# **Supporting Information**

## Visible-light Photoredox-Catalyzed Iminyl Radical Formation by N-H Cleavage with Hydrogen Release and Its Application in Synthesis of Isoquinolines

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## **General Information**

N-H diaryl imines **1a-1h** and **1j**,<sup>1</sup> **1k-1l**,<sup>2</sup> **1m**<sup>3</sup> and alkynes **2b-2l**,<sup>4</sup> were synthesized according to the reported procedures. The cobalt complexes  $Co(dmgH)(dmgH_2)Cl_2$ ,  $Co(dmgH)_2PyCl$ ,  $Co(dmgH)_2(4-NMe_2Py)Cl$ ,  $Co(dmgH)_2(4-CO_2MePy)Cl$ ,  $Co(dmgH)_2(4-CONMe_2Py)Cl$  and  $Co(dmgH)_2(4-CONEt_2Py)Cl$  were prepared according to the reported procedures.<sup>5</sup> DCM were freshly distilled over CaH<sub>2</sub>. If no special indicated, other reagents and solvents were used as commercially available without further purification. All the reactions were carried out in reaction tubes on Wattecs Parral Reactor under argon atmosphere. Column chromatographic purification of products was accomplished using 300-400 mesh silica gel.

NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the <sup>1</sup>H spectrum as 0.00 ppm, CDCl<sub>3</sub> resonance in the <sup>13</sup>C spectrum as 77.0 ppm. DMSO-*d*<sub>6</sub> resonance in the <sup>1</sup>H spectrum as 2.50 ppm and <sup>13</sup>C spectrum as 39.5 ppm. <sup>19</sup>F spectrum were determined relative to CFCl<sub>3</sub> as external standard. Coupling constants are reported in Hz with multiplicities denoted as br (broad), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (v max) are reported in wavenumbers (cm<sup>-1</sup>). HRMS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Analytical gas chromatography (GC) for liquid phase was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector and a TR-V1 column (0.32 mm × 30 m, Film: 1.8 µm). Analytical gas chromatography (GC) for gas sample were carried out on a SHIMDZU GC-2014ATF/SPL (TDX-01 60/80 mesh, 2.0 mm x 3.2mm x 2.1 mm-FID, TCD- permanent gases, N<sub>2</sub> carrier gas). The systems allow for the determination of H<sub>2</sub>, Ar, CO and CO<sub>2</sub> within the ranges:  $H_2 \ge 0.5$  vol% -100 vol%,  $CO \ge 2$  ppm,  $CO_2 \ge 100$  ppm. UV-vis absorption spectrum, the quantum yield measurement and steady-state emission spectra were recorded using a PerkinElmer Lambda or a HITACHI F-4500 Fluorescence Spectrometer. Cyclic voltammetry experiments were studied On a CHI660E Electrochemical Workstation equipped with the conventional three electrode system under argon atmosphere. The measurements were performed in CH<sub>3</sub>CN containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub> using ferrocene/ferrocenium ( $Fc^+/Fc^0$ ) as an internal reference. The working electrode was a glassy carbon disk electrode (d = 0.3 cm). The auxiliary and reference electrode consisted of a Pt tablets and an Ag/AgNO<sub>3</sub> (0.1 M in CH<sub>3</sub>CN), respectively. Glassy carbon disk electrode was polished with the d = 0.05 micron Alumina powder and a polishing cloth before each measurement.

#### General Procedure for Preparation of 1i, 1n and 1p-1u.

Following a literature procedure,<sup>1</sup> a mixture of the aryl nitrile (1 equiv) and the aryl Grignard reagent (2 equiv) was refluxed in THF for 12 h under Ar atmosphere. The reaction mixture was cooled to room temperature and then treated with anhydrous methanol. After stirring vigorously for 0.5 h, the mixture was diluted with Et<sub>2</sub>O and the resulting suspension was filtrated through Celite. The volatile materials were evaporated under vacuum. The residue was further purified by flash column chromatography with the eluent of petroleum ether/ethyl acetate (1.5 mL of Et<sub>3</sub>N was added into every 100 mL of petroleum ether/ethyl acetate).

#### Characterization data for 1i, 1n and 1p-1u.

Compound 1i



Applying 3-chlorobenzonitrile (21.8 mmol) and (3-chlorophenyl)magnesium bromide (43.6 mmol) following the general procedure, **1i** (3.29 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 60% yield as a pale yellow oil . <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  10.98 (s, 1H), 7.66 (s, 1H), 7.59-7.55 (m, 2H), 7.51-7.47 (m, 4H), 7.33 (d, *J* =

7.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  172.5, 140.5, 140.1, 133.4, 133.2, 130.3, 130.3, 130.2, 129.8, 127.9, 127.4, 127.4, 126.2. IR (cm<sup>-1</sup>): *v* 3255, 3056, 2939, 1668, 1588, 1558, 1426, 1337, 1192, 1159, 1076, 870, 804, 696. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>N, 250.0185; found 250.0179.

#### Compound 1n



Applying 1-cyanonaphthalene (10.0 mmol) and (4-fluorophenyl)magnesium bromide (20.0 mmol) following the general procedure, **1n** (1.79 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 72% yield as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$ 

10.69 (s, 1H), 8.02 (t, J = 8.2 Hz, 2H), 7.65-7.58 (m, 3H), 7.55-7.50 (m, 2H), 7.46-7.38 (m, 3H), 7.02 (m, 1H); <sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  173.7, 163.7 (d, <sup>1</sup> $J_{C-F} = 247.9$  Hz), 138.3, 135.3, 133.1, 130.2 (d, <sup>3</sup> $J_{C-F} = 9.1$  Hz, 2C), 129.6 (d, <sup>4</sup> $J_{C-F} = 5.4$  Hz), 128.8, 128.5, 126.8, 126.3, 125.6, 125.0, 124.9, 115.4 (d, <sup>2</sup> $J_{C-F} = 21.5$  Hz, 2C); <sup>19</sup>F NMR (376 MHz, DMSO): -109.2; IR (cm<sup>-1</sup>): v 3060, 2920, 2850, 1730, 1656, 1601, 1507, 1355, 1226, 1144, 902, 844, 808, 785, 734. MS: m/z: [M]<sup>+</sup>, 249.20.

#### Compound 1p



Applying 9-phenanthrenecarbonitrile (4.92 mmol) and (4methylphenyl)magnesium bromide (9.84 mmol) following the general procedure, **1p** (1.24 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 85% yield as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.71 (br, 1H), 8.67 (d, *J* = 8.0

Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.66-7.56 (m, 6H), 7.43 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  177.5, 141.3, 137.8, 135.7, 130.8, 130.3 (2C), 129.3, 129.1 (2C), 128.8, 128.2 (2C), 127.3, 126.9, 126.8 (2C), 126.5, 125.9, 122.8, 122.5, 21.3; IR (cm<sup>-1</sup>): *v* 3230, 3045, 26917, 1602, 1445, 1362, 1217, 1164, 876, 837, 747. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>18</sub>N, 296.1434; found 296.1432.

#### Compound **1q**



Applying 9-phenanthrenecarbonitrile (4.92 mmol) and (4methoxylphenyl)magnesium bromide (9.84 mmol) following the general procedure, **1q** (1.29 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 84% yield as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.63 (br, 1H), 8.74 (d, *J* = 8.8 Hz, 1H), 8.71 (d, *J* =

8.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.77-7.60 (m, 7H), 7.50-7.46 (m, 1H), 6.86-6.83 (m, 2H), 3.79 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  177.0, 161.9, 138.0, 131.2, 131.0, 130.4, 130.4, 130.1 (2C), 129.4, 129.0, 127.4, 127.1, 127.0 (2C), 126.7, 126.0, 123.0, 122.6, 113.7 (2C), 55.3. IR (cm<sup>-1</sup>): v 3263, 3069, 2934, 2833, 1601, 1509, 1446, 1353, 1245, 1153, 1027, 876, 835, 731. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>18</sub>NO, 312.1383; found 312.1383.

#### Compound 1r



Applying 9-phenanthrenecarbonitrile (3.94 mmol) and (4-tertbutyllphenyl)magnesium bromide (7.88 mmol) following the general procedure, **1r** (1.10 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 83% yield as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.71 (br, 1H), 8.70 (d, *J* = 8.0, 1H), 8.67 (d, *J* = 8.4 Hz, 1H),

7.83-7.57 (m, 8H), 7.47-7.44 (m, 1H), 7.35-7.33 (m, 2H), 1.28 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  177.6, 154.5, 137.8, 135.8, 131.0, 130.5, 130.5, 129.5, 129.0, 128.2 (2C), 127.4, 127.1, 127.0 (2C), 126.7, 126.1, 125.4 (2C), 123.0, 122.7, 34.9, 31.2 (3C); IR (cm<sup>-1</sup>): *v* 3254, 3061, 2965, 1664, 1596, 1445, 1408, 1348, 1162, 881, 750, 727. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>25</sub>H<sub>24</sub>N, 338.1903; found 338.1903.

#### Compound 1s



Applying 9-phenanthrenecarbonitrile (4.92 mmol) and (4-chlorophenyl)magnesium bromide (9.84 mmol) following the general procedure, **1s** (1.25 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 80% yield as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.89 (br, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 8.4 Hz, 1H),

7.84 (d, J = 7.6 Hz, 1H), 7.70-7.58 (m, 7H), 7.48-7.44 (m, 1H), 7.29 (d, J = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.7, 137.2 (2C), 136.9, 130.7, 130.4, 130.4, 129.7 (2C), 128.9 (2C), 128.6 (2C), 127.5, 127.1, 127.1, 127.0, 126.3, 126.1, 123.0, 122.6; IR (cm<sup>-1</sup>): v 3250, 3058, 2926, 1586, 1486, 1446, 1402, 1350, 1163, 1094, 1011, 877, 835, 750, 725. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>15</sub>ClN, 316.0888; found 316.0887.

Compound 1t



Applying 9-phenanthrenecarbonitrile (4.92 mmol) and (4-fluorophenyl)magnesium bromide (9.84 mmol) following the general procedure, **1t** (1.26 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 86% yield as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.81 (br, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H),

7.82-7.77 (m, 3H), 7.70-7.56 (m, 5H), 7.44 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 8.8 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.4, 164.5 (d, <sup>1</sup> $J_{C-F} = 250.2$  Hz), 137.3, 134.6 (d, <sup>4</sup> $J_{C-F} = 2.8$  Hz), 130.7, 130.5 (d, <sup>3</sup> $J_{C-F} = 8.6$  Hz, 2C), 130.3 (2C), 129.0, 128.9, 127.4, 127.1, 127.0, 126.9, 126.3, 126.0, 123.0, 122.5, 115.3 (d, <sup>2</sup> $J_{C-F} = 21.6$  Hz, 2C); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): -109.0; IR (cm<sup>-1</sup>): v 3255, 3063, 2924, 1597, 1506, 1447, 1410, 1346, 1220, 1148, 877, 839, 743, 722. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>15</sub>FN, 300.1183; found 300.1179.

#### Compound 1u



Applying 9-phenanthrenecarbonitrile (2.46 mmol) and (4-trifluorophenyl)magnesium bromide (4.92 mmol) following the general procedure, **1u** (0.73 g) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate/Et<sub>3</sub>N = 200/10/3) in 85% yield as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.13 (br, 1H), 8.74 (d, *J* = 8.8 Hz, 1H), 8.71 (d, *J* = 8.4 Hz, 1H),

7.89-7.87 (m, 3H), 7.73-7.59 (m, 7H), 7.49 (t, J = 7.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.8, 141.7, 136.9, 132.6 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32.3Hz), 130.7, 130.5, 130.5, 129.0, 128.9, 128.7 (2C), 127.7, 127.3, 127.2, 127.1, 126.3 (2C), 125.4 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz, 2C), 123.8 (q, <sup>1</sup>*J*<sub>C-F</sub> = 270.8 Hz), 123.2, 122.7; IR (cm<sup>-1</sup>): v 3248, 3038, 2922, 1687, 1616, 1514, 1410, 1380, 1112, 1017, 899, 733, 702. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>15</sub>F<sub>3</sub>N, 350.1151; found 350.1150.

#### General procedure for preparation of cobalt complexes

Following the literature procedure,<sup>5</sup> Co(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub> was suspended in methanol. Triethylamine (1 equiv) was then added to the flask. After stirring for 5 mins, the suspension turned to brown transparent solution. Afterwards, the corresponding pyridine derivatives (1 equiv) were added and the mixture was stirred for 1 h to form a brown precipitate. The suspension was filtered and the precipitate was washed with water, ethanol, and diethyl ether to afford the cobalt complexes.

#### Characterization data for new cobalt complexes

## Co(dmgH)2(4-CONMe2Py)Cl



According to the general procedure, *N*,*N*-dimethylisonicotinamide<sup>6</sup> (5.31 mmol) and Co(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub> (5.31 mmol) were employed as the substrate to give the product Co(dmgH)<sub>2</sub>(4-CONMe<sub>2</sub>Py)Cl (1.22 g) in 48% yield as a brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.34 (d, *J* = 6.4 Hz, 2H), 7.20 (d, *J* = 6.8 Hz, 2H), 3.49 (s, 2H), 3.09 (s, 3H), 2.29 (s, 3H), 2.42 (s, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.6, 152.8 (4C), 151.5 (2C), 146.7, 123.2 (2C), 39.0, 35.2, 13.2

(4C); IR (cm<sup>-1</sup>): v 3056, 2981, 2924, 1739, 1374, 1235, 1041, 731; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>16</sub>H<sub>25</sub>ClCoN<sub>6</sub>O<sub>5</sub>, 475.0901; found 475.0904.

## Co(dmgH)2(4-CONEt2Py)Cl



According to the general procedure, *N*,*N*-diethylisonicotinamide<sup>7</sup> (8.10 mmol) and Co(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub> (8.10 mmol) were employed as the substrate and finally give the product Co(dmgH)<sub>2</sub>(4-CONEt<sub>2</sub>Py)Cl (3.34 g) in 82% yield as a brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.32 (d, *J* = 6.0 Hz, 2H), 7.17 (d, *J* = 6.0 Hz, 2H), 3.50 (q, *J* = 7.2 Hz, 2H), 3.11 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 12H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 

166.2, 152.8 (4C), 151.5 (2C), 147.3, 122.8 (2C), 43.2, 39.5, 14.3, 13.2 (4C), 12.6; IR (cm<sup>-1</sup>): v 3057, 2968, 2920, 1631, 1558, 1429, 1236, 1090, 732; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>18</sub>H<sub>29</sub>ClCoN<sub>6</sub>O<sub>5</sub>, 503.1214; found 503.1215.

## General procedure for synthesis of isoquinolines 3

To a Schlenk tube containing a stirring bar was added  $Acr^+-Mes ClO_4^-$  (0.01 mmol),  $Co(dmgH)_2(CONMe_2Py)Cl$  (0.01 mmol), compound **1** (0.10 mmol) and compound **2** (0.20 mmol). Then anhydrous DCM (5.0 mL) was added to the reaction tube via syringe in glove box. The reaction mixture was stirred for 12 h at Wattecs Parallel Light Reactor (Blue LED Light source, every tube hole groove, 10 W) at ambient temperature. The gas phase was detected for the H<sub>2</sub> yield using methane as an internal

standard. Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel with the eluting (range petroleum ether/ $Et_2O/DCM = 250/1/1$  to 250/25/1) to afford compounds **3**.



## Wattecs Parallel Light Reactor (Blue LED Light source, every tube hole groove, 10 W)

## Procedure for gram-scale synthesis of 3aa



To a Schlenk flask containing a strring bar was added Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> (102.8 mg, 0.25 mmol, 0.05 equiv), Co(dmgH)<sub>2</sub>(CONMe<sub>2</sub>Py)Cl (129.8 mg, 0.25 mmol, 0.05 equiv), compound **1a** (1.05 g, 5.0 mmol, 1.0 equiv) and compound **2a** (1.78 g, 5.0 mmol, 2.0 equiv). The flask was sealed tightly with a Teflon-coated septum cap and evacuated and purged with Ar for three times. Then anhydrous DCM (500 mL) was added to the reaction flask via syringe. The reaction mixture was stirred for 24 h at Wattecs Parallel Light Reactor (Blue LED Light source, 10 W) at ambient temperature. The gas phase was detected for the H<sub>2</sub> yield using methane as an internal standard. Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) to afford compounds **3aa** (1.65 g) in 85% yield as a white solid with 83% H<sub>2</sub> yield.

#### Procedure for drawing the standard-curve for H<sub>2</sub> calculation

Five standard Schlenk tubes were filled with Ar. Then CH<sub>4</sub> (0.5 mL) as internal standard was injected to each tube. After that, H<sub>2</sub> (2.24 mL, 1.68 mL, 1.12 mL, 0.56 mL, 0.28 mL) was injected to each tube again, respectively. These amounts of H<sub>2</sub> were corresponding to H<sub>2</sub> yields (100%, 75%, 50%, 25% and 12.5%, respectively) in standard reaction. These tubes were kept for 3 h to make the gas mix uniformly. .Afterwards, these samples were detected by GC. The standard-curve was made by the different values of Area (H<sub>2</sub>)/Area (CH<sub>4</sub>) with the corresponding H<sub>2</sub> yields.



The standard-curve for the calculation of H<sub>2</sub> yield using CH<sub>4</sub> as an internal standard

Table S1. Optimization of reaction conditions.

Me	Me N H H H Ph	Ph Blue LEDs PS (5.0 mol%), Cat. (5 solvent, ambient temp	.0 mol%) perature, 12 h Me	Me N Ph	+ H <sub>2</sub>
	1a	2a		3aa	
entry <sup>a</sup>	photosensitizer (PS)	catalyst (Cat)	solvent (V, mL)	yield (%) <sup>b</sup>	H <sub>2</sub> (%) <sup>c</sup>
1	Acr <sup>+</sup> -Mes ClO <sub>4</sub>	Co(dmgH) <sub>2</sub> PyCl	MeCN (2.0)	32	24
2	PDI	Co(dmgH) <sub>2</sub> PyCl	MeCN (2.0)	14	8
3	TPT	Co(dmgH) <sub>2</sub> PyCl	MeCN (2.0)	8	5
4	Acr <sup>+</sup> -Mes CIO <sub>4</sub>	Co(dmgH) <sub>2</sub> PyCl	MeOH (2.0)	—	—
5	Acr <sup>+</sup> -Mes CIO <sub>4</sub>	Co(dmgH) <sub>2</sub> PyCl	DCE (2.0)	33	1
6	Acr <sup>+</sup> -Mes ClO <sub>4</sub>	Co(dmgH) <sub>2</sub> PyCl	DCM (2.0)	40	31
7	Acr <sup>+</sup> -Mes ClO <sub>4</sub>	Co(dmgH) <sub>2</sub> PyCl	DCM (5.0)	52	46
8	Acr <sup>+</sup> -Mes CIO <sub>4</sub>	Co(dmgH) <sub>2</sub> (4-CONMe <sub>2</sub> Py)Cl	DCM (5.0)	75	72
$9^d$	Acr <sup>+</sup> -Mes ClO <sub>4</sub>	Co(dmgH) <sub>2</sub> (4-CONMe <sub>2</sub> Py)Cl	MeCN (5.0)	56	51
10 <sup><i>d</i>,e</sup>	Acr <sup>+</sup> -Mes ClO <sub>4</sub>	Co(dmgH) <sub>2</sub> (4-CONMe <sub>2</sub> Py)Cl	DCM (5.0)	—	—
11 <i><sup>d</sup></i>	—	Co(dmgH) <sub>2</sub> (4-CONMe <sub>2</sub> Py)Cl	DCM (5.0)	—	—
12 <sup>d</sup>	Acr <sup>+</sup> -Mes ClO <sub>4</sub>	—	DCM (5.0)	35	27

<sup>&</sup>lt;sup>a</sup>Reaction conditions: **1a** (0.10 mmol), **2a** (0.20 mmol), DCM (5.0 mL), PS (5.0 mol%), Cat. (5.0 mol%), irradiation with blue LEDs for 12 h, the inner temperature was detected as 30 °C. <sup>b1</sup>H NMR yield was reported using Cl<sub>2</sub>CHCHCl<sub>2</sub> as an internal standard. <sup>c</sup>GC yield was reported using CH<sub>4</sub> as an internal standard. <sup>d</sup>PS (10.0 mol%), Cat. (10.0 mol%). <sup>e</sup>In dark.



GC spectrum of the H<sub>2</sub> yield under optimized conditions



Area (H<sub>2</sub>): 435105; Area (CH<sub>4</sub>): 56771.

 $y = 0.04322 + 0.1103 * [Area (H_2)/Area (CH_4)] = 89\%$ 

## Characterization data for products

#### Compound 3aa<sup>13</sup>



According to the general procedure, **3aa** (35.6 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 92% yield as a white solid with 89% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.42-7.39 (m, 3H), 7.37-7.34 (m, 5H), 7.30-7.27 (m, 2H), 7.19-7.14 (m, 3H), 2.46 (s, 3H), 2.43 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.5, 149.7, 141.1, 140.2, 138.3, 137.8, 137.2, 137.1, 131.4 (2C),

130.4 (2C), 130.1 (2C), 129.0, 128.9 (2C), 128.7, 128.3 (2C), 127.5, 127.4 (2C), 127.1, 126.8, 124.8, 123.8, 22.1, 21.4; IR (cm<sup>-1</sup>): *v* 3023, 1659, 1606, 1510, 1455, 1285, 751, 701. MS: m/z: [M + H]<sup>+</sup>, 386.3.

## Compound 3ba<sup>13</sup>



According to the general procedure, **3ba** (36.1 mg) was obtained by column chromatography with the eluting (petroleum ether/EtOAc = 10/1) in 87% yield as a white solid with 82% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (d, *J* = 9.2 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.42-7.34 (m, 5H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.17-7.12 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.96 (s, 1H), 3.89 (s, 3H), 3.72 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.5, 160.0, 158.8, 150.2, 141.2, 139.1, 137.9, 132.5, 131.5 (2C), 131.2 (2C), 130.4 (2C), 129.5, 128.7, 128.4 (2C), 127.4

(2C), 127.2, 126.9, 121.2, 118.7, 113.7 (2C), 104.2, 55.4, 55.2; IR (cm<sup>-1</sup>): *v* 3055, 3005, 2930, 2834, 1610, 1510, 1413, 1247, 1171, 1028, 841, 745, 696. MS: m/z: [M + H]<sup>+</sup>, 418.3.

#### Compound 3ca<sup>13</sup>



According to the general procedure, **3ca** (30.7 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 86% yield as a white solid with 83% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (d, *J* = 8.0 Hz, 1H), 7.84-7.81 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.61-7.48 (m, 5H), 7.44-7.36 (m, 5H), 7.31-7.29 (m, 2H), 7.21-7.16 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.8, 149.6, 140.9, 139.8, 137.5, 136.9, 131.3 (2C), 130.4 (2C), 130.2 (2C), 129.9, 129.8,

128.5, 128.3 (4C), 127.5 (2C), 127.5, 127.3, 127.0, 126.6, 126.0, 125.4; IR (cm<sup>-1</sup>): *v* 3023, 2926, 1610, 1546, 1504, 1440, 1381, 1338, 979, 760, 696. MS: m/z: 358.2.

## Compound 3da<sup>13</sup>



According to the general procedure, **3da** (35.4 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 83% yield as a white solid with 79% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (d, *J* = 8.8 Hz, 1H), 7.76-7.72 (m, 4H), 7.70 (d, *J* = 1.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.49-7.46 (m, 3H), 7.41-7.38 (m, 3H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.20-7.18 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.4, 150.9, 140.3, 138.1, 137.8, 136.7, 135.0, 131.5 (2C), 131.3, 131.2 (2C), 130.3 (2C), 129.3, 128.9, 128.7 (2C), 128.6 (2C),

127.7, 127.7, 127.6 (2C), 127.3, 125.0, 123.5; IR (cm<sup>-1</sup>): *v* 3059, 2926, 2856, 1648, 1589, 1482, 1397, 1259, 1087, 1011, 756, 696. MS: m/z: [M + H]<sup>+</sup>, 426.1.

## Compound 3ea<sup>13</sup>



According to the general procedure, **3ea** (30.8 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 78% yield as a white solid with 72% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.15 (dd, *J* = 9.2 Hz, *J* = 6.0 Hz, 1H), 7.80-7.77 (m, 2H), 7.42-7.37 (m, 5H), 7.32 (dd, *J* = 10.8 Hz, *J* = 2.4 Hz, 1H), 7.28-7.22 (m, 5H), 7.19-7.17 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.2 (d, <sup>1</sup>*J*<sub>C-F</sub> = 246.8 Hz), 163.2 (d, <sup>1</sup>*J*<sub>C-F</sub> = 250.4 Hz), 158.5, 150.6, 140.4, 139.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 9.7 Hz), 137.0, 135.6 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.3 Hz), 131.9 (d, <sup>3</sup>*J*<sub>C-F</sub> =

8.2 Hz, 2C), 131.1 (2C), 130.4 (d,  ${}^{3}J_{C-F} = 9.4$  Hz), 130.3 (2C), 129.6 (d,  ${}^{4}J_{C-F} = 5.2$  Hz), 128.5 (2C), 127.6 (2C), 127.6, 127.3, 122.7, 117.0 (d,  ${}^{2}J_{C-F} = 25.1$  Hz), 115.4 (d,  ${}^{2}J_{C-F} = 21.4$  Hz, 2C), 109.7 (d,  ${}^{2}J_{C-F} = 22.2$  Hz);  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -107.0, -112.8; IR (cm<sup>-1</sup>): *v* 3064, 3023, 2921, 2856, 1606, 1499, 1449, 1317, 1221, 1157, 970, 841, 696. MS: m/z: [M + H]<sup>+</sup>, 394.3.

Compound **3fa**<sup>13</sup>



According to the general procedure, **3fa** (31.1 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 63% yield as a white solid with 54% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.24 (d, *J* = 8.8 Hz, 1H), 8.07 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.44-7.40 (m, 5H), 7.31-7.29 (m, 2H), 7.22-7.20 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.3, 151.3, 142.6, 140.0, 136.4, 136.2, 131.8 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32.5 Hz), 131.1 (2C), 131.0, 130.6 (2C), 130.5 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32.6 Hz), 130.3 (2C),

128.7 (2C), 128.4, 128.0, 127.8 (2C), 127.6, 126.0, 125.5 (q,  ${}^{3}J_{C-F} = 3.4 \text{ Hz}$ , 2C), 124.1 (q,  ${}^{1}J_{C-F} = 273.9 \text{ Hz}$ ), 123.9 (q,  ${}^{3}J_{C-F} = 3.6 \text{ Hz}$ ), 122.6 (q,  ${}^{3}J_{C-F} = 2.1 \text{ Hz}$ ), 121.4 (q,  ${}^{1}J_{C-F} = 273.2 \text{ Hz}$ );  ${}^{19}\text{F}$  NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -62.6, -63.0; IR (cm<sup>-1</sup>):  $\nu$  2962, 2921, 2857, 1542, 1449, 1317, 1166, 1130, 1072, 745. MS: m/z: [M + H]<sup>+</sup>, 494.1.

Compound 3ga



According to the general procedure, **3ga** (31.4 mg) was obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O = 200/1) in 60% yield as a white solid with 56% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (d, *J* = 9.2 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.53 (s, 1H), 7.43-7.39 (m, 8H), 7.29-7.27 (m, 2H), 7.21-7.19 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.2, 151.0, 150.1 (q, <sup>3</sup>*J*<sub>C-F</sub> = 1.6 Hz), 149.7 (q, <sup>3</sup>*J*<sub>C-F</sub> = 1.8 Hz), 140.2, 138.3, 138.0, 136.5, 131.7 (2C), 131.1 (2C), 130.1, 129.8, 128.6 (2C), 127.8, 127.7 (2C), 127.4, 123.5, 121.0

(2C), 120.5 (q,  ${}^{1}J_{C-F} = 256.1$  Hz), 120.4, 120.4 (q,  ${}^{1}J_{C-F} = 257.2$  Hz), 116.3;  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -57.5, -57.7; IR (cm<sup>-1</sup>): *v* 3363, 3189, 2921, 2847, 1745, 1660, 1633, 1469, 1246, 1162, 1047, 698. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>18</sub>F<sub>6</sub>NO<sub>2</sub>, 526.1236; found 526.1237.

Compounds **3ha** and **3ha**'<sup>14</sup>



According to the general procedure, the mixture of **3ha** and **3ha'** (29.3 mg) were obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 10/1) in 76% yield as a white solid with 72% H<sub>2</sub> yield. The ratio of the isomers were determined based on the intergration of the character peak located at 8.03 ppm (H-1 of **3ha**) and 7.93 ppm (H-1' of **3ha'**).

**3ha**: **3ha**' = 2.0:1.0. **3ha**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.03 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.56 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.42-7.36 (m, 3H), 7.29-7.20 (m, 8H), 7.15-7.09 (m, 3H), 2.45 (s, 3H), 1.95 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.8, 151.9, 141.7, 140.7, 140.3, 137.9, 135.5, 135.3, 133.8, 131.7 (2C), 130.8, 130.2 (2C), 129.8, 129.0, 127.9, 127.4 (2C), 127.3, 127.2 (2C), 127.0, 126.9, 126.8, 126.4, 126.3, 24.7, 21.5; IR (cm<sup>-1</sup>): *v* 3053, 2915, 2858, 1540, 1503, 1441, 1383, 1318, 830, 763, 702. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>24</sub>N, 386.1903; found 386.1903. **3ha'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (s, 1H), 7.63-7.57 (m, 3H), 7.45-7.25 (m, 7H), 7.32-7.27 (m, 3H), 7.20-7.14 (m, 3H), 2.48 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.3, 148.9, 141.0, 140.0, 138.1, 137.7, 136.4, 135.1, 132.1, 131.3 (2C), 130.8, 130.4 (2C), 129.6, 129.1, 128.2 (2C), 128.0, 127.5 (2C), 127.3, 127.2, 126.8, 126.3, 125.9, 125.7, 21.8, 21.6; IR (cm<sup>-1</sup>): *v* 3356, 3062, 2953, 2918, 2855, 1652, 1601, 1539, 1497, 1446, 1383, 764, 700. HRMS: m/z: [M + H]<sup>+</sup>, 386.3.

Compounds **3ia**<sup>15</sup> and **3ia'** 



According to the general procedure, **3ia** (17.6 mg, 41%) and **3ia'** (13.5 mg, 32%) were obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 10/1) in 73% total yield as a white solid and 68% H<sub>2</sub> yield. **3ia:3ia'** = 1.3:1.0. **3ia**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.07 (d, *J* = 2.0 Hz, 1H), 7.81-7.80 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.67-7.64 (m, 1H), 7.54 (dd, *J* =

9.2 Hz, J = 2.0 Hz, 1H), 7.51-7.49 (m, 2H), 7.40-7.38 (m, 5H), 7.28-7.25 (m, 2H), 7.20-7.18 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.3, 150.1, 140.9, 140.2, 136.8, 135.4, 134.6, 132.8, 131.1 (2C), 131.0, 130.3 (2C), 130.2, 130.1, 129.7, 129.0, 128.5 (2C), 128.2, 128.1, 127.7 (2C), 127.7, 127.3, 125.9, 125.7; IR (cm<sup>-1</sup>): v 3055, 2921, 2848, 1734, 1536, 1498, 1374, 1318, 1240, 1076, 880, 771, 732, 699. MS: m/z: [M + H]<sup>+</sup>, 426.2; **3ia'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.06 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.74-7.71 (m, 2H), 7.62-7.60 (m, 1H), 7.48-7.42 (m, 3H), 7.26-7.18 (m, 7H), 7.17-7.13 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.9, 153.1, 141.5, 140.9, 138.6, 134.4, 133.9, 133.1, 131.7 (3C), 130.2, 130.1 (2C), 129.6, 129.1, 128.8, 128.4, 127.5, 127.4 (2C), 127.2 (2C), 127.2, 127.1, 126.9, 126.8; IR (cm<sup>-1</sup>): v 3061, 2918, 2856, 1742, 1537, 1494, 1382, 1238, 768, 696. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>27</sub>H<sub>18</sub>C<sub>12</sub>N, 426.0811; found 426.0811.

## Compound 3ja<sup>16</sup>



According to the general procedure, **3ja** (24.3 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 100/1) in 63% yield as a white solid with 57% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (d, *J* = 8.4 Hz, 1H), 7.46-7.25 (m, 13H), 7.17-7.12 (m, 3H), 2.21 (s, 3H), 2.04 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.4, 148.6, 143.9, 140.7, 138.1, 138.0, 136.2, 135.8, 131.5, 131.3, 130.3 (2C), 130.1, 130.0, 129.9, 129.5, 129.3, 128.3, 128.2, 128.0, 127.5 (2C),

127.2, 126.9, 125.9, 125.6, 124.9, 23.8, 20.1; IR (cm<sup>-1</sup>): *v* 3356, 3062, 3025, 2924, 2848, 1735, 1601, 1540, 1498, 1439, 1382, 1355, 1242, 1040, 779, 760, 700; MS: *m*/*z*: [M + H]<sup>+</sup>, 386.3.

## Compound 3ka<sup>16</sup>



According to the general procedure, **3ka** (19.2 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 100/1) in 57% yield as a colorless oil with 49% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.25-8.22 (m, 1H), 7.67-7.64 (m, 1H), 7.60-7.55 (m, 2H), 7.38-7.32 (m, 5H), 7.24-7.16 (m, 5H), 3.41 (t, *J* = 8.0 Hz, 2H), 1.95 (m, 2H), 1.57 (m, 2H), 1.03 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.5, 149.3, 141.1, 137.7, 136.3, 131.4 (2C), 130.3 (2C), 129.7,

128.9, 128.2 (2C), 127.5 (2C), 127.1, 126.9, 126.4, 126.3, 125.5, 125.3, 35.5, 32.1, 23.1, 14.1; IR (cm<sup>-1</sup>): *v* 3063, 2989, 2952, 2921, 2847, 2360, 2327, 1743, 1507, 1375, 1244, 1041, 768, 699; MS: *m/z*: [M + H]<sup>+</sup>, 338.3.

## Compound 3la<sup>16</sup>



According to the general procedure, **3la** (17.3 mg) was obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 51% yield as a colorless oil with 42% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.61-8.58 (m, 1H), 7.71-7.69 (m, 1H), 7.54-7.51 (m, 2H), 7.50-7.47 (m, 2H), 7.41-7.36 (m, 3H), 7.28-7.26 (m, 2H), 7.20-7.16 (m, 3H), 1.75 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  165.8,

147.0, 141.2, 138.2, 137.6, 131.4 (2C), 130.6 (2C), 128.7, 128.6, 128.4 (2C), 127.4 (2C), 127.1, 127.1, 126.9, 126.8, 125.1, 124.5, 40.2, 31.3 (3C); IR (cm<sup>-1</sup>): *v* 3355, 3181, 2955, 2921, 2952, 1744, 1678, 1634, 1469, 1373, 1274, 1240, 1174, 959, 715, 698. MS: *m/z*: [M + H]<sup>+</sup>, 338.3.

Compound **3ab**<sup>17</sup>



According to the general procedure, **3ab** (35.1 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 85% yield as a white solid with 79% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.07 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.34-7.29 (m, 5H), 7.21-7.15 (m, 4H), 6.98 (d, 2H), 2.45 (s, 3H), 2.41 (s, 6H), 2.26 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.2, 149.7, 139.9, 138.3, 138.2, 137.4, 137.2, 136.6, 136.4, 134.8, 131.2 (2C), 130.3 (2C), 130.1 (2C), 129.0 (2C), 128.9 (2C), 128.7, 128.4, 128.2 (2C), 127.4,

124.8, 123.7, 22.1, 21.3 (2C), 21.2; IR (cm<sup>-1</sup>): *v* 3059, 2925, 2838, 1759, 1626, 1512, 1453, 1255, 781, 711. MS: *m/z*: [M + H]<sup>+</sup>, 414.3.

#### Compound 3ac



According to the general procedure, **3ac** (35.9 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 66% yield as a white solid with 58% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.39 (s, 1H), 7.38-7.32 (m, 5H), 7.28-7.26 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.47 (s, 3H), 2.45(s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.0, 148.4, 140.7, 139.7, 138.6, 136.9, 136.7, 136.5, 133.0 (2C), 132.1 (2C), 131.8 (2C), 130.8 (2C), 130.0 (2C), 129.1, 129.0 (2C),

127.8, 127.6, 124.4, 123.9, 121.6, 121.5, 22.2, 21.4; IR (cm<sup>-1</sup>): v 2989, 2915, 1740, 1616, 1487, 1377, 1241, 1070, 1012, 836, 795. HRMS: m/z:  $[M + H]^+$  calculated for C<sub>29</sub>H<sub>22</sub>Br<sub>2</sub>N, 542.0114; found 542.0118.

## Compound **3ad**<sup>17</sup>



According to the general procedure, **3ad** (32.0 mg) was obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 70% yield as a white solid with 65% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.41-7.32 (m, 8H), 7.22-7.16 (m, 4H), 2.47 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.0, 148.5, 140.7, 139.3, 138.6, 137.0, 136.7, 136.0, 133.4, 133.1, 132.6 (2C), 131.7 (2C), 130.0 (2C), 129.0 (3C), 128.8 (2C), 127.8 (3C), 127.6, 124.4, 123.9, 22.2, 21.4; IR (cm<sup>-1</sup>): *v* 2961, 2927,

2858, 1739, 1617, 1491, 1380, 1262, 1098, 1043, 1014, 839, 797. MS: *m/z*: [M + H]<sup>+</sup>, 454.2.

## Compound 3ae<sup>17</sup>



According to the general procedure, **3ae** (13.9 mg) was obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 46% yield as a white solid with 39% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 1H), 7.38-7.34 (m, 5H), 7.24-7.22 (m, 2H), 7.13-7.09 (m, 2H), 6.90-6.86 (m, 2H), 2.46 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.1 (d, <sup>1</sup>*J*<sub>C-F</sub> = 245.4 Hz), 161.9 (d, <sup>1</sup>*J*<sub>C-F</sub> = 245.0 Hz), 159.8, 148.9, 140.5, 138.5, 137.2, 137.0 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.2 Hz), 136.8, 133.5 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.7

Hz), 132.9 (d,  ${}^{3}J_{C-F} = 8.0$  Hz, 2C), 131.1 (d,  ${}^{3}J_{C-F} = 8.0$  Hz, 2C), 130.0 (2C), 129.0 (2C), 128.9, 127.9, 127.6, 124.5, 123.8, 115.5 (d,  ${}^{2}J_{C-F} = 21.3$  Hz, 2C), 114.5 (d,  ${}^{2}J_{C-F} = 21.1$  Hz, 2C), 22.2, 21.4;  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -114.6, -115.3; IR (cm<sup>-1</sup>): *v* 2924, 2849, 1743, 1604, 1507, 1372, 1234, 1157, 843, 817, 794. MS: *m/z*: [M + H]<sup>+</sup>, 422.3.

Compound 3af



According to the general procedure, **3af** (42.2 mg) was obtained as the sole product by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 90% yield as a white solid with 87% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.6, 148.1, 144.9, 140.4, 138.5, 137.3, 137.2,

136.9, 134.0, 131.1 (2C), 130.7 (2C), 130.1 (2C), 130.0 (2C), 129.4 (q,  ${}^{2}J_{C-F} = 42.9$  Hz), 129.2 (2C), 129.1, 129.0, 127.5, 127.1 (q,  ${}^{1}J_{C-F} = 270.2$  Hz), 125.0, 124.4 (q,  ${}^{3}J_{C-F} = 3.8$  Hz, 2C), 124.1, 22.1, 21.4, 21.4;  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.4; IR (cm<sup>-1</sup>): *v* 2966, 2918, 1742, 1618, 1381, 1323, 1260, 1160, 1114, 1065, 1016, 849, 795. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>25</sub>F<sub>3</sub>N, 468.1934; found 468.1928.

Compounds 3ag and 3ag'



According to the general procedure, **3ag** (23.5 mg, 52%) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O/DCM = 100/1/10). **3ag** and **3ag'** were obtained in 67% <sup>1</sup>H NMR yield as a white solid with 61% H<sub>2</sub> yield. The ratio of the isomers were determined based on the intergration of the character peak located at 8.11 ppm (the sum of H-1 of **3ag** and H-1' of **3ag'**, defined as 1) and 7.47

ppm (H-2 of **3ag**, proved to be 0.78), **3ag:3ag'** = 0.78/(1-0.78) = 3.5:1.0. The characterization data of

the main product **3ag** was displaied below. **3ag** (23.5 mg, 53% yield, white solid): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.11 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.47 (s, 1H), 7.43-7.35 (m, 8H), 7.29-7.26 (m, 2H), 2.47 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.8, 148.1, 144.7, 140.6, 138.5, 137.2, 137.1, 136.8, 131.3 (2C), 130.7 (2C), 130.1 (2C), 129.6, 129.2, 129.0 (2C), 128.5 (2C), 128.8 (q, <sup>2</sup>*J*<sub>C-F</sub> = 28.6 Hz), 127.5 (2C), 124.9, 124.4 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.7 Hz, 2C), 124.3 (q, <sup>1</sup>*J*<sub>C-F</sub> = 270.3 Hz), 124.1, 22.1, 21.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.4; IR (cm<sup>-1</sup>):  $\nu$  2923, 2850, 1739, 1615, 1321, 1246, 1168, 1125, 1062, 852, 700. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>23</sub>F<sub>3</sub>N, 454.1777; found 454.1776. **3ag':** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7. 65 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.38-7.35 (m, 6H), 7.19-7.18 (m, 3H), 2.47 (s, 3H), 2.45 (s, 3H); MS: m/z: [M + H]<sup>+</sup>, 454.2.

Compounds 3ah and 3ah'



According to the general procedure, the mixture of **3ah** and **3ah'** (26.6 mg) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O = 100/10/1) in 64% yield as a white solid with 56% H<sub>2</sub> yield. The isomers were determined by LC-MS and the ratio of the isomers were determined based on the intergration of the character peaks located at 8.08 ppm

(the sum of H-1 of **3ah** and H-1' of **3ah'**, defined as 1) and 7.47 ppm (H-2 of **3ah**, proved to be 0.78), **3ah:3ah'** = 0.78/(1-0.78) = 3.5:1.0. **3ah**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.47 (s, 1H), 7.41-7.32 (m, 5H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.88-6.84 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.9 (d, <sup>1</sup>*J*<sub>C-F</sub> = 244.6 Hz), 159.4, 148.7, 140.2, 138.3, 137.3, 137.3 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.2 Hz), 137.0, 136.9, 134.5, 132.1 (d, <sup>3</sup>*J*<sub>C-F</sub> = 8.0 Hz, 2C), 131.1 (2C), 130.2, 130.1 (2C), 129.1 (2C), 129.0 (2C), 128.7, 127.4, 124.8, 123.9, 114.3 (d, <sup>2</sup>*J*<sub>C-F</sub> = 21.2 Hz, 2C), 22.1, 21.4, 21.3; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -115.7; IR (cm<sup>-1</sup>): *v* 2927, 2847, 1743, 1507, 1373, 1237, 1157, 1048, 845, 816, 736. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>25</sub>FN, 418.1966; found 418.1968.

Compounds 3ai and 3ai'



According to the general procedure, **3ai** (27.4 mg, 63%) and **3ai'** (10.0 mg, 23%) were obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O/DCM = 100/1/10) in 86% total yield as a white solid with 83% H<sub>2</sub> yield. **3ai:3ai'** = 2.7:1.0. **3ai**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 8.08 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.47 (s, 1H), 7.38-7.33 (m, 5H), 7.21 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.4 Hz, 4H), 2.46 (s, 3H), 2.43 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.5, 148.4, 140.3, 139.8, 138.4, 137.3, 137.0, 137.0, 134.3, 132.8, 131.8 (2C), 131.1 (2C), 130.1 (2C), 129.2 (2C), 129.2, 129.0 (2C), 128.8, 127.7 (2C), 127.5, 124.9, 123.9, 22.1, 21.4, 21.3; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>25</sub>ClN, 434.1670; found 434.1668. **3ai'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.09 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.39-7.37 (m, 3H), 7.35-7.32 (m, 3H), 7.28-7.27 (m, 2H), 7.24-7.22 (m, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.7, 149.8, 140.4, 138.4, 137.9, 137.1, 137.0, 136.7, 136.5, 133.1, 132.7 (2C), 130.3 (2C), 130.1 (2C), 128.9 (2C), 128.6, 128.6 (2C), 128.4 (2C), 127.6, 127.5, 124.4, 123.7, 22.1, 21.4, 21.2; IR (cm<sup>-1</sup>):  $\nu$  2959, 2925, 2846, 1739, 1492, 1372, 1259, 1102, 1026, 798; MS: m/z: [M + H]<sup>+</sup>, 434.5.

Compounds 3aj and 3aj'



According to the general procedure, **3aj** and **3aj'** (33.2 mg) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O = 200/5/1/1) in 83% yield as a white solid with 77% H<sub>2</sub> yield. The isomers were determined by LC-MS and the ratio of the isomers were determined based on the intergration of the character peak located at 8.09 ppm (the sum of H-1 of **3aj** and H-1' of **3aj'**, defined as 1)

and 7.49 ppm (H-2 of **3aj**, detected as 0.83), **3aj**:**3aj**' = 0.83/(1-0.83) = 4.9:1.0. **3aj**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.42-7.40 (dd, *J* = 8.0 Hz, 2.0Hz, 2H), 7.35-7.31 (m, 3H), 7.20-7.15 (m, 7H), 2.46 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.3, 149.8, 141.3, 140.1, 138.2, 137.3, 137.1, 136.7, 134.6, 131.2 (2C), 130.5 (2C), 130.1 (2C), 129.1, 129.0 (2C), 128.9 (2C), 128.6, 127.4 (3C), 126.7, 124.9, 123.8, 22.1, 21.4, 21.4; IR (cm<sup>-1</sup>): *v* 3354, 3185, 2921, 2849, 1739, 1654, 1630, 1468, 1411, 1371, 1246. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>26</sub>N, 400.2060; found 400.2057.

#### Compound 3ak



According to the general procedure, **3ak** (37.3 mg) was obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 90% yield as a white solid with 82% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.36-7.27 (m, 5H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.12-7.06 (m, 3H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.3, 149.7, 140.9, 140.0, 138.2, 137.7, 137.7, 137.2, 137.1, 136.9, 132.0, 131.2,

130.1 (2C), 129.1, 128.9 (2C), 128.6, 128.4, 128.1, 127.8, 127.6, 127.5, 127.4, 127.1, 124.9, 123.8, 22.1,

21.5, 21.4, 21.4; IR (cm<sup>-1</sup>): v 3031, 2923, 2852, 1740, 1620, 1543, 1496, 1377, 1239, 834, 782, 707. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>28</sub>N, 414.2216; found 414.2214.

## Compound 3al



According to the general procedure, **3al** (21.1 mg) was obtained by column chromatography with the eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 48% yield as a white solid with 41% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.38-7.32 (m, 5H), 7.26-7.24 (m, 3H), 2.47 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H), 0.04 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.4, 158.2, 156.4, 150.3, 139.7, 138.1, 137.6, 137.4, 136.6, 135.3, 132.1 (2C), 130.3 (2C), 129.0, 128.8 (2C), 127.1, 124.3, 123.4, 121.2 (2C), 22.0, 21.4, 21.3, -0.16

(3C); IR (cm<sup>-1</sup>): v 2960, 2917, 1937, 1370, 1247, 1199, 1046, 912, 840, 803. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>30</sub>NO<sub>2</sub>Si, 440.2040; found 440.2042.

## Compound 3ma<sup>15</sup>



According to the general procedure, **3ma** (35.1 mg) was obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 87% yield as a white solid with 82% H<sub>2</sub> yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.00 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.72-7.56 (m, 5H), 7.50-7.48 (m, 1H), 7.44-7.36 (m, 9H), 7.17-7.14 (m, 3H); <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>):  $\delta$  159.6, 149.9, 140.8, 137.5, 137.2, 136.5, 133.7, 132.5, 131.4, 131.3, 130.5 (2C), 130.1, 130.1, 128.8, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6 (2C), 127.3, 127.0, 126.9, 126.6, 126.3, 126.2, 125.9, 125.9, 125.3; IR (cm<sup>-1</sup>): *v* 3053, 2922, 2848, 1735, 1634, 1540, 1502, 1371, 1244, 968, 766, 701. MS: *m*/*z*: [M + H]<sup>+</sup>, 408.3.

#### Compound 3na



According to the general procedure, **3na** (35.2 mg) was obtained by column chromatography with eluting (petroleum ether/Et<sub>2</sub>O = 50/1) in 82% yield as a white solid with 78% H<sub>2</sub> yield. The structure of **3na** was confirmed by <sup>13</sup>C NMR, which displayed the character peak located at 138.6 ppm (d, <sup>3</sup>*J*<sub>C-F</sub> = 9.8 Hz, C-1) was a quaternary carbon. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.01 (d, J =

8.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.72-7.69 (m, 2H), 7.66-7.61 (m, 2H), 7.53-7.49 (m, 1H), 7.46-7.39 (m, 6H), 7.38-7.33 (m, 3H), 7.2-7.11 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.3 (d, <sup>1</sup>*J*<sub>C-F</sub> = 250.2 Hz), 159.4, 150.8, 140.5, 138.6 (d, <sup>3</sup>*J*<sub>C-F</sub> = 9.8 Hz), 137.1, 136.9, 133.8, 132.4, 131.3, 131.2, 131.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 9.5 Hz), 130.4 (2C), 129.9 (d, <sup>4</sup>*J*<sub>C-F</sub> = 5.2 Hz), 129.0, 128.6, 128.6, 128.3, 128.0, 127.7 (2C), 127.6, 127.2, 126.4, 126.1, 126.0, 125.3, 124.3, 117.0 (d, <sup>2</sup>*J*<sub>C-F</sub> = 25.2 Hz), 109.5 (d, <sup>2</sup>*J*<sub>C-F</sub> = 22.3 Hz);

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -106.8; IR (cm<sup>-1</sup>): *v* 3057, 2920, 2846, 1734, 1623, 1501, 1368, 1253, 981, 776, 705. HRMS: m/z:  $[M + H]^+$  calculated for C<sub>31</sub>H<sub>21</sub>FN, 426.1653; found 426.1653.

Compounds **3oa**<sup>13</sup> and **3oa'** 



According to the general procedure, **30a** (23.2 mg, 51%) and **30a'** (15.5 mg, 34%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 85% total yield as a white solid with 84% H<sub>2</sub> yield. The structure of **30a'** was confirmed by X-ray crystallography and the character

peak was located at around 8.4 ppm (mixture of H-1' and H-2'). The **30a**: **30a**' = 1.5:1.0. **30a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.79 (d, *J* = 8.0 Hz, 1H), 8.76 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.78-7.59 (m, 6H), 7.57-7.53 (m, 1H), 7.48-7.30 (m, 9H), 7.19-7.10 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.5, 149.9, 140.7, 137.4, 136.5, 135.9, 131.6, 131.4, 131.3, 131.3, 130.6, 130.5, 130.5 (2C), 130.2, 128.9 (2C), 128.4, 128.3, 127.7, 127.6 (2C), 127.3, 127.1, 127.1, 127.0, 127.0, 126.8, 126.7, 126.6, 126.6, 125.9, 122.8, 122.6; IR (cm<sup>-1</sup>): *v* 3055, 2919, 1610, 1541, 1501, 1444, 1369, 1331, 1261, 1154, 1030, 960, 772, 727. **30a**: MS: *m/z*: [M + H]<sup>+</sup>, 458.3. **30a**': <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.48 (d, *J* = 7.6 Hz, 1H), 8.45 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.81-7.78 (m, 2H), 7.54-7.47 (m, 3H), 7.42-7.37 (m, 5H), 7.29-7.23 (m, 3H), 7.21-7.15 (m, 6H), 7.08-7.04 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.3, 153.7, 143.2, 140.9, 140.6, 137.8, 132.8, 131.8 (2C), 131.3, 130.5 (2C), 130.3 (2C), 129.8, 129.5, 129.3, 129.2, 128.9 (2C), 128.9, 128.7 (2C), 128.6, 128.1, 127.4 (2C), 127.3, 127.1, 127.0, 126.1, 125.5, 123.8, 123.4, 123.2; IR (cm<sup>-1</sup>): *v* 3058, 2917, 2851, 1657, 1520, 1395, 1263, 763, 732, 700. **30a'**: HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>24</sub>N, 458.1903, found 458.1906.

Compounds 3pa and 3pa'



According to the general procedure, **3pa** (17.1 mg, 36%) and **3pa'** (13.1 mg, 28%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 64% total yield as a white solid with 70% H<sub>2</sub> yield. The structures of **3pa** and **3pa'** were confirmed by character peaks located at around

8.8 ppm (mixture of H-1 and H-2) and around 8.4 ppm (mixture of H-1' and H-2'). **3pa**: **3pa**' = 1.3:1.0. **3pa**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.82 (d, *J* = 8.4 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.73-7.62 (m, 5H), 7.53-7.37 (m, 9H), 7.21-7.14 (m, 4H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.2, 150.1, 140.9, 140.7, 137.7, 136.8, 136.1, 131.7, 131.5, 131.4, 131.4, 130.6, 130.6, 130.5 (2C), 129.8, 129.0, 128.9, 128.9, 128.4, 128.3, 127.6, 127.5 (2C), 127.3, 127.2, 127.0, 126.9, 126.9, 126.8, 126.6, 125.6, 124.7, 122.8, 122.6, 22.2; IR (cm<sup>-1</sup>): v 3058, 2932, 1628, 1541, 1494, 1441, 1367, 1263, 1072, 1028, 798, 733, 707. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>26</sub>N, 472.2060; found 472.2061. **3pa'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.47 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.53-7.47 (m, 3H), 7.39-7.36 (m, 2H), 7.27-7.17 (m, 11H), 7.08-7.03 (m, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.3, 153.6, 140.9, 140.6, 140.4, 138.6, 137.8, 132.8, 131.8 (2C), 131.3, 130.5 (2C), 130.2 (2C), 129.8, 129.7, 129.4 (2C), 129.1, 129.1, 128.9, 128.9 (2C), 128.0, 127.4 (2C), 127.2, 127.1, 127.0, 126.1, 125.5, 123.7, 123.4, 123.2, 21.4; IR (cm<sup>-1</sup>): v 2960, 2930, 2850, 1656, 1563, 1512, 1461, 758, 699; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>26</sub>N, 472.2060; found 472.2060.

#### Compounds 3qa and 3qa'



According to the general procedure, **3qa** (21.4 mg, 44%) and **3qa'** (12.6 mg, 26%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 70% total yield as a white solid with 65% H<sub>2</sub> yield. The structures of **3qa** and **3qa'** were confirmed by character peaks located at around

8.8 ppm (mixture of H-1 and H-2) and around 8.4 ppm (mixture of H-1' and H-2'). **3qa**: **3qa**' = 1.7:1.0. **3qa**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.81 (d, *J* = 8.0 Hz, 1H), 8.78 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.72-7.63 (m, 5H), 7.51-7.49 (m, 1H), 7.44-7.37 (m, 7H), 7.18-7.13 (m, 3H), 7.02-6.97 (m, 2H), 3.73 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.8, 158.8, 150.6, 141.0, 138.6, 137.8, 136.1, 131.6, 131.4, 131.3, 131.2, 130.6, 130.5, 130.4 (2C), 129.7, 129.5, 128.9, 128.8, 128.5, 128.4, 127.5 (2C), 127.3, 127.2, 127.0, 126.9, 126.8, 126.6, 126.6, 122.9, 122.8, 122.6, 119.1, 104.0, 55.2; IR (cm<sup>-1</sup>): *v* 3058, 2936, 2855, 1615, 1602, 1494, 1455, 1411, 1256, 1221, 1160, 1026, 753, 692. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>26</sub>NO, 488.2009; found 488.2009. **3qa'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.46 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.53-7.46 (m, 3H), 7.39-7.37 (m, 2H), 7.27-7.17 (m, 9H), 7.07-7.03 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.1, 153.7, 153.6, 141.0, 140.6, 137.8, 135.7, 132.8, 131.8 (2C), 131.7 (2C), 131.2, 130.5 (2C), 129.8, 129.8, 128.9 (3C), 128.9 (2C), 128.0, 127.4 (2C), 127.1, 127.0, 126.1, 125.5, 123.4, 123.3, 123.2, 114.1 (2C), 55.3; IR (cm<sup>-1</sup>): *v* 2958, 2925, 2849, 1654, 1608, 1512, 1458, 1394, 1248, 1172, 1030, 766, 703; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>26</sub>NO, 488.2009; found 488.2009; found 488.2009; found 488.2009, 128.9 (2C), 128.0, 127.4 (2C), 127.1, 127.1, 127.0, 126.1, 125.5, 123.4, 123.3, 123.2, 114.1 (2C), 55.3; IR (cm<sup>-1</sup>): *v* 2958, 2925, 2849, 1654, 1608, 1512, 1458, 1394, 1248, 1172, 1030, 766, 703; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>26</sub>NO, 488.2009; found 488.2012.



#### Compounds 3ra and 3ra'

According to the general procedure, **3ra** (17.6 mg, 34%) and **3ra'** (16.4 mg, 32%) were obtained by column

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chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 66% total yield as a white solid with 63% H<sub>2</sub> yield. The structures of 3ra and 3ra' were confirmed by character peaks located at around 8.8 ppm (mixture of H-1 and H-2) and around 8.4 ppm (mixture of H-1' and H-2'). **3ra:3ra'** = 1.1:1.0. **3ra**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.81 (d, J = 8.4 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H) 1H), 7.96-7.92 (m, 2H), 7.73-7.62 (m, 6H), 7.51-7.36 (m, 9H), 7.18-7.13 (m, 3H), 1.26 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.9, 153.3, 150.1, 141.0, 137.6, 136.6, 136.1, 131.7, 131.4, 131.4, 131.3, 130.6, 130.5, 130.5 (2C), 130.4, 128.9, 128.9, 128.3, 128.2, 127.5 (2C), 127.4, 127.3 (2C), 127.0, 126.9, 126.8, 126.6, 126.5, 125.6, 125.5, 122.8, 122.6, 120.9, 35.3, 30.9 (3C); IR (cm<sup>-1</sup>): v 3062, 2960, 2916, 2849, 1656, 1613, 1450, 1367, 1264, 1026, 737, 701. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>39</sub>H<sub>32</sub>N, 514.2529; found 514.2529. **3ra'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.47 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.53-7.46 (m, 3H), 7.42-7.37 (m, 4H), 7.26-7.24 (m, 3H), 7.20-7.17 (m, 6H), 7.06 (t, J = 7.6 Hz, 1H), 1.37 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): § 154.2, 153.7, 151.7, 141.0, 140.7, 140.2, 137.7, 132.9, 131.8 (2C), 131.2, 130.5 (2C), 129.9 (2C), 129.9, 129.7, 129.1, 129.1, 128.9, 128.9 (2C), 128.0, 127.4 (2C), 127.2, 127.1, 127.0, 126.1, 125.7 (2C), 125.5, 123.7, 123.4, 123.1, 34.7, 31.4 (3C); IR (cm<sup>-1</sup>): v 3059, 2961, 2918, 2851, 1656, 1601, 1519, 1395, 1265, 1016, 757, 726, 699; . HRMS: m/z:  $[M + H]^+$  calculated for C<sub>39</sub>H<sub>32</sub>N, 514.2529; found 514.2531.

Compounds 3sa and 3sa'



According to the general procedure, **3sa** (17.5 mg, 36%) and **3sa'** (15.7 mg, 32%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 68% total yield as a white solid with 60% H<sub>2</sub> yield. The structures of **3sa** and **3sa'** were confirmed by character peaks located at around

8.8 ppm (mixture of H-1 and H-2) and around 8.4 ppm (mixture of H-1' and H-2'). **3sa**: **3sa'** = 1.1:1.0. **3sa**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.82 (d, J = 8.4 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 7.97 (s, 1H), 7.94 (d, J = 7.2 Hz, 1H), 7.75-7.61 (m, 6H), 7.52-7.42 (m, 6H), 7.39-7.35 (m, 2H), 7.30 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.20-7.15 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.5, 151.1, 140.4, 137.6, 136.8, 135.4, 131.4, 131.3 (2C), 131.3, 131.2 (2C), 130.6, 130.4 (2C), 129.6, 129.5, 129.1, 129.0, 128.6, 128.6, 127.7 (2C), 127.6 (2C), 127.2, 127.2, 127.0, 127.0, 126.8, 126.7, 125.3, 124.8, 122.9, 122.6; IR (cm<sup>-1</sup>): v 2922, 2851, 1728, 1604, 1455, 1328, 963, 754, 727, 698. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>23</sub>ClN, 492.1514; found 492.1516. **3sa'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.48-8.44 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.54-7.47 (m, 3H), 7.39-7.35 (m, 4H), 7.29-7.24 (m, 3H), 7.22-7.18 (m, 6H), 7.09-7.04 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 153.8, 152.9, 141.6, 140.7, 140.4, 138.0, 134.7, 132.8, 131.8 (2C), 131.7 (2C), 131.4, 130.4 (2C), 129.8, 129.5, 129.2 (2C), 128.9 (4C), 128.8, 128.2, 127.5 (3C), 127.2, 127.1, 126.3, 125.7, 123.8, 123.5, 123.3; IR (cm<sup>-1</sup>): v 2963, 2921, 28461656, 1635, 1525, 1466, 1461, 1394, 1089, 1015, 760, 731, 706; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>23</sub>ClN, 492.1514; found 492.1514.

Compounds 3ta and 3ta'



According to the general procedure, **3ta** (16.9 mg, 36%) and **3ta'** (15.3 mg, 32%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 68% total yield as a white solid with 66% H<sub>2</sub> yield. The structures of **3ta** and **3ta'** were confirmed by character peaks located at around

8.8 ppm (mixture of H-1 and H-2) and around 8.4 ppm (mixture of H-1' and H-2'). 3ta:3ta' = 1.1:1.0. **3ta:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.82 (d, J = 8.4 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 7.97-7.93 (m, 2H), 7.79-7.62 (m, 5H), 7.52-7.34 (m, 9H), 7.19-7.09 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.3 (d,  ${}^{1}J_{C-F} = 250.2 \text{ Hz}$ , 159.3, 150.9, 140.4, 138.5 (d,  ${}^{3}J_{C-F} = 9.8 \text{ Hz}$ ), 137.1, 135.6, 131.5, 131.3, 131.2, 131.1, 131.0 (d,  ${}^{3}J_{C-F} = 9.6$  Hz), 130.6, 130.6, 130.4 (2C), 130.0 (d,  ${}^{4}J_{C-F} = 5.3$  Hz), 129.0, 129.0, 128.6, 128.5, 127.6 (3C), 127.2, 127.2, 127.0, 126.9, 126.7, 126.7, 124.4, 122.9, 122.6, 117.0 (d,  ${}^{2}J_{C-F} = 25.2$ Hz), 109.6 (d,  ${}^{2}J_{C-F} = 22.3$  Hz);  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>): -106.7; IR (cm<sup>-1</sup>): v 2964, 2923, 2952, 1624, 1508, 1449, 1370, 1258, 979, 750, 729, 708. HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>23</sub>FN, 476.1809; found 476.1813. **3ta'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.48-8.43 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 2H), 7.54-7.47 (m, 3H), 7.38-7.35 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.17 (m, 6H), 7.11-7.04 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.2 (d, <sup>1</sup>J<sub>C-F</sub> = 246.8 Hz), 153.7, 153.0, 140.8, 140.5, 139.2 (d,  ${}^{4}J_{C-F} = 3.4$  Hz), 138.0, 132.8, 132.1 (d,  ${}^{3}J_{C-F} = 8.1$  Hz, 2C), 131.8 (2C), 131.4, 130.4 (2C), 129.8, 129.4, 129.3, 129.0, 128.9 (2C), 128.8, 128.2, 127.5 (2C), 127.4, 127.2, 127.1, 126.2, 125.6, 123.6, 123.4, 123.3, 115.7 (d,  ${}^{2}J_{C-F} = 21.4$  Hz, 2C);  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>): -113.1; IR (cm<sup>-1</sup>): v 3059, 2922, 2946, 1603, 1504, 1447, 1393, 1268, 1222, 1153, 845, 761, 738, 700; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>23</sub>FN, 476.1809; found 476.1809.

#### Compounds 3ua and 3ua'



According to the general procedure, **3ua** (16.0 mg, 30%) and **3ua'** (17.6 mg, 33%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 63% total yield as a white solid with 63% H<sub>2</sub> yield. The structures of **3ua** and **3ua'** were confirmed by character peaks located at around

8.8 ppm (mixture of H-1 and H-2) and around 8.4 ppm (mixture of H-1' and H-2'). 3ua:3ua' = 1.0:1.1. **3ua**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.83 (d, J = 8.4 Hz, 1H), 8.80 (d, J = 8.4 Hz, 1H), 8.09 (s, 1H), 7.98-7.94 (m, 2H), 7.89 (d, J = 8.8 Hz, 1H), 7.77-7.64 (m, 3H), 7.60 (d, J = 8.0 Hz, 1H), 7.54-7.43 (m, 7H), 7.39-7.37 (m, 2H), 7.20-7.17 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.7, 151.4, 140.1, 136.4, 135.9, 135.2, 131.8 (q,  ${}^{2}J_{C-F} = 32.2$  Hz), 131.4, 131.3, 131.2, 131.2, 130.8, 130.7, 130.6, 130.4 (2C), 129.2, 129.1, 129.0, 128.7, 128.7, 127.9, 127.9, 127.7 (2C), 127.4, 127.3, 127.0, 126.9, 126.8, 126.8, 123.7 (q,  ${}^{1}J_{C-F} = 271.5$  Hz), 123.7 (q,  ${}^{3}J_{C-F} = 4.5$  Hz), 123.0, 122.7, 122.3 (q,  ${}^{3}J_{C-F} = 3.0$  Hz);  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>): -62.9; IR (cm<sup>-1</sup>): v 2958, 2925, 2854, 1654, 1539, 1509, 1457, 1330, 1308, 1174, 1125, 1069, 760, 697. HRMS: m/z:  $[M + H]^+$  calculated for C<sub>36</sub>H<sub>23</sub>F<sub>3</sub>N, 526.1777; found 526.1783. **3ua'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.49-8.45 (m, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.54-7.48 (m, 3H), 7.36-7.34 (m, 2H), 7.29-7.24 (m, 3H), 7.22-7.18 (m, 6H), 7.09-7.05 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 153.9, 152.6, 146.6, 140.6, 140.3, 138.1, 132.8, 131.7 (2C), 131.5, 130.6 (2C), 130.4 (2C), 130.4 (q,  ${}^{2}J_{C-F} = 32.1 \text{ Hz}$ ), 129.9, 129.8, 129.3, 129.0 (2C), 128.8, 128.7, 128.3, 127.6, 127.5 (2C), 127.3, 127.2, 126.3, 125.7, 125.6 (g,  ${}^{3}J_{C-F} = 3.7$  Hz, 2C), 124.2  $(q, {}^{1}J_{C-F} = 270.6 \text{ Hz}), 124.1, 123.5, 123.4; {}^{19}\text{F} \text{ NMR} (376 \text{ MHz}, \text{CDCl}_3): -62.4; \text{ IR} (cm^{-1}): v 2963, 2924,$ 2952, 1659, 1511, 1459, 1328, 1164, 1125, 1062, 764; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>23</sub>F<sub>3</sub>N, 526.1777; found 526.1777.

Compounds **3ob**<sup>13</sup> and **3ob'** 



According to the general procedure, **3ob** (15.4 mg, 32%) and **3ob'** (15.6 mg, 32%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 64% total yield as a white solid with 63% H<sub>2</sub> yield. The structure of **3ob'** was confirmed by character peaks located at 8.46-8.43

ppm (mixture of H-1' and H-2'). **3ob**:**3ob**' = 1.0:1.0. **3ob**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.82 (d, *J* = 8.4 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 7.97-7.93 (m, 2H), 7.78-7.63 (m, 6H), 7.59-7.54 (m, 1H), 7.50-7.46 (m, 1H), 7.37-7.32 (m, 3H), 7.29-7.23 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.26 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.2, 150.0, 138.0, 136.9, 136.8, 136.6, 136.1, 134.6, 131.7, 131.4, 131.3, 131.1, 130.6, 130.6, 130.4 (2C), 130.0, 130.0, 129.2, 129.1, 129.0, 128.9, 128.3 (2C), 127.7, 127.3, 127.0, 127.0, 126.8, 126.6, 126.5, 126.4, 126.0, 122.8, 122.6, 21.4, 21.2; IR (cm<sup>-1</sup>): *v* 2960, 1919, 1852, 1658, 1463, 1258, 1080, 1025, 809, 756. MS: m/z: [M + H]<sup>+</sup>, 486.3. **3ob'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.46 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 7.83-7.77 (m, 3H), 7.52-7.45 (m, 3H), 7.40-7.38 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.17-7.13 (m, 1H), 7.08-7.05 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.0, 153.7, 143.3, 138.0, 137.9, 137.8,

136.8, 136.7, 132.8, 131.6 (2C), 131.3, 130.4 (4C), 129.8, 129.7 (2C), 129.6, 129.2, 129.1, 129.1, 128.6 (2C), 128.5, 128.2 (2C), 127.9, 127.1, 126.0, 125.5, 123.6, 123.4, 123.1, 21.4, 21.2; IR (cm<sup>-1</sup>): v 3057, 2962, 2920, 2851, 1653, 1454, 1391, 1257, 1051, 1028, 822, 802, 734, 694; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>37</sub>H<sub>28</sub>N, 486.2216; found 486.2215.

Compounds **30e**<sup>13</sup> and **30e'** 



According to the general procedure, **30e** (15.6 mg, 32%) and **30e'** (17.0 mg, 34%) were obtained by column chromatography with eluting (petroleum ether/DCM/Et<sub>2</sub>O/Et<sub>3</sub>N = 250/5/1/1) in 66% total yield as a white solid with 65% H<sub>2</sub> yield. The structure of **30e'** was confirmed by character peaks located at 8.47-8.43

ppm (mixture of H-1' and H-2'). **30e**:**30e**' = 1.0:1.1. **30e**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.83 (d, J = 8.4 Hz, 1H), 8.79 (d, J = 8.0 Hz, 1H), 7.97-7.93 (m, 2H), 7.77-7.60 (m, 7H), 7.50-7.48 (m, 1H), 7.42-7.33 (m, 5H), 7.16-7.15 (m, 2H), 6.91-6.86 (m, 2H);  ${}^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.2 (d,  ${}^{1}J_{C-F} = 246.0$ Hz), 162.0 (d,  ${}^{1}J_{C-F} = 245.4$  Hz), 159.9, 149.2, 136.6 (d,  ${}^{4}J_{C-F} = 3.3$  Hz), 136.5, 135.7, 133.2 (d, {}^{4}J\_{C-F} = 3.3 Hz), 136.5, 135.7, 13 3.5 Hz), 133.0 (d,  ${}^{3}J_{C-F} = 7.9$  Hz), 132.9 (d,  ${}^{3}J_{C-F} = 8.0$  Hz), 132.2, 132.1, 131.5, 131.3, 130.6, 130.6, 130.5, 129.2, 129.0, 128.9, 127.9, 127.1 (2C), 127.0, 126.9 (d,  ${}^{2}J = 22.7$  Hz, 2C), 126.7 (2C), 125.6, 122.9, 122.6, 115.8 (d,  ${}^{3}J_{C-F} = 8.2$  Hz), 115.6 (d,  ${}^{3}J_{C-F} = 8.2$  Hz), 114.7 (d,  ${}^{2}J_{C-F} = 21.3$  Hz, 2C);  ${}^{19}F$ NMR (376 MHz, CDCl<sub>3</sub>): -114.2, -115.0; IR (cm<sup>-1</sup>): v 2964, 2927, 2849, 1605, 1507, 1371, 1214, 1157, 1017, 830, 752, 701. MS: m/z:  $[M + H]^+$ , 494.2. **30e'**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.47 (d, J = 8.0Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.78-7.76 (m, 2H), 7.55-7.40 (m, 6H), 7.34-7.31 (m, 2H), 7.18-7.08 (m, 4H), 6.99 (t, J = 8.4 Hz, 2H), 6.90 (t, J = 8.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.1 (d,  ${}^{1}J_{C-F} = 246.2$  Hz), 162.1 (d,  ${}^{1}J_{C-F} = 245.7$  Hz), 154.5, 152.7, 143.0, 137.9, 136.7 (d,  ${}^{4}J_{C-F} = 3.7$  Hz), 136.4 (d,  ${}^{4}J_{C-F} = 3.3$  Hz), 133.3 (d,  ${}^{3}J_{C-F} = 7.8$  Hz, 2C), 132.9, 132.1 (d,  ${}^{3}J_{C-F} = 8.1$  Hz, 2C), 131.3, 130.3 (2C), 129.6, 129.3, 129.1, 128.8 (3C), 128.5, 128.3, 128.0, 127.4, 126.2, 125.7, 124.0, 123.6, 123.2, 116.2 (d,  ${}^{2}J_{C-F} = 21.1$  Hz, 2C), 114.6 (d,  ${}^{2}J_{C-F} = 21.2$  Hz, 2C);  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>): -114.3, -114.8; IR (cm<sup>-1</sup>): v 2959, 2924, 2852, 1601, 1506, 1451, 1373, 1262, 1222, 1160, 1098, 1023, 837, 808, 755, 726, 697; HRMS: m/z:  $[M + H]^+$  calculated for  $C_{35}H_{22}F_2N$ , 494.1715; found 494.1715.

## X-ray Crystallography Studies of Compound 3oa'

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **30a'** in methanol in a loosely capped vial.



Table S2. Crystal data and structure refinement for **30a'**, hydrogen atoms have been omitted for clarity.

Summary of Data CCDC 1576204

\_\_\_\_\_

Compound Name: 30a'

Formula: C<sub>35</sub> H<sub>23</sub> N

Unit Cell Parameters: a 9.6484(9) b 14.1234(14) c 18.0080(17) P21/c

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## **Mechanistic studies**



Figure S1. UV-vis spectrum of substrate and catalyst.

#### **Radical Capture Experiments:**



Substrate **1a** (20.9 mg, 0.10 mmol, 1.0 equiv), diphenyacetylene **2a** (35.6 mg, 0.2 mmol, 2.0 equiv), TEMPO (31.2 mg, 0.20 mmol, 2.0 equiv), Mes<sup>+</sup>-Acr  $ClO_4^-$  (4.1 mg, 0.01 mmol, 0.1 equiv) and  $Co(dmgH)_2(4-CONMe_2Py)Cl$  (4.7 mg, 0.01 mmol, 0.1 equiv) were added into reaction tube. Then DCM (5 mL) was added under Ar atmosphere. The reaction mixture was stirred on Wattecs Parallel Light Reactor. Compound **3aa** was detected as 70% yield via crude <sup>1</sup>H NMR analysis using  $Cl_2CHCHCl_2$  as internal standard.



Substrate **1a** (20.9 mg, 0.10 mmol, 1.0 equiv), cis-diphenylene **4** or trans-diphenylene **4** (36.0 mg, 0.2 mmol, 2.0 equiv), TEMPO (31.2 mg, 0.20 mmol, 2.0 equiv), Mes<sup>+</sup>-Acr ClO<sub>4</sub><sup>-</sup> (4.1 mg, 0.01 mmol, 0.1 equiv) and Co(dmgH)<sub>2</sub>(4-CONMe<sub>2</sub>Py)Cl (4.7 mg, 0.01 mmol, 0.1 equiv) were added into a 50 mL reaction tube. Then DCM (5 mL) was added under Ar atmosphere. The reaction mixture was stirred on Wattees Parallel Light Reactor. Compound **5** (32.8 mg) was formed in 60% yield. **5**: <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  7.60 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.23-7.18 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.05-7.00 (m, 8H), 6.98-6.95 (m, 2H), 5.25 (d, *J* = 8.8 Hz, 1H), 5.01 (d, *J* = 9.2 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H), 1.62 (s, 3H), 1.44-1.24 (m, 6H), 1.02 (s, 6H), 0.21 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  165.9, 141.7, 141.0, 139.5, 137.7, 137.6, 134.2, 129.8 (2C), 128.8 (2C), 128.8 (2C), 128.6 (2C), 128.4 (2C), 128.2 (2C), 127.6 (2C), 127.0 (3C), 126.3, 91.1, 71.3, 61.1, 58.8, 41.1, 40.8, 34.0, 33.8, 21.5, 21.3, 20.8, 20.4, 17.1; IR (cm<sup>-1</sup>): *v* 3363, 3030, 2919, 1602, 1452, 1182, 1014, 696; HRMS: m/z: [M + H]<sup>+</sup> calculated for C<sub>38</sub>H<sub>45</sub>N<sub>2</sub>O, 545.3526; found 545.3526.

#### Quantum yield measurements:

#### Determination the light intensity at 450 nm:

According to the procedure of Yoon,<sup>18</sup> the photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry.<sup>19</sup> A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (1.47 g) in H<sub>2</sub>SO<sub>4</sub> (20 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving phenanthroline (25 mg) and sodium acetate (5.63 g) in H<sub>2</sub>SO<sub>4</sub> (25 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 seconds at  $\lambda = 450$  nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was allowed to rest in the dark for 1 hour to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq S4.

mol Fe<sup>2+</sup> = 
$$\frac{V \cdot \Delta A}{l \cdot \epsilon} = \frac{0.00235 \text{ L} \cdot 1.749}{1.000 \text{ cm} \cdot 11,100 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}} = 3.70 \times 10^{-7} \text{ mol}$$
 (eq S4)

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline,  $\Delta A$  is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, 1 is the path length (1.000 cm), and  $\varepsilon$  is the molar absorptivity at 510 nm (11,100 L mol<sup>-1</sup>cm<sup>-1</sup>). The photon flux can be calculated using eq S5.

Photon flux = 
$$\frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} = \frac{3.70 \times 10^{-7} \text{ mol}}{0.96 \cdot 90.0 \text{ s} \cdot 0.98280} = 4.36 \times 10^{-9} \text{ einstein s}^{-1} \text{ (eq S5)}$$

Where  $\Phi$  is the quantum yield for the ferrioxalate actinometer (0.96 for a 0.15 M solution at  $\lambda = 450$  nm),<sup>20</sup> t is the time (90.0 s), and f is the fraction of light absorbed at  $\lambda = 450$  nm (eq S5).

## Determination of fraction of light absorbed at 450 nm for the ferrioxalate solution:

The fraction of light absorbed (f) by this solution was calculated using eq S6, where A is the measured absorbance of the above ferrioxalate solution at 450 nm which was measured to be 1.7645 (Figure S2),

indicating the fraction of light absorbed (f) is 0.98280. Finally, the photon flux was calculated to be 4.36  $\times 10^{-9}$  einstein s<sup>-1</sup>.

$$f = 1 - 10^{-A} = 0.98280$$
 (eq S6)



Figure S2. UV-vis spectrum of 0.15 M ferrioxalate solution.

## Quantum yield calculation:

A cuvette was charged with **1a** (0.05 mmol, 1 equiv), diphenylacetylene (0.1 mmol, 2 equiv), Mes<sup>+</sup>-Acr  $ClO_4^-$  (2.0 mg, 0.005 mmol, 0.1 equiv) and  $Co(dmgH)_2(4$ -CONMe<sub>2</sub>Py)Cl (2.4 mg, 0.005 mmol, 0.1 equiv), and 2.5 mL degassed DCM in glovebox under Ar atmosphere. The cuvette was then capped with a PTFE stopper. The sample was irradiated ( $\lambda = 450$  nm, slit width = 10.0 nm) for 21,600 s (6 h). After irradiation, the yield of product formed was determined by <sup>1</sup>H NMR to be 36% using 1,1,2,2-tetrachloroethane as an internal standard. The quantum yield was determined using eq S7.

$$\Phi = \frac{\text{mol prod}}{\text{flux} \cdot \text{t} \cdot \text{f}} = \frac{0.36 \times 0.05 \times 10^{-3} \text{ mol}}{4.36 \times 10^{-9} \text{ einstein s}^{-1} \cdot 21,600 \text{ s} \cdot 0.99395} = 0.19 \quad (\text{eq S7})$$

The quantum yield  $\Phi$  for the reaction was calculated to be 0.19.

#### Absorbance of catalyst:

The absorbance of Mes<sup>+</sup>-Acr ClO<sub>4</sub><sup>-</sup> in DCM was measured at the reaction concentration of  $2 \times 10^{-3}$  M. The absorbance at 450 nm is 2.218 indicating the fraction of light absorbed (f) is 0.99395.



**Figure S3.** UV-vis absorption of  $2 \times 10^{-3}$  M Mes<sup>+</sup>-Acr ClO<sub>4</sub><sup>-</sup>.

#### **Emission Quenching Experiments:**

Emission intensities were recorded using an spectrofluorimeter. All Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> solutions were excited at 450 nm and the emission intensity at 507 nm was observed. DCM was degassed with a stream of argon for 30 min. In a typical experiment, the emission spectrum of the sample was collected after the sample was degassed with a stream of argon for 15 minutes. First, the emission spectrum of a  $5 \times 10^{-5}$  M solution of Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> in DCM was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.





**Figure S4.** Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> Emission Quenching by Co(dmgH)<sub>2</sub>(4-CONMe<sub>2</sub>Py)Cl catalyst.



Figure S5. Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> emission quenching by 1a.



Figure S6.  $Acr^+-Mes$   $ClO_4^-$  Emission Quenching by diphenylacetylene and 1,2-bis(4-methoxyphenyl)ethyne.



**Figure S7.** Emission-quenching experiments of Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> with Co(dmgH)<sub>2</sub>(4-CONMe<sub>2</sub>)Cl, 1,2-bis(4-methoxyphenyl)ethyne, **1a**, and **2a**.

#### Cyclic Voltammetry (CV) Experiments:

As CH<sub>3</sub>CN displays the widest detection window for the reduction oxidation potentials,<sup>21</sup> the most reported electrochemical data were detected in CH<sub>3</sub>CN.<sup>22</sup> Meanwhile, 56% yield of product was obtained in CH<sub>3</sub>CN (Table S1, entry 9) in our work. Thus the reduction oxidation potentials of **1a**, **2a**, **6** and the cobalt were detected in CH<sub>3</sub>CN.

For the electrochemical measurements a three-electrode system connected to an electrochemical station was used. The reference electrode,  $Ag/AgNO_3$  in 0.1 M AgNO<sub>3</sub>, was calibrated versus  $Fc^+/Fc^0$  using the same experimental conditions as for the sample. A glassy carbon electrode was used as working electrode. And a Pt wire was used as counter electrode. All electrochemical measurements were performed in acetonitrile under dry argon atmosphere.



Figure S8. CV spectra of 3 mM 1a in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in degassed CH<sub>3</sub>CN with scan rate 50 mV/s. The

oxidation potential  $E_{p/2}^{1a+\cdot/1a}$  (+ 1.62 V vs. SCE) was converted from internal standard Fc<sup>+</sup>/Fc<sup>0</sup>.



Figure S9. CV spectra of 1 mM Co(dmgH)<sub>2</sub>(4-CONMe<sub>2</sub>Py)Cl in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in degassed CH<sub>3</sub>CN with scan rate 50 mV/s. The reduction potential  $E_{p/2}^{Co(III)/Co(II)}$  (-0.77 V vs. SCE) and  $E_{p/2}^{Co(III)/Co(I)}$  (-1.04 V vs. SCE) was converted from internal standard Fc<sup>+</sup>/Fc<sup>0</sup>.



Figure S10. CV spectra of 3 mM 2a in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in degassed CH<sub>3</sub>CN with scan rate 50 mV/s. The oxidation potential  $E_{p/2}^{2a+*/2a}$  (+ 1.86 V vs. SCE) was converted from internal standard Fc<sup>+</sup>/Fc<sup>0</sup>, which values was in accordance with the reported leterature (+ 1.84 V vs. SCE).<sup>22e</sup>



**Figure S11**. CV spectra of 3 mM 1,2-bis(4-methoxyphenyl)ethyne in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in degassed CH<sub>3</sub>CN with scan rate 50 mV/s. The oxidation potential  $E_{p/2}$  (+ 1.28 V vs. SCE) was converted from internal standard Fc<sup>+</sup>/Fc<sup>0</sup>.



**Figure S12**. CV spectra of 3 mM Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in degassed CH<sub>3</sub>CN with scan rate 50 mV/s. The reduction potential  $E_{1/2}$  Acr<sup>+</sup>-MesClO<sub>4</sub><sup>-/</sup> Acr<sup>+</sup>-MesClO<sub>4</sub><sup>-/</sup> (- 0.55 V vs. SCE) was converted from internal standard Fc<sup>+</sup>/Fc<sup>0</sup>, which value was in accordance with repoeted literature (- 0.57 V vs SCE).<sup>8a</sup>

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## Spectrum




















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





.5 10.0 9.5 7.5 5.0 4.5 f1 (ppm) 9.0 8.5 8.0 7.0 6.5 6.0 5.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



f1 (ppm) 













f1 (ppm) Ó 













fl (ppm)







110 100 f1 (ppm) 210 200 190 180 160 150 140 130 120 Ó -10





. 50 fl (ppm)





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

### {<sup>1</sup>H-<sup>13</sup>C} HSQC (400 MHz, CDCl<sub>3</sub>)



### {1H-1H} COSY (400 MHz, CDCl3)



## {<sup>1</sup>H-<sup>13</sup>C} HMBC (400 MHz, CDCl<sub>3</sub>)









10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



{<sup>1</sup>H-<sup>13</sup>C} HSQC (400 MHz, CDCl<sub>3</sub>)





 ${^{1}H-^{1}H} COSY (400 \text{ MHz}, CDCl_{3})$ 





{<sup>1</sup>H-<sup>13</sup>C} HMBC (400 MHz, CDCl<sub>3</sub>)





8.100 8.089 8.079 8.068 8.068 -7.472



Range: 1.196e+2







# {<sup>1</sup>H-<sup>1</sup>H} COSY (400 MHz, CDCl<sub>3</sub>)




## {<sup>1</sup>H-<sup>13</sup>C} HMBC (400 MHz, CDCl<sub>3</sub>)









### {<sup>1</sup>H-<sup>1</sup>H} COSY (400 MHz, CDCl<sub>3</sub>)







LC-MS spectra of the mixture of 3aj and 3aj'





{<sup>1</sup>H-<sup>13</sup>C} HSQC (400 MHz, CDCl<sub>3</sub>)



{<sup>1</sup>H-<sup>1</sup>H} COSY (400 MHz, CDCl<sub>3</sub>)



## {<sup>1</sup>H-<sup>13</sup>C} HMBC (400 MHz, CDCl<sub>3</sub>)













100 90 f1 (ppm) 































210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)







10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)









10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)





Ó )0 f1 (ppm)






