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A new ferrocene-based bulky pyridine as an efficient reusable homogeneous catalyst†

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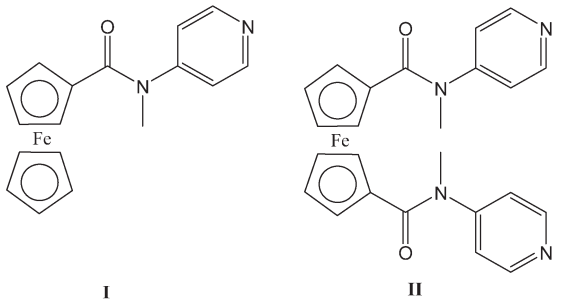
An effective approach to reusing a homogeneous catalyst has been demonstrated. A ferrocene-based bulky pyridine has been synthesized and utilized as a homogeneous catalyst for the synthesis of benzoylfumarates as well as for acetylation. After the reaction, the catalyst was separated by simple precipitation and reused without appreciable loss of activity.

Heterogeneous catalysts are widely used in industrial applications due to their ease of separation from the reaction mixture and their recyclability. On the other hand, even though homogeneous catalysts have many advantages such as high selectivity and activity, they only have limited application in industrial processes mainly due to the difficulty associated with their separation from the reaction mixture. Accordingly, it is highly desirable to develop a suitable approach that can provide the advantages of both homogeneous as well as heterogeneous catalysts. Consequently, a number of approaches have been explored for the separation and recycling of homogeneous catalysts. Among these strategies, the use of various supports for the immobilization of the catalyst, especially soluble supports, has been receiving great attention from synthetic chemists.[1] Over the last few years, soluble scaffolds such as perfluorinated tags,[2] ROMP gels,[3] JandaJel[4] and other soluble polymers[5] have been developed for the immobilization of the catalyst and reagents. Recently, a new technique known as ossification has also emerged as a new method for the immobilization of homogeneous catalysts.[6] This technique involves the modification of the coordinating ligands in such a way that the final catalytic complex is insoluble in most polar and nonpolar solvents. Eckart *et al.* have used tunable solvents for the separation of homogeneous catalysts from the reaction mixture.[7] Although this approach is efficient in catalyst separation, the high cost associated with this technique makes it unfavourable.

We herein report an alternative method where the homogeneous catalyst could be efficiently separated from the reaction mixture by simple precipitation. The product remains in the solution phase. This method allows easy separation as well as reuse of the catalyst. We have demonstrated the method on the example of the synthesis of benzoylfumarates by reacting benzaldehyde with dimethyl acetylenedicarboxylate (DMAD). Benzoylfumarates and their corresponding acids are known to be important building blocks for agrochemicals,[8] drugs[9] and other organic reactions.[10] Scarpati *et al.* have reported a general method for the synthesis of 2-benzoylfumarates from 2-methoxyfuranes as part of their extensive studies on the photosensitized oxidation of furanes.[11] Nair and co-workers and later Shi *et al.* have taken a better approach and prepared benzoylfumarates by one-pot reaction between DMAD and aldehydes in the presence of a Lewis base as the catalyst.[12] More recently, Bayat *et al.* obtained benzoylfumarates as unexpected products during the multicomponent reaction between DMAD, aldehyde and PPh_3,[13] and a few other methods are known in the literature.[14] In this paper, we describe for the first time a ferrocene based homogeneous reusable catalytic system for the preparation of benzoylfumarates from an aldehyde and DMAD.

To realize our goal, we designed the two ferrocene-based, bulky pyridines *N*-methyl-*N*-(pyridine-4-yl)ferroceneamide, (**I**) and *N*,*N*′-dimethyl-*N*,*N*′-di(pyridin-4-yl)ferrocene-1,1′-dicarboxamide (**II**) by attaching a 4-(methylamino)pyridine moiety to the ferrocene structure (Fig. 1).



I II

Fig. 1 Ferrocene based catalysts for the synthesis of benzoylfumarates and acetylation reactions.

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† Electronic supplementary information (ESI) available: Analytical data and NMR spectra of compounds, crystallographic information of catalyst **I** (CCDC 941950) & **II** (CCDC 893849). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra41674g

The redox properties of the catalyst were investigated by cyclic voltammetry in the presence of 0.1 M TBAP as the electrolyte in DMSO. The cyclic voltammograms of **I** and **II** showed well-defined single electron wave that was reversible in nature with $E_{1/2}$ = 0.385 V and $E_{1/2}$ = 0.275 V, respectively (Fig. 2).

Compound **I** (*N*-methyl-*N*-(pyridin-4-yl)ferroceneamide) was crystallized by slow evaporation from a 1 : 1 mixture of ethyl acetate and petroleum ether. The ORTEP diagram of compound **I** is shown in Fig. 3.

Similarly, compound **II** (*N*,*N*′-dimethyl-*N*,*N*′-di(pyridin-4-yl)ferrocene-1,1′-dicarboxamide) was crystallized by slow evaporation from a 1 : 1 mixture of ethyl acetate and petroleum ether (PE). Diffraction quality, block morphology single crystals were obtained after one day, and upon X-ray data collection, the structure was solved and refined in the monoclinic space group *C*2/*c*. The ORTEP diagram of compound **II** is shown in Fig. 4. Crystallographic data of compound **II** are presented in the ESI.†

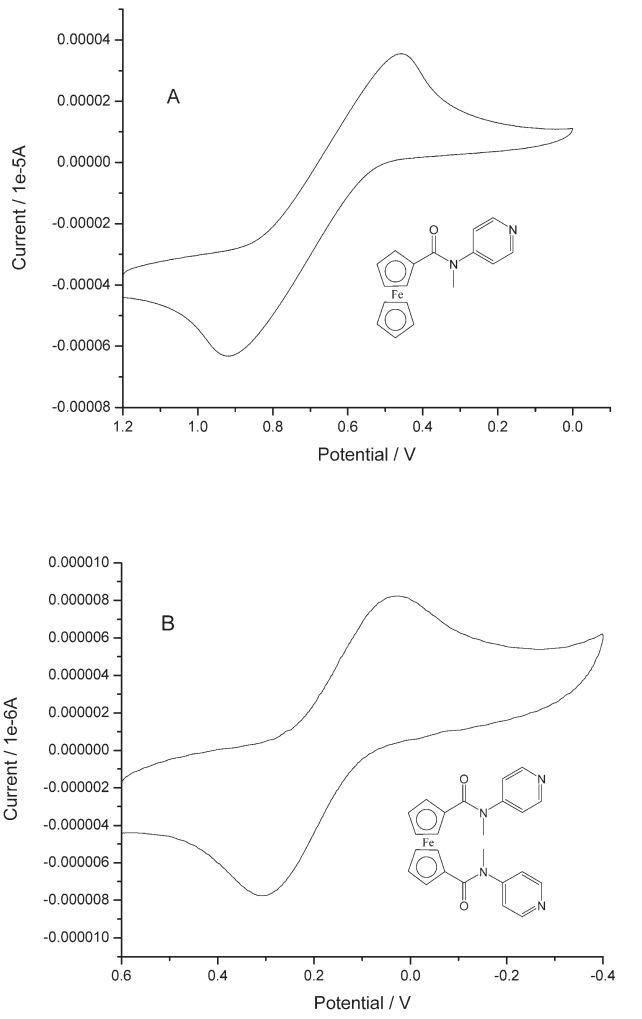


Fig. 2 Cyclic voltammograms of compound **I** (A) and compound **II** (B) in DMSO (0.1 M TBAP) at room temperature using glassy carbon as the working electrode, Ag/AgCl (3 M solution) as the reference electrode and Pt wire grid as the counter electrode; scan rate: 100 mV s^{-1}.

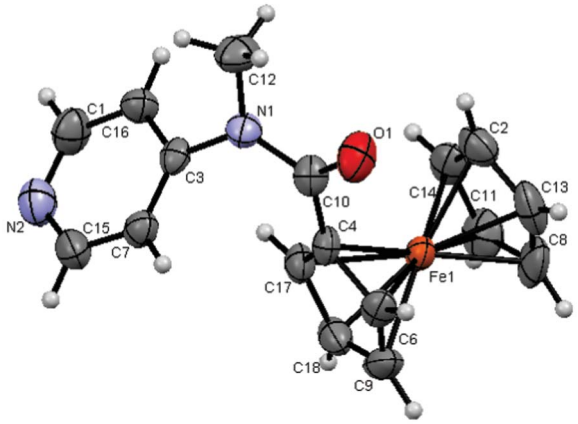


Fig. 3 ORTEP diagram of *N*-methyl-*N*-(pyridin-4-yl)ferroceneamide (**I**).

Initially, the reaction between 4-nitrobenzaldehyde and DMAD was selected as a model reaction to investigate the best reaction conditions (Table 1). In a typical reaction, a solution of the catalyst in DME (2 mL) was added dropwise with the help of a syringe to a mixture of 4-nitrobenzaldehyde (1 mmol) and DMAD (1 mmol) in DME (4 mL) at 0 °C under a N_2 atmosphere. The reaction was continued at room temperature for an appropriate time. After the usual workup, the crude product was purified using column chromatography to get the pure product. When 10 mol% of catalyst **I** was used, the yield of the product was found to be 79% after 10 h of reaction at room temperature. A slightly better yield was found within a shorter reaction time when catalyst **II** was used. The reaction in other solvents such as THF and acetonitrile produced a lower yield. The reaction in DCM did not proceed at all. Further reactions using 20 mol% of catalyst **II** did not improve the reaction. Finally, 10 mol% of catalyst **II** was found to be the optimum amount giving the best yield.

Having established the optimized reaction conditions, a variety of aldehydes were investigated under the same reaction conditions as described in Table 2. The general efficiency of

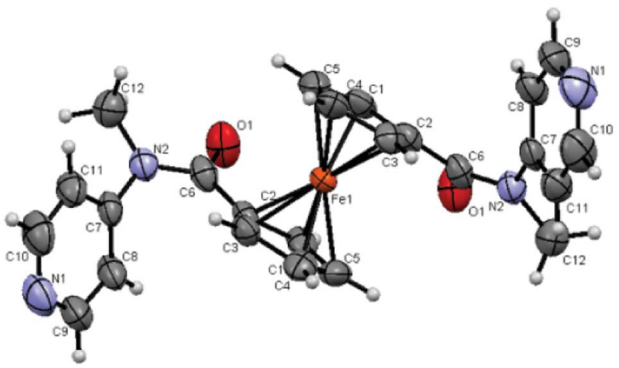
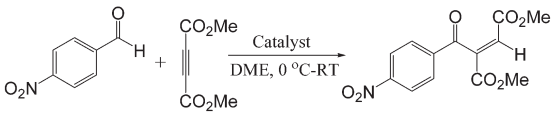


Fig. 4 ORTEP diagram of *N*,*N*́-dimethyl-*N*,*N*́-di(pyridine-4-yl)ferrocene-1,1′-dicarboxamide (**II**).

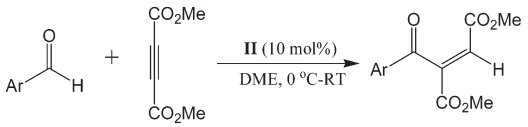
Table 1 Reaction of *p*-nitrobenzaldehyde with DMAD catalysed by **I** and **II** in different solvents[a]



Entry	Catalyst	Amount (mol%)	Solvent	Time (h)	Yield (%)[b]
1	**I**	10	DME	10	79
2	**II**	10	DME	7	81
3	**II**	10	THF	12	72
4	**II**	10	MeCN	12	30
5	**II**	10	DCM	12	Trace
6	**II**	20	DME	6	82
7	**II**	0	DME	24	0

[a] Reaction conditions: 4-nitrobenzaldehyde (1 mmol), DMAD (1 mmol), solvent (6 mL), 0 °C to rt. [b] Isolated yield.

Table 2 Reaction of aldehydes with DMAD catalysed by **II**[a]



Entry	Ar	Yield[b]
1	C_6H_5 (**4a**)	56
2	4-ClC_6H_4 (**4b**)	77
3	3-Cl C_6H_4 (**4c**)	73
4	4-NO_2 C_6H_4 (**4d**)	81
5	4-Br C_6H_4 (**4e**)	82
6	3-Br C_6H_4 (**4f**)	71
7	4-F C_6H_4 (**4g**)	69
8	4-OMe C_6H_4 (**4h**)	66
9	$C_{10}H_7$ (**4i**)	52
10	4-Me C_6H_4 (**4j**)	48
11	4-NO_2 C_6H_4	79[c]
12	4-NO_2 C_6H_4	76[d]
13	4-NO_2 C_6H_4	76[e]

[a] Reaction conditions: aldehyde (1 mmol), DMAD (1 mmol), catalyst **II** (10 mol%), DME (6 mL), 0 °C to rt, 7 h. [b] Isolated yield. [c] Catalyst **II** reused: 1st run. [d] Catalyst **II** reused: 2nd run. [e] Catalyst **II** reused: 3rd run.

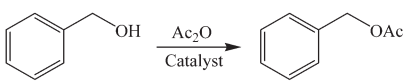
this reaction is evident from the variety of aldehydes, which react in good yields. It was observed that electron-withdrawing groups in the ring favor the reaction, which is evident from the high respective yields (Table 2, entries 2–8). However, the presence of electron-donating groups results in low yields (Table 2, entry 10).

After the reaction, the catalyst was recovered and reused. At this point, a model experiment was performed to check the feasibility of reusing catalysts **I** and **II** (Fig. S1–S3 in the ESI†). In two separate experiments, PE (10 mL) was added to a solution of compounds **I** and **II** in DCM (1 mL). We found that compound **II** precipitated out completely from the solution, whereas a small amount of compound **I** remained in solution, even after addition of more PE. Catalyst **II** was recovered by precipitation quantitatively, while only 70% recovery of catalyst **I** could be achieved. Hence, compound **II** was found to be suitable for the present study. To recover the catalyst from the reaction mixture, the solvent was removed and the residue dissolved in DCM (1 mL) followed by addition of PE (10 mL). The supernatant liquid was separated and the residue was washed three times with 1 : 10 DCM–PE. The combined organic phases were concentrated and purified using column chromatography to obtain the product. The residue was dried under vacuum to remove traces of PE. The dried catalyst was redissolved in DME (2 mL) and reused in the subsequent batch.

The catalyst was reused three times without any significant loss of activity (Table 2, entries 11–13). The efficiency of separation of catalyst **II** was further checked by electrochemical analysis. After evaporation of the filtrate, the crude mixture was analysed with the help of cyclic voltammetry, which indicated the absence of compound **II** in the filtrate (Fig. S4 in the ESI†). The cyclic voltammetry experiment confirms the full recovery of catalyst **II** after the reaction. The ^{1}H NMR spectrum (Fig. S5 in the ESI†) of the recovered catalyst confirms its stability.

To further extend the scope of our homogeneous reusable catalyst, it was applied to the acetylation of various functional groups. Initially, the acetylation of benzyl alcohol (1 mmol) was optimized by using different amounts of catalysts **I** and **II** and 1.2 mmol of acetic anhydride in different solvents (5 ml). It was observed that the use of solvent does not result in any good yields. However, when the reaction was performed without any solvent, a sharp increase in the rate of reaction as well as the yield was observed with both catalysts **I** and **II**. It was observed that 10 mol% of catalyst **I** gives the best result. A further increase of the catalyst does not have much effect on the yield. Almost the same yield was observed with 10 mol% of catalyst **II** in lesser time (Table 3, entry 13). It was further observed that an increased amount of acetic anhydride does

Table 3 Acetylation of benzyl alcohol under different reaction conditions[a]



Entry	Catalyst	Amount (mmol)	Ac_2O (mmol)	Solvent	Time (min)	Yield[b] (%)
1	**I**	5	1.2	DCM	120	60
2	**II**	5	1.2	DCM	70	62
3	**I**	5	1.2	EtOAc	120	70
4	**II**	5	1.2	EtOAc	65	73
5	**I**	5	1.2	CH_3CN	150	75
6	**II**	5	1.2	CH_3CN	80	79
7	**I**	5	1.2	—	65	82
8	**I**	10	1.2	—	60	91
9	**I**	15	1.2	—	60	93
10	**I**	20	1.2	—	40	90
11	**I**	10	1.5	—	60	92
12	**I**	10	2	—	60	92
13	**II**	10	10	—	30	95
14	—	—	1.2	—	300	0

[a] Reaction conditions: benzyl alcohol (1.2 mmol), rt. [b] Isolated yield.

not influence the yield. Accordingly, the use of 10 mol% of catalyst **I** or **II** was considered to be the optimum conditions for the reaction. The results are depicted in Table 3.

After optimization, a comparative study was carried out between both catalysts with a variety of alcohols, phenols, amines and thiophenols. The results are depicted in Table 4.

It is apparent from Table 4 that different types of alcohols including benzylic (entries 1, 12 and 13), primary (entries 14 and 17), secondary (entries 15, 16 and 37) and aliphatic (entry 18) were converted to their corresponding acetates in excellent yield. Phenolic compounds (entries 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11) reacted equally efficiently under the standard reaction conditions. Next, the procedure was extended to a variety of substrates such as amines and thiophenols. Aromatic (entries 19–28) as well as aliphatic (entry 29) amines were successfully acetylated using catalyst **II**. Similarly, the catalysts were found to be efficient in the acetylation of thiophenols (entries 30–33) with excellent yields. A comparative study was carried out between catalyst **I** and **II** for compounds **5I–5V** (entries 1–5). In all cases catalyst **II** was found to be more efficient than **I**.

The reusability of the catalysts was studied on benzyl alcohol as the model compound. After completion of the reaction, petroleum ether was added to the reaction mixture. The supernatant liquid was separated and the residue washed with petroleum ether three times. The combined organic phases were washed successively with 10% $NaHCO_3$ solution and brine, and dried over Na_2SO_4. The organic phase was passed through a short pad of silica gel and evaporated to give the pure product. The recovered catalyst was washed with petroleum ether and water successively, dissolved in DCM, and dried over Na_2SO_4. The solvent was evaporated and the recovered catalyst was kept in a desiccator over $CaCl_2$ overnight before use. As the catalyst **I** is slightly soluble in petroleum ether, a lower yield was observed in the subsequent step during the reuse of catalyst **I**. On the other hand, catalyst **II** was reused two times without any significant loss of activity.

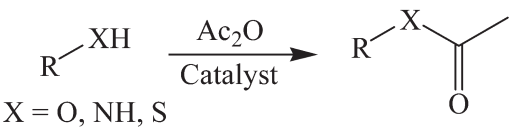
Conclusions

In conclusion, we have developed an effective approach to reuse a homogeneous ferrocene-based, bulky pyridine catalyst. The method was demonstrated for the preparation of benzoylfumarates from aromatic aldehydes. Various aromatic aldehydes were converted to the corresponding fumarates in high yield. After completion of the reaction, the catalyst was separated by simple precipitation and reused three times without any appreciable loss of activity.

Experimental section

All the chemicals used were of analytical grade. Melting points were determined in open capillaries in a paraffin bath and are uncorrected. IR spectra were recorded by using a Perkin Elmer Spectrum RX I FT-IR Spectrometer. Mass spectra were recorded on a Perkin Elmer Clarus 600 C mass spectrometer.

Table 4 Acetylation of alcohols, phenols, amines and thiophenols[a]



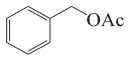
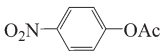
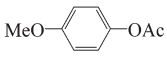
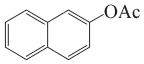
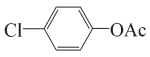
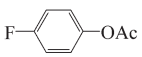
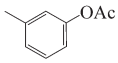
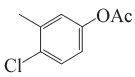
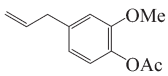
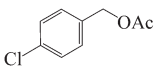
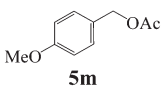
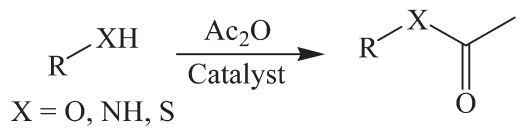
Entry	Product	Catalyst	Time (min)	Yield[b] (%)
1	 **5a**	**I**	60	91
		II	30	95
2	 **5b**	**I**	70	98
		II	30	98
3	 **5c**	**I**	120	84
		II	35	91
4	 **5d**	**I**	140	85
		II	40	90
5	 **5e**	**I**	120	80
		II	30	88
6	 **5f**	**II**	25	92
7	 **5g**	**II**	20	95
8	 **5h**	**II**	25	90
9	 **5i**	**II**	40	88
10	 **5j**	**II**	35	90
11	 **5k**	**II**	30	87
12	 **5l**	**II**	20	90
13	 **5m**	**II**	25	92

Table 4 (*Continued*)



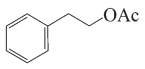
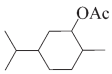
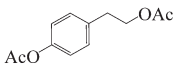
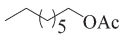
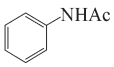
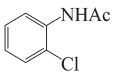
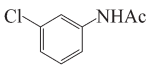
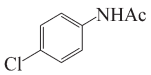
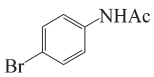
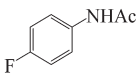
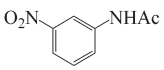
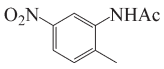
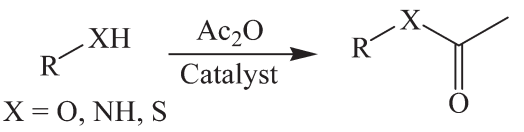
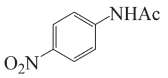
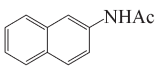
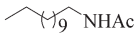
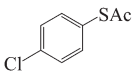
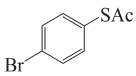
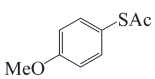
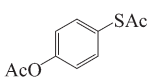
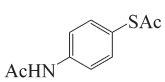
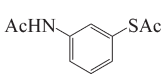
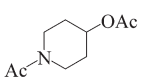
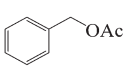
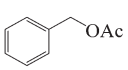
Entry	Product	Catalyst	Time (min)	Yield[b] (%)
14	 **5n**	**II**	20	86
15	 **5o**	**II**	45	89
16	 **5p**	**II**	35	85
17	 **5q**	**II**	40	85
18	 **5r**	**II**	45	75
19	 **5s**	**II**	20	96
20	 **5t**	**II**	25	92
21	 **5u**	**II**	30	93
22	 **5v**	**II**	35	93
23	 **5w**	**II**	30	95
24	 **5x**	**II**	35	89
25	 **5y**	**II**	40	88
26	 **5z**	**II**	35	89

Table 4 (*Continued*)



Entry	Product	Catalyst	Time (min)	Yield[b] (%)
27	 **5aa**	**II**	25	93
28	 **5ab**	**II**	25	94
29	 **5ac**	**II**	45	81
30	 **5ad**	**II**	45	84
31	 **5af**	**II**	30	88
32	 **5ag**	**II**	35	93
33	 **5ah**	**II**	30	90
34	 **5ai**	**II**	30	87
35	 **5aj**	**II**	35	83
36	 **5ak**	**II**	40	82
37	 **5al**	**II**	30	88
38		**II**	30	95[c]
39		**II**	30	93[d]

[a] Reaction conditions: substrate (1 mmol), acetic anhydride (1.2 mmol), catalyst (10 mol%), rt. [b] Isolated yield. [c] Catalyst reused: 1st run. [d] Catalyst reused: 2nd run.

^{1}H and ^{13}C-NMR spectra were obtained in $CDCl_3$ using a Bruker 300 MHz instrument.

Procedure for the synthesis of *N*-methyl-*N*-(pyridine-4-yl)ferroceneamide (I)

A) Synthesis of chlorocarbonyl ferrocene[1]. Oxalyl chloride was added dropwise to a suspension of ferrocene carboxylic acid in dry DCM under nitrogen. After the evolution of gas ceased, the reaction was stirred for a further 30 min. Then the solvent was removed under reduced pressure and the residue was extracted repeatedly with hexane. The combined organic extracts were concentrated under reduced pressure to give a dark red solid which was used directly in the next step without further purification.

B) Synthesis of *N*-methyl-*N*-(pyridine-4-yl)ferroceneamide (I). Chlorocarbonylferrocene (2.49 g, 0.01 mol) in DCM was added dropwise with the aid of a dropping funnel to a mixture of 4-(methylamino)pyridine (1.19 g, 0.011 mol), DMAP (0.05 g) and triethylamine (1.52 mL, 0.021 mol) in dichloromethane (20 mL) at 0 °C and the mixture was stirred overnight at room temperature. The reaction mixture was washed with water and brine, and then dried over anhydrous Na_2SO_4. The pure product (2.5 g, 75%) was isolated by passing it through a short pad of silica gel using ethyl acetate–petroleum ether as the eluent.

Red solid. Mp: 146–148 °C. IR (KBr, cm^{-1}): *ν* 846, 1124, 1345, 1496, 1576, 1638. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 3.42 (s, 3H), 4.17 (s, 5H), 4.20 (s, 2H), 4.17 (s, 2H), 7.02 (d, *J* = 6 Hz, 2H), 8.50 (d, *J* = 6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 37.5, 69.97, 70.11, 71.25, 102.67, 150.60, 152.38, 171.36. LC-MS (*m*/*z* (%)): 322 (100) [M^+], 226 (20), 211 (15), 109 (60). Anal. calculated for $C_{17}H_{16}FeN_2O$: C 63.77, H 5.04, N 8.75%. Found: C, 63.7, H 5.14, N 8.82%.

Procedure for the synthesis of *N*,*N*′-dimethyl-*N*,*N*′-di(pyridin-4-yl)ferrocene-1,1′-dicarboxamide (II)

A) Synthesis of Fc(COCl)$_2$. 1,1′-Ferrocenedicarbonyl chloride was prepared *via* the literature procedure.[2] A mixture of 1,1′-ferrocenedicarboxylic acid (8.79 g, 0.032 mol), oxalyl chloride (14 mL, 0.160 mol) and pyridine (0.5 mL) in 140 ml of dry dichloromethane was stirred under N_2 in the dark for 4 h at room temperature and then refluxed overnight. The reaction mixture was evaporated to dryness under reduced pressure and the residue extracted repeatedly with hexane. The solvent of the filtrate was removed under reduced pressure to give a red solid (9.20 g, 92%) which was kept under N_2 for further use.

B) Synthesis of *N*,*N*′-dimethyl-*N*,*N*′-di(pyridin-4-yl)ferrocene-1,1′-dicarboxamide (II). 1,1′-Ferrocenedicarbonyl chloride (3.11 g, 0.01 mol) in dichloromethane was added dropwise through a dropping funnel to a mixture of 4-(methylamino)-pyridine (2.27 g, 0.021 mol), *N*,*N*-dimethyl-4-aminopyridine (0.1 g) and triethylamine (2.9 mL, 0.021 mol) in dichloromethane (30 mL) at 0 °C, and the mixture was stirred overnight at room temperature. The reaction mixture was washed with water and brine, and then dried over anhydrous Na_2SO_4. The pure product (3.8 g, 83%) was isolated by passing it through a short silica gel column using ethyl acetate–petroleum ether as the eluent.

Red solid. Mp: 129–131 °C. IR (KBr, cm^{-1}): *ν* 829, 1114, 1350, 1496, 1585, 1643, 3421. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 3.12 (s, 6H), 3.43 (s, 4H), 4.20 (s, 4H), 6.66–7.21 (m, 4H), 8.35–8.90 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): *δ* 37.49, 71.61, 73.25, 118.42, 120.99, 147.64, 150.59, 150.92, 152.30, 169.92. LC-MS (*m*/*z* (%)): 456 (39) [M^+], 455 (100), 109 (22). Anal. calculated for $C_{24}H_{22}FeN_4O_2$: C 63.45, H 4.88, N 12.33%. Found: C 63.56, H 4.79, N 12.42%.

Typical procedure for the synthesis of benzoylfumarates

A solution of catalyst **II** in DME (2 mL) was added dropwise with the help of a syringe to a mixture of 4-nitrobenzaldehyde (1 mmol) and DMAD (1 mmol) in DME (4 mL) at 0 °C under a N_2 atmosphere. After completion of the reaction the solvent was removed, and the residue was dissolved in DCM (1 mL) followed by addition of petroleum ether (10 mL). The supernatant liquid was separated and the residue was washed with 1 : 10 DCM–PE three times. The combined organic phases were concentrated and purified using column chromatography to obtain the product.

Dimethyl (2*E*)-2-benzoylbut-2-enedioate[11,12] (4a). Colourless crystalline solid. Yield: 56%. Mp: 79–81 °C. IR (KBr, cm^{-1}): *ν* 1207, 1261, 1423, 1681, 1728, 2306, 2985, 3055. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 3.64 (s, 3H), 3.79 (s, 3H), 7.11 (s, 1H), 7.3–7.55 (m, 2H), 7.56–7.65 (m, 1H), 7.7–7.98 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 52.49, 53.29, 128.66, 128.82, 130.47, 133.91, 135.47, 145.21, 163.58, 164.18, 192.20. GC-MS (*m*/*z* (%)): 248 (15) [M^+], 217 (8), 105 (100), 77 (36), 28 (17).

Dimethyl (2*E*)-2-(4-chlorobenzoyl)but-2-enedioate[12*b*,13] (4b). Colourless crystalline solid. Yield: 77%. Mp: 78–80 °C. IR (KBr, cm^{-1}): *ν* 1207, 1273, 1423, 1589, 1685, 2985. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 3.66 (s, 3H), 3.79 (s, 3H), 7.10 (s, 1H), 7.465 (d, *J* = 9 Hz, 2H), 7.825(d, *J* = 9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 52.58, 53.35, 129.22, 129.97, 130.72, 133.90, 140.41, 144.79, 163.34, 164.14, 191.04. GC-MS (*m*/*z* (%)): 282 (26) [M^+], 251 (15), 139 (100), 111 (62), 75 (35), 53 (18).

Dimethyl (2*E*)-2-(3-chlorobenzoyl)but-2-enedioate[12*b*] (4c). Colourless crystalline solid. Yield: 73%. Mp: 76–77 °C IR (KBr, cm^{-1}): *ν* 774, 1072, 1253, 1424, 1580, 1731, 2976. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 3.65 (s, 3H), 3.78 (s, 3H), 7.10 (s, 1H), 7.37–7.48 (m, 1H), 7.555 (d, *J* = 9 Hz, 1H), 7.725 (d, *J* = 9 Hz, 1H), 7.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 52.53, 53.29, 126.72, 128.36, 130.11, 130.82, 133.73, 135.06, 136.92, 144.58, 163.14, 164.04, 190.92. GC-MS (*m*/*z* (%)): 282 (30) [M^+], 251 (20), 223 (23), 191 (17), 139 (100), 111 (68), 75 (56), 53 (24).

Dimethyl (2*E*)-2-(4-nitrobenzoyl)but-2-enedioate[12,13] (4d). Yellow crystalline solid. Yield: 81%. Mp: 115–117 °C. IR (KBr, cm^{-1}): *ν* 1194, 1359, 1453, 1665, 1721, 2943.^{1}H NMR (300 MHz, $CDCl_3$): *δ* 3.65 (s, 3H), 3.78 (s, 3H), 7.12 (s, 1H), 8.025 (d, *J* = 9 Hz, 2H), 8.305 (d, *J* = 9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 52.66, 53.36, 123.96, 129.46, 131.24, 139.67, 144.25, 150.46, 162.84, 164.07, 190.69. GC-MS (*m*/*z* (%)): 293 (73) [M^+], 262 (55), 234 (39), 171 (33), 150 (72), 120 (75), 104 (100), 92 (77), 76 (78), 53 (57).

Dimethyl (2*E*)-2-(4-bromobenzoyl)but-2-enedioate[11–13] (4e). White crystalline solid. Yield: 82%. Mp: 88–90 °C. IR (KBr,

cm^{-1}): *v* 1192, 1271, 1425, 1576, 1725, 2951 ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (s, 3H), 3.76 (s, 3H), 7.08 (s, 1H), 7.61 (d, J = 6 Hz, 2H), 7.73 (d, J = 6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.48, 53.23, 129.09, 129.95, 130.63, 132.08, 134.20, 144.64, 163.20, 164.02, 191.14. GC-MS (*m*/*z* (%)): 328 (22) [M^+ + 2], 326 (22) [M^+], 183 (100), 157 (44), 159 (45), 75 (52), 53 (35).

Dimethyl (2*E*)-2-(3-bromobenzoyl)but-2-enedioate (4f). Yellow oil. Yield: 71%. IR (KBr, cm^{-1}): *v* 1186, 121 254, 1430, 1577, 1732, 1941. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.79 (s, 3H), 7.11 (s, 1H), 7.30–7.45 (m, 1H), 7.65–7.86 (m, 2H), 8.01 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.60, 53.36, 123.13, 127.22, 130.38, 130.90, 131.34, 136.69, 137.15, 144.59, 163.18, 164.09, 190.88. GC-MS (*m*/*z* (%)): 328 (14) [M^+ + 2], 326 (14) [M^+], 185 (99), 183 (100), 157 (28), 155 (28), 75 (27), 53 (18). Anal. calculated for $C_{13}H_{11}BrO_5$: C 47.73, H 3.39%. Found: C 47.56; H 3.65%.

Dimethyl (2*E*)-2-(4-fluorobenzoyl)but-2-enedioate[15] (4g). Yellow oil. Yield: 69%. IR (KBr, cm^{-1}): *v* 1397, 1422, 1674, 1729, 2955.^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.79 (s, 3H), 7.10 (s, 1H), 7.11–7.22 (m, 2H), 7.86–7.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.54, 53.31, 115.95, 116.24, 130.55, 131.26, 131.39, 144.91, 163.43, 164.15, 190.64. GC-MS (*m*/*z* (%)): 266 (14) [M^+], 235 (8), 123 (100), 95 (40), 75 (12), 28 (19).

Dimethyl (2*E*)-2-(4-methoxybenzoyl)but-2-enedioate[13,15] (4h). Yellow oil. Yield: 66%. IR (KBr, cm^{-1}): *v* 1120, 1270, 1425, 1724, 2945. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (s, 3H), 3.78 (s,3H), 3.88 (s, 3H), 6.955 (d, J = 9 Hz, 2H), 7.08 (s, 1H), 7.855 (d, J = 9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.28, 52.69, 53.46, 129.33, 130.08, 130.83, 134.01, 140.52, 144.90, 163.45, 164.25, 191.15. GC-MS (*m*/*z* (%)): 278 (17), [M^+], 247 (6), 135 (100), 107 (12), 92 (13), 77 (18).

Dimethyl (2*E*)-2-(naphthalen-2-ylcaronyl)but-2-enedioate (4i). Yellow oil. Yield: 52%. IR (KBr, cm^{-1}): *v* 1265, 1422, 1571, 1672, 1731, 2956.^{1}H NMR (300 MHz, $CDCl_3$): δ 3.61 (s, 3H), 3.79 (s, 3H), 7.19 (s, 1H), 7.51–7.69 (m, 2H), 7.85–7.98 (m, 3H), 8.01–8.11 (m, 1H), 8.30 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.47, 53.30, 123.53, 126.89, 127.87, 128.88, 129.69, 130.61, 131.12, 132.44, 133.01, 136.02, 145.27, 163.69, 164.17, 192.09. GC-MS (*m*/*z* (%)): 298 (36) [M^+], 207 (16), 155 (100), 127 (99), 77 (12). Anal. calculated for $C_{17}H_{14}O_5$: C 68.45, H 4.73%. Found: C 68.58, H 4.82%.

Dimethyl (2*E*)-2-(4-methylbenzoyl)but-2-enedioate[11a,12,13] (4j). Colourless crystalline solid. Yield: 48%. Mp: 85–87 °C. IR (KBr, cm^{-1}): *v* 1169, 1278, 1433, 1609, 1721, 2956. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.64 (s, 3H), 3.78 (s, 3H), 7.09 (s, 1H), 7.285 (d, J = 9 Hz, 2H), 7.785 (d, J = 9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.28, 53.05, 53.85, 129.39, 130.15, 130.84, 133.69, 145.57, 145.92, 164.28, 164.80, 192.41. GC-MS (*m*/*z* (%)): 262 (26) [M^+], 231 (12), 119 (100), 91 (74), 65 (28).

Typical procedure for the acetylation

To a stirred mixture of Ac_2O (1.2 mmol) and the catalyst (10 mol%) at room temperature, the respective alcohol, phenol, amine or thiophenol (1 mmol) was added with continuous stirring. After completion of the reaction (TLC monitoring), petroleum ether was added, the supernatant liquid was separated, and the residue was washed with petroleum ether three times. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated, and purified using column chromatography to obtain the product. The recovered catalyst was washed with petroleum ether, dried under vacuum and then kept in a desiccator over $CaCl_2$ overnight before reuse.

Benzyl acetate[16,20,25] (5a). Thick oil. Yield: 95%. IR (KBr, cm^{-1}): *v* 876,1050, 1234, 1348, 1527, 1745,3099. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12 (s, 3H), 5.15 (s, 2H), 8.08–8.34 (m, 5H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.6, 66.3, 130.2, 132.7, 134.2, 135.7, 170.5. GC-MS (*m*/*z* (%)): 150 (94) [M^+], 108 (68), 91 (100), 77 (81), 65 (50), 51 (49).

4-Nitrophenyl acetate[16,21,28] (5b). White solid. Yield: 98%. Mp: 77–78 °C. IR (KBr, cm^{-1}): *v* 746, 865, 967, 1142, 1345, 1423, 1568, 1545, 1611, 1775, 2851, 2912, 3077. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H), 7.22 (dd, J = 6 Hz, 3 Hz, 2H), 8.18 (dd, J = 6 Hz, 3 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.7, 122.2, 124.8, 144.9, 155.1, 168.2. GC-MS (*m*/*z* (%)): 181 (71) [M^+], 139 (100), 123 (42), 109 (93), 63 (78).

4-Methoxyphenyl acetate[21,28] (5c). Thick oil. Yield: 91%. IR (KBr, cm^{-1}): *v* 731, 917, 1022, 1189, 1216, 1512, 1765. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H), 3.75 (s, 3H), 6.89 (d, J = 9 Hz, 2H), 7.02 (d, J = 9 Hz, 2H).^{13}C NMR (75 Hz, $CDCl_3$): δ 20.6, 55.1, 114.0, 122.0, 143.8, 156.9, 169.5. GC-MS (*m*/*z* (%)): 166 (49) [M^+], 124 (49), 109 (100), 81 (44).

Naphthalen-2-yl acetate[25,26] (5d). White solid. Yield: 90%. Mp: 68–69 °C. IR (KBr, cm^{-1}): *v* 824, 954, 1025, 1130, 1233, 1382, 1443, 1519, 1586, 1742, 2935, 3052. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 7.25–7.35 (m, 1H), 7.47–7.69 (m, 3H), 7.81–8.11 (m, 3H).^{13}C NMR (75 Hz, $CDCl_3$): δ 21.1, 118.4, 121.0, 125.6, 126.5, 127.5, 127.7, 129.3, 131.3, 133.6, 148.2, 169.6. GC-MS (*m*/*z* (%)): 186 (53) [M^+], 144 (100), 115 (81), 99 (25), 63 (25).

Naphthalen-1-yl acetate[25,26,28] (5e). White solid. Yield: 88%. Mp: 45–46 °C. IR (KBr, cm^{-1}): *v* 751, 823, 926, 1177, 1224, 1370, 1456, 1607, 1735, 2916. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 3H), 7.32–7.46 (m, 1H), 7.50–7.73 (m, 3H), 7.78–7.89 (m, 1H), 7.91–8.13 (m, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.7, 117.9, 120.9, 125.2, 125.8, 126.3, 126.6, 127.9, 134.4, 146.4, 169.3. GC-MS (*m*/*z* (%)): 186 (33) [M^+], 144 (100), 115 (74), 99 (21), 63 (22).

2-Nitrophenyl acetate[26] (5f). Thick oil. Yield: 92%. IR (KBr, cm^{-1}): *v* 850, 935, 1197, 1356, 1543, 1600, 1782, 2955. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H), 7.11–7.25 (m, 1H), 7.26–7.41 (m, 1H), 7.52–7.70 (m, 1H), 7.94–8.12 (m, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.3, 124.9, 125.3, 126.4, 134.6, 141.3, 143.6, 168.3. GC-MS (*m*/*z* (%)): 181 (15) [M^+], 139 (100), 109 (27), 81 (29), 63 (62).

4-Chlorophenyl acetate[16,26,28] (5g). Colourless liquid. Yield: 95%. IR (KBr, cm^{-1}): *v* 780, 1045, 1182, 1261, 1483, 1674, 2833, 3072. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H), 7.04 (dd, J = 6 Hz, 3 Hz, 2H), 7.35 (dd, J = 6 Hz, 3 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 21.0, 122.9, 129.4, 131.1, 149.0, 169.2. GC-MS (*m*/*z* (%)): 170 (37) [M^+], 128 (100), 99 (23), 73 (25), 65 (30).

4-Fluorophenyl acetate[28] (5h). Colourless liquid. Yield: 90%. IR (KBr, cm^{-1}): *v* 770, 1011, 1190, 1226, 1668, 3112. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 6.98–7.25 (m, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.7, 116.0, 122.9, 146.3, 161.6, 169.3. GC-MS (*m*/*z* (%)): 154 (68) [M^+], 112 (100), 83 (98), 57 (83).

3-Methylphenyl acetate[26] (5i). Colourless liquid. Yield: 88%. IR (KBr, cm^{-1}): *v* 751, 1161, 1222, 1368, 1771. ^{1}H NMR (300

MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.39 (s, 3H), 6.88–7.00 (m, 2H), 7.08 (d, *J* = 9 Hz, 1H), 7.29 (t, *J* = 6 Hz, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.9, 21.1, 118.4, 122.0, 126.5, 129.0, 139.4, 150.4, 169.5.

4-Chloro-3-methylphenyl acetate[27] (5j). Thick oil. Yield: 90%. IR (KBr, cm^{-1}): *v* 810, 1072, 1257, 1420, 1745, 3026. ^1H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.37 (s, 3H), 6.84–6.92 (m, 1H), 6.95–7.01 (m, 1H), 7.29–7.37 (m, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.0, 20.8, 120.1, 123,8, 129.5, 131.1, 137.2, 148.8, 169.2. GC-MS (*m*/*z* (%)): 184 (40) [M^+], 142 (55), 107 (100), 77 (78), 51 (42).

2-Methoxy-4-(prop-2-en-1-yl)phenyl acetate[20] (5k). Thick oil. Yield: 87%. IR (KBr, cm^{-1}): *v* 908, 1190, 1247, 1350, 1443, 1503, 1591, 1609, 1765. ^1H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 3.36 (d, *J* = 6 Hz, 2H), 3.75 (s, 3H), 5.04–5.24 (m, 2H), 5.87–6.08 (m, 1H), 6.70–6.88 (m, 2H), 6.91–7.07 (m, 1H).^{13}C NMR (75 Hz, $CDCl_3$): δ 19.9, 39.5, 55.0, 112.1, 115.5, 120.0, 122.0, 136.6, 137.5, 138.4, 150.4, 168.4. GC-MS (*m*/*z* (%)): 206 (15) [M^+], 164 (100), 149 (39), 91 (37), 77 (44), 65 (34).

4-Chlorobenzyl acetate[16,25] (5l). Thick oil. Yield: 90%. IR (KBr, cm^{-1}): *v* 1024, 1086, 1233, 1388, 1496, 1756, 2961. ^1H NMR (300 MHz, $CDCl_3$): δ 2.10 (s, 3H), 5.06 (s, 2H), 7.23–7.51 (m, 4H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.9, 65.4, 128.7, 129.6, 134.1, 134.3, 170.8. GC-MS (*m*/*z* (%)): 184 (63) [M^+], 142 (95), 125 (100), 107 (77), 99 (85), 77 (36).

4-Methoxybenzyl acetate[16,25] (5m). Thick oil. Yield: 92%. IR (KBr, cm^{-1}): *v* 743, 1012, 1178, 1235, 1522, 1737, 2952. ^1H NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 3H), 3.76 (s, 3H), 5.02 (s, 2H), 6.87 (d, *J* = 6 Hz, 2H), 7.28 (d, *J* = 6 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.7, 54.9, 65.8, 113.6, 127.7, 129.8, 159.3, 170.6. GC-MS (*m*/*z* (%)): 180 (74) [M^+], 138 (27), 121 (100), 91 (53), 77 (52).

2-Phenylethyl acetate[21] (5n). Thick oil. Yield: 86%. IR (KBr, cm^{-1}): *v* 714, 1037, 1233, 1372, 1455, 1741, 2952, 3030. ^1H NMR (300 MHz, $CDCl_3$): δ 1.97 (s, 3H), 2.91 (t, *J* = 6 Hz, 2H), 4.27 (t, *J* = 6 Hz, 2H), 7.14–7.25 (m, 3H), 7.26–7.34 (m, 2H).^{13}C NMR (75 Hz, $CDCl_3$): δ 20.1, 34.5, 64.3, 126.0, 127.9, 128.3, 137.3, 170.1.

Cyclohexyl acetate[16,25,26,28] (5o). Thick oil. Yield: 89%. IR (KBr, cm^{-1}): *v* 988, 1020, 1228, 1350, 1449, 1753, 2948. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99–1.56 (m, 6H), 1.57–1.88 (m, 4H), 1.94 (s, 3H), 4.55–4.90 (m, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 14.9, 17.3, 18.9, 25.2, 66.2, 164.1. GC-MS (*m*/*z* (%)): 142 (2) [M^+], 90 (10), 91 (75), 67 (100), 54 (42).

2-Methyl-5-(propan-2-yl)cyclohexyl acetate[21,25,27,28] (5p). Thick oil. Yield: 85%. IR (KBr, cm^{-1}): *v* 760, 1054, 1261, 1322, 1680, 1780, 3012. ^1H NMR (300 MHz, $CDCl_3$): δ 0.48 (d, *J* = 6 Hz, 3H), 1.02–1.49 (m, 4H), 1.50–1.83 (m, 6H), 1.88–1.99 (m, 2H), 4.34–4.46 (m, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 15.6, 20.3, 21.3, 22.8, 25.6, 30.7, 33.6, 40.3, 46.4, 73.2, 169.6.

4-[2-(Acetyloxy)ethyl]phenyl acetate (5q). Thick oil. Yield: 85%. IR (KBr, cm^{-1}): *v* 777, 1025, 1196, 1338, 1452, 1690, 1765, 3218. ^1H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H), 2.28 (s, 3H), 2.92 (t, *J* = 6 Hz, 2H), 4.25 (t, *J* = 6 Hz, 2H), 7.02 (d, *J* = 9 Hz, 2H), 7.22 (d, *J* = 9 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 21.0, 34.3, 64.6, 121.4, 129.7, 135.3, 149.2, 169.5, 170.9.

Octyl acetate[26] (5r). Thick oil. Yield: 81%. IR (KBr, cm^{-1}): *v* 890, 1039, 1280, 1447, 1545, 1743, 2927. ^1H NMR (300 MHz, $CDCl_3$): δ 0.78 (t, *J* = 6 Hz, 3H), 1.08–1.44 (m, 9H), 1.44–1.75 (m, 3H), 1.93 (s, 3H), 3.94 (t, *J* = 6 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 13.8, 20.6, 22.4, 25.7, 28.4, 29.0, 31.6, 64.3, 170.8.

***N*-phenylacetamide[16,17,23] (5s).** White Solid. Yield: 96%. Mp: 115–116 °C. IR (KBr, cm^{-1}): *v* 692, 752, 1262, 1320, 1368, 1434, 1486, 1499, 1557, 1596, 1661. ^1H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 3H), 7.05–7.16 (m, 1H), 7.23–7.36 (m, 2H), 7.50–7.63 (m, 2H), 8.71 (s, 1H).^{13}C NMR (75 Hz, $CDCl_3$): δ 24.1, 120.2, 124.1, 128.7, 138.0, 169.3. GC-MS (*m*/*z* (%)): 135 (32) [M^+], 93 (100), 66 (16), 51 (5).

***N*-(2-chlorophenyl)acetamide[23] (5t).** White Solid. Yield: 82%. Mp: 90–92 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 3H), 6.84–6.98 (m, 1H), 7.04–7.17 (m, 1H), 7.17–7.29 (m, 1H), 7.95–8.16 (m, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 23.9, 122.5, 123.4, 124.6, 126.9, 128.6, 134.1, 168.5. GC-MS (*m*/*z* (%)): 169 (17) [M^+], 134 (36), 127 (100), 92 (12), 63 (10).

***N*-(3-chlorophenyl)acetamide[23] (5u).** White Solid. Yield: 93%. Mp: 77–78 °C. IR (KBr, cm^{-1}): *v* 791,1250, 1422, 1540, 1580, 1690, 3354. ^1H NMR (300 MHz, $CDCl_3$): δ 2.16 (s, 3H), 7.05 (d, *J* = 6 Hz, 1H), 9.19 (t, *J* = 6 Hz, 1H), 7.33 (d, *J* = 6 Hz, 1H), 7.65 (s, 1H), 8.46 (s, 1H).^{13}C NMR (75 Hz, $CDCl_3$): δ 24.3, 118.0, 120.1, 124.2, 129.8, 134.3, 139.1, 169.3. GC-MS (*m*/*z* (%)): 169 (31) [M^+], 129 (35), 127 (100), 92 (11), 63 (10).

***N*-(4-chlorophenyl)acetamide (5v).** [16,23,26] White Solid. Yield: 93%. Mp: 178–180 °C. IR (KBr, cm^{-1}): *v* 850, 1330, 1500, 1607, 1675, 3300. ^1H NMR (300 MHz, $CDCl_3$): δ 1.94 (s, 3H), 7.04 (d, *J* = 9 Hz, 2H), 7.37 (d, *J* = 9 Hz, 2H), 9.26 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 24.1, 120.9, 128.5, 130.0, 137.5, 169.0. GC-MS (*m*/*z* (%)): 169 (32) [M^+], 129 (33), 127 (100), 92 (13), 63 (12).

***N*-(4-bromophenyl)acetamide[16] (5w).** White Solid. Yield: 95%. Mp: 166–168 °C. IR (KBr, cm^{-1}): *v* 810, 1300, 1388, 1492, 1523, 1680, 3289. ^1H NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 3H), 7.28 (d, *J* = 9 Hz, 2H), 7.44 (d, *J* = 9 Hz, 2H), 9.57 (s, 1H).^{13}C NMR (75 Hz, $CDCl_3$): δ 23.4, 114.9, 120.6, 130.7, 137.5, 168.4. GC-MS (*m*/*z* (%)): 213 (40) [M^+], 215 (38) [M^+ + 2], 171 (100), 92 (68), 65 (43).

***N*-(4-fluorophenyl)acetamide[23] (5x).** White Solid. Yield: 89%. Mp: 152–153 °C. IR (KBr, cm^{-1}): *v* 836, 1235, 1507, 1617, 1662, 2853, 2923, 3071, 3290. ^1H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 3H), 6.94–7.11 (m, 2H), 7.38–7.53 (m, 2H), 7.58 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 24.3, 115.4, 121.7, 133.8, 157.7, 168.5. GC-MS (*m*/*z* (%)):153 (64) [M^+], 111 (100), 83 (34), 57 (19).

***N*-(3-nitrophenyl)acetamide[16,17,26] (5y).** White Solid. Yield: 88%. Mp: 152–153 °C. IR (KBr, cm^{-1}): *v* 832, 1021, 1199, 1322, 1449, 1548, 1688, 3352. ^1H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 3H), 7.25 (t, *J* = 9 Hz, 1H), 7.64–7.71 (m, 1H), 7.77–7.85 (m, 1H), 7.33 (s, 1H), 9.77 (s, 1H).^{13}C NMR (75 Hz, $CDCl_3$): δ 23.8, 113.7, 117.4, 124.9, 129.0, 139.8, 147.8, 169.2. GC-MS (*m*/*z* (%)): 180 (25) [M^+], 138 (100), 92 (55), 65 (26).

***N*-(2-methyl-5-nitrophenyl)acetamide[22] (5z).** White Solid. Yield: 89%. Mp: 150–151 °C. IR (KBr, cm^{-1}): *v* 780, 1472, 1489, 1322, 1651, 1554, 1709, 3356. ^1H NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.34 (s, 3H), 7.23–7.38 (m, 1H), 7.42 (s, 1H), 7.90 (d, *J* = 6 Hz, 1H), 8.67 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 18.1, 24.2, 118.2, 119.8, 131.0, 136.5, 139.3, 146.7, 168.8. GC-MS (*m*/*z* (%)): 194 (14) [M^+], 177 (38), 152 (100), 106 (48), 77 (26).

***N*-(4-nitrophenyl)acetamide[25,26] (5aa).** White Solid. Yield: 93%. Mp: 113–115 °C. IR (KBr, cm^{-1}): *v* 725, 852, 1450, 1490,

1353, 1511, 1575, 1683, 3350. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (s, 3H), 6.98 (d, J = 9 Hz, 2H), 7.29 (d, J = 9 Hz, 2H), 9.41 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 23.4, 117.7, 123.6, 141.4, 144.4, 168.5. GC-MS (m/z (%)): 180 (31) [M^+], 138 (100), 108 (47), 92 (26), 65 (22).

***N*-(naphthalen-2-yl)acetamide[24] (5ab).** White Solid. Yield: 94%. Mp: 132–133 °C. IR (KBr, cm^{-1}): ν 741, 866, 1276, 1351, 1394, 1472, 1562, 1590, 1669, 3277. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 3H), 7.34–7.57 (m, 3H), 7.69–7.96 (m, 4H), 8.19 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 24.6, 116.7, 119.9, 122.4, 125.0, 126.4, 127.6, 128.7, 130.6, 133.7, 135.3, 168.7. GC-MS (m/z (%)): 185 (35) [M^+], 143 (100), 115 (41), 63 (6).

***N*-dodecylacetamide[29] (5ac).** White Solid. Yield: 81%. Mp: 51–52 °C. IR (KBr, cm^{-1}): ν 610, 1420, 1543, 1665, 2921, 3290. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.73 (t, J = 6 Hz, 3H), 1.04–1.26 (m, 18H), 1.29–1.44 (m, 2H), 1.83 (s, 3H), 2.99–3.14 (m, 2H), 6.98 (s, 1H).^{13}C NMR (75 Hz, $CDCl_3$): δ 13.7, 22.3, 22.6, 29.0, 29.1, 29.2, 29.3, 29.31, 31.6, 39.4, 170.2. GC-MS (m/z (%)): 227 (10) [M^+], 212 (9), 128 (17), 114 (42), 100 (40), 86 (52), 73 (100), 60 (43).

***S*-phenyl ethanethioate[16,28] (5ad).** Thick Oil. Yield: 84%. IR (KBr, cm^{-1}): ν 756, 980, 1225, 1489, 1502, 1715. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.34–7.57 (m, 5H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 29.9, 127.7, 128.9, 129.1, 134.2193.6. GC-MS (m/z (%)): 152 (50) [M^+], 110 (100), 84 (19), 65 (40), 51 (15).

***S*-(4-chlorophenyl) ethanethioate[17] (5af).** Thick Oil. Yield: 88%. IR (KBr, cm^{-1}): ν 750, 980, 1198, 1222, 1503, 1745. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H), 7.23–7.76 (m, 4H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 29.9, 126.1, 129.1, 135.4, 135.5, 193.0. GC-MS (m/z (%)): 186 (31) [M^+], 144 (100), 108 (55), 99 (14), 69 (21).

***S*-(4-bromophenyl) ethanethioate[30] (5ag).** White solid. Yield: 93%. Mp: 51–52 °C. IR (KBr, cm^{-1}): ν 980, 1009, 1224, 1478, 1567, 1734. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.27 (d, J = 9 Hz, 2H), 7.54 (d, J = 9 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 30.3, 124.1, 127.0, 132.4, 135.9, 193,2. GC-MS (m/z (%)): 230 (25) [M^+], 232 (26) [M^+ + 2], 188 (100), 108 (99), 82 (27), 69 (22).

***S*-(4-methoxyphenyl) ethanethioate[17] (5ah).** White solid. Yield: 90%. Mp: 98–101 °C. IR (KBr, cm^{-1}): ν 870, 1045, 1189, 1256, 1601, 1766. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H), 3.76 (s, 3H), 6.93 (d, J = 9 Hz, 2H), 7.32 (d, J = 9 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 29.4, 54.9, 114.4, 118.3, 135.7, 160.3, 194.5. GC-MS (m/z (%)): 182 (55) [M^+], 140 (100), 125 (95), 96 (37), 69 (25).

4-(Acetylsulfanyl)phenyl acetate[30] (5ai). White solid. Yield: 87%. Mp: 71–72 °C. IR (KBr, cm^{-1}): ν 983, 1124, 1378, 1511, 1567, 1702, 1744. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H), 2.30 (s, 3H), 7.09 (d, J = 6 Hz, 2H), 7.35 (d, J = 6 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 20.9, 30.0, 122.5, 125.1, 135.5, 151.6, 168.9, 193.5. GC-MS (m/z (%)): 210 (27) [M^+], 168 (78), 125 (100), 97 (37), 69 (23).

***S*-[4-(acetylamino)phenyl] ethanethioate[18] (5aj).** White solid. Yield: 83%. Mp: 127–129 °C. IR (KBr, cm^{-1}): ν 850, 1455, 1493, 1367, 1501, 1575, 1673, 1733, 3350. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (s, 3H), 2.15 (s, 3H), 7.06 (d, J = 9 Hz, 2H), 7.43 (d, J = 9 Hz, 2H), 9.37 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 23.7, 29.4, 119.5, 121.0, 134.5, 139.7, 168.7, 194.3. GC-MS (m/z (%)): 209 (18) [M^+], 167 (84), 125 (100), 80 (16).

***S*-[3-(acetylamino)phenyl] ethanethioate (5ak).** Thick oil. Yield: 82%. IR (KBr, cm^{-1}): ν 876, 1243, 1360, 1391, 1443, 1523, 1588, 1654, 1744, 3278. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.98 (s, 3H), 2.38 (s, 3H), 7.01–7.14 (m, 1H), 7.19–7.31 (m, 1H), 7.32–7.47 (m, 1H), 7.67 (s, 1H), 8.73 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 24.0, 30.1, 120.9, 125.5, 127.8, 129.3, 129.6, 139.0, 169.3, 195.5. GC-MS (m/z (%)): 209 (27) [M^+], 167 (98), 125 (100), 97 (16), 80 (46).

1-(2-Oxopropyl)piperidin-4-yl acetate[19] (5al). Thick oil. Yield: 88%. IR (KBr, cm^{-1}): ν 778, 1043, 1267, 1670 1745, 3011. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18–1.38 (m, 2H), 1.45–1.64 (m, 2H), 1.72 (s, 3H), 1.76 (s, 3H), 2.96–3.10 (m, 2H), 3.27–3.39 (m, 1H), 3.47–3.60 (m, 1H), 4.56–4.66 (m, 1H). ^{13}C NMR (75 Hz, $CDCl_3$): δ 29.4, 30.2, 37.7, 42.6, 68.4, 168.2, 169.4. GC-MS (m/z (%)): 185 (36) [M^+], 125 (37), 83 (100), 68 (36), 56 (28).

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