Supporting Information

Synthesis of 3-acylindoles by oxidative rearrangement of 2-aminochalcone using a hypervalent iodine reagent and cyclization sequence

Akira Nakamura,a Satoshi Tanaka,a Akira Imamiya,a Reo Tkane,a Kazuma Fujimura,a Tomohiro Maegawa**a and Yasuyoshi Miki**a,b

a. School of Pharmaceutical Sciences, Kindai University, 3-4-1 Kowakae, Higashi-osaka, Osaka 577-8502, Japan.
b. Research Organization of Science and Technology, Research Center for Drug Discovery and pharmaceutical Science, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan.
Experimental Section

General. Column chromatography and TLC were performed on Merck Silica gel 60 (230–400 mesh) and Merck Silica gel F254 plates (0.25 mm), respectively. The melting point was measured using the Stuart® melting point apparatus SMP3 with an AC input of 100 V. $^1$H and $^{13}$C NMR spectra were recorded on the JEOL JMN-400 spectrometer in CDCl$_3$ or DMSO-$d_6$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), and coupling constant (Hz). High-resolution mass spectra were obtained on the SHIMAZU IRAffinity-1 instrument with ionization voltages of 70 eV.

Materials: Unless otherwise noted, all reagents, including PhI(OCOCH$_3$)$_2$ (PIDA), PhI(OH)OTs and PhI(OCOCF$_3$)$_2$, and solvents were purchased from commercial suppliers and used without further purification.

General procedure for synthesis of chalcone

To the solution of aldehyde (1 equiv.) in toluene (0.2 M) was added ylide (1.2 equiv.) at 80 °C, and then stirred at same temperature. After cooling to room temperature, the resulting mixture was concentrated in vacuo. The residue was purified by SiO$_2$ column chromatography (eluent: Hexane/AcOEt) to give the desired chalcone.

$^{(E)}$-2,2,2-Trifluoro-$N$-(5-methoxy-2-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)acetamide (1a)

According to the general procedure, aldehyde (443 mg, 1.60 mmol) in toluene (8.0 mL) was added ylide (722 mg, 1.76 mmol) at 80 °C, then stirred at same temperature in 15 h. The resulting mixture was concentrated in vacuo. The residue was purified by SiO$_2$ column chromatography (eluent: Hexane/AcOEt = 1/1) to give 1a (537 mg, 89%) as ocher solid. mp 170-171 °C. $^1$H-NMR (CDCl$_3$) δ : 3.87 (3H, s, OMe), 3.88 (3H, s, OMe), 6.88 (1H, dd, $J$ = 2.4, 8.8 Hz), 6.95 (2H, d, $J$ = 8.8 Hz), 7.40 (1H, d, $J$ = 15.6 Hz), 7.45 (1H, d, $J$ = 2.4 Hz), 7.65 (1H, d, $J$ = 8.8 Hz), 7.84 (1H, d, $J$ = 16.0 Hz), 7.96 (2H, d, $J$ = 8.8 Hz), 8.54 (1H, s, NH); $^{13}$C-NMR (CDCl$_3$) δ : 55.7, 55.9, 112.9, 114.2, 114.7, 116.3 (q, $J$ = 287.3 Hz), 121.3, 123.6, 129.2, 130.7, 131.1, 136.1, 137.6, 155.9 (q, $J$ = 37.1 Hz), 161.5, 163.4, 187.4; HRFABMS: calcd for C$_{19}$H$_{17}$NO$_4$F$_3$ [M+H]$^+$: 380.1110, found 380.1086.

$^{(E)}$-N-(2-(3-(4-Chlorophenyl)-3-oxoprop-1-en-1-yl)-5-methoxyphenyl)-2,2,2-trifluoroacetamide (1b)

According to the general procedure, the reaction of aldehyde (395 mg, 1.60 mmol) with ylide (730 mg, 1.76 mmol) in toluene (8.0 mL) gave 1b (580 mg, 93%) as ocher solid. Reaction time: 15 h. Eluent of SiO$_2$ column chromatography: Hexane/AcOEt = 2/1.
mp 173-174 °C; $^1$H-NMR (CDCl$_3$) δ: 3.84 (3H, s, OMe), 7.01 (1H, d, J = 2.8 Hz), 7.06 (1H, dd, J = 2.4, 8.8 Hz), 7.63 (2H, d, J = 8.4 Hz), 7.71 (1H, d, J = 15.2 Hz), 7.83 (1H, d, J = 16.0 Hz), 8.16 (2H, d, J = 8.4 Hz), 8.19 (1H, d, J = 8.8 Hz), 11.42 (1H, s, NH); $^{13}$C-NMR (CDCl$_3$) δ: 55.9, 112.9, 114.7, 116.2 (q, J = 286.5 Hz), 120.9, 123.2, 129.1, 129.3, 130.6, 136.4, 136.5, 138.3, 139.0, 156.0 (q, J = 37.0 Hz), 161.8, 188.2; HRFABMS: calcd for C$_{18}$H$_{14}$NO$_3$F$_3$Cl [M+H]$^+$ 384.0614, found 384.0625.

(E)-2,2,2-Trifluoro-N-(2-(3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)-5-methoxyphenyl)acetamide (1c)

According to the general procedure, the reaction of aldehyde (49.4 mg, 0.20 mmol) with ylide (87.6 mg, 0.22 mmol) in toluene (1.0 mL) gave 1c (66.1 mg, 90%) as ocher solid. Reaction time: 2 h. Eluent of SiO$_2$ column chromatography: CH$_2$Cl$_2$.

mp 168-169 °C; $^1$H-NMR (CDCl$_3$) δ: 3.87 (3H, s, OMe), 6.89 (1H, dd, J = 2.4, 8.4 Hz), 7.15 (2H, t, J = 7.2 Hz), 7.37 (1H, d, J = 15.2 Hz), 7.41 (1H, d, J = 2.4 Hz), 7.67 (1H, d, J = 8.8 Hz), 7.85 (1H, d, J = 15.6 Hz), 7.99 (2H, dd, J = 5.6, 8.4 Hz), 8.44 (1H, s, NH); $^{13}$C-NMR (CDCl$_3$) δ: 55.7, 110.0, 114.3, 115.7, 115.8 (q, J = 286.5 Hz), 115.9 (d, J = 4.1 Hz), 120.9, 121.7, 128.9, 131.0 (d, J = 9.1 Hz), 134.1 (d, J = 2.5 Hz), 135.1, 138.3, 155.7 (q, J = 37.0 Hz), 162.1, 165.7 (d, J = 254.6 Hz), 188.3; HRFABMS: calcd for C$_{18}$H$_{14}$NO$_3$F$_4$ [M+H]$^+$ 368.0910, found 368.0958.

(E)-2,2,2-Trifluoro-N-(5-methoxy-2-(3-oxo-3-(o-tolyl)prop-1-en-1-yl)phenyl)acetamide (1d)

To the solution of aldehyde (98.8 mg, 0.40 mmol) and phosphonium salts (190 mg, 0.40 mmol) in THF (4.0 mL) was added DBU (89 μL, 0.6 mmol) at 40 °C. Then stirred at same temperature in 20 h. The reaction was quenched with NH$_4$Cl aq. The organic layer was extracted with AcOEt, washed with brine, dried over with Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by SiO$_2$ column chromatography (Hexane/AcOEt = 4/1) to give 1d (111.4 mg, 77%) as ocher solid.

mp 130-131 °C; $^1$H-NMR (CDCl$_3$) δ: 2.43 (3H, s, Me), 3.86 (3H, s, OMe), 6.89 (1H, dd, J = 2.8, 8.8 Hz), 7.04 (1H, d, J = 15.6 Hz), 7.24-7.28 (2H, m), 7.32 (1H, d, J = 2.4 Hz), 7.38 (1H, dt, J = 1.6, 8.0 Hz), 7.48 (1H, d, J = 8.8 Hz), 7.51 (1H, d, J = 15.6 Hz), 7.65 (1H, d, J = 8.8 Hz), 8.15 (1H, s, NH); $^{13}$C-NMR (CDCl$_3$) δ: 19.9, 55.5, 110.9, 114.4, 115.7 (q, J = 54.9 Hz), 121.7, 125.3, 126.0, 127.9, 128.5, 130.6, 131.2, 134.9, 136.8, 138.3, 139.8, 156.0 (q, J = 37.9 Hz), 161.9, 196.4; HRFABMS: calcd for C$_{19}$H$_{16}$NO$_3$F$_3$ [M+H]$^+$ 363.1082, found 363.1091.

(E)-2,2,2-Trifluoro-N-(5-methoxy-2-(3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)phenyl)acetamide (1e)

According to general procedure, the reaction of aldehyde (49.4 mg, 0.20 mmol) with ylide (87.6 mg, 0.22 mmol) in toluene (1.0 mL) gave 1e (66.1 mg, 90%) as yellow solid. Reaction time: 2 h. Eluent of SiO$_2$ column chromatography: CH$_2$Cl$_2$.

mp 213-214 °C; $^1$H-NMR (CDCl$_3$) δ: 3.87 (3H, s, OMe), 6.89 (1H, dd, J = 2.4, 8.8 Hz), 7.17 (1H, t, J = 4.0 Hz), 7.26 (1H, d, J = 7.6 Hz), 7.45 (1H, d, J = 2.4 Hz), 7.65-7.69 (2H, m), 7.80 (1H, d, J = 4.0 Hz), 7.89 (1H, d, J = 7.2 Hz),
Hz), 8.57 (1H, s, NH); $^{13}$C-NMR (DMSO-$d_6$) $\delta$: 55.7, 112.7, 114.5, 116.0 (q, $J = 288.4$ Hz), 121.0, 123.0, 128.9, 129.0, 133.6, 135.5, 136.1, 137.3, 145.6, 155.8 (q, $J = 38.0$ Hz), 161.5, 181.5; HRFABMS: calcd for C$_{16}$H$_{13}$NO$_3$F$_3$S [M+H]$^+$ 356.0568, found 356.0548.

(E)-2,2,2-Trifluoro-N-(5-methoxy-2-(3-oxobut-1-en-1-yl)phenyl)acetamide (1f)

According to the procedure for 1d, the reaction of aldehyde (74.1 mg, 0.30 mmol) with (2-oxopropyl)triphenylphosphonium bromide (107 mg, 0.30 mmol) and DBU (67 μL, 0.45 mmol) in THF (3.0 mL) gave 1f (66.2 mg, 77%) as colorless oil.

Reaction time: 1 h. Eluent of SiO$_2$ column chromatography: Hexane/AcOEt = 4/1.

mp 122-123 °C; $^1$H-NMR (CDCl$_3$) $\delta$: 2.33 (3H, s, Me), 3.86 (3H, s, OMe), 6.61 (1H, d, $J = 16.0$ Hz), 6.88 (1H, dd, $J = 2.8, 8.8$ Hz), 7.28 (1H, d, $J = 2.4$ Hz), 7.52 (1H, d, $J = 7.6$ Hz), 7.57 (1H, d, $J = 8.8$ Hz), 8.30 (1H, s, NH); $^{13}$C-NMR (CDCl$_3$) $\delta$: 27.7, 55.6, 110.8, 114.4, 115.8 (q, $J = 284.9$ Hz), 121.2, 126.6, 128.6, 134.7, 137.1, 156.1 (q, $J = 37.9$ Hz), 161.8, 198.5; HRFABMS: calcd for C$_{13}$H$_{13}$NO$_3$F$_3$ [M+H]$^+$ 288.0848, found 288.0821.

(E)-N-(2-(3-Cyclohexyl-3-oxoprop-1-en-1-yl)-5-methoxyphenyl)-2,2,2-trifluoroacetamide (1g)

To the solution of aldehyde (24.7 mg, 0.10 mmol) and phosphonium salts 1 (93.4 mg, 0.20 mmol) in THF (1.0 mL) and DMF (1.0 mL) was added DBU (22 μL, 0.15 mmol) at 65 °C. Then stirred at same temperature in 25 h and quenched with NH$_4$Cl aq. The organic layer was extracted with AcOEt, washed with brine, dried over with Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by SiO$_2$ column chromatography (CH$_2$Cl$_2$) to give 1g (22.4 mg, 63%) as white solid.

mp 137-138 °C; $^1$H-NMR (CDCl$_3$) $\delta$: 1.21-1.44 (5H, m), 1.60-1.90 (5H, m), 2.55 (1H, tt, $J = 3.6, 7.6$ Hz), 3.86 (3H, s, OMe), 6.72 (1H, d, $J = 15.6$ Hz), 6.86 (1H, dd, $J = 2.8, 8.8$ Hz), 7.42 (1H, d, $J = 3.2$ Hz), 7.58 (1H, d, $J = 8.8$ Hz), 7.62 (1H, d, $J = 15.6$ Hz), 8.16 (1H, s, NH); $^{13}$C-NMR (CDCl$_3$) $\delta$: 25.6, 25.7, 28.4, 49.9, 55.6, 110.3, 114.3, 115.9 (q, $J = 287.3$ Hz), 121.1, 124.2, 128.5, 135.1, 136.1, 155.9 (q, $J = 37.9$ Hz), 161.7, 202.9; HRFABMS: calcd for C$_{18}$H$_{20}$NO$_3$F$_3$ [M$^+$] 355.1395, found 355.1351.

(E)-2,2,2-Trifluoro-O-N-(2-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)acetamide (1h)

According to the general procedure, the reaction of aldehyde (65.1 mg, 0.30 mmol) with ylide (131 mg, 0.33 mmol) in toluene (1.5 mL) gave 1h (91.1 mg, 87%) as pale yellow solid. Reaction time: 2 h. Eluent of SiO$_2$ column chromatography: CH$_2$Cl$_2$.

mp 203-204 °C; $^1$H-NMR (DMSO-$d_6$) $\delta$: 3.87 (3H, s, OMe), 7.10 (1H, d, $J = 8.4$ Hz), 7.41 (1H, d, $J = 7.6$ Hz), 7.47 (1H, d, $J = 7.6$ Hz), 7.53 (1H, d, $J = 7.6$ Hz), 7.71 (1H, d, $J = 15.6$ Hz), 7.94 (1H, d, $J = 15.6$ Hz), 8.16-8.21 (3H, m), 11.4 (1H, s, NH); $^{13}$C-NMR (CDCl$_3$) $\delta$: 55.6, 114.1, 116.1 (q, $J = 288.4$ Hz), 123.7, 127.6, 127.8, 128.0, 130.2, 130.9, 130.9, 131.0, 134.2, 137.4, 155.8 (d, $J = 37.1$ Hz), 163.4, 187.3; HRFABMS: calcd for C$_{18}$H$_{13}$NO$_3$F$_3$ [M$^+$]$^+$ 350.1004, found 350.0963.
According to the general procedure, the reaction of aldehyde (355 mg, 1.20 mmol) with ylide (541 mg, 1.32 mmol) in toluene (6 mL) gave \( \text{1i} \) (456 mg, 89%) as pale yellow solid. Reaction time: 12 h. Eluent of SiO\(_2\) column chromatography: Hexane/AcOEt = 1/1. mp 202-203 °C; \(^1\)H-NMR (DMSO-\(d_6\)) \( \delta \): 3.86 (3H, s, OMe), 7.08 (1H, d, \( J = 8.8 \) Hz), 7.62-7.71 (3H, m), 7.99 (2H, d, \( J = 15.6 \) Hz), 8.16 (2H, d, \( J = 8.8 \) Hz), 11.5 (1H, s, NH); \(^1^3\)C-NMR (CDCl\(_3\)) \( \delta \): 55.6, 114.1, 115.9 (q, \( J = 287.6 \) Hz), 123.2, 124.3, 129.3, 130.15, 130.23, 130.4, 130.9, 131.1, 135.5, 136.3, 155.9 (q, \( J = 36.3 \) Hz), 163.4, 187.2; HRFABMS: calcd for C\(_{18}\)H\(_{14}\)NO\(_3\)F\(_3\)Br [M+H]^+ 428.0109, found 428.0102.

According to the general procedure, the reaction of aldehyde (443 mg, 1.6 mmol) with ylide (722 mg, 1.76 mmol) in toluene (8 mL) gave \( \text{1j} \) (622 mg, 95%) as pale yellow solid. Reaction time: 16 h. Eluent of SiO\(_2\) column chromatography: Hexane/AcOEt = 1/1. mp 210-212 °C; \(^1\)H-NMR (DMSO-\(d_6\)) \( \delta \): 3.82 (3H, s, OMe), 3.87 (3H, s, OMe), 3.93 (3H, s, OMe), 7.00 (1H, s), 7.10 (2H, d, \( J = 8.8 \) Hz), 7.65 (1H, s), 7.67 (1H, d, \( J = 15.2 \) Hz), 7.87 (1H, d, \( J = 15.2 \) Hz), 8.17 (2H, d, \( J = 8.8 \) Hz), 11.27 (1H, s, NH); \(^1^3\)C-NMR (DMSO-\(d_6\)) \( \delta \): 55.5, 55.9, 56.1, 109.2, 110.9, 114.0, 116.1 (q, \( J = 288.4 \) Hz), 121.3, 123.3, 128.4, 130.5, 130.9, 137.6, 148.4, 151.1, 155.9 (q, \( J = 36.3 \) Hz), 163.2, 187.3; HRFABMS: calcd for C\(_{20}\)H\(_{19}\)F\(_3\)NO\(_5\) [M+H]^+ 410.1215, found 410.1218.

**General procedure for synthesis of 3-acylindole**

To the solution of chalcone (0.1 mmol) in CH(OMe)\(_3\) (1 ml) was added BF\(_3\)•Et\(_2\)O (0.25 mmol) at room temperature. The resulting mixture was added PhI(OAc)\(_2\) (0.15 mmol), then stirred at same temperature for 1 h. THF and 30% aqueous K\(_2\)CO\(_3\) were then added, and the mixture was stirred at 60 °C for an appropriate time. The organic layer was extracted with CH\(_2\)Cl\(_2\), washed with brine, dried over with Na\(_2\)SO\(_4\) and concentrated in vacuo. The residue was purified by SiO\(_2\) column chromatography (eluent: hexane/AcOEt) to give the desired 3-acylindole.

\( \text{(6-Methoxy-1H-indol-3-yl)(4-methoxyphenyl)methanone (3a)} \)

99%; Eluent of SiO\(_2\) column chromatography: Hexane/AcOEt = 2/1; white solid; mp 216-217 °C; \(^1\)H-NMR (DMSO-\(d_6\)) \( \delta \): 3.80 (3H, s, OMe), 3.85 (3H, s, OMe), 6.86 (1H, dd, \( J = 1.6, 8.8 \) Hz), 7.00 (1H, s), 7.06 (2H, d, \( J = 8.8 \) Hz), 7.79 (2H, d, \( J = 8.8 \) Hz), 7.80 (1H, s), 8.07 (1H, d, \( J = 8.8 \) Hz), 11.79 (1H, s, NH); \(^1^3\)C-NMR (CDCl\(_3\)) \( \delta \): 55.4, 55.6, 95.3, 111.7, 113.8, 115.3, 120.6, 122.3, 130.7, 133.1, 134.1, 137.7, 156.7, 161.9, 188.8; HRFABMS: calcd for C\(_{17}\)H\(_{16}\)NO\(_3\) [M+H]^+ 282.1130, found 282.1118.
(4-Chlorophenyl)(6-methoxy-1H-indol-3-yl)methanone (3b)
99%; Eluent of SiO₂ column chromatography: Hexane/AcOEt = 1/1; yellow solid; mp 251-253 °C; ¹H-NMR (DMSO-d₆) δ : 3.80 (3H, s, OMe), 6.90 (1H, dd, J = 2.0, 8.8 Hz), 7.00 (1H, d, J = 2.0 Hz), 7.59 (2H, d, J = 7.6 Hz), 7.79 (2H, d, J = 8.4 Hz), 7.84 (1H, d, J = 2.8 Hz), 8.09 (1H, d, J = 8.8 Hz), 11.93 (1H, s, NH); ¹³C-NMR (DMSO-d₆) δ : 55.4, 95.5, 112.0, 115.1, 120.3, 122.3, 128.6, 130.4, 135.3, 136.0, 137.9, 139.3, 156.9, 188.7; HRFABMS: calcd for C₁₆H₁₃NO₂Cl [M+H]⁺ 286.0635, found 286.0620.

(4-Fluorophenyl)(6-methoxy-1H-indol-3-yl)methanone (3c)
91%; Eluent of SiO₂ column chromatography: Hexane/AcOEt = 2/1; ocher solid; mp 241-243 °C; ¹H-NMR (DMSO-d₆) δ : 3.80 (3H, s, OMe), 6.88 (1H, dd, J = 1.6, 8.8 Hz), 7.00 (1H, d, J = 2.0 Hz), 7.35 (2H, t, J = 8.8 Hz), 7.82-7.87 (3H, m), 8.09 (1H, d, J = 8.8 Hz), 11.91 (1H, s, NH); ¹³C-NMR (DMSO-d₆) 55.2, 95.2, 111.7, 114.9, 115.3 (d, J = 21.6 Hz), 120.2, 122.1, 130.9 (d, J = 9.1 Hz), 134.8, 137.0 (d, J = 3.0 Hz), 137.6, 156.6, 163.7 (d, J = 248.4 Hz), 188.3; HRFABMS: calcd for C₁₆H₁₃NO₂F [M+H]⁺ 270.0930, found 270.0970.

(6-Methoxy-1H-indol-3-yl)(o-tolyl)methanone (3d)
84%; Eluent of SiO₂ column chromatography: Hexane/AcOEt = 2/1; yellow solid; mp 216-217 °C; ¹H-NMR (DMSO-d₆) δ : 2.26 (3H, s, Me), 3.79 (3H, s, OMe), 6.87 (1H, dd, J = 2.0, 8.8 Hz), 6.99 (1H, d, J = 1.6 Hz), 7.28-7.32 (2H, m), 7.36-7.41 (2H, m), 7.46 (1H, d, J = 2.4 Hz), 8.03 (1H, d, J = 8.8 Hz), 11.82 (1H, s, NH); ¹³C-NMR (DMSO-d₆) δ : 19.4, 55.4, 95.6, 112.0, 116.9, 119.8, 122.1, 125.4, 127.4, 129.3, 130.7, 135.0, 135.6, 138.0, 141.1, 156.8, 192.1; HRFABMS: calcd for C₁₇H₁₆NO₂ [M+H]⁺ 266.1181, found 266.1139.

(6-Methoxy-1H-indol-3-yl)(thiophen-2-yl)methanone (3e)
94%; Eluent of SiO₂ column chromatography: Hexane/AcOEt = 2/1; ocher solid; mp 229-231 °C; ¹H-NMR (DMSO-d₆) δ : 3.80 (3H, s, OMe), 6.87 (1H, dd, J = 2.4, 8.8 Hz), 7.00 (1H, d, J = 2.4 Hz), 7.25 (1H, dd, J = 4.0, 4.8 Hz), 7.91-7.93 (2H, m), 8.07 (1H, d, J = 8.8 Hz), 8.22 (1H, d, J = 2.8 Hz), 11.92 (1H, s, NH); ¹³C-NMR (DMSO-d₆) δ : 45.0, 95.2, 111.6, 114.6, 120.2, 122.0, 128.2, 131.1, 132.1, 133.1, 137.4, 145.1, 156.6, 180.5; HRFABMS: calcd for C₁₄H₁₂NO₂S [M+H]⁺ 258.0589, found 258.0598.

1-(6-Methoxy-1H-indol-3-yl)ethan-1-one (3f)
91%; Eluent of SiO₂ column chromatography: Hexane/AcOEt = 1/1; ocher solid; ¹H-NMR (DMSO-d₆) δ : 2.41 (3H, s, Me), 3.77 (3H, s, OMe), 6.80 (1H, d, J = 8.8 Hz), 6.93 (1H, s, 8.01 (1H, d, J = 8.4 Hz), 8.16 (1H, s), 11.71 (1H, s, NH).
Cyclohexyl(6-methoxy-1H-indol-3-yl)methanone (3g)
89%; Eluent of SiO\textsubscript{2} column chromatography: Hexane/AcOEt = 2/1; beige solid; mp 161-163 °C; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \( \delta \): 1.25-1.42 (3H, m), 1.58-1.75 (3H, m), 1.84-1.93 (4H, m), 3.03 (1H, tt, \( J = 3.2, 12.0 \) Hz), 3.80 (3H, s, OMe), 6.86 (1H, d, \( J = 2.4 \) Hz), 6.93 (1H, dd, \( J = 2.4, 8.8 \) Hz), 7.79 (1H, d, \( J = 2.8 \) Hz), 8.27 (1H, d, \( J = 8.8 \) Hz), 9.06 (1H, s, NH); \textsuperscript{13}C-NMR (DMSO-\( d_6 \)) \( \delta \): 25.3, 25.7, 29.7, 46.0, 55.2, 95.0, 111.4, 115.2, 119.7, 122.1, 132.4, 137.7, 156.2, 198.7; HRFABMS: calcd for C\textsubscript{16}H\textsubscript{20}NO\textsubscript{2} [M+H]+ 258.1494, found 258.1447.

(1H-Indol-3-yl)(4-methoxyphenyl)methanone (3h)
81%; Eluent of SiO\textsubscript{2} column chromatography: Hexane/AcOEt = 2/1; beige solid; \textsuperscript{1}H-NMR (DMSO-\( d_6 \)) \( \delta \): 3.34 (3H, s), 7.06 (2H, d, \( J = 8.8 \) Hz), 7.20-7.26 (2H, m), 7.50 (1H, d, \( J = 7.2 \) Hz), 7.80 (2H, d, \( J = 8.8 \) Hz), 7.93 (1H, d, \( J = 3.2 \) Hz), 8.22 (1H, d, \( J = 7.2 \) Hz), 12.00 (1H, s, NH).

(6-Bromo-1H-indol-3-yl)(4-methoxyphenyl)methanone (3i)
51%; Eluent of SiO\textsubscript{2} column chromatography: Hexane/AcOEt = 2/1; beige solid; mp 208-209 °C; \textsuperscript{1}H-NMR (DMSO-\( d_6 \)) \( \delta \): 3.85 (3H, s, OMe), 7.07 (2H, d, \( J = 8.8 \) Hz), 7.36 (1H, d, \( J = 8.4 \) Hz), 7.71 (1H, s), 7.81 (2H, d, \( J = 8.8 \) Hz), 8.00 (1H, s), 8.15 (1H, d, \( J = 8.4 \) Hz), 12.1 (1H, s, NH); \textsuperscript{13}C-NMR (DMSO-\( d_6 \)) \( \delta \): 55.4, 113.7, 114.8, 115.0, 115.5, 123.2, 124.6, 125.5, 130.7, 132.5, 135.6, 137.5, 161.9, 188.6; HRFABMS: calcd for C\textsubscript{16}H\textsubscript{12}NO\textsubscript{2}Br [M+H]+ 330.0130, found 330.0102.

(5,6-Dimethoxy-1H-indol-3-yl)(4-methoxyphenyl)methanone (3j)
74%; Eluent of SiO\textsubscript{2} column chromatography: Hexane/AcOEt = 2/1; beige solid; mp 216-217 °C; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \( \delta \): 3.90 (3H, s, OMe), 3.92 (3H, s, OMe), 3.95 (3H, s, OMe), 6.90 (1H, s), 7.01 (1H, d, \( J = 8.8 \) Hz), 7.05 (1H, s), 8.01 (1H, d, \( J = 8.8 \) Hz), 9.54 (1H, s, NH); \textsuperscript{13}C-NMR (DMSO-\( d_6 \)) \( \delta \): 55.4, 113.7, 114.8, 115.0, 115.5, 123.2, 124.6, 125.5, 130.1, 132.5, 135.6, 137.5, 161.9, 188.6; HRFABMS: calcd for C\textsubscript{18}H\textsubscript{18}NO\textsubscript{4} [M+H]+ 312.1236, found 312.1247.

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\text{2,2,2-Trifluoro-N-(2-formyl-5-methoxyphenyl)acetamide (5)}
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To the solution of 4-methoxy-2-nitrobenzaldehyde (300 mg, 1.57 mmol) in EtOH (5 mL) and water (5 mL) was added Fe (292 mg, 4.71 mmol) and NH\textsubscript{4}Cl (466 mg, 7.85 mmol) then stirred at 60 °C for 1 h. Fe was removed by filtration and the solvent was extracted with CH\textsubscript{2}Cl\textsubscript{2}. The organic layer was concentrated in vacuo, and then added CH\textsubscript{2}Cl\textsubscript{2} (8 mL). Trifluoroacetic anhydride (TFAA) was slowly added to the solution at 0 °C. After 12 min, the reaction was quenched with sat. NaHCO\textsubscript{3} solution. The organic layer was extracted with CH\textsubscript{2}Cl\textsubscript{2}, washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. The
residue was purified by SiO2 column chromatography (Hexane/AcOEt = 4/1) to give 5 (308 mg, 72%) as yellow solid.

1H-NMR (CDCl3) δ: 3.93 (3H, s, OMe), 6.85 (1H, dd, J = 2.4, 8.4 Hz), 7.65 (1H, d, J = 8.4 Hz), 8.25 (1H, d, J = 2.0 Hz), 9.80 (1H, s), 12.49 (1H, s, NH); 13C-NMR (CDCl3) δ: 56.0, 105.2, 111.5, 115.4 (q, J = 287.3 Hz), 116.5, 137.9, 140.6, 156.0 (q, J = 37.9 Hz), 165.9, 193.7; HRFABMS: calcd for C10H9NO3 F3 [M+H]+ 248.0535, found 248.0525.

(E)-2,2,2-Trifluoro-N-(5-methoxy-2-(3-oxo-3-(3,4,5-trimethoxyphenyl) prop-1-en-1-yl)phenyl)acetamide (7)

According to the procedure for 1a, the reaction of aldehyde 5 (45.3 mg, 0.18 mmol) with ylide (94.7 mg, 0.20 mmol) in toluene (1.0 mL) gave 7 (78.5 mg, 98%) as ocher solid. Reaction time: 22 h. Eluent of SiO2 column chromatography: CH2Cl2.

mp 167-168 °C; 1H-NMR (DMSO-d6) δ: 3.75 (3H, s, OMe), 3.83 (3H, s, OMe), 3.89 (3H, s, OMe), 7.00 (1H, d, J = 2.4 Hz), 7.06 (1H, dd, J = 2.0, 8.8 Hz) 7.40 (2H, s), 7.68 (1H, d, J = 15.6 Hz), 7.82 (1H, d, J = 15.2 Hz), 8.18 (1H, d, J = 8.8 Hz), 11.40 (1H, s, NH); 13C-NMR (DMSO-d6) δ: 55.2, 55.9, 60.1, 95.1, 106.0, 111.6, 114.9, 120.4, 122.1, 134.7, 135.8, 137.6, 140.0, 152.6, 156.5, 188.8; HRFABMS: calcd for C21H21NO6F3 [M+H]+ 440.1321, found 440.1293.

(6-Methoxy-1H-indol-3-yl)(3,4,5-trimethoxyphenyl)methanone (SCB01A)

To the solution of 7 (44.0 mg, 0.10 mmol) in CH(OMe)3 (2.0 mL) was added BF3•Et2O (64 μL, 0.51 mmol) at room temperature. The resulting mixture was added Phl(OAc)2 (64.4 mg, 0.20 mmol), then stirred at same temperature for 1 h. The resulting mixture was added THF (4.0 mL) and 30% K2CO3 (1.0 mL) then stirred at 60 °C in 5 h. The organic layer was extracted with CH2Cl2, washed with brine, dried over with Na2SO4 and concentrated in vacuo. The residue was purified by SiO2 column chromatography (Hexane/AcOEt = 1/1) to give SCB01A (32.4 mg, 95%) as pale yellow solid.

mp 187-188 °C; 1H-NMR (DMSO-d6) δ: 3.76 (3H, s, OMe), 3.80 (3H, s, OMe), 3.86 (6H, s, OMe), 6.88 (1H, dd, J = 2.0, 8.8 Hz), 7.00 (1H, d, J = 2.0 Hz), 7.09 (2H, s), 7.97 (1H, d, J = 2.4 Hz), 8.11 (1H, d, J = 8.8 Hz), 11.84 (1H, s, NH); 13C-NMR (DMOSO-d6) δ: 55.2, 55.9, 60.1, 95.1, 106.0, 111.6, 114.9, 120.4, 122.1, 134.7, 135.8, 137.6, 140.0, 152.6, 156.5, 188.8; HRFABMS: calcd for C19H20NO5 [M+H]+ 342.1341, found 342.1327.

References
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1b

\[ \text{MeO-} \text{NHCOCF}_3 \text{Cl} \]
1d

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\text{MeO} \quad \text{NHOCOCF}_3
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1h

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\text{ONHCOCF}_3 \text{OMe}
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\text{ONHCOCF}_3
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