Supporting Information

Efficient synthesis of coumarin-based Tetra and Pentacyclic rings using Phospha-Palladacycles

Anant R. Kapdi,*[a] Amruta Karbelkar,[a] Minal Naik,[b] Suhas Pednekar,[b] Christian Fischer[c], Carola Schulzke[c] and Moniek Tromp[d]

[a] Department of Chemistry, Institute of Chemical Technology, Nathalal Parekh road, Matunga, Mumbai-400019, India. Fax: 00 91 22 3361 1020; Tel: 00 91 22 3361 2609; E-mail: ar.kapdi@ictmumbai.edu.in, anant.kapdi@gmail.com

[b] Department of Chemistry, Ramnarain Ruia College, L. Nappo road, Matunga, Mumbai-400019, India.

[c] Institut fur Biochemie, Ernst-Moritz-Arndt Universität Greifswald, Felix-Hausdorff-Straße 4, D-17487 Greifswald, Germany.

[d]Strukturanalytik in der Katalyse Chemie, Technische Universitat Munchen, Lichtenbergstrasse 4, 85748 Garching, Germany.

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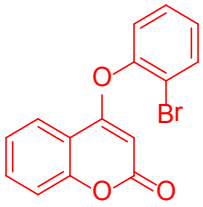
General Remarks

Aryl boronic acids and other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to isolated compounds, estimated to be >95 % pure as determined by ^{1}H-NMR. Flash chromatography: silica gel 60 (70-230 mesh). NMR data (^{1}H, ^{13}C) were recorded on Bruker 300 spectrometers. IR spectra were recorded on a Perkin-Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. UV-VIS analysis was performed on LAMBDA XLS & XLS+ UV/Vis Spectrophotometer. LC-MS analyses were performed on an Agilent VL mass-spectrometer. HRMS was carried out on ESI quadrapole mass analyzer. Elemental analysis was performed using a Carlo-Erba EA 1108. CEM Discover mono-mode Microwave Reactor used as the microwave source. UV-Vis studies performed on BioLogic SFM-400 having high power UV-Vis light source.

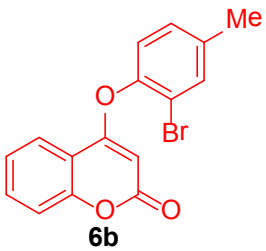
X-ray structural analysis: Diffraction data were collected at low temperature (-103.0 °C) using a STOE-IPDS 2T diffractometer with graphite-monochromated molybdenum K_{α} radiation, λ = 0.71073 Å. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques (SHELXL-97).[1] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^{3} carbon atoms and 1.2 times for all other carbon atoms. Copies of the data can be obtained free of charge by contacting the CCDC via e-mail: deposit@ccdc.cam.ac.uk.

Synthesis of Coumaryl and 2-pyronyl bromoethers:



6a

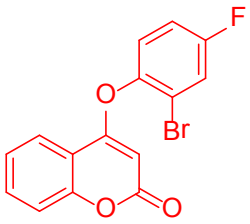
Synthesis of 4-(2-Bromophenoxy)-coumarin (6a): A solution of 4-bromo-coumarin (225 mg, 1 mmol, 1 eq.), 2-bromophenol (173 mg, 1 mmol), andK_2CO_3 (276 mg, 2 mmol) in acetonitrile (3 ml) was stirred at reflux for 16 hours. The reaction was allowed to cool to ambient temperature and quenched by addition of water (2 ml). The solid obtained was filtered to obtain the product as crude product which was purified by column chromatography r.f: 0.75 (E.A 20% : PE 80%) to yield the product as a white solid (92%). **Mpt**: 144-146 °C; **IR** (KBr, cm^{-1}): 3150, 2935, 1725, 1625, 1181, 1088; **^{1}H-NMR** (300 MHz, DMSO-d_6): 8.04-7.98 (m, 1H), 7.86-7.83 (m, 1H), 7.73-7.71 (m, 1H), 7.36-7.53 (m, 4H), 7.27-7.32 (m, 1H), 5.09 (s, 1H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 164.9, 161.4, 153.6, 149.3, 134.6, 134.1, 130.1, 129.4, 125.2, 124.2, 123.5, 117.2, 114.8, 93.4; **MS** (EI) *m/z*: 317 (100, M^+); **HRMS** (EI) calculated for $C_{15}H_9BrO_3$: 315.9735, found: 315.9739. The spectral data were in accordance with those reported in the literature.[2]



6b

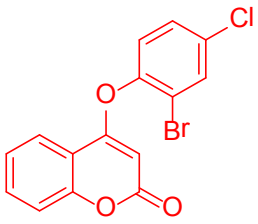
4-(2-Bromo-4-methyl-phenoxy)-coumarin (6b): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-4-methyl-phenol, to afford the crude product which on purification by column chromatography r.f: 0.70 (E.A 20% :PE 80%)

yield the product as a white solid (82%). **Mpt**: 150-152 °C; **IR** (KBr, cm^{-1}): 3165, 2935, 1721, 1482, 1181.08, 1089, 586; **^{1}H-NMR** (300 MHz, DMSO-d_6): 8.05-8.01 (m, 1H), 7.71-7.76 (m, 1H), 7.68-7.69 (m, 1H), 7.35-7.50 (m, 4H), 5.10 (s, 1H), 2.36 (s, 3H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 165.1, 161.3, 153.5, 147.0, 139.3, 134.6, 134.0, 130.9, 125.1, 123.6, 117.1, 114.9, 93.2, 20.5; **MS** (EI) *m/z*: 332 (100, M^+); **HRMS** (EI) calculated for $C_{16}H_{11}BrO_3$: 329.9892, found: 329.9886. The spectral data were in accordance with those reported in the literature.[3]



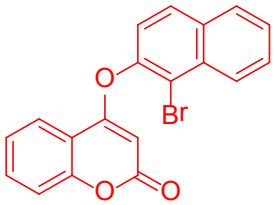
6c

4-(2-Bromo-4-fluoro-phenoxy)-coumarin (6c): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-4-fluoro-phenol, to afford the crude product which on purification by column chromatography r.f: 0.44 (E.A 20% : PE 80%) yield the product as a white solid (81%). **Mpt:** 152-154 °C; **IR** (KBr, cm^{-1}): 3087, 2851, 1731, 1481, 1182, 1093, 1005, 595; **^{1}H-NMR** (300 MHz, DMSO-d_6): 8.43-8.39 (m, 1H), 7.87-7.83 (m, 1H), 7.84-7.80 (m, 1H), 7.66-7.62 (m, 1H), 7.57-7.52 (m, 1H), 7.49 (s, 1H), 7.44-7.39 (m, 1H), 5.25 (s, 1H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 164.9, 161.3, 153.5, 145.9, 134.0, 125.3, 123.4, 121.7, 121.3, 117.5, 117.2, 117.1, 116.2, 116.1, 114.7, 93.5; **MS** (ESI) *m/z*: 336 (100, $M + H^+$); **HRMS** (ESI) calculated for $C_{15}H_7BrFO_3 + H^+$: 334.9714, found: 334.9719; Anal. calc. For $C_{15}H_7BrFO_3$: C, 53.76; H, 2.41. Found: C, 53.73; H, 2.43%.



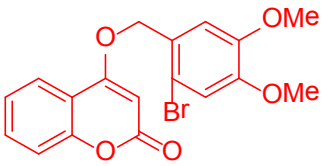
6d

4-(2-Bromo-4-chloro-phenoxy)-coumarin (6d): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-4-chloro-phenol, to afford the crude product which on purification by column chromatography r.f: 0.74 (E.A 20% :PE 80%) yield the product as a white solid (76%). **Mpt:** 172-173 °C; **IR** (KBr, cm^{-1}): 3089, 2924, 1728, 1466, 1229, 1092, 638, 580; **^{1}H-NMR** (300 MHz, $CDCl_3$): 7.96-7.92 (m, 1H), 7.65-7.67 (m, 1H), 7.55-7.58 (m, 1H), 7.27-7.38 (m, 2H), 7.13-7.07 (m, 2H), 5.23 (s, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$): 164.7, 162.0, 153.7, 148.2, 133.9, 133.2, 133.1, 129.5, 124.3, 124.0, 123.1, 116.9, 116.7, 114.7, 93.8; **MS** (ESI) *m/z*: 352 (100, M + H^+); **HRMS** (ESI) calculated for $C_{15}H_8BrClO_3$ + H^+: 350.9418, found: 350.9421. The spectral data were in accordance with those reported in the literature.[3]



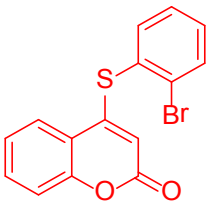
6e

4-(2-Bromo-naphthoxy)-coumarin (6e): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-1-naphthol, to afford the crude product which on purification by column chromatography r.f: 0.77 (E.A 20% : PE 80%) yield the product as a white solid (71%). **Mpt**: 168-170 °C; **IR** (KBr, cm^{-1}): 3100, 2923, 1722, 1183, 1090, 553; **^{1}H-NMR** (300 MHz, DMSO-d_6): 8.04 (s, 1H), 7.68-7.64 (m, 1H), 7.667.61 (m, 1H), 7.41-7.37 (m, 1H), 7.39-7.34 (m, 1H), 7.36-7.32 (m, 3H), 7.24-7.21 (m, 2H), 5.27 (s, 1H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 164.8, 162.4, 153.5, 149.2, 134.2, 132.8, 129.2, 128.2, 124.1, 123.1, 123.0, 116.7, 115.8, 114.8, 114.7, 93.5; **MS** (ESI) *m/z*: 367 (100, M + H^+); **HRMS** (ESI) calculated for $C_{19}H_{11}BrO_3$ + H^+: 366.9964, found: 366.9961; Anal. calc. For $C_{19}H_{11}BrO_3$: C, 62.15; H, 3.02. Found: C, 62.10; H, 3.04 %.



6f

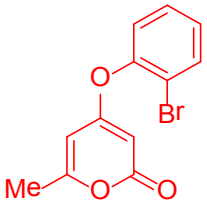
4-(2-Bromo-4,5-dimethoxybenzyloxy)-coumarin (6f): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-4,5-dimethoxy benzyl alcohol, to afford the crude product which on purification by column chromatography r.f: 0.65 (E.A 20% : PE 80%) yield the product as a white solid (68%). **Mpt**: 130-132 °C; **IR** (KBr, cm^{-1}): 3040, 2892, 1765, 1462, 1175, 1089; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.75-7.62 (m, 2H), 7.50-7.46 (m, 1H), 7.42-7.39 (m, 1H), 7.14-7.01 (m, 2H), 5.51 (s, 2H), 5.37 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (75 MHz, DMSO-d_6): 162.0, 158.5, 152.5, 151.1, 147.9, 132.9, 132.4, 131.5, 130.4, 129.6, 125.5, 118.3, 117.0, 116.4, 115.1, 69.4, 58.9, 58.7; **MS** (ESI) *m/z*: 392 (100, $M + H^+$); **HRMS** (ESI) calculated for $C_{18}H_{15}BrO_5 + H^+$: 391.0176, found: 391.0172; Anal. calc. For $C_{18}H_{15}BrO_5$: C, 55.26; H, 3.86. Found: C, 55.23; H, 3.87%.



6g

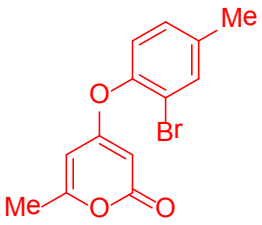
4-(2-Bromo-thiophenoxy)-coumarin (6g): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-thiophenol, to afford the crude product which on purification by column chromatography r.f: 0.70 (E.A 20% :PE 80%) yield the product as a white solid (76%). **Mpt**: 168-170 °C; **IR** (KBr, cm^{-1}): 3000, 2890, 1725, 1462, 1175, 1089; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.95-7.87 (m, 3H), 7.85-7.81 (m, 1H), 7.60-7.55 (m, 3H), 5.30 (s, 1H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 158.3, 155.1, 152.2, 138.6, 134.9, 133.7, 133.6, 130.2, 130.1, 127.5, 125.2, 124.2, 117.4, 117.2, 108.3; **MS** (ESI) *m/z*: 334 (100, $M + H^+$);

HRMS (ESI) calculated for $C_{15}H_9BrO_2S$ + H^+: 332.9579, found: 332.9582; Anal. calc. For $C_{15}H_9BrO_2S$: C, 54.07; H, 2.72; S, 9.62. Found: C, 54.04; H, 2.73; S, 9.65 %.



8a

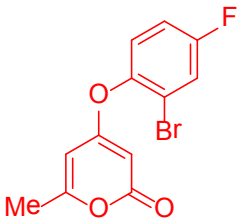
4-(2-Bromophenoxy)-6-methyl-2-pyrone (8a): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-phenol with 4-chloro-6-methyl-2-pyrone, to afford the crude product which on purification by column chromatography r.f: 0.49 (E.A 20% :Hexane 80%) yield the product as a white solid (79%). **Mpt**: 125-127 °C; **IR** (KBr, cm^{-1}): 3100, 2895, 1717, 1605, 1568, 1448, 1219, 1012, 926, 746; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.79-7.74 (m, 1H), 7.45-7.41 (m, 1H), 7.15-7.12 (m, 1H), 6.97-6.91 (m, 1H), 6.14-6.11 (m, 1H), 5.27-5.24 (m, 1H), 2.42 (d, 3H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 170.1, 164.8, 163.7, 158.8, 138.3, 130.1, 128.3, 122.3, 98.9, 89.7, 20.0; **MS** (ESI) *m/z*: 281 (100, M + H^+); **HRMS** (ESI) calculated for $C_{12}H_9BrO_3$ + H^+: 280.9808, found: 280.9802. The spectral data were in accordance with those reported in the literature.[2]



8b

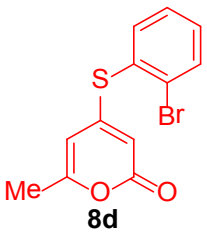
4-(2-Bromo-4-methylphenoxy)-6-methyl-2-pyrone (8b): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-4-methylphenol with 4-chloro-6-methyl-2-pyrone, to afford the crude product which on purification by column chromatography r.f: 0.55 (E.A 20% :Hexane 80%) yield the product as a white solid (84%). **Mpt**:

128-130 °C; **IR** (KBr, cm^{-1}): 3070, 2851, 1745, 1620, 1430, 1200,1047, 991, 951, 780, 773; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.69-7.67 (m, 1H), 7.39-7.35 (m, 1H), 7.16-7.13 (m, 1H), 6.39-6.37 (m, 1H), 4.98-4.96 (m, 1H), 2.56 (s, 3H), 2.41 (d, 3H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 169.7, 164.4, 162.9, 138.5, 132.9, 130.3, 123.0, 115.3, 111.6, 99.0, 89.7, 20.0, 19.4; **MS** (ESI) *m/z*: 294 (100, M + H^+); **HRMS** (ESI) calculated for $C_{13}H_{11}BrO_3$ + H^+: 294.9964, found: 294.9961. The spectral data were in accordance with those reported in the literature.[2]



8c

4-(2-Bromo-4-methylphenoxy)-6-methyl-2-pyrone (8c): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-4-fluorophenol with 4-chloro-6-methyl-2-pyrone, to afford the crude product which on purification by column chromatography r.f: 0.50 (E.A 20% :Hexane 80%) yield the product as a white solid (77%). **Mpt**: 156-158 °C; **IR** (KBr, cm^{-1}): 3075, 2840, 1735, 1600, 1573, 1130, 1031, 982, 797; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.82-7.78 (m, 1H), 7.51-7.37 (m, 2H), 6.36-6.34 (m, 1H), 5.00-4.97 (m, 1H), 2.46 (d, 3H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 170.0, 164.9, 163.4 (q), 161.9 (q), 158.6, 145.9, 125.2, 121.6, 117.4, 116.1, 99.4, 90.4, 19.9; **MS** (ESI) *m/z*: 300 (100, M + H^+); **HRMS** (ESI) calculated for $C_{12}H_8BrFO_3$ + H^+: 298.9714, found: 298.9718. The spectral data were in accordance with those reported in the literature.[2]

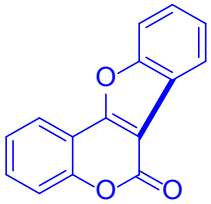


8d

4-(2-Bromo-thiophenoxy)-6-methyl-2-pyrone (8d): The title compound was prepared according to the above given general procedure, on a 1 mmol scale of 2-bromo-thiophenol with 4-chloro-6-methyl-2-pyrone, to afford the crude product which on purification by column chromatography r.f: 0.53 (E.A 20% :Hexane 80%) yield the product as a white solid (58%). **Mpt**: 135-138 °C; **IR** (KBr, cm^{-1}): 3023, 2900, 1723, 1625, 1585, 1340, 1196, 829, 762, 703; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.83-7.79 (m, 1H), 7.49-7.45 (m, 1H), 7.11-7.08 (m, 1H), 6.93-6.87 (m, 1H), 6.21-6.18 (m, 1H), 5.32-5.29 (m, 1H), 2.47 (d, 3H); **^{13}C-NMR** (75 MHz, DMSO-d_6): 169.8, 164.2, 162.9, 156.2, 137.1, 129.7, 128.32, 121.8, 100.2, 92.3, 20.0; **MS** (ESI) *m/z*: 298 (100, M + H^+); **HRMS** (ESI) calculated for $C_{12}H_9BrSO_2$ + H^+: 296.9579, found: 296.9573; Anal. calc. For $C_{12}H_9BrSO_2$: C, 48.50; H, 3.05; S, 10.79. Found: C, 48.54; H, 3.07; S, 10.77 %.

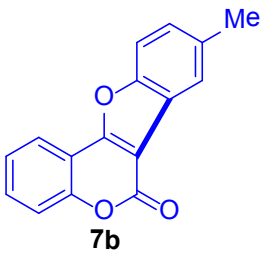
Representative procedure for C-H bond functionalization of 4-(2-Bromophenoxy)-coumarin

In a 30 mL Schlenk tube equipped with a magnetic stirring bar, **4** (2.0 mol %), 4-(2-bromophenoxy)-coumarin (0.158 g, 0.5 mmol) were taken in 1,4-dioxane (2 mL). The solution was degassed (three freeze–pump-thaw cycles) and stirred for 10 min. After this time period, to the solution K_2CO_3 (0.207 g, 1.5 mmol) was added and the mixture degassed. The reaction mixture was then refluxed for 24.0 hrs at 140 ^oC. The reaction was monitored by TLC (hexane:AcOEt, 8:2). The reaction mixture was evaporated in vacuo. The resultant residue was purified by flash chromatography (r.f: 0.63 (E.A 20% : PE 80%) to afford the product as a white solid.



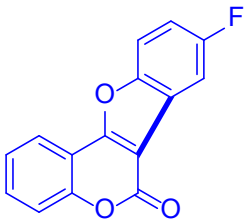
7a

Benzofuro[3,2-c]coumarin (Comestan) (7a): **Mpt:** 171–173 ^oC; **IR** (KBr, cm^{-1}): 3041, 2979, 1727, 1573, 1268, 1179, 1104, 1038, 858; **^{1}H-NMR** (300 MHz, $CDCl_3$): 8.07-8.02 (m, 2H), 7.67-7.70 (m, 1H), 7.60-7.63 (m, 1H), 7.51-7.55 (m, 1H), 7.46–7.49 (m, 2H), 7.42-7.44 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): 160.0, 158.0, 155.5, 153.7, 131.9, 126.7, 125.2, 124.6, 123.4, 121.8, 117.5, 112.6, 111.7, 105.8; **MS** (ESI) m/z (rel.%): 237 [M + H^+] (100), 211 (24); **HRMS** (ESI) calculated for $C_{15}H_8O_3$ + H^+: 237.0546, found: 237.0543. The spectral data were in accordance with those reported in the literature.[3]



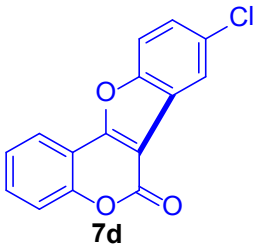
7b

4-Methyl-benzofuro[3,2-c]coumarin (7b): **r.f**: 0.63 (E.A 20% : PE 80%); **Mpt:** 201–202 ^{o}C; **IR** (KBr, cm^{-1}): 3023, 2985, 1725, 1570, 1278, 1164, 1104, 1038, 858; **^{1}H-NMR** (300 MHz, $CDCl_3$): 8.11-8.07 (m, 1H), 7.75-7.83 (m, 3H), 7.63-7.66 (m, 1H), 7.53-7.57 (m, 1H), 7.38–7.41 (m, 1H), 2.31 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): 159.6, 157.1, 153.3, 153.0, 134.9, 132.4, 131.4, 125.0, 122.8, 121.8, 120.5, 117.2, 112.0, 111.7, 104.9, 20.8; **MS** (ESI) m/z (rel.%): 251 [M + H^{+}] (100); **HRMS** (ESI) calculated for $C_{16}H_{10}O_3$ + H^{+}: 251.0708, found: 251.0695. The spectral data were in accordance with those reported in the literature.[3]



7c

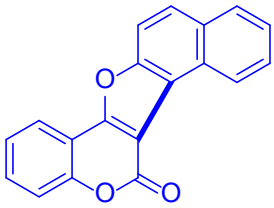
4-Fluoro-benzofuro[3,2-c]coumarin (7c): **r.f**: 0.65 (E.A 20% :PE 80%); **Mpt:** 223–224 ^{o}C; **IR** (KBr, cm^{-1}): 3034, 2935, 1755, 1632,1496, 1163, 1084, 979, 464; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.81-7.79 (m, 1H), 7.76-7.67 (m, 2H), 7.61-7.52 (m, 3H), 7.41-7.38 (m, 1H); **^{13}C NMR** (75 MHz, DMSO-d_6): 161.3, 161.1, 158.1, 156.9, 132.9, 125.1, 124.2, 124.0, 122.0, 117.3, 114.7, 113.9, 113.7, 111.8, 106.7, 106.4; **MS** (ESI) m/z (rel.%): 255 [M + H^{+}] (100); **HRMS** (ESI) calculated for $C_{15}H_7O_3F$ + H^{+}: 255.0452, found: 255.0456; Anal. calc. For $C_{15}H_7FO_3$: C, 70.87; H, 2.78. Found: C, 70.91; H, 2.77%.



7d

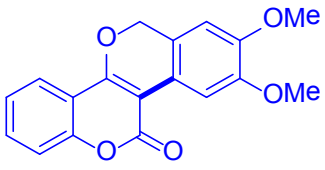
4-Chloro-benzofuro[3,2-c]coumarin (7d): **r.f**: 0.62 (E.A 20% :PE 80%); **Mpt:** 227–228 ^{o}C; **IR** (KBr, cm^{-1}): 3064, 2928, 1755, 1632,1496,1163, 1084, 979, 811, 464; **^{1}H-NMR** (300 MHz,

DMSO-d_6): 8.14-8.10 (m, 1H), 8.06-7.96 (m, 2H), 7.83-7.86 (m, 1H), 7.64-7.71 (m, 2H), 7.56-7.58 (m, 1H); **^{13}C NMR** (75 MHz, DMSO-d_6): 160.8, 156.8, 153.5, 153.3, 133.0, 129.9, 126.9, 125.2, 124.6, 122.1, 120.0, 117.3, 114.0, 111.8, 104.7; **MS** (ESI) m/z (rel.%): 271 [M + H^+] (100); **HRMS** (ESI) calculated for $C_{15}H_7O_3Cl$ + H^+: 271.0156, found: 271.0154. The spectral data were in accordance with those reported in the literature.[3]



7e

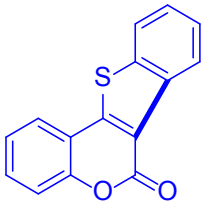
Naphthofuro[3,2-c]coumarin (7e): **r.f**: 0.70 (E.A 20% :PE 80%); **Mpt:** 225–227 ^{o}C; **IR** (KBr, cm^{-1}): 3030, 2935, 1710, 1624, 1552, 1342, 1185, 932, 752; **^{1}H-NMR** (300 MHz, DMSO-d_6): 8.25-8.08 (m, 3H), 7.78-7.75 (m, 2H), 7.64-7.59 (m, 2H), 7.55-7.50 (m, 1H), 7.39-7.36 (m, 1H), 7.31-7.27 (m, 1H); **^{13}C NMR** (75 MHz, DMSO-d_6): 157.9, 154.6, 151.8, 138.2, 134.4, 133.2, 131.1, 129.7, 129.6, 127.0, 124.8, 123.7, 117.0, 116.9, 116.7, 107.8; **MS** (ESI) m/z (rel.%): 287 [M + H^+] (100); **HRMS** (ESI) calculated for $C_{19}H_{10}O_3$ + H^+: 287.0703, found: 287.0707; Anal. calc. For $C_{19}H_{10}O_3$: C, 79.71; H, 3.52. Found: C, 79.75; H, 3.54 %.



7f

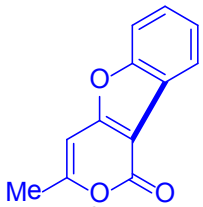
4,5-Dimethoxybenzopyrano[3,2-c]coumarin (7f): **r.f**: 0.69 (E.A 20% :PE 80%); **Mpt:** 214–216 ^{o}C; **IR** (KBr, cm^{-1}): 3147, 2934, 1703, 1616, 1453, 1391, 1262, 1081, 876, 768; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.92-7.89 (m, 1H), 7.70-7.61 (m, 2H), 7.49-7.47 (m, 1H), 7.42-7.36 (m, 1H), 7.12-7.02 (m, 1H), 5.34 (s, 2H), 3.92 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (75 MHz, DMSO-d_6): 160.0, 159.8, 153.2, 149.3, 149.2, 148.7, 133.0, 124.9, 124.7, 123.2, 121.1, 119.1, 116.6, 115.2,

108.6, 69.3, 56.3, 56.0; **MS** (ESI) m/z (rel.%): 311 [M + H^+] (100); **HRMS** (ESI) calculated for $C_{18}H_{14}O_5$ + H^+: 311.0914, found: 311.0915; Anal. calc. For $C_{18}H_{14}O_5$: C, 69.67; H, 4.55. Found: C, 69.69; H, 4.57 %.



7g

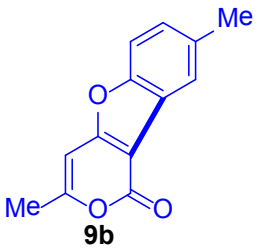
Benzothiopheno[3,2-c]coumarin (7g): **r.f**: 0.55 (E.A 20% :PE 80%); **Mpt:** 217–218 ^oC; **IR** (KBr, cm^{-1}): 3045, 2979, 1730, 1573, 1268, 1179, 1104, 1038, 858; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.91-7.89 (m, 1H), 7.85-7.83 (m, 1H), 7.75-7.72 (m, 1H), 7.64-7.60 (m, 1H), 7.50-7.47 (m, 1H), 7.45-7.42 (m, 1H), 7.40-7.33 (m, 2H); **^{13}C NMR** (75 MHz, DMSO-d_6): 162.0, 157.9, 155.0, 140.9, 137.3, 135.2, 135.1, 133.6, 131.8, 130.5, 126.9, 126.4, 120.8, 120.4; **MS** (ESI) m/z (rel.%): 253 [M + H^+] (100), 211; **HRMS** (ESI) calculated for $C_{15}H_8O_2S$ + H^+: 253.0318, found: 253.0317. The spectral data were in accordance with those reported in the literature.[4]



9a

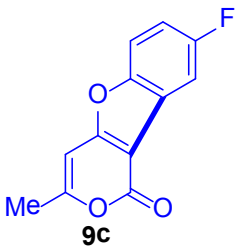
9-Methyl-benzofuro[3,2-*c*]-2-pyrone (9a): r.f: 0.46 (E.A 20% :PE 80%); **Mpt:** 149–150 ^oC; **IR** (KBr, cm^{-1}): 3105, 1720, 1607, 1558, 1448, 1431, 1219, 1171, 1012, 746; **^{1}H-NMR** (300 MHz, DMSO-d_6): 7.92-7.78 (m, 2H), 7.54-7.46 (m, 2H), 7.02-6.97 (m, 1H), 2.50 (d, 3H); **^{13}C NMR** (75 MHz, DMSO-d_6): 164.6, 163.8, 158.5, 154.2, 126.3, 125.1, 122.3, 120.2, 111.9, 102.4, 95.8, 20.0; **MS** (ESI) m/z (rel.%): 201 [M + H^+] (100); **HRMS** (ESI) calculated for $C_{12}H_8O_3$ + H^+:

201.0546, found: 201.0540. The spectral data were in accordance with those reported in the literature.[2]



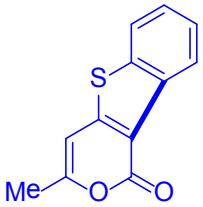
9b

4,9-Dimethyl-benzofuro[3,2-*c*]-2-pyrone (9b): r.f: 0.45 (E.A 20% :PE 80%); **Mpt:** 165–166 ^{o}C; **IR** (KBr, cm^{-1}): 3060, 2821, 1725, 1615, 1450, 1190, 1037, 971, 795, 773; **^{1}H-NMR** (300 MHz, DMSO-d$_6$): 7.82-7.76 (m, 2H), 7.50-7.44 (m, 1H), 7.04-6.91 (m, 1H), 2.60 (s, 3H), 2.43 (d, 3H); **^{13}C NMR** (75 MHz, DMSO-d$_6$): 164.6, 163.5, 158.5, 152.6, 134.5, 127.2, 122.3, 120.0, 111.4, 102.1, 95.8, 20.8, 20.0; **MS** (ESI) m/z (rel.%): 215 [M + H$^+$] (100); **HRMS** (ESI) calculated for $C_{13}H_{10}O_3$ + H$^+$: 215.0703, found: 215.0705. The spectral data were in accordance with those reported in the literature.[2]



9c

4-Fluoro-9-methyl-benzofuro[3,2-*c*]-2-pyrone (9c): r.f: 0.44 (E.A 20% :PE 80%); **Mpt:** 207–208 ^{o}C; **IR** (KBr, cm^{-1}): 3095, 2930, 1728, 1610, 1571, 1449, 1243, 1130, 1031, 797; **^{1}H-NMR** (300 MHz, DMSO-d$_6$): 8.00-7.82 (m, 1H), 7.72-7.66 (m, 1H), 7.42-7.34 (m, 1H), 7.07-6.96 (m, 1H), 2.50 (d, 3H); **^{13}C NMR** (75 MHz, DMSO-d$_6$): 165.0, 163.5, 160.8, 159.5, 151.6, 124.2, 114.3, 113.9, 106.7, 103.5, 96.3, 20.5; **MS** (ESI) m/z (rel.%): 219 [M + H$^+$] (100); **HRMS** (ESI) calculated for $C_{12}H_7FO_3$ + H$^+$: 219.0452, found: 219.0447. The spectral data were in accordance with those reported in the literature.[2]



9d

9-Methyl-benzothiopheno[3,2-*c*]-2-pyrone (9d): r.f: 0.43 (E.A 20% :PE 80%); **Mpt:** 153–155 ^{o}C; **IR** (KBr, cm^{-1}): 3013, 2931, 1733, 1624, 1575, 1443, 1196, 1130, 968, 829, 775; **^{1}H-NMR** (300 MHz, DMSO-d$_6$): 8.45-8.42 (m, 1H), 8.19-8.16 (m, 1H), 7.65-7.58 (m, 1H), 7.11-7.04 (m, 1H), 2.42 (d, 3H); **^{13}C NMR** (75 MHz, DMSO-d$_6$): 159.1, 157.5, 153.7, 137.1, 134.8, 126.1, 125.9, 123.0, 122.9, 114.7, 100.7, 19.5; **MS** (ESI) m/z (rel.%): 219 [M + H^{+}] (100); **HRMS** (ESI) calculated for $C_{12}H_8SO_2$ + H^{+}: 217.0318, found: 217.0315; Anal. calc. For $C_{12}H_8SO_2$: C, 66.65; H, 3.73; S, 14.83. Found: C, 66.67; H, 3.74; S, 14.85 %.

Representative procedure for Microwave-Assisted One-Pot C-H bond functionalization of 4-chlorocoumarin

To a microwaveable vial equipped with a magnetic stirring bar, was added **4** (2.0 mol %), 4-chlorocoumarin (0.5 mmol), 2-bromophenol (0.5 mmol) and 1,4-dioxane (2 mL) under nitrogen atmosphere. The solution was stirred for 10 min. After this time period, to the solution K_2CO_3 (3.0 mmol) was added under nitrogen. The reaction mixture was then microwaved for 2 hrs at 140 ^{o}C. The reaction was monitored by TLC (hexane:AcOEt, 8:2). The reaction mixture was evaporated in vacuo. The resultant residue was purified by flash chromatography (r.f: 0.63 (E.A 20% : PE 80%) to afford **7a** as a white solid.

References

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[2] Burns, M. J.; Thatcher, R. J.; Taylor, R. J. K.; Fairlamb, I. J. S. *Dalton Discussion 12*, *Dalton Trans.* **2010**, **39**, 10391.

[3] P. A. Shah, J. Garcia, M. D. Santana, J. L. Serrano, M. Naik, S. Pednekar and A. R. Kapdi, *Tetrahedron*, 2013, **69**, 1446.

[4] T. Yao, D. Yue and R. Larock, *J. Org. Chem*., 2005, **70**, 9985