Supporting Information

Straightforward Access to Anthrone Functionalized Benzylic Amines via Organocatalytic 1,2-Addition of Anthrones to Imines at Ambient Temperature

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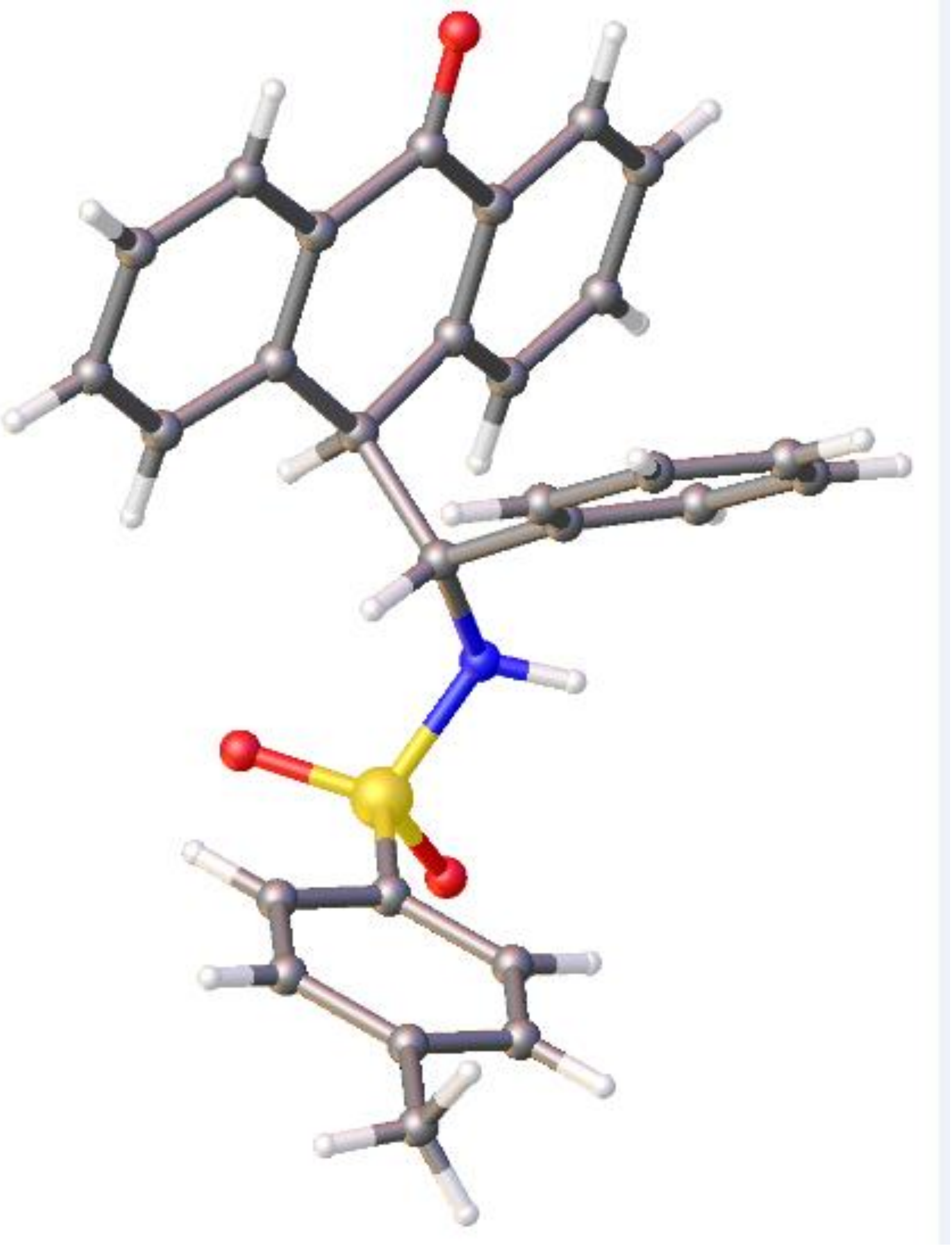
Figure S1. Single crystal X-ray structure of **3a** (ellipsoid contour at 50% probability level):

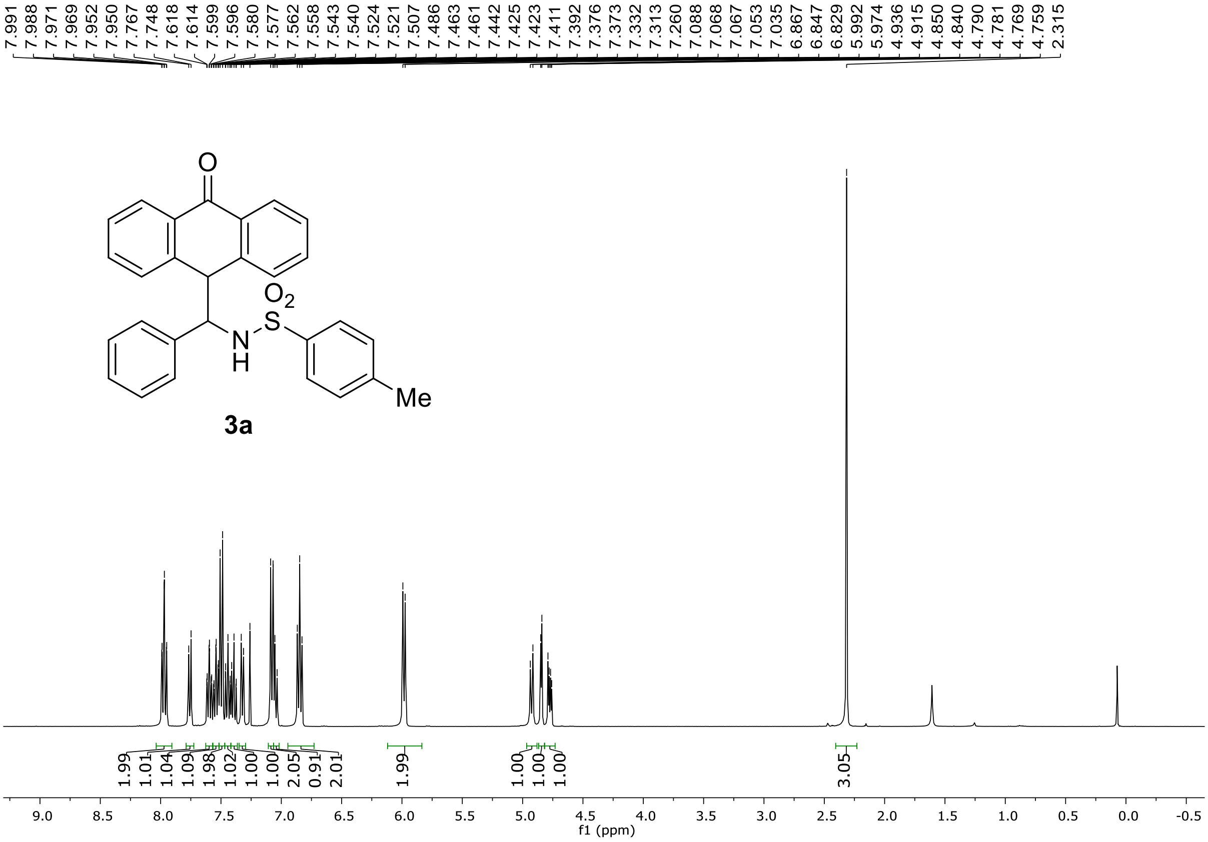


Crystal data and structure refinement for 3a

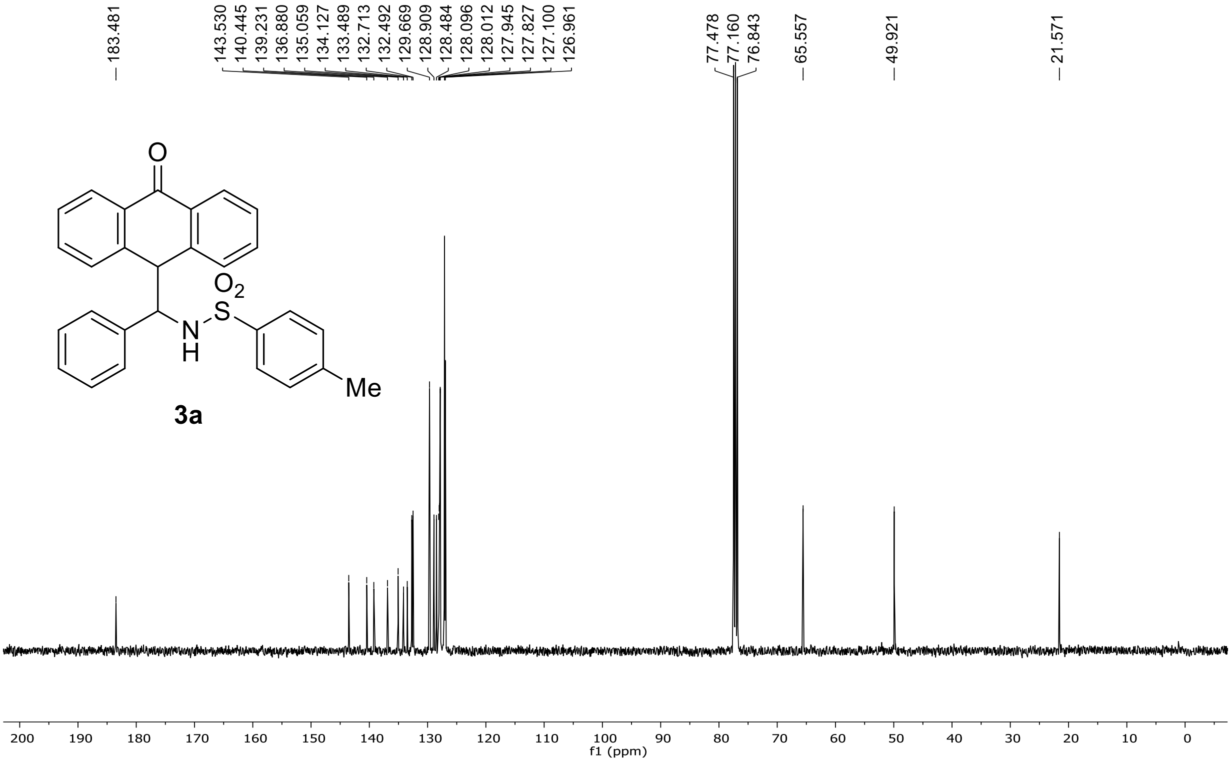
Empirical formula	$C_{28}H_{23}NO_3S$
Formula weight	453.53
Temperature/K	298.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.5969(8)
b/Å	10.3527(6)
c/Å	30.3432(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4585.4(5)
Z	8
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	0.172
F(000)	1904.0
Crystal size/mm^3	0.71 × 0.56 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.872 to 55.064
Index ranges	$-18 \leq h \leq 18$, $-13 \leq k \leq 13$, $-38 \leq l \leq 39$
Reflections collected	70506
Independent reflections	5268 [R_{int} = 0.0385, R_{sigma} = 0.0174]
Data/restraints/parameters	5268/267/302
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0533, wR_2 = 0.1181
Largest diff. peak/hole / e Å^{-3}	0.26/-0.42

^{1}H, ^{13}C{H} and ^{19}F NMR spectra of compounds:

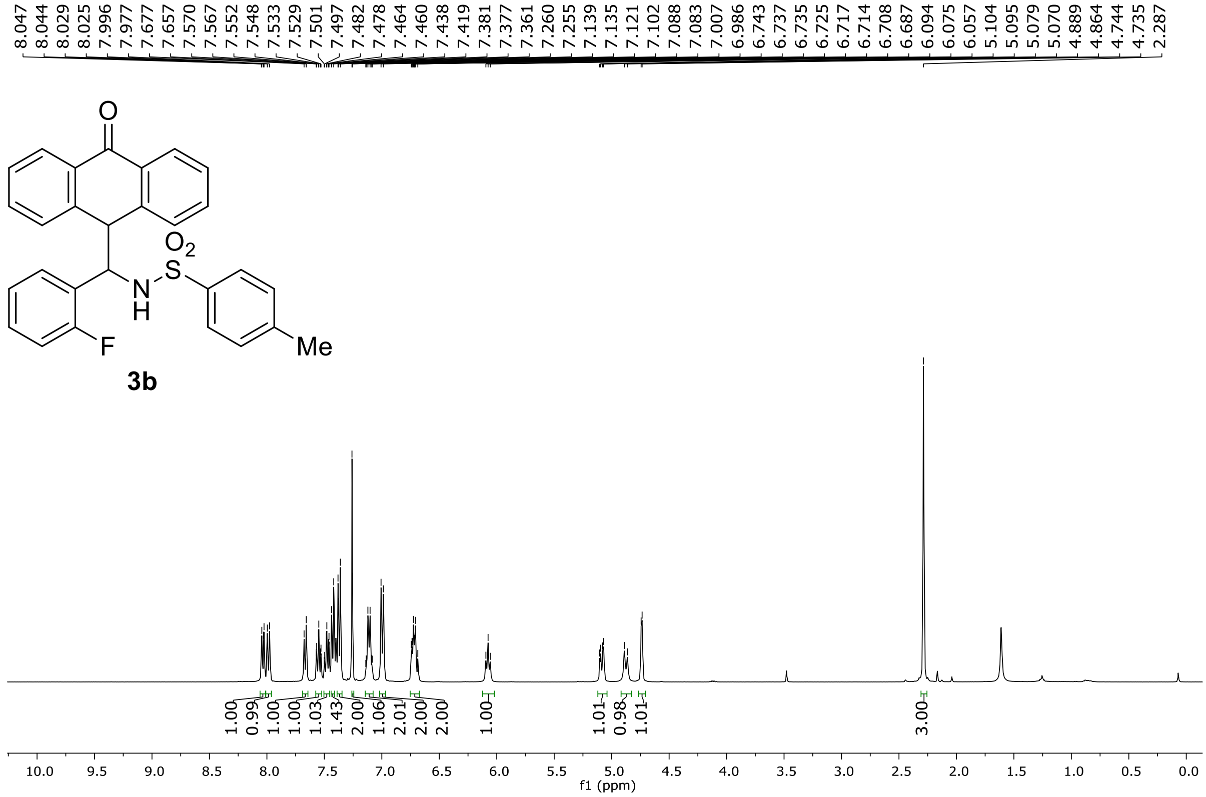
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$):



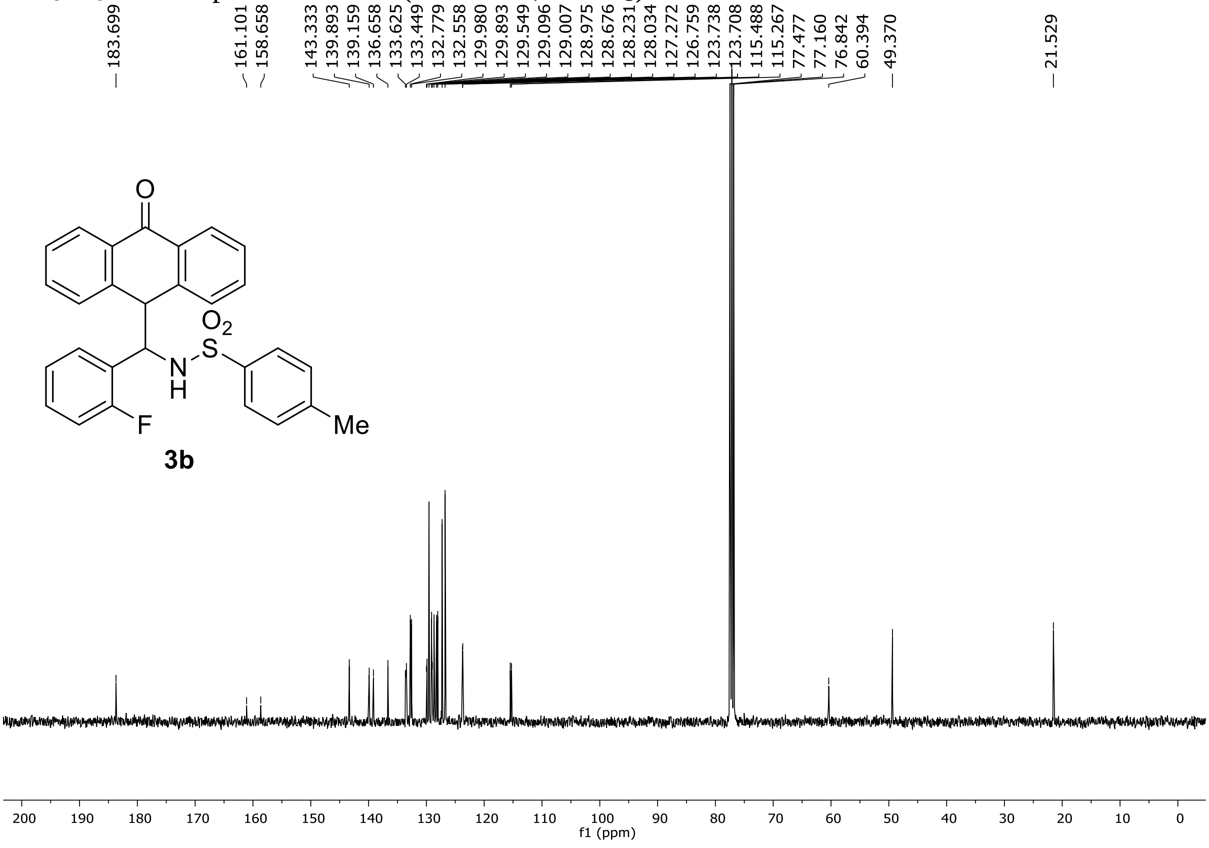
^{13}C{^{1}H} NMR spectrum of **3a** (100 MHz, $CDCl_3$):



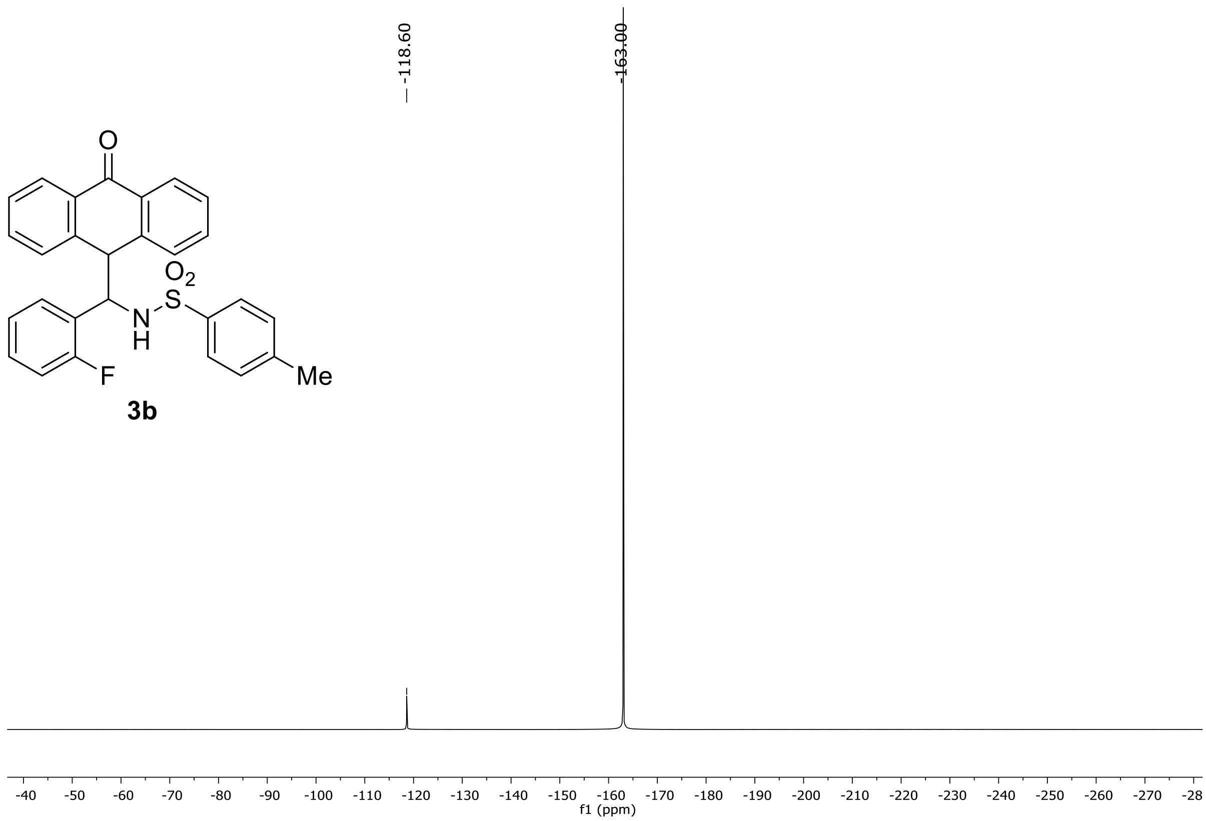
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$):



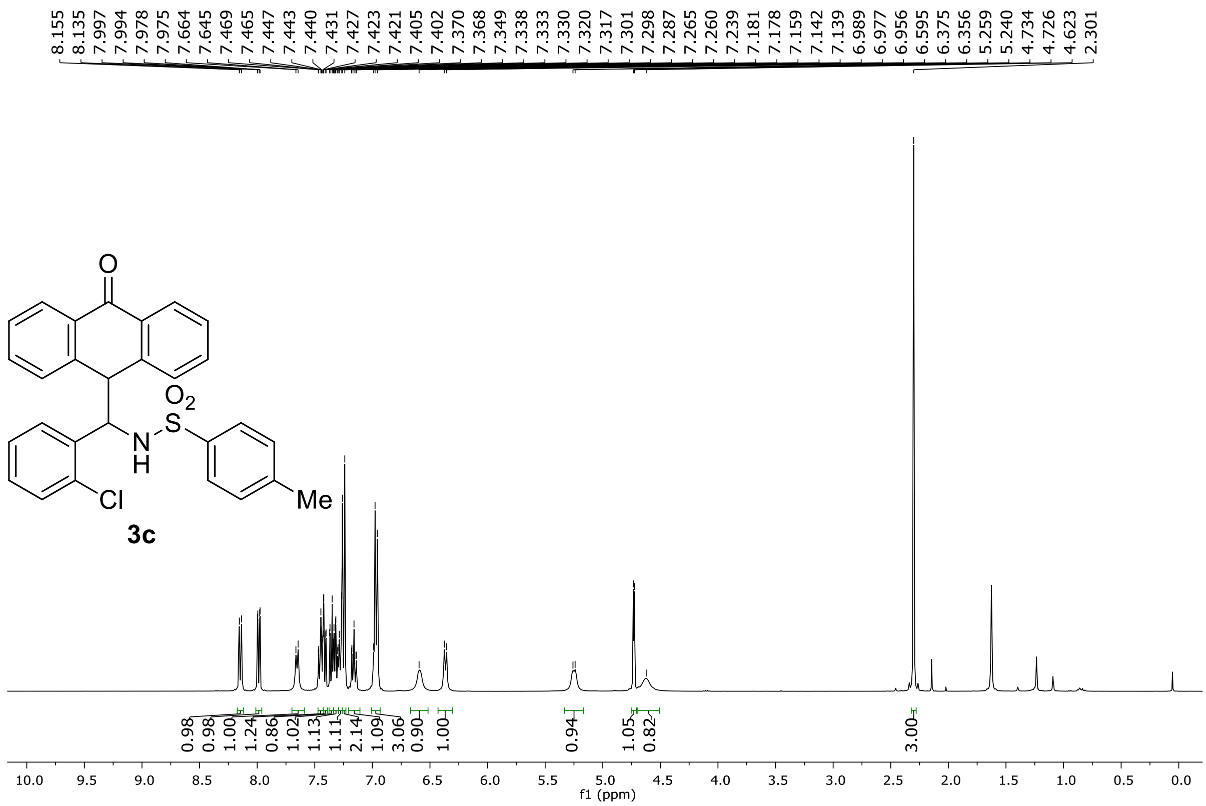
^{13}C{^{1}H} NMR spectrum of **3b** (100 MHz, $CDCl_3$):



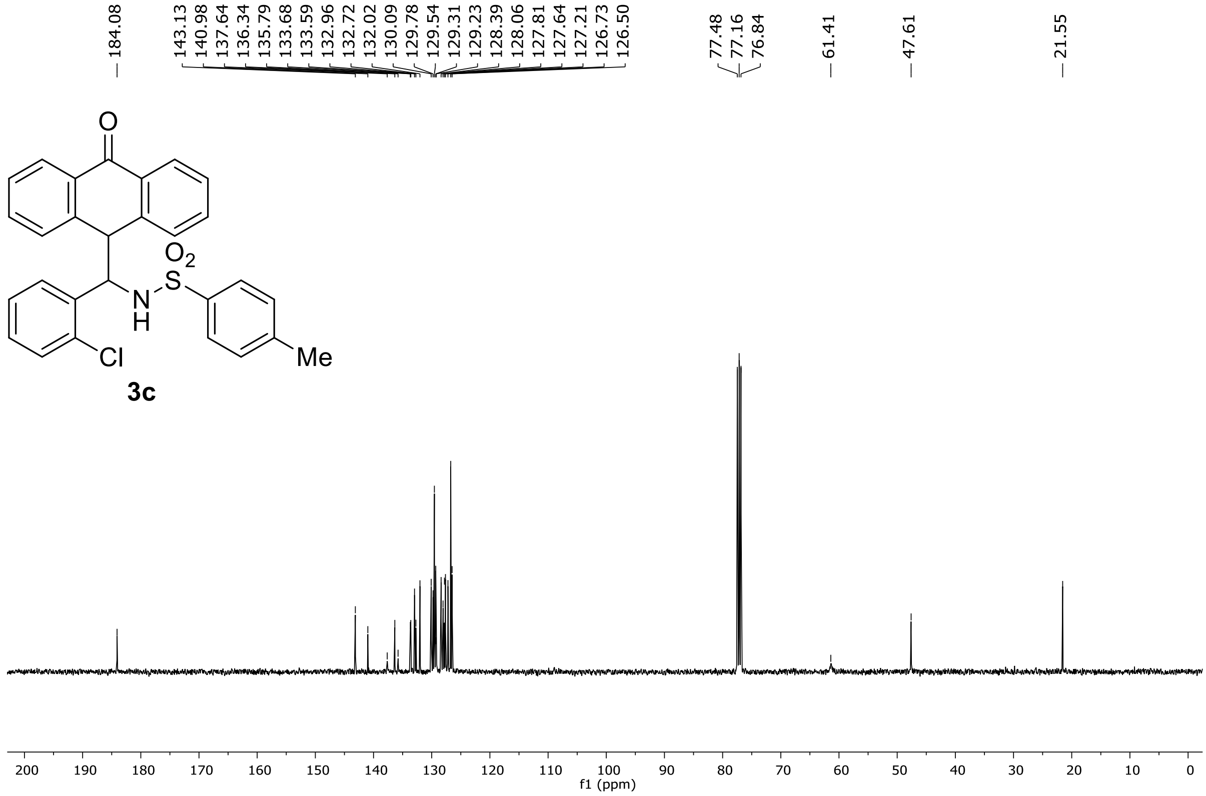
^{19}F NMR spectrum of **3b** (376 MHz, $CDCl_3$):



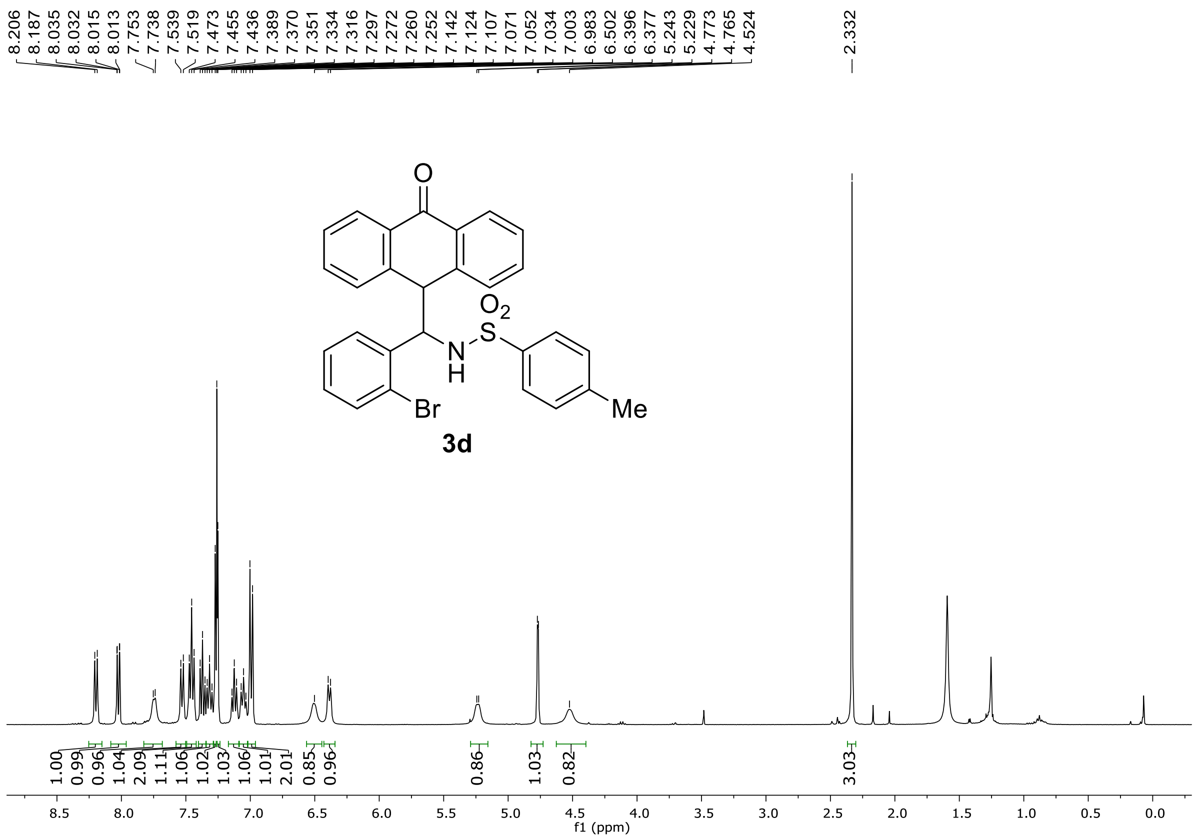
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$):



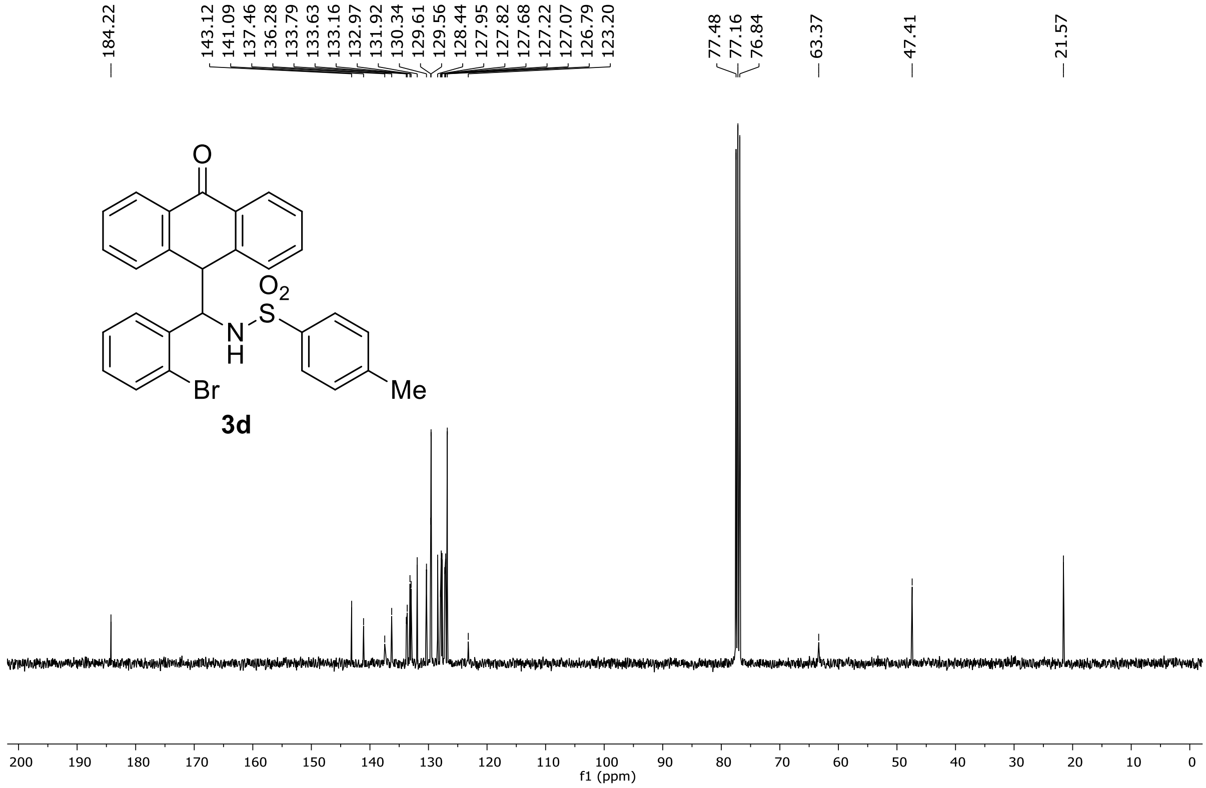
$^{13}C\{^{1}H\}$ NMR of **3c** (100 MHz, $CDCl_3$):



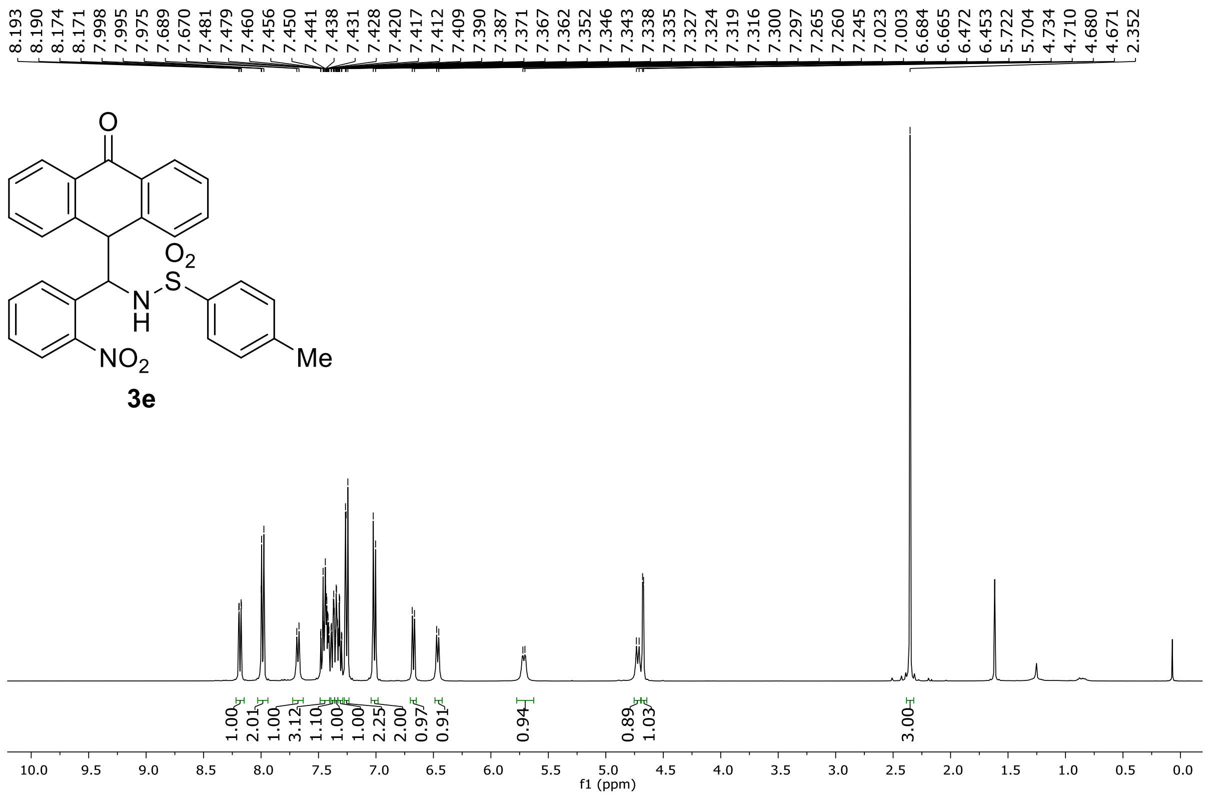
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$):



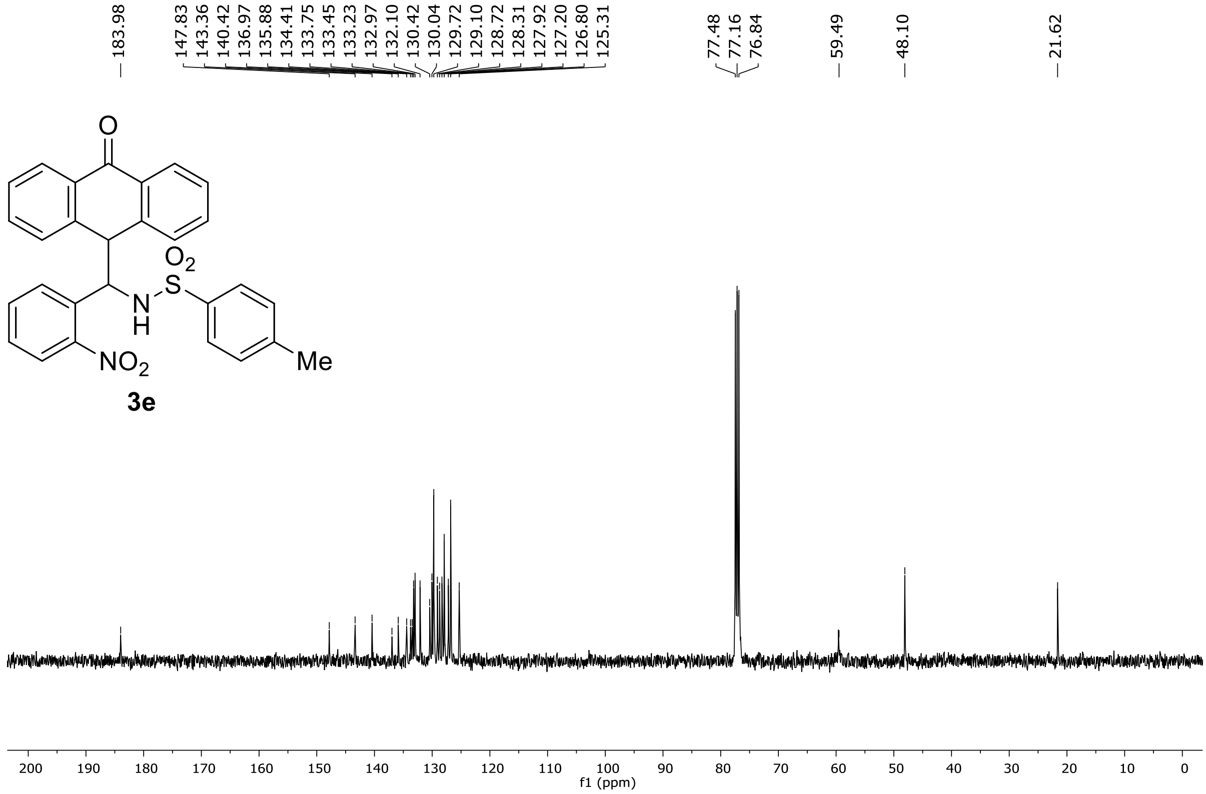
$^{13}C\{^{1}H\}$ NMR spectrum of **3d** (100 MHz, $CDCl_3$):



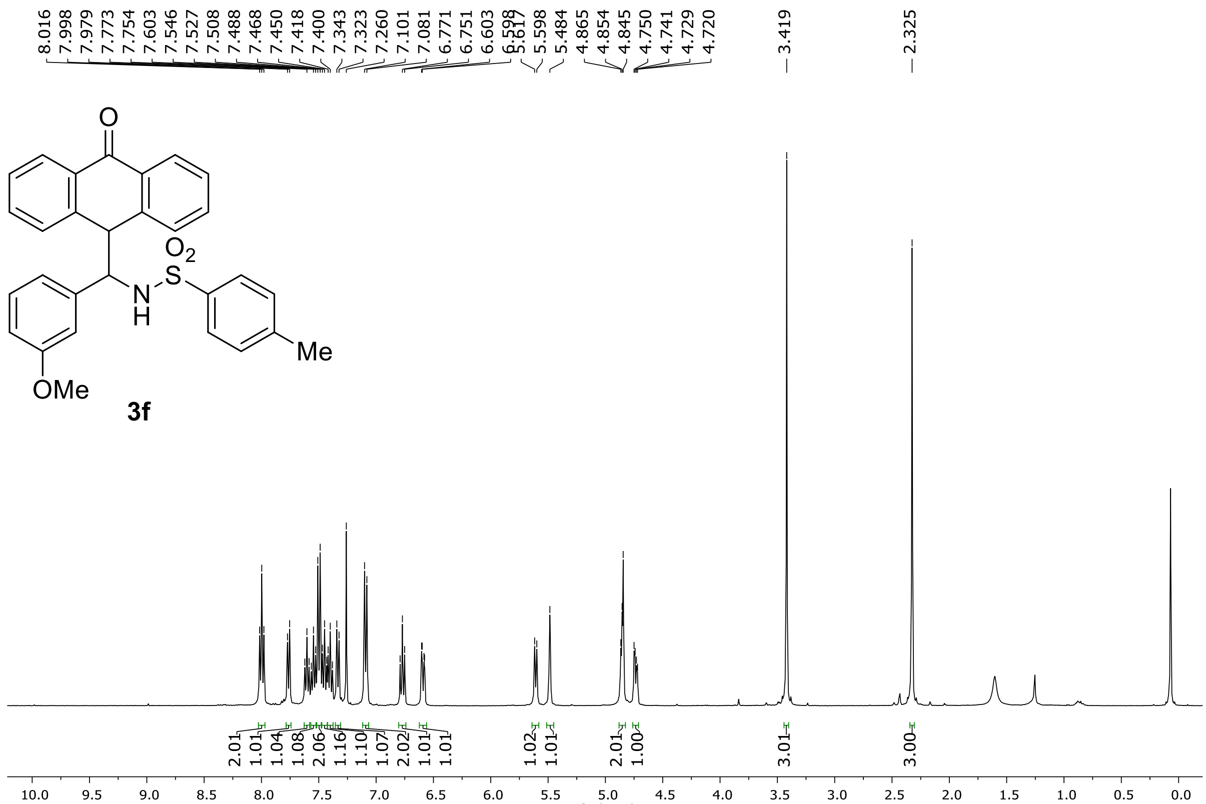
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$):



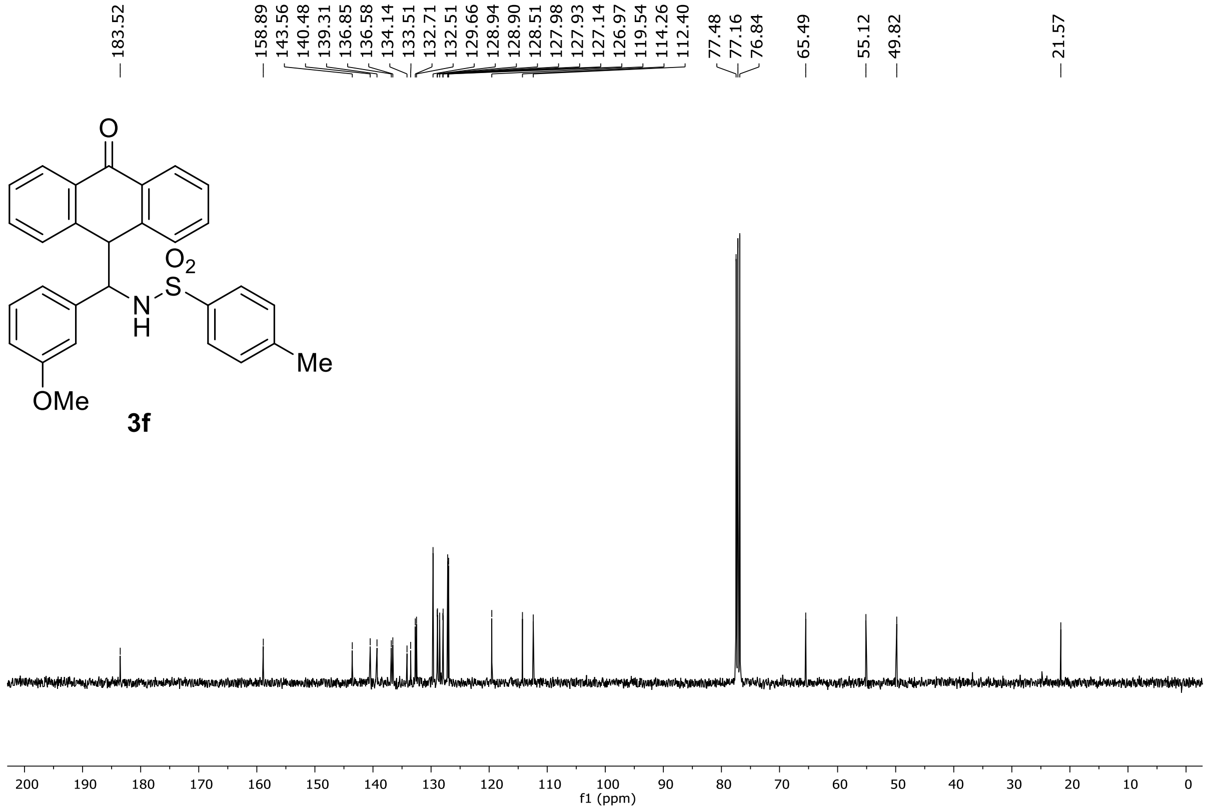
^{13}C{^{1}H} NMR spectrum of **3e** (100 MHz, $CDCl_3$):



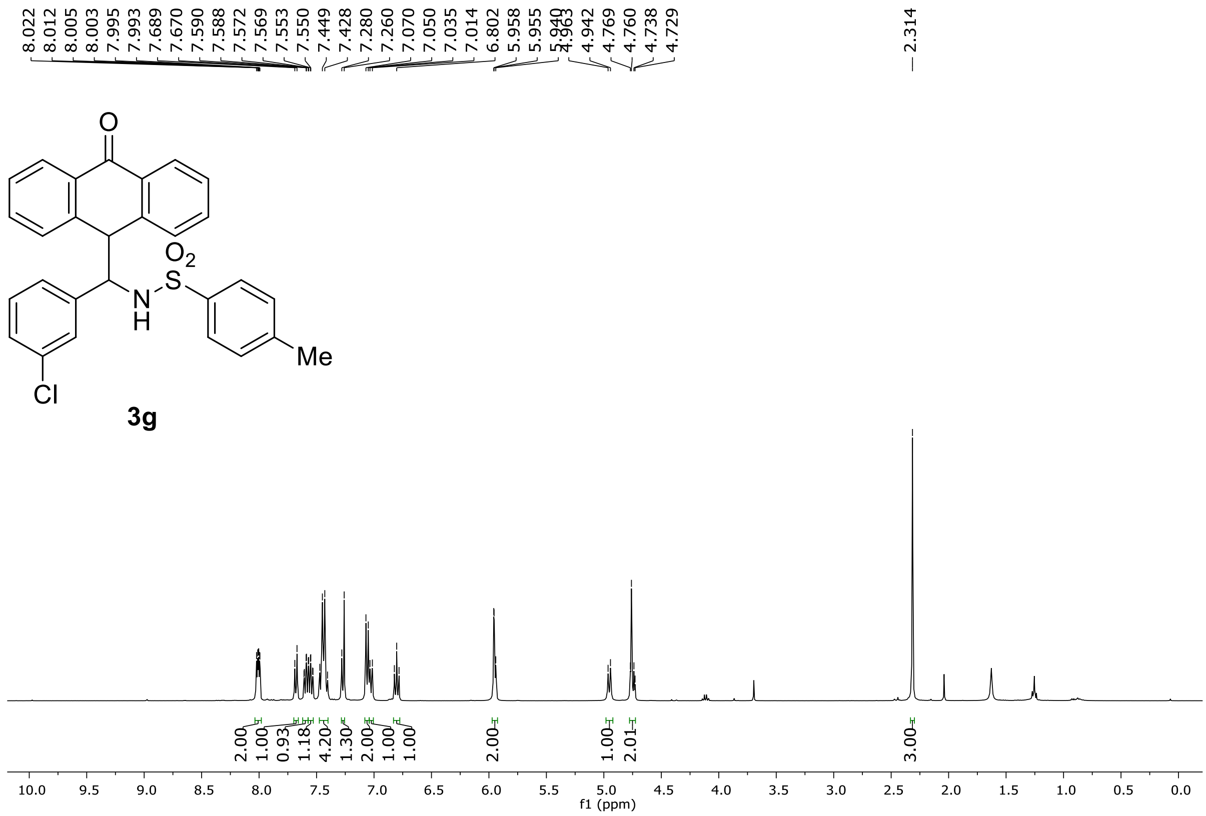
^{1}H NMR spectrumof **3f** (400 MHz, $CDCl_3$):



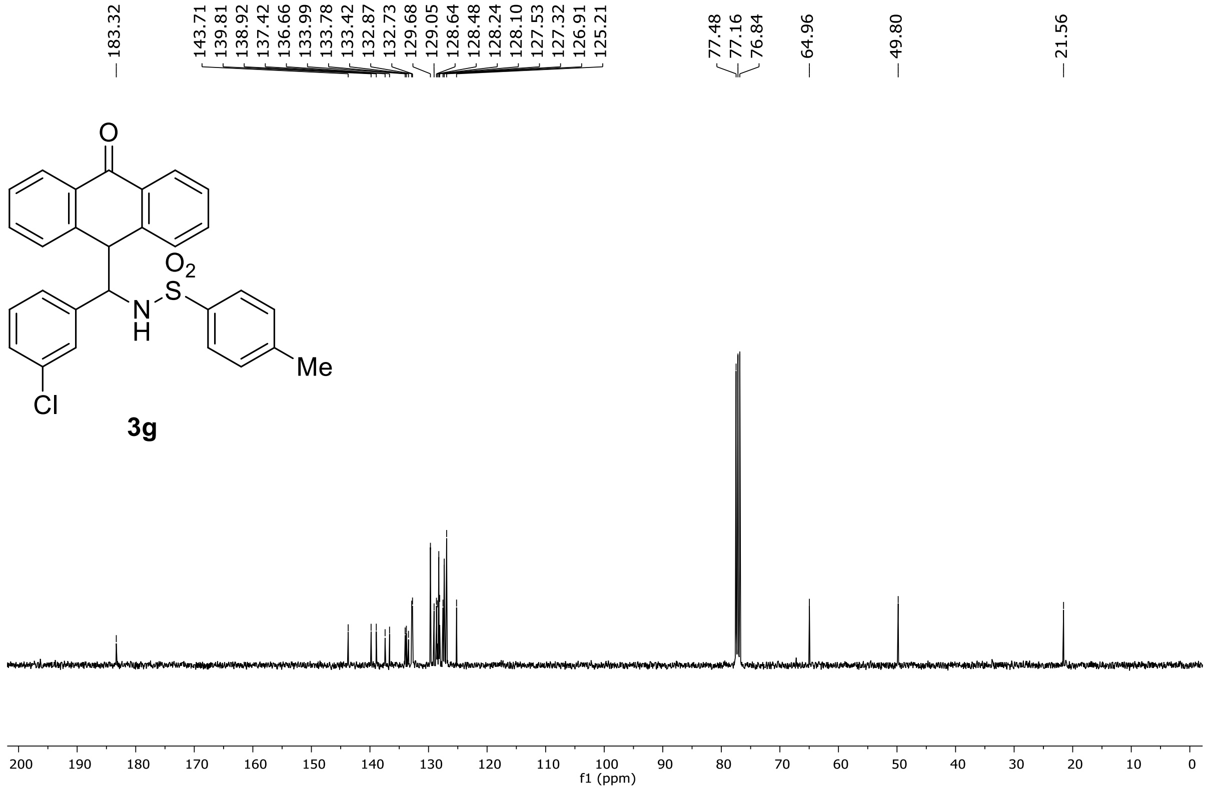
$^{13}C\{^{1}H\}$ NMR spectrum of **3f** (100 MHz, $CDCl_3$):



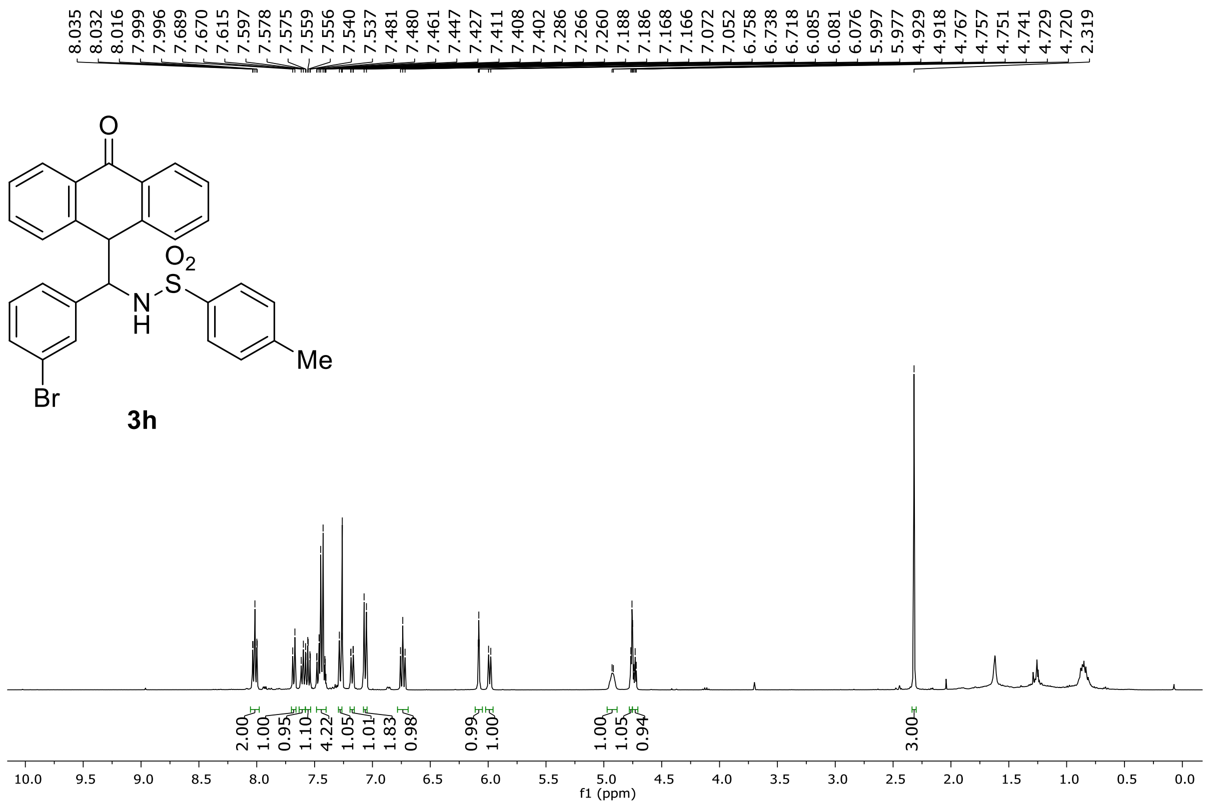
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$):



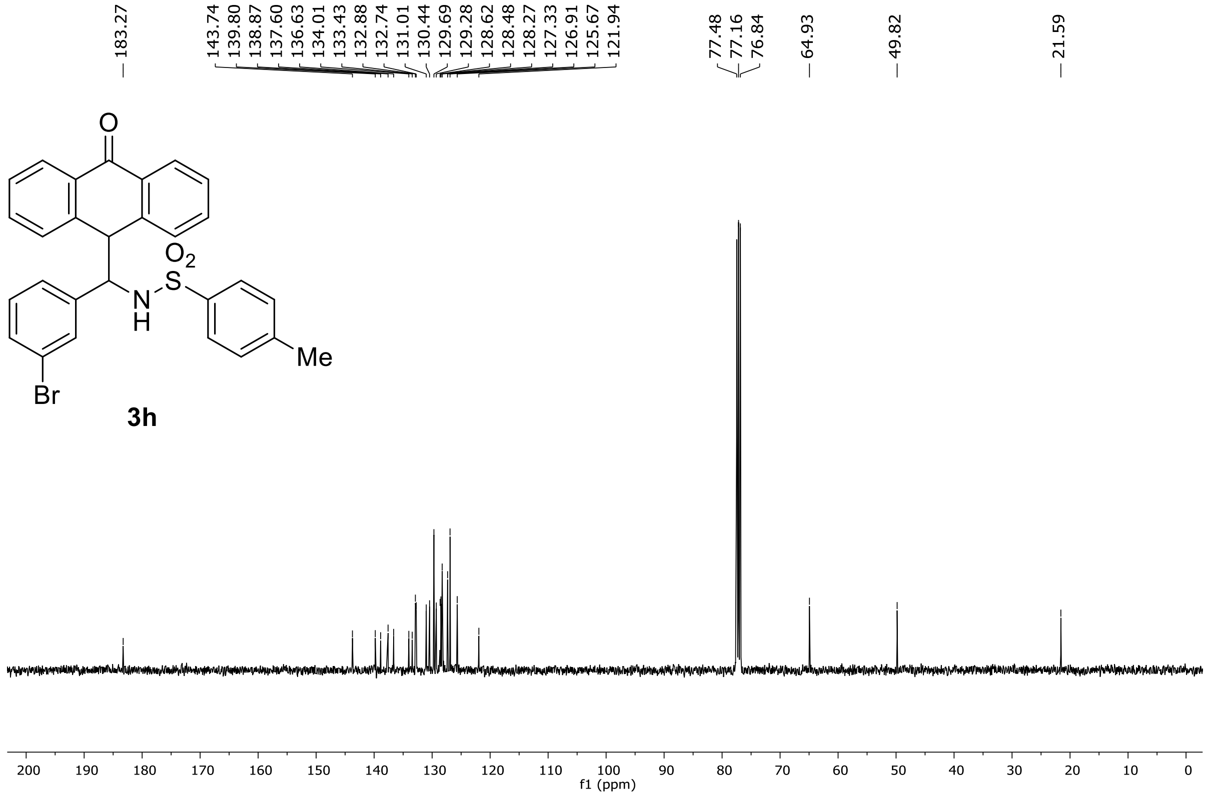
$^{13}C\{^1H\}$ NMR spectrum of **3g** (100 MHz, $CDCl_3$):



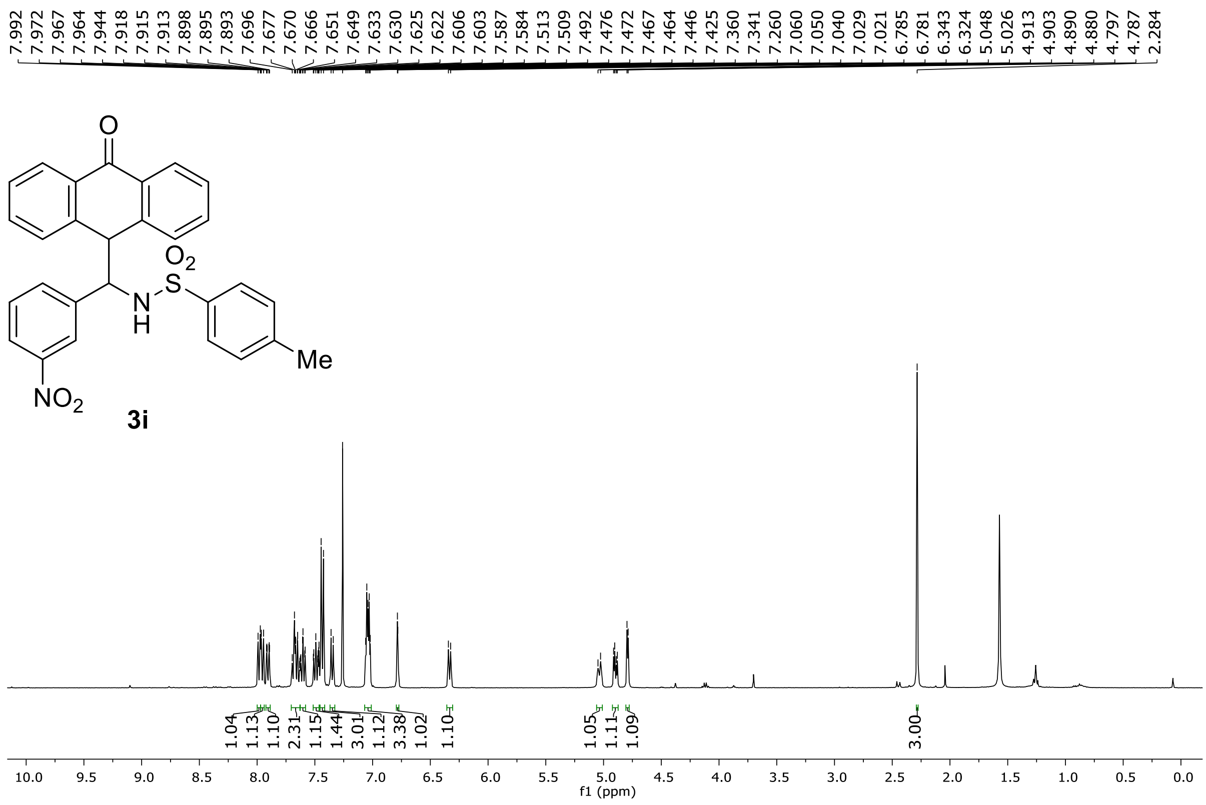
^1H NMR spectrumof **3h** (400 MHz, $CDCl_3$):



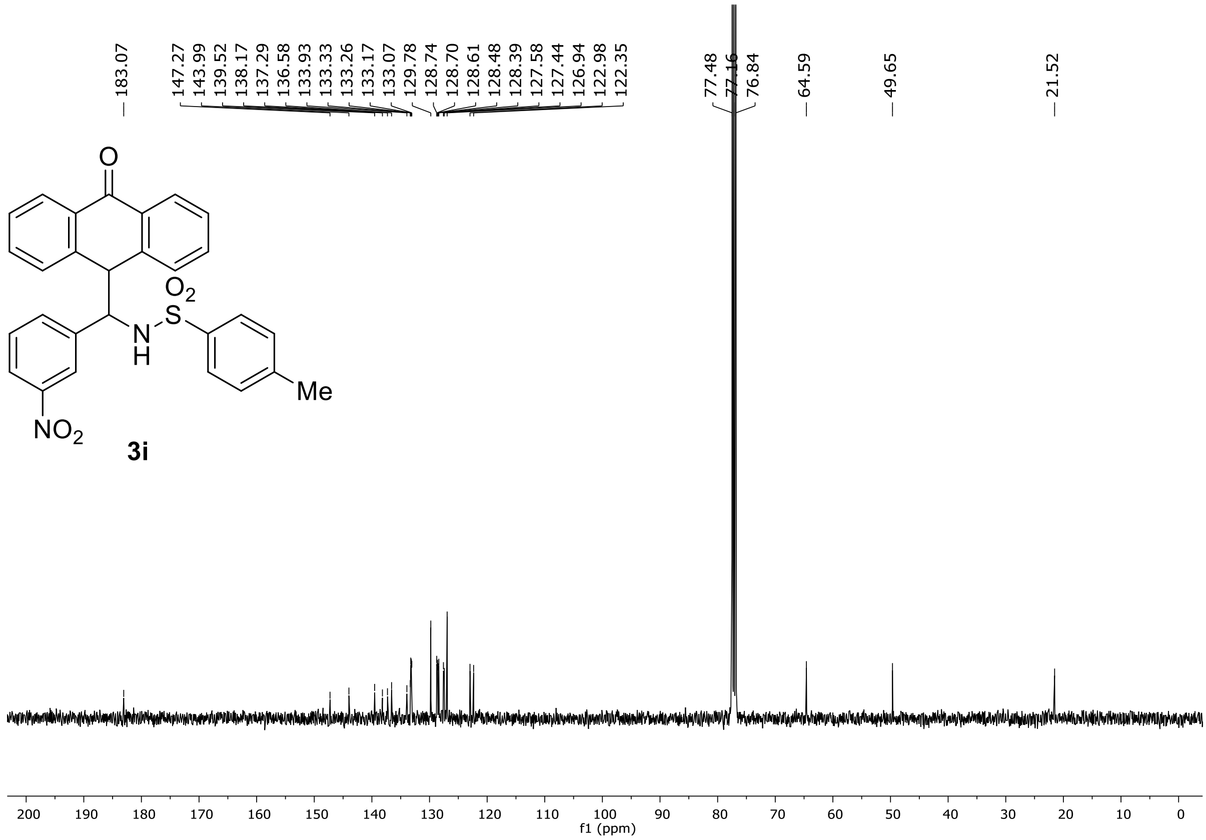
$^{13}C\{^1H\}$ NMR spectrum of **3h** (100 MHz, $CDCl_3$):



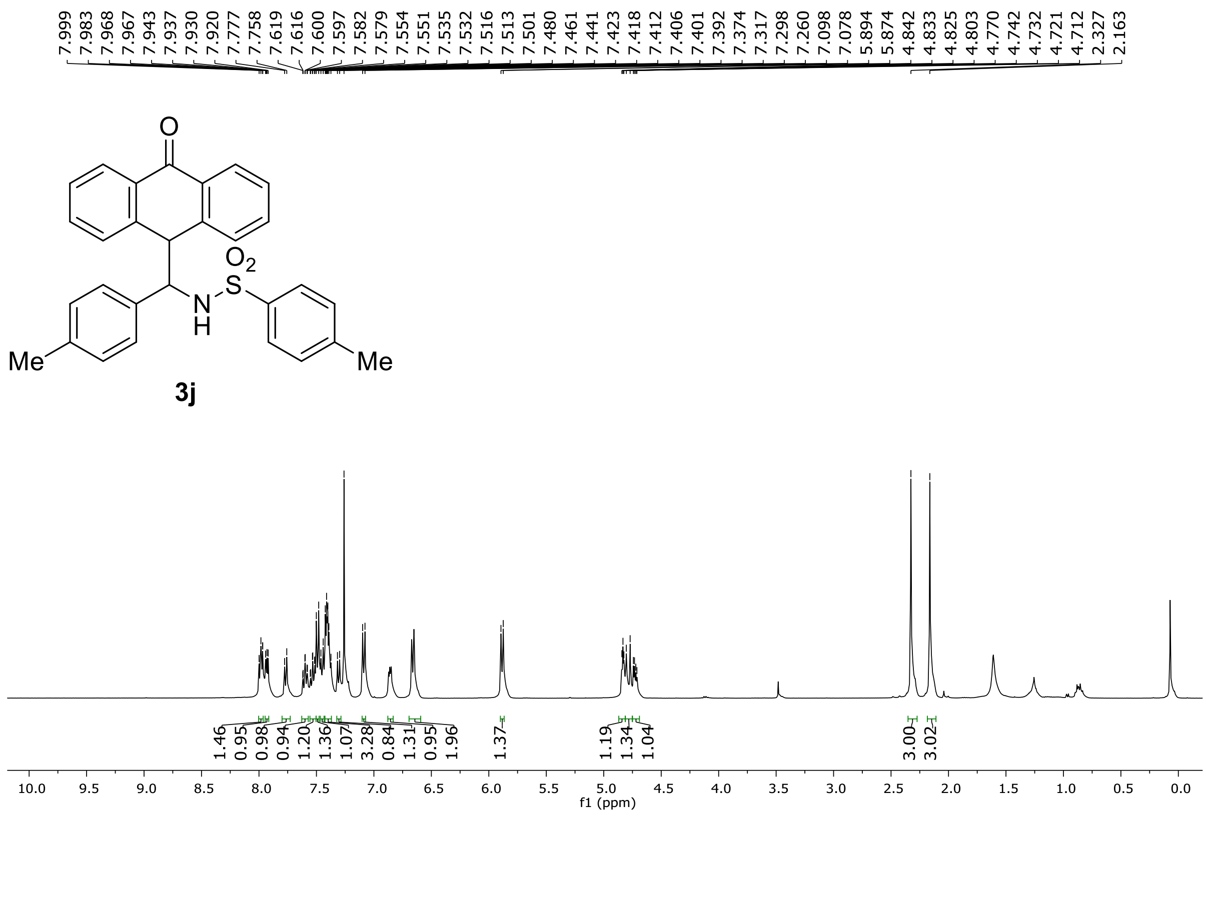
^1H NMR spectrum of **3i** (400 MHz, $CDCl_3$):



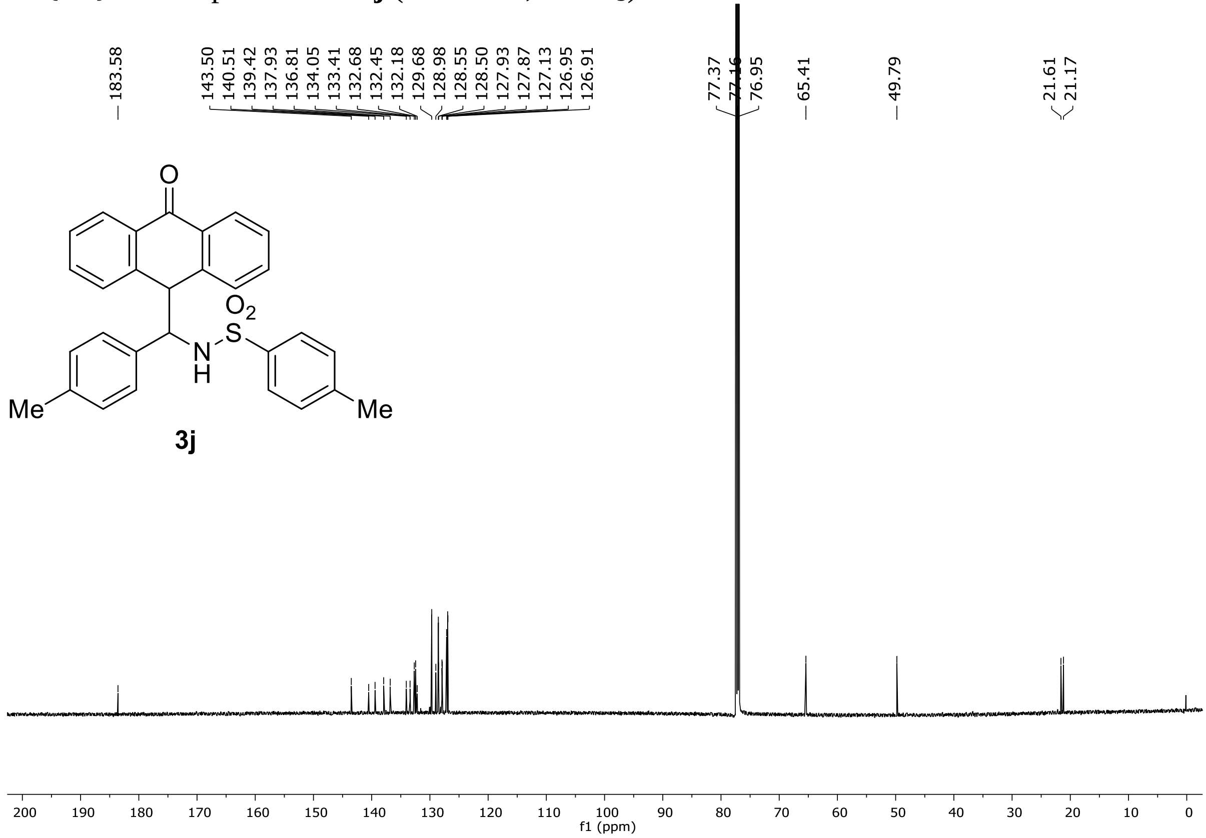
$^{13}C\{^{1}H\}$ NMR spectrum of **3i** (100 MHz, $CDCl_3$):



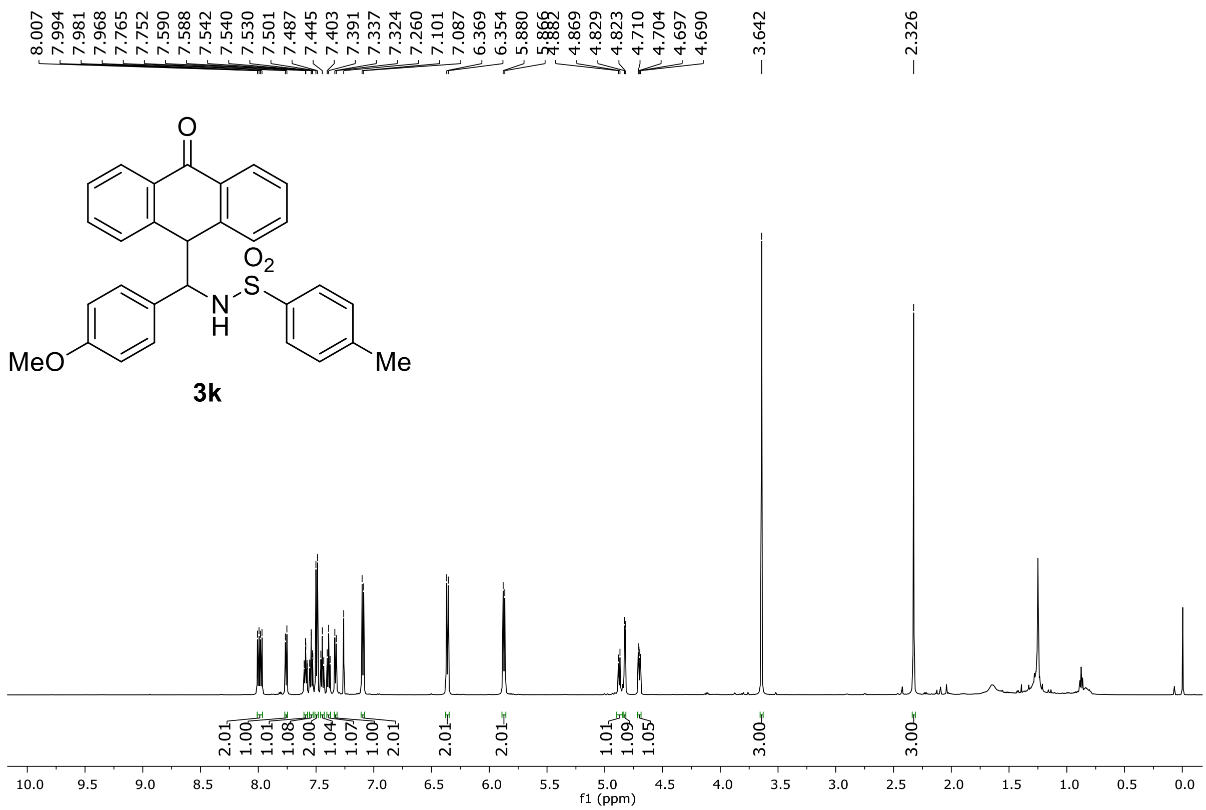
^{1}H NMR spectrumof **3j** (400 MHz, $CDCl_3$):



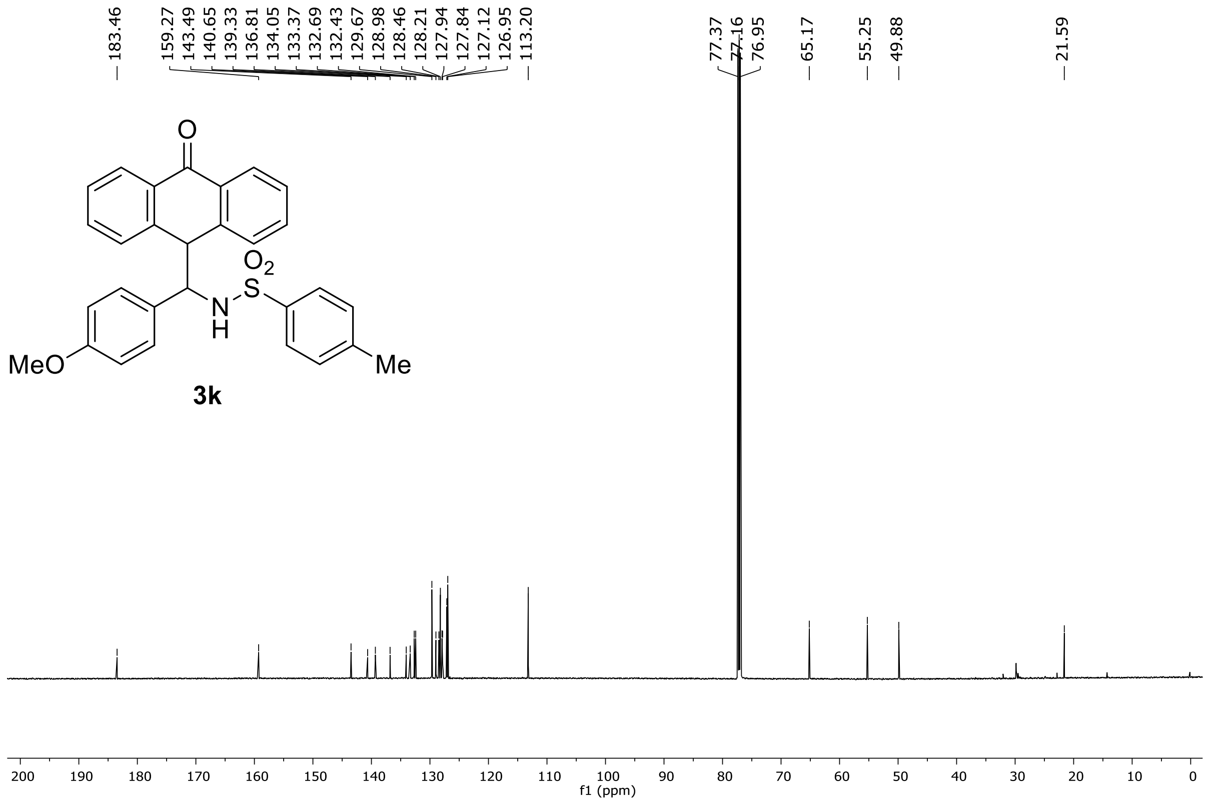
$^{13}C\{^1H\}$ NMR spectrum of **3j** (100 MHz, $CDCl_3$):



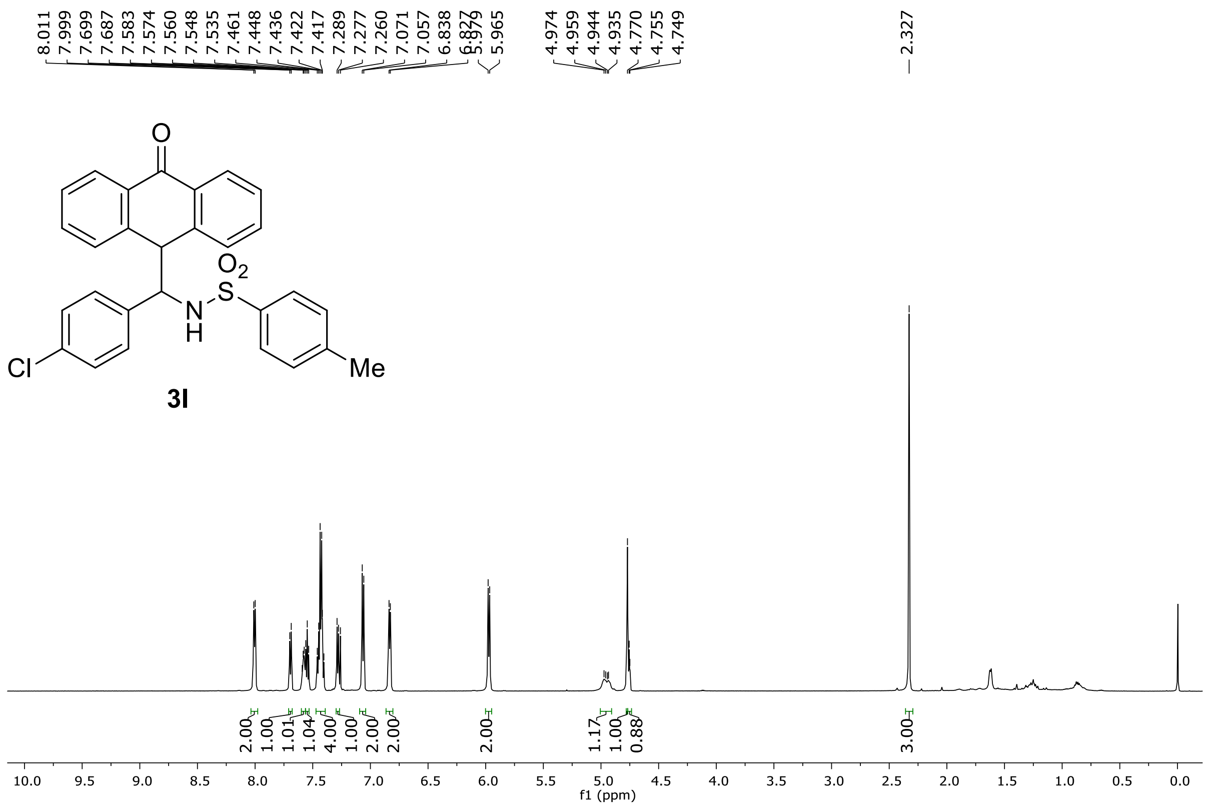
^1H NMR spectrum of **3k** (600 MHz, $CDCl_3$):



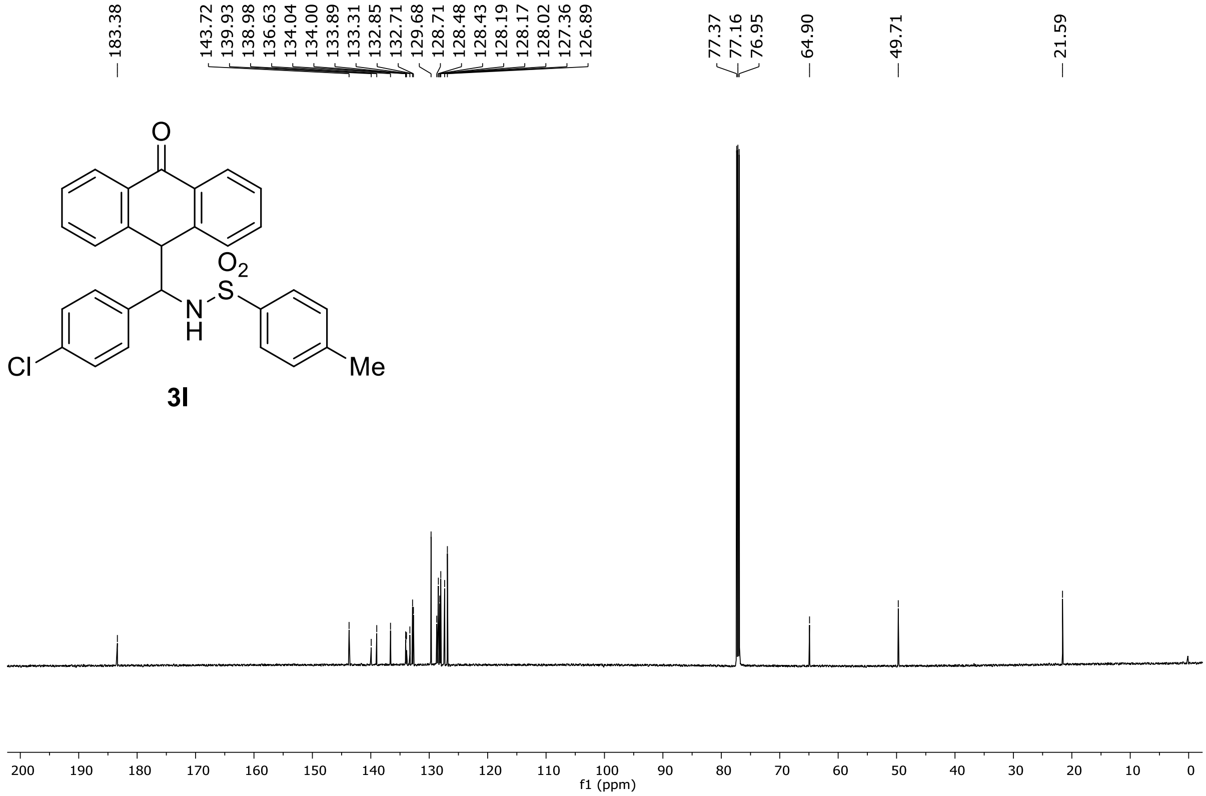
$^{13}C\{^{1}H\}$ NMR spectrum of **3k** (150 MHz, $CDCl_3$):



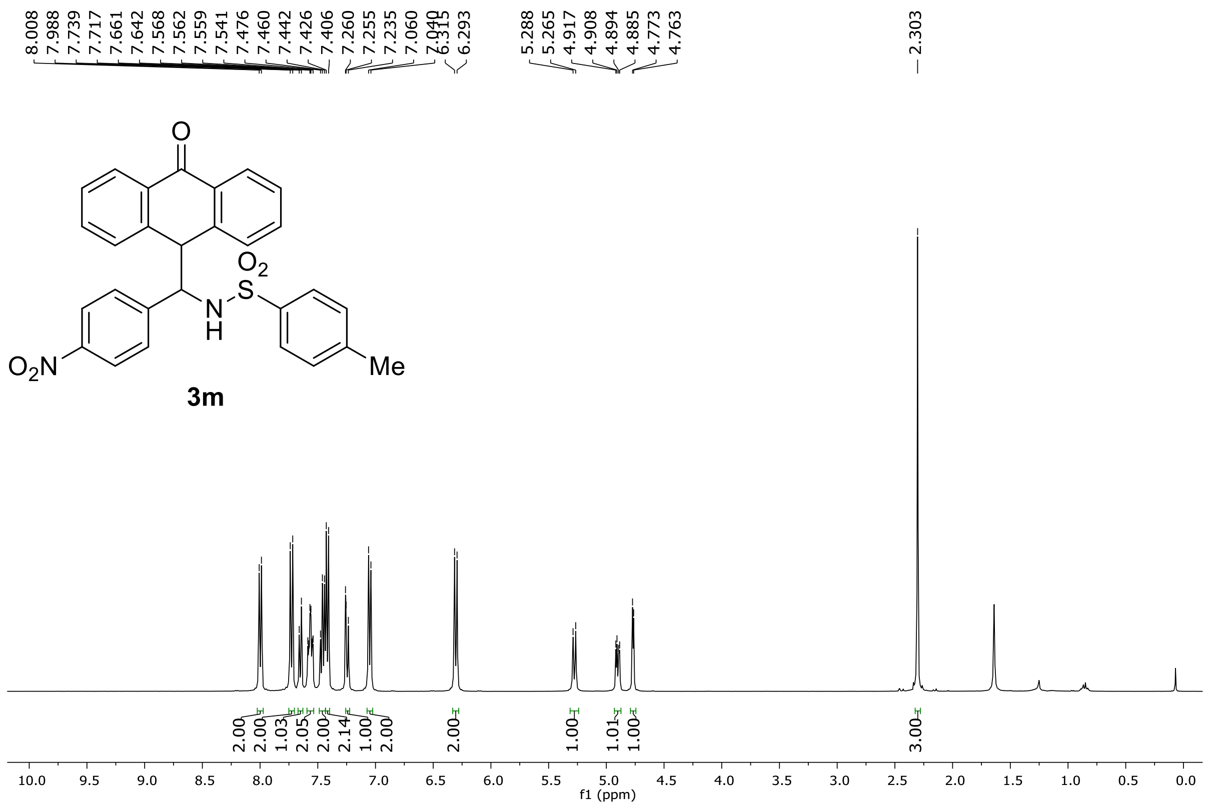
^{1}H NMR spectrum of **3l** (600 MHz, $CDCl_3$):



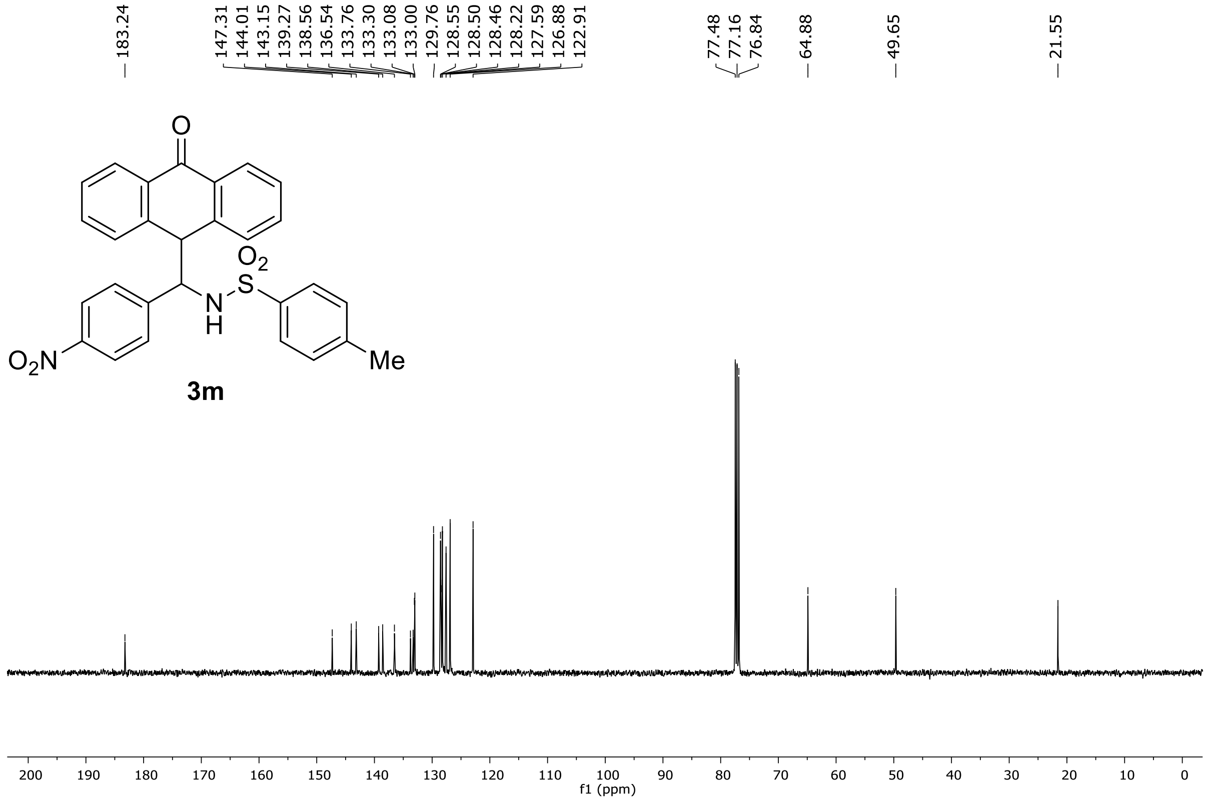
$^{13}C\{^1H\}$ NMR spectrum of **3l** (150 MHz, $CDCl_3$):



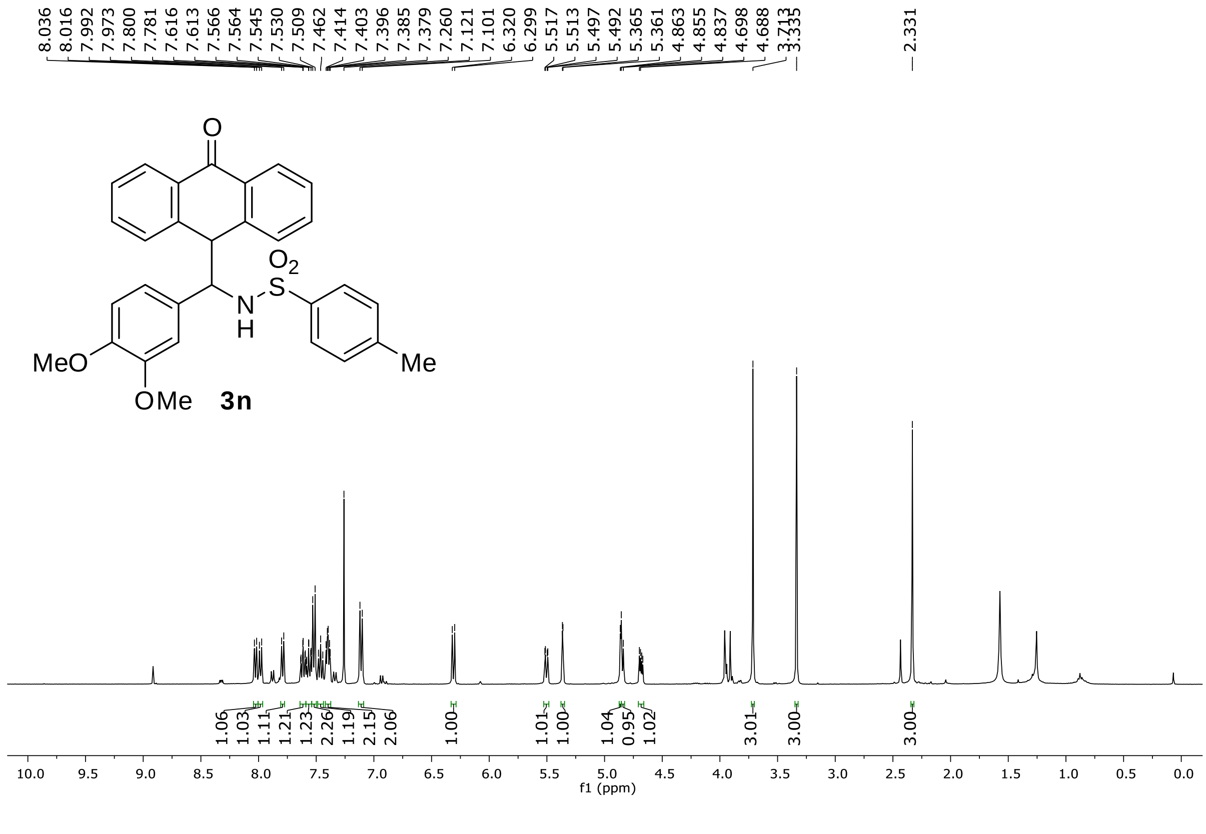
^1H NMR spectrum of **3m** (400 MHz, $CDCl_3$):



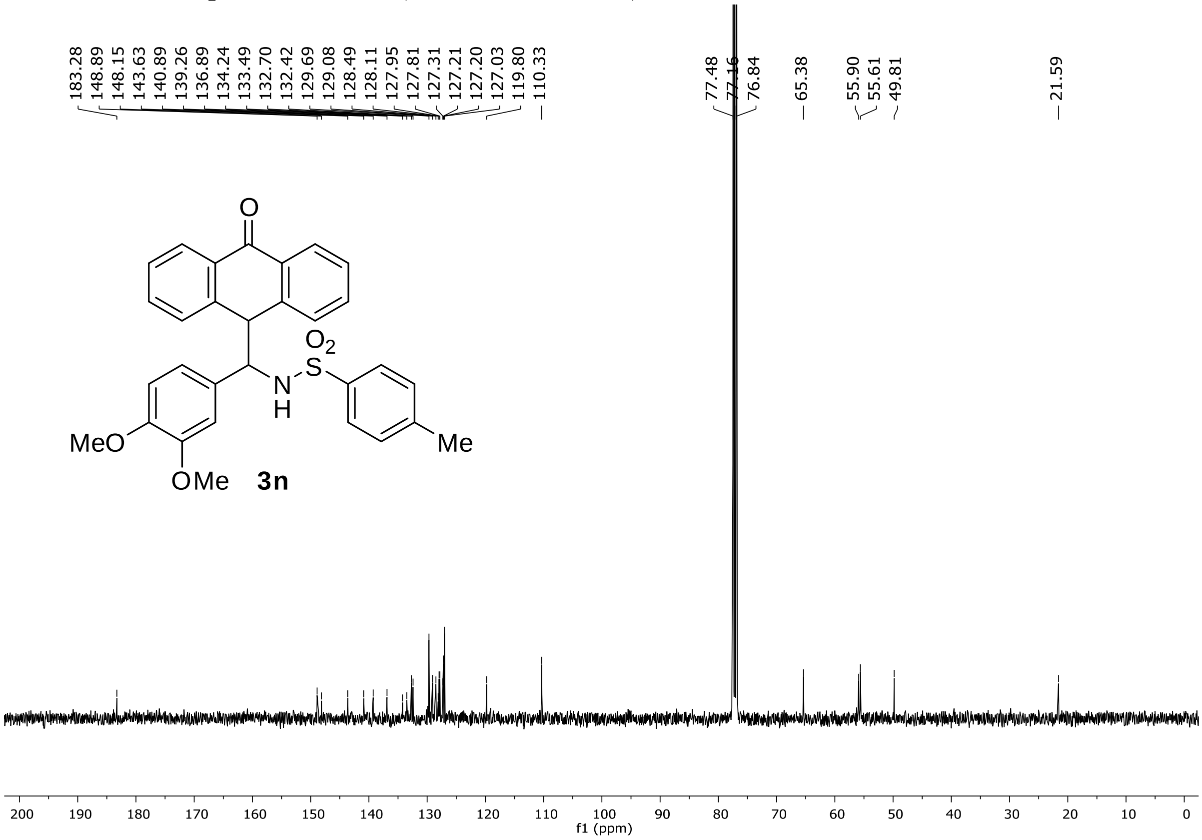
$^{13}C\{^1H\}$ NMR spectrum of **3m** (100 MHz, $CDCl_3$):



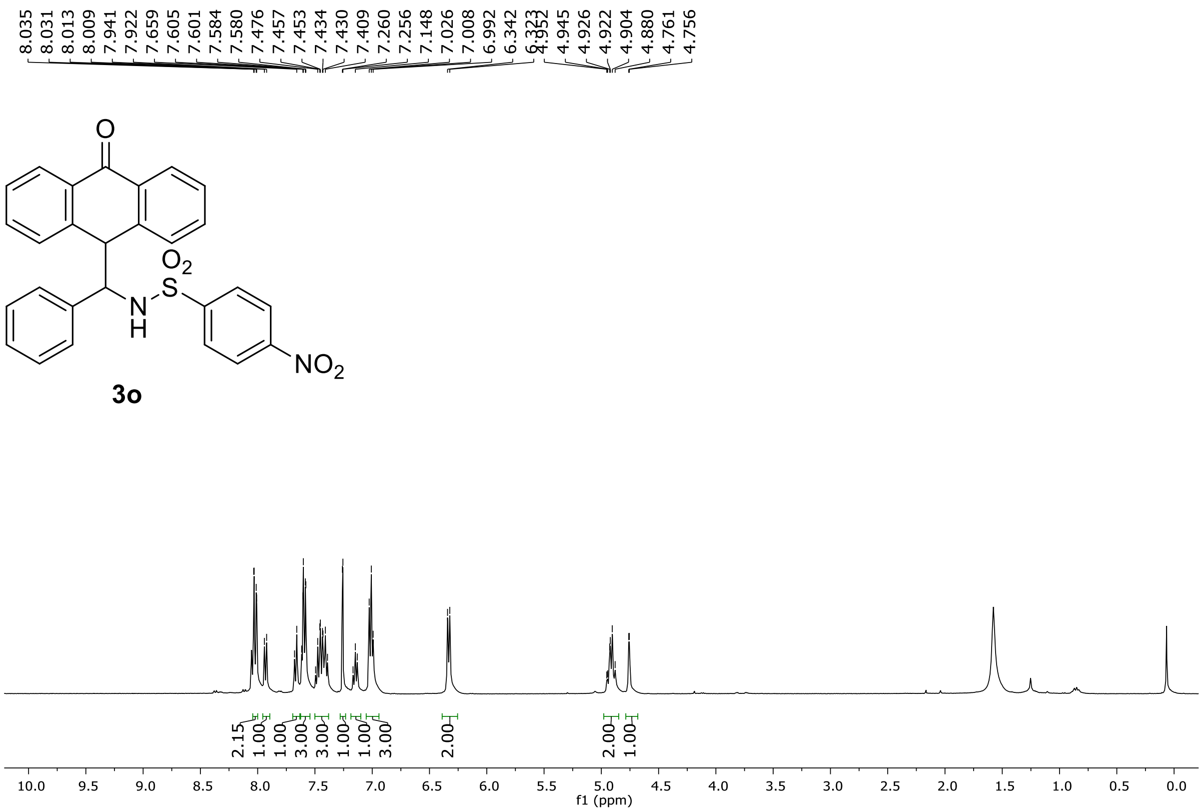
^1H NMR spectrum of **3n** (400 MHz, $CDCl_3$):



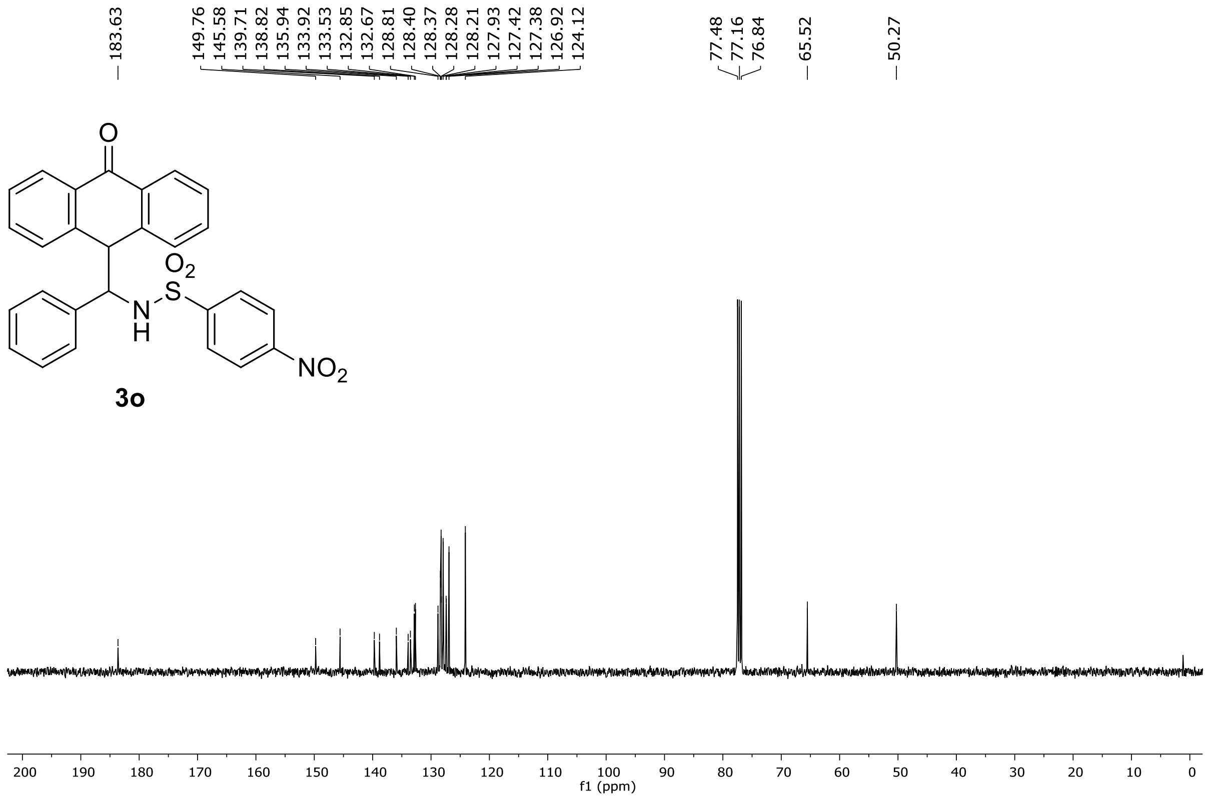
$^{13}C\{^{1}H\}$ NMR spectrum of **3n** (100 MHz, $CDCl_3$):



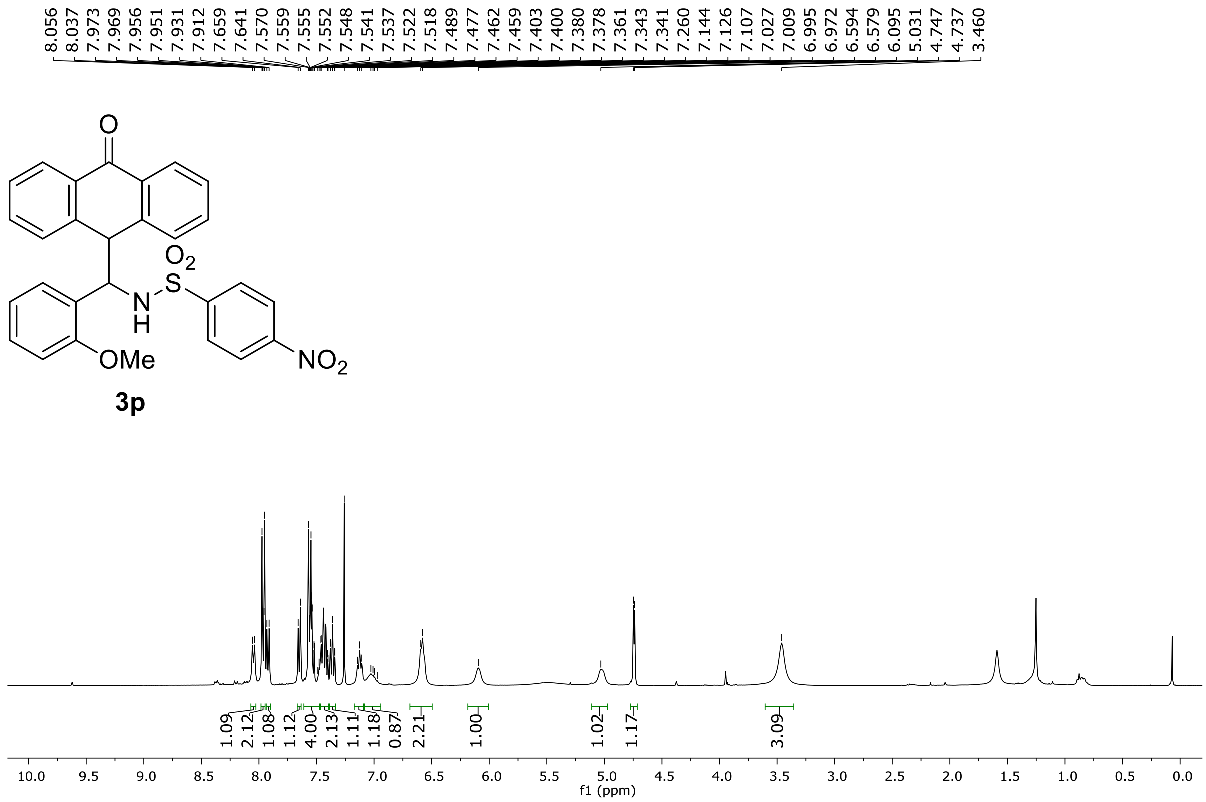
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$):



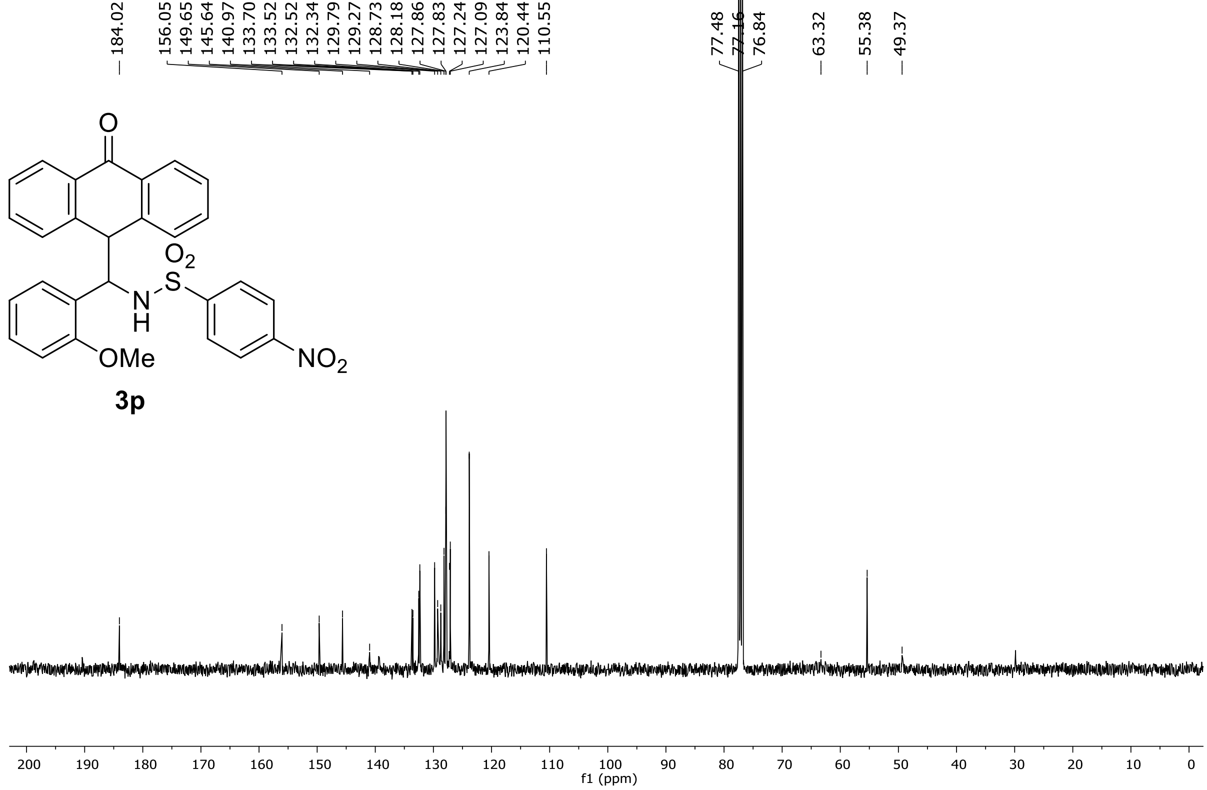
$^{13}C\{^{1}H\}$ NMR spectrum of **3o** (100 MHz, $CDCl_3$):



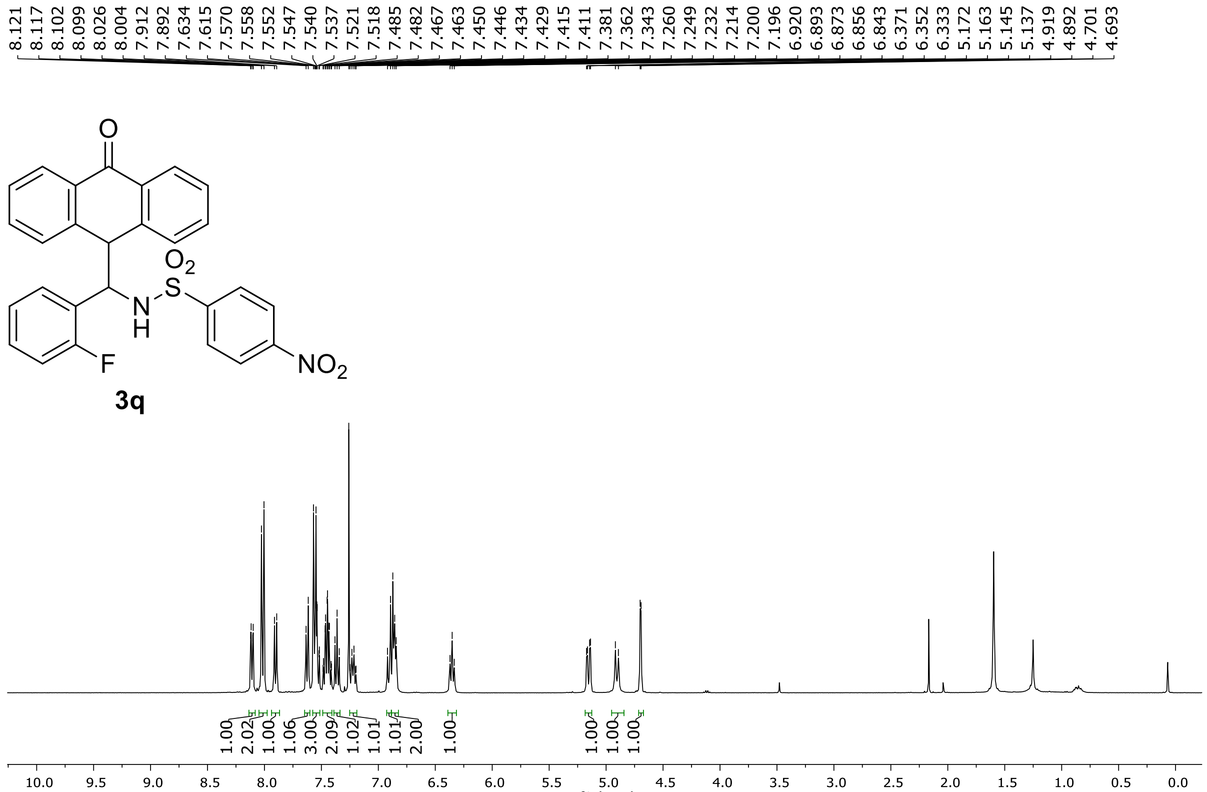
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$):



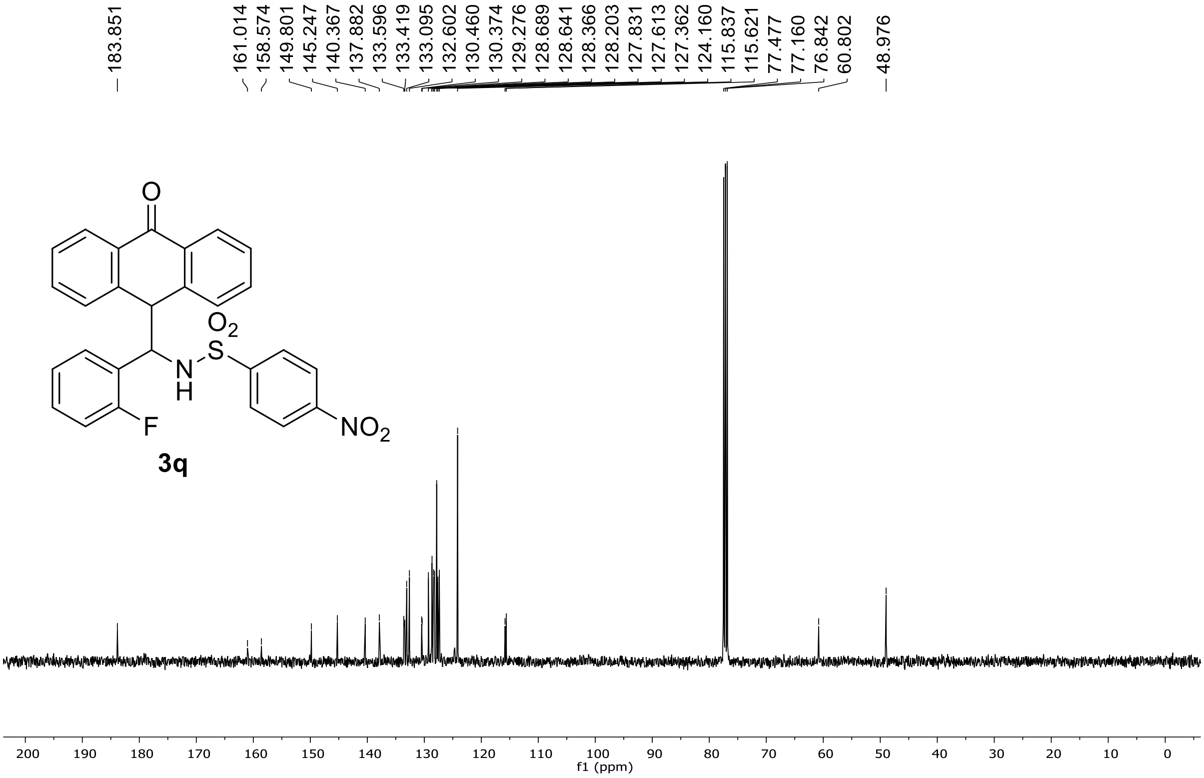
$^{13}C\{^1H\}$ NMR spectrum of **3p** (100 MHz, $CDCl_3$):



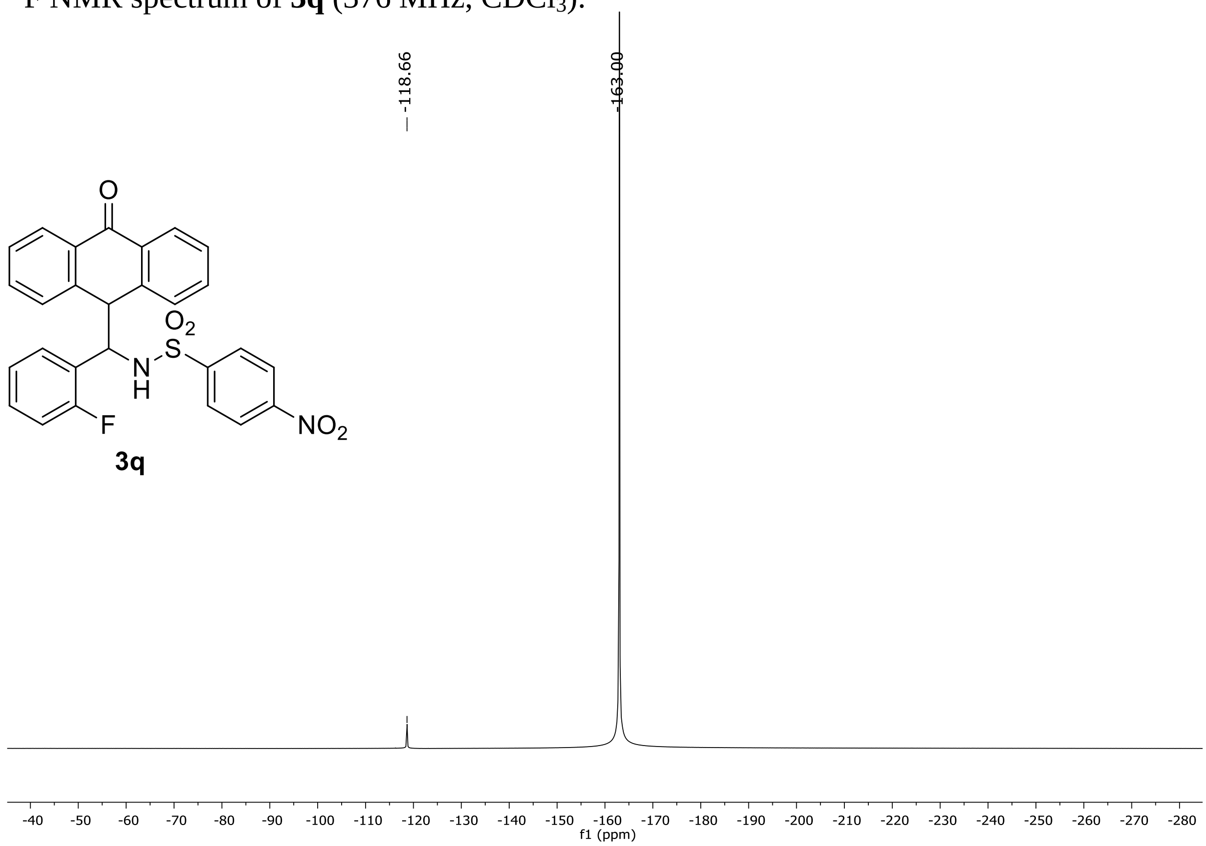
^1H NMR spectrum of **3q** (400 MHz, $CDCl_3$):



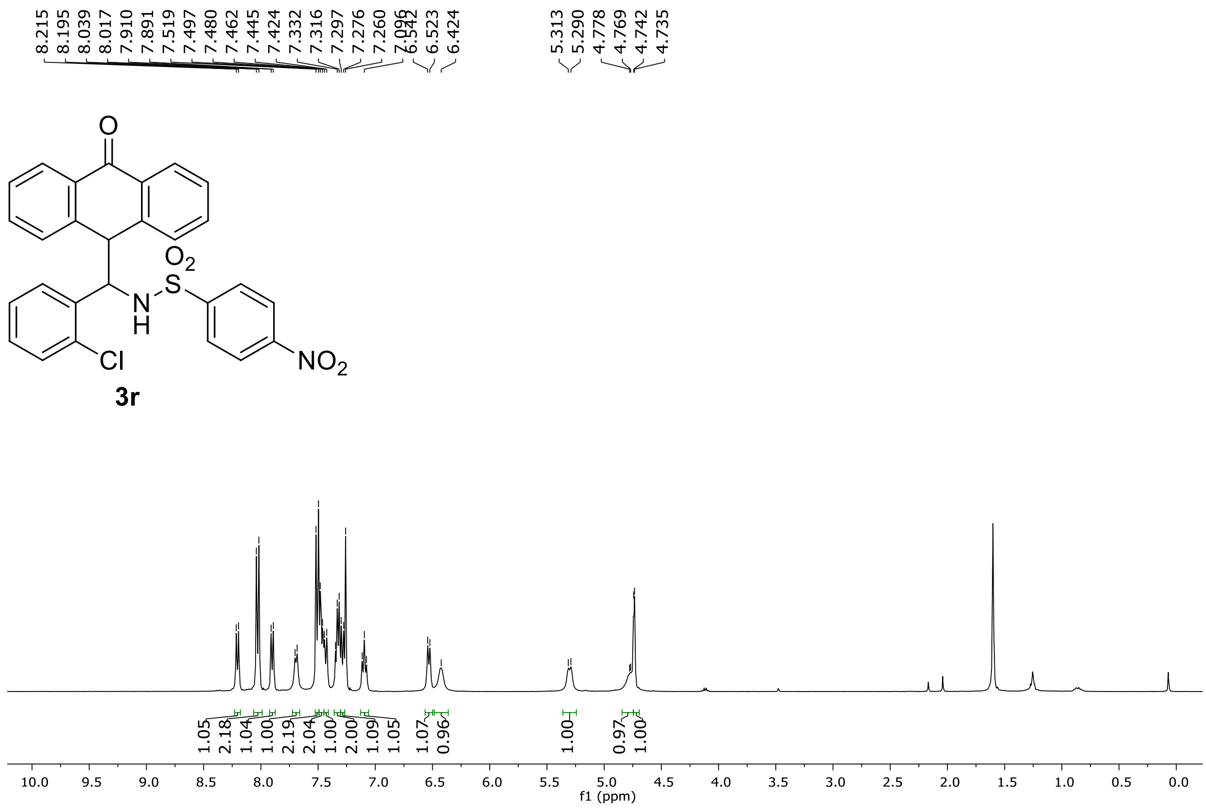
$^{13}C\{^{1}H\}$ NMR spectrum of **3q** (100 MHz, $CDCl_3$):



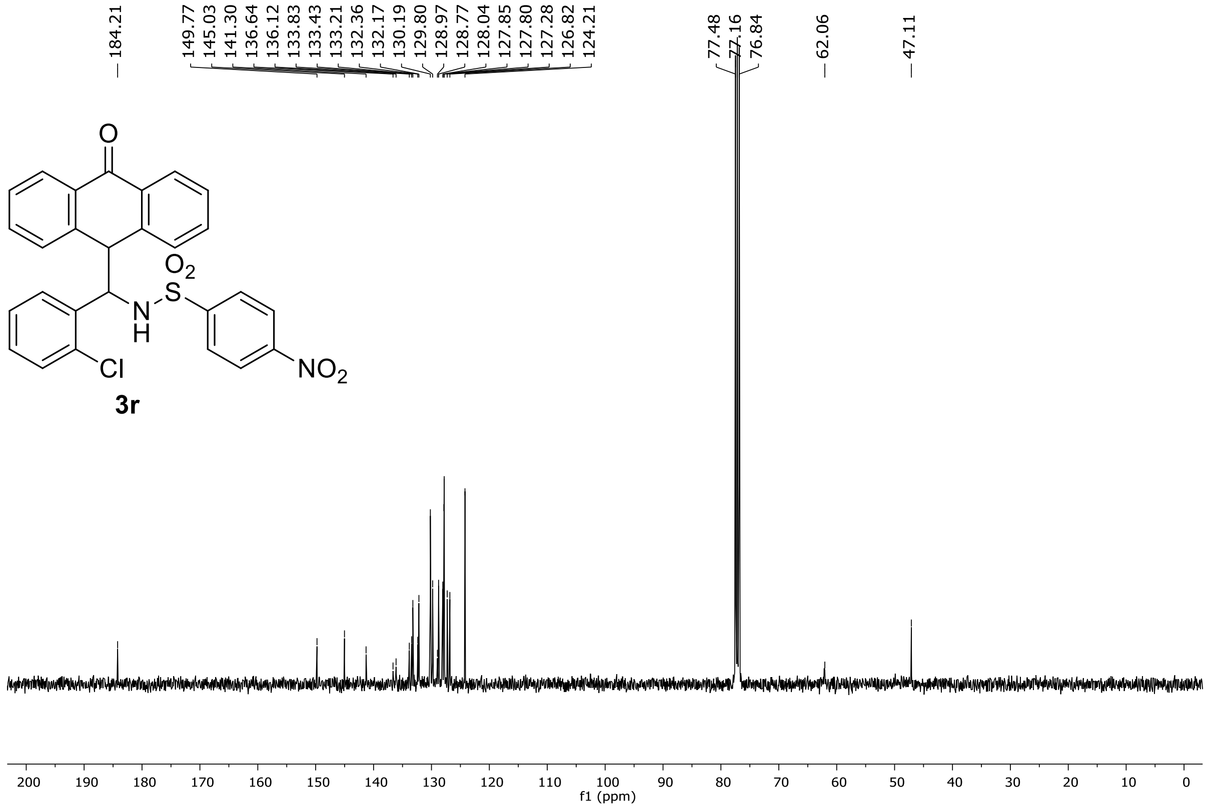
^{19}F NMR spectrum of **3q** (376 MHz, $CDCl_3$):



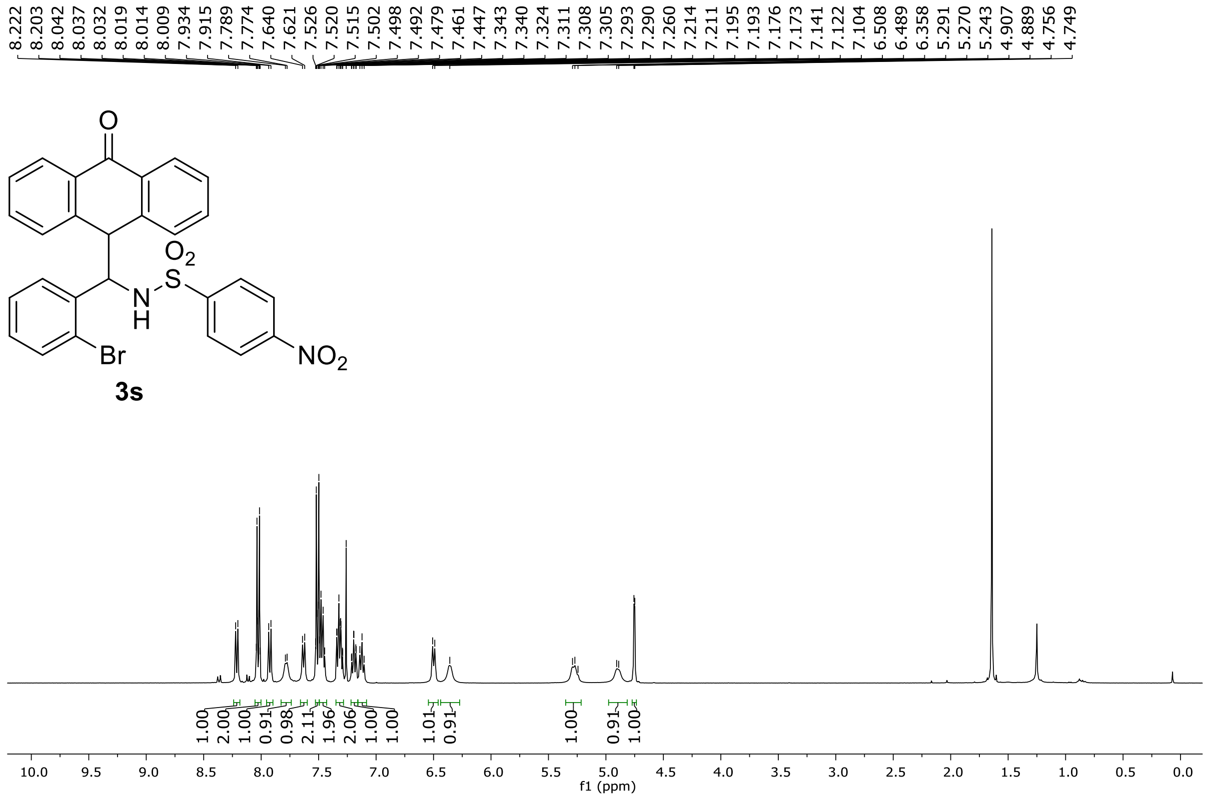
^{1}H NMR spectrumof **3r** (400 MHz, $CDCl_3$):



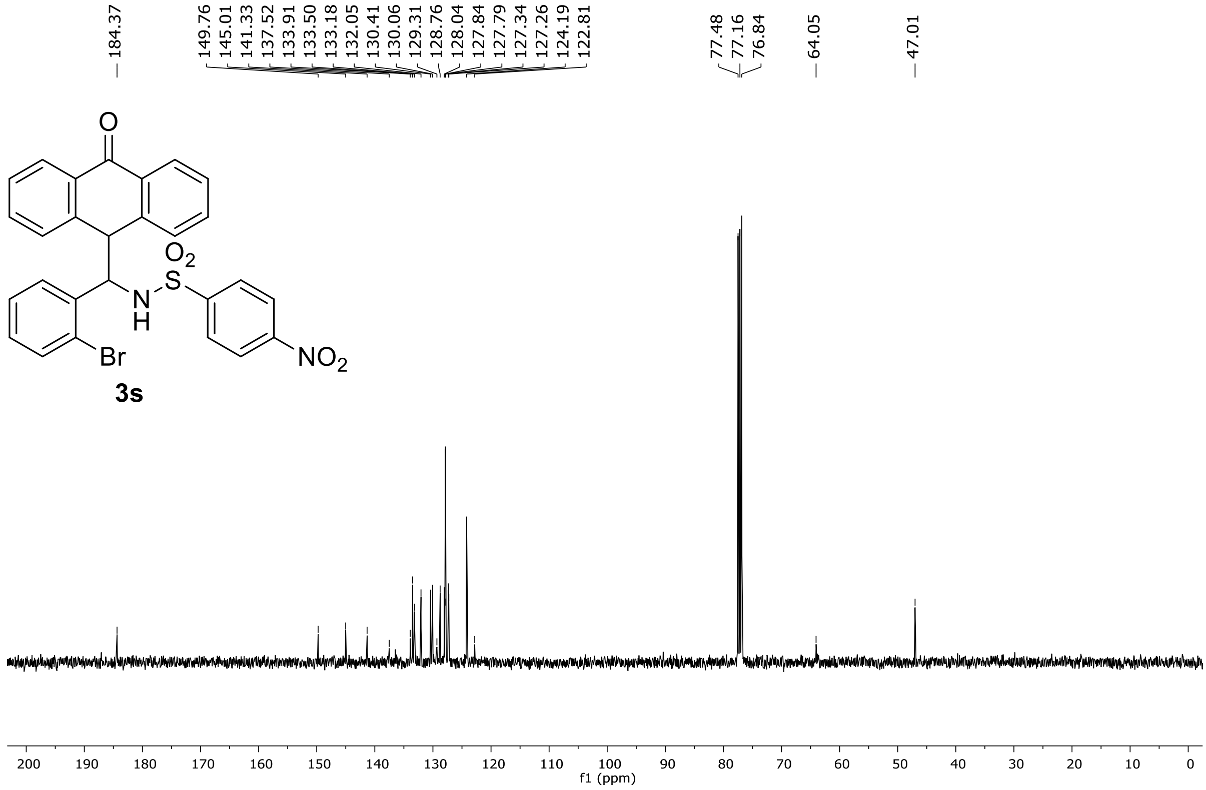
^{13}C{^{1}H} NMR spectrum of **3r** (100 MHz, $CDCl_3$):



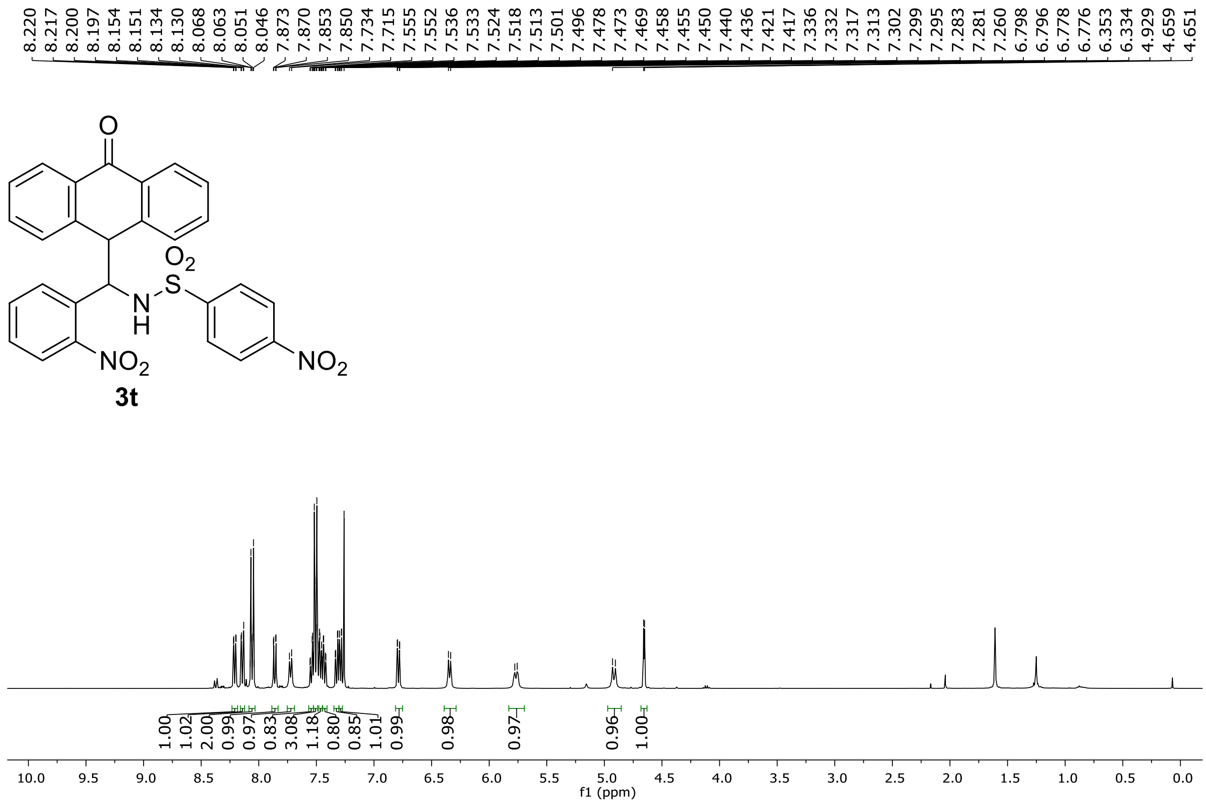
^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$):



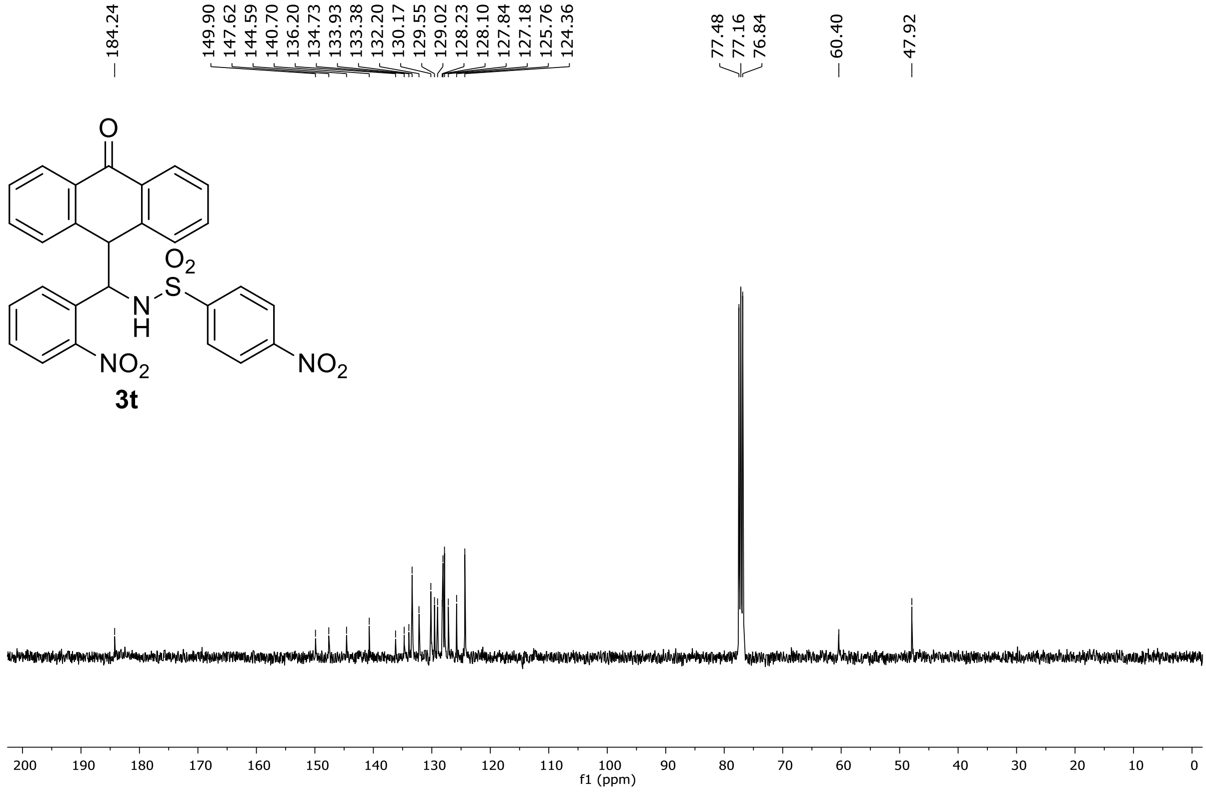
$^{13}C\{^{1}H\}$ NMR spectrum of **3s** (100 MHz, $CDCl_3$):



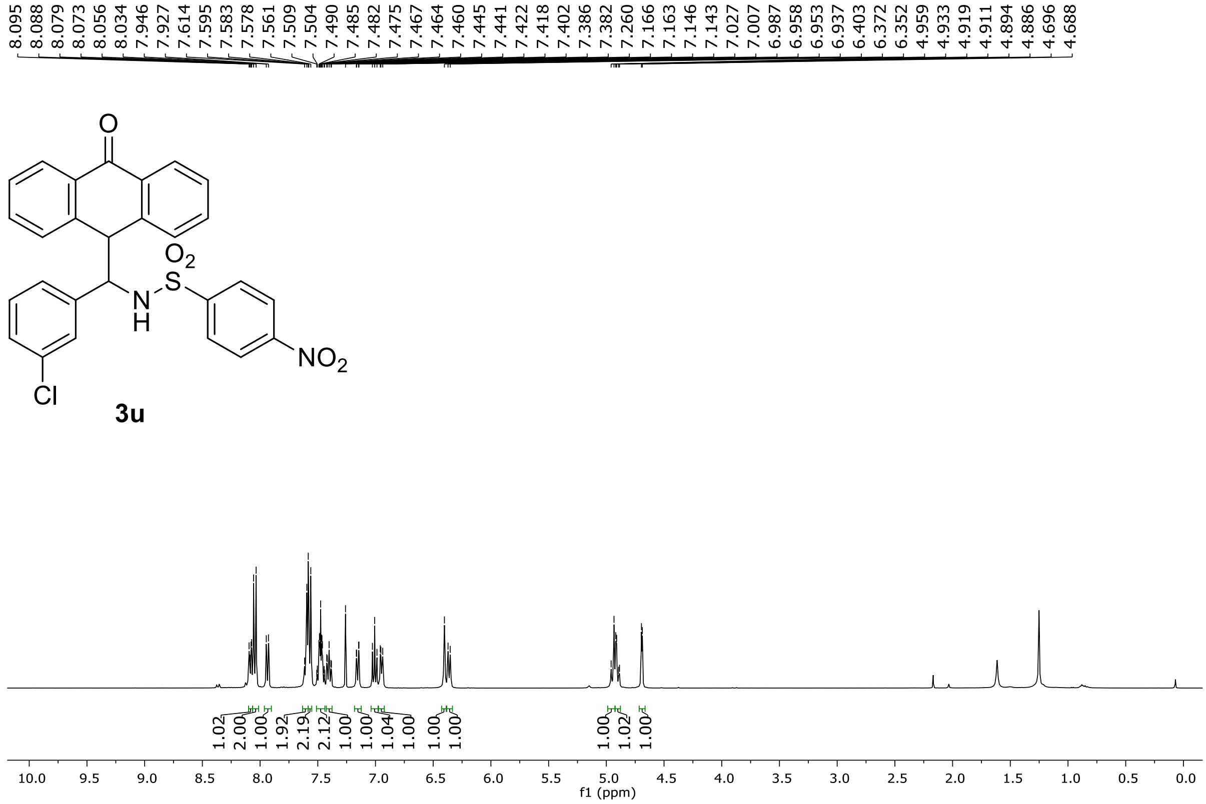
^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$):



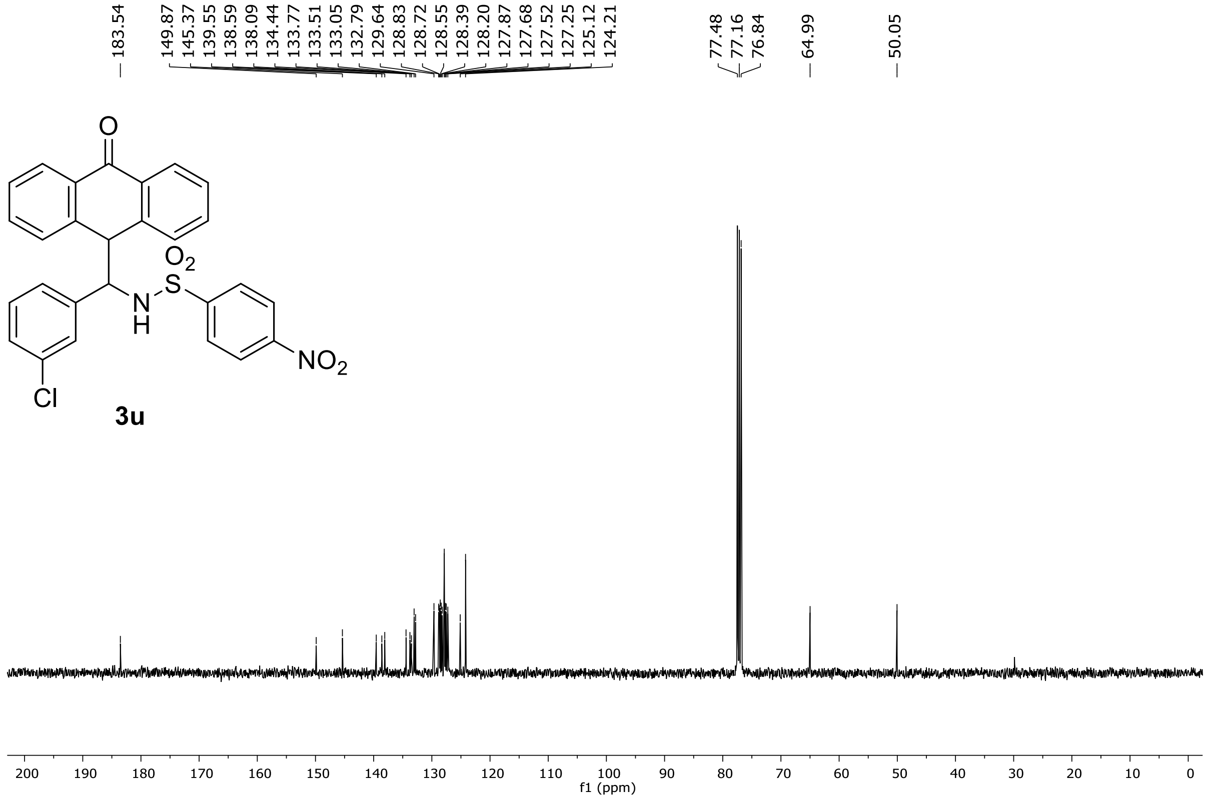
$^{13}C\{^1H\}$ NMR spectrum of **3t** (100 MHz, $CDCl_3$):



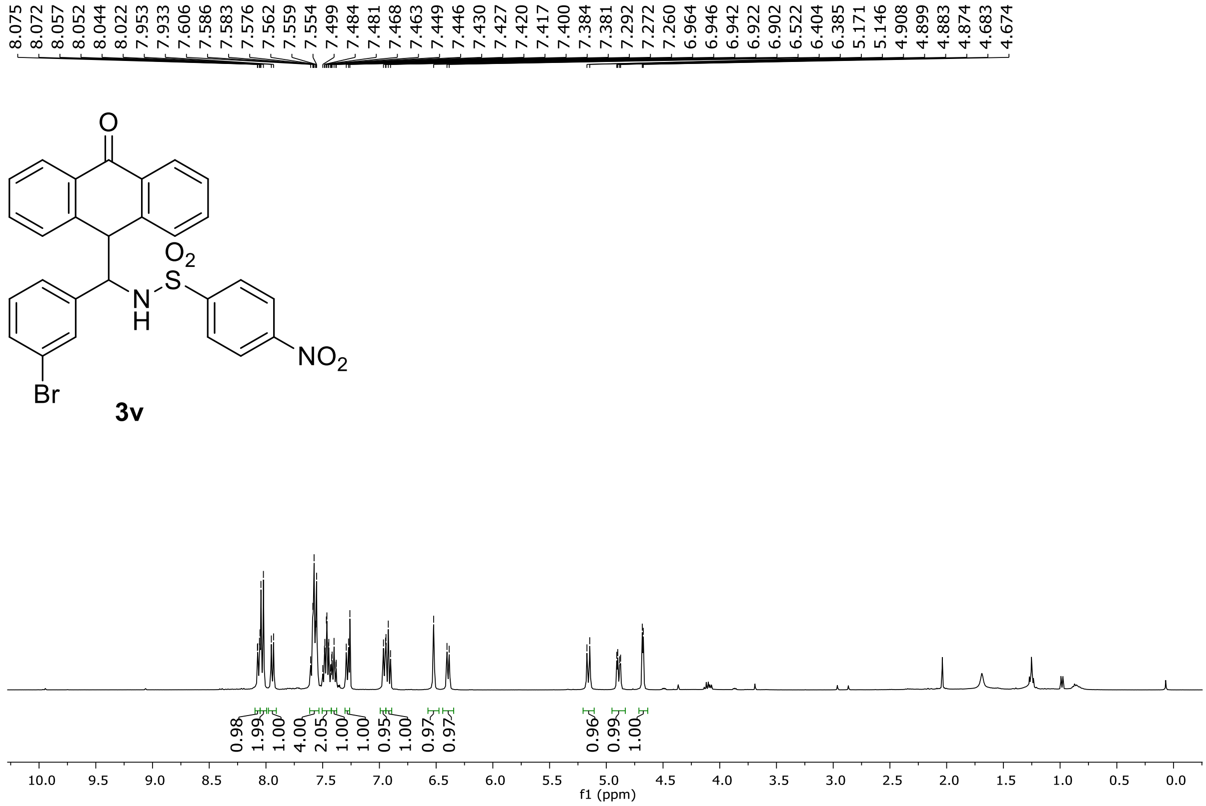
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$):



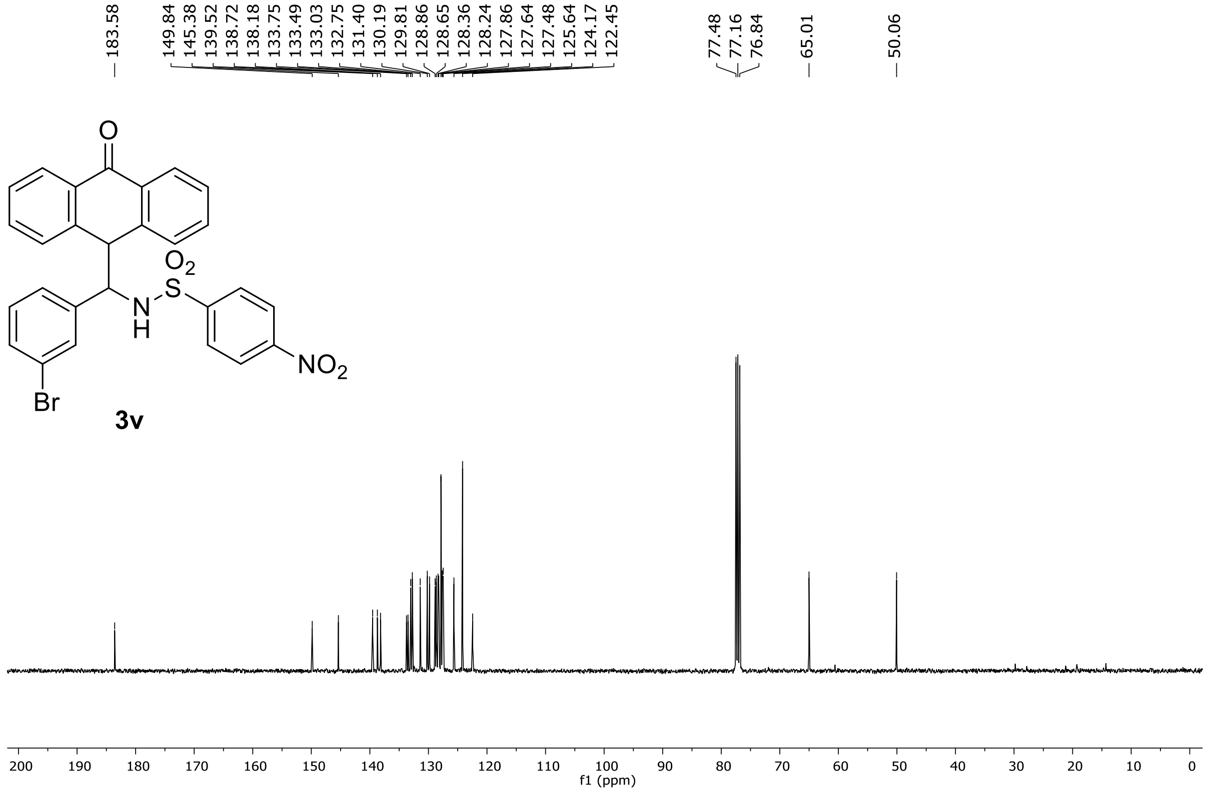
^{13}C{^{1}H} NMR spectrum of **3u** (100 MHz, $CDCl_3$):



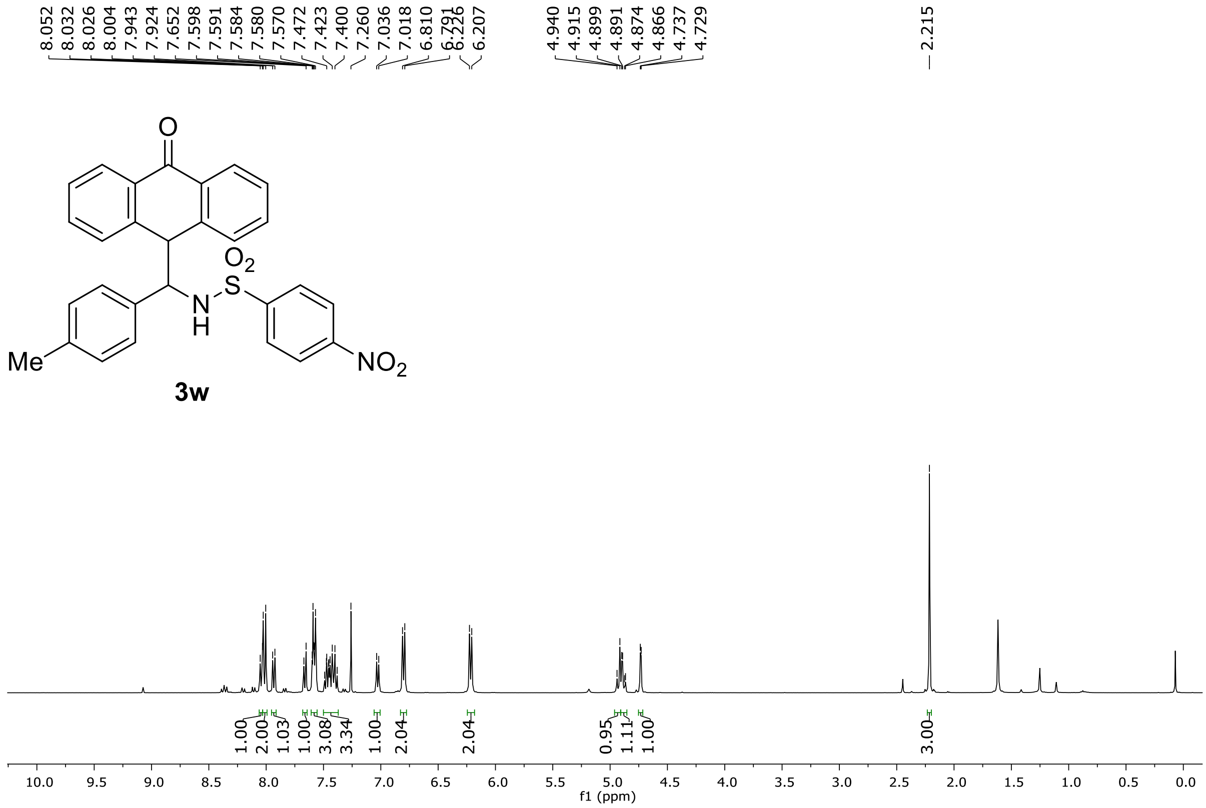
^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$):



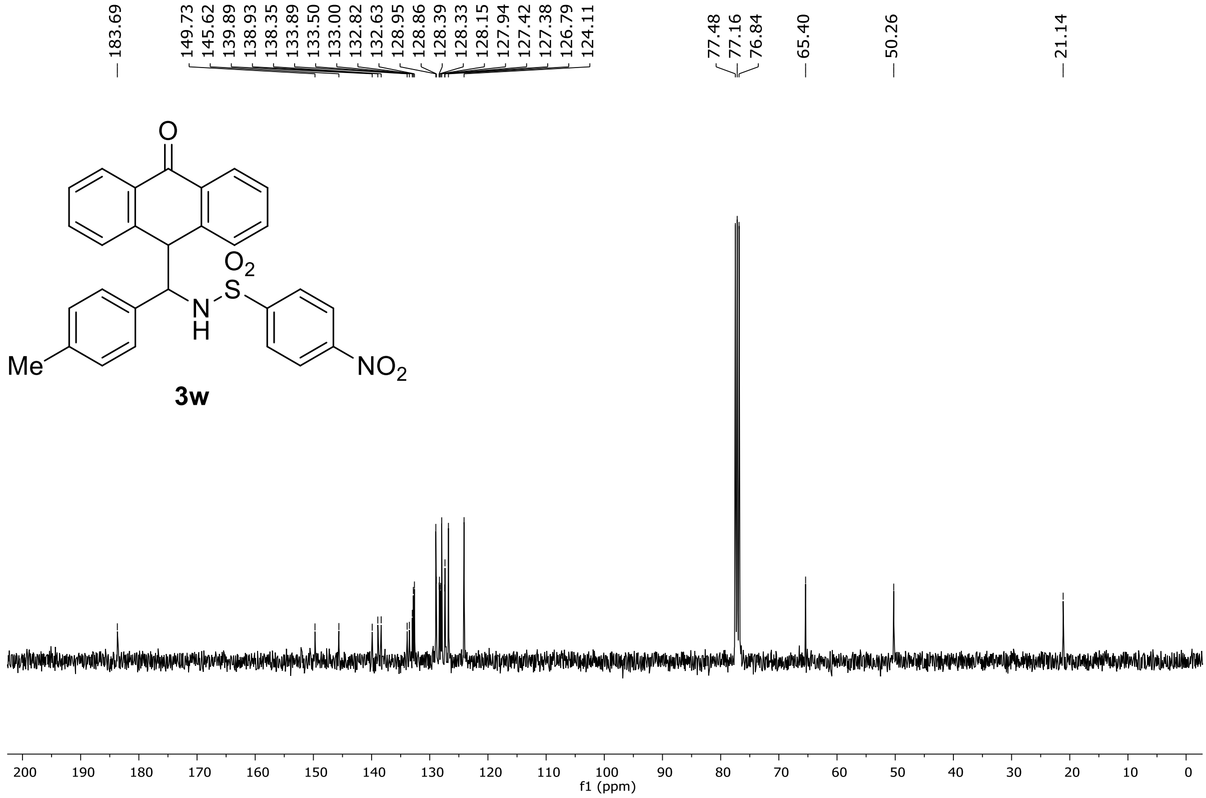
$^{13}C\{^{1}H\}$ NMR spectrum of **3v** (100 MHz, $CDCl_3$):



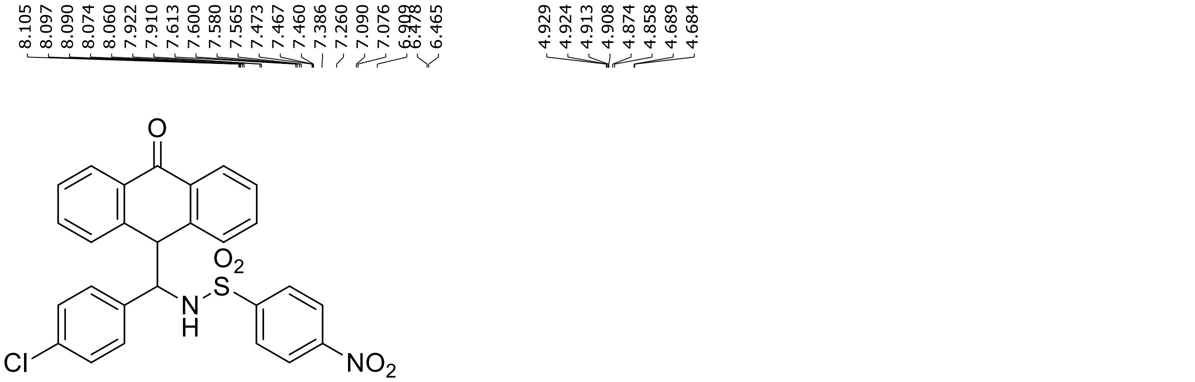
^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$):



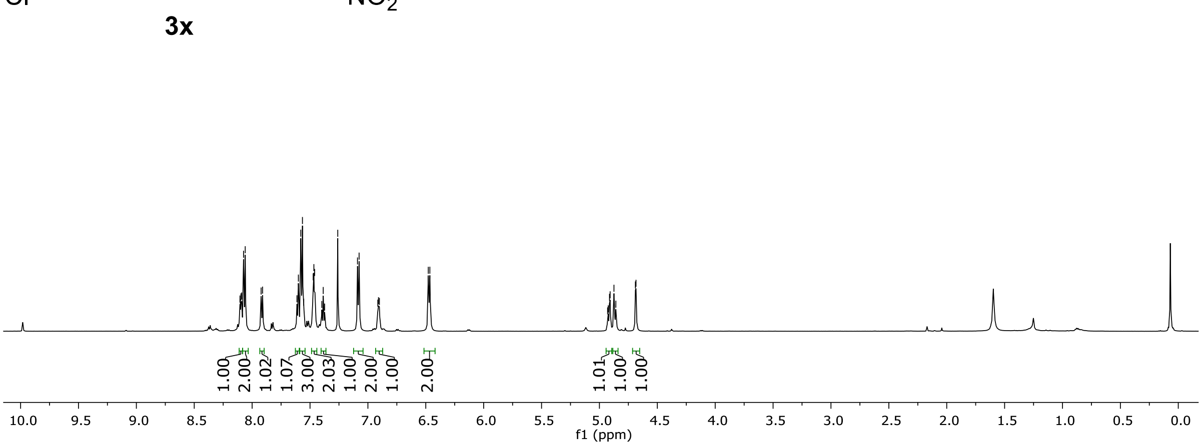
$^{13}C\{^1H\}$ NMR spectrum of **3w** (100 MHz, $CDCl_3$):



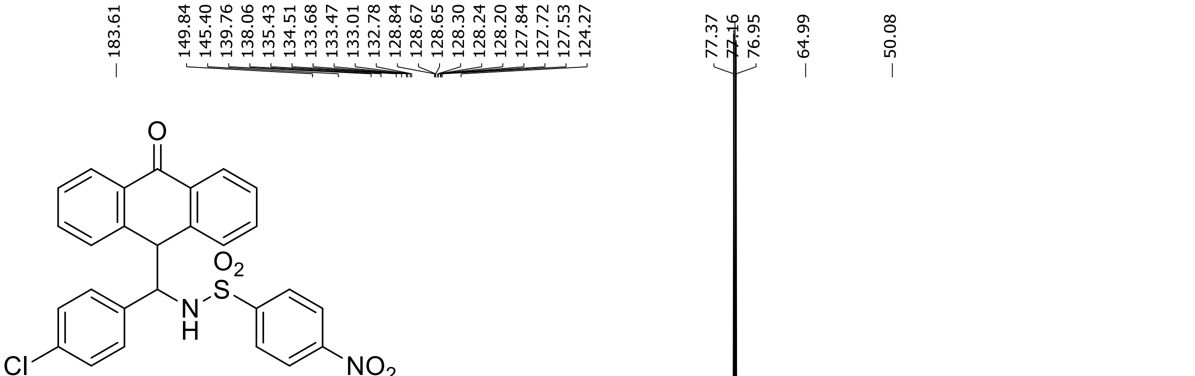
^{1}H NMR spectrum of **3x** (600 MHz, $CDCl_3$):



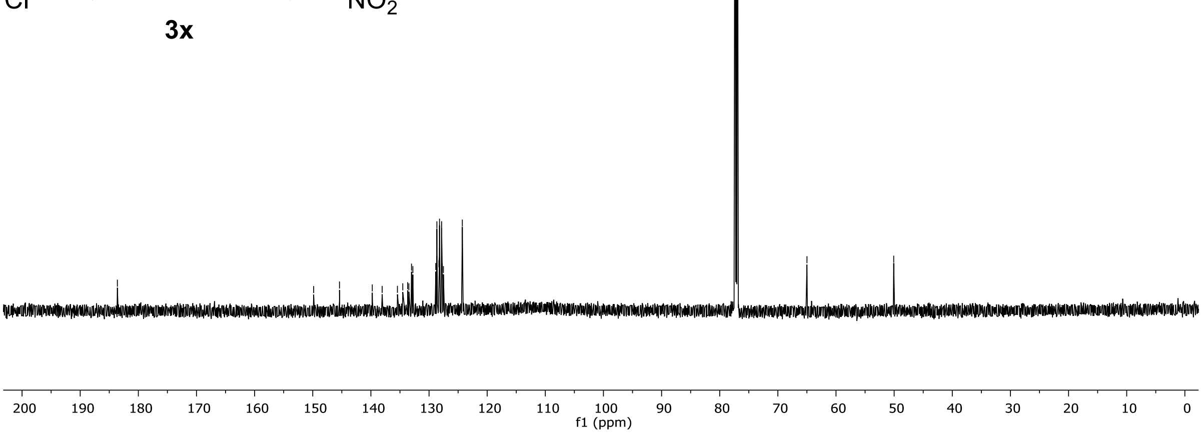
3x



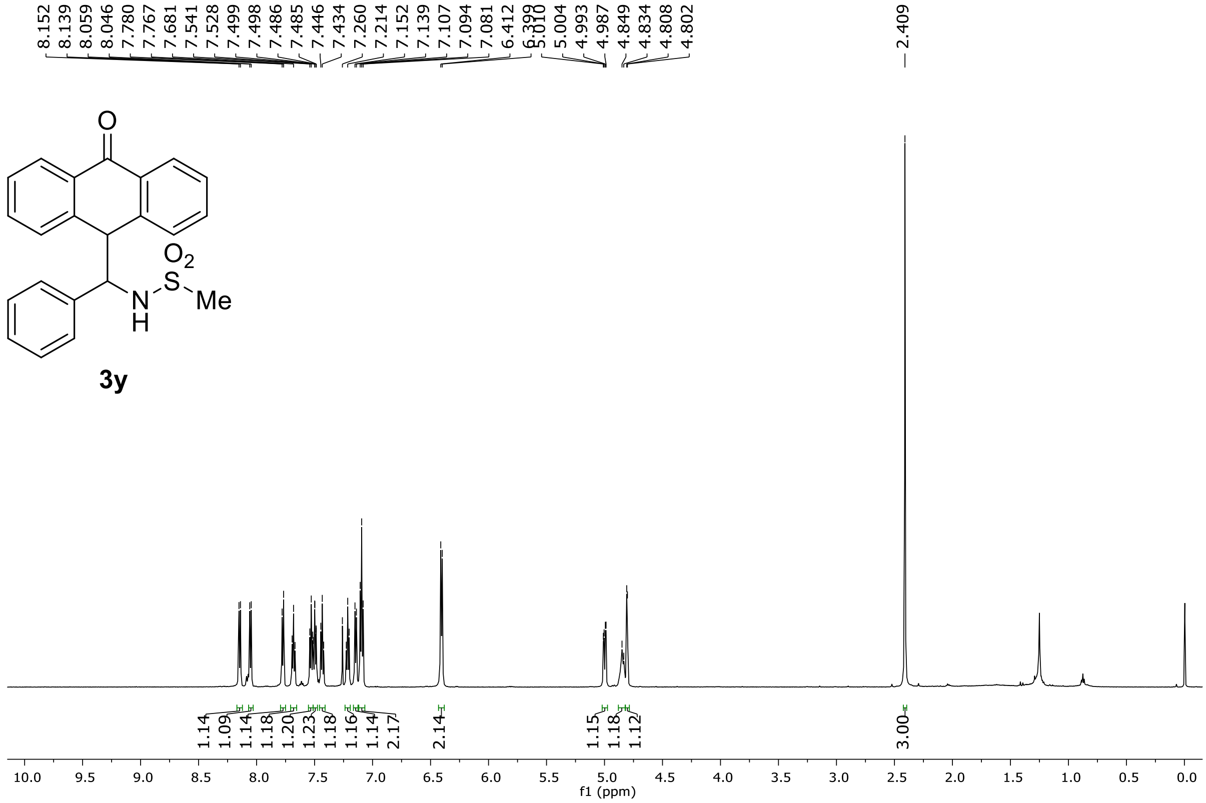
$^{13}C\{^{1}H\}$ NMR spectrum of **3x** (150 MHz, $CDCl_3$):



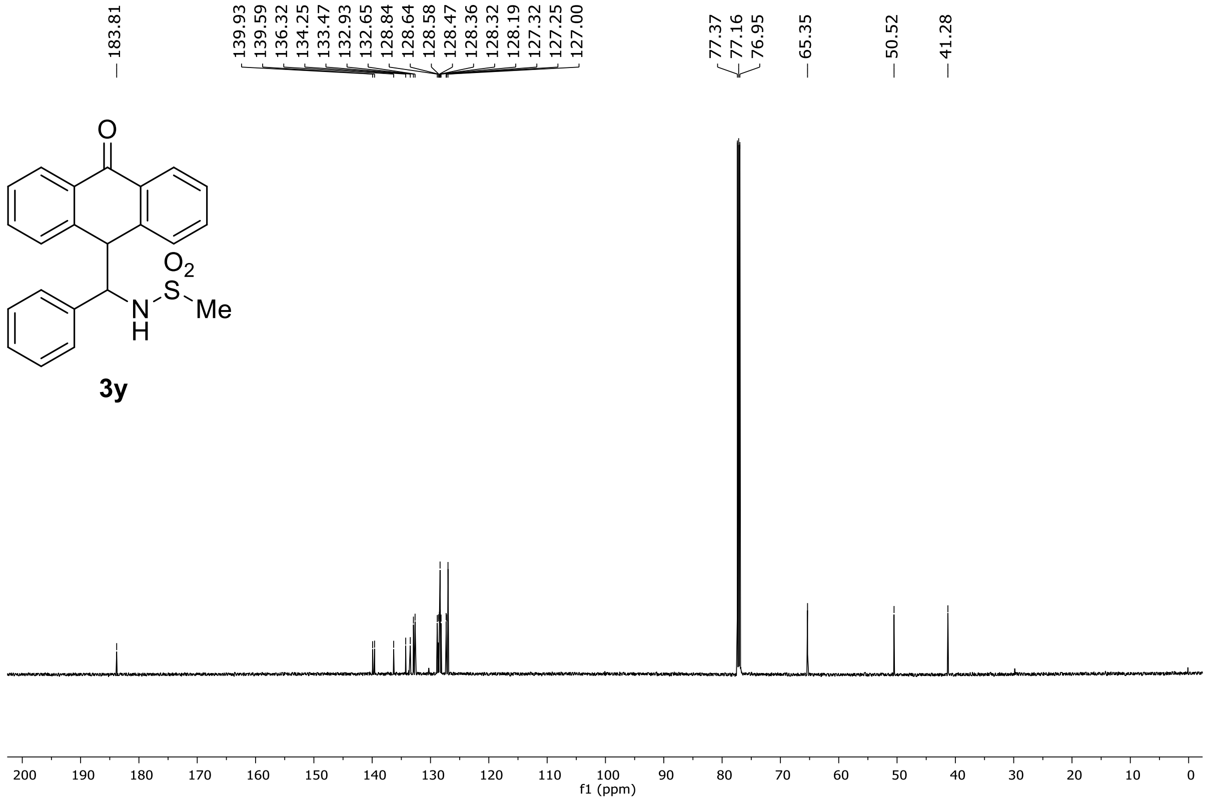
3x



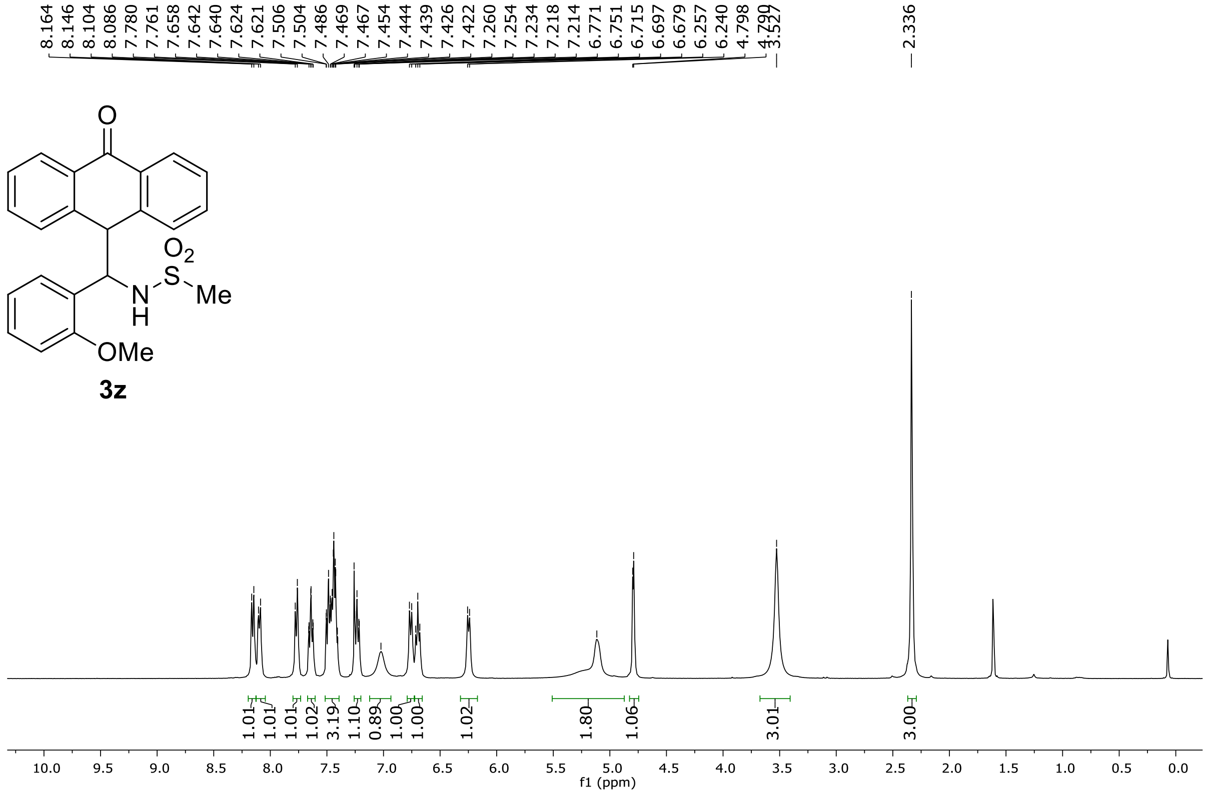
^{1}H NMR spectrum of **3y** (600 MHz, $CDCl_3$):



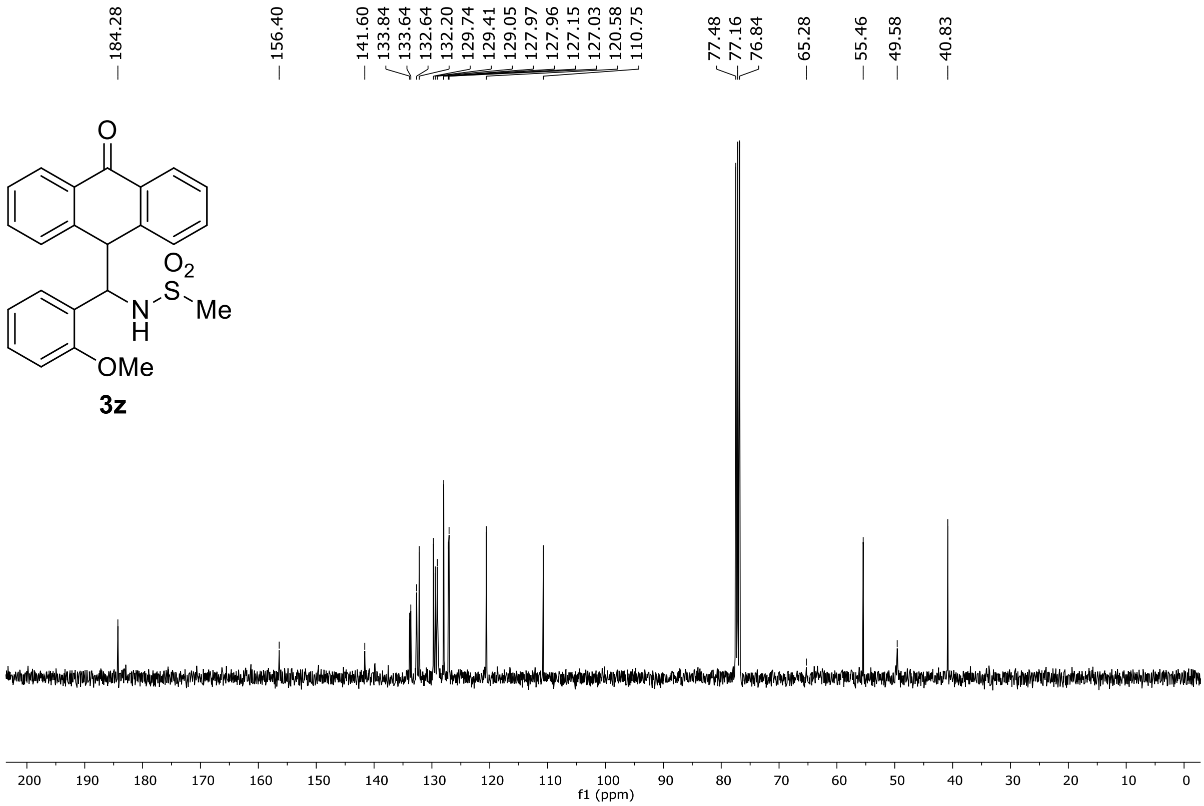
$^{13}C\{^1H\}$ NMR spectrum of **3y** (150 MHz, $CDCl_3$):



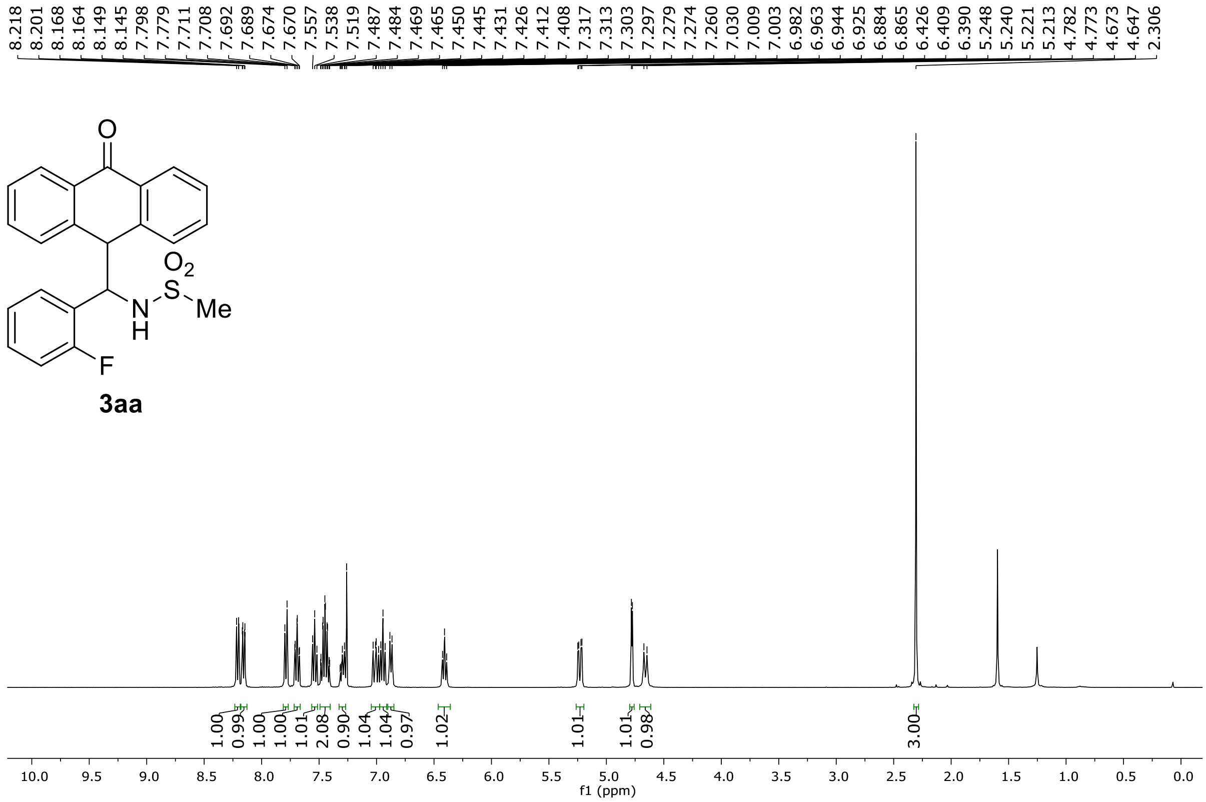
^{1}H NMR spectrum of **3z** (400 MHz, $CDCl_3$):



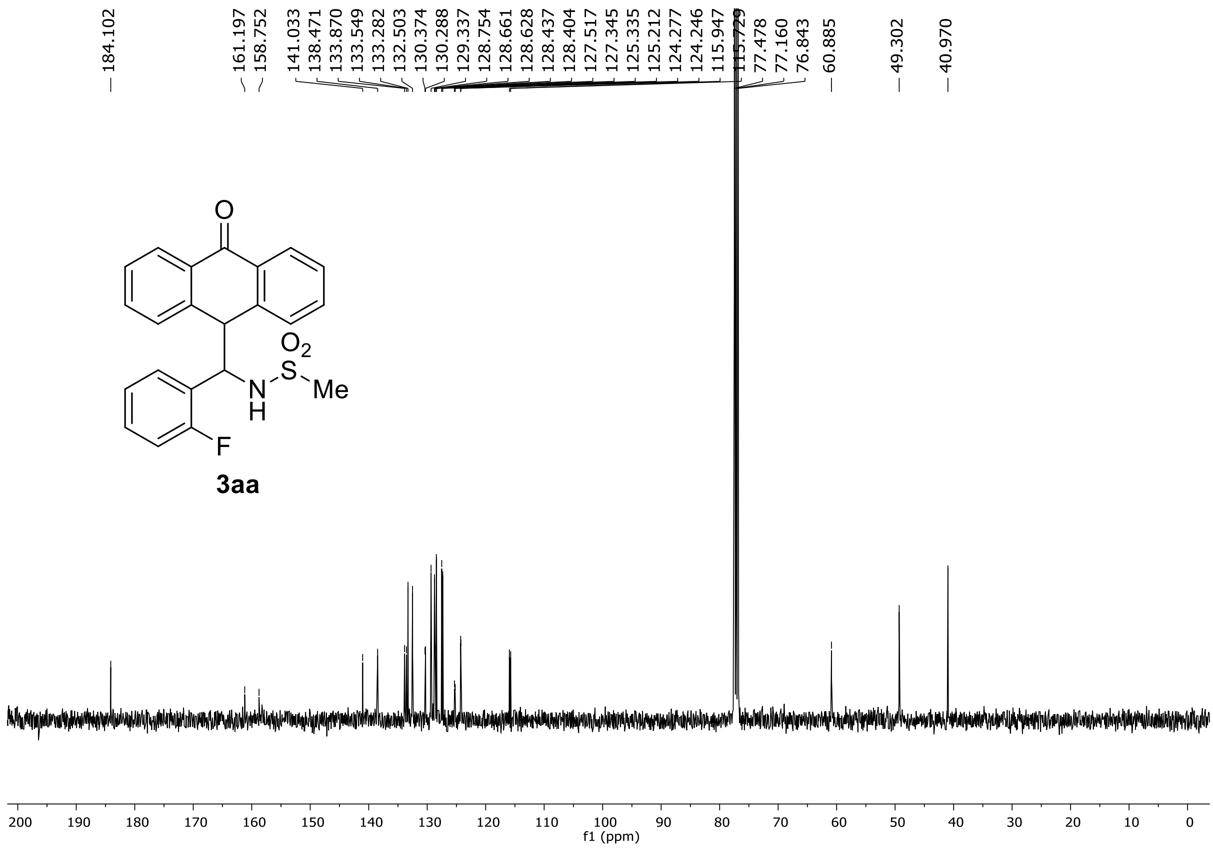
$^{13}C\{^{1}H\}$ NMR spectrum of **3z** (100 MHz, $CDCl_3$):



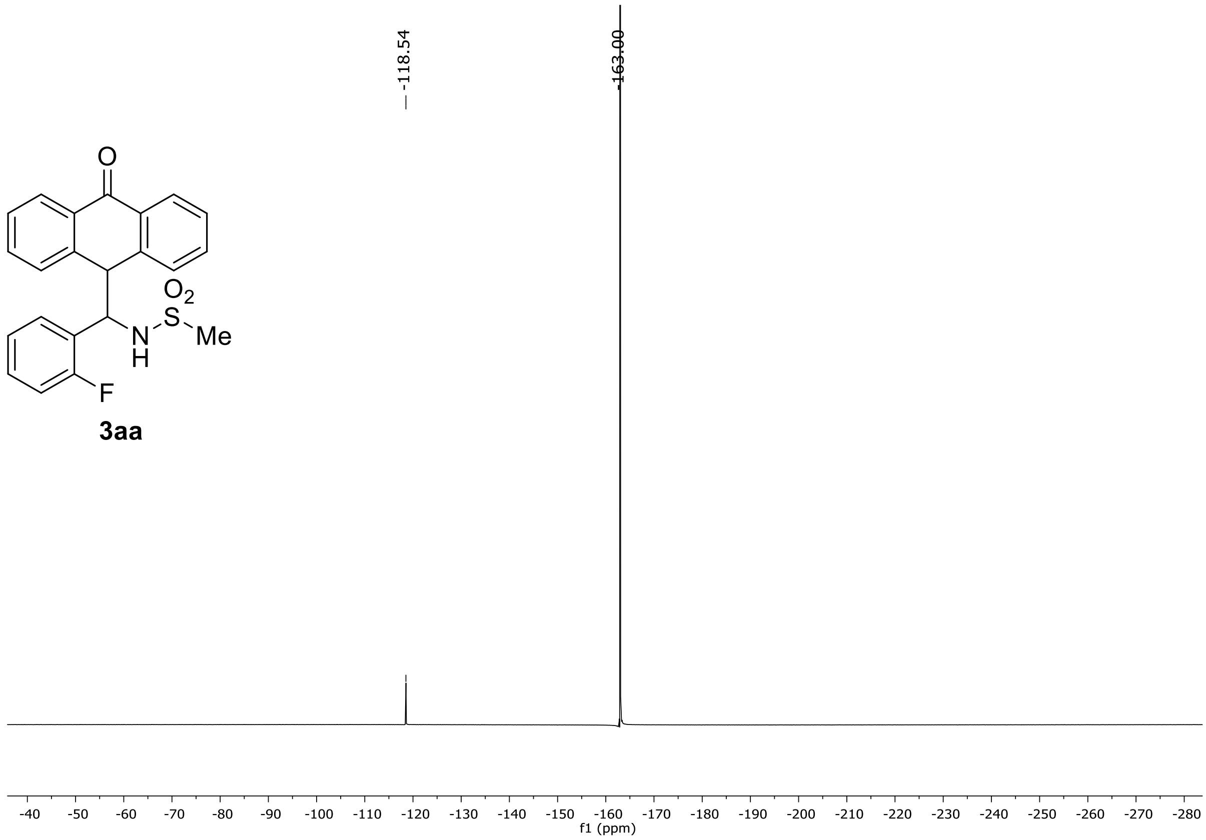
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$):



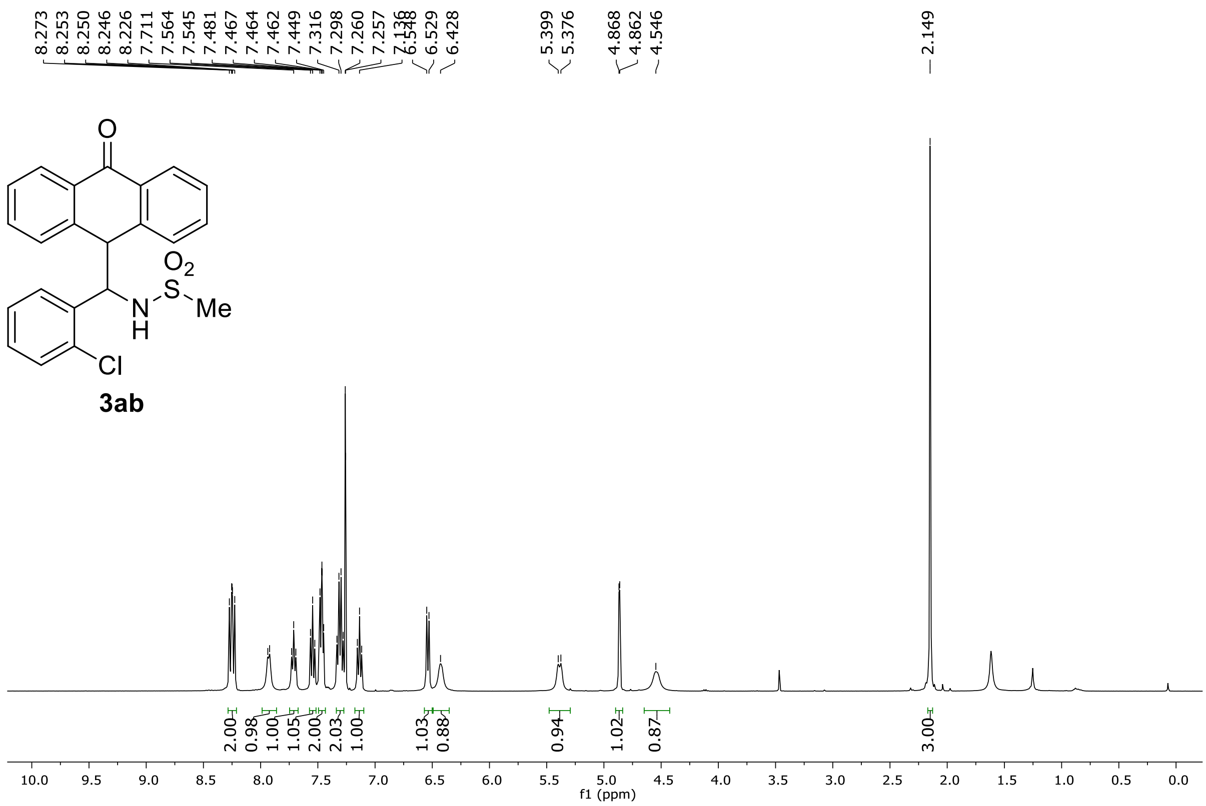
$^{13}C\{^{1}H\}$ NMR spectrum of **3aa** (100 MHz, $CDCl_3$):



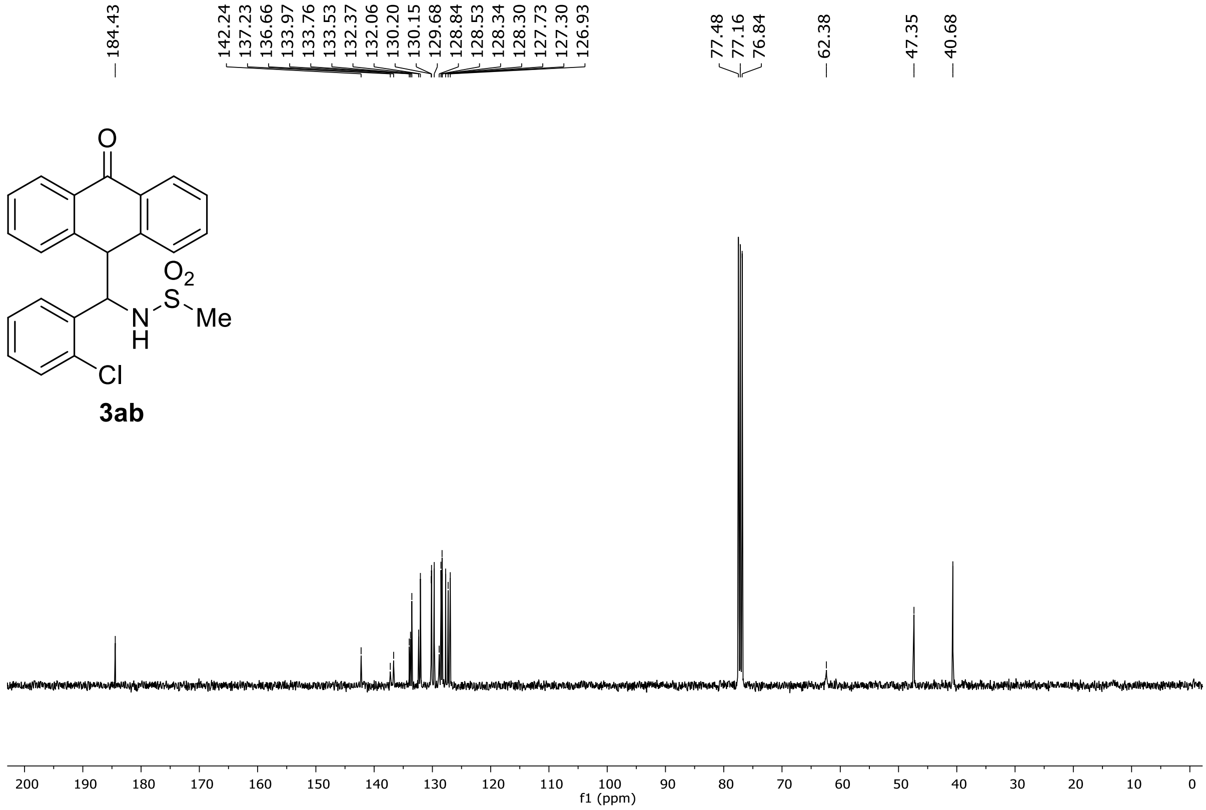
^{19}F NMR spectrum of **3aa** (376 MHz, $CDCl_3$):



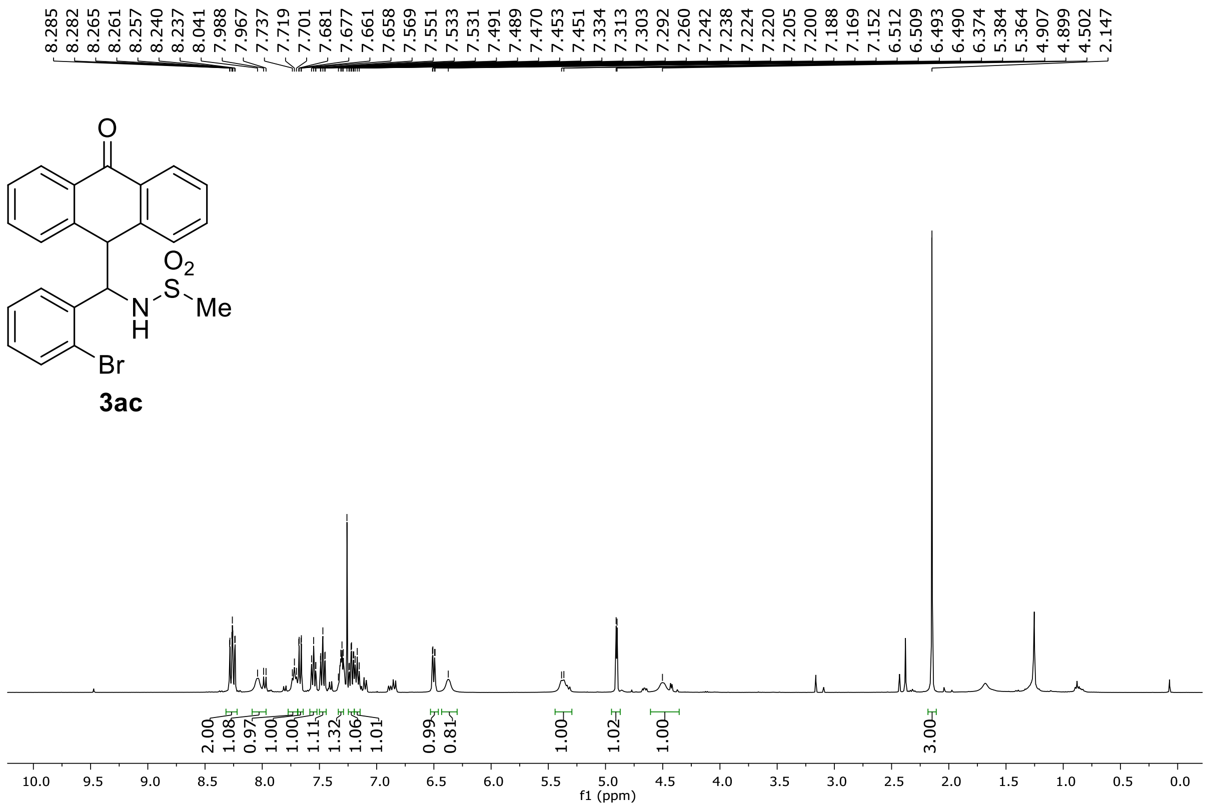
^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$):



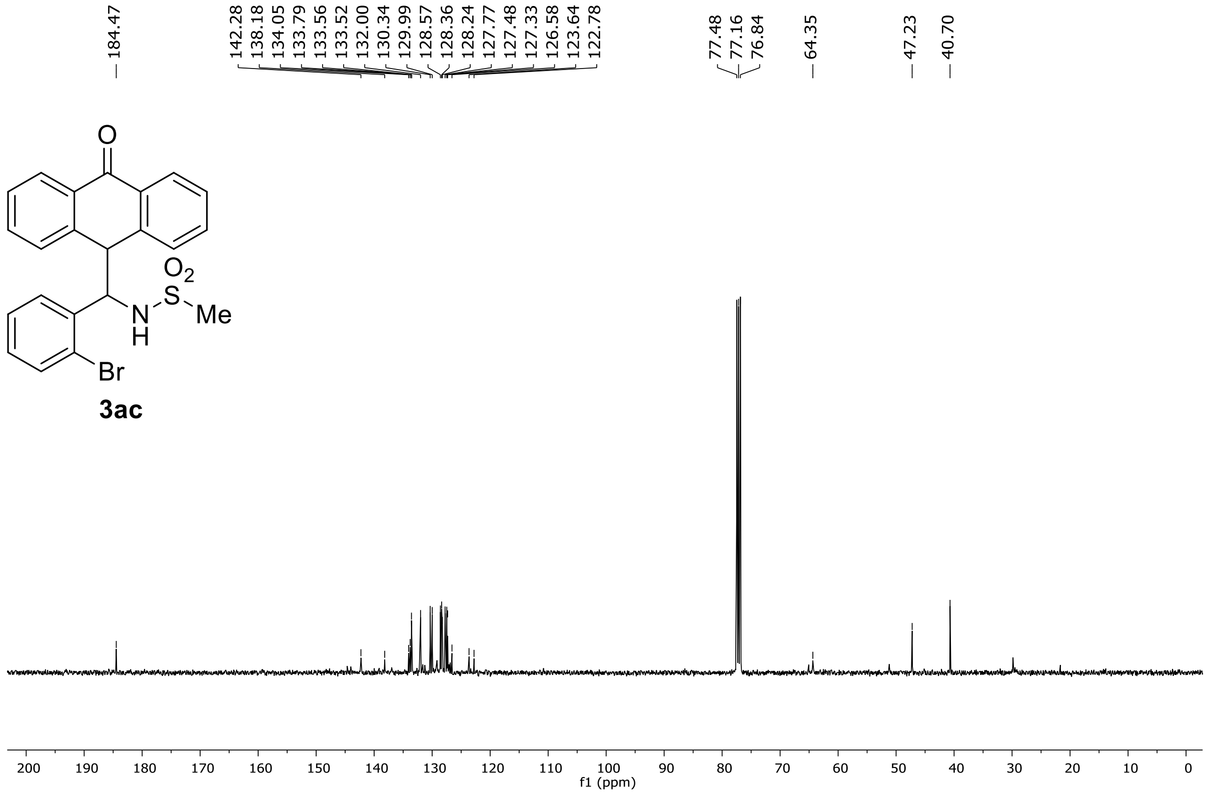
$^{13}C\{^{1}H\}$ NMR spectrum of **3ab** (100 MHz, $CDCl_3$):



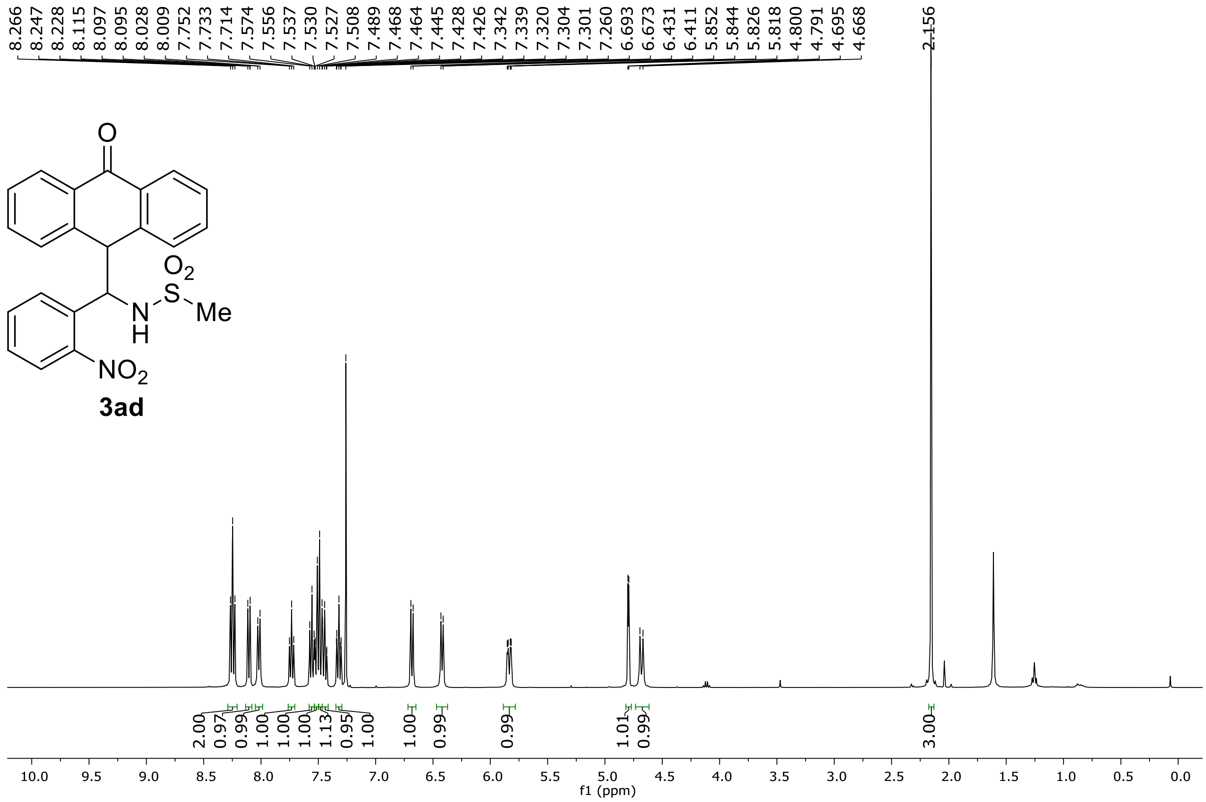
^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$):



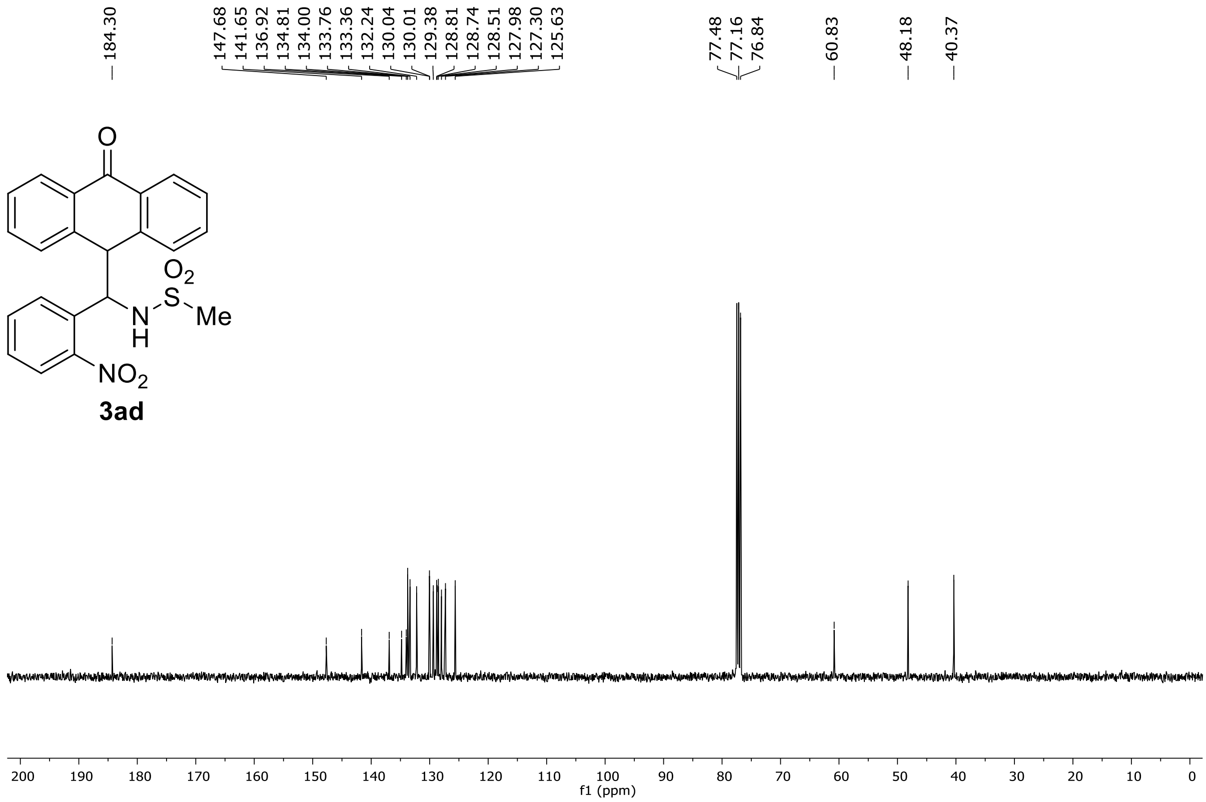
$^{13}C\{^1H\}$ NMR spectrum of **3ac** (100 MHz, $CDCl_3$):



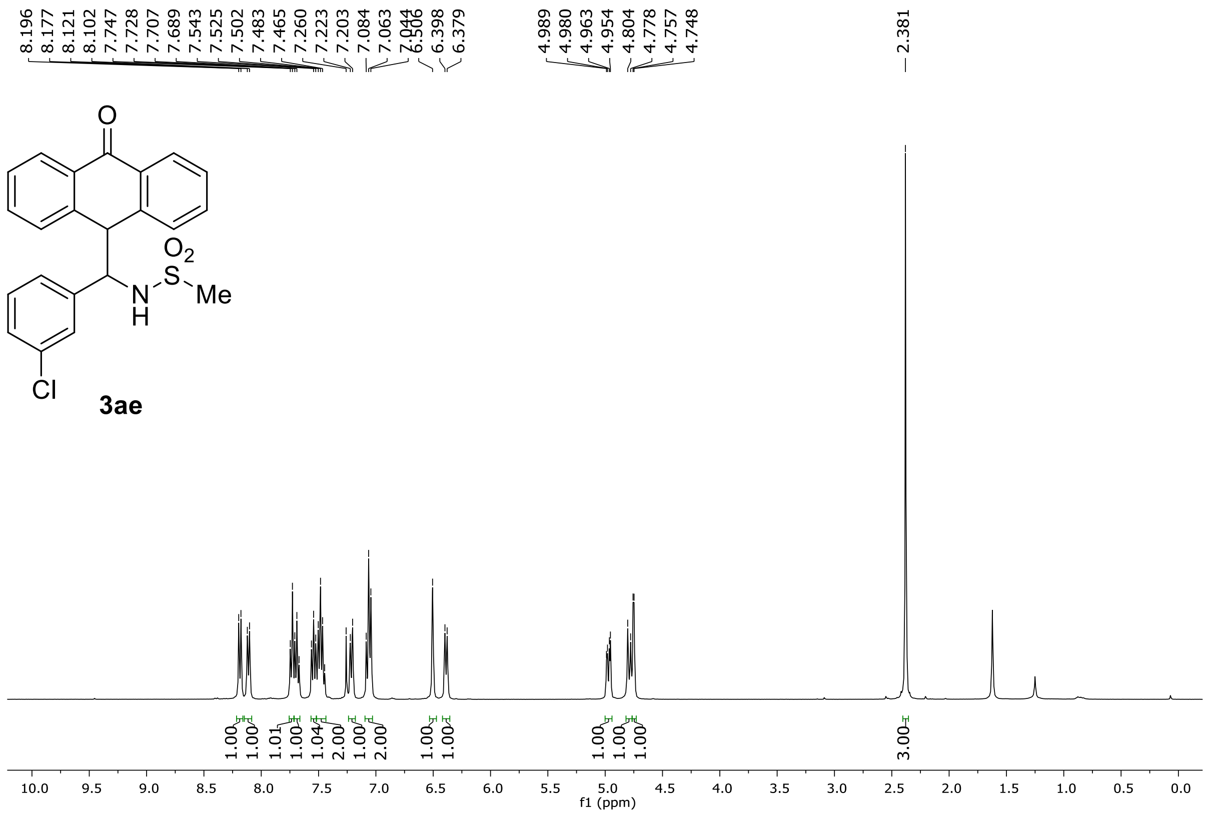
^1H NMR spectrum of **3ad** (400 MHz, $CDCl_3$):



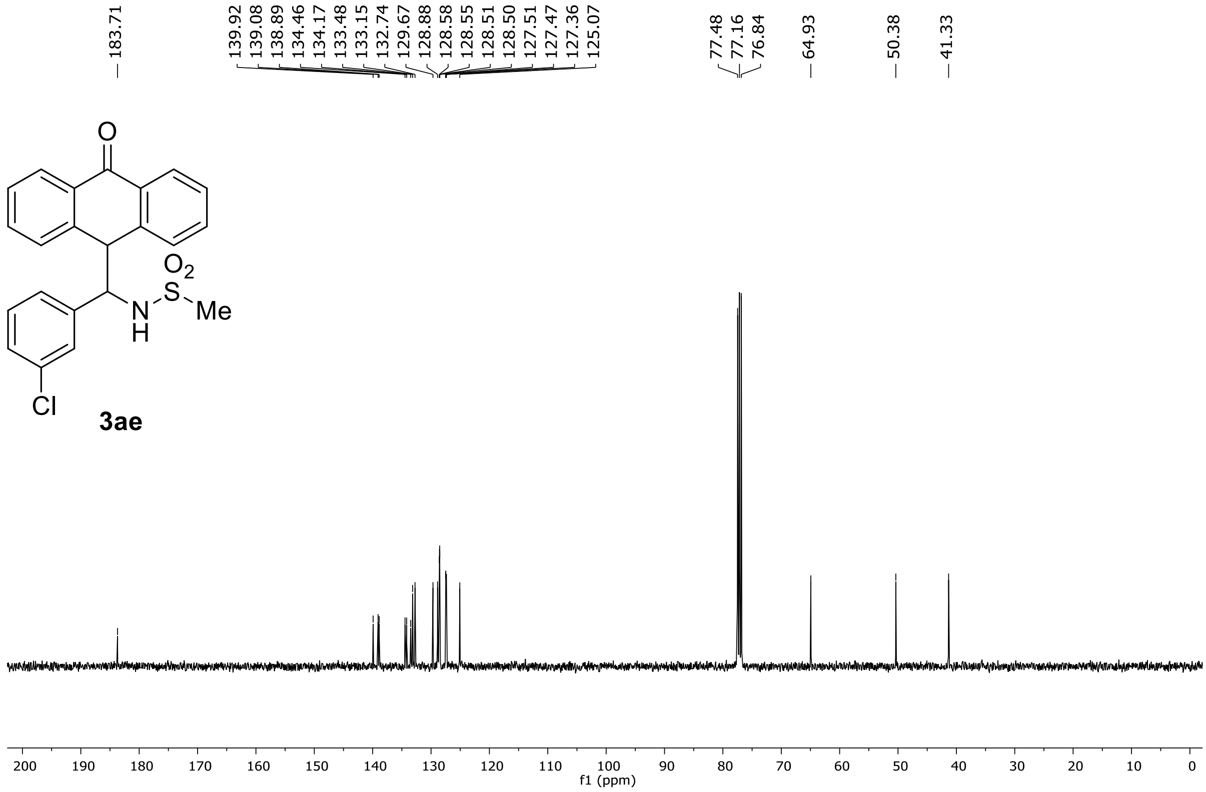
$^{13}C\{^{1}H\}$ NMR spectrum of **3ad** (100 MHz, $CDCl_3$):



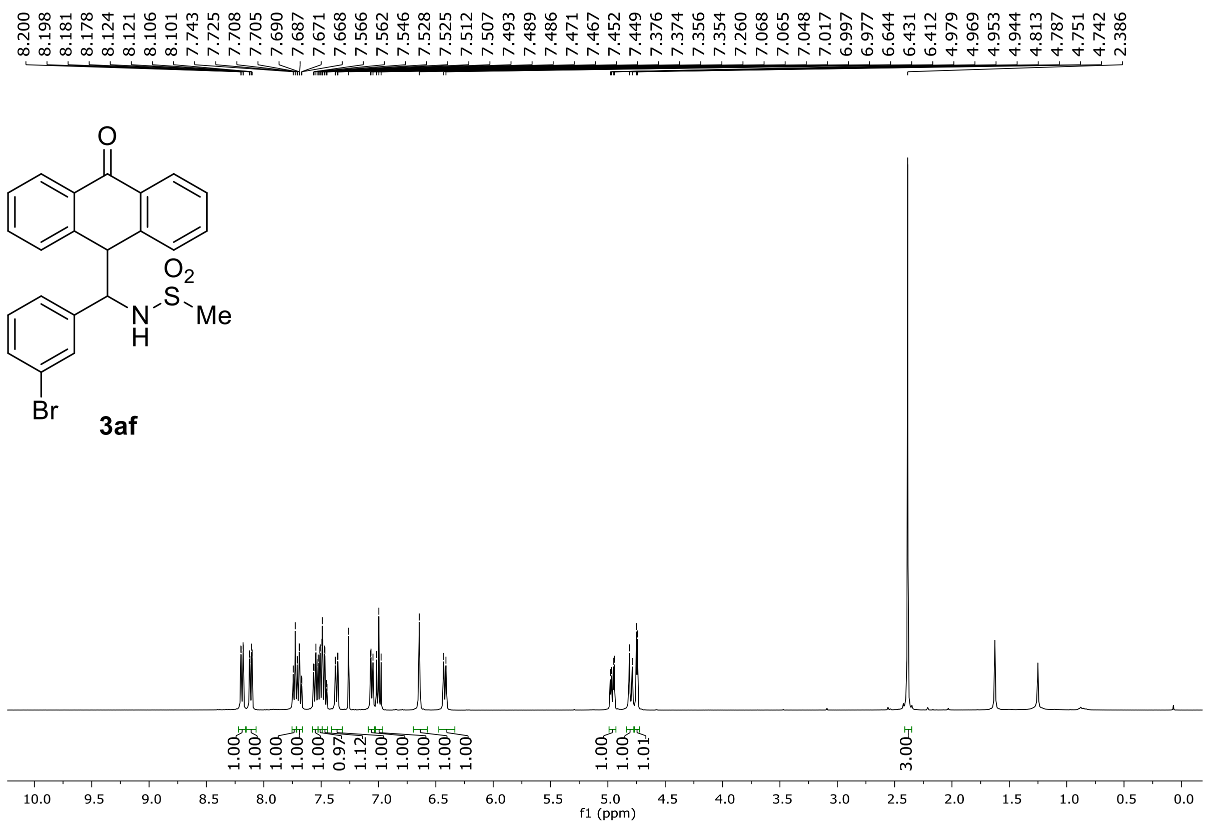
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$):



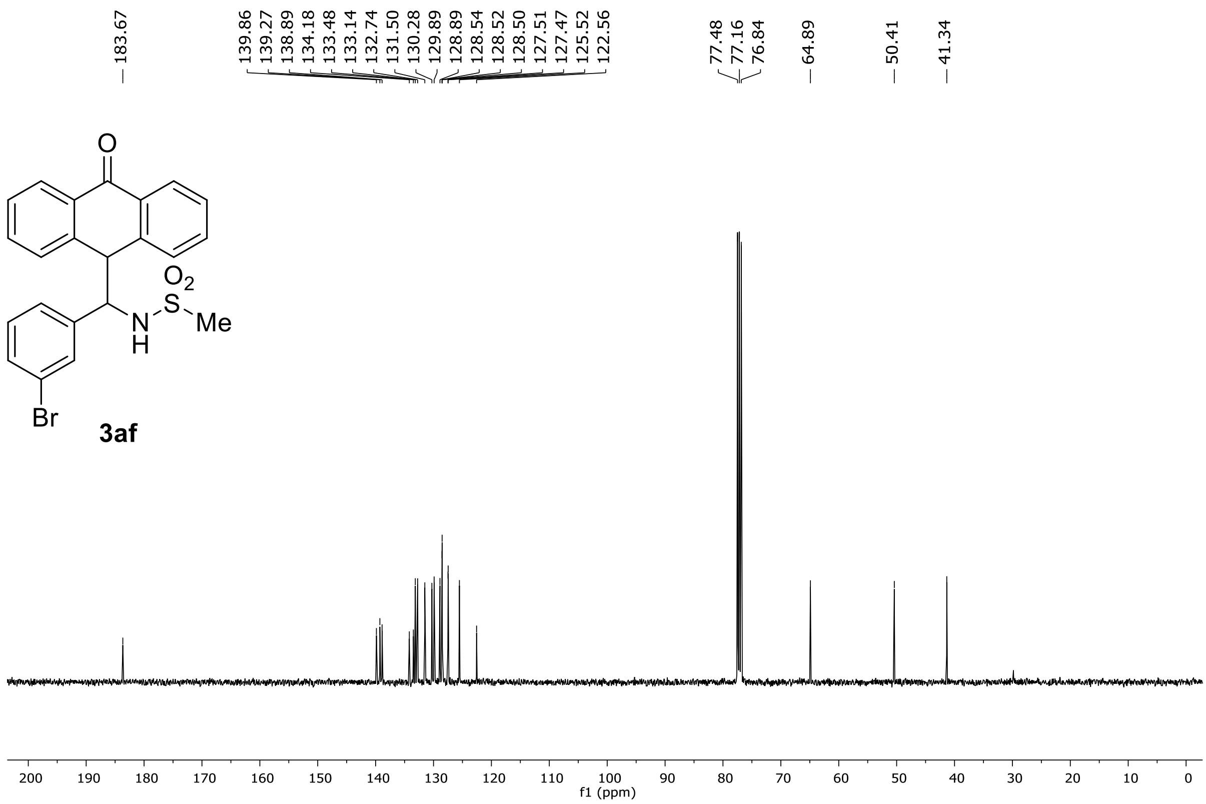
$^{13}C\{^{1}H\}$ NMR spectrum of **3ae** (100 MHz, $CDCl_3$):



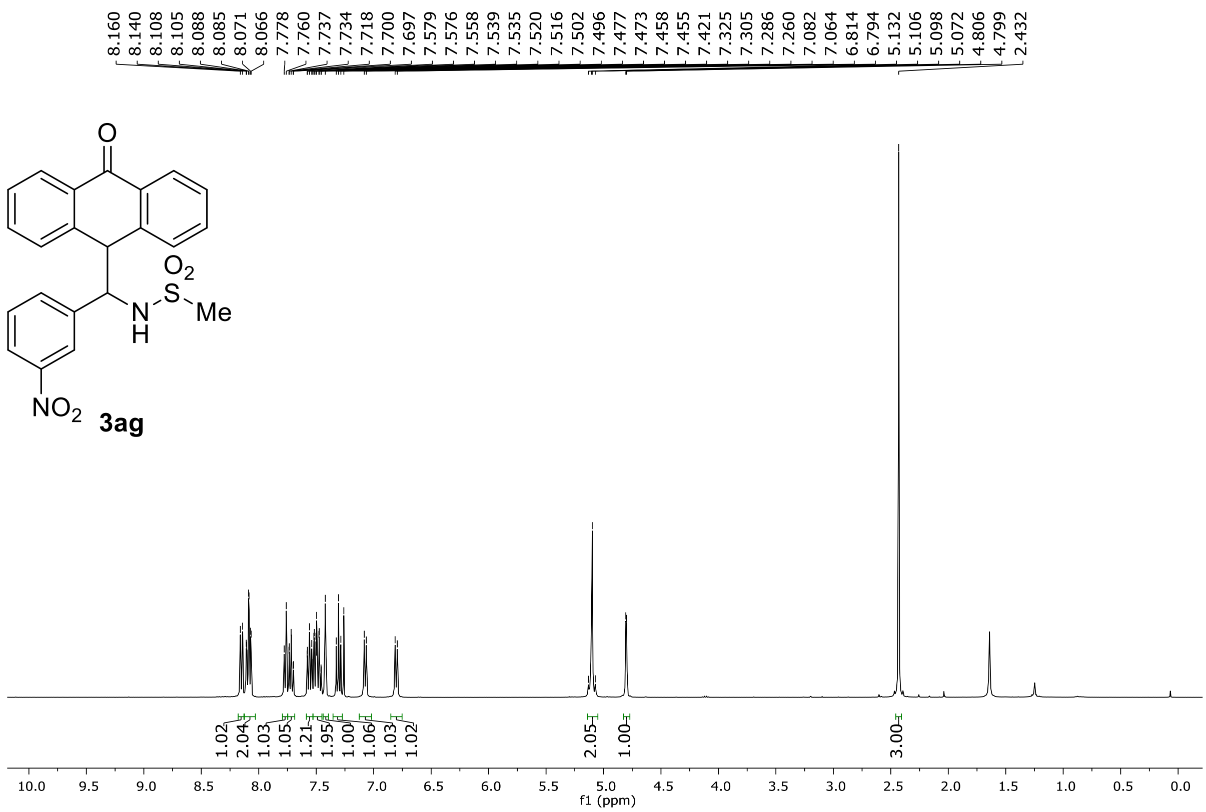
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$):



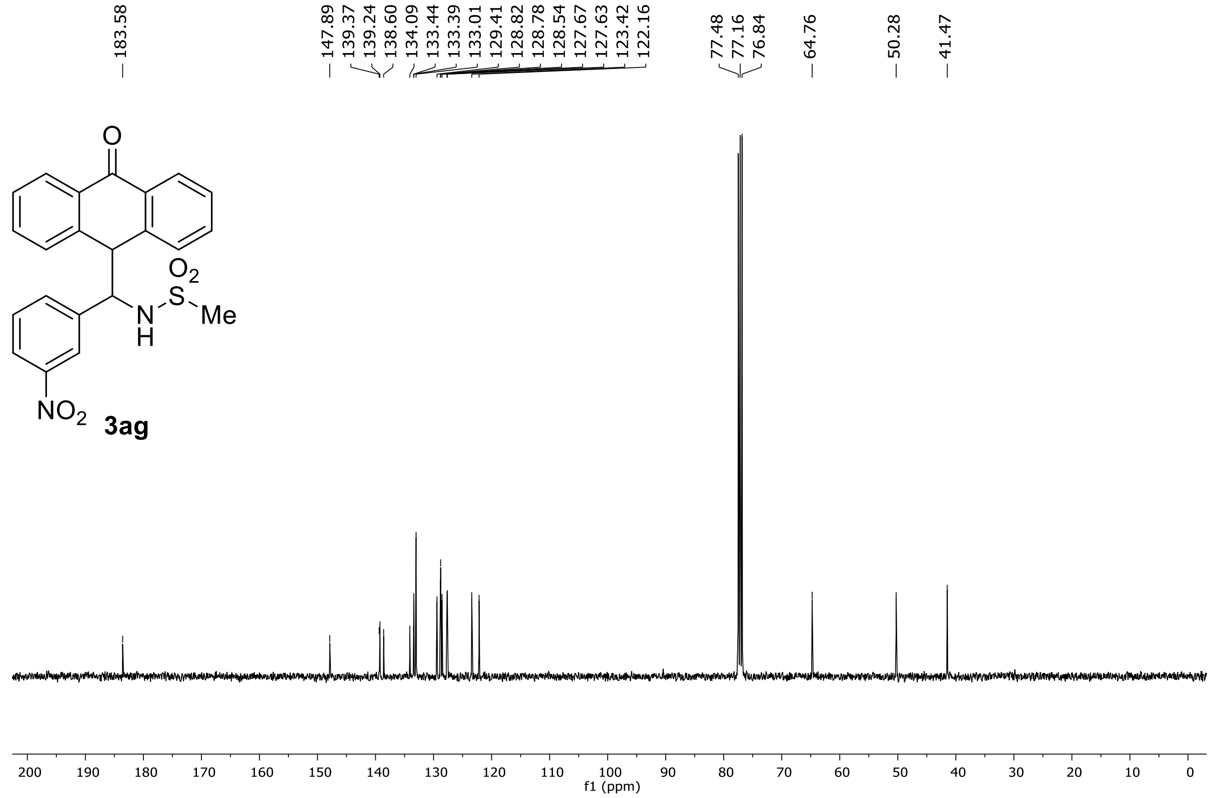
$^{13}C\{^{1}H\}$ NMR spectrum of **3af** (100 MHz, $CDCl_3$):



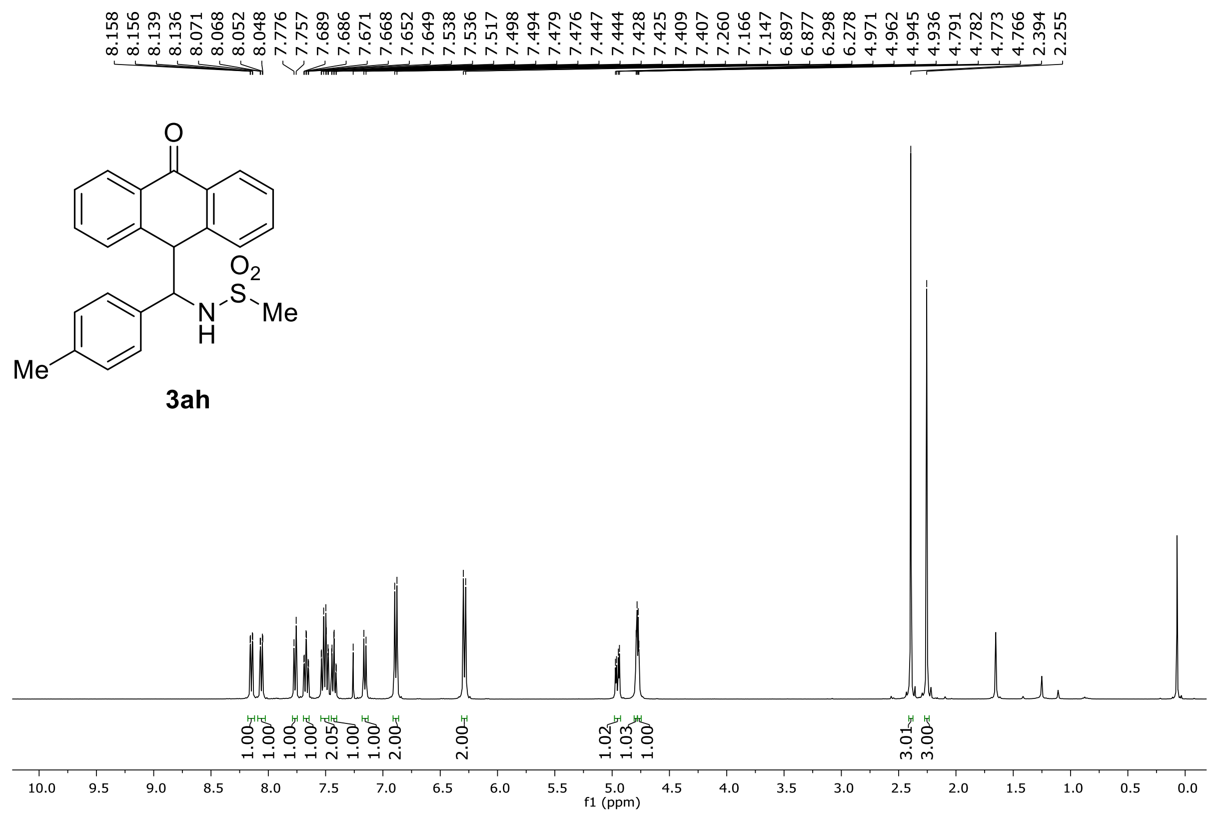
^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$):



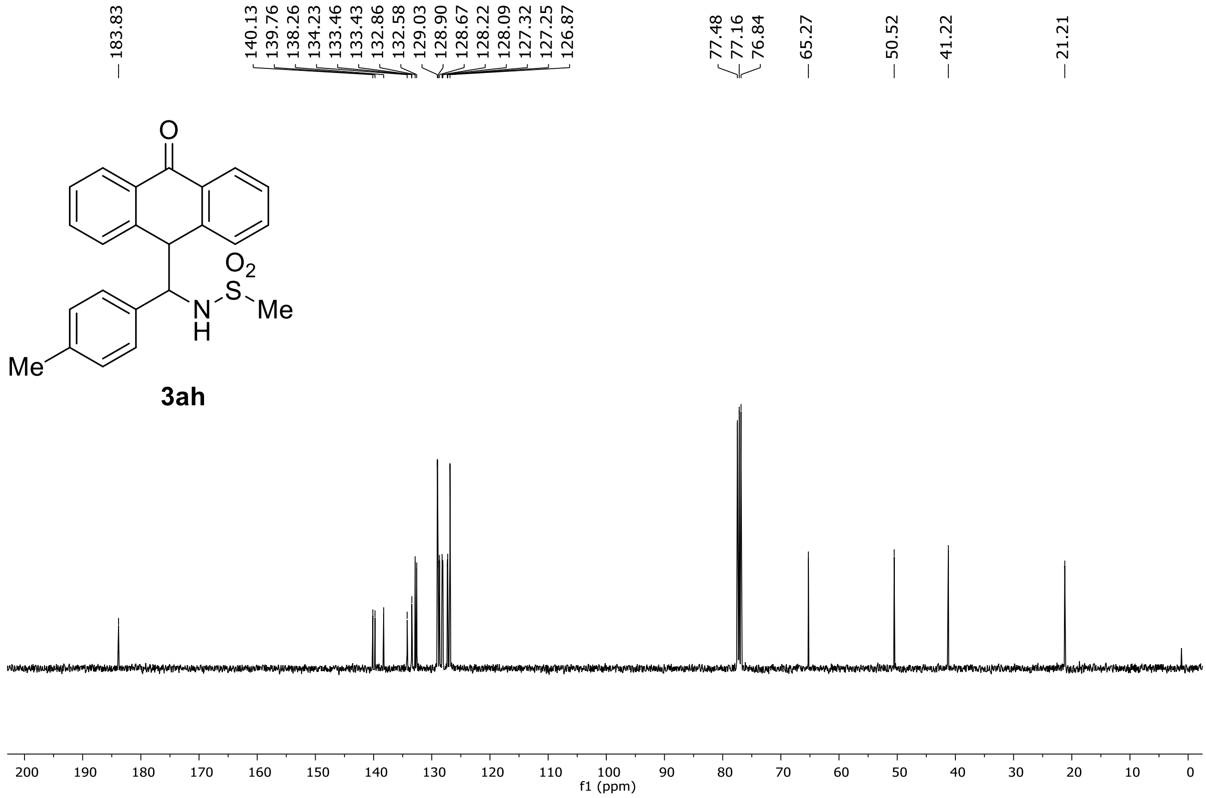
$^{13}C\{^1H\}$ NMR spectrum of **3ag** (100 MHz, $CDCl_3$):



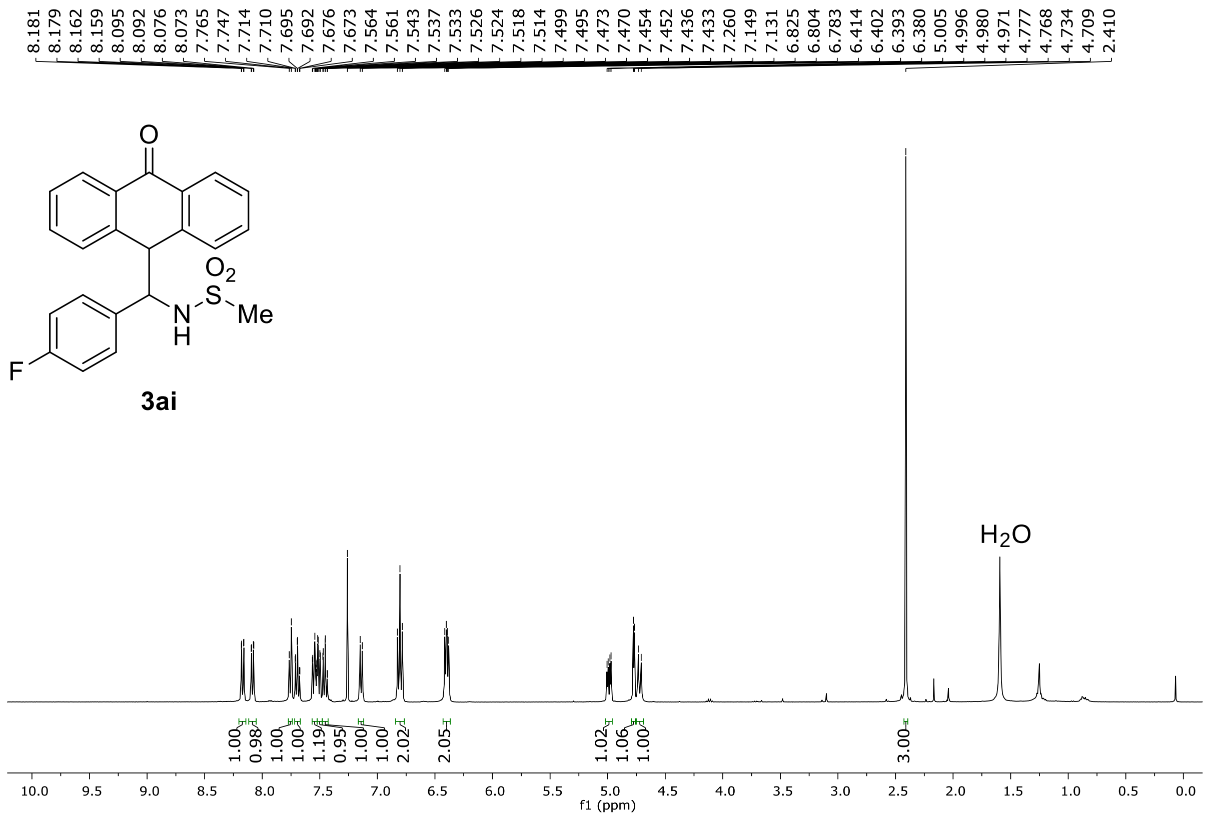
^1H NMR spectrum of **3ah** (400 MHz, $CDCl_3$):



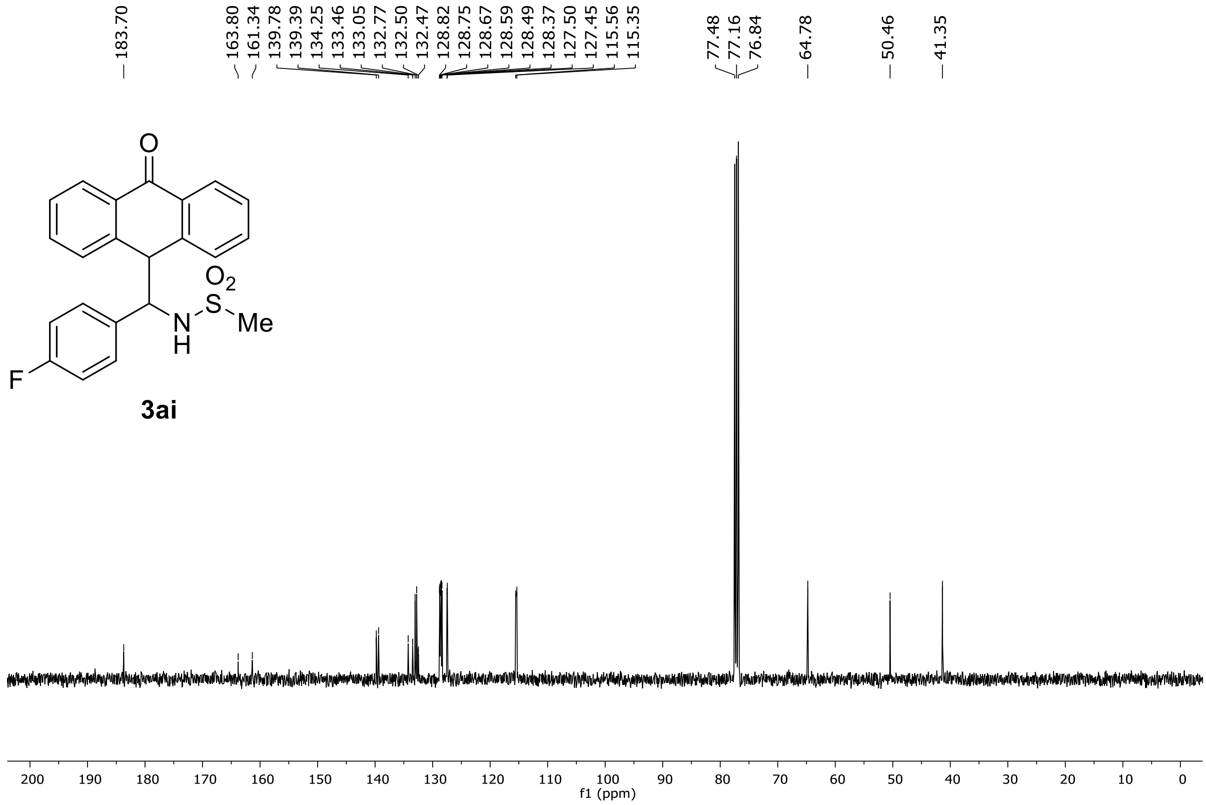
$^{13}C\{^{1}H\}$ NMR spectrum of **3ah** (100 MHz, $CDCl_3$):



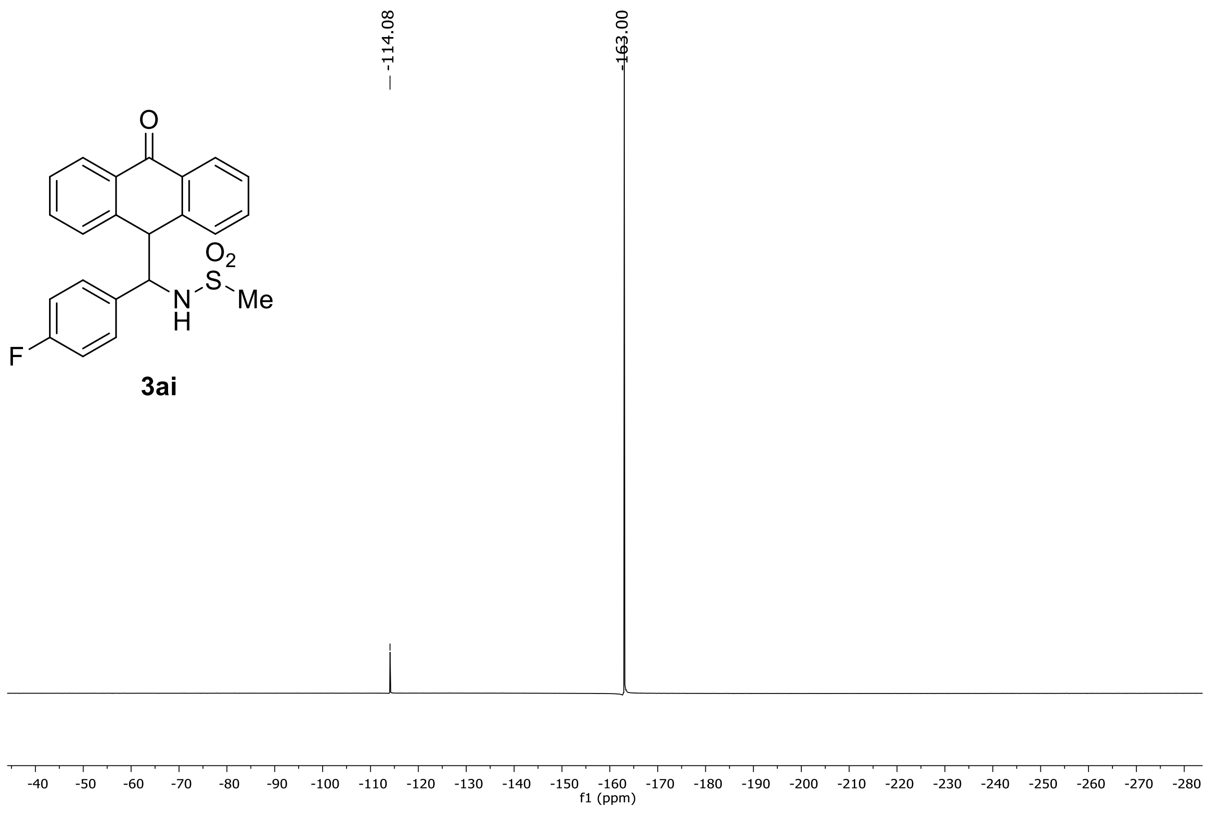
^{1}H NMR spectrum of **3ai** (400 MHz, $CDCl_3$):



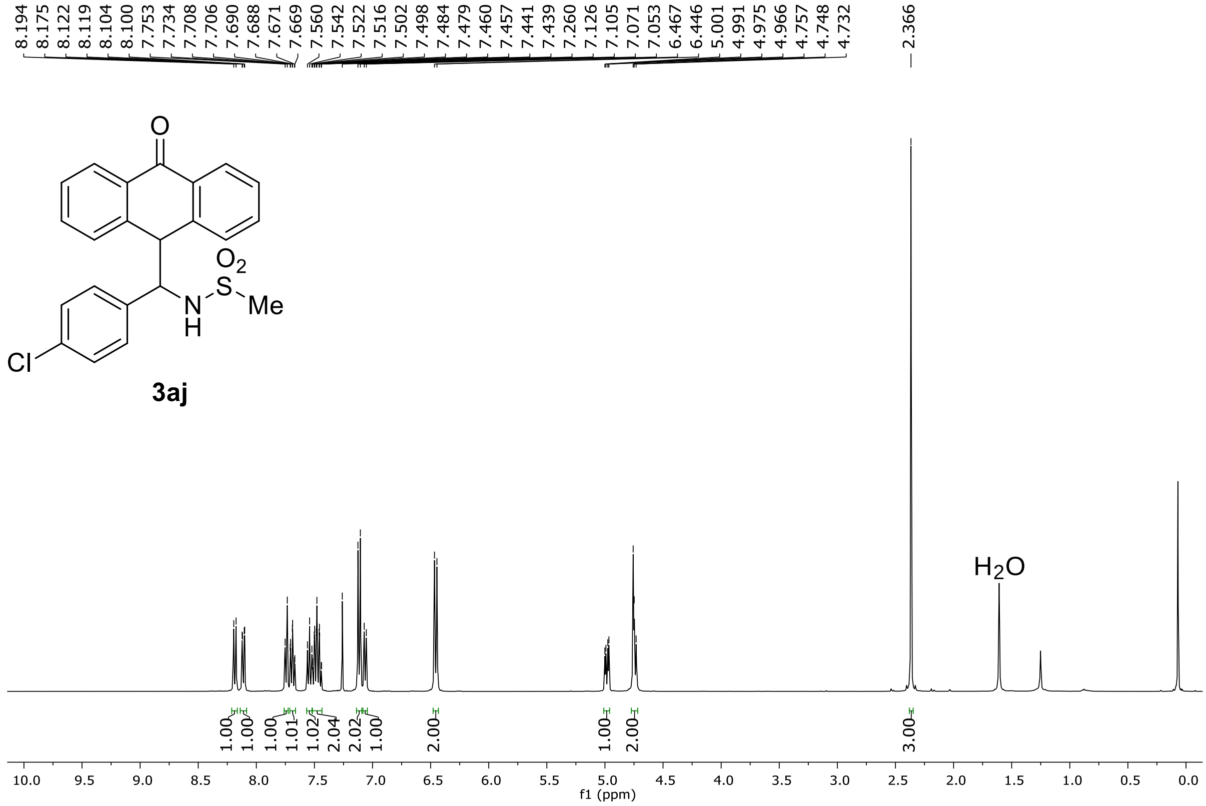
$^{13}C\{^1H\}$ NMR spectrum of **3ai** (100 MHz, $CDCl_3$):



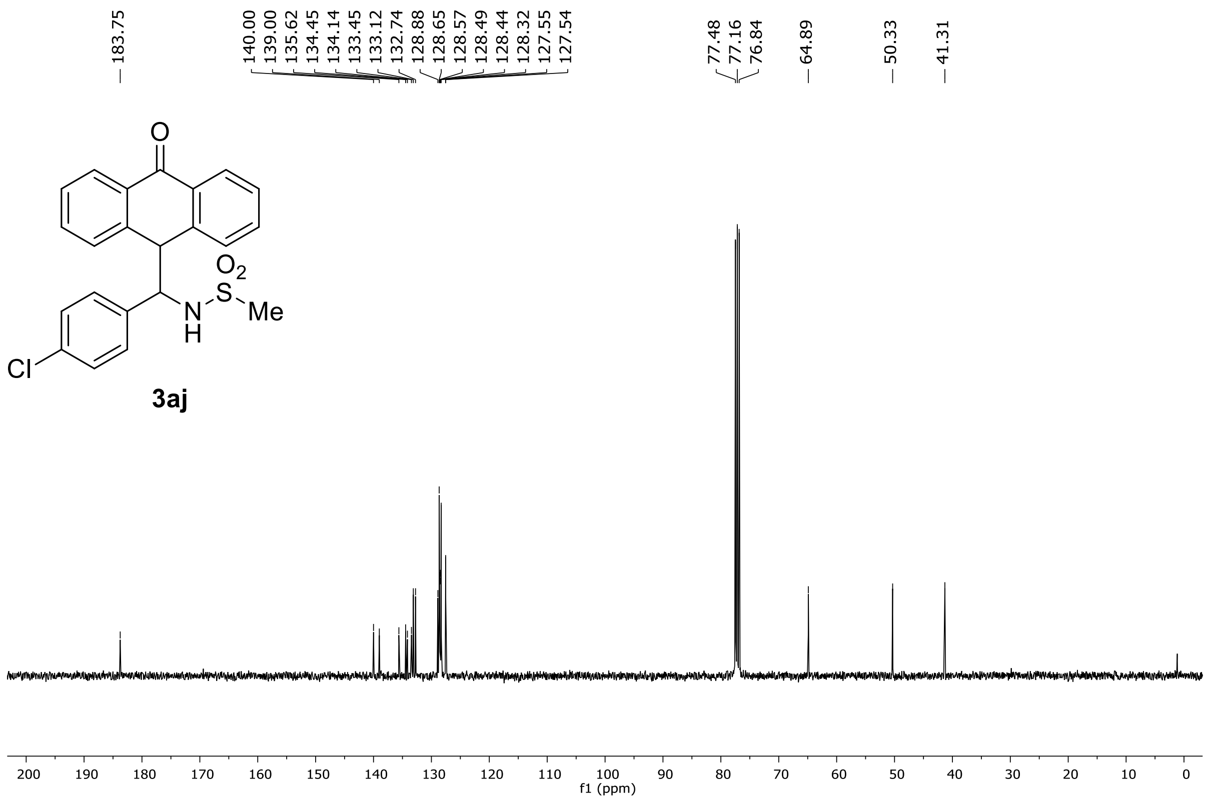
^{19}F NMR spectrum of **3ai** (376 MHz, $CDCl_3$):



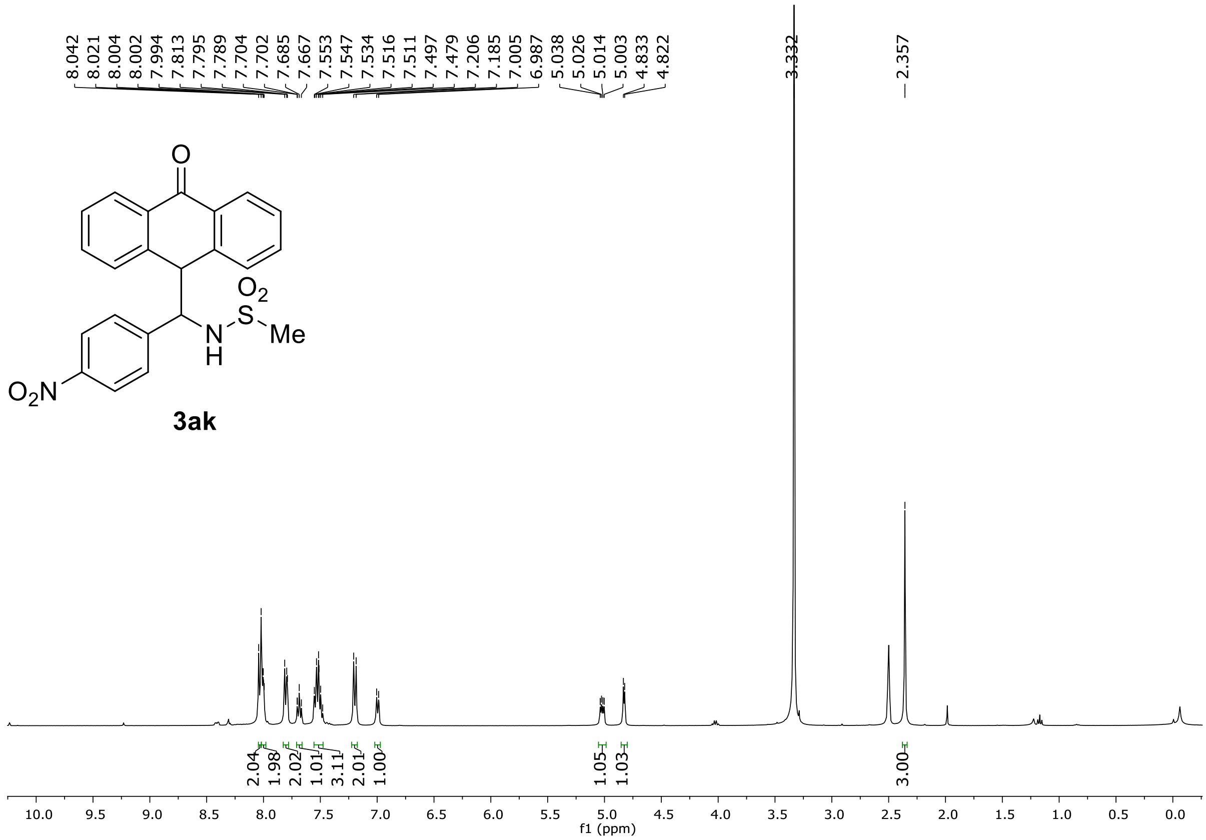
^{1}H NMR spectrum of **3aj** (400 MHz, $CDCl_3$):



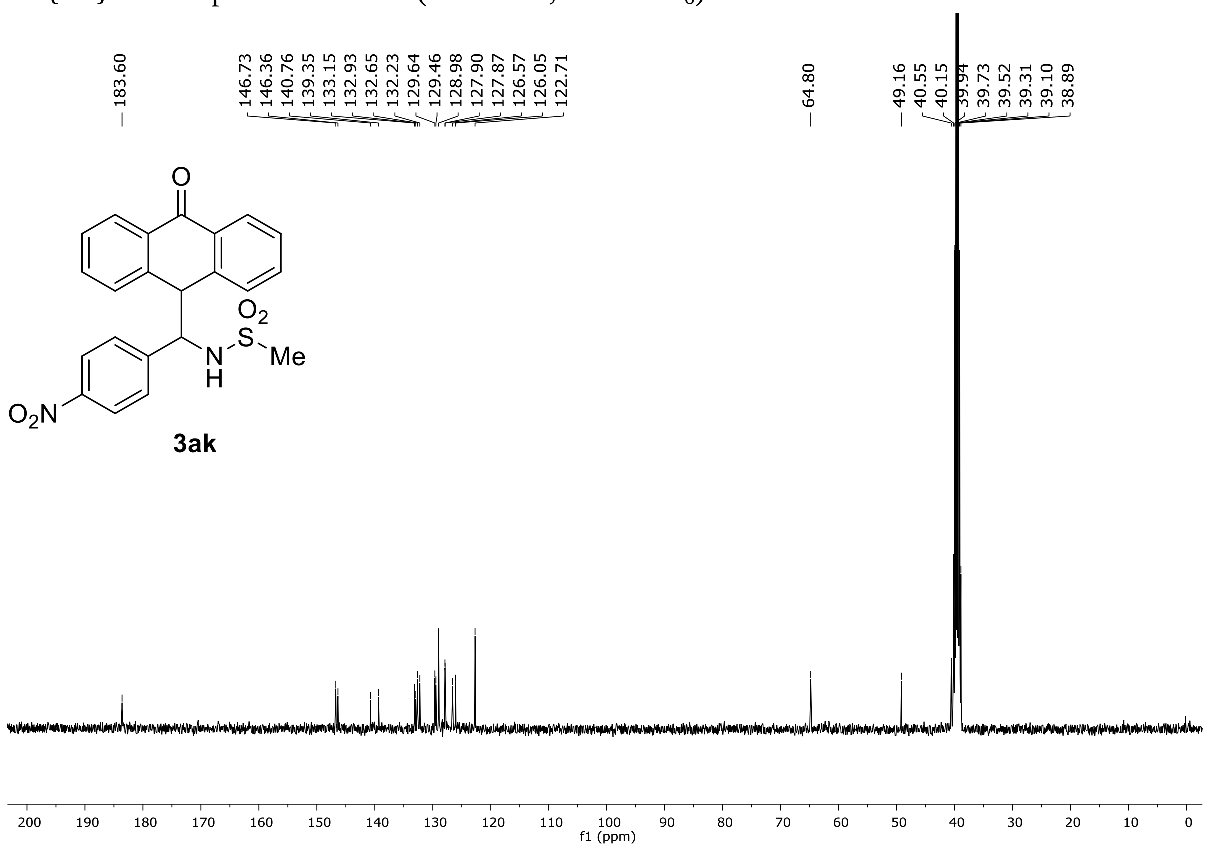
$^{13}C\{^{1}H\}$ NMR spectrum of **3aj** (100 MHz, $CDCl_3$):



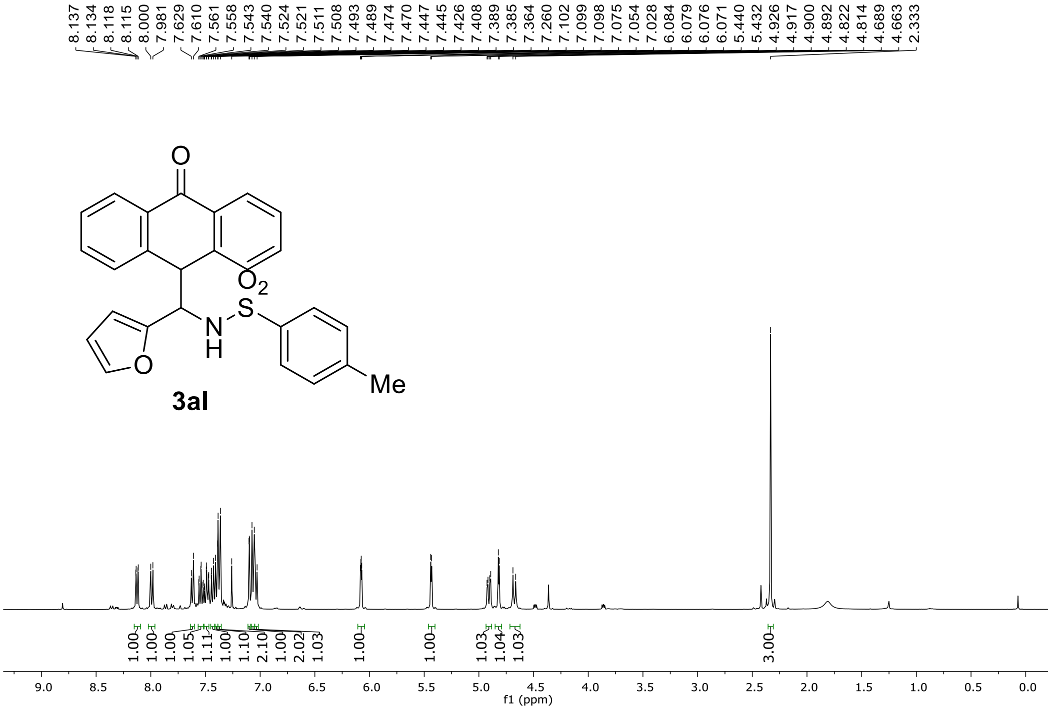
^{1}H NMR spectrum of **3ak** (400 MHz, DMSO-d_6):



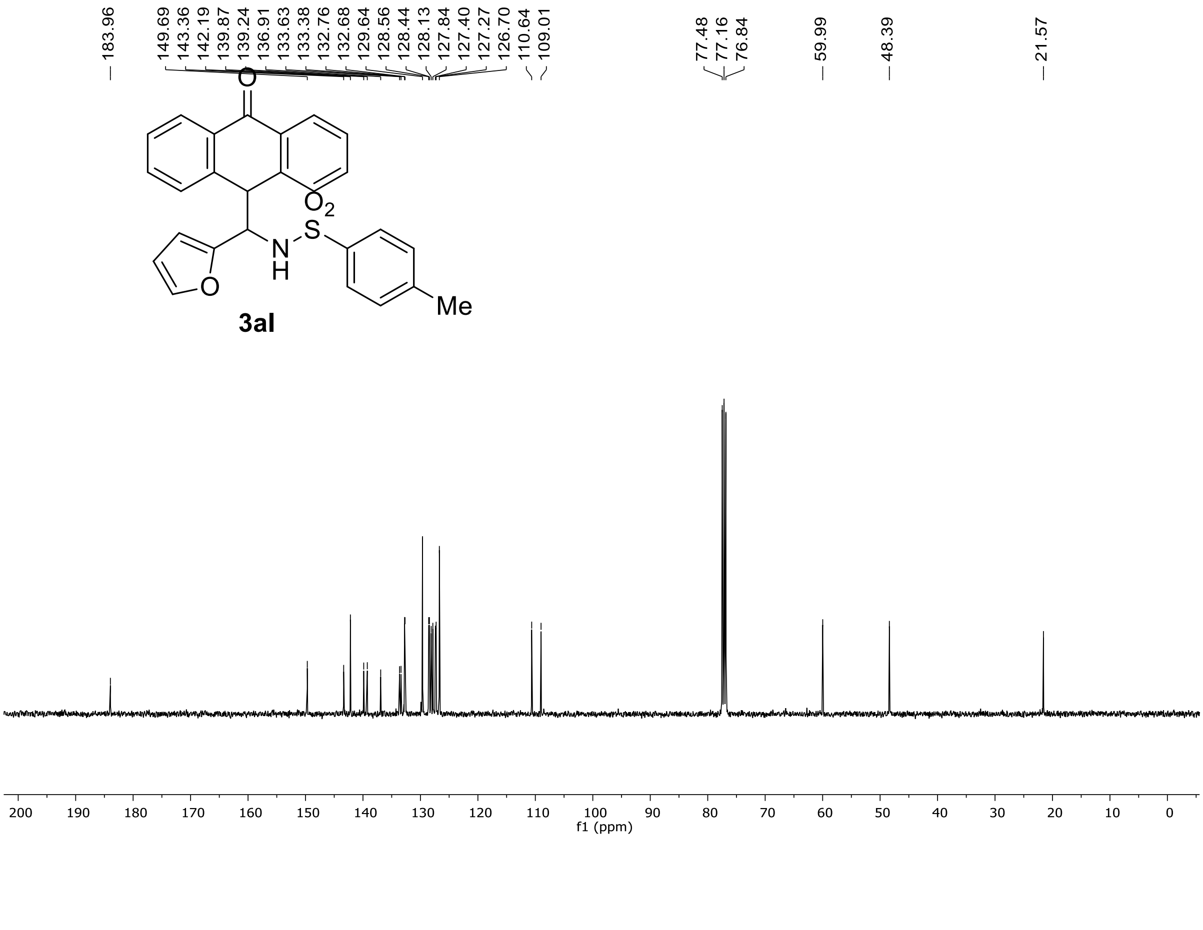
^{13}C{^{1}H} NMR spectrum of **3ak** (100 MHz, DMSO-d_6):



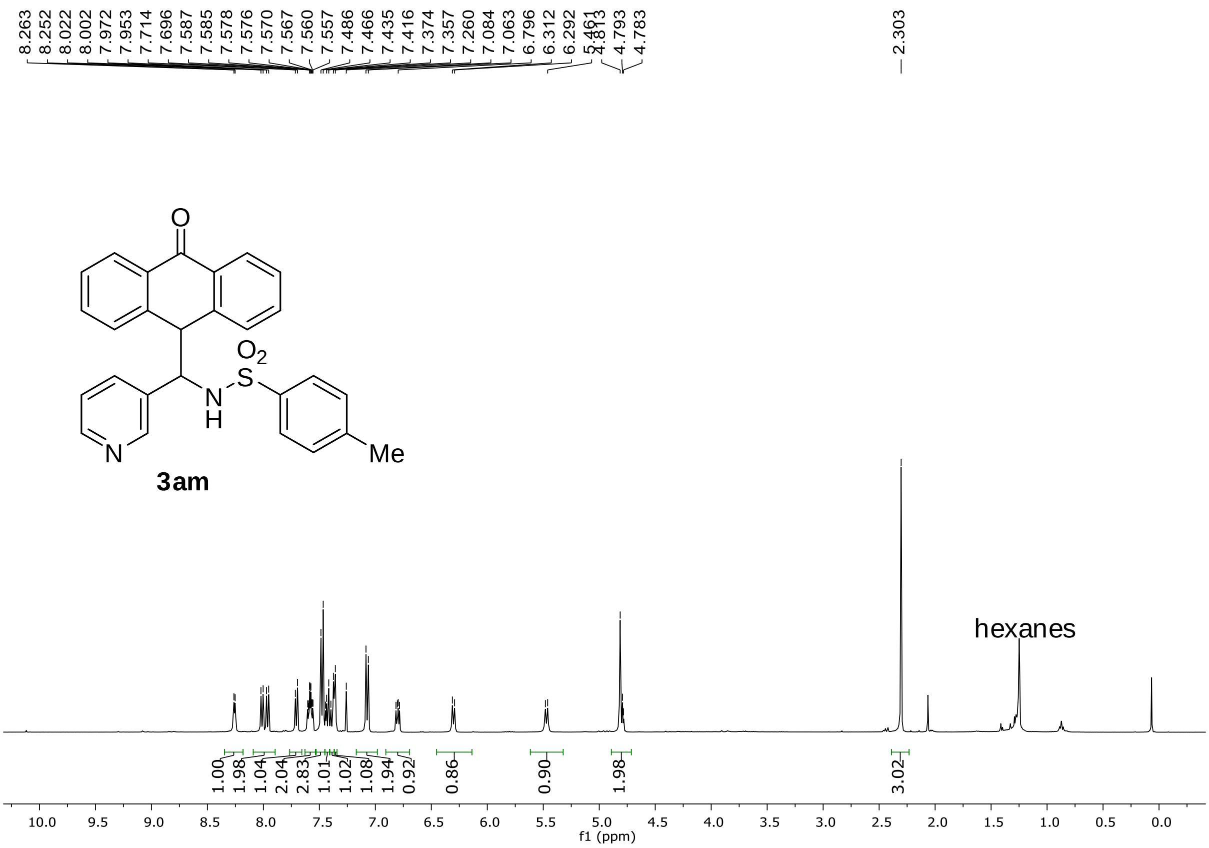
^{1}H NMR spectrum of **3al** (400 MHz, $CDCl_3$):



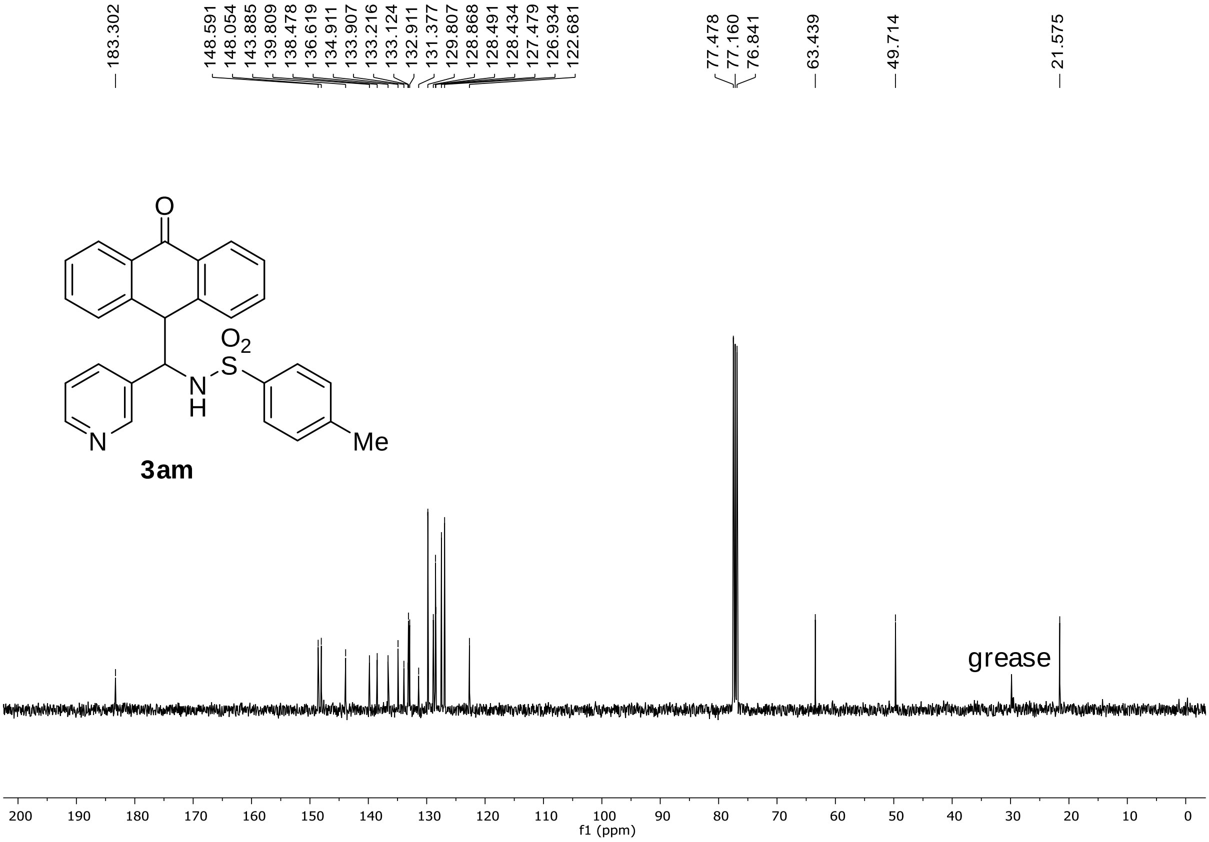
^{13}C{^{1}H} NMR spectrum of **3al** (100 MHz, $CDCl_3$):



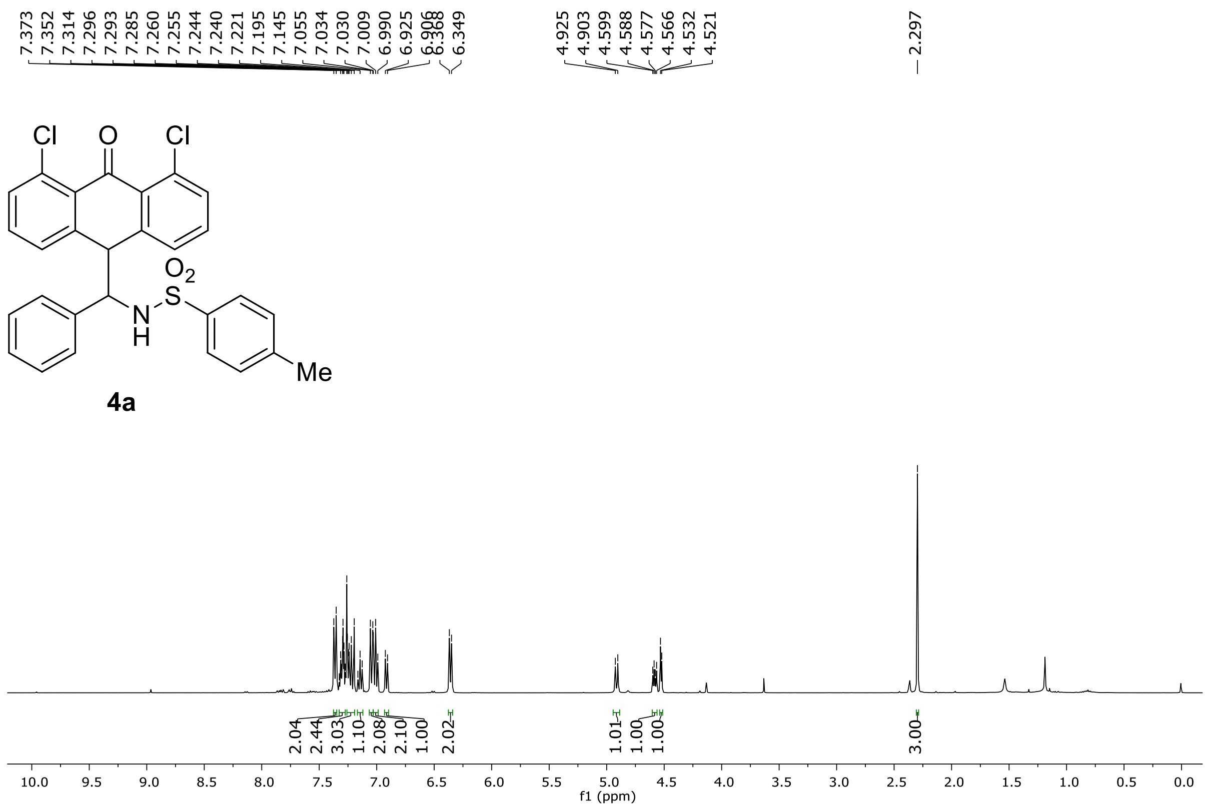
^{1}H NMR spectrum of **3am** (100 MHz, $CDCl_3$):



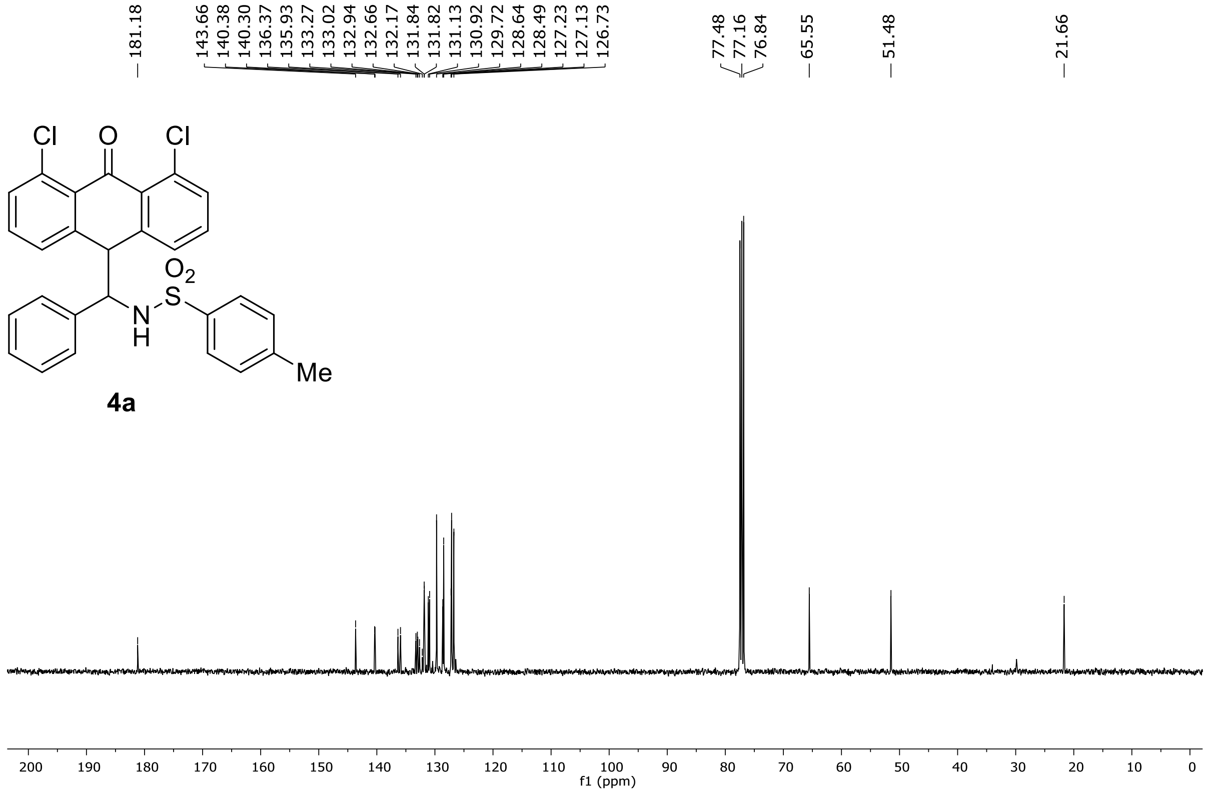
^{13}C{^{1}H} NMR spectrum of **3am** (100 MHz, $CDCl_3$):



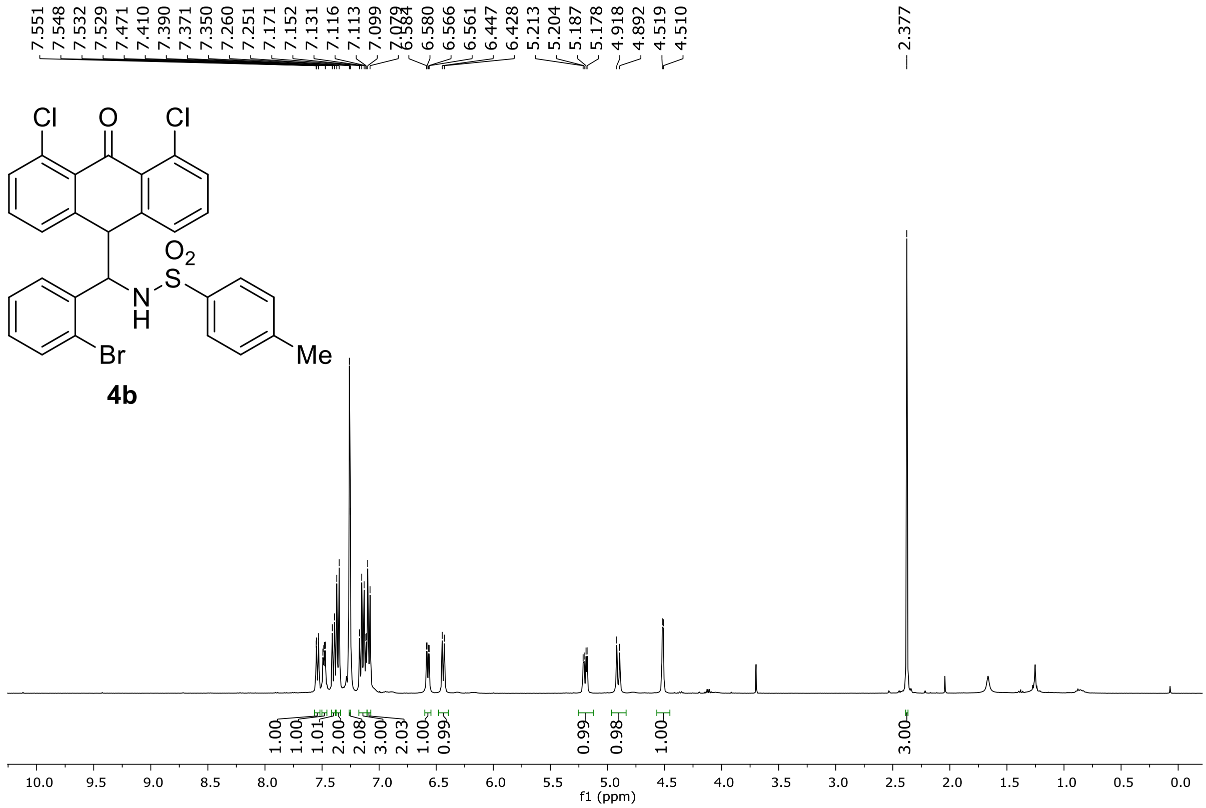
[1]H NMR spectrum of **4a** (400 MHz, $CDCl_3$):



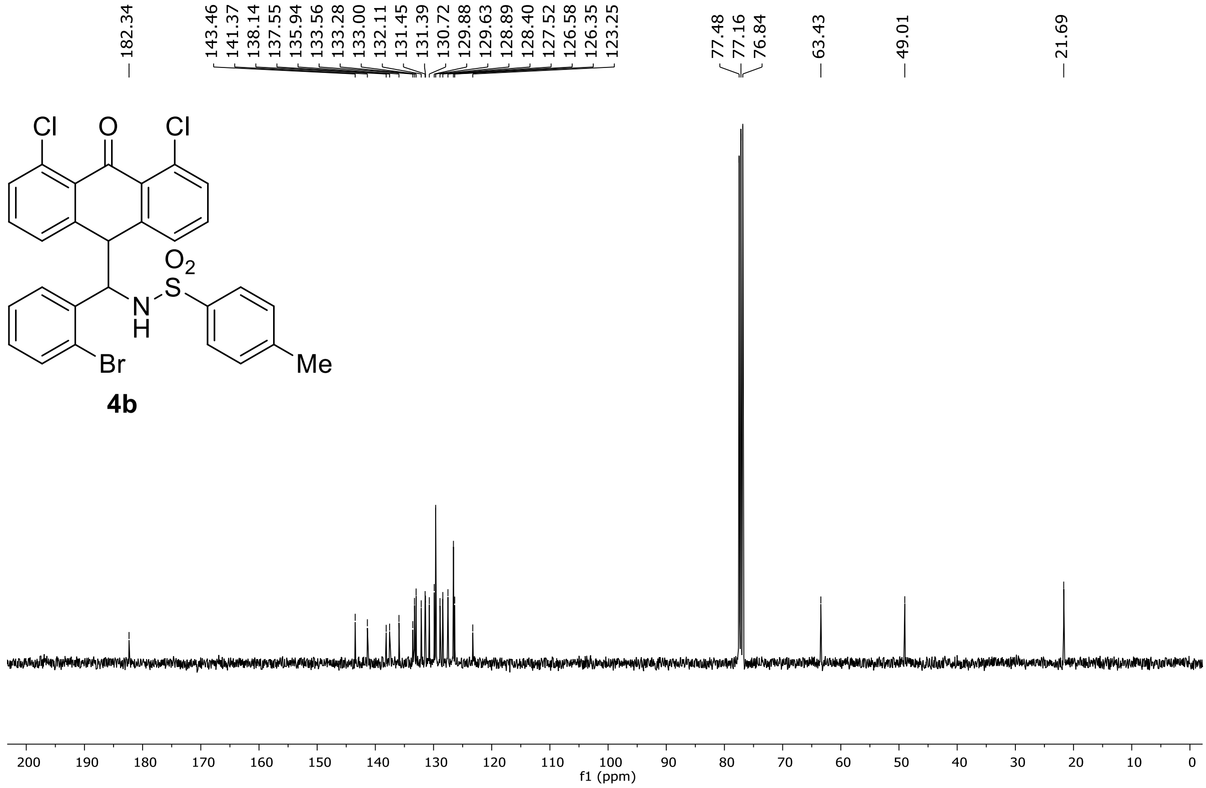
[13]C{[1]H} NMR spectrum of **4a** (100 MHz, $CDCl_3$):



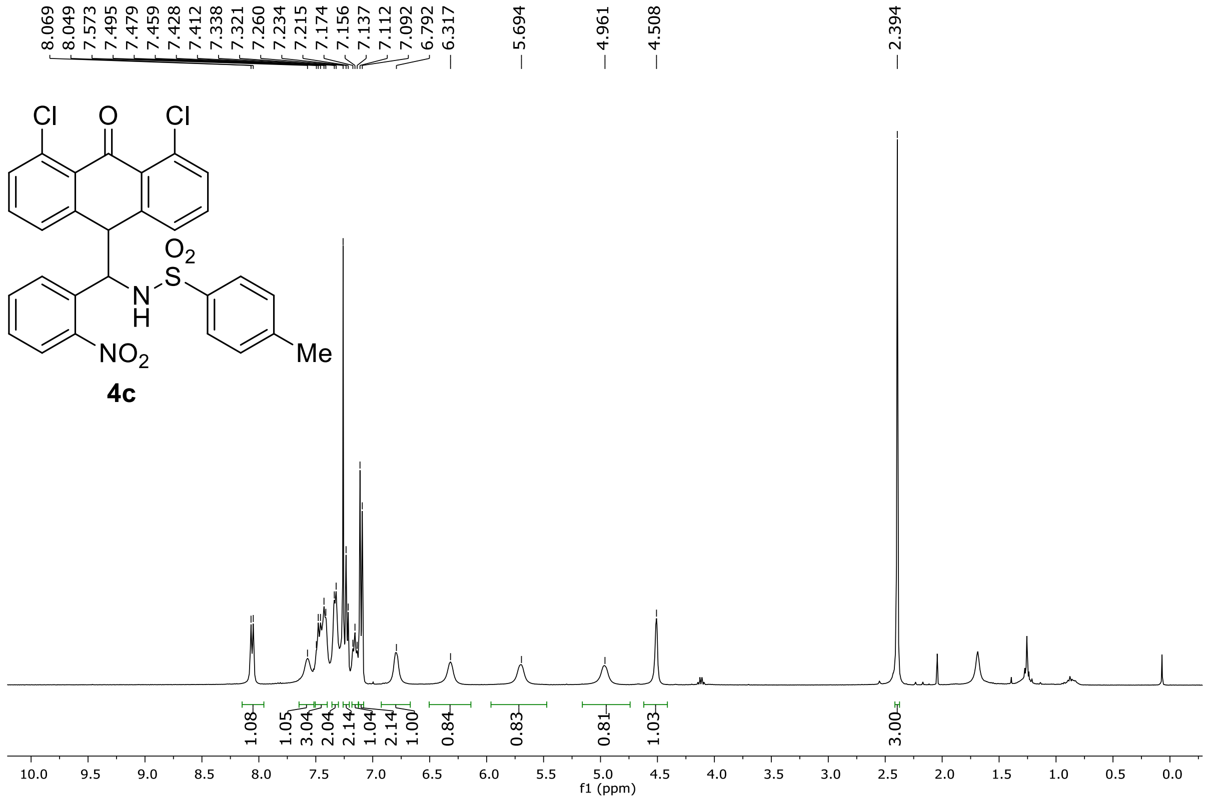
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$):



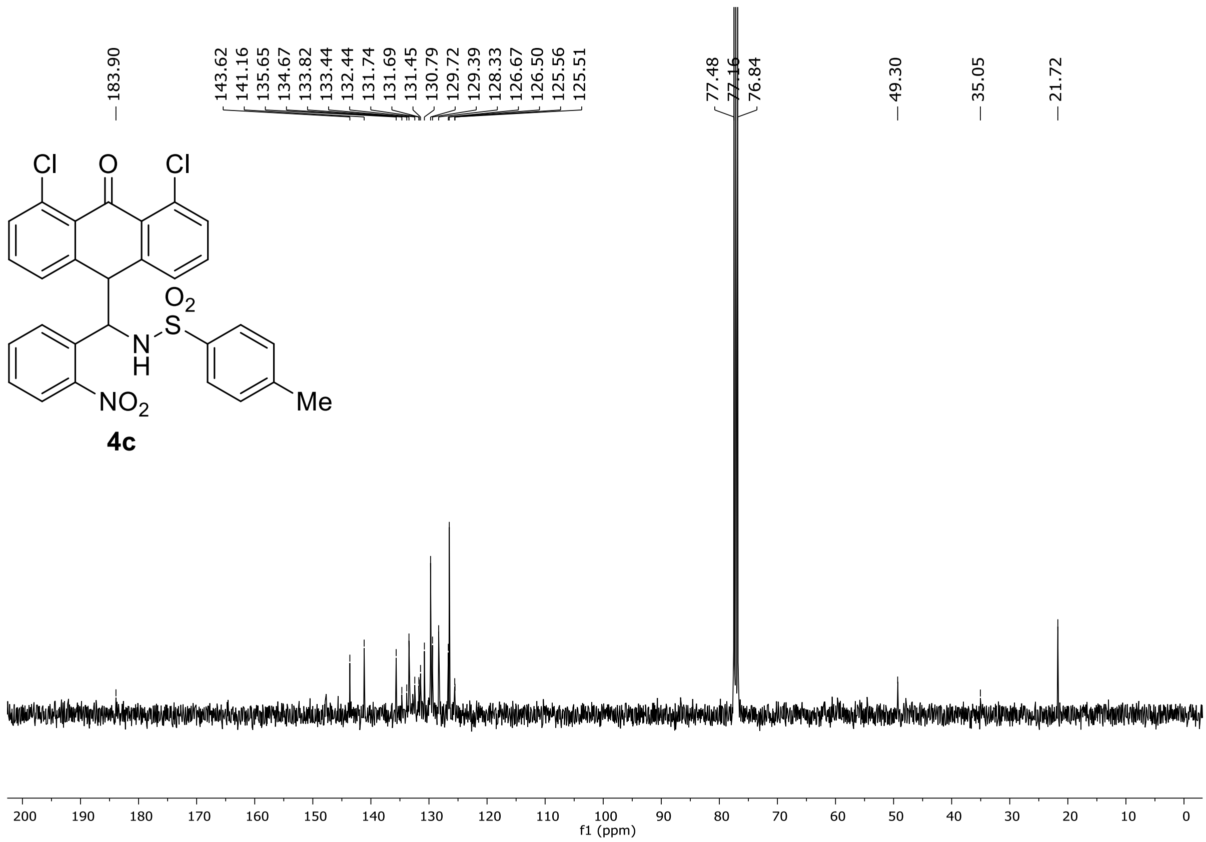
$^{13}C\{^{1}H\}$ NMR spectrum of **4b** (100 MHz, $CDCl_3$):



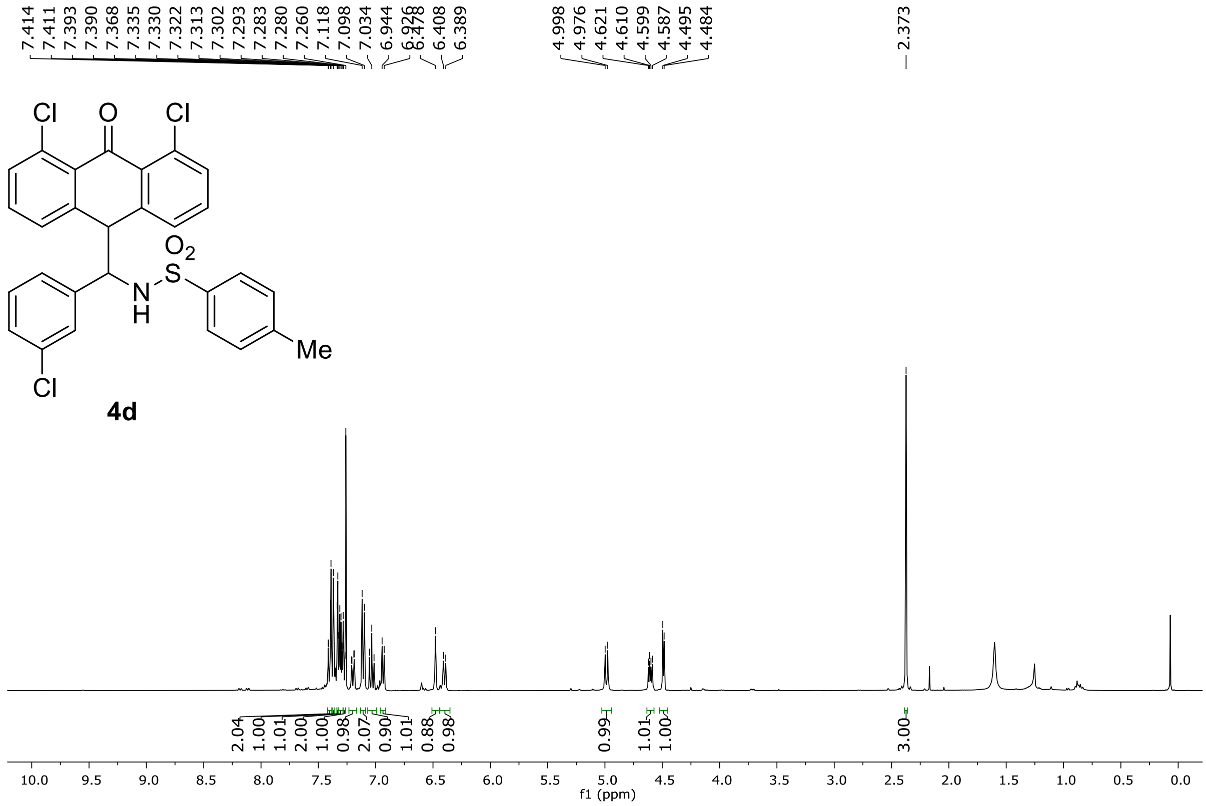
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$):



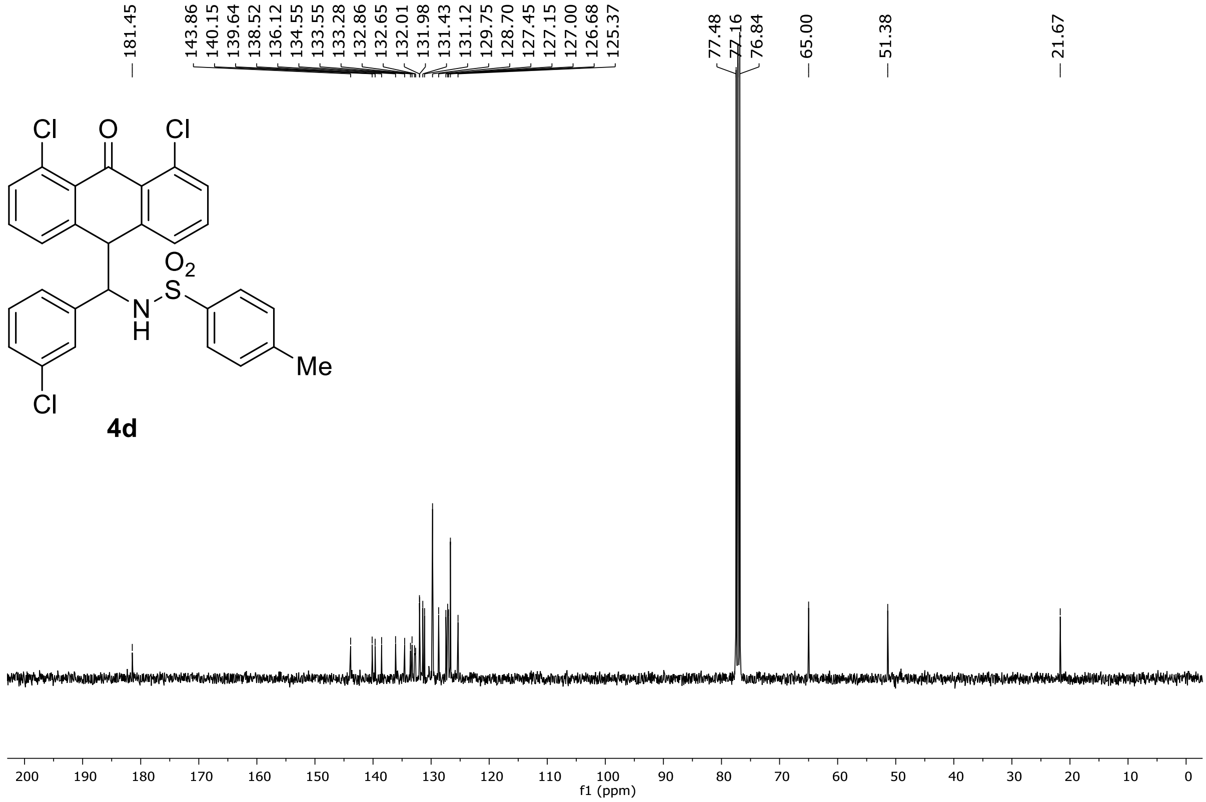
$^{13}C\{^{1}H\}$ NMR spectrum of **4c** (100 MHz, $CDCl_3$):



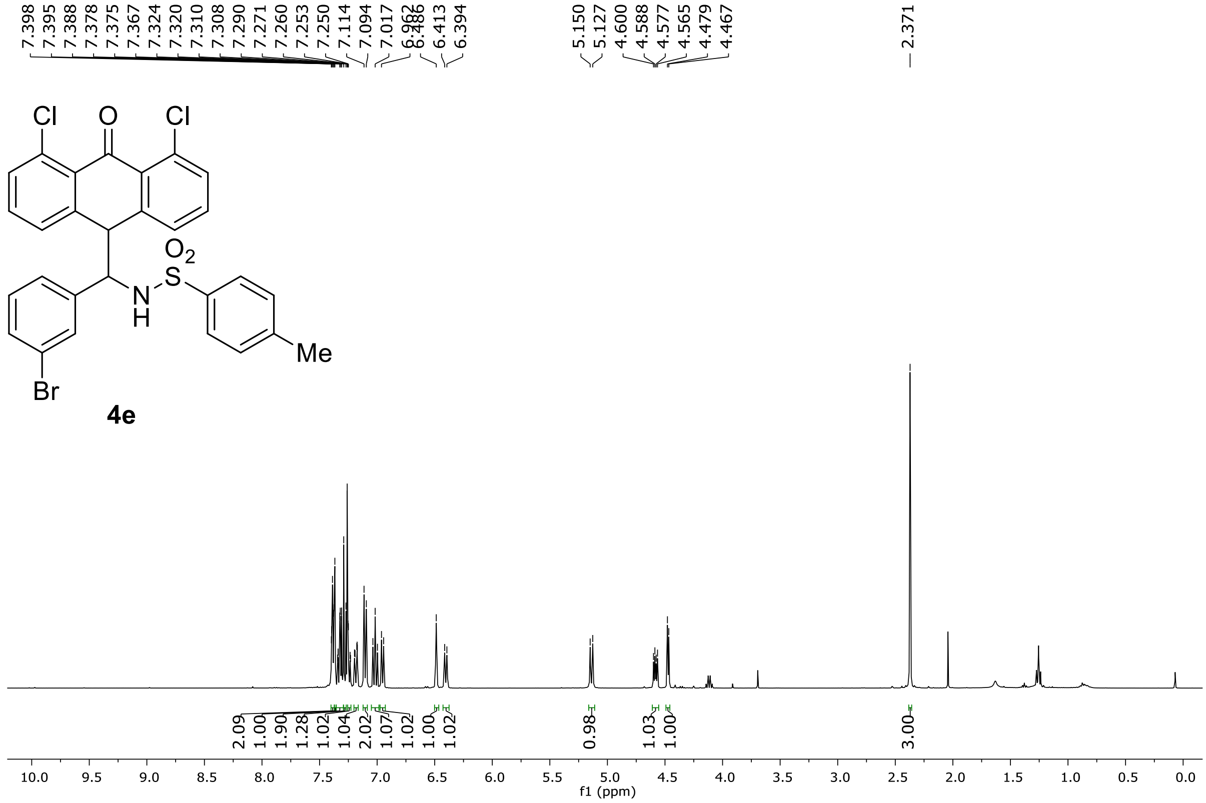
[1]H NMR spectrum of **4d** (400 MHz, $CDCl_3$):



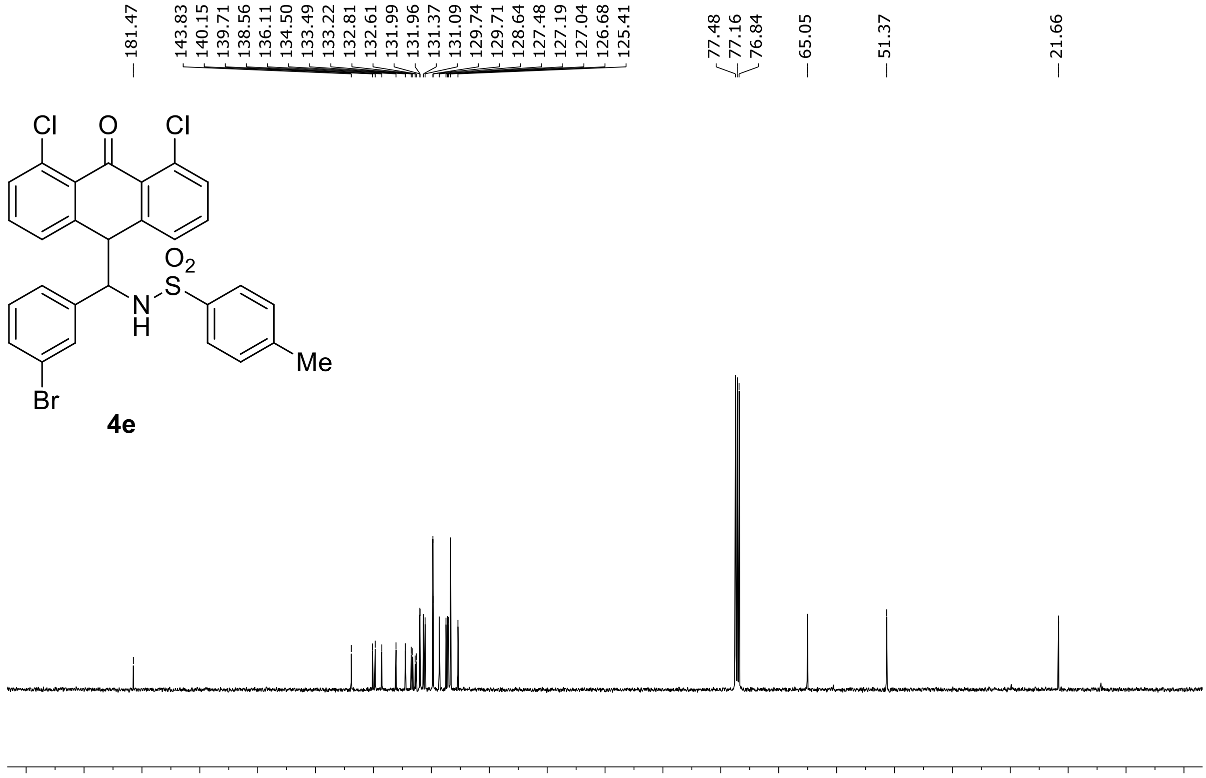
[13]C{[1]H} NMR spectrum of **4d** (100 MHz, $CDCl_3$):



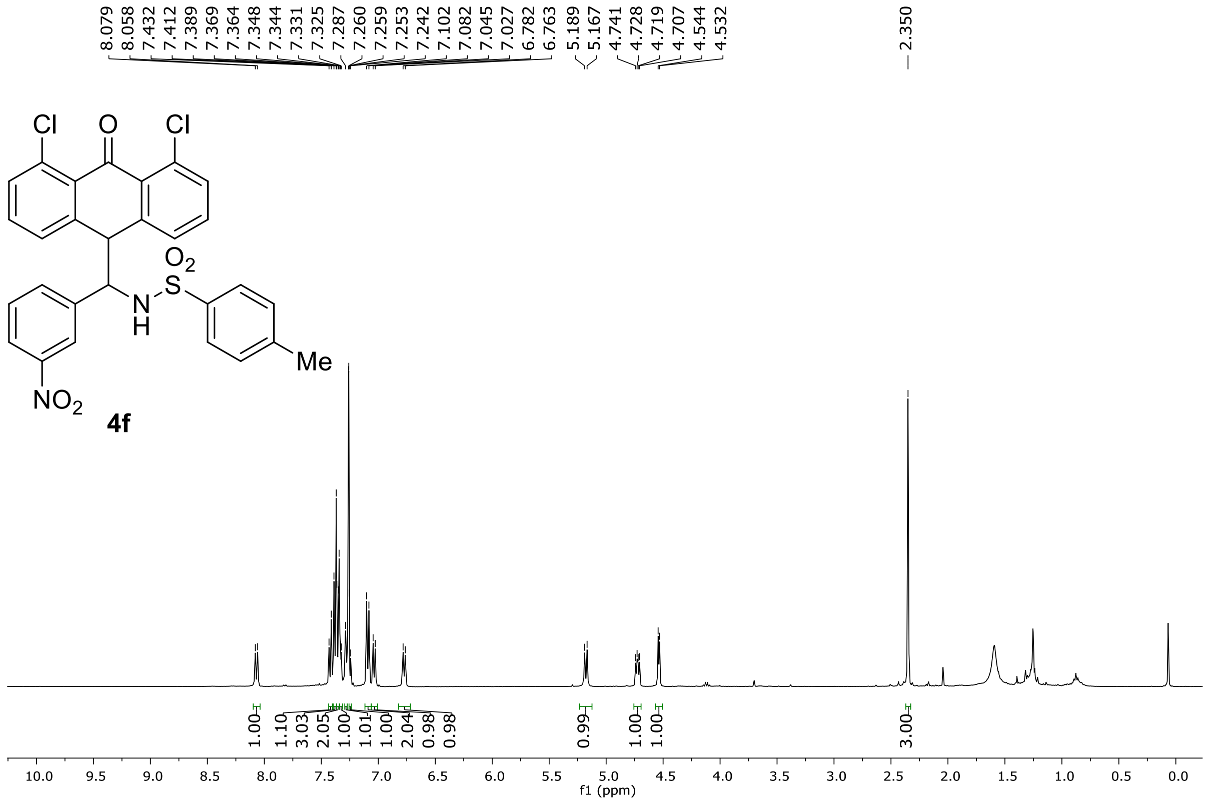
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$):



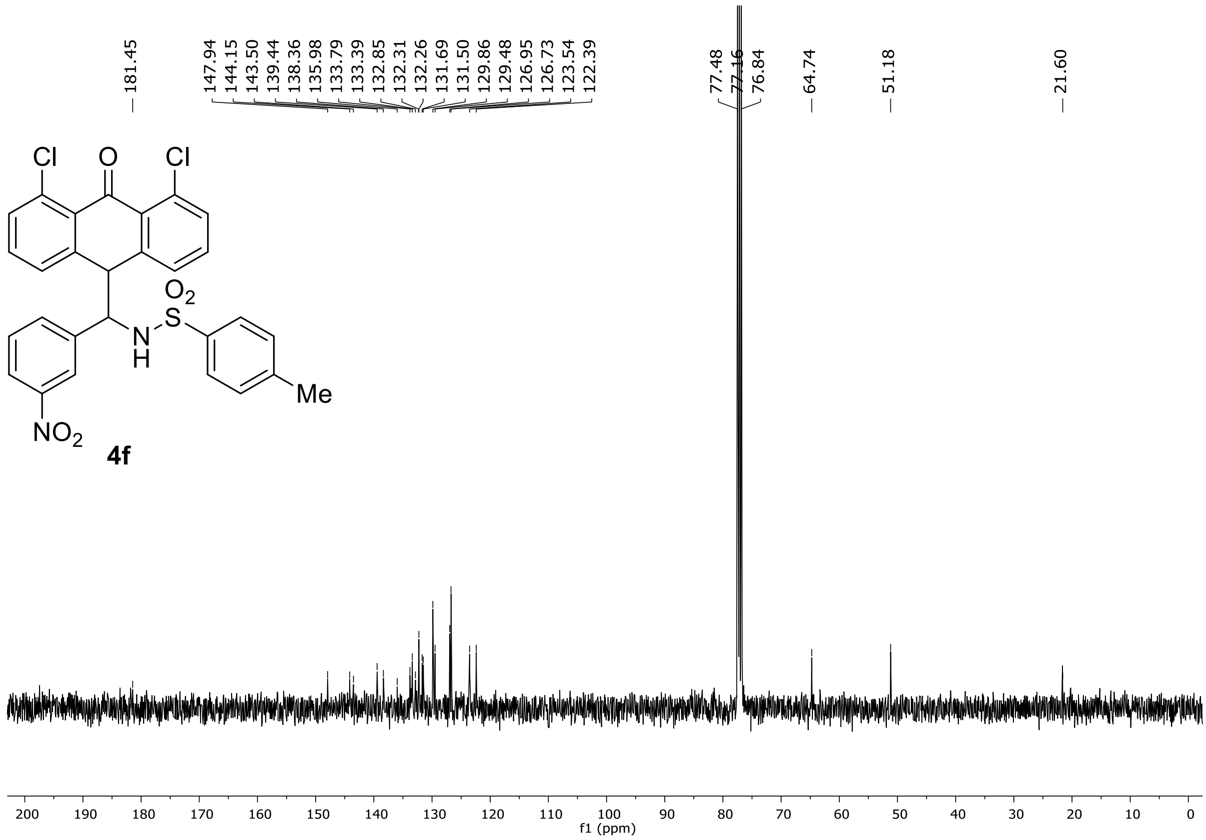
^{13}C{^{1}H} NMR spectrum of **4e** (100 MHz, $CDCl_3$):



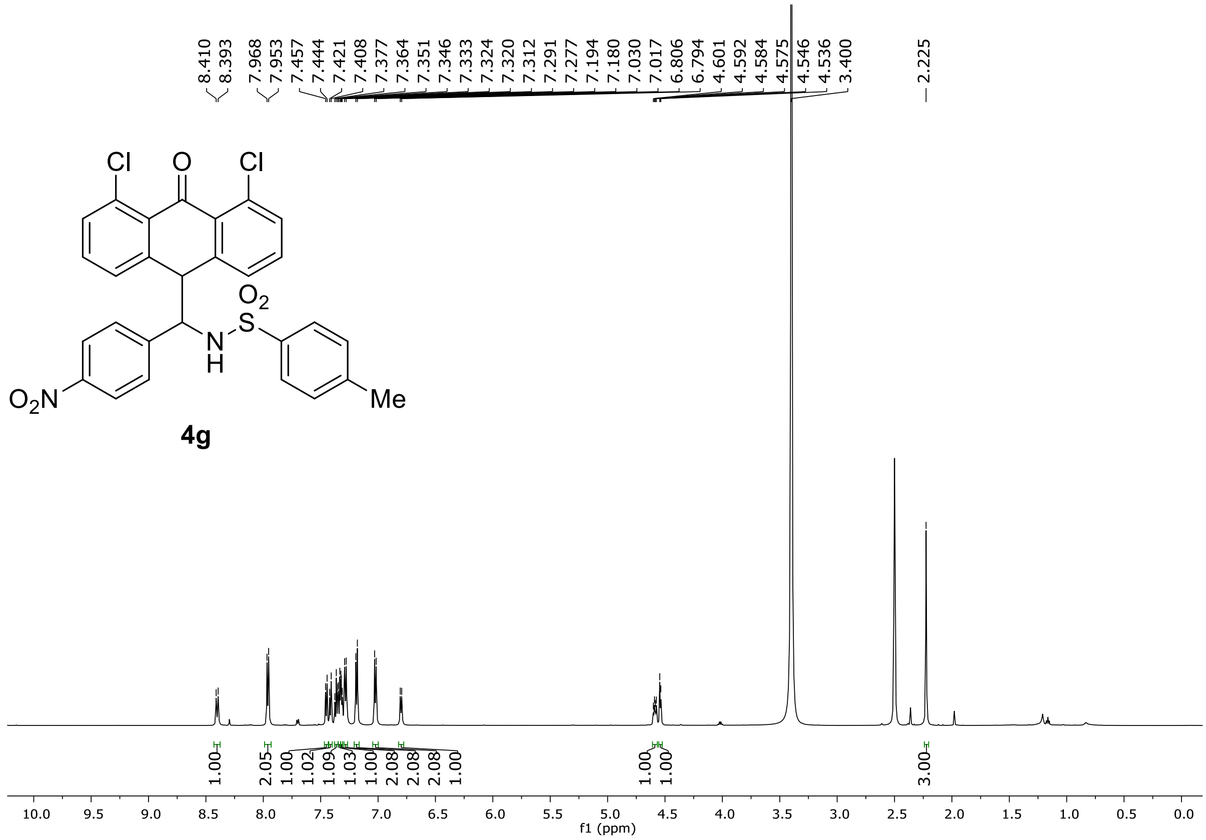
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$):



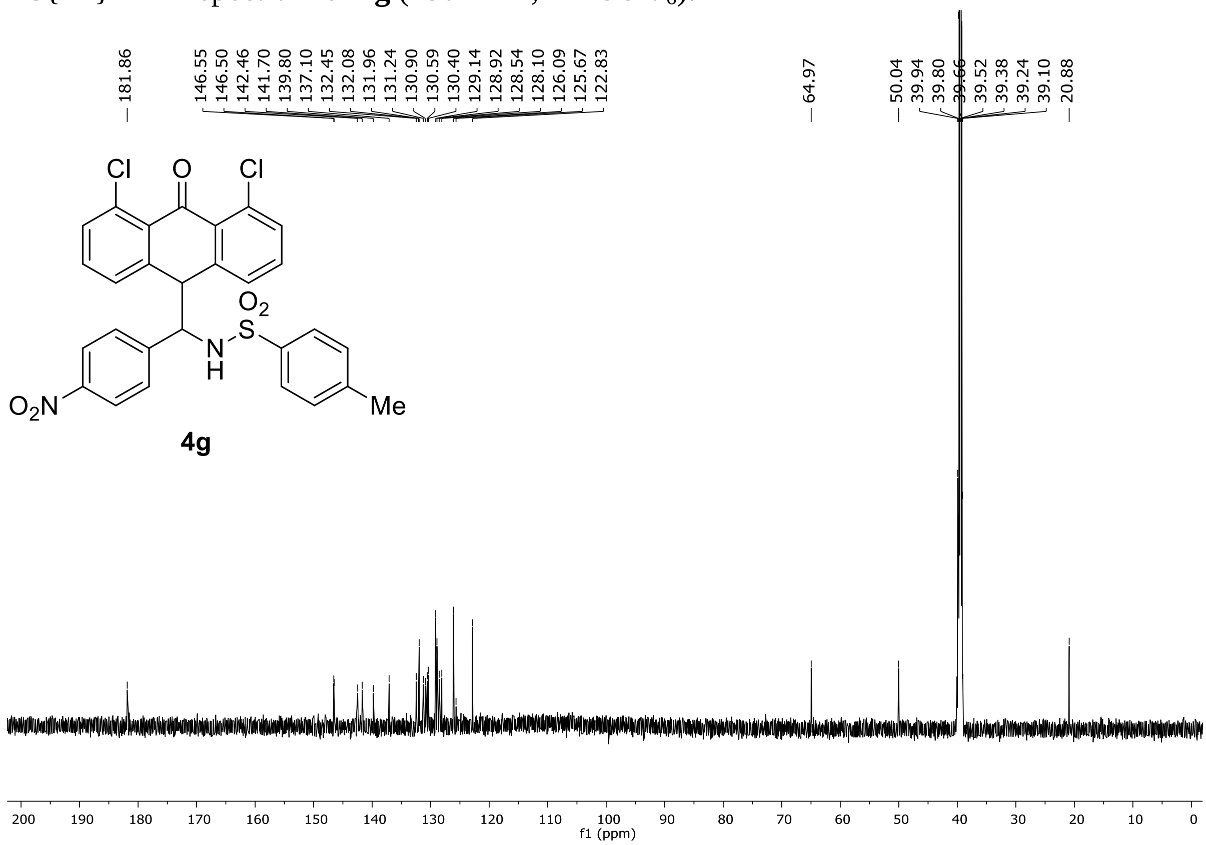
$^{13}C\{^1H\}$ NMR spectrum of **4f** (100 MHz, $CDCl_3$):



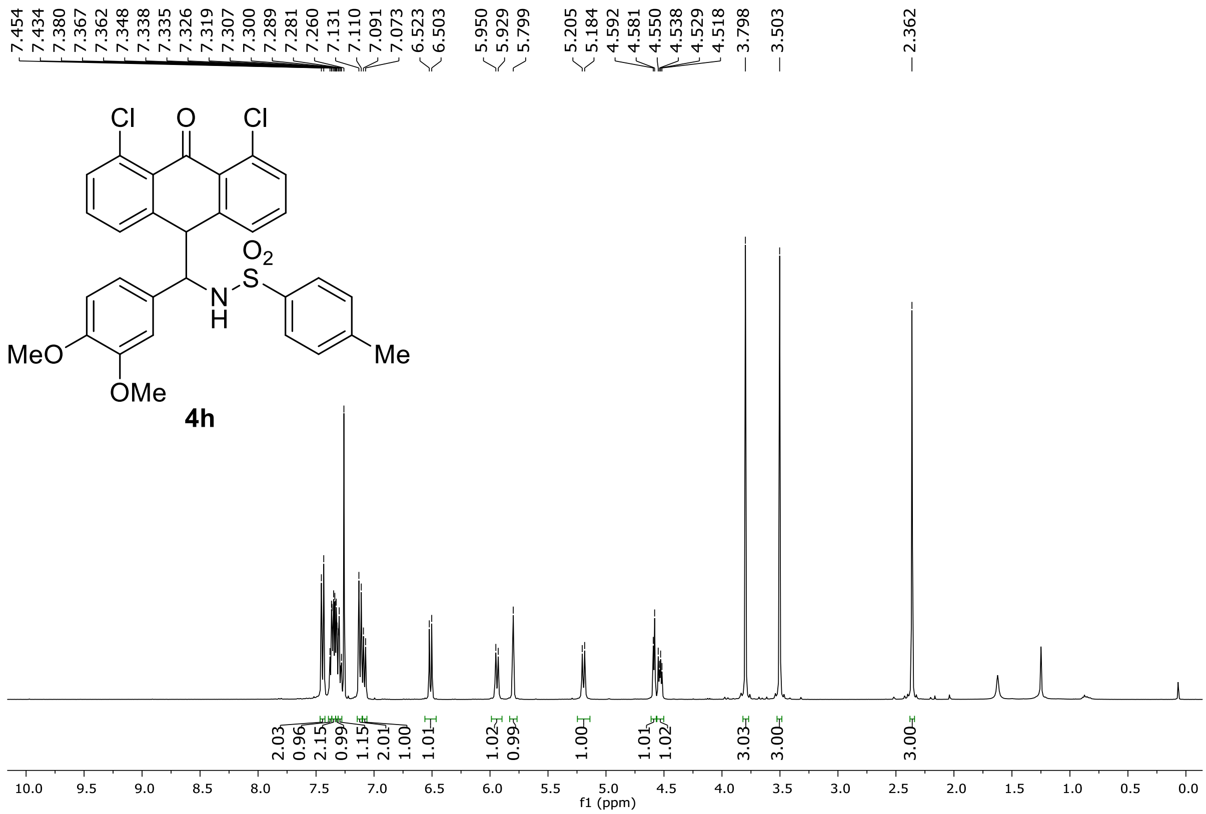
^{1}H NMR spectrum of **4g** (600 MHz, DMSO-d_6):



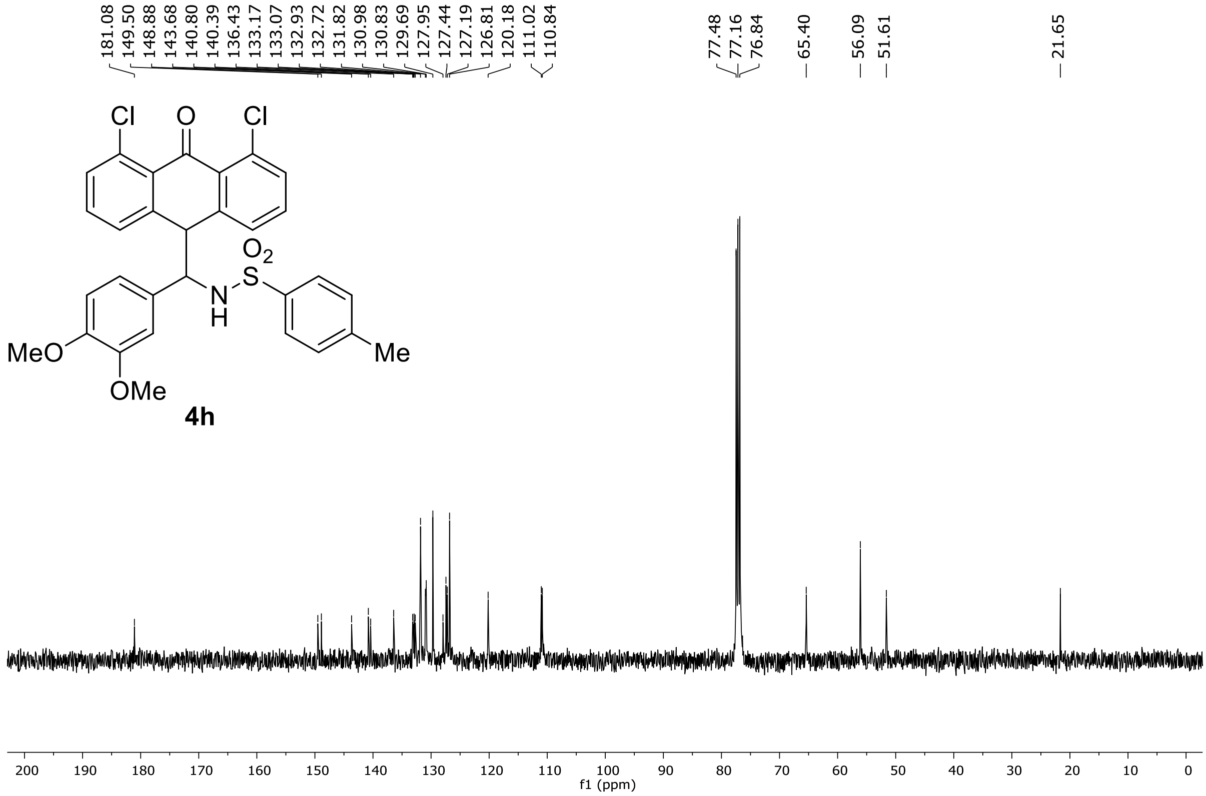
$^{13}C\{^{1}H\}$ NMR spectrum of **4g** (150 MHz, DMSO-d_6):



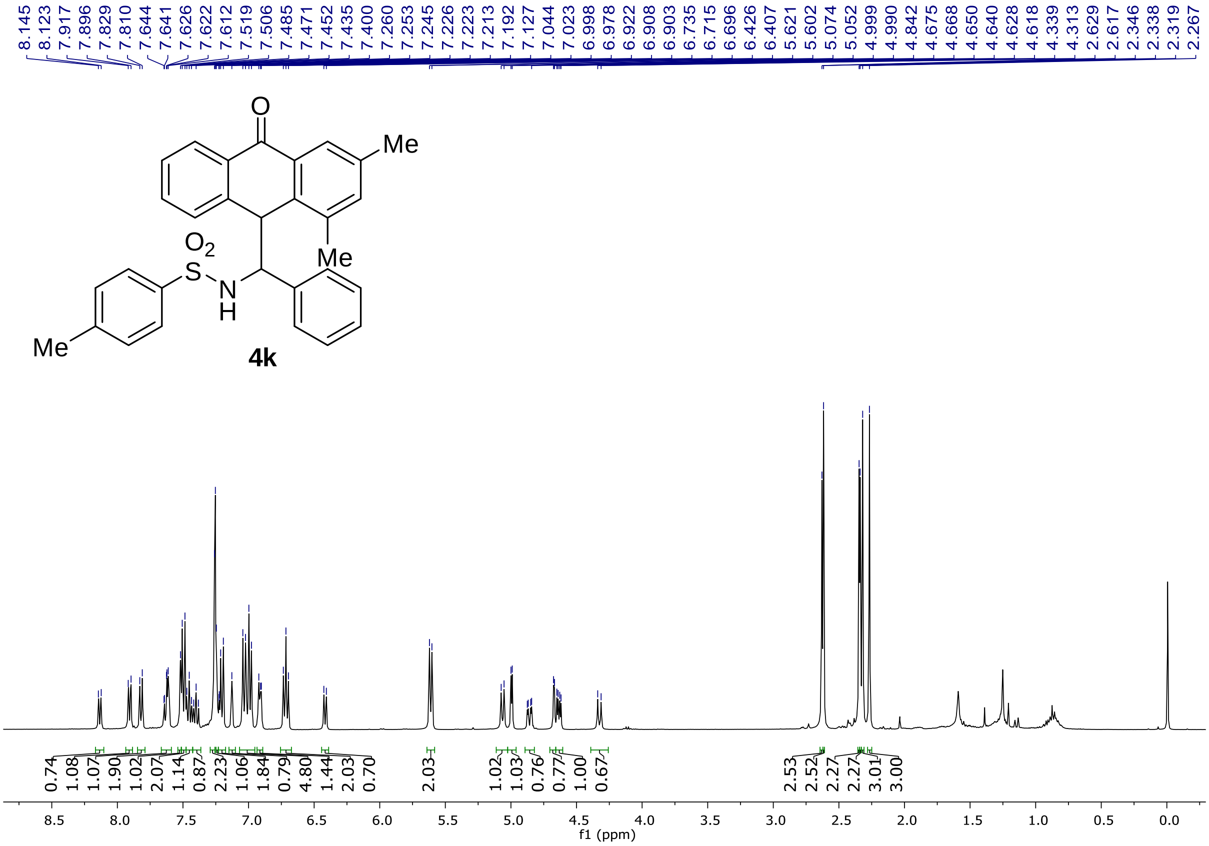
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$):



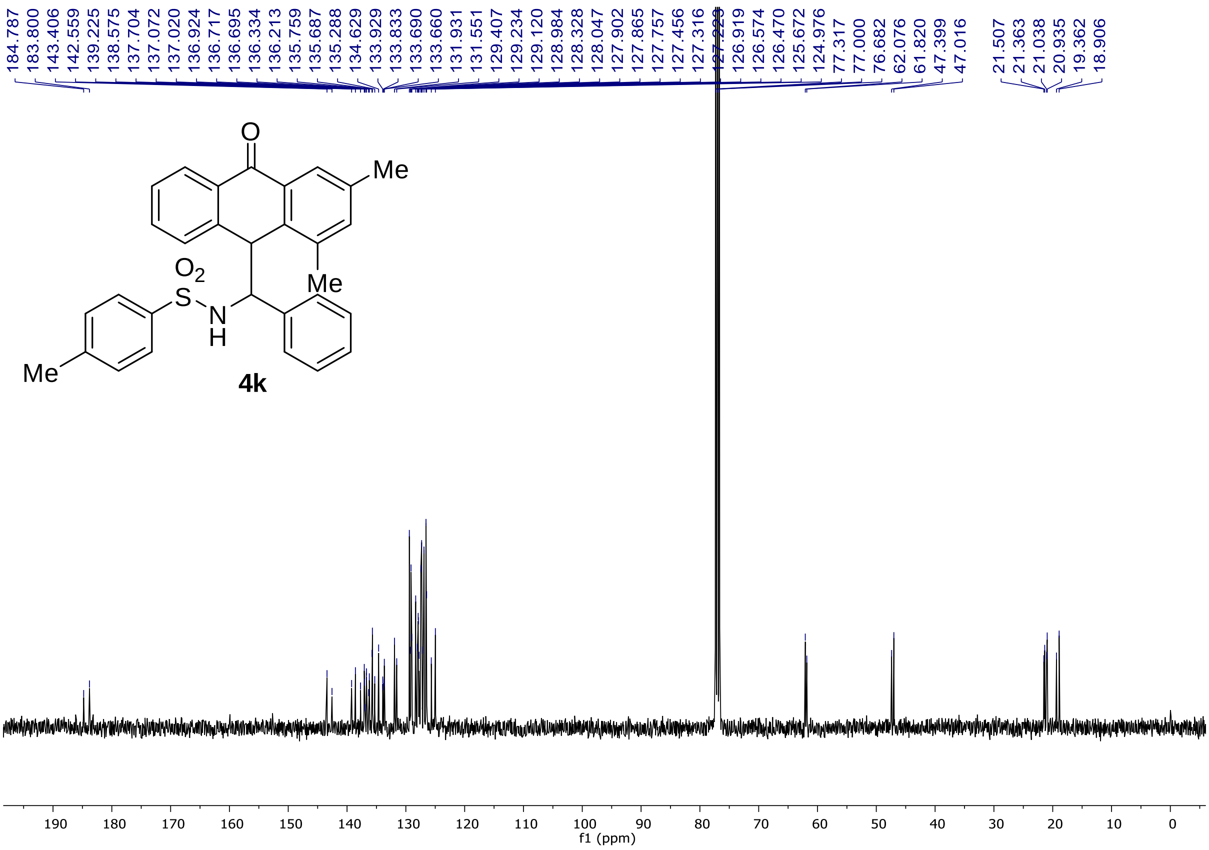
^{13}C{^{1}H} NMR spectrum of **4h** (100 MHz, $CDCl_3$):



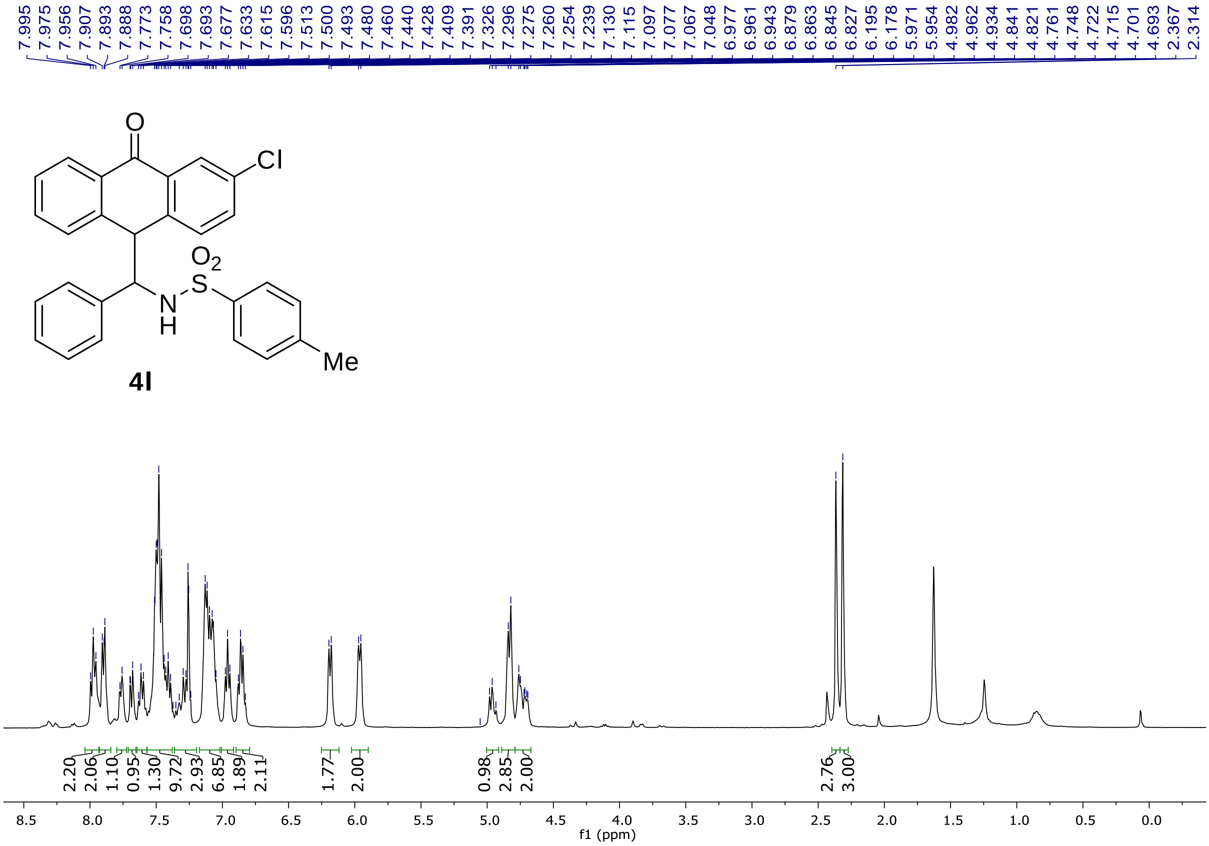
^{1}H NMR spectrum of **4k** (400 MHz, $CDCl_3$):



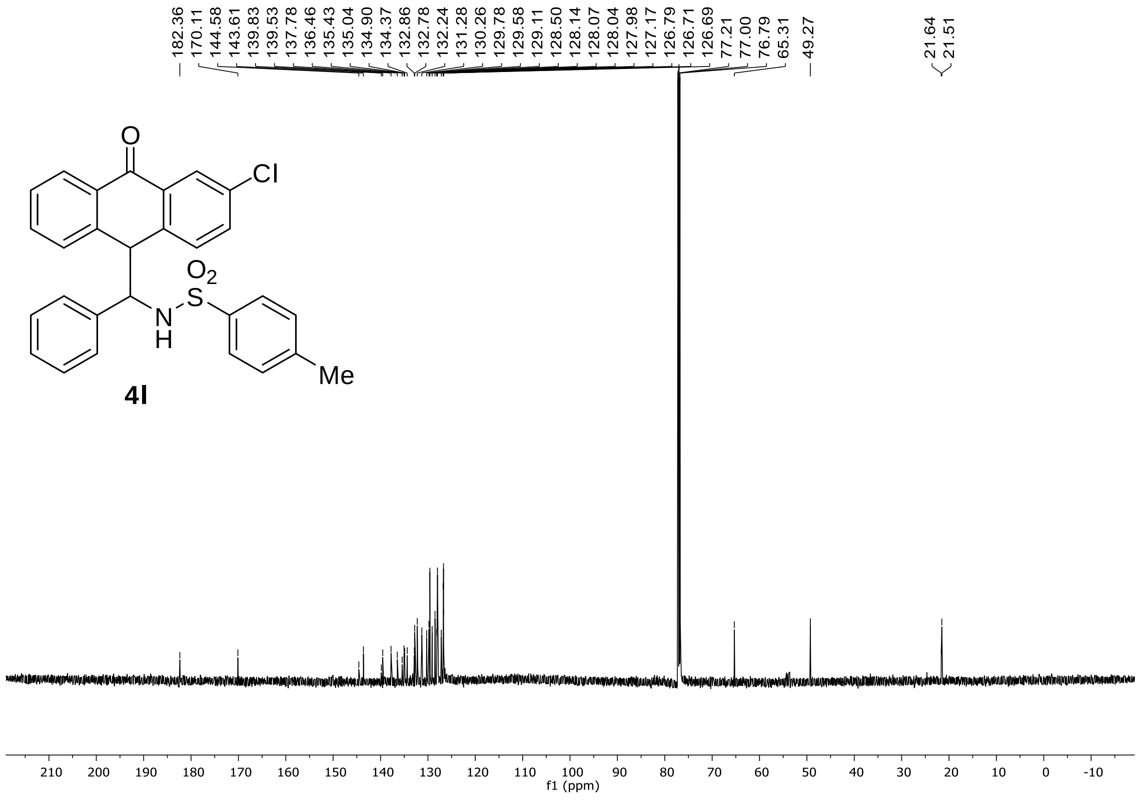
^{13}C{^{1}H} NMR spectrum of **4k** (100 MHz, $CDCl_3$):



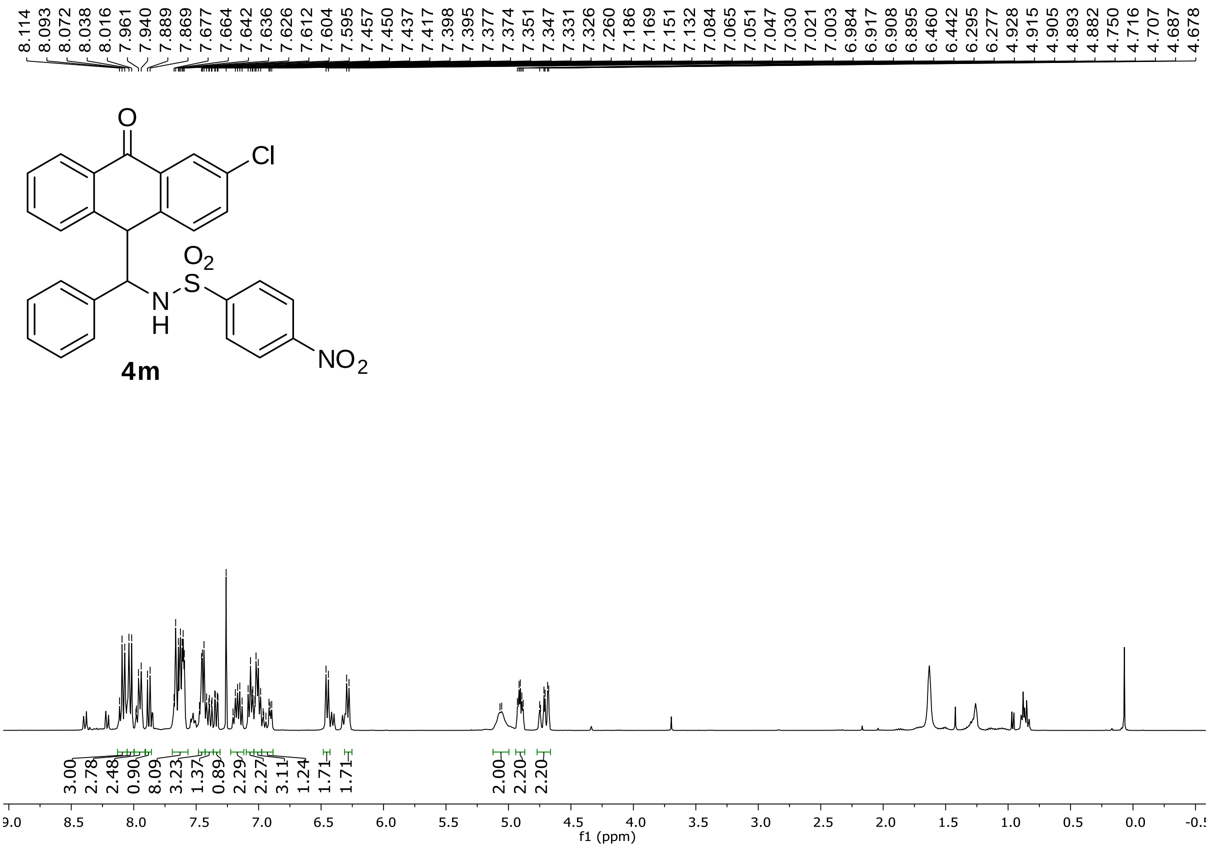
[1]H NMR spectrum of **4l** (400 MHz, $CDCl_3$):



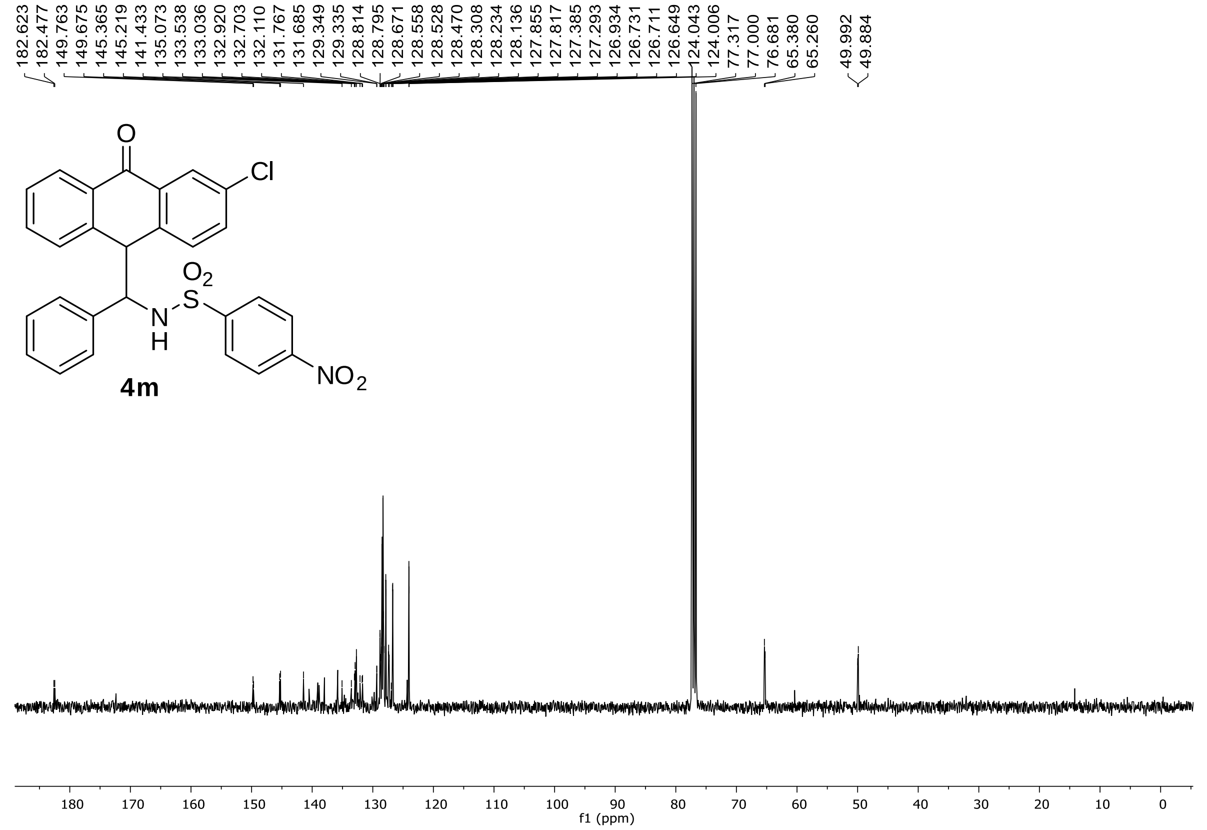
[13]C{[1]H} NMR spectrum of **4l** (100 MHz, $CDCl_3$):



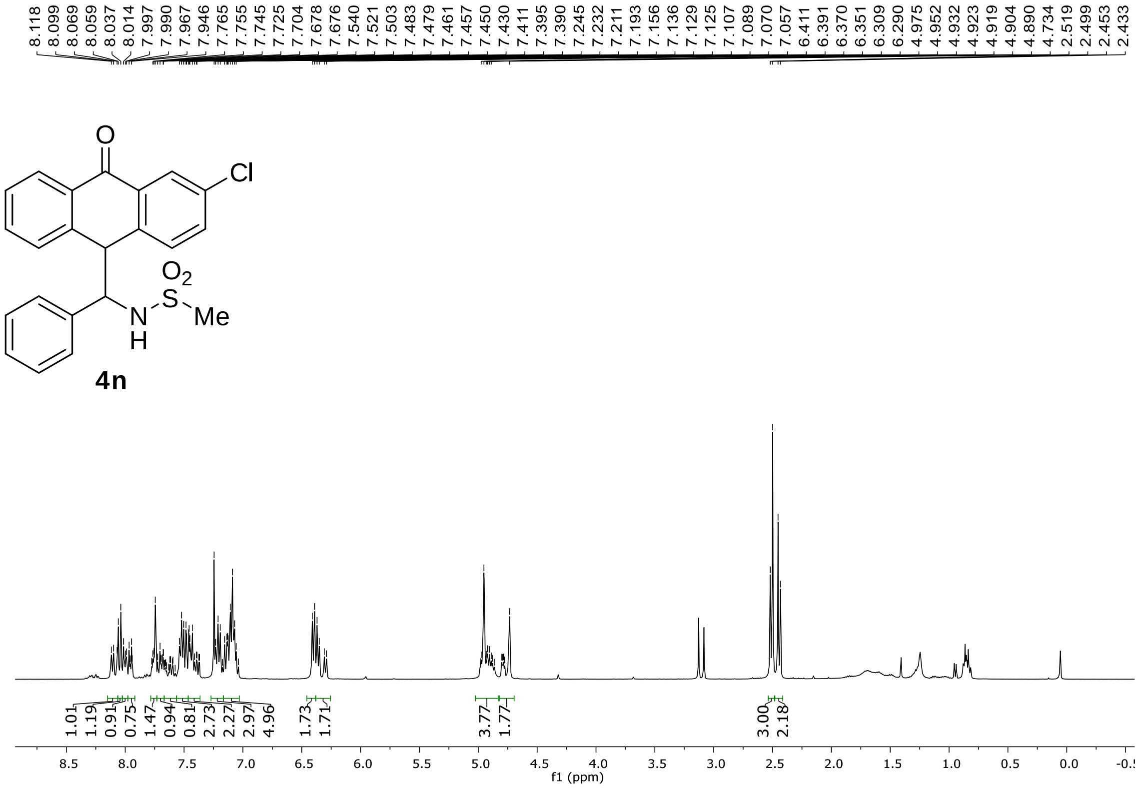
^{1}H NMR spectrum of **4m** (400 MHz, $CDCl_3$):



$^{13}C\{^{1}H\}$ NMR spectrum of **4m** (100 MHz, $CDCl_3$):



[1]H NMR spectrum of **4n** (400 MHz, $CDCl_3$):



[13]C{[1]H} NMR spectrum of **4n** (100 MHz, $CDCl_3$):

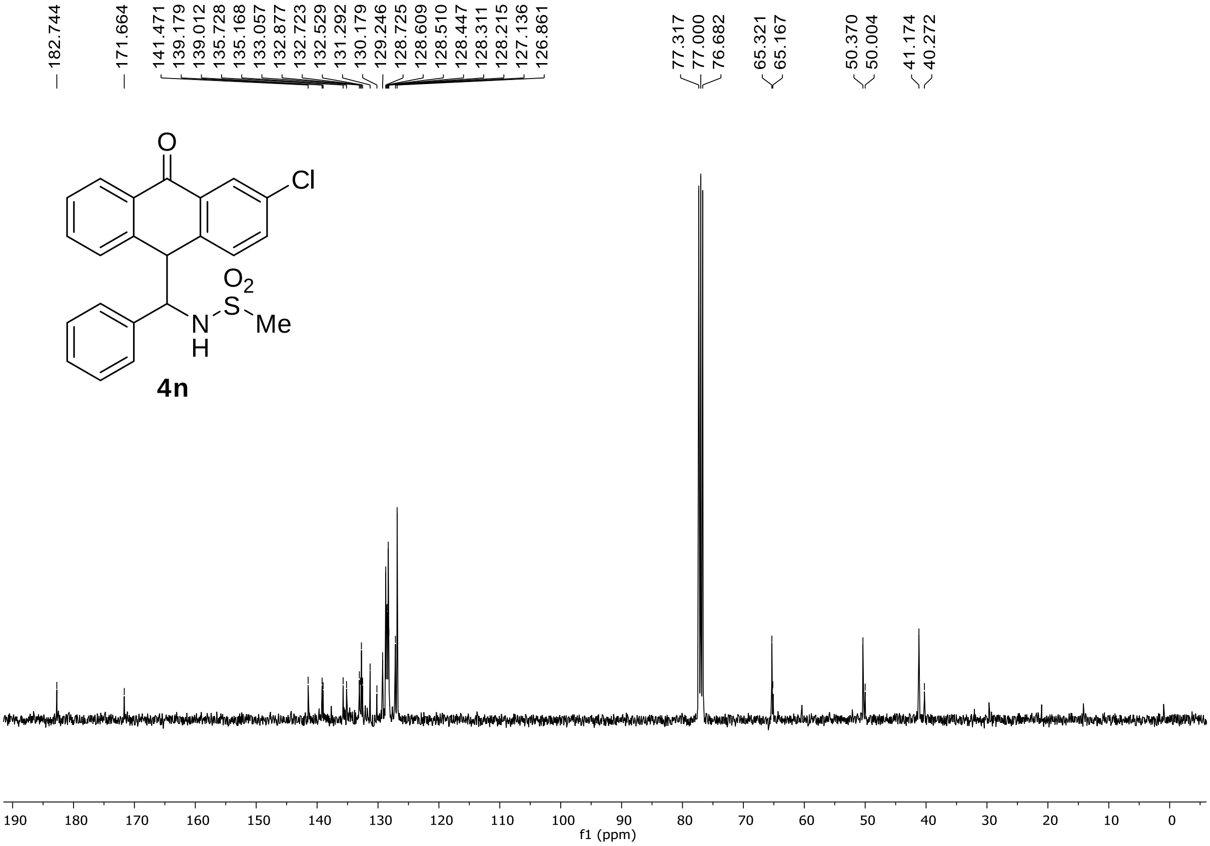
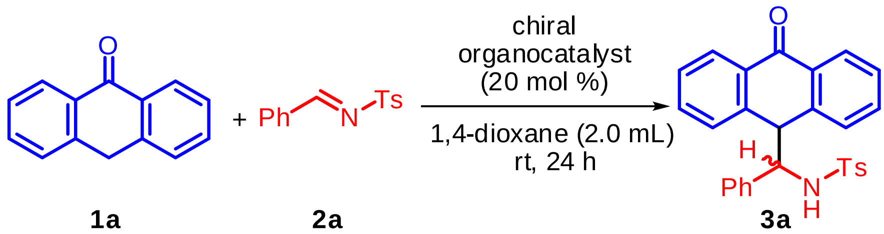


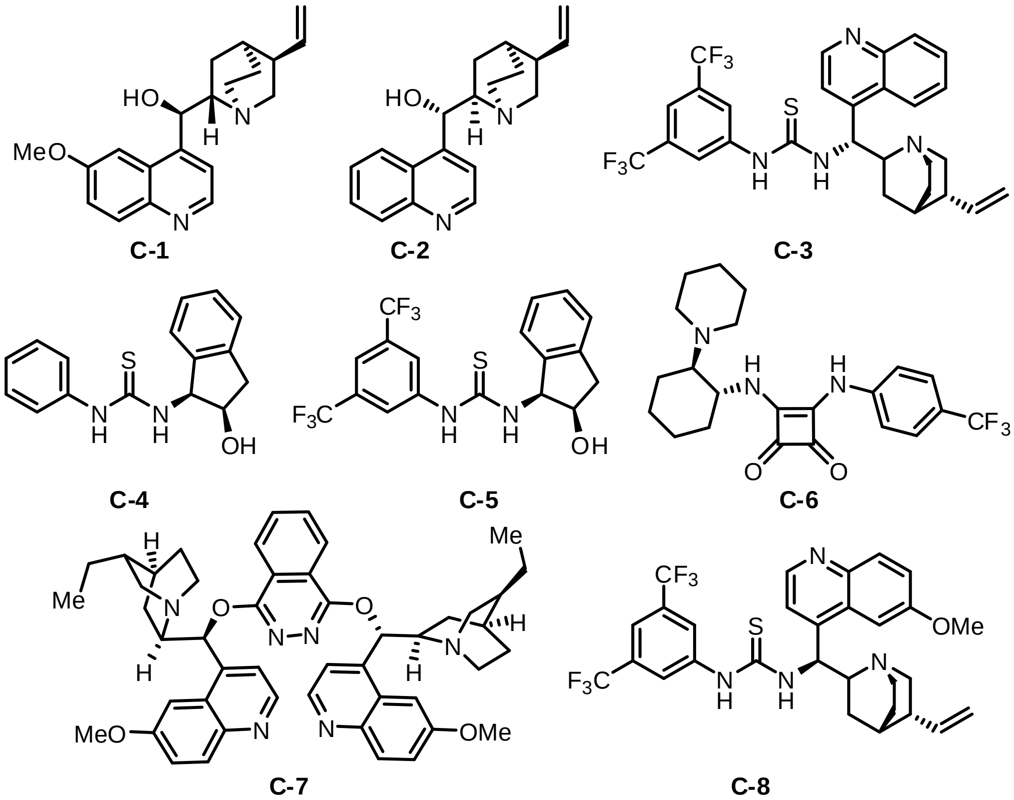
Table S1. Investigation of an asymmetric reaction using chiral organocatalyst[a]



entry[a]	Catalyst (20 mol %)	Yield of 3a[b] (%)	*er* (3a)[c]
1	C-1	40	50:50
2	C-2	41	47:53
3	C-3	55	49:51
4	C-4	36	53:47
5	C-5	61	51:49
6	C-6	34	49:51
7	C-7	57	51:49
8	C-8	68	44:56

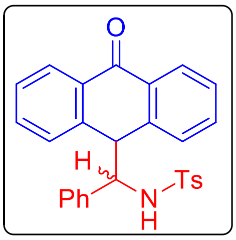
[a]In each case, the reaction was carried out with **1a** (0.2 mmol), **2a** (0.3 mmol) and catalyst (20 mol %) in 1,4-dioxane (2.0 mL) at room temperature (approx~32 °C). [b]Isolated yield. [c]Detected by HPLC analysis on chiral column.

Figure S2. Representative examples of chiral organocatalysts:

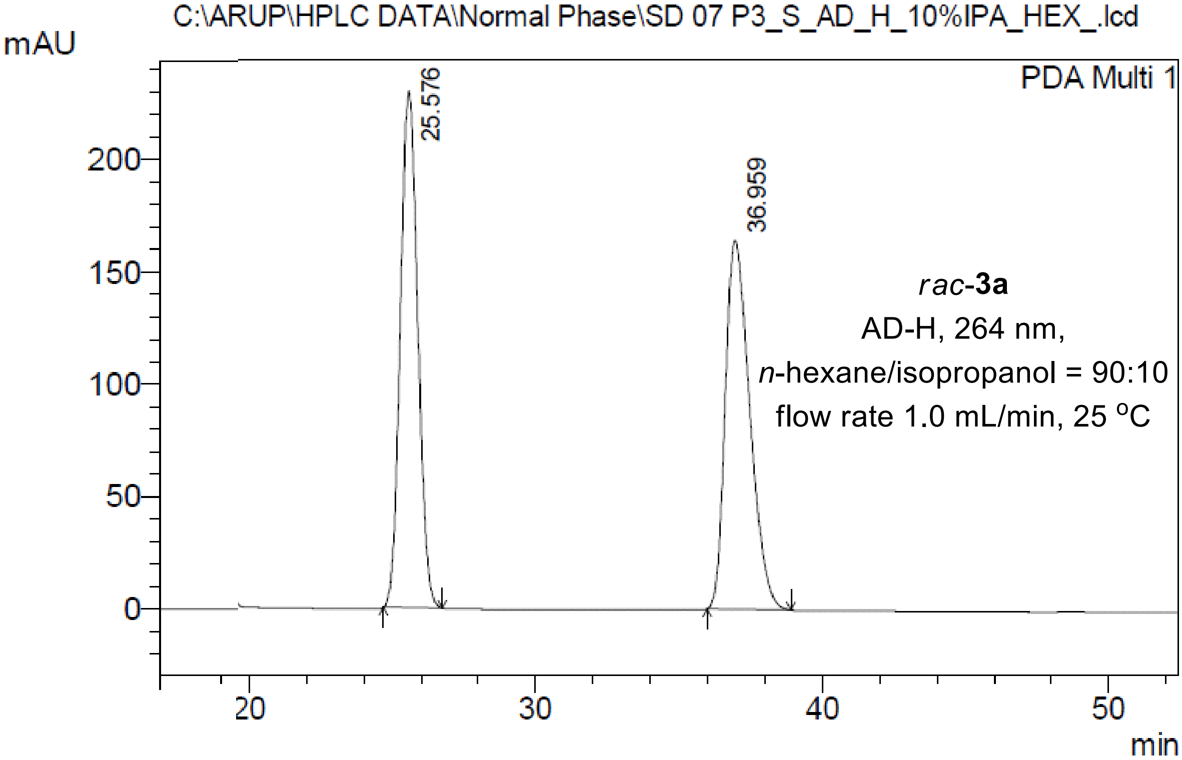


<u>HPLC Traces of *rac*-3a</u>

HPLC chromatogram of racemic **3a**



rac-**3a**



Peak#	Ret. Time	Area	Area %	Height
1	25.576	9704229	50.010	229234
2	36.959	9700482	49.990	163546
Total		19404711	100.000	392780