Supporting Information

Highly Substituted 2,3-Dihydroisoxazoles by Et_3N-Catalyzed Tandem Reaction of Electron-Deficient 1,3-Conjugated Enynes with Hydroxylamines.

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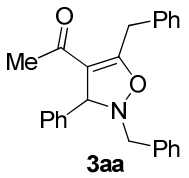
Typical Procedure for the synthesis of 2,3-dihydroisoxazole:

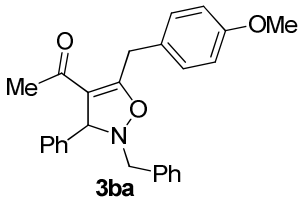
1. 1-(2,5-dibenzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)ethanone.



3aa

To a solution of 3-benzylidene-5-phenylpent-4-yn-2-one (**1a**) (0.3 mmol, 73.8 mg) and *N*-benzyl hydroxylamine (**2a**) (0.45 mmol, 55.4 mg) in 2.5 mL of DCE at 0 ^{o}C was added Et_3N (0.06 mmol, 6.1 mg) in one portion. The reaction mixture was then stirred till the enyne **1a** was consumed by TLC analysis. 3 mL of H_2O was added to quench the reaction and the mixture was extracted by ether. The combined organic layer was dried over $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography on silica gel (petroleum ether : acetate = 8 : 1) to give a white solid **3aa** (100.7 mg) in 91% yield. m.p.: 85 ~ 86℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 ~ 7.12 (m, 13 H), 7.12 ~ 7.04 (m, 2 H), 5.13 (s, 1 H), 4.25 (d, *J* = 14.4 Hz, 1 H), 4.20 (d, *J* = 14.4 Hz, 1 H), 3.96 (d, *J* = 13.5 Hz, 2 H), 1.97 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.37, 165.61, 140.73, 135.57, 135.02, 129.47, 128.95, 128.58, 128.55, 128.30, 127.97, 127.75, 127.42, 126.97, 112.50, 72.92, 63.40, 32.40, 29.68 ppm; MS (70 eV): m/z (%): 369 (M^+, 3.97), 91 (100). Anal, calcd for $C_{25}H_{23}NO_2$: C, 81.27, H, 6.27, N, 3.79; found: C, 81.23, H, 6.40, N, 3.82.

2. 1-(5-(4-methoxybenzyl)-2-benzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)ethanone.

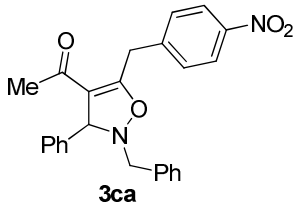


3ba

The reaction of **1b** (0.3 mmol, 82.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^{o}C for 4.5 h to afford a yellow solid **3ba** (106.5 mg) in 89% yield. m.p.: 47 ~ 48℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 ~ 7.17 (m, 10 H), 7.10 ~ 7.04 (m, 2 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 5.13 (s, 1 H), 4.20 (d, *J* = 12.9 Hz, 1 H), 4.19 (d, *J* = 14.4 Hz, 1 H), 3.96 (d, *J* = 12.9 Hz, 1 H), 3.90 (d, *J* =

14.4 Hz, 1 H), 3.78 (s, 3 H), 1.97 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.42, 166.10, 158.62, 140.76, 135.05, 130.01, 129.49, 128.56, 128.32, 127.97, 127.78, 127.61, 127.42, 113.99, 112.20, 72.89, 63.40, 55.18, 31.56, 29.71 ppm. MS (70 eV): m/z (%): 399 (M^+, 2.74), 105 (100). HRMS calcd for $C_{26}H_{25}NO_3$: 399.1834, found: 399.1828.

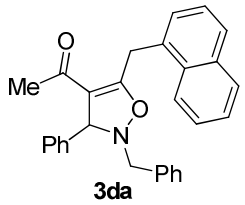
3. 1-(5-(4-nitrobenzyl)-2-benzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)ethanone.



3ca

The reaction of **1c** (0.3 mmol, 89.3 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 0.5 h to afford a yellow oil **3ca** (90.7 mg) in 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.33 ~ 7.18 (m, 8 H), 7.05 (t, *J* = 3.6 Hz, 2 H), 5.17 (s, 1 H), 4.32 (d, *J* = 14.1 Hz, 1 H), 4.24 (d, *J* = 12.9 Hz, 1 H), 4.11 (d, *J* = 14.1 Hz, 1 H), 4.03 (d, *J* = 12.9 Hz, 1 H), 1.91 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.84, 164.03, 147.00, 143.22, 140.15, 134.69, 129.94, 129.27, 128.73, 128.38, 128.31, 127.93, 127.43, 123.69, 112.40, 72.96, 63.42, 32.15, 29.79 ppm. MS (70 eV): m/z (%): 414 (M^+, 3.61), 91 (100). HRMS calcd for $C_{25}H_{22}N_2O_4$: 414.1580, found: 414.1580.

4. 1-(2-benzyl-5-(naphthalen-1-ylmethyl)-3-phenyl-2,3-dihydroisoxazol-4-yl)ethanone.

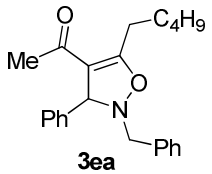


3da

The reaction of **1d** (0.3 mmol, 88.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 1.5 h to afford a white solid

3ca (110.9 mg) in 88% yield. m.p.: 93 ~ 94℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 ~ 8.08 (m, 1 H), 7.88 ~ 7.82 (m, 1 H), 7.78 (d, *J* = 8.1 Hz, 1 H), 7.53 ~ 7.42 (m, 3 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.28 ~ 7.05 (m, 8 H), 6.93 (d, *J* = 7.5 Hz, 2 H), 5.15 (s, 1 H), 4.80 (d, *J* = 15.3 Hz, 1 H), 4.46 (d, *J* = 15.3 Hz, 1 H), 4.02 (d, *J* = 12.9 Hz, 1 H), 3.87 (d, *J* = 12.9 Hz, 1 H), 1.97 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.89, 165.76, 140.65, 134.75, 133.78, 131.95, 131.74, 129.44, 128.59, 128.56, 128.16, 128.05, 127.79, 127.62, 127.52, 127.50, 126.23, 125.71, 125.43, 123.92, 112.53, 73.12, 63.42, 30.00, 29.88 ppm. MS (70 eV): m/z (%): 419 (M^+, 15.65), 91 (100). Anal, calcd for $C_{29}H_{25}NO_2$: C, 83.03, H, 6.01, N, 3.34; found: C, 82.82, H, 6.14, N, 3.33.

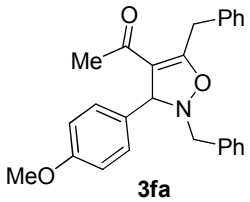
5. 1-(2-benzyl-5-pentyl-3-phenyl-2,3-dihydroisoxazol-4-yl)ethanone.



3ea

The reaction of **1c** (0.3 mmol, 67.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^{o}C for 24 h to afford a yellow oil **3ea** (66.0 mg) in 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 ~ 7.18 (m, 8 H), 7.11 (d, *J* = 7.5 Hz, 2 H), 5.15 (s, 1 H), 4.31 (d, *J* = 12.9 Hz, 1 H), 4.04 (d, *J* = 12.9 Hz, 1 H), 2.85 ~ 2.68 (m, 2 H), 1.99 (s, 3 H), 1.73 ~ 1.60 (m, 2 H), 1.46 ~ 1.28 (m, 4 H), 0.91 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.28, 168.31, 141.02, 135.20, 129.40, 128.54, 128.49, 128.39, 128.11, 127.83, 127.36, 112.44, 72.81, 63.46, 31.46, 29.49, 26.68, 22.23, 13.84 ppm. MS (70 eV): m/z (%): 349 (M^+, 3.54), 91 (100). HRMS calcd for $C_{23}H_{27}NO_2$: 349.2042, found: 349.2041.

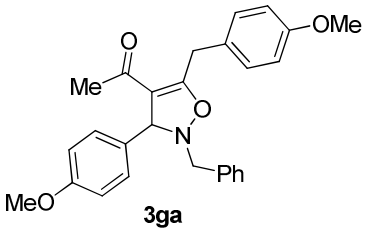
6. 1-(2,5-dibenzyl-3-(4-methoxyphenyl)-2,3-dihydroisoxazol-4-yl)ethanone.



3fa

The reaction of **1f** (0.3 mmol, 82.8 mg), **2a** (0.45 mmol, 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg,) in 2.5 mL of DCE was stirred at 0 ^oC for 5 h to afford straw yellow solid **3fa** (100 mg) in 84% yield. m.p.: 82 ~ 83℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 ~ 7.15 (m, 10 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.4 Hz, 2 H), 5.10 (s, 1 H), 4.26 (d, *J* = 14.4 Hz, 1 H), 4.19 (d, *J* = 12.9 Hz, 1 H), 3.97 (d, *J* = 14.4 Hz, 1 H), 3.95 (d, *J* = 12.9 Hz, 1 H), 3.75 (s, 3 H), 1.97 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.64, 165.65, 159.39, 135.71, 135.15, 132.90, 129.52, 129.03, 128.65, 128.61, 128.35, 127.77, 126.98, 114.02, 112.46, 72.45, 63.31, 55.19, 32.47, 29.73 ppm. MS (70 eV): m/z (%): 399 (M^+, 6.08), 91 (100). HRMS calcd for $C_{26}H_{25}NO_3$: 399.1834, found: 399.1834.

7. 1-(5-(4-methoxybenzyl)-2-benzyl-3-(4-methoxyphenyl)-2,3-dihydroisoxazol-4-yl)ethanone

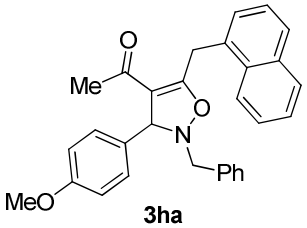


3ga

The reaction of **1g** (0.3 mmol, 91.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 23 h to afford a yellow solid **3ga** (100.8 mg) in 78% yield. m.p.: 72 ~ 73℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 ~ 7.17 (m, 7 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.4 Hz, 2 H), 5.09 (s, 1 H), 4.22 ~ 4.16 (m, 2 H), 3.97 ~ 3.87 (m, 2 H), 3.80 (s, 3 H), 3.76 (s, 3 H), 1.96 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.65, 166.10, 159.36, 158.63, 135.18, 132.93, 130.06, 129.52, 128.64, 128.35, 127.78, 127.76, 114.00 (2C), 112.15, 72.40, 63.30, 55.23, 55.19, 31.61, 29.75. ppm. ppm. MS (70 eV): m/z (%): 429 (M^+, 2.74), 91 (100). Anal, calcd for $C_{27}H_{27}NO_4$: C, 75.50, H, 6.34, N, 3.26; found: C, 75.38, H, 6.55, N, 3.24.

8. 1-(2-benzyl-3-(4-methoxyphenyl)-5-(naphthalen-1-ylmethyl)-2,3-dihydroisoxa

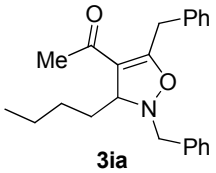
zol-4-yl)ethanone.



3ha

The reaction of **1c** (0.3 mmol, 97.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 24 h to afford a yellow oil **3ha** (104.4 mg) in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 ~ 8.09 (m, 1 H), 7.89 ~ 7.81 (m, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 7.52 ~ 7.47 (m, 3 H), 7.40 (t, *J* = 7.5 Hz, 1 H), 7.20 ~ 7.10 (m, 3 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 6.9 Hz, 2 H), 6.77 (d, *J* = 14.4 Hz, 2 H), 5.11 (s, 1 H), 4.79 (d, *J* = 15.3 Hz, 1 H), 4.47 (d, *J* = 15.3 Hz, 1 H), 4.01 (d, *J* = 12.9 Hz, 1 H), 3.86 (d, *J* = 12.9 Hz, 1 H), 3.72 (s, 3 H), 1.97 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 194.17, 165.73, 159.36, 134.83, 133.76, 132.73, 131.94, 131.81, 129.44, 128.71, 128.54, 128.15, 127.76, 127.59, 127.53, 126.21, 125.70, 125.43, 123.95, 113.98, 112.47, 72.58, 63.27, 55.12, 30.01, 29.87 ppm. MS (70 eV): m/z (%): 449 (M^+, 2.44), 84 (100). HRMS calcd for $C_{30}H_{27}NO_3$: 449.1991, found: 449.1993.

9. 1-(2,5-dibenzyl-3-butyl-2,3-dihydroisoxazol-4-yl)ethanone.

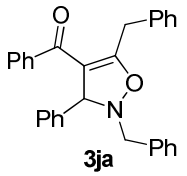


3ia

The reaction of **1c** (0.3 mmol, 67.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 0.5 h to afford a yellow oil **3ia** (93.1 mg) in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 ~ 7.14 (m, 10 H), 4.15 (d, *J* = 14.7 Hz, 1 H), 4.08 (dd, *J* = 8.4 Hz, 3.0 Hz, 1 H), 4.01 (d, *J* = 12.6 Hz, 1 H), 3.79 (d, *J* = 14.7 Hz, 1 H), 3.69 (d, *J* = 12.6 Hz, 1 H), 2.26 (s, 3 H), 1.60 ~ 1.40 (m, 2 H), 1.40 ~ 1.25 (m, 1 H), 1.25 ~ 1.08 (m, 3 H), 0.80 (t, *J* = 6.9 Hz, 3 H). ^{13}C

NMR (75.4 MHz, $CDCl_3$): δ = 192.99, 164.71, 135.38, 135.35, 129.49, 128.66, 128.56, 128.19, 127.58, 126.89, 113.83, 69.12, 63.10, 34.46, 32.46, 29.15, 27.42, 22.17, 13.89 ppm. MS (70 eV): m/z (%): 349 (M^+, 3.54), 91 (100). HRMS calcd for $C_{23}H_{27}NO_2$: 349.2042, found: 349.2042.

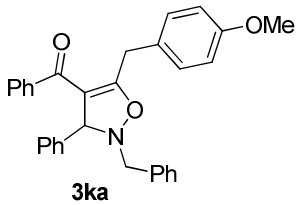
10. (2,5-dibenzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)(phenyl)methanone.



3ja

The reaction of **1c** (0.3 mmol, 92.4 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 4 h to afford a yellow oil **3ja** (120 mg) in 93% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52 ~ 7.36 (m, 3 H), 7.36 ~ 7.14 (m, 15 H), 7.04 (d, *J* = 7.2 Hz, 2 H), 5.47 (s, 1 H), 4.16 (d, *J* = 13.2 Hz, 1 H), 4.03 (d, *J* = 13.2 Hz, 1 H), 3.65 (d, *J* = 15.0 Hz, 1 H), 3.46 (d, *J* = 15.0 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.68, 163.62, 140.94, 139.91, 135.31, 135.18, 131.56, 129.47, 128.73, 128.48, 128.32, 128.31, 128.24, 127.86, 127.64, 127.56, 127.10, 126.89, 114.56, 73.83, 63.32, 32.71 ppm. MS (70 eV): m/z (%): 431 (M^+, 1.25), 105 (100). HRMS calcd for $C_{30}H_{25}NO_2$: 431.1885, found: 431.1886.

11. (5-(4-methoxybenzyl)-2-benzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)(phenyl)me thanone.

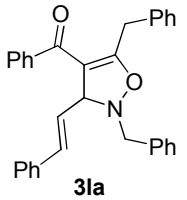


3ka

The reaction of **1k** (0.3 mmol, 101.4 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 1.5 h to afford colorless oil **3ka** (110.2 mg) in 80% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.8 Hz, 2 H), 7.42 (d, *J* = 6.9 Hz, 1 H), 7.33 (t, *J* = 7.5 Hz, 2 H), 7.26 ~ 7.14 (m, 10 H), 6.95 (d,

J = 8.4 Hz, 2 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 5.45 (s, 1 H), 4.17 (d, *J* = 13.2 Hz, 1 H), 4.03 (d, *J* = 13.2 Hz, 1 H), 3.75 (s, 3 H), 3.59 (d, *J* = 15.0 Hz, 1 H), 3.40 (d, *J* = 15.0 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.71, 164.09, 158.51, 140.96, 139.94, 135.20, 131.54, 129.78, 129.47, 128.30, 128.24, 127.87(2C), 127.64, 127.55, 127.54, 127.53, 127.29, 127.09, 114.24, 113.85, 73.79, 63.30, 54.14, 31.86 ppm. MS (70 eV): m/z (%): 461 (M^+, 1.58), 105 (100). HRMS calcd for $C_{31}H_{27}NO_3$: 461.1991, found: 465.1991.

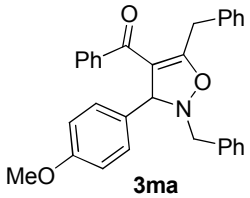
12. (*E*)-(2,5-dibenzyl-3-styryl-2,3-dihydroisoxazol-4-yl)(phenyl)methanone.



3la

The reaction of **1l** (0.3 mmol, 100.2 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^{o}C for 23 h to afford a brown oil **3la** (83.9 mg) in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 7.5 Hz, 2 H), 7.48 (t, *J* = 6.9 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 7.30 ~ 7.12 (m, 13 H), 7.06 ~ 6.98 (m, 2 H), 6.49 (d, *J* = 15.9 Hz, 1 H), 6.24 (dd, *J* = 15.9 Hz, 6.6 Hz, 1 H), 5.10 (d, *J* = 6.6 Hz, 1 H), 4.13 (d, *J* = 13.2 Hz, 1 H), 4.01 (d, *J* = 13.2 Hz, 1 H), 3.66 (d, *J* = 15.0 Hz, 1 H), 3.43 (d, *J* = 15.0 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.80, 164.38, 140.08, 136.61, 135.29, 135.26, 131.60, 131.37, 129.44, 128.77, 128.62, 128.51, 128.43, 128.35, 127.90, 127.72, 127.54, 127.22, 126.92, 126.57, 112.98, 72.06, 62.86, 32.81 ppm. MS (70 eV): m/z (%): 457 (M^+, 0.35), 91 (100). HRMS calcd for $C_{32}H_{27}NO_2$: 457.2042, found: 457.2047.

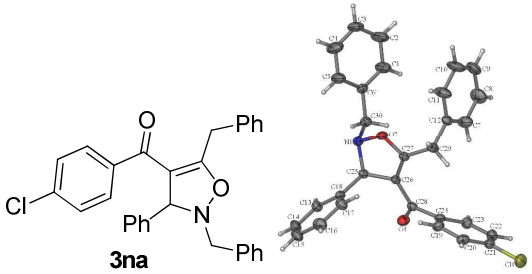
13. (2,5-dibenzyl-3-(4-methoxyphenyl)-2,3-dihydroisoxazol-4-yl)(phenyl)methanone.



3ma

The reaction of **1m** (0.3 mmol, 101.4 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 1 h to afford a yellow oil **3ma** (123.1 mg) in 89% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.5 Hz, 2 H), 7.45 ~ 7.40 (m, 1 H), 7.32 (t, *J* = 7.5 Hz, 2 H), 7.30 ~ 7.13 (m, 10 H), 7.05 (d, *J* = 7.5 Hz, 2 H), 6.76 (d, *J* = 8.1 Hz, 2 H), 5.42 (s, 1 H), 4.15 (d, *J* = 13.2 Hz, 1 H), 4.03 (d, *J* = 13.2 Hz, 1 H), 3.69 (s, 3 H), 3.66 (d, *J* = 15.0 Hz, 1 H), 3.47 (d, *J* = 15.0 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.74, 163.62, 159.00, 139.94, 135.36, 135.25, 133.06, 131.53, 129.46, 128.73, 128.46, 128.30, 128.23, 127.86, 127.61, 127.60, 126.87, 114.58, 113.72, 73.44, 63.18, 55.05, 32.73 ppm. MS (70 eV): m/z (%): 461 (M^+, 1.28), 91 (100). HRMS calcd for $C_{31}H_{27}NO_3$: 461.1991, found: 465.1993.

14. (4-chlorophenyl)(2,5-dibenzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)methanone.

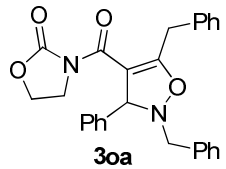


3na

The reaction of **1n** (0.3 mmol, 102.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 1.5 h to afford a white solid **3na** (122.4 mg) in 88% yield. m.p.: 102 ~ 103℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.1 Hz, 2 H), 7.35 ~ 7.15 (m, 15 H), 7.07 (d, *J* = 4.8 Hz, 2 H), 5.45 (s, 1 H), 4.18 (d, *J* = 13.2 Hz, 1 H), 4.07 (d, *J* = 13.2 Hz, 1 H), 3.70 (d, *J* = 15.0 Hz, 1 H), 3.52 (d, *J* = 15.0 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 190.33, 164.04, 140.78, 138.24, 137.86, 135.18, 135.09, 129.53, 129.35, 128.73, 128.66, 128.61, 128.43, 128.34, 127.76, 127.75, 127.17, 127.05, 114.33, 73.91, 63.33, 32.84 ppm. MS (70 eV):

m/z (%): 465 (M^+, 4.15), 91 (100). HRMS calcd for $C_{30}H_{24}NO_2Cl$: 465.1496, found: 465.1490. CCDC: 763753.

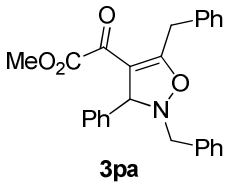
15. 3-(2,5-dibenzyl-3-phenyl-2,3-dihydroisoxazole-4-carbonyl)oxazolidin-2-one.



3oa

The reaction of **1o** (0.3 mmol, 95.1 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 24 h to afford a colorless oil **3la** (77.9 mg) in 59% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.38 ~ 7.15 (m, 13 H), 7.09 ~ 7.03 (m, 2 H), 5.64 (s, 1 H), 4.33 (d, *J* = 12.6 Hz, 1 H), 4.26 ~ 4.16 (m, 1 H), 4.16 (d, *J* = 12.6 Hz, 1 H), 4.04 (d, *J* = 14.7 Hz, 1 H), 3.98 ~ 3.87 (m, 3 H), 3.52 ~ 3.40 (m, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.84, 164.44, 152.84, 140.73, 135.47, 135.35, 129.74, 128.89, 128.53, 128.47, 128.19, 127.87, 127.55, 127.28, 126.87, 107.09, 72.27, 63.06, 62.41, 43.29, 32.57 ppm. MS (70 eV): m/z (%): 440 (M^+, 2.48), 91 (100). HRMS calcd for $C_{27}H_{24}N_2O_4$: 440.1736, found: 440.1734.

16. methyl 2-(2,5-dibenzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)-2-oxoacetate.

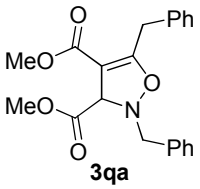


3pa

The reaction of **1p** (0.3 mmol, 87 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 1 h to afford a yellow solid **3pa** (105.0 mg) in 85% yield. m.p.: 85 ~ 87℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 ~ 7.15 (m, 13 H), 7.08 ~ 7.01 (m, 2 H), 5.52 (s, 1 H), 4.25 ~ 4.20 (m, 2 H), 4.05 ~ 3.95 (m, 2 H), 355 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 179.86, 171.78, 163.51, 140.44, 134.68, 134.65, 129.49, 129.10, 128.67, 128.41, 128.34, 127.98, 127.86, 127.53, 127.24, 110.18, 71.93, 63.60, 52.31, 32.74 ppm. MS (70 eV): m/z (%): 413

(M^+, 2.77), 91 (100). HRMS calcd for $C_{26}H_{23}NO_4$: 413.1627, found: 413.1629.

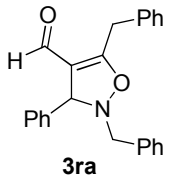
17. dimethyl 2,5-dibenzyl-2,3-dihydroisoxazole-3,4-dicarboxylate.



3qa

The reaction of **1q** (0.3 mmol, 73.2 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 5.5 h to afford a yellow solid **3qa** (95.4 mg) in 87% yield. m.p.: 70 ~ 71℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 ~ 7.16 (m, 8 H), 7.14 (bs, 2 H), 4.68 (s, 1 H), 4.30 (d, *J* = 14.1 Hz, 1 H), 4.07 (d, *J* = 12.9 Hz, 1 H), 3.88 (d, *J* = 12.9 Hz, 1 H), 3.77 (d, *J* = 14.1 Hz, 1 H), 3.74 (s, 3 H), 3.70 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 170.18, 167.36, 164.03, 135.28, 134.33, 129.49, 128.98, 128.57, 128.32, 127.93, 126.99, 99.09, 70.84, 64.12, 52.54, 51.33, 31.80 ppm. MS (70 eV): m/z (%): 367 (M^+, 0.28), 91 (100). HRMS calcd for $C_{21}H_{21}NO_5$: 367.1420, found: 367.1419.

18. 2,5-dibenzyl-3-phenyl-2,3-dihydroisoxazole-4-carbaldehyde.

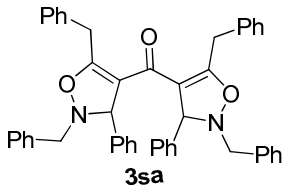


3ra

The reaction of **1r** (0.3 mmol, 69.6 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 1.5 h to afford a yellow oil **3ra** (41.5 mg) in 39% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.78 (s, 1 H), 7.40 ~ 7.10 (m, 15 H), 5.23 (s, 1 H), 4.14 (d, *J* = 12.9 Hz, 1 H), 4.01 (d, *J* = 15.0 Hz, 1 H), 3.95 (d, *J* = 12.9 Hz, 1 H), 3.80 (d, *J* = 15.0 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 183.74, 170.43, 140.31, 134.83, 134.32, 129.44, 128.95, 128.75, 128.37, 128.34, 127.83, 127.69, 127.50, 126.93, 116.54, 70.53, 63.57, 31.61 ppm. MS (70 eV): m/z

(%): 355 (M^+, 6.45), 91 (100). HRMS calcd for $C_{24}H_{21}NO_2$: 355.1572, found: 355.1570.

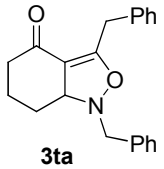
19. bis(2,5-dibenzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)methanone.



3sa

The reaction of **1p** (0.3 mmol, 130.2 mg), **2a** (0.90 mmol 110.7 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 0.5 h to afford yellow solid **3pa** (188.5 mg) in 92% yield. m.p.: 110 ~ 111℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 ~ 7.10 (m, 22 H), 6.85 (d, *J* = 7.2 Hz, 4 H), 6.74 (d, *J* = 7.2 Hz, 4 H), 5.31 (s, 2 H), 4.00 (d, *J* = 14.4 Hz, 2 H), 3.75 (d, *J* = 13.5 Hz, 2 H), 3.68 (d, *J* = 13.5 Hz, 2 H), 3.31 (d, *J* = 14.4 Hz, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 184.72, 162.10, 140.92, 135.35, 135.27, 129.48, 128.95, 128.74, 128.39, 128.11, 127.79, 127.47, 127.14, 126.76, 115.06, 73.26, 63.42, 32.05 ppm. MS (70 eV): m/z (%): 680 (M^+, 0.12), 91 (100). Anal, calcd for $C_{47}H_{40}N_2O_3$: C, 82.91, H, 5.92, N, 4.11; found: C, 82.64, H, 6.22, N, 4.10.

20. 1,3-dibenzyl-5,6,7,7a-tetrahydrobenzo[c]isoxazol-4(1H)-one.

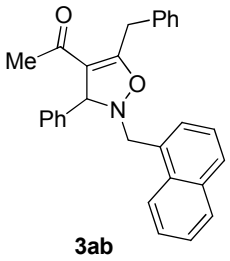


3ta

The reaction of **1t** (0.3 mmol, 58.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 17 h to afford a colorless oil **3ta** (69 mg) in 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 ~ 7.18 (m, 10 H), 4.35 (d, *J* = 12.6 Hz, 1 H), 4.16 ~ 3.98 (m, 3 H), 3.82 (d, *J* = 13.8 Hz, 1 H), 2.44 ~ 2.19 (m, 2 H), 1.98 ~ 1.88 (m, 1 H), 1.65 ~ 1.53 (m, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 194.64, 163.66, 135.59, 135.19, 129.19, 129.01, 128.40, 128.35, 127.73, 126.74, 109.90, 69.55, 63.15, 38.47, 32.18, 29.82, 20.87 ppm. MS (70 eV): m/z (%):

319 (M^+, 1.66), 91 (100). HRMS calcd for $C_{21}H_{21}NO_2$: 319.1572, found: 319.1569.

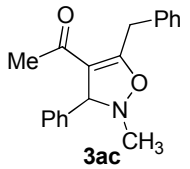
21. 1-(5-benzyl-2-(naphthalen-1-ylmethyl)-3-phenyl-2,3-dihydroisoxazol-4-yl)eth anone.



3ab

The reaction of **1u** (0.3 mmol, 73.8 mg), **2c** (0.45 mmol 77.9 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 12 h to afford a yellow solid **3u** (114.0 mg) in 91% yield. m.p.: 84 ~ 86℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 ~ 8.00 (m, 1 H), 7.85 ~ 7.75 (m, 2 H), 7.44 ~ 7.14 (m, 12 H), 7.04 ~ 6.98 (m, 2 H), 5.25 (s, 1 H), 4.61 (d, *J* = 12.9 Hz, 1 H), 4.38 (d, *J* = 12.9 Hz, 1 H), 4.27 (d, *J* = 14.4 Hz, 1 H), 3.96 (d, *J* = 14.4 Hz, 1 H), 1.99 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.60, 165.85, 140.53, 135.58, 133.60, 131.93, 130.67, 128.96, 128.77, 128.60, 128.46, 128.40, 128.33, 127.88, 127.37, 126.98, 126.17, 125.68, 124.99, 123.98, 112.35, 72.93, 61.24, 32.44, 29.74 ppm. MS (70 eV): m/z (%): 419 (M^+, 5.98), 141 (100). HRMS calcd for $C_{29}H_{25}NO_2$: 419.1885, found: 419.1881.

22. 1-(5-benzyl-2-methyl-3-phenyl-2,3-dihydroisoxazol-4-yl)ethanone.

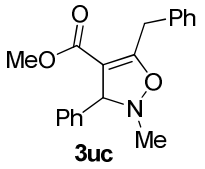


3ac

The reaction of **1a** (0.3 mmol, 73.8 mg), **2b** (*N*-methyl hydroxylamine hydrochloride, 0.45 mmol 37.6 mg), and Et_3N (0.51 mmol, 51.6 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 5 h to afford a yellow oil **3v** (54.4 mg) in 62% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 ~ 7.18 (m, 10 H), 4.94 (s, 1 H), 4.15 (d, *J* = 14.4 Hz, 1 H), 4.05 (d, *J* = 14.4 Hz, 1 H), 2.84 (s, 3 H), 1.98 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =

193.42, 165.09, 140.60, 135.45, 128.73, 128.66, 128.55, 128.17, 127.37, 126.92, 112.76, 76.28, 47.03, 32.36, 29.62 ppm. MS (70 eV): m/z (%): 293 (M^+, 23.30), 216 (100). HRMS calcd for $C_{19}H_{19}NO_2$: 293.1416, found: 293.1417.

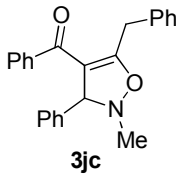
23. Methyl 5-benzyl-2-methyl-3-phenyl-2,3-dihydroisoxazole-4-carboxylate.



3uc

The reaction of **1a** (0.5 mmol, 131 mg), **2b** (*N*-methyl hydroxylamine hydrochloride, 0.75 mmol 62.6 mg), and Et_3N (0.85 mmol, 85.9 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 12 h to afford a white solid **3w** (136 mg) in 88% yield. m.p.: 93 ~ 94℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 ~ 7.27 (m, 10 H), 4.92 (s, 1 H), 4.22 (d, *J* = 14.4 Hz, 1 H), 4.04 (d, *J* = 14.4 Hz, 1 H), 3.68 (s, 3 H), 2.86 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.06, 164.69, 141.22, 135.67, 128.75, 128.48, 128.28, 127.67, 126.97, 126.82, 103.46, 75.23, 50.94, 47.09, 32.04 ppm. MS (70 eV): m/z (%): 309 (M^+, 13.24), 232 (100). HRMS calcd for $C_{19}H_{19}NO_3$: 309.1365, found: 309.1360.

24. (5-benzyl-2-methyl-3-phenyl-2,3-dihydroisoxazol-4-yl)(phenyl)methanone.

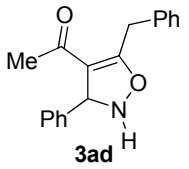


3jc

The reaction of **1j** (0.5 mmol, 154 mg), **2b** (*N*-methyl hydroxylamine hydrochloride, 0.75 mmol 62.6 mg), and Et_3N (0.85 mmol, 85.9 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 9 h to afford a yellow oil **3x** (125.1 mg) in 64% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.8 Hz, 2 H), 7.53 ~ 7.22 (m, 11 H), 7.15 (d, *J* = 7.5 Hz, 2 H), 5.30 (s, 1 H), 3.69 (d, *J* = 15.0 Hz, 1 H), 3.59 (d, *J* = 15.0 Hz, 1 H), 2.93 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.62, 163.14, 140.55, 139.75, 135.11, 131.53,

128.42, 128.39, 128.33, 128.25, 127.79, 127.67, 127.06, 126.78, 114.56, 77.09, 46.78, 32.56 ppm. MS (70 eV): m/z (%): 355 (M^+, 25.67), 105 (100). HRMS calcd for $C_{24}H_{21}NO_2$: 355.1572, found: 355.1566.

25. 1-(5-benzyl-3-phenyl-2,3-dihydroisoxazol-4-yl)ethanone.

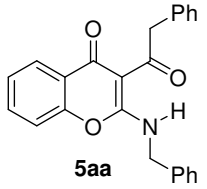


3ad

The reaction of **1a** (0.3 mmol, 73.8 mg), **2d** (hydroxylamine hydrochloride, 0.45 mmol 31.3 mg), and Et_3N (0.51 mmol, 51.6 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 10.5 h to afford a brown oil **3y** (65.6 mg) in 78% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 ~ 7.20 (m, 10 H), 6.79 (bs, 1 H), 5.50 (s, 1 H), 4.16 (d, *J* = 14.4 Hz, 1 H), 4.09 (d, *J* = 14.4 Hz, 1 H), 1.94 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 193.14, 168.40, 140.37, 135.55, 129.03, 128.92, 128.63, 127.47, 127.04, 114.06, 68.36, 32.24, 29.70 ppm. MS (70 eV): m/z (%): 279 (M^+, 50.80), 91 (100). HRMS calcd for $C_{18}H_{17}NO_2$:279.1259, found: 279.1261.

Typical Procedure for the synthesis of 1,3-amino ketone:

26. 2-(benzylamino)-3-(2-phenylacetyl)-4H-chromen-4-one.

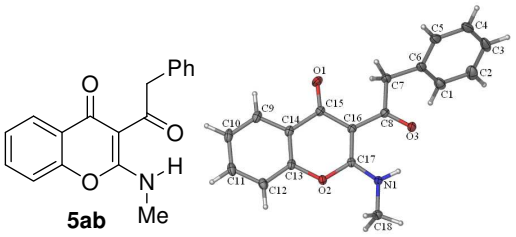


5aa

To a solution of 3-(phenylethynyl)-4H-chromen-4-one (**4a**) (0.3 mmol, 73.8 mg) and *N*-benzyl hydroxyl (**2a**) (0.45 mmol, 55.4 mg) in 2.5 mL of DCE at 0 ^oC was added Et_3N (0.06 mmol, 6.1 mg) in one portion. The reaction mixture was then stirred till the enyne **4a** was completely consumed by TLC analysis. 3 mL of H_2O was added to quench the reaction and the mixture was extracted by ether. The combined organic layer was dried over $MgSO_4$. After filtration and concentration,

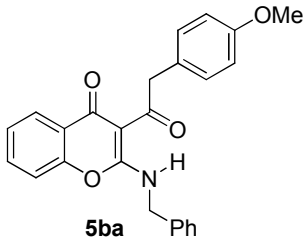
the residue was purified by column chromatography on silica gel (petroleum ether : DCM : acetate = 8 : 8 : 1) to give a white solid **5aa** (97 mg) in 88% yield. m.p.: 160 ~ 161℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.89 (s, 1 H), 8.24 (d, *J* = 7.8 Hz, 1 H), 7.58 (t, *J* = 7.8 Hz, 1 H), 7.40 ~ 7.21 (m, 12 H), 4.71 (d, *J* = 5.7 Hz, 2 H), 4.63 (s, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 199.55, 175.06, 165.49, 151.57, 136.27, 136.03, 133.17, 129.98, 128.97, 128.21, 128.08, 127.63, 126.80, 126.38, 125.44, 123.21, 115.90, 99.14, 49.76, 45.21 ppm. MS (70 eV): m/z (%): 369 (M^+, 28.51), 91 (100). HRMS calcd for $C_{24}H_{19}NO_3$: 369.1365, found: 369.1356.

27. 2-(methylamino)-3-(2-phenylacetyl)-4H-chromen-4-one.



The reaction of **4a** (0.3 mmol, 73.8 mg), **2b** (*N*-methyl hydroxylamine hydrochloride, 0.45 mmol 37.6 mg), and Et_3N (0.51 mmol, 51.5 mg) in 2.5 mL of DCE was stirred at 0 ^{o}C for 4 h to afford a white solid **5ab** (88 mg) in 88% yield. m.p.: 162 ~ 164℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.50 (bs, 1 H), 8.23 (d, *J* = 7.8 Hz, 1 H), 7.63 ~ 7.54 (m, 1 H), 7.39 ~ 7.18 (m, 7 H), 4.62 (s, 2 H), 3.13 (d, *J* = 4.8 Hz, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 199.37, 174.93, 166.12, 151.75, 136.36, 133.11, 129.90, 128.17, 126.71, 126.32, 125.34, 123.07, 115.90, 99.13, 49.61, 27.43 ppm. MS (70 eV): m/z (%): 293 (M^+, 38.65), 202 (100). HRMS calcd for $C_{18}H_{15}NO_3$: 293.1052, found: 293.1054. CCDC: 763754.

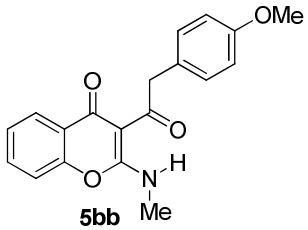
28. 2-(benzylamino)-3-(2-(4-methoxyphenyl)acetyl)-4H-chromen-4-one.



5ba

The reaction of **4b** (0.3 mmol, 82.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 9 h to afford a yellow solid **5ba** (93 mg) in 78% yield. m.p.: 118 ~ 120℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 11.89 (s, 1 H), 8.23 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.57 (td, *J* = 8.4 Hz, 1.8 Hz, 1 H), 7.40 ~ 7. 17 (m, 9 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 4.70 (d, *J* = 5.7 Hz, 2 H), 4.55 (s, 2 H), 3.77 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 199.90, 175.00, 165.44, 158.16, 151.73, 136.00, 133.12, 130.89, 128.93, 128.25, 128.05, 127.62, 126.74, 125.39, 123.19, 115.87, 113.68, 99.04, 55.13, 48.83, 45.18 ppm. MS (70 eV): m/z (%): 399 (M^+, 14.54), 91 (100). HRMS calcd for $C_{25}H_{21}NO_4$: 399.1471, found: 399.1471.

29. 3-(2-(4-methoxyphenyl)acetyl)-2-(methylamino)-4H-chromen-4-one.

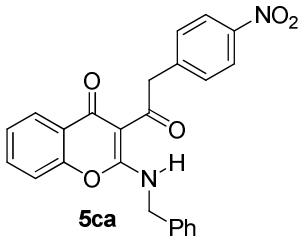


5bb

The reaction of **4b** (0.3 mmol, 82.8 mg), **2b** (*N*-methyl hydroxylamine hydrochloride, 0.45 mmol 37.6 mg), and Et_3N (0.51 mmol, 51.5 mg) in 2.5 mL of DCE was stirred at 0 ^oC for 9 h to afford a white solid **5bb** (83.7 mg) in 86% yield. m.p.: 146 ~ 147℃. ^1H NMR (300 MHz, $CDCl_3$): δ = 11.50 (bs, 1 H), 8.22 (d, *J* = 7.8 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 7.27 ~ 7.20 (m, 3 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 4.54 (s, 2 H), 3.77 (s, 3 H), 3.12 (q, *J* = 2.4 Hz, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 199.67, 174.80, 166.07, 158.09, 151.68, 133.00, 130.77, 128.36, 126.63, 125.23, 123.04, 115.83, 113.59, 98.99, 55.08, 48.56,

27.34 ppm. MS (70 eV): m/z (%): 323 (M^+, 27.36), 202 (100). HRMS calcd for $C_{19}H_{17}NO_4$: 323.1158, found: 323.1159.

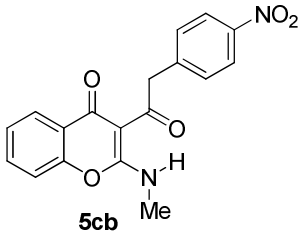
30. 2-(benzylamino)-3-(2-(4-nitrophenyl)acetyl)-4H-chromen-4-one.



5ca

The reaction of **4c** (0.3 mmol, 103.8 mg), **2a** (0.45 mmol 55.4 mg), and Et_3N (0.06 mmol, 6.1 mg) in 2.5 mL of DCE was stirred at 0 °C for 13 h to afford yellow solid **5ca** (108 mg) in 85% yield. m.p.: 188 ~ 190℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.76 (bs, 1 H), 8.22 (d, *J* = 7.8 Hz, 1 H), 8.16 (d, *J* = 8.1 Hz, 2 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.47 ~ 7.27 (m, 9 H), 4.74 (d, *J* = 5.7 Hz, 2 H), 4.71 (s, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 197.56, 175.12, 165.43, 151.76, 146.64, 144.17, 135.75, 133.48, 130.80, 129.03, 128.20, 127.61, 126.72, 125.62, 123.35, 122.88, 116.00, 99.02, 49.41, 45.29 ppm. MS (70 eV): m/z (%): 414 (M^+, 23.13), 91 (100). HRMS calcd for $C_{24}H_{18}N_2O_5$: 424.1216, found: 424.1216.

31. 2-(methylamino)-3-(2-(4-nitrophenyl)acetyl)-4H-chromen-4-one.

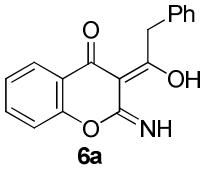


5cb

The reaction of **4c** (0.3 mmol, 103.8 mg), **2b** (*N*-methyl hydroxylamine hydrochloride, 0.45 mmol 37.6 mg), and Et_3N (0.51 mmol, 51.5 mg) in 2.5 mL of DCE was stirred at 0 °C for 9 h to afford a white solid **5cb** (100.5 mg) in 85% yield. m.p.: 205 ~ 206℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.40 (s, 1 H), 8.33 ~ 8.10 (m, 3 H), 7.78 ~ 7.27 (m, 5 H), 4.70 (s, 2 H), 3.19 (d, *J* = 4.5 Hz, 3 H). ^{13}C

NMR (75.4 MHz, $CDCl_3$): δ = 197.45, 175.05, 166.19, 151.81, 146.65, 144.34, 133.43, 130.75, 126.74, 125.57, 123.35, 122.84, 116.02, 99.10, 49.29, 27.57 ppm. MS (70 eV): m/z (%): 338 (M^+, 29.60), 202 (100). HRMS calcd for $C_{18}H_{14}N_2O_5$: 338.0903, found: 338.0904.

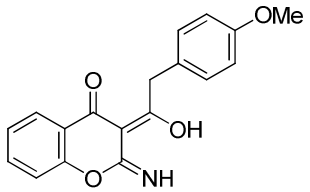
32. 3-(1-hydroxy-2-phenylethylidene)-2-iminochroman-4-one.



6a

The reaction of **4a** (0.3 mmol, 73.8 mg), **2d** (hydroxylamine hydrochloride, 0.45 mmol 31.3 mg), and Et_3N (0.51 mmol, 51.6 mg) in 2.5 mL of DCE was stirred at 0 °C for 16 h to afford a yellow solid **6a** (74 mg) in 88% yield. m.p.: 170 ~ 171℃. ^{1}H NMR (300 MHz, *d*-DMSO): δ = 11.51 (s, 1 H), 8.31 (s, 1 H), 8.06 (d, *J* = 7.8 Hz, 1 H), 7.78 (t, *J* = 7.5 Hz, 1 H), 7.56 (d, *J* = 8.4 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.44 ~ 7.20 (m, 5 H), 4.44 (s, 2 H). ^{13}C NMR (75.4 MHz, d-DMSO): δ = 176.26, 166.49, 155.74, 142.92, 136.60, 135.14, 129.34, 129.15, 127.42, 126.25, 125.62, 122.41, 118.61, 114.94, 38.42 ppm. MS (70 eV): m/z (%): 279 (M^+, 34.75), 262 (100). HRMS calcd for $C_{17}H_{13}NO_3$: 279.0895, found: 279.0895.

33. 3-(1-hydroxy-2-(4-methoxyphenyl)ethylidene)-2-iminochroman-4-one.

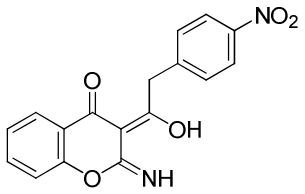


6b

The reaction of **4b** (0.3 mmol, 82.8 mg), **2d** (hydroxylamine hydrochloride, 0.45 mmol 31.3 mg), and Et_3N (0.51 mmol, 51.6 mg) in 2.5 mL of DCE was stirred at 0 °C for 16 h to afford a yellow solid **6b** (74 mg) in 90% yield. m.p.: 144 ~ 145℃. ^{1}H NMR (300 MHz, *d*-DMSO): δ = 11.49 (s, 1 H), 8.29 (s, 1 H), 8.05 (t, *J* = 7.5 Hz, 1 H), 7.90 (t, *J* = 7.5 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1

H), 7.32 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 4.35 (s, 2 H), 3.72 (s, 3 H). ^{13}C NMR (75.4 MHz, d-DMSO): δ = 176.23, 166.93, 158.71, 155.69, 142.88, 142.88, 135.07, 130.38, 128.34, 126.18, 125.57, 122.36, 118.56, 114.51, 55.50, 37.48 ppm. MS (70 eV): m/z (%): 309 (M^+, 47.13), 292 (100). HRMS calcd for $C_{18}H_{15}NO_4$: 309.1001, found: 309.1001.

34. 3-(1-hydroxy-2-(4-nitrophenyl)ethylidene)-2-iminochroman-4-one.



6c

The reaction of **4c** (0.3 mmol, 103.8 mg), **2d** (hydroxylamine hydrochloride, 0.45 mmol 31.3 mg), and Et_3N (0.51 mmol, 51.6 mg) in 2.5 mL of DCE was stirred at 0 ^{o}C for 9 h to afford a yellow solid **6c** (74 mg) in 74% yield. m.p.: 164 ~ 166℃. ^{1}H NMR (300 MHz, d-DMSO): δ = 11.54 (s, 1 H), 8.29 (s, 1 H), 8.19 (d, *J* = 8.7 Hz, 2 H), 8.06 (dd, *J* = 8.1 Hz, 1.5 Hz, 1 H), 7.82 ~ 7.76 (m, 1 H), 7.66 (d, *J* = 8.7 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 4.58 (s, 2 H). ^{13}C NMR (75.4 MHz, d-DMSO): δ = 176.18, 164.85, 155.76, 147.04, 144.57, 142.80, 135.21, 130.61, 126.35, 125.63, 124.18, 122.44, 118.63, 115.48, 38.43 ppm. MS (70 eV): m/z (%): 324 (M^+, 39.53), 307 (100). HRMS calcd for $C_{17}H_{12}N_2O_5$: 324.0746, found: 324.0746.