Supplementary Material (ESI) for Organic & Biomolecular Chemistry

(Electronic Supplementary Information)

A Base-Promoted Desalicyloylative Dimerization of 3-(1-Alkynyl)chromones: an Unusual Approach to 2-Alkynyl Xanthones

Fuchun Xie, Xuan Pan, Shijun Lin and Youhong Hu*

State Key Laboratory of Drug Research, Shanghi Institute of Materia Medica, Chinese Academy of Sciences, 555 Zu Chong Zhi Road, Shanghai, 201203, China

yhhu@mail.shcnc.ac.cn

List of contents

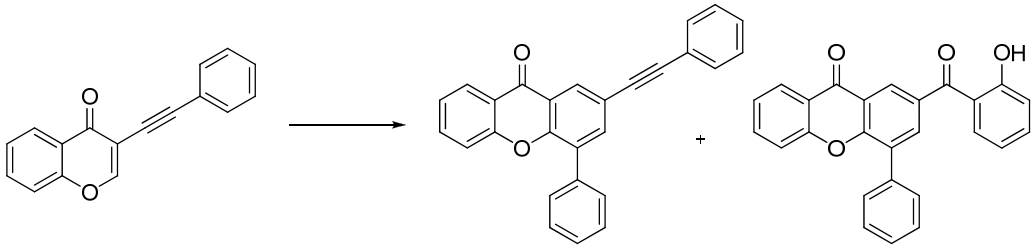
Experiment procedures……..…S1-S2
Characterization data:
2a-l, **3a**, **3f**, **3g$_1$, 3g$_2$, 2id, [D]2g, [D]3g$_1$, [D]3g$_2$**……S2-S9
^{1}H NMR and ^{13}C NMR spectra……S10-S29
X-ray crystal structures of **3a, 2b** and **3g$_1$**……S30

1. Experiment procedures

All reactions were performed under nitrogen atmosphere. Dry solvents were distilled prior to use: DMF was dried over microwave-dried molecular sieve; THF was distilled from sodium-benzophenone; Petroleum ether refers to the fraction with boiling point in the range 60 – 90 °C. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. High resolution mass spectra were recorded on a Finnigan MAT 95 mass spectrometer (EI). Column chromatography was performed with 200-300 mesh silica gel using flash column techniques. Melting points are uncorrected.

General Procedure:

Desalicyloylative Dimerization of 3-(1-Alkynyl)chromones to 2-alkynyl Xanthones 2a-l

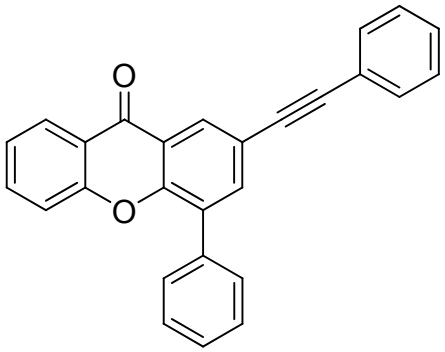


1a **2a** **3a**

A typical procedure for the preparation of **2a** and **3a**: 3-(1-Alkynyl)chromone **1a** (148 mg, 0.6 mmol), dry THF (3 mL), water (11 μL, 0.6 mmol) and DBU (90 μL, 0.6 mmol) were added sequentially to a 10 mL microwave vial containing a magnetic stir bar. The vial was sealed and then the resulting mixture was stirred at 50 ^{o}C for 5 h. When the reaction was complete (as monitored by TLC), it was quenched by

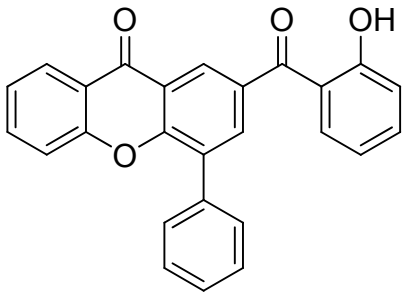
water (20 mL). The resulting mixture was extracted with dichloromethane (15 mL×3) and the combined organic layers were washed with brine(10 mL), dried over anhydrous Na_2SO_4 , filtered and concentrated to give the crude product, which was further purified by column chromatography (petroleum ether/ethyl acetate 20:1 to petroleum ether/ethyl acetate 8:1) to afford compounds **2a** as a white solid and **3a** as a light yellow solid.

2. Characterization Data:



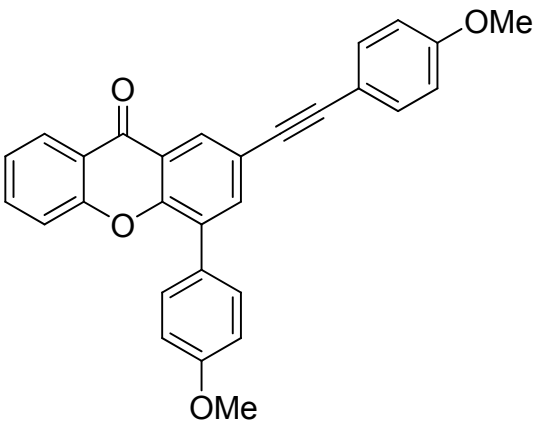
4-phenyl-2-(phenylethynyl)-9H-xanthen-9-one (2a)

As a white solid: m.p. 196-198 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ= 8.52 (d, *J* = 2.1 Hz, 1H), 8.36 (dd, *J* = 8.1 , 1.8 Hz, 1H), 7.9 (d, *J* = 2.2 Hz, 1H), 7.74-7.64 (m, 3H), 7.60-7.44 (m, 5H), 7.43-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.44, 155.70, 152.375, 138.215, 135.44, 134.83, 131.76, 131.575, 129.53, 129.03, 128.44, 128.39, 128.32, 128.12, 126.58, 124.18, 122.75, 122.13, 121.26, 119.13, 118.08, 90.12, 87.87; HRMS calcd for $C_{27}H_{16}O_2$: 372.1150, found: 372.1142.



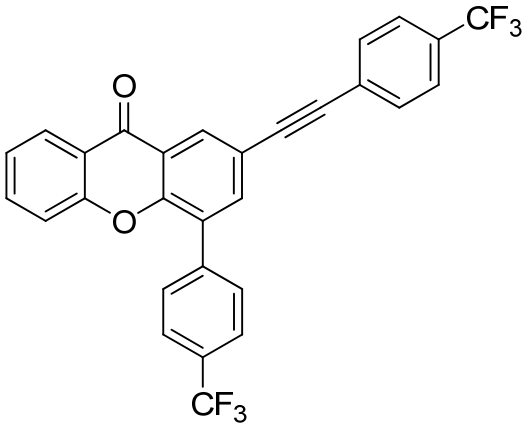
2-(2-hydroxybenzoyl)-4-phenyl-9H-xanthen-9-one (3a)

As a light yellow solid: m.p. 185-186 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ= 11.90 (s, 1H), 8.68 (d, *J* = 2.2 Hz, 1H), 8.36 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.14 (d, *J* = 2.3 Hz, 1H), 7.75 (td, *J* = 7.8, 1.5 Hz, 1H), 7.72-7.68 (m, 3H), 7.59-7.41 (m, 6H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 199.37, 176.62, 163.19, 155.77, 154.90, 136.61, 135.82, 135.265, 135.20, 133.21, 133.16, 132.36, 129.57, 128.55, 128.43, 127.82, 126.68, 124.69, 121.51, 121.38, 119.04, 118.87, 118.53, 118.23; HRMS calcd for $C_{26}H_{16}O_4$: 392.1049, found: 392.1045.



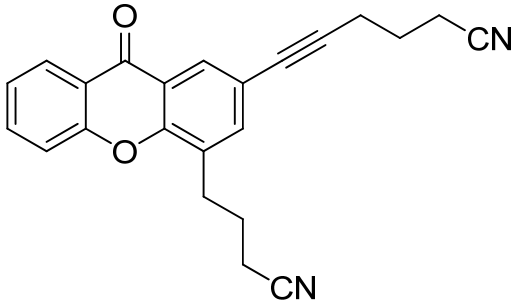
4-(4-methoxyphenyl)-2-((4-methoxyphenyl)ethynyl)-9H-xanthen-9-one (2b)

As a white solid: m.p. 200-202 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.46 (d, *J* = 2.2 Hz, 1H), 8.35 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.85 (d, *J* = 2.1 Hz, 1H), 7.70 (td, *J* = 7.8, 1.6 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.64, 159.745, 159.54, 155.80, 152.31, 137.87, 134.805, 133.09, 131.42, 130.75, 128.31, 127.85, 126.65, 124.14, 122.185, 121.33, 119.51, 118.12, 114.90, 114.01, 113.87, 90.10, 86.755, 55.31, 55.25; HRMS calcd for $C_{29}H_{20}O_4$: 432.1362, found: 432.1367.



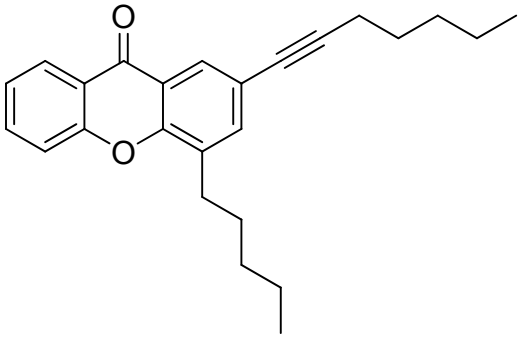
4-(4-(trifluoromethyl)phenyl)-2-((4-(trifluoromethyl)phenyl)ethynyl)-9H-xanthen-9-one (2c)

As a white solid: m.p. 223-224 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.59 (d, *J* = 2.2 Hz, 1H), 8.37 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.91 (d, *J* = 2.2 Hz, 1H), 7.84-7.78 (m, 4H), 7.74 (td, *J* = 7.8, 1.6 Hz, 1H), 7.69-7.62 (m, 4H), 7.43 (td, *J* = 7.6, 1.0 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ= 176.19, 155.70, 152.62, 139.01, 138.13, 135.24, 131.86, 130.64 (d, $^{2}J_{CF}$ = 32.3 Hz, 1C), 130.61, 130.31, 130.29 (d, $^{2}J_{CF}$ = 32.7 Hz, 1C), 129.97, 126.80, 126.47, 125.47 (q, $^{3}J_{CF}$ = 3.9 Hz, 2C), 125.37 (q, $^{3}J_{CF}$ = 3.3 Hz, 2C), 124.64, 124.09 (q, $^{1}J_{CF}$ =270.6 Hz, 1C), 123.85 (q, $^{1}J_{CF}$ =271.0 Hz, 1C), 122.42, 121.38, 118.68, 118.10, 89.82, 89.04; HRMS calcd for $C_{29}H_{14}O_2F_6$: 508.0898, found: 508.0903.



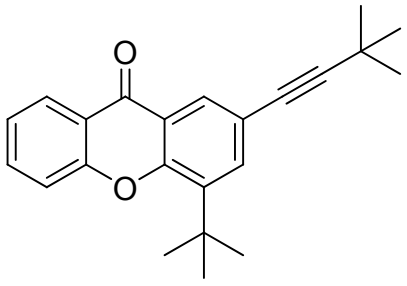
6-(4-(3-cyanopropyl)-9-oxo-9H-xanthen-2-yl)hex-5-ynenitrile (2d)

As a white solid: m.p. 112-114 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.26 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.19 (d, *J* = 2.1 Hz, 1H), 7.71 (td, *J* = 7.8, 1.8 Hz, 1H), 7.56-7.52 (m, 2H), 7.37 (td, *J* = 7.6, 1.1 Hz, 1H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 6.9 Hz, 2H), 2.09 (p, *J* = 7.2 Hz, 2H), 1.97 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.19, 155.39, 153.19, 137.42, 134.93, 129.24, 128.11, 126.34, 124.165, 121.425, 121.03, 119.18, 118.97, 118.75, 117.89, 87.76, 80.59, 28.11, 25.20, 24.26, 18.28, 16.59, 16.06; HRMS calcd for $C_{23}H_{18}N_2O_2$: 354.1368, found: 354.1359.



2-(hept-1-ynyl)-4-pentyl-9H-xanthen-9-one (2e)

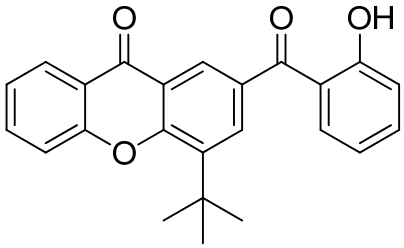
As a white solid: m.p. 54-56 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.32 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.22 (d, *J* = 2.1 Hz, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.78-1.57 (m, 4H), 1.51-1.32 (m, 8H), 0.97-0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.845, 155.81, 153.34, 137.53, 134.67, 132.05, 127.33, 126.65, 123.92, 121.51, 121.425, 119.54, 117.95, 90.78, 79.42, 31.515, 31.10, 29.45, 29.30, 28.38, 22.405, 22.21, 19.34, 13.96; HRMS calcd for $C_{25}H_{28}O_2$: 360.2089, found: 360.2083.



4-tert-butyl-2-(3,3-dimethylbut-1-ynyl)-9H-xanthen-9-one (2f)

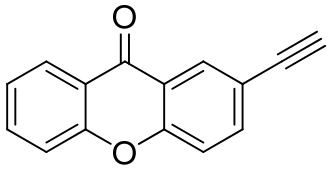
As a white solid: m.p.206-208 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.34 (dd, *J* = 8.0, 1.9 Hz, 1H), 8.27 (d, *J* = 2.1 Hz, 1H), 7.74 (td, *J* = 7.7, 1.6 Hz, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.54 (dd, *J* = 8.5, 1.1 Hz, 1H),

7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 1.56 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.98, 155.44, 154.08, 138.85, 134.87, 134.785, 128.01, 126.69, 124.05, 122.25, 121.27, 119.43, 117.85, 98.71, 78.22, 35.14, 30.99, 29.97, 27.96; HRMS calcd for $C_{23}H_{24}O_2$: 332.1776, found: 332.1787.



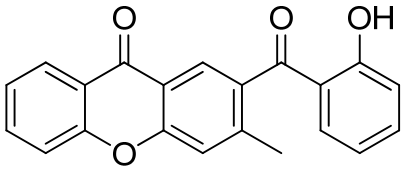
4-tert-butyl-2-(2-hydroxybenzoyl)-9H-xanthen-9-one (3f)

As a light yellow solid: m.p. 143-144 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 11.94 (s, 1H), 8.57 (d, *J* = 2.2 Hz, 1H), 8.36 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.10 (d, *J* = 2.2 Hz, 1H), 7.80 (td, *J* = 7.8, 1.6 Hz, 1H), 7.65 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.3, 0,8 Hz, 1H), 7.54 (td, *J* = 7.8, 1.6 Hz, 1H), 7.45 (td, *J* = 7.6, 1.1 Hz, 1H), 7.10 (dd, *J* = 8.5, 0.9 Hz, 1H), 6.92 (td, *J* = 7.6, 1.1 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 200.07, 176.98, 163.20, 157.01, 155.41, 140.07, 136.515, 135.29, 133.33, 132.58, 132.22, 127.10, 126.71, 124.66, 121.56, 121.31, 118.975, 118.49, 117.96, 35.48, 29.93; HRMS calcd for $C_{24}H_{20}O_4$: 372.1362, found: 372.1363.



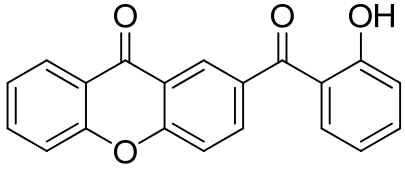
2-ethynyl-9H-xanthen-9-one (2g)

As a white solid: m.p. 157-159 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.47 (s, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 7.81-7.71 (m, 2H), 7.51-7.37 (m, 3H), 3.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.24, 155.91, 155.80, 137.83, 135.05, 130.74, 126.72, 124.24, 121.61, 121.58, 118.32, 118.03, 117.97, 82.07, 77.93; HRMS calcd for $C_{15}H_8O_2$: 220.0524, found: 220.0528.



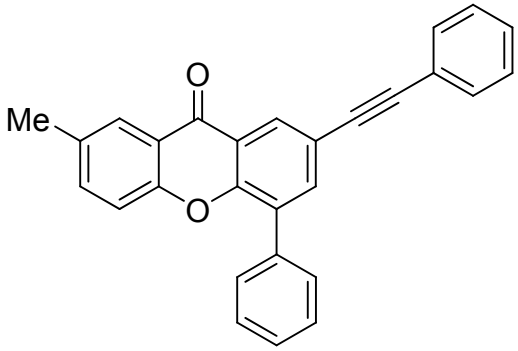
2-(2-hydroxybenzoyl)-3-methyl-9H-xanthen-9-one ($3g_1$)

As a white solid: m.p. 175-176 ^{o}C (lit.,[1] 144 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 12.12 (s, 1H), 8.33 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.28 (s, 1H), 7.76 (td, *J* = 7.8, 1.7 Hz, 1H), 7.57-7.50 (m, 2H), 7.45 (s, 1H), 7.42 (td, *J* = 7.5, 1.1 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.09 (dd, *J* = 8.7, 1.0 Hz, 1H), 6.83 (td, *J* = 7.7, 1.2 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 202.14, 176.38, 163.49, 156.70, 156.04, 144.32, 137.155, 135.08, 133.87, 133.47, 126.80, 126.73, 124.34, 121.84, 120.02, 119.70, 119.11, 119.05, 118.48, 118.04, 20.36; HRMS calcd for $C_{21}H_{14}O_4$: 330.0892, found: 330.0884.



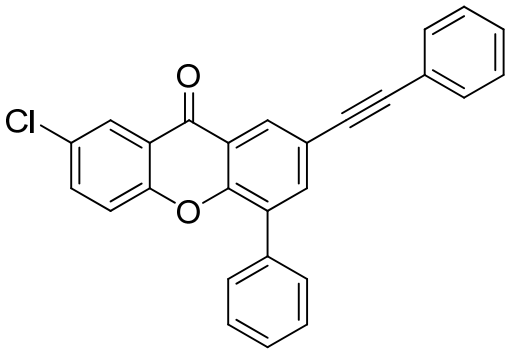
2-(2-hydroxybenzoyl)-9H-xanthen-9-one ($3g_2$)

As a white solid: m.p. 184-185 ^{o}C (lit.,[2] 185 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 11.87 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.12 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.79 (td, *J* = 7.8, 1.5 Hz, 1H), 7.67-7.52 (m, 4H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 199.31, 176.44, 163.16, 158.03, 155.93, 136.59, 135.345, 135.13, 133.31, 133.17, 128.83, 126.77, 124.61, 121.72, 120.98, 119.00, 118.84, 118.79, 118.53, 118.09; HRMS calcd for $C_{20}H_{12}O_4$: 316.0736, found: 316.0733.



7-methyl-4-phenyl-2-(phenylethynyl)-9H-xanthen-9-one (2h)

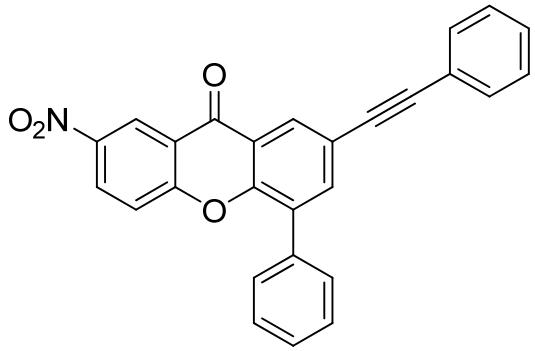
As a white solid: m.p.199-201 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.50 (d, *J* = 2.1 Hz, 1H), 8.11 (s, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.70-7.64 (m, 2H), 7.59-7.45 (m, 6H), 7.40-7.33 (m, 3H), 7.28 (d, *J* = 8.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ= 176.55, 154.01, 152.46, 138.06, 136.15, 135.57, 134.085, 131.75, 131.61, 129.575, 129.13, 128.44, 128.40, 128.35, 128.10, 125.94, 122.84, 122.135, 120.93, 118.95, 117.88, 90.025, 87.97, 20.76; HRMS calcd for $C_{28}H_{18}O_2$: 386.1307, found: 386.1307.



7-chloro-4-phenyl-2-(phenylethynyl)-9H-xanthen-9-one (2i)

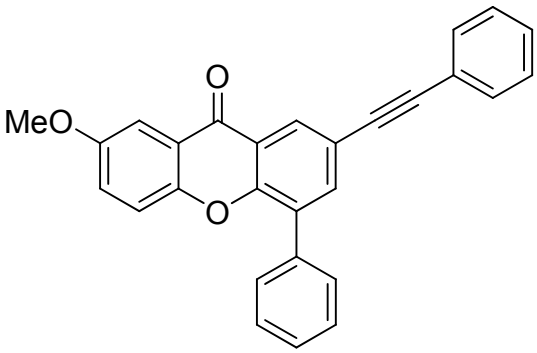
As a white solid: m.p. 213-215 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.50 (d, *J* = 2.2 Hz, 1H), 8.31 (d, *J* = 2.6 Hz, 1H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.69-7.61 (m, 3H), 7.59-7.46 (m, 5H), 7.41-7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 175.47, 154.11, 152.30, 138.61, 135.28, 134.99, 131.97, 131.64, 130.09, 129.55,

129.05, 128.58, 128.50, 128.39, 128.29, 125.97, 122.68, 122.16, 121.81, 119.92, 119.63, 90.46, 87.66; HRMS calcd for $C_{27}H_{15}ClO_2$: 406.0761, found: 406.0756.



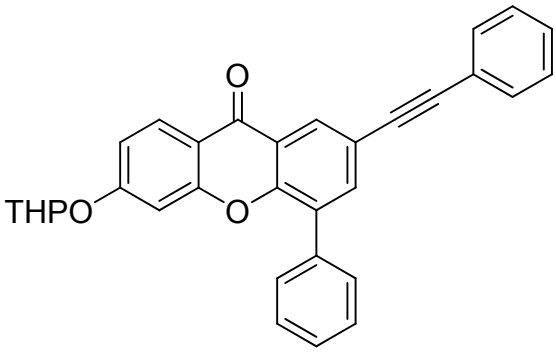
7-nitro-4-phenyl-2-(phenylethynyl)-9H-xanthen-9-one (2j)

As a yellow solid: m.p. 239-241 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 9.21 (d, *J* = 2.8 Hz, 1H), 8.50 (dd, *J* = 9.2, 2.7 Hz, 1H), 8.47 (d, *J* = 2.3 Hz, 1H), 7.67-7.63 (m, 2H), 7.59-7.49 (m, 6H), 7.39-7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 175.12, 158.71, 152.00, 143.96, 139.24, 134.84, 132.28, 131.65, 129.52, 129.00, 128.93, 128.78, 128.65, 128.56, 128.42, 123.435, 12.41, 121.71, 121.17, 120.65, 119.85, 91.06, 87.26; HRMS calcd for $C_{27}H_{15}NO_4$: 417.1001, found: 417.1002.



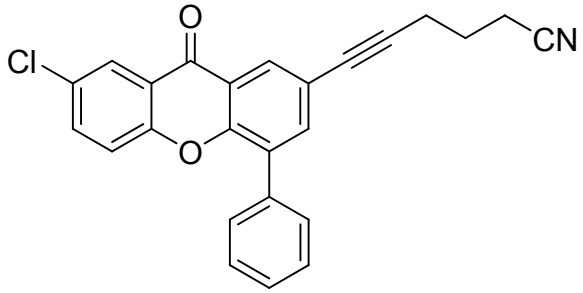
7-methoxy-4-phenyl-2-(phenylethynyl)-9H-xanthen-9-one (2k)

As a white solid: m.p. 227-229 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.53 (d, *J* = 2.2 Hz, 1H), 7.89 (d, *J* = 2.1 Hz, 1H), 7.73-7.65 (m, 3H), 7.60-7.46 (m, 5H), 7.40-7.27 (m, 5H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.435, 156.22, 152.44, 150.67, 138.04, 135.60, 131.84, 131.645, 129.60, 129.13, 128.49, 128.44, 128.39, 128.16, 125.08, 122.85, 121.67, 121.615, 119.625, 119.01, 105.65, 90.07, 87.99, 55.90; HRMS calcd for $C_{28}H_{18}O_3$: 402.1256, found:402.1252.



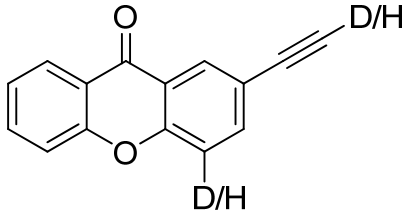
4-phenyl-2-(phenylethynyl)-6-(tetrahydro-2H-pyran-2-yloxy)-9H-xanthen-9-one (2l)

As a white solid: m.p. >300 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.50 (d, *J* = 2.0 Hz, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.69-7.63 (m, 2H), 7.59-7.46 (m, 5H), 7.40-7.34 (m, 3H), 7.06 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.00 (s, 1H), 5.59-5.54 (m, 1H), 3.87-3.77 (m, 1H), 3.68-3.58 (m, 1H), 2.06-1.85 (m, 3H), 1.79-1.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 175.70, 162.55, 157.51, 152.59, 137.92, 135.635, 131.62, 129.58, 129.09, 128.46, 128.36, 128.09, 128.08, 122.87, 122.31, 119.06, 115.83, 114.765, 103.39, 96.11, 90.00, 88.01, 61.83, 29.87, 24.935, 18.125; HRMS calcd for $C_{32}H_{24}O_4$: 472.1675, found: 472.1665.



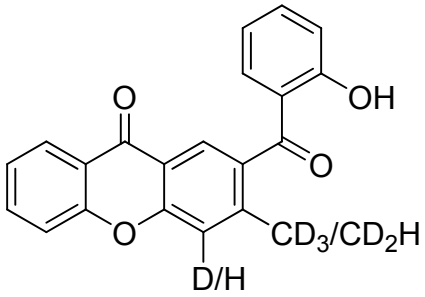
6-(7-chloro-9-oxo-4-phenyl-9H-xanthen-2-yl)hex-5-ynenitrile(2id)

As a white solid: m.p.153-154 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.35 (d, *J* = 1.8 Hz, 1H), 8.29 (d, *J* = 2.5 Hz, 1H), 7.77 (d, *J* = 2.2 Hz, 1H), 7.66-7.59 (m, 3H), 7.56-7.46 (m, 3H), 7.36 (d, *J* = 9.0 Hz, 1H), 2.65 (t, *J* = 6.8 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 1.99 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 175.475, 154.10, 152.155, 138.71, 135.20, 135.02, 131.915, 130.06, 129.49, 129.02, 128.485, 128.285, 125.94, 122.12, 121.71, 119.93, 119.51, 119.03, 88.19, 80.75, 24.48, 18.49, 16.255; HRMS calcd for $C_{25}H_{16}ClNO_2$: 397.8530, found:397.8523.



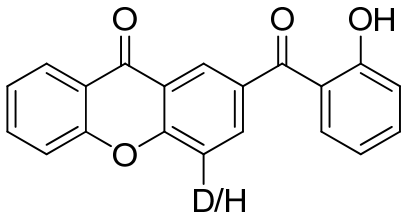
2-ethynyl-9H-xanthen-9-one ([D] 2g)

As a white solid: m.p. 155-157 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.45 (d, *J* = 2.1 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.72 (td, *J* = 7.8, 0.8 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 3.13 (s, 0.2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 176.02, 155.79, 155.63, 137.60, 134.91, 130.60, 126.60, 124.12, 121.51, 121.48, 117.96, 117.95 (t, $^{1}J_{CD}$ = 25.1 Hz, 1C) 117.87, 82.04, 81.60, 77.895; HRMS calcd for $C_{15}H_8O_2$: 220.0524, found: 220.0526, calcd for $C_{15}H_7DO_2$: 221.0587, found: 221.0589, calcd for $C_{15}H_6D_2O_2$: 222.0650, found: 222.0649.



2-(2-hydroxybenzoyl)-3-methyl-9H-xanthen-9-one ([D] 3g$_1$)

As a white solid: m.p. 175-176 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 12.12 (s, 1H), 8.33 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.28 (s, 1H), 7.76 (td, *J* = 7.8, 1.6 Hz, 1H), 7.57-7.49 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H),6.83 (t, *J* = 7.6 Hz), 2.50-2.45 (m, 0.1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 202.10, 176.34, 163.45, 156.63, 155.99, 144.13, 137.12, 135.06, 133.83, 133.45, 126.76, 126.68, 124.31, 121.79, 119.73 (t, $^{1}J_{CD}$ = 25.9 Hz, 1C), 119.67, 119.08, 119.00, 118.44, 118.01, 19.50 (h, *J* = 19.6 Hz, 1C); HRMS calcd for $C_{21}H_{12}D_2O_4$:332.1018, found: 332.1010, calcd for $C_{21}H_{11}D_3O_4$:333.1080, found: 333.1072, calcd for $C_{21}H_{10}D_4O_4$:334.1143, found: 334.1136.



2-(2-hydroxybenzoyl)-9H-xanthen-9-one ([D] 3g$_2$)

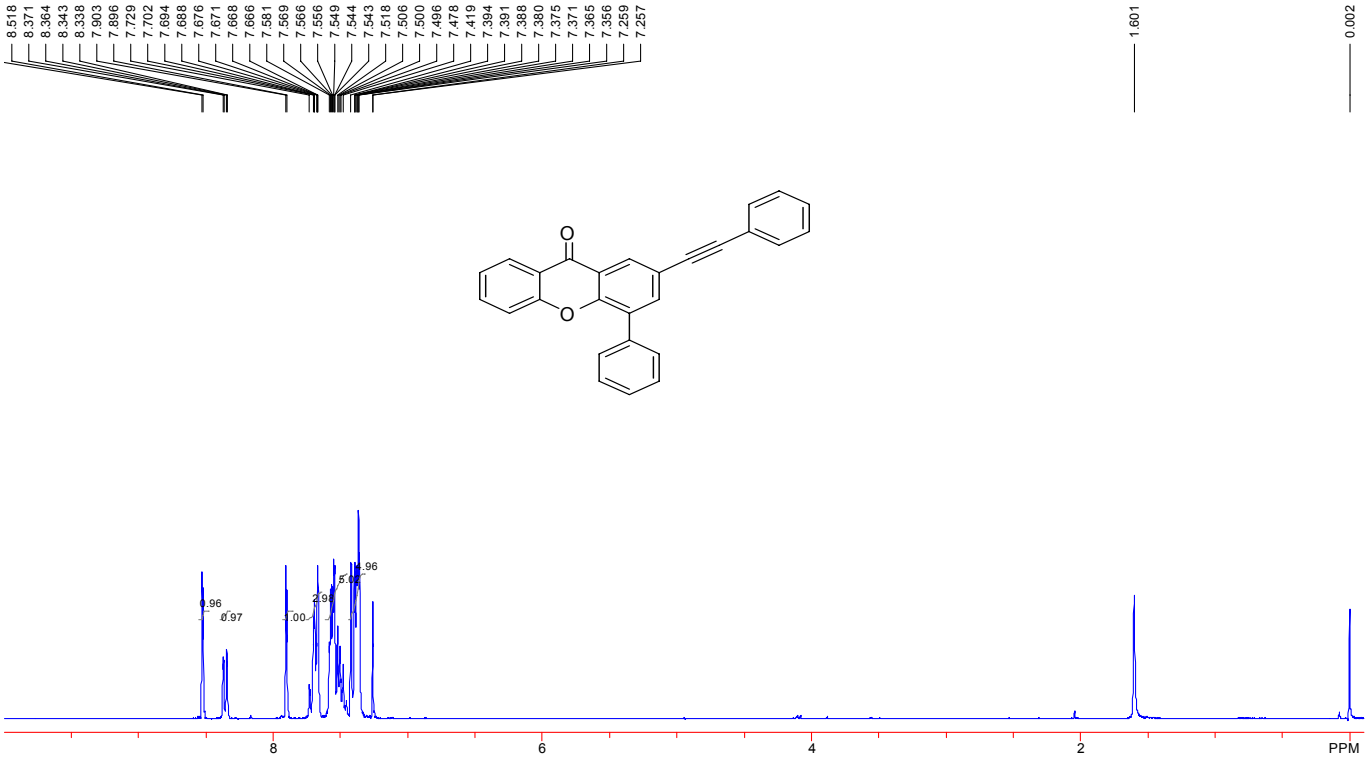
As a white solid: m.p. 183-184 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 11.87 (s, 1H), 8.67 (d, *J* = 1.7 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.13-8.08 (m, 1H), 7.79 (t, *J* = 7.9 Hz, 1H), 7.66-7.50 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.91 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 199.32, 176.44, 163.15, 157.99, 155.93, 136.59, 135.35, 135.13, 135.03, 133.30, 133.17, 128.82, 126.76, 124.61, 121.71, 120.975, 119.00, 118.83, 118.79, 118.52, 118.09; HRMS calcd for $C_{20}H_{12}O_4$: 316.0736, found: 316.0734, calcd for $C_{20}H_{11}DO_4$: 317.0798, found: 317.0802.

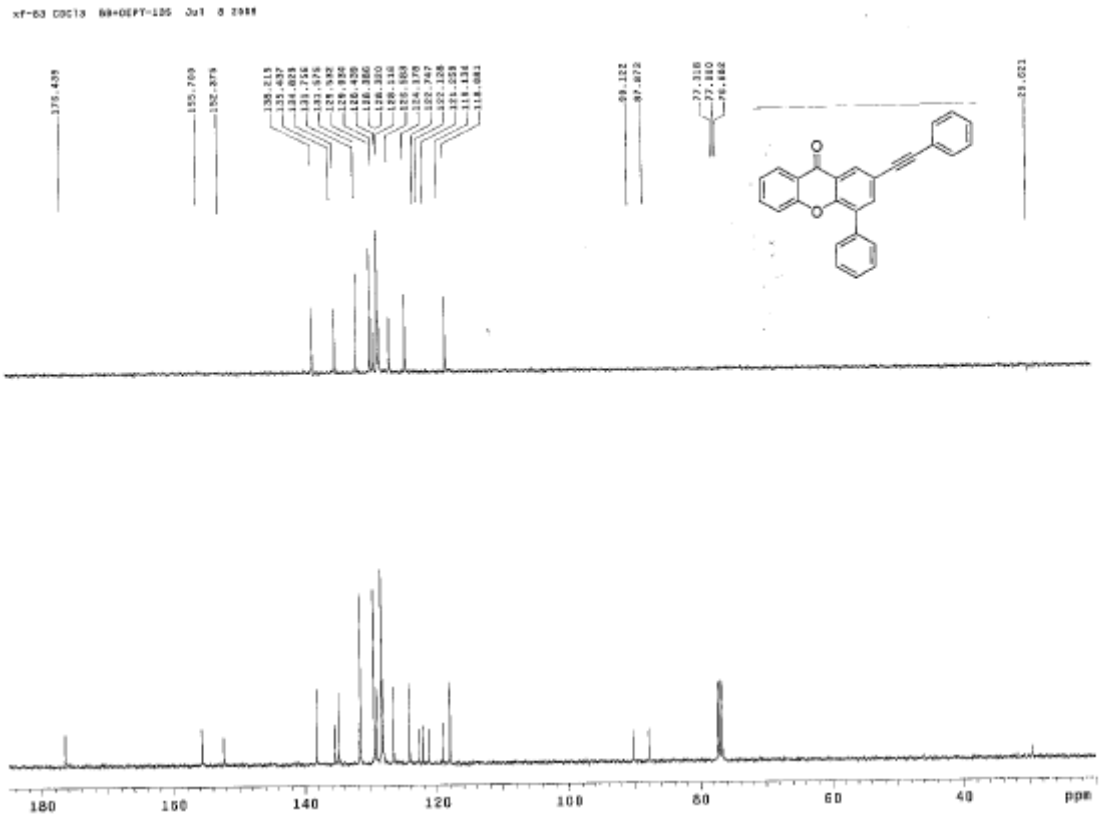
References

(1) Ghosh, C. K.; Sahana, S.; Patra, A. *Tetrahedron* **1993**, *49*, 4127-4134.
(2) Ghosh, C. K.; Bhattacharyya, S.; Patra, A. *J. Chem. Soc., Perkin. Trans. 1,* **1999**, 3005-3013.

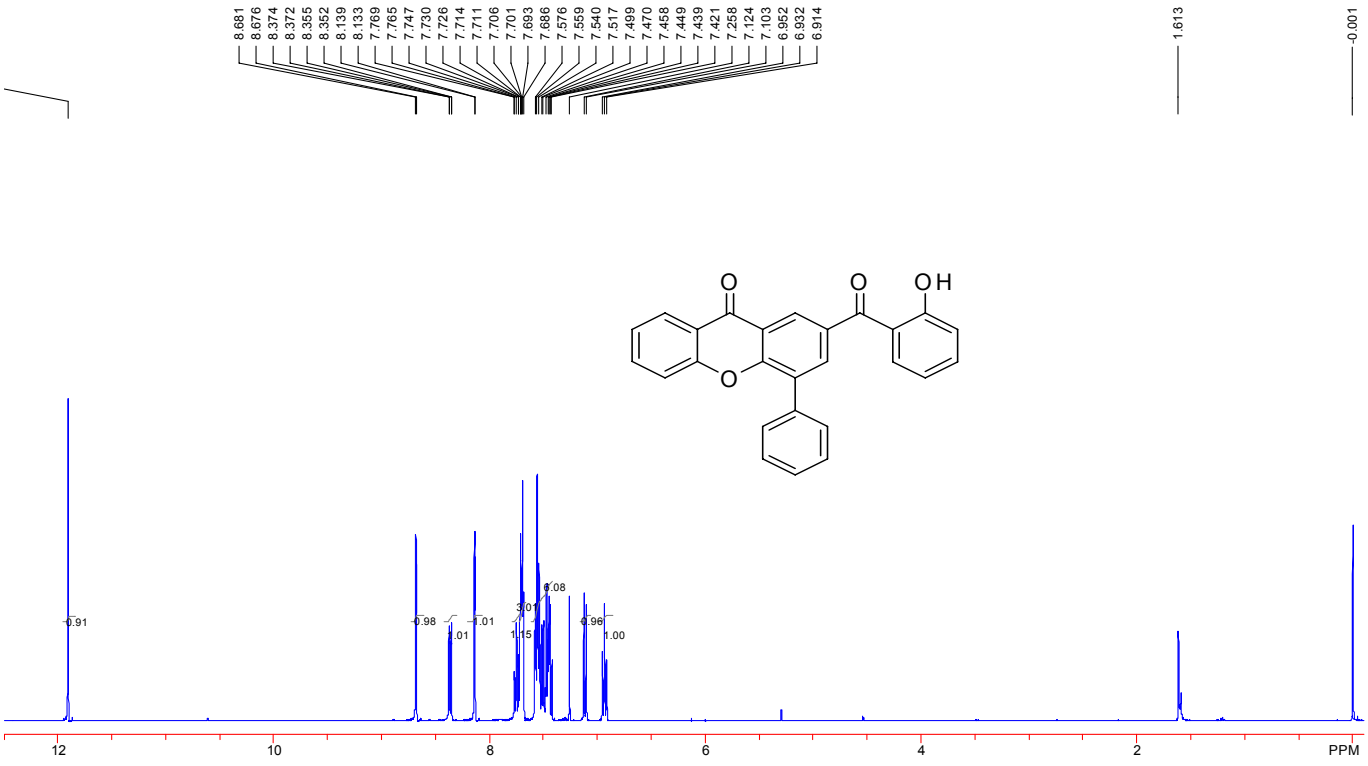
3. ^{1}H NMR and ^{13}C NMR spectra

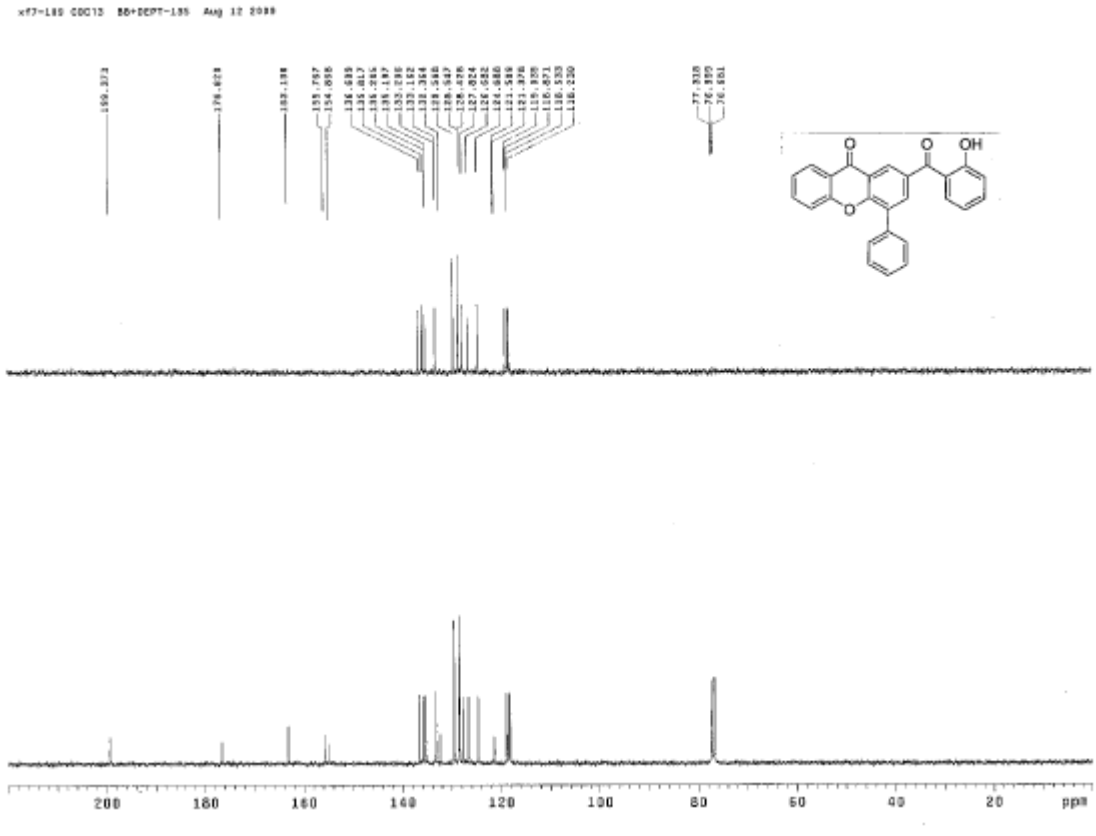
2a



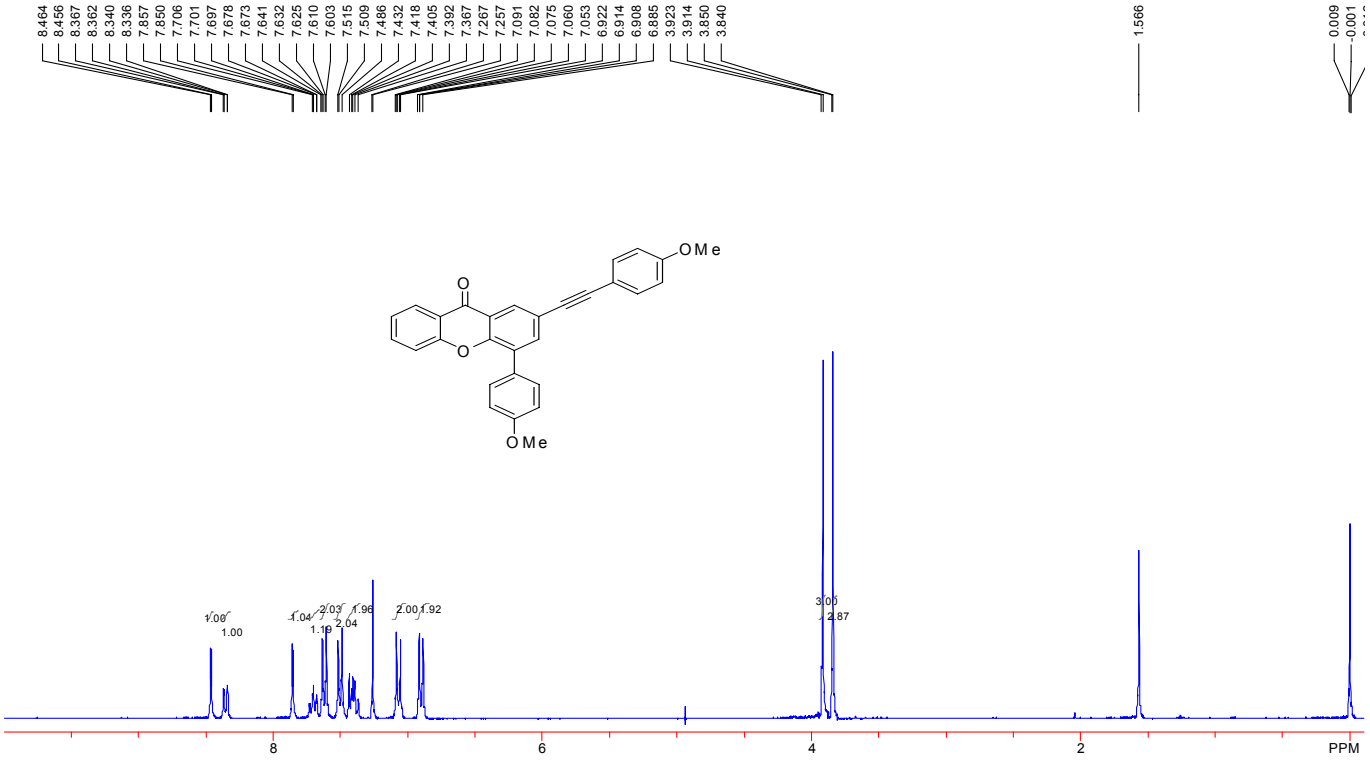


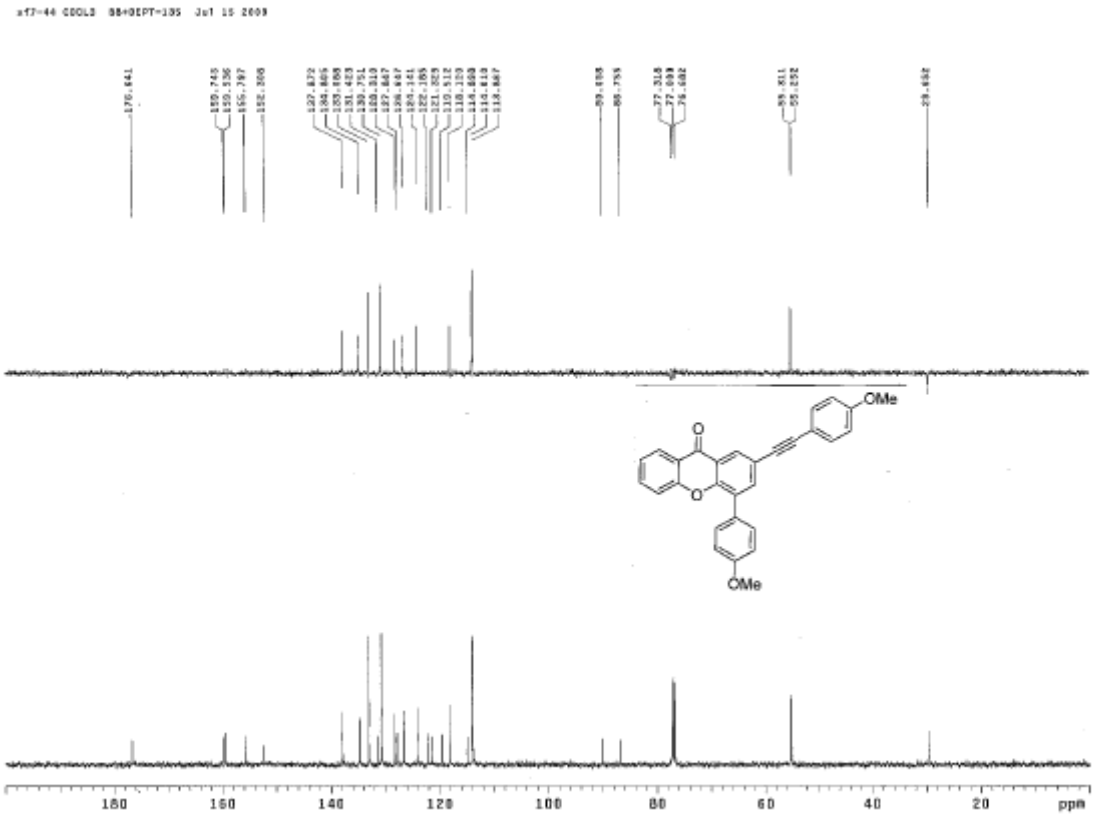
3a


8.681
8.676
8.374
8.372
8.355
8.352
8.139
8.133
7.769
7.765
7.747
7.730
7.726
7.714
7.711
7.706
7.701
7.693
7.686
7.576
7.559
7.540
7.517
7.499
7.470
7.458
7.449
7.439
7.421
7.258
7.124
7.103
6.952
6.932
6.914
1.613
0.001
O
O
OH
O
0.91
0.98
1.01
1.01
3.01
1.15
0.96
1.00
12
10
8
6
4
2
PPM

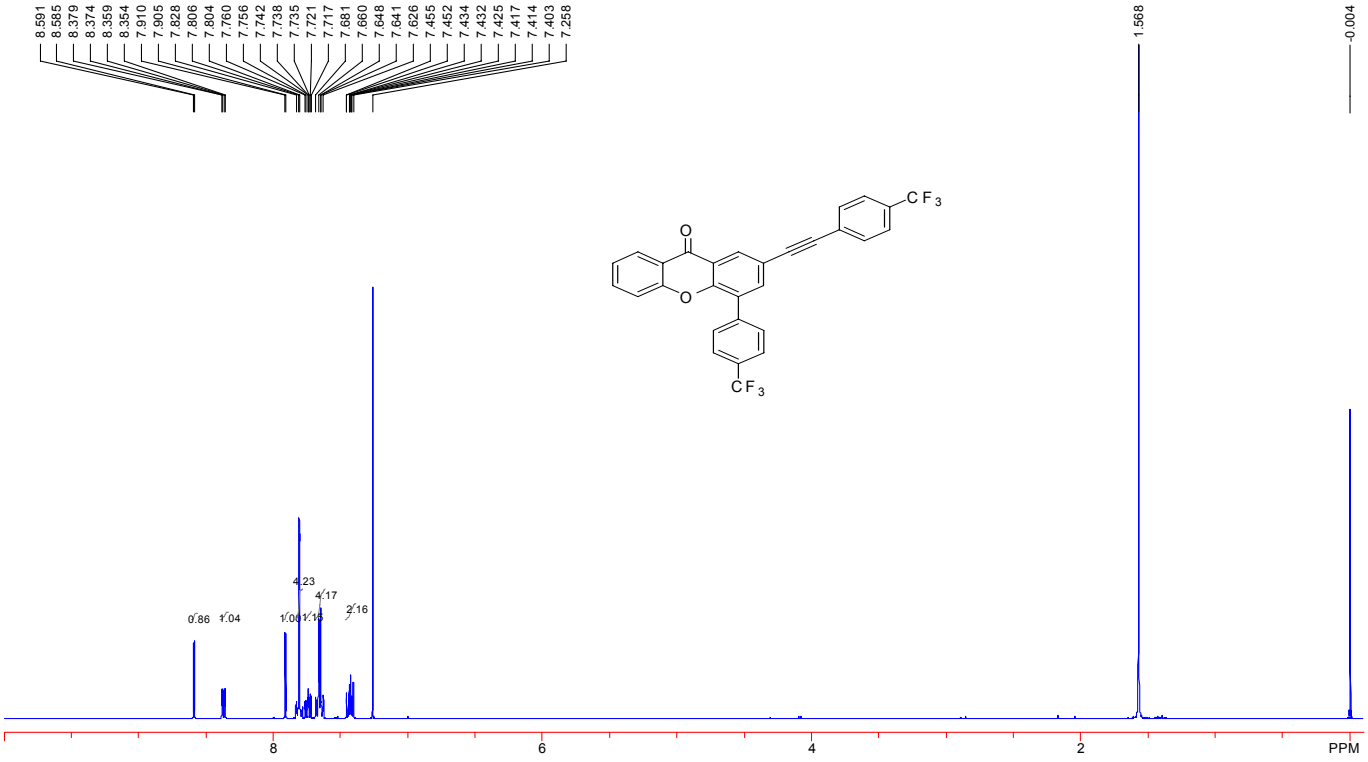

O
O
OH
O
200
180
160
140
120
100
80
60
40
20
ppm

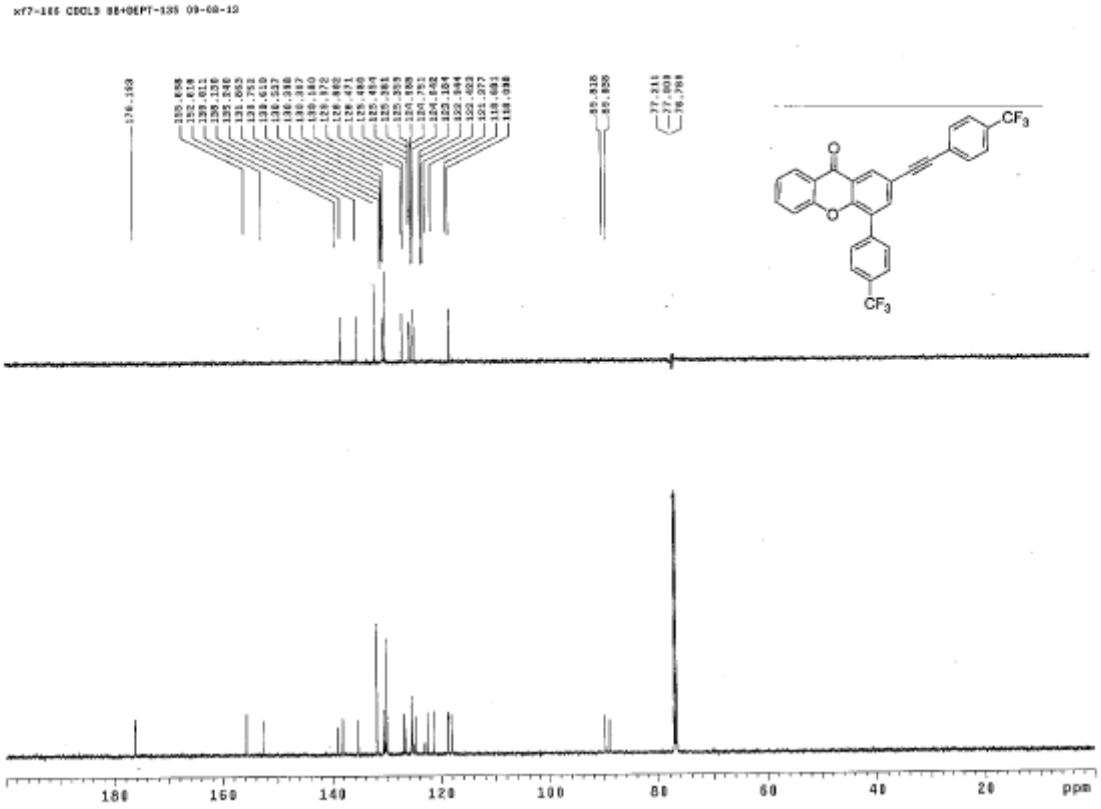
2b


8.464
8.456
8.367
8.362
8.340
8.336
7.857
7.850
7.706
7.701
7.697
7.678
7.673
7.641
7.632
7.625
7.610
7.603
7.515
7.509
7.486
7.432
7.418
7.405
7.392
7.367
7.267
7.257
7.091
7.082
7.075
7.060
7.053
6.922
6.914
6.908
6.885
3.923
3.914
3.850
3.840
1.566
0.009
-0.001
OMe
O
O
OMe
1.00
1.00
1.04
1.19
2.03
2.04
1.96
2.00
1.92
3.00
2.87
8
6
4
2
PPM


OMe
OMe
180
160
140
120
100
80
60
40
20
ppm

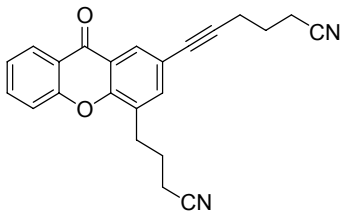
2c

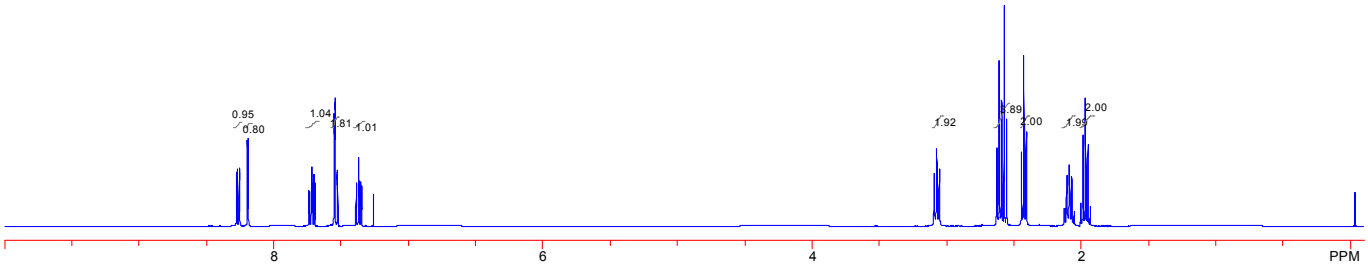

8.591
8.585
8.379
8.374
8.359
8.354
7.910
7.905
7.828
7.806
7.804
7.760
7.756
7.742
7.738
7.735
7.721
7.717
7.681
7.660
7.648
7.641
7.626
7.455
7.452
7.434
7.432
7.425
7.417
7.414
7.403
7.258
1.568
-0.004
CF3
O
O
CF3
4.23
4.17
2.16
0.86
1.04
1.00
1.16
8
6
4
2
PPM

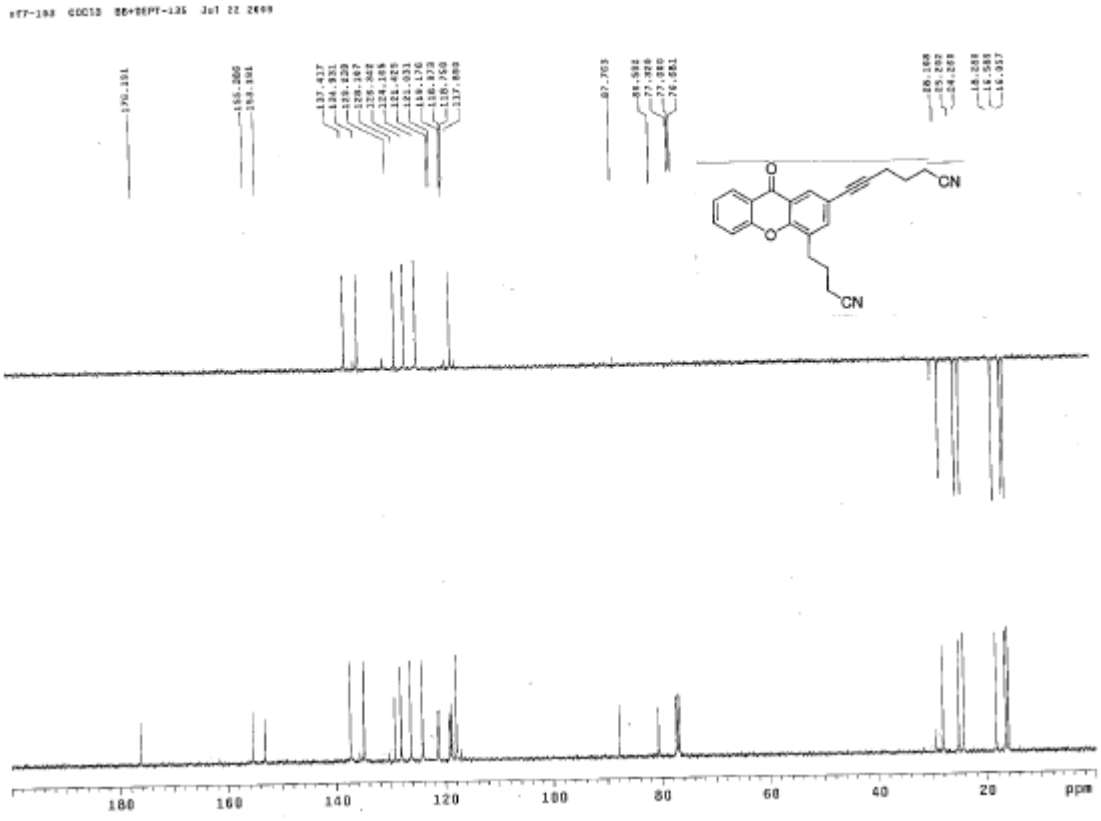

xf7-166 CDCL3 BB+DEPT-135 09-08-12
CF3
CF3
ppm

2d

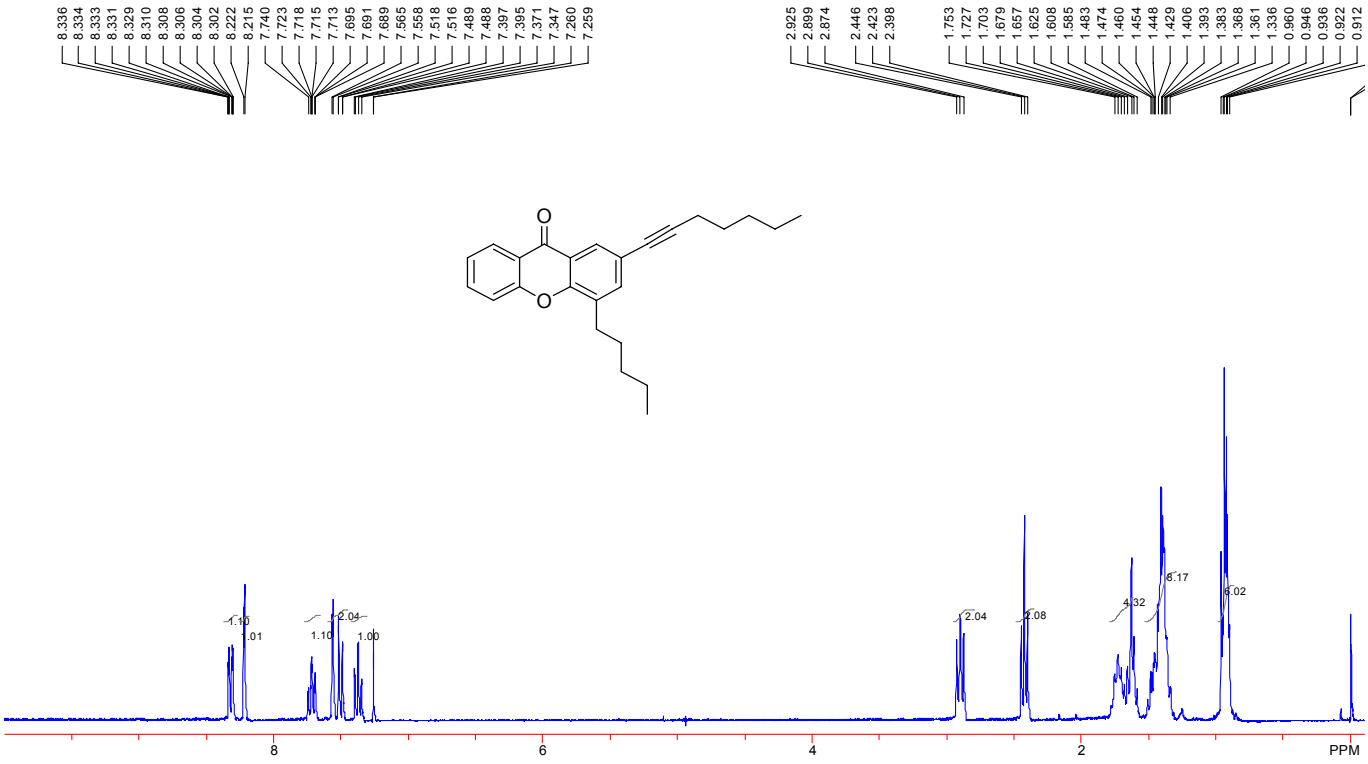

8.275
8.271
8.270
8.255
8.254
8.251
8.193
8.188
7.736
7.731
7.718
7.714
7.710
7.697
7.692
7.548
7.547
7.544
7.543
7.526
7.525
7.524
7.387
7.384
7.369
7.367
7.364
7.349
7.347
7.257
3.091
3.073
3.054
2.625
2.608
2.590
2.571
2.553
2.442
2.424
2.407
2.106
2.086
2.069
1.984
1.967
1.949
-0.032

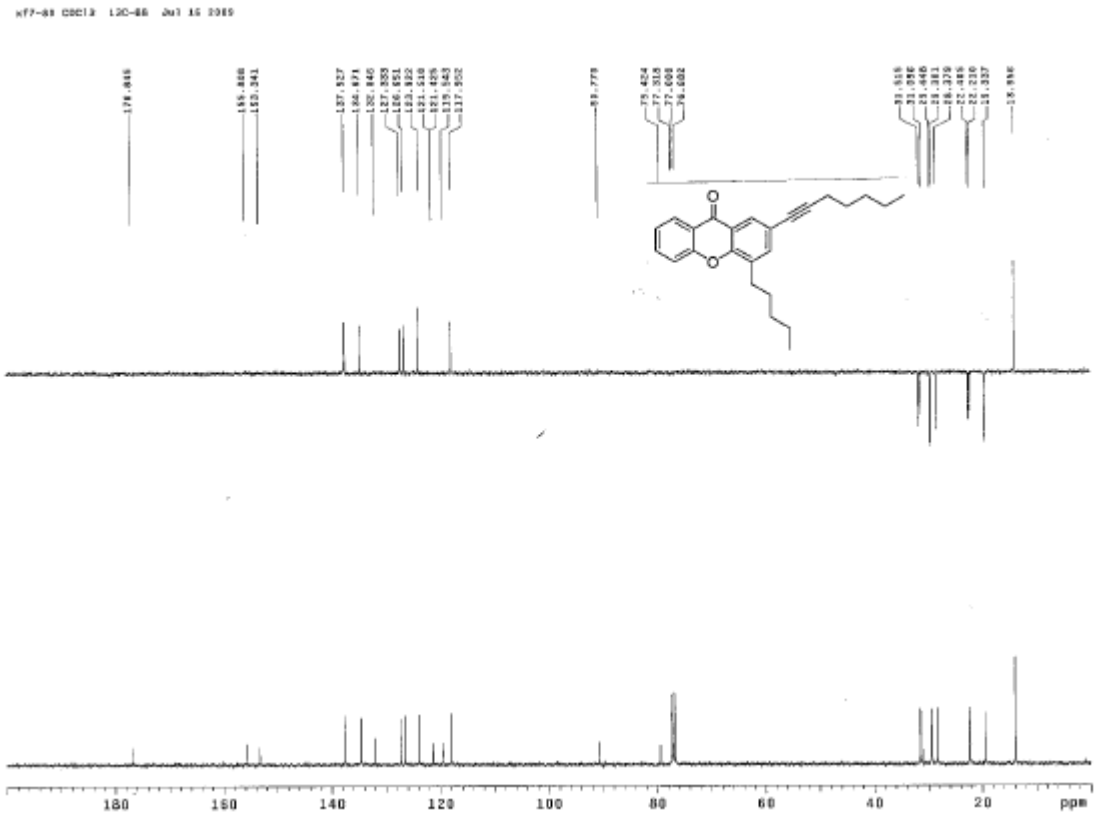

O
CN
O
CN


0.95
0.80
1.04
1.81
1.01
1.92
3.89
2.00
1.99
2.00
8
6
4
2
PPM

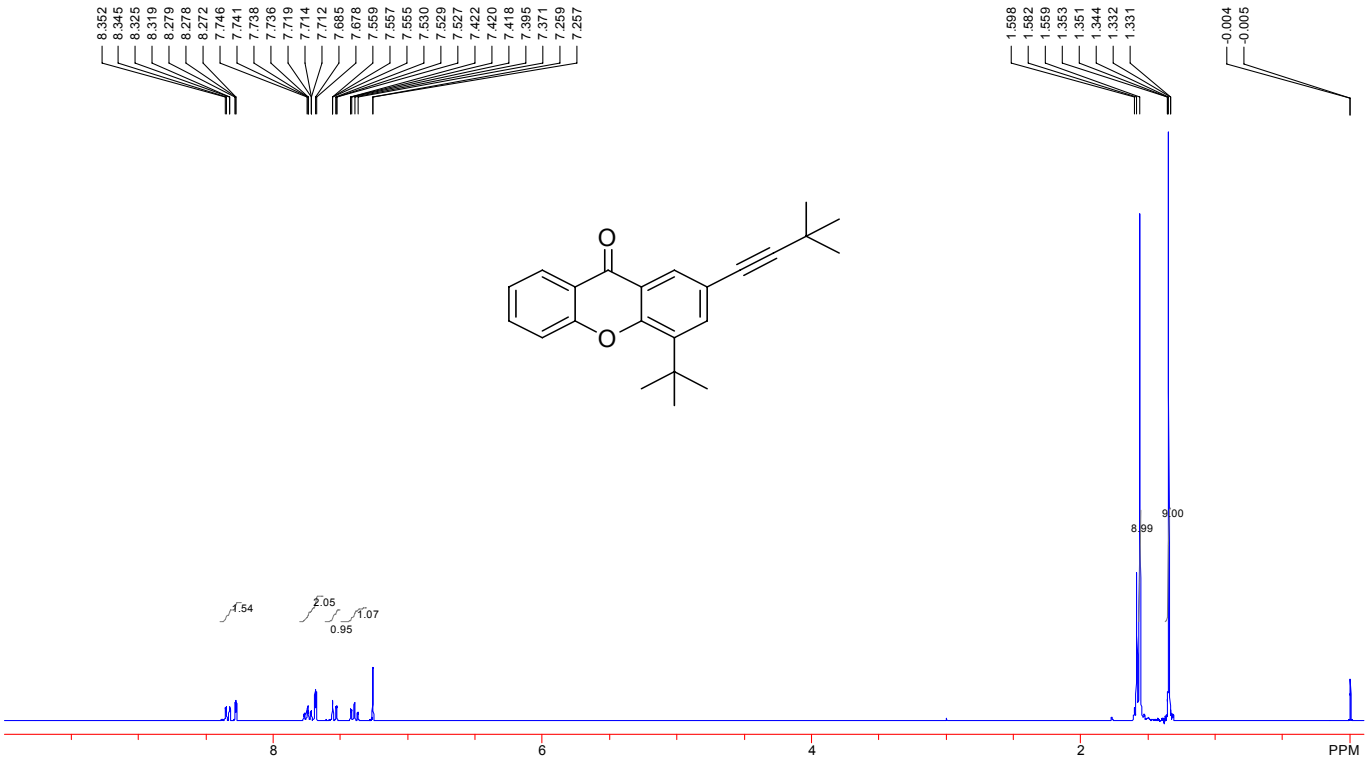

O
CN
CN
180
160
140
120
100
80
60
40
20
ppm

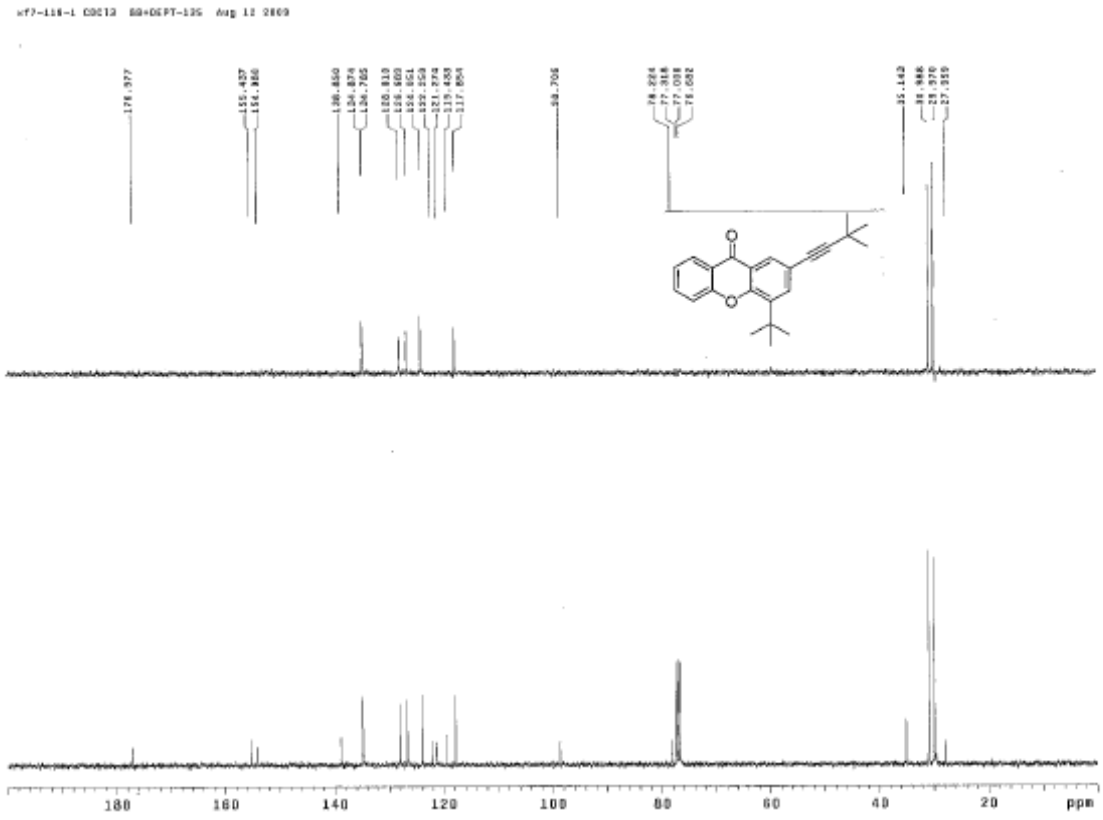
2e


8.336
8.334
8.333
8.331
8.329
8.310
8.308
8.306
8.304
8.302
8.222
8.215
7.740
7.723
7.718
7.715
7.713
7.695
7.691
7.689
7.565
7.558
7.518
7.516
7.489
7.488
7.397
7.395
7.371
7.347
7.260
7.259
2.925
2.899
2.874
2.446
2.423
2.398
1.753
1.727
1.703
1.679
1.657
1.625
1.608
1.585
1.483
1.474
1.460
1.454
1.448
1.429
1.406
1.393
1.383
1.368
1.361
1.336
0.960
0.946
0.936
0.922
0.912
O
O
1.10
1.01
2.04
1.10
1.00
2.04
2.08
4.32
6.17
4.02
8
6
4
2
PPM

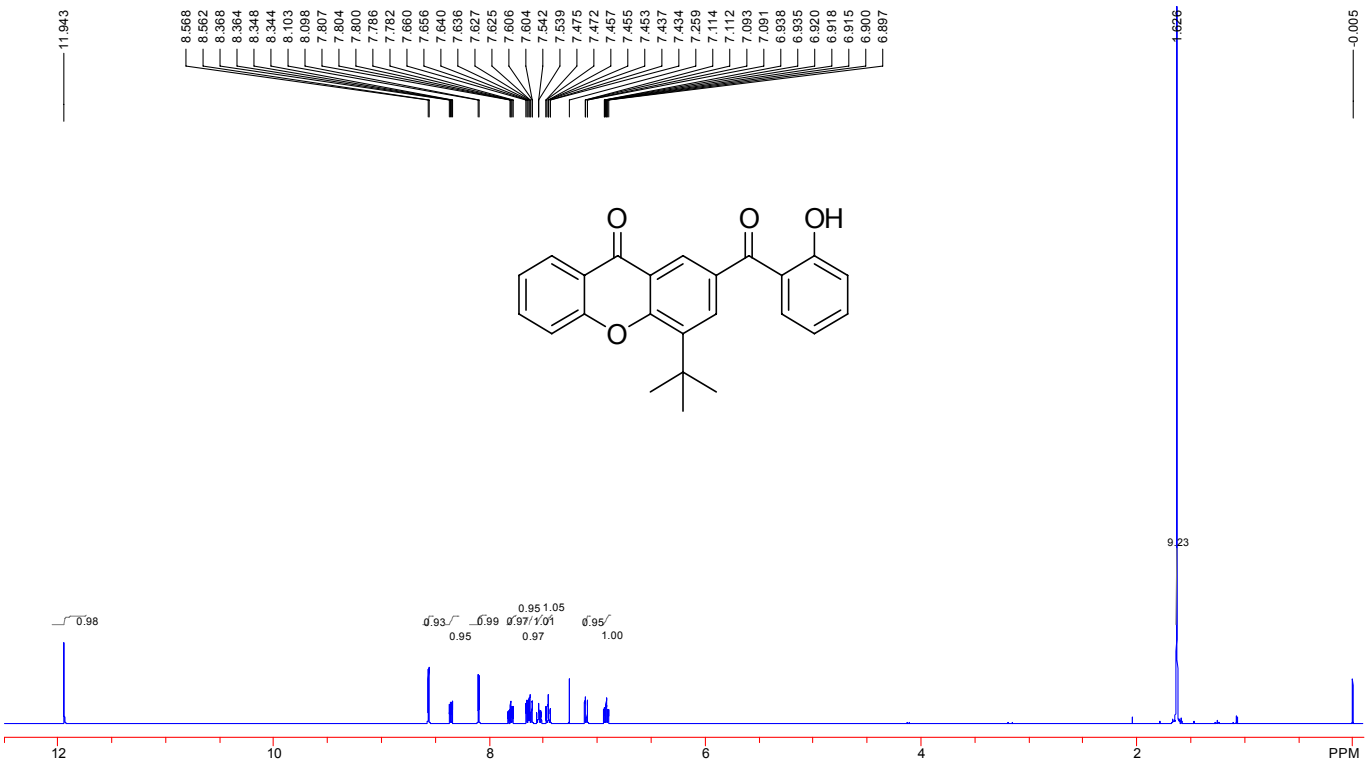

O
180
160
140
120
100
80
60
40
20
ppm

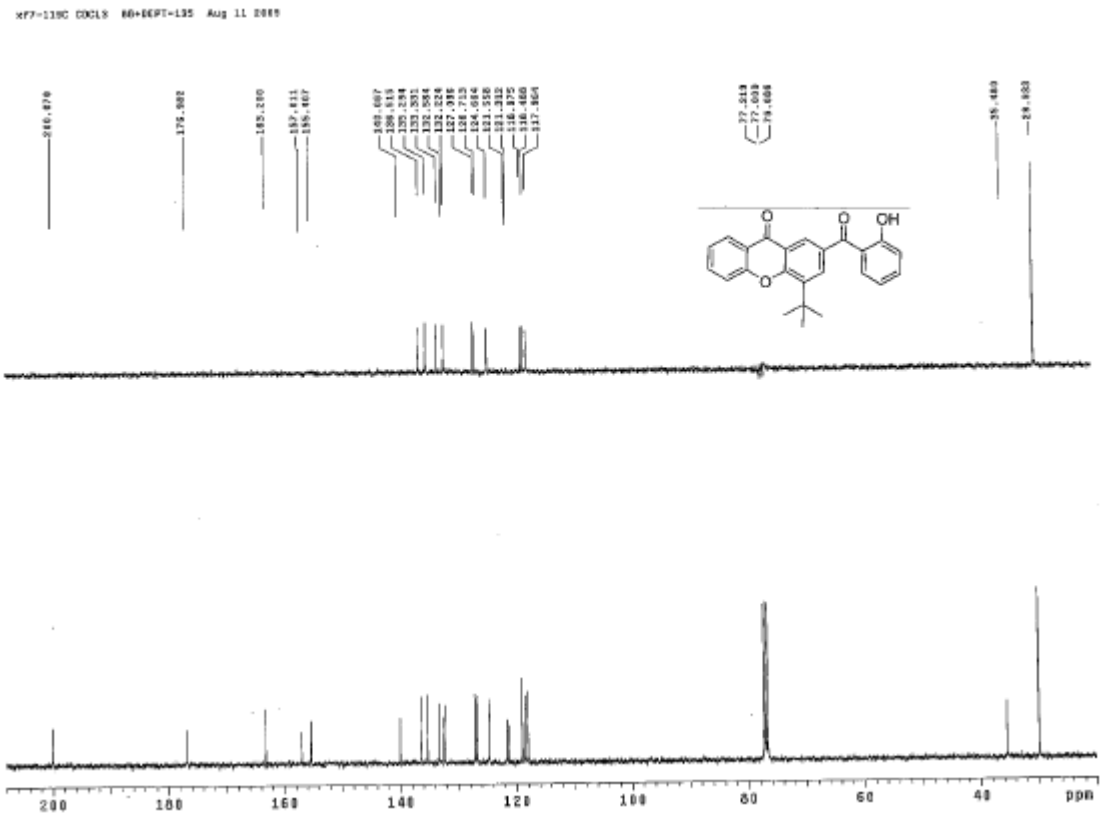
2f


8.352
8.345
8.325
8.319
8.279
8.278
8.272
7.746
7.741
7.738
7.736
7.719
7.714
7.712
7.685
7.678
7.559
7.557
7.555
7.530
7.529
7.527
7.422
7.420
7.418
7.395
7.371
7.259
7.257
1.598
1.582
1.559
1.559
1.353
1.351
1.344
1.332
1.331
-0.004
-0.005
O
O
1.54
2.05
0.95
1.07
8.99
9.00
8
6
4
2
PPM

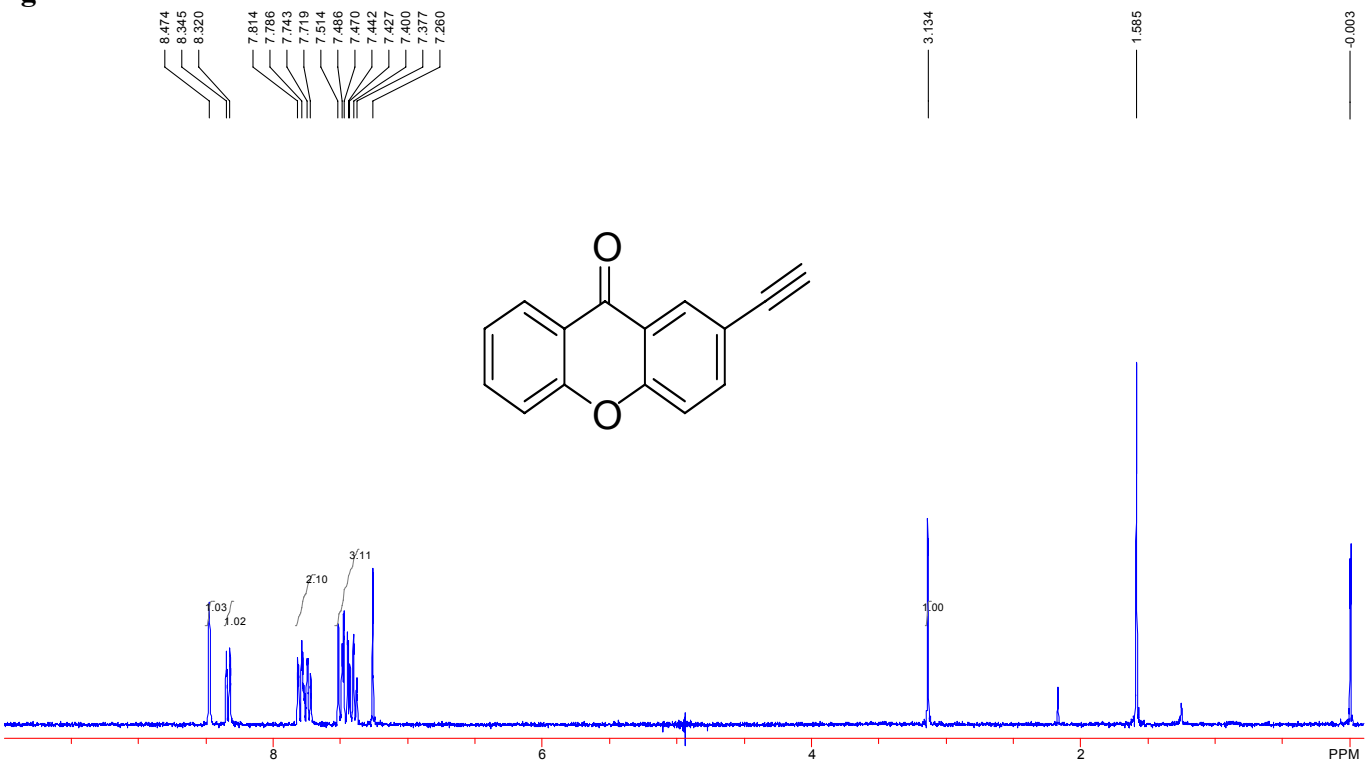

O
O
180
160
140
120
100
80
60
40
20
ppm

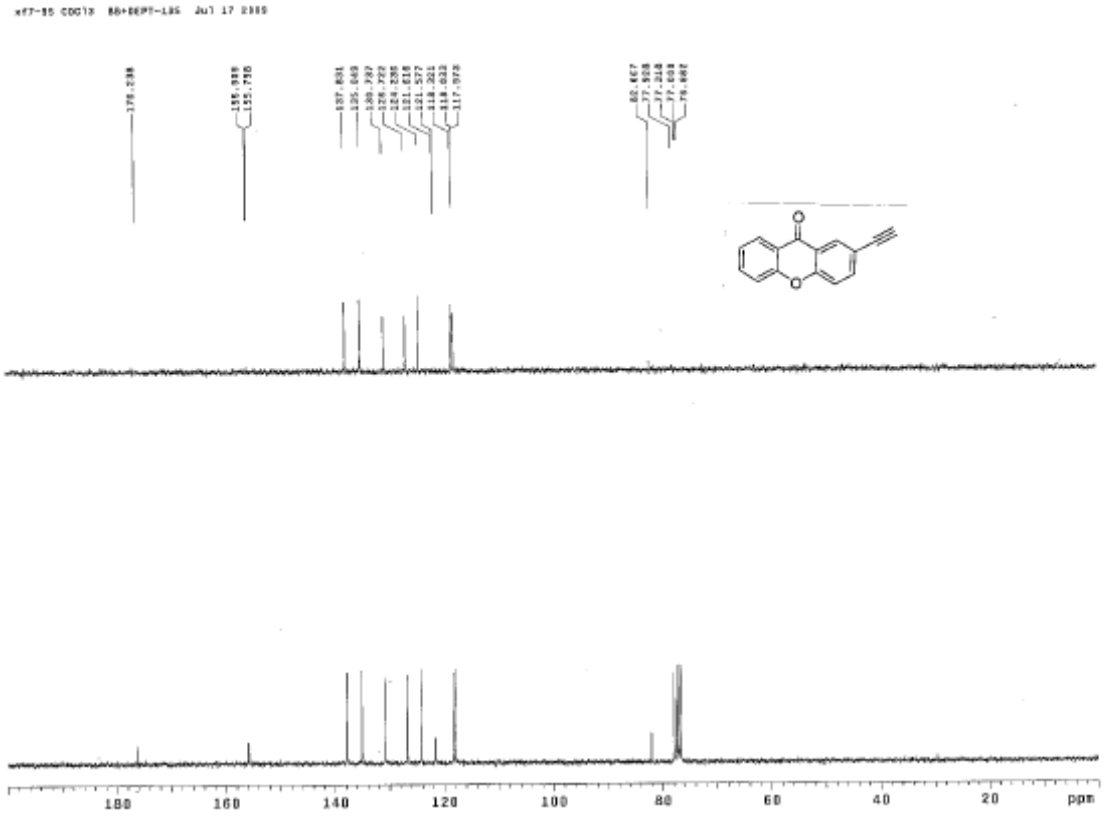
3f


11.943
8.568
8.562
8.368
8.364
8.348
8.344
8.103
8.098
7.807
7.804
7.800
7.786
7.782
7.660
7.656
7.640
7.636
7.627
7.625
7.606
7.604
7.542
7.539
7.475
7.472
7.457
7.455
7.453
7.437
7.434
7.259
7.114
7.112
7.093
7.091
6.938
6.935
6.920
6.918
6.915
6.900
6.897
1.626
-0.005
O
O
OH
O
9.23
0.98
0.93
0.95
0.99
0.95 1.05
0.97/1.01
0.97
0.95
1.00
12
10
8
6
4
2
PPM

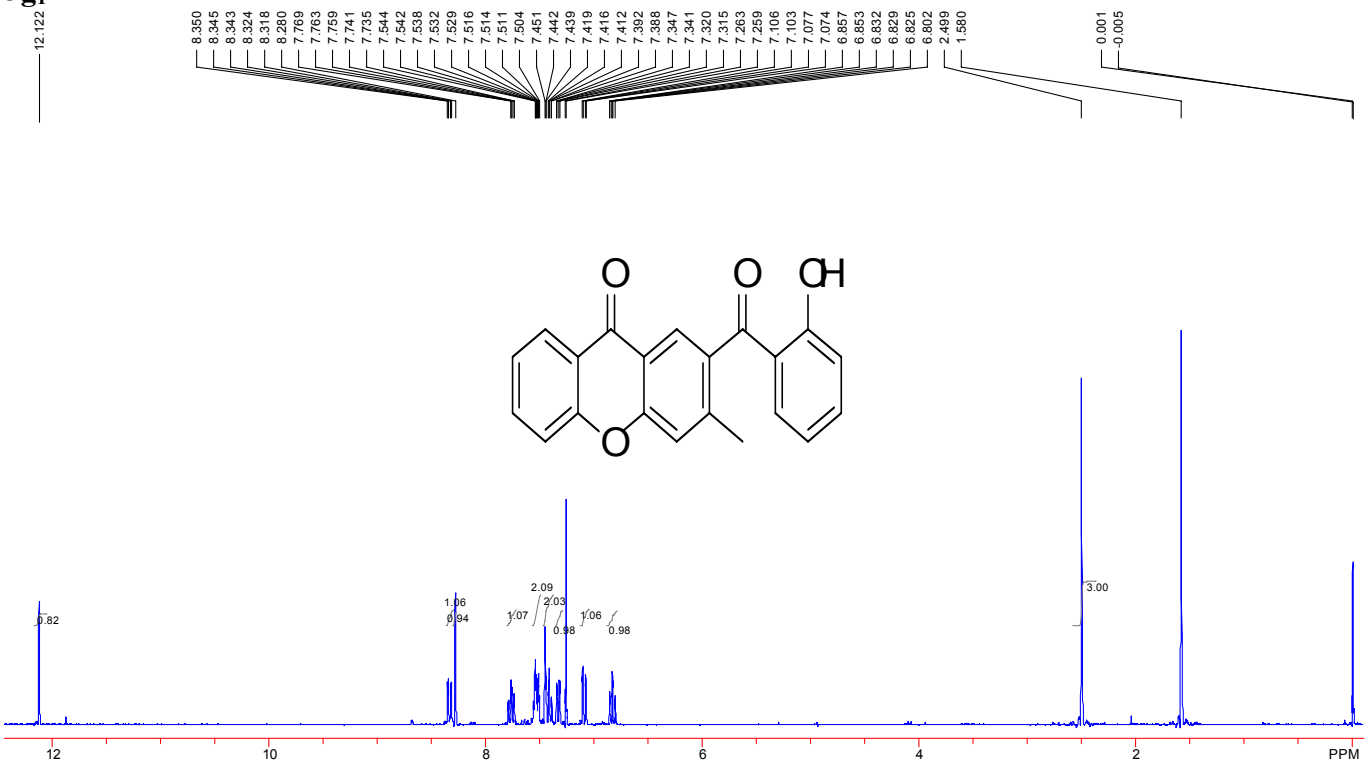

xF7-118C CDCL3 BB+DEPT-135 Aug 11 2009
O
O
OH
200
180
160
140
120
100
80
60
40
ppm

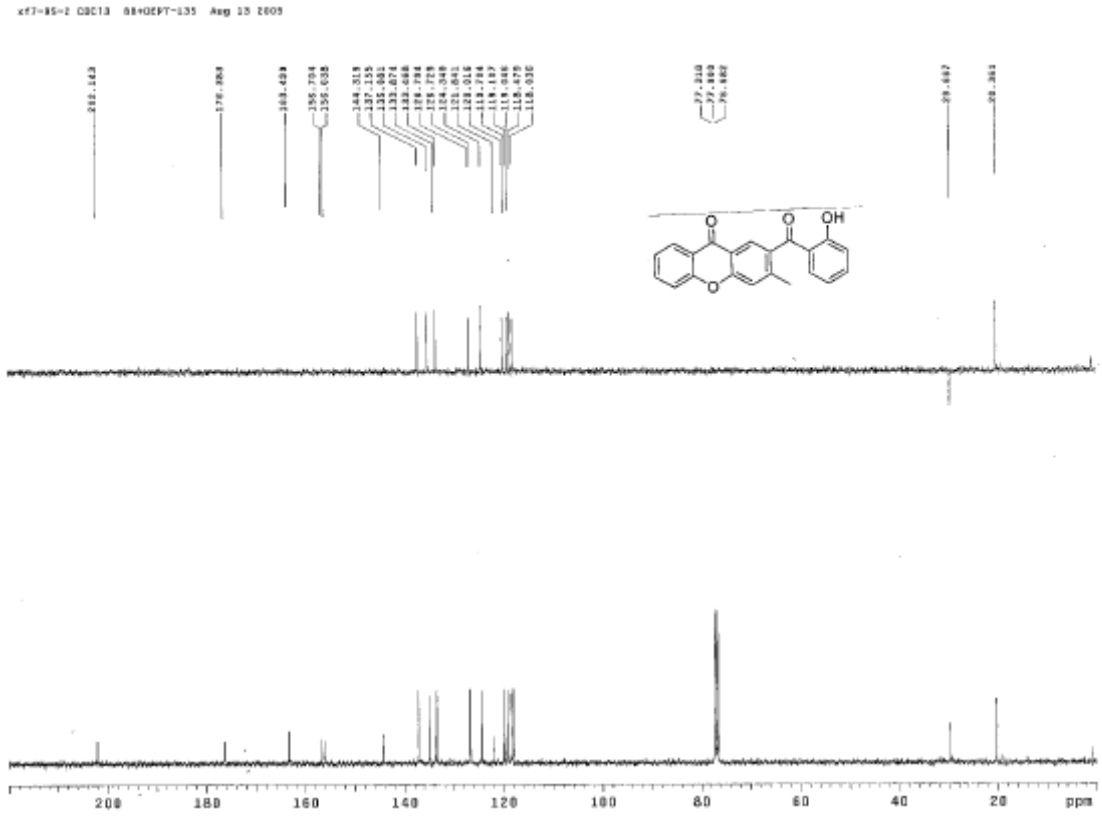
2g


8.474
8.345
8.320
7.814
7.786
7.743
7.719
7.514
7.486
7.470
7.442
7.427
7.400
7.377
7.260
3.134
1.585
-0.003
O
O
1.03
1.02
2.10
3.11
1.00
8
6
4
2
PPM

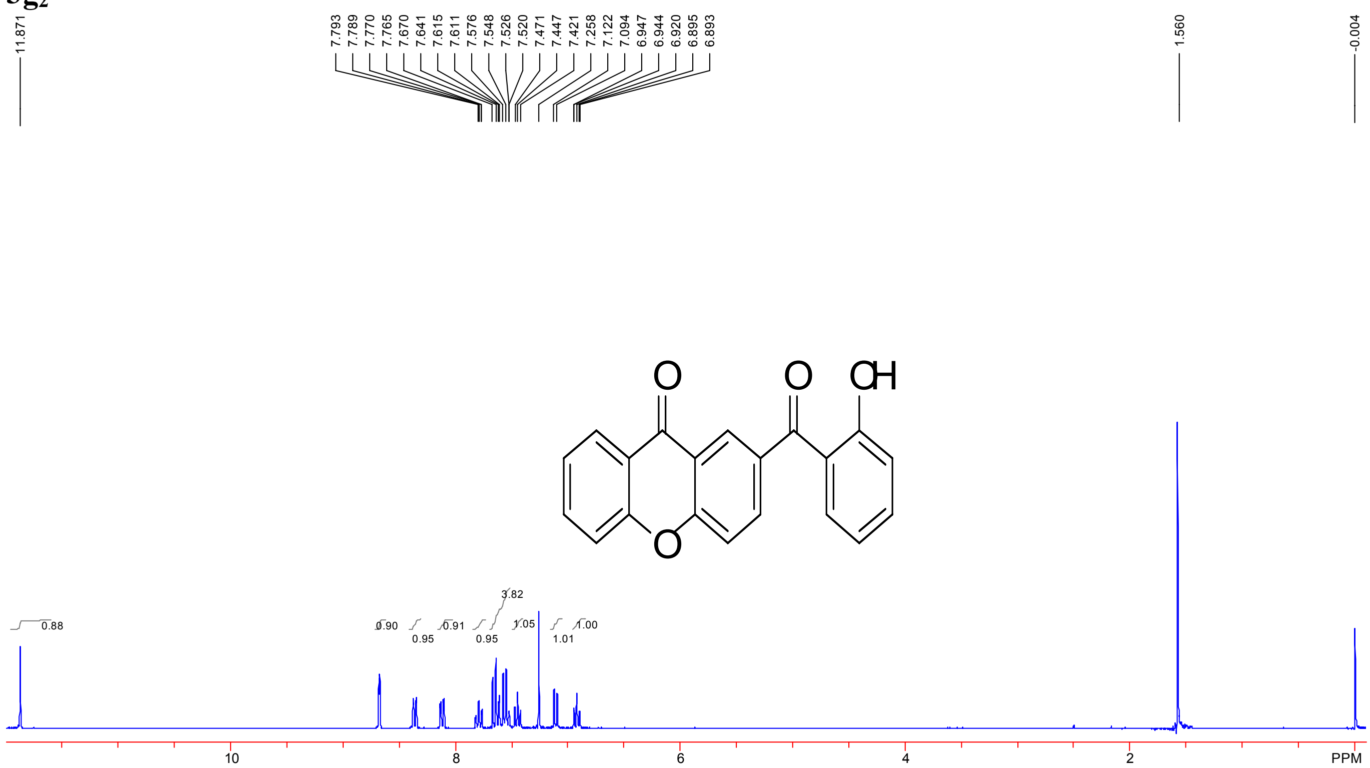

180
160
140
120
100
80
60
40
20
ppm

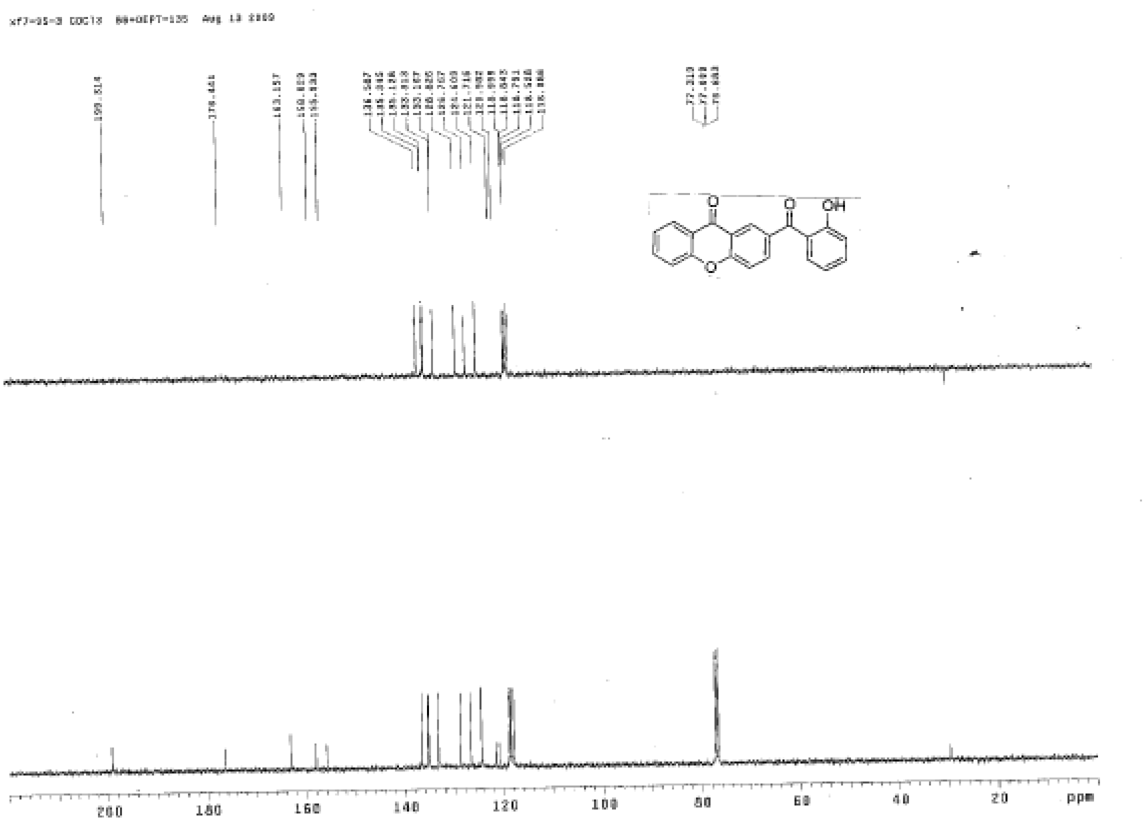
3g1


12.122
8.350
8.345
8.343
8.324
8.318
8.280
7.769
7.763
7.759
7.741
7.735
7.544
7.542
7.538
7.532
7.529
7.516
7.514
7.511
7.504
7.451
7.442
7.439
7.419
7.416
7.412
7.392
7.388
7.347
7.341
7.320
7.315
7.263
7.259
7.106
7.103
7.077
7.074
6.857
6.853
6.832
6.829
6.825
6.802
2.499
1.580
0.001
-0.005
O
O
OH
O
0.82
1.06
0.94
1.07
2.09
2.03
0.98
1.06
0.98
3.00
12
10
8
6
4
2
PPM

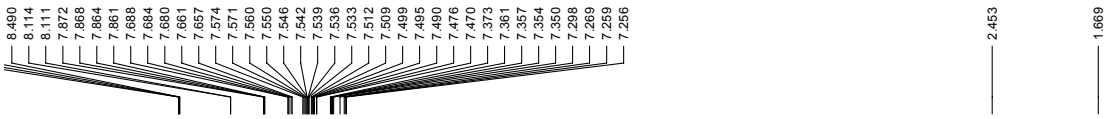

xf7-85-2 CDCl3 BB+DEPT-135 Aug 15 2005
O
O
OH
200
180
160
140
120
100
80
60
40
20
ppm

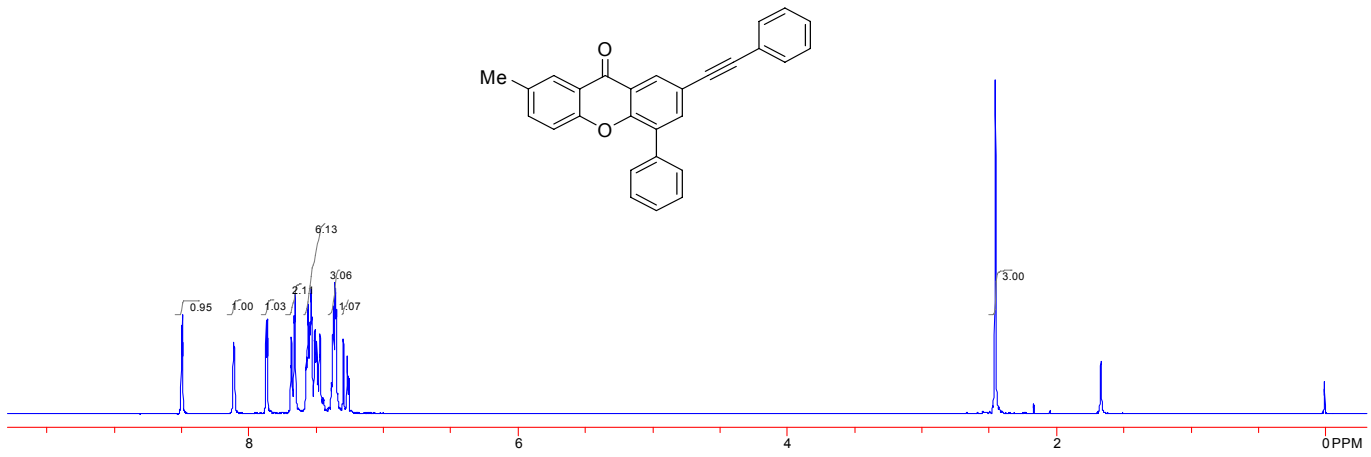
3g$_2$

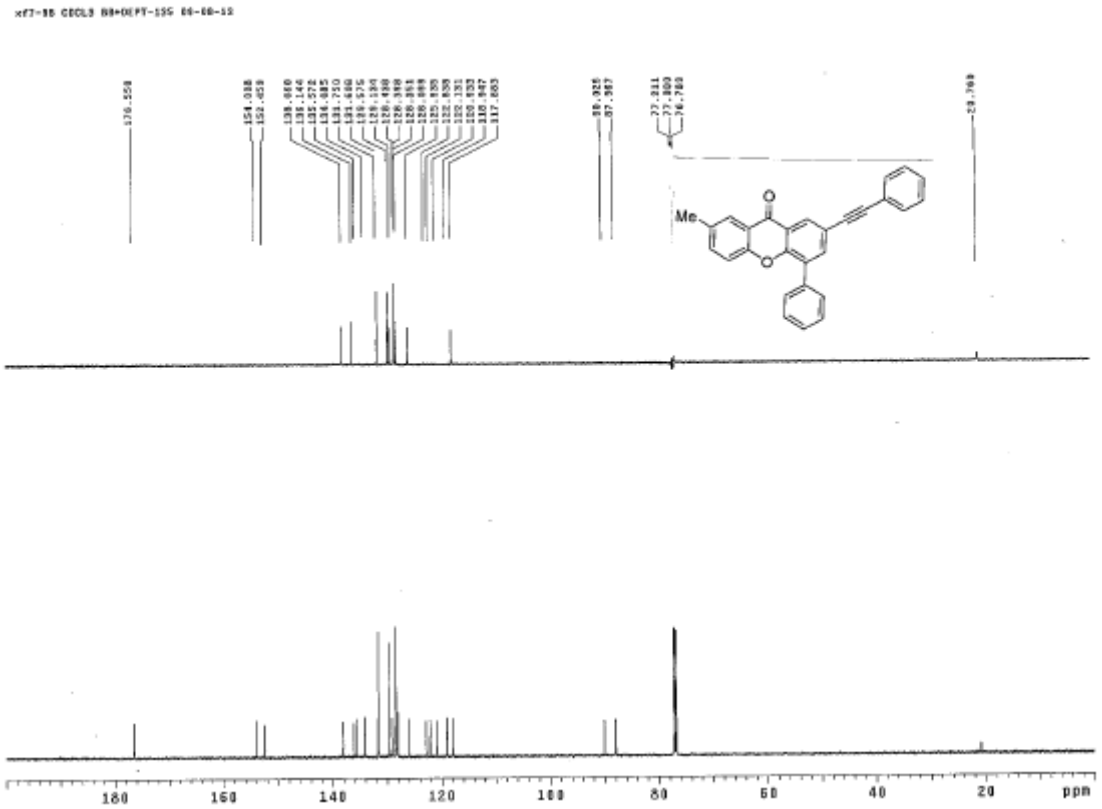

11.871
7.793
7.789
7.770
7.765
7.670
7.641
7.615
7.611
7.576
7.548
7.526
7.520
7.471
7.447
7.421
7.258
7.122
7.094
6.947
6.944
6.920
6.895
6.893
1.560
-0.004
O
O
OH
O
0.88
0.90
0.95
0.91
0.95
3.82
1.05
1.01
1.00
10
8
6
4
2
PPM


200
180
160
140
120
100
80
60
40
20
ppm

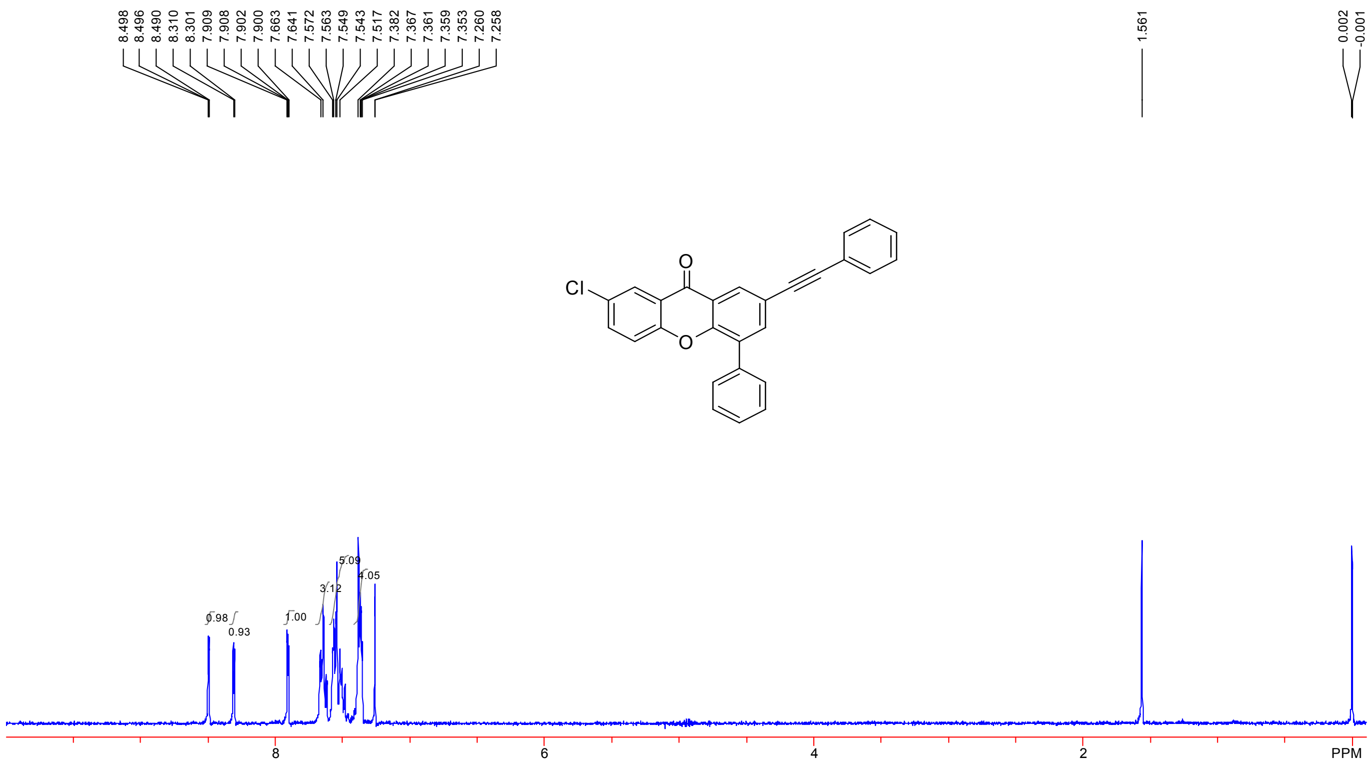
2h

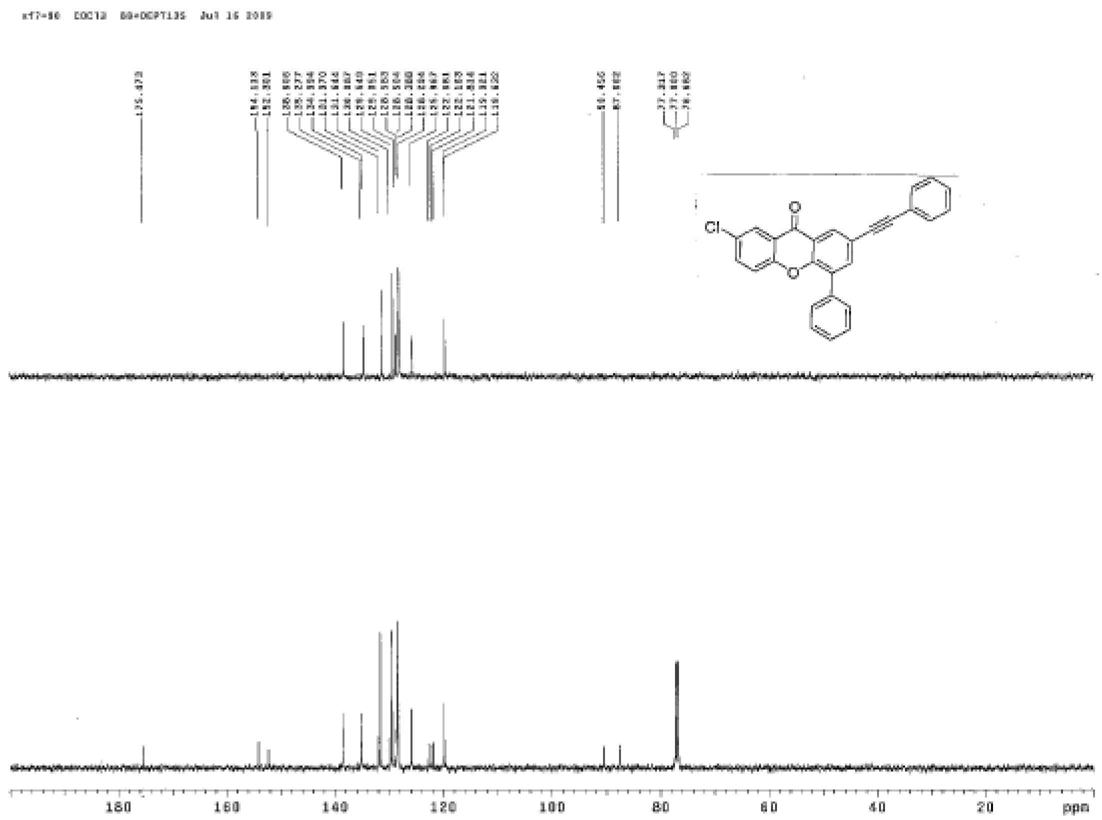

8.490
8.114
8.111
7.872
7.868
7.864
7.861
7.688
7.684
7.680
7.661
7.657
7.574
7.571
7.560
7.550
7.546
7.542
7.539
7.536
7.533
7.512
7.509
7.499
7.495
7.490
7.476
7.470
7.373
7.361
7.357
7.354
7.350
7.298
7.269
7.259
7.256
2.453
1.669


Me
O
O
6.13
3.06
2.11
0.95
1.00
1.03
1.07
3.00
8
6
4
2
0 PPM

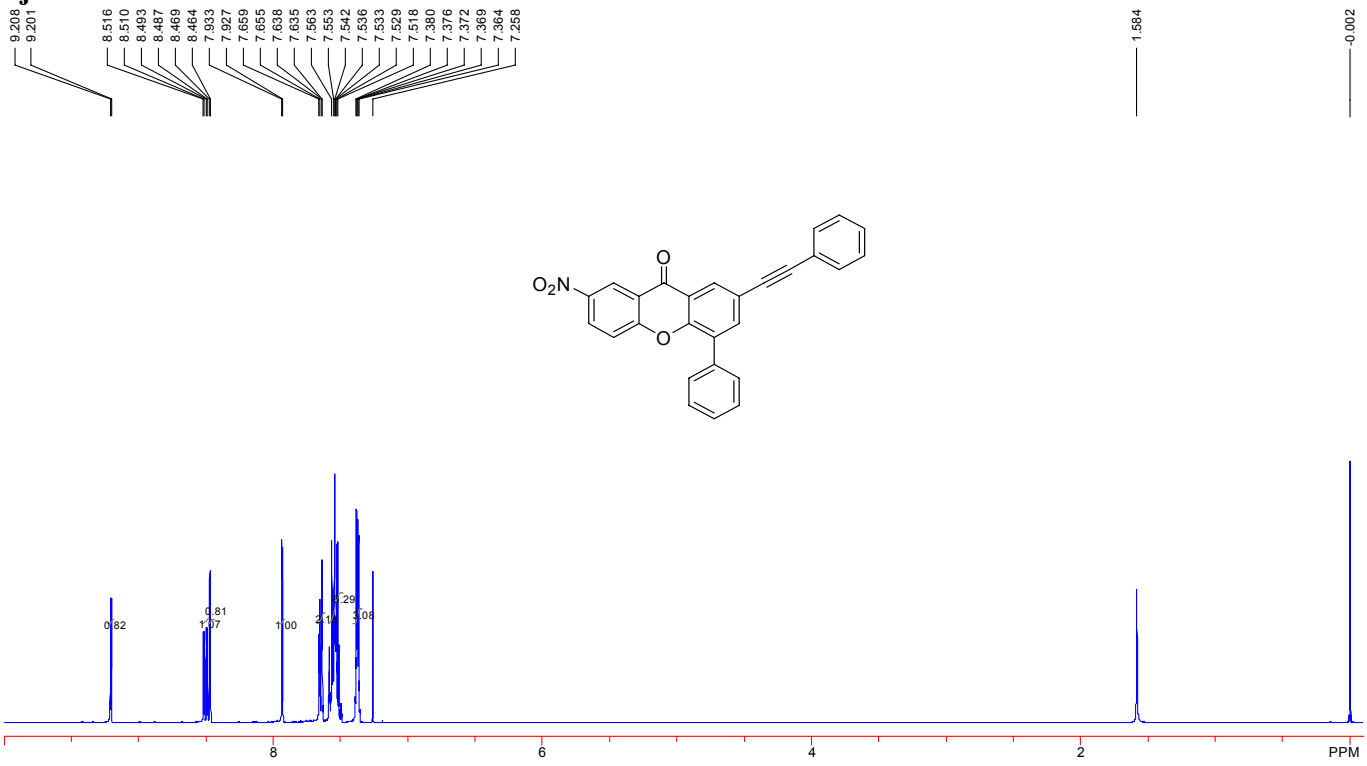

Me
180
160
140
120
100
80
60
40
20
ppm

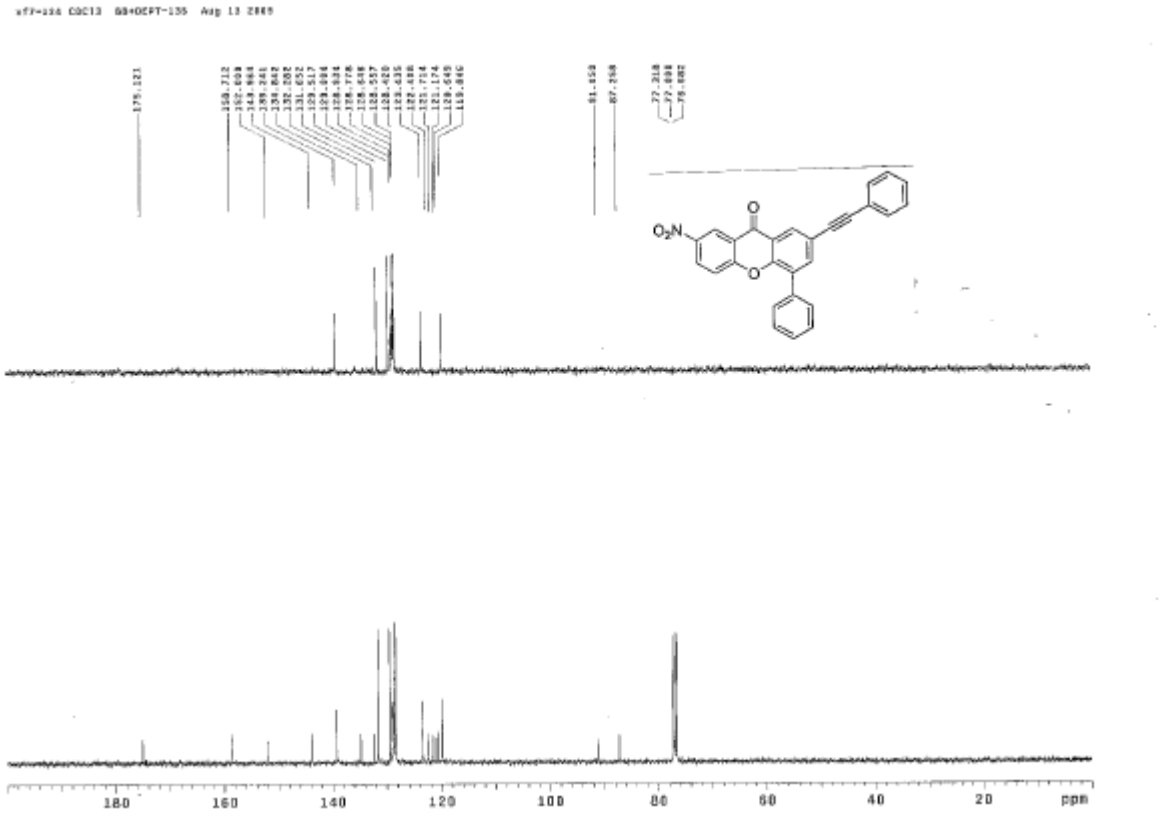
2i


8.498
8.496
8.490
8.310
8.301
7.909
7.908
7.902
7.900
7.663
7.641
7.572
7.563
7.549
7.543
7.517
7.382
7.367
7.361
7.359
7.353
7.260
7.258
1.561
0.002
-0.001
Cl
O
O
0.98
0.93
1.00
3.12
5.09
4.05
8
6
4
2
PPM

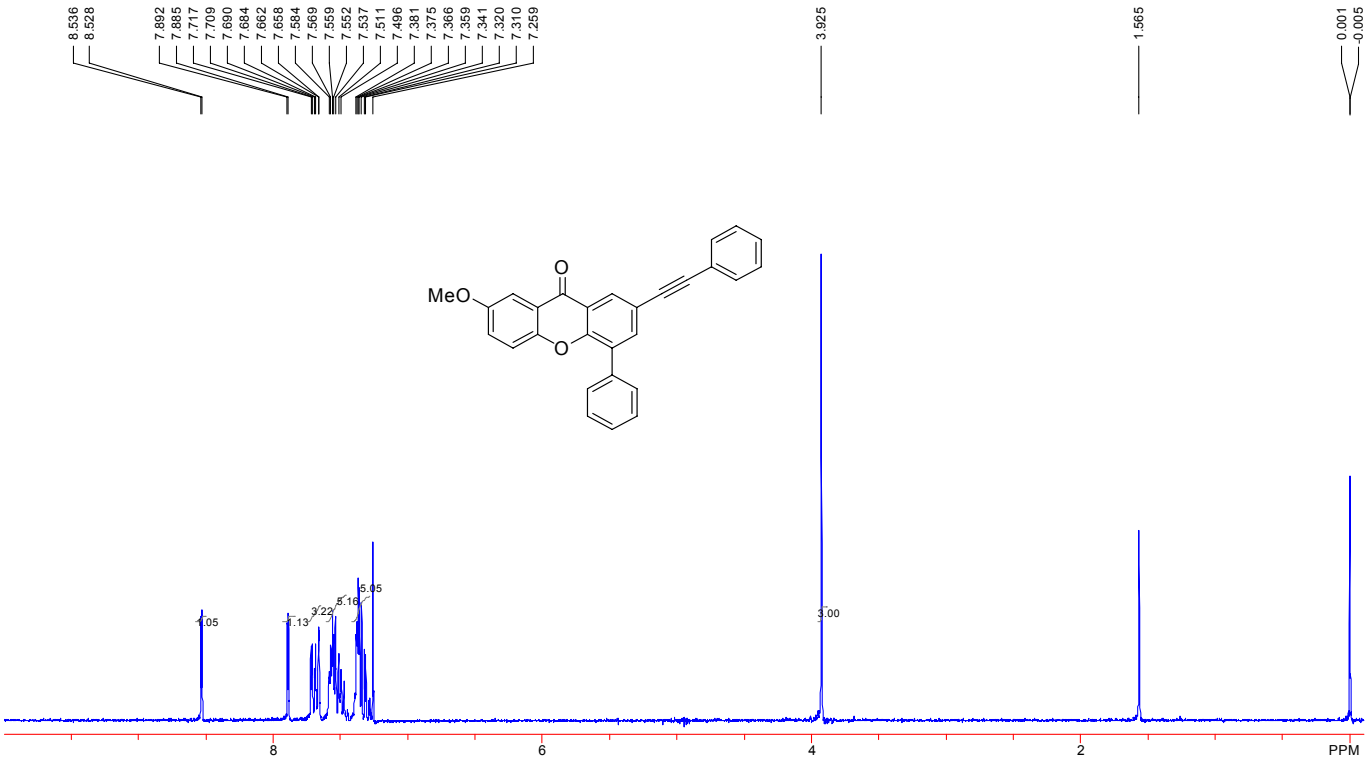

Cl
O
O
180
160
140
120
100
80
60
40
20
ppm

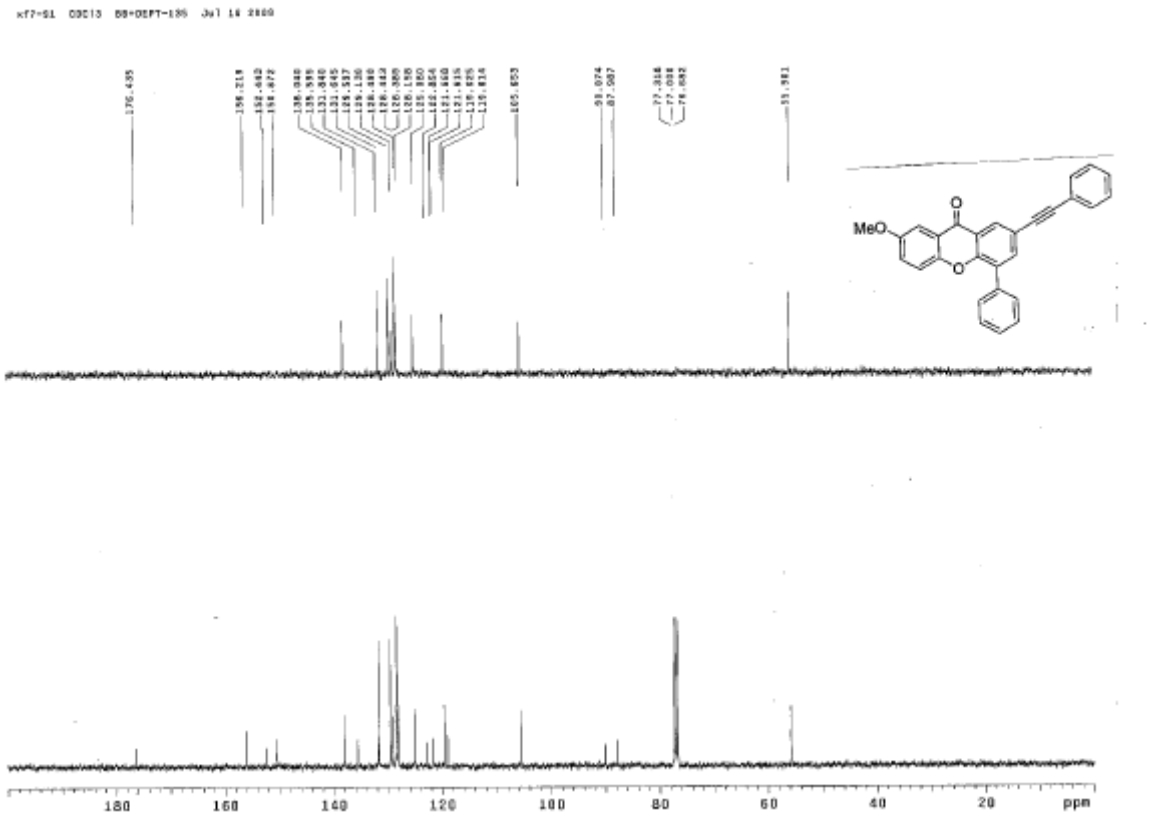
2j


9.208
9.201
8.516
8.510
8.493
8.487
8.469
8.464
7.933
7.927
7.659
7.655
7.638
7.635
7.563
7.553
7.542
7.536
7.533
7.529
7.518
7.380
7.376
7.372
7.369
7.364
7.258
1.584
-0.002
O2N
O
O
0.82
0.81
1.07
1.00
2.14
6.29
3.08
8
6
4
2
PPM

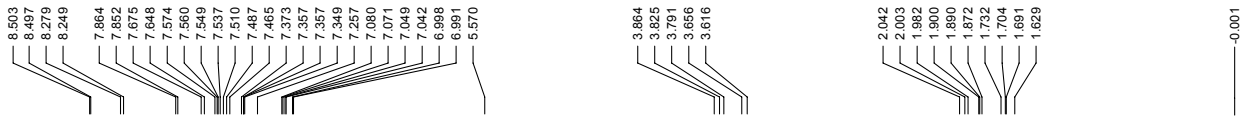

O2N
O
O
ppm

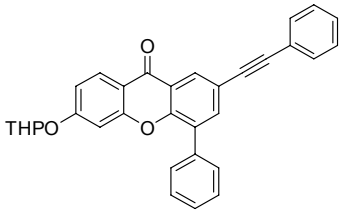
2k

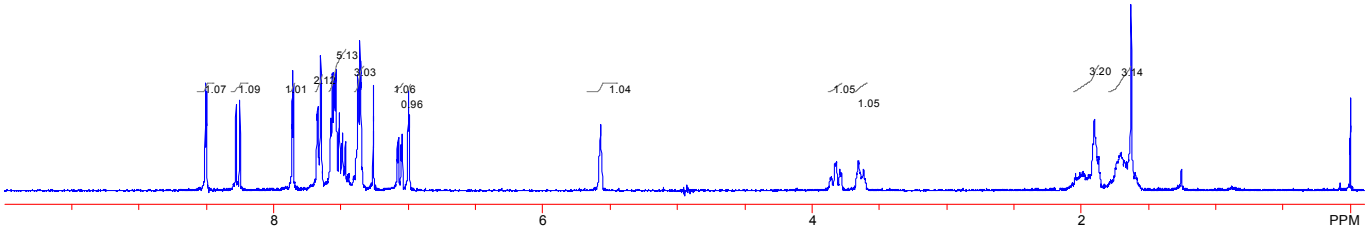

8.536
8.528
7.892
7.885
7.717
7.709
7.690
7.684
7.662
7.658
7.584
7.569
7.559
7.552
7.537
7.511
7.496
7.381
7.375
7.366
7.359
7.341
7.320
7.310
7.259
3.925
1.565
0.001
-0.005
MeO
O
O
1.05
1.13
3.22
5.16
5.05
3.00
8
6
4
2
PPM

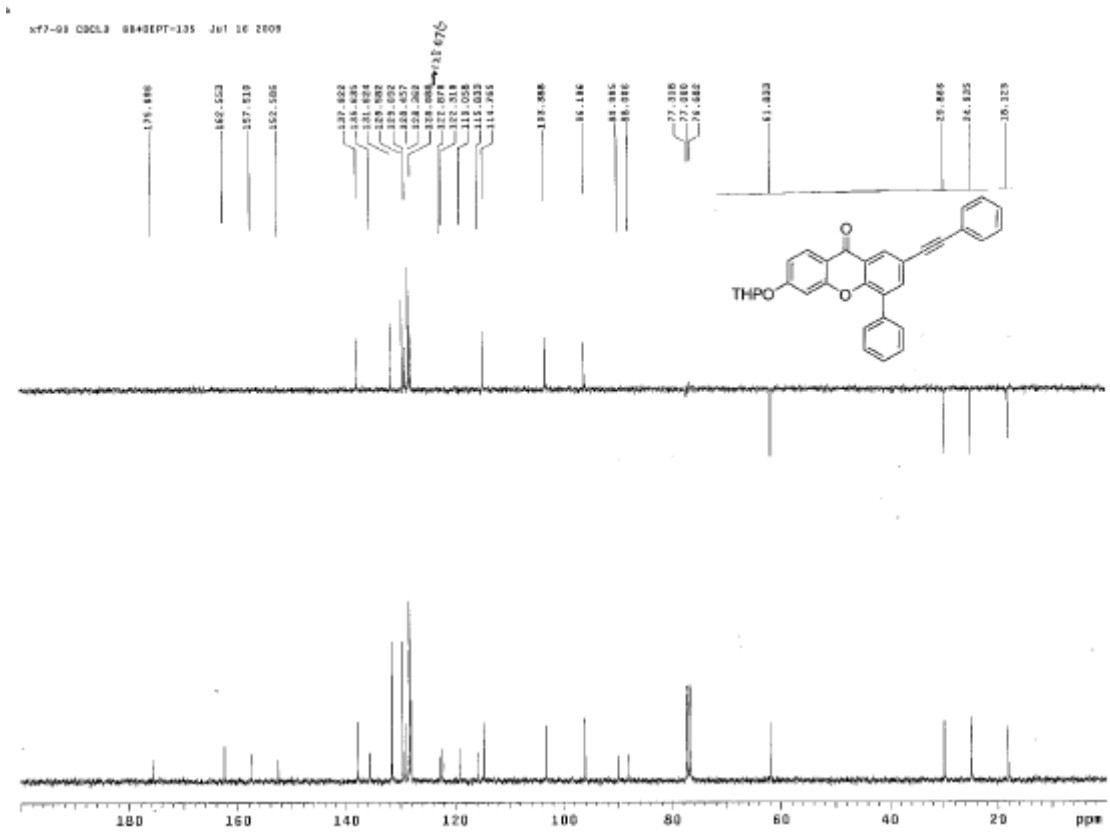

MeO
O
O
180
160
140
120
100
80
60
40
20
ppm

2l

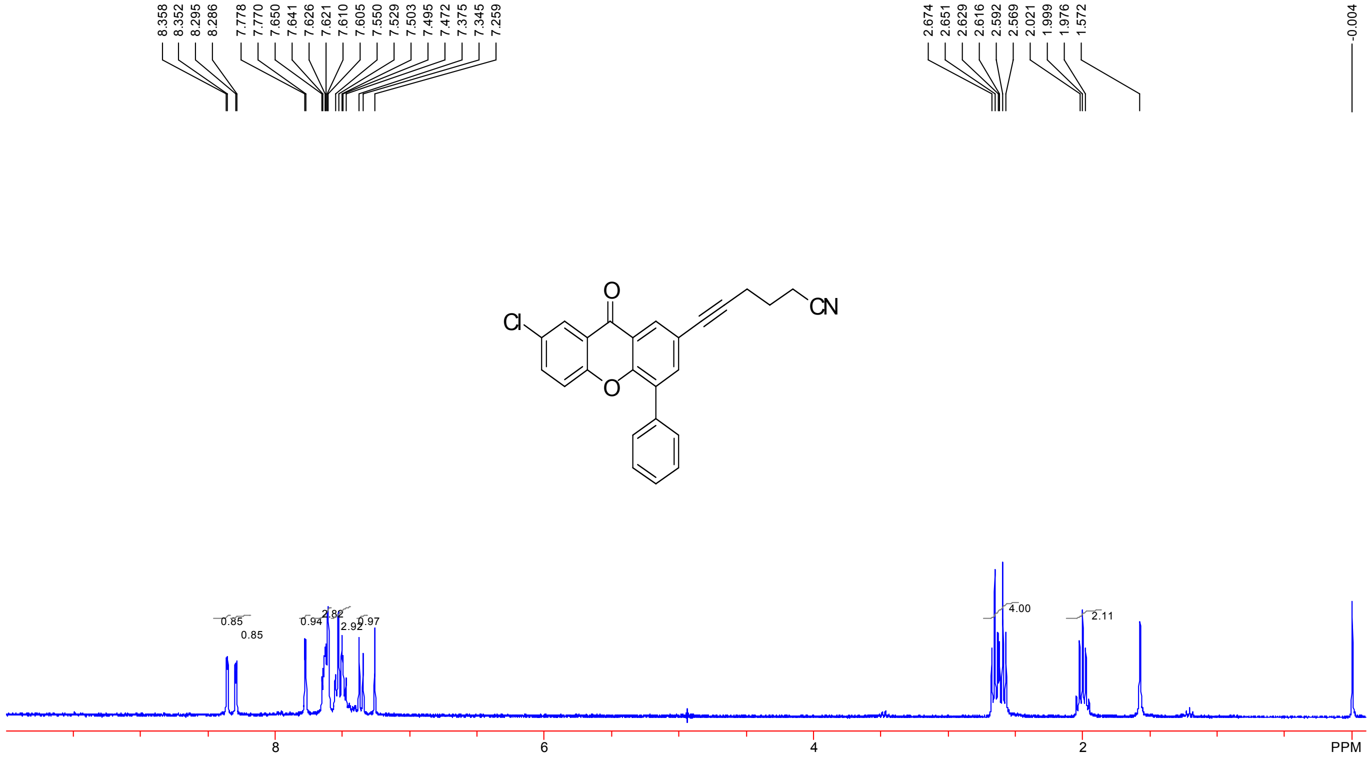

8.503
8.497
8.279
8.249
7.864
7.852
7.675
7.648
7.574
7.560
7.549
7.537
7.510
7.487
7.465
7.373
7.357
7.357
7.349
7.257
7.080
7.071
7.049
7.042
6.998
6.991
5.570
3.864
3.825
3.791
3.656
3.616
2.042
2.003
1.982
1.900
1.890
1.872
1.732
1.704
1.691
1.629
0.001

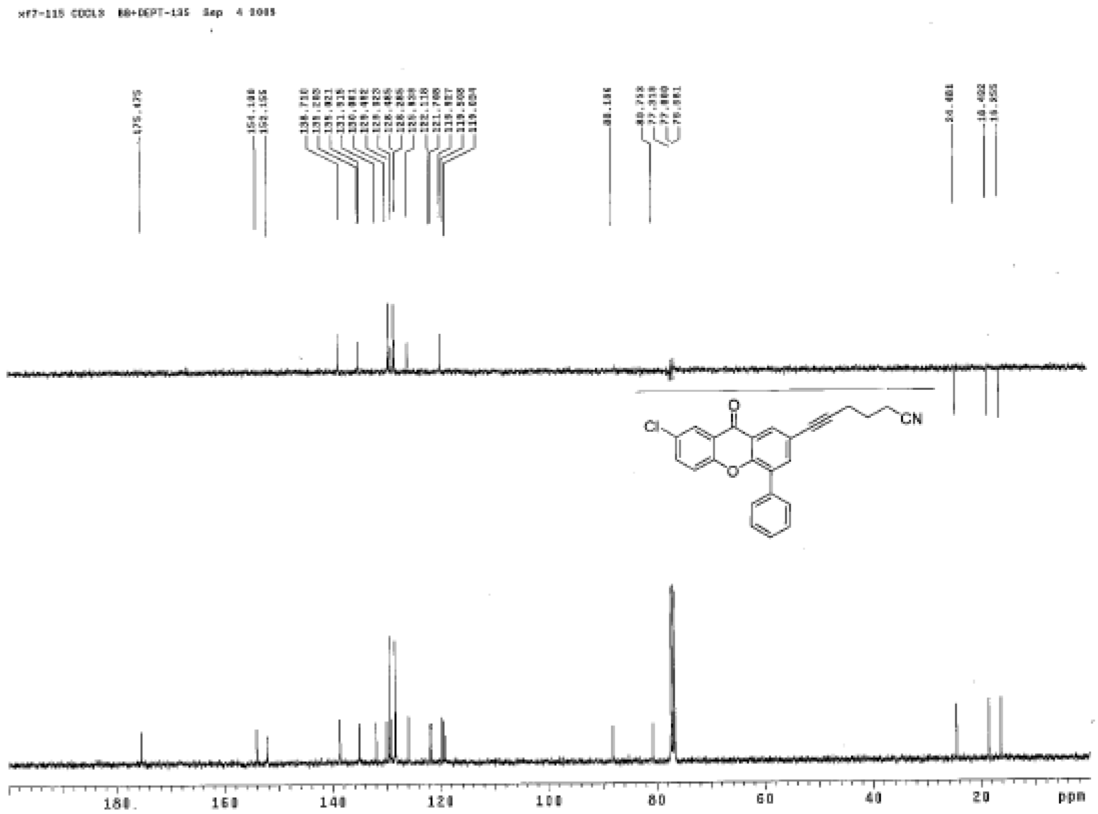

O
THPO
O


5.07
1.09
1.01
2.12
5.13
3.03
1.06
0.96
1.04
1.05
1.05
3.20
3.14
8
6
4
2
PPM

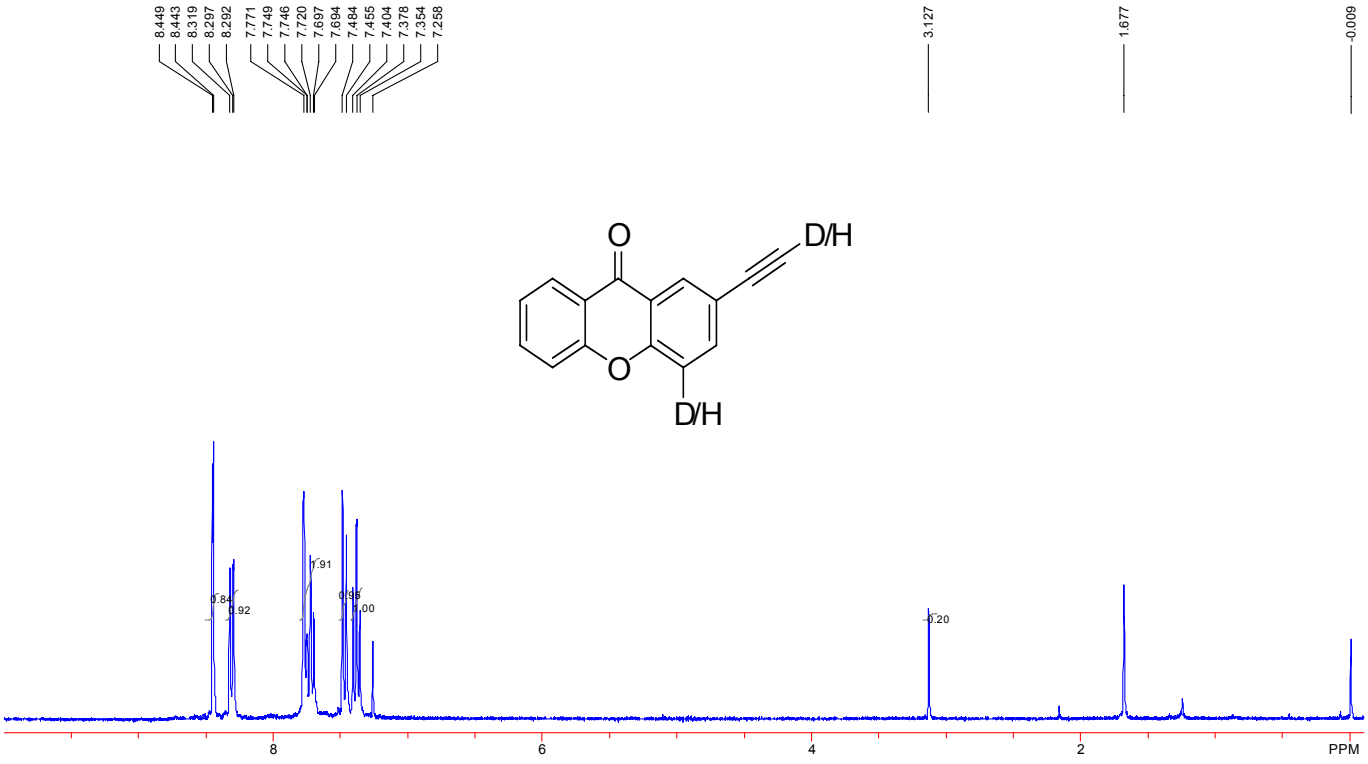

THPO
O
O
180
160
140
120
100
80
60
40
20
ppm

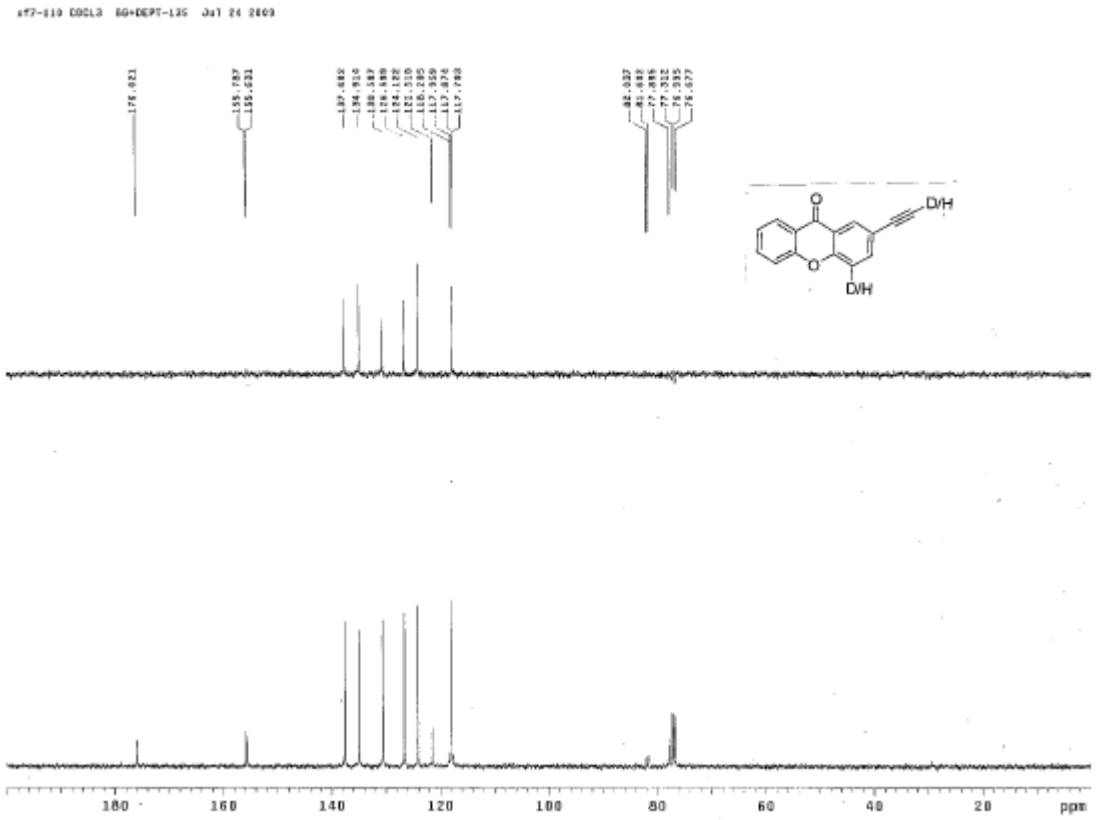
2id


8.358
8.352
8.295
8.286
7.778
7.770
7.650
7.641
7.626
7.621
7.610
7.605
7.550
7.529
7.503
7.495
7.472
7.375
7.345
7.259
2.674
2.651
2.629
2.616
2.592
2.569
2.021
1.999
1.976
1.572
-0.004
Cl
O
O
CN
0.85
0.85
0.94
2.82
2.92
0.97
4.00
2.11
8
6
4
2
PPM

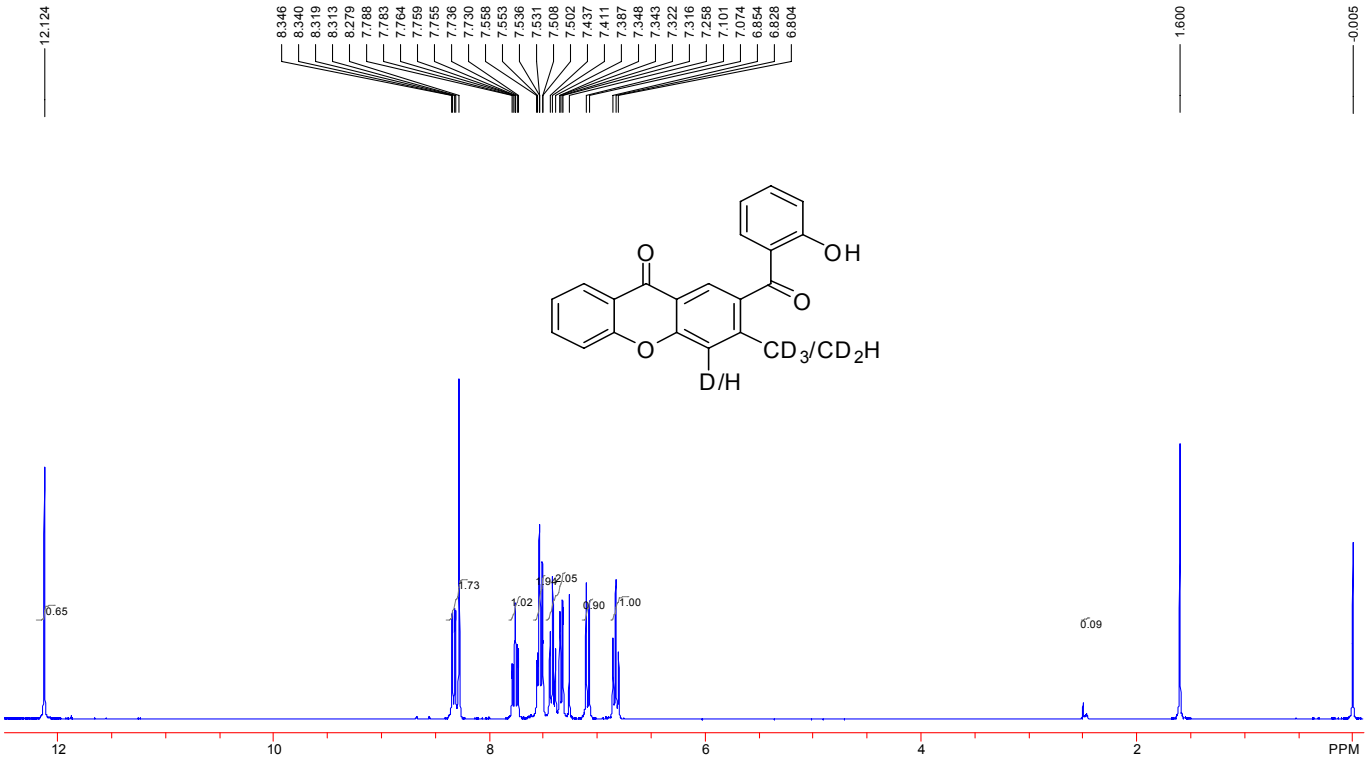

Cl
O
O
CN
180
160
140
120
100
80
60
40
20
ppm

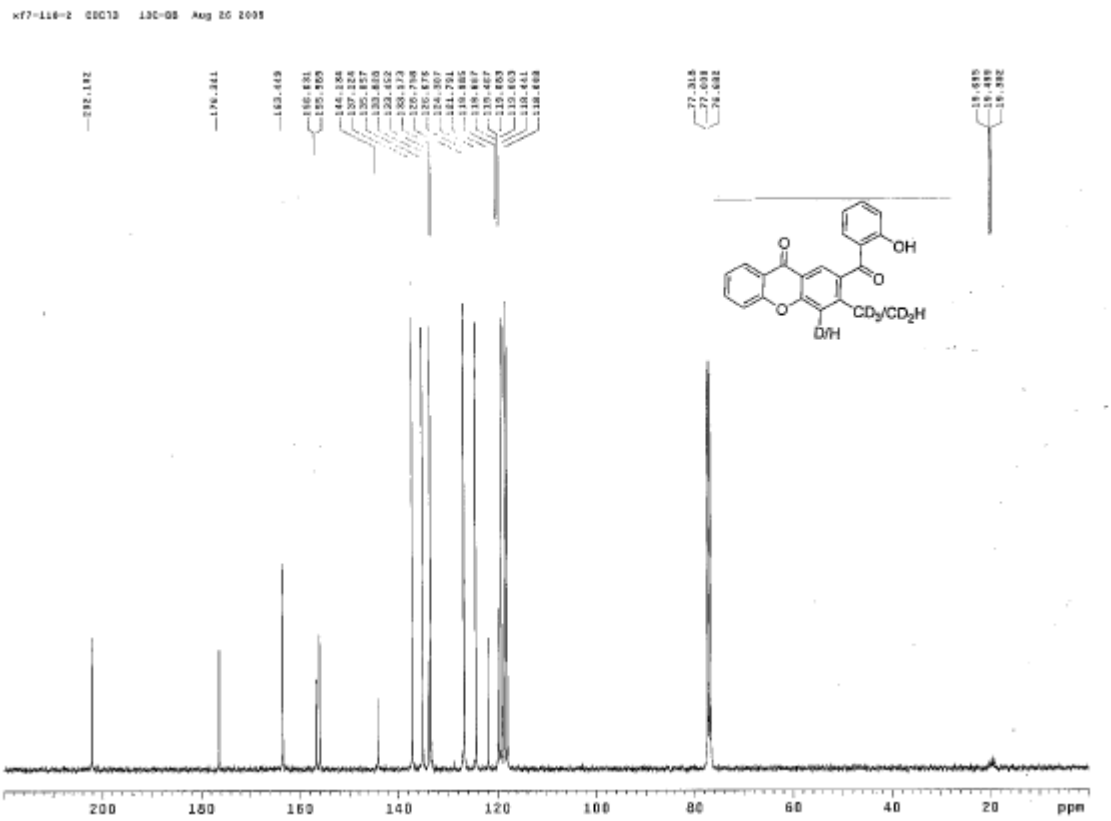
[D] 2g


8.449
8.443
8.319
8.297
8.292
7.771
7.749
7.746
7.720
7.697
7.694
7.484
7.455
7.404
7.378
7.354
7.258
3.127
1.677
0.009
O
D/H
O
D/H
7.91
0.84
0.92
0.95
1.00
0.20
8
6
4
2
PPM

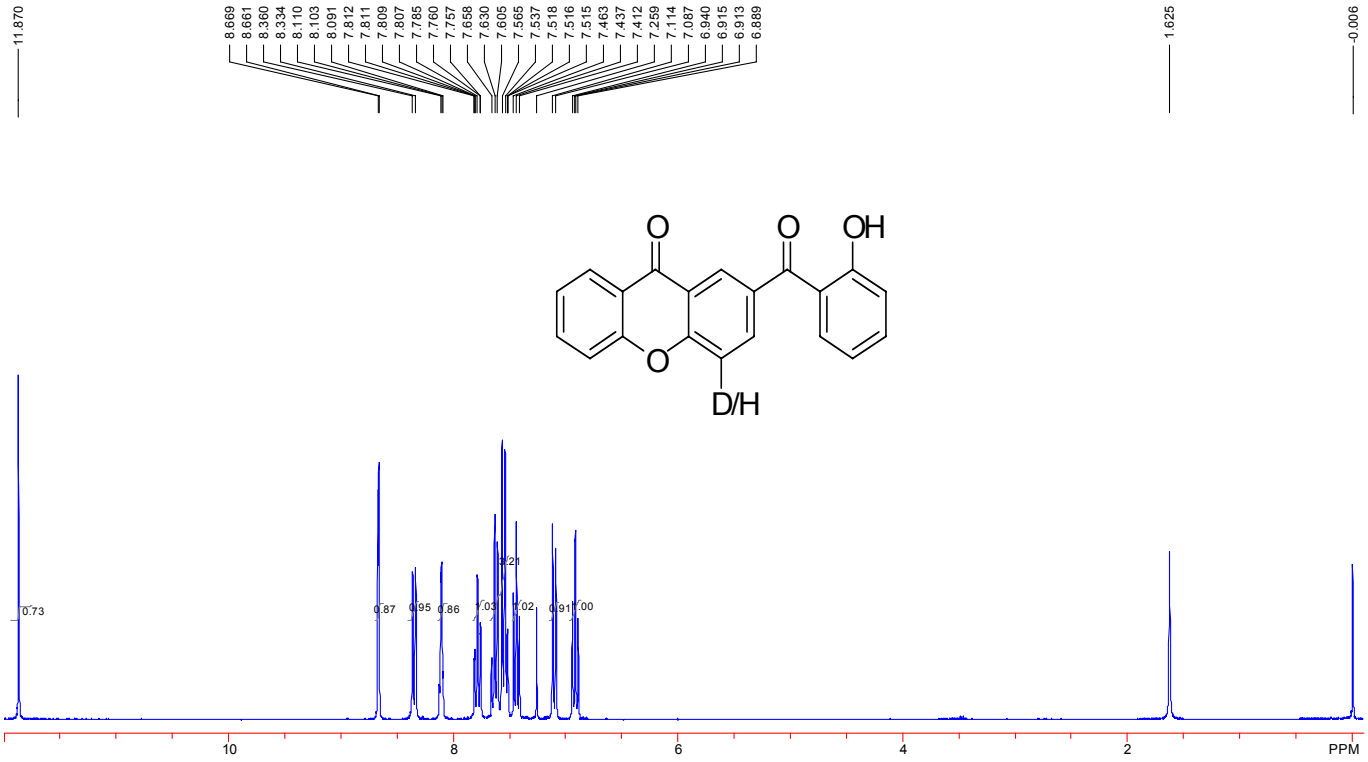

O
D/H
O
D/H
180
160
140
120
100
80
60
40
20
ppm

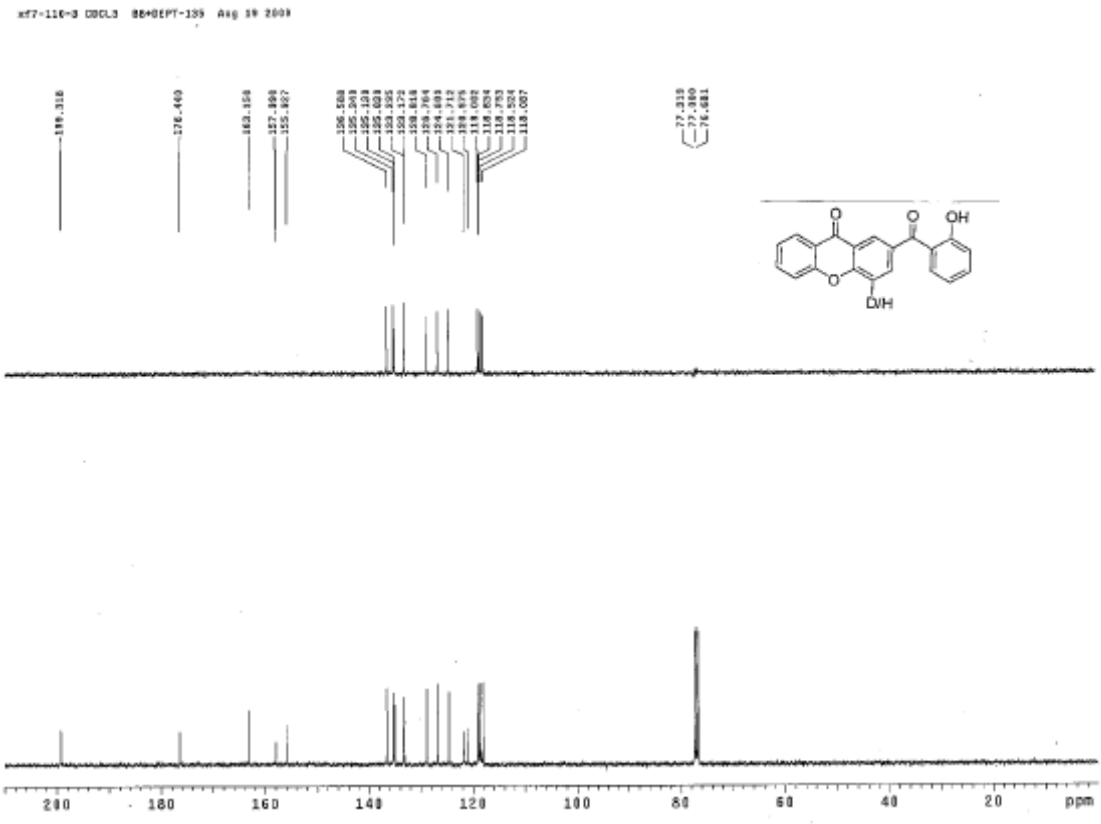
[D] $3g_1$


12.124
8.346
8.340
8.319
8.313
8.279
7.788
7.783
7.764
7.759
7.755
7.736
7.730
7.558
7.553
7.536
7.531
7.508
7.502
7.437
7.411
7.387
7.348
7.343
7.322
7.316
7.258
7.101
7.074
6.854
6.828
6.804
1.600
0.005
OH
O
O
O
CD3/CD2H
D/H
0.65
1.73
1.02
0.92
2.05
0.90
1.00
0.09
12
10
8
6
4
2
PPM

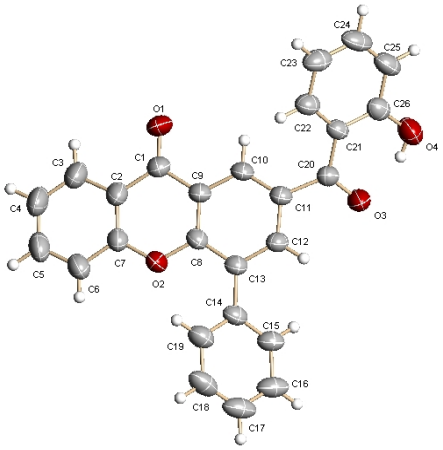

OH
O
O
O
CD3/CD2H
D/H
200
180
160
140
120
100
80
60
40
20
ppm

[D] $3g_2$

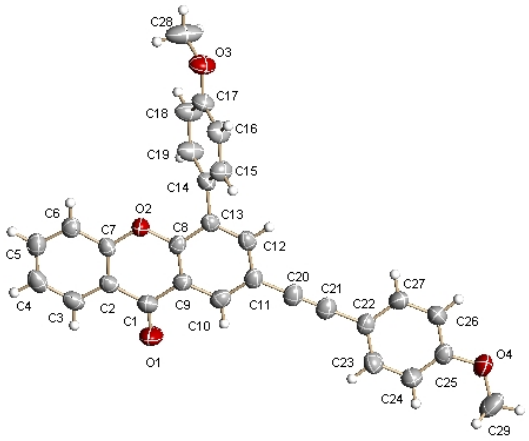

11.870
8.669
8.661
8.360
8.334
8.110
8.103
8.091
7.812
7.811
7.809
7.807
7.785
7.760
7.757
7.658
7.630
7.605
7.565
7.537
7.518
7.516
7.515
7.463
7.437
7.412
7.259
7.114
7.087
6.940
6.915
6.913
6.889
1.625
0.006
O
O
OH
O
D/H
0.73
0.87
0.95
0.86
1.03
2.21
1.02
0.91
1.00
10
8
6
4
2
PPM



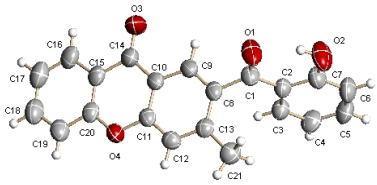
4, X-ray crystal structure of 3a, 2b and $3g_1$



ORTEP plot of **3a** shown with ellipsoids at the 50%



ORTEP plot of **2b** shown with ellipsoids at the 50%



ORTEP plot of **3g$_1$** shown with ellipsoids at the 50%