Supporting Information

High Pressure Diels-Alder Approach to Hydroxy-Substituted 6a-Cyano-Tetrahydro-6H-benzo[c]chromen-6-ones. A Route to Δ^6-*Cis*-Cannabidiol

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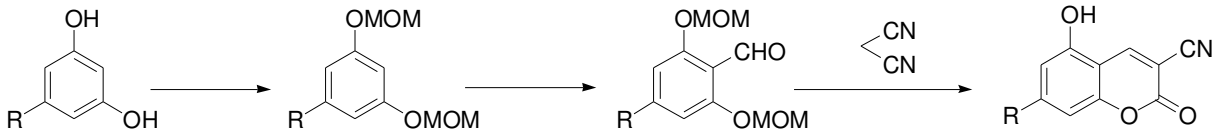
Experimental Section

NMR spectra were recorded at 400 or 200 MHz for proton and 100.6 or 50.3 MHz for carbon nuclei in $CDCl_3$ or CD_3COCD_3. GC-MS analyses were carried out by using a 70 eV electron energy EI. GC analyses were performed with an SPB-5 fused silica capillary column (30 m, 0.25 mm diameter) on an "on column" injector system and FID detector with hydrogen as the carrier gas. IR spectra were recorded with a FT-IR instrument, using $CHCl_3$ as solvent. Melting points are uncorrected. The 3-cyanocoumarins **1a**[1,2], **1c**[1b], **1d**[1]and **1e**[1] are known in the literature. The 3-cyanocoumarins **1b,h** were prepared by using Knoevenagel reaction in water between malonitrile and aldehyde **10b**[3] and **10h**[4], respectively[1], that were obtained from commercially available resorcinol **8b** and olivetol **8h** by protection of the phenolic groups and a subsequent formylation reaction. Mesylates **1f,g** were obtained by treating **1c,d** with methanesulfonylchloride according to the usual procedure[5]. Dienes **2** were purchased and used without further purification. The products were purified by column chromatography carried out on silica gel (230-400 mesh), using petroleum ether-ethyl acetate or petroleum ether-diethyl ether mixtures as eluent

The compounds **3ay**[6], **4ax,ay**[7], **5ax,ay**[7] and **4hy**[8] are known.

General procedure for preparing 3-cyanocoumarins 1b,h [1]



8b, R = H
h, R = C_5H_{11}

9b, R = H
h, R = C_5H_{11}

10b, R = H
h, R = C_5H_{11}

1b, R = H
h, R = C_5H_{11}

A three-necked round-bottom flask equipped with mechanical stirrer was charged with 0.22 mol of NaH (50 % suspension in mineral oil) under nitrogen atmpsphere. NaH was washed with 2 portions (100 mL) of n-hexane and then with 300 mL of dry diethyl ether; then 80 mL of anhydrous DMF were added. Then 0.09 mol of resorcinol **8b** or olivetol **8h,** dissolved in 100 mL of diethyl ether were added dropwise and the mixture was left under stirring at rt for 30 min. Then 0.18 mol of MOMCl were slowly added. After 1 h under stirring at rt, 250 mL of water were added and the organic layer was extracted with diethyl ether. The extracts were washed with brine, dried (Na_2SO_4), then concentrated to give the crude product that was purified by silical gel chromatography to give compound **9b** or **9h** (93 and 90 % yields, respectively).

A three-necked round-bottom flask was charged with 110 mL of n-hexane, 0.79 mol of BuLi and 9.4 mL of tetramethylethylendiamine (TMEDA) under nitrogen atmosphere. The mixture was cooled at –10 °C and 0.079 mol of bis-phenyl ether **9b** or **9h** were slowly added. The resulting mixture was left under magnetic stirring at –10 °C for 2 h. Then the temperature was raised to 0 °C and 0.067 mol of DMF were added dropwise. After 1 h, aqueous HCl was added until the pH was acidic; the mixture was then extracted with ethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated to give aldehyde **10b** or **10h** (84 and 80 % yields respectively).

2,6-bis(methoxymethoxy)benzaldehyde (10b): mp 58-59 °C (n-hexane); ; IR (KBr) ν: 1685 (C=O) cm^{-1}; 1H-NMR (400 MHz, $CDCl_3$) δ 3.51 (s, 6H, 2 OCH_3), 5.28 (s, 4H, 2 OCH_2O), 6.84 (d, 2H, J = 8.40 Hz, H-3, H-5), 7.41 (t, 1H, J = 8.40 Hz, H-4), 10.55 (s, 1H, CHO); MS, m/e (relative intensity) 226 (M^+, 3), 180 (4), 164 (14), 122 (2), 92 (2), 45 (100)**;** Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 57.98; H, 6.20.

2,6-bis(methoxymethoxy)-4-pentylbenzaldehyde (10h): mp 74-75 °C (n-hexane); IR (KBr) ν: 1678 (C=O) cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, J = 7.0 Hz, CH_3), 1.32 (m, 4H, CH_2CH_2), 1.60 (m, 2H, CH_2), 2.57 (t, 2H, J = 8.0 Hz, CH_2), 3.50 (s, 6H, 2 OCH_3), 5.25 (s, 4H, 2

OCH_2O), 6.66 (s, 2H, H-3, H-5), 10.48 (s, 1H, CHO); MS, m/e (relative intensity) 296 (M^+, 2), 251 (7), 234 (8), 178 (8), 164 (8), 45 (100); Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 65.02; H, 8.20.

A mixture of aldehyde **10b** or **10h** (10 mmol), malonitrile (0.80 g, 12.5 mmol) and 0.05 M aq $NaHCO_3$ solution (pH 8.3, 50 mL) were vigorously stirred at room temperature in a 100 mL round-bottom flask fitted with a mechanical stirrer for 24 h at rt. Then 25 mL of 37% HCl were added and the mixture was heated at 95 °C under stirring for 5 h. After cooling, the mixture was filtered under vacuum and the residue dried to obtain 3-cyanocoumarin **1b** or **1h** in 90 and 85 % yield, respectively.

3-Cyano-5-hydroxycoumarin (1b): Pale yellow solid, mp 159-160 °C (H_2O/EtOH); IR (KBr) ν: 2231 (CN), 1701 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 6.85 (dd, 1H, J = 4.17, 0.71 Hz, H-6), 6.91 (dd, 1H, J = 4.17, 0.40 Hz, H- 8), 7.59 (t, 1H, J = 4.17 Hz, H-7), 8.78 (s, 1H, H-4), 11.35 (s, 1H, OH)**;** ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 95.7, 100.8, 108.4, 108.6, 111.4, 115.1, 137.3, 148.5, 156.7, 157.6; Anal. Calcd for $C_{10}H_5NO_3$: C, 64.18; H, 2.96; N, 7.48. Found: C, 64.45; H, 2. 99; N, 7.39.

3-Cyano-5-hydroxy-7-pentylcoumarin (1h): Pale yellow solid, mp 173-174 °C ($CHCl_3$); IR (KBr) ν: 2225 (CN), 1737 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 0.88 (t, 3H, J = 6.7 Hz, CH_3), 1.33 (m, 4H, CH_2CH_2), 1.64 (m, 2H, CH_2), 2.66 (t, 2H, J = 7.5 Hz,CH_2), 6.77 (s, 2H, H-5, H-8), 8.74 (s, 1H, H-4). ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 14.2, 23.0, 31.0, 32.0, 36.9, 99.3, 106.8, 108.2, 111.6, 115.3, 148.4, 154.5, 156.3, 156.5, 157.9; Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.99; H, 5. 79; N, 5.44.

General procedure[5] for preparing of 6-mesyl-3-cyanocoumarins (1f) and 7-mesyl-3-cyanocoumarin (1g).

To a mixture of the hydroxy-3-cyanocoumarin **1c** or **1d** (3 mmol) in 20 mL of methylene chloride and 1.25 mL (9 mmol) of Et_3N, were added 0.46 mL (6 mmol) of methanesulfonylchloride. The resulting mixture was heated under stirring at 40 °C for 2h, then poured in water and extracted with methylene chloride. The combined extracts were washed with brine, dried (Na_2SO_4) and filtered. Evaporation of the solvent gave the crude product **1f** or **1g**, which was purified by cristallization (EtOH/EtOAc) (70 and 75 % yields respectively).

Methanesulfonic acid 3-cyano-2-oxo-2H-chromen-6 yl ester (6-mesyl-3-cyanocoumarin) (1f): Pale yellow solid, mp 163-164 °C (EtOH/EtOAc); ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 3.38 (s, 3H, SCH_3), 7.57 (d, 1H, J = 9.0 Hz, H-8), 7.77 (dd, 1H, J = 9.0, 2.8 Hz, H-7), 7.86 (d, 1H, J = 2.8 Hz, H-5), 8.82 (s, 1H, H-4). ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 37.7, 105.1, 114.6, 119.3, 119.5, 123.6, 130.0, 146.6, 152.8, 153.8, 157.0; Anal. Calcd for $C_{11}H_7NO_5S$: C, 49.81; H, 2.66; N, 5.28. Found: C, 49.87; H, 2.61; N, 5.25.

Methanesulfonic acid 3-cyano-2-oxo-2H-chromen-7 yl ester (7-mesyl-3-cyanocoumarin) (1g): Pale yellow solid, mp 161-162 °C (EtOH/EtOAc); ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 3.45 (s, 3H, SCH_3), 7.45 (dd, 1H, J = 8.4, 2.3 Hz, H-6), 7.47 (d, 1H, J = 2.3 Hz, H-8), 7.99 (d, 1H, J = 8.4 Hz, H-5), 8.83 (s, 1H, H-4). ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 38.3, 103.8, 111.7, 114.7, 117.5, 120.5, 132.4, 153.0, 154.7, 156.2, 157.0; Anal. Calcd for $C_{11}H_7NO_5S$: C, 49.81; H, 2.66; N, 5.28. Found: C, 49.75; H, 2.71; N, 5.31.

General procedure for the Diels-Alder reaction of 3-cyanocoumarins 1a-h with dienes 2x,y . The cycloadditions of **1** with **2** were accomplished (A) in water, toluene and SolFC at normal pressure and (B) under 11 kbar pressure conditions. Details are listed in Tables 1-3.

Conditions (A): Diene **2** (3 or 4 equiv) and few crystals of hydroquinone (1-2 mg) were added to a metal reactor containing coumarin **1** (0.3 mmol) and 3 mL of solvent (0.1 M). In the case of experiments without solvent (SolFC), diene **2** (7 or 10 equiv) and 1-2 mg of hydroquinone were added directly to coumarin **1**. The reactor was sealed and poured into an oil bath under magnetic stirring at the indicated reaction temperature and time. After cooling, the mixture was evaporated under vacuo and the residue was purified by column chromatography on silica gel followed by recrystallization.

Conditions (B): A solution of compound **1** (1.5 mmol), diene **2** (4 molar equiv) and a few crystals of hydroquinone in 10 ml of the appropriate solvent were placed in a 15 mL Teflon vial that was then filled with the solvent. The vial was closed and kept at 11 kbar at the indicated temperature for the appropriate time. After depressurizing, the solvent was removed in vacuo. The crude mixture

was purified by column chromatography on silica gel by using a mixture of petroleum ether/ethyl acetate (75/25) as eluent, followed by recrystallization.

Rel (6aR,10aS)-8,9-Dimethyl-6-oxo-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3ax): White solid, mp 84-85 °C (n-exane/chloroform); IR (KBr) ν: 2241 (CN), 1782 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.65 (s, 6H, 2 CH_3), 2.21 (dd broad, 1H, J = 17.6, 8.6 Hz, H-10α), 2.48 (dd broad, 1H, J = 17.6, 6.0 Hz, H-10β), 2.55 (d broad, 1H, J = 17.3 Hz, H-7α), 2.85 (d broad, 1H, , J = 17.3 Hz, H-7β), 3.45 (dd , 1H, J = 8.6, 6.0 Hz, H-10a), 7.10-7.39 (m, 4H, H-1, H-2, H-3, H-4); ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ 18.1, 18.5 (8-Me, 9-Me), 32.9, 34.4 (C-7, C-10), 37.6 (C-10a), 41.9 (C-6a), 116.8 (C-4), 117.3 (CN), 121.1, 123.1, 123.9 (C-8, C-9, C-10b), 125.4, 126.8 (C-2, C-3), 129.2 (C-1), 150.0 (C-4a), 162.4 (C-6); MS, m/e (relative intensity) 253 (M^+, 45), 121 (15), 120 (100), 115 (15), 82 (83), 77 (17), 67 (70). Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.83; H, 5. 99; N, 5.51.

Rel (6aR,10aS)-9-Methyl-6-oxo-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3ay): White solid, mp 97-98 °C (n-exane/ethyl acetate) (lit.[7b] mp 93-95°C); IR (KBr) ν: 2241 (CN), 1787 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.66 (s, 3H, CH_3), 2.17 (dd broad, 1H, J = 18.3, 8.0 Hz, H-10α), 2.36-2.64 (m, 2H, H-7α, H-10β), 2.85 (dddd, 1H, J = 17.6, 7.6, 3.7, 1.9 Hz, H-7β), 3.47 (dd , 1H, J = 8.0, 6.0 Hz, H-10a), 5.30 (s broad, 1H, H-8), 7.00-7.40 (m, 4H, H-1, H-2, H-3, H-4); ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ 23.0 (9-Me), 29.1 (C-10), 31.1 (C-7), 37.3 (C-10a), 41.0 (C-6a), 115.8, 116.9 (C-4, C-8), 117.3 (CN), 123.6 (C-10b), 125.5, 126.7 (C-2, C-3), 129.4 (C-1), 131.4 (C-9), 150.1 (C-4a), 162.6 (C-6); MS, m/e (relative intensity) 239 (M^+, 97), 210 (24), 172 (16), 120 (100), 77 (13), 68 (75). Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.39; H, 5. 45; N, 5.83.

Rel (6aR,10aS)-1-Hydroxy-8,9-dimethyl-6-oxo-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3bx): White solid, mp 173-174 °C (n-exane/ethyl acetate) ; IR ($CHCl_3$) ν: 2242 (CN), 1780 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.62 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.84 (m broad, 1H, H-10α), 2.41 (dd, 1H, J = 18.2, 6.2 Hz, H-10β), 2.80 (d broad, 1H, J = 17.6 Hz, H-7α), 3.05 (d broad, 1H, , J = 17.6 Hz, H-7β), 3.85 (dd , 1H, J = 11.4, 6.2 Hz, H-10a), 6.69 (dd, 1H, J = 8.2, 0.9 Hz, H-2), 6.83 (d, 1H, J = 8.2 Hz, H-4), 7.22 (t, 1H, J = 8.2 Hz, H-3), 9.26 (s broad, 1H,

OH); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 17.5, 17.6 (8-Me, 9-Me), 33.0 (C-10a), 33.3, 35.1 (C-7, C-10), 41.1 (C-6a), 107.7, 112.01 (C-2, C-4), 113.1 (C-10b), 117.5 (CN), 121.4, 123.0 (C-8, C-9), 129.3 (C-3), 151.4 (C-4a), 154.5 (C-1), 162.1 (C-6); MS, m/e (relative intensity) 269 (M^+, 79), 226 (12), 188 (15), 159 (10), 136 (873), 82 (100), 67 (54). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 70.83; H, 5. 99; N, 5.31.

Rel (6aR,10aS)-1-Hydroxy-9-Methyl-6-oxo-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3by): oil, IR (KBr) ν: 1776 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.67 (s, 3H, CH_3), 1.83 (m broad, 1H, H-10α), 2.45 (dd, 1H, J = 17.8, 5.8 Hz, H-10β), 2.80 (d broad, 1H, J = 18.4 Hz, H-7β), 3.19 (d broad, 1H, J = 18.4 Hz, H-7β), 3.90 (dd , 1H, J = 11.5, 6.2 Hz, H-10a), 5.45 (s broad, 1H, H-8),), 6.69 (d, 1H, J = 9.2 Hz, H-2), 6.84 (d, 1H, J = 9.2 Hz, H-4), 7.24 (t, 1H, J = 8.2 Hz, H-3),), 9.26 (s broad, 1H, OH); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 22.9 (9-Me), 30.7 (C-10), 32.7 (C-7), 33.8 (C-10a), 41.2 (C-6a), 108.7, 113.0 (C-2, C-4), 114.2 (C-10b), 117.2 (C-8), 118.6 (C- CN), 130.3 (C-3), 132.2 (C-9), 152.3 (C-4a), 155.4 (C-1), 162.6 (C-6); MS, m/e (relative intensity) 255 (M^+, 100), 226 (10), 212 (10), 187 (55), 159 (20), 136 (46), 68 (77). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.39; H, 5. 45; N, 5.63.

Rel (6aR,10aS)-2-Hydroxy-8,9-dimethyl-6-oxo-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3cx): White solid, mp 174-175 °C (n-exane/ethyl acetate) ; IR ($CHCl_3$) ν: 2242 (CN), 1772 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.65 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.23 (dd broad, 1H, J = 18.7, 7.9 H-10α), 2.53 (dd broad, 1H, J = 18.7, 6.1 Hz, H-10β), 2.56 (d, 1H, J = 16.6 Hz, H-7α), 2.74 (d, 1H, , J = 16.6 Hz, H-7β), 3.67 (dd , 1H, J = 7.9, 6.1 Hz, H-10a), 6.85 (dd, 1H, J = 8.6, 2.8 Hz, H-3), 6.88 (d, 1H, J = 2.8 Hz, H-1), 7.00 (d, 1H, J = 8.6 Hz, H-3), 8.62 (s broad, 1H, OH); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 17.5, 17.9 (8-Me, 9-Me), 32.5, 34.4 (C-7, C-10), 37.2 (C-10a), 42.2 (C-6a), 113.5 (C-3), 115.5 (C-1), 117.5 (C-4), 117.7 (CN), 121.2, 1234, 125.6 (C-8, C-9, C-10b), 143.4 (C-4a), 154.7 (C-2), 162.9 (C-6); MS, m/e (relative intensity) 269 (M^+, 52), 240 (20), 226 (11), 187 (28), 159 (9), 136 (100), 82 (23). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 70.95; H, 5. 89; N, 5.42.

Rel (6aR,10aS)-4-Hydroxy-8,9-dimethyl-6-oxo-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3ex): White solid, mp 141-142 °C (n-exane/ethyl acetate) ; IR ($CHCl_3$) ν: 2242 (CN), 1778 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.65 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 2.25 (dd broad, 1H, 18.3, 8.0 Hz, H-10α), 2.52 (dd broad, 1H, J = 18.3, 6.1 Hz, H-10β), 2.59 (d, 1H, J = 17.3

Hz, H-7α), 2.77 (d, 1H, , J = 17.3 Hz, H-7β), 3.72 (dd , 1H, J = 8.0, 6.1 Hz, H-10a), 6.89 (dd, 1H, J = 7.6, 1.5 Hz, H-3), 6.97 (dd, 1H, J = 8.2, 1.5 Hz, H-1), 7.08 (t, 1H, J = 8.1 Hz, H-2), 8.80 (s broad, 1H, OH); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 17.5, 17.9 (8-Me, 9-Me), 32.7, 34.4 (C-7, C-10), 37.4 (C-10a) 42.2 (C-6a), 116.8, 117.5 (C-1, C-3), 117.6 (CN), 121.1, 123.5, (C-8, C-9), 125.6 (C-2), 125.7 (C-10b), 138.4 (C-4a), 144.9 (C-4), 162.4 (C-6); MS, m/e (relative intensity) 269 (M^+, 71), 240 (18), 226 (29), 187 (13), 136 (100), 82 (39), 67 (23). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.73; H, 5. 29; N, 5.15.

Rel (6aR,10aS)-4-Hydroxy-9-Methyl-6-oxo-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3ey): White solid, mp 190-191 °C (n-exane/ethyl acetate), IR ($CHCl_3$) ν: 1775 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.73 (s, 3H, CH_3), 2.30 (dd broad, 1H, J = 18.3, 7.4 Hz H-10α), 2.54 (dd broad, 1H, J = 18.3, 6.0 Hz, H-10β), 2.62 (d broad, 1H, J = 17.6 Hz, H-7β), 2.81 (d broad, 1H, J = 18.4 Hz, H-7β), 3.80 (dd , 1H, J = 7.4, 6.0 Hz, H-10a), 5.37 (s broad, 1H, H-8),), 6.90 (dd, 1H, J = 8.9, 1.5 Hz, H-3), 6.98 (dd, 1H, J = 8.2, 1.5 Hz, H-1), 7.09 (t, 1H, J = 7.9 Hz, H-2), 8.77 (s broad, 1H, OH); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 23.2 (9-Me), 30.4, 31.7 (C-7, C-10), 38.0 (C-10a), 42.2 (C-6a), 116.8, 117.7, 118.2 (C-1, C-3, C-8), 118.6 (CN), 126.4 (C-10b), 126.6 (C-2), 132.7 (C-9), 139.1 (C-4a), 145.8 (C-4), 163.2 (C-6); MS, m/e (relative intensity) 255 (M^+, 100), 226 (35), 212 (32), 187 (39), 159 (15), 136 (84), 68 (21). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.22; H, 5. 11; N, 5.48.

Rel Methanesulfonic acid (6aR,10aS)-6a-cyano-8,9-dimethyl-6-oxo-6a,7,10,10a-tetrahydro-6H-benzo[c]chromen-2yl ester (3fx): Pale yellow solid, mp 112-113 °C (n-exane/ethyl acetate) ; IR ($CHCl_3$) ν: 2244 (CN), 1784 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.64(s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.38 (dd broad, 1H, J = 18.1, 6.7 Hz, H-10α), 2.62 (m, 2H, H-10β, H-7α), 2.70 (d broad, 1H, , J = 17.3 Hz, H-7β), 3.31 (s , 3H, SCH_3), 3.90 (t, 1H, J = 6.7 Hz, H-10a), 7.29 (d, 1H, J = 8.8 Hz, H-4), 7.42 (dd, 1H, J = 8.8, 2.8 Hz, H-3), 7.47 (d, 1H, J = 2.8 Hz, H-1); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 18.3, 18.7 (8-Me, 9-Me), 32.6, 34.9 (C-7, C-10), 37.5 (OSO_2CH_3), 37.6 (C-10a), 42.9 (C-6a), 118.2 (CN), 119.1 (C-4), 122.0, 124.2, 126.9 (C-8, C-9, C-10b), 122.1 (C-3), 124.1 (C-1), 147.3 (C-4a), 149.9 (C-2), 163.2 (C-6); MS, m/e (relative intensity) 347 (M^+, 44), 268 (21), 240 (17), 214 (100), 135 (26), 82 (52), 79 (12), 67 (25). Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.78; H, 4.93; N, 4.03; S, 9.23. Found: C, 58.83; H, 5. 09; N, 4.22; S, 9.33.

Rel (Methanesulfonic acid (6aR,10aS)-6a-cyano-9-methyl-6-oxo-6a,7,10,10a-tetrahydro-6H-benzo[c]chromen-2yl ester (3fy): Pale yellow solid, mp 100-101 °C (n-exane/ethyl acetate); IR ($CHCl_3$) ν: 2244 (CN), 1782 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.76 (s, 3H, CH_3), 2.45 (dd broad, 1H , J = 18.0, 6.6 Hz, H-10α), 2.64 (m, 2H, H-10β, H-7α), 2.73 (d broad, 1H, , J = 16.5 Hz, H-7β), 3.31 (s , 3H, SCH_3), 3.98 (t, 1H, J = 6.4 Hz, H-10a), 5.38 (s broad, 1 H, H-8), 7.29 (d, 1H, J = 8.8 Hz, H-4), 7.42 (dd, 1H, J = 8.8, 2.7 Hz, H-3), 7.49 (d, 1H, J = 2.7 Hz, H-1); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 23.2 (9-Me), 29.6, 30.7 (C-7, C-10), 37.3 (OSO_2CH_3), 37.6 (C-10a), 42.0 (C-6a), 116.7 (C-4), 118.2 (CN), 119.1, 122.1, 124.2 (C-1, C-3, C-8), 126.7, 132.6 (C-9, C-10b), 147.4 (C-4a), 149.9 (C-2), 163.4 (C-6); MS, m/e (relative intensity) 333 (M^+, 100), 254 (78), 226 (47), 214 (59), 199 (52), 186 (23), 128 (18), 68 (28). Anal. Calcd for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.54; N, 4.20; S, 9.62. Found: C, 57.77; H, 4. 65; N, 4.31; S, 9.35

Rel Methanesulfonic acid (6aR,10aS)-6a-cyano-8,9-dimethyl-6-oxo-6a,7,10,10a-tetrahydro-6H-benzo[c]chromen-3yl ester (3gx): Pale yellow oil; IR ($CHCl_3$) ν: 2244 (CN), 1787 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.64 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.39 (m broad, 1H, H-10α), 2.59 (m, 2H, H-10β, H-7α), 2.72 (d broad, 1H, , J = 18.3 Hz, H-7β), 3.36 (s , 3H, OSO_2CH_3), 3.88 (t, 1H, J = 6.7 Hz, H-10a), 7.22 (d, 1H, J = 2.4 Hz, H-4), 7.26 (dd, 1H, J = 8.4, 2.4 Hz, H-2), 7.58 (d, 1H, J = 8.4 Hz, H-1); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 17.4, 17.8 (8-Me, 9-Me), 31.8, 33.9 (C-7, C-10), 36.4 (C-10a), 36.9 (OSO_2CH_3), 42.1 (C-6a), 111.1 (C-4), 117.3 (CN), 119.1 (C-2), 121.0, 123.3 (C-8, C-9, C-10b), 128.5 (C-1), 149.5 (C-4a), 150.8 (C-3), 162.2 (C-6); MS, m/e (relative intensity) 347 (M^+, 24), 214 (94), 187 (13), 135 (6), 82 (100), 67 (42). Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.78; H, 4.93; N, 4.03; S, 9.23. Found: C, 59.03; H, 5. 19; N, 4.13; S, 9.15.

Rel Methanesulfonic acid (6aR,10aS)-6a-cyano-9-methyl-6-oxo-6a,7,10,10a-tetrahydro-6H-benzo[c]chromen-3yl ester (3gy): Pale yellow solid; mp 134-135 °C (n-exane/ethyl acetate); IR ($CHCl_3$) ν: 2244 (CN), 1789 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$] δ 1.76 (s, 3H, CH_3), 2.46 (dd broad, 1H, J = 18.3, 6.1 Hz, H-10α), 2.61 (d broad, 2H, J = 17.3 Hz, H-10β, H-7α), 2.71 (d broad, 1H, J = 15.7 Hz, H-7β), 3.36 (s , 3H, OSO_2CH_3), 3.97 (t, 1H, J = 6.1 Hz, H-10a), 5.38 (s broad, 1H, H-8), 7.23 (d, 1H, J = 2.3 Hz, H-4), 7.27 (dd, 1H, J = 8.4, 2.3 Hz, H-2), 7.60 (d, 1H, J = 8.4 Hz, H-1); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 22.4 (9-Me), 28.8, 29.9 (C-7, C-10), 36.2 (C-10a), 37.0 (OSO_2CH_3), 41.4 (C-6a), 111.2 (C-4), 115.8 (C-2), 117.4 (CN), 119.3 (C-8), 123.1 (C-10b), 128.5 (C-1), 131.7 (C-9), 149.7 (C-4a), 151.0 (C-3), 162.4 (C-6); MS, m/e (relative intensity)

333 (M^+, 59), 265 (26), 214 (59), 187 (64), 68 (100). Anal. Calcd for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.54; N, 4.20; S, 9.62. Found: C, 57.77; H, 4. 65; N, 4.31; S, 9.35

Rel (6aR,10aS)-1-Hydroxy-8,9-dimethyl-6-oxo-3-penthyl-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3hx): oil ; IR (KBr) ν: 2260 (CN), 1780 (C=O) cm^{-1}; ^{1}H-NMR [200 MHz, ($CDCl_3$] δ 0.89 (s, 3H, CH_3), 1.10-1.45 (m, 4H, CH_2CH_2), 1.45-1.75 (m, 2H CH_2), 1.59 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.86 (dd broad, 1H, J = 18.3, 11.4 Hz H-10α), 2.39 (dd, 1H, J = 18.3, 6.2 Hz, H-10β), 2.52 (t, 2H, J = 7.3 Hz, $ArCH_2$), 2.66 (d broad, 1H, J = 17.5 Hz, H-7α), 3.14 (d broad, 1H, J = 17.5 Hz, H-7β), 3.72 (dd , 1H, J = 11.4, 6.2 Hz, H-10a), 5.75 (s broad, 1H, OH), 6.45 (d, 1H, J = 1.3 Hz, H-4), 6.55 (d, 1H, J = 1.3 Hz, H-2); ^{13}C-NMR (50.3 MHz, $CHCl_3$) δ13.9 (C-5'), 18.3, 18.6 (8-Me, 9-Me), 22.4 (C-4'), 30.5, 31.4 (C-2', C-3'), 33.4 (C-10a), 33.8 (C-10), 35.7 (C-1', C-7), 41.3 (C-6a), 109.2 (C-4), 110.3 (C-10b), 112.2 (C-2), 117.7 (CN), 121.4, 123.4 (C-8, C-9), 145.2 (C-3), 151.2 (C-4a), 152.6 (C-1), 162.5 (C-6); MS, m/e (relative intensity) 339 (M^+, 39), 338 (31), 258 (20), 206 (26), 201 (56), 82 (100), 77 (9), 67 (33). Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.64; H, 7. 99; N, 4.31.

Rel (6aR,10aS)-1-Hydroxy-9-methyl-6-oxo-3-penthyl-10,10a-dihydro-7H-benzo[c]chromen-6a-carbonitrile (3hy): white solid; mp 139-140 °C (n-exane/ethyl acetate); IR (KBr) ν: 2400 (CN), 1772 (C=O) cm^{-1}; ^{1}H-NMR [200 MHz, ($CDCl_3$] δ 0.94 (s, 3H, CH_3), 1.10-1.50 (m, 4H, CH_2CH_2), 1.50-2.00 (m, 3H, CH_2, H-10α), 1.66 (s, 3H CH_3), 2.41 (dd broad, 1H, J = 18.1, 6.2 Hz, H-10β), 2.54 (t, 2H, J = 7.3 Hz, $ArCH_2$), 2.68 (d broad, 1H, J = 17.9 Hz, H-7α), 3.29 (d broad, 1H, J = 17.9 Hz, H-7β), 3.76 (dd , 1H, J = 11.4, 6.2 Hz, H-10a), 5.40 (m, 1H, H-8), 5.64 (s broad, 1H, OH), 6.47 (d, 1H, J = 1.3 Hz, H-4), 6.57 (d, 1H, J = 1.3 Hz, H-2); ^{13}C-NMR (50.3 MHz, $CHCl_3$) δ 13.9 (C-5'), 22.4 (C-4'), 22.8 (9-Me), 30.2, 30.5, 31.4, 32.3 (C-2', C-3', C-7, C-10), 33.1 (C-10a), 35.6 (C-1'), 40.4 (C-6a), 109.0 (C-4), 110.2 (C-10b), 112.3 (C-2), 116.0 (C-8), 117.7 (CN), 131.6 (C-9), 145.2 (C-3), 151.1 (C-4a), 152.8 (C-1), 162.4 (C-6); MS, m/e (relative intensity) 325 (M^+, 38), 269 (27), 257 (23), 201 (100), 173 (6), 150 (8), 77 (10), 68 (37). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 74.04; H, 6. 99; N, 4.31.

General Procedure for the Decyanation Reaction of Diels-Alder Cycloadducts 3bx,cx,ex,hy.

Cycloadduct **3** (0.15 mmol) was added to a 0.05 M aqueous solution of $NaHCO_3$ (3 mL) in a metal reactor and the mixture was heated at 150 °C (6 h for **3bx,cx,ex** and 2 h for **3hy**) under stirring. After cooling to room temperature, the mixture was then transferred into a separatory funnel and

extracted with ethyl acetate. The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure to led **4** and **5**. The products **4** and **5** were purified by column cromatography (silica gel, 4:1 petroleum ether-ethyl acetate).

Rel (6aS,10aR)-1-Hydroxy-8,9-dimethyl-6a,7,10,10a-tetrahydro-benzo[c]chromen-6-one (4bx): White solid, mp 208-210 °C (n-exane/ethyl acetate) ; IR (KBr) ν: 3270 (OH), 1764 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz, $(CD_3)_2CO$)] δ 1.58 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.75 (m, 1H, H-10α), 2.10-2.45 (m, 2H, H-7α, H-10β), 2.66 (d broad, 1H, J = 17.8 Hz, H-7β), 3.03 (t broad, 1H, , J = 5.6 Hz, H-6a), 3.46 (ddd, 1H, J = 11.3, 5.6, 5.6 Hz, H-10a), 6.50 (dd, 1H, J = 8.1, 1.1 Hz, H-4), 6.68 (dd, 1H, J = 8.1, 1.1 Hz, H-2), 7.06 (t, 1H, J = 8.1 Hz, H-3), 8.89 (s broad, 1H, OH); ^{13}C-NMR [50.3 MHz, $(CD_3)_2CO$] δ 18.0, 18.1 (8-Me, 9-Me), 28.7 (C-10a), 30.0 (C-10), 33.6 (C-7), 38.0 (C-6a), 107.6, 110.9 (C-2, C-4), 116.0 (C-10b), 123.0, 123.4 (C-8, C-9), 128.0 (C-3), 146.0 (C-4a), 154.2 (C-1), 169.6 (C-6); MS, m/e (relative intensity) 244 (M^+, 45), 201 (21), 162 (100), 134 (25), 77 (16), 67 (70). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; N, 5.20. Found: C, 73.80; H, 5. 21.

Rel (6aS,10aR)-2-Hydroxy-8,9-dimethyl-6a,7,10,10a-tetrahydro-benzo[c]chromen-6-one (4cx): White solid, mp 155-156 °C (diethyl ether) ; IR (KBr) ν: 3596 (OH), 1758 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$)] δ 1.58 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.87-2.37 (m, 3H, H-7α, H-10α, H-10β), 2.65 (d broad, 1H, J = 17.7 Hz, H-7β), 2.97 (t broad, 1H, , J = 5.5 Hz, H-6a), 3.04 (ddd, 1H, J = 10.9, 5.5, 5.5 Hz, H-10a), 6.50 (s broad, 1H, OH), 6.71 (s broad, 1H, H-1), 6.74 (dd, 1H, J = 8.7, 2.8 Hz, H-3), 6.88 (d, 1H, J = 8.7 Hz, H-4); ^{13}C-NMR [50.3 MHz, $CDCl_3$] δ 18.7, 18.9 (8-Me, 9-Me), 29.9 (C-10), 34.5 (C-6a), 34.9 (C-7), 38.5 (C-10a), 113.6, 114.7, 117.6 (C-1, C-3, C-4), 123.2, 123.6 (C-8, C-9), 129.2 (C-10b), 144.5 (C-4a), 152.6 (C-2), 171.7 (C-6); MS, m/e (relative intensity) 244 (M^+, 36), 216 (12), 162 (100), 134 (30), 94 (7), 77 (10). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.80; H, 6. 55.

Rel (6aR,10aR)-2-Hydroxy-8,9-dimethyl-6a,7,10,10a-tetrahydro-benzo[c]chromen-6-one (5cx): White solid, mp 195-196 °C (diethyl ether) ; IR (KBr) ν: 3596 (OH), 1758 (C=O) cm^{-1}; ^{1}H-NMR [200 MHz, $(CD_3)_2CO$)] δ 1.69 (s, 6H, 2 CH_3), 2.00-2.75 (m, 5H, H-7α, H-7β, H-6a, H-10α, H-10β), 2.94 (ddd, 1H, J = 13.4, 10.9, 5.6 Hz, H-10a), 6.67-6.87 (m, 3H, H-1, H-3, H-4); ^{13}C-NMR [50.3 MHz, $(CD_3)_2CO_3$] δ 18.9 (8-Me, 9-Me), 33.3 (C-10), 34.0 (C-6a), 36.6 (C-7), 39.8 (C-10a), 112.9, 115.3, 117.7 (C-1, C-3, C-4), 124.4, 125.0 (C-8, C-9), 128.8 (C-10b), 145.1 (C-4a), 154.9 (C-2), 170.6 (C-6); MS, m/e (relative intensity) 244 (M^+, 36), 216 (12), 162 (100), 134 (30), 94 (7), 77 (10). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.68; H, 6.66.

Rel (6aS,10aR)-4-Hydroxy-8,9-dimethyl-6a,7,10,10a-tetrahydro-benzo[c]chromen-6-one (4ex): White solid, mp 155-156 °C (diethyl ether) ; IR (KBr) ν: 3555 (OH), 1762 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$)] δ 1.60 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.90-2.40 (m, 3H, H-7α, H-10α, H-10β), 2.68 (d broad, 1H, J = 17.6 Hz, H-7β), 3.02 (t broad, 1H, J = 5.5 Hz, H-6a), 3.13 (ddd, 1H, J = 10.9, 5.5, 5.5 Hz, H-10a), 5.90 (s broad, 1H, OH), 6.70 (dd, 1H, J = 7.3, 1.8 Hz, H-3), 6.88 (dd, 1H, J = 8.2, 1.8 Hz, H-1), 6.98 (dd, 1H, J = 8.2, 7.3 Hz, H-2); ^{13}C-NMR [50.3 MHz, $CDCl_3$] δ 18.7, 18.9 (8-Me, 9-Me), 30.0 (C-10), 34.6 (C-6a), 35.1 (C-7), 38.8 (C-10a), 115.0, 117.9 (C-1, C-3), 123.3, 123.5 (C-8, C-9), 124.7 (C-2), 128.9 (C-10b), 138.4 (C-4a), 143.8 (C-4), 169.5 (C-6); MS, m/e (relative intensity) 244 (M^+, 46), 216 (19), 162 (100), 134 (15), 94 (10), 77 (12). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.68; H, 6. 51.

Rel (6aR,10aR)-4-Hydroxy-8,9-dimethyl-6a,7,10,10a-tetrahydro-benzo[c]chromen-6-one (5ex): White solid, mp 192-194 °C ($CHCl_3$) ; IR (KBr) ν: 3555 (OH), 1762 (C=O) cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$)] δ 1.72 (s, 6H, 2 CH_3), 2.10-2.75 (m, 5H, H-7α, H-7β, H-6a, H-10α, H-10β), 3.01 (ddd, 1H, J = 11.8, 10.8, 5.5 Hz, H-10a), 5.83 (s broad, 1H, OH), 6.78 (d, 1H, J = 7.5 Hz, H-3), 6.91 (d, 1H, J = 7.7 Hz, H-1), 7.04 (t, 1H, J = 7.6 Hz, H-2); ^{13}C-NMR [50.3 MHz, $CDCl_3$] δ 18.7, 18.8 (8-Me, 9-Me), 32.4 (C-10), 33.4 (C-6a), 36.0 (C-7), 39.6 (C-10a), 115.0, 116.4 (C-1, C-3), 123.6, 124.4 (C-8, C-9), 124.8 (C-2), 127.2 (C-10b), 138.5 (C-4a), 143.7 (C-4), 169.6 (C-6); MS, m/e (relative intensity) 244 (M^+, 46), 216 (19), 162 (100), 134 (15), 94 (10), 77 (12). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.70; H, 6. 68.

Rel (6aS,10aR)-1-Hydroxy-9-methyl-3-pentyl-6a,7,10,10a-tetrahydro-benzo[c]chromen-6-one (4hy):

White solid, mp 112-113 °C (lit.[6] 115-117 (n-hexane/ethyl acetate) ; IR ($CHCl_3$) ν: 3270 (OH), 1754 (C=O) cm^{-1}; ^{1}H-NMR [400 MHz, $(CD_3)_2CO$)] δ 0.89 (t, 3H, J = 6.9 Hz, CH_3), 1.29-1.35 (m, 4H, CH_2CH_2), 1.57-1.72 (m, 3H, CH_2, H-10α), 1.63 (s, 3H, CH_3), 2.22 (dd, 1H, J = 5.8, 17.4, H-10β), 2.36 (d broad, 1H, H-7α), 2.51 (t broad, 2H, J = 7.6 HZ, $ArCH_2$), 2.78 (d broad, 1H, J = 19.8 Hz, H-7β), 3.02 (t broad, 1H, J = 5.8 Hz, H-6a), 3.46 (ddd, 1H, J = 11.5, 5.8, 5.8 Hz, H-10a), 5.41 (s broad, 1H, H-8), 6.40 (d, 1H, J = 2.6 Hz, H-4), 6.68 (d, 1H, J = 2.6 Hz, H-2), 9.07 (s broad, 1H, OH); ^{13}C-NMR [100.6 MHz, $(CD_3)_2CO$] δ 13.4 (C-5'), 22.2 (C-4'), 22.6 (9-Me), 24.0 (C-3'), 28.2 (C-10a), 30.7, 31.2, 32.2, 35.3 (C-1', C-2', C-7, C-10), 36.9 (C-6a), 107.6 (C-4), 110.8 (C-2), 113.1 (C-10b), 118.8 (C-8), 131.2 (C-9), 143.4 (C-3), 152.2 (C-4a), 153.7 (C-1), 169.6 (C-6); MS, m/e

(relative intensity) 300 (M^+, 29), 232 (68), 190 (18), 176 (100), 147 (7), 91 (7). Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.88; H, 8. 13.

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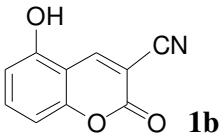

1b

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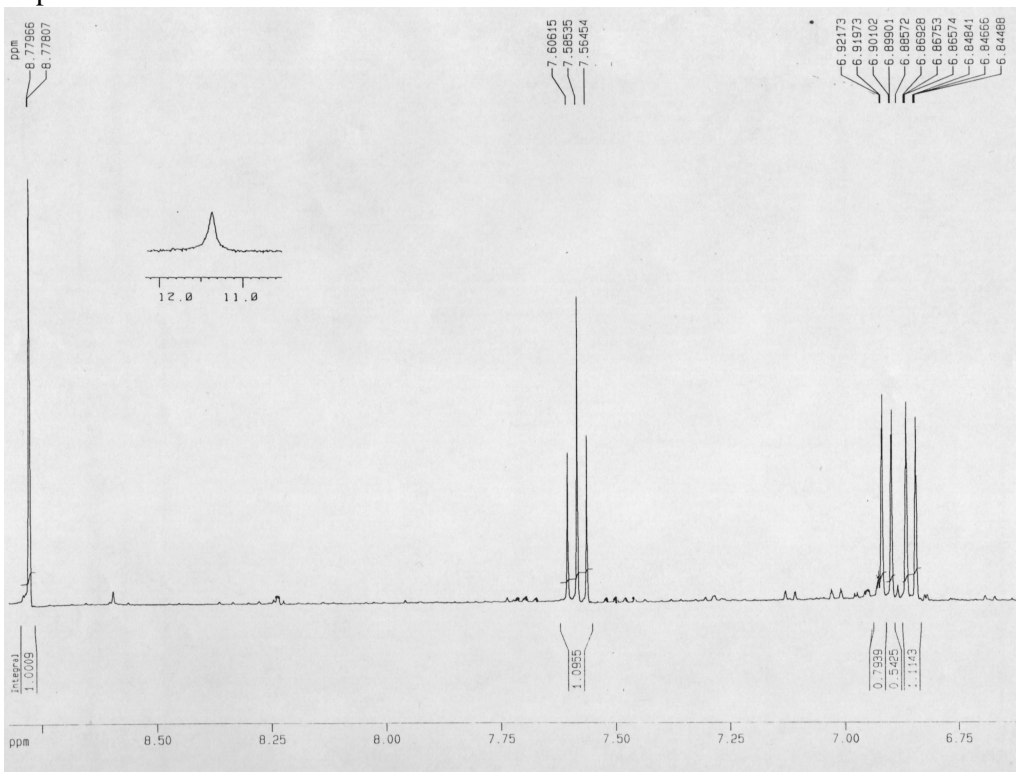
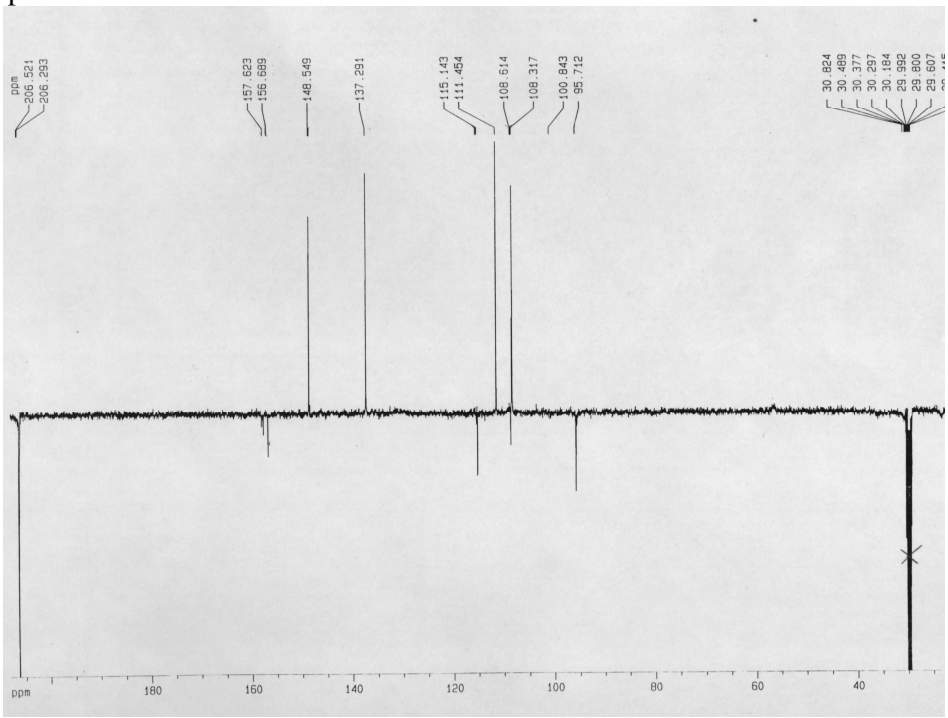
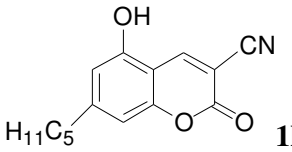


^{13}C-NMR spectrum





1h

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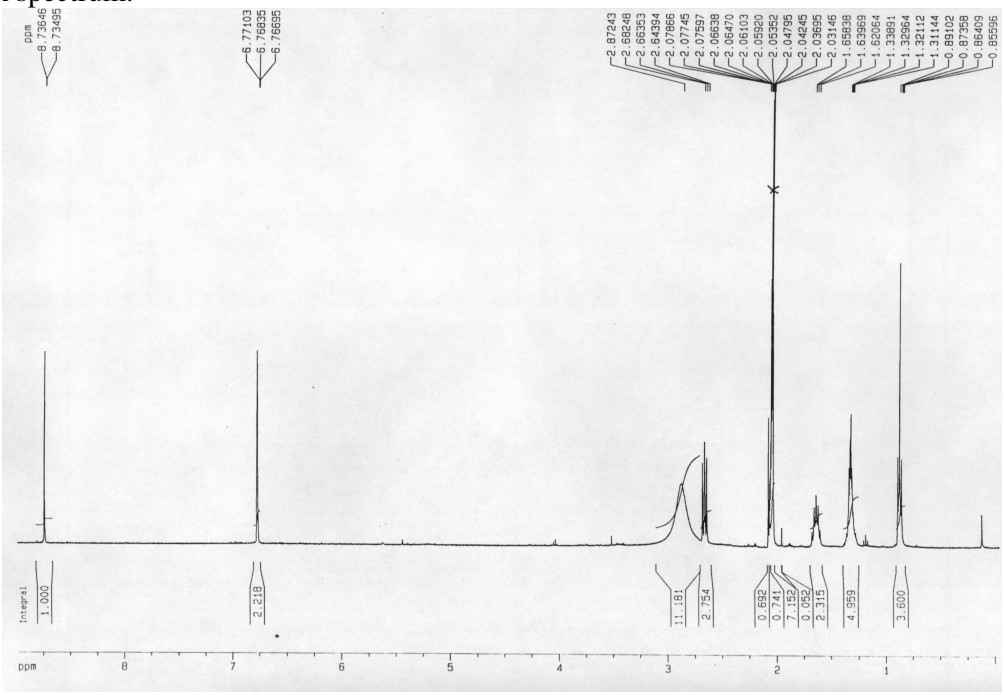

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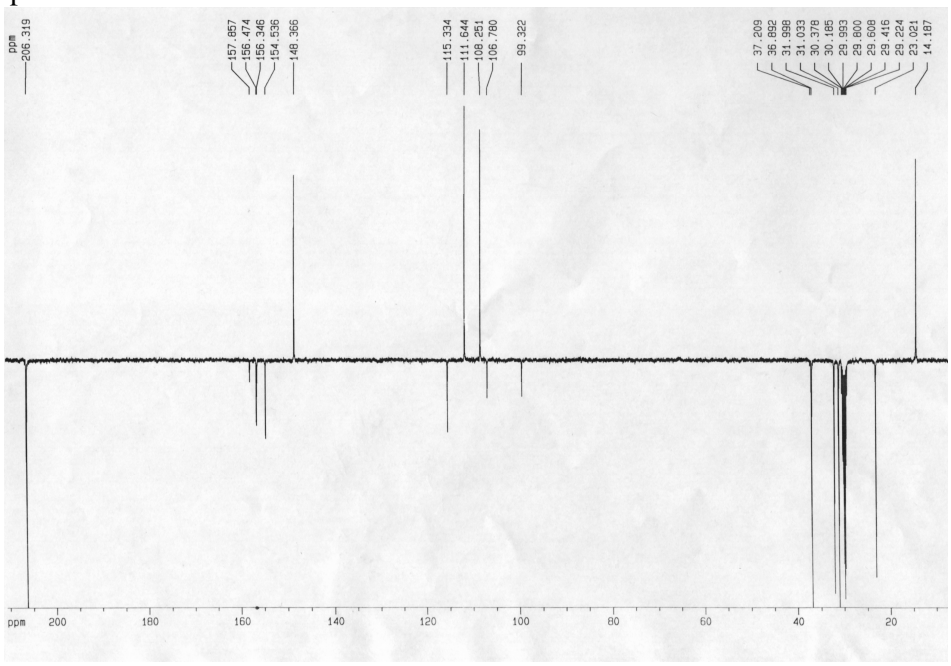

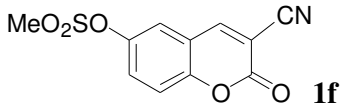

1f

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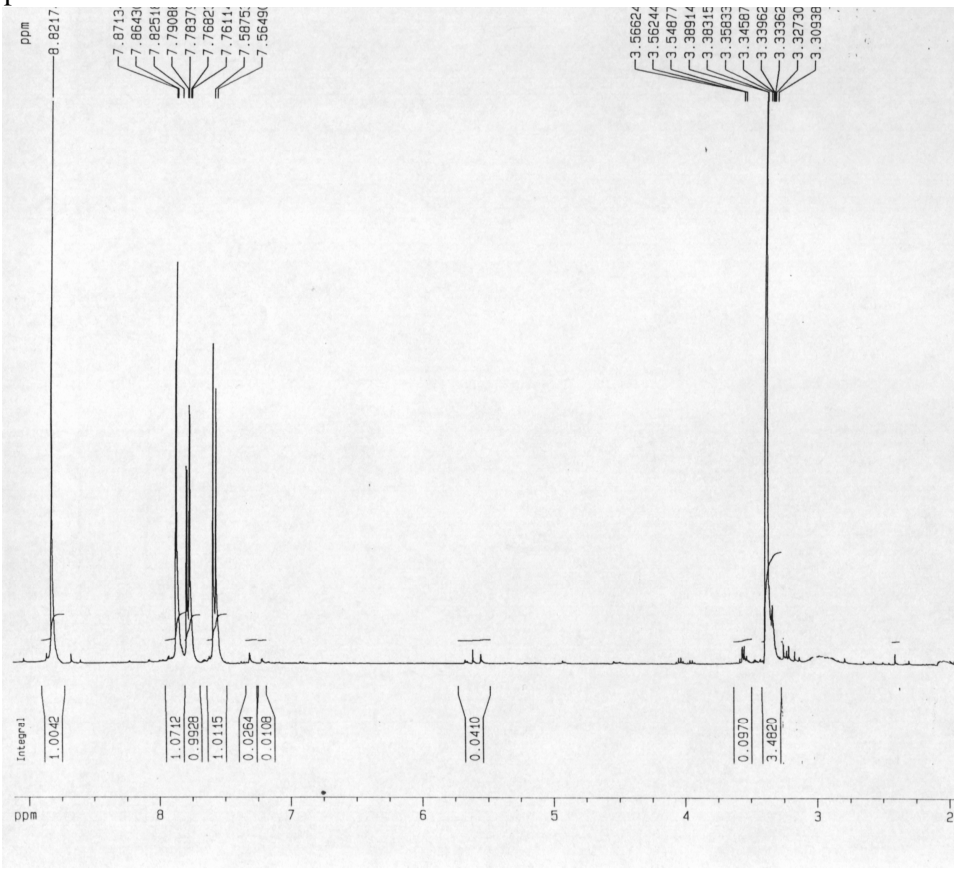
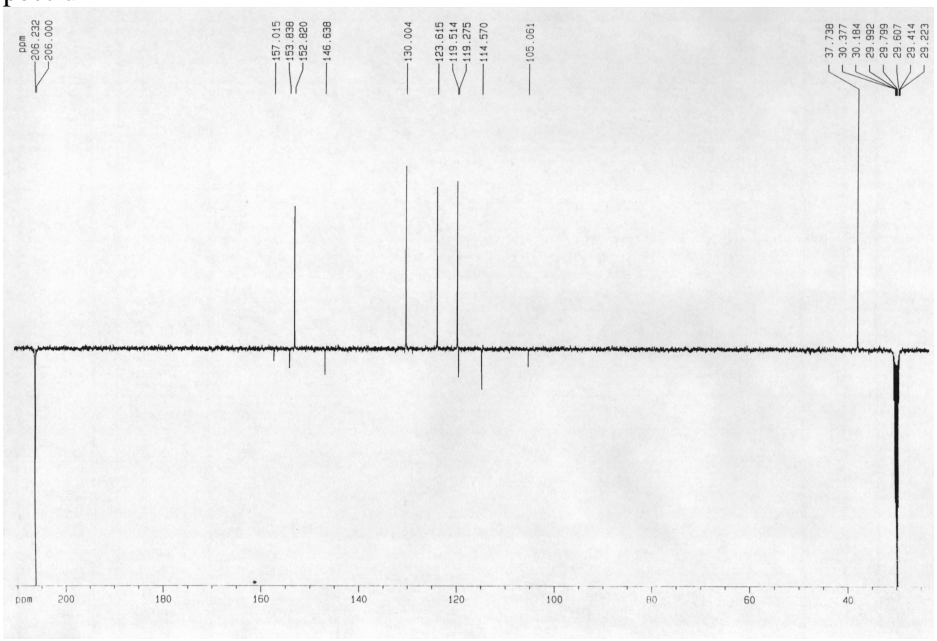
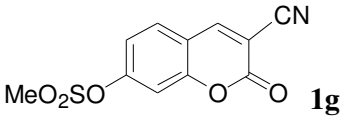


^{13}C-NMR spectrum





1g

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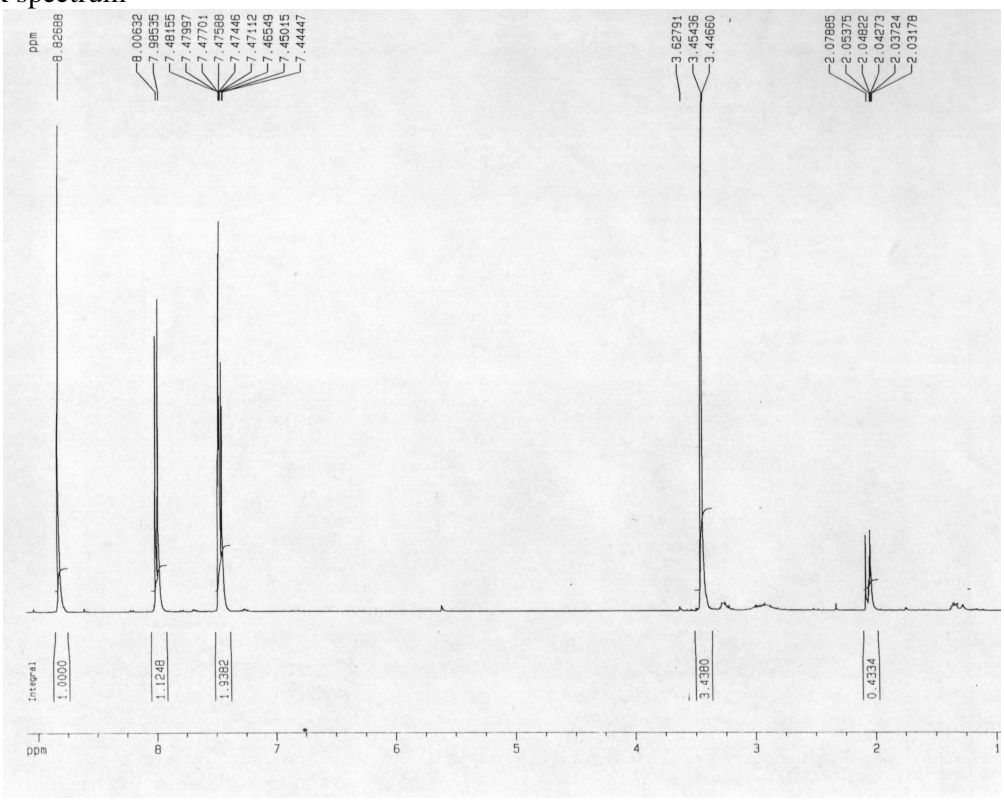

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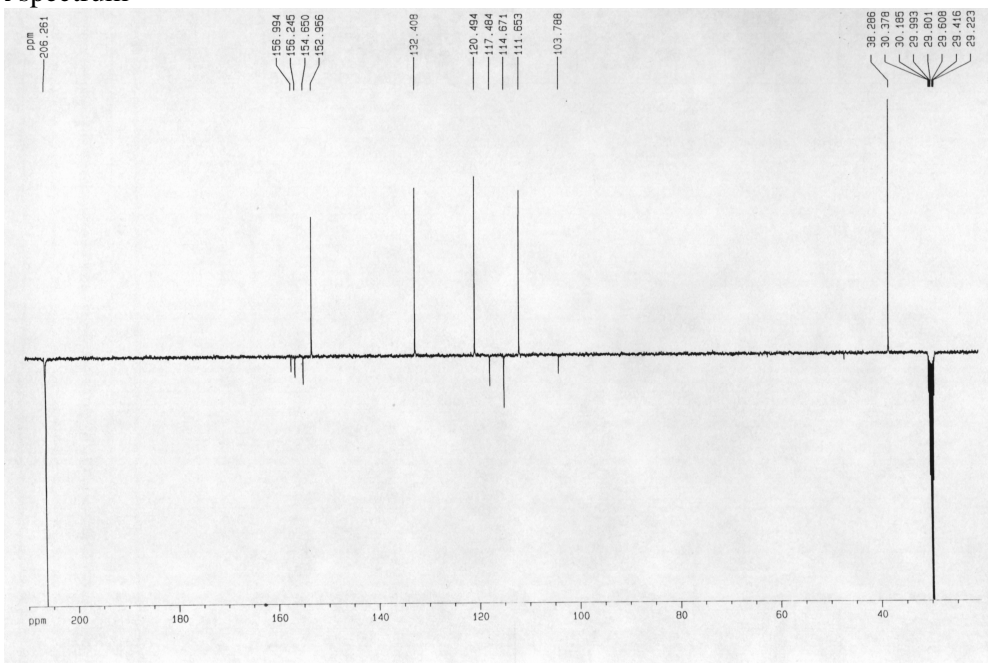

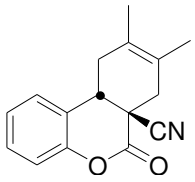

3ax

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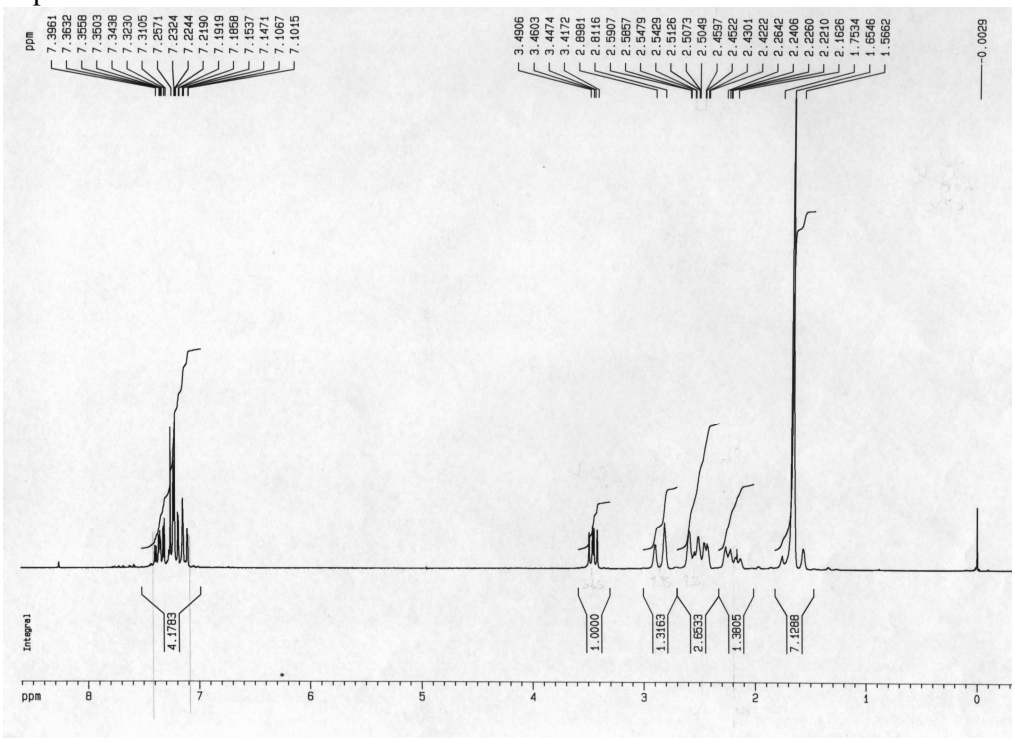

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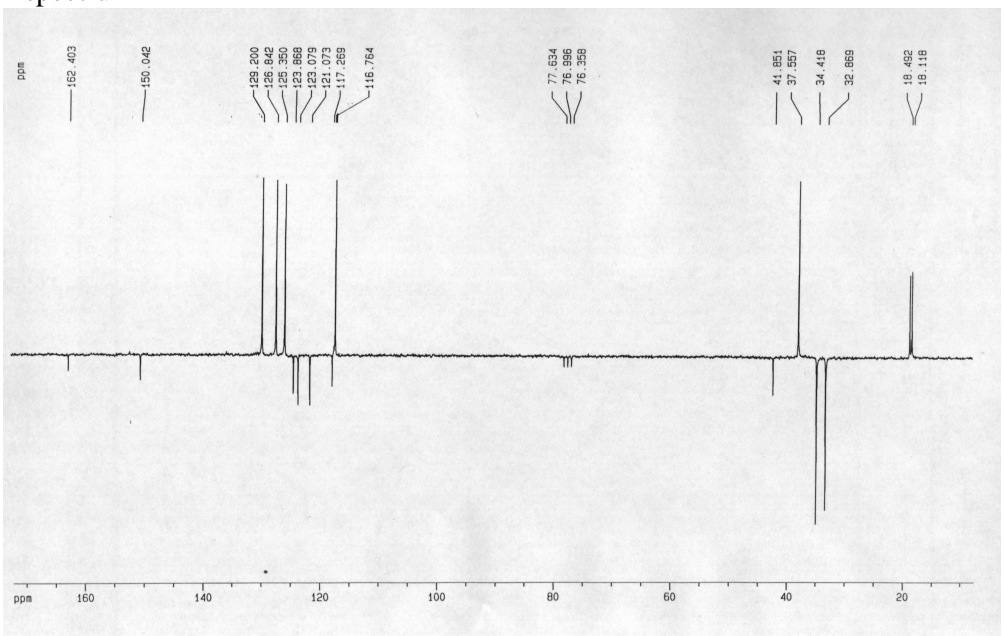
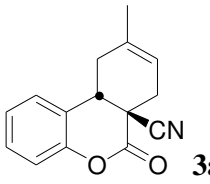
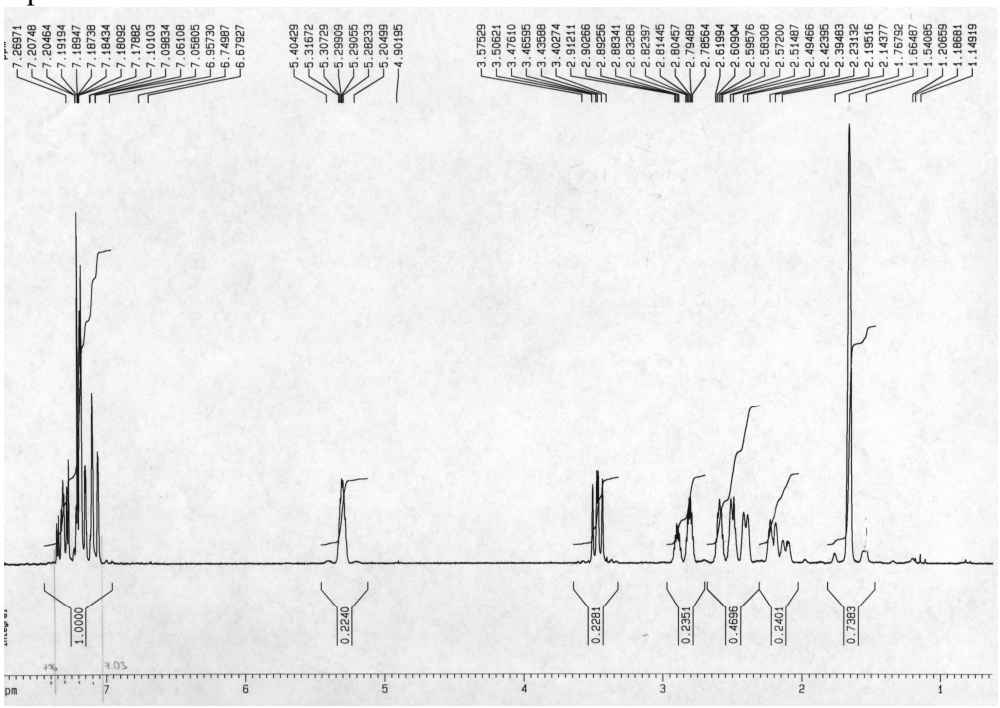


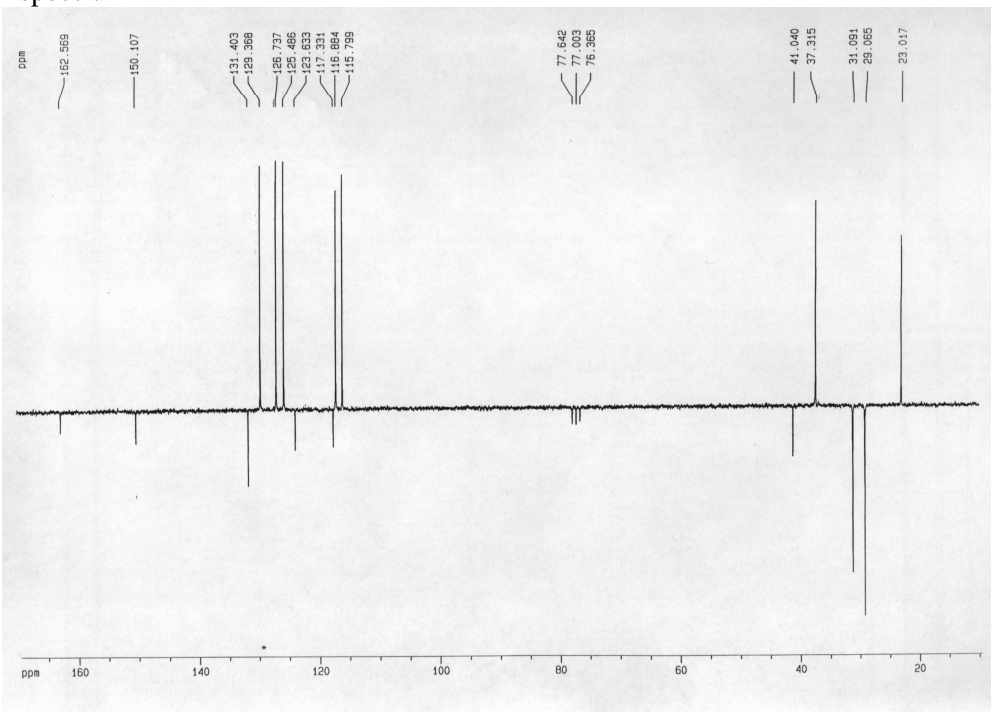


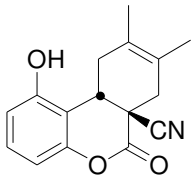
3ay

^{1}H-NMR spectrum



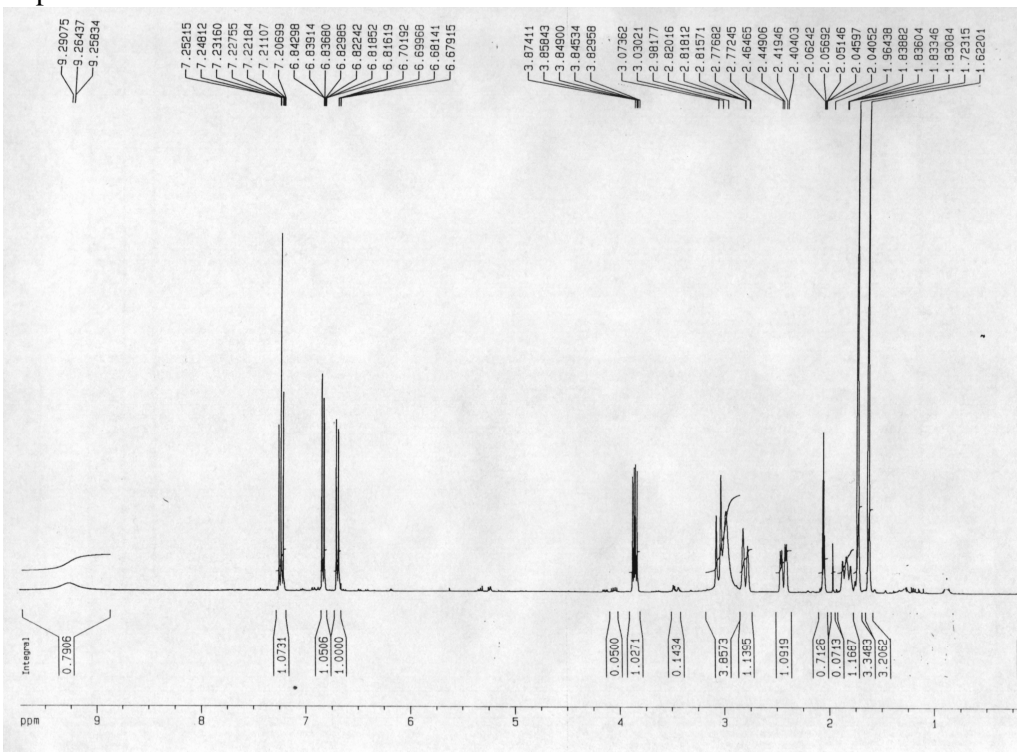
^{13}C-NMR spectrum





3bx

^{1}H-NMR spectrum



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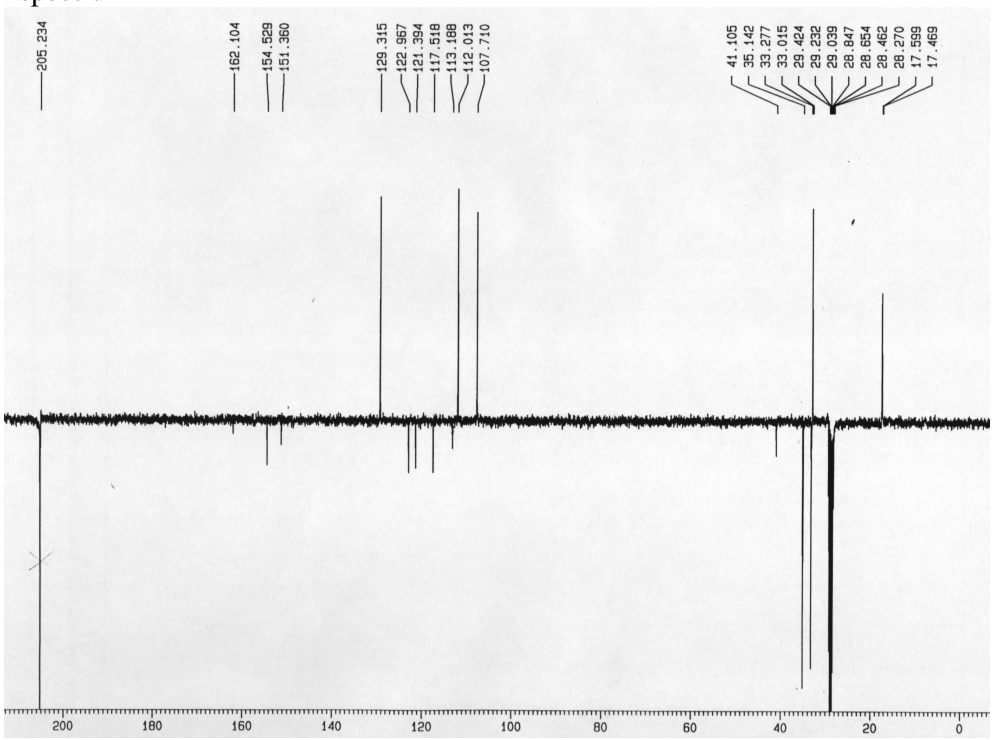

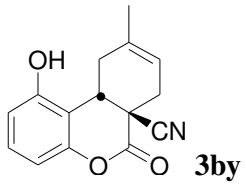

3by

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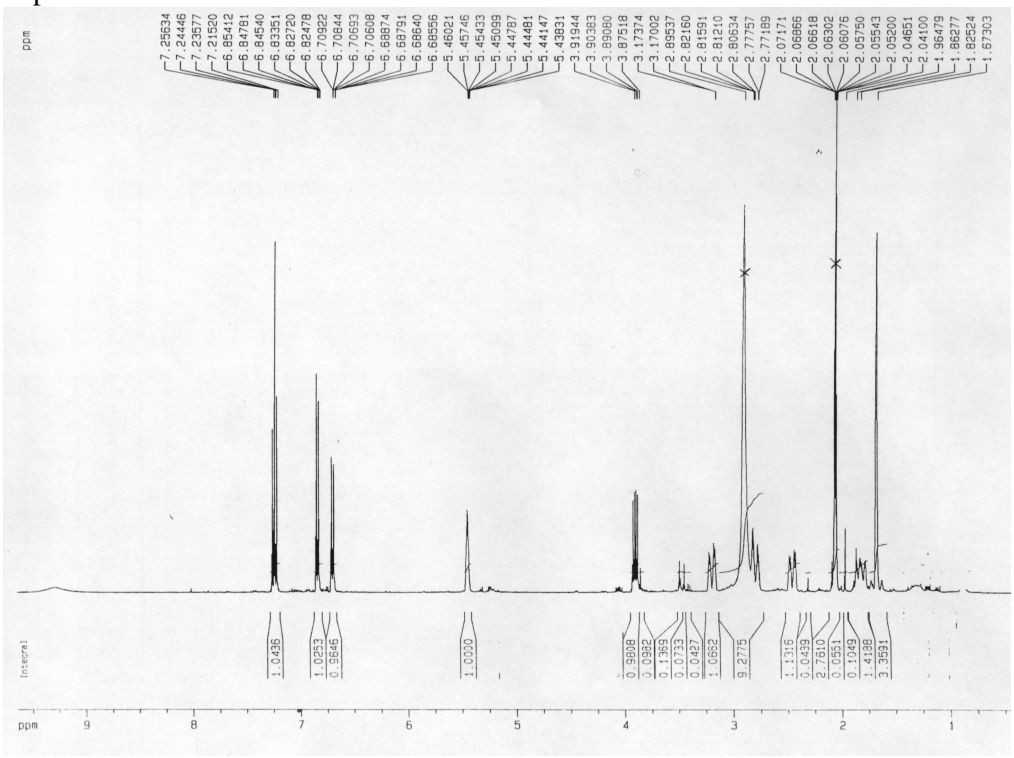

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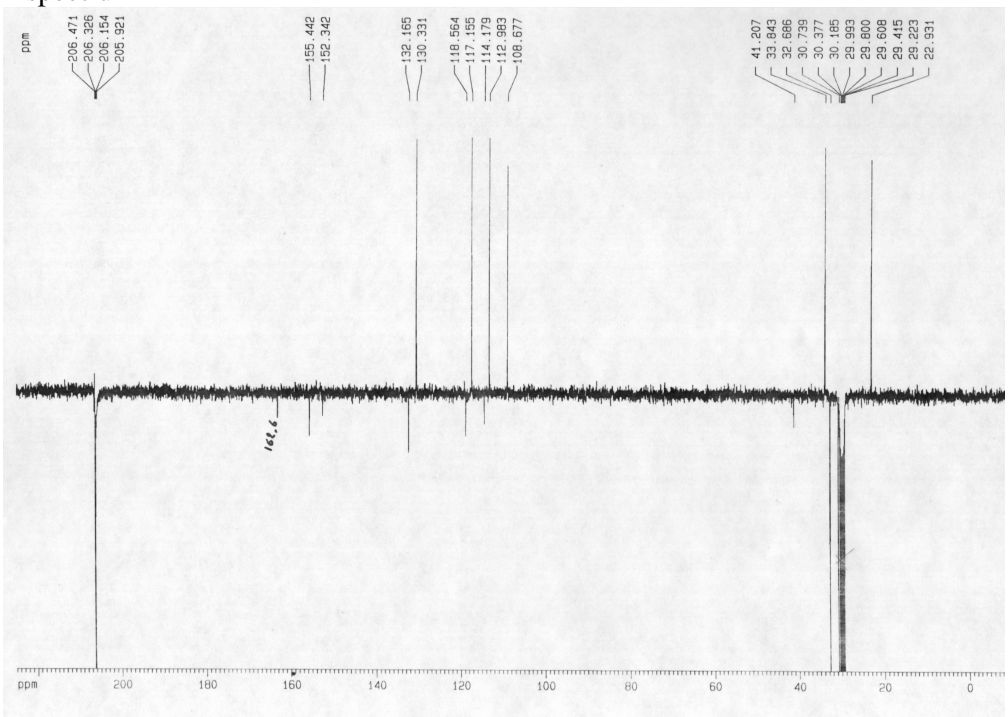
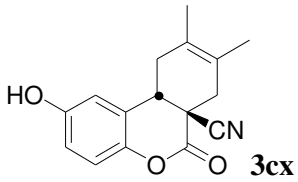
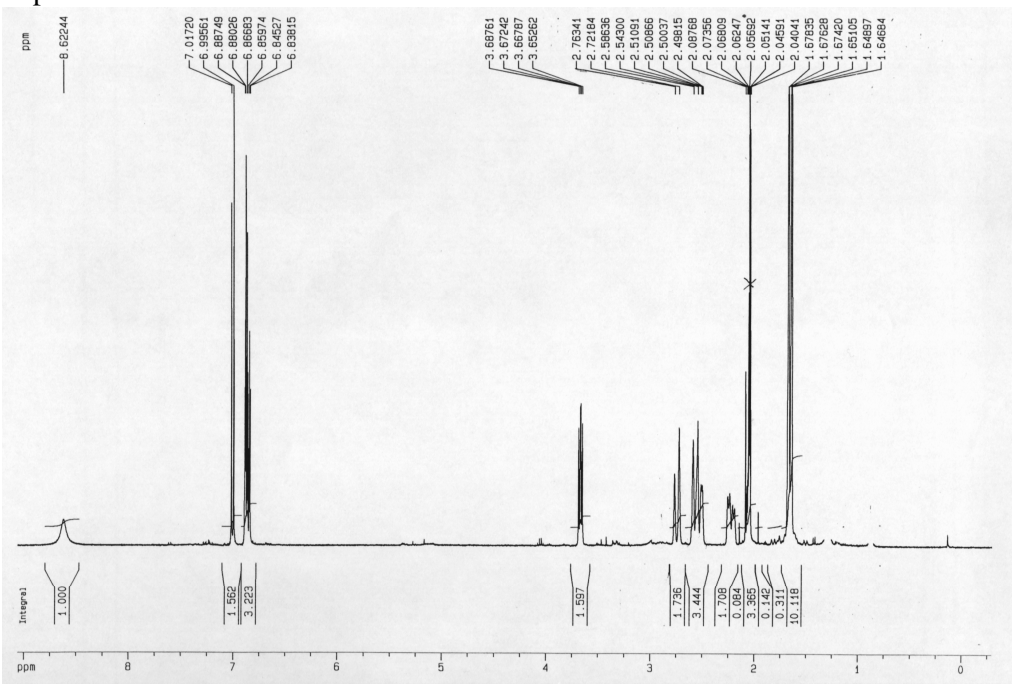




3cx

^{1}H-NMR spectrum



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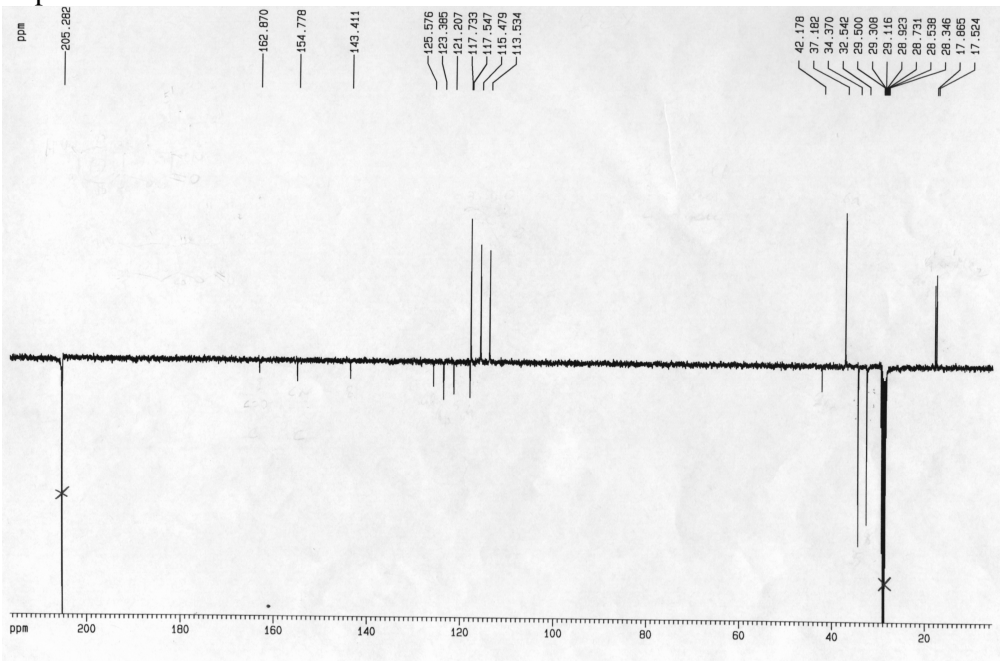
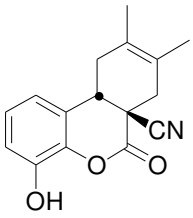
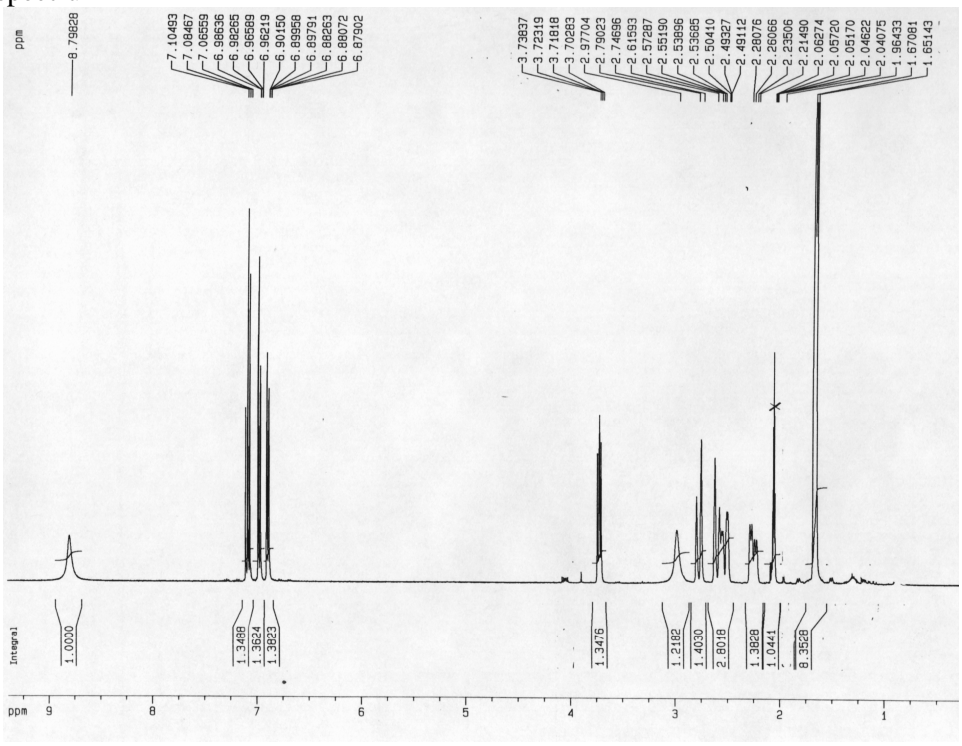




3ex

^{1}H-NMR spectrum



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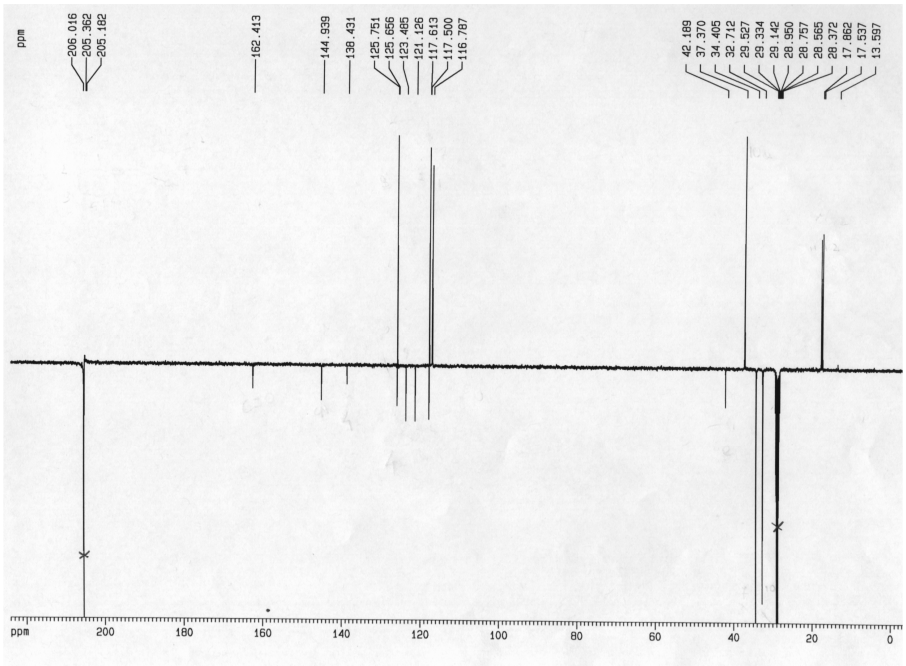
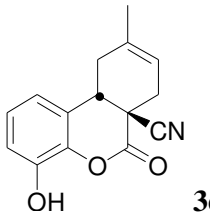
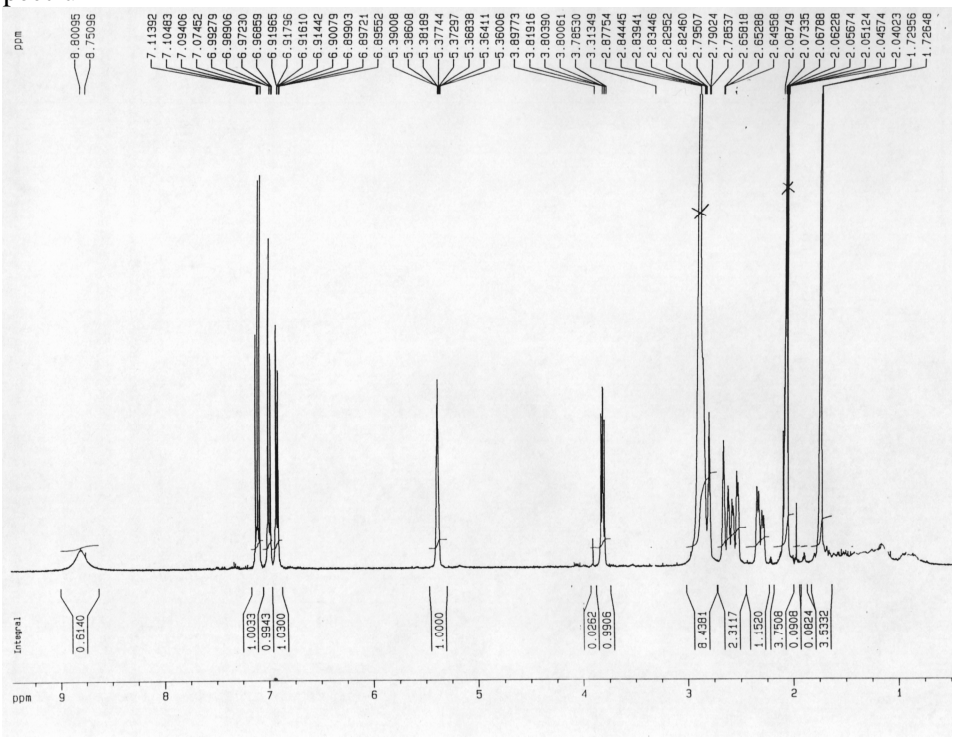




3ey

^{1}H-NMR spectrum



^{13}C-NMR spectrum