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Michael Addition of Indoles to Enones Catalyzed by a Cationic Iron Salt

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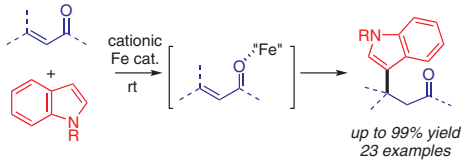

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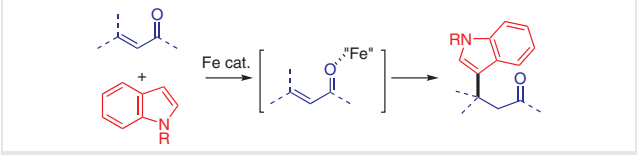
Abstract Indoles are one of the most valuable nucleophiles in Michael additions catalyzed by a proper Lewis acid. In this paper, we found that a cationic iron salt is effective to carry out the Michael addition of indoles. β-Mono- and disubstituted enones reacted smoothly with indoles under our conditions. The cationic iron catalyst is very active, and the maximum TON was up to 425. Moreover, cationic iron-catalyzed conditions enabled a chemoselective Michael addition of a substrate possessing both enone and α,β-unsaturated ester moieties.

Key words iron, enones, Michael addition, Friedel–Crafts reaction, chemoselectivity

The Friedel–Crafts-type conjugate (Michael) addition reaction of indoles is one of the most important reactions to synthesize substituted indole derivatives, which can be seen in important bioactive molecules.[1] Although various organocatalyst or metal catalyst systems for conjugate additions of indoles have been reported,[2–13] the desired reaction with sterically congested substrates such as β-mono- and disubstituted enones is still difficult.

In our previous studies, increasing the Lewis acidity of palladium was very effective to carry conjugate addition of arylboronic acids,[14] silanes[15] and bismuths,[16] and Fujiwara-type C–H functionalization reactions.[17] There are numerous coupling and addition reactions using palladium salts, whereas earth-abundant iron-catalyzed related reactions are still challenging.[17] One successful example of indole Michael additions was reported by Kawatsura's group who carried out iron-catalyzed Michael addition reactions of indoles and enones possessing a terminal vinyl group in ionic liquids.[18] But, the iron catalyst activity was not so high because sterically congested enones did not react with indoles under their conditions. On the other hand, there are a few reports on iron-catalyzed Michael additions using β-substituted enones,[19] but a turnover number (TON) of the iron catalyst was not high. In this context, we envisaged that a highly Lewis acidic iron catalyst (tuning cationicity of the iron salt) could realize an efficient conjugate addition of indole derivatives (Scheme 1). Herein, we would like to report cationic iron-catalyzed conjugate additions of indoles to β-substituted enones.



Scheme 1 This work

Initially, we screened various iron salts as a catalyst in the reaction of **1a** and **2a** in 1,2-dimethoxyethane (DME) at room temperature (Table 1). Without an iron catalyst, the reaction did not occur (Run 1). On the other hand, the corresponding Michael adduct **3a** was obtained in the presence of $FeCl_2$ (Run 2). More Lewis acidic $FeCl_3$ gave 49% yield of **3a** (Run 3). Other iron salts, such as $Fe(acac)_3$, $Fe(OAc)_2$, $[Cp\text{-}Fe(CO)_3]_2$, and $Fe_2(SO_4)_3$ hydrate, were not effective at all (Runs 4–7). In previous iron-catalyzed indole Michael additions with simple enones possessing a terminal vinyl group, $[Fe(H_2O)_6](BF_4)_2$ was effective,[18] but it did not show a good Lewis acidity in our reaction (Run 8). Finally, a cationic iron salt, $[Fe(H_2O)_6](OTs)_3$, was found to be the best catalyst, in which 72% yield of **3a** was obtained (Run 9). This catalyst was very active. For example, when 2 mol% $[Fe(H_2O)_6](OTs)_3$ was used, the yield was not decreased compared with the 10 mol% catalyst conditions. We also tested various solvents, such as THF, Et_2O, CH_2Cl_2, and EtOH, but the yield was not dramatically increased (see Supporting Information). When the reaction was carried out in the presence of in situ generated cationic iron salt, 69% yield of

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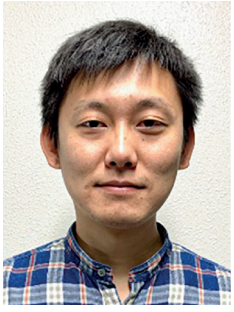
3a was obtained (Run 10). In this case, addition of water did not improve the chemical yield of **3a**. Therefore, water might not be important for the final protolysis process in the catalytic cycle (see Scheme 4).

A ligand effect is important to improve yields in transition-metal-catalyzed reactions. We screened various ligands, including phosphine, nitrogen, and amino acid ligands, in the presence of $[Fe(H_2O)_6](OTs)_3$ (Table 2). But, the yields were not higher than the conditions without ligand. In our previous cationic palladium chemistry in Michael additions, phosphorus ligands were effective, but no ligand was effective in the current cationic iron-catalyzed reaction. This could be attributed to decreased cationicity of the iron salt with ligands, which indicates that the cationic iron-catalyzed indole Michael addition could include a Friedel–Crafts-type reaction.

The reactivities of various **1** and **2** were examined under the optimized reaction conditions (Scheme 2). β-Methyl-substituted enones **1b**–**1e** possessing an α-aryl group gave 79–99% yield of **3b**–**3e**. Although aliphatic enone **1h** gave an excellent yield of **3h**, benzalacetone derivative **1f** possessing a bromine on the phenyl group and chalcone (**1g**) had moderate to low reactivity. According to the literature, the electrophilicity of **1g** is higher than that of **1a**,[20] but **1g** had low reactivity (**1g** was recovered after the reaction). α,β-Unsaturated carboxamide **1i** and ester **1j** were not suitable for this reaction due to low electrophilicity of each Michael acceptor. We also tried heating conditions with these substrates, but they were not effective. The reactivity of indole and substituted indoles **2** was tested. Thus, indoles possessing a boron moiety (**2f**, **2g**) or sterically hindered substituents (**2c**–**2e**) showed excellent reactivities to give the corresponding adducts **3k**–**3p** in high yields.

Biographical Sketches

Tsukasa Inishi received his BS degree from Yamaguchi University (Japan) in 2020. Since 2020, he has been a graduate student at the same university under the supervision of Prof. Takashi Nishikata.



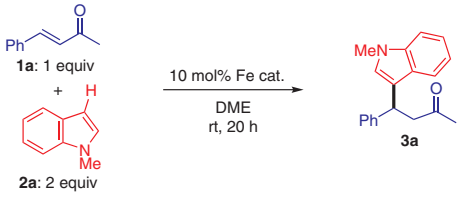
Goki Hirata received his Ph.D. from Nagasaki University (Japan) in 2017 under the supervision of Prof. Masanari Kimura. He spent two years as a postdoctoral fellow at Ritsumeikan University (Japan; Prof. Hiromitsu Maeda). Since 2019, he has been an assistant professor at Yamaguchi University (Japan).

Takashi Nishikata received his Ph.D. from Hokkaido University (Japan) in 2005 under the supervision of Prof. Norio Miyaura. He spent three years as a JST postdoctoral fellow in the same group. From 2008 to 2010, he worked as a postdoctoral fellow at the University of California, Santa Barbara (USA) under the direction of Prof. Bruce H. Lipshutz. In 2010, he joined Prof. Hideo Nagashima's group as an assistant professor at Kyushu University (Japan). In 2012, he was appointed as an associate professor at Yamaguchi University. Since 2020, he has been a full professor at Yamaguchi University.

We next tested a highly congested enone, namely β,β-dimethyl-substituted enone **1k** (Scheme 3). A highly congested enone to give a quaternary center is one of the most challenging substrates for iron-catalyzed Michael addition.[18,19] As we expected, the reactivity of **1k** was very low, and **1k** did not react with **2** at room temperature. But, elevated temperature (50 °C) was effective to obtain the corresponding adducts **3**. For example, **1k** and **2b** underwent the Michael addition reaction to produce **3q** in 76% yield. Halogen-substituted indoles **2h** and **2i** gave good yields of adducts **3u** and **3v**, respectively. Compounds **2j–2l** possessing an electron-withdrawing group gave moderate yields of adducts **3w**, and **3y**. When the reactions for those compounds were carried out in MeCN/MeOH, the yields were slightly improved. Sterically hindered indoles (**2c** and **2d**) were not suitable for this reaction.

The addition of indole to enone could give the corresponding enolate anion. The resulting enolate anion could be protonated to produce the Michael adduct **3**. Therefore, we next checked whether indole is a proton source (Scheme 4). As a result, when deuterated **2a** (**2a-D**) was used as a substrate in the presence of in situ generated cationic iron salt [$Fe(OTs)_3$: $FeCl_3$ + AgOTs], the corresponding deuterated adduct **3b-D** (70% D) was obtained without contact of H_2O or D_2O. This result indicated that the proton could come

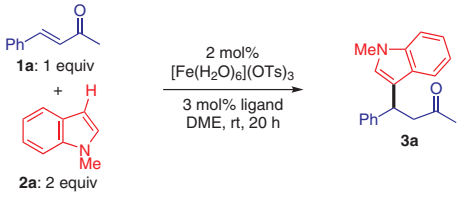
Table 1 Iron Salt Optimization[a]



Run	Iron catalyst	Yield (%) **3a**
1	none	0 (48 h)
2	$FeCl_2$	17
3	$FeCl_3$	49
4	$Fe(acac)_3$	0
5	$Fe(OAc)_2$	0
6	$[CpFe(CO)_3]_2$	0
7	$Fe_2(SO_4)_3nH_2O$	0
8	$[Fe(H_2O)_6](BF_4)_2$	9
9	$[Fe(H_2O)_6](OTs)_3$	72, 70[b]
10	$FeCl_3$ (5 mol%)/AgOTs (20 mol%)	69, 73[c]

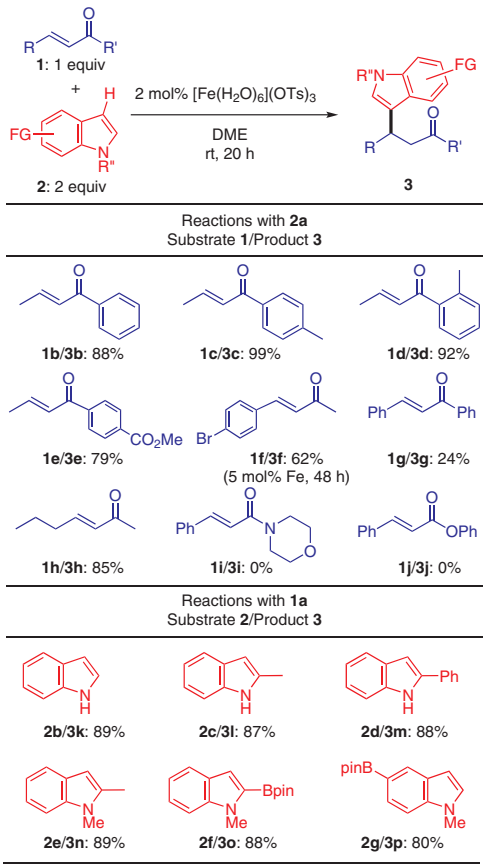
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), Fe salt (10 mol%), DME (1.0 mL), rt, 20 h. Isolated yields are shown.
[b] 2 mol% Fe catalyst was used.
[c] In the presence of 1 equivalent of water.

Table 2 Ligand Effects[a]



Run	Ligand	Yield (%) **3a**
1	none	70
2	dppm	14
3	dppe	13
4	DPEphos	15
5	Qphos	12
6	Bpy	19
7	picolic acid	33
8	phenylalanine	28
9	phenylglycine	20

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), $[Fe(H_2O)_6](OTs)_3$ (2 mol%), ligand (3 mol%), DME (1.0 mL), rt, 20 h. Isolated yields are shown.

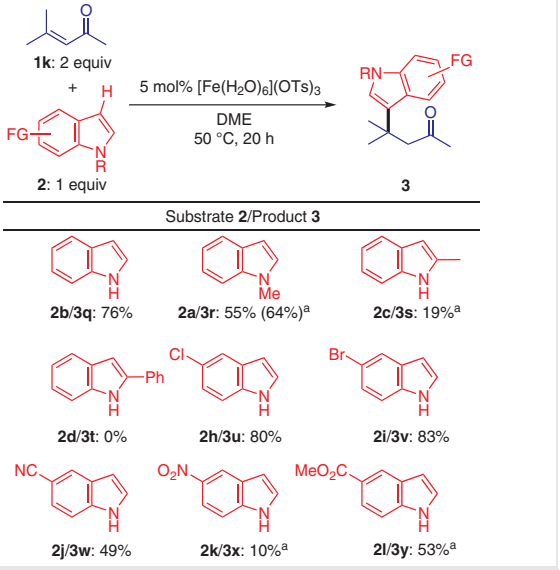


Scheme 2 Substrate scope 1. *Reagents and conditions*: **1** (0.5 mmol), **2** (1.0 mmol), $[Fe(H_2O)_6](OTs)_3$ (2 mol%), DME (1.0 mL), rt, 20 h. Isolated yields are shown.

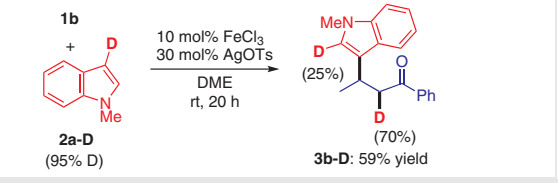
from indole **2**. In this reaction, we also obtained C-2 deuterated product (**3b-D**: 25% D), but the generation process for this product is not clear.

By using the different electrophilicity between enone and α,β-unsaturated ester,[20] we carried out a chemoselective Michael addition (Scheme 5). When substrate **1l** possessing both enone and α,β-unsaturated ester moieties reacted with **2a**, **2a** selectively added to the enone to produce **3z** as the sole adduct in 65% yield. Our mild addition conditions had realized a chemoselective Michael reaction.

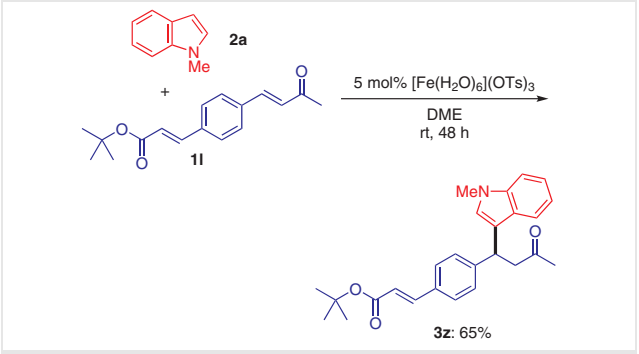
We next checked the maximum TON for the reaction of **1b** with **2a** in the presence of 2, 0.2, 0.1, 0.06, or 0.02 mol% iron catalyst (Figure 1). Although 2 mol% iron catalyst gave 88% yield of **3b** with a TON of 44, a better TON was achieved in the reaction with 0.2 mol% iron catalyst (TON = 425). When the reaction was carried out using 0.1 or 0.06 mol% iron catalyst, low yields of **3b** were obtained with a TON of ca. 200. The reaction was stopped when 0.02 mol% iron catalyst was employed.



Scheme 3 Substrate scope 2. *Reagents and conditions*: **1k** (1 mmol), **2** (0.5 mmol), $[Fe(H_2O)_6](OTs)_3$ (5 mol%), DME (1 mL), 50 °C, 20 h. Isolated yields are shown. [a] MeCN/MeOH (1:1) was used instead of DME.



Scheme 4 Reaction with deuterated indole **2a-D**



Scheme 5 Chemoselective Michael addition

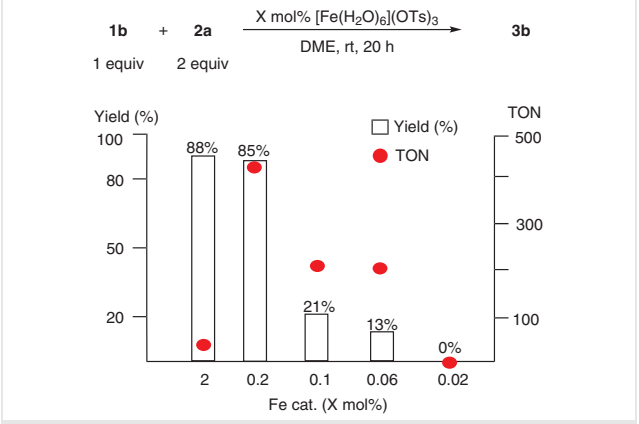


Figure 1 TON in this reaction

In conclusion, we have discovered that a cationic iron catalyst, $[Fe(H_2O)_6](OTs)_3$, is effective to carry out Michael additions of indoles with β-mono- and disubstituted enones. In this reaction, various indole adducts were obtained with TONs up to 425. These results are useful to carry out indole Michael additions with minimal amounts of inexpensive iron metals. Further improvements, including an asymmetric reaction, will be described in due course.

All reactions were carried out under nitrogen (99.95%) atmosphere. For TLC analyses, precoated Kieselgel 60 $_{F254}$ plates (Merck, 0.25 mm thick) were used; for column chromatography, SiliaFlash P60 (SiliCycle, 40–63 μm) was used. Visualization was accomplished by UV light (254 nm). ^{1}H and ^{13}C NMR spectra were obtained using a JEOL 400 or 500 MHz NMR spectrometer. Chemical shifts for ^{1}H NMR are described in parts per million (chloroform as an internal standard, δ = 7.26) in $CDCl_3$. Chemical shifts for ^{13}C NMR are expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.16). High-resolution mass analyses were obtained using an ACQUITY UPLC/TOF-MS for EI. Anhydrous solvents were purchased from Kanto Chemical Co., Ltd. Other chemicals were purchased from TCI, Sigma, and Wako, and directly used from the bottles.

Compounds 3a–3z; General Procedure

Fe salt (2–10 mol%), **1** (0.50 mmol or 1.0 mmol), and **2** (1.0 mmol or 0.5 mmol) were sequentially added under air to a dram vial equipped with a stir bar. Dried DME (1.0 mL) was added by syringe, and the resulting mixture was vigorously stirred under nitrogen atmosphere [charged by general N_2 (99.95%) gas flow] for 20 h, unless noted otherwise (**3f**, **3z**), at room temperature (**3a**–**3p**, **3z**) or 50 °C (**3q**–**3y**). After this time, the contents of the flask were filtered through a plug of silica gel and then concentrated by rotary evaporation. The residue was purified by silica gel column chromatography [*n*-hexane/EtOAc, 10:1 (v/v)] to afford the desired product **3**.

4-(1-Methyl-1*H*-indol-3-yl)-4-phenylbutan-2-one (3a)

4-Phenylbut-3-en-2-one (benzalacetone, **1a**; 73.1 mg, 0.50 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTs)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3a** (pale yellow oil, 97.1 mg, 70%).

IR (neat): 1709, 1154, 737, 700 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 2.09 (s, 3 H), 3.17 (dd, *J* = 7.7, 15.4 Hz, 1 H), 3.26 (dd, *J* = 6.7, 15.4 Hz, 1 H), 3.74 (s, 3 H), 4.84 (t, *J* = 7.7 Hz, 1 H), 6.85 (s, 1 H), 7.03 (t, *J* = 7.7 Hz, 1 H), 7.27–7.34 (m, 5 H), 7.33 (d, *J* = 7.7 Hz, 2 H), 7.45 (d, *J* = 7.7 Hz, 1 H), 7.45 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 30.4, 32.7, 38.5, 50.6, 109.4, 117.4, 117.5, 119.1, 119.7, 121.9, 126.3, 126.5, 127.1, 127.8, 127.8, 127.8, 127.8, 128.6, 128.6, 137.5, 144.3, 207.9.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{19}NO$ [M^+]: 277.1467; found: 277.1469.

3-(1-Methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3b)

Phenyl 1-propenyl ketone (**1b**; 73.1 mg, 0.50 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3b** (pale yellow oil, 122.0 mg, 88%).

IR (neat): 1680, 1277, 736, 689 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.8 Hz, 3 H), 3.25 (dd, *J* = 9.7, 15.9 Hz, 1 H), 3.49 (dd, *J* = 4.8, 15.9 Hz, 1 H), 3.75 (s, 3 H), 3.81–3.90 (m, 1 H), 6.91 (s, 1 H), 7.14 (t, *J* = 6.8 Hz, 1 H), 7.26 (t, *J* = 8.7 Hz, 1 H), 7.32 (d, *J* = 7.8 Hz, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 7.56 (t, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 8.7 Hz, 1 H), 7.99 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.2, 27.1, 32.6, 46.7, 109.5, 118.8, 119.4, 120.2, 121.7, 125.2, 126.8, 128.3, 128.7, 133.1, 137.4, 137.5, 199.9.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{19}NO$ [M^+]: 277.1467; found: 277.1464.

3-(1-Methyl-1*H*-indol-3-yl)-1-(4-tolyl)butan-1-one (3c)

1-(*p*-Tolyl)but-2-en-1-one (**1c**; 80.1 mg, 0.50 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3c** (pale yellow oil, 144.2 mg, 99%).

IR (neat): 1676, 1278, 1179, 806, 735 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.45 (d, *J* = 6.9 Hz, 3 H), 2.41 (s, 3 H), 3.22 (dd, *J* = 8.9, 15.8 Hz, 1 H), 3.46 (dd, *J* = 4.8, 15.8 Hz, 1 H), 3.74 (s, 3 H), 3.81–3.86 (m, 1 H), 6.90 (s, 1 H), 7.12 (t, *J* = 6.9 Hz, 1 H), 7.24–7.25 (m, 3 H), 7.30 (d, *J* = 8.3 Hz, 1 H), 7.69 (d, *J* = 8.1 Hz, 1 H), 7.88 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.3, 21.7, 27.3, 32.7, 46.7, 109.4, 118.8, 119.4, 120.3, 121.7, 125.1, 126.8, 128.4, 129.3, 135.0, 137.3, 143.7, 199.4.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{21}NO$ [M^+]: 291.1623; found: 291.1626.

3-(1-Methyl-1*H*-indol-3-yl)-1-(*o*-tolyl)butan-1-one (3d)

1-(*o*-Tolyl)but-2-en-1-one (**1d**; 80.1 mg, 0.50 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3d** (pale yellow oil, 134.0 mg, 92%).

IR (neat): 1681, 1270, 735 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 6.9 Hz, 3 H), 2.41 (s, 3 H), 3.16 (dd, *J* = 8.9, 16.5 Hz, 1 H), 3.39 (dd, *J* = 5.5, 16.5 Hz, 1 H), 3.72 (s, 3 H), 3.72–3.79 (m, 1 H), 6.85 (s, 1 H), 7.09 (t, *J* = 6.9 Hz, 1 H), 7.19–7.24 (m, 3 H), 7.28 (d, *J* = 8.3 Hz, 1 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.62 (d, *J* = 7.5 Hz, 1 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.1, 21.5, 27.5, 32.7, 50.0, 109.4, 118.8, 119.4, 120.0, 121.7, 125.2, 125.7, 126.8, 128.4, 131.1, 132.0, 137.3, 137.9, 138.7, 204.4.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{21}NO$ [M^+]: 291.1623; found: 291.1625.

Methyl 4-(3-(1-Methyl-1*H*-indol-3-yl)butanoyl)benzoate (3e)

Methyl 4-(but-2-enoyl)benzoate (**1e**; 102.1 mg, 0.50 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3e** (pale yellow oil, 132.5 mg, 79%).

IR (neat): 2768, 1450, 1360, 1022, 968 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.47 (d, *J* = 6.9 Hz, 3 H), 3.25 (dd, *J* = 8.3, 15.8 Hz, 1 H), 3.49 (dd, *J* = 4.8, 15.8 Hz, 1 H), 3.74 (s, 3 H), 3.81 (sext, *J* = 7.5 Hz, 1 H), 3.95 (s, 3 H), 6.89 (s, 1 H), 7.11 (t, *J* = 8.2 Hz, 1 H), 7.23 (d, *J* = 7.7 Hz, 1 H), 7.29 (d, *J* = 8.2 Hz, 1 H), 7.66 (d, *J* = 7.7 Hz, 1 H), 7.98 (d, *J* = 8.2 Hz, 2 H), 8.09 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.3, 27.2, 32.7, 47.2, 52.6, 109.5, 118.9, 119.4, 119.8, 121.8, 125.2, 126.7, 128.1, 129.9, 133.8, 137.3, 140.7, 166.4, 199.4.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{21}NO_3$ [M^+]: 335.1521; found: 335.1522.

4-(4-Bromophenyl)-4-(1-methyl-1*H*-indol-3-yl)butan-2-one (3f)

4-(4-Bromophenyl)but-3-en-2-one (**1f**; 112.5 mg, 0.5 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (33.4 mg, 0.05 mmol), and DME (1.0 mL) were used, with a reaction time of 48 h. The crude residue was purified by column chromatography to afford **3f** (pale yellow oil, 110.4 mg, 62%).

IR (neat): 1711, 1484, 1072, 1008, 737 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 2.14 (s, 3 H), 3.17 (dd, *J* = 7.6, 16.5 Hz, 1 H), 3.28 (dd, *J* = 6.8, 16.5 Hz, 1 H), 3.78 (s, 3 H), 4.85 (t, *J* = 7.5 Hz, 1 H), 6.87 (s, 1 H), 7.08 (t, *J* = 6.9 Hz, 1 H), 7.23–7.25 (m, 3 H), 7.31 (d, *J* = 8.2 Hz, 1 H), 7.42–7.43 (m, 3 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 30.5, 32.9, 37.8, 50.2, 109.4, 116.9, 119.2, 119.5, 120.2, 122.0, 126.2, 126.8, 129.6, 131.7, 137.5, 143.4, 207.2.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{18}BrNO$ [M^+]: 355.0572; found: 355.0575.

3-(1-Methyl-1*H*-indol-3-yl)-1,3-diphenylpropan-1-one (3g)[21]

Chalcone (**1g**; 104.1 mg, 0.50 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $Fe[(H_2O)_6](OTf)_3$ (16.8 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3g** (pale yellow oil, 40.7 mg, 24%).

IR (neat): 1711, 1484, 1072, 1008, 737 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.72–3.83 (m, 5 H), 5.06 (t, *J* = 7.2 Hz, 1 H), 6.84 (s, 1 H), 7.00–7.03 (m, 1 H), 7.14–7.20 (m, 2 H), 7.25 (m, 2 H), 7.27 (d, *J* = 4.3 Hz, 1 H), 7.36 (d, *J* = 7.6 Hz, 2 H), 7.42–7.45 (m, 3 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.93–7.94 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.8, 38.2, 45.5, 109.3, 117.9, 119.0, 119.7, 121.8, 126.4, 127.1, 127.9, 128.2, 128.6, 128.7, 133.1, 137.2, 137.5, 144.5, 198.7.

4-(1-Methyl-1*H*-indol-3-yl)heptan-2-one (3h)

3-Hepten-2-one (**1h**; 56 mg, 0.50 mmol), 1-methylindole (**2a**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3h** (pale yellow oil, 103.4 mg, 85%).

IR (neat): 1710, 1467, 735 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.5 Hz, 3 H), 1.26–1.32 (m, 2 H), 1.66–1.80 (m, 2 H), 2.04 (s, 3 H), 2.81 (dd, *J* = 6.9, 15.9 Hz, 1 H), 2.89 (dd, *J* = 7.5, 15.9 Hz, 1 H), 3.49 (quint, *J* = 6.2 Hz, 1 H), 3.74 (s, 3 H), 6.85 (s, 1 H), 7.12 (t, *J* = 6.9 Hz, 1 H), 7.23 (t, *J* = 6.9 Hz, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.66 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 14.2, 20.2, 30.5, 32.6, 32.7, 38.4, 50.5, 109.4, 117.6, 118.7, 119.5, 121.5, 126.1, 127.1, 137.3, 209.0.

HRMS (EI): *m*/*z* calcd for $C_{16}H_{21}NO$ [M^+]: 243.1623; found: 243.1622.

3-(1*H*-Indol-3-yl)-1-phenylbutan-1-one (3k)

4-Phenylbut-3-en-2-one (**1a**; 73.1 mg, 0.50 mmol), indole (**2b**; 117.15 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3k** (pale yellow oil, 117.2 mg, 89%).

IR (neat): 1674, 1278, 738, 688 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.49 (d, *J* = 6.9 Hz, 3 H), 3.27 (dd, *J* = 9.0, 16.5 Hz, 1 H), 3.51 (dd, *J* = 4.8, 16.5 Hz, 1 H), 3.87 (sext, *J* = 6.8 Hz, 1 H), 7.02 (s, 1 H), 7.15 (t, *J* = 6.9 Hz, 1 H), 7.22 (t, *J* = 8.2 Hz, 1 H), 7.36 (d, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.71 (d, *J* = 7.5 Hz, 1 H), 7.98 (d, *J* = 7.5 Hz, 2 H), 8.07 (s, 1 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.1, 27.3, 46.6, 111.4, 119.30, 119.33, 120.4, 121.5, 122.1, 126.4, 128.2, 128.7, 133.1, 136.7, 137.4, 200.0.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{17}NO$ [M^+]: 263.1310; found: 263.1310.

3-(2-Methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3l)

4-Phenylbut-3-en-2-one (**1a**; 73.1 mg, 0.50 mmol), 2-methylindole (**2c**; 131.2 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3l** (pale yellow oil, 120.7 mg, 87%).

IR (neat): 1673, 1458, 1281, 739, 688 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 6.8 Hz, 3 H), 2.38 (s, 3 H), 3.41 (dd, *J* = 7.8 and 15.4 Hz, 1 H), 3.57 (dd, *J* = 5.8 and 15.4 Hz, 1 H), 3.78 (quint, *J* = 6.8 Hz, 1 H), 7.09–7.15 (m, 2 H), 7.25 (d, *J* = 8.7 Hz, 1 H), 7.41 (t, *J* = 6.7 Hz, 2 H), 7.52 (t, *J* = 6.7 Hz, 1 H), 7.71–7.77 (m, 2 H), 7.91 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 11.8, 20.9, 27.3, 45.6, 110.5, 115.3, 118.8, 118.9, 120.5, 127.0, 127.9, 128.3, 130.3, 132.8, 135.5, 137.3, 200.1.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{19}NO$ [M^+]: 277.1467; found: 277.1468.

1-Phenyl-3-(2-phenyl-1*H*-indol-3-yl)butan-1-one (3m)

4-Phenylbut-3-en-2-one (**1a**; 73.1 mg, 0.50 mmol), 2-phenylindole (**2d**; 193.3 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3m** (pale yellow oil, 149.4 mg, 88%).

IR (neat): 1681, 1470, 1280, 735, 690 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.57 (d, *J* = 6.8 Hz, 3 H), 3.50 (dd, *J* = 5.8, 16.4 Hz, 1 H), 3.57 (dd, *J* = 8.7, 16.4 Hz, 1 H), 4.00 (sext, *J* = 6.8 Hz, 1 H), 7.16–7.25 (m, 2 H), 7.35–7.41 (m, 4 H), 7.44–7.53 (m, 4 H), 7.85–7.87 (m, 3 H), 8.04 (s, 1 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.3, 27.6, 45.8, 111.4, 117.3, 119.6, 120.5, 122.1, 127.5, 128.1, 128.3, 128.6, 128.9, 129.0, 133.0, 133.4, 134.3, 136.5, 137.3, 200.0.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{21}NO$ [M^+]: 339.1623; found: 339.1625.

3-(1,2-Dimethyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3n)

4-Phenylbut-3-en-2-one (**1a**; 73.1 mg, 0.50 mmol), 1,2-dimethylindole (**2e**; 145.2 mg, 1.0 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3n** (pale yellow oil, 129.7 mg, 89%).

IR (neat): 1681, 1470, 1280, 735, 690 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.44 (d, *J* = 6.7 Hz, 3 H), 2.31 (s, 3 H), 3.33 (dd, *J* = 7.7 and 16.4 Hz, 1 H), 3.47 (dd, *J* = 6.8 and 16.4 Hz, 1 H), 3.50 (s, 3 H), 3.70 (sext, *J* = 7.7 Hz, 1 H), 7.00 (t, *J* = 6.8 Hz, 1 H), 7.07 (t, *J* = 6.8 Hz, 1 H), 7.16 (d, *J* = 7.7 Hz, 1 H), 7.30 (t, *J* = 7.7 Hz, 1 H), 7.41 (t, *J* = 7.7 Hz, 1 H), 7.64 (d, *J* = 7.7 Hz, 1 H), 7.81 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 10.3, 21.2, 27.5, 29.3, 45.8, 108.8, 114.8, 118.4, 119.0, 120.1, 126.0, 127.9, 128.3, 132.2, 132.7, 136.9, 137.3, 200.0.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{21}NO$ [M^+]: 291.1623; found: 291.1618.

3-(1-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)-1-phenylbutan-1-one (3o)

4-Phenylbut-3-en-2-one (**1a**; 73.1 mg, 0.50 mmol), 1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**2f**; 257.1 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3o** (pale yellow oil, 177.5 mg, 88%).

IR (neat): 2925, 1115, 1005, 866 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 8.2 Hz, 12 H), 1.53 (d, *J* = 7.1 Hz, 3 H), 3.49–3.56 (m, 2 H), 3.93 (s, 3 H), 4.37–4.43 (m, 1 H), 7.10 (q, *J* = 7.5 Hz, 1 H), 7.28 (d, *J* = 7.5 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 2 H), 7.53 (d, *J* = 7.5 Hz, 1 H), 7.88 (d, *J* = 7.6 Hz, 1 H), 8.00 (d, *J* = 7.1 Hz, 2 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.5, 24.9, 25.0, 28.6, 32.3, 46.8, 83.6, 110.1, 118.7, 121.3, 123.2, 128.2, 128.5, 128.7, 132.7, 133.1, 137.5, 140.4, 200.3.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{30}NO_3B$ [M^+]: 403.2319; found: 403.2322.

3-(1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)-1-phenylbutan-1-one (3p)

4-Phenylbut-3-en-2-one (**1a**; 73.1 mg, 0.50 mmol), 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**2g**; 257.1 mg, 1.00 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3p** (pale yellow oil, 161.3 mg, 80%).

IR (neat): 1682, 1444, 1347, 1140, 689 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.39 (s, 12 H), 1.45 (d, *J* = 6.9 Hz, 3 H), 3.24 (dd, *J* = 8.9, 15.8 Hz, 1 H), 3.48 (dd, *J* = 4.8, 15.8 Hz, 1 H), 3.73 (s, 3 H), 3.82–3.86 (m, 1 H), 6.88 (s, 1 H), 7.29 (d, *J* = 8.2 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.98 (d, *J* = 8.2 Hz, 2 H), 8.20 (s, 1 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 21.5, 25.00, 25.02, 27.1, 32.7, 46.8, 83.5, 108.9, 121.1, 125.2, 126.6, 127.1, 128.0, 128.3, 128.6, 133.0, 137.4, 139.3, 199.8.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{30}NO_3B$ [M^+]: 403.2319; found: 403.2325.

4-(1*H*-Indol-3-yl)-4-methylpentan-2-one (3q)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), indole (**2b**; 58.4 mg, 0.5 mmol), $[Fe(H_2O)_6](OTf)_3$ (17.0 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3q** (pale yellow oil, 81.6 mg, 76%).

IR (neat): 3402, 2961, 1693, 1243, 740 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.57 (s, 6 H), 1.75 (s, 3 H), 2.98 (s, 2 H), 6.91 (m, 1 H), 7.16 (t, *J* = 7.7 Hz, 1 H), 7.22 (t, *J* = 7.7 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 8.13 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.1, 32.0, 32.8, 34.6, 55.3, 109.8, 118.7, 120.9, 121.4, 122.3, 125.5, 126.0, 137.9, 209.4.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{18}NO$ [M + H^+]: 216.1388; found: 216.1389.

4-Methyl-4-(1-methyl-1*H*-indol-3-yl)pentan-2-one (3r)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), 1-methylindole (**2a**; 62.3 μL, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.8 mg, 0.025 mmol), MeOH (0.5 mL), and MeCN (0.5 mL) were used. The crude residue was purified by column chromatography to afford **3r** (pale yellow oil, 73.2 mg, 64%).

IR (neat): 2960, 1699, 1355, 1239, 737 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.54 (s, 6 H), 1.74 (s, 3 H), 2.95 (s, 2 H), 3.74 (s, 3 H), 6.80 (s, 1 H), 7.12 (t, *J* = 7.4 Hz, 1 H), 7.23 (t, *J* = 7.4 Hz, 1 H), 7.31 (d, *J* = 8.2 Hz, 1 H), 7.80 (t, *J* = 8.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7, 30.4, 31.6, 36.2, 55.7, 110.6, 116.4, 119.0, 120.8, 120.8, 127.9, 130.1, 135.2, 209.8.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{19}NO$ [M^+]: 229.1467; found: 229.1467.

4-Methyl-4-(2-methyl-1*H*-indol-3-yl)pentan-2-one (3s)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), 2-methylindole (**2c**; 65.4 mg, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (17.3 mg, 0.025 mmol), MeOH (0.5 mL), and MeCN (0.5 mL) were used. The crude residue was purified by column chromatography to afford **3s** (pale yellow oil, 21.3 mg, 19%).

IR (neat): 3352, 2961, 1691, 1458, 740 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.62 (s, 6 H), 1.70 (s, 3 H), 2.51 (s, 3 H), 2.98 (s, 2 H), 7.04–7.11 (m, 2 H), 7.25 (d, *J* = 8.3 Hz, 1 H), 7.70 (br s, 1 H), 7.76 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7, 30.5, 31.6, 36.2, 55.7, 110.6, 116.5, 119.0, 120.8, 120.9, 127.9, 130.0, 135.4, 209.7.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{20}NO$ [M + H^+]: 230.1545; found: 230.1545.

4-(5-Chloro-1*H*-indol-3-yl)-4-methylpentan-2-one (3u)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), 5-chloroindole (**2h**; 76.0 mg, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3u** (pale yellow oil, 100.4 mg, 80%).

IR (neat): 3351, 2963, 1691, 1462, 797 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.52 (s, 6 H), 1.76 (s, 3 H), 2.91 (s, 2 H), 6.98 (d, *J* = 2.5 Hz, 1 H), 7.15 (dd, *J* = 2.0, 8.6 Hz, 1 H), 7.29 (d, *J* = 8.6 Hz, 1 H), 7.76 (d, *J* = 2.0 Hz, 1 H), 8.01 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.9, 32.0, 34.4, 55.0, 112.7, 120.1, 122.1, 122.2, 123.5, 124.9, 126.6, 135.6, 209.2.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{17}NOCl$ [M + H^+]: 250.0999; found: 250.1001.

4-(5-Bromo-1*H*-indol-3-yl)-4-methylpentan-2-one (3v)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), 5-bromoindole (**2i**; 98.2 mg, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (17.0 mg, 0.025 mmol), DME (1.0 mL) were used. The crude residue was purified by column chromatography to afford **3v** (pale yellow oil, 121.4 mg, 83%).

IR (neat): 3350, 2963, 1691, 1458, 795 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.52 (s, 6 H), 1.78 (s, 3 H), 2.92 (s, 2 H), 6.93 (t, *J* = 2.5 Hz, 1 H), 7.22–7.27 (m, 2 H), 7.91 (s, 1 H), 8.17 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.9, 32.0, 34.4, 55.0, 112.5, 113.2, 122.1, 123.1, 123.3, 124.6, 127.2, 135.9, 209.3.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{17}NOBr$ [M + H^+]: 294.0494; found: 294.0494.

3-(2-Methyl-4-oxopentan-2-yl)-1*H*-indole-5-carbonitrile (3w)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), 5-cyanoindole (**2j**; 71.5 mg, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (17.1 mg, 0.025 mmol), MeOH (0.5 mL), and MeCN (0.5 mL) were used. The crude residue was purified by column chromatography to afford **3w** (pale yellow oil, 59.3 mg, 49%).

IR (neat): 3324, 2217, 1697, 1349, 807 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.54 (s, 6 H), 1.83 (s, 3 H), 2.94 (s, 2 H), 7.06–7.07 (m, 1 H), 7.40–7.41 (m, 2 H), 8.14 (s, 1 H), 8.56 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.0, 32.1, 34.3, 54.9, 102.0, 112.7, 121.1, 123.1, 124.4, 124.5, 125.3, 126.2, 139.0, 208.7.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{17}N_2O$ [M + H^+]: 241.1341; found: 241.1345.

4-Methyl-4-(5-nitro-1*H*-indol-3-yl)pentan-2-one (3x)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), 5-nitroindole (**2k**; 81.4 mg, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.9 mg, 0.025 mmol), MeOH (0.5 mL), and MeCN (0.5 mL) were used. The crude residue was purified by column chromatography to afford **3x** (pale yellow solid, 12.5 mg, 10%); mp 143–145 °C.

IR (neat): 3280, 1520, 1330, 1082, 737 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.59 (s, 6 H), 1.85 (s, 3 H), 2.99 (s, 2 H), 7.12 (d, *J* = 2.5 Hz, 1 H), 7.40 (d, *J* = 9.0 Hz, 1 H), 8.11 (dd, *J* = 2.0, 9.0 Hz, 1 H), 8.43 (br s, 1 H), 8.76 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.1, 32.1, 34.4, 54.9, 111.7, 117.6, 117.8, 124.0, 124.9, 126.3, 140.3, 141.3, 208.4.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{17}N_2O_3$ [M + H^+]: 261.1239; found: 261.1240.

Methyl 3-(2-Methyl-4-oxopentan-2-yl)-1*H*-indole-5-carboxylate (3y)

4-Methylpent-3-en-2-one (**1k**; 115 μL, 1.00 mmol), methyl indole-5-carboxylate (**2l**; 87.6 mg, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), MeOH (0.5 mL), and MeCN (0.5 mL) were used. The crude residue was purified by column chromatography to afford **3y** (pale yellow oil, 71.8 mg, 53%).

IR (neat): 3339, 2955, 1690, 1237, 752 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.55 (s, 6 H), 1.75 (s, 3 H), 2.98 (s, 2 H), 3.95 (s, 3 H), 6.99 (d, *J* = 2.0 Hz, 1 H), 7.36 (d, *J* = 8.7 Hz, 1 H), 7.89 (dd, *J* = 1.6, 8.7 Hz, 1 H), 8.46 (br s, 1 H), 8.57 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.1, 31.9, 34.5, 52.1, 55.1, 111.5, 121.1, 122.2, 123.1, 123.5, 124.9, 125.2, 140.0, 168.5, 209.3.

HRMS (EI): *m*/*z* calcd for $C_{16}H_{20}NO_3$ [M + H^+]: 274.1443; found: 274.1443.

***tert*-Butyl 3-(4-(1-(1-Methyl-1*H*-indol-3-yl)-3-oxobutyl)phenyl)acrylate (3z)**

tert-Butyl 3-(4-(3-oxobut-1-en-1-yl)phenyl)acrylate (**1l**; 274.3 mg, 1.00 mmol), 1-methylindole (**2a**; 65.6 mg, 0.50 mmol), $[Fe(H_2O)_6](OTf)_3$ (16.7 mg, 0.025 mmol), and DME (1.0 mL) were used, with a reaction time of 48 h. The crude residue was purified by column chromatography to afford **3z** (pale yellow oil, 131.1 mg, 65%).

IR (neat): 1701, 1633, 1322, 1144, 737 cm^{-1}.

^1H NMR (396 MHz, $CDCl_3$): δ = 1.51 (s, 9 H), 2.08 (s, 3 H), 3.15 (dd, *J* = 8.3, 16.5 Hz, 1 H), 3.24 (dd, *J* = 7.6, 16.5 Hz, 1 H), 3.72 (s, 3 H), 4.83 (t, *J* = 7.6 Hz, 1 H), 6.27 (d, *J* = 15.8 Hz, 1 H), 6.83 (s, 1 H), 7.01 (t, *J* = 8.3 Hz, 1 H), 7.18 (t, *J* = 8.2 Hz, 1 H), 7.25 (t, *J* = 8.2 Hz, 1 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.38–7.40 (m, 3 H), 7.52 (d, *J* = 15.8 Hz, 1 H).

^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 28.3, 30.5, 32.8, 38.2, 50.2, 80.5, 109.4, 116.9, 119.1, 119.5, 119.7, 122.0, 126.3, 126.9, 128.3, 132.9, 137.4, 143.4, 146.6, 166.6, 207.3.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{29}NO_3$ [M^+]: 403.2147; found: 403.2147.

3-(1-Methyl-1*H*-indol-3-yl-2-*d*)-1-phenylbutan-1-one-2-*d* (3b-D)

The general procedure was followed using phenyl 1-propenyl ketone (**1b**; 73.1 mg, 0.50 mmol), 1-methylindole-3-*d* (**2a-D**; 131.2 mg, 1.00 mmol), $FeCl_3$ (8.1 mg, 0.05 mmol), AgOTs (48.8 mg, 0.17 mmol), and DME (1.0 mL) for 20 h. The crude residue was purified by column chromatography to afford **3b-D** (81.7 mg, 59%).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.45 (d, *J* = 6.8 Hz, 3 H), 3.20–3.27 (m, 0.3 H), 3.44–3.49 (m, 0.8 H), 3.75 (s, 3 H), 3.80–3.83 (m, 1 H), 6.89 (s, 0.75 H), 7.11 (t, *J* = 6.8 Hz, 1 H), 7.23 (t, *J* = 8.7 Hz, 1 H), 7.30 (d, *J* = 7.8 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 2 H), 7.55 (t, *J* = 7.8 Hz, 1 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.96 (d, *J* = 7.7 Hz, 2 H).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1705997.

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