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Supporting Information

Metal-free C(3)-H arylation of coumarins promoted by catalytic amounts of 5,10,15,20tetrakis(4-diethylaminophenyl)porphyrin

Masahiro Kojima, Kounosuke Oisaki*, and Motomu Kanai*

Graduate School of Pharmaceutical Sciences, The University of Tokyo

Kanai Life Science Catalysis Project, ERATO, Japan Science Technology Agency, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Phone: +81-3-5841-4835 (Oisaki); +81-3-5841-4830 (Kanai), Fax: +81-3-5684-5206 Email: oisaki@mol.f.u-tokyo.ac.jp (Oisaki); kanai@mol.f.u-tokyo.ac.jp (Kanai)

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1. General Method

¹H NMR spectra were recorded on JEOL ECX500 (500 MHz for ¹H NMR and 125.65 MHz for ¹³C NMR), and JEOL ECS400 (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR and 368 MHz for ¹⁹F NMR) spectrometer. For ¹H NMR and ¹³C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. For ¹⁹F NMR, chemical shifts were reported relative to hexafluorobenzene (δ = – 164.90 ppm) as an external reference. Electrospray ionization (ESI)-mass spectra were measured on a JEOL JMS-T100LC AccuTOF spectrometer for HRMS. Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. Microwave irradiation was performed with Biotage Initiator. ICP analysis was conducted with Shimadzu ICPS-7510. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). Gel permeation chromatography (GPC) purification was conducted on a JASICEL-1H and JAIGEL-2H, and CHCl₃ was used as an eluent. All non-

commercially available compounds were prepared and characterized as described in Section 4 of this SI. Other reagents were purchased from Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI), Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd. and were used as received.

2. General Procedure for the Arylation of Coumarins



4-Fluorobenzenediazonium tetrafluoroborate (2d) (52.5)mg, 0.25 mmol), 7-(**1d**) (238)mg, 1.25mmol) 5,10,15,20-tetrakis(4ethoxycoumarin and diethylaminophenyl)porphyrin (4e) (22.5 mg, 0.025 mmol) were added in a dry test tube under argon atmosphere. Degassed DMSO (0.5 ml) was added into the tube, and the reaction mixture was stirred for 16 hours at 40 °C. After cooling the reaction to room temperature, the mixture was absorbed in silica gel and subjected to column chromatography (EtOAc/n-hexane = 2/13), which afforded pure 3m (47.9 mg, 0.169 mmol) in 67% yield as white solid.

3. Preliminary Mechanistic Study

a) Aryl radical trapping experiment

Considering that Meerwein arylation proceeds *via* an aryl radical intermediate, we performed an aryl radical trapping experiment to see whether aryl radicals involve in the present reaction (Scheme S1).

Scheme S1: Detection of an aryl radical intermediate coumarin (1 eq) N_2BF_4 **4e** (10 mol%) DMSO (0.1 M) Ò٠ rt. 20 h 7a - 7d (20 mol%) product yield (based on ArN₂BF₄) R 7a 16% NO_2 7b 14% CO₂Et 12% 7c Н decomposed 7d OMe

To a stirred solution of TEMPO (6.2 mg, 0.040 mmol), coumarin (29.2 mg, 0.20 mmol) and **4e** (18.0 mg, 0.020 mmol) in DMSO (1.0 ml) was added a solution of aryldiazonium tetrafluoroborate (0.20 mmol) in DMSO (1.0 ml). After 20 hours, water (20 ml) was added, and products were extracted with EtOAc (20 ml x 3). The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified as described below. Attempts to isolate **7d** with column chromatography (with SiO₂, neutral silica or alumina) or GPC were unsuccessful possibly because of facile decomposition of **7d**. 3-Arylcoumarins were not observed in all the cases. The efficient TEMPO-trapping as well as the absence of 3-arylcoumarin products support that aryl radicals are the key intermediate for the present C-C bond formation.

2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine (7a)

 O_2N Purified by column chromatography (EtOAc/*n*-hexane = 2/55). NMR spectra of the obtained product were consistent with the reported one.¹

4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzoate (7b)

EtO₂C Purified by column chromatography (Et₃N/EtOAc/*n*-hexane = 1/2.5/100). ¹H NMR (CDCl₃): δ = 7.91 (2H, d, *J* = 9.2 Hz), 7.19 (2H, s), 4.31 (2H, q, *J* = 7.2 Hz), 1.67-1.54 (6H, m), 1.34 (3H, t, *J* = 7.2 Hz), 1.21 (6H, s), 0.97 (6H, s); ¹³C NMR (CDCl₃): δ = 167.38, 166.56, 130.99, 122.31, 113.69, 60.56, 60.42, 39.67, 32.35, 20.42, 16.95, 14.41; HRMS (ESI): *m*/*z* calcd for C₁₈H₂₇NO₃Na [M+Na]⁺ 328.1883 Found 328.1885; IR (KBr): 2977, 2932, 1715, 1602, 1501, 1272, 1252, 1150, 1109, 1095 cm⁻¹

2,2,6,6-tetramethyl-1-phenoxypiperidine (7c)

Purified by column chromatography (Et₃N/*n*-hexane = 1/100). NMR spectra of the obtained product were consistent with the reported one.²

b) Benzyl radical detection experiment

Compound **S1a** was prepared and subjected to the reaction conditions in order to determine the presence of benzyl radical intermediate. Based on a concept of "radical clock,"^{3a,3b} cyclopropane opening should occur if benzyl radical intermediate was generated. As the observed product **S3a** is formed through ring-opening of cyclopropane, benzyl radical intermediate is likely to have involved in the present reaction.^{3c} Product with the cyclopropane moiety remained (**S3b**) was not obtained. These results also indicate that 4-methoxybenzenediazonium tetrafluoroborate reacts via radical pathway.





4-methoxybenzenediazonium tetrafluoroborate (2a) (22.2 mg, 0.10 mmol), 4-

cyclopropyl-2*H*-chromen-2-one (**S1a**) (18.6 mg, 0.10 mmol) and 5,10,15,20-tetrakis(4diethylaminophenyl)porphyrin (**4e**) (9.0 mg, 0.010 mmol) were added in a dry test tube under argon atmosphere. Degassed DMSO (0.2 ml) was added into the tube, and the reaction mixture was stirred for 10 hours at 40 °C. After cooling the reaction to room temperature, the mixture was absorbed in silica gel and subjected to column chromatography (EtOAc/*n*-hexane = 1/5) and then subjected to GPC, which afforded pure **S3a** (2.0 mg, 0.0068 mmol) in 7% yield as white solid.

4-allyl-3-(4-methoxyphenyl)-2H-chromen-2-one (S3a)



¹H NMR (CDCl₃): δ = 7.65 (1H, dd, *J* = 7.4, 1.4 Hz), 7.50 (1H, dt, *J*

= 7.9, 1.4 Hz), 7.36 (1H, dd, J= 8.2, 1.1 Hz), 7.29-7.23 (3H, m), 6.95 (2H, d, J= 9.0 Hz), 5.93 (1H, m), 5.14 (1H, dd, J= 10.7, 1.4 Hz), 4.99 (1H, dd, J= 17.6, 1.2 Hz), 3.83 (3H, s), 3.44 (2H, d, J= 5.7 Hz), ; ¹³C NMR (CDCl₃): δ = 161.43, 159.58, 152.95, 148.46, 134.21, 131.13, 130.81, 127.85, 126.27, 125.87, 124.15, 119.61, 117.85, 116.97, 113.87, 55.29, 33.93; HRMS (ESI): m/z calcd for C₁₉H₁₆O₃Na [M+Na]⁺ 315.0992 Found 315.0994; IR (KBr): 1711, 1595, 1509, 1449, 1248, 1164, 1148, 835 cm⁻¹

c) Solubility measurement of 4d and 4e

In order to rationalize the difference in reactivity between 4d and 4e, their solubility in DMSO was evaluated. To an Eppendorf tube, 4d or 4e (50 mg) and DMSO (1 mL) were added. The tube was subjected to vortex mixing for 5 minutes and centrifuged (100,000 rpm for 5 minutes). Then 0.1 mL of their supernatant was transferred to a glass vial, which was freezed with liquid nitrogen and dried under high vacuum. After the removal of solvent, solid from the supernatant of 4d weighed 0.33 mg whereas that from 4e weighed 4.10 mg. These results suggested that the solubility of 4d is 3.3 g/L (= 4.2 mM) and 4e is 41.0 g/L (= 46 mM). Therefore, their maximum concentration in the standard reaction conditions (0.5 M to aryl diazonium tetrafluoroborate) corresponds to 0.84 mol% for 4d and 9.2 mol% for 4e. These inherent difference in solubility could be one crucial factor for the catalytic reactivity.

4. Syntheses of Catalysts and Substrates

(4-A) Synthesis of 4e

5,10,15,20-tetrakis(4-diethylaminophenyl)porphyrin (4e)



4e can be synthesized as was reported previously.⁴ We also developed a new reproducibility. procedure for shorter reaction time and better 4-Diethylaminobenzaldehyde (2.5 g, 14.1 mmol) and freshly distilled pyrrole (0.875 ml, 12.6 mmol) were heated to 250 °C under microwave irradiation in a sealed tube for 12 hours. Then the reaction mixture was cooled to room temperature and was suspended into acetone (125 ml). The suspension was filtered and washed several times with acetone. The solid was dried under vacuum and pure 5,10,15,20-tetrakis(4diethylaminophenyl)porphyrin was obtained (206.7 mg, 0.230 mmol) in 7% yield as black solid.

5,10,15,20-tetrakis(4-diethylaminophenyl)porphyrin (4e)



Et₂N

 NEt_2 1H NMR (CDCl₃): $\delta = 8.92$ (8H, s), 8.08 (8H, d, J = 8.8 Hz),

7.04 (8H, d, J = 9.1 Hz), 3.61 (16H, q, J = 7.1 Hz), 1.39 (24H, t, J = 7.1 Hz), -2.54 (2H, s); ¹³C NMR (CDCl₃): $\delta = 147.21$, 136.15, 129.71, 128.90, 120.41, 110.01, 44.57, 12.86 (one aromatic carbon is overlapped or unidentified); HRMS (ESI): m/z calcd for C₆₀H₆₇N₈ [M+H]+ 899.5483 Found 899.5484; IR (KBr): 2968, 1606, 1519, 1353, 1265, 1194, 800 cm⁻¹.

(4-B) Synthesis of aryl diazonium tetrafluoroborates

All the aryl diazonium tetrafluoroborates were synthesized according to the reported

procedure.5

6-Nitrocoumarin (1.91 g, 10 mmol) and SnCl₂ (6.17 g, 33 mmol) were suspended in concentrated HCl (100 ml) and heated to 75 °C for 1 hour. Then the reaction mixture was cooled to 0 °C on ice bath and basified with saturated NH₃ aqueous solution (120 ml). The resulting suspension was filtered, washed with H₂O and extracted with acetone. Concentration of the acetone extract afforded 6-aminocoumarin (**S2**) (1.22 g, 7.5 mmol) in 75% yield as yellow solid.

6-aminocoumarin (S2)

 \mathbb{NH}_2 NMR spectra of the obtained product were consistent with the reported one.⁶

A solution of 6-aminocoumarin (600 mg, 3.73 mmol) and Et₃N (0.624 ml, 4.48 mmol) in dichloromethane (7.5 ml) were cooled to 0 °C and PivCl (0.483 ml, 3.92 mmol) was added dropwise. The reaction mixture was warmed to room temperature and was stirred for 3 hours. Then the reaction mixture was washed with water three times. The organic layer was dried with Na₂SO₄, filtered and concentrated to afford N-(2-oxo-2H-chromen-6-yl)pivalamide (**1h**) (815 mg, 3.07 mmol) in 82% yield as white solid.

N-(2-oxo-2H-chromen-6-yl)pivalamide (1h)

O NHPiv ¹H NMR (CDCl₃): $\delta = 8.04$ (1H, d, J = 2.3 Hz), 7.65 (1H, d, J = 9.8

Hz), 7.38 (1H, s), 7.37 (1H, dd, J = 8.9, 2.3 Hz), 7.26 (1H, d, J = 8.9 Hz), 6.41 (1H, d, J = 9.8 Hz), 1.32 (9H, s); ¹³C NMR (CDCl₃): $\delta = 177.03$, 160.77, 150.24, 143.48, 134.62, 123.90, 118.83, 118.76, 116.97, 116.93, 39.59, 27.46; HRMS (ESI): m/z calcd for C₁₈H₁₈O₂Na

[M+Na]⁺ 268.0944 Found 268.0934; IR (KBr): 3262, 2984, 1735, 1650, 1573, 1536, 1435, 1156, 822 cm⁻¹

(4-D) Synthesis of S1a

4-cyclopropyl-2*H*-chromen-2-one (S1a)



To a flame-dried flask was added ZnCl₂ (1M in diethyl ether: 4.0 ml, 4.0 mmol) and cyclopropyl magnesium bromide (0.5 M in THF: 8.0 ml, 4.0 mmol). The resulting suspension was stirred at 50 °C for 40 minutes. The suspension was cooled to room temperature and its supernatant was used for the reaction.

2-oxo-2*H*-chromen-4-yl trifluoromethanesulfonate was prepared as reported previously.⁷ To a stirred suspension of Pd(PPh₃)₄ (46.0 mg, 0.040 mmol) and 2-oxo-2*H*chromen-4-yl trifluoromethanesulfonate (58.8 mg, 0.20 mmol) in dry THF (0.5 ml), the supernatant (1.8 ml, 0.6 mmol of cyclopropyl zinc chloride) was added. The mixture was stirred at 50 °C for 11 hours. After cooling to room temperature, the reaction was quenched with 1N HCl. After extraction with EtOAc, the combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by column chromatography (EtOAc/*n*-hexane = 1/10 to 1/5) afforded 4-cyclopropyl-2*H*chromen-2-one (**S1a**) (15.2 mg, 0.082 mmol) in 41% yield as white solid.

4-cyclopropyl-2H-chromen-2-one (S1a)



¹H NMR (CDCl₃): δ = 7.79 (1H, d, *J* = 8.6 Hz), 6.87 (1H, dd, *J* = 8.6, 2.6 Hz),

6.80 (1H, d, J = 2.6 Hz), 5.87 (1H, s), 3.86 (3H, s), 2.08-2.02 (1H, m), 1.13-1.09 (1H,m), 0.83-0.80 (1H, m); ¹³C NMR (CDCl₃): $\delta = 161.44$, 157.66, 153.37, 131.62, 124.63, 124.12, 120.17, 117.07, 110.33, 11.95, 8.01; HRMS (ESI): m/z calcd for C₁₂H₁₀O₂Na [M+Na]+ 209.0573 Found 209.0557; IR (KBr): 1719, 1609, 1408, 1281, 1208, 1137, 841 cm⁻¹

5. Characterization of Target Compounds 3-(4-methoxyphenyl)-2*H*-chromen-2-one (3a)



MeO

MeC

MeC

Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.⁸

3-(4-methoxyphenyl)-6-methyl-2*H*-chromen-2-one (3b)



Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.⁸

7-methoxy-3-(4-methoxyphenyl)-2H-chromen-2-one (3c)



Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.⁸

7-ethoxy-3-(4-methoxyphenyl)-2H-chromen-2-one (3d)



Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.⁸

7-hydroxy-3-(4-methoxyphenyl)-2H-chromen-2-one (3e)



Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.9

7-(diethylamino)-3-(4-methoxyphenyl)-2H-chromen-2-one (3f)

NEt₂

MeC

Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.⁸

3-(4-methoxyphenyl)-6-nitro-2H-chromen-2-one (3g)



Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.¹⁰

N-(3-(4-methoxyphenyl)-2-oxo-2H-chromen-6-yl)pivalamide (3h)



Purified by GPC. ¹H NMR (CDCl₃): $\delta = 8.05$ (1H, d, J = 2.5

Hz), 7.68 (1H, s), 7.63 (2H, d, J= 9.2 Hz), 7.44 (1H, s), 7.36 (1H, dd, J= 9.0, 2.5 Hz), 7.26 (1H, d, J= 8.9 Hz), 6.95 (2H, d, J= 9.2 Hz), 3.83 (3H, s), 1.32 (9H, s); ¹³C NMR (CDCl₃): δ = 176.85, 160.72, 160.21, 149.69, 138.31, 134.46, 129.83, 128.31, 126.95, 122.97, 119.99, 118.51, 116.59, 113.94, 55.35, 39.65, 27.57; HRMS (ESI): m/z calcd for C₂₁H₂₁NO₄Na [M+Na]⁺ 374.1363 Found 374.1363; IR (KBr): 3282, 2967, 1725, 1649, 1514, 1253, 826 cm⁻¹

7-(diethylamino)-3-(4-methoxyphenyl)-4-methyl-2H-chromen-2-one (3i)



Purified by GPC. ¹H NMR (CDCl₃): $\delta = 7.42$ (1H, d, J = 9.0

Hz), 7.20 (2H, d, J= 9.0 Hz), 6.94 (2H, d, J= 10 Hz), 6.59 (1H, dd, J= 9.0, 2.5 Hz), 6.52 (1H, d, J= 2.5 Hz), 3.40 (4H, q, J= 7.2 Hz), 1.19 (6H, t, J= 7.0 Hz); ¹³C NMR (CDCl₃): δ = 162.25, 158.87, 154.91, 150.03, 148.06, 131.58, 127.44, 125.98, 120.65, 113.65, 109.53, 108.47, 97.39, 55.20, 44.66, 16.26, 12.39; HRMS (ESI): m/z calcd for C₂₁H₂₃NO₃Na [M+Na]⁺ 360.1570 Found 360.1587; IR (KBr): 2966, 1703, 1617, 1578, 1524, 1273, 1248, 1073 cm⁻¹

4-hydroxy-3-(4-methoxyphenyl)-2H-chromen-2-one (3j)



Purified by GPC. NMR spectra of the obtained product were

consistent with the reported one.¹¹

7-ethoxy-3-phenyl-2*H*-chromen-2-one (3k)



Purified by column chromatography (EtOAc/*n*-hexane = 1/6). ¹H NMR (CDCl₃): δ = 7.73 (1H, s), 7.66 (2H, d, *J* = 7.1 Hz), 7.43-7.33 (4H, m), 6.85-6.79 (2H, m), 4.08 (2H, q, *J* = 7.2 Hz), 1.44 (3H, t, *J* = 7.1 Hz); ¹³C NMR (CDCl₃): δ = 161.97, 160.90, 155.28, 140.03, 135.03, 128.78, 128.37, 128.35, 124.61, 113.17, 113.11, 100.83, 64.15, 14.53 (one carbon is overlapped); HRMS (ESI): *m/z* calcd for C₁₇H₁₄O₃Na [M+Na]+ 289.0835 Found 289.0844; IR (KBr): 2977, 1711, 1604, 1274, 823, 783, 692 cm⁻¹

7-ethoxy-3-(p-tolyl)-2H-chromen-2-one (31)



Purified by column chromatography (EtOAc/*n*-hexane = 2/13).

¹H NMR (CDCl₃): δ = 7.70 (1H, s), 7.57 (2H, d, *J* = 8.2 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.22 (2H, d, *J* = 8.0 Hz), 6.82 (1H, dd, *J* = 8.5, 2.3 Hz), 6.81 (1H, d, *J* = 2.5 Hz), 4.08 (2H, q, *J* = 7.1 Hz), 2.37 (3H, s), 1.44 (3H, t, *J* = 7.1 Hz); ¹³C NMR (CDCl₃): δ = 161.81, 161.00, 155.17, 139.40, 138.34, 132.13, 129.08, 128.66, 128.22, 124.62, 113.27, 113.04, 100.82, 64.13, 21.22, 14.54; HRMS (ESI): *m*/*z* calcd for C₁₈H₁₆O₃Na [M+Na]⁺ 303.0992 Found 303.0994; IR (KBr): 1704, 1606, 1268, 1180, 1123, 1038, 822 cm⁻¹

7-ethoxy-3-(4-fluorophenyl)-2*H*-chromen-2-one (3m)



F^{*} Purified by column chromatography (EtOAc/*n*-hexane = 2/13). ¹H
 NMR (CDCl₃): δ = 7.70 (1H, s), 7.64 (2H, dd, J = 9.2, 5.5 Hz), 7.39 (1H, d, J = 8.7 Hz),

7.09 (2H, dd, J= 8.9, 8.9 Hz), 6.83 (1H, dd, J= 8.7, 2.5 Hz), 6.80 (1H, d, J= 2.3 Hz), 4.08 (2H, q, J= 7.2 Hz), 1.44 (3H, t, J= 7.2 Hz); ¹⁹F NMR (CDCl₃): δ = -115.96 (s, 1F); ¹³C NMR (CDCl₃): δ = 162.76 (d, J= 252 Hz), 162.06, 160.87, 155.26, 139.88, 131.03 (d, J= 3.8 Hz), 130.17 (d, J = 8.1 Hz), 128.78, 123.56, 115.34 (d, J = 21.5 Hz), 113.21, 113.04, 100.84, 64.18, 14.52; HRMS (ESI): m/z calcd for C₁₇H₁₃O₃FNa [M+Na]⁺ 307.0741 Found 307.0741; IR (KBr): 1706, 1604, 1513, 1274, 1240, 1177, 822 cm⁻¹

3-(4-chlorophenyl)-7-ethoxy-2H-chromen-2-one (3n)



Purified by column chromatography (EtOAc/*n*-hexane = 1/6). ¹H

NMR (CDCl₃): δ = 7.73 (1H, s), 7.62 (2H, d, *J* = 8.7 Hz), 7.40 (1H, d, *J* = 8.7 Hz), 7.37 (2H, d, *J* = 8.4 Hz), 6.84 (1H, dd, *J* = 8.7, 2.3 Hz), 6.81 (1H, d, *J* = 2.3 Hz), 4.09 (2H, q, *J* = 7.2 Hz), 1.45 (3H, t, *J* = 7.1 Hz); ¹³C NMR (CDCl₃): δ = 162.22, 160.69, 155.37, 140.11, 134.37, 133.45, 129.66, 128.88, 128.59, 123.37, 113.31, 112.99, 100.87, 64.22, 14.54; HRMS (ESI): *m/z* calcd for C₁₇H₁₃O₃Na [M+Na]⁺ 323.0445 Found 323.0438; IR (KBr): 1713, 1611, 1508, 1363, 1270, 818 cm⁻¹

3-(4-bromophenyl)-7-ethoxy-2H-chromen-2-one (30)



Purified by column chromatography (EtOAc/*n*-hexane = 1/6). ¹H

NMR (CDCl₃): δ = 7.73 (1H, s), 7.57-7.52 (4H,m), 7.40 (1H, d, *J* = 8.6 Hz), 6.84 (1H, dd, *J* = 8.6, 2.6 Hz), 6.81 (1H, d, *J* = 2.3 Hz), 4.06 (2H, q, *J* = 7.1, Hz), 1.45 (3H, t, *J* = 7.0 Hz); ¹³C NMR (CDCl₃): δ = 162.25, 160.62, 155.39, 140.11, 133.93, 131.55, 129.94, 128.90, 123.40, 122.60, 113.33, 113.00, 100.88, 64.23, 14.54; HRMS (ESI): *m/z* calcd for C₁₇H₁₃O₃BrNa [M+Na]⁺ 366.9940 Found 366.9947; IR (KBr): 1711, 1611, 1507, 1363, 1270, 1176, 817 cm⁻¹

7-ethoxy-3-(4-iodophenyl)-2H-chromen-2-one (3p)



Purified by column chromatography (EtOAc/*n*-hexane = 1/7). ¹H

NMR (CDCl₃): δ = 7.73 (2H, d, *J* = 8.6 Hz), 7.72 (1H, s), 7.41 (2H, d, *J* = 8.6 Hz), 7.39 (1H, d, *J* = 8.6 Hz), 6.83 (1H, dd, *J* = 8.6, 2.3 Hz), 6.80 (1H, d, *J* = 2.3 Hz), 4.08 (2H, q, *J* = 7.1 Hz), 1.44 (3H, t, *J* = 7.0 Hz); ¹³C NMR (CDCl₃): δ = 162.25, 160.53, 155.38, 140.07, 137.50, 134.51, 130.08, 128.91, 123.44, 113.30, 112.98, 100.87, 94.27, 64.22, 14.53; HRMS (ESI): *m/z* calcd for C₁₇H₁₃O₃INa [M+Na]+ 414.9802 Found 414.9809; IR (KBr): 1713, 1611, 1506, 1362, 1269, 1176, 816 cm⁻¹

ethyl 4-(7-ethoxy-2-oxo-2H-chromen-3-yl)benzoate (3q)



Purified by GPC. ¹H NMR (CDCl₃): $\delta = 8.06$ (2H, d, J = 8.9

Hz), 7.79 (1H, s), 7.75 (2H, d, J = 8.7 Hz), 7.41 (1H, d, J = 8.9 Hz), 6.84 (1H, dd, J = 8.9, 2.5 Hz), 6.80 (1H, d, J = 2.5 Hz), 4.37 (2H, q, J = 7.3 Hz), 4.08 (2H, q, J = 7.2 Hz), 1.44 (3H, t, J = 7.2 Hz), 1.38 (3H, t, J = 7.2 Hz); ¹³C NMR (CDCl₃): $\delta = 166.20$, 162.42, 160.45, 155.51, 140.90, 139.38, 130.09, 129.54, 129.07, 128.21, 123.40, 113.33, 112.90, 100.83, 64.22, 61.00, 14.50, 14.29; HRMS (ESI): m/z calcd for C₂₀H₁₈O₅Na [M+Na]⁺ 361.1046 Found 361.1057; IR (KBr): 1715, 1609, 1366, 1276, 1186, 1109, 783 cm⁻¹

7-ethoxy-3-(4-(trifluoromethyl)phenyl)-2H-chromen-2-one (3r)



Purified by column chromatography (EtOAc/n-hexane = 1/6).

¹H NMR (CDCl₃): δ = 7.79 (1H, s), 7.79 (2H, d, *J* = 8.2 Hz), 7.66 (2H, d, *J* = 8.7 Hz), 7.43 (1H, d, *J* = 8.7 Hz), 6.86 (1H, dd, *J* = 8.7, 2.5 Hz), 6.82 (1H, d, *J* = 2.3 Hz), 4.09 (2H, q, *J* = 7.1 Hz), 1.45 (3H, t, *J* = 7.1 Hz); ¹⁹F NMR (CDCl₃): δ = -65.51 (s, 3F); ¹³C NMR (CDCl₃): δ = 162.55, 160.53, 155.59, 141.07, 138.58 (q, *J* = 1.3 Hz), 130.25 (q, *J* = 33.2 Hz), 129.11, 128.69, 125.33 (q, *J* = 3.8 Hz), 124.04 (q, *J* = 276 Hz), 123.11, 113.45, 112.85, 100.91, 64.29, 14.52; HRMS (ESI): *m/z* calcd for C₁₈H₁₃O₃F₃Na [M+Na]⁺ 367.0709 Found 357.0710; IR (KBr): 1713, 1612, 1331, 1274, 178, 1117, 1071, 849 cm⁻¹

7-ethoxy-3-(4-nitrophenyl)-2H-chromen-2-one (3s)



Purified by GPC. ¹H NMR (CDCl₃): $\delta = 8.26$ (2H, d, J = 9.0 Hz),

7.88 (2H, d, J = 8.7 Hz), 7.87 (1H,s), 7.46 (1H, d, J = 8.7 Hz), 6.88 (1H, dd, J = 8.7, 2.3 Hz), 6.83 (1H, d, J = 2.3 Hz), 4.11 (2H, q, J = 7.1 Hz) 1.46 (3H, t, J = 7.1 Hz); ¹³C NMR (CDCl₃): $\delta = 162.98$, 160.19, 155.81, 147.41, 141.81, 141.52, 129.37, 129.14, 123.60, 122.08, 113.70, 112.67, 100.92, 64.38, 14.52; HRMS (ESI): m/z calcd for C₁₇H₁₃O₃INa [M+Na]⁺ 334.0686 Found 334.0700; IR (KBr): 1712, 1610, 1524, 1347, 1275, 1224, 1037, 852 cm⁻¹

3-(2-bromophenyl)-7-ethoxy-2*H*-chromen-2-one (3t)



Purified by column chromatography (EtOAc/*n*-hexane = 1/5). ¹H

NMR (CDCl₃): δ = 7.65 (1H, d, *J* = 7.8 Hz), 7.63 (1H, s), 7.40-7.34 (3H, m), 7.25-7.21 (1H, m), 6.86-6.83 (2H, m), 4.10 (2H, q, *J* = 7.0 Hz), 1.45 (3H, t, *J* = 7.0 Hz); ¹³C NMR (CDCl₃): δ = 162.33, 160.11, 155.80, 142.68, 136.07, 133.03, 131.47, 129.91, 128.98, 127.40, 125.01, 123.81, 113.19, 112.45, 101.10, 64.22, 14.53; HRMS (ESI): *m*/*z* calcd for C₁₇H₁₃O₃BrNa [M+Na]⁺ 366.9940 Found 366.9922; IR (KBr): 1734, 1615, 1356, 1274, 1180, 1125, 1036, 823 cm⁻¹

3-(3-bromophenyl)-7-ethoxy-2H-chromen-2-one (3u)



Br Purified by column chromatography (EtOAc/*n*-hexane = 1/6). ¹H NMR (CDCl₃): δ = 7.80 (1H, dd, *J* = 1.8, 1.8 Hz), 7.73 (1H, s), 7.62 (1H, dd, *J* = 8.0, 0.9 Hz), 7.47 (1H, dt, *J* = 8.2, 0.9 Hz), 7.40 (1H, d, *J* = 8.9 Hz), 7.27 (1H, t, *J* = 8.0 Hz), 6.84 (1H, dd, *J* = 8.7, 2.5 Hz), 6.80 (1H, d, *J* = 2.3 Hz), 4.08 (2H, q, *J* = 7.2 Hz), 1.44 (3H, t, *J* = 7.2 Hz); ¹³C NMR (CDCl₃): δ = 162.35, 160.49, 155.44, 140.63, 137.02, 131.31, 131.18, 129.85, 128.99, 127.05, 123.00, 122.40, 113.33, 112.88, 100.85, 64.23, 14.52; HRMS (ESI): m/z calcd for C₁₇H₁₃O₃BrNa [M+Na]+ 366.9940. Found 366.9928; IR (KBr): 1714, 1605, 1276, 1177, 822, 787, 686 cm⁻¹

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OE E



































RGAIN	BF	EXREF	SLVNT	CTEMP	IRNUC	PW1	PD	ACQTM	SCANS	FREQU	POINT	OBFIN	OBSET	OBFRQ	EXMOD	OBNUC	DATIM	COMNT	DFILE
60	0.12 Hz	77.00 ppm	CDCL3	25.0 c	1H	3.16 usec	2.0000 sec	1.0643 sec	125	30788.18 Hz	65535	8.74 Hz	4.64 KHz	98.52 MHz	carbon.jxp	13C	16-03-2015 23:08:15		0316mBrOEt13C-1-1.jdf



DFILE DATIM DATIM DATIM DATIM DATIM DATIM DATIM POINT FREQU DBFIN POINT FREQU PD ACQIM PD IRNUC CIEMP SLVNT SLVNT SLVNT SLVNT SLVNT M 2015-05-09 15:47:10 C 1H D proton.jxp S00.16 MHZ 2.41 KHZ N 2.6214 HZ 7507.51 HZ 5.0000 sec 5.55 usec CDCL3 0509cyclocoumarin-1-1.als 1H 7.24 ppm 0.12 Hz 30 21.5 c







RGAIN	BF	EXREF	SLVNT	CTEMP	IRNUC	PW1	PD	ACOTM	SCANS	FREQU	POINT	OBFIN	OBSET	OBFRQ	EXMOD	OBNUC	DATIM	COMNT	DFILE
60	0.10 Hz	77.00 ppm	CDCL3	21.9 c	1H	3.16 usec	2.0000 sec	1.0643 sec	94	30788.18 Hz	65535	8.74 Hz	4.64 KHz	98.52 MHz	carbon.jxp	13C	04-05-2015 21:30:26		0504cyclo13C-1-1.jdf





BF RGAIN	SLVNT	CTEMP	PW1	PD	ACQTM	SCANS	FREQU	POINT	OBFIN	OBSET	OBFRQ	EXMOD	OBNUC	DATIM	COMNT	DFILE
0.12 Hz 46	CDCL3 7.24 ppm	1H 21.8 c	4.99 usec	5.0000 sec	2.2282 sec	8	5882.35 Hz	26214	3.34 Hz	8.51 KHz	391.78 MHz	proton.jxp	1H	07-05-2015 05:38:32		0506radical3-1-1.als





BF RGAIN	SLVNT EXREF	IRNUC	PD PW1	ACQTM	FREQU	POINT	OBSET	OBFRO	EXMOD	OBNUC	DATIM	DFILE	
0.12 Hz 60	CDCL3 77.00 ppm	1H 21.9 c	2.0000 sec 3.16 usec	1.0643 sec	30788.18 Hz 4176	8.74 Hz 65535	4.64 KHz	98.52 MHz	carbon, jxp	13C	07-05-2015 05:40:30	0506radical313C-1-1.jdf	



EtO₂C 7b N, N,

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 DFILE
 0508esterTEMPO-2-1.als

 CCMNT
 2015-05-08
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 DBATIM
 13C
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 CBNUC
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 CBSERD
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 POLNT
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 SLVNT
 CDCL3
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 EXFRET
 77.00
 ppm

 EXFRET
 77.01
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 RGAIN
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EtO₂C

7b