



Supporting Information

for

Transition-metal-free intramolecular Friedel–Crafts reaction by alkene activation: A method for the synthesis of some novel xanthene derivatives

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Experimental and analytical data

Experimental

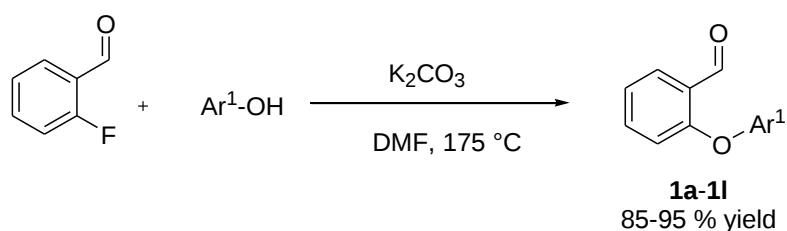
1. General information

The majority of the chemicals used in this work were commercially available from Merck or Aldrich. The starting compounds **1a–l** were prepared by Ullmann coupling of 2-fluorobenzaldehyde and substituted phenols. The further starting compounds **2a–l** were synthesized by Grignard reaction of **1a–l** and aryl(or alkyl)magnesium bromide. Then **3a–l** were prepared from oxidation of **2a–l** using PCC. The final starting alkene compounds **4a–l** were obtained with Wittig reaction using $\text{Me(Ph)}_3\text{PBr}$, $t\text{-BuOK}$, NaH . All substrates were purified by crystallization or column chromatography and were characterized by IR and GC-MS. All novel products were characterized by IR, ^1H NMR, ^{13}C NMR, elemental analysis and GC-MS. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh), eluting with hexane-ethyl acetate (v/v 9:1). NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C using Me_4Si as the internal standard in CDCl_3 . GC-MS were recorded on Shimadzu/QP2010 Plus. IR spectra were recorded on a Mattson 1000 spectrometer. Melting points were determined with Büchi Melting Point B-540.

2. General procedure for reduction of the Ullmann coupling:¹

To a solution of DMF (10 mL) containing 2-fluorobenzaldehyde (4 mmol) and phenol (4 mmol) was added K_2CO_3 (6 mmol) and the reaction mixture was stirred for 2 hours at 175 °C. It was cooled to room temperature and after usual workup and concentration, the product was purified over silica gel.

Thus, 2-arenoxybenzaldehydes were prepared in good yields with 85–95% (Scheme S1).

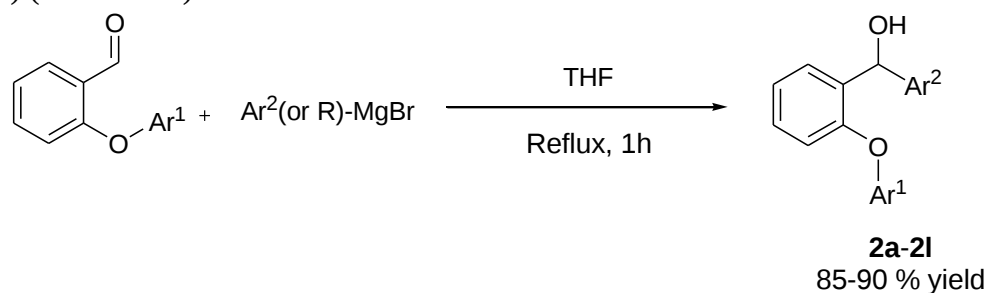


Scheme S1. The Ullmann type reaction of 2-fluorobenzaldehyde and hydroxy aryls.

3. General procedure for the Grignard reaction:

For the Grignard solution, to Mg (2 mmol) was added the respective bromo substrate (1.2 mmol) in dry THF and the mixture was heated under reflux and N_2 for 0.5–1 h then cooled to room temperature. 2-Arenoxybenzaldehydes (1 mmol) was dissolved in dry THF and cooled to 0 °C. Then the Grignard solution was added to the aldehyde solution and stirred for 1 hour. The end of the reaction was quenched with saturated NH_4Cl solution, extracted with DCM and water 2 times. After usual workup and concentration, the crude product was purified over silica gel.

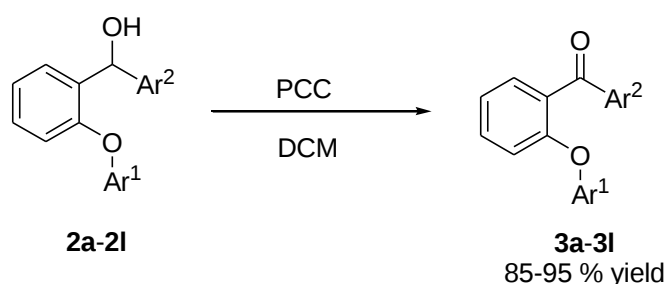
Diarylcarbinol compounds including an arenoxy group were obtained with very high yields (85–90%) (Scheme S2).



Scheme S2. The Grignard reaction of 2-arenoxybenzaldehyde.

4. General procedure for the alcohol oxidation:

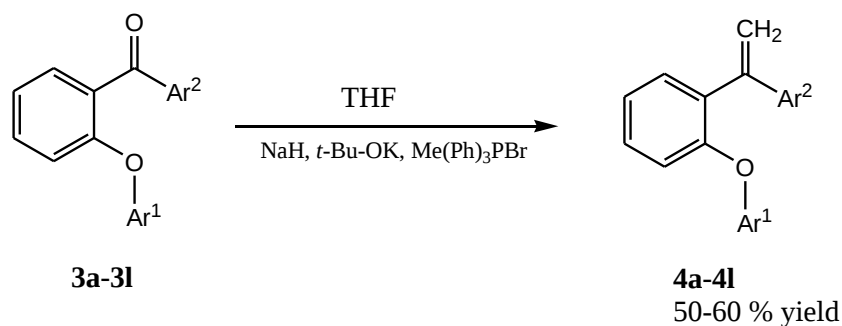
To the alcohol compound (1 mmol) were added PCC (1.5 mmol) and DCM (5 mL) as solvent then stirred for 2 hours. The end of the reaction was extracted with DCM and water 2 times. After usual reaction workup and concentration, the product was charged on silica gel (Scheme S3).



Scheme S3. The oxidation of diarylcarbinol compounds.

5. General procedure for the Wittig reaction:

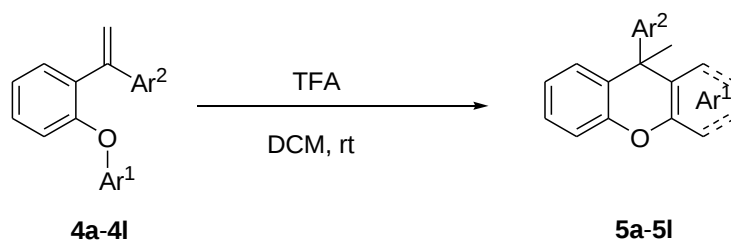
To the ketone compound (1 mmol) in dry THF were added $\text{Me(Ph)}_3\text{PBr}$ (2.2 mmol), *t*-BuOK (2.7 mmol) and NaH (2.5 mmol) and the reaction was stirred for 1-2 hours. At the end of the reaction it was extracted with DCM and water 2 times. After usual reaction workup and concentration, the product was charged on silica gel (Scheme S4).



Scheme S4. Wittig reaction of ketones **3a-3l**.

6. General procedure for intramolecular FCA of vinyl compounds

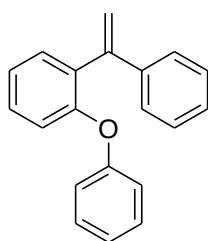
TFA (10 mol %) was added to a stirred solution of a starting alkene compound (**4a–4l**) (0.1 mmol) in DCM (1 mL), and the reaction was stirred for 6–24 h under room temperature. After the finishing of the reaction, as monitored with TLC the reaction mixture was washed with water two times. After the usual reaction workup and concentration, the product was charged on silica gel.



Scheme S5. The intramolecular FCA of vinyl compounds **4a–4l**.

7. Experimental and characterization data of 4a–l and 5a–l

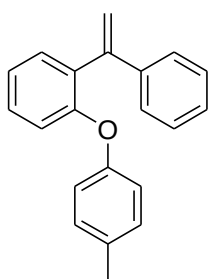
1-Phenoxy-2-(1-phenyl-vinyl)benzene (**4a**):



Colorless oily (85% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.37 (d, $J = 1.5$ Hz, 1H), 5.63 (d, $J = 1.5$ Hz, 1H), 6.72 (d, $J = 8.5$ Hz, 1H), 6.96 – 7.01 (m, 2H), 7.17 – 7.40 (m, 10H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 116.3, 117.9, 117.8, 119.9, 122.4, 123.7, 126.7, 127.3, 127.9, 129.0, 129.1, 129.2, 131.7, 134.0, 141.0, 146.3, 154.0, 157.4. **MS** (m/z) = 152, 165, 181, 194, 272

(M^+). Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{O}$: C, 88.20; H, 5.92. Found: C, 88.33; H, 5.93.

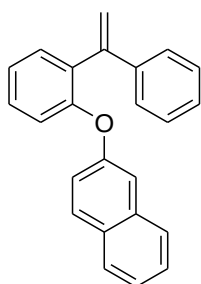
1-[4-Methylphenoxy]-2-(1-phenyl-vinyl)benzene (**4b**):



Colorless oily (53% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 2.30 (s, 3H), 5.40 (d, $J = 1.5$ Hz, 1H), 5.67 (d, $J = 1.5$ Hz, 1H), 6.66 (d, $J = 8.5$ Hz, 2H), 6.92 (d, $J = 9.0$ Hz, 1H), 6.95 – 7.18 (m, 4H), 7.24 – 7.39 (m, 6H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 20.6, 116.1, 118.2, 118.3, 119.1, 119.1, 123.2, 126.7, 127.3, 128.0, 128.9, 129.8, 130.2, 131.6, 132.1, 133.6, 141.1, 146.4, 154.6, 155.0. **MS** (m/z) = 77, 105, 211, 288 (M^+). Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{O}$:

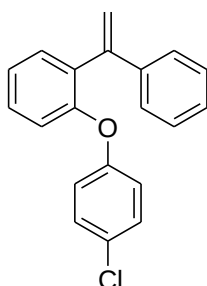
C, 88.08; H, 6.34. Found: C, 88.23; H, 6.26.

2-[2-(1-Phenylvinyl)phenoxy]naphthalene (4c):



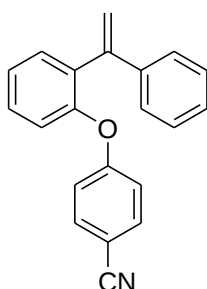
Pale yellow oily (57% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.40 (d, $J = 1.5$ Hz, 1H), 5.62 (d, $J = 1.5$ Hz, 1H), 6.97 (dd, $J_1 = 2.5$ Hz, $J_2 = 9.0$ Hz, 1H), 7.05 – 7.07 (m, 1H), 7.24 – 7.32 (m, 5H), 7.35 – 7.49 (m, 6H), 7.63 – 7.88 (m, 3H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 112.7, 114.1, 116.4, 119.1, 119.3, 120.0, 123.3, 123.4, 123.4, 124.0, 124.2, 126.3, 126.7, 127.6, 128.0, 129.1, 129.4, 129.8, 131.8, 134.1, 141.0, 146.3, 153.8, 155.3. **MS** (m/z) = 194, 215, 321, 322 (M^+). Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{O}$: C, 89.41; H, 5.63. Found: C, 89.56; H, 5.54.

1-[4-Chlorophenoxy]-2-(1-phenylvinyl)benzene (4d):



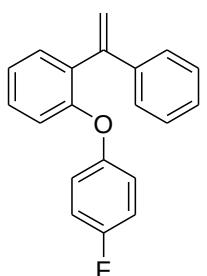
Colorless oily (64% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.34 (d, $J = 1.5$ Hz, 1H), 5.62 (d, $J = 1.5$ Hz, 1H), 6.62 (d, $J = 9.0$ Hz, 1H), 6.96 – 6.99 (m, 1H), 7.15 (d, $J = 9.0$ Hz, 2H), 7.22 – 7.43 (m, 9H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 116.5, 118.8, 118.9, 120.0, 120.2, 123.6, 124.3, 126.6, 127.2, 127.5, 128.0, 129.2, 129.7, 129.8, 131.8, 134.2, 140.9, 146.3, 153.4, 456.1. **MS** (m/z) = 152, 165, 181, 194, 306 (M^+). Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{ClO}$: C, 78.30; H, 4.93. Found: C, 78.48; H, 4.86.

4-[2-(1-Phenylvinyl)phenoxy]benzonitrile (4e):



Yellow oily (45% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.29 (d, $J = 1.0$ Hz, 1H), 5.55 (d, $J = 1.0$ Hz, 1H), 6.65 (d, $J = 1.0$ Hz, 2H), 7.06 (dd, $J_1 = 1.5$ Hz, $J_2 = 8.0$ Hz, 1H), 7.13 – 7.16 (m, 2H), 7.21 – 7.27 (m, 3H), 7.32 (dd, $J_1 = 1.0$ Hz, $J_2 = 7.5$ Hz, 1H), 7.40 – 7.48 (m, 4H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 105.0, 116.9, 117.9, 118.9, 120.4, 121.8, 125.7, 126.6, 127.6, 128.0, 129.5, 130.2, 132.1, 133.6, 134.1, 135.0, 140.5, 146.0, 151.4, 161.2. **MS** (m/z) = 152, 165, 181, 194, 296 (M^+). Anal. Calcd. for $\text{C}_{21}\text{H}_{15}\text{NO}$: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.75; H, 5.19; N, 4.54.

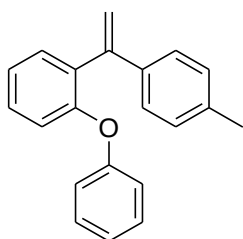
1-[4-Fluorophenoxy]-2-(1-phenylvinyl)benzene (4f):



Colorless oily (43% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.36 (s, 1H), 5.65 (s, 1H), 6.66 (dd, $J_1 = 4.5$ Hz, $J_2 = 9.0$ Hz, 1H), 6.88 – 6.92 (m, 2H), 6.99 – 7.07 (m, 2H), 7.21 – 7.27 (m, 1H), 7.25 – 7.41 (m, 7H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 115.6 (d, $^2J_{\text{CF}} = 27.9$ Hz), 115.8 (d, $^2J_{\text{CF}} = 27.9$ Hz),

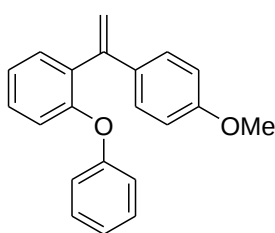
116.2, 118.2, 119.2 (d, $^3J_{CF}$ = 6.6 Hz), 119.3 (d, $^3J_{CF}$ = 6.6 Hz), 120.5, 120.5, 123.1, 123.7, 126.6, 127.4, 128.0, 129.1, 129.7, 131.8, 140.9, 146.4, 154.3- 159.2 (d, $^1J_{CF}$ = 287.1 Hz). **MS** (m/z) = 152, 165, 181, 194, 290 (M^+). Anal. Calcd. for $C_{20}H_{15}FO$: C, 82.74; H, 5.21. Found: C, 82.81; H, 5.29.

1-Phenoxy-2-(1-4-methylphenylvinyl)benzene (4g):



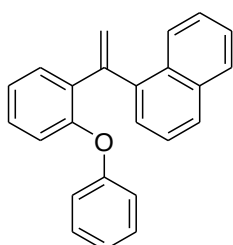
Colorless oily (66% yield). **1H NMR** (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.34 (d, J = 1.5 Hz, 1H), 5.64 (d, J = 1.5 Hz, 1H), 6.81 (d, J = 8.5 Hz, 2H), 7.00 – 7.05 (m, 2H), 7.11 – 7.12 (m, 2H), 7.19 – 7.28 (m, 5H), 7.28 – 7.33 (m, 1H), 7.40 (dd, J_1 = 1.5 Hz, J_2 = 9.0 Hz, 1H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 21.1, 115.5, 117.9, 118.9, 120.0, 122.4, 123.7, 126.6, 128.7, 128.9, 129.3, 129.7, 131.7, 134.3, 137.1, 138.2, 146.0, 154.0, 157.6. **MS** (m/z) = 165, 178, 195, 271, 286 (M^+). Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.35. Found: C, 88.12; H, 6.29.

1-Phenoxy-2-(1-4-methoxyphenylvinyl)benzene (4h):



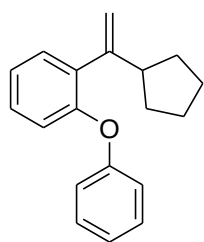
Colorless oily (40% yield). **1H NMR** (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 5.25 (d, J = 1.5 Hz, 1H), 5.56 (d, J = 1.5 Hz, 1H), 6.80 (d, J = 9.0 Hz, 2H), 7.01 – 7.06 (m, 2H), 7.17 – 7.24 (m, 5H), 7.31 – 7.39 (m, 4H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 55.2, 113.3, 114.6, 117.9, 118.8, 120.0, 122.4, 123.2, 123.7, 127.8, 128.9, 129.2, 129.7, 131.7, 133.6, 134.3, 145.6, 153.9, 157.2, 157.5, 159.1. **MS** (m/z) = 165, 211, 271, 287, 302 (M^+). Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.52; H, 6.08.

1-[1-(2-Phenoxyphenyl)vinyl]naphthalene (4i):



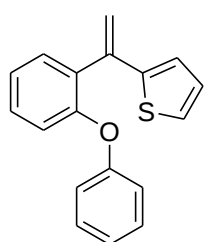
Orange oily (42% yield). **1H NMR** (500 MHz, $CDCl_3$) δ 5.56 (d, J = 1.5 Hz, 1H), 5.98 (d, J = 1.5 Hz, 1H), 6.60 (d, J = 10.0 Hz, 2H), 6.92 – 7.49 (m, 14H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 117.2, 118.8, 120.6, 120.8, 122.1, 124.0, 122.1, 124.0, 125.1, 125.3, 125.5, 126.1, 126.5, 127.4, 128.1, 128.8, 129.2, 129.7, 130.8, 144.9, 153.3, 157.4. **MS** (m/z) = 77, 115, 127, 155, 197, 231, 247, 322 (M^+). Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.48; H, 5.69.

1-(1-Cyclopentylvinyl)-2-phenoxybenzene (4j):



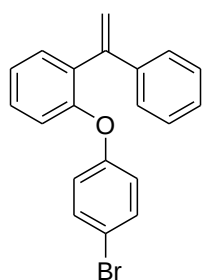
Colorless oily (51% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 1.27– 1.30 (m, 8H), 1.57– 1.58 (m, 1H), 5.28 (dd, $J_1 = 1.5$ Hz, $J_2 = 11.0$ Hz, 1H), 5.79 (dd, $J_1 = 1.5$ Hz, $J_2 = 19.0$ Hz, 1H), 6.92 – 7.28 (m, 9H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 22.6, 29.7, 31.9, 115.3, 117.7, 120.0, 119.4, 122.6, 124.0, 126.6, 128.9, 129.6, 130.0, 130.9, 135.7, 153.5, 157.8. **MS** (m/z) = 77, 93, 115, 127, 169, 171, 187, 195, 250, 264 (M^+). Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}$: C, 86.32; H, 7.63. Found: C, 86.41; H, 7.71.

2-[1-(2-Phenoxyphenyl)vinyl]thiophene (4k):



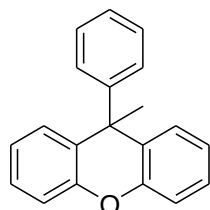
Pale brown oily (62% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.19 (s, 1H), 5.70 (s, 1H), 6.82 (dd, $J_1 = 1.0$ Hz, $J_2 = 3.5$ Hz, 1H), 6.86 – 6.88 (m, 2H), 6.93 (dd, $J_1 = 3.5$ Hz, $J_2 = 5.0$ Hz, 1H), 6.98 (dd, $J_1 = 1.0$ Hz, $J_2 = 8.0$ Hz, 1H), 7.02 – 7.05 (m, 1H), 7.16 – 7.20 (m, 2H), 7.24 – 7.28 (m, 2H), 7.32 – 7.38 (m, 1H), 7.40 (dd, $J_1 = 3.5$ Hz, $J_2 = 5.0$ Hz, 1H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 114.8, 118.2, 118.8, 119.6, 122.7, 123.5, 124.5, 125.5, 127.1, 129.2, 129.4, 129.7, 131.3, 133.1, 139.4, 144.9, 154.1, 157.5. **MS** (m/z) = 77, 83, 93, 127, 169, 171, 185, 201, 250, 264, 278 (M^+). Anal. Calcd. for $\text{C}_{18}\text{H}_{14}\text{OS}$: C, 77.66; H, 5.07; S, 11.52. Found: C, 77.58; H, 5.12; S, 11.42.

1-[4-Bromophenoxy]-2-(1-phenylvinyl)benzene (4l):



Yellow oily (54% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.32 (d, 1H, $J = 1.5$ Hz), 5.60 (d, 1H, $J = 1.5$ Hz), 6.55 (d, $J = 9.0$ Hz, 1H), 6.90 (d, $J = 9.0$ Hz, 1H), 6.93 – 7.03 (dd, $J_1 = 15.5$ Hz, $J_2 = 9.0$ Hz, 2H), 7.22 – 7.38 (m, 8H), 7.44 (d, $J = 9.0$ Hz, 1H). $^{13}\text{C NMR}$ (150MHz, CDCl_3) δ 116.5, 119.0, 119.2, 120.4, 124.4, 126.5, 127.5, 128.8, 129.2, 129.8, 132.1, 132.6, 134.3, 140.8, 145.2, 153.2, 156.7. **MS** (m/z) = 154, 170, 179, 195, 271, 336, 350 (M^+). Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{BrO}$: C, 68.39; H, 4.30. Found: C, 68.51; H, 4.28.

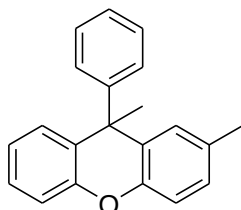
9-Methyl-9-phenyl-9H-xanthene (5a):^{2,3}



White solid (90% yield); mp: 105.3-106.8 °C. **IR** (cm^{-1}) ν = 3018, 2958, 1594, 1597, 1468, 1431, 1245, 1021. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.96 (s, 3H), 6.87 (d, $J_1 = 7.5$ Hz, 2H), 6.96 (dd, $J_1 = J_2 = 7.5$ Hz, 2H), 7.12 (d, $J_1 = 8.0$ Hz, 2H), 7.19 – 7.38 (m, 7H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 32.1, 42.9, 116.1, 123.0, 126.2, 127.4, 127.8, 128.0, 128.6, 128.0, 130.0, 130.2, 149.0, 150.2.

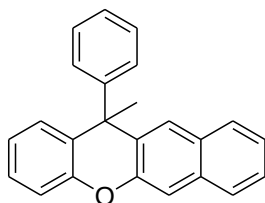
MS (m/z) = 195, 257, 272 (M^+). Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.12; H, 5.83.

2,9-Dimethyl-9-phenyl-9H-xanthene (5b):



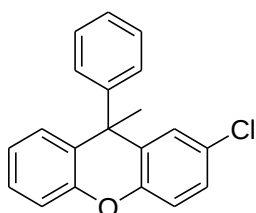
Colorless oily (88% yield). **IR** (cm^{-1}) ν = 3018, 2965, 2908, 1591, 1574, 1475, 1445, 1245, 750. **1H NMR** (500 MHz, $CDCl_3$) δ 1.95 (s, 3H), 2.21 (s, 3H), 6.66 (d, J = 2.0 Hz, 1H), 6.85 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1H), 6.92 – 7.38 (m, 10H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 20.8, 32.1, 42.9, 115.9, 116.1, 118.3, 119.1, 122.8, 126.1, 127.3, 128.0, 128.2, 128.6, 129.0, 129.0, 129.6, 130.2, 132.2, 148.1, 150.3, 150.3. **MS (m/z)** = 209, 286, 271 (M^+). Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.13; H, 6.41.

12-Methyl-12-phenyl-12H-benzo[b]xanthene (5c):



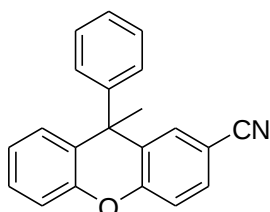
Beige solid (50% yield); mp: 137.8-140.9 °C. **IR** (cm^{-1}) ν = 3041, 3024, 2961, 2911, 1584, 1485, 1448, 1245, 743. **1H NMR** (500 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.91 – 6.96 (m, 2H), 7.08 – 7.60 (m, 11H), 7.72 – 7.87 (m, 2H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 30.3, 42.9, 114.0, 115.8, 118.1, 119.1, 119.9, 123.2, 123.4, 124.6, 125.6, 125.8, 126.0, 126.5, 127.1, 127.7, 127.8, 128.4, 128.9, 129.6, 131.4, 148.2, 150.1, 155.0. **MS (m/z)** = 245, 307, 308, 322 (M^+). Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.78; H, 5.71.

2-Chloro-9-methyl-9-phenyl-9H-xanthene (5d):



Colorless oily (57% yield). **IR** (cm^{-1}) ν = 3051, 3018, 2965, 2911, 1594, 1561, 1468, 1438, 1269, 1235, 750. **1H NMR** (500 MHz, $CDCl_3$) δ 1.93 (s, 3H), 6.83 (d, J = 2.5 Hz, 1H), 6.84 (dd, J_1 = 2.0 Hz, J_2 = 7.5 Hz, 1H), 6.95 – 7.35 (m, 10H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 32.1, 43.1, 116.1, 117.6, 118.9, 120.0, 123.3, 126.5, 127.6, 128.2, 128.5, 128.6, 128.9, 129.5, 129.7, 129.8, 131.0, 148.2, 148.8, 149.9. **MS (m/z)** = 51, 75, 152, 165, 181, 194, 271, 306 (M^+). Anal. Calcd. for $C_{20}H_{15}ClO$: C, 78.30; H, 4.93. Found: C, 78.41; H, 4.89.

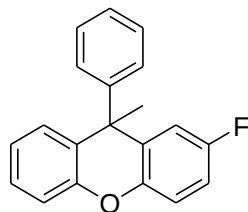
9-Methyl-9-phenyl-9H-xanthene-2-carbonitrile (5e):



Yellow oily (90% yield). **IR** (cm^{-1}) ν = 3049, 2970, 2225, 1600, 1479, 1447, 1240, 1044. **1H NMR** (500 MHz, $CDCl_3$) δ 1.93 (s, 3H), 7.01 – 7.79 (m, 12H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 32.5, 42.9, 105.0,

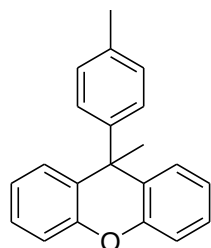
116.9, 118.9, 121.8, 124.1, 125.7, 126.6, 127.6, 128.0, 128.4, 129.0, 129.5, 132.1, 133.6, 134.0, 135.0, 146.0, 151.4, 161.2. **MS (m/z)** = 51, 77, 152, 165, 181, 194, 296 (M^+). Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.75; H, 5.15; N, 4.59.

2-Fluoro-9-methyl-9-phenyl-9H-xanthene (5f):



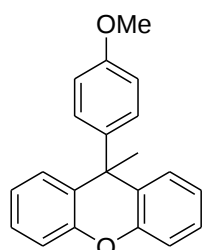
White solid (40% yield); mp: 89.5-90.5 °C. **IR** (cm^{-1}) ν = 3054, 3028, 2961, 2921, 1598, 1471, 1448, 1259, 750. **1H NMR** (500 MHz, $CDCl_3$) δ 1.94 (s, 3H), 6.56 (dd, J_1 = 3.0 Hz, J_2 = 9.5 Hz, 1H), 6.85 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1H), 6.89 – 7.35 (m, 10H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 31.9, 43.3, 114.4 (d, $^2J_{CF}$ = 23.8 Hz), 114.7, 114.9 (d, $^2J_{CF}$ = 23.9 Hz), 116.1, 117.3 (d, $^3J_{CF}$ = 8.4 Hz), 118.2, 120.5 (d, $^3J_{CF}$ = 8.4 Hz), 123.2, 126.5, 127.6, 128.1, 128.8, 129.2, 129.7, 148.2, 150.2, 157.5-158.4 (d, $^1J_{CF}$ = 240.1 Hz). **MS (m/z)** = 213, 275, 290 (M^+). Anal. Calcd. for $C_{20}H_{15}FO$: C, 82.74; H, 5.21. Found: C, 82.68; H, 5.28.

9-Methyl-9-p-tolyl-9H-xanthene (5g):



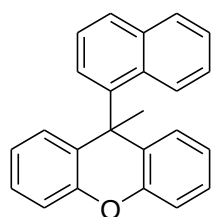
White solid (97% yield); mp: 81.6-82.4 °C. **IR** (cm^{-1}) ν = 3018, 2958, 2918, 1568, 1468, 1441, 1298, 1239, 746. **1H NMR** (500 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.36 (s, 3H), 6.89 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 2H), 6.99 (ddd, J_1 = 1.5 Hz, J_2 = J_3 = 7.5 Hz, 2H), 7.05 – 7.28 (m, 8H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 20.9, 32.2, 42.5, 116.1, 118.9, 123.2, 127.3, 128.5, 128.9, 129.7, 130.3, 135.7, 146.1, 150.2, 157.2. **MS (m/z)** = 195, 255, 271, 286 (M^+). Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.13; H, 6.41.

9-(4-Methoxy-phenyl)-9-methyl-9H-xanthene (5h):



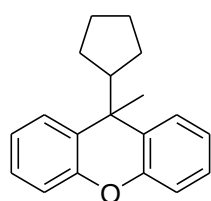
Pale yellow solid (83% yield); mp: 108.5-109.4°C. **IR** (cm^{-1}) ν = 3068, 3018, 2955, 2918, 1594, 1438, 1239, 1022, 750. **1H NMR** (500 MHz, $CDCl_3$) δ 1.91 (s, 3H), 3.81 (s, 3H), 6.84 (d, J = 8.5 Hz, 1H), 6.87 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 2H), 6.95 (ddd, J_1 = 1.5 Hz, J_2 = J_3 = 7.5 Hz, 2H), 7.10 (dd, J_1 = 1.5 Hz, J_2 = 8.5 Hz, 2H), 7.19 (ddd, J_1 = 1.5 Hz, J_2 = J_3 = 8.0 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 7.28 (s, 1H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 32.4, 42.3, 55.2, 113.2, 116.1, 123.0, 127.3, 128.9, 129.6, 130.4, 141.2, 150.2, 157.7. **MS (m/z)** = 152, 165, 195, 243, 287, 302 (M^+). Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.51; H, 6.08.

9-Methyl-9-naphthalen-1-yl-9H-xanthene (5i):



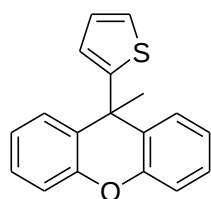
White solid (76% yield); mp: 134.0-136.2 °C. **IR** (cm⁻¹) ν = 3044, 2965, 1594, 1568, 1475, 1438, 1298, 1242, 743. **¹H NMR** (400 MHz, CDCl₃) δ 1.98 (s, 3H), 7.14 – 7.27 (m, 5H), 7.60 – 7.64 (d, J = 7.5 Hz, 2H), 7.80 – 7.82 (d, J = 7.2 Hz, 2H), 7.89 – 7.91 (d, J = 7.0 Hz, 2H), 7.99 – 8.01 (d, J = 7.2 Hz, 2H). **¹³C NMR** (150 MHz, CDCl₃) δ 35.6, 43.2, 116.1, 123.1, 123.3, 124.4, 124.8, 125.0, 126.1, 127.4, 127.5, 128.7, 128.9, 129.1, 135.2, 140.9, 149.8. **MS** (m/z) = 153, 165, 195, 307, 322 (M⁺). Anal. Calcd. for C₂₄H₁₈O: C, 89.41; H, 5.63. Found: C, 89.54; H, 5.73.

9-Cyclopentyl-9-methyl-9H-xanthene (5j):



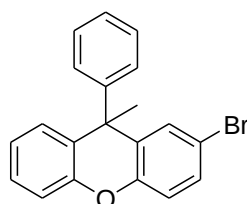
Yellow oily (20% yield). **IR** (cm⁻¹) ν = 3061, 3034, 2958, 2918, 1688, 1574, 1475, 1451, 1222, 1009, 796, 750. **¹H NMR** (500 MHz, CDCl₃) δ 1.33 – 1.39 (m, 2H), 1.56 – 1.66 (m, 6H), 1.67 (s, 3H), 2.54 (q, J = 7.5 Hz, 1H), 6.91 (dd, J_1 = 1.0 Hz, J_2 = 8.0 Hz, 1H), 7.08 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 2H), 7.21 (dd, J_1 = J_2 = 7.5 Hz, 2H), 7.41 (dd, J_1 = 7.5 Hz, J_2 = 8.5 Hz, 2H), 7.53 (ddd, J_1 = 2.0 Hz, J_2 = J_3 = 8.0 Hz, 1H). **¹³C NMR** (150MHz, CDCl₃) δ 29.3, 29.7, 30.2, 31.9, 53.4, 118.4, 119.4, 123.3, 124.3, 124.3, 128.4, 130.0, 135.7, 156.3, 159.9. **MS** (m/z) = 77, 104, 180, 189, 195, 249, 264 (M⁺), 265, 266. Anal. Calcd. for C₁₉H₂₀O: C, 86.32; H, 7.63. Found: C, 86.48; H, 7.76.

9-Methyl-9-thiophen-2-yl-9H-xanthene (5k):



Pale brown solid (99% yield); mp: 134.0-136.2 °C. **IR** (cm⁻¹) ν = 3064, 3024, 2958, 2915, 1598, 1468, 1431, 1235, 750. **¹H NMR** (500 MHz, CDCl₃) δ 2.02 (s, 3H), 6.97 (dd, J_1 = 4.0 Hz, J_2 = 5.0 Hz, 1H), 7.01 – 7.05 (m, 3H), 7.13 (ddd, J_1 = 1.5 Hz, J_2 = J_3 = 8.0 Hz, 4H), 7.22 – 7.28 (m, 3H). **¹³C NMR** (150MHz, CDCl₃) δ 33.7, 40.9, 116.3, 118.8, 123.1, 125.4, 125.9, 127.9, 128.4, 129.2, 149.7, 154.9. **MS** (m/z) = 83, 92, 110, 173, 180, 195, 264, 278 (M⁺). Anal. Calcd. for C₁₈H₁₄OS: C, 77.66; H, 5.07; S, 11.52. Found: C, 77.71; H, 5.12; S, 11.41.

2-Bromo-9-methyl-9-phenyl-9H-xanthene (5l):



Colorless oily (93% yield). **IR** (cm⁻¹) ν = 3066, 3025, 2987, 2933, 1594, 1463, 1451, 1278, 758. **¹H NMR** (500 MHz, CDCl₃) δ 1.93 (s, 3H), 6.89 – 6.91 (m, 3H), 7.01 – 7.03 (d, J = 8.5 Hz, 2H), 7.13 – 7.16 (m, 1H), 7.34 – 7.45 (m, 6H). **¹³C NMR** (150MHz, CDCl₃) δ 29.7, 43.0, 110.3, 115.5, 119.02, 119.1, 119.9, 120.4, 123.5, 123.7, 129.8, 132.6,

132.8, 136.1, 147.7, 153.3, 156.5, 156.7. **MS (m/z)** = 78, 152, 168, 181, 257, 271, 335, 350 (M^+). Anal. Calcd. for $C_{20}H_{15}BrO$: C, 68.39; H, 4.30. Found: C, 68.45; H, 4.24.

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NMR Spectra of all the reported compounds:

