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ORIGINAL PAPER

Meglumine: an efficient, biodegradable, and recyclable green catalyst for one-pot synthesis of functionalized dihydropyridines

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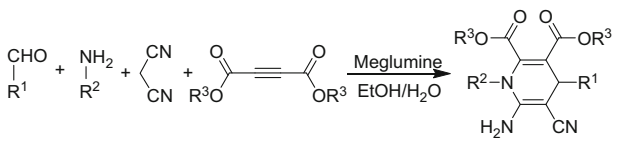
Abstract A green and efficient one-pot synthesis of functionalized dihydropyridines by four-component reaction of aldehydes, amine, malononitrile, and dimethyl acetylenedicarboxylate in presence of meglumine has been developed. The main advantages of this new methodology are reusability of catalyst, simplicity of the starting materials, short reaction time, one-pot and high yields of products.

Graphical abstract



Keywords Multicomponent reaction · Functionalized dihydropyridines · Meglumine · Recyclable catalyst

Introduction

In medicinal chemistry, the synthesis of biologically active molecules is one of the main challenges. Heterocycles constitute the largest diversity of organic molecules of chemical, biomedical, and industrial significance [1–3]. Functionalized dihydropyridines are an important class of biologically active heterocycles [4–7]. Dihydropyridine derivatives have attracted considerable attention because of their wide variety of biological activities, including antihypertension [8], antioxidant [9], anticancer [10], and antitumor activity [11]. Functionalized dihydropyridines are also potential calcium channel antagonists, which are structurally similar to biologically active 4*H*-pyran derivatives [12]. Consequently, various methods have been developed for the synthesis of these compounds [13–17]. Yan et al. [18] have synthesized poly-substituted dihydropyridine derivatives using triethylamine as a base, as well as solvent and catalyst. Pal and coworkers [19, 20] have reported the synthesis of functionalized dihydropyridines used KF/Al_2O_3 or NaOH as catalysts. Pal [21] also has synthesized them with the use of PEG as solvent without catalyst. Kumar and coworker [22] have synthesized the functionalized dihydropyridines under grinding condition without catalyst and solvent. Although these procedures worked nicely in many cases, sometimes, however, some of these procedures are associated with one or more shortcomings such as long reaction time [19–21], toxic solvent and catalyst [18], unsatisfactory yield [19–21], or the lack of generality [22]. Due to the importance of functionalized dihydropyridines from pharmaceutical, industrial, and synthetic points of view, the development of a more practical and economical method for the preparation of these compounds is still highly desirable.

In recent years, the target of science and technology has been shifting more towards environmentally friendly, sustainable resources and reusable catalysts. Some biological catalysts such as chitosan [23–25], cellulose sulfate [26–30], xanthan sulfuric acid [31–35], and starch sulfuric acid [36–38] have been widely used in organic synthesis. However, the number of biological catalyst is still limited

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at this stage. More recently, meglumine as a biological catalyst has been introduced in organic synthesis [39–42]. Meglumine is an amino sugar derived from sorbitol with the IUPAC name of (2*R*,3*R*,4*R*,5*S*)-6-(methylamino)hexane-1,2,3,4,5-pentol. It contains an amino group, primary and secondary hydroxyl groups that can activate the nucleophilic as well as electrophilic components of the reactions by hydrogen bonding and donation of a lone pair of electrons, respectively. Meglumine possesses environmentally benign properties such as bio-degradability, physiological inertness, inexpensiveness, non-corrosivity, stability to air and moisture, and largely available in the market.

Meanwhile, multicomponent reactions (MCRs) represent a highly valuable synthetic tool for the construction of novel and complex molecular structures because of their environmentally friendly, atom economy, and high throughput generation of organic compounds. Multicomponent reactions take significant advantages over conventional stepwise strategies by reducing waste production, saving energy, shortening reaction periods, and avoiding protection and deprotection of functional groups; thus resulting in both economical and environmental benefits [43–60]. Therefore, the development of MCRs using meglumine as catalyst has been considered in our research work. Herein, we report a novel, efficient, and environmentally benign procedure for the synthesis of functionalized dihydropyridines by a one-pot, four-component reaction of aldehydes, amine, malononitrile, and dimethyl acetylenedicarboxylate in the presence of meglumine in aqueous ethanol solution (Scheme 1).

Results and discussion

To optimize the reaction conditions, we conducted the reaction of 4-chlorobenzaldehyde, 4-methylaniline, malononitrile, and dimethyl acetylenedicarboxylate at room temperature in various conditions. As shown in Table 1, in the absence of catalyst, no product was formed. Some commercially available catalysts including DMU, urea, Al_2O_3, Et_3N, CuO, ZnO, CH_3COONa, $NaHCO_3$, K_2CO_3, NaOH, and choline chloride were also tested, in which the product was obtained in low yields. Meglumine was found to be the most effective catalyst for this transformation since it gave the highest yield of product. The efficiency of the catalyst was found to be affected the quantity of the catalyst used in the reaction. It was also found that the use of 10 mmol% meglumine is sufficient to promote the reaction (Table 1, entry 14).

Next, the effects of solvents were evaluated for this model reaction, and the results are summarized in Table 2. As shown in Table 2, the results showed that the efficiency and the yield of the reaction in aqueous ethanol solution were higher than those obtained in other solvents such as H_2O, MeOH, EtOH, and PEG400 or under solvent-free conditions.

To examine the efficiency of this multicomponent reaction, a series of different aldehydes was employed. As shown in Table 3, this protocol can be applied to aromatic aldehydes either with electron-withdrawing groups or electron-donating groups. Furthermore, a series of different substituted aldehydes gave excellent yields. It has been observed that the benzaldehyde with electron-withdrawing groups led to products in shorter reaction time. *Para*-substituted and *meta*-substituted benzaldehyde needed shorter reaction time than those with *ortho*-substituted benzaldehyde. To our disappointment, when aliphatic aldehyde instead of aromatic aldehyde, such as pelargonic aldehyde was subjected to the reaction system in 24 h, no reaction was observed.

Aliphatic amines show less reactivity than aromatic amines for this reaction, for example cyclopropylamine gave the corresponding product in 80 % yield (Table 3, entry 19), whereas 4-methylaniline provided 93 % yield (Table 3, entry 20). Aromatic amines with stronger electron-donor groups showed less reactivity, and more reaction time was required than electron-withdrawing substituents. *Para*-substituted as well as *meta*-substituted amines were found to react well to give the corresponding product in high yields, however, *ortho*-substituted cannot get the products.

Dimethyl and diethyl acetylenedicarboxylate were also tested. As revealed in Table 3, these reactants worked well and furnished the desired products in high yields. To extend

Scheme 1

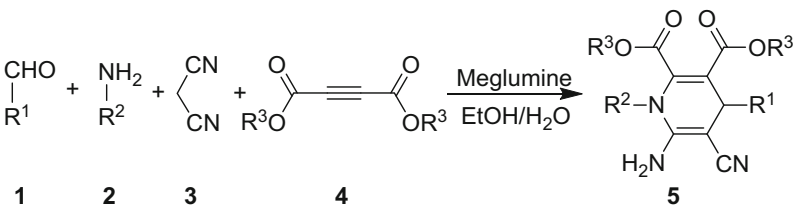


Table 1 Influence of different catalysts for the reaction of 4-chlorobenzaldehyde, 4-methylaniline, malononitrile, and dimethyl acetylenedicarboxylate

Entry	Catalyst	Catalyst loading/mol%	Time/h	Yield/%[a]
1	No [21]		10	0
2	CeO_2	10	10	40
3	DMU	10	10	35
4	K_2CO_3	10	10	80
5	CH_3COONa	10	10	50
6	$NaHCO_3$	10	10	50
7	Urea	10	10	35
8	Choline chloride	10	10	85
9	ZnO	10	10	50
10	CuO	10	10	60
11	NaOH [20]	10	10	85
12	Al_2O_3 [19]	10	10	10
13	Et_3N [18]	10	10	15
14	Meglumine	10	4.5	94
15	Meglumine	5	4.5	90
16	Meglumine	15	4.5	94

Reaction condition: 4-chlorobenzaldehyde (1 mmol), 4-methylaniline (1 mmol), malononitrile (1 mmol), dimethyl acetylenedicarboxylate (1 mmol), catalyst (0.01 mmol)

[a] Yield refers to isolated pure product

Table 2 Optimization of reaction conditions

Entry	Solvent	Time/h	Yield/%[a]
1	No	10	0
2	H_2O	10	0
3	EtOH	10	90
4	PEG400	10	50
5	MeOH	10	80
6	EtOH:H_2O = 9:1	4.5	94

Reaction condition: 4-chlorobenzaldehyde (1 mmol), 4-methylaniline (1 mmol), malononitrile (1 mmol), dimethyl acetylenedicarboxylate (1 mmol), meglumine (0.01 mmol), solvent (3 cm^3)

[a] Yield refers to isolated pure product

the utility and generality of this method, ethyl cyanocaetate was also explored, only 60 % product was observed.

To explain the mechanism of this multicomponent reaction, we proposed a plausible reaction course (Scheme 2). Arylamine was added to acetylenedicarboxylate to give the 1,3-dipole intermediate (**A**). Knoevenagel condensation of aldehyde with malononitrile and meglumine as base catalyst yielded arylidene malononitrile (**B**), and Michael addition of **A** and **B** to give intermediate **C**, followed by migration of the hydrogen atom, intramolecular addition, and tautomerization to give **D**.

In conclusion, we have developed a new, one-pot synthesis of functionalized dihydropyridines by the reaction of aldehydes, amine, malononitrile, and dimethyl acetylenedicarboxylate using meglumine as an efficient, eco-friendly, reusable, and biodegradable catalyst. This method is found to be more advantageous than the previously reported methods. This catalyst could be directly reused at least three additional times.

Experimental

Melting points were determined using an X-4 apparatus. IR spectra were taken as KBr discs using a Bruker-TENSOR 27 spectrometer instrument. NMR spectra were taken with a Bruker DRX-500 spectrometer, using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as an internal standard.

Representative procedure for the synthesis of dimethyl 6-amino-5-cyano-1-(p-tolyl)-4-(4-chlorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate

A solution of 140 mg 4-chlorobenzaldehyde (1.0 mmol), 66 mg malononitrile (1.0 mmol), and meglumine (0.1 mmol) were stirred in 1 cm^3 of aqueous ethanol solution at room temperature. Then, a solution of 107 mg 4-methylaniline (1.0 mmol) and 142 mg dimethyl acetylenedicarboxylate (1.0 mmol) in 2 cm^3 aqueous ethanol solution was added. The resulting mixture was stirred until the reaction was completed as indicated by thin-layer chromatography (TLC). The resulting precipitates were collected by filtration and washed with ethanol. The crude product was purified via recrystallization from ethanol to give pure product.

Dimethyl 6-amino-5-cyano-1-(p-tolyl)-4-[3-(trifluoro methyl)phenyl]-1,4-dihydropyridine-2,3-dicarboxylate (**5d**, $C_{24}H_{20}F_3N_3O_4$)

White solid; m.p.: 117–118 °C; IR (KBr): $\bar{\nu}$ = 3,473, 3,322, 2,188, 1,743, 1,654, 1,225 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 3.47 (s, 3H), 3.61 (s, 3H), 4.15 (s, 2H), 4.74 (s, 1H), 7.21 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.48–7.54 (m, 2H), 7.57 (d, J = 7.5 Hz, 1H), 7.62 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3, 38.6, 52.1, 52.7, 61.7, 104.6, 120.3, 124.1 ($^3J_{CF}$ = 3.75 Hz), 125.3, 127.4 ($^1J_{CF}$ = 270.8 Hz), 129.3, 129.8, 130.6, 130.7, 130.9, 131.1 ($^2J_{CF}$ = 31.6 Hz), 132.1, 141.1, 142.3, 145.8, 150.3, 163.3, 165.5 ppm.

Dimethyl 6-amino-5-cyano-4-(3-phenoxyphenyl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5e**, $C_{29}H_{25}N_3O_5$)

Light green solid; m.p.: 83–85 °C; IR (KBr): $\bar{\nu}$ = 3,467, 3,341, 2,182, 1,710, 1,648, 1,227 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 3.44 (*s*, 3H), 3.61 (s, 3H), 4.08 (s, 2H), 4.62 (s, 1H), 6.91 (dd, J = 8.0,

Table 3 Preparation of functionalized dihydropyridines catalyzed by meglumine

Compounds	Aldehyde	Amine	R^3	Time/h	Yield[a]/%	m.p./°C	
						Found	Reported
5a	4-ClC_6H_4CHO	4-$CH_3C_6H_4NH_2$	Me	4.5	94	197–198	188–189 [16]
5b	4-$CH_3OC_6H_4CHO$	4-$CH_3C_6H_4NH_2$	Me	5.5	93	182–183	168–169 [16]
5c	3-ClC_6H_4CHO	4-$CH_3C_6H_4NH_2$	Me	4	90	180–182	181–182 [16]
5d	3-$CF_3C_6H_4CHO$	4-$CH_3C_6H_4NH_2$	Me	3.5	93	117–118	
5e	3-$PhOC_6H_4CHO$	4-$CH_3C_6H_4NH_2$	Me	6	90	83–85	
5f	Furan-2-carbaldehyde	4-$CH_3C_6H_4NH_2$	Me	4	93	186–188	
5g	Thiophen-2-carbaldehyde	4-$CH_3C_6H_4NH_2$	Me	4	95	164–166	
5h	Pyridin-4-carbaldehyde	4-$CH_3C_6H_4NH_2$	Me	3.5	95	151–152	
5i	Naphthalene-1-carbaldehyde	4-$CH_3C_6H_4NH_2$	Me	6.5	90	260–262	
5j	2-ClC_6H_4CHO	4-$CH_3C_6H_4NH_2$	Me	5	93	213–215	
5k	2-$CH_3OC_6H_4CHO$	4-$CH_3C_6H_4NH_2$	Me	6	90	192–194	
5l	2,4-$Cl_2C_6H_3CHO$	4-$CH_3C_6H_4NH_2$	Me	8	92	288–290	
5m	2,3,4-$(MeO)_3C_6H_2CHO$	4-$CH_3C_6H_4NH_2$	Me	8.5	90	210–212	
5n	4-ClC_6H_4CHO	4-$CH_3OC_6H_4NH_2$	Me	5	90	185–187	173–174 [16]
5o	4-ClC_6H_4CHO	4-$BrC_6H_4NH_2$	Me	3.5	90	181–183	
5p	4-ClC_6H_4CHO	3-$CH_3OC_6H_4NH_2$	Me	5	91	173–175	
5q	4-ClC_6H_4CHO	3-$ClC_6H_4NH_2$	Me	4	92	122–123	120–121 [16]
5r	4-ClC_6H_4CHO	1-Naphthylamine	Me	4.5	90	192–193	
5s	4-ClC_6H_4CHO	Cyclopropylamine	Me	3	80	154–156	
5t	3-$NO_2C_6H_4CHO$	4-$CH_3C_6H_4NH_2$	Me	4.5	93	210–212	213–214 [16]
5u	4-$CH_3(CH_2)_4OC_6H_4CHO$	4-$CH_3C_6H_4NH_2$	Et	5	90	148–149	
5v	3-FC_6H_4CHO	4-$CH_3C_6H_4NH_2$	Et	4	92	101–102	
5w	3-$CF_3C_6H_4CHO$	4-$CH_3C_6H_4NH_2$	Et	3.5	93	215–216	
5x	4-$(CH_3)_3CC_6H_5CHO$	4-$CH_3C_6H_4NH_2$	Et	4	90	112–113	
5y	6-Nitrobenzo[*d*] [1, 3] dioxol-5-carbaldehyde	4-$CH_3C_6H_4NH_2$	Et	6	87	229–231	
5z	4-ClC_6H_4CHO	4-$PhOC_6H_4NH_2$	Et	6	90	161–163	
5aa	4-ClC_6H_4CHO	3-$CH_3C_6H_4NH_2$	Et	5	92	76–78	
5ab	4-ClC_6H_4CHO	9H-Fluoren-2-amine	Me	6.5	91	288–289	
5ac	4-$(CH_3)_3CC_6H_5CHO$	4-$CH_3OC_6H_4NH_2$	Me	4.5	93	240–242	

[a] Yields refer to isolated products

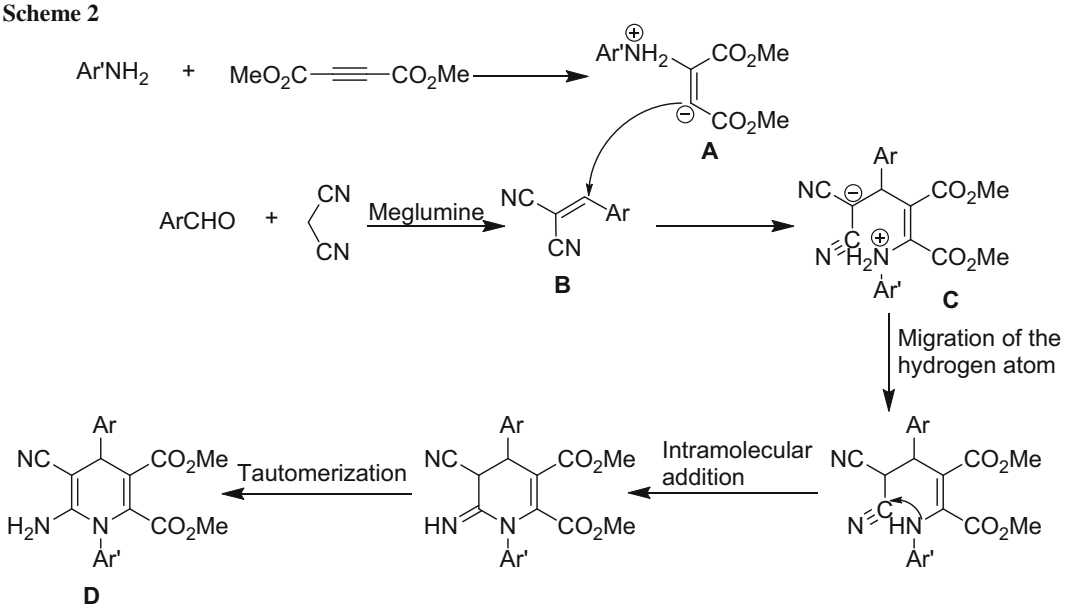
1.5 Hz, 1H), 7.02 (s, 1H), 7.07–7.15 (m, 6H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3, 38.5, 52.0, 52.6, 62.0, 104.9, 117.1, 117.4, 119.3, 120.6, 121.9, 123.6, 129.8, 129.9, 130.0, 130.5, 132.2, 140.9, 141.9, 147.0, 150.1, 156.9, 157.8, 163.5, 165.7$ ppm.

Dimethyl 6-amino-5-cyano-4-(furan-2-yl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5f**, $C_{21}H_{19}N_3O_5$)
Red solid; m.p.: 186–188 °C; IR (KBr): $\overline{\nu} = 3{,}472, 3{,}341, 2{,}178, 1{,}743, 1{,}642, 1{,}250$ cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.40$ (s, 3H), 3.47 (s, 3H), 3.69 (s, 3H), 4.15 (s, 2H), 4.78 (s, 1H), 6.17 (s, 1H), 6.32 (s, 1H), 7.22–7.25 (m, 4H), 7.38 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 21.3, 32.3, 52.1, 52.6, 59.1, 103.0, 105.4, 110.4, 120.5, 129.9, 130.6, 132.5, 140.9, 142.2, 142.2, 151.2, 156.0, 163.5, 165.6$ ppm.

Dimethyl 6-amino-5-cyano-4-(thiophen-2-yl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5g**, $C_{21}H_{19}N_3O_4S$)
White solid; m.p.: 164–166 °C; IR (KBr): $\overline{\nu} = 3{,}422, 3{,}336, 2{,}187, 1{,}751, 1{,}573, 1{,}230$ cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.40$ (s, 3H), 3.46 (*s*, 3H), 3.71 (s, 3H), 4.17 (s, 2H), 4.98 (s, 1H), 6.95–6.97 (m, 1H), 6.99 (d, $J = 3.5$ Hz, 1H), 7.20–7.24 (m, 3H), 7.28 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3, 33.6, 52.1, 52.6, 62.2, 105.5, 120.4, 123.8, 124.5, 127.2, 129.9, 130.6, 132.3, 141.0, 141.4, 149.6, 150.4, 163.4, 165.5$ ppm.

Dimethyl 6-amino-5-cyano-1-(p-tolyl)-1,4-dihydro-4,4′-bipyridine-2,3-dicarboxylate (**5h**, $C_{22}H_{20}N_4O_4$)
White solid; m.p.: 151–152 °C; IR (KBr): $\overline{\nu} = 3{,}568, 3{,}463, 2{,}180, 1{,}747, 1{,}649, 1{,}226$ cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H), 3.48 (s, 3H), 3.60

Scheme 2



(s, 3H), 4.16 (s, 2H), 4.68 (s, 1H), 7.02–7.21 (m, 2H), 7.29–7.30 (m, 4H), 8.61–8.63 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3$, 38.1, 52.2, 52.7, 60.5, 103.4, 120.2, 122.0, 129.8, 130.6, 132.0, 141.2, 143.0, 150.3, 150.5, 153.1, 163.2, 165.5 ppm.

Dimethyl 6-amino-5-cyano-4-(naphthalene-2-yl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5i**, $C_{27}H_{20}N_3O_4$)
White solid; m.p.: 260–262 °C; IR (KBr): $\overline{\nu} = 3{,}457$, 3,366, 2,183, 1,745, 1,705, 1,644, 1,572, 1,202 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H), 3.42 (s, 3H), 3.51 (s, 3H), 4.03 (s, 2H), 5.60 (s, 1H), 7.27–7.32 (m, 4H), 7.49–7.56 (m, 2H), 7.56 (d, $J = 6.0$ Hz, 1H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.87 (d, $J = 8.5$ Hz, 1H), 8.47 (d, $J = 8.5$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3$, 33.2, 51.9, 52.7, 62.9, 105.5, 120.7, 123.5, 125.5, 125.8, 125.9, 126.3, 127.9, 128.6, 130.0, 130.6, 130.8, 132.4, 134.0, 141.0, 141.8, 142.4, 150.0, 163.7, 165.9 ppm.

Dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5j**, $C_{23}H_{20}ClN_3O_4$)
White solid; m.p.: 213–215 °C; IR (KBr): $\overline{\nu} = 3{,}473$, 3,377, 2,180, 1,745, 1,645, 1,251 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H), 3.45 (s, 3H), 3.55 (s, 3H), 4.07 (s, 2H), 5.29 (s, 1H), 7.17–7.20 (m, 1H), 7.24 (m, 2H), 7.28–7.31 (m, 3H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.42 (dd, $J = 7.5$, 1.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3$, 35.7, 51.9, 52.6, 61.2, 104.0, 120.3, 127.5, 128.3, 129.9, 130.0, 130.7, 132.2, 132.7, 141.0, 142.4, 142.8, 150.3, 163.5, 165.7 ppm.

Dimethyl 6-amino-5-cyano-4-(2-methoxyphenyl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5k**, $C_{24}H_{23}N_3O_5$)
White solid; m.p.: 192–194 °C; IR (KBr):$\overline{\nu} = 3{,}441$, 3,319, 2,188, 1,747, 1,701, 1,251 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.40$ (s, 3H), 3.50 (s, 3H), 3.56 (s, 3H), 3.92 (s, 3H), 4.00 (s, 2H), 5.11 (s, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H),7.20–7.27 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3$, 32.2, 51.9, 52.6, 55.8, 62.2, 104.2, 111.4, 120.9, 127.9, 128.2, 129.9, 130.5, 132.7, 132.9, 140.7, 142.9, 150.4, 156.8, 163.9, 166.0 ppm.

Dimethyl 6-amino-5-cyano-4-(2,4-dichlorophenyl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5l**, $C_{23}H_{19}Cl_2N_3O_4$)
White solid; m.p.: 288–290 °C; IR (KBr): $\overline{\nu} = 3{,}467$, 3,367, 2,182, 1,740, 1,648, 1,253 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H), 3.47 (s, 3H), 3.56 (s, 3H), 4.08 (s, 2H), 5.24 (s, 1H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.28–7.30 (m, 3H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.40 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 21.3$, 35.6, 52.1, 52.7, 61.3, 103.7, 119.9, 127.8, 129.7, 130.0, 130.6, 130.8, 132.1, 133.3, 140.9, 141.2, 142.9, 150.0, 163.3, 165.4 ppm.

Dimethyl 6-amino-5-cyano-1-(p-tolyl)-4-(2,3,4-trimethoxy phenyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5m**, $C_{26}H_{27}N_3O_7$)
White solid; m.p.: 210–212 °C; IR (KBr): $\overline{\nu} = 3{,}423$, 3,323, 2,188, 1,747, 1,654, 1,223 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.41$ (s, 3H), 3.47 (s, 3H), 3.57 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 3.99 (s, 2H), 4.01 (s,

3H), 4.95 (s, 1H), 6.68 (d, $J = 9.0$ Hz, 1H), 6.98 (*d*, $J = 8.5$ Hz, 1H), 7.24–7.29 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3$, 33.0, 51.9, 52.5, 55.9, 60.7, 61.5, 62.6, 104.7, 107.3, 120.9, 123.1, 129.9, 130.5, 130.8, 132.6, 140.7, 142.1, 142.2, 149.9, 151.5, 152.8, 163.8, 166.0 ppm.

Dimethyl 6-amino-1-(4-bromophenyl)-4-(4-chlorophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate
(**5o**, $C_{22}H_{17}BrClN_3O_4$)
White solid; m.p.: 181–183 °C; IR (KBr): $\overline{\nu} = 3{,}470$, 3,336, 2,184, 1,717, 1,654, 1,224 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.50$ (s, 3H), 3.60 (s, 3H), 4.05 (s, 2H), 4.66 (s, 1H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 38.0$, 52.2, 52.9, 63.2, 105.3, 119.9, 125.2, 128.4, 129.1, 131.8, 133.1, 133.4, 134.0, 141.5, 143.0, 149.2, 163.3, 165.4 ppm.

Dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(3-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5p**, $C_{23}H_{20}ClN_3O_5$)
White solid; m.p.: 173–175 °C; IR (KBr): $\overline{\nu} = 3{,}475$, 3,352, 2,179, 1,702, 1,647, 1,265 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.50$ (s, 3H), 3.60 (s, 3H), 3.84 (s, 3H), 4.16 (s, 2H), 4.66 (s, 1H), 6.84 (s, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 7.03 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.29 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.39 (t, $J = 8.0$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 38.1$, 52.1, 52.7, 55.7, 61.9, 104.8, 115.7, 116.3, 120.5, 122.0, 128.5, 128.9, 130.6, 132.9, 135.9, 141.9, 143.4, 149.9, 160.5, 163.4, 165.6 ppm.

Dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(naphthalene-1-yl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5r**, $C_{26}H_{20}ClN_3O_4$)
White solid; m.p.: 192–193 °C; IR (KBr): $\overline{\nu} = 3{,}420$, 3,324, 2,178, 1,747, 1,709, 1,644, 1,228 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.24$ (s, 3H), 3.60 (s, 3H), 3.84 (s, 3H), 4.06 (s, 2H), 4.86 (s, 1H), 7.38–7.46 (m, 4H), 7.51–7.62 (m, 4H), 7.77 (dd, $J = 9.0$, 2.0 Hz, 1H, HAr), 7.93 (dd, $J = 6.0$, 2.0 Hz, 1H, HAr), 8.00 (dd, $J = 7.0$, 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 38.1$, 52.1, 52.5, 61.9, 104.6, 120.6, 122.1, 125.0, 127.5, 128.3, 128.5, 128.6, 128.9, 129.1, 131.2, 131.4, 133.0, 134.3, 142.9, 143.3, 150.1, 163.3, 165.7 ppm.

Dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-cyclopropyl-1,4-dihydropyridine-2,3-dicarboxylate
(**5s**, $C_{19}H_{18}ClN_3O_4$)
White solid; m.p.: 154–156 °C; IR (KBr): $\overline{\nu} = 3{,}356$, 3,284, 2,359, 1,669, 1,050 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.79$–0.82 (m, 1H), 0.90–0.96 (m, 2H), 1.03–1.07 (m, 1H), 2.83–2.86 (m, 1H), 3.67 (s, 3H), 3.92 (s, 3H), 4.47 (s, 1H), 4.70 (s, 2H), 7.09 (dd, $J = 8.5$, 2.5 Hz, 2H), 7.25–7.26 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 8.8$, 9.8, 27.5, 37.4, 52.3, 53.2, 61.7, 107.7, 120.5, 127.8, 128.9, 132.8, 142.3, 143.4, 153.0, 164.0, 165.3 ppm.

Diethyl 6-amino-5-cyano-4-(4-pentyloxyphenyl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5u**, $C_{30}H_{35}N_3O_5$)
White solid; m.p.: 148–149 °C; IR (KBr): $\overline{\nu} = 3{,}465$, 3,369, 2,185, 1,735, 1,643, 1,227 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.92$–0.98 (m, 6H), 1.13 (t, 3H), 1.36–1.46 (m, 4H), 1.75–1.81 (m, 2H), 2.40 (s, 3H), 3.85–3.96 (m, 4H), 4.02–4.06 (m, 4H), 4.62 (s, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.26–7.28 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.5$, 13.9, 14.1, 21.3, 22.5, 28.2, 29.0, 37.9, 60.8, 61.9, 68.0, 105.5, 114.6, 120.9, 128.3, 130.2, 130.4, 132.6, 137.3, 140.8, 141.4, 149.7, 158.2, 163.2, 165.3 ppm.

Diethyl 6-amino-5-cyano-4-(3-fluorophenyl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5v**, $C_{25}H_{24}FN_3O_4$)
White solid; m.p.: 101–102 °C; IR (KBr): $\overline{\nu} = 3{,}406$, 3,329, 2,184, 1,716, 1,653, 1,418, 1,221 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.5$ Hz, 3H), 1.11 (t, $J = 7.0$ Hz, 3H), 2.41 (t, 3H), 3.88–4.06 (m, 4H), 4.09 (s, 2H), 4.69 (s, 1H), 6.96 (t, $J = 8.0$ Hz, 1H), 7.08 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 7.23–7.25 (m, 1H), 7.28–7.33 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.4$, 13.8, 21.2, 38.4, 60.9, 61.9, 62.1, 104.7, 113.9, 114.0, 114.1, 114.2 ($^3J_{CF} = 9.0$ Hz), 120.3, 122.9, 130.1, 130.5, 132.2, 141.0, 141.9, 147.5, 147.6, 149.8, 162.9, 162.1, 164.1($^1J_{CF} = 245.0$ Hz), 164.9 ppm.

Diethyl 6-amino-5-cyano-1-(p-tolyl)-4-[3-(trifluoromethyl)phenyl]-1,4-dihydropyridine-2,3-dicarboxylate
(**5w**, $C_{26}H_{24}F_3N_3O_4$)
White solid; m.p.: 215–216 °C; IR (KBr): $\overline{\nu} = 3{,}469$, 3,309, 2,189, 1,740, 1,654, 1,222 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.0$ Hz, 3H), 1.11 (t, $J = 7.0$ Hz, 3H), 2.41 (s, 3H), 3.80–4.10 (m, 4H), 4.13 (s, 2H), 4.74 (s, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.41–7.53 (m, 2H), 7.57 (d, $J = 7.5$ Hz, 1H), 7.63 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.4$, 13.8, 21.2, 38.7, 61.0, 61.3, 62.0, 104.6, 120.5, 124.0, 124.1 ($^3J_{CF} = 4.0$ Hz), 123.1, 125.3 ($^1J_{CF} = 270.9$ Hz), 129.3, 130.1, 130.6, 130.8, 132.1, 141.1, 142.2, 146.1, 150.4, 162.8, 164.9 ppm.

Diethyl 6-amino-4-[4-(tert-butyl)phenyl]-5-cyano-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate
(**5x**, $C_{29}H_{33}N_3O_4$)
White solid; m.p.: 112–113 °C; IR (KBr): $\overline{\nu} = 3{,}428$, 3,328, 2,185, 1,742, 1,649, 1,226 cm^{-1}; ^{1}H NMR

(500 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.0$ Hz, 3H), 1.11 (t, $J = 7.0$ Hz, 3H), 1.32 (s, 9H), 2.41 (s, 3H), 3.85–4.07 (m, 6H), 4.65 (s, 1H), 7.23–7.30 (m, 6H), 7.36 (d, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.5$, 13.9, 21.3, 31.4, 34.5, 38.1, 60.8, 61.9, 62.8, 105.5, 125.6, 126.8, 130.2, 130.4, 132.6, 131.5, 140.8, 141.5, 142.0, 149.7, 149.8, 163.2, 165.3 ppm.

Diethyl 6-amino-5-cyano-4-(6-nitrobenzo[d][1, 3]dioxol-5-yl)-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5y**, $C_{26}H_{24}N_4O_8$)

Brown solid; m.p.: 229–231 °C; IR (KBr): $\overline{\nu} = 3{,}441$, 3,327, 2,185, 1,727, 1,680, 1,222 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.5$ Hz, 3H), 1.03 (t, $J = 7.0$ Hz, 3H), 2.42 (s, 3H), 3.86–3.98 (m, 4H), 4.17 (s, 2H), 5.62 (s, 1H), 6.12 (s, 2H), 7.03 (s, 1H), 7.28–7.31 (m, 4H), 7.35 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.4$, 13.7, 21.3, 33.5, 61.1, 62.1, 102.9, 104.5, 104.7, 109.4, 119.9, 130.2, 130.5, 131.9, 137.2, 141.2, 142.4, 142.5, 146.8, 150.5, 151.9, 162.7, 164.7 ppm.

Diethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(4-phenoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5z**, $C_{30}H_{26}ClN_3O_5$)

White solid; m.p.: 161–163 °C; IR (KBr): $\overline{\nu} = 3{,}457$, 3,331, 2,192, 1,739, 1,651, 1,220 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.03$ (t, $J = 7.0$ Hz, 3H), 1.11 (t, $J = 7.0$ Hz, 3H), 3.90–4.06 (m, 4H), 4.12 (s, 2H), 4.66 (s, 1H), 7.04 (d, $J = 8.5$ Hz, 4H), 7.22 (d, $J = 7.5$ Hz, 1H), 7.27–7.34 (m, 6H), 7.41 (d, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.6$, 13.9, 38.3, 60.9, 61.9, 62.1, 104.9, 118.5, 120.1, 120.6, 124.9, 128.6, 128.8, 128.9, 130.2, 131.9, 132.8, 142.0, 143.6, 150.1, 155.4, 159.5, 162.9, 165.0 ppm.

Diethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(m-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5aa**, $C_{25}H_{24}ClN_3O_4$)

White solid; m.p.: 76–78 °C; IR (KBr): $\overline{\nu} = 3{,}418$, 3,355, 2,185, 1,751, 1,669, 1,203 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.5$ Hz, 3H), 1.13 (t, $J = 7.5$ Hz, 3H), 2.43 (s, 3H), 3.87–3.98 (m, 2H), 4.06 (dd, $J = 7.5$, 7.0 Hz, 2H), 4.15 (s, 2H), 4.69 (s, 1H), 7.18 (s, 2H), 7.32–7.39 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.4$, 13.9, 21.2, 29.7, 38.3, 60.9, 61.9, 104.8, 120.6, 127.3, 128.6, 128.8, 129.7, 130.9, 131.3, 132.8, 134.9, 140.3, 141.8, 143.7, 149.9, 162.9, 165.0 ppm.

Dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(9H-fluoren-2-yl)-1,4-dihydropyridine-2,3-dicarboxylate (**5ab**, $C_{29}H_{22}ClN_3O_4$)

White solid; m.p.: 288–289 °C; IR (KBr): $\overline{\nu} = 3{,}441$, 3,327, 2,180, 1,749, 1,708, 1,654, 1,570, 1,254 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.44$ (s, 3H), 3.61 (s, 3H), 3.97 (s, 2H), 4.16 (s, 2H), 4.67 (s, 1H), 7.32–7.44 (m, 7H), 7.50 (s, 1H), 7.61 (d, $J = 7.5$ Hz, 1H), 7.82–7.87 (m, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 37.0$, 38.7, 52.4, 52.9, 59.5, 104.3, 121.2, 121.4, 125.8, 127.5, 128.1, 129.1, 129.2, 129.3, 132.0, 134.0, 140.4, 142.8, 143.1, 144.2, 144.7, 145.0, 151.5, 163.4, 165.5 ppm.

Dimethyl 6-amino-4-[4-(tert-butyl)phenyl]-5-cyano-1-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5ac**, $C_{27}H_{29}N_3O_5$)

White solid; m.p.: 240–242 °C; IR (KBr): $\overline{\nu} = 3{,}471$, 3,309, 2,189, 1,654, 1,576, 1,223 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.32$ (s, 9H), 3.48 (s, 3H), 3.61 (s, 3H), 3.85 (s, 3H), 4.06 (s, 2H), 4.63 (s, 1H), 6.96 (d, $J = 8.5$ Hz, 2H), 7.25–7.29 (m, 4H), 7.37 (d, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 31.4$, 34.5, 37.8, 52.0, 52.6, 55.6, 62.8, 105.2, 114.9, 120.8, 125.7, 126.6, 127.3, 131.5, 141.8, 142.0, 149.8, 150.0, 160.7, 163.7, 165.9 ppm.

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