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Highly effective capture and subsequent catalytic transformation of low-concentration  $CO_2$  by superbasic guanidines<sup>†</sup>

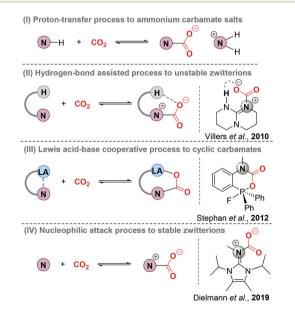
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Herein, we present a highly efficient and convenient approach for carbon dioxide ( $CO_2$ ) capture and catalytic transformation under mild conditions using N,N'-bis(imidazolyl)guanidines (BIGs, organoguanidine-based strong superbases) as the organocatalyst, even from simulated flue gas ( $10\% CO_2/90\% N_2$ , v/v) or directly from dry air ( $\sim$ 400 ppm  $CO_2$ ). The zwitterionic BIG $-CO_2$  adducts were successfully isolated and characterized. X-ray single crystal analysis revealed the bent geometry of the binding  $CO_2$  in the BIG $-CO_2$  adduct with an O-C-O angle of  $129.7^\circ$  and increased C-O bond distances (1.253 and 1.237 Å) in comparison with free  $CO_2$ . Notably, the resulting BIG $-CO_2$  adducts were found to be capable of catalyzing the novel cycloaddition of various propiolamidines with simulated flue gas to generate functionalized (4E,5Z)-4-imino-5-benzylideneoxazolidine-2-ones in good yields and excellent selectivity.

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#### Introduction

Nitrogen base-involving carbon dioxide (CO2) capture and sequestration (CCS), as a kind of climate change mitigation technology, has attracted so much global attention with the aim of reducing anthropogenic CO<sub>2</sub> emissions.<sup>1</sup> Understanding the interaction pattern of nitrogen bases and CO<sub>2</sub> is critical to boost the development of CCS technology (Scheme 1). As is well known, primary and secondary amines could react with CO2 by rapid nucleophilic attack to form zwitterionic nitrogen base-CO2 adducts (N-CO2 adducts). Due to the inherent instability, N-CO2 adducts easily react with another molecule of an amine via a proton transfer process to form stable ammonium carbamate salts (Scheme 1, I). This method has been widely applied to remove CO2 from highly concentrated and stationary CO2 emission sources, such as power plants and industrial sectors.<sup>2</sup> In 2010, the first N-CO<sub>2</sub> adduct derived from 1,5,7triazabicyclo[4.4.0]dec-5-ene (TBD) was successfully isolated and characterized by the Villiers group.3 Note that X-ray single-crystal diffraction data indicate that the intramolecular hydrogen bonding leads to an increased stability of TBD-CO2 adducts (Scheme 1, II). With the assistance of Lewis acids, N– $\rm CO_2$  adducts could also be stabilized, thus generating cyclic frustrated Lewis pair (FLP)– $\rm CO_2$  adducts (Scheme 1, III). Furthermore, N-heterocyclic imines (NHI) as more electron-rich nitrogen donors were recently developed to activate the pressured  $\rm CO_2$  by the Dielmann group and the corresponding stable NHI– $\rm CO_2$  adducts were obtained through a nucleophilic attack process (Scheme 1, IV).



Scheme 1 Representative methods for  $CO_2$  capture and sequestration by nitrogen base derivatives.

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Obviously, the donor strength of Lewis bases is a vital factor for CO<sub>2</sub> activation and sequestration. As a consequence, a series of Lewis base-CO2 adducts have been synthesized,6 employing strong basic carbon, phosphine, and oxygen bases. 9 N,N'-Bis(imidazolyl)guanidine (BIG) bases, formed by direct attachment of imidazolyl substituents to guanidine derivatives, have emerged as a new class of nitrogen bases.<sup>10</sup> Importantly, the  $pK_a$  values of the resulting BIG bases were determined to be between 26.1 and 29.3 in THF. Although commonly known organoguanidines have widely been applied for CO<sub>2</sub> capture, activation, and chemical transformation, <sup>11</sup> no literature regarding the use of strong basic BIG systems for CO<sub>2</sub> capture and sequestration has been reported. Herein, we report the synthesis, isolation and structural characterization of zwitterionic BIG-CO2 adducts via a nucleophilic addition process. More importantly, this system is even effective in extracting CO<sub>2</sub> from the ambient air. Additionally, we demonstrate that BIG-CO2 adducts also have the ability to catalyze the novel cycloaddition of propiolamidines with simulated flue gas to selectively form functionalized (4E,5Z)-4-imino-4imino-5-benzylideneoxazolidine-2-ones with high activity.

#### Results and discussion

#### Synthesis and characterization of BIG-CO2 adducts

Firstly, BIG hydrotetrafluoroborates 1a-1d were synthesized as previously reported by Ullrich Jahn et al. 10a BIG bases were prepared by the deprotonation of 1a-1d with KN(SiMe<sub>3</sub>)<sub>2</sub> in THF solution and further purified by extraction with n-hexane. When the n-hexane solution of BIG bases 2a-2d was placed under an atmosphere of pure CO<sub>2</sub> at room temperature, white precipitates of BIG-CO2 adducts (3a-3d) were rapidly formed and isolated in good to excellent yields (Scheme 2).

Furthermore, BIG-CO<sub>2</sub> adducts (3a-3d) were structurally characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and MS (ESI).† <sup>13</sup>C NMR spectra of 3a-3d show the chemical shifts of the carbonyl group in the range of 162.1-162.3 ppm, which are quite close

Scheme 2 CO<sub>2</sub> activation and fixation by BIG bases. Reaction conditions: (I) KN(SiMe<sub>3</sub>)<sub>2</sub>, THF, 25 °C, 2 h; (II) CO<sub>2</sub> (1 atm), n-hexane, 25 °C,

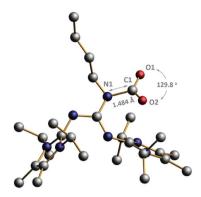


Fig. 1 POV-Ray illustrations of the molecular structure of BIG-CO<sub>2</sub> adduct 3b. Hydrogen atoms have been omitted for clarity. C: black, O: red, and N: dark blue. Selected bond lengths (Å) and angles (°): N1-C1. 1.484(6); O1-C1, 1.253(6); O2-C1, 1.237(4); O1-C1-O2, 129.78(7).

to those of reported NHI-CO<sub>2</sub> adducts. 10a Meanwhile, a 13C isotope labeling experiment was conducted, in which the CO<sub>2</sub> resonance of 3a (162.1 ppm) obtained from <sup>13</sup>CO<sub>2</sub> was enhanced obviously. And also, the C=O stretching frequencies of 3a-3d were investigated in the range of 1610-1631 cm<sup>-1</sup>. Gratifyingly, the single crystal of 3a was obtained and determined by X-ray single crystal diffraction, as shown in Fig. 1. The crystal structure data show that the C1-O1 and C1-O2 bond distances, 1.253(6) and 1.237(4) Å, respectively, are both elongated, in comparison with that of free gaseous CO<sub>2</sub> (1.160 Å). A bent geometry of the binding CO<sub>2</sub> with an O1-C1-O2 angle of 129.78(7)° was observed in the BIG-CO2 adduct, indicating that CO2 is activated through nucleophilic attack by BIG bases. Moreover, the dihedral angles between the plane of the guanidine core and the two imidazole planes are 109.85 (4)° and 119.54(4)°, respectively.

In addition, the thermal stability of BIG-CO2 adducts 3a-3d was investigated by means of thermogravimetric analysis (TGA). From the results (ESI, Fig. S1-S4†), the reversible decarboxylation of 3a-3d began in the range of 129.2-135.8 °C, and the observed weight losses were matched well with the theoretical content of CO<sub>2</sub> in BIG-CO<sub>2</sub> adducts.

#### CO<sub>2</sub> capture ability of BIG bases under various concentrations of CO<sub>2</sub>

Reversible CO2 capture and release of BIG bases was also studied by Density Functional Theory (DFT) calculations (ESI, Fig. S5†). The free energy barriers of BIG bases 2a-2d for CO<sub>2</sub> capture are very low (5.5-7.6 kcal mol<sup>-1</sup>), and the formation of BIG-CO<sub>2</sub> adducts 3a-3c is even more exergonic. Based on this observation, BIG bases have the potential to be applied for CO2 activation and capture. Up to now, most of the existing CCS technologies are applied in highly concentrated and stationary CO2 emission sources. Direct CO2 capture from ambient air, by contrast, is becoming more promising to permanently lower the atmospheric CO2 concentration, thus achieving negative carbon emissions. 12 As shown in Fig. 2, the CO2 capture ability of BIG bases with 2a as an example was

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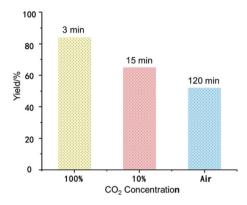


Fig. 2  $CO_2$  fixation ability of a BIG base (2a) under various concentrations of  $CO_2$ . Reaction conditions: BIG base (2a) (0.1 mmol), hexane (5 mL), 25 °C,  $CO_2$  (balloon); simulated flue gas (100 mL min<sup>-1</sup>); dry air (100 mL min<sup>-1</sup>).

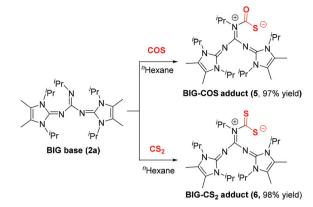
measured under various concentrations of  $CO_2$ . When the commercially pure  $CO_2$  was introduced with a balloon, a white precipitate was formed immediately to obtain 3a in 84% isolated yield within 3 minutes. Moreover,  $CO_2$  capture from simulated flue gas (10%  $CO_2/90\%$   $N_2$ , v/v) could also be carried out at a flow rate of 100 mL min<sup>-1</sup>, and the corresponding 3a was formed in 65% yield within 15 minutes. When switching to dry air containing about 400 ppm of  $CO_2$ , a yield of 52% could be obtained with an enhanced reaction time of 2 hours.

#### Protonation of BIG-CO<sub>2</sub> adducts in the presence of H<sub>2</sub>O

Most of the known Lewis base– $\mathrm{CO}_2$  adducts are sensitive to protic solvents, such as water and alcohols. <sup>13</sup> Surprisingly, recently reported NHI– $\mathrm{CO}_2$  adducts bearing a methyl group at the exocyclic nitrogen atom showed unprecedented chemical stability towards hydrolysis, probably due to the hydrophobic nature of the  $\mathrm{CO}_2$  binding site. <sup>5</sup> The stability of BIG– $\mathrm{CO}_2$  adducts toward water was also evaluated in THF solution at ambient temperature. In the presence of 1.2 equiv.  $\mathrm{H}_2\mathrm{O}$ ,  $\mathrm{2a-2c}$  was rapidly hydrolyzed via a decarboxylation process to form ammonium bicarbonates  $\mathrm{4a-c}$  in 90–98% isolated yields. Meanwhile, the X-ray crystal structure of  $\mathrm{4a}$  was also determined (ESI, Fig. S7†).

#### Application of BIG for COS and CS2 capture and activation

Because of the structural similarity of COS and CS<sub>2</sub> molecules to CO<sub>2</sub>,<sup>14</sup> their capture using BIG base **2a** was also investigated under the same reaction conditions. As shown in Scheme 3, the COS and CS<sub>2</sub> capture processes could smoothly proceed at room temperature and the corresponding BIG–COS adduct 5 and CS<sub>2</sub> adduct **6** were isolated in 97% and 98% yields, respectively. The solid-state structure of the BIG–CS<sub>2</sub> adduct **6** shows that CS<sub>2</sub> binds to the nitrogen atom with a N1–C1 bond of 1.427(7) Å and a S–C–S angle of 122.96(4)° (Fig. 3). Note that the BIG–CS<sub>2</sub> adduct **6** is the first example of a nitrogen-based zwitterionic adduct. The groups of Vlasse<sup>15</sup> and Jessop<sup>16</sup> independently reported the reaction of CS<sub>2</sub> with cyclic amidines to



Scheme 3 COS/CS<sub>2</sub> activation and fixation by BIG bases.

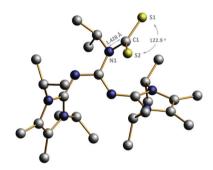


Fig. 3 POV-Ray illustrations of the molecular structure of 6. Hydrogen atoms have been omitted for clarity. C: black, S: yellow, and N: dark blue. Selected bond lengths (Å) and angles (°): N1–C1, 1.427(7); S1–C1, 1.703(6): S2–C1, 1.680(9): S1–C1–S2, 122.96(4).

form cyclic carbamic carboxylic trithioanhydride rings, while acyclic acetamidines were cleaved by  $CS_2$  at room temperature to give an isothiocyanate and a thioacetamide. In addition, Cantat *et al.* showed that TBD reacted with  $CS_2$  and the guanidinium dithiocarbamate was selectively synthesized via a proton transfer process.<sup>17</sup>

# Application of BIG–CO $_2$ adducts as organocatalysts for CO $_2$ catalytic transformation

As an additional CO<sub>2</sub>-mitigation strategy to CCS, CO<sub>2</sub> capture and utilization (CCU) is attracting global interest. Recently, Lewis base–CO<sub>2</sub> adducts, as a new class of organic catalysts, have exhibited unique reactivity and selectivity for CO<sub>2</sub> transformation to value-added chemicals, which inspires us to further investigate the application of BIG–CO<sub>2</sub> adducts in the CCU process. Gratifyingly, BIG–CO<sub>2</sub> adduct 3b could efficiently catalyze the novel cycloaddition of propargylamidine 7a with simulated flue gas at 80 °C in 24 hours (for detailed optimized conditions, see ESI, Table S1†), thus generating 4-imino-5-benzylideneoxazolidine-2-one 8a in 90% isolated yield. The reactions of propargylamidines (7b–7f) bearing methyl, methoxyl or halogen groups (–F, –Cl, and –Br) on the aryl ring gave the corresponding products 8b–8f in moderate to excellent yields. When the R<sup>2</sup> group was transformed to the cyclohexyl group,

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Table 1 BIG-CO<sub>2</sub> adduct 3b catalyzed cycloaddition of propargylamidines with CO<sub>2</sub> (simulated flue gas)<sup>a</sup>

 $^a$  General reaction conditions: Sub. 7 (0.25 mmol), BIG–CO<sub>2</sub> adduct **3b** (0.025 mmol, 10 mol%), CO<sub>2</sub> balloon (10% CO<sub>2</sub>, 90% N<sub>2</sub>), DMSO (1.0 mL), 80 °C, 24 h. Isolated yields.  $^b$  POV-ray depiction of single crystal. C: black, O: red, and N: dark blue.

the corresponding substrate **7g** was converted to **8g** with 90% yield. Meanwhile, the absolute stereostructures of (4*E*,5*Z*)-**8a** and **8g** were clearly confirmed by single-crystal X-ray diffraction study (Table 1).

To demonstrate the synthetic utility of this transformation, the gram-scale synthesis and further transformations of the products were next elucidated, as shown in Scheme 4. Under the standard conditions, the reaction of 7f (1.2 g) with simulated flue gas proceeded smoothly, isolating the corresponding

**Scheme 4** Gram-scale synthesis and synthetic applications oproducts.

product **8f** in 81% yield (Scheme 4, I). Moreover, the carbon-carbon double bond of product **8a** was selectively reduced by H<sub>2</sub> in the presence of Pd/C catalyst at room temperature, and the reduced product **9** was isolated in 95% yield (Scheme 4, **II**). Oxazolidine-2,4-diones, as a significant class of heterocyclic scaffolds, are frequently found in biologically active and medicinally useful molecules.<sup>20</sup> Note that the hydrolysis of **8f** could take place smoothly in an aqueous solution of hydrochloric acid, thus affording oxazolidine-2,4-dione **10** in 98% yield (Scheme 4, III).

#### Conclusions

In summary, we have demonstrated the high efficiency of superbasic guanidines for reversible capture of low-concentration CO<sub>2</sub> at room temperature and atmospheric pressure, affording the corresponding CO<sub>2</sub> adducts in good and excellent yields. Moreover, the resulting BIG–CO<sub>2</sub> adducts were demonstrated to be efficient organocatalysts for the cyclization of CO<sub>2</sub> (10% CO<sub>2</sub>/90% N<sub>2</sub>, v/v) and propiolamidines to produce various functionalized (4*E*,5*Z*)-4-imino-5-benzylideneoxazolidine-2-ones in high yields and excellent selectivity. The present study provides an alternative method for CO<sub>2</sub> capture and subsequent catalytic transformation of low-concentration CO<sub>2</sub> under mild conditions. Further explorations regarding the applications of organocatalytic systems for the synthesis of various heterocyclic chemicals are now in progress.

## Experimental

# Representative experimental procedure for the synthesis of BIG-CO<sub>2</sub> adducts (3a-3d)

In a nitrogen-filled glove box, BIG salt 1a (545 mg, 1.0 mmol) was added to a suspension of KHMDS (199 mg, 1.0 mmol) in THF (10 mL) and the mixture was stirred at 25 °C for 2 h. Then the solvent was removed in vacuo and the residues were extracted with n-hexane (10 mL). After filtration to remove the inorganic salt, the filtrate was exposed to 1.0 atm of CO2 at room temperature for 2 h. The resulting precipitates were collected *via* filtration, washed with *n*-hexane  $(3 \times 5 \text{ mL})$  and then dried in vacuo to afford BIG-CO2 adduct 3a as a white solid (476 mg, 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.52 (dt, J = 14.1, 7.0 Hz, 4H), 4.06 (dt, J = 13.1, 6.5 Hz, 1H), 2.23 (s, 12H), 1.47 (d, J = 7.1 Hz, 24H), 1.21 (d, J = 6.5 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.1, 156.2, 147.6, 120.2, 47.9, 44.0, 23.1, 21.3, 10.1. **IR**  $\nu_{C=0}$ : 1650 cm<sup>-1</sup>. **HRMS (ESI)**: calcd for  $C_{27}H_{47}N_7O_2$ : 458.3966 [M -  $CO_2$  + H]<sup>+</sup>. Found: 458.3962  $[M - CO_2 + H]^+$ .

**3b.** White solid (464 mg, 90% yield). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.49 (dt, J = 14.1, 7.0 Hz,4 H), 3.60–3.07 (m, 2H), 2.19 (s, 12H), 1.54 (dt, J = 15.0, 7.5 Hz, 2H), 1.44 (d, J = 7.0 Hz, 24H), 1.31 (dt, J = 15.0, 7.4 Hz, 2H), 0.86 (dt, J = 14.1, 7.2 Hz, 3H). <sup>13</sup>C **NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.1, 157.4, 147.9, 120.1, 47.9, 42.3, 32.5, 21.3, 20.2, 13.9, 10.1. **IR**  $\nu_{\text{C}}$ : 1647 cm<sup>-1</sup>.

**HRMS** (ESI): calcd for  $C_{28}H_{49}N_7O_2$ : 472.4122 [M -  $CO_2$  + H]<sup>+</sup>. Found: 472.4155 [M -  $CO_2$  + H]<sup>+</sup>.

3c. White solid (434 mg, 82% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.76–4.24 (m, 4H), 3.23 (s, 2H), 2.25 (s, 12H), 1.48 (d, J = 7.1 Hz, 24H), 0.92 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.2, 157.3, 147.6, 120.3, 53.6, 47.9, 32.2, 27.4, 21.4, 10.1. IR  $\nu_{\text{C}=\text{O}}$ : 1654 cm<sup>-1</sup>. HRMS (ESI): calcd for C<sub>29</sub>H<sub>51</sub>N<sub>7</sub>O<sub>2</sub>: 486.4279 [M – CO<sub>2</sub> + H]<sup>+</sup>. Found: 486.4271 [M – CO<sub>2</sub> + H]<sup>+</sup>.

**3d.** White solid (542 mg, 82% yield). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.19 (dt, J = 11.6, 5.6 Hz, 1H), 4.13–3.97 (m, 4H), 2.24 (s, 12H), 1.79 (dd, J = 62.7, 9.0 Hz, 28H), 1.44–0.99 (m, 18H); <sup>13</sup>C **NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.3, 155.3, 147.8, 120.6, 56.8, 44.1, 31.0, 26.2, 25.1, 23.5, 10.9. **IR**  $\nu_{\text{C}=\text{O}}$ : 1639 cm<sup>-1</sup>. **HRMS** (**ESI**): calcd for C<sub>39</sub>H<sub>63</sub>N<sub>7</sub>O<sub>2</sub>: 618.5218 [M – CO<sub>2</sub> + H]<sup>+</sup>. Found: 618.5205 [M – CO<sub>2</sub> + H]<sup>+</sup>.

# Representative experimental procedure for the cycloaddition of propiolamidines with simulated flue gas to (4*E*,5*Z*)-4-imino-5-benzylideneoxazolidine-2-ones

In a nitrogen-filled glove box, a 10 mL Schlenk flask equipped with a magnetic stirring bar was charged with propiolamidine 7a (57.1 mg, 0.25 mmol), Cat. 3b (12.9 mg, 0.025 mmol, 10 mol%) and DMSO (1.0 mL). Then the Schlenk flask was immediately transferred from the glovebox, and exchanged with CO<sub>2</sub> (10% CO<sub>2</sub>/90% N<sub>2</sub>, v/v) using a balloon. The reaction was stirred at 80 °C for 24 h. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the desired (4E,5Z)-4imino-5-benzylideneoxazolidine-2-one 8a (61.2 mg, 90%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77–7.63 (m, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 6.35 (s, 1H), 4.10 (tt, J = 12.3, 3.9 Hz, 1H), 3.84 (t, J = 9.1 Hz, 1H), 2.21 (dq, J = 12.5, 3.3 Hz, 2H), 1.85 (d, J = 9.7 Hz, 6H), 1.68 (t, J = 11.8Hz, 4H), 1.61–1.13 (m, 10H);  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 152.7, 142.8, 136.1, 132.8, 130.5, 129.0, 128.9, 113.1, 57.0, 52.0, 33.9, 28.6, 26.1, 26.0, 25.3, 24.5. IR: 2930, 2855, 1797, 1670, 1647, 1450, 1367, 1331, 1232, 1201, 1089. HRMS (ESI): calcd for  $C_{22}H_{28}N_2O_2$ : 353.2224 [M + H]<sup>+</sup>. Found: 353.2212 [M + H]<sup>+</sup>.

**8b.** White solid (80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 6.40 (s, 1H), 4.52 (hept, J = 6.8 Hz, 1H), 4.17 (hept, J = 6.1 Hz, 1H), 2.37 (s, 3H), 1.43 (d, J = 6.9 Hz, 6H), 1.28 (d, J = 6.1 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.5, 143.0, 139.4, 135.6, 130.5, 129.9, 129.6, 113.5, 49.0, 44.1, 24.1, 21.5, 19.0. IR: 2971, 2935, 1794, 1670, 1647, 1407, 1385, 1349, 1330, 1313, 1252, 1178, 1024. HRMS (ESI): calcd for  $C_{17}H_{22}N_2O_2$ : 287.1754 [M + H]<sup>+</sup>. Found: 287.1752 [M + H]<sup>+</sup>.

8c. White solid (78%). <sup>1</sup>H NMR (400 MHz, CDC<sub>13</sub>)  $\delta$  7.67 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 6.38 (s, 1H), 4.69–4.36 (m, 1H), 4.32–4.08 (m, 1H), 3.84 (s, 3H), 1.42 (d, J = 6.9 Hz, 6H), 1.27 (d, J = 6.2 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.3, 152.6, 143.1, 134.8, 132.2, 125.5, 114.4, 113.3, 55.5, 49.0, 44.1, 24.1, 19.1. IR: 2957, 2927, 1793, 1670, 1646, 1604, 1513, 1408, 1385, 1256, 1178, 1026. HRMS (ESI): calcd for  $C_{17}H_{22}N_2O_3$ : 303.1703 [M + H]<sup>+</sup>. Found: 303.1693 [M + H]<sup>+</sup>.

**8d.** White solid (98%). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87–7.54 (m, 2H), 7.21–6.87 (m, 2H), 6.38 (s, 1H), 4.52 (hept, J = 7.0 Hz, 1H), 4.31–4.01 (m, 1H), 1.42 (d, J = 7.0 Hz, 6H), 1.27 (d, J = 6.2 Hz, 6H). **IR**: 2972, 1797, 1673, 1650, 1602, 1509, 1408, 1386, 1252, 1163, 1023. **HRMS** (**ESI**): calcd for  $C_{16}H_{19}FN_2O_2$ : 291.1503 [M + H]<sup>+</sup>. Found: 291.1493 [M + H]<sup>+</sup>.

8e. White solid (82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 6.36 (s, 1H), 4.51 (m, J = 6.9 Hz, 1H), 4.30–4.00 (m, 1H), 1.42 (d, J = 7.0 Hz, 6H), 1.27 (d, J = 6.2 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.1, 142.6, 136.4, 134.9, 131.6, 131.3, 129.1, 111.9, 49.2, 44.3, 24.1, 19.0. IR: 2972, 1794, 1673, 1648, 1490, 1409, 1385, 1349, 1251, 1180, 1080, 1022. HRMS (ESI): calcd for  $C_{16}H_{19}ClN_2O_2$ : 307.1208 [M + H]<sup>+</sup>. Found: 307.1198 [M + H]<sup>+</sup>.

8f. White solid (90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 6.27 (s, 1H), 4.44 (m, J = 6.9 Hz, 1H), 4.08 (m, J = 6.1 Hz, 1H), 1.35 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.2 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.1, 142.6, 136.5, 132.1, 131.9, 131.7, 123.3, 112.0, 49.2, 44.2, 24.1, 19.0. IR: 2970, 2938, 1794, 1671, 1646, 1486, 1408, 1385, 1348, 1307, 1250, 1176, 1074, 1021. HRMS (ESI): calcd for  $C_{16}H_{19}BrN_2O_2$ : 351.0703 [M + H]<sup>+</sup>. Found: 351.0693 [M + H]<sup>+</sup>.

**8g.** White solid (90%). <sup>1</sup>H **NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77–7.63 (m, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 6.35 (s, 1H), 4.10 (tt, J = 12.3, 3.9 Hz, 1H), 3.84 (t, J = 9.1 Hz, 1H), 2.21 (qd, J = 12.5, 3.3 Hz, 2H), 1.85 (d, J = 9.7 Hz, 6H), 1.68 (t, J = 11.8 Hz, 4H), 1.61–1.13 (m, 10H). <sup>13</sup>C **NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.7, 142.8, 136.1, 132.8, 130.5, 129.0, 128.9, 113.1, 57.0, 52.0, 33.9, 28.6, 26.1, 26.0, 25.3, 24.5. **IR**: 2930, 2855, 1797, 1670, 1647, 1450, 1367, 1331, 1232, 1201, 1089. **HRMS** (**ESI**): calcd for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: 353.2224 [M + H]<sup>+</sup>. Found: 353.2212 [M + H]<sup>+</sup>.

### Conflicts of interest

There are no conflicts to declare.

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