Supporting Information

Desulfitative Sonogashira Cross-Coupling of Thiopyronin for the Synthesis of NIR Arylacetylene-Containing Rhodamines

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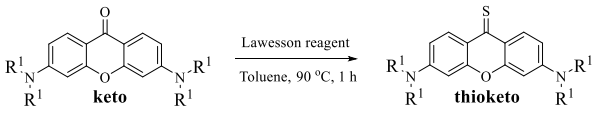
1. General information

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. All commercial solvents were used without further purification. The following solvents and reagents have been abbreviated: ethyl acetate (EtOAc), dichloromethane (DCM), dichloroethane (DCE), petroleum ether (PE), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF) and acetonitrile (ACN). ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Ascend III 400 and Avance III 600 instruments, using $CDCl_3$ or DMSO-d_6 at room temperature. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Chemical shifts are given in δ relative to TMS, coupling constants (*J*) are reported in Hertz (Hz). UV measurements were carried out on HITACHI U-3900 Spectrophotometer. Fluorescence measurements were carried out on Edinburgh FLS980 spectrophotometer, using a 450 W Xenon lamp. Absolute quantum yields were measured using an integrating sphere detector from Edinburgh Instruments. High-resolution mass spectrometry (HRMS) was performed with a TOF MS instrument with an ESI source. Column chromatography was performed using EM silica gel 60 (300−400 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254, 0.25 mm) were used, using UV light as the visualizing agent. The ground state geometries of **3a**, **3c**, **3i** and **4a** were optimized by using DFT method at B3LYP/6-31G (d, p) level. All of the calculations were carried out by the methods implemented in Gaussian 09 package.

2. Synthesis and reaction

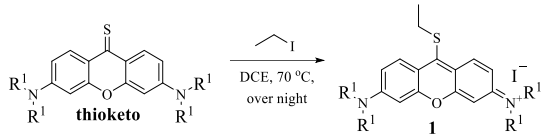
2.1 General procedure for the synthesis of thiopyronins.

The synthesis of different ketos was according to reported methods[1].



R^1 = methyl, cyclohexyl

To a solution of keto compound (1mmol, 1eq) in toluene was added Lawesson reagent (400mg, 1mmol, 1eq). The reaction was stirred at reflux temperature until complete consumption of keto (monitored by TLC). The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to get the thioketo compound.

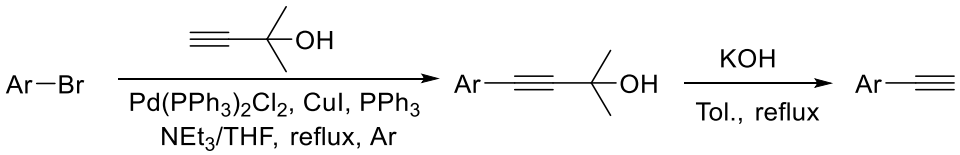


R^1 = methyl, cyclohexyl

To a solution of thioketo (0.16 mmol, 1eq) in dry DCE was added ethyl iodide (262 mg, 1.6 mmol, 10 eq). The reaction mixture was stirred at reflux temperature until complete consumption of thioketo (monitored by TLC). The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to get compound **1**.

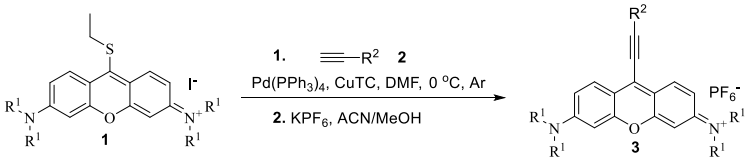
2.2 General procedure for the synthesis of arylacetylenes.

Most of the terminal alkynes were obtained from commercial sources and used without further purification. Other alkynes were prepared according to the following procedures.



To a solution of aryl bromide (5.00 mmol, 1 eq) in a mixture of Et_3N (15 mL) and THF (15 mL) was added $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (0.5 mmol, 0.1 eq) and PPh_3 (10 mol%) under Argon atmosphere. After the reaction mixture was stirred for 5 min at room temperature, 2-methylbut-3-yn-2-ol (6.00 mmol, 1.2 eq) was added by a syringe. The reaction mixture was stirred at reflux temperature until complete consumption of the aryl bromide (monitored by TLC). After cooling to room temperature, the reaction mixture was diluted with DCM, washed with H_2O, saturated aq. NH_4Cl and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. Purification by flash chromatography yielded the corresponding propargyl alcohols.
To a solution of propargyl alcohol (5.00 mmol, 1 eq) in toluene (30 mL) was added KOH (25 mmol, 5 eq) under Ar. The reaction was stirred at reflux temperature until complete consumption of staring materials (monitored by TLC). The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to get the corresponding alkyne **2**.

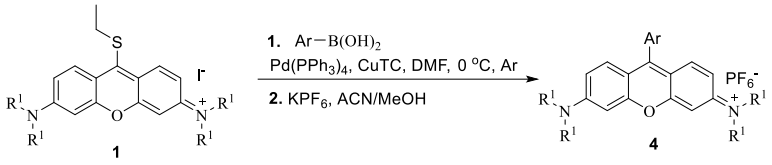
2.3 General procedure for the desulfitative Sonogashira cross-coupling rection.



To a solution of **Rho-SEt** (0.10 mmol, 1eq), **arylacetylene** (0.12 mmol, 1.2 eq) in dry

DMF (10 mL) at 0 °C under argon was added $Pd(PPh_3)_4$ (5 mmol%), CuTC (0.15mmol, 1.5eq). The reaction mixture was stirred at 0 °C until the starting material completely depleted monitored by LCMS. The reaction mixture was diluted with DCM, washed with H_2O and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. Purification by flash chromatography (30:1 DCM/MeOH, v/v) yielded the desired compound. Anion exchange by addition of KPF_6 (92 mg, 0.5 mmol, 5eq) to obtain all hexafluorophosphate products and the anion will not be emphasized in subsequent structure.

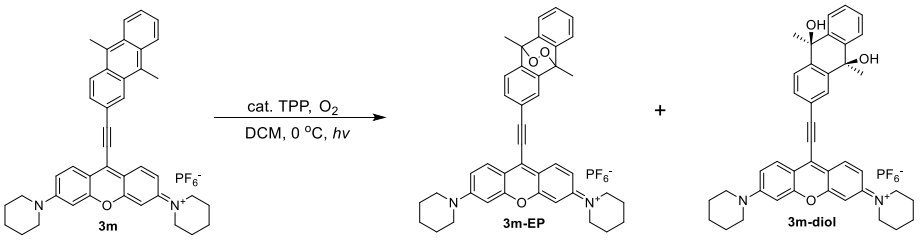
2.4 General procedure for rhodamine compounds without triple bond.



4a : R^1 = cyclohexyl, Ar = Ph;
4b : R^1 = cyclohexyl, Ar = 4-OCH_3Ph;
4c : R^1 = cyclohexyl, Ar = 9,10-dimethylanthryl;
4d : R^1 = cyclohexyl Ar = 3-thienyl;
4e : R^1 = methyl, Ar = Ph

To a solution of **Rho-SEt** (0.10 mmol, 1eq), arylboronic acid (0.15 mmol, 1.5 eq) in dry DMF (10 mL) at room temperature under Argon was added $Pd(PPh_3)_4$ (5 mmol%), CuTC (0.15mmol, 1.5eq). The reaction mixture was stirred at 90 °C until the **Rho-SEt** was completely depleted, monitored by LCMS. After cooled to room temperature, the reaction mixture was diluted with DCM, washed with H_2O and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. Purification by flash chromatography (30:1 DCM/MeOH, v/v) yielded the desired compound. Anion exchange by addition of KPF_6 (92 mg, 0.5 mmol, 5eq) to obtain all hexafluorophosphate products.

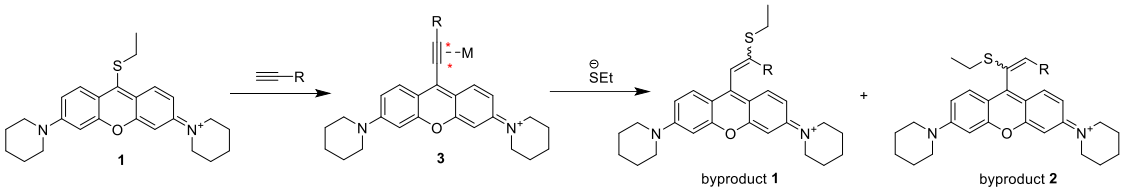
2.5 General procedure for the photooxygenation of 3m.



To a solution of **3m** (5 mg) in 5 mL PBS solution was added TPP (1 mg) subsequently, and oxygen was bubbled through the solution with vigorous stirring for 5 min. The reaction mixture was kept under an oxygen atmosphere with a balloon at 0 °C. Then the mixture was irradiated for 0.5 h with a high-pressure sodium lamp. Both of **3m-EP** and **3m-diol** were detected by LCMS during the reaction, but the final product yielded

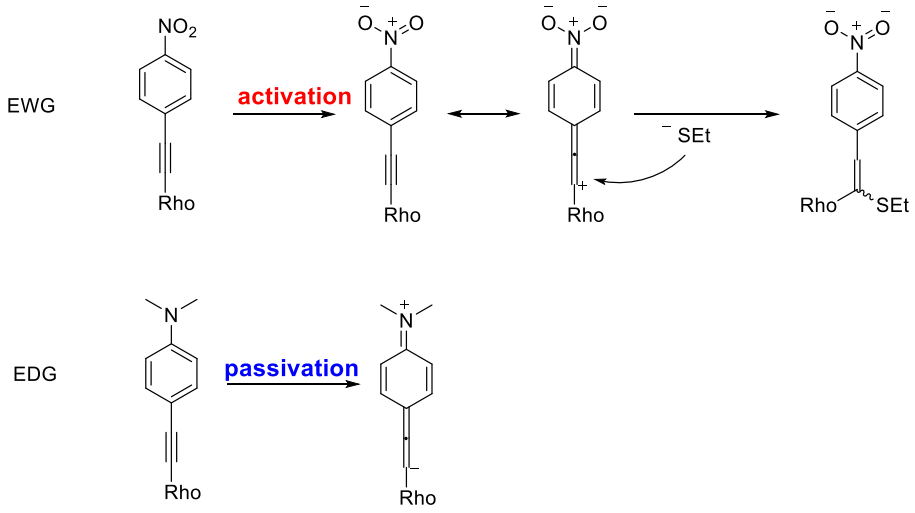
only diol. The solution was concentrated in vacuo, and the residue was purified by flash column chromatography (50:1 DCM/MeOH v/v) yielded the **3m-diol** as a blue solid.

2.6 Structure and mechanism of by-products



Based on the monitoring of the experimental process by LCMS and the results of experiments, it was found that compound **1** was readily converted to the target product **3**, however, the by-products were mainly generated by nucleophilic addition to the triple bond of **3** by alkylthio group , which may be mediated by metal ions in the reaction system. However, due to the lack of a clear positioning effect, the by-product olefins are typically a mixture with different substitution sites.

The experimental results indicate that electron-withdrawing groups (such as -NO_2, -CF_3) accelerate the nucleophilic addition of alkylthio groups to alkynes， probably due to the activation of the triple bond by the strong inducing effect of EDGs (Scheme S1)， whereas the electron donating groups (such as: -NMe_2, -OH, -OMe) decrease the activity of alkynes, leading to a significant increase in the proportion of alkynes obtained.



Scheme S1. Mechanism of the effect of substituents in alkyne on side reaction

3. Photophysical properties

3.1 The optical properties of **products.**

Table S1. Optical properties of arylacetylene-containing rhodamines in MeOH[a,b]

Compound	λ_{abs} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{em} (nm)	Stokes shift (nm)	Φ (%)
3a	626	12.1	656	30	28
3b	626	13.6	651	25	25
3c	623	8.5	650	27	26
3d	613	15.7	647	34	23
3e	631	8.1	656	25	24
3f	611	3.4	643	42	0.4
3g	626	15.6	655	29	26
3h	634	4.5	656	22	15
3i	639	7.9	666	27	19
3j	628	10.8	654	26	21
3k	619	17.9	666	47	0.2
3l	630	18.9	666	36	0.7
3m	630	5.5	658	28	0.3
3n	624	6.7	668	44	0.6
3o	621	3.3	666	45	22
3p	624	8.8	650	26	23
3q	621	9.3	646	25	25
3r	612	15.8	634	22	31
3s	606	14.9	626	20	29
3t	595	7.6	640	45	22
3u	607	6.5	631	24	26

[a]Concentration: 10 *u*M. [b]Room temperature.

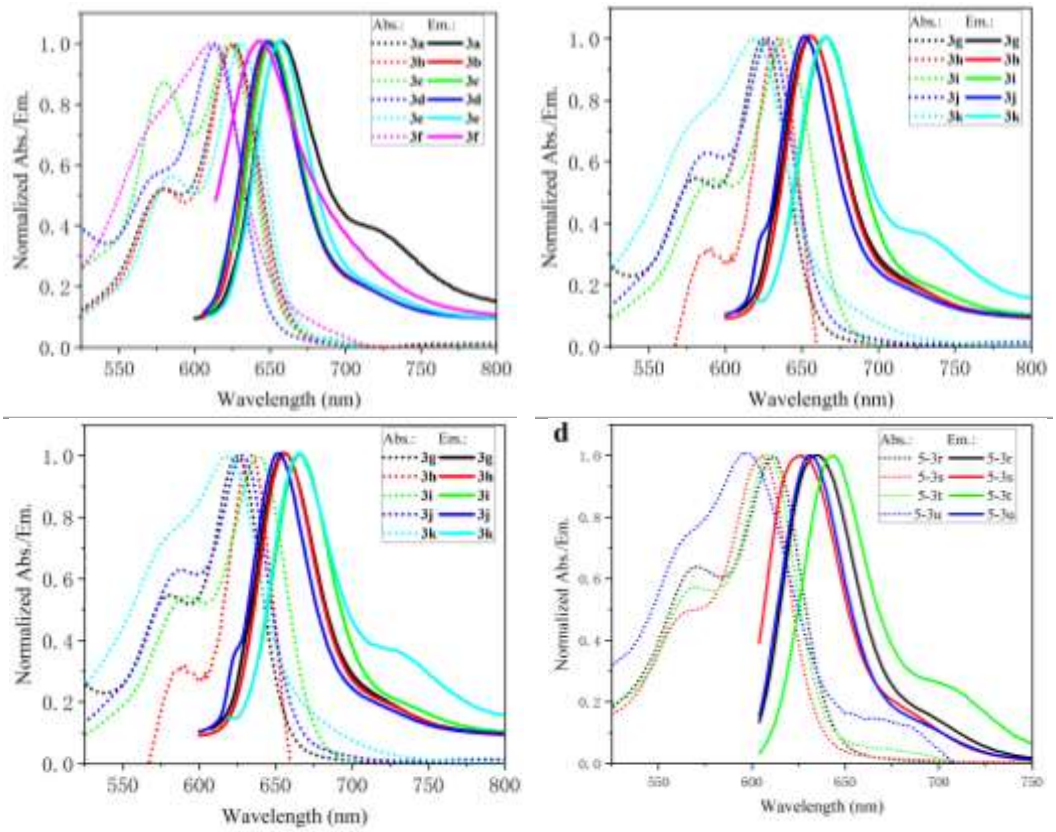


Figure S1. Normalized UV-vis absorption and emission spectra of **3a–3u** in MeOH.

Compared to **3a**, the introduction of strong EDGs lead to hypochromic shift both of λ_{abs} and λ_{em} (**3b**, **3c**, **3d**, **3f**), while EWGs lead to bathochromic shift (**3h**, **3i**). The result was consistent with DFT calculations at the B3LYP/6-31 G(d, p) level of theory (Fig. S2–S3). All calculations showed that HOMO was located on the pyronin moiety, while LUMO was distributed throughout the molecule. The -OMe group on compound 3c contributed to the increase in LUMO level, on the contrary, the -COMe group of compound **3i** decreased. Therefore, the energy gap increased in compound **3c** (2.55 eV) and decreased in compound **3i** (2.45 eV) compared to **3a** (2.51 eV), which explained the shift of λ_{abs} and λ_{em}.

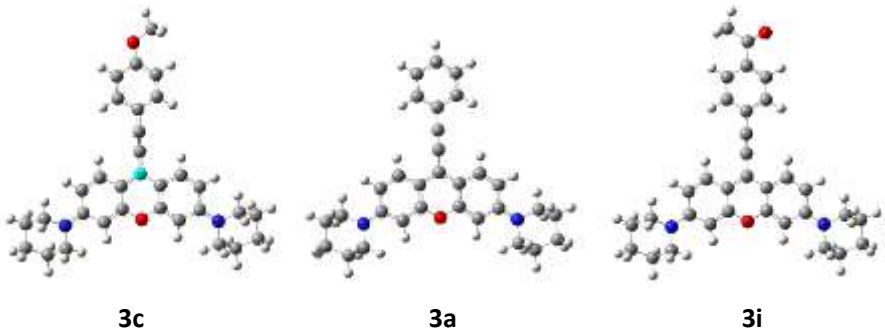


Figure S2. Most stable conformation for **3a**, **3c** and **3i** obtained by DFT calculations at the B3LYP/6–31G(d,p) level.

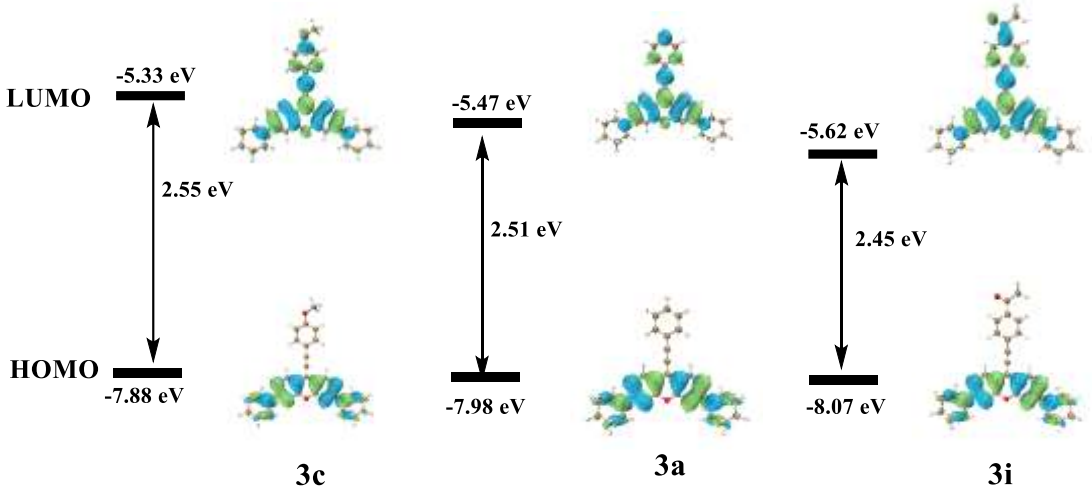


Figure S3. Energy diagrams and HOMOs-LUMOs for **3a**, **3c** and **3i** obtained by DFT calculations at the B3LYP/6–31G(d,p) level.

3.2 The effect of acetylene-bridge on optical properties

Table S2. Difference in Optical Data between Rhodamines with and without Alkyne Group in MeOH at 25 °C.

Compound	λ_{abs} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{em} (nm)	Stokes shift (nm)	Φ (%)
4a	565	11.1	592	27	31
3a	626	12.1	656	30	28
Δ	61		64		
4b	562	10.2	590	28	33
3c	623	8.5	650	27	26
Δ	61		60		
4c	568	12.8	590	22	5
3m	630	5.5	658	28	0.3
Δ	62		68		
4d	568	15.6	589	21	26
3p	624	8.8	650	26	23
Δ	56		61		
4e	550	17.8	572	22	33
3r	612	15.8	634	22	31
Δ	62		62		

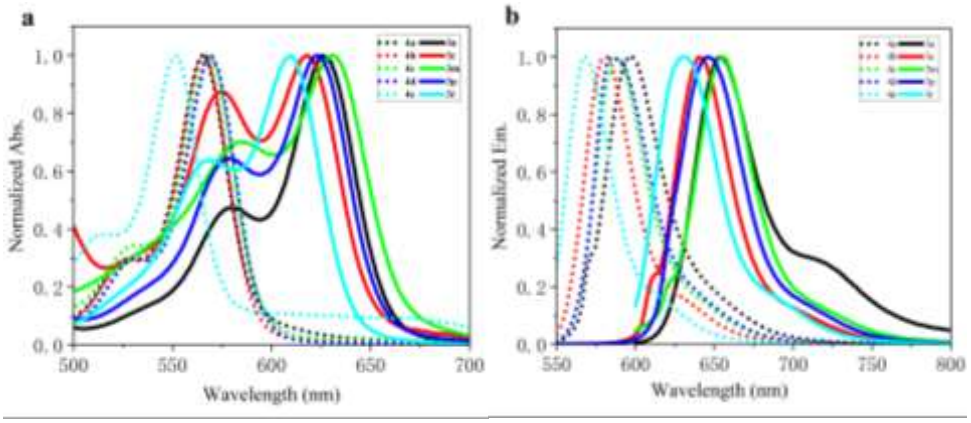


Figure S4. (a) Normalized UV-vis absorption (b) emission spectra of **4a–4e, 3a, 3c, 3m, 3p, 3r** in MeOH. Concentration:10 μM at room temperature.

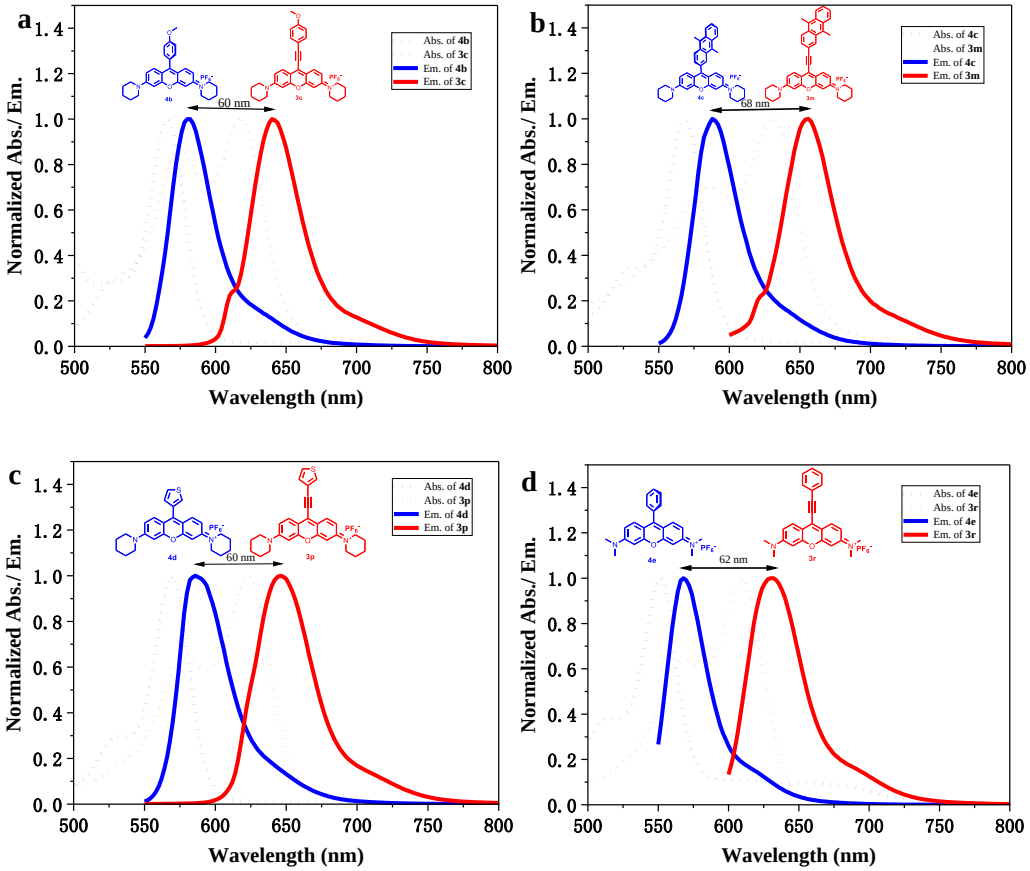
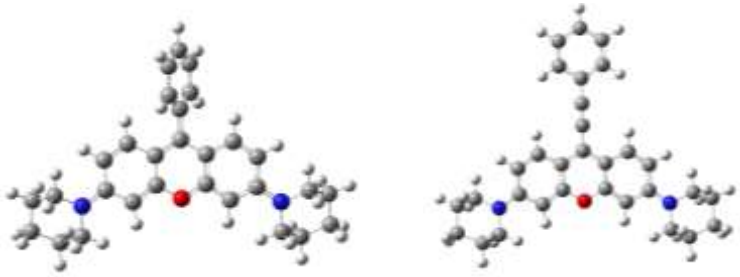


Figure S5. Normalized UV-vis absorption and emission spectra of (a) **4b** vs **3c**, (b) **4c** vs **3m,** (c) **4d** vs **3p** and (d) **4e** vs **3r** (d) in MeOH. Concentration:10 μM at room temperature.



4a **3a**

Figure S6. Most stable conformation for compound **4a** and **3a** obtained by DFT calculations at the B3LYP/6-31 G (d,p) level.

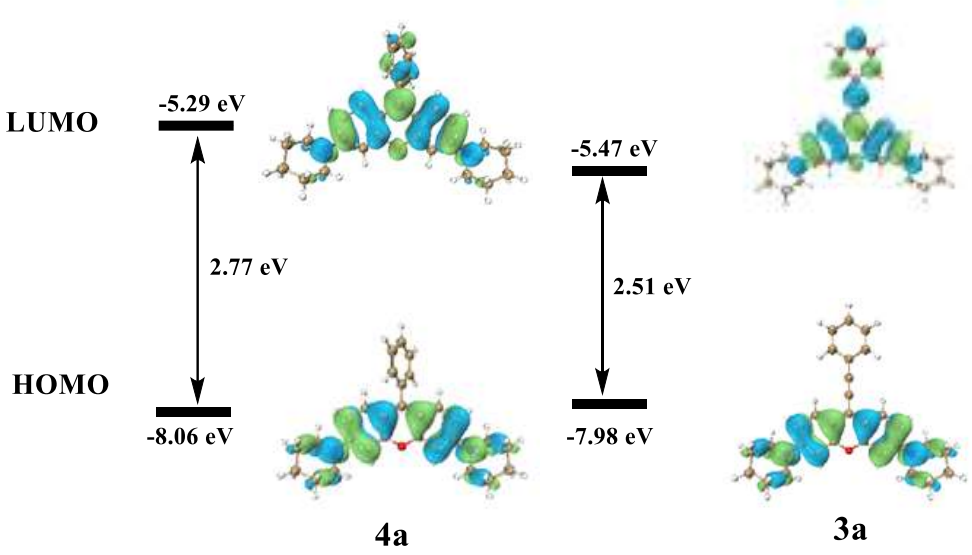


Figure S7. Energy diagrams and HOMOs-LUMOs for compound **4a** and **3a** obtained by DFT calculations at the B3LYP/6–31 G (d,p) level.

3.3 Changes in optical properties of 3m upon reaction with $^1O_2$

Table S3. Optical properties of **3m** and oxidized compound

Compound	λ_{abs} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{em} (nm)	stokes shift (nm)	Φ (%)
3m	630	5.5	658	28	0.3
3m-diol	624	4.8	668	44	12

Conditions: 10 μM in PBS buffer (50 mM, pH 7.4), 25 °C.

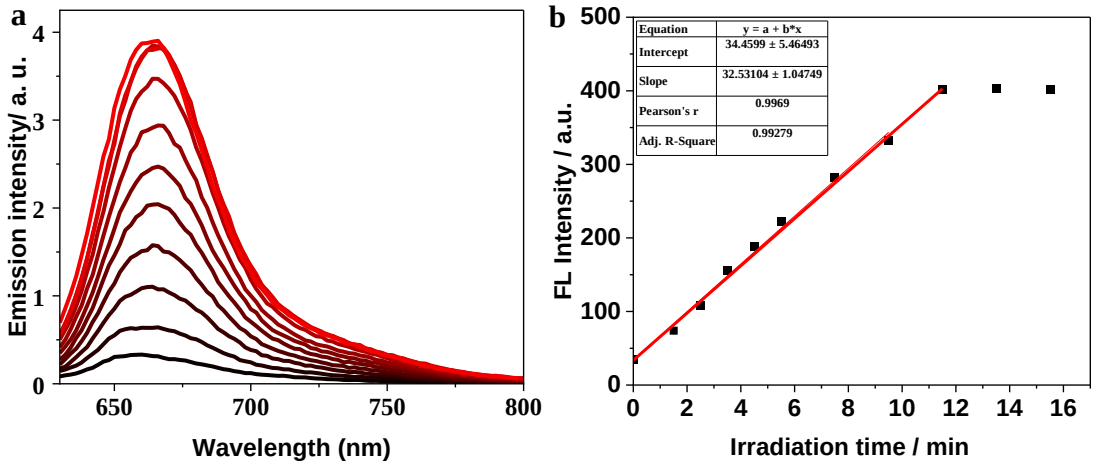
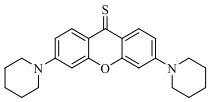


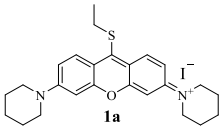
Fig. S8. Emission intensity changes of **3m** in PBS buffer upon photoirradiation of codissolved TPP for 16 min (black to red). [**3m**] = 20 μM, [TPP] = 10 μM.

4. Characterization data



3,6-di(piperidin-1-yl)-9*H*-xanthene-9-thione

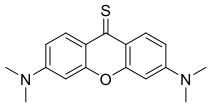
Purified by column chromatography on silica gel (20:1, DCM/ MeOH, v/v) to get the title compound (94% yield) as a brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 9.3 Hz, 2H), 6.79 (dd, *J* = 9.4, 2.6 Hz, 2H), 6.49 (d, *J* = 2.5 Hz, 2H), 3.35 (t, *J* = 4.3 Hz, 8H), 1.61 (q, *J* = 3.0 Hz, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 155.2, 153.2, 131.6, 120.8, 112.4, 98.2, 48.5, 25.3, 24.4. HRMS (ESI-TOF) m/z: calcd. for $C_{23}H_{26}N_2OS$ $[M+H]^+$: 379.1844; found: 379.1842.



1a

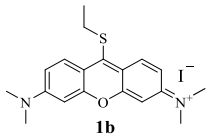
1-(9-(ethylthio)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium iodide (1a)

1a was purified by column chromatography on silica gel (10:1, DCM/ MeOH, v/v) to get the title compound (94% yield) as a red solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (d, *J* = 9.6 Hz, 2H), 7.42 (dd, *J* = 9.6, 2.1 Hz, 2H), 7.05 (d, *J* = 2.1 Hz, 2H), 3.78 (s, 8H), 3.24 (q, *J* = 7.3 Hz, 2H), 1.77 – 1.60 (m, 12H), 1.21 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 157.0, 156.6, 131.6, 116.6, 115.6, 97.1, 49.0, 33.4, 26.2, 24.2, 16.0. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{25}H_{31}N_2OS^+$: 407.2152; found: 407.2151.



3,6-bis(dimethylamino)-9*H*-xanthene-9-thione

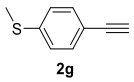
Prepared according to the similar procedure to **1a** using 3,6-bis(dimethylamino)-9*H*-xanthen-9-one as starting material and purified by flash column chromatography using DCM as the eluent to give the title compound (86% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 9.3 Hz, 2H), 6.73 (dd, *J* = 9.3, 2.5 Hz, 2H), 6.41 (d, *J* = 2.5 Hz, 2H), 3.11 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 154.6, 153.0, 131.8, 120.0, 110.5, 96.1, 40.2. HRMS (ESI-TOF) m/z: calcd. for $C_{17}H_{18}N_2OS$ $[M+H]^+$: 299.1218; found: 299.1215.



1b

***N*-(6-(dimethylamino)-9-(ethylthio)-3*H*-xanthen-3-ylidene)-*N*-methylmethanaminium iodide (1b)**

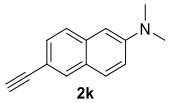
1b was purified by flash column chromatography (10:1, DCM/ MeOH, v/v) to give the title compound (85% yield) as a dark-red solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, *J* = 9.6 Hz, 2H), 7.24 (dd, *J* = 9.6, 2.3 Hz, 2H), 6.83 (d, *J* = 2.3 Hz, 2H), 3.30 (s, 12H), 3.28 – 3.19 (m, 2H), 1.20 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 157.9, 157.4, 156.2, 131.2, 116.3, 115.3, 96.5, 41.1, 33.5, 15.9. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{19}H_{23}N_2OS^+$: 327.1526; found: 327.1525.



2g

(4-ethynylphenyl)(methyl)sulfane (2g)

Prepared according to the general procedure using (4-bromophenyl)(methyl)sulfane and purified by flash column chromatography using PE to PE/EA(20/1, v/v) as the eluent to give the title compound (79% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 2.99 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0 131.3, 124.7, 117.3, 82.4, 14.3.

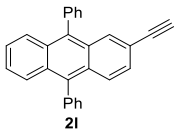


2k

6-ethynyl-*N*,*N*-dimethylnaphthalen-2-amine (2k)

Prepared according to the general procedure using 6-bromo-2-

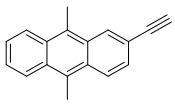
dimethylaminonaphthalene and purified by flash column chromatography using DCM/PE (1/6, v/v) as the eluent to give the title compound (79% yield) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.06 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 3.00 (s, 1H), 2.98 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 134.8, 132.1, 129.0, 128.7, 126.2, 125. 9, 116.6, 114.8, 105.9, 84.8, 76.0, 40.6.



2l

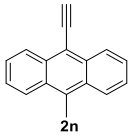
2-ethynyl-9,10-diphenylanthracene (2l)

Prepared according to the general procedure using 2-bromo-9,10-diphenylanthracene and purified by flash column chromatography using DCM/PE (1/5, v/v) as the eluent to give the title compound (50% yield) as yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 1.6 Hz, 1H), 7.73 – 7.56 (m, 9H), 7.51 – 7.46 (m, 4H), 7.39 – 7.31 (m, 3H), 3.10 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.3, 136.3, 136.2, 130.7, 130.2, 130.2, 129.5, 129.3, 128.1, 128.0, 127.5, 127.4, 126.7, 126.6, 126.2, 126.1, 126.0, 124.6, 124.4, 117.4, 83.4, 76.9.


2m

2-ethynyl-9,10-dimethylanthracene (2m)

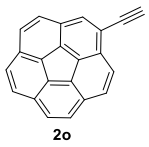
Prepared according to the general procedure using 2-bromo-9,10-dimethylanthracene and purified by flash column chromatography using DCM/PE (1/5, v/v) as the eluent to give the title compound (60% yield) as yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 1.3 Hz, 1H), 8.22 (m, 2H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.59 – 7.50 (m, 3H), 3.38 (s, 1H), 2.95 (s, 3H), 2.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.2, 129.0, 128.9, 127.7, 127.6, 127.4, 127.1, 125.3, 124.2, 124.1, 124.0, 123.9, 123.8, 116.6, 83.8, 76.5, 12.7, 12.7.


2n

9-ethynyl-10-methylanthracene (2n)

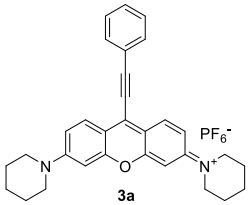
Prepared according to the general procedure using 9-bromo-10-methylanthracene and purified by flash column chromatography using DCM/PE (1/5, v/v) as the eluent to give

the title compound (63% yield) as yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (dd, *J* = 7.7, 1.0 Hz, 2H), 8.18 (dt, *J* = 8.5, 1.0 Hz, 2H), 7.52 – 7.39 (m, 4H), 3.87 (s, 1H), 2.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 132.6, 129.7, 127.4, 126.3, 125.6, 125.1, 114.8, 88.0, 80.8, 14.4.



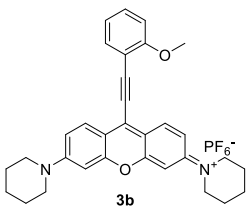
1-ethynylcorannulene (2o)

Prepared according to the general procedure using monobromocorannulene and purified by flash column chromatography using DCM/PE (1/10, v/v) as the eluent to give the title compound (70% yield) as yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.66 (m, 5H), 7.63 (d, *J* = 8.8 Hz, 1H), 3.34 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 134.6, 134.5, 134.4, 134.0, 131.2, 130.2, 130.1, 129.9, 129.9, 129.0, 126.6, 126.5, 126.4, 126.4, 126.1, 126.1, 125.5, 124.8, 119.1, 80.8, 79.6. All spectroscopic data are consistent with published results.[2]



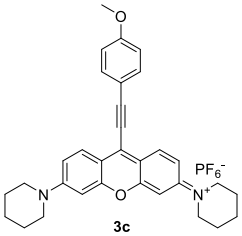
1-(9-(phenylethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3a)

3a was obtained as a blue solid in 75% yield after column chromatography on silica gel (30:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, *J* = 9.5 Hz, 2H), 7.98 – 7.86 (m, 2H), 7.70 – 7.64 (m, 1H), 7.61 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.38 (dd, *J* = 9.5, 2.5 Hz, 2H), 7.01 (d, *J* = 2.5 Hz, 2H), 3.76 (t, *J* = 5.2 Hz, 8H), 1.84 – 1.58 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.5, 156.5, 135.3, 133.5, 132.3, 131.4, 129.7, 120.4, 115.7, 114.4, 111.8, 97.3, 82.8, 49.0, 26.3, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{32}H_{33}N_2O_2^+$: 447.2436; found: 447.2442.



1-(9-((2-methoxyphenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3b)

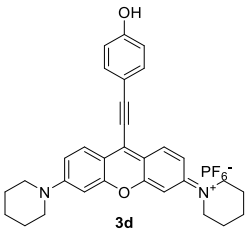
3b was obtained as a blue solid in 92% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 9.5 Hz, 2H), 7.80 (dd, J = 7.6, 1.7 Hz, 1H), 7.64 (ddd, J = 8.6, 7.6, 1.7 Hz, 1H), 7.44 (dd, J = 9.5, 2.4 Hz, 2H), 7.26 (d, J = 8.6 Hz, 1H), 7.13 (td, J = 7.6, 0.9 Hz, 1H), 6.97 (d, J = 2.4 Hz, 2H), 4.06 (s, 3H), 3.75 (t, J = 5.3 Hz, 8H), 1.76 – 1.51 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.1, 157.5, 156.5, 135.8, 134.7, 134.6, 131.3, 121.5, 115.7, 114.1, 112.3, 109.9, 109.4, 97.2, 87.8, 56.8, 49.0, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{32}H_{33}N_2O_2^+$: 477.2537; found: 477.2544.



3c

1-(9-((4-methoxyphenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3c)

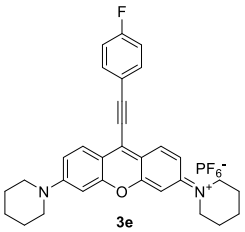
3c was obtained as a blue solid in 90% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, J = 9.5 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.39 (dd, J = 9.5, 2.5 Hz, 1H), 7.16 (J = 8.8 Hz, 2H), 7.04 (d, J = 2.4 Hz, 1H), 3.90 (s, 3H), 3.80 – 3.73 (t, J = 5.5 Hz, 8H), 1.80 – 1.52 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.7, 157.5, 156.5, 136.2, 135.9, 131.6, 115.5, 115.5, 114.1, 114.1, 112.1, 97.3, 83.1, 56.2, 48.9, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{32}H_{33}N_2O_2^+$: 477.2537; found: 477.2544.



3d

1-(9-((4-hydroxyphenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3d)

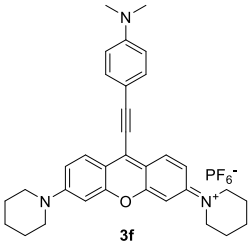
3d was obtained as a blue solid in 82% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (s, 1H), 8.13 (d, J = 9.4 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.45 (dd, J = 9.5, 2.4 Hz, 2H), 7.09 (d, J = 2.4 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 3.82 (t, J = 5.3 Hz, 8H), 1.75 (dt, J = 23.1, 5.5 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.9, 157.5, 156.5, 136.5, 136.2, 131.5, 117.0, 115.5, 115.5, 114.0, 110.3, 97.3, 83.2, 49.0, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{31}H_{31}N_2O_2^+$: 463.2380; found: 463.2384.



3e

1-(9-((4-fluorophenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3e)

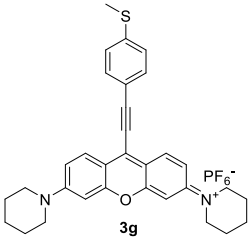
3e was obtained as a blue solid in 75% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, J = 9.5 Hz, 2H), 8.08 (dd, J = 8.7, 5.5 Hz, 2H), 7.49 (t, J = 8.9 Hz, 2H), 7.43 (dd, J = 9.5, 2.4 Hz, 2H), 7.10 (d, J = 2.4 Hz, 2H), 3.80 (t, J = 5.0 Hz, 8H), 1.71 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.4(d, $J_{(CF)}$ = 253 Hz), 157.5, 156.6, 136.4 (d, $J_{(CF)}$ = 9 Hz), 135.4, 131.6, 117.2 (d, $J_{(CF)}$ = 22 Hz), 117.0 (d, $J_{(CF)}$ = 3 Hz), 115.7, 114.4, 110.8, 97.3, 82.8, 49.1, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{31}H_{30}FN_2O^+$: 465.2337; found: 465.2343.



3f

1-(9-((4-(dimethylamino)phenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3f)

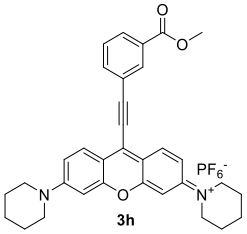
3f was obtained as a dark-blue solid in 90% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (dd, J = 9.4, 2.4 Hz, 2H), 7.73 (d, J = 8.9 Hz, 2H), 7.34 (dd, J = 9.4, 2.4 Hz, 2H), 6.97 (d, J = 2.4 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 3.73 (t, J = 5.3 Hz, 8H), 3.11 (s, 6H), 1.96 – 1.38 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.2, 156.3, 152.9, 136.7, 135.9, 131.4, 120.2, 115.2, 113.4, 112.5, 105.3, 97.3, 85.9, 48.8, 40.6, 26.1, 24.3. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{33}H_{36}N_3O^+$: 490.2853; found: 490.2861.



3g

1-(9-((4-(methylthio)phenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3g)

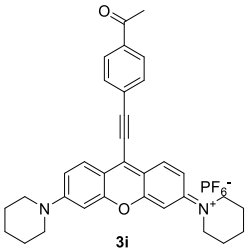
3g was obtained as a purple solid in 78% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (d, J = 9.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.41 (dd, J = 9.6, 2.5 Hz, 2H), 7.06 (d, J = 2.4 Hz, 2H), 3.78 (t, J = 5.4 Hz, 8H), 1.67 (d, J = 5.0 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.5, 156.6, 145.1, 135.7, 134.0, 131.6, 126.0, 115.9, 115.6, 114.3, 113.0, 97.4, 83.7, 49.0, 26.2, 24.2, 14.5. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{32}H_{33}N_2OS^+$: 493.2308; found: 493.2314.



3h

1-(9-((3-(methoxycarbonyl)phenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3h)

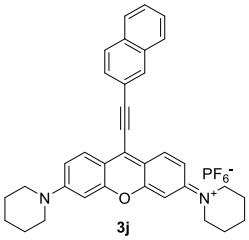
3h was obtained as a dark-red solid in 56% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.41 (t, J = 1.7 Hz, 1H), 8.20 (dt, J = 7.9, 1.4 Hz, 1H), 8.17 (dt, J = 7.9, 1.4 Hz, 1H), 8.11 (d, J = 9.5 Hz, 2H), 7.75 (t, J = 7.8 Hz, 1H), 7.40 (dd, J = 9.5, 2.4 Hz, 2H), 7.04 (d, J = 2.4 Hz, 2H), 3.94 (s, 3H), 3.78 (t, J = 5.3 Hz, 8H), 1.76 – 1.63 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.7, 157.5, 156.6, 137.9, 134.8, 133.7, 132.4, 131.6, 131.1, 130.3, 121.1, 115.8, 114.6, 109.8, 97.3, 83.3, 53.1, 49.1, 26.3, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{33}H_{33}N_2O_3^+$: 505.2486; found: 505.2489.



3i

1-(9-((4-acetylphenyl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3i)

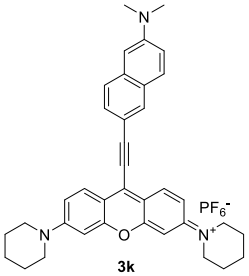
3i was obtained as a blue solid in 58% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, J = 9.5 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H), 8.11 (d, J = 8.6 Hz, 2H), 7.45 (dd, J = 9.5, 2.4 Hz, 2H), 7.11 (d, J = 2.4 Hz, 2H), 3.81 (t, J = 5.3 Hz, 8H), 2.68 (s, 3H), 1.71 (d, J = 19.9 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 197.9, 157.6, 156.6, 138.7, 134.7, 133.8, 131.6, 129.1, 124.7, 115.9, 114.7, 109.8, 97.4, 84.8, 49.2, 27.5, 26.3, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{33}H_{33}N_2O_2^+$: 489.2537; found: 489.2542.



3j

1-(9-(naphthalen-2-ylethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3j)

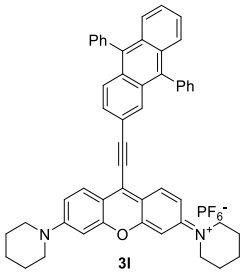
3j was obtained as a purple solid in 80% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (d, J = 1.6 Hz, 1H), 8.19 (d, J = 9.5 Hz, 2H), 8.13 (d, J = 8.6 Hz, 1H), 8.07 (m, 2H), 7.95 (dd, J = 8.4, 1.7 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.44 (dd, J = 9.5, 2.4 Hz, 2H), 7.09 (d, J = 2.4 Hz, 2H), 3.79 (t, J = 5.0 Hz, 8H), 1.78 – 1.60 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.6, 156.6, 135.4, 135.0, 134.3, 132.9, 131.6, 129.4, 129.2, 128.9, 128.8, 128.5, 128.0, 117.7, 115.7, 114.5, 112.5, 97.4, 83.4, 49.1, 26.3, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{35}H_{33}N_2O^+$: 497.2587; found: 497.2589.



3k

1-(9-((6-(dimethylamino)naphthalen-2-yl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3k)

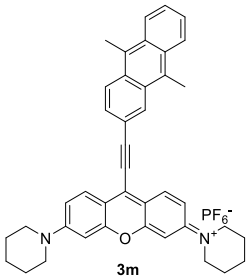
3k was obtained as a dark-blue solid in 87% yield after column chromatography on silica gel (15:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 (d, J = 1.6 Hz, 1H), 8.11 (d, J = 9.4 Hz, 2H), 7.85 (d, J = 9.4 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.70 (dd, J = 8.6, 1.7 Hz, 1H), 7.39 (dd, J = 9.4, 2.4 Hz, 2H), 7.32 (dd, J = 9.4, 2.4 Hz, 1H), 7.02 (d, J = 2.4 Hz, 2H), 6.99 (d, J = 2.5 Hz, 1H), 3.75 (t, J = 5.3 Hz, 8H), 3.12 (s, 6H), 1.83 – 1.53 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.4, 156.4, 150.8, 136.7, 136.1, 135.5, 131.5, 130.2, 129.2, 127.1, 125.5, 117.3, 116.6, 115.4, 114.0, 112.0, 105.5, 97.3, 84.3, 48.9, 40.6, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{37}H_{38}N_3O^+$: 540.3009; found: 540.3016.



3l

1-(9-((9,10-diphenylanthracen-2-yl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3l)

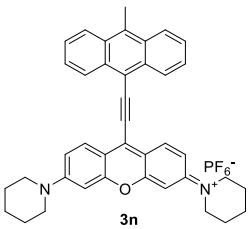
3l was obtained as a blue solid in 62% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 – 8.02 (d, J = 1.2 Hz, 1H), 7.83 (d, J = 9.4 Hz, 2H), 7.79 – 7.58 (m, 10H), 7.57 – 7.50 (m, 4H), 7.42 (d, J = 9.1 Hz, 1H), 7.40 (dd, J = 9.1, 1.2 Hz, 1H), 7.34 (dd, J = 9.5, 2.4 Hz, 2H), 6.99 (d, J = 2.4 Hz, 2H), 3.75 (t, J = 5.4 Hz, 8H), 1.79 – 1.54 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.4, 156.5, 138.7, 137.8, 137.7, 137.6, 134.8, 133.5, 131.6, 131.3, 131.3, 131.0, 130.5, 129.4, 129.3, 129.1, 128.8, 128.7, 128.6, 128.1, 127.5, 127.3, 127.2, 127.1, 127.0, 117.3, 115.7, 114.4, 112.0, 97.3, 84.1, 49.1, 26.3, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{51}H_{43}N_2O^+$: 699.3370; found: 699.3376.



3m

1-(9-((9,10-dimethylanthracen-2-yl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3m)

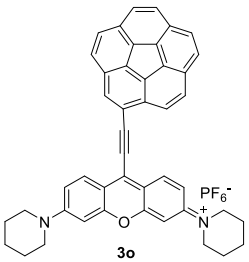
3m was obtained as a blue solid in 73% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (d, J = 1.6 Hz, 1H), 8.47 (d, J = 9.1 Hz, 1H), 8.44 – 8.34 (m, 2H), 8.22 (d, J = 9.6 Hz, 2H), 7.86 (dd, J = 9.1, 1.6 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.46 (dd, J = 9.6, 2.4 Hz, 2H), 7.04 (d, J = 2.4 Hz, 2H), 3.80 (t, J = 5.4 Hz, 8H), 3.21 – 3.13 (m, 3H), 3.06 – 2.99 (m, 3H), 1.83 – 1.61 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.5, 156.6, 135.5, 134.0, 132.7, 131.7, 131.5, 131.2, 130.6, 130.0, 129.5, 129.0, 127.1, 126.6, 126.4, 126.3, 126.0, 116.7, 115.7, 114.4, 113.6, 97.4, 84.2, 49.1, 26.3, 24.3, 14.7, 14.4. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{41}H_{39}N_2O^+$: 575.3057; found: 575.3063.



3n

1-(9-((10-methylanthracen-9-yl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3n)

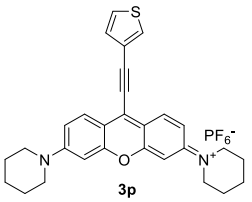
3n was obtained as a blue solid in 60% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 (dd, *J* = 8.7, 1.2 Hz, 2H), 8.29 (d, *J* = 8.9, 1.3 Hz, 2H), 7.75 (d, *J* = 9.5 Hz, 2H), 7.64 (ddd, *J* = 8.9, 7.2, 1.2 Hz, 2H), 7.57 (ddd, *J* = 8.7, 7.3, 1.3 Hz, 2H), 7.21 (dd, *J* = 9.5, 2.4 Hz, 2H), 6.63 (d, *J* = 2.4 Hz, 2H), 3.74 (t, *J* = 5.3 Hz, 8H), 3.08 (s, 3H), 1.76 (d, *J* = 23.2 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.6, 156.0, 138.7, 134.4, 133.0, 130.3, 129.4, 128.7, 126.6, 126.5, 126.1, 115.6, 113.6, 112.1, 109.7, 97.0, 94.9, 48.8, 26.3, 24.2, 15.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{40}H_{37}N_2O^+$: 561.2900; found: 561.2901.



3o

1-(9-(dibenzo[*ghi*,*mno*]fluoranthen-1-ylethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3o)

3o was obtained as a blue solid in 52% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 (s, 1H), 8.09 – 7.93 (m, 9H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.30 (dd, *J* = 9.4, 2.3 Hz, 2H), 6.69 (d, *J* = 2.3 Hz, 2H), 3.39 (t, *J* = 5.1 Hz, 8H), 1.61 – 1.33 (m, 12H). ^{13}C NMR (101 MHz, DMSO) δ 157.0, 156.1, 136.4, 135.7, 135.6, 135.1, 134.7, 134.5, 134.3, 132.3, 131.4, 130.9, 129.6, 129.5, 129.4, 129.2, 128.7, 128.7, 128.3, 128.1, 127.3, 125.2, 118.0, 115.6, 114.2, 110.2, 97.1, 86.4, 48.8, 26.0, 24.1. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{45}H_{35}N_2O^+$: 619.2749; found: 619.2751.

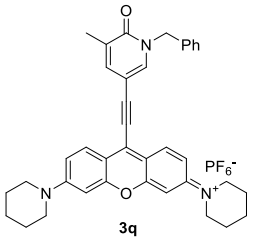


3p

1-(6-(piperidin-1-yl)-9-(thiophen-3-ylethynyl)-3*H*-xanthen-3-ylidene)piperidin-1-

ium hexafluorophosphate (3p)

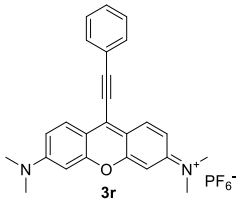
3p was obtained as a blue solid in 75% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (dd, J = 2.9, 1.2 Hz, 1H), 8.11 (d, J = 9.4 Hz, 2H), 7.85 (dd, J = 5.0, 2.9 Hz, 1H), 7.64 (dd, J = 5.0, 1.2 Hz, 1H), 7.43 (dd, J = 9.5, 2.5 Hz, 2H), 7.09 (d, J = 2.4 Hz, 2H), 3.80 (t, J = 5.1 Hz, 8H), 1.76 – 1.60 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.6, 156.6, 136.8, 135.9, 131.6, 130.7, 128.7, 119.6, 115.7, 114.4, 107.9, 97.4, 83.0, 49.1, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{29}H_{29}N_2OS^+$: 453.1995; found: 453.1995.



3q

1-(9-((1-benzyl-5-methyl-6-oxo-1,6-dihydropyridin-3-yl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (3q)

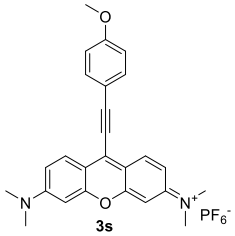
3q was obtained as a blue solid in 75% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (d, J = 2.4 Hz, 1H), 8.11 (d, J = 9.4 Hz, 2H), 7.83 (s, 1H), 7.46 – 7.36 (m, 5H), 7.34 (dd, J = 9.4, 2.4 Hz, 2H), 7.05 (d, J = 2.4 Hz, 2H), 5.23 (s, 2H), 3.77 (t, J = 5.1 Hz, 8H), 2.10 (s, 3H), 1.78 – 1.61 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.5, 157.5, 156.5, 146.0, 138.7, 137.0, 136.0, 131.7, 129.7, 129.2, 128.3, 128.2, 115.4, 113.8, 111.7, 98.8, 97.4, 85.0, 52.9, 49.0, 40.6, 26.2, 24.2, 17.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{38}H_{38}N_3O_2^+$: 568.2959; found: 568.2964.



3r

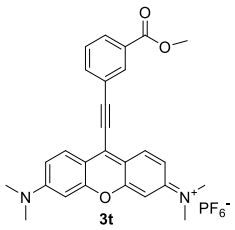
***N*-(6-(dimethylamino)-9-(phenylethynyl)-3*H*-xanthen-3-ylidene)-*N*-methylmethanaminium hexafluorophosphate (3r)**

3r was obtained as a dark-red solid in 83% yield after column chromatography on silica gel (15:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 9.4 Hz, 2H), 7.90 – 7.83 (m, 2H), 7.70 – 7.63 (m, 1H), 7.62 – 7.54 (m, 2H), 7.13 (dd, J = 9.4, 2.4 Hz, 2H), 6.69 (d, J = 2.4 Hz, 2H), 3.22 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.2, 156.6, 136.0, 133.6, 132.3, 131.0, 129.6, 120.3, 115.3, 113.9, 112.1, 96.5, 82.7, 41.0. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{25}H_{23}N_2O^+$: 367.1805; found: 367.1809.



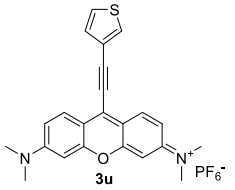
***N*-(6-(dimethylamino)-9-((4-methoxyphenyl)ethynyl)-3*H*-xanthen-3-ylidene)-*N*-methylmethanaminium hexafluorophosphate (3s)**

3s was obtained as a blue solid in 91% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (dd, J = 9.4, 2.3 Hz, 2H), 7.87 – 7.80 (m, 1H), 7.18 – 7.07 (m, 2H), 6.69 (d, J = 2.5 Hz, 1H), 3.91 (s, 2H), 3.23 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.7, 157.1, 156.6, 136.8, 135.9, 131.0, 115.4, 115.0, 114.4, 113.6, 112.1, 96.5, 83.1, 56.2, 41.0. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{26}H_{25}N_2O_2^+$: 397.1911; found: 397.1914.



***N*-(6-(dimethylamino)-9-((3-(methoxycarbonyl)phenyl)ethynyl)-3*H*-xanthen-3-ylidene)-*N*-methylmethanaminium hexafluorophosphate (3t)**

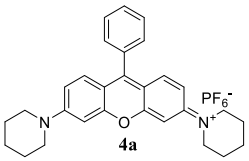
3t was obtained as a purple-blue solid in 55% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 (t, J = 1.7 Hz, 1H), 8.19 (dt, J = 7.9, 1.7 Hz, 1H), 8.16 (dt, J = 7.9, 1.7 Hz, 1H), 8.11 (d, J = 9.4 Hz, 2H), 7.74 (t, J = 7.9 Hz, 1H), 7.20 (dd, J = 9.4, 2.4 Hz, 2H), 6.80 (d, J = 2.4 Hz, 2H), 3.94 (s, 3H), 3.28 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.7, 157.4, 156.8, 138.1, 135.8, 133.8, 132.5, 131.3, 131.0, 130.3, 121.1, 115.4, 114.2, 110.2, 96.7, 83.3, 53.1, 41.1. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{27}H_{25}N_2O_3^+$: 425.1860; found: 425.1862.



***N*-(6-(dimethylamino)-9-(thiophen-3-ylethynyl)-3*H*-xanthen-3-ylidene)-*N*-methylmethanaminium hexafluorophosphate (3u)**

3u was obtained as a blue solid in 68% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.57 (dd, J = 2.9, 1.2 Hz,

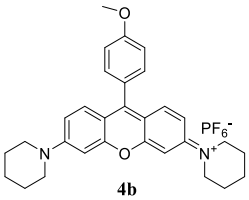
1H), 8.15 (d, *J* = 9.4 Hz, 2H), 7.86 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.26 (dd, *J* = 9.4, 2.4 Hz, 2H), 6.89 (d, *J* = 2.4 Hz, 2H), 3.32 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.2, 156.6, 136.9, 136.5, 131.0, 130.7, 128.7, 119.6, 115.2, 113.8, 108.2, 96.5, 82.9, 41.0. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{23}H_{21}N_2OS^+$: 373.1369; found: 373.1371.



4a

1-(9-phenyl-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (4a)

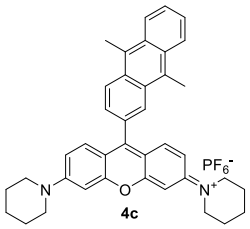
4a was obtained as a red solid in 68% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.72 – 7.69 (m, 3H), 7.55 – 7.50 (m, 2H), 7.34 (dd, *J* = 9.6, 2.4 Hz, 2H), 7.23 (d, *J* = 9.6 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 2H), 3.82 – 3.71 (t, *J* =5.4 Hz, 8H), 1.81 – 1.59 (m, 12H). ^{13}C NMR (101 MHz, DMSO-*d6*) δ 158.2, 156.5, 156.5, 132.2, 132.0, 130.7, 129.9, 129.3, 115.5, 113.5, 97.3, 48.9, 26.2, 24.3. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{29}H_{31}N_2O^+$: 423.2431; found: 423.2434.



4b

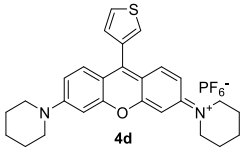
1-(9-(4-methoxyphenyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (4b)

4b was obtained as a red solid in 70% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.34 (s, 4H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 1.7 Hz, 2H), 3.91 (s, 3H), 3.76 (t, *J* = 5.4 Hz, 9H), 1.75 – 1.61 (m, 14H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.3, 158.3, 156.4, 132.3, 132.0, 124.1, 115.3, 114.9, 113.5, 97.3, 56.0, 48.9, 26.2, 24.3. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{30}H_{33}N_2O_2^+$: 453.2537; found: 453.2542.



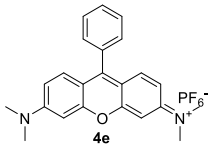
1-(9-(9,10-dimethylanthracen-2-yl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (4c)

4c was obtained as a violet solid in 47% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.61 (d, J = 9.0 Hz, 1H), 8.51 (s, 1H), 8.49 – 8.38 (m, 2H), 7.72 – 7.64 (m, 2H), 7.63 – 7.58 (m, 1H), 7.35 (d, J = 9.6 Hz, 2H), 7.27 (dd, J = 9.7, 2.0 Hz, 2H), 7.16 (d, J = 2.0 Hz, 2H), 3.75 (t, J = 5.6 Hz, 8H), 3.14 (s, 3H), 3.04 (s, 3H), 1.68 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.2, 156.8, 156.4, 132.3, 130.8, 130.6, 130.2, 129.5, 129.4, 128.9, 128.7, 128.0, 126.7, 126.5, 126.3, 126.0, 115.4, 113.7, 97.3, 48.9, 26.2, 24.3, 14.5, 14.4. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{39}H_{39}N_2O^+$: 551.3057; found: 551.3063



1-(6-(piperidin-1-yl)-9-(thiophen-3-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (4d)

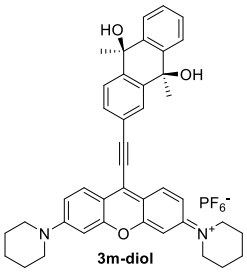
4d was obtained as a red solid in 52% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (dd, J = 2.9, 1.3 Hz, 1H), 7.98 (dd, J = 4.9, 2.9 Hz, 1H), 7.45 (d, J = 9.6 Hz, 2H), 7.41 (dd, J = 4.9, 1.3 Hz, 1H), 7.34 (dd, J = 9.6, 2.4 Hz, 2H), 7.11 (d, J = 2.4 Hz, 2H), 4.12 – 3.64 (t, J = 5.4 Hz, 8H), 1.68 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 156.4, 151.9, 132.1, 131.9, 130.2, 130.0, 128.7, 115.4, 113.4, 97.3, 48.9, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{27}H_{29}N_2OS^+$: 429.1995; found: 429.2001.



***N*-(6-(dimethylamino)-9-phenyl-3*H*-xanthen-3-ylidene)-*N*-methylmethanaminium hexafluorophosphate (4e)**

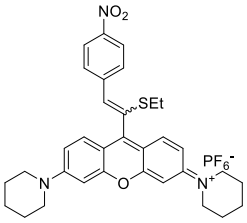
4e was obtained as a red solid in 73% yield after column chromatography on silica gel (20:1 DCM/MeOH, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 – 7.68 (m, 3H), 7.56 – 7.51 (m, 2H), 7.27 (d, 2H), 7.17 (dd, J = 9.6, 2.5 Hz, 2H), 6.97 (d, J = 2.4 Hz, 2H),

3.29 (s, 12H). ^{13}C NMR (01 MHz, DMSO-d_6) δ 157.5, 157.5, 157.3, 132.2, 131.7, 130.7, 129.9, 129.3, 115.2, 113.2, 96.8, 41.0. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{23}H_{23}N_2O^+$: 343.1805; found: 343.1808.



1-(9-(((9R,10S)-9,10-dihydroxy-9,10-dimethyl-9,10-dihydroanthracen-2-yl)ethynyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate

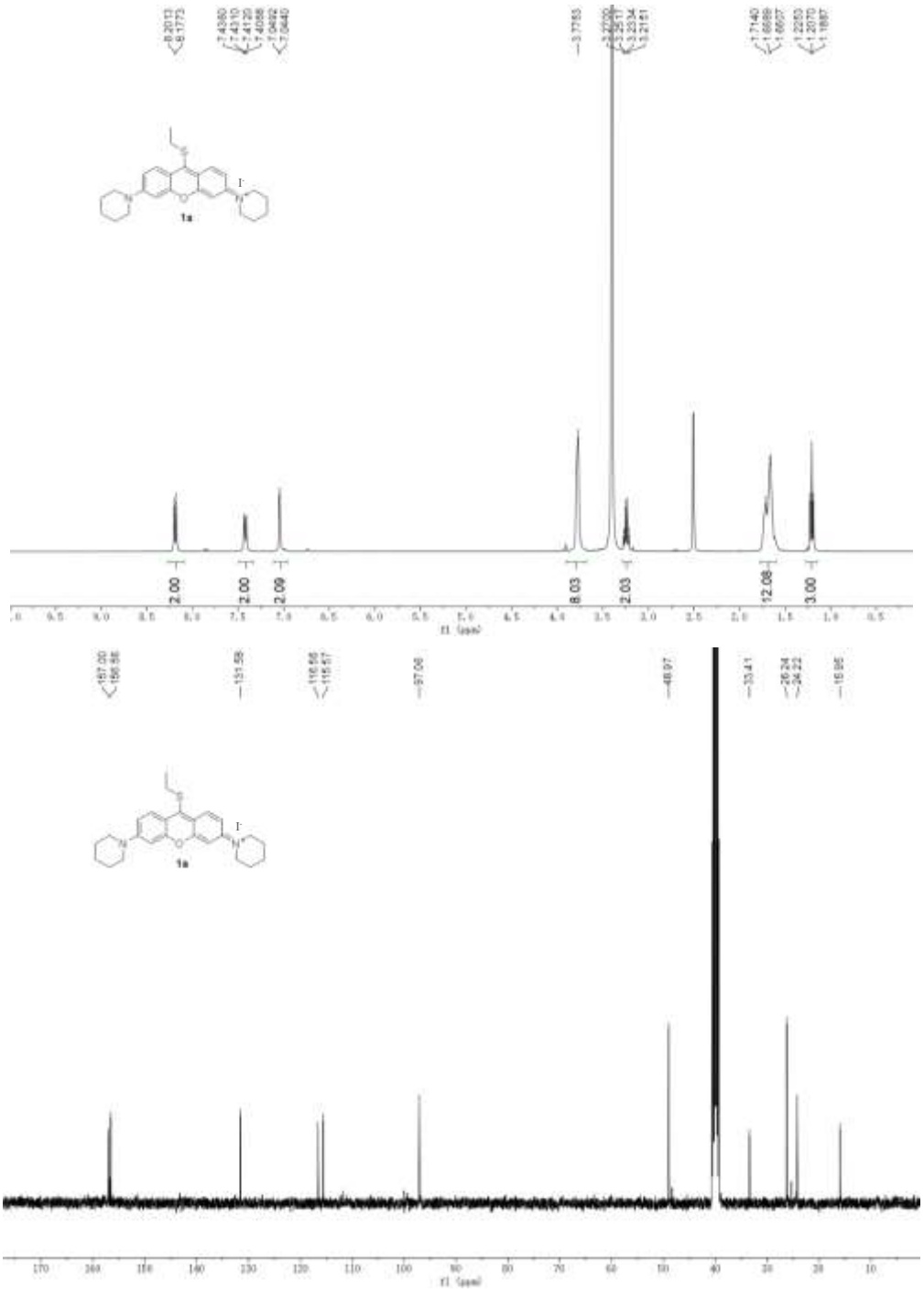
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (d, *J* = 1.8 Hz, 1H), 8.11 (d, *J* = 9.5 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.81 (dq, *J* = 7.0, 3.5 Hz, 2H), 7.47 (dd, *J* = 9.5, 2.4 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.06 (d, *J* = 2.4 Hz, 2H), 6.10 (s, 1H), 6.06 (s, 1H) 3.79 (t, *J* = 5.1 Hz, 8H), 1.92 – 1.59 (m, 12H), 1.57 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.6, 156.6, 146.4, 143.5, 141.5, 141.3, 135.6, 132.1, 131.4, 130.8, 127.7, 127.7, 126.8, 125.6, 118.9, 115.9, 114.5, 112.7, 97.4, 82.7, 69.2, 69.0, 49.1, 36.6, 36.5, 26.2, 24.2. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{41}H_{41}N_2O_3^+$: 609.3112; found: 609.3117.



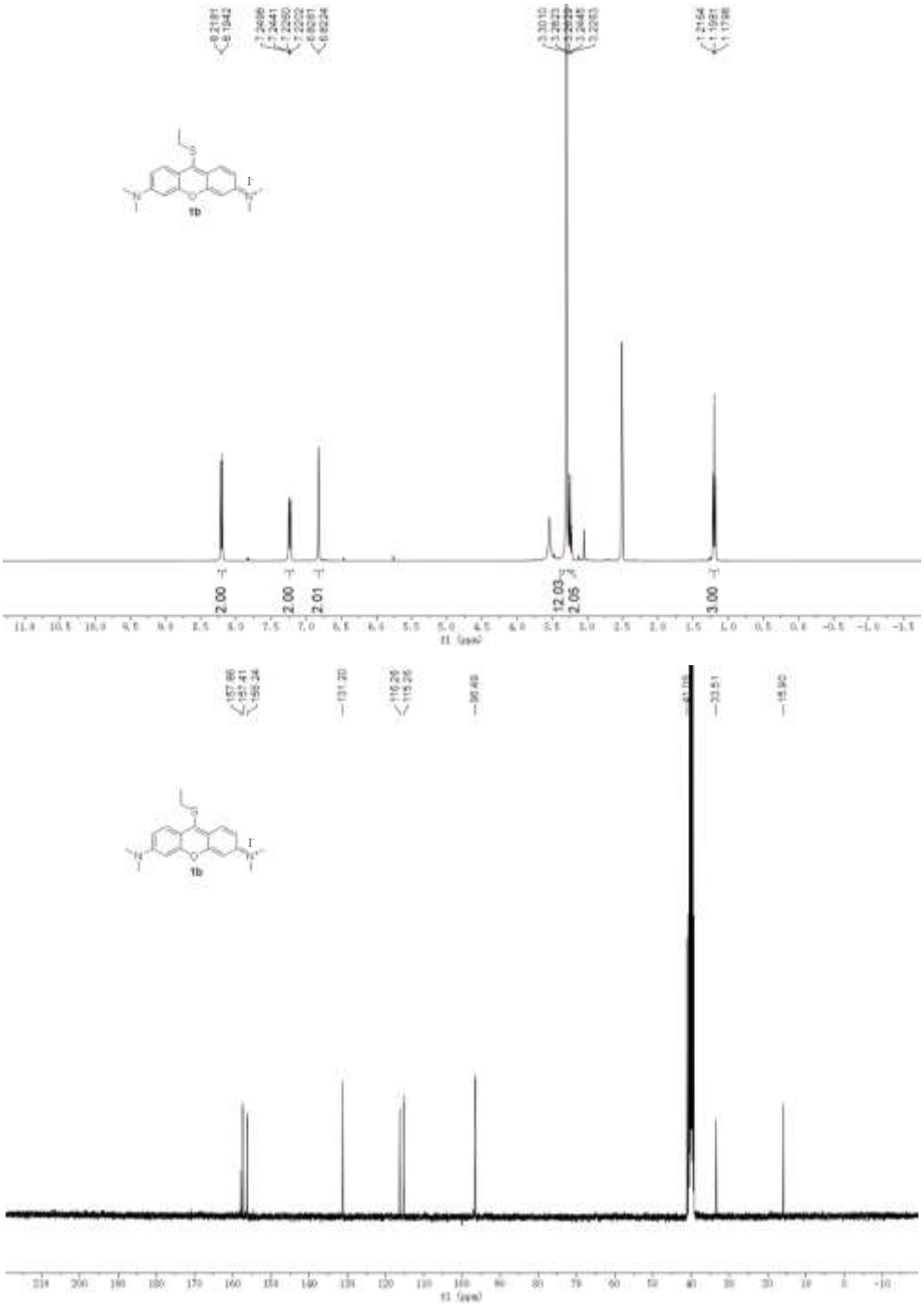
1-**(9-(1-(ethylthio)-2-(4-nitrophenyl)vinyl)-6-(piperidin-1-yl)-3*H*-xanthen-3-ylidene)piperidin-1-ium hexafluorophosphate (NO_2-byproduct)**

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 9.5 Hz, 2H), 7.50 (s, 1H), 7.40 (dd, *J* = 9.6, 2.5 Hz, 2H), 7.14 (d, *J* = 2.3 Hz, 2H), 3.79 (m, 8H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.70 (m, 12H), 0.88 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 156.7, 152.6, 148.3, 144.8, 144.4, 131.8, 130.1, 126.7, 124.5, 115.3, 112.6, 97.4, 48.9, 26.6, 26.2, 24.2, 15.5. HRMS (ESI-TOF) m/z: $[M]^+$ calcd. for $C_{33}H_{36}N_3O_3S^+$: 554.2472; found: 554.2474.

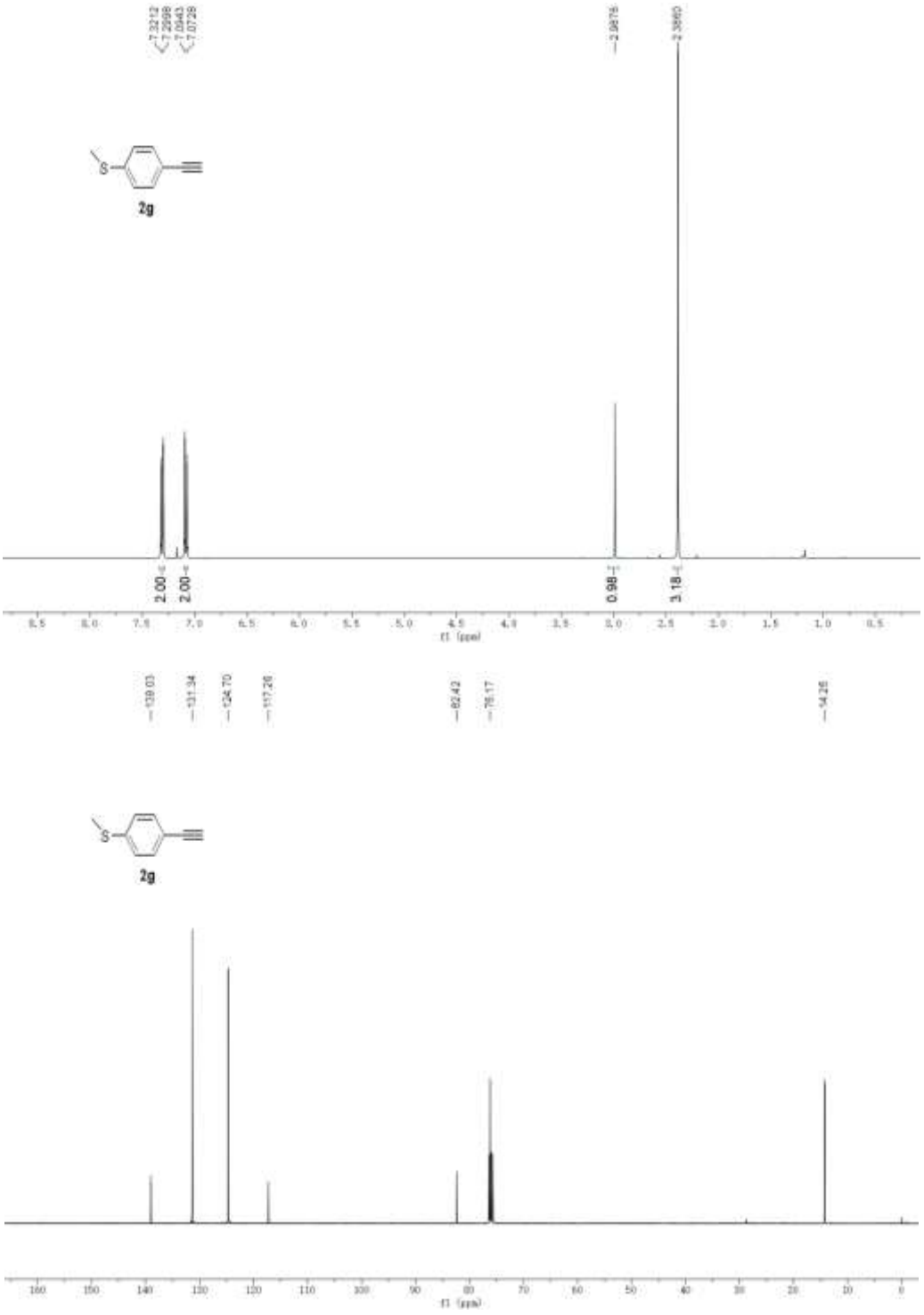
5. ^{1}H NMR and ^{13}C NMR spectra



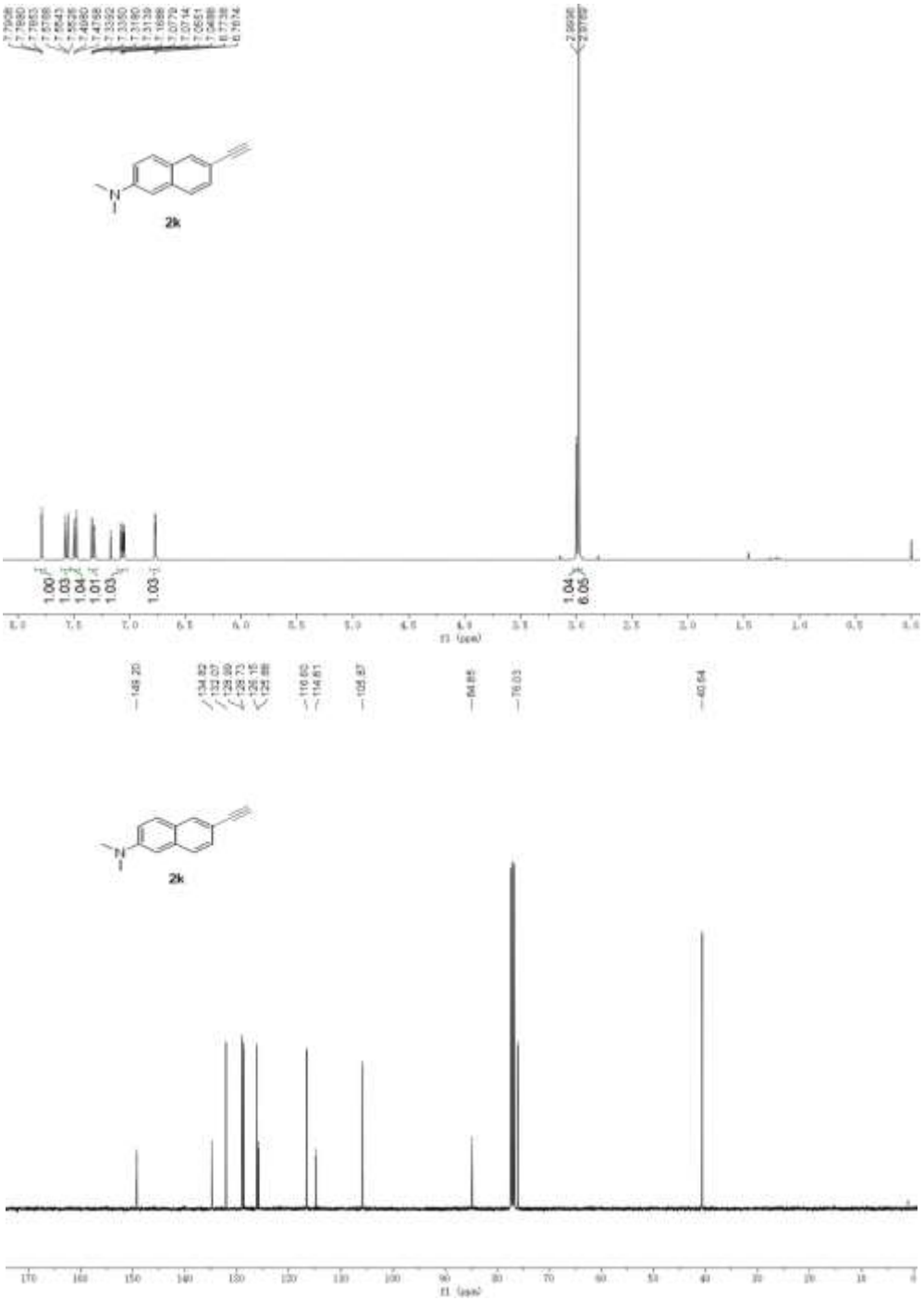
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **1a** in DMSO-d_6.



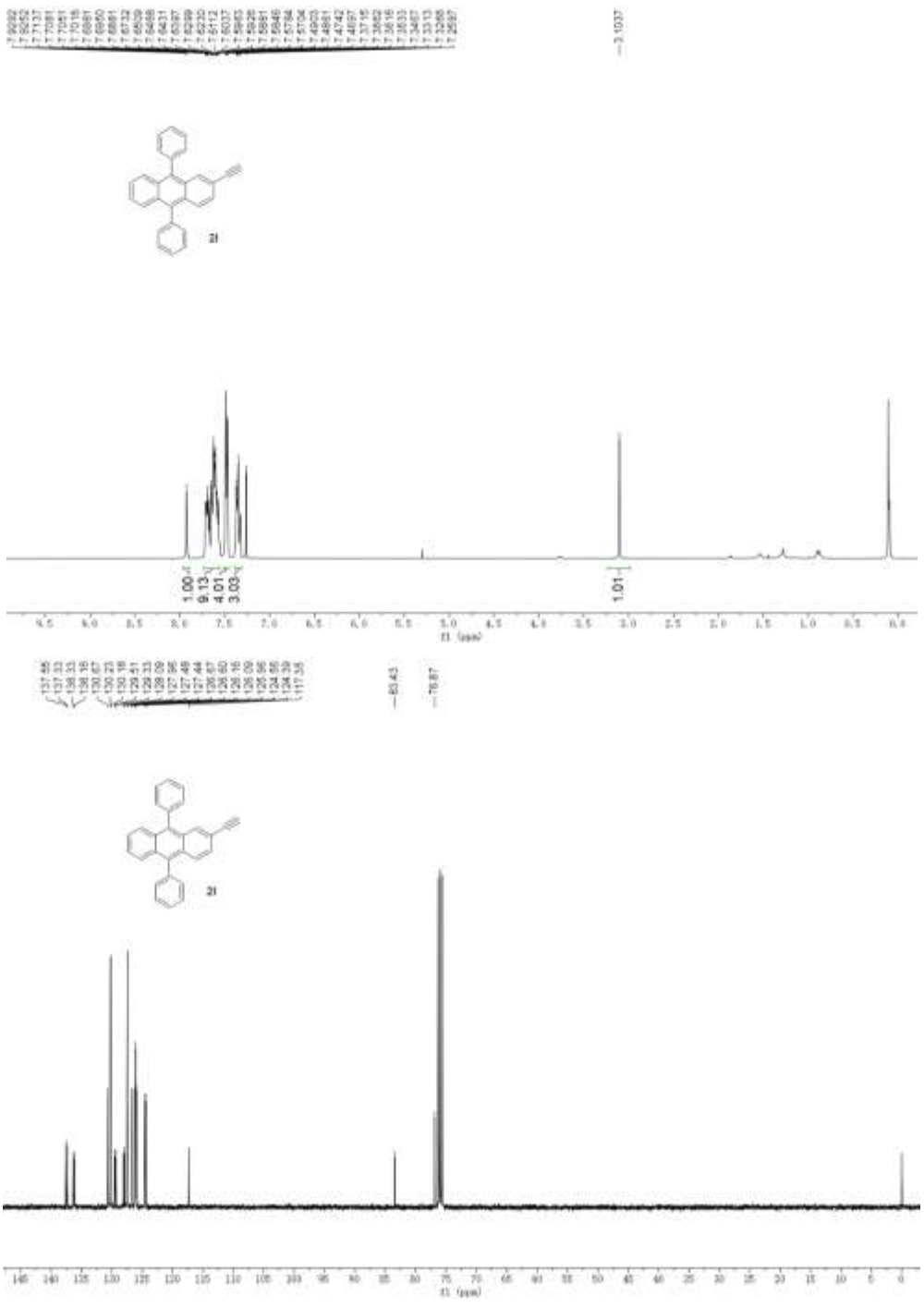
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **1b** in DMSO-d_6.



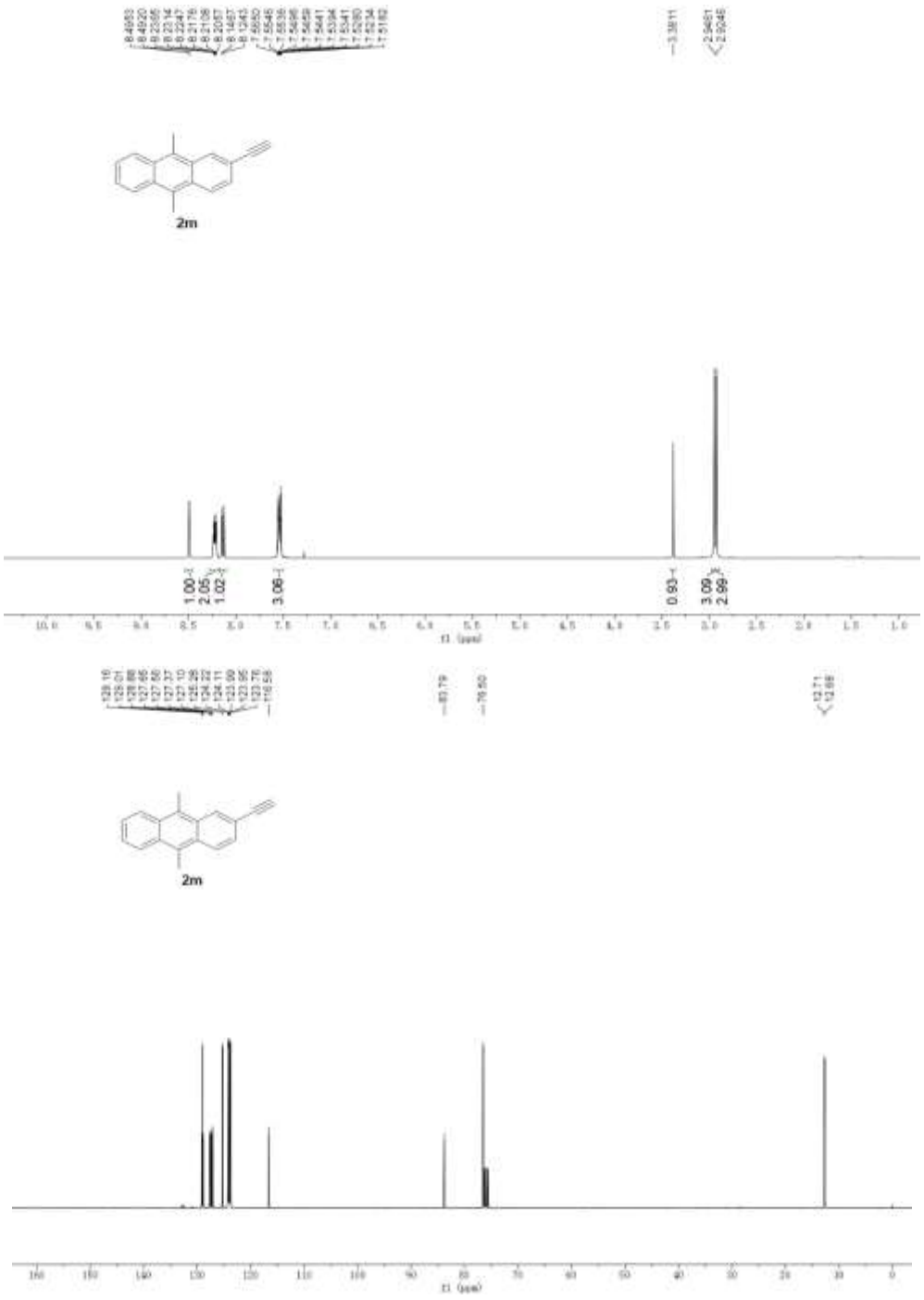
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **2g** in $CDCl_3$.



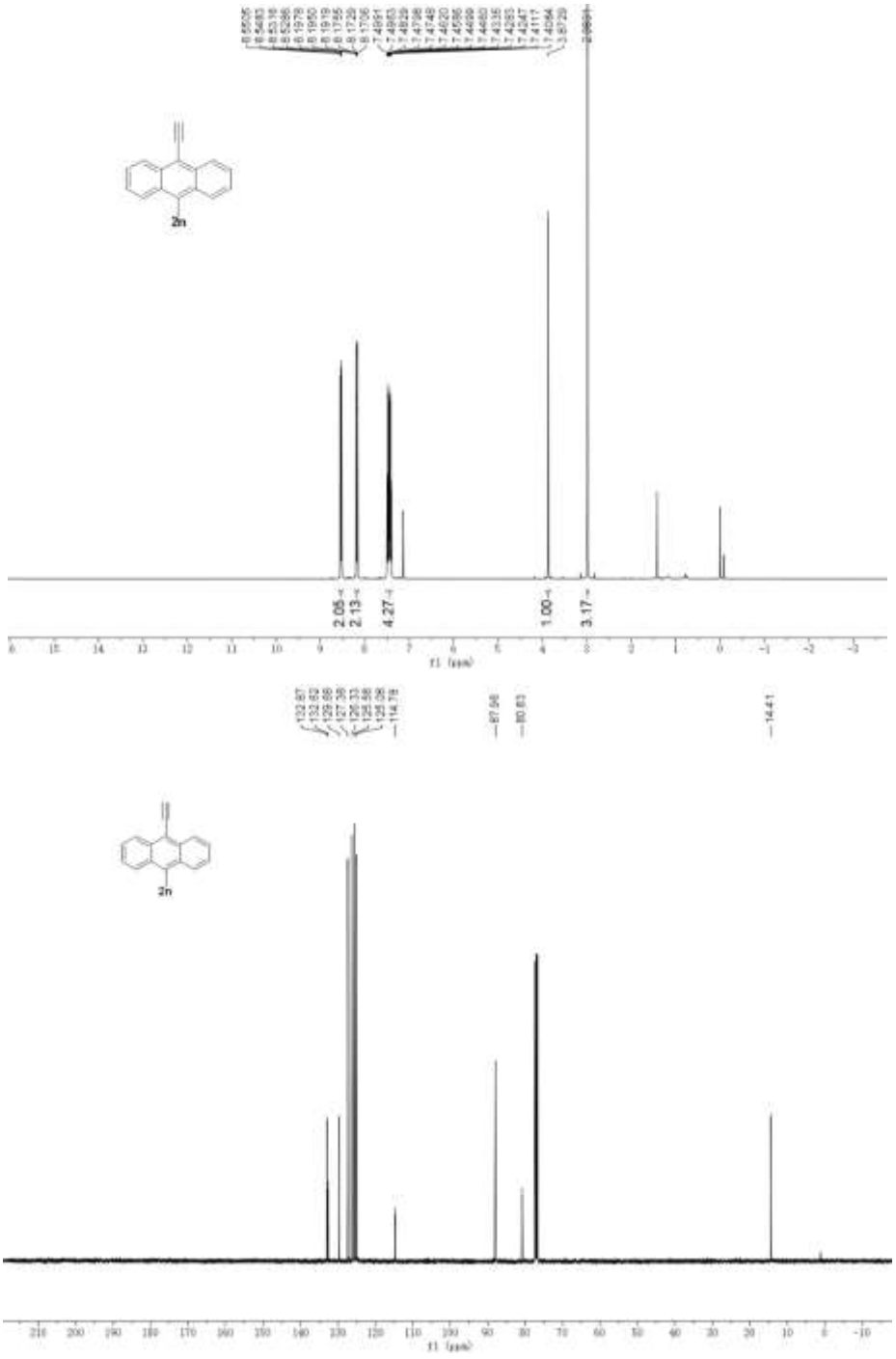
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **2k** in $CDCl_3$.



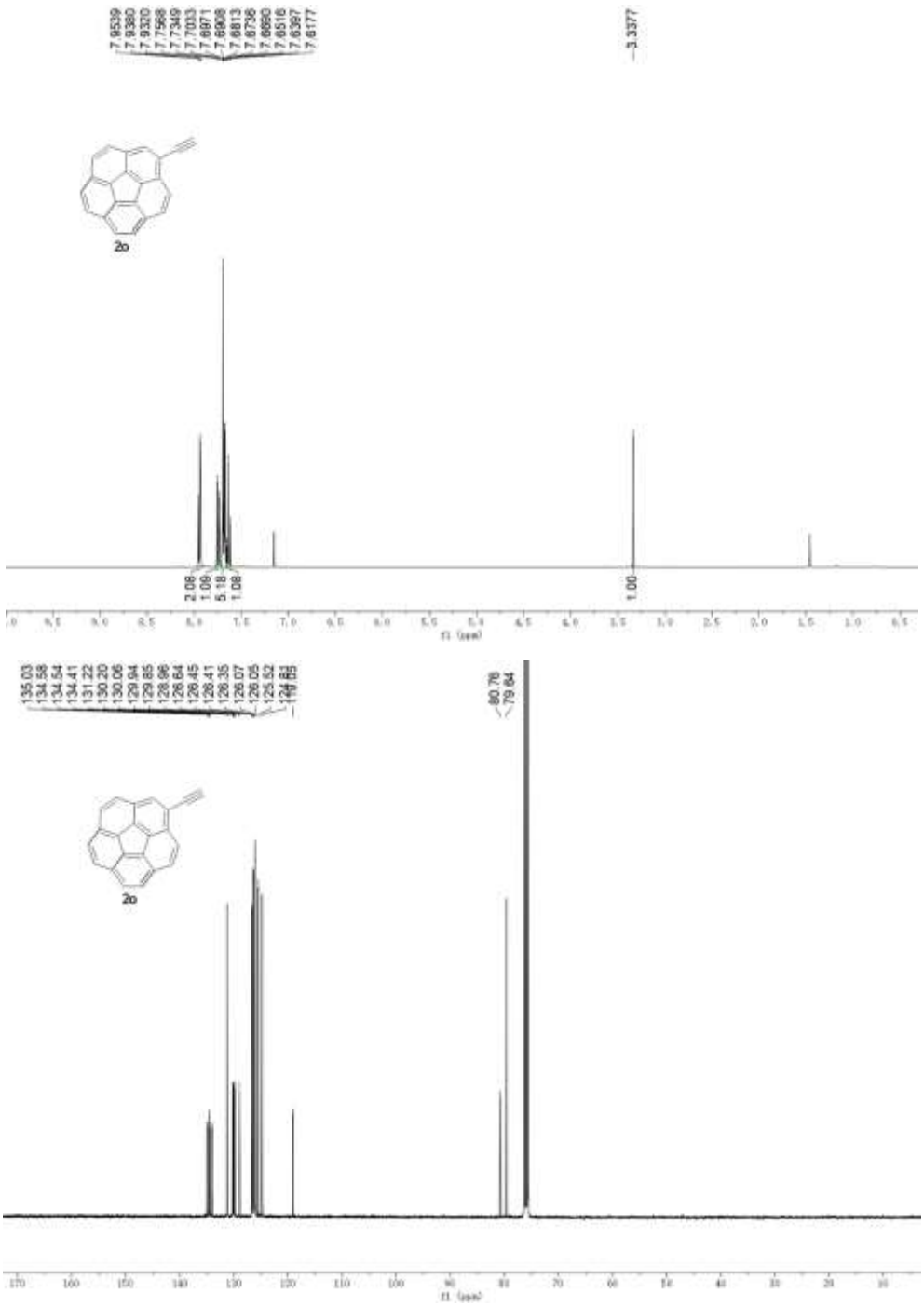
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **2l** in $CDCl_3$.



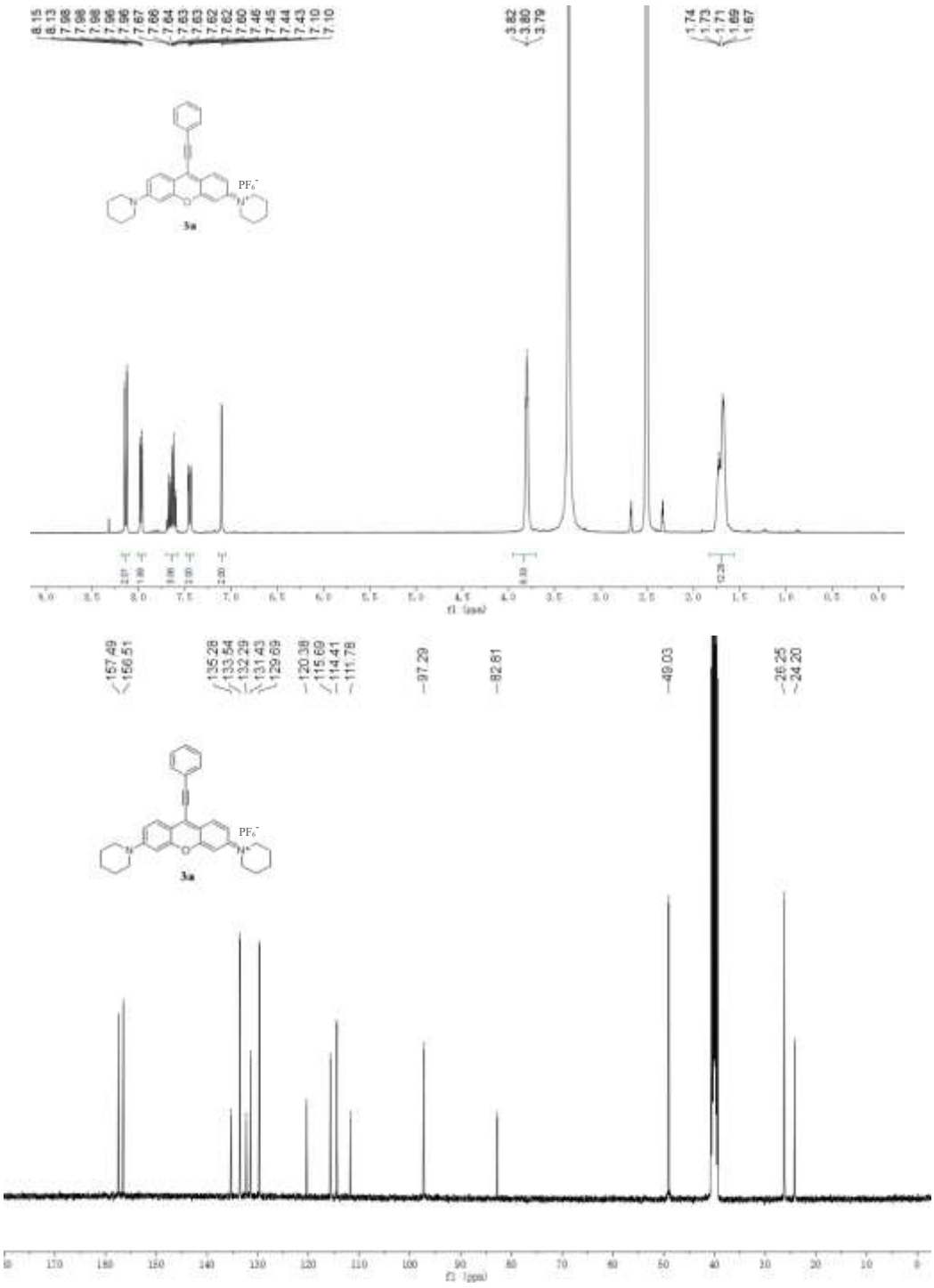
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **2m** in $CDCl_3$.



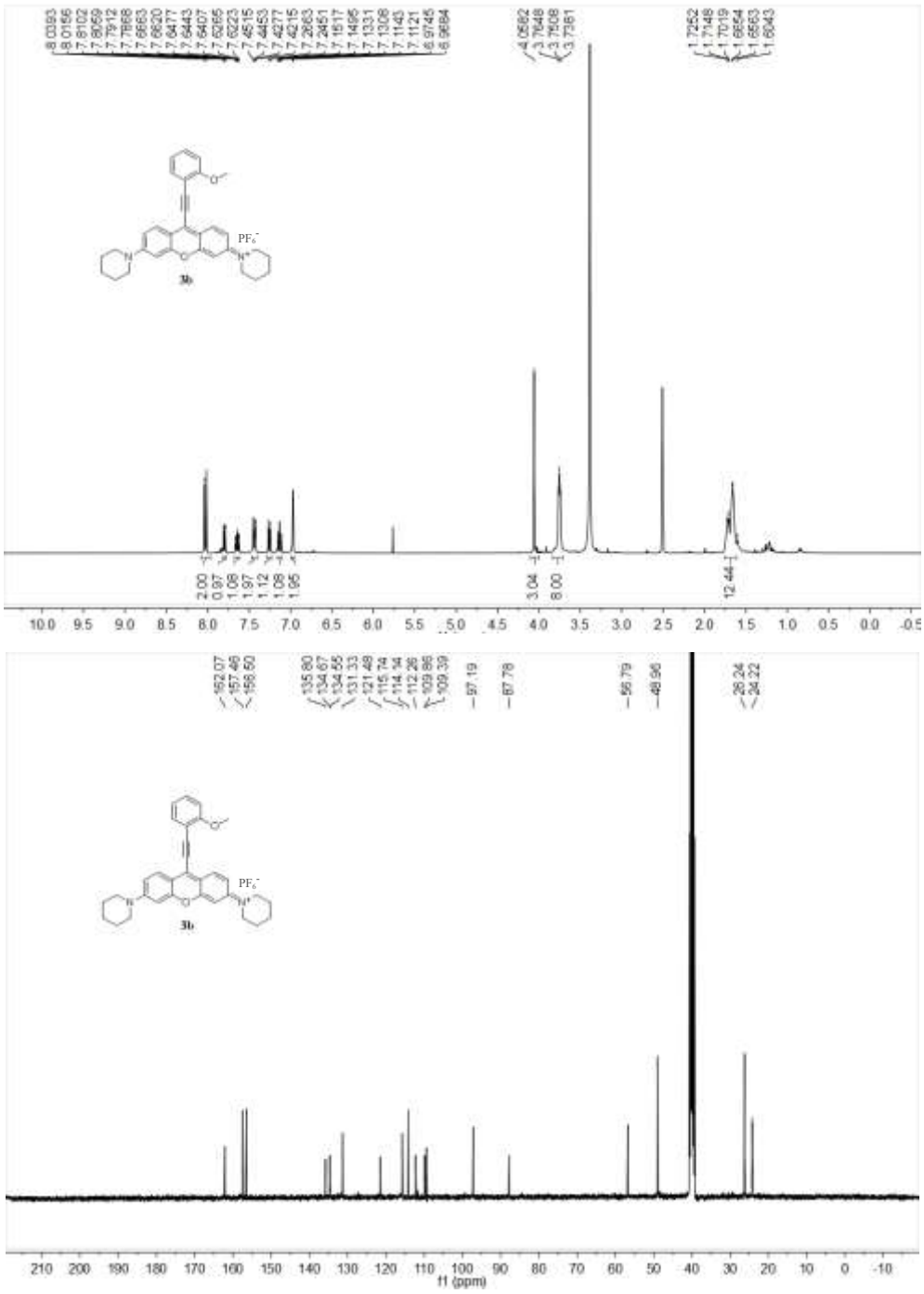
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **2n** in $CDCl_3$.



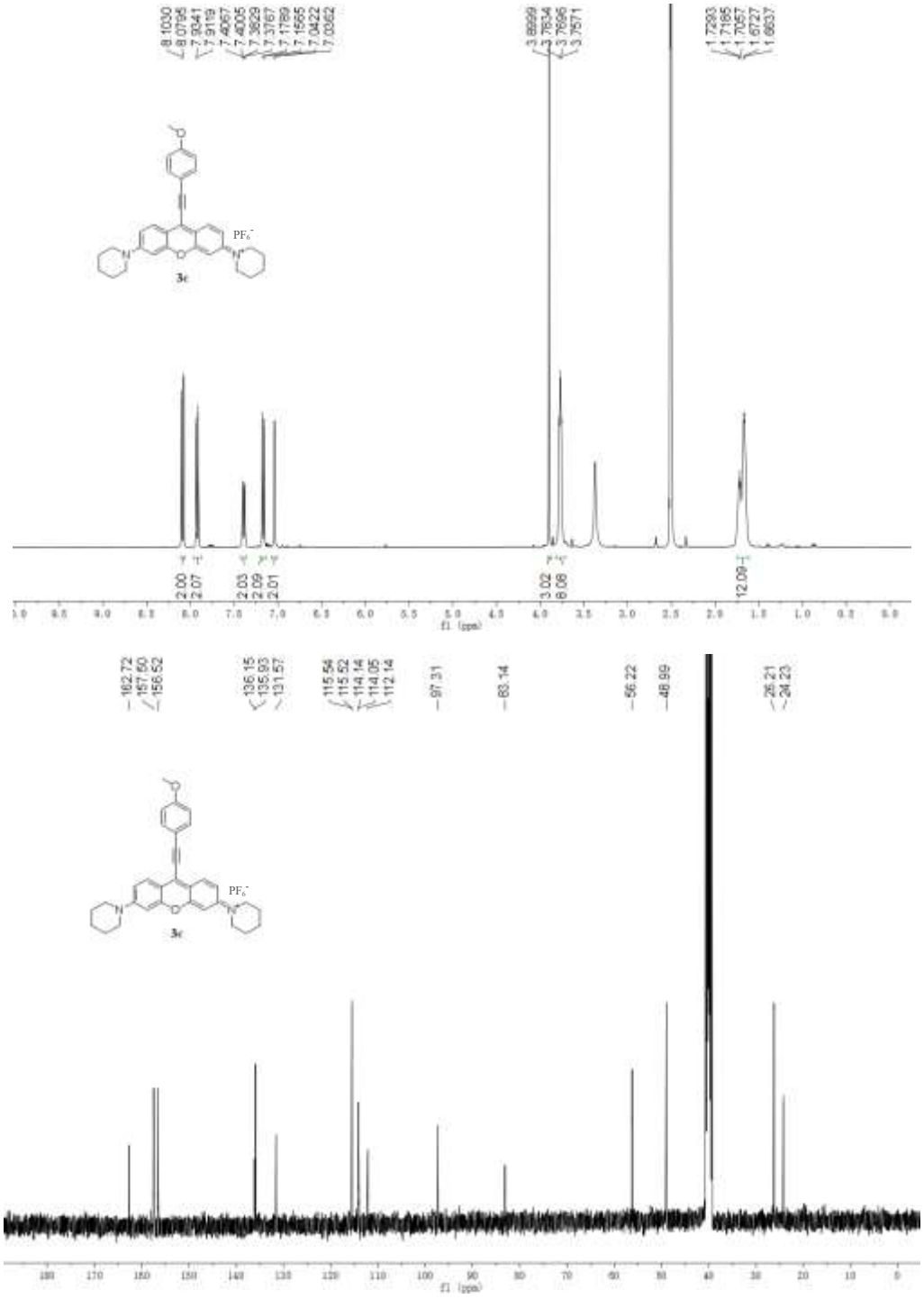
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **2o** in $CDCl_3$.



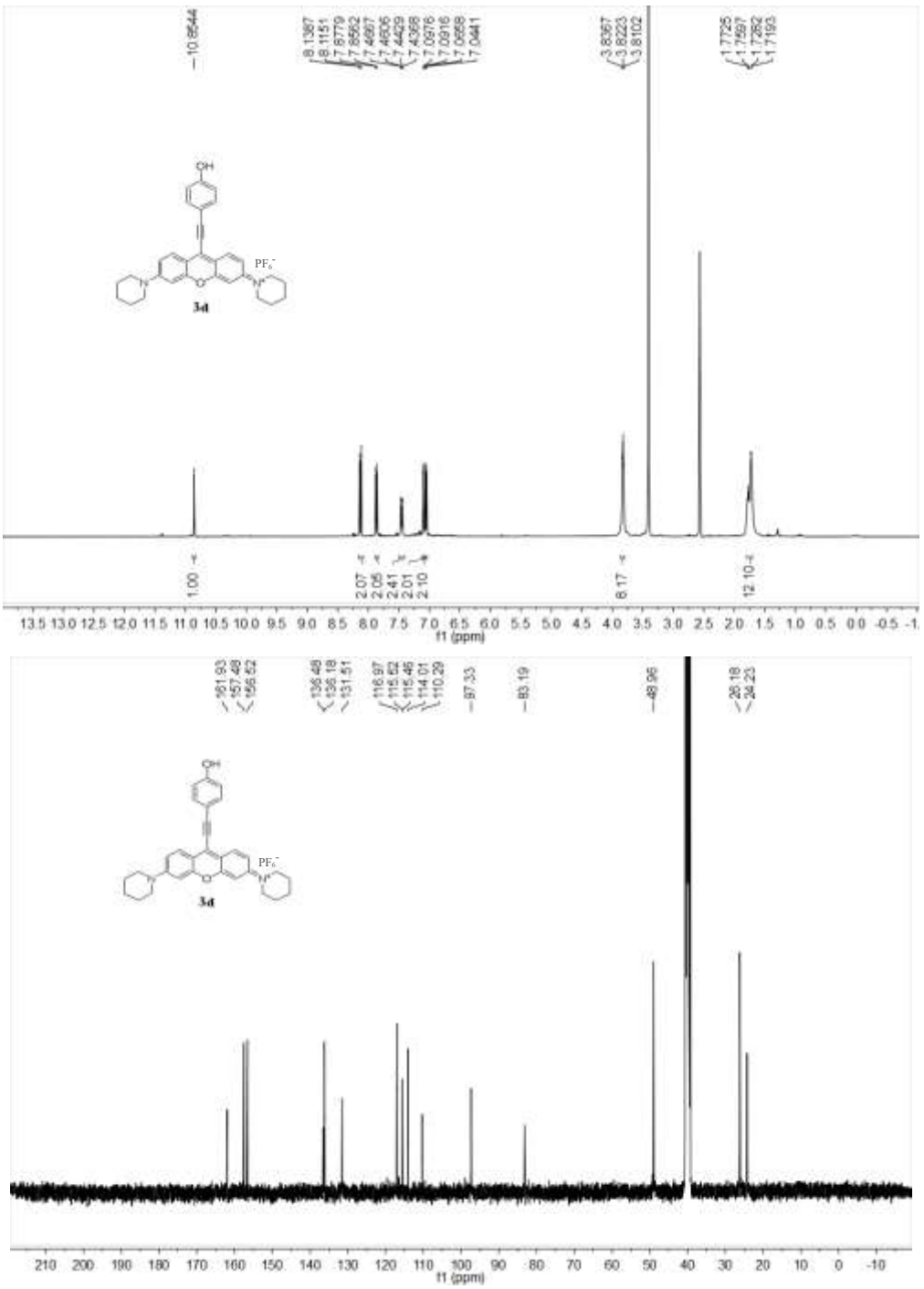
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3a** in DMSO-d_6.



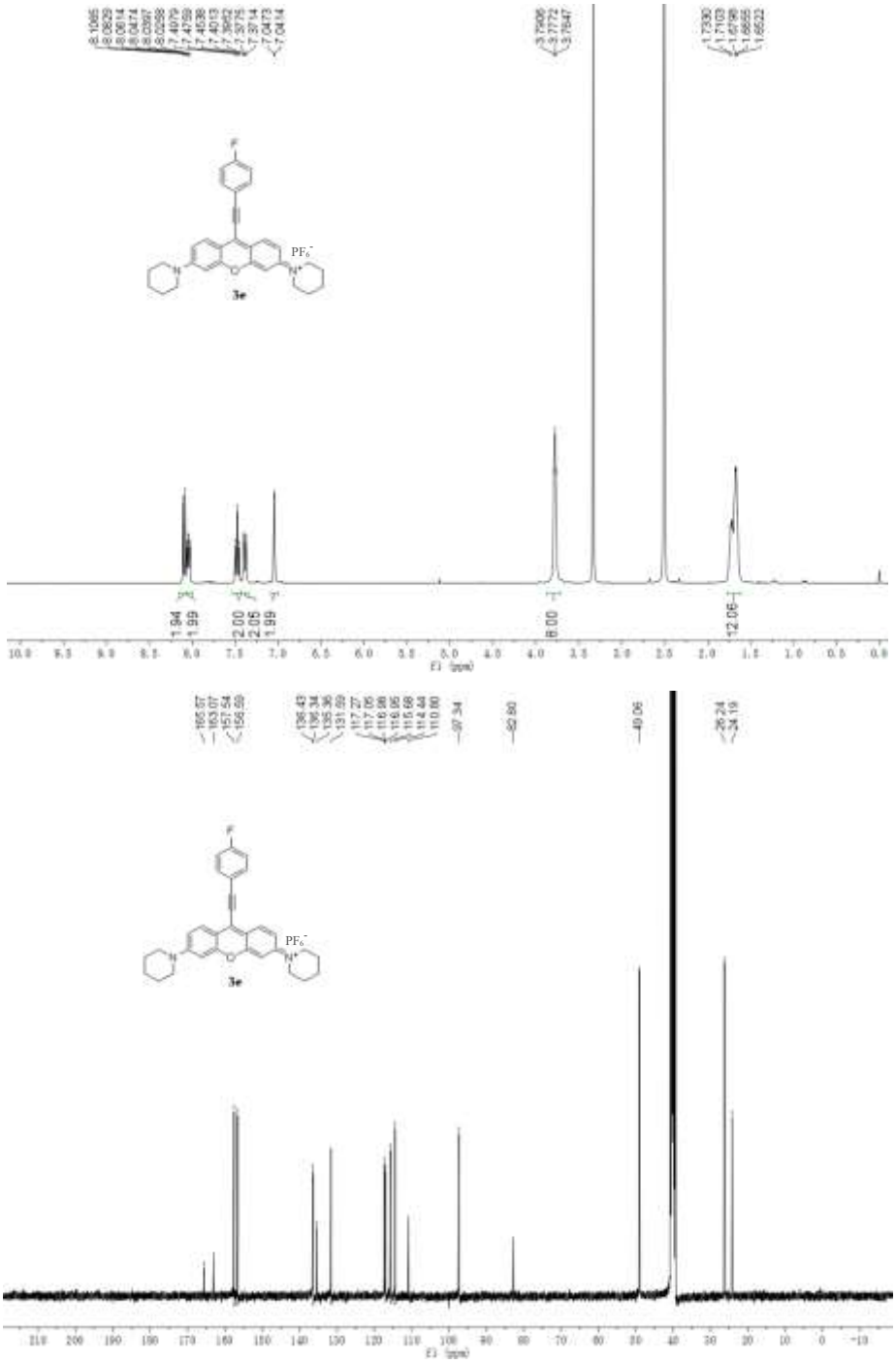
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3b** in DMSO-d_6.



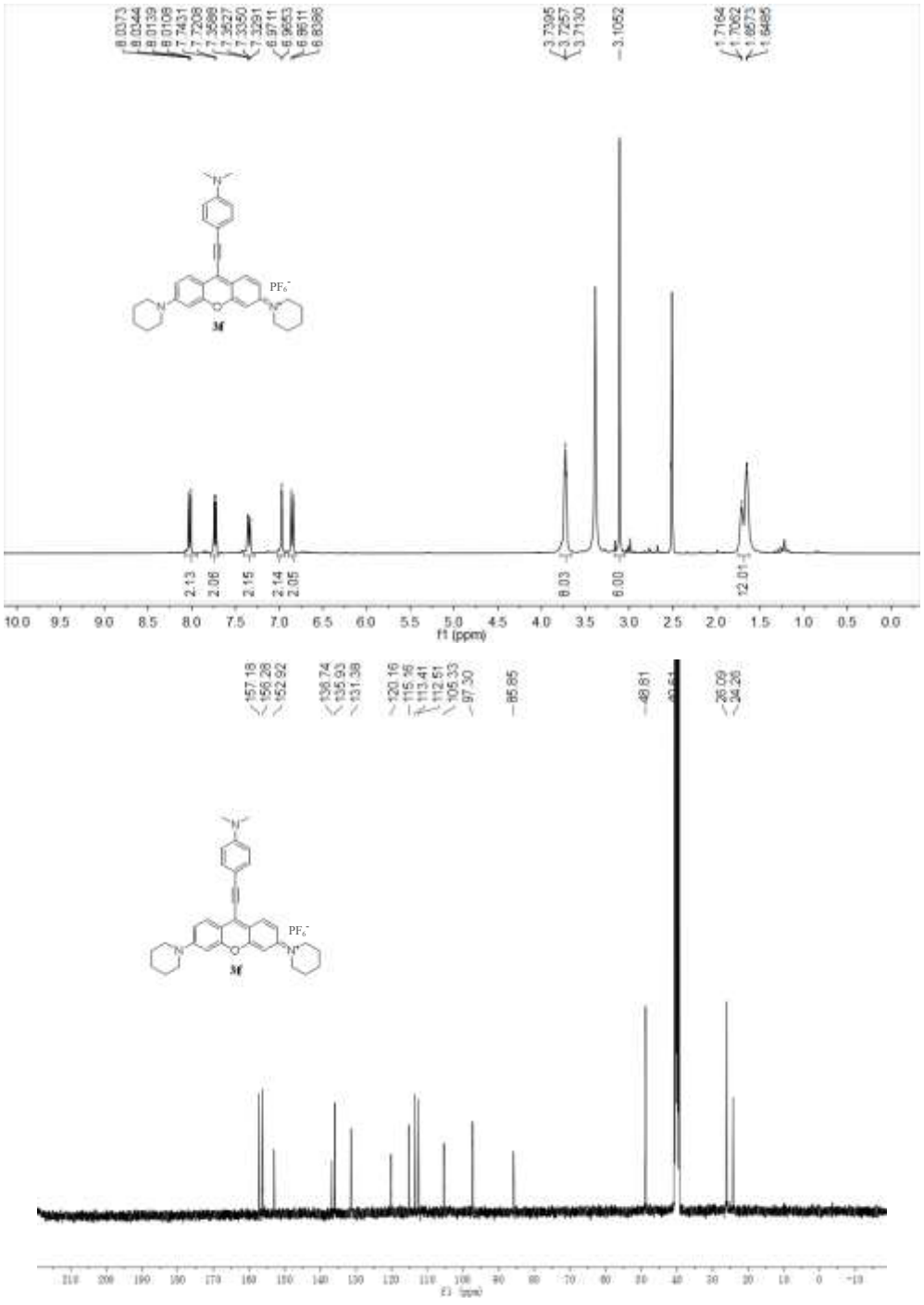
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3c** in DMSO-d_6.



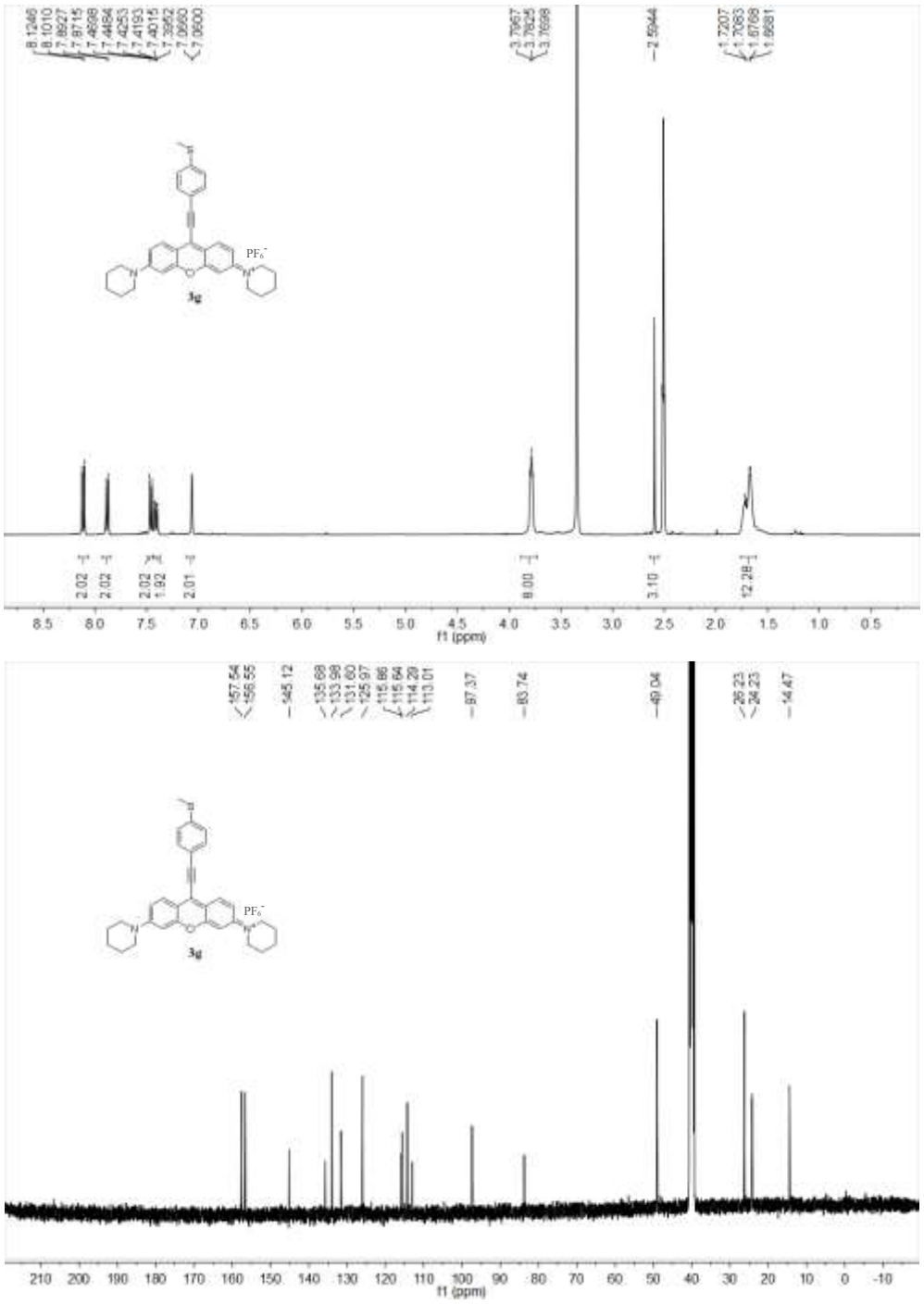
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3d** in DMSO-d_6.



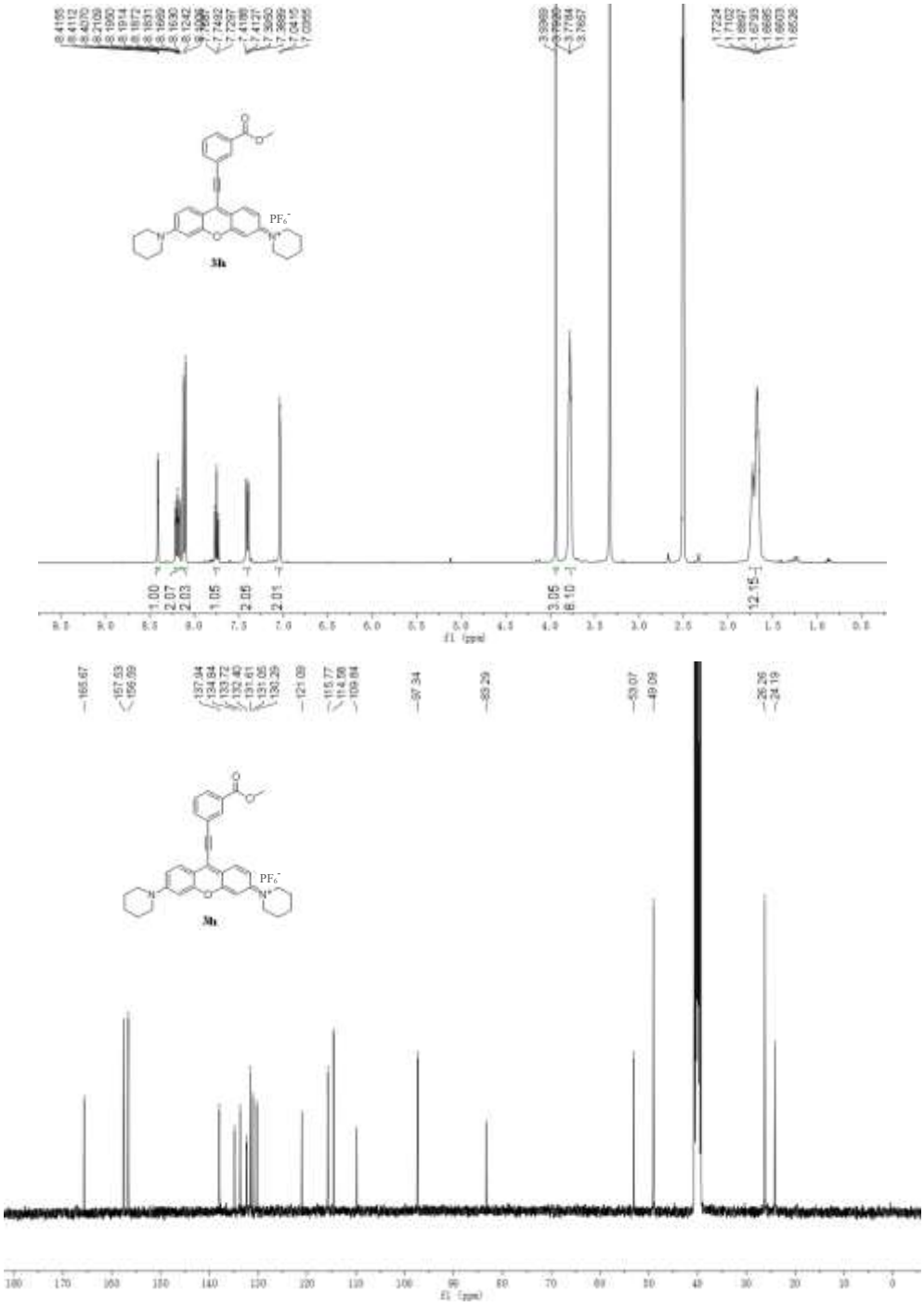
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3e** in DMSO-d_6.



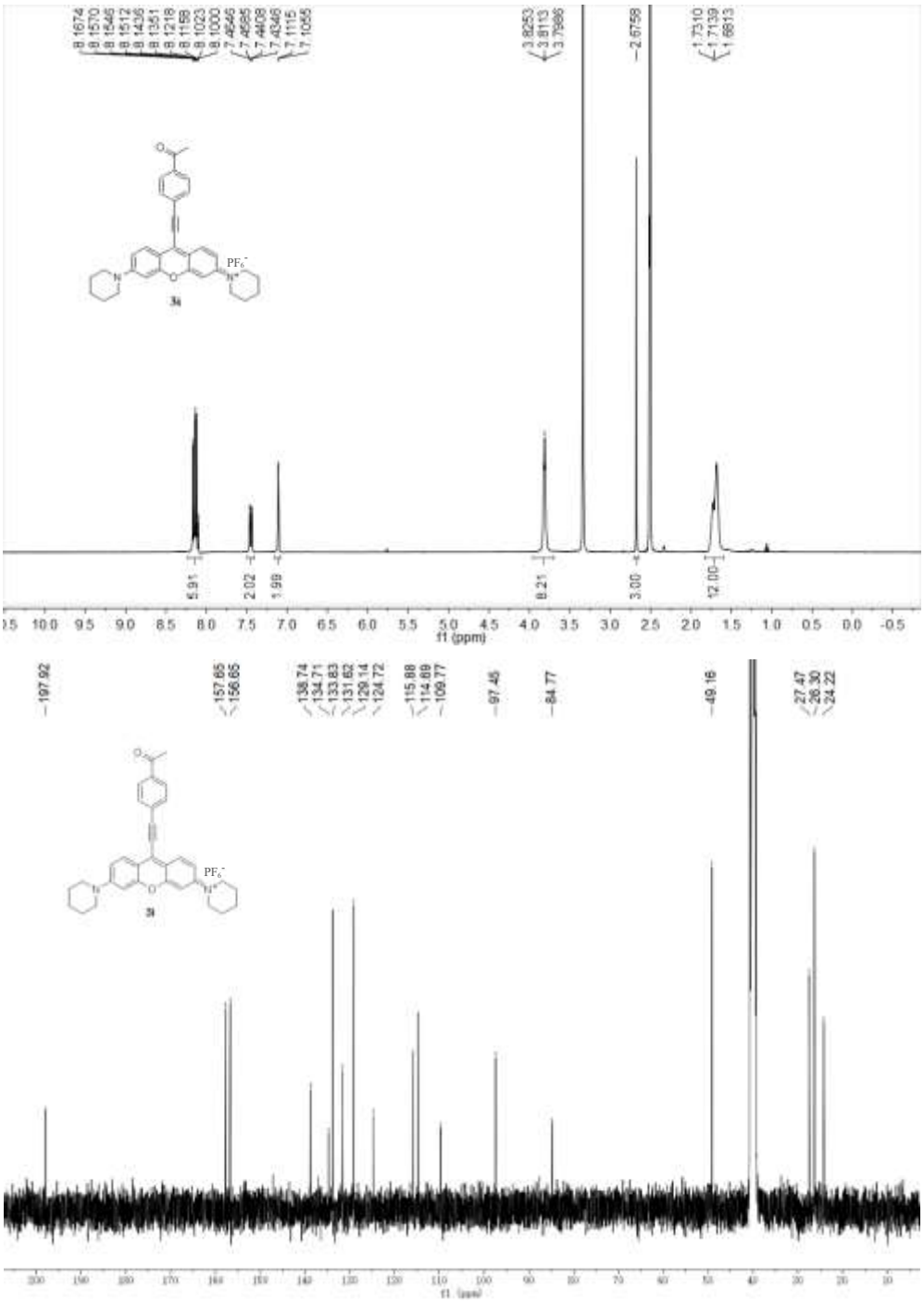
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3f** in DMSO-d_6.



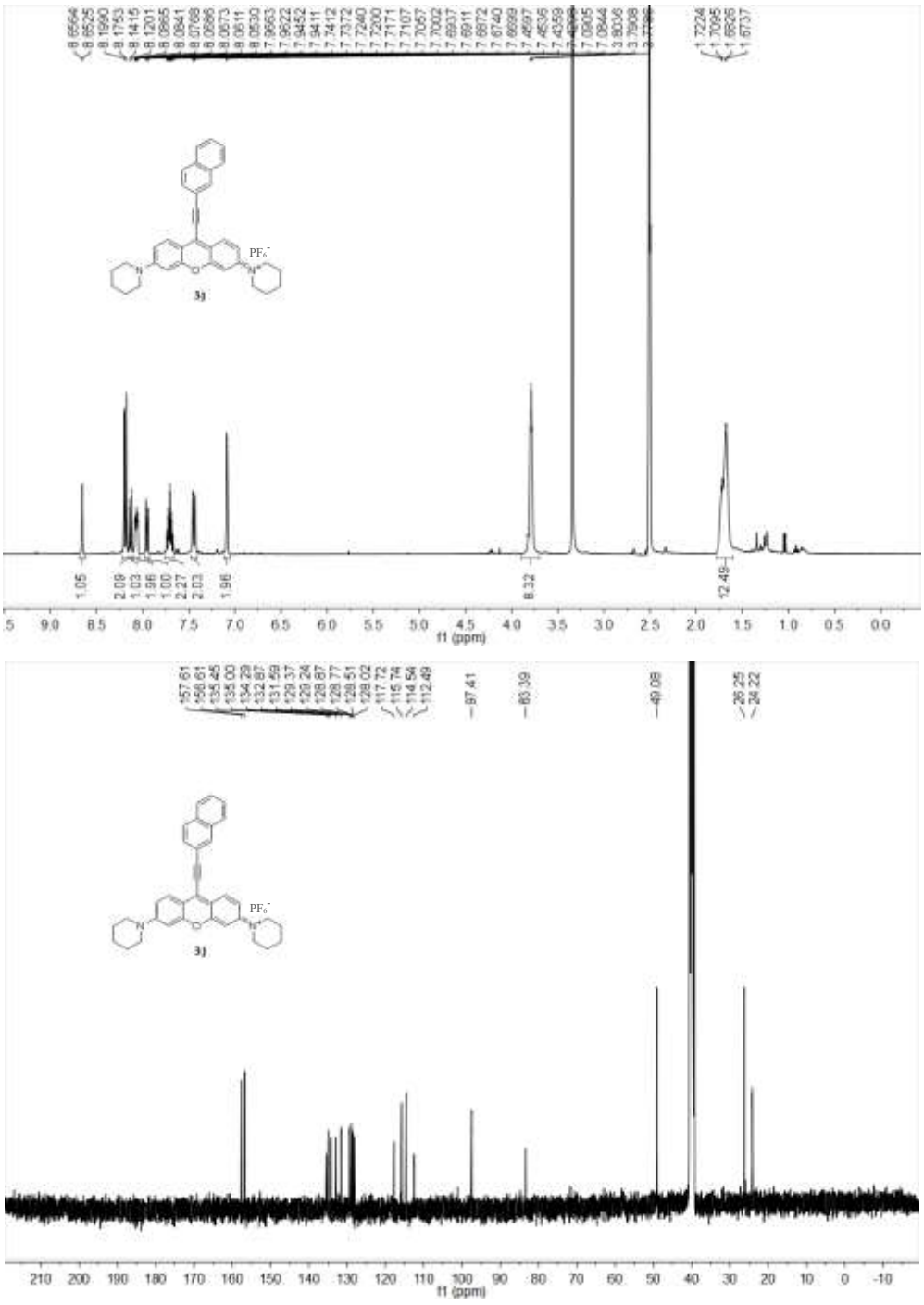
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3g** in DMSO-d_6.



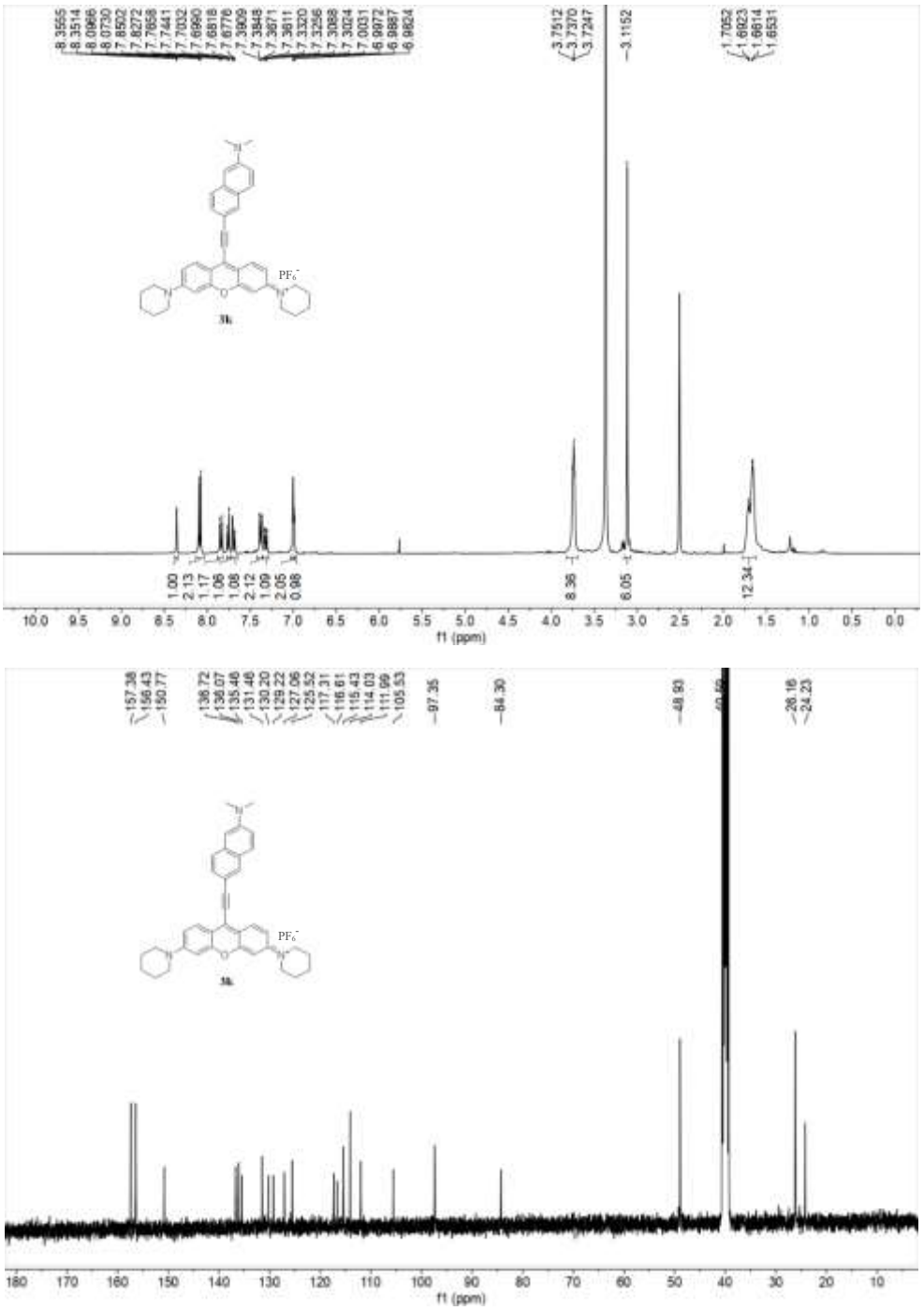
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3h** in DMSO-d_6.



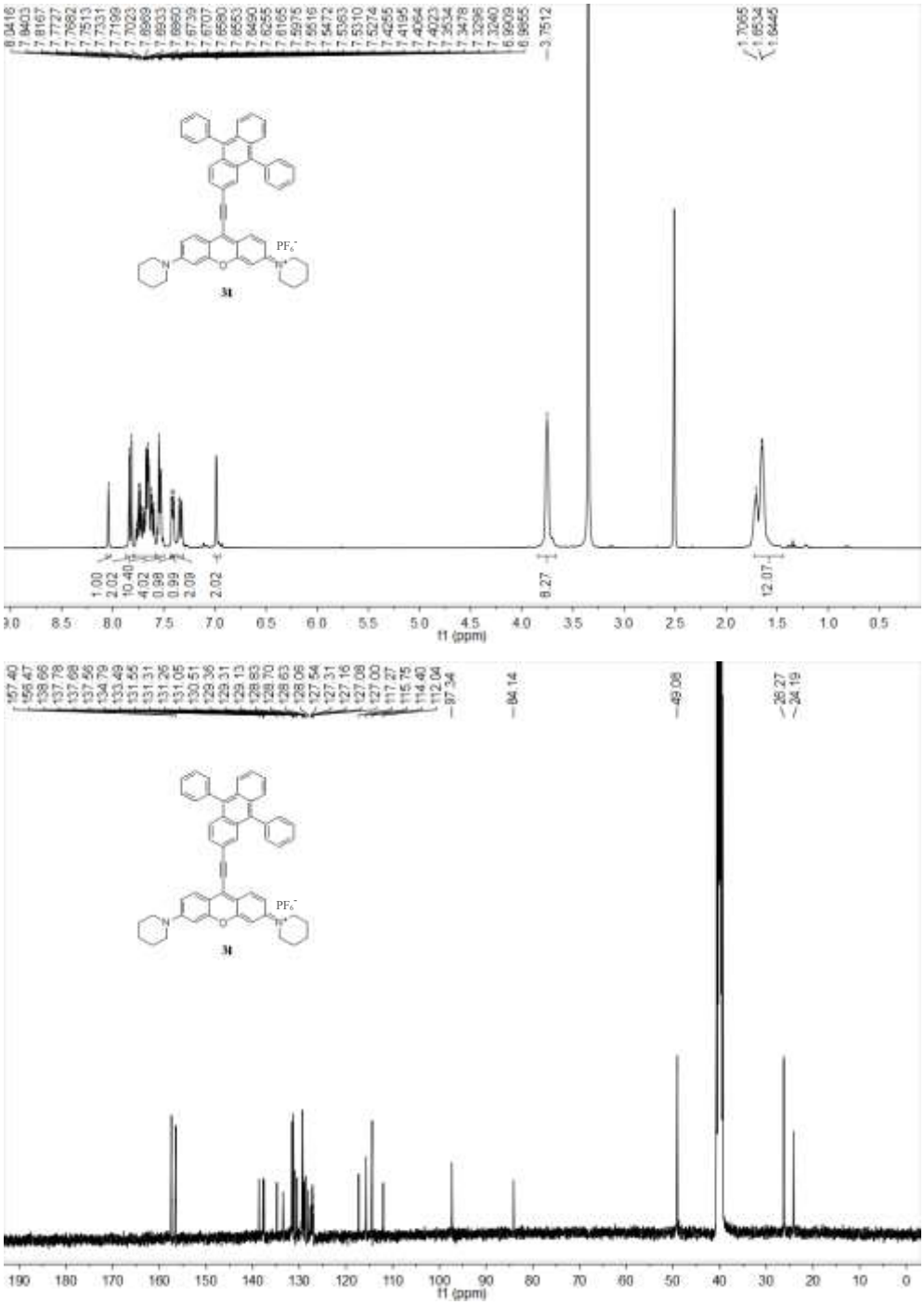
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3i** in DMSO-d_6.



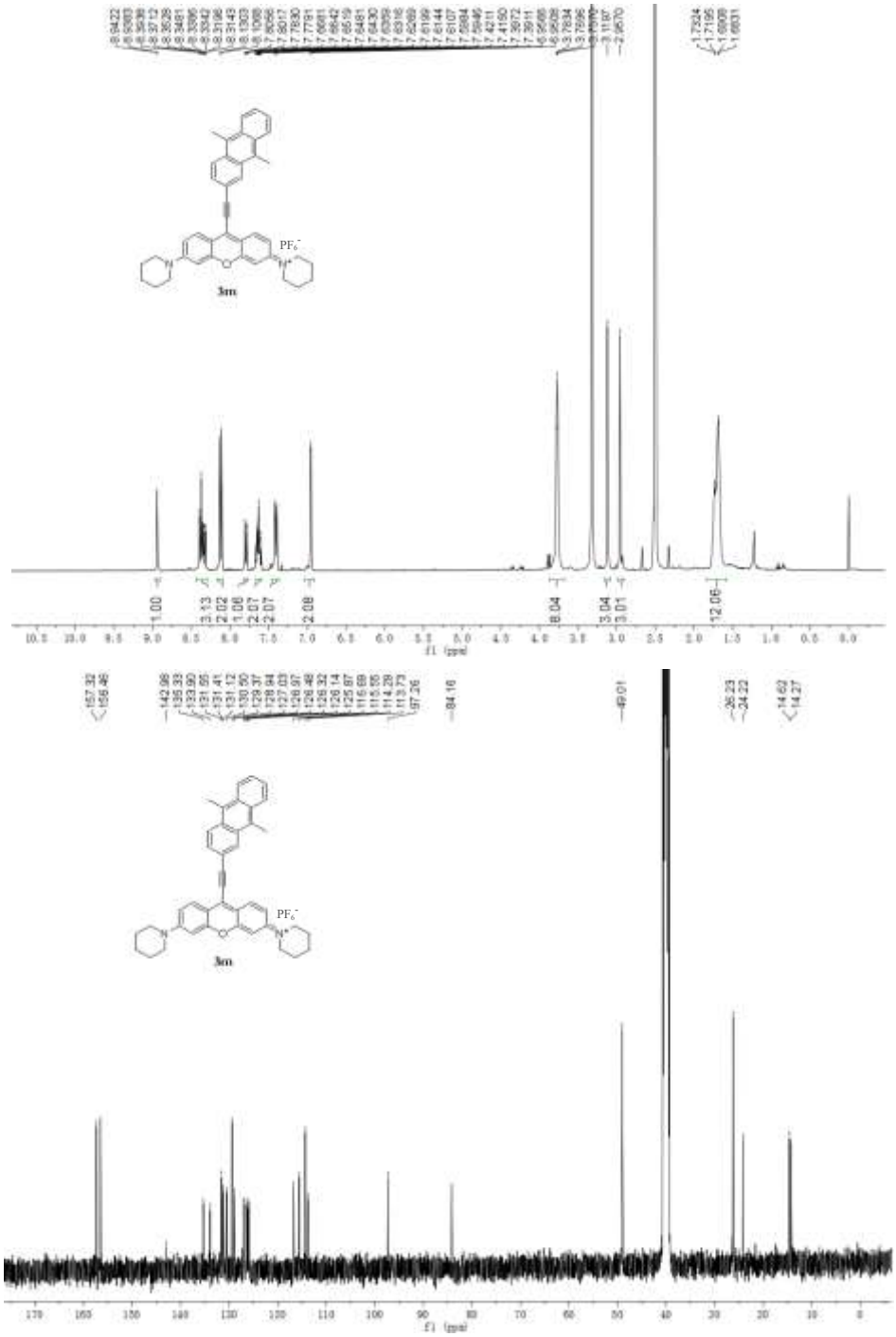
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3j** in DMSO-d_6.



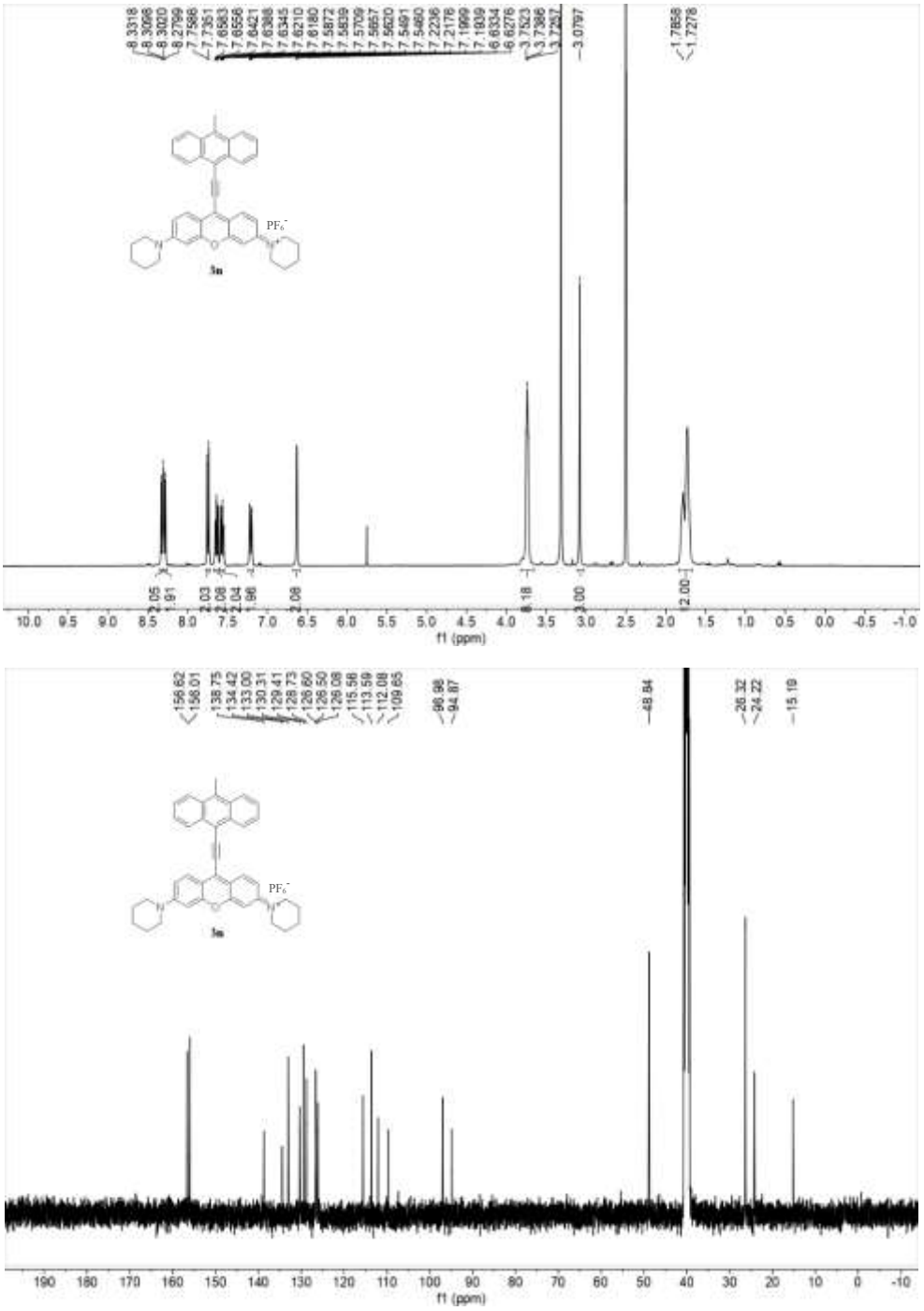
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3k** in DMSO-d_6.



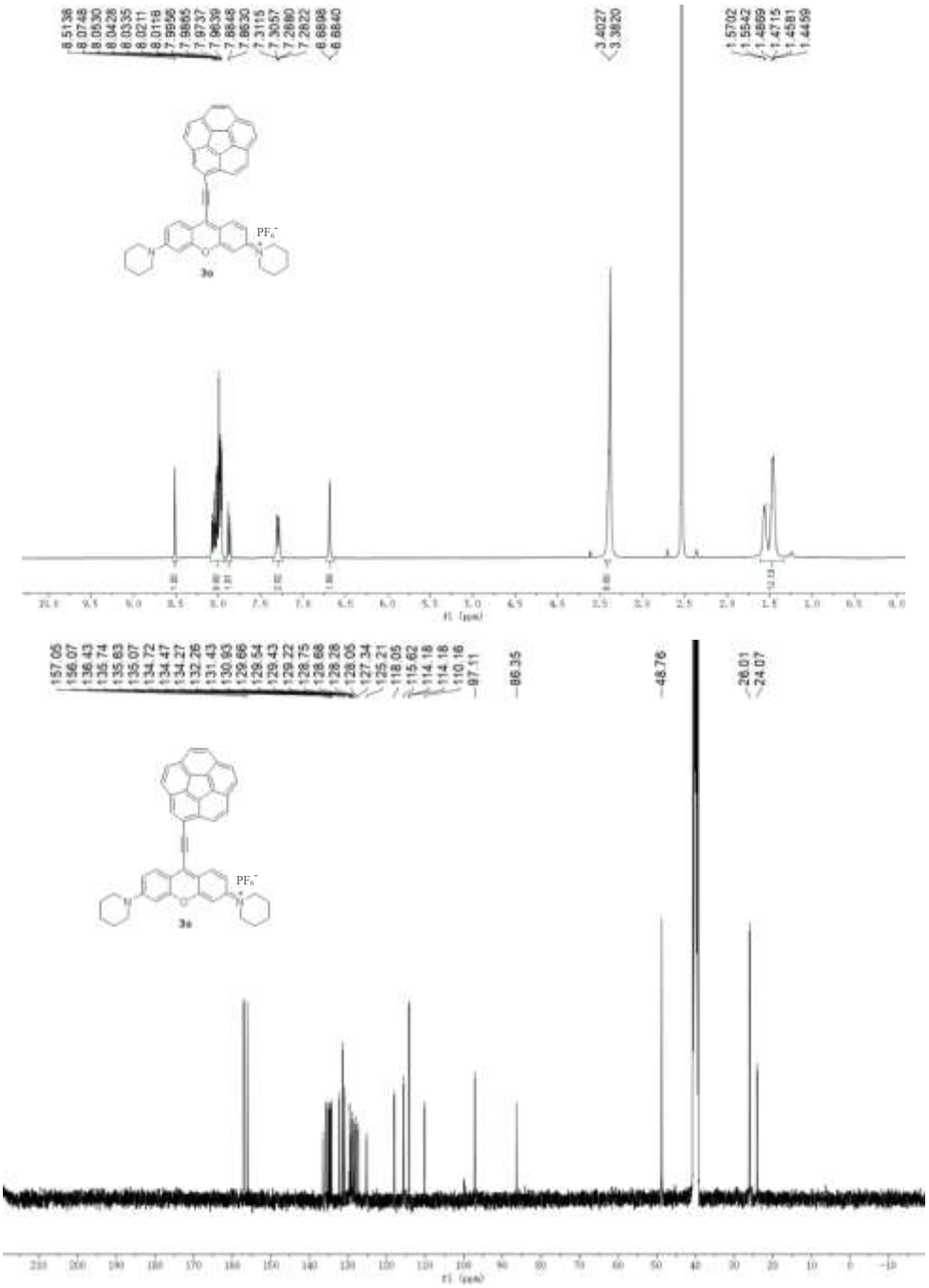
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3l** in DMSO-d_6.



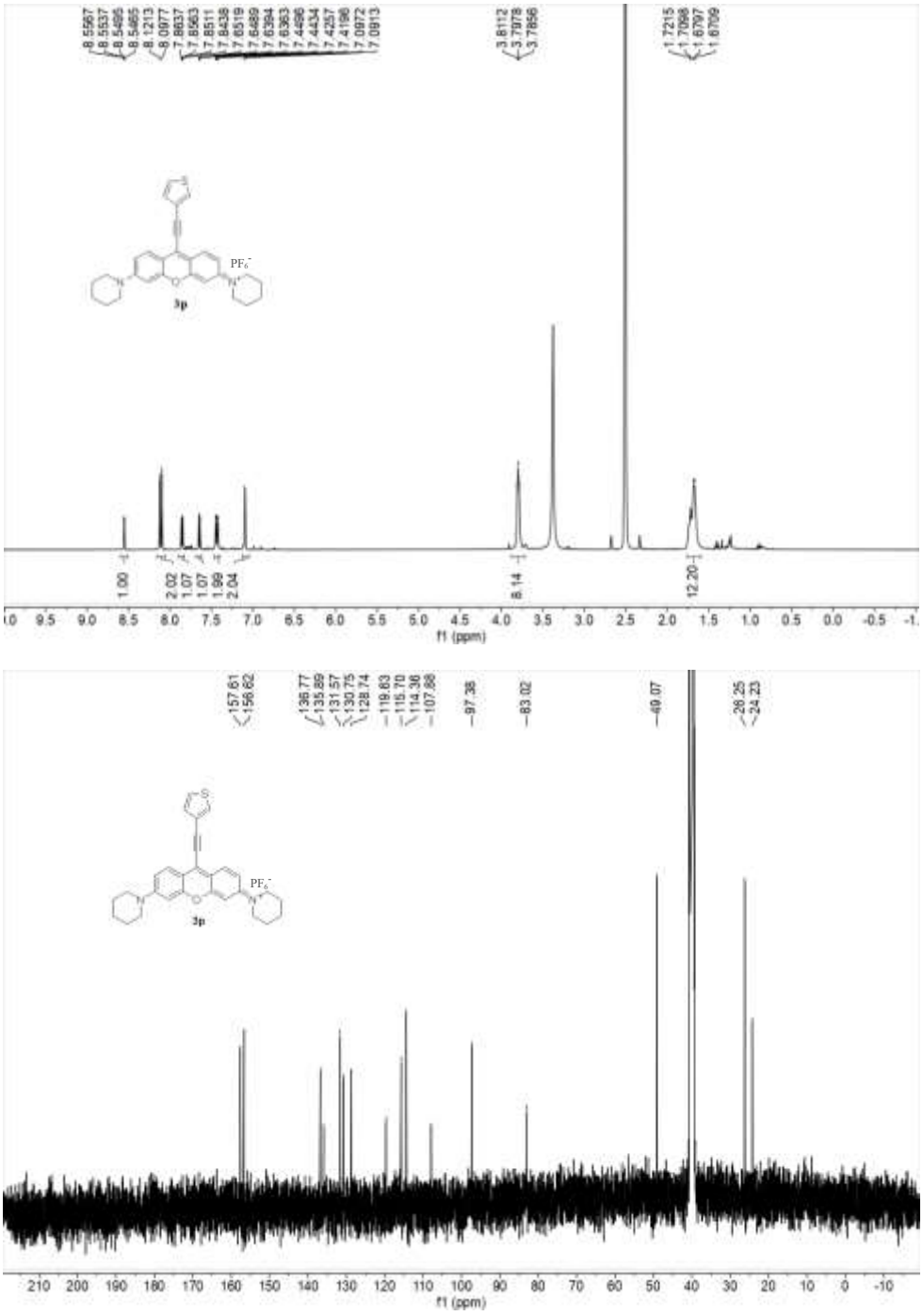
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3m** in DMSO-d_6.



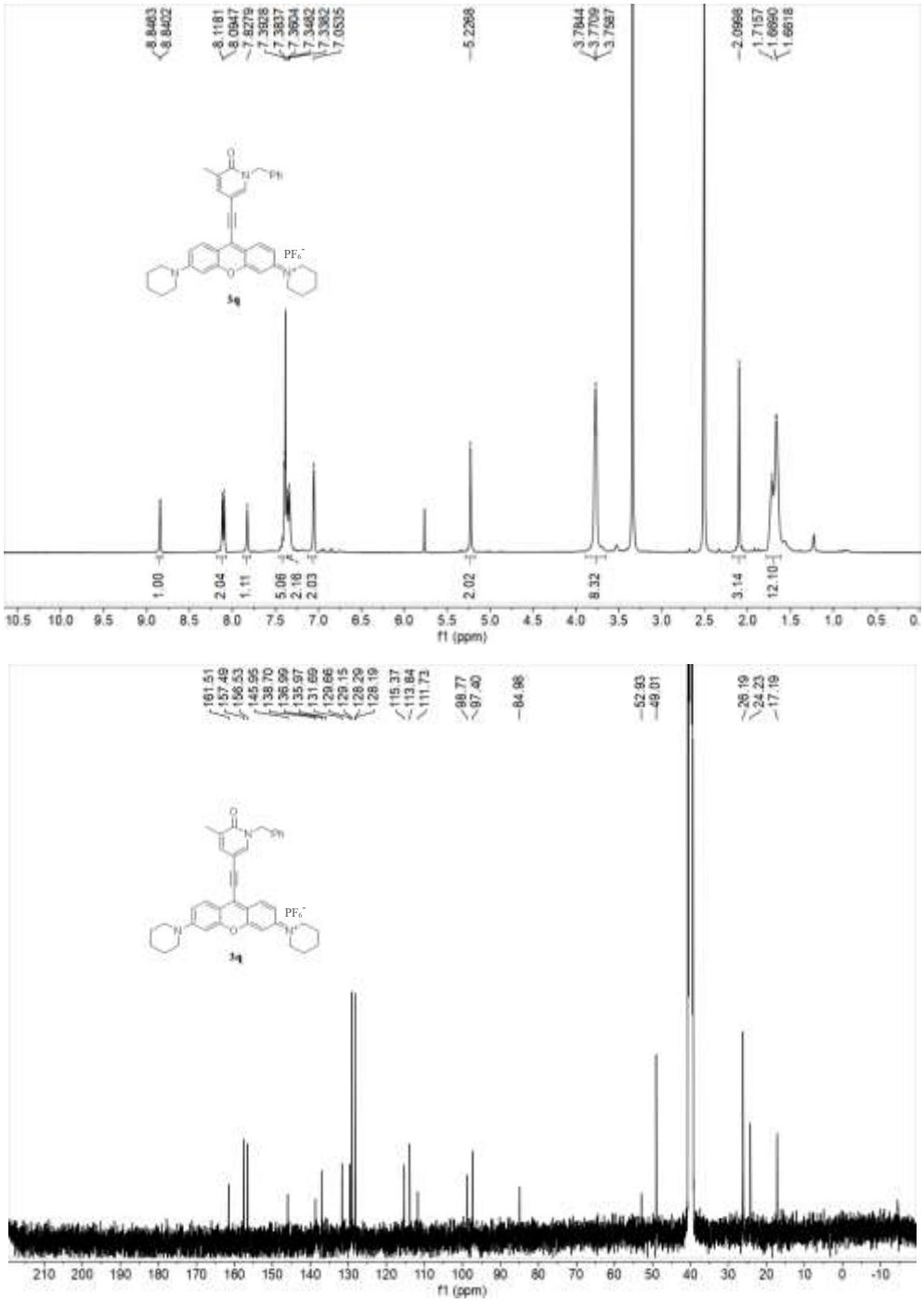
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3n** in DMSO-d_6.



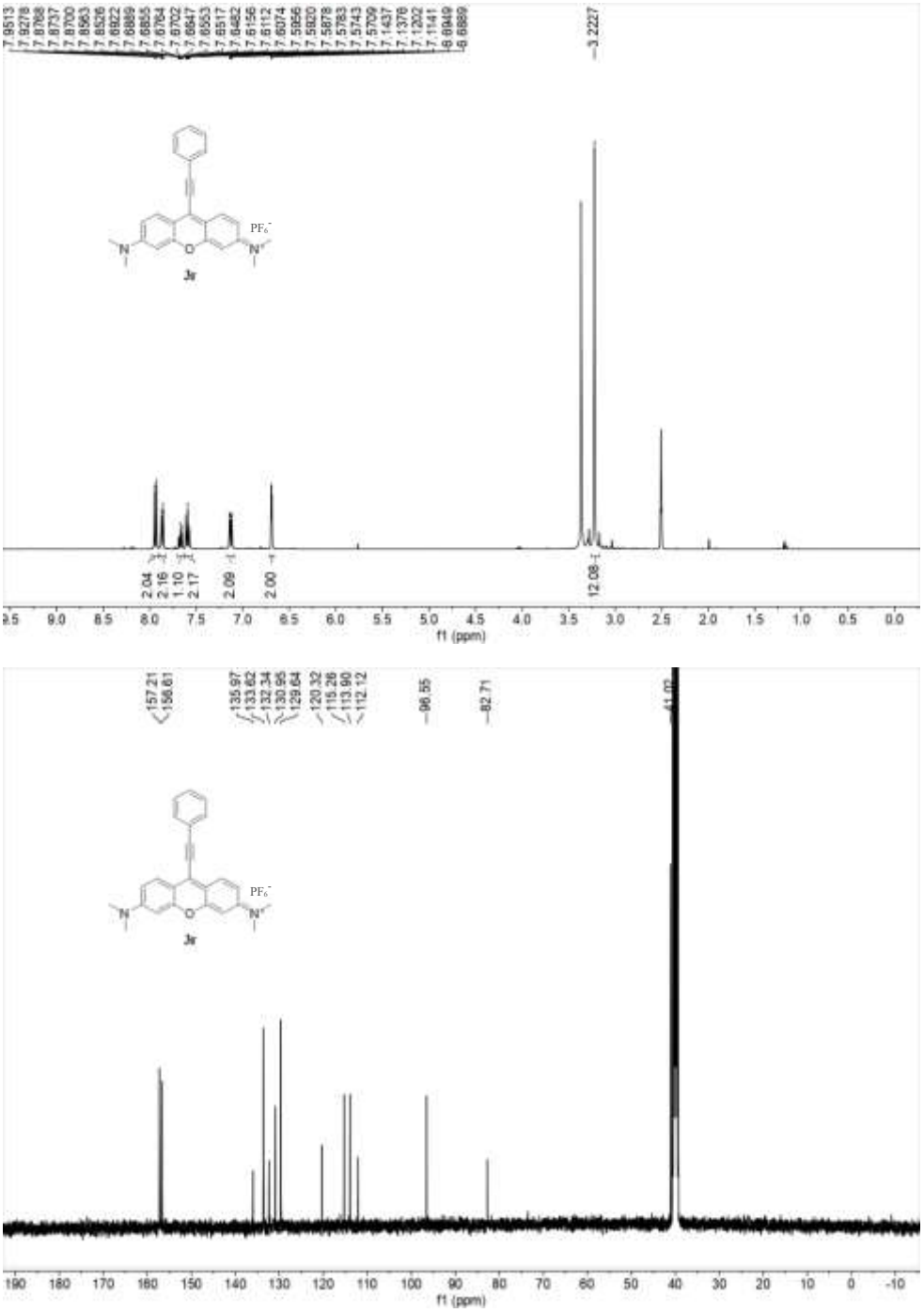
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3o** in DMSO-d_6.



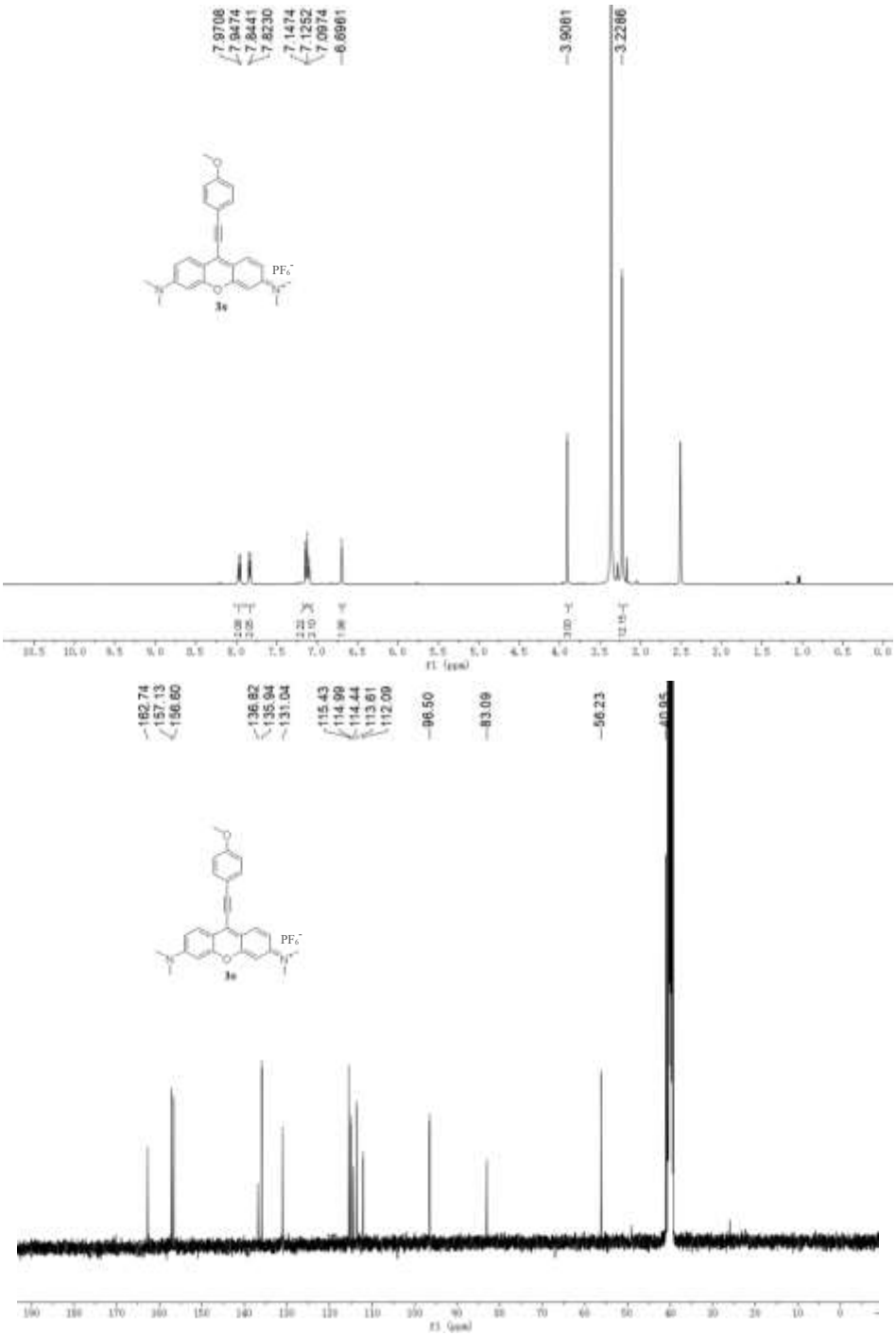
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3p** in DMSO-d_6.



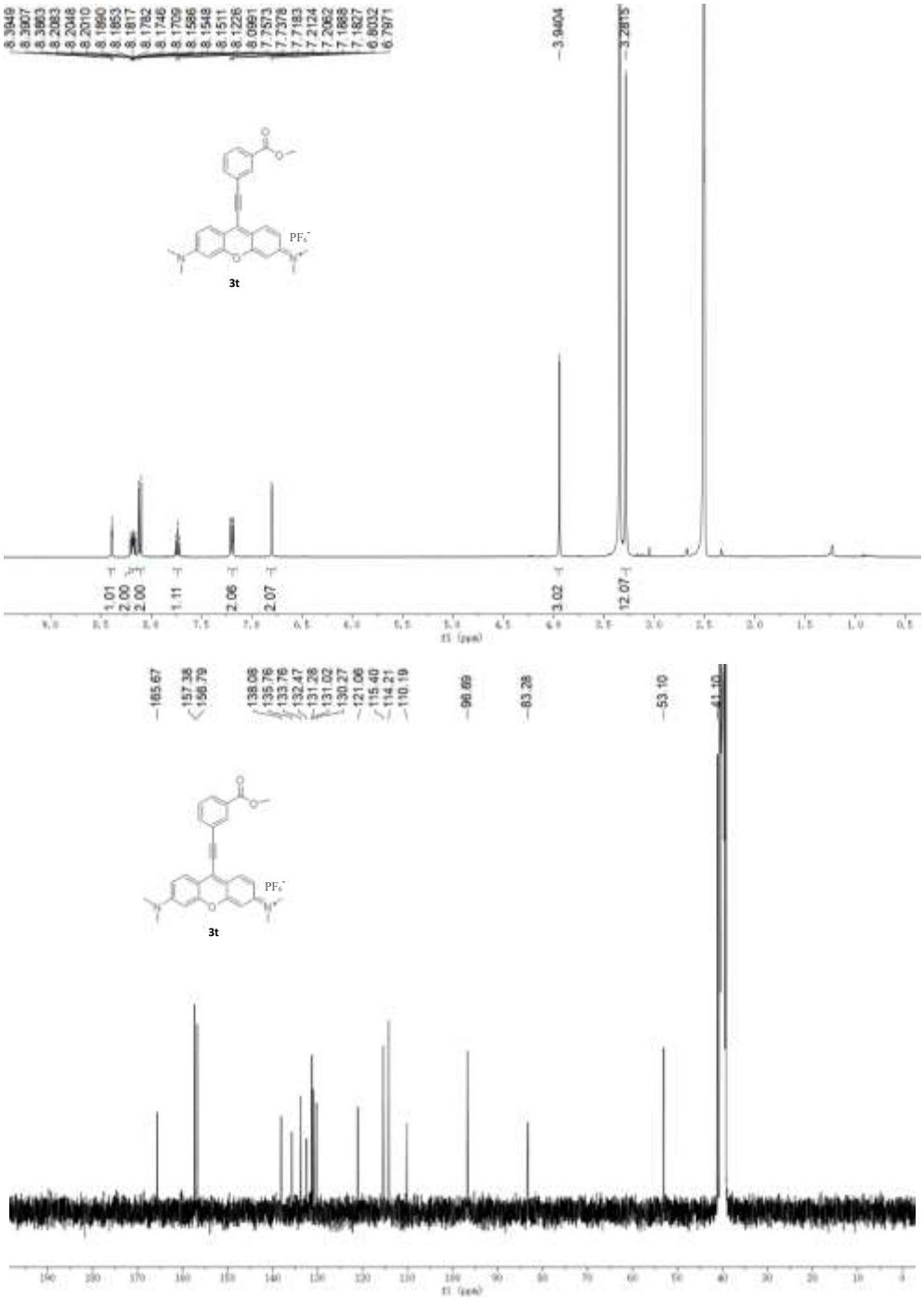
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3q** in DMSO-d_6.



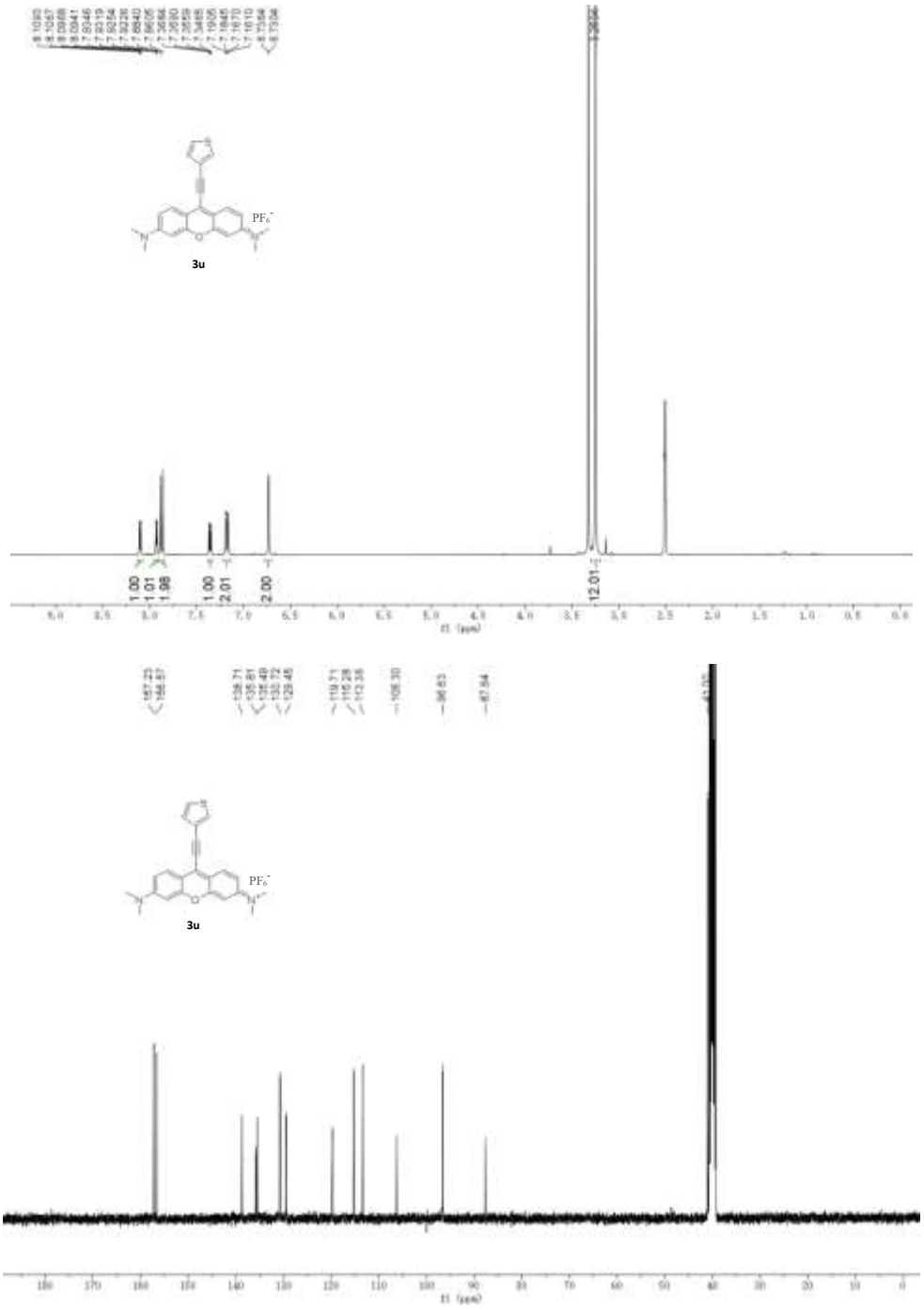
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3r** in DMSO-d_6.



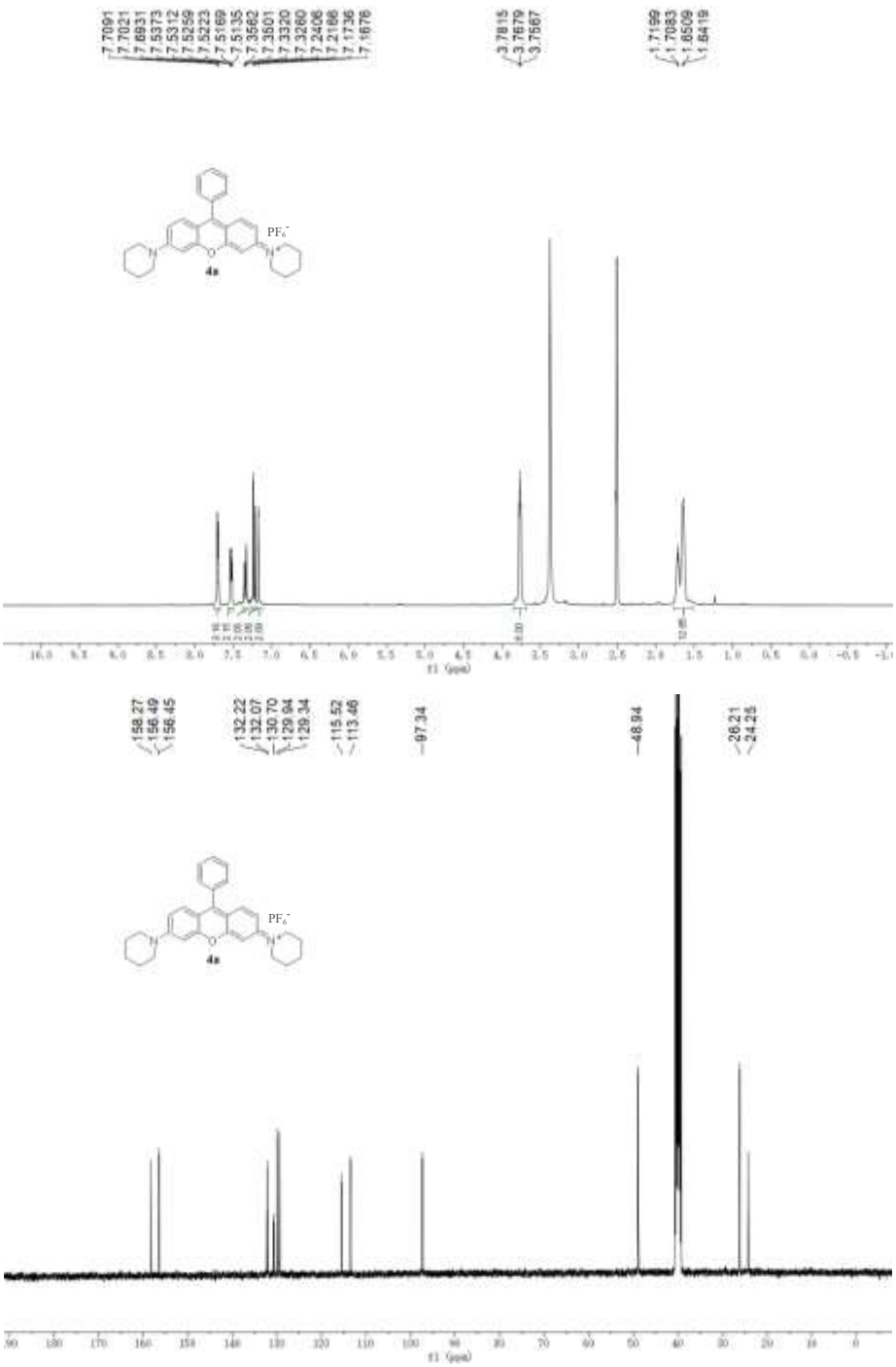
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3s** in DMSO-d_6.



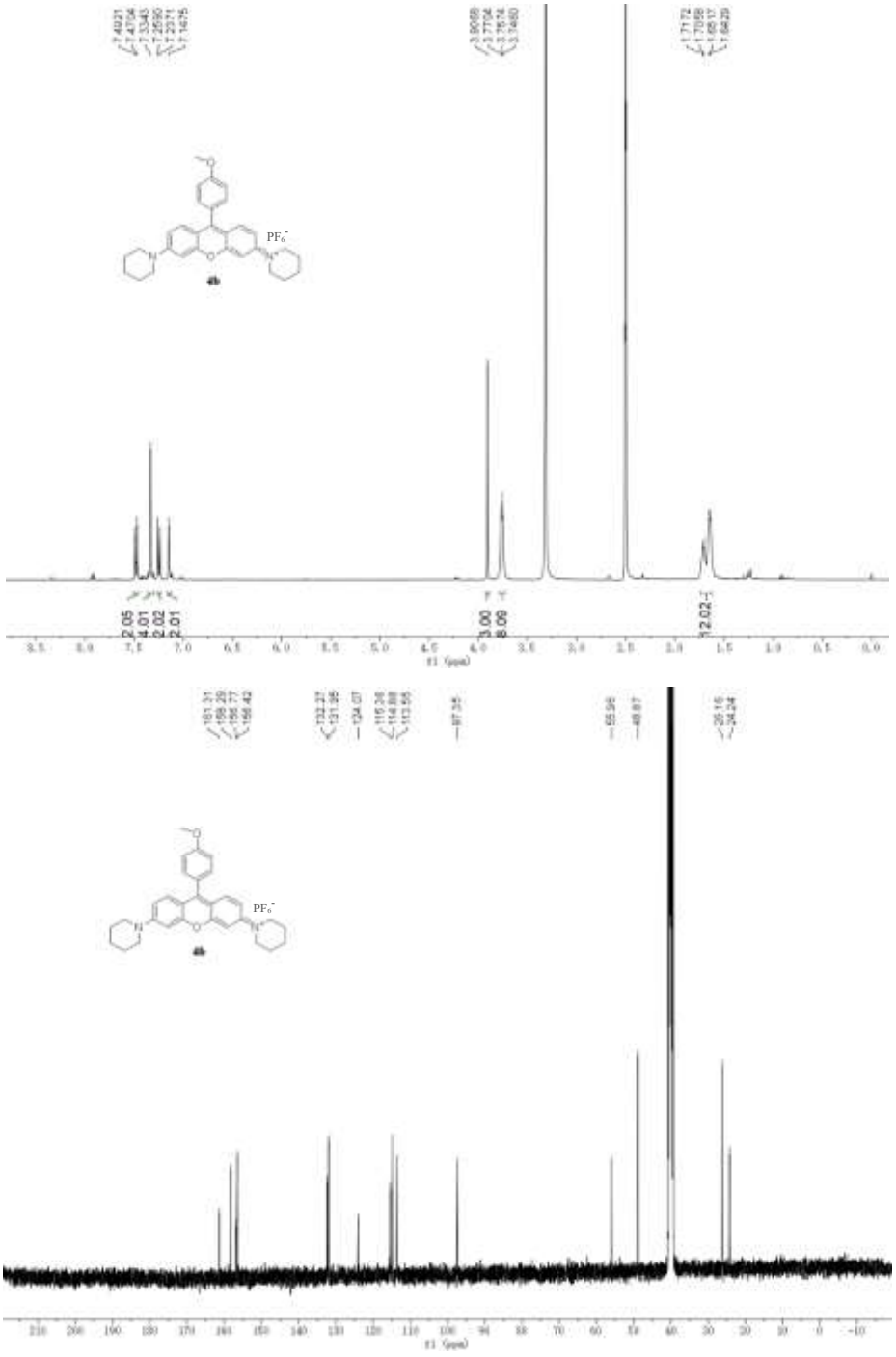
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3t** in DMSO-d_6.



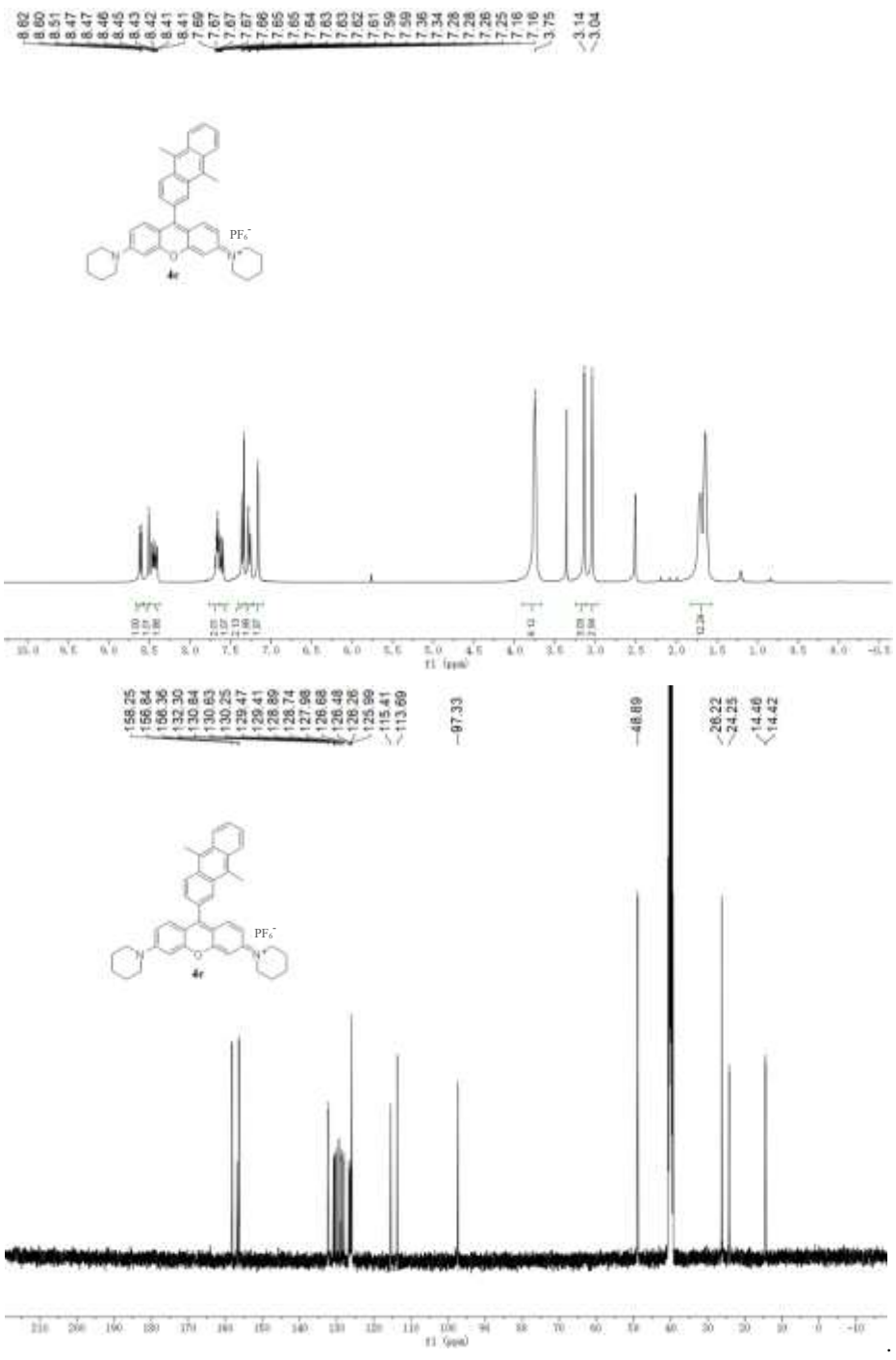
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3u** in DMSO-d_6.



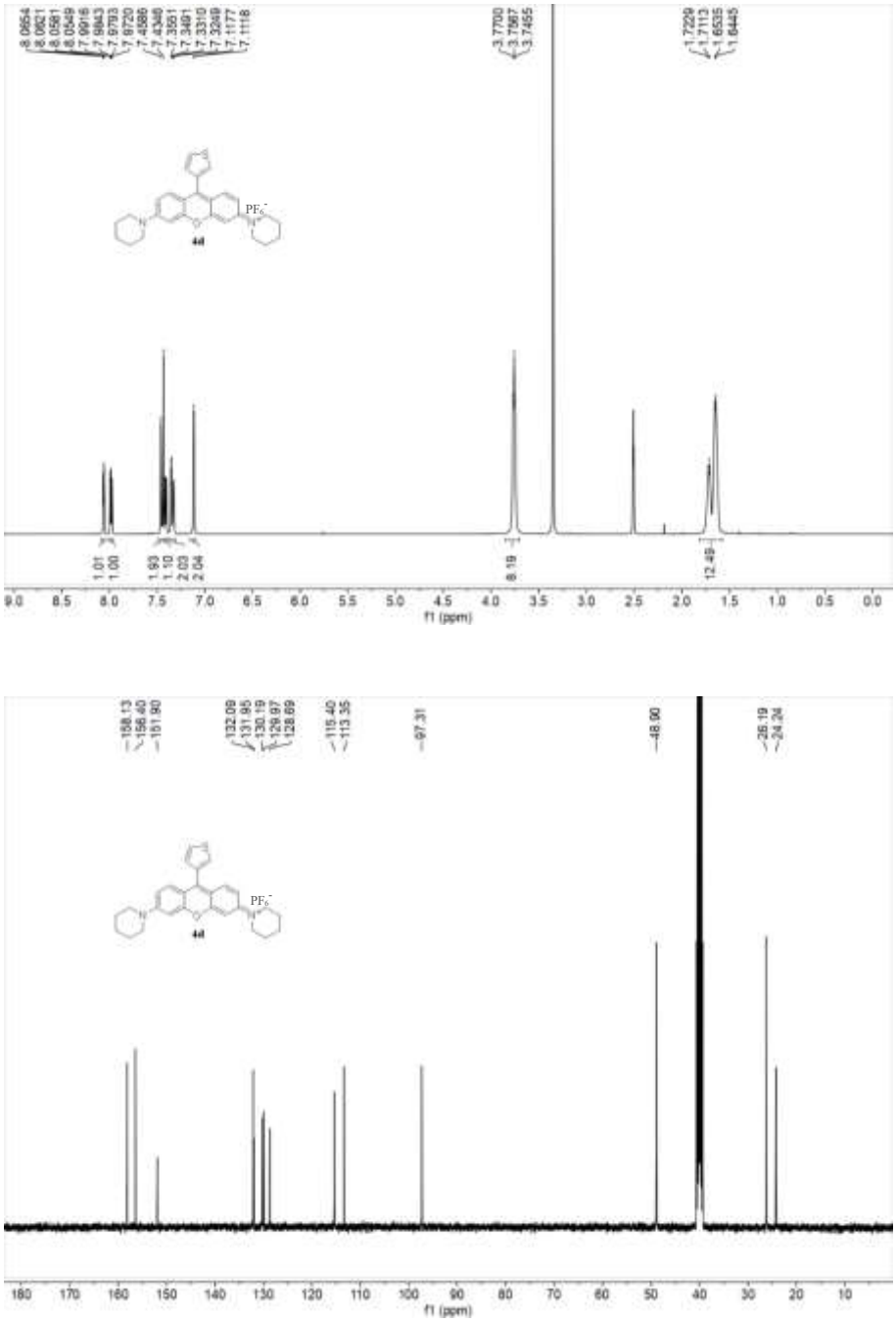
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **4a** in DMSO-d_6.



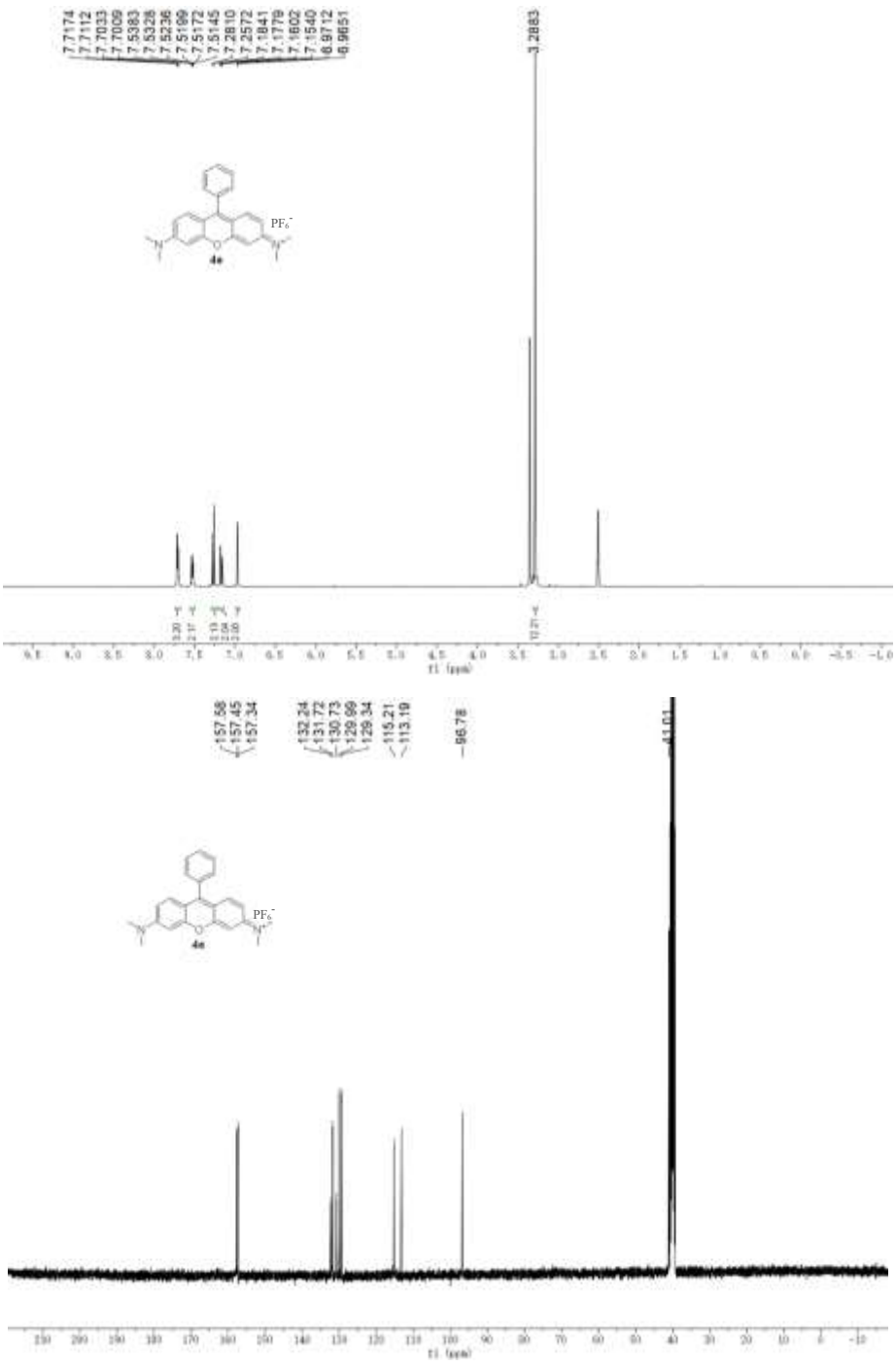
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **4b** in DMSO-d_6.



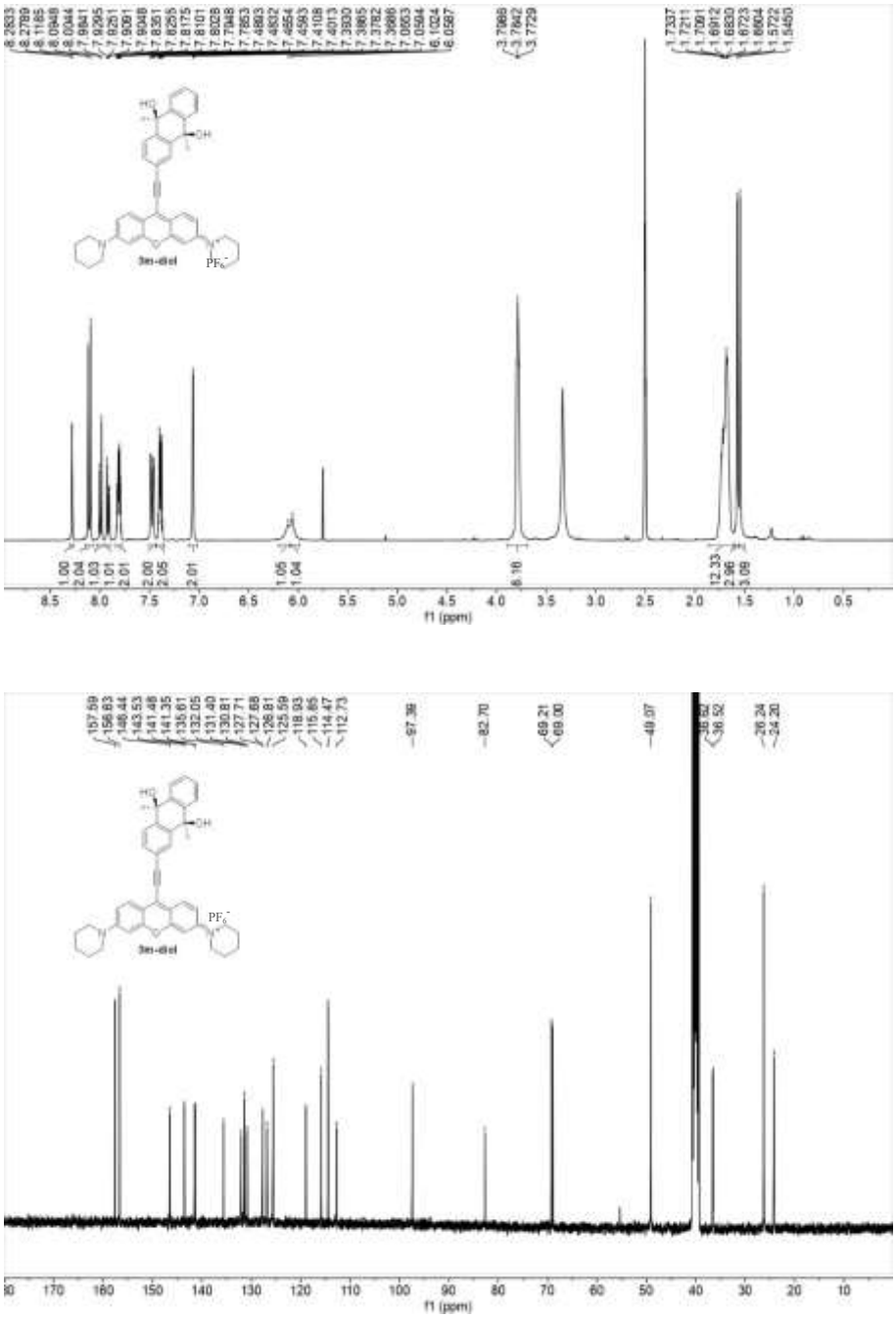
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **4c** in DMSO-d_6.



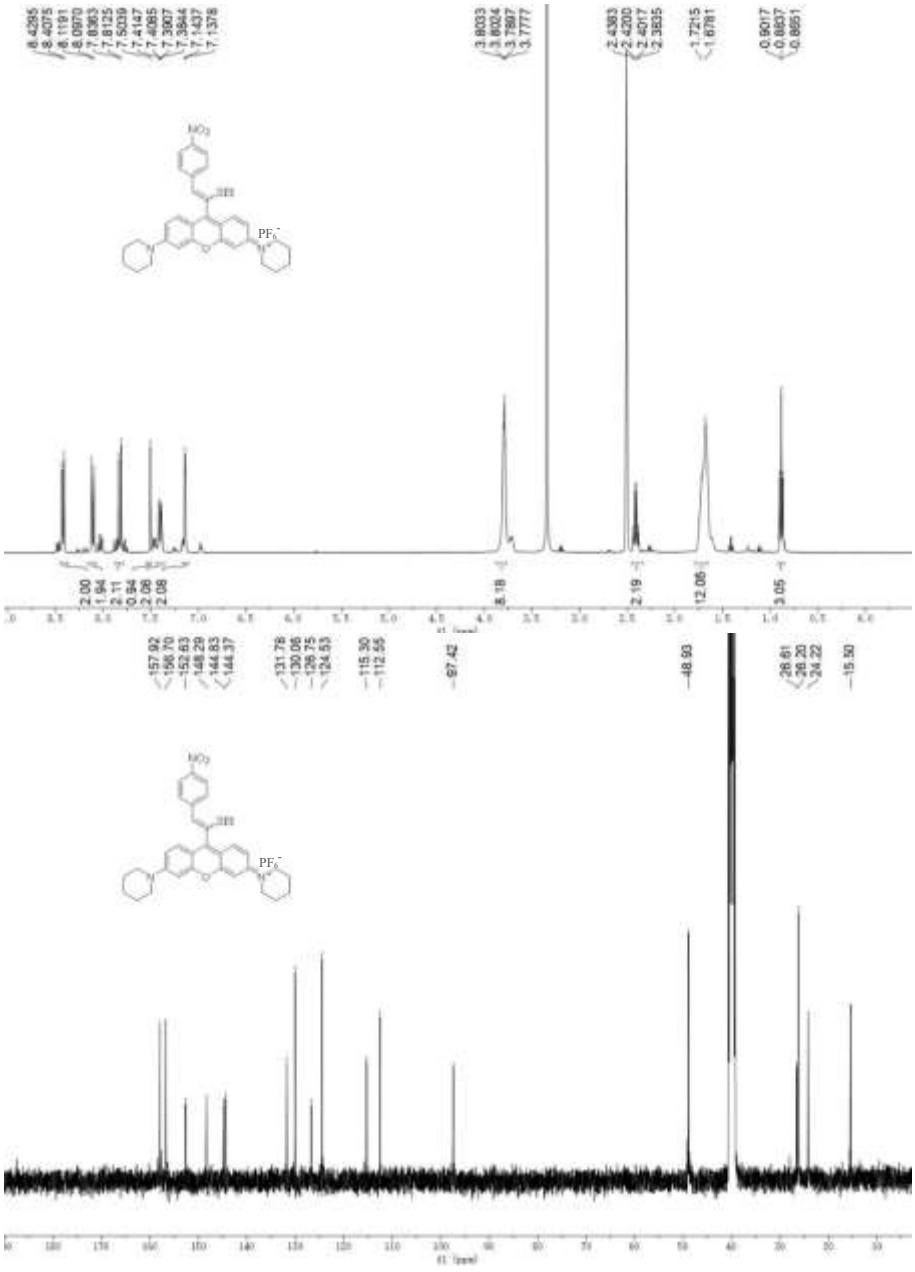
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **4d** in DMSO-d_6.



^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **4e** in DMSO-d_6.



^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3m-diol** in DMSO-d_6.



^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **NO_2-byproduct** in DMSO-d_6.

6. Reference

1. Sabatini, R. P.; Mark, M. F.; Mark, D. J.; Kryman, M. W.; Hill, J. E.; Brennessel, W. W.; Detty, M. R.; Eisenberg, R.; McCamant, D. W., *Photochem Photobiol Sci* 2016, **15,** 1417-1432.

2. Niamnont, N.; Kimpitak, N.; Wongravee, K.; Rashatasakhon, P.; Baldridge, K. K.; Siegel, J. S.; Sukwattanasinitt, M., *Chem. Commun. (Camb.)* 2013, **49,** 780-2.