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Electrocyclization of *cis*-dienal in organic synthesis: a new and versatile synthetic method for the preparation of aryl- and heteroaryl-fused coumarins

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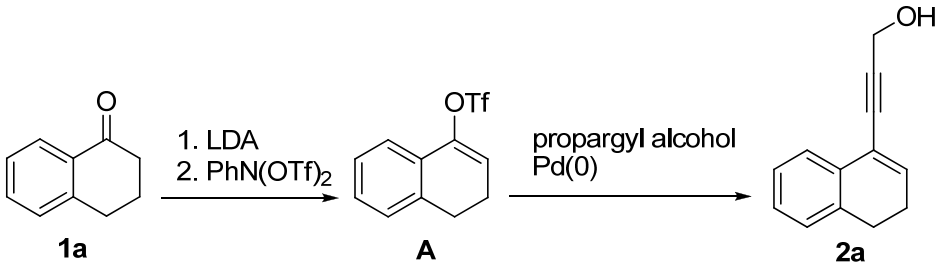
1. Preparation of 3-(3,4-dihydronaphthalen-1-yl)prop-2-yn-1-ol (2a) from α-tetralone (1a) *via* enol triflate A:



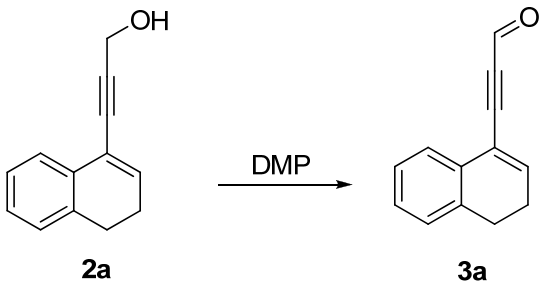
1.1. Typical procedure for the enol triflate A formation: [1]

To a solution of α-tetralone (**1a**)(1.0 g, 6.84 mmol) in THF (5 mL) was added a solution of lithium diisopropylamide (4.6 mL, 8.9 mmol) at –78 °C under nitrogen atomosphere and the reaction mixture was stirred at –78 °C for 1 h. To the resulted solution was added a solution of $PhNTf_2$ (3.0 g, 8.2mmol) in THF (5 mL) and the reaction mixture was warmed slowly to rt and stirred for another 12 h. The reaction was diluted with 1 *N* NH_4Cl (10 mL), extracted with ether. The combined organic phase was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on silica gel column (Hexane/EtOAc = 10:1) to afford enol triflate **A** as a pale yellow oil (1.62 g, 88%).

1.2. Typical procedure for the enynol 2a formation by Sonogashira coupling: [2]

To a degassed solution of $Pd(Ph_3)_4$ (100 mg, 0.09 mmol) and enol triflate **A** (500 mg, 1.8 mmol) in pyrrolidine (10 mL) was added propargyl alcohol (0.2 mL, 3.6 mmol) at rt and the reaction mixture was stirred at rt for 6 h. The reaction was quenched with 1 *N* NH_4Cl, extracted with ether. The combined organic phase was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on silica gel column to afford enynol **2a** as a brown liquid (258 mg, 78%).

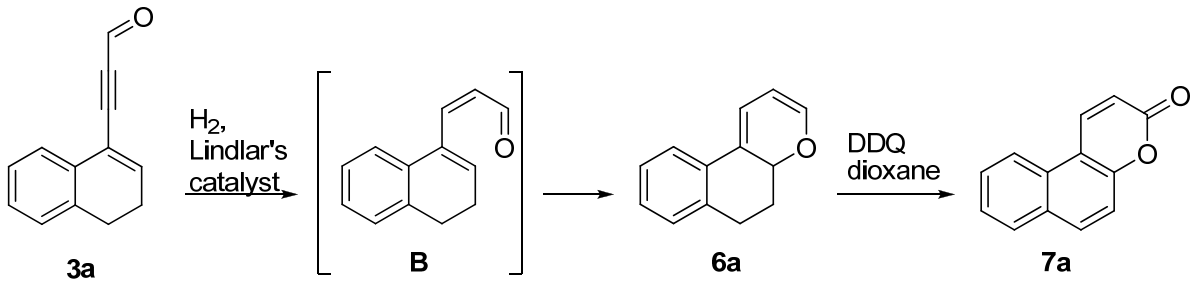
2. General procedure for Dess-Martin periodinane oxidation of enynol 2a to enynal 3a:



3-(3,4-dihydronaphthalen-1-yl)propiolaldehyde(3a): To a solution of enynol **2a**

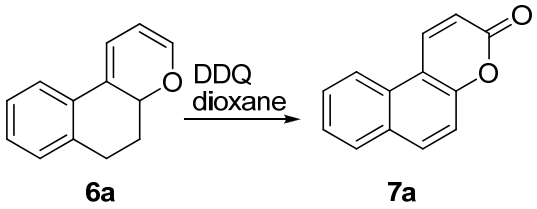
(100 mg, 0.54 mmol) in CH_2Cl_2 (5 mL) was added Dess-Martin periodinane (252 mg, 0.59 mmol) at rt and the resulting solution was stirred for 2 h at rt. The reaction mixture was quenched with a saturated solution of Na_2SO_3 and $NaHCO_3$ (7.5 mL each). The reaction mixture was passed through a pad of celite. The combined organic phase was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on silica gel column to afford enynal 3**a** (67 mg, 68%).

3. General procedure for the formation of benzocoumarin 7a from the oxidation of dihydropyran 6a, which was formed from the electrocyclization of dienal B intermediate:



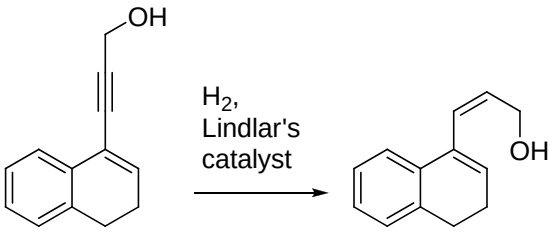
3.1. 5,6-Dihydro-4a*H*-benzo[*f*]chromene (6a):[3] A mixture of enynal **3a** (340 mg, 1.85 mmol), ethyl acetate 10 mL, and Lindlar's catalyst (200 mg) was stirred at rt under a balloon atomosphere of hydrogen for 1 h. The reaction mixture was filtered through a pad of celite using a Büchner funnel and the filtrate was concentrated in *vacuo*. The crude product was chromatographed on silica gel column to give dihydropyran **6a**.

3.2. General procedure for the formation of benzocoumarin 7a from DDQ oxidation of dihydropyran 6a:[4]



5,6-benzocoumarin (7a): To a solution of dihydropyran **6a** (100 mg, 5.43 mmol) in 1,4-dioxane (2.2 mL) was added DDQ (394 mg, 1.74 mmol) and the reaction mixture was stirred under nitrogen atomosphere at rt for 8 h. The reaction mixture was filtered through a pad of aluminum oxide and washed with EtOAc. The filtrate was concentrated in *vacuo* and the crude product was purified by flash chromatography to yield benzocoumarin 7**a** (75 mg, 70%).

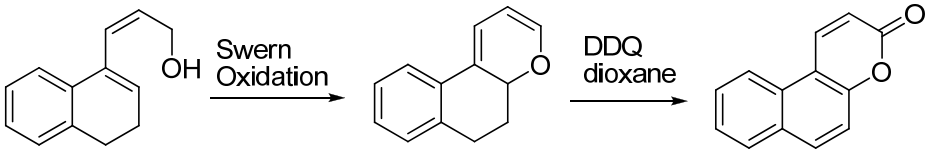
3.3. General procedure for the formation of *cis*-dienol 4a from enynol 2a:



2a **4a**

(*Z*)-3-(3,4-Dihydronaphthalen-1-yl)prop-2-en-1-ol (4a): A mixture of enynol 2**a** (500 mg, 5.43 mmol), ethyl acetate (20 mL), and Lindlar's catalyst (250 mg) was stirred at rt under a balloon atomosphere of hydrogen for 6 h. The reaction mixture was filtered through a pad of celite using a Büchner funnel. The filtrate was concentrated in *vacuo* and the crude product was chromatographed on silica gel column to yield *cis*-dienol 4**a** (404 mg, 80%).

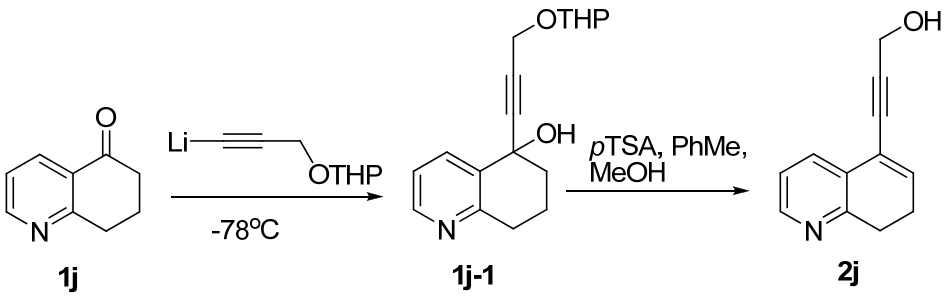
3.4. General procedure for the formation of dihydropyran 6a from the Swern oxidation of *cis*-dienol 4a followed by *in situ* electrocyclization:



4a **6a** **7a**

5,6-Dihydro-4a*H*-benzo[*f*]chromene (6a):[5] To a stirred solution of oxalyl chloride (0.6 mL, 9.4 mmol) in CH_2Cl_2 (10 mL) was added anhydrous DMSO (1.4 mL, 18.9 mmol) at –78 °C. The resulted solution was stirred for 20 min at –78 °C and a solution of alcohol **4a** (880 mg, 4.72 mmol) in CH_2Cl_2 (37 mL) was added. After stirring for 20 min, triethylamine (3.3 mL, 24.0 mmol) was added at –78 °C and the mixture was allowed to warm slowly to rt and stirred for another 6 h. The reaction was quenched with 1 *N* NH_4Cl, extracted with ether. The combined organic phase was dried over anhydrous $MgSO_4$, concentrated, chromatographed on silica gel column to give dihydropyran **6a** (592 mg) in 88% yield.

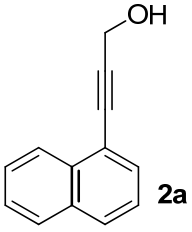
4. General procedure for enynol formation from the addition of lithium alkynide to ketone 1j followed by dehydration:



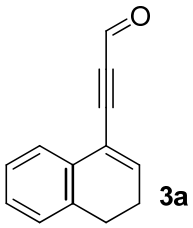
5-(3-(Tetrahydro-2*H*-pyran-2-yloxy)prop-1-ynyl)-5,6,7,8-tetrahydroquinolin-5-ol (1j-1):[6] To a stirred solution THP-protected propargyl alcohol (1.86 g, 13.2 mmol) in THF (15 mL) was added dropwise *n*-BuLi (9.1 mL, 14.6 mmol, 1.60 M solution in hexane) under nitrogen atomosphere at –78 °C and stirred at this temperature for 1 h. To the resulted solution was added a solution of ketone **1j** (1.50 g, 10.2mmol) in THF (15 mL) at –78 °C and stirred at this temperature for 1 h. The reaction mixture was warmed slowly to rt and stirred for another 12 h. The reaction mixture was quenched with 1 *N* HN_4Cl and extracted with ether. The combined extracts was washed with brine, dried over anhydrous $MgSO_4$, concentrated and chromatographed on silica gel column to get propargylic alcohol **1j-1** (2.41 g, 83%). TLC R_f = 0.27 (Hexane/EtOAc=1:2).

3-(7,8-dihydroquinolin-5-yl)prop-2-yn-1-ol (2j):[7] To a stirred solution of propargylic alcohol **1j-1** (5.40 g, 18.8 mmol) in PhMe (85 mL) was added a catalytic amount of *p*-TsOH monohydrate (1.07 g, 5.6 mmol) under nitrogen atomosphere with Dean-Stark apparatus. The reaction was heated to reflux for 10 h. The reaction mixture was cooled to rt and added MeOH (30 mL). The resulted solution was stirred at rt for 1 h. The reaction mixture was concentrated to about 20 mL, diluted with saturated aqueous $NaHCO_3$, extracted with EtOAc. The combined extracts was washed with brine, dried over anhydrous $MgSO_4$, concentrated, and chromatographed on silica gel column to get enynol **2j** (2.30 g, 69%). TLC R_f = 0.29 (Hexane/EtOAc=1:1).

5. Spectral data

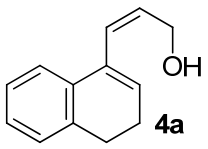


3-(3,4-Dihydronaphthalen-1-yl)prop-2-yn-1-ol (2a): TLC R_f = 0.51 (Hexane/EtOAc=3:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, *J* = 7.2 Hz, 1H, Ph-*H*), 7.20 (t, *J* = 7.2 Hz, 1H, Ph-*H*), 7.14 (t, *J* = 7.2 Hz, 1H, Ph-*H*), 7.07 (d, *J* = 7.2 Hz, 1H, Ph-*H*), 6.43 (t, *J* = 4.8 Hz, 1H, -C=C*H*CH_2CH_2), 4.47 (d, *J* = 4.0 Hz, 2H, -C*H*$_2$OH), 2.75 (t, *J* = 8.0 Hz, 2H, -C=CHCH$_2$C*H*$_2$), 2.33 (dt, *J* = 8.0 and 4.8 Hz, 2H, -C=CH$_2$C*H*$_2$CH$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.8 (d), 134.8 (s), 132.3 (s), 127.6 (d), 127.2 (d), 126.5 (d), 124.8 (d), 121.0 (s), 88.2 (s), 83.3 (s), 51.3 (t), 26.9 (t), 23.5 (t); IR (thin film, KBr plates): 3359, 3054, 2935, 2217, 1265, 1018, 736 cm^{-1}; EI Mass (m/z): 184 (M^+, 100), 153 (84), 152 (97), 141 (66), 128 (95) , 115 (69) , 77 (31); HRMS m/z calcd for $C_{13}H_{12}O$ 184.0888, Found: 184.0886.



3a

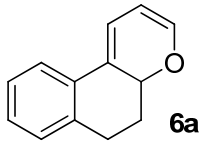
3-(3,4-Dihydronaphthalen-1-yl)propiolaldehyde (3a): TLC R_f = 0.85 (Hexane/EtOAc=4:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.43 (s, 1H, -CHO), 7.54 (d, *J* = 7.5 Hz, 1H, Ph-*H*), 7.31–7.20 (m, 2H, Ph-*H*), 7.14 (d, *J* = 7.5 Hz, 1H, Ph-*H*), 6.84 (t, *J* = 4.9 Hz, 1H, -C=C*H*CH_2CH_2), 2.84 (t, *J* = 8.2 Hz, 2H, -C=CHCH$_2$C*H*$_2$), 2.49 (td, *J* = 8.2 and 4.9 Hz, 2H, -C=CHC*H*$_2$CH$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.6 (s), 143.5 (d), 134.6 (s), 130.8 (s), 128.5 (d), 127.7 (d), 126.9 (d), 124.9 (d), 120.0 (s), 93.5 (s), 89.8 (s), 26.5 (t), 24.2 (t); IR (thin film, KBr plates): 3048, 2923, 2205, 1687, 766 cm^{-1}; ESI Mass (m/z): 205 (M^++23); HRMS m/z calcd for $C_{13}H_{10}ONa$ 205.0629, Found: 205.0630.



4a

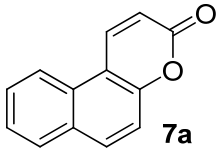
(*Z*)-3-(3,4-Dihydronaphthalen-1-yl)prop-2-en-1-ol (4a): TLC R_f = 0.49

(Hexane/EtOAc=4:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15–7.17 (m, 4H, Ph-*H*), 6.36 (dd, *J* = 11.2 and 1.6 Hz, 1H, -C*H*=CHCH$_2$OH), 5.92 (dt, *J* = 11.2 and 6.4 Hz, 1H, -CH=C*H*CH$_2$OH), 5.87 (t, *J* = 4.4 Hz, 1H, -C*H*CH$_2$CH$_2$), 4.30 (dd, *J* = 6.4 and 1.6 Hz, 2H, -CH=CHC*H*$_2$OH), 2.79 (t, *J* = 8.0 Hz, 2H, -CHCH$_2$C*H*$_2$), 2.37 (m, 2H, -CHC*H*$_2$CH$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0 (s), 134.4 (s), 133.4 (s), 132.0 (d), 129.4 (d), 128.4 (d), 127.5 (d), 127.1 (d), 126.4 (d), 124.0 (d), 59.7 (t), 27.8 (t), 23.0 (q); IR (thin film, KBr plates): 3388, 3019, 2931, 1679, 1051, 757 cm^{-1}; EI Mass (m/z): 186 (M$^+$, 64), 158 (49), 129 (100), 115 (46), 84 (20); HRMS m/z calcd for $C_{13}H_{14}O$ 186.1045, Found: 186.1044.



6a

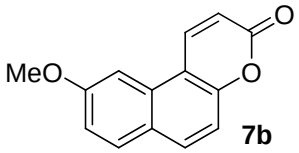
5,6-Dihydro-4a*H*-benzo[*f*]chromene (6a): TLC R_f = 0.90 (Hexane/EtOAc=10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, *J* = 8.4 Hz, 1H, Ph-*H*), 7.06–7.22 (m, 3H, Ph-*H*), 6.61 (d, *J* = 5.6 Hz, 1H, -C=C*H*CH=CH), 6.43 (dd, *J* = 5.6 and 2.4 Hz, 1H, -C=CHCH=C*H*), 5.50 (dd, *J* = 5.6 and 5.6 Hz, 1H, -C=CHC*H*=CH), 4.79 (ddd, 1H, *J* = 10.8 and 5.6 and 2.4 Hz, -OC*H*CH$_2$CH$_2$), 2.79–2.84 (m, 2H, -OCHC*H*$_2$CH$_2$ and -OCHCH$_2$C*H*$_2$), 2.29–2.35 (m, 1H, -OCHCH$_2$C*H*$_2$), 2.00–2.10 (m, 1H, -OCHC*H*$_2$CH$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5 (d), 136.3 (s), 132.2 (s), 128.6 (d), 126.8 (d), 126.5 (d), 124.8 (s), 123.3 (d), 114.6 (d), 105.3 (d), 74.9 (d), 28.4 (t), 27.7 (t); IR (thin film, KBr plates): 2955, 2860, 1744, 1696, 1435, 1236, 1024, 734 cm^{-1}; EI Mass (m/z): 184 (M$^+$, 59), 183 (39), 141 (61), 128 (100), 115 (89), 77 (82); HRMS m/z calcd for $C_{13}H_{12}O$ 184.0888, Found: 184.0886.



7a

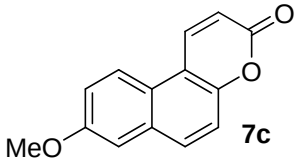
5,6-benzocoumarin (7a): TLC R_f = 0.47 (Hexane/EtOAc = 5:1); mp 115-116 ^{o}C; pale yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (d, *J* = 9.6 Hz, 1H,

-C*H*=CHC(O)), 8.24 (d, *J* = 8.8 Hz, 1H, Ph-*H*), 8.00 (d, *J* = 9.2 Hz, 1H, -C*H*=CHCO), 7.93 (d, *J* = 8.8 Hz, 1H, Ph-*H*), 7.70 (dd, *J* = 7.2 and 7.2 Hz, 1H, Ph-*H*), 7.58 (dd, *J* = 7.6 and 7.6 Hz, 1H, Ph-*H*), 7.48 (d, *J* = 9.2 Hz, 1H, -CH=C*H*CO), 6.59 (d , *J* = 9.6 Hz, 1H, -CH=C*H*C(O)); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7 (s), 153.5 (s), 138.8 (d), 132.8 (d), 130.0 (s), 128.8 (d), 128.7 (s), 128.1 (d), 125.9 (d), 121.1 (d), 116.7 (d), 115.3 (d), 112.7 (s); IR (thin film, KBr plates): 3054, 2929, 1727, 1265, 738 cm^{-1}; EI Mass (m/z): 196 (M^+, 31), 168 (72), 140 (27), 139 (100), 70 (23); HRMS m/z calcd. for $C_{13}H_8O_2$ 196.0524, Found: 196.0525.



7b

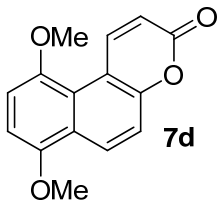
9-methoxybenzo[*f*]coumarin (7b): TLC R_f = 0.22 (Hexane/EtOAc=5:1); mp 143-144 ^{o}C; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (d, *J* = 10.0 Hz, 1H, -C*H*=CHC(O)), 7.90 (d, *J* = 8.8 Hz, 1H, -C*H*=CHCO), 7.81 (d, *J* = 8.8 Hz, 1H, -CH=C*H*CO), 7.50 (d, *J* = 2.4 Hz, 1H, =C*H*-C-OMe), 7.31 (d, *J* = 9.2 Hz, 1H, =C*H*-CH=C-OMe), 7.21 (dd, *J* = 9.2 and 2.4 Hz, 1H, =CH-C*H*=C-OMe), 6.54 (d, *J* = 10.0 Hz, 1H, -CH=C*H*C(O)), 3.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0 (s), 157.1 (s), 152.4 (4^o), 139.1 (d), 131.8 (d), 131.6 (s), 123.8 (s), 122.8 (d), 120.4 (d), 117.4 (d), 115.8 (d), 113.2 (s), 107.5 (d), 55.4 (q); IR (thin film, KBr plates): 3028, 1731, 1285, 1247, 779 cm^{-1}; ESI Mass (m/z): 249 (M^++23); HRMS m/z calcd. for $C_{14}H_{10}O_3Na$ 249.0528, Found: 249.0529.



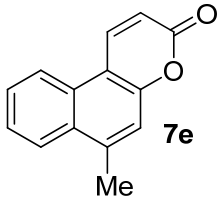
7c

8-methoxybenzo[*f*]coumarin (7c): TLC R_f = 0.23 (Hexane/EtOAc=5:1); mp 154-155 ^{o}C; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, *J* = 9.8 Hz, 1H, -C*H*=CHC(O)), 8.11 (d, *J* = 9.2 Hz, 1H, =C*H*-CH=C-OMe), 7.87 (d, *J* = 9.0 Hz, 1H, -C*H*=CHCO), 7.43 (d, *J* = 9.0 Hz, 1H, -CH=C*H*CO), 7.34 (dd, *J* = 9.2 and 2.4

Hz, 1H, =CH-C*H*=C-OMe), 7.21 (d, *J* = 2.4 Hz, 1H, =C*H*-C-OMe), 6.55 (d, *J* = 9.8 Hz, 1H, -C*H*=CHC(O)), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0 (s), 159.7 (s), 154.6 (4 ^{o}), 139.2 (d), 132.9 (d), 130.7 (s), 130.6 (d), 125.5 (s), 117.6 (d), 114.9 (d), 114.5 (d), 112.2 (s), 101.2 (d), 55.5 (q); IR (thin film, KBr plates): 3015, 1717, 1285, 1247, 799 cm^{-1}; ESI Mass (m/z): 249 (M^++23); HRMS m/z calcd. for $C_{14}H_{10}O_3Na$ 249.0528, Found: 249.0527.

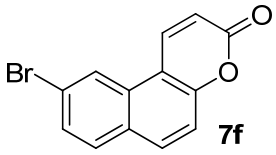


7,9-dimethoxybenzo[*f*]coumarin (7d): TLC R_f = 0.19 (Hexane/EtOAc=5:1); mp 172-173 ^{o}C; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.54 (d, *J* = 10.0 Hz, 1H, -C*H*=CHC(O)), 8.48 (d, *J* = 9.2 Hz, 1H, -C*H*=CHCO), 7.45 (d, *J* = 9.2 Hz, 1H, -CH=C*H*CO), 7.00 (d, *J* = 8.4 Hz, 1H, MeO-C-C*H*=CH-C-OMe), 6.83 (d, *J* = 8.4 Hz, 1H, MeO-C-CH=C*H*-C-OMe), 6.47 (d, *J* = 10.0 Hz, 1H, -CH=C*H*C(O)), 4.02 (s, 3H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8 (s), 155.3 (s), 151.1 (4 ^{o}), 150.1 (4 ^{o}) 144.9 (d), 130.0 (s), 129.7 (s), 127.4 (d), 116.9 (d), 114.1 (d), 113.5 (s), 108.7 (d), 104.1 (d), 55.9 (q), 55.9 (q); IR (thin film, KBr plates): 3029, 1677, 907, 732 cm^{-1}; ESI Mass (m/z): 279 (M^++23); HRMS m/z calcd. for $C_{15}H_{12}O_4Na$ 279.0633, Found: 279.0634.



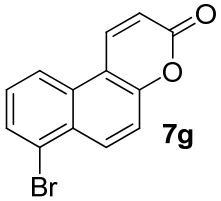
6-methylbenzo[*f*]coumarin (7e): TLC R_f = 0.31 (Hexane/EtOAc=5:1); mp 118-119 ^{o}C; yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (d, *J* = 9.6 Hz, 1H, -C*H*=CHC(O)), 8.25 (d, *J* = 8.4 Hz, 1H, Ph-*H*), 8.08 (d, *J* = 8.4 Hz, 1H, Ph-*H*), 7.72-7.68 (dd, *J* = 7.9 and 7.4Hz, 1H, Ph-*H*), 7.63-7.59 (dd, *J* = 7.9 and 7.4 Hz, 1H, Ph-*H*), 7.34 (s, 1H, -CH=C*H*CO), 6.53 (d, *J* = 9.6 Hz, 1H, -CH=C*H*C(O)), 2.78 (s,

3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0 (s), 153.5 (s), 140.9 (s), 139.0 (d), 129.7 (s), 128.9 (s), 127.8 (d), 125.8 (d), 125.0 (d), 121.7 (d), 117.4 (d), 114.5 (d), 111.5 (s), 19.9 (q); IR (thin film, KBr plates): 2928, 1718, 1560, 910, 733 cm^{-1}; ESI Mass (m/z): 233 (M^++23); HRMS m/z calcd. for $C_{14}H_{10}O_2Na$ 233.0578, Found: 233.0576.



7f

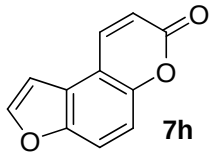
9-bromobenzo[*f*]coumarin (7f): TLC R_f = 0.33 (Hexane/EtOAc=5:1); mp 152-153 ^{o}C; yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.40 (d, *J* = 10.0 Hz, 1H, -C*H*=CHC(O)), 8.38 (s, 1H), 7.95 (d, *J* = 9.2 Hz, 1H, -CH=C*H*CO), 7.78 (d, *J* = 8.4 Hz, 1H, =C*H*-CH=C-Br), 7.65 (d, *J* = 8.4 Hz, 1H, =C*H*-CH=C-Br), 7.48 (d, *J* = 9.2 Hz, 1H, =CH-C*H*=C-Br), 6.60 (d, *J* = 10.0 Hz, 1H, -CH=C*H*C(O)); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5 (s), 154.4 (s), 138.6 (3 ^{o}), 132.8 (d), 130.5 (d), 130.3 (s), 129.5 (d), 128.7 (s), 124.1 (d), 123.0 (s), 117.6 (d), 116.1 (d), 112.2 (s); IR (thin film, KBr plates): 3154, 2902, 1727, 1276, 768, 650 cm^{-1}; ESI Mass (m/z): 297 (M^++23); HRMS m/z calcd. for $C_{13}H_7{}^{79}BrO_2Na$ 296.9527, Found: 296.9525.



7g

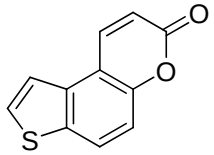
7-bromobenzo[*f*]coumarin (7g): TLC R_f = 0.27 (Hexane/EtOAc=5:1); mp 149-150 ^{o}C; yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (d, *J* = 9.6 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 1H, =C*H*-CH=CH-C-Br), 7.87 (d, *J* = 7.8 Hz, 1H, =CH-CH=C*H*-C-Br), 7.56 (d, *J* = 9.6 Hz, 1H), 7.51 (dd, *J* = 8.4 and 7.8 Hz, 1H, =CH-C*H*=CH-C-Br), 6.60 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3 (s), 154.1 (s), 138.8 (d), 132.1 (d), 130.4 (s), 130.1 (d), 128.8 (s), 128.5 (d), 124.0 (d), 121.1 (s), 118.3 (d), 116.2 (d), 112.9 (s); IR (thin film, KBr plates): 3104, 2873, 1729, 1326, 788, 649 cm^{-1}; ESI Mass (m/z): 297 (M^++23); HRMS m/z calcd

for $C_{13}H_7{}^{79}BrO_2Na$ 296.9527, Found: 296.9524, 298.9503.



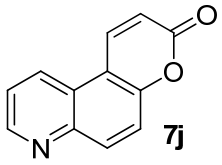
7h

5a*H*-Furo[3,2-*f*]chromen-7(9a*H*)-one (7h): TLC R_f = 0.47 (Hexane/EtOAc=3:1); mp 147-148 ^oC; yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, *J* = 9.6 Hz, 1H, -CH=CHC(O)), 7.81 (d, *J* = 2.0 Hz, 1H, furan-*H*), 7.65 (dd, *J* = 9.2 and 0.4 Hz, 1H, Ph-*H*), 7.27 (d, *J* = 9.2 Hz, 1H, Ph-*H*), 7.02 (dd, *J* = 2.0 and 0.4 Hz, 1H, furan-*H*), 6.51 (d, *J* = 9.6 Hz, 1H, CH=C*H*C(O)); ^{13}C NMR ($CDCl_3$, 100 MHz) 161.0 (s), 150.96 (s), 150.92 (s), 147.4 (d), 140.0 (d), 124.5 (s), 116.1 (d), 114.9 (d), 113.3 (d), 111.4 (s), 104.6 (d); IR (thin film, KBr plates): 3054, 2987, 2931, 1725, 1427, 1265, 896, 738, 707 cm^{-1}; EI Mass (m/z): 186 (M^+, 83), 158 (100), 130 (33), 102 (68), 75 (46) HRMS m/z calcd for $C_{11}H_6O_3$ 186.0317, Found: 186.0317.



7i

7*H*-Thieno[3,2-*f*]chromen-7-one (7i): TLC R_f = 0.47 (Hexane/EtOAc=3:1); mp 141-142 ^oC; yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, *J* = 9.6 Hz, 1H, -C*H*=CHC(O)), 7.99 (d, *J* = 8.8 Hz, 1H, Ph-*H*), 7.72 (d, *J* = 5.6 Hz, 1H, thiophene-*H*), 7.64 (d, *J* = 5.6 Hz, 1H, thiophene-*H*), 7.36 (d, *J* = 8.8 Hz, 1H, Ph-*H*), 6.54 (d, *J* = 9.6 Hz, 1H, CH=C*H*CO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7 (s), 152.7 (s), 140.3 (d), 136.2 (s), 135.7 (s), 130.3 (d), 125.8 (d), 120.2 (d), 116.1 (d), 114.2 (d), 113.3 (s); IR (thin film, KBr plates): 3054, 2964, 1725, 1265, 738 cm^{-1} ; EI Mass (m/z): 202 (M^+, 84), 174 (100), 145 (35), 102 (30), 69 (38); ; HRMS m/z calcd for $C_{11}H_6O_2S$ 202.0088, Found: 202.0089.



7j

Pyrido[3,2-*f*]coumarin (7j): TLC R_f = 0.33 (Hexane/EtOAc=1:2); mp 124-125 ^{o}C; brown solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.00 (dd, *J* = 4.4 and 1.6 Hz, 1H, pyridine-*H*), 8.56 (d, *J* = 8.4 Hz, 1H, pyridine-*H*), 8.43 (d, *J* = 9.6 Hz, 1H, -C*H*=CHC(O)), 8.28 (d, *J* = 9.2 Hz, 1H, -C*H*=CHCO), 7.72 (d, *J* = 9.2 Hz, 1H, -CH=C*H*CO), 7.61 (dd, *J* = 8.4 and 4.4 Hz, 1H, pyridine-*H*), 6.64 (d , *J* = 9.6 Hz, 1H, -CH=C*H*C(O)); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3 (s), 153.2 (s), 150.0 (d), 145.4 (d), 138.0 (d), 134.4 (d), 129.6 (d), 124.1 (s), 122.6 (d), 120.6 (d), 116.4 (s), 112.6 (s); IR (thin film, KBr plates): 2925, 2854, 1737, 1504, 1465, 912, 742 cm^{-1}; ESI Mass (m/z): 220 (M^++23); HRMS m/z calcd for $C_{12}H_7NO_2Na$ 220.0374, Found: 220.0373.

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