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Catalyst-Free [3 + 3] Annulation/Oxidation of Cyclic Amidines with Activated Olefins: When the Substrate Olefin Is Also an Oxidant

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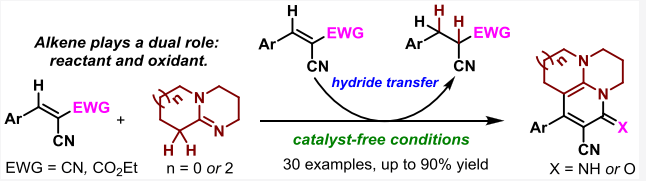
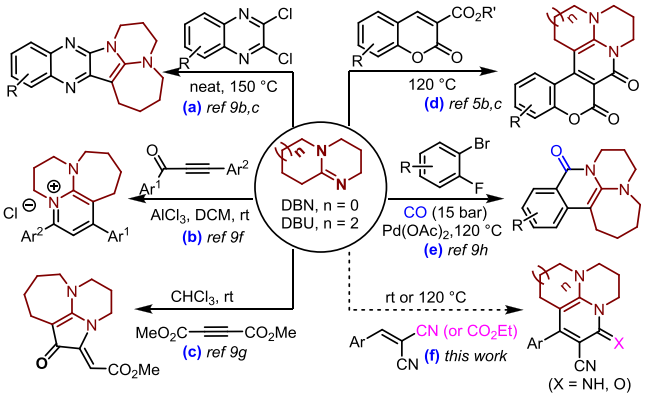
ABSTRACT: Herein we describe a catalyst-free regioselective [3 + 3] annulation/oxidation reaction of cyclic amidines such as DBU (1,8-diazabicyclo(5.4.0)undec-7-ene) and DBN (1,5-diazabicyclo(4.3.0)non-5-ene) with activated olefins, *i.e.*, 2-arylidenemalononitriles and 2-cyano-3-aryl acrylates, to afford tricyclic 2-pyridones and pyridin-2(1*H*)-imines, respectively. The mechanism has been proposed based on DFT calculations. In the reaction, the cyclic amidines serve as *C,N*-bisnucleophiles for the cyclization, while the olefins play a dual role by acting as both reactants and oxidants.



2-Pyridones are embedded as important core units in various biologically active compounds[1] and functional organic materials.[2] They are also used as versatile intermediates in organic synthesis that can be converted into pyridines, piperidines, quinolizidines, indolizidines, *etc.*[3] In this regard, a type of tricyclic 2-pyridone derivatives has recently gained significant attention[4] due to their intriguing optical properties.[5] However, a survey of the literature showed that the construction of this tricyclic system is tedious, often requiring complex substrates and multiple steps of synthesis.[6] Thus, developing efficient and simple approaches to access tricyclic 2-pyridone structures is desirable.

Cyclic amidines such as DBU (1,8-diazabicyclo(5.4.0)-undec-7-ene) and DBN (1,5-diazabicyclo(4.3.0)non-5-ene) are commercially available substances, which are commonly used as strong bases.[7] However, the use of DBU and DBN as nucleophiles acting as catalysts or reagents has also been well documented.[8] In particular, it has been reported that DBU and DBN can be used as *C,N*-bisnucleophiles for cyclization reactions to build multicyclic structues.[9] Notably, Gryko and co-workers[9b,c] have reported a cyclocondensation of DBU with 2,3-dichloroquinoxalines to form pentacyclic structures possessing strong fluorescence (Scheme 1a). The $AlCl_3$-promoted [3 + 3] annulation of alkynones and DBU to deliver tricyclic 2-aminopyridinium salts bearing intensive blue luminescence was disclosed by the Müller group[9f] (Scheme 1b). Dolphin and Ma[9g] have developed a [3 + 2] annulation of DBU with dimethyl acetylenedicarboxylate, which has a high regio- and stereoselectivity (Scheme 1c). Tang[5b] and Gryko[5c] have demonstrated the annulation of alkyl coumarins with DBU or DBN for the construction of pentacyclic blue emitters (Scheme 1d). Wu et al.[9h] have also described a palladium-catalyzed carbonylative annulation of 1-bromo-2-fluorobenzenes with DBU to form multicyclic systems (Scheme 1e). Herein, as part of our interest in Lewis base-promoted reactions,[10] we report the use of DBU and DBN as *C,N*-bisnucleophiles for a regioselective [3 + 3] annulation/oxidation tandem reaction with activated alkenes, *i.e.*, 2-arylidenemalononitriles and 2-cyano-3-aryl acrylates, for an efficient synthesis of tricyclic 2-pyridones and pyridin-2(1*H*)-imines, respectively (Scheme 1f). In the reaction, the substrate olefin plays a dual role as both a reactant for the annulation and an oxidant for an intermolecular hydrogen transfer (*vide infra*).

Scheme 1. DBU and DBN Used As *C,N*-Bisnucleophiles for Cyclization Reactions



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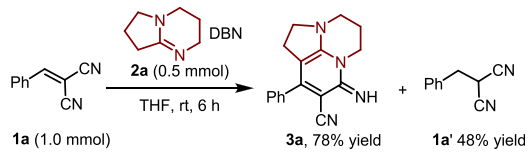
Upon employing DBN as a Lewis base to promote consecutive transformations, we serendipitously found an interesting cyclization between benzylidenemalononitrile **1a** and DBN. Under the optimized conditions (for details, see the Supporting Information), the reaction of 2.0 equiv of **1a** (1.0 mmol) and DBN (**2a**, 0.5 mmol) in THF at room temperature for 6 h afforded a tricyclic pyridin-2(1*H*)-imine product **3a** as a precipitate in a 78% yield together with a hydrogenated product **1a′**, which was isolated in a 48% yield (Scheme 2).

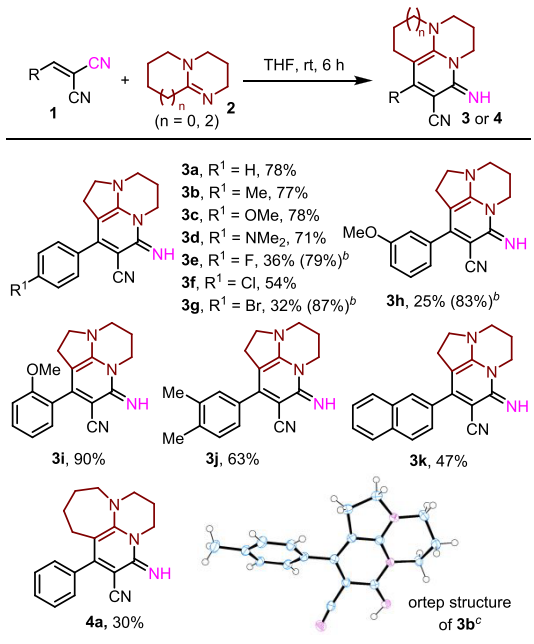
Scheme 2. An Unexpected Cyclization of DBN with 1a



Structure analysis revealed that **3a** was resulted from a [3 + 3] annulation of **1a** and DBN, followed by oxidation by another molecule of **1a** through intermolecular hydrogen transfer. Of note, a similar reactivity between alkyl coumarins with DBU or DBN has been disclosed previously,[5b,c] yet the reaction scope and the mechanism have not been thoroughly investigated.

The substrate scope of the [3 + 3] annulation/oxidation of DBN with 2-arylidenemalononitriles **1** was then briefly examined (Scheme 3). 2-Arylidenemalononitriles **1** bearing -Me, -OMe, -NMe_2, -F, -Cl, and -Br on the phenyl ring were all compatible, delivering the corresponding products **3a**–**j** in 32–90% yields. As seen from the results, substitutions at the *para*-, *meta*-, and *ortho*- positions of the benzene ring were all tolerated. 2-Naphthylidenemalononitrile also reacted with DBN to produce product **3k** in a 47% yield. Of note, all the products **3** were collected by precipitation with THF as the solvent. Our attempt to isolate products **3** by column chromatography failed, probably because the imino (=NH) group of the products is sensitive toward the stationary phase (silica gel and aluminum oxide). The yields of some products were relatively low, which is mainly due to the precipitation being insufficient. For example, while the products **3e**, **3g**, and **3h** precipitated in low yields, using NMR methods for the yield determination showed the good conversion of the reaction (Scheme 3).

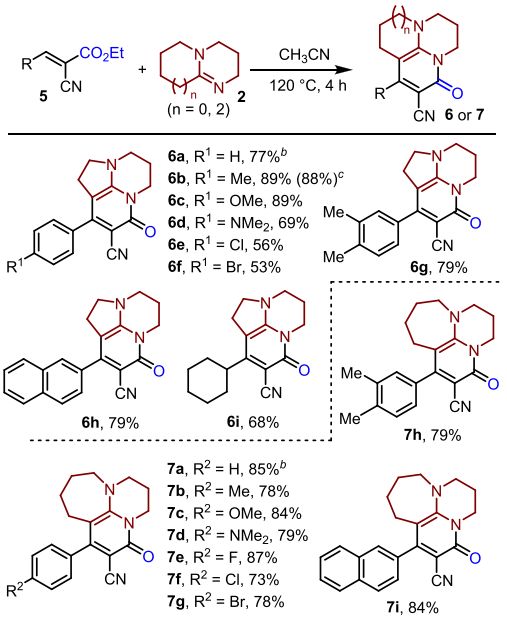
Scheme 3. [3 + 3] Annulation/Oxidation of DBN or DBU with 2-Arylidenemalononitriles[a]



Similar to DBN, DBU was also reactive toward the reaction with arylidenemalononitriles. However, the precipitation of the products was less efficient, presumably due to the more flexible backbone of DBU moiety that is detrimental to precipitation. Accordingly, for the reaction of DBU and benzylidenemalononitrile **1a**, product **4a** was collected in only a 30% yield by precipitation (Scheme 3).

Based on the [3 + 3] annulation/oxidation of DBN or DBU with 2-arylidenemalononitriles **1**, we reasoned that 2-cyano-3-aryl acrylates **5** might also be feasible C_3-units in the reaction, with the ester participating in the annulation. However, it was found that substrates **5** were less reactive, and their annulations were accomplished at a higher temperature. At 120 °C with CH_3CN as a solvent (for the conditions survey, see the Supporting Information), the [3 + 3] annulation/oxidation of DBN with **5** proceeded smoothly, delivering tricyclic 2-pyridone products **6a**–**h** in 53–89% yields with a good functionality tolerance (Scheme 4, top). Notably, an alkyl-substituted alkene, 2-cyano-3-cyclohexyl acrylate, was also reactive for the reaction, generating the corresponding product

Scheme 4. [3 + 3] Annulation/Oxidation of DBN or DBU with 2-Cyano-3-arylacrylates[a]



[a]Reaction conditions are as follows: **1** (1.0 mmol) and **2** (0.5 mmol) were stirred in THF (2.0 mL) at room temperature under a N_2 atmosphere for 6 h; products were collected from precipitation. [b]Yield in parentheses was measured by ^{1}H NMR using dibromomethane as an internal standard. [c]Displacement ellipsoids are drawn at the 50% probability level.

[a]Reaction conditions are as follows: **5** (0.4 mmol) and **2** (0.2 mmol) were stirred in CH_3CN (1.0 mL) at 120 °C under a N_2 atmosphere for 4 h; products, except **6a** and **7a**, were isolated by column chromatography. [b]Products were collected by precipitation. [c]Yield in parentheses is from a 20 mmol scale reaction.

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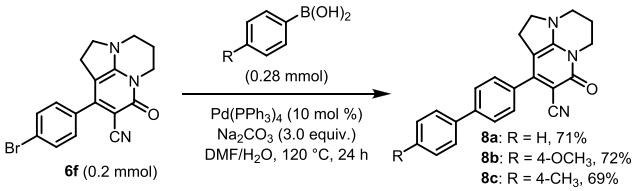
6i in a 68% yield. As shown, DBU also exhibited a comparable reactivity in the annulation with **5**, providing products **7a**−**i** in 73−87% yields (Scheme 4, bottom). Of note, products **6** and **7** could be isolated by column chromatography due to the better stabilities compared to those of **3** and **4**. To demonstrate the practicality, a scaled-up synthesis of compound **6b** was carried out (20 mmol), which afforded **6b** in 2.54 g and an 88% yield (Scheme 4).

The structures of all the products[11] **3**, **4**, **6**, and **7** have been well established by ^{1}H and ^{13}C NMR, IR, HRMS, and X-ray crystallographic analysis (for **3b**, CCDC 2021247). It is noteworthy that the reaction shows an excellent regioselectivity; all products were obtained as single regioisomers. Although DBN and DBU are used as *C,N*-bisnucleophiles in the reaction, their *C*-nucleophile selectively attacks at the alkene, while the *N*-nucleophile only adds to the carbonyl or nitrile.

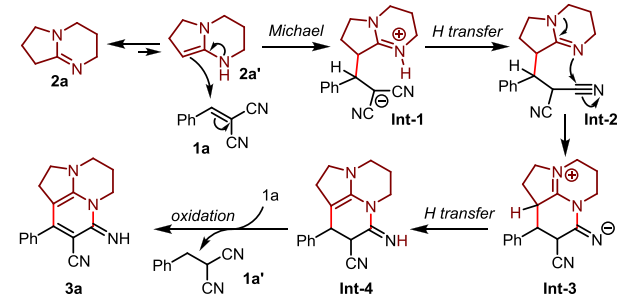
To demonstrate the application of the products, Suzuki cross-couplings of the product **6f** with arylboronic acids under the catalysis of $Pd(PPh_3)_4$ were conducted, which afforded the biphenyl products **8** in good yields (Scheme 5).

Scheme 5. Elaboration of the Product



A possible mechanism for the formation of **3a** is proposed in Scheme 6. First, the tautomerization of DBN gives an enamine

Scheme 6. Proposed Mechanism for the Cyclization



intermediate **2a′**, which adds to the olefin **1a** via a Michael reaction to furnish intermediate **Int-1**.[12] A proton transfer occurs to deliver adduct **Int-2**, which cyclizes to form species **Int-3** by the intramolecular attack of the sp^2 N on a cyano group. Another hydrogen transfer then gives **Int-4**, which undergoes the final oxidation[13] by another molecule of **1a** to afford the product **3a**. A DFT calculation was performed to inspect the mechanism (Figure 1, see details in the Supporting Information). It shows that the tautomerization of DBN to **2a′** is endothermic (+14.1 kcal mol^{-1}), while the attack of **2a′** at **1a** to form the zwitterion **Int-1** is fast (activation barrier of 7.6 kcal mol^{-1}) and exothermic (−25.0 kcal mol^{-1}). The formation of **Int-3** for the cyclization was found to be endergonic (**Int-1** ⇌ **Int-2** ⇌ **Int-3**, +16.0 kcal mol^{-1}), whereas the hydrogen shift from **Int-3** to **Int-4** is energy-releasing (−10.8 kcal mol^{-1}). For the oxidation of **Int-4** by another molecule of **1a**, it was computed that a stepwise

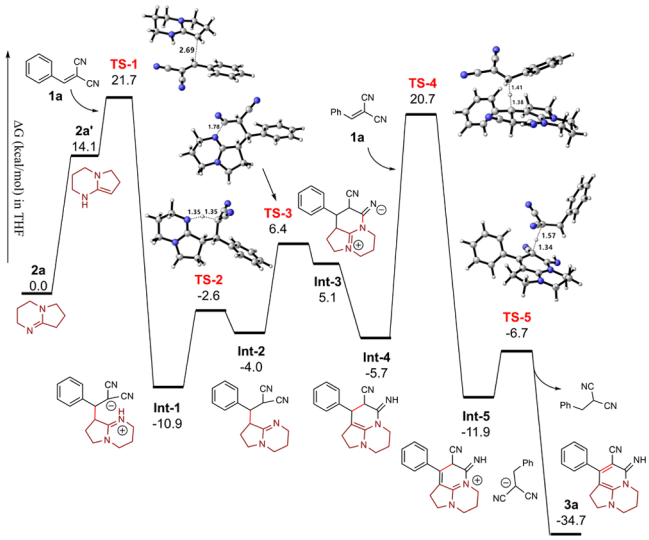


Figure 1. Relative Gibbs free-energy profile computed for the annulation of **1a** and DBN.

process (**TS-4** and **TS-5**) may be responsible. The first step is associated with a direct hydride transfer,[13,14] forming an ion-pair intermediate **Int-5**. A charge population analysis of **Int-5** confirms the 0.97 electron transfer from the dehydrogenated form of **Int-4** to the hydrogenated form of **1a**. The second step is a fast proton transfer within the ion pair, which is driven by aromatization, to finally afford products **3a** and **1a′**. The oxidation is reminiscent of the biomimetic hydrogenation of active olefins by the Hantzsch 1,4-dihydropyridine ester through self-catalysis by decreasing the HOMO−LUMO energy gap.[14f,g] The overall tandem reaction is exergonic and releases 34.7 kcal mol^{-1} of energy.

In summary, we have reported the use of DBU and DBN as *C,N*-bisnucleophiles for a highly regioselective [3 + 3] annulation/oxidation tandem reaction with activated olefins such as 2-arylidenemalononitriles and 2-cyano-3-arylacrylates. The reaction provides an easy access to tricyclic 2-pyridones and tricyclic pyridin-2(1*H*)-imines in good yields under catalyst-free conditions. Interestingly, the substrate olefin plays a dual role in the reaction, serving as both a reactant for the annulation and an oxidant for an intermolecular hydrogen transfer. A DFT calculation was performed to clarify the mechanism. Given the importance of the tricyclic 2-pyridone structure in materials, we anticipate that this method will be useful to the chemistry community. Future efforts will focus on the application of the current method for the synthesis of functional organic materials.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were performed in oven-dried or flame-dried glassware under a nitrogen atmosphere. All solvents were purified prior to use according to standard procedures. 2-Arylidenemalononitriles **1**[15] and 2-cyano-3-arylacrylates **5**[16] were prepared according to reported methods. All other reagents were purchased from commercial sources and used without further purification. For reactions that require heating, an oil bath was used as the heating source. All reactions were monitored by thin layer chromatography (TLC) and visualized by UV irradiation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer. Chemical shifts (δ values) were reported in parts per million (ppm) with TMS (^{1}H NMR) and $CDCl_3$ (^{13}C NMR) as internal standards, respectively. Peak multiplicities are reported as follows: s = singlet, t =

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triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. High-resolution ESI mass spectra were determined on a WATERS I-Class VION IMS Q TOF LC/MS system. X-ray crystallographic analysis was performed on a Bruker D8 Quest system. IR data were measured on a Nicolet iS10 FT-IR spectrometer. Melting points were measured on a WRX-4 apparatus and are uncorrected.

General Procedure for the Synthesis of Compounds 3 and 4. 2-Arylidenemalononitriles **1** (1.0 mmol) were placed in a Schlenk tube (10 mL), and the vessel was evacuated and refilled with nitrogen three times. THF (2.0 mL) was subsequently was added, followed by either DBN **2a** (0.5 mmol) or DBU **2b** (0.5 mmol) to get a yellow suspension. The mixture was stirred vigorously at room temperature for 6 h. The reaction was monitored by TLC (ethyl acetate/petroleum ether = 1:20). After the complete consumption of the starting material, the mixture was filtered to afford crude products **3** or **4**. Pure products of **3** or **4** were obtained via recrystallization from ethanol or a mixed solvent of $CHCl_3$ and hexane. The filtrate was concentrated, and the residue was purified by preparative TLC (ethyl acetate/petroleum ether = 1:20) to afford the hydrogenated product **1′**.

General Procedure for the Synthesis of Compounds 6 and 7. Ethyl (*E*)-2-cyano-3-arylacrylates **5** (0.4 mmol) was placed in a Schlenk tube (10 mL), and the vessel was evacuated and refilled with nitrogen three times. CH_3CN (1.0 mL) was subsequently added, followed by either DBN **2a** (0.2 mmol) or DBU **2b** (0.2 mmol). The mixture was stirred vigorously at 120 °C under a nitrogen atmosphere for 4 h. After the completion of the reaction (as monitored by TLC), all volatiles were evaporated *in vacuo*. The residue was then purified by column chromatography (ethyl acetate/petroleum ether = 1:10, then ethyl acetate/methanol = 5:1) to obtain the hydrogenated product **5′** and products **6** or **7**. Products **6a** and **7a** could also be isolated by precipitation due to their poor solubility in the solvent CH_3CN.

3a. Starting from 2-benzylidenemalononitrile **1a** (154.2 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3a** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 108.0 mg (78%) yield as a yellow solid. 2-Benzylmalononitrile **1a′**, which is a known compound,[17] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 37.5 mg (48%) yield. Analytical data for **3a**: mp 272−273 °C. IR (ATR): $\tilde{\nu}$ 2940, 2860, 2167, 1615, 1578, 1490, 1440, 1408, 1371, 1308, 1275, 1245, 1193, 1132, 1078, 1027, 945, 748, 713 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45−7.35 (m, 5H), 4.08−3.89 (m, 2H), 3.66 (t, J = 8.0 Hz, 2H), 3.33 (t, J = 8.6 Hz, 2H), 2.77 (t, J = 8.1 Hz, 2H), 2.25−2.10 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.4, 154.0, 151.1, 136.3, 129.1, 128.5, 127.8, 120.8, 97.2, 79.6, 52.0, 42.1, 39.4, 24.3, 20.3. HRMS (ESI): m/z calcd for $C_{17}H_{17}N_4^+$ $[M + H]^+$ 277.1448. Found: 277.1437.

3b. Starting from 2-(4-methylbenzylidene)malononitrile **1b** (168.2 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3b** was obtained via recrystallization from ethanol in a 112.2 mg (77%) yield as a yellow solid. 2-(4-Methylbenzyl)malononitrile **1b′**, which is a known compound,[17] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 59.8 mg (70%) yield. Analytical data for **3b**: mp 235−236 °C. IR (ATR): $\tilde{\nu}$ 3312, 2860, 2170, 1616, 1572, 1513, 1445, 1417, 1378, 1334, 1305, 1277, 1254, 1200, 1175, 1147, 1112, 1040, 1018, 978, 958, 922, 891, 824, 742, 651 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.7 Hz, 2H), 3.97 (t, J = 5.8 Hz, 2H), 3.65 (t, J = 8.3 Hz, 2H), 3.31 (t, J = 5.5 Hz, 2H), 2.78 (t, J = 8.3 Hz, 2H), 2.38 (s, 3H), 2.23−2.12 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.5, 153.9, 151.2, 139.1, 133.3, 129.2, 127.8, 121.0, 97.0, 79.6, 52.0, 42.1, 39.3, 24.4, 21.4, 20.3. HRMS (ESI): m/z calcd for$C_{18}H_{19}N_4^+$ $[M + H]^+$ 291.1604. Found: 291.1596.

3c. Starting from 2-(4-methoxybenzylidene)malononitrile **1c** (184.2 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3c** was obtained via recrystallization from ethanol in a 119.4 mg (78%) yield as a yellow solid. 2-(4-Methoxybenzyl)malononitrile **1c′**, which is a known compound,[17] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 65.3 mg (70%) yield. Analytical data for **3c**: mp 209−211 °C. IR (ATR): $\tilde{\nu}$ 3296, 2942, 2861, 2173, 1609, 1579, 1558, 1509, 1442, 1422, 1376, 1294, 1276, 1247, 1174, 1148, 1115, 1026, 922, 890, 844, 820, 751, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.00−3.92 (m, 2H), 3.83 (s, 3H), 3.65 (t, J = 8.4 Hz, 2H), 3.31 (t, J = 5.8 Hz, 2H), 2.79 (t, J = 8.4 Hz, 2H), 2.21−2.12 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.1, 158.6, 153.9, 150.7, 129.4, 128.4, 121.3, 113.9, 97.2, 79.2, 55.3, 51.9, 42.1, 39.3, 24.4, 20.3. HRMS (ESI): m/z calcd for $C_{18}H_{19}N_4O^+$ $[M + H]^+$ 307.1546. Found: 307.1543.

3d. Starting from 2-(4-(dimethylamino)benzylidene)malononitrile **1d** (197.2 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3d** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 113.0 mg (71%) yield as a yellow solid. 2-(4-(Dimethylamino)-benzyl)malononitrile **1d′**, which is a known compound,[18] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:3) in a 75.2 mg (76%) yield. Analytical data for **3d**: mp 248−250 °C. IR (ATR): $\tilde{\nu}$ 3538, 3214, 2866, 2171, 1607, 1579, 1516, 1446, 1365, 1333, 1310, 1268, 1199, 1170, 1064, 1038, 961, 944, 921, 821, 746, 734, 651 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.9 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 4.02−3.94 (m, 2H), 3.65 (t, J = 8.4 Hz, 2H), 3.31 (t, J = 5.7 Hz, 2H), 3.00 (s, 6H), 2.86 (t, J = 8.3 Hz, 2H), 2.23−2.13 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.8, 153.8, 151.3, 150.8, 129.2, 123.3, 121.6, 111.6, 96.9, 79.3, 52.0, 42.2, 40.2, 39.4, 24.8, 20.4. HRMS (ESI): m/z calcd for $C_{19}H_{22}N_5^+$ $[M + H]^+$ 320.1870. Found: 320.1865.

3e. Starting from 2-(4-fluorobenzylidene)malononitrile **1e** (172.2 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3e** was obtained via recrystallization from ethanol in a 53.4 mg (36%) yield. 2-(4-Fluorobenzyl)malononitrile **1e′**, which is a known compound,[17] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a less than 5% yield. Analytical data for **3e**: mp 225−226 °C. IR (ATR): $\tilde{\nu}$ 3304, 2945, 2861, 2167, 1616, 1579, 1505, 1417, 1373, 1333, 1305, 1274, 1251, 1226, 1159, 1138, 1100, 1033, 1014, 974, 956, 918, 891, 834, 787, 753, 739, 706, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.35 (m, 2H), 7.13 (t, J = 8.7 Hz, 2H), 4.10−4.00 (m, 2H), 3.70 (t, J = 8.4 Hz, 2H), 3.35 (t, J = 5.7 Hz, 2H), 2.79 (t, J = 8.4 Hz, 2H), 2.27−2.17 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.1 (d, J_{F-C} = 249.2 Hz), 157.9, 154.0, 149.9, 131.9 (d, J_{F-C} = 3.4 Hz), 129.9 (d, J_{F-C} = 8.4 Hz), 120.2, 115.8 (d, J_{F-C} = 21.8 Hz), 98.5, 79.5, 52.0, 42.1, 39.9, 24.2, 20.2. HRMS (ESI): m/z calcd for $C_{17}H_{16}FN_4^+$ $[M + H]^+$ 295.1353. Found: 295.1346.

3f. Starting from 2-(4-chlorobenzylidene)malononitrile **1f** (188.6 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3f** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 84.1 mg (54%) yield as a yellow solid. 2-(4-Chlorobenzyl)malononitrile **1f′**, which is a known compound,[17] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 45.4 mg (48%) yield. Analytical data for **3f**: mp 232−224 °C. IR (ATR): $\tilde{\nu}$ 3305, 2863, 2175, 1616, 1583, 1554, 1519, 1488, 1419, 1377, 1333, 1310, 1280, 1256, 1200, 1181, 1147, 1106, 1088, 1041, 1010, 976, 959, 922, 893, 831, 756, 709, 661 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 4.07−3.94 (m, 2H), 3.76−3.63 (m, 2H), 3.35 (t, J = 5.8 Hz, 2H), 2.83−2.70 (m, 2H), 2.27−2.15 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.2, 154.1, 149.7, 135.1, 134.7, 129.3, 128.9, 120.7, 97.0, 79.3, 51.9, 42.1, 39.3, 24.2, 20.3. HRMS (ESI): m/z calcd for $C_{17}H_{16}ClN_4^+$ $[M + H]^+$ 311.1058. Found: 311.1053.

3g. Starting from 2-(4-bromobenzylidene)malononitrile **1g** (232.1 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3g** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 57.0 mg (32%) yield as a yellow solid. 2-(4-Bromobenzyl)malononitrile **1g′**, which is a known compound,[19] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 71.8 mg (61%) yield. Analytical data for **3g**: mp 209−210 °C. IR (ATR): $\tilde{\nu}$ 3304, 2862, 2175, 1615, 1582, 1550, 1519, 1485, 1417, 1377, 1333, 1310, 1277, 1254, 1199, 1145, 1105, 1072, 1038, 1006, 974, 957, 920, 892, 842, 829, 755, 739, 656 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.04−3.92 (m, 2H), 3.68 (t, J = 8.3 Hz, 2H), 3.33 (t, J = 5.7 Hz, 2H), 2.75 (t, J = 8.3 Hz, 2H), 2.25−

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2.13 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.2, 154.1, 149.6, 135.2, 131.8, 129.6, 123.3, 120.8, 97.0, 79.1, 51.9, 42.1, 39.3, 24.2, 20.2. HRMS (ESI): m/z calcd for $C_{17}H_{16}BrN_4^+$ $[M + H]^+$ 355.0553. Found: 355.0553.

3h. Starting from 2-(3-methoxybenzylidene)malononitrile **1h** (184.2 mg, 1.0 mmol) and DBN **3a** (62.1 mg, 0.5 mmol), product **3h** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 38.2 mg (25%) yield as a yellow solid. 2-(3-Methoxybenzyl)malononitrile **1h′** which is a known compound,[20] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 57.1 mg (61%) yield,. Analytical data for **3h**: mp 184−186 °C. IR (ATR): $\tilde{\nu}$ 3292, 2951, 2852, 2169, 1617, 1585, 1554, 1523, 1489, 1461, 1422, 1377, 1336, 1304, 1273, 1245, 1162, 1142, 1081, 1052, 1031, 995, 952, 910, 894, 856, 821, 764, 749, 734, 664 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 9.0, 7.6 Hz, 1H), 7.04−6.90 (m, 3H), 4.05−3.92 (m, 2H), 3.82 (s, 3H), 3.66 (t, J = 8.4 Hz, 2H), 3.32 (t, J = 5.8 Hz, 2H), 2.78 (t, J = 8.4 Hz, 2H), 2.27−2.11 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.5, 158.4, 154.0, 150.8, 137.6, 129.7, 120.9, 120.2, 114.7, 113.4, 97.2, 79.3, 55.4, 51.9, 42.0, 39.3, 24.3, 20.3. HRMS (ESI): m/z calcd for $C_{18}H_{18}KN_4O^+$ $[M + K]^+$ 345.1120. Found: 345.1121.

3i. Starting from 2-(2-methoxybenzylidene)malononitrile **1i** (184.2 mg, 1.0 mmol) and DBN **3a** (62.1 mg, 0.5 mmol), product **3i** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 137.9 mg (90%) yield as a yellow solid. 2-(2-Methoxybenzyl)malononitrile **1i′**, which is a known compound,[20] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 63.0 mg (68%) yield. Analytical data for **3i**: mp 242−243 °C. IR (ATR): $\tilde{\nu}$ 3301, 2927, 2867, 2173, 1616, 1591, 1548, 1520, 1487, 1455, 1432, 1408, 1373, 1335, 1307, 1281, 1196, 1156, 1050, 1024, 957, 918, 793, 743, 714, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41−7.32 (m, 1H), 7.23 (dd, J = 7.5, 1.6 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 7.00−6.96 (m, 1H), 3.96 (td, J = 5.8, 1.8 Hz, 2H), 3.85 (s, 3H), 3.70−3.58 (m, 2H), 3.31 (t, J = 5.8 Hz, 2H), 2.77−2.53 (m, 2H), 2.24−2.11 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.4, 155.9, 153.7, 148.4, 130.4, 129.6, 125.0, 120.8, 120.8, 111.4, 98.7, 80.4, 55.7, 51.9, 42.0, 39.2, 24.1, 20.3. HRMS (ESI): m/z calcd for $C_{18}H_{19}N_4O^+$ $[M + H]^+$ 307.1553. Found: 307.1545.

3j. Starting from 2-(3,4-dimethylbenzylidene)malononitrile **1j** (182.2 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3j** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 96.4 mg (63%) yield as a yellow solid. 2-(3,4-Dimethylbenzyl)-malononitrile **1j′**, which is a known compound,[21] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 44.1 mg (48%) yield. Analytical data for **3j**: mp 210−211 °C. IR (ATR): $\tilde{\nu}$ 3322, 2868, 2169, 1622, 1574, 1554, 1531, 1503, 1452, 1419, 1378, 1311, 1279, 1249, 1209, 1159, 1137, 1124, 1105, 1003, 974, 958, 932, 906, 879, 828, 763, 663 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20−7.13 (m, 3H), 4.01−3.94 (m, 2H), 3.65 (t, J = 8.4 Hz, 2H), 3.32 (t, J = 5.7 Hz, 2H), 2.79 (t, J = 8.4 Hz, 2H), 2.29 (s, 6H), 2.23−2.14 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.6, 153.9, 151.2, 137.7, 136.7, 133.8, 129.7, 128.9, 125.3, 121.1, 97.0, 79.5, 51.9, 42.1, 39.3, 24.4, 20.3, 19.9, 19.7. HRMS (ESI): m/z calcd for $C_{19}H_{21}N_4^+$ $[M + H]^+$ 305.1761. Found: 305.1756.

3k. Starting from 2-(naphthalen-2-ylmethylene)malononitrile **1k** (204.2 mg, 1.0 mmol) and DBN **2a** (62.1 mg, 0.5 mmol), product **3k** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 76.0 mg (47%) yield as a yellow solid. 2-(Naphthalen-2-ylmethyl)-malononitrile **1k′**, which is a known compound,[19] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:20) in a 68.8 mg (67%) yield. Analytical data for **3k**: mp 220−221 °C. IR (ATR): $\tilde{\nu}$ 2925, 2171, 1609, 1581, 1548, 1527, 1467, 1409, 1378, 1303, 1274, 1251, 1199, 1143, 1032, 959, 890, 855, 813, 772, 758, 746, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93−7.83 (m, 4H), 7.57−7.45 (m, 3H), 4.06−3.98 (m, 2H), 3.67 (t, J = 8.4 Hz, 2H), 3.34 (t, J = 5.8 Hz, 2H), 2.81 (t, J = 8.3 Hz, 2H), 2.25−2.16 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.4, 154.0, 151.0, 133.7, 133.4, 133.0, 128.4, 127.8, 127.4, 126.8, 126.5, 125.3, 120.8, 100.0, 97.6, 79.8, 52.0, 42.1, 39.5, 24.4, 20.3. HRMS (ESI) calcd for $C_{21}H_{22}N_5^+$ $[M + NH_4]^+$ 344.1870. Found: 344.1873.

4a. Starting from 2-benzylidenemalononitrile **1a** (154.2 mg, 1.0 mmol) and DBU **2b** (76.1 mg, 0.5 mmol), product **4a** was obtained via recrystallization ($CHCl_3$/hexane = 1:4) in a 45.6 mg (30%) yield as a green solid. The hydrogenated compound 2-benzylmalononitrile **1a′** was not isolated. Analytical data for **4a**: mp 250−251 °C. IR (ATR): $\tilde{\nu}$ 2929, 2846, 2183, 1582, 1540, 1482, 1379, 1335, 1313, 1278, 1238, 1196, 1154, 1132, 1084, 1025, 993, 962, 938, 926, 909, 790, 756, 715, 699, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.36 (m, 3H), 7.25 (dd, J = 7.8, 1.6 Hz, 2H), 4.21−4.13 (m, 2H), 3.58−3.51 (m, 2H), 3.37 (t, J = 6.4 Hz, 2H), 2.25−2.17 (m, 2H), 2.15−2.07 (m, 2H), 1.95−1.84 (m, 2H), 1.68−1.57 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.7, 157.6, 153.5, 137.7, 128.7, 128.6, 128.0, 119.2, 99.4, 86.3, 52.8, 49.3, 41.4, 27.5, 24.4 (2C), 22.3. HRMS (ESI) calcd for $C_{19}H_{20}LiN_4^+$ $[M + Li]^+$ 311.1843. Found:311.1849.

6a. Starting from ethyl (*E*)-2-cyano-3-phenylacrylate **5a** (80.5 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6a** was obtained by precipitation from the reaction) in a 42.5 mg (77%) yield as a yellow solid. Ethyl 2-cyano-3-phenylpropanoate **5a′**, which is a known compound,[17] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:10) in a 28.8 mg (71%) yield. Analytical data for **6a**: mp > 290 °C. IR (ATR): $\tilde{\nu}$ 3675, 2973, 2794, 1700, 1614, 1557, 1538, 1495, 1440, 1392, 1366, 1308, 1273, 1209, 1180, 1081, 889, 788, 764, 740, 708, 670 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 7.54−7.39 (m, 5H), 3.83−3.75 (m, 2H), 3.72 (t, J = 8.3 Hz, 2H), 3.32−3.29 (t, 2H), 2.76 (t, J = 8.2 Hz, 2H), 2.11−1.98 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 161.2, 154.9, 150.2, 136.4, 129.4, 129.0, 128.3, 120.4, 102.4, 78.4, 51.8, 41.9, 38.1, 24.1, 19.6. HRMS (ESI): m/z calcd for $C_{17}H_{16}N_3O^+$ $[M + H]^+$ 278.1288. Found: 278.1284.

6b. Starting from ethyl (*E*)-2-cyano-3-(*p*-tolyl)acrylate **5b** (86.0 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6b** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 51.4 mg (89%) yield as a yellow solid. Ethyl 2-cyano-3-(p-tolyl)propanoate **5b′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 28.9 mg (67%) yield. Analytical data for **6b**: mp 212−214 °C. IR (ATR): $\tilde{\nu}$ 3526, 2970, 2902, 2249, 2190, 1734, 1700, 1650, 1615, 1554, 1536, 1512, 1454, 1393, 1374, 1259, 1185, 1049, 890, 832, 800, 769, 753, 666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 4.00−3.92 (m, 2H), 3.73 (t, J = 8.4 Hz, 2H), 3.34 (t, J = 5.8 Hz, 2H), 2.88 (t, J = 8.4 Hz, 2H), 2.38 (s, 3H), 2.15 (dt, J = 11.7, 5.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.5, 154.1, 152.4, 139.3, 132.7, 129.2, 127.9, 119.4, 101.1, 81.6, 52.0, 42.2, 37.9, 24.6, 21.4, 19.9. HRMS (ESI): m/z calcd for $C_{18}H_{21}N_4O^+$ $[M + NH_4]^+$ 309.1710. Found: 309.1730.

6c. Starting from ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)acrylate **5c** (92.4 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6c** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 54.4 mg (89%) yield as a yellow solid. Ethyl 2-cyano-3-(4-methoxyphenyl)propanoate **5c′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 38.1 mg (82%) yield. Analytical data for **6c**: mp 224−225 °C. IR (ATR): $\tilde{\nu}$ 3547, 2913, 2190, 1711, 1614, 1535, 1510, 1459, 1418, 1392, 1372, 1307, 1278, 1252, 1175, 1117, 1025, 973, 891, 842, 771, 755, 725, 700, 655 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.95−3.89 (m, 2H), 3.83 (s, 3H), 3.73 (t, J = 8.4 Hz, 2H), 3.33 (t, J = 5.8 Hz, 2H), 2.89 (t, J = 8.4 Hz, 2H), 2.16−2.07 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.5, 160.2, 154.2, 151.6, 129.6, 127.9, 119.8, 113.9, 101.3, 81.0, 55.3, 51.9, 42.1, 37.9, 24.7, 19.8. HRMS (ESI): m/z calcd for $C_{18}H_{18}N_3O_2^+$ $[M + H]^+$ 308.1394. Found: 308.1389.

6d. Starting from ethyl (*E*)-2-cyano-3-(4-(dimethylamino)phenyl)-acrylate **5d** (97.5 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6d** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 44.5 mg (69%) yield as a green solid. Ethyl 2-cyano-3-(4-(dimethylamino)phenyl)propanoate **5d′**, which is a known compound,[22] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:5) in a 27.7 mg (56%) yield. Analytical data for **6d**: mp 287−289 °C. IR (ATR): $\tilde{\nu}$ 2883, 2189,

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1631, 1604, 1519, 1444, 1394, 1355, 1303, 1272, 1212, 1193, 1163, 1126, 1100, 1043, 942, 825, 762, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.9 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 3.95−3.89 (m, 2H), 3.71 (t, J = 8.4 Hz, 2H), 3.31 (t, J = 5.8 Hz, 2H), 3.00 (s, 6H), 2.93 (t, J = 8.4 Hz, 2H), 2.14−2.07 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.8, 154.0, 152.4, 150.8, 129.5(2C), 120.1, 111.7, 100.7, 81.2, 52.0, 42.3, 40.3, 37.9, 25.0, 20.0. HRMS (ESI): m/z calcd for $C_{19}H_{20}LiN_4O^+$ $[M + Li]^+$ 327.1792. Found: 327.1776.

6e. Starting from ethyl (*E*)-3-(4-chlorophenyl)-2-cyanoacrylate **5f** (94.0 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6e** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 35.0 mg (56%) yield as a yellow solid. Ethyl 3-(4-chlorophenyl)-2-cyanopropanoate **5f′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 33.2 mg (70%) yield. Analytical data for **6e**: mp 237−238 °C. IR (ATR): $\tilde{\nu}$ 3545, 2912, 2194, 1617, 1554, 1534, 1488, 1406, 1371, 1307, 1279, 1187, 1151, 1108, 1089, 1043, 1009, 977, 891, 833, 768, 754, 700, 651 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42−7.32 (m, 4H), 3.97−3.89 (m, 2H), 3.75 (t, J = 8.4 Hz, 2H), 3.35 (t, J = 5.8 Hz, 2H), 2.86 (t, J = 8.4 Hz, 2H), 2.19−2.08 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.2, 154.3, 150.7, 135.3, 134.1, 129.5, 128.8, 119.3, 101.4, 80.8, 51.9, 42.1, 37.9, 24.3, 19.8. HRMS (ESI): m/z calcd for $C_{17}H_{15}ClN_3O^+$ $[M + H]^+$ 312.0898. Found: 312.0885.

6f. Starting from ethyl (*E*)-3-(4-bromophenyl)-2-cyanoacrylate **5g** (111.6 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6f** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 37.6 mg (53%) yield as a yellow solid. Ethyl 3-(4-bromophenyl)-2-cyanopropanoate **5g′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 30.7 mg (55%) yield. Analytical data for **6f**: mp 270−272 °C. IR (ATR): $\tilde{\nu}$ 2972, 2189, 1636, 1611, 1550, 1486, 1401, 1369, 1309, 1275, 1182, 1153, 1104, 1073, 1046, 1007, 904, 835, 764, 698, 653 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.00−3.92 (m, 2H), 3.75 (t, J = 8.4 Hz, 2H), 3.35 (t, J = 5.8 Hz, 2H), 2.86 (t, J = 8.4 Hz, 2H), 2.22−2.11 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.2, 154.3, 151.0, 134.5, 131.9, 129.7, 123.6, 119.1, 101.0, 81.3, 51.9, 42.2, 37.9, 24.4, 19.9. HRMS (ESI): m/z calcd for $C_{17}H_{15}BrN_3O^+$ $[M + H]^+$ 356.0393. Found: 356.0374.

6g. Starting from ethyl (*E*)-2-cyano-3-(3, 4-dimethylphenyl)-acrylate **5h** (91.6 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6g** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 48.3 mg (79%) yield as a yellow solid. Ethyl 2-cyano-3-(3,4-dimethylphenyl)propanoate **5h′**, which is a known compound,[21] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 32.3 mg (70%) yield. Analytical data for **6g**: mp 229−231 °C. IR (ATR): $\tilde{\nu}$ 2910, 2188, 1620, 1582, 1539, 1503, 1451, 1411, 1366, 1309, 1276, 1242, 1210, 1196, 1173, 1151, 1125, 1106, 1049, 1027, 1001, 923, 836, 791, 753, 662 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.19−7.11 (m, 3H), 3.97−3.90 (m, 2H), 3.77−3.69 (m, 2H), 3.34 (t, J = 5.8 Hz, 2H), 2.87 (t, J = 8.4 Hz, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 2.18−2.09 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.5, 154.2, 152.3, 137.8, 136.7, 133.2, 129.7, 129.1, 125.5, 119.6, 101.2, 81.2, 51.9, 42.1, 37.9, 24.6, 19.9, 19.8, 19.7. HRMS (ESI): m/z calcd for $C_{19}H_{20}N_3O^+$ $[M + H]^+$ 306.1601. Found: 306.1602.

6h. Starting from ethyl (*E*)-2-cyano-3-(naphthalen-2-yl)acrylate **5i** (100.4 mg, 0.4 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6h** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 51.6 mg (79%) yield as a yellow solid. Ethyl 2-cyano-3-(naphthalen-2-yl)propanoate **5i′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:5) in a 38.1 mg (75%) yield. Analytical data for **6h**: mp 224−225 °C. IR (ATR): $\tilde{\nu}$ 2867, 2190, 1717, 1611, 1559, 1536, 1470, 1398, 1367, 1307, 1272, 1175, 1144, 1043, 956, 920, 865, 825, 750, 663 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91−7.78 (m, 4H), 7.55−7.44 (m, 3H), 3.99−3.91 (m, 2H), 3.73 (t, J = 8.4 Hz, 2H), 3.33 (t, J = 5.8 Hz, 2H), 2.89 (t, J = 8.4 Hz, 2H), 2.15−2.07 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.4, 154.3, 152.0, 133.4, 133.1, 132.9, 128.4, 128.3, 127.7(2C), 126.9, 126.5, 125.5, 119.5, 101.6, 81.4, 51.6, 42.2, 38.0, 24.6, 19.8. HRMS (ESI): m/z calcd for $C_{21}H_{18}N_3O^+$ $[M + H]^+$ 328.1444. Found: 328.1438.

6i. Starting from ethyl (*E*)-2-cyano-3-cyclohexylacrylate **5j** (82.9 mg, 0.2 mmol) and DBN **2a** (24.8 mg, 0.2 mmol), product **6i** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 38.4 mg (68%) yield as a yellow solid. Ethyl 2-cyano-3-cyclohexylpropanoate **5j′**, which is a known compound,[22] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:20) in a 28.3 mg (68%) yield. Analytical data for **6i**: mp 243−244 °C. IR (ATR): $\tilde{\nu}$ 3413, 2924, 2851, 2190, 1609, 1537, 1474, 1373, 1271, 1239, 1169, 1085, 1040, 976, 909, 890, 764, 706, 680, 640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.89 (t, J = 5.4 Hz, 2H), 3.72 (t, J = 8.4 Hz, 2H), 3.31 (t, J = 5.7 Hz, 2H), 3.01 (t, J = 8.4 Hz, 2H), 2.18−2.07 (m, 2H), 1.91−1.56 (m, 7H), 1.42−1.29 (m, 2H), 1.25 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.6, 158.5, 154.4, 119.5, 100.1, 100.0, 52.0, 43.9, 42.3, 37.9, 30.1, 26.5, 25.9, 25.1, 20.0. HRMS (ESI): m/z calcd for $C_{17}H_{22}N_3O^+$ $[M + H]^+$ 284.1757. Found: 284.1749.

7a. Starting from ethyl (*E*)-2-cyano-3-phenylacrylate **5a** (80.5 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7a** was obtained by precipitation from the reaction in a 52.0 mg (85%) yield as a yellow solid. Ethyl 2-cyano-3-phenylpropanoate **5a′**, which is a known compound,[17] was obtained by preparative TLC (ethyl acetate/petroleum ether = 1:10) in a 28.7 mg (71%) yield. Analytical data for **7a**: mp > 290 °C. IR (ATR): $\tilde{\nu}$ 2932, 2200, 1630, 1543, 1476, 1453, 1402, 1375, 1310, 1283, 1257, 1216, 1187, 1156, 1131, 1104, 1079, 1042, 1023, 991, 959, 934, 802, 774, 755, 727, 667 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 7.53−7.40 (m, 3H), 7.32−7.24 (m, 2H), 3.98−3.90 (m, 2H), 3.64−3.56 (m, 2H), 3.38 (d, J = 6.3 Hz, 2H), 2.25−2.17 (m, 2H), 2.06−1.97 (m, 2H), 1.91−1.81 (m, 2H), 1.62−1.53 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 159.1, 157.51, 157.49, 153.7, 137.3, 128.5, 128.4, 127.8, 118.5, 102.2, 84.1, 51.7, 49.0, 27.0, 23.7, 23.5, 21.1. HRMS (ESI): m/z calcd for $C_{19}H_{19}N_3NaO^+$ $[M + Na]^+$ 328.1420. Found: 328.1400.

7b. Starting from ethyl (*E*)-2-cyano-3-(*p*-tolyl)acrylate **5b** (86.0 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7b** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 50.0 mg (78%) yield as a light yellow solid. Ethyl 2-cyano-3-(p-tolyl)propanoate **5b′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 13.0 mg (30%) yield. Analytical data for **7b**: mp 231−233 °C. IR (ATR): $\tilde{\nu}$ 2930, 2200, 1740, 1634, 1543, 1479, 1403, 1378, 1314, 1285, 1257, 1219, 1175, 1156, 1108, 1083, 1041, 993, 959, 939, 908, 878, 827, 786, 768, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 4.16−4.08 (m, 2H), 3.64−3.55 (m, 2H), 3.38 (t, J = 6.5 Hz, 2H), 2.37 (s, 3H), 2.32 (dd, J = 11.8, 5.6 Hz, 2H), 2.14−2.05 (m, 2H), 1.99−1.87 (m, 2H), 1.67 (dt, J = 12.8, 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 159.8, 153.3, 138.8, 134.2, 129.3, 128.0, 118.1, 102.9, 88.1, 52.6, 49.6, 39.8, 27.7, 24.4, 24.3, 22.4, 21.4. HRMS (ESI): m/z calcd for $C_{20}H_{21}N_3NaO^+$ $[M + Na]^+$ 342.1577. Found: 342.1559.

7c. Starting from ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)acrylate **5c** (92.4 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7c** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 56.1 mg (84%) yield as a light yellow solid. Ethyl 2-cyano-3-(4-methoxyphenyl)propanoate **5c′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 29.3 mg (63%) yield. Analytical data for **7c**: mp 217−218 °C. IR (ATR): $\tilde{\nu}$ 3526, 2970, 2902, 2249, 2190, 1734, 1700, 1650, 1615, 1554, 1536, 1512, 1454, 1393, 1374, 1259, 1185, 1049, 890, 832, 800, 769, 753, 666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 4.16−4.05 (m, 2H), 3.83 (s, 3H), 3.66−3.54 (m, 2H), 3.38 (t, J = 6.5 Hz, 2H), 2.40−2.28 (m, 2H), 2.16−2.02 (m, 2H), 2.00−1.87 (m, 2H), 1.67 (dt, J = 12.8, 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0 (2C), 159.4, 153.4, 129.7, 129.4, 118.4, 113.9, 103.1, 87.8, 55.3, 52.5, 49.5, 39.8, 27.8, 24.5, 24.3, 22.3. HRMS (ESI): m/z calcd for $C_{20}H_{21}KN_3O_2^+$ $[M + K]^+$ 374.1265. Found: 374.1280.

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7d. Starting from ethyl (*E*)-2-cyano-3-(4-(dimethylamino)phenyl)-acrylate **5d** (97.4 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7d** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 54.5 mg (79%) yield as an orange solid. Ethyl 2-cyano-3-(4-(dimethylamino)phenyl)propanoate **5d′**, which is a known compound,[22] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:5) in a 27.5 mg (56%) yield. Analytical data for **7d**: mp 277−278 °C. IR (ATR): $\tilde{\nu}$ 2922, 2196, 1632, 1608, 1553, 1528, 1490, 1442, 1409, 1381, 1346, 1312, 1282, 1224, 1189, 1165, 1149, 1079, 1059, 980, 945, 913, 885, 832, 797, 770, 725, 696, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 4.15−4.05 (m, 2H), 3.58 (dd, J = 6.7, 4.7 Hz, 2H), 3.37 (t, J = 6.5 Hz, 2H), 2.99 (s, 6H), 2.45−2.36 (m, 2H), 2.13−2.02 (m, 2H), 1.97−1.88 (m, 2H), 1.69 (dt, J = 12.8, 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 160.2, 153.3, 150.7, 129.6(2C), 118.6, 111.7, 103.0, 88.0, 52.5, 49.4, 40.3, 39.7, 28.11, 24.6, 24.4, 22.4. HRMS (ESI): m/z calcd for $C_{21}H_{25}N_4O^+$ $[M + H]^+$ 349.2023. Found: 349.2023.

7e. Starting from ethyl (*E*)-2-cyano-3-(4-fluorophenyl)acrylate **5e** (87.6 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7e** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 56.0 mg (87%) yield as a white solid. Ethyl 2-cyano-3-(4-fluorophenyl)propanoate **5e′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 17.5 mg (40%) yield. Analytical data for **7e**: mp 237−239 °C. IR (ATR): $\tilde{\nu}$ 3838, 3588, 2987, 2902, 2291, 2201, 2162, 2026, 1985, 1701, 1639, 1553, 1483, 1403, 1381, 1294, 1254, 1153, 1066, 939, 879, 790, 750, 703, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.29−7.25 (m, 2H), 7.13 (t, J = 8.6 Hz, 2H), 4.18−4.03 (m, 2H), 3.65−3.55 (m, 2H), 3.39 (dd, J = 14.8, 8.6 Hz, 2H), 2.34−2.26 (m, 2H), 2.14−2.06 (m, 2H), 1.98−1.90 (m, 2H), 1.68 (dd, J = 12.1, 6.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.9 (d, J_{F-C} = 248.4 Hz), 159.8, 158.4, 153.6, 133.1 (d, J_{F-C} = 3.4 Hz), 130.1 (d, J_{F-C} = 8.3 Hz), 118.0, 115.7 (d, J_{F-C} = 21.8 Hz), 103.0, 87.7, 52.6, 49.6, 39.9, 27.6, 24.4, 24.2, 22.2. HRMS (ESI): m/z calcd for $C_{19}H_{19}FN_3O^+$ $[M + H]^+$ 324.1507. Found: 324.1508.

7f. Starting from ethyl (*E*)-3-(4-chlorophenyl)-2-cyanoacrylate **5f** (94.0 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7f** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 49.5 mg (73%) yield as a light yellow solid. Ethyl 3-(4-chlorophenyl)-2-cyanopropanoate **5f′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 27.5 mg (58%) yield. Analytical data for **7f**: mp 248−250 °C. IR (ATR): $\tilde{\nu}$ 2940, 2195, 1627, 1542, 1503, 1477, 1407, 1376, 1317, 1285, 1258, 1221, 1190, 1175, 1158, 1103, 1088, 111, 964, 941, 909, 883, 848, 827, 800, 774, 762, 731, 687, 663 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.14−4.05 (m, 2H), 3.65−3.56 (m, 2H), 3.40 (t, J = 6.4 Hz, 2H), 2.35−2.25 (m, 2H), 2.15−2.04 (m, 2H), 1.99−1.90 (m, 2H), 1.72−1.61 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.8, 158.1, 153.7 135.6, 134.9, 129.6, 128.9, 118.0, 102.8, 87.3, 52.6, 49.7, 39.9, 27.6, 24.4, 24.2, 22.2. HRMS (ESI): m/z calcd for $C_{19}H_{19}ClN_3O^+$ $[M + H]^+$ 340.1211. Found: 340.1208.

7g. Starting from ethyl (*E*)-3-(4-bromophenyl)-2-cyanoacrylate **5g** (111.6 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7g** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 59.7 mg (78%) yield as a light yellow solid. Ethyl 3-(4-bromophenyl)-2-cyanopropanoate **5g′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in 76.3 mg (>99%) yield. Analytical data for **7g**: mp 258−260 °C. IR (ATR): $\tilde{\nu}$ 2936, 2860, 2202, 1628, 1551, 1504, 1476, 1450, 1407, 1379, 1363, 1337, 1311, 1213, 1173, 1148, 1100, 1069, 1028, 1007, 972, 910, 882, 844, 826, 793, 768, 754, 728, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61−7.51 (m, 2H), 7.21−7.10 (m, 2H), 4.17−4.03 (m, 2H), 3.65−3.55 (m, 2H), 3.39 (t, J = 6.4 Hz, 2H), 2.36−2.24 (m, 2H), 2.13−2.04 (m, 2H), 1.99−1.90 (m, 2H), 1.66 (dt, J = 12.9, 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.8, 158.0, 153.7, 136.1, 131.8, 129.9, 123.2, 118.0, 102.8, 87.1, 52.6, 49.7, 39.9, 27.6, 24.3, 24.2, 22.2. HRMS (ESI): m/z calcd for $C_{19}H_{18}BrLiN_3O^+$ $[M + Li]^+$ 390.0788. Found: 390.0768.

7h. Starting from ethyl (*E*)-2-cyano-3-(3, 4-dimethylphenyl)-acrylate **5h** (91.6 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7h** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 52.9 mg (79%) yield as a light yellow solid. Ethyl 2-cyano-3-(3,4-dimethylphenyl)propanoate **5h′**, which is a known compound,[21] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:10) in a 19.3 mg (42%) yield. Analytical data for **7h**: mp 213−215 °C. IR (ATR): $\tilde{\nu}$ 2942, 2200, 1740, 1627, 1541, 1482, 1410, 1378, 1336, 1313, 1227, 1173, 1146, 1123, 1076, 1035, 960, 910, 892, 856, 838, 788, 770, 759, 734, 722, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 7.5 Hz, 1H), 7.03−6.96 (m, 2H), 4.18−4.02 (m, 2H), 3.64−3.54 (m, 2H), 3.38 (t, J = 6.4 Hz, 2H), 2.38−2.36 (t, 2H) 2.36−2.18 (s, 6H), 2.13−2.03 (m, 2H), 1.97−1.88 (m, 2H), 1.66 (dt, J = 12.9, 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.96, 159.91, 153.3, 137.3, 136.7, 134.7, 129.7, 129.1, 125.5, 118.2, 103.0, 87.9, 52.5, 49.5, 39.8, 27.7, 24.4, 24.3, 22.3, 19.9, 19.7. HRMS (ESI): m/z calcd for $C_{21}H_{24}N_3O^+$ $[M + H]^+$ 334.1914. Found: 334.1927.

7i. Starting from ethyl (*E*)-2-cyano-3-(naphthalen-2-yl)acrylate **5i** (100.4 mg, 0.4 mmol) and DBU **2b** (30.4 mg, 0.2 mmol), product **7i** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 60.0 mg (84%) yield as a light yellow solid. Ethyl 2-cyano-3-(naphthalen-2-yl)propanoate **5i′**, which is a known compound,[17] was obtained by column chromatography (ethyl acetate/petroleum ether = 1:5) in a 62.6 mg (>99%) yield. Analytical data for **7i**: mp 254−256 °C. IR (ATR): $\tilde{\nu}$ 2930, 2197, 1625, 1543, 1492, 1465, 1407, 1378, 1313, 1284, 1227, 1175, 1077, 963, 935, 903, 860, 831, 791, 762, 743, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 6.8 Hz, 2H), 7.76 (s, 1H), 7.55−7.48 (m, 2H), 7.36 (dd, J = 8.4, 1.5 Hz, 1H), 4.21−4.05 (m, 2H), 3.64−3.55 (m, 2H), 3.37 (t, J = 6.4 Hz, 2H), 2.36−2.27 (m, 2H), 2.09 (dd, J = 11.7, 6.0 Hz, 2H), 1.99−1.88 (m, 2H), 1.71−1.58 (m, 2H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 159.4, 153.5, 134.7, 133.2, 133.0, 128.40, 128.38, 127.8, 127.5, 126.7, 126.5, 125.8, 118.1, 103.1, 87.9, 52.6, 49.6, 39.9, 27.7, 24.4, 24.3, 22.3. HRMS (ESI): m/z calcd for $C_{23}H_{22}N_3O^+$ $[M + H]^+$ 356.1757. Found: 356.1754.

A Scaled-Up Synthesis of 6b. Ethyl (*E*)-2-cyano-3-(p-tolyl)-acrylate **5b** (20 mmol) was placed in a Schlenk tube (100 mL), and the vessel was evacuated and refilled with nitrogen three times. CH_3CN (20.0 mL) was subsequently added, followed by DBN **2a** (10 mmol). The mixture was stirred vigorously at 120 °C under a nitrogen atmosphere for 4 h. It was observed that a small amount of the product **6b** was precipitated from the reaction. After the completion of the reaction as monitored by TLC, the mixture was filtered to afford one part of product **6b**. Then, the filtrate was collected, concentrated, and purified by column chromatography (ethyl acetate/methanol = 5:1) to afford another part of the product **6b**. The pure product **6b** was obtained in a total of 2.54 g in an 88% yield.

Synthesis of Compounds 8. A mixture of 8-(4-bromophenyl)-6-oxo-1,2,4,5-tetrahydro-3*H*,6*H*-2a,5a-diazaacenaphthylene-7-carbonitrile **6f** (71.0 mg, 0.2 mmol), arylboronic acid (0.28 mmol), sodium carbonate (63.6 mg, 0.6 mmol), and $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) was evacuated and refilled with nitrogen three times. *N*,*N*-Dimethylformamide (1.0 mL) and water (5 drops) were subsequently added. The mixture was stirred vigorously at 120 °C under a nitrogen atmosphere for 24 h, diluted with dichloromethane, and then washed with water and brine. The organic phase was dried over sodium sulfate, filtered, and concentrated to get a dark residue. The crude was purified by column chromatography to obtain compounds **8**.

8a. Starting from **6f** (71.0 mg, 0.2 mmol) and phenylboronic acid (34.1 mg, 0.28 mmol), product **8a** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 50.4 mg (71%) yield as a yellow solid: mp > 250 °C. IR (ATR): $\tilde{\nu}$ 3752, 3655, 2956, 2918, 2850, 2375, 2353, 2317, 2189, 1615, 1597, 1541, 1483, 1468, 1407, 1371, 1312, 1299, 1276, 1195, 1178, 1120, 1045, 977, 923, 892, 849, 753, 701, 655, 627 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.54−7.48 (m, 4H), 7.41 (t, J = 7.3 Hz, 1H), 3.84−3.77 (t, J = 5.8 Hz, 2H), 3.73 (t, J = 8.2 Hz, 2H), 3.33 (t, J = 5.2 Hz, 2H), 2.83 (t, J = 8.2 Hz, 2H), 2.07 (t, J = 5.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ

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161.2, 154.9, 149.7, 141.1, 139.8, 135.4, 129.5, 129.1, 128.3, 127.23, 127.18, 120.5, 102.5, 78.2, 51.9, 41.9, 38.1, 24.2, 19.6. HRMS (ESI): m/z calcd for $C_{23}H_{20}N_3O^+$ $[M + H]^+$ 354.1601. Found: 354.1584.

8b. Starting from **6f** (71.0 mg, 0.2 mmol) and (4-methoxyphenyl) boronic acid (42.5 mg, 0.28 mmol), product **8b** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 55.2 mg (72%) yield as a yellow solid: mp 243−244 °C. IR (ATR): 3751, 3657, 3359, 3199, 2920, 2851, 2375, 2194, 1634, 1615, 1550, 1502, 1471, 1403, 1374, 1327, 1278, 1168, 1120, 1071, 829, 762, 745, 702, 667, 603, 526, 443 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.72−7.67 (m, 2H), 7.67−7.62 (m, 2H), 7.49−7.42 (m, 2H), 7.04−6.99 (m, 2H), 3.77 (s, 3H), 3.76−3.72 (t, J = 5.8 Hz, 2H), 3.69 (t, J = 8.2 Hz, 2H), 3.29 (t, J = 5.7 Hz, 2H), 2.78 (t, J = 8.2 Hz, 2H), 2.07−1.97 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 161.3, 159.7, 154.9, 149.8, 148.3, 140.8, 134.6, 132.1, 129.1, 128.4, 126.6, 120.6, 115.0, 102.5, 78.3, 55.7, 51.9, 38.1, 24.3, 19.6. HRMS (ESI): m/z calcd for $C_{24}H_{22}N_3O_2^+$ $[M + H]^+$ 384.1707. Found: 384.1706.

8c. Starting from **6f** (71.0 mg, 0.2 mmol) and p-tolylboronic acid (38.1 mg, 0.28 mmol), product **8c** was obtained by column chromatography (ethyl acetate/methanol = 5:1) in a 50.9 mg (69%) yield as a yellow solid: mp > 250 °C. IR (ATR): 3824, 3751, 3715, 3656, 3613, 3360, 3201, 2959, 2919, 2851, 2375, 2309, 2195, 1873, 1633, 1617, 1548, 1488, 1470, 1405, 1376, 1313, 1277, 1188, 1052, 892, 824, 757, 701, 668, 586, 491, 455 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.77−3.72 (t, J = 5.8 Hz, 2H), 3.69 (t, J = 8.2 Hz, 2H), 3.29 (t, J = 5.6 Hz, 2H), 2.78 (t, J = 8.2 Hz, 2H), 2.32 (s, 3H), 2.07−1.98 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 161.3 154.9, 149.8, 141.1, 137.8, 137.0, 135.1, 130.2, 129.1, 127.1, 126.9, 120.6, 102.6, 78.3, 51.9, 42.0, 38.1, 24.3, 21.3, 19.6. HRMS (ESI): m/z calcd for $C_{24}H_{22}N_3O^+$ $[M + H]^+$ 368.1757. Found: 368.1763.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00717.

Optimization of conditions, X-ray crystallographic data, DFT calculation data, and NMR spectra (PDF)

Accession Codes

CCDC 2021247 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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