Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electricity-Driven Redox-Neutral C(sp^3)-H Amidation with *N*-alkoxyamide as Amidating Reagent

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Supporting Information

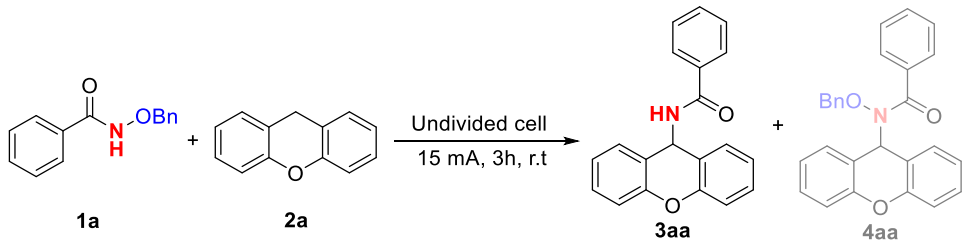
Table of Contents

1. General Information

^{1}H NMR and ^{13}C NMR were recorded on a Bruker 400 MHz spectrometer (^{1}H NMR: 400MHz, ^{13}C NMR: 100MHz). The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. ^{1}H NMR spectra were referenced to the solvent residual peak (TMS, δ 0 ppm) and ^{13}C{1H} NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.0 ppm, DMSO-d_6, δ 39.5 ppm). High Resolution mass spectra were obtained using ThermoFisher LTQ Orbitrap XL mass spectrometer. All solvents were purified and dried according to the standard procedures unless otherwise noted. Commercially substrates were purchased and used directly. *N*-alkoxyamides[1,2], xanthanes[3], 9*H*-thioxanthene[4] and 5*H*-dibenzo[*a,d*][7]annulene[5] were prepared according to the literature procedures.

2. Optimization of reaction conditions

Table S1. Optimization of redox-neutral C(sp^3)-H amidation [a]



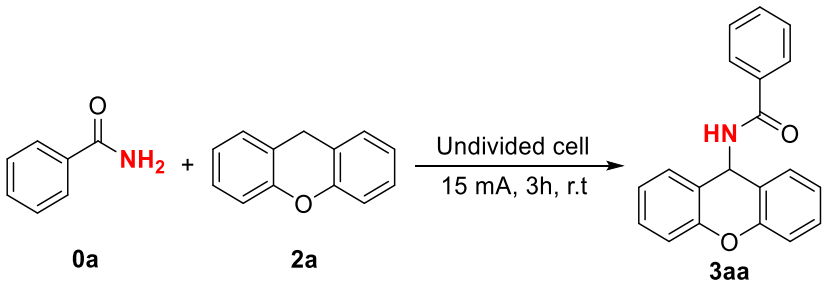
1a **2a** **3aa** **4aa**

Entry	Electrolyte	Electrodes	Solvent	Yield of **3aa**/**4aa** (%)[b]
1	^{n}Bu$_4$NClO$_4$	Pt(+)-C(-)	MeCN	81/9
2	^{n}Bu$_4$NClO$_4$	Pt(+)-C(-)	MeCN/DCM(1/2)	48/11
3	^{n}Bu$_4$NClO$_4$	Pt(+)-C(-)	MeCN/MeOH(1/2)	18/23
4	^{n}Bu$_4$NClO$_4$	Pt(+)-C(-)	MeCN/THF(1/2)	91/trace
5	^{n}Bu$_4$NBF$_4$	Pt(+)-C(-)	MeCN/THF(1/2)	54/23
6	^{n}Bu$_4$NOAc	Pt(+)-C(-)	MeCN/THF(1/2)	trace/trace
7	^{n}Bu$_4$NBr	Pt(+)-C(-)	MeCN/THF(1/2)	trace/47
8	^{n}Bu$_4$NClO$_4$	C(+)-C(-)	MeCN/THF(1/2)	63/18
9	**^{n}Bu$_4$NClO$_4$**	**Pt(+)-Pb(-)**	MeCN/THF(1/2)	**99/trace**
10	^{n}Bu$_4$NClO$_4$	Pt(+)-Ni(-)	MeCN/THF(1/2)	83/11

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), electrolyte (1 mmol), solvent (9 mL), graphite rod electrode (0.6*10 cm), metal plate electrode (1.5*1.5 cm), 15 mA, 3h (3.7 F/mol), room temperature. [b] Isolated yield of **3aa** and the yield of **4aa.**

In an undivided cell, various solvents were first screened (entries 1-4, Table S1). It was found that mixed solvent of acetonitrile and tetrahydrofuran (1/2, v/v) could exclusively afford the desired product **3aa** with the best yield (entry 4). In sharp contrast, protic solvent MeOH led to mixed products **3aa** and **4aa** in diminished yields (entry 3), owning to undesired cathodic hydrogen evolution. Varying ^{n}Bu$_4$NClO$_4$ to other electrolytes failed to give better results (entries 5-7). Specifically, ^{n}Bu$_4$NBr could only afford dehydrogenative aminated product **4aa** (entry 7). Investigation on the electrodes (entries 8-10) showed that platinum anode and lead cathode are the most efficient one to afford the desired product **3aa** with nearly quantitative yield (99%, entry 9).

Table S2. Optimization of electrochemical oxidative C(sp^3)-H amidation [a]



0a **2a** **3aa**

Entry	Electrodes	Solvent	Electrolyte	Yield (%)[b]
1	Pt(+)-C(-)	MeCN	^{n}Bu$_4$NClO$_4$	64
2	Pt(+)-C(-)	MeCN/MeOH (8/1)	^{n}Bu$_4$NClO$_4$	34
3	**Pt(+)-C(-)**	**MeCN/DCM(1/2)**	**^{n}Bu$_4$NClO$_4$**	**70**
4	Pt(+)-C(-)	MeCN/THF(1/2)	^{n}Bu$_4$NClO$_4$	68
5	Pt(+)-C(-)	MeCN/DCM(1/2)	^{n}Bu$_4$NBF$_4$	67
6	Pt(+)-C(-)	MeCN/ DCM (1/2)	^{n}Bu$_4$NOAc	61
7	Pt(+)-C(-)	MeCN/ DCM (1/2)	^{n}Bu$_4$NBr	trace
8	C(+)-C(-)	MeCN/DCM(1/2)	^{n}Bu$_4$NClO$_4$	61
9	C(+)-Pt(-)	MeCN/DCM(1/2)	^{n}Bu$_4$NClO$_4$	59
10	Ni(+)-C(-)	MeCN/DCM(1/2)	^{n}Bu$_4$NClO$_4$	68

[a] Reaction conditions: **0a** (0.5 mmol), **2a** (0.75 mmol), electrolyte (1 mmol), solvent (9 mL), graphite rod electrode (0.6*10 cm), metal plate electrode (1.5*1.5 cm), 15 mA, 3h (3.7 F/mol), room temperature. [b] Isolated yield of **3aa.**

We also investigated electrochemical oxidative C(sp^3)-H amidation using benzamide as amidating reagent (Table S2). First, various solvent was screened (entries 1-4), and it showed that mixed solvent of acetonitrile and dichloromethane gave the desired product **3aa** with the best yield (70%, entry 3). Second, replacing ^{n}Bu$_4$NClO$_4$ with other electrolytes failed to give better results (entries 5-7). Finally, various electrodes were studied. Changing platinum anode or graphite cathode led to decreased yields (entries 8-10).

3. General procedure for the electrochemical amidation

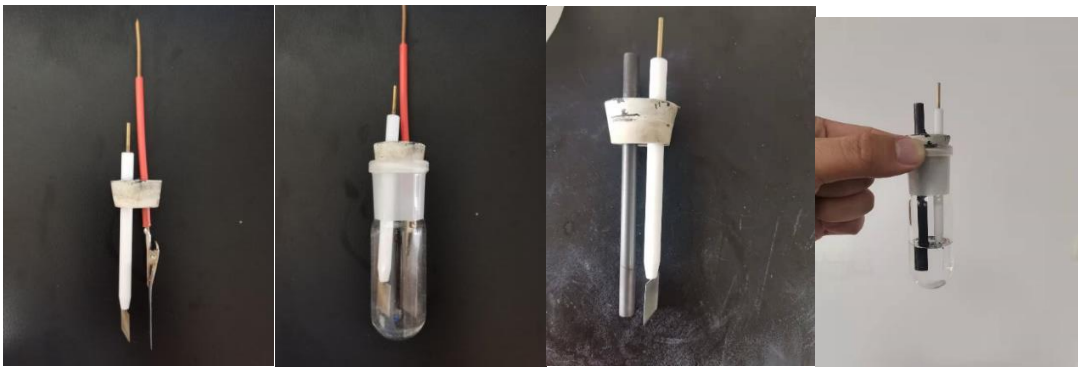
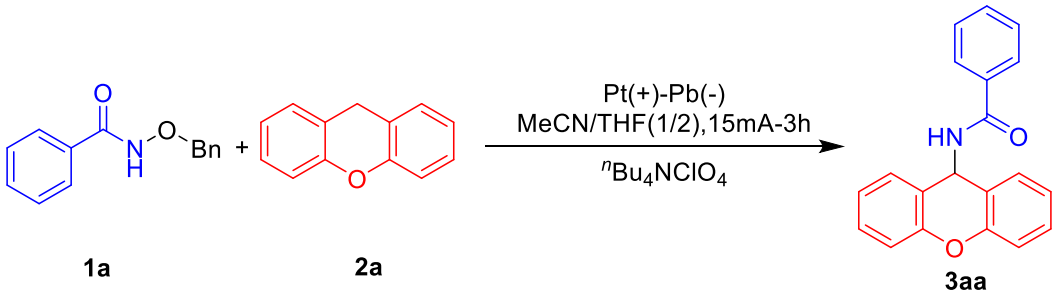


Figure S1 Electrolysis setup (graphite rod: diameter 0.6 cm, length 10 cm; lead plate: 1.5 cm (width) *1.5 cm (immersion depth); platinum plate: 1.5 cm *1.5 cm)

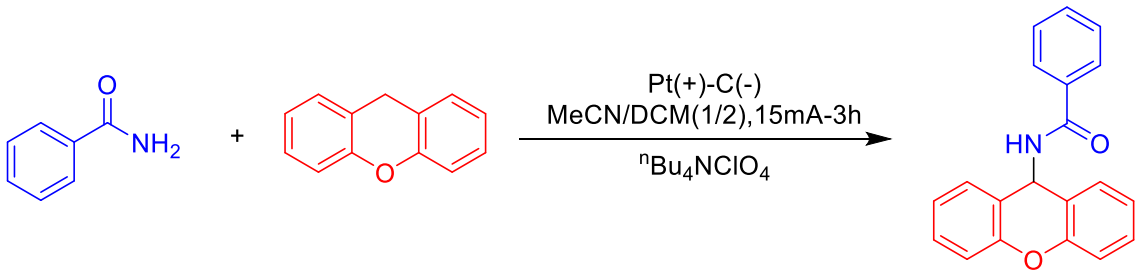
Condition I (3aa as example)



1a **2a** **3aa**

An undivided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), lead plate (1.5*1.5 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S1). The substrate *N*-(benzyloxy)benzamide **1a** (114 mg, 0.5 mmol), 9*H*-xanthene **2a** (137 mg, 0.75 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 1 mmol) were added to the solvent MeCN/THF (3/6 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. The reaction mixture was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **3aa** (149 g) in 99 % yield.

Condition II (3aa as example)



0a **2a** **3aa**

An undivided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), graphite rod (0.6*10 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S1). The substrate benzamide **0a** (61 mg, 0.5 mmol), 9*H*-xanthene **2a** (137 mg, 0.75 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 1 mmol) were added to the solvent MeCN/DCM (3/6 mL). The resulting

mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. The reaction mixture was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **3aa** (211 g) in 70 % yield.

4. Procedure for gram scale reaction and the reaction using solar cell

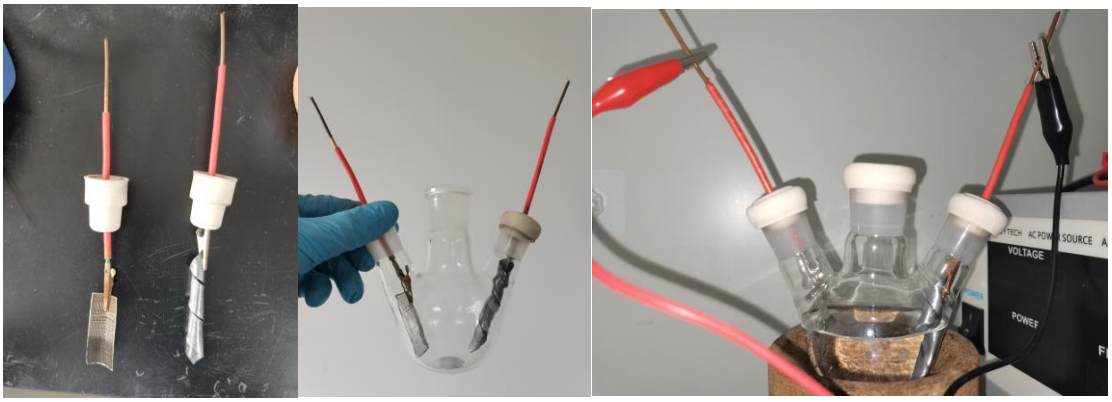
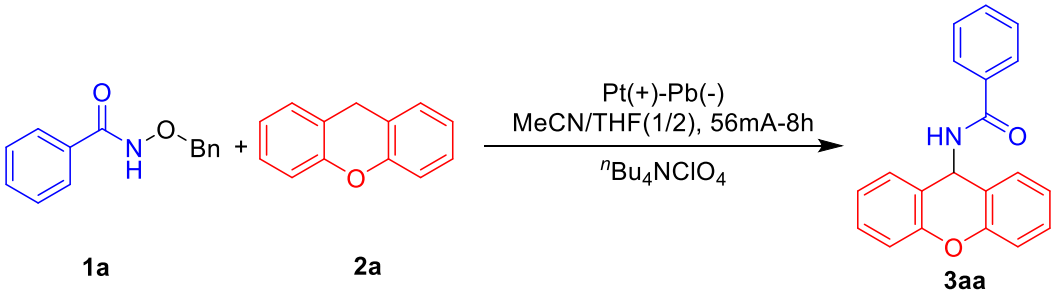


Figure S2 Gram electrolysis device (platinum mesh: length 5.0 cm, width 2.0 cm, immersion depth 2.0 cm; Lead sheet: length 10.0 cm, width 1.5 cm, immersion depth 4.0 cm)



An undivided cell was equipped with a magnet stirrer, platinum mesh (2.0 *2.0 cm^2), lead plate (1.5*4.0 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S2). The substrate *N*-(benzyloxy)benzamide **1a** (1.14 g, 5 mmol), 9*H*-xanthene **2a** (1.37 g, 7.5 mmol) and $^{n}Bu_4NClO_4$ (1.71 g, 5 mmol) were added to the solvent MeCN/THF (15/30 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (56 mA) at room temperature for 8 hours (the initial voltage is 10 V). The reaction mixture was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **3aa** (1.37 g) in 91 % yield.

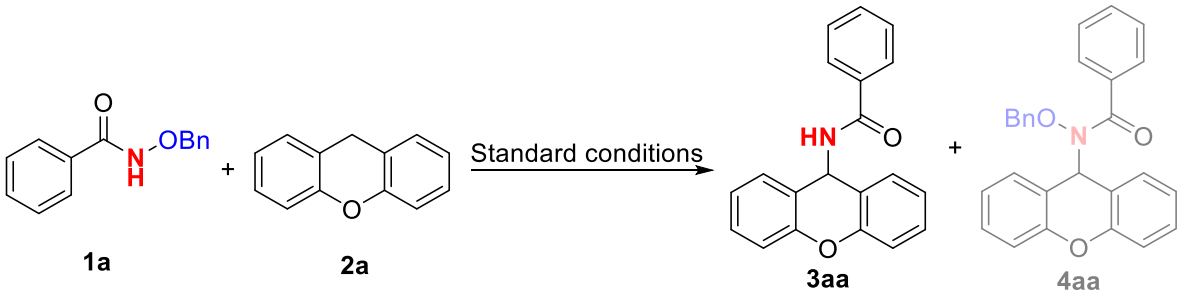
Using solar cell as electricity supply

Figure S3 Electrolysis setup with solar cell (135 mm*165mm) as electricity supply (10:00-12:00 am, May 16th, 2022 at Hefei, China)

An undivided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), lead plate (1.5*1.5 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S3). The substrate *N*-(benzyloxy)benzamide **1a** (114 mg, 0.5 mmol), 9*H*-xanthene **2a** (137 mg, 0.75 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 1 mmol) were added to the solvent MeCN/THF (3/6 mL). The resulting mixture was allowed to stir and electrolyze using a solar cell as electricity supply under sunlight for 2 hours. The reaction mixture was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **3aa** (149 g) in 99 % yield.

5. Control experiments

Reaction progress monitoring



To better understand the reaction intermediate, we performed the reaction under the standard conditions with 0.5 h, 1h, 1.5h, 2h, and 2.5h. Corresponding products **3aa** and **4aa** were isolated and the yields are listed below.

Time(h)	0	0.5	1	1.5	2	2.5	3
3aa (%)	0	0	19	39	57	68	99
4aa (%)	0	26	31	34	46	14	0

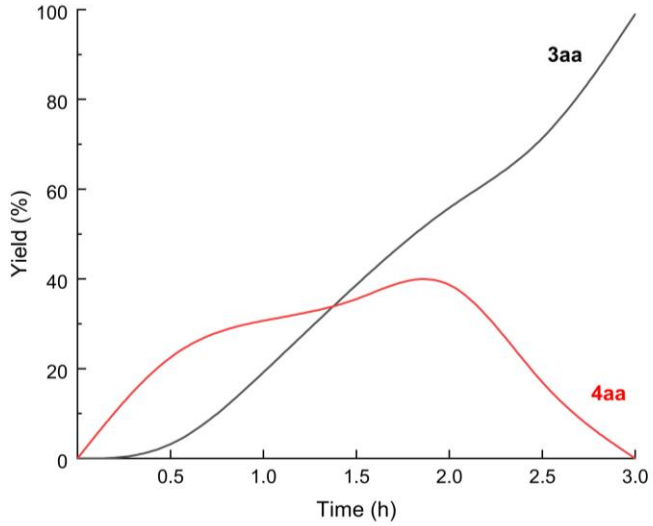
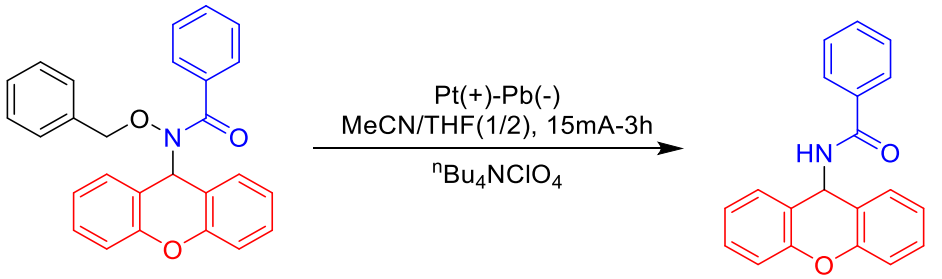


Figure S4. Reaction progress monitoring (smoothed curve)

Reaction of 4aa under standard conditions



4aa **3aa** , 91% yield

An undivided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), lead plate (1.5*1.5 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S1). The substrate *N*-(benzyloxy)benzamide **4aa** (204 mg, 0.5 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 1 mmol) were added to the solvent MeCN/THF (3/6 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. The reaction mixture was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **3aa** (137 g) in 99 % yield.

Reaction in divided cell

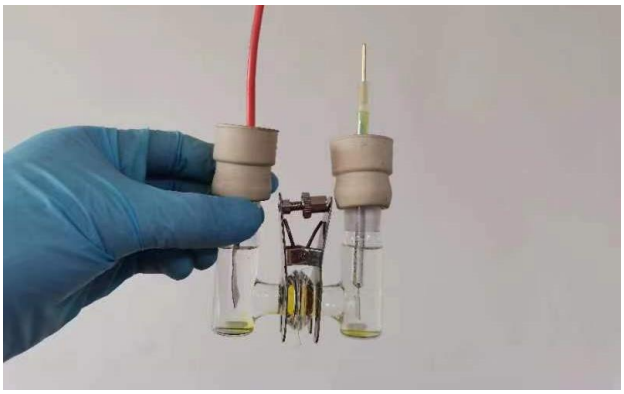
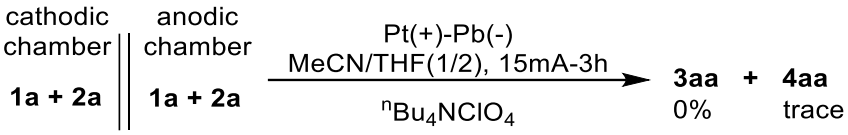
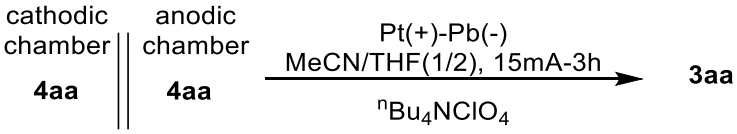


Figure S5 Divided cell setup (lead plate: 1.5 cm (width) *1.5 cm (immersion depth); platinum plate: 1.5 cm *1.5 cm)

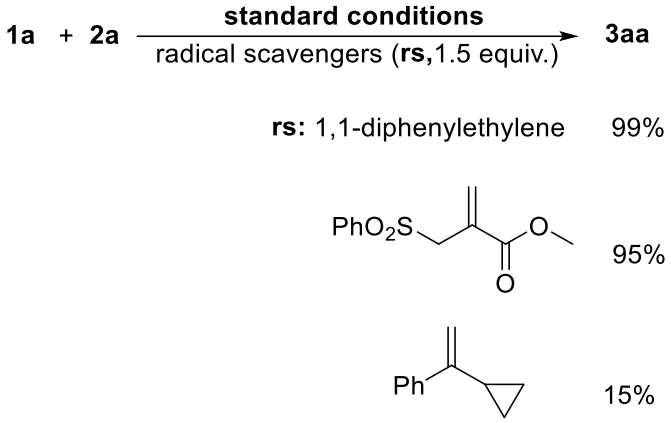


An divided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), lead plate (1.5*1.5 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S5). The substrate *N*-(benzyloxy)benzamide **1a** (114 mg, 0.5 mmol), 9*H*-xanthene **2a** (137 mg, 0.75 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 2 mmol) were added to the solvent MeCN/THF (6/12 mL). The resulting mixture was divided equally between two chambers and was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. Only trace of **4aa** was detected in the anodic chamber



A divided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), lead plate (1.5*1.5 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S5). The substrate *N*-(benzyloxy)benzamide **4aa** (204 mg, 0.5 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 2 mmol) were added to the solvent MeCN/THF (6/12 mL). The resulting mixture was divided equally between two chambers and was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. Then the solvent in cathodic chamber was removed with a rotary evaporator. The residue was purified by column chromatography ((PE/ EA= 20/1-10/1) on silica gel to afford product **3aa** (68 mg) in 90 % yield.

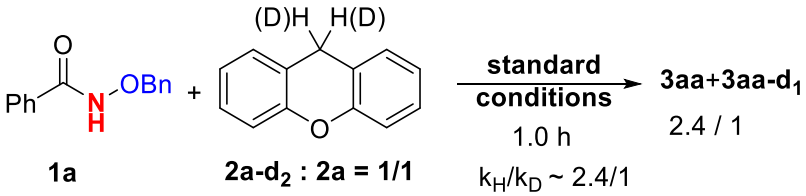
Radical suppression experiment



An undivided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), lead plate (1.5*1.5 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S1). The substrate *N*-(benzyloxy)benzamide **1a** (114 mg, 0.5 mmol), 9*H*-xanthene **2a** (137 mg, 0.75 mmol) radical scavengers (1.5 equiv.) and $^{n}Bu_4NClO_4$ (342 mg, 1 mmol) were added to the solvent MeCN/THF (3/6 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. The reaction mixture was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **3aa**.

As shown above, 1.5 equivalents of 1,1-diphenylethylenen and methyl 2-((phenylsulfonyl)methyl)acrylate marginally affected the reaction performance, indicating an ionic pathway. Nevertheless, reactive scavenger (1-cyclopropylvinyl)benzene led to diminished yield (15%). This result suggests a radical intermediate may be involved in the reaction. Given these results, aromatic cation arising from the anodic oxidation of 9*H*-xanthene are proposed to be the major intermediate, while radical species is a transient intermediate and can be further oxidized to aromatic cation.

KIE study



An undivided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), lead plate (1.5*1.5 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S1). The substrate *N*-(benzyloxy) benzamide **1a** (114 mg, 0.5 mmol), 9*H*-xanthene **2a-d_2** (70 mg, 0.325 mmol), **2a** (69 mg, 0.325 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 1 mmol) were added to the solvent MeCN/THF (3/6 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 1 hours. The reaction mixture was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **3aa** and **3aa-d_1** and the ratio of product was determined by ^{1}H NMR.

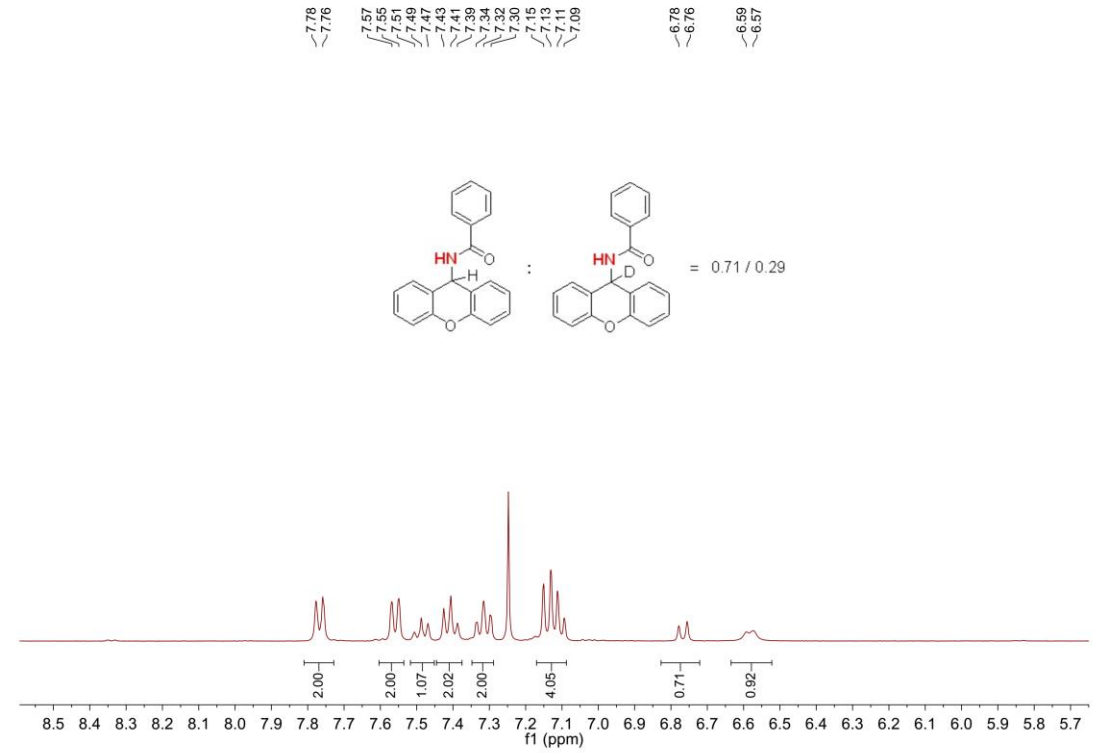
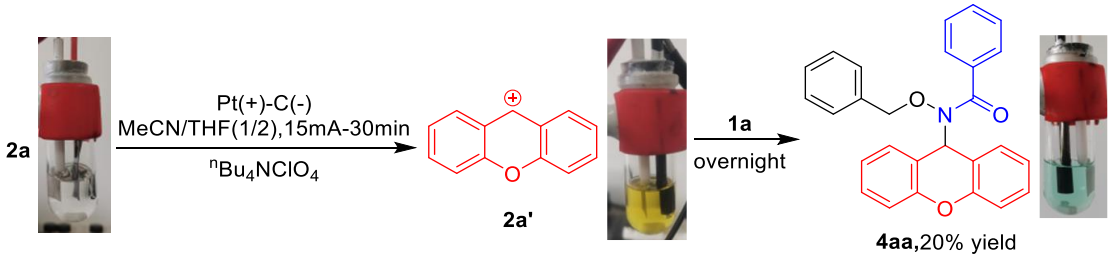


Figure S6. Reaction mixture of 3aa and **3aa-d$_1$**

Carbocation capture experiment



An undivided cell was equipped with a magnet stirrer, platinum plate (1.5 *1.5 cm^2), graphite rod (0.6 *10 cm), as anode and cathode, respectively (the electrolysis setup is shown in Figure S1). The substrate 9*H*-xanthene **2a** (136.5 mg, 0.75 mmol) and ^{n}Bu$_4$NClO$_4$ (342 mg, 1 mmol) were added to the solvent MeCN/THF (3/6 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA,) at room temperature for 30 minutes. The colorless reaction mixture changed to yellow. Then the substrate *N*-(benzyloxy)benzamide **1a** (113.5 mg, 0.5 mmol) was added to the reaction mixture. The resulting mixture was allowed to stir at room temperature overnight and the resulting mixture turned to cyan. The combined organic phase was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 20/1-10/1) on silica gel to afford the desired product **4aa** (41.7 mg, 20% yield) .

6. Cyclic voltammetric experiments

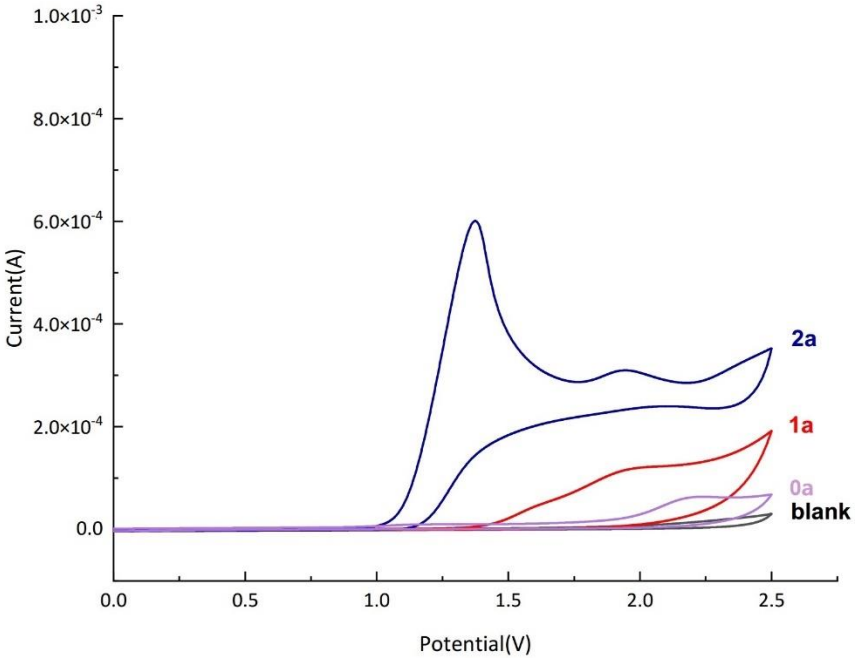


Figure S7. Cyclic voltammograms of substrates in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 $mV \cdot s^{-1}$ scan rate.

As shown in the Fig. S7, substrate **2a** is more susceptible to oxidation when compared with **1a**, with anodic peaks at 1.38V and 1.91V respectively. By contrast, the anodic peak of primary amide **0a** is 2.18 V, which further verifies the inert reactivity of **0a**.

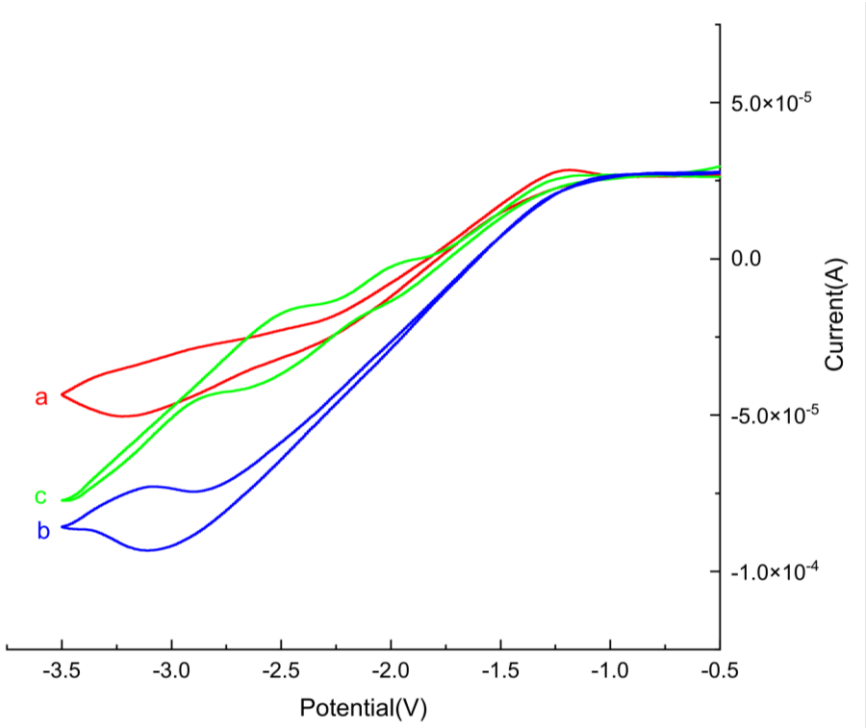


Figure S8. Cyclic voltammograms of substrates in 0.1 M $^nBu_4ClO_4$ (EtOAc), using a glassy carbon working electrode and Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes

at a 100 mV·s^{-1} scan rate: a. 9*H*-xanthene. b. *N*-(benzyloxy)benzamide. c. **4aa**.

The cathodic behavior of substrates **1a, 2a** and intermediate **4aa** was also explored (Fig. S8). The intermediate **4aa** was found to be the cathodic active species in the reaction with a peak at -2.66 V, which is less negative than that of **1a** (-3.11V) and **2a** (-3.20V)

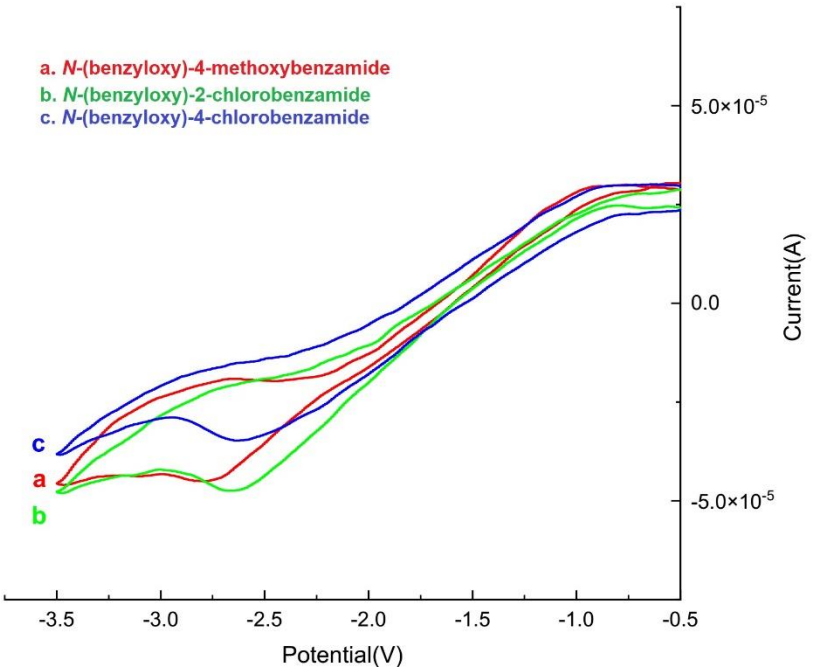


Figure S9. Cyclic voltammograms of substrates in 0.1 M $^{n}Bu_4ClO_4$ (EtOAc), using a glassy carbon working electrode and Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV·s^{-1} scan rate.

Reduction potential of various *N*-benzyloxy amides were investigated. It showed that electron-deficient substrate is more reducible than the electron-rich one. Reducible *N*-benzyloxy amides might lead to direct cathodic N-O cleavage rather than sequential oxidative C-H amidation and N-O cleavage.

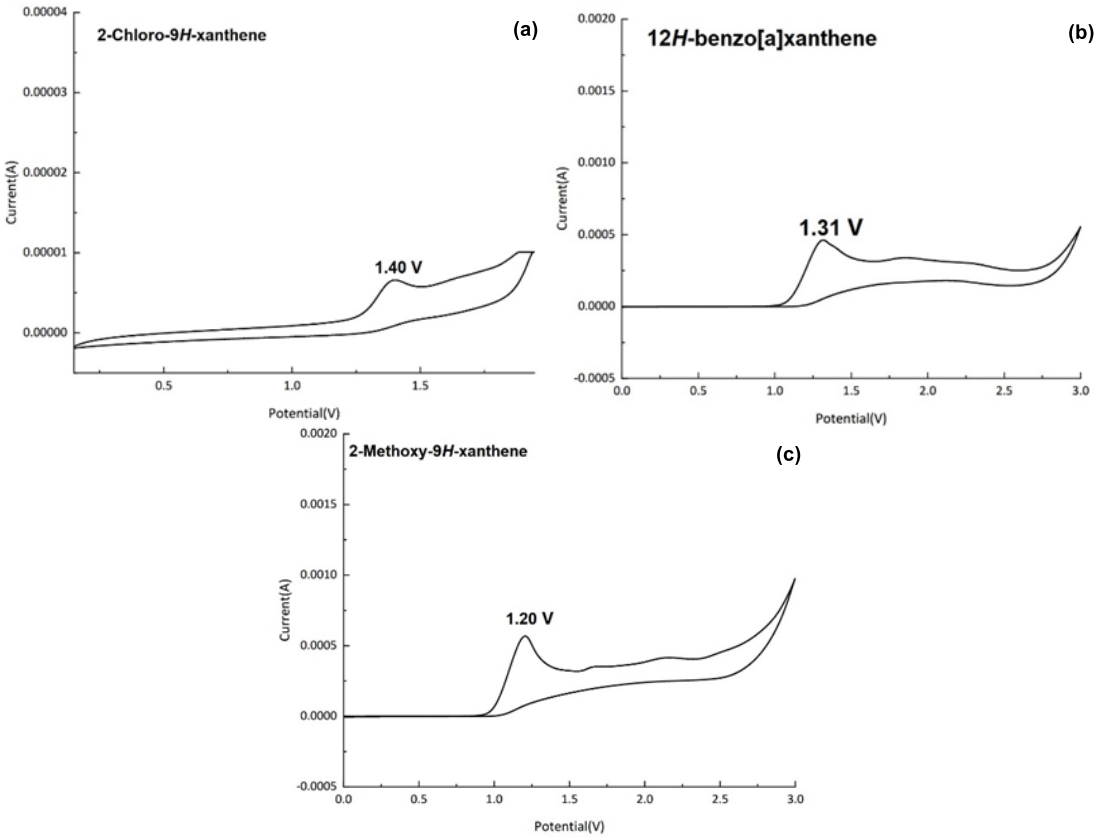
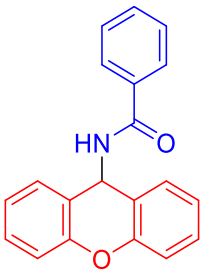


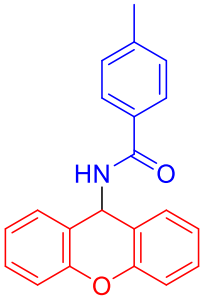
Figure S10. Cyclic voltammograms of substrates in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 $mV \cdot s^{-1}$ scan rate.

We also studied oxidation potential of 9*H*-xanthanes. Substitution of 9*H*-xanthanes slightly affected their oxidation potential, and all of the oxidation peaks are around 1.2-1.4 V, which are all lower than that of *N*-benzyloxy amide. These results could serve as explanation of the uniform yields arising from variation of 9*H*-xanthanes.

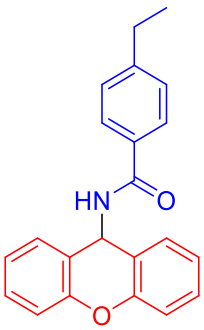
7. Experimental data for products



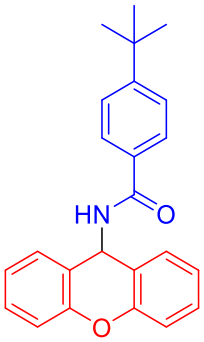
N-(9*H*-Xanthen-9-yl)benzamide (**3aa**): 149 mg, 99% yield (**condition I**); 105 mg, 70% yield (**condition II**); 1.37 g, 91% yield (gram scale); white solid, mp 227-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.13 (m, 4H), 6.78 (d, *J* = 12.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 151.1, 134.0, 131.8, 129.7, 129.4, 128.6, 127.0, 123.7, 121.0, 116.7, 44.3. These data are in accordance with the literature. [6]



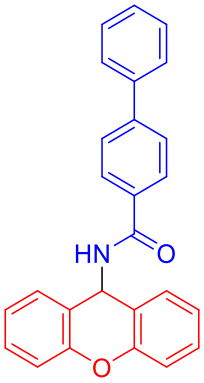
4-Methyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3ab**): 156 mg, 99% yield (**condition I**); 79 mg, 50% yield (**condition II**); white solid, mp 216-219 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.36 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.15 (m,4H), 6.55 (d, *J* = 8.0 Hz, 1H), 2.34 (s,3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.7, 150.6, 141.3, 131.1, 129.0, 128.9, 128.8, 127.5, 123.4, 121.8, 116.1, 43.0, 20.9. These data are in accordance with the literature. [7]



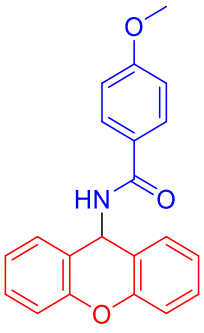
4-Ethyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3ac**): 163 mg, 99% yield; white solid, mp 238-240 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.38 (d, *J* = 4.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 4.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 4.0 Hz,2H), 7.14 (t, *J* = 4.0 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 1H), 2.64 (q, 2H), 1.18 (t, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.7, 150.6, 147.6, 131.4, 129.0, 128.9, 127.6, 123.4, 121.8, 116.1, 43.0, 28.0, 15.4; HRMS (ESI): cacld. for $C_{22}H_{19}NO_2$ $[M+Na]^+$: 352.1308, found 352.1317.



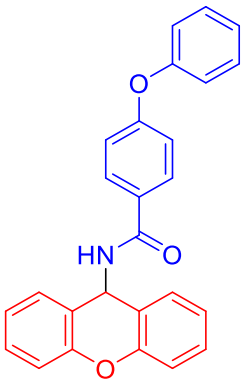
4-(*tert*-Butyl)-*N*-(9*H*-xanthen-9-yl)benzamide (**3ad**): 175 mg, 98% yield; white solid, mp 217-219 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.39 (s, 1H), 7.87 (s, 2H), 7.38 (m, 6H) , 7.15 (s, 4H), 6.55 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.7, 154.3, 150.6, 131.1, 128.9, 127.4, 125.0, 123.4, 121.9, 116.1, 42.9, 34.6, 30.9; HRMS (ESI): cacld. for $C_{24}H_{23}NO_2$ $[M+Na]^+$: 380.1621, found 380.1628.



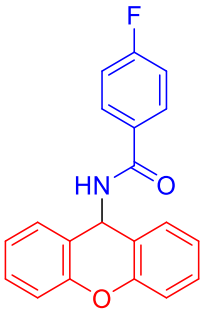
N-(9*H*-Xanthen-9-yl)-[1,1'-biphenyl]-4-carboxamide (**3ae**): 149 mg, 79% yield; white solid, mp 284-285 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.51 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 3H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.16 (m, 4H), 6.58 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.5, 150.6, 143.0, 139.1, 132.7, 129.0, 128.9, 128.2, 128.1, 126.9, 126.5, 123.5, 121.8, 116.1, 43.1; HRMS (ESI): cacld. for $C_{26}H_{19}NO_2$ $[M+Na]^+$: 400.1308, found 400.1323.



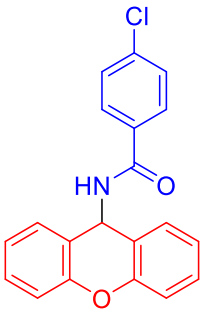
4-Methoxy-*N*-(9*H*-xanthen-9-yl)benzamide (**3af**): 128 mg, 77% yield; white solid, mp 243-244 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.29 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.15 (m, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.3, 161.8, 150.6, 129.4, 129.0, 128.9, 126.0, 123.4, 122.0, 116.1, 113.5, 55.3, 42.9; HRMS (ESI): cacld. for $C_{21}H_{17}NO_3$ $[M+Na]^+$: 354.1101, found 354.1109.



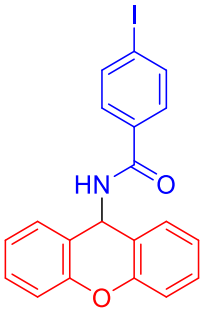
4-Phenoxy-*N*-(9*H*-xanthen-9-yl)benzamide (**3ag**): 133 mg, 68% yield; white solid, mp 222-224 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.41 (d, *J* = 12.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.42 (m, 4H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.18 (m, 5H), 7.05 (m, 4H), 6.55 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.0, 159.6, 155.6, 150.6, 130.2, 129.7, 129.0, 128.9, 128.5, 124.2, 123.4, 121.8, 119.4, 117.4, 116.1, 43.0; HRMS (ESI): cacld. for $C_{26}H_{19}FNO_3$ [M+Na]$^+$: 416.1257, found 416.1243.



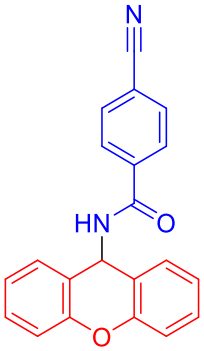
4-Fluoro-*N*-(9*H*-xanthen-9-yl)benzamide (**3ah**): 158 mg, 99% yield (**condition I**); 97 mg, 61% yield (**condition II**); white solid, mp 230-231 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.47 (d, *J* = 8.0 Hz, 1H), 8.00 (t, *J* = 4.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.32 (m, 4H), 7.16(m, 4H) , 6.55 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.7, 164.0 (d, $J_{F\text{-}C}$ = 247.0 Hz), 150.6, 130.3 (d, $J_{F\text{-}C}$ = 3.0 Hz), 130.2 (d, $J_{F\text{-}C}$ = 9.0 Hz), 129.0 (d, $J_{F\text{-}C}$ = 5.0 Hz), 123.5, 121.7, 116.1, 115.3, 115.1, 43.1; HRMS (ESI): cacld. for $C_{20}H_{14}FNO_2$ [M+Na]$^+$: 342.0901, found 342.0901.



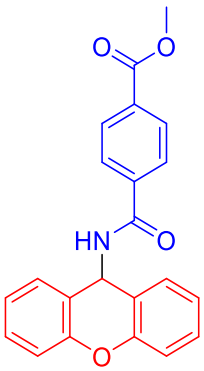
4-Chloro-*N*-(9*H*-xanthen-9-yl)benzamide (**3ai**): 129 mg, 77% yield; white solid, mp 224-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.14 (q, 4H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.8, 150.6, 136.3, 132.6, 129.4, 129.03, 128.99, 128.4, 123.5, 121.6, 116.1, 43.2; HRMS (ESI): cacld. for $C_{20}H_{14}NO_2Cl$ [M+Na]$^+$: 358.0605, found 358.0610.



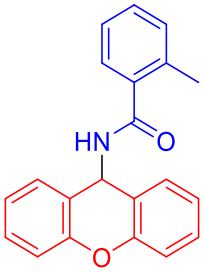
4-Iodo-*N*-(9*H*-xanthen-9-yl)benzamide (**3aj**): 70 mg, 33% yield; white solid, mp 268-269 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 12.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.14 (q, 4H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.1, 150.6, 137.2, 133.3, 129.5, 129.02, 128.98, 123.5, 121.6, 116.1, 99.1, 43.2; HRMS (ESI): cacld. for $C_{20}H_{14}INO_2$ $[M+Na]^+$: 449.9961, found 449.9960.



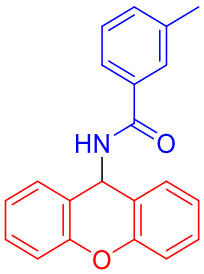
4-Cyano-*N*-(9*H*-xanthen-9-yl)benzamide (**3ak**): 119 mg, 73% yield (**condition I**); 70 mg, 43% yield (**condition II**); white solid, mp 216-220 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.70 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 4.0 Hz, 2H), 7.16 (m, 4H), 6.56 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.4, 150.6, 137.9, 132.4, 129.08, 129.05, 128.3, 123.5, 121.3, 118.3, 116.2, 113.8, 43.4; HRMS (ESI): cacld. for $C_{21}H_{14}N_2O_2$ $[M+Na]^+$: 349.0948, found 349.0953.



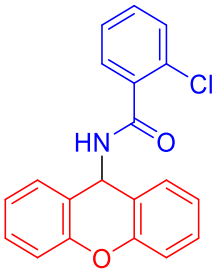
Methyl 4-((9*H*-xanthen-9-yl)carbamoyl)benzoate (**3al**): 178 mg, 99% yield; white solid, mp 249-251 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.65 (d, *J* = 12.0 Hz, 1H), 8.03 (s, 4H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.16 (m, 4H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.7, 165.0, 150.6, 138.0, 131.9, 129.1, 129.0, 127.9, 123.5, 121.5, 116.2, 52.3, 43.3; HRMS (ESI): cacld. for $C_{22}H_{17}NO_4$ $[M+Na]^+$: 382.1050, found 382.1056.



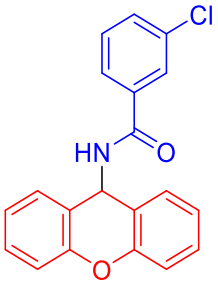
2-Methyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3am**): 139 mg, 88% yield (**condition I**); 85 mg, 54% yield (**condition II**); white solid, mp 204-205 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.29 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.34 (m, 4H), 7.21 (m, 6H), 6.51 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 150.8, 134.4, 133.2, 131.8, 131.7, 131.6, 129.7, 128.6, 128.5, 128.3, 123.6, 123.2, 115.9, 45.1; HRMS (ESI): cacld. for $C_{21}H_{17}NO_2$ [M+Na]$^+$: 338.1151, found 338.1154.



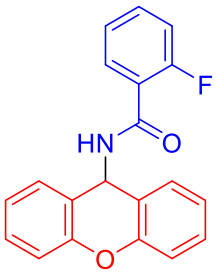
3-Methyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3an**): 156 mg, 99% yield(**condition I**); 103 mg, 65% yield (**condition II**); white solid, mp 204-205 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.39 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 12.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (m, 4H), 7.16 (m, 4H), 6.56 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.8, 150.6, 137.5, 133.8, 132.0, 129.0, 128.9, 128.2, 128.0, 124.7, 123.4, 121.8, 116.1, 43.0, 20.9; HRMS (ESI): cacld. for $C_{21}H_{17}NO_2$ [M+Na]$^+$: 338.1152, found 338.1148.



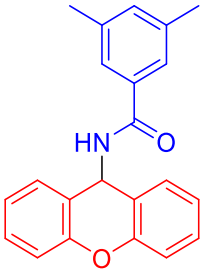
2-Chloro-*N*-(9*H*-xanthen-9-yl)benzamide (**3ao**): 62 mg, 37% yield; white solid, mp 223-224 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.47 (d, *J* = 12.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.48 (m, 2H), 7.40 (m, 4H), 7.20 (m, 4H), 6.51 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 166.1, 150.4, 136.5, 130.8, 129.8, 129.5, 129.0, 128.7, 127.1, 123.5, 121.2, 116.2, 42.8; HRMS (ESI): cacld. for $C_{20}H_{14}ClNO_2$ [M+Na]$^+$: 358.0605, found 358.0609.



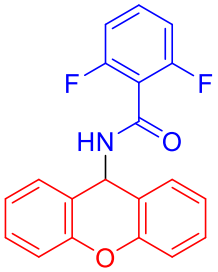
3-Chloro-*N*-(9*H*-xanthen-9-yl)benzamide (**3ap**): 142 mg, 85% yield; white solid, mp 231-232 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.56 (d, *J* = 8.0 Hz, 1H), 7.90 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.16 (m, 4H), 6.55 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.3, 150.6, 135.8, 133.2, 131.3, 130.3, 129.1, 129.0, 127.2, 126.3, 123.5, 121.5, 116.2, 43.3; HRMS (ESI): cacld. for $C_{20}H_{14}NO_2Cl$ $[M+Na]^+$: 358.0605, found 358.0610.



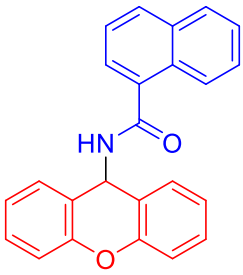
2-Fluoro-*N*-(9*H*-xanthen-9-yl)benzamide **(3aq)**: 139 mg, 87% yield; 1.20 g, 75% yield (gram scale); white solid, mp 192-193 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.38 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.51 (m, 3H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 4H), 6.50 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.8 (d, $J_{F\text{-}C}$ = 10.0 Hz), 159.1 (d, $J_{F\text{-}C}$ = 248 Hz), 150.6, 132.4 (d, $J_{F\text{-}C}$ = 8.0 Hz), 129.9 (d, $J_{F\text{-}C}$ = 2.0 Hz), 129.0, 128.9, 124.4 (d, $J_{F\text{-}C}$ = 3.0 Hz), 123.5, 121.4 (d, $J_{F\text{-}C}$ = 3.0 Hz), 116.2, 116.0, 43.20 (d, $J_{F\text{-}C}$ = 8.0 Hz); HRMS (ESI): cacld. for $C_{20}H_{14}FNO_2$ $[M+Na]^+$: 342.0901, found 342.0888.



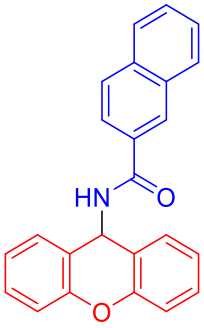
3,5-Dimethyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3ar**): 163 mg, 99% yield; white solid, mp 243-247 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.32 (d, *J* =8.0 Hz, 1H), 7.53 (s, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* =8.0 Hz, 2H), 7.16 (m, 5H), 6.55 (d, *J* = 8.0 Hz, 1H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.9, 150.6, 137.4, 133.8, 132.6, 129.0, 128.9, 125.2, 123.4, 121.8, 116.1, 42.9, 20.8; HRMS (ESI): cacld. for $C_{22}H_{19}NO_2$ $[M+Na]^+$: 352.1308, found 352.1314.



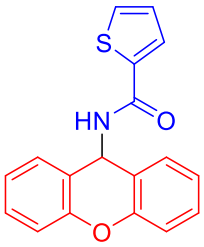
2,6-Difluoro-*N*-(9*H*-xanthen-9-yl)benzamide (**3as**): 85 mg, 50% yield; white solid, mp 213-215 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.73 (d, *J* = 8.0 Hz, 1H), 7.50 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.19 (m, 6H), 6.53 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 159.5, 153.7 (dd, $J_{F\text{-}C}$ = 8.0 Hz, $J_{F\text{-}C}$ = 247.0 Hz), 150.4, 131.7 (t, $J_{F\text{-}C}$ = 9.5 Hz), 129.2, 128.7, 123.6, 121.0, 116.3, 115.1 (t, $J_{F\text{-}C}$ = 23.0 Hz), 111.9 (dd, $J_{F\text{-}C}$ = 5.0 Hz, $J_{F\text{-}C}$ = 19.0 Hz), 43.1. HRMS (ESI): cacld. for $C_{20}H_{13}F_2NO_2$ $[M+Na]^+$: 360.0807, found 360.0809.



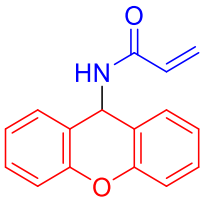
N-(9*H*-Xanthen-9-yl)-1-naphthamide (**3at**): 174 mg, 99% yield (**condition I**); 107 mg, 61% yield (**condition II**); white solid, mp 243-245 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.57 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.00 (t, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 5H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.21 (m, 4H), 6.64 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.1, 150.6, 134.0, 133.1, 130.0, 129.8, 129.0, 128.2, 126.8, 126.2, 125.3, 125.2, 124.9, 123.6, 121.6, 116.2, 40.1; HRMS (ESI): cacld. for $C_{24}H_{17}NO_2$ $[M+Na]^+$: 374.1151, found 374.1154.



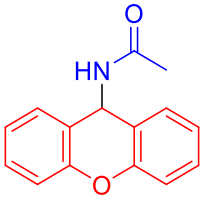
N-(9*H*-Xanthen-9-yl)-2-naphthamide (**3au**): 174 mg, 99% yield (**condition I**); 109 mg, 62% yield (**condition II**); white solid, mp 249-250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 7.87 (t, *J* = 8.0 Hz, 4H), 7.57 (d, *J* = 4.0 Hz, 2H), 7.52 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.16 (m, 4H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.8, 150.7, 134.2, 132.1, 131.2, 129.1, 129.0, 128.8, 127.83, 127.78, 127.7, 127.6, 126.7, 124.4, 123.5, 121.8, 116.2, 43.2; HRMS (ESI): cacld. for $C_{24}H_{17}NO_2$ $[M+Na]^+$: 374.1152, found 374.1159.



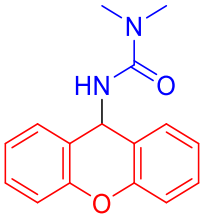
N-(9*H*-Xanthen-9-yl)thiophene-2-carboxamide (**3av**): 152 mg, 99% yield; yellow solid, mp 217-220 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.45 (d, *J* = 12.0 Hz, 1H), 7.80 (s, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.15 (m, 5H), 6.50 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.7, 150.6, 139.5, 131.3, 129.1, 129.0, 128.5, 128.0, 123.5, 121.5, 116.2, 43.0; HRMS (ESI): cacld. for $C_{18}H_{13}NO_2S$ [M+Na]$^{+}$: 330.0559, found 330.0562.



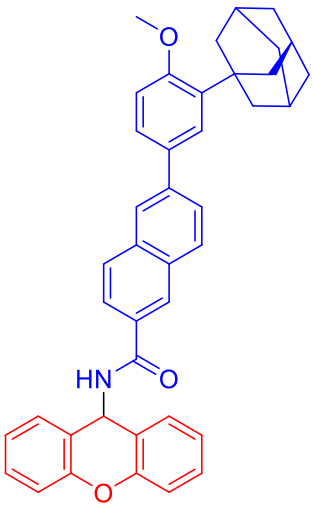
N-(9*H*-Xanthen-9-yl)acrylamide (**3aw**): 104 mg, 83% yield (**condition I**); 62 mg, 49% yield (**condition II**); white solid, mp 249-250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.12 (q, 4H), 6.62 (d, *J* = 12.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.05 (m, 2H), 5.73 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.0, 150.6, 131.3, 129.2, 129.1, 126.3, 123.6, 121.6, 116.2, 42.6. These data are in accordance with the literature. [8]



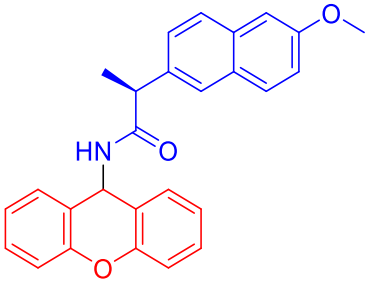
N-(9*H*-Xanthen-9-yl)acetamide (**3ax**): 51 mg, 43% yield; white solid, mp 227-232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.11 (m, 4H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.03 (d, *J* = 8.0 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.0, 151.1, 129.7, 129.3, 123.6, 121.1, 116.6, 43.9, 23.4. These data are in accordance with the literature.[6]



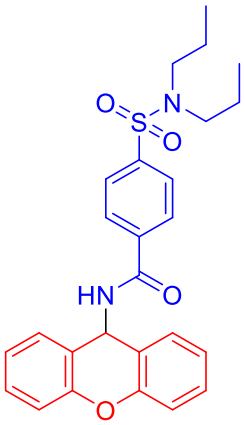
1,1-Dimethyl-3-(9*H*-xanthen-9-yl)urea (**3ay**): 44 mg, 33% yield; white solid, mp 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 4H), 6.40 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 8.0 Hz, 1H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 151.0, 129.7, 128.9, 123.4, 122.4, 116.4, 44.9, 36.2; HRMS (ESI): cacld. for $C_{16}H_{16}N_2O_2$ [M+Na]$^{+}$: 291.1104, found 291.1100.



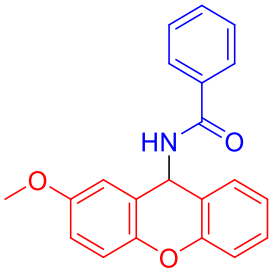
6-(3-(Adamantan-1-yl)-4-methoxyphenyl)-*N*-(9*H*-xanthen-9-yl)-2-naphthamide (**3az**): 186 mg, 63% yield (**condition I**); trace (**condition II**); white solid, mp 241-242 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.59 (d, *J* = 8.0 Hz, 1H), 8.52 (s, 1H), 8.19 (s, 1H), 8.04 (m, 3H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 3H), 2.13 (s, 6H), 2.06 (s, 3H), 1.75 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.8, 158.5, 150.7, 139.5, 138.0, 134.8, 131.5, 130.84, 130.78, 129.4, 129.1, 129.0, 128.0, 127.5, 125.8, 125.6, 125.0, 124.7, 124.0, 123.5, 121.8, 116.2, 112.7, 55.3, 43.2, 40.1, 36.6, 36.5, 28.4; HRMS (ESI): cacld. for $C_{27}H_{23}NO_3$ $[M+Na]^+$: 614.2666, found 614.2661.



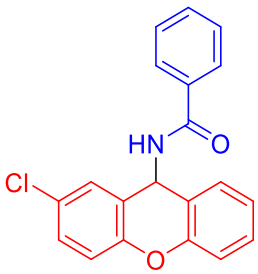
(*S*)-2-(6-Methoxynaphthalen-2-yl)-*N*-(9*H*-xanthen-9-yl)propanamide (**3ba**): 55 mg, 27% yield; white solid, mp 211-215 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.01 (d, *J* = 8.0 Hz, 1H), 7.76 (m, 3H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36 (m, 2H), 7.26 (m, 2H), 7.11 (m, 4H), 7.04 (d, *J* = 4.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.78 (d, *J* = 4.0 Hz, 1H), 1.49 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 173.1, 157.0, 150.4, 137.2, 133.1, 129.0, 128.7, 128.4, 126.6, 126.4, 125.3, 123.5, 123.2, 121.78, 121.71, 118.6, 116.1, 55.1, 44.9, 42.3, 18.5; HRMS (ESI): cacld. for $C_{27}H_{23}NO_3$ $[M+Na]^+$: 432.1570, found 432.1576.



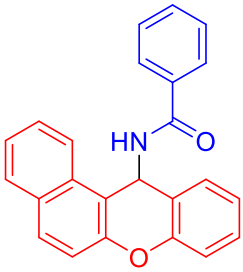
4-(*N*,*N*-Dipropylsulfamoyl)-*N*-(9*H*-xanthen-9-yl)benzamide (**3bb**): 100 mg, 49% yield; white solid, mp 183-184 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.68 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 4.0 Hz, 2H), 7.36 (t, *J* = 4.0 Hz, 2H), 7.16 (m, 4H), 6.56 (d, *J* = 8.0 Hz, 1H), 3.03 (t, *J* = 4.0 Hz, 4H), 1.46 (m, 4H), 0.80 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.6, 150.6, 141.9, 137.4, 129.09, 129.06, 128.5, 126.8, 123.5, 121.4, 116.2, 49.6, 43.3 21.6, 10.9; HRMS (ESI): cacld. for $C_{26}H_{28}N_2O_4S$ [M+Na]$^+$: 487.1662, found 487.1645.



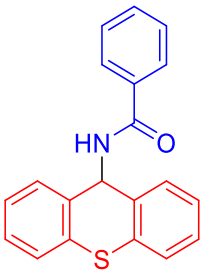
N-(2-Methoxy-9*H*-xanthen-9-yl)benzamide (**3bc**): 137 mg, 83% yield; white solid, mp 256-257 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.43 (d, *J* = 12.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 4.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.12 (m, 3H), 6.94 (m, 2H), 6.53 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 3H); ^{13}C (100 MHz, DMSO-d_6) δ: 165.9, 155.1, 150.8, 144.7, 133.9, 131.4, 129.0, 128.9, 128.3, 127.5, 123.2, 122.4, 121.2, 117.1, 116.1, 115.1, 112.7, 55.4, 43.5; HRMS (ESI): cacld. For $C_{21}H_{17}NO_3$ [M+Na]$^+$: 354.1101, found 354.1094.



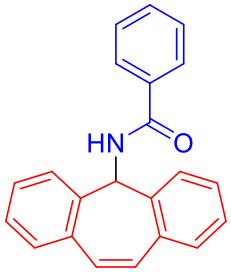
N-(2-Chloro-9*H*-xanthen-9-yl)benzamide **(3bd)**: 140 mg, 84% yield; white solid, mp 217-218 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.50 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 4.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 3H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.17 (q, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.9, 150.4, 149.5, 133.7, 131.6, 129.1, 129.0, 128.9, 128.3, 128.2, 127.5, 126.8, 123.9, 123.8, 121.1, 118.2, 116.2, 43.1; HRMS (ESI): cacld. for $C_{20}H_{14}ClNO_2$ [M+Na]$^+$: 358.0605, found 358.0597.



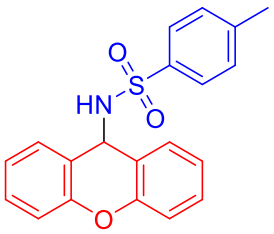
N-(12*H*-Benzo[a]xanthen-12-yl)benzamide **(3be)**: 172 mg, 98% yield; white solid, mp 242-244 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.37 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.97 (t, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.47 (m, 3H), 7.38 (t, *J* = 8.0 Hz, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.9, 150.2, 149.5, 133.7, 131.6, 131.4, 130.1, 130.0, 129.4, 129.0, 128.6, 128.2, 127.4, 127.3, 124.5, 124.0, 122.5, 122.3, 117.7, 116.1, 112.4, 40.9; HRMS (ESI): cacld. for $C_{24}H_{17}NO_2$ $[M+Na]^+$: 374.1151, found 374.1143.



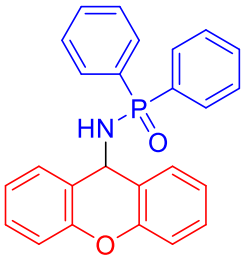
N-(9*H*-Thioxanthen-9-yl)benzamide (**3bf**): 68 mg, 43% yield (**condition I**); trace (**condition II**); yellow solid, mp 176-178 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.59 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 6H), 7.34 (m, 4H), 6.03 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 166.7, 136.0, 133.9, 131.7, 131.7, 128.4, 127.7, 127.3, 126.7, 125.7, 51.8; HRMS (ESI): cacld. for $C_{20}H_{15}NOS$ $[M+Na]^+$: 340.0767, found 340.0772.



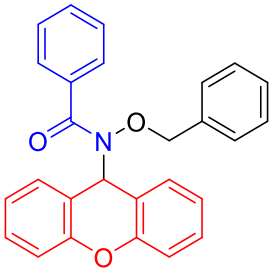
N-(5*H*-Dibenzo[a,d][7]annulen-5-yl)benzamide (**3bg**): 62 mg, 40% yield (**condition I**); trace (**condition II**); white solid, mp 232-233 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.47 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 4H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 5.95 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 166.2, 138.6, 134.4, 133.5, 131.4, 131.3, 128.3, 128.2, 128.1, 127.7, 126.5, 124.4, 53.3; HRMS (ESI): cacld. for $C_{22}H_{17}NO$ $[M+Na]^+$: 334.1202, found 334.1210.



4-Methyl-*N*-(9*H*-xanthen-9-yl)benzenesulfonamide **(3bh)**: 109 mg, 62% yield (**condition I**); trace (**condition II**); 1.27 g, 72% yield (gram scale); white solid, mp 232-233 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.41 (t, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 4.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 152.2, 144.8, 132.3, 131.4, 130.6, 129.2, 129.0, 123.2, 116.1, 113.9, 65.1, 21.1. These data are in accordance with the literature.[7]



P,P-Diphenyl-*N*-(9*H*-xanthen-9-yl)phosphinic amide (**3bi**): 60 mg, 30% yield; white solid, mp 256-258 °C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.91 (q, 4H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.46 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 4H), 5.59 (t, *J* = 12.0 Hz, 1H), 3.41 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.5, 133.2, 132.3, 132.2, 132.02, 131.99, 131.9, 130.2, 128.9, 128.6, 128.5, 123.5, 123.0, 122.9, 116.5, 46.6; HRMS (ESI): cacld. for $C_{25}H_{20}NO_2P$ $[M+Na]^+$: 420.1124, found 420.1132.



N-(Benzyloxy)-*N*-(9*H*-xanthen-9-yl)benzamide (**4aa**): 53 mg, 26% yield (**condition I**, reaction time 0.5 h); white solid, mp 136-140 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.57 (m, 5H), 7.46 (m, 4H), 7.26 (t, *J* = 8.0 Hz, 4H), 7.18 (m, 3H), 6.94 (s, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 169.9, 152.2, 134.4, 133.5, 130.6, 129.9, 129.4, 128.9, 128.6, 128.3, 128.2, 127.5, 123.8, 118.6, 116.4, 78.0, 52.9; HRMS (ESI): cacld. for $C_{27}H_{21}NO_3$ $[M+Na]^+$: 430.1414, found 430.1420.

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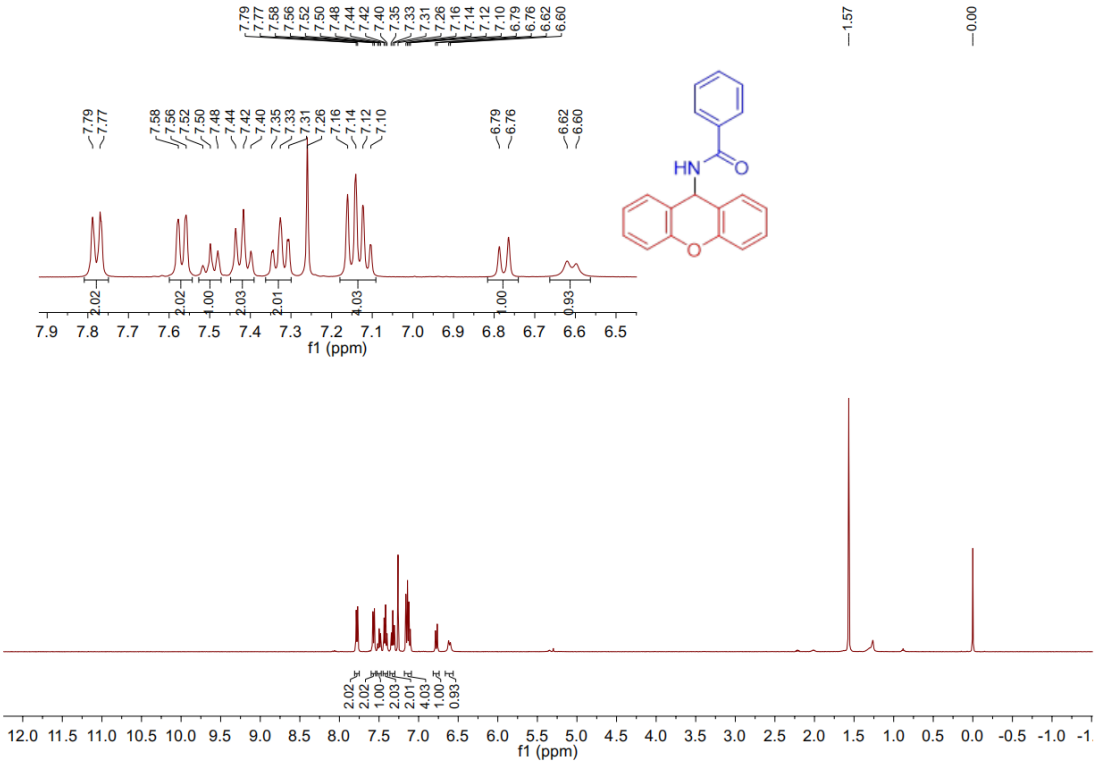
NMR spectra

3aa ^{1}H NMR



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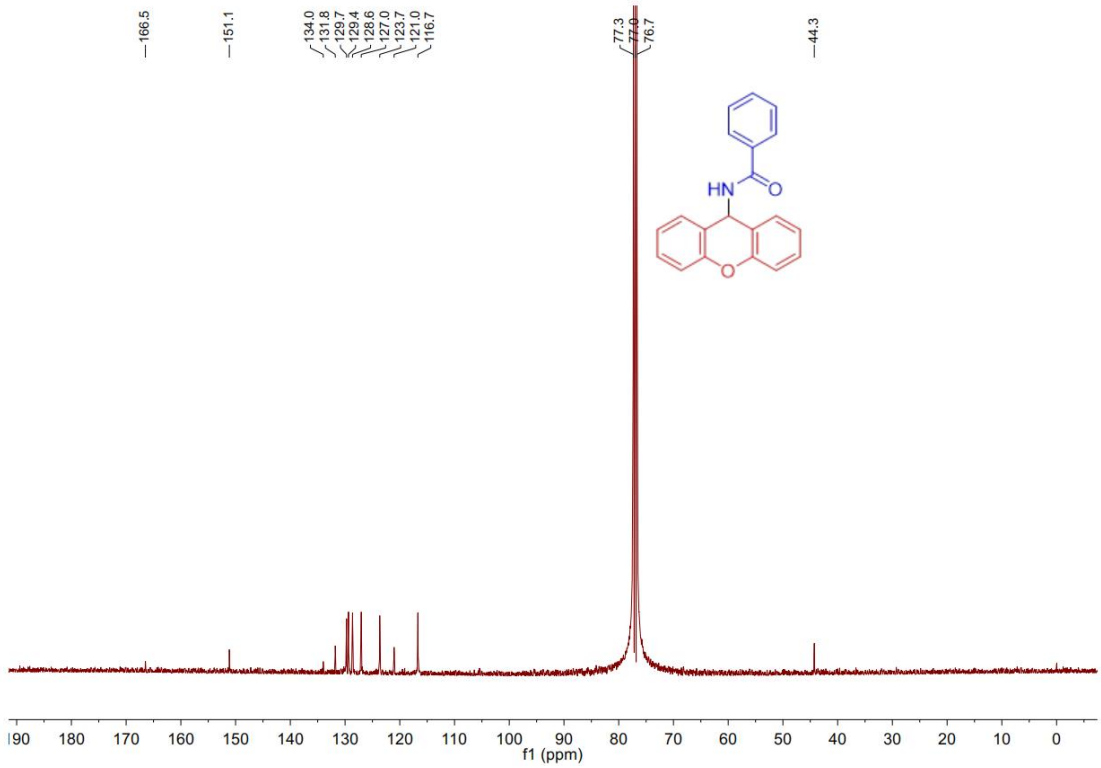

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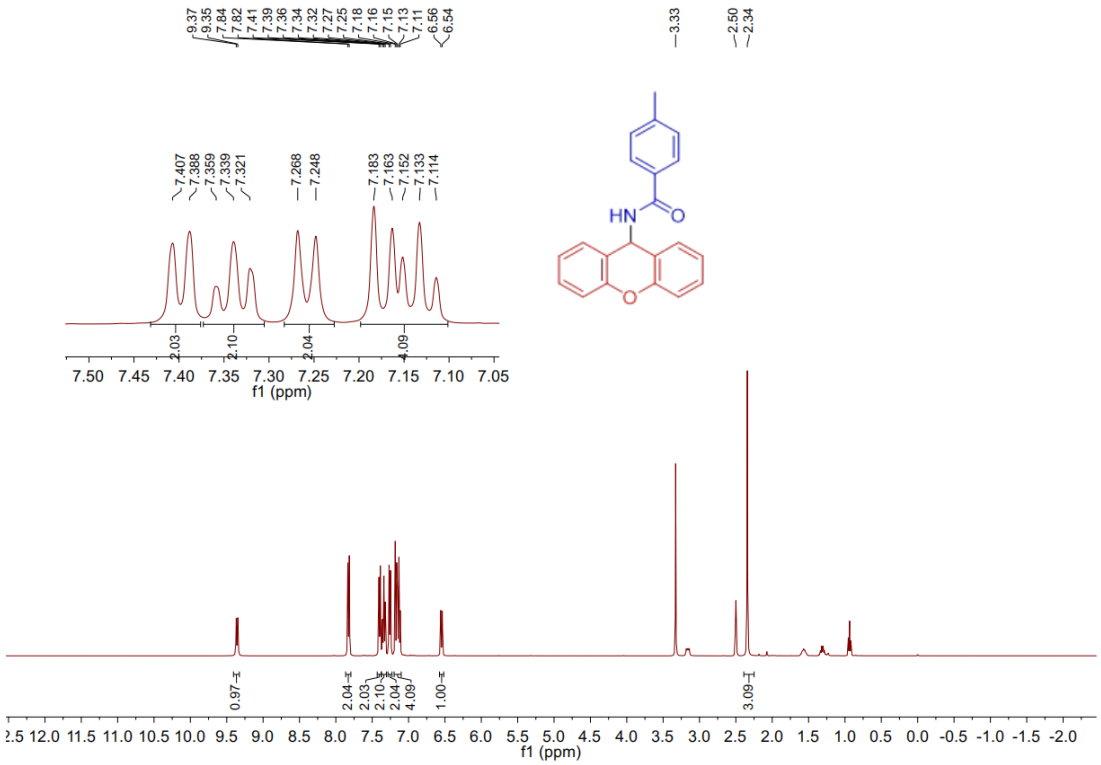

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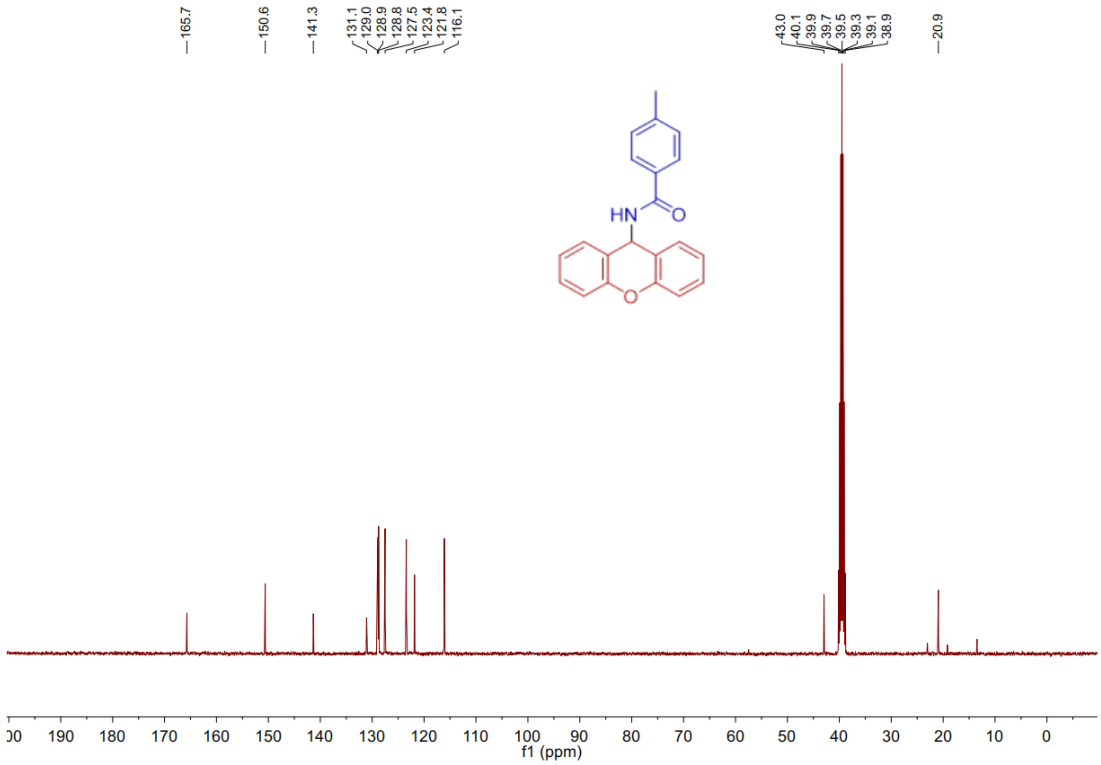

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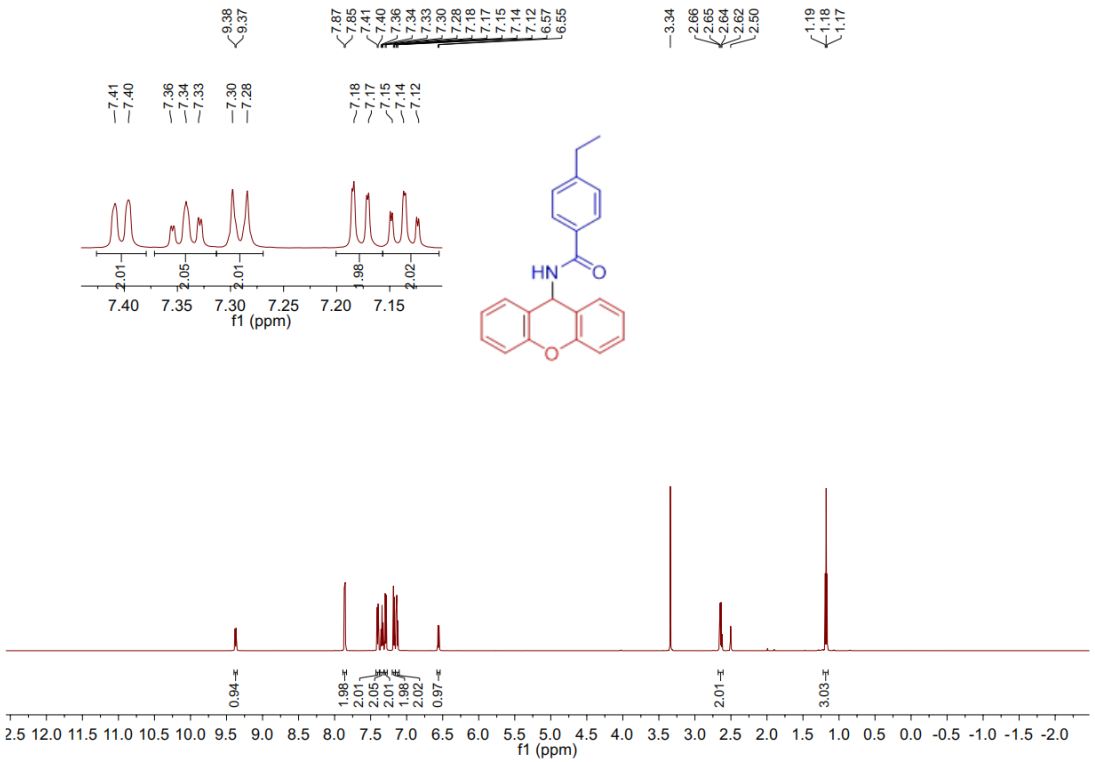

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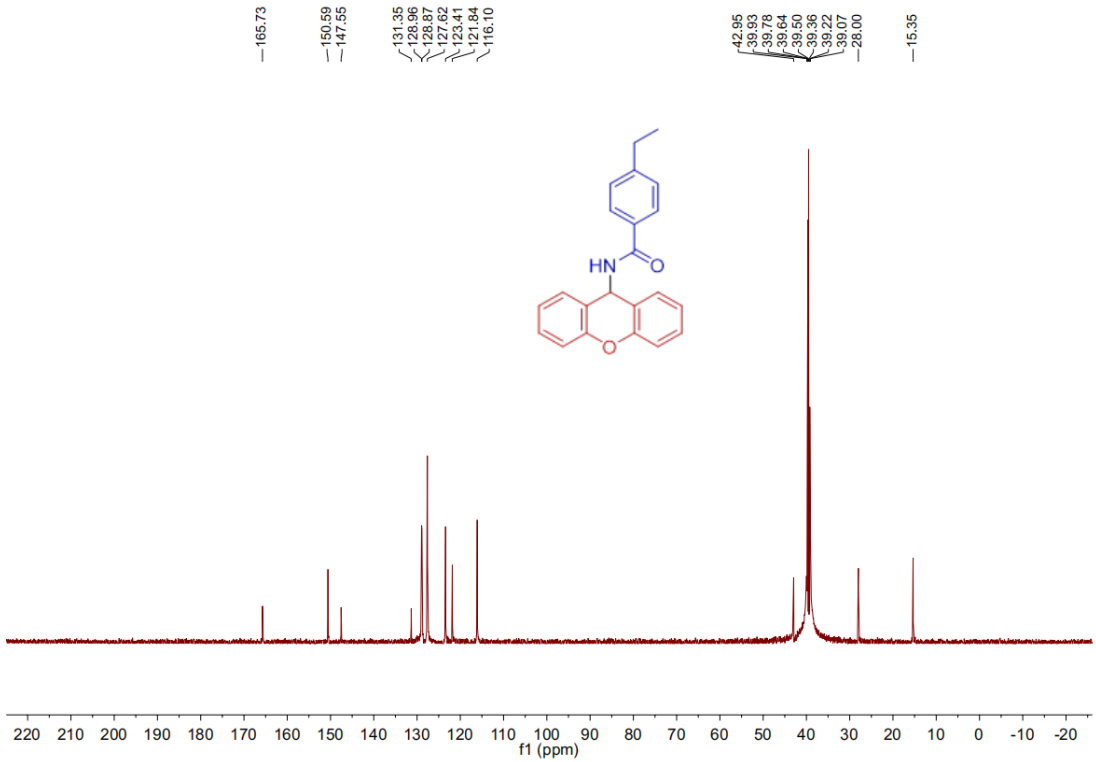

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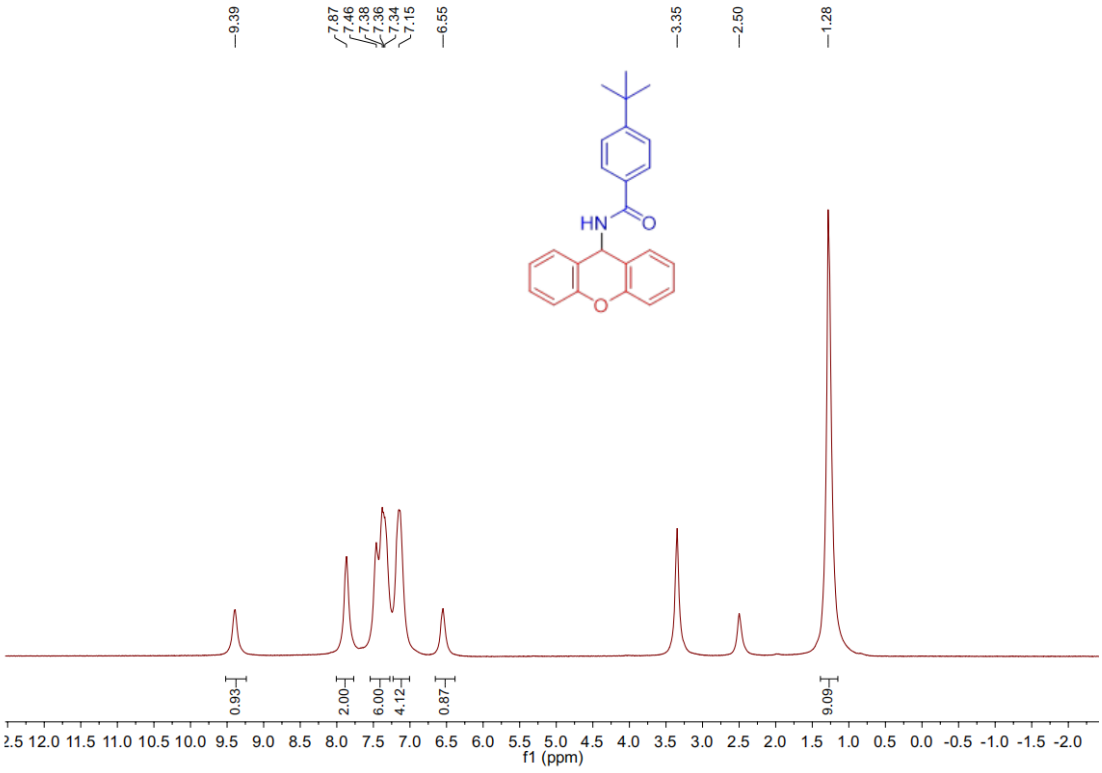

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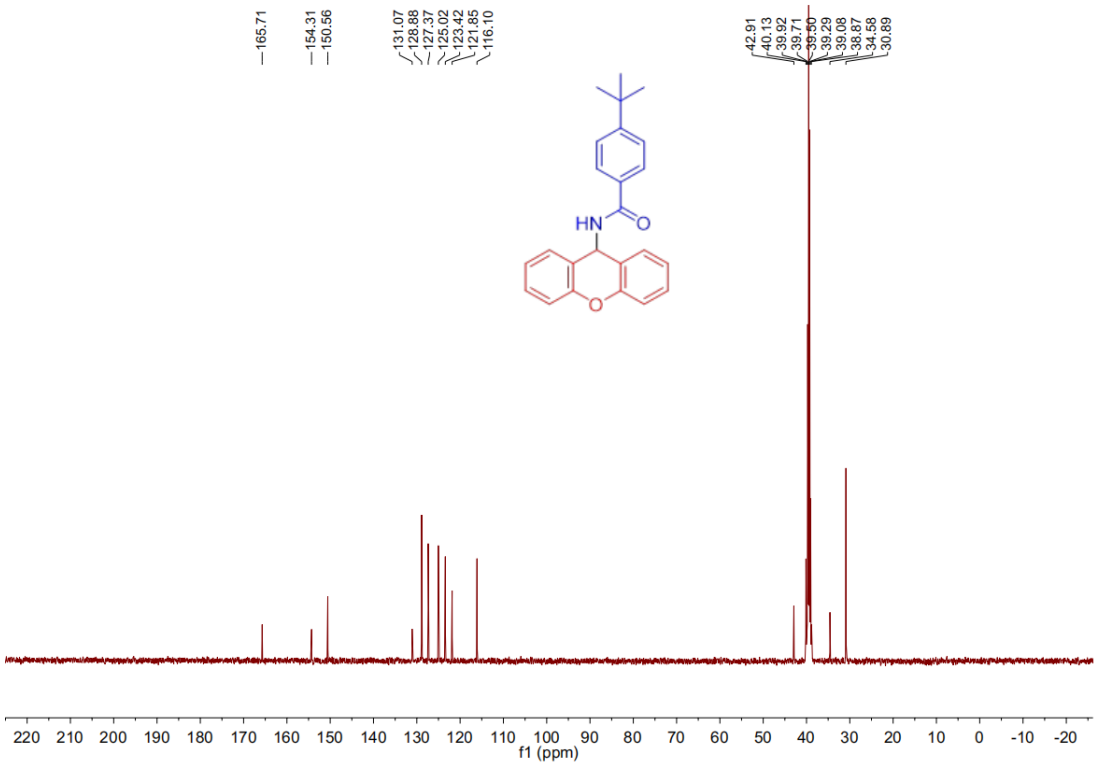

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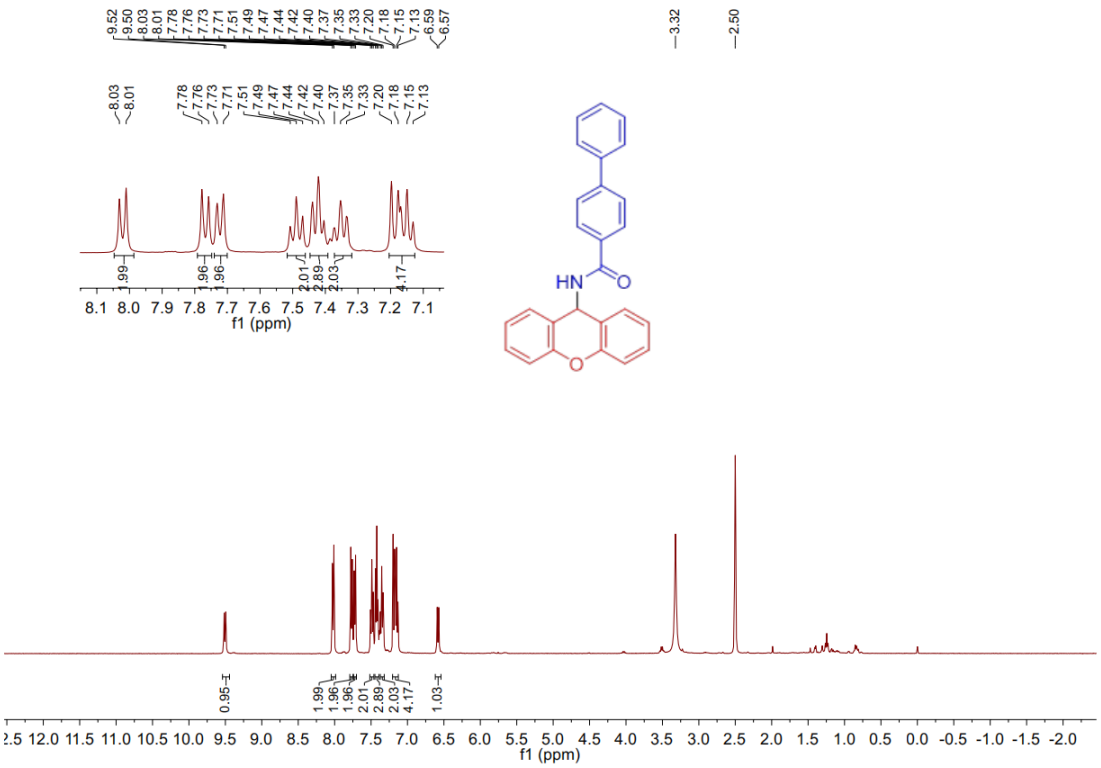

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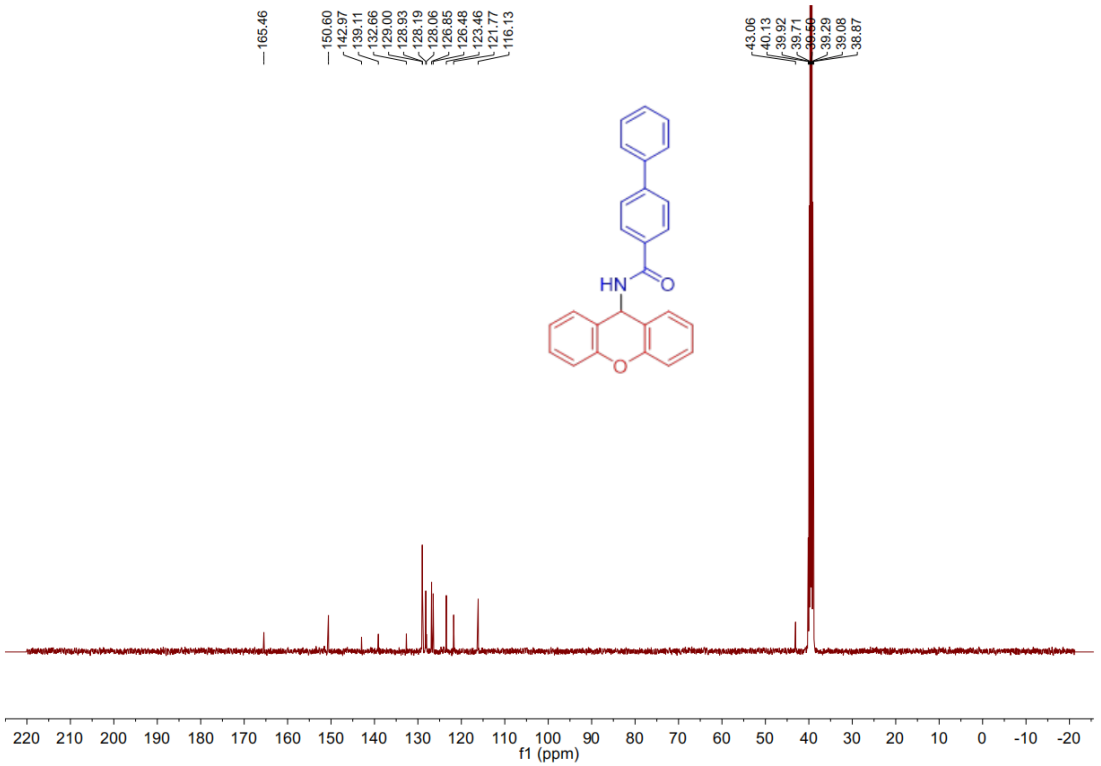

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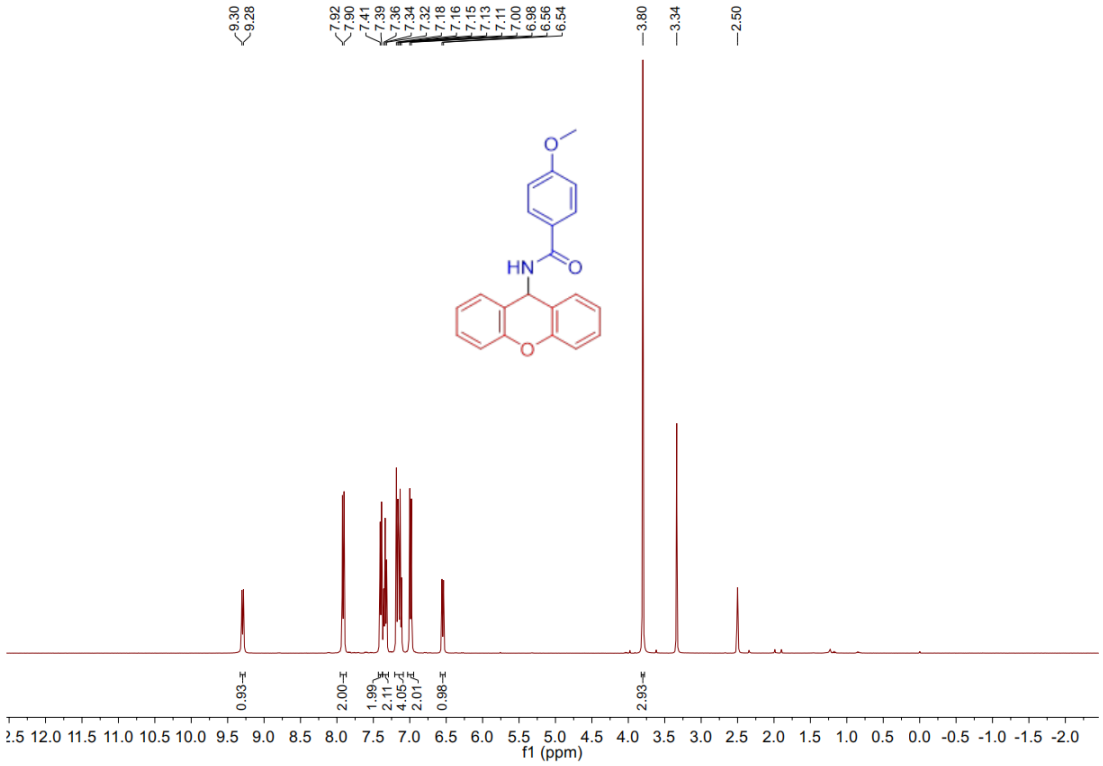

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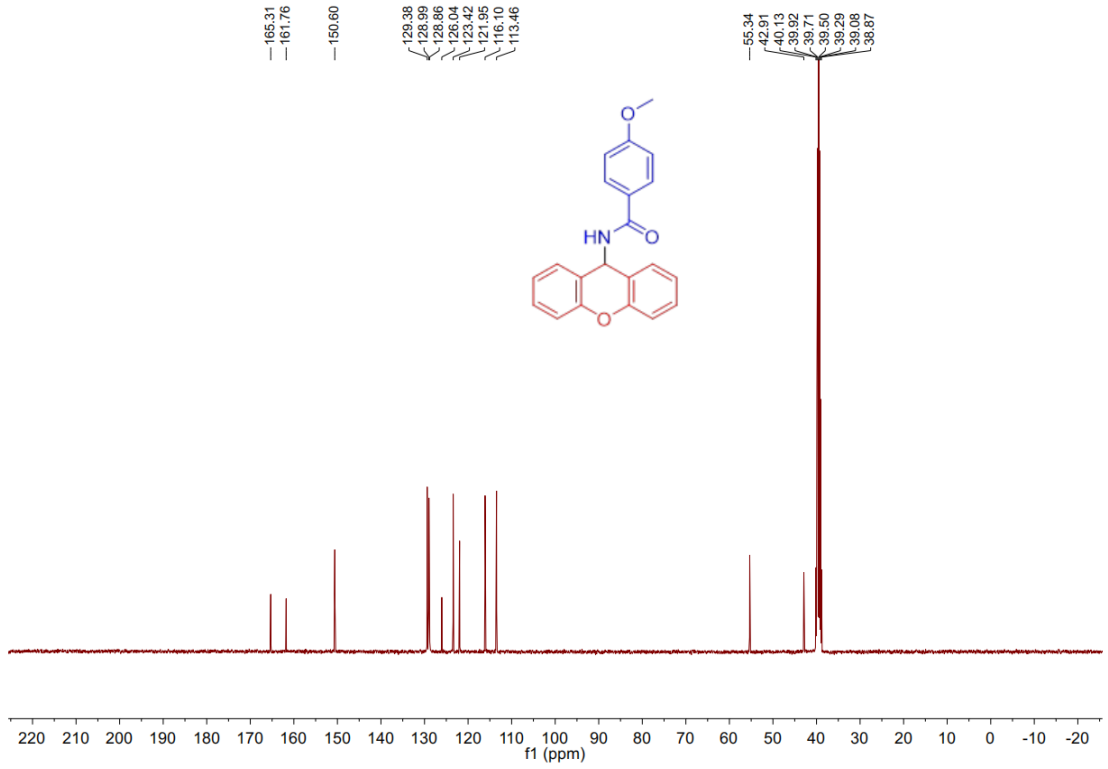

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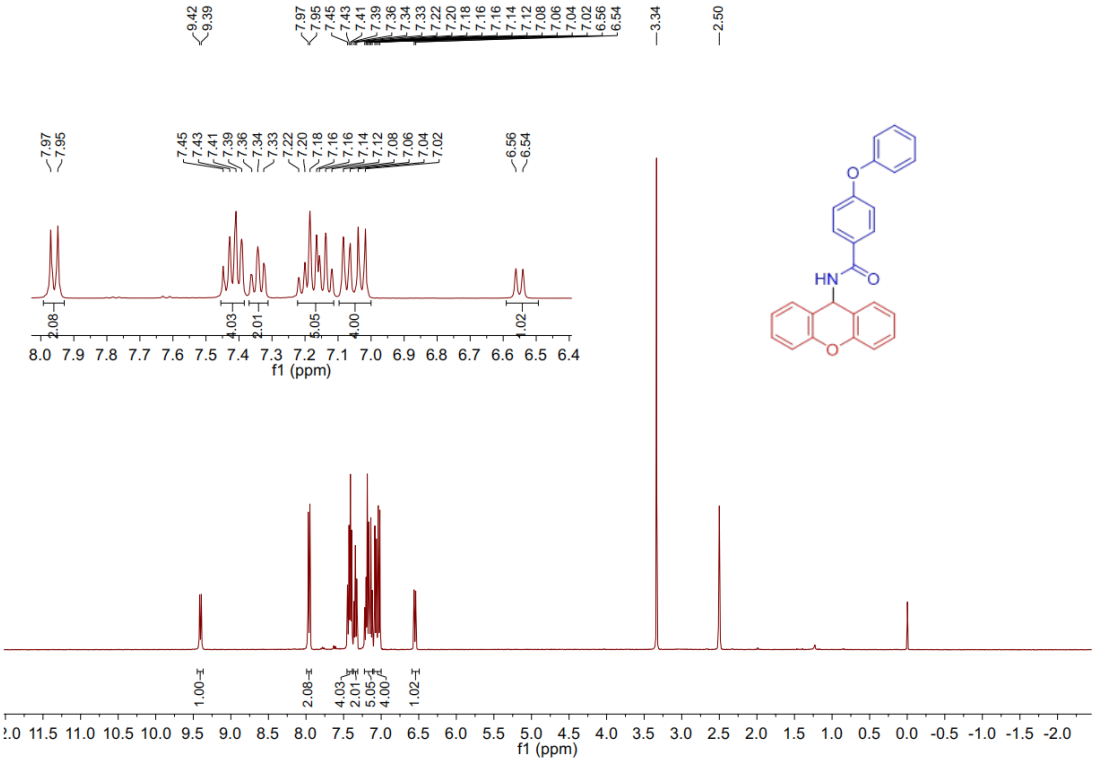

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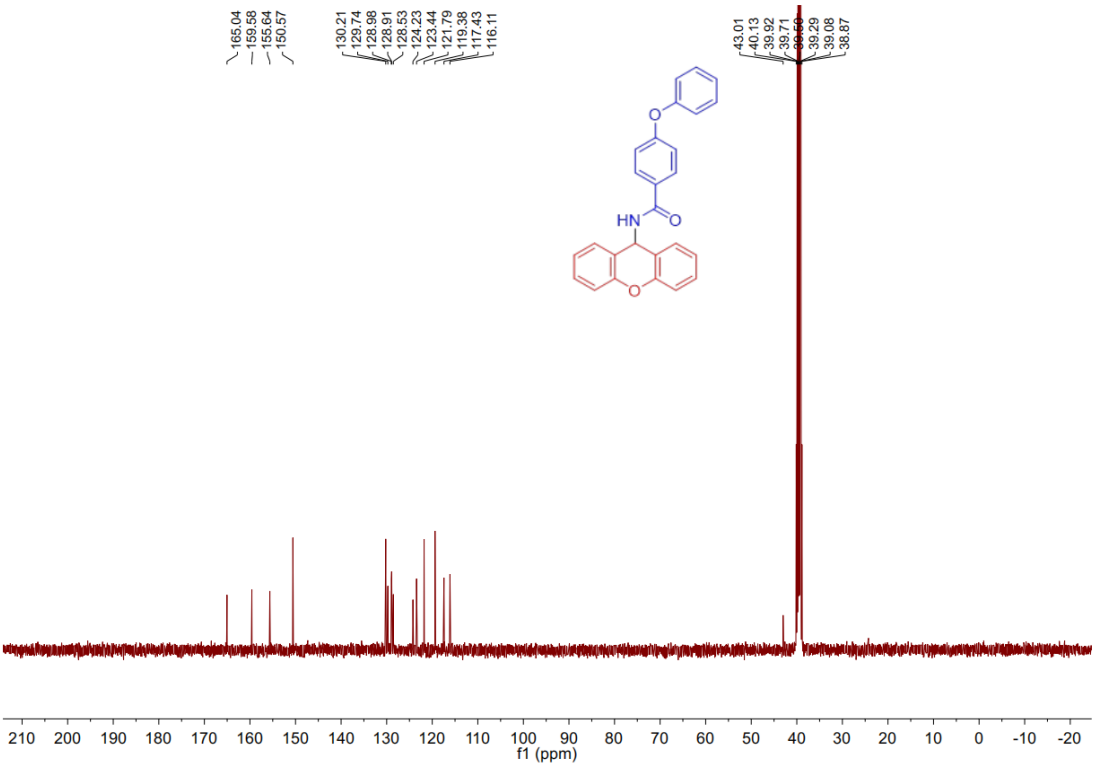

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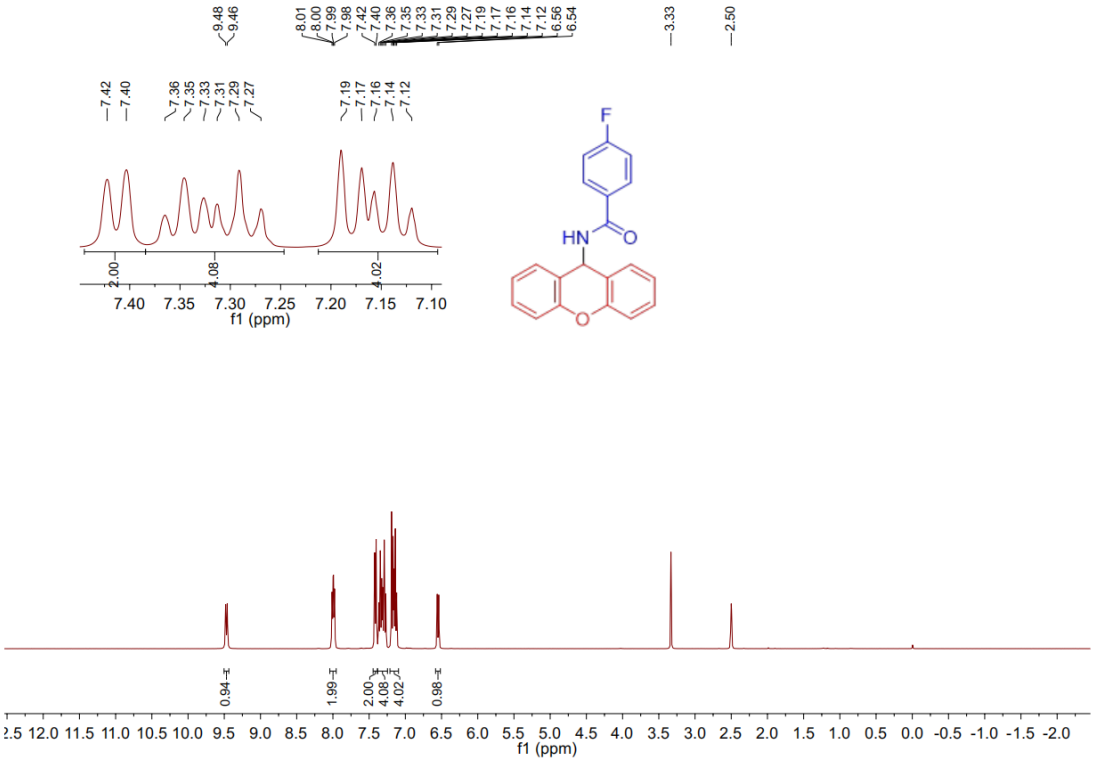

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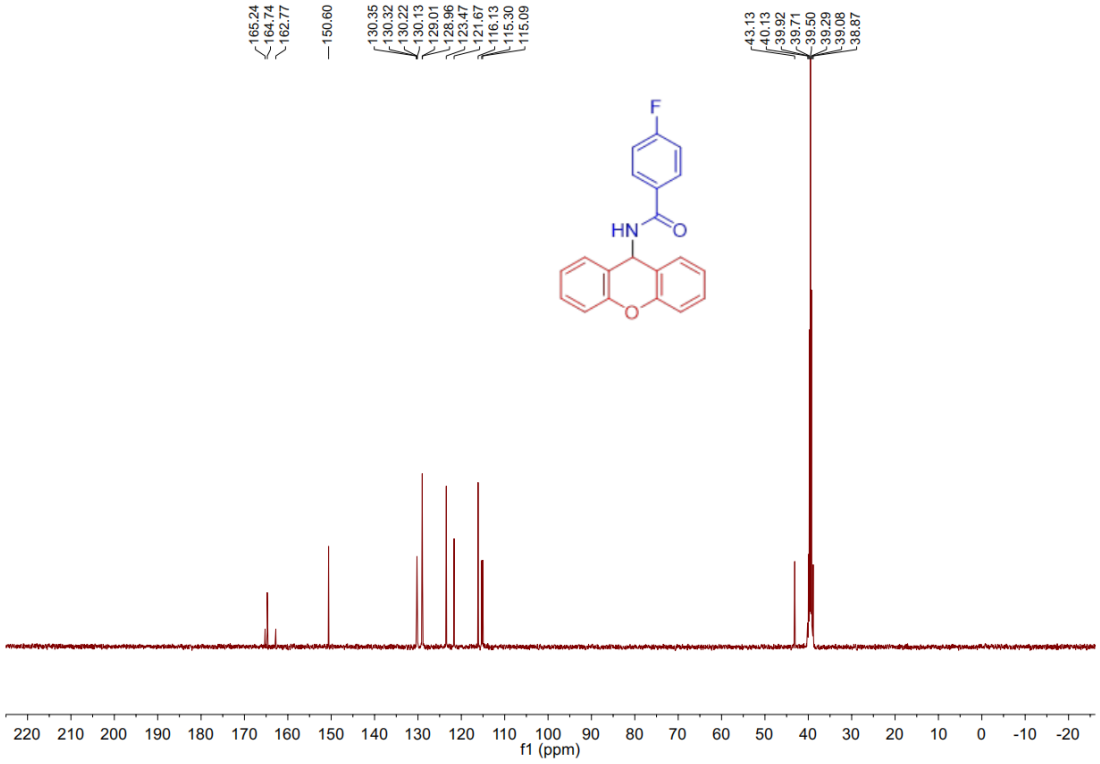

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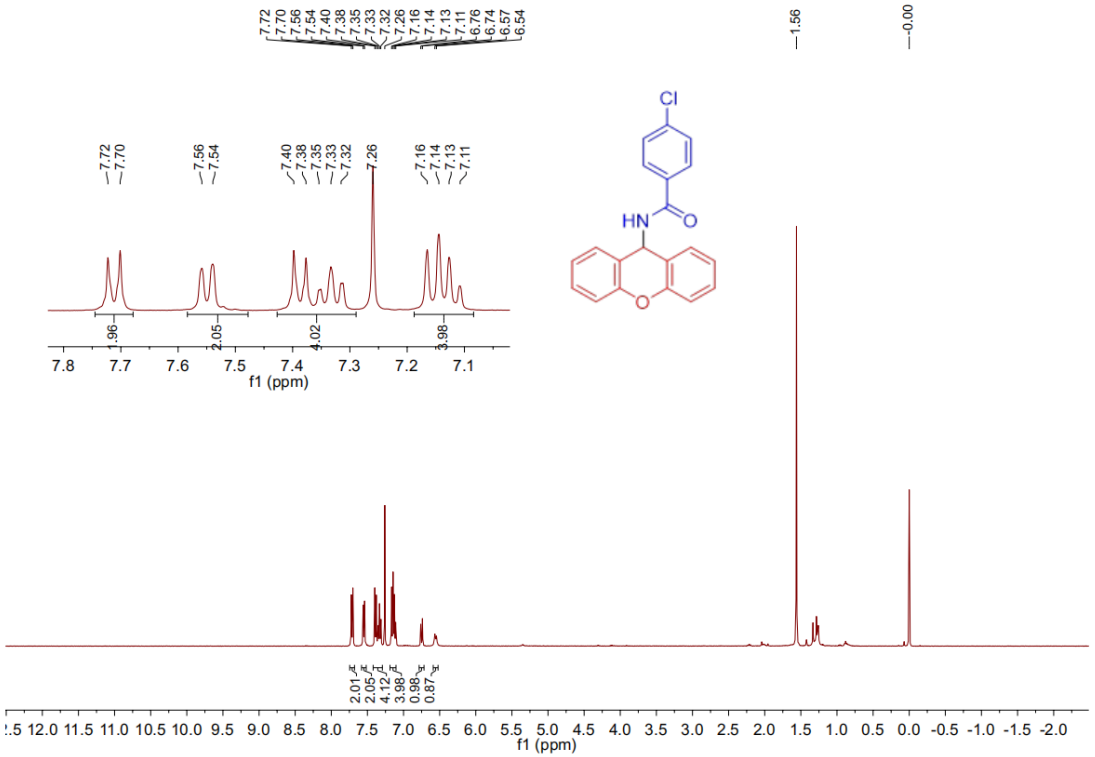

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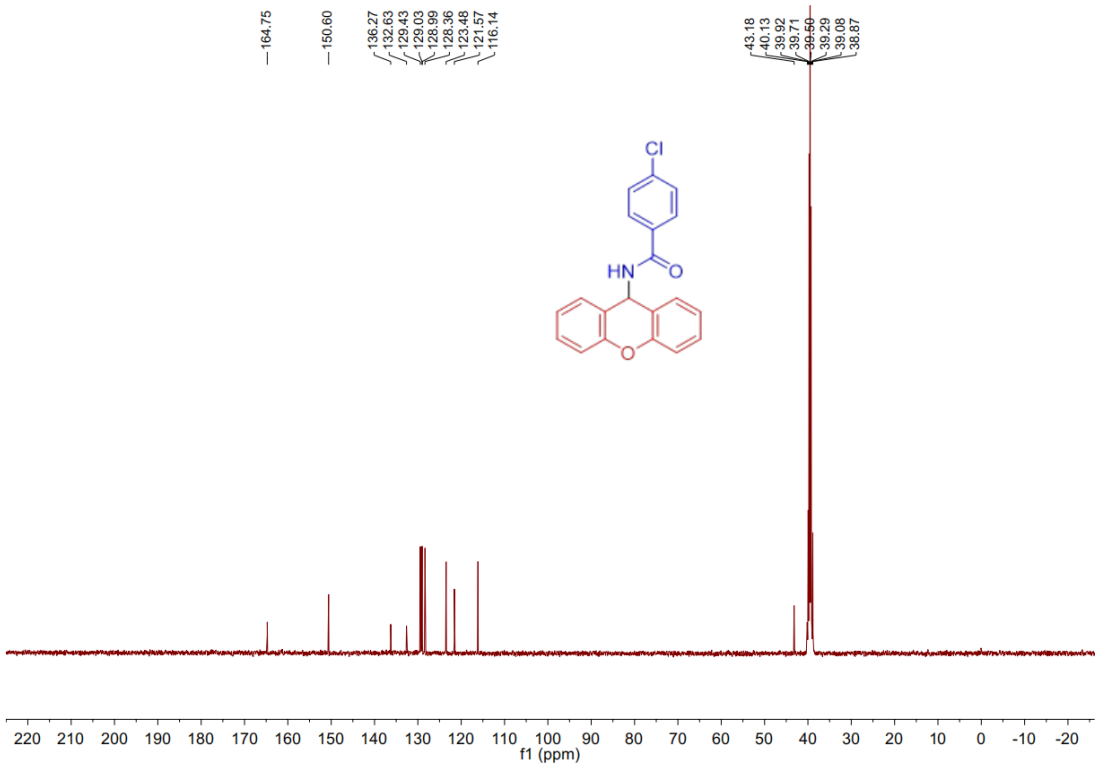

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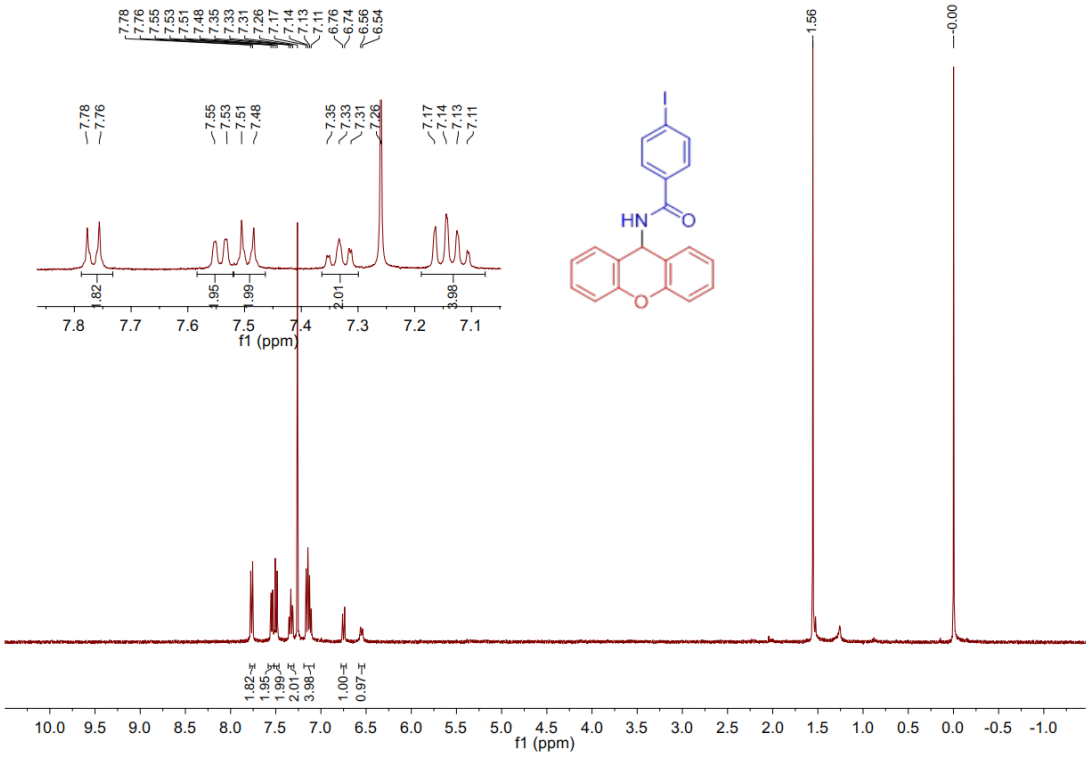

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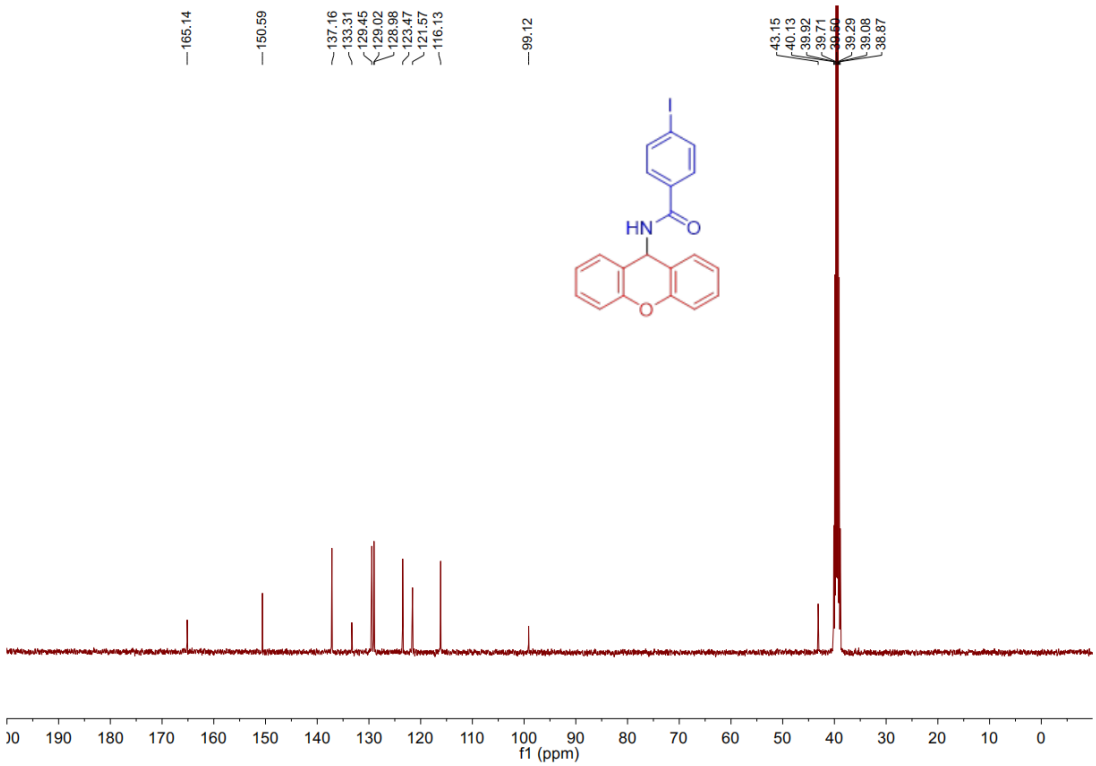

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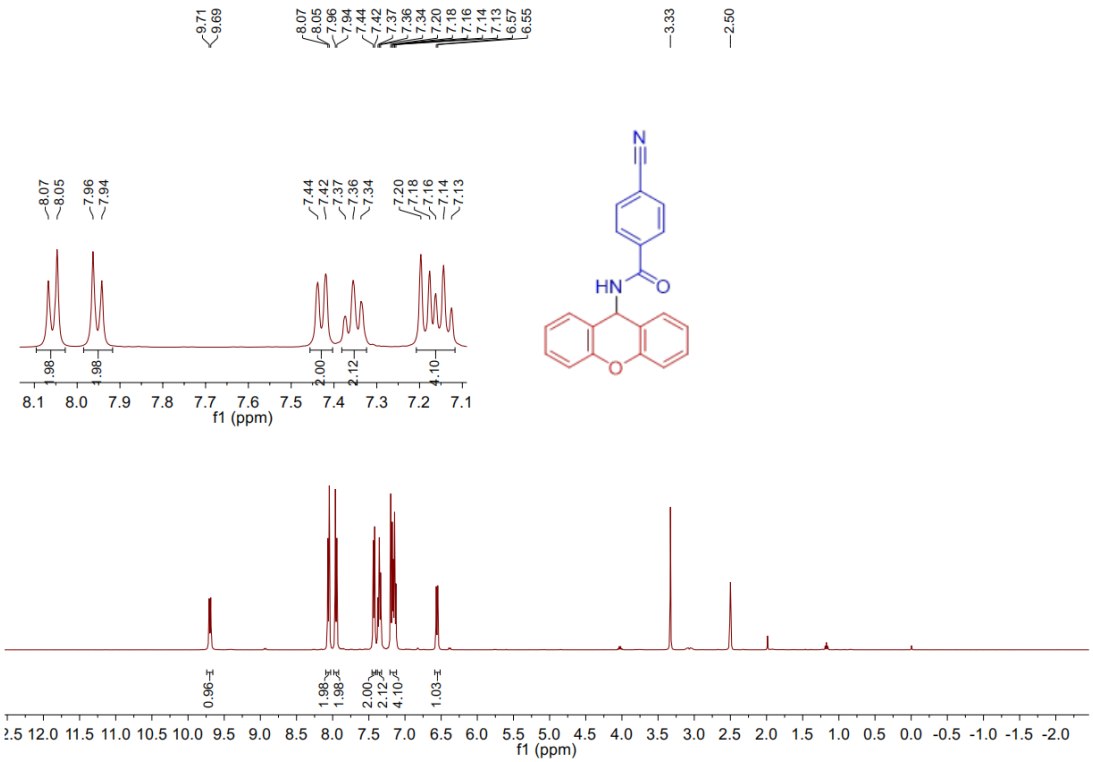

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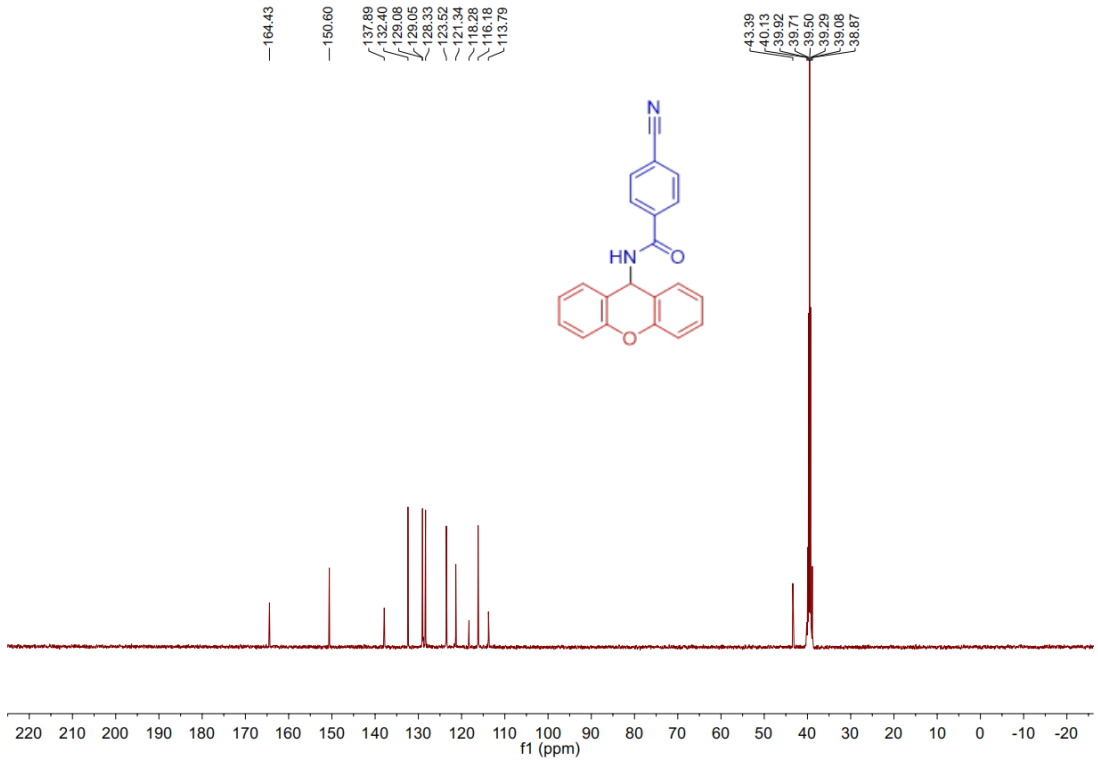

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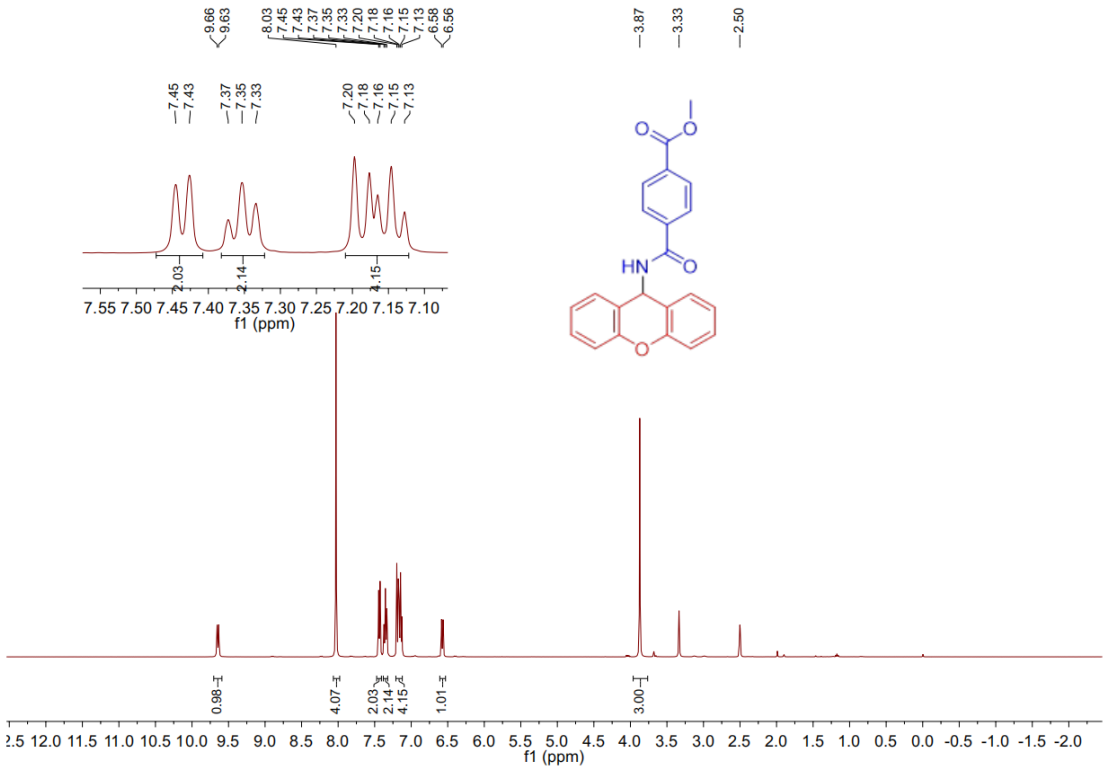

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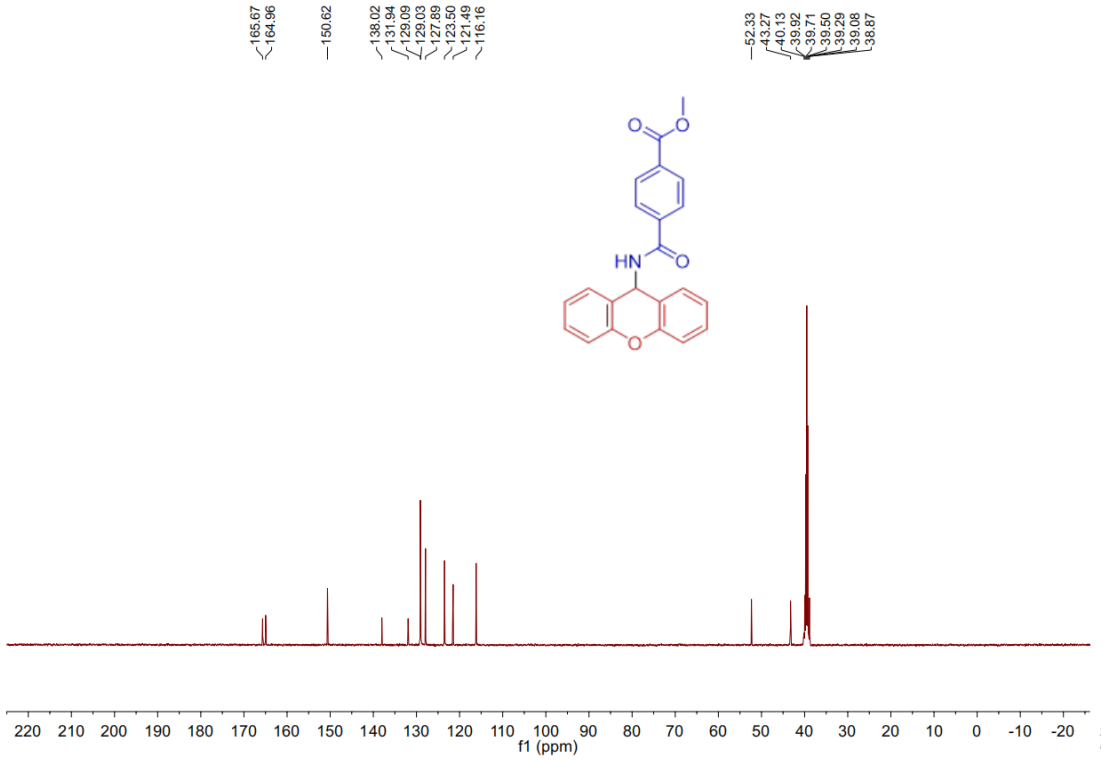

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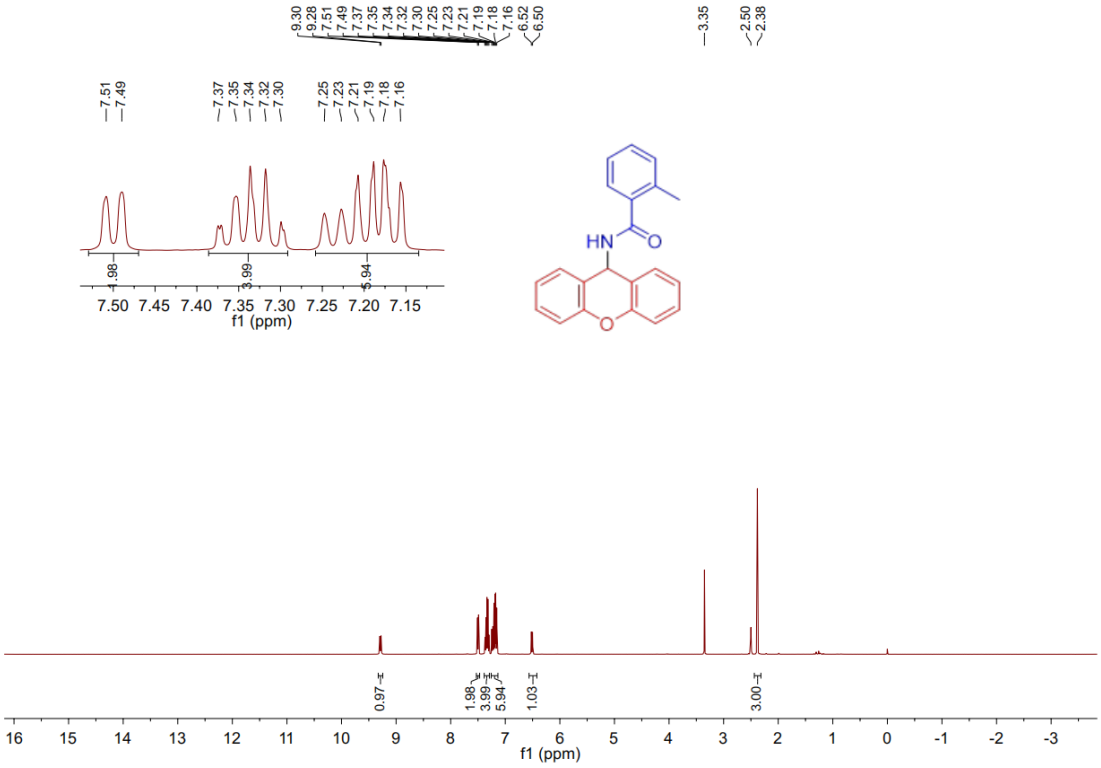

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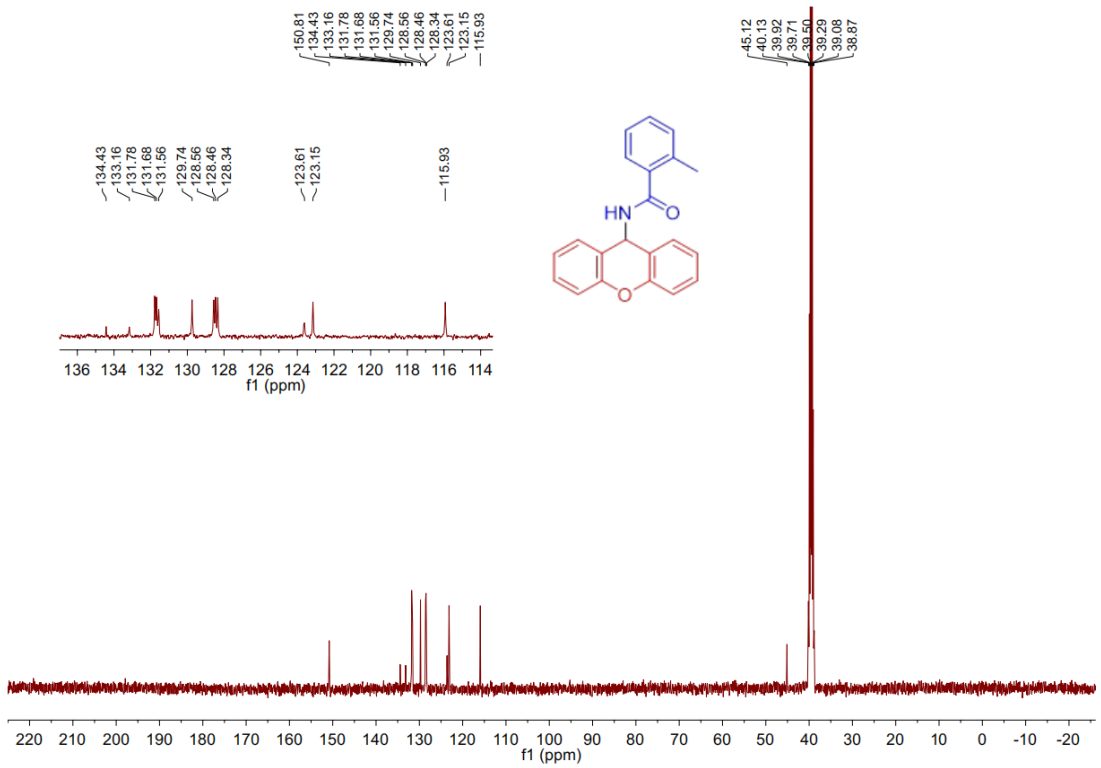

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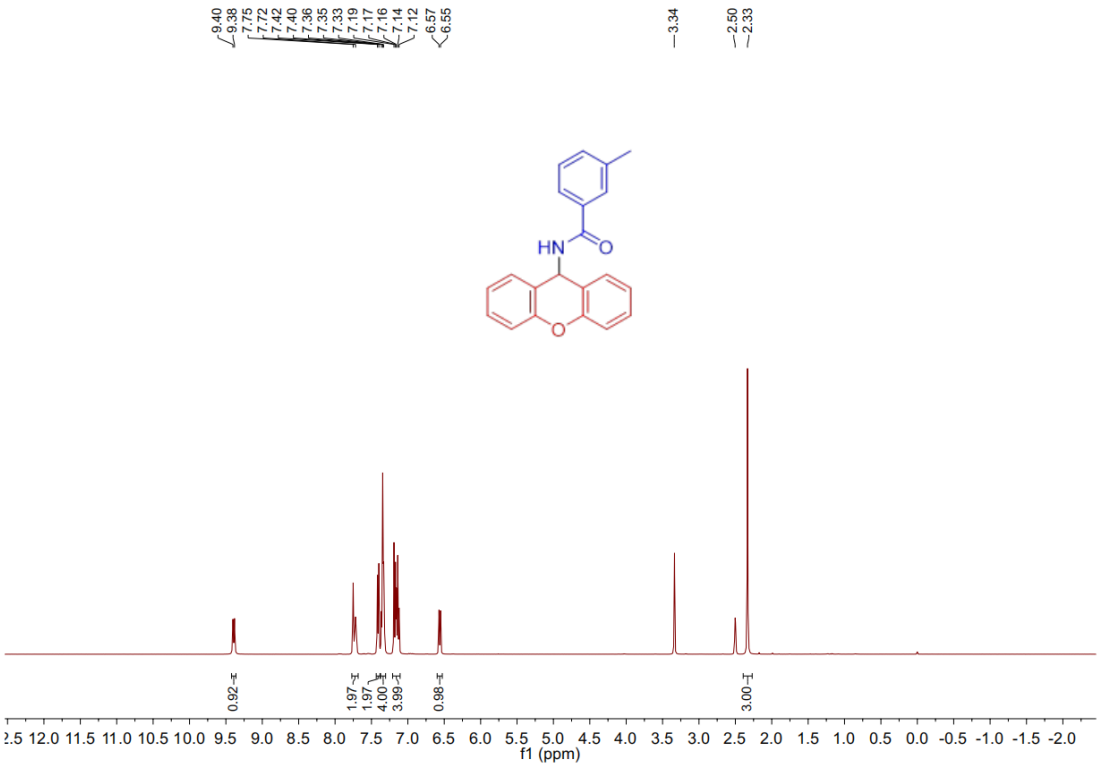

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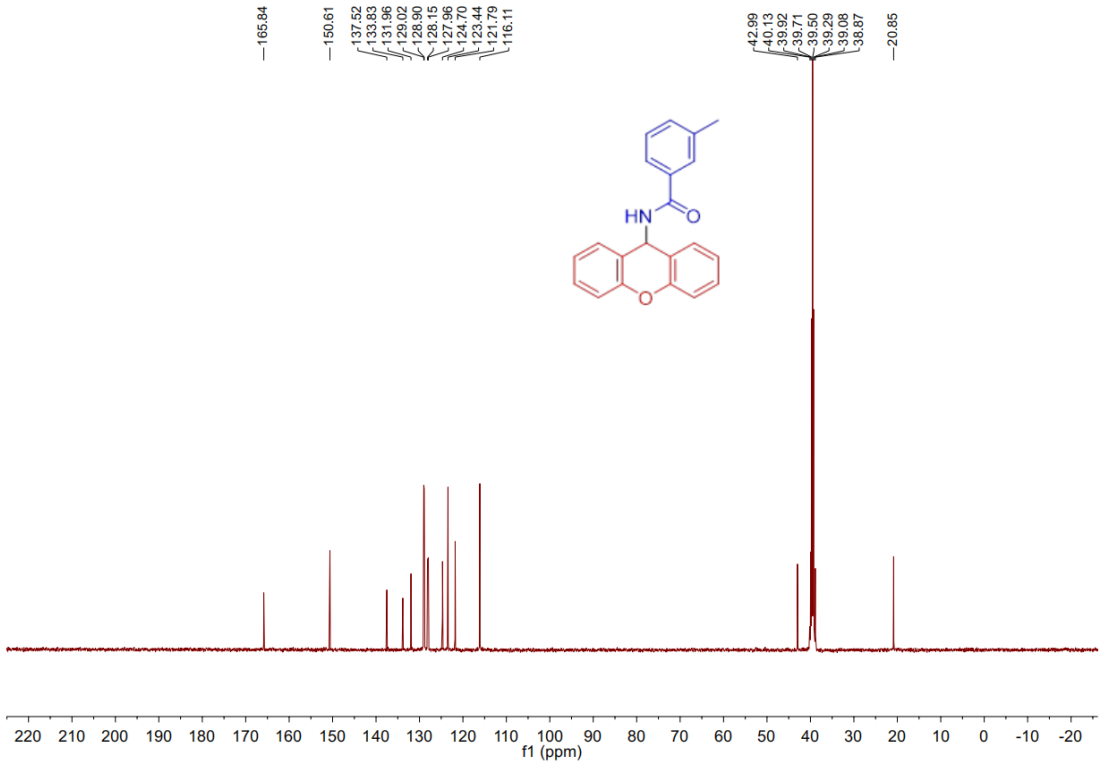

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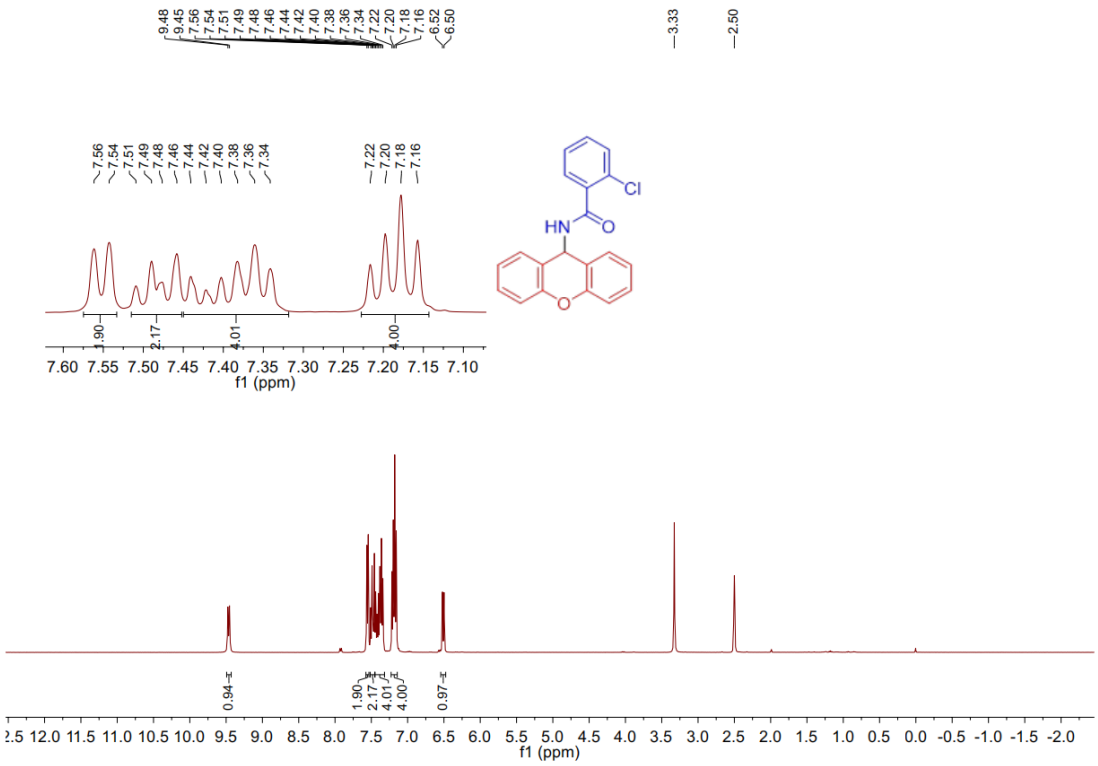

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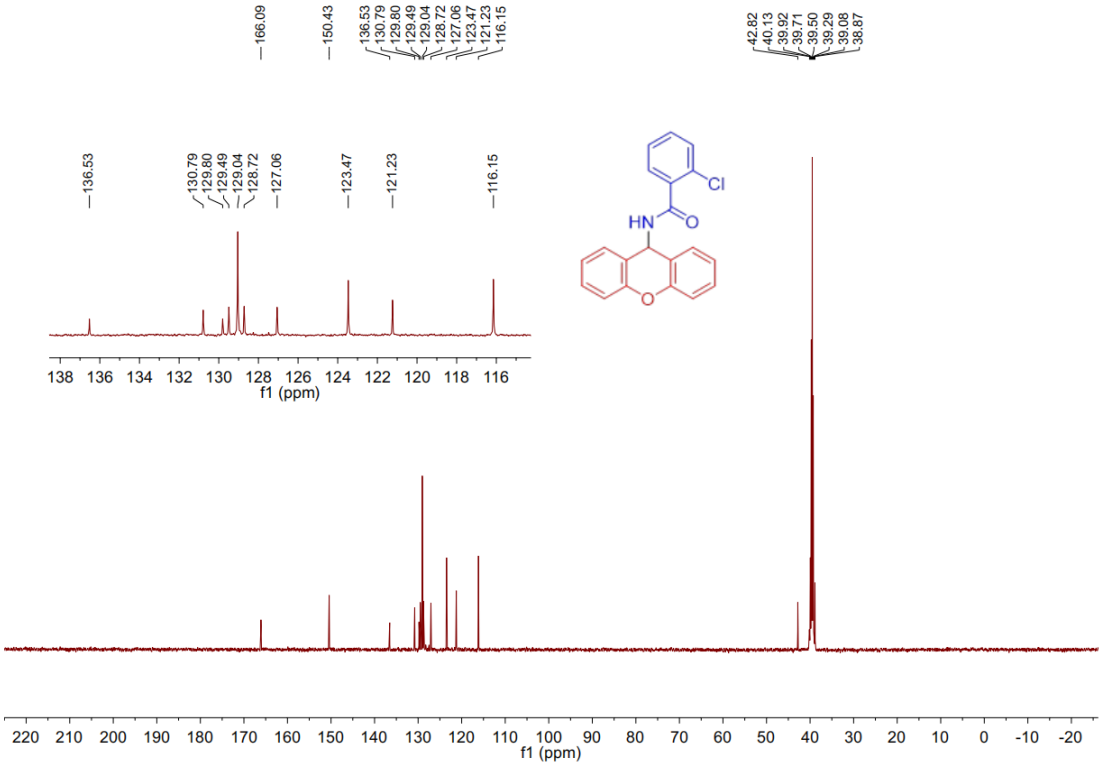

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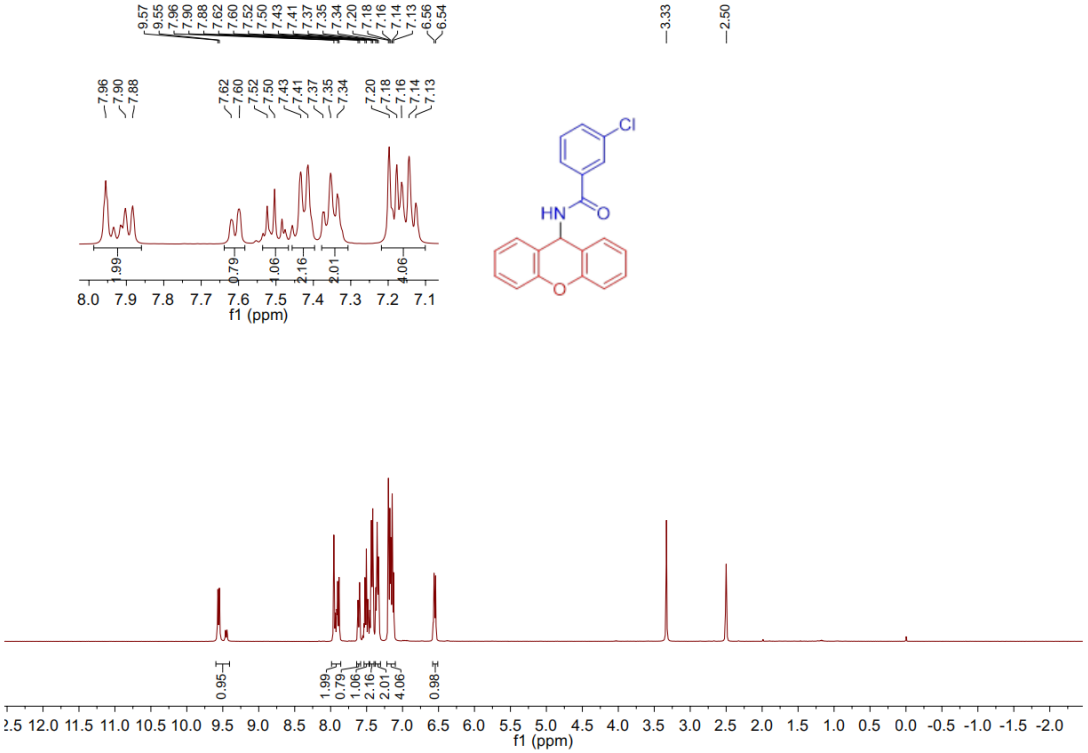

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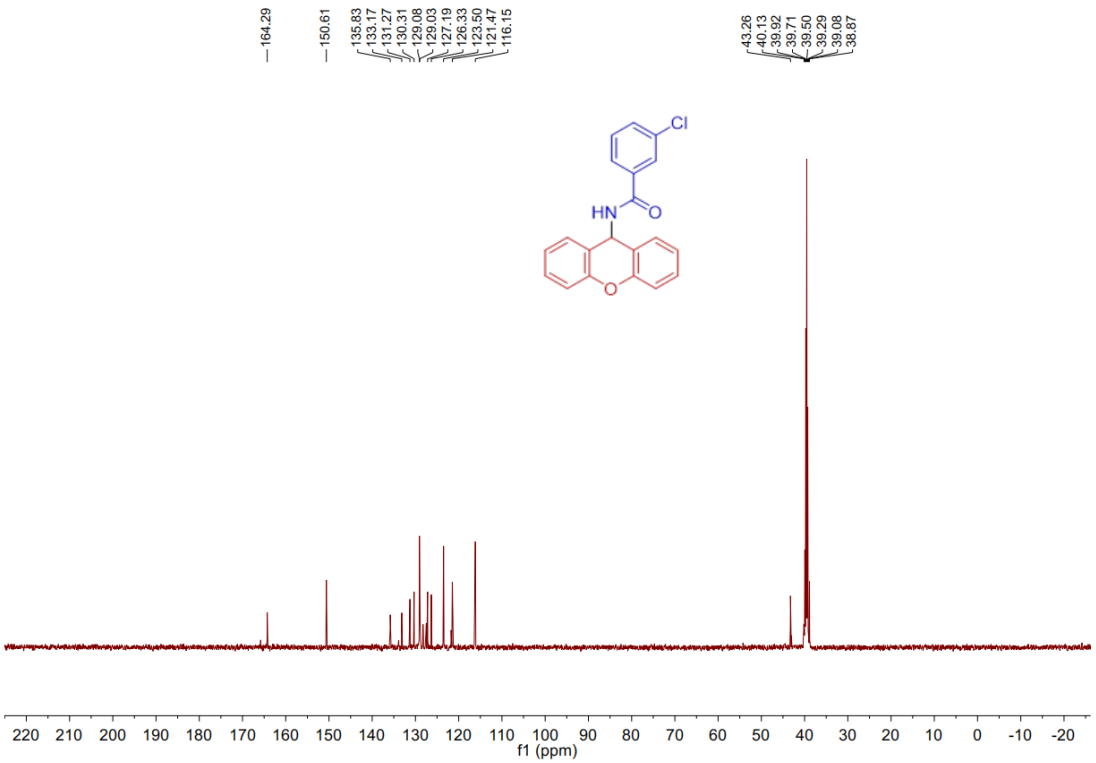

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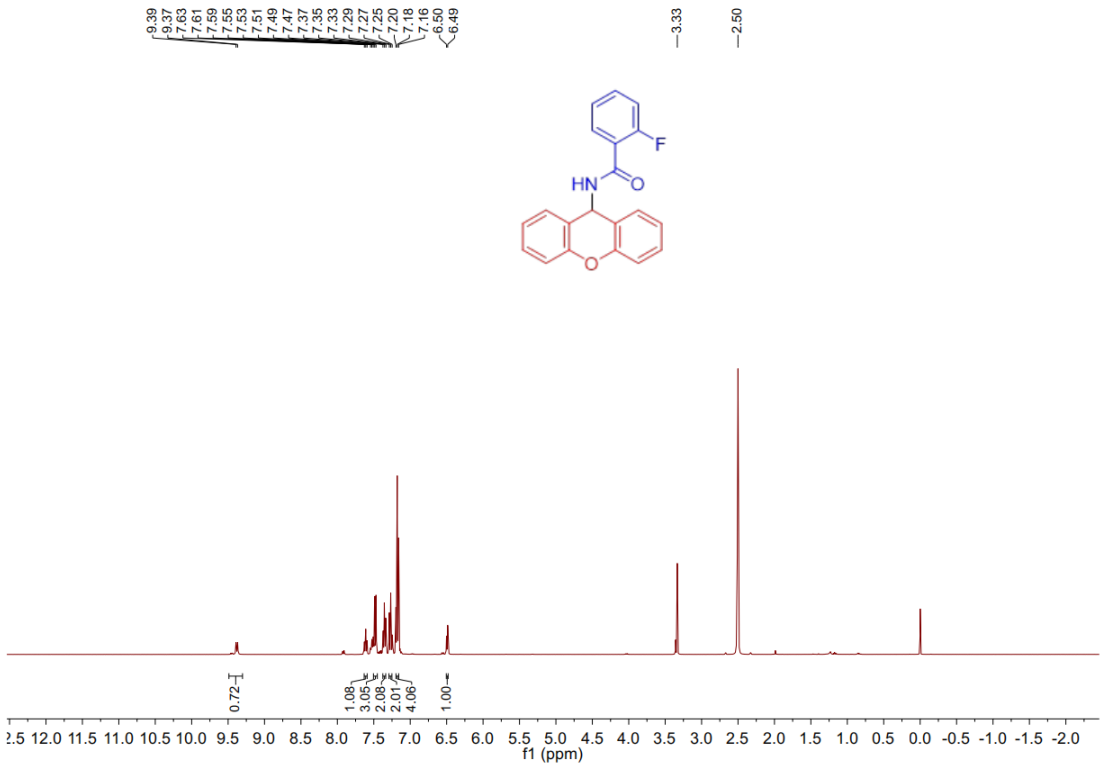

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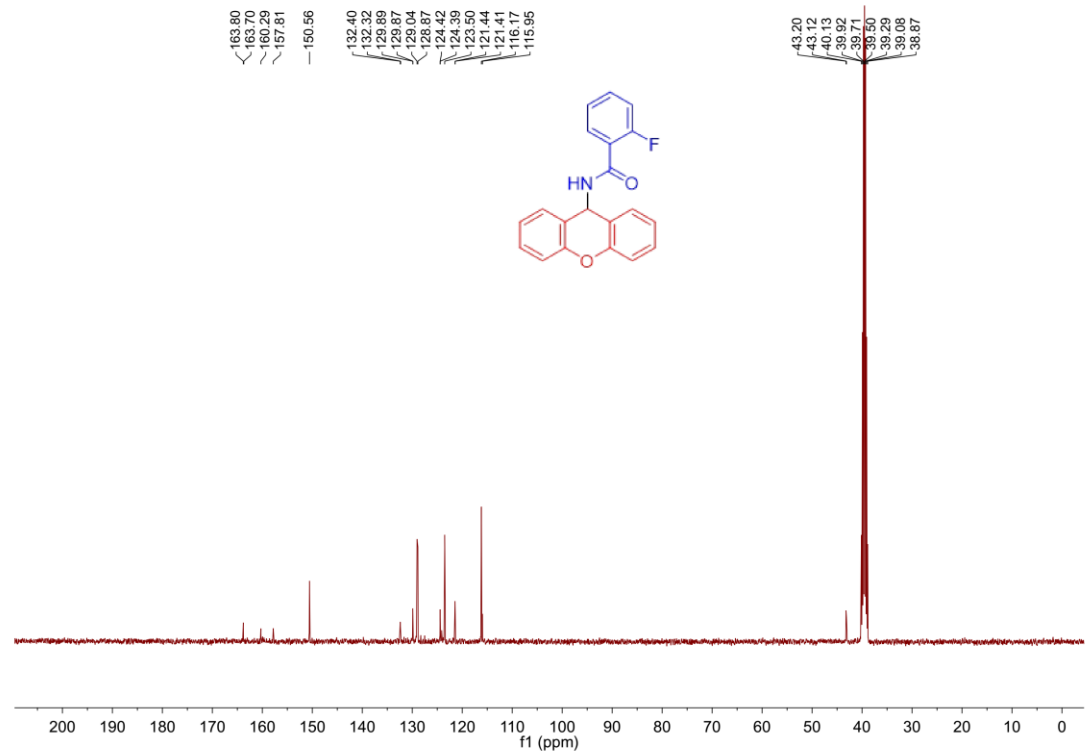

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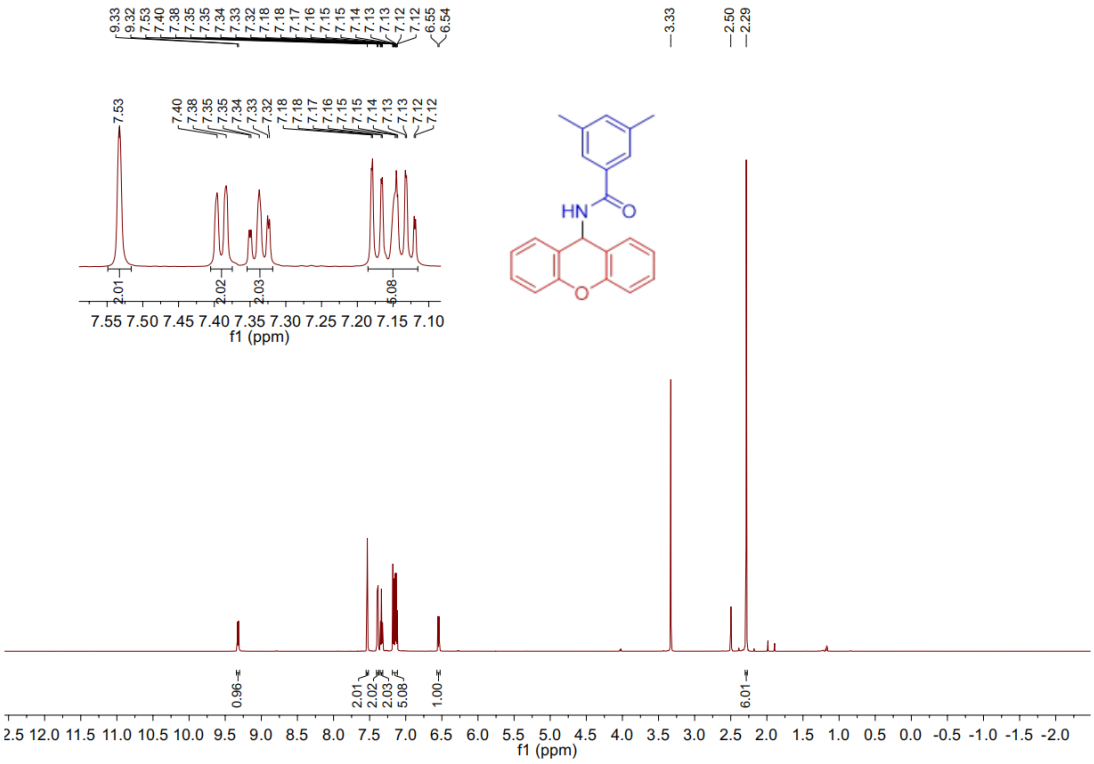

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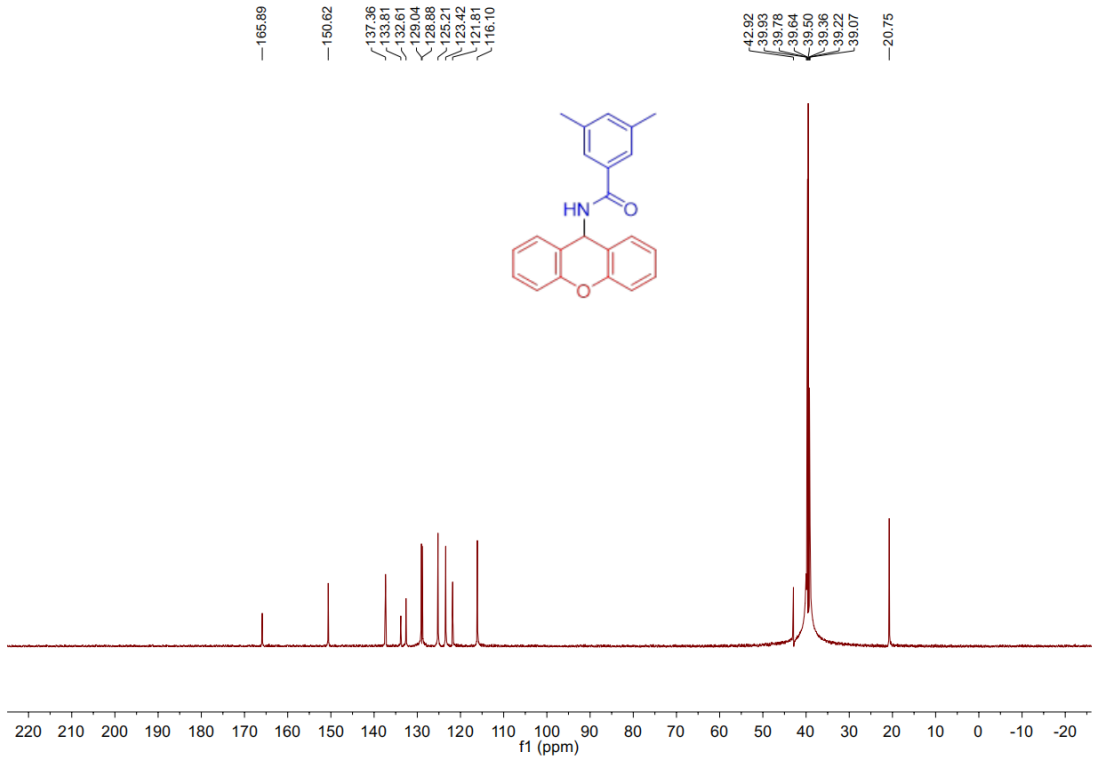

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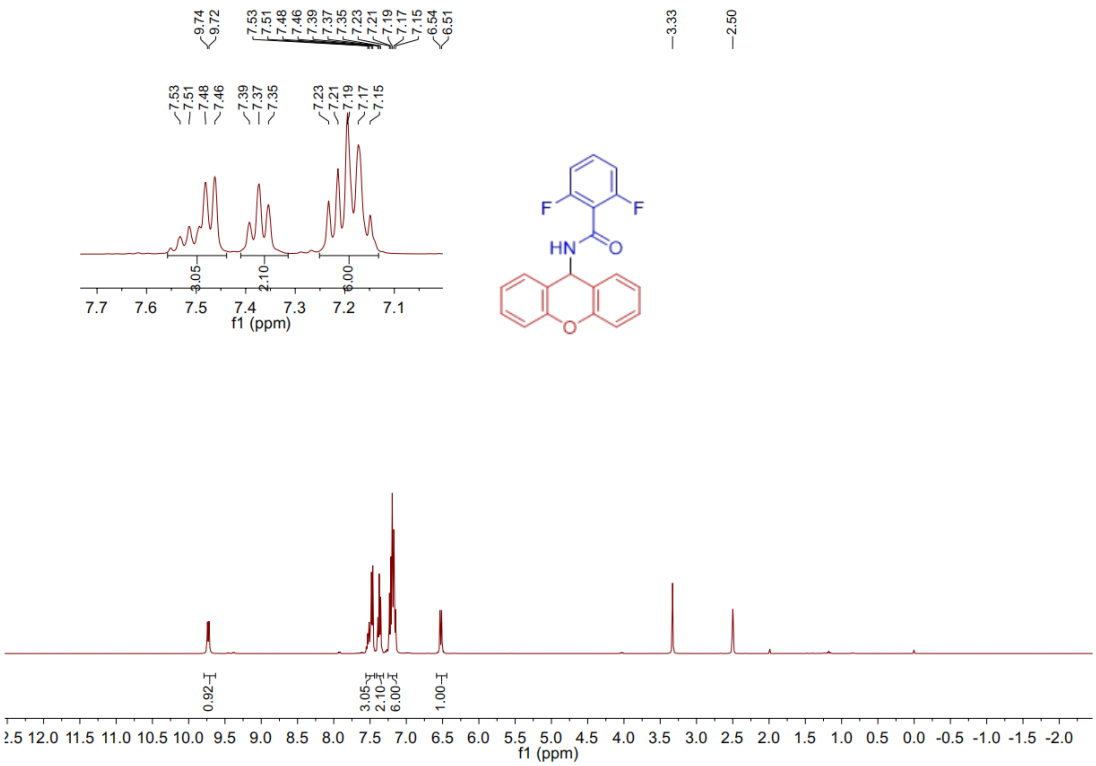

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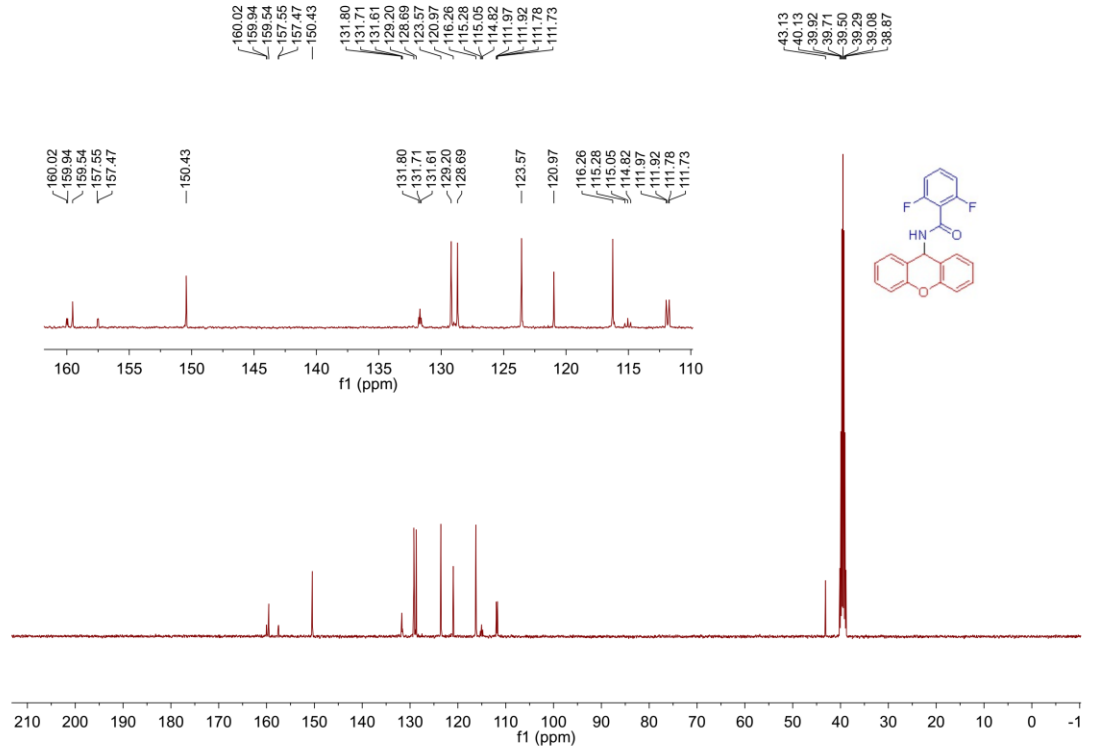

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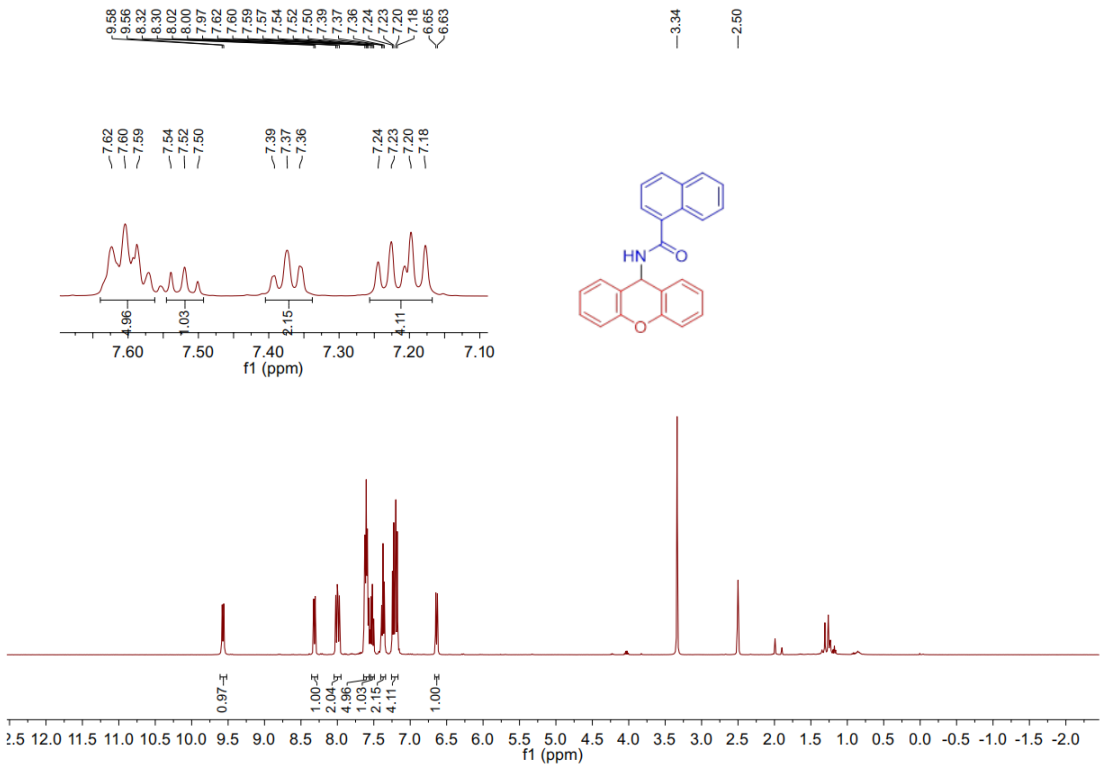

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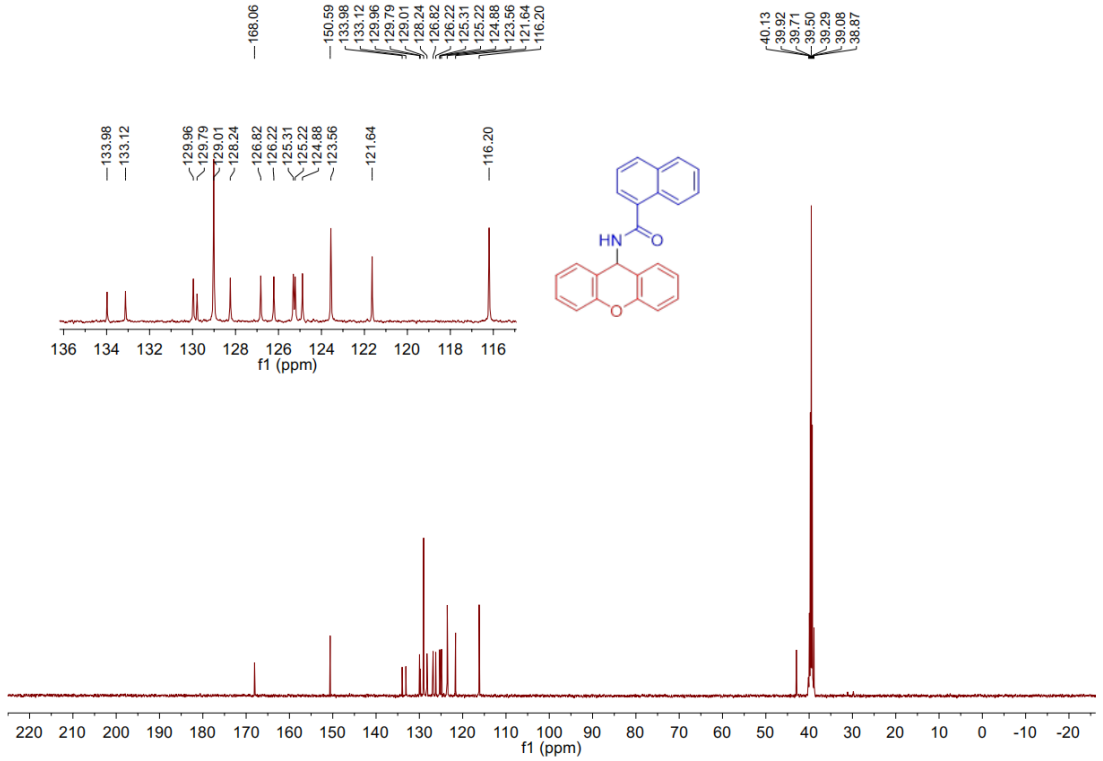

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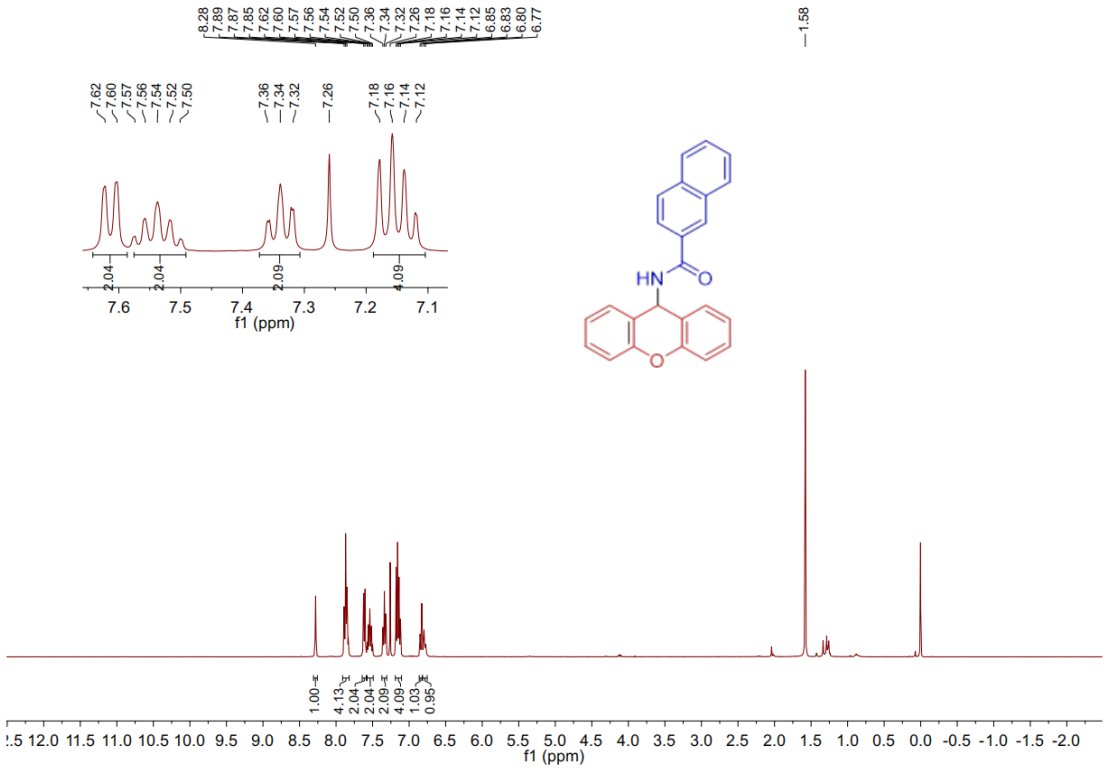

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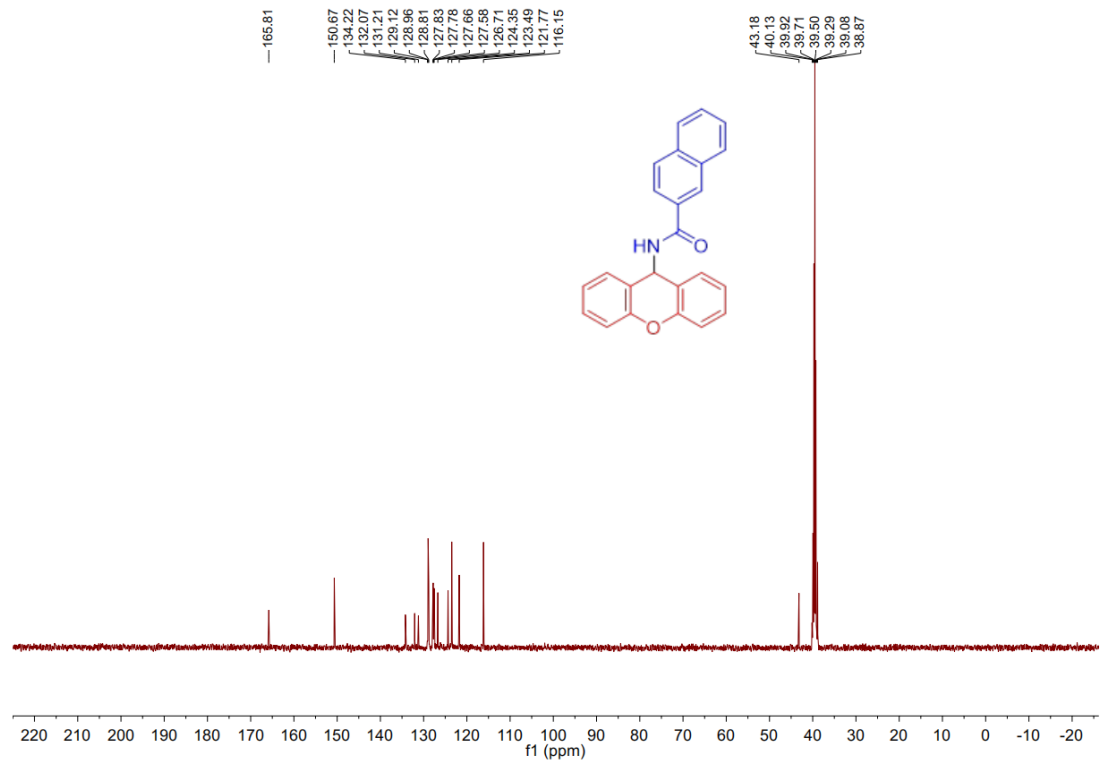

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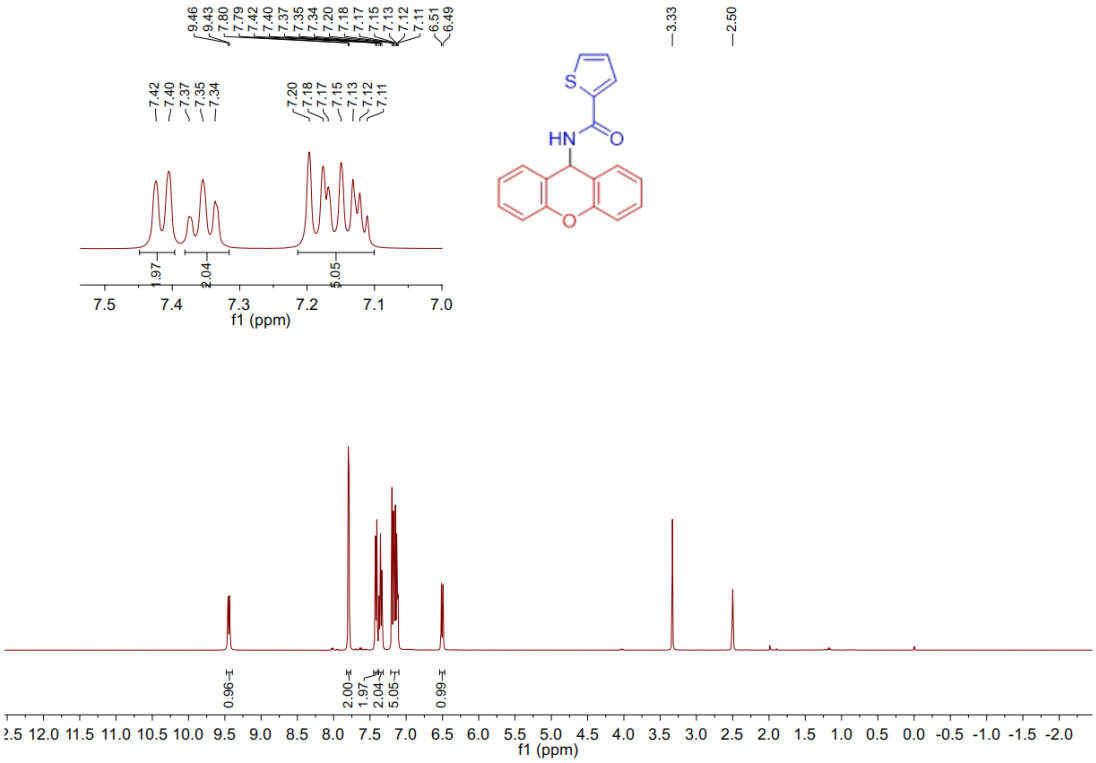

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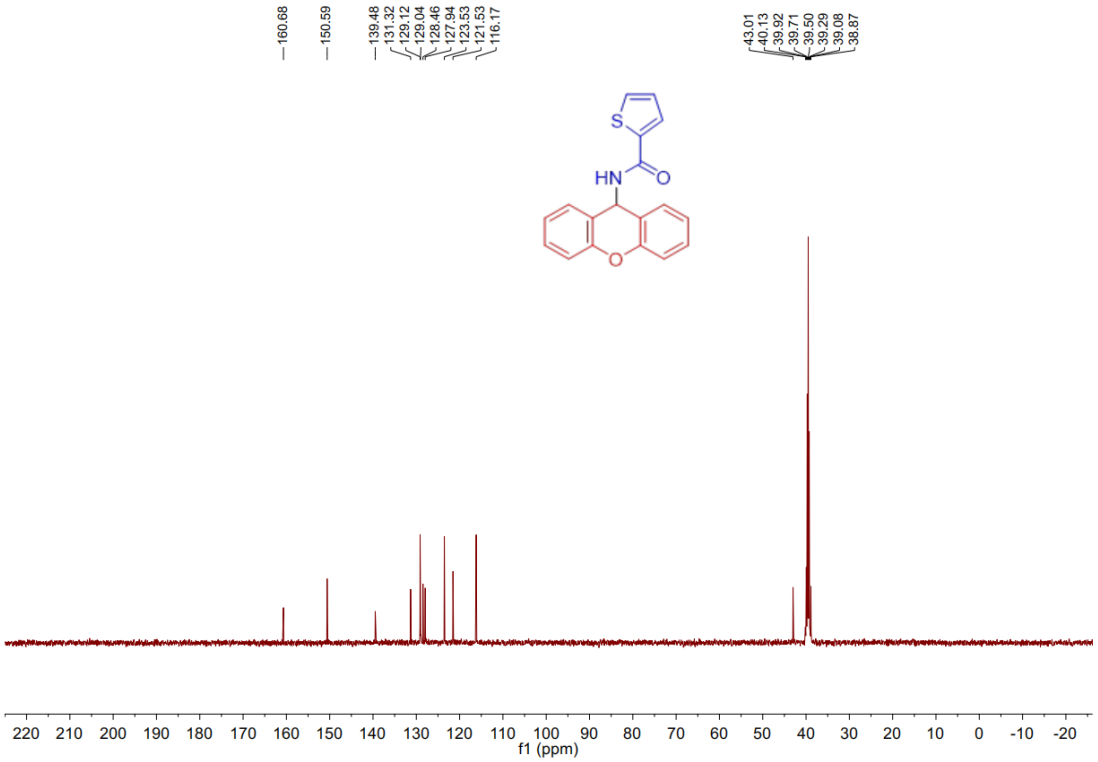

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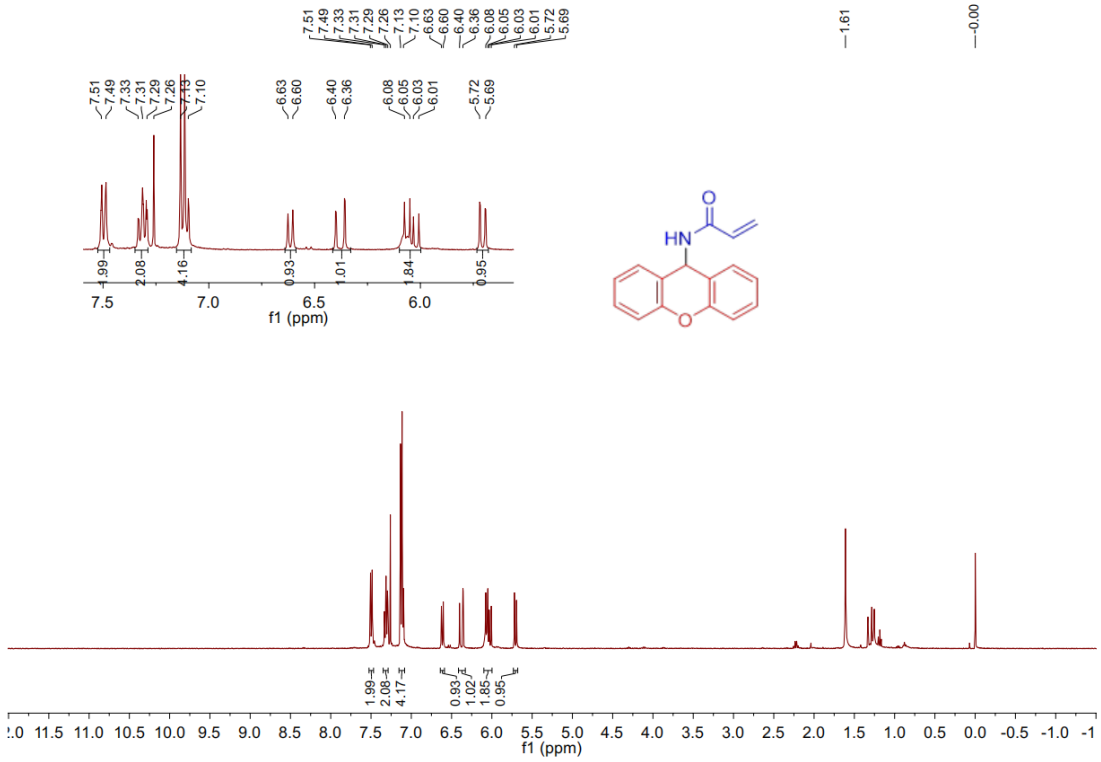

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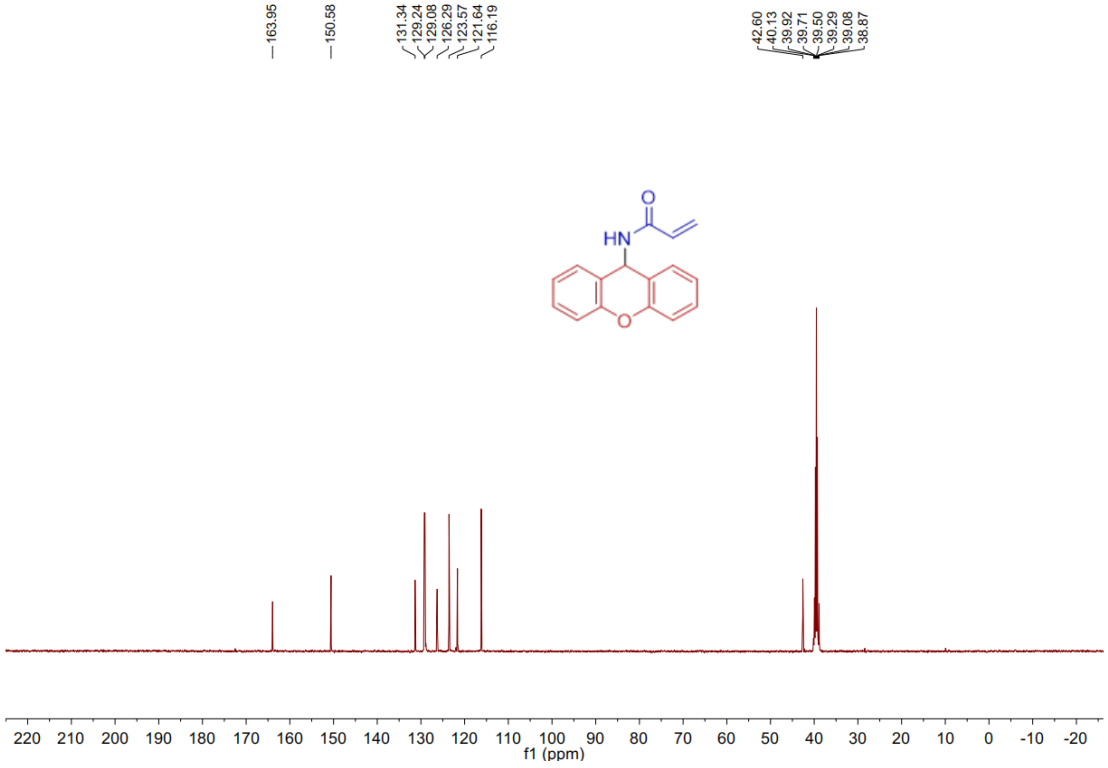

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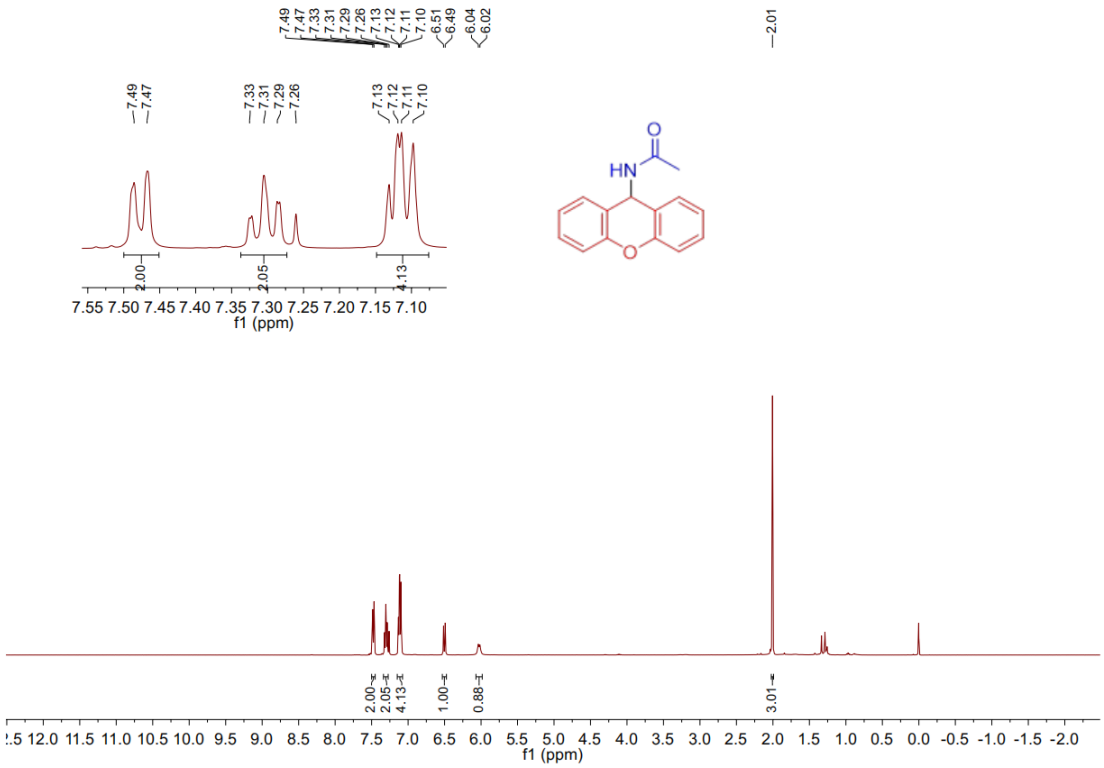

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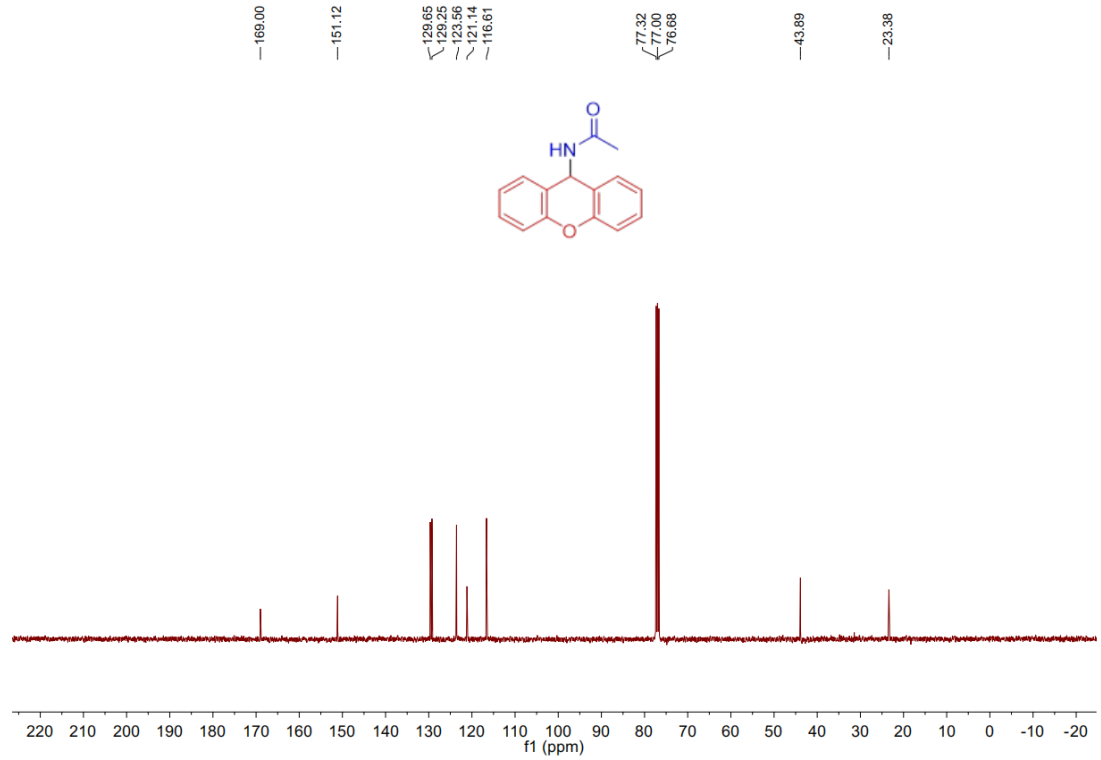

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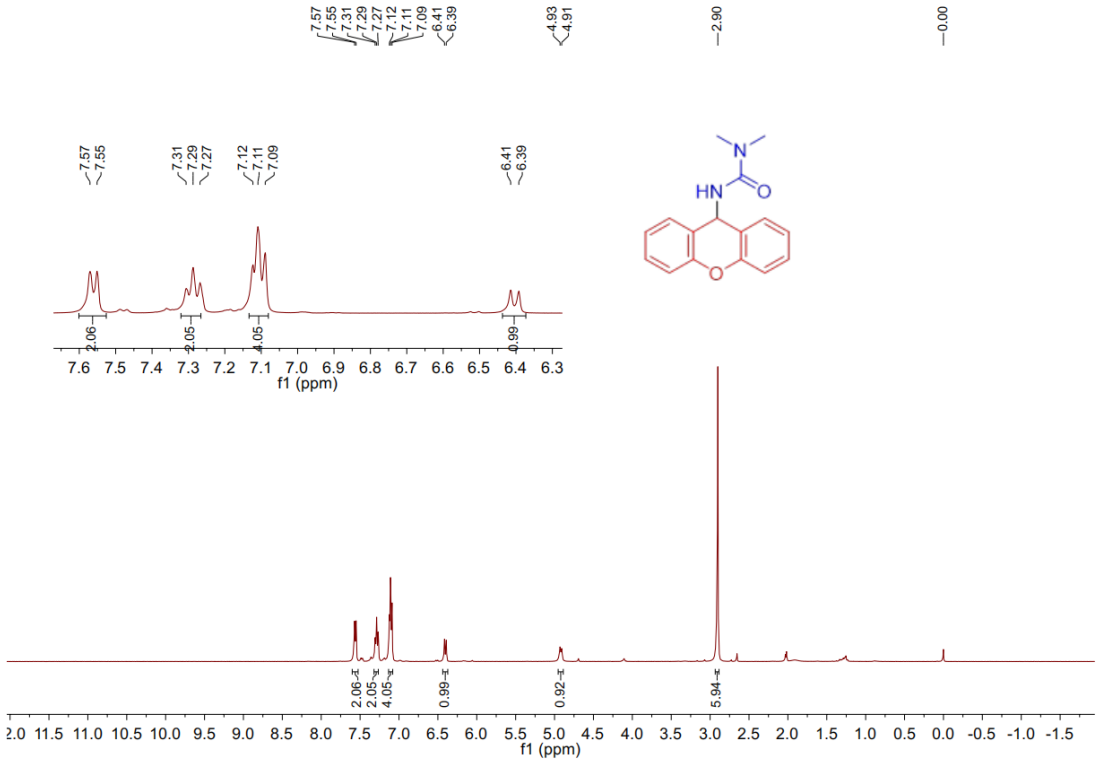

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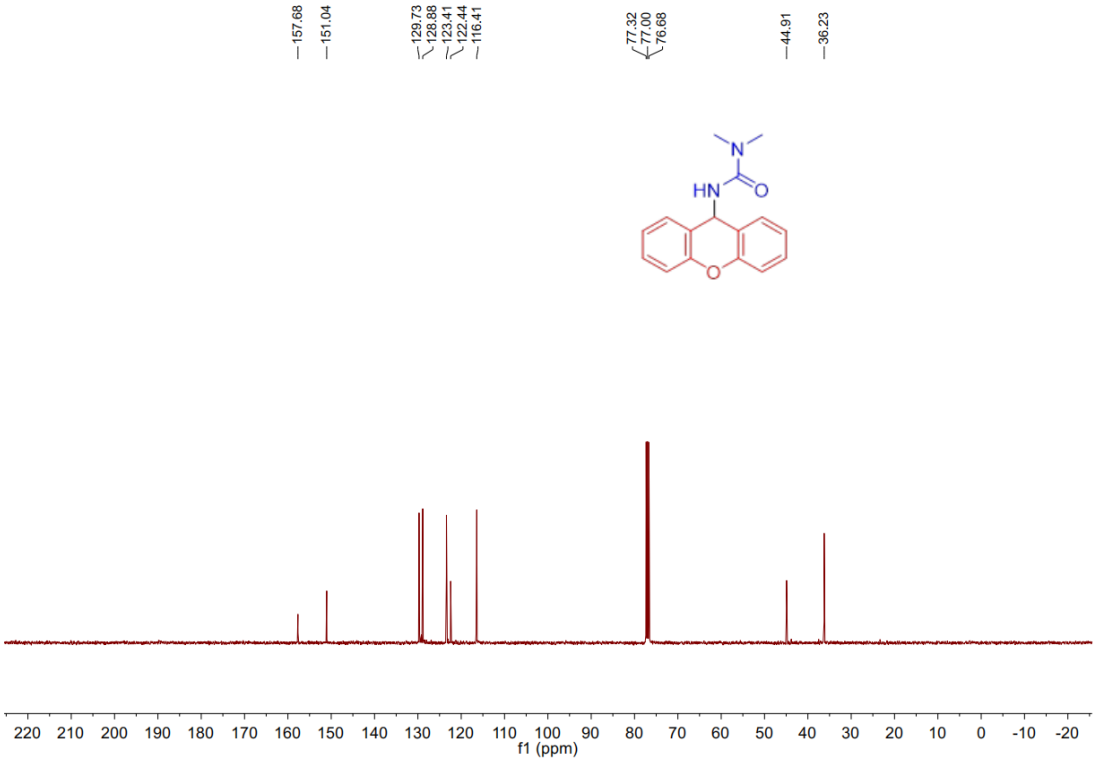
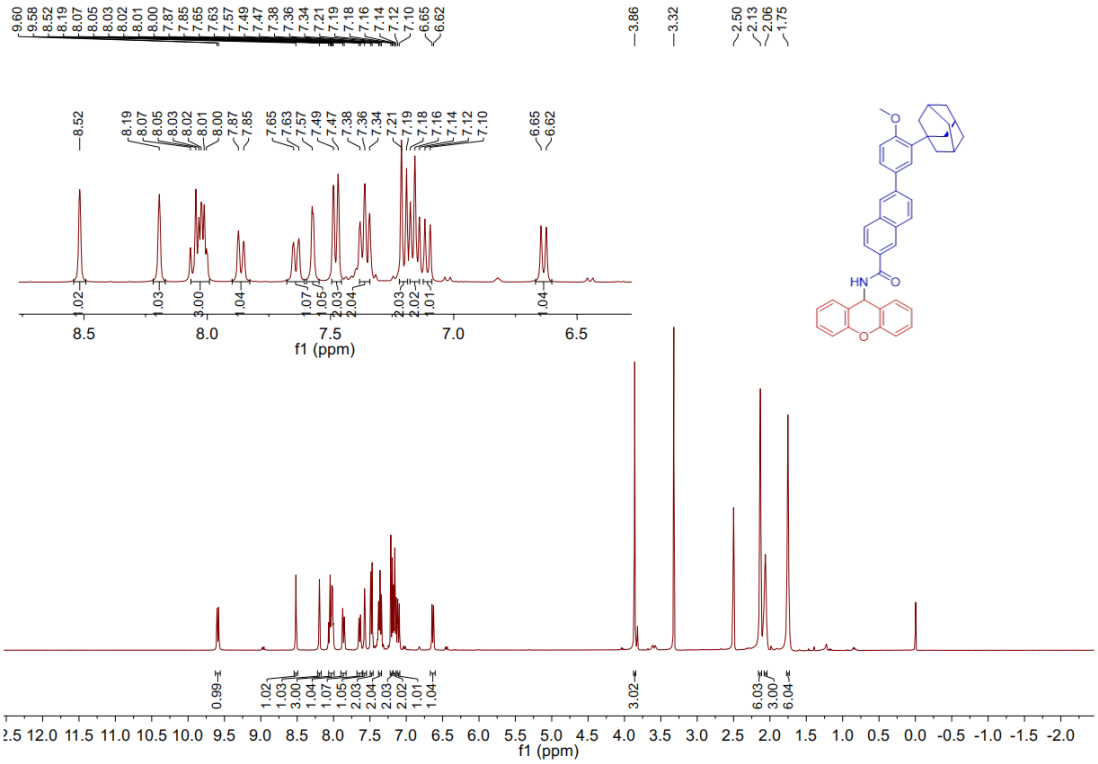
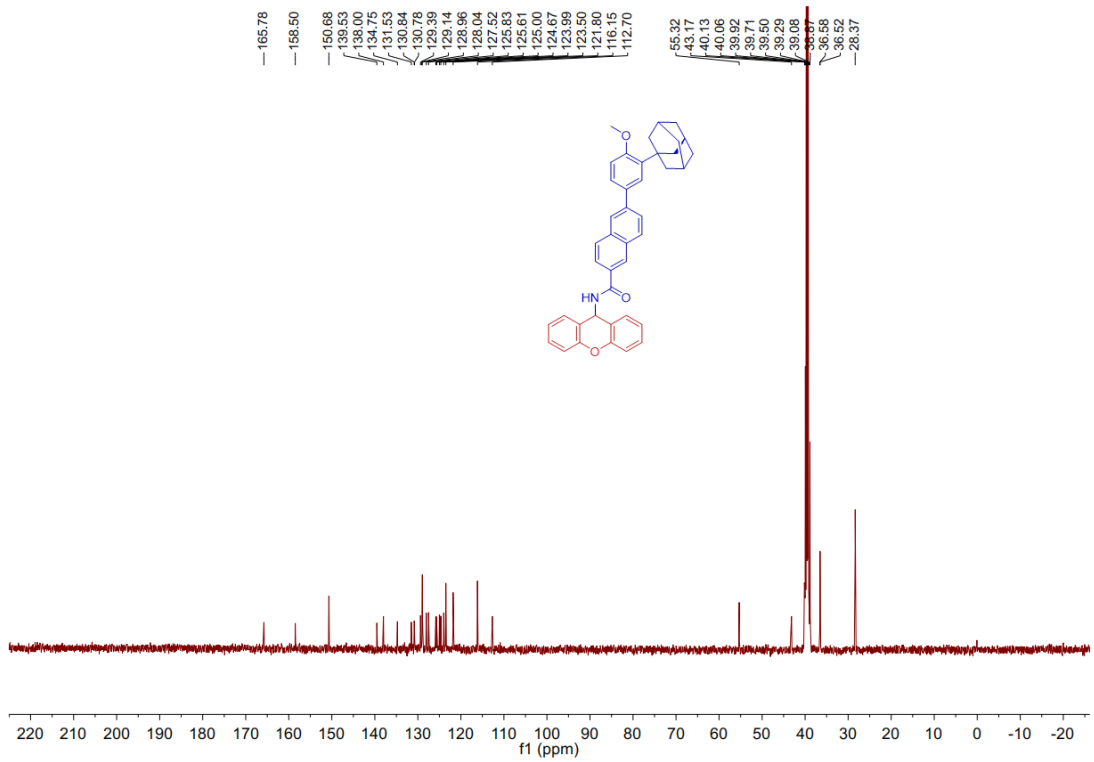


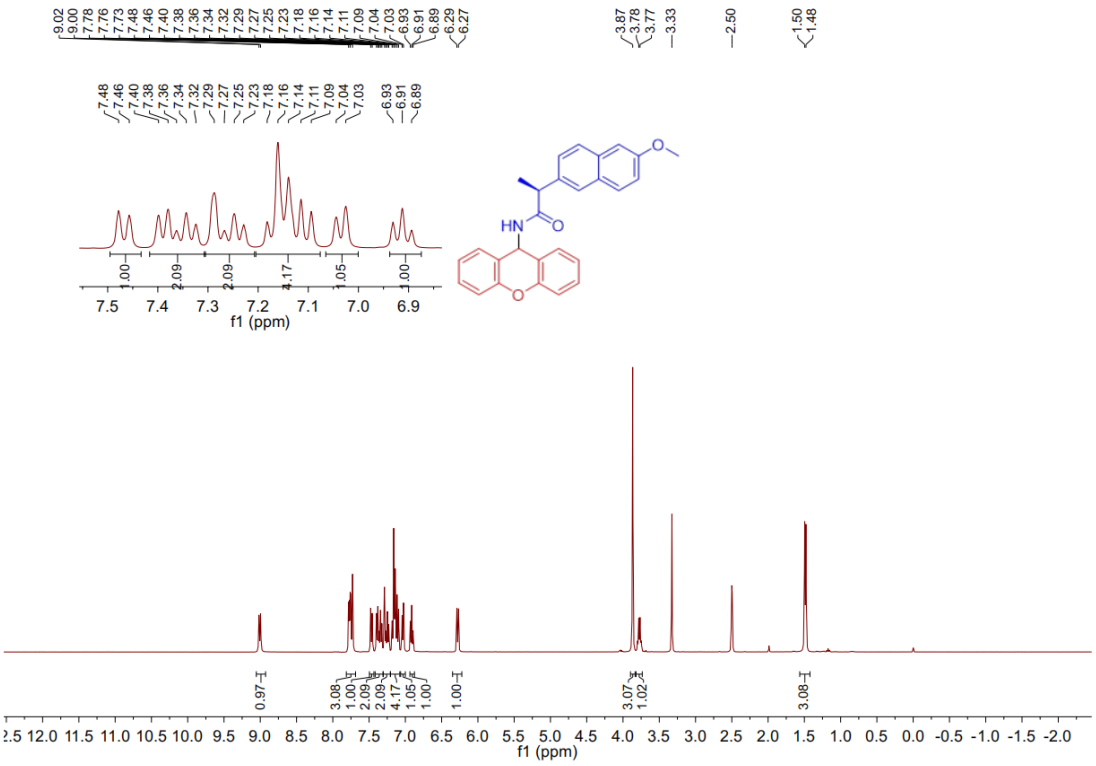
3az ^{1}H NMR



3az ^{13}C NMR



3ba ^{1}H NMR



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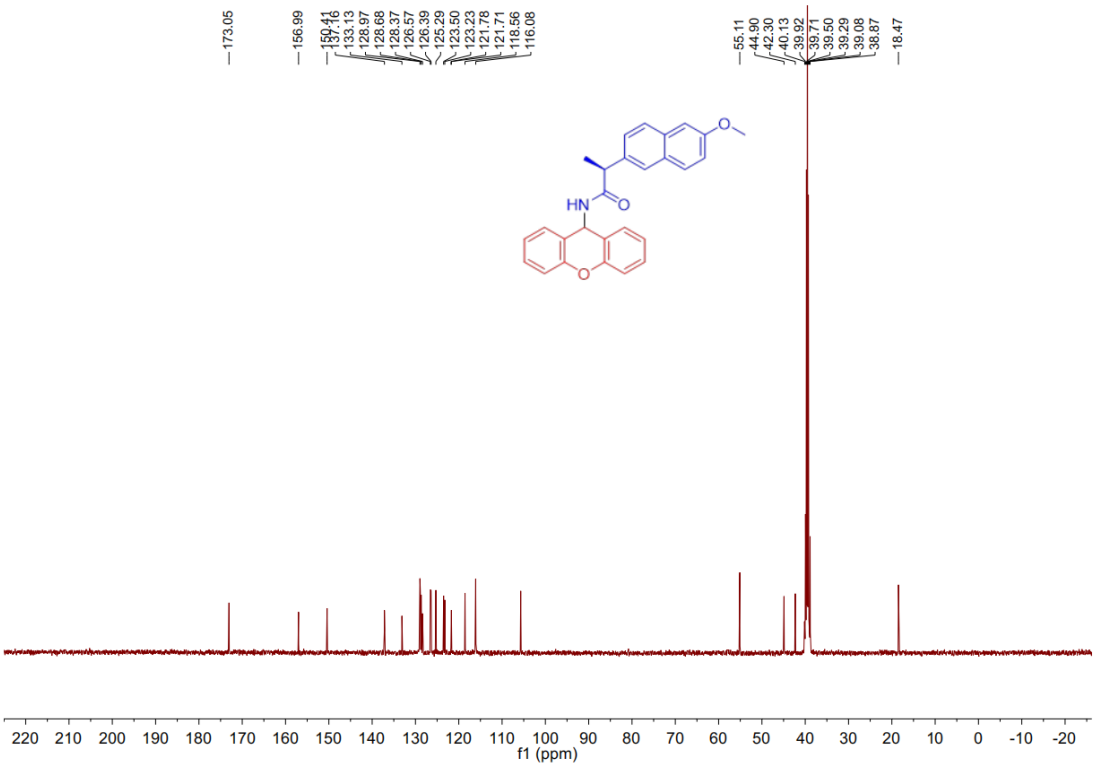

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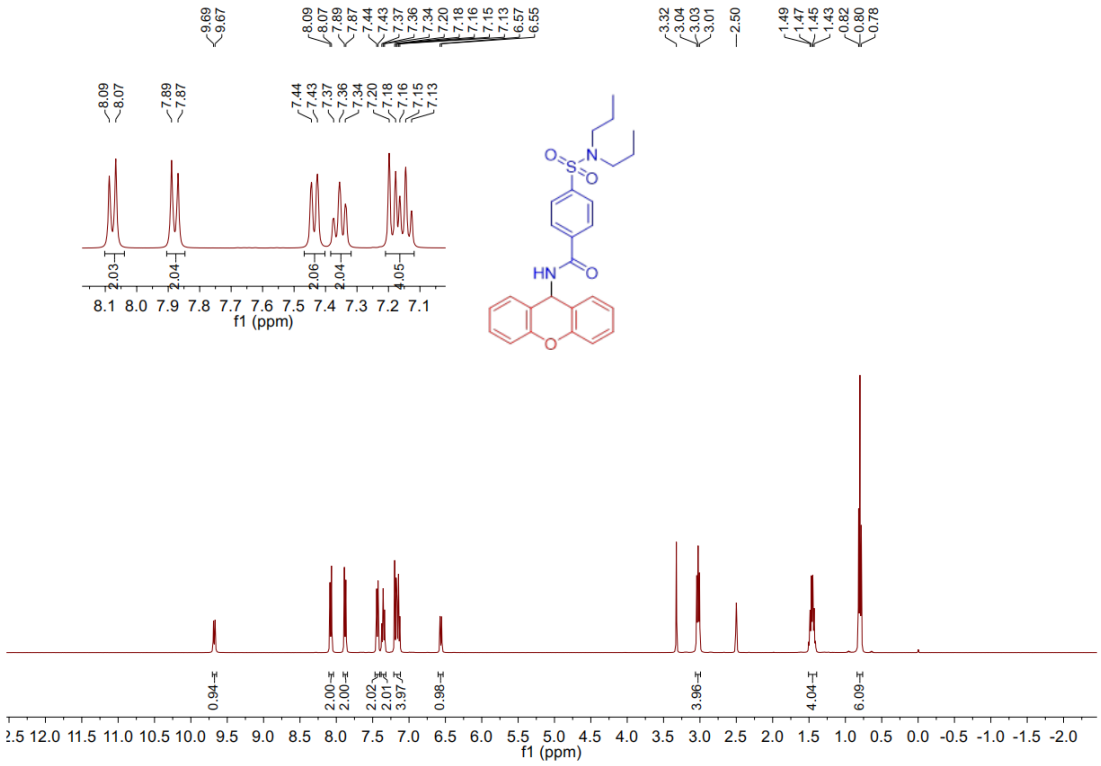

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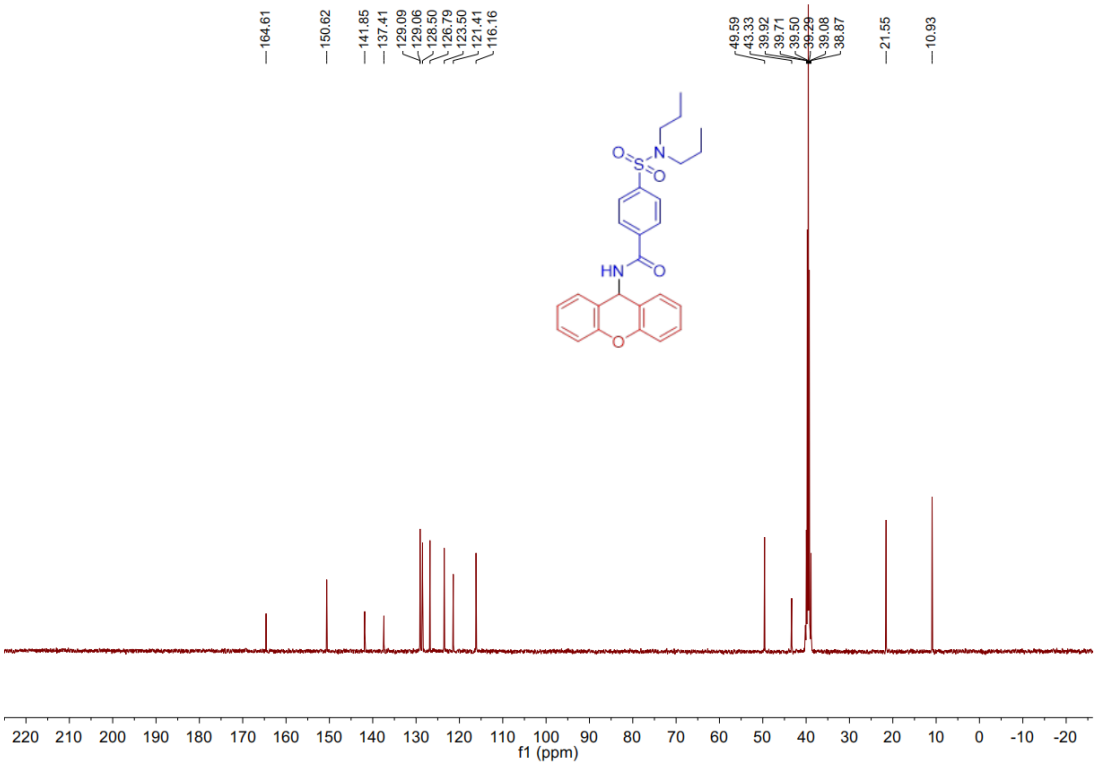

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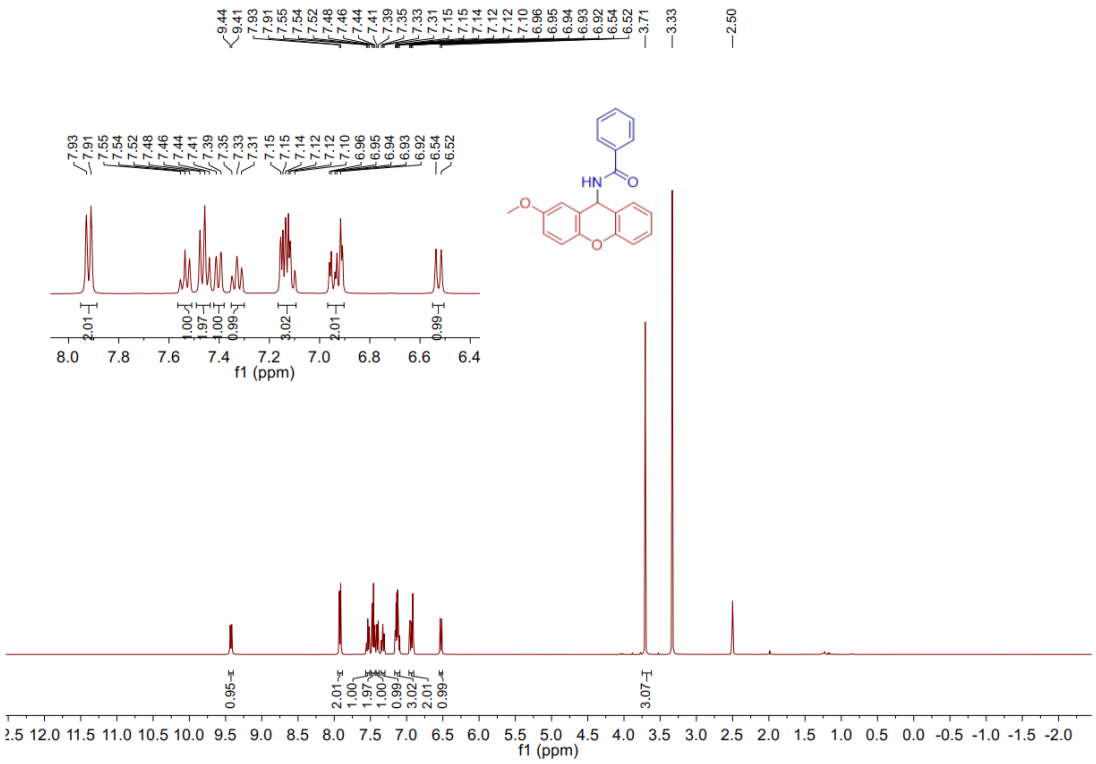

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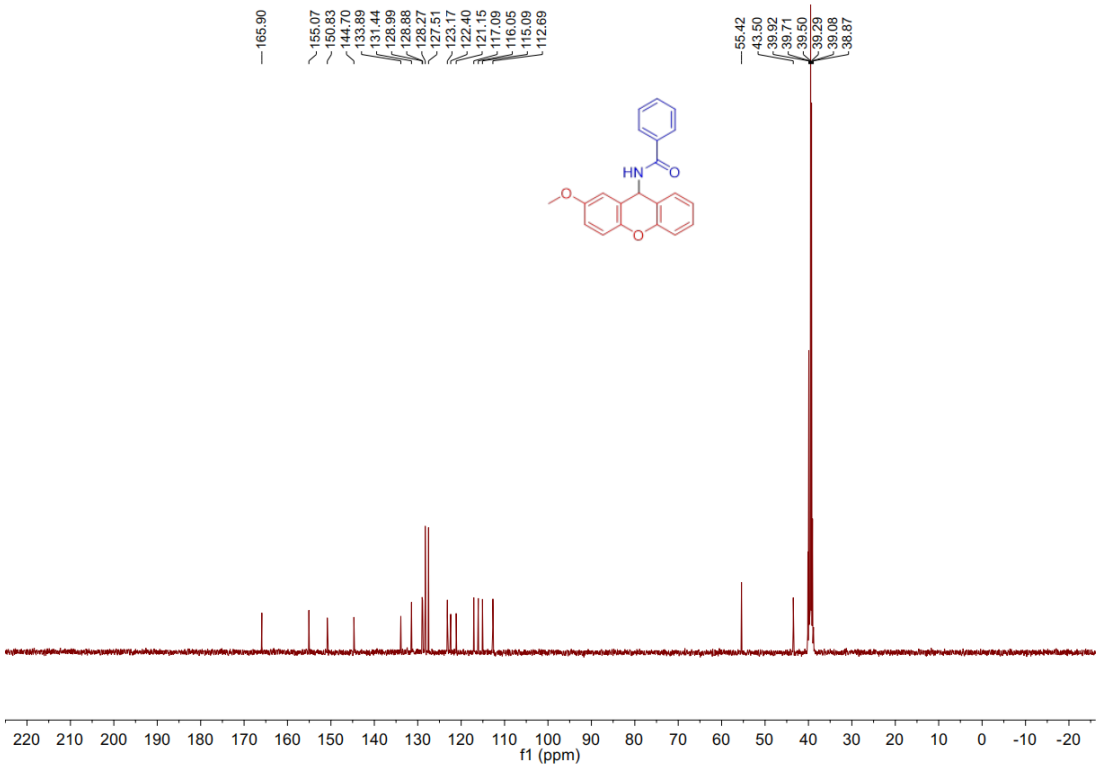

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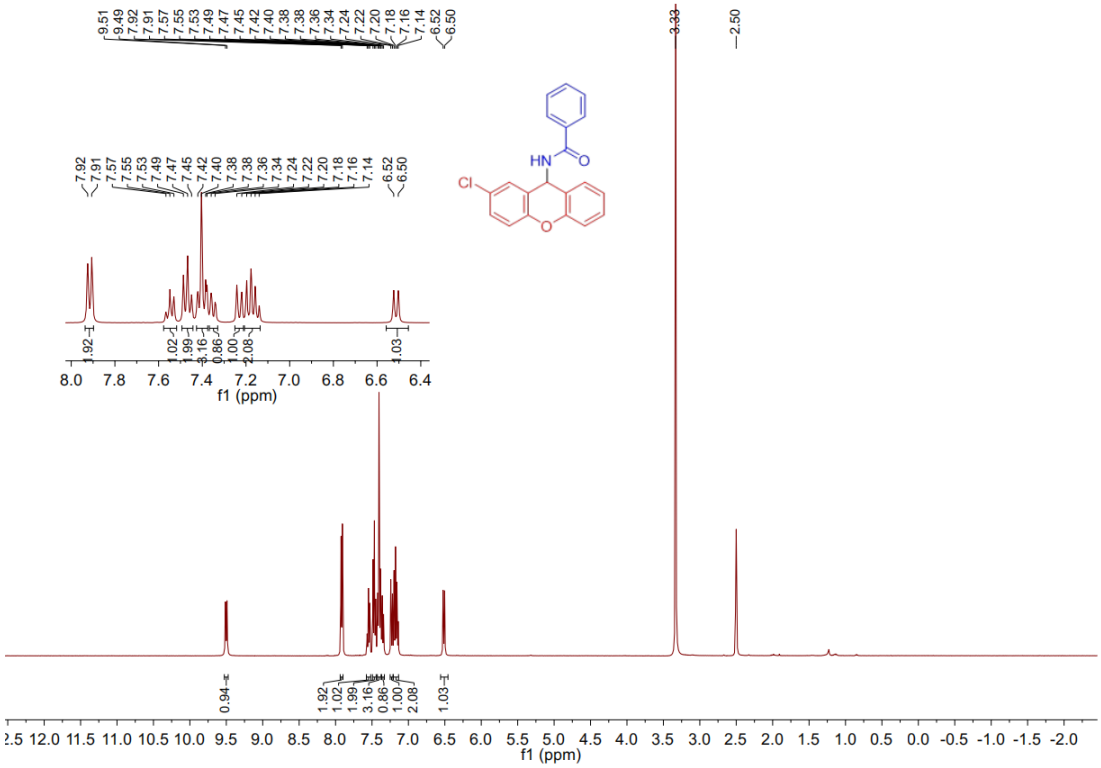

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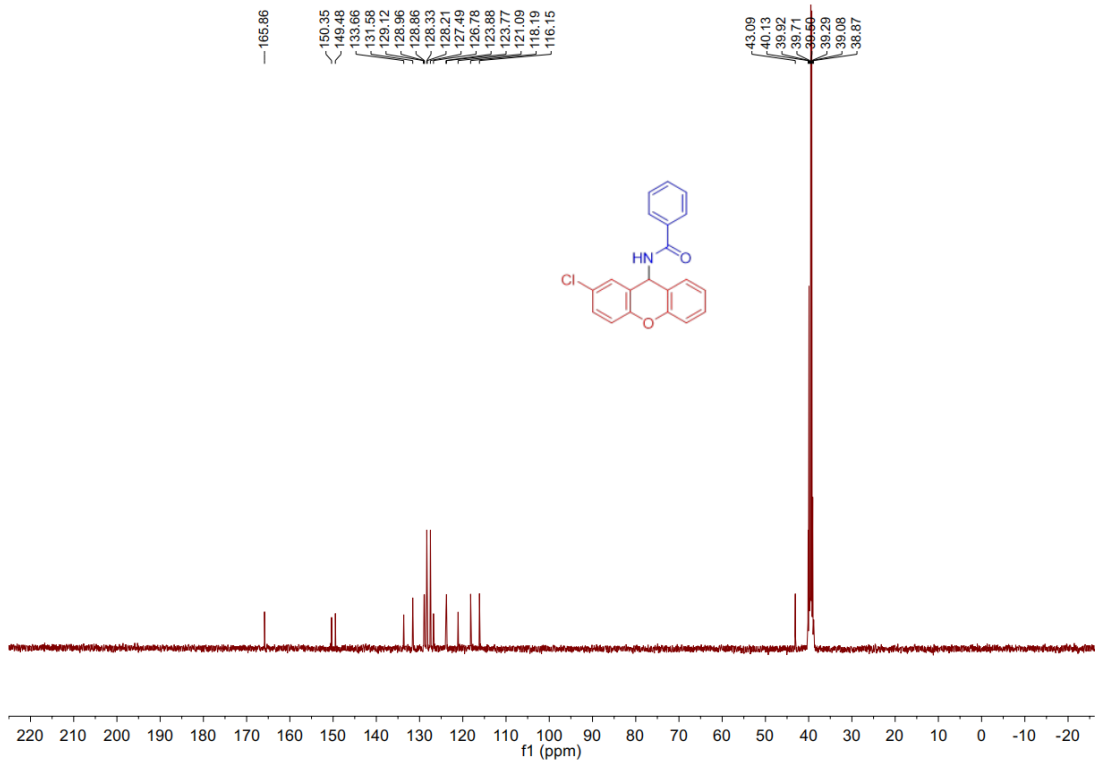

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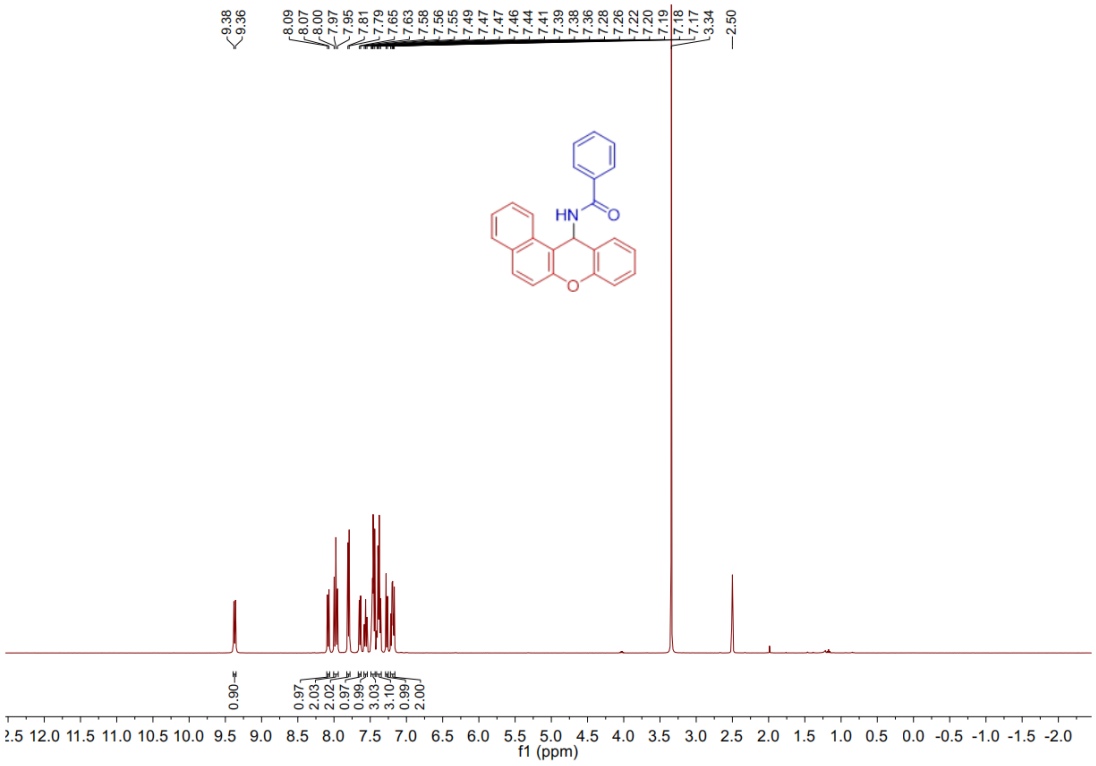

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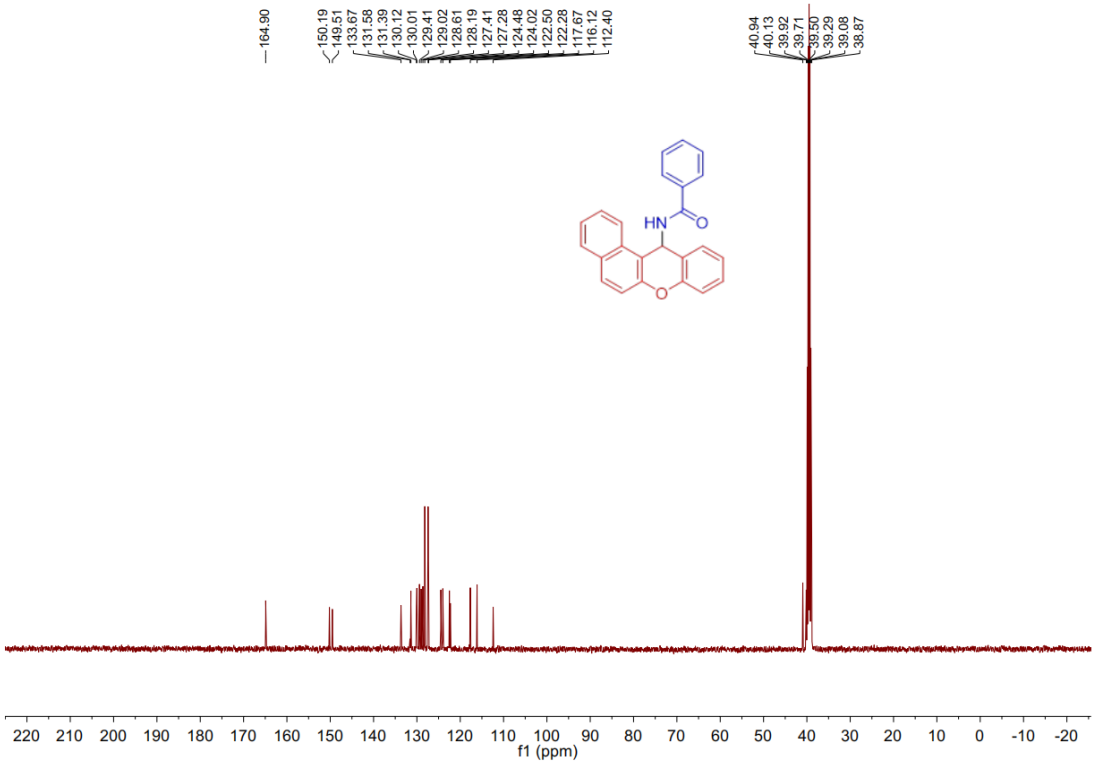

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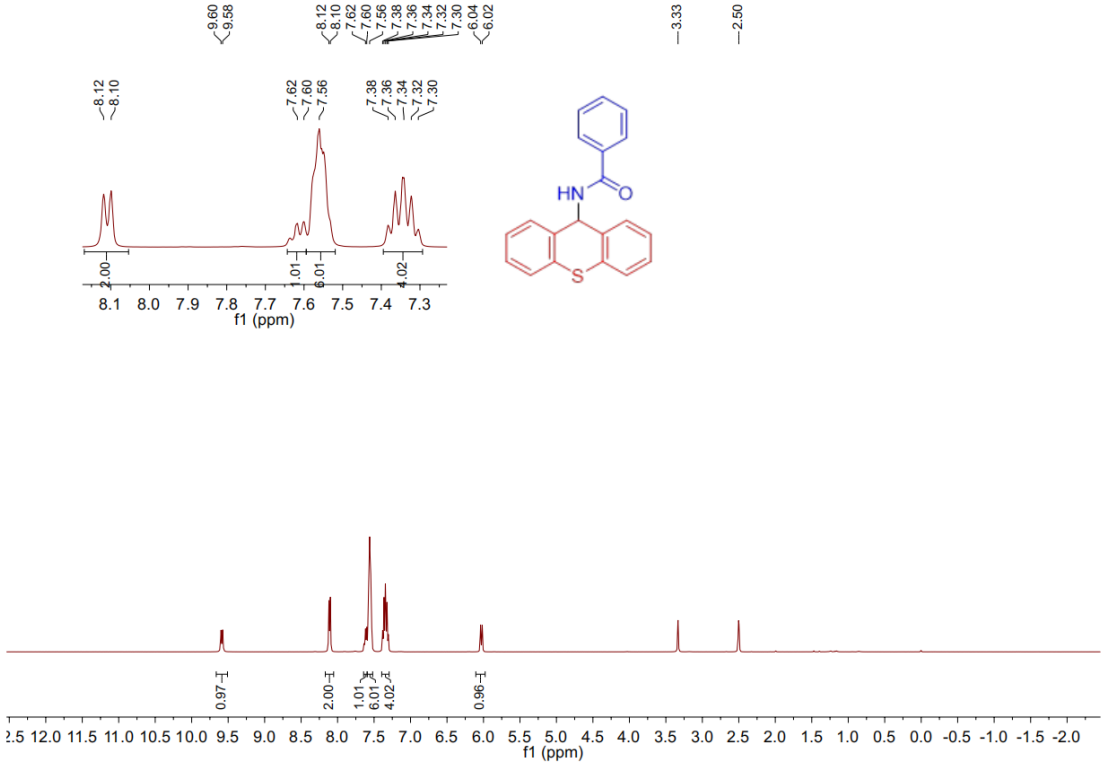

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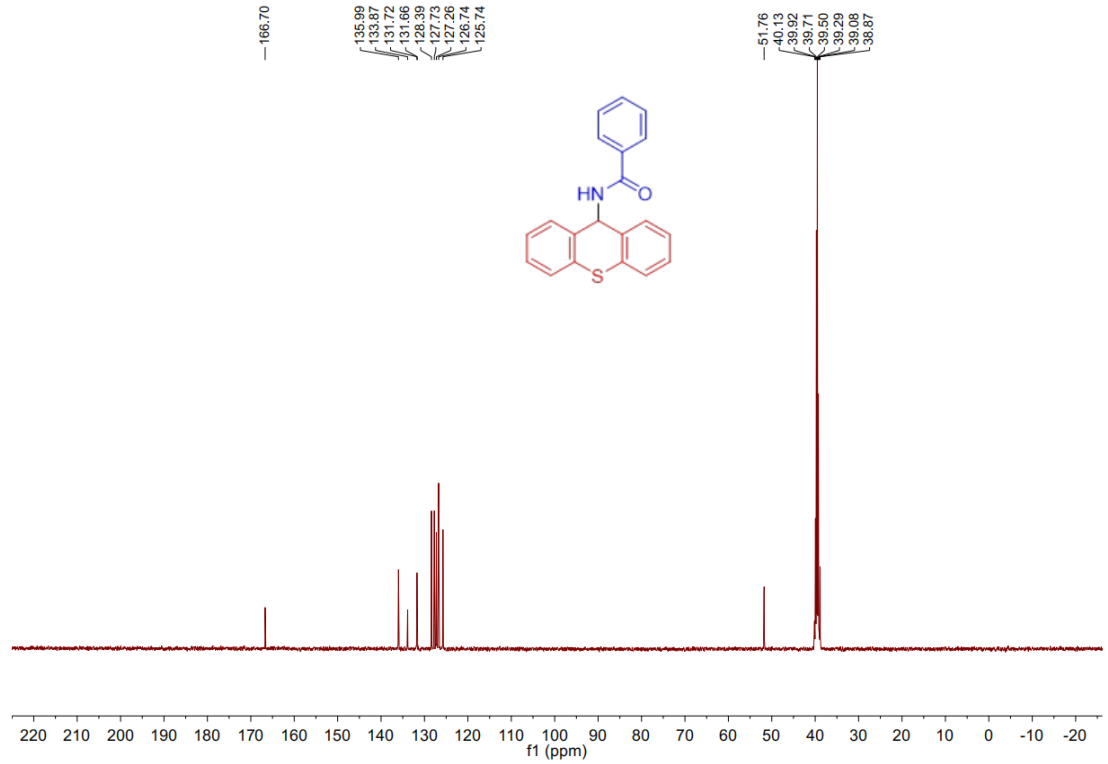

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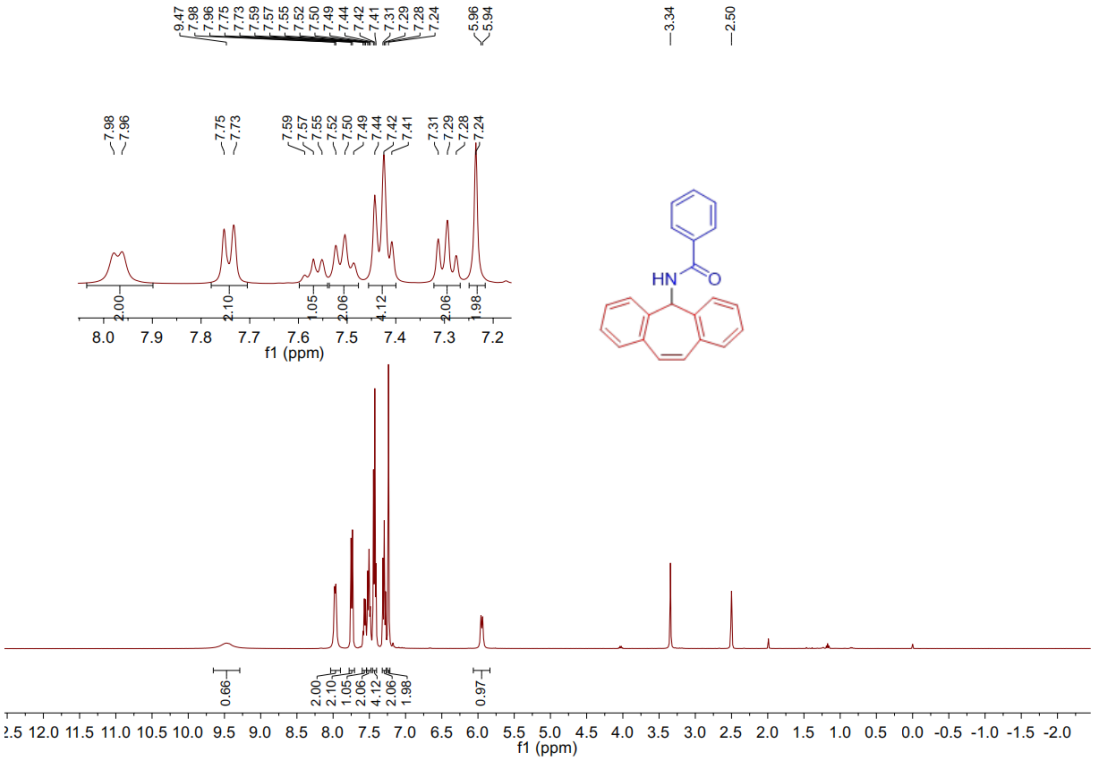

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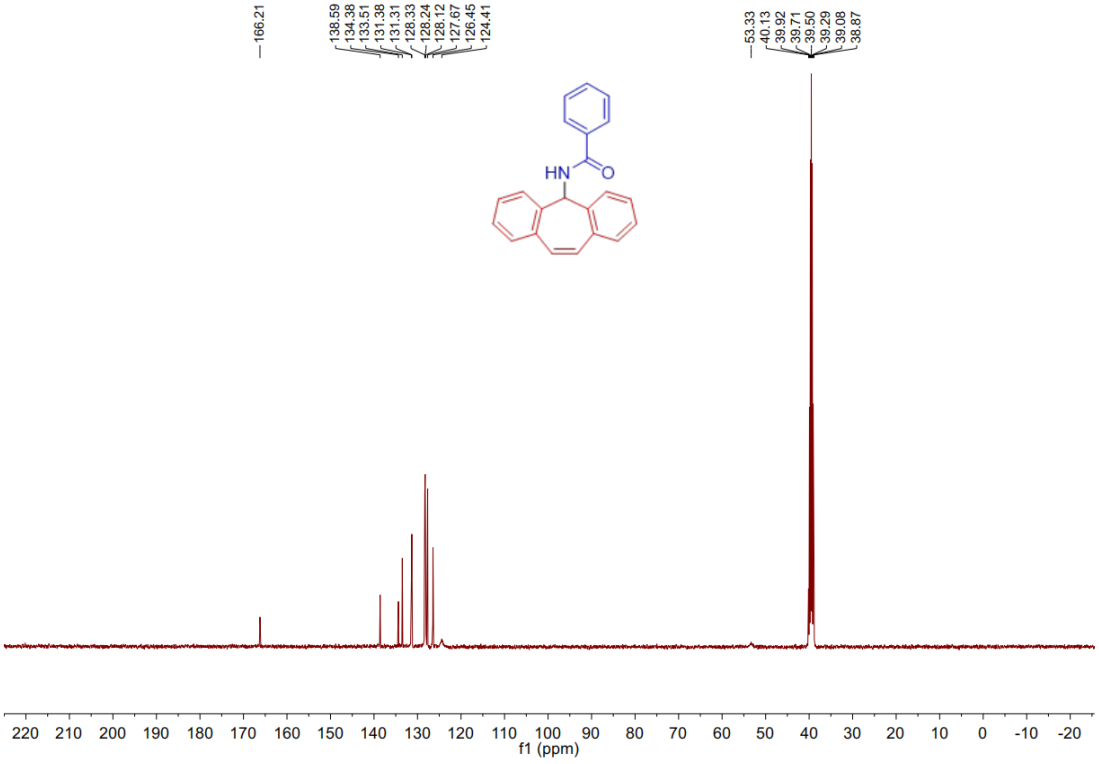

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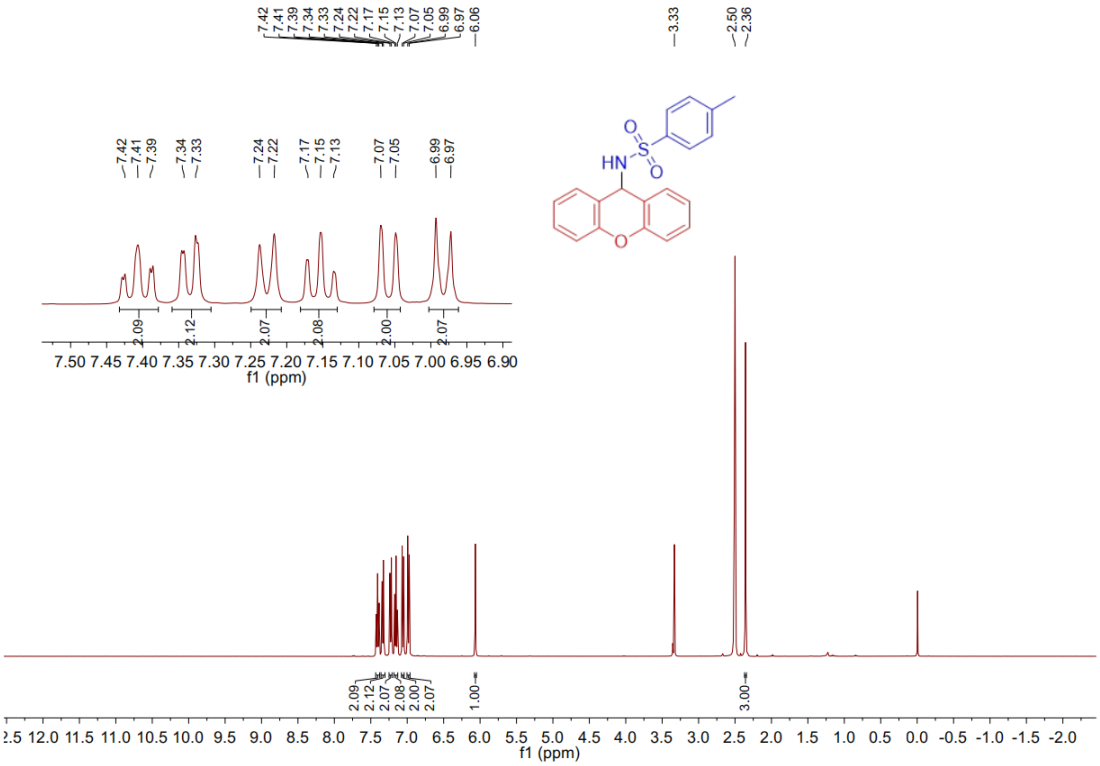
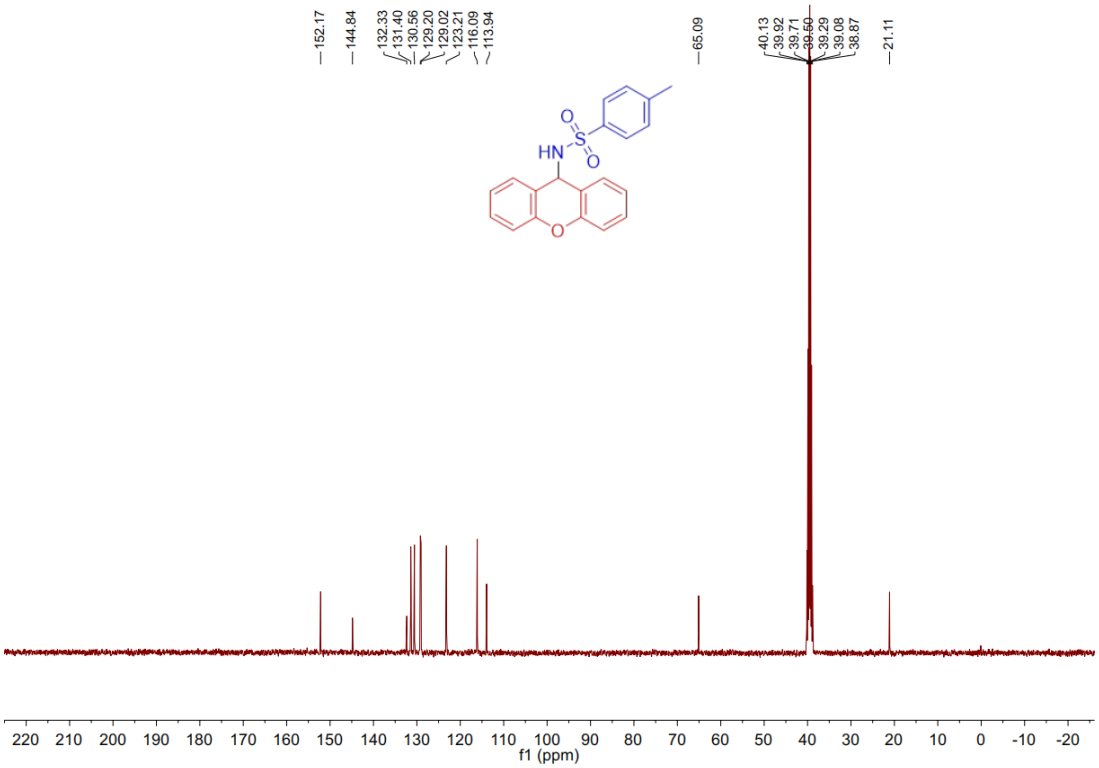
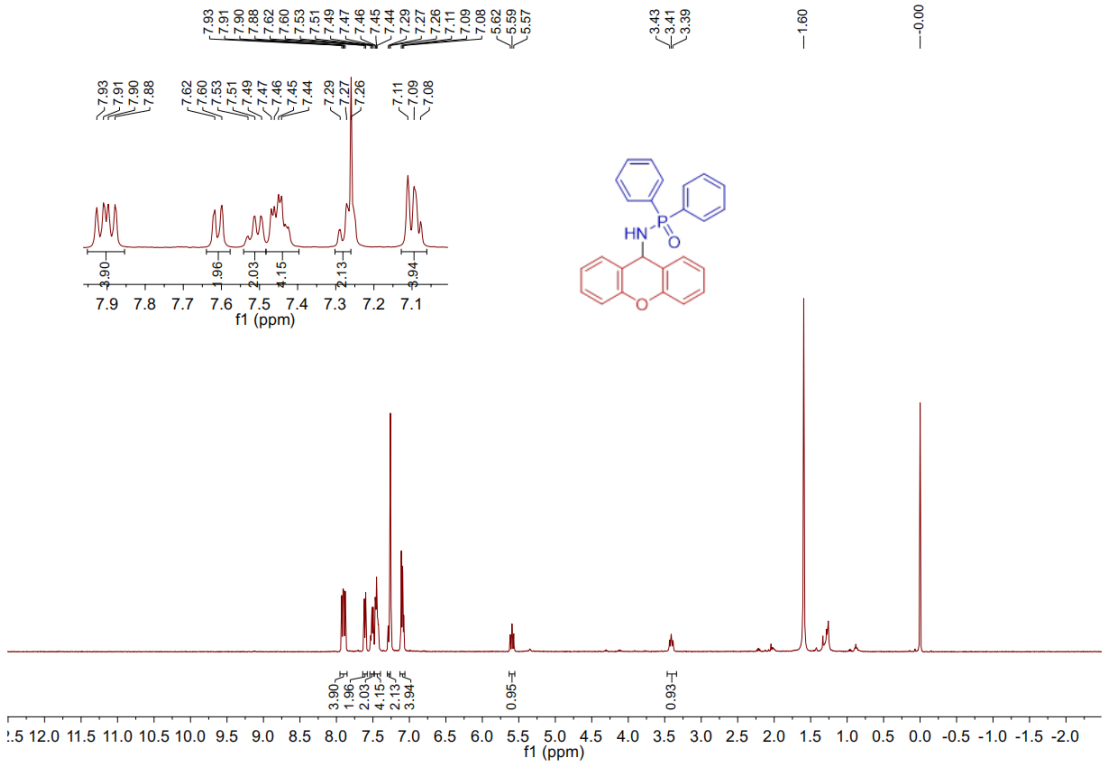


3bh ^{13}C NMR



3bi ^{1}H NMR



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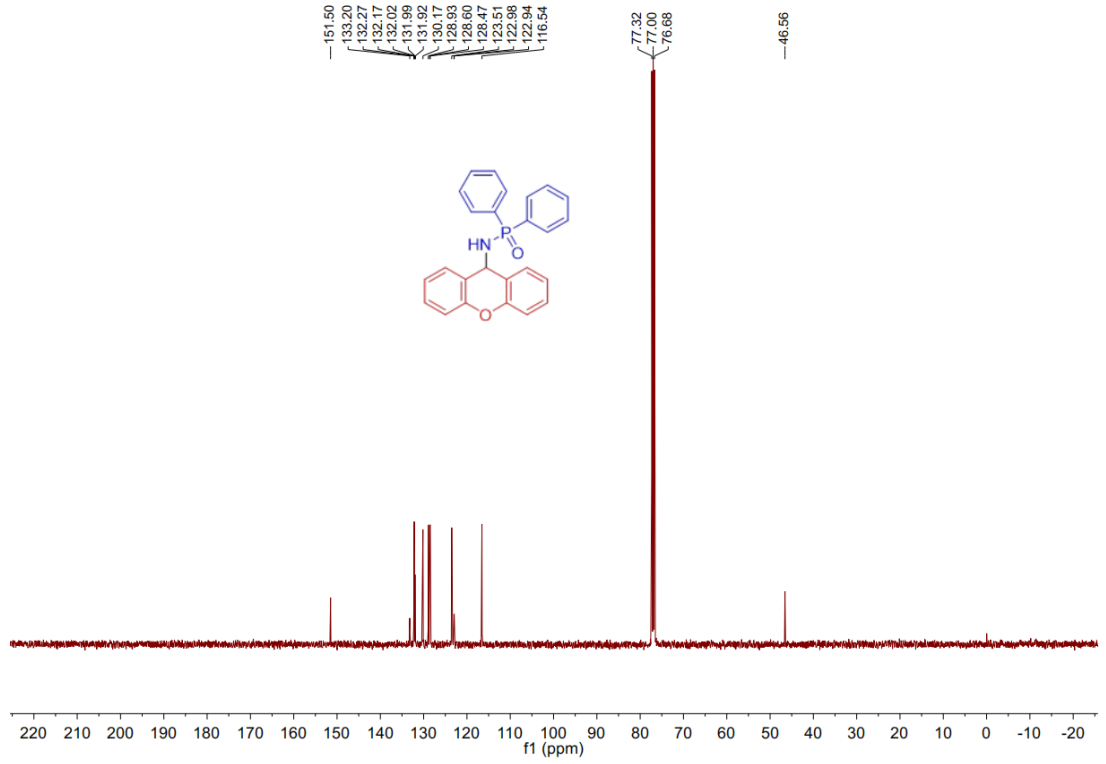

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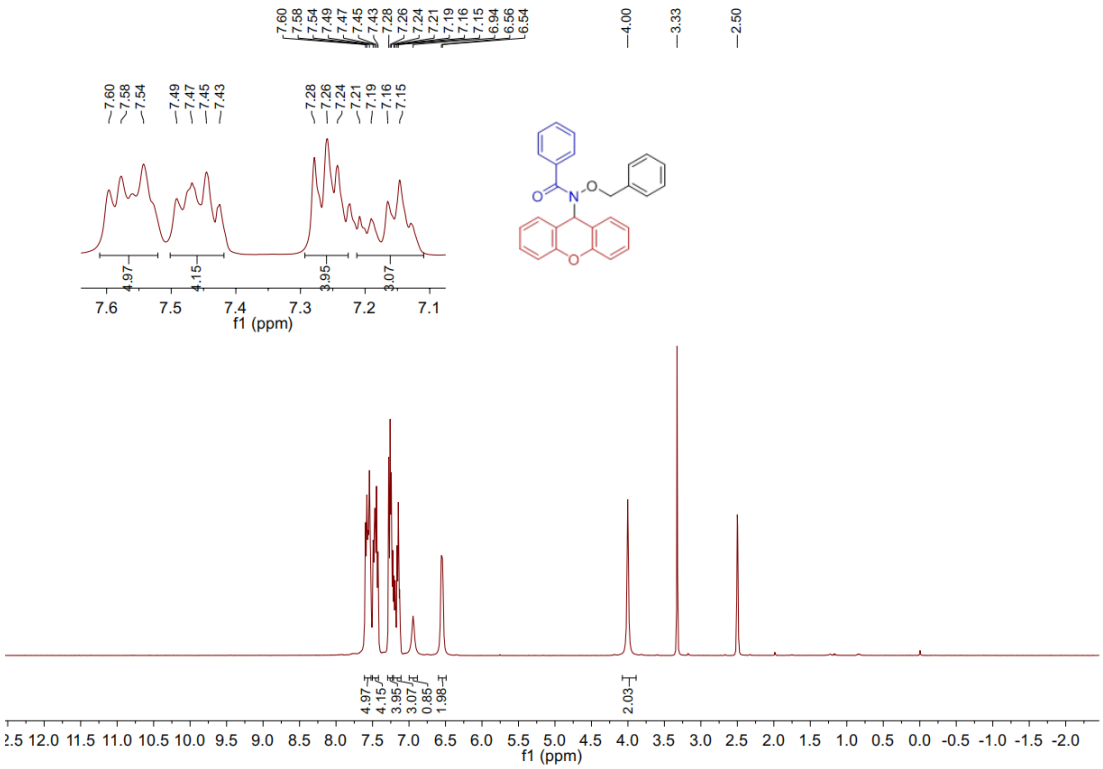

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