Supplementary Information

Regioselective Ruthenium Catalyzed Hydrohydroxyalkylation of Dienes with

3-Hydroxy-2-Oxindoles: Prenylation, Geranylation and Beyond

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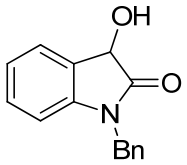
General Experimental Details

All reactions were run under an atmosphere of argon, unless otherwise indicated. Toluene was distilled from sodium/benzophenone and transferred via an oven-dried syringe. Reaction tubes were oven-dried and cooled under a stream of argon. Reactions tubes were purchased from Fischer Scientific (catalog number 14-959-35C). $Ru_3(CO)_{12}$ and PCy_3 were used as received from commercial suppliers. 3-Hydroxy-2-oxindoles (**1a-1f**) were prepared via reduction between benzylated isatins and $NaBH_4$. Isoprene and dienes (**2c-2f**) were distilled immediately before each use, and myrcene was distilled after purchase from commercial suppliers. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}) and products were visualized by UV, $KMnO_4$, magic stain and/or *p*-anisaldehyde stain. Preparative column chromatography employing silica gel was performed according to the method of Still.[1] Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+H]^+$ or a suitable fragment ion. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected. Proton and deuteron nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Gemini 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform and the center of the quintet at 2.49 ppm (J = 1.7 Hz) for deuteriodimethyl sulfoxide. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 400 spectrometer (100 MHz). Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform and the center of the septet at 39.5 ppm for deuteriodimethyl sulphoxide. ^{13}C NMR spectra were routinely run with broadband decoupling.

[1]Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem*. **1978**, *43*, 2923.

Experimental Procedures and Spectroscopic Data for Preparation of 3-Hydroxy-2-oxindole 1a-1e

1-benzyl-3-hydroxyindolin-2-one (1a)



Compound 1a: $NaBH_4$ (1.7 mmol, 64.3 mg, 0.5 equiv) was added in small portions to a stirred suspension of commercially available 1-benzylindoline-2,3-dione (0.8 g, 3.4 mmol, 1.0 equiv) in 20.5 mL of a 1:1 dichloromethane/ethanol mixture at -30 ºC. The mixture was vigorously stirred at this temperature until the suspension became colorless. Then distilled water was added and the reaction mixture was stirred until bubbling stopped. The mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using a 4:1 mixture of dichloromethane /diethyl ether as elution solvent to give 0.4 g (50%) **1a**[2] as a white solid.

^{1}H NMR (400 MHz, D_6-DMSO): δ 7.35-7.18 (m, 7H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H) 5.03 (d, *J* = 7.6 Hz, 1H), 4.83 (s, 2H)

.

^{13}C NMR (100 MHz, D_6-DMSO): δ 176.2, 142.6, 136.3, 128.9, 128.7, 128.6, 127.4, 127.3, 124.6, 122.3, 109.0, 68.8, 42.4

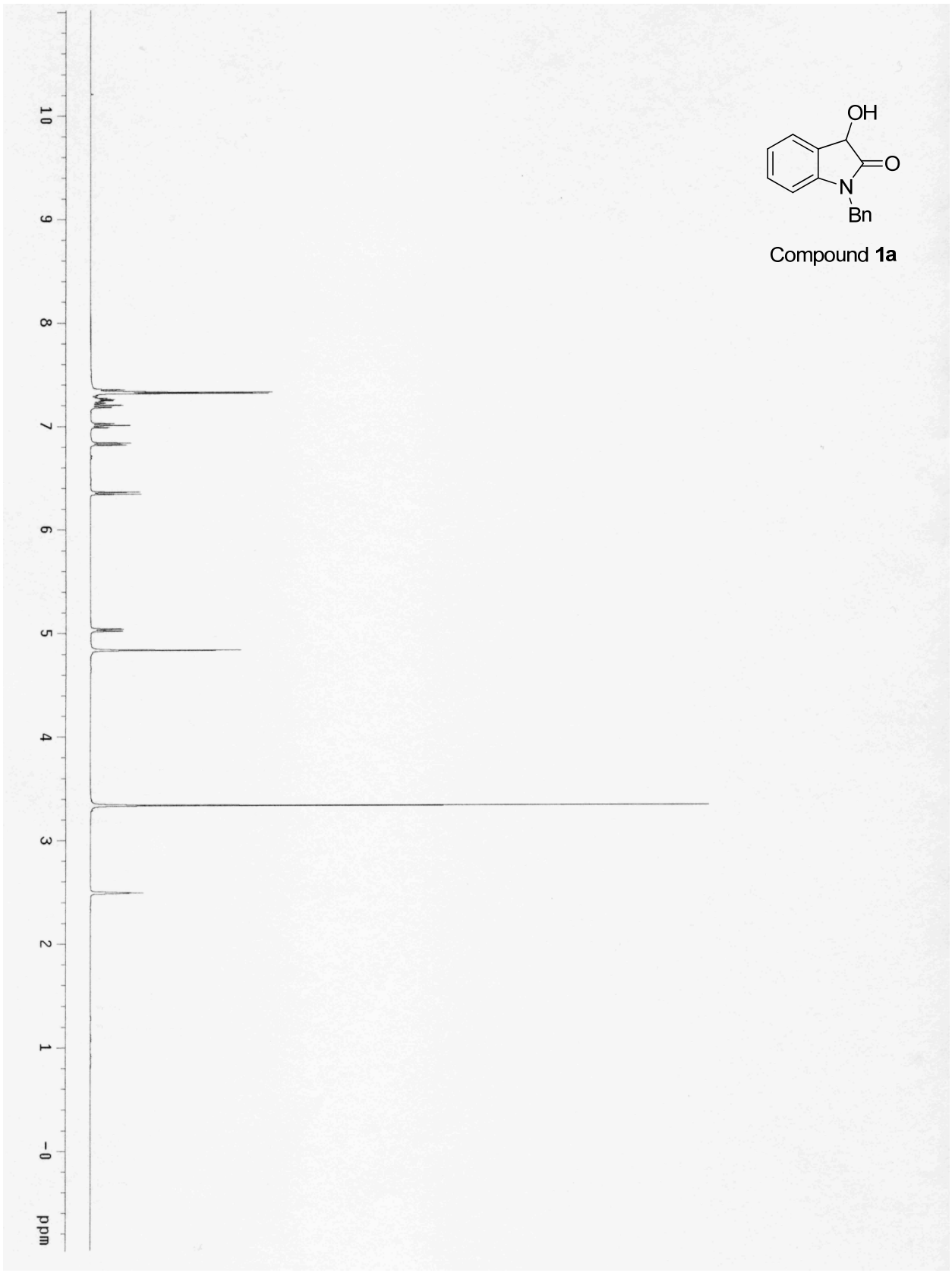
LRMS (CI) Calcd. For $C_{15}H_{12}NO_2$ $[M-H]^+$: 238, Found: 238

FTIR (neat): 3461, 3261, 2251, 2113, 1650, 1049, 1023, 1005, 814, 752 cm^{-1}

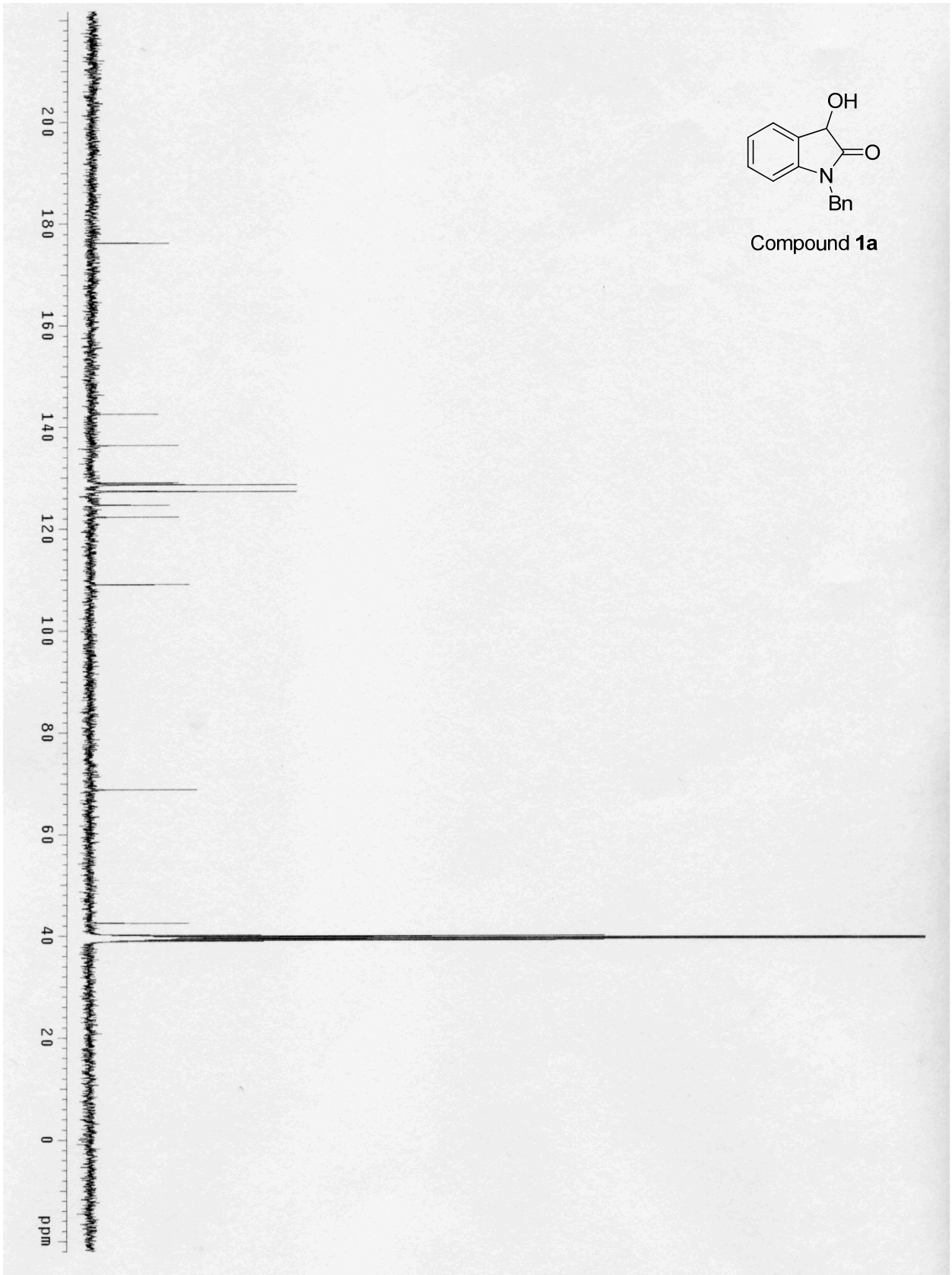
Mp: 140.8-141.2 °C

TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 1:4)

[2]M. Retini, G. Bergonzinia and P. Melchiorre, *Chem. Commun.*, 2012, **48**, 3336

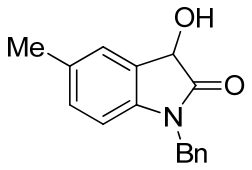


Compound **1a**



Compound **1a**

1-benzyl-3-hydroxy-5-methylindolin-2-one (1b)



Compound 1b: $NaBH_4$ (2.6 mmol, 98.8 mg, 0.5 equiv) was added in small portions to a stirred suspension of commercially available 1-benzyl-5-methylindoline-2,3-dione (1.3 g, 5.2 mmol, 1.0 equiv) in 31.2 mL of a 1:1 dichloromethane/ethanol mixture at -30 ºC. The mixture was vigorously stirred at this temperature until the suspension became colorless. Then distilled water was added and the reaction mixture was stirred until bubbling stop. The mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using a 4:1 mixture of dichloromethane /diethyl ether as elution solvent to give 0.53 g (40%) **1b**[3] as a white solid.

^{1}H NMR (400 MHz, D_6-DMSO): 7.25-7.16 (m, 6H), 7.10 (s, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.29 (d, J = 7.6 Hz 1H), 4.94 (d, J = 7.6 Hz, 1H), 4.75 (s, 2H), 2.17 (s, 2H)

^{13}C NMR (100 MHz, D_6-DMSO): δ 176.2, 140.3, 136.4, 131.3, 129.0, 128.7, 128.6, 127.3, 127.2, 125.4, 108.8, 68.9, 42.5, 20.6

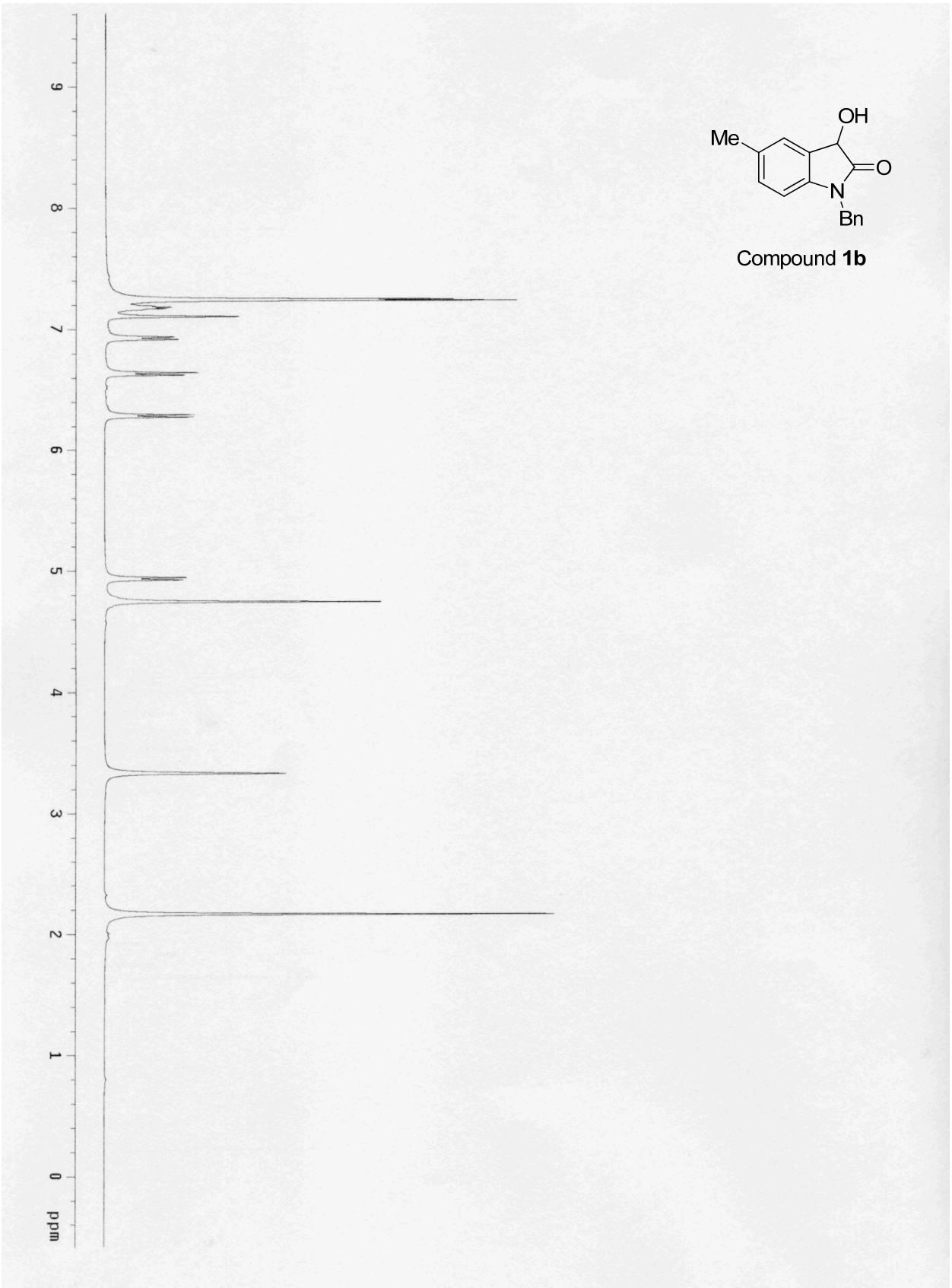
LRMS (CI) Calcd. For $C_{16}H_{14}NO_2$ $[M-H]^+$: 252, Found: 252

FTIR (neat): 3377, 2918, 2358, 1701, 1619, 1490, 1432, 1343, 1192, 1129, 1014, 804 cm^{-1}

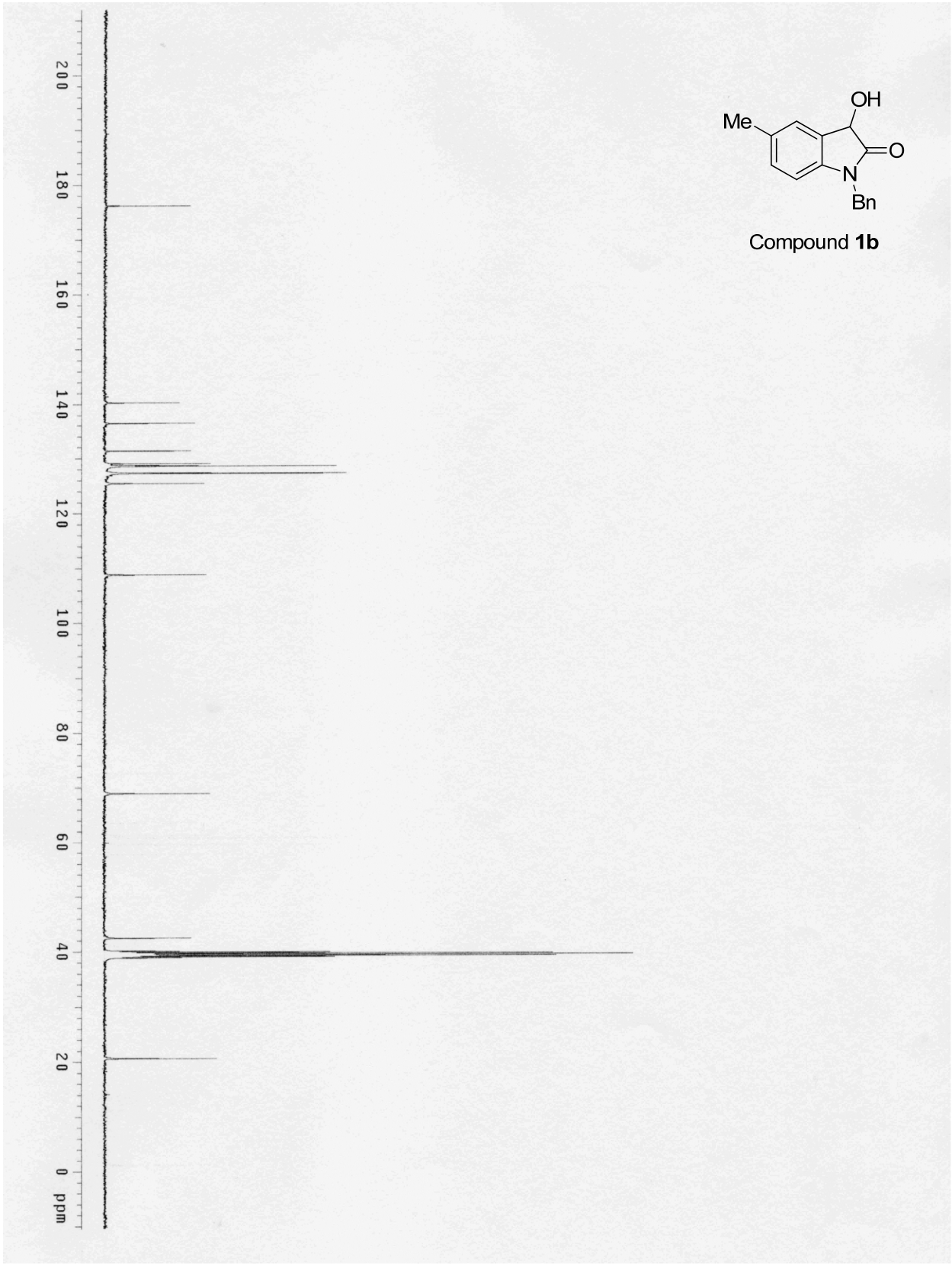
Mp: 130.5-131.1 °C

TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 1:4)

[3]M. Retini, G. Bergonzinia and P. Melchiorre, *Chem. Commun.*, 2012, **48**, 3336

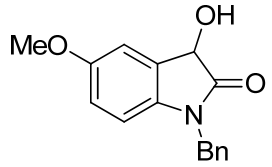


Compound **1b**



Compound **1b**

1-benzyl-3-hydroxy-5-methoxyindolin-2-one (1c)



Compound 1c: $NaBH_4$ (1.9 mmol, 72.2 mg, 0.5 equiv) was added in small portions to a stirred suspension of commercially available 1-benzyl-3-hydroxy-5-methoxyindolin-2-one (1.0 g, 3.7 mmol, 1.0 equiv) in 21.8 mL of a 1:1 dichloromethane/ethanol mixture at -30 ºC. The mixture was vigorously stirred at this temperature until the suspension became colorless. Then distilled water was added and the reaction mixture was stirred until bubbling stop. The mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using a 4:1 mixture of dichloromethane /diethyl ether as elution solvent to give 0.4 g (40%) **1c** as a white solid.

^{1}H NMR (400 MHz, D_6-DMSO): δ 7.34-7.29 (m, 4H), 7.26-7.23 (m, 1H), 6.97 (d, J = 2.0 Hz, 1H), 6.78-6.71 (m, 2H), 6.37 (d, J = 8.0 Hz, 1H), 5.01 (d, J = 7.6 Hz, 1H), 4.81 (s, 2H), 3.69 (s, 3H)

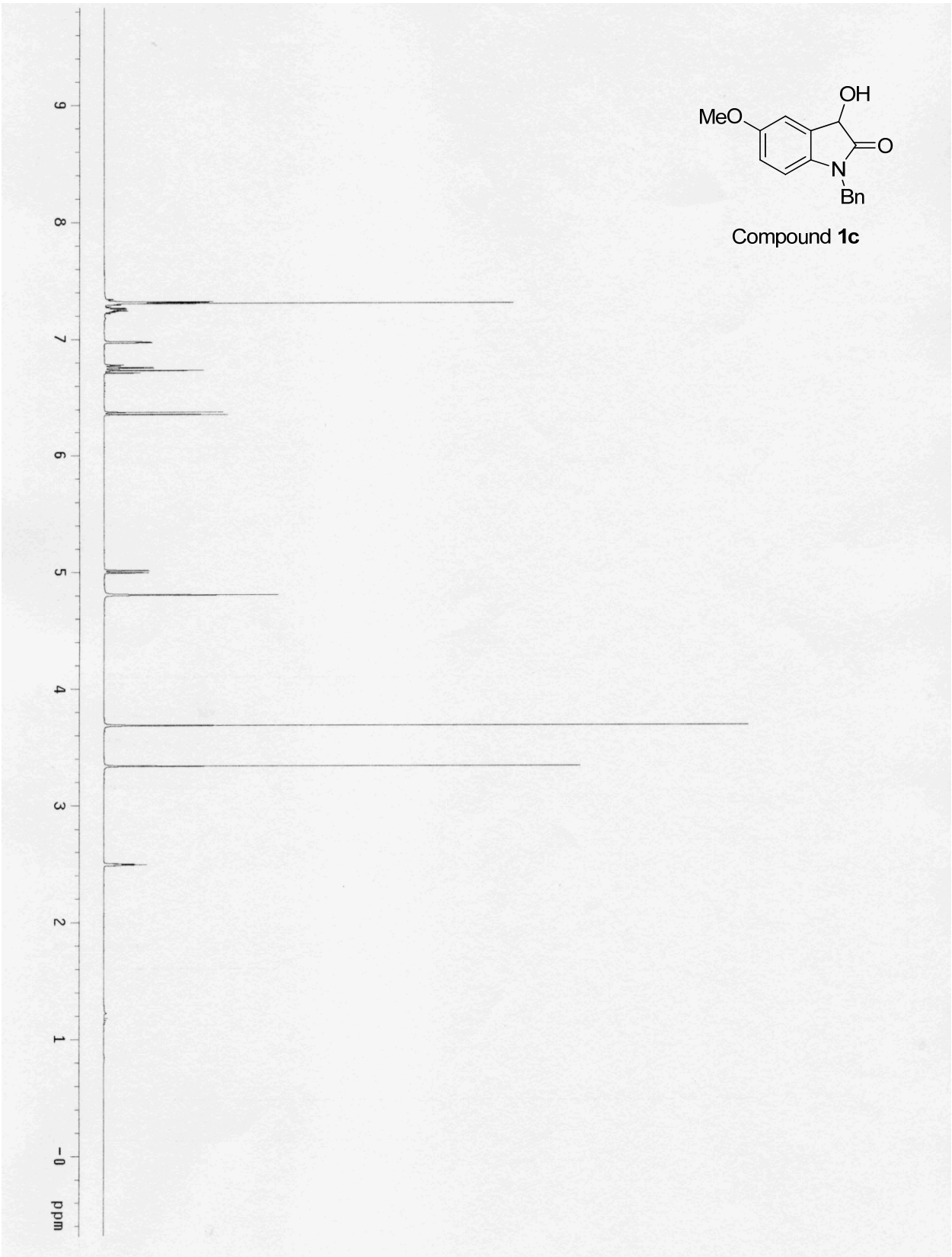
^{13}C NMR (100 MHz, D_6-DMSO): δ 175.9, 155.5, 136.4, 135.9, 129.9, 128.6, 127.3, 127.2, 113.4, 111.7, 109.5, 69.1, 55.5, 42.5

LRMS (CI) Calcd. For $C_{16}H_{16}NO_3$ $[M+H]^+$: 270, Found: 270

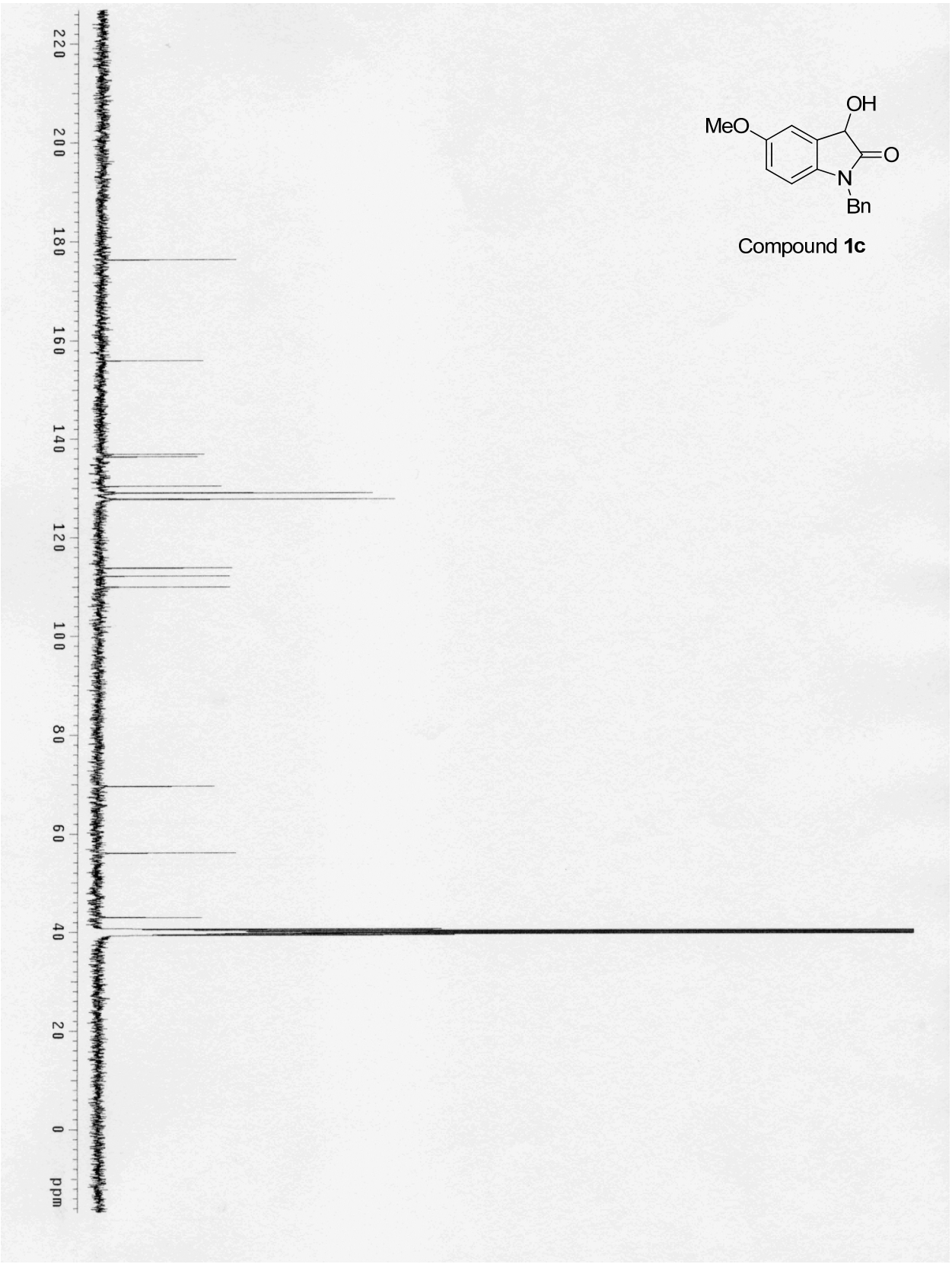
FTIR (neat): 3434, 2249, 2123, 1711, 1054, 1043, 1006, 821, 758 cm^{-1}

Mp: 122.7-123.1 °C

TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 1:4)

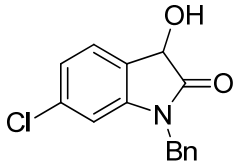


Compound **1c**



Compound **1c**

1-benzyl-6-chloro-3-hydroxyindolin-2-one (1d)



Compound 1d: $NaBH_4$ (2.4 mmol, 91.2 mg, 0.5 eq) was added in small portions to a stirred suspension of commercially available 1-benzyl-6-chloro-3-hydroxyindolin-2-one (1.3 g, 4.8 mmol, 1.0 equiv) in 28.2 mL of a 1:1 dichloromethane/ethanol mixture at -30 ºC. The mixture was vigorously stirred at this temperature until the suspension became colorless. Then distilled water was added and the reaction mixture was stirred until bubbling stop. The mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using a 4:1 mixture of dichloromethane /diethyl ether as elution solvent to give 0.5 g (38%) **1d** as a pale yellow solid.

^{1}H NMR (400 MHz, D_6-DMSO): δ 7.36-7.31 (m, 5H), 7.28-7.25 (m, 1H), 7.06 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 5.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.86 (s, 2H)

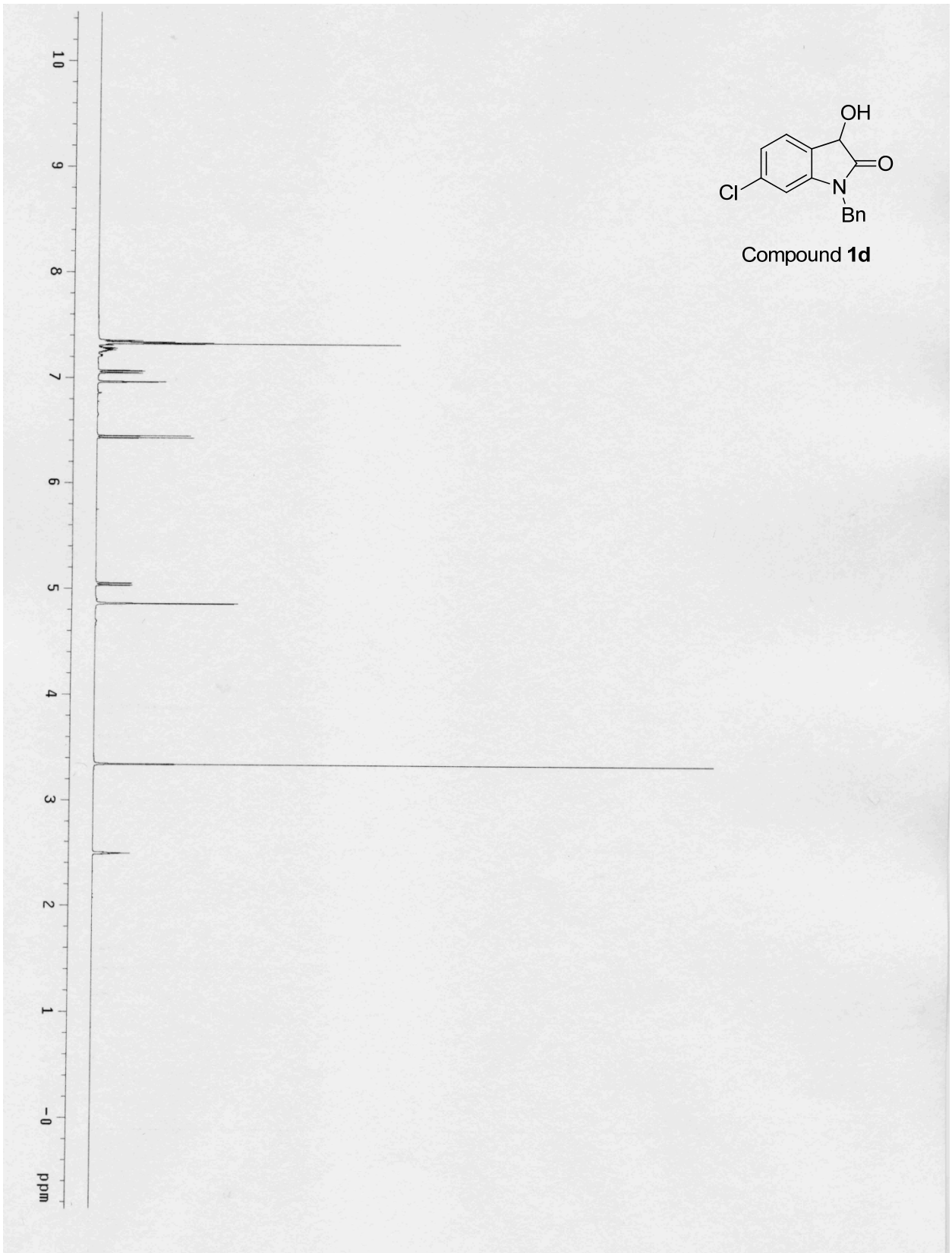
^{13}C NMR (100 MHz, D_6-DMSO): δ 176.3, 144.2, 135.9, 133.3, 128.6, 127.6, 127.5, 127.3, 126.0, 121.9, 109.3, 68.3, 42.4

LRMS (CI) Calcd. For $C_{15}H_{13}ClNO_2$ $[M+H]^+$: 274, Found: 274

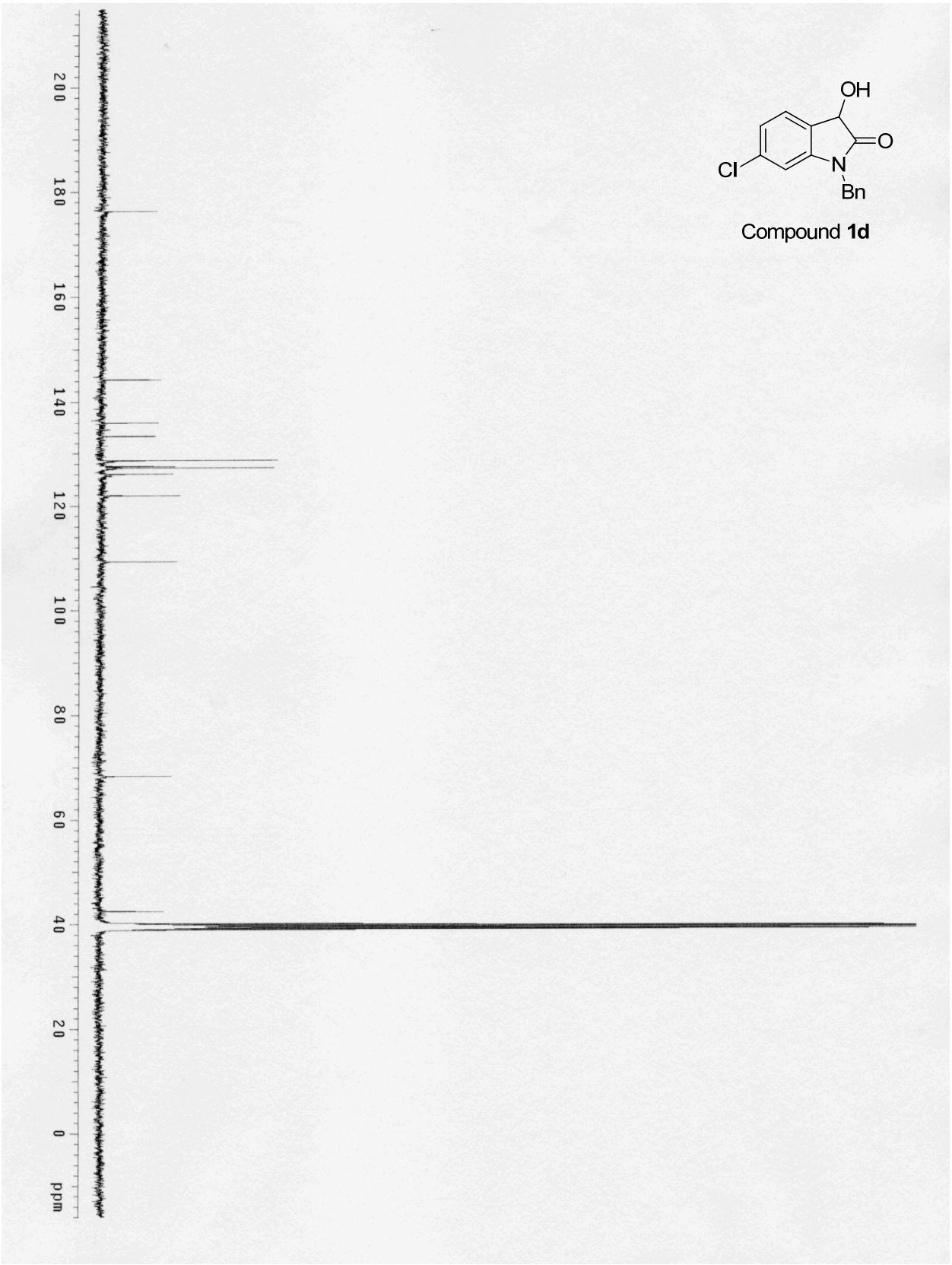
FTIR (neat): 3451, 2249, 2124, 1725, 1613, 1489, 1433, 1372, 1174, 1065, 1037, 1026, 821, 758 cm^{-1}

Mp: 136.5-137.2 °C

TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 1:4)

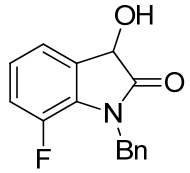


Compound **1d**



Compound **1d**

1-benzyl-7-fluoro-3-hydroxyindolin-2-one (1e)



Compound 1e: $NaBH_4$ (4.35 mmol, 165.3 mg, 0.5 eq) was added in small portions to a stirred suspension of commercially available 1-benzyl-7-fluoro-3-hydroxyindolin-2-one (2.22 g, 8.7 mmol, 1.0 equiv) in 51.2 mL of a 1:1 dichloromethane/ethanol mixture at -30 ºC. The mixture was vigorously stirred at this temperature until the suspension became colorless. Then distilled water was added and the reaction mixture was stirred until bubbling stop. The mixture was extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using a 4:1 mixture of dichloromethane /diethyl ether as elution solvent to give 1.2 g (54%) **1e** as a white solid.

^{1}H NMR (400 MHz, D_6-DMSO): δ 7.34-7.30 (m, 2H), 7.26-7.18 (m, 4H), 7.13-7.00 (m, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 7.6 Hz, 1H), 4.92 (dd, *J* = 24.8, 16.0 Hz, 2H)

^{13}C NMR (100 MHz, D_6-DMSO): δ 176.1, 146.5 (d, *J* = 241.1 Hz), 137.1, 131.9, 128.9, 128.5, 127.3, 126.6, 123.4 (d, *J* = 6.7 Hz), 120.9, 117.0 (d, *J* = 19.4), 68.8, 44.3

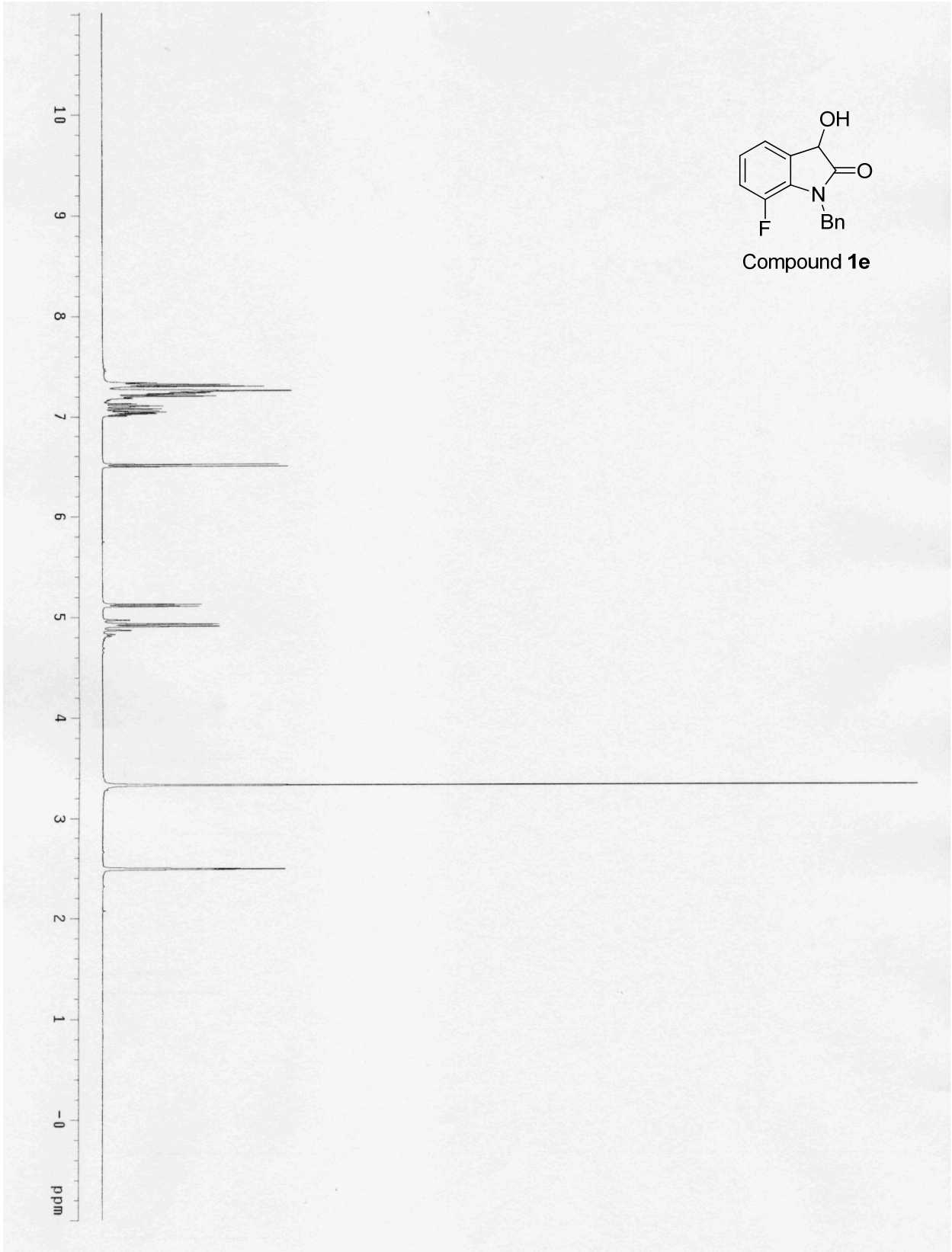
^{19}F NMR (376 MHz, D_6-DMSO): δ –135.0– –135.1 (m)

LRMS (CI) Calcd. For $C_{15}H_{12}FNO_2$ $[M]^+$: 257, Found: 257

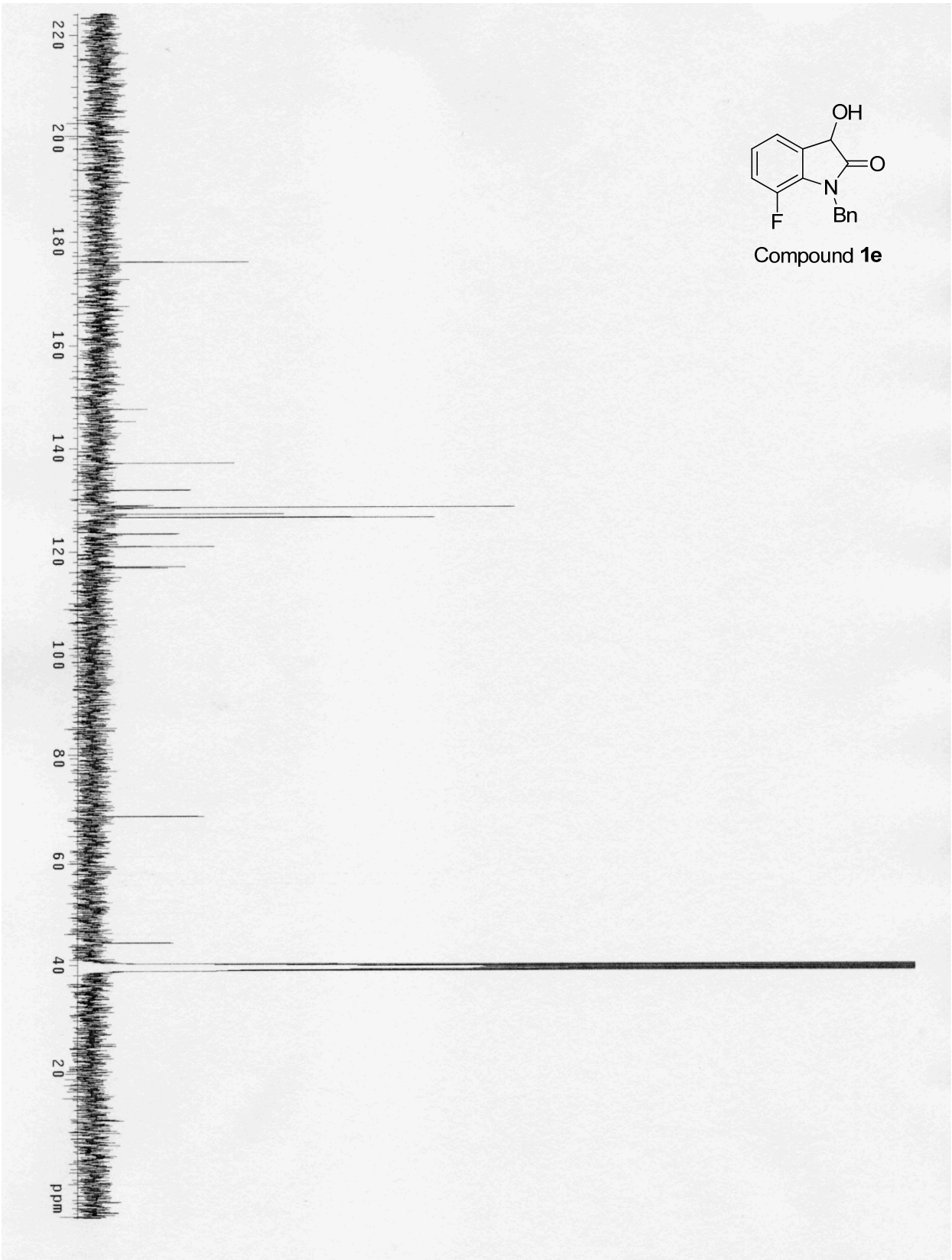
FTIR (neat): 3341, 2349, 1734, 1628, 1481, 1343, 1245, 1192, 1107, 814, 707 cm^{-1}

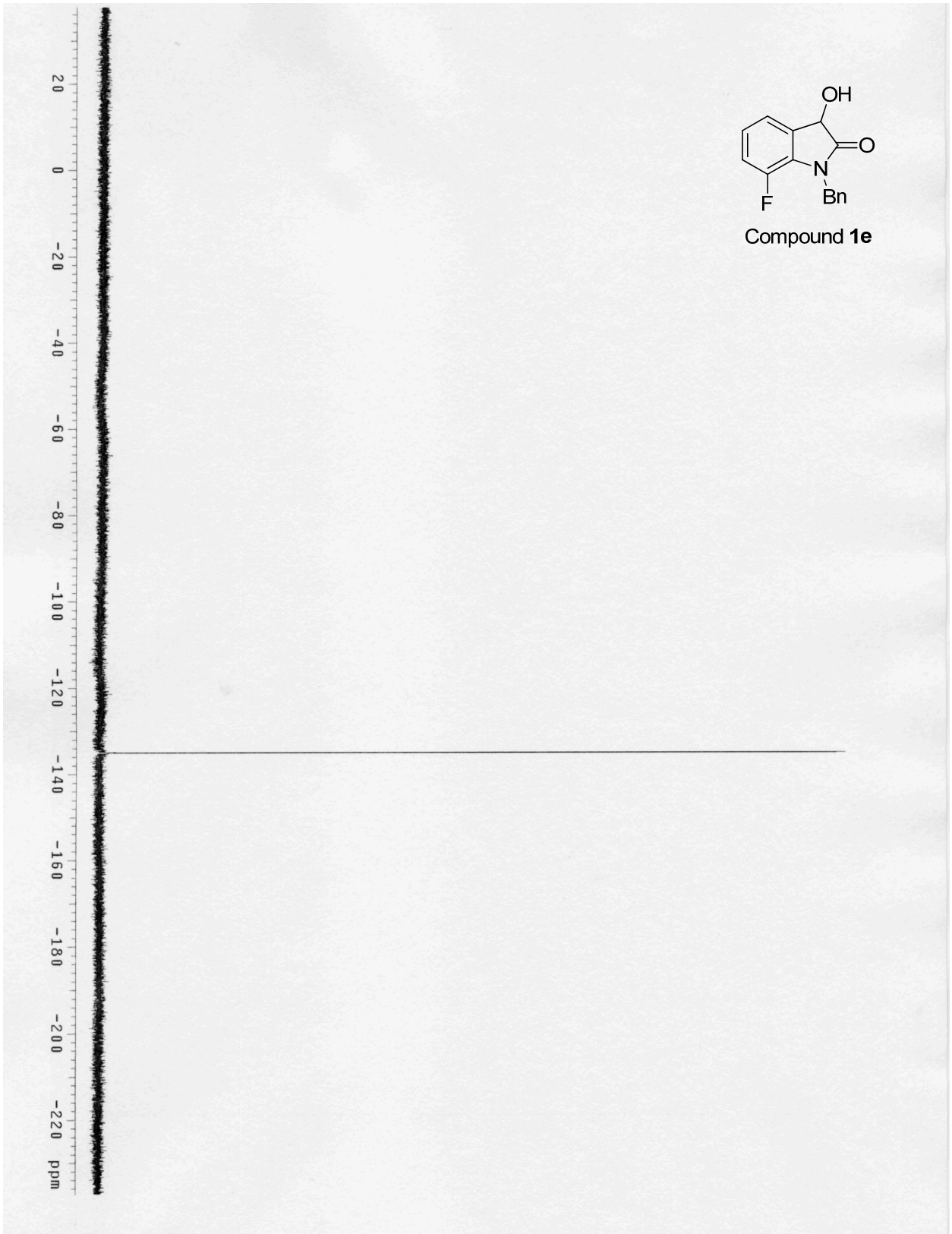
Mp: 113.2-113.7 °C

TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 1:4)



Compound **1e**

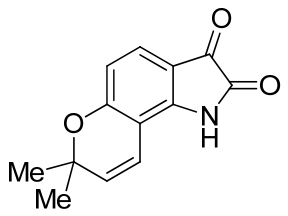

OH
O
N
Bn
F
Compound 1e
220
200
180
160
140
120
100
80
60
40
20
ppm



Compound **1e**

Experimental Procedures and Spectroscopic Data for Preparation of 1-Benzyl-3-hydroxy-7,7-dimethyl-3,7-dihydropyrano[2,3-g]indol-2(1H)-one (1f)

7,7-dimethylpyrano[2,3-g]indole-2,3(1H,7H)-dione (1f-I)



Compound 1f-I: Oxalyl chloride (16.7 mL, 194.92 mmol, 10.0 equiv) and DCM (78 mL) were added to a 3-necked 500 mL RBF and the solution was cooled to 0 °C with an ice bath. A solution of 2,2-dimethyl-2H-chromen-5-amine[4] (3.42 g, 19.49 mmol, 1.0 equiv) in DCM (78 mL) was added via syringe over 5-10 min. The ice bath was removed upon completion of addition and the brown solution was stirred at room temperature for 1 h. $AlCl_3$ (2.73 g, 20.47 mmol, 1.05 equiv) was added in one portion and the reaction mixture was stirred at room temperature for 3 hours. The crude reaction mixture was transferred to an Erlenmeyer flask containing ice and was stirred until the ice was melted. The mixture was extracted with DCM (3 x 100 mL). The combined organic layers were dried over $MgSO_4$, then filtered and concentrated under reduced pressure to a red-orange solid. Purification on flash column chromatography (2.5-5% EtOAc/DCM) gave the desired isatin **1f-I** (1.25 g) in 36% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.44 (dd, *J* = 8.4, 0.6 Hz,1H), 6.46 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.40 (dd, *J* = 10.0, 0.6 Hz, 1H), 5.78 (d, *J* = 10.0 Hz, 1H), 1.50 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 162.4, 146.1, 131.4, 127.8, 114.4, 112.1, 111.3, 106.1, 78.9, 77.2, 28.5

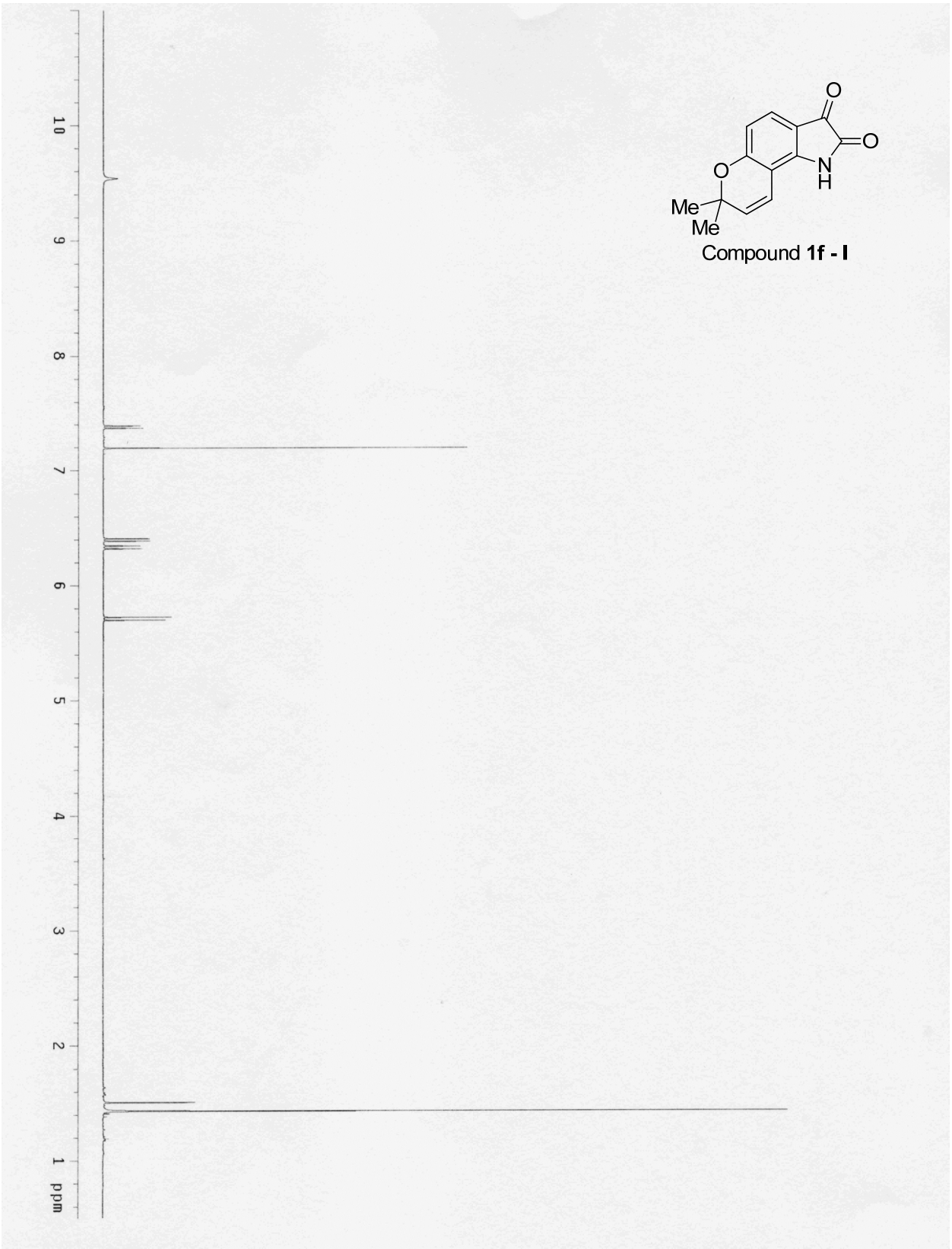
LRMS (CI) Calcd. For $C_{13}H_{12}NO_3$ $[M+H]^+$: 230, Found: 230

FTIR (neat): 3159, 2358, 1735, 1729, 1637, 1588, 1432, 1339, 1112, 1059, 729 cm^{-1}

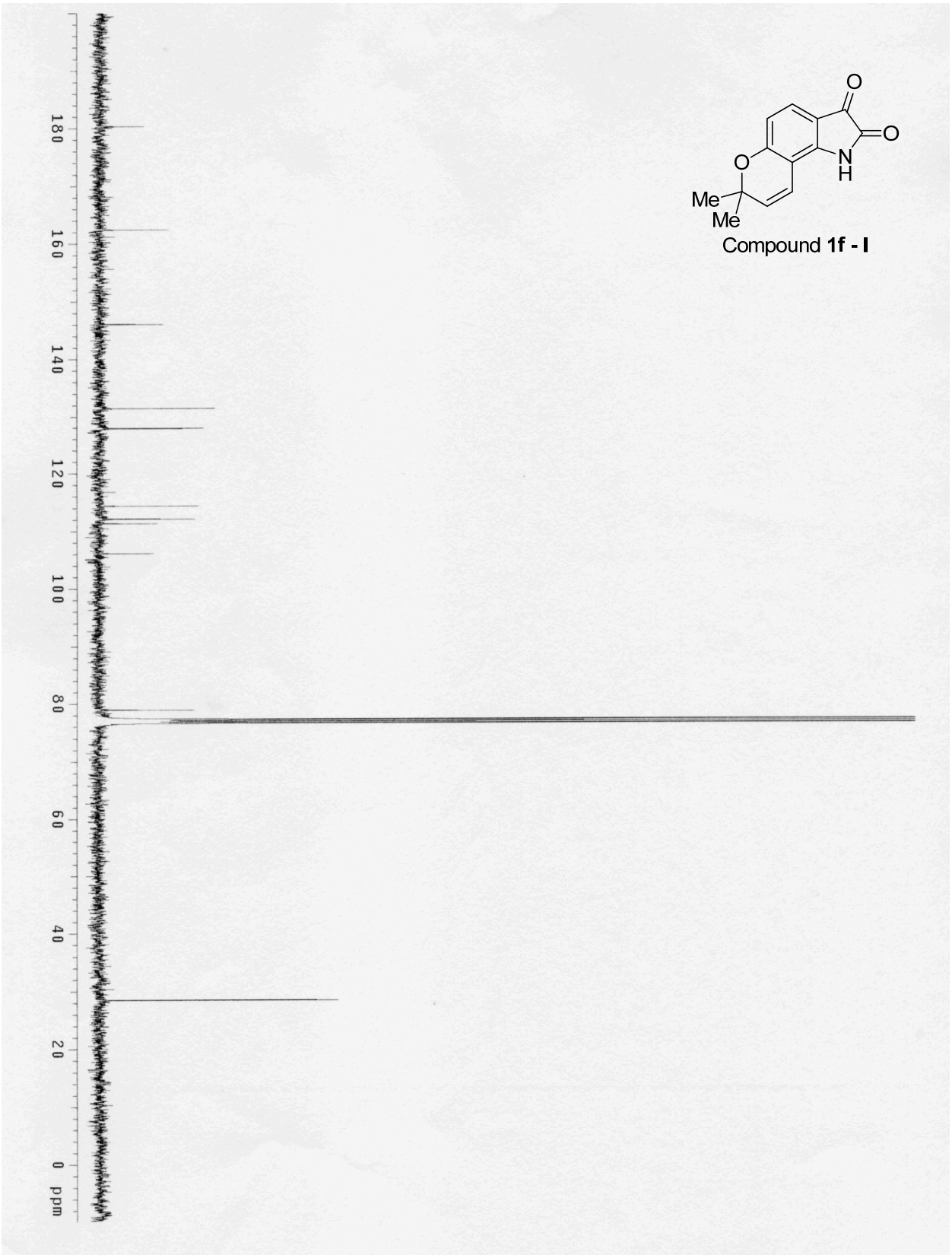
Mp: 240.6-241.1 °C

TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 1:4)

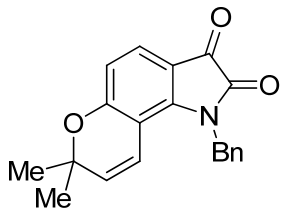
[4]P. E. Brown and R. A. Lewis, *J. CHEM. SOC. PERKIN TRANS.* 1, 1992, **5**, 573



Compound **1f - l**


O
O
N
H
O
Me
Me
Compound 1f - l
180
160
140
120
100
80
60
40
20
0 ppm

1-benzyl-7,7-dimethylpyrano[2,3-g]indole-2,3(1H,7H)-dione (1f-II)



Compound 1f-II: A solution of 1.61 g of isatin **1f-I** (6.9 mmol, 1.0 equiv) in 20.9 mL of dry DMF was slowly added to a suspension of NaH (331 mg, 13.8 mmol, 2.0 equiv, 60 % in mineral oil) in 20.9 mL of dry DMF at 0 ºC. The suspension was stirred for 2 hours at 0 ºC. Then, benzyl bromide (1.5 equiv) was added. The mixture was stirred for 2 hours at room temperature and water was added until precipitation of the N-protected isatin **1f-II**. Crystallization from hexane/ethyl acetate afforded the pure product in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.37-7.21 (m, 5H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 5.57 (d, *J* = 10.4 Hz, 1H), 5.13 (s, 2H), 1.38 (s, 6H)

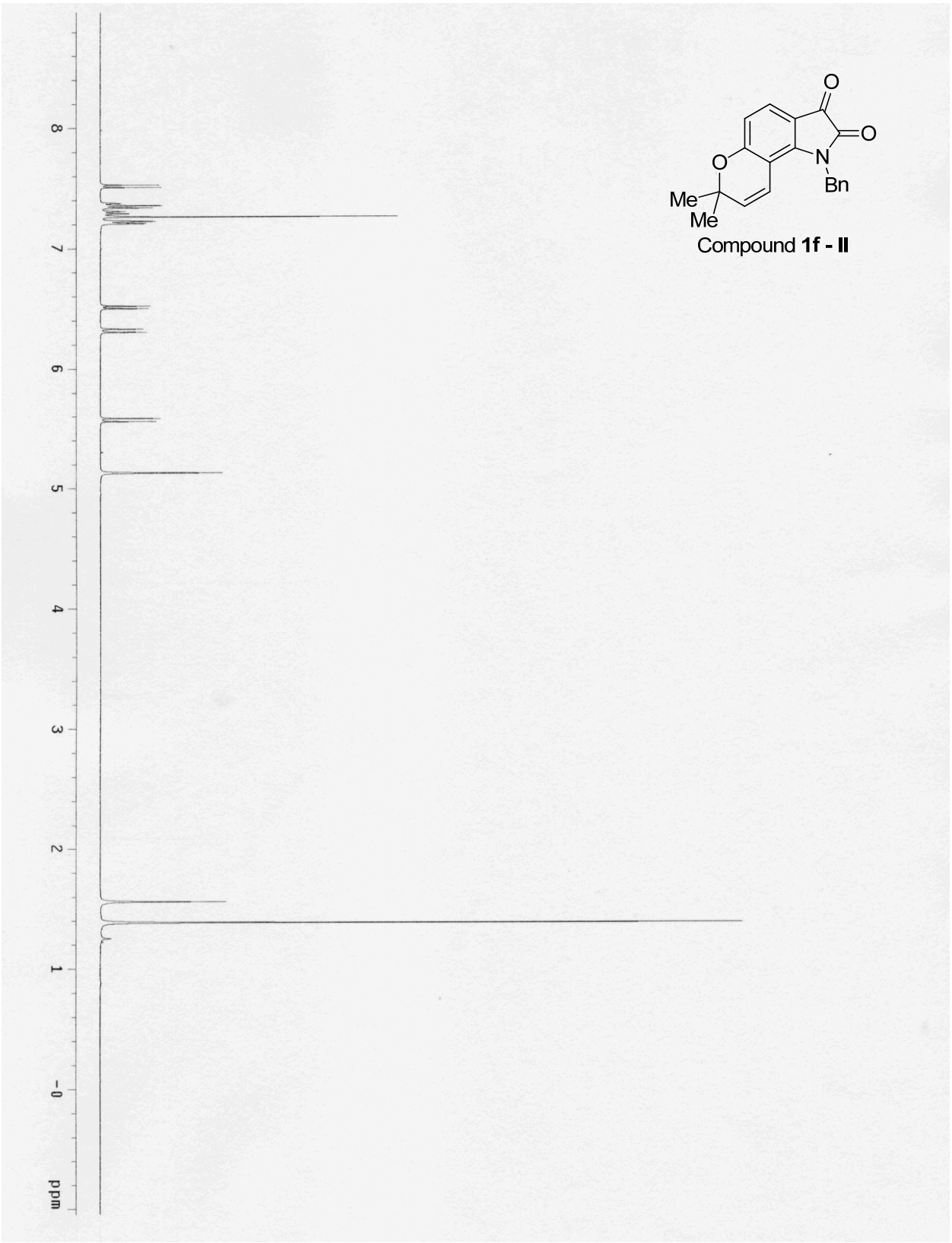
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 163.1, 161.0, 147.5, 135.4, 131.3, 129.1, 127.8, 127.4, 125.8, 116.2, 112.5, 112.4, 107.2, 77.4, 45.9, 27.7

LRMS (CI) Calcd. For $C_{20}H_{18}NO_3$ $[M+H]^+$: 320, Found: 320

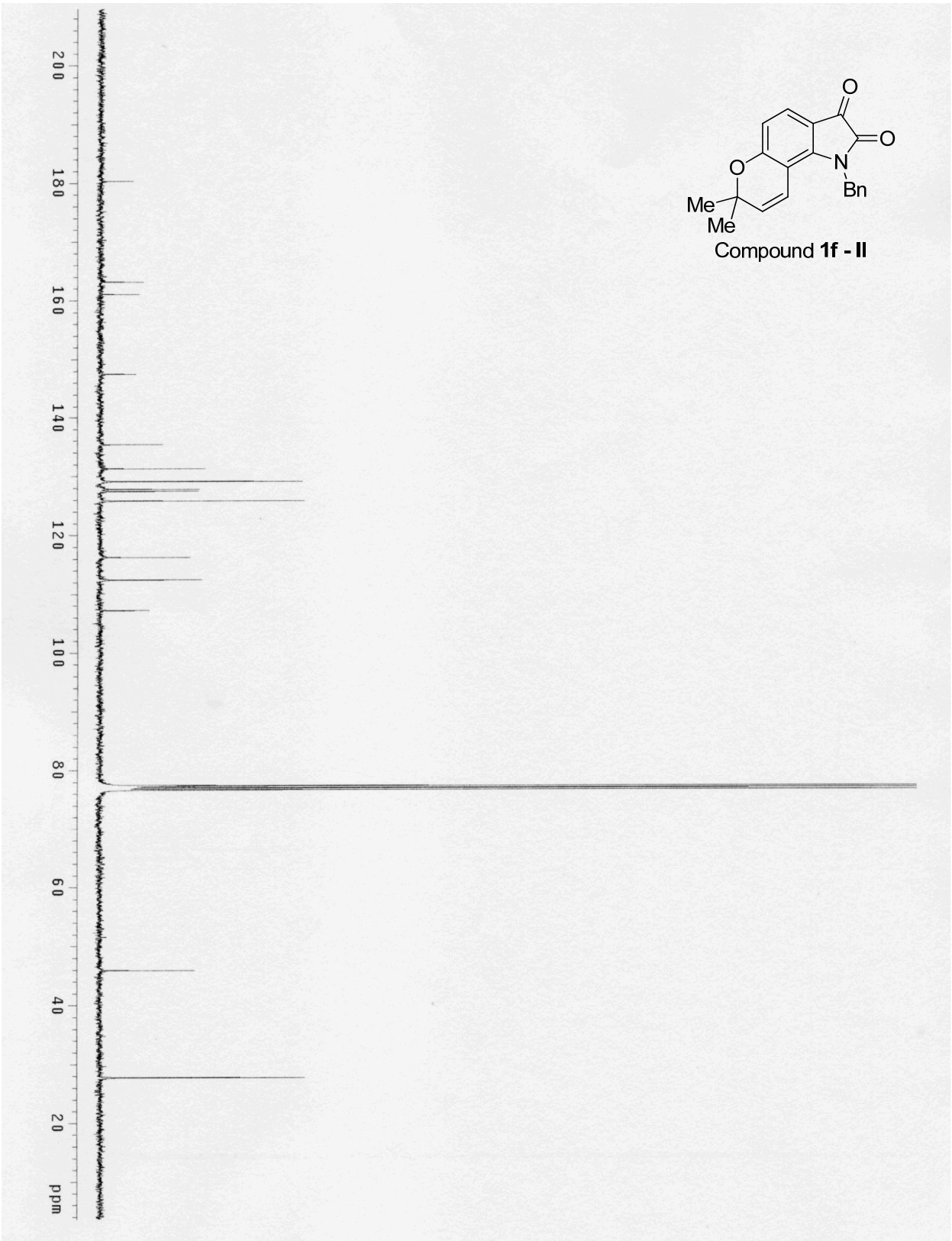
FTIR (neat): 3065, 2972, 2927, 2345, 1735, 1637, 1584, 1419, 1361, 1237, 1148, 1108, 1045, 1005, 753 cm^{-1}

Mp: 117.9-118.3 °C

TLC (SiO_2): R_f = 0.2 (ethyl acetate: hexanes, 1:4)

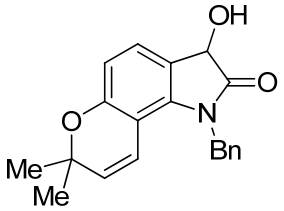


Compound **1f - II**



Compound **1f - II**

1-benzyl-3-hydroxy-7,7-dimethyl-3,7-dihydropyrano[2,3-g]indol-2(1H)-one (1f)



Compound 1f: $NaBH_4$ (2.9 mmol, 110.0 mg, 0.5 equiv) was added in small portions to a stirred suspension of **1f-II** (1.85 g, 5.8 mmol, 1.0 equiv) in 34.0 mL of a 1:1 dichloromethane/ethanol mixture at -30 ºC. The mixture was vigorously stirred at this temperature until the suspension became colorless. Then distilled water was added and the reaction mixture was stirred until bubbling stop. The mixture was extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using a 4:1 mixture of dichloromethane /diethyl ether as elution solvent to give 1.0 g (54%) **1f** as a white solid.

^{1}H NMR (400 MHz, D_6-DMSO): δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz,1H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.13 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.37 (d, *J* = 10.0 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 5.58 (d, *J* = 10.4 Hz, 1H), 5.03 (s, 2H), 4.98 (dd, *J* = 7.6, 1.0 Hz, 1H), 1.26 (s, 3H), 1.20 (s, 3H)

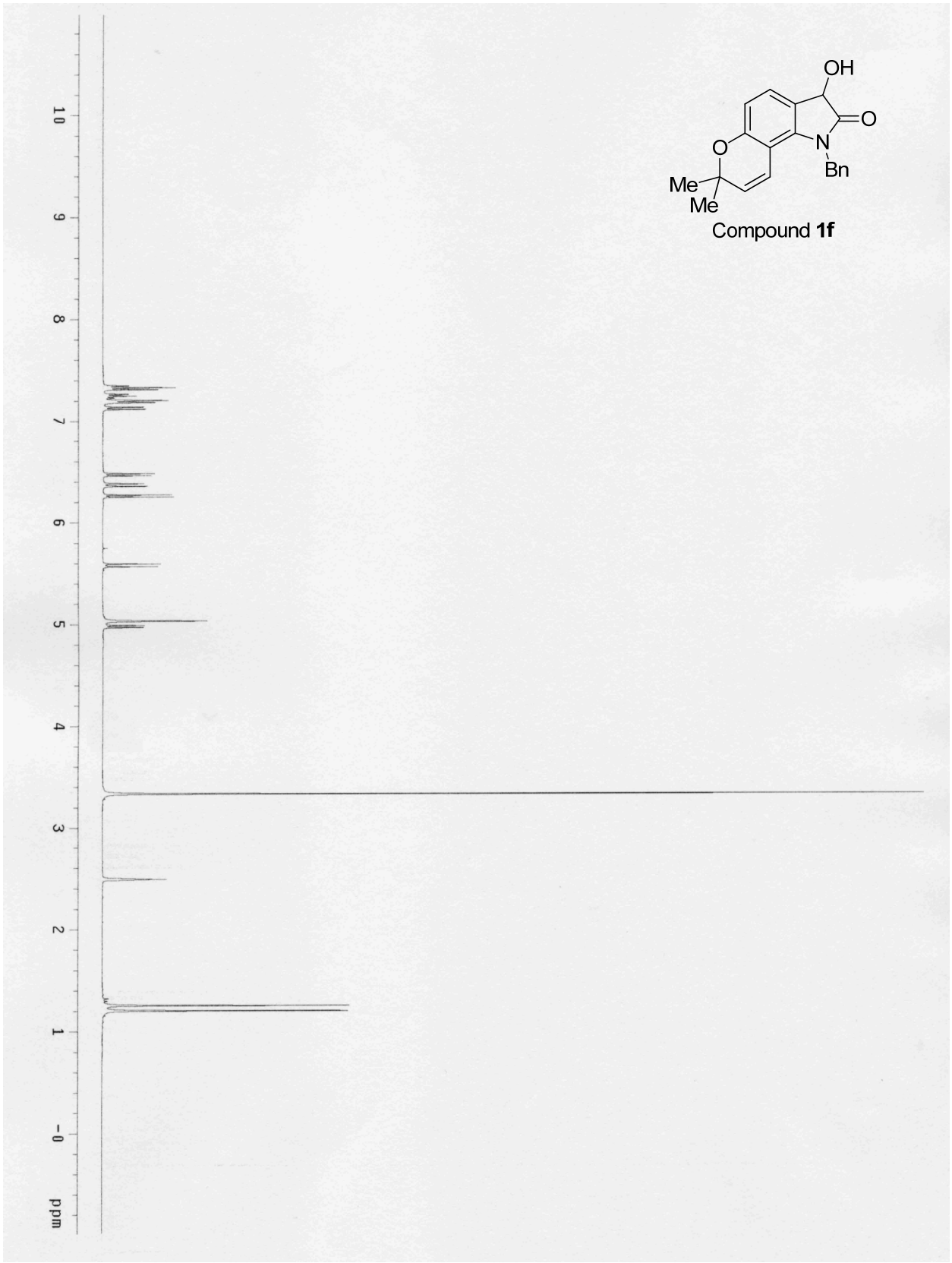
^{13}C NMR (100 MHz, D_6-DMSO): δ 177.8, 153.6, 138.4, 136.6, 130.9, 128.7, 127.2, 125.8, 124.9, 121.7, 116.9, 110.1, 106.4, 74.7, 67.8, 44.3, 26.9, 26.5

LRMS (CI) Calcd. For $C_{20}H_{20}NO_3$ $[M+H]^+$: 322, Found: 322

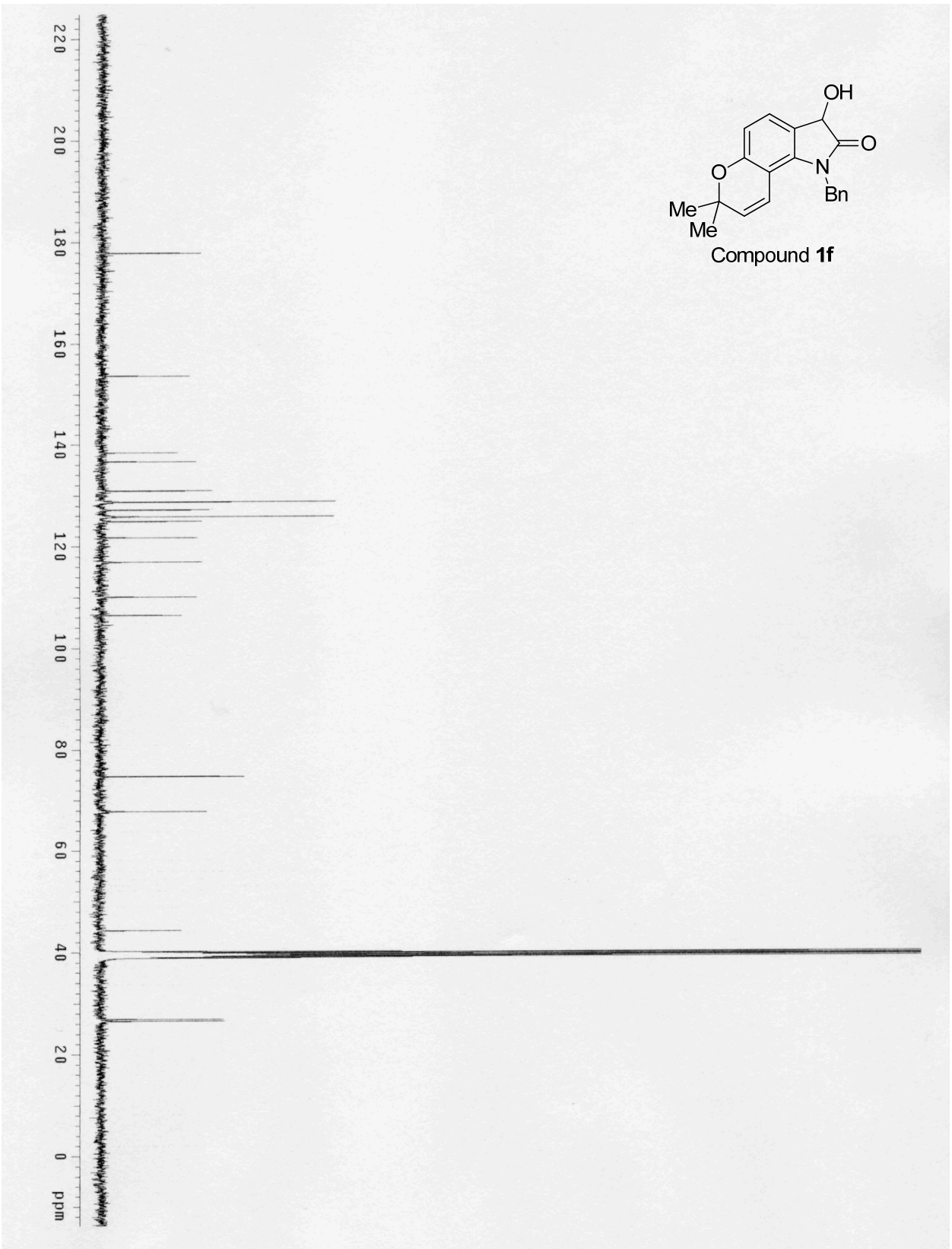
FTIR (neat): 3368, 2972, 2349, 2046, 1690, 1593, 1459, 1375, 1152, 987, 720 cm^{-1}

Mp: 177.3-177.5 °C

TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 1:4)



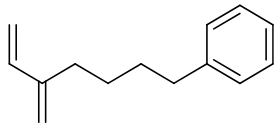
Compound **1f**



Compound **1f**

Experimental Details and Spectroscopic Data for Diene 2f

(5-methylenehept-6-en-1-yl)benzene



Compound 2f: 2f was prepared by modifying an iron catalyzed coupling method reported by Cossy[5]. To a flam dried one neck round bottom flask equipped with a magnetic stir bar was added $FeCl_3$ (0.49 mg, 3.0 mmol, 20 mol%) and THF (50ml). It was cooled to 0°C followed by addition of 1-iodo-4-phenylbutane[6] (3.9 g, 15 mmol, 1.0 equiv.) The resulting solution was stirred at 0°C for 10 min and a solution of chloroprene Grignard (43 ml, 30 mmol, 0.7M in THF, 2.0 equiv) and TMEDA (4.3 ml, 29 mmol, 1.9 equiv) was added drop-wise over 1 hour. After 2 hours at 0°C, the reaction mixture was quenched by adding an aqueous saturated NH_4Cl solution. After extractive work-up and evaporation of the solvent, the residue was purified by flash column chromatography (SiO_2, 100% hexane) to furnish the title compound (1.5 g, 53%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.31 (m, 2H), 7.24-7.20 (m, 3H), 6.42 (dd, *J* = 18.0, 10.8 Hz, 1H), 5.27 (d, *J* = Hz, 1H), 5.07 (dd, *J* = 22.8, 10.8 Hz, 3H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.76-1.68 (m, 2H), 1.64-1.56 (m, 2H)

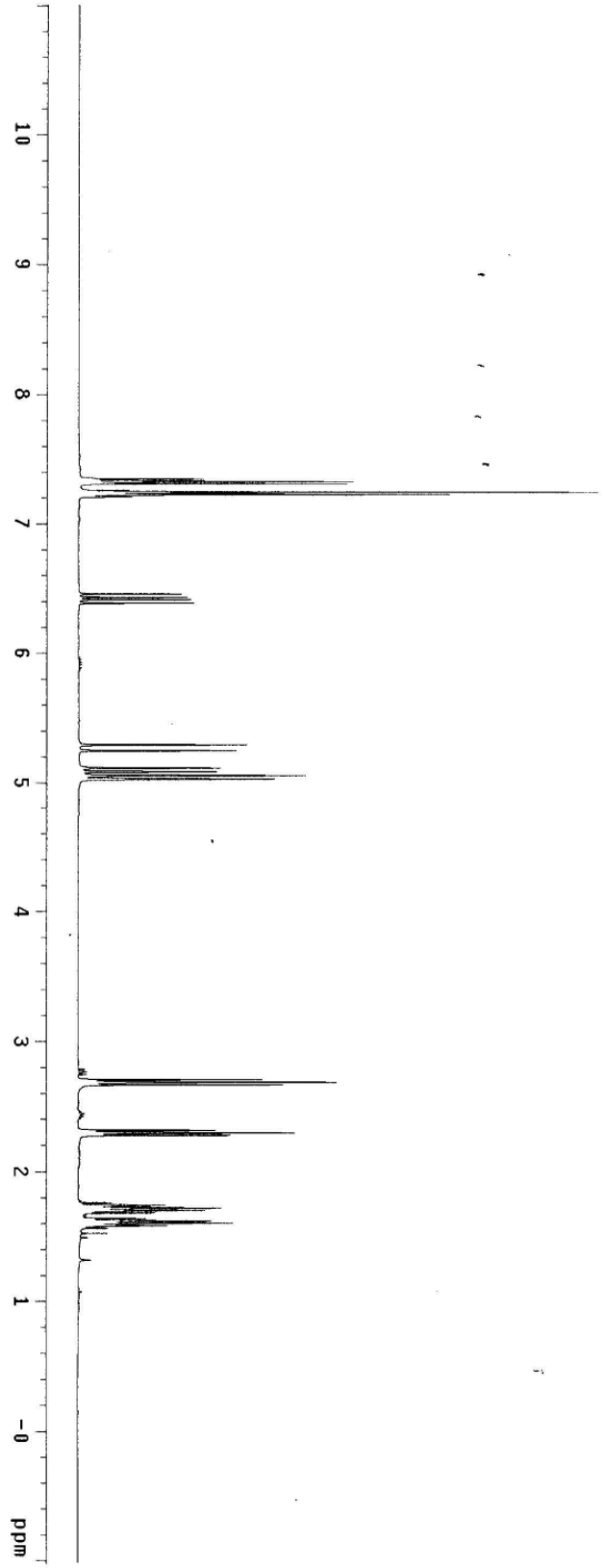
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 142.6, 138.9, 128.3, 128.2, 125.6, 115.6, 113.1, 35.8, 31.4, 31.2, 27.7

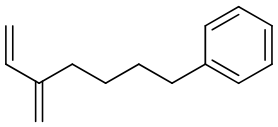
LRMS (CI) Calcd. For $C_{14}H_{18}$ $[M]^+$: 186, Found: 186

FTIR (neat): 3086, 3026, 2932, 2858, 1594, 1496, 1453, 1030, 991, 893, 744, 697 cm^{-1}

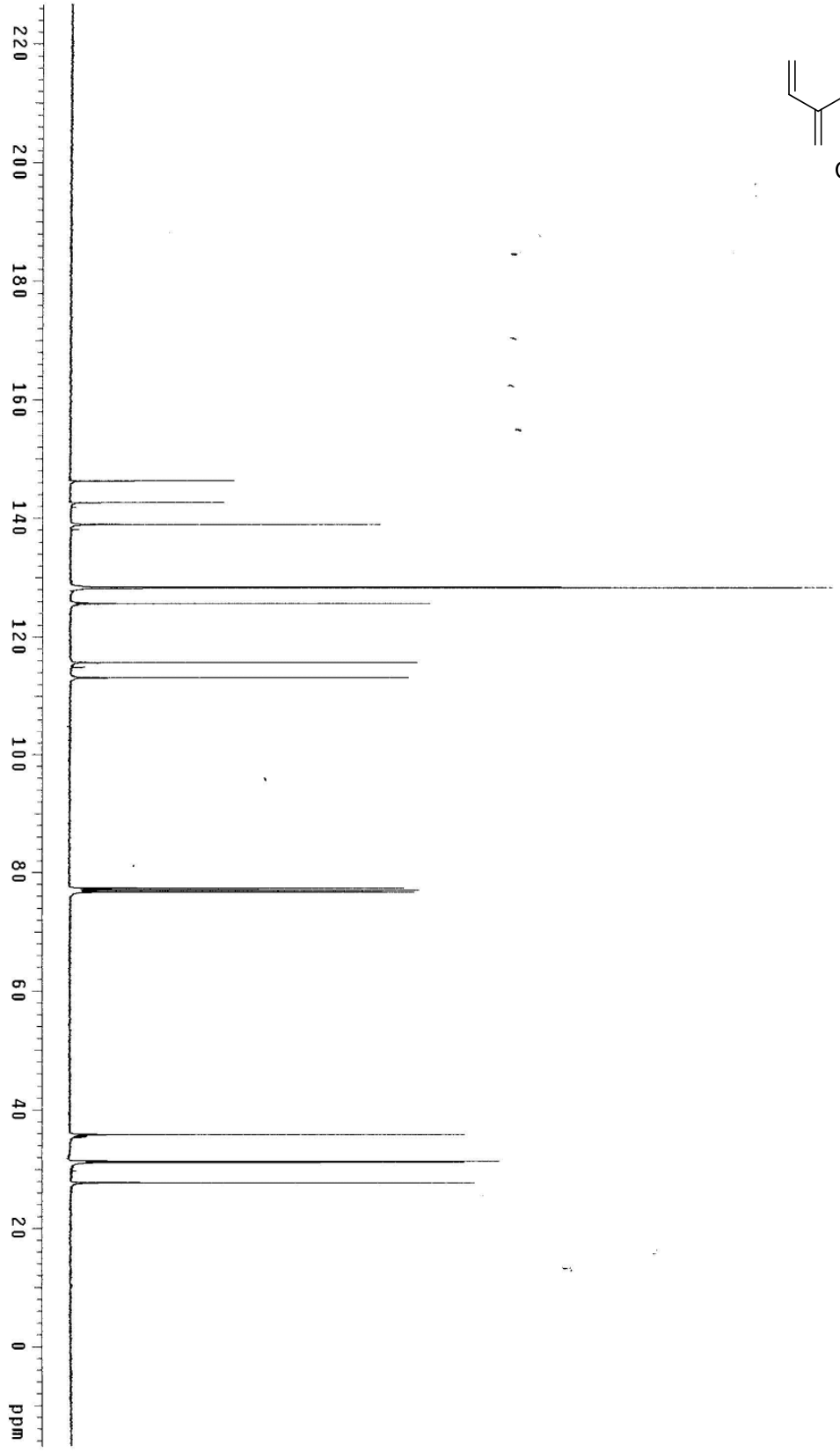
[5] Guerinot, A.; Reymond, S.; Cossy, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 6521

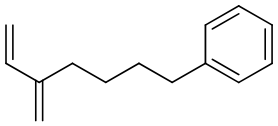
[6] Smith, S.M.; Takacs, J.M. *J. AM. CHEM. SOC.* **2010**, *132*, 1740





Compound **2f**





Compound **2f**

Experimental Procedures and Spectroscopic Data for the Coupling of Dienes with 3-Hydroxy-2-oxindole

General Procedures for the Coupling of Isoprene with 3-Hydroxy-2-oxindole 1a-1f

To a pressure tube equipped with magnetic stir bar was added $Ru_3(CO)_{12}$ (2.5 mg, 0.004 mmol, 2 mol%) and PCy_3 (6.7 mg, 0.024 mmol, 12 mol%). The tube was then sealed with a rubber septum and purged with argon. At this stage, 3-hydroxy-2-oxindole **1a-1f** (0.200 mmol, 100 mol%), PhMe (0.1 mL, 2.0 M concentration with respect to 3-hydroxy-2-oxindole), and isoprene (20.0 μL, 0.200 mmol, 100 mol%) were added. The rubber septum was quickly replaced with a screw cap. The reaction was heated to 110 °C for the indicated time. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) under the conditions noted to furnish prenylated 3-hydroxy-2-oxindole.

General Procedures for the Coupling of Myrcene with 3-Hydroxy-2-oxindole 1a-1f

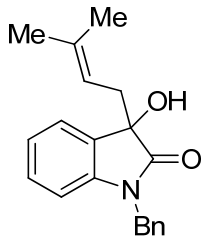
To a pressure tube equipped with magnetic stir bar was added $Ru_3(CO)_{12}$ (2.5 mg, 0.004 mmol, 2 mol%) and PCy_3 (6.7 mg, 0.024 mmol, 12 mol%). The tube was then sealed with a rubber septum and purged with argon. At this stage, 3-hydroxy-2-oxindole **1a-1f** (0.200 mmol, 100 mol%), PhMe (0.1 mL, 2.0 M concentration with respect to 3-hydroxy-2-oxindole), and myrcene (34.3 μL, 0.200 mmol, 100 mol%) were added. The rubber septum was quickly replaced with a screw cap. The reaction was heated to 110 °C for the indicated time. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) under the conditions noted to furnish geranylated 3-hydroxy-2-oxindole.

General Procedures for the Coupling of Dienes 2c-2f with 3-Hydroxy-2-oxindole 1a

To a pressure tube equipped with magnetic stir bar was added $Ru_3(CO)_{12}$ (2.5 mg, 0.004 mmol, 2 mol%) and PCy_3 (6.7 mg, 0.024 mmol, 12 mol%). The tube was then sealed with a rubber septum and purged with argon. At this stage, 3-hydroxy-2-oxindole **1a** (0.200 mmol, 100 mol%), PhMe (0.1 mL, 2.0 M concentration with respect to 3-hydroxy-2-oxindole), and dienes **2c-2f** (100-300 mol%) were added. The rubber septum was quickly replaced with a screw cap. The reaction was heated to 110 °C for the indicated time. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2).

Experimental Procedures and Spectroscopic Data for Prenylated 3-Hydroxy-2-oxindole 3a-3f

1-benzyl-3-hydroxy-3-(3-methylbut-2-en-1-yl)indolin-2-one (3a)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (51.0 mg, 83%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.32-7.24 (m, 5H), 7.18 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (td, *J* = 7.6, 1.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.14 (d, *J* = 16.0 Hz, 1H), 4.91-4.86 (m, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 3.66 (s, 1H), 2.84 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.74 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.61 (s, 3H), 1.55 (s, 3H)

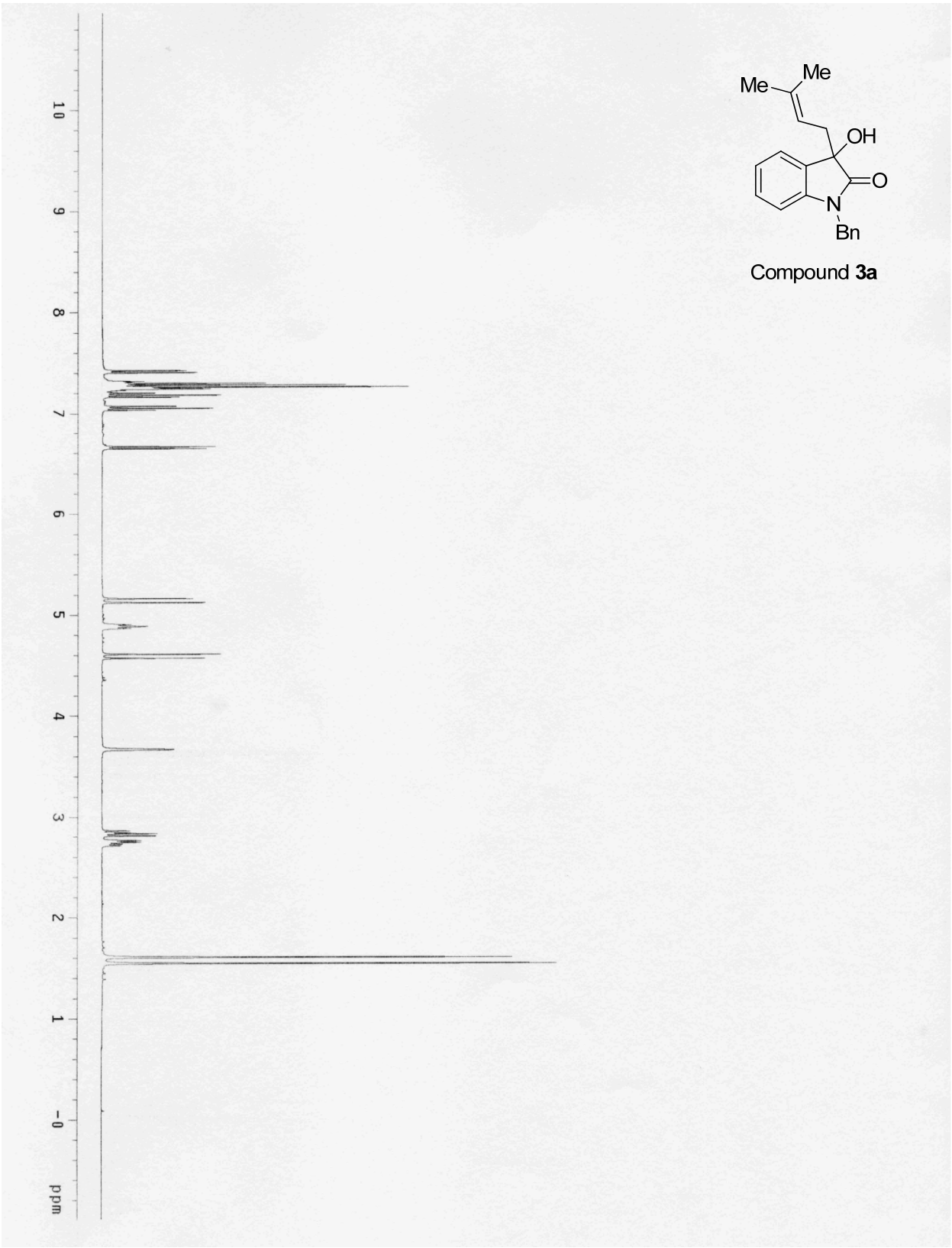
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 142.5, 137.1, 135.5, 130.0, 129.4, 128.7, 127.5, 127.0, 123.9, 122.9, 115.9, 109.3, 76.4, 43.7, 37.5, 25.9, 17.9

LRMS (CI) Calcd. For $C_{20}H_{22}NO_2$ $[M+H]^+$: 308, Found: 308

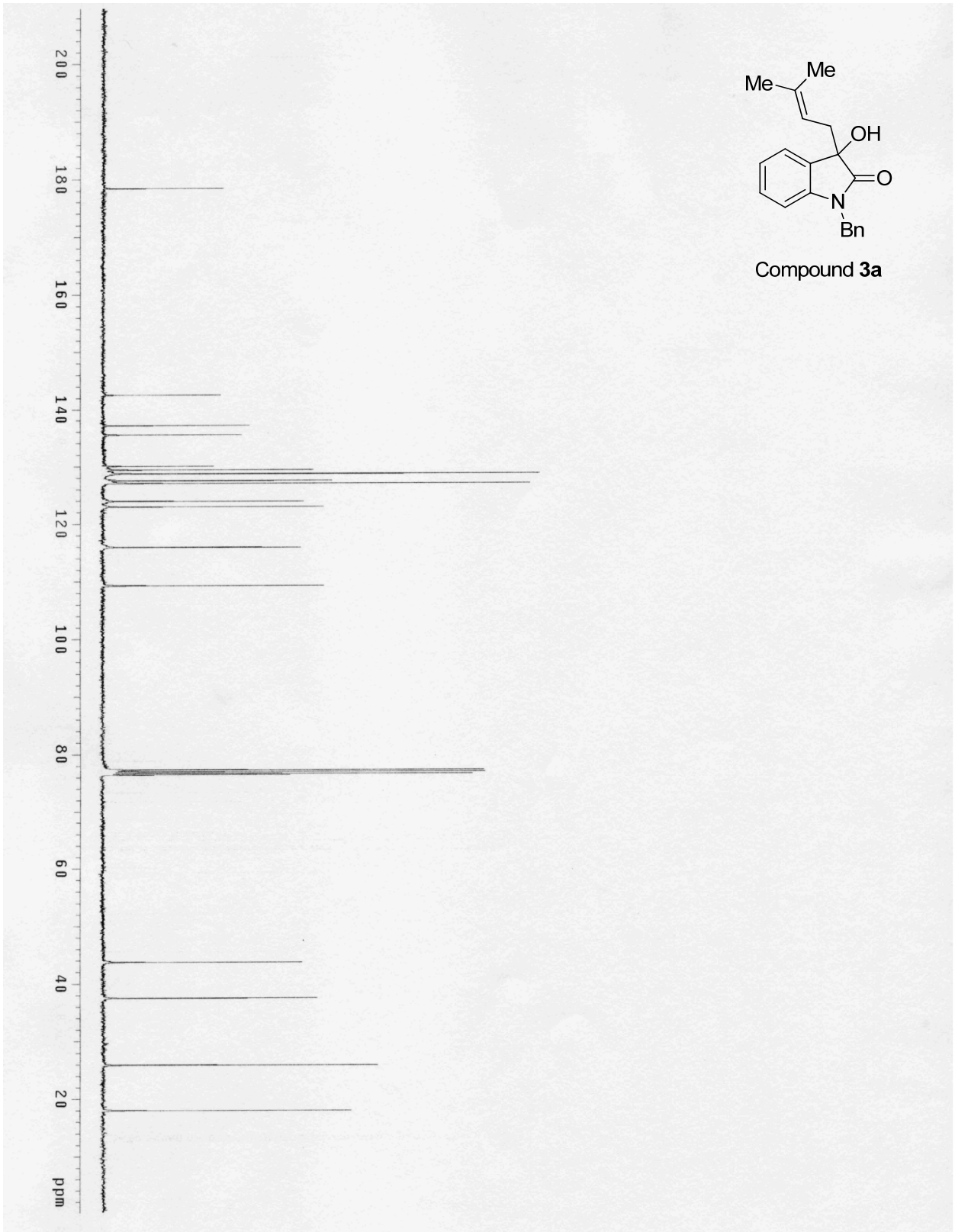
FTIR (neat): 2969,2398, 2287, 1736, 1436, 1373, 1229, 1216, 1045, 905 cm^{-1}

Mp: 112.1-112.5 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

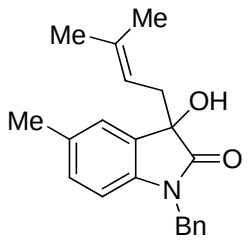


Compound **3a**



Compound **3a**

1-benzyl-3-hydroxy-5-methyl-3-(3-methylbut-2-en-1-yl)indolin-2-one (3b)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (57.8 mg, 90%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.22 (m, 6H), 6.99-6.97 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.11 (d, *J* = 15.6 Hz, 1H), 4.92-4.88 (m, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 3.02 (s, 1H), 2.81 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.68 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.31 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H)

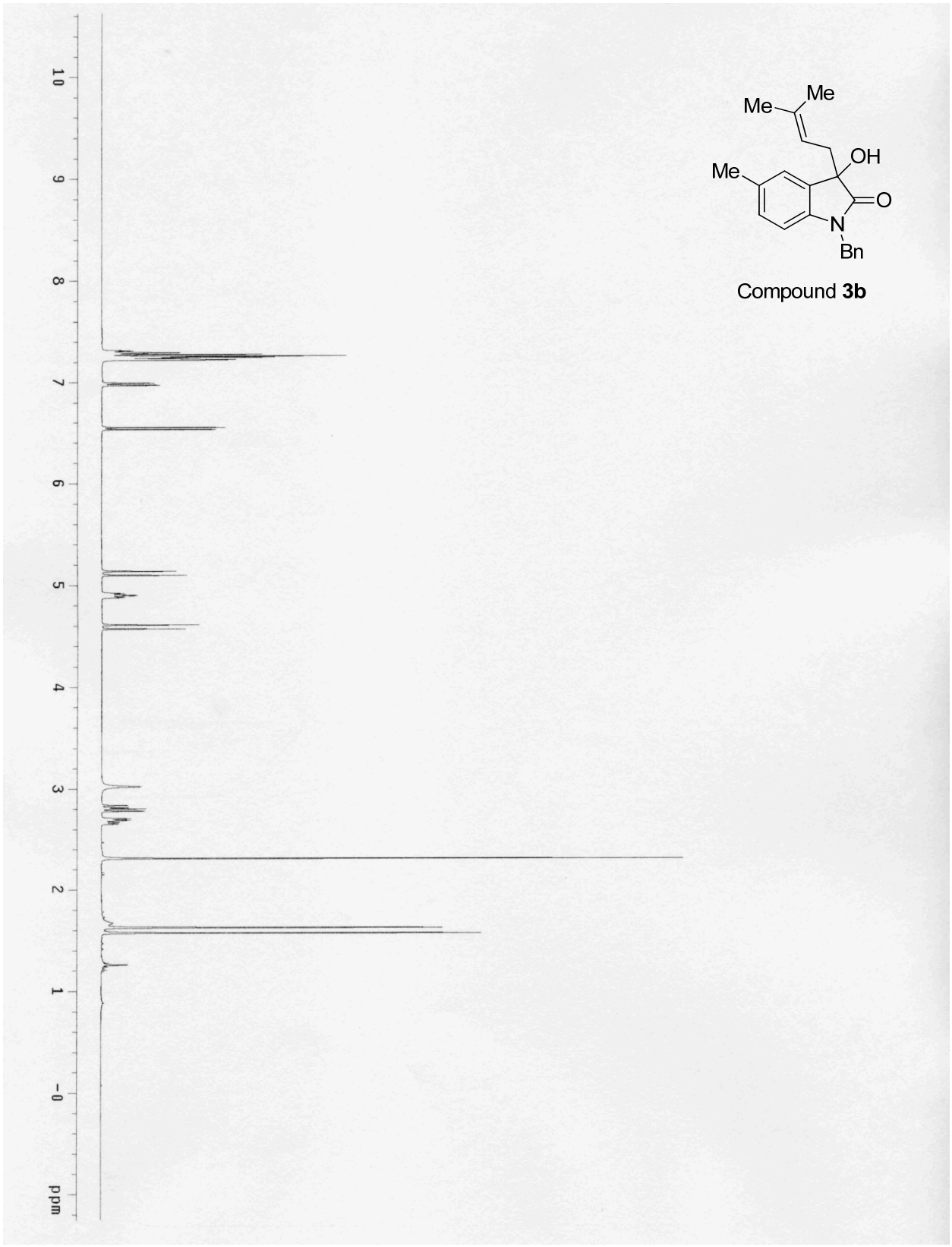
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 140.2, 137.3, 135.6, 132.6, 129.9, 129.7, 128.7, 127.5, 127.1, 124.7, 115.9, 109.1, 76.4, 43.7, 37.6, 25.9, 21.0, 18.0

LRMS (CI) Calcd. For $C_{21}H_{24}NO_2$ $[M+H]^+$: 322, Found: 322

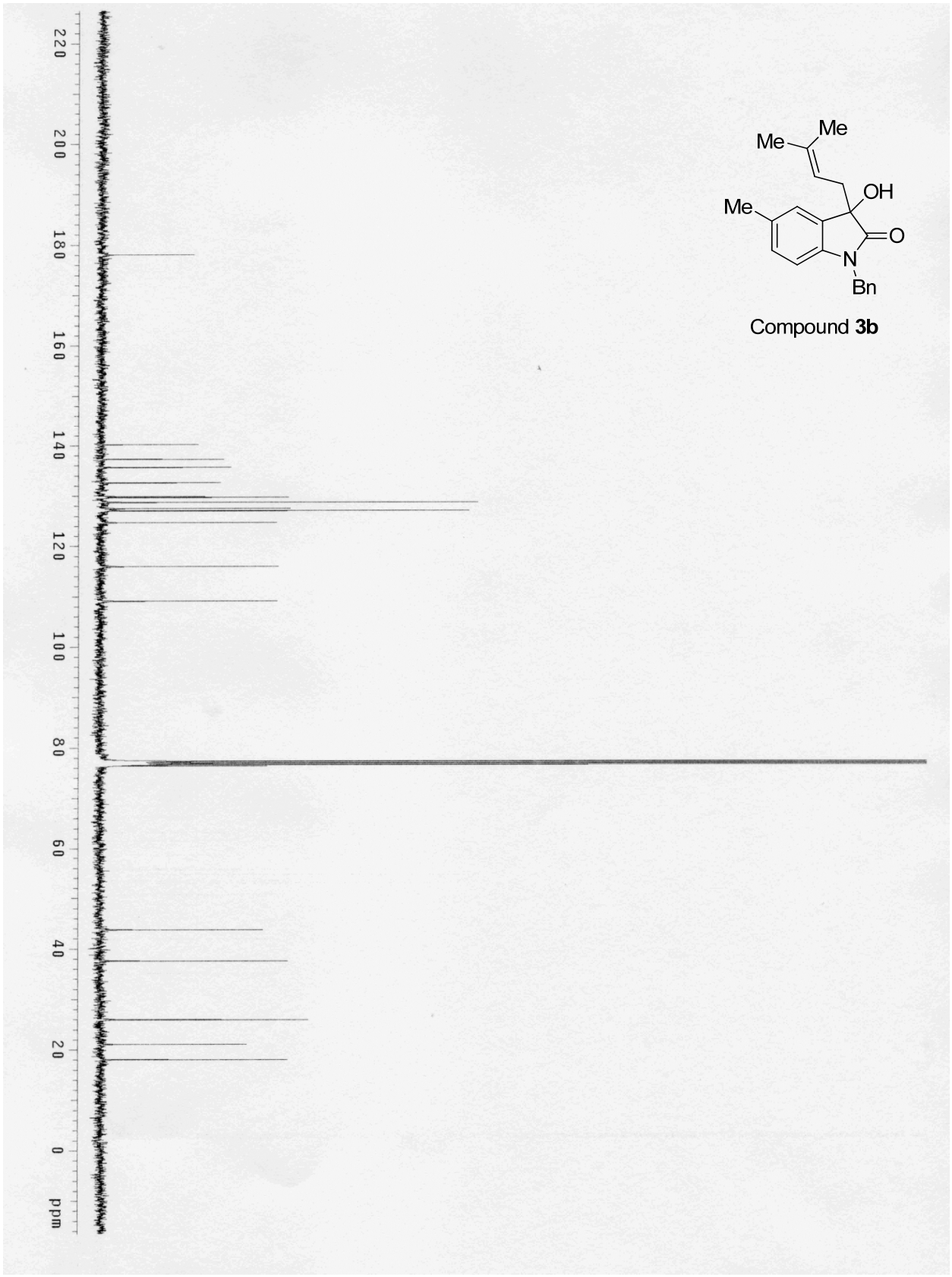
FTIR (neat): 3336, 2914, 1690, 1619, 1601, 1490, 1436, 1370, 1343, 1285, 1192, 1138, 1080, 1001, 800, 693 cm^{-1}

Mp: 178.0-178.6 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

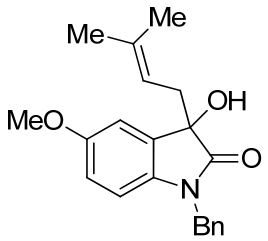


Compound **3b**



Compound **3b**

1-benzyl-3-hydroxy-5-methoxy-3-(3-methylbut-2-en-1-yl)indolin-2-one (3c)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (59.9 mg, 89%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 5H), 7.23 (d, *J* = 2.4 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.95-4.90 (m, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 3.77 (s, 3H), 3.84 (s, 1H), 2.79 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.68 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 3H)

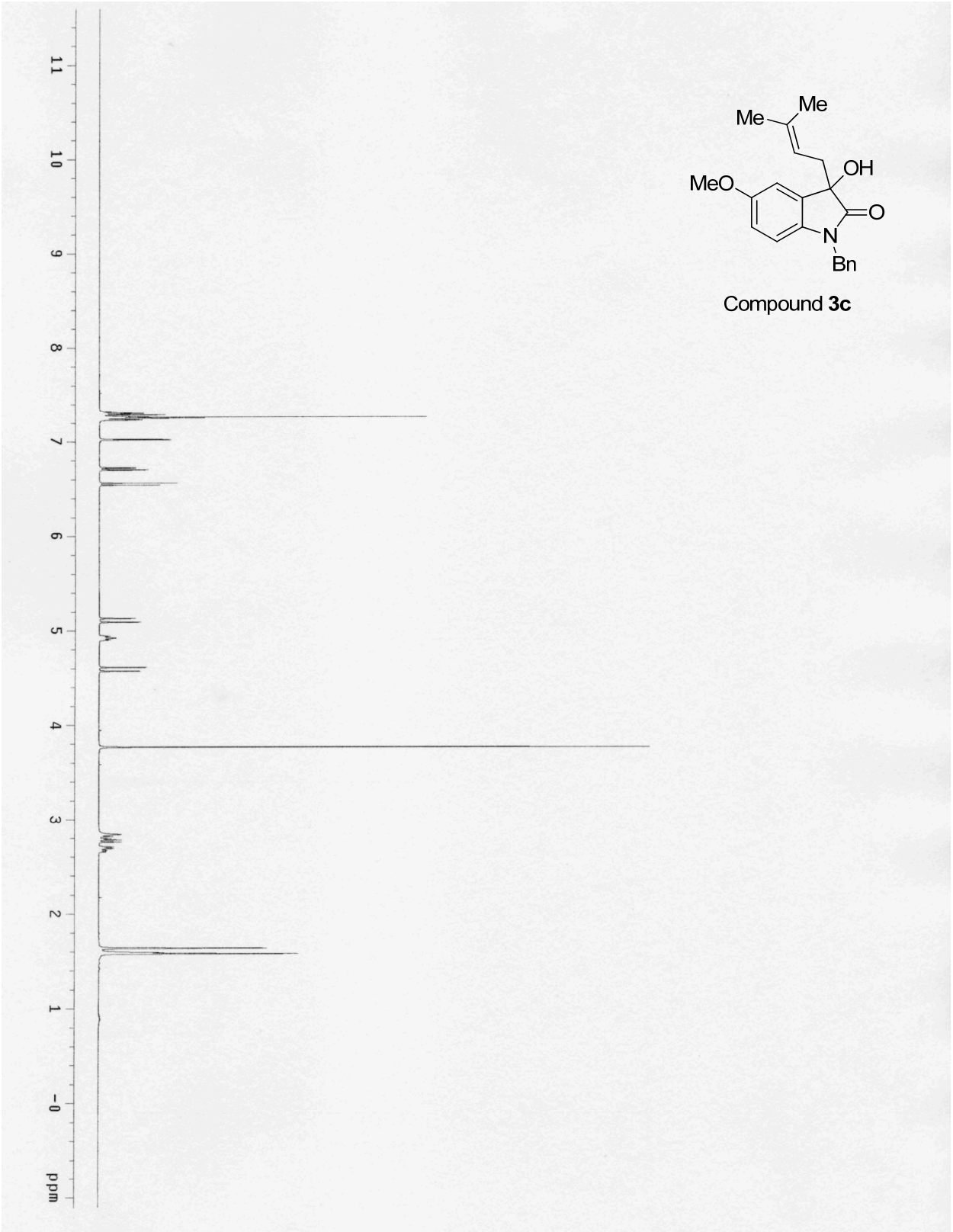
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 156.2, 137.3, 135.9, 135.6, 131.1, 128.7, 127.5, 127.1, 115.8, 114.1, 110.9, 109.9, 76.6, 55.8, 43.8, 37.6, 25.9, 18.0

LRMS (CI) Calcd. For $C_{21}H_{24}NO_3$ $[M+H]^+$: 338, Found: 338

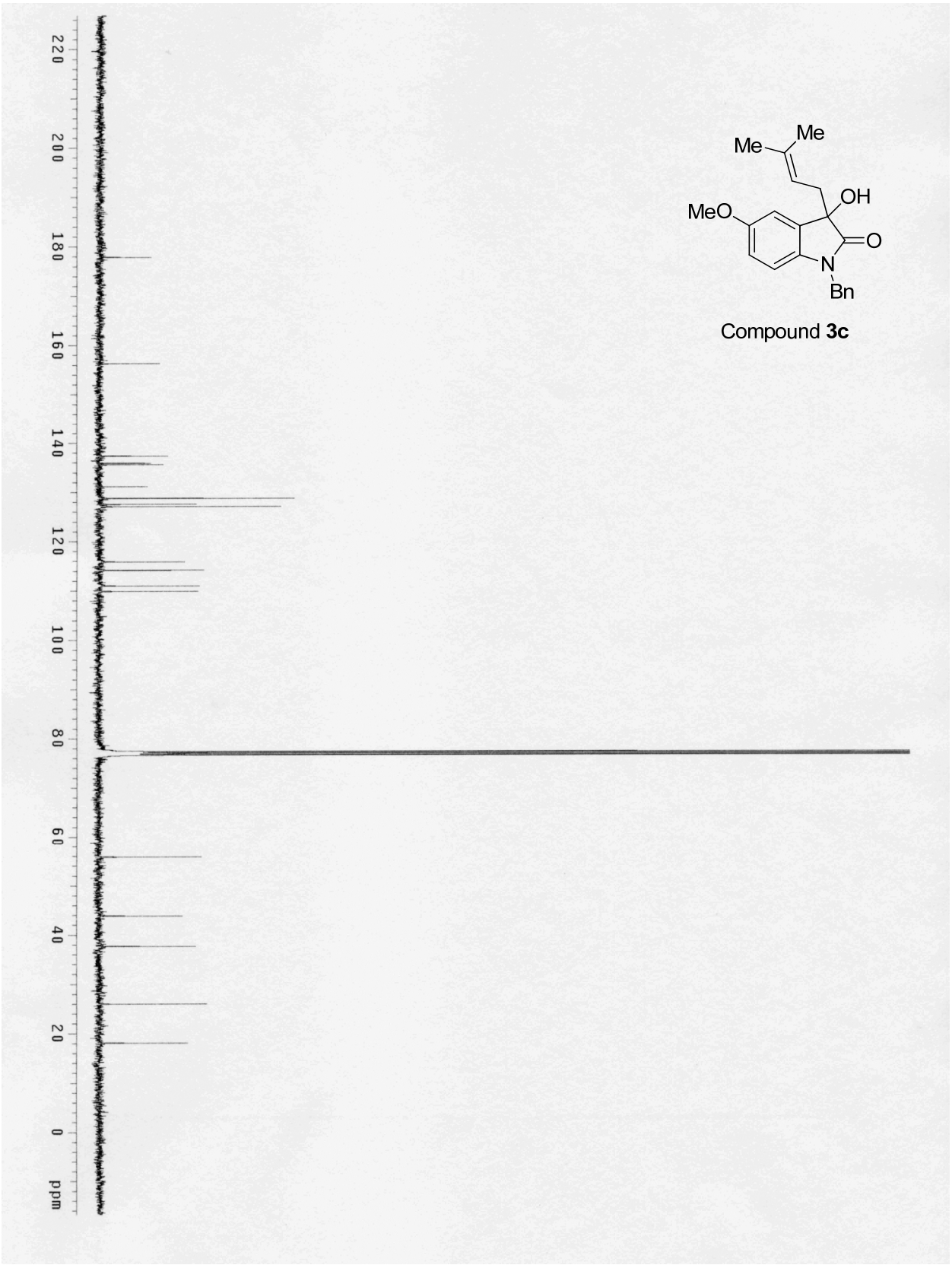
FTIR (neat): 3377, 2919, 1698, 1601, 1492, 1436, 1281, 1032, 694 cm^{-1}

Mp: 165.8-166.3 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

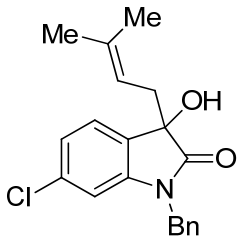


Compound **3c**



Compound **3c**

1-benzyl-6-chloro-3-hydroxy-3-(3-methylbut-2-en-1-yl)indolin-2-one (3d)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (58.1 mg, 85%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 6H), 7.03 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.65 (d, *J* = 2.0 Hz, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.91-4.87 (m, 1H), 4.58 (d, *J* = 16.0 Hz, 1H), 2.77 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.75 (s, 1H), 2.68 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.63 (s, 3H), 1.56 (s, 3H)

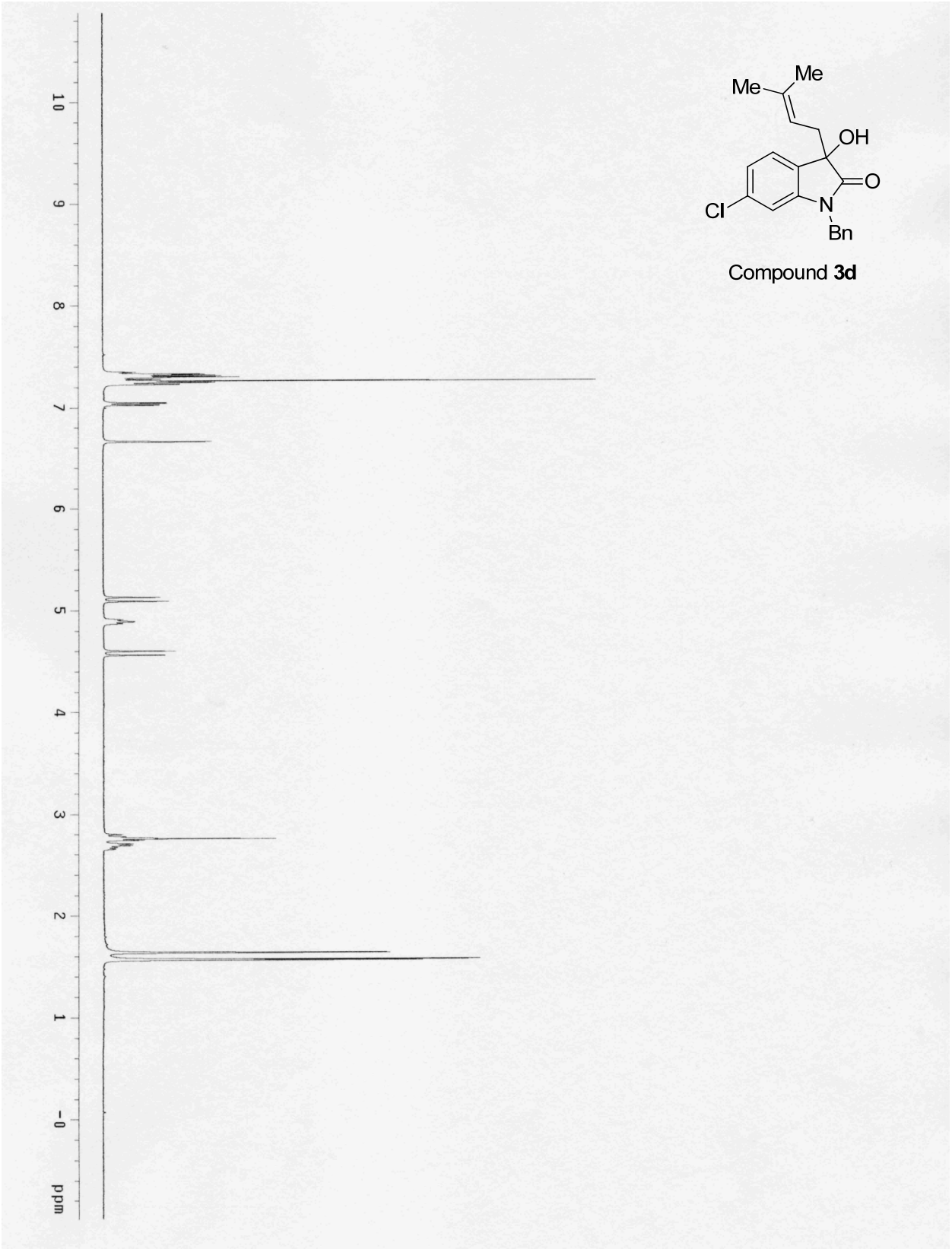
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 143.9, 137.9, 135.3, 134.9, 128.9, 128.2, 127.8, 127.0, 124.9, 122.9, 115.4, 109.9, 75.9, 43.9, 37.5, 25.9, 18.0

LRMS (CI) Calcd. For $C_{20}H_{21}ClNO_2$ $[M+H]^+$: 342, Found: 342

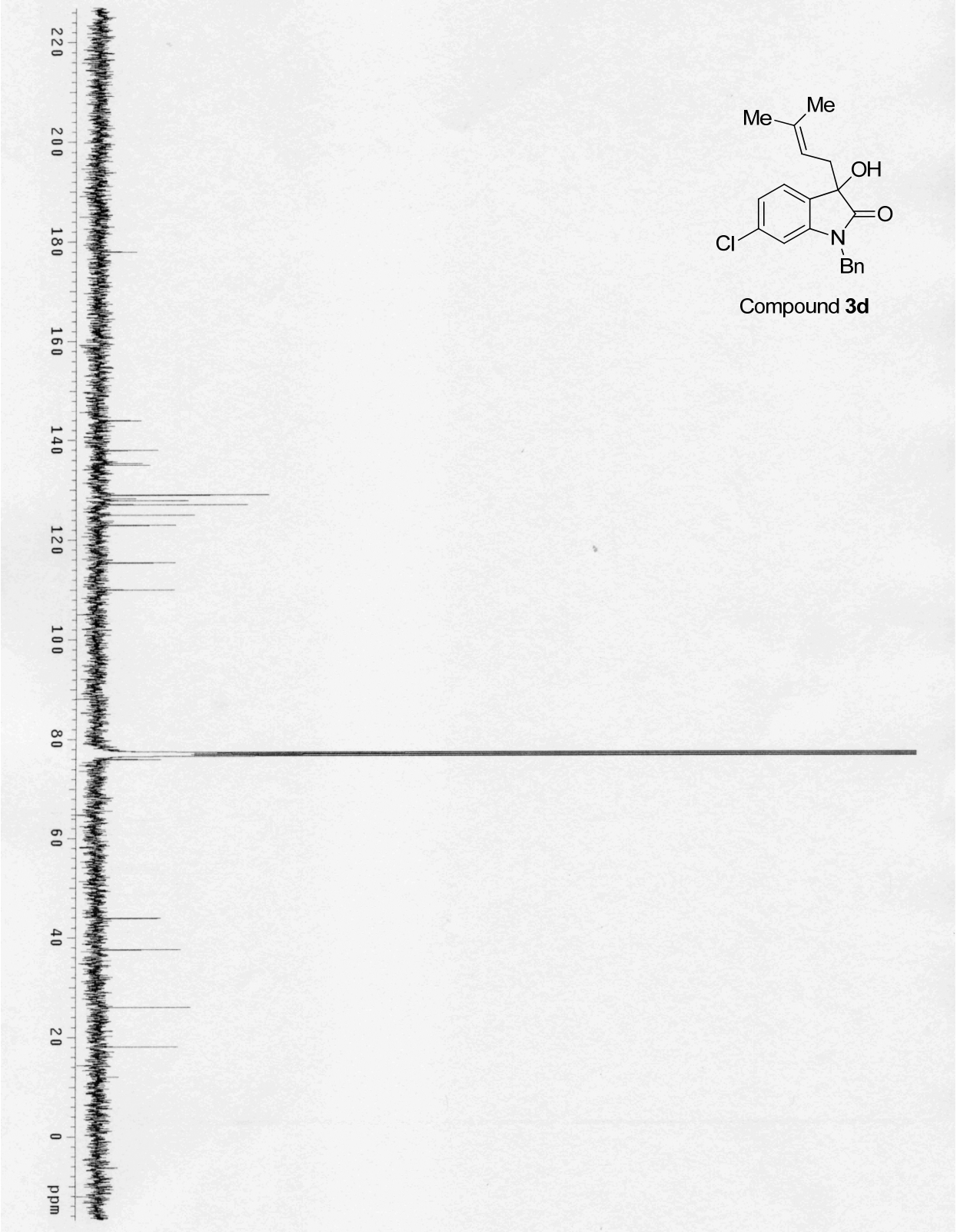
FTIR (neat): 3390, 2919, 1717, 1606, 1490, 1432, 1375, 1067, 987, 845, 698 cm^{-1}

Mp: 175.5-176.0 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

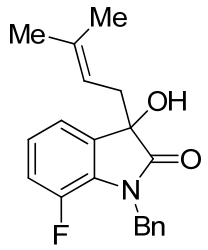


Compound **3d**



Compound **3d**

1-benzyl-7-fluoro-3-hydroxy-3-(3-methylbut-2-en-1-yl)indolin-2-one (3e)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (53.3 mg, 82%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.18 (m, 6H), 7.04-6.95 (m, 2H), 5.14 (d, *J* = 15.6 Hz, 1H), 4.91-4.86 (m, 2H), 2.82 (s, 1H), 2.75 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.66 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.60 (s, 3H), 1.54 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 147.4 (d, *J* = 243.3 Hz), 137.7, 136.7, 132.9, 129.1 (d, *J* = 8.1 Hz), 128.6, 127.5, 127.3 (d, *J* = 8.2 Hz), 123.8 (d, *J* = 6.0 Hz), 119.8 (d, *J* = 2.9 Hz), 117.7 (d, *J* = 20.1 Hz), 115.3, 76.3, 45.3 (d, *J* = 4.4 Hz), 37.6, 25.9, 17.9

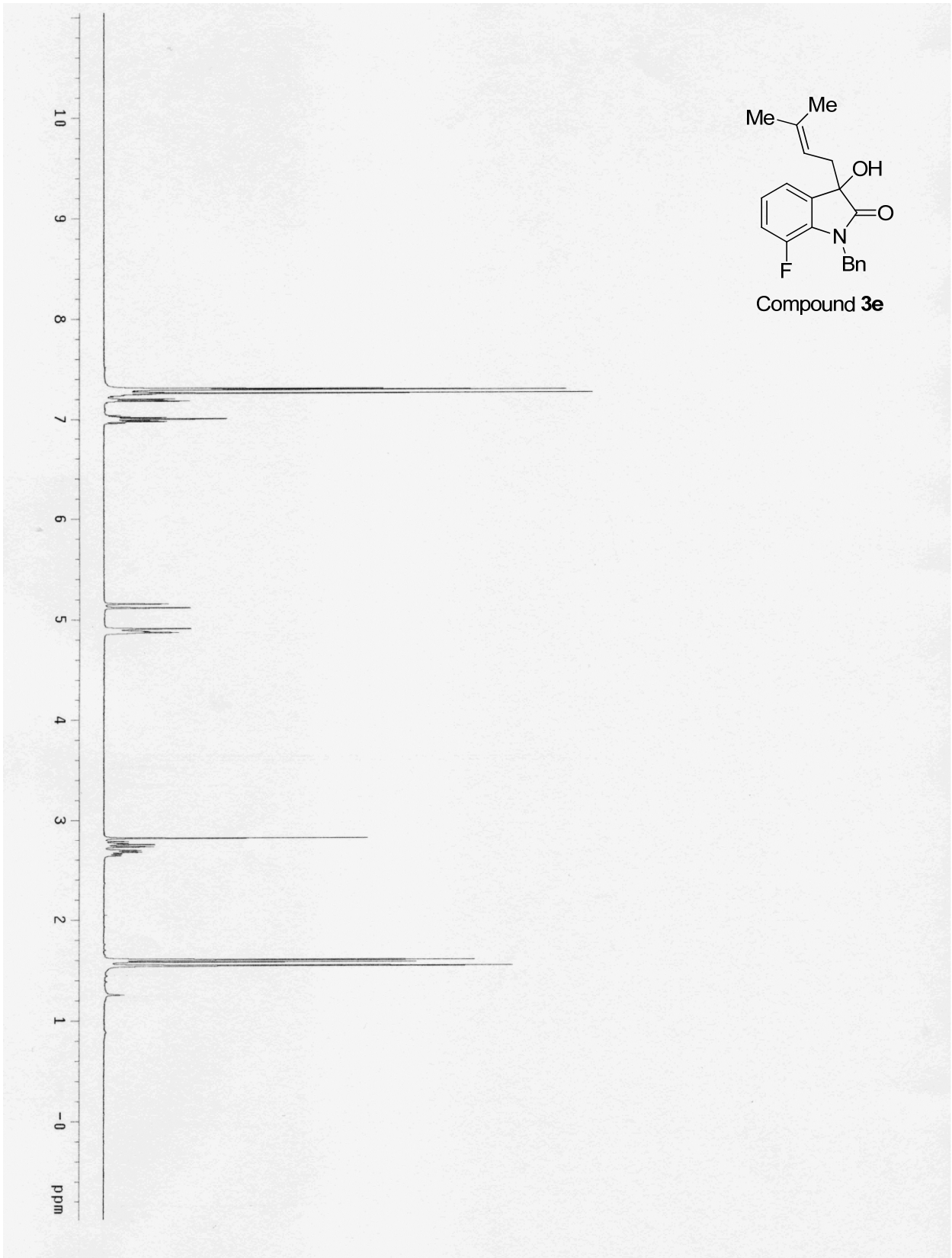
^{19}F NMR (376 MHz, $CDCl_3$): δ −133.58– −133.59 (m)

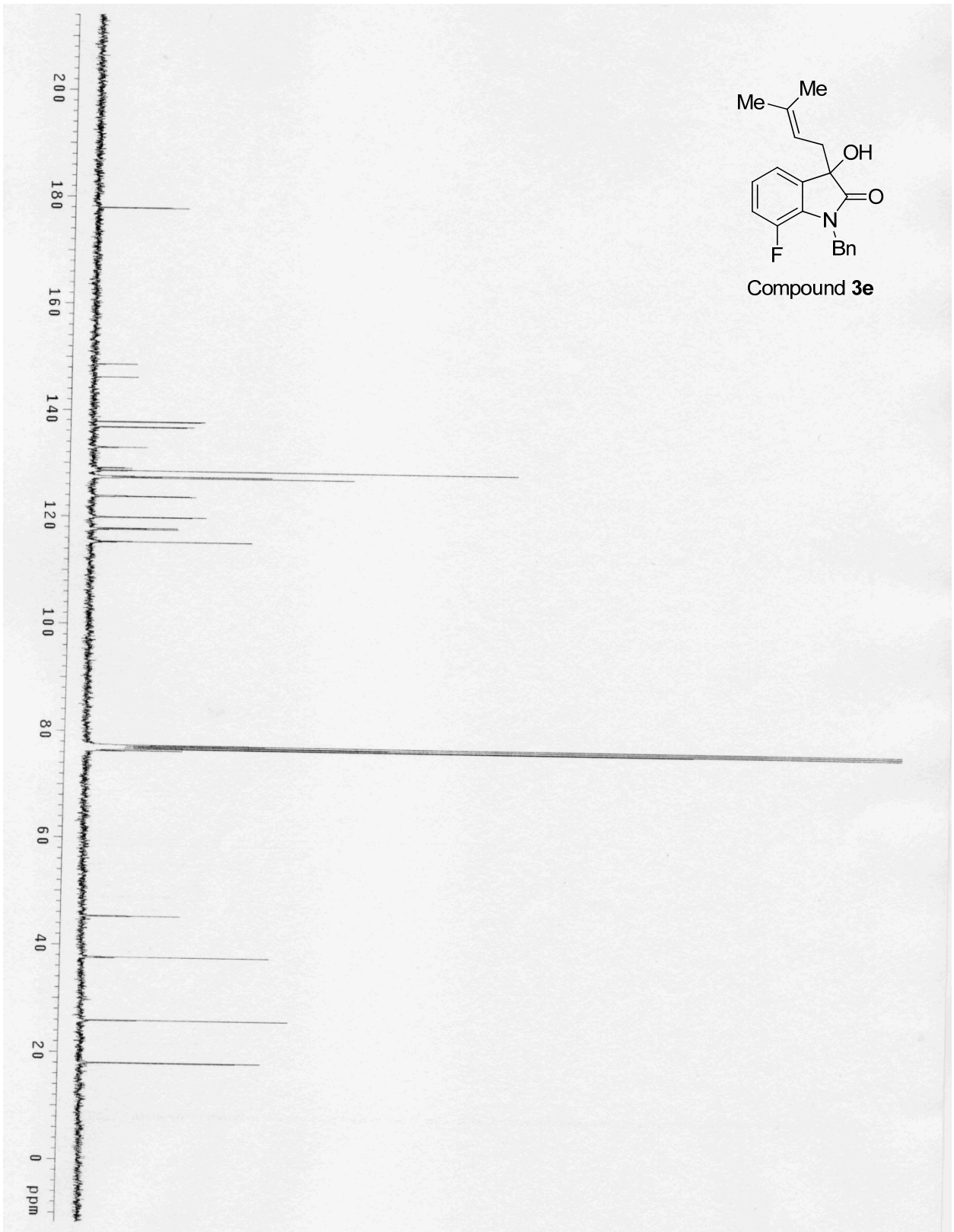
LRMS (CI) Calcd. For $C_{20}H_{21}FNO_2$ $[M+H]^+$: 326, Found: 326

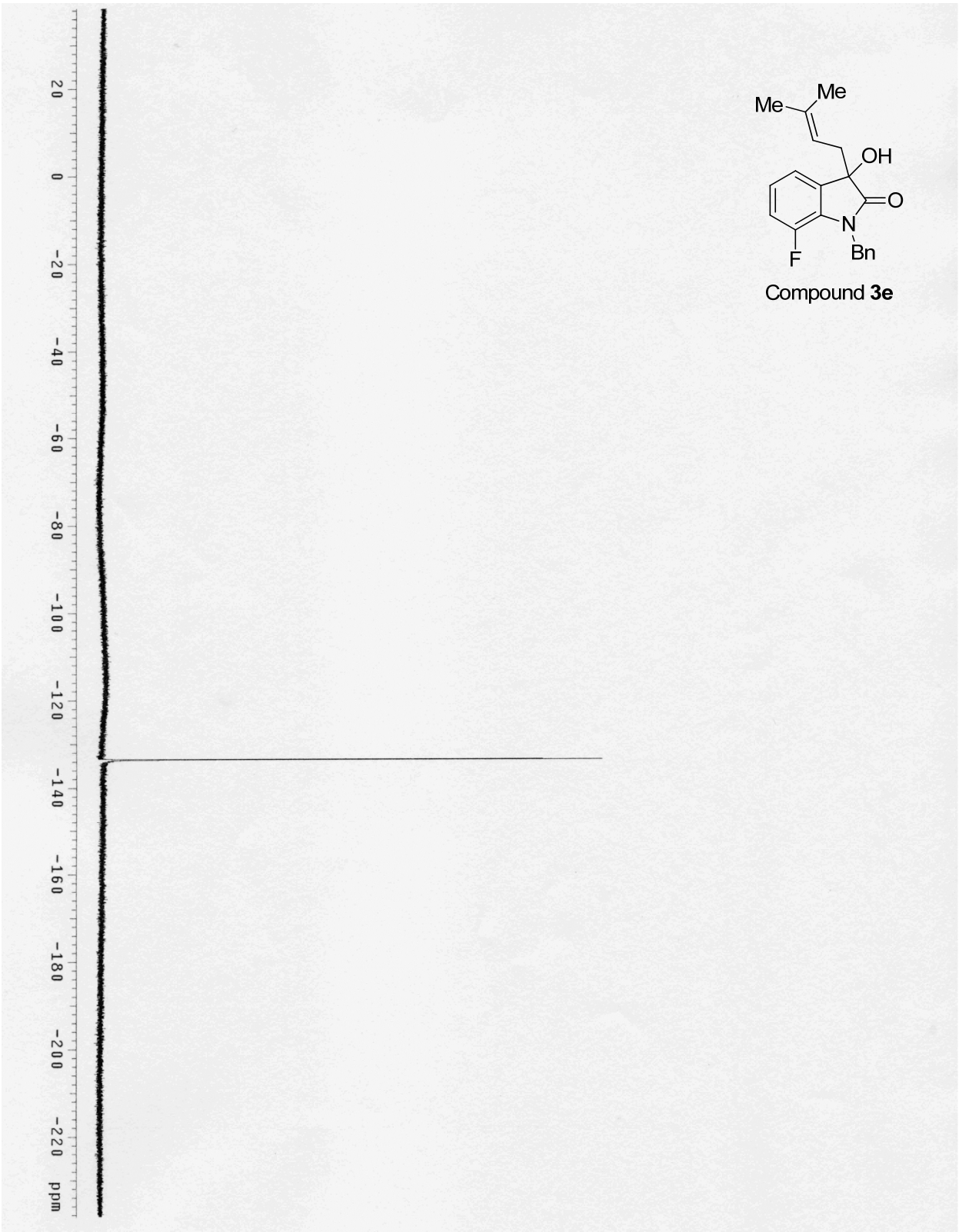
FTIR (neat): 3373, 2923, 2358, 2336, 1722, 1633, 1486, 1357, 1245, 1192, 1081, 912, 725, 694 cm^{-1}

Mp: 145.5-146.0 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

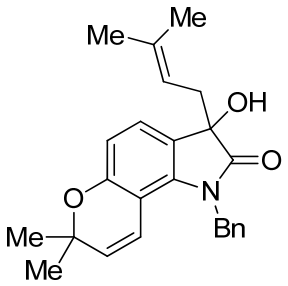

Me
Me
OH
O
N
Bn
F
Compound 3e
10
9
8
7
6
5
4
3
2
1
-0
ppm


Me
Me
OH
O
N
Bn
F
Compound 3e
200
180
160
140
120
100
80
60
40
20
0
ppm



Compound **3e**

1-benzyl-3-hydroxy-7,7-dimethyl-3-(3-methylbut-2-en-1-yl)-3,7-dihydropyrano[2,3-g]indol-2(1H)-one (3f)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (69.8 mg, 90%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.14 (m, 6H), 6.58 (dd, *J* = 8.0, 0.4 Hz, 1H), 6.27 (d, *J* = 10.0 Hz, 1H), 5.48 (d, *J* = 10.0 Hz, 1H), 5.35 (d, *J* = 16.8 Hz, 1H), 4.96-4.92 (m, 1H), 4.80 (d, *J* = 17.2 Hz, 1H), 2.89 (s, 1H), 2.82 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.68 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.68 (s, 3H), 1.57 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H)

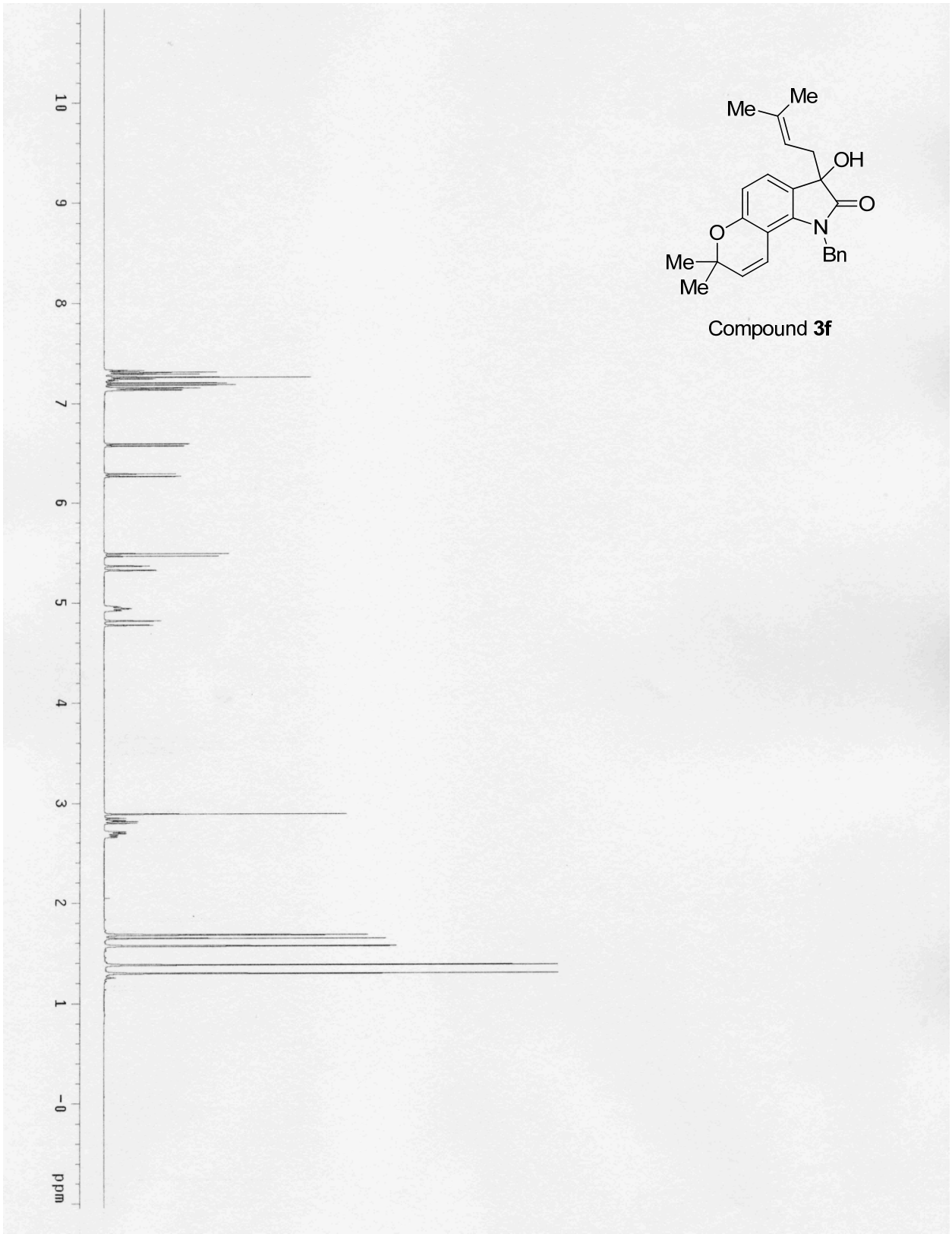
^{13}C NMR (100 MHz, $CDCl_3$): δ 179.6, 154.8, 138.8, 137.4, 136.4, 131.1, 128.9, 127.3, 125.7, 124.1, 122.6, 117.3, 116.1, 111.3, 107.2, 75.3, 75.0, 45.5, 37.7, 27.7, 26.4, 26.0, 18.1

LRMS (CI) Calcd. For $C_{25}H_{28}NO_3$ $[M+H]^+$: 390, Found: 390

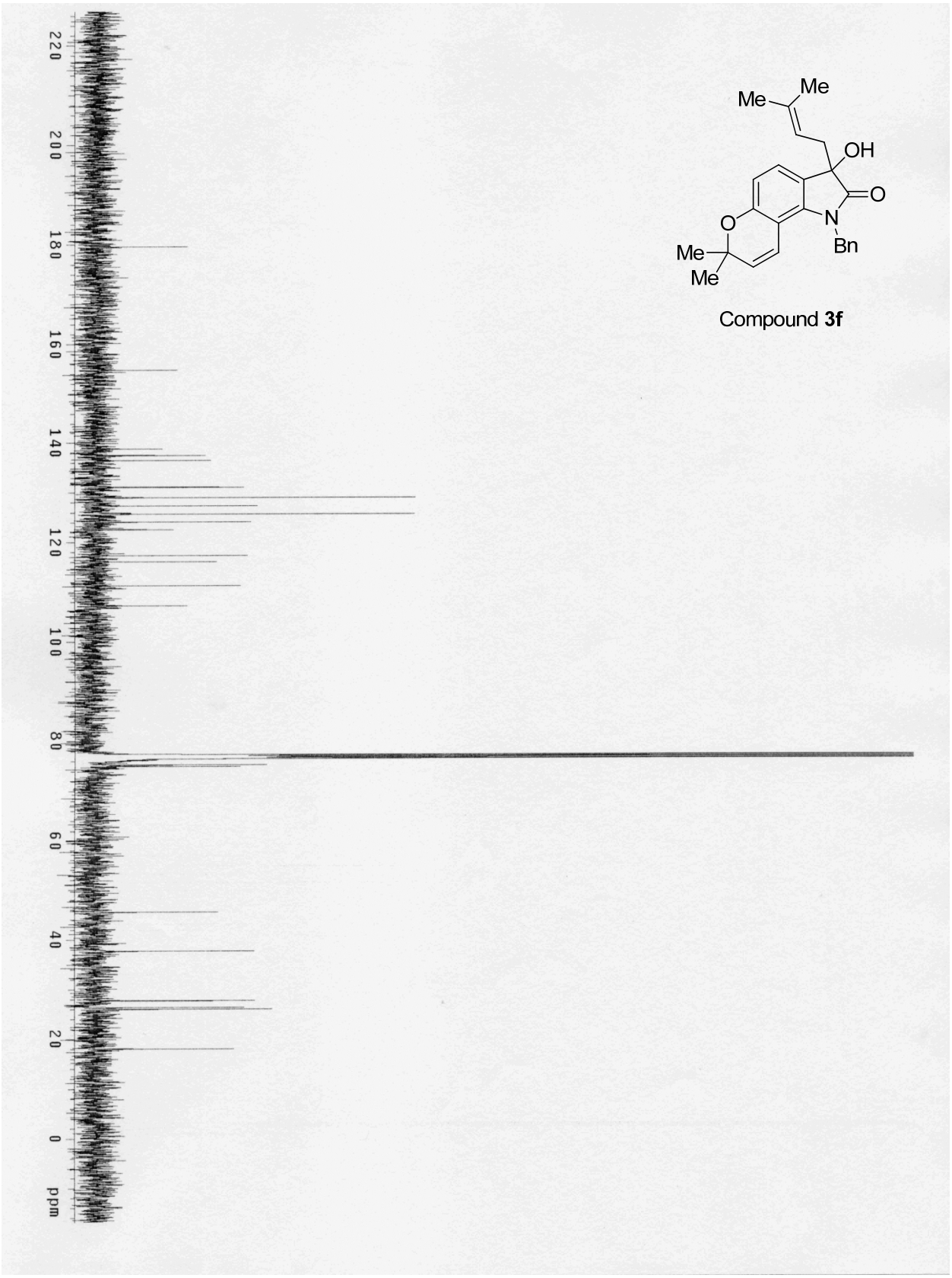
FTIR (neat): 3386, 2977, 2928, 2349, 1713, 1601, 1450, 1375, 1165, 1112, 974, 729 cm^{-1}

Mp: 157.3-157.7 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)



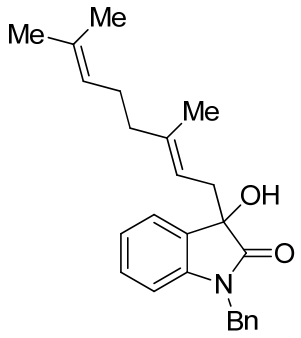
Compound **3f**



Compound **3f**

Experimental Procedures and Spectroscopic Data for Geranylated 3-Hydroxy-2-oxindole 4a-4f

(E)-1-benzyl-3-(3,7-dimethylocta-2,6-dien-1-yl)-3-hydroxyindolin-2-one (4a)



General Procedure: The reaction was heated for 48 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (57.0 mg, 76%, >20:1 *E*:*Z*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.31-7.22 (m, 5H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (td, *J* = 7.6, 0.8 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.99-4.95 (m, 2H), 4.67 (d, *J* = 16.0 Hz, 1H), 3.46-3.43 (m, 1H), 2.81-2.71 (m, 2H), 1.97-1.87 (m, 4H), 1.64 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H)

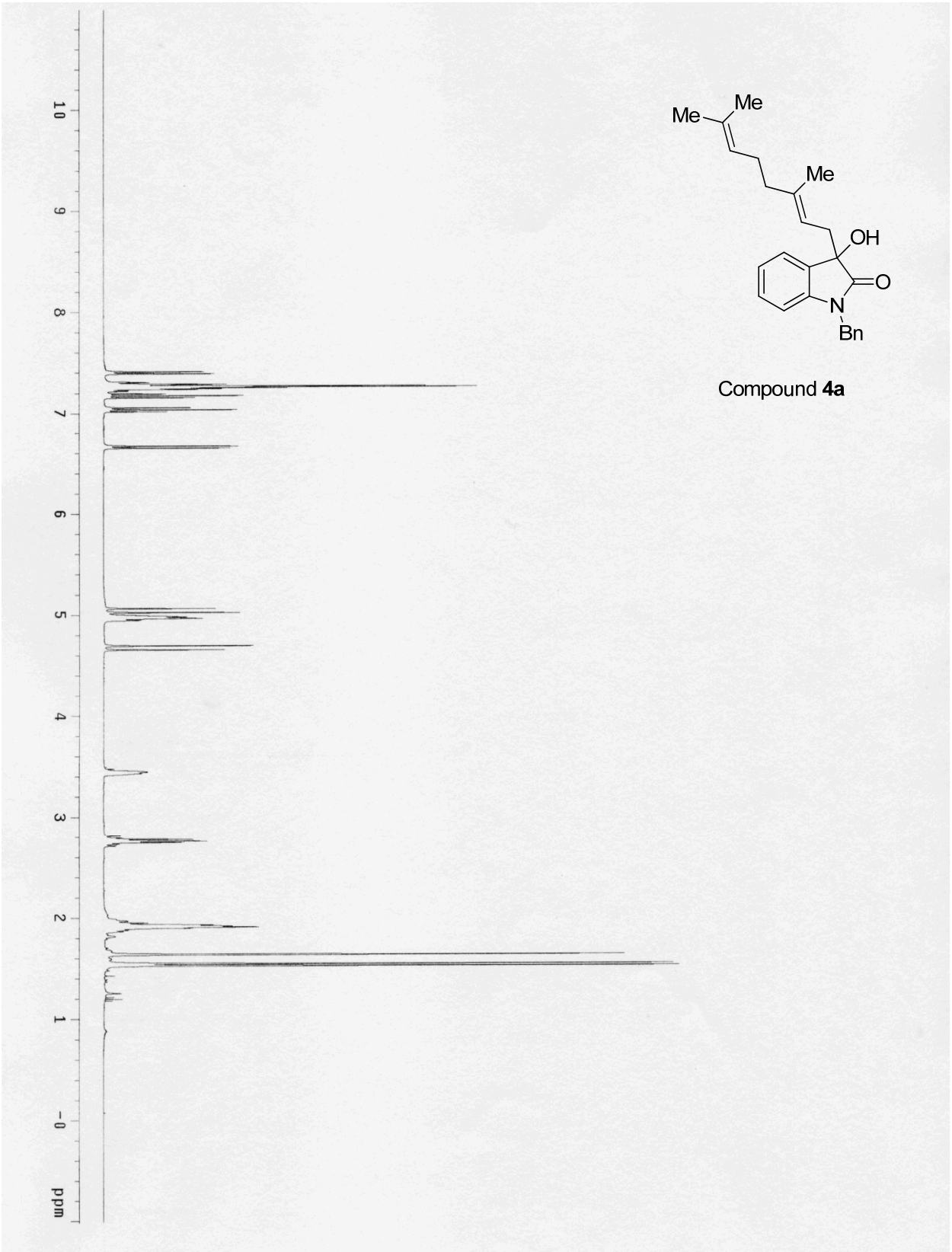
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 143.5, 140.8, 135.5, 131.6, 130.1, 129.4, 128.7, 127.6, 127.1, 124.0, 123.9, 122.9, 115.7, 109.3, 76.3, 43.7, 39.8, 37.4, 26.4, 25.7, 17.6, 16.3

LRMS (CI) Calcd. For $C_{25}H_{30}NO_2$ $[M+H]^+$: 376, Found: 376

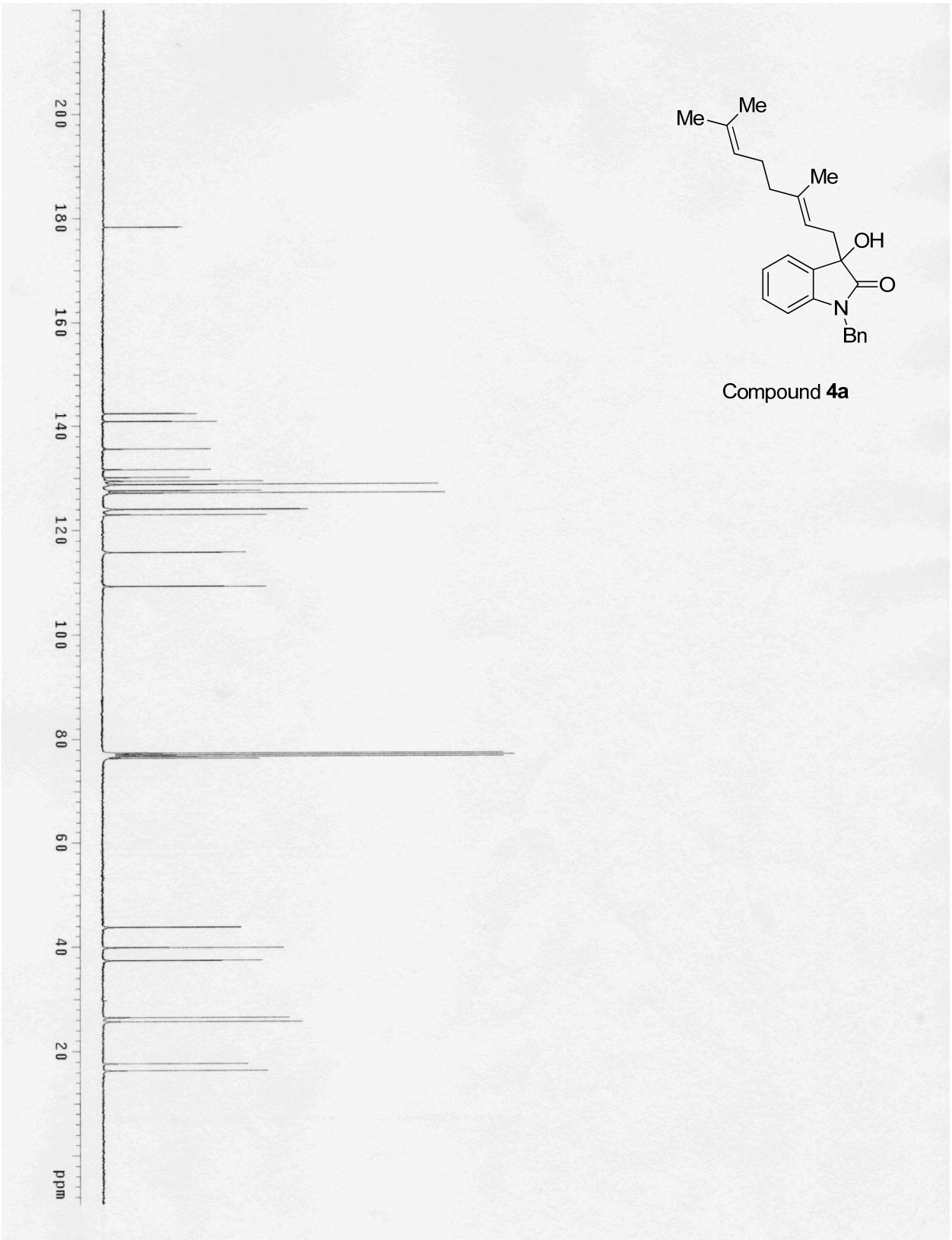
FTIR (neat): 3329, 2969, 2929, 1738, 1695, 1615, 1494, 1434, 1371, 1284, 1227, 1216, 1113, 1089, 996, 907, 768, 756, 730, 694 cm^{-1}

Mp: 139.2-139.5 °C

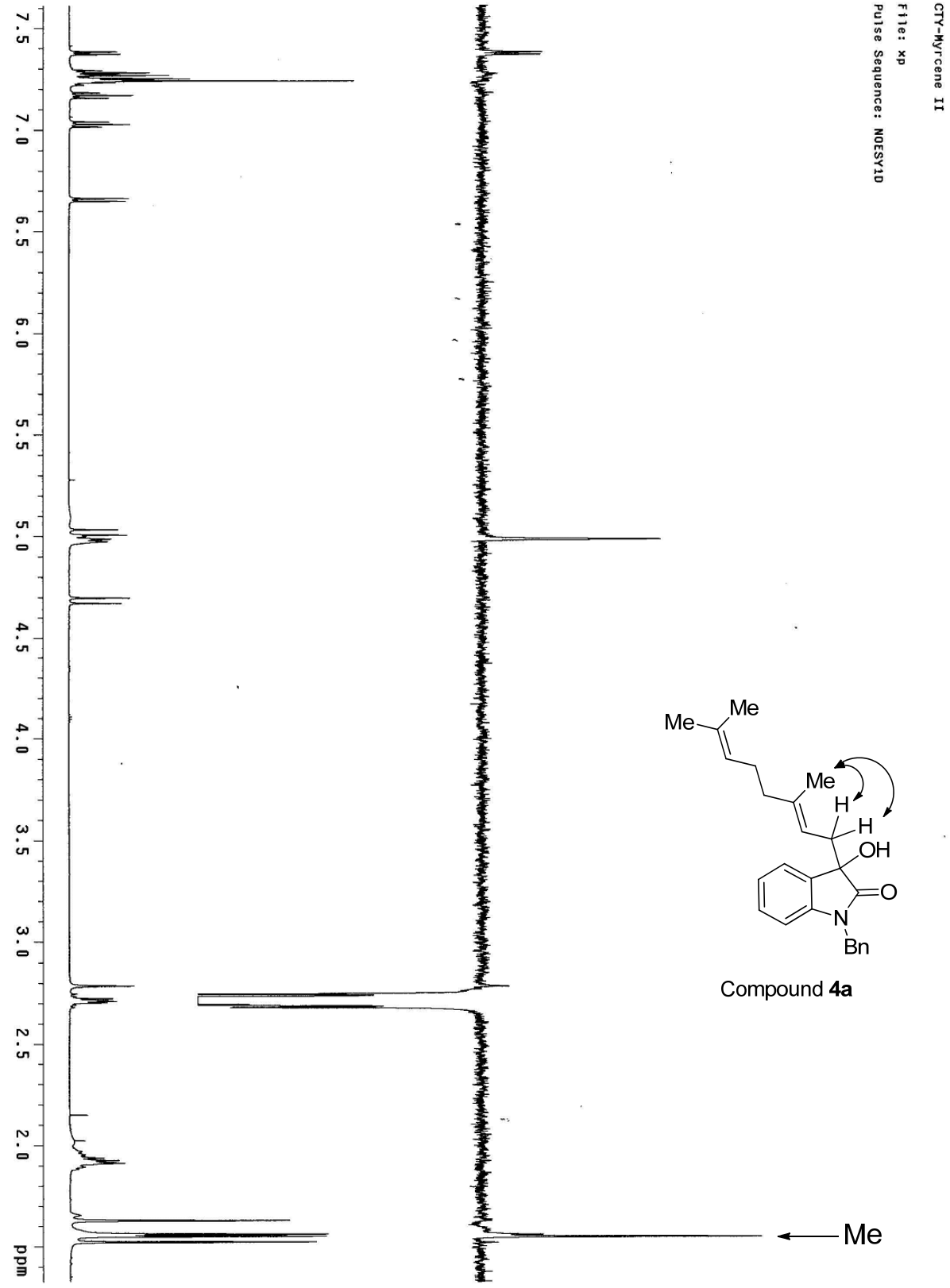
TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)



Compound **4a**

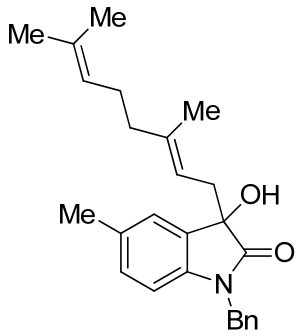


Compound **4a**


CTY-Myrcene II
File: xp
Pulse Sequence: NOESY1D
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
Me
Me
Me
H
H
OH
O
N
Bn
Me

Compound **4a**

(E)-1-benzyl-3-(3,7-dimethylocta-2,6-dien-1-yl)-3-hydroxy-5-methylindolin-2-one (4b)



General Procedure: The reaction was heated for 48 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (73.2 mg, 94%, >20:1 *E*:*Z*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.21 (m, 6H), 6.99-6.97 (m, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 5.03-4.99 (m, 3H), 4.68 (d, *J* = 15.6 Hz, 1H), 2.78 (s, 1H), 2.75 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.68 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.30 (s, 3H), 1.97-1.94 (m, 4H), 1.65 (s, 3H), 1.58 (s, 3H), 1.55(s, 3H)

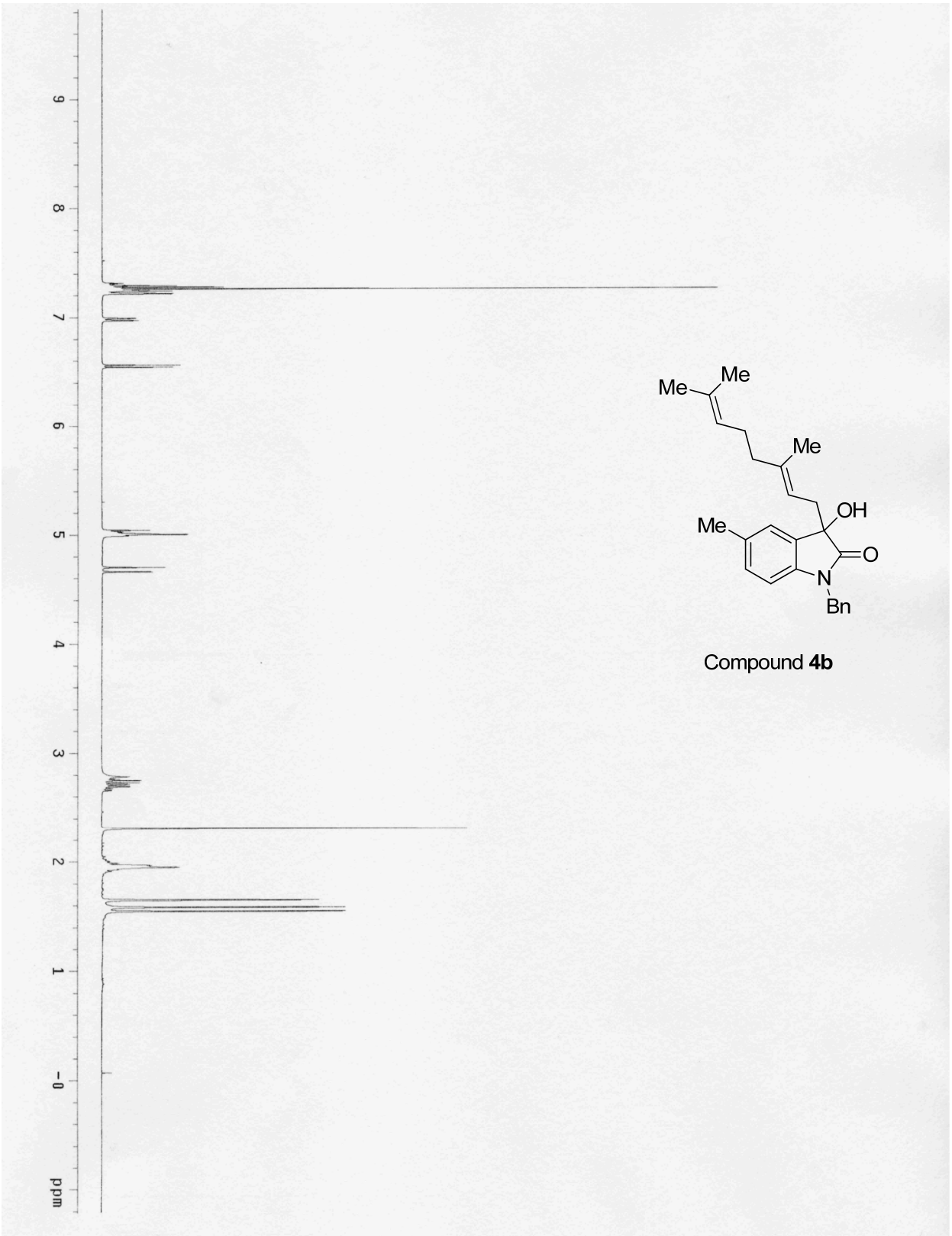
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 140.9, 140.1, 135.6, 132.5, 131.6, 129.9, 129.6, 128.7, 127.5, 127.1, 124.7, 123.9, 115.8, 109.0, 76.3, 43.7, 39.9, 37.4, 26.5, 25.7, 21.0, 17.6, 16.3

LRMS (CI) Calcd. For $C_{26}H_{32}NO_2$ $[M+H]^+$: 390, Found: 390

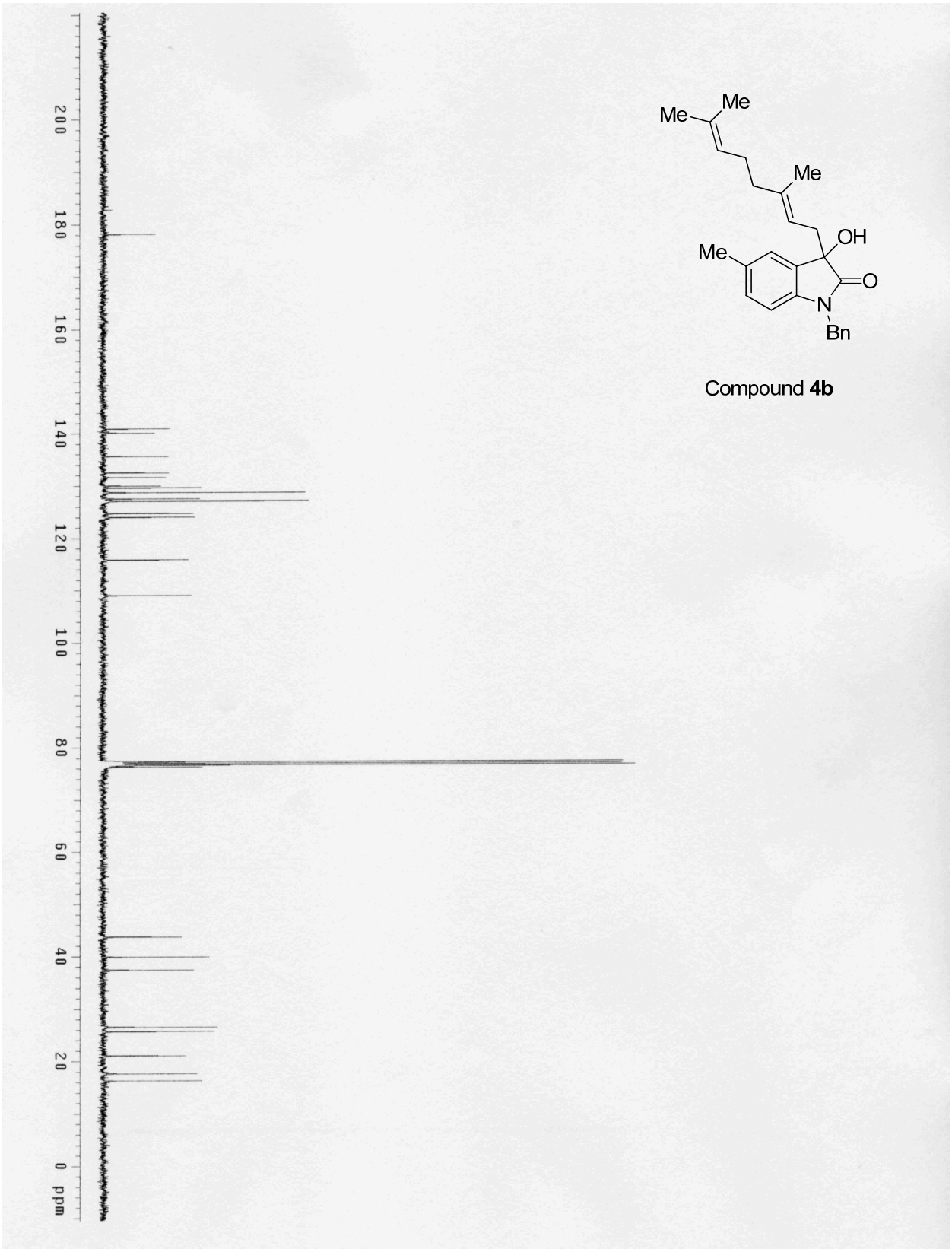
FTIR (neat): 3319, 2927, 2362, 1694, 1619, 1494, 1432, 1347, 1276, 1192, 1147, 1085, 978, 809, 742, 693 cm^{-1}

Mp: 142.3-142.9 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

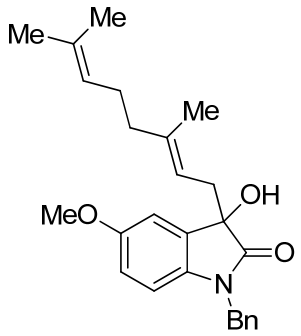


Compound **4b**



Compound **4b**

(E)-1-benzyl-3-(3,7-dimethylocta-2,6-dien-1-yl)-3-hydroxy-5-methoxyindolin-2-one (4c)



General Procedure: The reaction was heated for 48 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (78.5 mg, 97%, >20:1 *E*:*Z*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 5H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 5.04-4.97 (m, 3H), 4.67 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H), 3.01 (s, 1H), 2.79-2.67 (m, 2H), 2.01-1.94 (m, 4H), 1.65 (s, 3H), 1.58 (s, 3H), 1.54 (s, 3H)

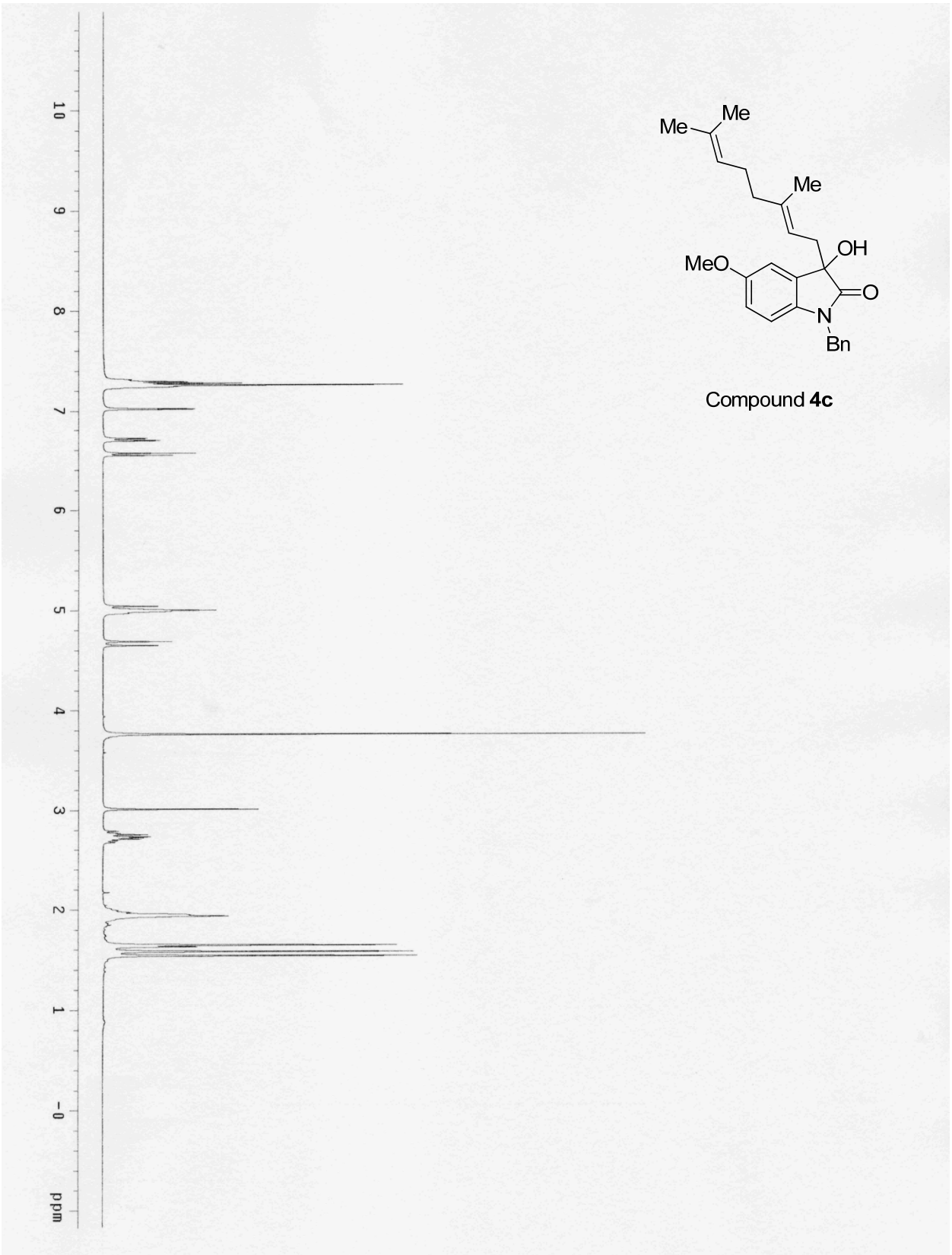
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 156.2, 140.9, 135.8, 135.6, 131.7, 131.3, 128.8, 127.6, 127.1, 123.9, 115.7, 114.1, 111.0, 109.8, 76.6, 55.8, 43.9, 39.9, 37.5, 26.5, 25.7, 17.7, 16.4

LRMS (CI) Calcd. For $C_{26}H_{32}NO_3$ $[M+H]^+$: 406, Found: 406

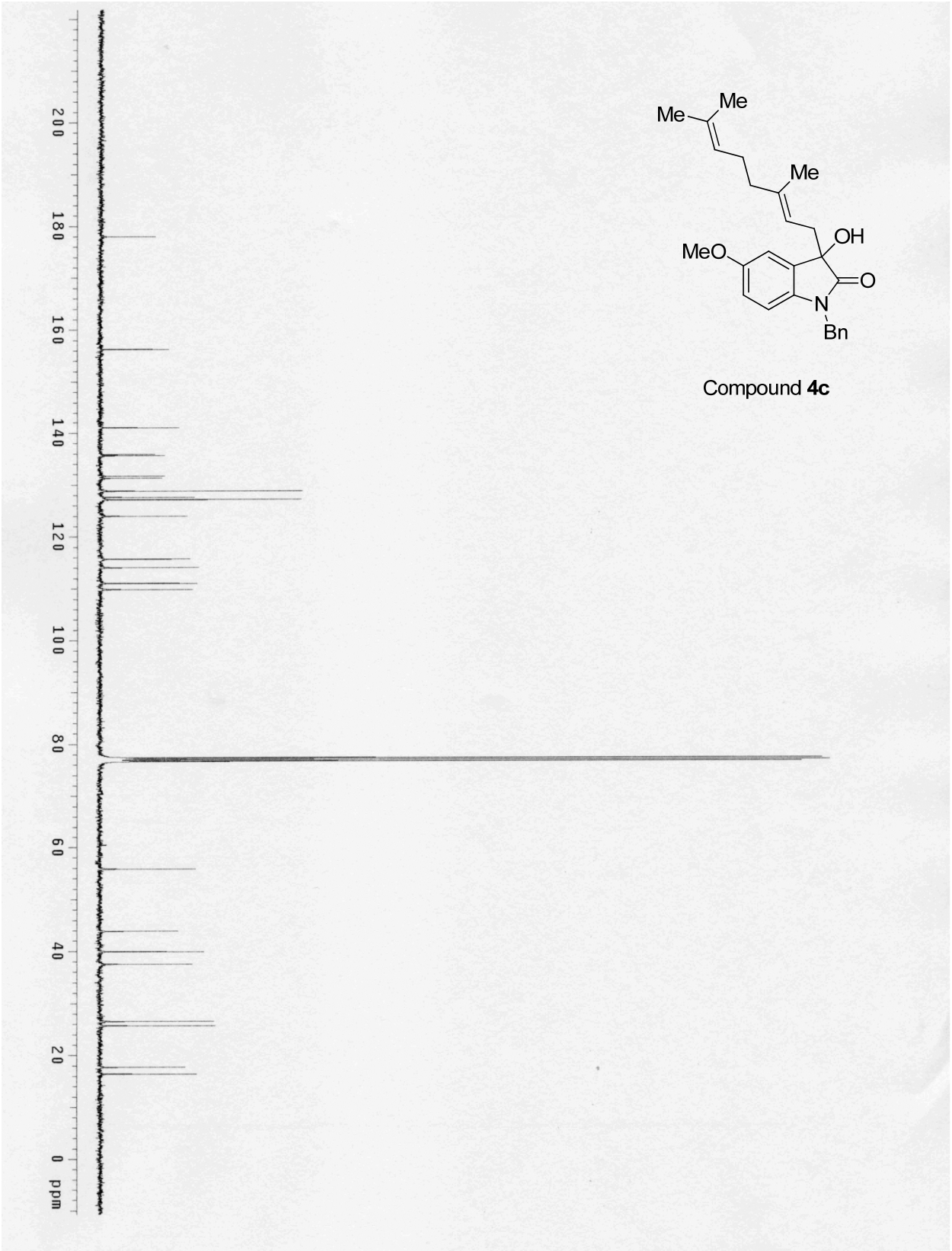
FTIR (neat): 3385, 2918, 1964, 1601, 1432, 1347, 1276, 1174, 1022, 809, 698 cm^{-1}

Mp: 135.7-136.1 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

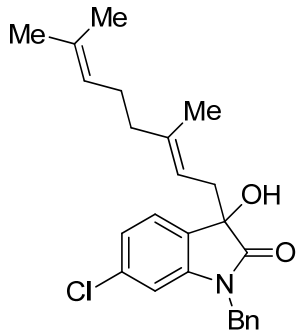


Compound **4c**



Compound **4c**

(E)-1-benzyl-6-chloro-3-(3,7-dimethylocta-2,6-dien-1-yl)-3-hydroxyindolin-2-one (4d)



General Procedure: The reaction was heated for 48 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (68.1 mg, 83%, >20:1 *E*:*Z*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.24 (m, 6H), 7.02 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 5.04-4.96 (m, 3H), 4.66 (d, *J* = 15.6 Hz, 1H), 2.84 (s, 1H), 2.76-2.66 (m, 2H), 2.04-1.91 (m, 4H), 1.65 (s, 3H), 1.57 (s, 3H), 1.55 (s, 3H)

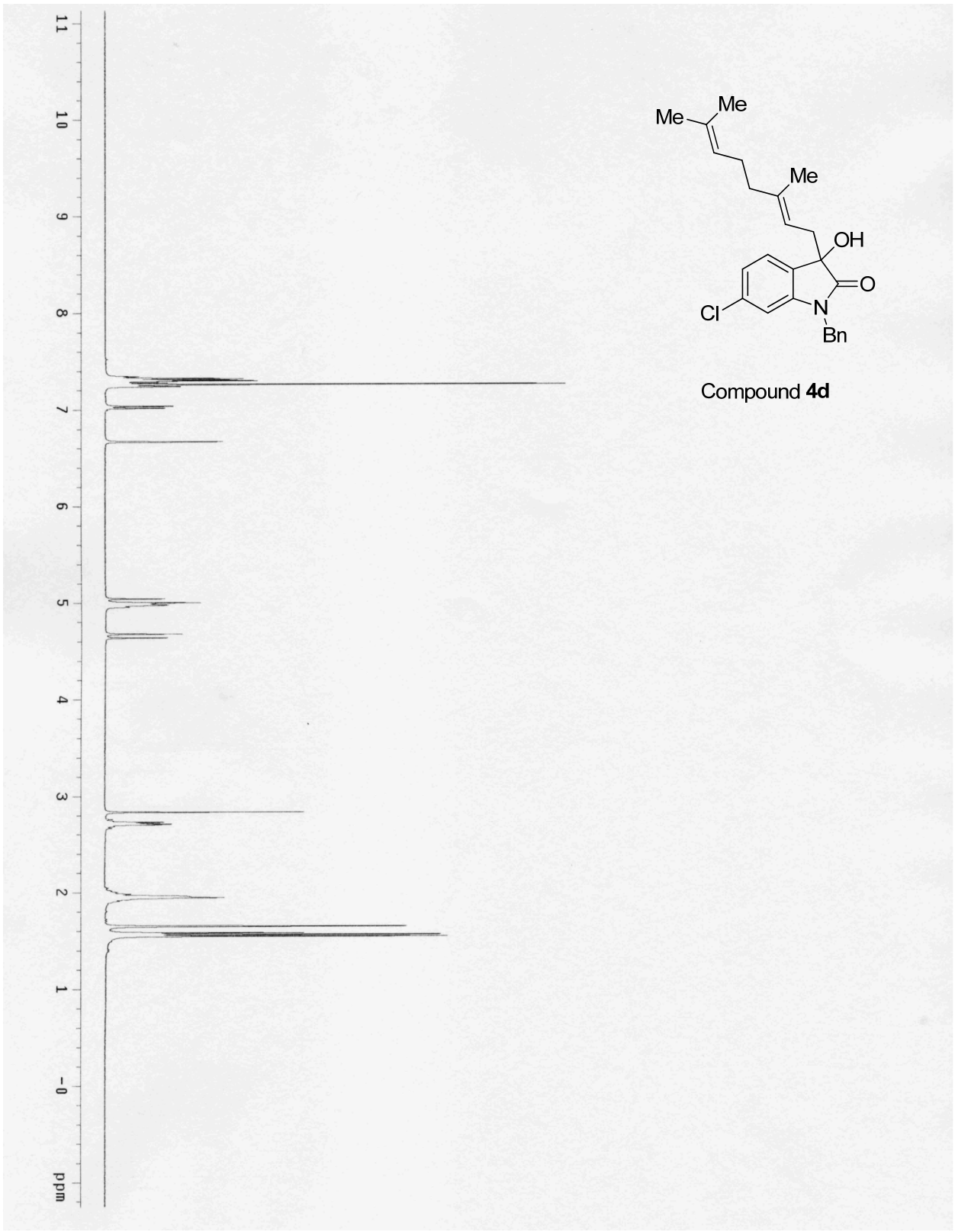
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 143.8, 141.5, 135.2, 134.9, 131.8, 128.9, 128.3, 127.8, 127.1, 124.9, 123.8, 122.8, 115.3, 109.9, 75.8, 43.9, 39.9, 37.4, 26.4, 25.7, 17.7, 16.3

LRMS (CI) Calcd. For $C_{25}H_{29}ClNO_2$ $[M+H]^+$: 410, Found: 410

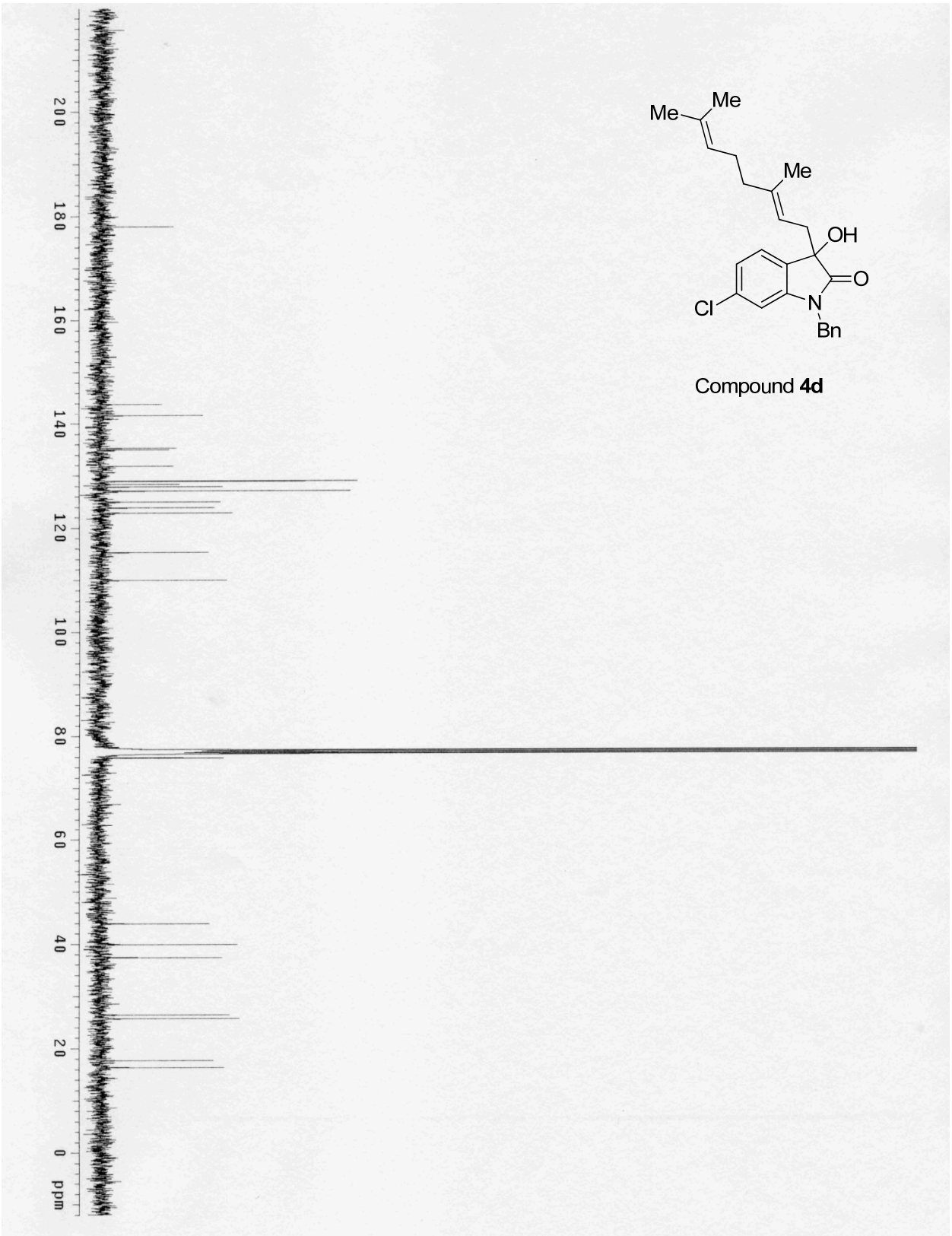
FTIR (neat): 3372, 2914, 1708, 1605, 1490, 1441, 1374, 1103, 1067, 991, 844, 693 cm^{-1}

Mp: 134.8-135.1 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

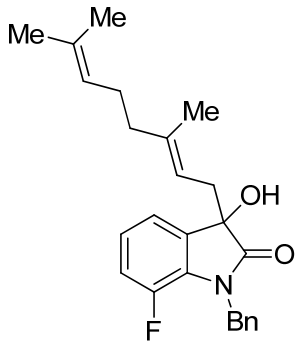


Compound **4d**



Compound **4d**

(E)-1-benzyl-3-(3,7-dimethylocta-2,6-dien-1-yl)-7-fluoro-3-hydroxyindolin-2-one (4e)



General Procedure: The reaction was heated for 48 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (69.0 mg, 88%, >20:1 *E*:*Z*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.18 (m, 6H), 7.03-6.95 (m, 2H), 5.08 (d, *J* = 15.2 Hz, 1H), 4.99-4.92 (m, 3H), 2.79 (s, 1H), 2.75-2.65 (m, 2H), 1.99-1.87 (m, 4H), 1.65 (s, 3H), 1.57 (s, 3H), 1.55 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8, 147.4 (d, *J* = 243.3 Hz), 141.5, 136.7, 132.9, 131.7, 129.0 (d, *J* = 9.0 Hz), 128.6, 127.6, 127.4 (d, *J* = 8.2 Hz), 123.9, 123.7 (d, *J* = 5.9 Hz), 119.9, 117.7 (d, *J* = 19.3 Hz), 115.2, 76.2 (d, *J* = 2.2 Hz), 45.3 (d, *J* = 4.5 Hz), 39.8, 37.6, 26.4, 25.7, 17.7, 16.3

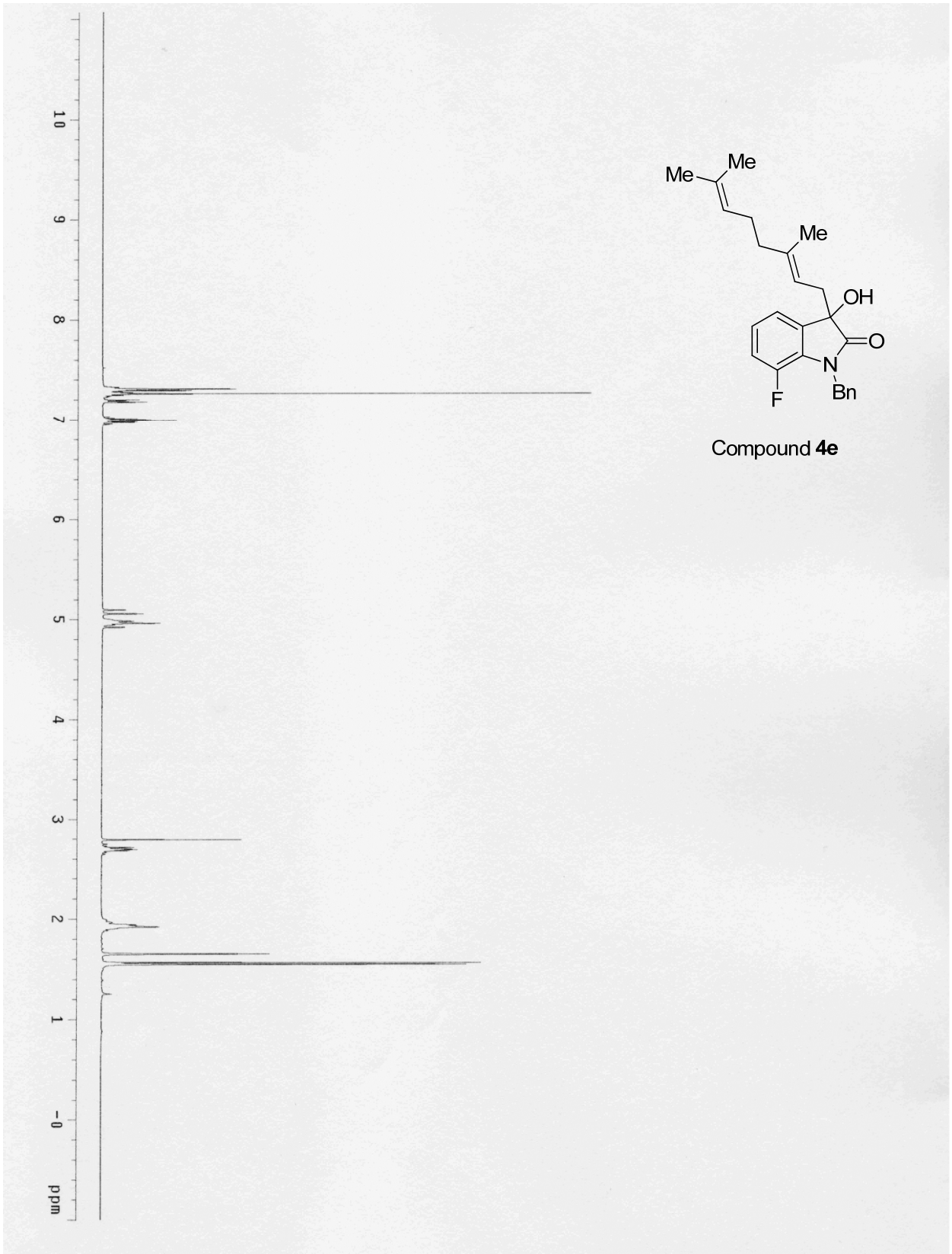
^{19}F NMR (376 MHz, $CDCl_3$): δ −133.5– −133.6 (m)

LRMS (CI) Calcd. For $C_{25}H_{29}FNO_2$ $[M+H]^+$: 394, Found: 394

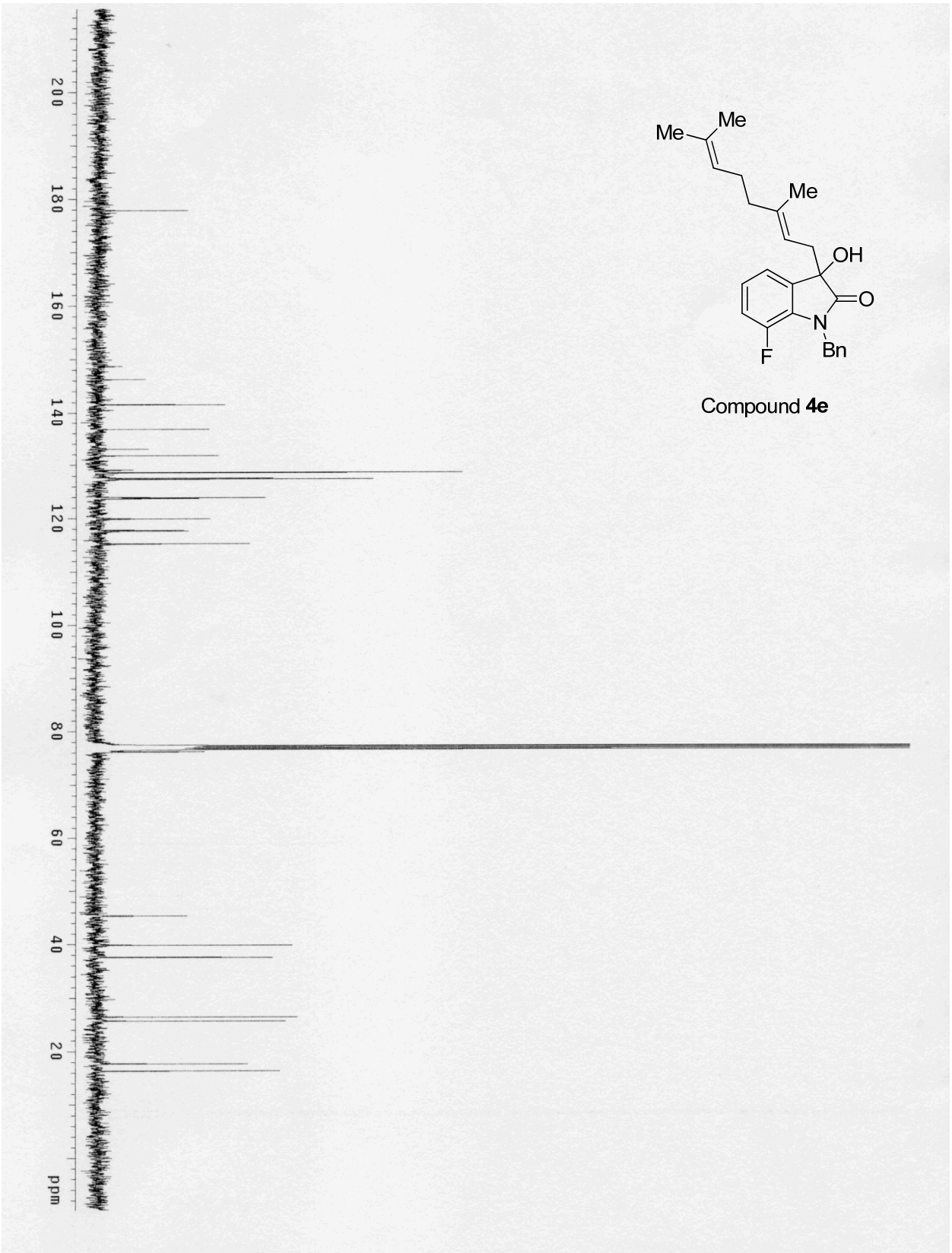
FTIR (neat): 3359, 2918, 2375, 2335, 1726, 1628, 1481, 1352, 1245, 1178, 1080, 778, 729, 693 cm^{-1}

Mp: 85.1-85.4 °C

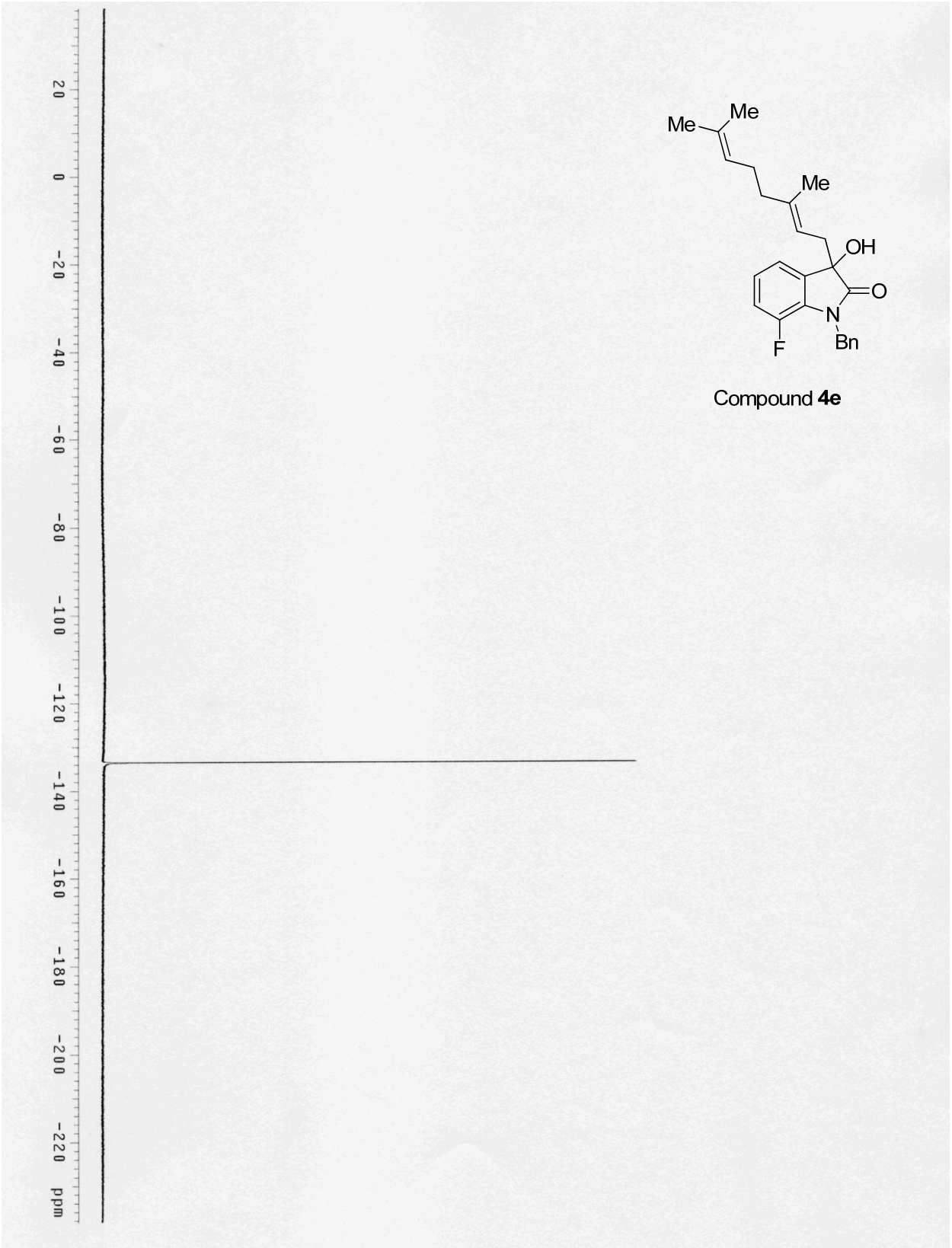
TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)



Compound **4e**

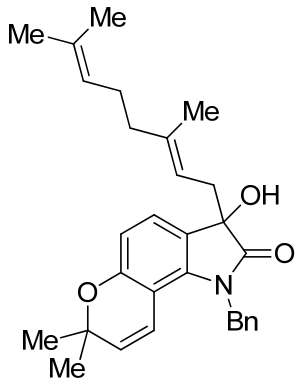


Compound **4e**



Compound **4e**

(*E*)-ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-hydroxy-5,9-dimethyldeca-4,8-dienoate (4f)



General Procedure: The reaction was heated for 48 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (70.4 mg, 77%, >20:1 *E*:*Z*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.14 (m, 6H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.28 (d, *J* = 10.0 Hz, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.03-4.99 (m, 2H), 4.86 (d, *J* = 16.8 Hz, 1H), 3.18 (s, 1H), 2.80 (dd, *J* = 13.2, 8.8 Hz, 1H), 2.70 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.03-1.93 (m, 4H), 1.65 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H), 1.29 (s, 3H)

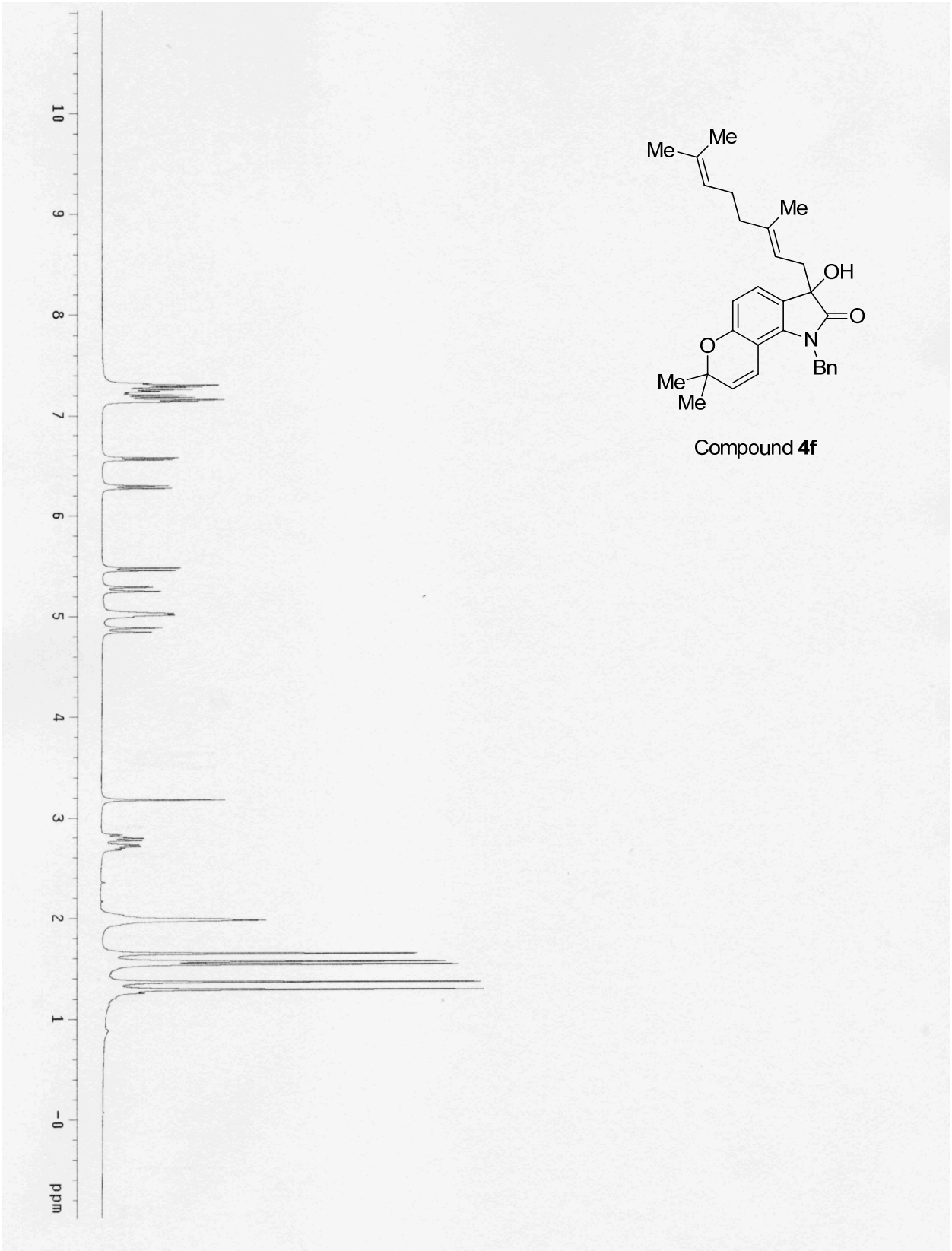
^{13}C NMR (100 MHz, $CDCl_3$): δ 179.8, 154.7, 140.9, 138.6, 136.3, 131.7, 130.9, 128.9, 127.3, 125.7, 124.1, 123.9, 122.7, 117.3, 115.9, 111.2, 107.1, 75.3, 74.9, 45.6, 39.9, 37.5, 27.6, 26.5, 26.4, 25.7, 17.7, 16.3

LRMS (CI) Calcd. For $C_{30}H_{36}NO_3$ $[M+H]^+$: 458, Found: 458

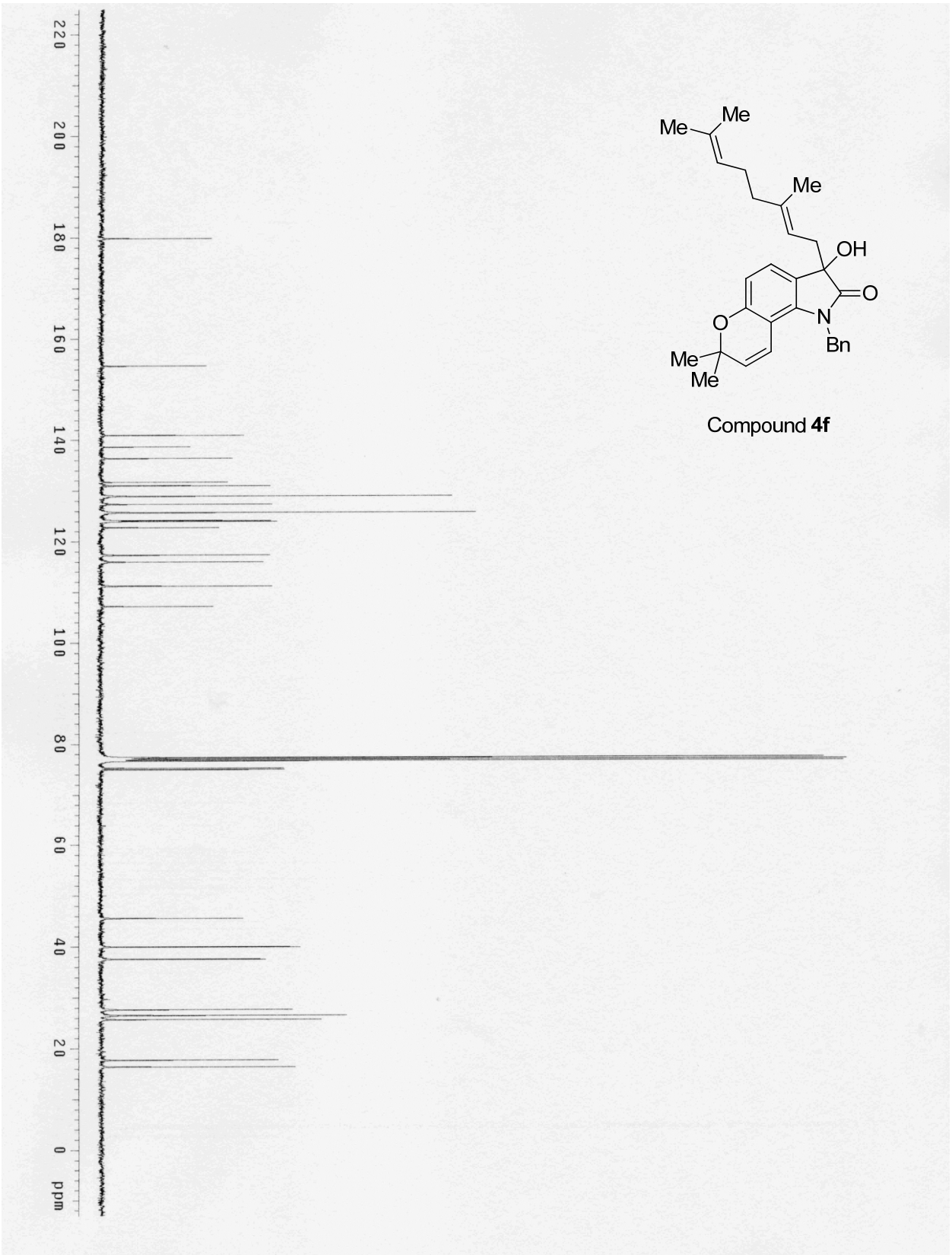
FTIR (neat): 3385, 2976, 2932, 2362, 2246, 1712, 1605, 1454, 1365, 1152, 911, 747 cm^{-1}

Mp: 147.3-147.7 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)



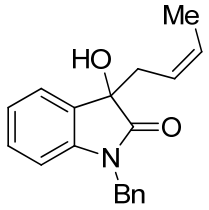
Compound **4f**


220
200
180
160
140
120
100
80
60
40
20
0
ppm
Me
Me
Me
OH
O
O
N
Bn
Me
Me

Compound **4f**

Experimental Procedures and Spectroscopic Data for 3-Hydroxy-2-oxindoles 5a-5d

(Z)-1-benzyl-3-(but-2-en-1-yl)-3-hydroxyindolin-2-one (5a)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (43.9 mg, 75%, >20:1 *Z*:*E*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.33-7.24 (m, 5H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (td, *J* = 8.0, 1.2 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.58 (dddd, *J* = 14.4, 6.8, 0.8 Hz, 1H), 5.58 (dddd, *J* = 17.6, 8.8, 3.6, 2.0 Hz, 1H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.71 (d, *J* = 15.6 Hz, 1H), 2.91 (s, 1H), 2.84 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.74 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.57 (d, *J* = 6.8, 3H)

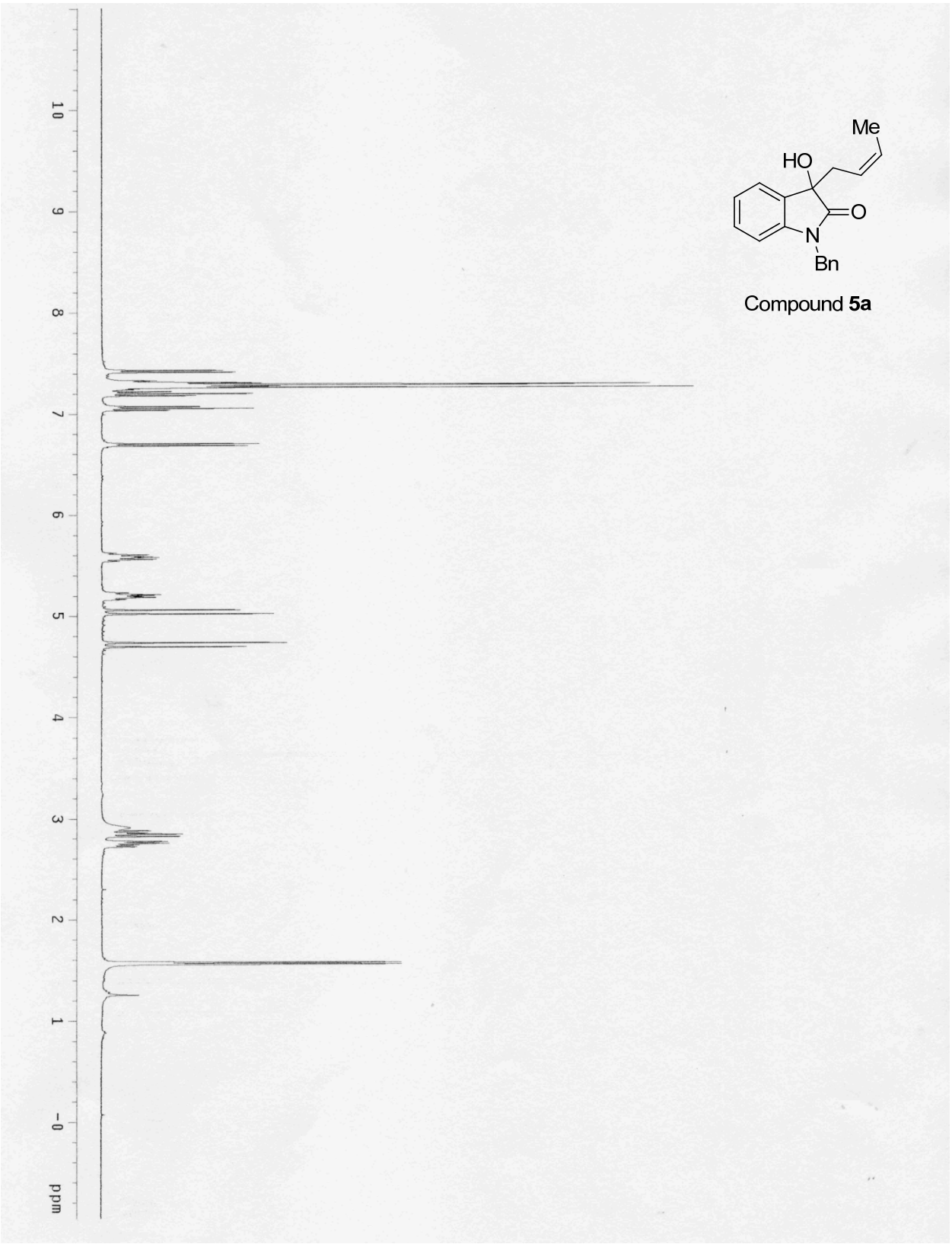
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 142.5, 135.4, 129.7, 129.6, 129.3, 128.7, 127.6, 127.2, 123.9, 123.0, 121.7, 109.4, 76.1, 43.8, 36.1, 13.0

LRMS (CI) Calcd. For $C_{19}H_{20}NO_2$ $[M+H]^+$: 294, Found: 294

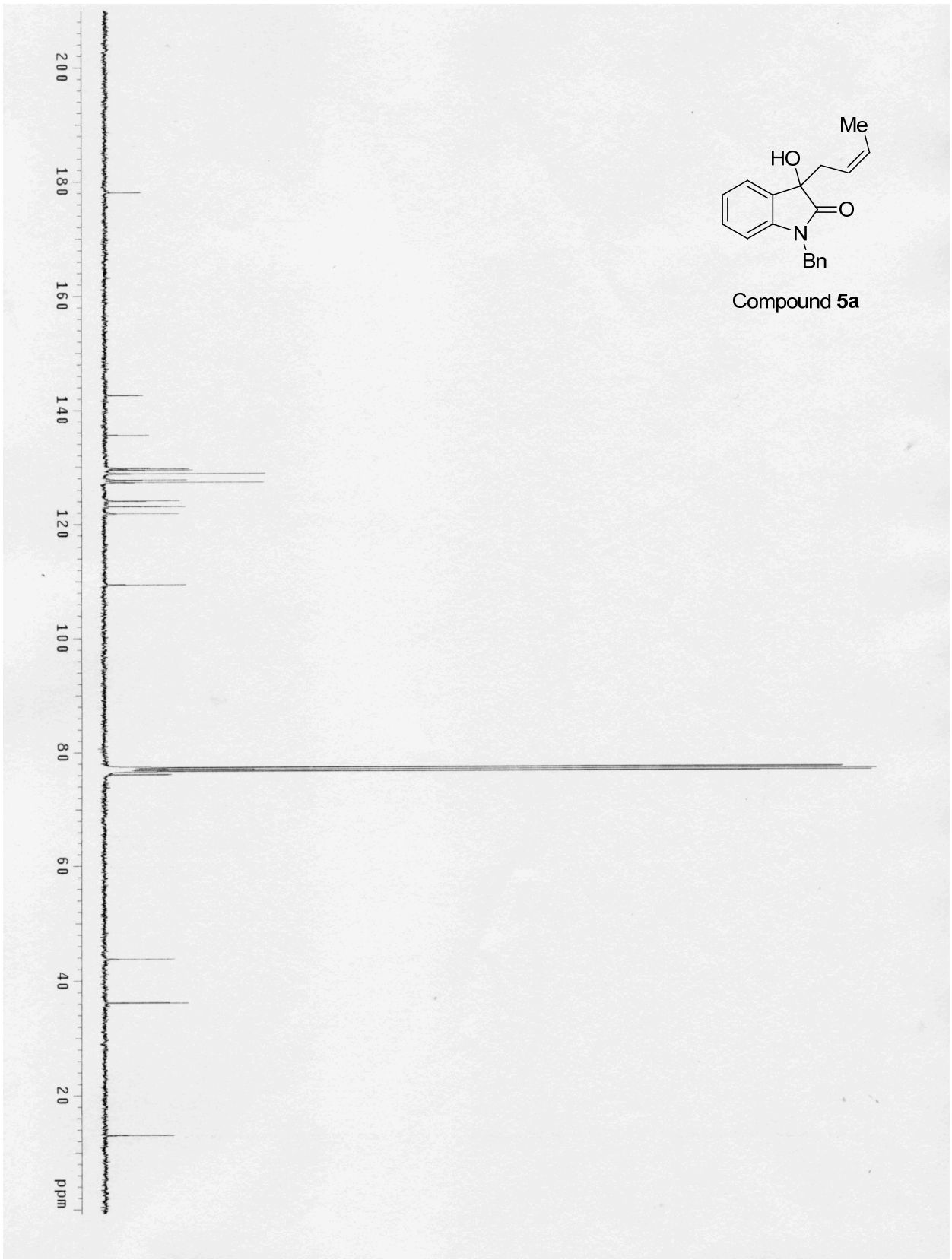
FTIR (neat): 3319, 3029, 2936, 1690, 1610, 1463, 1365, 1178, 751, 698 cm^{-1}

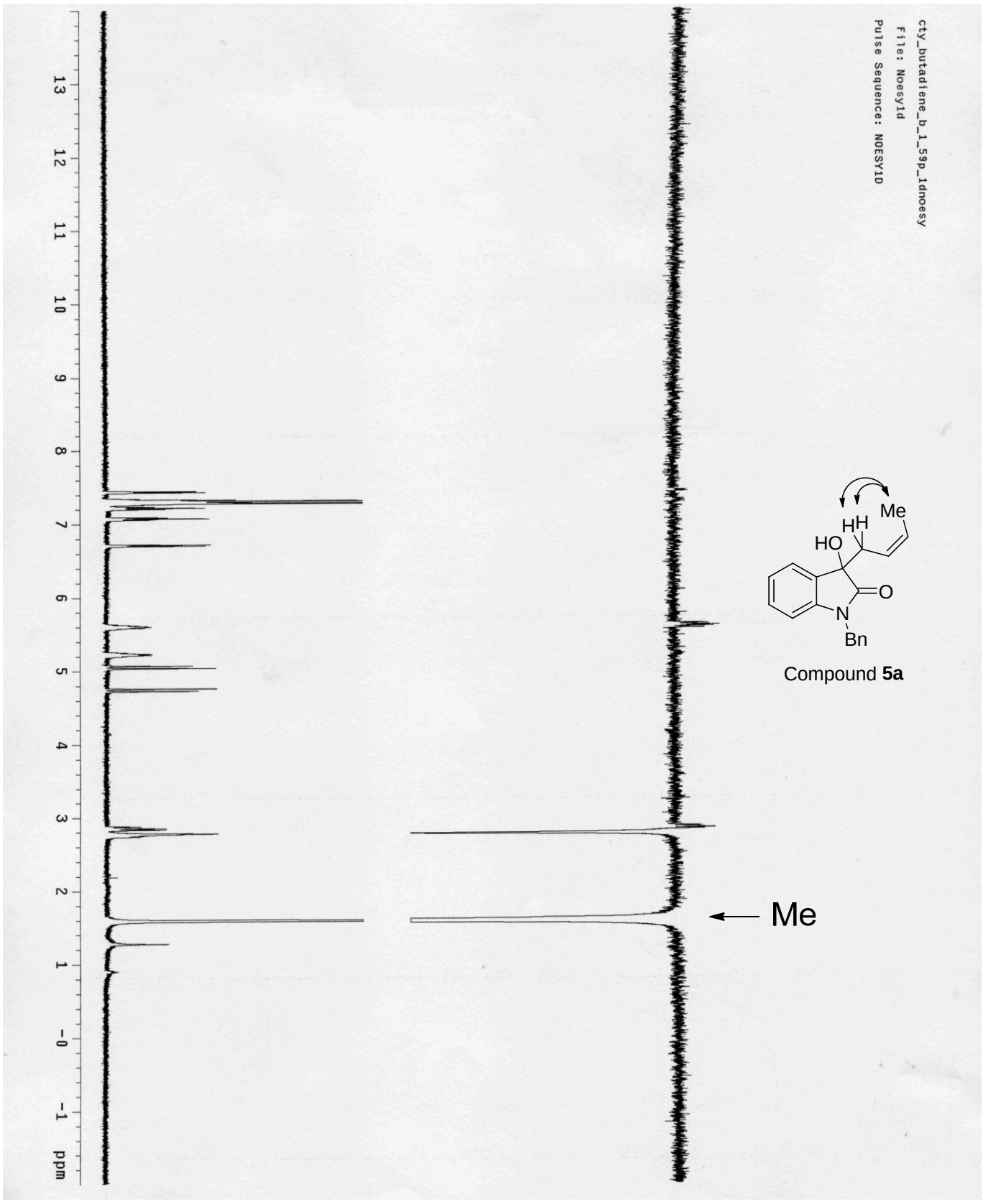
Mp: 146.4-146.8 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

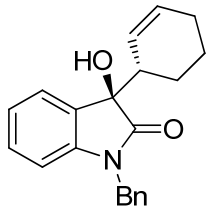


Compound **5a**


Me
HO
O
N
Bn
Compound 5a
200
180
160
140
120
100
80
60
40
20
ppm


cty_butadiene_b_1_59p_1dnoesy
File: Noesy1d
Pulse Sequence: NOESY1D
Me
H
H
HO
O
N
Bn
Compound 5a
Me
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

1-benzyl-3-(cyclohex-2-en-1-yl)-3-hydroxyindolin-2-one (5b)



General Procedure: The reaction was heated for 24 hours and cyclohexadiene (200 mol%) was added, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (48.5 mg, 76%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.29-7.22 (m, 5H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 10.0 Hz, 1H), 5.89 (m, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.69 (d, *J* = 15.6 Hz, 1H), 2.84 (m, 1H), 2.79 (s, 1H), 1.93-1.34 (m, 5H), 0.81 (dd, *J* = 12.8, 3.2, 1H)

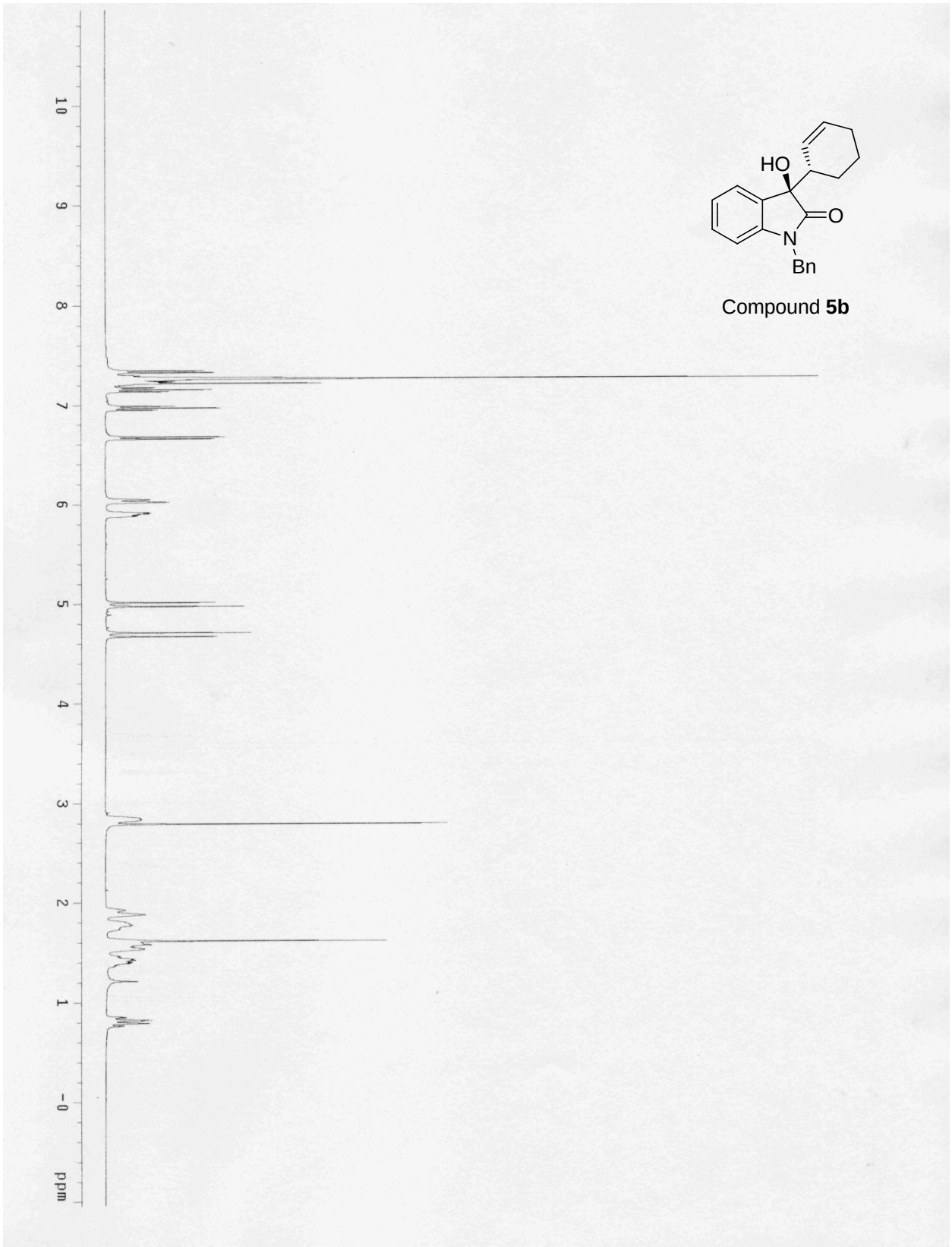
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 143.0, 135.5, 130.9, 129.4, 128.7, 128.3, 127.6, 127.3, 125.1, 124.6, 122.8, 109.1, 78.3, 43.8, 43.7, 24.8, 23.4, 21.2

LRMS (CI) Calcd. For $C_{21}H_{22}NO_2$ $[M+H]^+$: 320, Found: 320

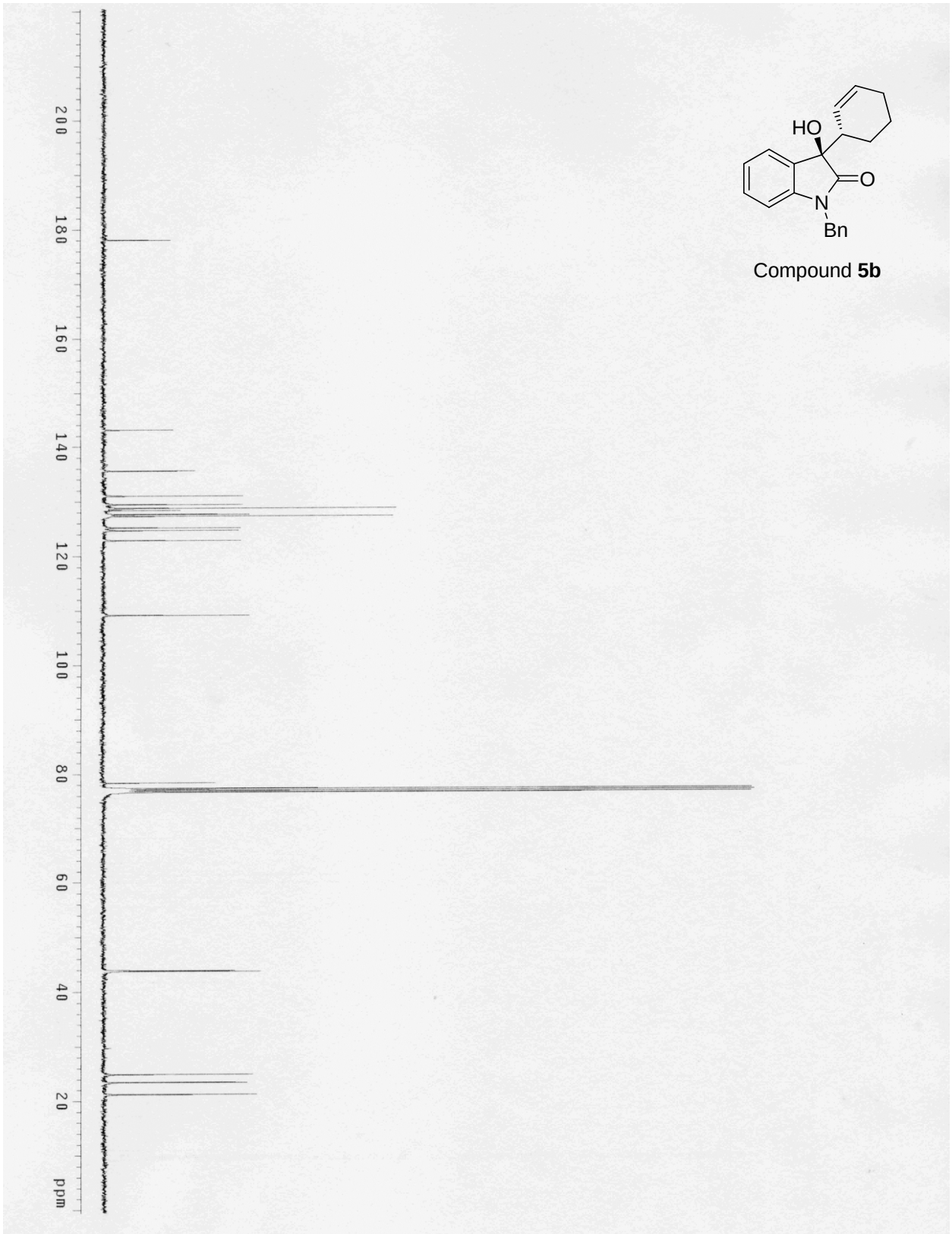
FTIR (neat): 3336, 2936, 2353, 1703, 1610, 1472, 1383, 1169, 1107, 1005, 902, 738, 693 cm^{-1}

Mp: 170.3-171.0 °C

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

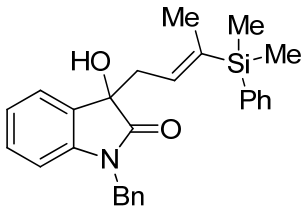


Compound **5b**



Compound **5b**

(E)-1-benzyl-3-(3-(dimethyl(phenyl)silyl)but-2-en-1-yl)-3-hydroxyindolin-2-one (5c)



General Procedure: The reaction was heated for 24 hours under 120°C and silylprene (300 mol%) was added, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (60.2 mg, 71%, >20:1 *E*:*Z*) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.22 (m, 11H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 6.99 (td, *J* = 7.2, 0.8 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.60 (td, *J* = 7.6, 2.0 Hz, 1H), 4.80 (s, 2H), 2.90 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.80 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.74 (s, 1H), 1.57 (t, *J* = 1.2, 3H), 0.21 (s, 3H), 0.17 (s, 3H)

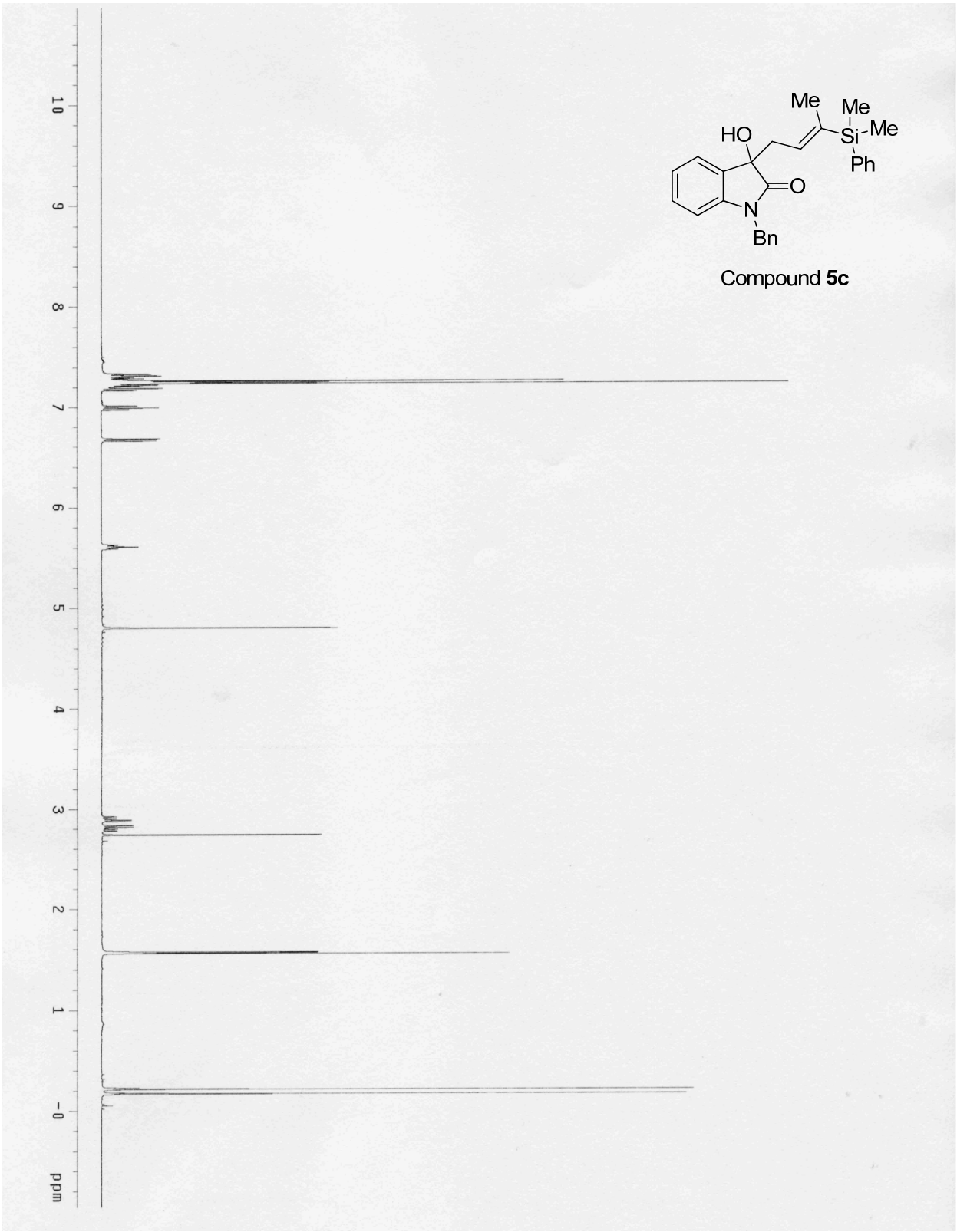
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 142.4, 139.9, 137.9, 135.4, 133.8, 132.1, 129.6, 129.5, 128.8, 127.7, 127.2, 124.1, 122.9, 109.4, 76.2, 43.8, 37.5, 15.1, -3.5, -3.7

LRMS (CI) Calcd. For $C_{27}H_{30}NO_2Si$ $[M+H]^+$: 428, Found: 428

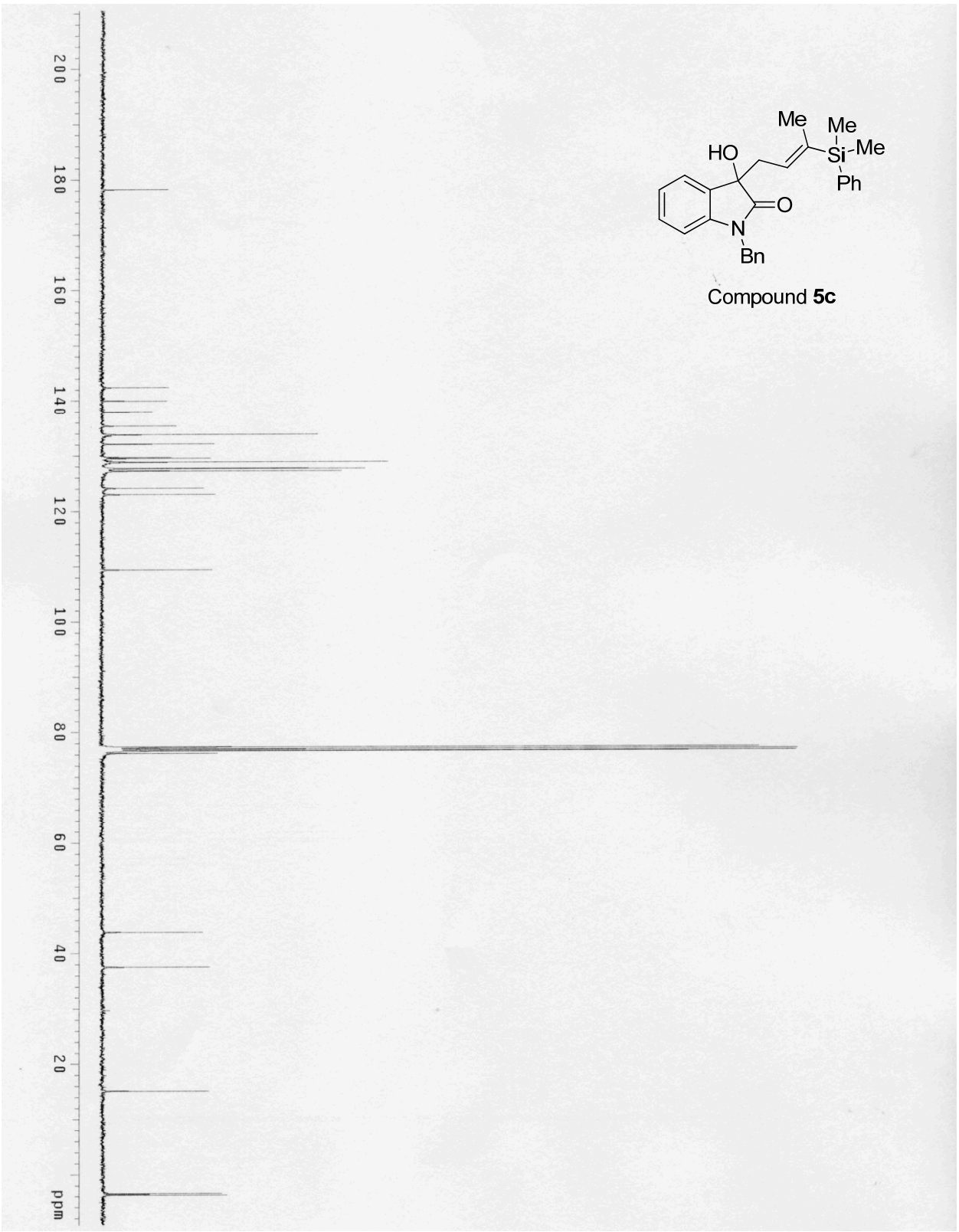
FTIR (neat): 3394, 2936, 2322, 1721, 1610, 1463, 1356, 1249, 1165, 1107, 996, 822, 751, 698 cm^{-1}

Mp: 122.6-123.1 °C

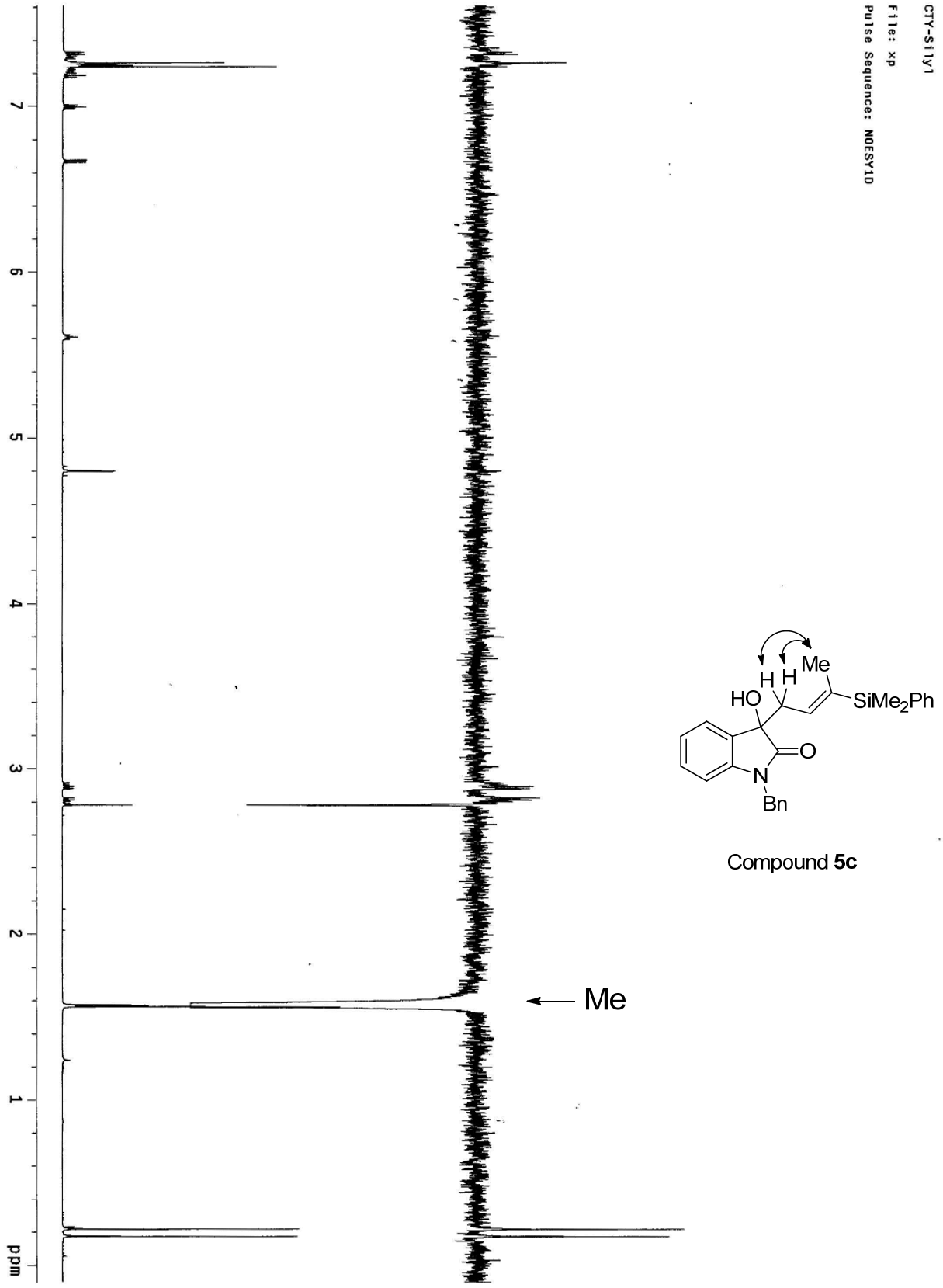
TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)



Compound **5c**

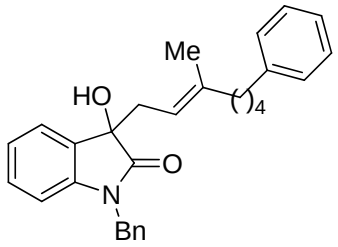


Compound **5c**


CTY-Silyl
File: xp
Pulse Sequence: NOESY1D
7
6
5
4
3
2
1
ppm
Me
H
H
Me
HO
SiMe2Ph
O
N
Bn

Compound **5c**

(E)-1-benzyl-3-hydroxy-3-(3-methyl-7-phenylhept-2-en-1-yl)indolin-2-one (5d)



General Procedure: The reaction was heated for 24 hours, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 15% EtOAc/Hexane) to furnish the title compound (68.5 mg, 81%, >20:1 *E*:*Z*) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.31-7.24 (m, 7H), 7.19-7.11 (m, 4H), 7.02 (td, *J* = 8.0, 0.8 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 4.97-4.89 (m, 2H), 4.67 (d, *J* = 16.0 Hz, 1H), 2.76-2.73 (m, 2H), 2.69 (s, 1H), 2.51 (t, *J* = 7.6 Hz, 1H), 1.95-1.86 (m, 2H), 1.52 (s, 3H), 1.45-1.20 (m, 5H)

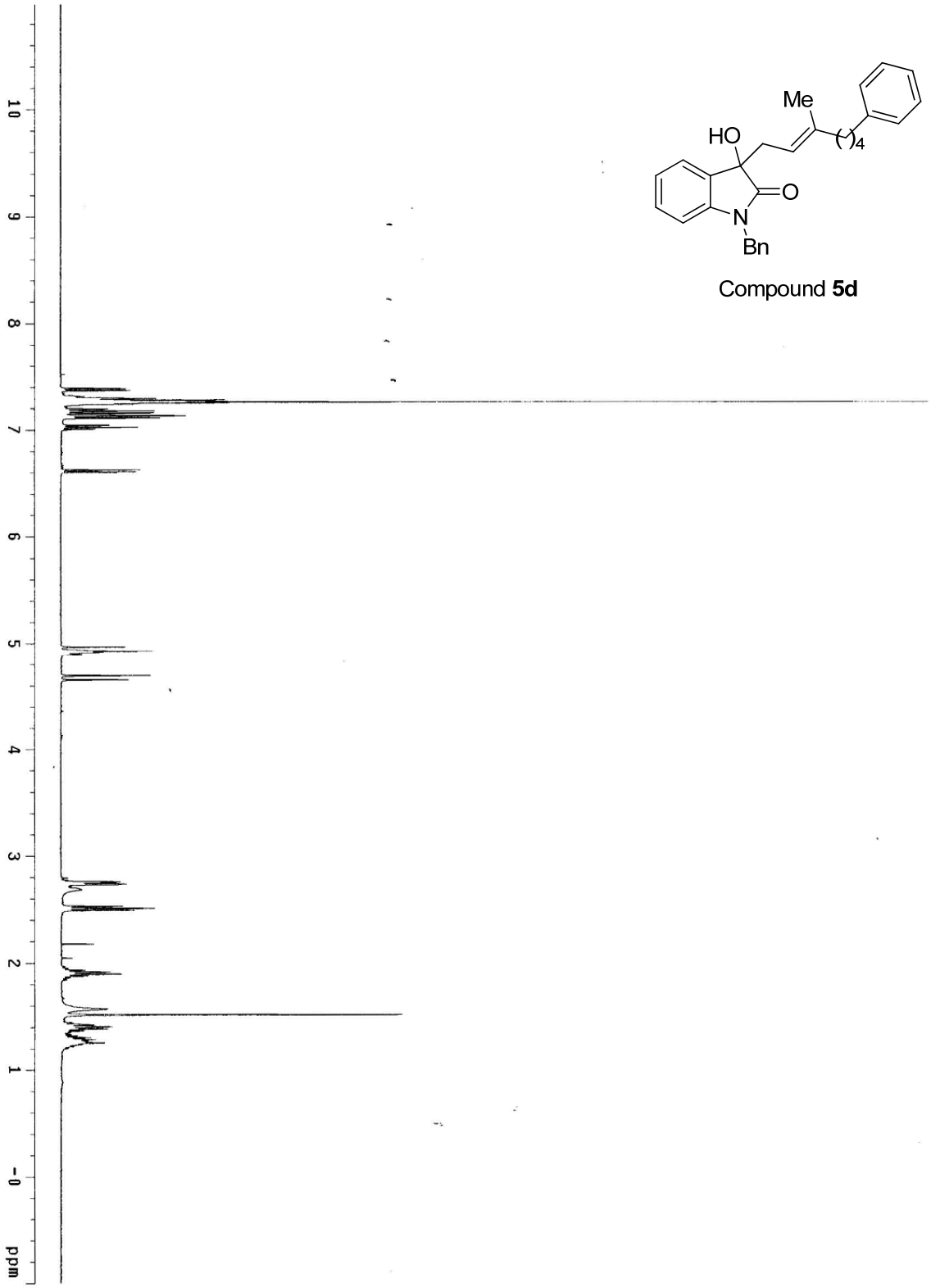
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 142.6, 142.5, 140.8, 135.5, 129.8, 129.5, 128.7, 128.4, 128.2, 127.6, 127.2, 125.6, 123.9, 122.9, 115.7, 109.3, 76.4, 43.7, 39.7, 37.4, 35.8, 30.8, 27.3, 16.1

LRMS (CI) Calcd. For $C_{29}H_{32}NO_2$ $[M+H]^+$: 426, Found: 426

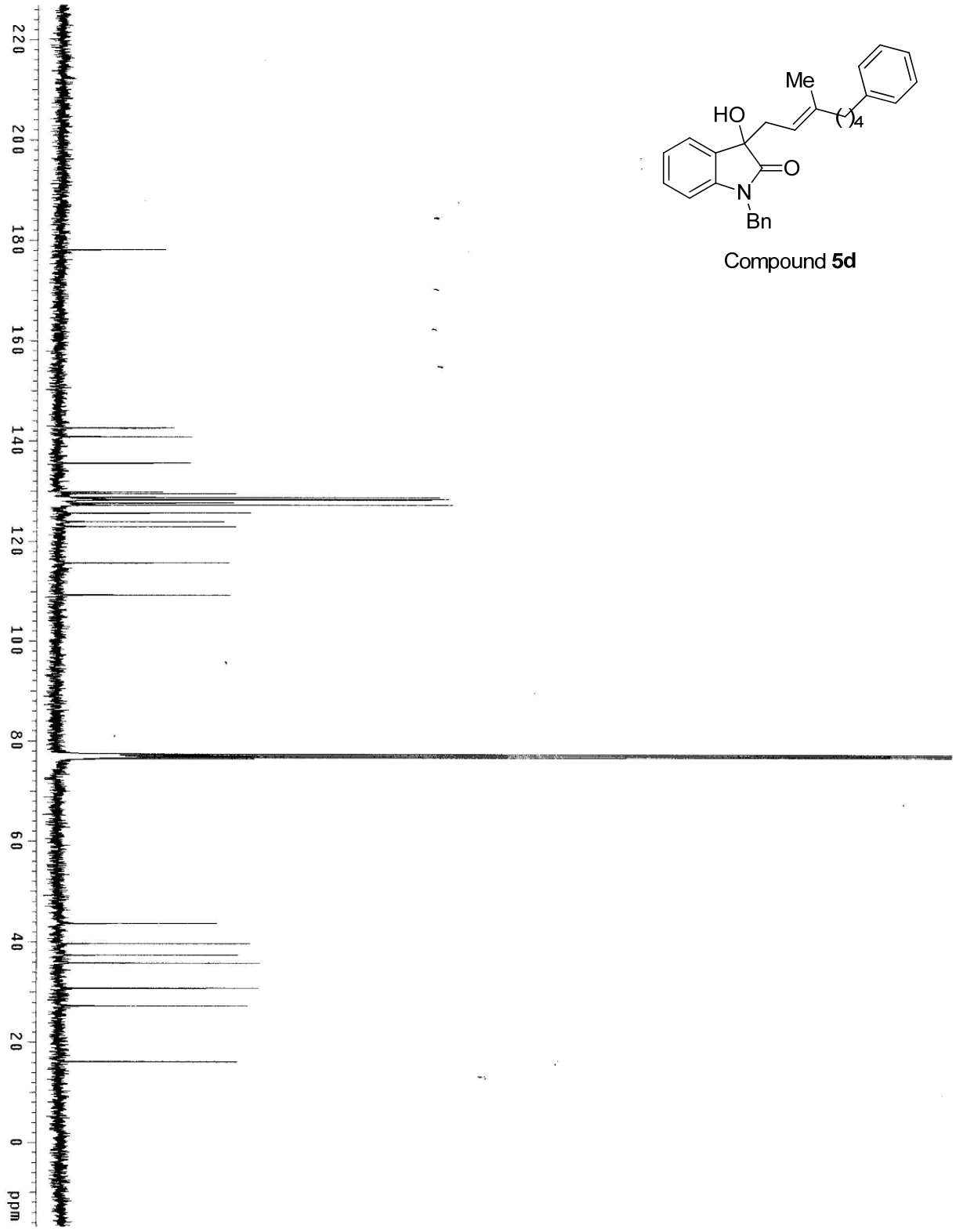
FTIR (neat): 3323, 2923, 2847, 2349, 1690, 1619, 1445, 1370, 1294, 1178, 1085, 996, 742, 693 cm^{-1}

Mp: 127.8-128.3 °C

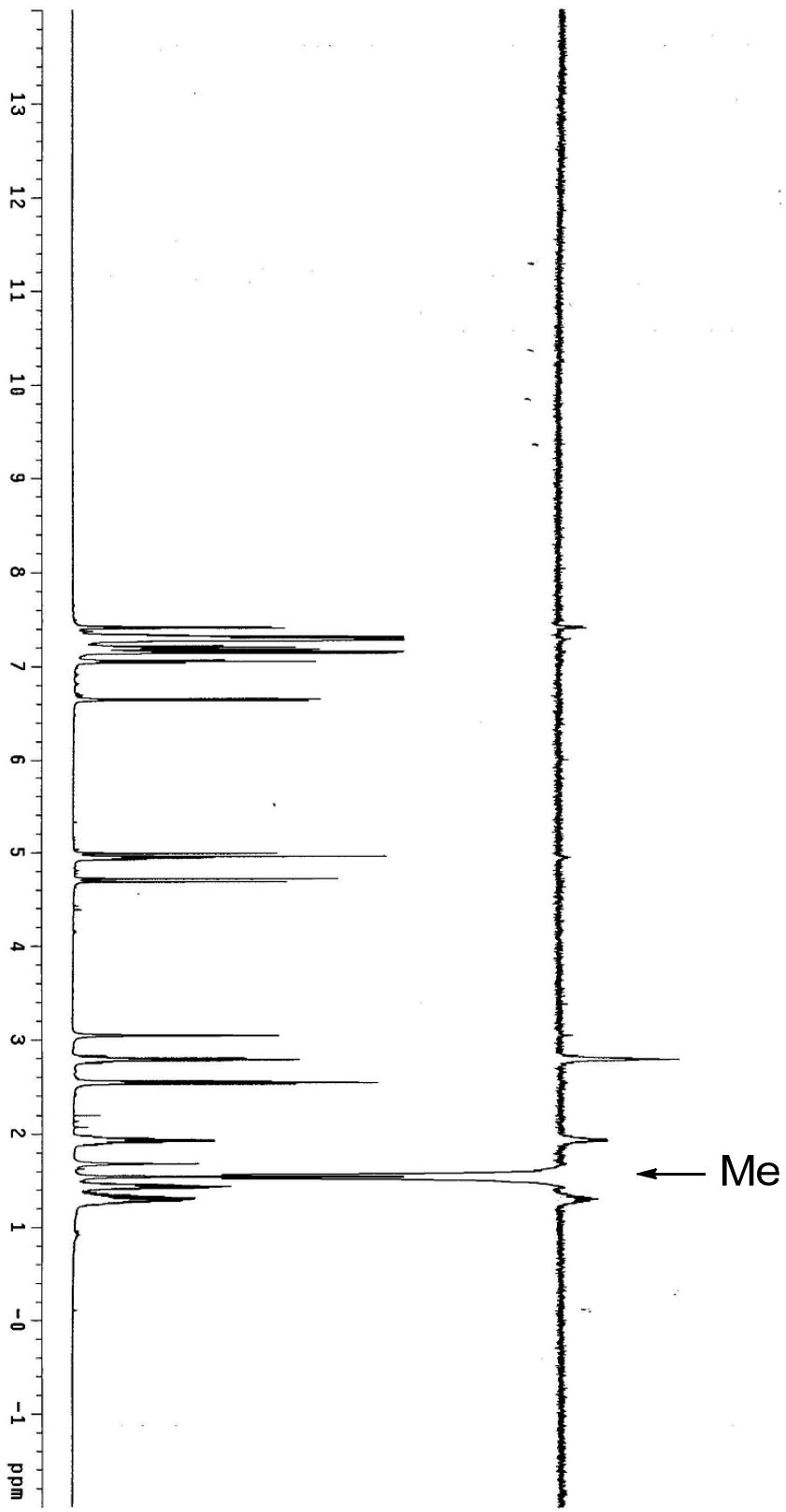
TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:4)

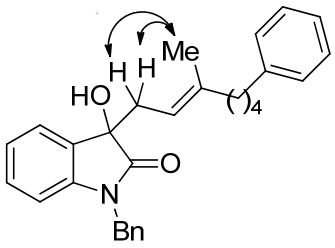


Compound **5d**



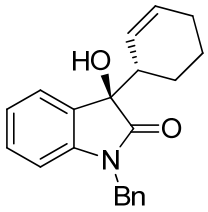
Compound **5d**


cty_BuPh_1_54p_noesy1d
File: Noesy1d
Pulse Sequence: NOESY1D
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
Me


Me
H H
HO
4
O
N
Bn

Compound **5d**

Crystal structure of product 1-benzyl-3-(cyclohex-2-en-1-yl)-3-hydroxyindolin-2-one (5b)



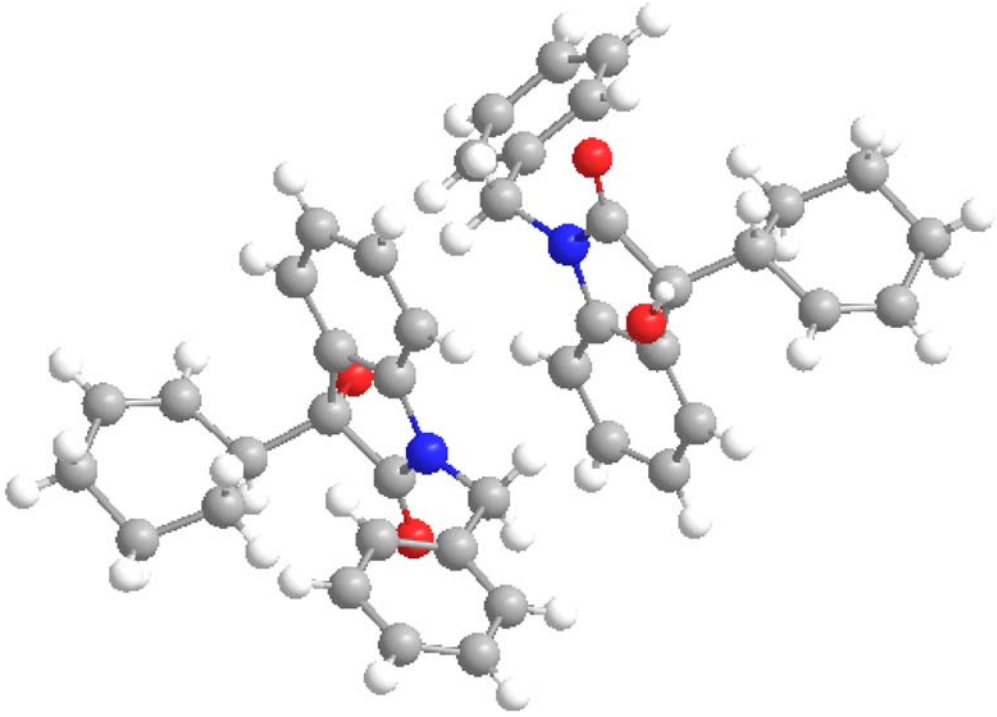


Table 1. Crystal data and structure refinement for 1.

Empirical formula	C21 H21 N O2	
Formula weight	319.39	
Temperature	153(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 9.4044(15) Å	α= 90°.
	b = 19.072(2) Å	β= 101.853(3)°.
	c = 18.984(2) Å	γ = 90°.
Volume	3332.4(7) $Å^3$	
Z	8	

Density (calculated)	1.273 Mg/m^3
Absorption coefficient	0.081 mm^{-1}
F(000)	1360
Crystal size	0.48 x 0.05 x 0.02 mm
Theta range for data collection	3.06 to 25.00°.
Index ranges	-11<=h<=11, -22<=k<=22, -22<=l<=22
Reflections collected	50065
Independent reflections	5869 [R(int) = 0.1784]
Completeness to theta = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.513
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5869 / 0 / 441
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0844, wR2 = 0.1457
R indices (all data)	R1 = 0.1653, wR2 = 0.1740
Largest diff. peak and hole	0.222 and -0.308 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	4752(4)	5949(2)	2138(2)	30(1)
C2	4754(4)	6042(2)	2945(2)	29(1)
C3	6315(4)	5863(2)	3293(2)	28(1)
C4	7041(4)	5876(2)	4003(2)	35(1)
C5	8527(4)	5709(2)	4162(2)	41(1)
C6	9247(4)	5538(2)	3617(2)	41(1)
C7	8522(4)	5526(2)	2898(2)	39(1)
C8	7049(4)	5686(2)	2748(2)	29(1)
C9	3583(4)	5552(2)	3145(2)	27(1)
C10	3543(4)	5596(2)	3930(2)	32(1)
C11	3321(4)	5042(2)	4325(2)	35(1)
C12	3033(5)	4314(2)	4024(2)	40(1)
C13	2676(4)	4322(2)	3204(2)	40(1)
C14	3738(4)	4787(2)	2920(2)	32(1)
C15	6497(4)	5560(2)	1388(2)	36(1)
C16	6480(4)	4784(2)	1211(2)	30(1)
C17	6394(4)	4267(2)	1715(2)	33(1)
C18	6380(4)	3556(2)	1526(2)	40(1)
C19	6454(4)	3367(2)	838(2)	44(1)
C20	6540(4)	3872(2)	331(2)	44(1)
C21	6561(4)	4577(2)	518(2)	41(1)
C22	10502(4)	7113(2)	2524(2)	32(1)
C23	10438(4)	7015(2)	1707(2)	29(1)
C24	8844(4)	7170(2)	1402(2)	31(1)
C25	8059(4)	7166(2)	705(2)	37(1)
C26	6556(4)	7308(2)	580(2)	40(1)
C27	5897(4)	7441(2)	1154(2)	41(1)
C28	6667(4)	7451(2)	1859(2)	35(1)
C29	8142(4)	7317(2)	1968(2)	32(1)
C30	11515(4)	7505(2)	1461(2)	31(1)
C31	11530(4)	7423(2)	671(2)	36(1)

C32	11831(4)	7940(2)	262(2)	39(1)
C33	12245(5)	8661(2)	542(2)	44(1)
C34	12440(4)	8718(2)	1356(2)	37(1)
C35	11321(4)	8281(2)	1624(2)	32(1)
C36	8810(4)	7379(2)	3341(2)	36(1)
C37	8630(4)	8136(2)	3554(2)	29(1)
C38	9692(4)	8638(2)	3518(2)	45(1)
C39	9540(5)	9318(2)	3747(2)	48(1)
C40	8345(5)	9505(2)	4028(2)	43(1)
C41	7275(4)	9015(2)	4055(2)	43(1)
C42	7424(4)	8333(2)	3818(2)	39(1)
N1	6094(3)	5718(2)	2067(2)	29(1)
N2	9161(3)	7293(2)	2631(2)	30(1)
O1	3721(3)	6055(1)	1637(1)	35(1)
O2	4486(3)	6761(1)	3094(1)	34(1)
O3	11587(3)	7031(1)	3008(1)	37(1)
O4	10709(3)	6293(1)	1574(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for 1.

C1-O1	1.228(4)	C15-H15A	0.99
C1-N1	1.369(4)	C15-H15B	0.99
C1-C2	1.542(5)	C16-C17	1.387(5)
C2-O2	1.433(4)	C16-C21	1.392(5)
C2-C3	1.520(5)	C17-C18	1.403(5)
C2-C9	1.551(5)	C17-H17	0.95
C3-C4	1.380(5)	C18-C19	1.372(5)
C3-C8	1.397(5)	C18-H18	0.95
C4-C5	1.405(5)	C19-C20	1.376(5)
C4-H4	0.95	C19-H19	0.95
C5-C6	1.387(5)	C20-C21	1.391(5)
C5-H5	0.95	C20-H20	0.95
C6-C7	1.395(5)	C21-H21	0.95
C6-H6	0.95	C22-O3	1.235(4)
C7-C8	1.390(5)	C22-N2	1.363(5)
C7-H7	0.95	C22-C23	1.552(5)
C8-N1	1.416(4)	C23-O4	1.432(4)
C9-C10	1.501(5)	C23-C30	1.519(5)
C9-C14	1.536(5)	C23-C24	1.521(5)
C9-H9	1.00	C24-C25	1.377(5)
C10-C11	1.335(5)	C24-C29	1.400(5)
C10-H10	0.95	C25-C26	1.410(5)
C11-C12	1.505(5)	C25-H25	0.95
C11-H11	0.95	C26-C27	1.383(5)
C12-C13	1.523(5)	C26-H26	0.95
C12-H12A	0.99	C27-C28	1.386(5)
C12-H12B	0.99	C27-H27	0.95
C13-C14	1.515(5)	C28-C29	1.384(5)
C13-H13A	0.99	C28-H28	0.95
C13-H13B	0.99	C29-N2	1.418(5)
C14-H14A	0.99	C30-C31	1.511(5)
C14-H14B	0.99	C30-C35	1.531(5)
C15-N1	1.448(4)	C30-H30	1.00
C15-C16	1.518(5)	C31-C32	1.322(5)

C31-H31	0.95	C36-H36B	0.99
C32-C33	1.497(5)	C37-C42	1.383(5)
C32-H32	0.95	C37-C38	1.395(5)
C33-C34	1.522(5)	C38-C39	1.386(5)
C33-H33A	0.99	C38-H38	0.95
C33-H33B	0.99	C39-C40	1.386(5)
C34-C35	1.511(5)	C39-H39	0.95
C34-H34A	0.99	C40-C41	1.381(5)
C34-H34B	0.99	C40-H40	0.95
C35-H35A	0.99	C41-C42	1.393(5)
C35-H35B	0.99	C41-H41	0.95
C36-N2	1.460(4)	C42-H42	0.95
C36-C37	1.518(5)	O2-H2O	1.02(5)
C36-H36A	0.99	O4-H4O	0.89(4)

O1-C1-N1	125.0(4)	C8-C7-C6	117.6(4)
O1-C1-C2	126.2(3)	C8-C7-H7	121.2
N1-C1-C2	108.8(3)	C6-C7-H7	121.2
O2-C2-C3	108.8(3)	C7-C8-C3	121.7(4)
O2-C2-C1	110.0(3)	C7-C8-N1	127.9(3)
C3-C2-C1	102.1(3)	C3-C8-N1	110.4(3)
O2-C2-C9	111.5(3)	C10-C9-C14	110.7(3)
C3-C2-C9	115.5(3)	C10-C9-C2	111.9(3)
C1-C2-C9	108.5(3)	C14-C9-C2	113.1(3)
C4-C3-C8	120.4(4)	C10-C9-H9	106.9
C4-C3-C2	131.3(3)	C14-C9-H9	106.9
C8-C3-C2	108.2(3)	C2-C9-H9	106.9
C3-C4-C5	118.5(4)	C11-C10-C9	123.5(3)
C3-C4-H4	120.7	C11-C10-H10	118.3
C5-C4-H4	120.7	C9-C10-H10	118.3
C6-C5-C4	120.6(4)	C10-C11-C12	123.6(3)
C6-C5-H5	119.7	C10-C11-H11	118.2
C4-C5-H5	119.7	C12-C11-H11	118.2
C5-C6-C7	121.2(4)	C11-C12-C13	111.3(3)
C5-C6-H6	119.4	C11-C12-H12A	109.4
C7-C6-H6	119.4	C13-C12-H12A	109.4

C11-C12-H12B	109.4	C20-C21-C16	121.0(4)
C13-C12-H12B	109.4	C20-C21-H21	119.5
H12A-C12-H12B	108.0	C16-C21-H21	119.5
C14-C13-C12	110.3(3)	O3-C22-N2	124.7(4)
C14-C13-H13A	109.6	O3-C22-C23	125.9(3)
C12-C13-H13A	109.6	N2-C22-C23	109.4(3)
C14-C13-H13B	109.6	O4-C23-C30	112.5(3)
C12-C13-H13B	109.6	O4-C23-C24	108.5(3)
H13A-C13-H13B	108.1	C30-C23-C24	115.5(3)
C13-C14-C9	110.4(3)	O4-C23-C22	108.6(3)
C13-C14-H14A	109.6	C30-C23-C22	110.0(3)
C9-C14-H14A	109.6	C24-C23-C22	100.9(3)
C13-C14-H14B	109.6	C25-C24-C29	119.6(4)
C9-C14-H14B	109.6	C25-C24-C23	131.0(3)
H14A-C14-H14B	108.1	C29-C24-C23	109.3(3)
N1-C15-C16	114.0(3)	C24-C25-C26	118.8(4)
N1-C15-H15A	108.8	C24-C25-H25	120.6
C16-C15-H15A	108.8	C26-C25-H25	120.6
N1-C15-H15B	108.8	C27-C26-C25	119.9(4)
C16-C15-H15B	108.8	C27-C26-H26	120.0
H15A-C15-H15B	107.7	C25-C26-H26	120.0
C17-C16-C21	118.3(3)	C26-C27-C28	122.3(4)
C17-C16-C15	122.7(3)	C26-C27-H27	118.9
C21-C16-C15	119.0(3)	C28-C27-H27	118.9
C16-C17-C18	120.7(4)	C29-C28-C27	116.8(4)
C16-C17-H17	119.7	C29-C28-H28	121.6
C18-C17-H17	119.7	C27-C28-H28	121.6
C19-C18-C17	119.9(4)	C28-C29-C24	122.6(4)
C19-C18-H18	120.1	C28-C29-N2	127.7(3)
C17-C18-H18	120.1	C24-C29-N2	109.6(3)
C18-C19-C20	120.3(4)	C31-C30-C23	112.6(3)
C18-C19-H19	119.9	C31-C30-C35	109.1(3)
C20-C19-H19	119.9	C23-C30-C35	114.7(3)
C19-C20-C21	119.9(4)	C31-C30-H30	106.7
C19-C20-H20	120.0	C23-C30-H30	106.7
C21-C20-H20	120.0	C35-C30-H30	106.7

C32-C31-C30	123.6(4)	C37-C36-H36B	108.7
C32-C31-H31	118.2	H36A-C36-H36B	107.6
C30-C31-H31	118.2	C42-C37-C38	118.7(4)
C31-C32-C33	123.2(4)	C42-C37-C36	120.0(3)
C31-C32-H32	118.4	C38-C37-C36	121.3(3)
C33-C32-H32	118.4	C39-C38-C37	120.4(4)
C32-C33-C34	113.3(3)	C39-C38-H38	119.8
C32-C33-H33A	108.9	C37-C38-H38	119.8
C34-C33-H33A	108.9	C40-C39-C38	120.3(4)
C32-C33-H33B	108.9	C40-C39-H39	119.8
C34-C33-H33B	108.9	C38-C39-H39	119.8
H33A-C33-H33B	107.7	C41-C40-C39	119.7(4)
C35-C34-C33	110.9(3)	C41-C40-H40	120.1
C35-C34-H34A	109.5	C39-C40-H40	120.1
C33-C34-H34A	109.5	C40-C41-C42	119.8(4)
C35-C34-H34B	109.5	C40-C41-H41	120.1
C33-C34-H34B	109.5	C42-C41-H41	120.1
H34A-C34-H34B	108.0	C37-C42-C41	121.0(4)
C34-C35-C30	110.2(3)	C37-C42-H42	119.5
C34-C35-H35A	109.6	C41-C42-H42	119.5
C30-C35-H35A	109.6	C1-N1-C8	110.4(3)
C34-C35-H35B	109.6	C1-N1-C15	124.7(3)
C30-C35-H35B	109.6	C8-N1-C15	124.8(3)
H35A-C35-H35B	108.1	C22-N2-C29	110.7(3)
N2-C36-C37	114.3(3)	C22-N2-C36	123.9(3)
N2-C36-H36A	108.7	C29-N2-C36	125.2(3)
C37-C36-H36A	108.7	C2-O2-H2O	107(3)
N2-C36-H36B	108.7	C23-O4-H4O	108(3)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	30(2)	19(2)	43(3)	3(2)	10(2)	-1(2)
C2	34(2)	21(2)	34(2)	-1(2)	13(2)	1(2)
C3	25(2)	21(2)	38(3)	3(2)	8(2)	-1(2)
C4	36(3)	30(2)	40(3)	1(2)	11(2)	-5(2)
C5	33(3)	42(3)	43(3)	4(2)	-2(2)	-4(2)
C6	28(2)	41(3)	56(3)	3(2)	12(2)	0(2)
C7	34(3)	32(2)	56(3)	1(2)	18(2)	3(2)
C8	31(2)	20(2)	39(3)	4(2)	11(2)	0(2)
C9	26(2)	24(2)	30(2)	3(2)	8(2)	-2(2)
C10	33(2)	23(2)	42(3)	-1(2)	13(2)	0(2)
C11	33(2)	36(2)	36(2)	-2(2)	8(2)	3(2)
C12	51(3)	28(2)	43(3)	4(2)	14(2)	-7(2)
C13	48(3)	23(2)	49(3)	-4(2)	14(2)	-6(2)
C14	37(2)	24(2)	37(2)	-2(2)	10(2)	1(2)
C15	44(3)	28(2)	39(3)	2(2)	19(2)	3(2)
C16	23(2)	33(2)	36(2)	1(2)	10(2)	1(2)
C17	31(2)	33(2)	38(2)	-2(2)	12(2)	5(2)
C18	39(3)	29(2)	52(3)	2(2)	10(2)	5(2)
C19	36(3)	33(3)	59(3)	-7(2)	2(2)	5(2)
C20	38(3)	50(3)	45(3)	-10(2)	9(2)	12(2)
C21	40(3)	41(3)	45(3)	7(2)	13(2)	6(2)
C22	32(3)	17(2)	51(3)	5(2)	12(2)	0(2)
C23	30(2)	21(2)	35(2)	-3(2)	8(2)	-3(2)
C24	24(2)	23(2)	44(3)	-3(2)	6(2)	-4(2)
C25	30(2)	34(2)	45(3)	-3(2)	6(2)	-2(2)
C26	36(3)	34(2)	45(3)	-2(2)	-2(2)	-5(2)
C27	27(2)	28(2)	66(3)	-2(2)	6(2)	-2(2)
C28	33(3)	25(2)	48(3)	-3(2)	10(2)	1(2)
C29	31(2)	22(2)	42(3)	-1(2)	8(2)	-2(2)
C30	26(2)	23(2)	45(3)	3(2)	12(2)	2(2)
C31	30(2)	35(2)	44(3)	-8(2)	14(2)	-2(2)

C32	38(3)	47(3)	33(3)	-1(2)	8(2)	0(2)
C33	45(3)	42(3)	49(3)	11(2)	19(2)	2(2)
C34	38(3)	28(2)	49(3)	3(2)	17(2)	-1(2)
C35	33(2)	26(2)	39(2)	-1(2)	10(2)	-1(2)
C36	39(3)	30(2)	43(3)	5(2)	14(2)	4(2)
C37	26(2)	30(2)	34(2)	2(2)	10(2)	3(2)
C38	33(3)	46(3)	60(3)	-6(2)	19(2)	-4(2)
C39	41(3)	44(3)	60(3)	-12(2)	14(2)	-15(2)
C40	44(3)	31(2)	56(3)	-8(2)	12(2)	4(2)
C41	32(3)	44(3)	54(3)	-7(2)	13(2)	3(2)
C42	30(2)	39(2)	49(3)	-1(2)	13(2)	-3(2)
N1	33(2)	30(2)	28(2)	0(2)	13(2)	1(2)
N2	28(2)	27(2)	37(2)	3(2)	13(2)	2(2)
O1	33(2)	33(2)	39(2)	3(1)	6(1)	4(1)
O2	35(2)	19(1)	51(2)	-5(1)	14(1)	0(1)
O3	31(2)	32(2)	45(2)	3(1)	5(1)	7(1)
O4	33(2)	23(2)	56(2)	-6(1)	13(2)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1.

	x	y	z	U(eq)
H4	6547	5995	4375	42
H5	9044	5712	4648	49
H6	10253	5428	3735	49
H7	9017	5413	2524	47
H9	2620	5722	2873	32
H10	3683	6041	4159	38
H11	3346	5111	4822	42
H12A	2211	4105	4203	48
H12B	3901	4017	4193	48
H13A	2726	3839	3020	48
H13B	1674	4498	3032	48
H14A	3550	4755	2388	39
H14B	4742	4623	3111	39
H15A	7485	5746	1400	43
H15B	5820	5807	998	43
H17	6345	4397	2193	40
H18	6319	3206	1875	48
H19	6445	2885	710	52
H20	6585	3739	-147	53
H21	6632	4923	166	50
H25	8520	7069	315	44
H26	5998	7312	102	48
H27	4881	7528	1061	49
H28	6204	7545	2249	42
H30	12502	7367	1732	37
H31	11312	6975	457	43
H32	11782	7850	-235	47
H33A	11485	8996	313	53
H33B	13164	8798	402	53
H34A	13426	8557	1586	45

H34B	12343	9215	1491	45
H35A	10334	8436	1388	38
H35B	11429	8347	2150	38
H36A	9591	7161	3704	44
H36B	7898	7123	3349	44
H38	10525	8512	3335	54
H39	10259	9659	3711	57
H40	8262	9967	4201	52
H41	6440	9143	4234	52
H42	6686	7998	3839	46
H4O	11670(50)	6230(20)	1650(20)	56(14)
H2O	3390(60)	6820(30)	3050(30)	107(19)

Table 6. Torsion angles [°] for 1.

O1-C1-C2-O2	-62.6(5)	C12-C13-C14-C9	-64.2(4)
N1-C1-C2-O2	118.2(3)	C10-C9-C14-C13	47.1(4)
O1-C1-C2-C3	-178.0(3)	C2-C9-C14-C13	173.5(3)
N1-C1-C2-C3	2.8(4)	N1-C15-C16-C17	-13.1(5)
O1-C1-C2-C9	59.7(4)	N1-C15-C16-C21	167.3(3)
N1-C1-C2-C9	-119.6(3)	C21-C16-C17-C18	-0.5(6)
O2-C2-C3-C4	60.5(5)	C15-C16-C17-C18	179.9(3)
C1-C2-C3-C4	176.8(4)	C16-C17-C18-C19	0.1(6)
C9-C2-C3-C4	-65.7(5)	C17-C18-C19-C20	-0.1(6)
O2-C2-C3-C8	-117.1(3)	C18-C19-C20-C21	0.4(6)
C1-C2-C3-C8	-0.9(4)	C19-C20-C21-C16	-0.7(6)
C9-C2-C3-C8	116.6(3)	C17-C16-C21-C20	0.8(6)
C8-C3-C4-C5	0.2(5)	C15-C16-C21-C20	-179.6(4)
C2-C3-C4-C5	-177.2(3)	O3-C22-C23-O4	64.8(5)
C3-C4-C5-C6	0.3(6)	N2-C22-C23-O4	-114.3(3)
C4-C5-C6-C7	-0.1(6)	O3-C22-C23-C30	-58.7(5)
C5-C6-C7-C8	-0.5(6)	N2-C22-C23-C30	122.2(3)
C6-C7-C8-C3	0.9(5)	O3-C22-C23-C24	178.8(3)
C6-C7-C8-N1	179.1(3)	N2-C22-C23-C24	-0.3(4)
C4-C3-C8-C7	-0.8(5)	O4-C23-C24-C25	-64.9(5)
C2-C3-C8-C7	177.1(3)	C30-C23-C24-C25	62.5(5)
C4-C3-C8-N1	-179.2(3)	C22-C23-C24-C25	-178.9(4)
C2-C3-C8-N1	-1.3(4)	O4-C23-C24-C29	113.1(3)
O2-C2-C9-C10	-60.3(4)	C30-C23-C24-C29	-119.5(3)
C3-C2-C9-C10	64.5(4)	C22-C23-C24-C29	-0.9(4)
C1-C2-C9-C10	178.4(3)	C29-C24-C25-C26	-0.2(5)
O2-C2-C9-C14	173.9(3)	C23-C24-C25-C26	177.6(4)
C3-C2-C9-C14	-61.3(4)	C24-C25-C26-C27	-0.7(5)
C1-C2-C9-C14	52.6(4)	C25-C26-C27-C28	1.0(6)
C14-C9-C10-C11	-14.8(5)	C26-C27-C28-C29	-0.4(5)
C2-C9-C10-C11	-141.9(4)	C27-C28-C29-C24	-0.6(5)
C9-C10-C11-C12	-2.2(6)	C27-C28-C29-N2	-179.7(3)
C10-C11-C12-C13	-13.5(5)	C25-C24-C29-C28	0.9(5)
C11-C12-C13-C14	45.7(4)	C23-C24-C29-C28	-177.4(3)

C25-C24-C29-N2	-179.9(3)	C38-C37-C42-C41	-1.0(6)
C23-C24-C29-N2	1.9(4)	C36-C37-C42-C41	176.4(4)
O4-C23-C30-C31	57.4(4)	C40-C41-C42-C37	-0.1(6)
C24-C23-C30-C31	-67.9(4)	O1-C1-N1-C8	177.0(3)
C22-C23-C30-C31	178.6(3)	C2-C1-N1-C8	-3.8(4)
O4-C23-C30-C35	-177.1(3)	O1-C1-N1-C15	-0.3(6)
C24-C23-C30-C35	57.5(4)	C2-C1-N1-C15	179.0(3)
C22-C23-C30-C35	-55.9(4)	C7-C8-N1-C1	-175.1(4)
C23-C30-C31-C32	149.6(4)	C3-C8-N1-C1	3.3(4)
C35-C30-C31-C32	21.1(5)	C7-C8-N1-C15	2.2(6)
C30-C31-C32-C33	2.3(6)	C3-C8-N1-C15	-179.5(3)
C31-C32-C33-C34	6.0(6)	C16-C15-N1-C1	-100.4(4)
C32-C33-C34-C35	-38.0(5)	C16-C15-N1-C8	82.7(4)
C33-C34-C35-C30	62.6(4)	O3-C22-N2-C29	-177.6(3)
C31-C30-C35-C34	-52.5(4)	C23-C22-N2-C29	1.5(4)
C23-C30-C35-C34	-179.8(3)	O3-C22-N2-C36	-3.4(5)
N2-C36-C37-C42	130.9(4)	C23-C22-N2-C36	175.7(3)
N2-C36-C37-C38	-51.8(5)	C28-C29-N2-C22	177.1(4)
C42-C37-C38-C39	0.4(6)	C24-C29-N2-C22	-2.1(4)
C36-C37-C38-C39	-177.0(4)	C28-C29-N2-C36	3.0(6)
C37-C38-C39-C40	1.3(6)	C24-C29-N2-C36	-176.2(3)
C38-C39-C40-C41	-2.4(6)	C37-C36-N2-C22	106.0(4)
C39-C40-C41-C42	1.8(6)	C37-C36-N2-C29	-80.6(4)

Table 7. Hydrogen bonds for 1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O4-H4O...O1#1	0.89(4)	1.96(4)	2.847(4)	170(4)
O2-H2O...O3#2	1.02(5)	1.73(5)	2.746(4)	172(5)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x-1,y,z