One-step synthesis of xanthones catalyzed by a highly efficient copper-based magnetically recoverable nanocatalyst

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Supporting Information

Table of Contents

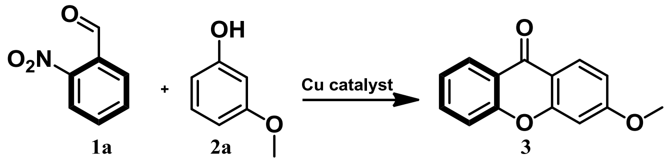
1. General experimental details

All operations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled in accordance with standard procedure.[1] Reactions were monitored by thin-layer chromatography on silica gel plates (60F-254) visualized under UV light and/or using 5% phosphomolybdic acid in ethanol. All ^{1}H and ^{13}C NMR spectra were recorded at room temp. in $CDCl_3$ or Acetone-d_6 on a Bruker Avance ARX-300 spectrophotometer. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (TMS) using the residual solvent resonance ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; brs = broad signal). IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the ATR mode at room temp. Melting points were determined using a Büchi 510 apparatus and are not corrected. Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a GC Shimadzu (GC-14B) with a flame ionization detector equipped with a HP-5MS column (30 m × 0.25 mm × 0.25 μm) using nitrogen as carrier gas. High resolution mass spectra were recorded on Thermo Fisher LTQ Orbitrap XL, (for EI) and a Finnigen MAT 95 (for ESI). Flash column chromatography was performed using Macherey Nagel MN Kieselgel 60M (0.040- 0.063 mm / 230-240 mesh ASTM). All starting materials were of the best available grade (Aldrich, Merck, Acros or TCI) and were used without further purification. Commercially available copper (II) chloride dihydrate was dehydrated upon heating in oven (150 °C, 45 min) prior to use for the preparation of CuNPs. MagSilica® was provided by Evonik Industries AG (Essen, Germany).

Copper content in the supported catalyst was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), in a Spectro Arcos instrument. The freshly prepared catalyst was characterized by Transmission Electron Microscopy (TEM) in a JEOL JEM-2100F-UHR instrument, operated at an acceleration voltage of 200 kV. Approximately one hundred metal particles were measured to perform the particle size distribution. The reducibility of the supported catalyst was analyzed by Temperature Programmed Reduction (TPR) in a in-house-made equipment. Before reduction, the samples were treated with flowing Ar at 300 ºC. Then, a flowing mixture (20 mL/min) of 10 % H_2/Ar was introduced, raising the temperature at 8 ºC/min from room temperature up to 550 ºC. The TPR profile was obtained following the H_2 consumption with a TCD detector. X-ray diffraction (XRD) analysis were performed using a Bruker AXS D8 Advance diffractometer, equipped with a Cu-Kα1,2 radiation source. Atomic absorption spectroscopy was carried out in a Perkin Elmer AA700 spectrometer.

2. Optimization of reaction conditions for the synthesis of xanthones

Table 1. *Initial screening of some copper-catalysts*[a]



Entry	Catalyst	Yield (%)[b]
1	$CuCl_2 \cdot H_2O$	---
2	$CuCl_2$	75
3	Cu	71
4	CuCl	65
5	**CuNPs/MagSilica**	**89**[c]
6	CuO	62

[a] ***Standard reaction conditions**:* 2-nitro- benzaldehyde (1 mmol), 3-methoxyphenol (1.3 mmol), Cu catalyst (5 mol %), PPh_3 (7.5 mmol), K_3PO_4 (2.2 equiv.) in toluene, 24 h. [b] Determined by GC using internal standard. [c] The same yield was obtained by using only 0.9 mol% (8 mg) of CuNPs/MagSilica catalyst.

Table 2: *Effect of ligand and solvent on copper-mediated coupling reaction*[a]

Entry	ligand	solvent	Yield (%)[b]
1	PPh_3	toluene	89
2	---	***toluene***	***95***
3	PPh_3	H_2O	---
4	---	H_2O	---
5	PPh_3	DMF	64
6	---	DMF	62
7	PPh_3	DMSO	51
8	---	DMSO	51

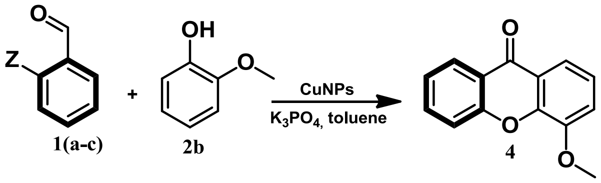
[a] ***Reaction conditions***: 2-nitrobenzaldehyde (1 mmol), 3-methoxyphenol (1.1 mmol), CuNPs (0.9 mol %), PPh_3 (7.5 mmol), K_3PO_4 (2.2 equiv.), 24 h.
[b] Determined by GC using internal standard.

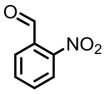
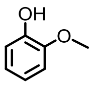
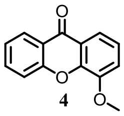
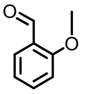
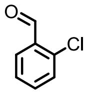
Table 3. *Temperature effect on copper-catalyzed reaction*[a]

Entry	T (°C)	t (h)	Yield (%)[b]
1	0	48	---
2	RT	48	---
3	70	24	53
4	***110***	***2***	***95***

[a] ***Reaction conditions***: 2-nitrobenzaldehyde (1 mmol), 3-methoxyphenol (1.1 mmol), CuNPs (0.9 mol %), K_3PO_4 (2.2 equiv.). [b] Isolated yield after purification.

Table 4. *Scope of 2-substituted benzaldehydes*[a]



Entry	Aryl aldehyde	Phenol	Xanthone	Yield (%)[b]
1	 **1a**	 **2b**	 **4**	84
2	 **1b**	**2b**	**4**	65
3	 **1c**	**2b**	**4**	61

[a]***Reaction conditions***: aryl aldehyde (1 mmol), 2-methoxy-phenol (1.1 mmol), CuNPs (0.9 mol %), K_3PO_4 (2.2 equiv.), 2 h, under argon. [b]Isolated yield after purification**.**

3. General Procedure for One-step Synthesis of Xanthones

Phenols (1.1 mmol), 2-substituted benzaldehydes (1 mmol), K_3PO_4 (2.2 equiv.), CuNPs (0.9 mol%), and toluene (3 mL) were added to a Schlenk tube under argon. The resulting solution was stirred at 110 °C for 2 h. The progress of the reaction was monitored by TLC. The mixture was extracted with EtOAc, washed with water, brine, and then the combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired xanthones.

4. Preparation and characterization of the catalyst

A mixture of lithium sand (21 mg, 3.0 mmol) and 4,4'-di-*tert*-butylbiphenyl (DTBB, 26 mg, 0.1 mmol) in THF (3 mL), was stirred at room temperature under nitrogen atmosphere. When the reaction mixture turned dark green (15-30 min), indicating the formation of the corresponding lithium arenide, anhydrous $CuCl_2$ was added (134 mg, 1.0 mmol). The resulting suspension was stirred until it turned black (5-10 min), indicating the formation of copper(0) nanoparticles. Then, it was diluted with THF (10 mL) and MagSilica (500 mg) was added. The resulting suspension was stirred for 1 h, and then bidistilled water (2 mL) was added for eliminating the excess of lithium. The resulting solid was filtered under vacuum in a Buchner funnel and successively washed with water (10 mL) and acetone (10 mL). Finally, the solid was dried under vacuum (5 Torr) for 2 h.

The CuNPs/MagSilica catalyst was characterized by means of transmission electron microscopy (TEM), energy dispersive X-ray (EDX), powder X-ray diffraction (XRD), temperature programmed reduction (TPR), and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The copper loading fixed to the magnetic support was 6.8 wt% as determined by ICP-AES. For this analysis, two subsamples, 100 mg each, where microwave digested in Teflon beakers using 4 ml HNO_3 (65 %; subboiled) and 3 ml HF (50%; p.a.). MW program: 10 min heating, 600 W to 150°C;and 20 min heating, 800 W to 210°C. Due to undissolved black particles in the sample solution, 3 ml HCl (ca.25% p.a.) and 2 ml HF were added and the MW program repeated. The resulting solution was free of solid particles, clear and brown-greenish in color.

The TPR profile of the catalyst showed only one peak, which was assigned to the reduction of copper oxidized species (CuO). The presence of this species indicates that CuNPs have been oxidized during handling of the catalyst under air. No peaks attributable to the support reduction were detected. The lack of iron species available for reduction strongly suggests that the magnetic core is fully coated by the SiO_2 shell.

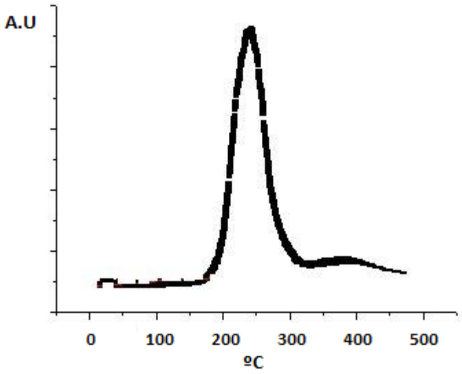


Figure 1. TPR profile of the catalyst. The amount of hydrogen consumed corresponds to the reduction of the whole CuO present in the catalyst. No peaks attributable to the support reduction are observed.

Analysis by TEM showed the presence of well dispersed spherical nanoparticles on the magnetic support, with a narrow size distribution and an average particle size of 3.0 ± 0.8 nm.

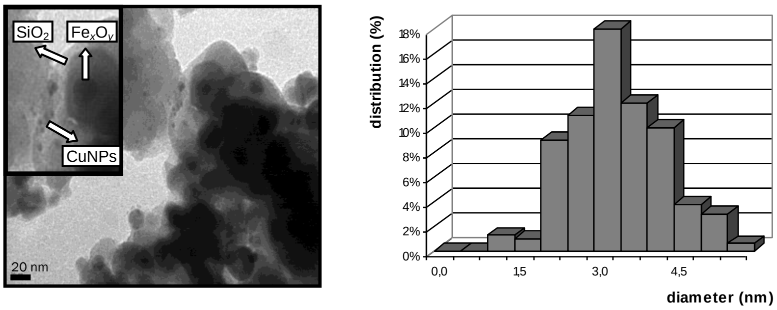


Figure 2. TEM micrograph of CuNPs/MagSilica catalyst (left), and size distribution graphic of supported CuNPs (right). The sizes were determined for 100 nanoparticles selected at random.

Analysis by TEM after a reaction cycle showed that the size and shape of the CuNPs remained similar to that of the fresh sample. TEM micrograph of the recovered catalyst after one reaction cycle in the synthesis of xanthone **3** is shown below.

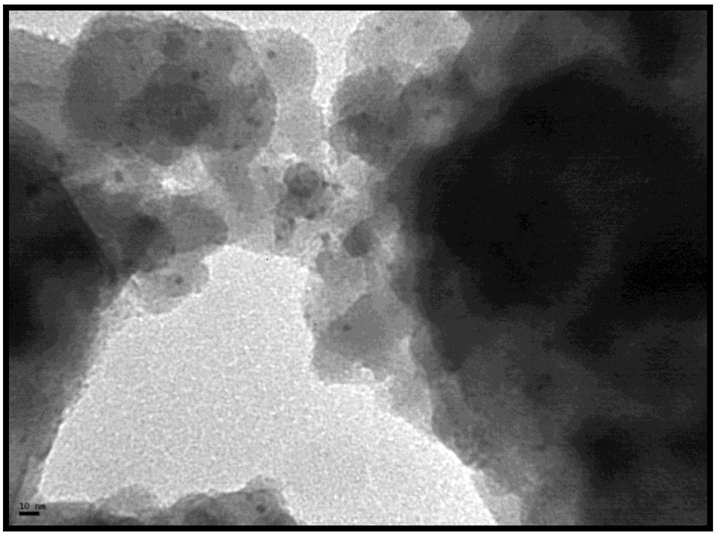


Figure 3. TEM micrograph of the CuNPs present in the catalyst after a reaction cycle. The scale bar corresponds to 10 nm.

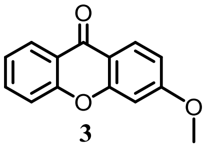
Energy dispersive X-ray analysis on various regions confirmed the presence of copper, with energy bands of 8.04, 8.90 (K lines) and 0.92 keV (L line). Since the spot of the probe is larger than the dimension of copper nanoparticles, this characterization corresponds to a global analysis of copper in the sample.

The XRD diffractogram showed the support diffraction pattern, but no diffraction peaks owing to copper species were detected, this could be attributed to the nanometric character of the CuNPs deposited on the support.

For the analysis of copper and iron leaching under the experimental conditions, 2-nitrobenzaldehyde (**1a**) and 3-nitrophenol (**2a**) were allowed to react under the optimized conditions. After total conversion of the reactants the catalyst was recovered by means of an external magnet. Then, the solvent was evaporated under vacuum and the residue was digested by using a microwave digestor (MARS-5, CEM Corporation), utilizing nitric acid pro-analysis, according to standard SRM 1577a. Quantification of the metal content of the samples was carried out by external calibration using certified standards (Chem-Lab, Zedelgem B-8210). The ICP-AES analysis gave <50 ppb of copper (iron was not detected at ppb levels).

5. Experimental characterization data

3-methoxy-*9H*-xanthen-9-one (3):[2] the title compound was prepared from **1a** and **2a** to give a colorless solid (192 mg, 0.86 mmol, 86 % yield), mp 113-114 °C. SiO_2 (cyclohexane/EtOAc = 10:1).^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 6.86 (d, *J* = 2.3 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 7.34-7.38 (m, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.66-7.70 (m, 1H), 8.27 (d, *J* = 8.9 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 56.1, 100.4, 113.5, 116.0, 117.9, 122.2, 124.2, 126.9, 128.5, 134.5, 156.4, 158.3, 165.3, 176.5. IR (film) ν [cm^{-1}] = 3068, 2950, 2843, 1650. HRMS (EI) for $C_{14}H_{10}O_3$: calcd. 226.0630, found 226.0633.



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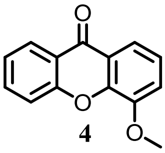
4-methoxy-*9H*-xanthen-9-one (4):[2] the title compound was prepared from **1a** and **2b** to give a colorless solid (190 mg, 0.84 mmol, 84 % yield), mp 110-111 °C. SiO_2 (hexane/EtOAc = 12:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.03 (s, 3H), 7.22-7.31 (m, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.71-7.75 (m, 1H), 7.90 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 56.7, 115.5, 117.8, 118.5, 121.9, 122.9, 123.7, 124.3, 126.9, 135.1, 146.7, 148.8, 156.2, 177.4. IR (film) ν [cm^{-1}] = 3026, 2951, 2849, 1660. HRMS (EI) for $C_{14}H_{10}O_3$: calcd. 226.0630, found 226.0634.



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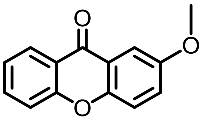
2-methoxy-*9H*-xanthen-9-one (5):[2] the title compound was prepared from **1a** and **2c** to give a white solid (200 mg, 0.89 mmol, 89 % yield), mp 131-133 °C. SiO_2 (hexane/EtOAc = 10:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.03 (s, 3H), 7.22-7.31 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.71-7.75 (m, 1H), 7.90 (dd, J = 7.9, 1.5 Hz, 1H), 8.33 (d, *J* = 7.9 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 56.7, 115.5, 117.8, 118.5, 121.9, 122.9, 123.7, 124.3, 126.9, 135.0, 146.7, 148.8, 156.2, 177.4. IR (film) ν [cm^{-1}] = 3026, 2951, 2849, 1660. HRMS (EI) for $C_{14}H_{10}O_3$: calcd. 226.0630, found 226.0632.



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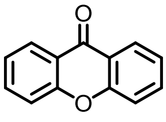
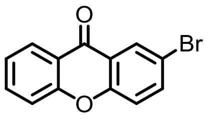
***9H*-xanthen-9-one (6):**[2,3] the title compound was prepared from **1a** and **2d** to give a white solid (150 mg, 0.76 mmol, 76 % yield), mp 174-175 °C. SiO_2 (hexane/EtOAc = 12:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.35 (t, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 6.4 Hz, 2H), 7.70-7.74 (m, 2H), 8.33 (dd, *J* = 6.0, 1.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 117.9, 121.8, 123.9,



6

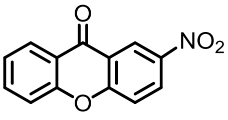
126.7, 134.8, 156.1, 171.1. IR (film) ν [cm^{-1}] = 2914, 2874, 1654, 1456. HRMS (EI) for $C_{13}H_8O_2$: calcd. 196.0524, found 196.0528.

2-bromo-*9H*-xanthen-9-one (7):[4,5] the title compound was prepared from **1a** and **2e** to give a white solid (190 mg, 0.70 mmol, 70 % yield), mp 176-178 °C. SiO_2 (hexane/EtOAc = 14:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.58-7.61 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.98-8.01 (m, 2H), 8.30 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.42 (d, *J* = 2.5 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 117.3, 118.3, 120.2, 121.8, 123.3, 124.5, 127.0, 129.4, 135.5, 137.8, 155.1, 156.2, 176.1. IR (film) ν [cm^{-1}] = 3075, 2919, 1663. HRMS (EI) for $C_{13}H_7BrO_2$: calcd. 273.9629, found 273.9631.



7

2-nitro-*9H*-xanthen-9-one (8):[6] the title compound was prepared from **1a** and **2f** to give a colorless solid (120 mg, 0.51 mmol, 51 % yield), mp 153-154 °C. SiO_2 (hexane/EtOAc = 20:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75-7.77 (m, 2H), 7.98 (dd, *J* = 9.2, 0.3 Hz, 1H), 8.01-8.05 (m, 1H), 8.40-8.42 (m, 1H), 8.85 (dd, *J* = 9.1, 2.8 Hz, 1H), 9.21-9.22 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 118.4, 119.9, 121.6, 121.9, 123.8, 125.5, 127.2, 129.4, 136.1, 156.1, 159.5, 175.9. IR (film) ν [cm^{-1}] = 3077, 1667, 1611. HRMS (EI) for $C_{13}H_7NO_4$: calcd. 241.0375, found 241.0378.



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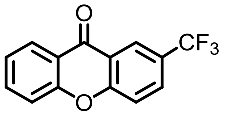
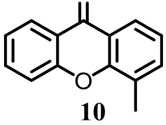
2-trifluoromethyl-*9H*-xanthen-9-one (9):[3] the title compound was prepared from **1a** and **2g** to give a yellow solid (140 mg, 0.54 mmol, 54 % yield), mp 122-124 °C. SiO_2 (hexane/EtOAc =25:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.57-7.62 (m, 3H), 7.86 (td, *J* = 7.8 Hz, 1.5 Hz, 1H), 8.10 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.55 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 118.1, 119.2, 121.5, 121.6, 123.7, 124.7, 124.8, 126.6, 126.8, 131.1, 135.5, 156.0, 157.7, 176.1. IR (film) ν [cm^{-1}] = 3077, 2961, 1667, 1611. HRMS (EI) for $C_{14}H_7F_3O_2$: calcd. 264.0398, found 264.0402.



9

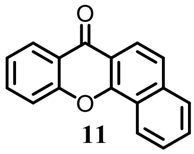
4-methyl-*9H*-xanthen-9-one (10):[2] the title compound was prepared from **1a** and **2h** to give a colorless solid (170 mg, 0.80 mmol, 80 % yield), mp 125-127 °C. SiO_2 (hexane/EtOAc =40:1). ^{1}H-RMN (300 MHz, $CDCl_3$): δ 2.54 (s, 3H), 7.25 (dd, 1H, *J*= 7.6 Hz, 7.0 Hz), 7.36 (dd, *J*= 7.6 Hz, 7.0 Hz), 7.50 (d, 1H, *J*= 7.6 Hz), 7.53 (d, 1H, *J*=7.2 Hz), 7.70 (dd, 1H, *J* = 7.2



10

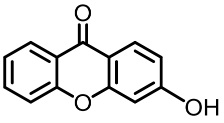
Hz), 8.17 (d, 1H, *J* = 7.6 Hz), 8.32 (d, 1H, *J*=8.0 Hz).^{13}C-RMN (75 MHz, CDCl$_3$): δ 16.0, 118.3, 121.8, 121.9, 123.6, 124.1, 124.5, 126.9, 127.5, 134.9, 135.9, 154.7, 156.26, 177.8. IR (film) ν [cm^{-1}] = 3071, 2990, 1665, 1610. HRMS (EI) for $C_{14}H_{10}O_2$: calcd. 210.0681, found 210.0685.

***7H*-benzo[c]xanthen-7-one (11):**[3,5] the title compound was prepared from **1a** and **2i** to give a white solid (190 mg, 0.77 mmol, 77 % yield), mp 155-157 °C. SiO$_2$ (hexane/EtOAc =10:1). ^{1}H-RMN (300 MHz, CDCl$_3$): δ 7.46 (t, 1H, *J*=7.4 Hz), 7.70-7.81 (m, 5H), 7.95 (d, 1H, *J*=8.6 Hz), 8.29 (d, 1H, *J*=8.8 Hz), 8.42 (d, 1H, *J*=7.9 Hz), 8.70 (d, 1H, *J*=7.4 Hz). ^{13}C-RMN (75 MHz, CDCl$_3$): δ 117.8, 118.2, 121.7, 122.6, 123.1, 124.2, 124.6, 126.8, 127.1, 128.3, 129.7, 134.5, 136.7, 153.8, 155.3, 155.9, 177.1. IR (film) ν [cm^{-1}] = 3073, 1663, 1612. HRMS (EI) for $C_{17}H_{10}O_2$: calcd. 246.0681, found 246.0684.



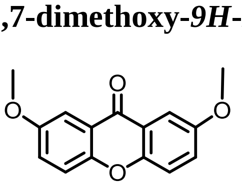
11

3-hydroxy-*9H*-xanthen-9-one (12):[7] the title compound was prepared from **1a** and **2j** to give a white solid (140 mg, 0.68 mmol, 68 % yield), mp 254-255 °C. SiO$_2$ (hexane/EtOAc =2:1). ^{1}H-RMN (300 MHz, DMSO-*d$_6$*): δ 2.44 (s, 1H), 6.94 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.99 (d, *J* = 1.4 Hz, 1H), 7.49-7.51 (m, 2H), 7.78 (td, *J* = 7.5, 1.4 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 8.15-8.17 (m, 1H). ^{13}C-NMR (75 MHz, DMSO-*d$_6$*): δ 103.1, 114.0, 118.7, 122.3, 123.9, 126.1, 128.2, 133.9, 134.5, 155.2, 158.9, 164.8, 175.5. IR (KBr) ν [cm^{-1}] = 3455, 3073, 1667, 1612, 1120. HRMS (EI) for $C_{13}H_8O_3$: calcd. 212.0473, found 212.0477.



12

2,7-dimethoxy-*9H*-xanthen-9-one (13):[8] the title compound was prepared from **1d** and **2c** to give a white solid (180 mg, 0.72 mmol, 72 % yield), mp 172-174 °C. SiO$_2$ (hexane/EtOAc =15:1). ^{1}H-NMR (CDCl$_3$, 300 MHz): δ 3.80 (s, 6H), 6.92 (d, *J*= 9.2 Hz, 1H), 6.94 (d, *J* = 9.2 Hz, 1H), 7.04-7.06 (m, 4H). ^{13}C-NMR (CDCl$_3$, 75 MHz): δ 56.2, 106.6, 119.9, 120.4, 123.7, 155.0, 161.0, 174.1. IR (film) ν [cm^{-1}] = 3075, 1661, 1610. HRMS (ESI) for $C_{15}H_{12}O_4$: calcd. 256.0736, found 256.0740.



13

6. References

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7. NMR Spectra

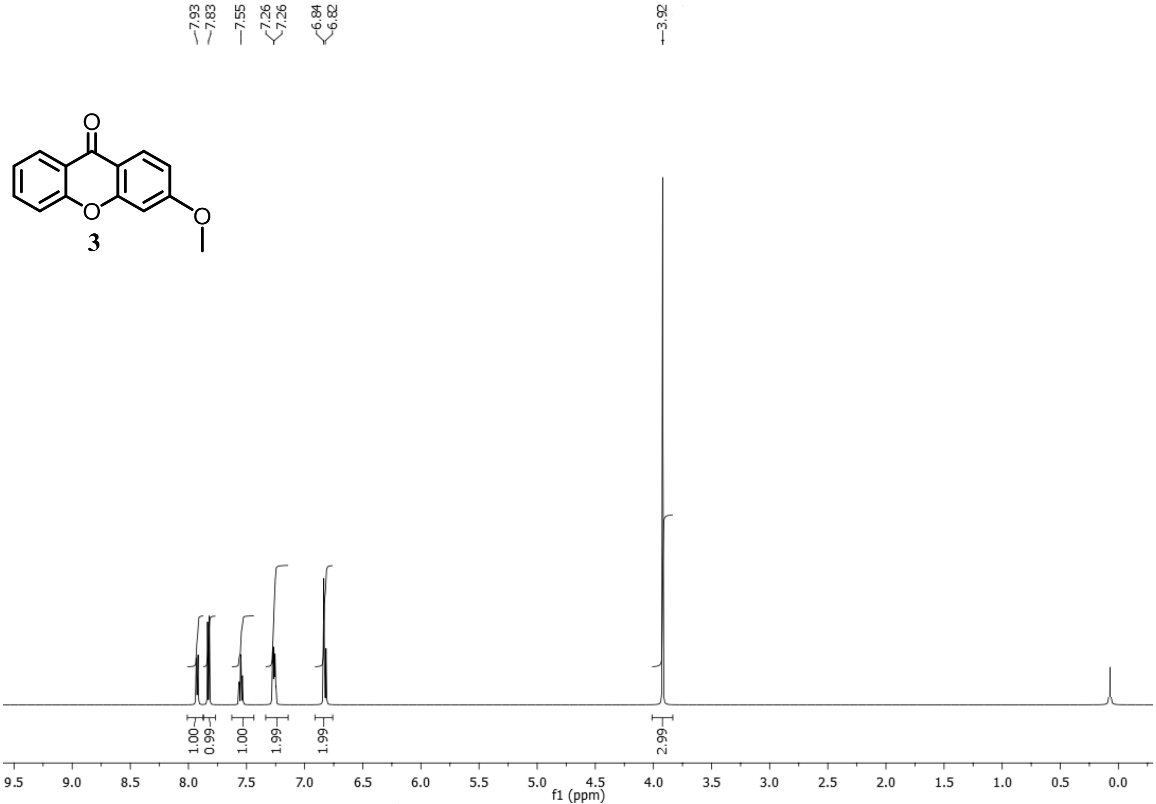


Figure 1. ^{1}H spectrum of **3** (300 MHz, $CDCl_3$).

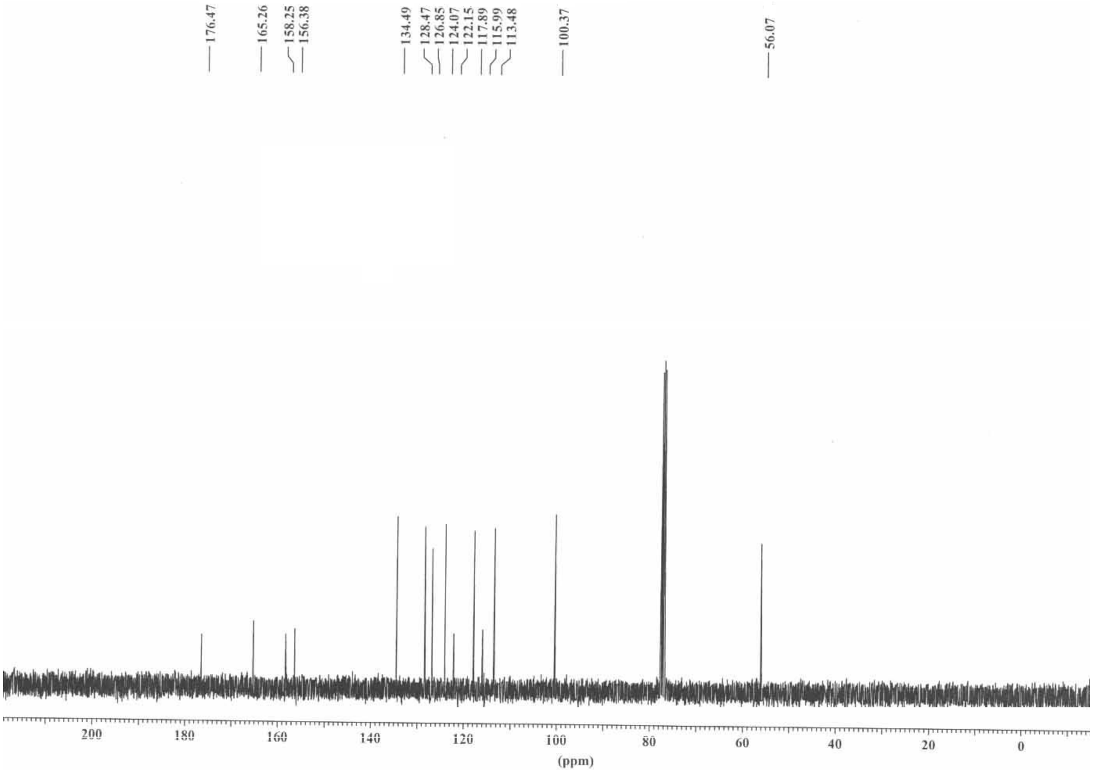


Figure 2. ^{13}C spectrum of **3** (75 MHz, $CDCl_3$).

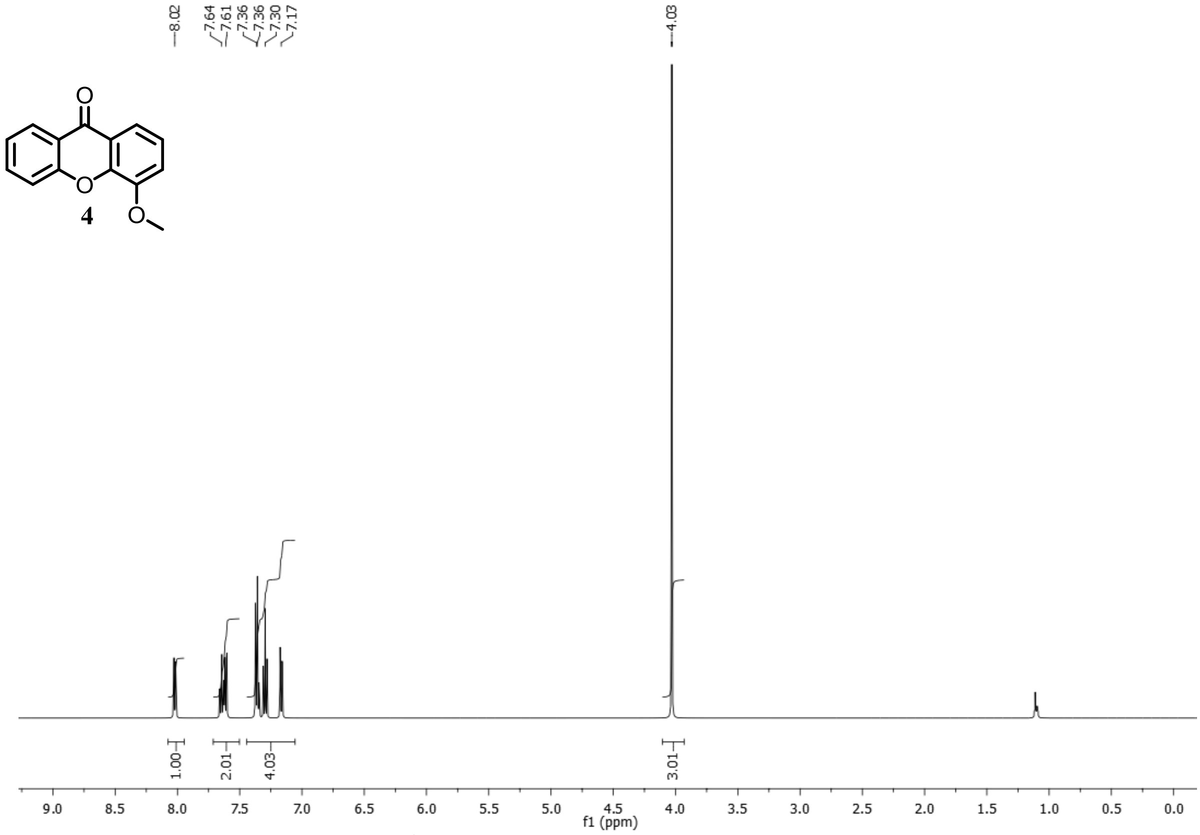


Figure 3. ^{1}H spectrum of **4** (300 MHz, CDCl$_3$).

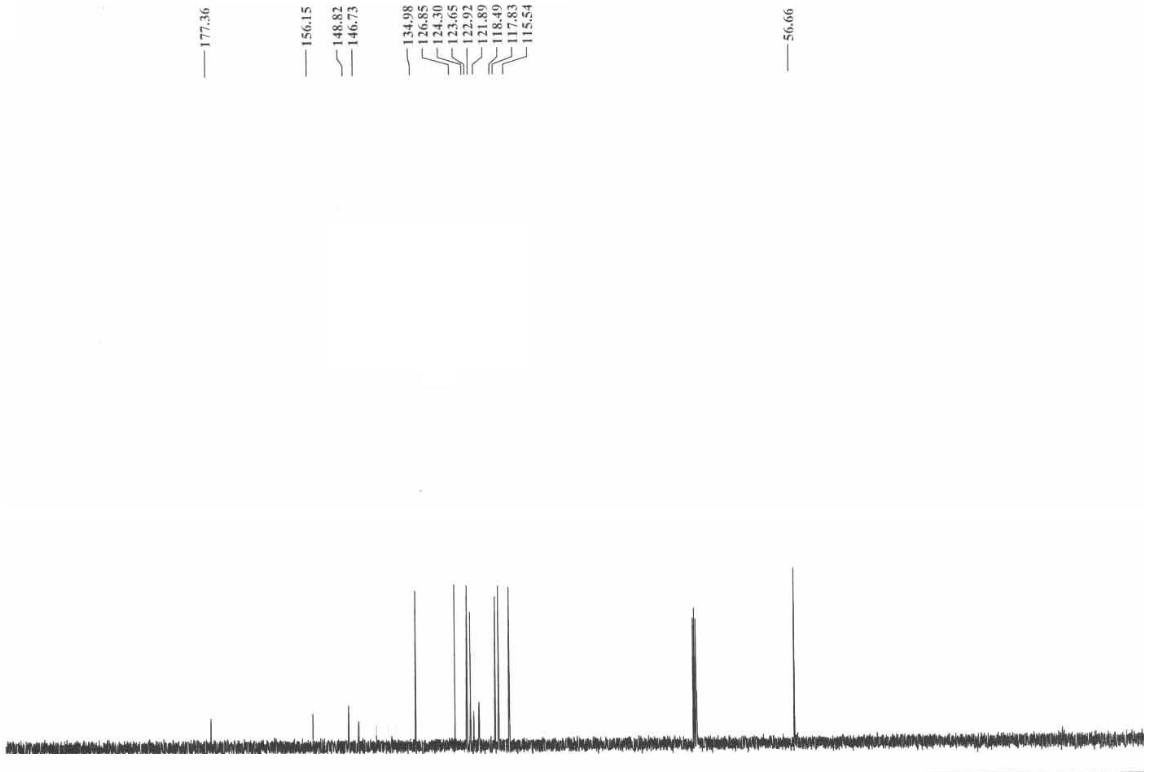


Figure 4. ^{13}C spectrum of **4** (75 MHz, CDCl$_3$).

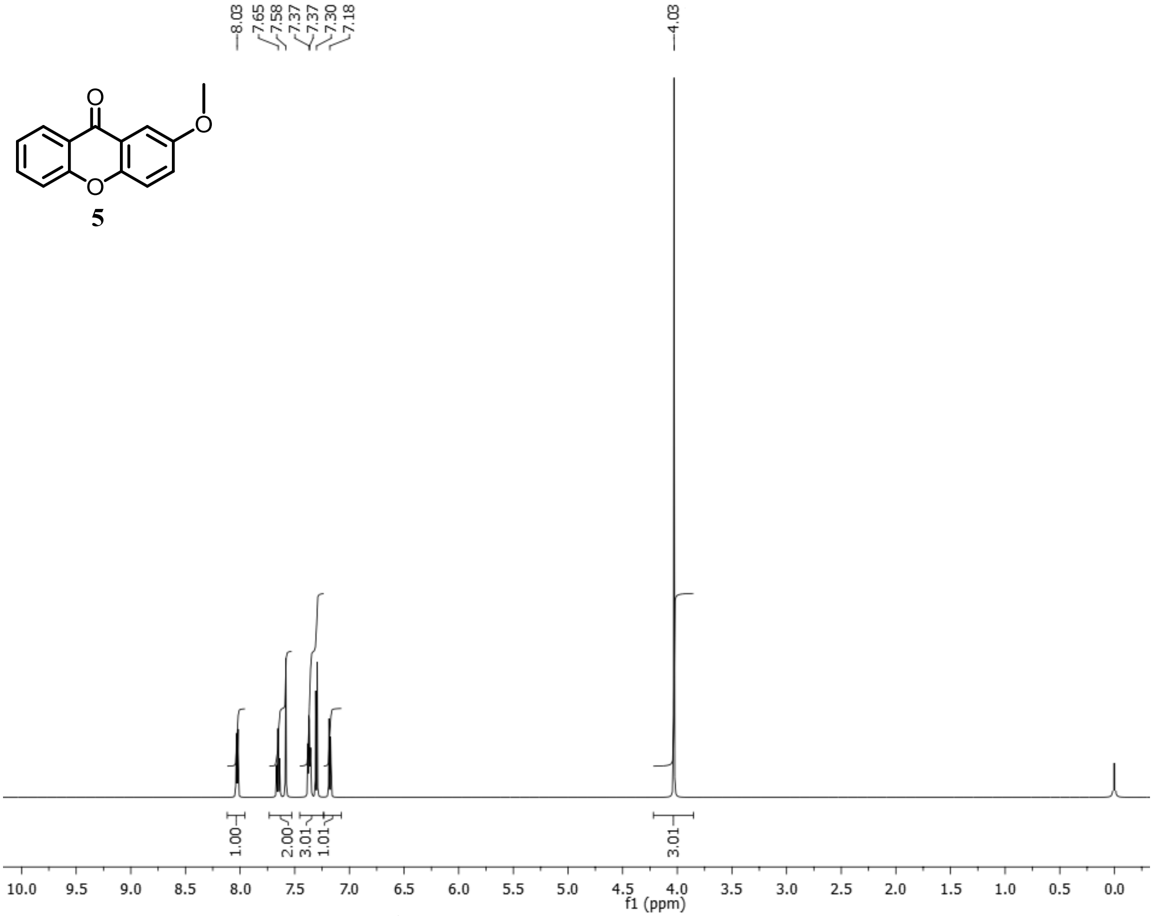


Figure 5. ${}^{1}H$ spectrum of **5** (300 MHz, $CDCl_3$).

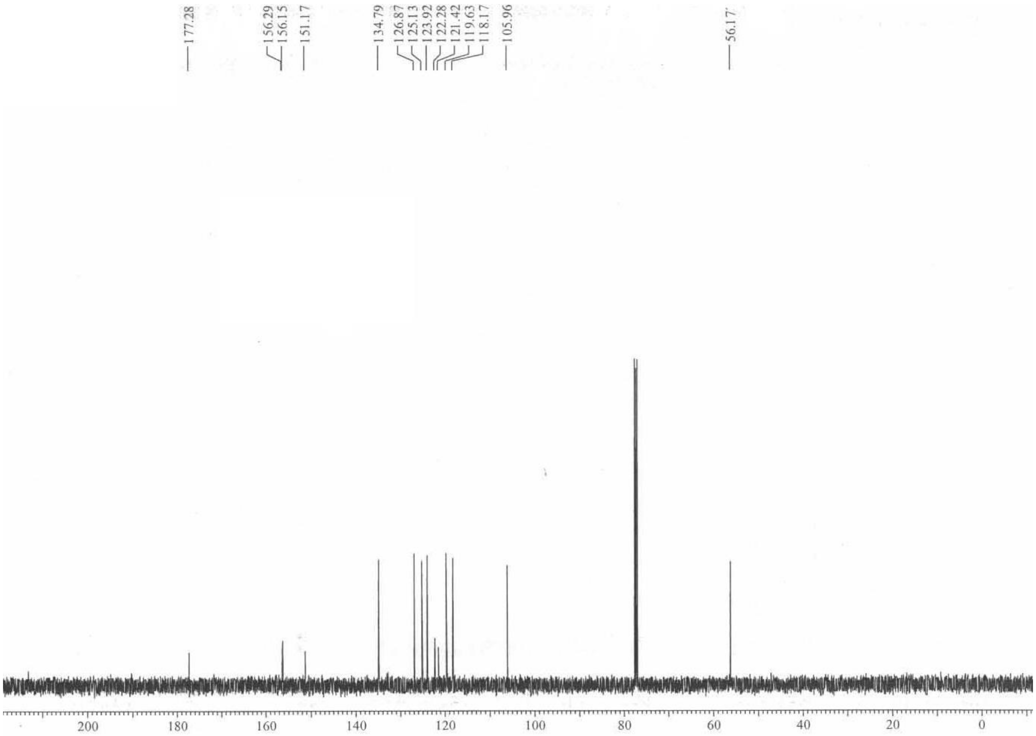
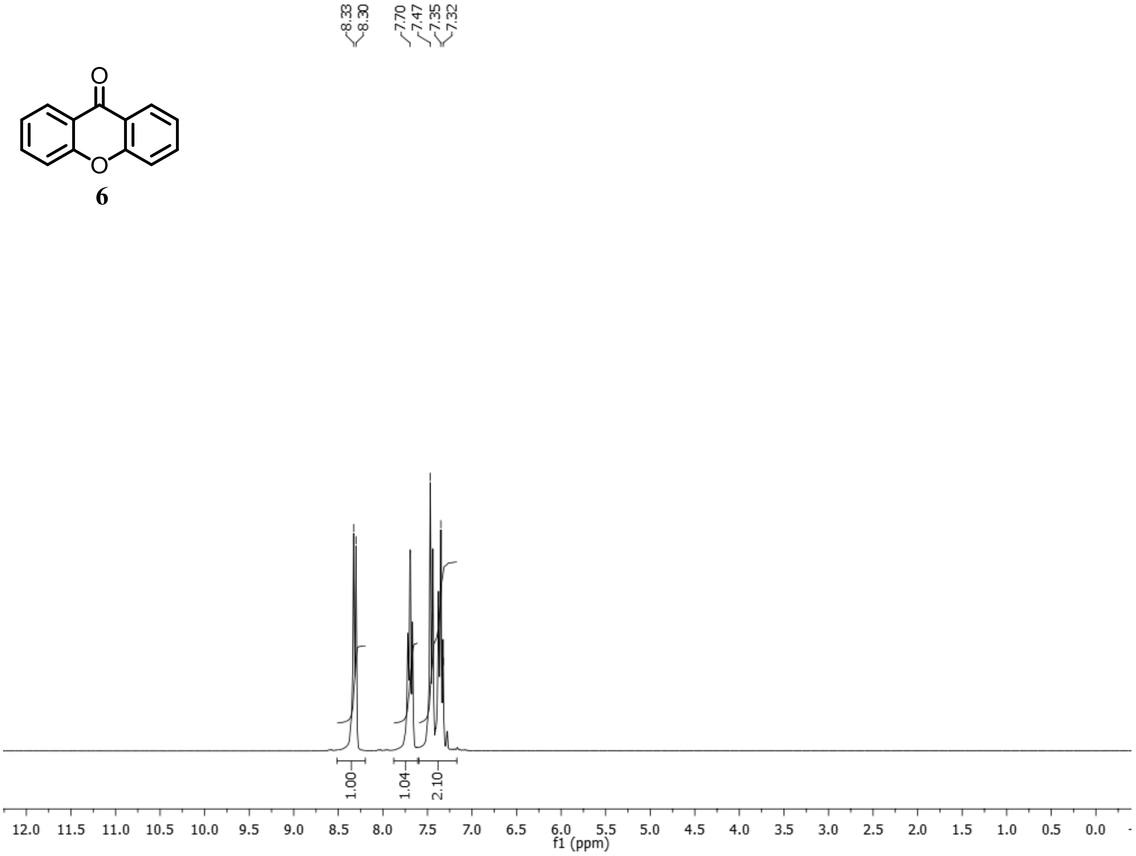


Figure 6. ${}^{13}C$ spectrum of **5** (75 MHz, $CDCl_3$).



6

Figure 7. ^{1}H spectrum of **6** (300 MHz, $CDCl_3$).

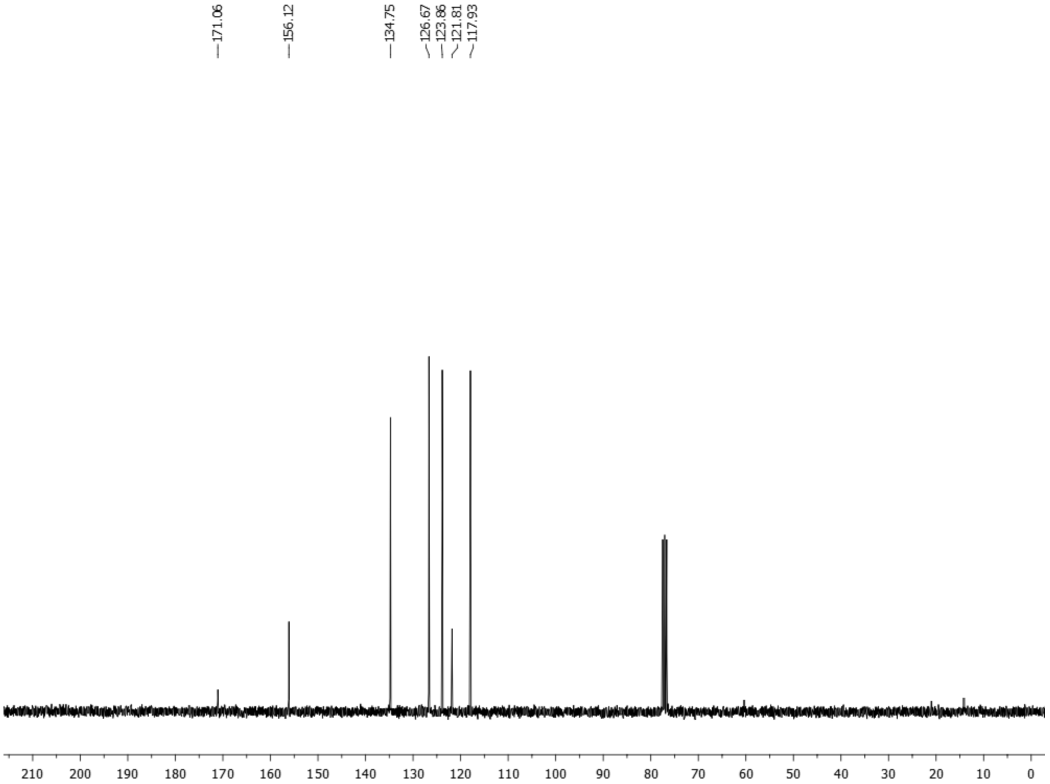


Figure 8. ^{13}C spectrum of **6** (75 MHz, $CDCl_3$).

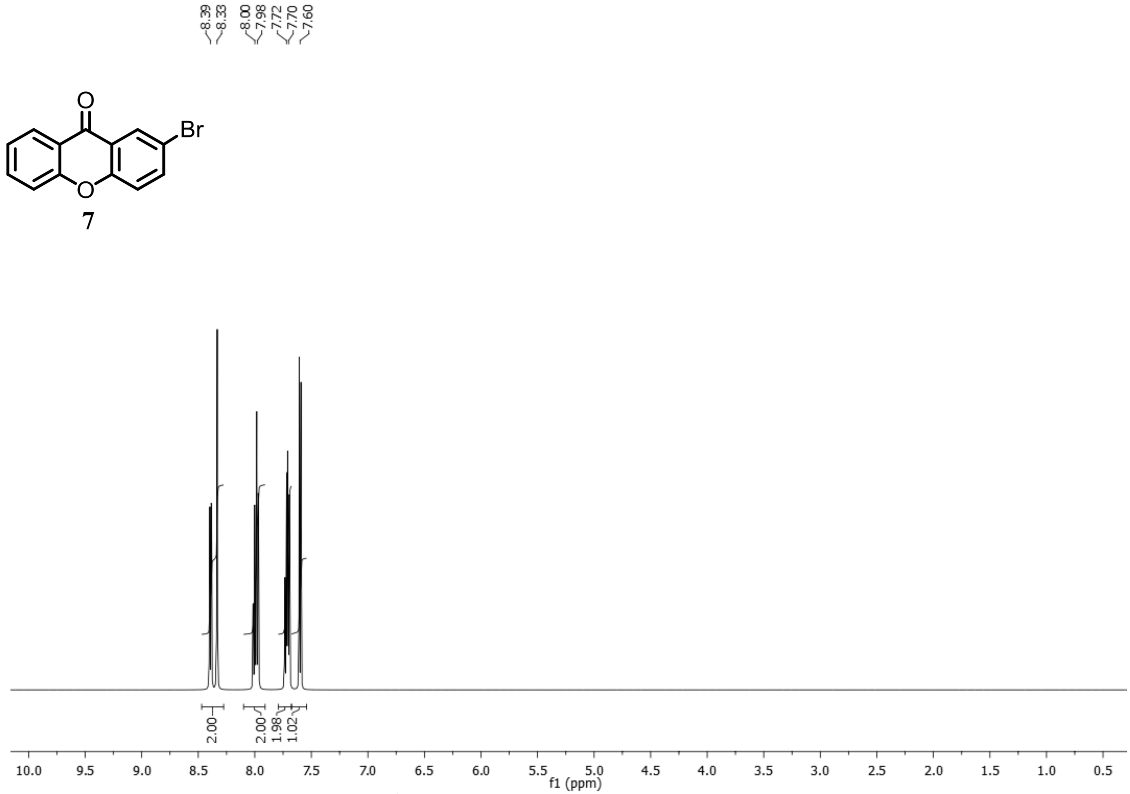


Figure 9. ^{1}H spectrum of **7** (300 MHz, CDCl$_3$).

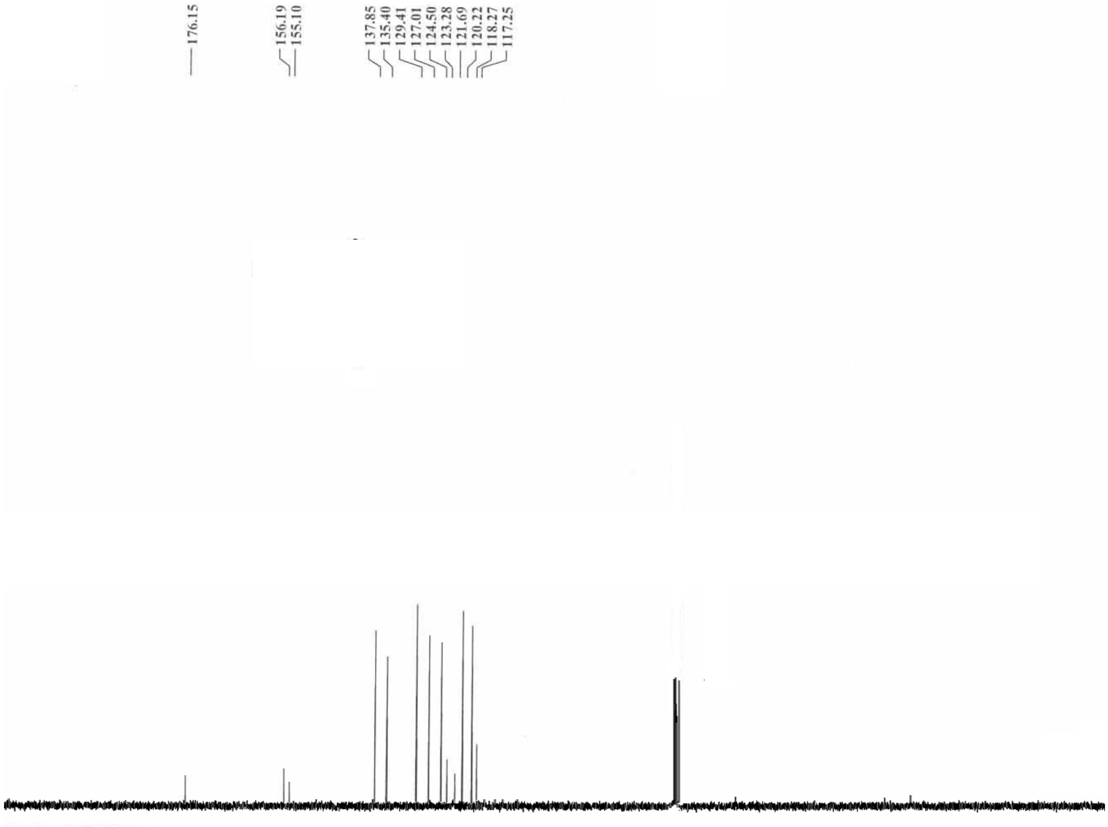


Figure 10. ^{13}C spectrum of **7** (75 MHz, CDCl$_3$).

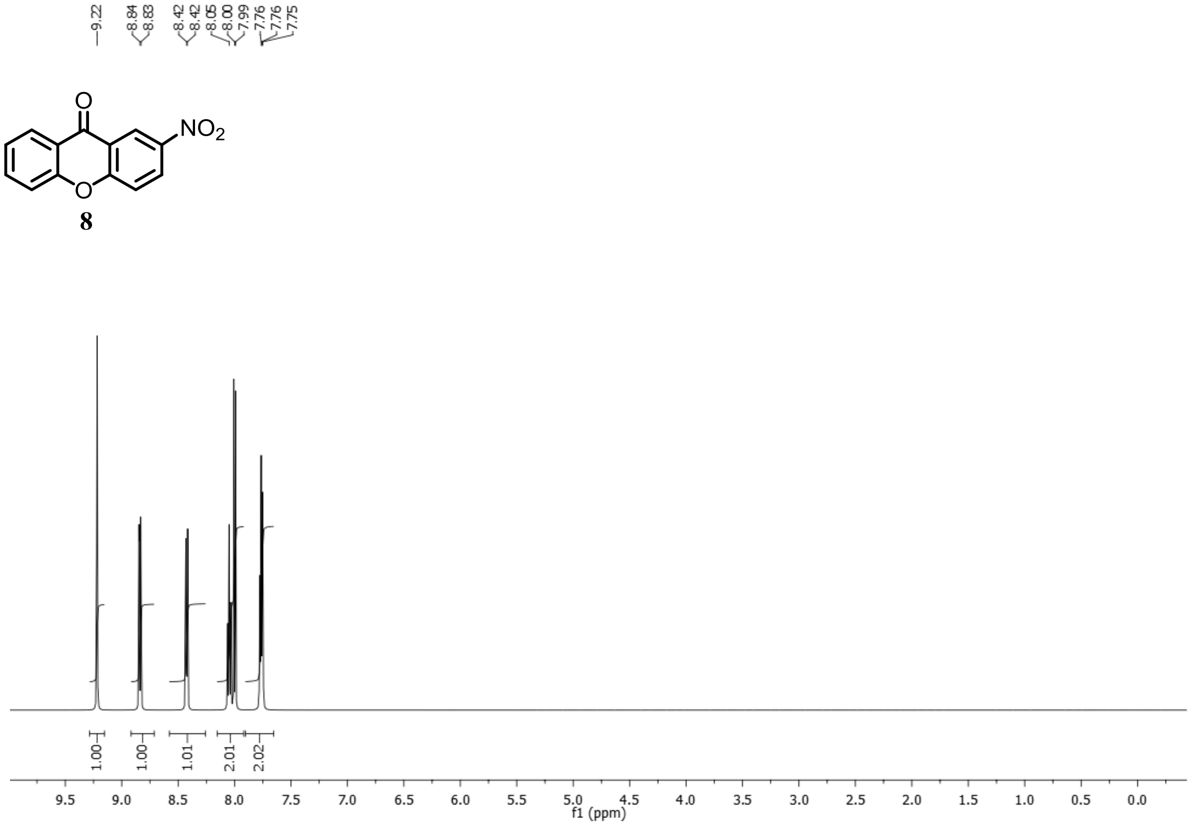


Figure 11. ^{1}H spectrum of **8** (300 MHz, CDCl$_3$).

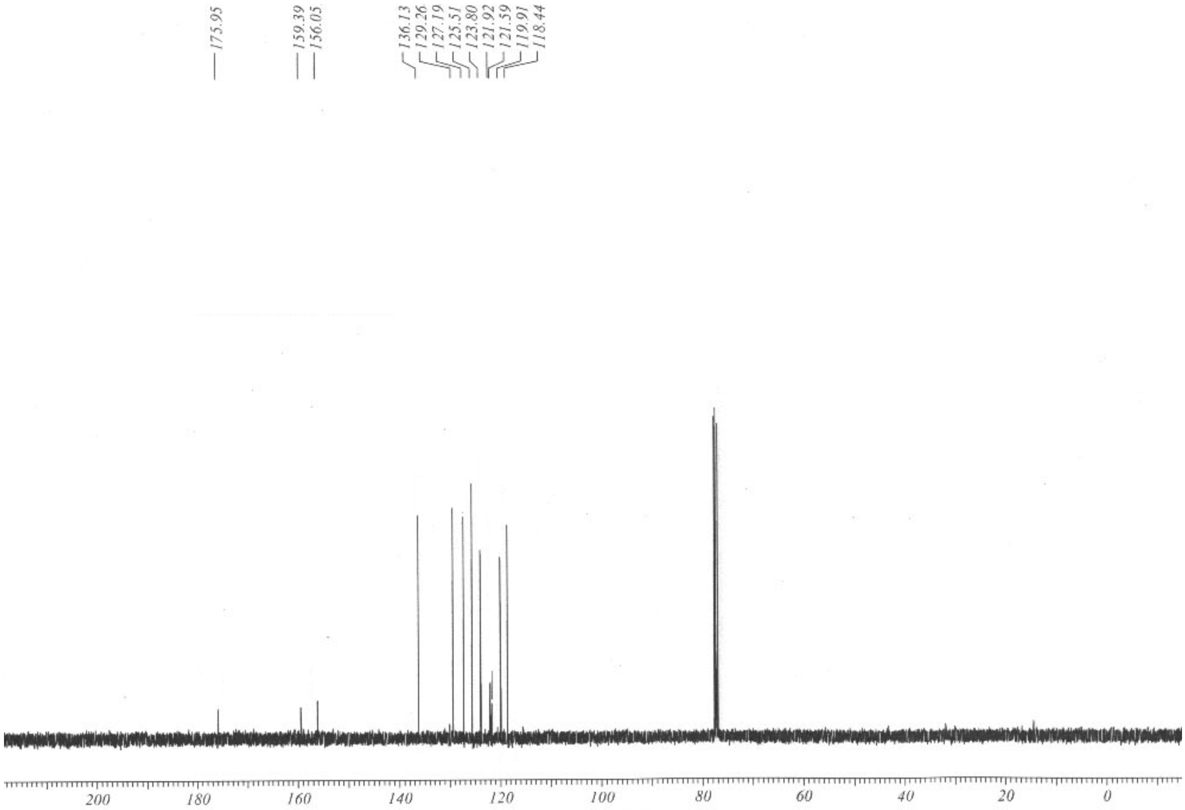


Figure 12. ^{13}C spectrum of **8** (75 MHz, CDCl$_3$).

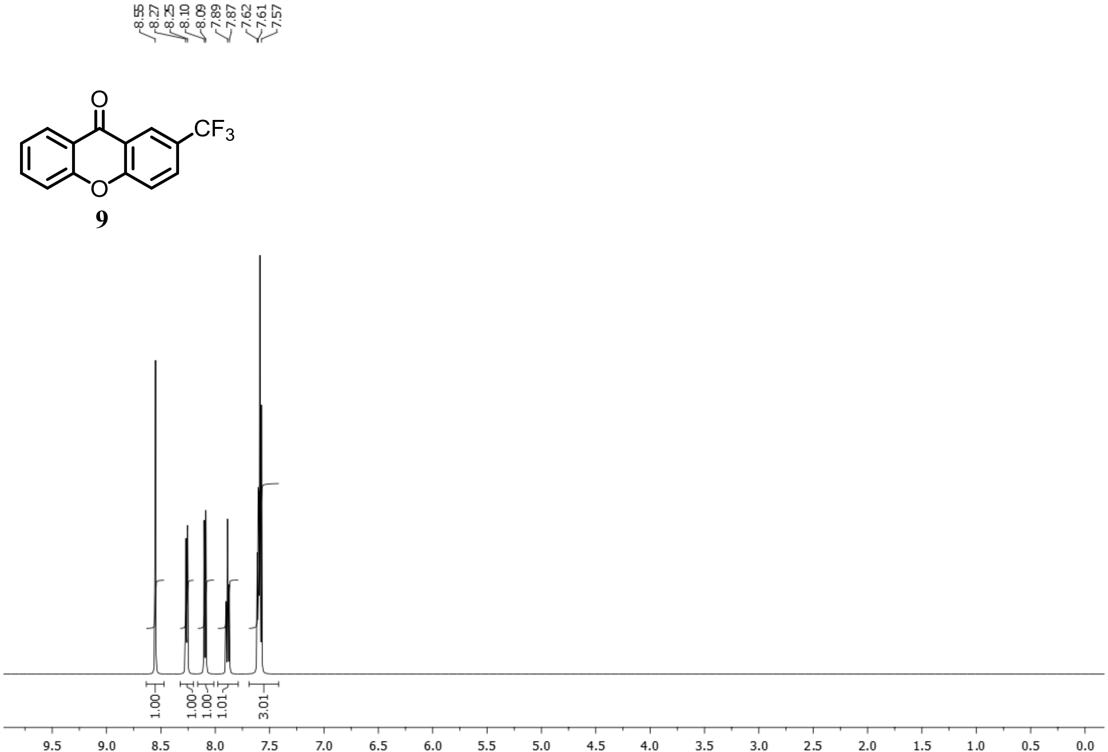


Figure 13. ^{1}H spectrum of **9** (300 MHz, CDCl$_3$).

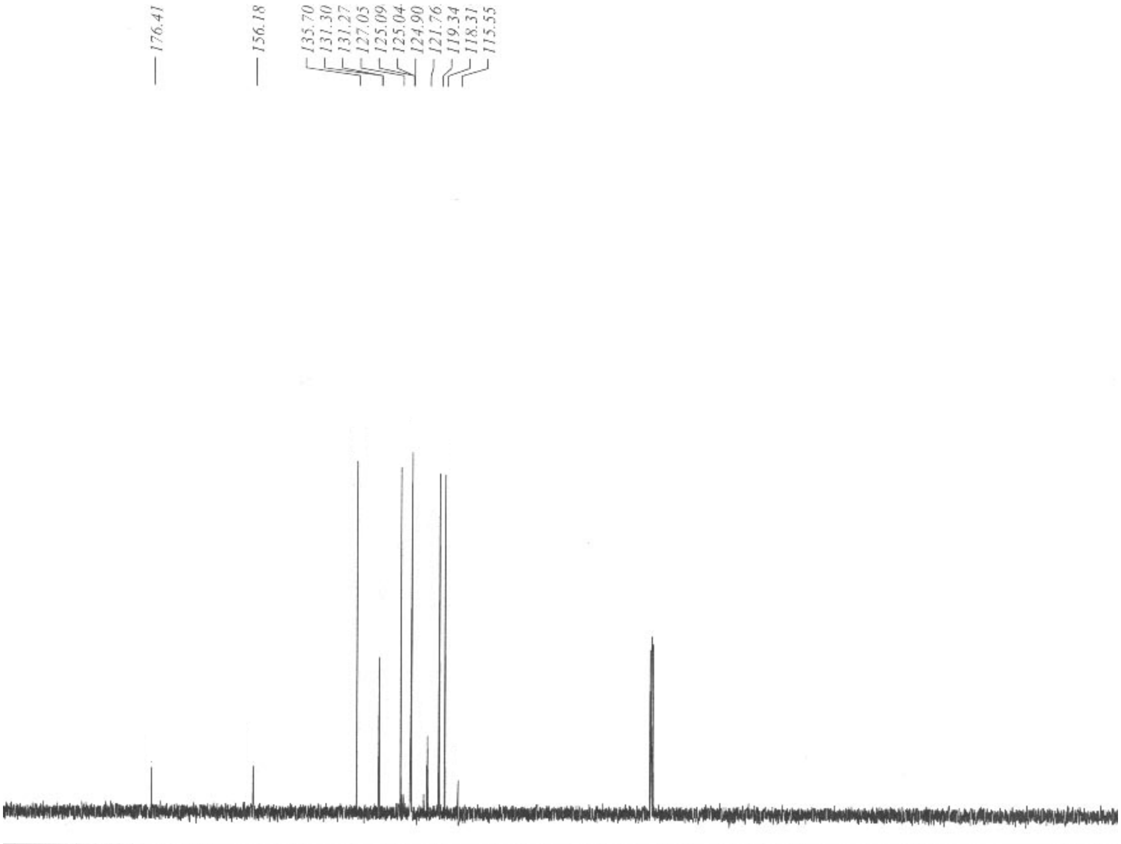


Figure 14. ^{13}C spectrum of **9** (75 MHz, CDCl$_3$).

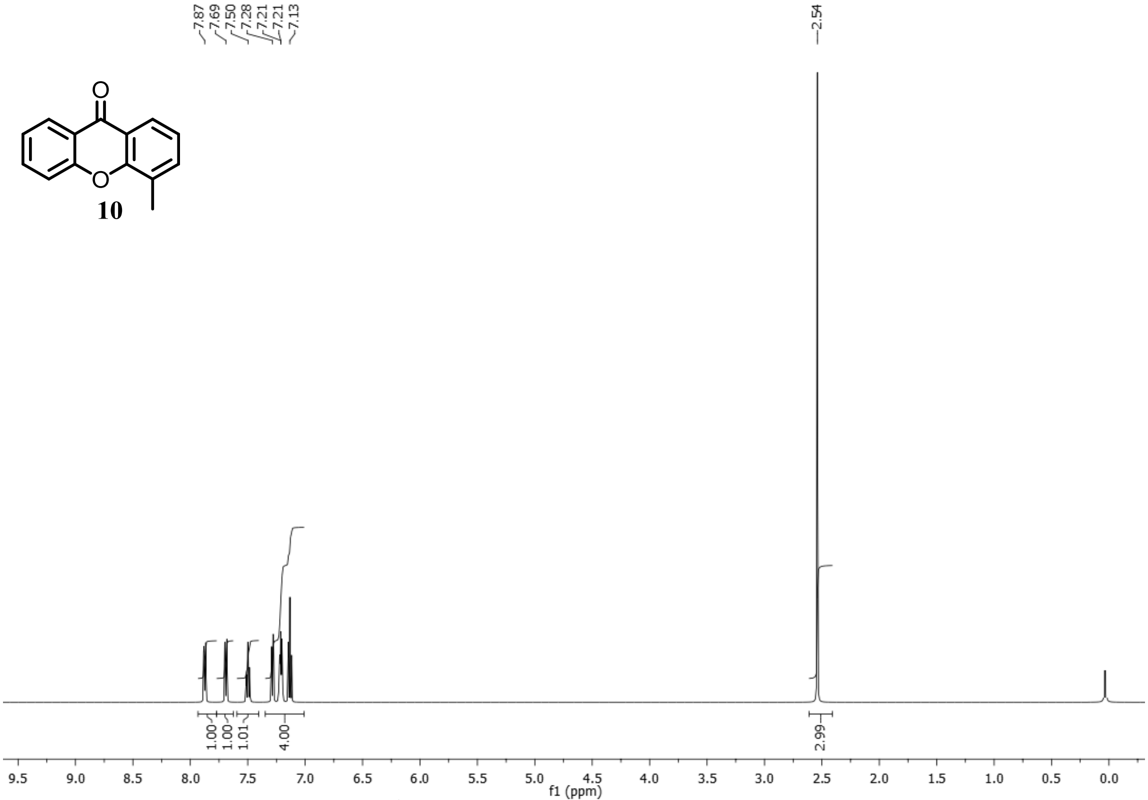


Figure 15. ^{1}H spectrum of **10** (300 MHz, $CDCl_3$).

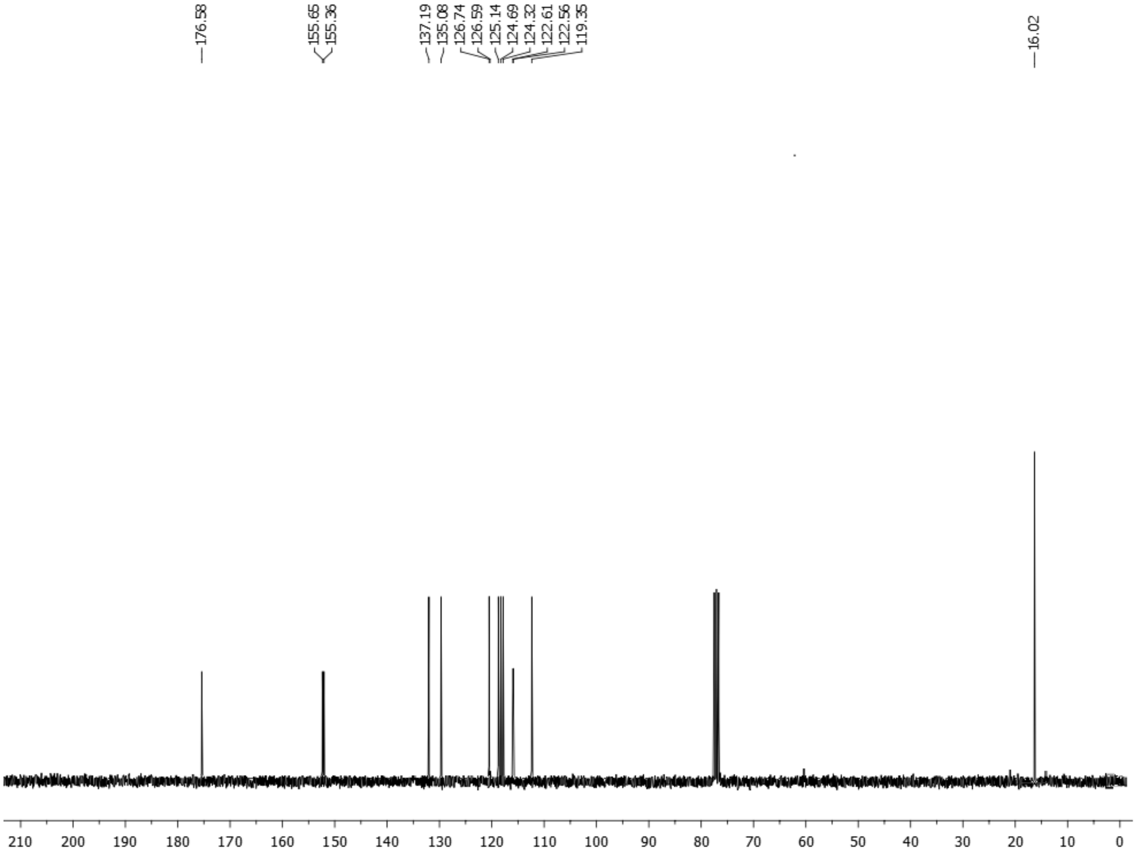


Figure 16. ^{13}C spectrum of **10** (75 MHz, $CDCl_3$).

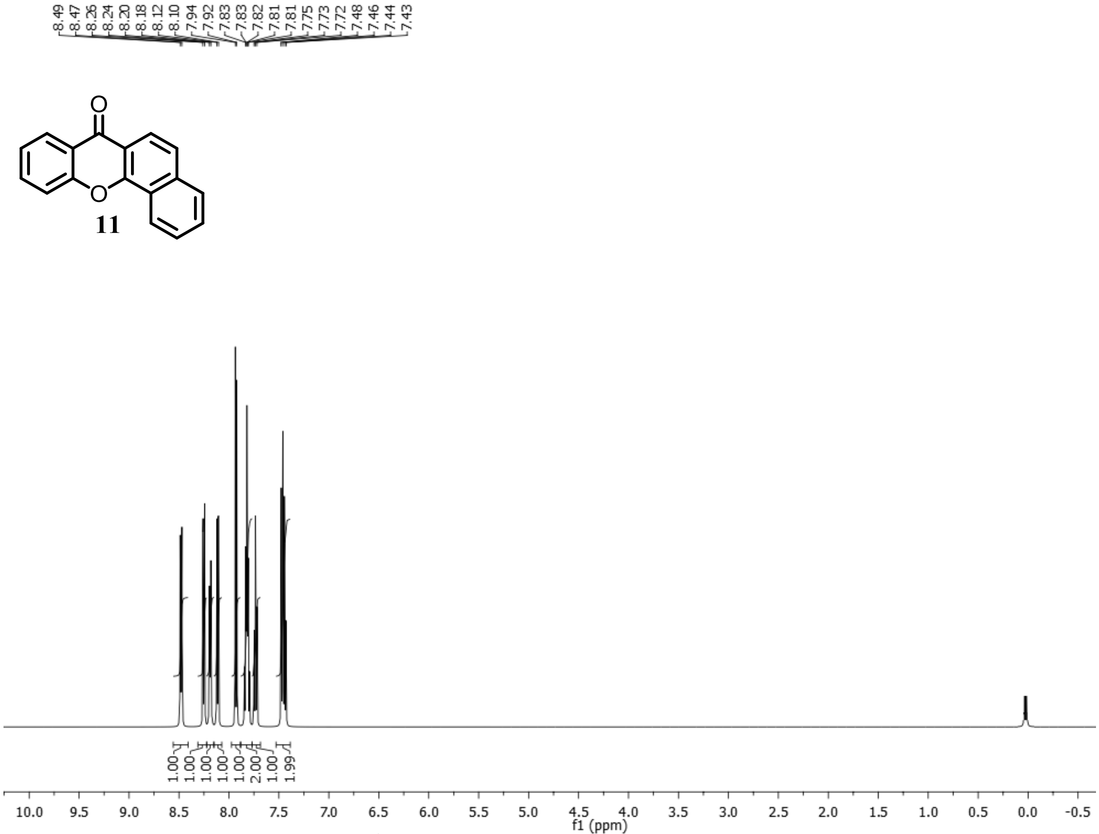


Figure 17. ^{1}H spectrum of **11** (300 MHz, $CDCl_3$).

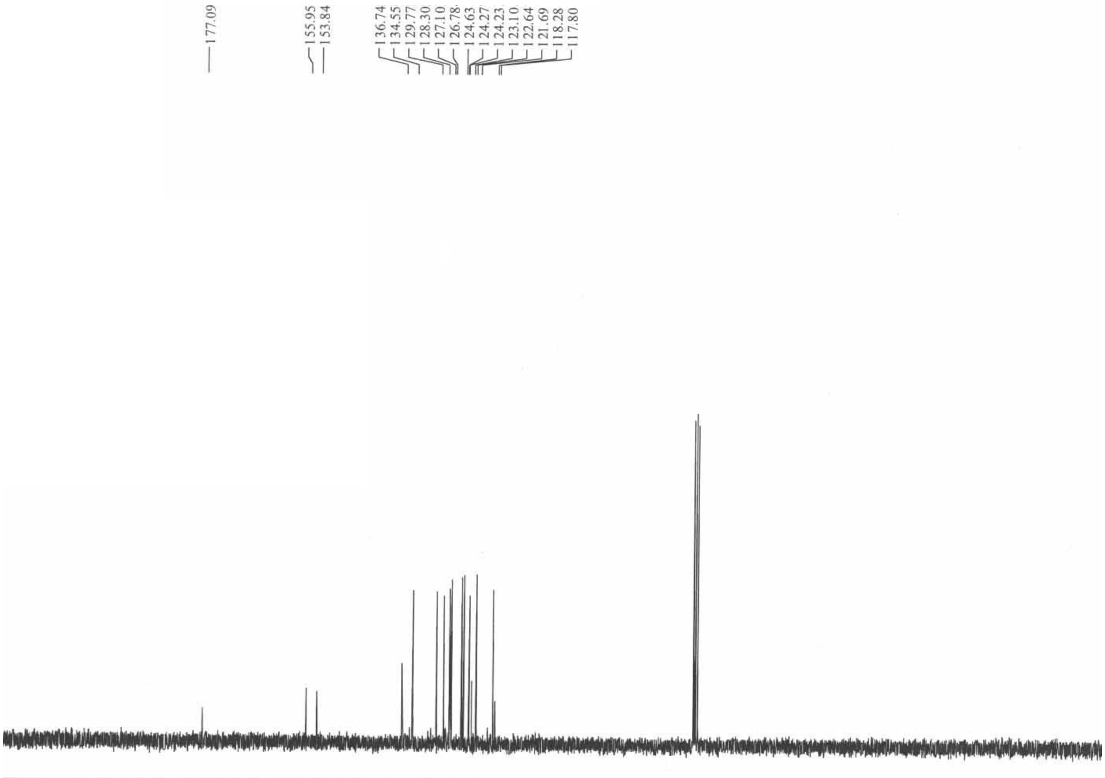


Figure 18. ^{13}C spectrum of **11** (75 MHz, $CDCl_3$).

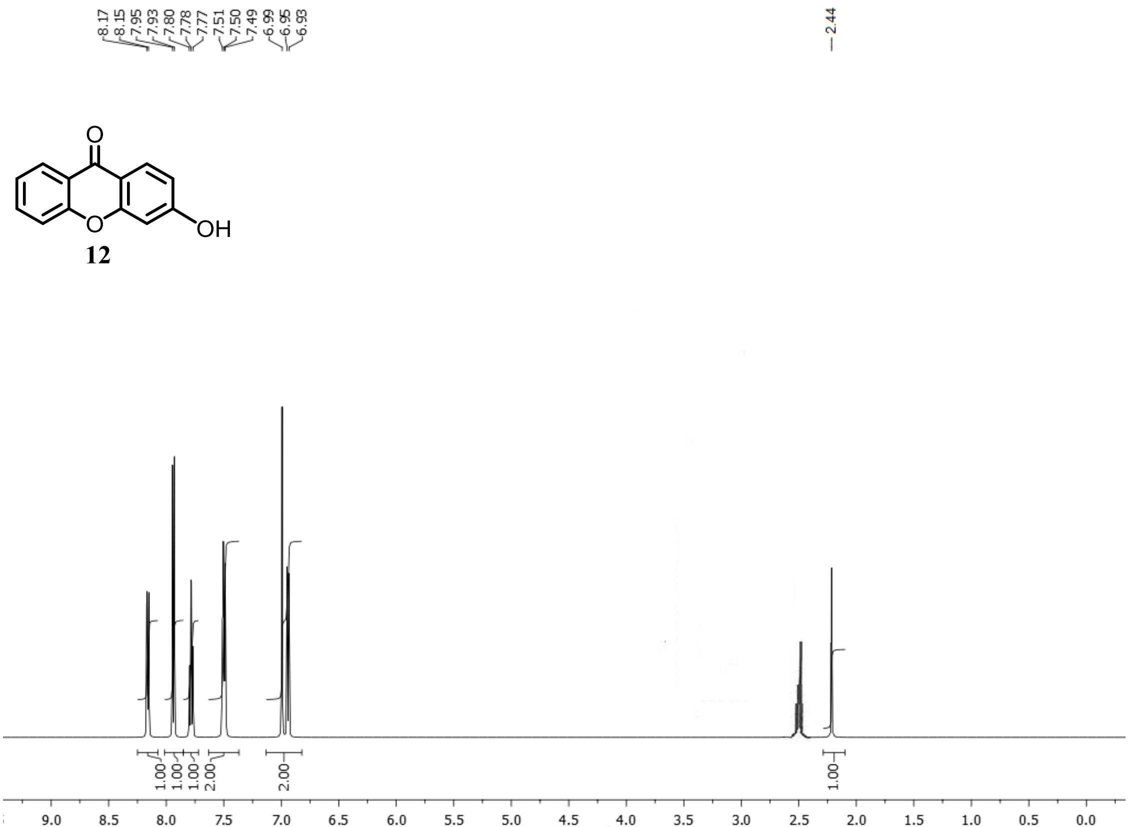


Figure 19. ^{1}H spectrum of **12** (300 MHz, DMSO- d_6).

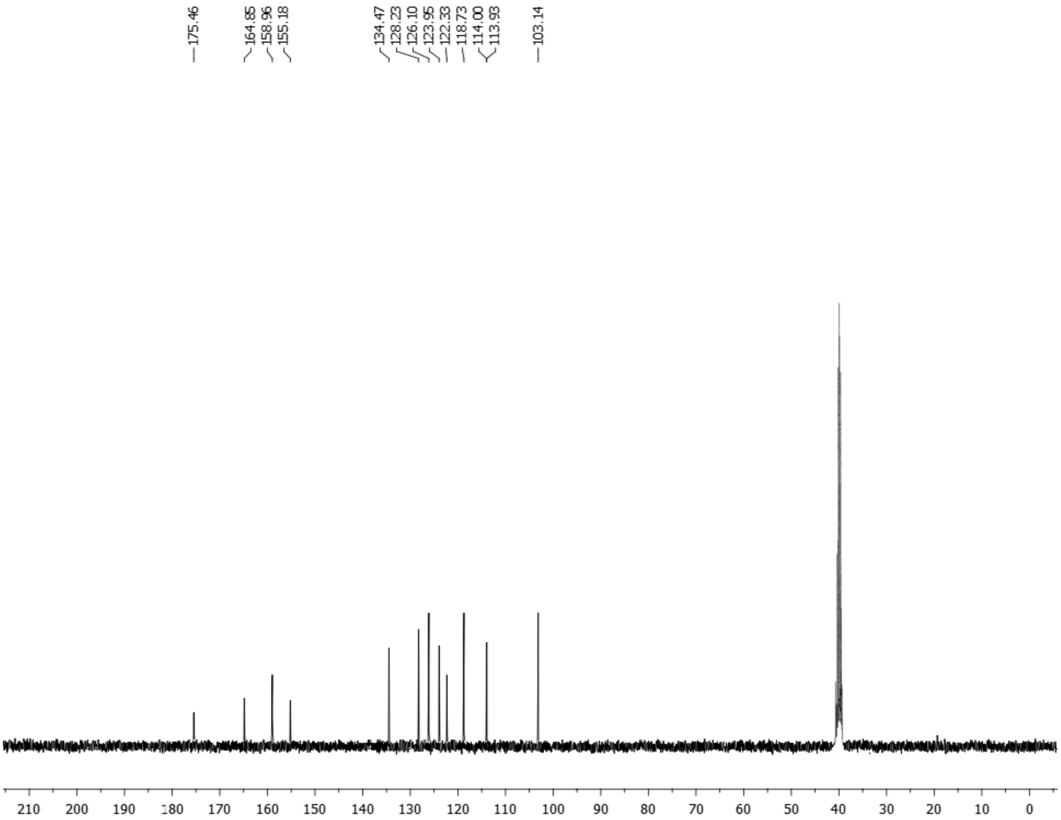


Figure 20. ^{13}C spectrum of **12** (75 MHz, DMSO-d_6).

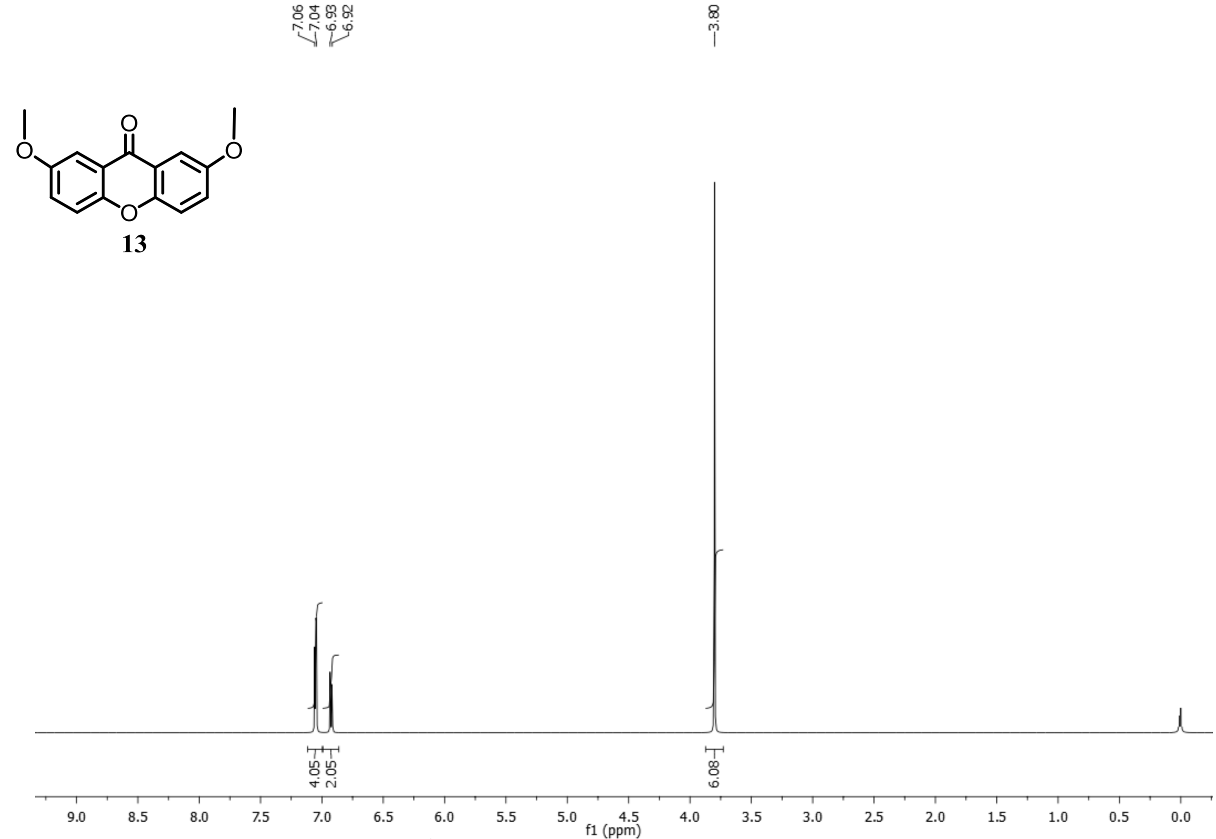


Figure 21. ^{1}H spectrum of **13** (300 MHz, CDCl$_3$).

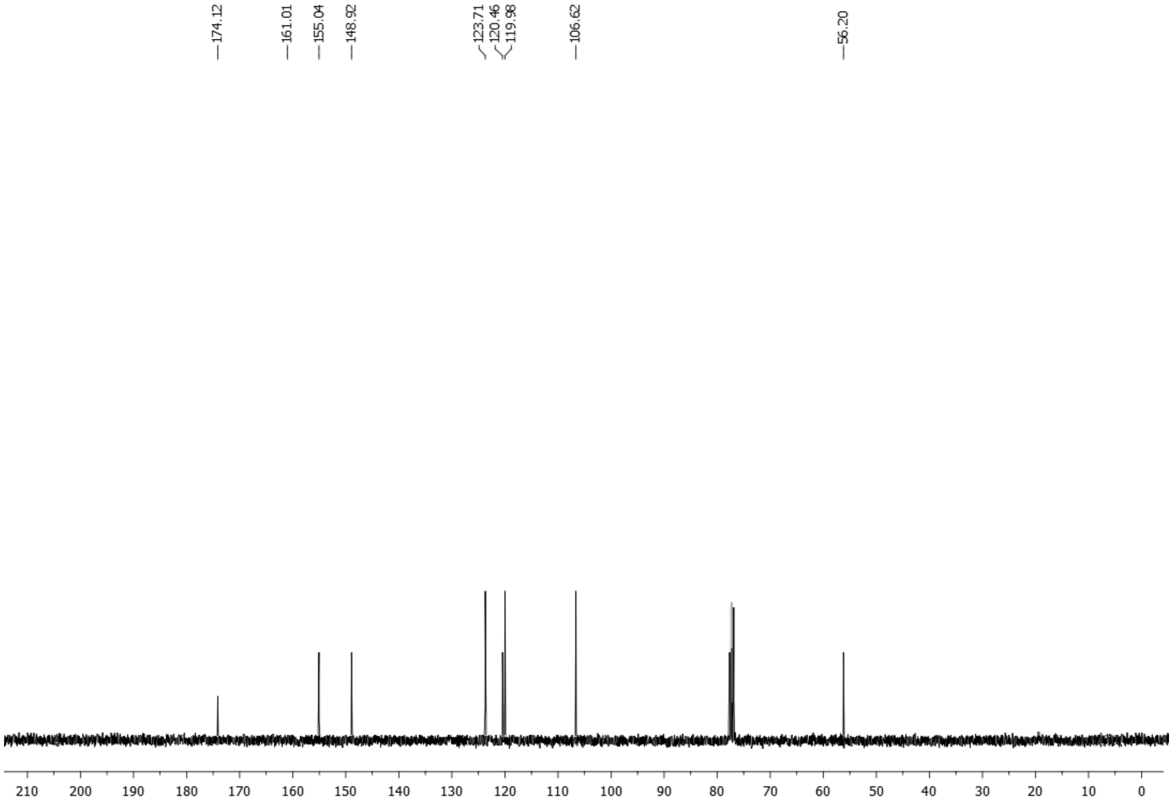


Figure 22. ^{13}C spectrum of **13** (75 MHz, CDCl$_3$).