Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of Novel Functional Polycyclic Chromones through Michael Addition and Double Cyclizations

Yang Liu, Liping Huang, Fuchun Xie, Xuxing Chen 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

Supporting Information

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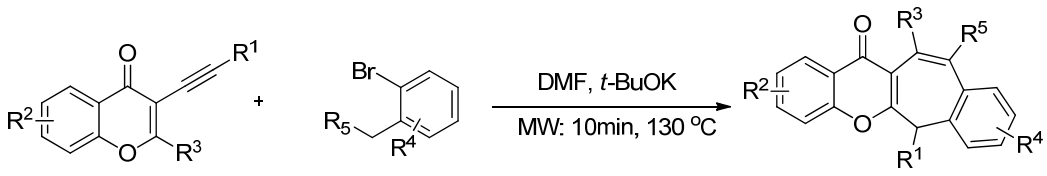
1. Experiment procedures

All reactions were performed under nitrogen atmosphere. Dry solvents were distilled prior to use: DMF was dried over microwave-dried molecular sieve; 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 $CDCl_3$ or d_6-DMSO 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 was uncorrected.

General Procedure:

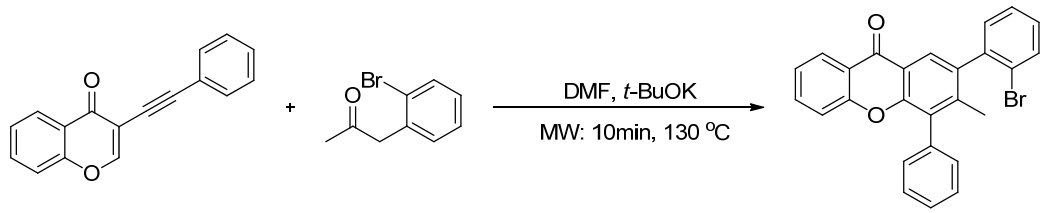
1.1 Tandem reaction of 3-(1-Alkynyl)chromones and 2-(2-bromophenyl)acetonitrile compounds to novel functional polycyclic chromenones 3



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

A typical procedure for the preparation of 3**aa**: To a solution of 2-(2-bromophenyl)acetonitrile **2aa** (40 mg, 0.2 mmol) in dry DMF (1 mL) was added *t*-BuOK (24 mg, 0.2 mmol) at room temperature under nitrogen atmosphere. After stirring for 5 min, compound **1a** (50 mg, 0.2 mmol) was added and the resulting dark red solution was irradiated for 10 min at 130 °C (monitored by TLC). The mixture was extracted with ethyl acetate (10 mL×3). 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 6:1) to afford compound **3aa** as a white solid.

1.2 Tandem reaction of 1a with 2g to Xanthone 4b



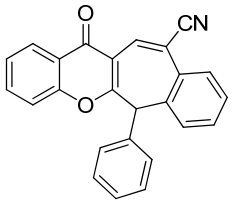
1a **2g** **4b 91%**

To a solution of 1-(2-bromophenyl)propan-2-one **2g** (44 mg, 0.2 mmol) in dry DMF (1 mL) was added *t*-BuOK (24 mg, 0.2 mmol) at room temperature under nitrogen atmosphere. After stirring for 5 min, compound **1a** (50 mg, 0.2 mmol) was added and the resulting dark red solution was irradiated for 10 min at 130 °C (monitored by TLC). The mixture was extracted with ethyl acetate (10 mL×3). 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 10:1) to afford compound **4b** as a white solid.

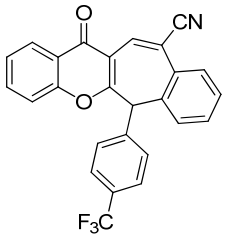
2. Characterization Data:

2.1 3aa-3ma



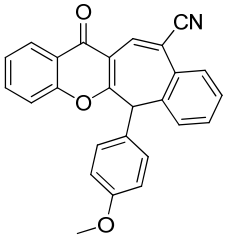
13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3aa)

As a white solid: m.p. 235-236 ^oC; IR (KBr) ν_{max} 3429, 3053, 2212, 1651, 1620, 1570, 1464, 1400, 1365, 1217, 1167, 764, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.27 (dd, *J* = 1.8, 7.9 Hz, 1H), 7.91 (dd, *J* = 1.4, 7.4 Hz, 1H), 7.70-7.79 (m, 2H), 7.44-7.67 (m, 5H), 7.12-7.21 (m, 3H), 6.70-6.77 (m, 2H), 5.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.8, 166.0, 155.9, 136.2, 135.8, 134.3, 133.9, 131.2, 131.1, 128.9, 128.6, 128.3, 127.6, 126.4, 126.3, 126.1, 122.6, 118.8, 118.1, 116.1, 114.9, 55.0. HRMS $[M]^+$ Calculated for $C_{25}H_{15}NO_2$ 361.1103, found 361.1106.



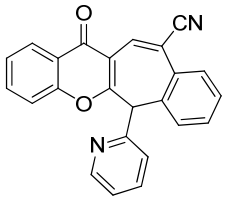
13-oxo-6-(4-(trifluoromethyl)phenyl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ba)

As a white solid: m.p. 225-226 ^oC; IR (KBr) ν_{max} 3425, 3041, 2216, 1657, 1620, 1570, 1466, 1400, 1327, 1217, 1180, 1130, 1016, 941, 845, 766, 492 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.27 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.94 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.74-7.80 (m, 2H), 7.67 (td, *J* = 1.5, 7.4 Hz, 1H), 7.53-7.62 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 5.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 164.8, 155.8, 140.0, 135.4, 134.5, 133.9, 131.5, 131.1, 131.0, 130.1, 129.8, 129.1, 129.0, 126.7, 126.5, 126.3, 125.3, 125.1, 122.5, 122.4, 118.5, 118.1, 116.2, 115.0, 54.7. HRMS $[M]^+$ Calculated for $C_{26}H_{14}F_3NO_2$ 429.0977, found 429.0973.



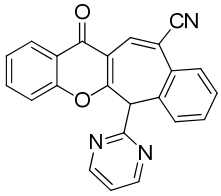
6-(4-methoxyphenyl)-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ca)

As a white solid: m.p. 244-245 ^{o}C; IR (KBr) ν_{max} 3432, 3037, 2926, 2829, 2218, 1645, 1566, 1510, 1464, 1400, 1254, 1178, 1038, 939, 835, 768, 669, 517 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.72-7.78 (m, 2H), 7.45-7.64 (m, 5H), 7.63-7.73 (m, 4H), 5.45 (s, 1H), 3.74 (s, 1H). ^{13}C NMR (100 MHz, CDCl3) δ: 175.8, 166.3, 158.8, 155.8, 136.5, 134.3, 133.9, 131.2, 131.0, 130.9, 128.8, 128.5, 127.6, 127.4, 126.4, 126.1, 122.5, 118.9, 118.1, 115.9, 114.9, 113.6, 55.1, 54.3. HRMS $[M]^+$ Calculated for $C_{26}H_{17}NO_3$ 391.1208, found 391.1204.



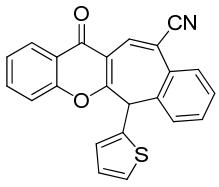
13-oxo-6-(pyridin-2-yl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3da)

As a light brown solid: m.p. 215-216 ^{o}C; IR (KBr) ν_{max} 3425, 3036, 2924, 2218, 1720, 1651, 1568, 1466, 1400, 1223, 1175, 995, 908, 770, 673 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 4.1 Hz, 1H), 8.25 (dd, *J* = 1.7, 8.0 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.66-7.77 (m, 2H), 7.54-7.65 (m, 4H), 7.43-7.52 (m, 2H), 7.11 (dd, *J* = 4.7, 7.4 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0, 165.9, 156.1, 156.0, 149.0, 136.3, 135.4, 134.6, 134.1, 131.2, 131.1, 128.7, 126.2, 125.9, 122.6, 122.4, 121.1, 118.7, 118.2, 115.9, 114.1, 57.5. HRMS $[M]^+$ Calculated for $C_{24}H_{14}N_2O_2$ 362.1055, found 362.1057.



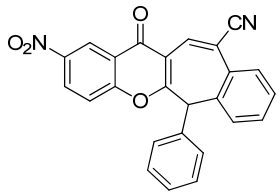
13-oxo-6-(pyrimidin-2-yl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ea)

As a light yellow solid: m.p. 221-222 ^{o}C; IR (KBr) ν_{max} 3431, 3037, 2222, 1641, 1562, 1464, 1402, 1213, 889, 770, 635 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.06 (s, 1H), 8.19-8.29 (m, 3H), 7.94 (dd, *J* = 1.0, 7.7 Hz, 1H), 7.73-7.82 (m, 2H), 7.67 (td, *J* = 1.4, 7.4 Hz, 1H), 7.56-7.63 (m, 3H), 7.50 (td, *J* = 1.0, 7.4 Hz, 1H), 5.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.2, 162.6, 158.1, 155.8, 154.8, 134.7, 133.9, 133.6, 131.9, 130.8, 129.7, 129.5, 129.4, 126.6, 126.5, 122.5, 118.0, 116.4, 115.3, 51.0. HRMS $[M]^+$ Calculated for $C_{23}H_{13}N_3O_2$ 363.1008, found 363.1003.



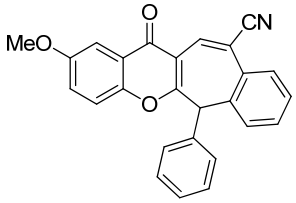
13-oxo-6-(thiophen-2-yl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3fa)

As a white solid: m.p. 208-209 ^{o}C; IR (KBr) ν_{max} 3425, 3041, 2922, 2216, 1649, 1620, 1562, 1485, 1402, 1223, 1020, 847, 764, 717 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.85 (s, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.42-7.65 (m, 5H), 7.12 (d, *J* = 5.2 Hz, 1H), 6.83 (t, *J* = 4.3 Hz, 1H), 6.50 (s, 1H), 5.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 155.8, 136.4, 134.4, 133.8, 131.3, 131.0, 130.2, 129.0, 128.9, 126.5, 126.4, 126.1, 124.9, 122.6, 118.8, 118.1, 116.1, 115.2, 51.5. HRMS $[M]^+$ Calculated for $C_{23}H_{13}NO_2S$ 367.0667, found 367.0662.



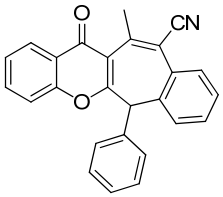
2-nitro-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ga)

As a light yellow solid: m.p. 277-278 ^{o}C; IR (KBr) ν_{max} 3431, 3088, 2220, 1655, 1529, 1452, 1344, 1254, 1221, 1161, 908, 839, 746, 677 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.13 (d, *J* = 2.8 Hz, 1H), 8.58 (dd, *J* = 2.9, 9.2 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 9.3 Hz, 1H), 7.63-7.70 (m, 2H), 7.56-7.62 (m, 1H), 7.54 (dd, *J* = 1.4, 7.4 Hz, 1H), 7.14-7.23 (m, 3H), 6.71-6.76 (m, 2H), 5.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 166.0, 158.6, 145.4, 136.1, 135.2, 132.5, 131.7, 131.1, 131.0, 129.2, 128.9, 128.6, 128.5, 127.9, 126.3, 123.1, 122.8, 120.0, 118.3, 116.5, 54.8. HRMS $[M]^+$ Calculated for $C_{25}H_{14}N_2O_4$ 406.0954, found 406.0953.



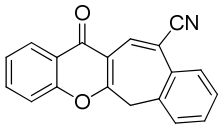
2-methoxy-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ha)

As a white solid: m.p. 267-268 ^{o}C; IR (KBr) ν_{max} 3425, 2935, 2220, 1649, 1485, 1394, 1296, 1207, 1032, 895, 825, 764, 708 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.91 (dd, *J* = 1.1, 7.7 Hz, 1H), 7.74 (s, 1H), 7.59-7.65 (m, 2H), 7.56 (dd, *J* = 1.7, 7.3 Hz, 1H), 7.32 (dd, *J* = 2.9, 8.9 Hz, 1H), 7.13-7.20 (m, 3H), 6.69-6.75 (m, 2H), 5.49 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 165.7, 157.5, 150.5, 136.1, 135.9, 134.1, 131.1, 131.0, 128.8, 128.5, 128.2, 127.5, 126.3, 124.2, 123.2, 119.5, 118.8, 115.3, 114.6, 56.0, 54.9. HRMS $[M]^+$ Calculated for $C_{26}H_{17}NO_3$ 391.1208, found 391.1201.



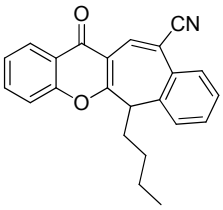
12-methyl-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ia)

As a white solid: m.p. 244-245 ^{o}C; IR (KBr) ν_{max} 3431, 3057, 2929, 2214, 1647, 1556, 1466, 1389, 1338, 1223, 1138, 1065, 764, 710, 658 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (dd, *J* = 1.4, 8.0 Hz, 1H), 7.67-7.77 (m, 2H), 7.48-7.57 (m, 4H), 7.44 (dd, *J* = 1.4, 7.4 Hz, 1H), 7.18-7.24 (m, 3H), 6.80-6.87 (m, 2H), 5.41 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0, 166.9, 155.3, 148.1, 139.2, 136.4, 134.0, 131.4, 130.0, 129.5, 128.5, 128.4, 127.5, 126.3, 125.8, 123.3, 117.8, 117.6, 117.2, 114.5, 55.0, 21.8. HRMS $[M]^+$ Calculated for $C_{26}H_{17}NO_2$ 375.1259, found 375.1254.



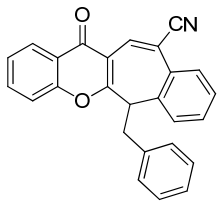
13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ja)

As a light yellow solid: m.p. 173-174 ^{o}C; IR (KBr) ν_{max} 3425, 3039, 2214, 1734, 1643, 1556, 1460, 1402, 1360, 1217, 1155, 1020, 766, 683, 635 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.22 (dd, *J* = 1.7, 8.0 Hz, 1H), 8.07 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.69 (td, *J* = 1.7, 7.2 Hz, 1H), 7.38-7.54 (m, 5H), 3.79 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 162.2, 155.7, 135.9, 134.1, 133.2, 131.6, 131.1, 128.9, 128.0, 127.5, 126.3, 125.9, 122.6, 119.0, 117.9, 116.2, 115.1, 38.9. HRMS $[M]^+$ Calculated for $C_{19}H_{11}NO_2$ 285.0790, found 285.0789.



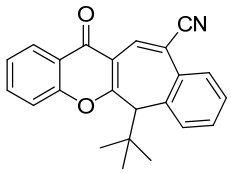
6-butyl-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ka)

As a white solid: m.p. 161-162 ^{o}C; IR (KBr) ν_{max} 3431, 3049, 2955, 2862, 2216, 1637, 1616, 1554, 1466, 1400, 1227, 770 cm^{-1}; ^{1}H NMR (300 MHz, d_6-DMSO, TEMP=70 ^{o}C) δ: 8.06 (dd, *J* = 1.3, 7.8 Hz, 1H), 7.86 (s, 1H), 7.81 (td, *J* = 1.6, 7.8 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.46-7.54 (m, 3H), 4.20 (s, 1H), 1.51-1.79 (m, 2H), 0.98-1.35 (m, 4H), 0.75 (s, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 174.6, 167.3, 155.3, 137.1, 134.9, 133.9, 131.5, 131.1, 129.2, 128.2, 128.0, 126.3, 125.5, 121.6, 119.1, 118.4, 114.7, 113.3, 50.6, 28.7, 27.7, 21.5, 13.6. HRMS $[M]^+$ Calculated for $C_{23}H_{19}NO_2$ 341.1416, found 341.1414.



6-benzyl-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3la)

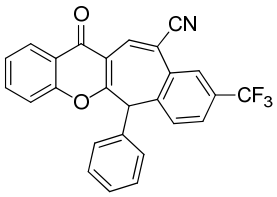
As a white solid: m.p. 179-180 ^{o}C; IR (KBr) ν_{max} 3429, 3030, 2924, 2858, 2218, 1641, 1564, 1464, 1406, 1346, 1225, 1180, 1022, 920, 760, 702, 503 cm^{-1}; ^{1}H NMR (300 MHz, d_6-DMSO, TEMP=70 ^{o}C) δ: 8.05 (d, J = 7.8 Hz, 1H), 7.98 (s, 1H), 7.74-7.84 (m, 2H), 7.37-7.60 (m, 5H), 6.97-7.24 (m, 5H), 4.55 (s, 1H), 2.81-3.09 (m, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 174.6, 166.2, 155.2, 137.2, 136.4, 134.9, 133.9, 131.4, 131.3, 131.2, 129.5, 129.0, 128.8, 128.3, 128.1, 128.0, 126.5, 126.2, 125.4, 121.4, 119.2, 118.1, 115.3, 113.5, 52.5, 33.6. HRMS [M]$^{+}$ Calculated for $C_{26}H_{17}NO_2$ 375.1259, found 375.1264.



6-(tert-butyl)-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile(3ma)

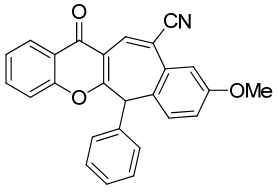
As a white solid: m.p. 194-195 ^{o}C; IR (KBr) ν_{max} 3431, 2964, 2868, 2210, 1649, 1620, 1564, 1465, 1402, 1221, 1157, 906, 770 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.24 (dd, J = 1.6, 8.0 Hz, 1H), 7.95 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.3 Hz, 1H), 7.39-7.55 (m, 4H), 7.23 (d, J = 7.8 Hz, 1H), 3.64 (s, 1H), 0.91 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 164.9, 155.7, 134.4, 134.3, 133.8, 133.4, 131.0, 130.9, 128.8, 128.1, 126.3, 125.8, 122.1, 119.5, 118.0, 117.3, 115.7, 63.1, 40.2, 28.4. HRMS [M]$^{+}$ Calculated for $C_{23}H_{19}NO_2$ 341.1416, found 341.1421.

2.2 3ab-3af



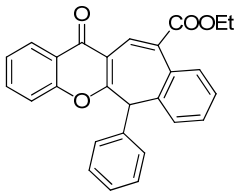
13-oxo-6-phenyl-9-(trifluoromethyl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ab)

As a white solid: m.p. 212-213 ^{o}C; IR (KBr) ν_{max} 3429, 3049, 2222, 1653, 1618, 1564, 1462, 1392, 1319, 1126, 764, 710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.27 (dd, J = 1.4, 8.0 Hz, 1H), 8.15 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.77 (td, J = 1.7, 7.2 Hz, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.18-7.24 (m, 3H), 6.70-6.76 (m, 2H), 5.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.5, 165.6, 155.9, 139.5, 135.6, 134.8, 134.6, 131.8, 131.4, 131.1, 128.6, 128.0, 127.7, 126.6, 126.4, 126.3, 125.8, 122.6, 118.1, 116.3, 113.9, 54.8. HRMS [M]$^{+}$ Calculated for $C_{26}H_{14}F_3NO_2$ 429.0977, found 429.0975.



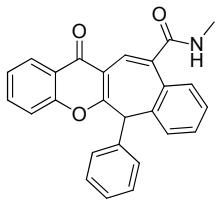
9-methoxy-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carbonitrile (3ac)

As a white solid: m.p. 229-230 ^{o}C; IR (KBr) ν_{max} 3431, 3054, 2937, 2837, 2224, 1726, 1651, 1610, 1572, 1498, 1464, 1265, 1217, 1034, 858, 762 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26 (dd, *J* = 1.7, 8.0 Hz, 1H), 7.70-7.79 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 2.8 Hz, 1H), 7.15-7.20 (m, 4H), 6.73-6.79 (m, 2H), 5.45 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.8, 166.6, 159.6, 155.9, 136.3, 134.3, 134.2, 132.3, 132.2, 128.7, 128.3, 127.5, 126.5, 126.3, 126.1, 122.6, 118.8, 118.1, 117.9, 115.9, 114.8, 112.9, 55.6, 54.2. HRMS $[M]^+$ Calculated for $C_{26}H_{17}NO_3$ 391.1208, found 391.1207.



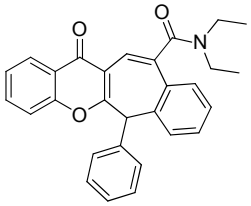
Ethyl 13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carboxylate (3ad)

As a white solid: m.p. 172-173 ^{o}C; IR (KBr) ν_{max} 3431, 2991, 2220, 1709, 1657, 1464, 1402, 1246, 1113, 1028, 905, 760, 704, 611 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.25 (dd, *J* = 1.7, 7.9 Hz, 1H), 7.94 (s, 1H), 7.64-7.75 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.39-7.53 (m, 4H), 7.08-7.17 (m, 3H), 6.79-6.92 (m, 2H), 5.47 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 166.5, 166.4, 155.9, 137.8, 136.2, 133.9, 133.3, 132.6, 130.8, 129.9, 129.5, 128.5, 127.9, 127.3, 127.0, 126.5, 126.2, 125.6, 122.8, 118.0, 116.1, 61.0, 55.2, 14.2. HRMS $[M]^+$ Calculated for $C_{27}H_{20}NaO_4$ 431.1259, found 431.1265.



N-methyl-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carboxamide (3ae)

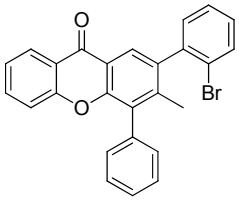
As a light yellow solid: m.p. 183-184 ^{o}C; IR (KBr) ν_{max} 3433, 3248, 3057, 2931, 1651, 1543, 1466, 1400, 1300, 1219, 1157, 764, 702, 611 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.23 (dd, *J* = 1.7, 8.0 Hz, 1H), 7.66-7.74 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.47-7.53 (m, 2H), 7.39-7.46 (m, 2H), 7.33 (s, 1H), 7.12-7.19 (m, 3H), 6.85-6.95 (m, 2H), 5.65 (br. s., 1H), 5.45 (s, 1H), 2.82 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.9, 169.3, 164.5, 156.0, 138.5, 138.0, 136.7, 133.8, 132.8, 130.3, 129.9, 129.7, 128.0, 127.8, 127.2, 126.6, 126.2, 125.6, 122.8, 122.4, 118.0, 116.1, 55.1, 26.6. HRMS $[M]^+$ Calculated for $C_{26}H_{19}NO_3$ 393.1365, found 393.1361.



N,N-diethyl-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-*b*]chromene-11-carboxamide (3af)

As a white solid: m.p. 197-198 ^{o}C; IR (KBr) ν_{max} 3442, 2972, 1637, 1466, 1402, 1277, 1221, 1165, 762, 706, 600 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.27 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.68 (td, *J* = 1.7, 7.1 Hz, 1H), 7.49-7.62 (m, 4H), 7.38-7.46 (m, 2H), 7.13-7.20 (m, 4H), 6.89-6.98 (m, 2H), 5.50 (s, 1H), 3.43 (q, *J* = 7.0 Hz, 2H), 2.51 (s, 2H), 1.17 (t, *J* = 7.0 Hz, 3H), 0.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 169.8, 156.0, 138.3, 136.8, 136.2, 133.7, 132.6, 131.4, 130.0, 128.5, 128.2, 128.1, 127.2, 126.7, 126.3, 125.4, 122.7, 119.7, 118.0, 117.2, 55.5, 42.2, 38.7, 13.8, 12.6. HRMS $[M]^+$ Calculated for $C_{29}H_{25}NO_3$ 435.1834, found 435.1835.

2.3 4b

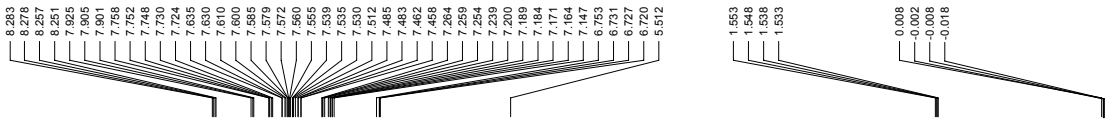


2-(2-bromophenyl)-3-methyl-4-phenyl-9H-xanthen-9-one (4b)

As a white solid: m.p. 185-186 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.33 (dd, *J* = 1.7, 7.9 Hz, 1H), 8.15 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (td, *J* = 1.6, 7.7 Hz, 1H), 7.26-7.58 (m, 9H), 7.23 (d, *J* = 8.8 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.3, 156.1, 153.0, 143.0, 141.5, 137.9, 135.5, 134.5, 132.6, 131.3, 131.1, 130.3, 130.0, 129.2, 128.4, 128.3, 127.6, 127.4, 126.4, 126.0, 124.0, 123.8, 121.5, 119.5, 118.2, 18.9. HRMS $[M]^+$ Calculated for $C_{26}H_{17}BrO_2Na$ 463.0310, found 463.0298.

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

3aa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7.610
7.600
7.585
7.579
7.572
7.560
7.555
7.539
7.535
7.530
7.512
7.485
7.483
7.462
7.458
7.264
7.259
7.254
7.239
7.200
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7.184
7.171
7.164
7.147
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6.731
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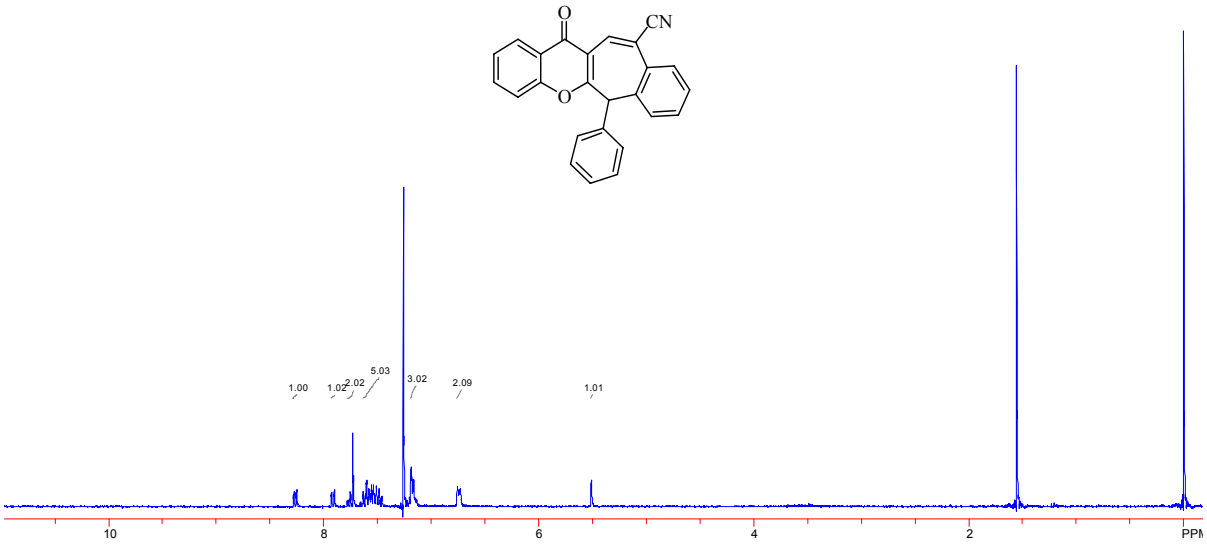
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6
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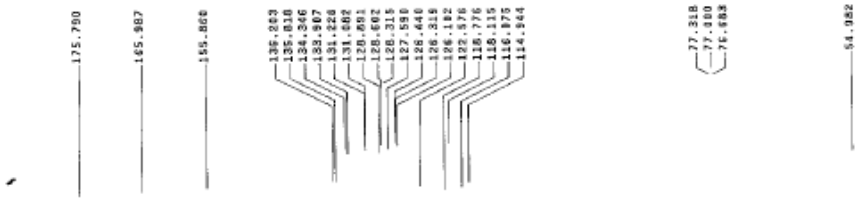
PPM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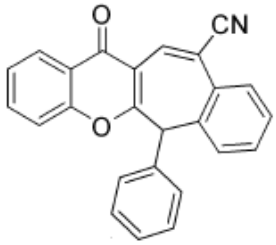
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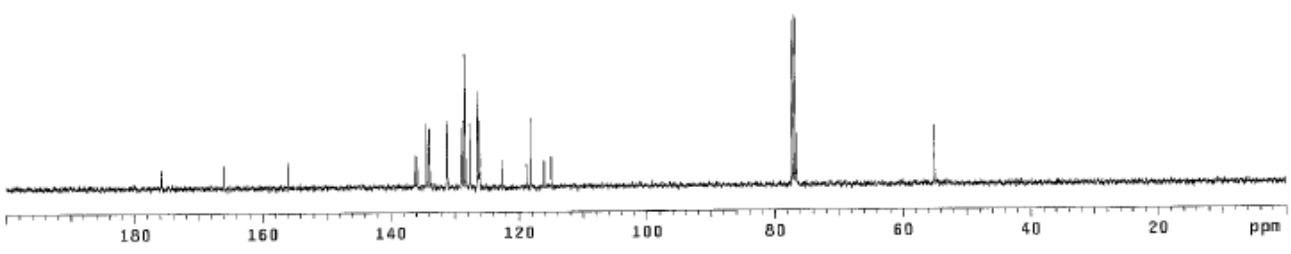
CN
O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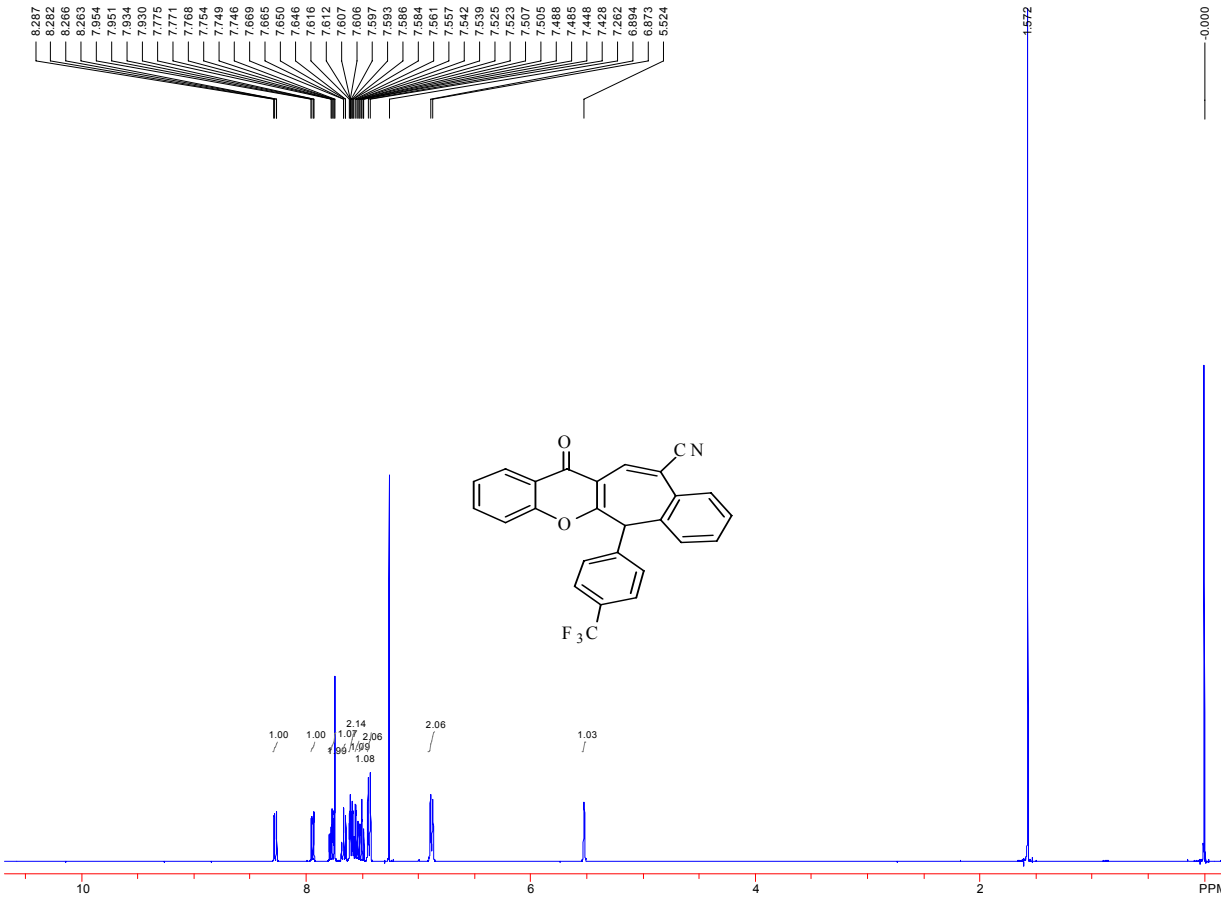
ppm

3ba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7.746
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7.665
7.650
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7.612
7.607
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7.597
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7.539
7.525
7.523
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CN
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1.08
2.06
1.03
10
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4
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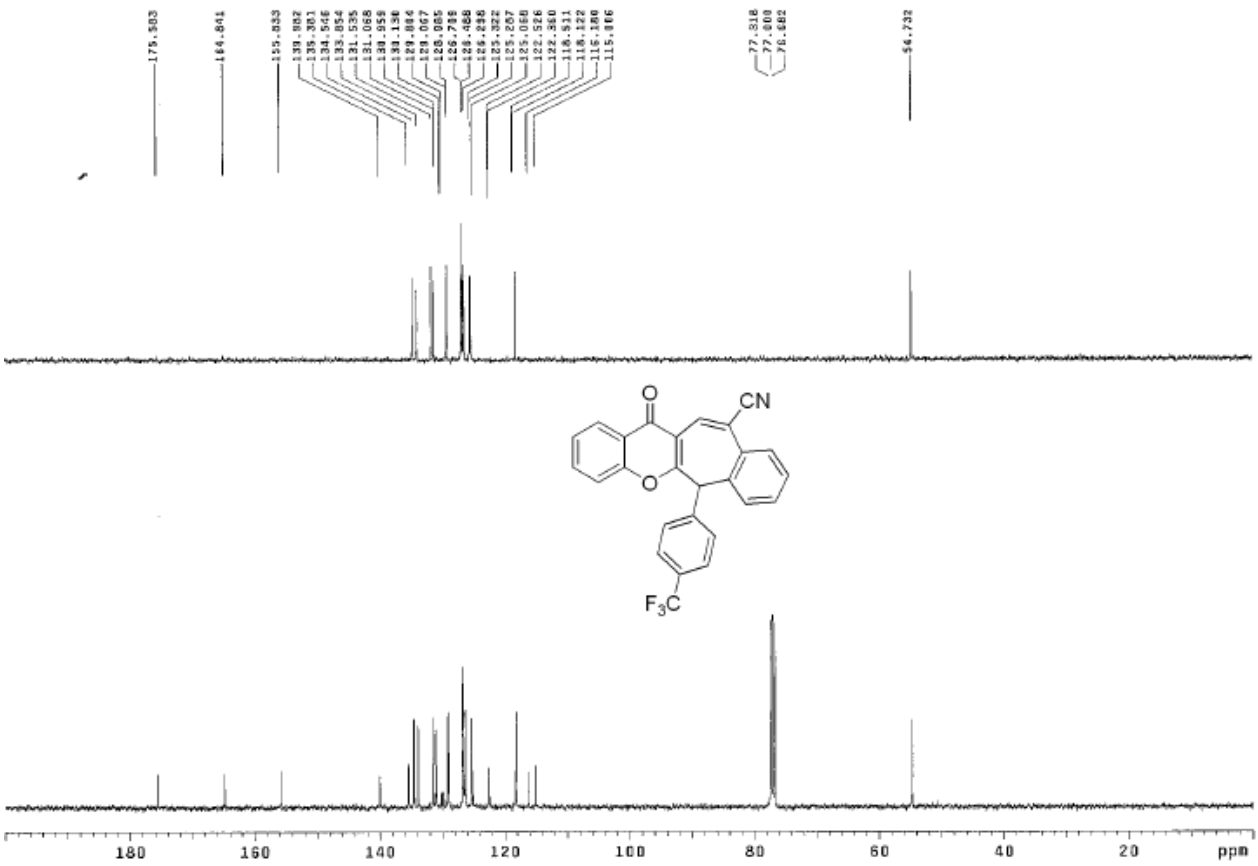
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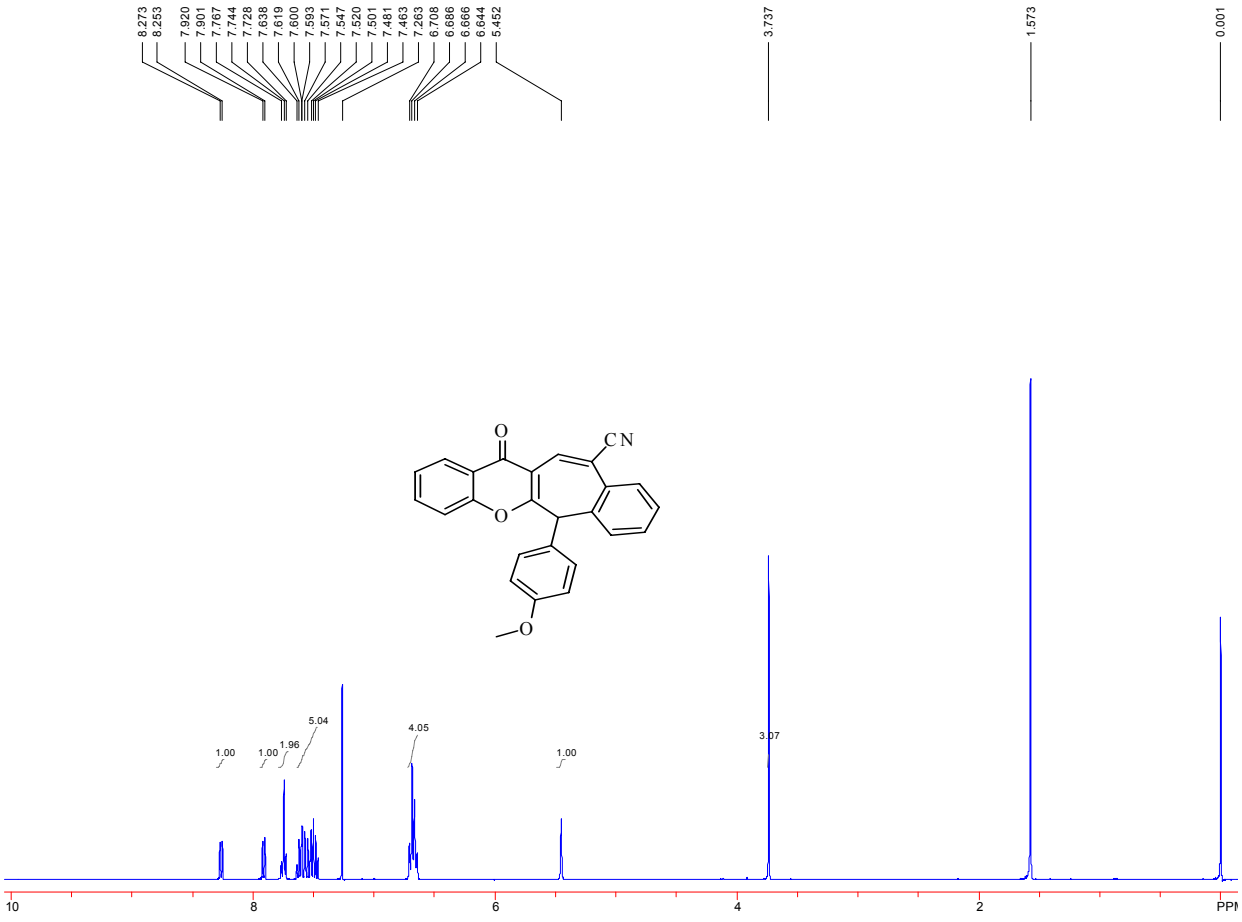
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7.547
7.520
7.501
7.481
7.463
7.263
6.708
6.686
6.666
6.644
5.452
3.737
1.573
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1.00
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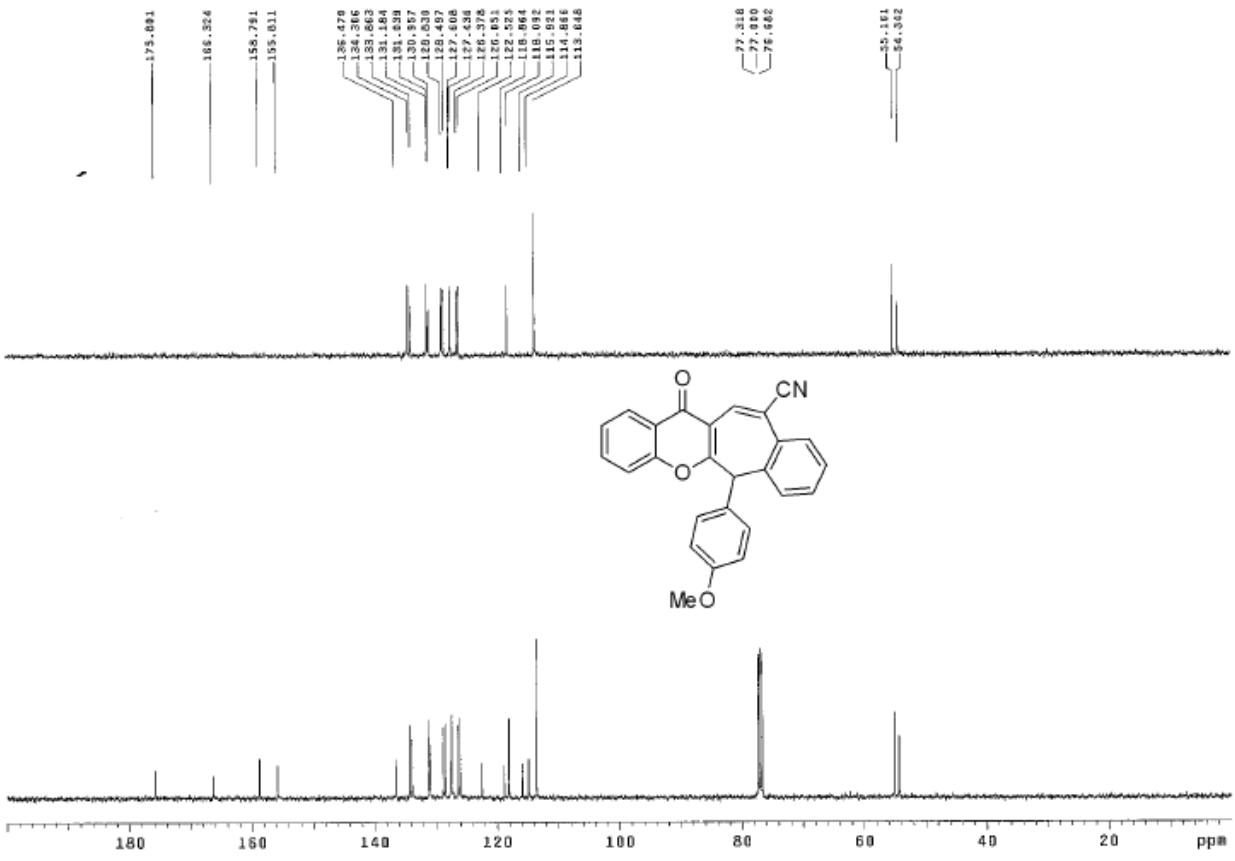
1.00
3.07
10
8
6
4
2
PPM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127.434
126.378
126.051
122.525
118.864
118.092
115.921
114.866
113.648
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77.010
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MeO
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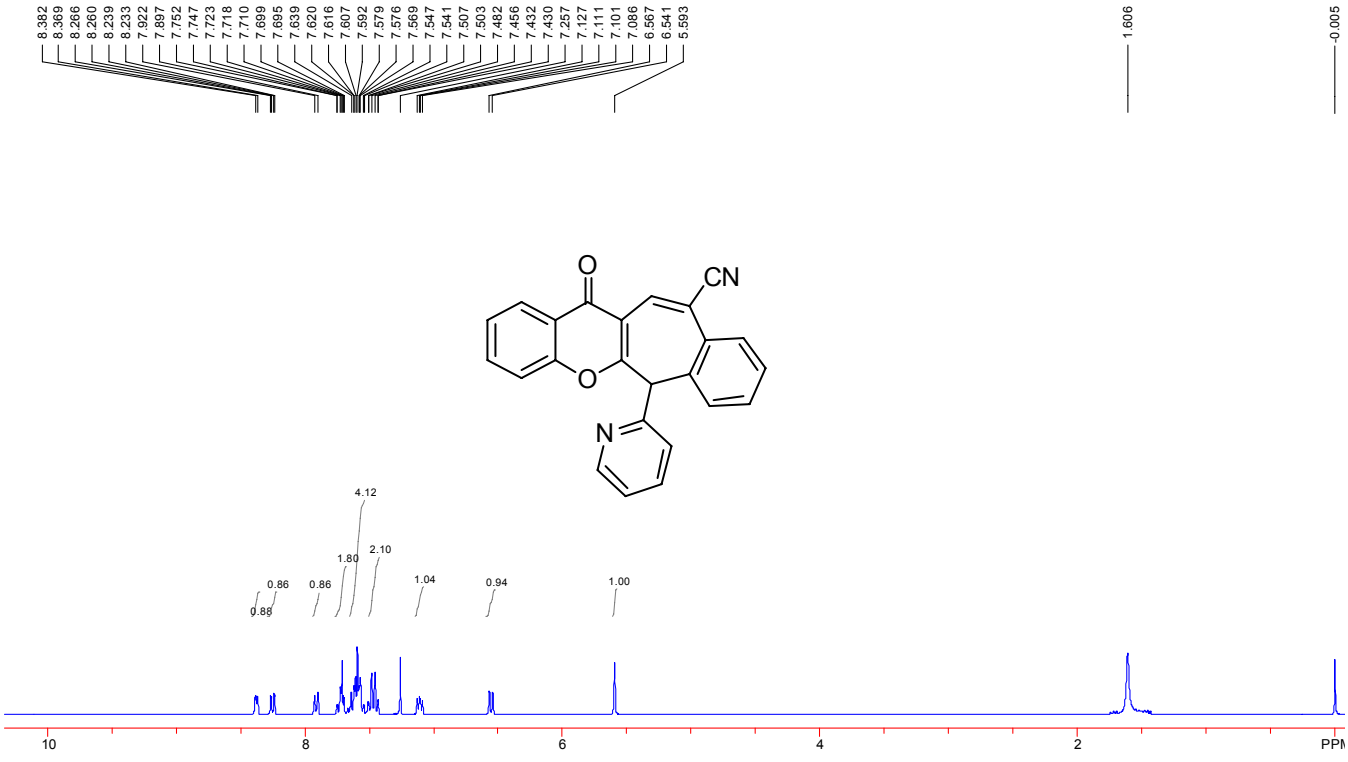
40
20
ppm

3da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7.710
7.699
7.695
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7.620
7.616
7.607
7.592
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7.576
7.569
7.547
7.541
7.507
7.503
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7.456
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6.593
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CN
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2
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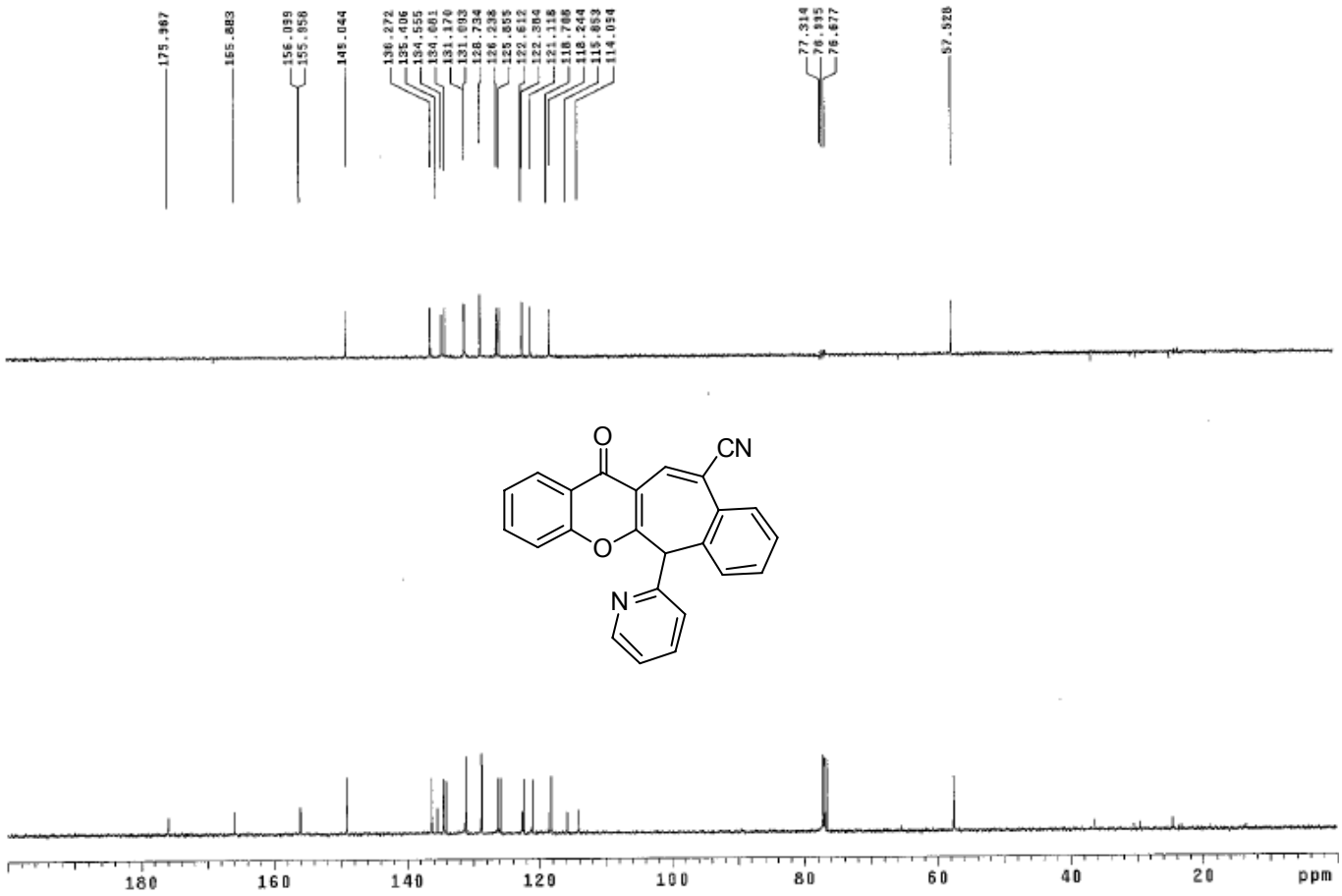
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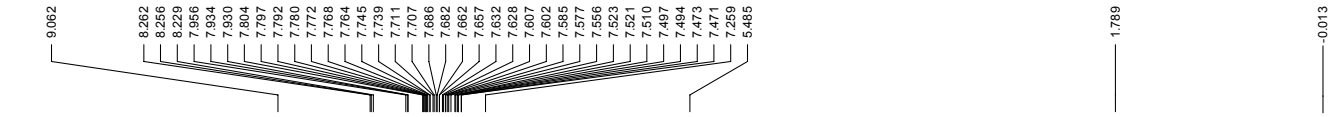
ppm

3ea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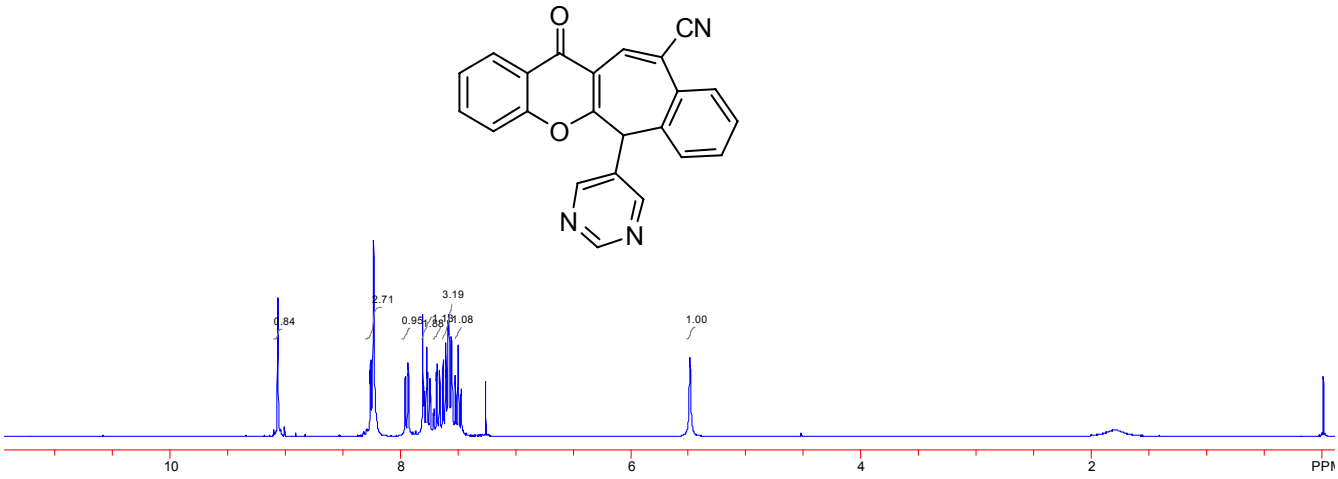
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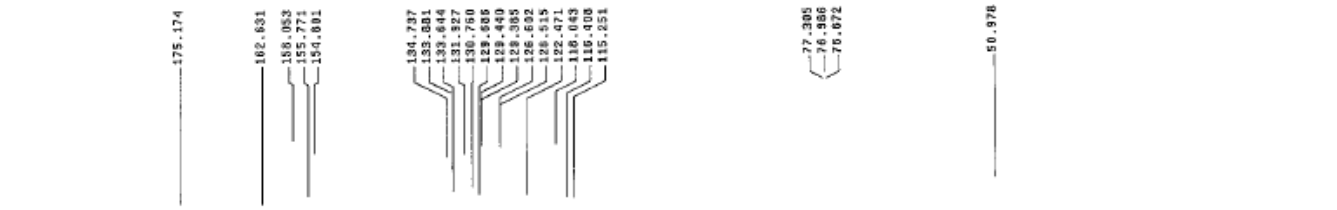
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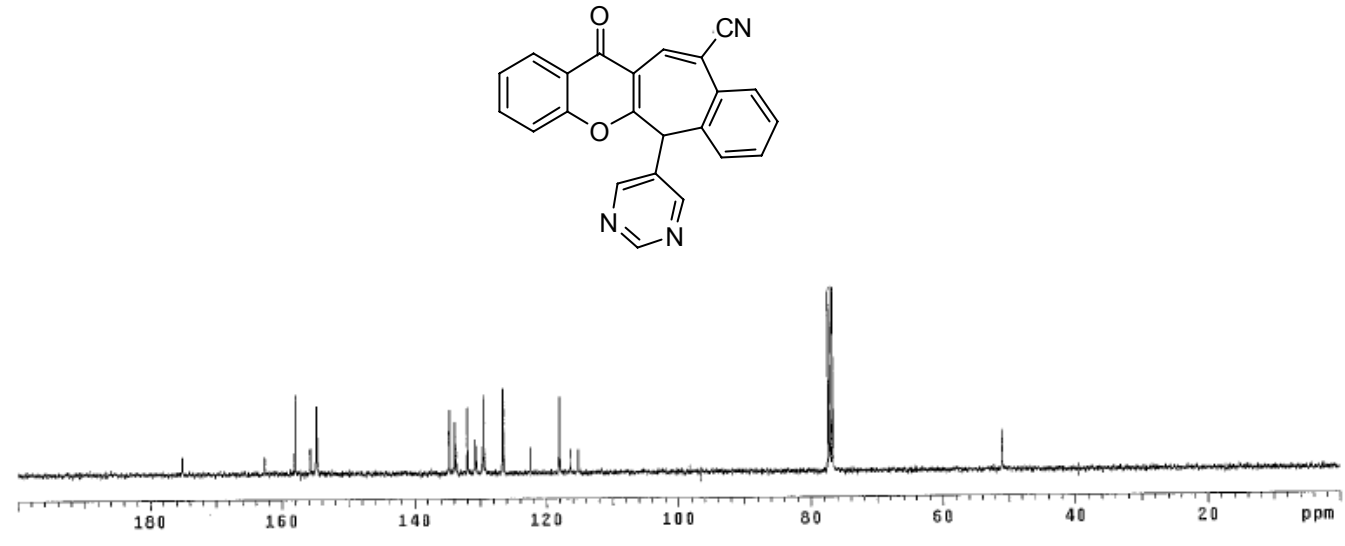
50.978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N
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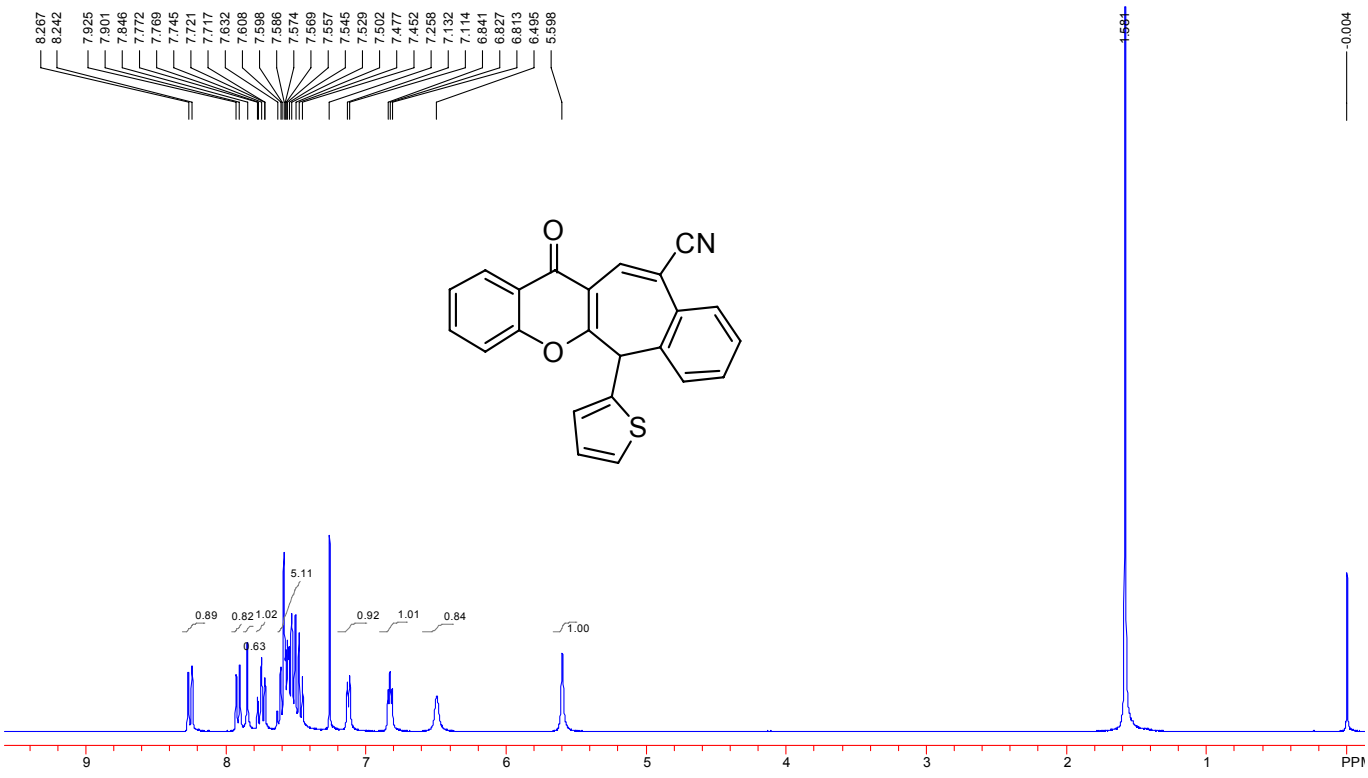
60
40
20
ppm

3fa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CN
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1.00
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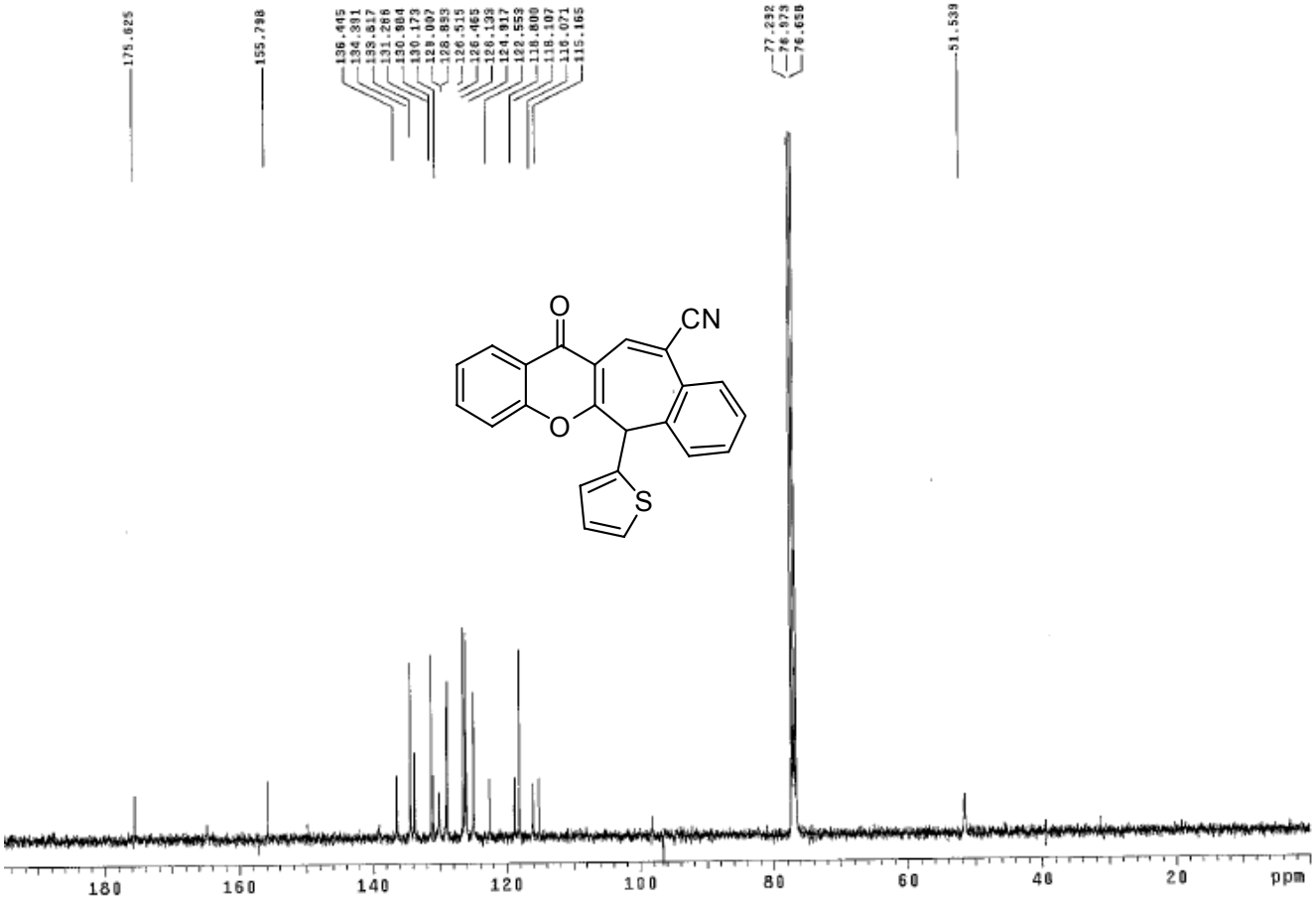
7
6
5
4
3
2
1
PPM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116.071
115.165
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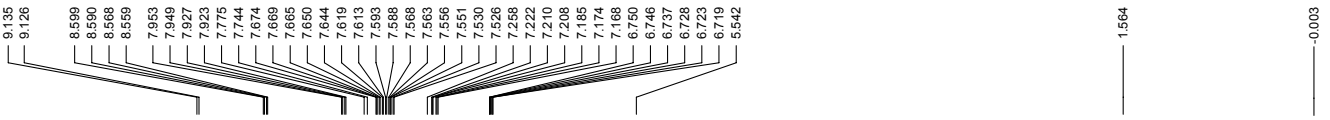
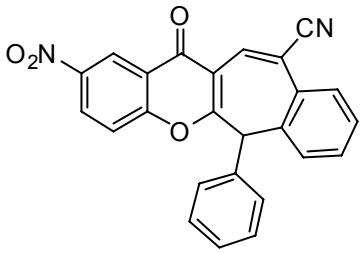
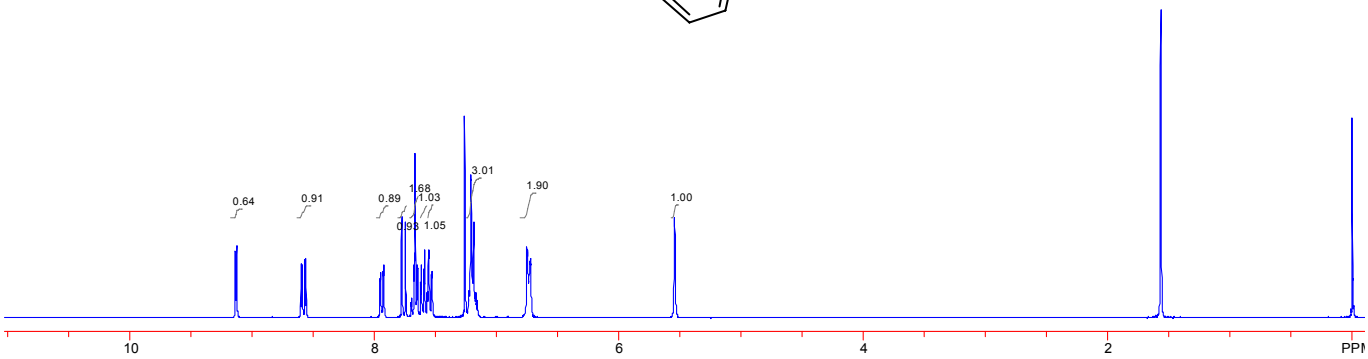
CN
O
S
180
160
140
120
100
80
60
40
20
ppm

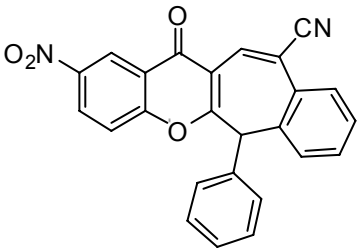
3ga


9.135
9.126
8.599
8.590
8.588
8.559
7.953
7.949
7.927
7.923
7.775
7.744
7.674
7.669
7.665
7.650
7.644
7.619
7.613
7.593
7.588
7.568
7.563
7.556
7.551
7.530
7.526
7.258
7.222
7.210
7.208
7.185
7.174
7.168
6.750
6.746
6.737
6.728
6.723
6.719
5.542
1.564
0.003


O
CN
O2N
O


0.64
0.91
0.89
1.68
1.03
0.98
1.05
3.01
1.90
1.00
10
8
6
4
2
PPM


174.356
166.047
158.554
145.350
136.062
135.179
132.476
131.722
131.120
130.961
129.166
128.948
128.588
128.515
127.814
126.274
123.977
122.782
120.002
118.312
116.518
77.319
77.000
76.681
54.809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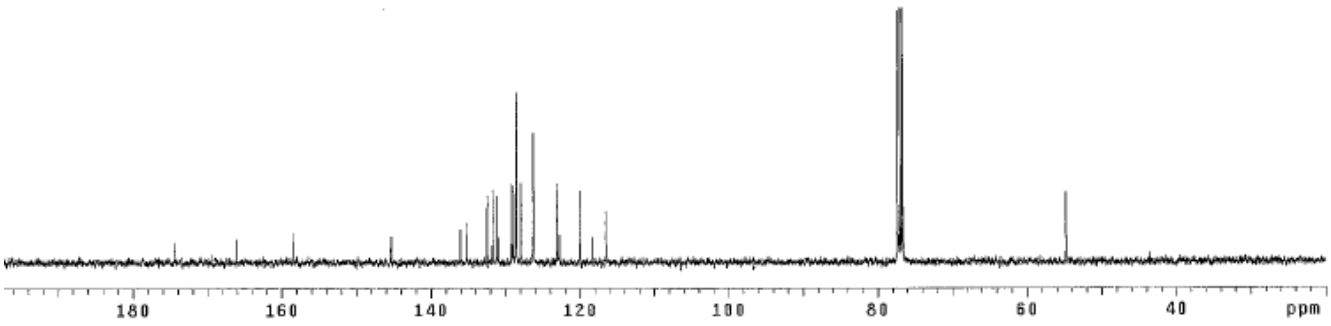
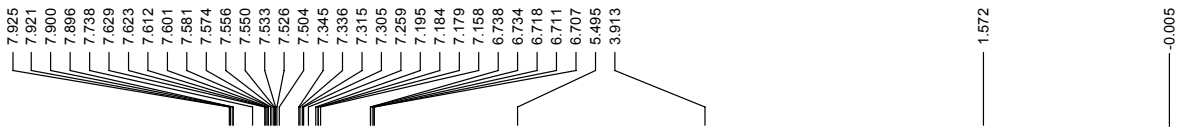
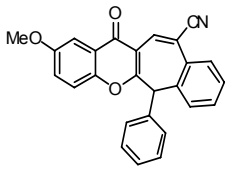
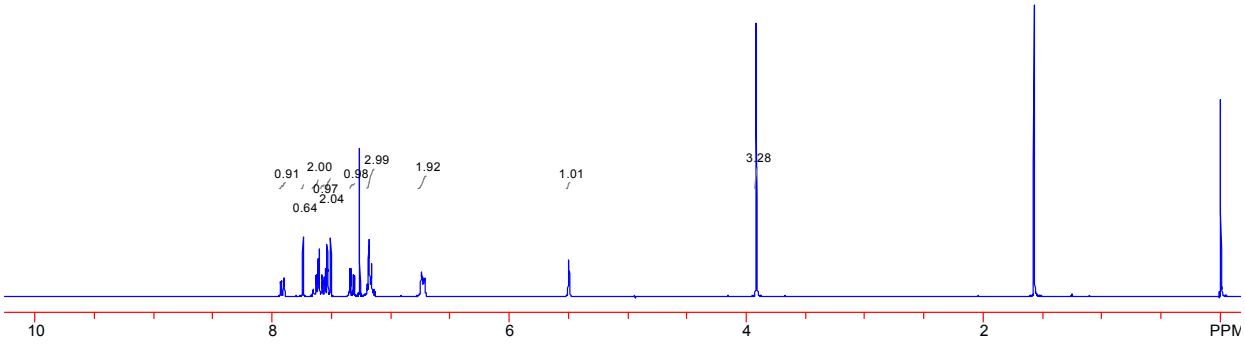
CN
O2N
O

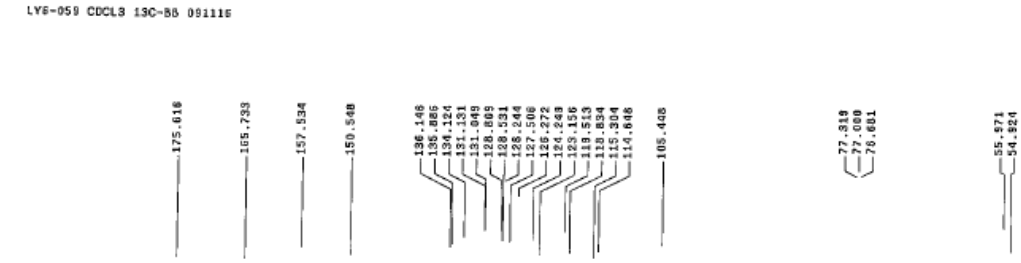

180
160
140
120
100
80
60
40
ppm

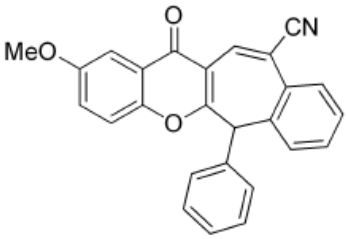
3ha

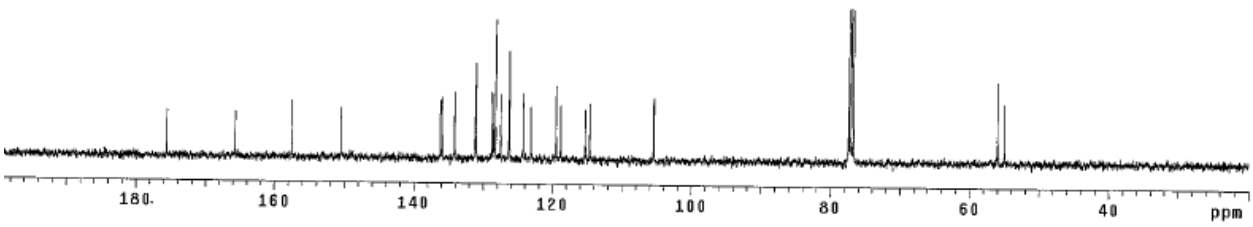

7.925
7.921
7.900
7.896
7.738
7.629
7.623
7.612
7.601
7.581
7.574
7.556
7.550
7.533
7.526
7.504
7.345
7.336
7.315
7.305
7.259
7.195
7.184
7.179
7.158
6.738
6.734
6.718
6.711
6.707
5.495
3.913
1.572
-0.005


MeO
O
CN
O

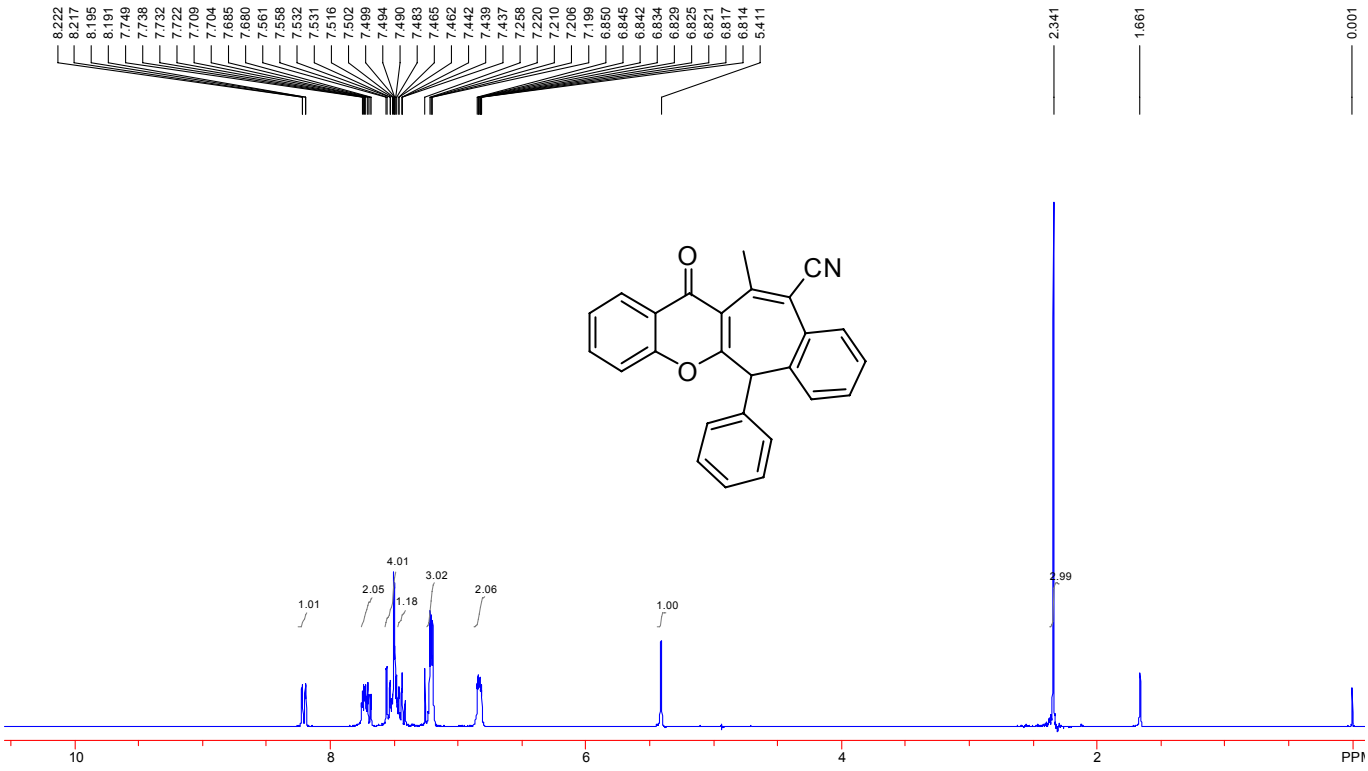

0.91
2.00
0.97
2.04
0.64
0.98
2.99
1.92
1.01
3.28
10
8
6
4
2
PPM

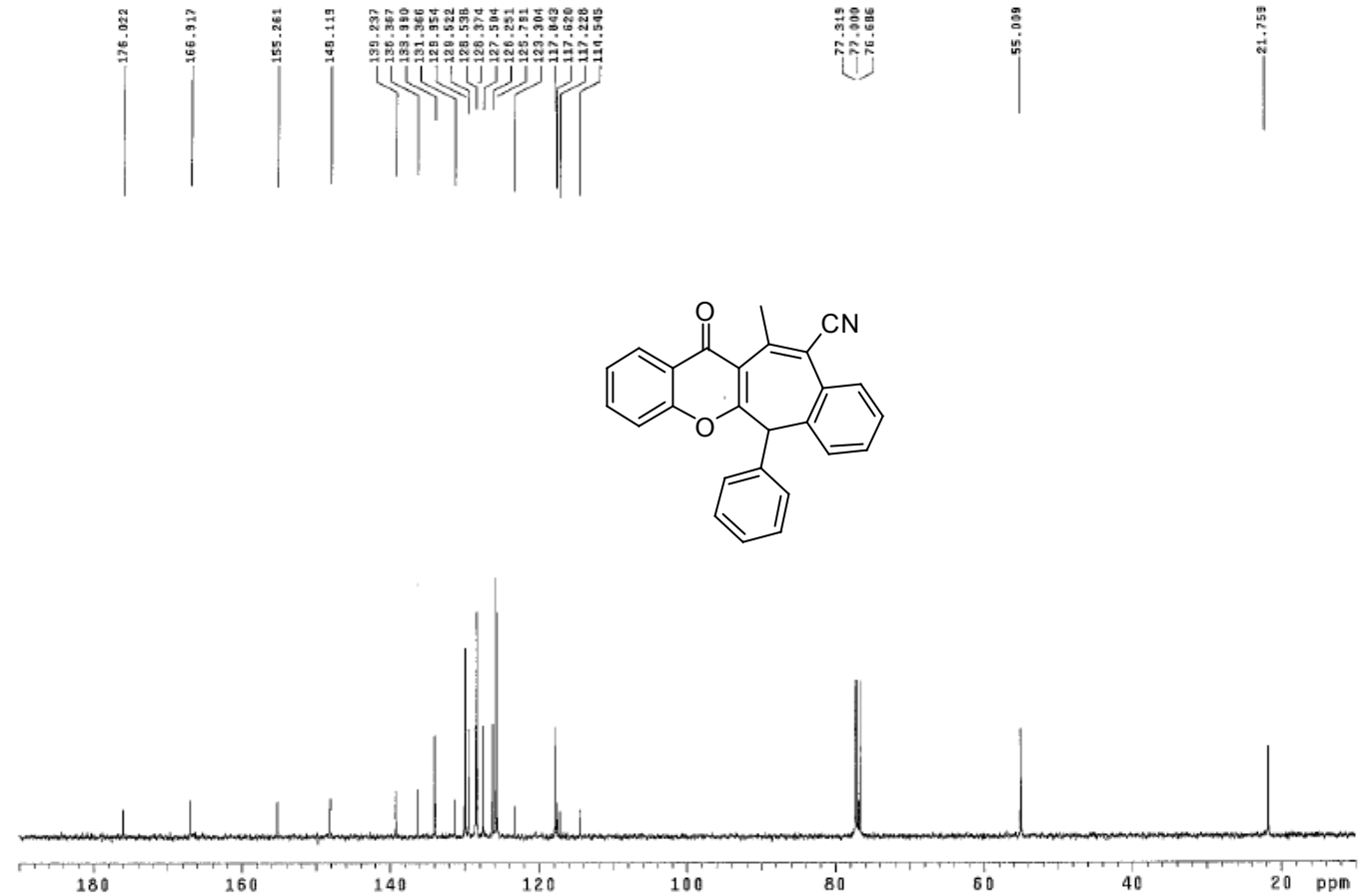

LY6-059 CDCL3 13C-88 091116
175.616
165.733
157.534
150.548
136.146
135.886
134.124
131.131
131.049
128.869
128.531
126.244
125.506
125.272
124.243
123.156
119.513
118.834
115.304
114.648
105.448
77.318
77.000
76.681
55.471
54.924


MeO
O
CN
O

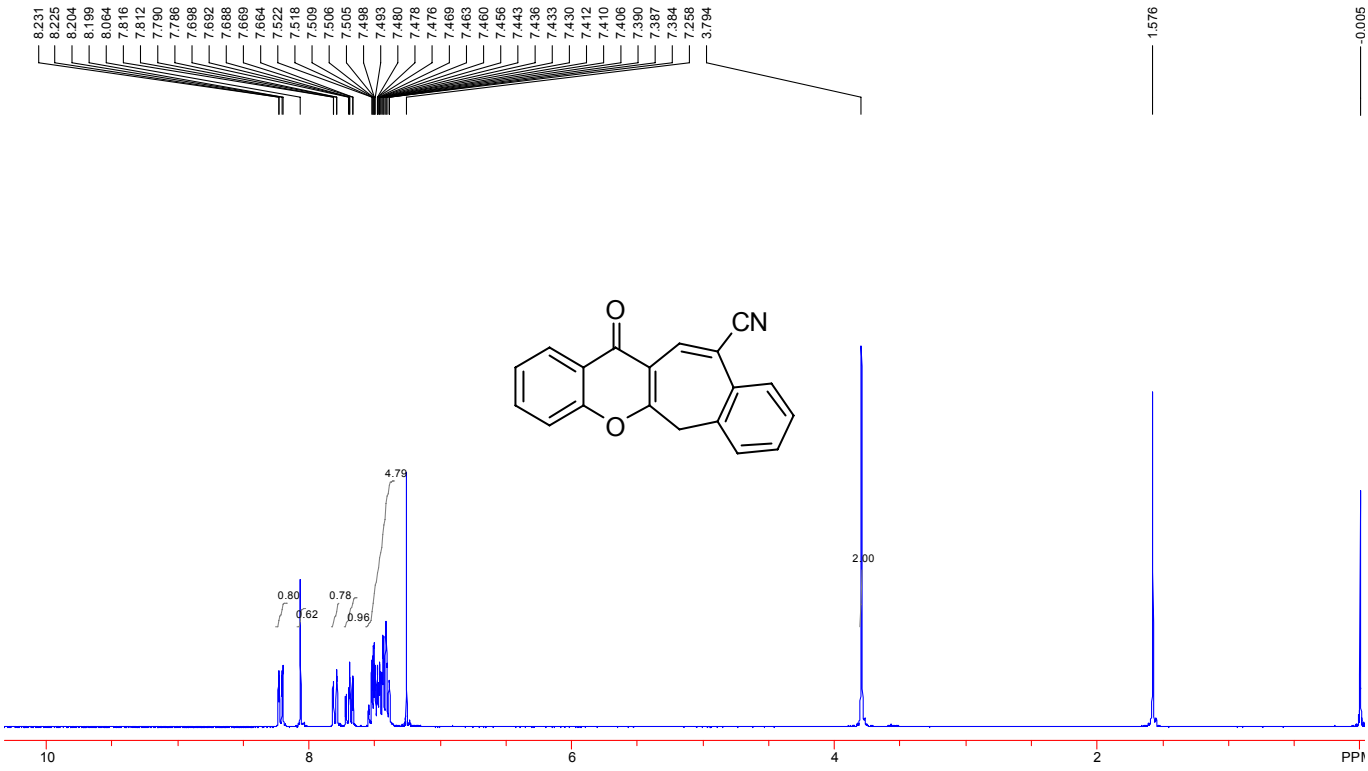

180.
160
140
120
100
80
60
40
ppm

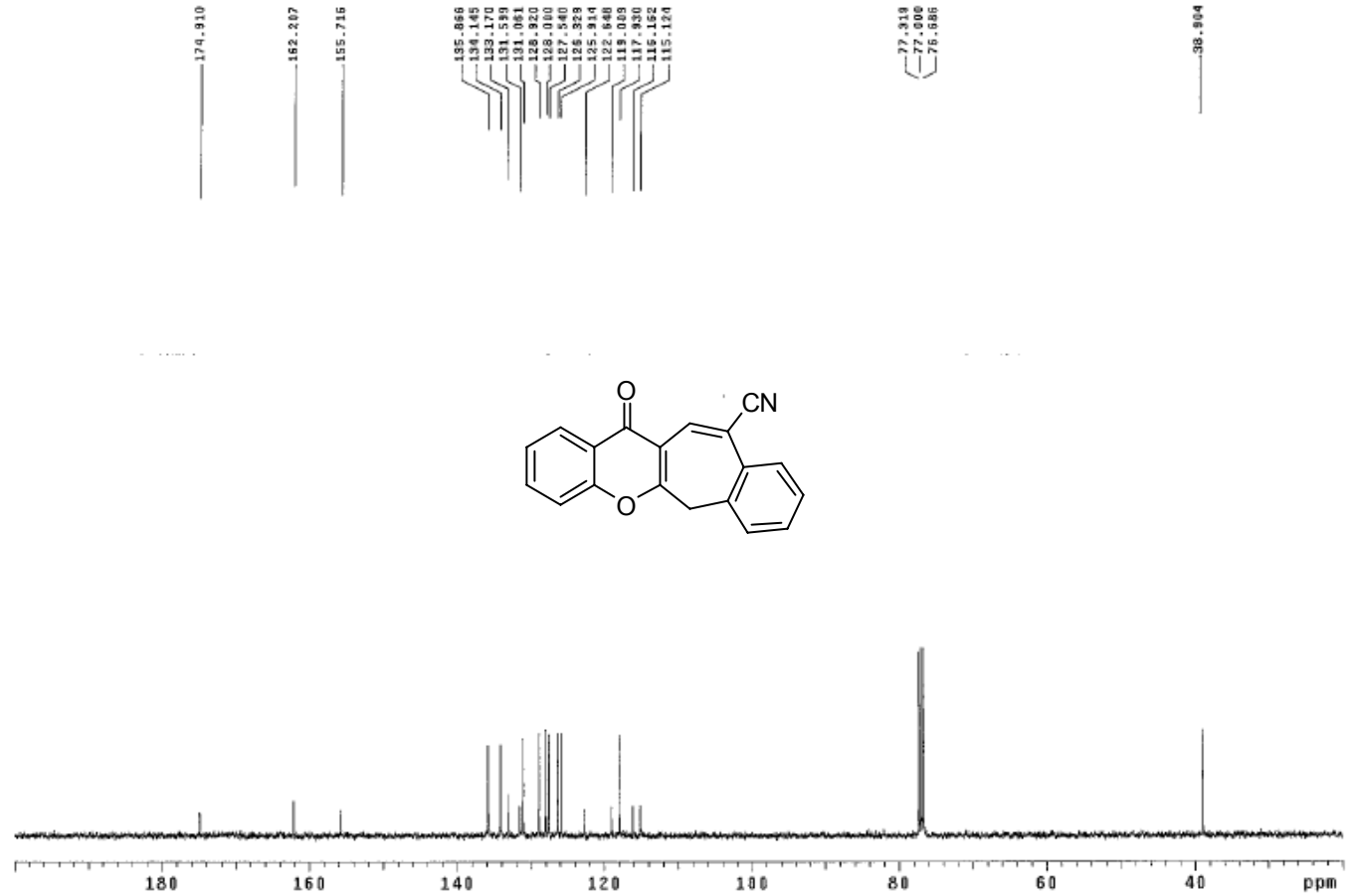
3ia


8.222
8.217
8.195
8.191
7.749
7.738
7.732
7.722
7.709
7.704
7.685
7.680
7.561
7.558
7.532
7.531
7.516
7.502
7.499
7.494
7.490
7.483
7.465
7.462
7.442
7.439
7.437
7.258
7.220
7.210
7.206
7.199
6.850
6.845
6.842
6.834
6.829
6.825
6.821
6.817
6.814
5.411
2.341
1.661
0.001
O
CN
O
4.01
3.02
2.05
2.06
1.18
1.01
1.00
2.99
10
8
6
4
2
PPM

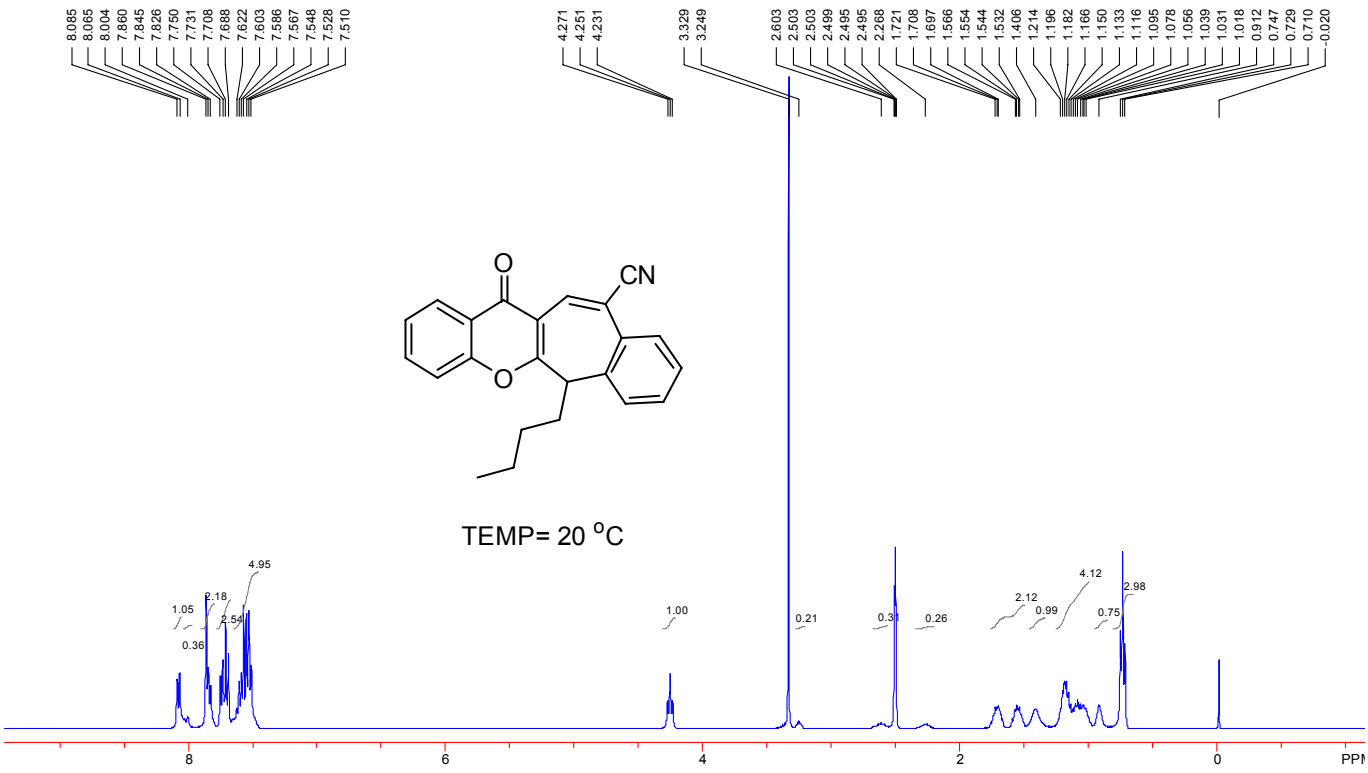

176.022
166.917
155.261
148.113
139.237
136.367
133.990
131.366
129.954
129.522
128.536
128.374
127.594
126.251
125.781
123.304
117.843
117.620
117.220
114.545
77.315
77.000
76.686
55.099
21.753
O
CN
O
180
160
140
120
100
80
60
40
20
ppm

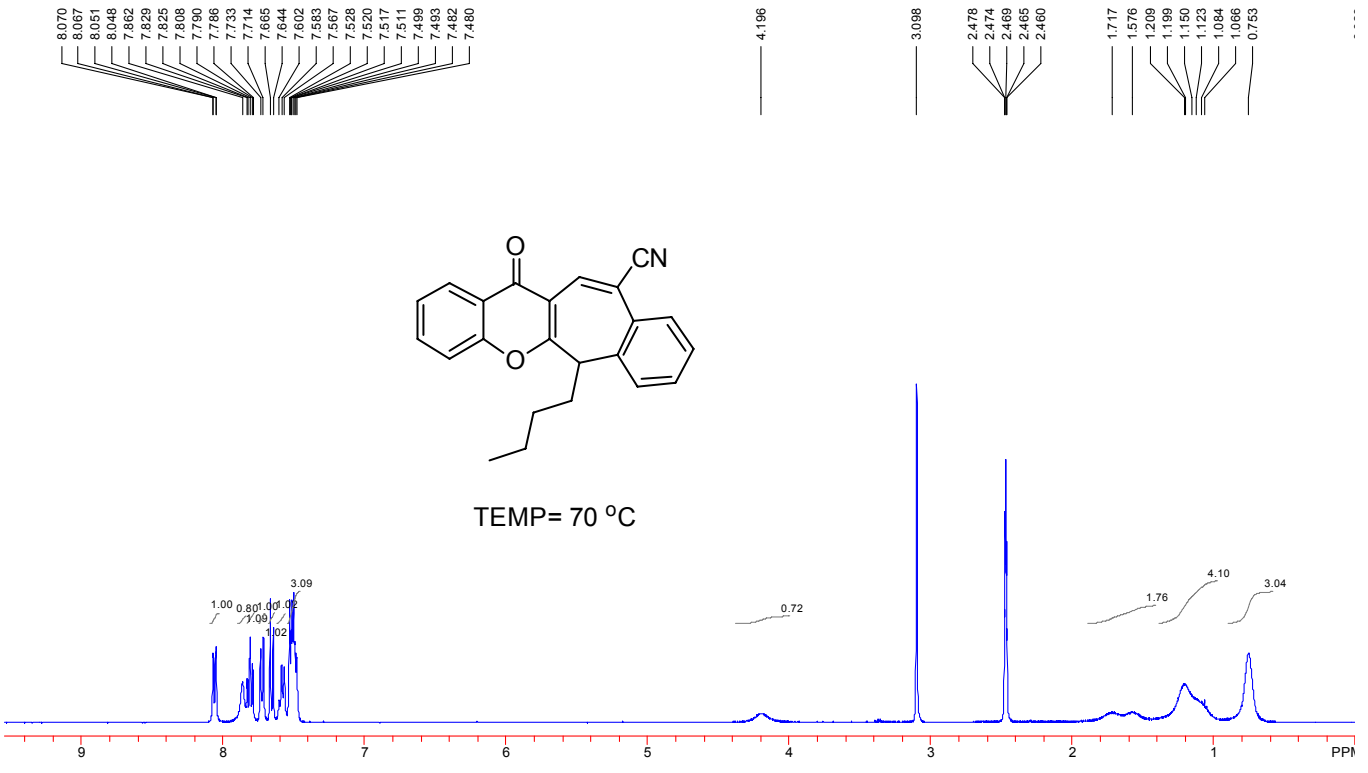
3ja

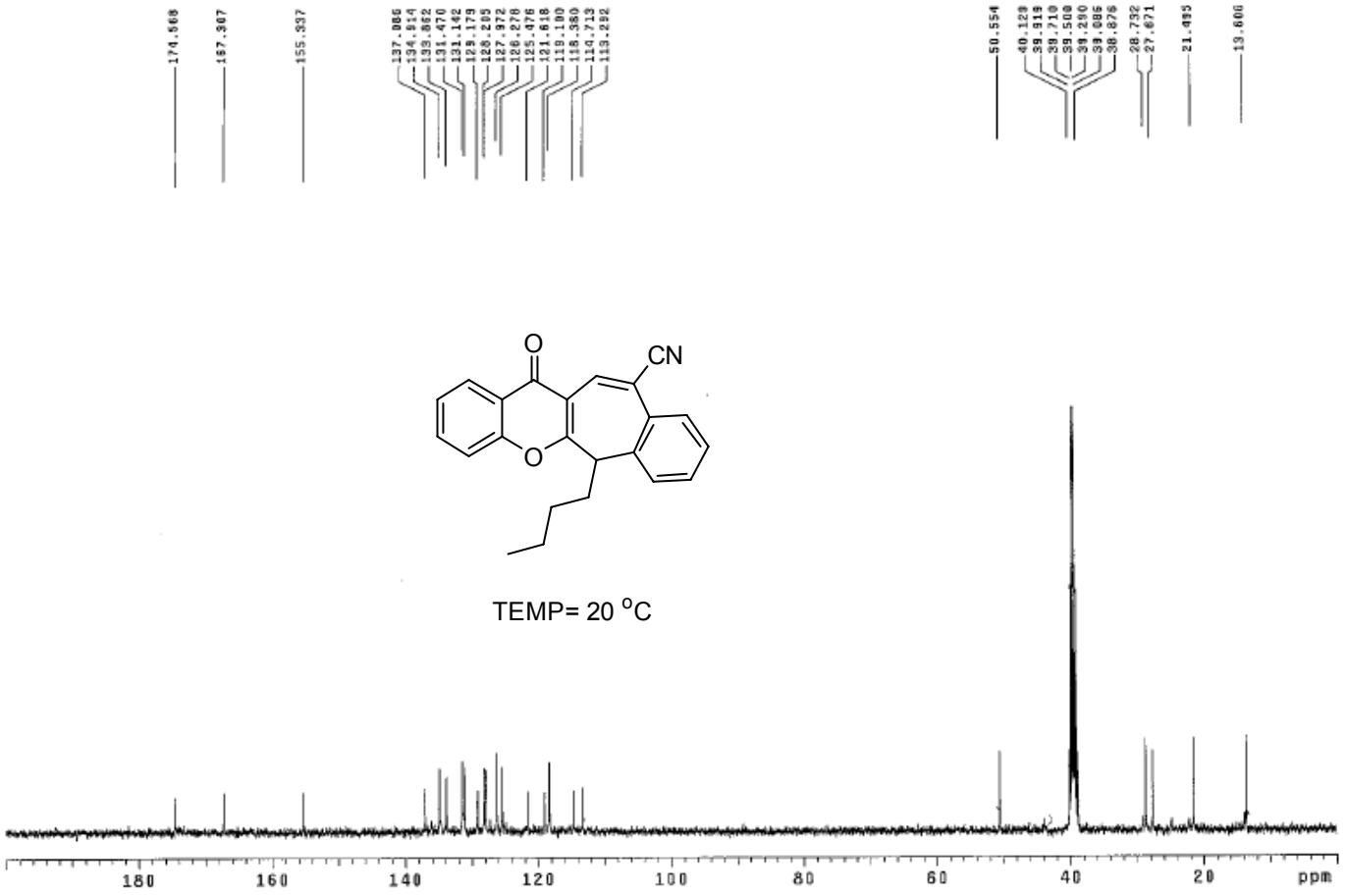

8.231
8.225
8.204
8.199
8.064
7.816
7.812
7.790
7.786
7.698
7.692
7.688
7.669
7.664
7.522
7.518
7.509
7.506
7.505
7.498
7.493
7.480
7.478
7.476
7.469
7.463
7.460
7.456
7.443
7.436
7.433
7.430
7.412
7.410
7.406
7.390
7.387
7.384
7.258
3.794
1.576
-0.005
O
CN
O
4.79
2.00
0.80
0.62
0.78
0.96
10
8
6
4
2
PPM


174.910
162.207
155.716
135.866
134.145
133.170
131.549
131.061
128.920
128.000
127.540
126.329
125.914
122.648
119.009
117.930
116.162
115.124
77.319
77.000
76.686
38.904
O
CN
O
180
160
140
120
100
80
60
40
ppm

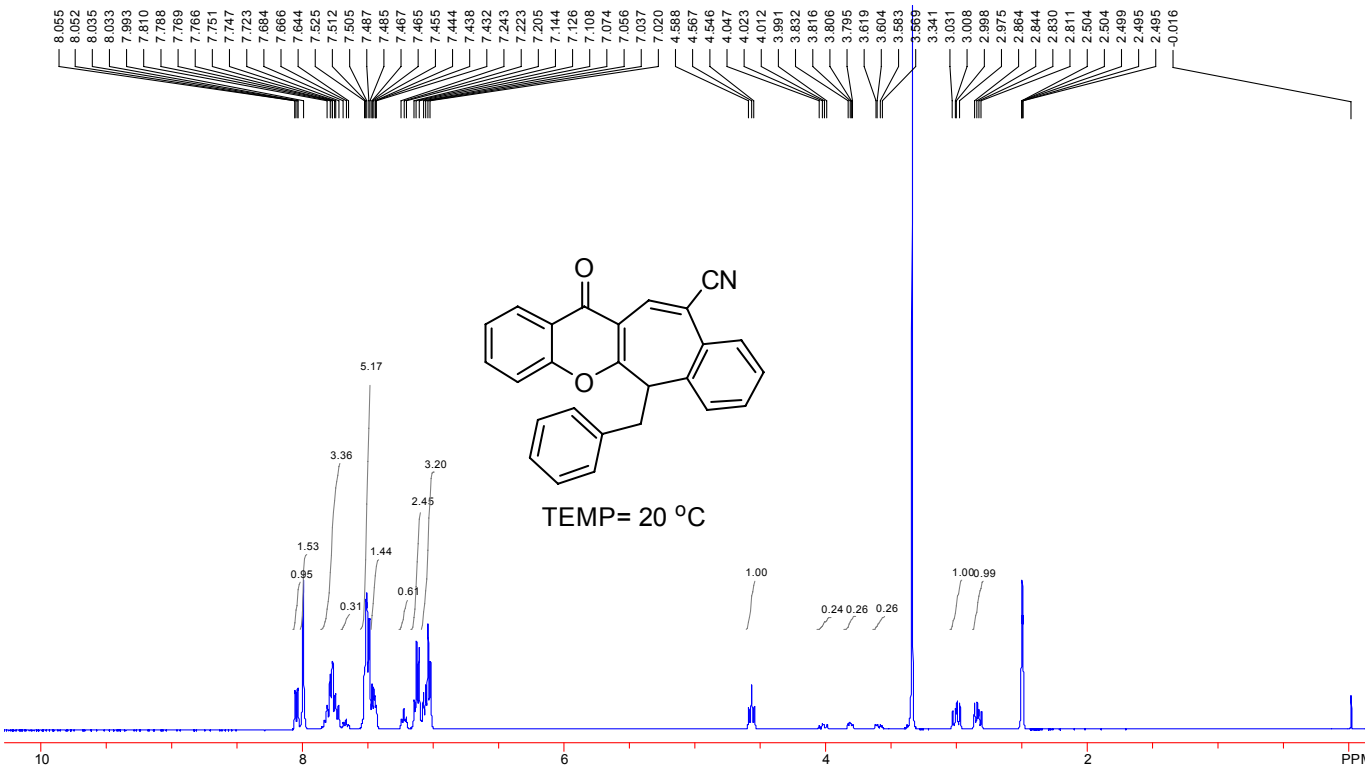
3ka


8.085
8.065
8.004
7.860
7.845
7.826
7.750
7.731
7.708
7.688
7.622
7.603
7.586
7.567
7.548
7.528
7.510
4.271
4.251
4.231
3.329
3.249
2.603
2.503
2.503
2.499
2.495
2.495
2.268
1.721
1.708
1.697
1.566
1.554
1.544
1.532
1.406
1.214
1.196
1.182
1.166
1.150
1.133
1.116
1.095
1.078
1.056
1.039
1.031
1.018
0.912
0.747
0.729
0.710
-0.020
O
CN
O
TEMP= 20 °C
4.95
2.18
1.05
2.54
0.36
1.00
0.21
0.31
0.26
2.12
0.99
4.12
0.75
2.98
8
6
4
2
0
PPM

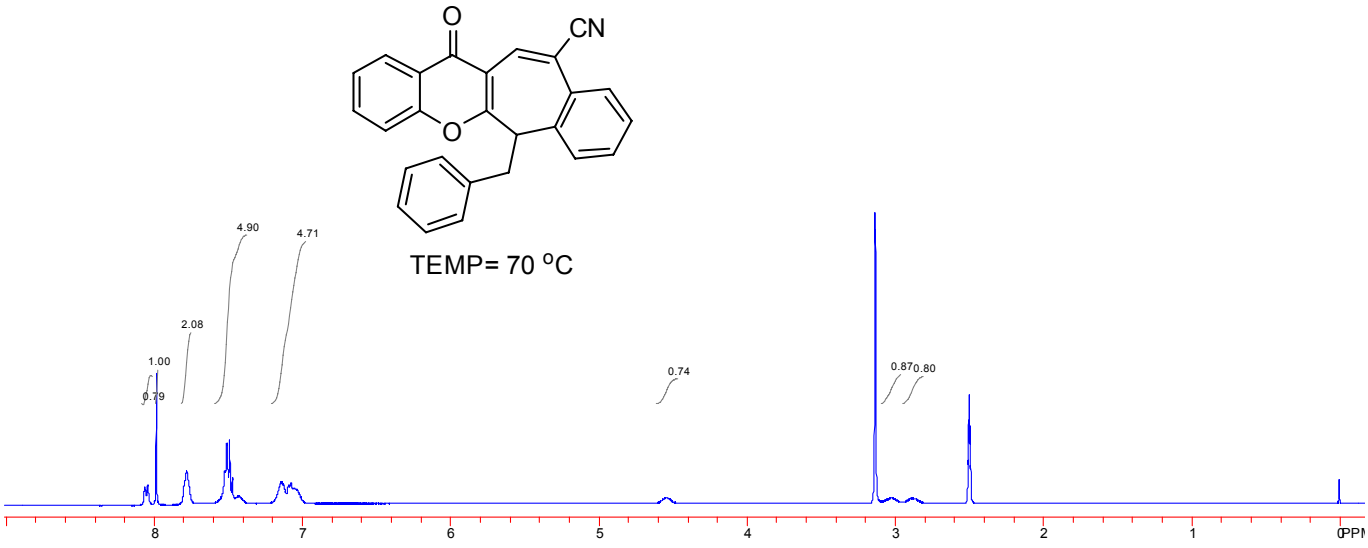

8.070
8.067
8.051
8.048
7.862
7.829
7.825
7.808
7.790
7.786
7.733
7.714
7.665
7.644
7.602
7.583
7.567
7.528
7.520
7.517
7.511
7.499
7.493
7.482
7.480
4.196
3.098
2.478
2.474
2.469
2.465
2.460
1.717
1.576
1.209
1.199
1.150
1.123
1.084
1.066
0.753
O
CN
O
TEMP= 70 °C
3.09
1.00
0.80
1.01
1.02
1.09
1.02
0.72
4.10
1.76
3.04
9
8
7
6
5
4
3
2
1
PPM

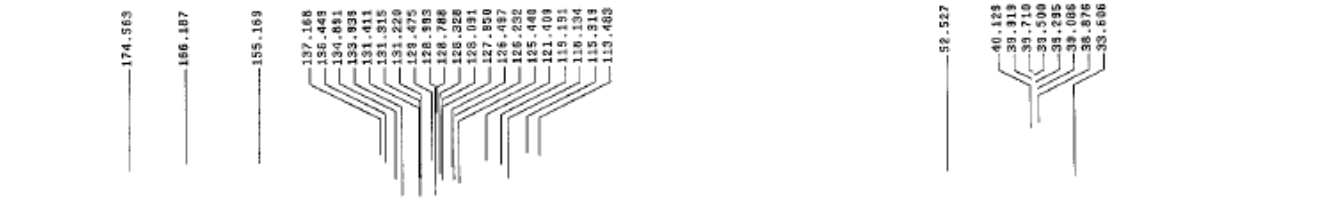

174.568
167.307
155.337
137.086
134.514
133.062
131.470
131.142
129.179
128.285
127.972
126.278
125.476
121.618
119.190
118.380
114.713
113.292
50.554
40.129
39.919
39.710
39.500
39.290
39.086
38.876
28.732
27.671
21.495
13.606
O
CN
O
TEMP= 20 °C
180
160
140
120
100
80
60
40
20
ppm

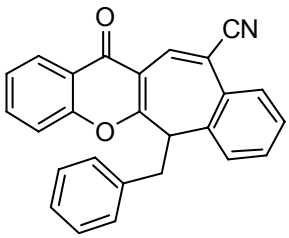
3la


8.055
8.052
8.035
8.033
7.993
7.810
7.788
7.769
7.766
7.751
7.747
7.723
7.684
7.666
7.644
7.525
7.512
7.505
7.487
7.485
7.467
7.465
7.455
7.444
7.438
7.432
7.243
7.223
7.205
7.144
7.126
7.108
7.074
7.056
7.037
7.020
4.588
4.567
4.546
4.047
4.023
4.012
3.991
3.832
3.816
3.806
3.795
3.619
3.604
3.583
3.569
3.341
3.031
3.008
2.998
2.975
2.864
2.844
2.830
2.811
2.504
2.504
2.499
2.495
2.495
-0.016
O
CN
O
TEMP= 20 °C
5.17
3.36
3.20
2.45
1.53
1.44
0.95
0.61
0.31
1.00
0.24
0.26
0.26
1.00
0.99
10
8
6
4
2
PPM


8.063
8.044
7.986
7.792
7.780
7.778
7.525
7.511
7.509
7.491
7.473
7.471
7.427
7.144
7.132
7.131
7.116
7.114
7.108
7.094
7.077
7.056
4.545
3.136
3.021
2.875
2.508
2.504
2.499
2.495
2.490
0.003


O
CN
O
TEMP= 70 °C
4.90
4.71
2.08
1.00
0.79
0.74
0.87
0.80
8
7
6
5
4
3
2
1
PPM

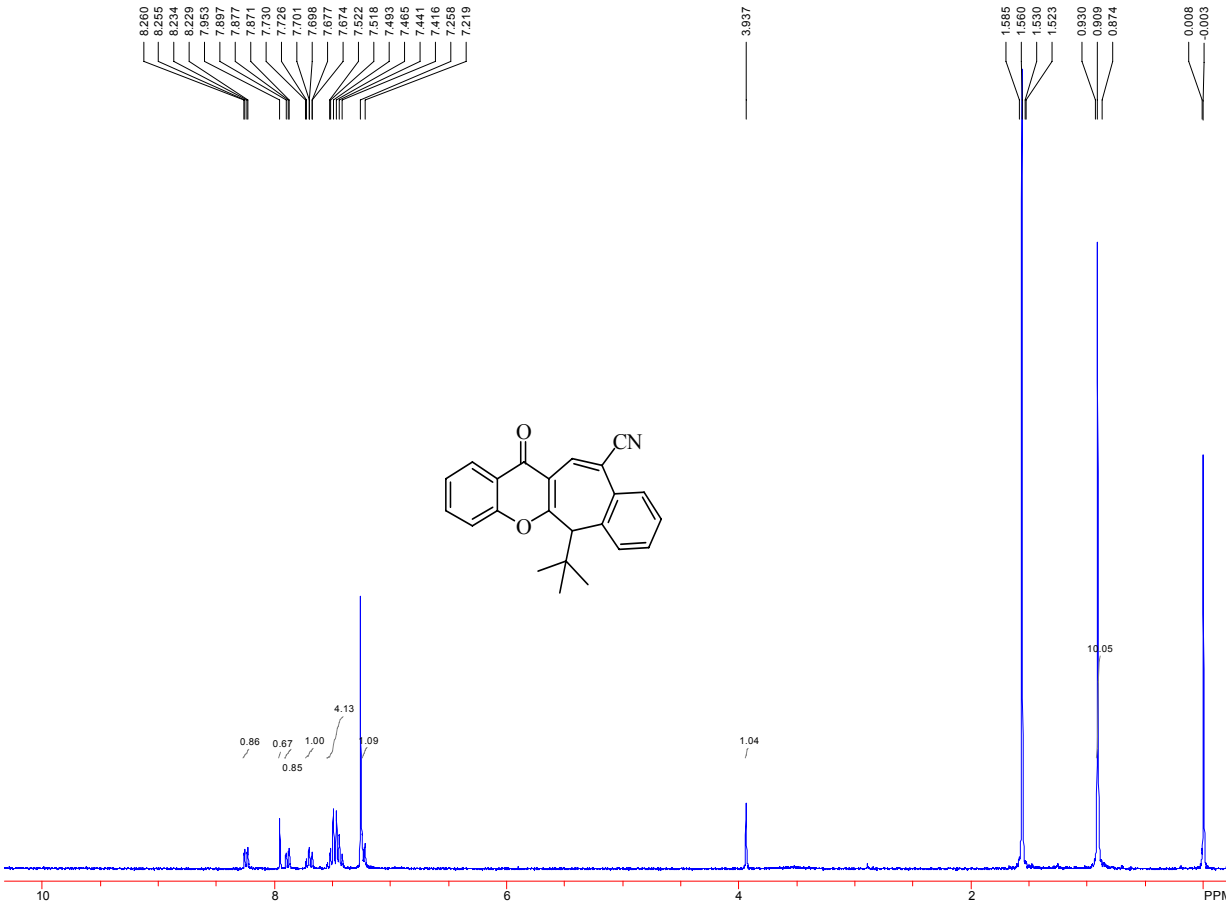

174.563
166.187
155.169
137.168
136.449
134.691
133.938
131.411
131.315
131.220
129.475
128.593
128.788
128.328
128.091
127.850
126.497
126.252
125.440
121.009
119.191
118.134
115.913
113.483
52.527
40.124
39.913
39.710
39.500
39.295
39.086
38.876
33.606

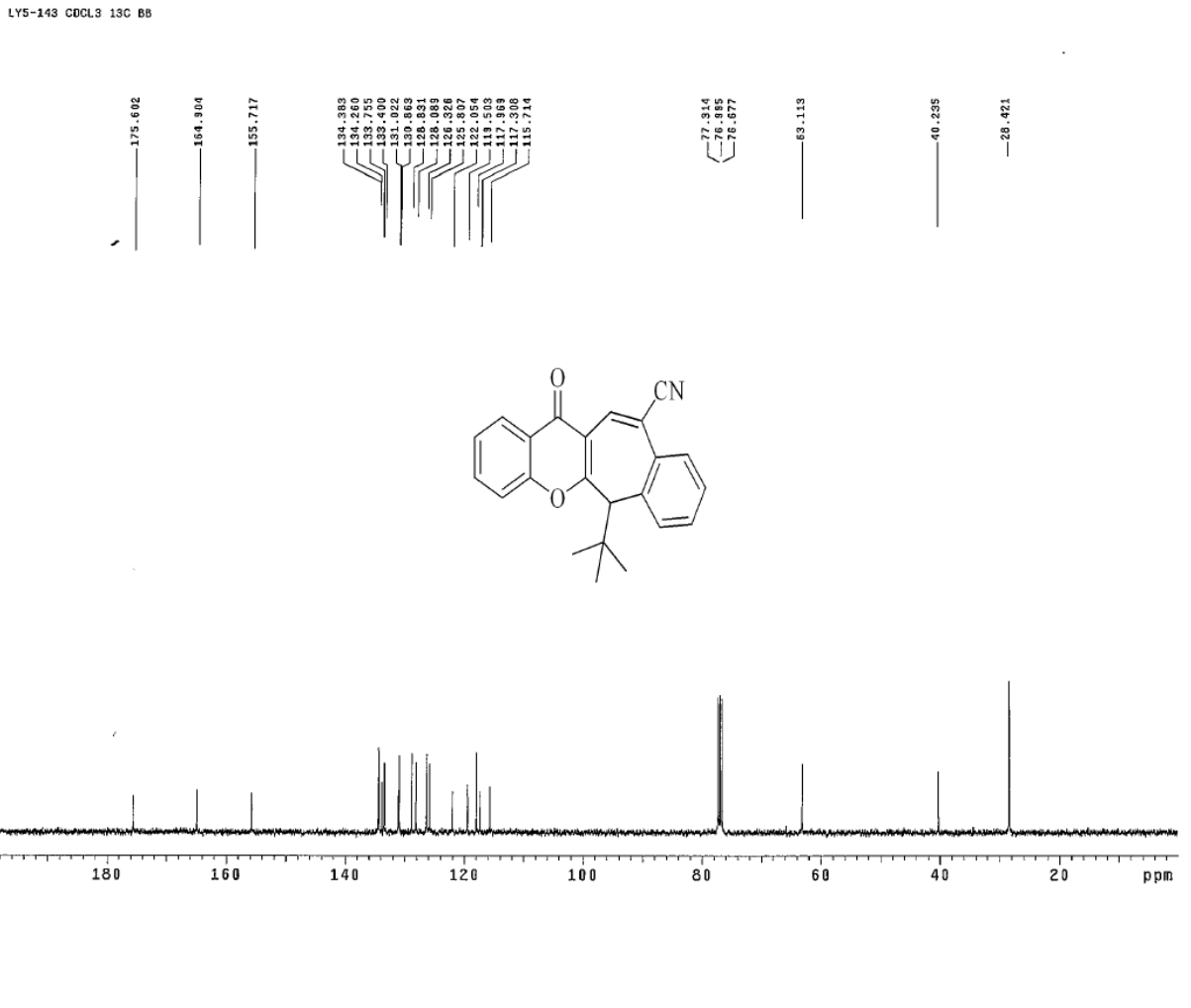

O
CN
O

TEMP= 20 °C

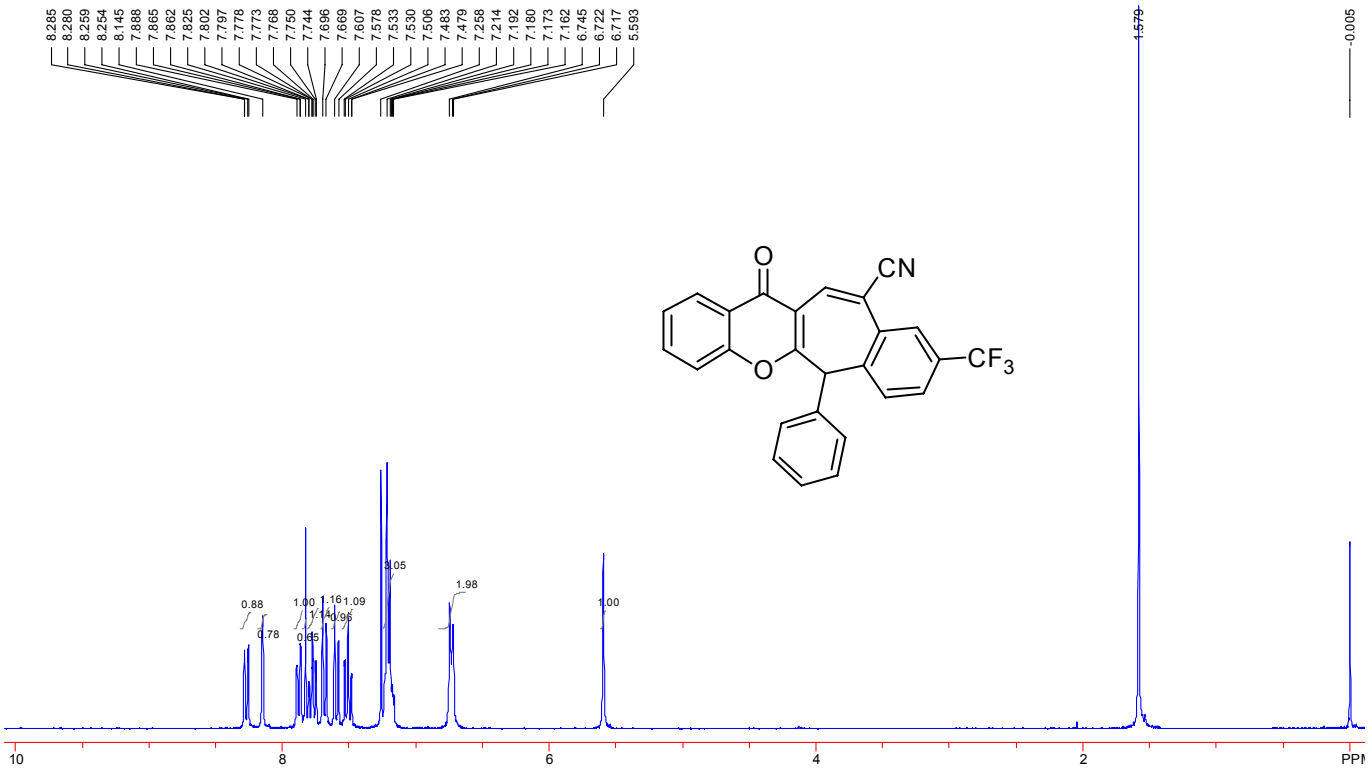
180
160
140
120
100
80
60
40
20
ppm

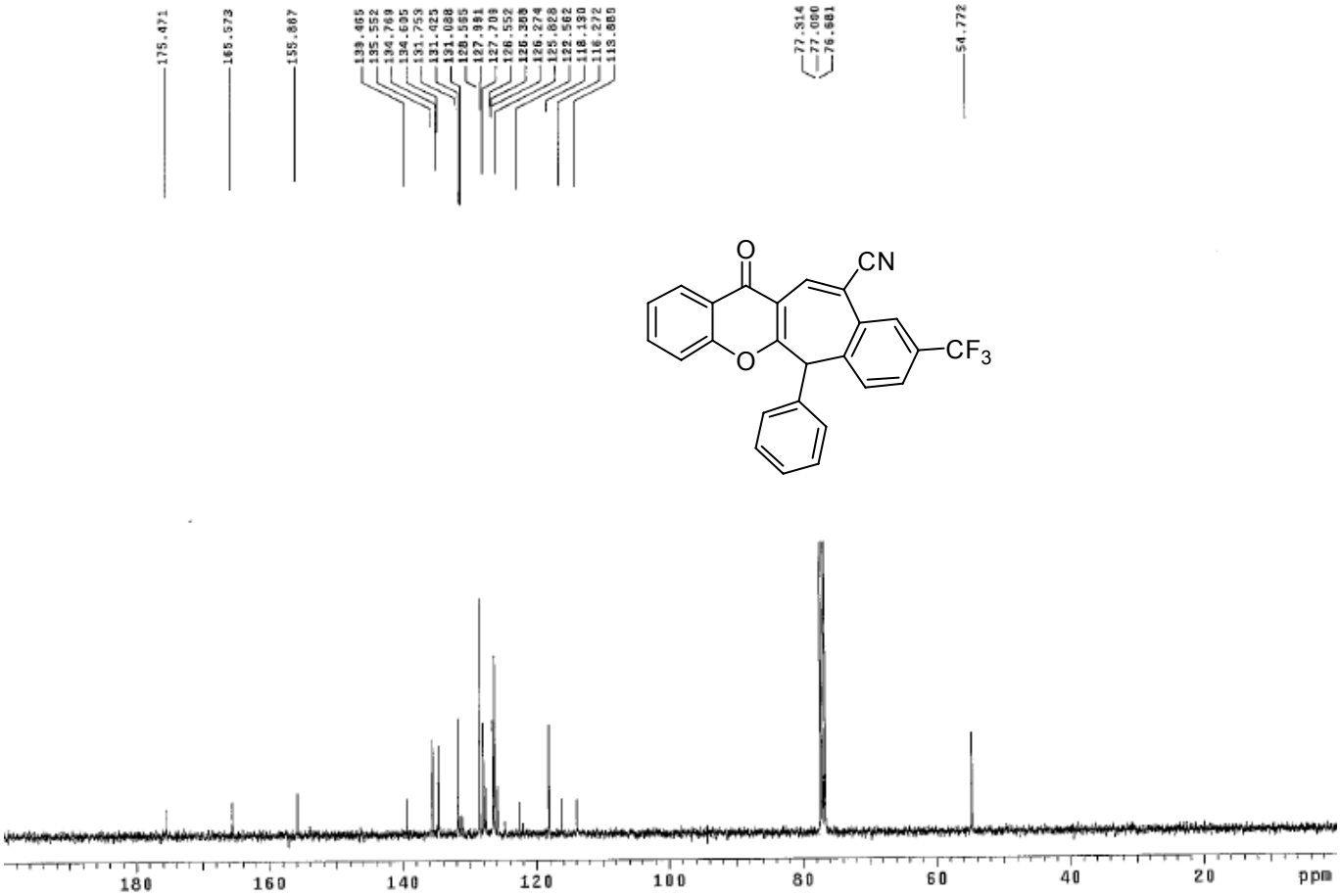
3ma


8.260
8.255
8.234
8.229
7.953
7.897
7.877
7.871
7.730
7.726
7.701
7.698
7.677
7.674
7.522
7.518
7.493
7.465
7.441
7.416
7.258
7.219
3.937
1.585
1.560
1.530
1.523
0.930
0.909
0.874
0.008
-0.003
O
CN
O
4.13
0.86
0.67
1.00
1.09
0.85
1.04
10.05
10
8
6
4
2
PPM


LY5-143 CDCL3 13C BB
175.602
164.904
155.717
134.383
134.260
133.755
133.400
131.022
130.863
128.831
128.089
126.326
125.837
122.054
119.503
117.969
117.308
115.714
77.314
76.985
76.677
63.113
40.295
28.421
O
CN
O
180
160
140
120
100
80
60
40
20
ppm

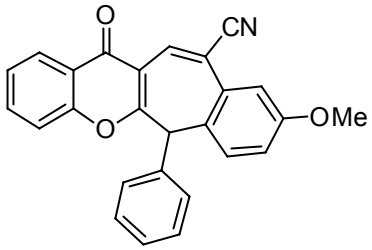
3ab

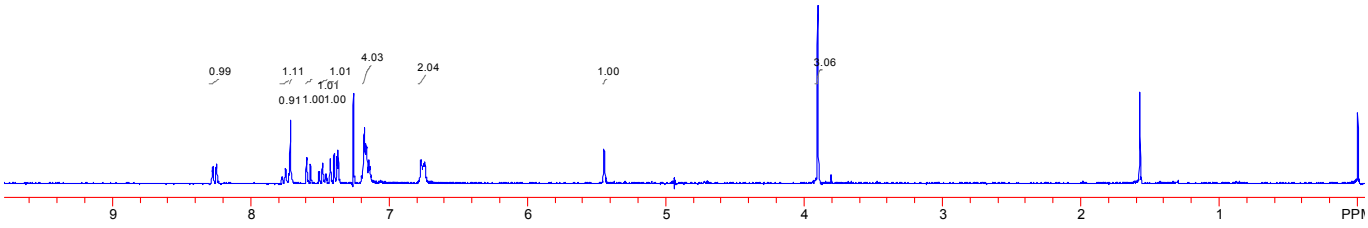

8.285
8.280
8.259
8.254
8.145
7.888
7.865
7.862
7.825
7.802
7.797
7.778
7.773
7.768
7.750
7.744
7.696
7.669
7.607
7.578
7.533
7.530
7.506
7.483
7.479
7.258
7.214
7.192
7.180
7.173
7.162
6.745
6.722
6.717
5.593
1.579
-0.005
O
CN
O
CF3
0.88
0.78
1.00
1.14
1.16
0.95
1.09
0.85
3.05
1.98
1.00
10
8
6
4
2
PPM


175.471
165.573
155.867
77.514
77.090
76.681
54.772
O
CN
O
CF3
180
160
140
120
100
80
60
40
20
ppm

3ac


8.274
8.247
7.773
7.771
7.748
7.725
7.721
7.713
7.597
7.595
7.569
7.504
7.480
7.456
7.424
7.397
7.376
7.369
7.257
7.250
7.193
7.184
7.176
7.167
7.162
7.146
7.139
6.767
6.750
6.742
5.445
3.901
1.572
-0.004


O
CN
O
OMe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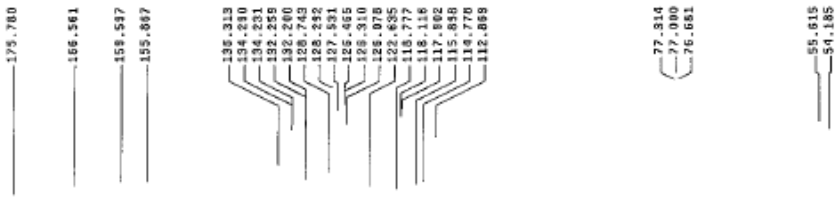
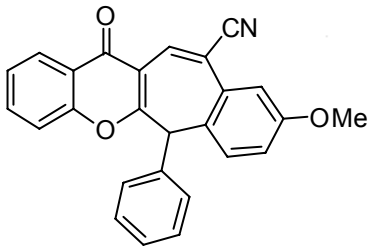
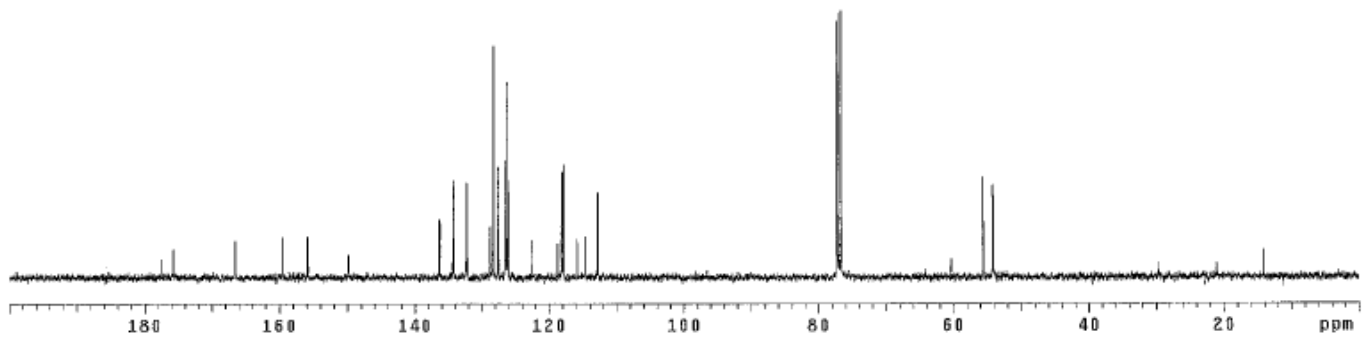
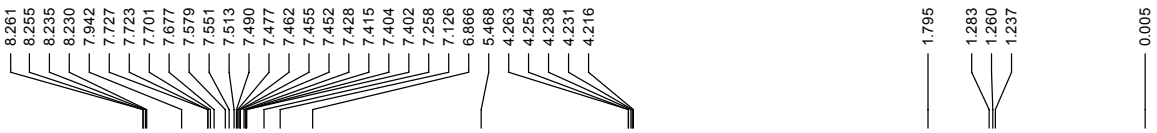
1.11
0.91
1.01
1.01
1.00
4.03
2.04
1.00
3.06
9
8
7
6
5
4
3
2
1
PPM

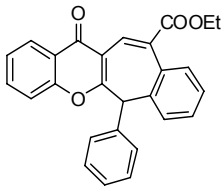

175.780
166.561
158.597
155.867
130.313
134.290
134.231
132.255
132.200
128.743
128.292
127.591
126.465
125.310
122.635
118.777
118.116
117.862
115.858
114.776
112.869
77.314
77.000
76.651
55.615
54.185

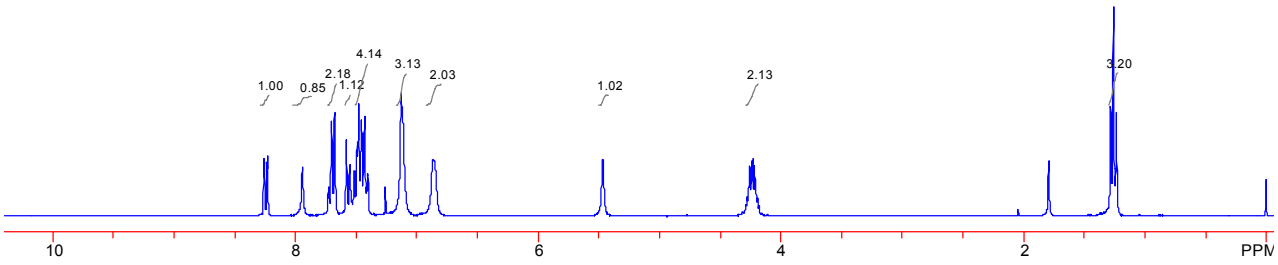

O
CN
O
OMe

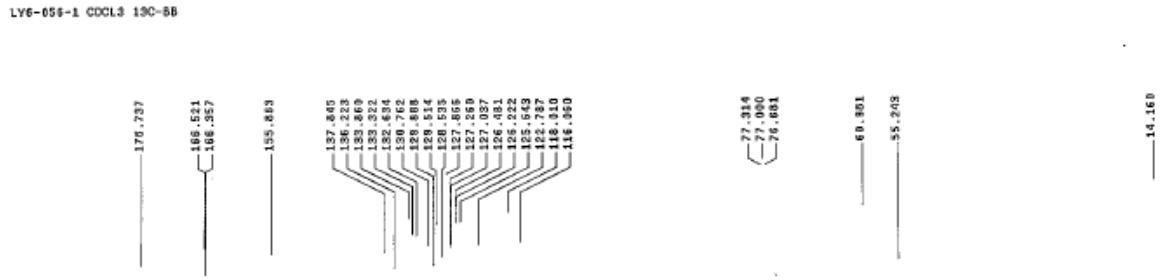

180
160
140
120
100
80
60
40
20
ppm

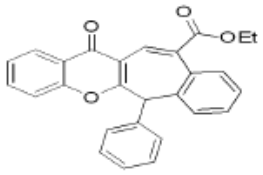
3ad

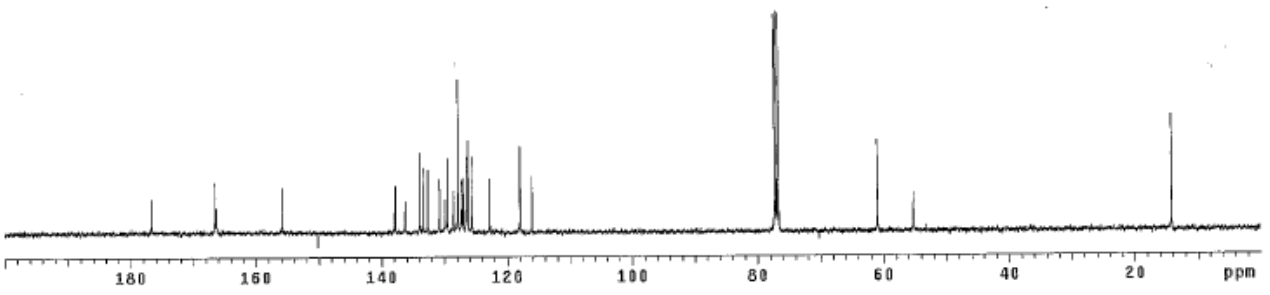

8.261
8.255
8.235
8.230
7.942
7.727
7.723
7.701
7.677
7.579
7.551
7.513
7.490
7.477
7.462
7.455
7.452
7.428
7.415
7.404
7.402
7.258
7.126
6.866
5.468
4.263
4.254
4.238
4.231
4.216
1.795
1.283
1.260
1.237
0.005


O
COOEt
O

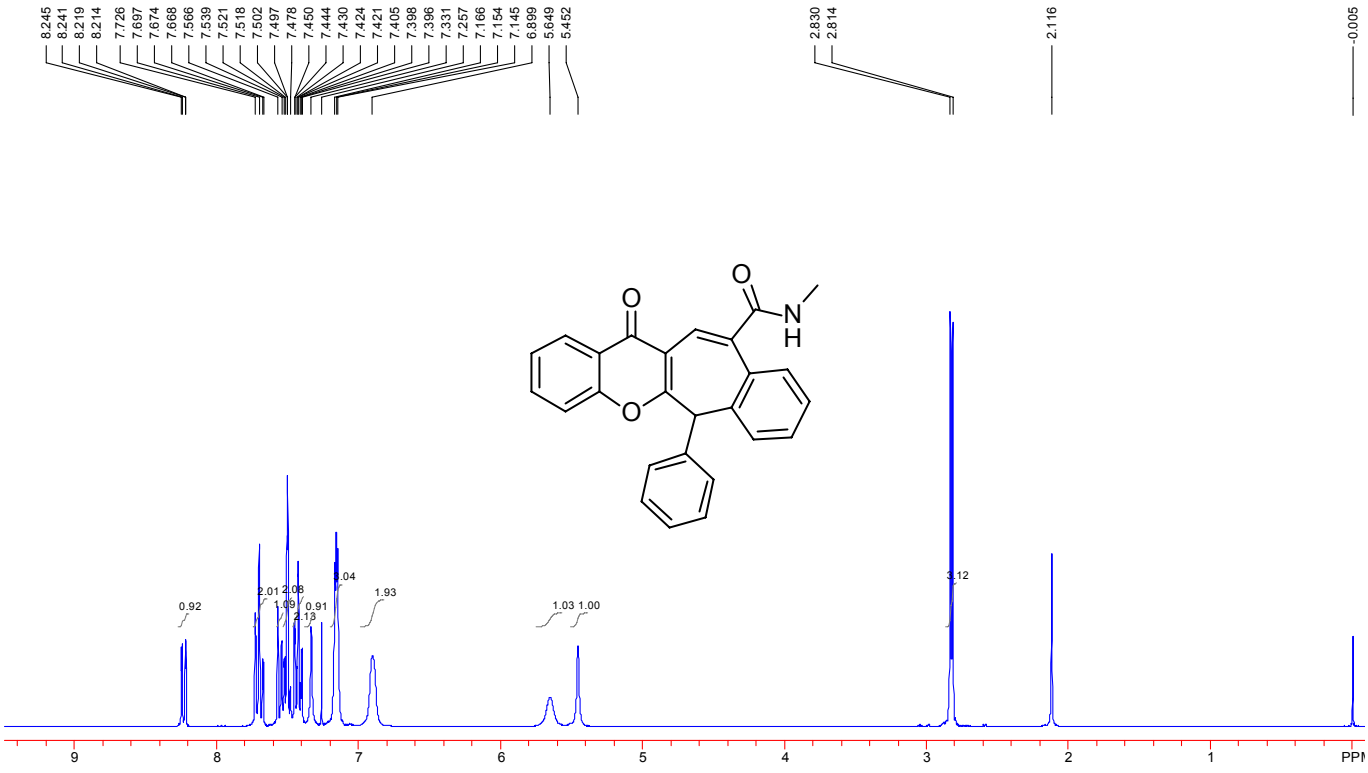

1.00
0.85
2.18
4.14
1.12
3.13
2.03
1.02
2.13
3.20
10
8
6
4
2
PPM

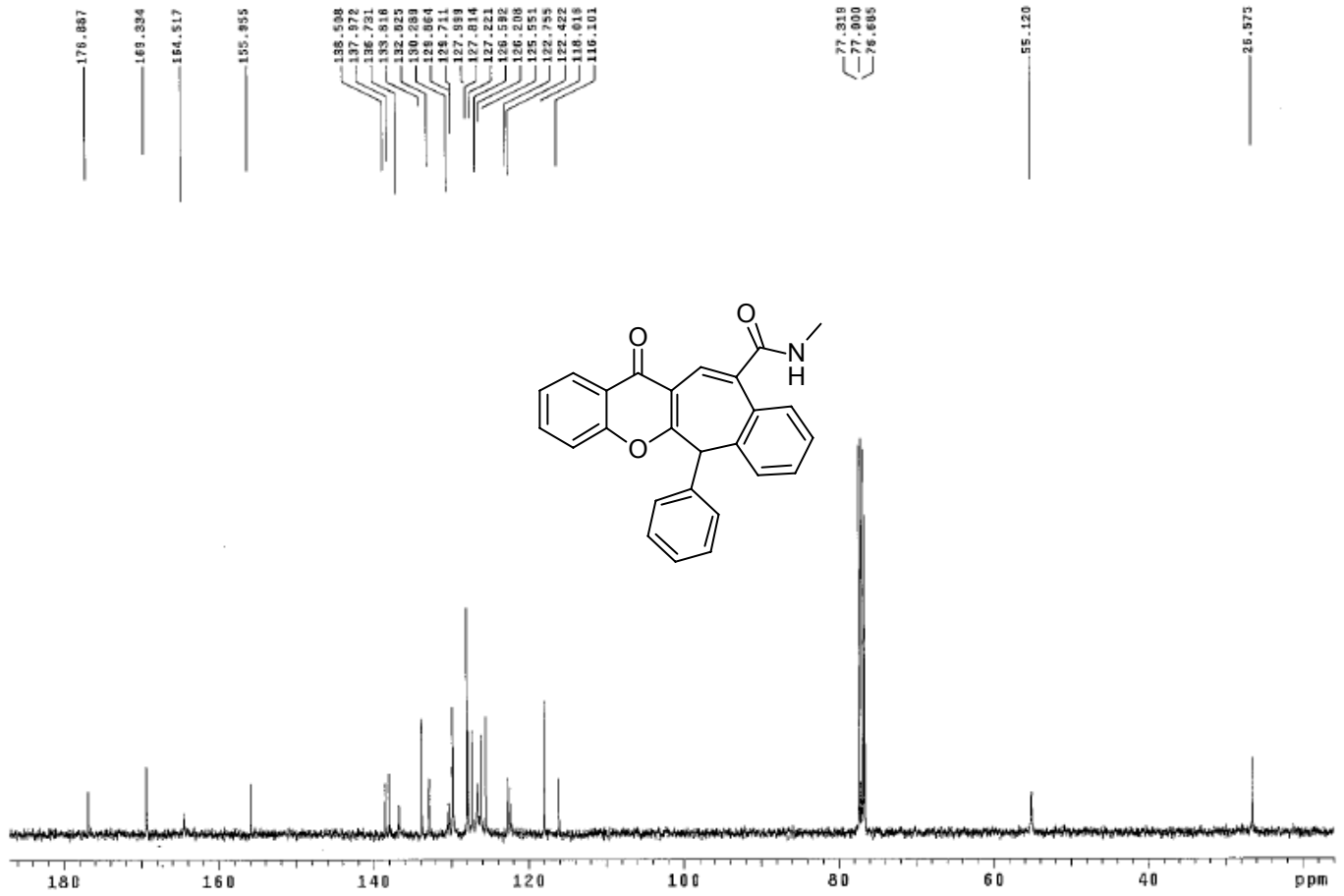

LY6-056-1 CDCL3 13C-BB
176.737
166.521
166.357
155.863
137.845
136.223
133.869
133.322
132.634
130.762
128.888
128.514
128.535
127.865
127.260
127.037
126.481
125.222
125.643
122.787
118.010
116.960
77.314
77.000
76.681
60.801
55.243
14.160


O
OEt
O


180
160
140
120
100
80
60
40
20
ppm

3ae


8.245
8.241
8.219
8.214
7.726
7.697
7.674
7.668
7.566
7.539
7.521
7.518
7.502
7.497
7.478
7.450
7.444
7.430
7.424
7.421
7.405
7.398
7.396
7.331
7.257
7.166
7.154
7.145
6.899
5.649
5.452
2.830
2.814
2.116
-0.005
O
O
N
H
0.92
2.01
2.08
1.09
0.91
2.13
1.04
1.93
1.03
1.00
3.12
9
8
7
6
5
4
3
2
1
PPM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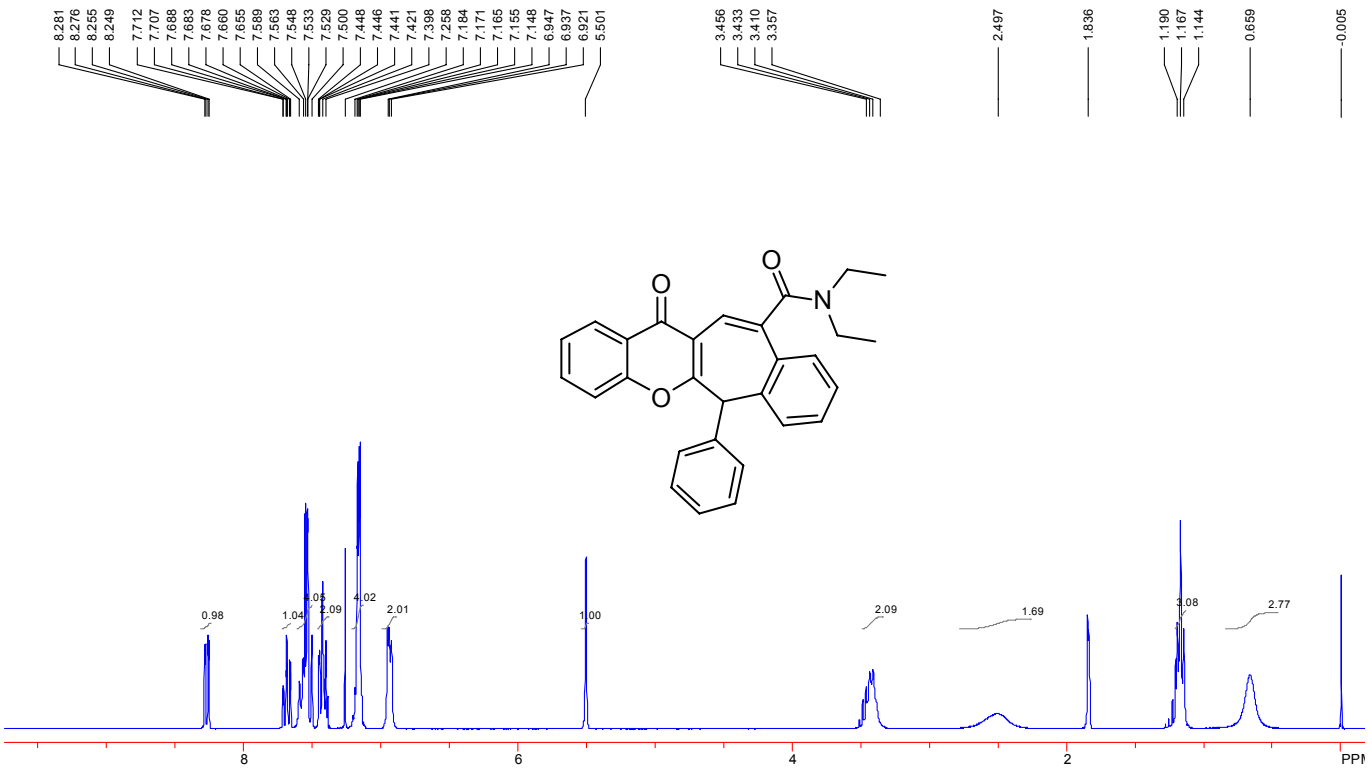
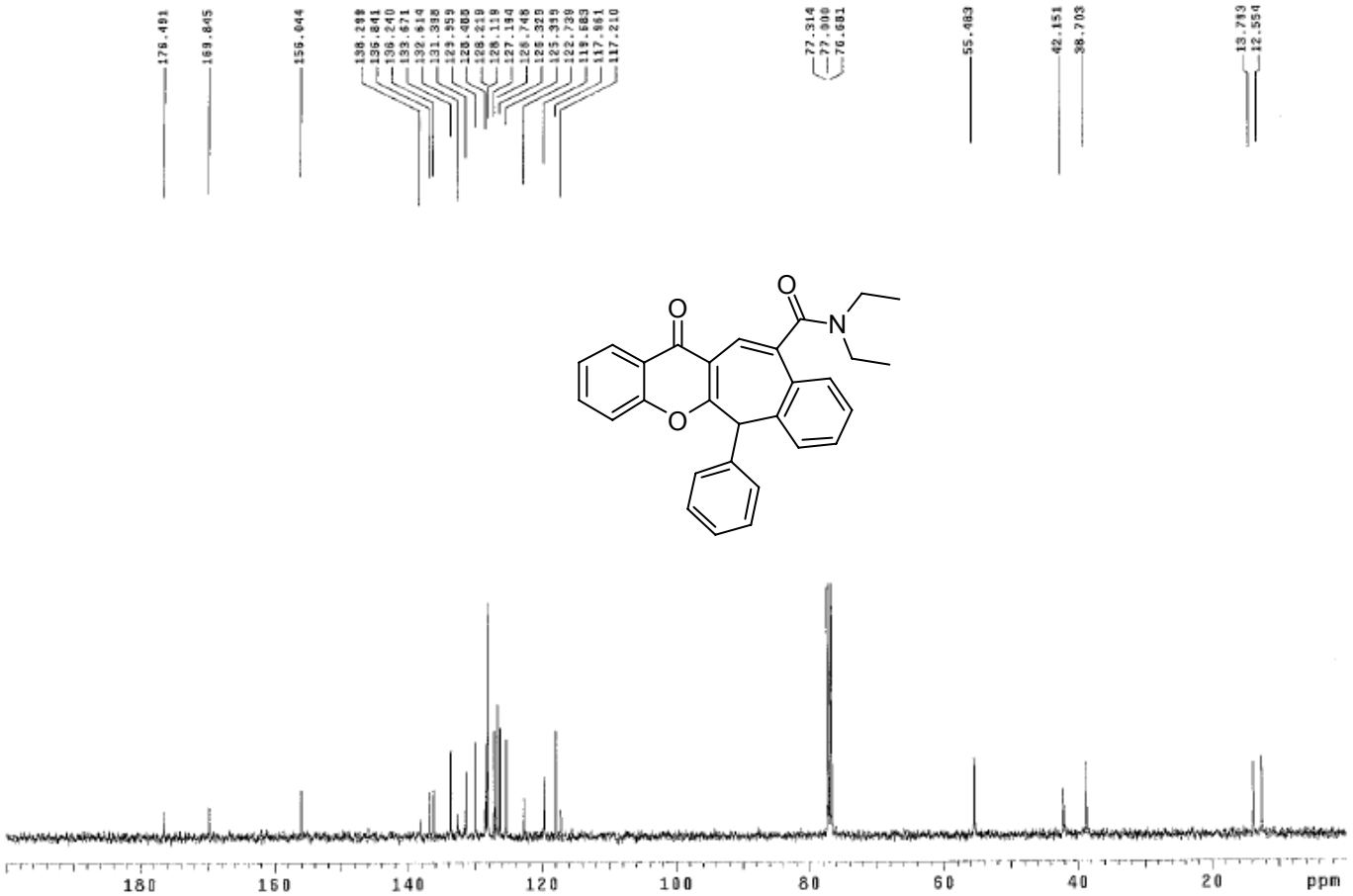
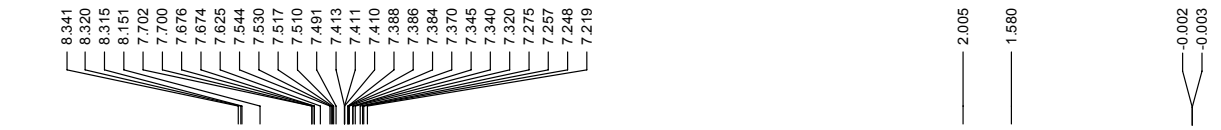
169.334
164.517
155.955
138.508
137.972
136.731
133.816
132.025
130.289
128.864
128.711
127.989
127.814
127.221
126.592
126.208
125.551
122.755
122.422
118.016
116.101
77.318
77.000
76.685
55.120
28.573
O
O
N
H
180
160
140
120
100
80
60
40
ppm

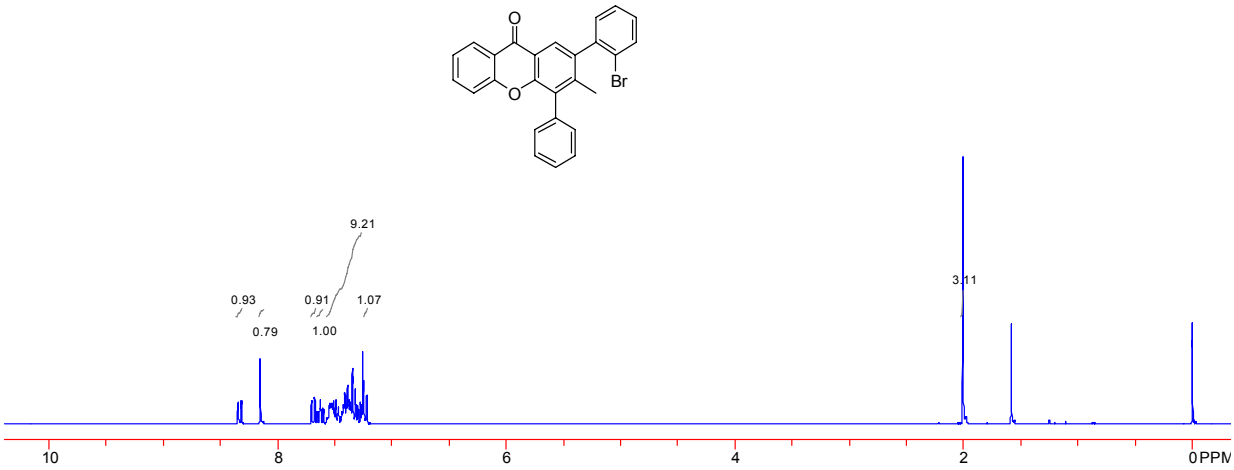
3af

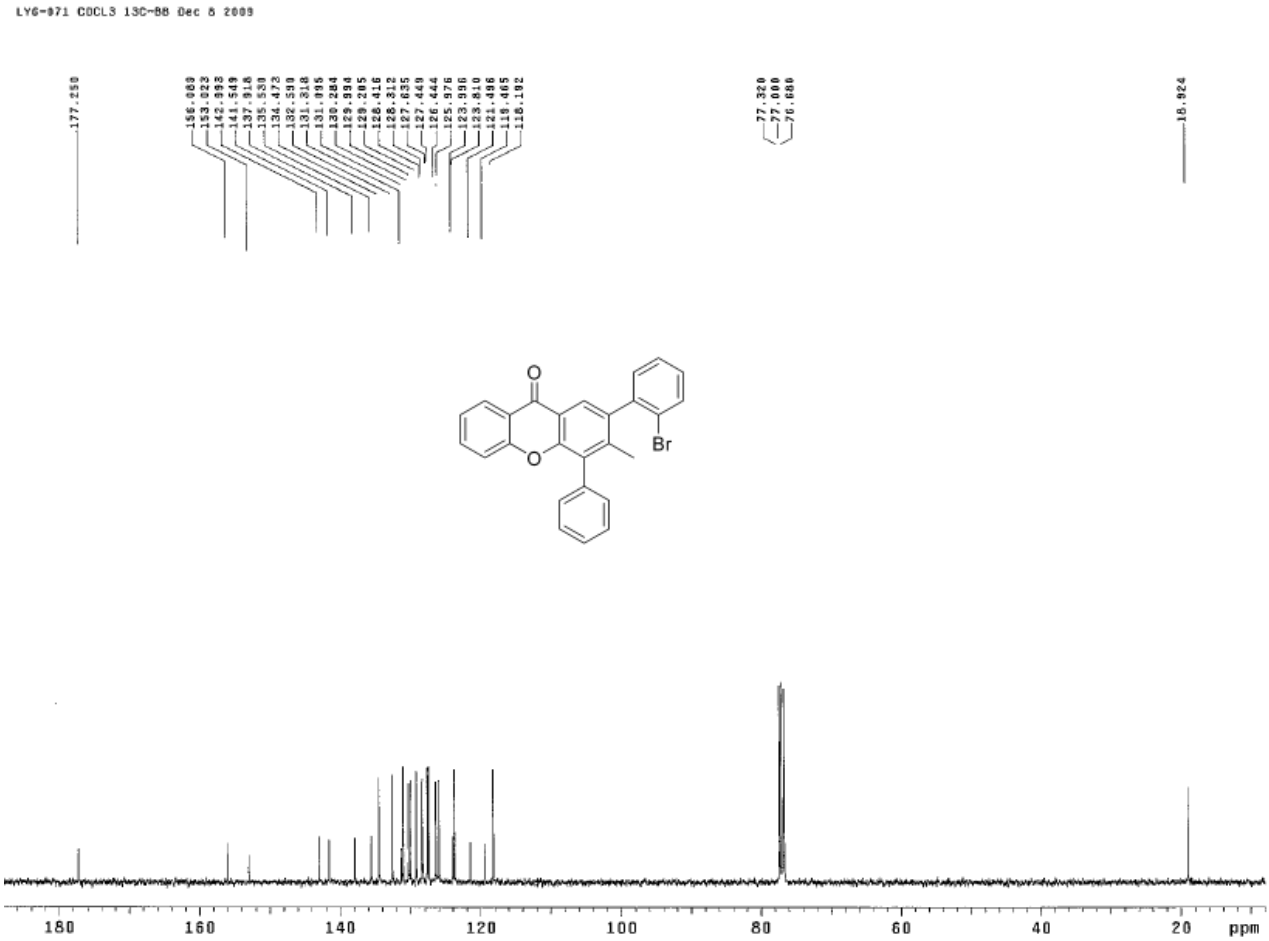

8.281
8.276
8.255
8.249
7.712
7.707
7.688
7.683
7.678
7.660
7.655
7.589
7.563
7.548
7.533
7.529
7.500
7.448
7.446
7.441
7.421
7.398
7.258
7.184
7.171
7.165
7.155
7.148
6.947
6.937
6.921
5.501
3.456
3.433
3.410
3.357
2.497
1.836
1.190
1.167
1.144
0.659
-0.005
O
O
N
0.98
1.04
3.05
2.09
4.02
2.01
1.00
2.09
1.69
3.08
2.77
8
6
4
2
PPM


176.491
169.845
156.044
138.218
136.841
136.240
133.671
132.614
131.388
129.959
128.480
128.219
128.119
127.194
126.748
126.329
125.349
122.739
119.683
117.801
117.210
77.314
77.000
76.681
55.483
42.151
38.703
13.713
12.554
O
O
N
180
160
140
120
100
80
60
40
20
ppm

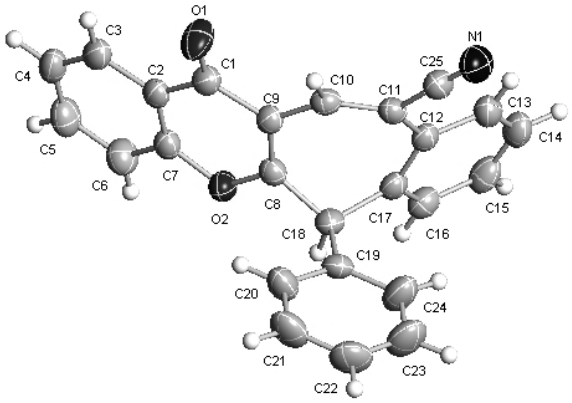
4b


8.341
8.320
8.315
8.151
7.702
7.700
7.676
7.674
7.625
7.544
7.530
7.517
7.510
7.491
7.413
7.411
7.410
7.388
7.386
7.384
7.370
7.345
7.340
7.320
7.275
7.257
7.248
7.219
2.005
1.580
-0.002
-0.003

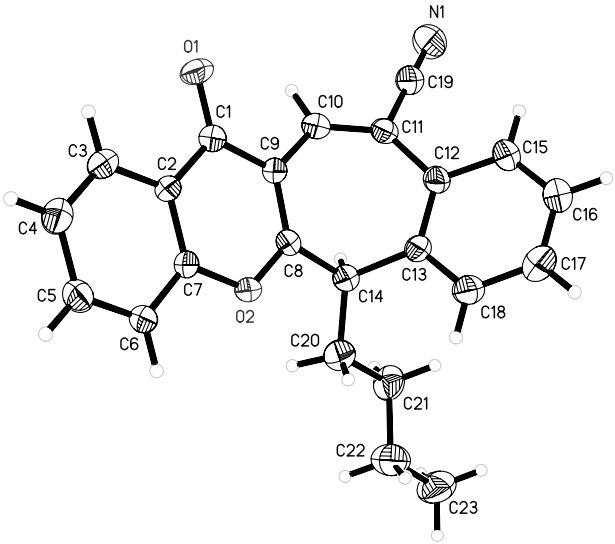

O
O
Br
9.21
0.93
0.91
1.07
0.79
1.00
3.11
10
8
6
4
2
0 PPM


LY6-071 CDCL3 13C-BB Dec 5 2009
177.250
156.060
153.023
142.993
141.549
137.916
135.530
134.473
132.590
131.318
131.095
130.284
129.934
129.205
128.416
128.312
127.635
127.469
126.444
125.976
123.996
123.810
121.496
119.465
118.192
77.320
77.000
76.680
18.924
O
O
Br
180
160
140
120
100
80
60
40
20
ppm

4. X-ray crystal structure of 3aa and 3ka



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



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