Supporting Information

Electrochemical oxidation-induced benzylic C(sp^3)–H functionalization towards atom-economic synthesis of oxazole heterocycles

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1. General Information

NMR spectra were recorded on Bruker-600 (600 MHz for ^{1}H; 151 MHz for ^{13}C). ^{1}H NMR spectra were referenced relative to internal $Si(Me)_4$ (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 ^{1}H, ^{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. using ESI-TOF (electrospray ionization-time of flight) and Aglient Technologies 7250 GCQTOF using EI-TOF. Amount of H_2O in CH_3CN was analyzed with 831 KF Coulometer (Metrohm). *n*-Bu_4NBF_4, phenylacetylene and CH_3CN were purchased from Energy Chemical Company and Taitan Chemical Company in China. Other substituted xanthenes and thioxanthenes were synthesized according to the known methods.[1-2] The commercially available CH_3CN contains about 2188.9 ppm of water that directly determined by 831 KF Coulometer.

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×10 mm×0.3 mm) and a platinum plate cathode (10 mm×10 mm×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.

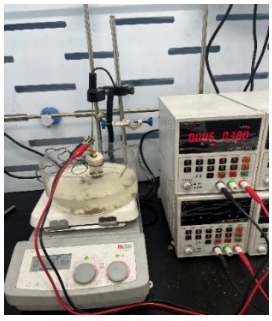
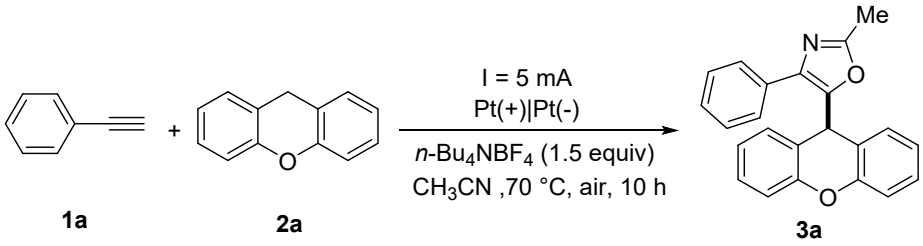


Figure S1 Experiment setup for the oxidation-induced benzylic C(sp^3)–H functionalization toward atom-economic synthesis of oxazole heterocycles

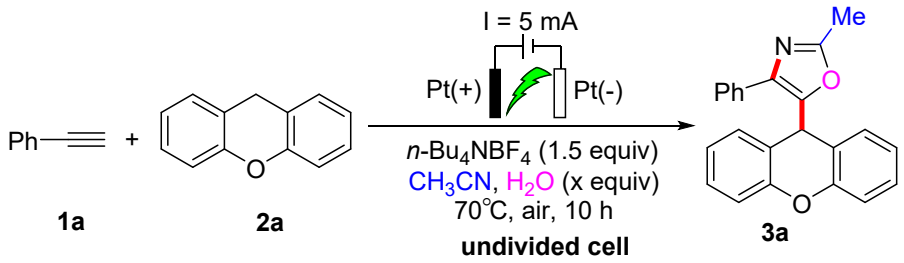
2.2 Typical Procedure for the Synthesis of 3a



To an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) fitted with a platinum anode (10 mm×10 mm×0.3 mm) and a platinum cathode (10 mm×10 mm×0.3 mm), the solid reagents xanthene (0.45 mmol) and *n*-Bu_4NBF_4 (0.45 mmol) were added. Then, the liquid reagents phenylacetylene (0.3 mmol) and CH_3CN (5 mL) were added in sequence via syringe. The electrolysis was carried out with constant current (5 mA) at 70 °C for 10 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 Effect of Water on the Electrochemical Synthesis of Oxazole 3a

Table S1. Effect of water on the synthesis of oxazole 3a [a,b]



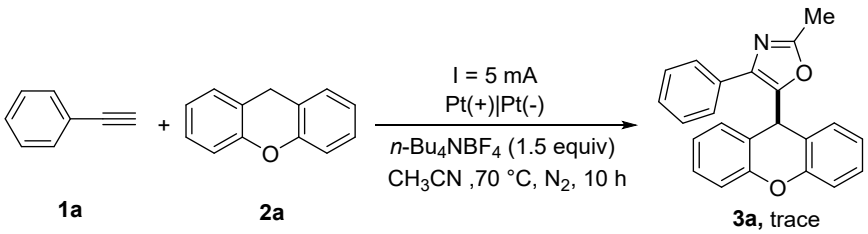
Entry	H_2O (x equiv)	Yield (%)
1	none	trace
2	1	80
3	1.6	79 [c]
4	3	82
5	4	70
6	5	54

[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.45 mmol), *n*-Bu_4NBF_4 (1.5 equiv), *anhydrous* CH_3CN (5.0 mL), H_2O (x equiv), Pt plate (1 cm × 1 cm) anode, Pt plate (1 cm × 1 cm) cathode, constant

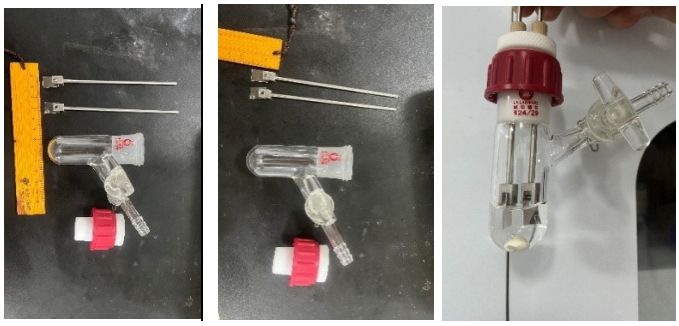
current = 5 mA, 70 °C, air, 10 h. [b] Isolated yields. [c] *Commercially available CH_3CN (Water content determined by 831 KF Coulometer: 2188.9 ppm, about 1.6 equiv. H_2O in 5 mL of CH_3CN*)

2.4 Typical Procedure for the Electrochemical Reaction Performed under N_2 Atmosphere

As experimental setup, we used a platinum plate anode (10 mm×10 mm×0.3 mm) and a platinum plate cathode (10 mm×10 mm×0.3 mm), rubber stoppers, an undivided 15 mL Electrochemical Schlenk flask (LH-618-F) (LH LABWARE), a DC adjustable power supply regulator (HY3005MT) (Made in China) and a magnetic stirrer.



To an undivided cell (15 mL columnar Electrochemical round-bottom flask with a 24# mouth) fitted with a platinum anode (10 mm×10 mm×0.3 mm) and a platinum cathode (10 mm×10 mm×0.3 mm), the solid reagents xanthene (0.45 mmol) and *n*-Bu_4NBF_4 (0.45 mmol) were added, the liquid reagents phenylacetylene (0.3 mmol) and Extra Dry CH_3CN (5 mL) were added in sequence via syringe. Then, degassing with liquid nitrogen removes water as well as oxygen from CH_3CN. The electrolysis was carried out with constant current (5 mA) at 70 °C for 10 h, and almost no product was observed therein.



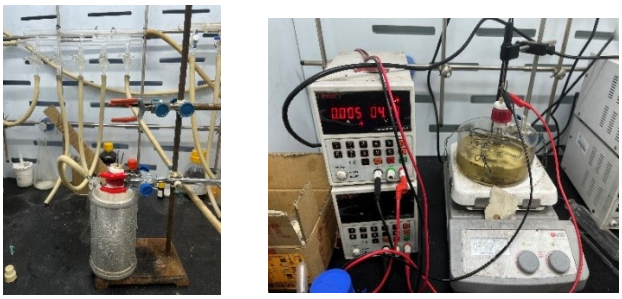
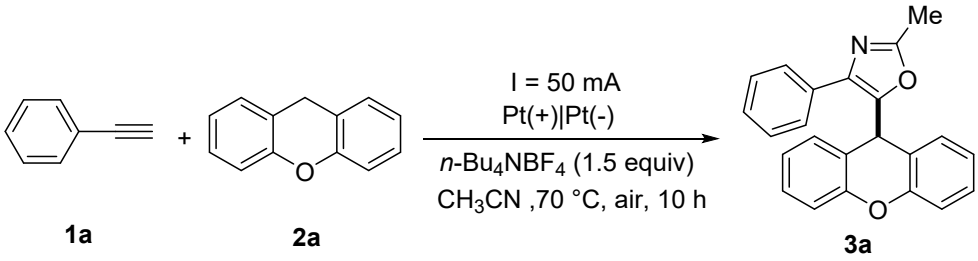


Figure S2 Experiment setup for electrochemical reaction performed under N_2.

2.5 Gram-scale Synthesis of 3a



To an 100 mL oven-dried undivided three neck bottle fitted with a platinum anode (15 mm×15 mm×0.3 mm) and a platinum cathode (15 mm×15 mm×0.3 mm), the solid reagents xanthene (819.3 mg, 4.5 mmol,1.5 equiv) and *n*-Bu_4NBF_4 (1.48g, 4.5 mmol, 1.5 equiv) were added. Then, the liquid reagents phenylacetylene (306.2 mg, 3 mmol) and CH_3CN (50 mL) were added in sequence via syringe. The electrolysis was carried out with constant current (50 mA) at 70 °C for 10 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** (579.9 mg, 57% yield).

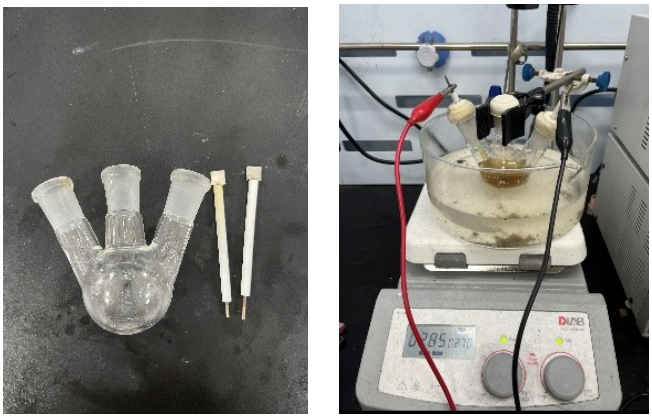


Figure S3 Experiment setup for the gram-scale synthesis of **3a**.

3. Mechanistic Experiments

3.1 Cyclic Voltammetry Studies

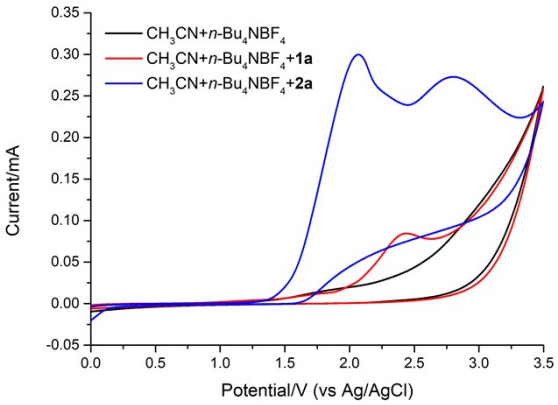
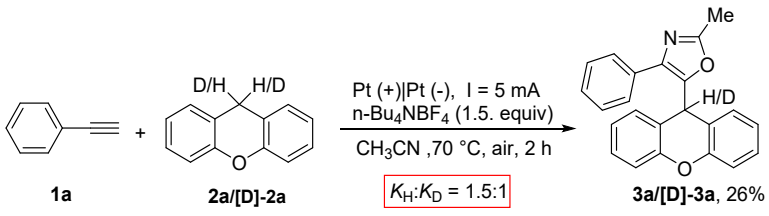


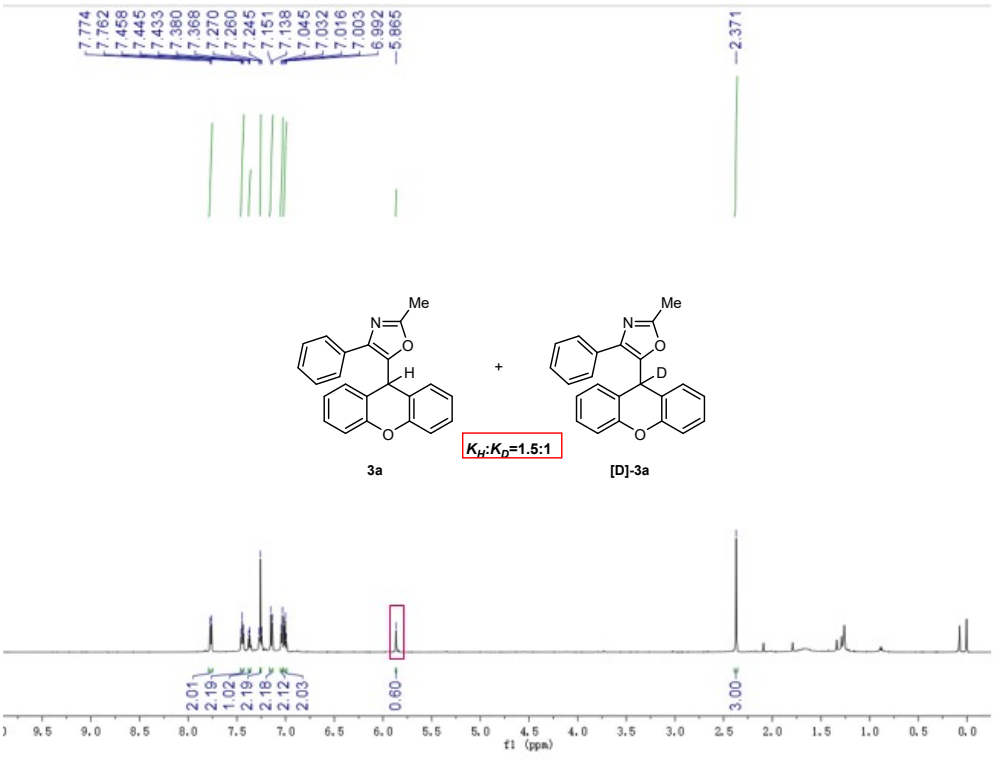
Figure S4 The cyclic voltammograms recorded in CH_3CN with 0.1 M *n*-Bu_4NBF_4 as the supporting electrolyte [**1a** (10 mM), **2a** (10 mM)].

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. 10 mL of CH_3CN containing 0.1 M *n*-Bu_4NBF_4 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



Phenylacetylene (**1a**, 30.6 mg, 0.3 mmol, 1.0 equiv), xanthene (**2a**, 41.0 mg, 0.225 mmol), [D]-xanthene (**[D]-2a**, 41.5 mg, 0.225 mmol), *n*-Bu_4NBF_4 (148.2 mg, 0.45 mmol, 1.5 equiv), CH_3CN (5 mL) was sequentially added to an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) fitted with a platinum anode (10 mm×10 mm×0.3 mm) and a platinum cathode (10 mm×10 mm×0.3 mm). The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under air at 70 ℃ for 2 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 26% yield.



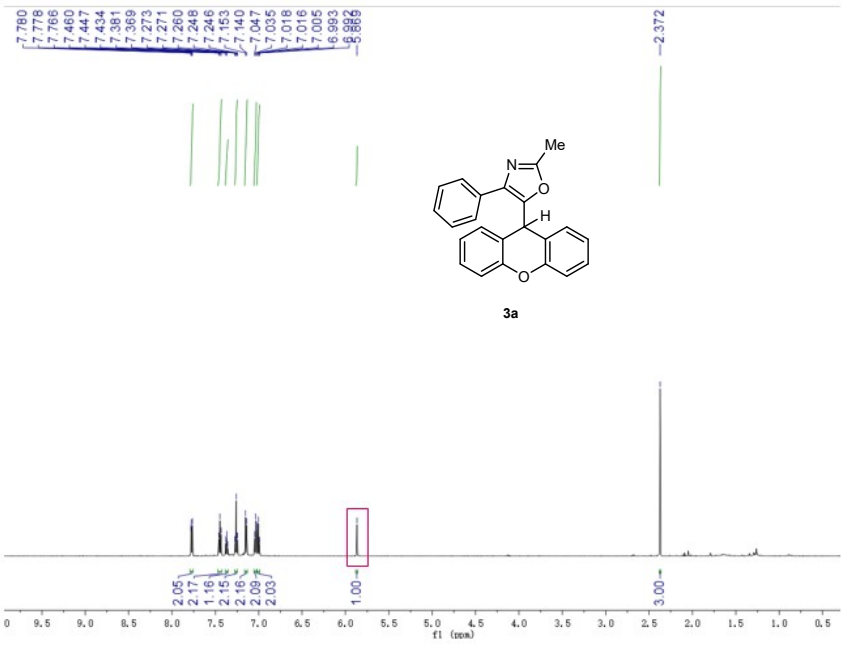
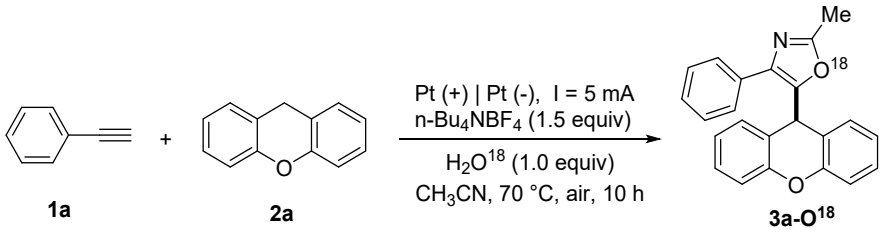


Figure S5 NMR spectra of **3a/[D]-3a**

3.3 Isotope-labeling Experiment



Phenylacetylene (**1a**, 30.6 mg, 0.3 mmol, 1.0 equiv), xanthene (**2a**, 82.0 mg, 4.5 mmol, 1.5 equiv), *n*-Bu_4NBF_4 (148.0 mg, 0.3 mmol, 1.5 equiv), CH_3CN (5 mL), H_2O^{18} (6.0 mg, 0.3 mmol, 1.0 equiv) was sequentially added to an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) fitted with a platinum anode (10 mm×10 mm×0.3 mm) and a platinum cathode (10 mm×10 mm×0.3 mm). The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under air at 70 ℃ for 10 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-O^{18}**, which could be detected by HRMS (data of $[M+H]^+$ are showed).

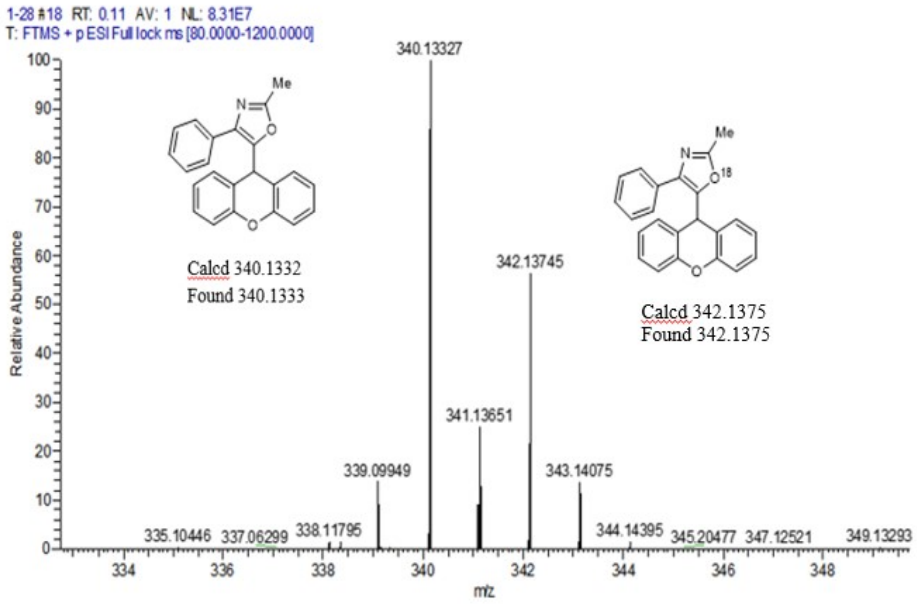
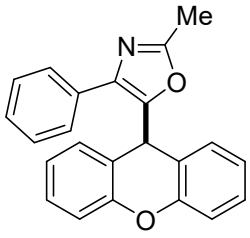


Figure S6 HRMS Analysis Reports for **3a/** [O^{18}]-**3a**

4. Characterization Data for the Products



3a

2-Methyl-4-phenyl-5-(9*H*-xanthen-9-yl)oxazole (3a)

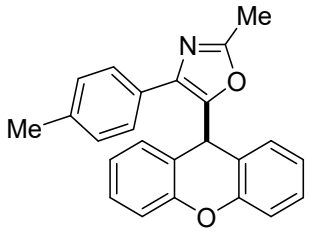
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA=20:1) to afford the product **3a** (80.3 mg, 79% yield).

White solid; m.p.: 165~166 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.76 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.27–7.24 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.02–6.99 (m, 2H), 5.87 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.2, 147.3, 137.0, 131.7, 128.9, 128.7, 128.6, 128.1, 127.1, 123.3, 120.3, 116.9, 34.9, 14.0.

HRMS (ESI) calcd. for $C_{23}H_{18}NO_2^+$ ([M+H]$^+$): 340.1332, found: 340.1333.



3b

2-Methyl-4-(*p*-tolyl)-5-(9*H*-xanthen-9-yl)oxazole (3b)

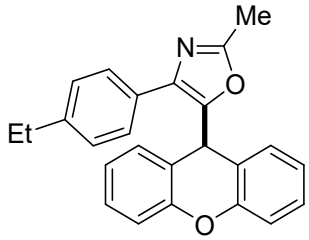
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA=20:1) to afford the product **3b** (77.3 mg, 73% yield).

White solid; m.p.: 163~164 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.26–7.24 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.01–7.00 (m, 2H), 5.86 (s, 1H), 2.40 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 151.2, 146.9, 137.9, 137.0, 129.5, 128.8, 128.7, 128.6, 126.9, 123.3, 120.4, 116.9, 34.9, 21.3, 14.1

HRMS (ESI) calcd. for $C_{24}H_{20}NO_2^+$ ([M+H]$^+$): 354.1489, found 354.1488.



3c

4-(4-Ethylphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3c)

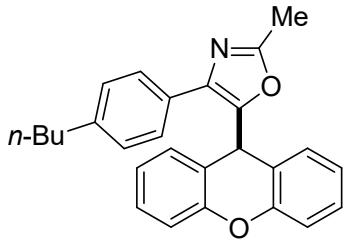
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3c** (78.1 mg, 71% yield).

White solid; m.p.: 169~170 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.29–7.24 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.02–6.99 (m, 2H), 5.87 (s, 1H), 2.72–2.68 (q, *J* = 7.8 Hz ,2H), 2.36 (s, 3H) , 1.27 (t, *J* = 7.8 Hz, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 151.2, 145.8, 143.2, 136.1, 128.0, 127.7, 127.5, 127.3, 126.0, 122.2, 119.4, 115.8, 33.9, 27.6, 14.5, 13.0.

HRMS (ESI) calcd. for $C_{25}H_{22}NO_2^+$ ([M+H]$^+$): 368.1645, found: 368.1649.



3d

4-(4-Butylphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3d)

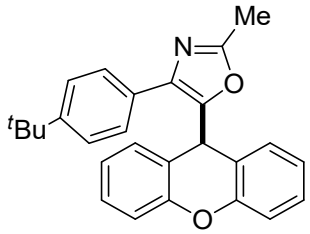
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3d** (88.9 mg, 75% yield).

White solid; m.p.: 173~174 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.27–7.24 (m, 4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 7.01–6.99 (m, 2H), 5.87 (s, 1H), 2.67–2.64 (m, 2H), 2.36 (s, 3H), 1.65–1.62(m, 2H), 1.40–1.36 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.3, 146.9, 143.0, 137.2, 129.1, 129.0, 128.8, 128.7, 127.0, 123.4, 120.5, 117.0, 35.5, 35.0, 33.6, 22.4, 14.1, 14.1.

HRMS (ESI) calcd. for $C_{27}H_{26}NO_2^+$ ([M+H]$^+$): 396.1958, found: 396.1960.



3e

4-(4-(*tert*-Butyl)phenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3e)

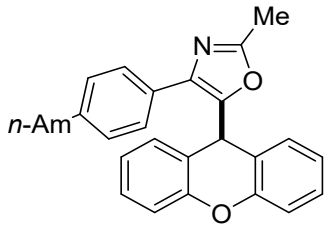
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3e** (90.1 mg, 76% yield).

White solid; m.p.: 153~154 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.26–7.24 (m, 2H), 7.15 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.02–6.99 (m, 2H), 5.88 (s, 1H), 2.36 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.4, 151.2, 146.9, 137.2, 128.9, 128.8, 128.7, 126.8, 125.9, 123.4, 120.6, 117.0, 35.0, 34.8, 31.4, 14.2.

HRMS (ESI) calcd. for $C_{27}H_{26}NO_2^+$ ([M+H]$^+$): 396.1958, found: 396.1961.



3f

2-Methyl-4-(4-pentylphenyl)-5-(9*H*-xanthen-9-yl)oxazole (3f)

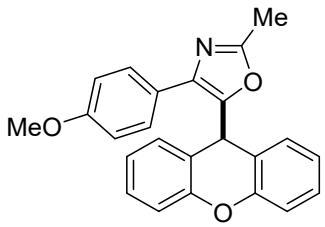
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3f** (88.9 mg, 75% yield).

White solid; m.p.: 179~180 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.27–7.23 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.02–6.98 (m, 2H), 5.86 (s, 1H), 2.64. (t, *J* = 7.8 Hz, 2H) , 2.36 (s, 3H), 1.67–1.62 (m, 2H)， 1.37–1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.4, 146.9, 143.1, 137.3, 129.1, 129.0, 128.8, 128.7, 127.1, 123.4, 120.6, 117.0, 35.8, 35.0, 31.6, 31.12, 22.7, 14.2, 14.2.

HRMS (ESI) calcd. for $C_{28}H_{28}NO_2^+$ ([M+H]$^+$): 410.2114, found: 410.2116.



3g

4-(4-Methoxyphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3g)

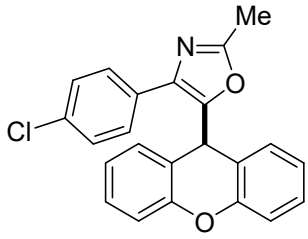
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 10:1) to afford the product **3g** (88.4 mg, 80% yield).

White solid; m.p.: 160~161 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.27–7.22 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 7.01–6.98 (m, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 1H), 3.96 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 159.6, 151.4, 146.6, 136.9, 128.8, 128.7, 128.5, 124.4, 123.4, 120.6, 117.0, 114.4, 55.5, 35.0, 14.2.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_3^+$ ([M+H]$^+$): 370.1438, found 370.1439.



3h

4-(4-Chlorophenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3h)

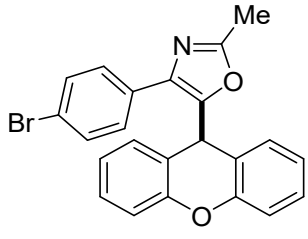
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3h** (48.1 mg, 43% yield).

White solid; m.p.: 154~155 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.27–7.24 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* =4.2 Hz, 4H), 5.81 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 151.3, 147.8, 136.0, 134.0, 130.3, 129.1, 128.9, 128.7, 128.5, 123.5, 120.2, 117.1, 35.2, 14.1.

HRMS (ESI) calcd. for $C_{23}H_{17}ClNO_2^+$ ([M+H]$^+$): 374.0942, found: 374.0944.



3i

4-(4-Bromophenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3i)

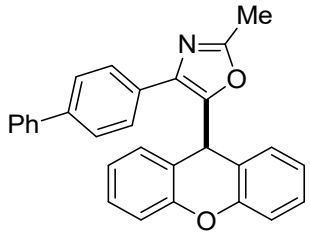
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3i** (62.6 mg, 50% yield).

White solid; m.p.: 158~159 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.28–7.24 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 4.2 Hz, 4H), 5.81 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 151.3, 147.8, 136.0, 134.0, 130.3, 129.1, 128.9, 128.7, 128.5, 123.5, 120.2, 117.1, 35.2, 14.1.

HRMS (ESI) calcd. for $C_{23}H_{17}BrNO_2^+$ ([M+H]$^+$): 418.0437, found: 418.0437.



3j

4-([1,1'-Biphenyl]-4-yl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3j)

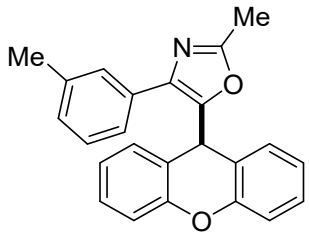
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3j** (81.0 mg, 65% yield).

White solid; m.p.: 170~171 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7. 47–7.44 (m, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.28–7.26 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 7.02–7.00 (m, 2H), 5.92 (s, 1H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ161.0, 151.2, 147.4, 140.8, 140.6, 136.6, 130.7, 128.8, 128.7, 128.7, 127.5, 127.4, 127.0, 123.3, 120.3, 116.9, 35.0, 14.1.

HRMS (ESI) calcd. for $C_{29}H_{22}NO_2^+$ ([M+H]$^+$): 416.1645, found: 416.1645.



3k

2-Methyl-4-(*m*-tolyl)-5-(9*H*-xanthen-9-yl)oxazole (3k)

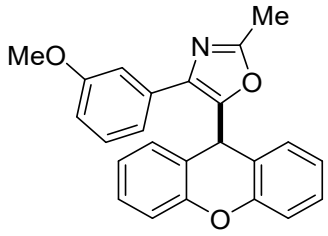
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3k** (72.0 mg, 68% yield).

White solid; m.p.: 143~144 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.27–7.24 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 7.8, 0.6 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.02–6.99 (m, 2H), 5.88 (s, 1H), 2.41 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.3, 147.4, 138.7, 137.2, 131.7, 129.0, 128.8, 128.8, 128.7, 128.0, 124.1, 123.4, 120.5, 117.0, 35.0, 21.6, 14.2.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_2^+$ ($[M+H]^+$): 354.1488, found: 354.1488.



3l

4-(3-Methoxyphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3l)

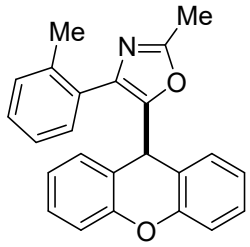
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 10:1) to afford the product **3l** (79.7 mg, 72% yield).

White solid; m.p.: 149~151 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36–7.34 (m, 2H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.27–7.24 (m, 2H), 7.14 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.04 (d, *J* = 6.6 Hz, 2H), 7.01–6.99 (m, 2H), 6.93–6.90 (m, 1H), 5.88 (s, 1H), 3.84 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 156.8, 151.3, 149.2, 133.4, 131.7, 129.7, 129.3, 128.5, 123.2, 121.1, 121.0, 120.9, 116.8, 111.1, 55.4, 35.0, 14.3.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_3^+$ ([M+H]$^+$): 370.1438, found: 370.1438.



3m

2-Methyl-4-(*o*-tolyl)-5-(9*H*-xanthen-9-yl)oxazole (3m)

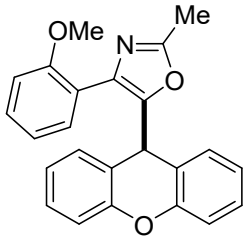
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3m** (66.7 mg, 63% yield).

White solid; m.p.: 142~143 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, J = 7.2, 4.2 Hz, 2H), 7.28 (d, J = 1.2 Hz, 1H), 7.25–7.22 (m, 2H), 7.21–7.18 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 6.0 Hz, 2H), 7.03–7.00 (m, 2H), 5.40 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 151.6, 148.7, 138.1, 136.9, 131.0, 130.6, 130.2, 128.8, 128.6, 125.8, 123.4, 120.8, 117.0, 34.8, 20.4, 14.3.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_2^+$ ([M+H]$^+$): 354.1489, found: 354.1489



3n

4-(2-Methoxyphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3n)

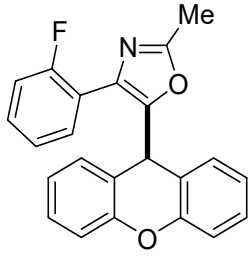
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3n** (74.2 mg, 67% yield).

White solid; m.p.: 163~164 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.37–7.34 (m, 1H), 7.24–7.21 (m, 2H), 7.11–7.09 (m, 3H), 7.08–7.05 (m, 2H), 7.00–6.96 (m, 3H), 5.66 (s, 1H), 3.81 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 156.7, 151.3, 149.2, 133.4, 131.6, 129.7, 129.2, 128.4, 123.2, 121.1, 121.0, 120.8, 116.7, 111.1, 55.4, 35.0, 14.2.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_3^+$ ($[M+H]^+$): 370.1438, found: 370.1438.



3o

4-(2-Fluorophenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (3o)

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3o** (51.4 mg, 48% yield).

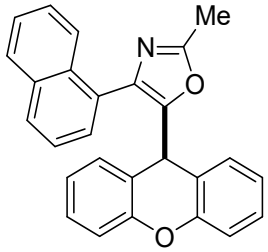
White solid; m.p.: 137~138 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.45–7.40 (m, 1H), 7.29–7.27 (m, 1H), 7.17–7.16 (m, 2H), 7.07 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.03 (d, *J* = 6.6 Hz, 2H), 7.02–7.01 (m, 2H), 5.87 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 151.4, 147.4, 137.1, 131.8, 130.5, 129.0, 128.8, 128.8, 128.2, 127.2, 123.4, 120.4, 117.0, 116.5, 35.0, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ –112.4.

HRMS (ESI) calcd. for $C_{23}H_{17}FNO_2^+$ ([M+H]$^+$): 358.1238, found: 358.1238.



3p

2-Methyl-4-(naphthalen-1-yl)-5-(9*H*-xanthen-9-yl)oxazole (3p)

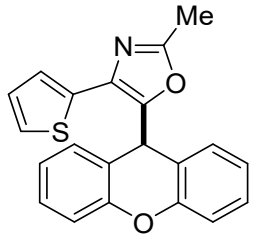
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3p** (77.2 mg, 66% yield).

White solid; m.p.: 181~182 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05–8.02 (m, 1H), 7.93–7.90 (m, 2H), 7.59 (d, *J* = 6.6, 0.6 Hz, 1H), 7.55–7.52 (m, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.23–7.19 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.00–6.96 (m, 2H), 5.47 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ160.8, 151.4, 149.8, 135.8, 133.9, 132.6, 129.2, 128.9, 128.8, 128.5, 128.3, 127.8, 126.6, 126.1, 125.9, 125.2, 123.3, 120. 4, 116.8, 34. 8, 14.2.

HRMS (ESI) calcd. for $C_{27}H_{20}NO_2^+$ ([M+H]$^+$): 390.1489, found: 390.1487.



3q

2-Methyl-4-(thiophen-2-yl)-5-(9*H*-xanthen-9-yl)oxazole (3q)

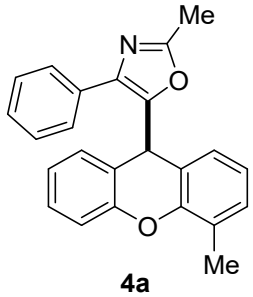
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **3q** (63.2 mg, 61% yield).

White solid; m.p.: 140~141 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.48 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.42–7.40 (m, 1H), 7.27–7.24 (m, 2H), 7.15 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.01–6.99 (m, 2H), 5.86 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.3, 147.1, 133.0, 132.8, 128.9, 128.8, 126.6, 126.3, 123.4, 122.2, 120.2, 117.0, 35.1, 14.1.

HRMS (ESI) calcd. for $C_{21}H_{16}NO_2S^+$ ($[M+H]^+$): 346.0896, found 346.0897.



4a

2-Methyl-5-(4-methyl-9*H*-xanthen-9-yl)-4-phenyloxazole (4a)

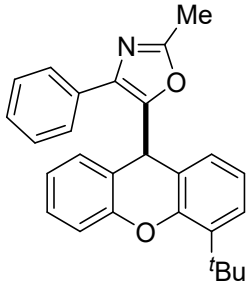
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4a** (72.0 mg, 68% yield).

White solid; m.p.: 157~158°C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.11 (d, J = 7.1 Hz, 1H), 7.07–6.99 (m, 3H), 6.90–6.86 (m, 2H), 5.85 (s, 1H), 2.43 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 151.5, 149.6, 147.6, 137.0, 131.9, 130.0, 128.0, 128.7, 128.6, 128.2, 127.3, 127.3, 126.2, 123.3, 122.8, 120.6, 120.0, 117.1, 35.2, 16.2, 14.2.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_2^+$ ([M+H]$^+$): 354.1489, found: 354.1489.



4b

5-(4-(*tert*-Butyl)-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazol (4b)

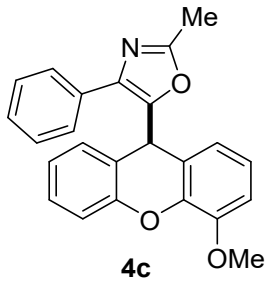
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4b** (77.1 mg, 65% yield).

White solid; m.p.: 149~150 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.26–7.23 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.08–7.05 (m, 2H), 7.01–6.98 (m, 2H), 5.83 (s, 1H), 2.39 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.6, 149.2, 147.8, 146.3, 136.9, 131.9, 128.91, 128.9, 128.7, 128.1, 127.3, 125.9, 125.2, 123.2, 120.5, 119.6, 117.0, 116.4, 35.4, 34.3, 31.5, 14.1.

HRMS (ESI) calcd. for $C_{27}H_{26}NO_2^+$ ([M+H]$^+$): 396.1958, found: 396.1961.



4c

5-(4-Methoxy-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazol (4c)

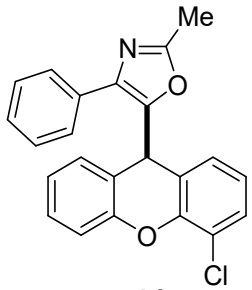
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4c** (79.7 mg, 72% yield).

White solid; m.p.: 151~152 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.27–7.23 (m, 2H), 7.03–6.98 (m, 2H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 1H), 3.96 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 151.2, 148.3, 147.5, 141.2, 136.9, 131.9, 129.0, 128.7, 128.2, 127.2, 123.6, 123.0, 121.3, 120.3, 120.3, 117.3, 110.9, 56.4, 35.09, 14.2.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_3^+$ ($[M+H]^+$): 370.1438, found 370.1437.



4d

5-(4-Chloro-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazole (4d)

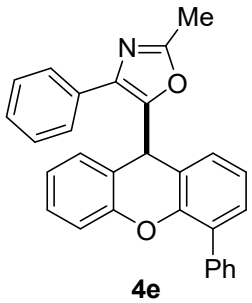
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4d** (63.8 mg, 57% yield).

White solid; m.p.: 142~143 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.02–6.99 (m, 3H), 5.87 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 151.9, 150.9, 147.2, 137.1, 131.7, 130.0, 129.0, 128.9, 128.8, 128.3, 127.2, 123.8, 120.2, 117.0, 116.2, 110.7, 104.4, 104.3, 34.6, 14.1.

HRMS (ESI) calcd. for $C_{23}H_{17}ClNO_2^+$ ([M+H]$^+$): 374.0942, found: 374.0945.



4e

2-Methyl-4-phenyl-5-(4-phenyl-9*H*-xanthen-9-yl)oxazole (4e)

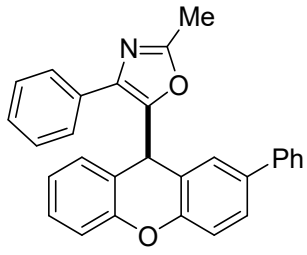
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4e** (77.2 mg, 62% yield).

White solid; m.p.: 173~174 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.46–7.43 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.38–7.35 (m, 1H), 7.30 (d, *J* = 6.6 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.07–6.98 (m, 5H), 5.90 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 151.4, 148.3, 147.2, 137.7, 137.3, 131.8, 130.4, 130.2, 129.9, 129.0, 128.6, 128.5, 128.2, 128.0, 127.4, 127.3, 123.5, 123.3, 121.2, 120.7, 117.1, 35.5, 14.2.

HRMS (ESI) calcd. for $C_{29}H_{22}NO_2^+$ ([M+H]$^+$): 416.1645, found: 416.1645.



4f

2-Methyl-4-phenyl-5-(2-phenyl-9*H*-xanthen-9-yl)oxazole (4f)

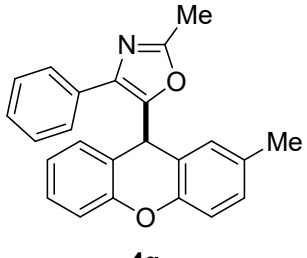
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4f** (74.7 mg, 60% yield).

White solid; m.p.: 170~171 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.49 (dd, J = 8.4, 1.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 4H), 7.39 (t, *J* = 7.8 Hz, 3H), 7.32–7.27 (m, 2H), 7.25–7.21 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H), 5.93 (s, 1H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 151.2, 150.8, 147.3, 140.3, 137.2, 136.5, 131.8, 128.9, 128.9, 128.8, 128.8, 128.2, 127.5, 127.2, 126.9, 123.5, 120.6, 120.3, 117.4, 117.0, 35.1, 14.1.

HRMS (ESI) calcd. for $C_{29}H_{22}NO_2^+$ ($[M+H]^+$): 416.1645, found: 416.1646.



4g

2-Methyl-5-(2-methyl-9H-xanthen-9-yl)-4-phenyloxazole (4g)

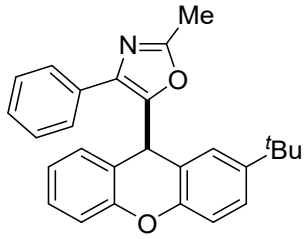
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4g** (73.1 mg, 69% yield).

White solid; m.p.: 156~157 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.47–7.44 (m, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.06–7.03 (m, 2H), 7.02–6.98 (m, 2H), 6.83 (s, 1H), 5.84 (s, 1H), 2.38 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 151.4, 149.2, 147.6, 136.9, 132.8, 131.9, 129.5, 129.0, 129.0, 128.8, 128.7, 128.2, 127.2, 123.2, 120.4, 119.9, 117.0, 116.7, 35.0, 20.9, 14.2.

HRMS (ESI) calcd. for $C_{24}H_{20}NO_2^+$ ($[M+H]^+$): 354.1489, found: 354.1485.



4h

5-(2-(*tert*-Butyl)-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazole (4h)

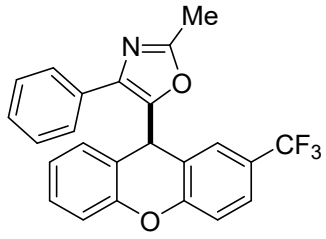
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4h** (75.8 mg, 64% yield).

White solid; m.p.: 167~168 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.28–7.24 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.08–7.04 (m, 2H), 7.01–6.98 (m, 2H), 5.83 (s, 1H), 2.38 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 151.5, 149.2, 147.7, 146.3, 136.9, 131.9, 128.9, 128.8, 128.6, 128.1, 127.3, 125.8, 125.2, 123.2, 120.5, 119.5, 116.9, 116.4, 35.3, 34.3, 31.4, 14.1.

HRMS (ESI) calcd. for $C_{27}H_{26}NO_2^+$ ([M+H]$^+$): 396.1958, found: 396.1958.



4i

2-Methyl-4-phenyl-5-(2-(trifluoromethyl)-9*H*-xanthen-9-yl)oxazole (4i)

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4i** (64.7 mg, 53% yield).

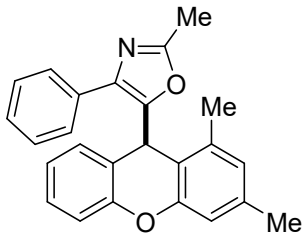
White solid; m.p.: 133~134 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.8k Hz, 1H), 7.30–7.27 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 6.6 Hz, 2H), 5.86 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 152.8, 149.7, 145.6, 136.5, 130.5, 128.1, 128.0, 127.8, 127.4, 126.3, 126.2, 125.8 (q, *J* = 271.6Hz), 125.3 (q, *J* = 3.2 Hz), 125.0 (q, *J* = 3.8 Hz), 123.2, 120.0, 118.9, 116.6, 116.1, 34.0, 13.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ –61.8.

HRMS (ESI) calcd. for $C_{20}H_{17}O_2^+$ ([M+H]$^+$): 408.1206, found: 408.1206.



4j

5-(1,3-Dimethyl-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazo (4j)

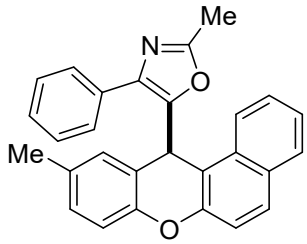
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4j** (69.8 mg, 70% yield).

White solid; m.p.: 186~187 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8. Hz, 2H), 7.26–7.24 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 6.6 Hz, 1H), 7.02–6.97 (m, 2H), 6.91–6.85 (m, 2H), 5.84 (s, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.5, 149.6, 147.2, 138.0, 137.1, 130.0, 129.7, 129.0, 128.7, 128.6, 127.1, 126.3, 126.2, 123.3, 122.8, 120.7, 120.1, 117.1, 35.2, 21.4, 16.2, 14.2.

HRMS (ESI) calcd. for $C_{25}H_{22}NO_2^+$ ([M+H]$^+$): 368.1645, found 368.1644.



4k

2-Methyl-5-(10-methyl-12*H*-benzo[a]xanthen-12-yl)-4-phenyloxazole (4k)

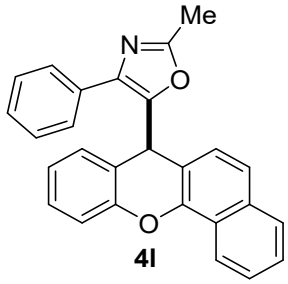
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4k** (76.1 mg, 63% yield).

White solid; m.p.: 195~196 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79–7.75 (m, 4H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.3–7.33 (m, 3H), 7.32–7.29 (m, 2H), 7.25–7.20 (m, 2H), 7.12–7.09 (m, 1H), 6.30 (s, 1H), 2.47 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 151.2, 149.5, 148.5, 138.0, 134.0, 131.7, 130.6, 129.8, 129.6, 129.5, 129.1, 128.7, 127.3, 127.0, 124.3, 123.8, 122.6, 121.1, 118.2, 117.1, 112.3, 33.0, 21.5, 14.1.

HRMS (ESI) calcd. for $C_{28}H_{22}NO_2^+$ ([M+H]$^+$): 404.1645, found 404.1648.



4l

5-(7*H*-benzo[c]xanthen-7-yl)-2-methyl-4-phenyloxazole (4l)

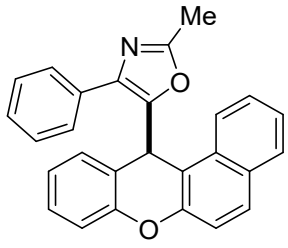
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4l** (76.8 mg, 66% yield).

White solid; m.p.: 185~186 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97–7.94 (m, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.52–7.50 (m, 1H), 7.47–7.45 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 7.92–7.88 (m, 2H), 5.39 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 151.2, 150.8, 147.3 140.3, 137.2, 136.5, 131.8, 129.9, 128.9 128.9, 128.8, 128.76, 128.2, 127.5, 127.2, 126.9, 123.5, 120.6, 120.3, 117.4, 117.0, 35.1, 14.1.

HRMS (ESI) calcd. for $C_{28}H_{22}NO_2^+$ ([M+H]$^+$): 390.1489, found 390.1488.



4m

5-(12*H*-benzo[a]xanthen-12-yl)-2-methyl-4-phenyloxazole (4m)

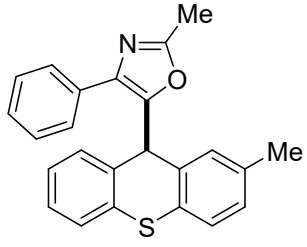
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4m** (66.4 mg, 57% yield).

White solid; m.p.: 175~176 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.67–7.64 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.41–7.38 (m, 1H), 7.33–7.31 (m, 1H), 7.25–7.21 (m, 1H), 7.10–7.07 (m, 2H), 7.01 (d, J = 7.2 Hz, 1H), 5.92 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 151.5, 148.4, 147.3, 137.8, 137.3, 131.9, 130.4, 130.3, 129.9, 129.8, 129.0, 128.7, 128.6, 128.3, 128.0, 127.5, 127.3, 123.6, 123.4, 121.3, 120.8, 117.2, 35.5, 14.2.

HRMS (ESI) calcd. for $C_{28}H_{22}NO_2^+$ ($[M+H]^+$): 390.1489, found 390.1485.



4n

2-Methyl-5-(2-methyl-9*H*-thioxanthen-9-yl)-4-phenyloxazole (4n)

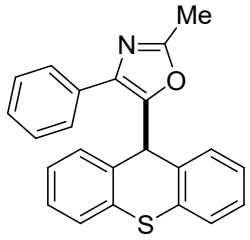
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4n** (66.5 mg, 60% yield).

White solid; m.p.: 160~161 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.05–7.03 (m, 2H), 7.00–6.95 (m, 2H), 6.82 (s, 1H), 5.83 (s, 1H), 2.38 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 151.4, 149.2, 147.6, 136.9, 132.8, 131.86, 129.4, 128.9, 128.9, 128.8, 128.6, 128.1, 127.1, 123.1, 120.4, 119.9, 116.9, 116.7, 35.0, 20.8, 14.1.

HRMS (ESI) calcd. for $C_{24}H_{20}NOS^+$ ($[M+H]^+$): 370.1260, found: 370.1254.



4o

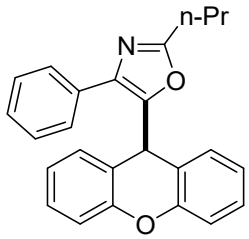
2-Methyl-4-phenyl-5-(9*H*-thioxanthen-9-yl)oxazole (4o)

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 20:1) to afford the product **4o** (61.8 mg, 58% yield).

White solid; m.p.: 166~167 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37–7.35 (m, 1H), 7.27–6.24 (m, 2H), 7.14 (d, *J* = 8.4, 2H), 7.04 (d, *J* = 6.6 Hz, 2H), 7.02–6.99 (m, 2H), 5.87 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 151.4, 147.4, 137.1, 131.9, 129.0, 128.8, 128.8, 128.3, 127.2, 123.4, 120.5, 117.0, 35.0, 14.2.



5a

4-Phenyl-2-propyl-5-(9*H*-xanthen-9-yl)oxazole (5a)

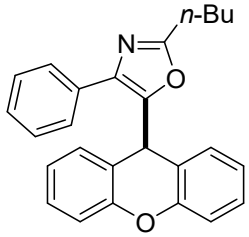
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **5a** (67.2 mg, 61% yield).

White solid; m.p.: 211~212 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.37–7.34 (m, 1H), 7.26–7.24 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.01–7.68 (m, 4H), 5.85 (s, 1H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.74–1.67 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 151.4, 146.8, 137.4, 132.0, 128.9, 128.7, 128.6, 128.2, 127.3, 123.4, 120.7, 117.0, 35.1, 30.1, 20.7, 13.7.

HRMS (ESI) calcd. for $C_{25}H_{21}NO_2^+$ ($[M+H]^+$): 368.1645, found: 368.1642.



5b

2-Butyl-4-phenyl-5-(9*H*-xanthen-9-yl)oxazole (5b)

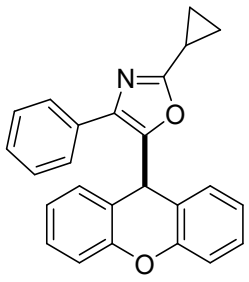
Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **5b** (49.3 mg, 43% yield).

White solid; m.p.: 211~212 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.26–7.24 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.02–7.98 (m, 4H), 5.85 (s, 1H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.68–1.63 (m, 2H), 1.32–1.26 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.8, 151.4, 146.8, 137.3, 132.0, 128.9, 128.6, 128.1, 127.3, 126.9, 123.4, 120.6, 116.9, 35.1, 29.2, 28.0, 22.3, 13.7.

HRMS (ESI) calcd. for $C_{26}H_{23}NO_2^+$ ($[M+H]^+$): 382.1802, found: 382.1798.



5c

2-Cyclopropyl-4-phenyl-5-(9*H*-xanthen-9-yl)oxazole (5c)

Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **5c** (60.1 mg, 55% yield).

White solid; m.p.: 198~199 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.26– .23 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.03–6.99 (m, 4H), 5.81 (s, 1H), 1.98–1.93 (m, 1H), 1.00–0.97 (m, 2H), 0.96–0.92 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 151.3, 146.0, 137.3, 131.8, 128.8, 128.6, 128.5, 128.0, 127.2, 123.3, 120.6, 116.8, 35.0, 8.9, 8.5.

HRMS (ESI) calcd. for $C_{25}H_{19}NO_2^+$ ($[M+H]^+$): 366.1489, found: 366.1485.

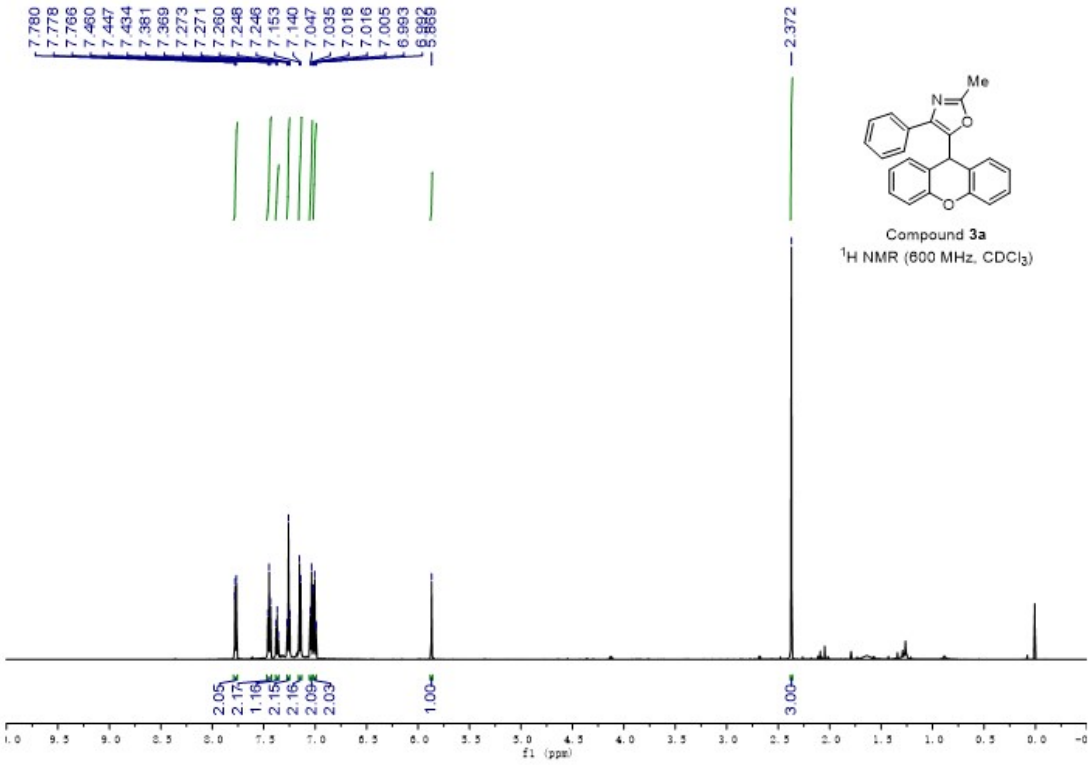
5. References:

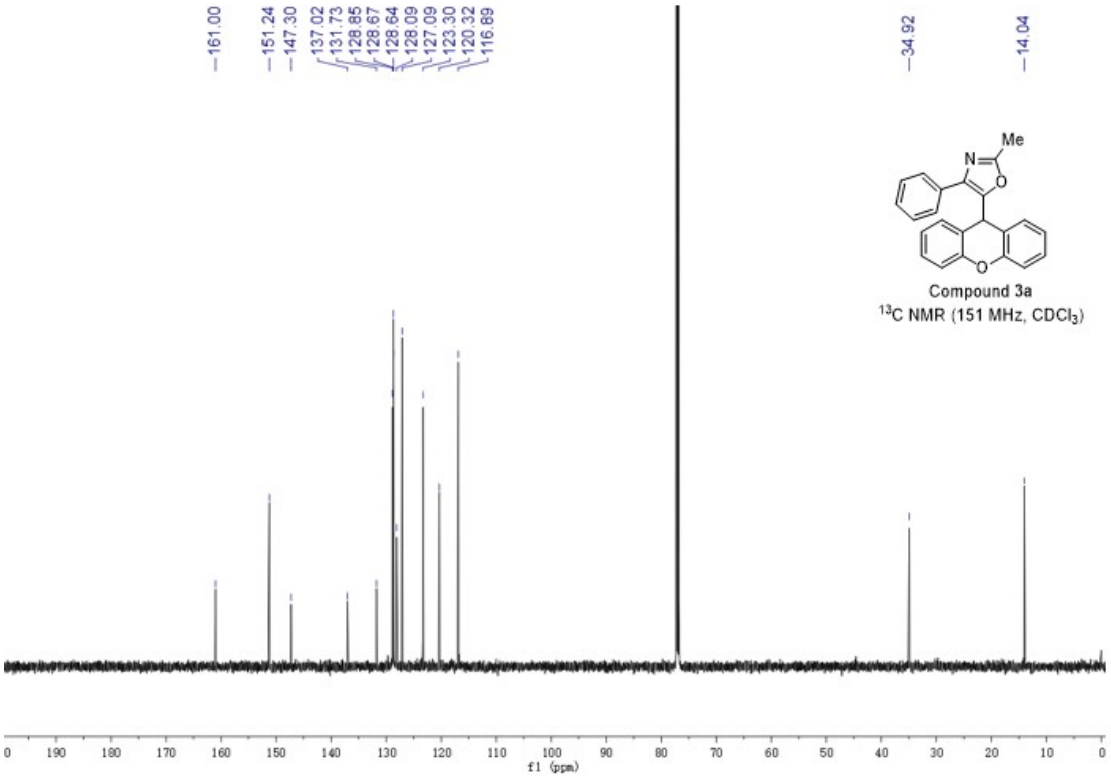
1. Chen, X.; Liu, H.; Gao, H.; Li, P.; Miao, T.; Li, H. *J. Org. Chem.* **2022**, *87*, 1056–1064.

2. Gao, H.; Chen, X.; Wang, P.-L.; Shi, M.-M.; Shang, L.-L.; Guo, H.-Y.; Li, H.; Li, P. *Org. Chem. Front.*, **2022**, *9*, 1911–1916.

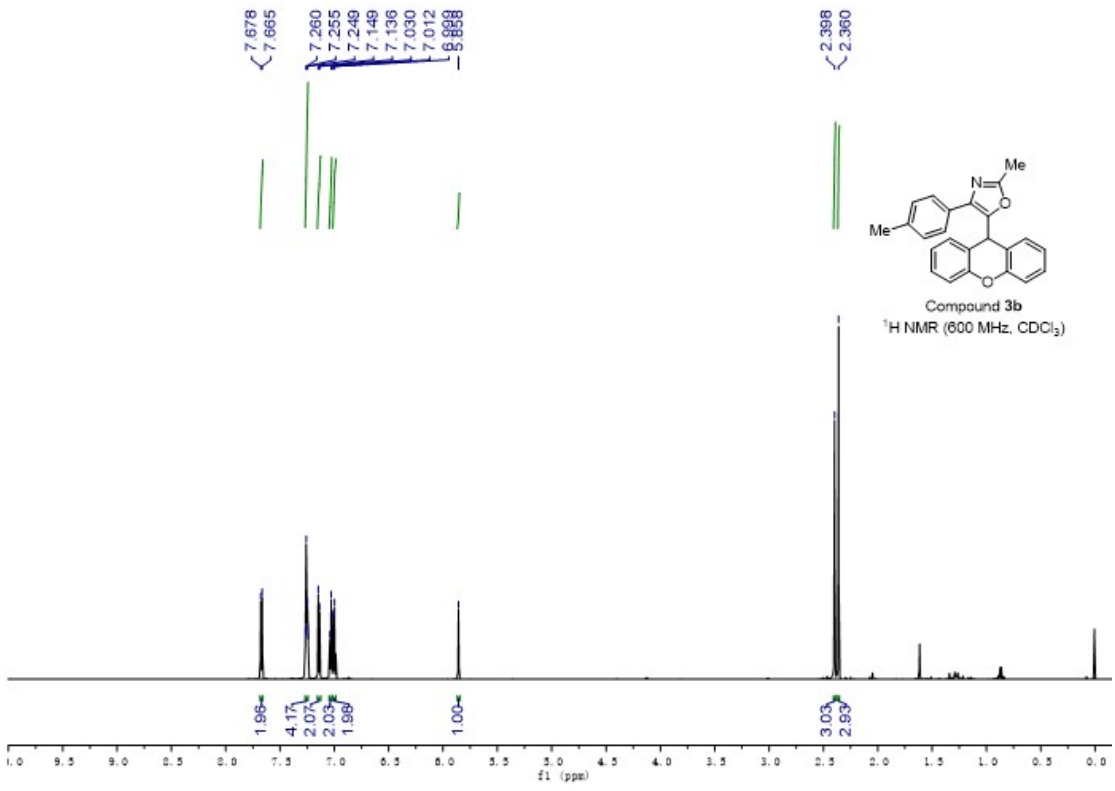
6. NMR Spectra of the Products

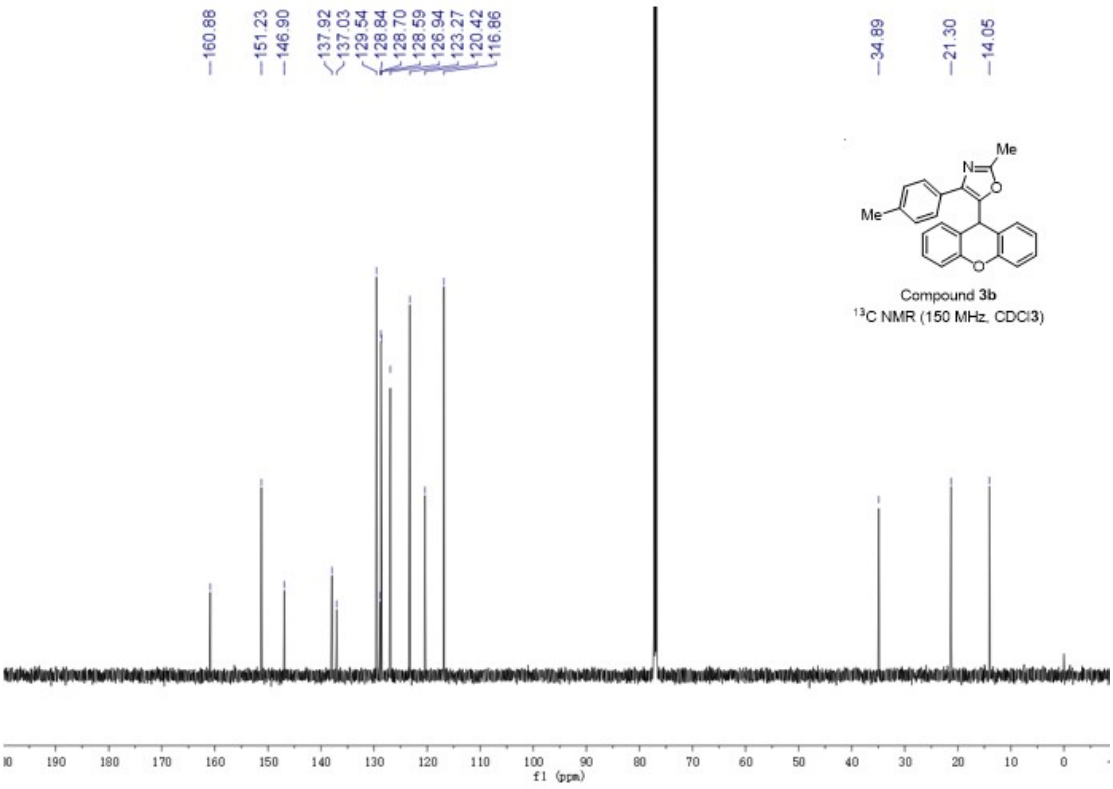
NMR spectra of 2-methyl-4-phenyl-5-(9*H*-xanthen-9-yl)oxazole (**3a**)



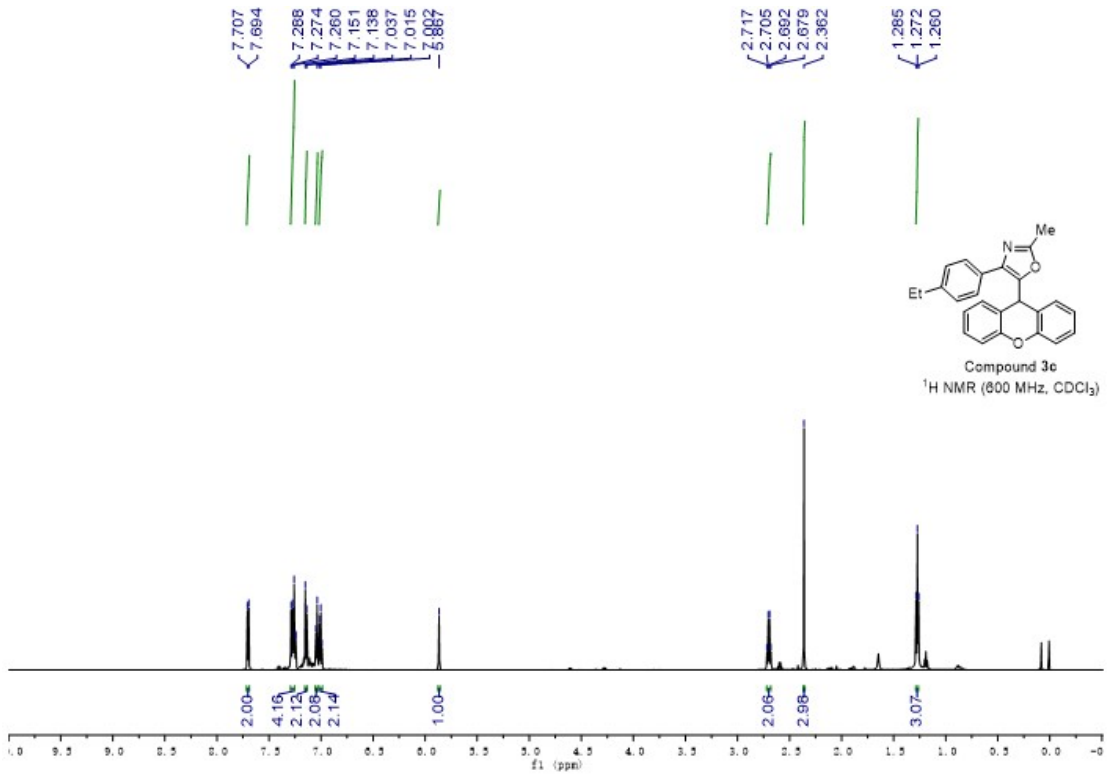


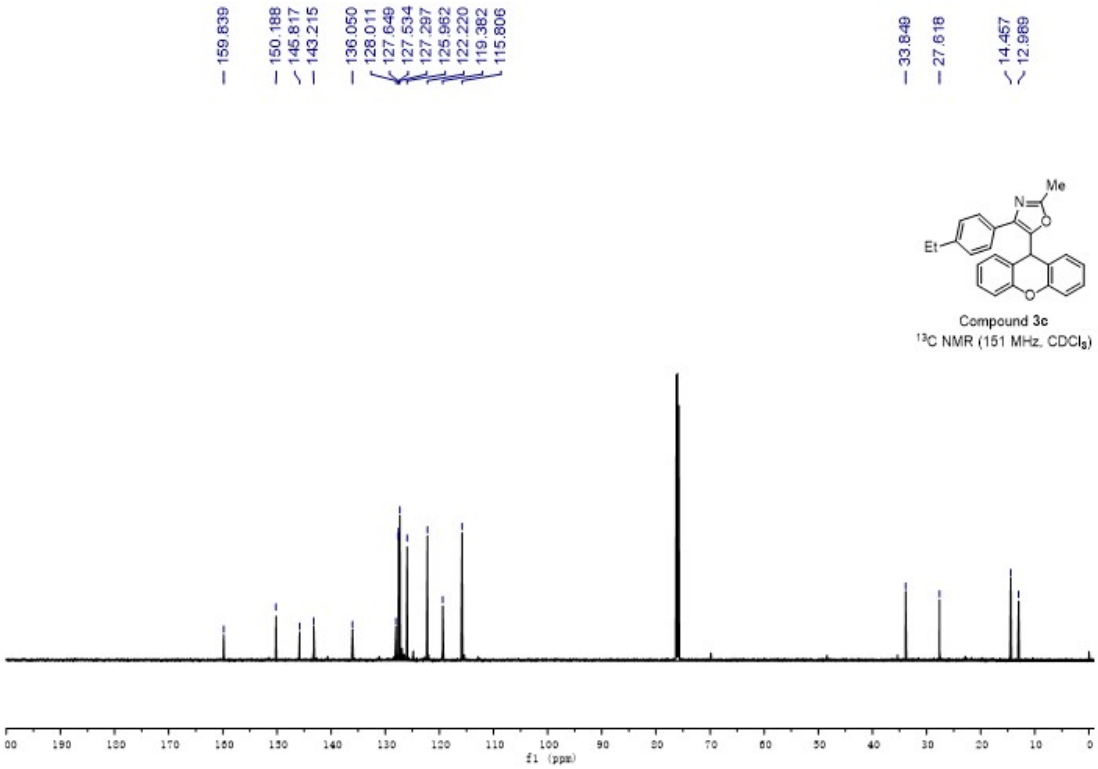
NMR spectra of 2-methyl-4-(*p*-tolyl)-5-(9*H*-xanthen-9-yl)oxazole (**3b**)



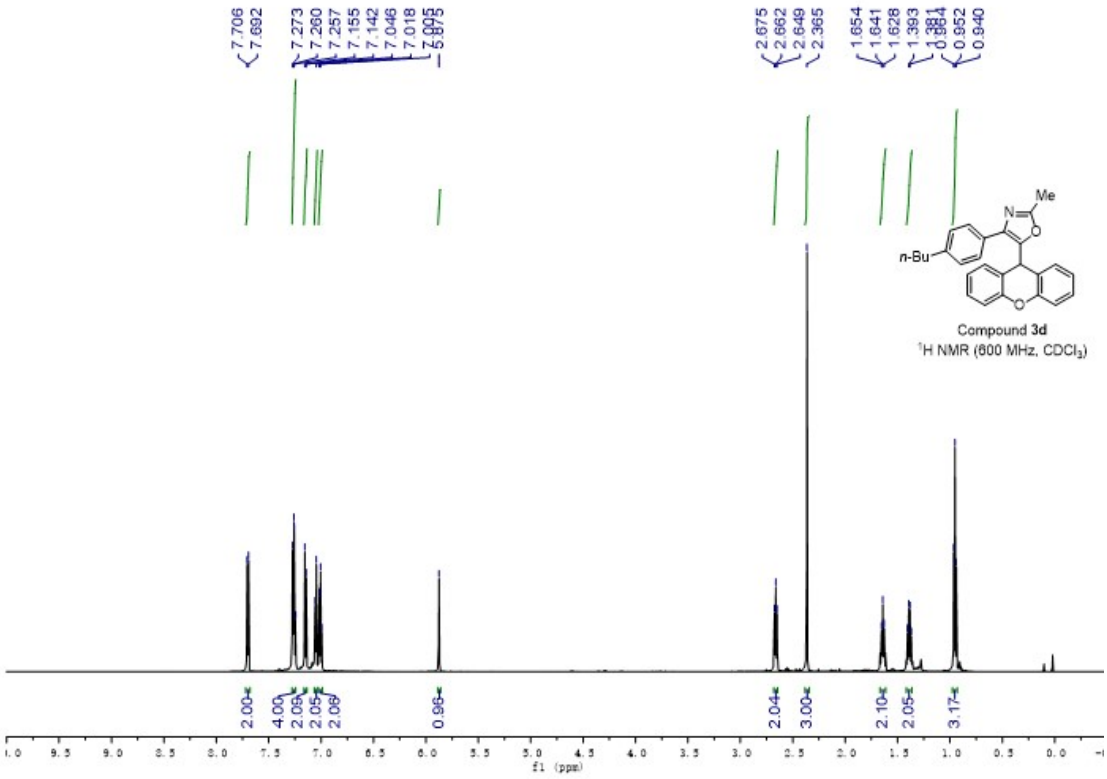


NMR spectra of 4-(4-ethylphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3c**)

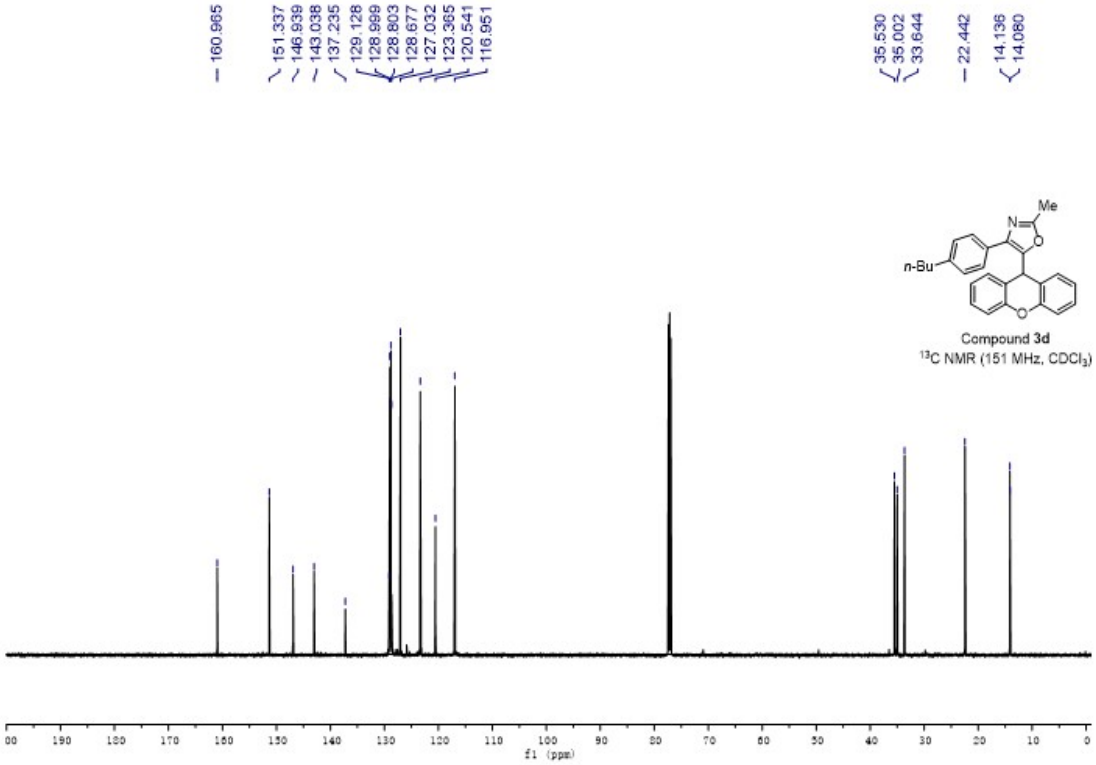




NMR spectra of 4-(4-butylphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3d**)

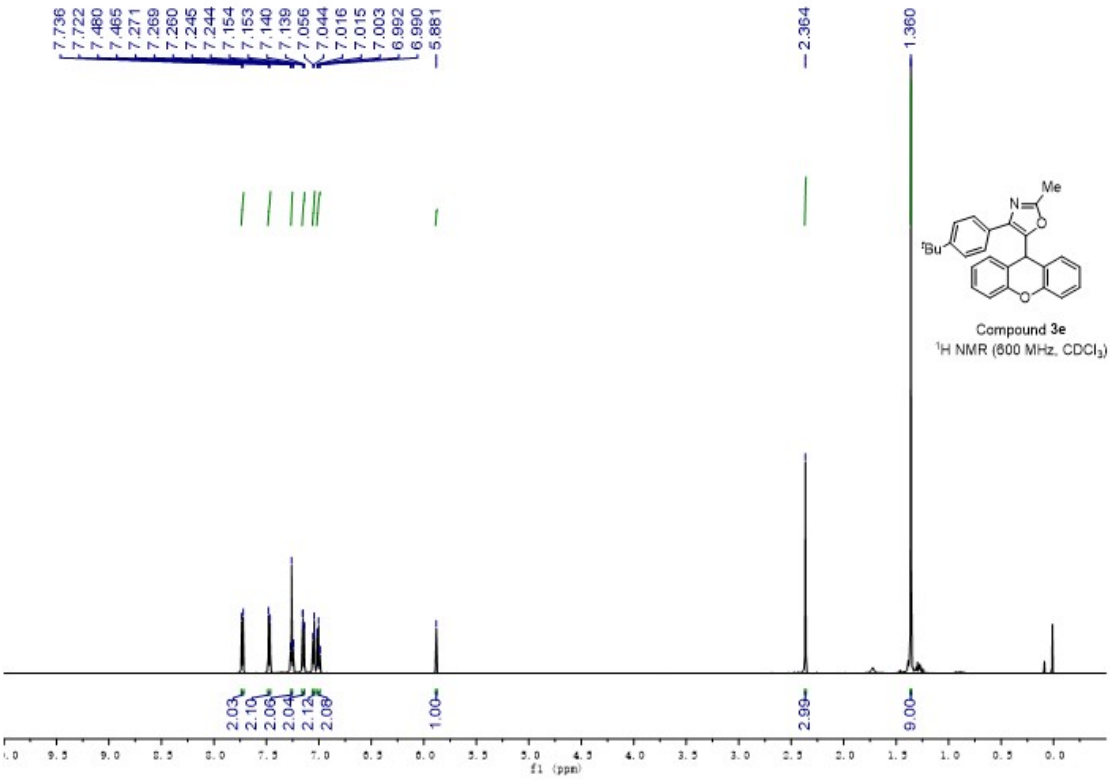


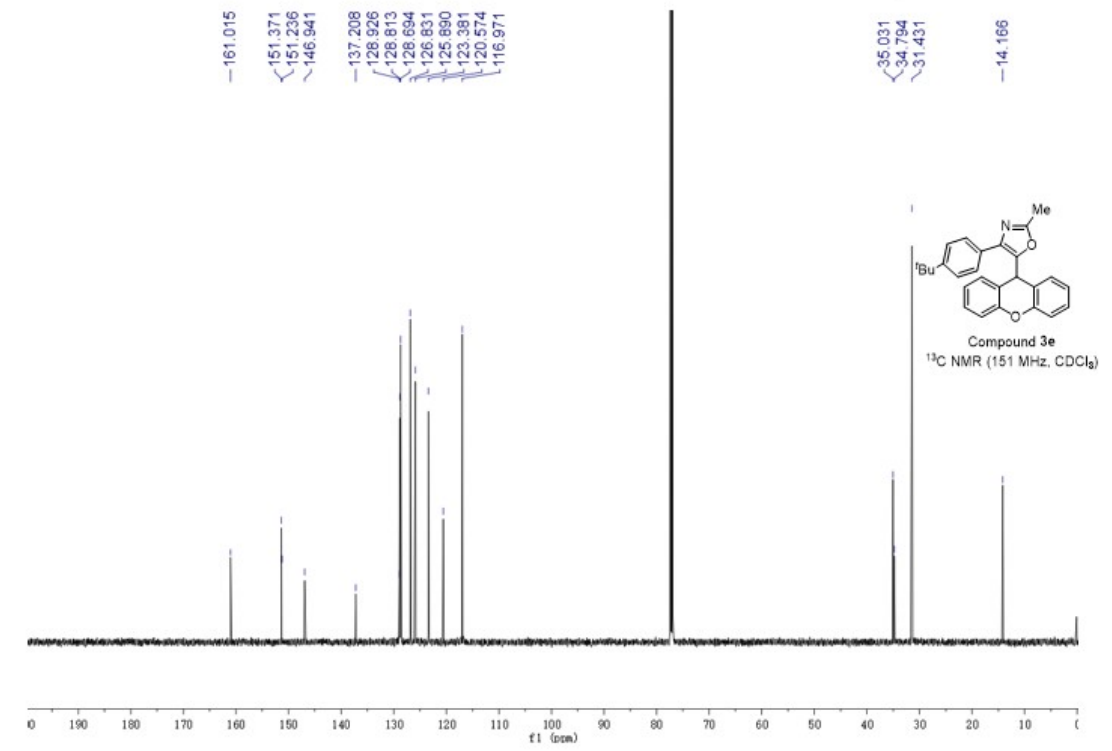
Compound **3d**
^{1}H NMR (800 MHz, $CDCl_3$)



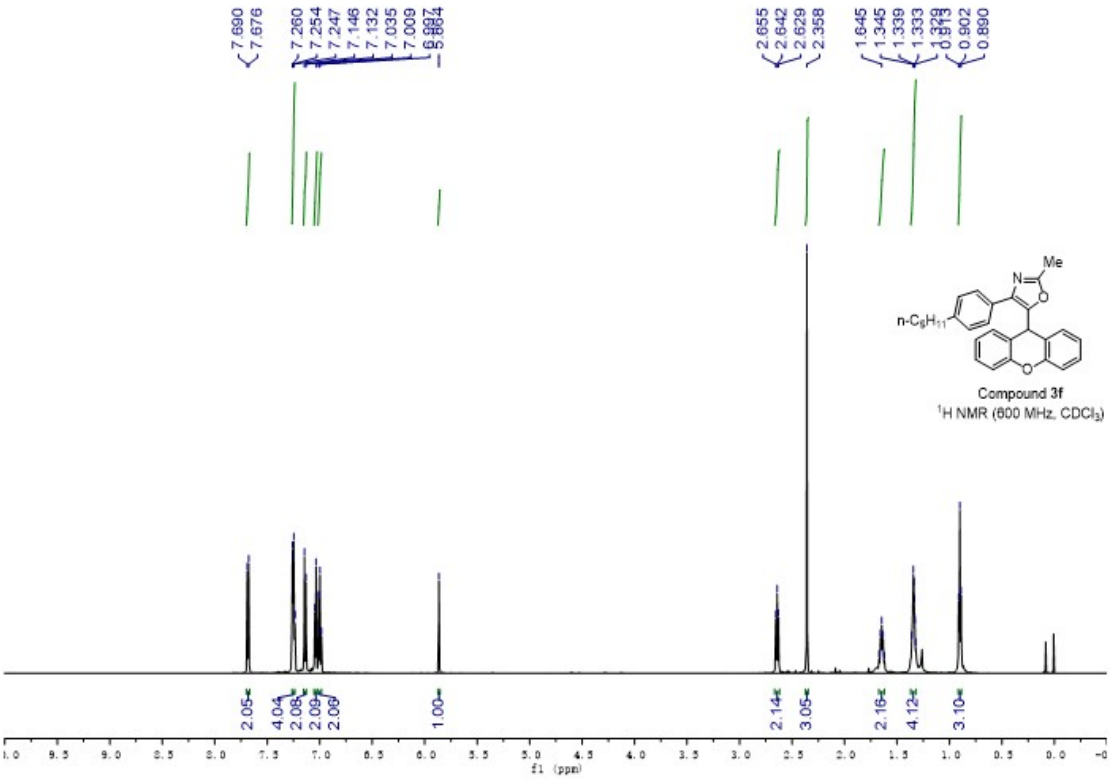
Compound **3d**
^{13}C NMR (151 MHz, $CDCl_3$)

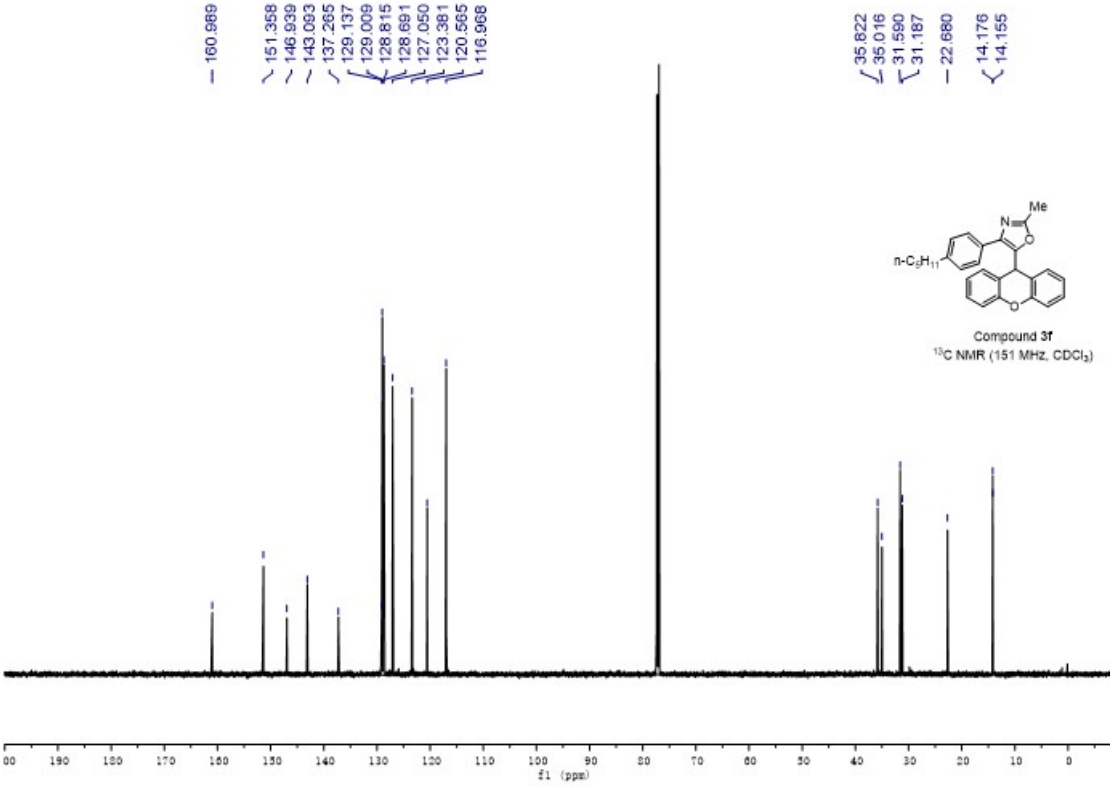
NMR spectra of 4-(4-(*tert*-Butyl)phenyl)-2-methyl-5-(9H-xanthen-9-yl)oxazole **(3e)**



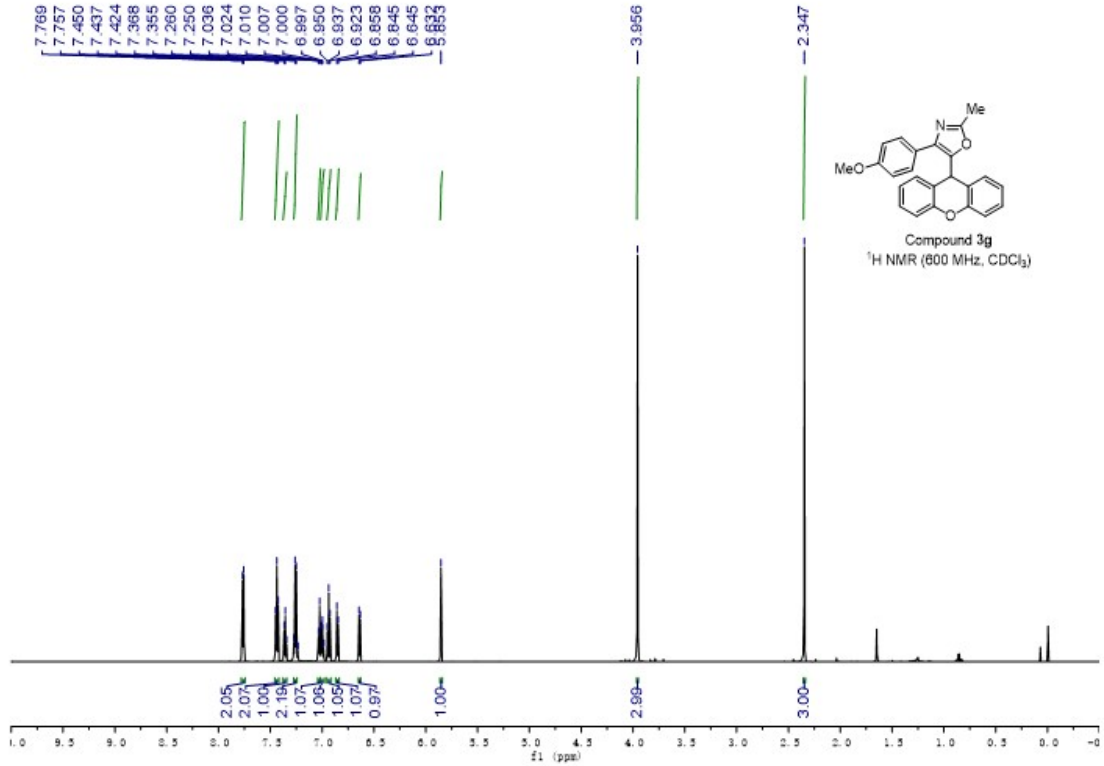


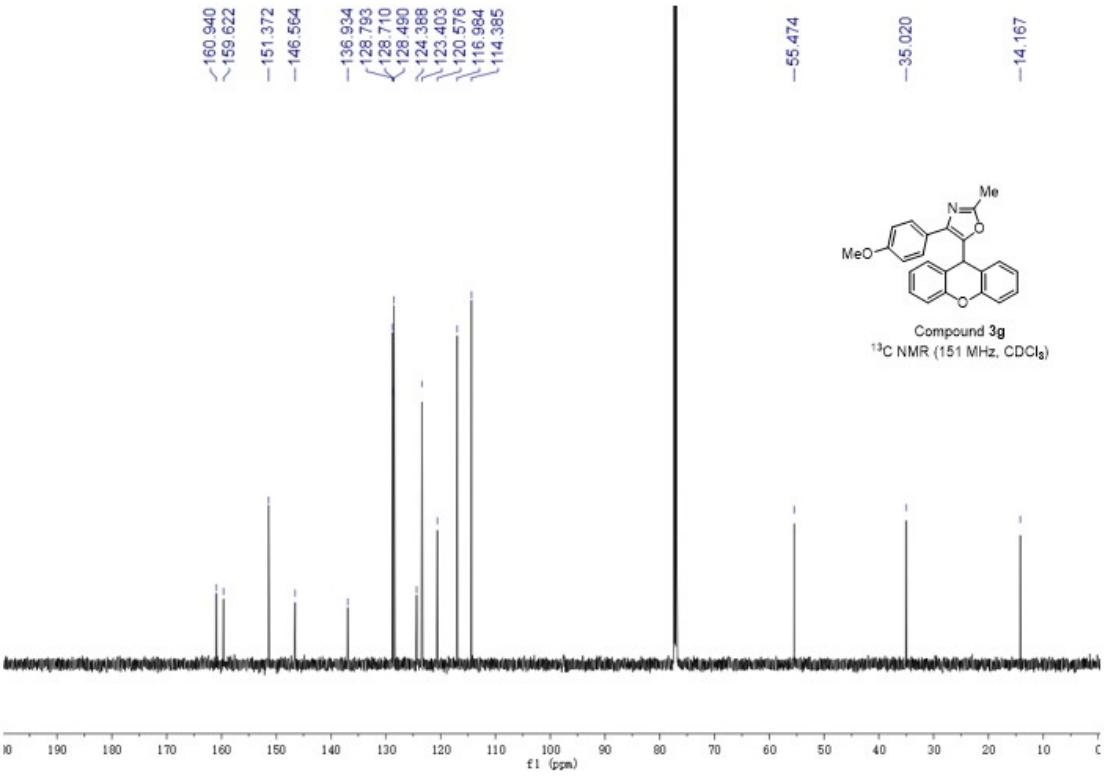
NMR spectra of 2-Methyl-4-(4-pentylphenyl)-5-(9*H*-xanthen-9-yl)oxazole (**3f**)



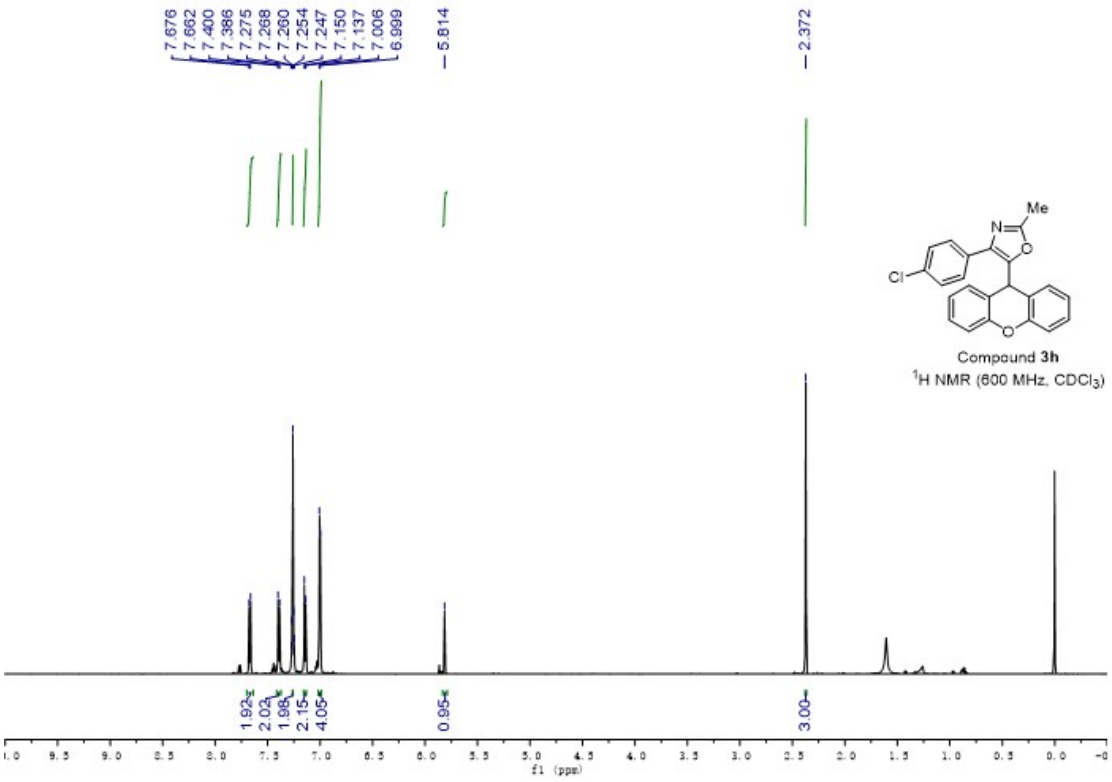


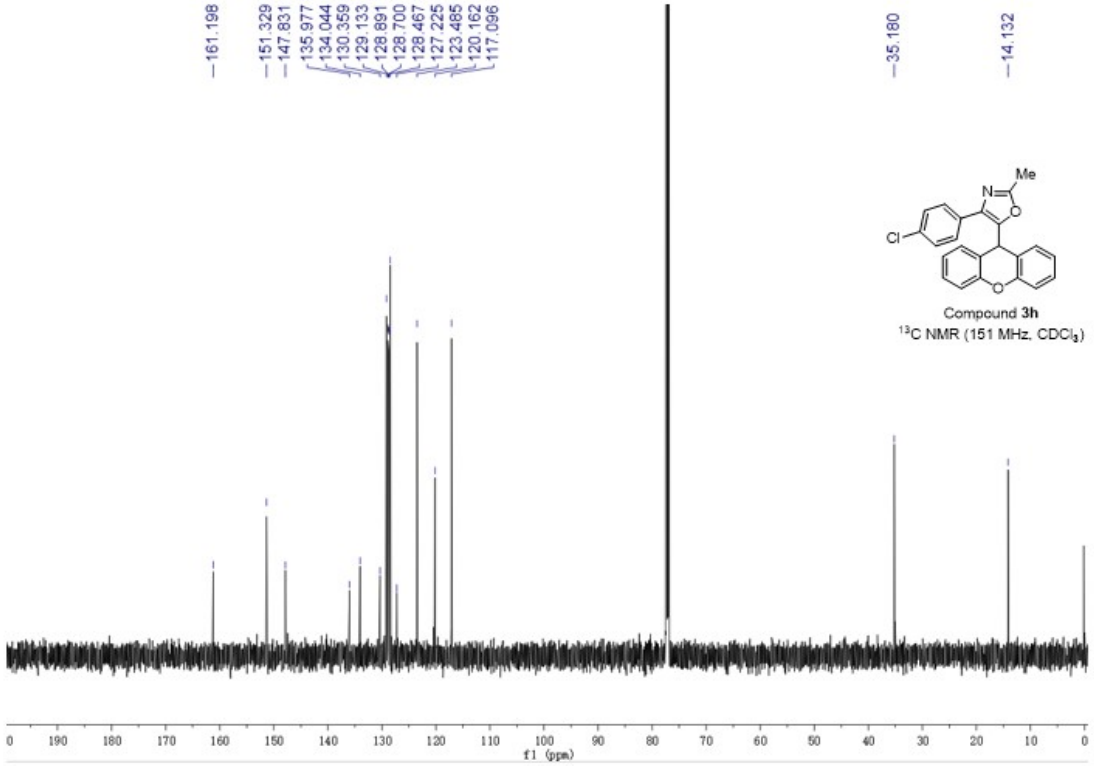
NMR spectra of 4-(4-methoxyphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3g**)



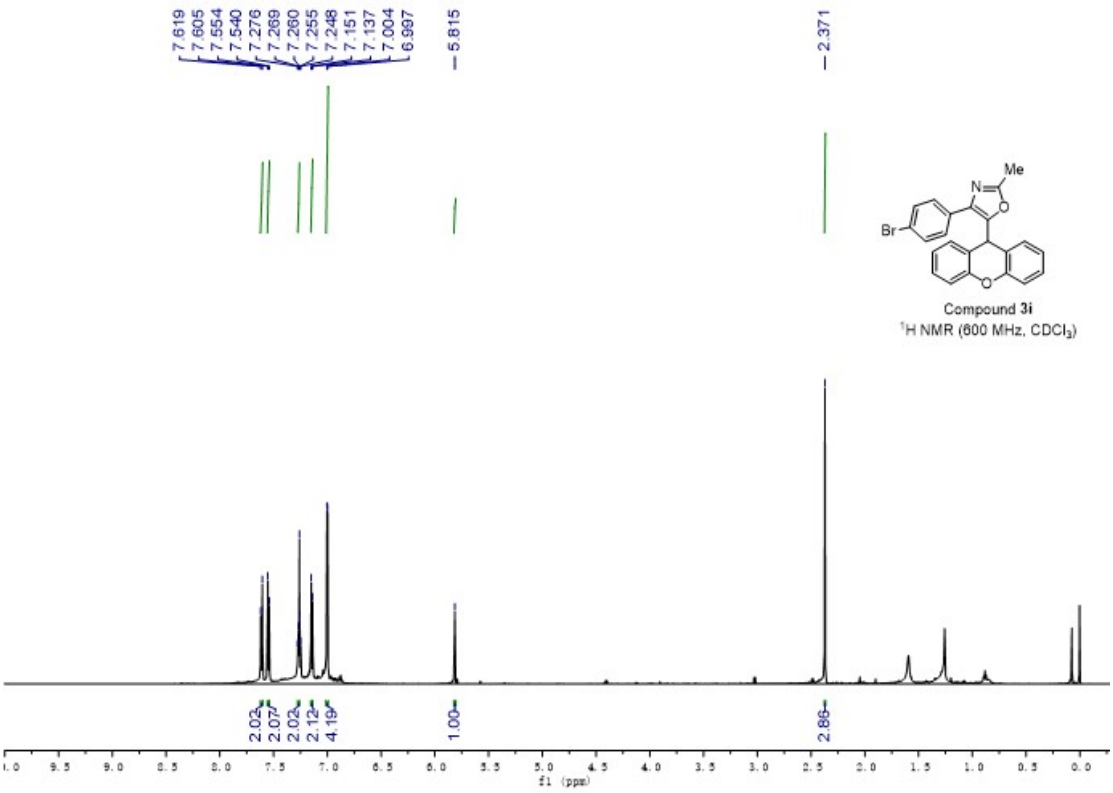


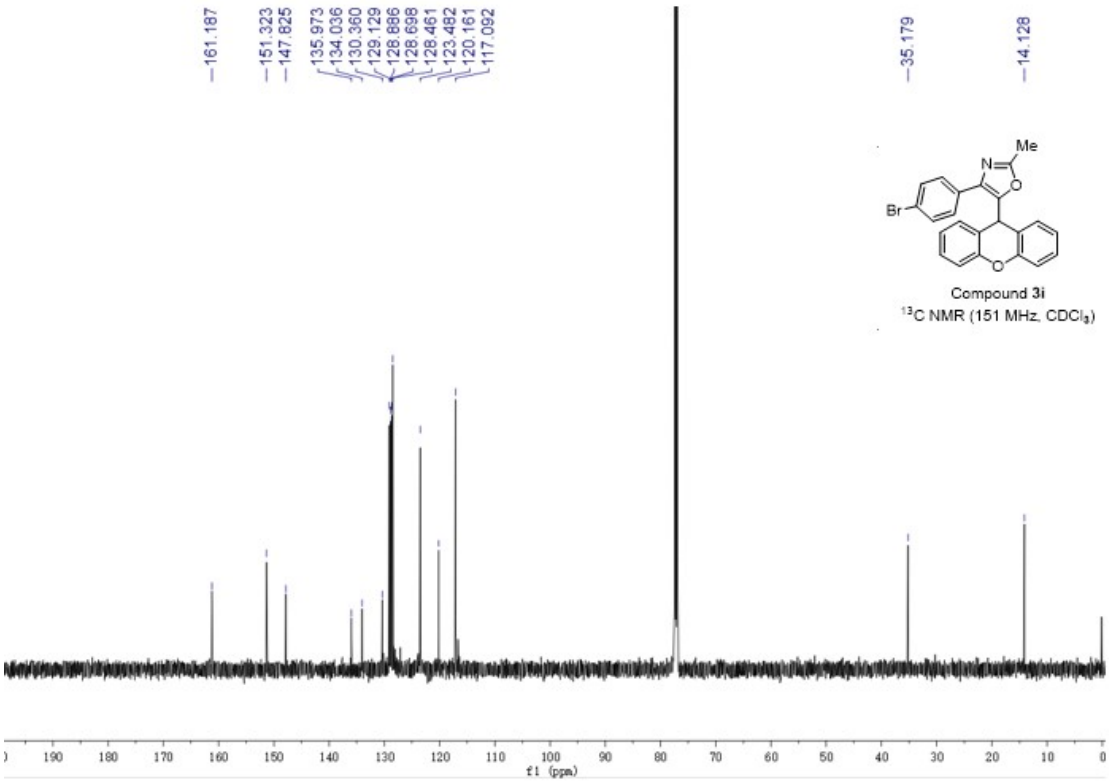
NMR spectra of 4-(4-chlorophenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3h**)



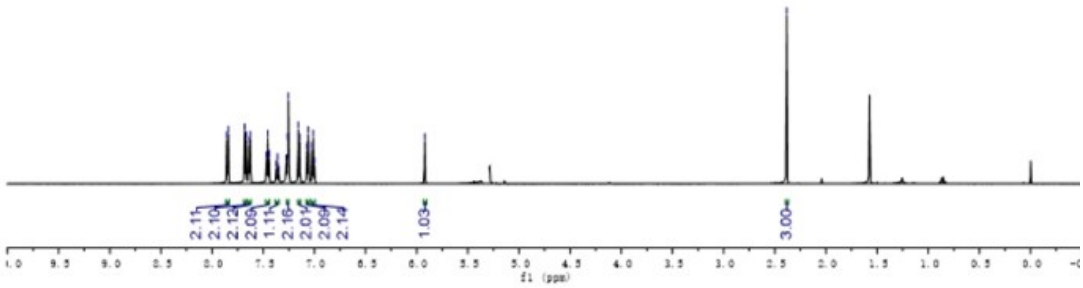


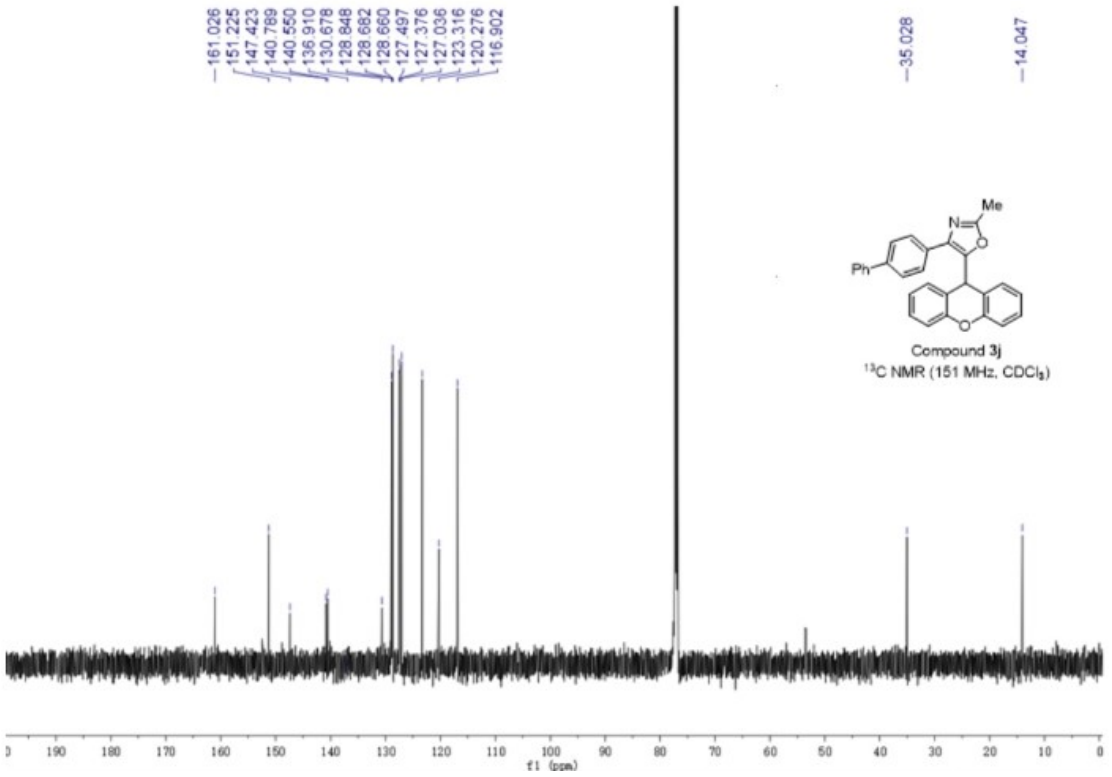
NMR spectra of 4-(4-Bromophenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3i**)



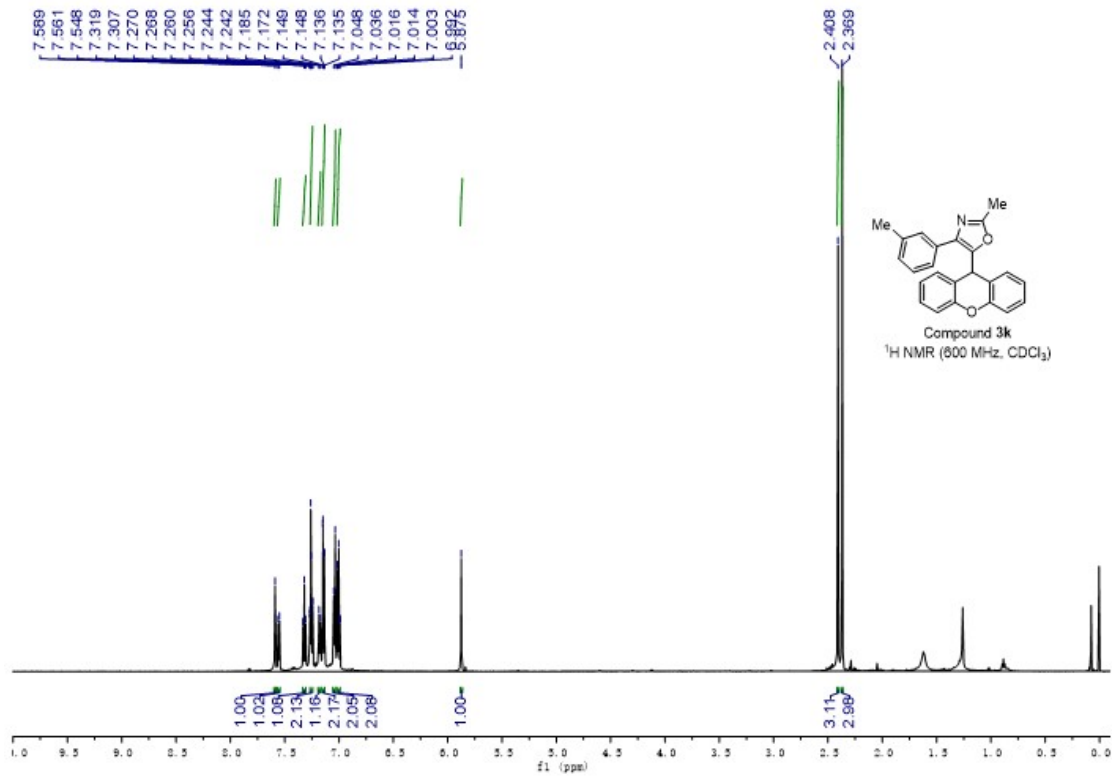


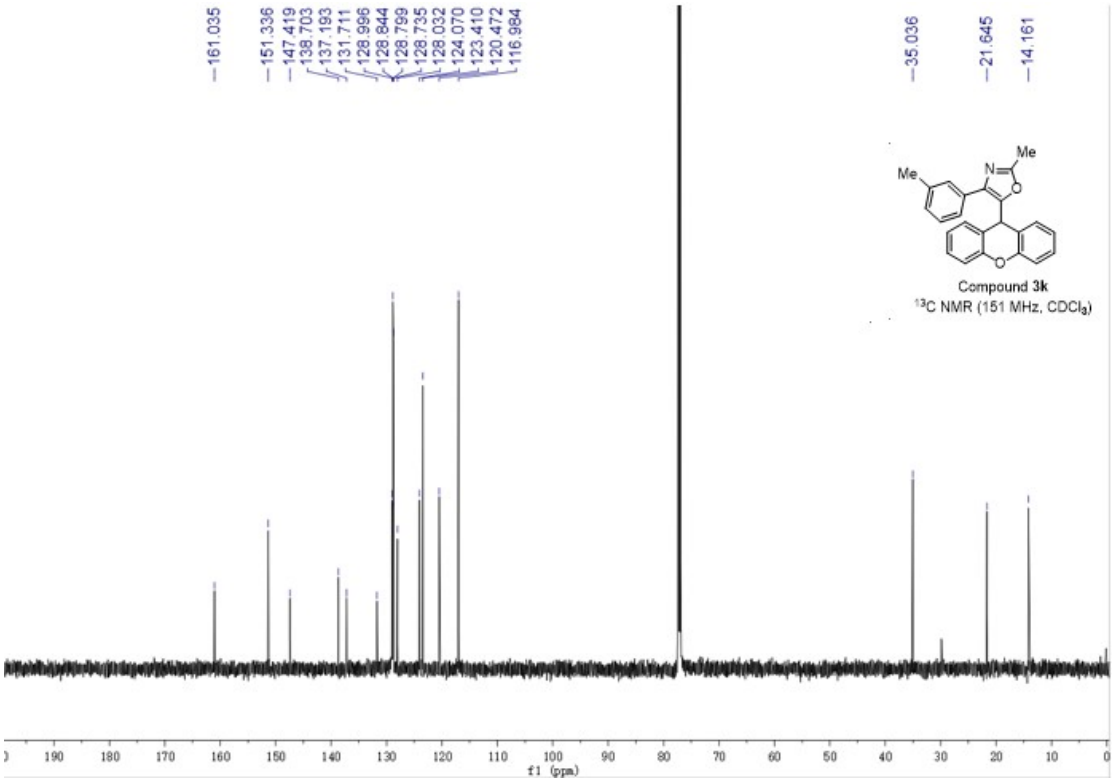
NMR spectra of 4-([1,1'-Biphenyl]-4-yl)-2-methyl-5-(9H-xanthen-9-yl)oxazole (**3j**)



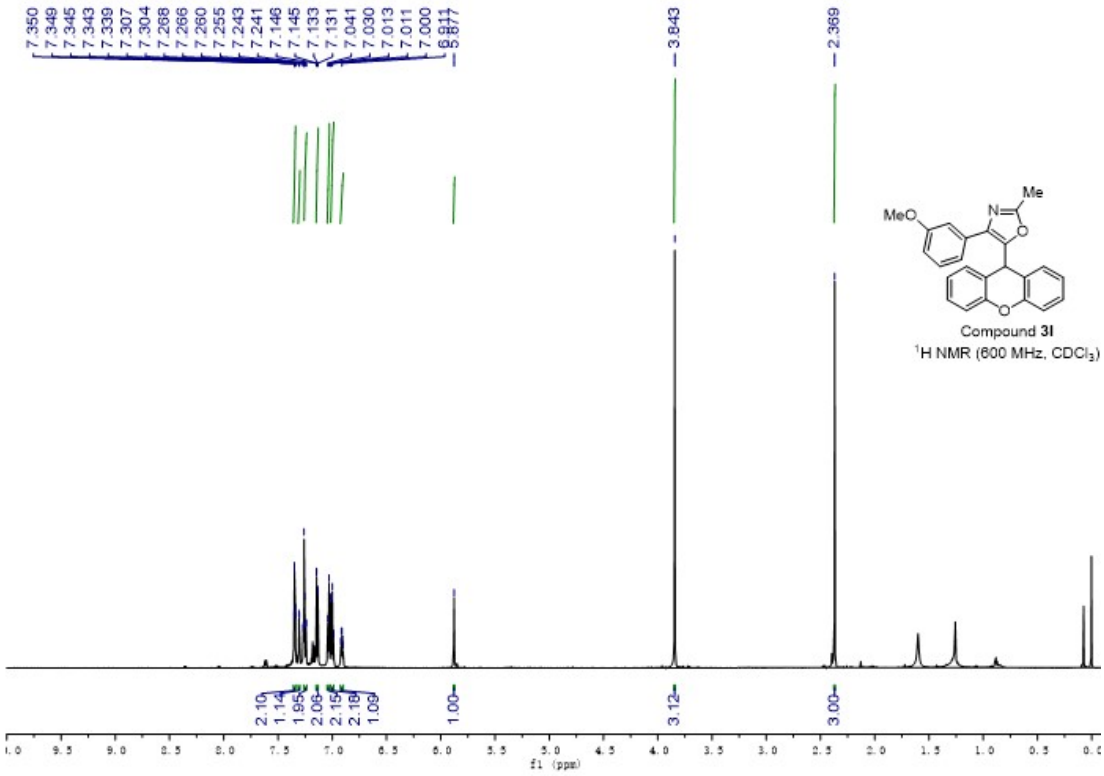


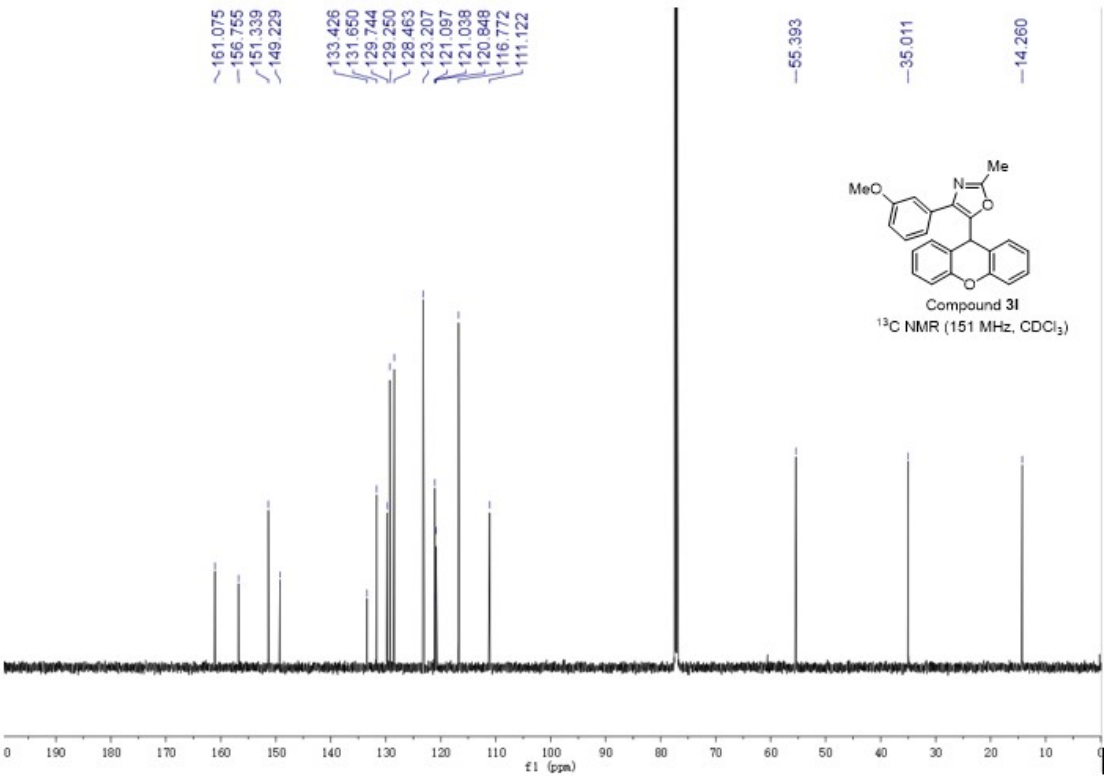
NMR spectra of 2-methyl-4-(m-tolyl)-5-(9*H*-xanthen-9-yl)oxazole (**3k**)



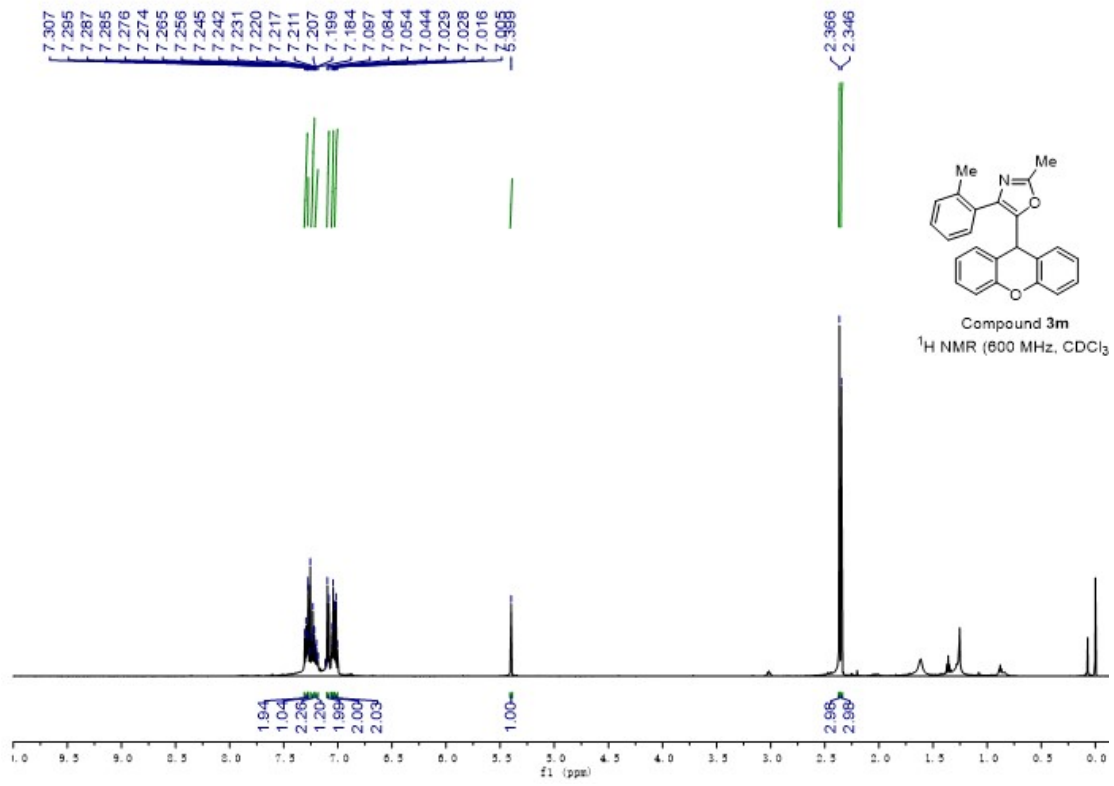


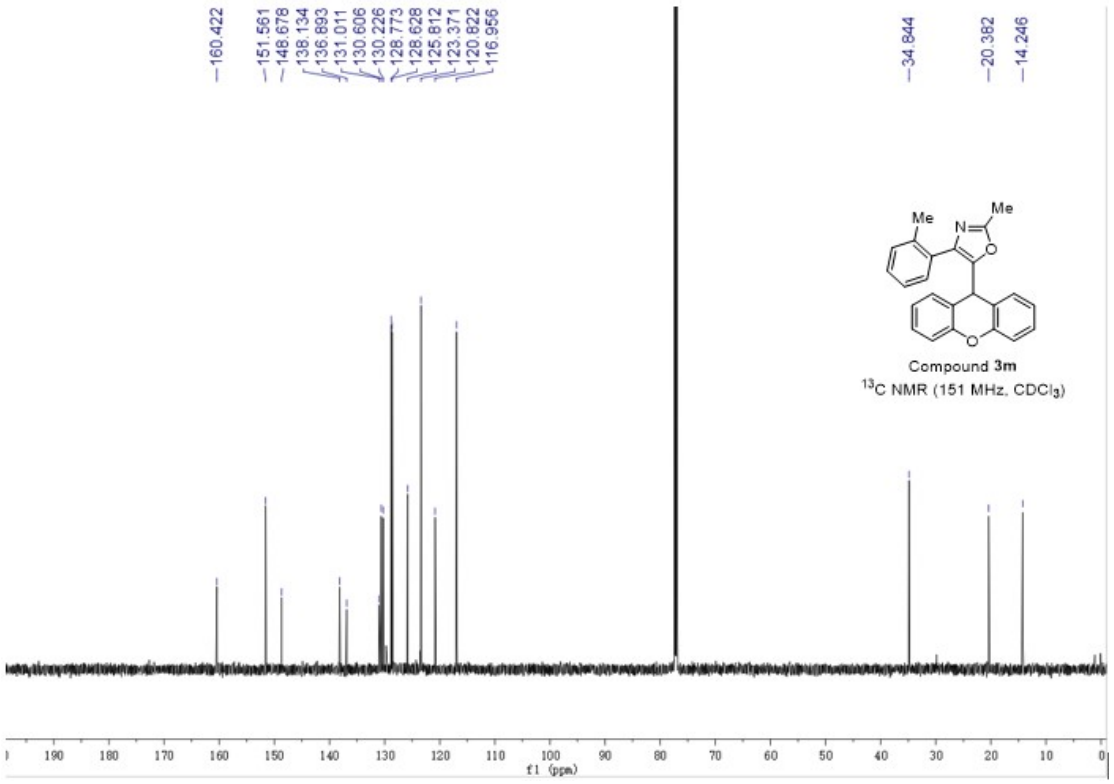
NMR spectra of 4-(3-methoxyphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3l**)



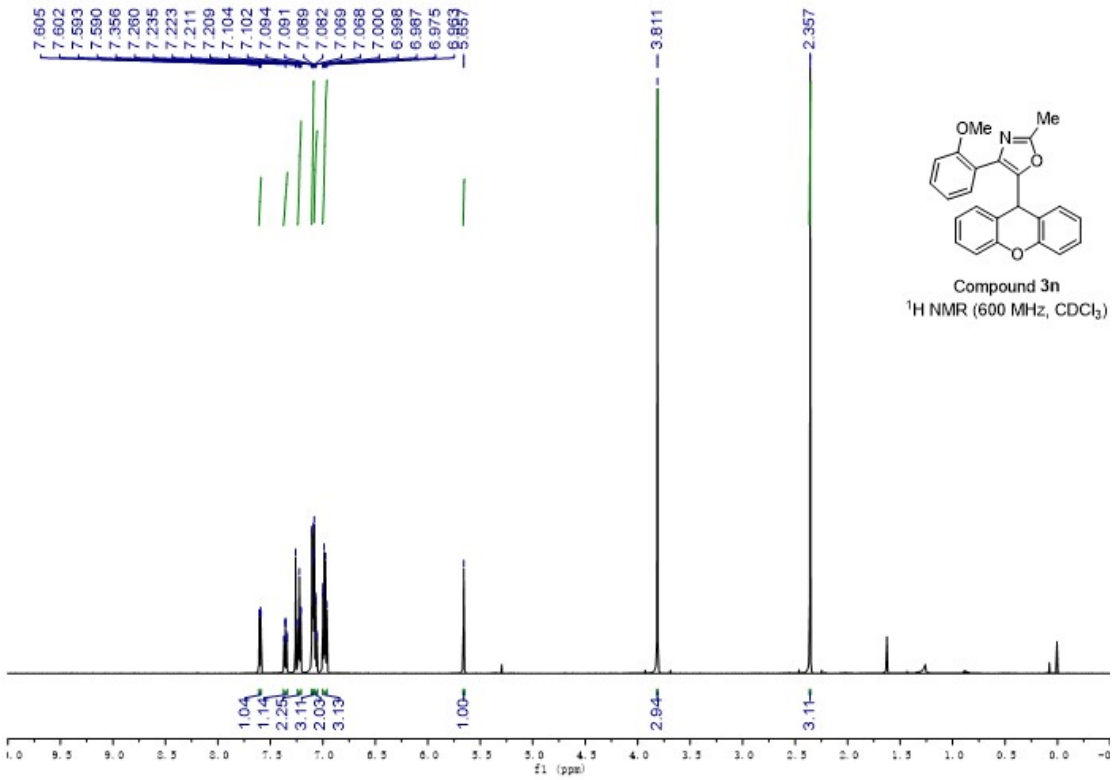


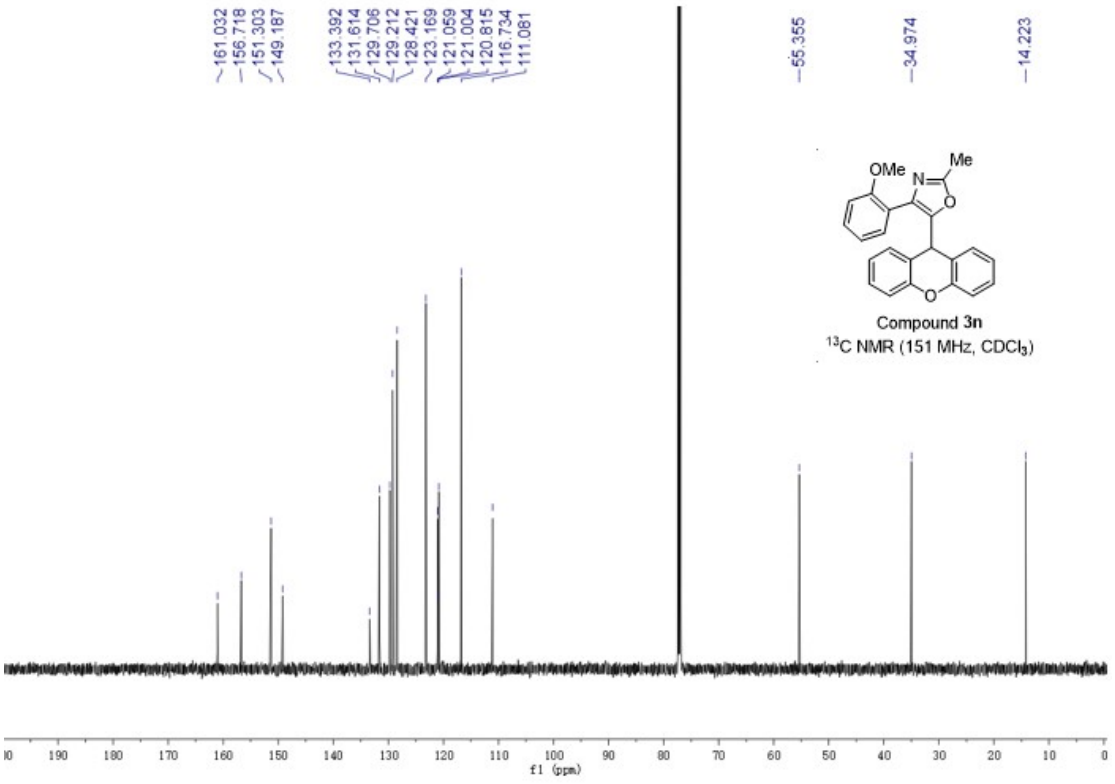
NMR spectra of 2-methyl-4-(*o*-tolyl)-5-(9*H*-xanthen-9-yl)oxazole (**3m**)



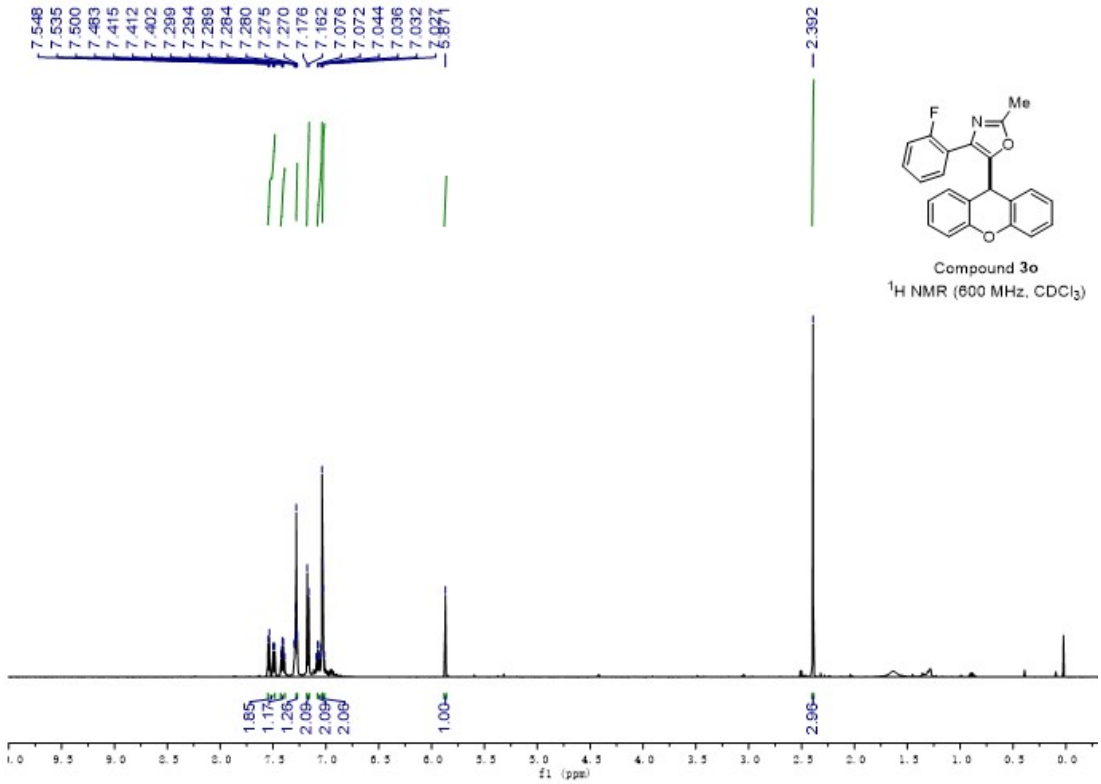


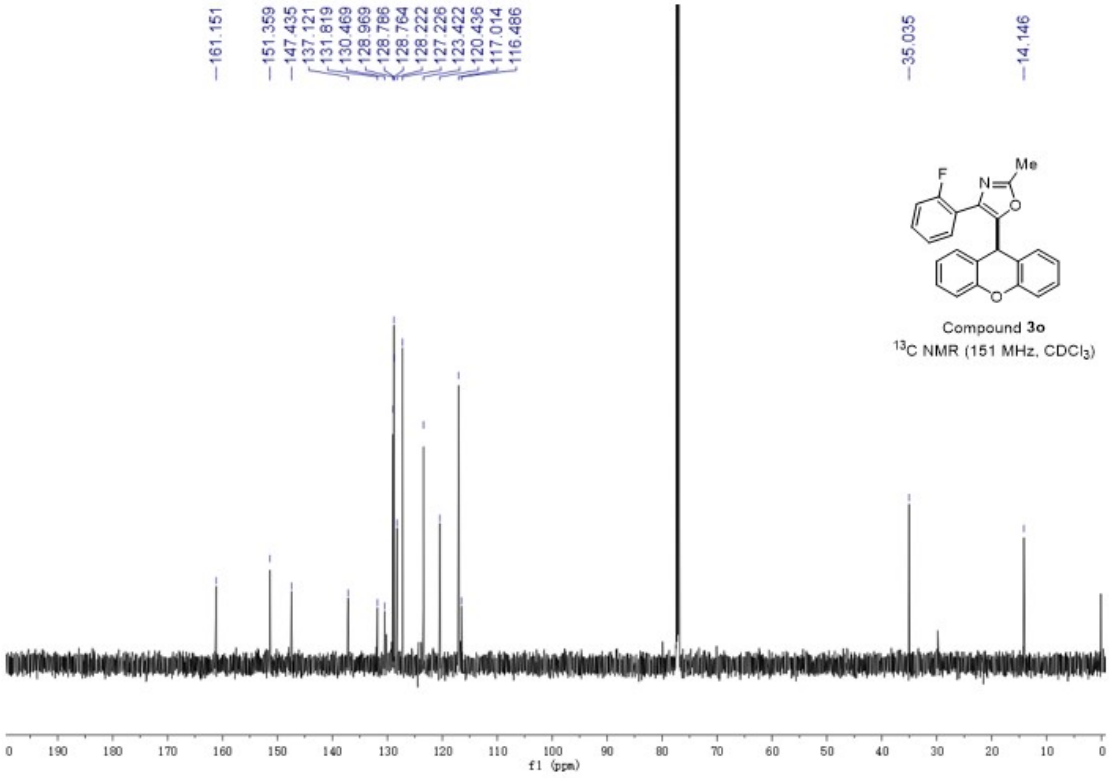
NMR spectra of 4-(2-methoxyphenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3n**)

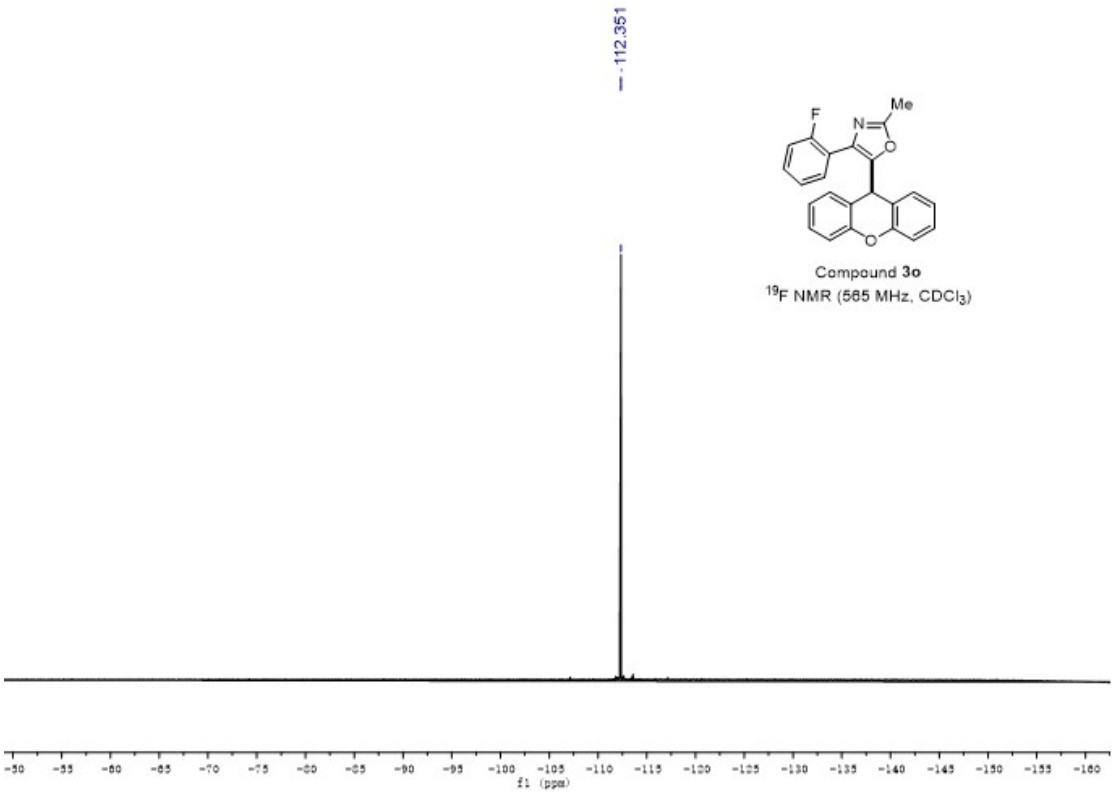




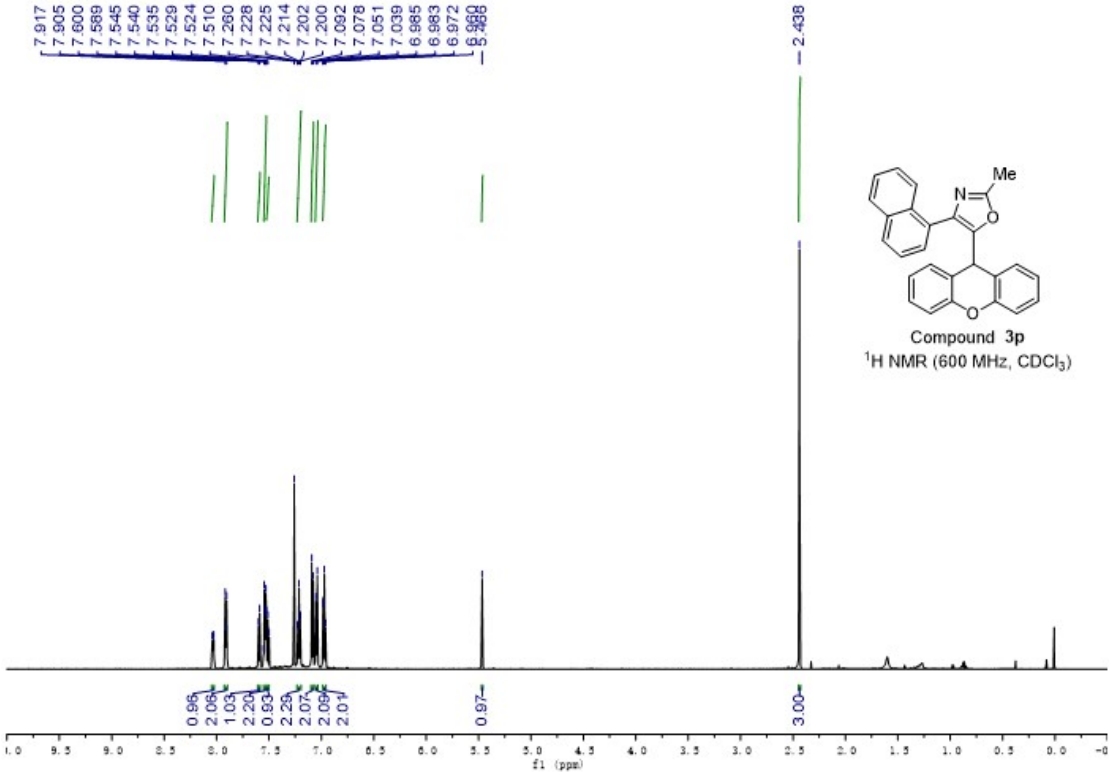
NMR spectra of 4-(2-fluorophenyl)-2-methyl-5-(9*H*-xanthen-9-yl)oxazole (**3o**)

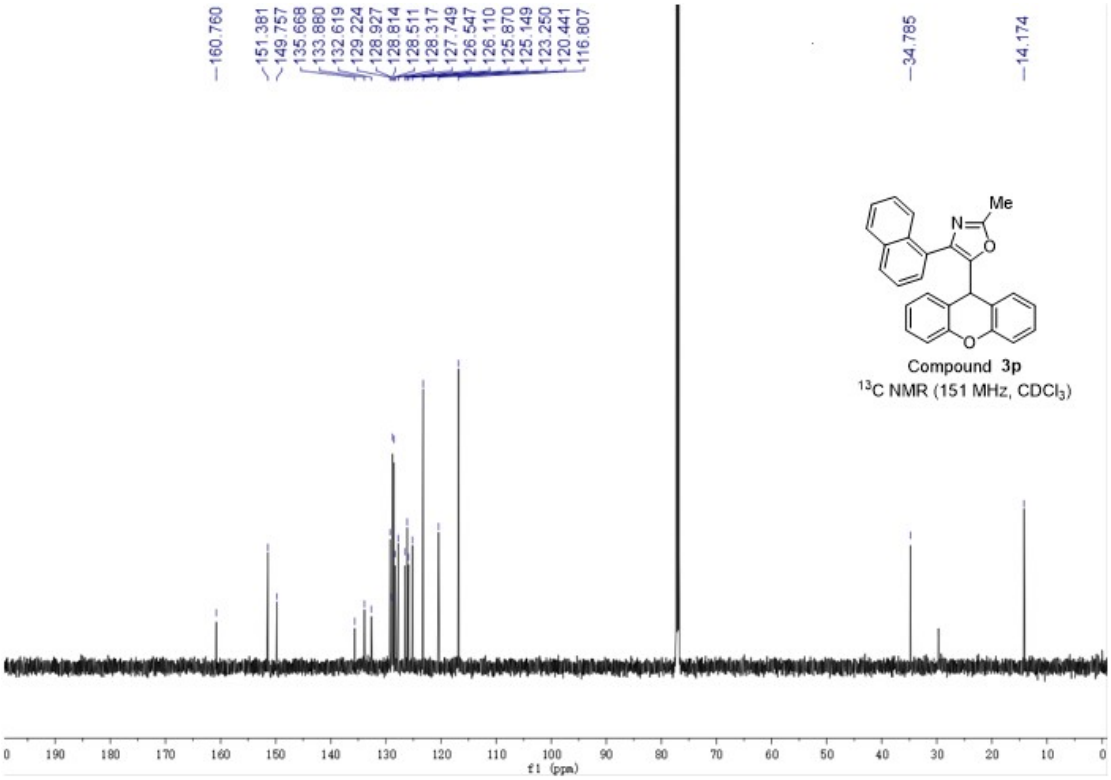




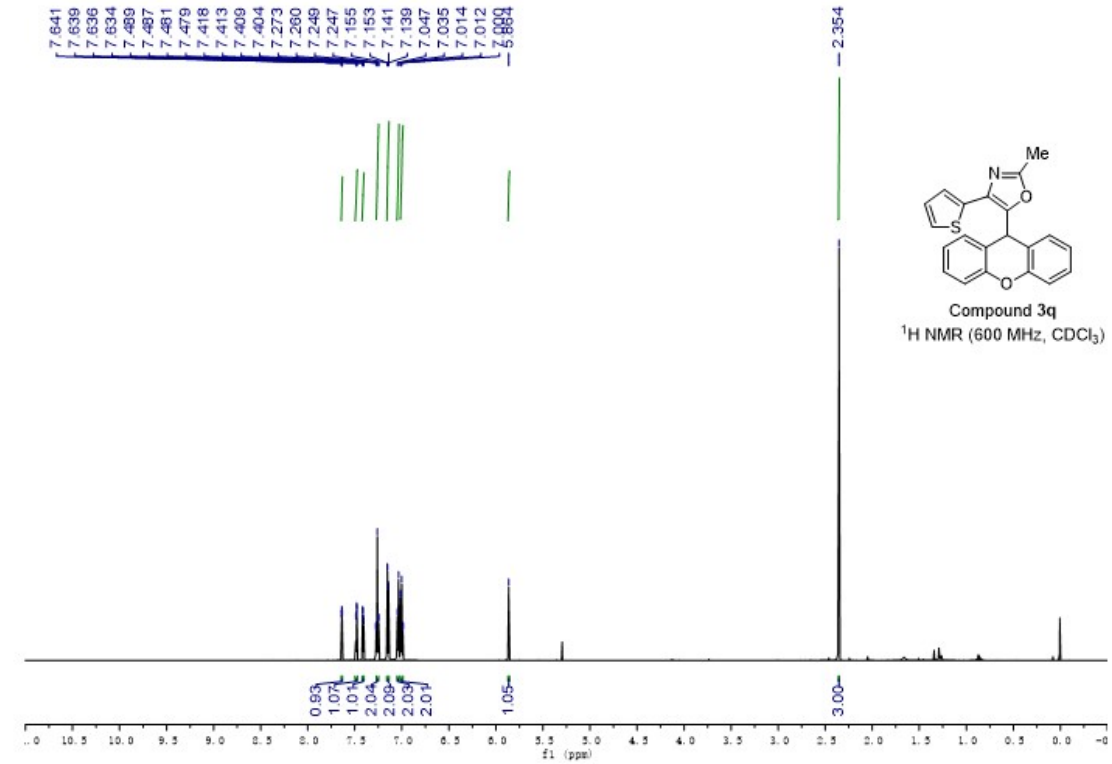


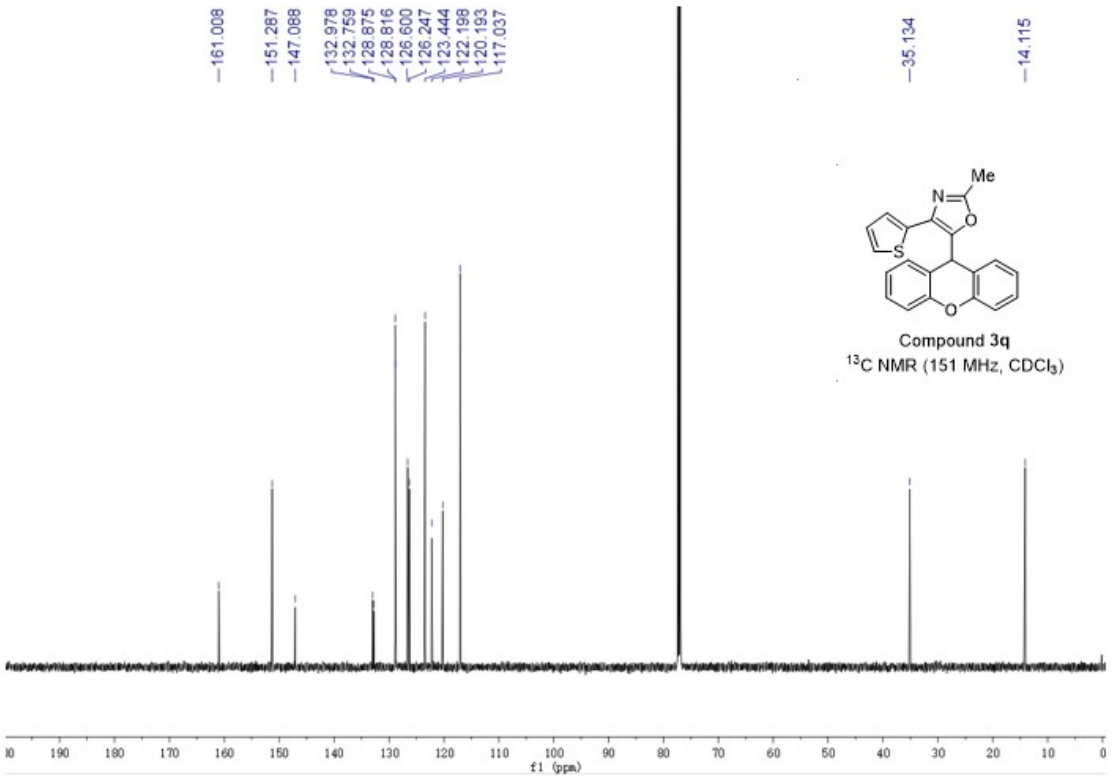
NMR spectra of 2-Methyl-4-(naphthalen-1-yl)-5-(9*H*-xanthen-9-yl)oxazole (**3p**)



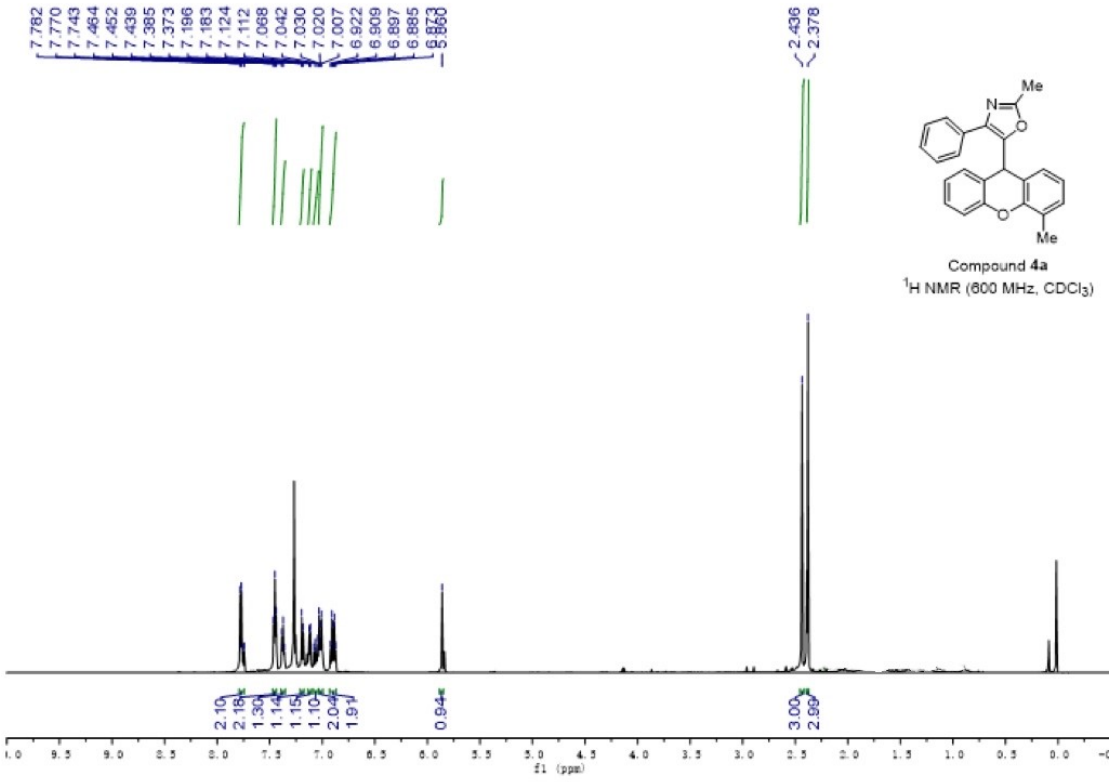


NMR spectra of 2-Methyl-4-(thiophen-2-yl)-5-(9*H*-xanthen-9-yl)oxazole (**3q**)



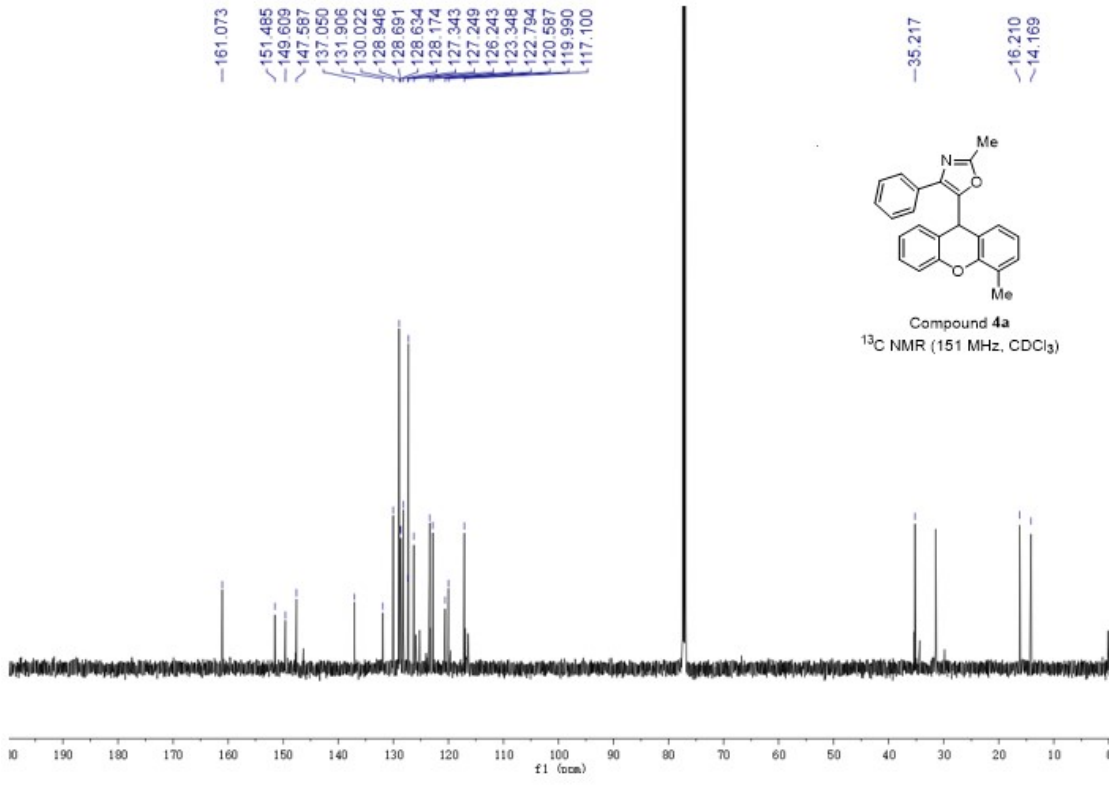


NMR spectra of 2-Methyl-5-(4-methyl-9*H*-xanthen-9-yl)-4-phenyloxazole (**4a**)



Compound **4a**

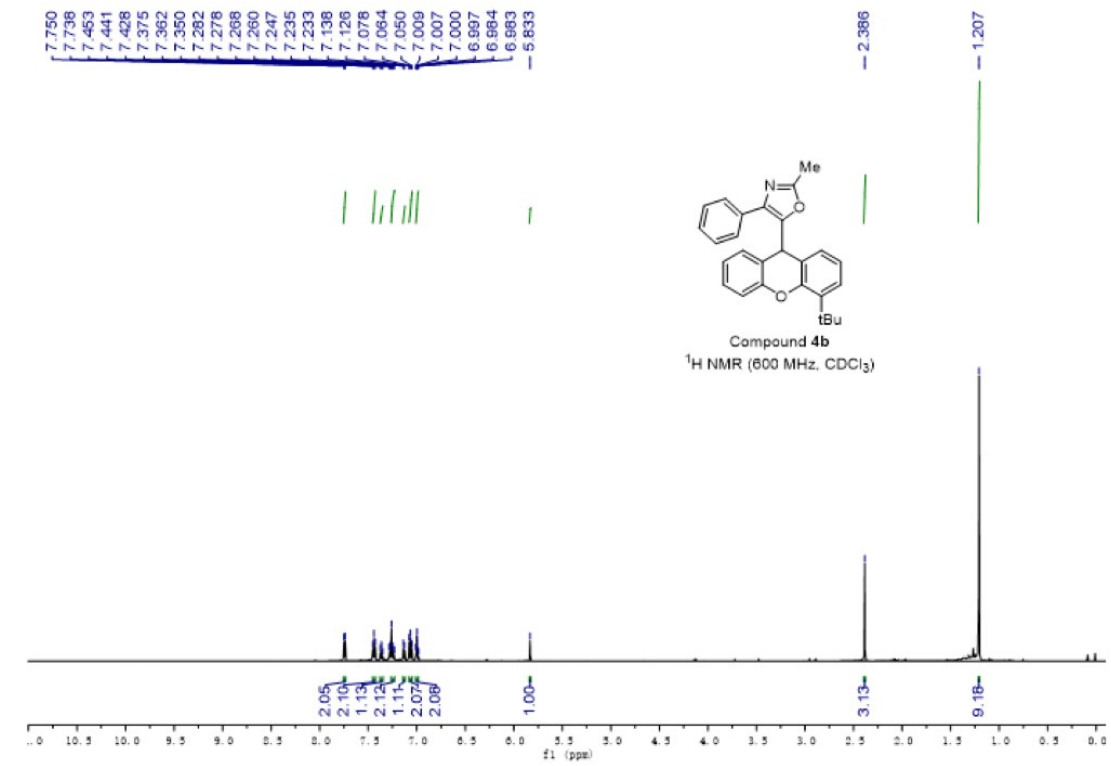
^{1}H NMR (600 MHz, $CDCl_3$)

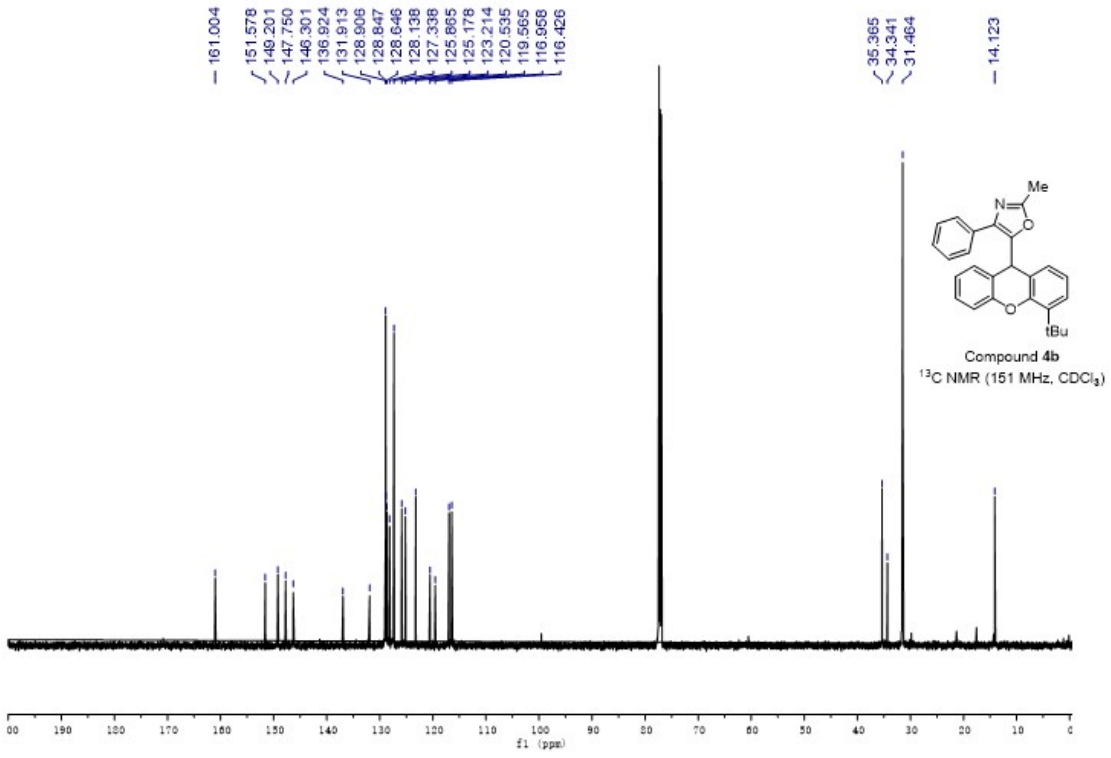


Compound **4a**

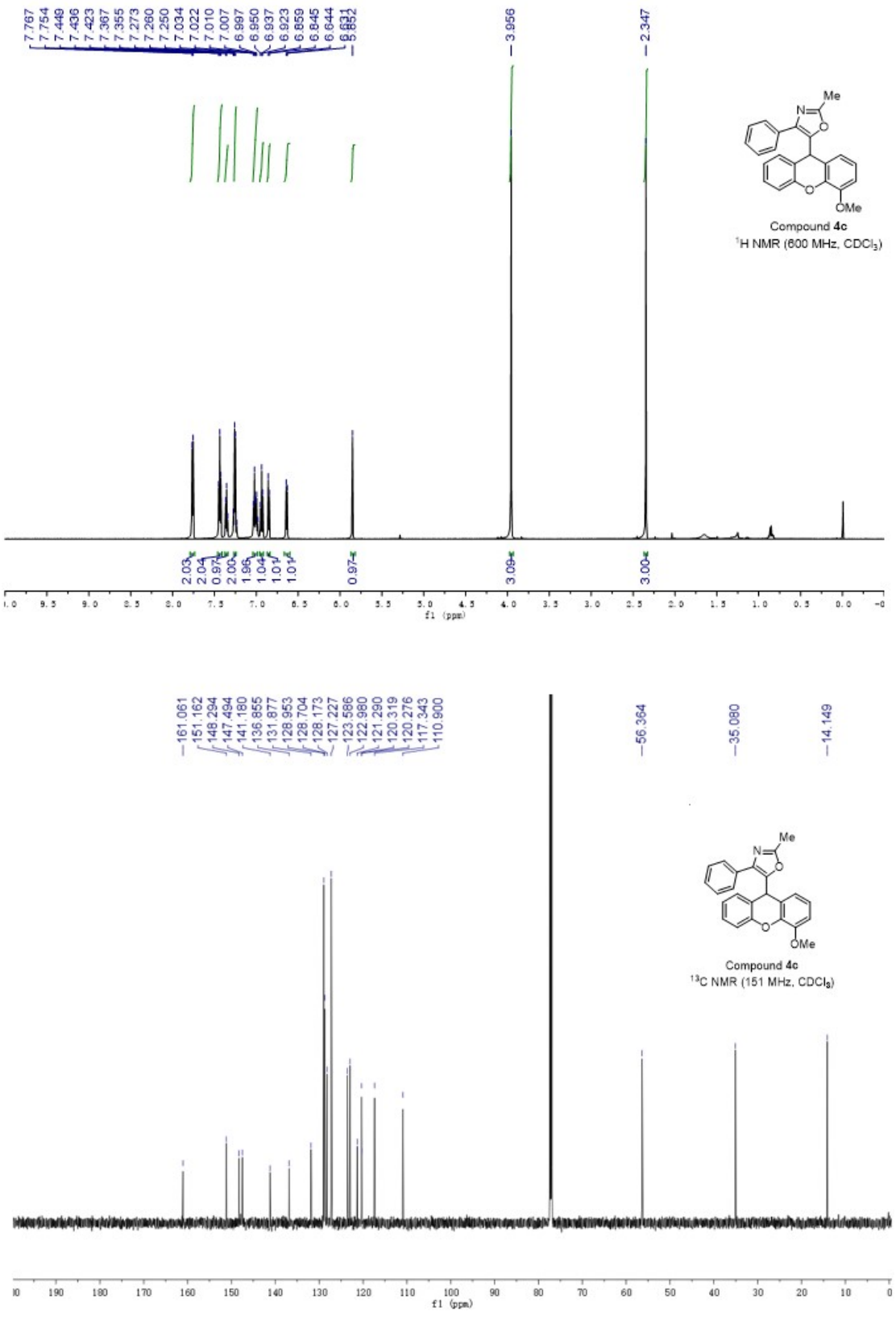
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 5-(4-(*tert*-butyl)-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazol (**4b**)

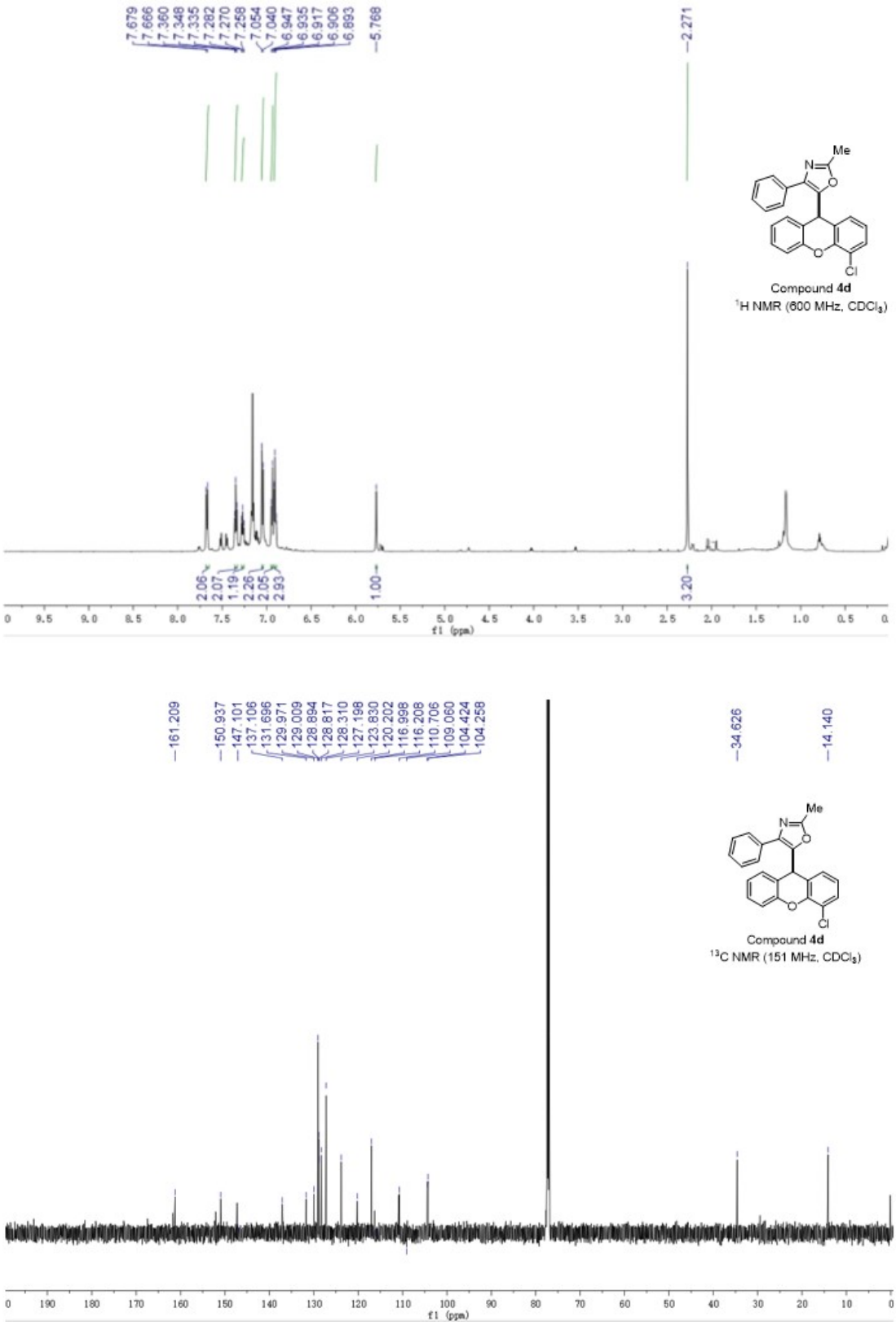




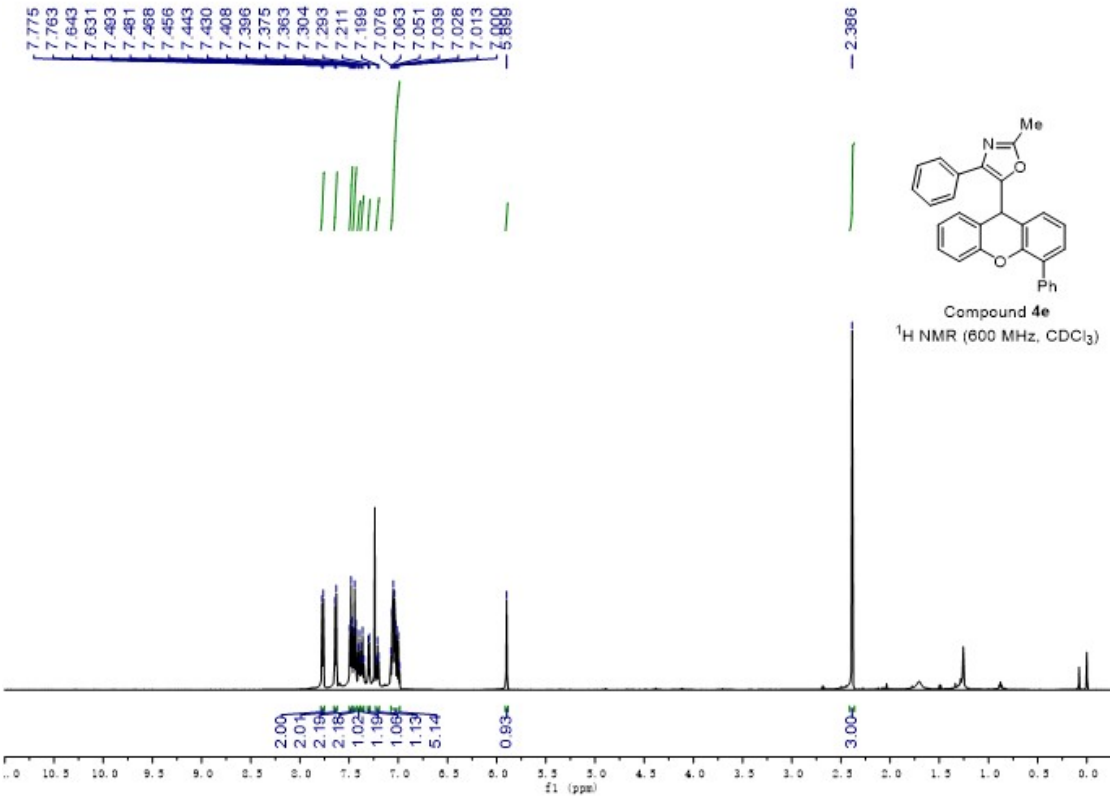
NMR spectra of 5-(4-methoxy-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazol (**4c**)

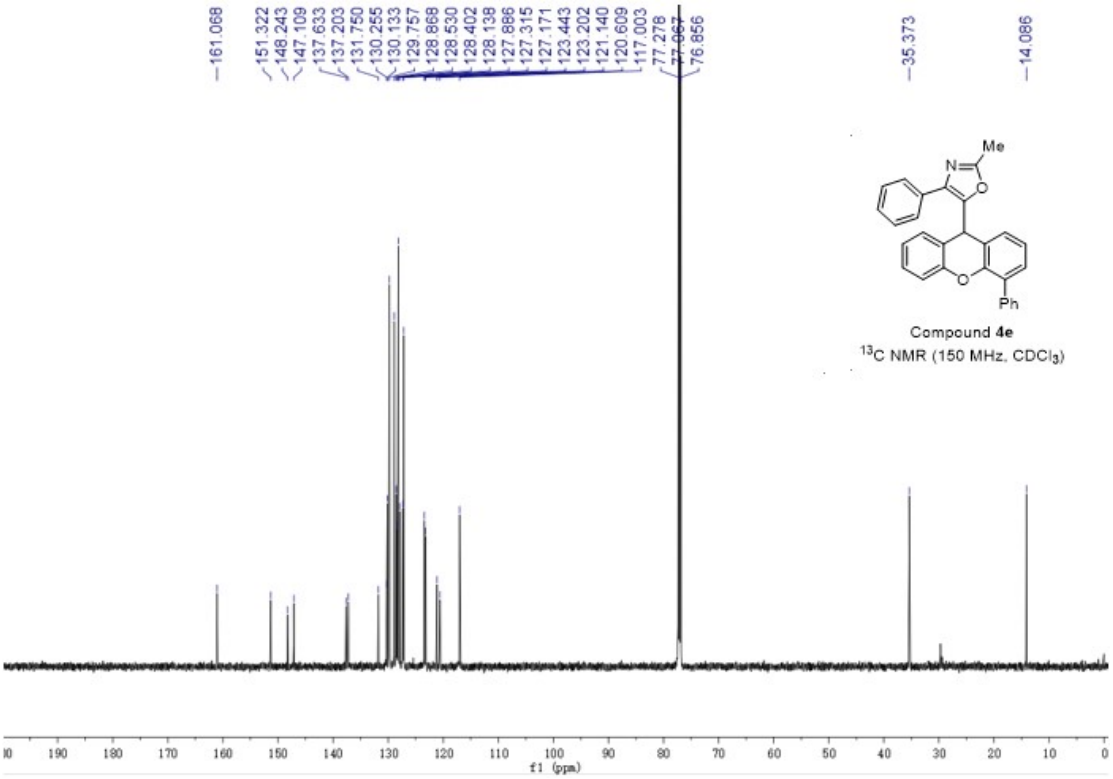


NMR spectra of 5-(4-chloro-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazole (**4d**)

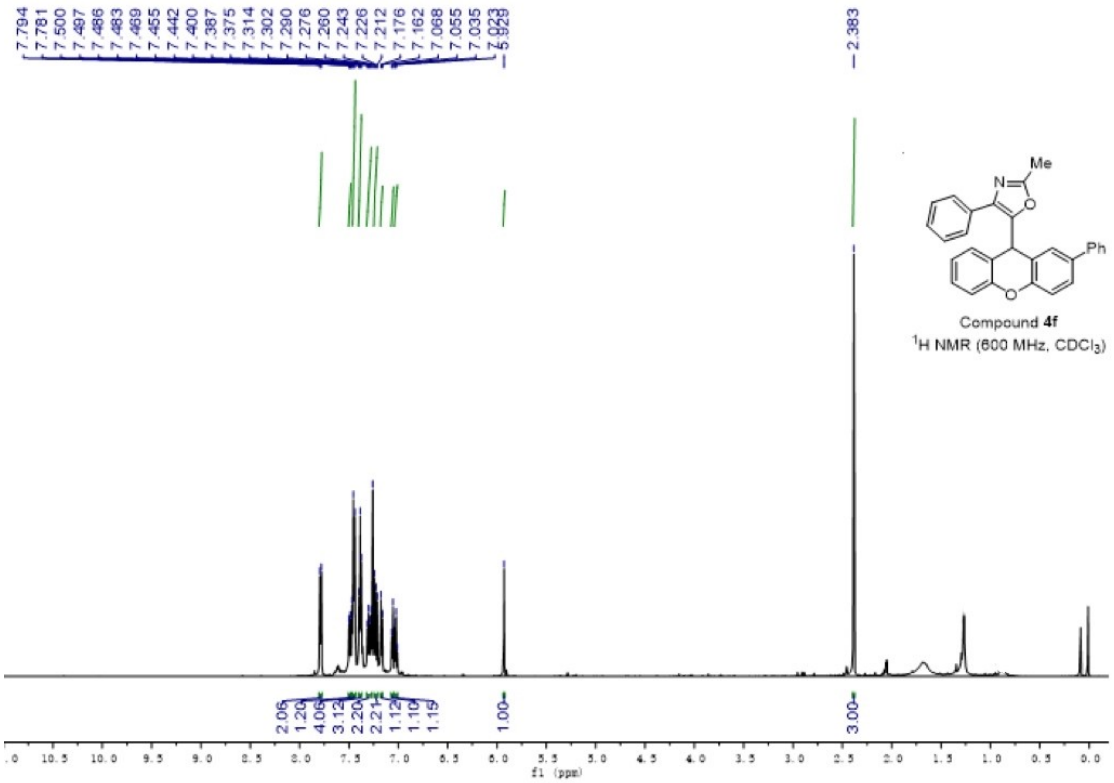


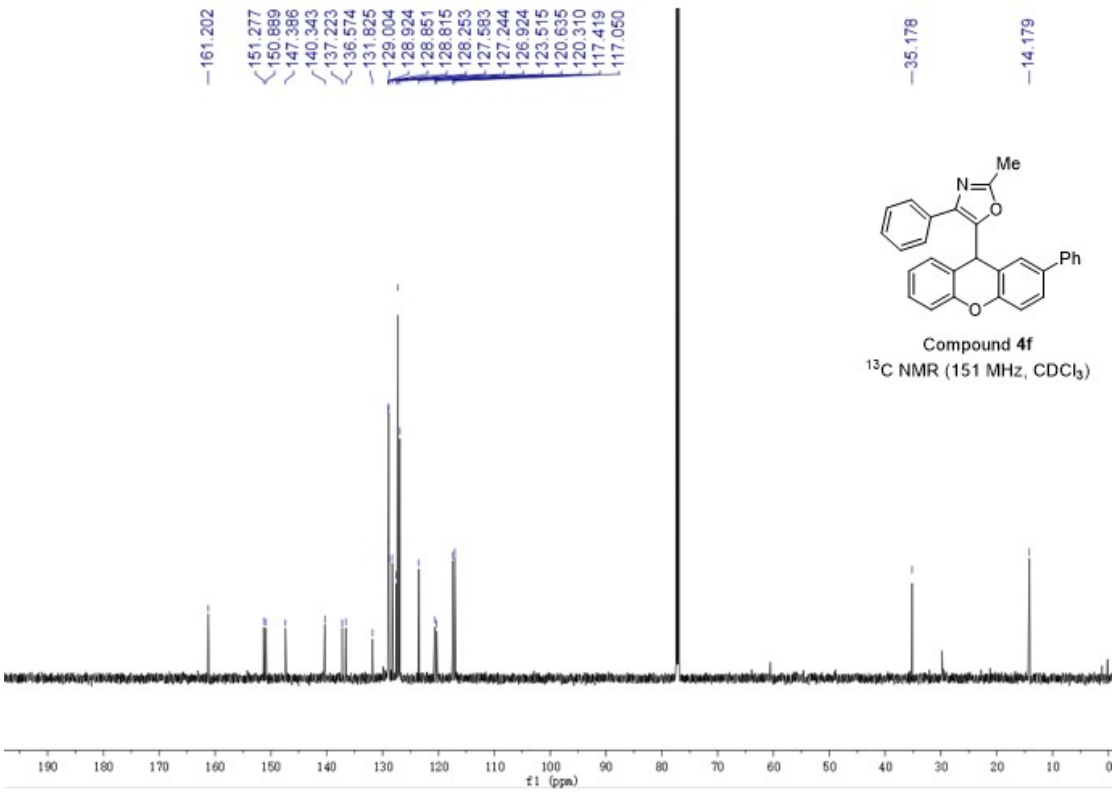
NMR spectra of 2-methyl-4-phenyl-5-(4-phenyl-9*H*-xanthen-9-yl)oxazole (**4e**)



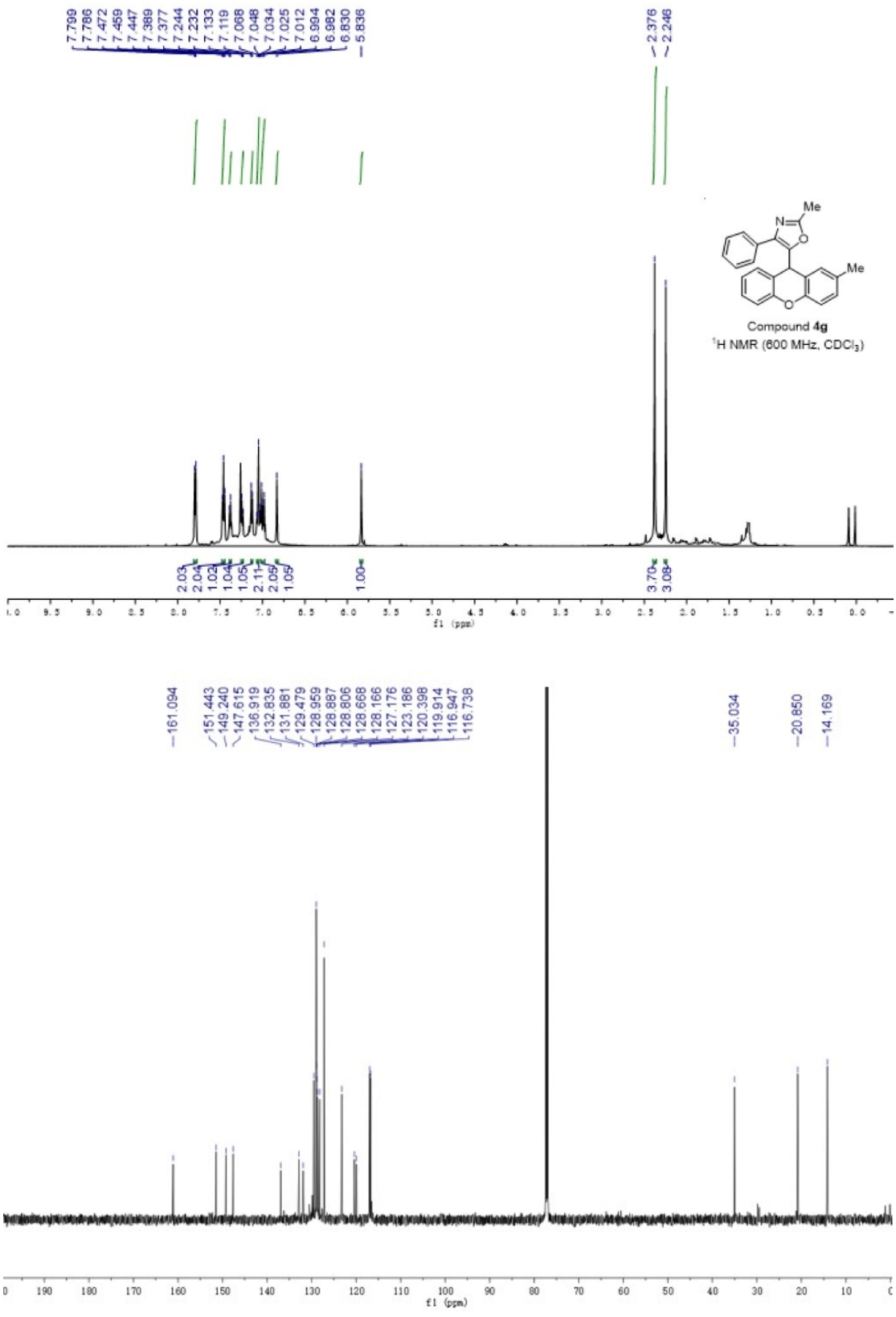


NMR spectra of 2-methyl-4-phenyl-5-(2-phenyl-9*H*-xanthen-9-yl)oxazole (**4f**)

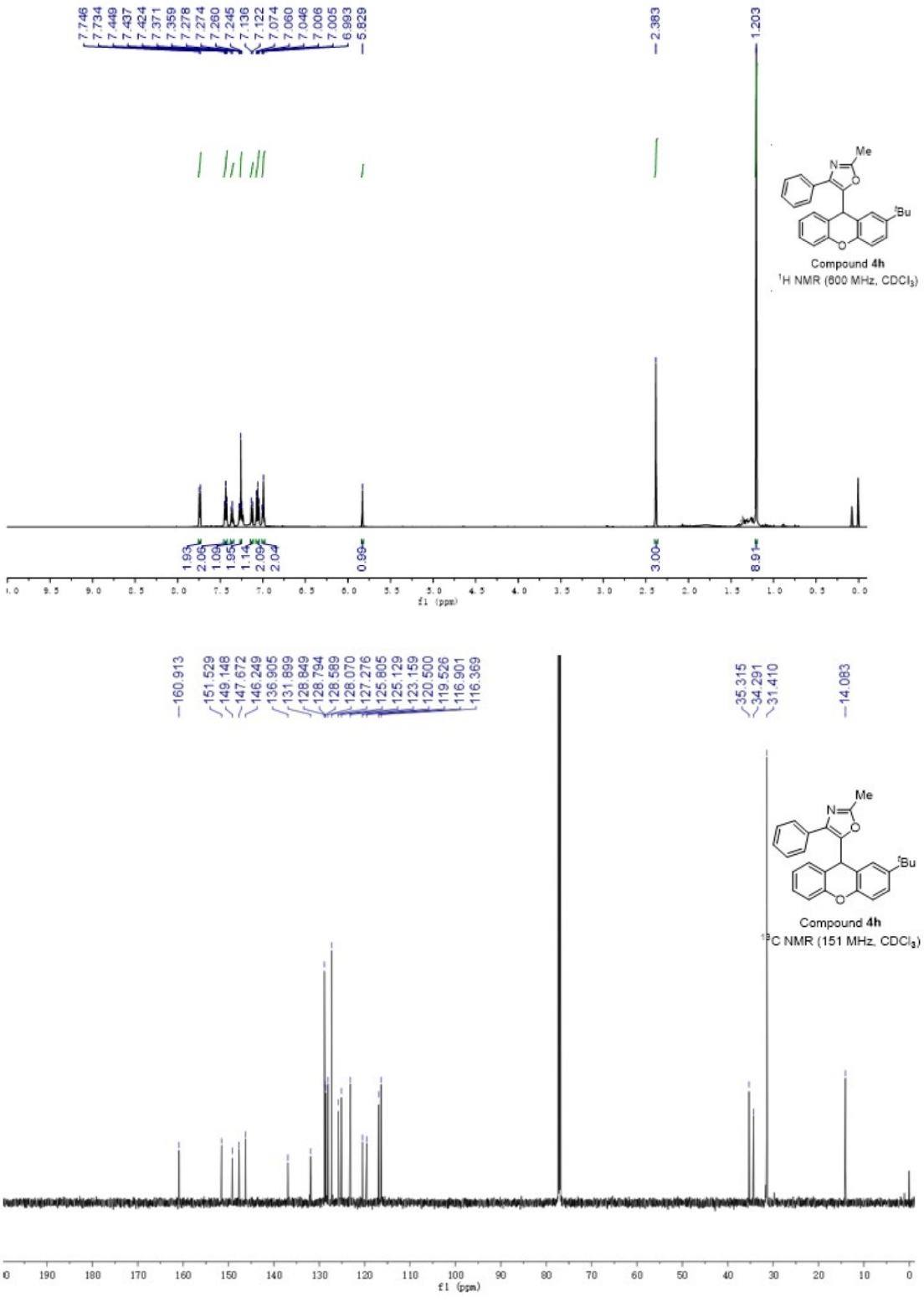




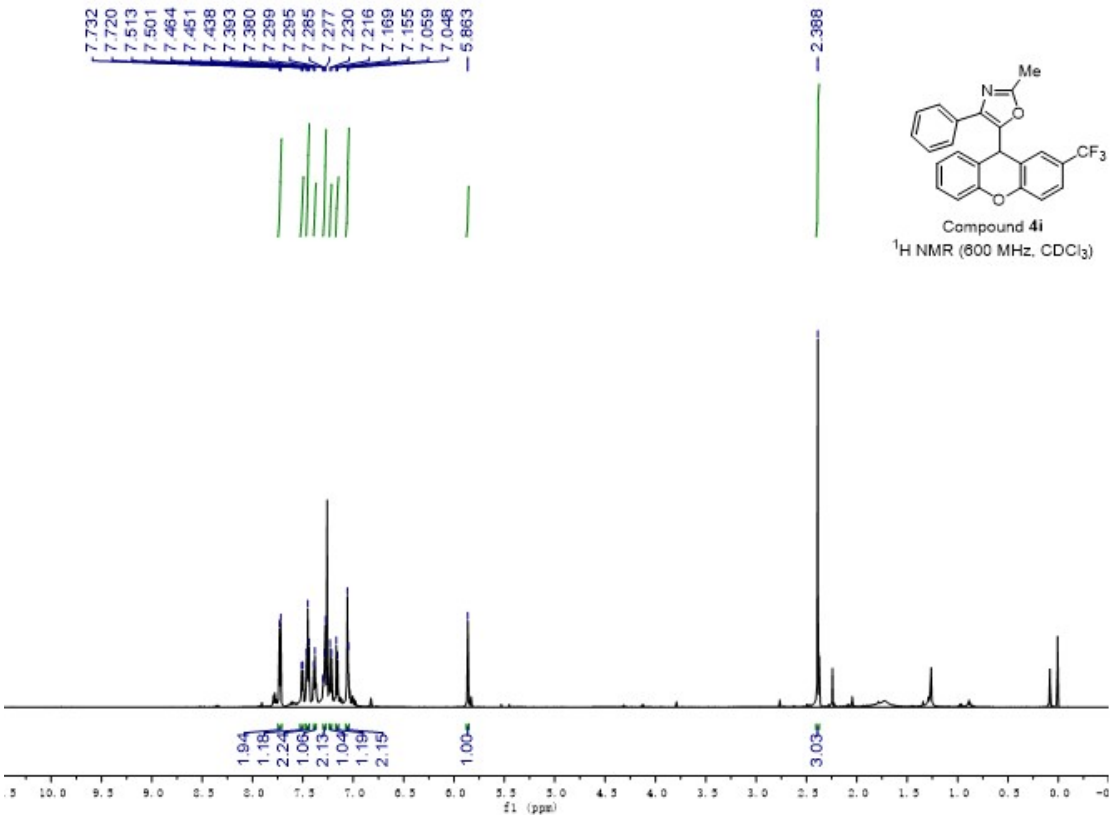
NMR spectra of 2-Methyl-5-(2-methyl-9H-xanthen-9-yl)-4-phenyloxazole (**4g**)



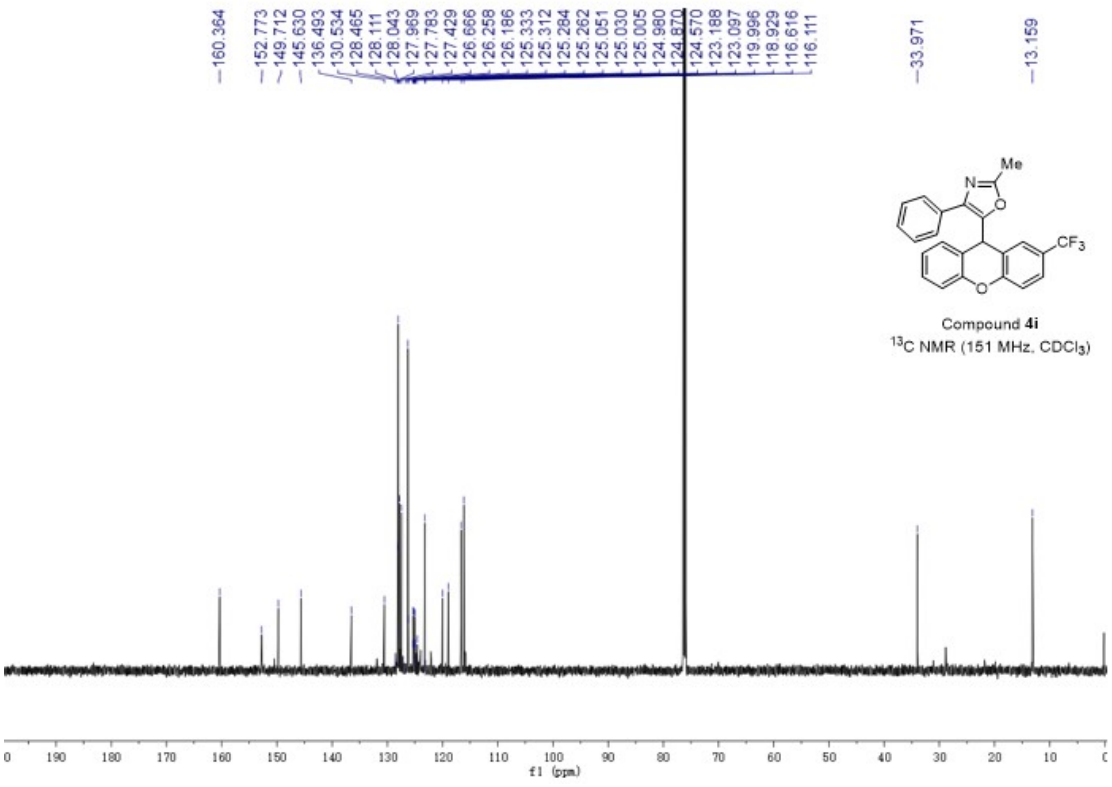
NMR spectra of 5-(2-(*tert*-butyl)-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazole (**4h**)



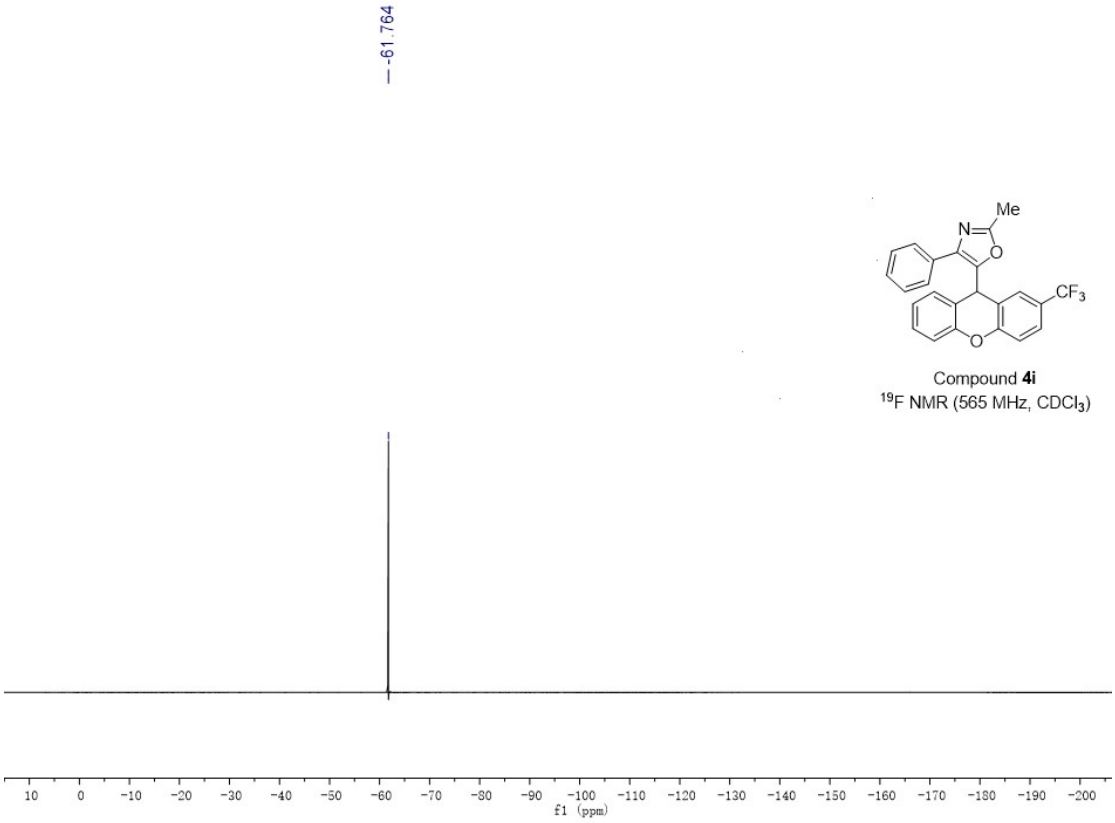
NMR spectra of 2-methyl-4-phenyl-5-(2-(trifluoromethyl)-9*H*-xanthen-9-yl)oxazole (**4i**)



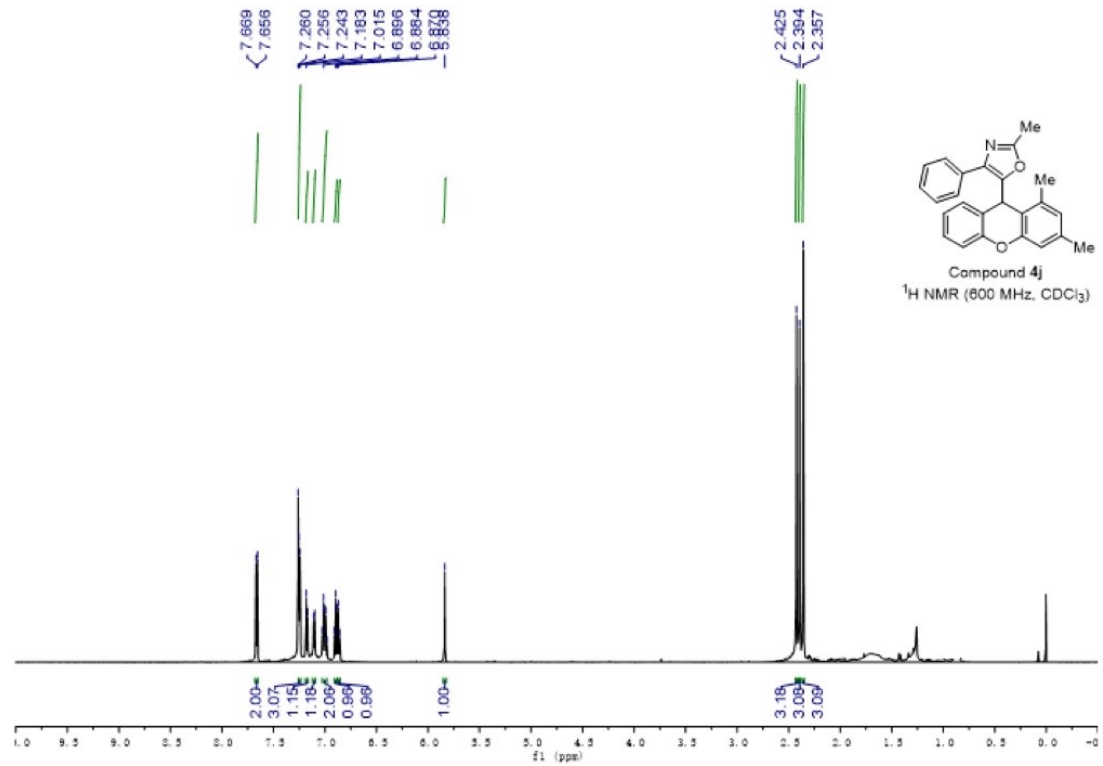
Compound **4i**
^{1}H NMR (600 MHz, $CDCl_3$)

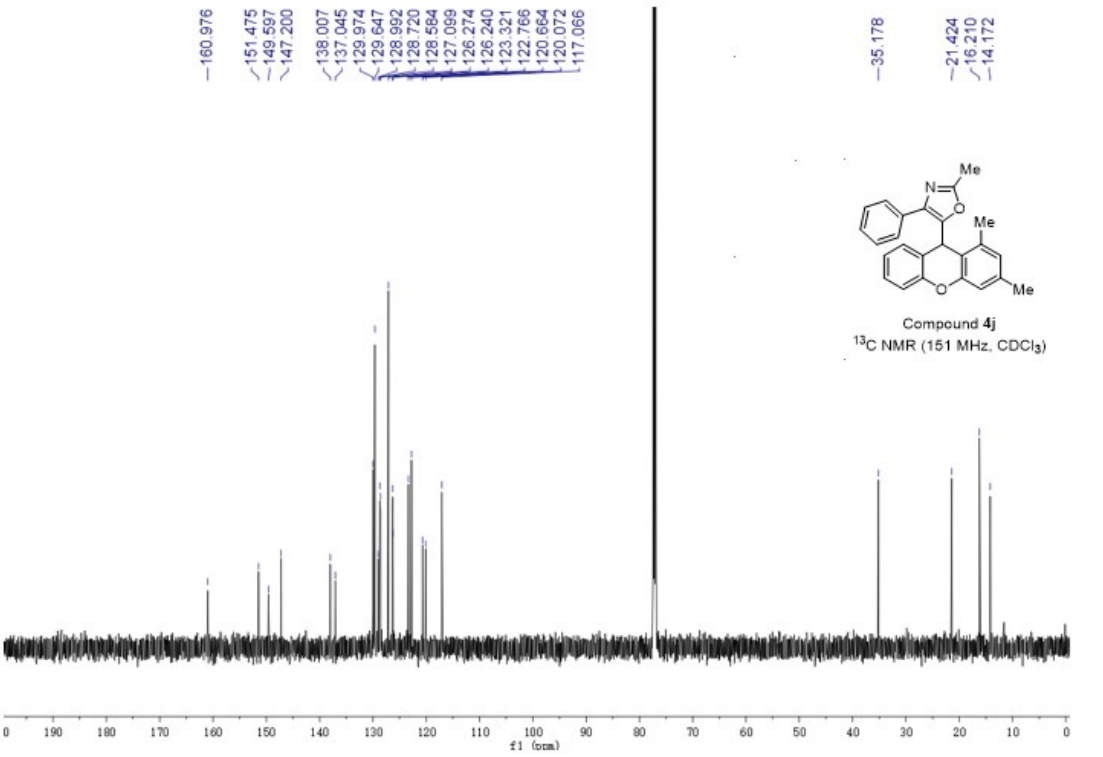


Compound **4i**
^{13}C NMR (151 MHz, $CDCl_3$)

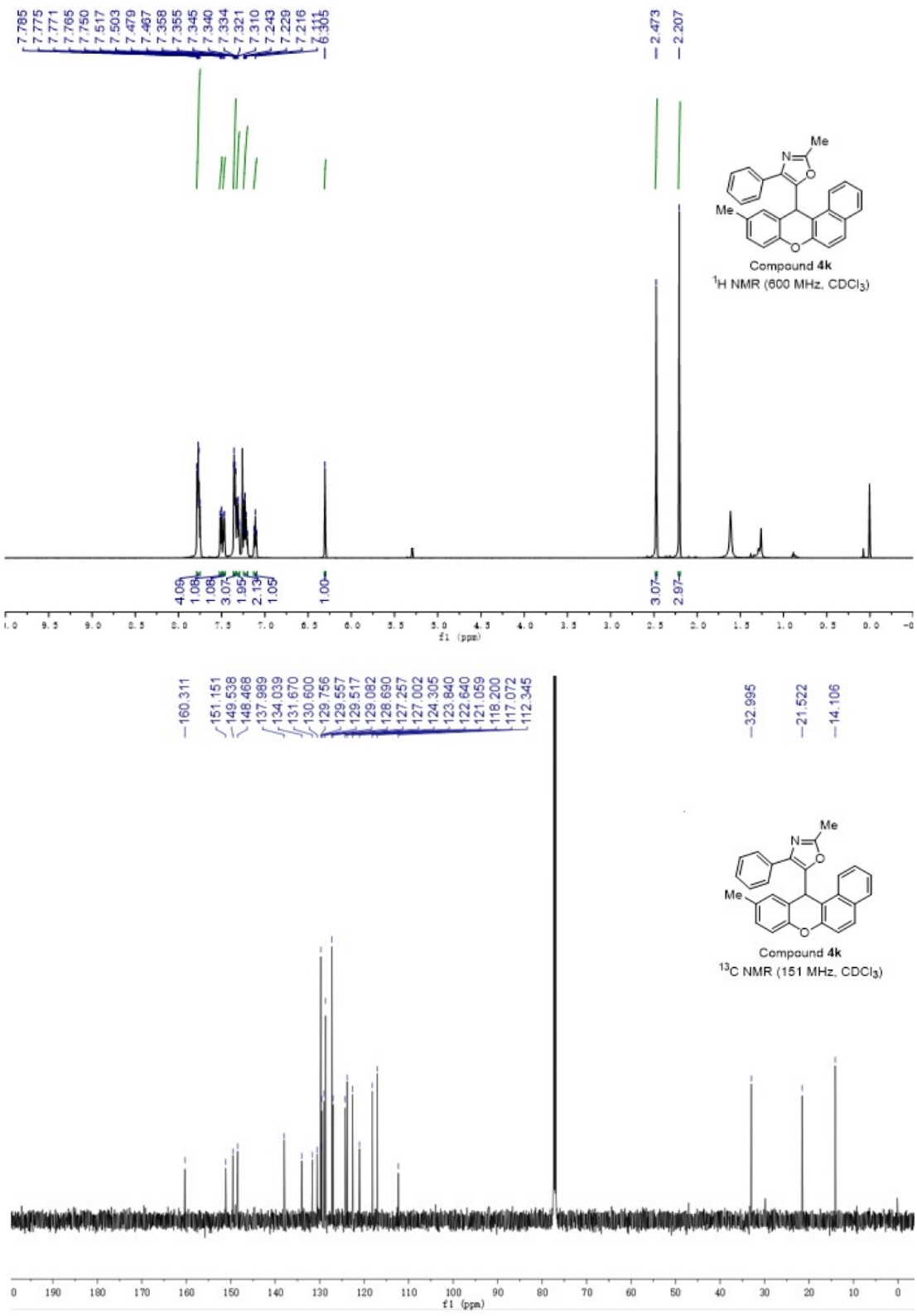


NMR spectra of 5-(1,3-Dimethyl-9*H*-xanthen-9-yl)-2-methyl-4-phenyloxazo **(4j)**

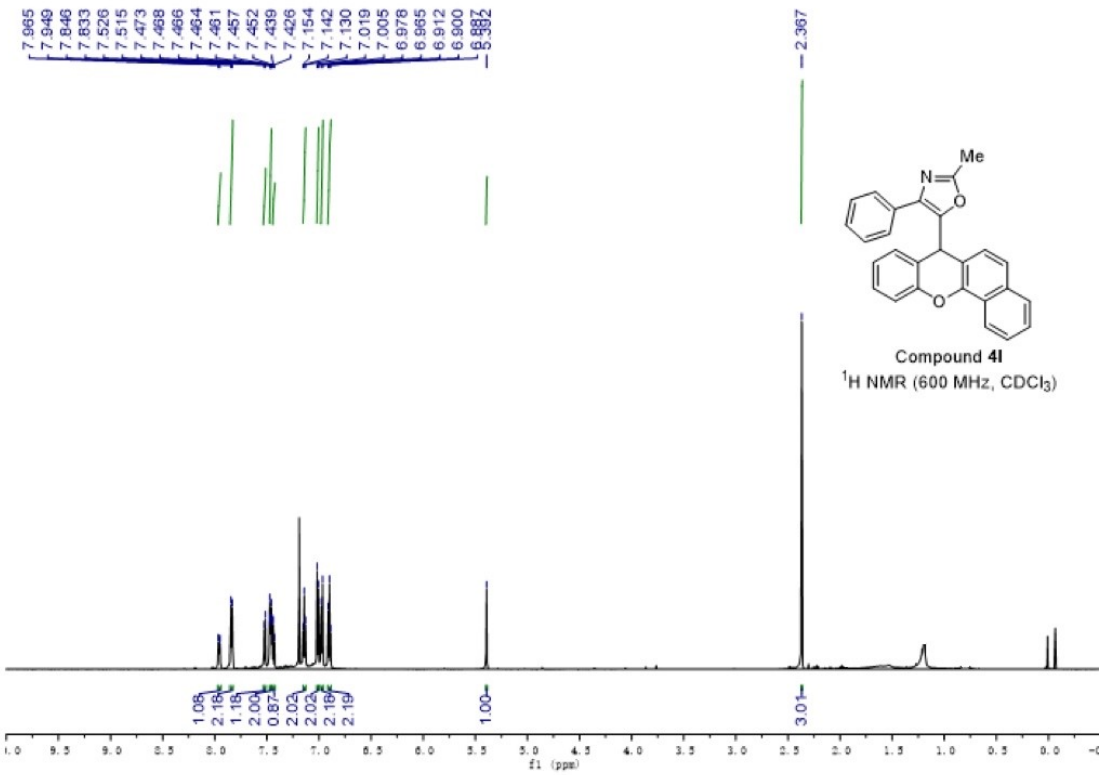


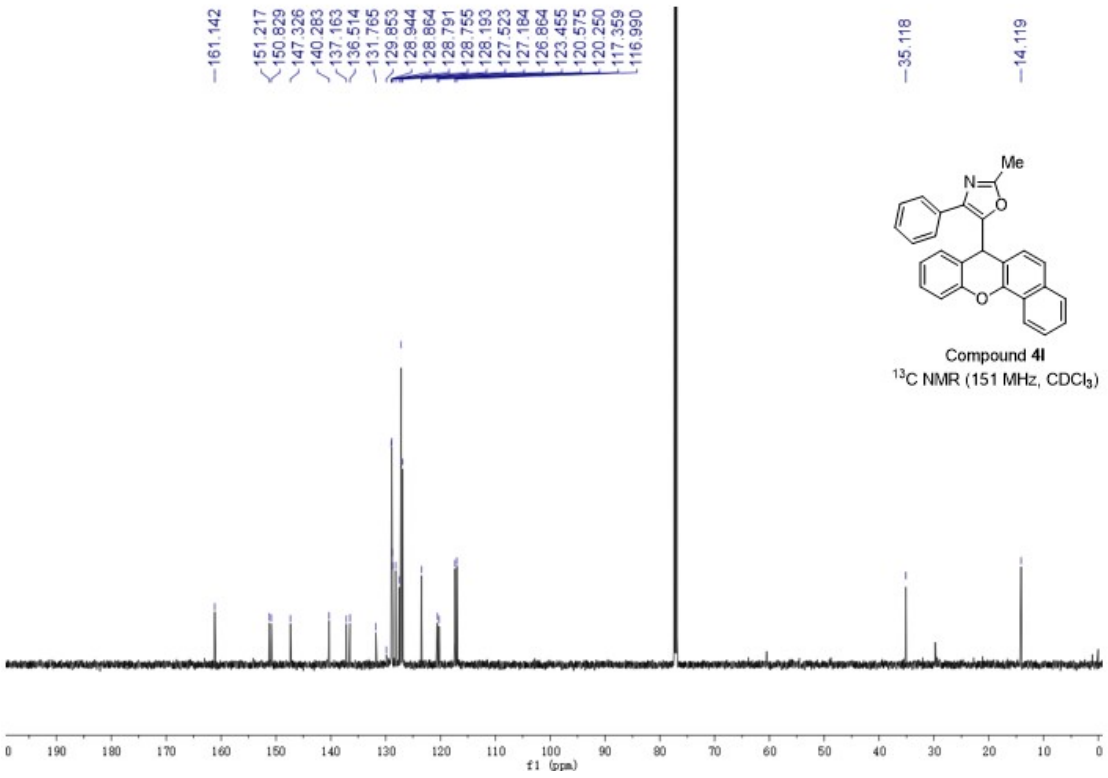


NMR spectra of 2-Methyl-5-(10-methyl-12H-benzo[a]xanthen-12-yl)-4-phenyloxazole **(4k)**

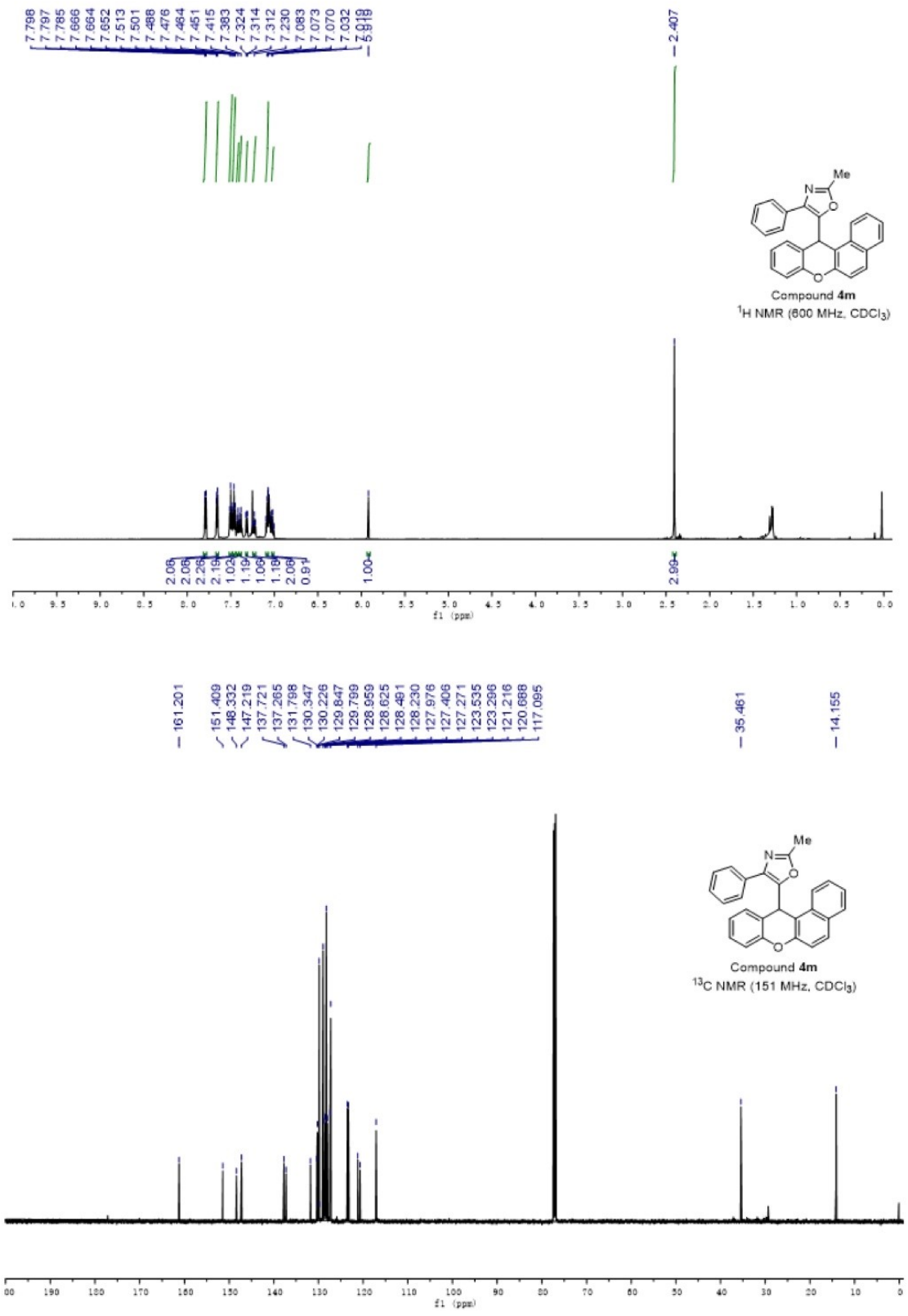


NMR spectra of 5-(7*H*-benzo[c]xanthen-7-yl)-2-methyl-4-phenyloxazole (**4l**)

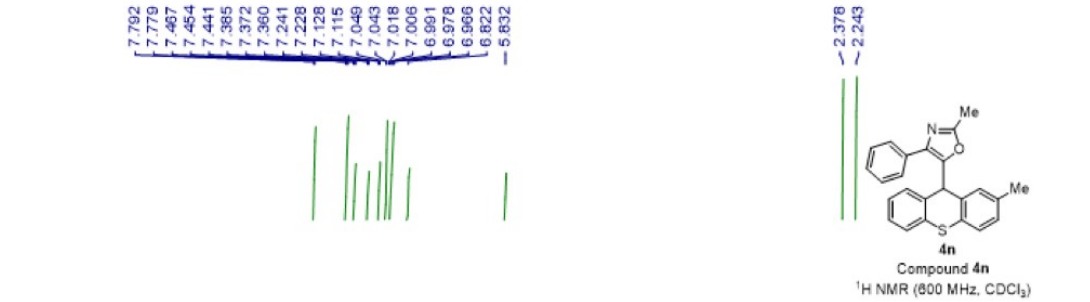




NMR spectra of 5-(12*H*-benzo[a]xanthen-12-yl)-2-methyl-4-phenyloxazole (**4m**)

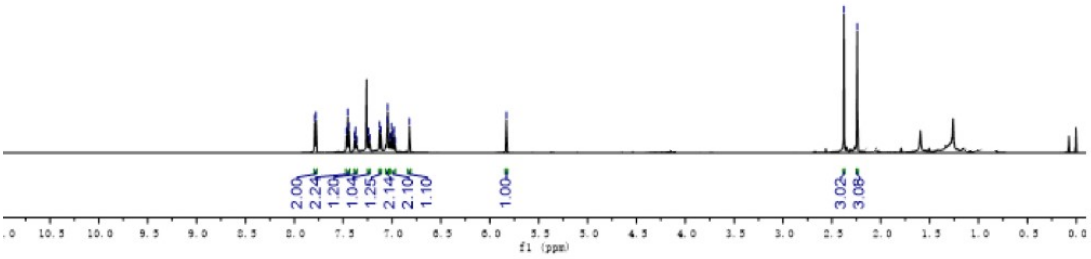


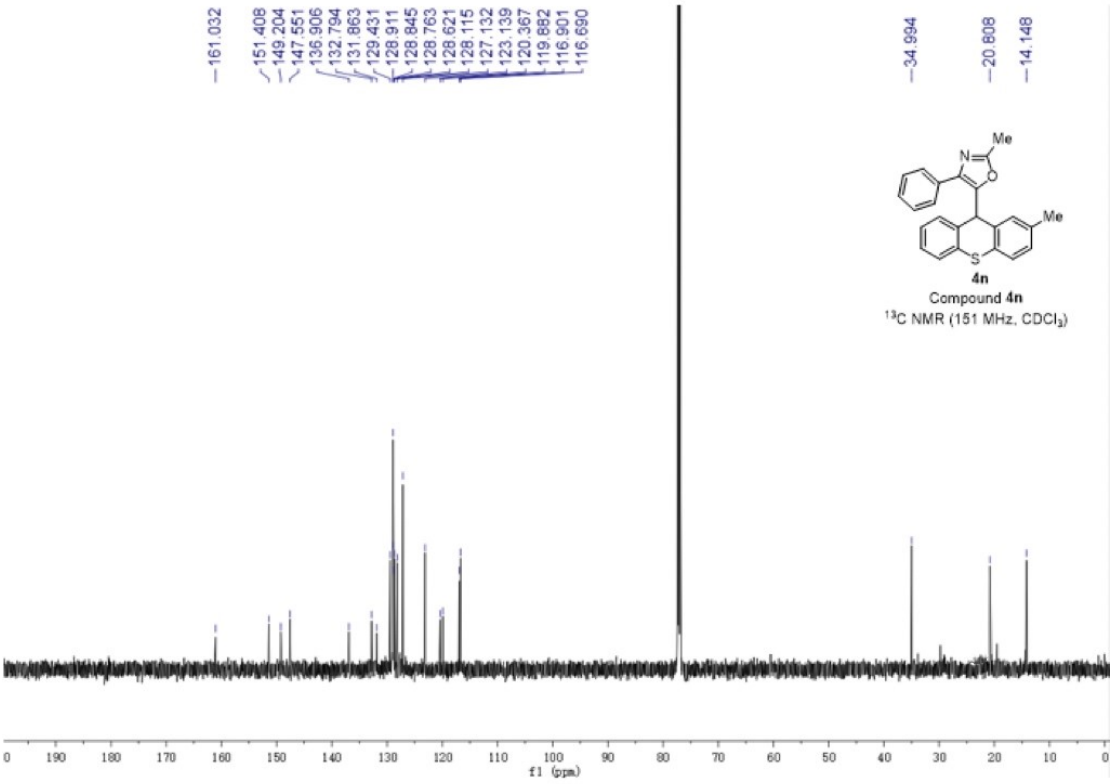
NMR spectra of 2-Methyl-5-(2-methyl-9*H*-thioxanthen-9-yl)-4-phenyloxazole **(4n)**



Compound **4n**

^{1}H NMR (600 MHz, $CDCl_3$)

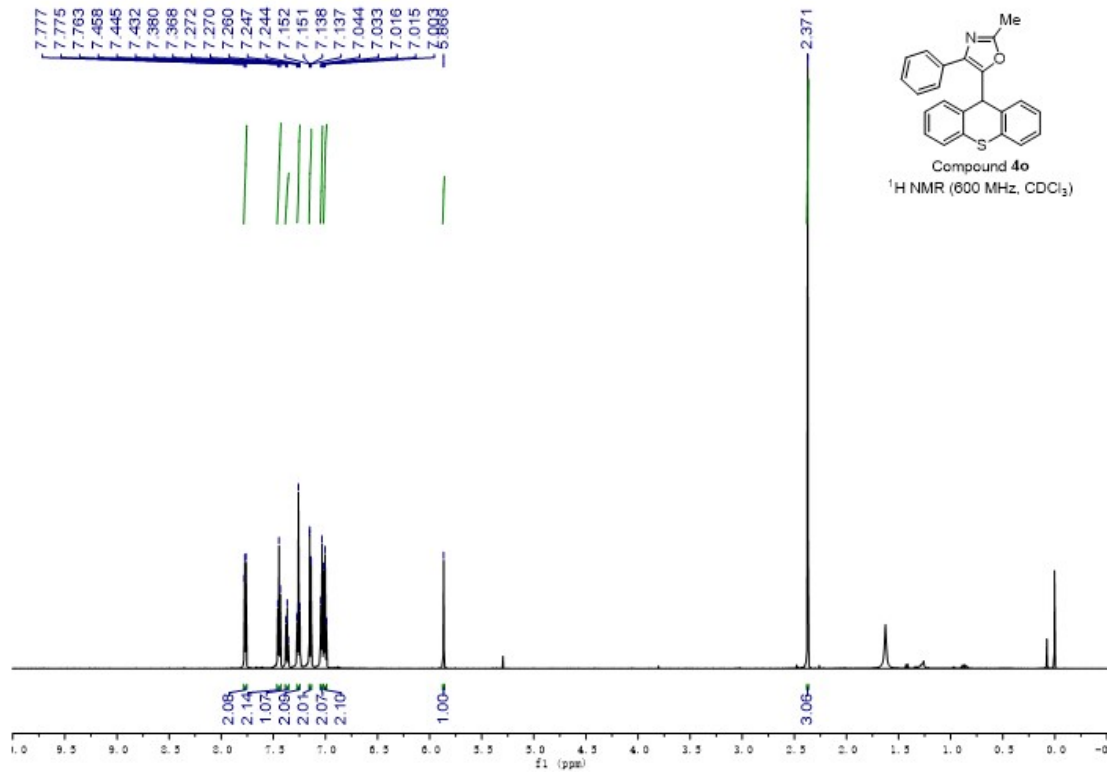


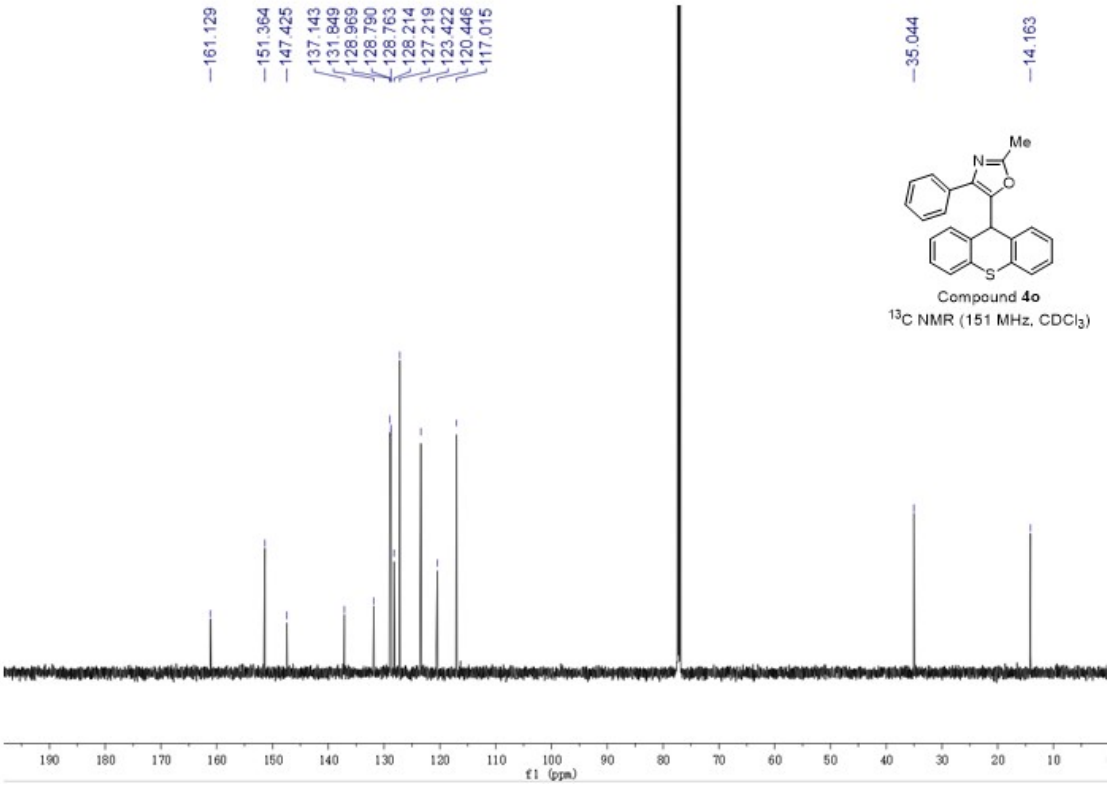


Compound **4n**

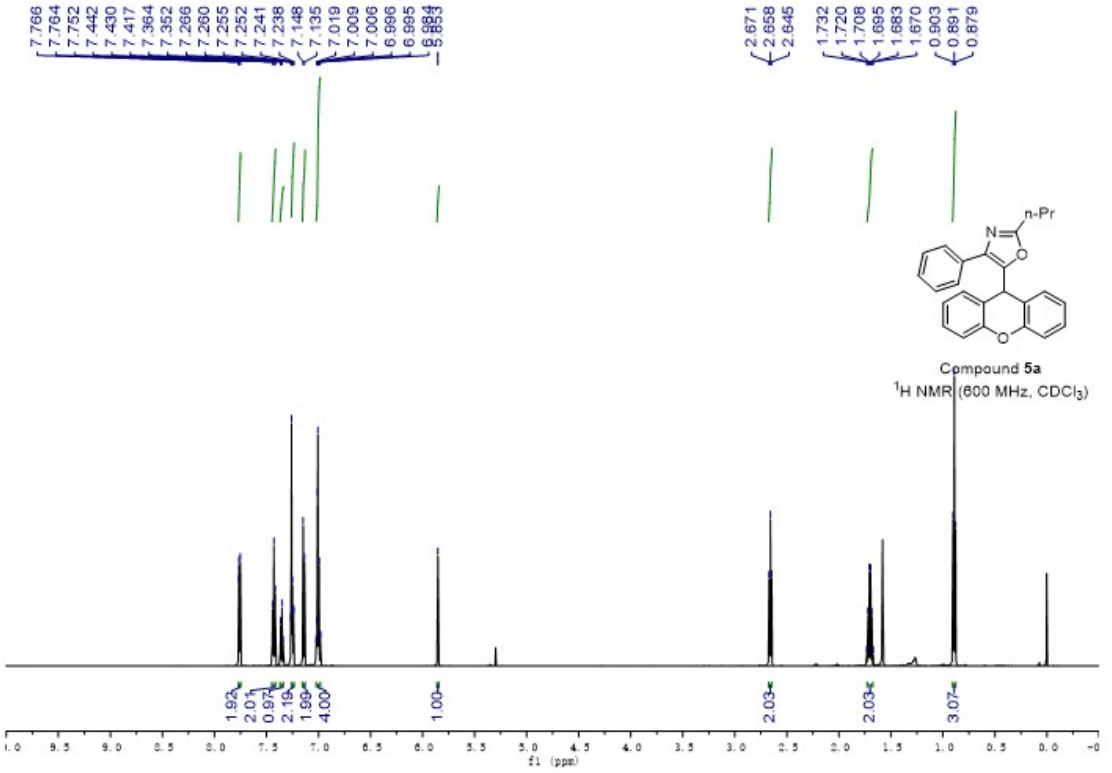
^{13}C NMR (151 MHz, $CDCl_3$)

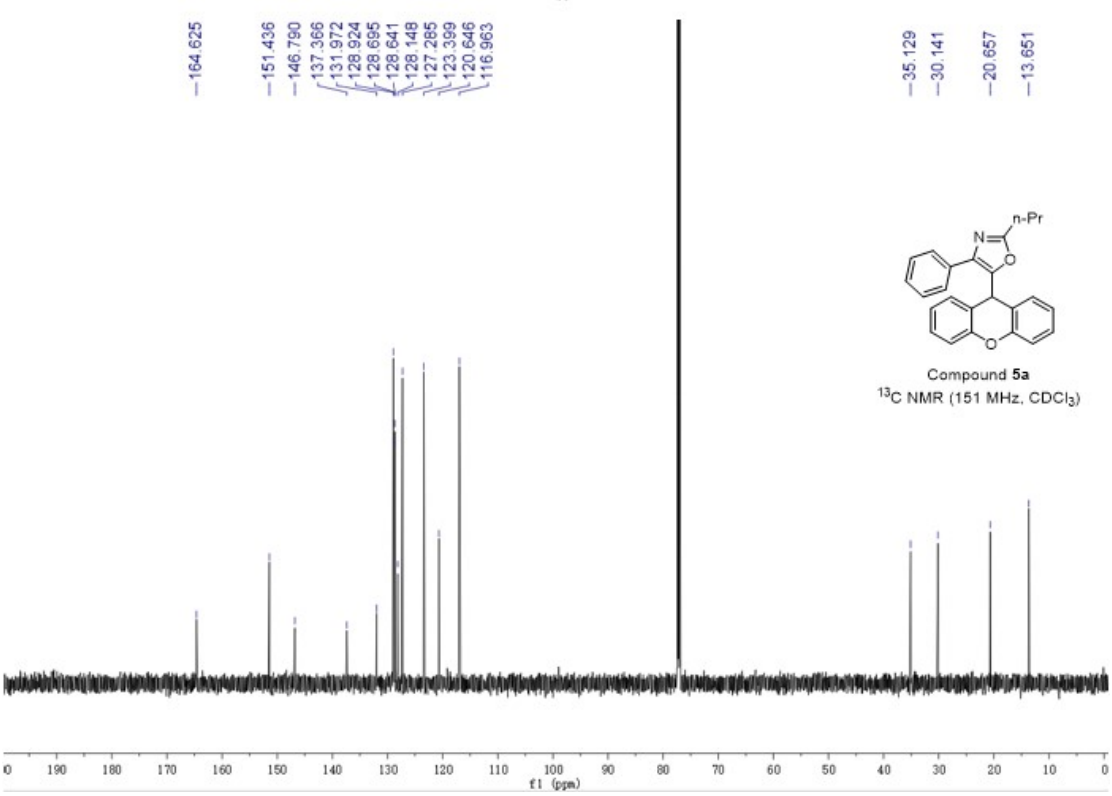
NMR spectra of 2-Methyl-4-phenyl-5-(9H-thioxanthen-9-yl)oxazole **(4o)**



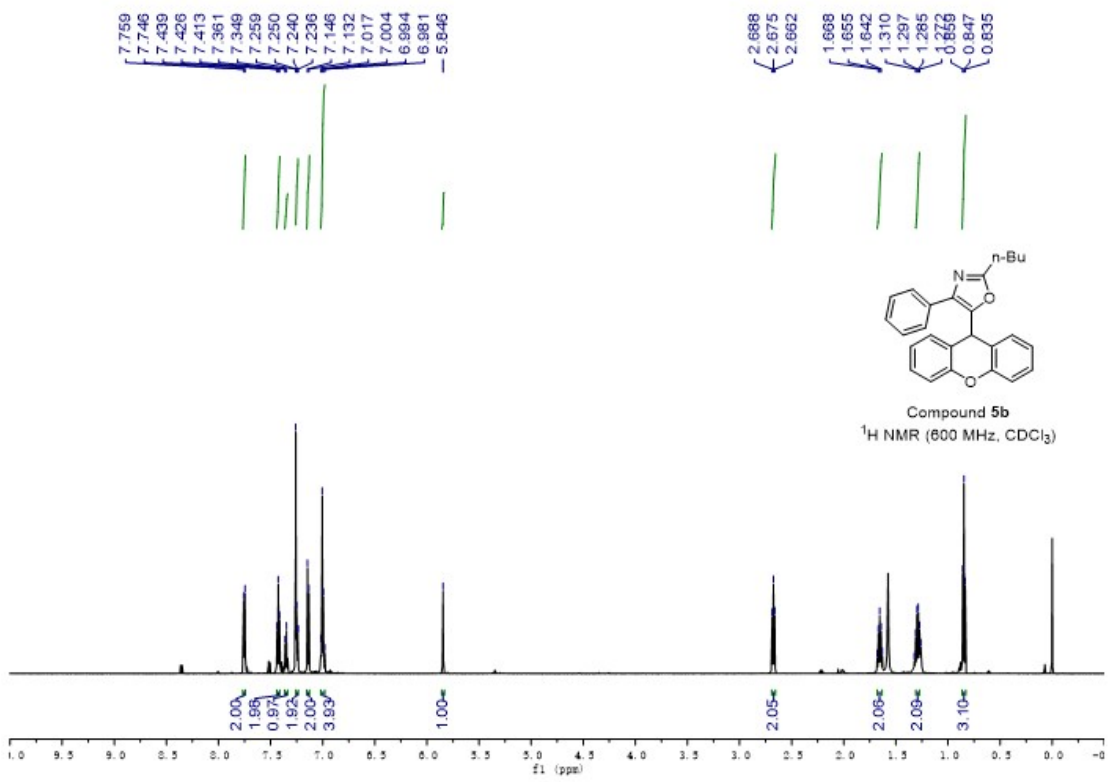


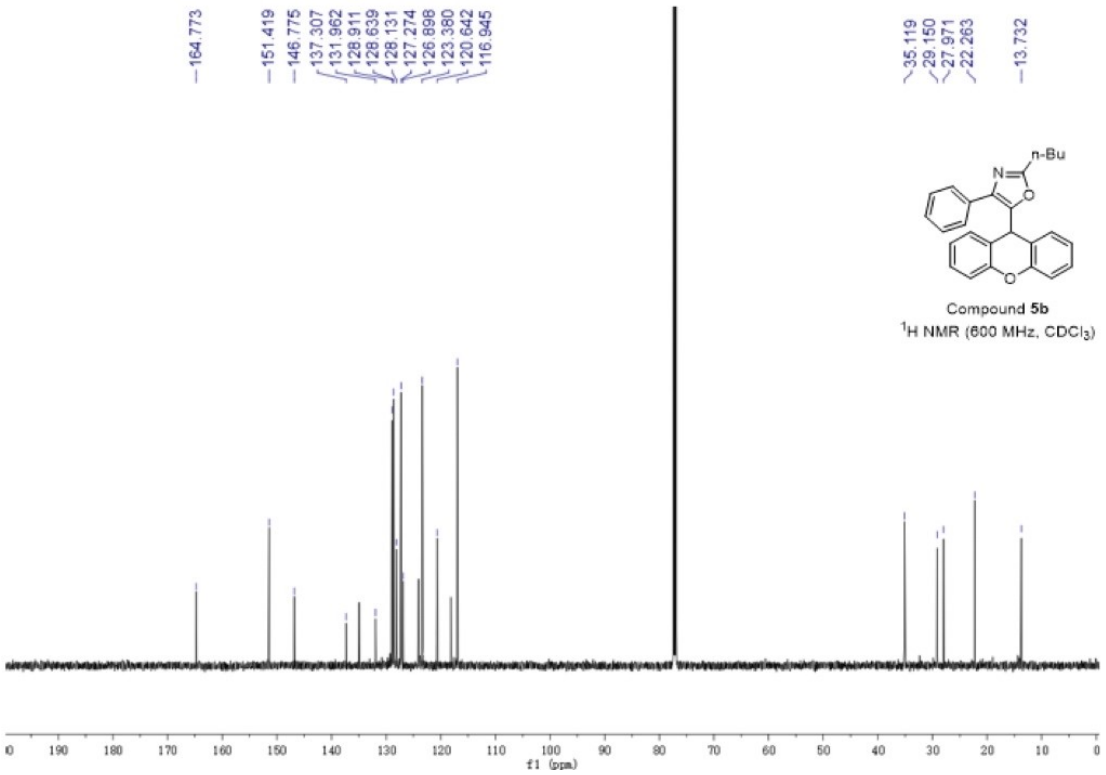
NMR spectra of 4-Phenyl-2-propyl-5-(9*H*-xanthen-9-yl)oxazole (**5a**)



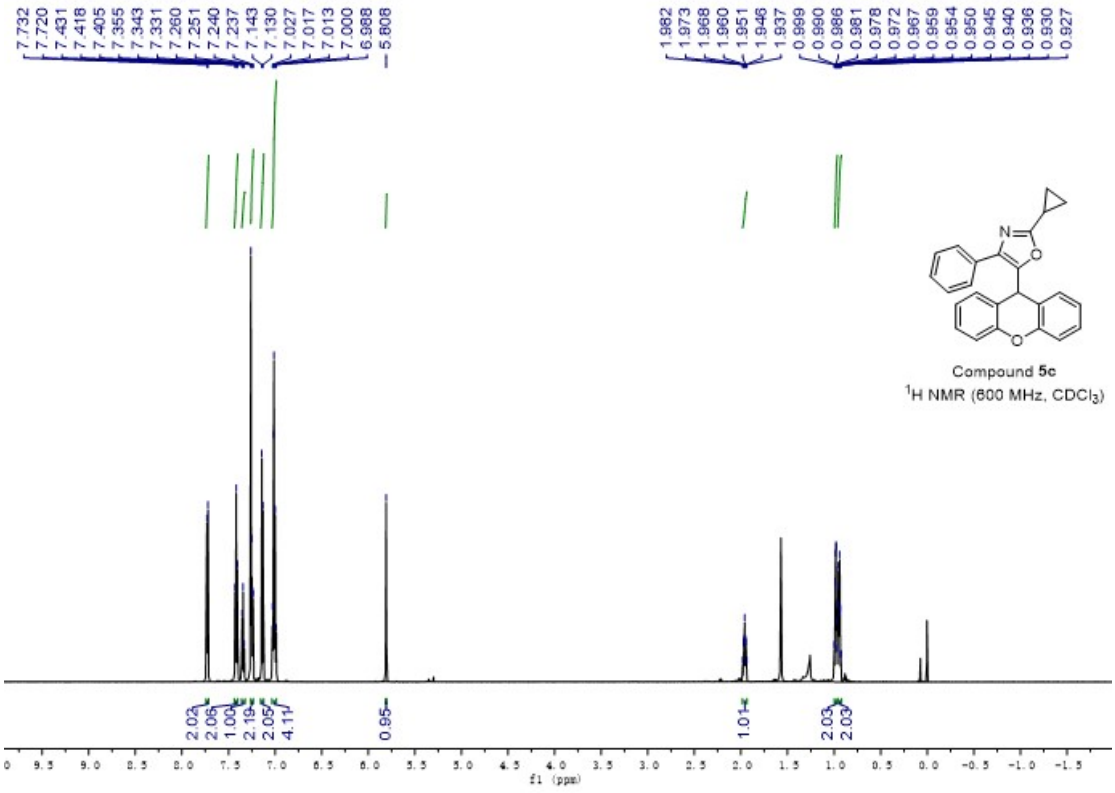


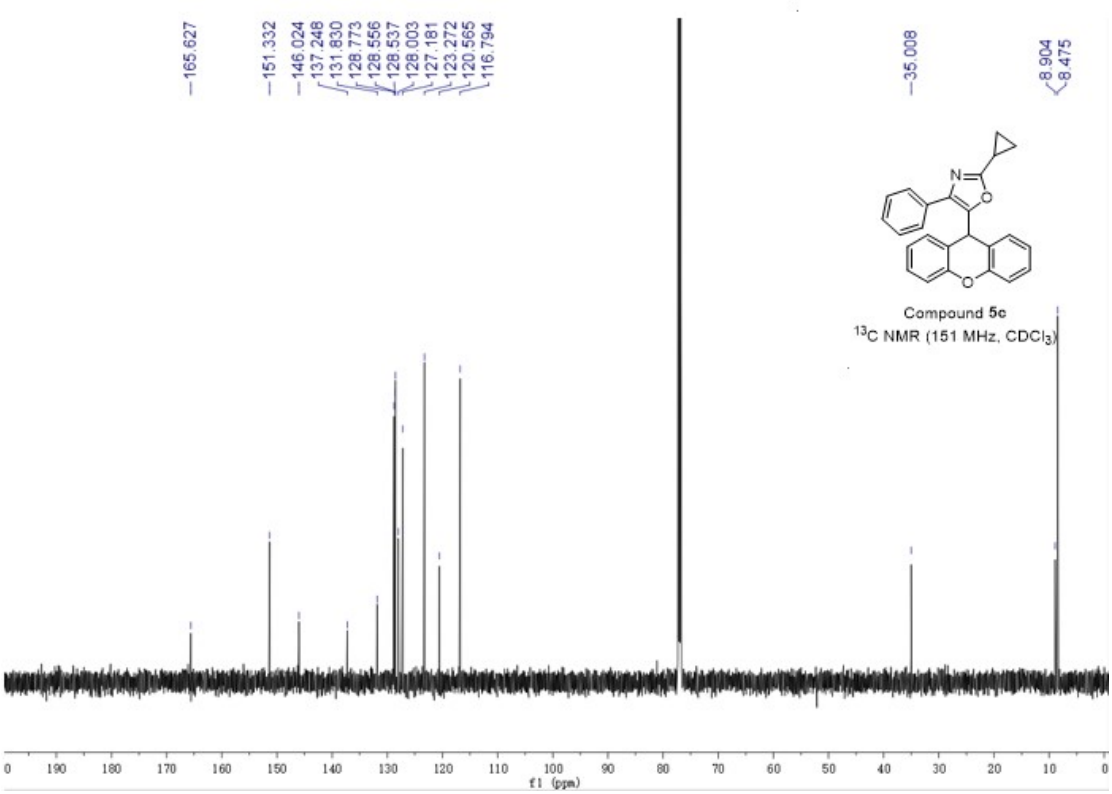
NMR spectra of 2-Butyl-4-phenyl-5-(9H-xanthen-9-yl)oxazole (**5b**)





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





7. Crystallographic Data for 3n

The compound **3n** was crystalized over a solution of **3n** (50 mg) in CH_2Cl_2/petroleum (1 mL/1 mL) at room temperature. The mixed solvent spontaneously evaporates in open air to obtain the crystals of **3n**. 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 **3n** is 2157488.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 2

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2

Bond precision: C-C = 0.0019 A Wavelength=0.71073

Cell: a=8.998(3) b=13.804(4) c=14.731(4)
alpha=90 beta=92.647(10) gamma=90
Temperature: 273 K

	Calculated	Reported
Volume	1827.8(9)	1827.9(9)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H19 N O3	C24 H19 N O3
Sum formula	C24 H19 N O3	C24 H19 N O3
Mr	369.40	369.40
Dx,g cm-3	1.342	1.342
Z	4	4
Mu (mm-1)	0.089	0.089
F000	776.0	776.0
F000'	776.36	
h,k,lmax	11,18,19	11,17,19
Nref	4268	4241
Tmin,Tmax	0.988,0.991	0.727,0.746
Tmin'	0.988	

Correction method= # Reported T Limits: Tmin=0.727 Tmax=0.746
AbsCorr = NONE

Data completeness= 0.994 Theta(max)= 27.654

R(reflections)= 0.0401(3453) wR2(reflections)= 0.1142(4241)

S = 1.057 Npar= 257

Datablock 2 - ellipsoid plot

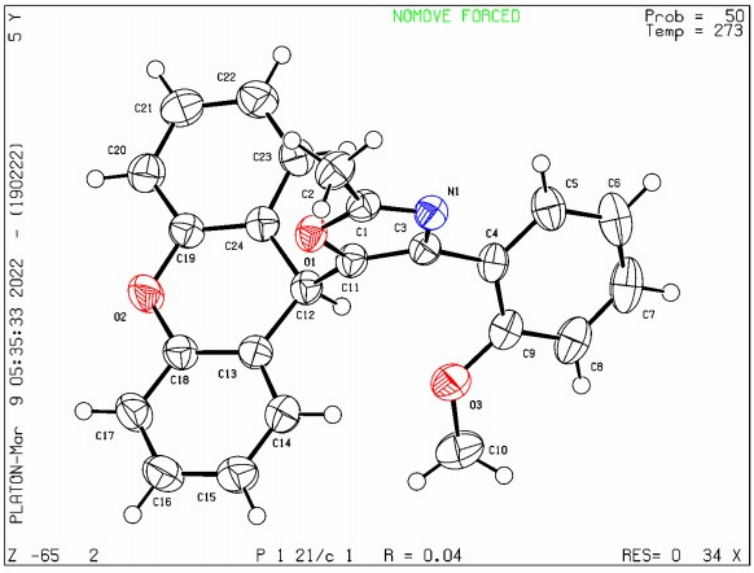

Figure S7 X-ray structure of **3n** (ORTEP diagram with ellipsoid contour 50% probability)

8. Determination of the Faradaic Efficiency

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

$$= \frac{4 \times 96485\ \text{C mol}^{-1} \times 0.3\ \text{mmol} \times 10^{-3} \times 79\ \%}{5\ \text{mA} \times 10^{-3} \times 10\ \text{h} \times 3600} \times 100\ \%$$

$$= 50.8\%$$

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.