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Hydroalkylation leading to heterocyclic compounds (Part 2): practical synthesis of polysubstituted 1,2,3,4-tetrahydropyridines through multicomponent reactions (MCRs)

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ABSTRACT

Polysubstituted 1,2,3,4-tetrahydropyridines were synthesized through hydroalkylation of electron-deficient alkynes, followed by double Mannich addition reactions, which is a practical protocol with atom efficiency and good substrate scope.

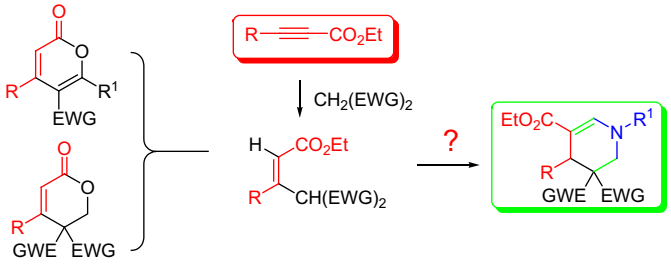
1. Introduction

Small heterocyclic molecules are one of the predominant types of building block of biologically active compounds and designed medicinal agents in medicinal chemistry.[1] Especially, nitrogen containing heterocycles are prevalent in many drugs,[2] thus synthetic chemists are increasingly motivated to discover new methods for rapid construction of pharmacologically important drug-like compounds.[3] As part of the research interest to construct the small heterocyclic molecules in our laboratory,[4] a variety of nitrogen containing heterocycles have been successfully achieved via hydroamination of electron-deficient alkynes and primary amines with interesting cyclization reaction.[5]

In view of the convergent and modular nature of our previous hydroamination, we planned and investigated the hydroalkylation of electron-deficient alkynes with activated methylenes to synthesize various oxygen and nitrogen containing heterocycles. Previously, we have successfully synthesized a range of oxygen containing heterocycles,[6] such as 2*H*-pyran-2-ones and 5,6-dihydro-2*H*-pyran-2-ones through different multicomponent reactions (MCRs).[7] In this part, we will report a practical procedure to prepare multisubstituted 1,2,3,4-tetrahydropyridines through MCRs combined hydroalkylation with double Mannich reaction in one pot (Scheme 1).

2. Results and discussion

To start the research, we used diethyl but-2-ynedioate, malononitrile, formaldehyde, and benzylamine as the model reaction to systematically evaluate the reaction conditions (Table 1). Using NaOH as the base and 1,4-dioxane as the solvent, the product tetrahydropyridine could be formed in 4% GC yields (Table 1, entry 1). According to the ^{1}H, ^{13}C NMR spectra, the product is 1,2,3,4-tetrahydropyridine, which isomerized from the expected product 1,2,5,6-tetrahydropyridine. This isomerization is consistent with the similar results reported by Fowler and Cook.[8,9]



Scheme 1. Synthesis of six-membered heterocycles based on alkynoates.

Both the bases and solvents posed significant influence to the reaction results. When the reaction was conducted in dioxane at room temperature (Table 1, entries 1–6), different bases furnish large difference. Sodium acetate (CH_3CO_2Na) is the base of choice, affording the product in 50% GC yield (Table 1, entry 4). While other bases, like Na_2CO_3, Et_3N, NaOH, and EtONa were much less efficient, furnishing the desired product with less than 22% yields (Table 1, entries 1–3 and 5). To exclude the background reaction, we also set a control reaction without addition of the base (Table 1, entry 6), no desired product was detected. It was also found that the suitable solvents for this reaction are dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) (Table 1, entries 8 and 9). The desired product decreased dramatically when the reaction was performed

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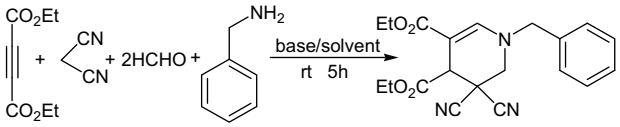
Table 1
Optimization of reaction conditions[a]



Entry	Additive	Solvent	*t*(h)	Yield (%)[b]
1	Et_3N	Dioxane	5	4
2	NaOH	Dioxane	5	4
3	Na_2CO_3	Dioxane	5	22
4	CH_3CO_2Na	Dioxane	5	50
5	EtONa	Dioxane	5	11
6	None	Dioxane	5	none
7	CH_3CO_2Na	CH_3CN	5	56
8	CH_3CO_2Na	DMF	5	83
9	CH_3CO_2Na	DMSO	5	90
10	CH_3CO_2Na	THF	5	50
11	CH_3CO_2Na	Toluene	5	31
12[c]	CH_3CO_2Na	DMSO	5	6
13[d]	CH_3CO_2Na	DMSO	5	30
14[e]	CH_3CO_2Na	DMSO	5	96

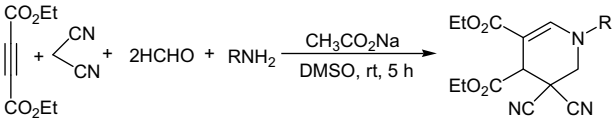
[a] All the reactions were carried out using 0.25 mmol of but-2-ynedioic acid diethyl ester, 0.25 mmol of malononitrile, 0.5 mmol of formaldehyde, 0.25 mmol of benzylamine, and 1 equiv of base in solvent (6.0 mL).
[b] GC yield.
[c] CH_3CO_2Na (10 mol%).
[d] CH_3CO_2Na (30 mol%).
[e] CH_3CO_2Na (2 equiv).

in tetrahydrofuran (THF), acetonitrile, and toluene (Table 1, entries 7, 10 and 11). There was evident difference when the amount of sodium acetate (CH_3CO_2Na) was employed in 10 mol%, 30 mol% and 200 mol%, the product yield was increasing accordingly from 6% to 96% (Table 1, entries 12–14).

Based on the optimized reaction conditions, the substrate scope of the MCRs system was then examined. In addition to benzylamine, which was a good substrate for this MCRs reaction to form the corresponding tetrahydropyridines, as shown in Table 2, the aromatic amines with electron-withdrawing, electron-donating, and electron-neutral substituted groups except 4-methoxy- and 3,4-dimethyl-aromatic amines, proceeded smoothly to furnish the corresponding polysubstituted tetrahydropyridines in moderate to excellent yields (Table 2, entries 2–6, 12, 13). Electron-rich aromatic amines were less reactive for this reaction. For example, *p*-toluidine and *o*-toluidine afforded 40, 45% isolated yields, respectively (Table 2, entry 5), and the 3,4-dimethylbenzenamine and methoxybenzenamine resulted only trace desired product (Table 2, entries 12, 13). Aliphatic amines, which were typically less reactive substrate compared with aromatic amines, were converted into the desired products in moderate to good yield as well (Table 2, entries 1, 6–11). However, when other types of electron-deficient alkynes, such as ethyl 3-phenylpropiolate and methyl oct-2-ynoate, are used as partners of diethyl but-2-ynedioate in the reaction, it resulted in no desired products. Except formaldehyde, other kinds of aldehydes, such as acetaldehyde, propanal, benzaldehyde, 4-nitrobenzaldehyde, 4-iodobenzaldehyde, 2-iodobenzaldehyde, were also examined, and unfortunately, all gave trace products.

On the basis of all the results obtained, we proposed a plausible mechanism for the MCRs, as outlined in Scheme 2. The overall transformation commenced from the highly active carbon anion, which was formed from malononitrile during the reaction course in the presence of the base, and the nucleophilic attack of carbanion on the C–C triple bond in but-2-ynedioic acid diethyl ester to form Michael adduct product **I**, which reacted with formaldehyde and amines and underwent double Mannich reactions lead to the formation of linear intermediate **II** and cyclic intermediate **III**, then in the basic conditions, the latter was isomerized to the final product.

Table 2
Synthesis of multisubstituted 1,2,3,4-tetrahydropyridines[a]



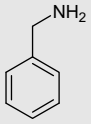
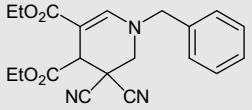
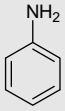
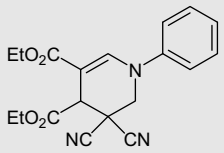
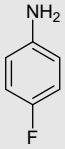
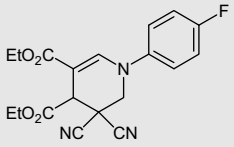
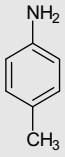
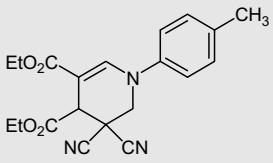
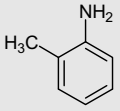
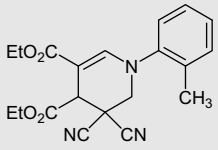
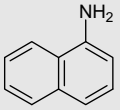
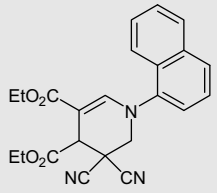
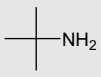
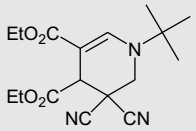
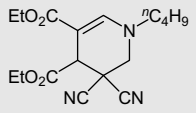
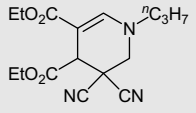
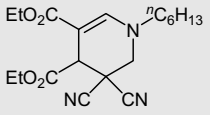
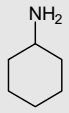
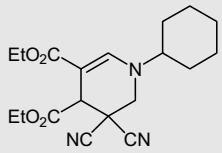
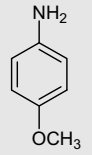
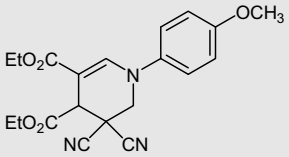
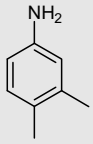
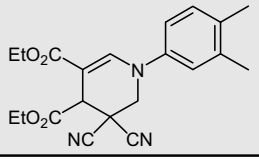
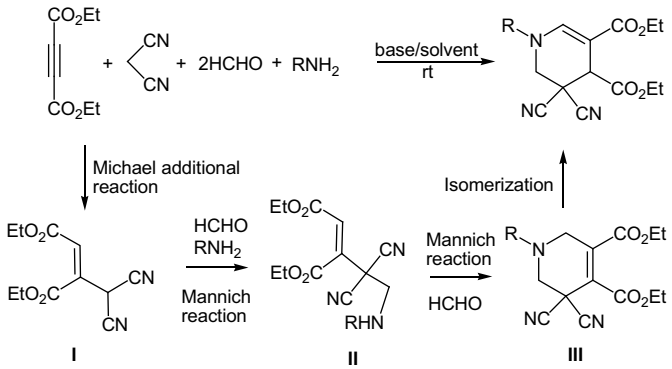
Entry	RNH_2	Product	Yield (%)[b]
1			90
2			92
3			78
4			40
5			45
6			89
7			60
8	$^nC_4H_9NH_2$		57
9	$^nC_3H_7NH_2$		55
10	$^nC_6H_{13}NH_2$		62

Table 2 (*continued*)

Entry	RNH_2	Product	Yield (%)[b]
11			59
12			Trace
			Trace

[a] All the reactions were carried out using 1 mmol of but-2-ynedioic acid diethyl ester, 1 mmol of malononitrile, 2 mmol of formaldehyde, 1 mmol of amineand 2 equiv of AcONa in DMSO (6.0 mL) at room temperature for the desired reaction time.

[b] Isolated yield.



Scheme 2. Proposed route to synthesize 1,2,3,4-tetrahydropyridine derivatives.

It was not very clear why the aniline with electron-donating groups in the reaction afforded the unsatisfied results and further research was needed.

3. Conclusion

In summary, we have described a novel sodium acetate-promoted five-component synthesis of 1,2,3,4-tetrahydropyridines from readily accessible starting materials. It allows the direct introduction of ester and nitrile functionalities onto the tetrahydropyridine skeleton with atom efficiency, operational simplicity, and good yields. To the best of our knowledge, this represented a typical hydroalkylation reaction of electron-deficient alkynes leading to synthesis of highly functionalized nitrogen containing heterocycle compounds and the strategy of hydroalkylation of electron-deficient alkynes hold the potential to construct of various heterocyclic compounds.

4. Experimental

4.1. General

All the reactions were carried out under air atmosphere in a round bottom flask equipped with magnetic stir bar. Solvents and all reagents were used as received. ^{1}H NMR spectra were recorded in CD_3COCD_3 at 400 MHz and ^{13}C NMR spectra were recorded in CD_3COCD_3 at 100 MHz in Guangzhou Institute of Chemistry, Chinese Academy of Sciences. Respectively, the chemical shifts (d) were referenced to TMS. GC–MS was obtained using electron ionization (EI). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucher Vector 22 spectrometer. TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

4.2. Typical procedure for the reaction of but-2-ynedioic acid diethyl ester, malononitrile, formaldehyde, and benzylamine (Table 2, entry 1)

To a mixture of but-2-ynedioic acid diethyl ester (170 mg, 1 mmol) and malononitrile (66 mg, 1 mmol), AcONa (164 mg, 2 mmol) and 6 ml of DMSO were added successively, under air atmosphere with stirring in a round bottom flask. The reaction was kept at air atmosphere for 2 h, after which time 35% formaldehyde (86 mg, 1 mmol) was added to the resulting reaction mixture. The reaction was kept at air atmosphere for 1 h and then, added benzylamine (107 mg, 1 mmol) to the reaction system, after reacting for 1 h, the 35% formaldehyde (86 mg, 1 mmol) was added dropwise to the system to continue to react for 1 h. After completion of the reaction, the solvent was diluted with water and extracted with diethyl ether. The ether layer was washed with saturated salt water, and dried with anhydrous $MgSO_4$. The resulting mixture was then analyzed by GC and GC–MS. Volatiles were removed under reduced pressure and the crude product was subjected to isolation by PTLC (GF_{254}), eluted with a 10:1 petroleum ether/diethyl ether mixture to afford the desired product diethyl 1-benzyl-5,5-dicyano-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate.

4.2.1. Diethyl 1-benzyl-5,5-dicyano-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate(Table 2, entry 1). Yellow viscous oil, IR ν_{max} (KBr): 2192, 1726, 1626, 1516, 1454, 1367, 1271, 1165, 1087, 989, 854, 738, 698 cm^{-1}; ^{1}H NMR (400 MHz, CD_3COCD_3): δ ppm=7.93 (s, 1H), 7.25–7.41 (m, 5H), 4.80–4.66 (q, 2H, J=15.2), 4.33 (s, 1H), 4.21–4.04 (m, 5H), 3.97 (d, 1H), 1.23 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=170.3, 166.2, 146.2, 136.6, 129.7, 129.0, 128.9, 114.1, 113.7, 90.6, 62.7, 60.2, 59.8, 48.3, 44.5, 31.7, 14.7, 14.3; GC–MS m/z (% rel inten.): 368.08 (M^+, 10.83), 90.9 (100). Anal. Calcd for $C_{20}H_{21}N_3O_4$: C, 65.38; H, 5.76; N, 11.44. Found: C, 65.30; H, 5.80; N, 11.38.

4.2.2. Diethyl 5,5-dicyano-1-phenyl-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 2). Colorless crystals; mp: 132–133 °C, IR ν_{max} (KBr): 2982, 2262, 1730, 1686, 1628, 1593, 1496, 1456, 1394, 1373, 1195, 1159, 1098, 990, 943, 763, 695 cm^{-1}; ^{1}H NMR (400 MHz, CD_3COCD_3): δ ppm=8.03 (s, 1H), 7.49–7.24 (m, 5H), 4.75–4.53 (q, 2H, J=15.2), 4.43 (s, 1H), 4.30–4.13 (m, 4H), 1.28 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=170.0, 166.0, 145.4, 141.8. 130.6, 126.2, 120.8, 113.8, 113.3, 96.7, 63.0, 60.7, 49.6, 45.1, 32.3, 14.6, 14.3; GC–MS m/z (% rel inten.): 353.10 (M^+, 29.96), 280.07 (100). Anal. Calcd for $C_{19}H_{19}N_3O_4$: C, 64.58; H, 5.42; N, 11.89. Found: C, 64.57; H, 5.44; N, 11.99.

4.2.3. Diethyl 5,5-dicyano-1-(4-fluorophenyl)-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 3). Colorless crystals; mp: 141–142 °C, IR ν_{max} (KBr): 2262, 1730, 1678, 1629, 1510, 1454, 1421, 1374, 1278, 1221, 1192, 1093, 988, 840, 787, 717 cm^{-1}; ^{1}H NMR (400 MHz, CD_3COCD_3): δ ppm=7.96 (s, 1H), 7.45–7.23 (m, 4H), 4.69–4.52 (q, 2H, J=15.2), 4.43 (s, 1H), 4.28–4.14 (m, 4H), 1.28 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=170.0, 166.0, 142.1, 142.0. 123.4, 124.3, 117.3, 113.8, 113.3, 96.7, 63.0, 60.7, 50.0, 45.0,

32.2, 14.6, 14.3; GC–MS *m*/*z* (% rel inten.): 370.95 (M^+, 21.11), 297.85 (100). Anal. Calcd for $C_{19}H_{18}FN_3O_4$: C, 61.45; H, 4.89; N, 11.32. Found: C, 64.55; H, 4.98; N, 11.44.

4.2.4. Diethyl 5,5-dicyano-1-(4-methylphenyl)-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 4). Colorless crystals; mp: 124–125 °C, IR ν_{max} (KBr): 2250, 1726, 1629, 1513, 1455, 1374, 1277, 1195, 1091, 988, 856, 817, 712 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=7.97 (s, 1H), 7.27–7.24 (m, 4H), 4.70–4.50 (q, 2H, *J*=15.2), 4.41 (s, 1H), 4.28–4.14 (m, 4H), 2.33 (s, 3H), 1.28 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=170.1, 166.0, 143.2, 142.1, 136.1, 131.1, 120.9, 113.8, 113.4, 96.0, 63.0, 60.6, 49.8, 45.1, 32.2, 20.7, 14.6, 14.3; GC–MS *m*/*z* (% rel inten.): 367.15 (M^+, 20.02), 294.13 (100). Anal. Calcd for $C_{20}H_{21}N_3O_4$: C, 65.38; H, 5.76; N, 11.44. Found: C, 65.40; H, 5.77; N, 11.55.

4.2.5. Diethyl 5,5-dicyano-1-(2-methylphenyl)-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 5). Colorless crystals; mp: 137–138 °C, IR ν_{max} (KBr): 2257, 1732, 1680, 1632, 1496, 1456, 1377, 1277, 1196, 1089, 988, 858, 771, 722 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=7.67 (s, 1H), 7.36–7.24 (m, 4H), 4.44 (m, 3H), 4.27 (m, 2H), 4.14 (m, 2H), 2.37 (s, 3H), 1.32–1.20 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=170.1, 166.0, 144.9, 144.5, 135.0, 132.6, 129.0, 128.3, 127.2, 114.3, 113.5, 93.9, 63.0, 60.5, 50.8, 44.8, 32.1, 17.9, 14.6, 14.4; GC–MS *m*/*z* (% rel inten.): 367.15 (M^+, 14.25), 294.05 (100). Anal. Calcd for $C_{20}H_{21}N_3O_4$: C, 65.38; H, 5.76; N, 11.44. Found: C, 65.22; H, 5.79; N, 11.60.

4.2.6. Diethyl 5,5-dicyano-1-(naphthalene-1-yl)-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 6). Colorless crystals; mp: 140–142 °C, IR ν_{max} (KBr): 2257, 1733, 1681, 1629, 1512, 1446, 1396, 1273, 1229, 1194, 1082, 988, 933, 858, 770, 682 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=8.07–7.99 (m, 3H), 7.84 (s, 1H), 7.65–7.55 (m, 4H), 4.54 (m, 3H), 4.32 (m, 2H), 4.14 (m, 2H), 1.37–1.19 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=169.4, 165.3, 144.6, 134.8, 132.5, 128.8, 128.7, 127.5, 126.9, 125.8, 121.9, 113.4, 112.5, 93.7, 62.3, 59.8, 50.8, 44.1, 32.1, 13.7, 13.5; GC–MS *m*/*z* (% rel inten.): 403.1 (M^+, 45.29), 330.1 (100). Anal. Calcd for $C_{23}H_{21}N_3O_4$: C, 68.47; H, 5.25; N, 10.42. Found: C, 68.55; H, 5.20; N, 10.38.

4.2.7. Diethyl 1-tert-butyl-5,5-dicyano-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 7). Colorless crystals; mp: 71–72 °C, IR ν_{max} (KBr): 2258, 1729, 1679, 1619, 1472, 1444, 1402, 1374, 1334, 1279, 1196, 1099, 989, 917 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=7.91 (s, 1H), 4.41 (d, 1H), 4.24 (d, 1H), 4.22–40.7 (m, 4H), 3.98 (d, 1H), 1.44 (s, 9H), 1.28–1.19 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=170.6, 166.5, 141.9, 114.1, 113.9, 89.7, 62.6, 60.0, 59.3, 32.3, 28.2, 14.7, 14.3; GC–MS *m*/*z* (% rel inten.): 333.02 (M^+, 17.78), 56.90 (100). Anal. Calcd for $C_{17}H_{23}N_3O_4$: C, 61.25; H, 6.95; N, 12.60. Found: C, 61.20; H, 7.03; N, 12.74.

4.2.8. Diethyl 1-butyl-5,5-dicyano-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 8). Colorless crystals; mp: 73–75 °C, IR ν_{max} (KBr): 1644, 1376, 1279, 1198, 1084, 988, 854 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=7.74 (s, 1H), 4.26–4.08 (m, 7H), 3.53 (t, 2H), 1.70 (m, 2H), 1.40 (m, 2H), 1.32–1.23 (m, 6H), 0.99 (t, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) : δ ppm=169.6, 165.5, 145.4, 113.3, 112.9, 88.6, 61.8, 59.2, 55.3, 47.6, 43.8, 30.3, 29.5, 19.2, 13.8, 13.4, 13.0; GC–MS *m*/*z* (% rel inten.): 333.07 (M^+, 8.03), 259.99 (100). Anal. Calcd for $C_{17}H_{23}N_3O_4$: C, 61.25; H, 6.95; N, 12.60. Found: C, 61.25; H, 6.96; N, 12.66.

4.2.9. Diethyl 5,5-dicyano-1-propyl-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 9). Colorless crystals; mp: 69–71 °C, IR ν_{max} (KBr): 2259, 1724, 1679, 1626, 1469, 1374, 1346, 1277, 1174, 1098, 988, 863, 692 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=7.72 (s, 1H), 4.30–4.08 (m, 7H), 3.47 (t, 2H), 1.70 (m, 2H), 1.29–1.20 (m, 6H), 0.96 (t, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=169.6, 165.5, 145.5, 113.3, 112.9, 88.6, 61.8, 59.2, 57.1, 47.6, 43.8, 30.8, 21.4, 13.8, 13.4, 10.1; GC–MS *m*/*z* (% rel inten.): 319.1 (M^+, 12.40), 246.1 (100). Anal. Calcd for $C_{16}H_{21}N_3O_4$: C, 60.17; H, 6.63; N, 13.16. Found: C, 60.33; H, 6.49; N, 13.30.

4.2.10. Diethyl 5,5-dicyano-1-hexyl-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 10). Pale yellow viscous oil, IR ν_{max} (KBr): 2360, 1736, 1627, 1564, 1515, 1462, 1368, 1271, 1195, 1091, 989, 852 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=7.69 (s, 1H), 4.28–4.03 (m, 7H), 3.48 (t, 2H), 1.70 (m, 2H), 1.31 (m, 6H), 1.27–1.18 (m, 6H), 0.86 (t, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=169.6, 165.5, 145.5, 113.3, 112.9, 88.6, 61.8, 59.2, 55.5, 47.5, 43.8, 43.7, 31.18, 31.16, 25.7, 22.2, 13.8, 13.4, 13.3; GC–MS *m*/*z* (% rel inten.): 361.1 (M^+, 10.71), 288.1 (100). Anal. Calcd for $C_{19}H_{27}N_3O_4$: C, 63.14; H, 7.53; N, 11.63. Found: C, 63.10; H, 7.60; N, 11.71.

4.2.11. Diethyl 5,5-dicyano-1-cyclohexyl-1,4,5,6-tetrahydropyridine-3,4-dicarboxylate (Table 2, entry 11). Yellow viscous oil, IR ν_{max} (KBr): 2362, 1646, 1565, 1516, 1370, 1268, 1194, 1086, 989, 851 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3): δ ppm=7.74 (s, 1H), 4.26–3.98 (m, 7H), 3.10 (m, 1H), 1.84 (m, 4H), 1.66 (m, 4H), 1.40 (m, 2H), 1.27–1.09 (m, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ ppm=169.6, 165.6, 143.9, 113.3, 113.0, 88.6, 64.2, 61.8, 59.2, 45.4, 44.3, 31.0, 25.2, 24.8, 24.6, 13.8, 13.4; GC–MS *m*/*z* (% rel inten.): 359.1 (M^+, 16.20), 286.1 (100). Anal. Calcd for $C_{19}H_{25}N_3O_4$: C, 63.49; H, 7.01; N, 11.69. Found: C, 63.64; H, 6.81; N, 11.8.

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