Supplementary Information

Electrochemical benzylic C-H arylation of xanthenes and thioxanthenes without a catalyst and oxidant

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Tabel of Contents

I. General Information	S2
II. Experimental procedures and data	S3
1. Procedure for the synthesis of xanthene substrate 1g	S3
2. Optimization of the solvent on the reaction (TS1)	S4
3. Optimization of the electrolyte, temperature, and ratio of 1a/2a on the reaction (TS2)	S5
4. General procedure for the electrochemical C-H arylation of xanthenes/thioxanthenes	S6
5. General procedure for cyclic voltammetry (CV)	S6
6. Characterization data for the products	S7
III. References	S27
IV. NMR spectra of the products	S28

I. General Information

NMR spectra were recorded on Bruker-600 (600 MHz for ¹H; 150 MHz for ¹³C). ¹H NMR spectra were referenced relative to internal Si(Me)₄ (TMS) at δ 0.00 ppm or CDCl₃ at δ 7.26 ppm. ¹³C NMR spectra were recorded at ambient temperature on Bruker-600 (150 MHz) spectrometers and are referenced relative to CDCl₃ at δ 77.16 ppm. Data for ¹H, ¹³C NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, quint = quintet, br = broad), integration, and coupling constant (Hz). High resolution mass spectra were recorded on P-SIMS-Gly of BrukerDaltonics Inc. using ESI-TOF (electrospray ionization-time of flight) and Aglient Technologies 7250 GCQTOF using EI-TOF. *n*-Bu₄NBF₄ and DCE were purchased from Energy Chemical. Anisole was purchased from Sinopharm. Methanesulfonic acid was purchased from Tianjin Heowns Biochemical Technology Co. Ltd. was purchased from Bidepharm. Other substituted xanthenes and thioxanthene were synthesized through the known methods.¹⁻²

II. Experimental procedures and data

1. Procedure for the synthesis of xanthene substrate 1g



To a suspension of Sc(OTf)₃ (0.615 g, 1.25 mmol, 5 mol%) in chlorobenzene (100 mL), substrate 2hydroxy-5-methylbenzaldehyde (3.744 g, 27.5 mmol) and 3,4-dihydronaphthalen-2(1*H*)-one (3.655 g, 25 mmol) were quickly added. The reaction mixture was refluxed for 24 h. After that, the reaction mixture was cooled to room temperature and DCM (300 mL) and saturated aqueous NaHCO₃ (300 mL) were added in sequence. After the two layers were separated, the aqueous phase was extracted with DCM (3×300 mL) and the combined organic layers were dried with Na₂SO₄. The solvent was evaporated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel to give product **1g** (4.9201 g, 80% yield).

10-Methyl-12*H*-benzo[*a*]xanthene (1g)



White solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.83 (dd, *J* = 16.8, 8.2 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.58–7.55 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.24–7.23 (m, 1H), 7.10 (s, 1H), 7.03–6.98 (m, 2H), 4.32 (s, 2H), 2.34 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 149.0, 149.0, 132.6, 132.3, 130.2, 129.9, 128.6, 128.5, 128.3, 126. 8, 124.2, 122.4, 119.2, 118.1, 116.3, 111.6, 24.9, 20.9.

HRMS (EI) calcd. for C₁₈H₁₃O⁺ ([M-H]⁺): 245.0961, found: 245.0958.

2. Optimization of the solvent on the reaction (TS1)

Table S1. Optimization of the solvent on the reaction

H U Ia	$H = 6 \text{ mA}$ $C(+) \qquad Pt(-)$ $MsOH (2 \text{ equiv})$ $n-Bu_4NBF_4 (1.5 \text{ equiv})$ solvent, air, 80 °C, 5 h $2a \qquad undivided \ cell$	OMe J J J J J J J J J J J J J J J J J J J
Entry	Solvent	Yield (%)
1	CH ₃ CN	64
2	DMSO	26
3	DMF	12
4	EtOH	64
5	MeOH	43
6	AcOH	72
7	DCE	87
8	DCE/CH ₃ CN(1:1)	74
9	DCE/EtOH (1:1)	70
10	DCE/AcOH (1:1)	76

^{*a*} Reaction conditions: C anode (Φ 6 mm), Pt cathode (1 cm x 1 cm), I = 6 mA, **1** (0.5 mmol), **2** (1.5 mmol), MsOH (2 equiv.), *n*-Bu₄NBF₄ (1.5 equiv.) and DCE (5 mL) at 80 °C under an air atmosphere for 5 h. ^{*b*} Isolated yields.

3. Optimization of the electrolyte, temperature, and ratio of 1a/2a on the reaction (TS2)

Table S2	. Effect	of the	electrolyte,	temperature,	and ratio	of 1a / 2a ^{<i>a</i>,<i>b</i>}
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	H + 1a 2	$C(+) \square Pt(-)$ $MsOH (2 equiv)$ $n-Bu_4NBF_4 (1.5 equiv)$ $DCE, air, 80 °C, 5$ $undivided cell$) hiv) h 3a	
Entry	Electrolyte	Temp. (°C)	Ratio of 1a/2a	Yield (%)
1	<i>n</i> -Bu ₄ NBF ₄	80	1:3	87
2	<i>n</i> -Bu ₄ NOAc	80	1:3	55
3	<i>n</i> -Bu ₄ NHSO ₄	80	1:3	62
4	<i>n</i> -Bu ₄ NPF ₆	80	1:3	60
5	<i>n</i> -Bu ₄ NBr	80	1:3	43
6	<i>n</i> -Bu ₄ NI	80	1:3	42
7	<i>n</i> -Bu ₄ NClO ₄	80	1:3	78
8	<i>n</i> -Bu ₄ NBF ₄	70	1:3	74
9	<i>n</i> -Bu ₄ NBF ₄	90	1:3	85
10	<i>n</i> -Bu ₄ NBF ₄	80	1:5	87
11	<i>n</i> -Bu ₄ NBF ₄	80	1:1	51
12	<i>n</i> -Bu ₄ NBF ₄	80	2:1	33
13	<i>n</i> -Bu ₄ NBF ₄	80	1:3	71 ^c
14	<i>n</i> -Bu ₄ NBF ₄	80	1:3	85 ^d

OMe

^{*a*} Reaction conditions: C anode (Φ 6 mm), Pt cathode (1 cm x 1 cm), I = 6 mA, **1** (0.5 mmol), **2** (1.5 mmol), MsOH (2 equiv.), *n*-Bu₄NBF₄ (1.5 equiv.) and DCE (5 mL) at 80 °C under an air atmosphere for 5 h. ^{*b*} Isolated yields. ^{*c*} 1.0 equiv. of *n*-Bu₄NBF₄. ^{*d*} 2.0 equiv. of *n*-Bu₄NBF₄.

4. General procedure for the electrochemical C-H arylation of xanthenes/thioxanthenes.

To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) fitted with a graphite rod anode (6 mm diameter, 120 mm length) and a piece of Pt (1 cm \times 1 cm \times 0.02 cm) cathode, the solid reagents xanthene or thioxanthene (0.5 mmol), *n*-Bu₄NBF₄ (0.75 mmol) were added. Then, the liquid reagents arene (1.5 mmol), DCE (5 mL), MsOH (1 mmol) were added in sequence via syringe. The electrolysis was carried out with constant current (6 mA) at 80 °C for 5 h. After that, the reaction mixture was cooled to room temperature and filtered through a plug of silica (eluted with 80 mL EtOAc). The filtrate was washed with saturated Na₂CO₃ solution, and extrated with EtOAc for two times (2×80 mL). Then combined organic layer was washed with water for two times (2×80 mL). Then the organic layer was washed with brine and dried over Na₂SO₄. The solvent was evaporated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel to give product **3**.

5. General procedure for cyclic voltammetry (CV):

Cyclic voltammetry was performed in a three electrode cell connected to a Schlenk line at room temperature. The working electrode was a glassy carbon electrode, and the counter electrode was a platinum electrode. The reference was an Ag/AgCl. 10 mL of DCE containing 0.1 M n-Bu₄NBF₄ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3 V. The test concentrations of MsOH, **1a** and **2a** are 5 mM. Theses experiment results show that MsOH palys an critical role in decreasing the oxidation potential of the xanthene (**Figure S3a**), thus promoting the electrochemical cross-coupling reaction in an efficient manner. Moreover, the addition of MsOH dose not affect the oxidation potential of the anisole (**Figure S3b**).



Figure S3. CV of compounds 1a, 1a+MsOH and 2a, 2a+MsOH

6. Characterization data for the products

9-(4-Methoxyphenyl)-9*H*-xanthene (**3a**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3a** (125.1 mg, 87% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.22 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 2H), 7.14 (dd, *J* = 8.4, 7.2 Hz, 4H), 7.08–7.06 (m, 2H), 7.00 (td, *J* = 7.2, 1.2 Hz, 2H), 6.85–6.82 (m, 2H), 5.23 (s, 1H), 3.77 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.2, 151.0, 138.8, 129.6, 129.4, 127.7, 124.7, 123.2, 116.5, 114.1, 55.2, 43.5.

HRMS (ESI) calcd. for $C_{20}H_{17}O_2^+$ ([M+H]⁺): 289.1223, found: 289.1220.

9-(3,4-Dimethoxyphenyl)-9*H*-xanthene (**3b**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 10:1) to afford the product **3b** (104.6 mg, 69% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.10 (t, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.93–6.83 (m, 4H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.07 (s, 1H), 3.71–3.65 (m, 3H), 2.05 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 156.5, 151.0, 138.4, 130.7, 129.8, 127.7, 127.0, 126.6, 124.9, 123.2, 116.5, 109.9, 55.3, 43.6, 16.4.

HRMS (ESI) calcd. for $C_{21}H_{18}NaO_2^+$ ([M+Na]⁺): 325.1199, found: 325.1200.

9-(3,4-Dimethoxyphenyl)-9*H*-xanthene (**3c**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 10:1) to afford the product 3c (124.1 mg, 78% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.22–7.28 (m, 2H), 7.13 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.06 (d, *J* = 7.0 Hz, 2H), 6.98 (td, *J* = 7.5, 1.2 Hz, 2H), 6.79 (d, *J* = 1.0 Hz, 2H), 6.66 (s, 1H), 5.20 (s, 1H), 3.84 (s, 3H), 3.76 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 151.2, 149.4, 148.0, 139.1, 129.8, 128.0, 124.7, 123.3, 120.8, 116.6, 111.7, 111.2, 56.0, 44.1.

HRMS (ESI) calcd. for $C_{21}H_{18}NaO_3^+$ ([M+Na]⁺): 341.1148, found: 341.1147.

9-(Benzo[d][1,3]dioxol-5-yl)-9*H*-xanthene (**3d**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 10:1) to afford the product **3d** (127.6 mg, 84% yield).

Pale yellow solid.

¹**H** NMR (600 MHz, CDCl₃) δ 7.23–7.18 (m, 2H), 7.14–7.10 (m, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.01–6.97 (m, 2H), 6.75–6.71 (m, 2H), 6.59 (d, *J* = 1.2 Hz, 1H), 5.88 (s, 2H), 5.17 (s, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 150.96, 148.10, 146.36, 140.66, 129.65, 127.92, 124.38, 123.23, 121.29, 116.59, 108.89, 108.05, 100.99, 44.03.

HRMS (ESI) calcd. for $C_{20}H_{14}O_3Na^+$ ([M+Na]⁺): 325.0835, found: 325.0836.

9-(2,3-Dihydrobenzofuran-5-yl)-9H-xanthene (3e)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3e** (114.5 mg, 76% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.23–7.18 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 3H), 6.95 (s, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.19 (s, 1H), 4.50 (t, *J* = 9.0 Hz, 2H), 3.10 (t, *J* = 9.0 Hz, 2H).

¹³C NMR (150 MHz, CDCl₃) δ 158.9, 151.0, 139.0, 129.7, 127.9, 127.8, 124.9, 123.2, 116.5, 109.0, 71.3, 43.8, 29.7.

HRMS (ESI) calcd. for C₂₁H₁₆O₂Na ([M+Na]⁺): 323.1043, found: 323.1041.

9-(4-Isopropoxyphenyl)-9H-xanthene (3f)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3f** (134.0 mg, 85% yield).

Pale yellow liquid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.23–7.18 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.01–6.97 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 1H), 4.50–4.46 (m, 1H), 1.32 (s, 3H), 1.31 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 156.6, 151.1, 138.5, 129.7, 129.4, 127.8, 124.8, 123.2, 116.5, 115.9, 69.8, 43.6, 22.1.

HRMS (ESI) calcd. for C₂₂H₂₀O₂Na⁺ ([M+Na]⁺): 339.1356, found: 339.1354.

9-(4-Ethoxyphenyl)-9*H*-xanthene (**3**g)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3g** (122.7 mg, 81% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.20–7.16 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.98–6.95 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.19 (s, 1H), 3.98–3.89 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (150 MHz, CDCl₃) δ 157.7, 151.0, 138.7, 129.7, 129.4, 127.8, 124.8, 123.2, 116.5, 114.6, 63.4, 43.5, 14.9.

HRMS (ESI) calcd. for $C_{21}H_{18}O_2$ Na ([M+Na]⁺): 325.1199, found: 325.1202.

4-(9*H*-xanthen-9-yl)phenol (**3h**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 20:1) to afford the product **3h** (84.8 mg, 62% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.22–7.19 (m, 2H), 7.13 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.08–7.04 (m, 4H), 6.98 (td, *J* = 7.6, 1.2 Hz, 2H), 6.76–6.69 (m, 2H), 5.20 (s, 1H), 4.79 (s, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 154.2, 151.0, 139.1, 129.7, 129.6, 127.8, 124.7, 123.2, 116.5, 115.6, 43.5.

HRMS (ESI) calcd. for C₁₉H₁₄O₂Na ([M+Na]⁺): 297.0886, found: 297.0881.

2-Methyl-4-(9*H*-xanthen-9-yl)phenol (3i)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **3i** (93.1 mg, 65% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.20–7.16 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.04 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 5.14 (s, 1H), 4.63 (s, 1H), 2.15 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 152.6, 151.0, 139.1, 131.0, 129.8, 127.8, 127.1, 124.9, 124.1, 123.2, 116.6, 115.1, 43.6, 15.9.

HRMS (ESI) calcd. for $C_{20}H_{17}O_2^+$ ([M+H]⁺): 289.1223, found: 289.1218.

2-(*tert*-Butyl)-4-(9*H*-xanthen-9-yl)phenol (**3j**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 10:1) to afford the product **3j** (110.4 mg, 67% yield).

Pale yellow liquid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.25–7.22 (m, 2H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.13–7.10 (m, 2H), 7.02 (td, *J* = 7.8, 1.2 Hz, 2H), 6.80 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 5.21 (s, 1H), 4.71 (s, 1H), 1.42 (s, 9H).

¹³C NMR (150 MHz, CDCl₃) δ 152.7, 151.1, 138.4, 135.9, 129.6, 127.6, 127.0, 126.7, 125.0, 123.1, 116.9, 116.4, 43.9, 34.5, 29.6.

HRMS (EI) calcd. for C₂₃H₂₂O₂Na ([M+Na]⁺): 353.1512, found: 353.1512.

2,6-Dimethyl-4-(9*H*-xanthen-9-yl)phenol (**3**k)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 20:1) to afford the product 3k (104.2 mg, 69% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.22–7.18 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 7.01–6.95 (m, 2H), 6.80 (s, 2H), 5.12 (s, 1H), 4.49 (s, 1H), 2.17 (s, 6H).

¹³C NMR (150 MHz, CDCl₃) δ 151.0, 150.9, 138.4, 129.7, 128.5, 127.7, 124.9, 123.2, 123.2, 116.5, 43.6, 16.0.

HRMS (ESI) calcd. for $C_{21}H_{17}O_2^{-}$ ([M-H]⁻): 301.1234, found: 301.1238.

N,*N*-Dimethyl-4-(9*H*-xanthen-9-yl)aniline (**3m**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 20:1) to afford the product **3m** (120.7 mg, 80% yield).

Pale yellow liquid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.20–7.16 (m, 2H), 7.11 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.06 (t, *J* = 8.4 Hz, 4H), 6.97 (td, *J* = 7.8, 1.2 Hz, 2H), 6.71–6.63 (m, 2H), 5.16 (s, 1H), 2.90 (s, 6H).

¹³C NMR (150 MHz, CDCl₃) δ 151.1, 149.3, 134.7, 129.8, 129.1, 127.6, 125.2, 123.1, 116.4, 112.7, 43.4, 40.6.

HRMS (ESI) calcd. for C₂₁H₁₉NONa⁺ ([M+Na]⁺): 324.1359, found: 324.1358.

9-(Benzofuran-2-yl)-9*H*-xanthene (3n)



Prepared following general procedure using MeCN as a solvent instead of DCE, and the reaction mixture was purified by flash column chromatography with petroleum ether to afford the product **3n** (127.9 mg, 86% yield).

Yellow solid.

¹H NMR (600 MHz, CDCl₃) δ 7.44 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.40–7.37 (m, 1H), 7.34 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.29 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 2H), 7.20 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.19–7.14 (m, 3H), 7.08 (td, *J* = 7.2, 1.2 Hz, 2H), 6.29 (s, 1H), 5.51 (s, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 159.9, 155.2, 151.6, 129.7, 128.7, 128.7, 128.4, 123.9, 123.4, 122.7, 120.8, 116.9, 111.3, 103.6, 38.6.

HRMS (EI) calcd. for $C_{21}H_{14}O_2^+$ (M⁺): 298.0988, found: 298.0984.

9-(5-Iodothiophen-2-yl)-9*H*-xanthene (**30**)



Prepared following general procedure using MeCN as a solvent instead of DCE, and the reaction mixture was purified by flash column chromatography with petroleum ether to afford the product **30** (152.8 mg, 78% yield).

Brown Solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.25 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 2H), 7.21 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.12 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.05 (td, *J* = 7.4, 1.2 Hz, 2H), 6.99 (d, *J* = 3.7 Hz, 1H), 6.45 (d, *J* = 3.6 Hz, 1H), 5.49 (s, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 156.1, 151.0, 136.4, 129.3, 128.5, 126.2, 123.4, 123.2, 116.8, 72.7, 39.8.

HRMS (EI) calcd. for $C_{17}H_{11}IOS^+$ (M⁺): 389.9570, found: 389.9575.

9-(4-Methoxyphenyl)-9*H*-thioxanthene (**3p**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 50:1) to afford the product **3p** (117.1 mg, 77% yield).

Pale yellow solid.

¹**H** NMR (600 MHz, CDCl₃) δ 7.43 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.39 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.26–7.21 (m, 4H), 6.94–6.89 (m, 2H), 6.75–6.71 (m, 2H), 5.26 (s, 1H), 3.71 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.1, 137.6, 133.1, 132.8, 129.4, 128.9, 127.2, 126.8, 126.6, 113.5, 55.1, 52.3.

HRMS (EI) calcd. for $C_{20}H_{16}OS^+$ (M⁺): 304.0916, found: 304.0910.

9-(3,4-Dimethoxyphenyl)-9*H*-thioxanthene (**3q**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA=10:1) to afford the product 3q (137.3 mg, 82% yield).

White solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.44 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.39 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.27–7.22 (m, 4H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 6.54–6.52 (m, 1H), 5.24 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 148.7, 147.7, 137.5, 133.6, 133.0, 129.4, 127.1, 126.8, 126.6, 112.0, 111.4, 110.7, 55.8, 55.7, 52.6.

HRMS (ESI) calcd. for $C_{21}H_{18}NaO_2S^+$ ([M+Na]⁺): 357.0920, found: 357.0921.



9-(2,4-Dimethoxyphenyl)-9*H*-thioxanthene (**3r**)

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product 3r (106.1 mg, 63% yield).

Pale yellow oil.

¹**H NMR** (600 MHz, CDCl₃) δ 7.41–7.38 (m, 2H), 7.37–7.33 (m, 2H), 7.17–7.13 (m, 4H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 6.33 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.64 (s, 1H), 3.85 (s, 3H), 3.73 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 159.8, 157.6, 137.7, 133.1, 130.3, 129.7, 126.8, 126.6, 126.5, 122.3, 104.1, 98.9, 55.4, 55.4, 45.8.

HRMS (EI) calcd. for $C_{21}H_{18}O_2S^+$ (M⁺): 334.1022, found: 334.1019.

9-(2,5-Dimethoxyphenyl)-9*H*-thioxanthene (3s)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 50:1) to afford the product **3s** (97.2 mg, 58% yield).

Pale yellow oil.

¹**H NMR** (600 MHz, CDCl₃) δ 7.43–7.39 (m, 4H), 7.20–7.16 (m, 4H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 3.0 Hz, 1H), 5.78 (s, 1H), 3.87 (s, 3H), 3.64 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 153.4, 150.6, 137.1, 132.8, 131.3, 129.7, 126.7, 126.6, 126.4, 116.1, 111.9, 111.7, 55.9, 55.5, 45.9.

HRMS (ESI) calcd. for $C_{21}H_{19}O_2S^+$ ([M+H]⁺): 335.1100, found: 335.1103.

9-(2,4,6-Trimethoxyphenyl)-9H-thioxanthene (3t)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 50:1) to afford the product **3t** (101.5 mg, 56% yield).

White solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.39 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.12 (tt, *J* = 7.8, 1.2 Hz, 2H), 7.05 (td, *J* = 7.8, 1.2 Hz, 2H), 6.88 (dt, *J* = 7.8, 1.2 Hz, 2H), 6.30 (s, 2H), 5.54 (s, 1H), 3.90 (s, 3H), 3.65 (s, 6H).

¹³C NMR (150 MHz, CDCl₃) δ 160.9, 159.7, 137.9, 132.5, 127.2, 125.9, 125.8, 125.8, 108.2, 91.1, 55.6, 55.4, 41.1.

HRMS (EI) calcd. for C₂₂H₂₀O₃S⁺ (M⁺): 364.1128, found: 364.1133.

9-(4-(Methylthio)phenyl)-9*H*-thioxanthene (**3u**)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 100:1) to afford the product 3u (105.3 mg, 66% yield).

Yellow solid.

¹**H** NMR (600 MHz, CDCl₃) δ 7.36 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.32 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.29–7.26 (m, 2H), 7.25–7.23 (m, 2H), 7.04–6.99 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.21 (s, 1H), 2.32 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 137.8, 137.2, 136.4, 133.1, 129.5, 128.3, 127.2, 126.9, 126.6, 126.5, 52.5, 15.8.

HRMS (EI) calcd. for $C_{20}H_{16}S_2^+$ (M⁺): 320.0688, found: 320.0685.

2-Methyl-4-(9*H*-thioxanthen-9-yl)phenol (**3**v)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 10:1) to afford the product 3v (109.5 mg, 72% yield).

Yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.44 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.39 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.25–7.21 (m, 3H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 5.23 (s, 1H), 4.60 (s, 1H), 2.13 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 152.4, 137.7, 133.1, 133.0, 130.5, 129.4, 127.2, 126.7, 126.6, 126.5, 123.4, 114.6, 52.3, 15.9.

HRMS (EI) calcd. for C₂₀H₁₆OS⁺ (M⁺): 304.0916, found: 304.0916.

2,6-Dimethyl-4-(9*H*-thioxanthen-9-yl)phenol (**3**w)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 10:1) to afford the product **3w** (119.6 mg, 75% yield).

Yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.43 (d, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.26–7.20 (m, 4H), 6.63 (s, 2H), 5.19 (s, 1H), 4.44 (s, 1H), 2.11 (s, 6H).

¹³C NMR (150 MHz, CDCl₃) δ 151.0, 137.9, 133.1, 132.7, 129.6, 128.2, 127.3, 126.8, 126.7, 122.8, 52.5, 16.2.

HRMS (EI) calcd. for C₂₁H₁₈OS⁺ (M⁺): 318.1073, found: 318.1069.

9-(4-Methoxyphenyl)-2-methyl-9*H*-xanthene (4a)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **4a** (110.1 mg, 73% yield).

Yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.19–7.16 (m, 1H), 7.12-7.08 (m, 3H), 7.04–6.94 (m, 4H), 6.83–6.79 (m, 3H), 5.15 (s, 1H), 3.75 (s, 3H), 2.22 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.2, 151.1, 148.9, 139.0, 132.5, 129.8, 129.7, 129.3, 128.5, 127.7, 124.8, 124.3, 123.0, 116.4, 116.2, 114.1, 55.2, 43.6, 20.7.

HRMS (ESI) calcd. for $C_{21}H_{19}O_2^+$ ([M+H]⁺): 303.1380, found: 303.1380.

2-Methoxy-9-(4-methoxyphenyl)-9H-xanthene (4b)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4b** (97.4 mg, 61% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.19 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 1H), 7.13 – 7.09 (m, 3H), 7.06 (d, *J* = 9.0 Hz, 1H), 7.04 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.96 (td, *J* = 7.8, 1.2 Hz, 1H), 6.83–6.79 (m, 2H), 6.77 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.56 (dd, *J* = 3.0, 0.6 Hz, 1H), 5.17 (s, 1H), 3.76 (s, 3H), 3.70 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.3, 155.3, 151.3, 145.2, 138.6, 129.6, 129.3, 127.7, 125.4, 124.2, 122.9, 117.2, 116.4, 114.1, 113.9, 113.7, 55.6, 55.2, 44.0.

HRMS (ESI) calcd. for $C_{21}H_{19}O_3^+$ ([M+H]⁺): 319.1329, found: 319.1327.

9-(4-Methoxyphenyl)-9*H*-xanthen-2-ol (4c)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product 4c (80.3 mg, 53% yield).

Brown solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.20–7.17 (m, 1H), 7.12–7.09 (m, 3H), 7.02–7.00 (m, 2H), 6.95 (td, *J* = 7.4, 1.2 Hz, 1H), 6.82–6.80 (m, 2H), 6.68 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.48 (d, *J* = 2.9 Hz, 1H), 5.13 (s, 1H), 4.84 (brs, 1H), 3.76 (s, 3H).

¹³**C NMR** (150 MHz, CDCl₃) δ 158.4, 151.2, 151.1, 145.2, 138.5, 129.6, 129.4, 127.8, 125.6, 124.1, 123.0, 117.4, 116.4, 115.4, 115.1, 114.2, 55.3, 43.8.

HRMS (EI) calcd. for $C_{20}H_{16}O_3^+$ (M⁺): 304.1094, found: 304.1086.

4-Methoxy-9-(4-methoxyphenyl)-9H-xanthene (4d)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 5:1) to afford the product **4d** (120.9 mg, 76% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.25 (dd, *J* = 6.6, 1.8 Hz, 1H), 7.19 (td, *J* = 8.4, 7.8, 1.8 Hz, 1H), 7.12– 7.08 (m, 2H), 7.04 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.97 (td, *J* = 7.2, 1.2 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.79 (dq, *J* = 9.6, 3.0, 2.4 Hz, 3H), 6.65 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.19 (s, 1H), 3.95 (s, 3H), 3.74 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.3, 150.8, 147.9, 140.7, 138.9, 129.5, 129.2, 127.7, 125.6, 124.5, 123.4, 122.7, 121.2, 116.9, 114.1, 109.9, 56.2, 55.2, 43.6.

HRMS (ESI) calcd. for $C_{21}H_{19}O_3^+$ ([M+H]⁺): 319.1329, found: 319.1330.

9-(4-Methoxyphenyl)-2-(trifluoromethyl)-9H-xanthene (4e)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 30:1) to afford the product **4e** (142.7 mg, 80% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.34–7.31 (m, 1H), 7.20 (s, 1H), 7.11–7.07 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4Hz, 2H), 6.92 (d, *J* = 6.6 Hz, 1H), 6.90–6.86 (m, 1H), 6.74–6.64 (m, 2H), 5.07 (s, 1H), 3.62 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.6, 153.4, 150.5, 138.0, 129.7, 129.4, 128.2, 127.2 (q, *J* = 4.2 Hz), 125.1 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 270 Hz), 124.2, 124.0, 123.3, 121.5, 117.2, 116.6, 114.4, 55.2, 43.4.

¹⁹**F NMR** (565 MHz, CDCl₃) δ -61.6.

HRMS (ESI) calcd. for $C_{21}H_{15}F_3O_2Na^+$ ([M+Na]⁺): 379.0916, found: 379.0917.

12-(4-Methoxyphenyl)-12*H*-benzo[a]xanthene (4f)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 30:1) to afford the product **4f** (111.3 mg, 66% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 9.0 Hz, 2H), 7.43–7.37 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.20–7.13 (m, 4H), 7.05–7.01 (m, 1H), 6.72–6.68 (m, 2H), 5.75 (s, 1H), 3.64 (d, *J* = 1.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.0, 150.1, 149.3, 138.8, 131.6, 130.8, 129.2, 129.0, 128.5, 128.3, 127.5, 126.7, 125.2, 124.0, 123.6, 123.1, 118.0, 116.6, 116.0, 114.1, 55.1, 41.1.

HRMS (ESI) calcd. for $C_{24}H_{19}O_2^+$ ([M+H]⁺): 339.1380, found: 339.1386.

12-(4-Methoxyphenyl)-10-methyl-12*H*-benzo[a]xanthene (4g)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 10:1) to afford the product **4g** (103.3 mg, 59% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.76 (dd, *J* = 13.2, 8.4 Hz, 2H), 7.42–7.39 (m, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.98–6.95 (m, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.70 (s, 1H), 3.64 (s, 3H), 2.27 (s, 3H).

¹³**C NMR** (150 MHz, CDCl₃) δ 158.1, 149.5, 148.1, 139.0, 133.0, 131.8, 130.8, 129.5, 128.9, 128.6, 128.4, 126.7, 124.8, 124.0, 123.1, 118.1, 116.4, 116.1, 114.2, 55.1, 41.2, 20.9.

HRMS (EI) calcd. for $C_{25}H_{20}O_2^+$ (M⁺): 352.1458, found: 352.1458.

2-Chloro-9-(4-methoxyphenyl)-9*H*-xanthene (4h)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleumether and ethylacetate (PE/EA = 30:1) to afford the product **4h** (138.5 mg, 86% yield).

Pale yellow solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.21 (s, 1H), 7.16–7.13 (m, 1H), 7.12–7.08 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.03–6.97 (m, 3H), 6.84–6.81 (m, 2H), 5.16 (s, 1H), 3.77 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 158.5, 150.7, 149.6, 138.0, 129.7, 129.4, 129.3, 128.0, 127.9, 127.8, 126.3, 124.0, 123.5, 117.9, 116.5, 114.2, 55.2, 43.4.

HRMS (EI) calcd. for $C_{20}H_{15}ClO_2^+$ (M⁺): 322.0755, found: 322.0752.

9-(Benzofuran-2-yl)-2-chloro-9H-xanthene (4i)



Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether to afford the product **4i** (129.4 mg, 78% yield).

White solid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.45 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.31–7.26 (m, 3H), 7.23–7.19 (m, 2H), 7.16 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.14 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.09–7.05 (m, 2H), 6.31 (s, 1H), 5.44 (s, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 158.9, 151.1, 150.0, 129.5, 129.1, 128.8, 128.7, 128.2, 128.0, 124.0, 123.6, 122.8, 122.2, 120.8, 119.9, 118.2, 116.8, 111.3, 103.9, 38.3.

HRMS (EI) calcd. for $C_{21}H_{13}ClO_2^+$ (M⁺): 332.0599, found: 332.0595.

III. References:

- 1. E. Böβ, T. Hillringhaus, J. Nitsch and M. Klussmann, Org. Biomol. Chem., 2011, 9, 1744.
- 2. M. Bhanuchandra, H. Yorimitsu, A. Osuka, Org. Lett., 2016, 18, 384.

IV. NMR spectra of the products



Figure SI 2. ¹C NMR of **1g**.









f1 (ppm)






Figure SI 6. ¹³C NMR of **3b**.



f1 (ppm)

Figure SI 8. ¹³C NMR of **3c**.







Figure SI 10. ¹³C NMR of **3d**.







Figure SI 12. ¹³C NMR of **3e**.



Figure SI 14. ¹³C NMR of **3f**.



Figure SI 16. ¹³C NMR of **3g**.



200 180 160 140 120 100 80 60 40 20 0 f1 (ppm)

Figure SI 18. ¹³C NMR of **3h**.



Figure SI 20. ¹³C NMR of **3i**.







Figure SI 22. ¹³C NMR of **3**j.



Figure SI 24. ¹³C NMR of **3k**.



Figure SI 25. ¹H NMR of **3m**.



Figure SI 26. ¹³C NMR of **3m**.

7,452 7,450 7,450 7,450 7,3382 7,352 7,352 7,352 7,352 7,352 7,352 7,352 7,352 7,352 7,352 7,352 7,352 7,352 7,159 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,179 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170 7,170







Figure SI 28. ¹³C NMR of **3n**.



Figure SI 30. ¹³C NMR of **30.**







Figure SI 32. ¹³C NMR of **3p**







Figure SI 34. ¹³C NMR of **3q**.







Figure SI 36. ¹³C NMR of **3r**.







Figure SI 38. ¹³C NMR of **3s**.



Figure SI 40. ¹³C NMR of **3t**.





Figure SI 42. ¹³C NMR of **3u**.







Figure SI 44. ¹³C NMR of **3v**.



Figure SI 46. ¹³C NMR of **3w**.



Figure SI 48. ¹³C NMR of **4a**.







Figure SI 50. ¹³C NMR of **4b**.







Figure SI 52. ¹³C NMR of **4c**.







Figure SI 54. ¹³C NMR of 4d.







Figure SI 56. ¹³C NMR of **4e**.





Figure SI 58. ¹H NMR of 4f.



Figure SI 60. ¹H NMR of **4g**.







Figure SI 62. ¹H NMR of **4h**.





7.454 7.452 7.452 7.452 7.2336 7.2336 7.2336 7.2297 7.2297 7.2261 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216 7.2216



Figure SI 63. ¹H NMR of 4i.



Figure SI 64. ¹³C NMR of **4i**.