

Supporting Information

Tuning Benzylic C–H Functionalization of (Thio)xanthenes with Electrochemistry

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Table of Contents

1. General Information	S1
2. General Procedure for the Reactions.....	S1
2.1 Graphical Guide for the Set-up	S1
2.2 Typical Procedure for the Synthesis of 3a	S2
2.3 Typical Procedure for the Synthesis of 4a	S2
2.4 Effect of Water on the Electrochemical Synthesis of 3a	S3
3. Mechanistic Experiments.....	S3
3.1 Cyclic Voltammetry Studies	S3
3.2 Kinetic Isotope Effect Experiment.....	S3
4. Characterization Data for the Products.....	S5
5. NMR Spectra of the Products.....	S22
6. Determination of Faradaic Efficiency.....	S47

1. General Information

NMR spectra were recorded on Bruker-600 (Bruker, Germany, 600 MHz for ^1H ; 151 MHz for ^{13}C). ^1H NMR spectra were referenced relative to internal $\text{Si}(\text{Me})_4$ (TMS) at δ 0.00 ppm or CDCl_3 at δ 7.26 ppm. ^{13}C NMR spectra were recorded at ambient temperature on Bruker-600 (151 MHz) spectrometers and are referenced relative to CDCl_3 at δ 77.16 ppm. Data for ^1H , ^{13}C NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, quint = quintet, br = broad), integration, and coupling constant (Hz). High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. (Bruker, Germany) using ESI-TOF (electrospray ionization-time of flight) and Agilent Technologies 7250 GCQTOF using EI-TOF (Agilent Technologies, California, America). $n\text{-Bu}_4\text{NBF}_4$, phenylacetylene and CH_3CN were purchased from Energy Chemical Company and Taitan Chemical Company in China. Some other substituted xanthenes and thioxanthenes were synthesized according to the known methods.

2. General Procedure for the Reactions

2.1 Graphical Guide for the Set-up

As experimental setup, we used a platinum plate anode (10 mm \times 10 mm \times 0.3 mm) and a platinum plate cathode (10 mm \times 10 mm \times 0.3 mm), rubber stoppers, an undivided 15 mL single-necked flask, a DC adjustable power supply regulator (HY3005MT) (Made in China) and a magnetic stirrer.

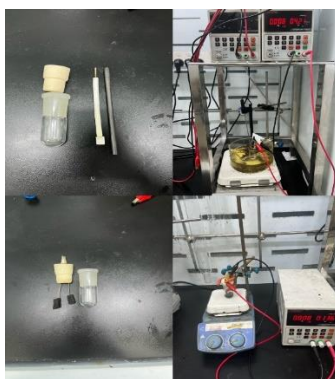
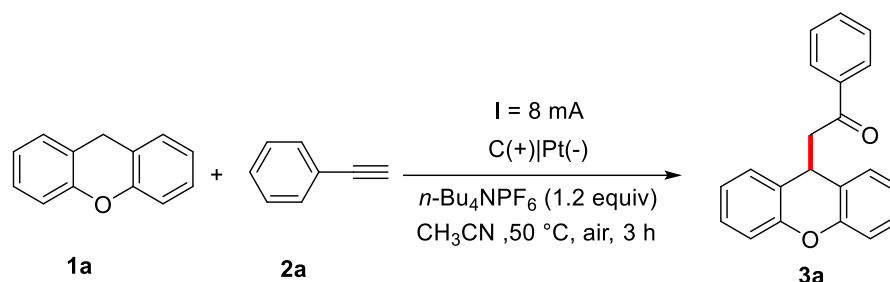


Figure S1 Electrochemical benzylic C-H functionalization of (thio)xanthenes with terminal

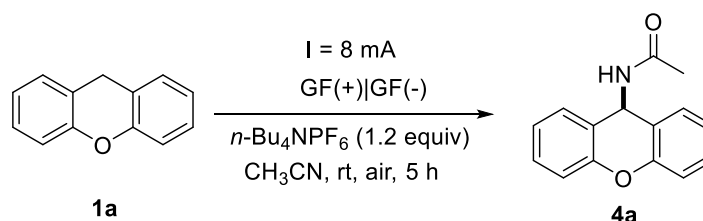
alkynes and nitriles

2.2 Typical Procedure for the Synthesis of 3a



To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) fitted with a carbon rod anode (Φ 6 mm) and a platinum cathode (10 mm×10 mm×0.3 mm), the solid reagents xanthene (0.45 mmol) and $n\text{-Bu}_4\text{NPF}_6$ (0.36 mmol) were added. Then, the liquid reagents phenylacetylene (0.3 mmol), H_2O (4 equiv) and CH_3CN (5 mL) were added in sequence via syringe. The electrolysis was carried out with constant current (8 mA) at 50°C for 3 h. Then the solvent was evaporated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel to give product 3a.

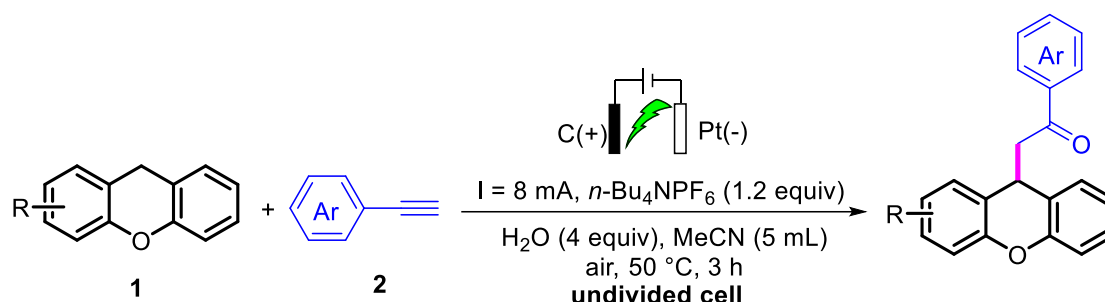
2.3 Typical Procedure for the Synthesis of 4a



To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) fitted with a graphite felt anode (10 mm×10 mm×3 cm) and a graphite felt cathode (10 mm×10 mm×3 cm), the solid reagents xanthene (0.3 mmol) and $n\text{-Bu}_4\text{NPF}_6$ (0.36 mmol) were added. Then, CH_3CN (5 mL) were added in sequence via a syringe. The electrolysis was carried out with constant current (8 mA) at room temperature for 5 h. Then the solvent was evaporated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel to give product 4a.

2.4 Effect of Water on the Electrochemical Synthesis of 3a

Table S1. Effect of water on the synthesis of 3a ^{a,b}



Entry	H ₂ O (x equiv)	Yield (%)
1	none	trace
2	1	45
3	2	59
4	3	66
5	4	71
6	5	68

^a Reaction conditions: **1** (0.3 mmol), **2a** (0.2 mmol), *n*-Bu₄NPF₆ (1.2 equiv), dry CH₃CN (5.0 mL), H₂O (x equiv), carbon rod (Φ 6 mm) anode, Pt plate (1 cm × 1 cm) cathode, constant current = 8 mA, 50 °C, air, 3 h. ^b Isolated yields.

3. Mechanistic Experiments

3.1 Cyclic Voltammetry Studies

Cyclic voltammetry was performed in a three electrode cell connected to a Schlenk line at room temperature. The working electrode was a glassy carbon electrode, and the counter electrode was a platinum electrode. The reference was an Ag/AgCl. 10 mL of CH₃CN containing 0.1 M *n*-Bu₄NPF₆ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3.5 V. The test concentrations of **1a** and **2a** are 10 mM.

3.2 Kinetic Isotope Effect Experiment

Xanthene (**1a**, 41.0 mg, 0.225 mmol), [D]-xanthene ([D]-**1a**, 41.5 mg, 0.225 mmol), phenylacetylene (**2a**, 30.6 mg, 0.3 mmol, 1.0 equiv), *n*-Bu₄NBF₄ (118.5 mg, 0.45 mmol, 1.2 equiv), CH₃CN (5 mL) was sequentially added to an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) fitted with a carbon rod anode (Φ

6 mm) and a platinum cathode (10 mm×10 mm×0.3 mm). The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at 50 °C 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/ethyl acetate = 20:1), to give the desired product **3a**/[D]-**3a** in 18% yield.

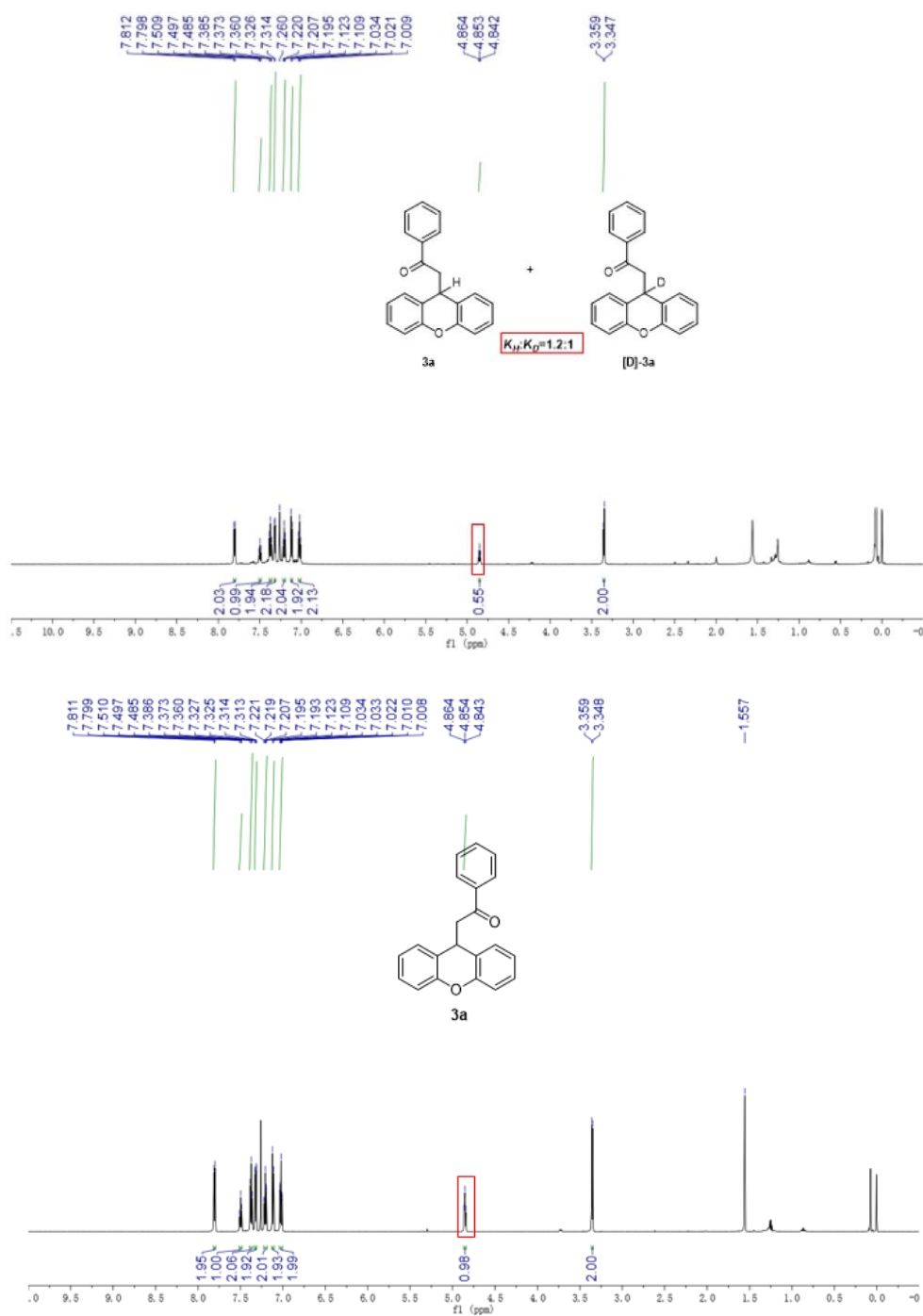
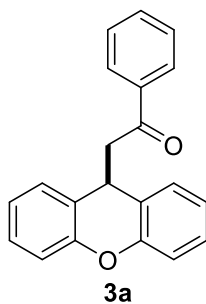


Figure S2 NMR spectra of **3a**/[D]-**3a**

4. Characterization Data for the Products



1-Phenyl-2-(9H-xanthen-9-yl)ethan-1-one (3a)

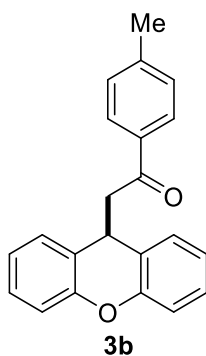
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3a** (63.8 mg, 71% yield).

White solid; m.p.: 105~106 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.32 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.23–7.19 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.04–7.00 (m, 2H), 4.85 (t, *J* = 6.0 Hz, 1H), 3.35 (d, *J* = 6.6 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 197.9, 152.4, 137.0, 133.1, 128.8, 128.5, 128.1, 127.9, 125.5, 123.5, 116.6, 49.7, 34.7.

HRMS (ESI) calcd. for C₂₁H₁₆NaO₂⁺ ([M+Na]⁺): 323.1043, found: 323.1044.



1-(*p*-Tolyl)-2-(9H-xanthen-9-yl)ethan-1-one (3b)

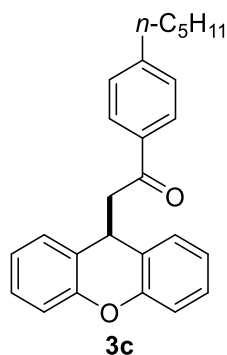
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3b** (59.2 mg, 63% yield).

White solid; m.p.: 108~109 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.32 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.22–7.19 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.11 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.03–7.00 (m, 2H), 4.85 (t, *J* = 6.6 Hz, 1H), 3.32 (d, *J* = 6.6 Hz, 2H), 2.36 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 197.69, 152.46, 144.09, 134.68, 129.33, 128.98, 128.36, 127.95, 125.75, 123.59, 116.65, 49.77, 34.81, 21.73.

HRMS (ESI) calcd. for C₂₂H₁₈NaO₂⁺ ([M+Na]⁺): 337.1199, found: 337.1203.



1-(4-Pentylphenyl)-2-(9H-xanthen-9-yl)ethan-1-one (**3c**)

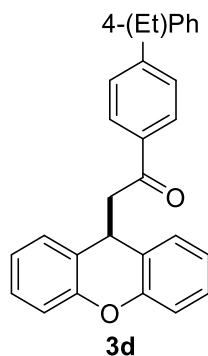
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3c** (82.2 mg, 75% yield).

White solid; m.p.: 117~118 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.22–7.16 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.03–7.00 (m, 2H), 4.85 (t, *J* = 6.6 Hz, 1H), 3.33 (d, *J* = 6.6 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.58–1.32 (m, 2H), 1.31–1.25 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 197.5, 152.3, 148.9, 134.7, 128.9, 128.6, 128.3, 127.8, 125.7, 123.5, 116.5, 49.7, 34.6, 31.4, 30.8, 22.5, 22.3, 14.0.

HRMS (ESI) calcd. for $C_{26}H_{26}NaO_2^+$ ($[M+Na]^+$): 393.1825, found: 393.1826.



1-(4'-Ethyl-[1,1'-biphenyl]-4-yl)-2-(9H-xanthen-9-yl)ethan-1-one (3d)

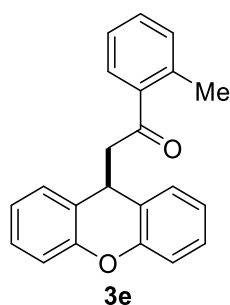
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3d** (78.6 mg, 65% yield).

White solid; m.p.: 122~123 °C.

1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.34 (dd, J = 7.8, 1.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.23–7.20 (m, 2H), 7.13 (dd, J = 7.8, 0.6 Hz, 2H), 7.03 (td, J = 7.2, 1.2 Hz, 2H), 4.88 (t, J = 6.6 Hz, 1H), 3.38 (d, J = 6.6 Hz, 2H), 2.70 (q, J = 7.8 Hz, 2H), 1.28 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 152.5, 145.9, 144.8, 137.2, 135.6, 129.0, 128.8, 128.6, 128.0, 127.3, 127.0, 125.7, 123.6, 116.7, 49.9, 34.9, 28.7, 15.7.

HRMS (ESI) calcd. for $C_{29}H_{24}NaO_2^+$ ($[M+Na]^+$): 427.1669, found: 427.1668.



1-(o-Tolyl)-2-(9H-xanthen-9-yl)ethan-1-one (3e)

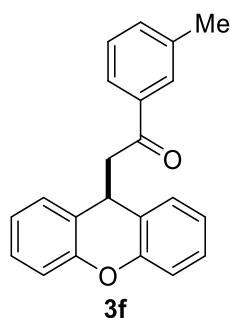
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3e** (49.8 mg, 53% yield).

White solid; m.p.: 105~106 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.33 (d, *J* = 7.2 Hz, 2H), 7.30–7.27 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.12–7.09 (m, 3H), 7.04 (t, *J* = 7.2 Hz, 2H), 4.84 (t, *J* = 6.6 Hz, 1H), 3.26 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 202.1, 152.5, 138.2, 132.0, 131.4, 128.9, 128.6, 128.0, 125.7, 125.7, 123.6, 116.7, 52.7, 35.0, 21.2.

HRMS (ESI) calcd. for C₂₂H₁₈NaO₂⁺ ([M+Na]⁺): 337.1199, found: 337.1201.



1-(*m*-Tolyl)-2-(9H-xanthen-9-yl)ethan-1-one (**3f**)

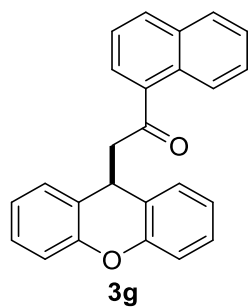
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3f** (60.0 mg, 68% yield).

White solid; m.p.: 111~112 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.54–7.50 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.20–7.16 (m, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 2H), 4.77 (t, *J* = 6.6 Hz, 1H), 3.26 (d, *J* = 6.6 Hz, 2H), 2.26 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) 198.3, 152.6, 138.6, 137.2, 134.1, 129.1, 128.9, 128.6, 128.1, 125.8, 125.5, 123.7, 116.8, 50.0, 34.9, 21.5.

HRMS (ESI) calcd. for C₂₂H₁₈NaO₂⁺ ([M+Na]⁺): 337.1199, found 337.1198.



1-(Naphthalen-1-yl)-2-(9H-xanthen-9-yl)ethan-1-one (3g)

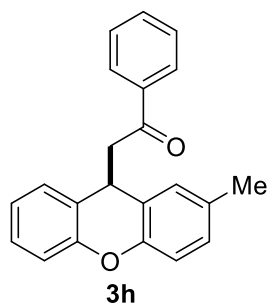
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3g** (64.2 mg, 61% yield).

White solid; m.p.: 116~117 °C.

¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.59–7.55 (m, 1H), 7.59–7.50 (m, 1H), 7.48 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.38 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.36–7.32 (m, 1H), 7.24–7.21 (m, 2H), 7.12 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.06–7.03 (m, 2H), 4.94 (t, *J* = 6.6 Hz, 1H), 3.42 (d, *J* = 6.6 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 202.2, 152.5, 136.1, 134.0, 132.9, 130.2, 128.9, 128.6, 128.1, 127.9, 126.6, 125.8, 125.5, 124.4, 123.7, 53.2, 35.5.

HRMS (ESI) calcd. for C₂₅H₁₈NaO₂⁺ ([M+Na]⁺): 373.1199, found: 373.1200.



2-(2-Methyl-9H-xanthen-9-yl)-1-phenylethan-1-one (3h)

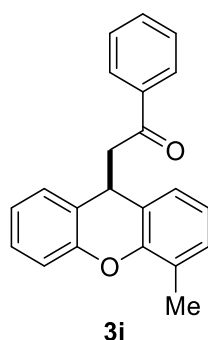
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3h** (65.8 mg, 70% yield).

White solid; m.p.: 102~103 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.02–6.89 (m, 3H), 4.80 (t, *J* = 6.6 Hz, 1H), 3.35 (d, *J* = 6.6 Hz, 2H), 2.27 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 198.2, 152.6, 150.3, 137.2, 133.21, 133.0, 129.2, 129.0, 128.6, 128.6, 128.2, 127.9, 125.7, 125.3, 123.4, 116.6, 116.4, 49.9, 34.8, 20.8.

HRMS (ESI) calcd. for C₂₂H₁₈NaO₂⁺ ([M+Na]⁺): 337.1199, found: 337.1199.



2-(4-Methyl-9H-xanthen-9-yl)-1-phenylethan-1-one (**3i**)

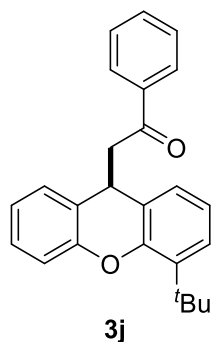
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3i** (67.8 mg, 72% yield).

White solid; m.p.: 107~108 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.23–7.20 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 2H), 4.86 (t, *J* = 6.6 Hz, 1H), 3.33 (d, *J* = 6.6 Hz, 2H), 2.36 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 197.5, 152.3, 143.9, 134.5, 130.0, 129.8, 129.5, 129.5, 129.2, 128.8, 128.3, 128.2, 127.8, 127.3, 125.6, 123.4, 116.5, 49.6, 34.7, 21.6.

HRMS (ESI) calcd. for C₂₂H₁₈NaO₂⁺ ([M+Na]⁺): 337.1199, found: 337.1196.



2-(4-(*tert*-Butyl)-9H-xanthen-9-yl)-1-phenylethan-1-one (3j)

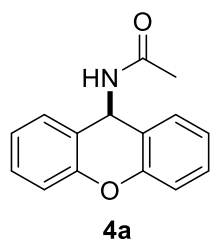
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3j** (74.0 mg, 70% yield).

White solid; m.p.: 113~114 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.78–7.75 (m, 2H), 7.41–7.38 (m, 2H), 7.32 (dd, J = 7.8, 1.2 Hz, 2H), 7.22–7.19 (m, 2H), 7.12 (dd, J = 8.4, 1.2 Hz, 2H), 7.02 (td, J = 7.2, 1.2 Hz, 2H), 4.87 (t, J = 6.6 Hz, 1H), 3.34 (d, J = 6.6 Hz, 2H), 1.30 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 196.4, 155.9, 151.3, 133.4, 128.8, 128.7, 127.8, 127.3, 127.0, 126.8, 126.3, 124.7, 124.6, 124.4, 122.4, 121.8, 115.5, 48.7, 34.0, 33.5, 29.9.

HRMS (ESI) calcd. for C₂₅H₂₄NaO₂⁺ ([M+Na]⁺): 379.1669, found: 379.1670.



N-(9H-xanthen-9-yl)acetamide (4a)

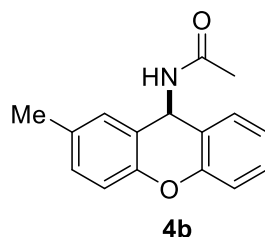
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA=5:1) to afford the product **2a** (48.7 mg, 68% yield).

White solid; m.p.: 238~239 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.48–7.46 (m, 2H), 7.32–7.28 (m, 2H), 7.13–7.10 (m, 4H), 6.49 (d, *J* = 9.0 Hz, 1H), 6.05 (br, d, *J* = 9.0 Hz, 1H), 2.00 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.2, 151.3, 129.8, 129.4, 123.7, 121.3, 116.8, 44.0, 23.5.

HRMS (ESI) calcd. for C₁₅H₁₃NNaO₂⁺ ([M+Na]⁺): 262.0838, found: 262.0839.



***N*-(2-Methyl-9*H*-xanthen-9-yl)acetamide (**4b**)**

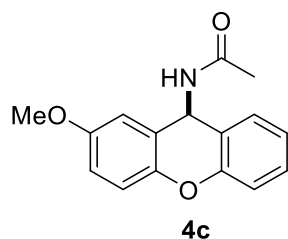
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA=5:1) to afford the product **2b** (49.5 mg, 65% yield).

White solid; m.p.: 242~243 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.31–7.27 (m, 1H), 7.11–7.08 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.46 (d, *J* = 9.0 Hz, 1H), 6.00 (br, d, *J* = 9.0 Hz, 1H), 2.32 (s, 3H), 2.01 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.2, 151.4, 149.2, 133.2, 130.2, 129.8, 129.8, 129.3, 123.5, 121.3, 120.8, 116.7, 116.5, 44.1, 23.6, 20.8.

HRMS (ESI) calcd. for C₁₆H₁₅NNaO₃⁺ ([M+Na]⁺): 276.0095, found: 276.0092.



***N*-(2-Methoxy-9*H*-xanthen-9-yl)acetamide (4c)**

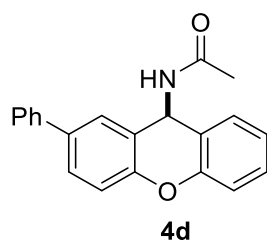
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4c** (60.3 mg, 75% yield).

White solid; m.p.: 251~252 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.31–7.27 (m, 1H), 7.11–7.07 (m, 2H), 7.04 (d, *J* = 9.0 Hz, 1H), 6.98 (d, *J* = 3.0 Hz, 1H), 6.87 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.47 (d, *J* = 9.0 Hz, 1H), 6.01 (br, d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H), 2.01 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.2, 155.7, 151.5, 145.4, 129.8, 129.4, 123.5, 121.7, 120.7, 117.7, 116.7, 116.4, 112.8, 55.9, 44.5, 23.6.

HRMS (ESI) calcd. for C₁₆H₁₅NNaO₃⁺ ([M+Na]⁺): 292.0944, found 292.0947.



***N*-(2-Phenyl-9*H*-xanthen-9-yl)acetamide (4d)**

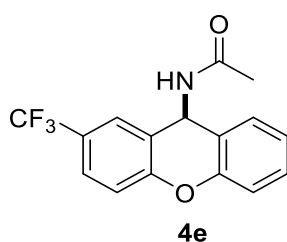
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4d** (57.7 mg, 61% yield).

White solid; m.p.: 247~248 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, *J* = 1.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.54 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.51–7.49 (m, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.36–7.30 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.14–7.11 (m, 2H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.06 (br, *J* = 9.6 Hz, 1H), 2.01 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.2, 151.2, 150.8, 140.2, 136.9, 129.9, 129.5, 129.0, 128.2, 128.2, 127.4, 127.0, 123.8, 121.5, 121.2, 117.2, 116.8, 44.1, 23.6.

HRMS (ESI) calcd. for C₂₁H₁₇NNaO₂⁺ ([M+Na]⁺): 338.1151, found: 338.1147.



***N*-(2-(Trifluoromethyl)-9*H*-xanthen-9-yl)acetamide (**4e**)**

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4e** (51.6 mg, 56% yield).

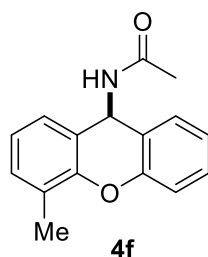
White solid; m.p.: 244~245 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.75 (s, 1H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.35–7.31 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 9.0 Hz, 1H), 6.10 (br, s, 1H), 2.04 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.4, 153.5, 150.7, 129.8, 129.64, 127.4 (q, *J* = 3.6), 126.5 (q, *J* = 3.2), 125.9 (q, *J* = 271.5), 124.5, 123.1, 121.8, 121.3, 120.7, 117.4, 116.9, 43.7, 23.5.

¹⁹F NMR (565 MHz, CDCl₃) δ -77.30.

HRMS (ESI) calcd. for C₁₆H₁₂F₃NNaO₂⁺ ([M+Na]⁺): 330.0172, found: 330.0175.



***N*-(4-Methyl-9*H*-xanthen-9-yl)acetamide (**4f**)**

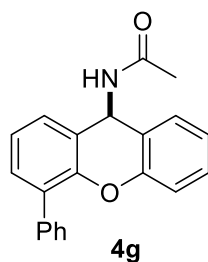
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4f** (52.5 mg, 69% yield).

White solid; m.p.: 239~240 °C.

¹H NMR (600 MHz, CDCl₃) 7.50 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.13–7.10 (m, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 9.0 Hz, 1H), 5.92 (br, d, *J* = 8.4 Hz, 1H), 2.40 (s, 3H), 2.00 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.0, 151.2, 151.0, 139.6, 129.7, 129.4, 129.2, 124.6, 123.5, 121.3, 118.1, 116.9, 116.6, 43.8, 23.4, 21.2.

HRMS (ESI) calcd. for C₁₆H₁₅NNaO₂⁺ ([M+Na]⁺): 276.0995, found: 276.0997.



***N*-(4-Phenyl-9*H*-xanthen-9-yl)acetamide (**4g**)**

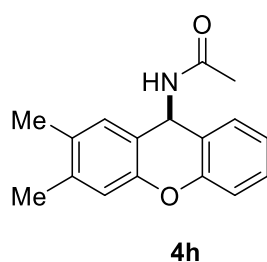
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4g** (54.7 mg, 58% yield).

White solid; m.p.: 251~152 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, *J* = 7.0 Hz, 2H), 7.51–7.46 (m, 4H), 7.42–7.38 (m, 1H), 7.36 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.29–7.26 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (td, *J* = 7.8, 1.2 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 9.0 Hz, 1H), 6.06 (br, *J* = 8.4 Hz, 1H), 2.02 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.2, 151.3, 148.3, 137.5, 130.8, 130.2, 129.8, 129.6, 129.3, 129.1, 128.3, 127.5, 123.9, 123.7, 122.0, 121.3, 116.9, 44.5, 23.6.

HRMS (ESI) calcd. for C₂₁H₁₇NNaO₂⁺ ([M+Na]⁺): 338.1151, found: 338.1151.



***N*-(2,3-Dimethyl-9,10-dihydroanthracen-9-yl)acetamide (4h)**

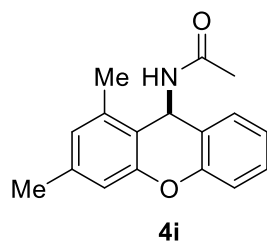
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4h** (57.2 mg, 72% yield).

White solid; m.p.: 247~248 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.66 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.30–7.27 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.10–7.07 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 9.0 Hz, 1H), 5.85 (br, d, *J* = 7.8 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.91 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 168.4, 151.1, 150.8, 136.8, 131.9, 130.7, 130.2, 129.2, 123.6, 122.8, 119.0, 116.3, 114.1, 42.9, 23.3, 20.2, 15.2.

HRMS (ESI) calcd. for C₁₇H₁₇NNaO₂⁺ ([M+Na]⁺): 290.1151, found: 290.1152.



***N*-(1,3-Dimethyl-9,10-dihydroanthracen-9-yl)acetamide (4i)**

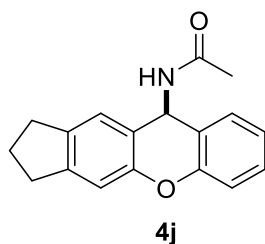
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4i** (51.6 mg, 67% yield).

White solid; m.p.: 244~245 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.66–7.63 (m, 1H), 7.29 (td, *J* = 7.8, 1.8 Hz, 1H), 7.11–7.08 (m, 2H), 6.82 (d, *J* = 4.8 Hz, 2H), 6.47 (d, *J* = 9.6 Hz, 1H), 5.78 (br, d, *J* = 9.0 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.91 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 168.4, 152.4, 151.3, 139.4, 138.6, 130.2, 129.2, 126.4, 123.7, 122.9, 116.5, 116.2, 115.1, 42.4, 23.4, 21.2, 18.7.

HRMS (ESI) calcd. for C₁₇H₁₇NNaO₂⁺ ([M+Na]⁺): 290.1151, found: 290.1155.



***N*-(1,2,3,10-Tetrahydrocyclopenta[*b*]xanthen-10-yl)acetamide (4j)**

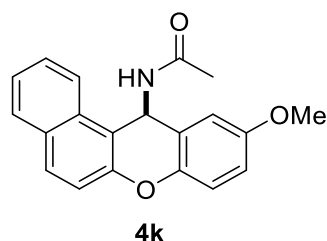
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4j** (51.9 mg, 70% yield).

White solid; m.p.: 236~237 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.58 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.30–7.27 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.11–7.07 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 5.81 (br, d, *J* = 9.6 Hz, 1H), 2.99–2.94 (m, 1H), 2.90 (t, *J* = 8.4 Hz, 2H), 2.87–2.81 (m, 1H), 2.17–2.08 (m, 2H), 1.96 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 168.5, 151.327, 150.6, 144.8, 139.4, 130.2, 129.3, 125.1, 123.6, 122.2, 116.6, 116.4, 114.9, 42.8, 32.5, 31.4, 25.7, 23.4.

HRMS (ESI) calcd. for C₁₈H₁₇NNaO₂⁺ ([M+Na]⁺): 302.1151, found 302.1154.



***N*-(10-Methoxy-12*H*-benzo[a]xanthen-12-yl)acetamide (4k)**

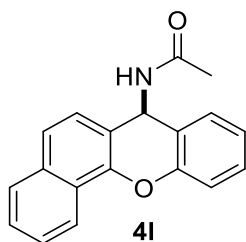
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 3:1) to afford the product **4k** (61.3 mg, 64% yield).

White solid; m.p.: 258~259 °C.

¹H NMR (600 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 6.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 6.6 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.25 (d, *J* = 3.0 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 9.4 Hz, 1H), 6.92 (dd, *J* = 8.4, 3.0 Hz, 1H), 5.85 (br, d, *J* = 9.6 Hz, 1H), 3.83 (s, 3H), 1.92 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 168.7, 156.2, 150.3, 144.8, 131.8, 130.5, 130.4, 128.7, 127.8, 124.8, 123.0, 122.5, 118.0, 117.6, 116.8, 112.6, 111.5, 56.0, 42.2, 23.4.

HRMS (ESI) calcd. for C₂₀H₁₇NNaO₂⁺ ([M+Na]⁺): 342.1101, found 342.1102.



***N*-(7*H*-benzo[*c*]xanthen-7-yl)acetamide (4l)**

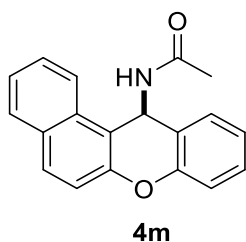
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4l** (47.6 mg, 55% yield).

White solid; m.p.: 250~251 °C.

¹H NMR (600 MHz, CDCl₃) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.60–7.54 (m, 4H), 7.51–7.48 (m, 1H), 7.38–7.35 (m, 1H), 7.30 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.19–7.16 (m, 1H), 6.66 (d, *J* = 9.0 Hz, 1H), 6.04 (br, d, *J* = 9.0 Hz, 1H), 2.02 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.1, 151.0, 146.3, 134.0, 129.9, 129.3, 127.6, 127.0, 126.3, 126.3, 124.0, 123.9, 123.3, 121.8, 121.2, 116.8, 114.8, 44.2, 23.5.

HRMS (ESI) calcd. for C₁₉H₁₅NNaO₂⁺ ([M+Na]⁺): 312.0095, found 312.0098.



***N*-(12*H*-benzo[*a*]xanthen-12-yl)acetamide (4m)**

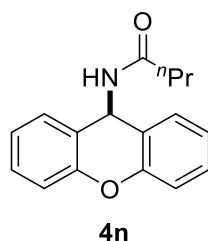
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4m** (50.3 mg, 58% yield).

White solid; m.p.: 249~250 °C.

¹H NMR (600 MHz, CDCl₃) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.60–7.54 (m, 4H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.01 (br, *J* = 9.0 Hz, 1H), 2.02 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.1, 151.1, 146.4, 134.1, 130.0, 129.4, 127.8, 127.1, 126.4, 126.4, 124.1, 123.4, 121.9, 121.4, 116.9, 114.9, 44.4, 23.6.

HRMS (ESI) calcd. for C₁₉H₁₅NNaO₂⁺ ([M+Na]⁺): 312.0095, found 312.0098.



***N*-(9*H*-xanthen-9-yl)butyramide (4n)**

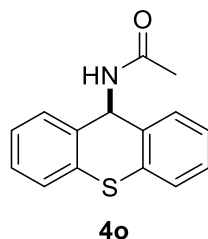
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 9:1) to afford the product **4n** (40.1 mg, 50% yield).

White solid; m.p.: 262~263 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.12–7.09 (m, 4H), 6.52 (d, *J* = 9.0 Hz, 1H), 6.05 (br, d, *J* = 8.4 Hz, 1H), 2.17 (t, *J* = 7.8 Hz, 2H), 1.72–1.67 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 172.2, 151.2, 129.8, 129.4, 123.7, 121.4, 116.8, 43.8, 38.9, 19.3, 13.9.

HRMS (ESI) calcd. for C₁₈H₁₉NO₂⁺ ([M+H]⁺): 267.1379, found: 267.1377.



***N*-(9*H*-thioxanthen-9-yl)acetamide (4o)**

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **4o** (48.9 mg, 64% yield).

White solid; m.p.: 237~238 °C.

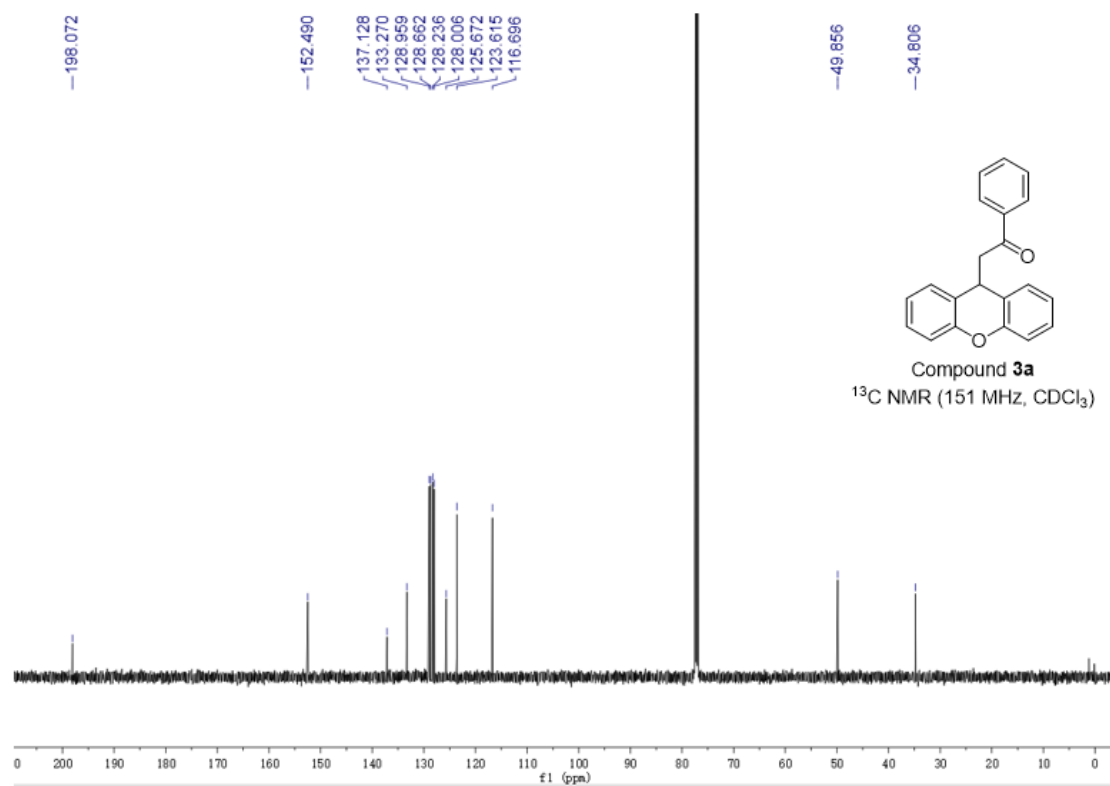
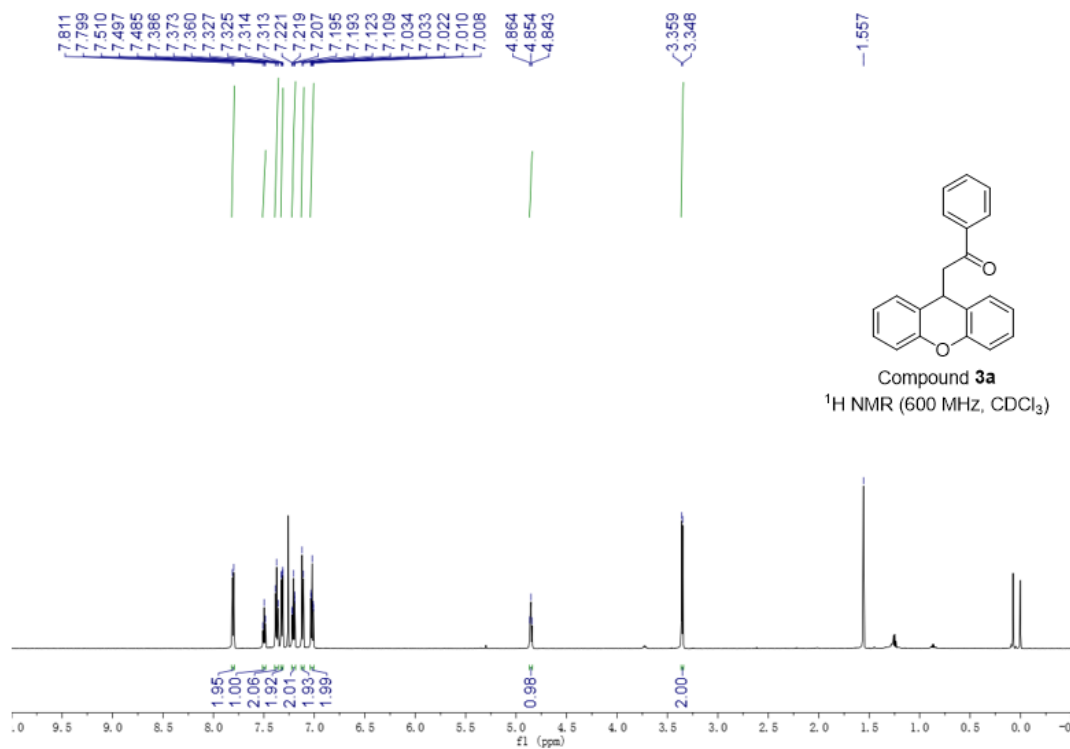
¹H NMR (600 MHz, CDCl₃) δ 7.58 (dd, *J* = 6.0, 2.4 Hz, 2H), 7.47–7.45 (m, 2H), 7.28–7.25 (m, 4H), 6.30 (d, *J* = 9.0 Hz, 1H), 6.23 (br, d, *J* = 7.2 Hz, 1H), 1.88 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.0, 134.9, 133.0, 129.6, 128.0, 127.2, 127.2, 53.4, 23.5.

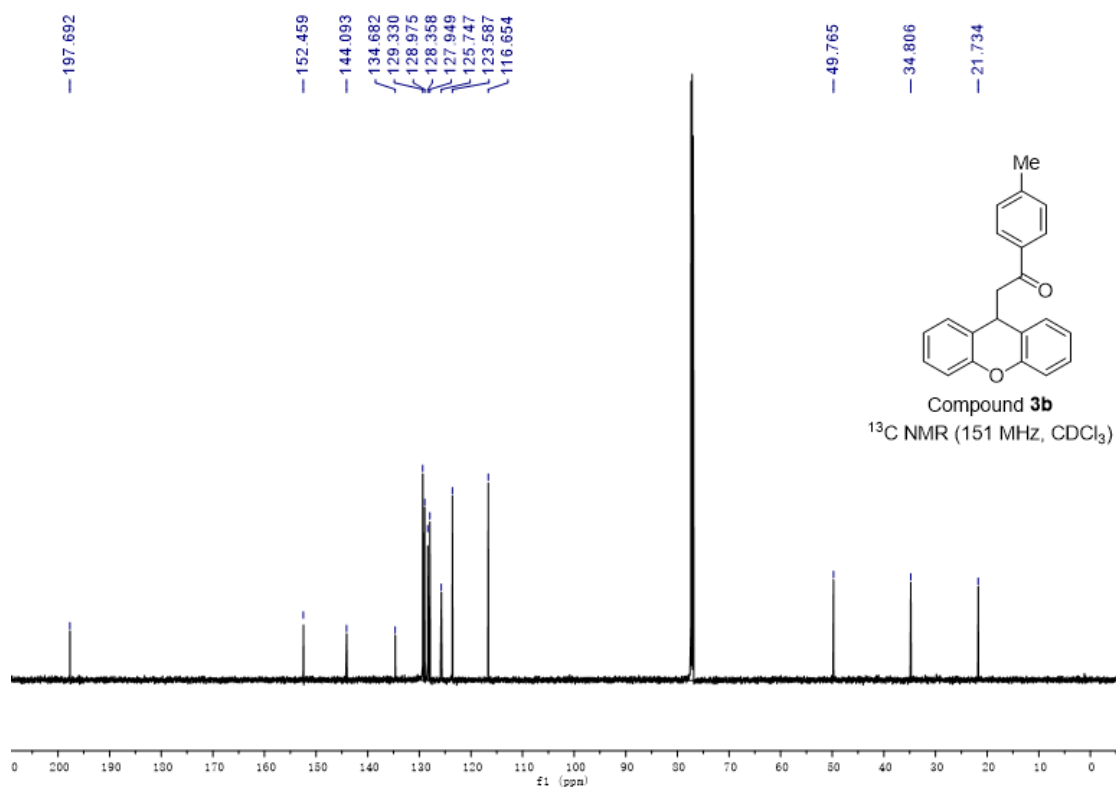
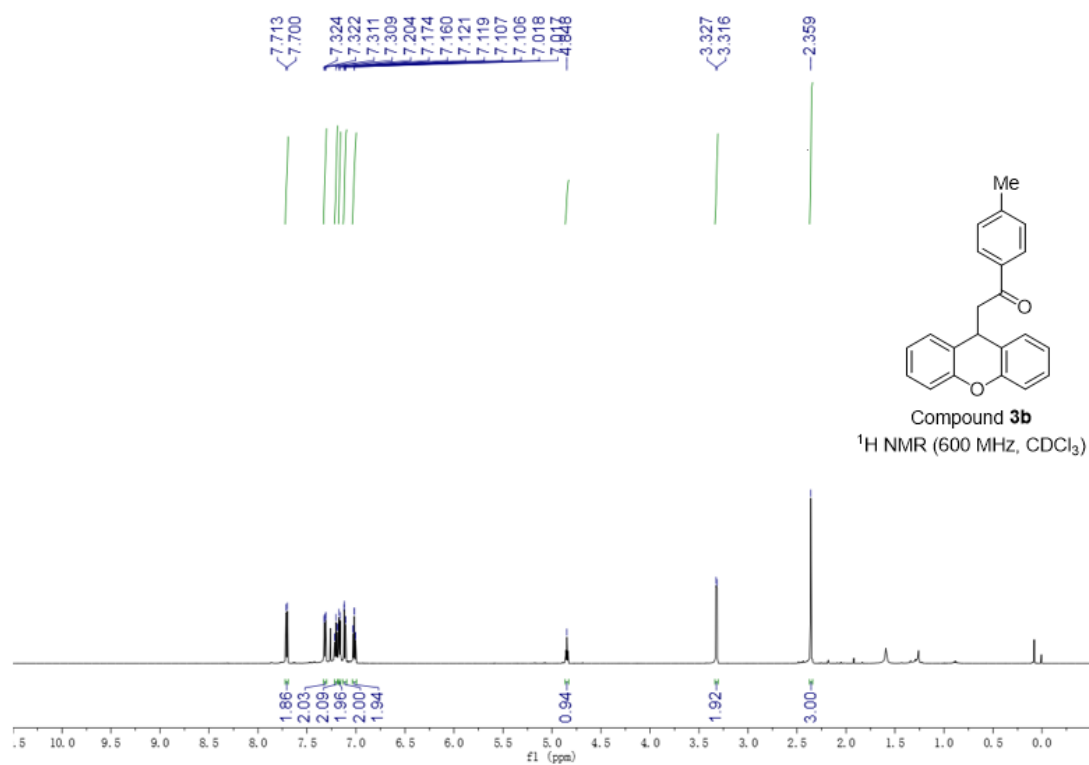
HRMS (ESI) calcd. for C₁₅H₁₃NNaOS⁺ ([M+Na]⁺): 278.0610, found: 278.0613.

5. NMR Spectra of the Products

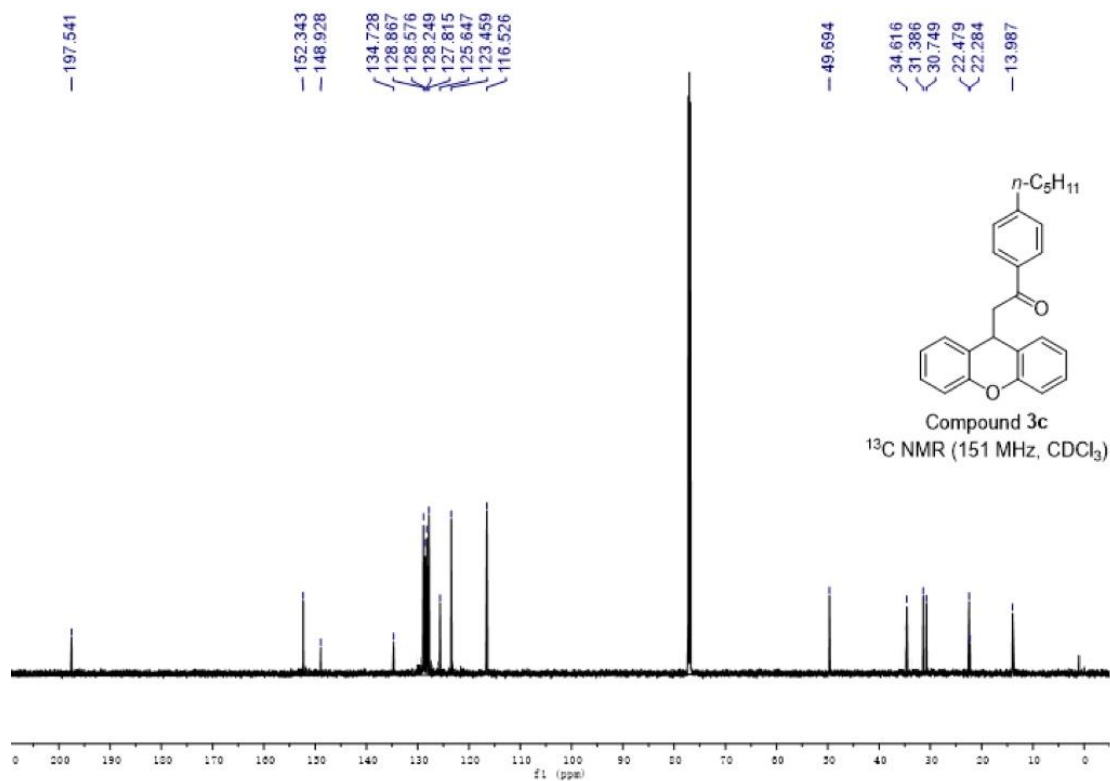
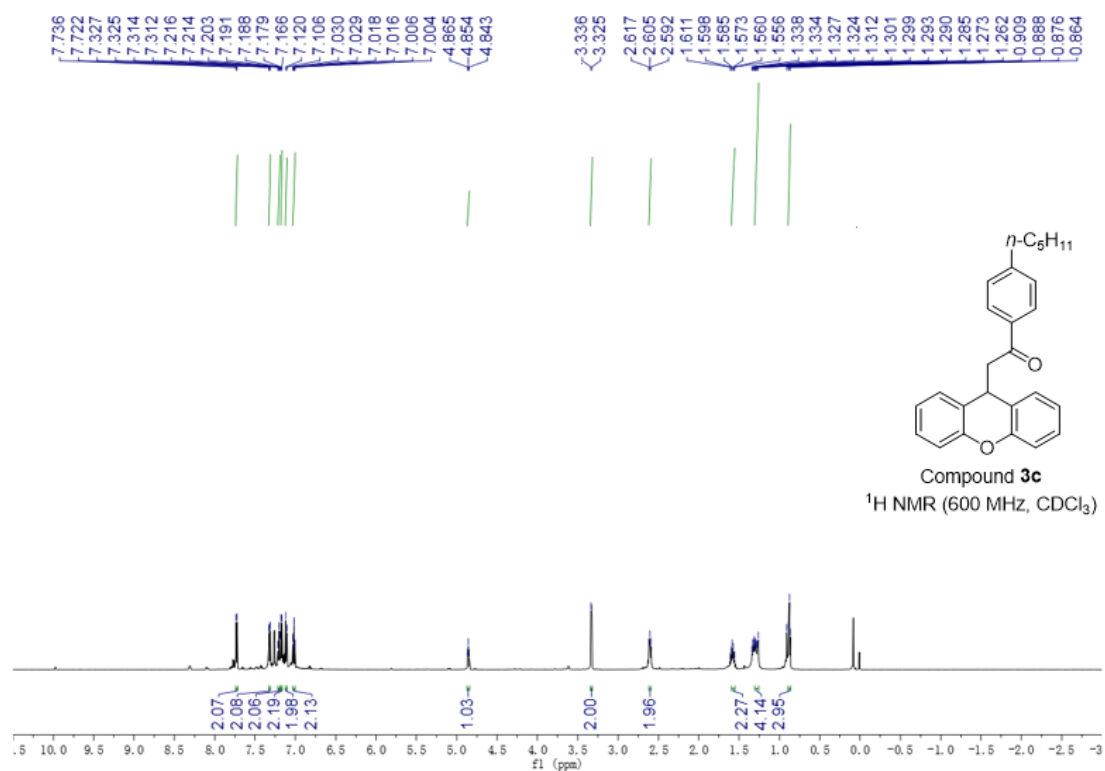
NMR spectra of 1-phenyl-2-(9*H*-xanthen-9-yl)ethan-1-one (**3a**)



NMR spectra of 1-(*p*-tolyl)-2-(9*H*-xanthen-9-yl)ethan-1-one (**3b**)

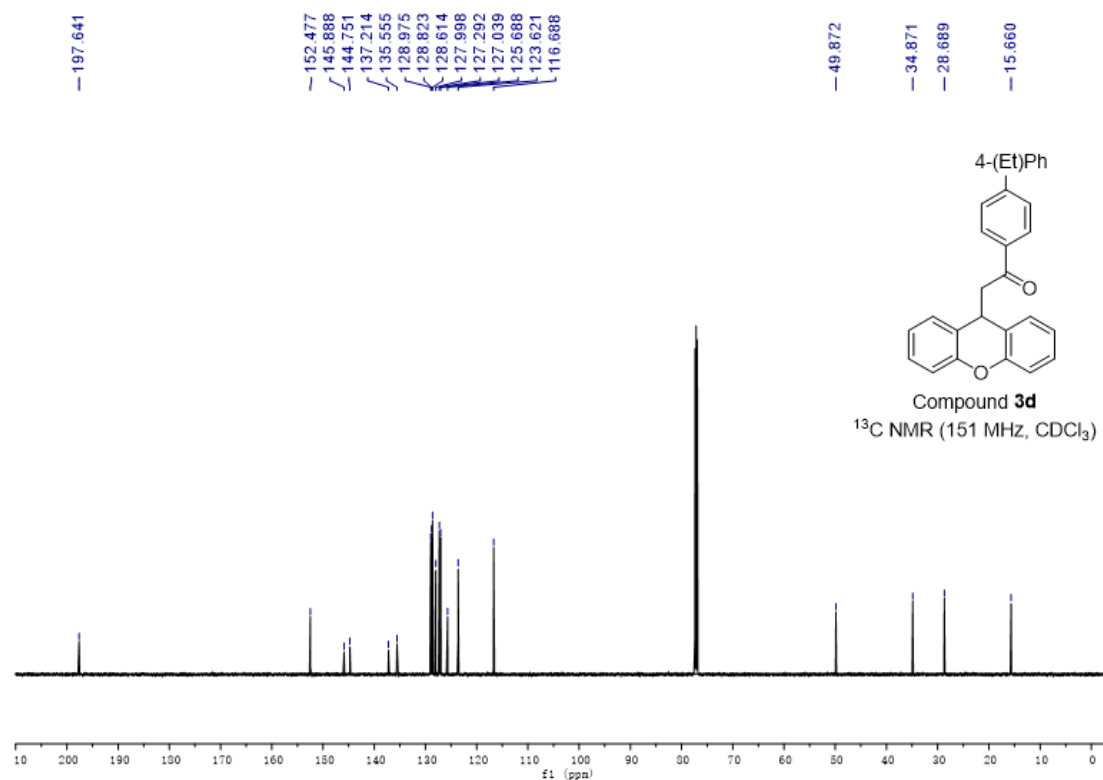
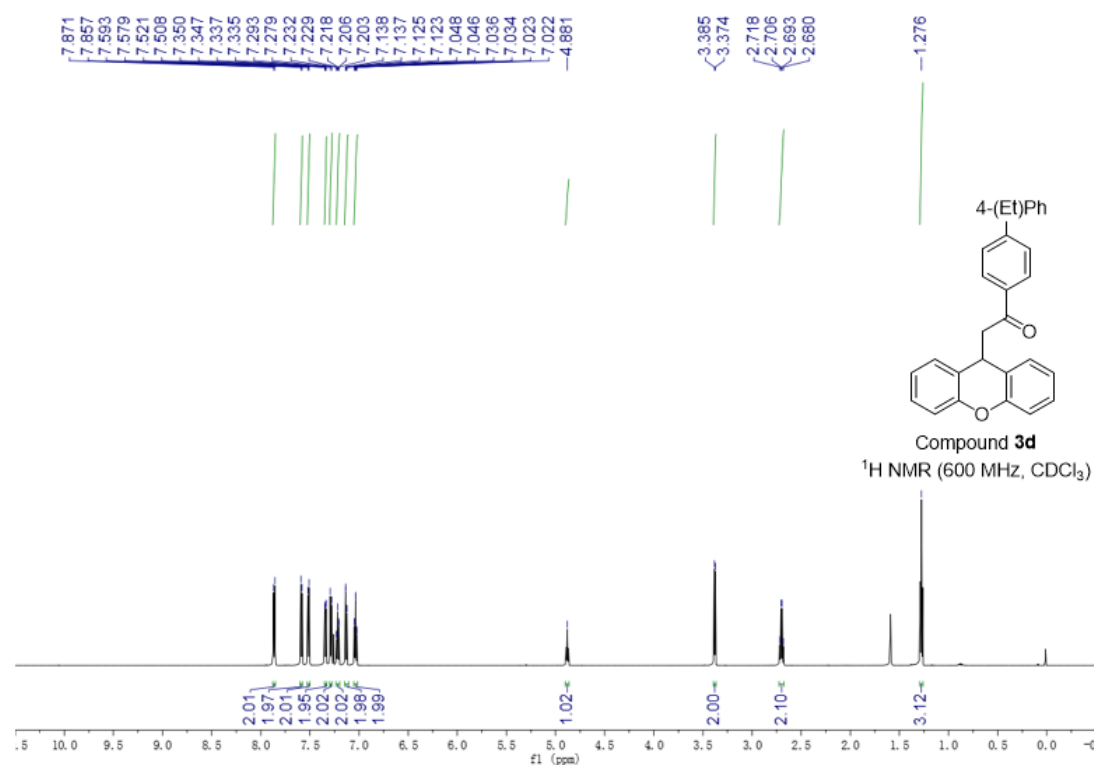


NMR spectra of 1-(4-pentylphenyl)-2-(9*H*-xanthen-9-yl)ethan-1-one (**3c**)

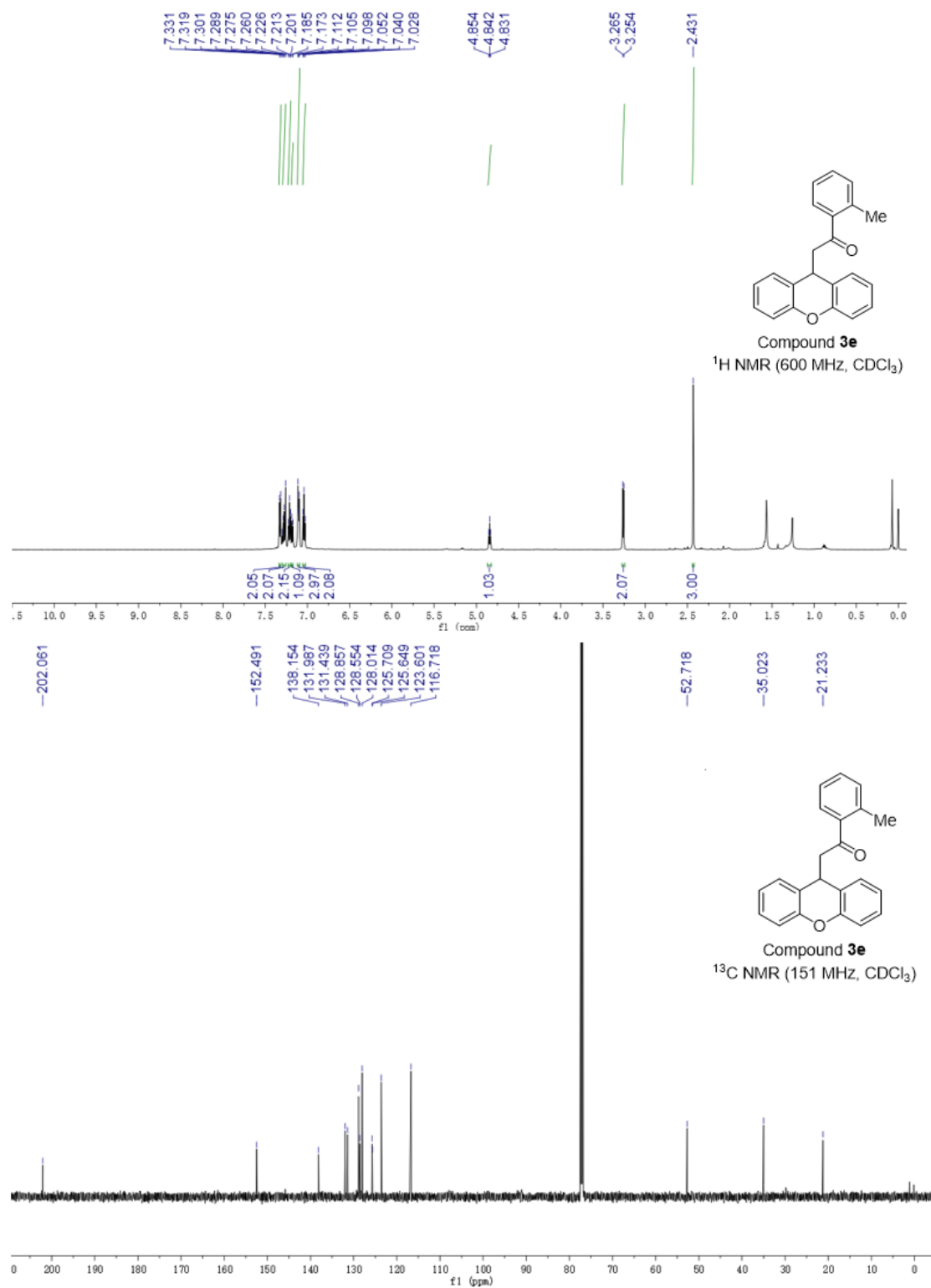


NMR spectra of 1-(4'-ethyl-[1,1'-biphenyl]-4-yl)-2-(9*H*-xanthen-9-yl)ethan-1-one

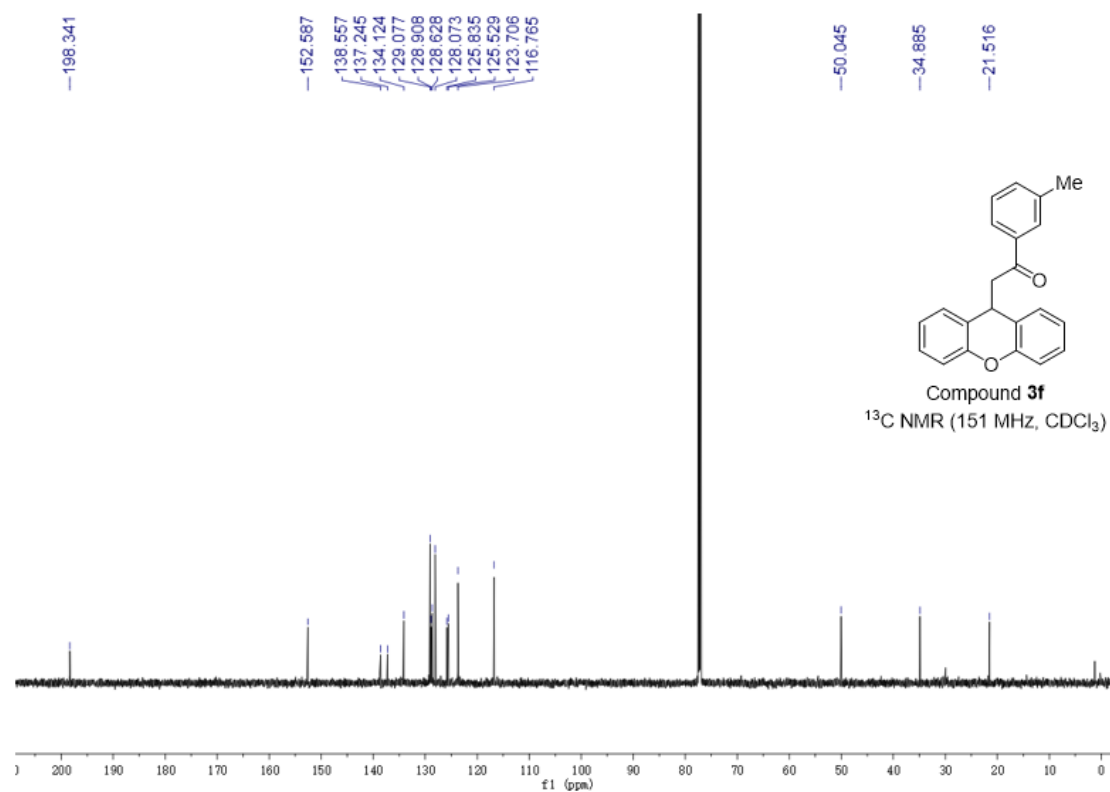
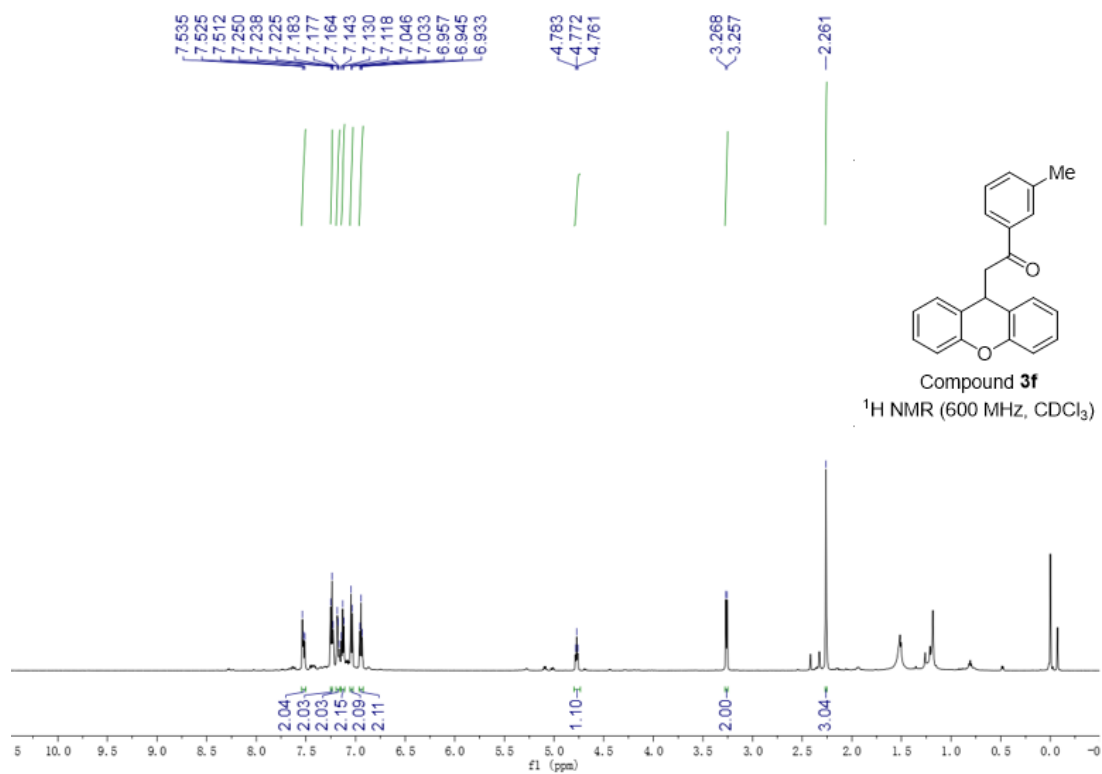
(3d)



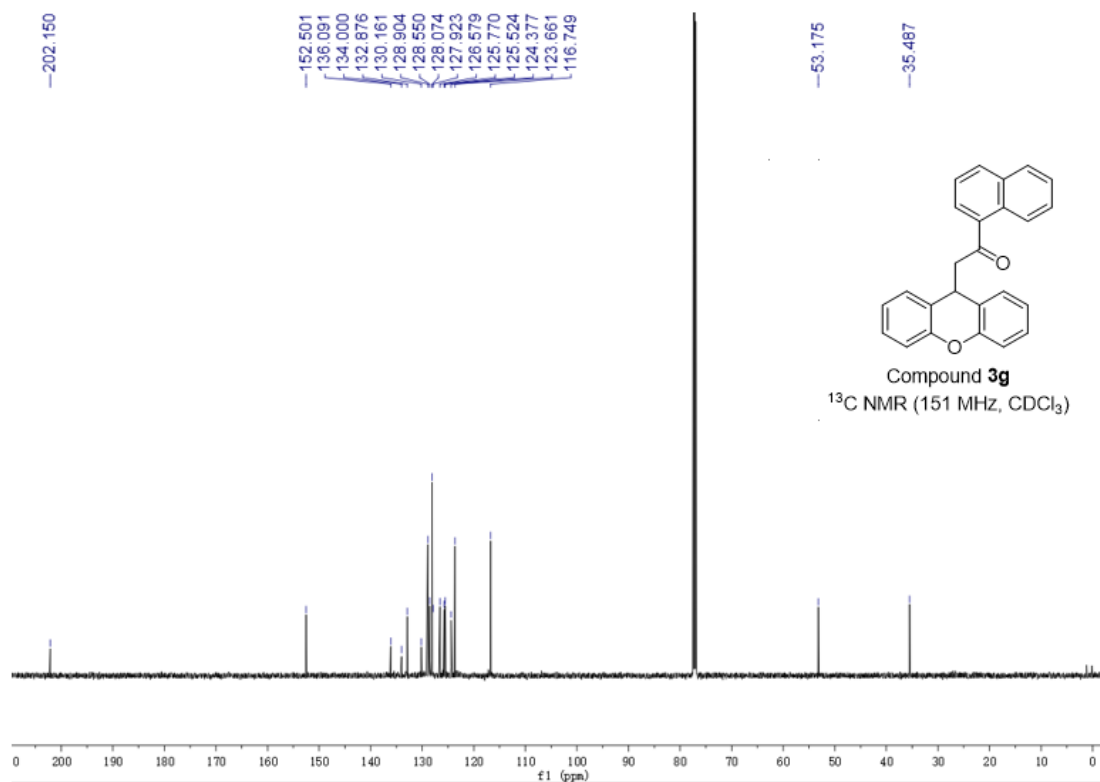
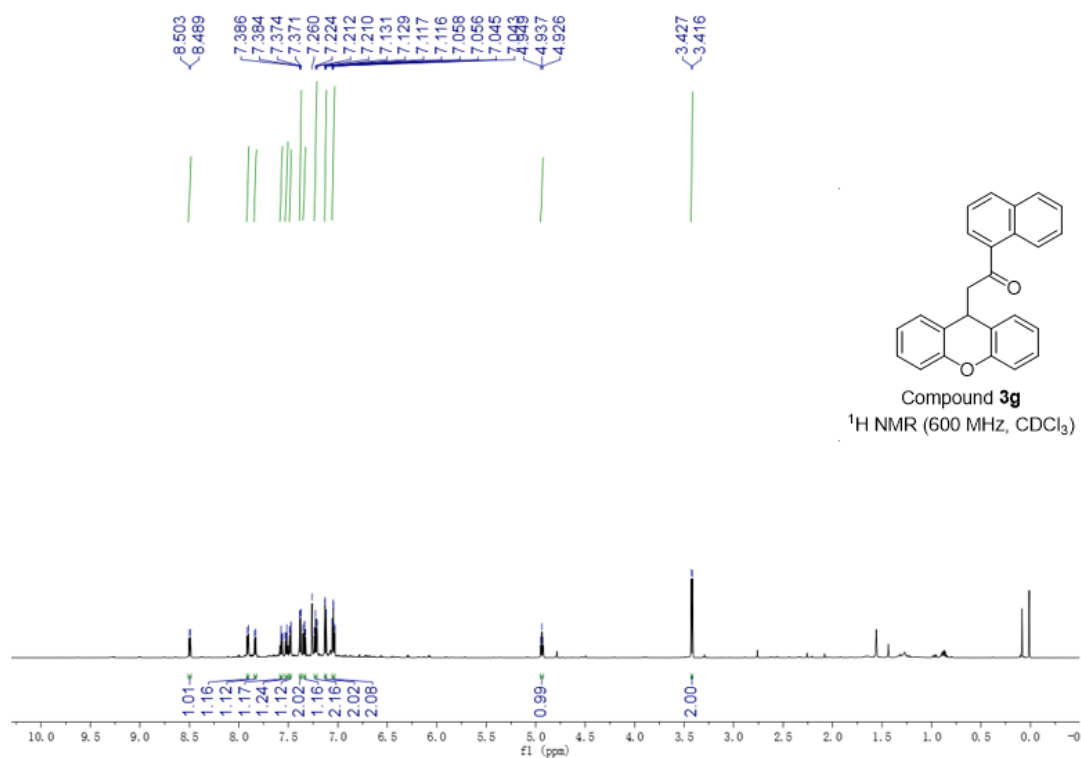
NMR spectra of 1-(*o*-tolyl)-2-(9*H*-xanthen-9-yl)ethan-1-one (**3e**)



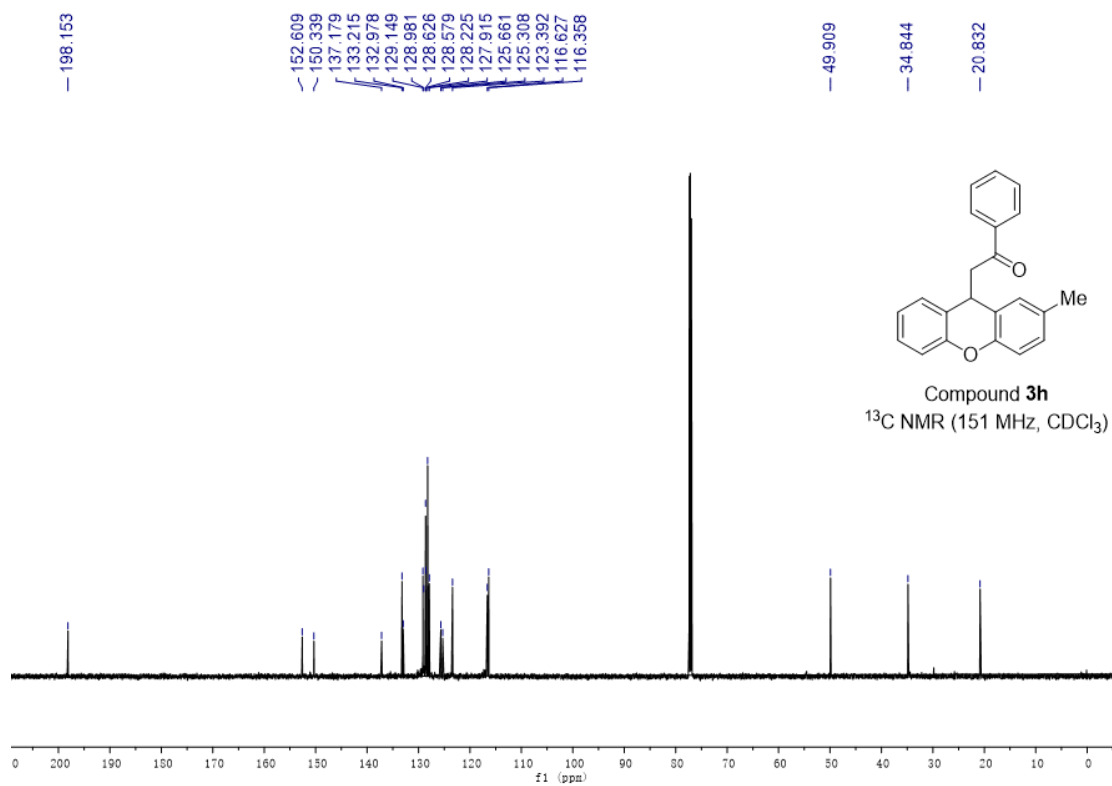
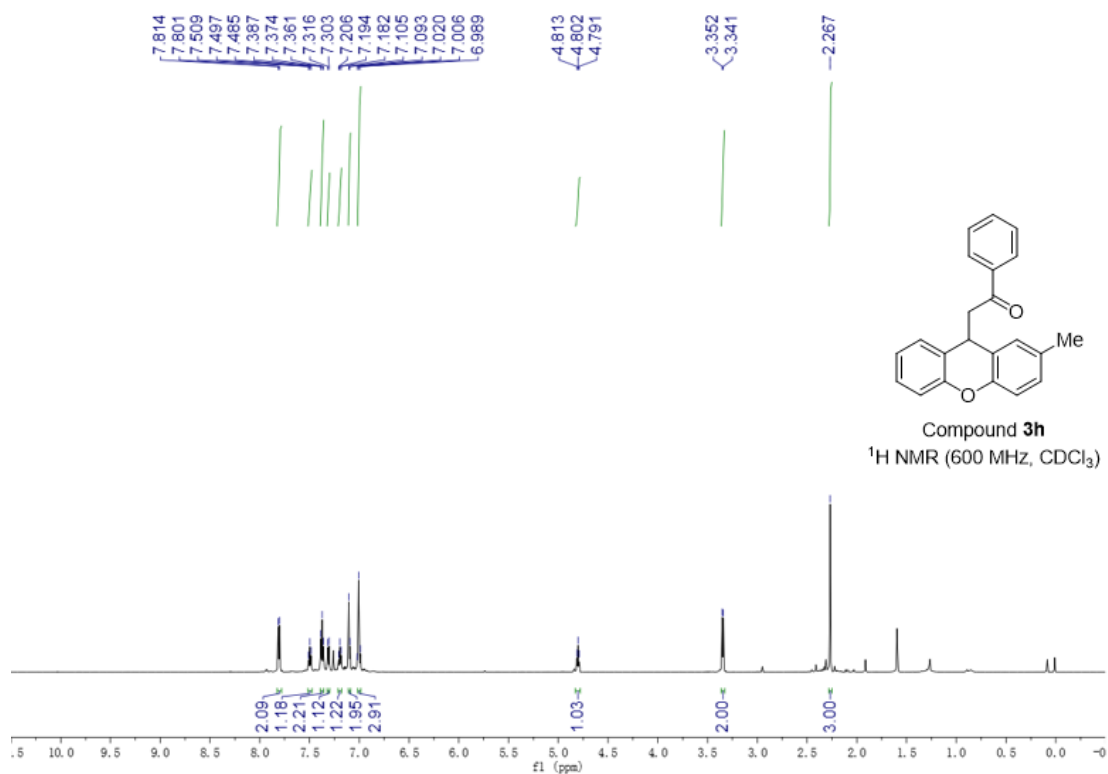
NMR spectra of 1-(*m*-tolyl)-2-(9*H*-xanthen-9-yl)ethan-1-one (**3f**)



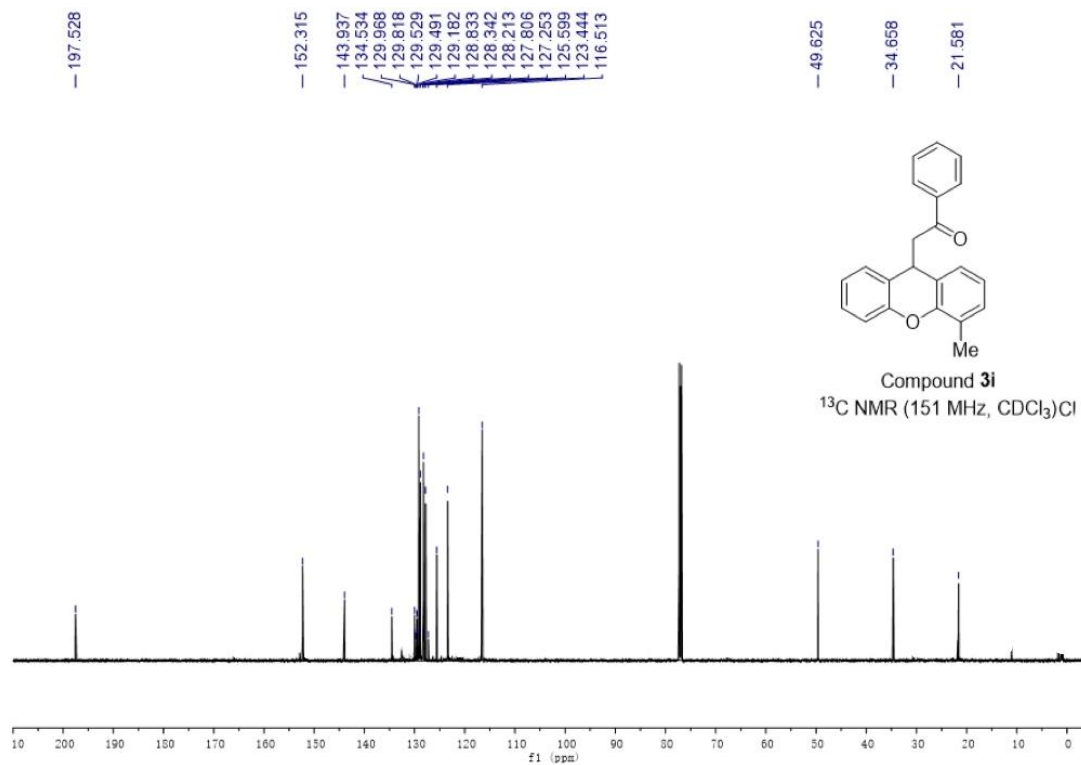
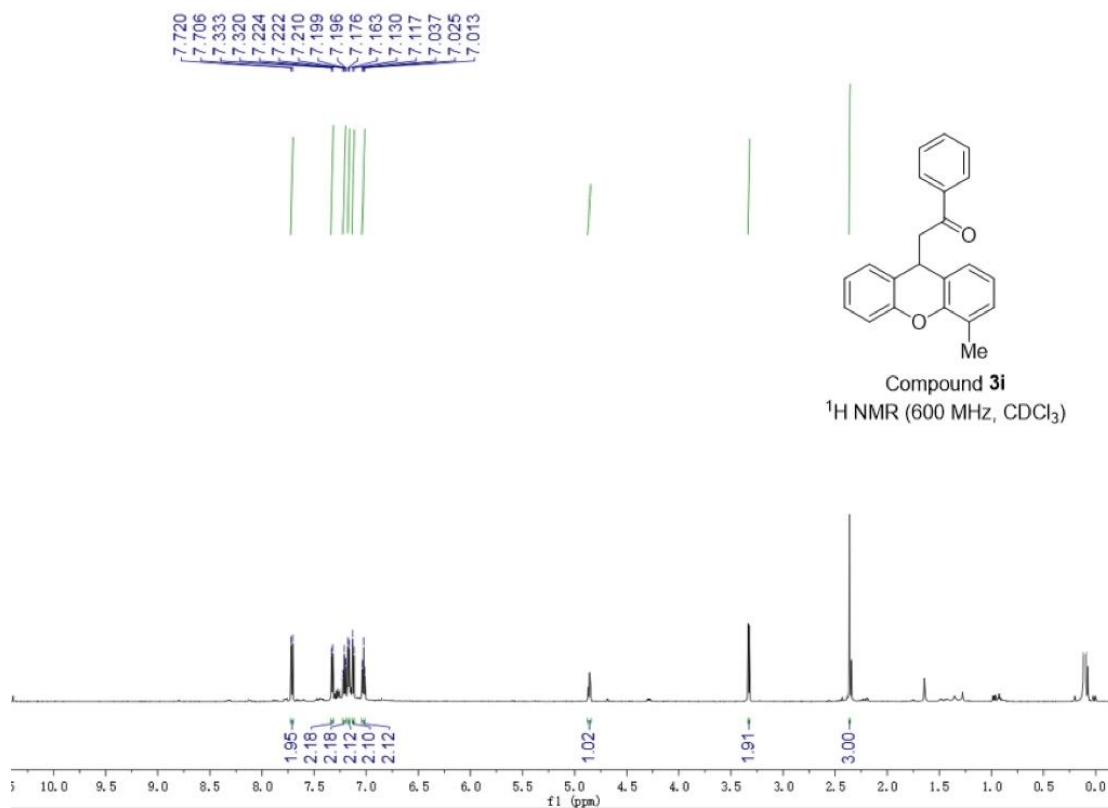
NMR spectra of 1-(naphthalen-1-yl)-2-(9*H*-xanthen-9-yl)ethan-1-one (**3g**)



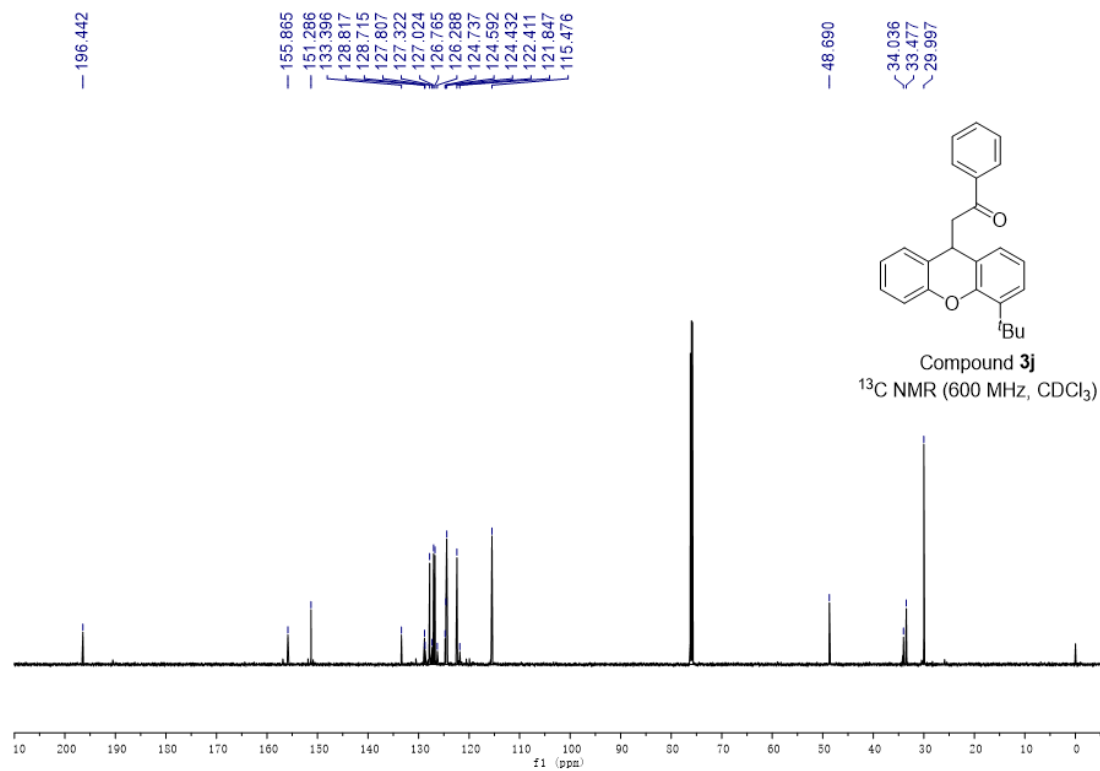
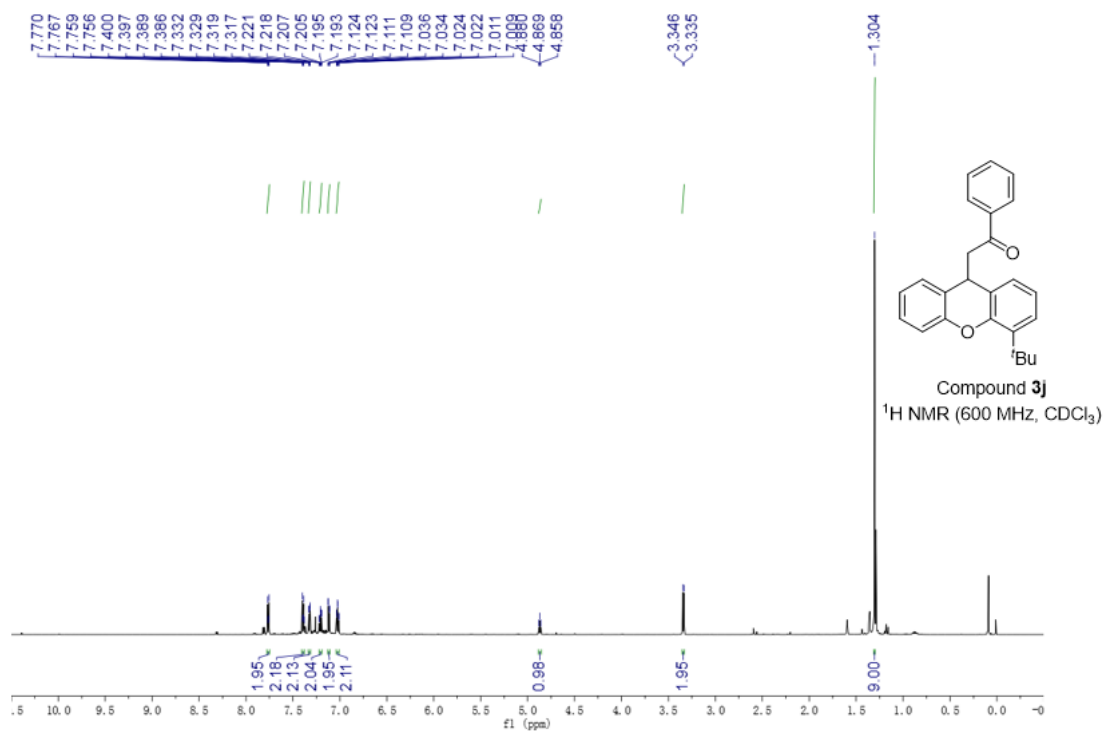
NMR spectra of 2-(2-methyl-9*H*-xanthen-9-yl)-1-phenylethan-1-one (**3h**)



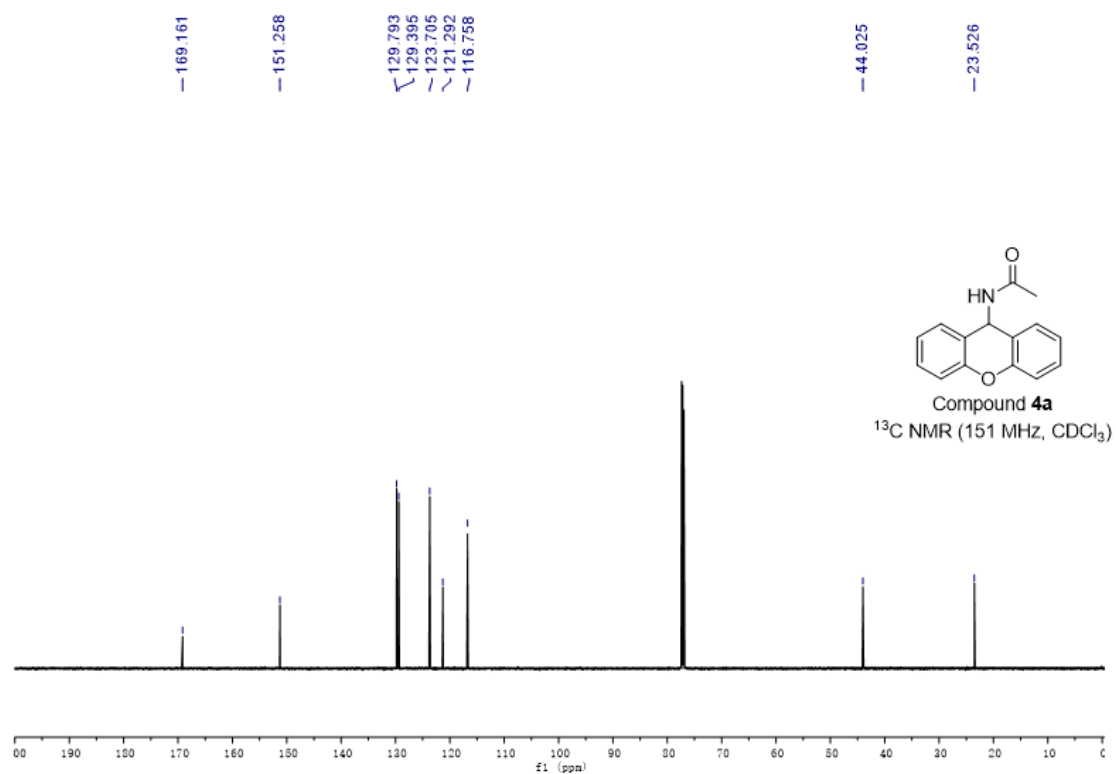
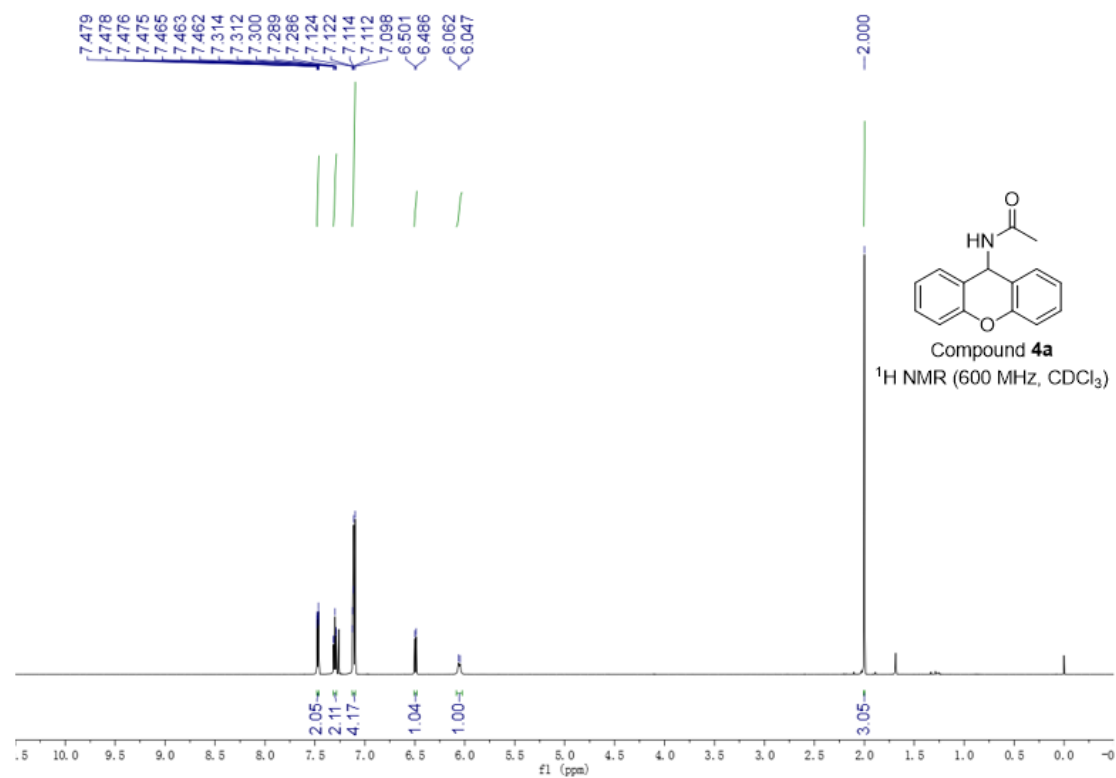
NMR spectra of 2-(4-methyl-9*H*-xanthen-9-yl)-1-phenylethan-1-one (**3i**)



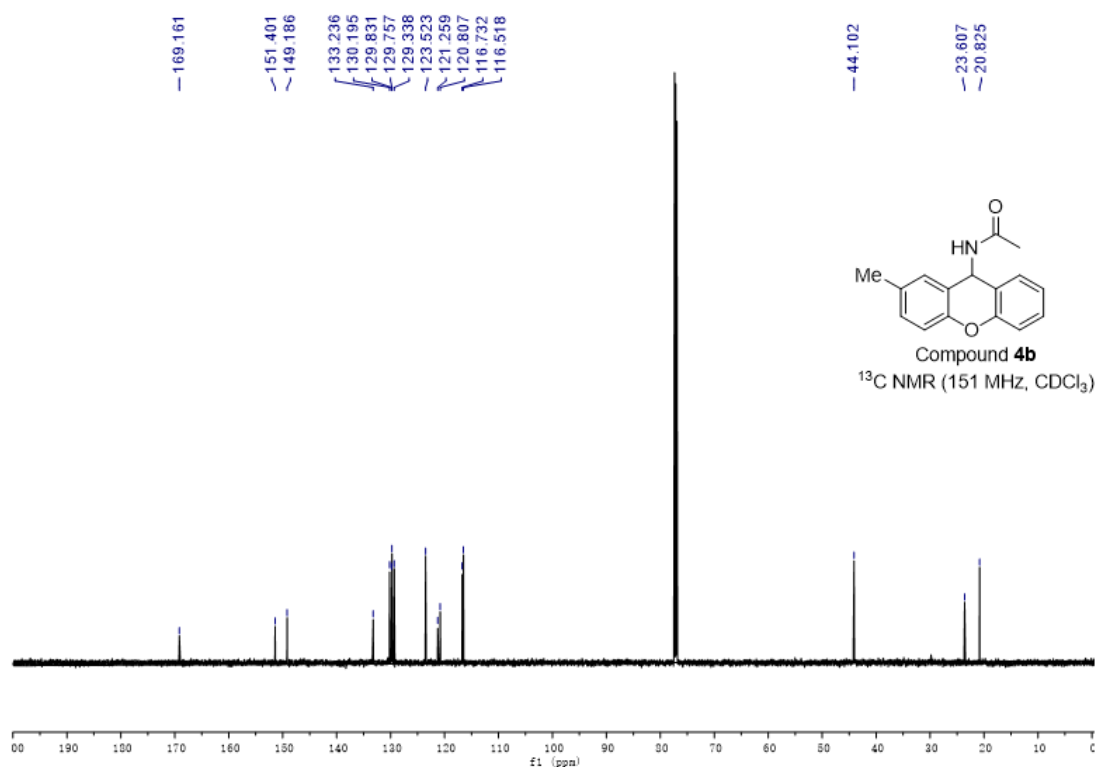
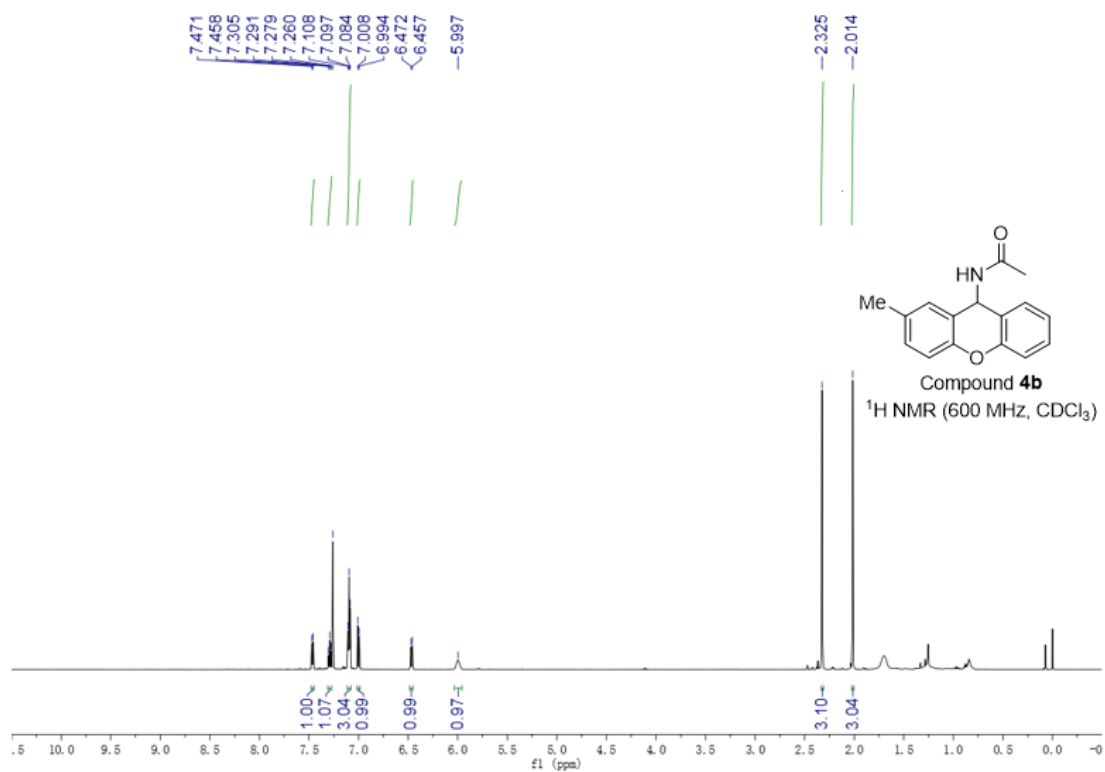
NMR spectra of 2-(4-(*tert*-butyl)-9*H*-xanthen-9-yl)-1-phenylethan-1-one (**3j**)



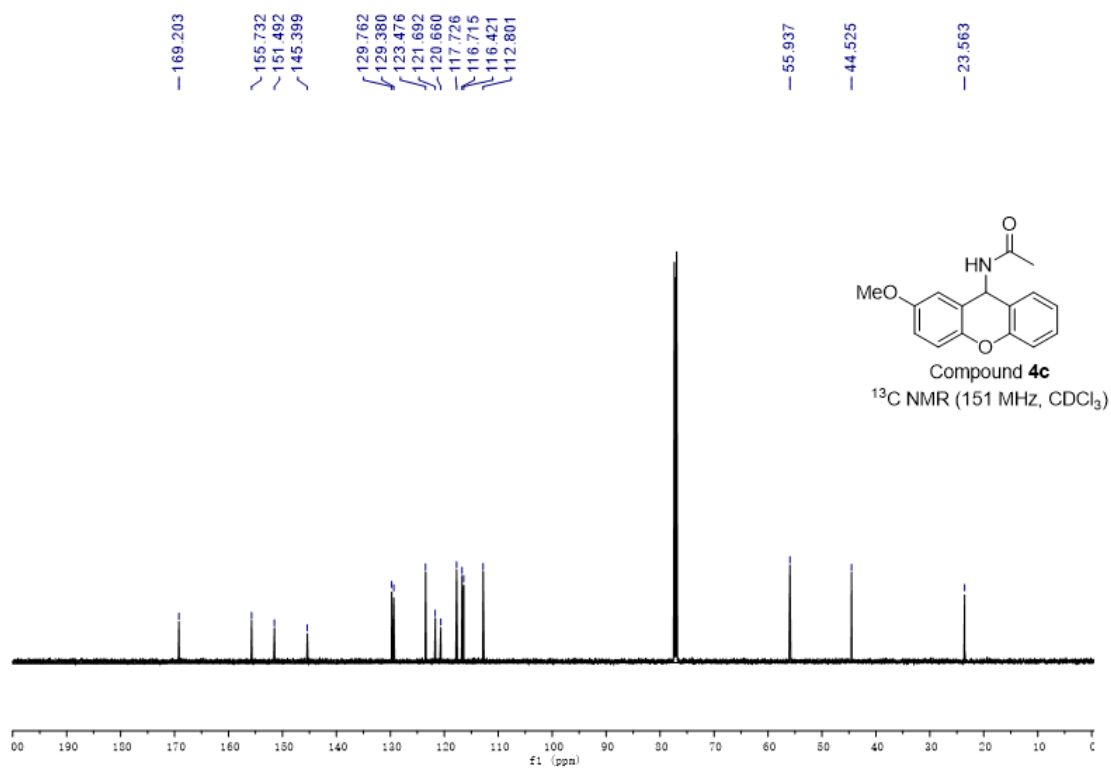
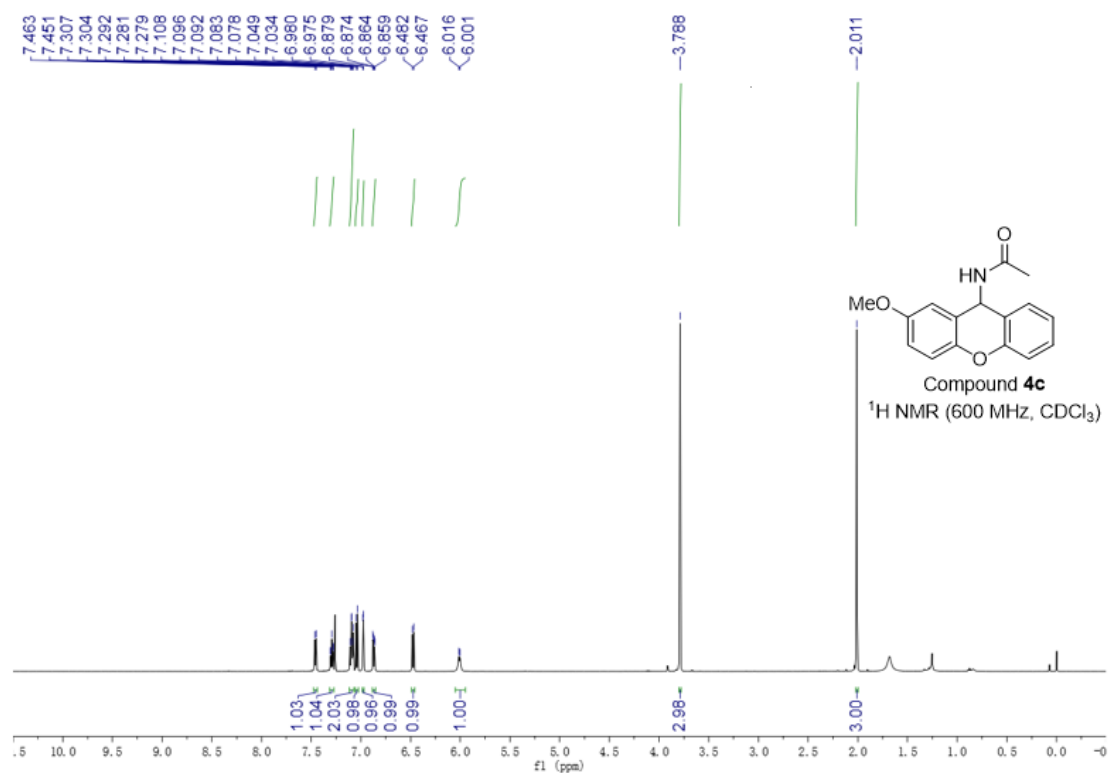
NMR spectra of *N*-(9*H*-xanthen-9-yl)acetamide (**4a**)



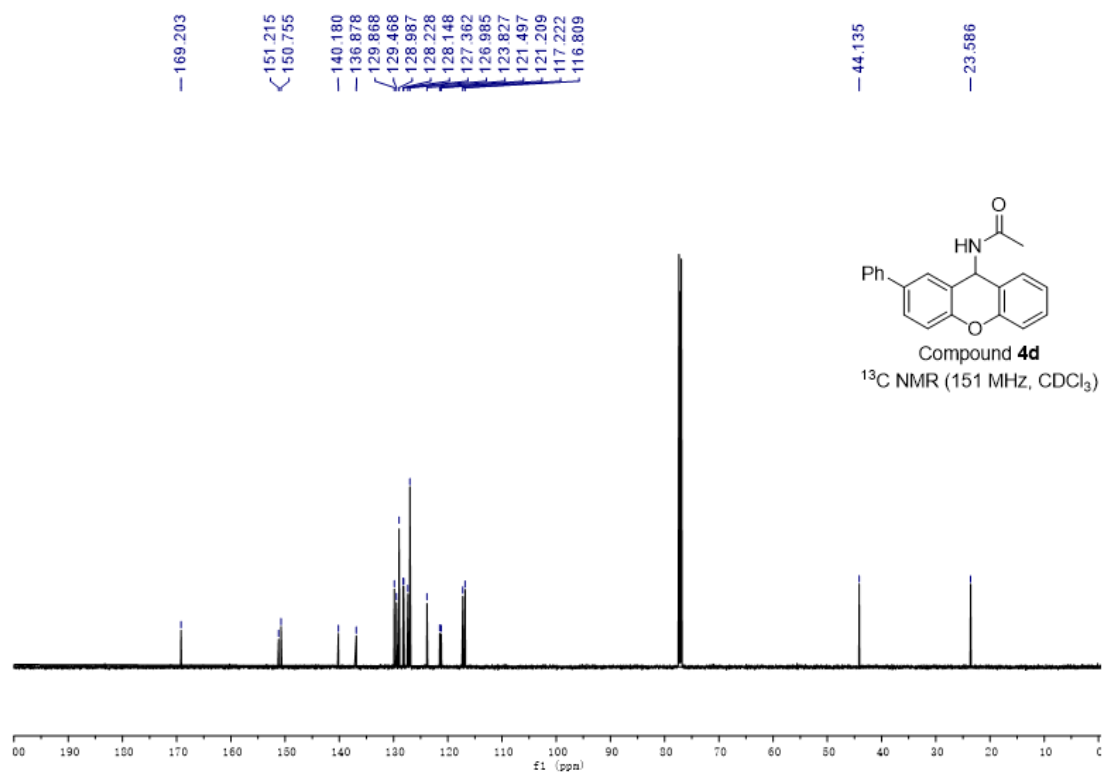
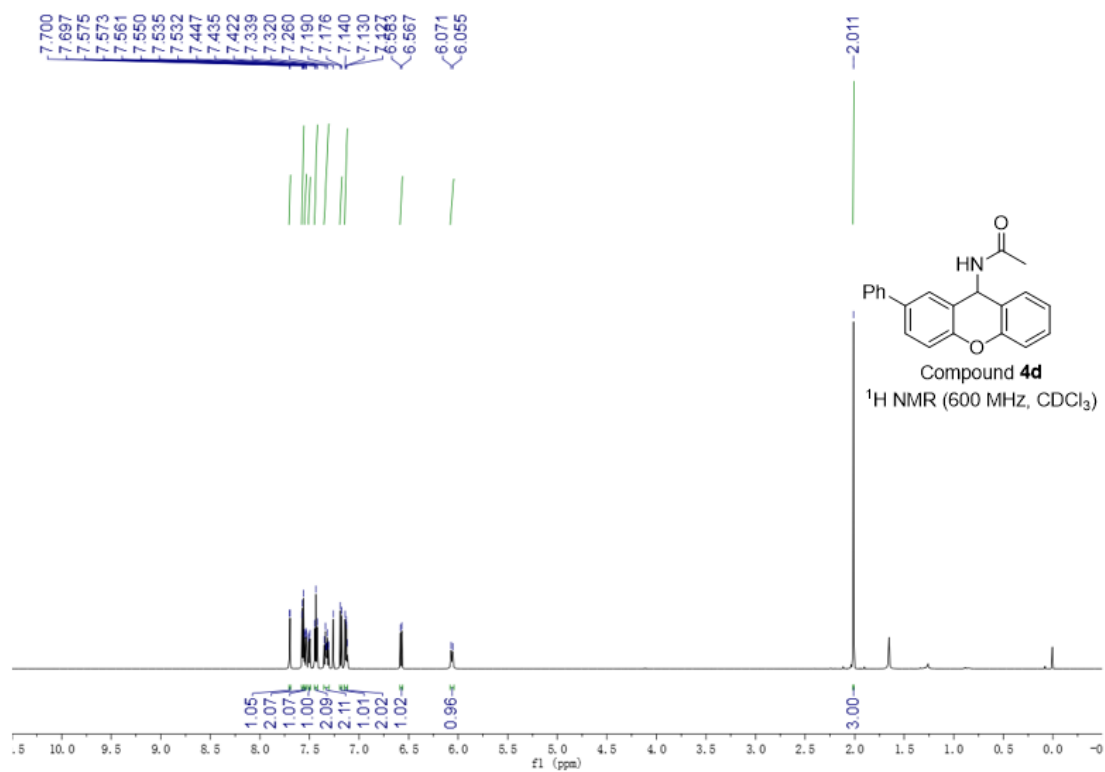
NMR spectra of *N*-(2-methyl-9*H*-xanthen-9-yl)acetamide (**4b**)



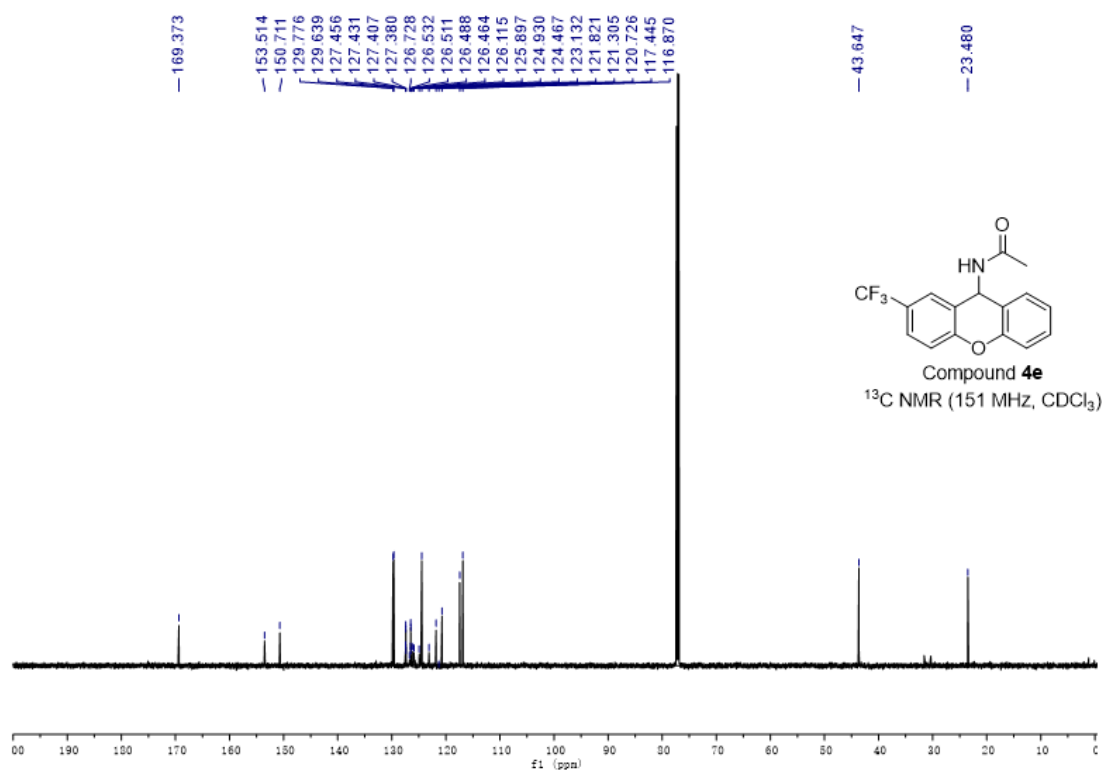
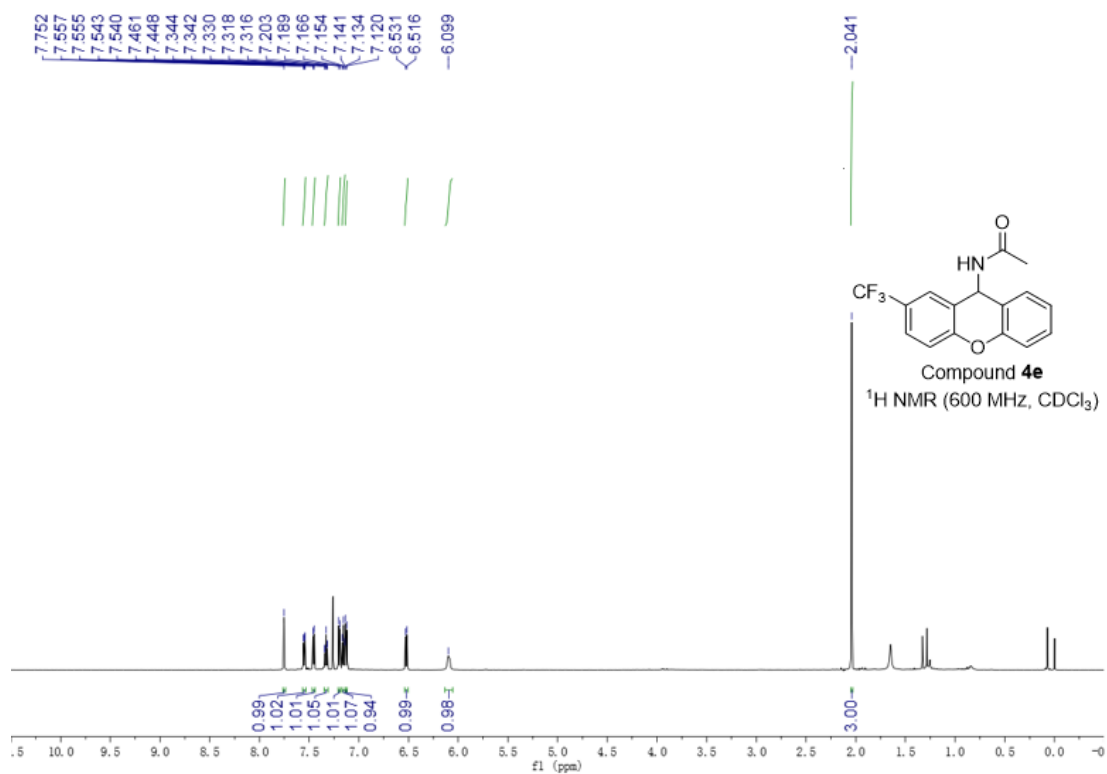
NMR spectra of *N*-(2-methoxy-9*H*-xanthen-9-yl)acetamide (**4c**)

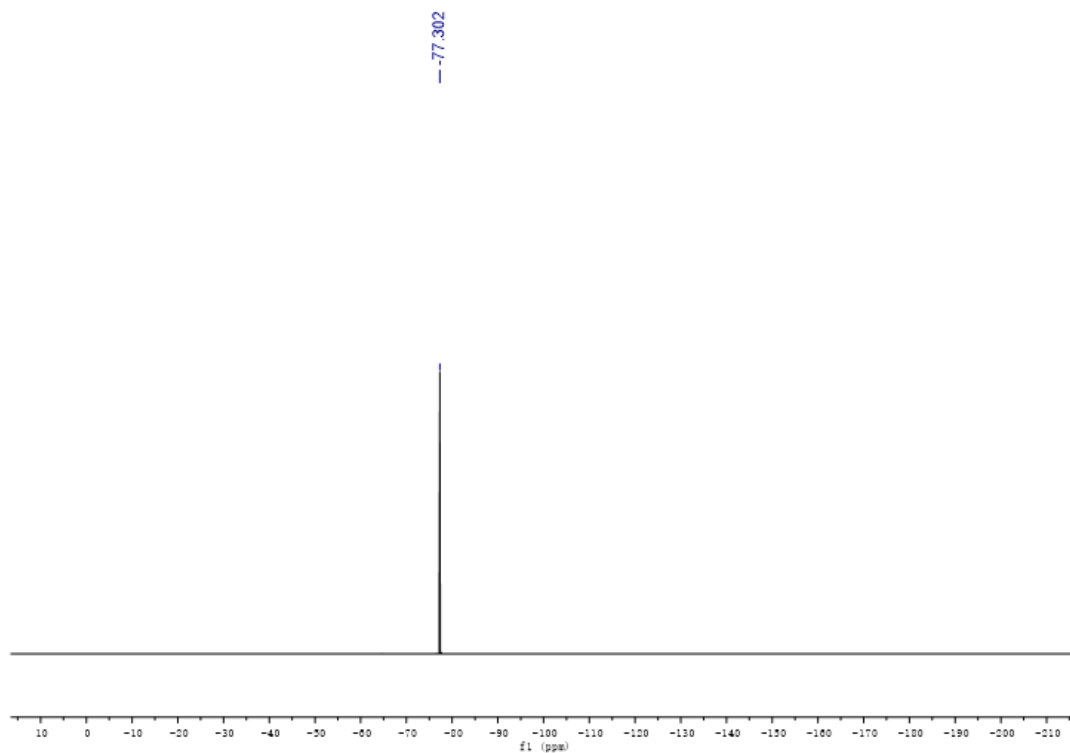


NMR spectra of *N*-(2-phenyl-9*H*-xanthen-9-yl)acetamide (**4d**)

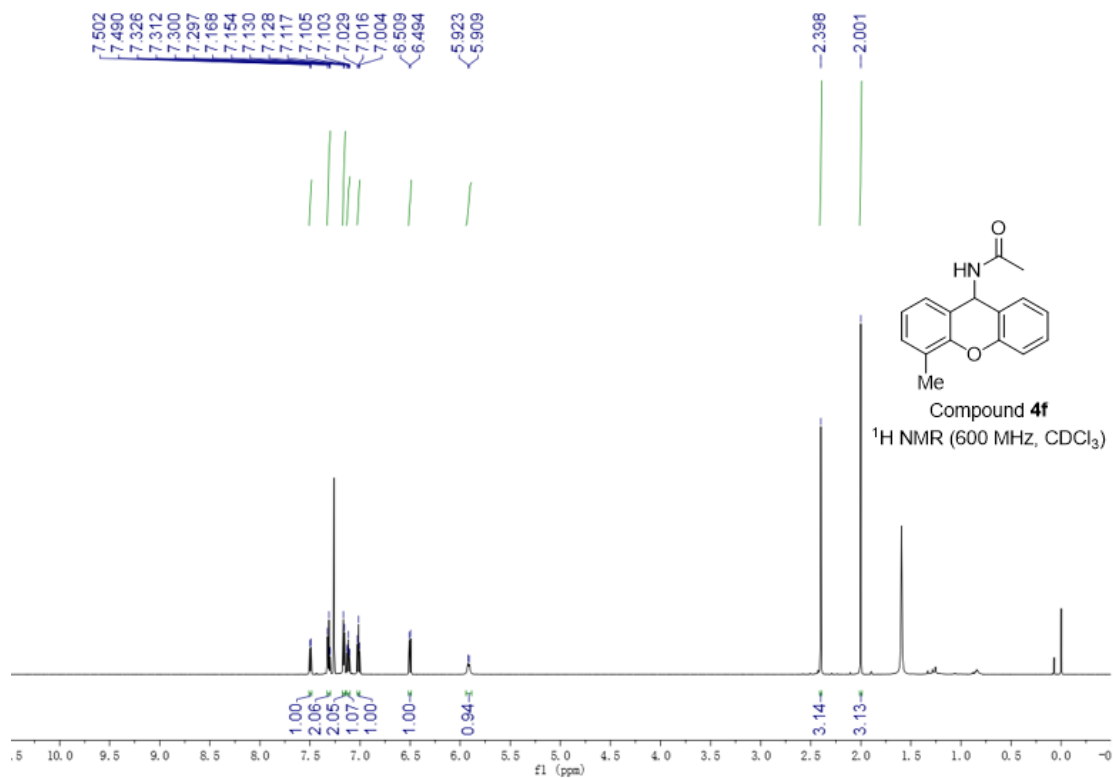


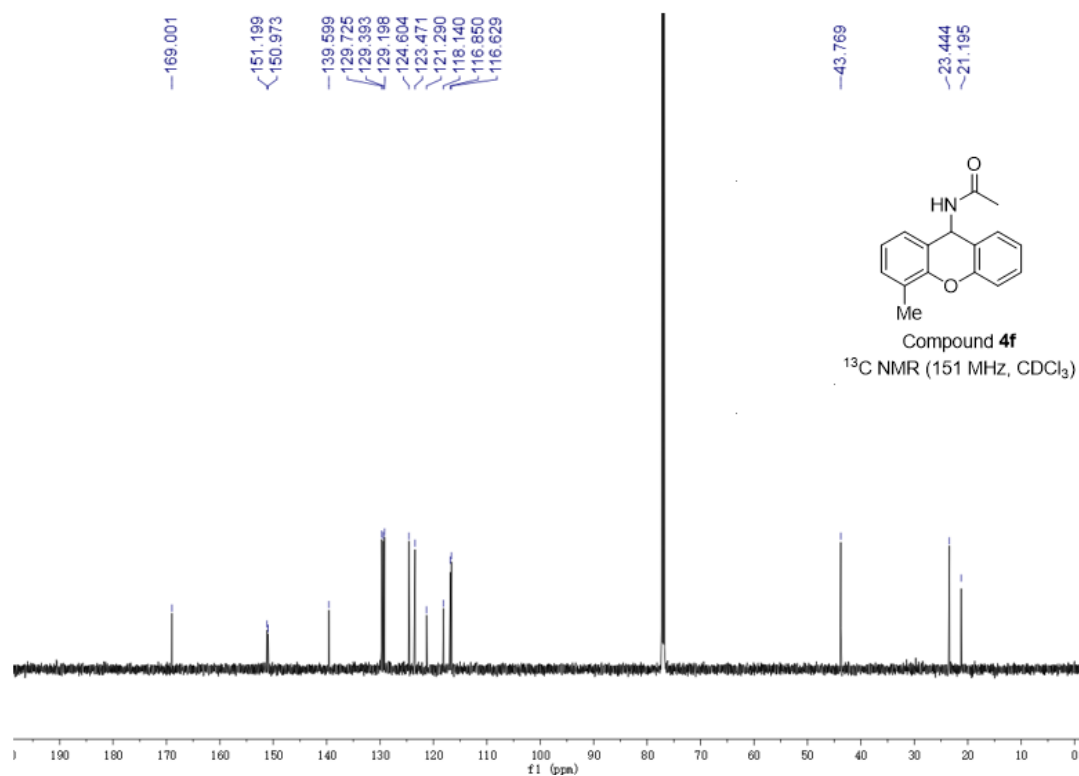
NMR spectra of *N*-(2-(trifluoromethyl)-9*H*-xanthen-9-yl)acetamide (**4e**)



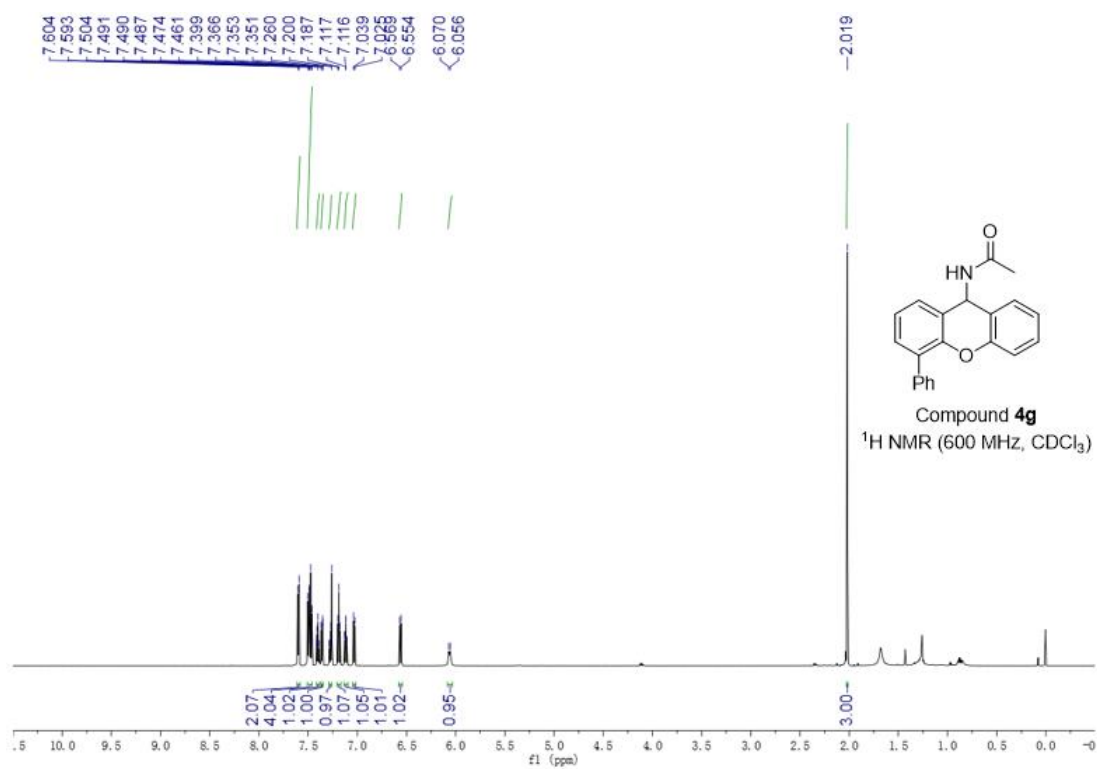


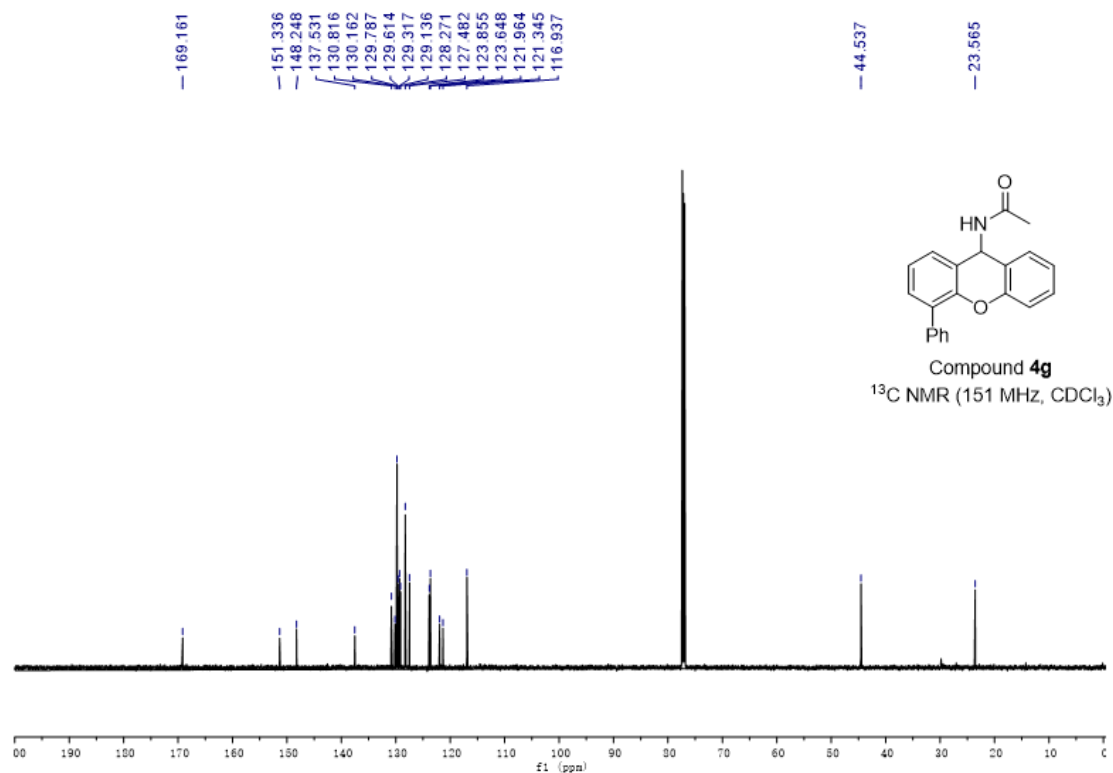
NMR spectra of 2-methyl-4-phenyl-5-(2-phenyl-9*H*-xanthen-9-yl)oxazole (**4f**)



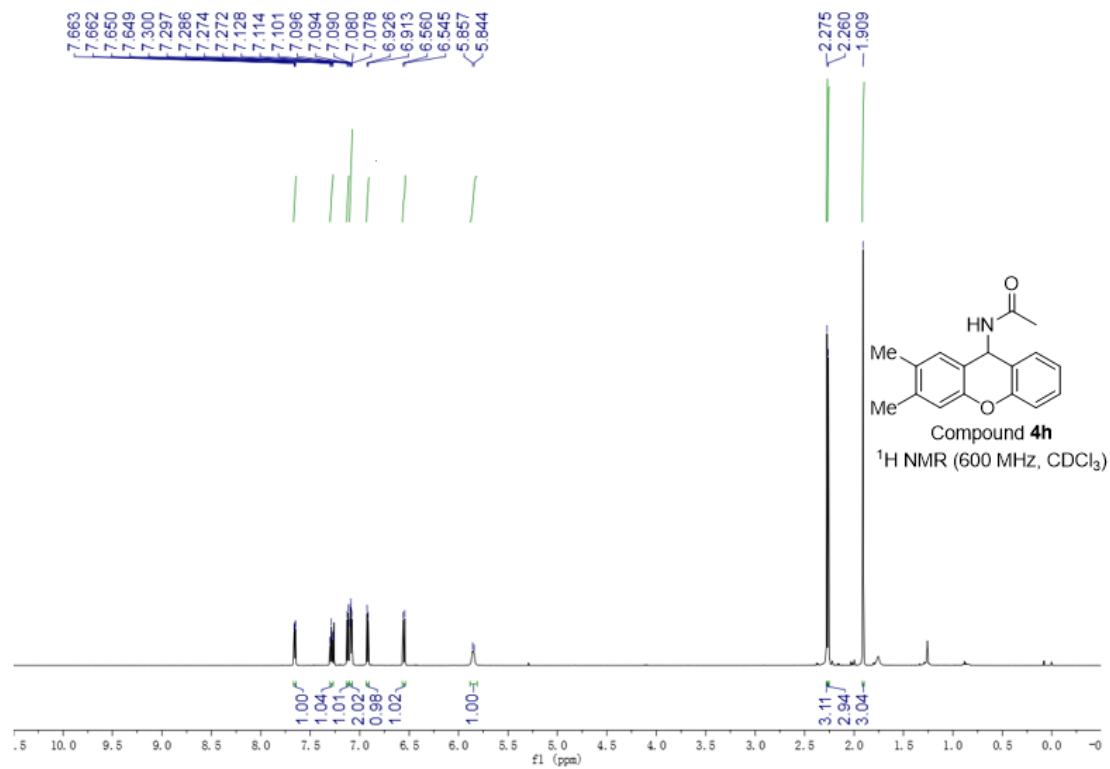


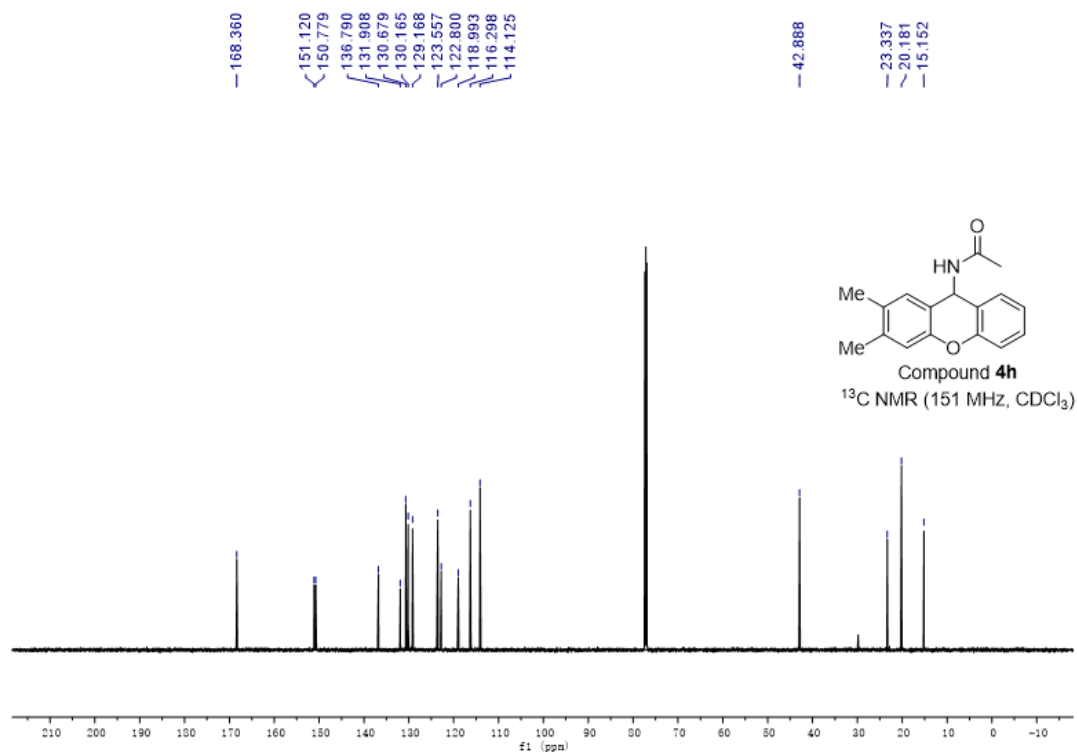
NMR spectra of *N*-(4-phenyl-9*H*-xanthen-9-yl)acetamide (**4g**)



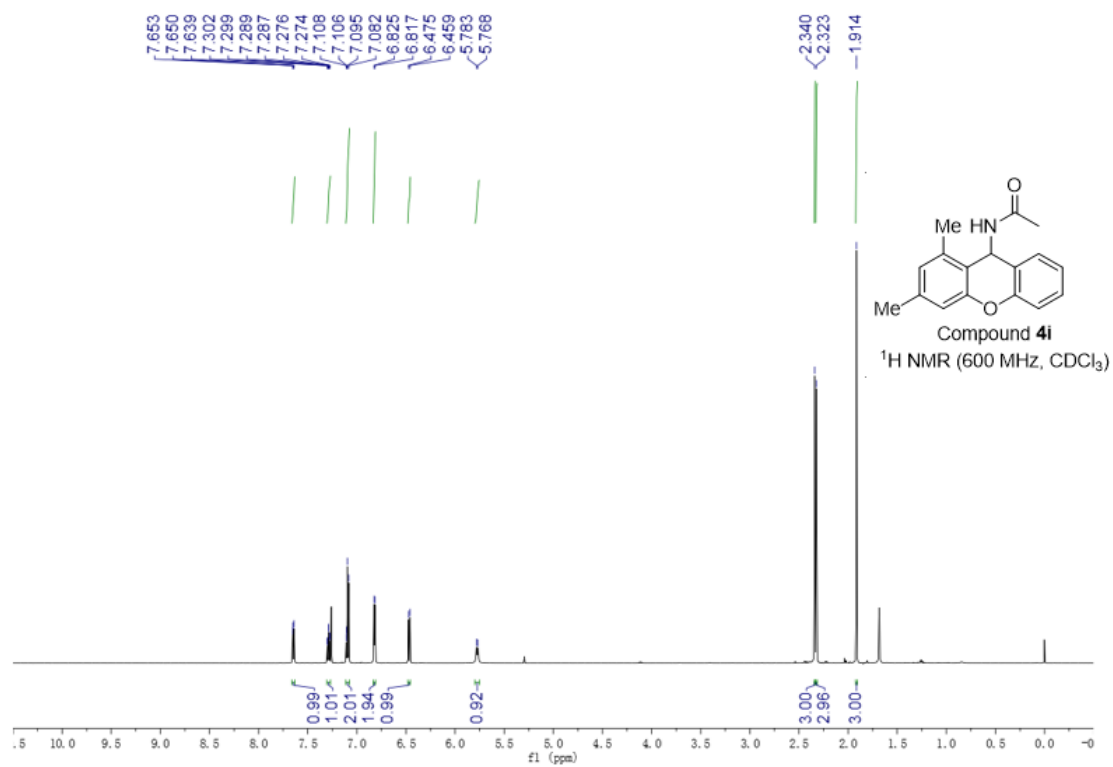


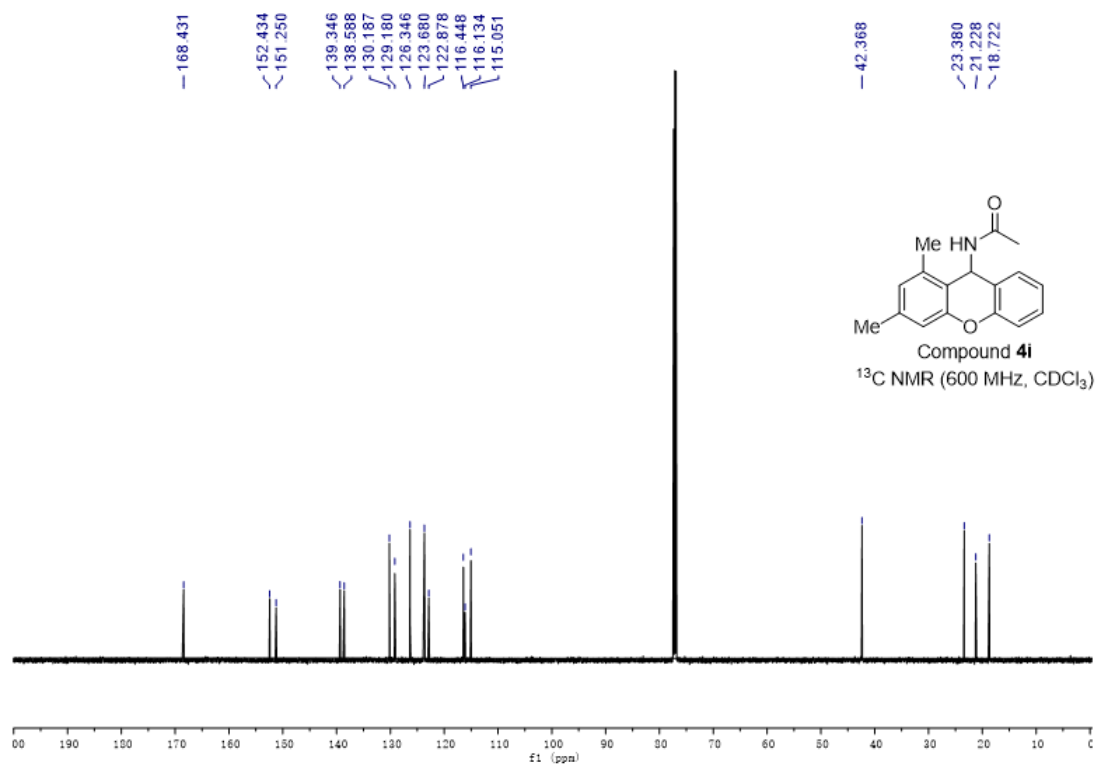
NMR spectra of *N*-(2,3-dimethyl-9,10-dihydroanthracen-9-yl)acetamide (**4h**)



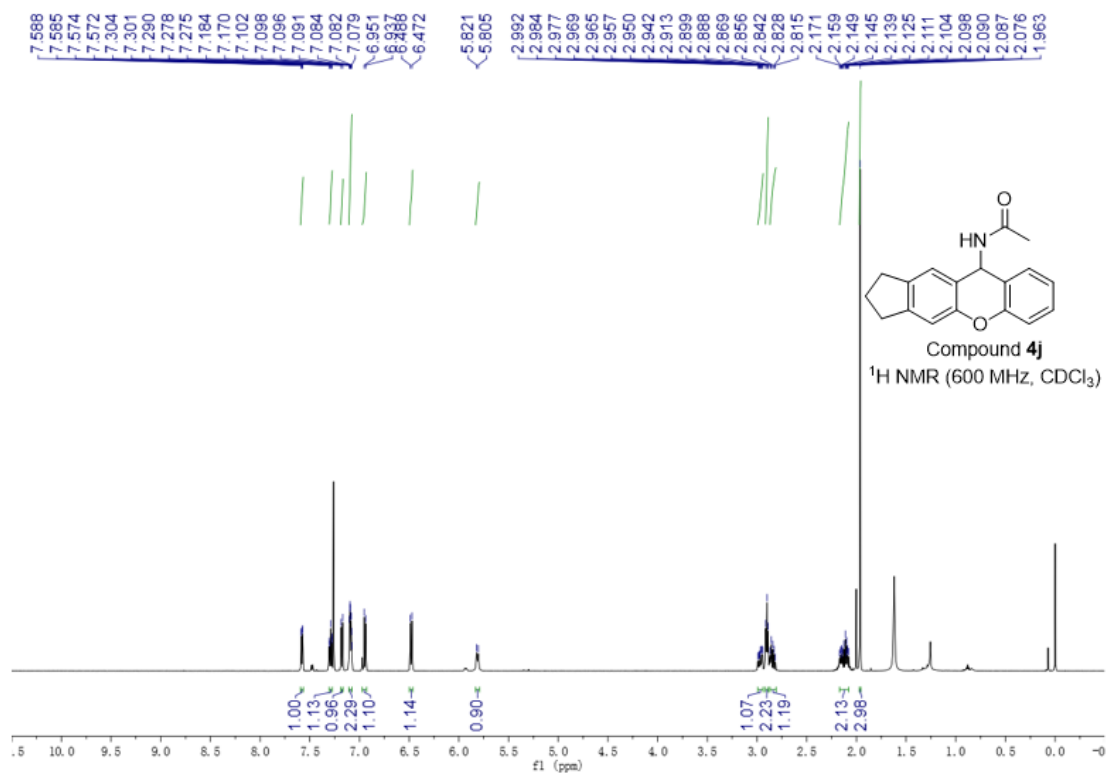


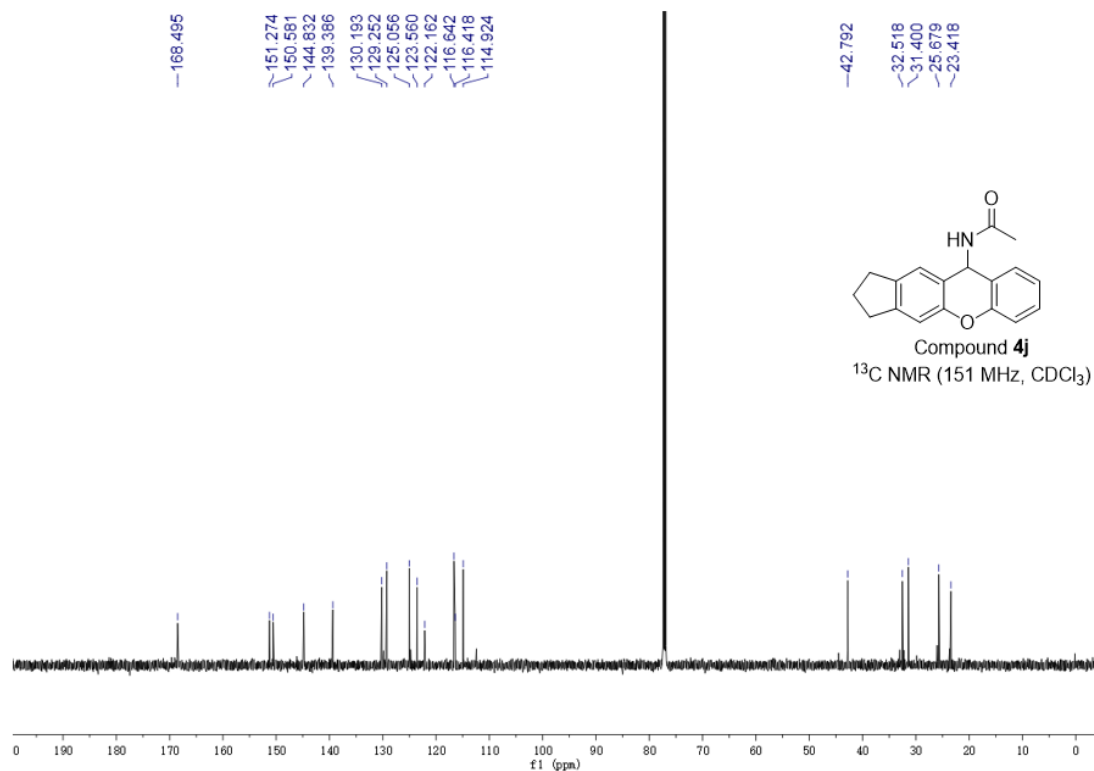
NMR spectra of *N*-(1,3-dimethyl-9,10-dihydroanthracen-9-yl)acetamide (**4i**)



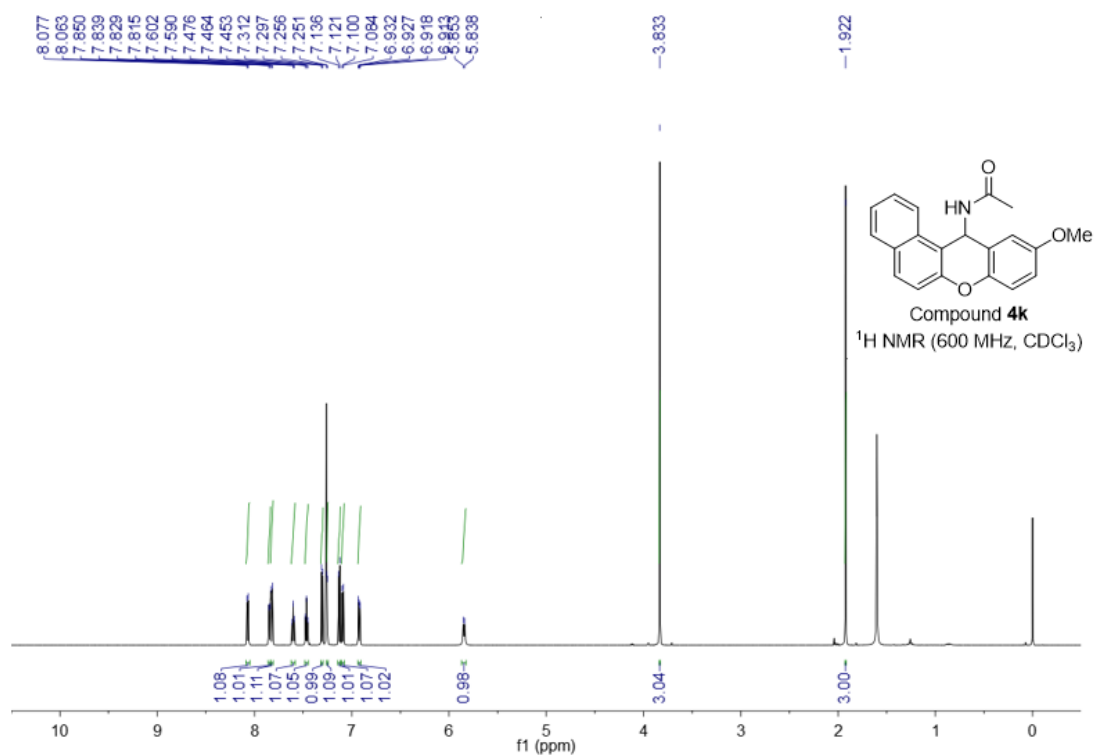


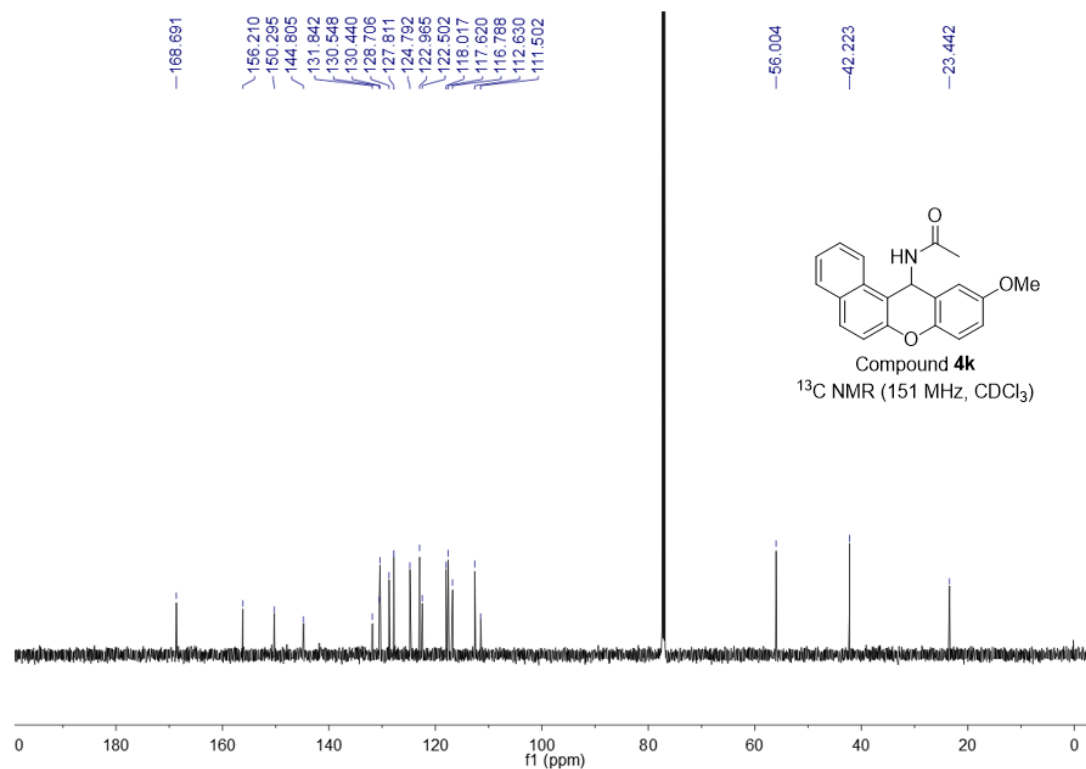
NMR spectra of *N*-(1,2,3,10-tetrahydrocyclopenta[*b*]xanthen-10-yl)acetamide (**4j**)



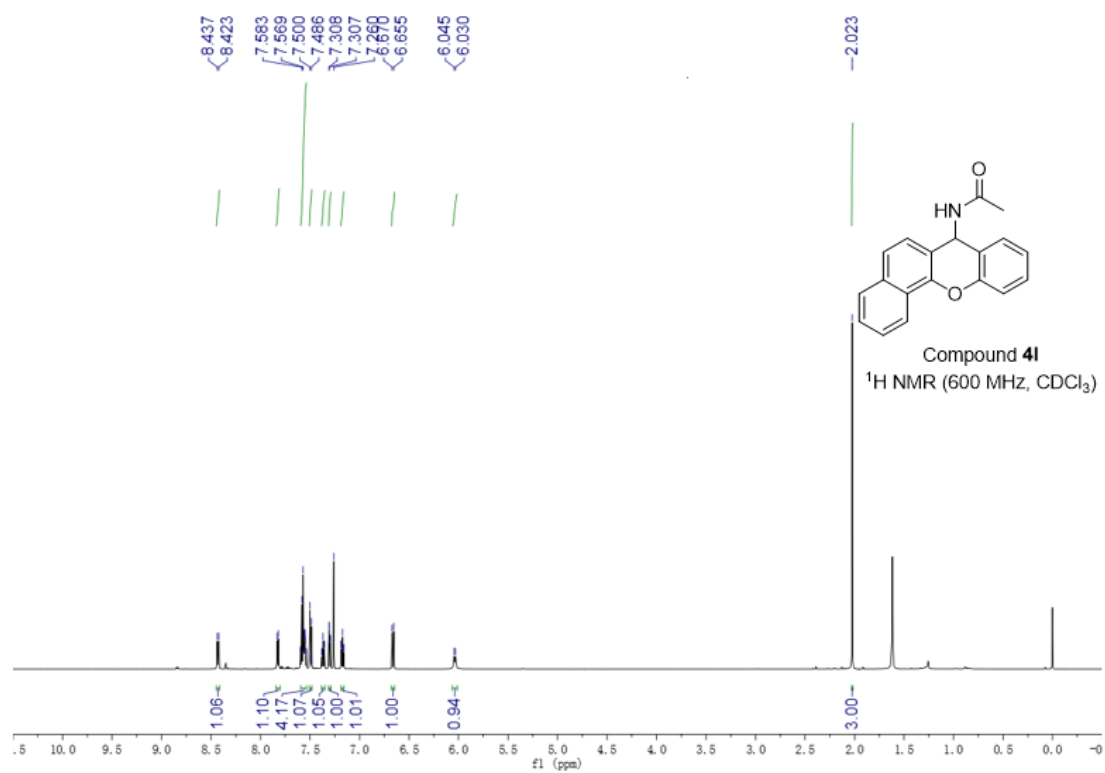


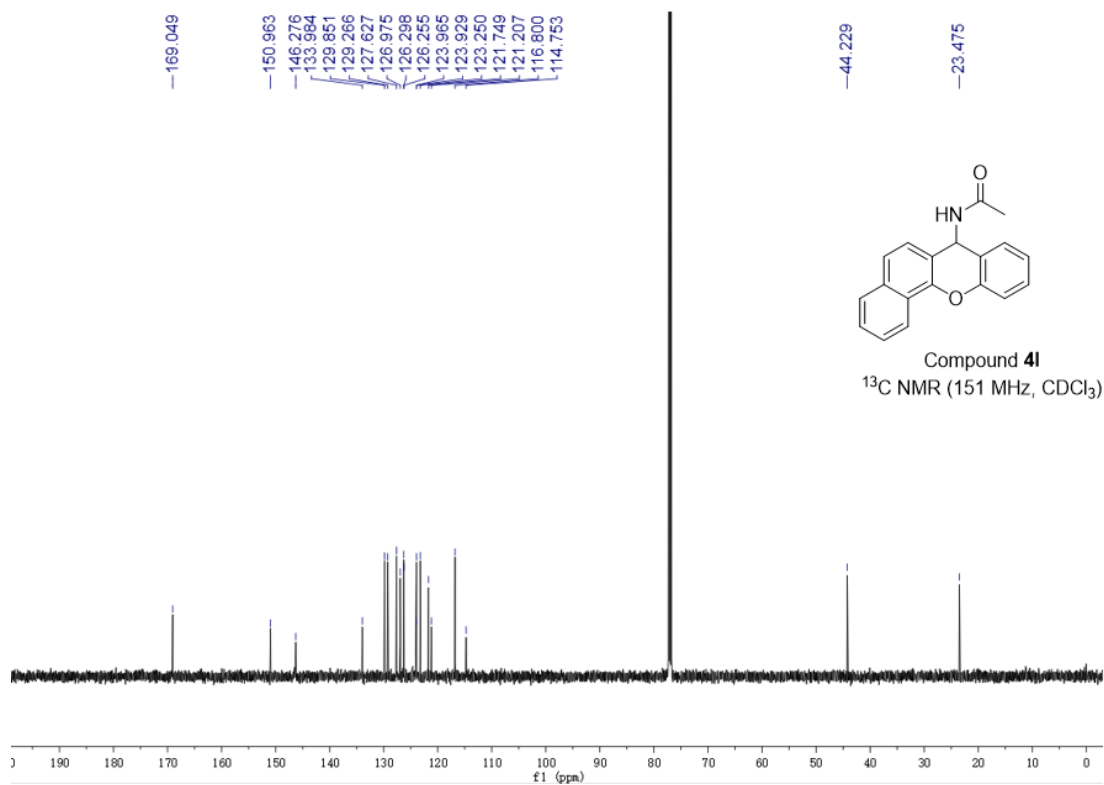
NMR spectra of *N*-(10-methoxy-12*H*-benzo[*a*]xanthen-12-yl)acetamide (**4k**)



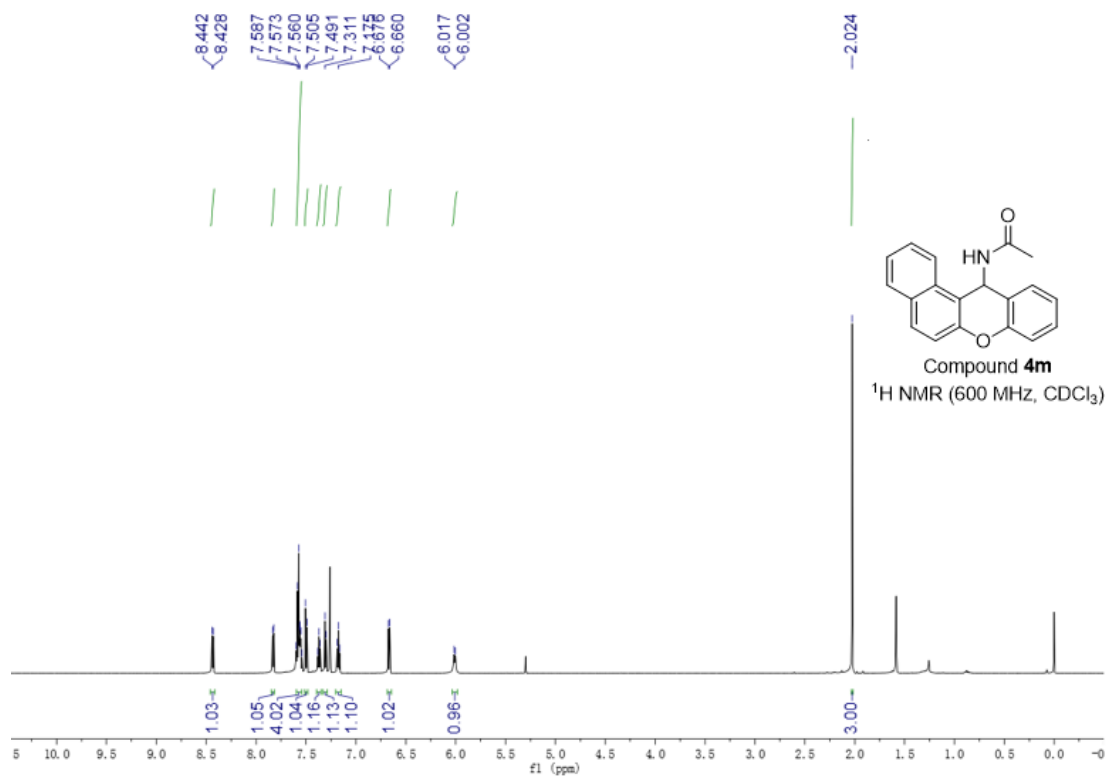


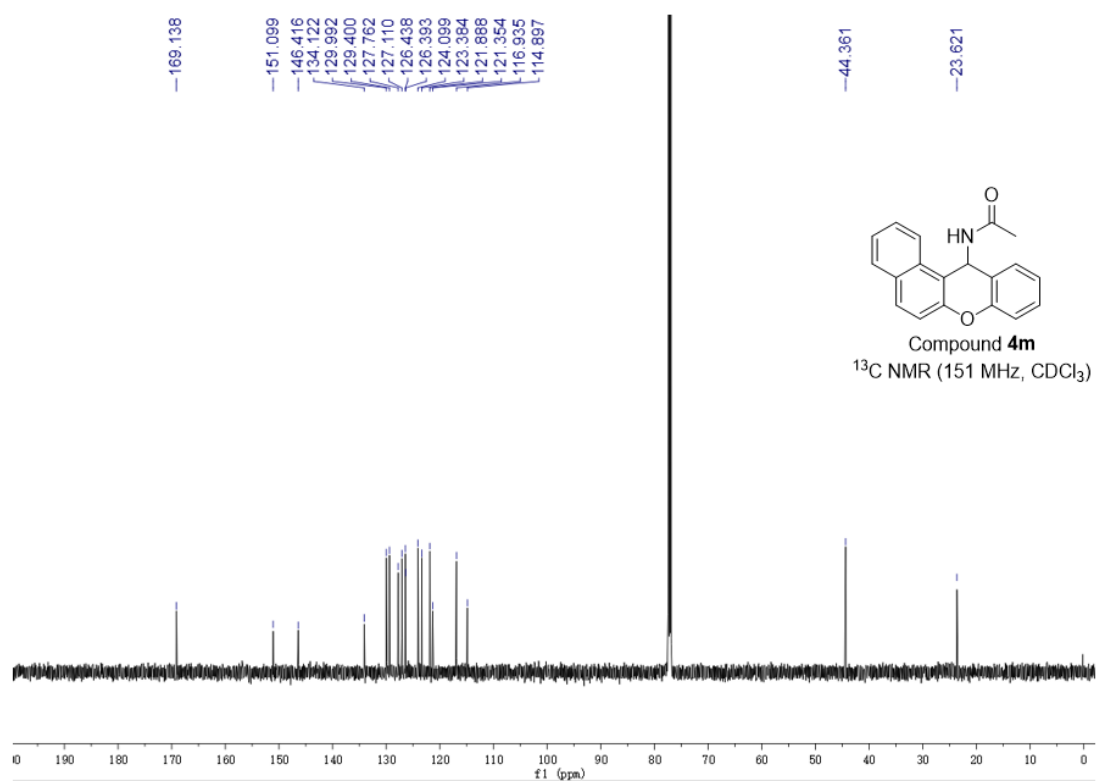
NMR spectra of *N*-(7*H*-benzo[*c*]xanthen-7-yl)acetamide (**4l**)



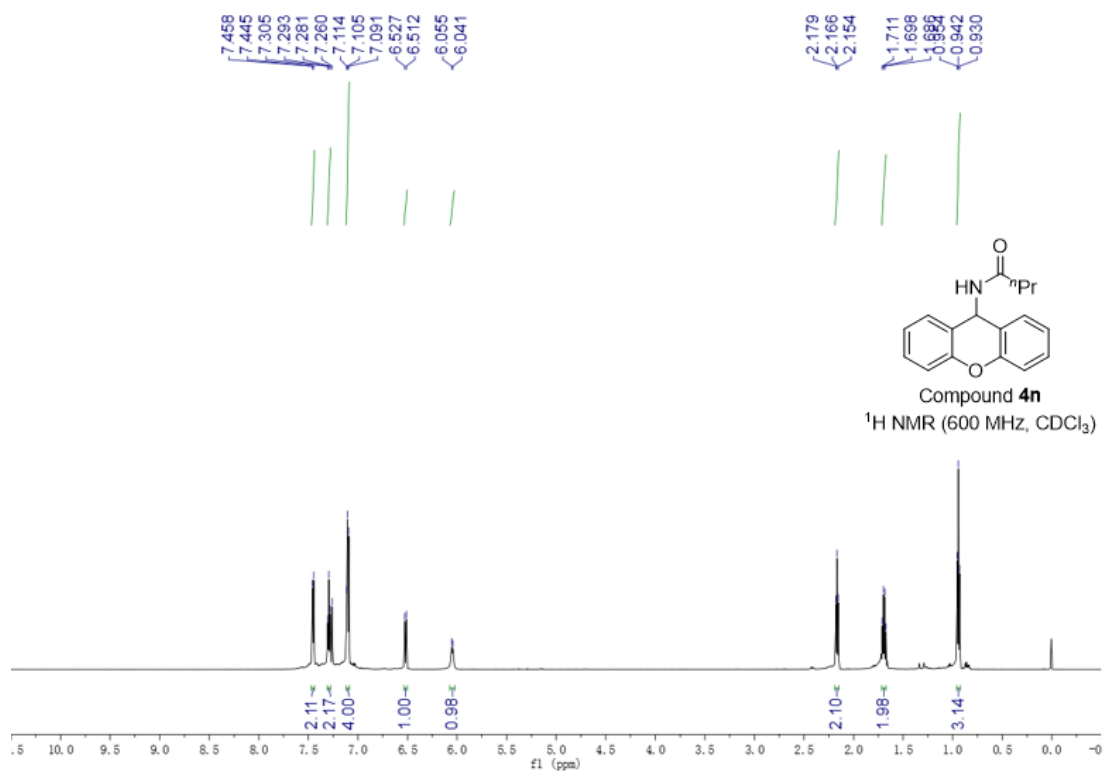


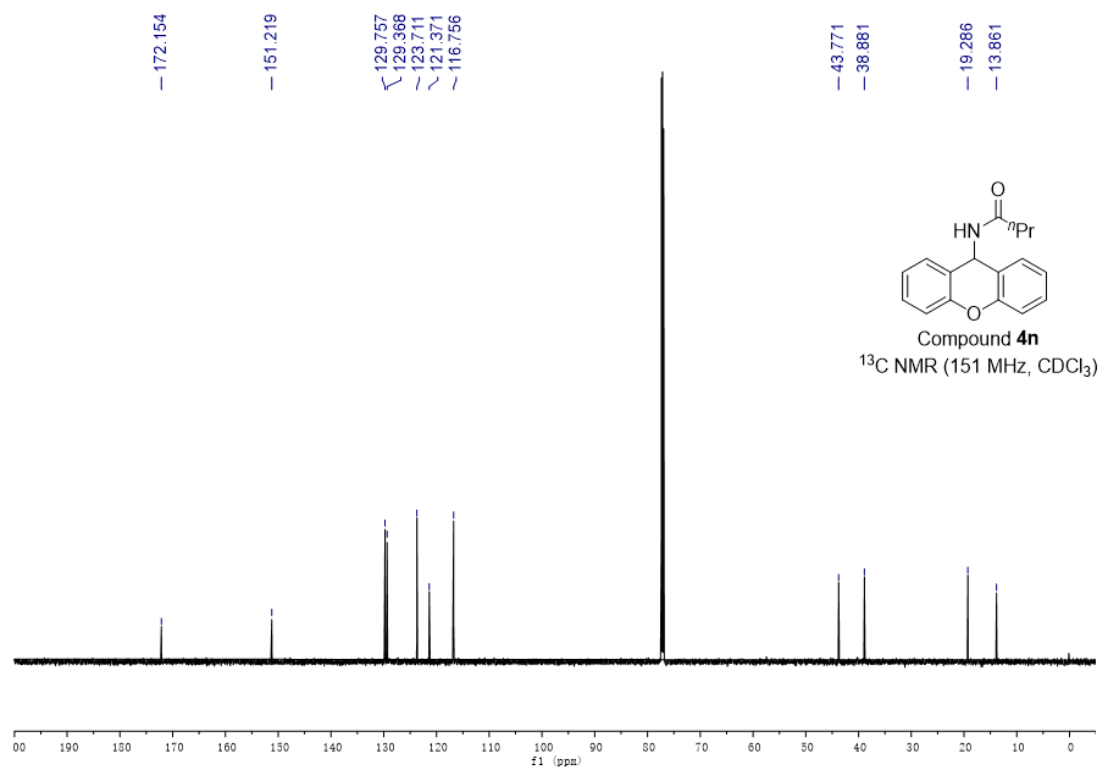
NMR spectra of *N*-(12*H*-benzo[*a*]xanthen-12-yl)acetamide (**4m**)



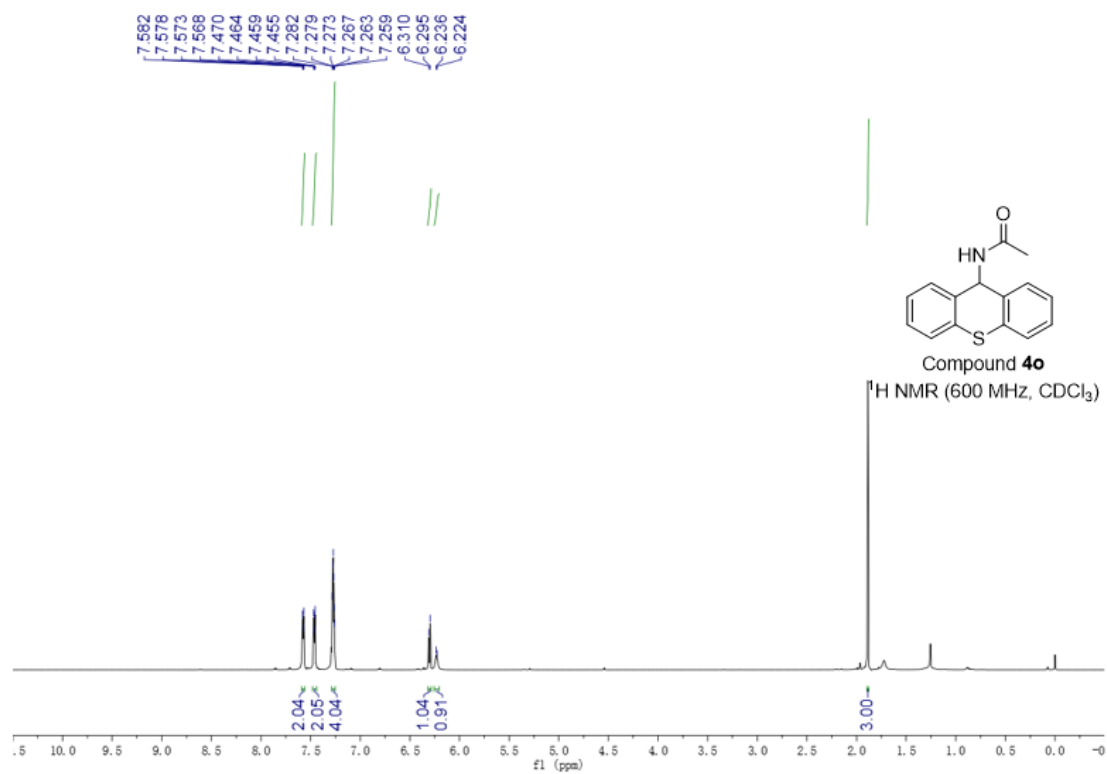


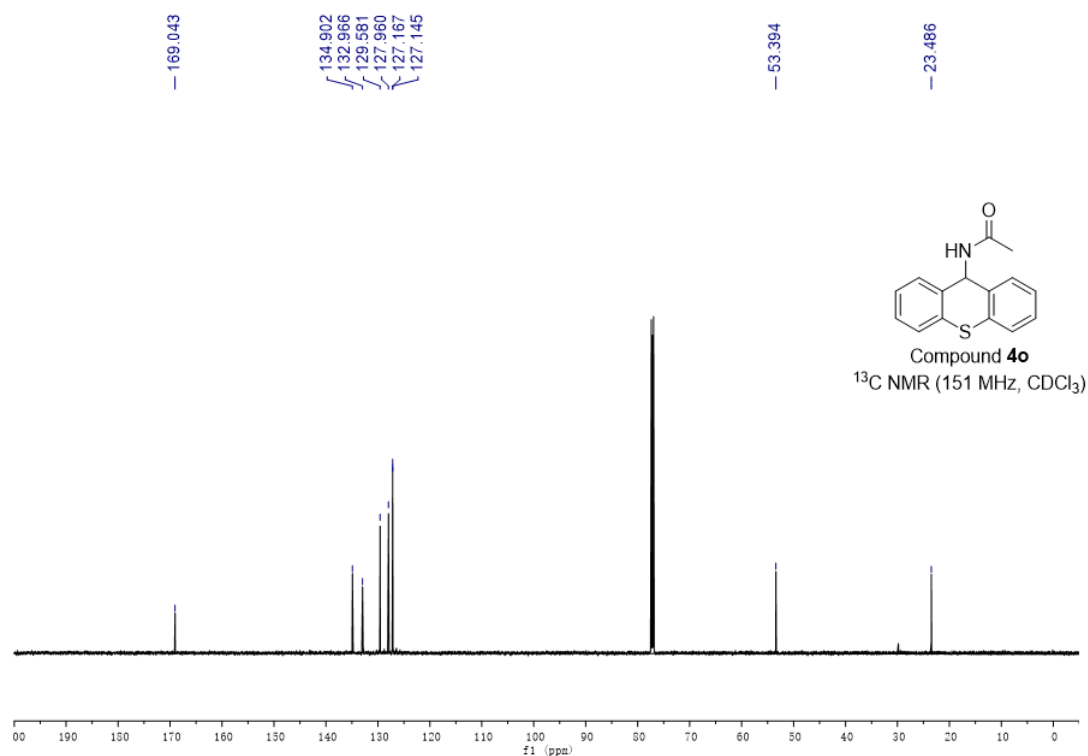
NMR spectra of *N*-(9*H*-xanthen-9-yl)butyramide (**4n**)





NMR spectra of *N*-(9*H*-thioxanthen-9-yl)acetamide (**4o**)





6. Determination of Faraday Efficiency

$$\begin{aligned}
 \text{F.E.}(\%) &= \frac{n \times F \times \text{mol of product or intermediate formed}}{\text{accumulated charge (C)}} \times 100 \% \\
 &= \frac{2 \times 96485 \text{ C mol}^{-1} \times 0.3 \text{ mmol} \times 10^{-3} \times 68 \%}{8 \text{ mA} \times 10^{-3} \times 3 \text{ h} \times 3600} \times 100 \% \\
 &= 45.6\%
 \end{aligned}$$

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.

$$\begin{aligned}
 \text{F.E.}(\%) &= \frac{n \times F \times \text{mol of product or intermediate formed}}{\text{accumulated charge (C)}} \times 100 \% \\
 &= \frac{2 \times 96485 \text{ C mol}^{-1} \times 0.3 \text{ mmol} \times 10^{-3} \times 71 \%}{8 \text{ mA} \times 10^{-3} \times 5 \text{ h} \times 3600} \times 100 \% \\
 &= 28.5\%
 \end{aligned}$$

The F.E. (%) of the product **4a** 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.