

Supporting Information

Catalyst-free benzylic C(sp³)-H cross-coupling with organotrifluoroborates enabled by electrochemistry

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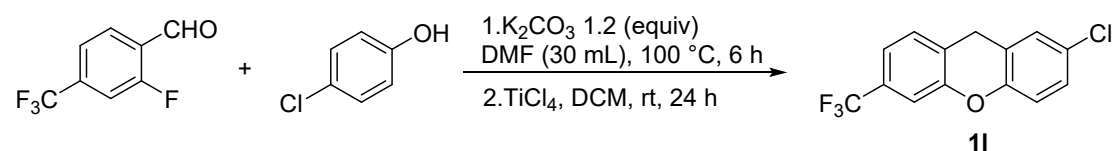
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1. General Considerations

All ^1H NMR and ^{13}C NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer (600 MHz and 151 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) and a Thermo Fisher Scientific LTQ FTICR-MS instrument. Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus.

The starting materials, such as xanthene and potassium benzyltrifluoroborate reagents, are prepared according to the reported methods.^{1,2} All the solvents are commercially available and directly used in this electrochemical system. Products were purified by flash chromatography on silica gels, eluting with petroleum ether.

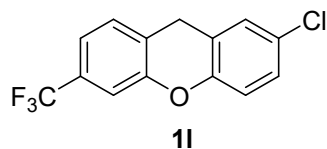
2. Typical procedure for the synthesis of 2-chloro-6-(trifluoromethyl)-9H-xanthene (11).¹



DMF (30 mL), 2-fluoro-4-(trifluoromethyl)benzaldehyde (10 mmol, 1.9 g), 4-chlorophenol (12 mmol, 1.5 g), and potassium carbonate (12 mmol, 1.65 g) were added to a 100 mL round-bottom flask, and the mixture was stirred at 100 °C for 6 h. After addition of water, the reaction solution was extracted with dichloromethane (3 × 100 mL), washed with saturated brine, filtered through Na_2SO_4 and dried, and concentrated to obtain the crude product. The crude product does not require further processing.

To a solution of the crude product from the previous step in DCM (10 mL) was added TiCl_4 (1 M solution in DCM, 40 mL, 4.0 equiv.) at room temperature, and the mixture was stirred at room temperature for 24 h. The reaction was quenched by the

addition of H₂O, stirred for 30 min, then was extracted three times with DCM (20 mL), washed with brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified by silica gel flash column chromatography (PE) to afford the desired products **11**.



2-Chloro-6-(trifluoromethyl)-9H-xanthene (**11**)

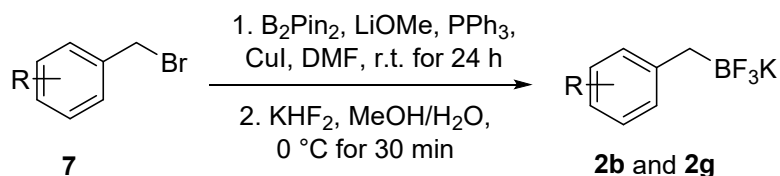
The titled compound was obtained as a white powder, 0.9 g (32 % yield).

¹H NMR (600 MHz, CDCl₃) δ 7.30 (s, 1H), 7.29–7.28 (m, 2H), 7.19–7.17 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 2H).

¹⁹F NMR (565 MHz, CDCl₃) δ -62.69.

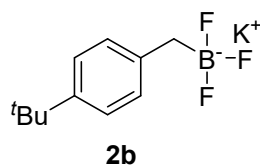
EI calcd for C₁₄H₈ClF₃O⁺ [M]⁺ 284.0210, found 284.0208.

3. General procedure for the synthesis of potassium benzyltrifluoroborates²



Bis(pinacolato)diboron (11.58 g, 45 mmol, 1.5 equiv), triphenylphosphine (1.02 g, 3.9 mmol, 13 mol%), CuI (0.57 g, 3.0 mmol, 10 mol%), and LiOMe (2.28 g, 60 mmol, 2 equiv), were mixed in 50 mL dry DMF under Ar. Then, benzylic bromide (30 mmol, 1 equiv) was added. The reaction mixture was stirred at room temperature for 24 h under inert atmosphere. The resultant black mixture was decanted into 200 mL water and extracted by EtOAc (3×150 mL). The organic phases were combined and washed with saturated NaCl solution (3×100 mL). After drying under vacuum, the residue was suspended in 100 mL CH₃OH. And then, KHF₂ (1:1 ratio of KF and HF) (18.7 g, 240 mmol, 8 equiv) in 60 mL water solution was added dropwise at 0 °C over 30 min. The obtained suspension was warmed up to room temperature and concentrated under reduced pressure. The resultant residue was suspended in 50 mL

EtOH and dried by rotary evaporation, which was repeated for 3 times to remove pinacol and H₂O. The obtained solid was further suspended in hot acetone (3×200 mL) and filtered. The filtrate was dried by rotary evaporation. The resultant residue was further purified by washing with CH₂Cl₂ (2×20 mL) and hexane (2×30 mL) to afford the desired potassium benzylic trifluoroborate salts.



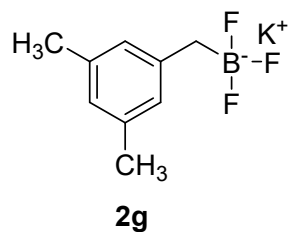
Potassium (4-(*tert*-butyl)benzyl)trifluoroborate (**2b**)

The titled compound was obtained as a white powder, 5.5 g (72 % yield).

¹H NMR (600 MHz, DMSO-*d*₆) δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 1.36 (s, 2H), 1.19 (s, 9H).

¹⁹F NMR (565 MHz, DMSO-*d*₆) δ -136.48.

ACPI-MS calcd for C₁₁H₁₅BF₃⁻ [M]⁻ 215.1224, found 215.1224.



Potassium (3,5-dimethylbenzyl)trifluoroborate (**2g**)

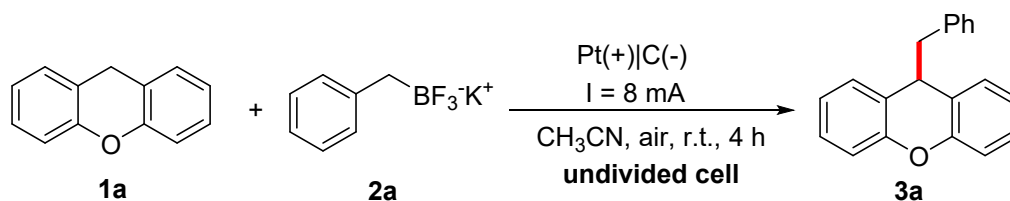
The titled compound was obtained as a white powder, 4.5 g (67 % yield).

¹H NMR (600 MHz, DMSO-*d*₆) δ 6.55 (s, 2H), 6.45 (s, 1H), 2.10 (s, 6H), 1.34 (s, 2H).

¹⁹F NMR (565 MHz, DMSO-*d*₆) δ -136.51.

ACPI-MS calcd for C₉H₁₁BF₃⁻ [M]⁻ 187.0911, found 187.0911.

4. Typical Procedure for the Synthesis of 3a



Xanthene (**1a**, 0.30 mmol, 1.0 equiv), potassium benzyltrifluoroborate (**2a**, 0.40 mmol, 1.3 equiv), CH₃CN (5.0 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A platinum electrode (10 mm×10 mm×0.3 mm) anode and a carbon rod (Φ 6 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at room temperature for 4 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether) to give the desired product **3a** as a white solid (66.5 mg, 81% yield).

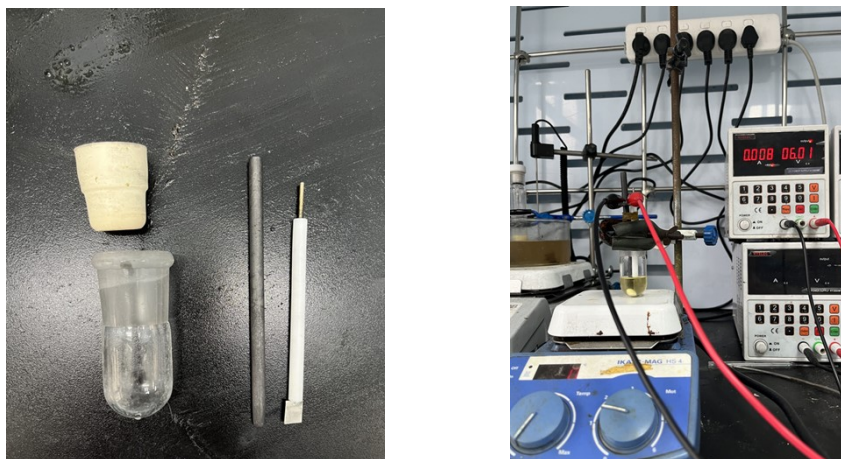
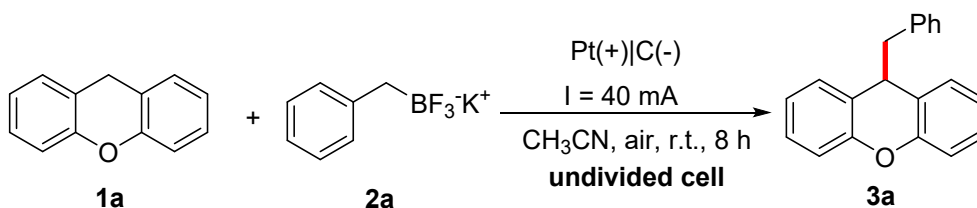


Figure S1 Experiment setup for the benzylic C(sp³)-H cross-coupling with organotrifluoroborates

5. Gram-scale Synthesis of **3a**



Xanthene (**1a**, 546.6 mg, 3.0 mmol, 1.0 equiv), potassium benzyltrifluoroborate (**2a**, 792.2 mg, 4.0 mmol, 1.3 equiv), CH₃CN (20 mL) was sequentially added to a 50 mL oven-dried undivided three neck bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A platinum electrode (10 mm×10 mm×0.3 mm) anode and a carbon rod (Φ 6 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 40 mA under air at room temperature for 8 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography to give the desired product **3a** (562.8 mg, 69 % yield).

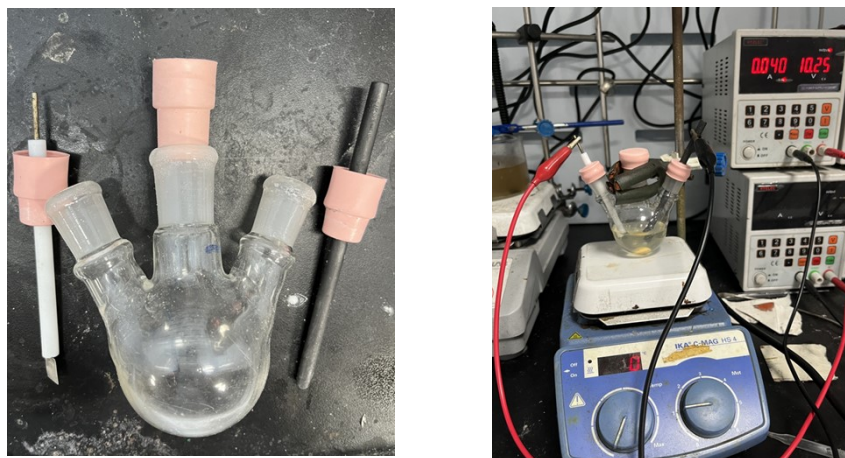


Figure S2 Experiment setup for the gram-scale synthesis of **3a**.

6. Mechanistic experiments

6.1 Cyclic voltammetry studies

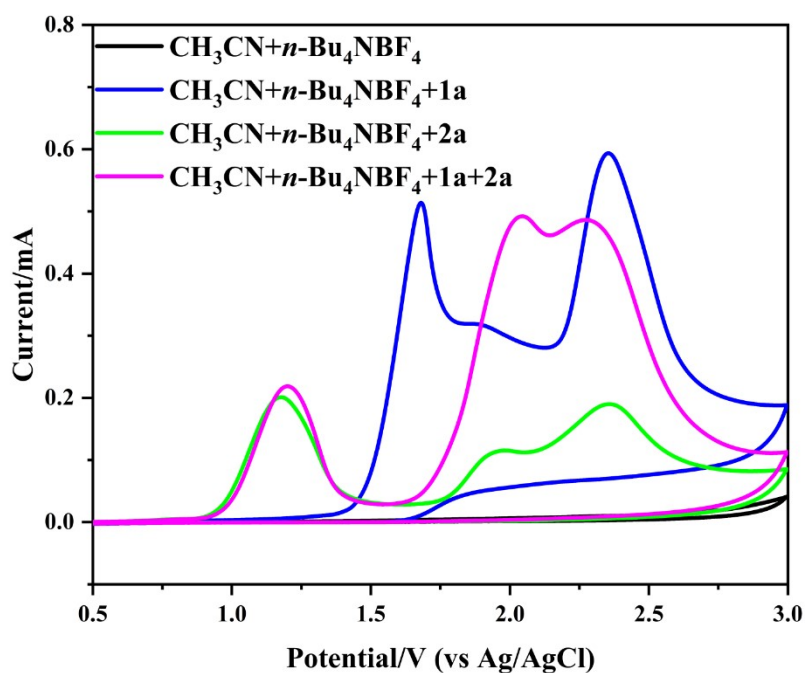
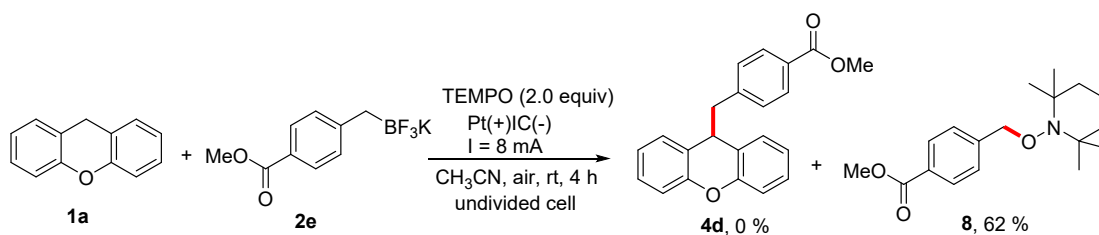


Figure S3 A cyclic voltammogram recorded in CH₃CN with 0.1 M *n*-Bu₄NBF₄ as the supporting electrolyte. **1a** (1 mM), **2a** (1 mM), **1a+2a** (1 mM).

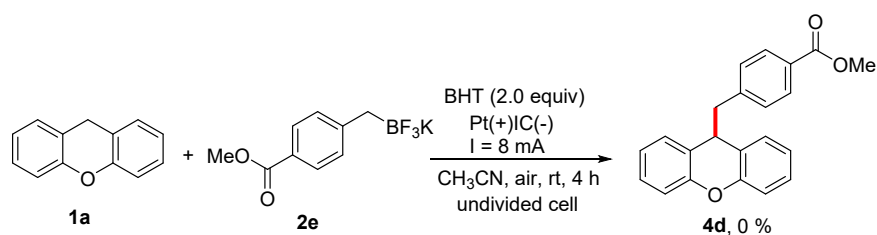
Cyclic voltammetry was performed in a three electrode cell connected to a Schlenk line at room temperature. The working electrode was a glassy carbon electrode, and the counter electrode was a platinum electrode. The reference was an Ag/AgCl wire, and CH₃CN (10 mL) containing 0.1 M *n*-Bu₄NBF₄ was poured into the electrochemical cell in all experiments. Under ambient conditions, the LK98C electrochemical workstation was used with an applied potential range of 0.5 V to 3.0 V and a scan rate of 0.1 V/s. The test concentrations of **1a**, **2a** and **1a+2a** are 1 mM, respectively.

6.2 Radical-trapping experiment with TEMPO



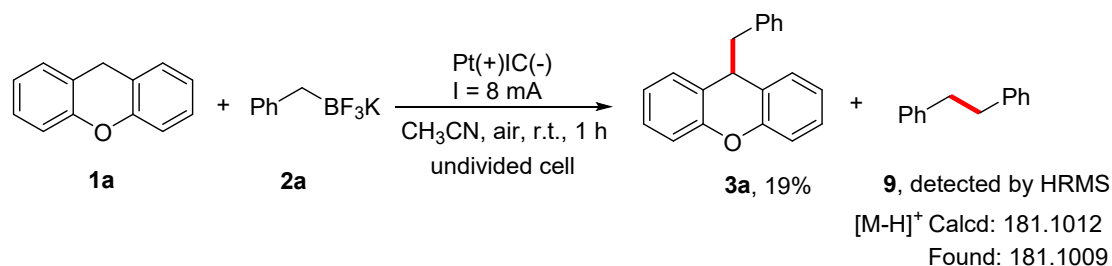
Xanthene **1a** (0.30 mmol, 1.0 equiv), **2e** (0.40 mmol, 1.3 equiv), TEMPO (0.6 mmol, 2.0 equiv), CH₃CN (5.0 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A platinum electrode (10 mm×10 mm×0.3 mm) anode and a carbon rod (Φ 6 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at room temperature for 4 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether/ethylacetate = 50:1) to give the desired product **8** (75.8 mg, 62%).

6.3 Radical-trapping experiment with BHT



Xanthene **1a** (0.30 mmol, 1.0 equiv), **2e** (0.40 mmol, 1.3 equiv), BHT (0.6 mmol, 2.0 equiv), CH₃CN (5.0 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A platinum electrode (10 mm×10 mm×0.3 mm) anode and a carbon rod (Φ 6 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at room temperature for 4 h.

6.4 Radical-trapping experiment with HRMS



Xanthene (**1a**, 0.30 mmol, 1.0 equiv), potassium benzyltrifluoroborate (**2a**, 0.40 mmol, 1.3 equiv), CH₃CN (5.0 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A platinum electrode (10 mm×10 mm×0.3 mm) anode and a carbon rod (Φ 6 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at room temperature for 1 h. After completion of the reaction, the resulted mixture is detected by HRMS (Figures S3, data of [M-H]⁺ was showed). The reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether) to give the desired product **3a** (15.7 mg, 19%).

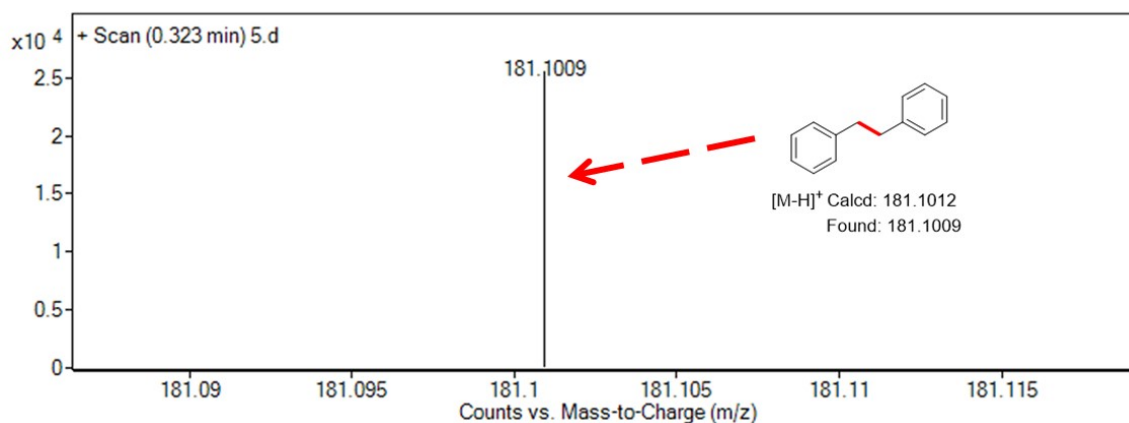
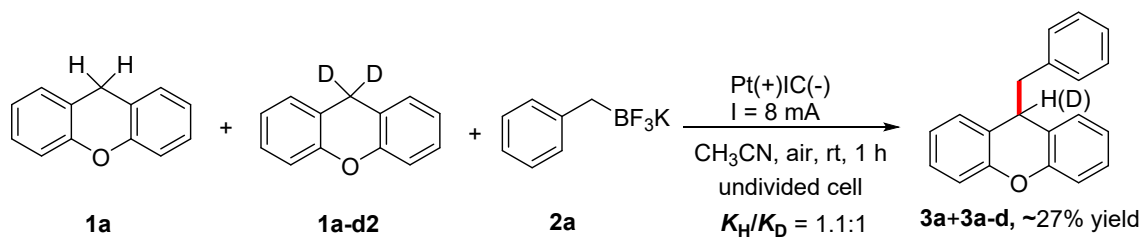
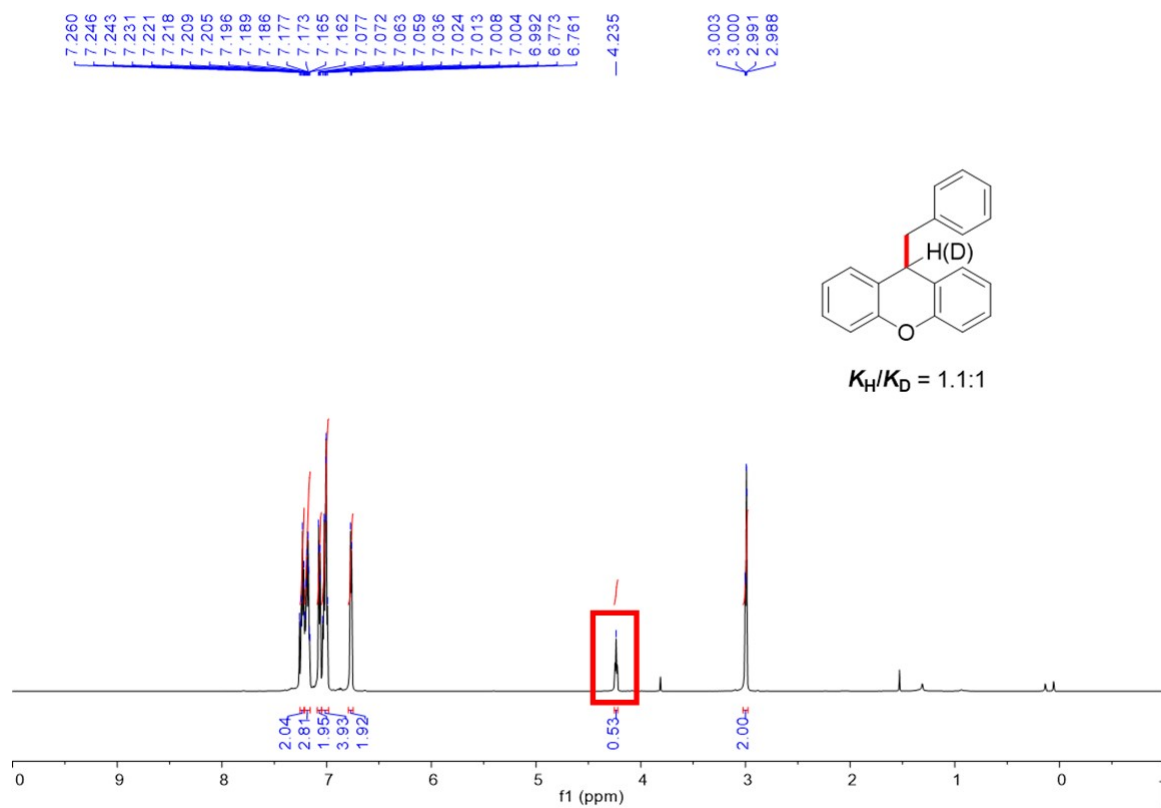
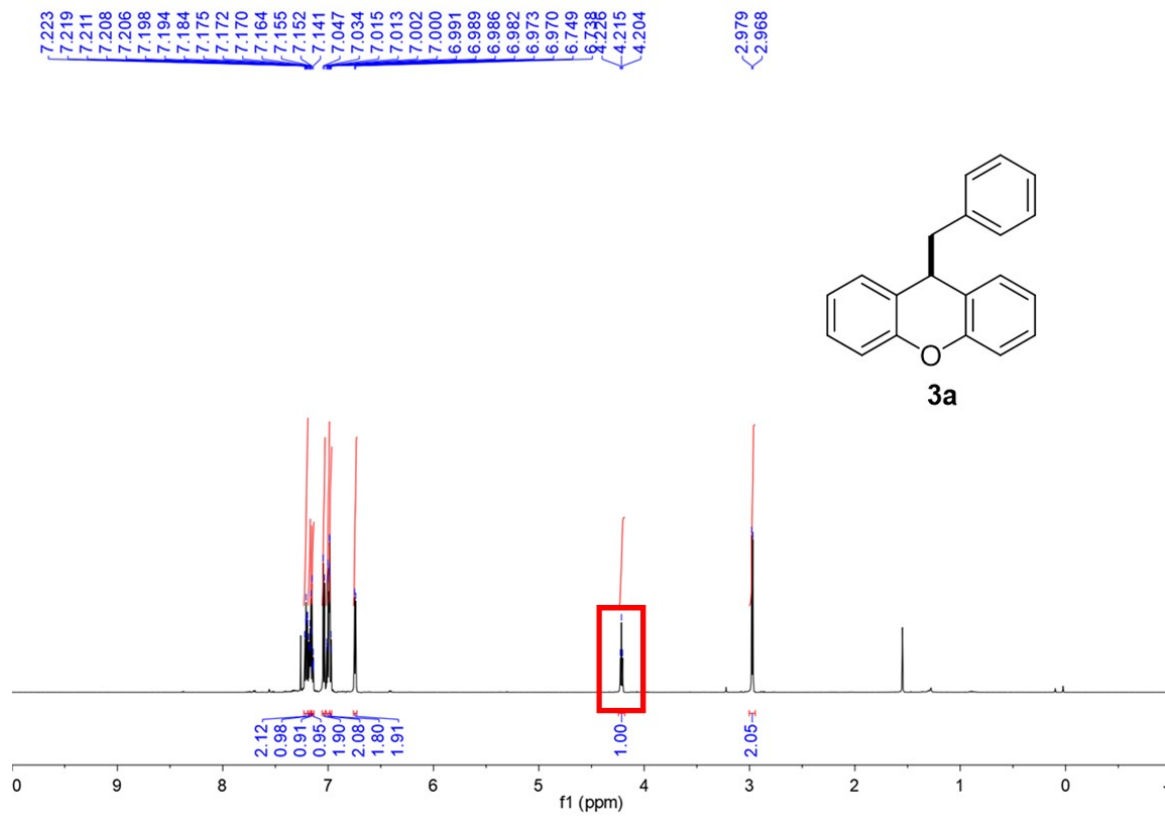


Figure S4 Detection of **9** with HRMS

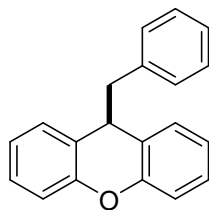
6.5 KIE experiments



Xanthene **1a** (0.15 mmol, 1.0 equiv), **1a-d2** (0.15 mmol, 1.0 equiv), **2a** (0.40 mmol, 1.3 equiv), CH₃CN (5.0 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A platinum electrode (10 mm×10 mm×0.3 mm) anode and a carbon rod (Φ 6 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at room temperature for 1 h. After that, the mixture in reaction tube was detected by TLC. The crude product was purified by flash chromatography (silica gel, petroleum ether), affording the desired product **3a** and **3a-d** as a White solid (22.1 mg, 27% yield). The ratio of **3a/3a-d** was determined as 1.1:1 by ¹H NMR analysis.



7. Characterization data for the products



3a

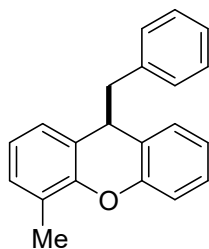
9-Benzyl-9H-xanthene (3a)³: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3a** (66.5 mg, 81% yield).

White solid; m.p.: 122.1~124.4 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.22–7.19 (m, 2H), 7.18–7.17 (m, 1H), 7.16 (d, *J* = 5.4 Hz, 1H), 7.15–7.14 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.02–6.99 (m, 2H), 6.99–6.97 (m, 2H), 6.74 (d, *J* = 6.6 Hz, 2H), 4.22 (t, *J* = 6.6 Hz, 1H), 2.97 (d, *J* = 6.6 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 152.3, 138.1, 129.8, 128.9, 127.8, 127.6, 126.2, 124.6, 122.8, 116.2, 47.5, 41.7.

HRMS (ESI) calcd for C₂₀H₁₅O⁺ [M-H]⁺ 271.1129, found 271.1127.



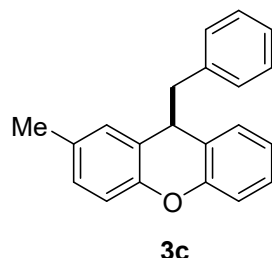
3b

9-Benzyl-4-methyl-9H-xanthene (3b): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3b** (61.7 mg, 72% yield).

White solid; m.p.: 104.3~106.2 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.22 (t, *J* = 7.8 Hz, 1H), 7.19 – 7.17 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 2H), 4.18 (t, *J* = 6.6 Hz, 1H), 2.99–2.92 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.4, 150.5, 138.4, 129.8, 128.9, 128.8, 127.8, 127.4, 126.3, 126.2, 125.4, 124.9, 124.4, 122.7, 122.3, 116.3, 47.5, 42.1, 15.8.
ACPI-MS calcd for $\text{C}_{21}\text{H}_{19}\text{O}^+$ $[\text{M}+\text{H}]^+$ 287.1430, found 287.1431.



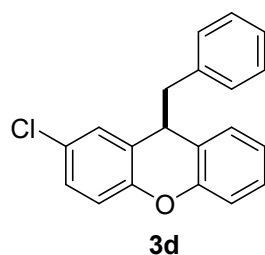
9-Benzyl-2-methyl-9H-xanthene (3c): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3c** (66.9 mg, 78% yield).

White solid; m.p.: 105.2~107.4 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21–7.16 (m, 4H), 7.03 (t, $J = 9.6$ Hz, 2H), 6.98 (t, $J = 7.2$ Hz, 1H), 6.95–6.93 (m, 2H), 6.78 (s, 1H), 6.76 (d, $J = 7.2$ Hz, 2H), 4.16 (t, $J = 6.6$ Hz, 1H), 3.00–2.94 (m, 2H), 2.29 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.4, 150.1, 138.3, 132.1, 129.8, 129.2, 128.9, 128.2, 127.8, 127.5, 126.2, 124.5, 124.3, 122.6, 116.2, 115.9, 47.5, 41.8, 20.7.

ACPI-MS calcd for $\text{C}_{21}\text{H}_{19}\text{O}^+$ $[\text{M}+\text{H}]^+$ 287.1430, found 287.1433.



9-Benzyl-2-chloro-9H-xanthene (3d): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3d** (59.9 mg, 65% yield).

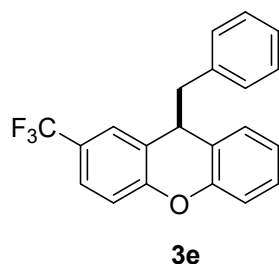
White solid; m.p.: 112.5~114.6°C.

^1H NMR (600 MHz, CDCl_3) δ 7.23 (d, $J = 7.8$ Hz, 1H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.17 (m, $J = 6.6$ Hz, 3H), 7.03–7.02 (m, 2H), 6.98 (d, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz,

1H), 6.95 (s, 1H), 6.73 (d, $J = 7.8$ Hz, 2H), 4.16 (t, $J = 6.6$ Hz, 1H), 2.97 (d, $J = 6.0$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.9, 150.8, 137.5, 129.7, 128.8, 128.5, 127.9, 127.8, 127.6, 127.4, 126.5, 126.2, 123.7, 123.1, 117.5, 116.2, 47.3, 41.6.

ACPI-MS calcd for $\text{C}_{20}\text{H}_{14}\text{OCl}^+$ $[\text{M}-\text{H}]^+$ 305.0728, found 305.0729.



9-Benzyl-2-(trifluoromethyl)-9H-xanthene (3e): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3e** (63.7 mg, 62% yield).

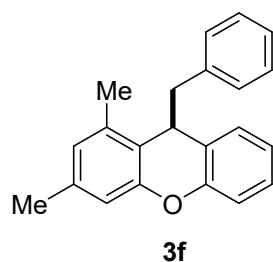
White solid; m.p.: 103.1~105.4 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 1H), 7.25–7.22 (m, 1H), 7.19 (t, $J = 7.2$ Hz, 1H), 7.15 (t, $J = 7.2$ Hz, 2H), 7.12–7.07 (m, 2H), 7.06–7.04 (m, 3H), 6.70 (d, $J = 6.6$ Hz, 2H), 4.22 (t, $J = 6.6$ Hz, 1H), 3.00 (dd, $J = 13.2, 6.6$ Hz, 1H), 2.93 (dd, $J = 13.2, 6.6$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 154.6, 151.6, 137.4, 129.7, 128.8, 128.0, 128.0, 126.6, 126.5, 126.4 (q, $J = 3.8$ Hz), 124.9, 124.9, 124.0, 123.6, 122.3 (q, $J = 267.9$ Hz), 116.6, 116.4, 47.5, 41.6.

^{19}F NMR (565 MHz, CDCl_3) δ -57.9.

ACPI-MS calcd for $\text{C}_{21}\text{H}_{14}\text{OF}_3^+$ $[\text{M}-\text{H}]^+$ 339.0991, found 339.0995.



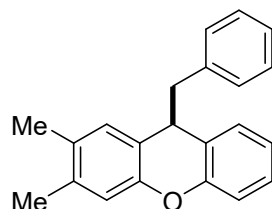
9-Benzyl-1,3-dimethyl-9H-xanthene (3f): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3f** (53.4 mg, 59% yield).

White solid; m.p.: 116.3.1~118.0 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.20–7.16 (m, 4H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.79 (s, 2H), 6.74 (d, *J* = 6.6 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.22 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.96 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.77 (dd, *J* = 12.6, 7.8 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 152.8, 152.7, 138.5, 137.0, 135.7, 129.7, 128.9, 127.9, 127.4, 126.2, 125.9, 125.4, 122.3, 121.2, 116.0, 114.8, 44.9, 39.3, 21.0, 18.3.

ACPI-MS calcd for C₂₂H₂₁O⁺ [M+H]⁺ 301.1587, found 301.1588.



3g

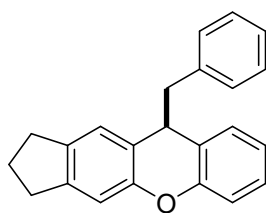
9-Benzyl-2,3-dimethyl-9H-xanthene (3g): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3g** (63.1 mg, 70% yield).

White solid; m.p.: 118.2~120.4 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.21–7.17 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.86 (s, 1H), 6.79 (d, *J* = 7.8 Hz, 2H), 6.76 (s, 1H), 4.15 (t, *J* = 7.2 Hz, 1H), 3.01–2.93 (m, 2H), 2.27 (s, 3H), 2.20 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 152.4, 150.1, 138.5, 135.9, 130.8, 129.8, 129.5, 129.0, 127.8, 127.4, 126.1, 124.6, 122.4, 121.7, 117.0, 116.1, 47.6, 41.3, 19.6, 18.9.

ACPI-MS calcd for C₂₂H₂₁O⁺ [M+H]⁺ 301.1587, found 301.1587.



3h

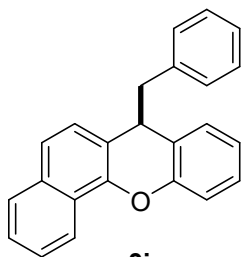
10-Benzyl-1,2,3,10-tetrahydrocyclopenta[b]xanthene (3h): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3h** (69.1 mg, 74% yield).

White solid; m.p.: 101.6.1~103.5 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.19–7.16 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.93 (s, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.85 (s, 1H), 6.79 (d, *J* = 6.0 Hz, 2H), 4.14 (t, *J* = 6.6 Hz, 1H), 2.98 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.95–2.87 (m, 3H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.14–2.05 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 152.6, 151.0, 143.8, 138.6, 138.5, 129.8, 128.9, 127.8, 127.4, 126.1, 124.8, 124.0, 122.6, 122.4, 116.1, 112.0, 47.6, 42.2, 32.8, 32.1, 25.8.

ACPI-MS calcd for C₂₃H₂₁O⁺ [M+H]⁺ 313.1587, found 313.1589.



3i

7-Benzyl-7H-benzo[c]xanthene (3i): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3i** (70.2 mg, 73% yield).

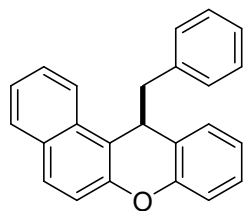
White solid; m.p.: 133.6~134.8 °C.

¹H NMR (600 MHz, CDCl₃) δ 8.38 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 2H), 7.27–7.25 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 6.6 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.05 (t,

$J = 6.6$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.78 (d, $J = 7.2$ Hz, 2H), 4.36 (t, $J = 6.6$ Hz, 1H), 3.09–3.02 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.2, 147.0, 138.2, 133.3, 129.8, 128.9, 127.9, 127.6, 127.46, 126.6, 126.2, 126.0, 125.7, 124.5, 124.1, 123.1, 122.3, 121.5, 118.5, 116.4, 47.4, 41.8.

ACPI-MS calcd for $\text{C}_{24}\text{H}_{19}\text{O}^+$ $[\text{M}+\text{H}]^+$ 323.1430, found 323.1432.



3j

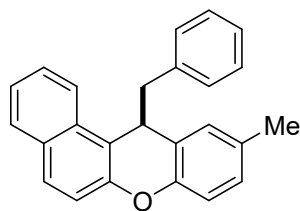
12-Benzyl-12H-benzo[a]xanthene (3j): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3j** (63.8 mg, 66% yield).

White solid; m.p.: 131.6~132.4 °C.

^1H NMR (600 MHz, CDCl_3) δ 8.17 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.75 (d, $J = 9.0$ Hz, 1H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.23 (t, $J = 8.4$ Hz, 2H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.10 (t, $J = 7.2$ Hz, 2H), 7.07 (d, $J = 7.8$ Hz, 1H), 7.01 (t, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 2H), 4.95 (dd, $J = 7.8, 4.2$ Hz, 1H), 3.17 (dd, $J = 13.2, 4.2$ Hz, 1H), 3.01 (dd, $J = 13.2, 8.4$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.1, 150.1, 138.1, 131.2, 130.7, 129.8, 129.2, 128.9, 128.32, 127.7, 127.6, 126.7, 126.2, 124.0, 123.8, 122.9, 122.0, 117.8, 116.5, 115.9, 44.6, 37.7.

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{O}^+$ $[\text{M}-\text{H}]^+$ 321.1284, found 321.1281.



3k

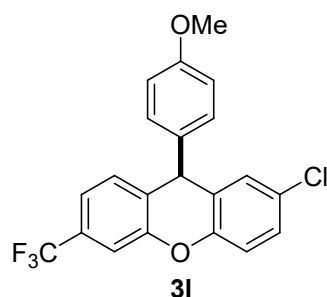
12-Benzyl-10-methyl-12*H*-benzo[*a*]xanthene (3k): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3k** (76.5 mg, 76% yield).

White solid; m.p.: 135.1~136.5 °C.

¹H NMR (600 MHz, CDCl₃) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.67 (s, 1H), 6.60 (d, *J* = 7.2 Hz, 2H), 4.87 (dd, *J* = 7.8, 5.4 Hz, 1H), 3.15 (dd, *J* = 13.2, 4.2 Hz, 1H), 2.98 (dd, *J* = 13.2, 7.8 Hz, 1H), 2.25 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 150.3, 145.0, 138.2, 132.1, 131.3, 130.6, 129.8, 129.5, 128.8, 128.2, 128.1, 127.6, 126.7, 126.2, 123.9, 123.4, 122.0, 117.8, 116.4, 115.5, 44.6, 37.8, 20.7.

ACPI-MS calcd for C₂₅H₂₁O⁺ [M+H]⁺ 337.1587, found 337.1584.



2-chloro-9-(4-methoxyphenyl)-6-(trifluoromethyl)-9*H*-xanthene (3l): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3l** (59.4 mg, 51% yield).

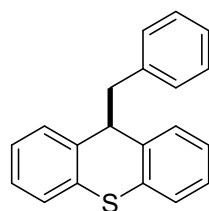
White solid; m.p.: 125.3~126.8 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.38 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.09–7.07 (m, 3H), 7.00 (d, *J* = 1.8 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.18 (s, 1H), 3.78 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 158.8, 150.7, 149.1, 137.1, 131.0, 130.4, 129.5, 129.3, 128.5, 128.3, 125.4 (q, *J* = 272.0 Hz), 127.8, 125.6, 120.0 (q, *J* = 7.2 Hz), 118.0, 114.5, 114.0 (q, *J* = 4.4 Hz), 55.3, 43.3.

^{19}F NMR (565 MHz, CDCl_3) δ -62.7.

EI calcd for $\text{C}_{21}\text{H}_{14}\text{ClF}_3\text{O}_2^+$ $[\text{M}]^+$ 390.0629, found 390.0635.



3m

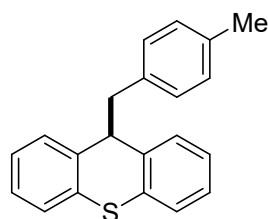
9-Benzyl-9H-thioxanthene (3m): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3m** (59.6 mg, 69% yield).

White solid; m.p.: 126.1~128.5 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.44 (d, J = 7.8 Hz, 2H), 7.20–7.16 (m, 5H), 7.09 (t, J = 7.2 Hz, 2H), 6.96 (d, J = 7.8 Hz, 2H), 6.85–6.83 (m, 2H), 4.19 (t, J = 7.8 Hz, 1H), 3.01 (d, J = 7.8 Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.3, 137.2, 132.2, 129.5, 129.2, 127.9, 126.7, 126.5, 126.2, 126.0, 52.2, 38.9.

ACPI-MS calcd for $\text{C}_{20}\text{H}_{17}\text{S}^+$ $[\text{M}+\text{H}]^+$ 289.1045, found 289.1042.



3n

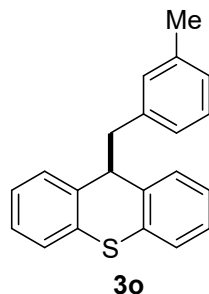
9-(4-Methylbenzyl)-9H-thioxanthene (3n): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3n** (66.4 mg, 73% yield).

White solid; m.p.: 129.3~130.6 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.45 (d, J = 7.8 Hz, 2H), 7.20 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.8 Hz, 2H), 6.99 (t, J = 7.2 Hz, 4H), 6.75 (d, J = 7.8 Hz, 2H), 4.18 (t, J = 7.8 Hz, 1H), 2.99 (d, J = 7.8 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 137.4, 136.2, 135.4, 132.1, 129.3, 129.2, 128.6, 126.6, 126.4, 126.2, 52.2, 38.5, 21.0.

ACPI-MS calcd for $\text{C}_{21}\text{H}_{19}\text{S}^+$ $[\text{M}+\text{H}]^+$ 303.1202, found 303.1203.



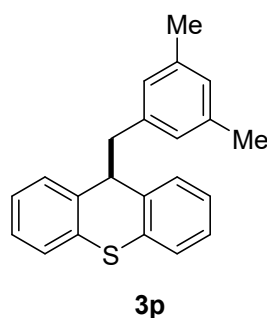
9-(3-Methylbenzyl)-9H-thioxanthene (3o): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3o** (63.4 mg, 70% yield).

White solid; m.p.: 116.1~118.4 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.46 (d, $J = 7.8$ Hz, 2H), 7.21 (t, $J = 7.2$, 2H), 7.12 (t, $J = 7.8$, 2H), 7.08 (t, $J = 7.8$ Hz, 1H), 6.99 (t, $J = 7.2$ Hz, 3H), 6.66 (d, $J = 6.0$ Hz, 2H), 4.19 (t, $J = 7.8$ Hz, 1H), 3.00 (d, $J = 7.8$ Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.1, 137.4, 137.3, 132.1, 130.4, 129.2, 127.7, 126.7, 126.6, 126.5, 126.1, 52.1, 38.8, 21.3.

ACPI-MS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{S}^+$ $[\text{M}+\text{H}]^+$ 303.1202, found 303.1202.



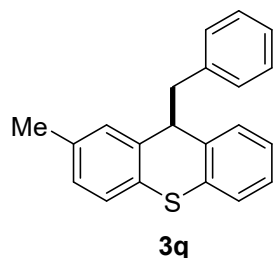
9-(3,5-Dimethylbenzyl)-9H-thioxanthene (3p): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3p** (64.9 mg, 68% yield).

White solid; m.p.: 119.8~120.4 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.49 (d, $J = 7.8$ Hz, 2H), 7.23 (t, $J = 7.8$ Hz, 2H), 7.14 (t, $J = 7.2$ Hz, 2H), 7.01 (d, $J = 7.2$ Hz, 2H), 6.85 (s, 1H), 6.48 (s, 2H), 4.20 (t, $J = 7.8$ Hz, 1H), 2.99 (d, $J = 7.8$ Hz, 2H), 2.25 (s, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.1, 137.4, 137.2, 132.1, 129.3, 127.5, 127.4, 126.6, 126.4, 126.0, 52.1, 38.8, 21.1.

ACPI-MS calcd for $\text{C}_{22}\text{H}_{21}\text{S}^+$ $[\text{M}+\text{H}]^+$ 317.1358, found 317.1358.



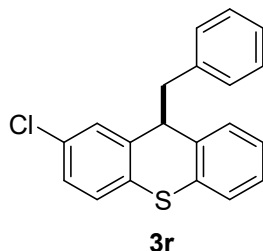
9-Benzyl-2-methyl-9H-thioxanthene (3q): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3q** (64.6 mg, 71% yield).

White solid; m.p.: 125.3~126.4 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.44 (d, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 7.8$ Hz, 1H), 7.20–7.17 (m, 4H), 7.07 (t, $J = 7.8$ Hz, 1H), 7.02 (d, $J = 8.4$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.86–6.84 (m, 3H), 4.14 (t, $J = 7.8$ Hz, 1H), 3.06 (dd, $J = 13.2, 8.4$ Hz, 1H), 2.99 (dd, $J = 13.2, 7.8$ Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.4, 137.3, 137.1, 136.0, 132.5, 129.8, 129.5, 129.3, 128.7, 127.8, 127.3, 126.6, 126.5, 126.4, 126.0, 125.9, 52.2, 38.9, 20.9.

ACPI-MS calcd for $\text{C}_{21}\text{H}_{19}\text{S}^+$ $[\text{M}+\text{H}]^+$ 303.1202, found 303.1202.



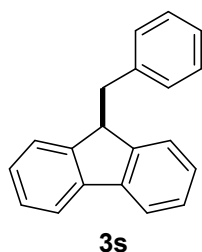
9-Benzyl-2-chloro-9H-thioxanthene (3r): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3r** (63.9 mg, 66% yield).

White solid; m.p.: 113.6~114.9 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.42 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.21–7.16 (m, 5H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.96 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.84–6.83 (m, 2H), 4.13 (t, *J* = 7.8 Hz, 1H), 3.04–2.95 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 139.0, 138.7, 136.4, 131.9, 131.7, 130.8, 129.4, 129.3, 129.0, 128.0, 127.7, 126.7, 126.6, 126.5, 126.4, 126.2, 52.0, 38.7.

ACPI-MS calcd for C₂₀H₁₄SCl⁺ [M-H]⁺ 323.0499, found 323.0495.



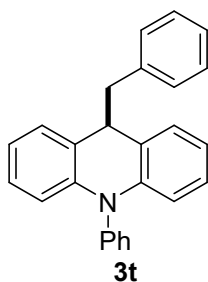
9-Benzyl-9H-fluorene (3s): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **3s** (36.1 mg, 47% yield).

White solid; m.p.: 125.3~126.6 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 3H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.23 (t, *J* = 7.8 Hz, 1H), 3.11 (d, *J* = 7.8 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 146.8, 139.8, 138.8, 128.5, 127.3, 126.1, 125.6, 125.3, 123.8, 118.8, 47.7, 39.1.

ACPI-MS calcd for C₂₀H₁₇⁺ [M+H]⁺ 257.1325, found 257.1325.



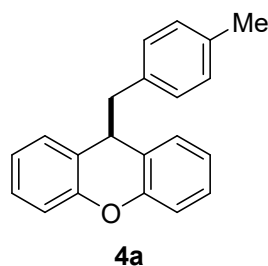
9-Benzyl-10-phenyl-9,10-dihydroacridine (3t): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3t** (58.3 mg, 56% yield).

White solid; m.p.: 136.9~138.1 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.54 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.97–6.93 (m, 4H), 6.85 (t, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 7.8 Hz, 2H), 6.12 (d, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 6.0 Hz, 1H), 2.99 (d, *J* = 6.0 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 142.1, 140.7, 138.5, 131.1, 130.6, 130.0, 128.6, 128.0, 127.6, 126.6, 125.9, 123.6, 120.3, 113.6, 47.8, 44.7.

ACPI-MS calcd for C₂₆H₂₂N⁺ [M+H]⁺ 348.1747, found 348.1748.



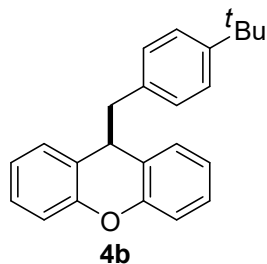
9-(4-Methylbenzyl)-9H-xanthene (4a): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4a** (71.1 mg, 83% yield).

White solid; m.p.: 105.2~107.5 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.21–7.19 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.01–6.95 (m, 6H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.17 (t, *J* = 7.2 Hz, 1H), 2.92 (d, *J* = 6.6 Hz, 2H), 2.30 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 152.2, 135.7, 135.1, 129.6, 128.9, 128.6, 127.5, 124.8, 122.79, 116.2, 47.1, 41.8, 21.1.

ACPI-MS calcd for C₂₁H₁₉O⁺ [M+H]⁺ 287.1430, found 287.1433.



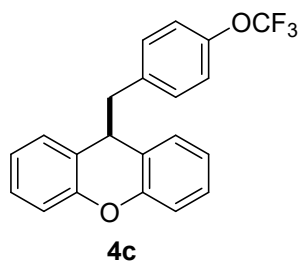
9-(4-Butylbenzyl)-9H-xanthene (4b): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4b** (83.4 mg, 85% yield).

White solid; m.p.: 102.6~104.2 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21 (t, $J = 7.8$ Hz, 4H), 7.07 (d, $J = 8.4$ Hz, 2H), 6.98 (t, $J = 7.2$ Hz, 2H), 6.93 (d, $J = 7.2$ Hz, 2H), 6.75 (d, $J = 7.8$ Hz, 2H), 4.15 (t, $J = 6.6$ Hz, 1H), 2.93 (d, $J = 6.6$ Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.2, 149.1, 135.3, 129.4, 129.0, 127.5, 125.0, 124.8, 122.7, 116.2, 47.1, 41.9, 34.4, 31.4.

ACPI-MS calcd for $\text{C}_{24}\text{H}_{25}\text{O}^+$ $[\text{M}+\text{H}]^+$ 329.1900, found 329.1902.



9-(4-(Trifluoromethoxy)benzyl)-9H-xanthene (4c): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4c** (81.2 mg, 76% yield).

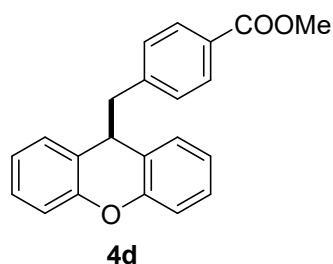
White solid; m.p.: 119.3~121.6 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.22–7.19 (m, 2H), 7.01 (d, $J = 7.8$ Hz, 3H), 7.00–6.97 (m, 4H), 6.96 (s, 1H), 6.67 (d, $J = 8.4$ Hz, 2H), 4.21 (t, $J = 6.6$ Hz, 1H), 2.96 (d, $J = 6.6$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.3, 147.9, 136.8, 131.0, 128.7, 127.8, 124.1, 123.0, 120.5 (q, $J = 256.1$ Hz) 120.3, 116.4, 46.6, 41.5.

^{19}F NMR (565 MHz, CDCl_3) δ -57.91.

ACPI-MS calcd for $C_{21}H_{16}O_2F_3^+$ $[M+H]^+$ 357.1097, found 357.1100.



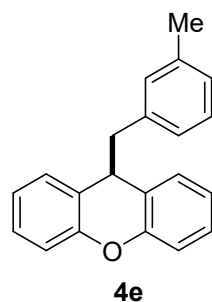
Methyl 4-((9*H*-xanthen-9-yl)methyl)benzoate (4d): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4d** (52.7 mg, 53% yield).

White solid; m.p.: 121.8~123.5 °C.

1H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, $J = 8.4$ Hz, 2H), 7.22–7.19 (m, 2H), 7.01–6.99 (m, 6H), 6.74 (d, $J = 8.4$ Hz, 2H), 4.26 (t, $J = 6.6$ Hz, 1H), 3.89 (s, 3H), 3.02 (d, $J = 6.0$ Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 152.2, 143.5, 129.8, 129.1, 128.7, 128.2, 127.8, 124.0, 123.0, 116.3, 52.0, 47.3, 41.3.

HRMS (ESI) calcd for $C_{22}H_{18}O_3Na^+$ $[M+Na]^+$ 353.1148, found 353.1145.



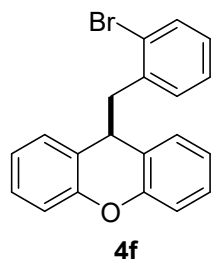
9-(3-Methylbenzyl)-9*H*-xanthene (4e): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4e** (67.0 mg, 78% yield).

White solid; m.p.: 114.1~113.4 °C.

1H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, $J = 8.4$ Hz, 2H), 7.07–7.04 (m, 3H), 7.00 (t, $J = 7.2$ Hz, 3H), 6.97 (d, $J = 7.2$ Hz, 2H), 6.56 (d, $J = 6.0$ Hz, 2H), 4.19 (t, $J = 6.6$ Hz, 1H), 2.93 (d, $J = 6.6$ Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.3, 138.1, 137.3, 130.6, 128.9, 127.7, 127.6, 126.9, 126.8, 124.8, 122.8, 116.2, 47.5, 41.8, 21.2.

ACPI-MS calcd for $\text{C}_{21}\text{H}_{17}\text{O}^+$ $[\text{M}-\text{H}]^+$ 285.1274, found 285.1275.



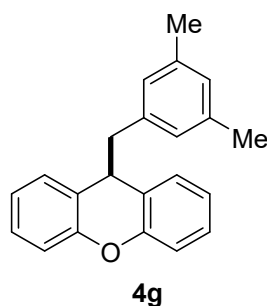
9-(2-Bromobenzyl)-9H-xanthene (4f): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4f** (67.1 mg, 64% yield).

White solid; m.p.: 134.6~136.1 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21–7.18 (m, 2H), 7.17 (d, $J = 6.6$ Hz, 1H), 7.14 (t, $J = 6.6$ Hz, 2H), 7.03 (d, $J = 7.8$ Hz, 2H), 7.00 (d, $J = 7.2$ Hz, 1H), 6.98–6.96 (m, 2H), 6.73 (d, $J = 6.6$ Hz, 2H), 4.20 (t, $J = 6.6$ Hz, 1H), 2.96 (d, $J = 6.6$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.3, 138.2, 129.8, 128.9, 127.8, 127.6, 126.2, 124.6, 122.82, 116.2, 47.5, 41.7.

ACPI-MS calcd for $\text{C}_{20}\text{H}_{16}\text{OBr}^+$ $[\text{M}+\text{H}]^+$ 363.0379, found 363.0378.



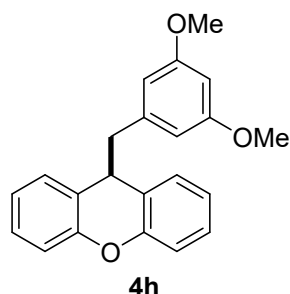
9-(3,5-Dimethylbenzyl)-9H-xanthene (4g): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4g** (71.1 mg, 79% yield).

White solid; m.p.: 116.2~118.1 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21 (t, $J = 7.2$ Hz, 2H), 7.06 (d, $J = 8.4$ Hz, 2H), 7.00 (t, $J = 7.8$ Hz, 2H), 6.96 (d, $J = 6.0$ Hz, 2H), 6.83 (s, 1H), 6.38 (s, 2H), 4.16 (t, $J = 6.6$ Hz, 1H), 2.88 (d, $J = 6.6$ Hz, 2H), 2.20 (s, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.3, 138.1, 137.2, 129.0, 127.7, 127.7, 127.5, 124.9, 122.7, 116.1, 47.5, 41.8, 21.1.

ACPI-MS calcd for $\text{C}_{22}\text{H}_{21}\text{O}^+$ $[\text{M}+\text{H}]^+$ 301.1587, found 301.1589.



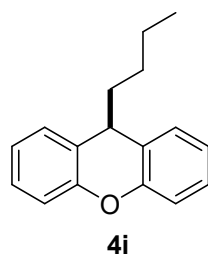
9-(3,5-Dimethoxybenzyl)-9H-xanthene (4h): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4h** (82.7 mg, 83% yield).

White solid; m.p.: 134.6~136.1 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21 (t, $J = 7.2$ Hz, 2H), 7.05–7.01 (m, 6H), 6.30 (s, 1H), 5.87 (s, 1H), 5.87 (s, 1H), 4.22 (t, $J = 6.6$ Hz, 1H), 3.61 (s, 6H), 2.91 (d, $J = 6.6$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 160.1, 152.3, 140.3, 128.9, 127.6, 124.5, 122.8, 116.2, 107.5, 99.0, 55.1, 47.7, 41.5.

ACPI-MS calcd for $\text{C}_{22}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 333.1485, found 333.1484.



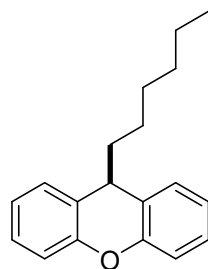
9-Butyl-9H-xanthene (4i): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4i** (44.5 mg, 62% yield).

White solid; m.p.: 103.3~104.6 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.23–7.20 (m, 4H), 7.09–7.05 (m, 4H), 3.98 (t, $J = 6.0$ Hz, 1H), 1.74–1.70 (m, 2H), 1.23–1.19 (m, 2H), 1.18–1.14 (m, 2H), 0.80 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.3, 128.6, 127.4, 125.8, 123.0, 116.3, 40.5, 39.1, 27.6, 22.7, 13.9.

ACPI-MS calcd for $\text{C}_{17}\text{H}_{19}\text{O}^+$ $[\text{M}+\text{H}]^+$ 239.1430, found 239.1432.



4j

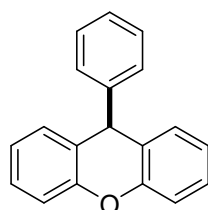
9-Hexyl-9H-xanthene (4j): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4j** (51.9 mg, 65% yield).

White solid; m.p.: 91.3~92.6 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21 (t, $J = 8.4$ Hz, 4H), 7.09–7.05 (m, 4H), 3.97 (t, $J = 6.0$ Hz, 1H), 1.72–1.69 (m, 2H), 1.26–1.17 (m, 8H), 0.79 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.3, 128.6, 127.4, 125.8, 123.0, 116.3, 40.7, 39.1, 31.8, 25.2, 22.5, 14.0.

ACPI-MS calcd for $\text{C}_{19}\text{H}_{23}\text{O}^+$ $[\text{M}+\text{H}]^+$ 267.1743, found 267.1748.



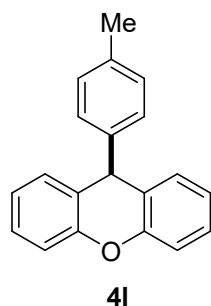
4k

9-Phenyl-9H-xanthene (4k): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4k** (67.4 mg, 87% yield).

White solid; m.p.: 138.9~140.7 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.27 (t, $J = 7.2$ Hz, 2H), 7.22–7.17 (m, 5H), 7.13 (d, $J = 7.8$ Hz, 2H), 7.06 (d, $J = 7.2$ Hz, 2H), 6.98 (t, $J = 7.2$ Hz, 2H), 5.26 (s, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.0, 146.5, 129.7, 128.7, 128.4, 127.9, 126.6, 124.4, 123.2, 116.5, 44.4.

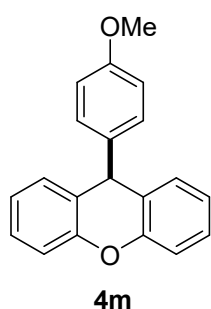


9-(*p*-Tolyl)-9*H*-xanthene (4l)⁴: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4l** (67.5 mg, 83% yield).

White solid; m.p.: 121.7~122.5 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21 (t, $J = 7.2$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 7.10 (t, $J = 9.0$ Hz, 4H), 7.07 (d, $J = 7.8$ Hz, 2H), 6.98 (t, $J = 7.2$ Hz, 2H), 5.23 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.0, 143.6, 136.2, 129.7, 129.4, 128.2, 127.8, 124.6, 123.2, 116.5, 44.0, 21.0.



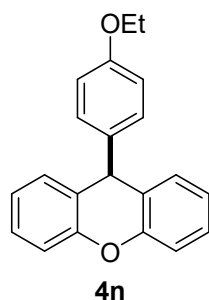
9-(4-Methoxyphenyl)-9*H*-xanthene (4m)^{1b}: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4m** (73.0 mg, 84% yield).

White solid; m.p.: 121.7~122.5 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.22 (t, $J = 7.8$ Hz, 2H), 7.15 – 7.13 (m, 4H), 7.07 (d, $J = 7.8$ Hz, 2H), 7.00 (t, $J = 7.2$ Hz, 2H), 6.83 (d, $J = 9.0$ Hz, 2H), 5.23 (s, 1H), 3.77 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.3, 151.0, 138.8, 129.6, 129.4, 127.8, 124.7, 123.2, 116.5, 114.1, 55.2, 43.5.

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{O}_2^+([\text{M}+\text{H}]^+)$: 289.1223, found: 289.1220.

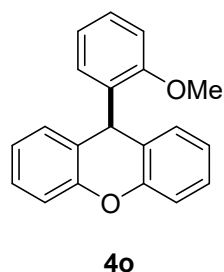


9-(4-Ethoxyphenyl)-9H-xanthene (4n)^{1b}: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4n** (79.1 mg, 87% yield). White solid; m.p.: 134.6~135.9 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.21 (t, $J = 7.8$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 7.12 (d, $J = 9.0$ Hz, 2H), 7.07 (d, $J = 7.2$ Hz, 2H), 6.99 (t, $J = 7.2$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 5.22 (s, 1H), 3.99 (q, $J = 13.8, 7.2$ Hz, 2H), 1.39 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.7, 151.0, 138.6, 129.7, 129.4, 127.7, 124.8, 123.1, 116.5, 114.6, 63.3, 43.5, 14.8.

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{18}\text{O}_2 \text{Na}^+([\text{M}+\text{Na}]^+)$: 325.1199, found: 325.1202.



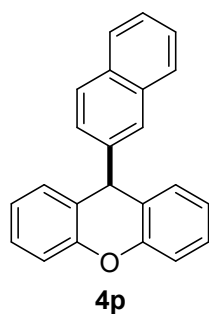
9-(2-Methoxyphenyl)-9H-xanthene (4o)⁵: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4o** (58.3 mg, 67% yield).

White solid; m.p.: 136.1~128.3 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.1 (t, $J = 7.8$ Hz, 2H), 7.15 (d, $J = 7.2$ Hz, 1H), 7.12–7.10 (m, 4H) 6.95 (t, $J = 7.8$ Hz, 3H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.83 (t, $J = 7.8$ Hz, 1H), 5.82 (s, 1H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 156.2, 151.5, 135.3, 130.3, 129.5, 127.7, 127.5, 124.8, 123.0, 121.1, 116.2, 111.0, 55.6, 36.9.

HRMS Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2^+$ $[\text{M}]^+$, 288.1150. Found 288.1159.



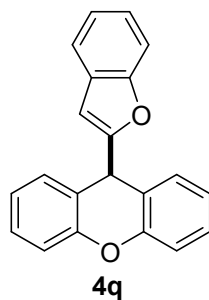
9-(Naphthalen-2-yl)-9H-xanthene (4p): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4p** (59.2 mg, 64% yield).

White solid; m.p.: 142.9~144.2 °C.

^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 7.8$ Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.7 (s, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 6.6$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 1H), 7.22 (t, $J = 6.6$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 7.06 (d, $J = 7.2$ Hz, 2H), 6.95 (t, $J = 6.6$ Hz, 2H), 5.43 (s, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.0, 143.5, 133.3, 132.3, 129.9, 128.9, 128.0, 127.8, 127.7, 126.8, 126.7, 126.2, 125.8, 124.0, 123.2, 116.6, 44.5.

ACPI-MS calcd for $\text{C}_{23}\text{H}_{17}\text{O}^+$ $[\text{M}+\text{H}]^+$ 309.1274, found 309.1271.

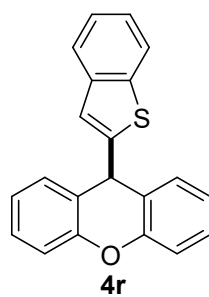


9-(Benzofuran-2-yl)-9H-xanthene (4q)^{1b}: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4q** (51.6 mg, 58% yield). White solid; m.p.: 142.9~144.2 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 8.4 Hz, 1H), 7.19 (s, 1H), 7.17 (t, *J* = 3.6 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.29 (s, 1H), 5.52 (s, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 159.8, 155.1, 151.5, 129.6, 128.6, 128.3, 123.8, 123.3, 122.6, 120.7, 120.7, 116.8, 111.2, 103.5, 38.5.

HRMS (EI) calcd. for C₂₁H₁₄O₂⁺(M⁺): 298.0988, found: 298.0984.



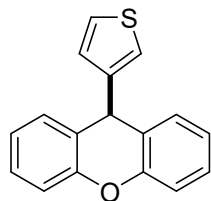
9-(Benzo[*b*]thiophen-2-yl)-9H-xanthene (4r): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4r** (67.8 mg, 72% yield).

White solid; m.p.: 137.5 ~139.3°C.

¹H NMR (600 MHz, CDCl₃) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.36 (s, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 5.4 Hz, 2H), 7.19 (s, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 6.6 Hz, 2H), 5.76 (s, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 151.0, 141.2, 138.9, 137.1, 129.1, 128.1, 124.7, 124.2, 124.0, 123.2, 122.9, 122.8, 122.7, 116.5, 38.6.

ACPI-MS calcd for C₂₁H₁₅OS⁺ [M+H]⁺ 315.0838, found 315.0837.



4s

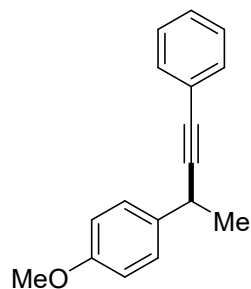
9-(Thiophen-3-yl)-9H-xanthene (4s): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **4s** (54.7 mg, 69% yield).

White solid; m.p.: 126.6 ~127.8°C.

^1H NMR (600 MHz, CDCl_3) δ 7.27–7.23 (m, 4H), 7.14 (d, $J = 8.4$ Hz, 3H), 7.06 (t, $J = 7.8$ Hz, 2H), 6.88 (dd, $J = 4.8, 3.0$ Hz, 1H), 6.80 (d, $J = 3.6$ Hz, 1H), 5.56 (s, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.0, 150.0, 129.5, 128.3, 126.5, 124.9, 124.8, 123.9, 123.3, 116.7, 39.5.

ACPI-MS calcd for $\text{C}_{17}\text{H}_{13}\text{OS}^+$ $[\text{M}+\text{H}]^+$ 265.0682, found 265.0681.



7a

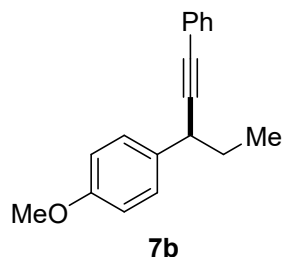
1-Methoxy-4-(4-phenylbut-3-yn-2-yl)benzene (7a): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **7a** (39.3 mg, 55% yield).

Colorless liquid

^1H NMR (600 MHz, CDCl_3) δ 7.44–7.43 (m, 2H), 7.37 (d, $J = 9.0$ Hz, 2H), 7.30–7.27 (m, 3H), 6.89 (d, $J = 8.4$ Hz, 2H), 3.94 (q, $J = 7.2$ Hz, 1H), 3.81 (s, 3H), 1.56 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.3, 135.5, 131.6, 128.2, 127.9, 127.7, 123.8, 113.9, 92.9, 82.2, 55.3, 31.6, 24.6.

EI calcd for $\text{C}_{17}\text{H}_{16}\text{O}^+$ $[\text{M}]^+$ 236.1196, found 236.1199.



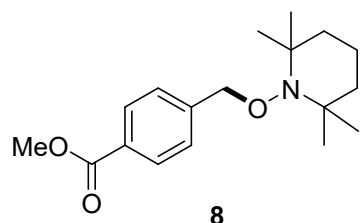
1-Methoxy-4-(1-phenylpent-1-yn-3-yl)benzene (7b): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether (PE) to afford the product **7b** (32.1 mg, 43% yield).

Colorless liquid

^1H NMR (600 MHz, CDCl_3) δ 7.44 (dd, $J = 7.2, 1.8$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.33–7.28 (m, 3H), 6.88 (d, $J = 8.4$ Hz, 2H), 3.81 (s, 3H), 3.74 (t, $J = 7.2$ Hz, 1H), 1.86–1.81 (m, 2H), 1.04 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.4, 134.2, 131.6, 128.5, 128.2, 127.7, 123.9, 113.8, 91.8, 83.2, 55.3, 39.1, 31.7, 11.8.

EI calcd for $\text{C}_{18}\text{H}_{18}\text{O}^+$ $[M]^+$ 250.1352, found 250.1357.



Methyl 4-(((2,2,5,5-Tetramethylpyrrolidin-1-yl)oxy)methyl)benzoate (8)²:

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **8** (75.8 mg, 62% yield).

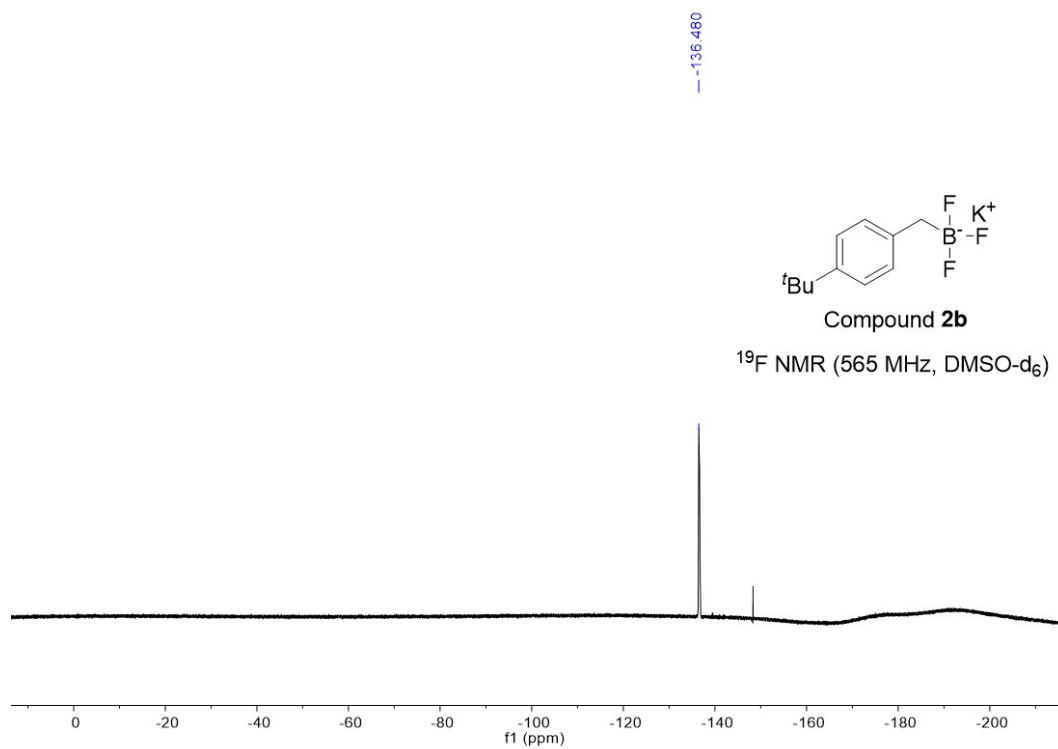
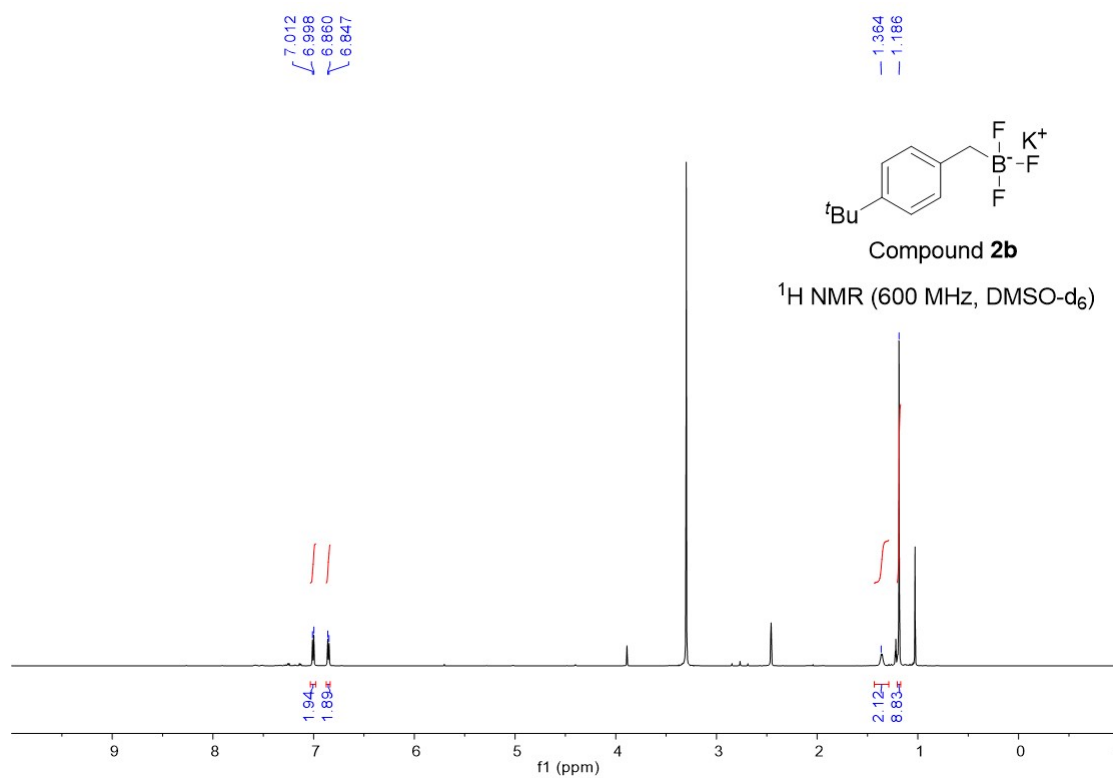
White solid; m.p.: 116.2~118.1 °C.

^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 4.88 (s, 2H), 3.91 (s, 3H), 1.53–1.49 (m, 4H), 1.36–1.24 (m, 2H), 1.22 (s, 6H), 1.16 (s, 6H).

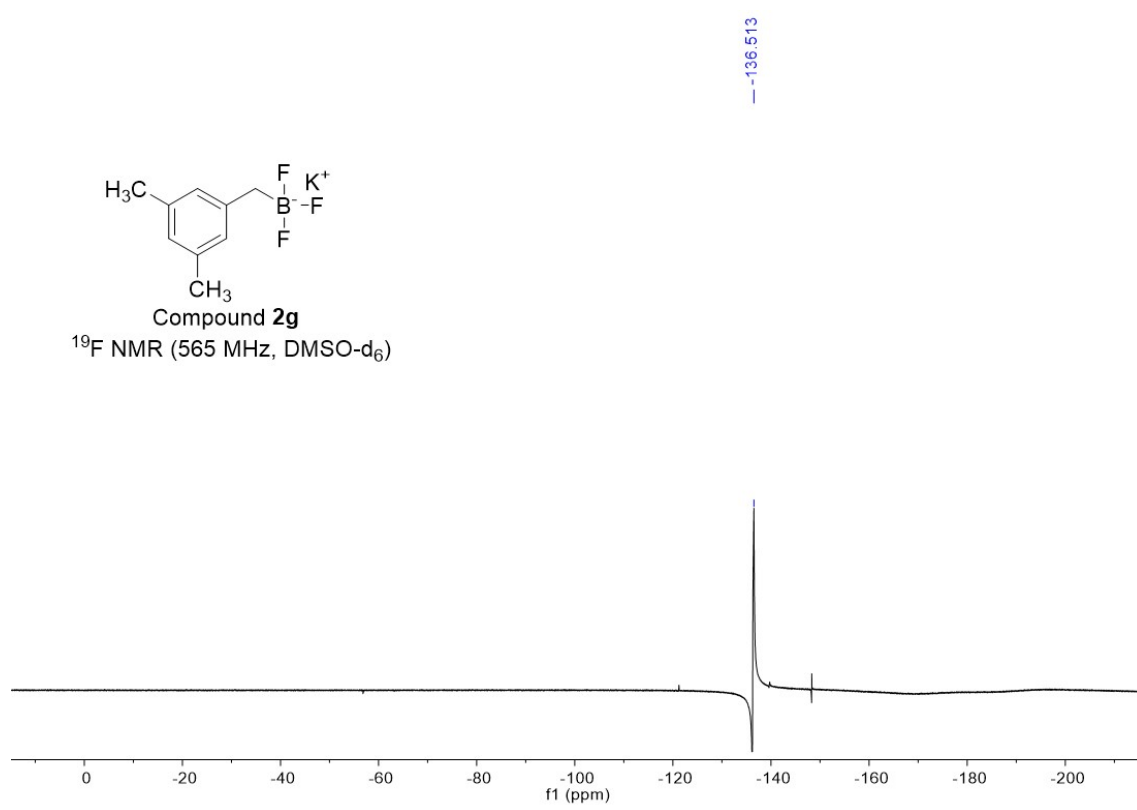
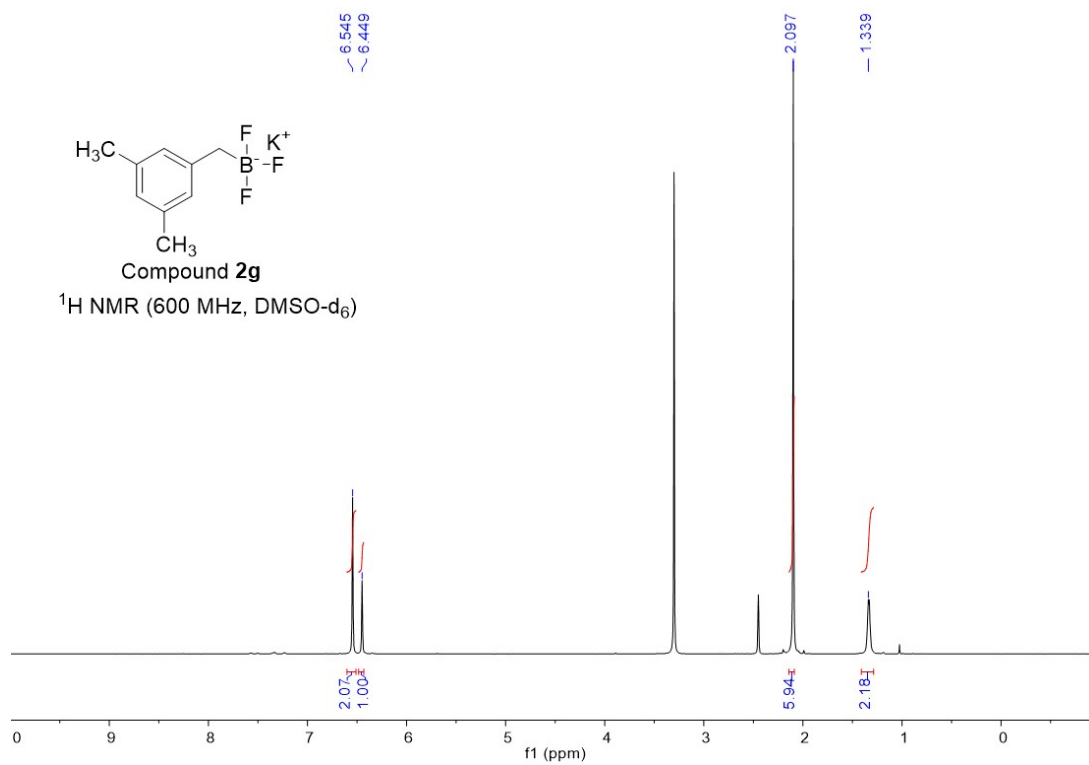
^{13}C NMR (151 MHz, CDCl_3) δ 167.0, 143.7, 129.6, 129.0, 126.9, 78.2, 60.1, 52.0, 39.7, 33.0, 20.3, 17.1.

8. ^1H , ^{13}C , ^{19}F NMR spectra of the products

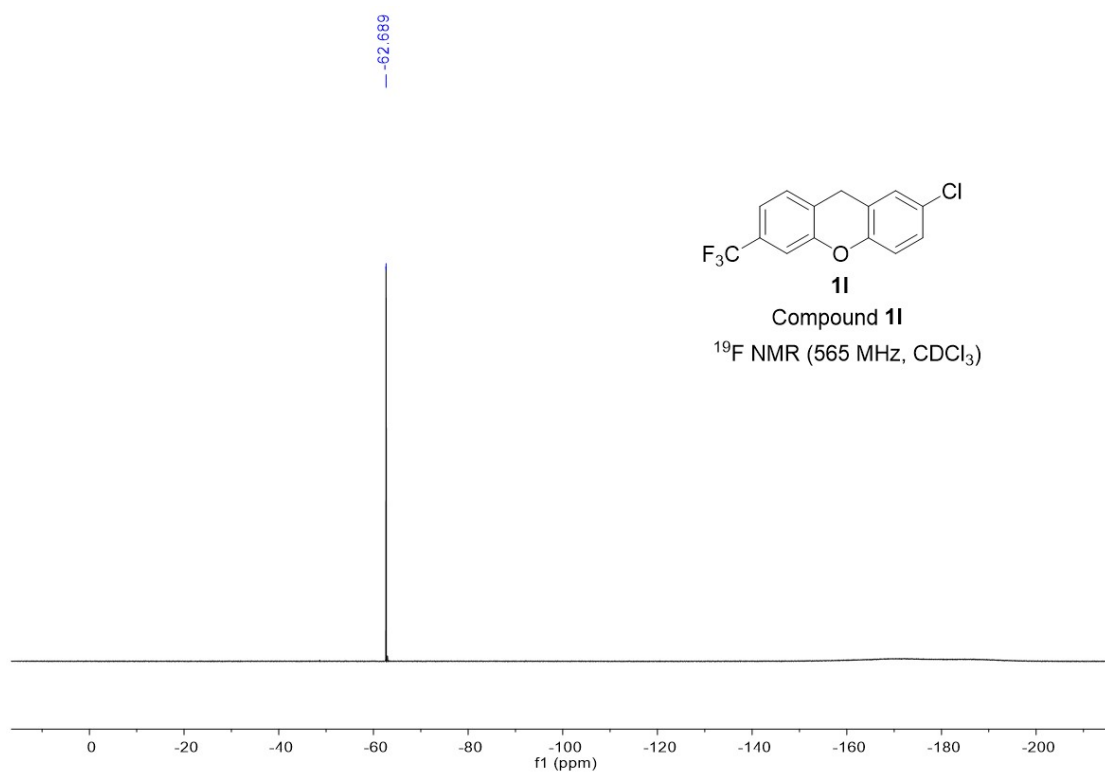
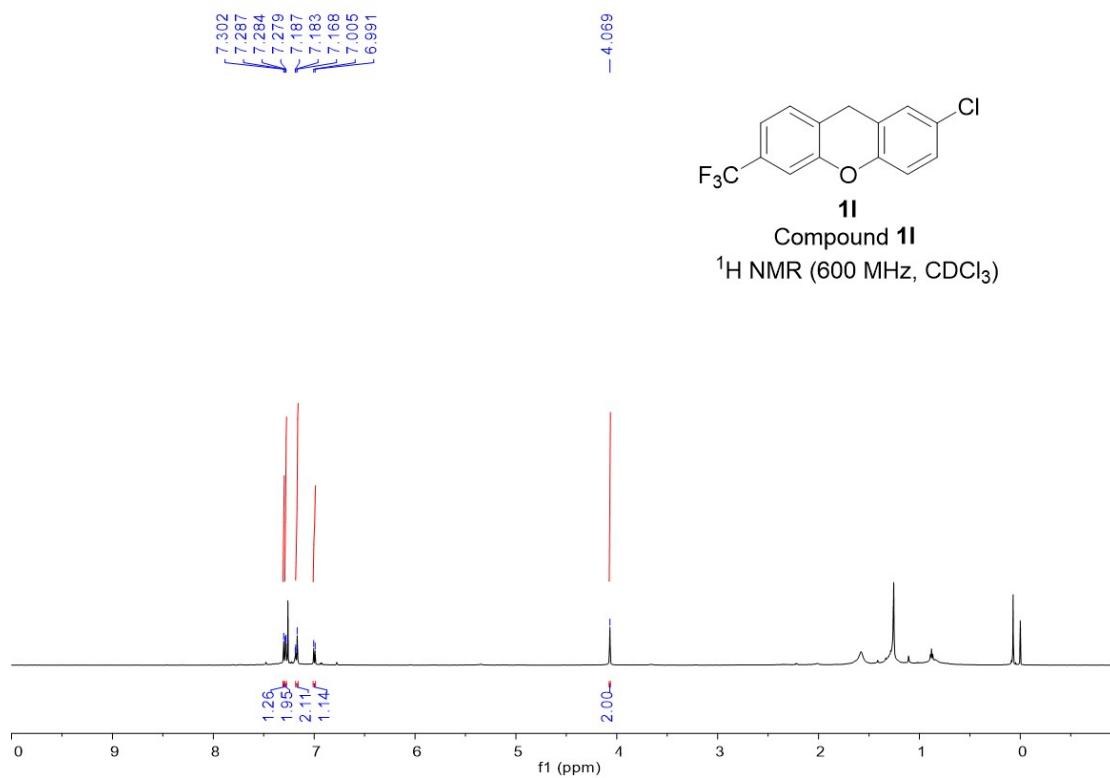
NMR spectra of Potassium (4-(tert-butyl)benzyl)trifluoroborate (**2b**)



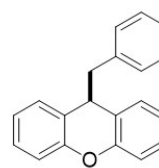
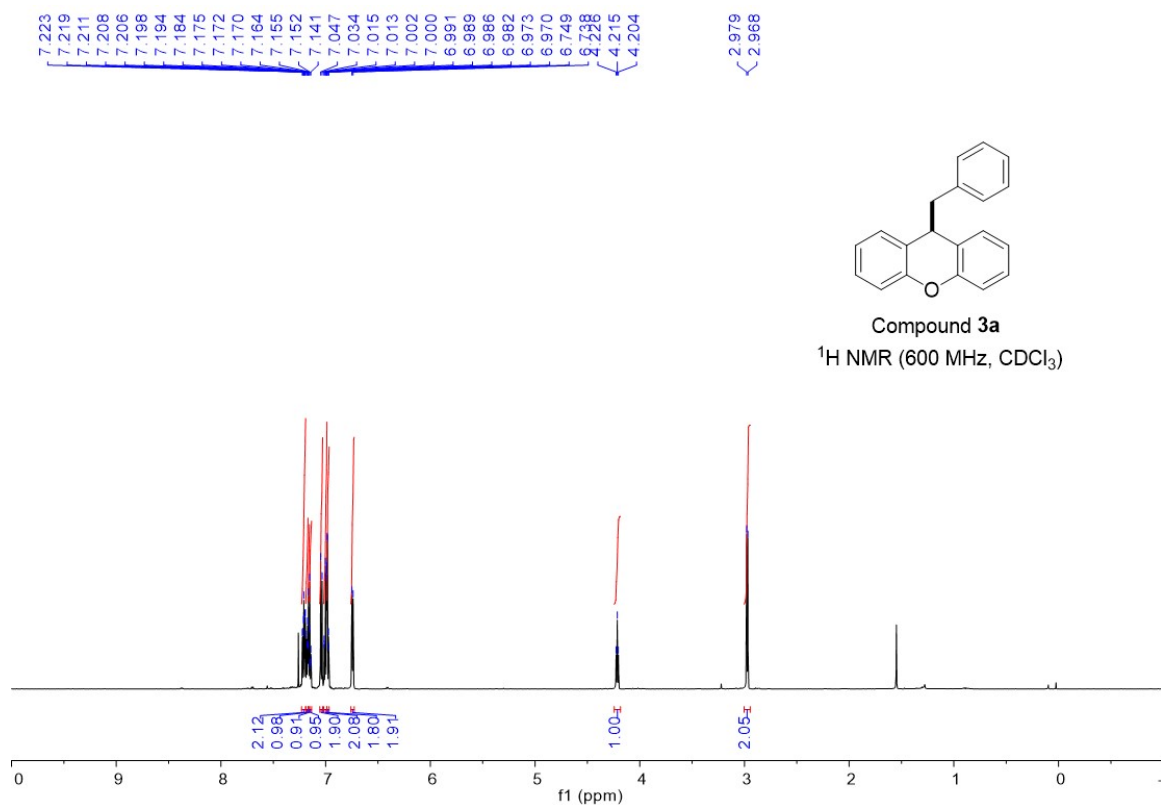
NMR spectra of Potassium (3,5-dimethylbenzyl)trifluoroborate (**2g**)



NMR spectra of 2-chloro-6-(trifluoromethyl)-9H-xanthene (**11**)

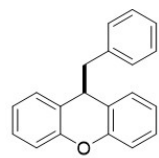


NMR spectra of 9-benzyl-9*H*-xanthene (**3a**)

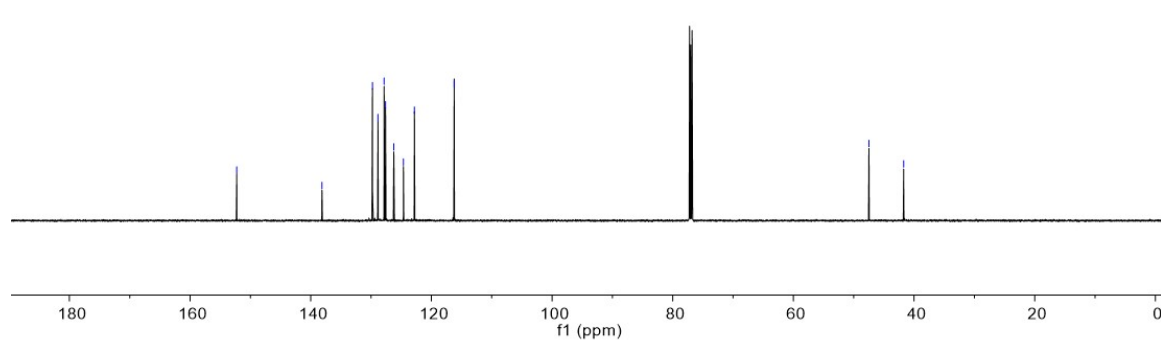


Compound 3a
¹H NMR (600 MHz, CDCl₃)

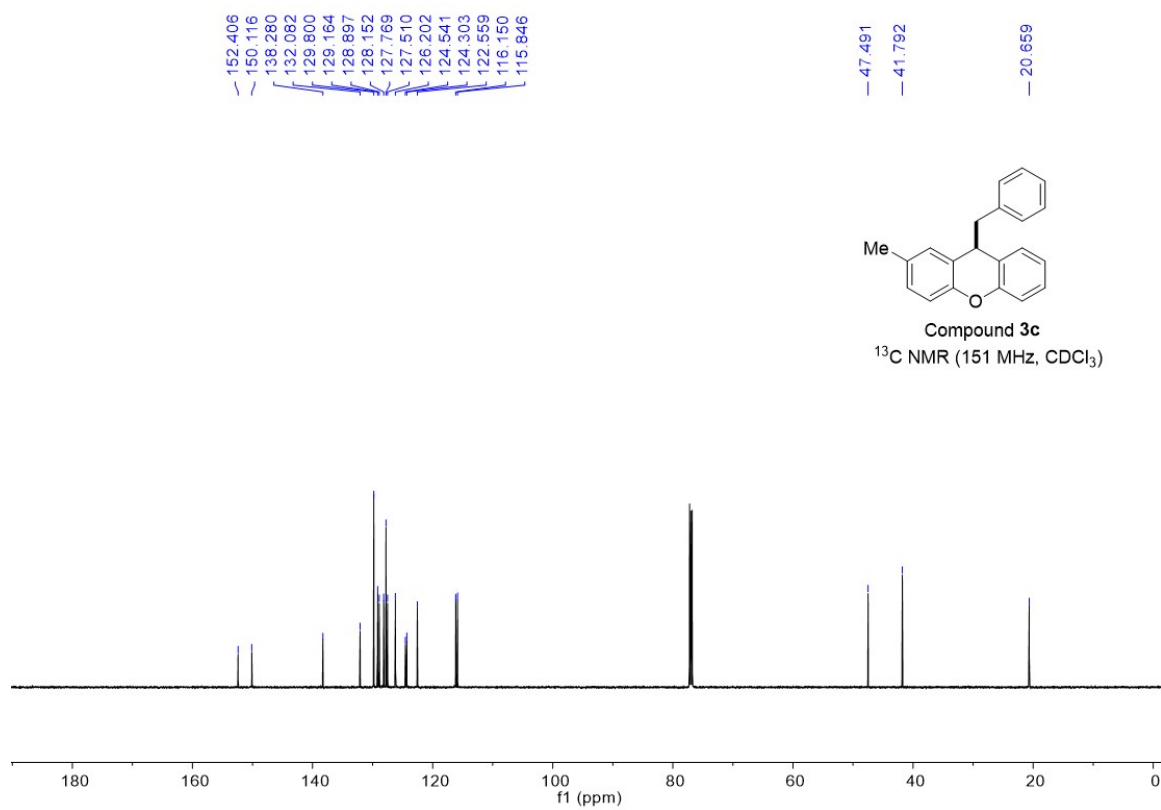
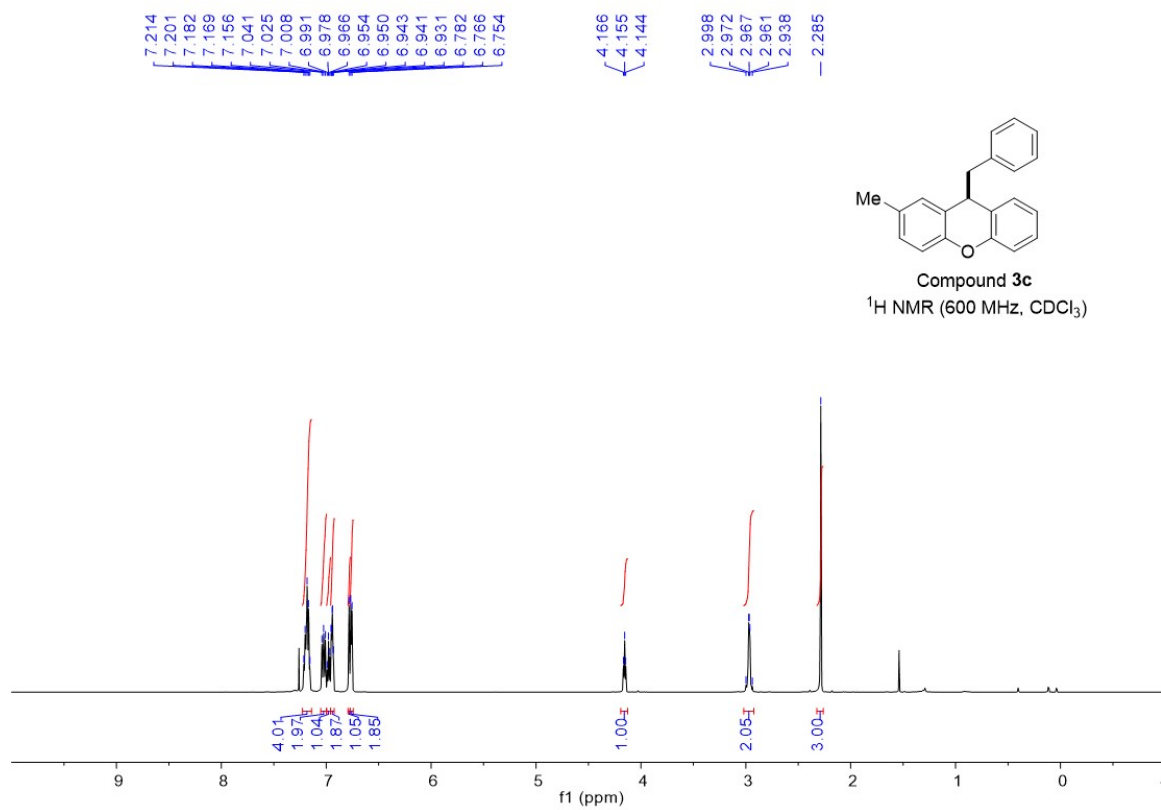
152.263
 138.136
 129.765
 128.847
 127.829
 127.599
 126.233
 124.630
 122.817
 116.216
 47.478
 41.714



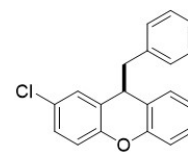
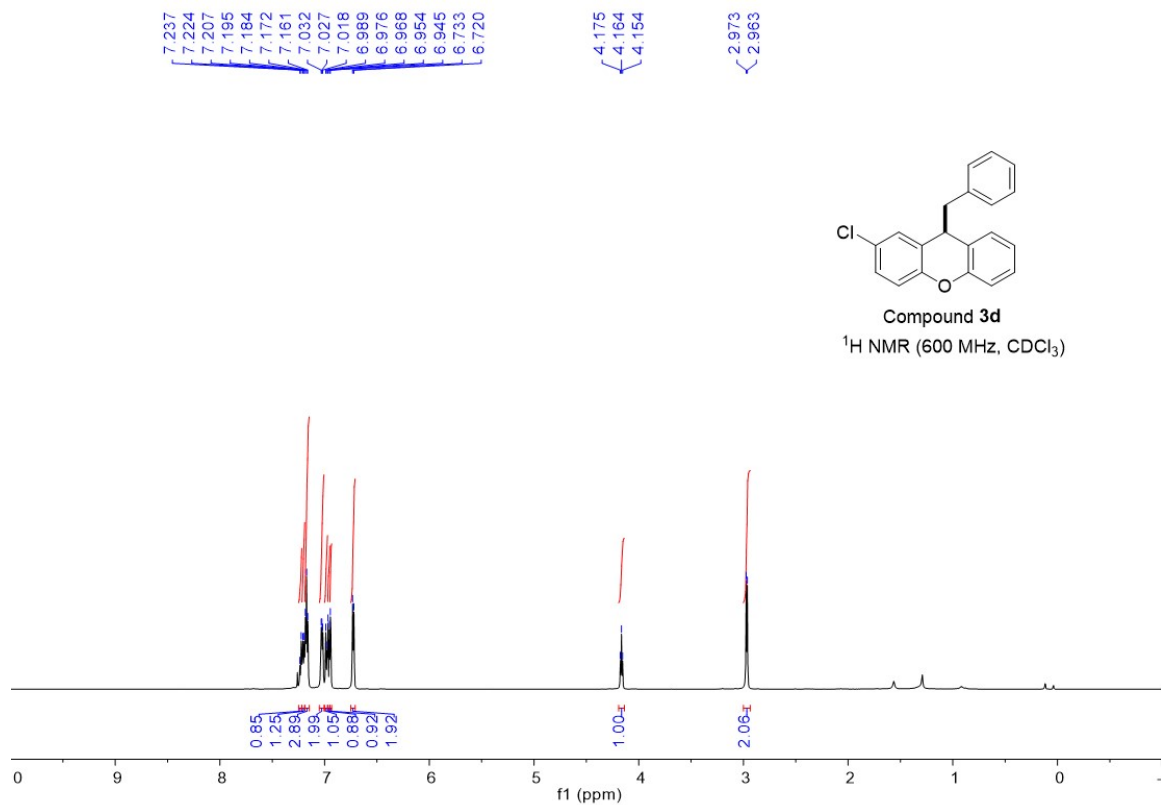
Compound 3a
¹³C NMR (151 MHz, CDCl₃)



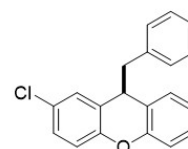
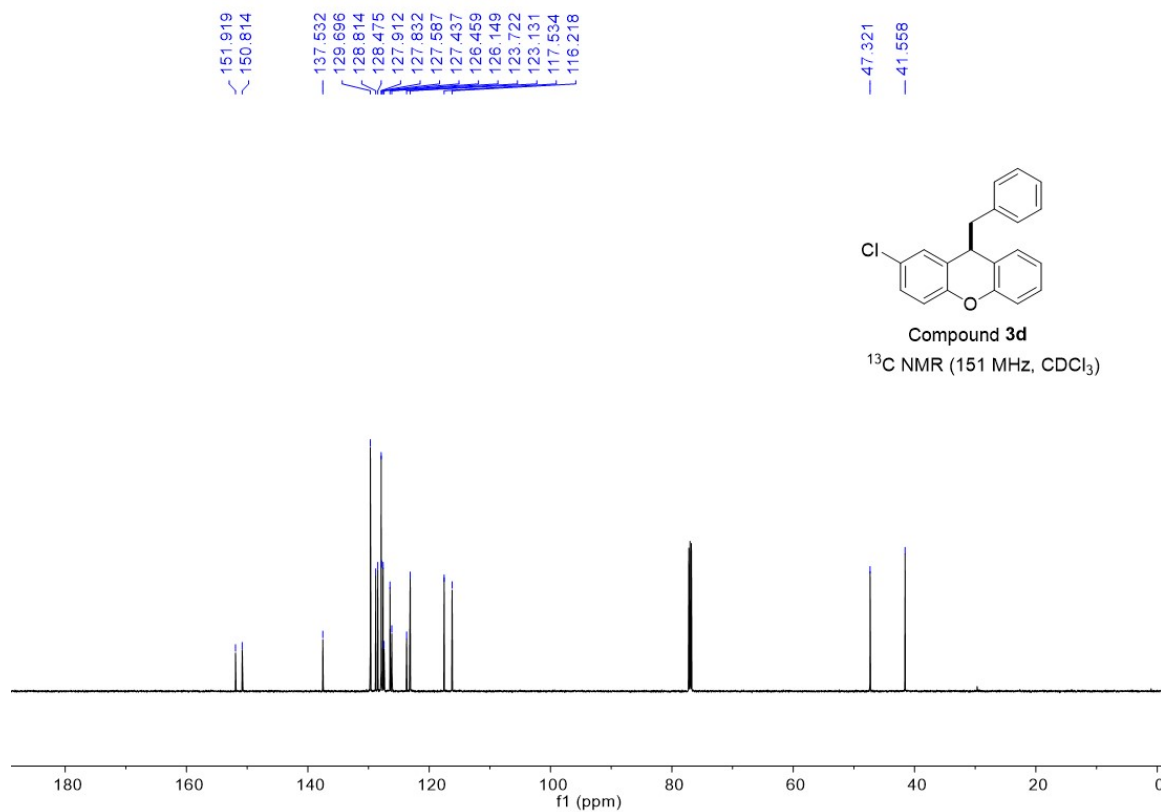
NMR spectra of 9-benzyl-4-methyl-9*H*-xanthene (**3b**)



NMR spectra of 9-benzyl-2-chloro-9H-xanthene (**3d**)

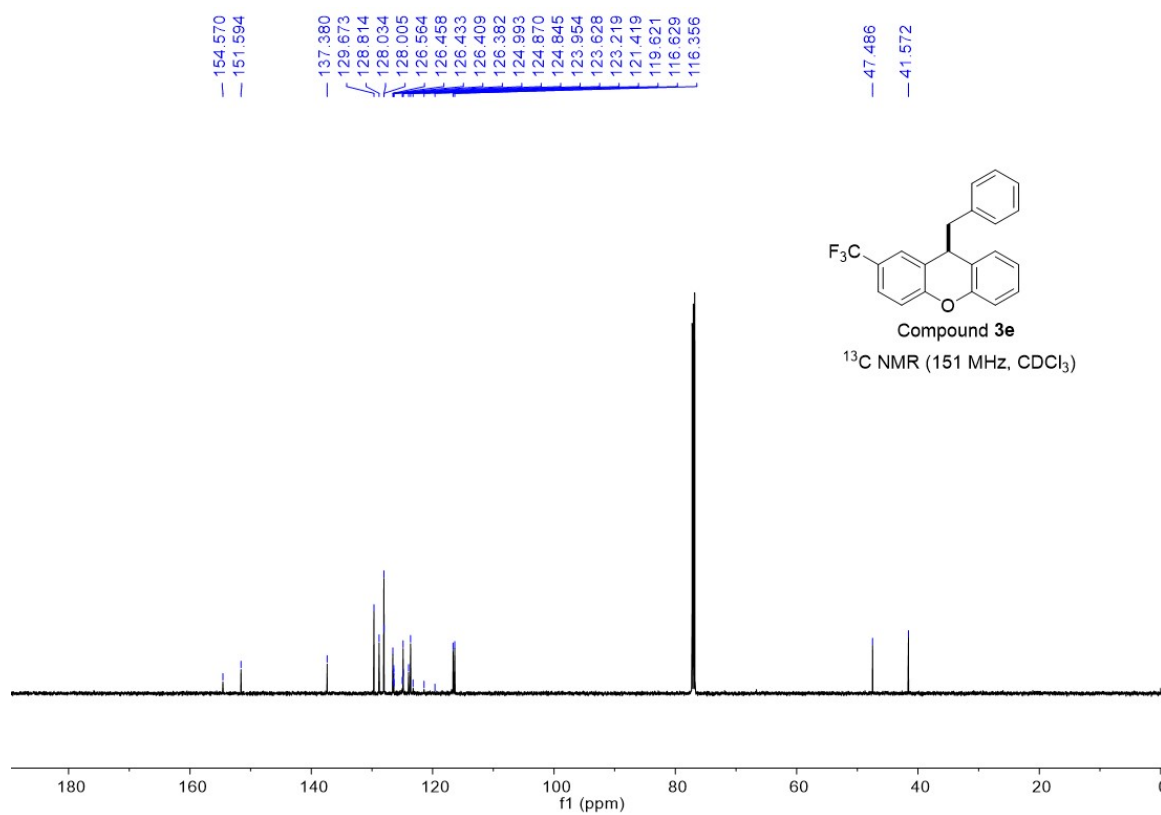
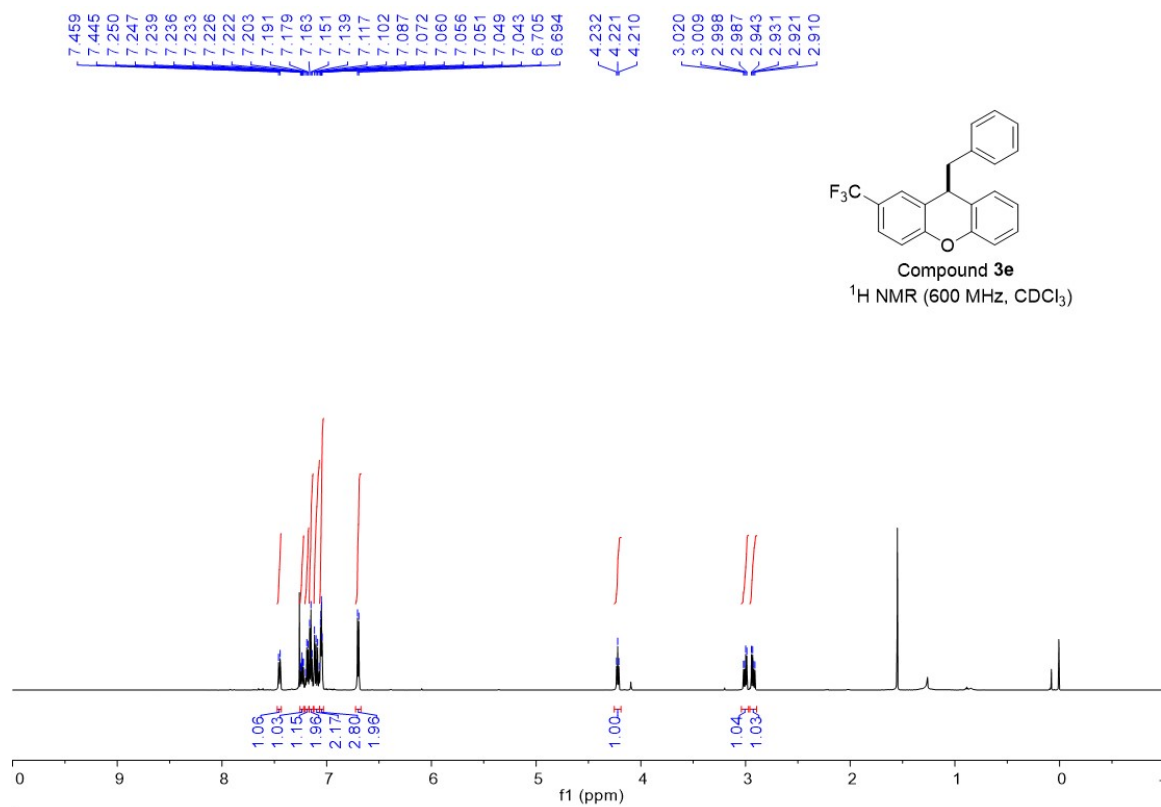


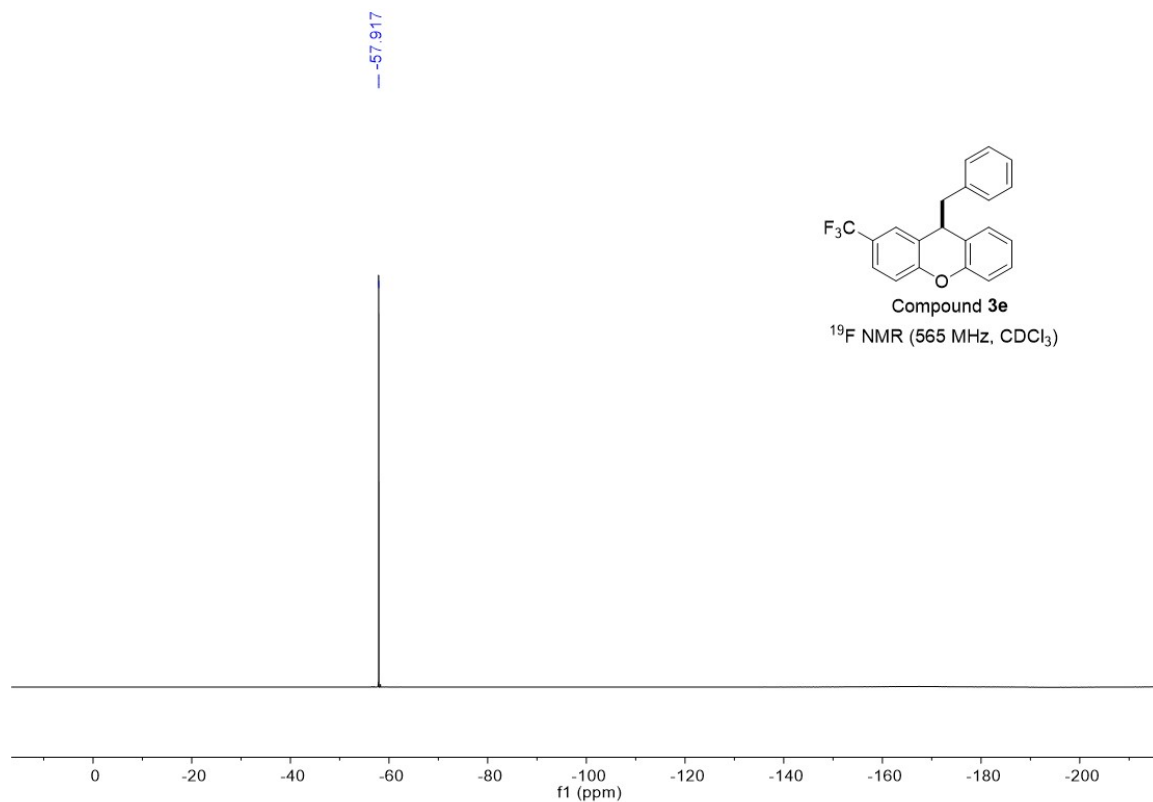
Compound **3d**
¹H NMR (600 MHz, CDCl₃)



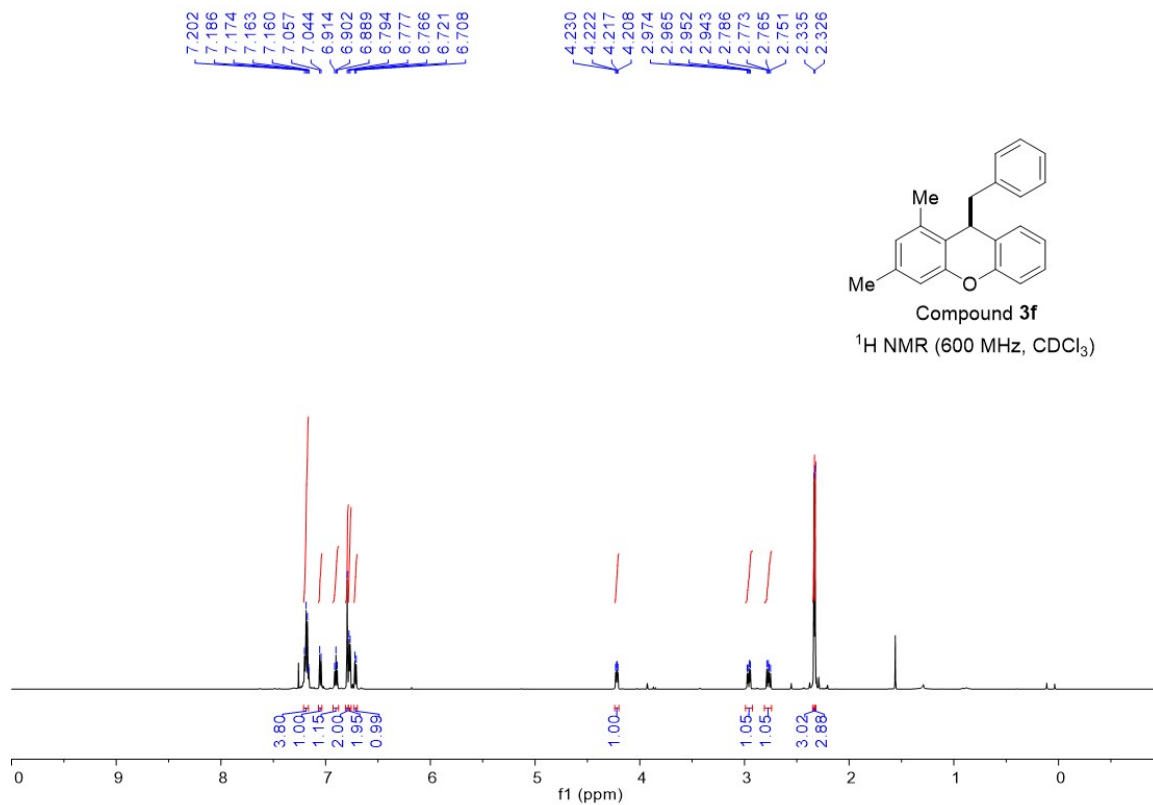
Compound **3d**
¹³C NMR (151 MHz, CDCl₃)

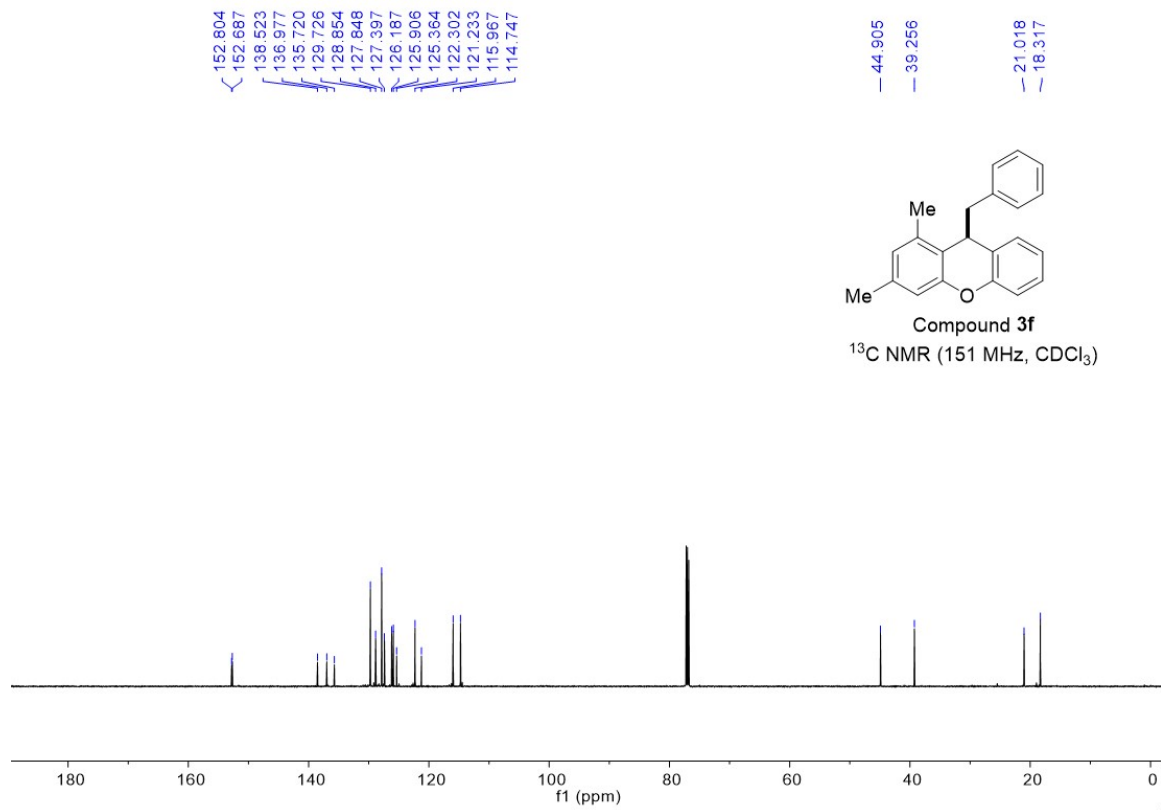
NMR spectra of 9-benzyl-2-(trifluoromethyl)-9*H*-xanthene (**3e**)



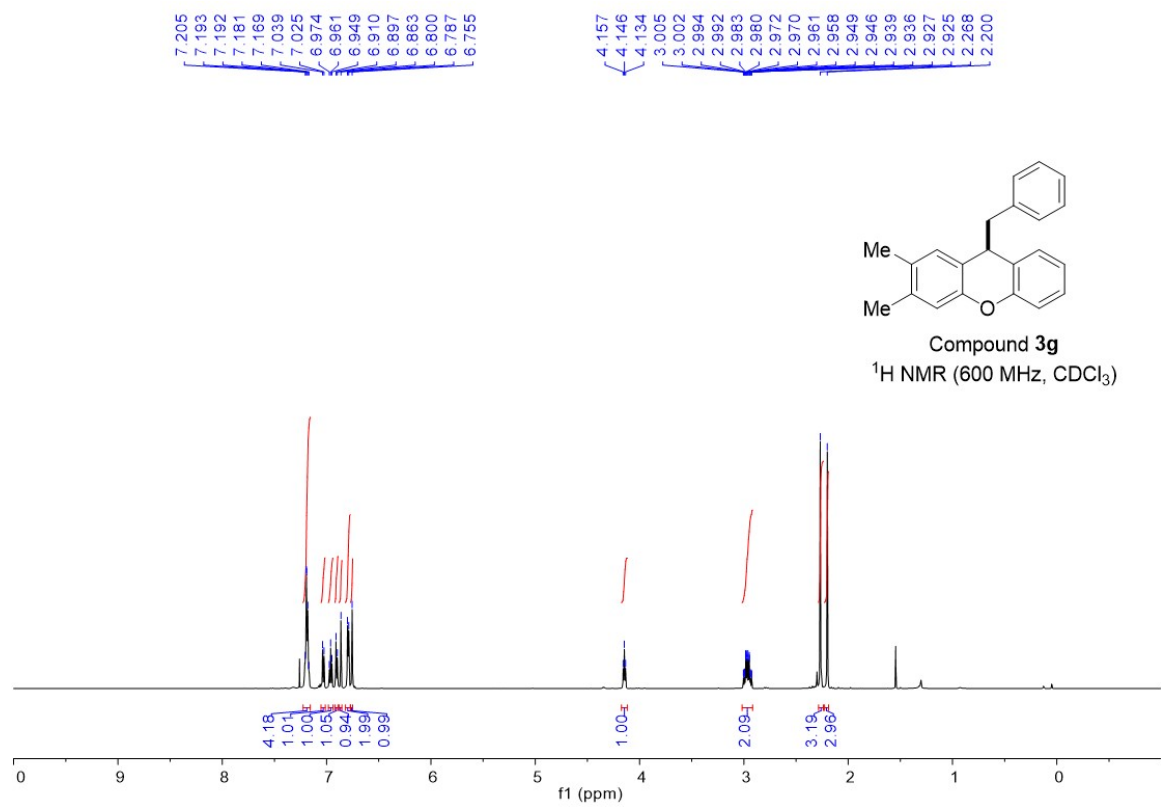


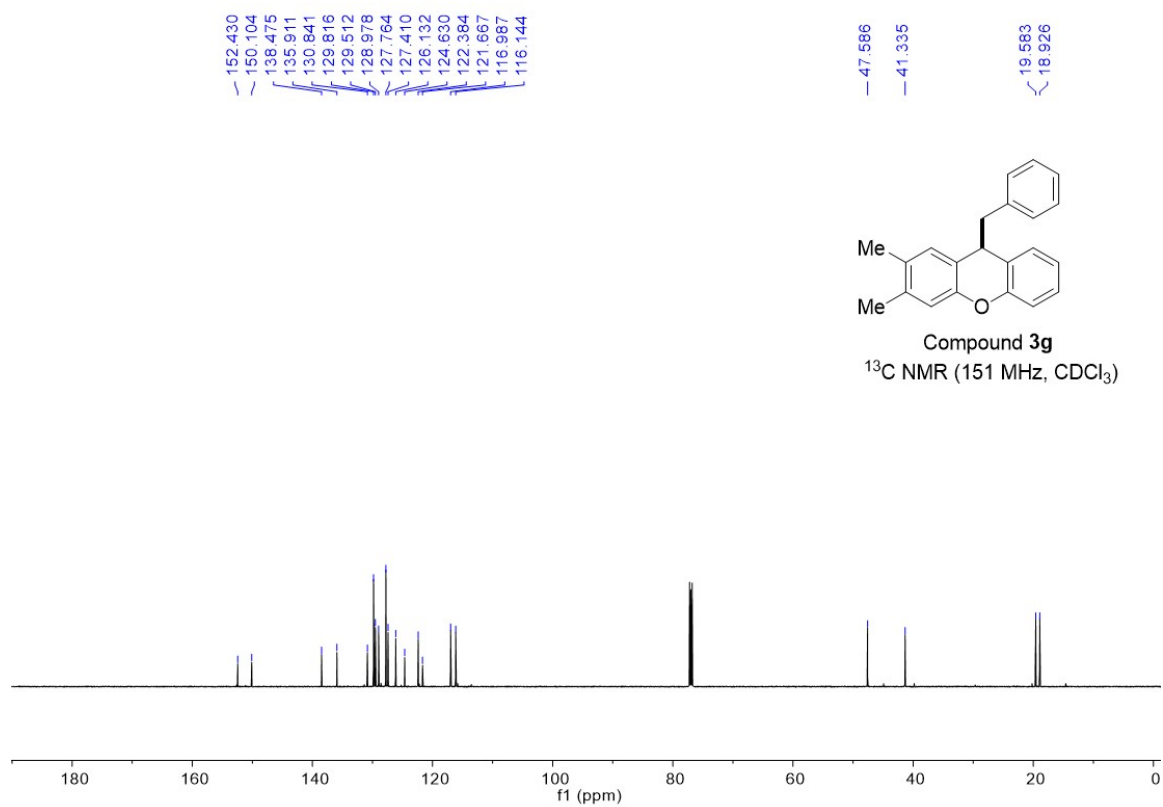
NMR spectra of 9-benzyl-1,3-dimethyl-9H-xanthene (3f)



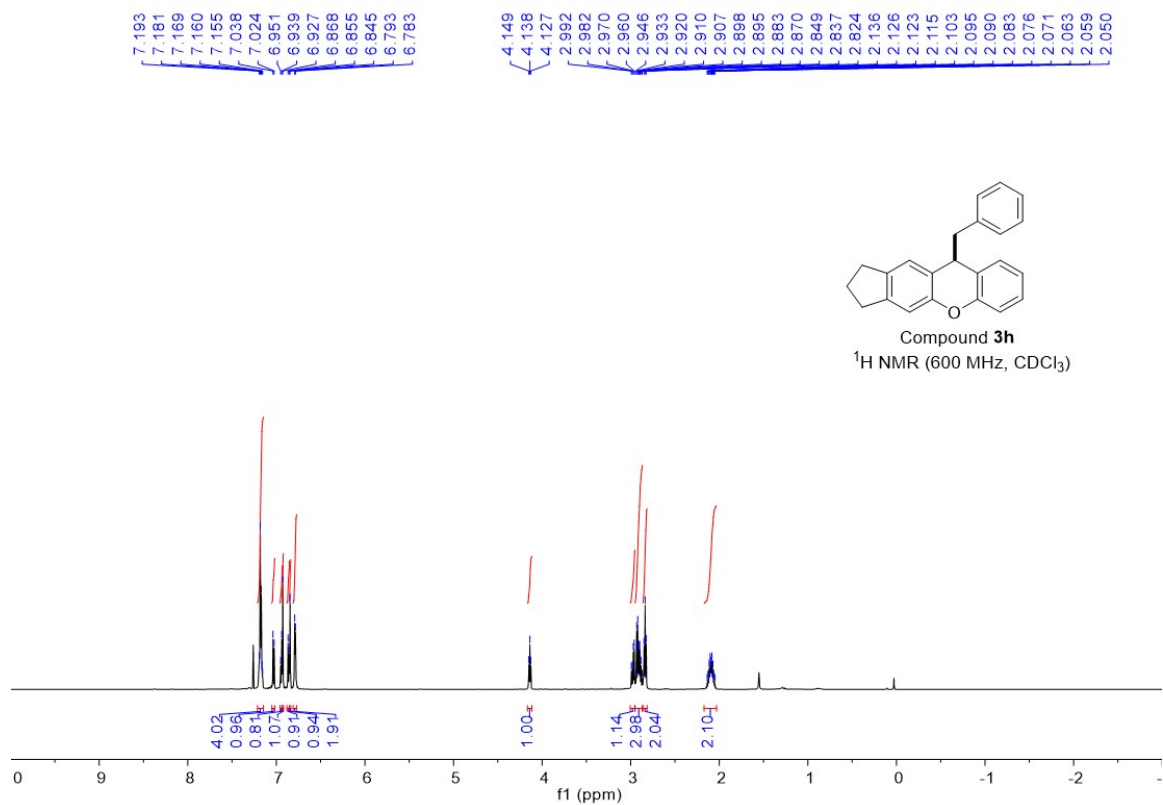


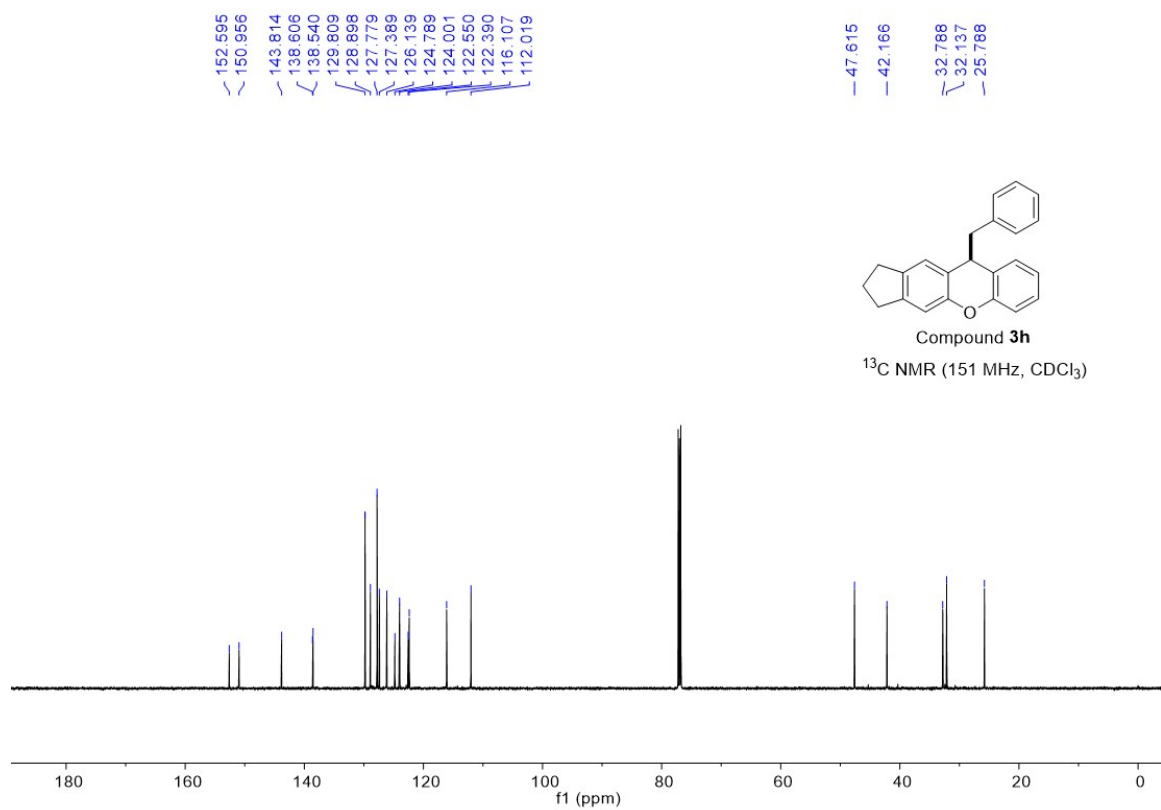
NMR spectra of 9-benzyl-2,3-dimethyl-9H-xanthene (**3g**)



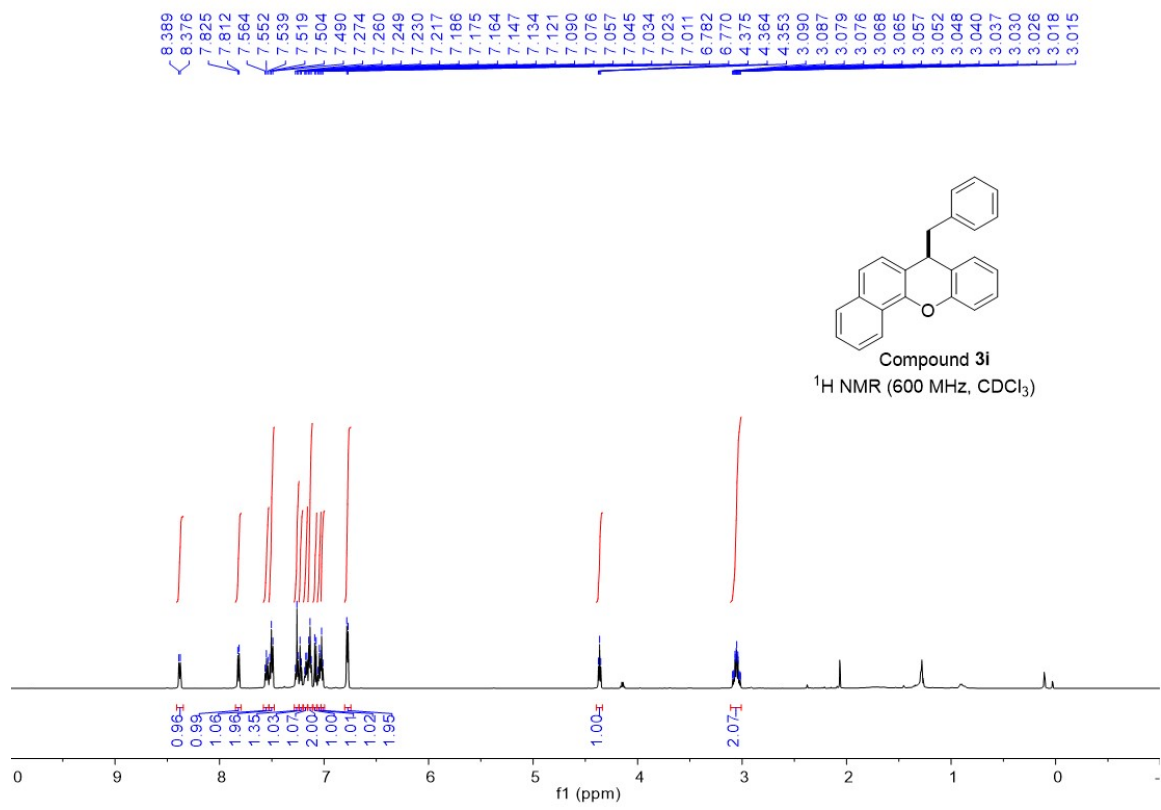


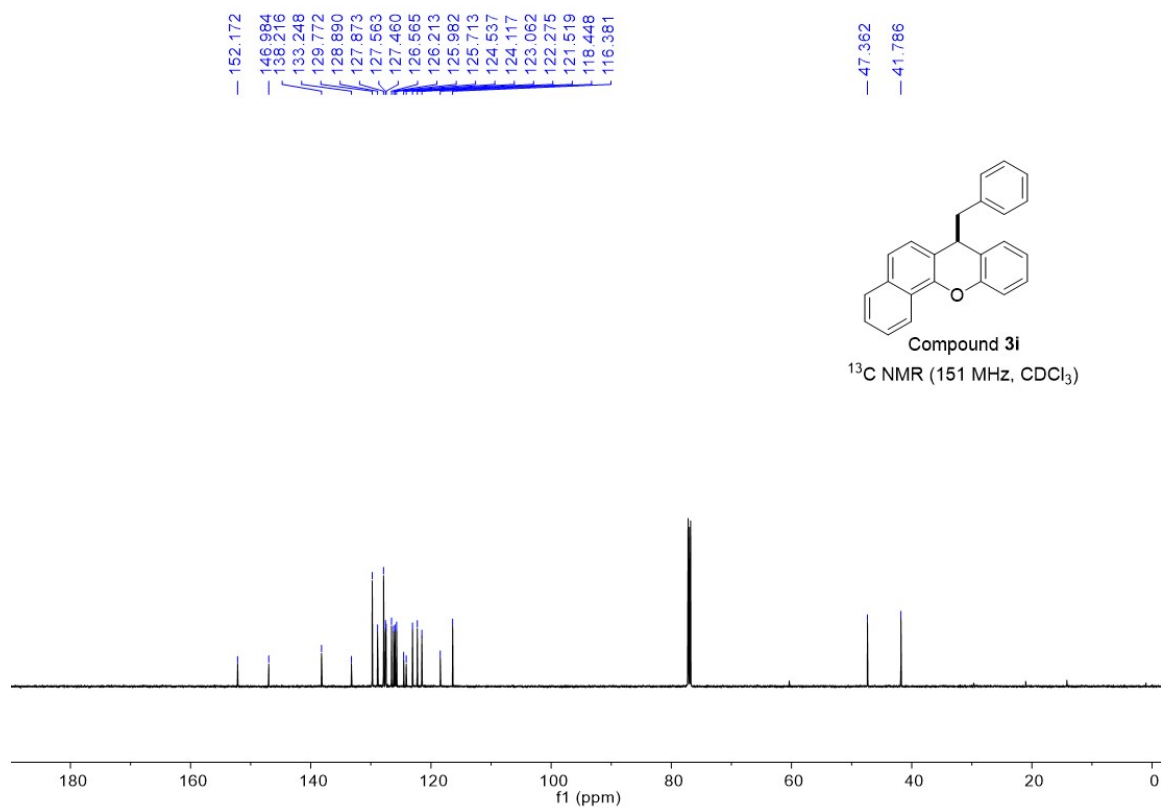
NMR spectra of 10-benzyl-1,2,3,10-tetrahydrocyclopenta[*b*]xanthene (**3h**)



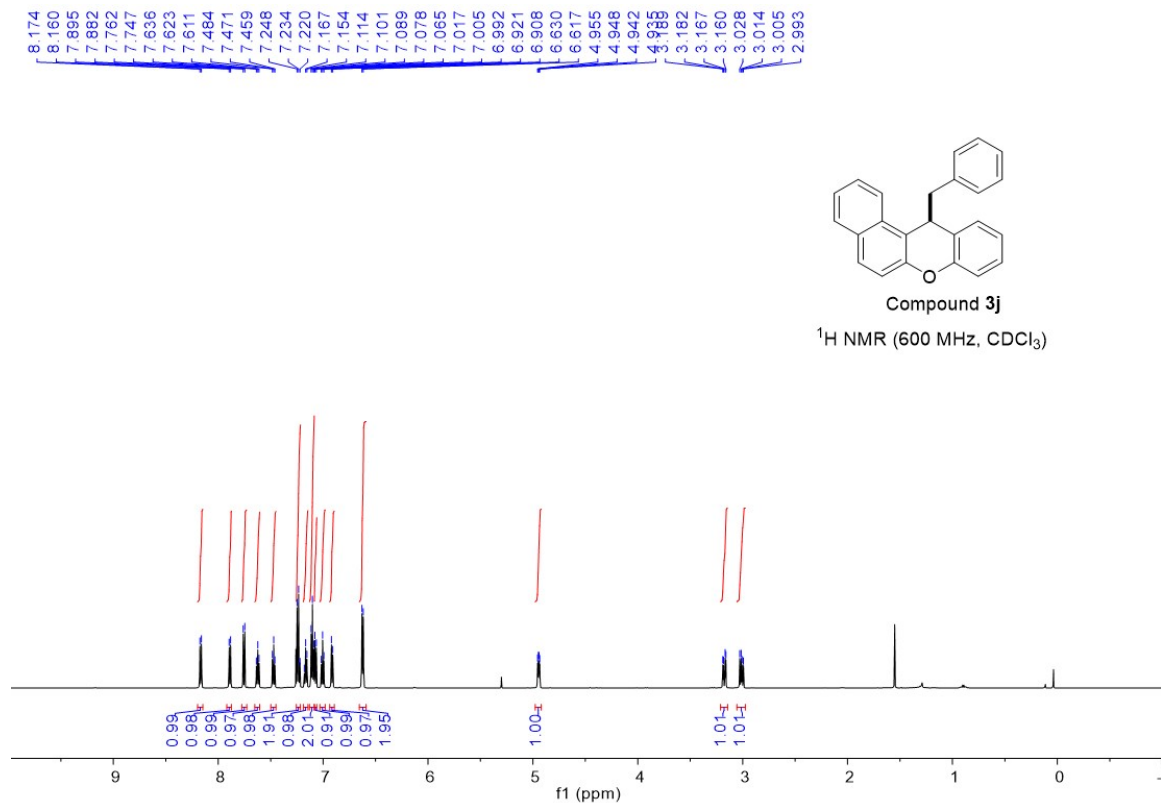


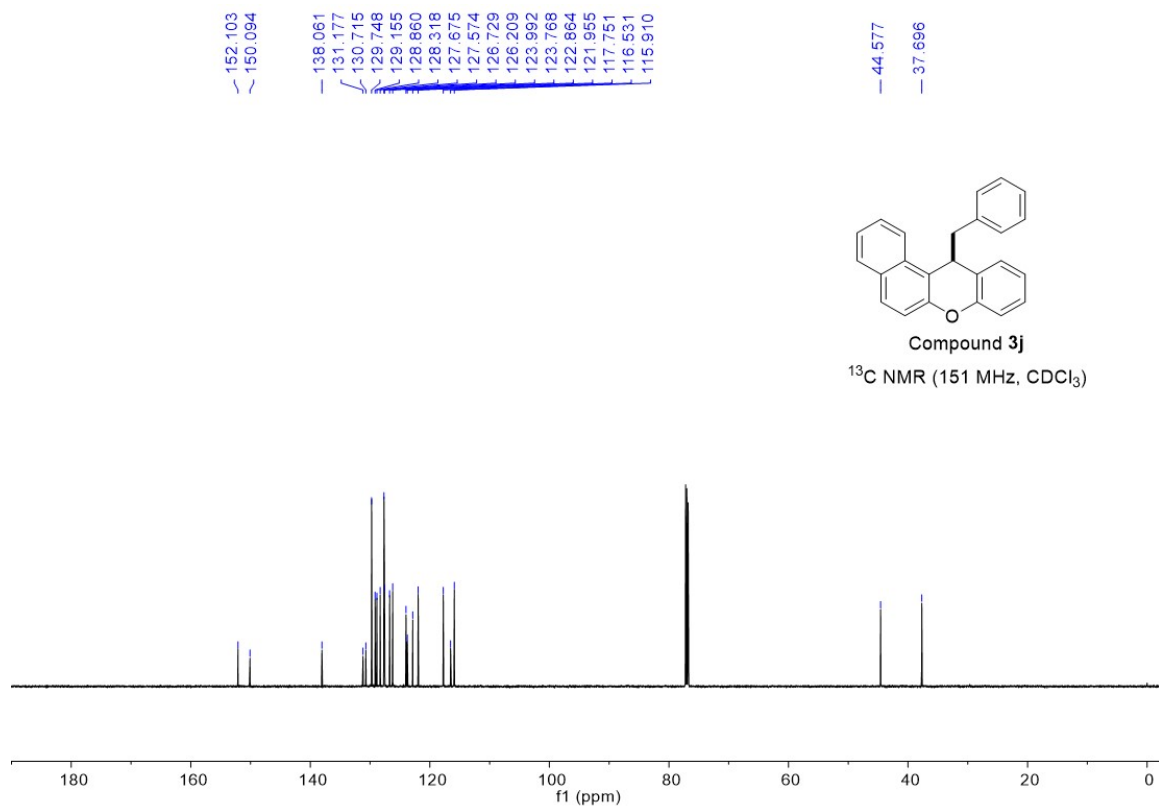
NMR spectra of 7-benzyl-7H-benzo[c]xanthene (**3i**)



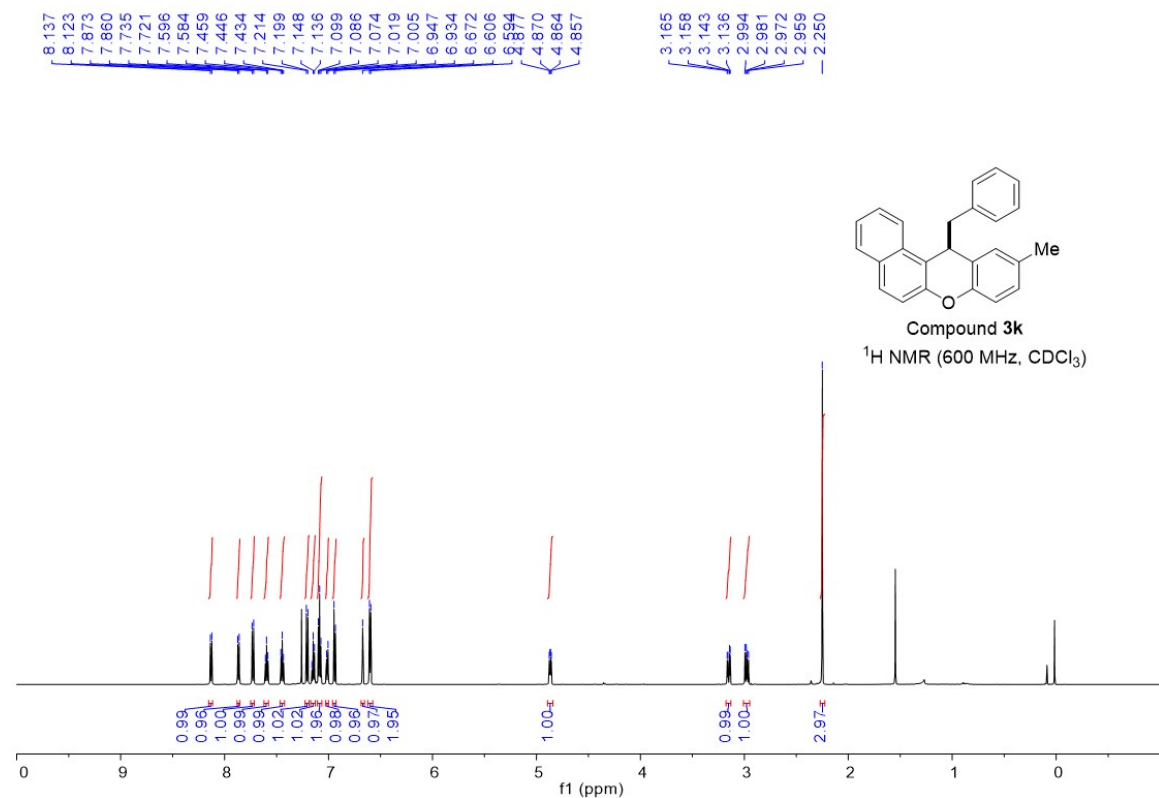


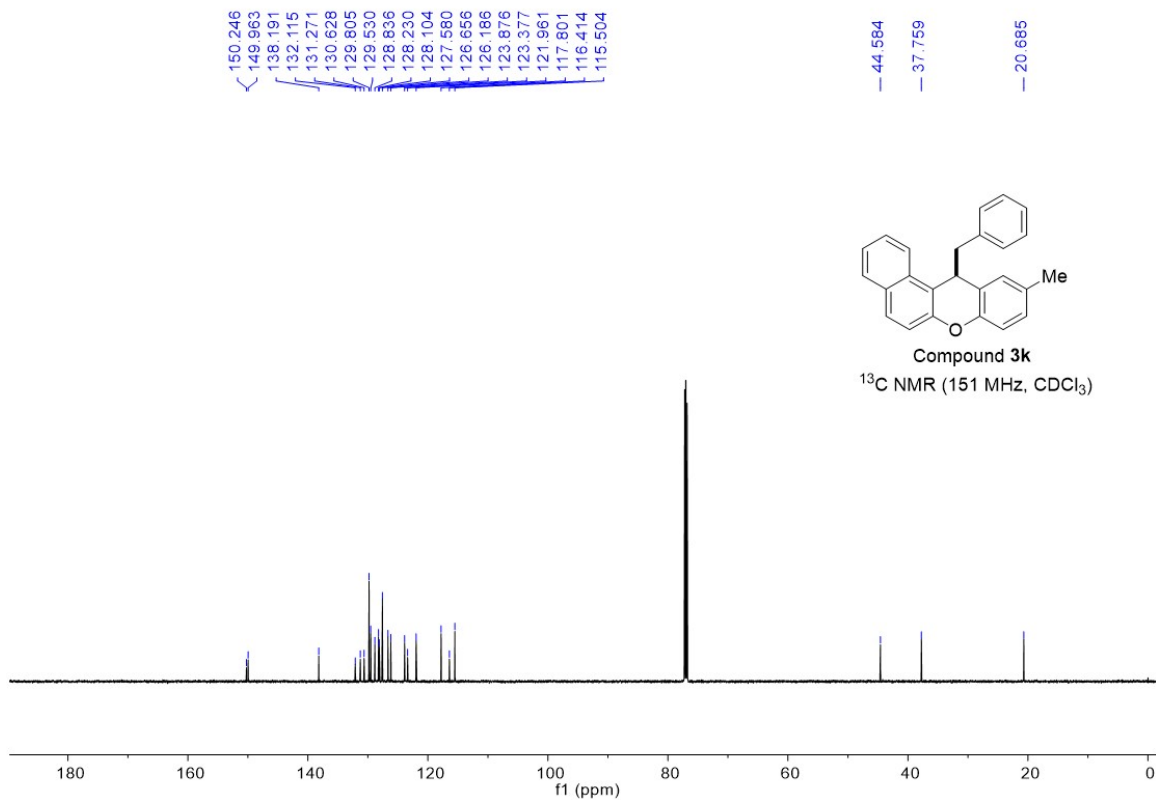
NMR spectra of 12-benzyl-12*H*-benzo[*a*]xanthene (**3j**)



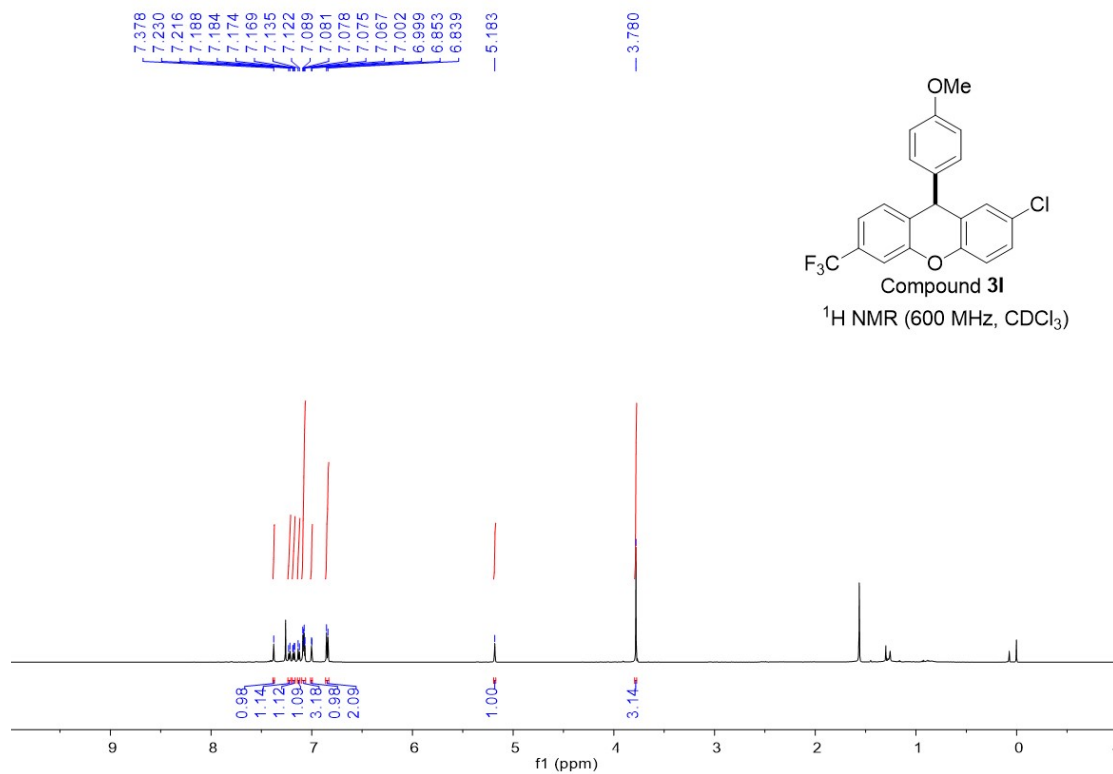


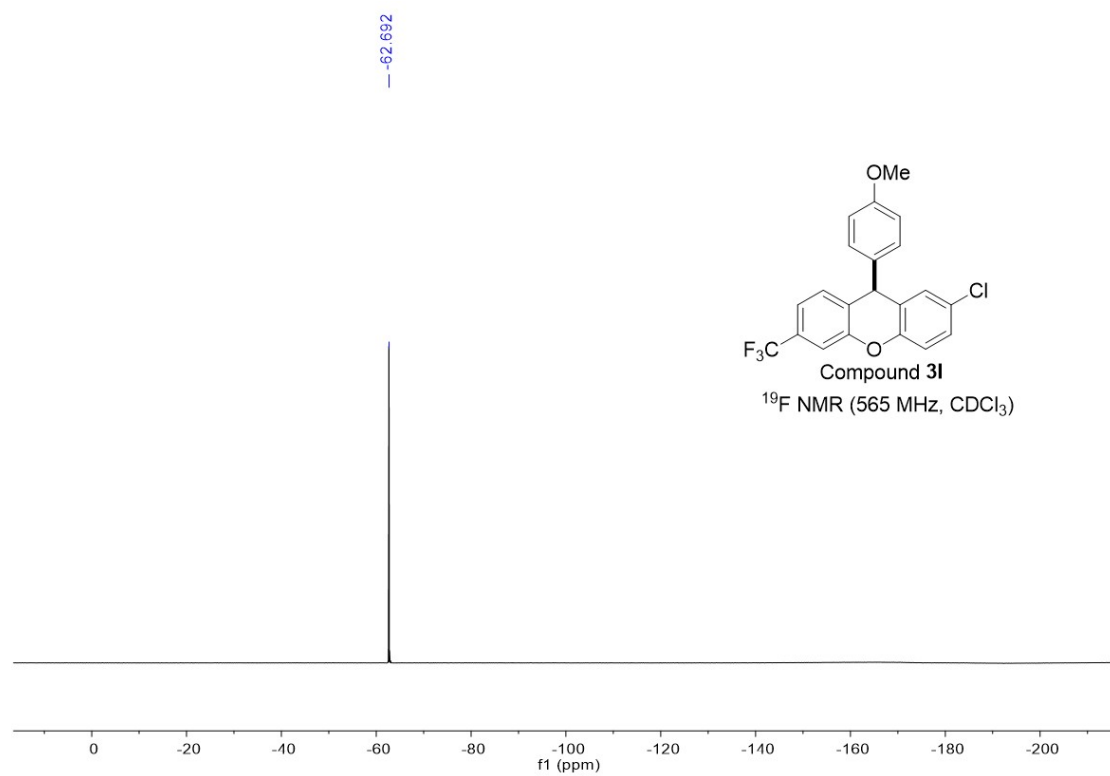
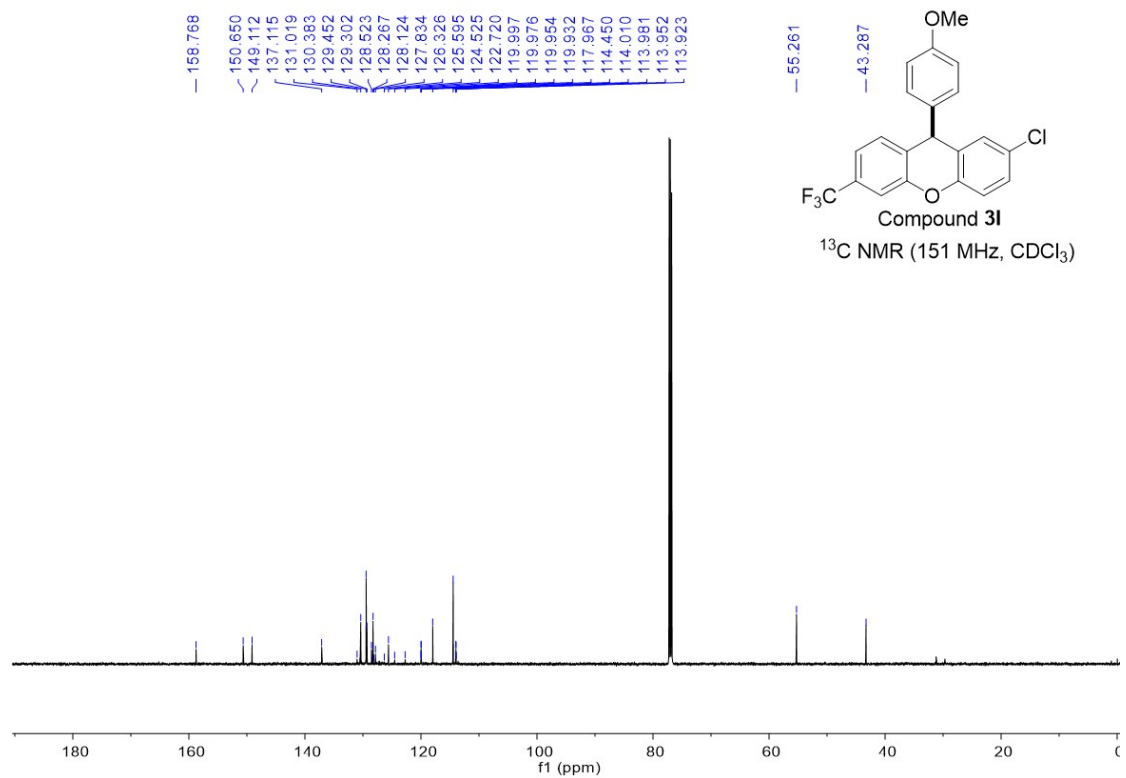
NMR spectra of 12-benzyl-10-methyl-12*H*-benzo[*a*]xanthene (**3k**)



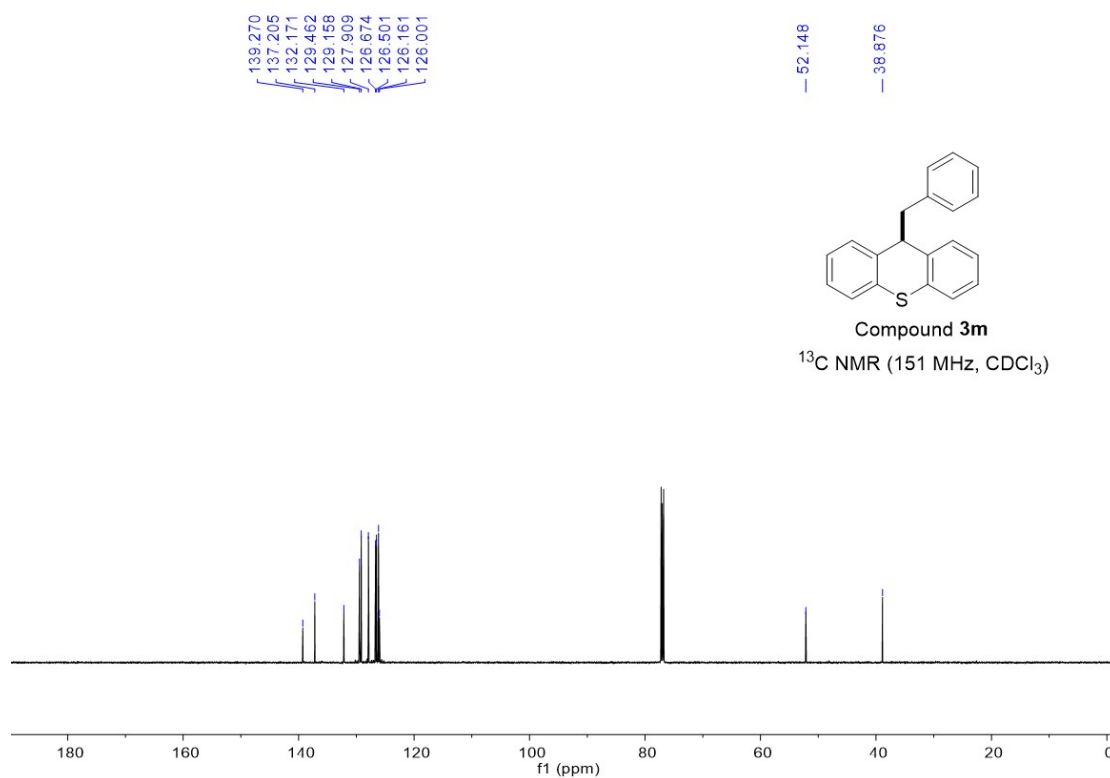
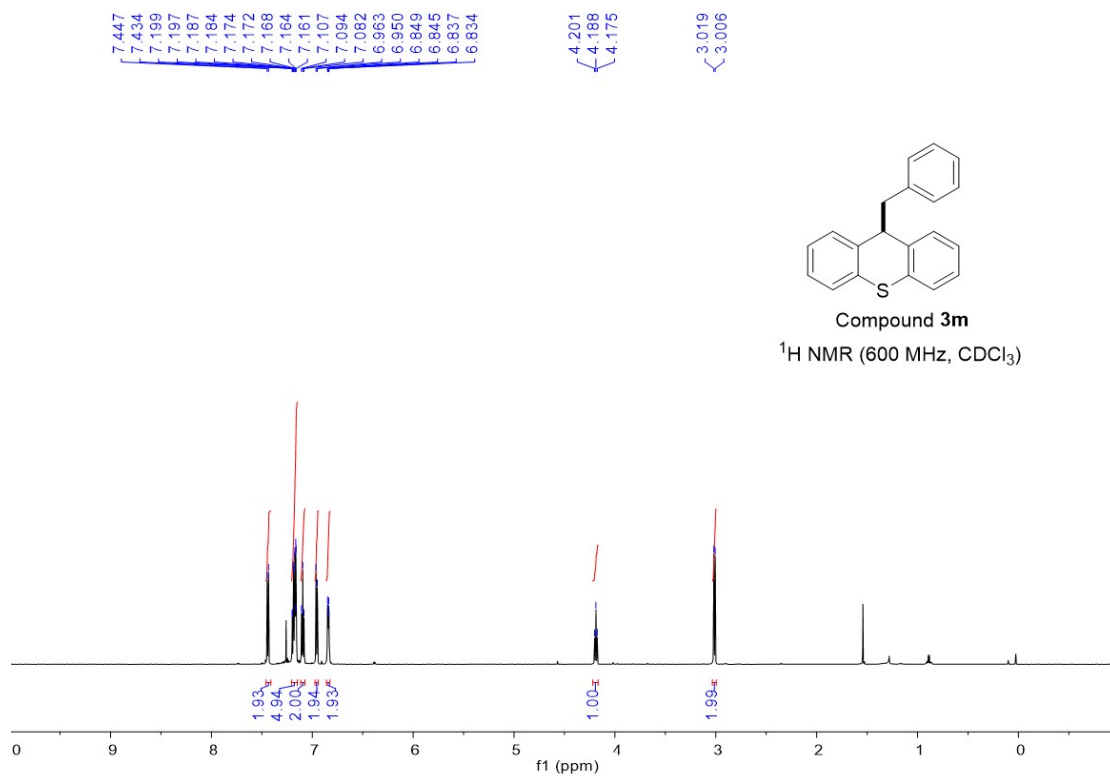


NMR spectra of 2-chloro-9-(4-methoxyphenyl)-6-(trifluoromethyl)-9H-xanthene (**3I**)

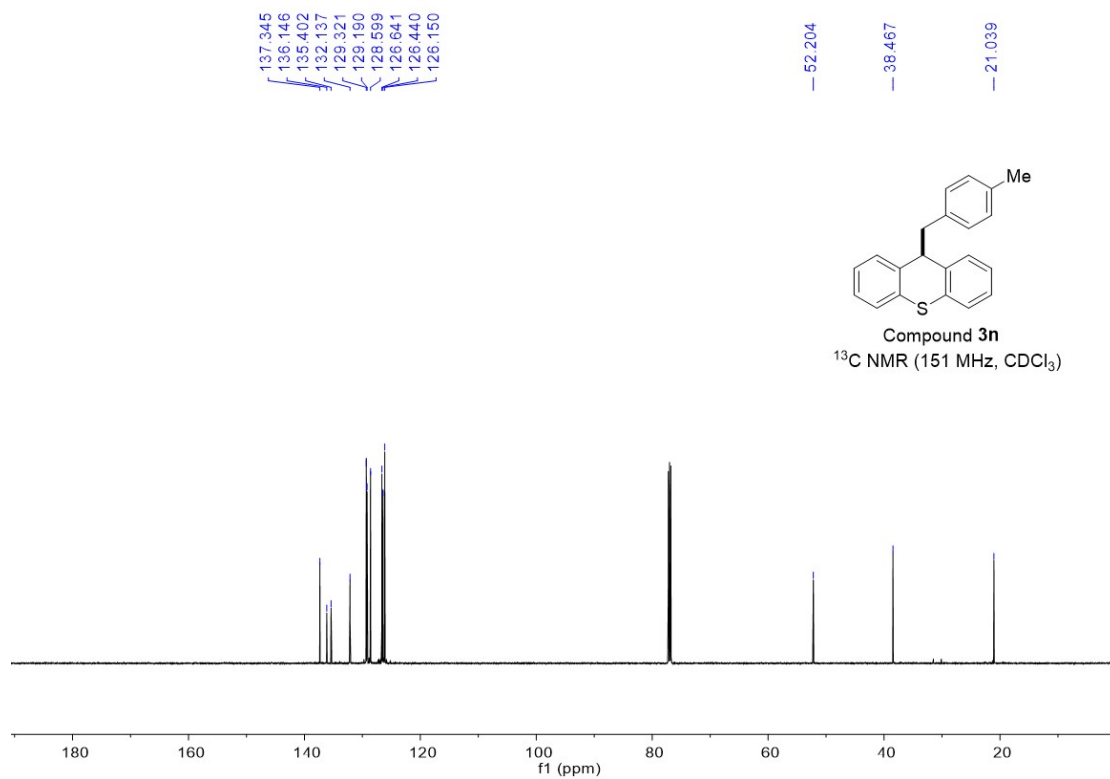
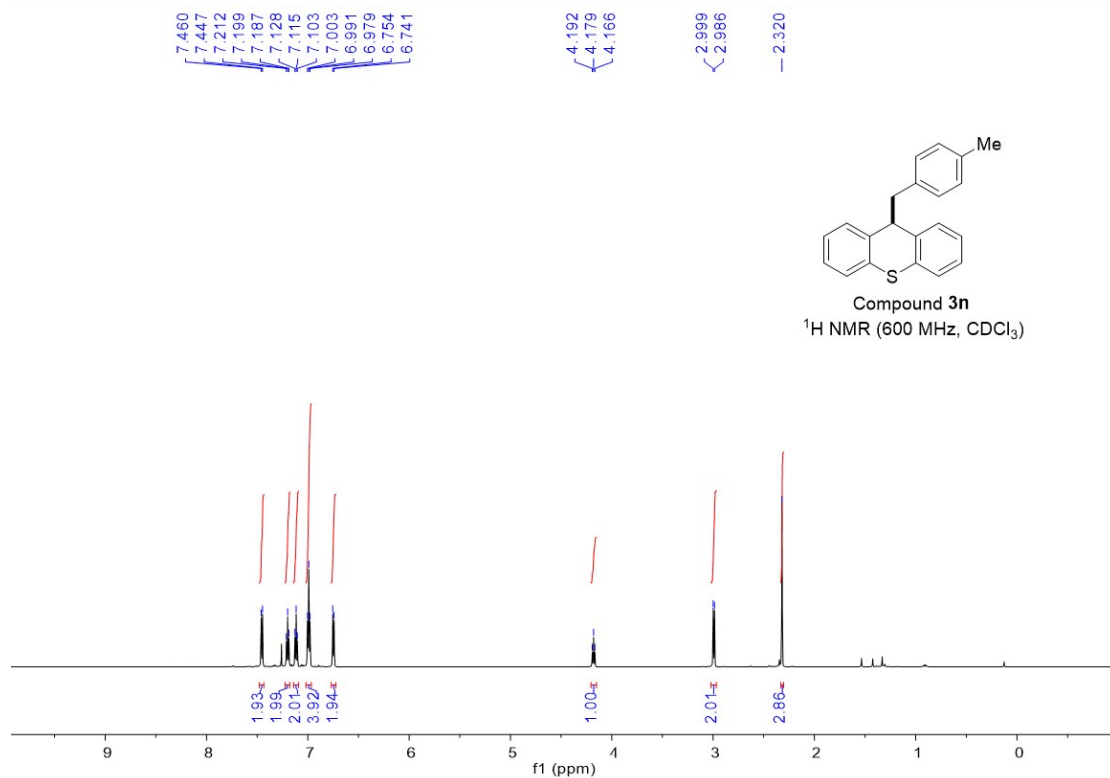




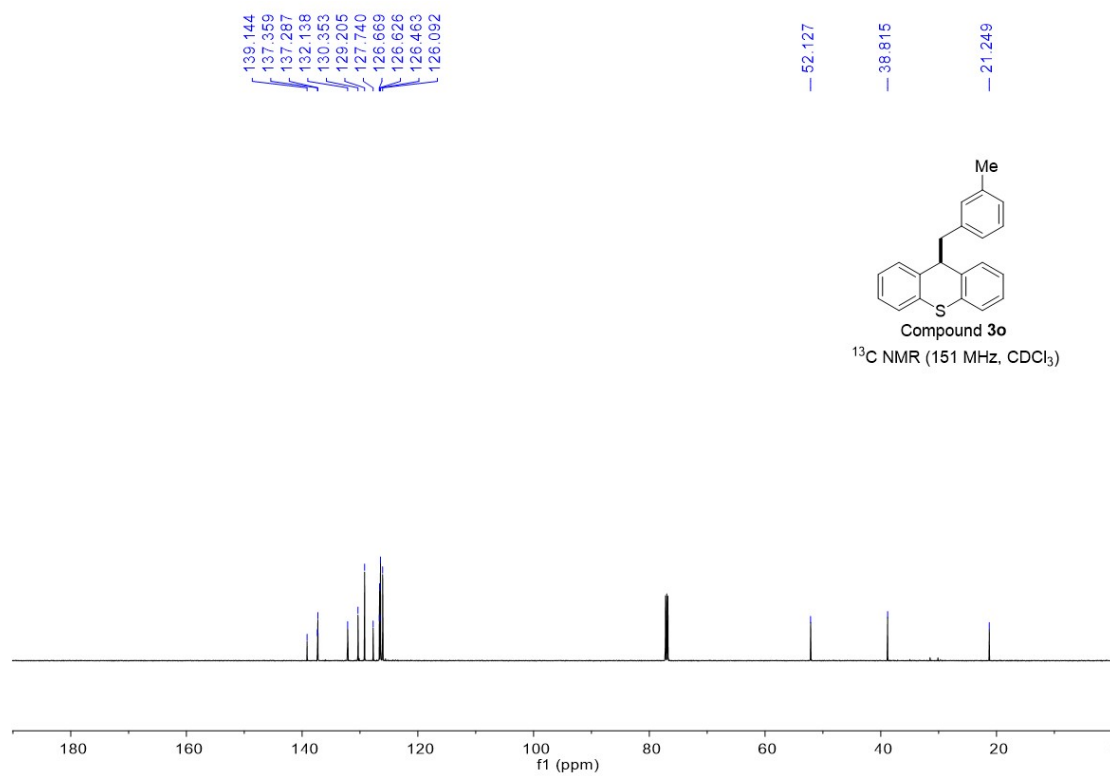
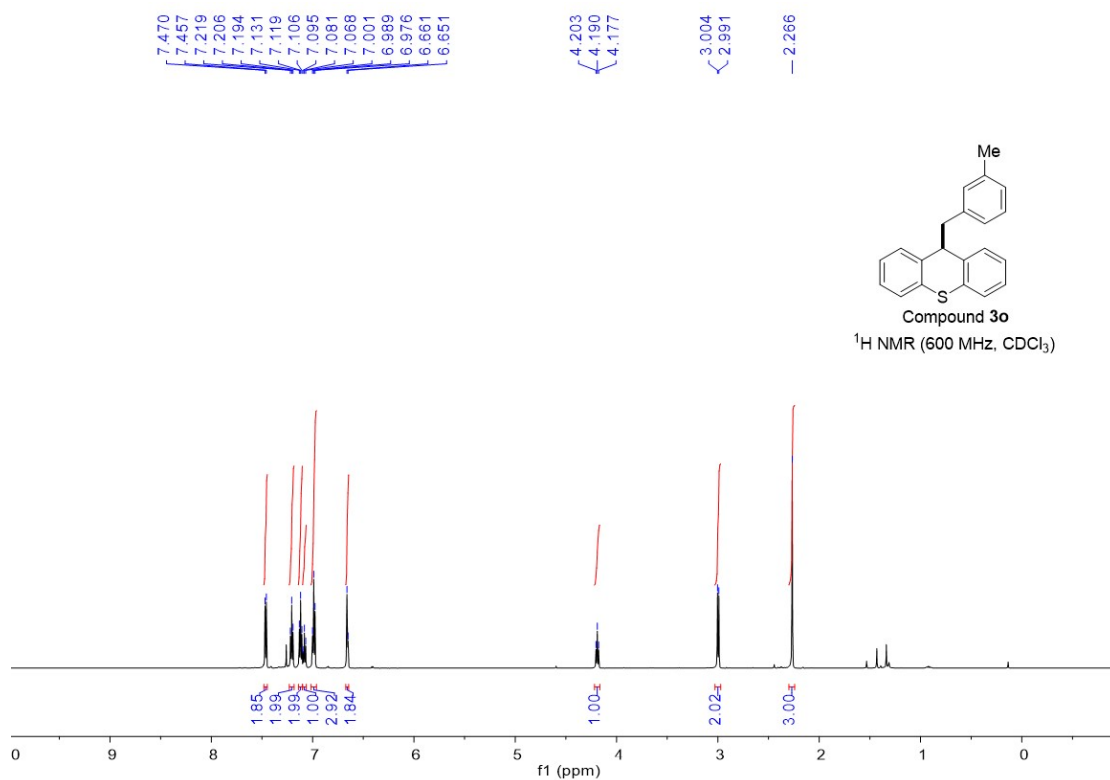
NMR spectra of 9-benzyl-9*H*-thioxanthene (**3m**)



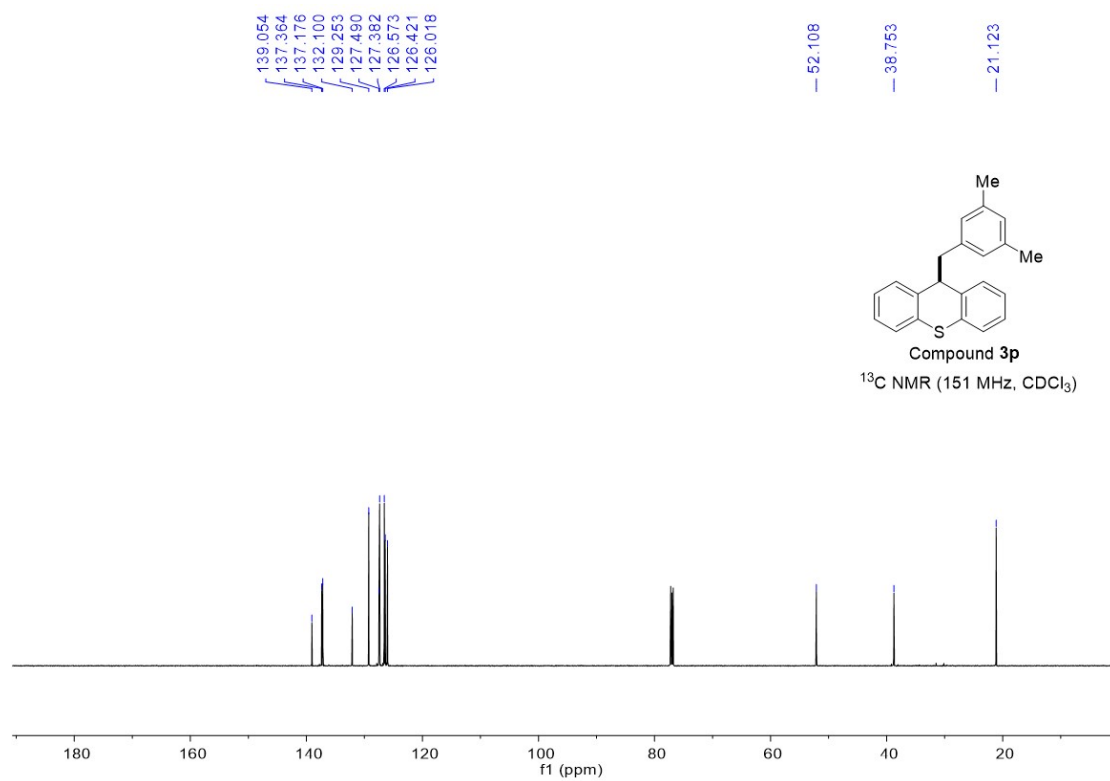
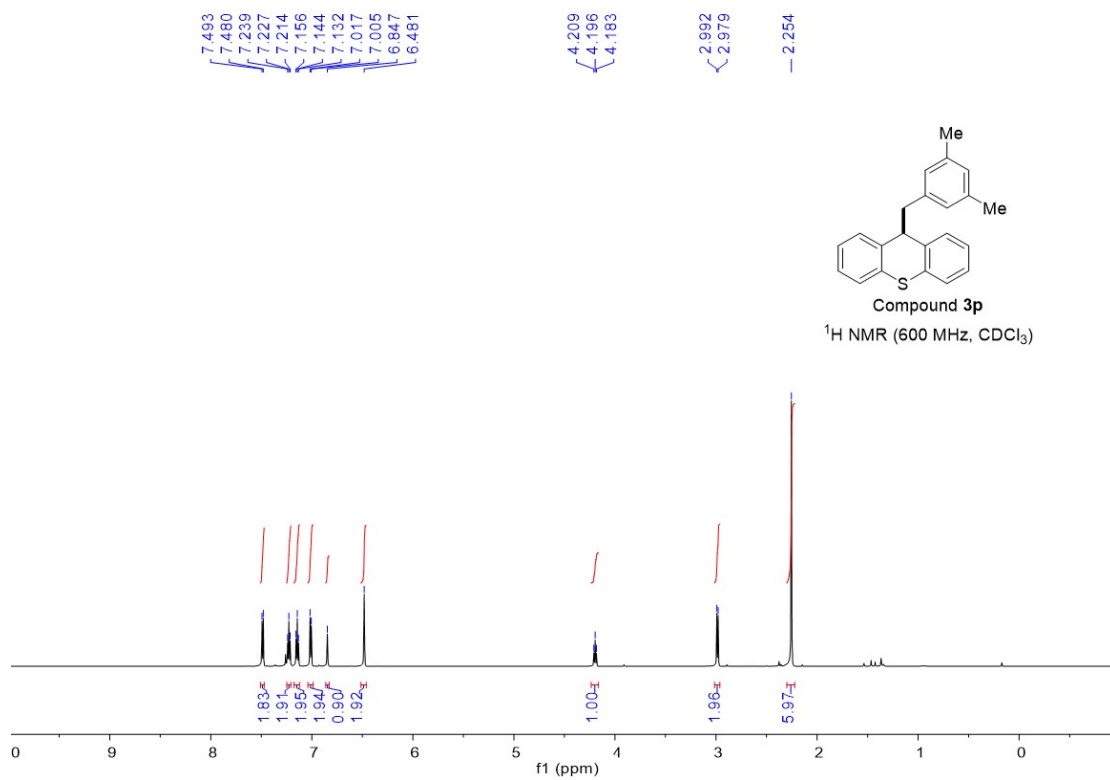
NMR spectra of 9-(4-methylbenzyl)-9H-thioxanthene (**3n**)



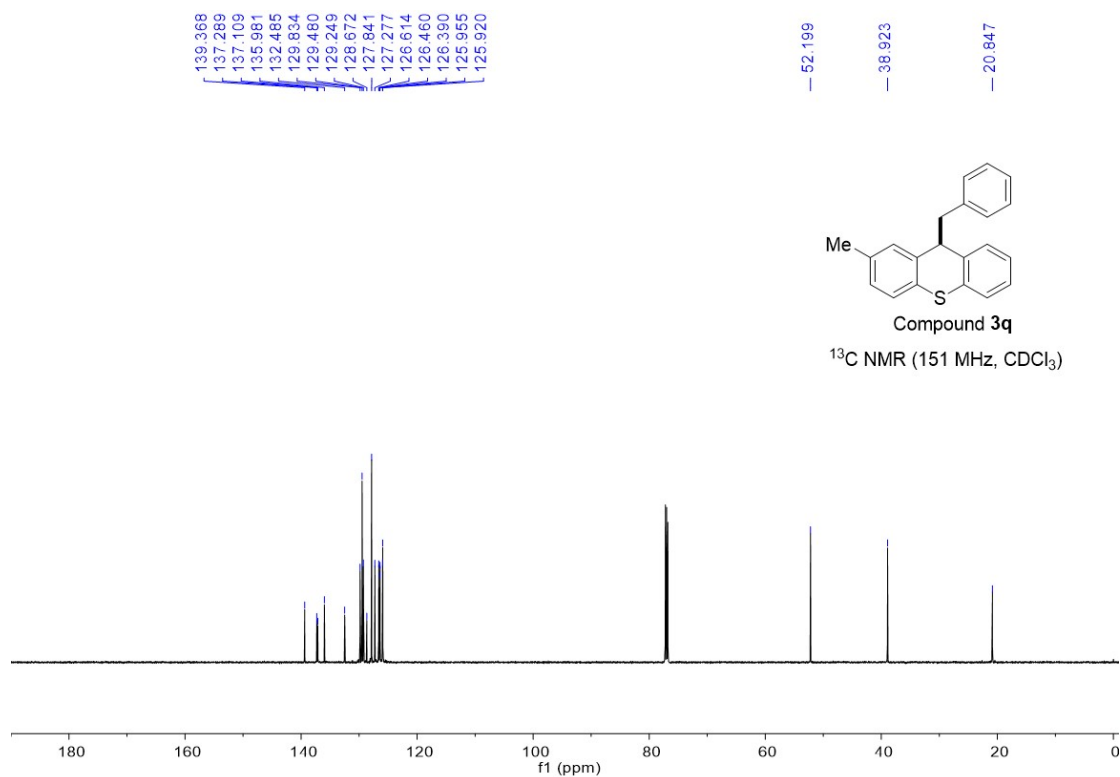
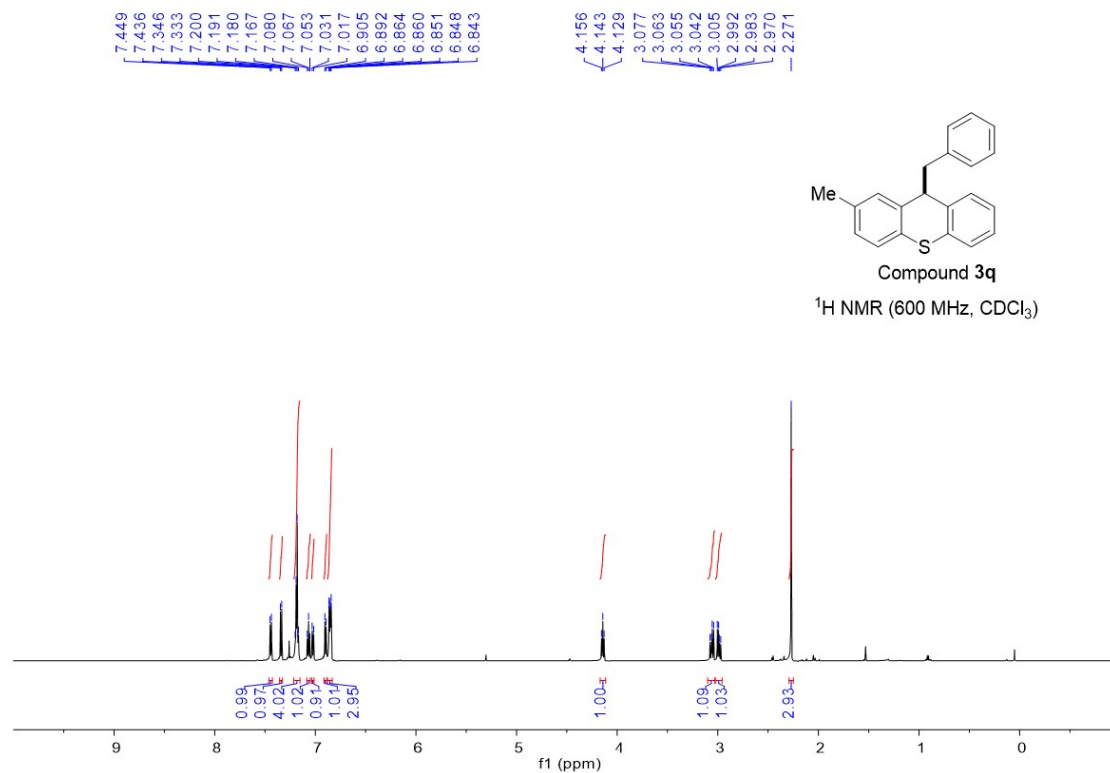
NMR spectra of 9-(3-methylbenzyl)-9*H*-thioxanthene (**3o**)



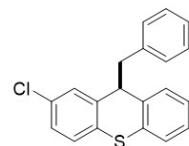
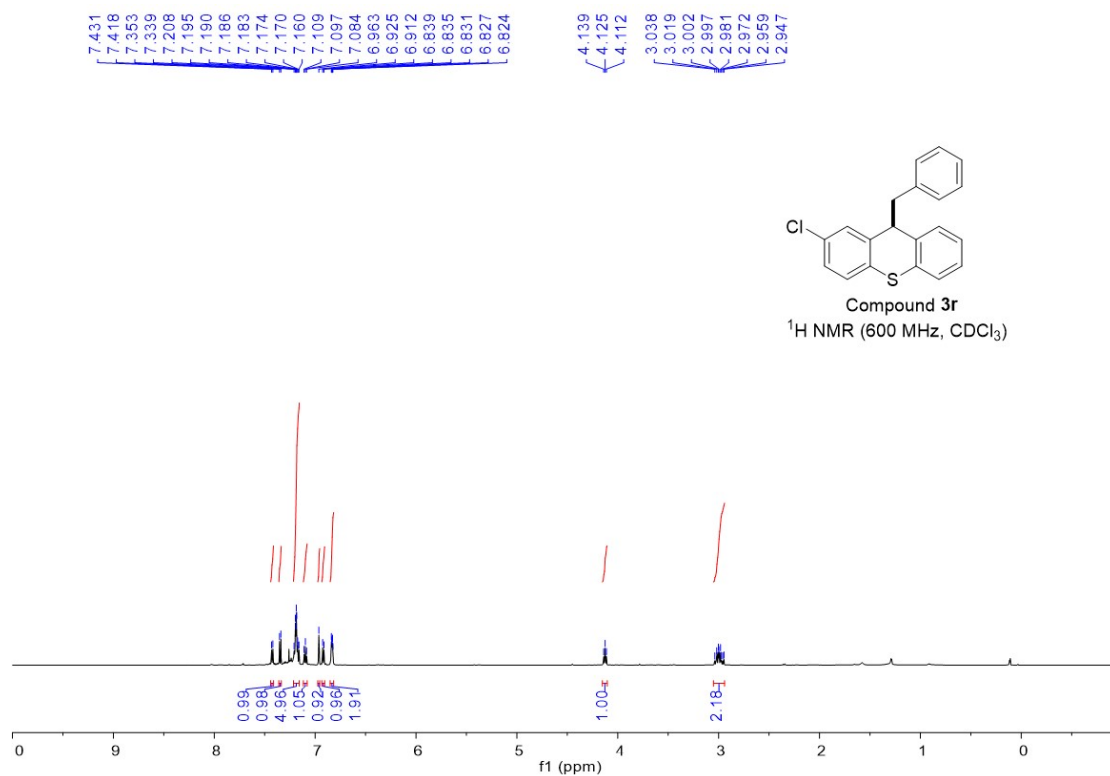
NMR spectra of 9-(3,5-dimethylbenzyl)-9H-thioxanthene (**3p**)



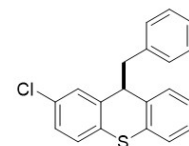
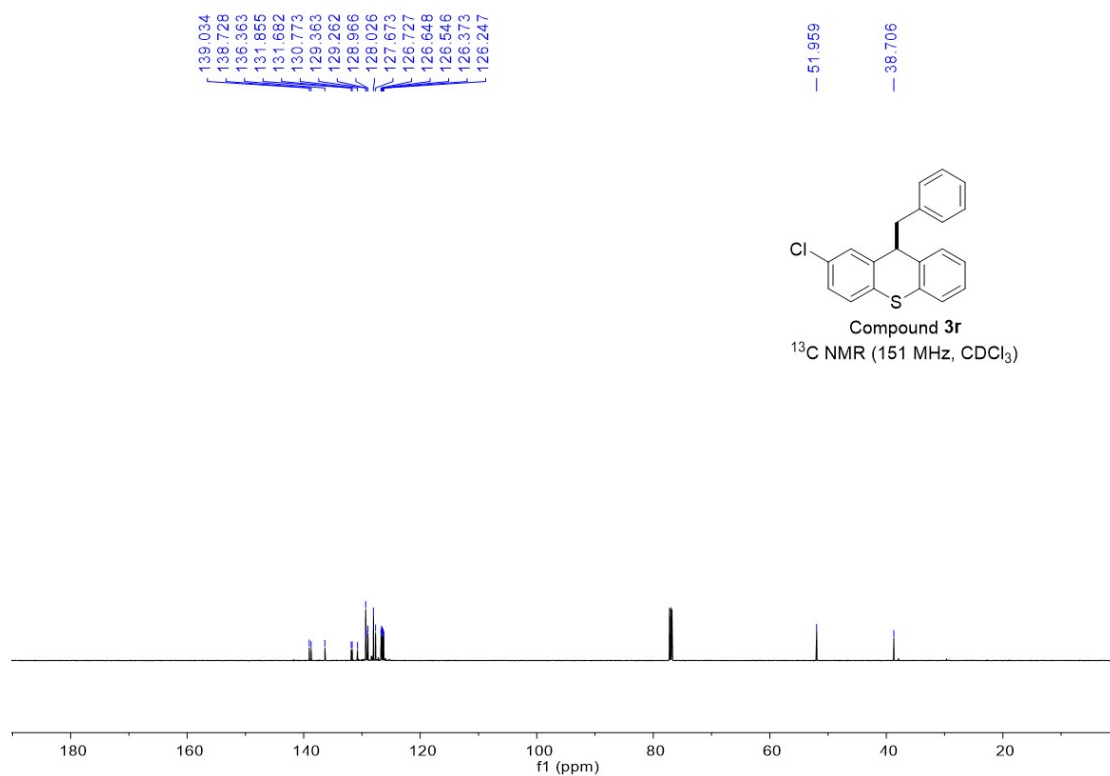
NMR spectra of 9-benzyl-2-methyl-9H-thioxanthene (**3q**)



NMR spectra of 9-benzyl-2-chloro-9H-thioxanthene (**3r**)

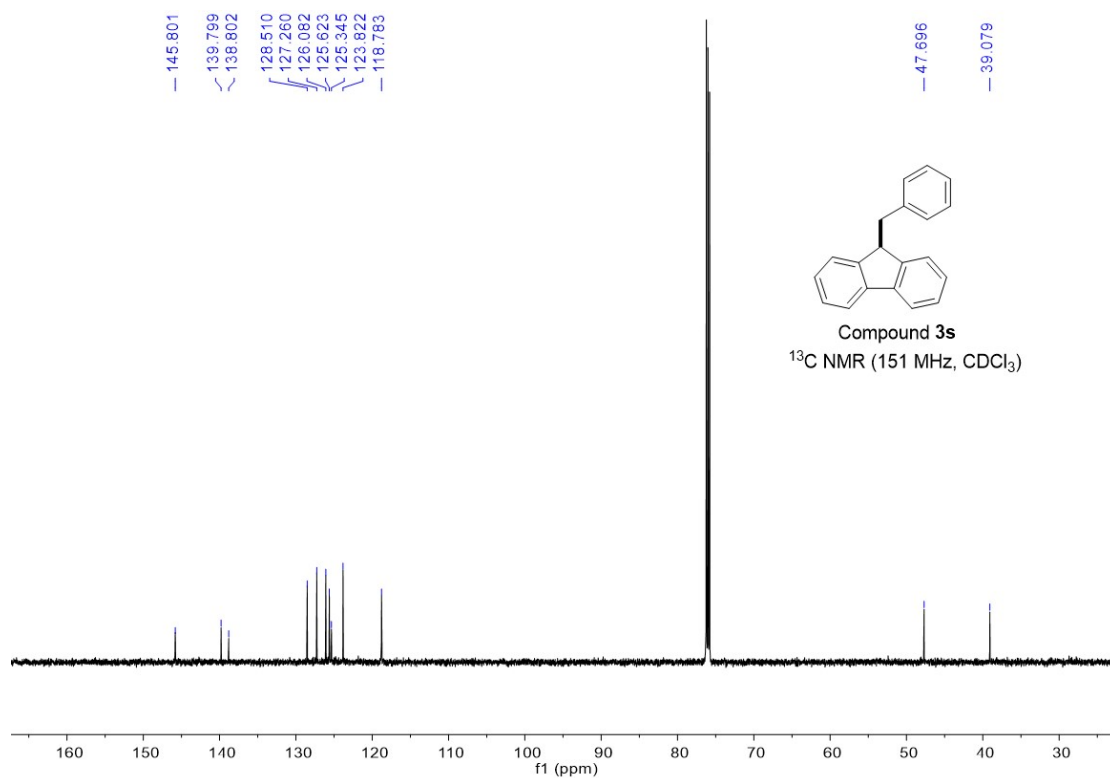
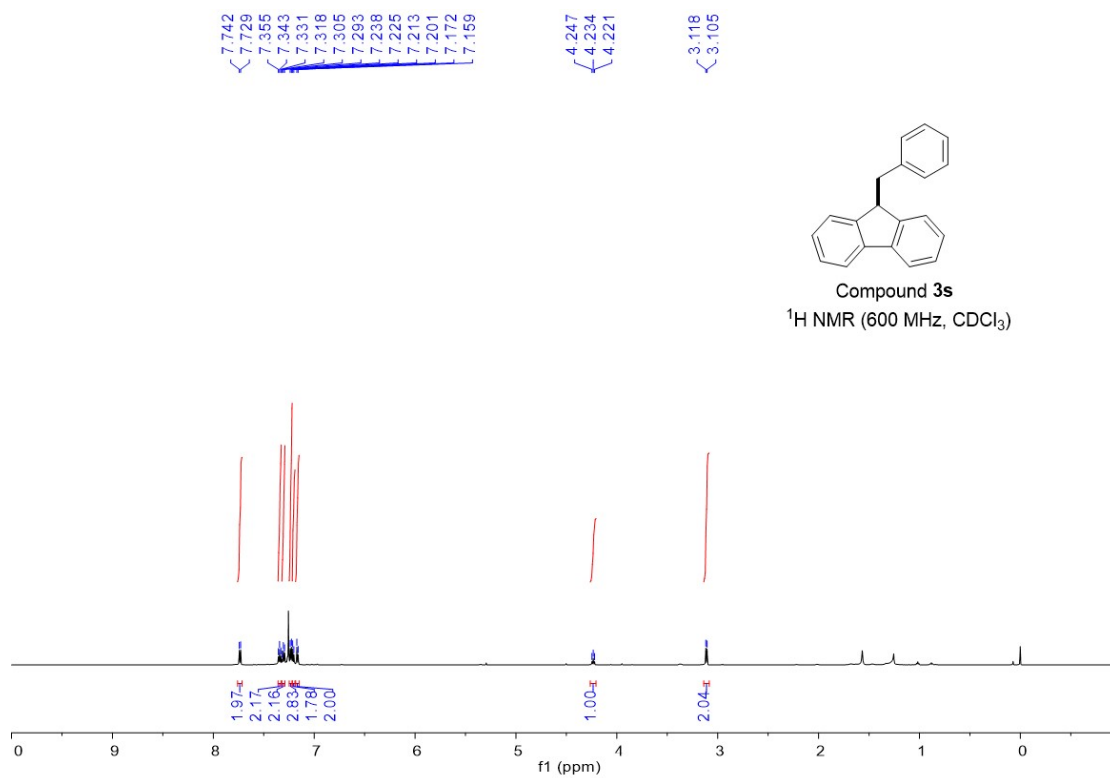


Compound **3r**
¹H NMR (600 MHz, CDCl₃)

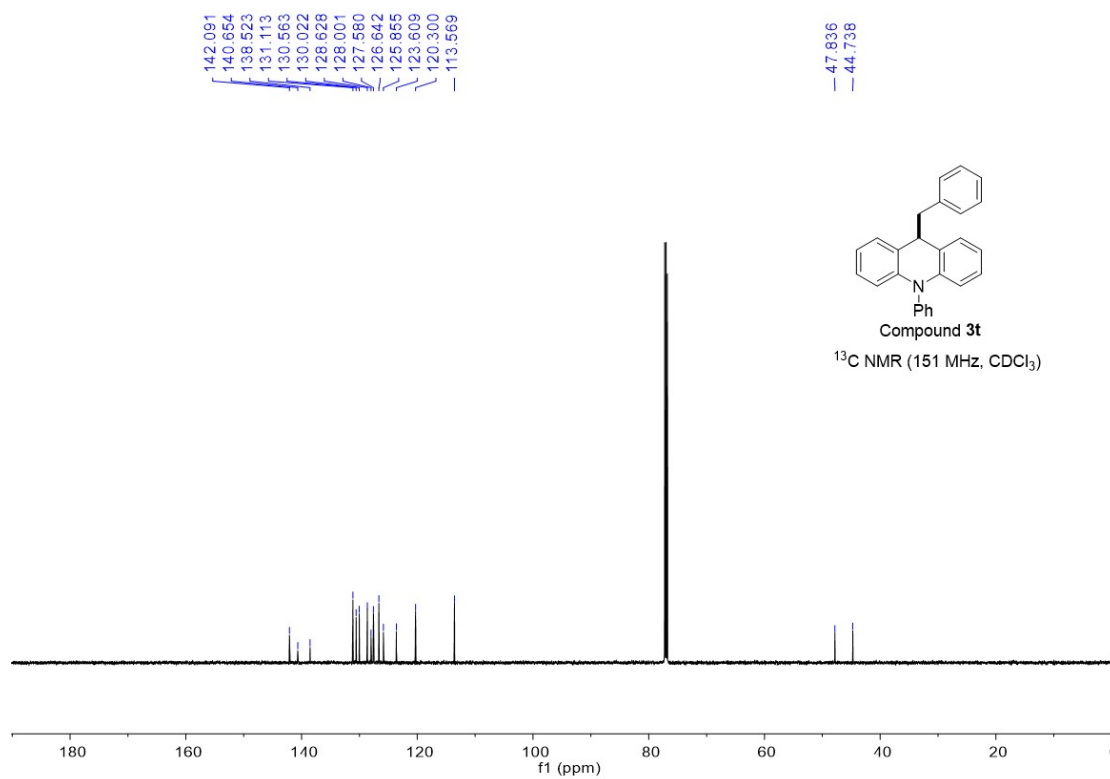
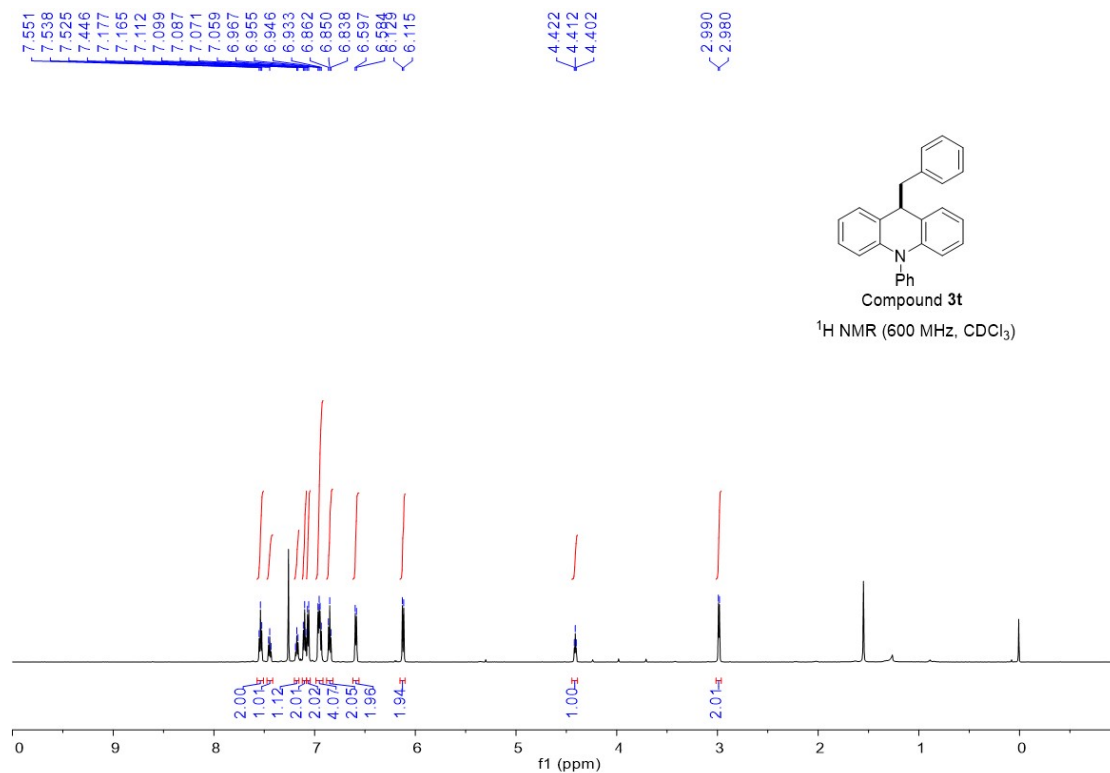


Compound **3r**
¹³C NMR (151 MHz, CDCl₃)

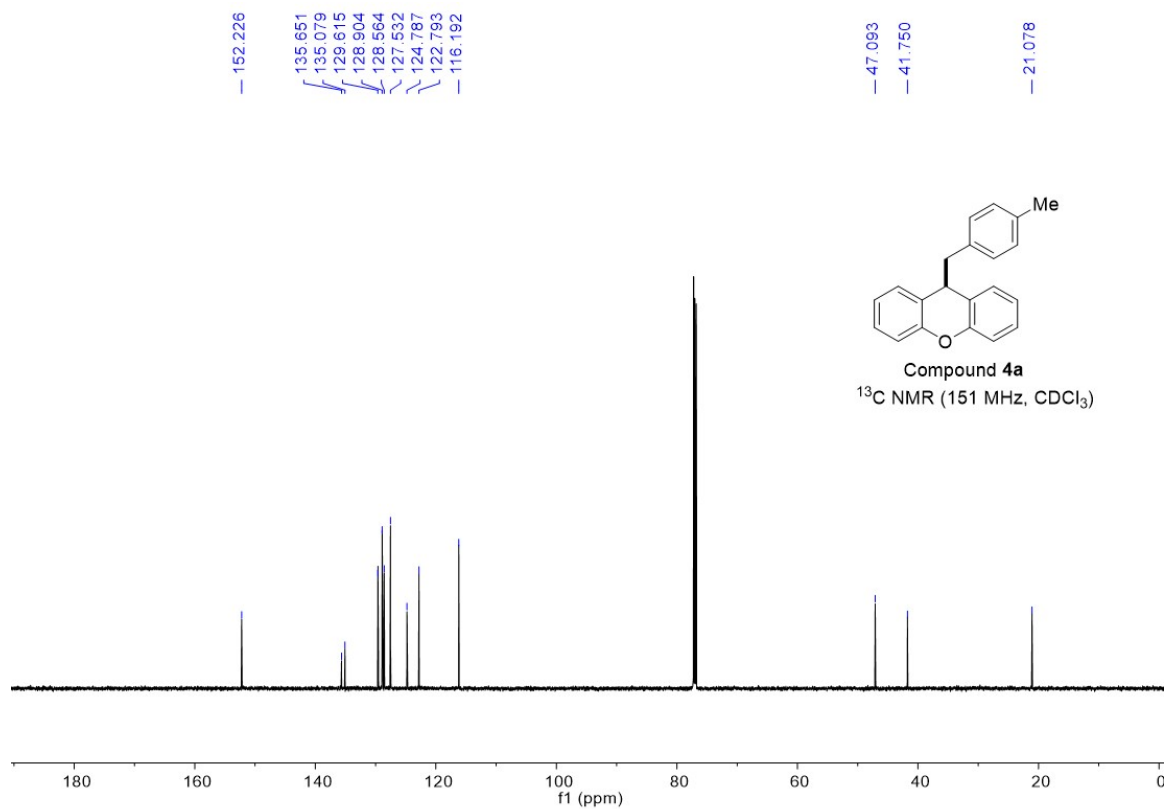
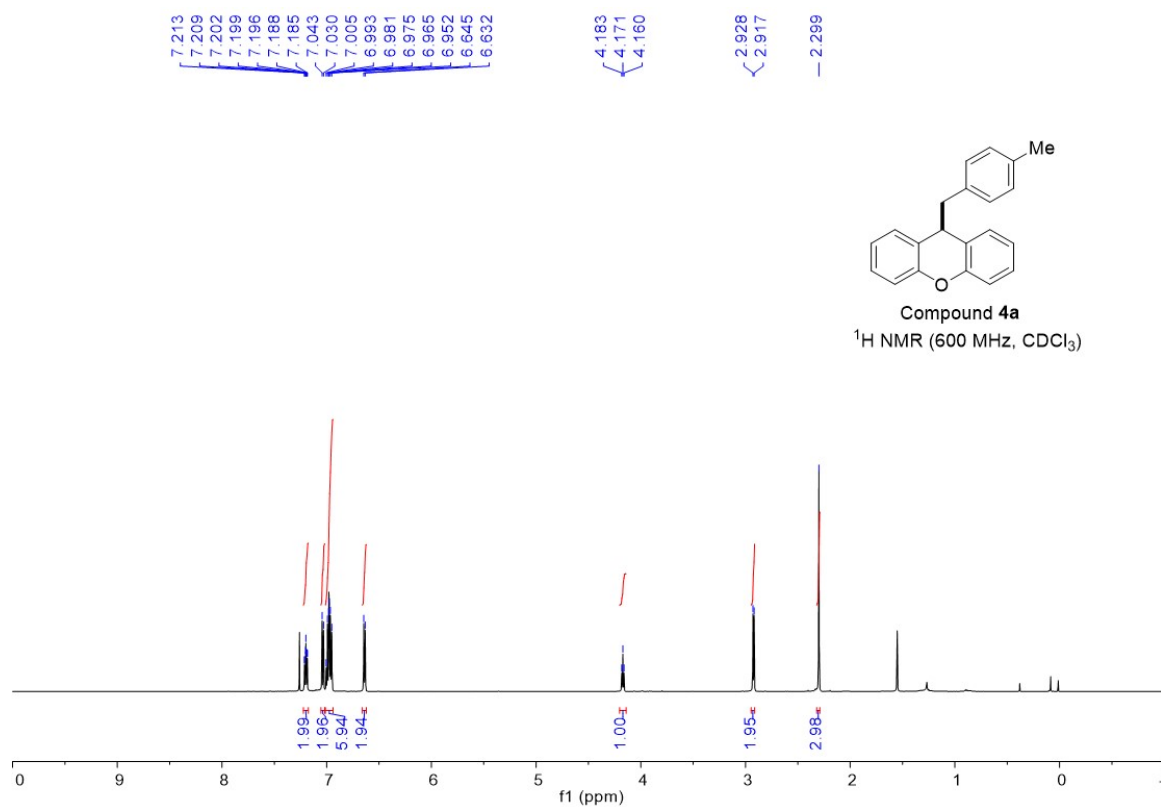
NMR spectra of 9-benzyl-9H-fluorene (3s)



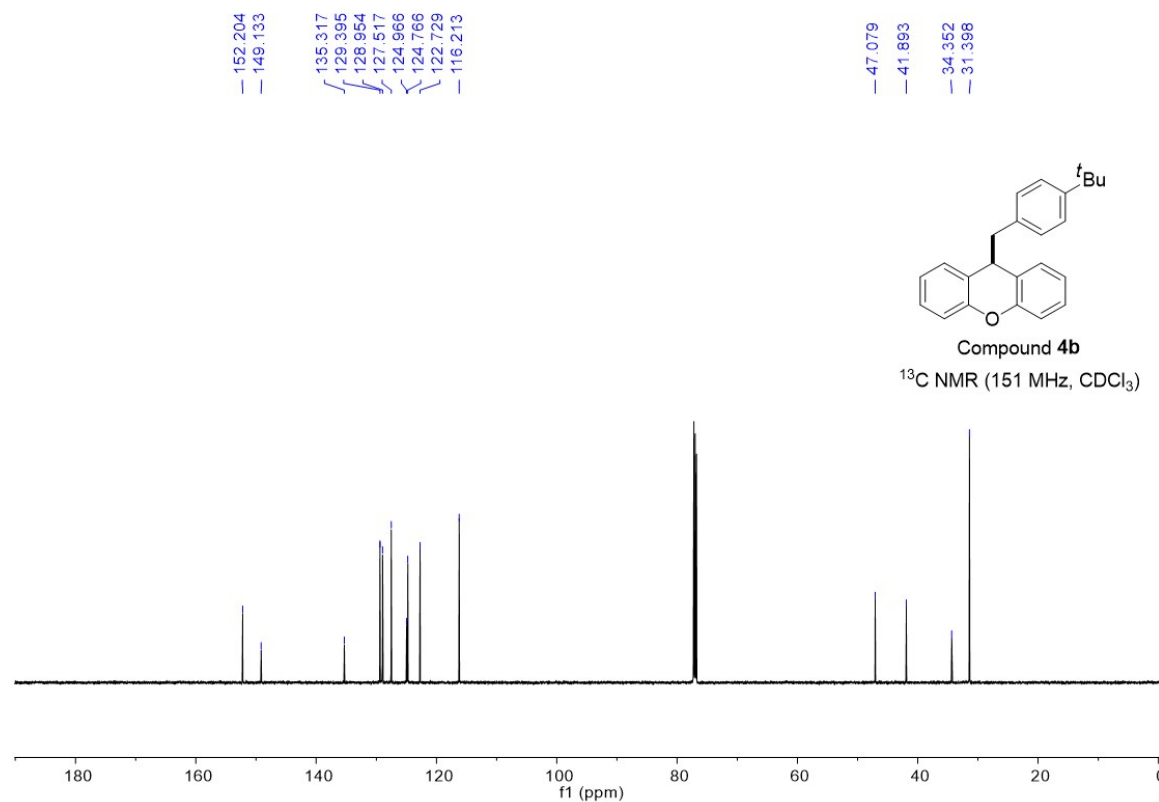
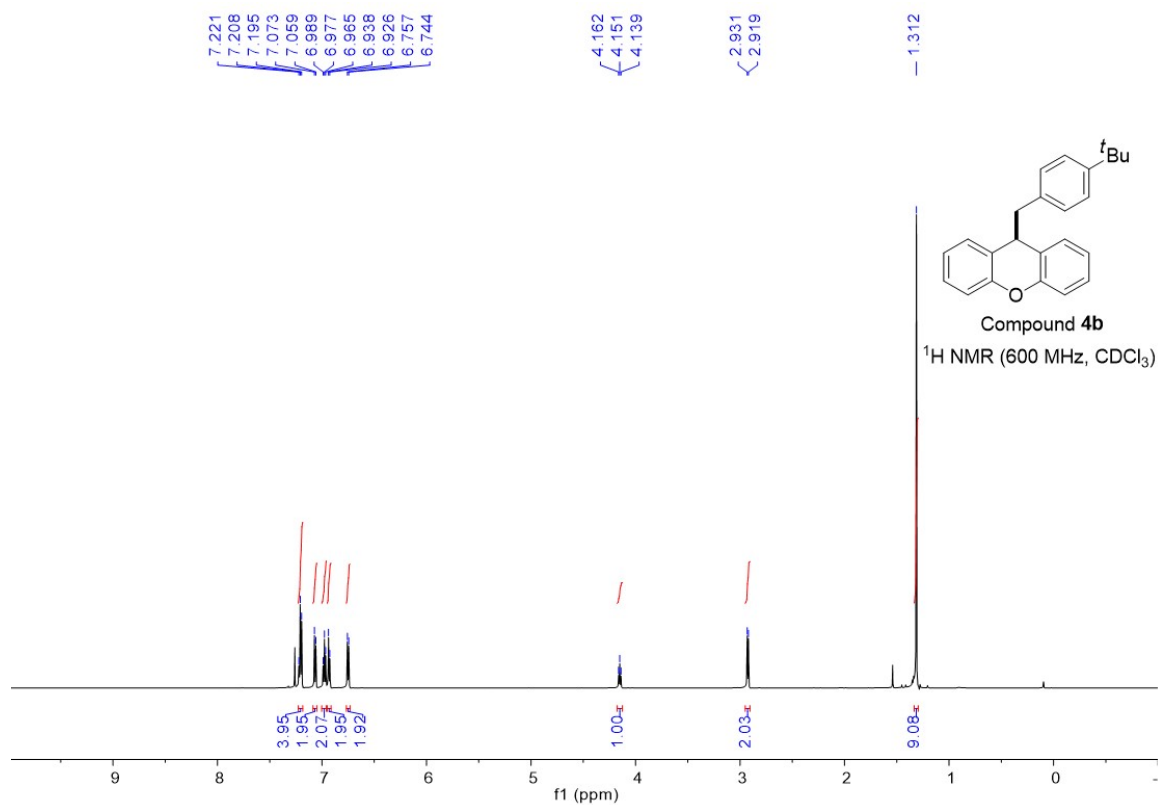
NMR spectra of 9-benzyl-10-phenyl-9,10-dihydroacridine (**3t**)



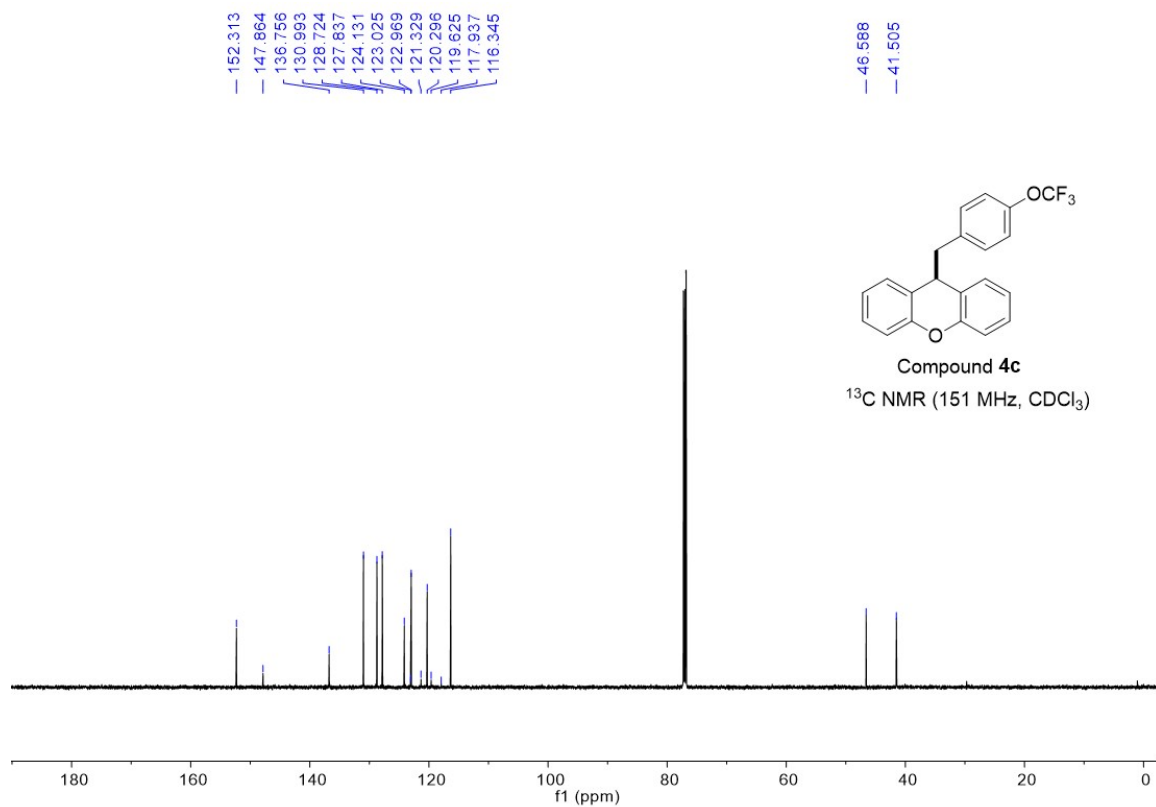
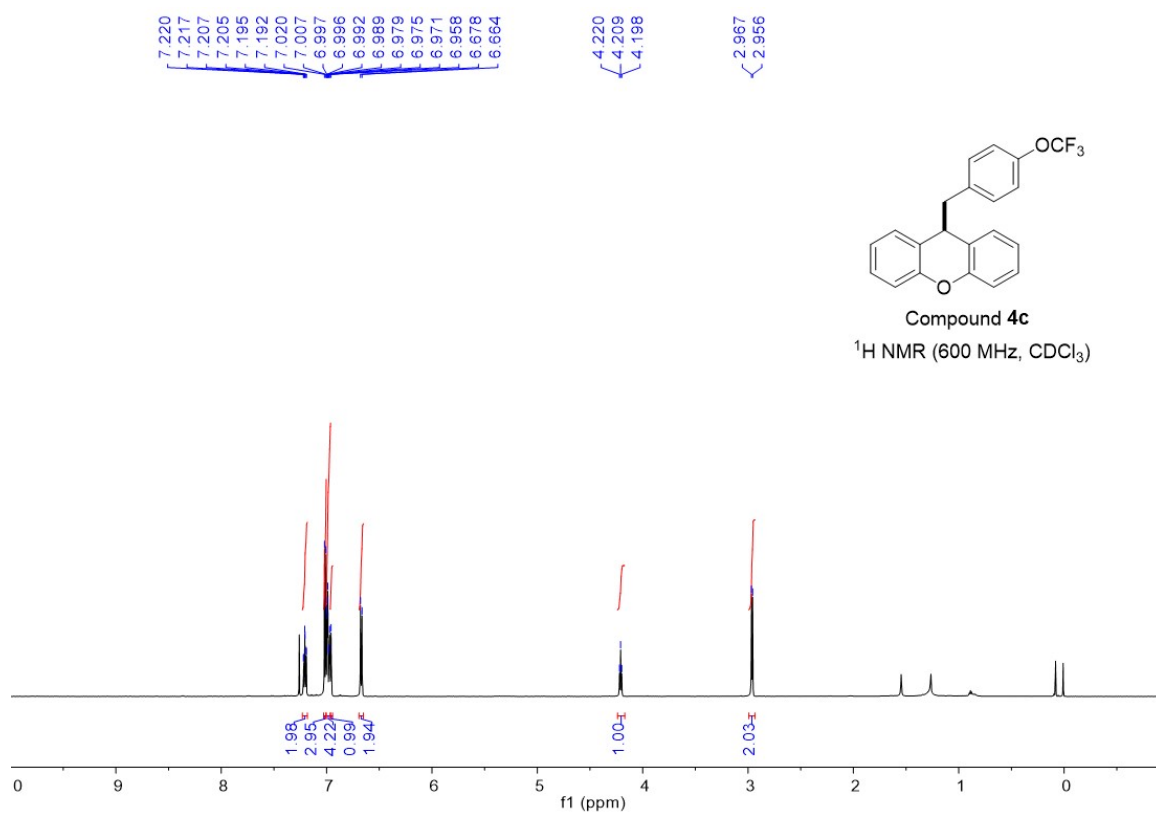
NMR spectra of 9-(4-methylbenzyl)-9H-xanthene (**4a**)

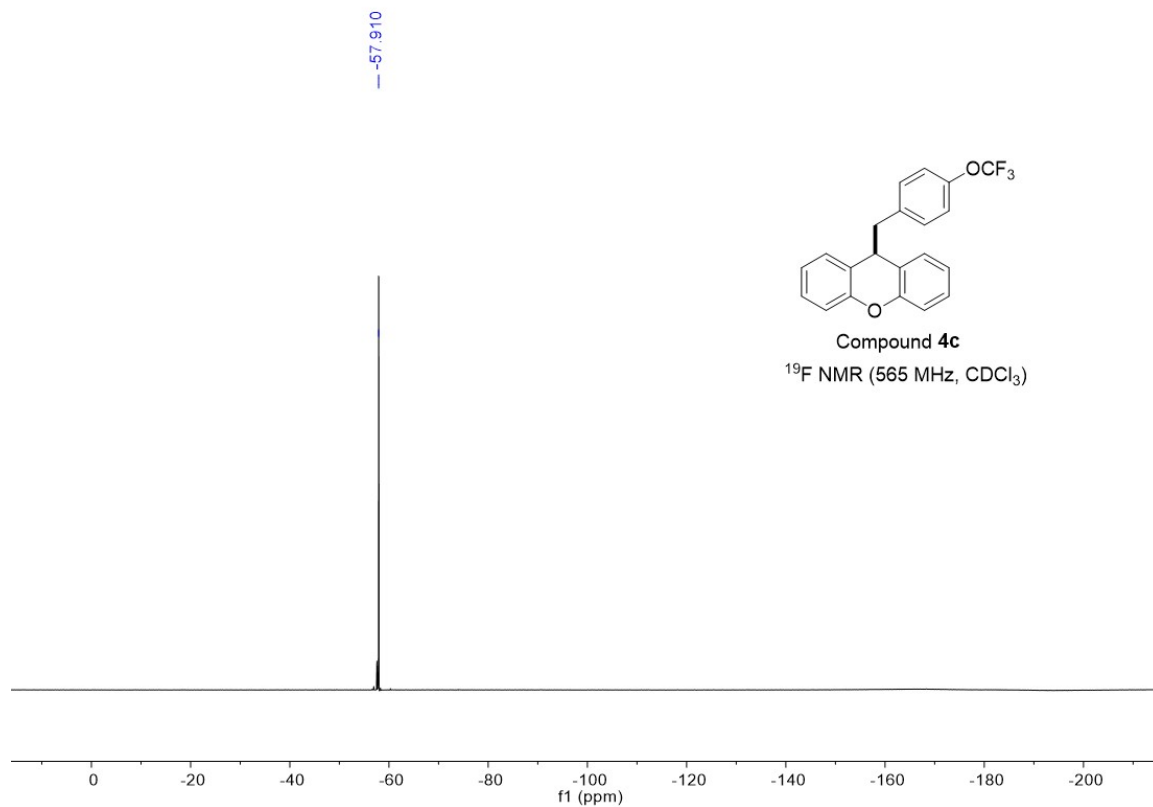


NMR spectra of 9-(4-butylbenzyl)-9H-xanthene (**4b**)

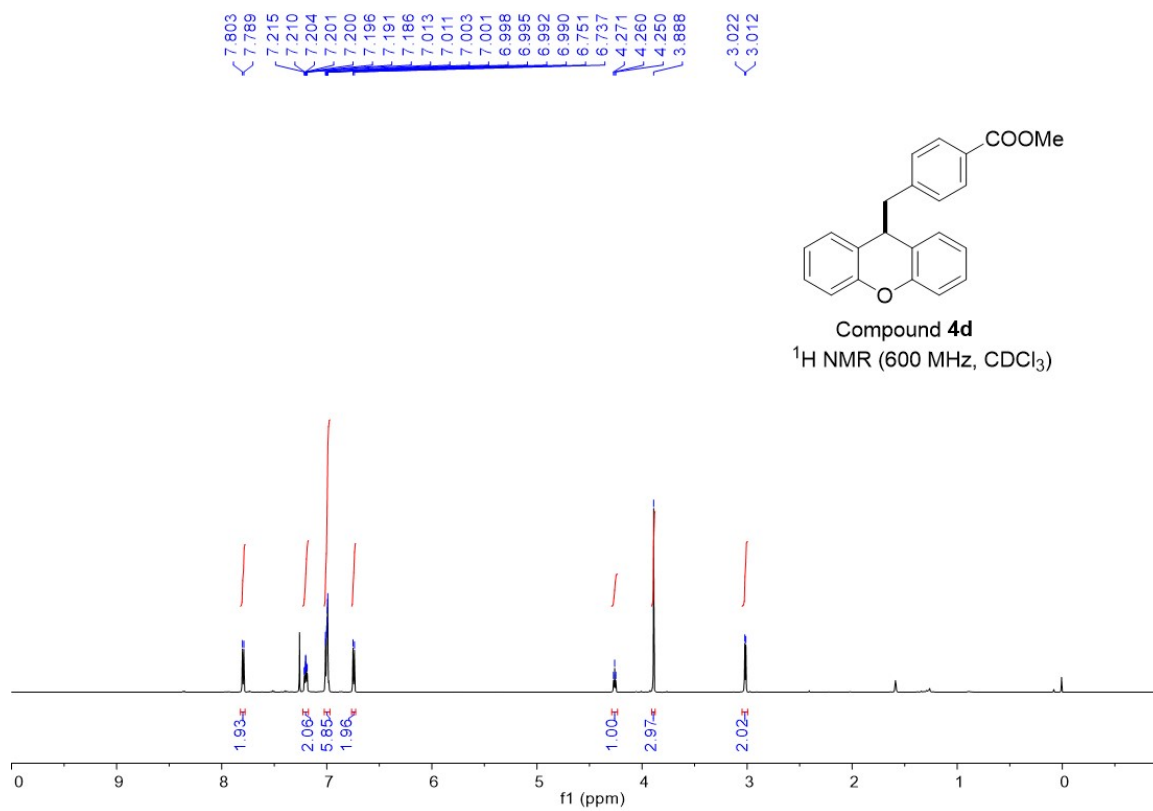


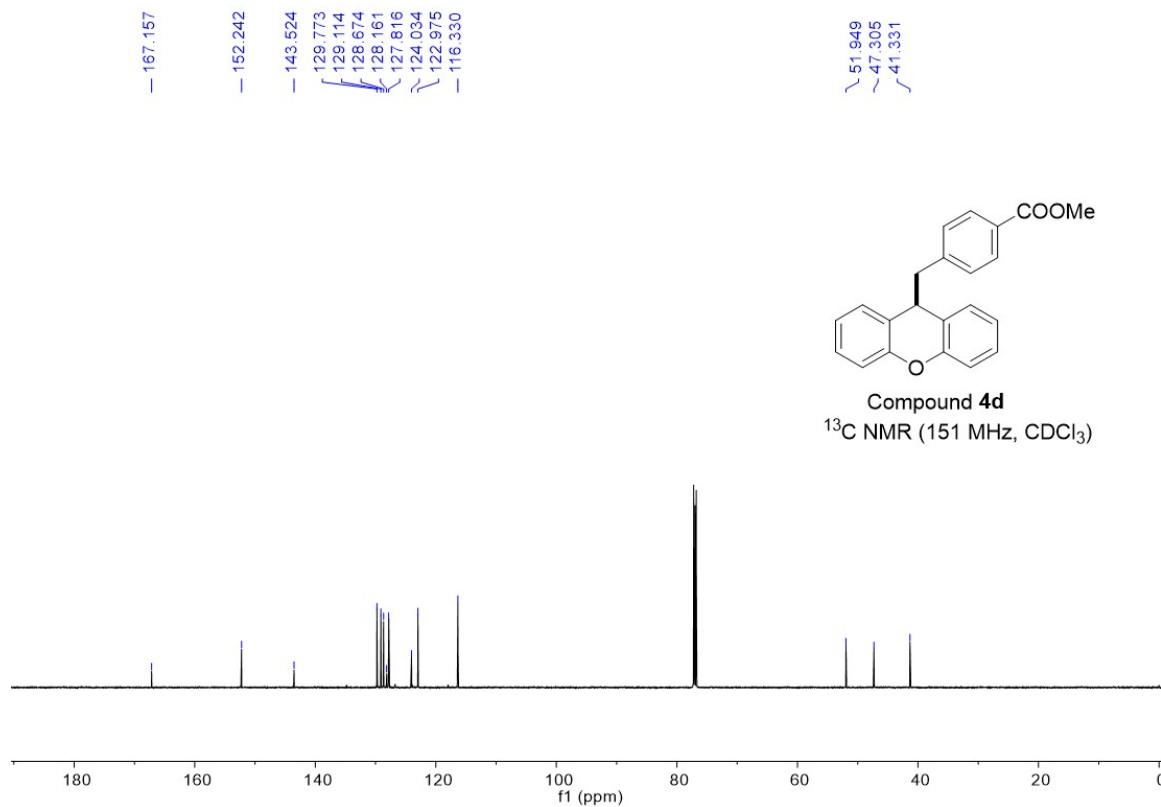
NMR spectra of 9-(4-(trifluoromethoxy)benzyl)-9H-xanthene (**4c**)



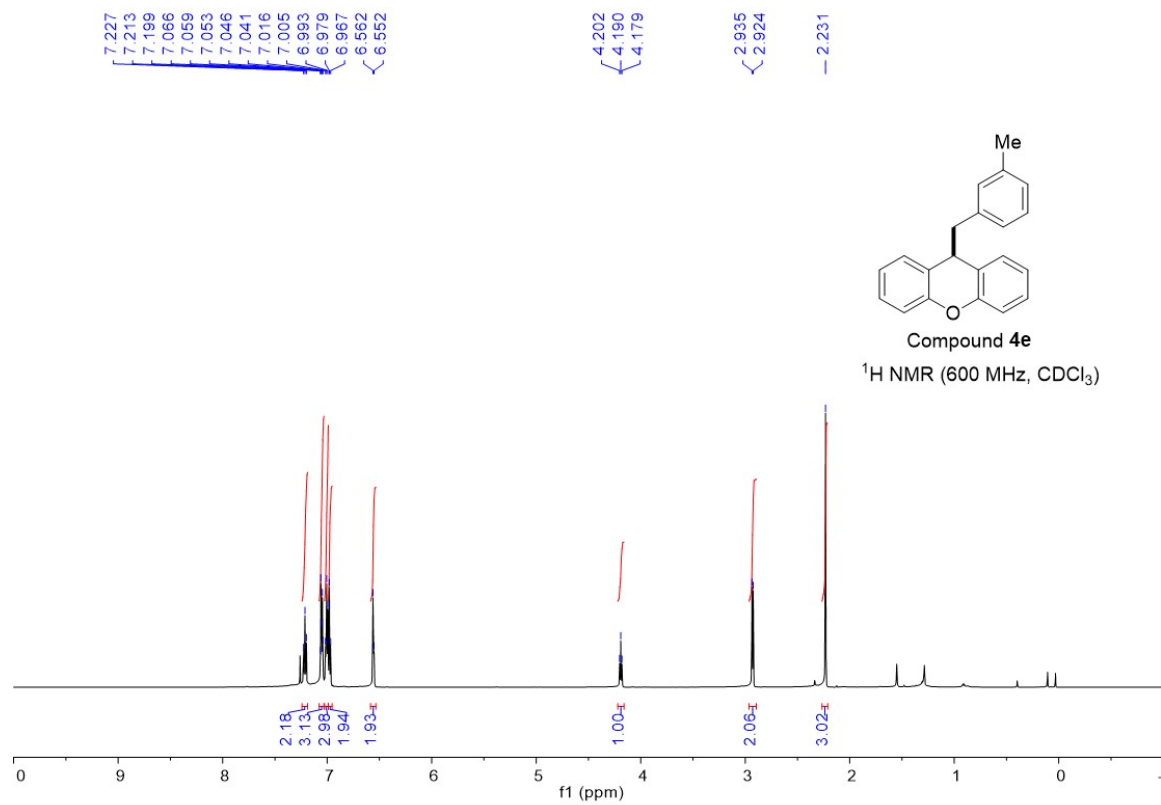


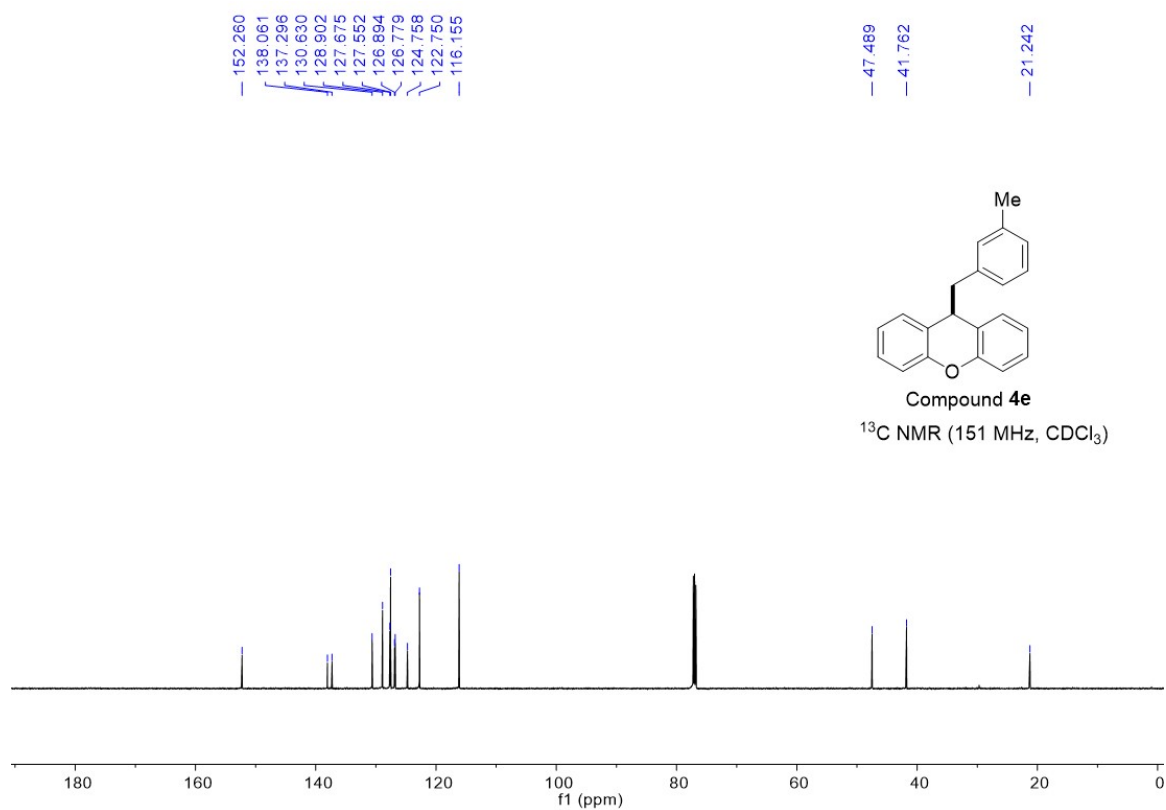
NMR spectra of methyl 4-((9H-xanthen-9-yl)methyl)benzoate (**4d**)



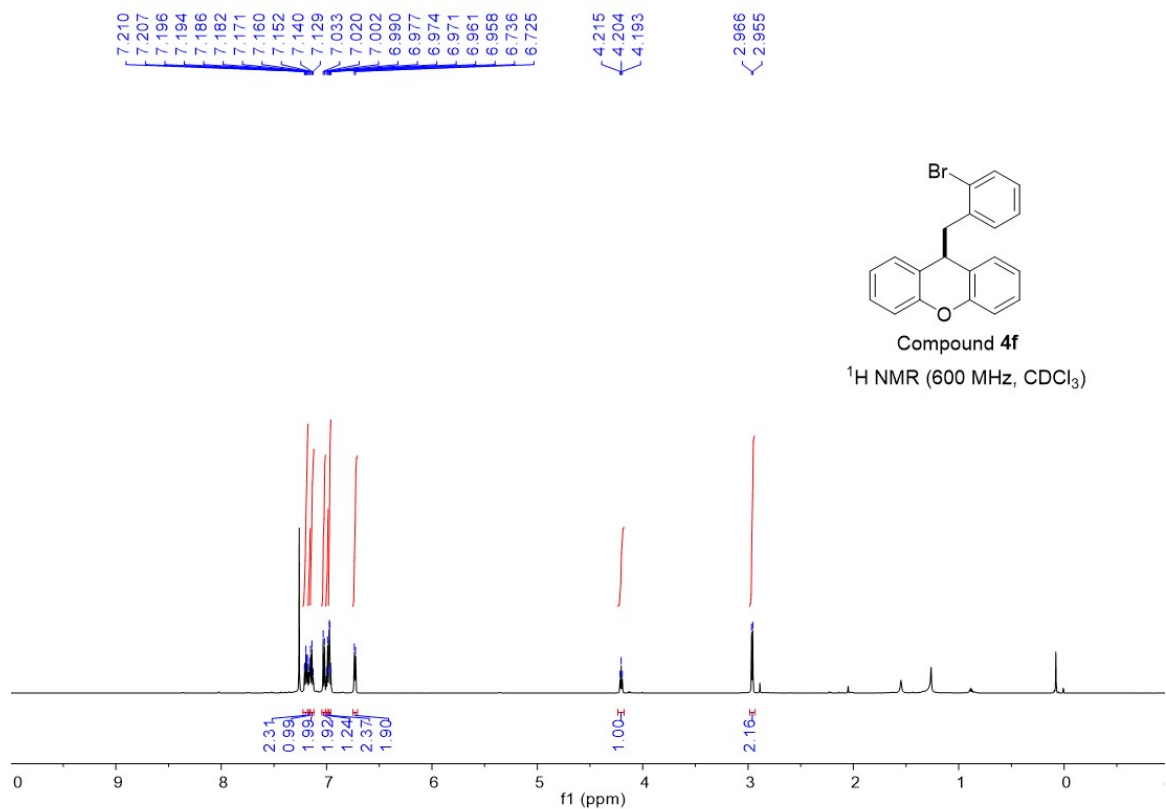


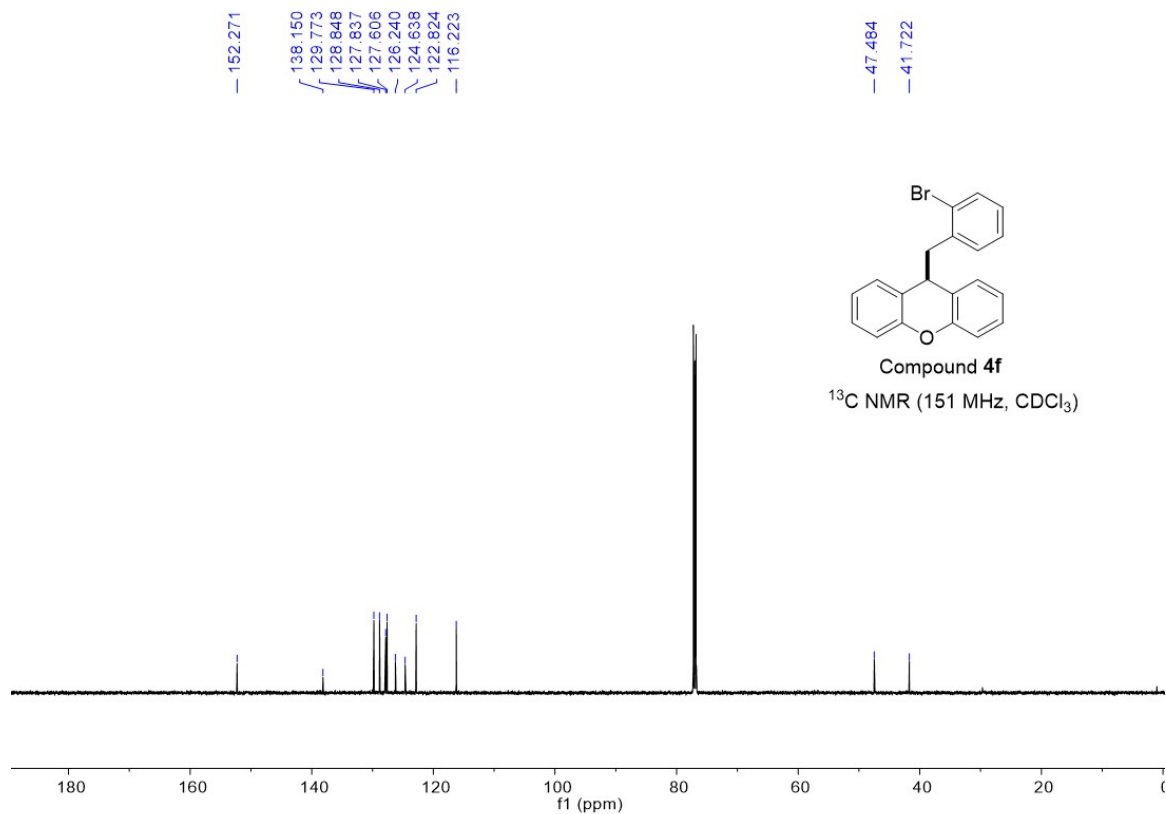
NMR spectra of 9-(3-methylbenzyl)-9*H*-xanthene (**4e**)



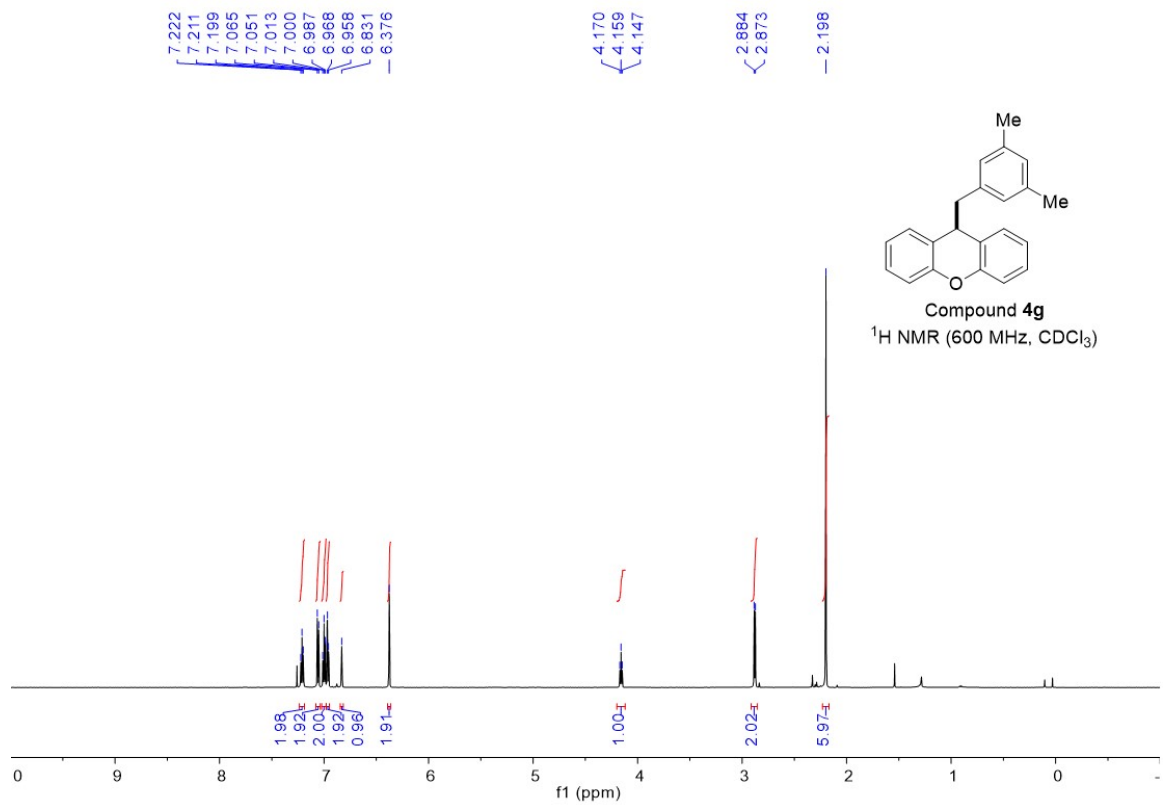


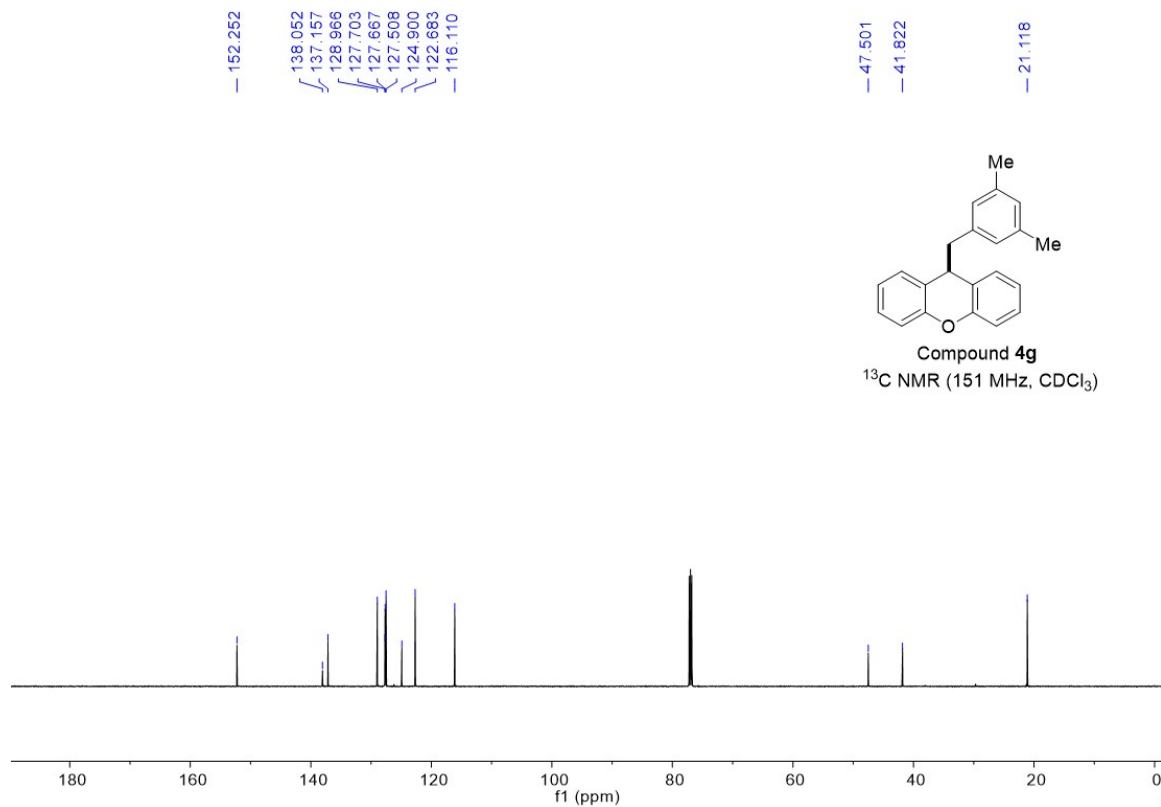
NMR spectra of 9-(2-bromobenzyl)-9H-xanthene (**4f**)



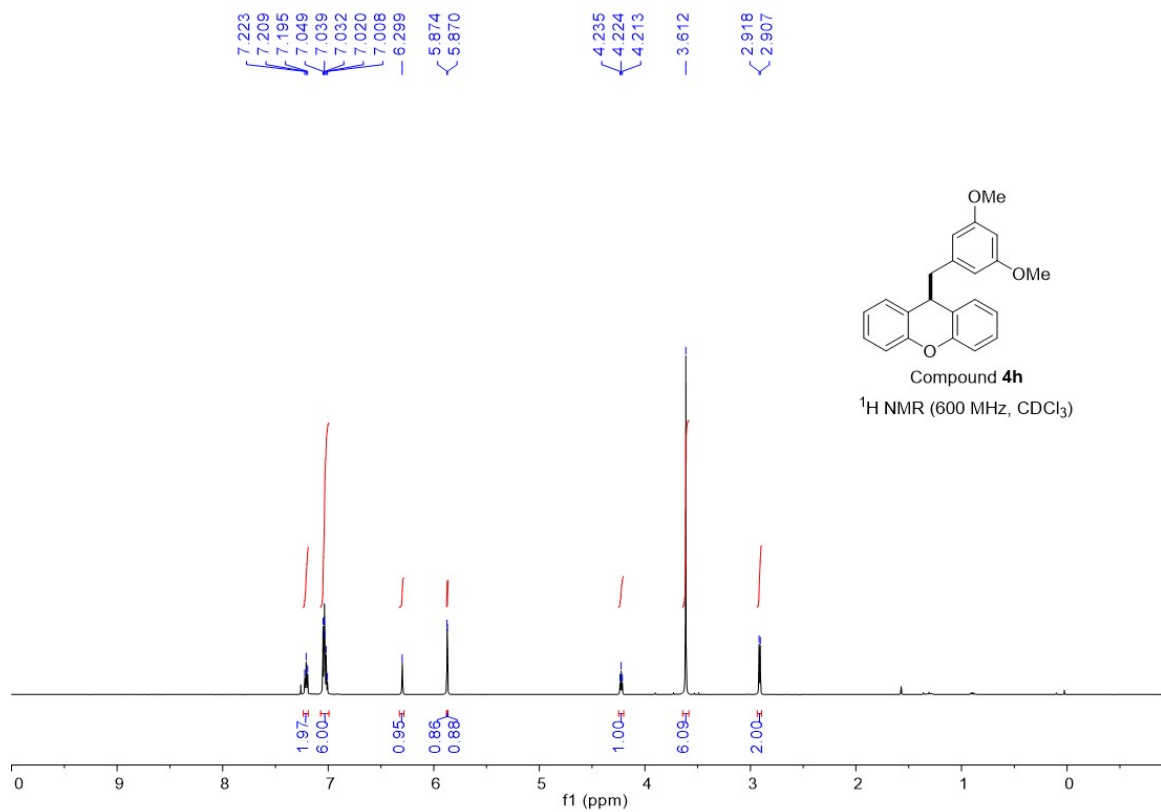


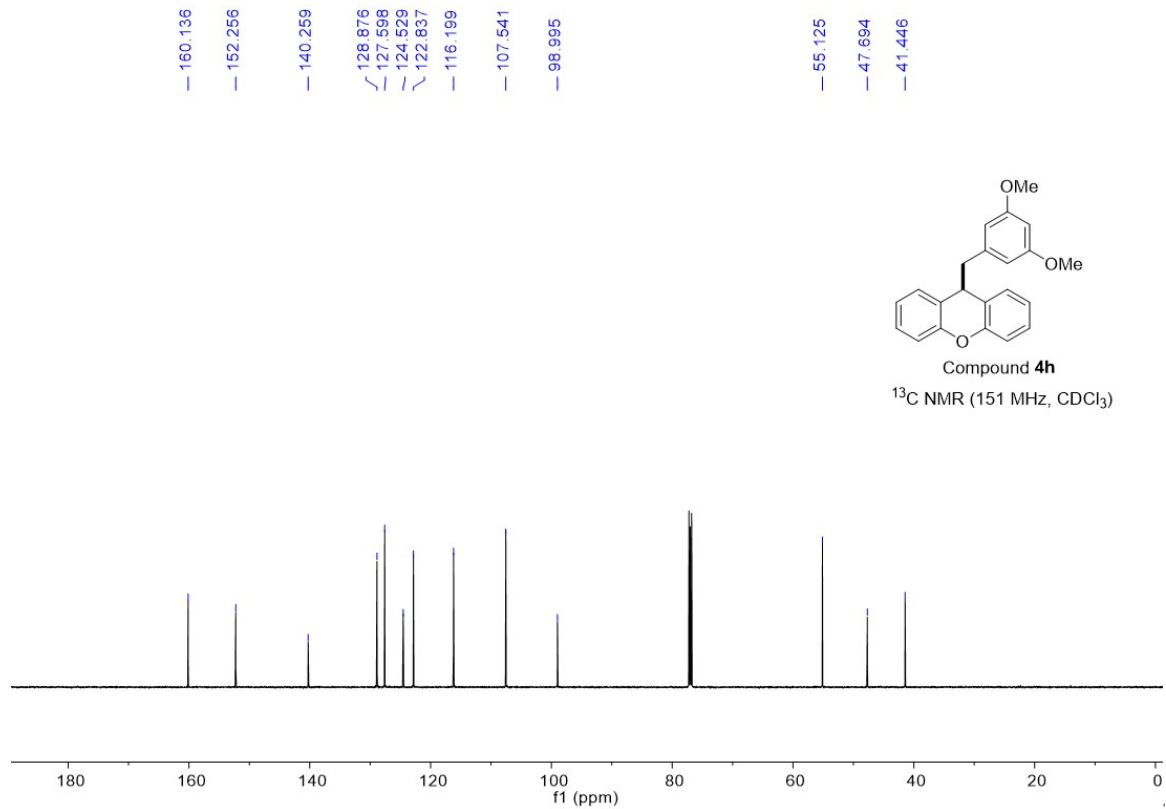
NMR spectra of 9-(3,5-dimethylbenzyl)-9*H*-xanthene (**4g**)



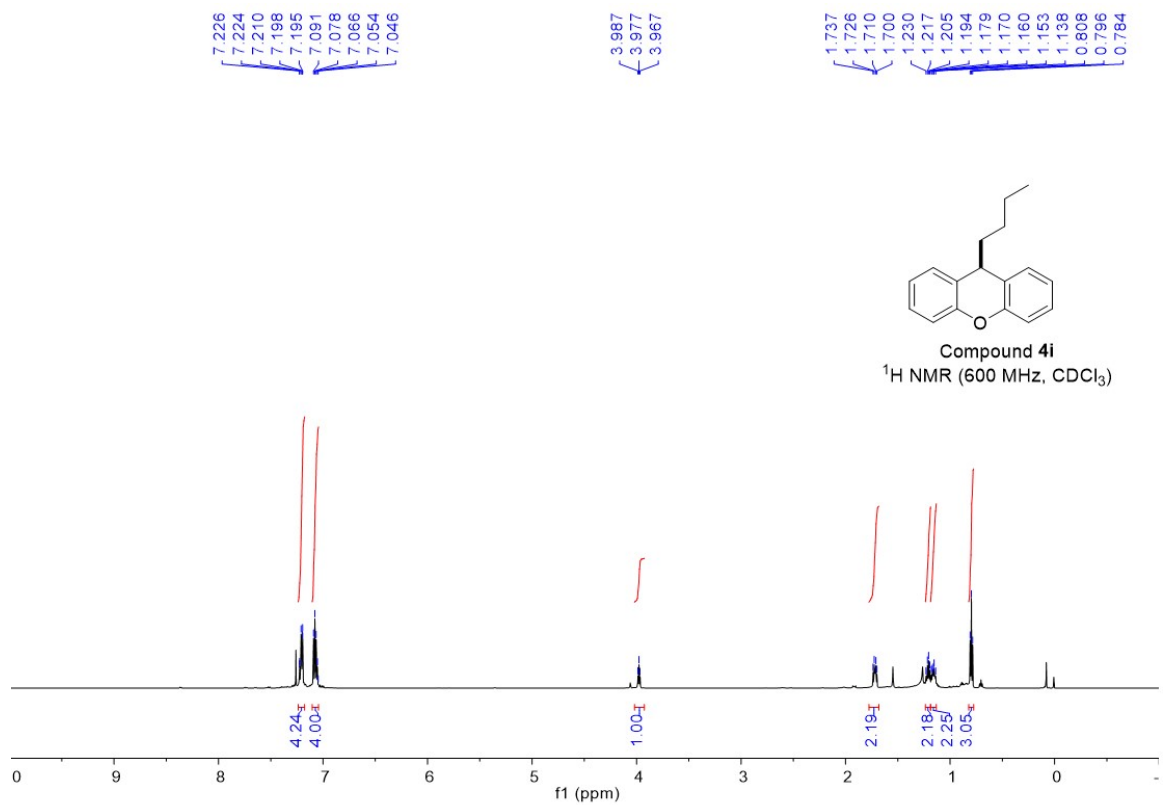


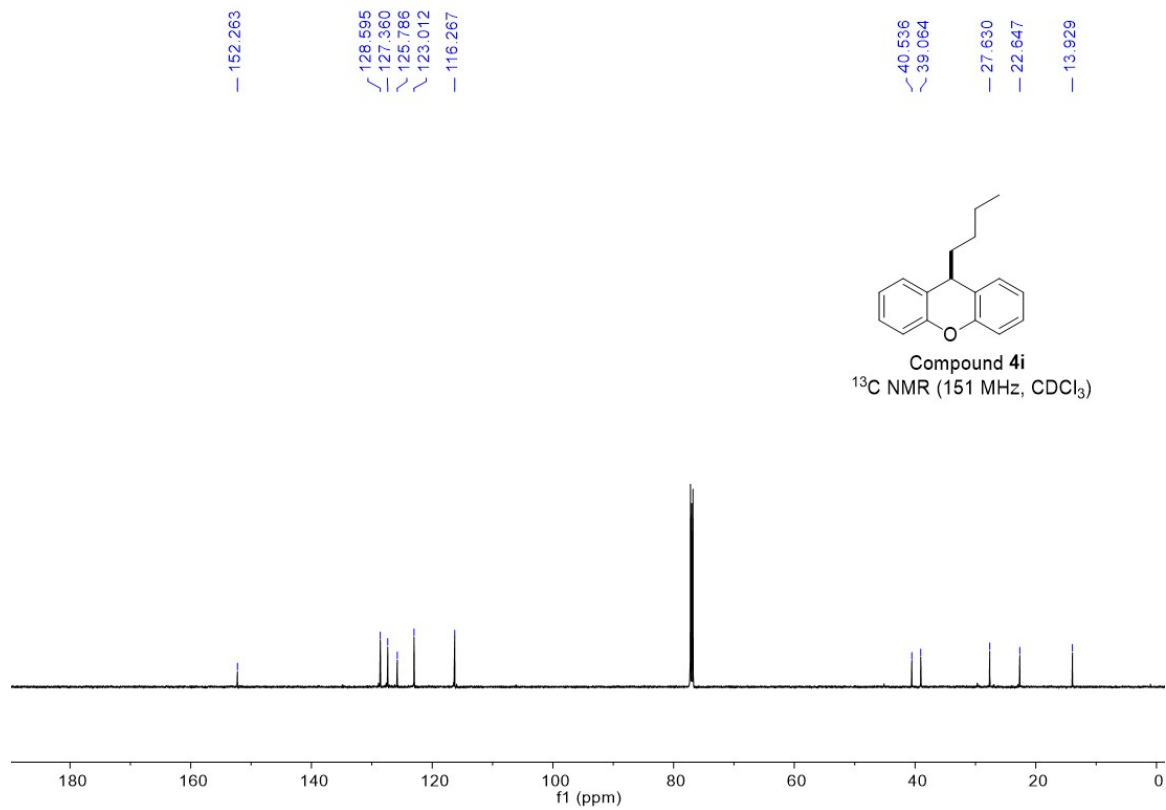
NMR spectra of 9-(3,5-dimethoxybenzyl)-9H-xanthene (**4h**)



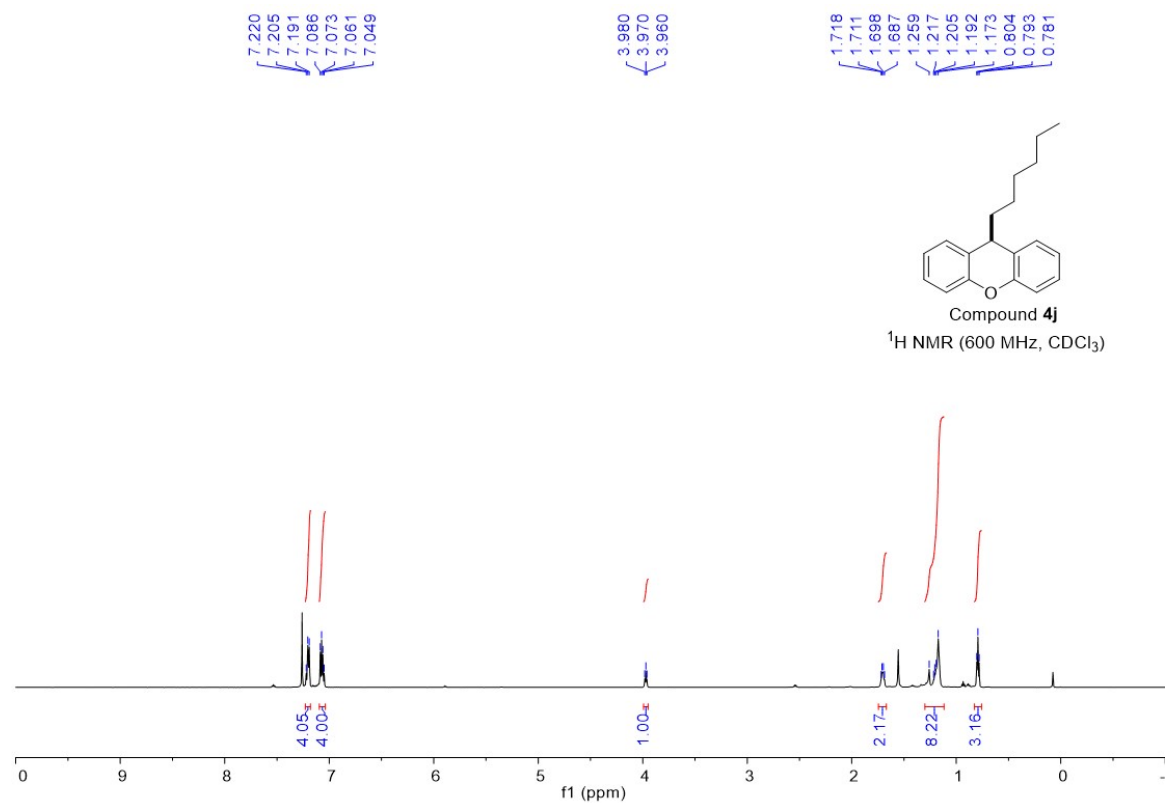


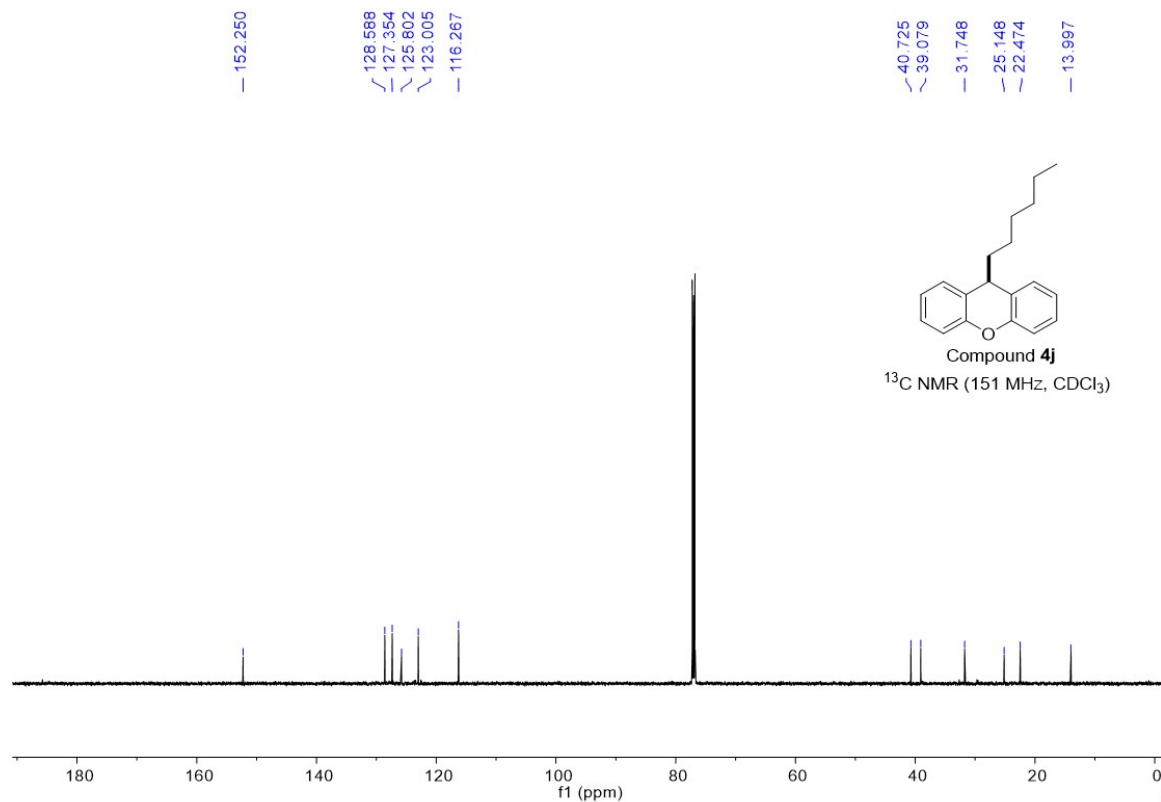
NMR spectra of 9-butyl-9H-xanthene (4i)



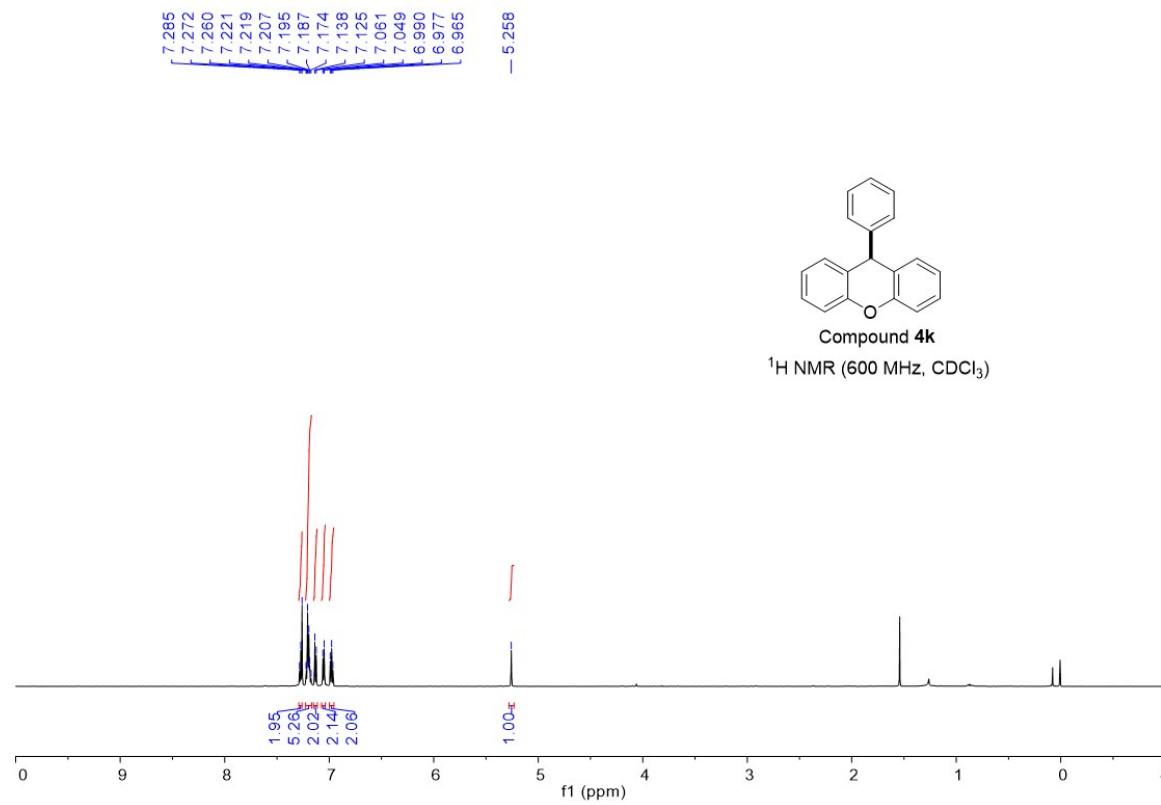


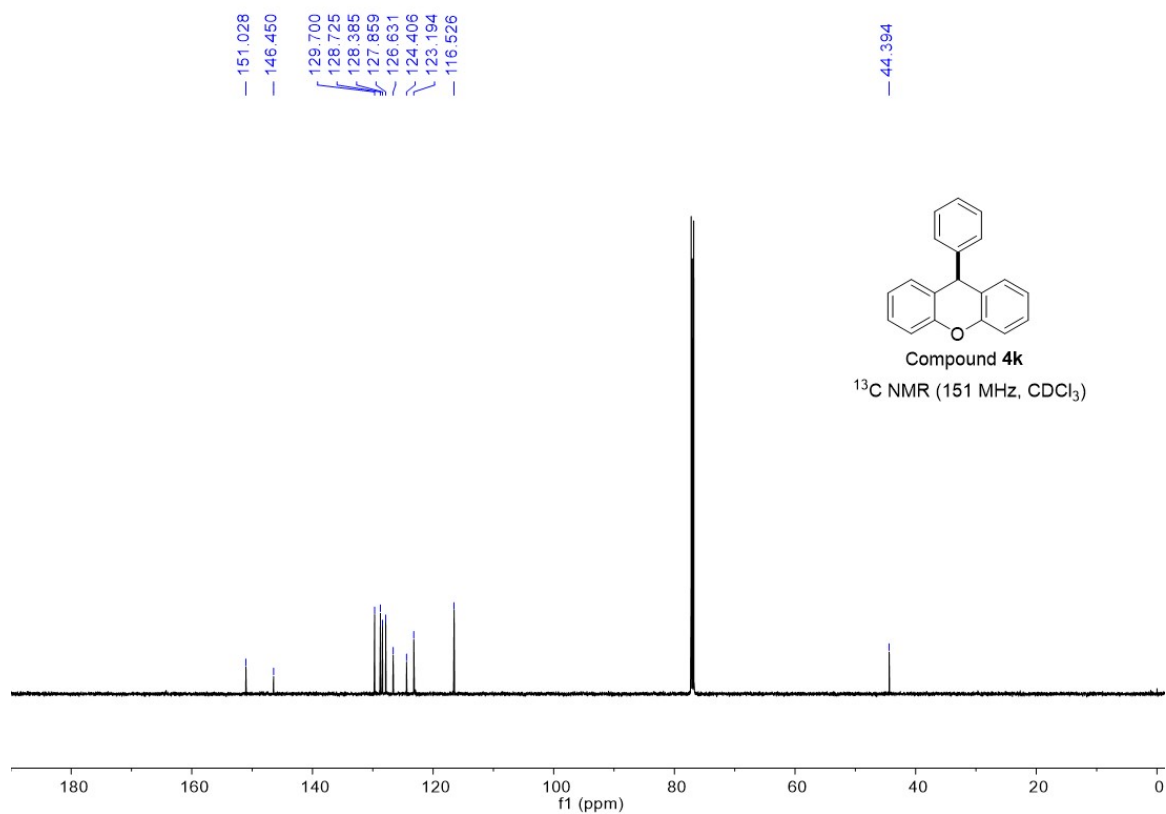
NMR spectra of 9-hexyl-9H-xanthene (**4j**)



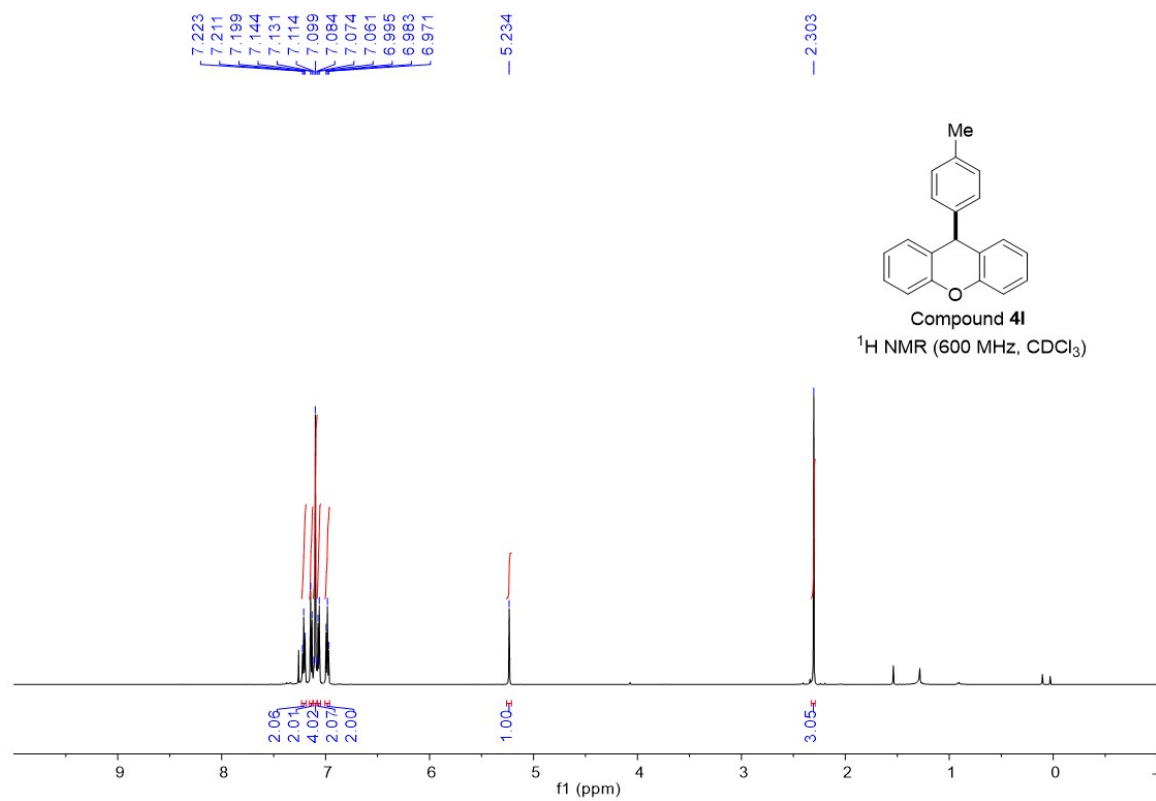


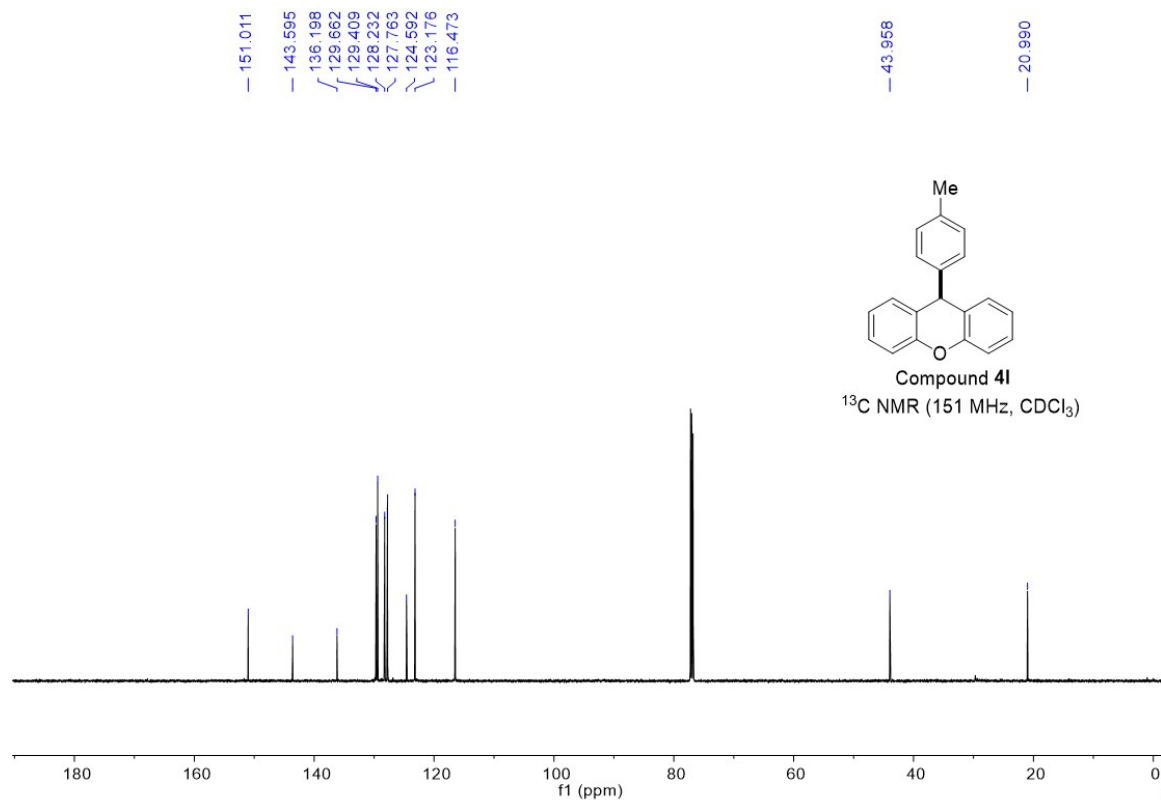
NMR spectra of 9-phenyl-9*H*-xanthene (**4k**)



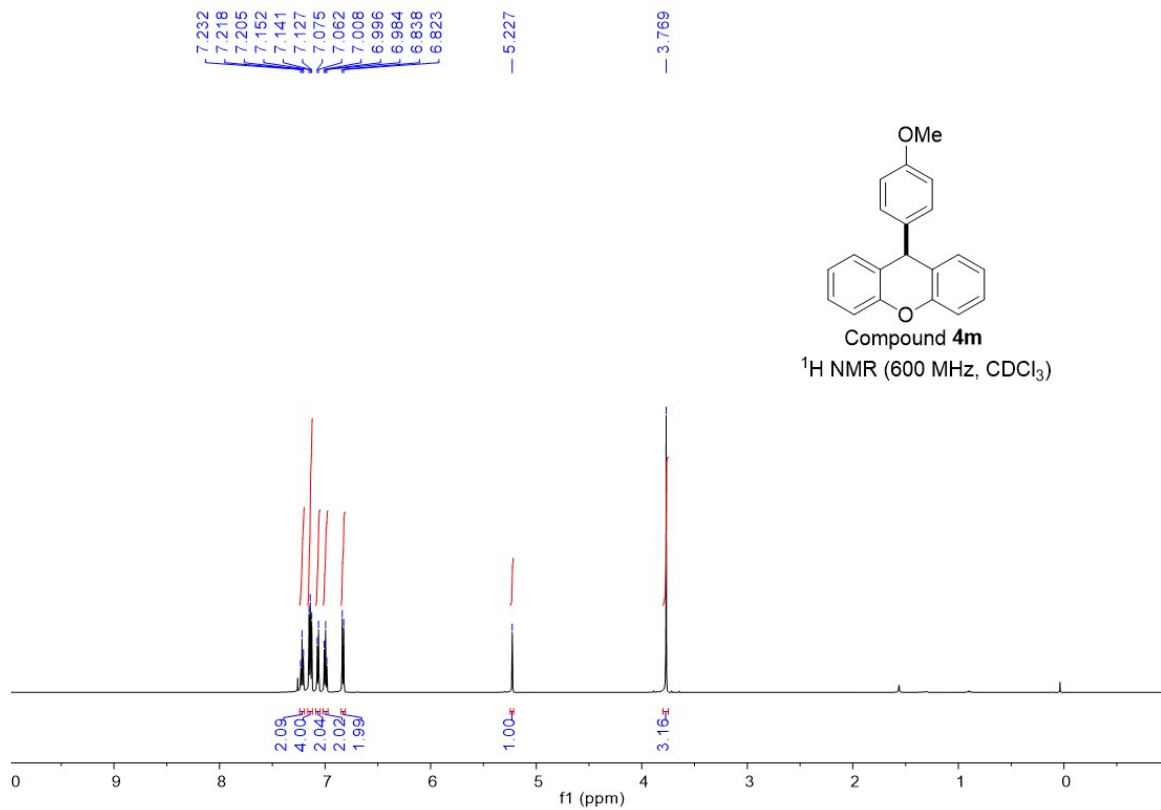


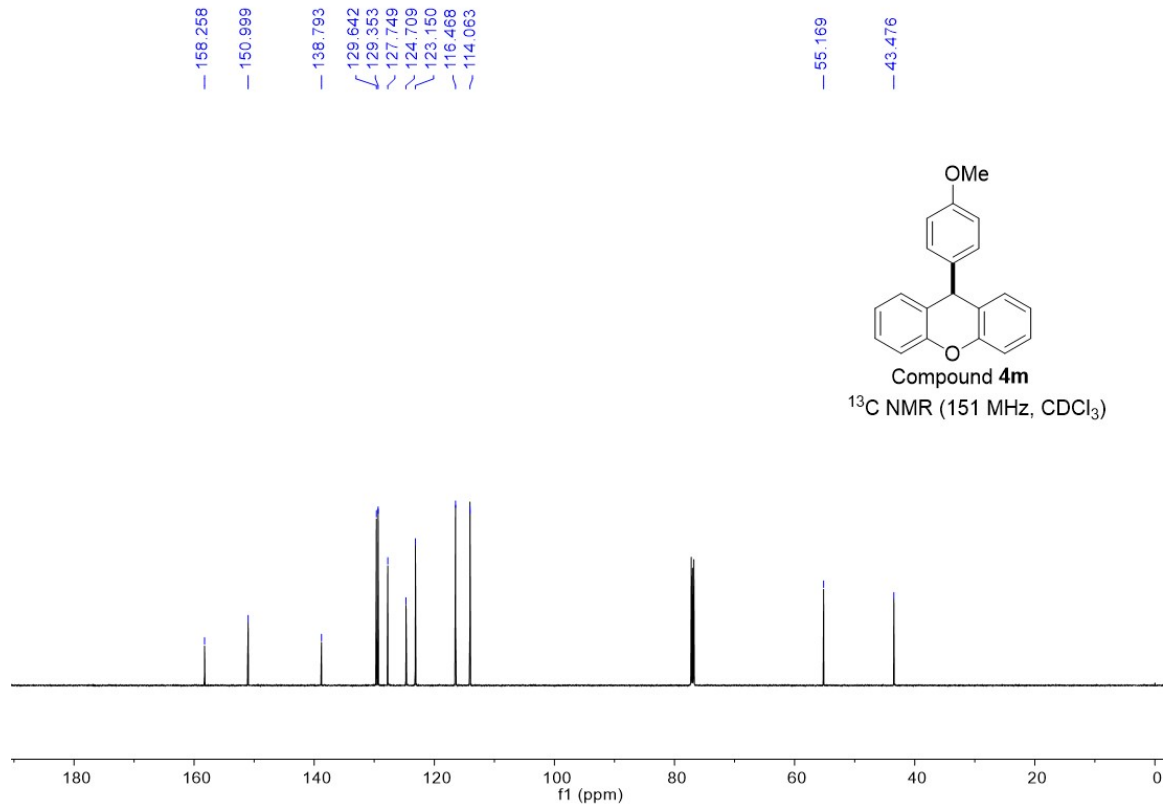
NMR spectra of 9-(*p*-tolyl)-9*H*-xanthene (**4l**)



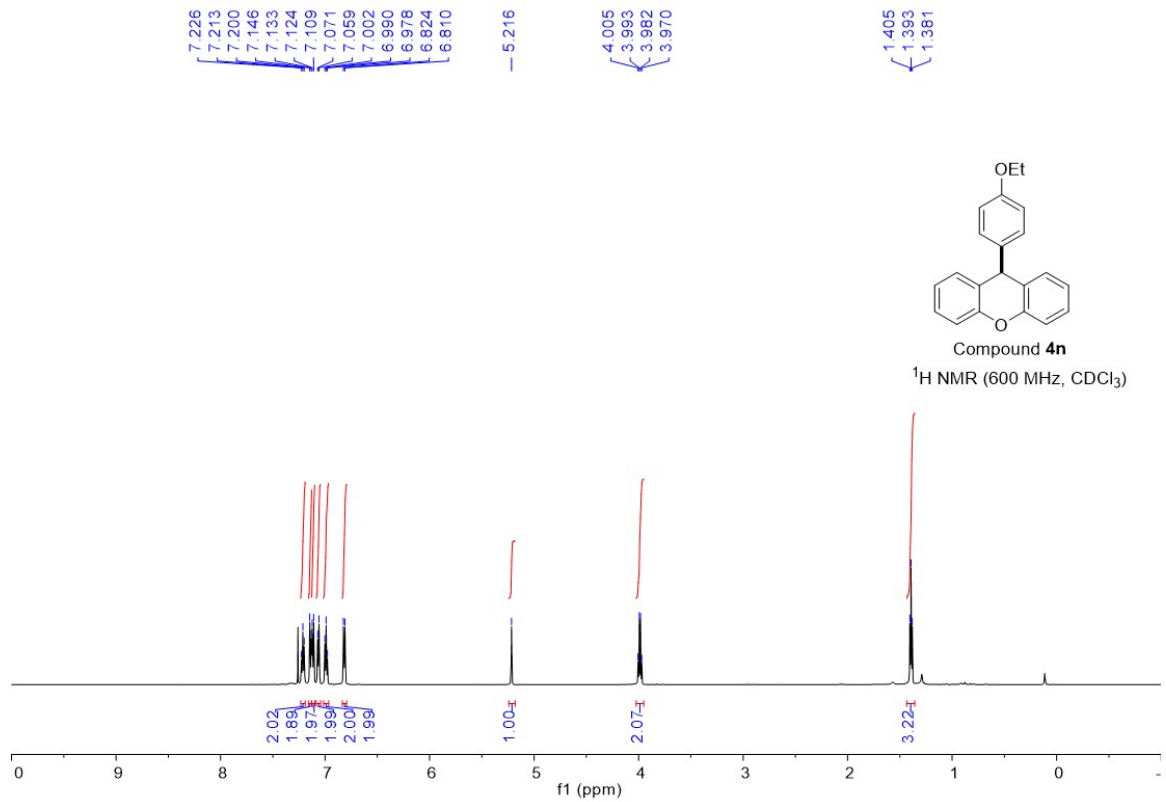


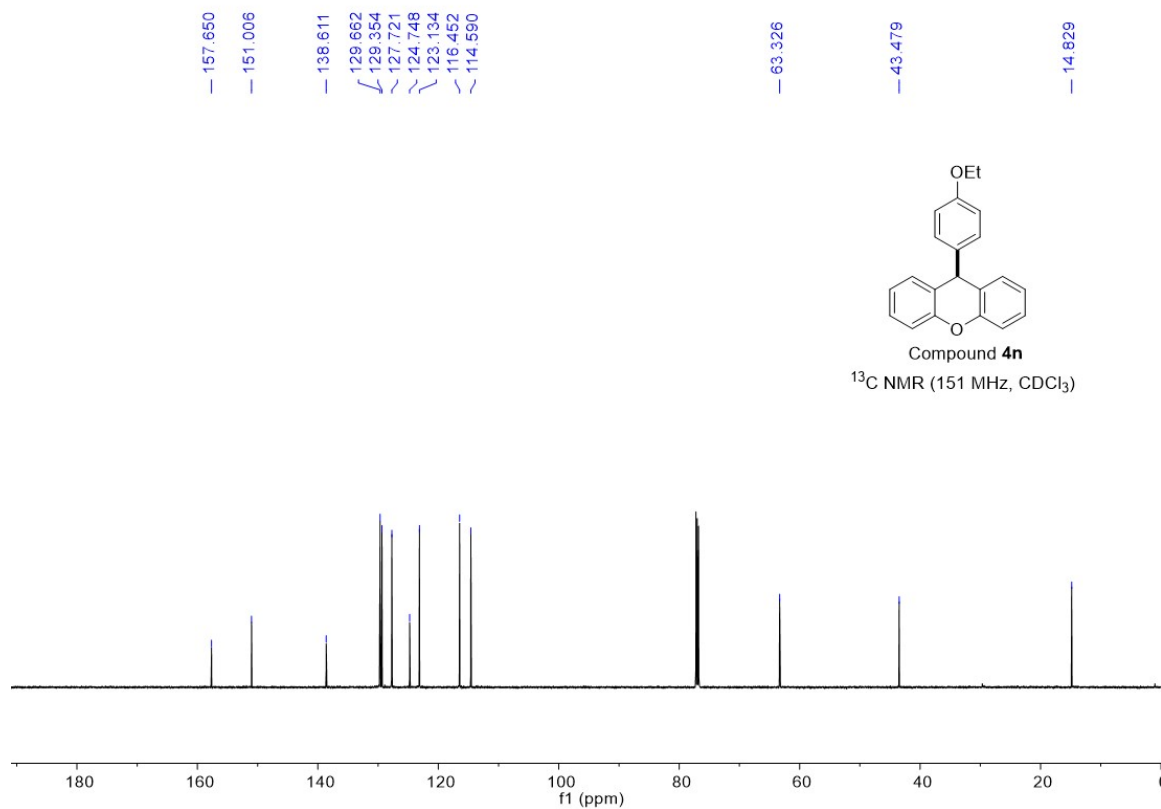
NMR spectra of 9-(4-methoxyphenyl)-9H-xanthene (**4m**)



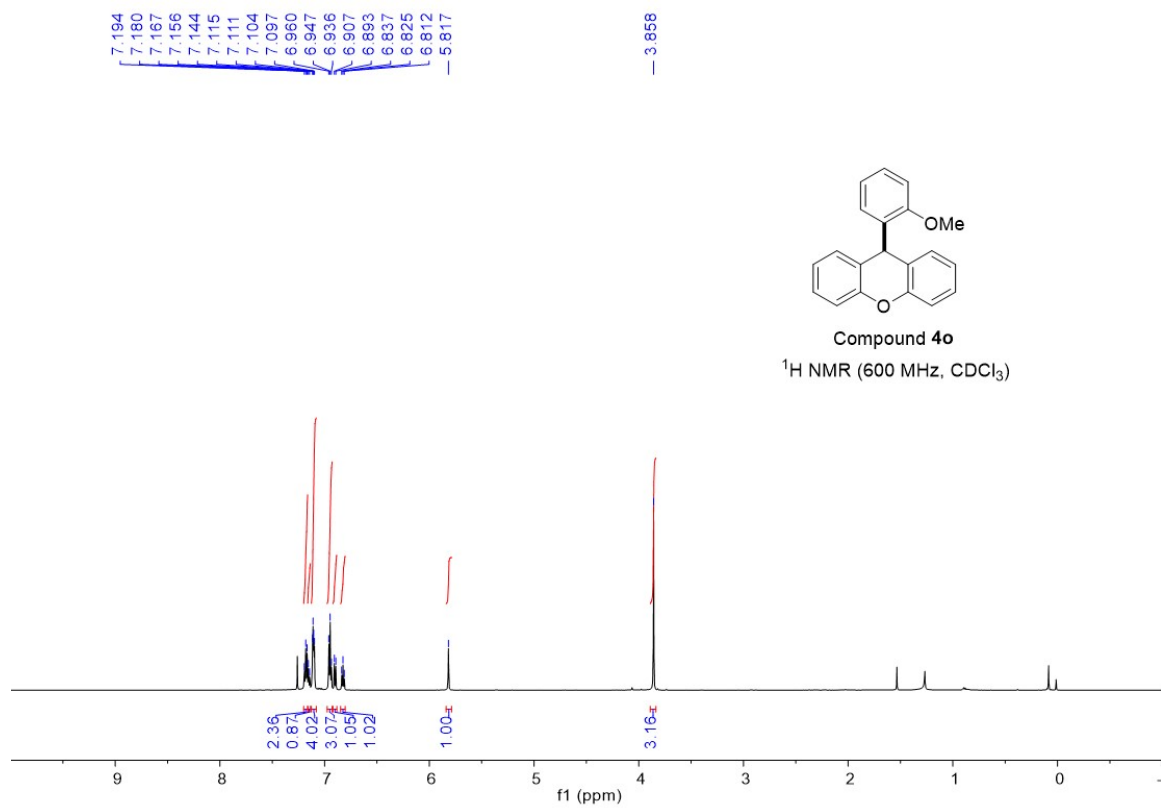


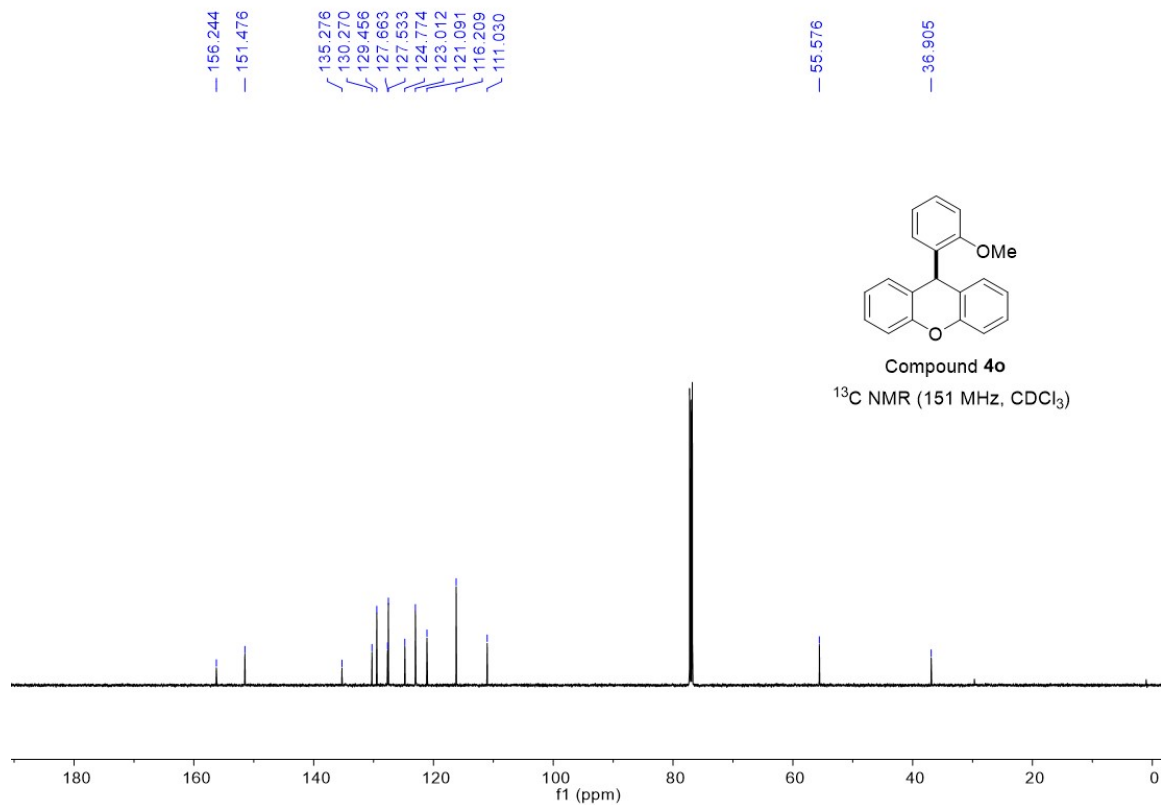
NMR spectra of 9-(4-ethoxyphenyl)-9*H*-xanthene (**4n**)



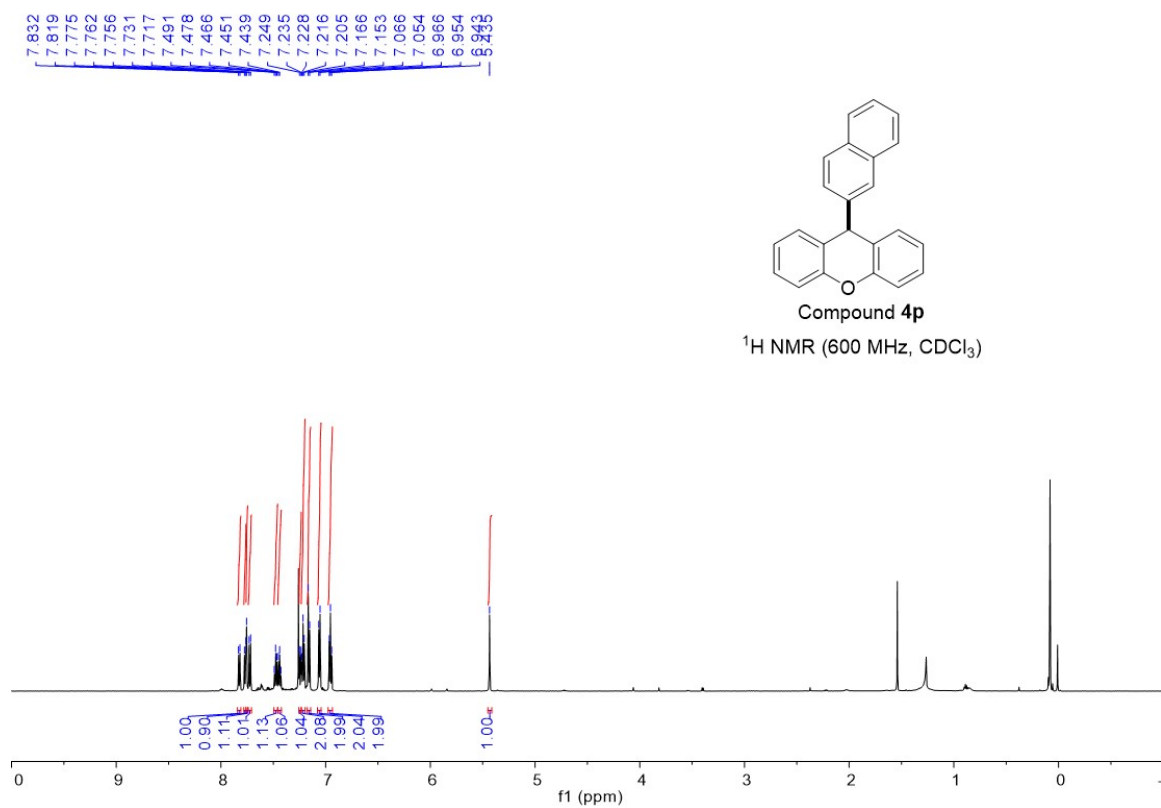


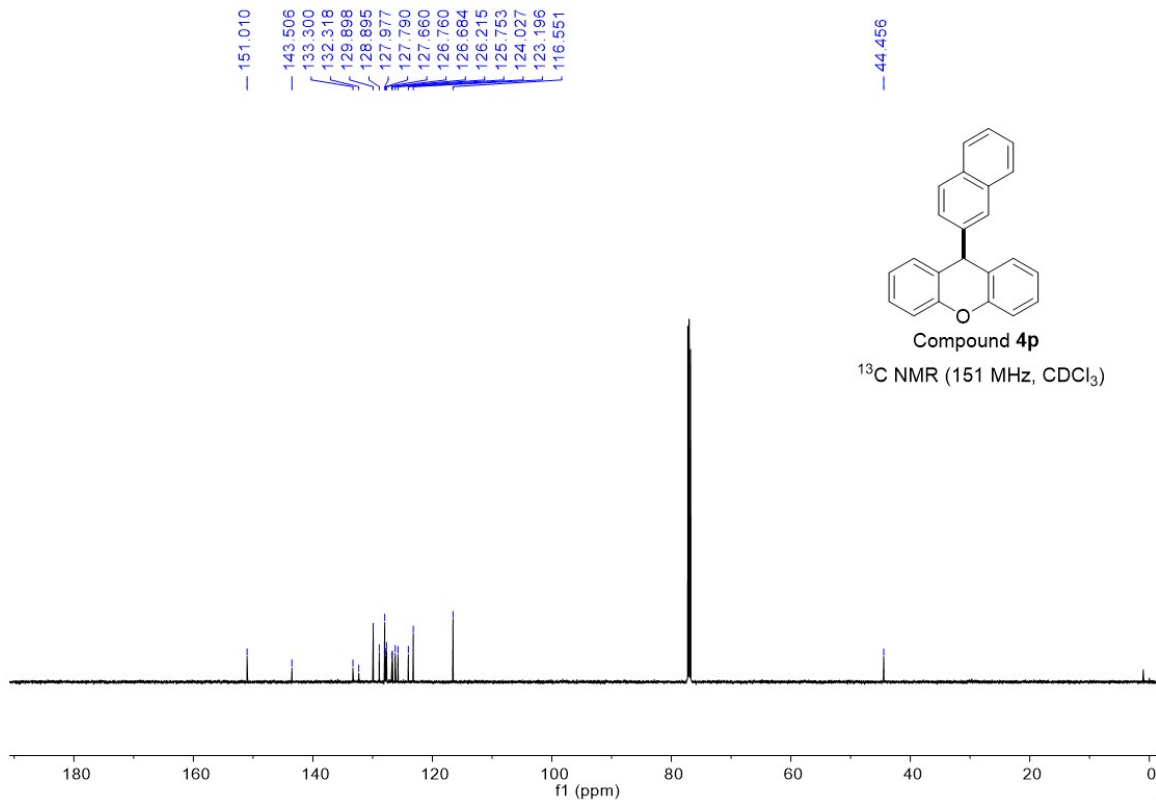
NMR spectra of 9-(2-methoxyphenyl)-9*H*-xanthene (**4o**)



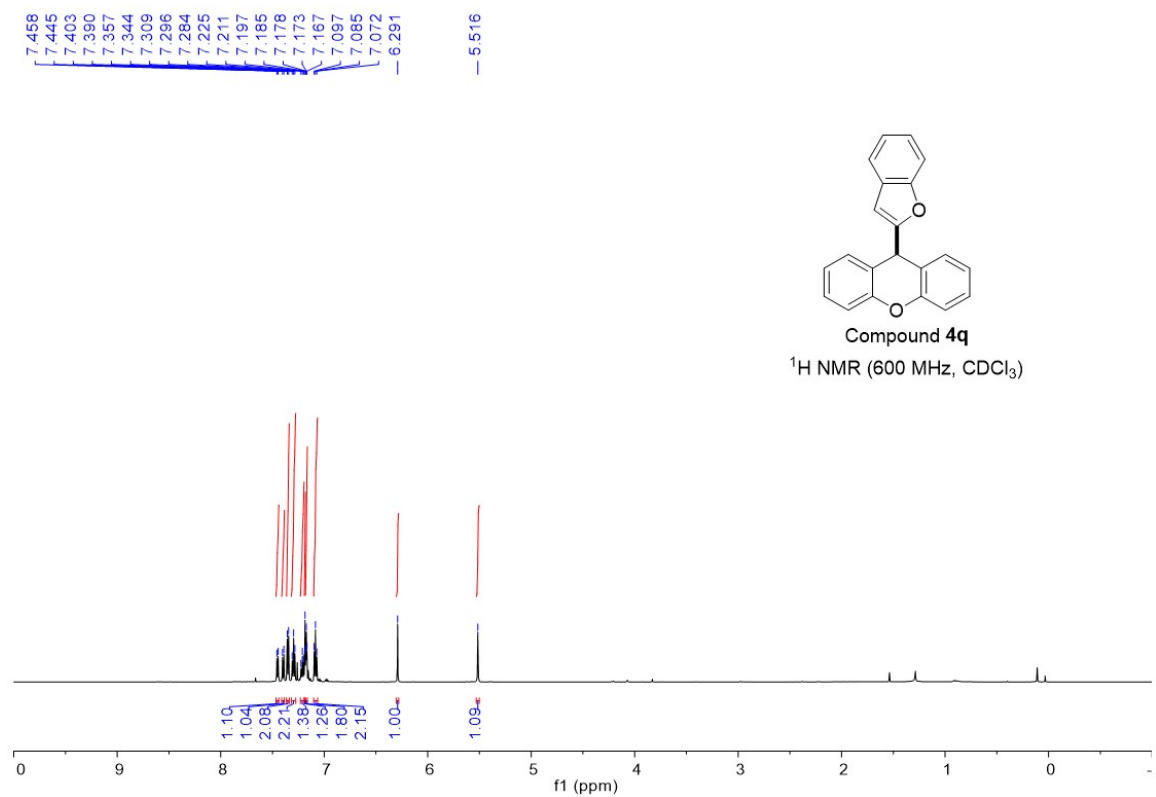


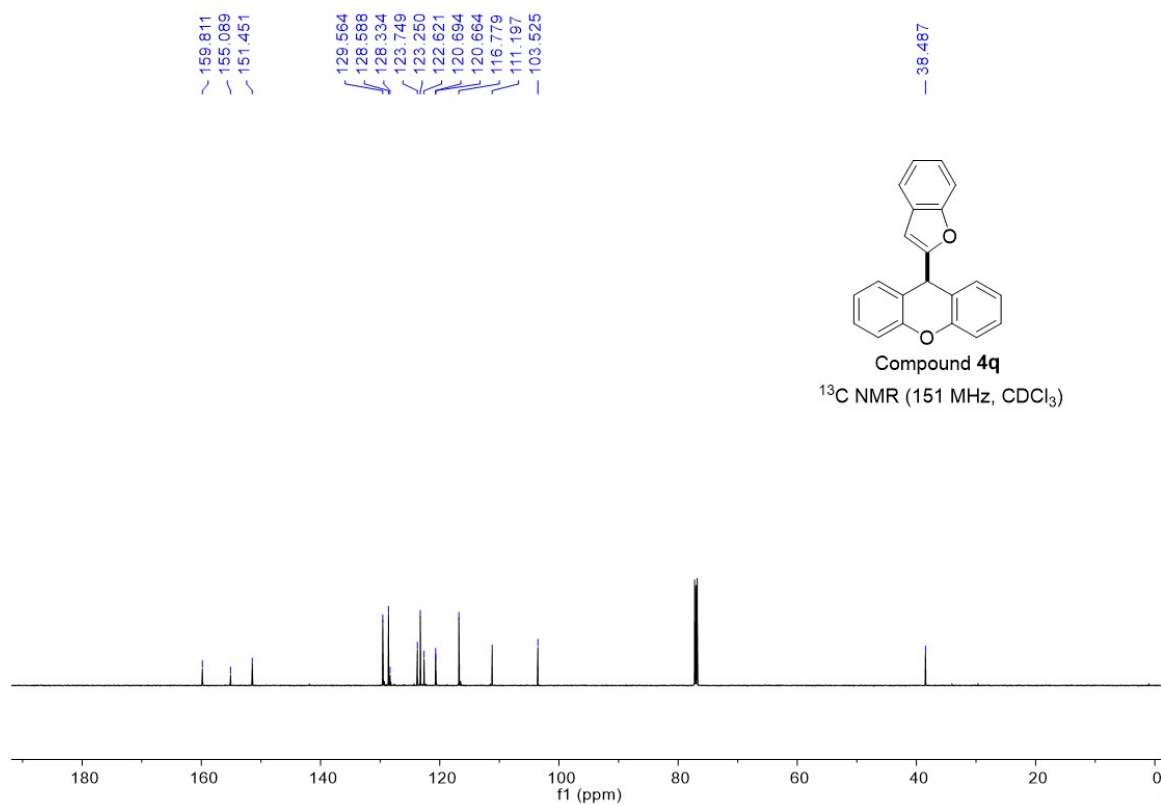
NMR spectra of 9-(naphthalen-2-yl)-9H-xanthene (**4p**)



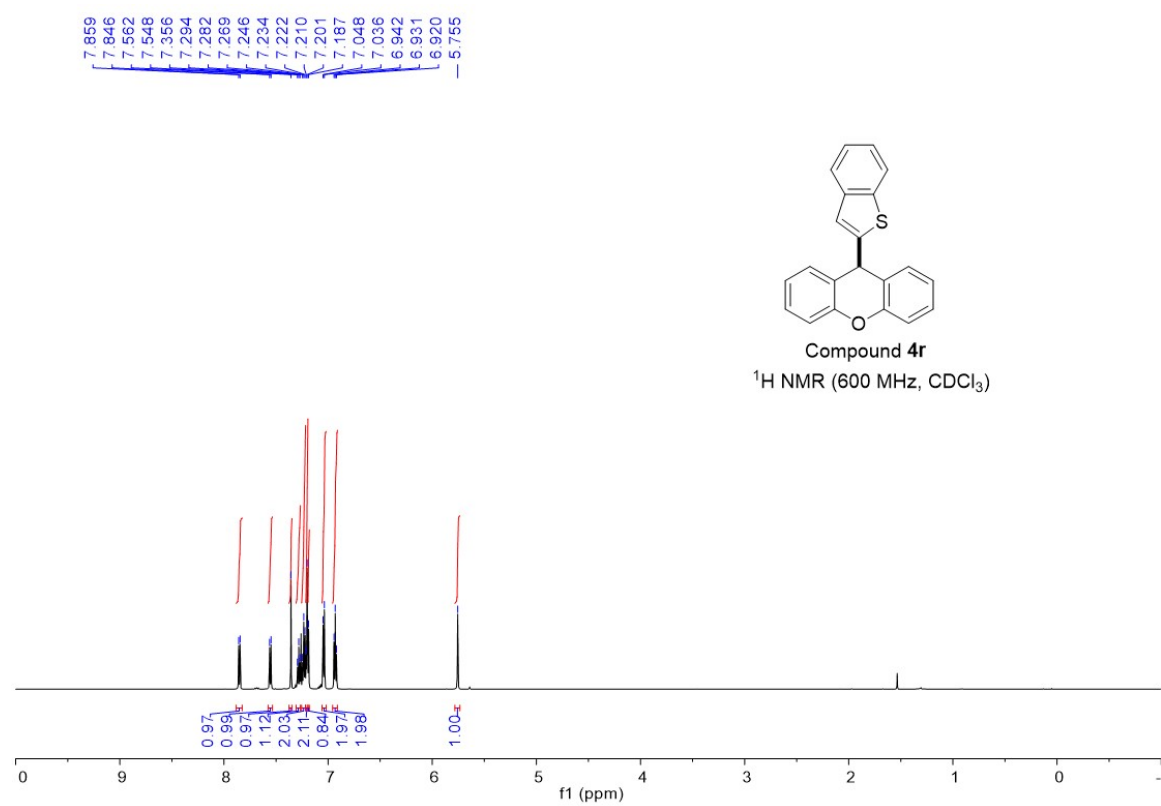


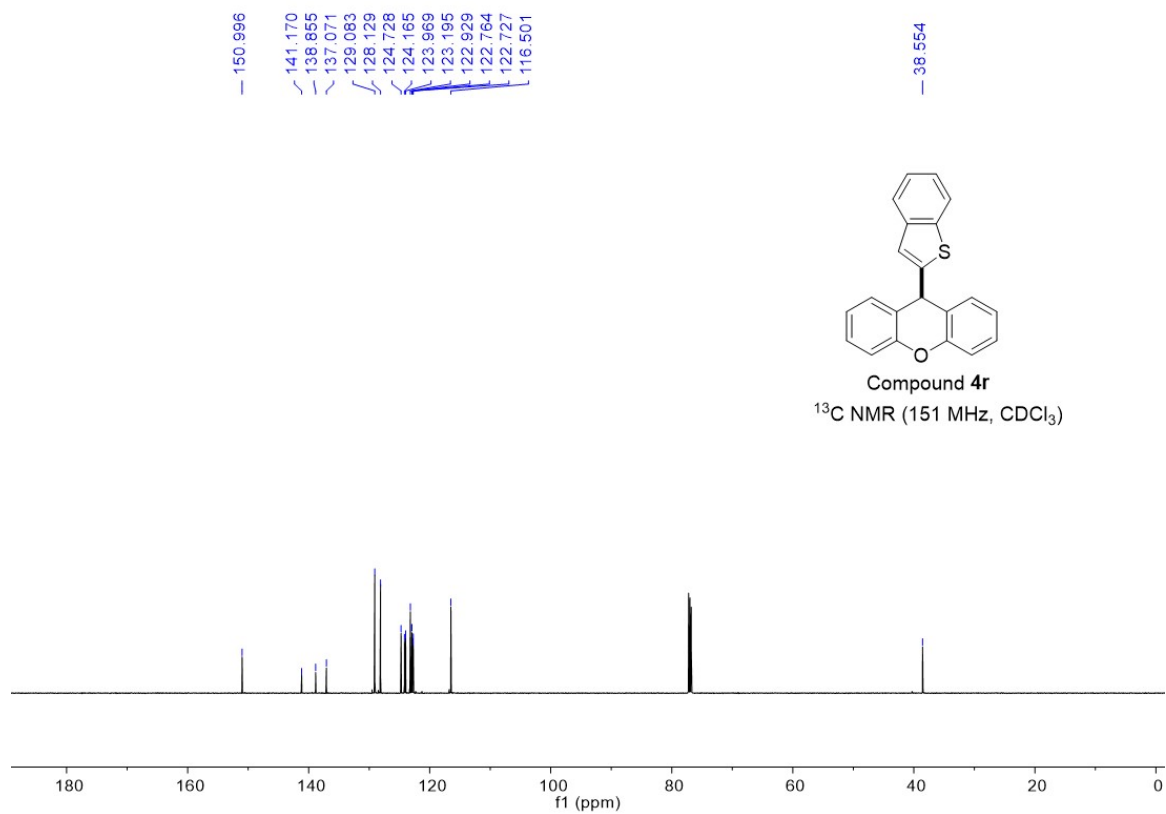
NMR spectra of 9-(benzofuran-2-yl)-9H-xanthene (**4q**)



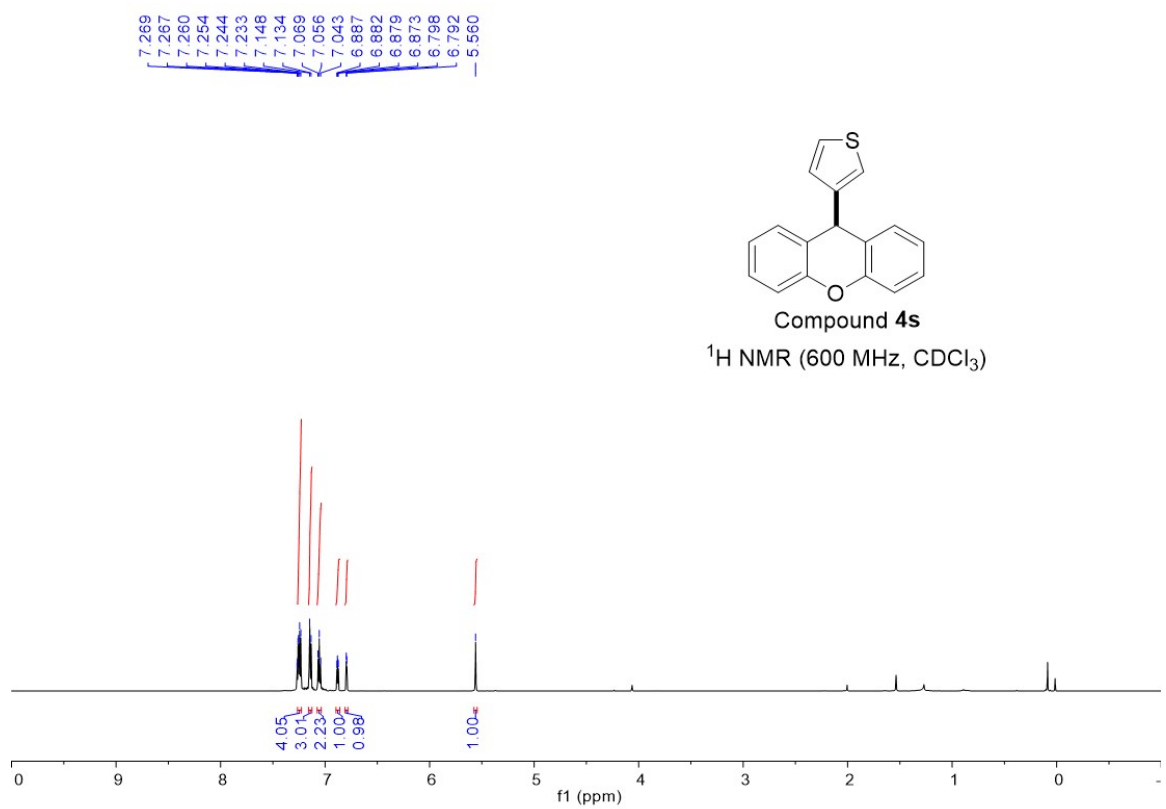


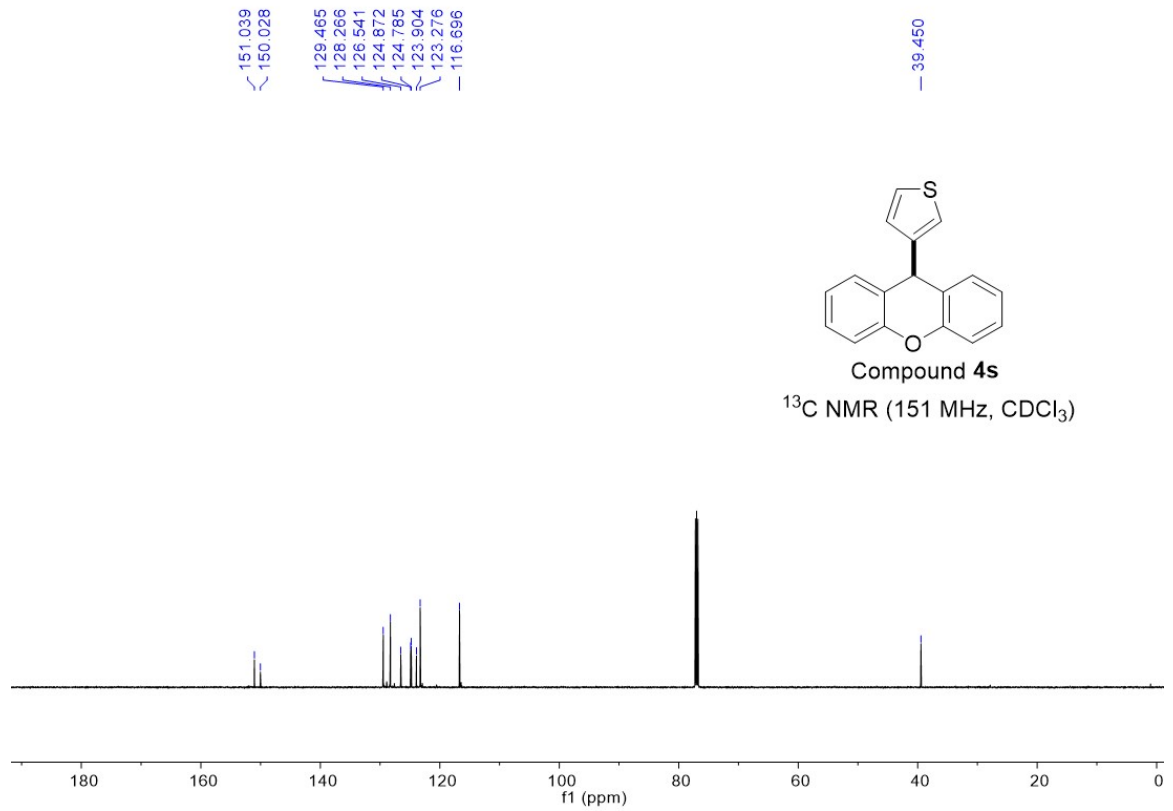
NMR spectra of 9-(benzo[*b*]thiophen-2-yl)-9*H*-xanthene (**4r**)



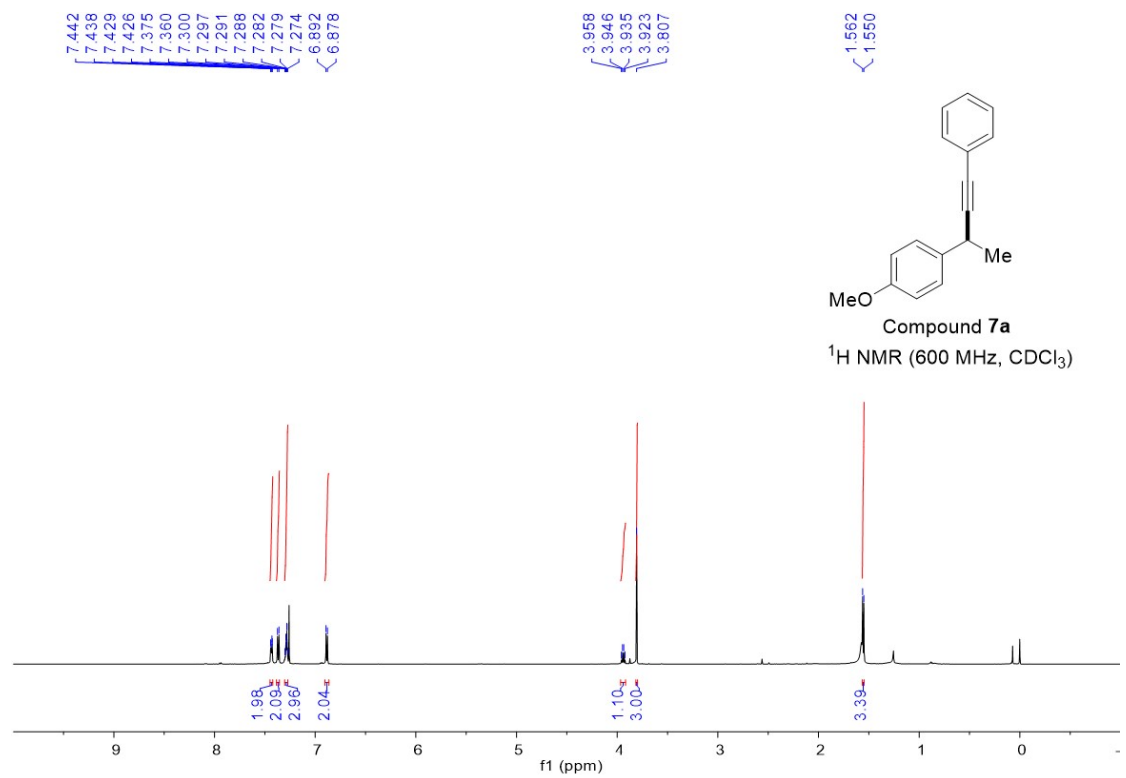


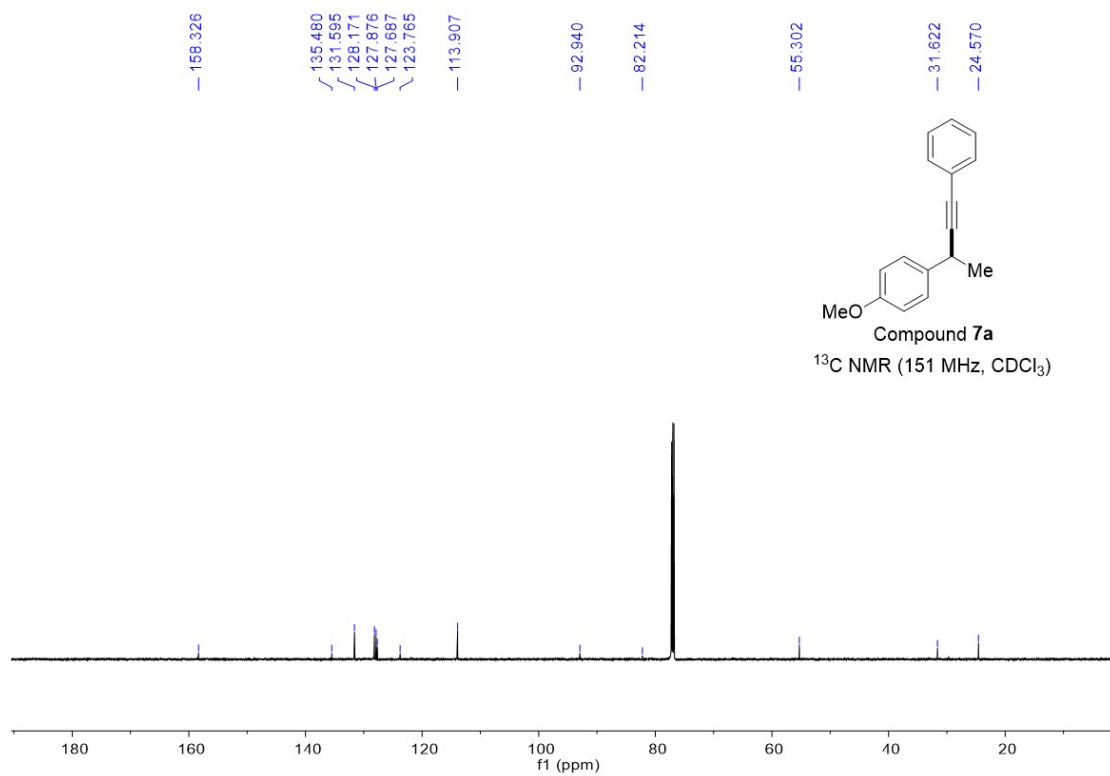
NMR spectra of 9-(thiophen-3-yl)-9H-xanthene (**4s**)



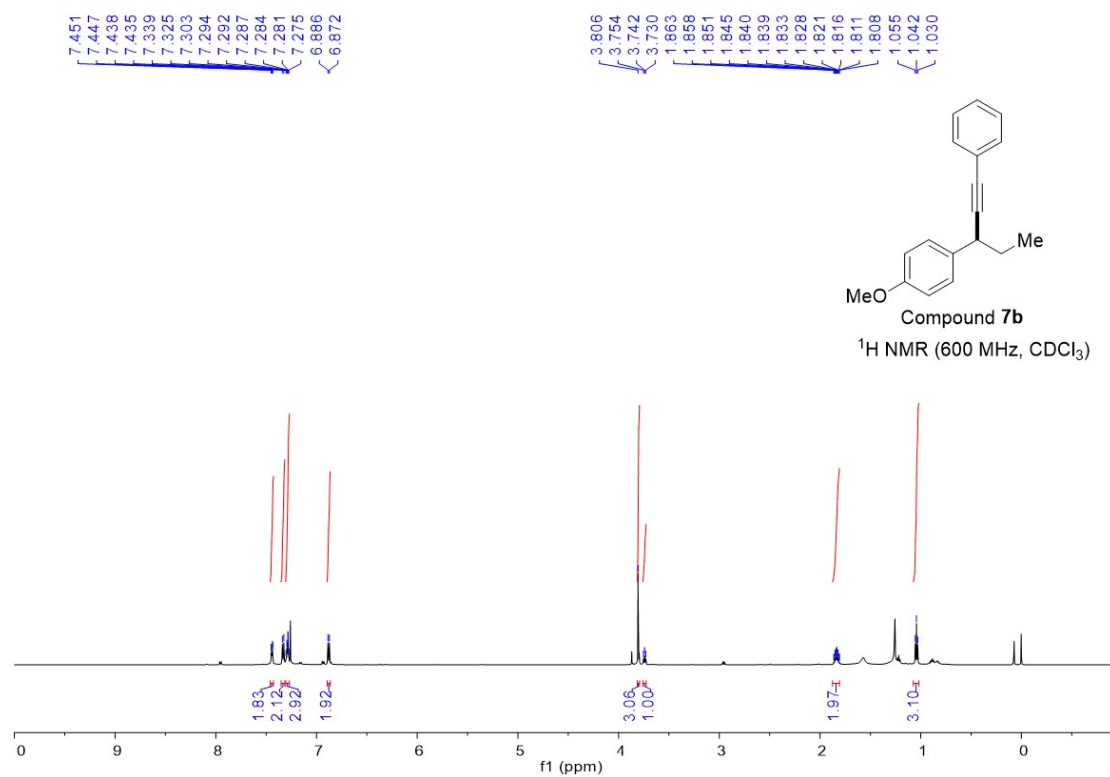


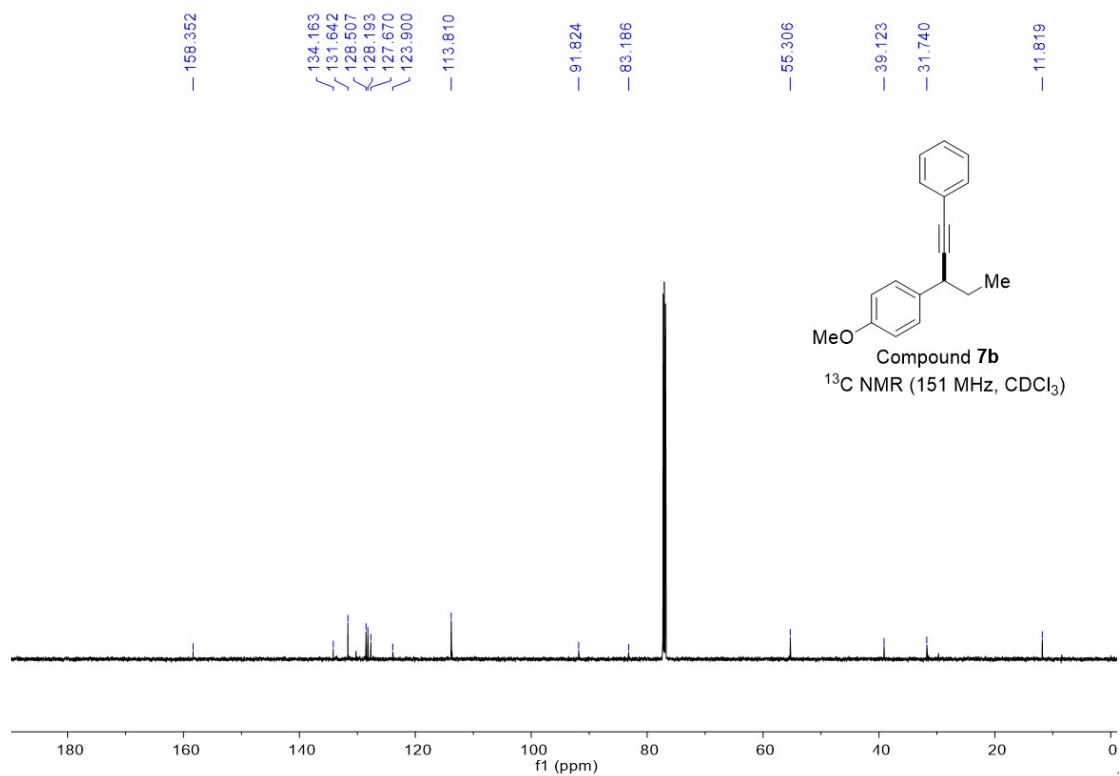
NMR spectra of methyl 1-methoxy-4-(4-phenylbut-3-yn-2-yl)benzene (**7a**)





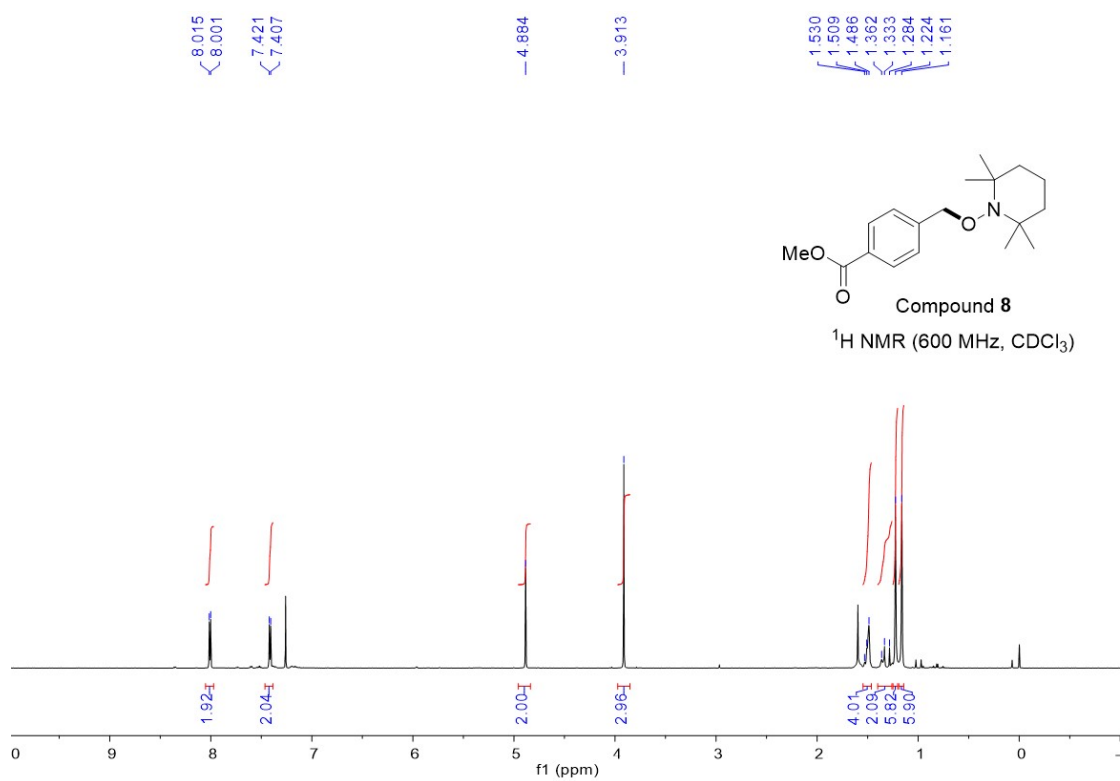
NMR spectra of methyl 1-methoxy-4-(1-phenylpent-1-yn-3-yl)benzene (**7b**)

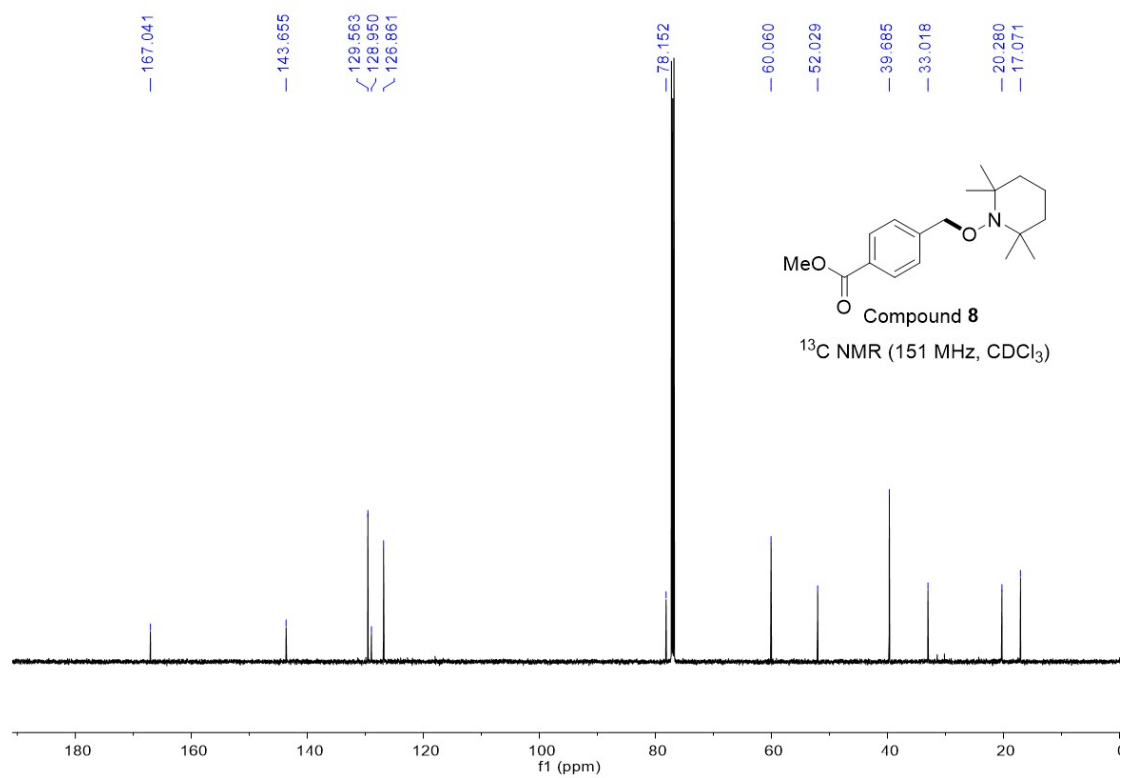




NMR spectra of Methyl 4-(((2,2,5,5-tetramethylpyrrolidin-1-yl)oxy)methyl)benzoate

(8)





9. Crystallographic data for 3a

The compound **3a** was crystalized over a solution of **3a** (80 mg) in CH₂Cl₂/petroleum (2 mL/2 mL) at room temperature. The mixed solvent spontaneously evaporates in open air to obtain the crystals of **3a**. Then the crystals were carefully collected and used for X-ray diffraction analysis. The crystal structure was further determined by Bruker D8 QUEST X-ray single crystal diffractometer. The CCDC number of **3a** is 2129581.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: t1

Bond precision:	C-C = 0.0021 A	Wavelength=0.71073	
Cell:	a=5.6133(16)	b=11.125(3)	c=23.100(6)
	alpha=91.600(12)	beta=90.153(12)	gamma=90.094(13)
Temperature:	273 K		
	Calculated	Reported	
Volume	1442.0(7)	1442.0(7)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C20 H16 O	C20 H16 O	
Sum formula	C20 H16 O	C20 H16 O	
Mr	272.33	272.33	
Dx, g cm ⁻³	1.254	1.254	
Z	4	4	
Mu (mm ⁻¹)	0.076	0.076	
F000	576.0	576.0	
F000'	576.24		
h, k, lmax	7, 14, 30	7, 14, 30	
Nref	6749	6682	
Tmin, Tmax	0.977, 0.985	0.721, 0.746	
Tmin'	0.977		
Correction method=	# Reported T Limits: Tmin=0.721 Tmax=0.746		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.990	Theta(max)=	27.656
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S =	1.070	Npar=	379

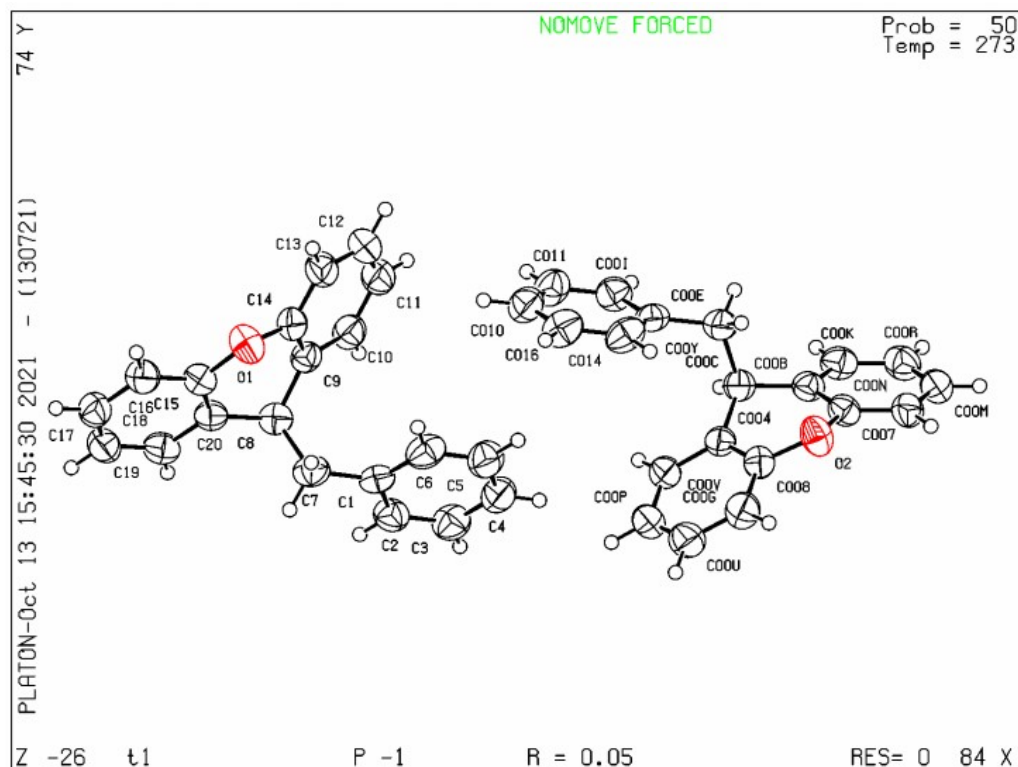


Figure S5 X-ray structure of **3a** (ORTEP diagram with ellipsoid contour 50% probability)

10. Determination of faradaic efficiency

$$(1) \text{ F. E. (\%)} = \frac{n \times F \times \text{mol of product or intermediate formed}}{\text{accumulated charge (C)}} \times 100 \%$$

$$\text{F. E. (\%)} = \frac{2 \times 96485 \text{ C mol}^{-1} \times 0.3 \text{ mmol} \times 10^{-3} \times 81\%}{8 \text{ mA} \times 10^{-3} \times 4 \text{ h} \times 3600} \times 100 \%$$

$$= 40.7 \%$$

The F.E. (%) of the product **3a** was calculated by (1). The F.E. is the proportion of electrons consumed in each electrochemical reaction of the total applied charge and represents the selectivity of the electrochemical system for each reaction. In Eq (1), F is the Faradaic constant (96485 C mol⁻¹), and n is the number of electrons required for the production of products. The yield is the proportion of reactant converted to target product.

11. DFT calculation for the mechanism proposal

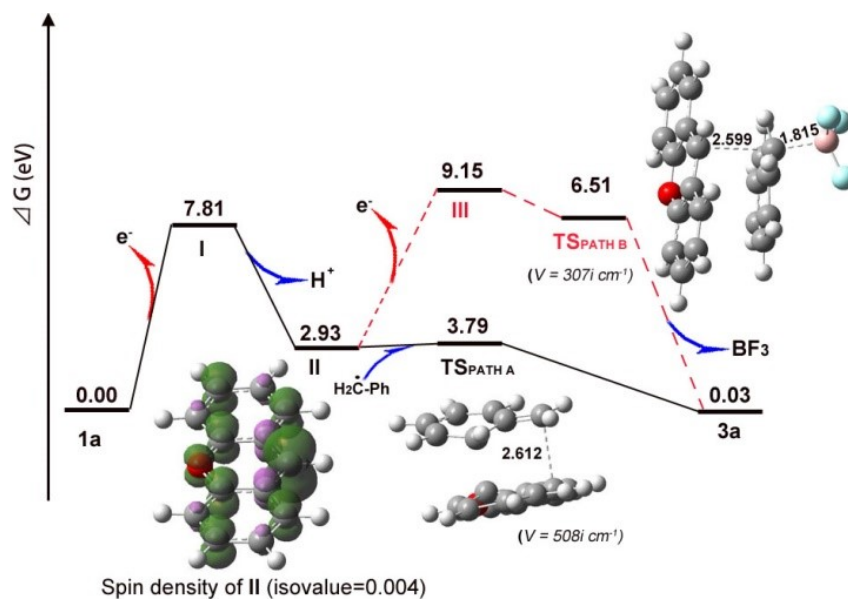


Figure S6 DFT calculation for the electrochemical benzylic C(sp³)-H cross-coupling with organotrifluoroborates

To verify the mechanism proposal in Scheme 3 of the maintext, a density functional theory (DFT) study with the empirical dispersion correction D3 developed by Grimme *et al.*^{6,7} was carried out, using the Minnesota density functional (M06)^{8,9} with the augmented correlation consistent basis set 6-311+G(d),¹⁰ and the results is listed in Figure S6. In this electrochemical system, the formation of a key intermediate radical **II** on the anode is proposed through successive oxidation reaction and deprotonation. In the case of the organotrifluoroborates salt, the **2a** undergoes anodic oxidation to generate a benzyl radical (Scheme 4). For the path A, the intermediate **II** could couple with the benzyl radical to yield product **3a**, which only requires a calculated energy barrier of only 0.66 eV (for the transition state TS_{PATH A}) to finish this radical coupling process. Theoretically, the path B listed in Figure S3 seems to be a barrierless reaction, but higher energy (6.22 eV) is requisite for the following anodic oxidation of **II** into **III** (transition state TS_{PATH B}). Remarkably, path A involving the radical coupling of **II** with benzyl radical is a favorable pathway (with the energy barrier 0.66 eV).

12. Oxidation potential measurement of **1t** and **1u**

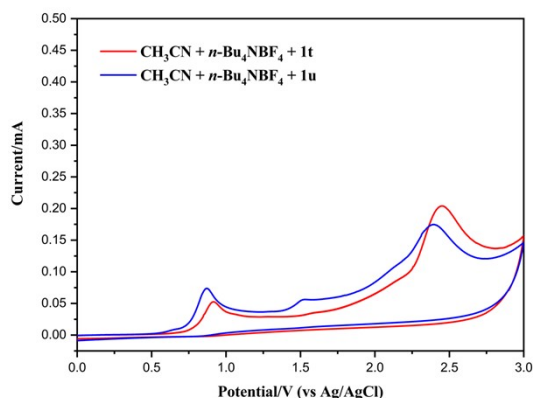


Fig.S7 A cyclic voltammogram recorded in CH₃CN with 0.1 M *n*-Bu₄NBF₄ as the supporting electrolyte. **1t** (1 mM), **1u** (1 mM). Scan direction: From negative to positive.

13. References

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