In(OTf)₃-Catalyzed reorganization/cycloaddition of two imine units and subsequently modular assembly of acridinium photocatalysts

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A. General information

All reagents were used as received unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh). Proton-1 nuclear magnetic

resonance (¹H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (¹³C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for CDCl₃. Fluorine-19 nuclear magnetic resonance (¹⁹F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 spectrometer. Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm⁻¹). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. UV-Vis spectra were determined on a Hitachi U-2900 spectrometer. Fluorescence spectra were acquired on a Hitachi F-4600 fluorescence spectrometer with a 10-mm quartz cuvette. The Substrates 1a-1z, 1a'-1i'^{[1][2][3][4]} was prepared according to the literature methods, Naphthylamines and aromatic aldehydes required for the synthesis of 1a can be directly purchased from Well-known chemical reagent companies such as Energy, Innochem, Sigma-Aldrich, Acros, Alfa Aesar, or TCI.

Photoreactor Configuration

The reaction device consists of a quartz beaker with a 240V blue LED lamp winding, a stirrer with a temperature detector and an external tin box. In order to control the reaction temperature, two high-power fans are installed on both sides of the reactor. Once reaction can accommodate 5 quartz sealing tubes.



B. Optimization Studies



Table 1Optimization of the Reaction Conditions					
Entry	Catalyst	Solvent	Temp/°C	yield (%) ^[b]	
1	Yb(OTf) ₃	EG	120	51	
2	Sc(OTf) ₃	EG	120	47	
3	Cu(OTf) ₂	EG	120	43	
4	Al(OTf) ₃	EG	120	77	
5	In(OTf) ₃	EG	120	87	
6	La(OTf) ₃	EG	120	trace	
7	$BF_3 \cdot OEt_2$	EG	120	trace	
8	FeCl ₃	EG	120	54	
9	$ZnCl_2$	EG	120	trace	
10	TiCl ₄	EG	120	trace	
11	In(OTf) ₃	DCE	120	56	
12	In(OTf) ₃	THF	120	30	
13	In(OTf) ₃	HFIP	120	32	
14	In(OTf) ₃	MeOH	120	29	
15	In(OTf) ₃	EtOH	120	57	
16	In(OTf) ₃	EG	50	51	
17	In(OTf) ₃	EG	80	67	
18	In(OTf) ₃	EG	140	79	
19 ^[c]	In(OTf) ₃	EG	120	80	
20	none	EG	120	trace	

^[a]Reaction conditions: **1a** (0.4 mmol), catalyst (20 mmol%) in solvent (0.8 mL) were stirred at indicated temperatures for 12 h under Ar atmosphere. ^[b]Isolated yields. ^[c]Air

atmosphere.

C. Preparation of substrates



A round bottom flask equipped with a stir bar was charged with the mixture of naphthalen-2-amines (0.57 g, 4.0 mmol) and MgSO₄ (0.96 g, 2 equiv.), then added 15 mL CH₂Cl₂ and stirred the mixture for 5 minutes. After that, added benzaldehydes (0.43 g, 4.0 mmol) and stirred at room temperature overnight. When the starting materials were completely converted, the reaction mixture was filtered and concentrated in vacuo. Then the residue was recrystallized to afford the product **1**.

D. Synthesis of dihydroacridines



An oven-dried vial equipped with a stir bar was charged with N-(naphthalen-2-yl)-1-phenylmethanimines **1** (0.4 mmol) and In(OTf)₃ (22.5 mg, 0.04 mmol). The reaction mixture was placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. Ethylene glycol (typically, 0.8 mL) was added and the reaction mixture was stirred at 120 °C for 12 hours in an oil bath. After the reaction was completed, it was cooled to room temperature. The mixture was diluted with EtOAc and washed with saturated aqueous NaHCO₃, then concentrated in vacuo. The residue was purified by silica gel chromatography to afford the dihydroacridine products **2**.

E. Synthesis of acridinium photocatalysts



Under argon atmosphere, $Pd(OAc)_2$ (0.01 mmol), xantphos (0.02 mmol), 'BuOK (2 equiv.) were added to the pressure tube equipped with a stir bar and dissolved with 1 mL toluene, then aryl iodides (0.3 mmol) was slowly added and the mixture stirred for 5 minutes. After that, product **2** (0.2 mmol) dissolved with 1 mL toluene was slowly added and the mixture stirred at 120 °C for 4 hours. After the reaction was completed, it was filtered and concentrated in vacuo.

The residue from previous step was dissolved with 5 mL CH₃CN and added to a round

bottom stir with was 0 °C flask equipped а bar, it stirred at and 2,3-dichloro-5,6-dicyano-1,4-benz-oquinone (90.8 mg, 2 equiv.) was slowly added. The mixture was stirred at room temperature for 2 hours. After the reaction was completed, the mixture was diluted with CH₂Cl₂ and washed with pure water, then concentrated in vacuo. The residue was dissolved with 8 mL CH_2Cl_2 and added to a round bottom flask equipped with a stir bar, it was stirred with 10 mL NaBF₄ aqueous solution for 8 hours. After the reaction was completed, it was washed with pure water and the organic phase was concentrated in vacuo. The residue was purified by silica gel chromatography to afford the acridinium photocatalysts 8.



(6aR,14R)-14-Phenyl-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2a)

White solid (62.1 mg, 87% yield). PE / EA = 10:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.50 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.65 (t, J = 7.8 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.80 (s, 1H), 6.46 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.1, 136.0, 132.2, 130.3, 128.8, 128.4, 128.3, 127.9, 126.9, 126.2, 123.0, 122.2, 116.8, 114.6, 39.1. IR (KBr): 3467, 3017, 1631, 1521, 1509, 1477, 1420, 1285, 1206, 1155, 871 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₂₀N [M+H]⁺ 358.1596, found 358.1589.



(6a*R*,14*R*)-14-(p-tolyl)-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2b)

White solid (49.1 mg, 66% yield). PE / EA = 10:1, $R_f = 0.28$. ¹H NMR (400 MHz, CDCl₃): δ 8.47 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.6 Hz, 3H), 7.63 (t, J = 7.8 Hz, 3H), 7.45 (d, J = 7.8 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 6.99 (d, J = 7.7 Hz, 3H), 6.75 (s, 1H), 6.51 (s, 1H), 2.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 143.2, 135.9, 135.6, 132.1, 130.3, 129.0, 128.8, 128.2, 127.6, 126.8, 123.0, 122.1, 116.7, 114.8, 38.6, 20.9. IR (KBr): 3462, 3023, 2898, 1621, 1549, 1538, 1485, 1453, 1430, 1388, 1295, 1050 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₂₂N [M+H]⁺ 372.1752, found 372.1746.



(6aR,14R)-14-(4-(tert-butyl)phenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2c)

White solid (56.9 mg, 69% yield). PE / EA = 10:1, $R_f = 0.29$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.61 (s, 1H), 8.64 (d, *J* = 7.8 Hz, 2H), 7.91–7.80 (m, 4H), 7.67–7.55 (m, 4H), 7.54–7.45 (m, 2H), 7.41–7.30 (m, 2H), 7.21–7.06 (m, 2H), 6.78 (s, 1H), 1.11 (s, 9H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 148.5, 144.7, 136.9, 132.3, 130.0, 129.0, 128.3, 127.6, 127.0, 125.3, 122.9, 122.7, 117.7, 114.2, 38.3, 34.3, 31.4. IR (KBr): 3469, 3019, 2998, 1659, 1578, 1561, 1474, 1451, 1391, 1289, 1255, 729 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₁H₂₈N [M+H]⁺ 414.2222, found 414.2213.



(6aR, 14R) - 14 - (4 - methoxyphenyl) - 6a, 7, 14, 14a - tetrahydrodibenzo[a, j] a cridine (2d)

White solid (48.8 mg, 63% yield). PE / EA = 8:1, $R_f = 0.27$. ¹H NMR (400 MHz, d₆-DMSO): δ 9.56 (s, 1H), 8.56 (d, *J* = 8.5 Hz, 2H), 7.85–7.71 (m, 4H), 7.57–7.46 (m, 4H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 6.71–6.59 (m, 3H), 3.52 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 157.7, 140.3, 136.7, 132.2, 129.9, 128.9, 128.3, 127.0, 122.9, 122.8, 117.7, 114.3, 113.9, 55.2, 37.9. IR (KBr): 3461, 3031, 2933, 1631, 1555, 1534, 1473, 1441, 1289, 1187, 746 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₂₂NO [M+H]⁺ 388.1701, found 388.1695.



(6aR,14R)-14-(4-(methylthio)phenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2e)

Yellow solid (45.2 mg, 56% yield). PE / EA = 10:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.60 (t, J = 7.1 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.71 (s, 1H), 6.55 (s, 1H), 2.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 143.2, 135.9, 135.6, 132.0, 130.2, 128.8, 128.4, 128.2, 126.9, 126.8, 123.0, 122.0, 116.7, 114.4, 38.5, 15.9. IR (KBr): 3458, 3031, 1626, 1523, 1515, 1445, 1413, 1289, 1062, 745 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₂₂NS [M+H]⁺ 404.1473, found 404.1467.



(6a*R*,14*R*)-14-([1,1'-biphenyl]-4-yl)-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2f)

White solid (52.8 mg, 61% yield). PE / EA = 10:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.56 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 7.73–7.62 (m, 4H),

7.51–7.38 (m, 8H), 7.34 (d, J = 7.4 Hz, 1H), 7.14 (d, J = 8.7 Hz, 2H), 6.88 (s, 1H), 6.48 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 145.1, 140.9, 139.0, 136.1, 132.2, 130.4, 128.9, 128.6, 128.4, 128.2, 127.2, 127.1, 127.0, 127.0, 123.1, 122.2, 116.8, 114.6, 38.7. IR (KBr): 3451, 3021, 1642, 1577, 1518, 1470, 1422, 1268, 1042 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₃H₂₄N [M+H]⁺ 434.1909, found 434.1902.



(6aR,14R)-14-(4-chlorophenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2g)

White solid (56.3 mg, 72% yield). PE / EA = 10:1, $R_f = 0.28$. ¹H NMR (400 MHz, CDCl₃): δ 8.37 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.60 (t, J = 8.6 Hz, 2H), 7.44 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.72 (s, 1H), 6.55 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 144.5, 135.9, 131.9, 131.7, 130.2, 129.1, 128.9, 128.6, 128.4, 127.0, 123.1, 121.8, 116.7, 114.1, 38.4. IR (KBr): 3475, 3027, 1619, 1518, 1502, 1466, 1421, 1290, 733 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₉ClN [M+H]⁺ 392.1206, found 392.1198.



(6a*R*,14*R*)-14-(4-fluorophenyl)-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2h)

Yellow solid (49.6 mg, 66% yield). PE / EA = 10:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.43 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.64 (t, J = 7.9 Hz, 2H), 7.50 (t, J = 6.9 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.86 (t, J = 8.6 Hz, 2H), 6.77 (s, 1H), 6.49 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.1 (d, J = 244.5 Hz), 141.9 (d, J = 3.5 Hz), 135.9, 132.0, 130.2, 129.2, 129.2, 128.9, 128.5, 127.0, 123.1, 121.9, 116.8, 115.1 (d, J = 21.3 Hz), 114.4, 38.2. ¹⁹F NMR (376 MHz, d₆-DMSO): δ -116.9. IR (KBr): 3442, 3012, 1614, 1569, 1528, 1467, 1414, 1349, 1248, 1207 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₉FN [M+H]⁺ 376.1502, found 376.1443.



(6a*R*,14*R*)-14-(4-(trifluoromethyl)phenyl)-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2i)

White solid (61.2 mg, 72% yield). PE / EA = 10:1, $R_f = 0.33$. ¹H NMR (400 MHz, CDCl₃): δ 8.42 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.73–7.62 (m, 4H),

7.45 (d, J = 7.6 Hz, 4H), 7.19 (d, J = 8.5 Hz, 2H), 6.84 (s, 1H), 6.58 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 149.8, 136.0, 132.0, 130.3, 129.0, 128.8, 128.3 (q, J = 32.3 Hz), 128.0, 127.1, 125.4 (q, J = 3.8 Hz), 124.2 (q, J = 270.1 Hz), 123.3, 121.8, 116.8, 113.8, 39.0. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.4. IR (KBr): 3450, 3017, 1634, 1558, 1512, 1460, 1438, 1332, 1261, 1212, 1108 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₁₉F₃N [M+H]⁺ 426.1470, found 426.1466.



(6a*R*,14*R*)-14-(4-((trifluoromethyl)thio)phenyl)-6a,7,14,14a-tetrahydrodibenzo[*a,j*]acridine (2j)

White solid (74.1 mg, 81% yield). PE / EA = 10:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.63 (t, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.46–7.37 (m, 4H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.79 (s, 1H), 6.55 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 136.3, 136.1, 132.0, 130.2, 129.5 (q, *J* = 306.3 Hz), 128.9, 128.8, 128.7, 127.1, 123.2, 121.8, 121.6, 116.8, 113.7, 38.6. ¹⁹F NMR (376 MHz, CDCl₃): δ -42.6. IR (KBr): 3469, 3018, 1623, 1562, 1254, 1229, 1038, 738 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₁₉F₃NS [M+H]⁺ 458.1190, found 458.1182.



4-((6aR,14R)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridin-14-yl)benzonitrile (2k)

Yellow solid (53.4 mg, 70% yield). PE / EA = 7:1, $R_f = 0.29$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.70 (s, 1H), 8.60 (d, J = 8.5 Hz, 2H), 7.86–7.80 (m, 6H), 7.63–7.54 (m, 4H), 7.41 (d, J = 8.8 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 6.87 (s, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 152.9, 136.9, 132.7, 132.1, 129.9, 129.0, 128.9, 128.8, 127.3, 123.2, 122.5, 119.2, 117.7, 112.9, 109.3, 38.8. IR (KBr): 3479, 3020, 2237, 1616, 1541, 1517, 1441, 1420, 1260, 1197 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₁₉N₂ [M+H]⁺ 383.1548, found 383.1542.



(6aR, 14R) - 14 - (4 - nitrophenyl) - 6a, 7, 14, 14a - tetrahydrodibenzo[a, j] acridine (2l)

Yellow solid (57.0 mg, 71% yield). PE / EA = 4:1, $R_f = 0.31$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.71 (s, 1H), 8.61 (d, J = 8.6 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.87–7.78 (m, 4H), 7.57 (t, J = 7.9 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 6.94 (s, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 154.9, 146.1, 136.9, 132.0, 129.9, 129.0, 128.9, 127.3,

124.0, 123.2, 122.5, 117.7, 112.7, 38.7. IR (KBr): 3460, 3321, 3024, 1587, 1522, 1447, 1408, 1368, 1269, 1043 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{27}H_{19}N_2O_2$ [M+H]⁺ 403.1447, found 403.1441.



(6aR, 14R)-14-(4-(1H-1, 2, 4-triazol-1-yl)phenyl)-6a, 7, 14, 14a-tetrahydrodibenzo[a, j]acridine (2m)

Yellow solid (49.2 mg, 58% yield). PE / EA = 5:1, $R_f = 0.30$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.67 (s, 1H), 9.06 (s, 1H), 8.65 (d, J = 8.6 Hz, 2H), 8.15 (s, 1H), 7.87–7.81 (m, 6H), 7.64–7.56 (m, 4H), 7.43 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 6.86 (s, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 152.6, 147.6, 142.6, 136.8, 135.1, 132.1, 129.9, 129.0, 129.0, 128.7, 127.1, 123.0, 122.6, 120.1, 117.7, 113.5, 38.3. IR (KBr): 3916, 3022, 1756, 1588, 1524, 1472, 1402, 1277, 1147, 1020 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₉H₂₁N₄ [M+H]⁺ 425.1766, found 425.1752.



(6aR,14R)-14-(3-bromophenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2n)

White solid (59.9 mg, 69% yield). PE / EA = 10:1, $R_f = 0.31$. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.71–7.62 (m, 3H), 7.56 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.21–7.11 (m, 3H), 7.06 (t, J = 7.8 Hz, 1H), 6.74 (s, 1H), 6.51 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.3, 135.9, 131.9, 130.8, 130.2, 129.8, 129.4, 128.9, 128.6, 127.1, 126.3, 123.2, 122.8, 121.8, 116.8, 113.8, 38.9. IR (KBr): 3448, 3029, 1644, 1560, 1478, 1434, 1269, 1238, 578 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₉BrN [M+H]⁺ 436.0701, found 436.0696.



(6aR,14R)-14-(3-iodophenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (20)

White solid (70.6 mg, 73% yield). PE / EA = 10:1, $R_f = 0.30$. ¹H NMR (400 MHz, CDCl₃): δ 8.37 (d, J = 8.5 Hz, 2H), 7.89–7.80 (m, 3H), 7.75 (d, J = 8.7 Hz, 2H), 7.62 (t, J = 7.4 Hz, 2H), 7.56 (d, J = 7.7 Hz, 1H), 7.44–7.32 (m, 3H), 7.14 (d, J = 8.6 Hz, 2H), 6.89 (t, J = 7.8 Hz, 1H), 6.68 (s, 1H), 6.52 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 136.7, 135.9, 135.3, 131.9, 130.2, 123.0, 128.9, 128.6, 127.0, 127.0, 123.2, 121.8, 116.8, 113.9, 94.9, 38.9. IR (KBr): 3467, 3024, 1631, 1554, 1474, 1429, 1059, 637 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{29}H_{19}IN [M+H]^+$ 484.0562, found 484.0557.



(6aR,14S)-14-(2-bromophenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2p)

White solid (59.2 mg, 68% yield). PE / EA = 10:1, $R_f = 0.30$. ¹H NMR (400 MHz, CDCl₃): δ 8.97 (d, J = 8.6 Hz, 2H), 7.84–7.73 (m, 5H), 7.65 (t, J = 7.7 Hz, 2H), 7.45–7.35 (m, 3H), 7.18 (d, J = 8.6 Hz, 2H), 6.99 (t, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.58 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 135.8, 132.9, 132.4, 132.0, 130.2, 128.6, 128.5, 127.9, 126.8, 123.6, 123.2, 119.7, 116.9, 115.9, 38.8. IR (KBr): 3451, 3031, 1616, 1529, 1511, 1478, 1434, 1264, 1220, 657 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₉BrN [M+H]⁺ 436.0701, found 436.0696.



(6aR,14R)-14-(naphthalen-2-yl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2q)

White solid (45.6 mg, 56% yield). PE / EA = 10:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, *J* = 8.5 Hz, 2H), 8.00 (s, 1H), 7.84–7.68 (m, 7H), 7.68–7.52 (m, 5H), 7.42–7.32 (m, 4H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.92 (s, 1H), 6.61 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 143.4, 135.9, 133.1, 132.2, 132.0, 130.3, 128.8, 128.5, 128.4, 128.0, 127.4, 126.9, 126.7, 125.7, 125.6, 125.3, 123.0, 122.1, 116.8, 114.3, 39.4. IR (KBr): 3463, 3032, 1637, 1559, 1538, 1466, 1439, 1261, 1198 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₁H₂₂N [M+H]⁺ 408.1752, found 408.1744.



(6aR,14S)-14-(thiophen-2-yl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2r)

Yellow solid (50.8 mg, 70% yield). PE / EA = 10:1, $R_f = 0.29$. ¹H NMR (400 MHz, CDCl₃): δ 8.45 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.66 (t, J = 8.6 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.13 (d, J = 8.7 Hz, 2H), 7.09 (s, 1H), 6.97 (d, J = 4.5 Hz, 1H), 6.78–6.70 (m, 2H), 6.59 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 149.2, 136.0, 131.9, 130.2, 128.8, 128.6, 127.1, 126.3, 124.1, 123.8, 123.2, 122.0, 116.7, 113.7, 33.8. IR (KBr): 3472, 3022, 2915, 1667, 1559, 1462, 1279, 1241, 688 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{25}H_{18}NS$ [M+H]⁺ 364.1160, found 364.1153.



(6aR,14R)-14-(benzofuran-6-yl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2s)

White solid (41.2 mg, 52% yield). PE / EA = 10:1, $R_f = 0.30$. ¹H NMR (400 MHz, CDCl₃): δ 8.48 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 7.64 (t, J = 8.4 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.35–7.24 (m, 2H), 7.16 (d, J = 8.7 Hz, 2H), 7.13–7.02 (m, 2H), 7.00 (s, 1H), 6.63 (s, 1H), 6.15 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 160.2, 136.2, 132.3, 130.1, 128.8, 128.6, 127.0, 123.1, 122.3, 122.2, 120.4, 116.6, 111.1, 110.7, 103.2, 33.5. IR (KBr): 3461, 2979, 1633, 1523, 1466, 1400, 1259, 1065, 742 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₉H₂₀NO [M+H]⁺ 398.1545, found 398.1537.



(6aR,14R)-14-(3,5-dimethylphenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2t)

White solid (57.8 mg, 75% yield). PE / EA = 10:1, $R_f = 0.33$. ¹H NMR (400 MHz, CDCl₃): δ 8.47 (d, J = 8.6 Hz, 2H), 7.81 (d, J = 8.0, 1.2 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.60 (t, J = 8.2 Hz, 2H), 7.38 (t, J = 8.2 Hz, 2H), 7.19–7.14 (m, 4H), 6.67 (d, J = 8.2 Hz, 2H), 6.49 (s, 1H), 2.19 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 146.1, 137.5, 135.9, 132.2, 130.3, 128.7, 128.2, 128.0, 126.7, 125.7, 122.9, 122.2, 116.8, 114.9, 39.1, 21.5. IR (KBr): 3461, 3015, 2989, 1642, 1543, 1519, 1451, 1384, 1266, 998 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₉H₂₄N [M+H]⁺ 386.1909, found 386.1903.



(6aR,14R)-14-(3,5-dimethoxyphenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2u)

Yellow solid (64.2 mg, 77% yield). PE / EA = 10:1, $R_f = 0.29$. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.70–7.57 (m, 4H), 7.40 (t, J = 7.4 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.79 (s, 2H), 6.73 (s, 1H), 6.50 (s, 1H), 6.19 (s, 1H), 3.67 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 160.6, 148.4, 136.0, 132.2, 130.3, 128.8, 128.3, 126.8, 123.0, 122.2, 116.8, 114.2, 106.9, 97.2, 55.1, 39.2. IR (KBr): 3455, 3010, 2987, 1661, 1579, 1460, 1429, 1278,



(6aR, 14R) - 14 - (3, 4 - dimethylphenyl) - 6a, 7, 14, 14a - tetrahydrodibenzo[a, j] a cridine (2v)

White solid (54.6 mg, 71% yield). PE / EA = 10:1, $R_f = 0.31$. ¹H NMR (400 MHz, CDCl₃): δ 8.56–8.44 (m, 2H), 7.84 (t, *J* = 7.7 Hz, 2H), 7.77 (t, *J* = 7.6 Hz, 2H), 7.70–7.57 (m, 2H), 7.46–7.36 (m, 2H), 7.36–7.26 (m, 2H), 7.25–7.13 (m, 2H), 7.01–6.90 (m, 1H), 6.73 (s, 1H), 6.51 (s, 1H), 2.21–2.06 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 143.6, 136.3, 135.9, 134.3, 132.2, 130.3, 129.4, 129.1, 128.7, 128.1, 126.8, 125.2, 122.9, 122.2, 116.7, 115.0, 38.7, 19.9, 19.1. IR (KBr): 3459, 3008, 2989, 1645, 1533, 1520, 1454, 1382, 1280, 1048 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₉H₂₄N [M+H]⁺ 386.1909, found 386.1901.



(6aR,14R)-14-(3,4-dimethoxyphenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2w)

White solid (65.1 mg, 78% yield). PE / EA = 10:1, $R_f = 0.27$. ¹H NMR (400 MHz, CDCl₃): δ 8.48 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.13 (d, J = 8.7 Hz, 2H), 7.10–6.99 (m, 2H), 6.75 (s, 1H), 6.66 (d, J = 8.1Hz, 1H), 6.59 (s, 1H), 3.72 (s, 3H), 3.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 149.0, 147.4, 138.8, 136.1, 132.2, 130.3, 128.8, 128.2, 126.8, 123.0, 122.1, 119.8, 116.7, 114.7, 111.8, 111.0, 55.7, 55.7, 38.3. IR (KBr): 3445, 3023, 2966, 1654, 1545, 1532, 1473, 1424, 1257, 1206, 1169 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₉H₂₄NO₂ [M+H]⁺ 418.1807, found 418.1802.



(6aR,14S)-14-(2-bromo-4-methoxyphenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2x)

White solid (50.2 mg, 54% yield). PE / EA = 10:1, $R_f = 0.27$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.70 (s, 1H), 8.76 (d, J = 8.6 Hz, 2H), 7.81 (t, J = 9.0 Hz, 4H), 7.62–7.48 (m, 3H), 7.42 (d, J = 8.7 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 6.96 (s, 1H), 6.72–6.59 (m, 2H), 3.54 (s, 3H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 158.5, 140.6, 137.0, 132.4, 132.3, 129.9, 129.1, 128.7, 126.9, 123.1, 123.0, 119.3, 118.0, 117.1, 116.2, 114.4, 55.7, 37.8. IR (KBr): 3458, 3014, 2987, 1671, 1568, 1531, 1466, 1418, 1281, 1234, 1045, 949, 641 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₂₁BrNO [M+H]⁺ 486.0807, found 486.0802.



(6a*R*,14*R*)-14-(4-bromo-3-fluorophenyl)-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2y)

White solid (56.2 mg, 62% yield). PE / EA = 7:1, $R_f = 0.29$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.68 (s, 1H), 8.62 (d, J = 8.5 Hz, 2H), 7.85–7.78 (m, 4H), 7.69 (d, J = 10.1 Hz, 1H), 7.58 (t, J =7.7 Hz, 2H), 7.46–7.30 (m, 6H), 6.82 (s, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 158.4 (d, J =245.1 Hz), 150.0 (d, J = 5.3 Hz), 136.8, 133.7, 132.0, 129.9, 129.0, 128.9, 127.3, 125.7 (d, J = 3.0Hz), 123.2, 122.5, 117.7, 115.8 (d, J = 21.9 Hz), 113.0, 105.6 (d, J = 20.7 Hz), 38.1. ¹⁹F NMR (376 MHz, d_6 -DMSO): δ -107.3. IR (KBr): 3471, 3007, 1626, 1541, 1511, 1474, 1445, 1333, 1261, 1234, 652 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₈BrFN [M+H]⁺ 454.0607, found 454.0602.



(6aR,14S)-14-(2-bromo-4-methylphenyl)-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2z)

Yellow solid (49.4 mg, 55% yield). PE / EA = 10:1, $R_f = 0.29$. ¹H NMR (400 MHz, CDCl₃): δ 8.95 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.67–7.58 (m, 3H), 7.38 (t, J = 7.5 Hz, 2H), 7.23 (s, 1H), 7.12 (d, J = 8.6 Hz, 2H), 6.86 (s, 1H), 6.76 (d, J = 8.2 Hz, 1H), 6.51 (s, 1H), 2.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 144.8, 137.9, 135.8, 133.1, 132.4, 131.5, 130.2, 129.6, 128.5, 128.5, 126.7, 123.7, 123.1, 119.4, 116.9, 115.9, 38.4, 20.2. IR (KBr): 3479, 3018, 2972, 1664, 1528, 1466, 1422, 1387, 1228, 1014, 677 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₈H₂₁BrN [M+H]⁺ 450.0857, found 450.0849.



(6aR,14R)-2,12-dimethoxy-14-phenyl-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2a')

White solid (50.8 mg, 61% yield). PE / EA = 7:1, $R_f = 0.28$. ¹H NMR (400 MHz, CDCl₃): δ 7.76–7.69 (m, 4H), 7.69–7.64 (m, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.20 (t, J = 7.5 Hz, 2H), 7.09–7.03 (m, 3H), 7.04–6.98 (m, 2H), 6.50 (s, 1H), 6.44 (s, 1H), 4.09 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 158.4, 146.1, 136.1, 133.4, 130.2, 128.3, 128.1, 128.0, 126.1, 125.5, 114.3, 114.1, 113.8, 102.5, 55.4, 40.3. IR (KBr): 3455, 3009, 2986, 1654, 1545, 1473, 1424, 1257, 1206, 1109 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₉H₂₄NO₂ [M+H]⁺ 418.1807, found 418.1799.



(6a*R*,14*R*)-2,12-dibromo-14-phenyl-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2b')

White solid (68.6 mg, 67% yield). PE / EA = 8:1, $R_f = 0.31$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.82 (s, 1H), 8.90 (s, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 7.1 Hz, 2H), 7.45–7.35 (m, 4H), 7.15 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.73 (s, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 147.6, 137.5, 133.7, 131.1, 128.8, 128.6, 127.9, 126.6, 126.1, 125.3, 121.2, 118.2, 113.5, 38.4. IR (KBr): 3465, 3010, 1679, 1519, 1485, 1453, 1276, 1227, 689 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₈Br₂N [M+H]⁺ 513.9806, found 513.9801.



(6a*R*,14*R*)-3,11-dimethyl-14-phenyl-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2c')

White solid (44.5 mg, 58% yield). PE / EA = 8:1, $R_f = 0.31$. ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.59 (s, 2H), 7.50 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.17–7.10 (m, 4H), 7.01 (t, J = 7.2 Hz, 1H), 6.70 (s, 1H), 6.44 (s, 1H), 2.52 (s, 6H).¹³C NMR (100 MHz, CDCl₃): δ 146.2, 135.4, 132.3, 130.4, 130.3, 128.9, 128.2, 127.9, 127.8, 127.6, 126.0, 122.0, 116.8, 114.6, 39.1, 21.3. IR (KBr): 3463, 3011, 2991, 1625, 1568, 1525, 1431, 1377, 1278, 1225, 994 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₉H₂₄N [M+H]⁺ 386.1909, found 386.1901.



(6aR,14R)-3,11-dicyclopropyl-14-phenyl-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2d')

White solid (68.2 mg, 78% yield). PE / EA = 10:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.30 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.52–7.44 (m, 4H), 7.29 (s, 2H), 7.16–7.07 (m, 4H), 6.98 (t, J = 7.4 Hz, 1H), 6.64 (s, 1H), 6.44 (s, 1H), 2.11–1.98 (m, 2H), 1.08–0.98 (m, 4H), 0.85–0.74 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 146.2, 138.2, 135.3, 130.5, 130.3, 128.2, 127.8, 127.6, 126.0, 125.6, 124.8, 122.2, 116.9, 114.6, 39.2, 15.3, 9.0, 8.8. IR (KBr): 3545, 3401, 3003, 2922, 1599, 1520, 1485, 1401, 943 804, 749, 510 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₃H₂₈N [M+H]⁺ 438.2222, found 438.2218.



(6a*R*,14*R*)-3,11-dibromo-14-phenyl-6a,7,14,14a-tetrahydrodibenzo[*a*,*j*]acridine (2e')

White solid (69.6 mg, 68% yield). PE / EA = 8:1, $R_f = 0.28$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.74 (s, 1H), 8.52 (d, J = 9.1 Hz, 2H), 8.04 (s, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 9.1 Hz, 2H), 7.53 (d, J = 7.7 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.09 (t, J = 7.7 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1H), 6.67 (s, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 152.1, 141.7, 136.0, 135.5, 135.4, 134.4, 133.4, 132.6, 132.5, 131.2, 123.0, 123.6, 120.6, 118.8, 43.2. IR (KBr): 3462, 3032, 1618, 1555, 1528, 1461, 1421, 1266, 1212, 677 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₈Br₂N [M+H]⁺ 513.9806, found 513.9798.



(6aR,14R)-3,11,14-triphenyl-6a,7,14,14a-tetrahydrodibenzo[a,j]acridine (2f')

Yellow solid (60.9 mg, 60% yield). PE / EA = 8:1, R_f = 0.31. ¹H NMR (400 MHz, CDCl₃): δ 8.52 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 2.0 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 9.6 Hz, 4H), 7.57 (d, 2H), 7.52 (t, *J* = 7.7 Hz, 4H), 7.44–7.37 (m, 2H), 7.22–7.15 (m, 4H), 7.04 (t, *J* = 6.9 Hz, 1H), 6.79 (s, 1H), 6.56 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.0, 141.1, 135.9, 135.7, 131.4, 130.6, 128.8, 128.7, 128.4, 127.8, 127.1, 127.0, 126.6, 126.4, 126.2, 122.7, 117.1, 114.6, 39.3. IR (KBr): 3451, 3019, 1638, 1559, 1541, 1477, 1438, 1409, 1259, 1223 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₉H₂₈N [M+H]⁺ 510.2222, found 510.2218.



(6a*R*,14*R*)-14-phenyl-3,11-di(thiophen-3-yl)-6a,7,14,14a-tetrahydrodibenzo[*a,j*]acridine (2g') Yellow solid (84.4 mg, 83% yield). PE / EA = 10:1, $R_f = 0.29$. ¹H NMR (400 MHz, d₆-DMSO): δ 9.81 (s, 1H), 8.72 (d, *J* = 9.0 Hz, 2H), 8.26 (s, 2H), 8.07–7.98 (m, 4H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.80–7.66 (m, 6H), 7.53 (d, *J* = 8.8, 1.9 Hz, 2H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H). ¹³C NMR (100 MHz, d₆-DMSO): δ 148.0, 141.9, 136.7, 131.4, 130.3, 129.8, 128.8, 128.6, 128.1, 127.5, 126.7, 126.4, 125.8, 125.6, 123.6, 120.9, 118.2, 114.2, 39.0. IR (KBr): 3467, 3031, 2955, 1704, 1561, 1518, 1444, 1408, 1272, 1230, 1015, 655 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₅H₂₄NS₂ [M+H]⁺ 522.1350, found 522.1342.



(7a*R*,17*R*)-17-phenyl-7a,8,17,17a-tetrahydrodinaphtho[2,3-a:2',3'-j]acridine (2h')

Yellow solid (70.4 mg, 77% yield). PE / EA = 7:1, $R_f = 0.27$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.79 (s, 1H), 9.17 (s, 2H), 8.43 (s, 2H), 8.19 (d, J = 8.5 Hz, 2H), 7.97 (t, J = 9.6 Hz, 4H), 7.80 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.46–7.38 (m, 4H), 7.08 (t, J = 7.6 Hz, 2H), 6.98 (s, 1H), 6.87 (t, J = 7.4 Hz, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 148.1, 135.5, 132.4, 130.7, 129.6, 129.4, 129.0, 128.5, 128.3, 128.3, 127.3, 126.2, 126.2, 124.8, 120.3, 119.4, 111.7, 39.1. IR (KBr): 3451, 3031, 1644, 1558, 1511, 1470, 1438, 1280, 1231 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₅H₂₄N [M+H]⁺ 458.1909, found 458.1903.



(6a*R*,14*R*)-3,11-dibromo-14-(4-(trifluoromethyl)phenyl)-6a,7,14,14a-tetrahydrodibenzo[*a,j*]a cridine (2i')

Yellow solid (98.6 mg, 85% yield). PE / EA = 7:1, $R_f = 0.31$. ¹H NMR (400 MHz, d_6 -DMSO): δ 9.62 (s, 1H), 8.25 (d, J = 9.2 Hz, 2H), 7.74 (s, 2H), 7.55–7.44 (m, 4H), 7.35 (d, J = 9.2 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.55 (s, 1H). ¹³C NMR (100 MHz, d_6 -DMSO): δ 151.4, 137.1, 131.3, 130.7, 130.7, 129.9, 128.4, 128.2, 127.3 (q, J = 31.7 Hz), 125.6 (q, J = 4.5 Hz), 124.9, 124.5 (q, J = 270.3 Hz), 119.0, 116.1, 113.2, 38.6. ¹⁹F NMR (376 MHz, d_6 -DMSO): δ -61.1. IR (KBr): 3463, 3023, 1631, 1518, 1477, 1422, 1324, 1285, 1206 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{28}H_{17}Br_2FN$ [M+H]⁺ 581.9680, found 581.9672.



(R)-2-bromo-14-phenyl-7,14-dihydrodibenzo[a,j]acridine (2l')

White solid (38.3 mg, 44% yield). PE / EA = 10:1, $R_f = 0.34$. ¹H NMR (400 MHz, CDCl₃): δ 8.54 (s, 1H), 8.42 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.70–7.58 (m, 3H), 7.49 (d, J = 9.3 Hz, 2H), 7.43–7.35 (m, 2H), 7.20–7.12 (m, 4H), 7.03 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 12.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 145.7, 136.7, 135.5, 133.5, 132.0, 130.3, 128.8, 128.6, 128.5, 128.5, 128.2, 127.7, 127.0, 126.3, 126.2, 124.6, 123.2, 122.2, 121.5, 117.2, 116.6, 114.5, 113.7, 39.1. IR (KBr): 3458, 3012, 1669, 1513, 1477, 1448, 1271, 1224, 682 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₇H₁₉BrN [M+H]⁺ 436.0717, found 436.0711.



7,14-diphenyldibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (8a)

Yellow solid (81.8 mg, 79% yield). DCM / MeOH = 100:1, R_f = 0.24. ¹H NMR (400 MHz, CDCl₃): δ 8.26 (d, J = 9.3 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 7.94–7.82 (m, 4H), 7.79–7.70 (m, 4H), 7.68–7.57 (m, 4H), 7.39–7.22 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 156.2, 142.7, 140.7, 140.4, 138.3, 132.4, 132.0, 131.7, 131.5, 130.7, 129.9, 129.4, 129.3, 129.1, 128.9, 128.3, 128.0, 125.0, 117.1. ¹⁹F NMR (376 MHz, d₆-DMSO): δ -154.2. IR (KBr): 3465, 3048, 1586, 1461, 1345, 1221, 1084 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₃H₂₂N⁺ [M]⁺ 432.1747 found 432.1744.



7-phenyl-14-(p-tolyl)dibenzo[a,j]acridin-7-ium tetrafluoroborate (8b)

Red solid (76.6 mg, 72% yield). DCM / MeOH = 100:1, $R_f = 0.25$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.56 (d, J = 9.4 Hz, 2H), 8.24 (d, J = 7.8 Hz, 2H), 8.05–7.98 (m, 3H), 7.94–7.88 (m, 2H), 7.78 (t, J = 7.9 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.45–7.30 (m, 6H), 2.68 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 155.9, 143.0, 141.3, 140.5, 139.0, 138.1, 132.6, 132.3, 132.0, 131.9, 130.5, 129.4, 129.3, 129.2, 129.2, 128.8, 128.8, 128.3, 124.8, 117.9, 21.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.4. IR (KBr): 3661, 2981, 1686, 1531, 1371, 1242, 1072, 752 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₄H₂₄N⁺ [M]⁺ 446.1903 found 446.1898.



14-(4-(tert-butyl)phenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8c)

Yellow solid (82.9 mg, 72% yield). DCM / MeOH = 100:1, $R_f = 0.27$. ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 9.4 Hz, 2H), 8.02 (d, J = 7.9 Hz, 2H), 7.94–7.89 (m, 3H), 7.80 (d, J = 8.1 Hz, 2H), 7.71–7.63 (m, 4H), 7.51 (d, J = 8.1 Hz, 2H), 7.36 (t, J = 9.1 Hz, 4H), 7.24 (t, J = 8.2 Hz, 2H), 1.59 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 156.6, 155.0, 142.6, 140.6, 138.3, 137.9, 132.5, 132.1, 131.8, 130.0, 129.3, 129.3, 129.0, 128.9, 128.5, 128.3, 127.9, 125.1, 117.1, 35.3, 31.6. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3463, 2959, 1634, 1520, 1371, 1213, 1055, 827, 758 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₇H₃₀N⁺ [M]⁺ 488.2373 found 488.2369.



14-(4-methoxyphenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8d)

Yellow solid (64.8 mg, 59% yield). DCM / MeOH = 100:1, $R_f = 0.23$. ¹H NMR (400 MHz, CDCl₃): δ 8.23 (t, J = 8.0 Hz, 2H), 8.06–7.81 (m, 7H), 7.65 (d, J = 7.4 Hz, 2H), 7.53–7.24 (m, 10H), 4.09 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 161.8, 156.3, 142.6, 140.2, 138.3, 132.6, 132.4, 131.9, 131.6, 130.9, 129.8, 129.3, 129.0, 128.9, 128.5, 128.0, 125.2, 117.2, 117.1, 55.7. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3671, 2897, 1669, 1534, 1361, 1254, 1206, 1102, 742 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₄H₂₄NO⁺ [M]⁺ 462.1852 found 462.1843.



14-(4-(methylthio)phenyl)-7-phenyldibenzo[*a*₃*j*]acridin-7-ium tetrafluoroborate (8e)

Yellow solid (76.8 mg, 68% yield). DCM / MeOH = 100:1, R_f = 0.28. ¹H NMR (400 MHz, d₆-DMSO): δ 8.53 (d, J = 9.7 Hz, 2H), 8.23 (d, J = 7.5 Hz, 2H), 8.02–7.67 (m, 9H), 7.50 (d, J = 7.3 Hz, 2H), 7.46–7.37 (m, 4H), 7.33 (d, J = 9.3 Hz, 2H), 2.70 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 155.1, 143.0, 142.9, 140.5, 138.9, 136.9, 132.6, 132.3, 131.9, 130.5, 130.1, 129.4, 129.1, 128.8, 128.3, 124.8, 117.8, 15.1. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.4. IR (KBr): 3471, 3056, 1750, 1590, 1519, 1371, 1052, 821, 755 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₄H₂₄NS⁺ [M]⁺ 478.1624 found 478.1605.



14-(4-nitrophenyl)-7-phenyldibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (8f)

Yellow solid (64.3 mg, 57% yield). DCM / MeOH = 100:1, $R_f = 0.23$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.72 (d, J = 8.2 Hz, 2H), 8.61 (d, J = 9.4 Hz, 2H), 8.29 (d, J = 7.8 Hz, 2H), 8.10–8.02 (m, 3H), 7.98 (d, J = 8.2 Hz, 2H), 7.95–7.88 (m, 2H), 7.82 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.41 (d, J = 9.4 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, d₆-DMSO): δ 152.9, 149.3, 147.2, 143.1, 140.8, 138.8, 132.7, 132.4, 132.0, 131.7, 130.7, 129.7, 129.2, 128.7, 128.5, 127.0, 124.4, 117.9. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.2. IR (KBr): 3688, 3049, 1636,

1514, 1371, 1216, 751 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{33}H_{21}N_2O_2^+$ [M]⁺ 477.1598 found 477.1589.



14-(4-cyanophenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8g)

Yellow solid (69.6 mg, 64% yield). DCM / MeOH = 100:1, $R_f = 0.27$. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (d, J = 9.4 Hz, 2H), 7.99 (d, J = 7.8 Hz, 4H), 7.92–7.83 (m, 5H), 7.74 (d, J = 6.2 Hz, 2H), 7.65 (t, J = 7.4 Hz, 2H), 7.33–7.25 (m, 4H), 7.21 (d, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 153.2, 145.4, 142.9, 140.2, 138.3, 134.6, 132.6, 131.9, 131.5, 131.2, 130.1, 129.3, 129.0, 128.6, 128.4, 127.9, 124.7, 118.1, 117.2, 114.2. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3918, 3068, 1733, 1521, 1371, 1052, 758 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₄H₂₁N₂⁺ [M]⁺ 457.1699 found 457.1694.



14-(3,4-dimethylphenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8h)

Yellow solid (68.9 mg, 63% yield). DCM / MeOH = 100:1, R_f = 0.28. ¹H NMR (400 MHz, CDCl₃): δ 8.30 (d, *J* = 9.3 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 6.1 Hz, 3H), 7.74–7.65 (m, 4H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.38–7.27 (m, 6H), 2.62 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 156.7, 142.5, 140.5, 139.8, 138.2, 138.0, 132.7, 132.4, 132.0, 131.8, 129.9, 129.3, 129.2, 129.0, 128.2, 127.9, 126.4, 125.0, 117.0, 20.0, 19.9. ¹⁹F NMR (376 MHz, d₆-DMSO): δ -154.4. IR (KBr): 3669, 3050, 2991, 1673, 1562, 1370, 1276, 1033, 759 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₅H₂₆N⁺ [M]⁺ 460.2060 found 460.2055.



14-(3,4-dimethoxyphenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8i)

Yellow solid (68.4 mg, 59% yield). DCM / MeOH = 100:1, R_f = 0.23. ¹H NMR (400 MHz, d₆-DMSO): δ 8.57 (d, J = 9.6 Hz, 2H), 8.26 (d, J = 7.9 Hz, 2H), 8.07–7.77 (m, 7H), 7.53–7.42 (m, 5H), 7.37 (d, J = 9.5 Hz, 2H), 7.19–7.08 (m, 2H), 4.07 (s, 3H), 3.63 (s, 3H). ¹³C NMR (100 MHz,

d₆-DMSO): δ 155.8, 152.1, 151.6, 142.9, 140.5, 138.9, 132.9, 132.5, 132.3, 132.0, 130.4, 129.4, 129.3, 128.8, 128.3, 125.0, 122.1, 117.7, 115.1, 113.1, 56.6. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3677, 3049, 2889, 1724, 1643, 1551, 1326, 1224, 1022, 741 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{35}H_{26}NO_2^+$ [M]⁺ 492.1958 found 492.1952.



14-(3,5-dimethylphenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8j)

Yellow solid (83.2 mg, 76% yield). DCM / MeOH = 100:1, R_f = 0.24. ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, J = 9.3 Hz, 2H), 8.01 (d, J = 7.8 Hz, 2H), 7.94–7.86 (m, 3H), 7.71–7.61 (m, 4H), 7.46 (s, 1H), 7.42 (d, J = 8.7 Hz, 2H), 7.36–7.26 (m, 4H), 7.16 (s, 2H), 2.43 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 156.8, 142.5, 141.7, 140.6, 140.4, 138.2, 132.4, 132.3, 132.0, 131.8, 130.0, 129.4, 129.2, 129.1, 128.2, 128.0, 126.4, 124.8, 117.0, 21.5. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.2. IR (KBr): 3647, 2977, 1633, 1551, 1370, 1249, 1208, 805 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₅H₂₆N⁺ [M]⁺ 460.2060 found 460.2049.



14-(3,5-dimethoxyphenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8k)

Yellow solid (71.6 mg, 69% yield). DCM / MeOH = 100:1, $R_f = 0.25$. ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 9.5 Hz, 2H), 8.03 (d, J = 7.8 Hz, 2H), 7.97–7.87 (m, 3H), 7.74–7.64 (m, 6H), 7.46–7.33 (m, 4H), 6.92 (s, 1H), 6.80 (d, J = 2.2 Hz, 2H), 3.82 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 163.7, 156.1, 142.6, 142.1, 140.4, 138.4, 132.3, 131.9, 131.7, 129.9, 129.3, 129.1, 129.0, 128.3, 128.1, 124.8, 117.0, 106.9, 103.0, 56.0. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.5. IR (KBr): 3675, 3061, 2878, 1641, 1553, 1338, 1239, 1055, 776 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₅H₂₆NO₂⁺ [M]⁺ 492.1958 found 492.1951.



14-(2-bromo-4-methylphenyl)-7-phenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (81)

Yellow solid (68.3 mg, 56% yield). DCM / MeOH = 100:1, R_f = 0.27. ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 9.3 Hz, 2H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.95–7.86 (m, 4H), 7.79 (s, 1H), 7.70 (t, *J* = 7.4 Hz, 2H), 7.62–7.52 (m, 3H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.36 (t, *J* = 8.1 Hz, 4H), 2.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 154.1, 143.3, 142.7, 140.5, 138.3, 138.2, 135.4, 132.3, 132.1, 132.0, 131.7, 131.6, 131.3, 130.2, 129.1, 129.0, 128.7, 128.0, 127.6, 125.0, 122.0, 117.2, 21.4. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.4. IR (KBr): 3654, 3031, 2978, 1664, 1527, 1370, 1221, 648 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₄H₂₃BrN⁺ [M]⁺ 524.1008 found 524.1003.



14-(2-bromo-4-methoxyphenyl)-7-phenyldibenzo[*a*₃*j*]acridin-7-ium tetrafluoroborate (8m)

Yellow solid (52.6 mg, 42% yield). DCM / MeOH = 100:1, $R_f = 0.24$. ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, J = 9.2 Hz, 2H), 8.03 (d, J = 7.9 Hz, 2H), 7.94–7.88 (m, 4H), 7.71 (t, J = 7.4 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.51–7.40 (m, 6H), 7.32–7.24 (m, 2H), 4.07 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 162.2, 154.0, 142.6, 140.5, 138.3, 133.2, 132.7, 132.2, 132.1, 132.0, 131.3, 130.1, 129.3, 129.1, 128.9, 128.7, 127.9, 127.6, 125.3, 122.8, 120.6, 117.1, 116.7, 56.1. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3663, 3048, 2878, 1674, 1537, 1280, 1209, 1064 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₄H₂₃BrNO⁺ [M]⁺ 540.0958 found 540.0951.



14-(naphthalen-2-yl)-7-phenyldibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (8n)

Yellow solid (49.8 mg, 44% yield). DCM / MeOH = 100:1, $R_f = 0.28$. ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 8.7 Hz, 3H), 8.15 (d, J = 8.3 Hz, 1H), 8.10 (s, 1H), 8.00 (d, J = 7.9 Hz, 2H), 7.96–7.90 (m, 3H), 7.87 (d, J = 8.2 Hz, 1H), 7.80–7.64 (m, 5H), 7.57 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 9.3 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.05 (t, J = 7.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 156.0, 142.7, 140.4, 138.3, 137.8, 134.5, 133.8, 132.5, 132.0, 131.7, 131.5, 129.9, 129.3, 129.2, 129.2, 128.9, 128.3, 128.1, 127.9, 127.5, 126.3, 125.2, 117.1. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.2. IR (KBr): 3662, 3048, 1666, 1540, 1347, 1261, 1206 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₇H₂₄N⁺ [M]⁺ 482.1904 found 482.1898.



3,7,11,14-tetraphenyldibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (80)

Yellow solid (95.1 mg, 71% yield). DCM / MeOH = 100:1, R_f = 0.28. ¹H NMR (400 MHz, d₆-DMSO): δ 8.67–8.56 (m, 4H), 8.07–7.92 (m, 8H), 7.88 (d, *J* = 7.6 Hz, 4H), 7.75–7.64 (m, 4H), 7.55 (t, *J* = 7.5 Hz, 4H), 7.51–7.39 (m, 4H), 7.36 (d, *J* = 9.1 Hz, 2H). ¹³C NMR (100 MHz, d₆-DMSO): δ 155.4, 142.9, 140.8, 140.4, 139.0, 138.3, 133.3, 132.4, 132.2, 132.0, 131.5, 129.6, 129.5, 129.0, 128.7, 128.1, 127.8, 127.5, 126.4, 124.8, 118.3. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3665, 3049, 1581, 1473, 1331, 1251, 1043 cm⁻¹. HRMS (ESI) m/z Calcd for C₄₅H₃₀N⁺ [M]⁺ 584.2373 found 584.2367.



7,14-di-p-tolyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8p)

Yellow solid (81.1 mg, 74% yield). DCM / MeOH = 100:1, R_f = 0.29. ¹H NMR (400 MHz, d₆-DMSO): δ 8.56 (d, J = 9.4 Hz, 2H), 8.24 (d, J = 7.8 Hz, 2H), 7.85–7.74 (m, 6H), 7.70 (d, J = 7.7 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H), 7.44–7.35 (m, 6H), 2.68 (s, 6H). ¹³C NMR (100 MHz, d₆-DMSO): δ 155.8, 143.1, 142.3, 141.2, 140.4, 138.1, 136.5, 132.6, 132.6, 132.3, 130.5, 129.4, 129.2, 128.8, 128.5, 128.2, 124.8, 117.9, 21.8, 21.5. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3673, 3051, 2959, 1737, 1541, 1373, 1241, 752 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₅H₂₆N⁺ [M]⁺ 460.2060 found 460.2053.



7-(4-chlorophenyl)-14-(p-tolyl)dibenzo[a,j]acridin-7-ium tetrafluoroborate (8q)

Yellow solid (75.8 mg, 67% yield). DCM / MeOH = 100:1, $R_f = 0.27$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.57 (d, J = 9.4 Hz, 2H), 8.27 (d, J = 7.9 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.78 (t, J = 7.5 Hz, 2H), 7.70 (d, J = 7.7 Hz, 2H), 7.5–7.34 (m, 8H), 2.68 (s, 3H).

¹³C NMR (100 MHz, d₆-DMSO): δ 156.0, 143.0, 141.3, 140.6, 138.0, 137.7, 137.1, 132.6, 132.1, 130.8, 130.5, 129.4, 129.4, 129.2, 128.8, 128.3, 124.8, 117.9, 21.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.2. IR (KBr): 3917, 3060, 1734, 1520, 1370, 1051, 824, 757 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{34}H_{23}CIN^+$ [M]⁺ 480.1514 found 480.1505.



7-(4-(methoxycarbonyl)phenyl)-14-(p-tolyl)dibenzo[a,j]acridin-7-ium tetrafluoroborate (8r)

Yellow solid (68.6 mg, 58% yield). DCM / MeOH = 100:1, $R_f = 0.27$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.53 (d, J = 8.8 Hz, 4H), 8.24 (d, J = 7.9 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H), 7.76 (t, J = 7.4 Hz, 2H), 7.68 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.7 Hz, 2H), 7.43–7.32 (m, 6H), 4.04 (s, 3H), 2.66 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 165.8, 156.2, 142.7, 142.6, 141.3, 140.7, 138.0, 133.1, 132.7, 132.6, 130.6, 129.6, 129.4, 129.3, 129.2, 128.8, 128.3, 124.8, 117.8, 53.3, 21.7. ¹⁹F NMR (376 MHz, d₆-DMSO): δ -143.7. IR (KBr): 3364, 2921, 2853, 1722, 1642, 1517, 1371, 1214, 1054, 531 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₆H₂₆NO₂+ [M]+ 504.1958 found 504.1949.



7-(3-nitrophenyl)-14-(p-tolyl)dibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (8s)

Yellow solid (78.5 mg, 68% yield). DCM / MeOH = 100:1, $R_f = 0.25$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.96 (s, 1H), 8.84 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 9.5 Hz, 2H), 8.40 (d, J = 8.0 Hz, 1H), 8.34–8.24 (m, 3H), 7.80 (t, J = 7.3 Hz, 2H), 7.73 (d, J = 7.7 Hz, 2H), 7.50 (d, J = 8.6 Hz, 4H), 7.46–7.36 (m, 4H), 2.69 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 156.3, 150.2, 143.1, 141.4, 140.8, 139.5, 138.0, 135.4, 133.5, 132.7, 132.7, 130.6, 129.4, 129.3, 129.3, 128.8, 128.4, 127.1, 124.9, 124.8, 118.0, 21.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -153.7. IR (KBr): 3467, 3087, 1602, 1529, 1359, 1214, 1055, 822, 744 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₄H₂₃N₂O₂⁺ [M]⁺ 491.1754 found 491.1744.



7-(3,5-dimethylphenyl)-14-(p-tolyl)dibenzo[*a,j*]acridin-7-ium tetrafluoroborate (8t)

Yellow solid (81.8 mg, 73% yield). DCM / MeOH = 100:1, $R_f = 0.29$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.58 (d, J = 9.4 Hz, 2H), 8.25 (d, J = 7.8 Hz, 2H), 7.82–7.64 (m, 5H), 7.57–7.38 (m, 10H), 2.69 (s, 3H), 2.56 (s, 6H). ¹³C NMR (100 MHz, d₆-DMSO): δ 155.8, 142.9, 141.6, 141.3, 140.4, 138.8, 138.1, 133.6, 132.7, 132.6, 130.5, 129.4, 129.4, 129.2, 128.9, 128.2, 126.1, 124.8, 118.0, 21.8, 21.4. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3475, 2922, 1605, 1519, 1370, 1212, 1053, 823, 756 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₆H₂₈N⁺ [M]⁺ 474.2216 found 474.2207.



7-(3,5-dimethoxyphenyl)-14-(p-tolyl)dibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (8u)

Yellow solid (66.5 mg, 56% yield). DCM / MeOH = 100:1, R_f = 0.26. ¹H NMR (400 MHz, d₆-DMSO): δ 8.61 (d, J = 9.4 Hz, 2H), 8.28 (d, J = 7.8 Hz, 2H), 7.80 (t, J = 7.2 Hz, 2H), 7.73 (d, J = 7.7 Hz, 2H), 7.59 (d, J = 9.4 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.45–7.37 (m, 4H), 7.22 (s, 2H), 7.12 (s, 1H), 3.94 (s, 6H), 2.70 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 162.7, 155.9, 142.8, 141.3, 140.5, 140.3, 138.0, 132.7, 132.7, 130.5, 129.4, 129.3, 129.2, 128.8, 128.3, 124.7, 118.1, 107.3, 103.7, 56.5, 21.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.3. IR (KBr): 3661, 3057, 2899, 1728, 1553, 1326, 1218, 1035, 754 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₆H₂₈NO₂⁺ [M]⁺ 506.2115 found 506.2107.



7-(3,5-bis(trifluoromethyl)phenyl)-14-(p-tolyl)dibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (8v)

Yellow solid (85.5 mg, 64% yield). DCM / MeOH = 100:1, $R_f = 0.28$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.82 (s, 3H), 8.58 (d, J = 9.5 Hz, 2H), 8.30 (d, J = 7.9 Hz, 2H), 7.80 (t, J = 7.4 Hz,

2H), 7.72 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 9.4 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.46–7.36 (m, 4H), 2.69 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 156.3, 143.2, 141.5, 141.1, 140.4, 137.9, 134.0 (q, J = 34.2 Hz), 132.7, 132.7, 130.7, 129.5, 129.3, 129.2, 128.7, 128.5, 126.8 (q, J = 3.7 Hz), 124.8, 123.2 (q, J = 271.6 Hz), 118.0, 21.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.7, -154.2. IR (KBr): 3468, 2980, 1612, 1521, 1369, 1278, 1186, 1053, 747 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₆H₂₂F₆N⁺ [M]⁺ 582.1651 found 582.1648.



7-(naphthalen-2-yl)-14-(p-tolyl)dibenzo[a,j]acridin-7-ium tetrafluoroborate (8w)

Yellow solid (71.2 mg, 61% yield). DCM / MeOH = 100:1, $R_f = 0.27$. ¹H NMR (400 MHz, d₆-DMSO): δ 8.62–8.49 (m, 4H), 8.37 (d, J = 8.2 Hz, 1H), 8.26 (d, J = 7.8 Hz, 2H), 8.21 (d, J = 7.9 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.95–7.83 (m, 2H), 7.83–7.76 (m, 2H), 7.74 (d, J = 7.3 Hz, 2H), 7.54 (d, J = 7.3 Hz, 2H), 7.49–7.40 (m, 6H), 2.71 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ 156.0, 143.2, 141.3, 140.5, 138.1, 136.3, 134.3, 133.7, 132.7, 132.6, 132.2, 130.5, 129.4, 129.3, 129.2, 128.9, 128.7, 128.6, 128.3, 125.3, 124.9, 118.1, 21.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.2. IR (KBr): 3648, 3039, 2931, 1674, 1528, 1370, 1216, 749 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₈H₂₆N⁺ [M]⁺ 496.2060 found 496.2052.



7-(dibenzo[*b*,*d*]thiophen-2-yl)-14-(p-tolyl)dibenzo[*a*,*j*]acridin-7-ium tetrafluoroborate (8x)

Yellow solid (70.2 mg, 55% yield). DCM / MeOH = 100:1, $R_f = 0.26$. ¹H NMR (400 MHz, CDCl₃): δ 8.61 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 7.9 Hz, 1H), 8.17 (d, J = 9.5 Hz, 2H), 8.02–7.93 (m, 3H), 7.74 (d, J = 8.5 Hz, 1H), 7.66–7.56 (m, 5H), 7.53–7.48 (m, 3H), 7.45 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 9.4 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 2.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 156.7, 143.0, 142.7, 141.0, 140.5, 140.2, 138.0, 137.8, 135.0, 134.3, 132.4, 132.1, 129.8, 129.4, 129.3, 129.3, 128.8, 128.4, 127.9, 125.7, 125.6, 125.4, 125.2, 123.0, 122.9, 121.8, 117.2, 21.7. ¹⁹F NMR (376 MHz, CDCl₃): δ -154.2. IR (KBr): 3468, 2924, 1723, 1600, 1519, 1473, 1370, 1216, 1055, 823, 602 cm⁻¹. HRMS (ESI) m/z Calcd for C₄₀H₂₆NS⁺ [M]⁺ 552.1780 found 552.1774.



2-bromo-7,14-diphenyldibenzo[a,j]acridin-7-ium tetrafluoroborate (8y)

Yellow solid (93.1 mg, 78% yield). DCM / MeOH = 100:1, $R_f = 0.32$. ¹H NMR (400 MHz, d6-DMSO): δ 8.65–8.51 (m, 2H), 8.26 (d, J = 7.9 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 8.05–7.88 (m, 9H), 7.79 (t, J = 7.4 Hz, 1H), 7.63 (d, J = 7.4 Hz, 2H), 7.44–7.35 (m, 4H), 7.30 (s, 1H). ¹³C NMR (100 MHz, d6-DMSO): δ 155.9, 143.5, 143.1, 141.1, 140.5, 139.8, 138.9, 132.7, 132.4, 132.3, 132.0, 131.7, 131.7, 131.3, 130.8, 130.4, 129.6, 129.3, 129.1, 128.9, 128.7, 128.5, 124.8, 123.7, 122.5, 118.6, 118.0. ¹⁹F NMR (376 MHz, d6-DMSO): δ -148.2. IR (KBr): 3657, 3032, 2973, 1658, 1519, 1365, 1217, 677 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₃H₂₁BrN⁺ [M]⁺ 510.0852, found 510.0847.

F. Mechanism studies



An oven-dried vial equipped with a stir bar was charged with naphthalen-2-amine **3** (28.6 mg, 0.2 mmol), $In(OTf)_3$ (11.2 mg, 0.02 mmol) and dissolved with 1 mL ethylene glycol, then stirred the mixture for 5 minutes. After that, benzaldehyde **4** (10.6 mg, 0.1 mmol) was slowly added. Under argon atmosphere, the mixture was stirred at 120 °C for 12 hours in an oil bath. After the reaction was completed, it was cooled to room temperature. The mixture was diluted with 25 mL CH_2Cl_2 and washed with saturated aqueous NaHCO₃, then concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product **2a** (16.1 mg, 45% yield).



An oven-dried vial equipped with stir bar was charged with а N-(naphthalen-2-yl)-1-phenylm-ethanimine 1a (46.2 mg, 0.2 mmol), In(OTf)₃ (11.2 mg, 0.02 mmol), naphthalen-2-ol 6 (28.8 mg, 0.2 mmol) and dissolved with 1.5 mL ethylene glycol. Under argon atmosphere, the mixture was stirred at 120 °C for 12 hours in an oil bath. After the reaction was completed, The mixture was diluted with 25 mL EtOAc and washed with saturated aqueous NaHCO₃, then concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product 2a (23.2 mg, 65% yield) and product 7 (6.2 mg, 17% yield).



14-phenyl-14H-dibenzo[*a*,*j*]xanthene (7)

White solid (12.2 mg, 17% yield). PE / EA = 50:1, $R_f = 0.34$. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (d, J = 7.4 Hz, 2H), 7.98–7.78 (m, 4H), 7.74–7.41 (m, 8H), 7.24 (t, J = 7.4 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.58 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 145.1, 131.5, 131.1, 128.9, 128.8, 128.5, 128.3, 126.8, 126.4, 124.3, 122.8, 118.1, 117.4, 38.1. The identity of **10** was confirmed based on reported NMR spectra.^[5]



An oven-dried vial equipped with a stir bar was charged with (E)-N-(6-bromonaphthalen-2-y -l)-1-phenylmethanimine **1e'** (30.9 mg, 0.1 mmol), (E)-N-(naphthalen-2-yl)-1-(4-(trifluoromethyl) -phenyl)methanemine **1i** (29.9 mg, 0.1 mmol), $In(OTf)_3$ (5.7 mg, 0.02 mmol) and dissolved with 0.4 mL ethylene glycol. Under argon atmosphere, the mixture was stirred at 120 °C for 12 hours in an oil bath. After the reaction was completed, it was cooled to room temperature. The mixture was diluted with 25 mL EtOAc and washed with saturated aqueous NaHCO₃, then concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product **2a** (2.9 mg, 8% yield), **2i** (13.6 mg, 32% yield), **2e'** (9.4 mg, 24% yield), **2i'** (11.1 mg, 19% yield).



An oven-dried vial equipped with a stir bar was charged with naphthalen-2-amine **3** (14.1 mg, 0.1 mmol), $In(OTf)_3$ (11.2 mg, 0.02 mmol), (2-aminophenyl)(phenyl)methanol **5** (20.0 mg, 0.1 mmol) and dissolved with 0.4 mL ethylene glycol. Under argon atmosphere, the mixture was stirred at 120 °C for 12 hours in an oil bath. After the reaction was completed, the mixture was diluted with 25 mL EtOAc and washed with saturated aqueous NaHCO₃, then concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product **2j'** (23.6 mg, 77% yield).



(S)-12-phenyl-7,12-dihydrobenzo[a]acridine (2j')

White solid (23.6 mg, 77% yield). PE / DCM = 8:1, $R_f = 0.31$. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.51–7.44 (m, 2H), 7.40–7.30 (m, 3H), 7.26–7.08 (m, 5H), 6.99 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.33 (s, 1H), 6.03 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 147.1, 137.8, 136.8, 132.2, 129.8, 129.4, 128.7, 128.6, 128.6, 127.1, 127.1, 126.8, 126.2, 123.9, 122.8, 122.3, 121.5, 116.7, 114.1, 113.6, 44.1. IR (KBr): 3448, 3015, 1629, 1519, 1467, 1420, 1285, 1206, 1155 cm⁻¹. HRMS (ESI) m/z Calcd for C₃₁H₂₀N [M+H]⁺ 308.1439, found 308.1433.

G. Synthetic transformation of products



An oven-dried vial equipped with a stir bar was charged with photoredox catalyst **8c** (5.8 mg, 10 mmol%), [1,1'-biphenyl]-2-carboxylic acid **9** (19.8 mg, 0.1 mmol) and dissolved with 1 mL MeCN. Under oxygen atomsphere, 1,8-Diazabicyclo[5.4.0]-undec-7-ene was slowly added to the tube(3.1 mg, 0.02 mmol) and the mixture was stirred in photoreactor at room temperature for 20 hours. After the reaction was completed, the reaction mixture was concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product **10** (12.5 mg, 64% yield). White solid (12.5 mg, 64% yield). PE/ EA = 20:1, R_f = 0.34. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.83 (t, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 8.5 Hz, 1H), 7.41–7.32 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 161.1, 151.3, 134.8, 134.7, 130.5, 130.4, 128.8, 124.5, 122.7, 121.6, 121.3, 118.0, 117.7. The identity of **10** was confirmed based on reported NMR spectra.^[6]



An oven-dried vial equipped with a stir bar was charged with photoredox catalyst **8c** (5.8 mg, 10 mmol%), pyrazole **12** (13.6 mg, 0.2 mmol) and 2,2,6,6-Tetramethylpiperidine-1-oxyl (3.1 mg, 0.02 mmol). Under oxygen atomsphere, Anisole **11** (10.8 mg, 0.1 mmol) dissolved with 1 mL CH₂Cl₂ and slowly added to the tube and the mixture was stirred in photoreactor at room temperature for 20 hours. After the reaction was completed, the reaction mixture concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product **13** (9.5 mg, 54% yield). PE / EA = 10:1, R_f = 0.32. ¹H NMR (400 MHz,

CDCl₃): δ 7.91 (d, *J* = 2.7 Hz, 1H), 7.84–7.64 (m, 3H), 7.07 (d, *J* = 9.4 Hz, 2H), 6.53 (s, 1H), 3.94 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 158.3, 140.6, 126.8, 120.9, 114.5, 107.1, 55.5. The identity of **13** was confirmed based on reported NMR spectra.^[7]



A quartz tube was charged with **8c** (11.6 mg, 10 mmol%), 1-phenylethan-1-ol (24.4 mg, 0.2 equiv.) was diluted with 1 mL MeCN and added to the tube. The mixture was stirred in photoreactor at room temperature for 20 hours under O₂. After the reaction was completed, the reaction mixture was diluted with 5.0 mL DCM and concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product **15** (13.4 mg, 56% yield). Colorless solid (13.4 mg, 56% yield). PE/EA = 30:1, $R_f = 0.32$. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.56–7.45 (m, 2H), 2.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.0, 137.2, 133.0, 128.5, 128.3, 26.5.



An oven-dried vial equipped with a stir bar was charged with N-(naphthalen-2-yl)-1-phenylmethanimines **1a** (1.16 g, 5.0 mmol) and In(OTf)₃ (281.0 mg, 0.5 mmol). The reaction mixture was placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. Ethylene glycol (typically, 15 mL) was added and the reaction mixture was stirred at 120 °C for 12 hours in an oil bath. After the reaction was completed, it was cooled to room temperature. The mixture was diluted with EtOAc and washed with saturated aqueous NaHCO₃, then concentrated in vacuo. The residue was purified by silica gel chromatography to afford the dihydroacridine products **2a** (731.8 mg, 82% yield).

Under an Ar atomsohere, $Pd(OAc)_2$ (23.9 mg, 0.1 mmol), xantphos (115.8 mg, 0.2 mmol) and t-BuOK (459.2 mg, 2 equiv.) were added to the pressure tube equipped with a stir bar and dissolved with 15 mL toluene, then iodobenzene(611.1 mg, 3.0 mmol) was slowly added and the mixture stirred for 10 minutes. After that, product **2a** (731.3 mg, 2.0 mmol) dissolved with 10 mL toluene was slowly added and the mixture stirred at 120 °C for 4 hours. After the reaction was completed, the reaction mixture was filtered and concentrated in vacuo.

The residue from previous step was dissolved with 30 mL CH₃CN and added to a round bottom flask equipped with a stir bar, it was stirred at 0 °C and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (926.6 mg, 2 equiv.) was slowly added at 0 °C. The reaction was stirred at room temperature for 2 hours. After the reaction was completed, the mixture concentrated in vacuo, the mixture was diluted with 50 mL CH₂Cl₂ and washed with pure water, the organic phases were dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (50 mL) and added to a round bottom flask equipped with a stir bar, it was stirred with NaBF₄ aqueous solution (40 mL) for 8 hours. After the reaction was completed, it was washed with pure water. The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product **8a** (789.2 mg, 76% yield).



An oven-dried vial equipped with a stir bar was charged with (E)-N-(7-bromonaphthale -n-2-yl)-1-phenylmethanimine **1b'** (61.8 mg, 0.2 mmol), 2-Naphthylamine **3** (28.6 mg, 0.2 mmol) and $In(OTf)_3$ (22.5 mg, 0.04 mmol). The reaction mixture was placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. Ethylene glycol (typically, 0.8 mL) was added and the reaction mixture was stirred at 120 °C for 12 hours in an oil bath. After the reaction was completed, it was cooled to room temperature. The mixture was diluted with EtOAc and washed with saturated aqueous NaHCO₃, then concentrated in vacuo. The residue was purified by silica gel chromatography to afford the dihydroacridine products **2l'** (38.3 mg, 44% yield).

Under argon atmosphere, $Pd(OAc)_2$ (0.01 mmol), xantphos (0.02 mmol), 'BuOK (2 equiv.) were added to the pressure tube equipped with a stir bar and dissolved with 1 mL toluene, then aryl iodobenzene (61.2 mg, 0.3 mmol) was slowly added and the mixture stirred for 5 minutes. After that, product **2l'** (87.1 mg, 0.2 mmol) dissolved with 1 mL toluene was slowly added and the mixture stirred at 120 °C for 4 hours. After the reaction was completed, it was filtered and concentrated in vacuo.

The residue from previous step was dissolved with 5 mL CH₃CN and added to a round bottom flask equipped with a stir bar, it was stirred at 0 °C and 2,3-dichloro-5,6-dicyano -1,4-benz-oquinone (90.8 mg, 2 equiv.) was slowly added. The mixture was stirred at room temperature for 2 hours. After the reaction was completed, the mixture was diluted with CH₂Cl₂ and washed with pure water, then concentrated in vacuo. The residue was dissolved with 8 mL CH₂Cl₂ and added to a round bottom flask equipped with a stir bar, it was stirred with 10 mL NaBF₄ aqueous solution for 8 hours. After the reaction was completed, it was washed with pure water and the organic phase was concentrated in vacuo. The residue was purified by silica gel chromatography to afford the acridinium photocatalysts **8**y (93.1 mg, 78% yield).

H. References

1. Hu, Y., Nan, J., Yin, J., Huang, G., Ren, X., Ma, Y. Rhodium-Catalyzed Dehydrogenative Annulation of N-Arylmethanimines with Vinylene Carbonate for Synthesizing Quinolines. *Org. Lett.* **23**, 8527–8532 (2021).

2. Suresh, R., Sakthinathan, S. P., Kamalakkannan, D., Ranganathan, K., Sathiyamoorthi, K., Mala, V., Arulkumaran, R., Vijayakumar, S., Sundararajan, R., Vanangamudi, G., Subramanian, M., Thirunarayanan, G., Vanaja, G., Kanagambal, P. Solvent-free synthesis of azomethines, spectral correlations and antimicrobial activities of some E-benzylidene-4-chlorobenzenamines *Bull. Chem. Soc. Ethiop.* **29**, 275–290 (2015).

3. Saha, S., Rajput, L., Joseph, S., Mishra, M. K., Ganguly, S., Desiraju, G. R. *CrystEngComm*. IR spectroscopy as a probe for C–H···X hydrogen bonded supramolecular synthons. **17**, 1273–1290 (2015).

4. Sek, D., Siwy, M., Bijak, K., Filapek, M., Malecki, G., Nowak, E., Sanetra, J., Jedryka, A. J., Laba, K., Lapkowski, M., Balcerzak, E. Optical and electrochemical properties of novel thermally stable Schiff bases bearing naphthalene unit. *J. Electroanal. Chem.* **751**, 128–136 (2015).

5. Sek, D., Siwy, M., Grucela, M., Małecki, G., Nowak, E. M., Lewinska, G., Santera, J., Laba, K., Lapkowski, M., Kotowicz, S., Balcerzak, E. S. New anthracene-based Schiff bases: Theoretical and experimental investigations of photophysical and electrochemical propertiesSpectrochim. *Acta. A Mol. Biomol. Spectrosc.* **175**, 24-35 (2017).

6. Niu, K., Zhou, P., Ding, L., Hao, Y., Liu, Y., Song, H., Wang, Q. Photoelectrochemical Decarboxylative C–H Alkylation of Quinoxalin-2(*1H*)-ones. *ACS. Sustain. Chem. Eng.* **9**, 16820–16828 (2021).

7. Romero, N. A., Margrey, K. A., Tay, N. E., Nicewicz, D. A. Site-selective arene C-H amination via photoredox catalysis. *Science*. **349**, 1326–1330 (2015).

I. Spectrophotometric and electrochemical data







Spectrophotometric and electrochemical data of **8a** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8b** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.



^tBu

Spectrophotometric and electrochemical data of **8c** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.





Spectrophotometric and electrochemical data of **8d** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.





Spectrophotometric and electrochemical data of **8e** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.






Spectrophotometric and electrochemical data of **8f** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8g** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8h** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.



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Spectrophotometric and electrochemical data of 8i top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V vs SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8k** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8l** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.





Spectrophotometric and electrochemical data of **8m** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission (λ_{ex} = 485 nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, λ_{ex} = 340 nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8n** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 485$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.





Spectrophotometric and electrochemical data of **80** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.

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Spectrophotometric and electrochemical data of **8p** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8q** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.





Spectrophotometric and electrochemical data of **8r** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.





Spectrophotometric and electrochemical data of **8s** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 485$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







100







Spectrophotometric and electrochemical data of **8u** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8v** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 485$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8w** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.







Spectrophotometric and electrochemical data of **8x** top left: Cyclic voltammograms measured in a deaerated DCM with 0.1 M nBu₄N·PF₆ with a scan rate of 100 mV/s, a platinum working electrode and with ferrocene as the internal reference (Fc/Fc⁺ = 0.38 V *vs* SCE in DCM). top right: UV-visible absorption (red line) and emission ($\lambda_{ex} = 447$ nm, black line) spectra, in DCM. bottom: Fitting of luminescence decays in DCM at 298 K (c $\approx 10^{-5}$ M, $\lambda_{ex} = 340$ nm). Experimental decays in yellow, exponential fits in red, residual traces in green.

J. NMR spectra

¹H NMR of **2a** (400 MHz, CDCl₃)





12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



S56





220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 fl (ppm)







S58



¹³C NMR of **2d** (100 MHz, d₆-DMSO)







¹H NMR of **2f** (400 MHz, CDCl₃)







S61

¹H NMR of **2g** (400 MHz, CDCl₃)









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¹⁹F NMR of **2i** (376 MHz, CDCl₃)

~№ н́

-60 fl (ppm) -22 80 60 40 20 0 -20 -40 -80 -100 -120 -140 -160 -180 -200





¹⁹F NMR of **2j** (376 MHz, CDCl₃)













¹H NMR of **2m** (400 MHz, d_6 -DMSO)



¹H NMR of **2n** (400 MHz, CDCl₃)





¹³C NMR of **20** (100 MHz, CDCl₃)






¹H NMR of 2q (400 MHz, CDCl₃)





¹H NMR of 2r (400 MHz, CDCl₃)

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12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



¹H NMR of **2s** (400 MHz, CDCl₃)



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)











 ¹H NMR of 2v (400 MHz, CDCl₃)

 Image: Construction of the second se

12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



¹H NMR of 2w (400 MHz, CDCl₃)









12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



$^{19}\mathrm{F}$ NMR of $\mathbf{2y}$ (376 MHz, d_6-DMSO)

-60 fl (ppm) -22 80 60 40 20 0 -20 -40 -80 -100 -120 -140 -160 -180 -200









70 60

50

40 30

20

10

80

0

200 190 180 170 160 150 140 130 120 110 100 90 f1 (ppm)

¹H NMR of **2b'** (400 MHz, d_6 -DMSO)





¹³C NMR of **2b'** (100 MHz, d₆-DMSO)



f1 (ppm) 160 150





f1 (ppm) 190 180 170 160 150 140 130 120





110 100 f1 (ppm) 190 180 170 160 150 140 130 120



 $^{13}\mathrm{C}$ NMR of 2e' (100 MHz, d_6-DMSO) 141.7 136.0 135.5 135.5 135.4 135.4 135.4 133.4 133.5 133.5 133.5 133.5 133.5 133.5 133.5 133.5 1131.2 130.0 1123.6 118.8 - 152.1 Br В f1 (ppm)





200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)





110 100 f1 (ppm)

¹H NMR of **2h'** (400 MHz, d_6 -DMSO)







210 200 190 180 170 160 150 140 130 120 110 100 90 f1 (ppm) 70 60 50 40 30 20 10 0 -10 -20 -3 80

¹H NMR of **2i'** (400 MHz, d₆-DMSO)





¹³C NMR of **2i'** (100 MHz, d₆-DMSO)



f1 (ppm) 160 150 140 130 120

¹⁹F NMR of **2i'** (376 MHz, d₆-DMSO)





— -61.1

¹H NMR of 2l' (400 MHz, CDCl₃)

 $\begin{array}{c} 88.8\\ 88.5\\ 88.5\\ 77.7\\ 77.8\\ 77.6\\ 77.6\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\ 77.5\\$





12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)



¹⁹F NMR of 8a (376 MHz, CDCl₃)

BF₄

-90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)



 $^{13}\mathrm{C}$ NMR of **8b** (100 MHz, d_6-DMSO)



f1 (ppm) 160 150

Me BF_4

-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 -21 fl (ppm)





¹⁹F NMR of 8c (376 MHz, CDCl₃)







¹³C NMR of 8d (100 MHz, CDCl₃)

¹⁹F NMR of 8d (376 MHz, CDCl₃)

ОМе _____ BF₄

-90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 fl (ppm)





¹⁹F NMR of 8e (376 MHz, CDCl₃)



-75 -85 -95 -105 -115 -125 -135 -145 -155 -165 -175 -185 -195 -205 -2. f1 (ppm)







f1 (ppm) 190 180 170 160 150

¹⁹F NMR of 8f (376 MHz, CDCl₃)



-105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 f1 (ppm)



¹H NMR of **8g** (400 MHz, CDCl₃)



$^{19}\mathrm{F}$ NMR of 8g (376 MHz, CDCl_3)



-145 -150 f1 (ppm) -110 -115 -120 -125 -130 -135 -140 -155 -160 -165 -170 -175 -180 -185 -190





f1 (ppm) 160 150

S105

¹⁹F NMR of 8h (376 MHz, CDCl₃)

Me ^{Me} BF_4

-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -20 fl (ppm)





¹⁹F NMR of 8i (376 MHz, CDCl₃)



-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 f1 (ppm)




Me Me BF_4

-105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -1! f1 (ppm)



S109

¹³C NMR of **8k** (100 MHz, CDCl₃)



¹⁹F NMR of 8k (376 MHz, CDCl₃)



-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 f1 (ppm)





110 100 f1 (ppm) 190 180



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115	-120	-125	-130	-135	-140	-145	-150	-155	-160	-165	-170	-175	-180	-185	-190	
							f	1 (ppm)								



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



¹⁹F NMR of 8m (376 MHz, CDCl₃)



.34 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160 -162 -164 -166 -168 -170 -172 -174 -176 f1 (ppm)





S114

¹⁹F NMR of 8n (376 MHz, CDCl₃)



-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 f1 (ppm)



¹H NMR of **80** (400 MHz, d₆-DMSO)

12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



¹⁹F NMR of 80 (376 MHz, CDCl₃)







¹³C NMR of **8p** (100 MHz, d₆-DMSO)



^{110 100} f1 (ppm) 160 150

S117



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



110 100 f1 (ppm)

 $^{19}\mathrm{F}$ NMR of $\mathbf{8q}$ (376 MHz, CDCl_3)



-150 f1 (ppm) -80 -90 -100 -110 -120 -130 -140 -160 -170 -180 -190 -200 -210 -220

¹H NMR of **8r** (400 MHz, d_6 -DMSO)



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)



f1 (ppm)

S120



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)



 $^{19}\mathrm{F}$ NMR of 8s (376 MHz, CDCl_3)



-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 f1 (ppm)





¹³C NMR of **8t** (100 MHz, d₆-DMSO)



f1 (ppm) 160 150



· · ·																	· · · ·
110	-115	-120	-125	-130	-135	-140	-145	-150	-155	-160	-165	-170	-175	-180	-185	-190	-19
								f1	(ppm)								



S124



¹⁹F NMR of 8u (376 MHz, CDCl₃)



^{-90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205} f1 (ppm)





 ^{13}C NMR of 8v (100 MHz, d₆-DMSO)

f1 (ppm) 190 180 170 160 150 130 120

¹⁹F NMR of 8v (376 MHz, CDCl₃)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)



¹⁹F NMR of 8w (376 MHz, CDCl₃)



^{95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195} f1 (ppm)





f1 (ppm) 140 130



-115 -150 fl (ppm) -1 -125 -185 -120 -130 -135 -140-145 -155 -160 -165 -170 -175 -180



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm)



¹⁹F NMR of **8y** (376 MHz, d₆-DMSO)



-140 -150 fl (ppm) -60 -70 -80 -90 -100 -110 -120 -130 -160 -170 -180 -190 -200 -210 -220

¹H NMR of **10** (400 MHz, CDCl₃)





12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)







¹H NMR of **15** (400 MHz, CDCl₃)



¹³C NMR of **15** (100 MHz, CDCl₃)

- 198.0	- 137.2 7 / 138.5 7 / 138.5	- 26.5
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^{110 100} f1 (ppm) 190 180

¹H NMR of **7** (400 MHz, CDCl₃)





f1 (ppm) 200 190 180 170 160 150 140 130 120





f1 (ppm) 200 190 180 170 160 150 140 130 120