Supporting Information:

A rapid entry to *C*-prenylcarbazoles: total synthesis of clausamine C-D, clausevatine D and clausine F

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List of Contents:

1) General methods and X-ray crystal structure of compound 27:

General methods: Melting points were determined in open-end capillary tubes and are uncorrected. Solvents were dried and distilled following the standard procedures. TLC was carried out on precoated plates (Merck silica gel 60, GF254), and the spots were visualized with UV and fluorescent light. Column chromatography was performed on silica gel (60-120 or 230-400 mesh). ^{1}H and ^{13}C NMR spectra for all the compounds were recorded at 200/400 MHz and 50/100 MHz in $CDCl_3$ and $(CD_3)_2CO$ respectively. IR spectra were recorded on a FT-IR using KBr pellet on a Thermo Nicolet Nexus 870 FT-IR spectrophotometer. Mass spectra were taken using a VG Autospec M mass spectrometer. The phase "usual work-up" or "worked up in usual manner" refers to washing of the organic phase with water (2 x 1/3 of the volume of organic phase) and brine (1 x 1/4 the volume of organic phase), drying (Na_2SO_4), filtration and concentrated under reduced pressure. All chromatographic separations were done using silica gel.

X-ray crystal structure of prenylated carbazole 27:

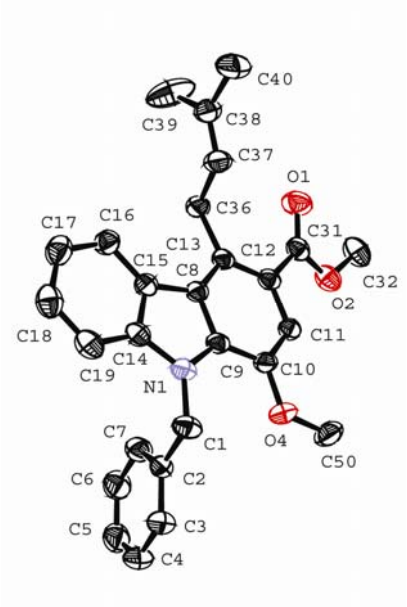
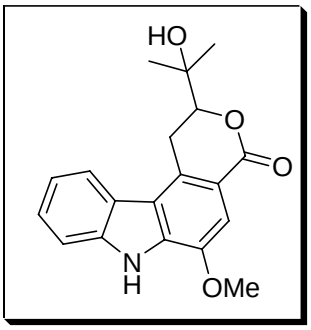


Figure 1. ORTEP diagram of prenylated carbazole **27**

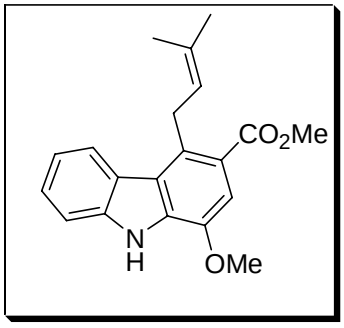
2) Experimental procedures and characterization data:

1,7-Dihydro-6-methoxy-2-(1-hydroxy-1-methylethyl)pyrano[3,4-*c*]carbazole-(2*H*)-4-one (Clausamine C) (3):



To a stirred solution of compound **11** (15 mg, 0.05 mmol) in acetone (5 mL) were added K_2CO_3 (20 mg, 0.15 mmol) and MeI (0.1 mL, 1.0 mmol) and the mixture was stirred for 2 h. After completion of the reaction, the solvent was evaporated and the residue was extracted with EtOAc (3 x 20 mL) and worked up in usual manner. The crude product was purified by column chromatography to give compound **3** (12 mg, 77%) as a pale yellow solid. The spectroscopic data for synthetic clausamine C are in agreement with lit.[1,2] values, with the exception of the optical rotation. R_f: 0.40 (1:1 ethyl acetate : petroleum ether); mp: 182-185 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (br s, 1H), 8.08 (d, 1H, J = 8 Hz), 7.63 (s, 1H), 7.55 (d, 1H, J = 8.0 Hz), 7.49 (t, 1H, J = 7.4 Hz), 7.32 (t, 1H, J = 7.4 Hz), 4.47 (dd, 1H, J = 12.8, 3.2 Hz), 4.06 (s, 3H), 3.66 (dd, 1H, J = 16.4, 2.8 Hz), 3.46 (dd, 1H, J = 16.4, 12.8 Hz), 1.49 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C), 144.6 (C), 139.5 (C), 133.6 (C), 128.9 (C), 126.3 (CH), 123.4 (C), 122.0 (CH), 120.7 (CH), 120.5 (C), 116.0 (C), 111.6 (CH), 106.4 (CH), 84.0 (CH), 71.4 (C), 55.9 (CH_3), 26.0 (CH_3), 25.5 (CH_2), 24.9 (CH_3); HRMS (ES) Calcd. for $C_{19}H_{19}NO_4$ $[M+Na]^+$ 348.1211; Found 346.1223.

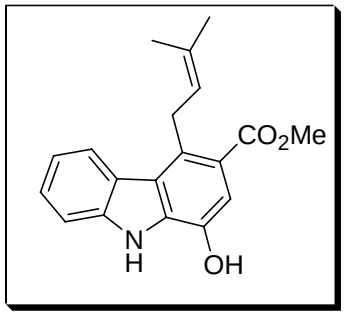
Methyl 1-methoxy-4-(3-methylbut-2-enyl)-9*H*-carbazole-3-carboxylate (Clausamine D) (4):



Compound **9** (50 mg, 0.16 mmol) was *O*-methylated using K_2CO_3 (90 mg, 1.0 mmol) and MeI (0.2 mL, 2.5 mmol) in 8 mL acetone to afford compound **4** (38 mg, 72%) as a white solid. The procedures for the work-up and the purification were very similar to the ones described for conversion of **11** to **3**. R_f: 0.5 (1:3 ethyl acetate : petroleum ether); mp: 158-160 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (br s, 1H), 8.13 (d, 1H, J = 8 Hz), 7.51-7.43 (m, 3H), 7.29-7.26 (m, 1H), 5.29 (m, 1H), 4.31 (d, 2H, J = 4.8 Hz), 4.03 (s, 3H), 3.93 (s, 3H), 1.92 (s, 3H), 1.71

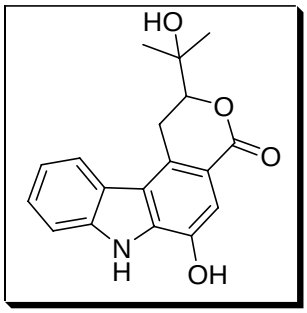
(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (C), 142.9 (C), 139.4 (C), 133.6 (C), 132.3 (C), 132.2 (C), 125.6 (CH), 123.8 (C), 123.3 (CH), 123.1 (C), 122.8 (CH), 120.6 (C), 120.1 (CH), 111.0 (CH), 108.0 (CH), 55.6 (CH_3), 51.9 (CH_3), 29.3 (CH_2), 25.6 (CH_3), 18.4 (CH_3) ; ν_{max} (KBr, cm^{-1}): 3388, 2931, 1687, 1610, 1446, 1350, 1242; HRMS (ES) Calcd. for $C_{20}H_{21}NO_3$ $[M+Na]^+$ 346.1419; Found 346.1418.

Methyl 1-hydroxy-4-(3-methyl-but-2-enyl)-9*H*-carbazole-3-carboxylate (Clausine F) (9):



To a stirred solution of compound **33** (40 mg, 0.2 mmol) in dry acetone were added DBU (0.05 mL, 0.5 mmol) and MeI (0.1 mL, 2.0 mmol). After 3 h at rt, solvent was evaporated and the residue was extracted with EtOAc (3 x 20 mL) and worked up in the usual manner. The solvent was removed under reduced pressure and the residue was purified by column chromatography to get a white solid product of **9** (32 mg, 76%). R_f: 0.3 (1:3 ethyl acetate : petroleum ether); mp: 196-198 ºC; Lit[3] mp: 200-202 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (br s, 1H), 8.13 (d, 1H, J = 8 Hz), 7.49-7.44 (m, 3H), 7.30-7.24 (m, 1H), 5.28 (m, 1H), 4.27 (d, 2H, J = 4.8 Hz), 3.91 (s, 3H), 1.88 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (C), 139.7 (C), 138.7 (C), 133.6 (C), 132.3 (C), 131.8 (C), 125.8 (CH), 123.9 (C), 123.4 (CH), 123.1 (C), 122.9 (CH), 120.5 (C), 120.2 (CH), 112.8 (CH), 111.1 (CH), 52.0 (CH_3), 29.4 (CH_2), 25.7 (CH_3), 18.4 (CH_3) ; ν_{max} (KBr, cm^{-1}): 3350, 1674, 1620, 1444, 1342, 1255, 1091, 1024, 804.

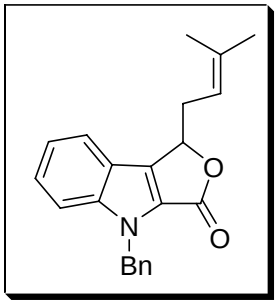
1,7-Dihydro-6-hydroxy-2-(1-hydroxy-1-methylethyl)pyrano[3,4-*c*]carbazole-(2*H*)-4-one (Clausevatine D) (11):



To a stirred solution of carboxylic acid **33** (40 mg, 0.13 mmol) in dry CH_2Cl_2 (5 mL) cooled to 0 - 5 °C was added *m*-CPBA (35 mg, 0.2 mmol) and further stirred at rt for 2 h. After total consumption of starting material, the mixture was concentrated and extracted with EtOAc (2 x 15 mL). The combined extracts were washed two times with aq $NaHCO_3$ solution (10 mL) followed by

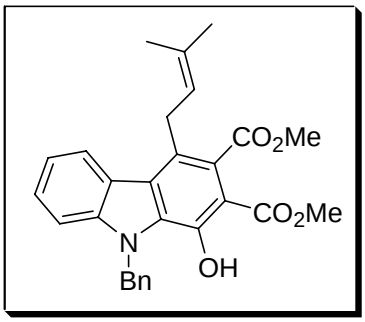
water and brine. The organic phase was concentrated and the residue purified by column chromatography to furnish **11** (25 mg, 60%) as a yellow solid. The spectroscopic data for synthetic clausamine C are in agreement with literature[1,4] data with the exception of the optical rotation. R_f: 0.30 (1:1 ethyl acetate : petroleum ether); mp: 238-240 ºC; ^{1}H NMR (400 MHz, Acetone-d_6): δ 10.87 (br s, 1H), 9.16 (br s, 1H), 8.21 (d, 1H, J = 8 Hz), 7.67 (d, 1H, J = 8 Hz), 7.55 (s, 1H), 7.46 (t, 1H, J = 7.6 Hz), 7.27 (t, 1H, J = 7.6 Hz), 4.43 (dd, 1H, J = 12.6, 3.0 Hz), 3.96 (br s, 1H), 3.78 (dd, 1H, J = 16.4, 3.2 Hz), 3.42 (dd, 1H, J = 16.4, 12.8 Hz),1.42 (s, 6H); ^{13}C NMR (100 MHz, Acetone-d_6): δ 166.5 (C), 142.9 (C), 141.6 (C), 134.5 (C), 129.2 (C), 126.7 (CH), 124.5 (C), 123.0 (CH), 121.9 (C), 120.9 (CH), 117.1 (C), 112.8 (CH), 110.9 (CH), 84.9 (CH), 71.4 (C), 26.9 (CH_3), 26.1 (CH_2), 25.5 (CH_3).

1,4-Dihydro-4-phenylmethyl-1-(3-methylbut-2-enyl)furo[3,4-*b*]indol-3-one (21):



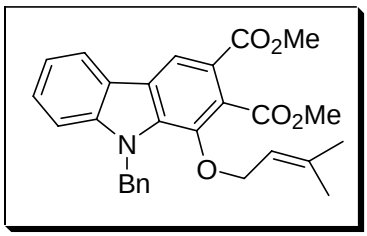
To a stirred solution of diisopropylamine (0.1 mL, 1.1 mmol) in THF (3 mL) at -78 ºC under N_2 atmosphere was added 1.6 M *n*-BuLi (0.7 mL, 1.1 mmol) in hexane. The reaction mixture was allowed to stir at -78 ºC for 0.5 h. To it was added *N*-benzylfuroindolone **20**[5] (100 mg, 0.5 mmol) in THF (2 mL). After 45 min, the resulting mixture was treated with prenyl bromide (0.1 mL, 1.1 mmol), stirred for an additional 1 h at -78 ºC and then allowed to warm to rt. After 6 h, THF was evaporated under reduced pressure and the residue was acidified with 15% aq HCl (15 mL) solution and worked up in usual manner. The resulting residue was column chromatographed to furnish **21** (110 mg, 87%). R_f: 0.5 (1:5 ethyl acetate : petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, 1H, J = 8.4 Hz), 7.41 (d, 1H, J = 8.4 Hz), 7.35 (t, 1H, J = 8 Hz), 7.31-7.27 (m, 5H), 7.19 (t, 1H, J = 7.6 Hz), 5.57 (dd, 1H, J = 6 Hz, J = 7.2 Hz), 5.54 (s, 2H), 5.27 (t, 1H, J = 7.6 Hz), 2.84-2.79 (m, 1H), 2.66-2.59 (m, 1H), 1.77 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 (C), 143.5 (C), 137.8 (C), 136.7 (C), 136.6 (C), 128.9 (CH), 128.7 (C), 127.8 (CH), 127.3 (CH), 126.0 (CH), 121.6 (CH), 121.1 (CH), 120.8 (C), 117.0 (CH), 112.0 (CH), 78.9 (CH), 47.5 (CH_2), 33.6 (CH_2), 25.8 (CH_3), 18.0 (CH_3); ν_{max} (KBr, cm^{-1}): 2922, 1753, 1631, 1444, 1305, 1082, 744; HRMS (ES) Calcd. for $C_{22}H_{21}NO_2$ (MH^+) 332.1643; Found 332.1652.

Dimethyl 9-phenylmethyl-1-hydroxy-4-(3-methylbut-2-enyl)-9*H*-carbazole-2,3-dicarboxylate (22):



A solution of compound **24** (100 mg) in *N*,*N*-dimethylaniline (10 mL) was heated at reflux for 10 min. Then the reaction mixture was acidified with 25% aq HCl (20 mL) and extracted thrice with ethyl acetate (60 mL). The combined organic extracts were washed with brine and dried with Na_2SO_4. The solvent was removed under reduced pressure to give a gummy residue, which was purified by column chromatography to furnish **22** (65 mg, ~65%) as a white solid. It was not fully pure. R_f: 0.40 (1:5 ethyl acetate : petroleum ether); mp: 145-150 ºC; ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.81 (s, 1H), 8.08 (d, 1H, J = 8 Hz), 7.45-7.38 (m, 2H), 7.24-7.18 (m, 3H), 7.11-7.07 (m, 3H), 5.99 (s, 2H), 5.28-5.25 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.79 (d, 2H, J = 5.8 Hz), 1.81 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7 (C), 170.3 (C), 149.4 (C), 142.3 (C), 138.4 (C), 132.8 (C), 128.9 (C), 128.6 (CH), 127.2 (CH), 127.0 (CH), 126.4 (C), 126.3 (CH), 125.8 (C), 124.7 (C), 123.8 (CH), 122.5 (C), 121.8 (CH), 120.3 (CH), 110.1 (CH), 105.1 (C), 52.9 (CH_3), 52.5 (CH_3), 48.7 (CH_2), 29.8 (CH_2), 25.7 (CH_3) 18.4 (CH_3) ; ν_{max} (KBr, cm^{-1}): 3444, 1732, 1668, 1444, 1321, 1215, 1034, 740.

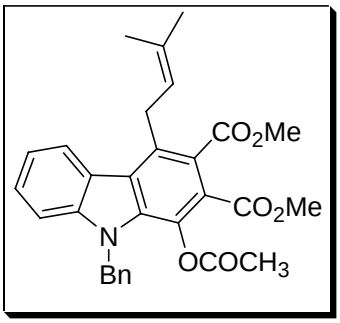
Dimethyl 1-(3-methyl-2-butenyloxy)-9-phenylmethyl-9*H*-carbazole-2,3-dicarboxylate (24):



To a stirred solution of compound **23** (400 mg, 1.0 mmol) in dry acetone (20 mL) at rt was added K_2CO_3 (0.7 g, 5.0 mmol) and stirred for 20 min. Then NaI (154 mg, 1.0 mmol) followed by prenyl bromide (0.2 mL, 1.7 mmol) was added and further stirred for 2 h. After completion of the reaction (TLC), the solvent was evaporated and after extraction with EtOAc (3 x 80 mL) and usual work-up, the crude product was purified by column chromatography to furnish **24** (330 mg, 71%) as a yellow solid. R_f: 0.45 (1:4 ethyl acetate : petroleum ether); mp: 123 ºC ; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.14 (d, 1H, J = 7.8 Hz), 7.47-7.30 (m, 2H), 7.28-7.22 (m, 4H), 7.08-7.04 (m, 2H), 5.92 (s, 2H), 5.30-5.26 (m, 1H), 4.48 (d, 2H, J = 7.2 Hz), 4.00 (s, 3H), 3.95 (s, 3H), 1.70 (s, 3H), 1.48 (s, 3H);

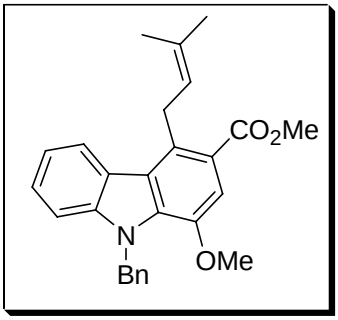
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (C), 166.2 (C), 142.0 (C), 141.9 (C), 138.9 (C), 137.1 (C), 135.4 (C), 128.7 (CH), 128.2 (C), 127.3 (CH), 127.1 (CH), 125.8 (CH), 125.6 (C), 123.2 (C), 120.7 (CH), 120.6 (CH), 119.5 (CH), 119.2 (CH), 119.1, 110.5 (CH), 73.8 (CH_2), 52.8 (CH_3), 52.3 (CH_3), 47.9 (CH_2), 25.7 (CH_3), 17.9 (CH_3) ; ν_{max} (KBr, cm^{-1}): 2946, 1722, 1598, 1442, 1358, 1268, 1152, 1038, 738; HRMS (ES) Calcd. for $C_{28}H_{27}NO_5$ $[M+Na]^+$ 480.1787; Found 480.1784.

Dimethyl 9-phenylmethyl-1-acetoxy-4-(3-methyl-but-2-enyl)-9*H*-carbazole-2,3-dicarboxylate (25):



Compound **22** (30 mg, 0.06 mmol) was acetylated by treating it with Et_3N (0.12 mL, 0.8 mmol), CH_3COCl (0.05 mL, 0.65 mmol) and DMAP (2 mg) in dry CH_2Cl_2 (8 mL) to give compound **25** (20 mg, 60%) as a white solid. R_f: 0.4 (1:3 ethyl acetate : petroleum ether); mp: 180 ºC ; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.17 (d, 1H, J = 8 Hz), 7.54-7.46 (m, 1H), 7.38-7.30 (m, 2H), 7.28-7.23 (m, 3H), 7.04-7.00 (m, 2H), 5.73 (s, 2H), 5.32 (m, 1H), 4.04 (d, 2H, J = 5.8 Hz), 3.88 (s, 3H), 3.81 (s, 3H), 1.96 (s, 3H), 1.72 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (C), 168.9 (C), 166.1 (C), 142.8 (C), 137.1 (C), 134.0 (C), 133.3 (C), 133.2 (C), 133.1 (C), 128.9 (CH), 127.5 (CH), 127.3 (CH), 126.4 (C), 125.4 (CH), 124.9 (C), 123.9 (CH), 122.5 (C), 121.9 (C), 121.4 (CH), 120.9 (CH), 109.5 (CH), 52.6 (CH_3), 52.5 (CH_3), 48.4 (CH_2), 29.8 (CH_2), 25.7 (CH_3), 20.6 (CH_3), 18.4 (CH_3) ; ν_{max} (KBr, cm^{-1}): 2946, 1728, 1446, 1364, 1222, 1028, 742; HRMS (ES) Calcd. for $C_{30}H_{29}NO_6$ (MH^+- MeOH) 468.1813; Found 468.1809.

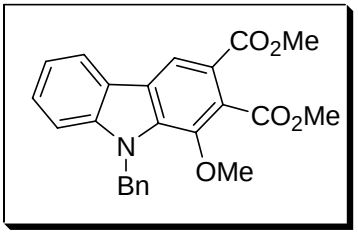
Methyl 1-methoxy-4-(3-methyl-but-2-enyl)-9-phenylmethyl-9*H*-carbazole-3-carboxylate (27):



To a solution of **22** (100 mg) in MeOH (5 mL) was added 60% KOH solution (20 mL). Then the resulting solution was heated at reflux under inert atm for 6 h. After completion of the reaction, the reaction mixture was acidified with 20% aq HCl (20 mL) and extracted with EtOAc (3 x 60 mL). The combined organic phase was washed with water then brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to

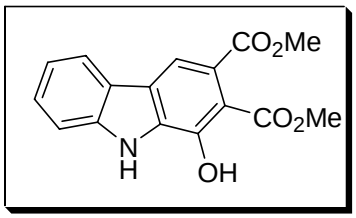
yield the crude carboxylic acid **26**. Then the crude product was dissolved in dry acetone (8 mL) and then treated with DBU (0.1 mL) and MeI (0.5 mL). After the complete consumption of starting materials (indicated by TLC), the solvent was evaporated, the residue extracted with EtOAc (3 x 50 mL) and worked up in usual manner. The solvent was removed under reduced pressure and purified by column chromatography to furnish **27** (50 mg, 55% over two steps) as a white crystalline solid. R_f: 0.6 (1:10 ethyl acetate : petroleum ether); mp: 108-110 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, 1H, J = 8 Hz), 7.48 (s, 1H), 7.44-7.38 (m, 2H), 7.24-7.17 (m, 5H), 7.11 (d, 1H, J = 7.2 Hz), 5.92 (s, 2H), 5.31 (m, 1H), 4.33 (d, 2H, J = 5.2 Hz), 3.93 (s, 3H), 3.89 (s, 3H), 1.93 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8 (C), 144.3 (C), 141.3 (C), 138.6 (C), 133.6 (C), 132.4 (C), 132.4 (C), 128.5 (CH), 126.9 (CH), 126.2 (CH), 125.6 (CH), 123.7 (C), 123.4 (CH), 122.8 (CH), 120.5 (C), 120.0 (CH), 109.5 (CH), 109.4 (CH), 55.8 (CH_3), 51.9 (CH_3), 48.7 (CH_2), 29.2 (CH_2), 25.7 (CH_3), 18.4 (CH_3), one carbon missing; ν_{max} (KBr, cm^{-1}): 2928, 1710, 1586, 1452, 1360, 1218, 1024, 746; HRMS (ES) Calcd. for $C_{27}H_{27}NO_3$ $[M+Na]^+$ 436.1888; Found 436.1898.

Dimethyl 1-methoxy-9-phenylmethyl-9*H*-carbazole-2,3-dicarboxylate (28):



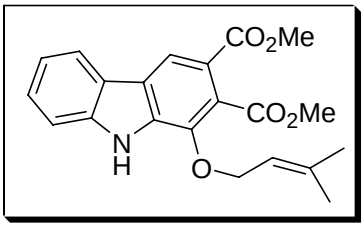
Compound **23** was prepared by annulation of compound **20** (300 mg, 1.1 mmol) with dimethyl maleate (1 mL, 1.4 mmol) in 68% yield by adopting the annulation procedure of Mal[5] et al. but by replacing LDA with LTB (365 mg, 4.6 mmol) and TMEDA (0.5 mL, 3.65 mmol) in dry THF (8 mL). Then compound **23** (200 mg, 0.5 mmol) was *O*-methylated using K_2CO_3 (250 mg, 2.5 mmol) and MeI (0.16 mL, 2.5 mmol) in dry acetone (8 mL) according to the conversion of **11** to **3** to afford compound **28** (180 mg, 87%) as a yellow solid. R_f: 0.5 (1:5 ethyl acetate : petroleum ether); mp: 127 ºC ; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.14 (d, 1H, J = 8.2 Hz), 7.47-7.42 (m, 1H), 7.36-7.21 (m, 5H), 7.09-7.06 (m, 2H), 5.87 (s, 2H), 4.00 (s, 3H), 3.95 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6 (C), 166.2 (C), 143.0 (C), 142.1 (C), 137.2 (C), 135.0 (C), 128.8 (CH), 127.7 (C), 127.3 (CH), 127.2 (CH), 125.8 (CH), 125.6 (C), 123.1 (C), 120.8 (CH), 120.6 (CH), 119.5 (CH), 119.2 (C), 110.3 (CH), 64.1 (CH_3), 52.9 (CH_3), 52.3 (CH_3), 48.0 (CH_2); ν_{max} (KBr, cm^{-1}): 1728, 1444, 1356, 1263, 1143, 1051, 976, 742; HRMS (ES) Calcd. for $C_{24}H_{21}NO_5$ (MH^+) 404.1498; Found 404.1488.

Dimethyl 1-hydroxy-9*H*-carbazole-2,3-dicarboxylate (29):



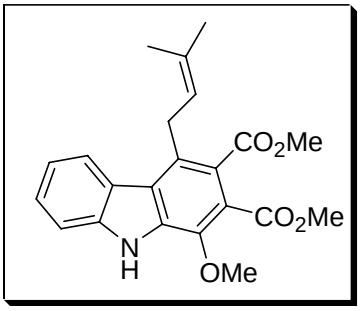
To a stirred solution of compound **28** (50 mg, 0.12 mmol) in dry CH_2Cl_2 (8 mL) was added anhyd $AlCl_3$ (80 mg, 0.6 mmol) at 0-5˚C and stirring was continued for 2 h. After total consumption of the starting material, the reaction mixture was concentrated, acidified with 10% aq HCl (10 mL) and extracted with EtOAc (3 x 30 mL). The combined extracts were washed with water, then brine and finally dried over Na_2SO_4. The organic phase was concentrated in vacuo and the residue purified by column chromatography to furnish a white solid product **29** (30 mg, 78%). R_f: 0.5 (1:3 ethyl acetate : petroleum ether); mp: 125 ºC ; ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.08 (s, 1H), 8.69 (br s, 1H), 8.08 (d, 1H, J = 7.6 Hz), 7.84 (s, 1H), 7.57-7.54 (m, 2H), 7.39-7.28 (m, 1H), 4.00 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4 (C), 170.1 (C), 148.3 (C), 140.2 (C), 129.3 (C), 127.6 (CH), 126.1 (C), 125.5 (C), 122.9 (C), 121.1 (CH), 120.5 (CH), 113.0 (CH), 111.6 (CH), 106.1 (C), 52.7 (CH_3), 52.5 (CH_3) ; ν_{max} (KBr, cm^{-1}): 3382, 2358, 1730, 1668, 1442, 1336, 1261, 1151, 1020, 771; HRMS (ES) Calcd. for $C_{16}H_{13}NO_5$ (MH^+- MeOH) 268.0612; Found 268.0623.

Dimethyl 1-(3-Methyl-2-butenyloxy)-9*H*-carbazole-2,3-dicarboxylate (30):



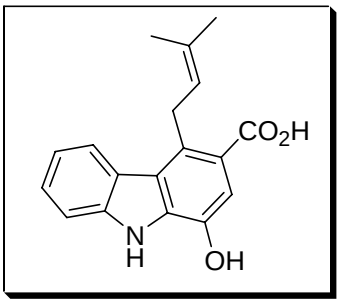
Compound **29** (100 mg) was *O*-prenylated following the procedure for the preparation of compound **24** from **23** using 1.5 eq of K_2CO_3 to furnish compound **30** (80 mg, 65%) as a semisolid. R_f: 0.55 (1:3 ethyl acetate : petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.49 (br s, 1H), 8.10 (d, 1H, J = 7.6 Hz), 7.51-7.47 (m, 2H), 7.35-7.27 (m, 1H), 5.63 (t, 1H, J = 7.2 Hz), 4.70 (d, 2H, J = 7.2 Hz), 4.01 (s, 3H), 3.94 (s, 3H), 1.79 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6 (C), 166.5 (C), 141.4 (C), 140.1 (C), 139.8 (C), 135.8 (C), 127.2 (CH), 126.6 (C), 124.9 (C), 123.5 (C), 121.0 (CH), 120.8 (CH), 120.1 (CH), 119.7 (C), 119.4 (CH), 111.3 (CH), 71.9 (CH_2), 52.8 (CH_3), 52.4 (CH_3), 25.8 (CH_3), 18.1 (CH_3) ; ν_{max} (KBr, cm^{-1}): 3373, 1716, 1637, 1442, 1251, 1142, 1039, 754; HRMS (ES) Calcd. for $C_{21}H_{21}NO_5$ $[M+Na]^+$ 390.1318; Found 390.1316.

Dimethyl 1-methoxy-4-(3-methyl-but-2-enyl)-9*H*-carbazole-2,3-dicarboxylate (32):



Compound **30** (50 mg, 0.14 mmol) was dissolved in dry *N*,*N*-diethylaniline (4 mL) and heated at reflux for 10 min. After the completion, the reaction mixture was extracted with EtOAc (3 x 30 mL) and washed with 10% aq HCl (4 x 10 mL) four times to remove *N*,*N*-diethylaniline. After usual work-up, the crude product was subjected to column chromatography to furnish the diester **31**, which was not fully pure. For further purification, the product was dissolved in dry acetone (10 mL). To the solution were added K_2CO_3 (30 mg, 0.2 mmol) and MeI (0.06 mL, 1.0 mmol). After 2 h, the solvent was evaporated and extracted with EtOAc (2 x 30 mL) and worked up in usual manner. The solution was removed under reduced pressure and purified by column chromatography on silica gel (ethyl acetate-petroleum ether as eluent) to furnish **32** (25 mg, 48% over two steps) as a white solid. R_f: 0.3 (1:3 ethyl acetate : petroleum ether); mp: 190-192 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (br s, 1H), 8.11 (d, 1H, J = 8 Hz), 7.54-7.47 (m, 2H), 7.29 (t, 1H, J = 7.4 Hz), 5.27 (m, 1H), 4.04-4.02 (m, 5H), 3.94 (s, 3H), 3.89 (s, 3H), 1.84 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 (C), 167.4 (C), 141.9 (C), 140.2 (C), 133.8 (C), 133.0 (C), 132.9 (C), 126.8 (CH), 125.0 (C), 123.7 (C), 123.6 (CH), 123.4 (C), 122.2 (C), 121.7 (CH), 120.6 (CH), 111.2 (CH), 62.6 (CH_3), 52.7 (CH_3), 52.5 (CH_3), 29.7 (CH_2), 25.6 (CH_3), 18.4 (CH_3) ; ν_{max} (KBr, cm^{-1}): 3440, 2927, 2360, 1649, 1462, 1091; HRMS (ES) Calcd. for $C_{22}H_{23}NO_5$ $[M+Na]^+$ 404.1474; Found 404.1465.

1-Hydroxy-4-(3-methylbut-2-enyl)-9*H*-carbazole-3-carboxylic acid (33):



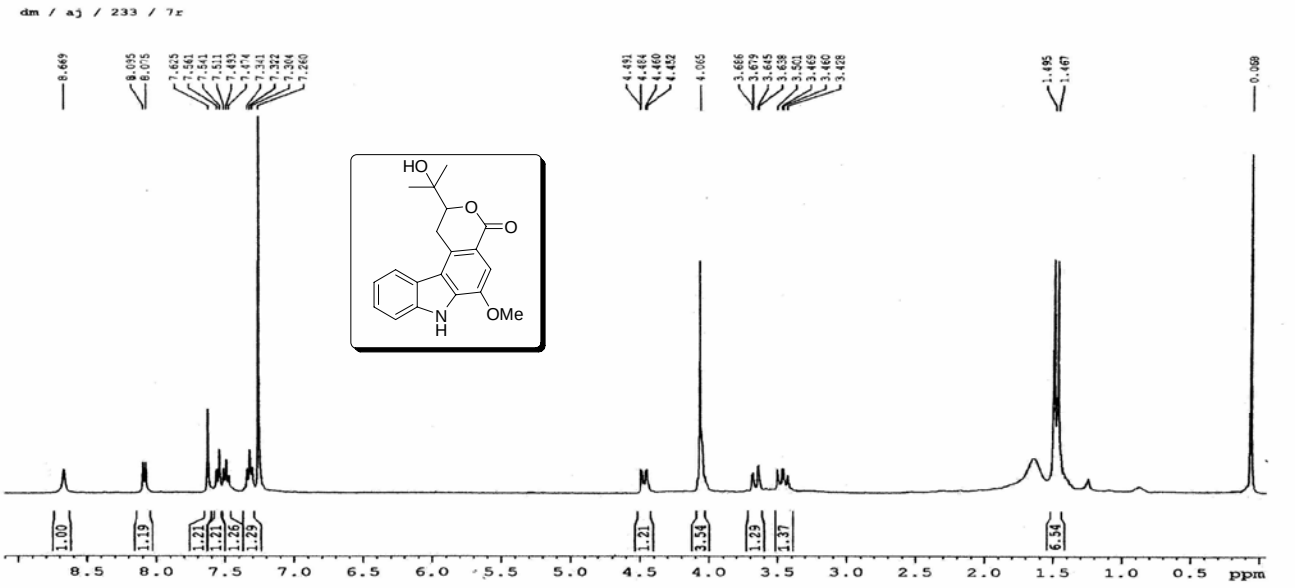
Carbazole diester **31** (40 mg), obtained from the above Claisen reaction was dissolved in MeOH (1 mL) containing 30% aq KOH solution (8 mL). The mixture was heated at reflux for 3.5 h and brought into rt and acidified with 20% HCl (10 mL). The resulting mixture was extracted with EtOAc (2 x 30 mL) and worked up in usual manner. Column chromatography of the residue afforded hydroxy acid **33** (22 mg, 68%) as a white solid. R_f:

0.3 (1:1 ethyl acetate : petroleum ether); mp: 160-166 ºC; ^{1}H NMR (200 MHz, Acetone-d_6): δ 10.98 (br s, 1H), 8.09 (d, 1H, *J* = 8 Hz), 7.69 (d, 1H, *J* = 8 Hz), 7.49 (t, 2H, *J* = 7.6 Hz), 7.24 (t, 2H, *J* = 7.6 Hz), 5.25 (m, 1H), 3.93 (d, 2H, *J* = 5.6 Hz), 1.86 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (C), 140.5 (C), 140.2 (C), 132.2 (C), 130.9 (C), 128.7 (C), 128.3 (C), 126.0 (C), 125.2 (CH), 123.8 (CH), 122.8 (CH), 120.2 (C), 119.5 (CH), 112.3 (CH), 111.4 (CH), 24.9 (CH_3), 17.5 (CH_3) ; ν_{max} (KBr, cm^{-1}): 3404, 2920, 1676, 1448, 1254, 742.

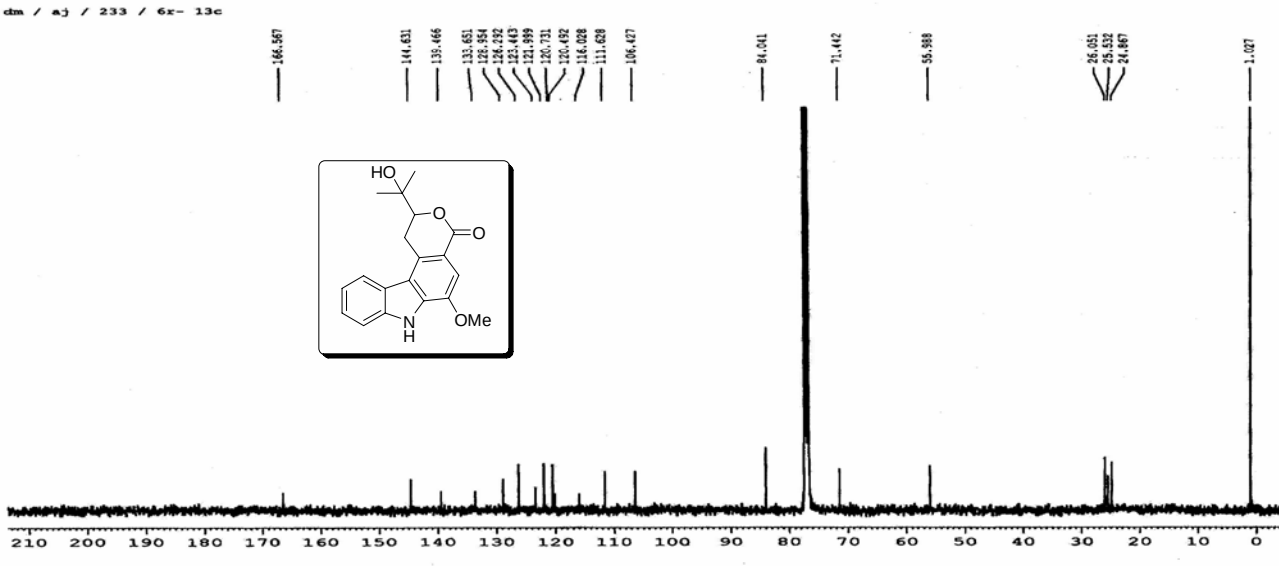
Reference:

1) Lebold, T. P.; Kerr, M. A. *Org. Lett.* **2008**, *10*, 997-1000.
2) Ito, C.; Katsuno, S.; Ruangrungsi, N.; Furukawa, H. *Chem. Pharm. Bull.* **1998**, *46*, 344-346.
3) Wu, T. S.; Huang, S. C.; *Chem. Pharm. Bull*. **1992**, *40*, 1069-1071.
4) Wu, T-S.; Huang, S-C.; Wu, P-L. *Chem. Pharm. Bull*. **1992**, *40*, 1069-1071.
5) Mal, D.; Senapati, B. K.; Pahari, P. *Tetrahedron* **2007**, *63*, 3768-3781.

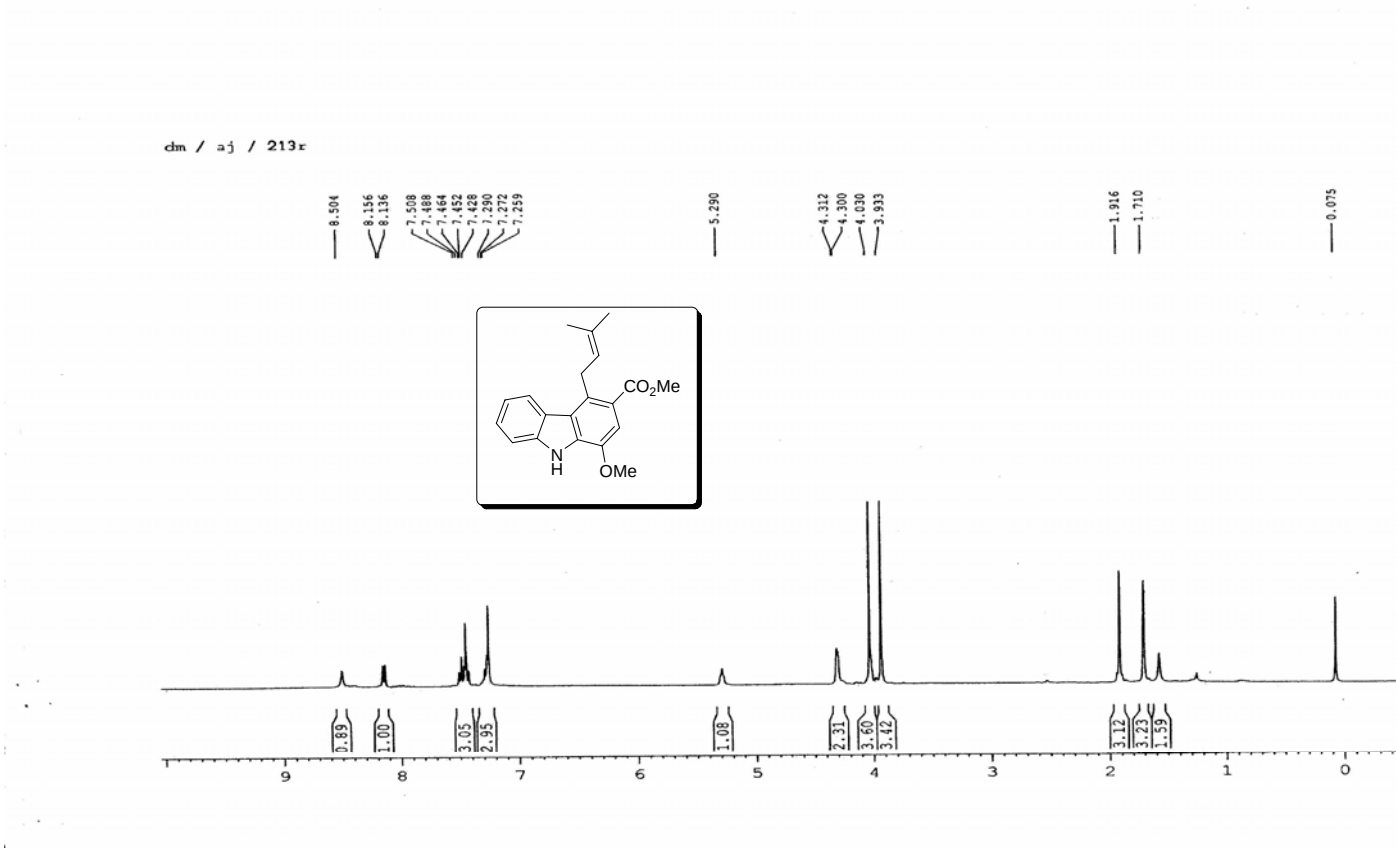
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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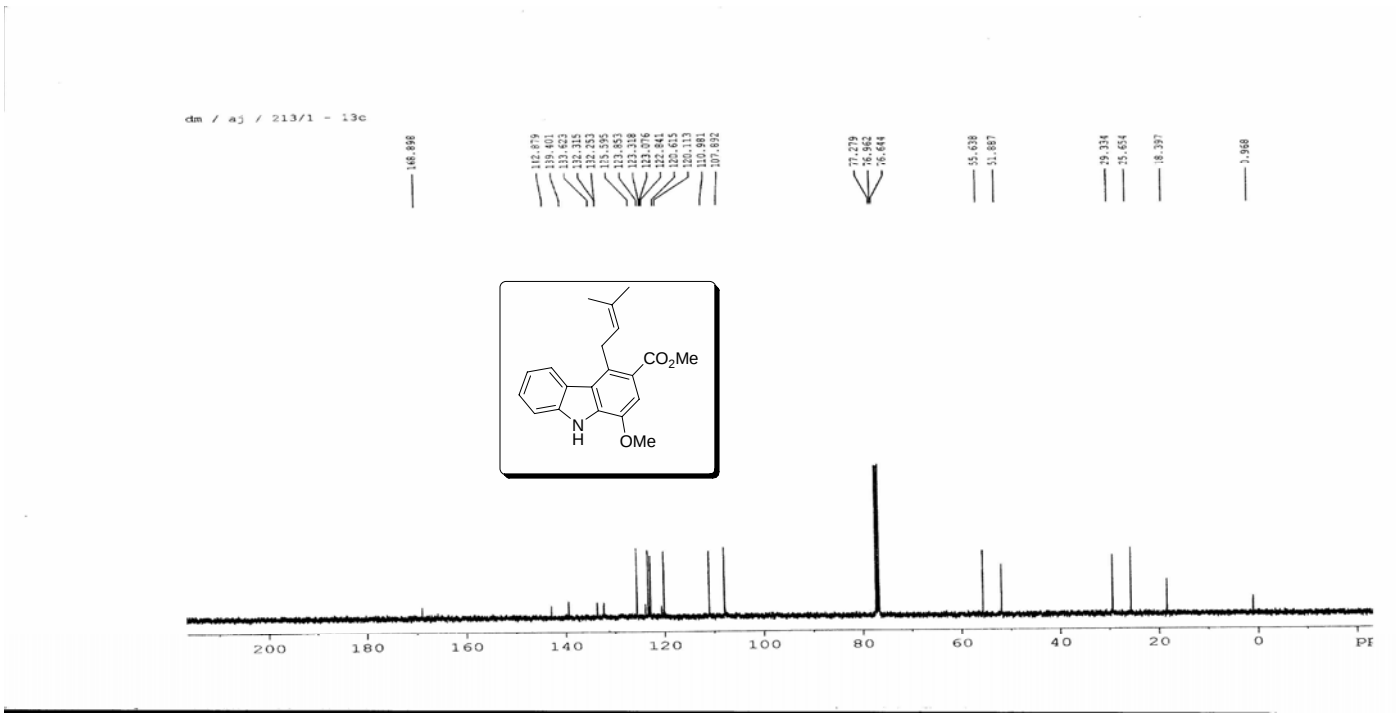

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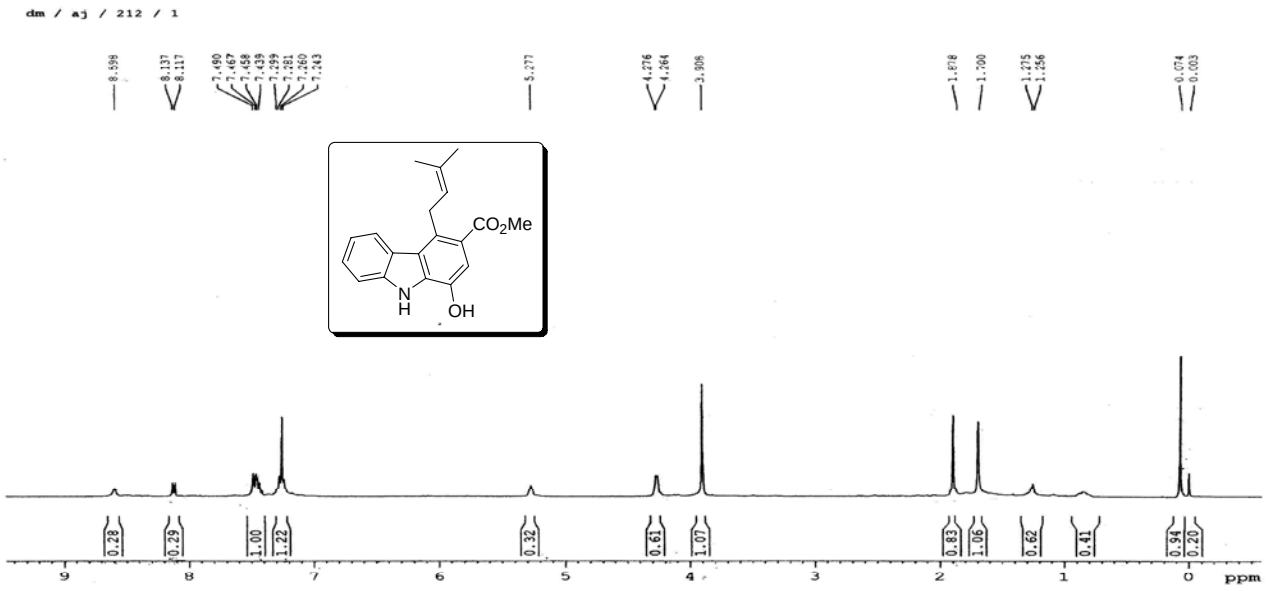

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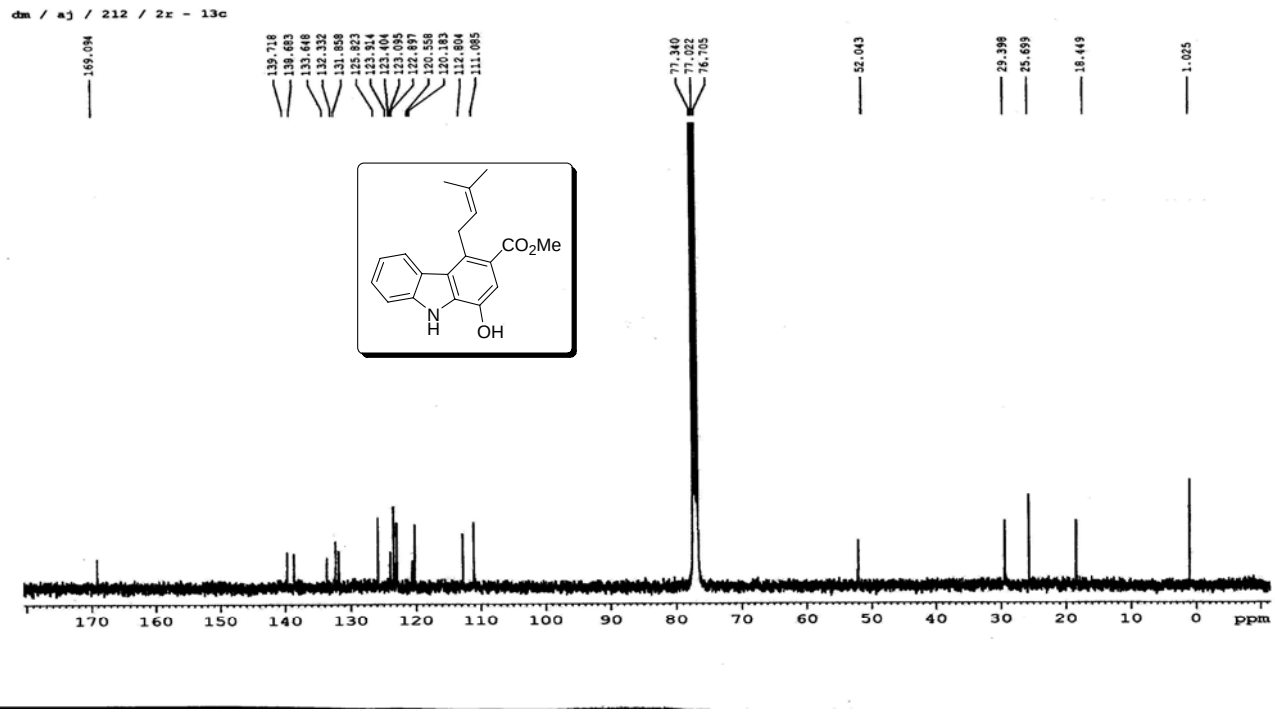
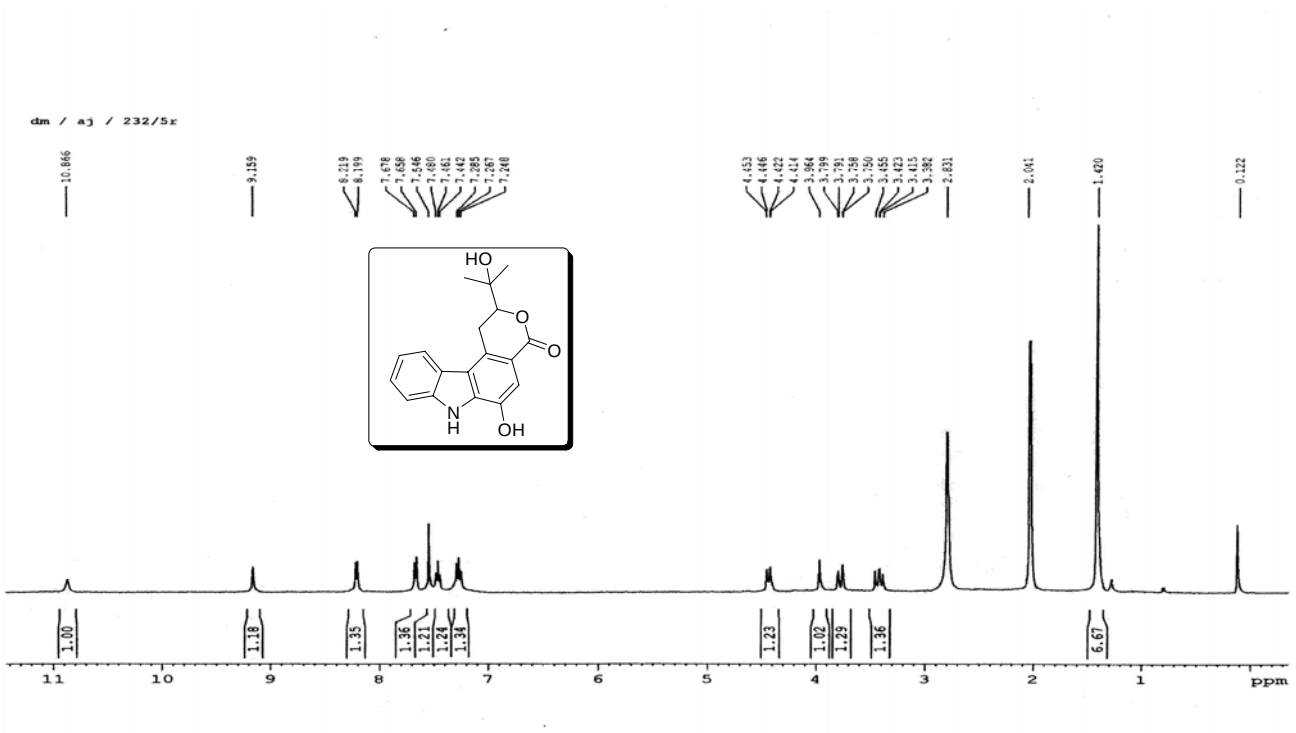


^{1}H NMR (400 MHz, Acetone-d_6)



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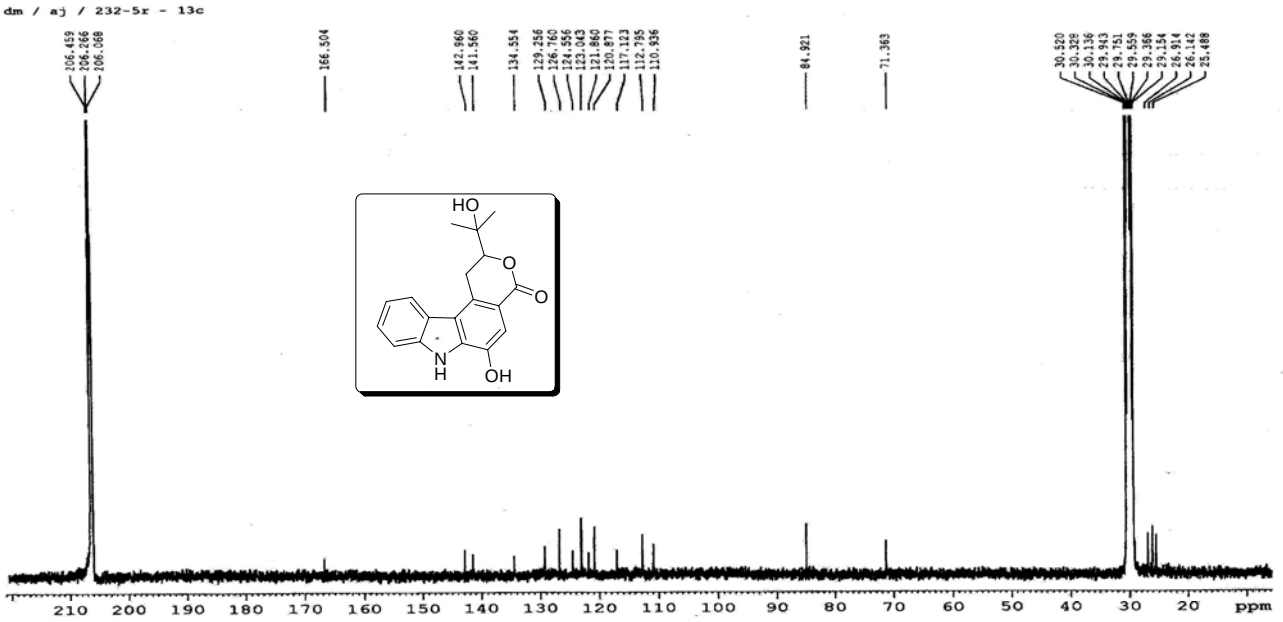

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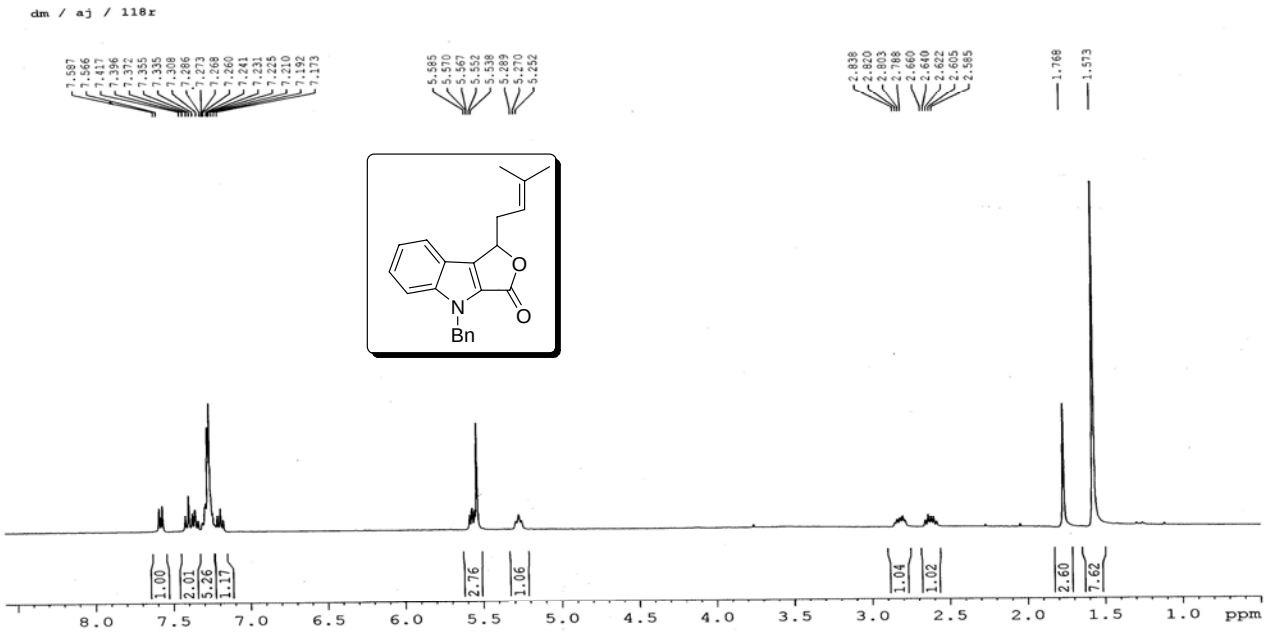

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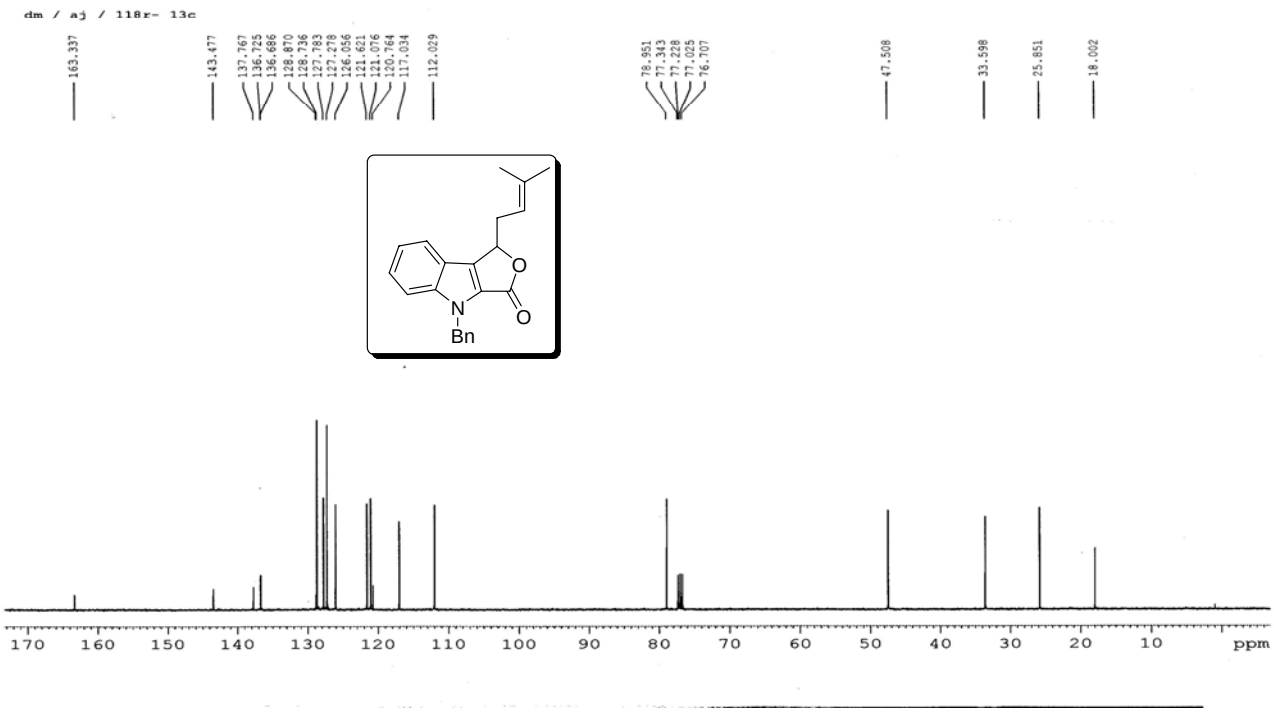

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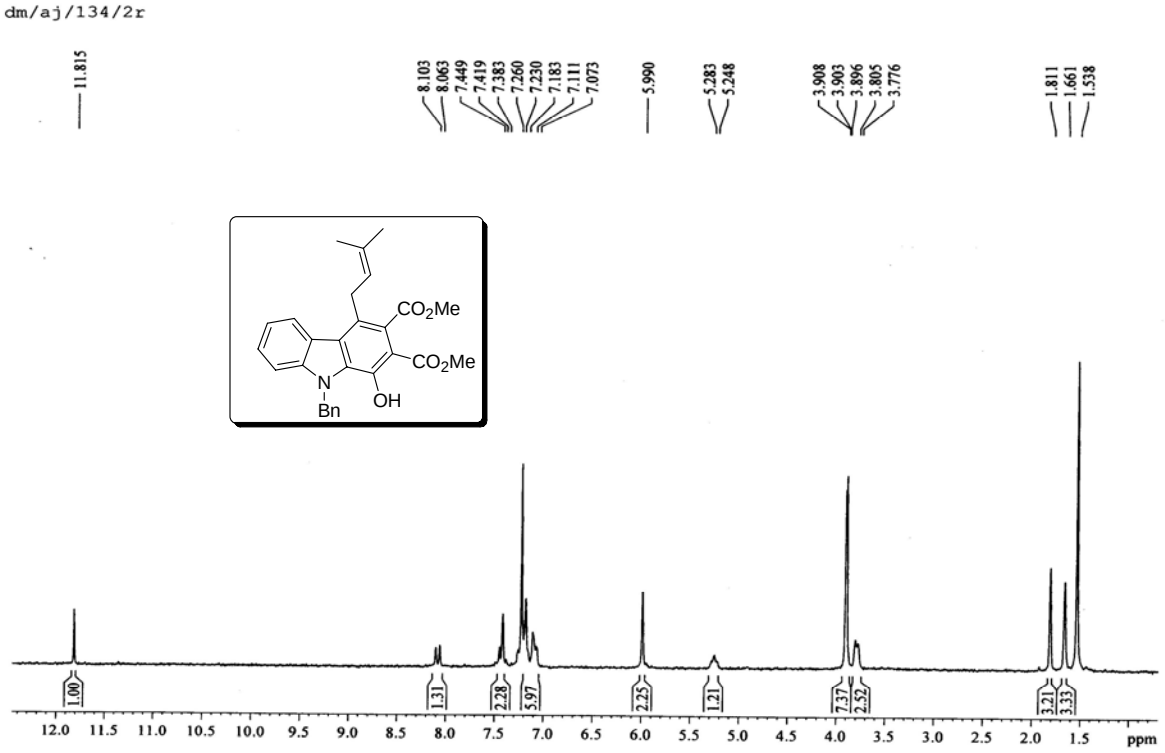

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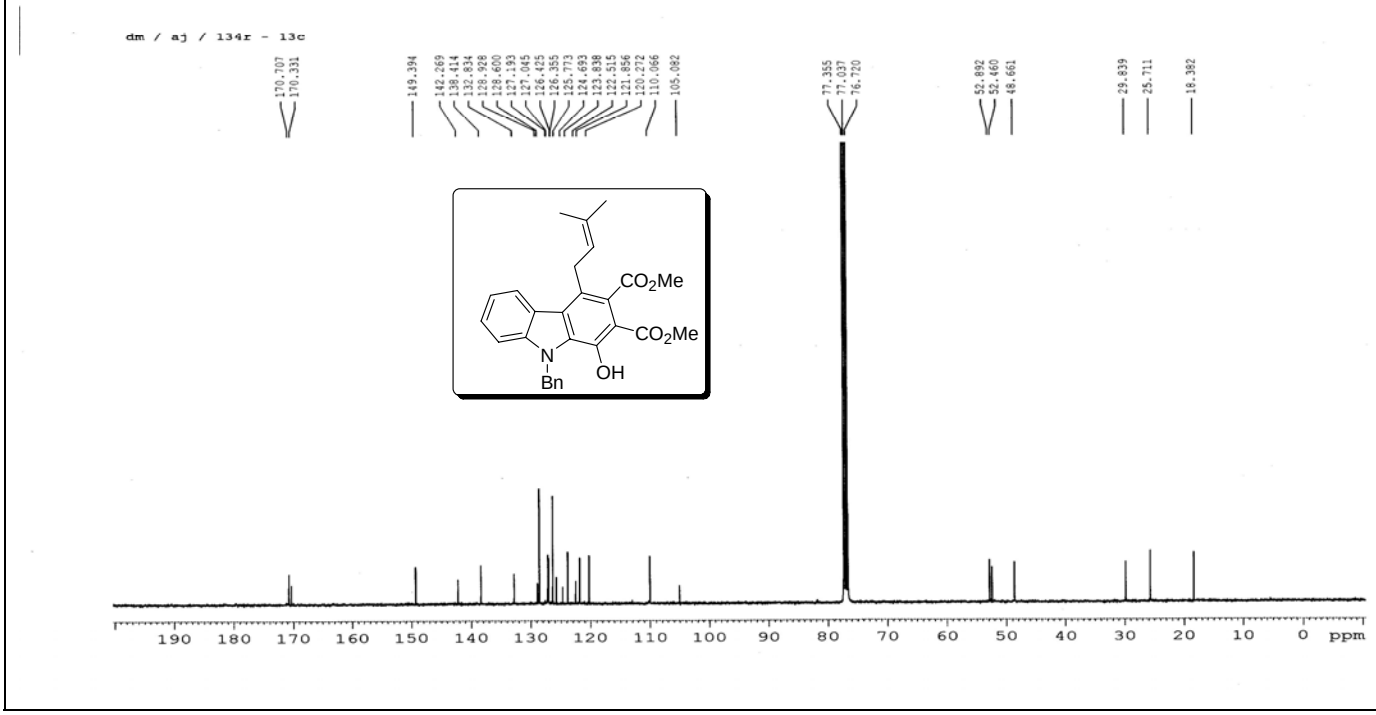

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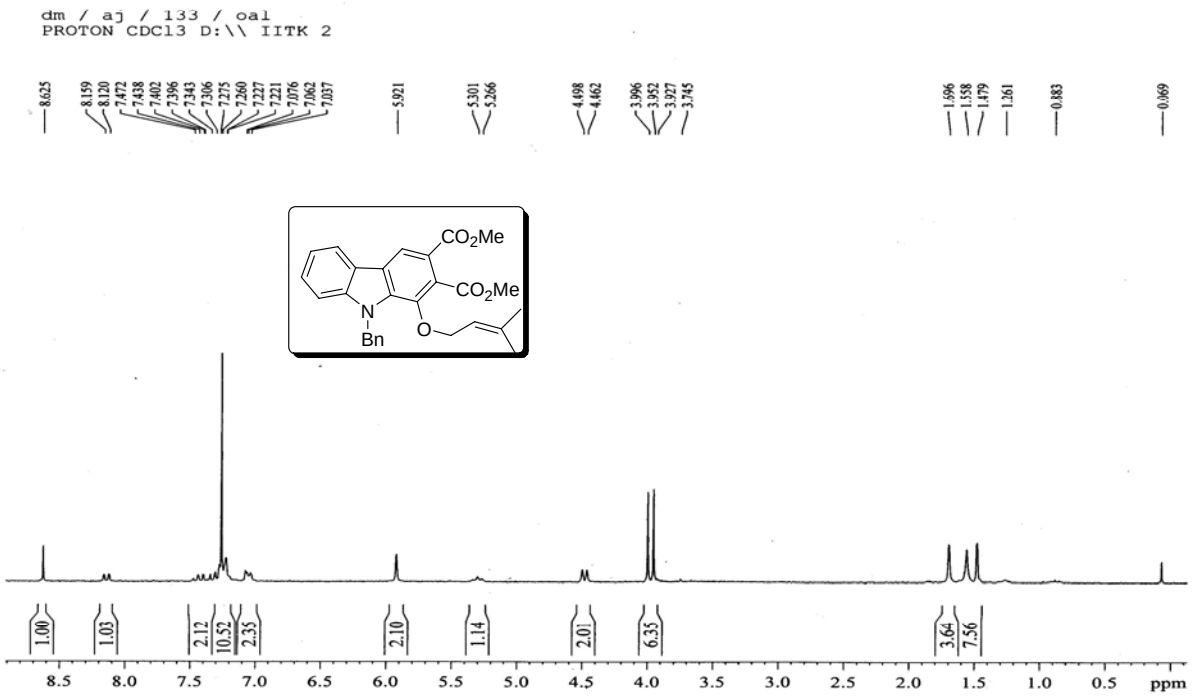

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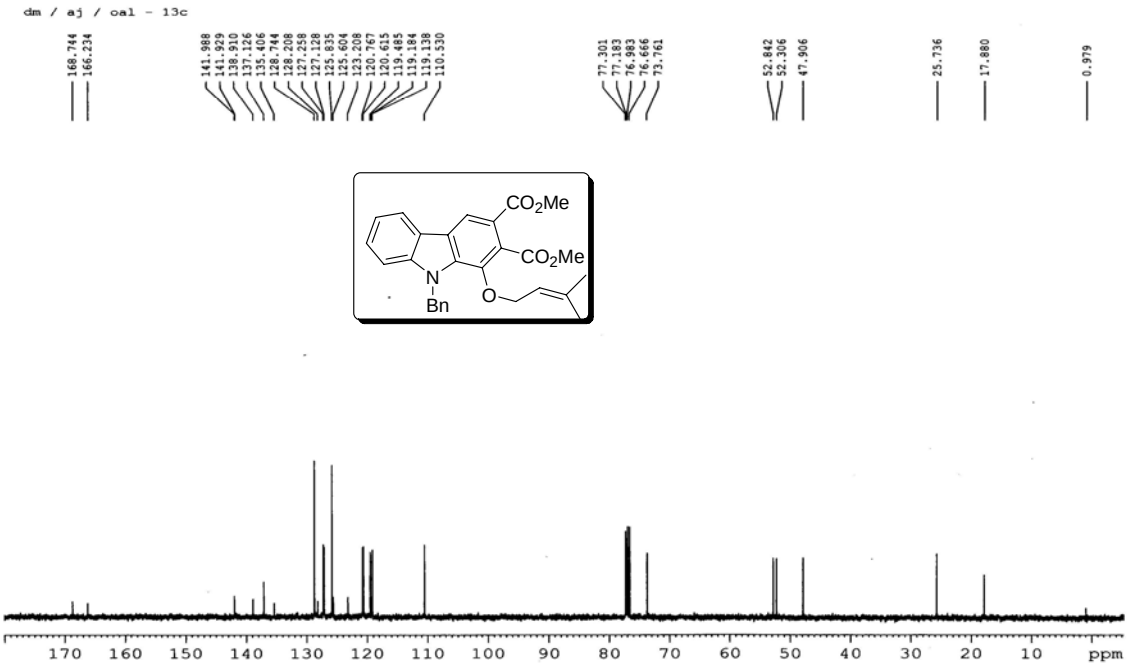

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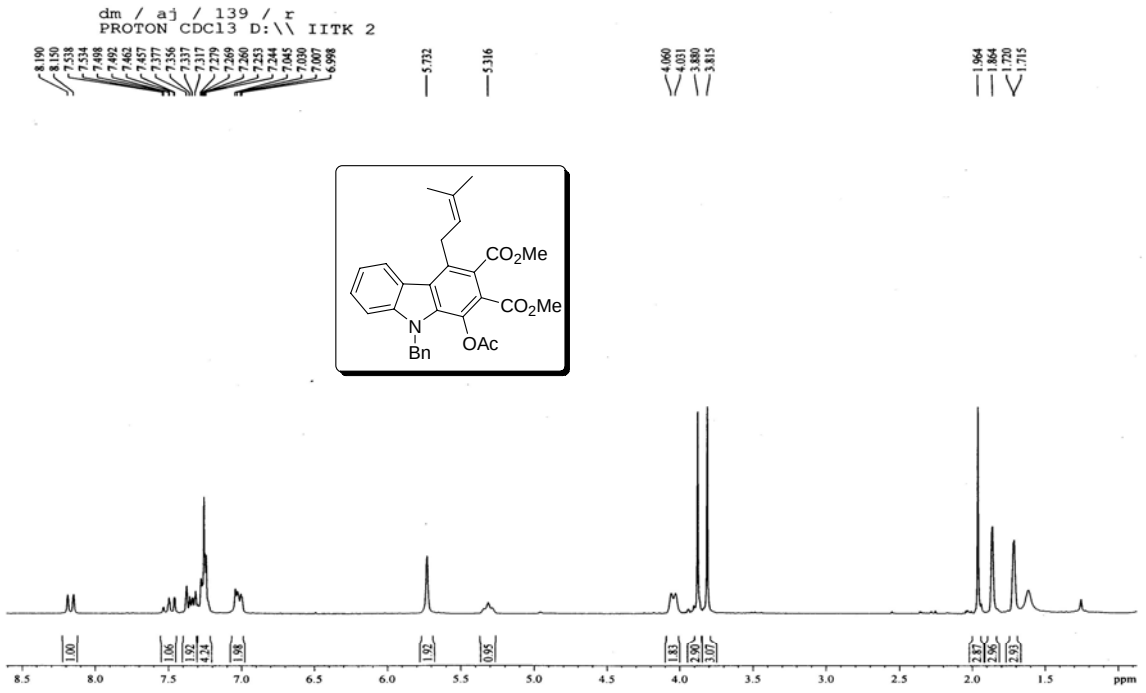

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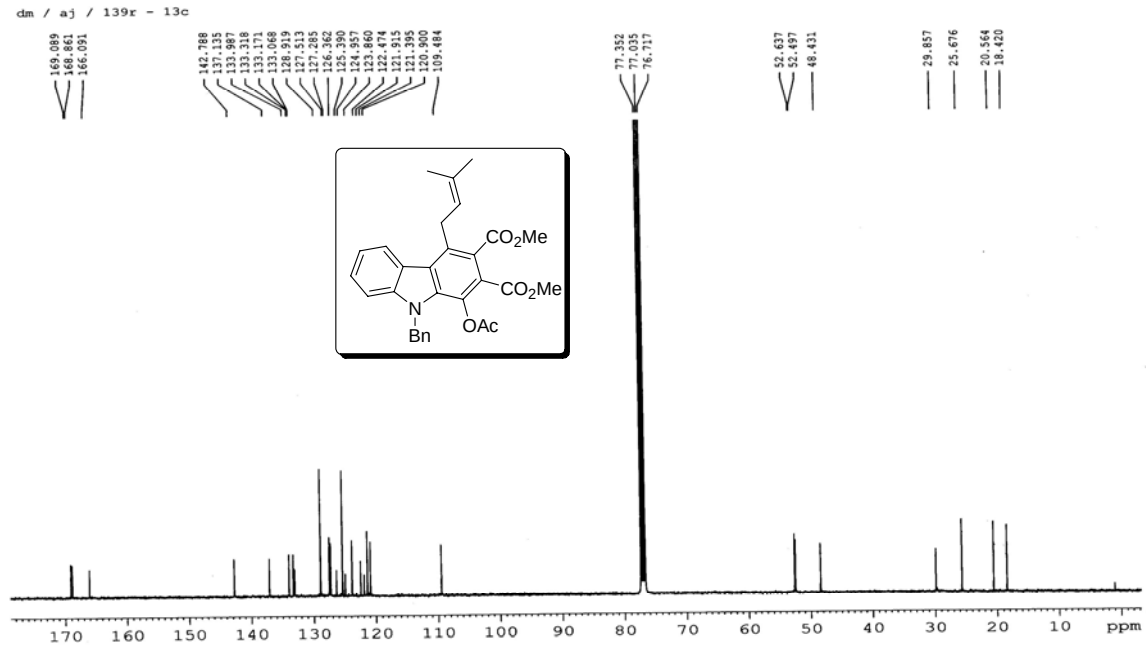

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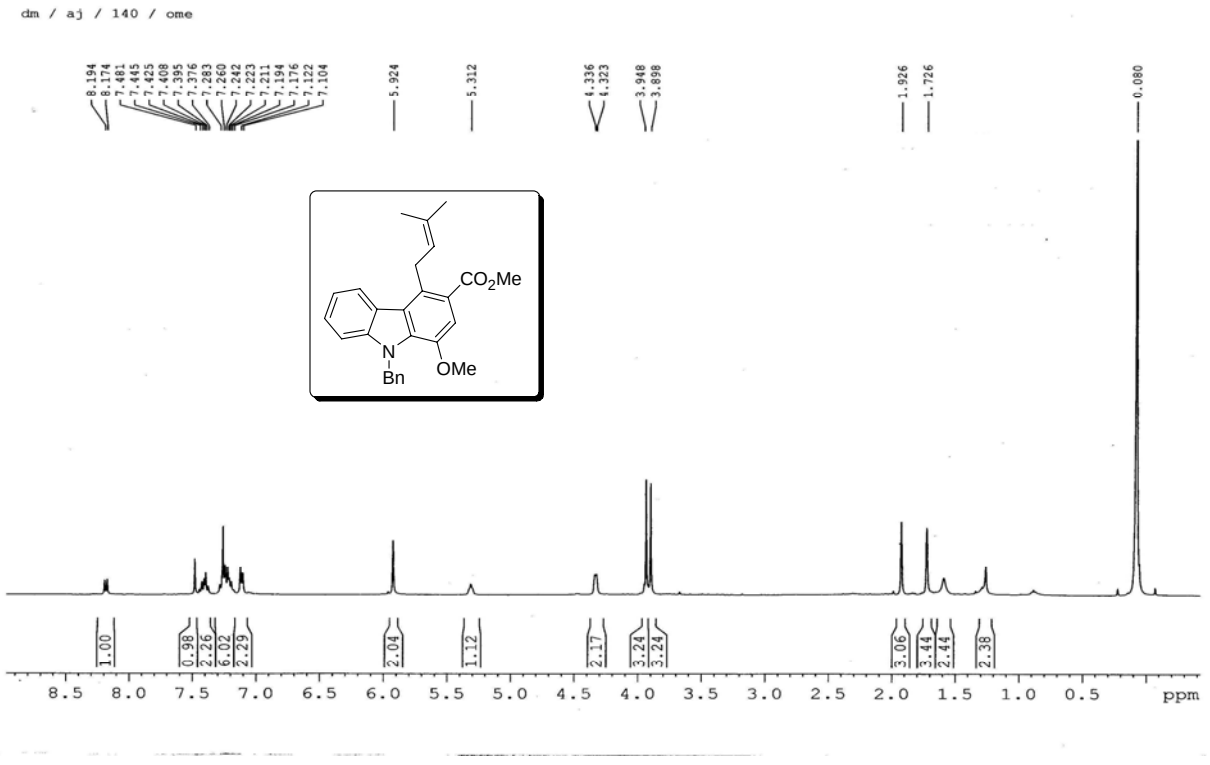

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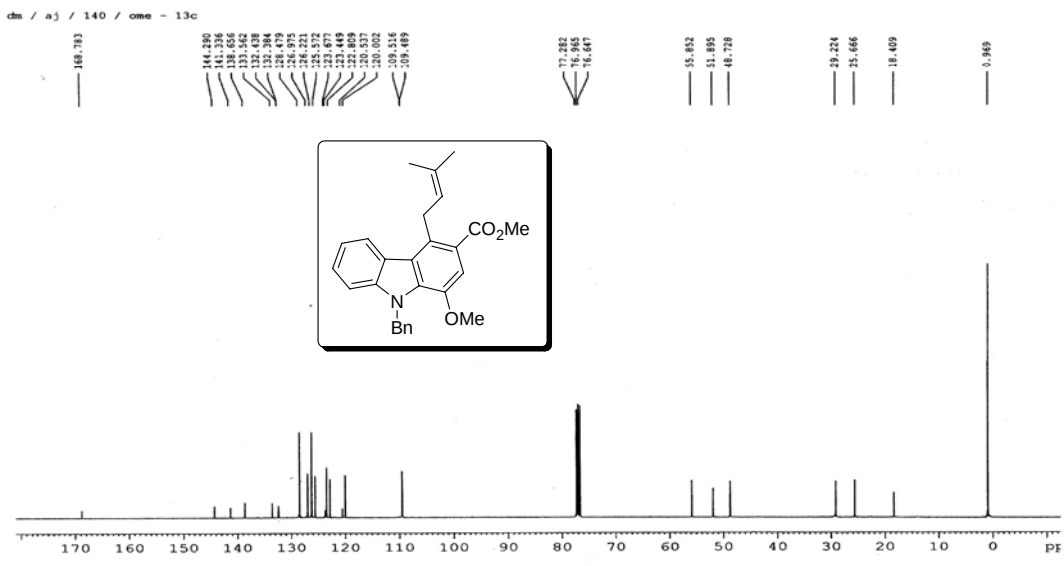

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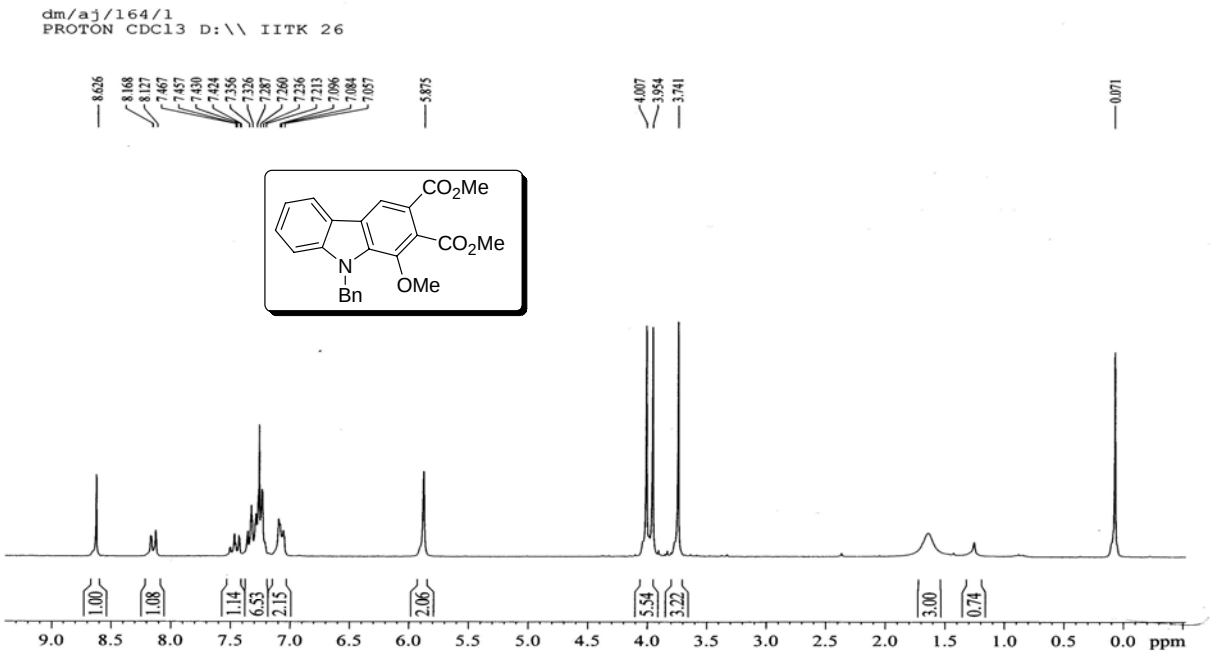

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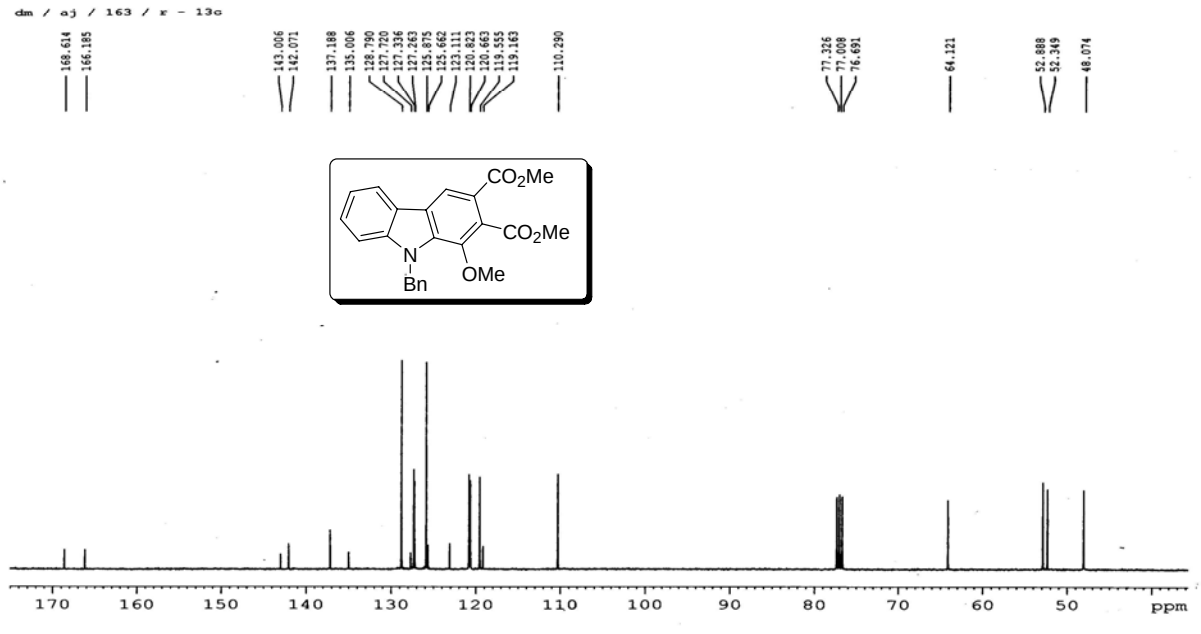

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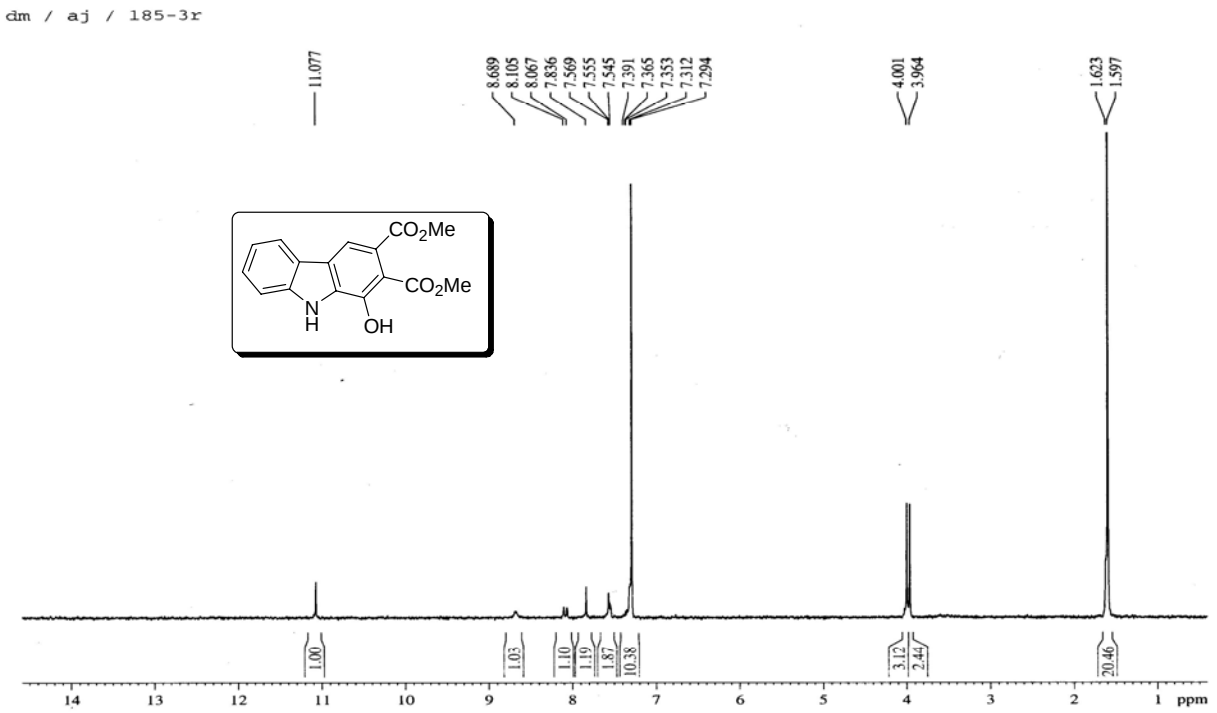

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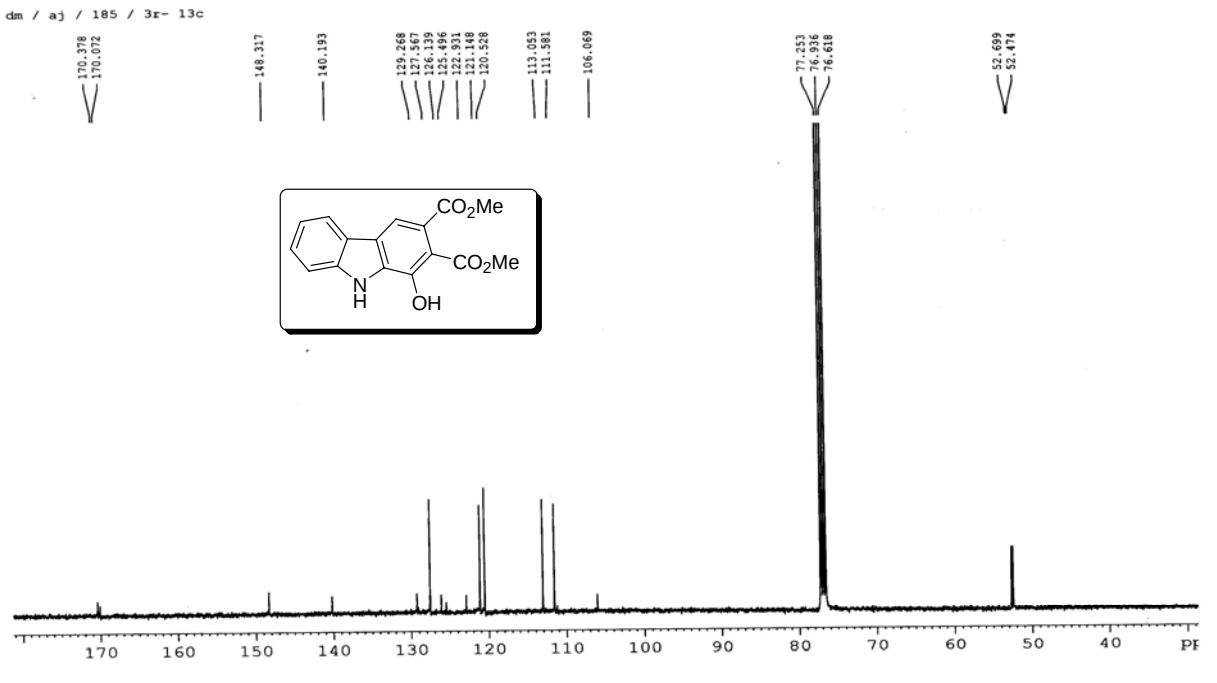

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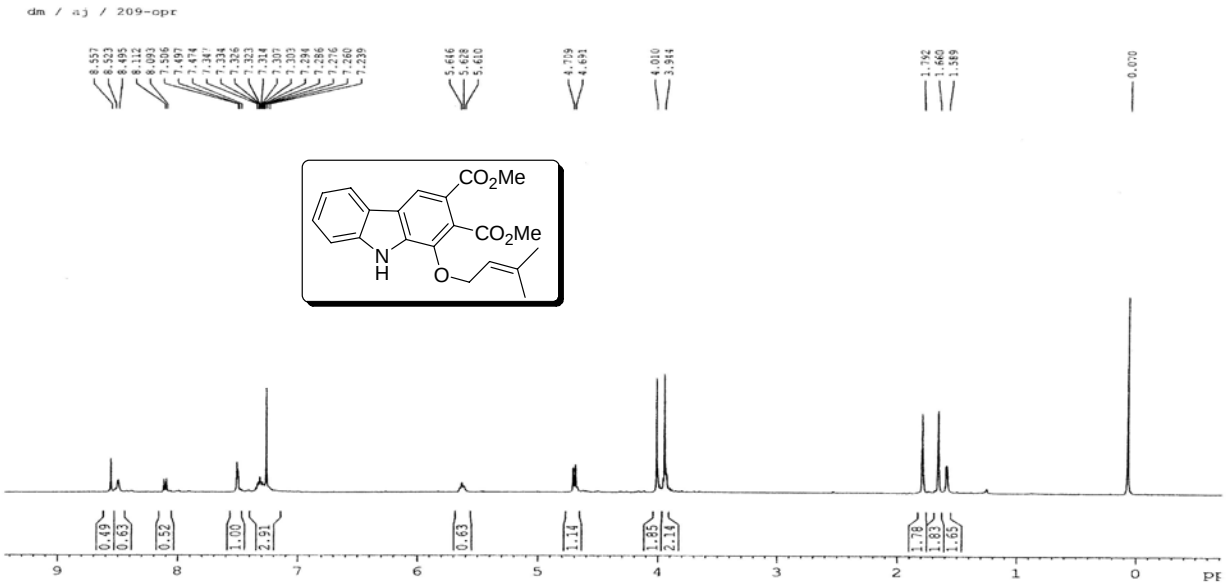

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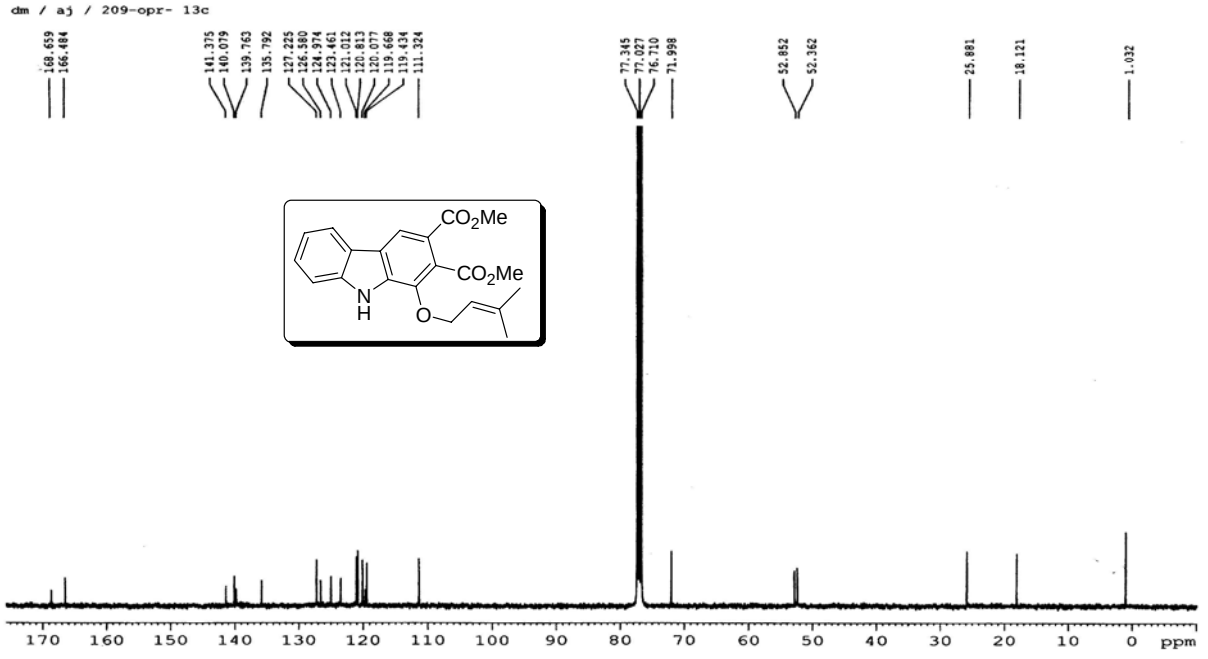

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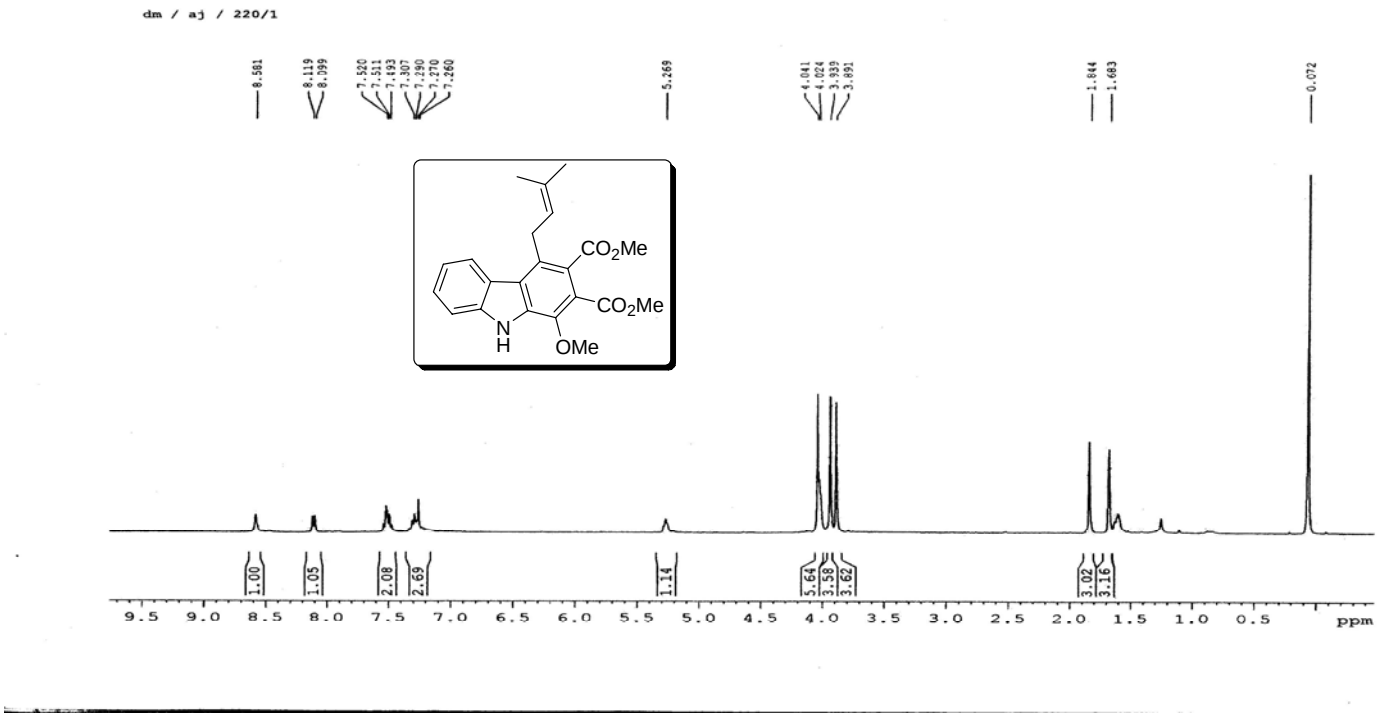

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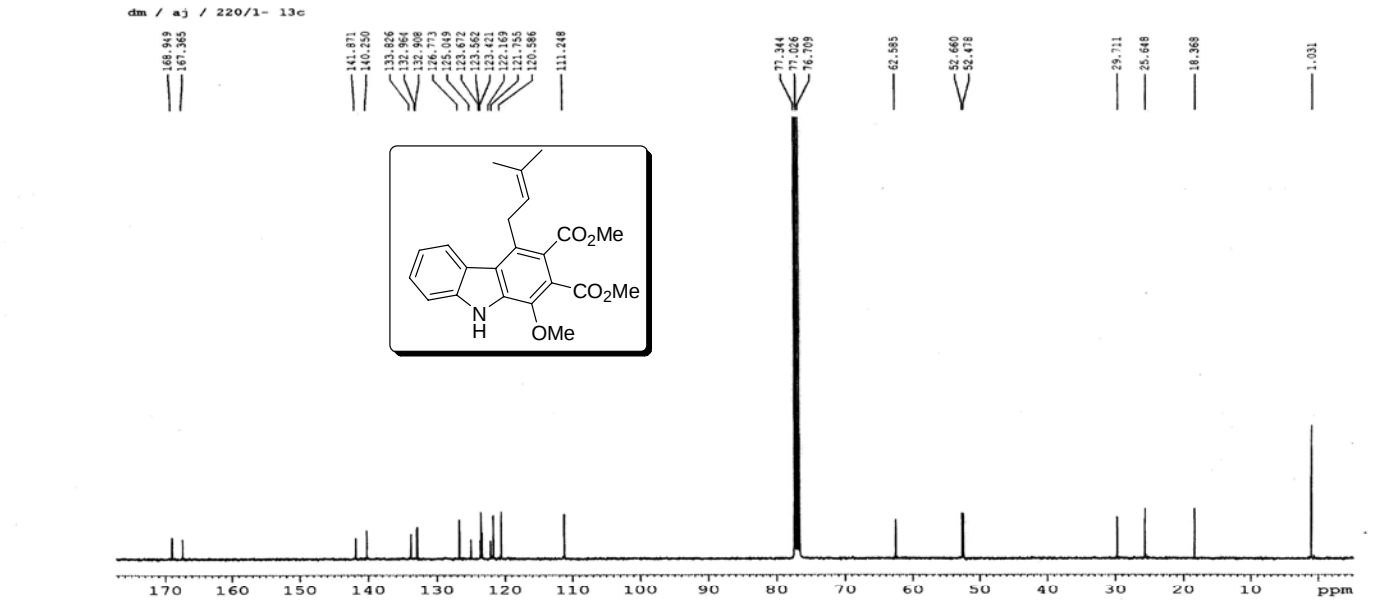

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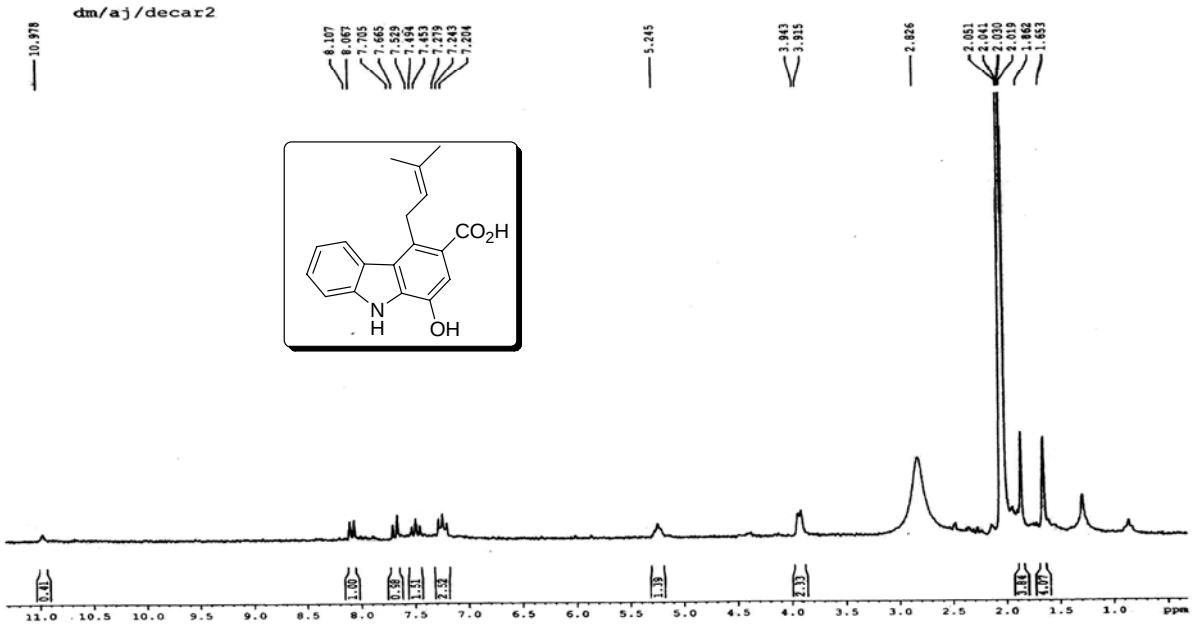

^{13}C NMR (100 MHz, Acetone-d_6)