

Fur-Imine-Functionalized Graphene Oxide-Immobilized Copper Oxide Nanoparticle Catalyst for the Synthesis of Xanthene Derivatives

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Materials and Characterization Techniques

Graphite powder (~200 mesh, 99.9%) and 3-aminopropyltriethoxysilane (3-APTES) were purchased from Alfa Aesar, India. $\text{Cu}(\text{CH}_3\text{COO})_2$ was obtained from SRL, India. All other materials used were of AR grade. X-ray diffraction patterns were obtained using X-ray diffractometer (Model No. D8 DISCOVER). X-Ray photoelectron spectroscopy (XPS) (PHI 5000 Versa Prob II, FEI Inc.) with Auger electron spectroscopy module was used for obtaining XPS spectra. Morphological characterization was carried out using TECNAI 200 kV Transmission Electron Microscopy (TEM) (Fei, Electron Optics) equipped with digital imaging and 35 mm photography system and Field Emission Scanning Electron Microscope (FESEM) Model No.- ZEISS Gemini SEM-500. Raman spectra were recorded by Renishaw inViaTM Reflex Micro-Raman spectrometer using 514 nm wavelength Ar^+ laser for sample excitation.

Table S1 Effect of solvent on the catalytic efficacy of Cu(II)-Fur-APTES/GO for the synthesis of 1,8-dioxo-octahydroxanthenes^a

Entry	Solvent/Solvent Mixture	Temperature (°C)	Time (min)	Yield ^b (%)
1	Acetonitrile	85	150	68
2	Methanol	70	120	72
3	Water	100	90	81
4	Ethanol(EtOH)	82	90	86
5	Water:EtOH (4:1)	60	60	91
6	Water:EtOH (1:1)	60	30	95
7	Water:EtOH (1:1)	50	30	95

^aReaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol), catalyst (20 mg), solvent (5 ml).

^bIsolated yields

Table S2 Reusability of Cu(II)-Fur-APTES/GO^a.

Entry	Time (min)	Yield (%)
1	30	95
2	30	95
3	30	93
4	30	91
5	35	90

^aReaction conditions: Dimedone (2 mmol), Benzaldehyde (1 mmol), Cu(II)-Fur-APTES/GO (20 mg), 50 °C, 5ml aq. ethanolic solution (1:1).

Table S3 EDX data of Cu (II)- APTES/GO

Element	Weight %	Atomic %
C K	45.50	57.23
N K	8.17	8.81
O K	28.05	26.49
CuL	7.90	1.88
SiK	10.39	5.59

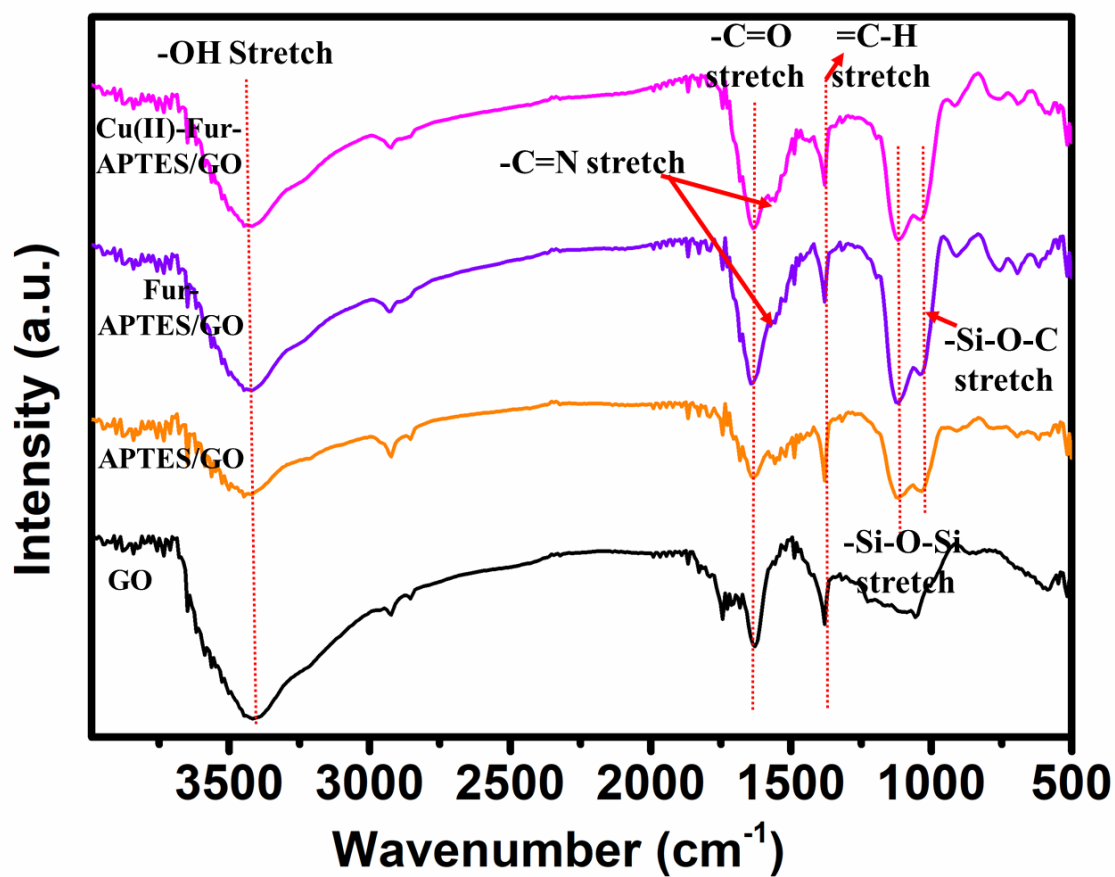


Figure S1 FTIR Spectra of GO, APTES/GO, Fur-APTES/GO, Cu(II)-Fur-APTES/GO nanocatalyst.

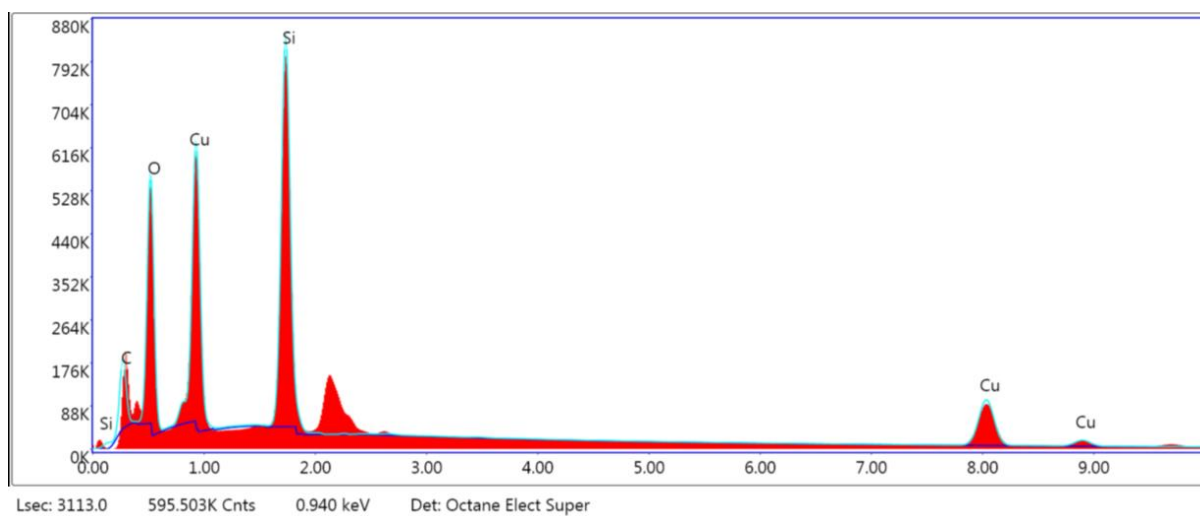


Figure S2 EDX spectrum of the nano-catalyst Cu(II)-Fur-APTES/GO.

^1H and ^{13}C -NMR spectra of the different xanthene derivatives reported in Table 2.

Figure S3. ^1H and ^{13}C NMR of **3a**

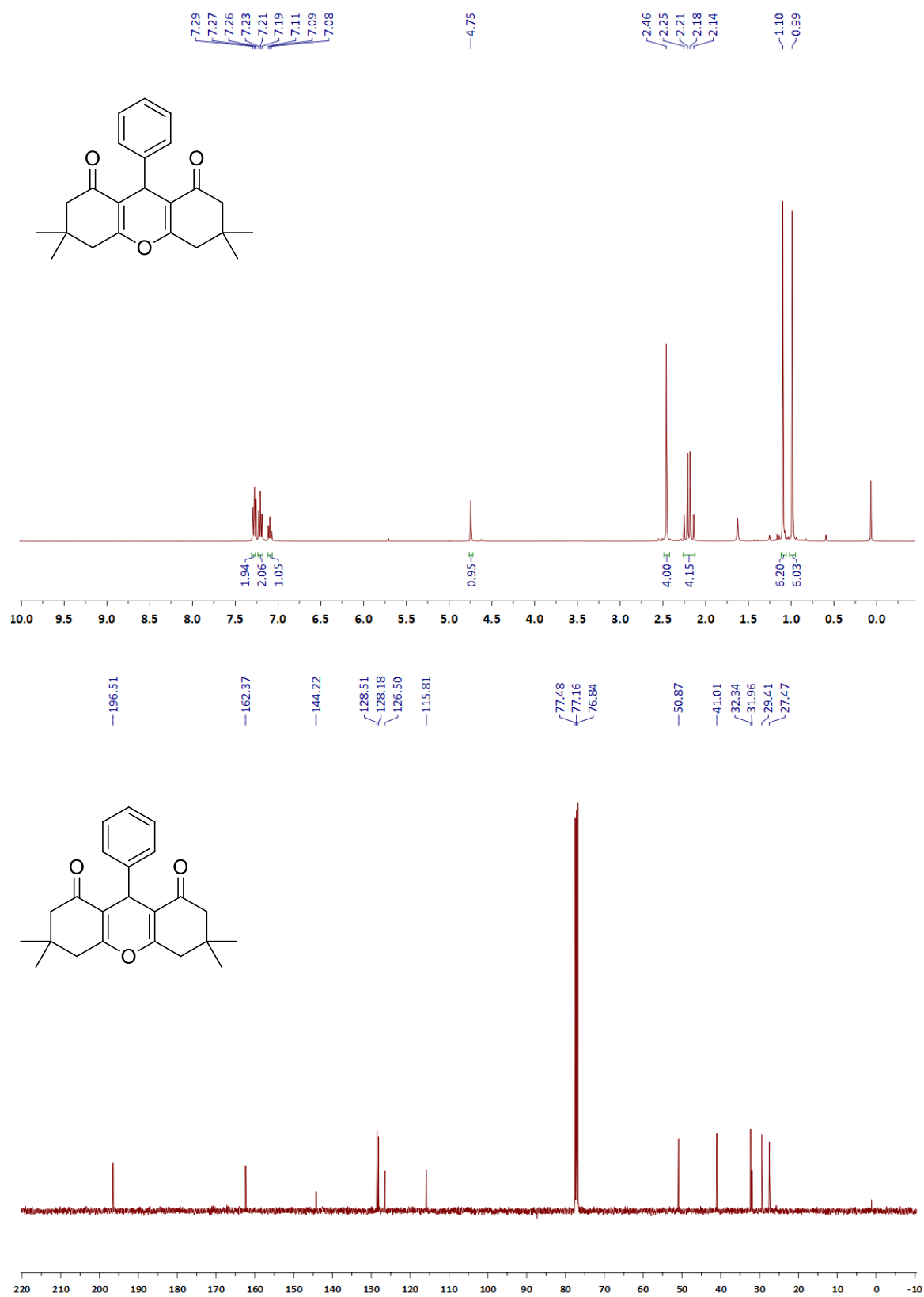


Figure S4. ^1H and ^{13}C NMR of **3b**

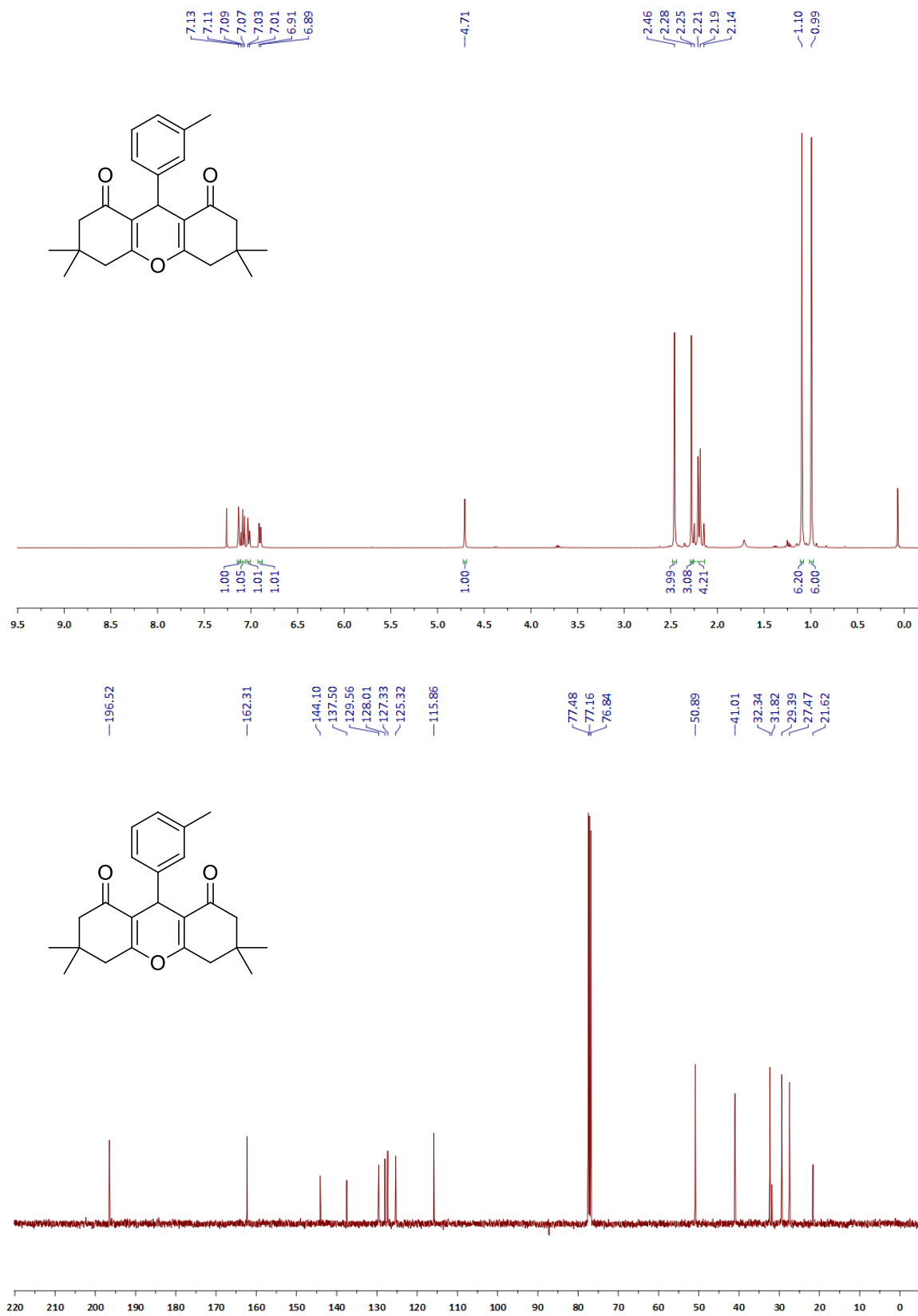


Figure S5. ^1H and ^{13}C NMR of **3c**

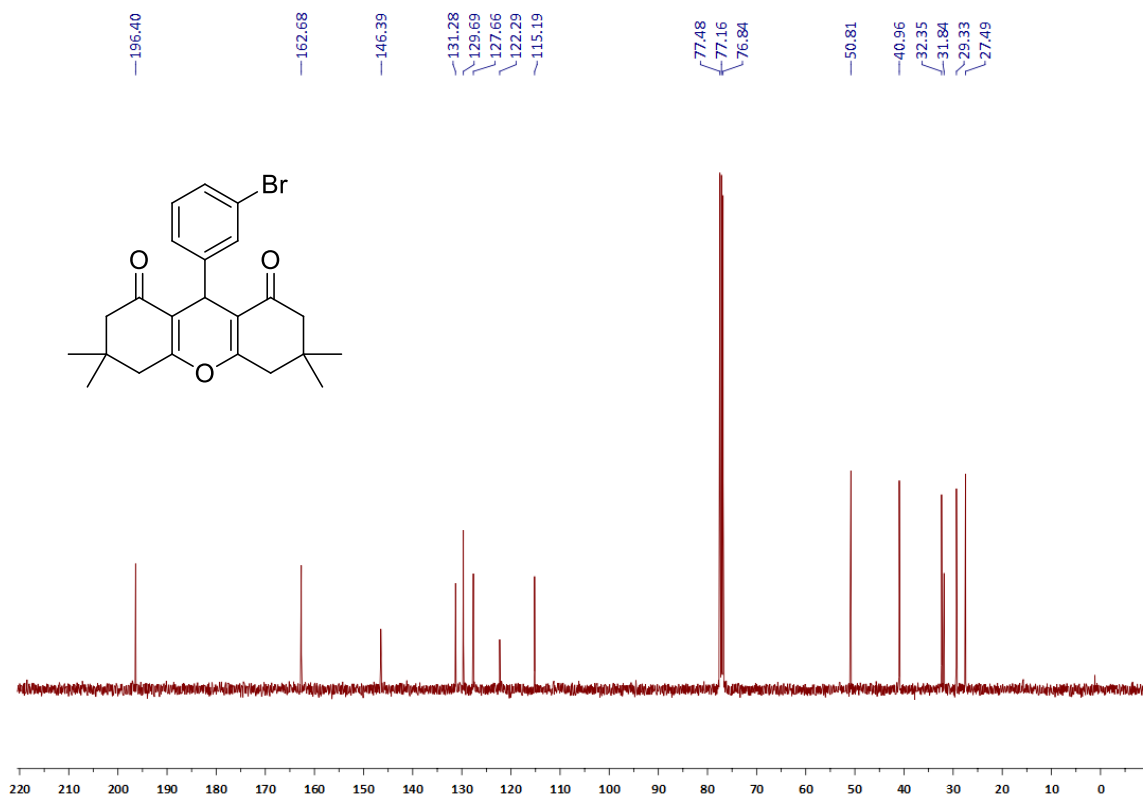
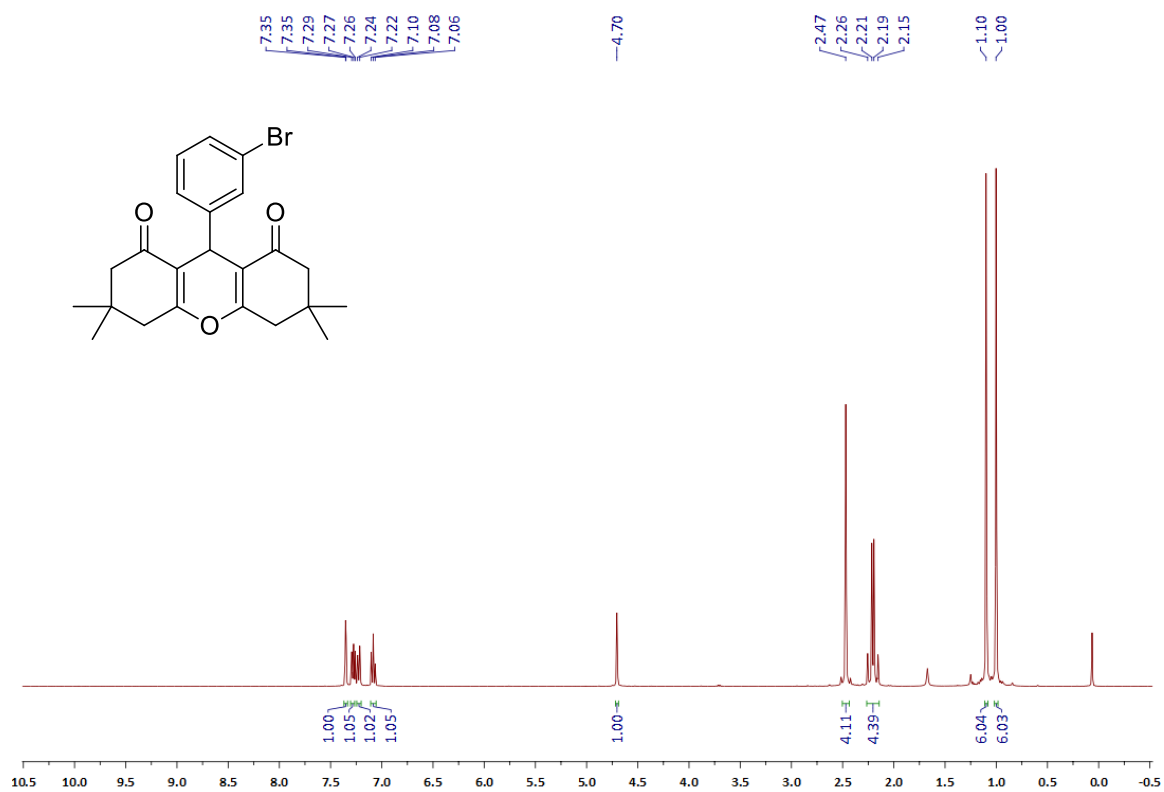


Figure S6. ^1H and ^{13}C NMR of **3d**

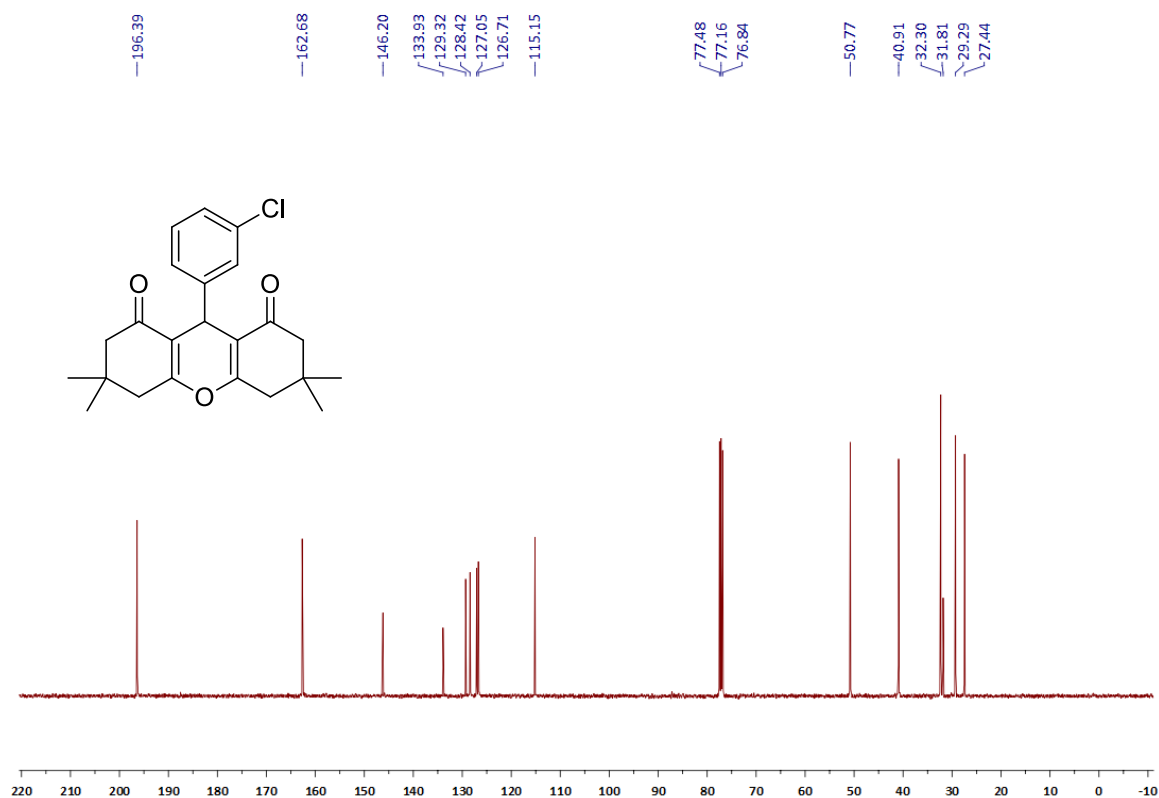
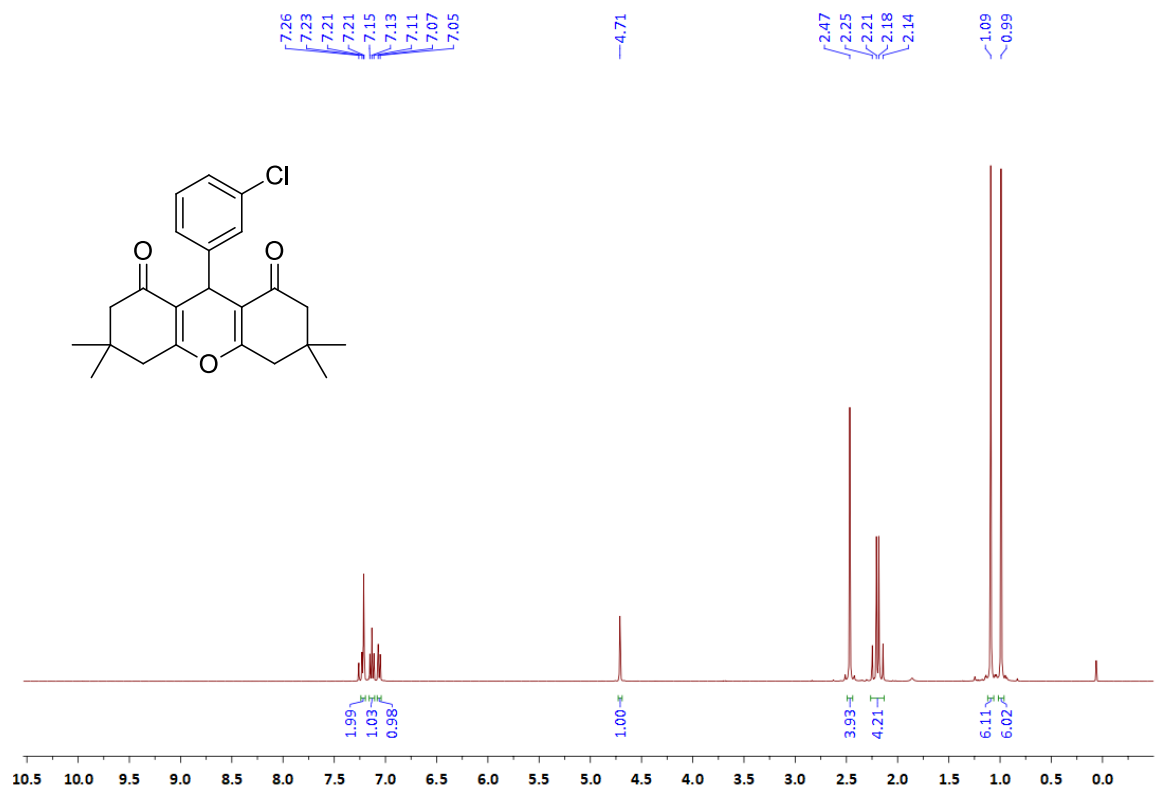


Figure S7. ^1H and ^{13}C NMR of **3e**

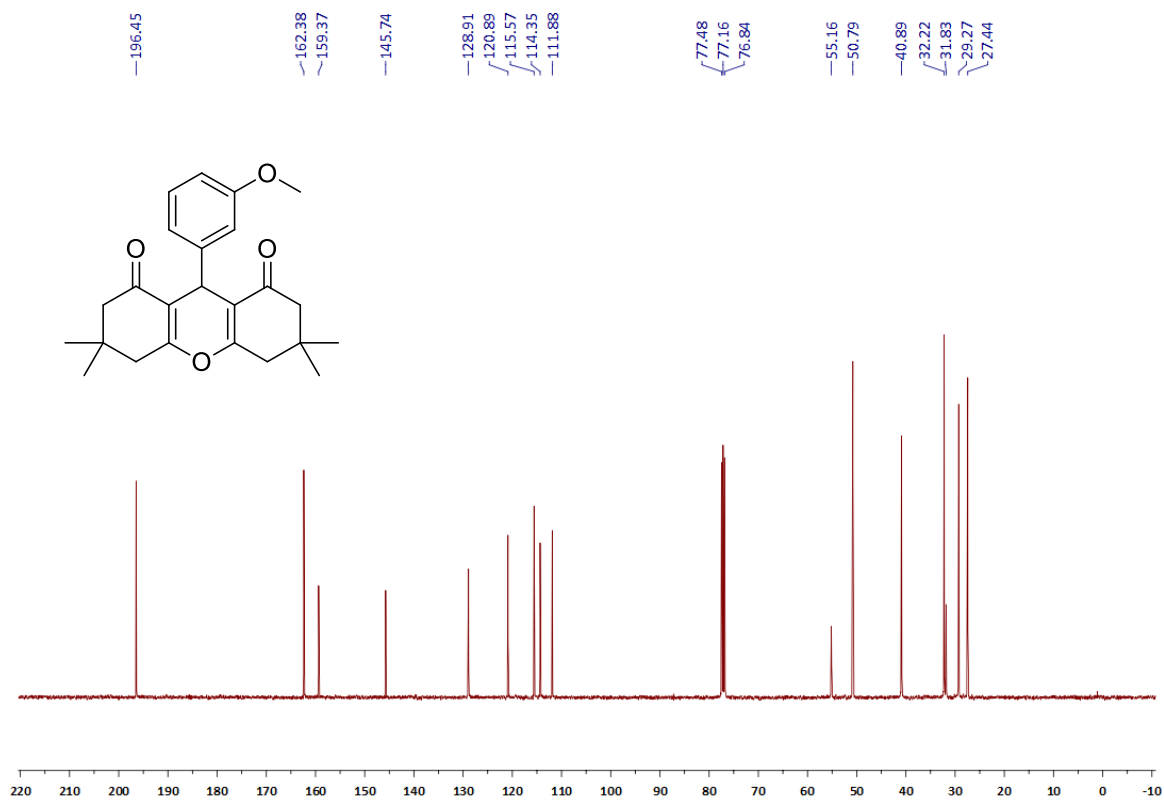
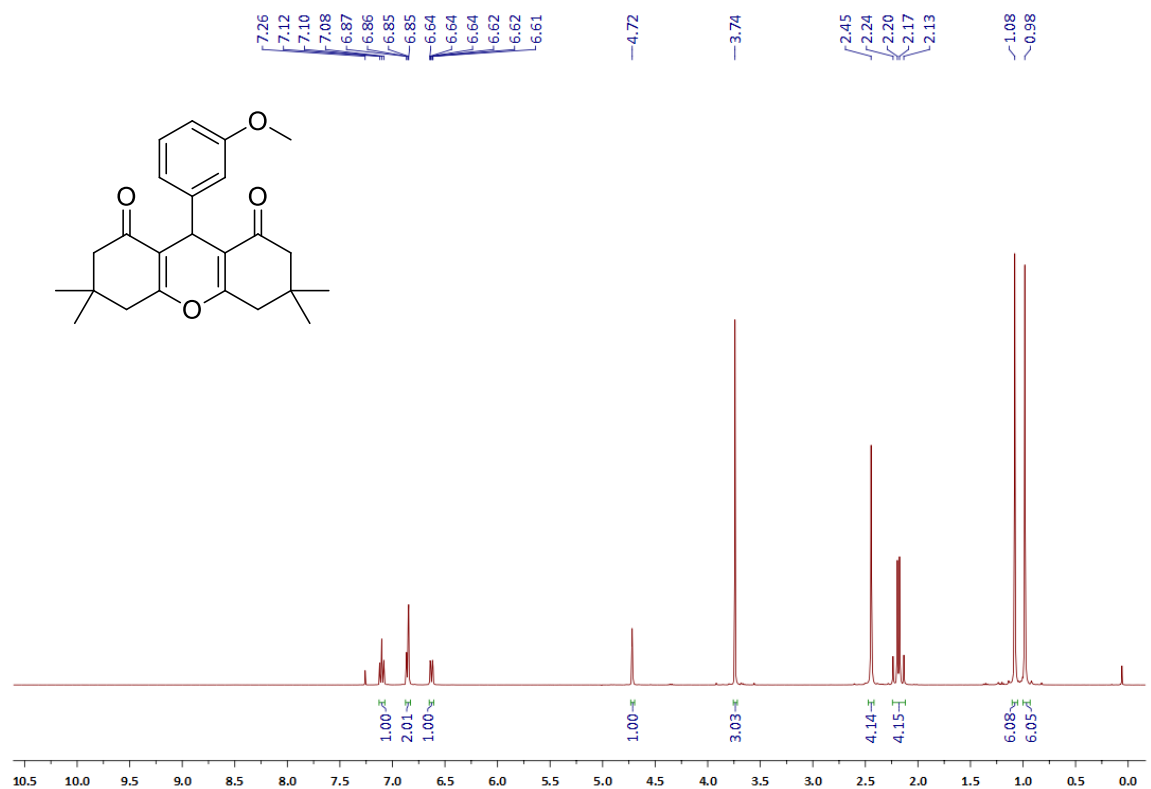


Figure S8. ^1H and ^{13}C NMR of **3f**

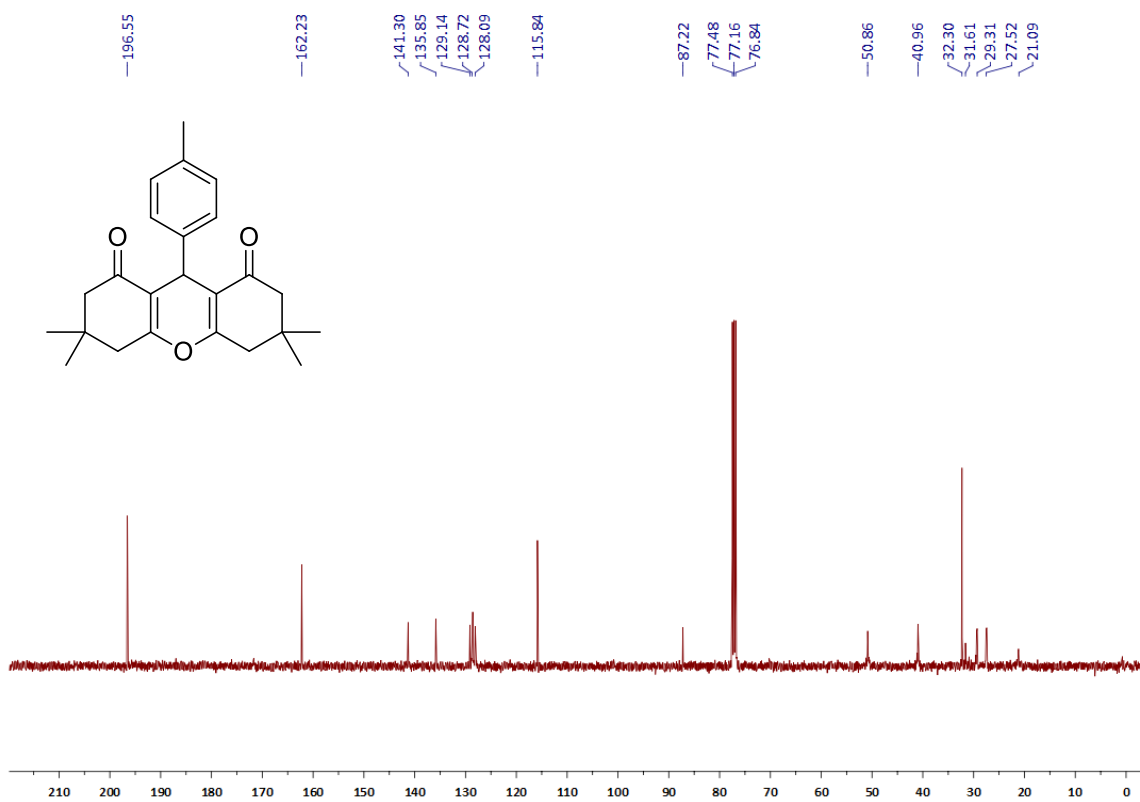
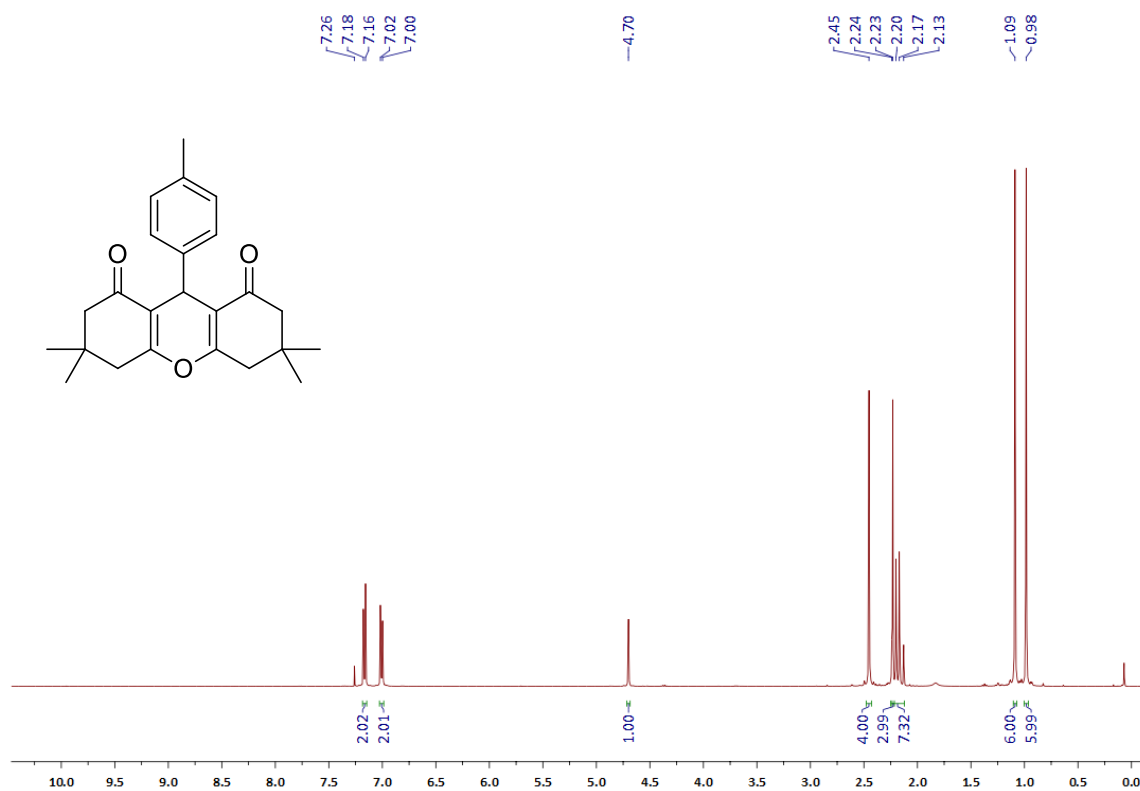


Figure S9. ^1H and ^{13}C NMR of **3g**

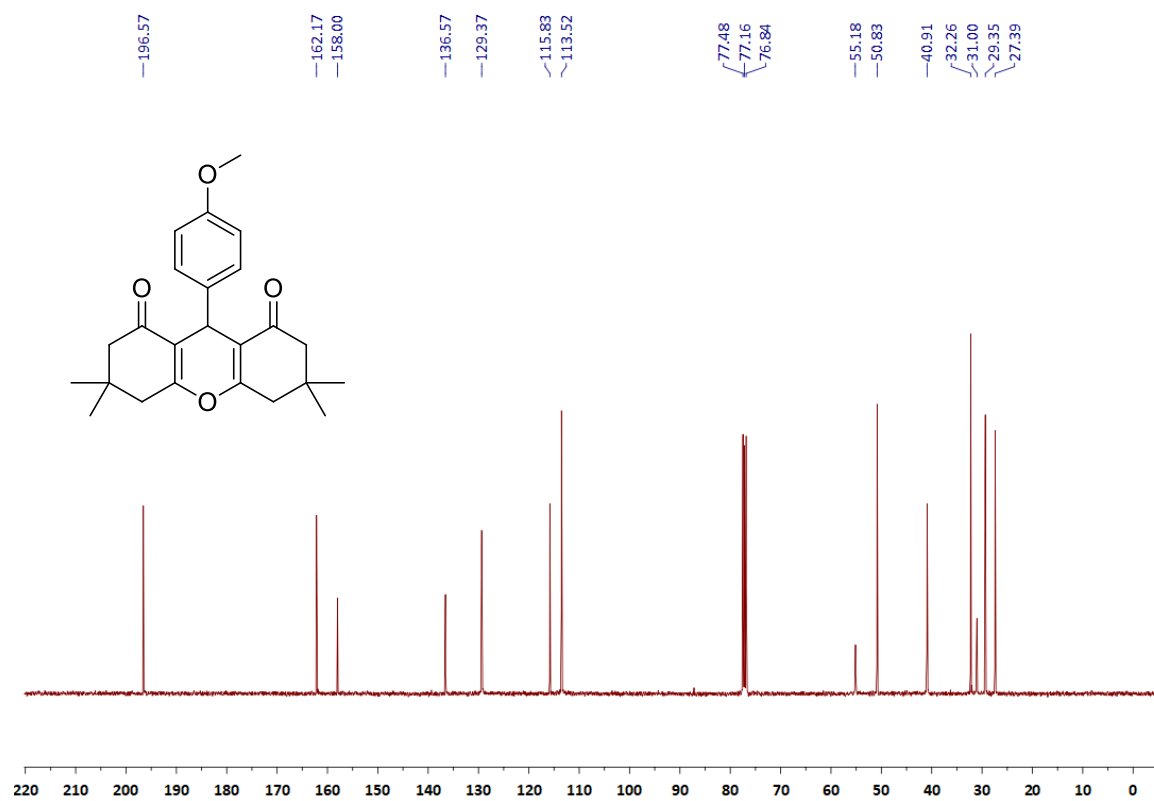
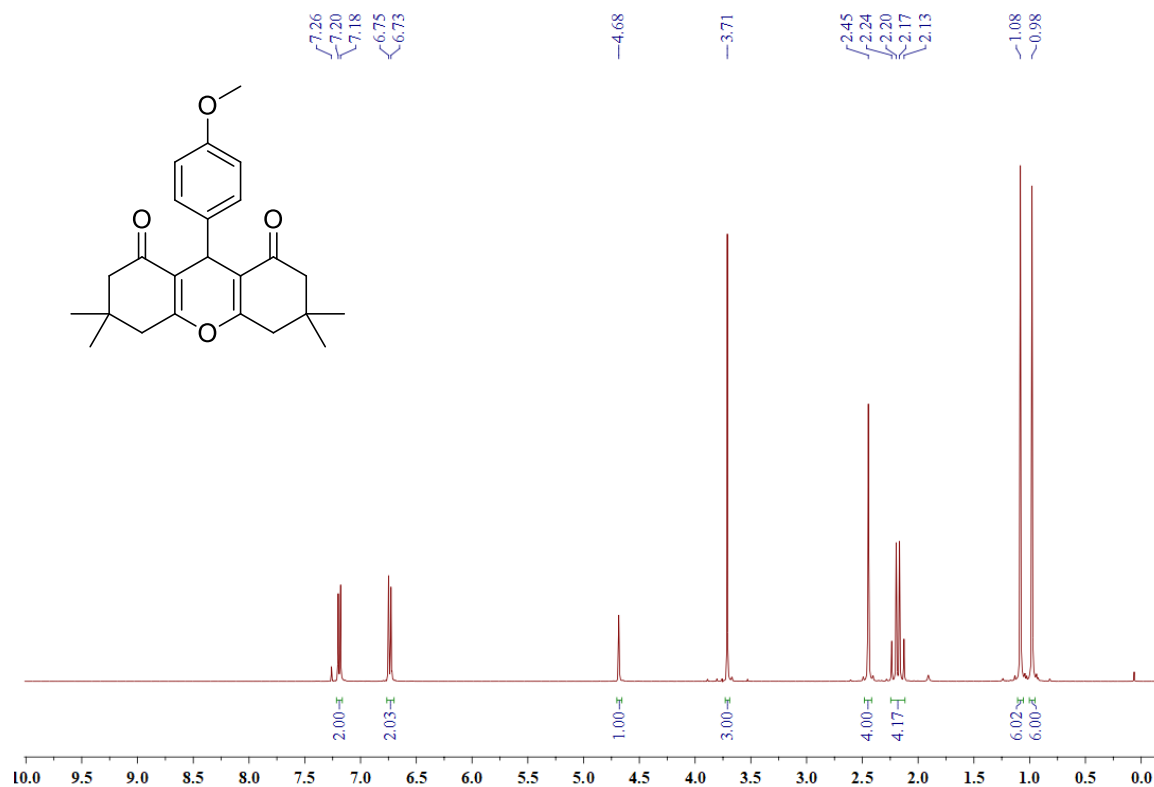


Figure S10. ^1H and ^{13}C NMR of **3h**

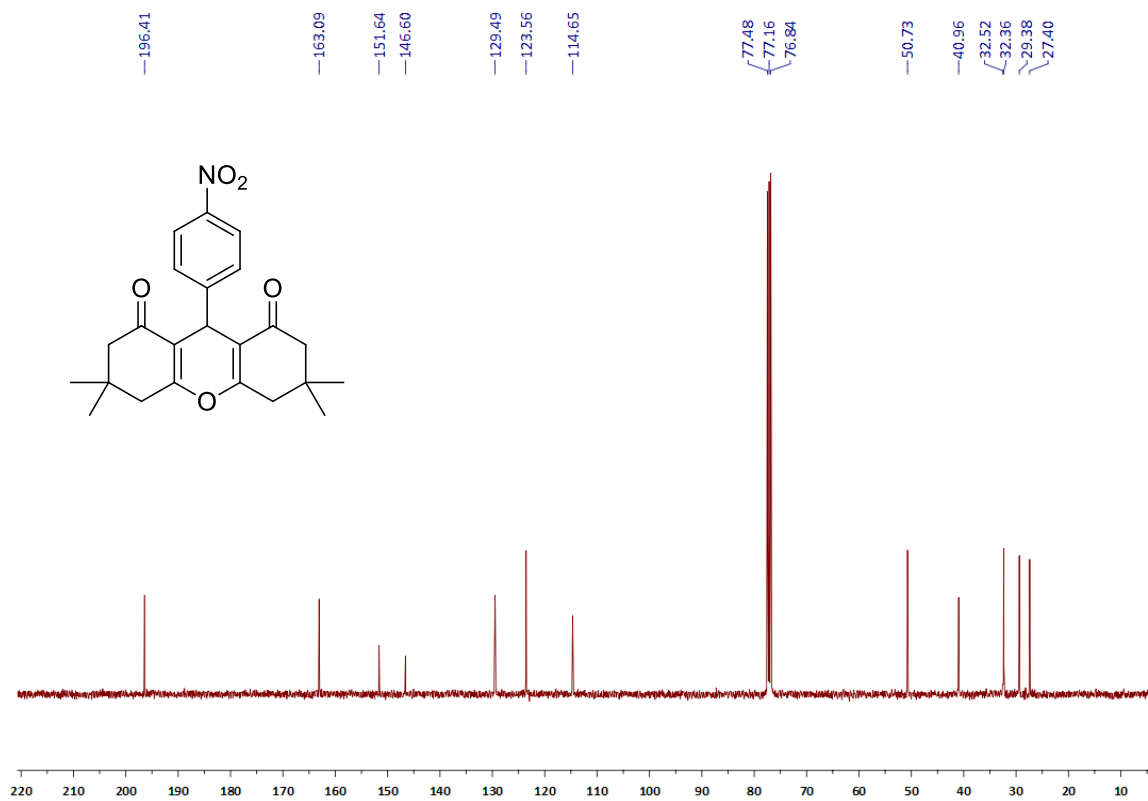
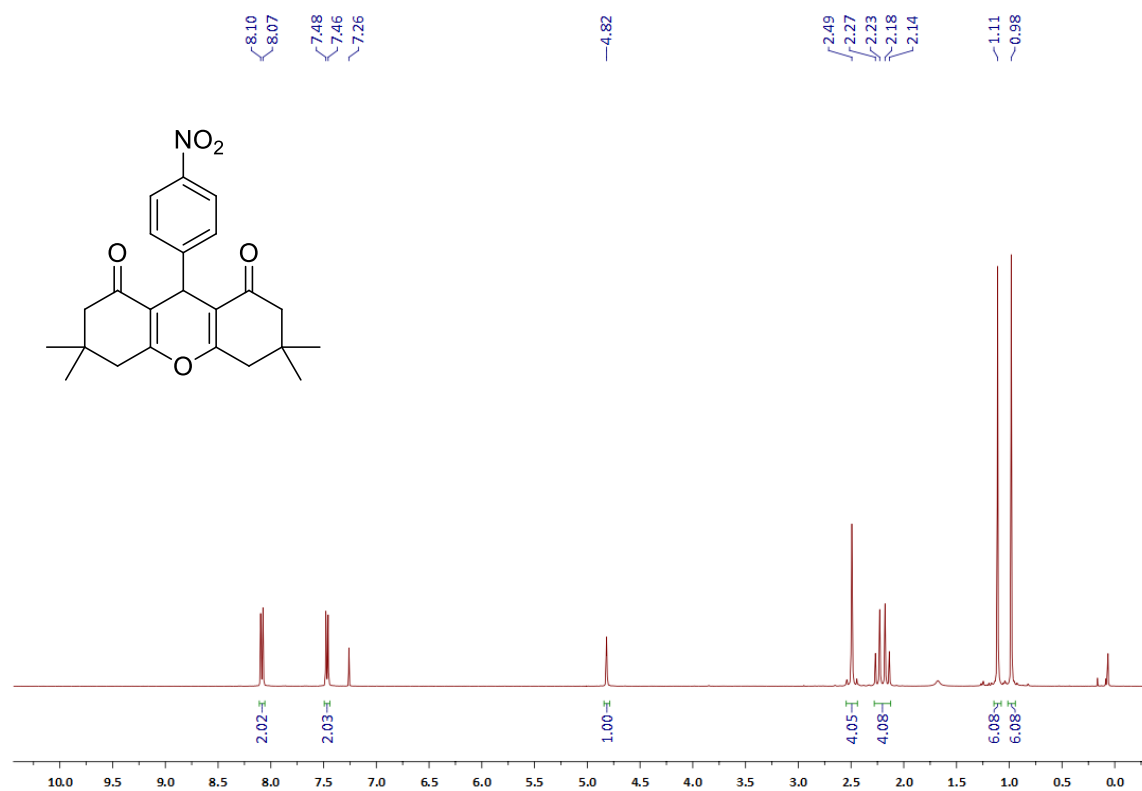


Figure S11. ^1H and ^{13}C NMR of **3i**

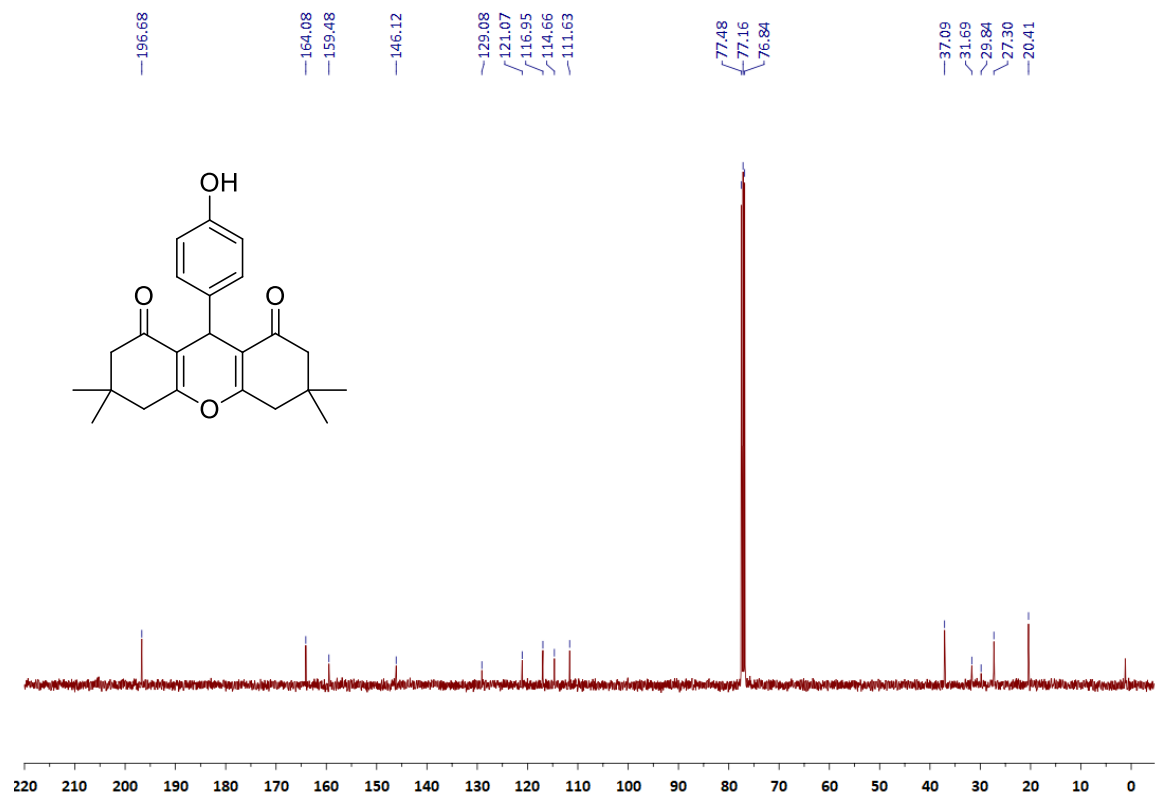
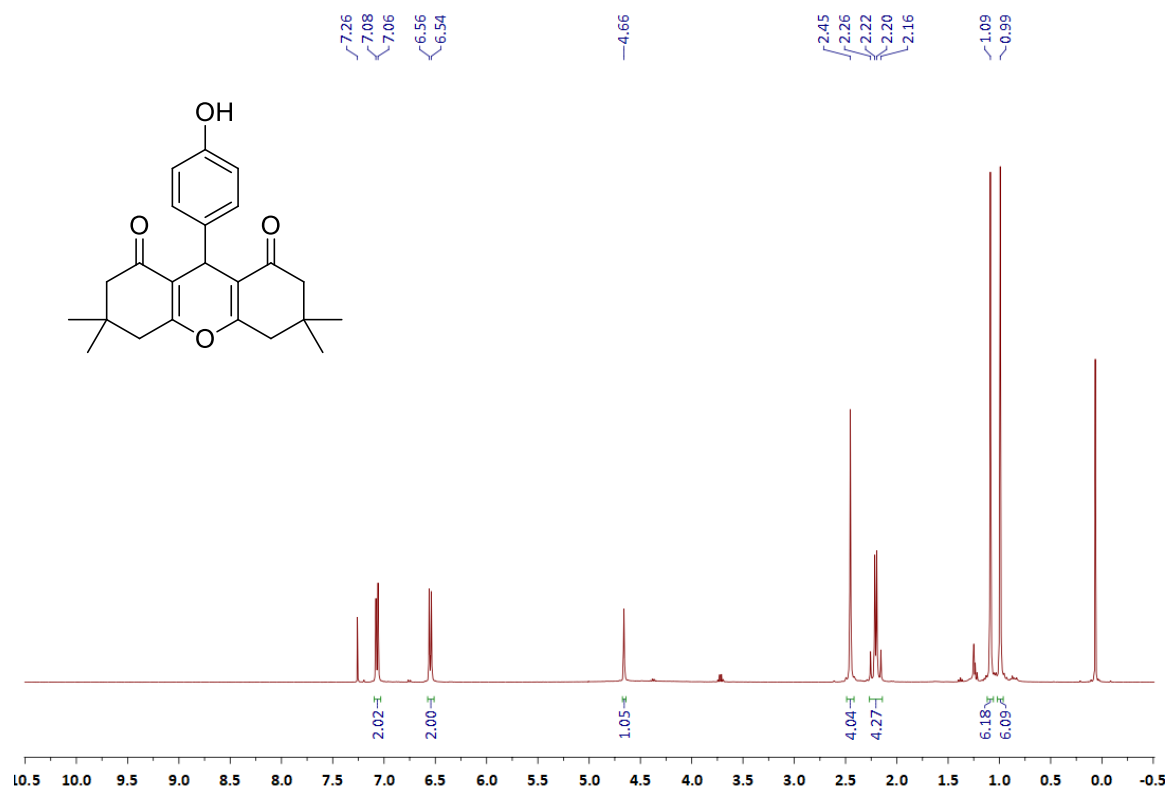


Figure S12. ^1H and ^{13}C NMR of **3j**

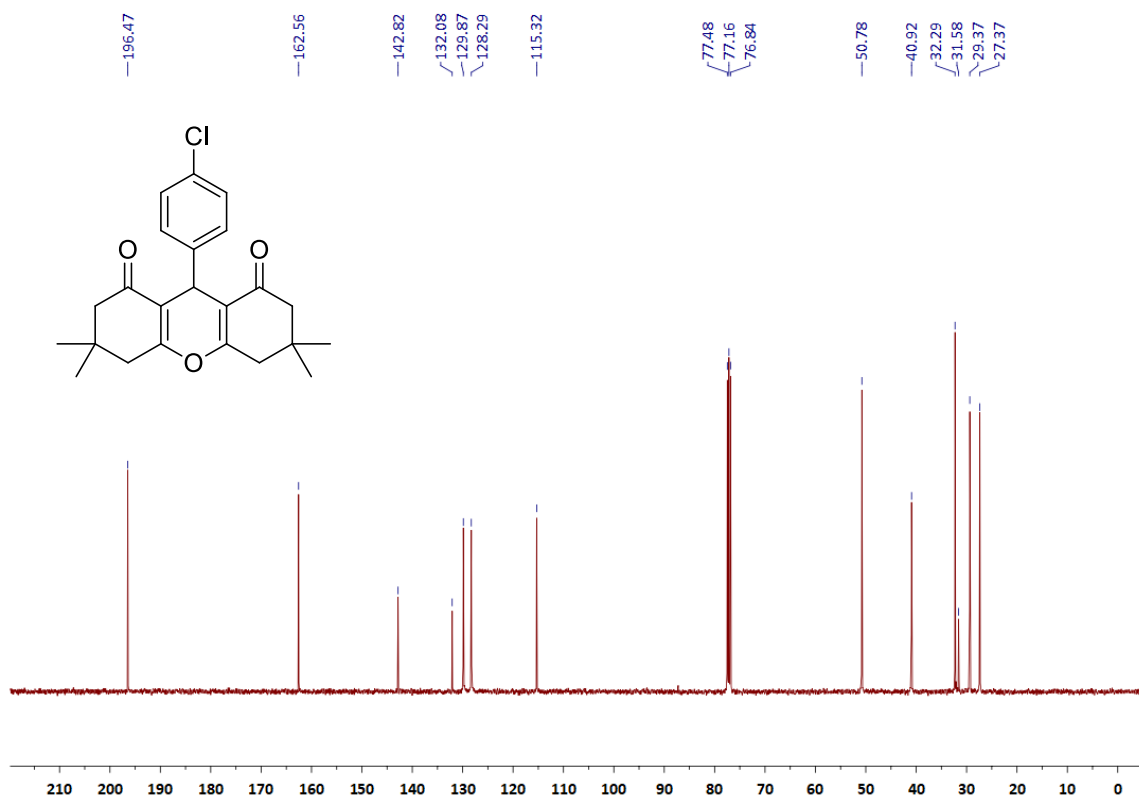
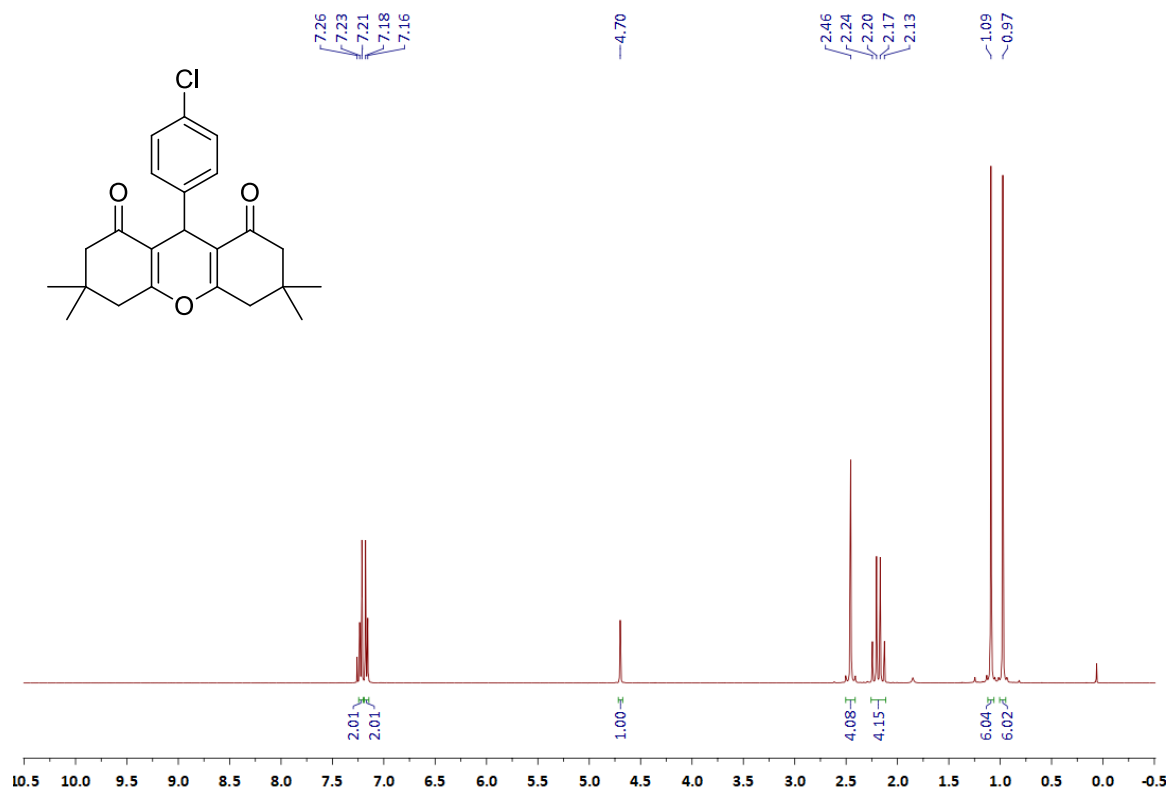


Figure S13. ^1H and ^{13}C NMR of **3k**

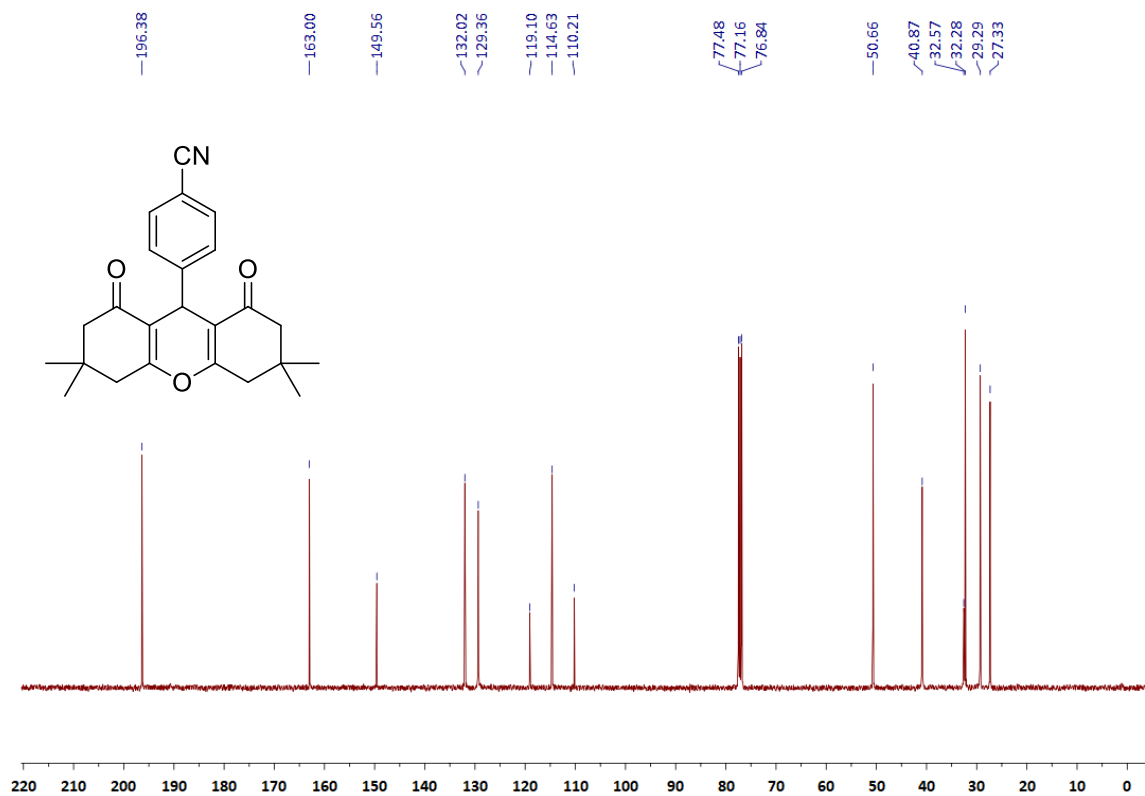
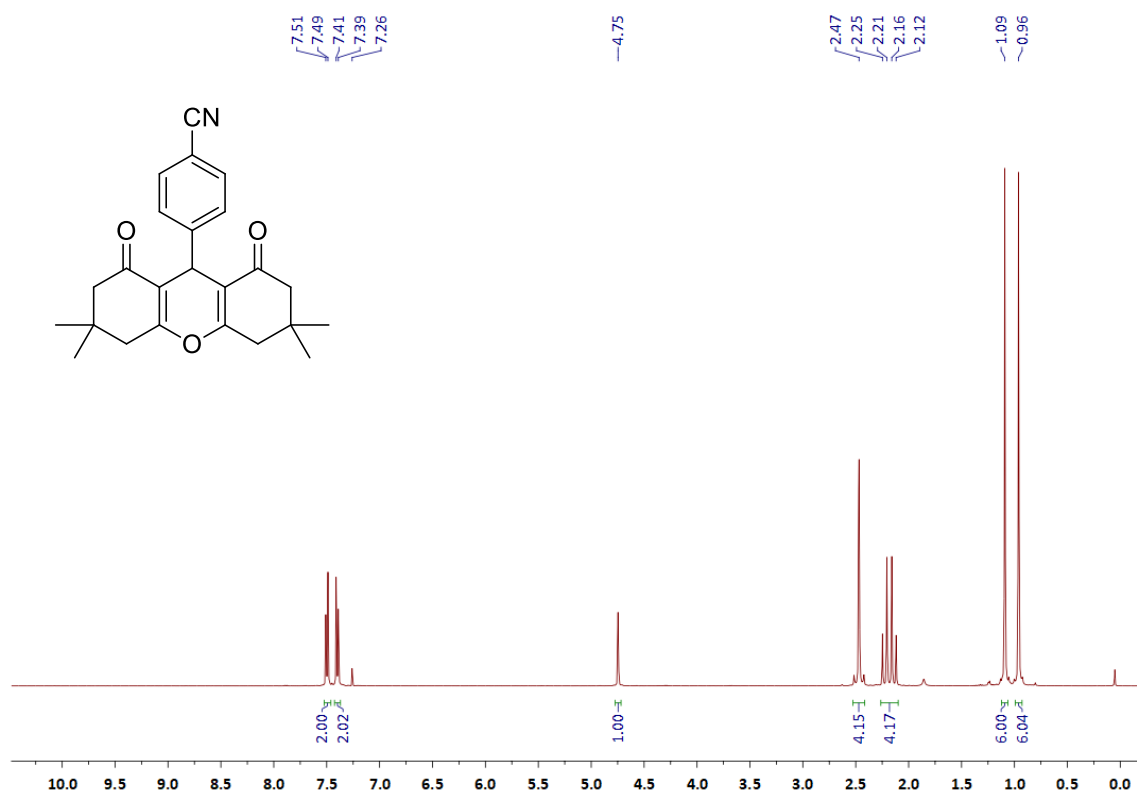


Figure S14. ^1H and ^{13}C NMR of **31**

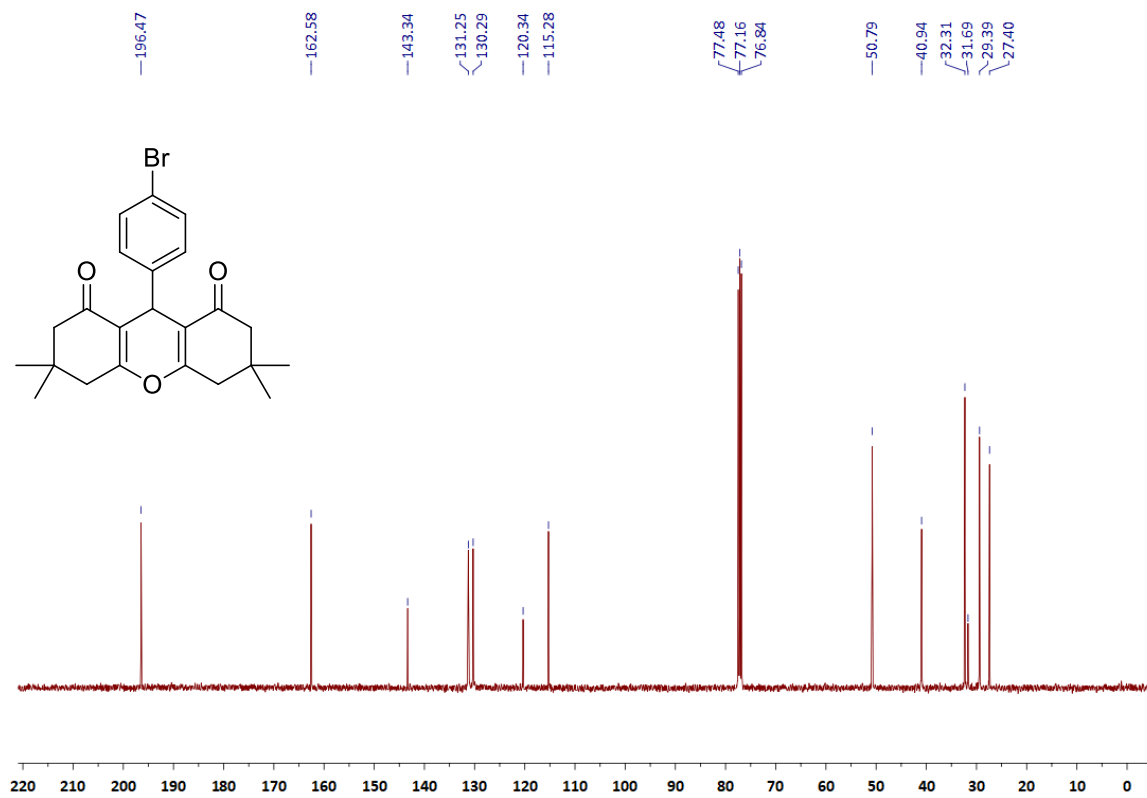
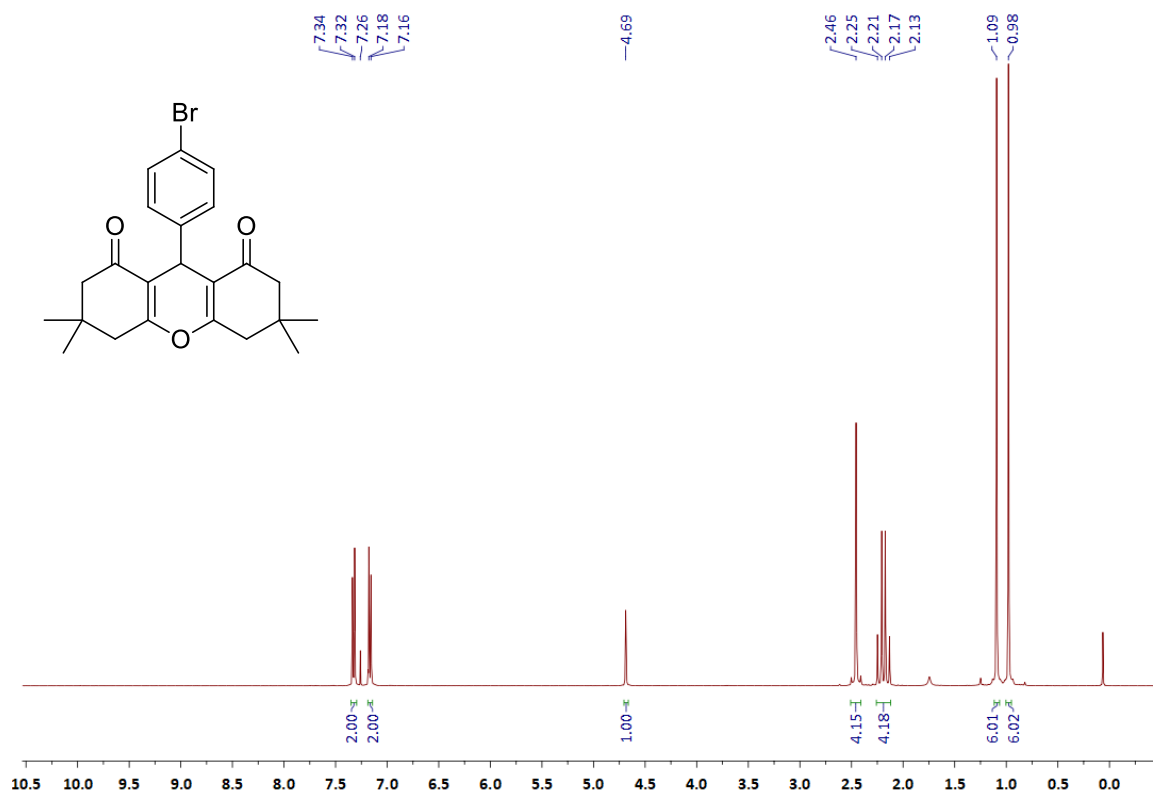


Figure S15. ^1H and ^{13}C NMR of **3m**

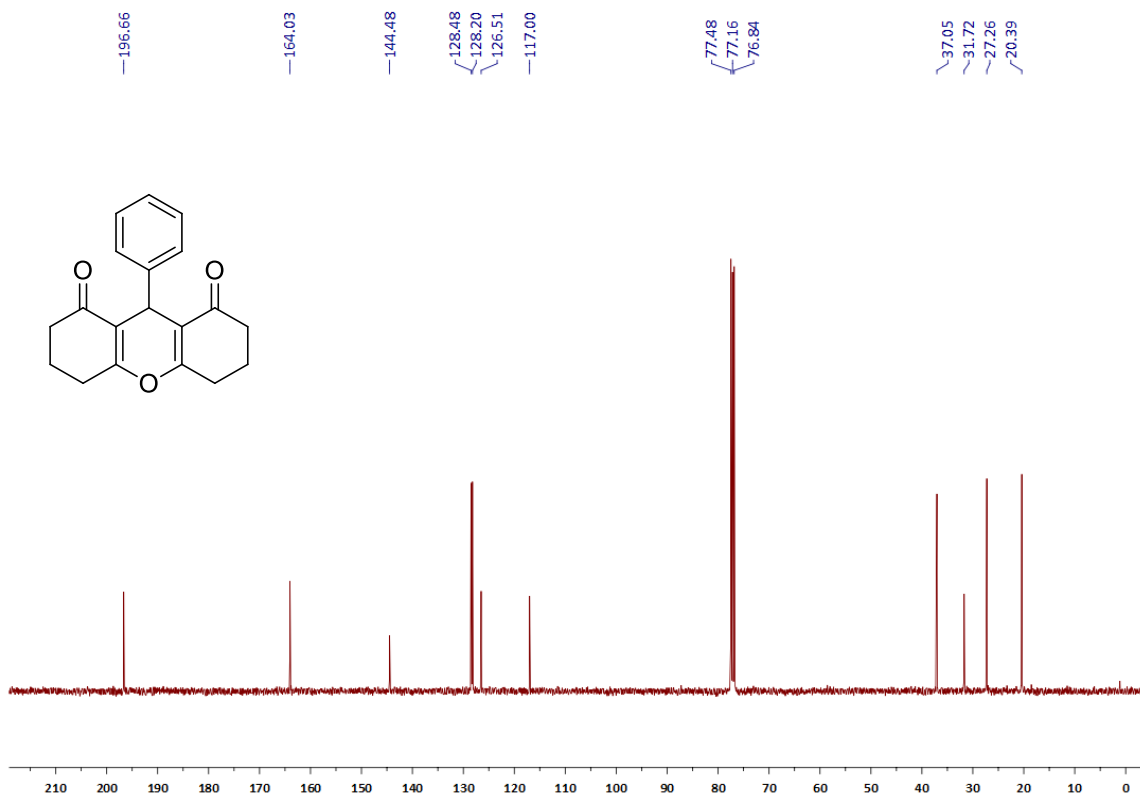
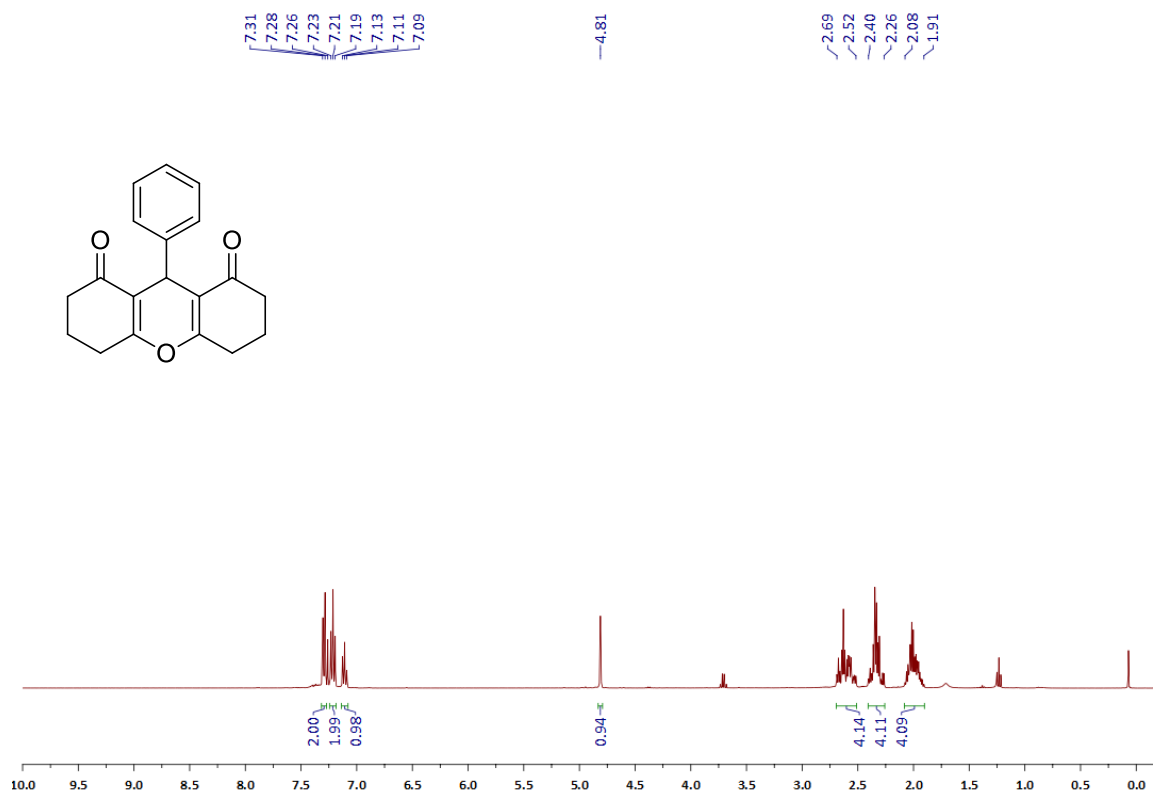


Figure S16. ^1H and ^{13}C NMR of **3n**

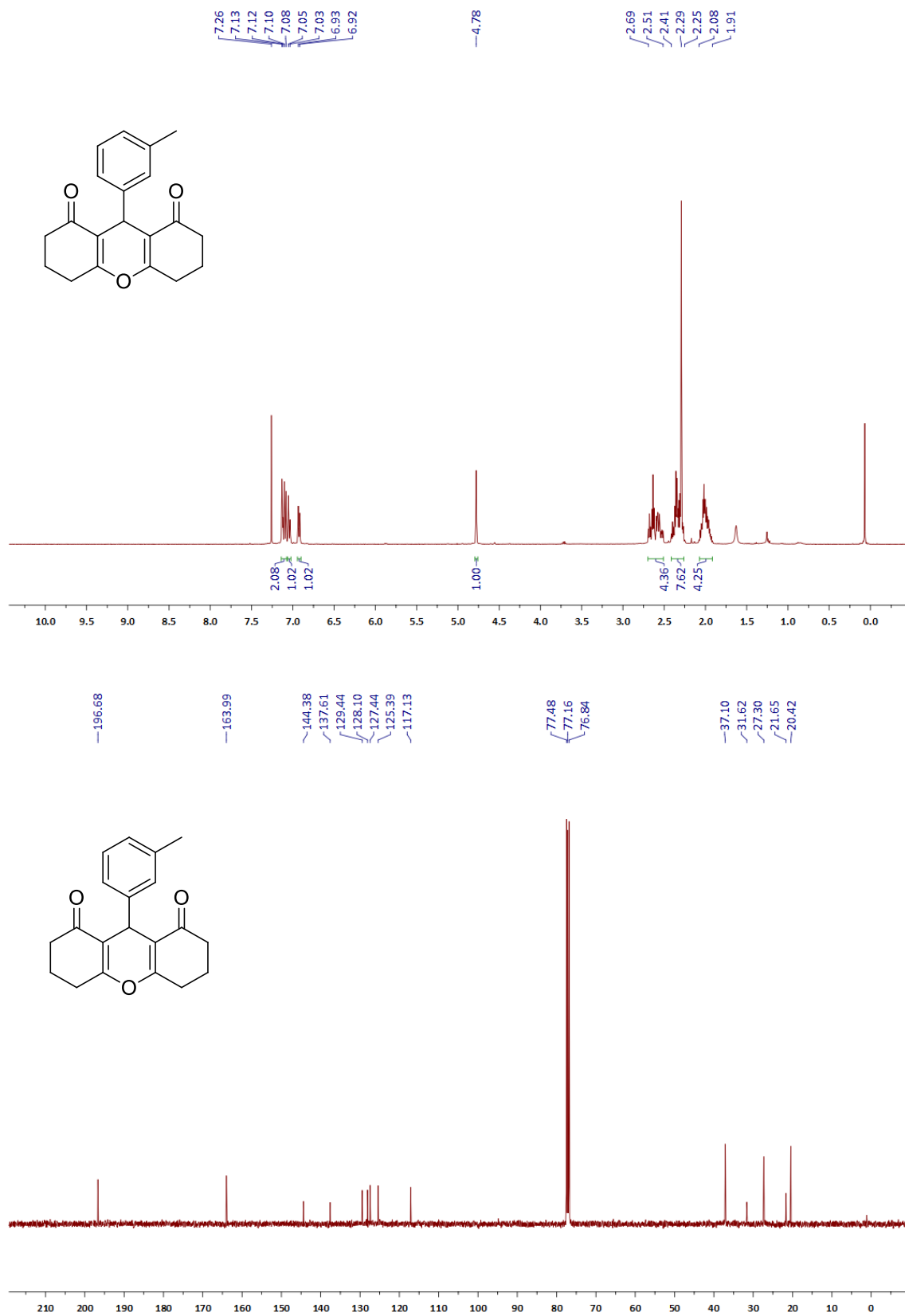


Figure S17. ^1H and ^{13}C NMR of **30**

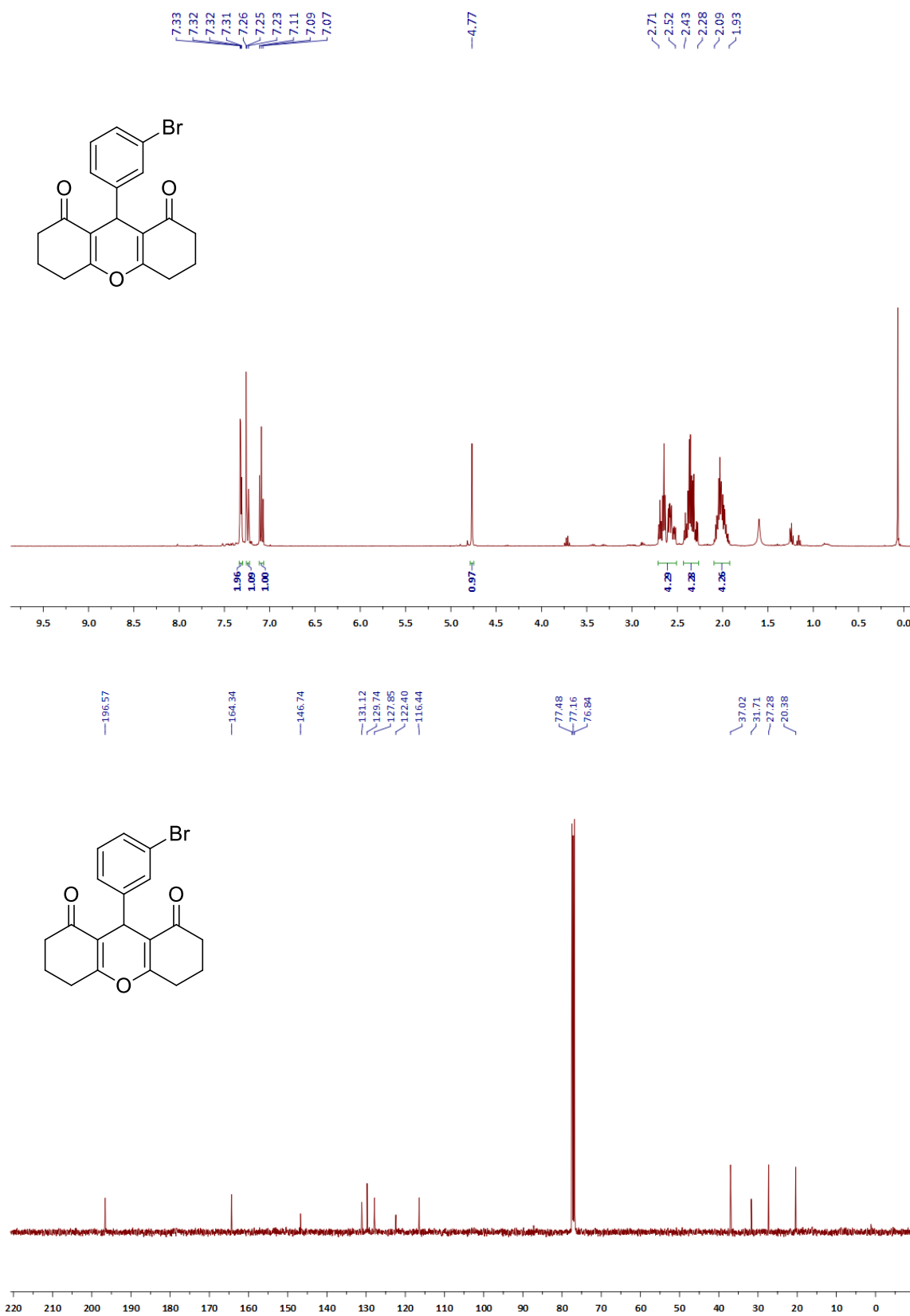


Figure S18. ^1H and ^{13}C NMR of **3p**

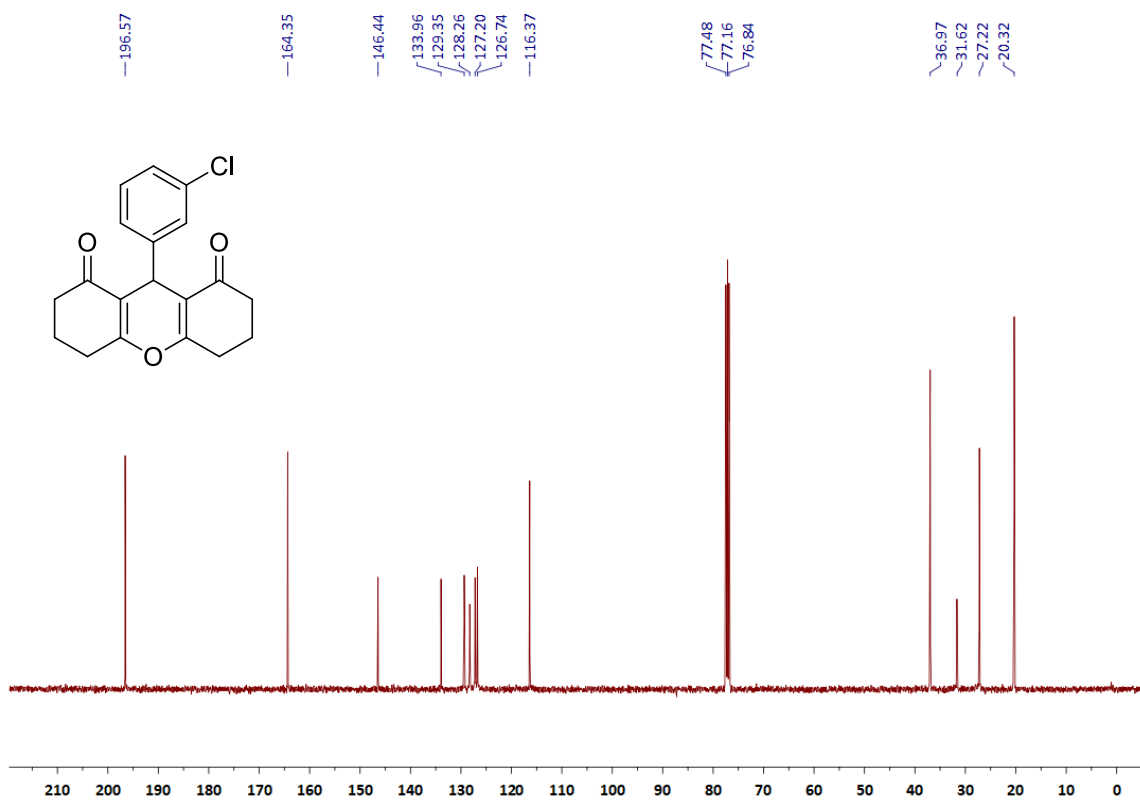
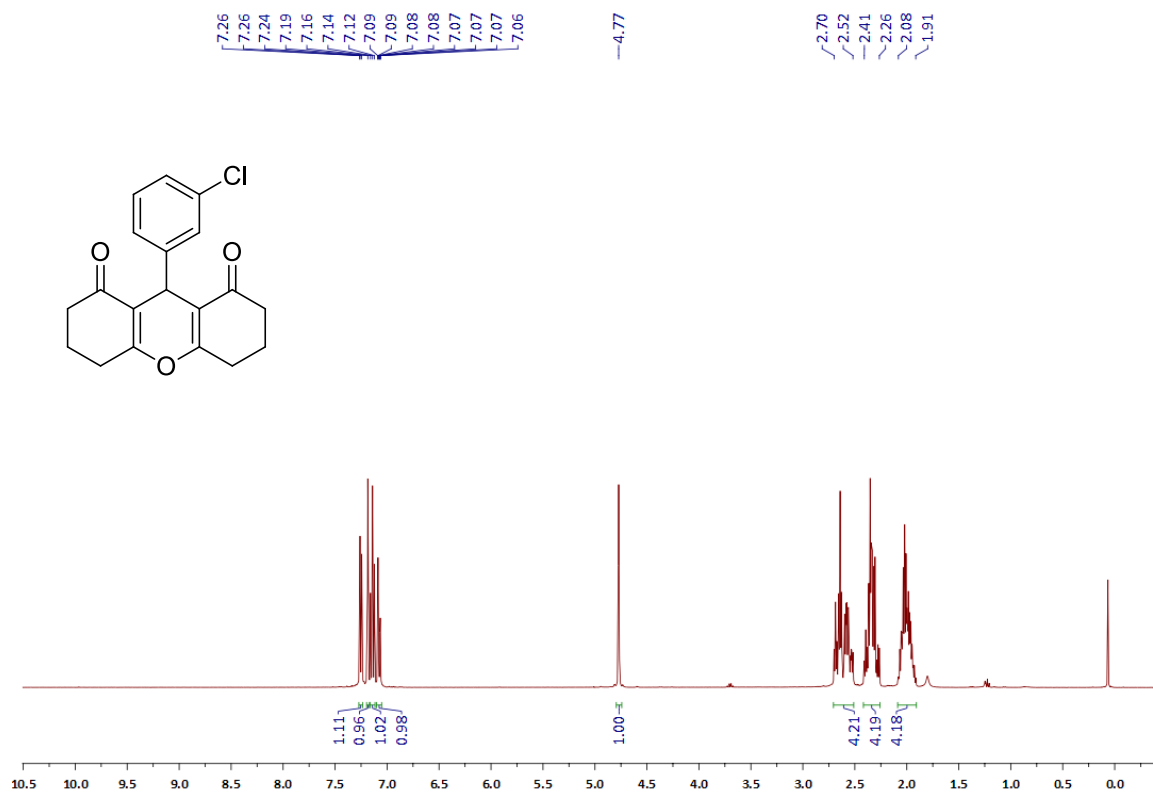


Figure S19. ^1H and ^{13}C NMR of **3q**

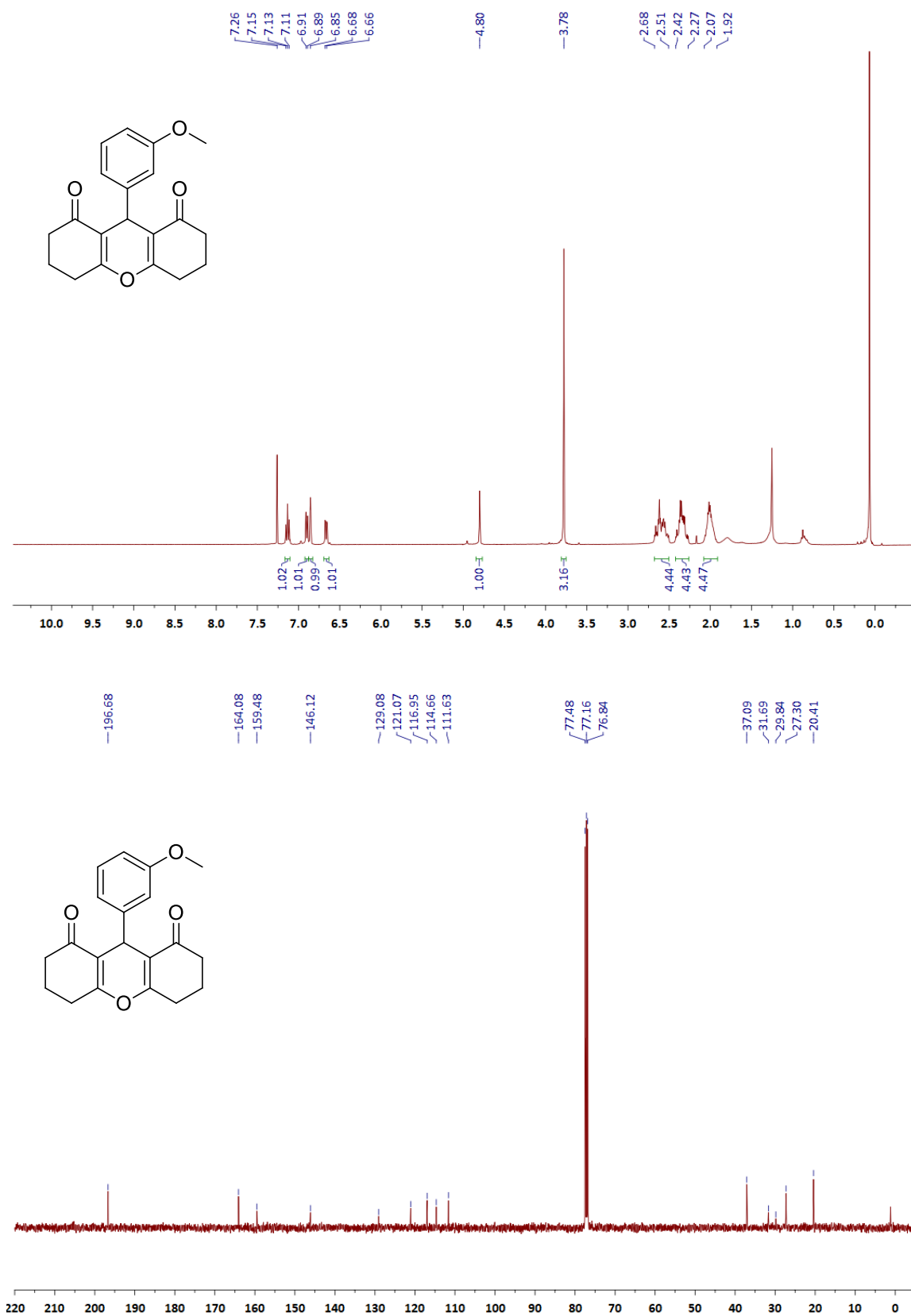


Figure S20. ^1H and ^{13}C NMR of **3r**

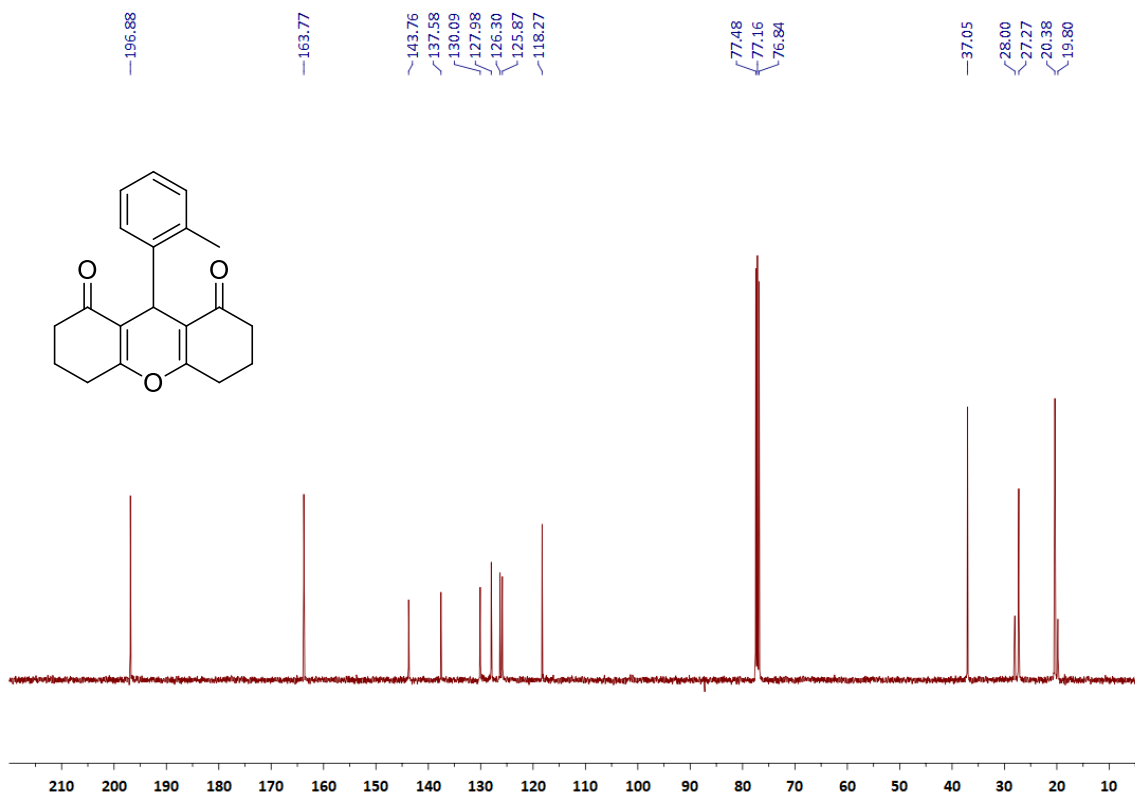
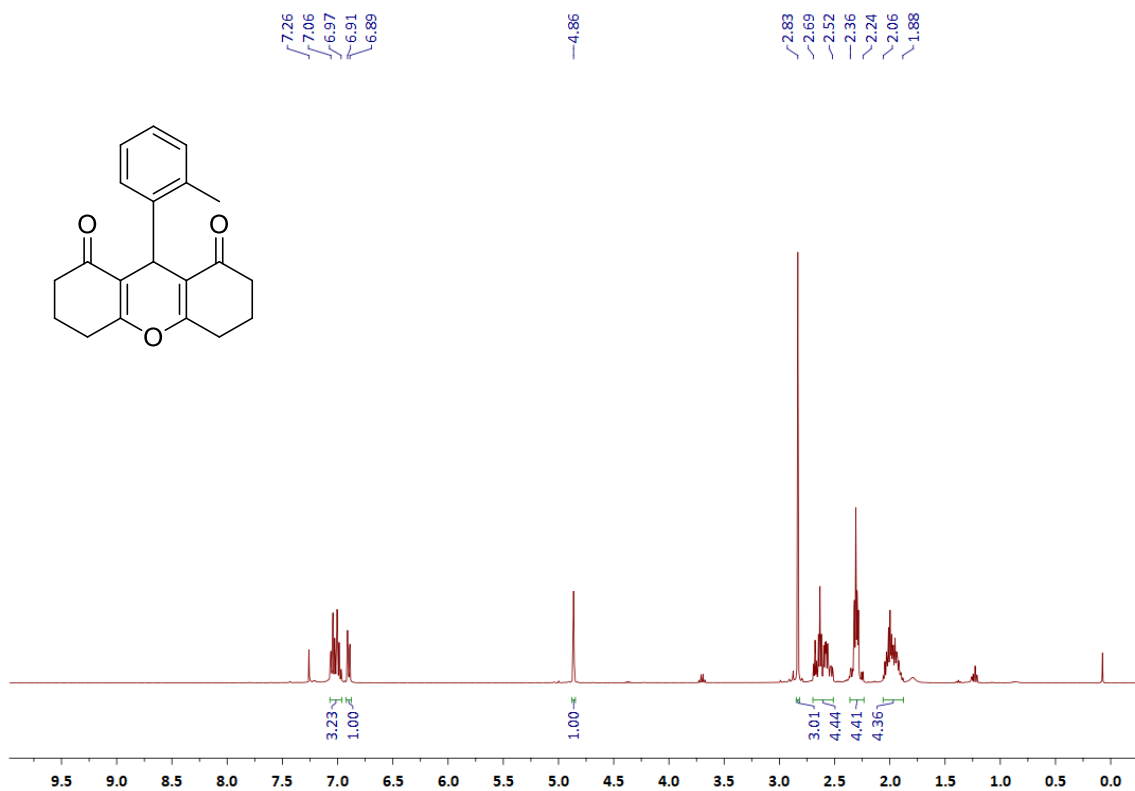


Figure S21. ^1H and ^{13}C NMR of **3s**

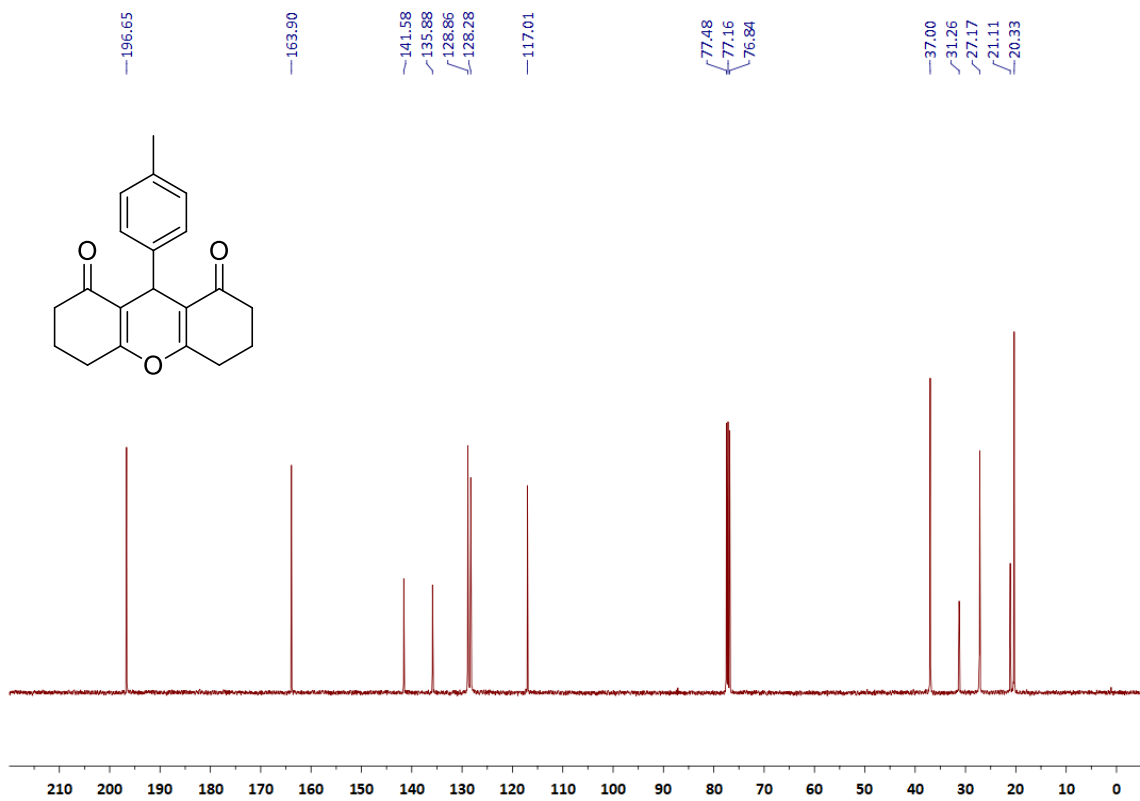
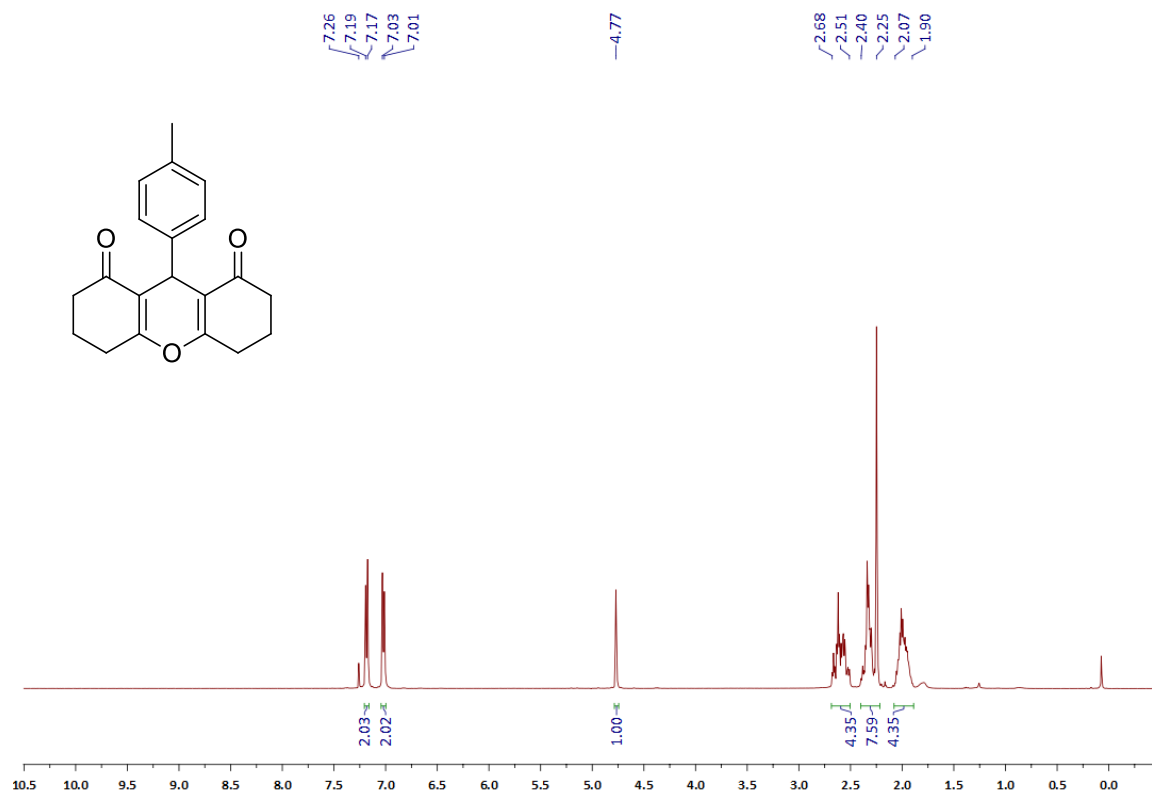
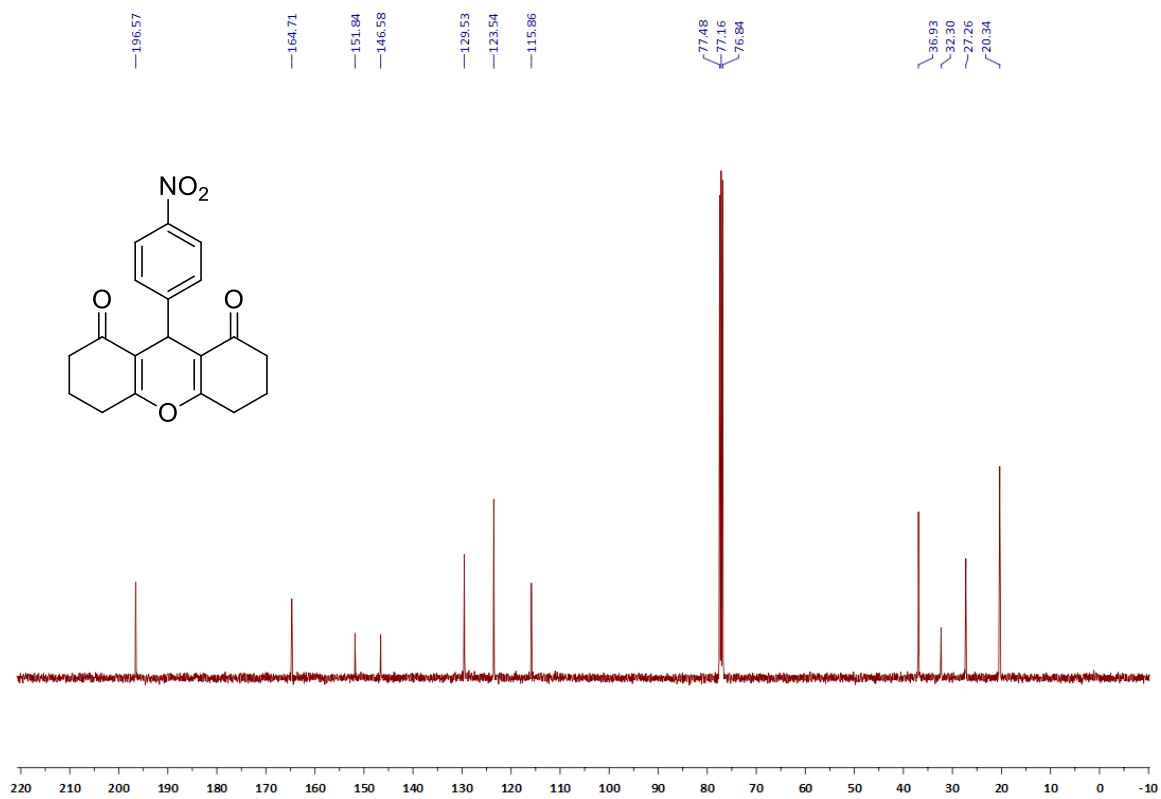
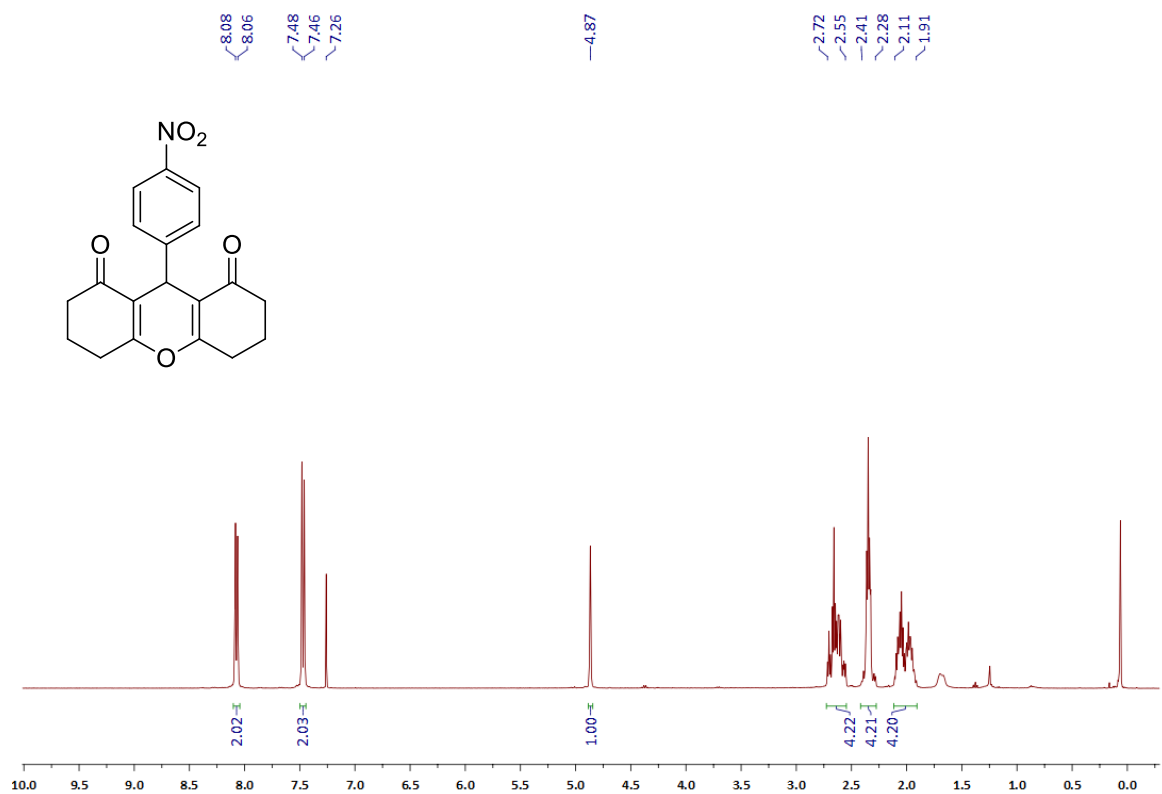


Figure S22. ^1H and ^{13}C NMR of **3t**



¹H and ¹³C NMR chemical shifts for different xanthene derivatives reported in the Table 2.

- 3a.** ¹H NMR (CDCl₃, 400 MHz): δ_H (ppm) = 7.28 (d, J=8.4 Hz, 2H), 7.21 (t, J=7.6 Hz, 2H), 7.09 (t, J=7.6 Hz, 1H), 4.75 (s, 1H, CH), 2.46 (s, 4H, 2x CH₂), 2.25-2.14 (m, 4H, 2x CH₂), 1.10 (s, 6H, 2x CH₃), 0.99 (s, 6H, 2x CH₃)
¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 196.51, 162.37, 144.22, 128.51, 128.18, 126.50, 115.81, 50.87, 41.01, 32.34, 31.96, 29.41, 27.47
- 3b.** ¹H NMR (CDCl₃, 400 MHz): δ_H (ppm) = 7.13 (s, 1H), 7.09 (t, J=7.2Hz, 1H), 7.02 (d, J=7.6Hz, 1H), 6.90 (d, J=7.2Hz, 1H), 4.71 (s, 1H, CH), 2.46 (s, 4H, 2x CH₂), 2.28 (s, 3H, CH₃), 2.25-2.14 (m, 4H, 2x CH₂), 1.10 (s, 6H, 2x CH₃), 0.99 (s, 6H, 2x CH₃)
¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 196.52, 162.31, 144.10, 137.10, 129.56, 128.01, 127.33, 125.32, 115.86, 50.89, 41.01, 32.34, 31.82, 29.39, 27.47, 21.62
- 3c.** ¹H NMR (CDCl₃, 400 MHz): δ_H (ppm) = 7.35 (s, 1H), 7.28 (d, J=7.6 Hz, 1H), 7.23 (d, J=8Hz, 1H), 7.08 (t, J=8Hz, 1H), 4.70 (s, 1H, CH), 2.47 (s, 4H, 2x CH₂), 2.26-2.15 (m, 4H, 2x CH₂), 1.10 (s, 6H, 2x CH₃), 1.00 (s, 6H, 2x CH₃)
¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 196.40, 162.68, 146.39, 131.28, 129.69, 127.66, 122.29, 115.19, 50.81, 40.96, 32.35, 31.84, 29.33, 27.49
- 3d.** ¹H NMR (CDCl₃, 400 MHz): δ_H (ppm) = 7.23-7.21 (m, 2H), 7.13 (t, J=8Hz, 1H), 7.06 (d, J=8Hz, 1H), 4.71 (s, 1H, CH), 2.47 (s, 4H, 2x CH₂), 2.25-2.14 (m, 4H, 2x CH₂), 1.09 (s, 6H, 2x CH₃), 0.99 (s, 6H, 2x CH₃)
¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 196.39, 162.88, 146.20, 133.92, 129.32, 128.42, 127.05, 126.71, 115.15, 50.77, 32.30, 31.81, 29.29, 27.44
- 3e.** ¹H NMR (CDCl₃, 400 MHz): δ_H (ppm) = 7.10 (t, J=8Hz, 1H), 6.87-6.85 (m, 2H), 6.63 (dt, J₁=9.2Hz, J₂=1.8Hz, 1H), 4.72 (s, 1H, CH), 3.74 (s, 3H, OCH₃), 2.45 (s, 4H, 2x CH₂), 2.24-2.13 (m, 4H, 2x CH₂), 1.08 (s, 6H, 2x CH₃), 0.98 (s, 6H, 2x CH₃)
¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 196.45, 162.38, 159.37, 145.74, 128.91, 120.89, 115.57, 114.35, 111.88, 55.16, 50.79, 40.89, 32.22, 31.83, 29.27, 27.44

- 3f.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.17 (d, $J=8\text{Hz}$, 2H), 7.01 (d, $J=8\text{Hz}$, 2H), 4.70 (s, 1H, CH), 2.45 (s, 4H, 2x CH_2), 2.24-2.13 (m, 7H, 2x CH_2 , CH_3), 1.09 (s, 6H, 2x CH_3), 0.98 (s, 6H, 2x CH_3)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.55, 162.23, 141.30, 135.85, 129.14, 128.72, 128.09, 115.84, 87.22, 50.86, 40.96, 32.30, 31.61, 29.31, 27.52, 21.09
- 3g.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.19 (d, $J=8.8\text{Hz}$, 2H), 6.74 (d, $J=8.7\text{Hz}$, 2H), 4.68 (s, 1H, CH), 3.71 (s, 3H, OCH_3), 2.45 (s, 4H, 2x CH_2), 2.24-2.13 (m, 4H, 2x CH_2), 1.08 (s, 6H, 2x CH_3), 0.98 (s, 6H, 2x CH_3)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.57, 162.17, 158.00, 136.57, 129.37, 115.83, 113.52, 55.18, 50.83, 40.91, 32.26, 31.00, 29.35, 27.39
- 3h.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 8.08 (d, $J=8.8\text{Hz}$, 2H), 7.47 (d, $J=8.4\text{Hz}$, 2H), 4.82 (s, 1H, CH), 2.49 (s, 4H, 2x CH_2), 2.27-2.14 (m, 4H, 2x CH_2), 1.11 (s, 6H, 2x CH_3), 0.98 (s, 6H, 2x CH_3)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.41, 163.09, 151.64, 146.60, 129.49, 123.56, 114.66, 50.73, 40.96, 32.52, 32.36, 29.38, 27.40
- 3i.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.07 (d, $J=8.8\text{Hz}$, 2H), 6.55 (d, $J=8.4\text{Hz}$, 2H), 4.66 (s, 1H, CH), 2.45 (s, 4H, 2x CH_2), 2.26-2.16 (m, 4H, 2x CH_2), 1.09 (s, 6H, 2x CH_3), 0.99 (s, 6H, 2x CH_3)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 197.30, 162.51, 154.74, 135.81, 129.49, 116.00, 115.35, 50.89, 40.99, 32.39, 31.11, 29.31, 27.52
- 3j.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.22 (d, $J=8.4\text{Hz}$, 2H), 7.17 (d, $J=8.4\text{Hz}$, 2H), 4.70 (s, 1H, CH), 2.46 (s, 4H, 2x CH_2), 2.24-2.13 (m, 4H, 2x CH_2), 1.09 (s, 6H, 2x CH_3), 0.97 (s, 6H, 2x CH_3)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.47, 162.56, 142.82, 132.08, 129.87, 128.29, 115.32, 50.78, 40.92, 32.29, 31.58, 29.37, 27.37

- 3k.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.50 (d, $J=8.4\text{Hz}$, 2H), 7.40 (d, $J=8.4\text{Hz}$, 2H), 4.75 (s, 1H, CH), 2.47 (s, 4H, 2x CH_2), 2.25-2.12 (m, 4H, 2x CH_2), 1.09 (s, 6H, 2x CH_3), 0.96 (s, 6H, 2x CH_3)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.38, 163.00, 149.56, 132.02, 129.36, 119.10, 114.63, 110.21, 50.66, 40.87, 32.57, 32.28, 29.29, 27.33
- 3l.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.33 (d, $J=8.4\text{Hz}$, 2H), 7.17 (d, $J=8.4\text{Hz}$, 2H), 4.69 (s, 1H, CH), 2.46 (s, 4H, 2x CH_2), 2.25-2.13 (m, 4H, 2x CH_2), 1.09 (s, 6H, 2x CH_3), 0.98 (s, 6H, 2x CH_3)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.47, 162.58, 143.34, 131.25, 130.29, 120.34, 115.28, 50.79, 40.94, 32.31, 31.69, 29.39, 27.40
- 3m.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.30 (d, $J=8\text{Hz}$, 2H), 7.21 (t, $J=7.6\text{Hz}$, 2H), 7.11 (t, $J=7.2\text{ Hz}$, 1H), 4.81 (s, 1H), 2.69-2.52 (m, 4H, 2x CH_2), 2.40-2.26 (m, 4H, 2x CH_2), 2.08-1.91 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.66, 164.03, 144.48, 128.48, 128.20, 126.51, 117.00, 37.05, 31.72, 27.26, 20.39
- 3n.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.13-7.08 (m, 2H), 7.04 (d, $J=7.6\text{Hz}$, 1H), 6.92 (d, $J=7.2\text{Hz}$, 1H), 4.78 (s, 1H, CH), 2.69-2.51 (m, 4H, 2x CH_2), 2.41-2.25 (m, 7H, 2x CH_2 , CH_3), 2.08-1.91 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.68, 163.99, 144.38, 137.61, 129.44, 128.10, 127.44, 125.39, 117.13, 37.10, 31.62, 27.30, 21.65, 20.42
- 3o.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.33-7.31 (m, 2H), 7.24 (d, $J=7.6\text{Hz}$, 1H), 7.09 (t, $J=8\text{Hz}$, 1H), 4.77 (s, 1H, CH), 2.71-2.52 (m, 4H, 2x CH_2), 2.43-2.28 (m, 4H, 2x CH_2), 2.09-1.93 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.57, 164.34, 146.74, 131.12, 129.74, 127.85, 122.40, 116.44, 37.02, 31.71, 27.28, 20.38

- 3p.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.25 (d, $J=7.6\text{Hz}$, 1H), 7.19 (s, 1H), 7.14 (t, $J=8\text{Hz}$, 1H), 7.09-7.06 (m, 1H), 4.77 (s, 1H, CH), 2.70-2.52 (m, 4H, 2x CH_2), 2.41-2.26 (m, 4H, 2x CH_2), 2.08-1.91 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.57, 164.35, 146.44, 133.96, 129.35, 128.26, 127.20, 126.74, 116.37, 36.97, 31.62, 27.22, 20.32
- 3q.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.13 (t, $J=8\text{Hz}$, 1H), 6.90 (d, $J=8\text{Hz}$, 1H), 6.85 (s, 1H), 6.67 (d, $J=8\text{Hz}$, 1H), 4.80 (s, 1H, CH), 3.78 (s, 3H, CH_3), 2.68-2.51 (m, 4H, 2x CH_2), 2.42-2.27 (m, 4H, 2x CH_2), 2.07-1.92 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.68, 164.08, 159.48, 146.12, 129.08, 121.07, 116.95, 114.66, 111.63, 37.09, 31.69, 29.84, 27.30, 20.41
- 3r.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.06-6.97 (m, 3H), 6.90 (d, $J=8.7\text{ Hz}$, 1H), 4.86 (s, 1H, CH), 2.83 (s, 3H, CH_3), 2.69-2.52 (m, 4H, 2x CH_2), 2.36-2.24 (m, 4H, 2x CH_2), 2.06-1.88 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.88, 163.77, 143.76, 137.58, 130.09, 127.98, 126.30, 125.87, 118.27, 37.05, 28.00, 27.27, 20.38, 19.80
- 3s.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 7.19 (d, $J=8\text{Hz}$, 2H), 7.02 (d, $J=8\text{Hz}$, 2H), 4.77 (s, 1H, CH), 2.68-2.51 (m, 4H, 2x CH_2), 2.40-2.25 (m, 7H, 2x CH_2 , CH_3), 2.07-1.90 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.65, 163.90, 141.58, 135.88, 128.86, 128.28, 117.01, 37.00, 31.26, 27.17, 21.11, 20.33
- 3t.** ^1H NMR (CDCl_3 , 400 MHz): δ_{H} (ppm) = 8.07 (d, $J=8.8\text{Hz}$, 2H), 7.47 (d, $J=8.6\text{Hz}$, 2H), 4.87 (s, 1H, CH), 2.72-2.55 (m, 4H, 2x CH_2), 2.41-2.28 (m, 4H, 2x CH_2), 2.11-1.91 (m, 4H, 2x CH_2)
 ^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) = 196.57, 164.71, 151.84, 146.58, 129.53, 123.54, 115.86, 36.93, 32.30, 27.26, 20.34