Direct Synthesis of 1-Indanones via Pd-Catalyzed Olefination and Ethylene Glycol-Promoted Aldol-type Annulation Cascade

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Supporting Information

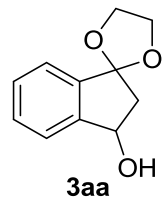
Table of contents

Experimental

Materials: All the reactions were carried out under a nitrogen atmosphere. Silica gel plates (GF_{254}) were used for TLC monitoring and silica gel (230-400 mesh) was used for flash column chromatography. The following chemicals were purchased from Aldrich, Acros, Alfa Aesar, or TCI, and used as received: all the aryl chlorides, aryl bromides, *n*-butyl vinyl ether, 1-ethoxyprop-1-ene, $Pd(OAc)_2$, Et_3N, ethylene glycol, and 1,3-bis(diphenylphosphino)propane (dppp). $H_2N^iPr_2{\cdot}BF_4$ was synthesized by mixing HN^iPr_2 and aqueous HBF_4 (1.2:1) and then removing the excess amine and water.[1] The ligand 1,3-bis(bis(4-methoxyphenyl)phosphino)propane (4-MeO-dppp) was synthesized by following a similar literature procedure.[2] The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer with TMS as the internal standard. The mass spectra were obtained by chemical ionization (CI).

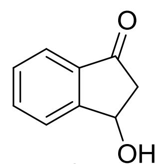
General procedure for the Heck olefination-aldol annulation cascade: An oven-dried carousel reaction tube containing a stirrer bar was charged with aryl bromide **1** (1.0 mmol), $Pd(OAc)_2$ (0.01 mmol), and dppp (0.015 mmol). After degassing three times with nitrogen, ethylene glycol (4 mL), *n*-butyl vinyl ether **2a** (3.0 mmol), and Et_3N (1.5 mmol) were injected sequentially. The reaction mixture was vigorously stirred at 115 °C for 16 h. After cooling down to room temperature, 2 mL aqueous HCl (3 M) and 10 mL EtOAc were added; the mixture was stirred for 1 h. After separation of the EtOAc phase, the aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using a mixture of ethyl acetate and hexane (20/80 to 50/50) as eluant.

^{1}H NMR, ^{13}C NMR, MS, and elemental analysis data of the products 3, 4, and 6



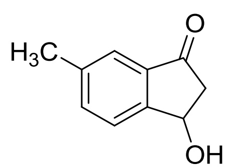
3aa

3-Hydroxy-1-indanone ethylene ketal (3aa).[3] ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42-7.39 (m, 2H), 7.38-7.34 (m, 2H), 5.14-5.10 (m, 1H), 4.18-4.10 (m, 2H), 4.08-4.00 (m, 2H), 2.63 (dd, *J* = 6.8, 13.6 Hz, 1H), 2.46 (d, *J* = 7.6 Hz, 1H), 2.09 (dd, *J* = 4.8, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 147.7, 144.0, 132.4, 131.1, 126.7, 125.3, 116.7, 73.9, 67.8, 67.5, 50.1; MS (CI, *m/z*, %) 210 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.65; H, 6.35.



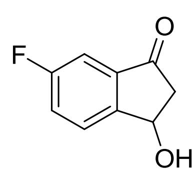
3a

3-Hydroxy-1-indanone (3a).[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.68 (m, 3H), 7.52-7.48 (m, 1H), 5.44 (dd, *J* = 2.8, 6.8 Hz, 1H), 3.11 (dd, *J* = 6.8, 18.8 Hz, 1H), 2.62 (dd, *J* = 2.8, 18.8 Hz, 1H), 2.40 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 155.5, 136.8, 135.8, 129.9, 126.3, 123.7, 68.9, 47.6; MS (CI, *m/z*, %) 166 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.76; H, 5.37.



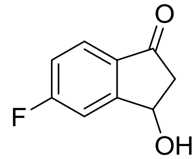
3b

3-Hydroxy-6-methyl-1-indanone (3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 5.38 (dd, *J* = 2.8, 6.4 Hz, 1H), 3.09 (dd, *J* = 6.4, 19.2 Hz, 1H), 2.60 (br, 1H), 2.58 (dd, *J* = 2.8, 19.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 153.1, 140.1, 136.9 (2C), 126.0, 123.5, 68.7, 47.9, 21.7; MS (CI, *m/z*, %) 180 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.00; H, 6.23.



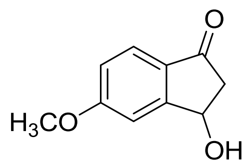
3c

6-Fluoro-3-hydroxy-1-indanone (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.68 (m, 1H), 7.42-7.33 (m, 2H), 5.44-5.40 (m, 1H), 3.16 (dd, *J* = 6.8, 19.2 Hz, 1H), 2.77 (br, 1H), 2.65 (dd, *J* = 2.8, 19.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7 (d, *J* = 2.7 Hz), 164.0 (d, *J* = 249.3 Hz), 151.1 (d, *J* = 2.3 Hz), 138.7 (d, *J* = 7.6 Hz), 128.2 (d, *J* = 8.4 Hz), 123.5 (d, *J* = 23.6 Hz), 109.5 (d, *J* = 21.7 Hz), 68.4, 48.2; MS (CI, *m/z*, %) 184 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_9H_7FO_2$: C, 65.06; H, 4.25. Found: C, 65.24; H, 4.18.



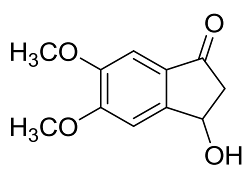
3d

5-Fluoro-3-hydroxy-1-indanone (3d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 5.2, 8.4 Hz, 1H), 7.37 (dd, J = 2.4, 8.4 Hz, 1H), 7.17 (ddd, J = 2.4, 8.4, 8.4 Hz, 1H), 5.40 (dd, J = 3.2, 6.8 Hz, 1H), 3.13 (dd, J = 6.8, 18.8 Hz, 1H), 2.92 (br, 1H), 2.64 (dd, J = 3.2, 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 167.6 (d, J = 256.1 Hz), 158.6 (d, J = 9.2 Hz), 133.1 (d, J = 1.9 Hz), 126.1 (d, J = 9.9 Hz), 118.2 (d, J = 24.0 Hz), 113.1 (d, J = 22.5 Hz), 68.4 (d, J = 1.9 Hz), 47.7; MS (CI, *m/z*, %) 184 $[M+NH_3+H]^+$; Anal. calcd for $C_9H_7FO_2$: C, 65.06; H, 4.25. Found: C, 65.04; H, 4.21.



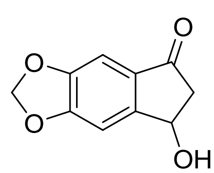
3e

3-Hydroxy-5-methoxy-1-indanone (3e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 2.0 Hz, 1H), 6.98 (dd, J = 2.0, 8.4 Hz, 1H), 5.34 (dd, J = 2.8, 6.8 Hz, 1H), 3.90 (s, 3H), 3.07 (dd, J = 6.8, 18.8 Hz, 1H), 2.88 (br, 1H), 2.58 (dd, J = 2.8, 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 166.2, 158.8, 129.9, 125.4, 117.9, 109.2, 68.8, 56.2, 47.8; MS (CI, *m/z*, %) 179 (100) $[M+H]^+$, 196 (90) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.54; H, 5.60.



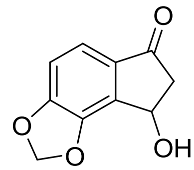
3f

3-Hydroxy-5,6-dimethoxy-1-indanone (3f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 5.34 (dd, J = 2.4, 6.4 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 3.08 (dd, J = 6.4, 18.8 Hz, 1H), 2.71 (br, 1H), 2.57 (dd, J = 2.4, 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 156.3, 151.3, 150.8, 129.8, 107.0, 103.9, 68.7, 56.8, 56.6, 47.8; MS (CI, *m/z*, %) 209 (100) $[M+H]^+$; Anal. calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.37; H, 5.69.



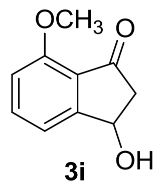
3g

3-Hydroxy-5,6-methylenedioxy-1-indanone (3g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.12 (s, 1H), 6.99 (s, 1H), 6.18 (s, 2H), 5.69-5.66 (m, 1H), 5.10 (br, 1H), 2.96 (dd, J = 6.4, 18.4 Hz, 1H), 2.36 (dd, J = 2.4, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 201.4, 154.8, 154.2, 149.4, 130.9, 105.6, 102.9, 100.9, 66.9, 47.4; MS (CI, *m/z*, %) 193 (96) $[M+H]^+$, 210 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.76; H, 4.22.



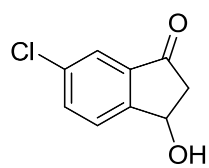
3h

3-Hydroxy-4,5-methylenedioxy-1-indanone (3h). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.24 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.23 (s, 1H), 6.20 (s, 1H), 5.70-5.73 (m, 1H), 5.30 (br, 1H), 3.00 (dd, J = 6.8, 18.4 Hz, 1H), 2.39 (dd, J = 2.4, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 201.9, 153.2, 144.4, 136.0, 132.2, 117.9, 110.2, 102.9, 64.6, 47.7; MS (CI, *m/z*, %) 193 (61) $[M+H]^+$, 210 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.25; H, 4.16.



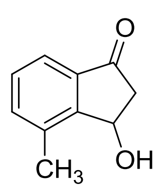
3i

3-Hydroxy-7-methoxy-1-indanone (3i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.6, 8.4 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 5.31 (dd, J = 3.2, 6.8 Hz, 1H), 3.92 (s, 3H), 3.03 (dd, J = 6.8, 18.8 Hz, 1H), 2.99 (br, 1H), 2.59 (dd, J = 3.2, 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 158.3, 157.8, 137.6, 124.6, 117.9, 111.2, 68.2, 56.2, 47.9; MS (CI, *m/z*, %) 196 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.49; H, 5.76.



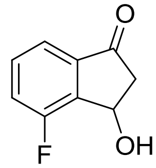
3j

6-Chloro-3-hydroxy-1-indanone (3j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.64 (m, 3H), 5.42 (dd, J = 2.8, 6.8 Hz, 1H), 3.15 (dd, J = 6.8, 18.8 Hz, 1H), 2.65 (dd, J = 2.8, 18.8 Hz, 1H), 2.38 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 153.5, 138.3, 136.5, 135.8, 127.7, 123.5, 68.5, 47.9; MS (CI, *m/z*, %) 183:185=3:1 (100) $[M+H]^+$; Anal. calcd for $C_9H_7ClO_2$: C, 59.20; H, 3.86. Found: C, 59.01; H, 3.99.



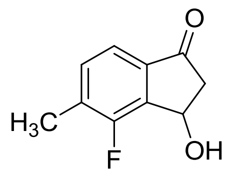
3k

3-Hydroxy-4-methyl-1-indanone (3k). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.36 (dd, J = 7.2, 7.6 Hz, 1H), 5.42 (dd, J = 2.0, 6.8 Hz, 1H), 3.02 (dd, J = 6.8, 19.2 Hz, 1H), 2.91 (br, 1H), 2.55 (dd, J = 2.0, 19.2 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 153.3, 137.6, 137.0, 136.8, 130.2, 121.1, 68.3, 47.5, 18.1; MS (CI, *m/z*, %) 180 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.82; H, 6.17.



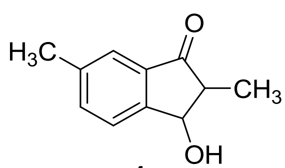
3l

4-Fluoro-3-hydroxy-1-indanone (3l). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.52-7.46 (m, 1H), 7.37-7.31 (m, 1H), 5.68 (dd, *J* = 2.4, 6.8 Hz, 1H), 3.12 (dd, *J* = 6.8, 19.2 Hz, 1H), 2.82 (br, 1H), 2.69 (dd, *J* = 2.4, 19.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7 (d, *J* = 1.9 Hz), 160.8 (d, *J* = 251.1 Hz), 141.1 (d, *J* = 17.1 Hz), 139.7 (d, *J* = 3.8 Hz), 132.2 (d, *J* = 6.5 Hz), 122.1 (d, *J* = 19.8 Hz), 119.7 (d, *J* = 3.8 Hz), 66.2, 46.6; MS (CI, *m/z*, %) 184 $[M+NH_3+H]^+$; Anal. calcd for $C_9H_7FO_2$: C, 65.06; H, 4.25. Found: C, 65.15; H, 4.16.



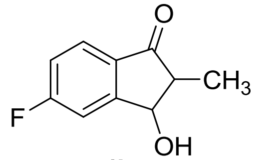
3m

4-Fluoro-3-hydroxy-5-methyl-1-indanone (3m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.36-7.31 (m, 1H), 5.68-5.62 (m, 1H), 3.10 (dd, *J* = 6.8, 19.2 Hz, 1H), 2.70 (br, 1H), 2.67 (dd, *J* = 2.4, 19.2 Hz, 1H), 2.39 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4 (d, *J* = 1.9 Hz), 158.9 (d, *J* = 248.9 Hz), 140.9 (d, *J* = 17.5 Hz), 137.5 (d, *J* = 3.5 Hz), 134.0 (d, *J* = 3.8 Hz), 133.1 (d, *J* = 16.0 Hz), 119.2 (d, *J* = 4.2 Hz), 66.2, 46.8, 15.2 (d, *J* = 3.9 Hz); MS (CI, *m/z*, %) 198 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_9FO_2$: C, 66.66; H, 5.03. Found: C, 66.43; H, 5.00.



4a

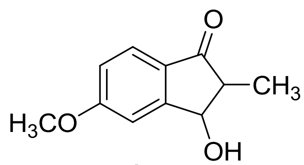
3-Hydroxy-2,6-dimethyl-1-indanone (4a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.48 (m, 3H), 5.32 (d, *J* = 6.8 Hz, 0.7H), 4.88 (d, *J* = 4.0 Hz, 0.3H), 2.90-2.81 (m, 0.7H), 2.60-2.53 (m, 0.3H), 2.42 (s, 3H), 2.29 (br, 1H), 1.37 (d, *J* = 7.2 Hz, 0.9H), 1.26 (d, *J* = 7.6 Hz, 2.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7 (0.7C), 205.4 (0.3C), 152.0 (0.7C), 151.3 (0.3C), 140.3 (0.7C), 139.9 (0.3C), 136.9 (0.7C), 136.8 (0.3C), 136.2 (0.3C), 136.0 (0.7C), 126.4 (0.7C), 125.5 (0.3C), 123.9 (0.7C), 123.6 (0.3C), 76.7 (0.3C), 70.9 (0.7C), 54.0 (0.3C), 48.4 (0.7C), 21.7 (0.7C), 21.6 (0.3C), 13.4 (0.3C), 10.7 (0.7C); MS (CI, *m/z*, %) 194 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.90; H, 6.93.



4b

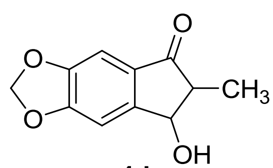
5-Fluoro-3-hydroxy-2-methyl-1-indanone (4b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 1H), 7.39-7.35 (m, 1H), 7.20-7.15 (m, 1H), 5.35 (d, *J* = 6.0 Hz, 0.7H), 4.90 (d, *J* = 2.4 Hz, 0.3H), 3.08 (br, 0.3H), 2.95-2.86 (m, 0.7H), 2.64-2.60 (m, 0.3H), 2.53 (br, 0.7H), 1.39 (d, *J* = 7.6 Hz, 0.9H), 1.27 (d, *J* =

7.6 Hz, 2.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7 (0.7C), 203.4 (0.3C), 167.9 (d, *J* = 255.7 Hz, 1C), 157.5 (d, *J* = 9.2 Hz, 0.7C), 156.8 (d, *J* = 9.1 Hz, 0.3C), 132.3 (d, *J* = 1.9 Hz, 0.3C), 132.1 (d, *J* = 1.9 Hz, 0.7C), 126.4 (d, *J* = 9.9 Hz, 0.7C), 126.2 (d, *J* = 9.9 Hz, 0.3C), 118.2 (d, *J* = 24.0 Hz, 0.7C), 118.0 (d, *J* = 24.0 Hz, 0.3C), 113.5 (d, *J* = 22.1 Hz, 0.7C), 112.6 (d, *J* = 22.5 Hz, 0.3C), 76.4 (d, *J* = 2.0 Hz, 0.3C), 70.6 (d, *J* = 1.5 Hz, 0.7C), 54.0 (0.3C), 48.3 (0.7C), 13.2 (0.3C), 10.7 (0.7C); MS (CI, *m/z*, %) 198 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_9FO_2$: C, 66.66; H, 5.03. Found: C, 66.79; H, 5.00.



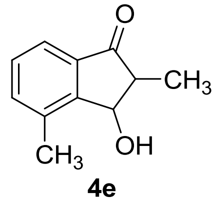
4c

3-Hydroxy-5-methoxy-2-methyl-1-indanone (4c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.59 (m, 1H), 7.14-7.11 (m, 1H), 6.98-6.93 (m, 1H), 5.28 (d, *J* = 7.2 Hz, 0.4H), 4.82 (d, *J* = 4.0 Hz, 0.6H), 3.88 (s, 1.2H), 3.87 (s, 1.8H), 3.22 (br, 1H), 2.87-2.81 (m, 0.4H), 2.59-2.54 (m, 0.6H), 1.33 (dd, *J* = 1.6, 7.6 Hz, 1.8H), 1.23 (dd, *J* = 1.2, 7.6 Hz, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3 (0.4C), 204.0 (0.6C), 166.3 (0.4C), 166.2 (0.6C), 157.9 (0.4C), 157.2 (0.6C), 128.9 (0.6C), 128.7 (0.4C), 125.6 (0.4C), 125.4 (0.6C), 118.0 (0.4C), 117.8 (0.6C), 109.6 (0.4C), 108.7 (0.6C), 76.7 (0.6C), 70.8 (0.4C), 56.2 (1C), 53.7 (0.6C), 48.2 (0.4C), 13.5 (0.6C), 10.9 (0.4C); MS (CI, *m/z*, %) 193 (100) $[M+H]^+$, 210 (85) $[M+NH_3+H]^+$; Anal. calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.70; H, 6.37.



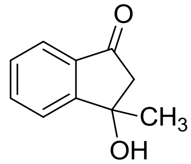
4d

3-Hydroxy-2-methyl-5,6-methylenedioxy-1-indanone (4d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-7.03 (m, 2H), 6.09 (s, 0.6H), 6.08 (s, 1.4H), 5.23 (d, *J* = 6.0 Hz, 0.7H), 4.78 (d, *J* = 4.0 Hz, 0.3H), 3.04 (br, 0.3H), 2.90-2.81 (m, 0.7H), 2.58-2.50 (m, 0.3H), 2.46 (br, 0.7H), 1.34 (d, *J* = 7.2 Hz, 0.9H), 1.24 (d, *J* = 7.6 Hz, 2.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5 (0.7C), 203.3 (0.3C), 154.9 (1C), 152.1 (0.7C), 151.4 (0.3C), 150.2 (0.7C), 150.1 (0.3C), 130.8 (0.3C), 130.7 (0.7C), 105.9 (0.7C), 105.2 (0.3C), 102.9 (0.7C), 102.8 (0.3C), 102.4 (0.7C), 102.2 (0.3C), 76.6 (0.3C), 70.7 (0.7C), 53.9 (0.3C), 48.3 (0.7C), 13.6 (0.3C), 11.1 (0.7C); MS (CI, *m/z*, %) 207 (83) $[M+H]^+$, 224 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.20; H, 4.87.



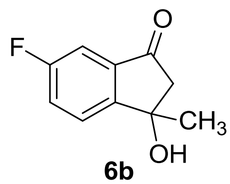
4e

3-Hydroxy-2,4-dimethyl-1-indanone (4e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.39 (dd, *J* = 7.2, 7.6 Hz, 1H), 5.42 (d, *J* = 6.4 Hz, 0.6H), 5.01 (d, *J* = 2.4 Hz, 0.4H), 2.85-2.76 (m, 0.6H), 2.64-2.56 (m, 0.4H), 2.54 (s, 3H), 1.96 (br, 0.6H), 1.76 (br, 0.4H), 1.35 (d, *J* = 7.2 Hz, 1.2H), 1.30 (d, *J* = 7.6 Hz, 1.8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9 (0.6C), 206.4 (0.4C), 152.2 (0.6C), 151.3 (0.4C), 137.6 (0.4C), 137.5 (0.6C), 137.1 (0.4C), 136.8 (0.6C), 136.2 (0.4C), 136.1 (0.6C), 130.3 (0.6C), 130.2 (0.4C), 121.4 (0.6C), 121.3 (0.4C), 76.8 (0.4C), 70.4 (0.6C), 53.4 (0.4C), 47.9 (0.6C), 18.4 (0.4C), 18.0 (0.6C), 14.3 (0.4C), 9.8 (0.6C); MS (CI, *m/z*, %) 194 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.85; H, 6.90.



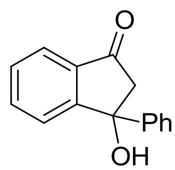
6a

3-Hydroxy-3-methyl-1-indanone (6a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.65 (m, 3H), 7.48-7.44 (m, 1H), 2.92 (br, 1H), 2.84 (s, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 159.2, 135.9, 135.7, 129.7, 124.1, 123.5, 74.8, 54.1, 29.6; MS (CI, *m/z*, %) 180 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.19; H, 6.12.



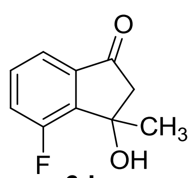
6b

6-Fluoro-3-hydroxy-3-methyl-1-indanone (6b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 4.4, 8.4 Hz, 1H), 7.39 (ddd, J = 2.4, 8.4, 8.4 Hz, 1H), 7.27 (dd, J = 2.4, 7.6 Hz, 1H), 2.90 (s, 2H), 2.89 (s, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8 (d, J = 2.7 Hz), 163.8 (d, J = 248.9 Hz), 154.8 (d, J = 2.3 Hz), 137.6 (d, J = 7.2 Hz), 126.0 (d, J = 8.4 Hz), 123.6 (d, J = 23.6 Hz), 109.3 (d, J = 22.1 Hz), 74.4, 54.5, 29.6; MS (CI, *m/z*, %) 198 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_9H_7FO_2$: C, 66.66; H, 5.03. Found: C, 66.64; H, 5.10.



6c

3-Hydroxy-3-phenyl-1-indanone (6c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 1H), 7.61 (ddd, J = 1.0, 7.6, 7.6 Hz, 1H), 7.46 (ddd, J = 1.0, 7.6, 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.33-7.24 (m, 5H), 3.28 (s, 1H), 3.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 158.7, 145.7, 136.3, 136.2, 129.9, 129.0, 127.9, 125.7, 125.5, 123.6, 78.9, 56.5; MS (CI, *m/z*, %) 242 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_{10}H_{10}O_2$: C, 80.34; H, 5.39. Found: C, 80.49; H, 5.32.



6d

4-Fluoro-3-hydroxy-3-methyl-1-indanone (6d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.44 (m, 2H), 7.34-7.28 (m, 1H), 2.98 (s, 1H), 2.95 (d, J = 19.2 Hz, 1H), 2.83 (d, J = 19.2 Hz, 1H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7 (d, J = 1.5 Hz), 160.3 (d, J = 251.2 Hz), 144.0 (d, J = 15.2 Hz), 138.9 (d, J = 3.4 Hz), 131.8 (d, J = 6.5 Hz), 122.6 (d, J = 20.2 Hz), 119.6 (d, J = 3.8 Hz), 74.5, 53.9, 28.9; MS (CI, *m/z*, %) 198 (100) $[M+NH_3+H]^+$; Anal. calcd for $C_9H_7FO_2$: C, 66.66; H, 5.03. Found: C, 66.74; H, 4.98.

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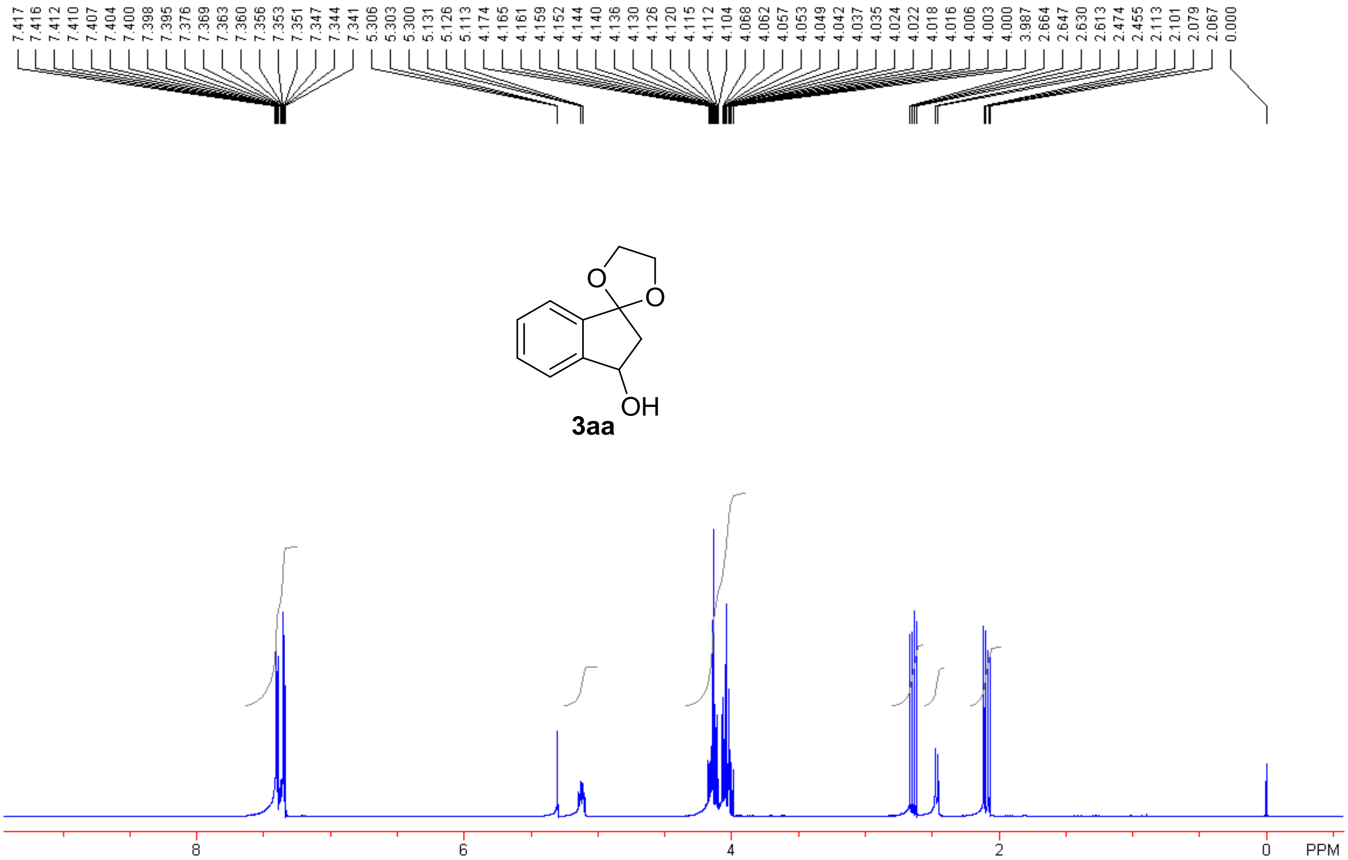
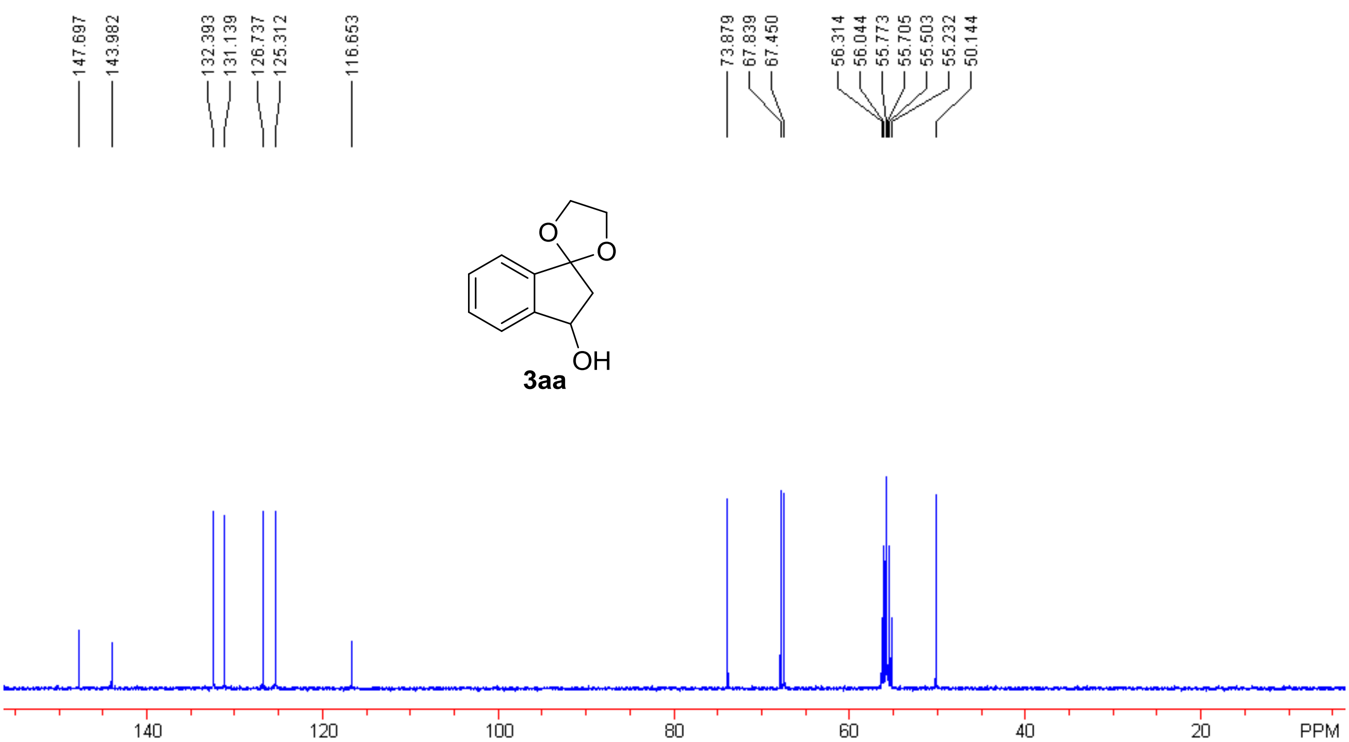
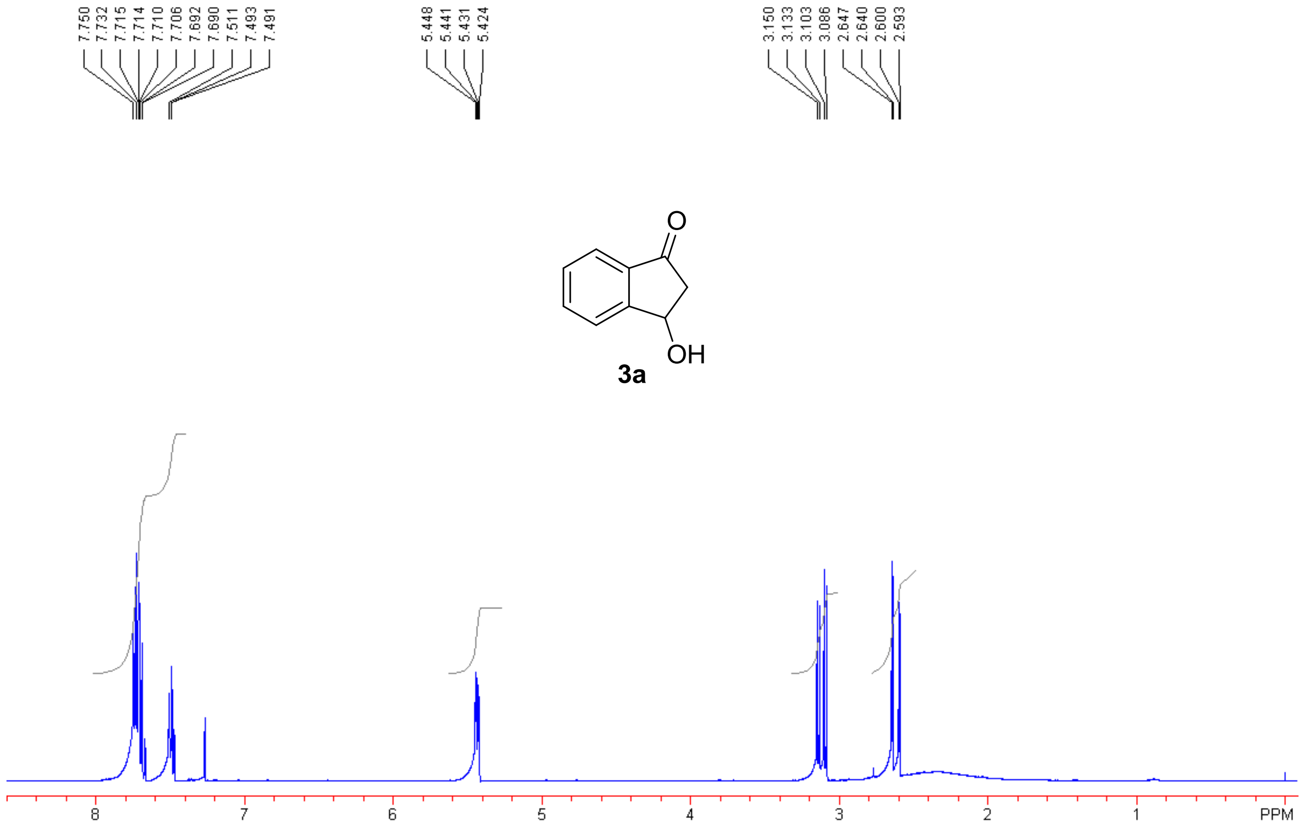
[1]H NMR and [13]C NMR spectra of the products 3, 4, and 6



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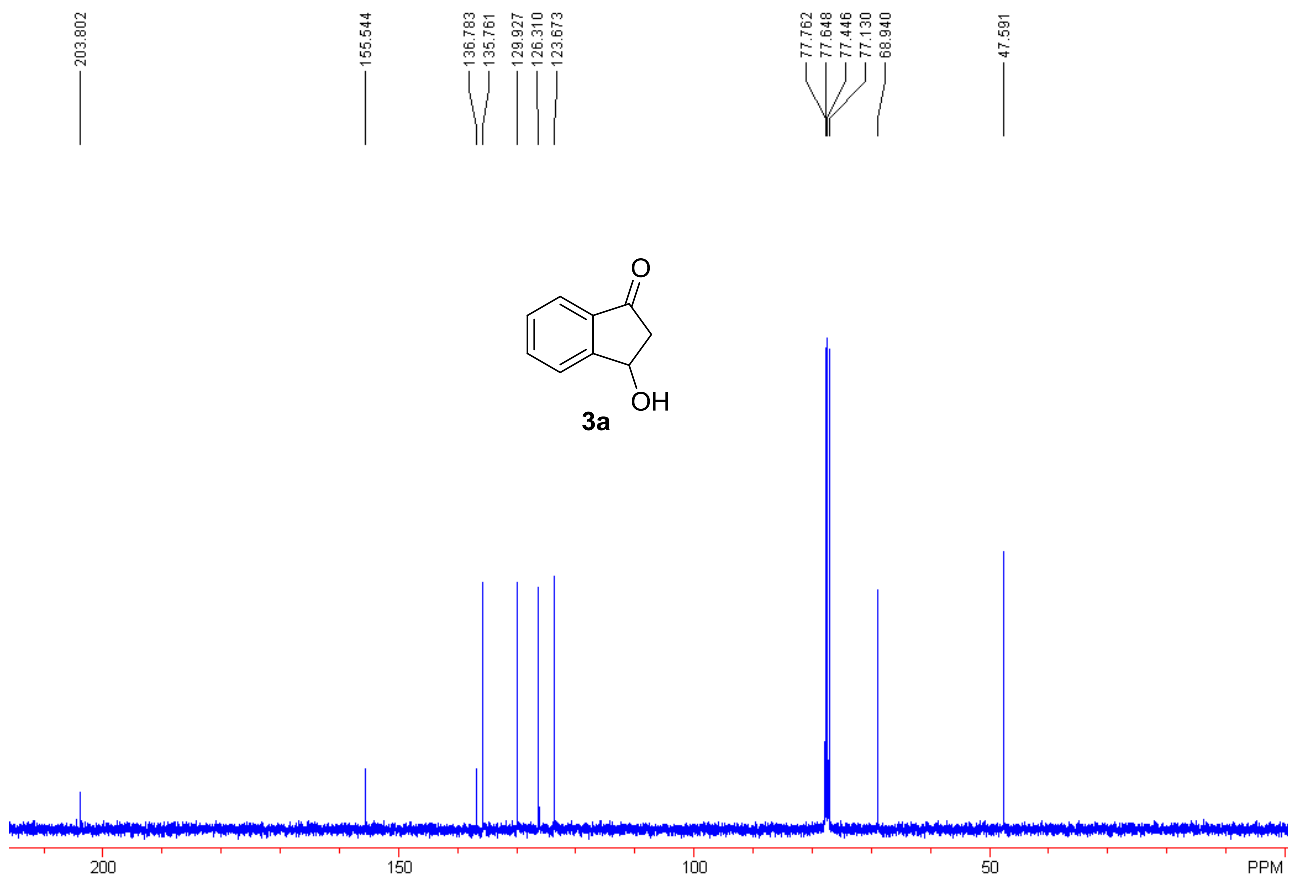
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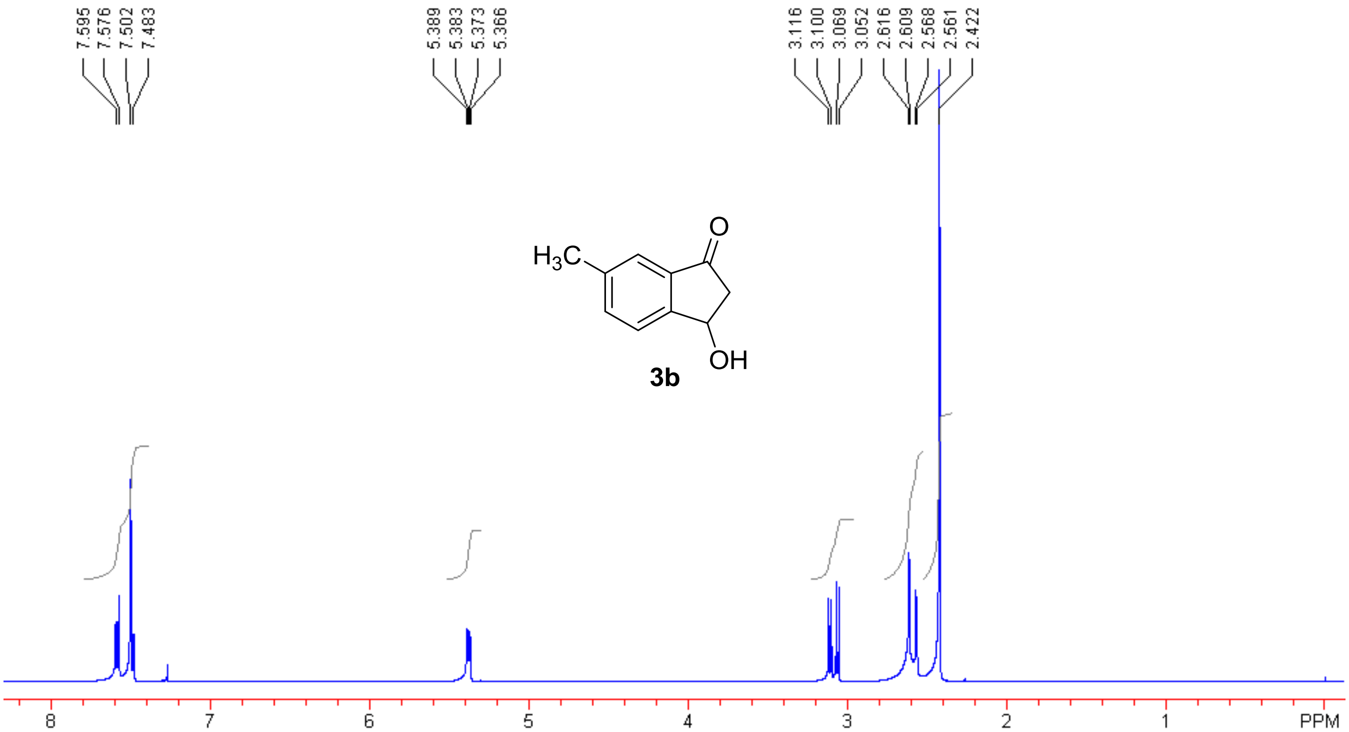
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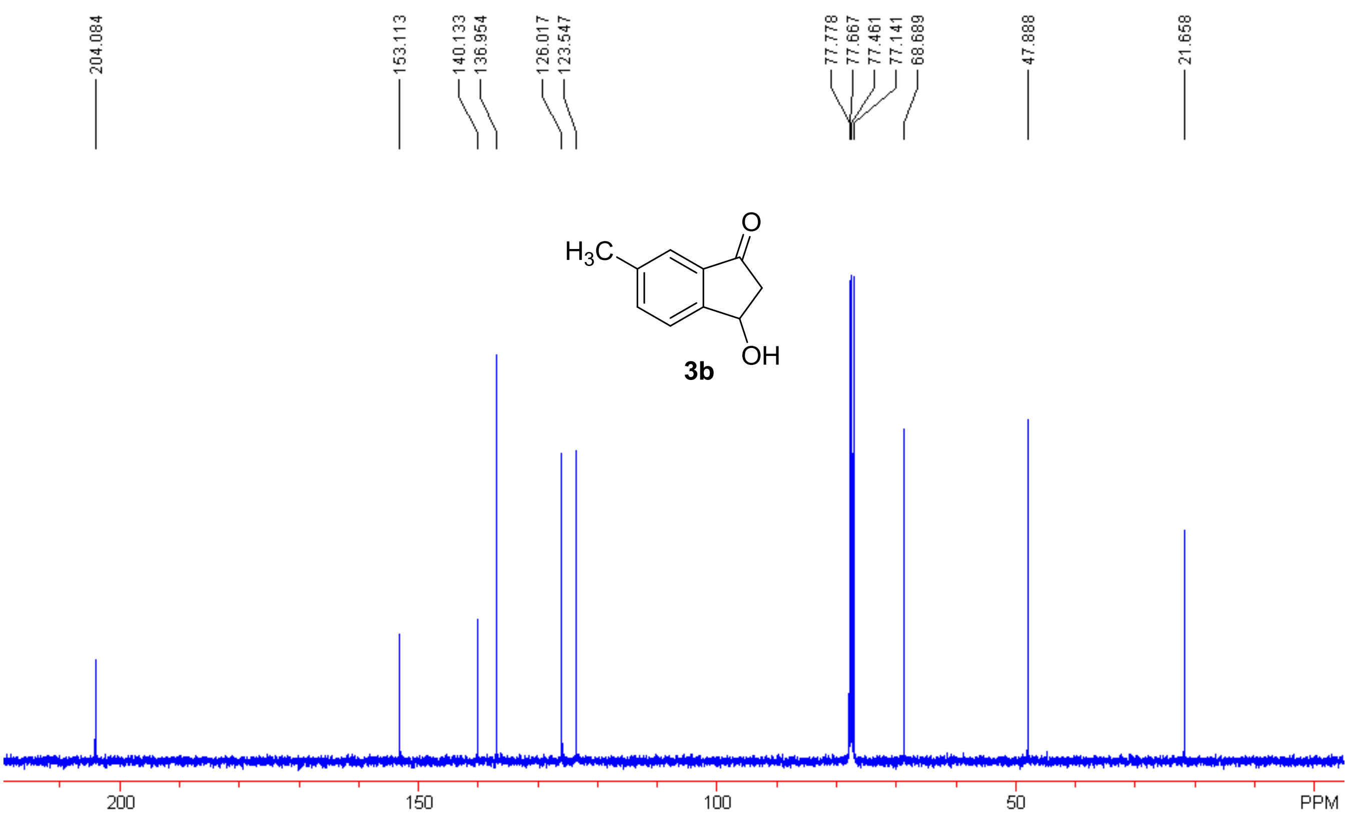
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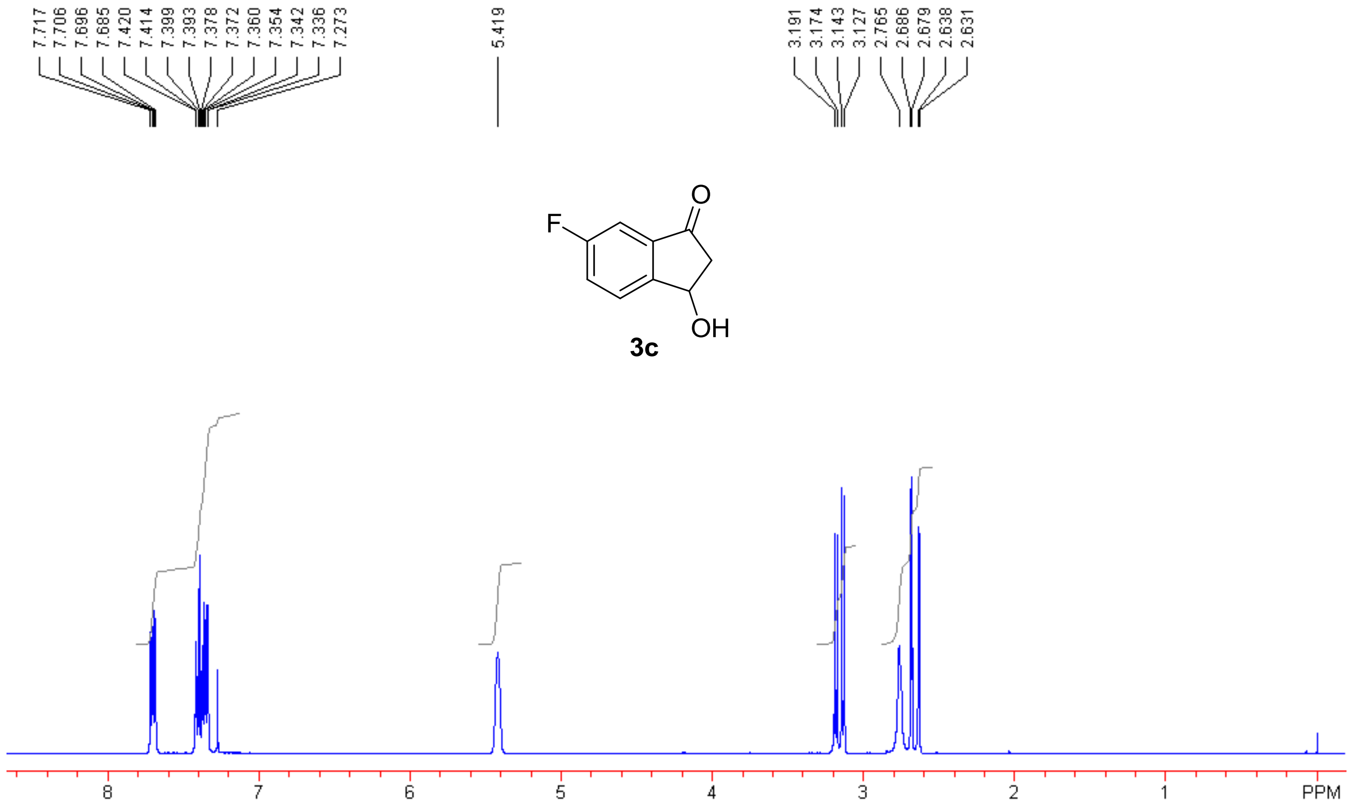
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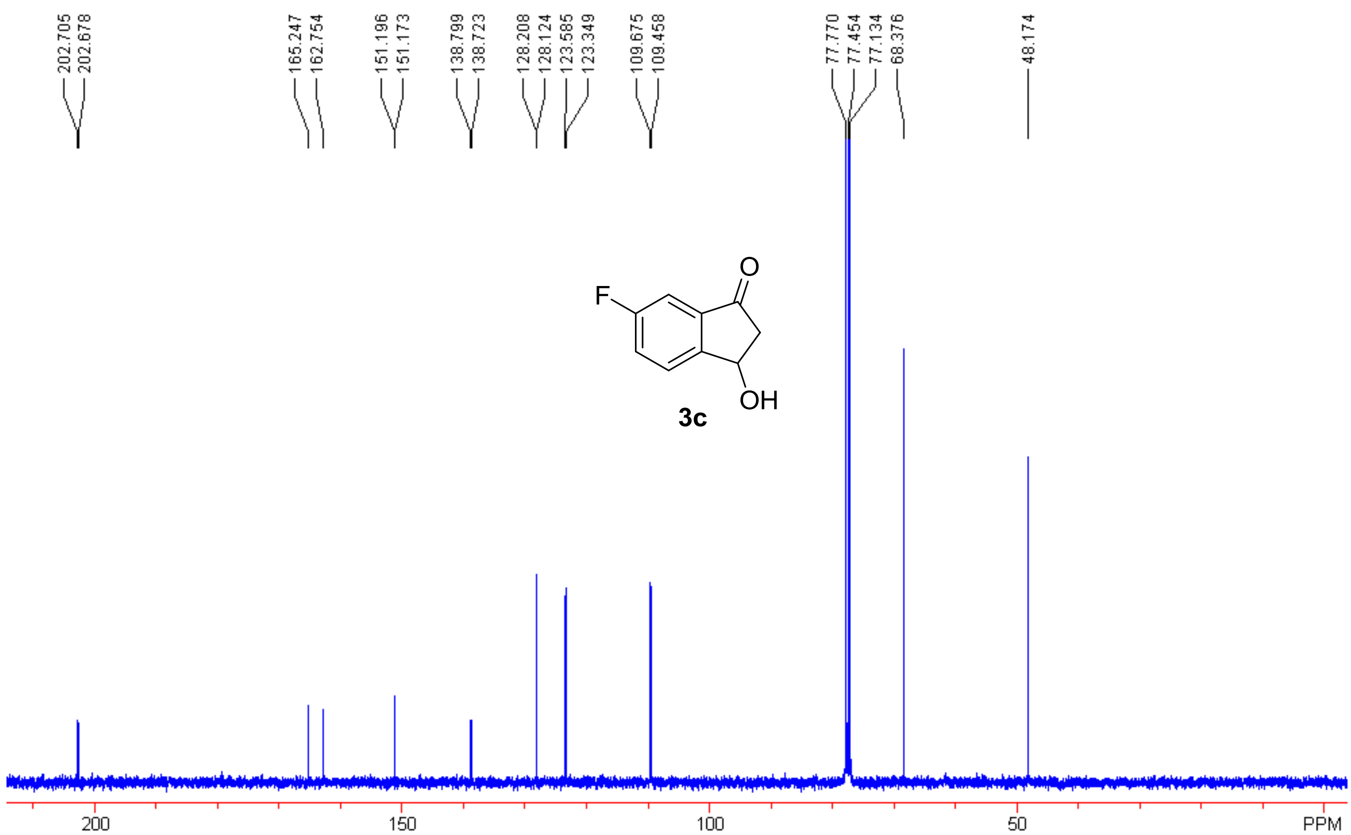
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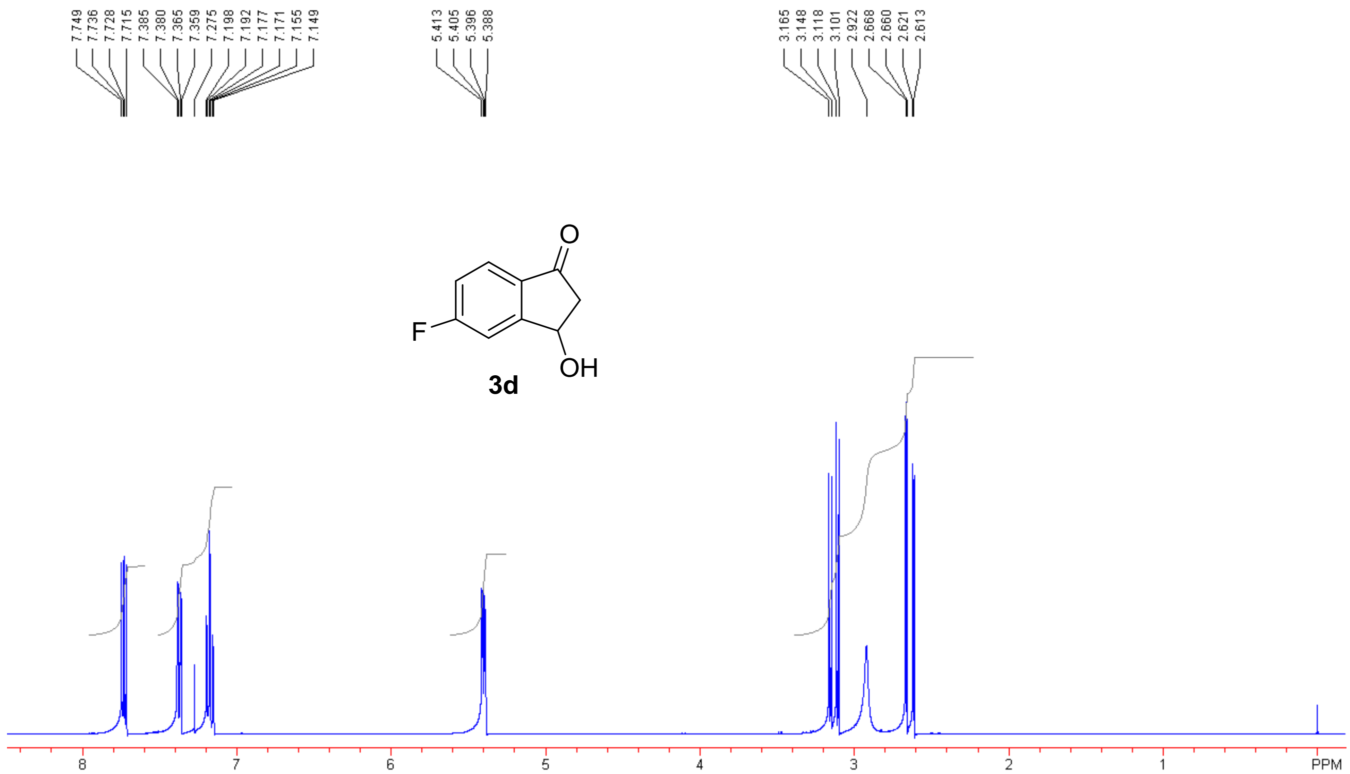
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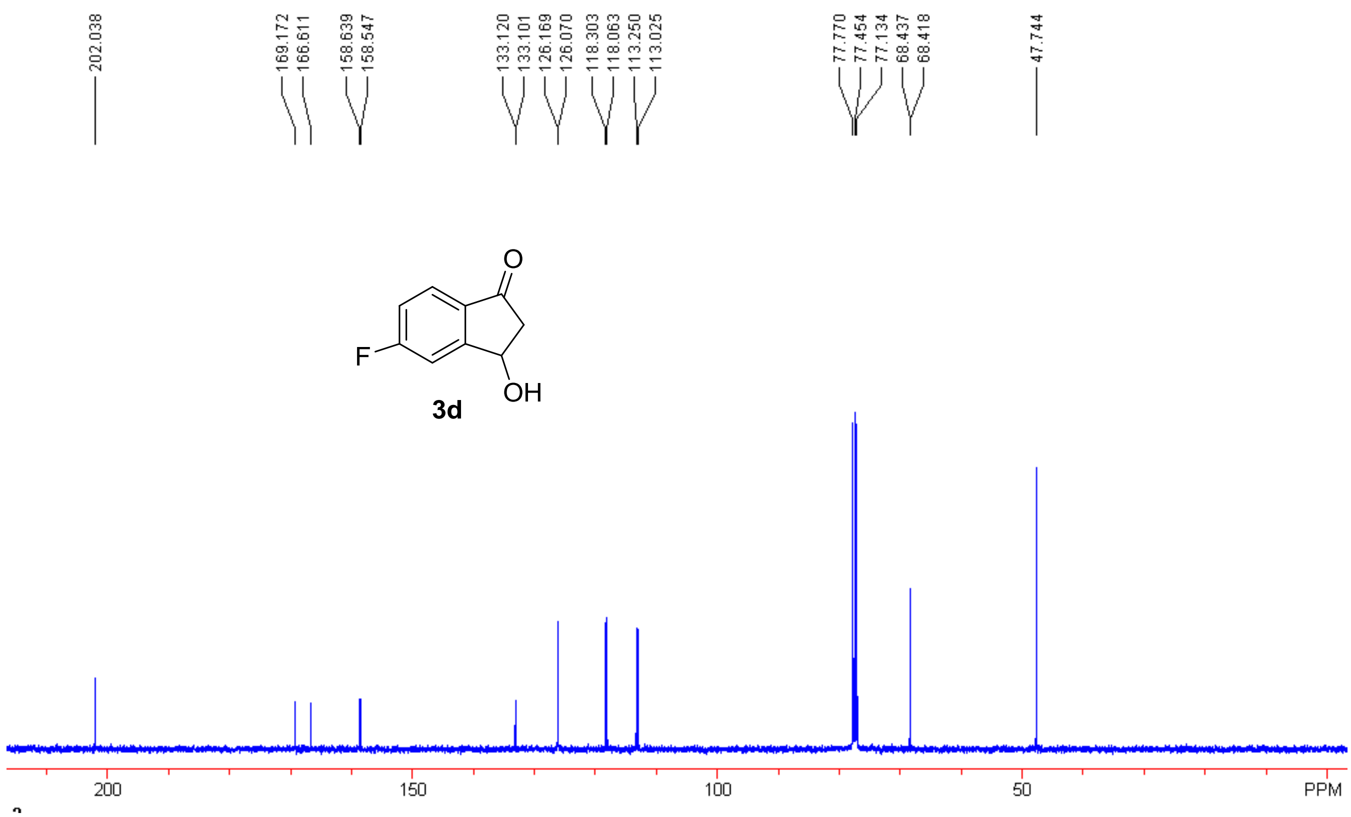
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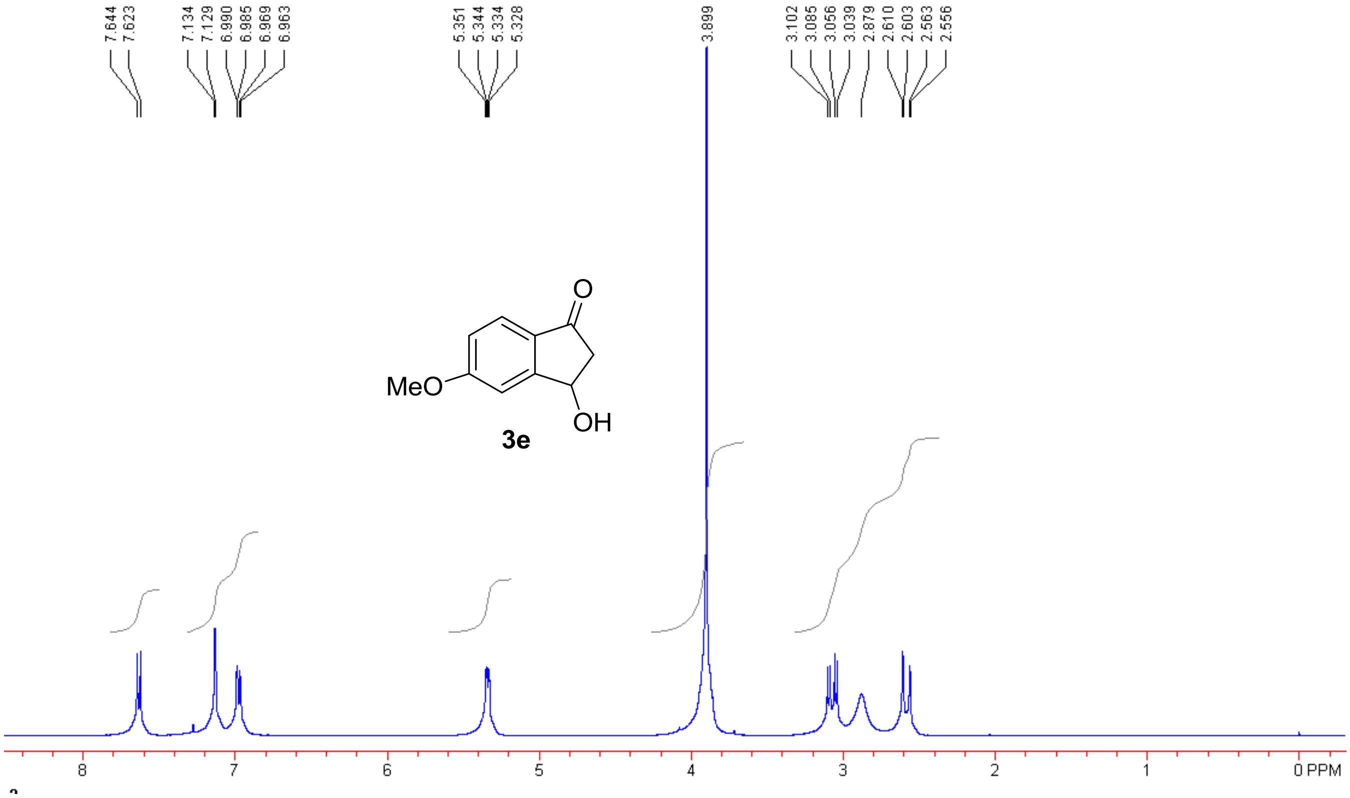
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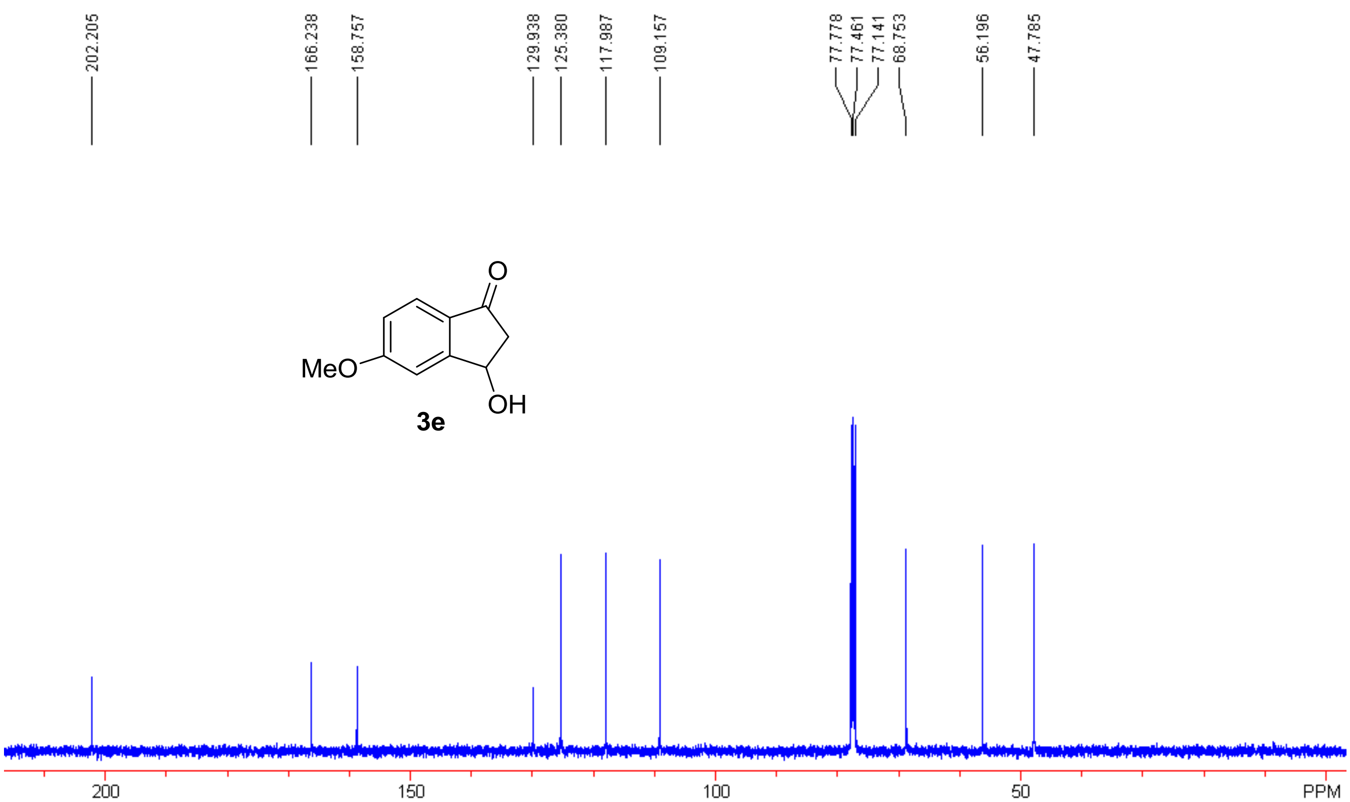
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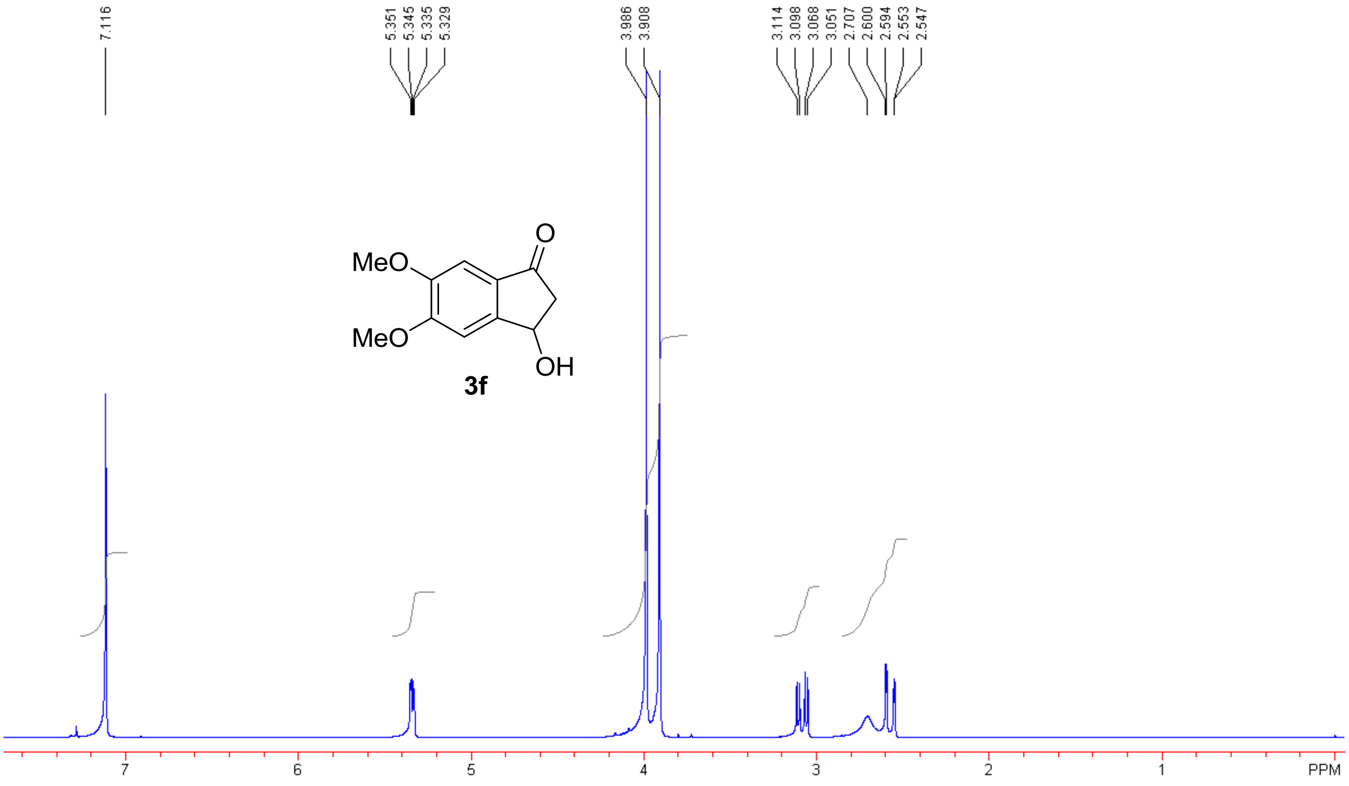
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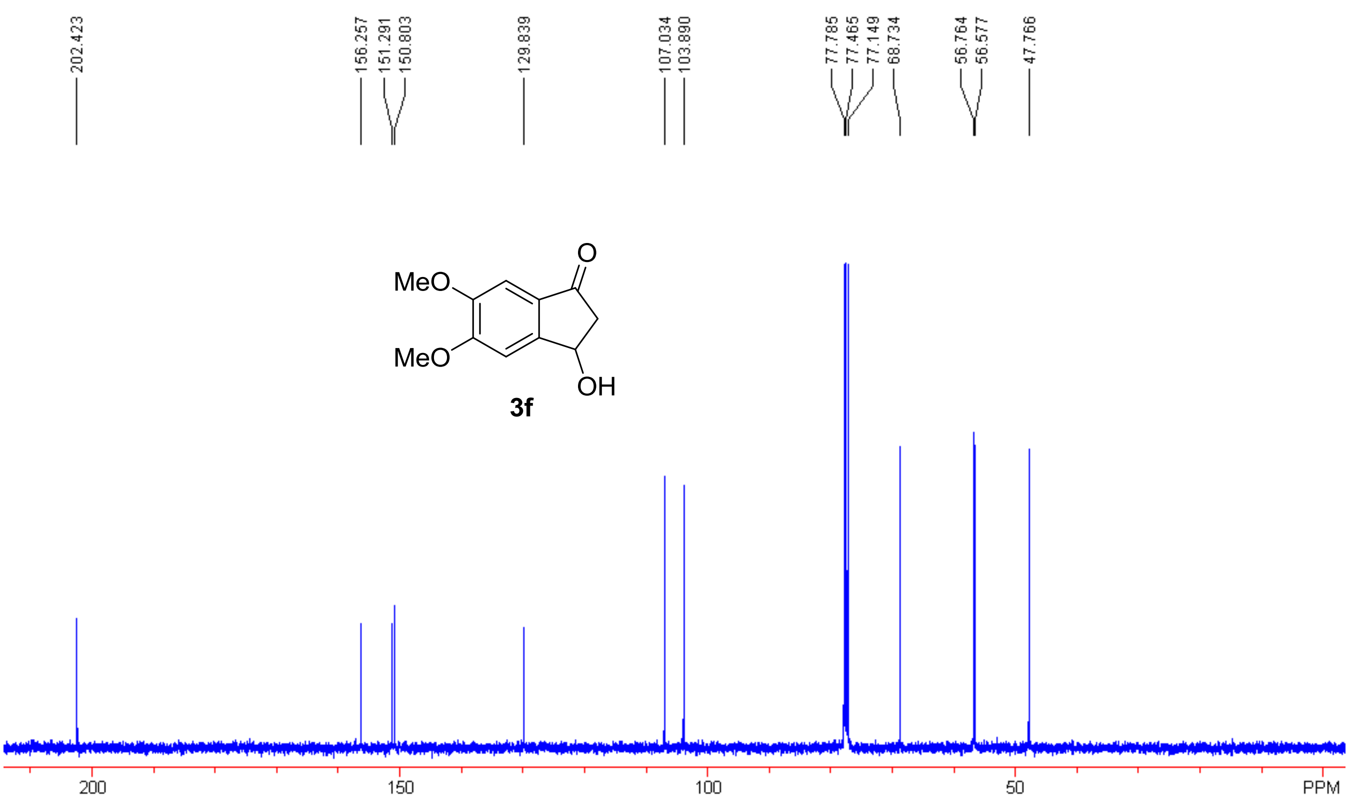
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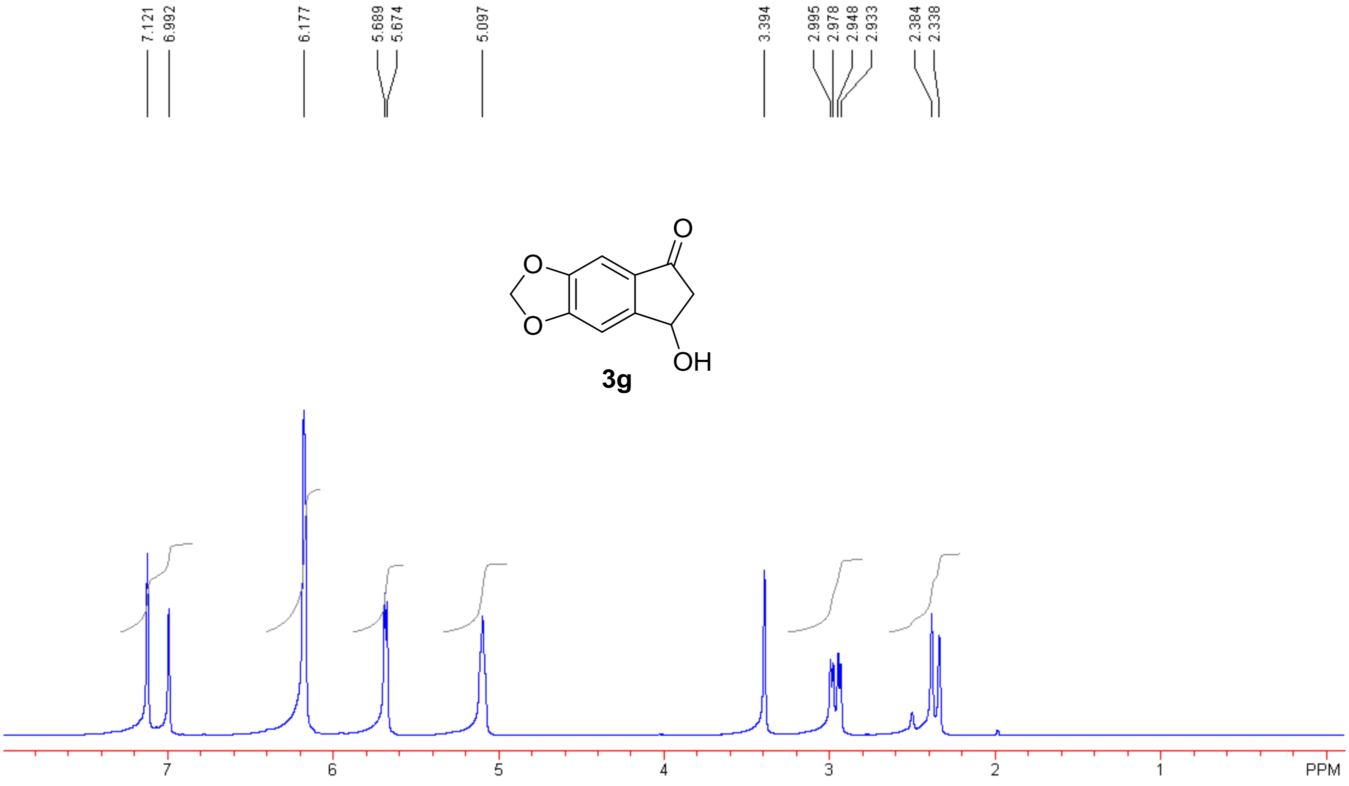
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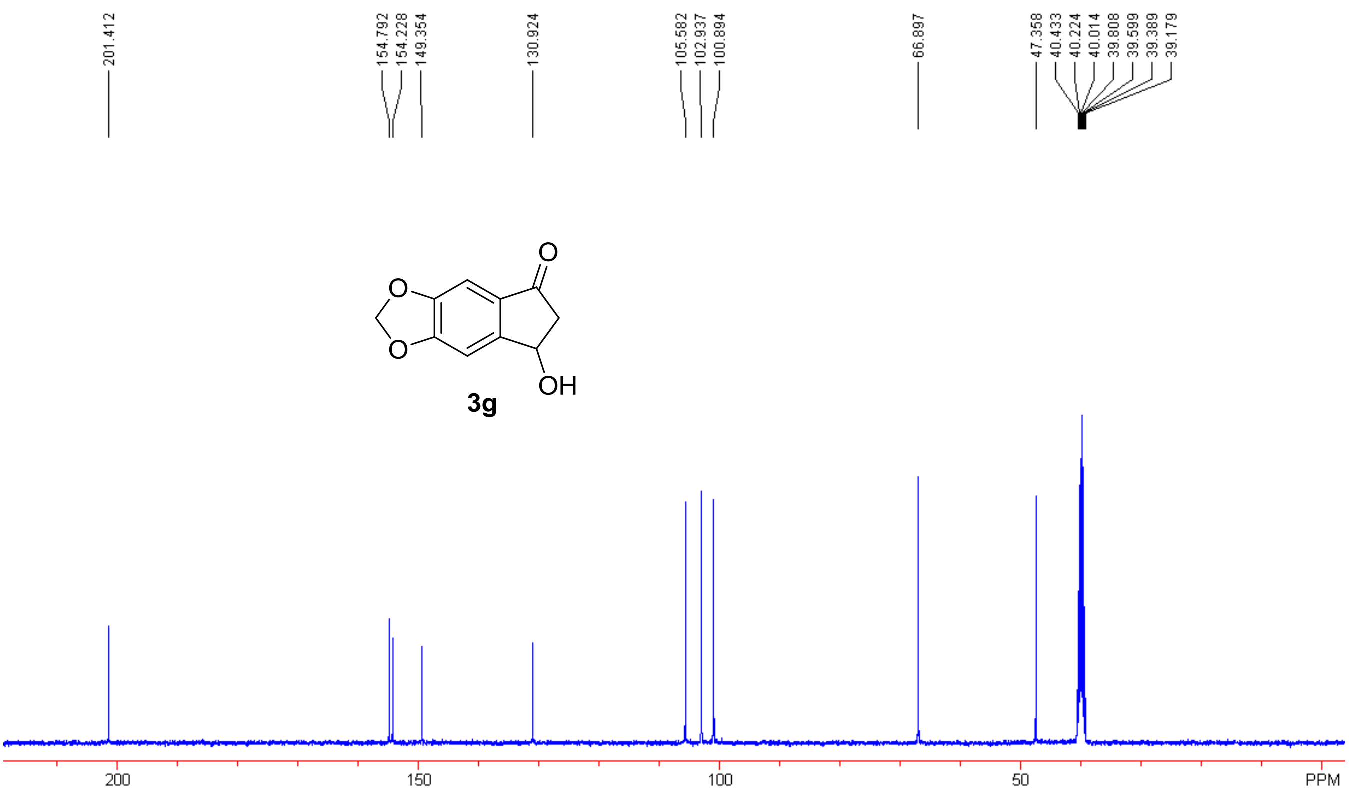
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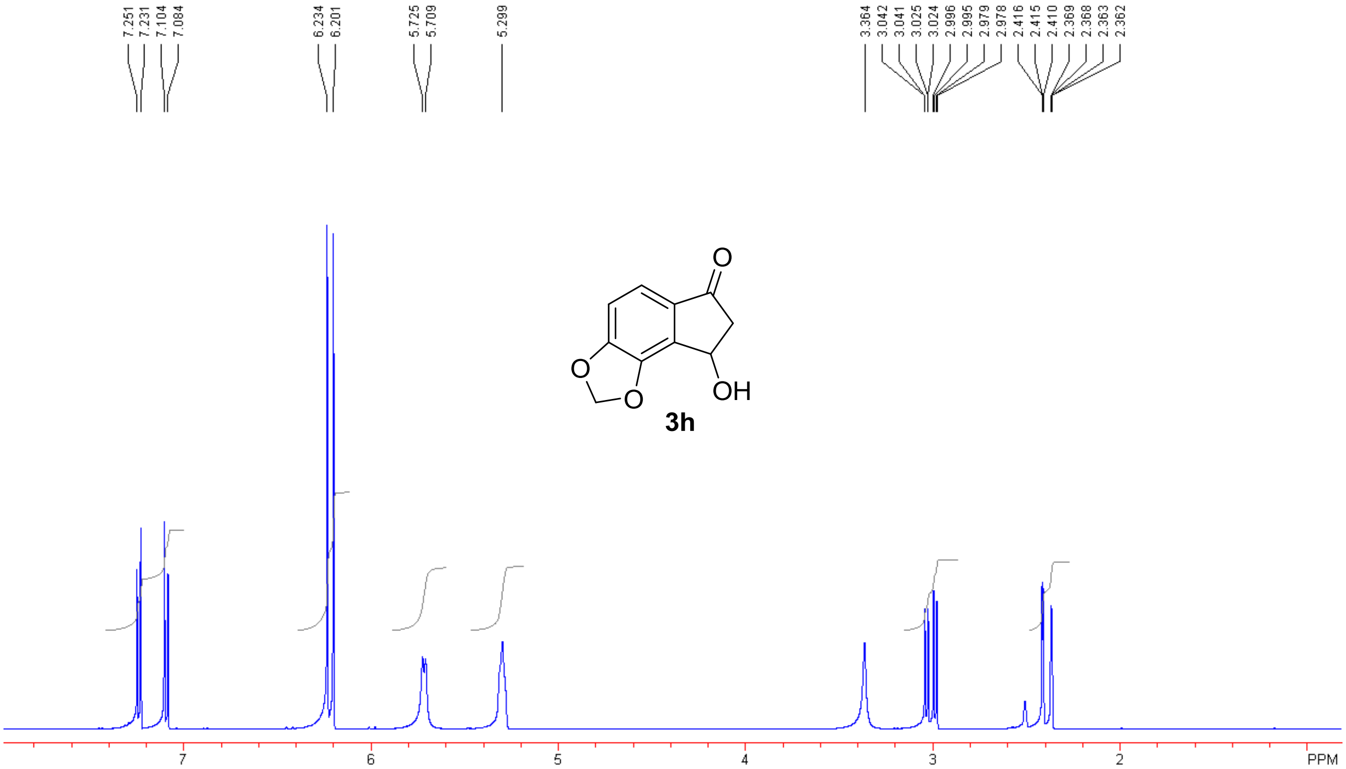

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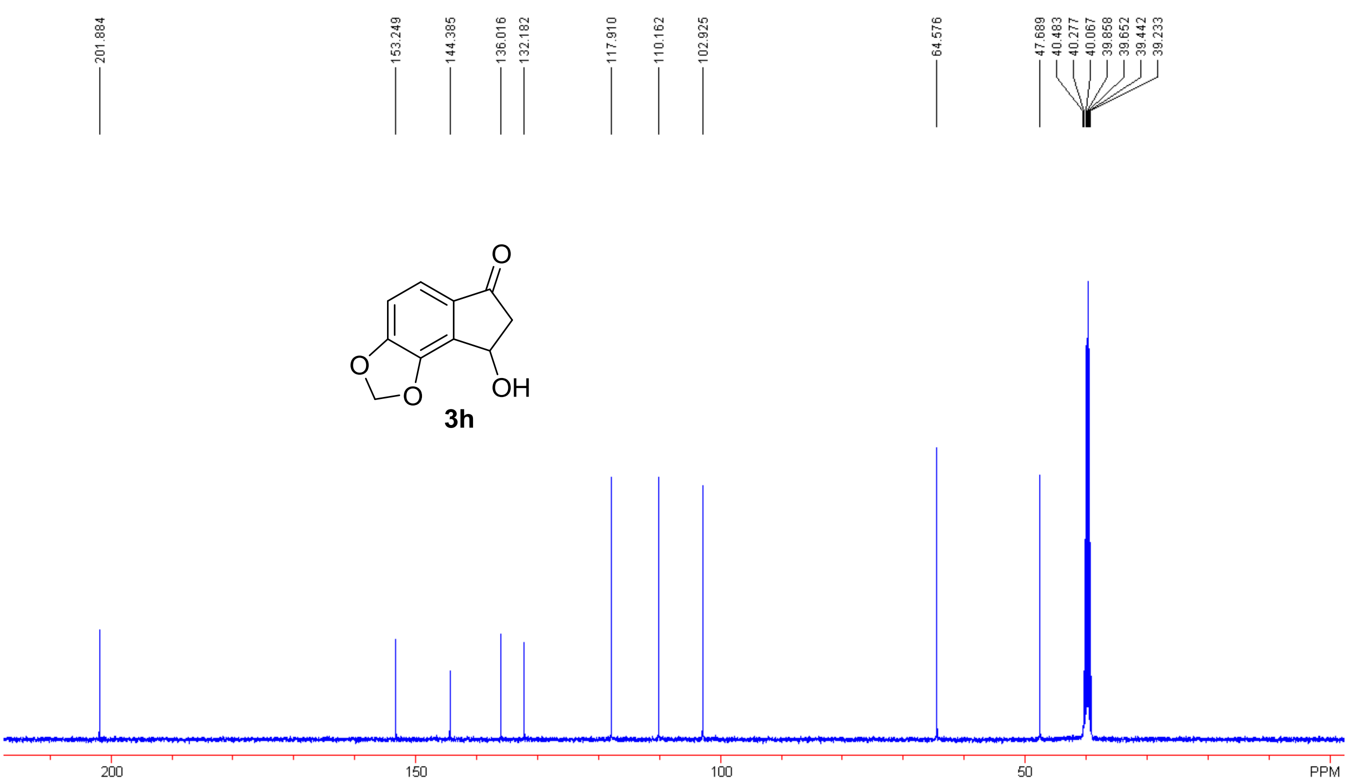

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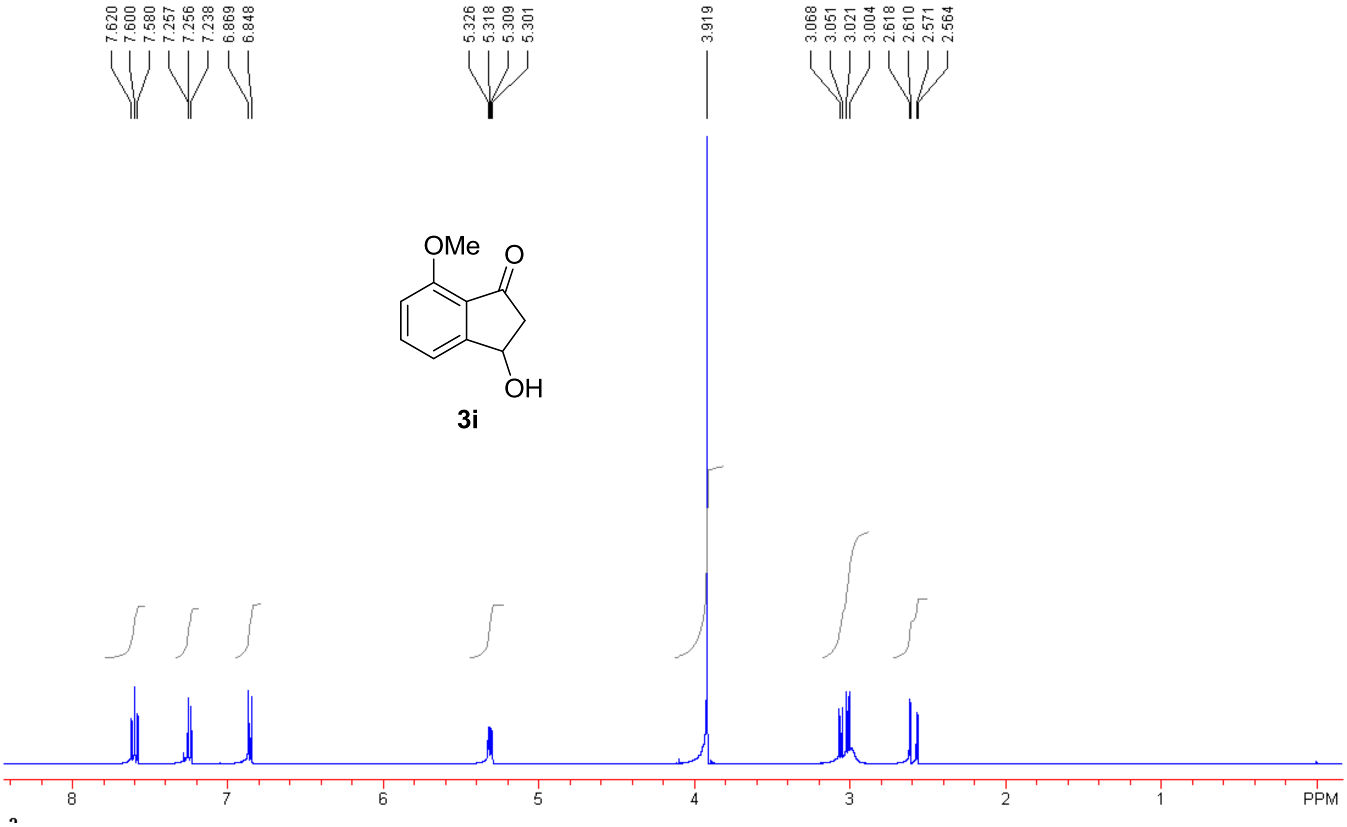
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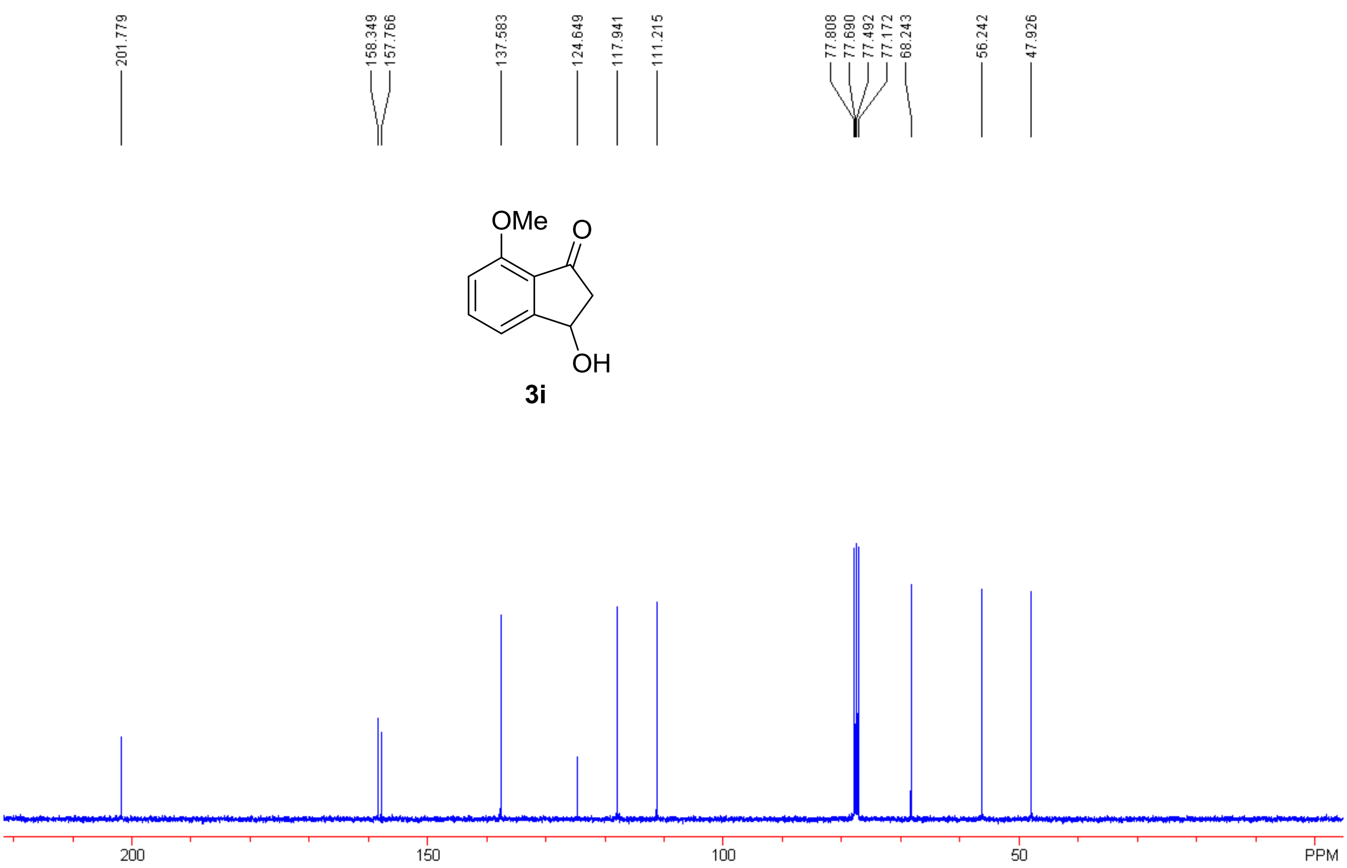
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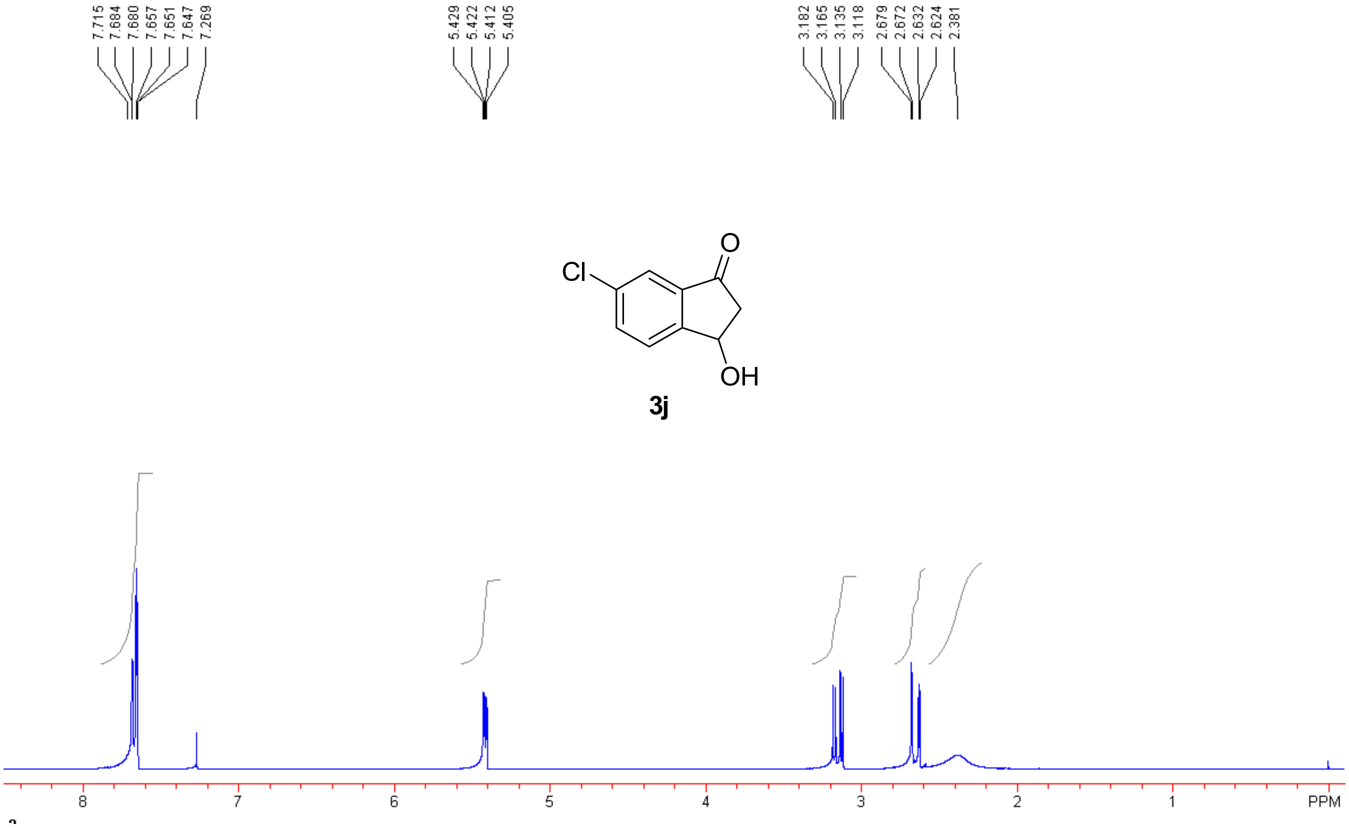
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3.135
3.118
2.679
2.672
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Cl
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OH
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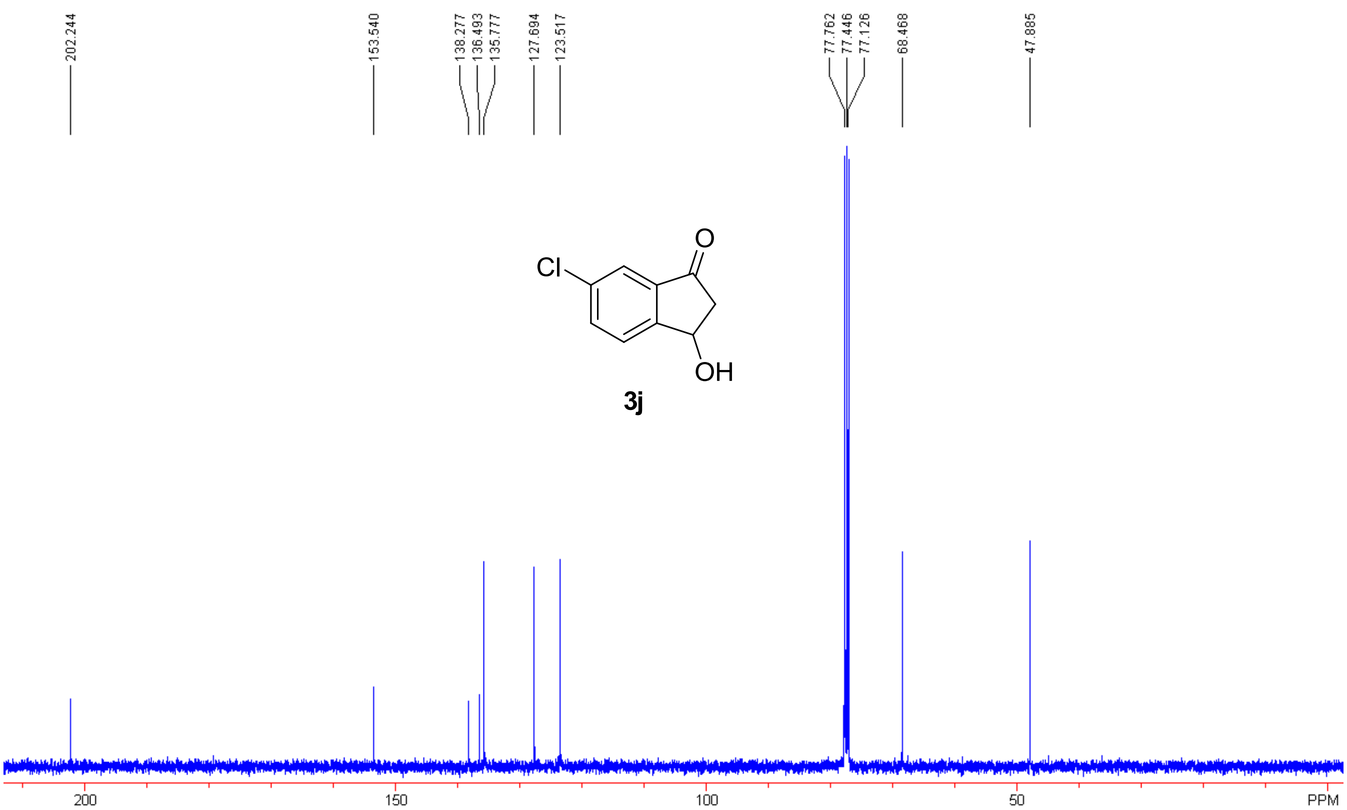
PPM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OH
3j
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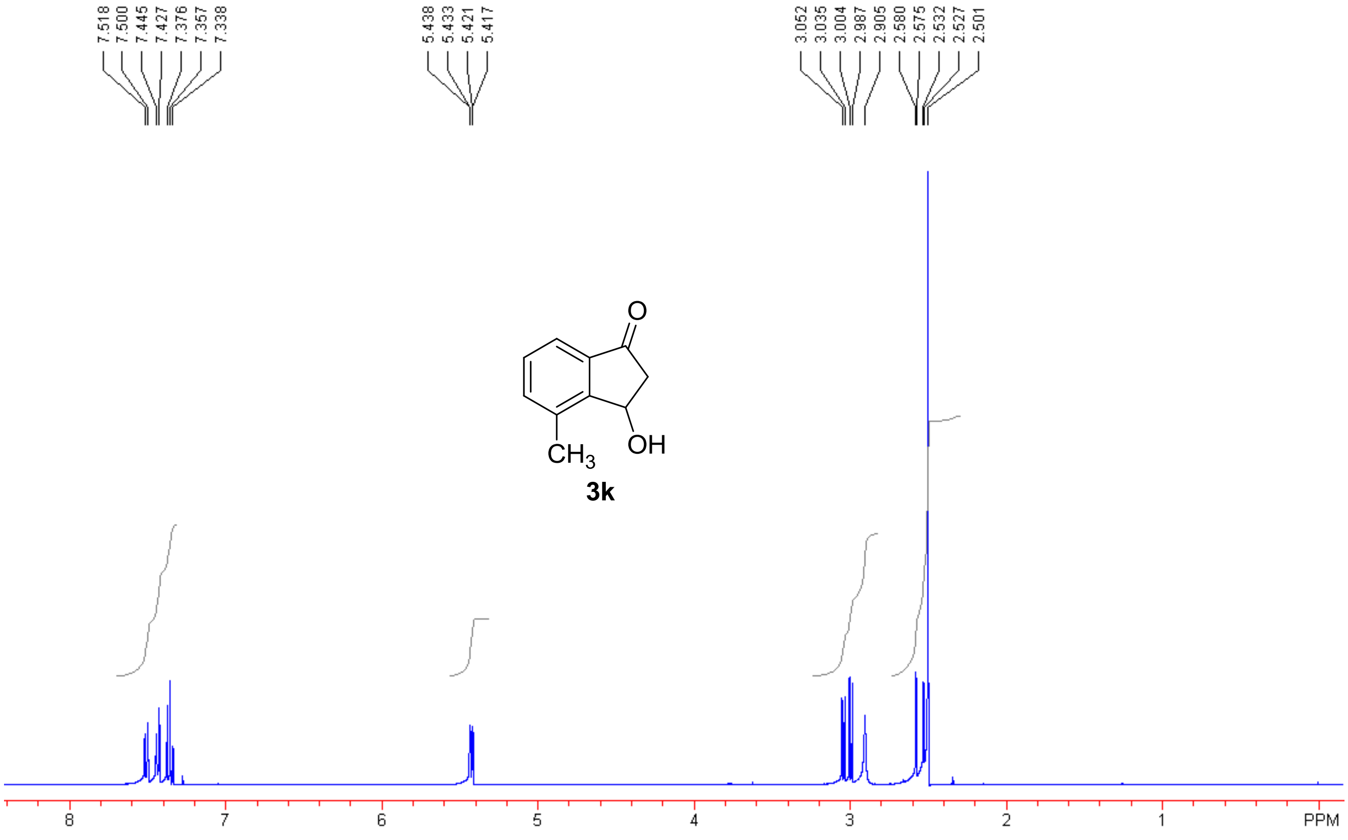
PPM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3.004
2.987
2.905
2.580
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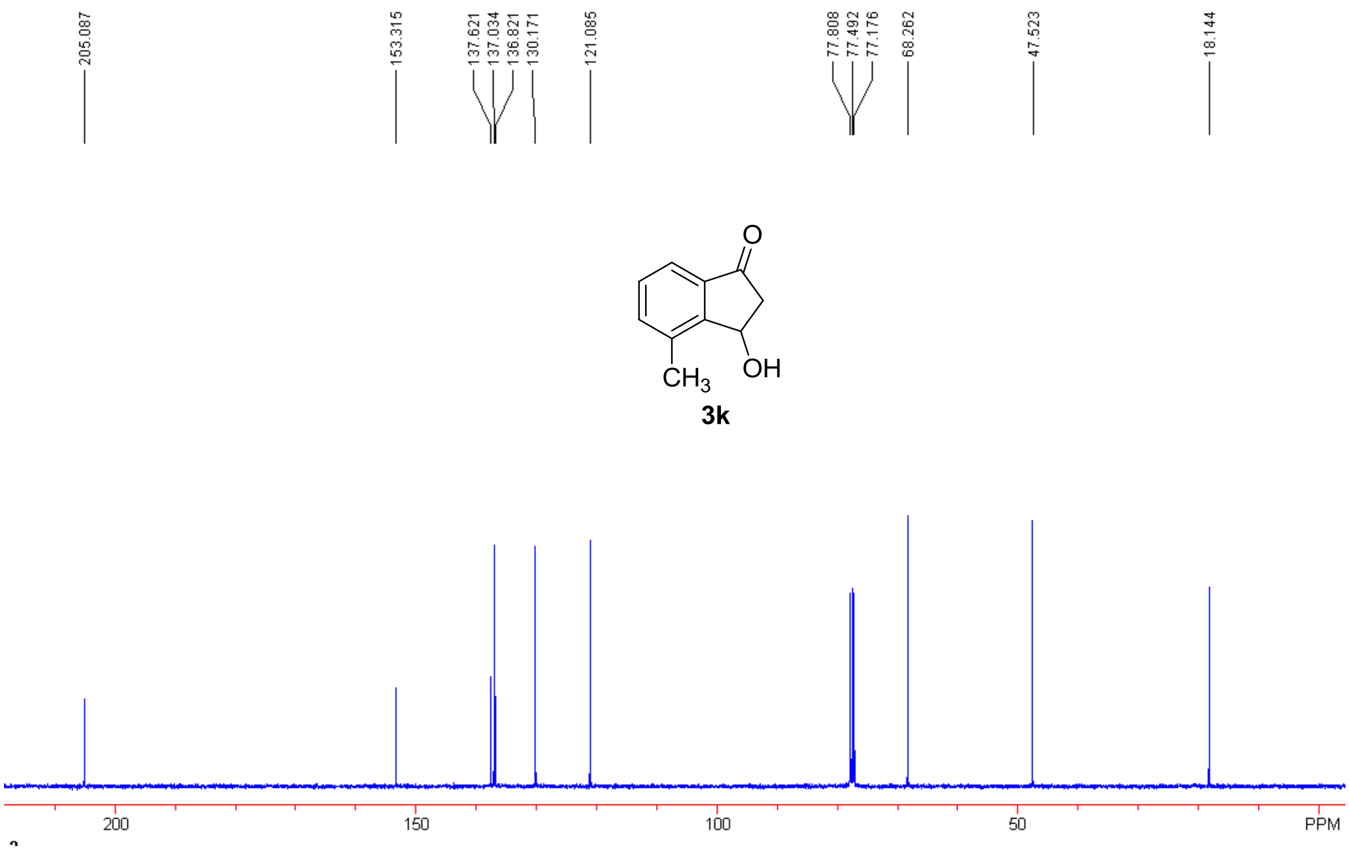
2.501
O
CH3
OH
8
7
6
5
4
3
2
1
PPM

3k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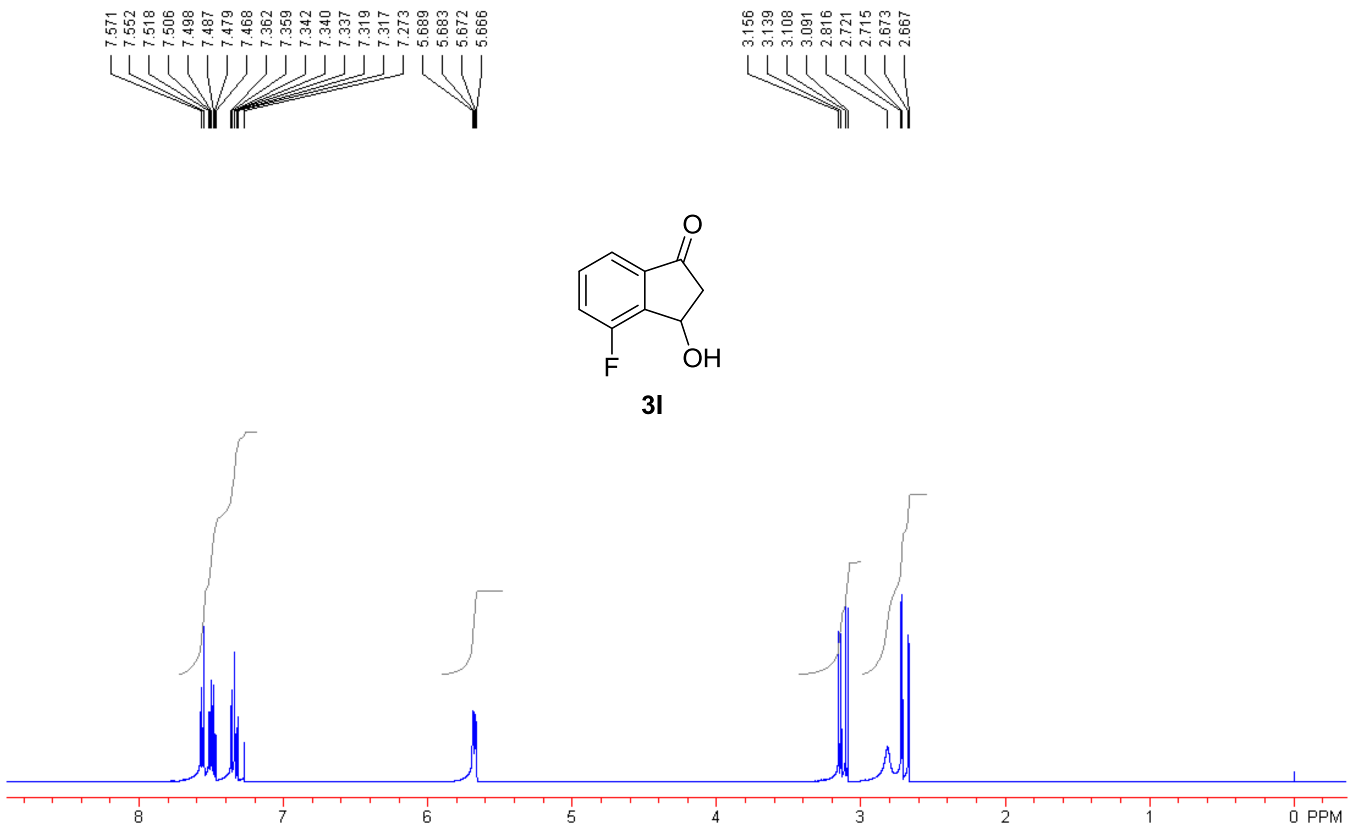
OH
200
150
100
50
PPM

3k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7.337
7.319
7.317
7.273
5.689
5.683
5.672
5.666
3.156
3.139
3.108
3.091
2.816
2.721
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2.667
O
F
OH
3l
8
7
6
5
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2
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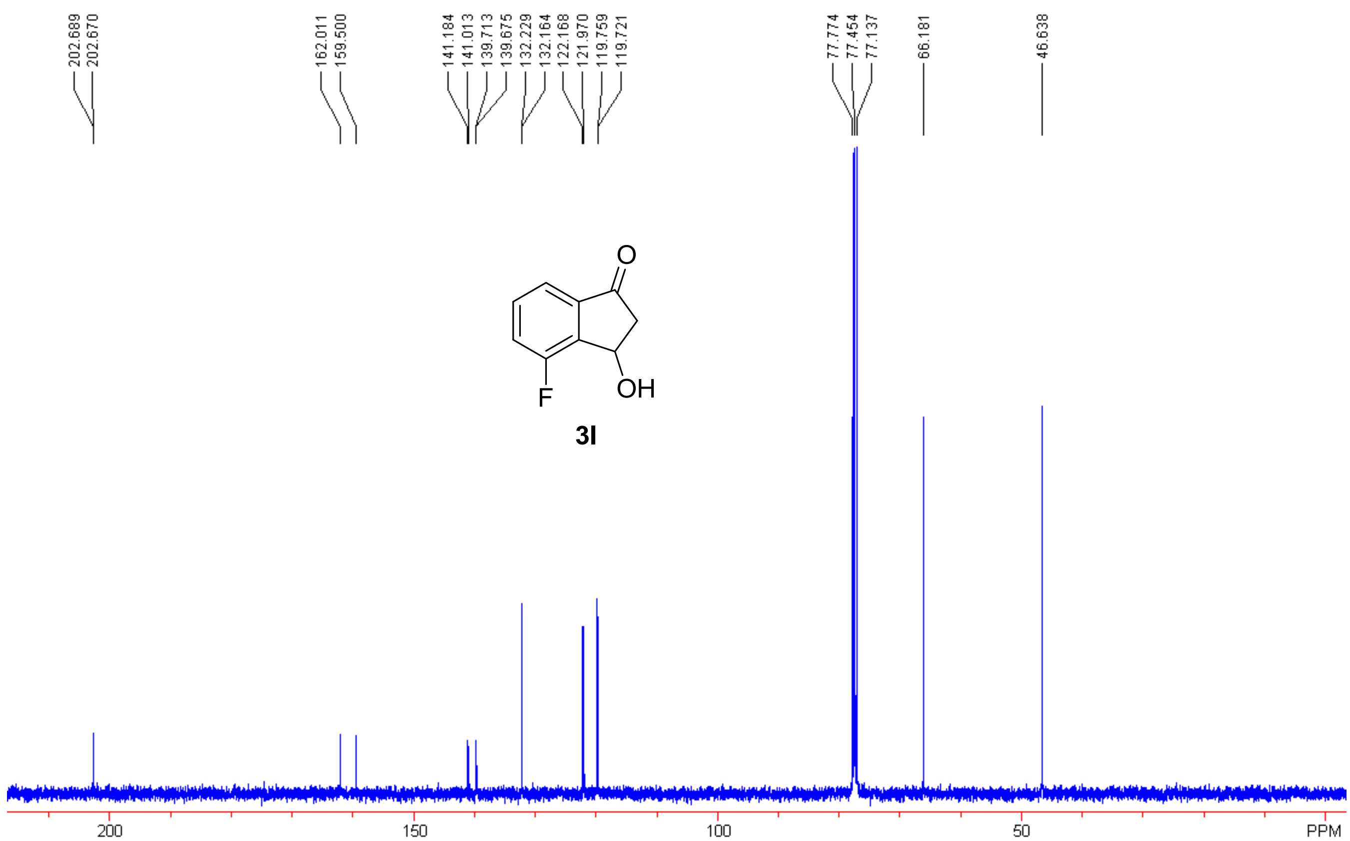
0 PPM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F
OH
3l
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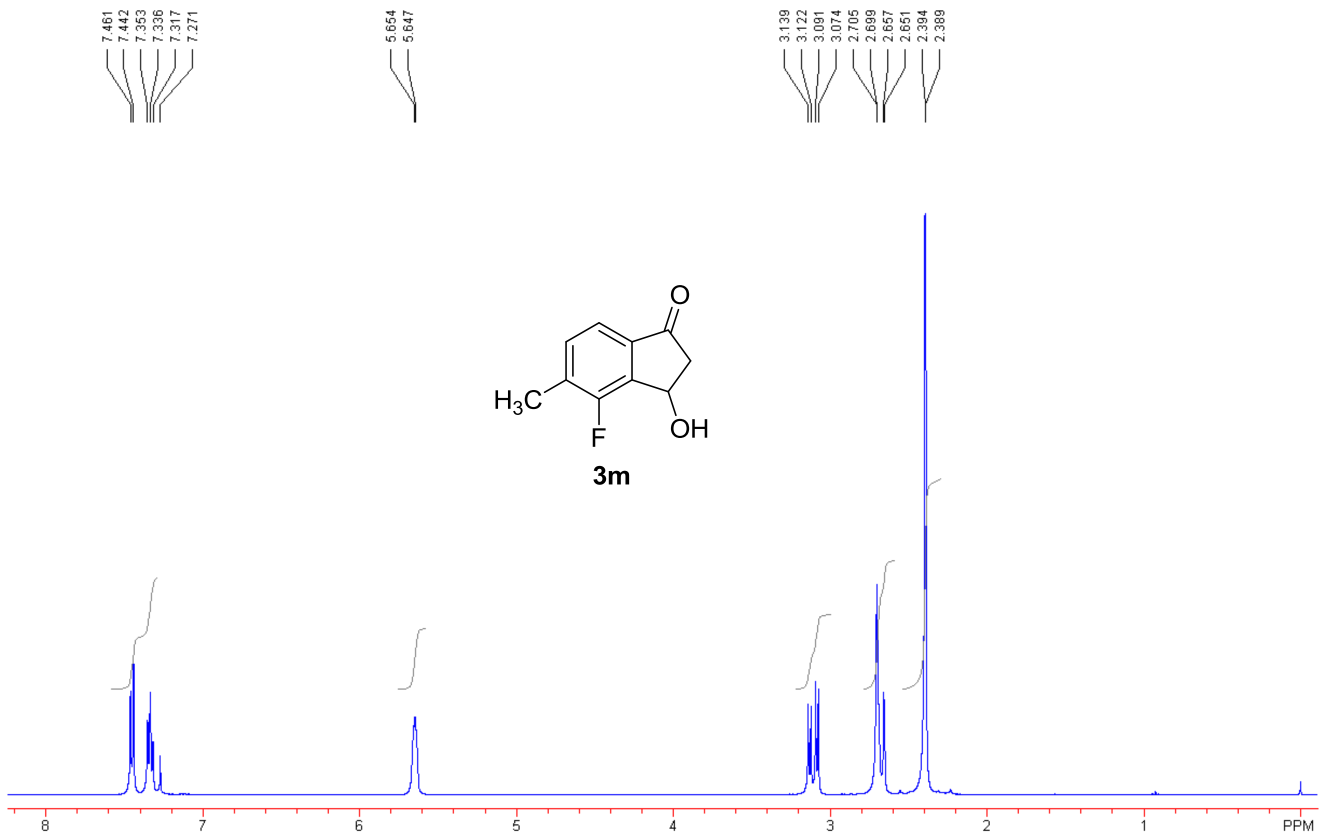
PPM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2.705
2.699
2.657
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O
H3C
F
OH
3m
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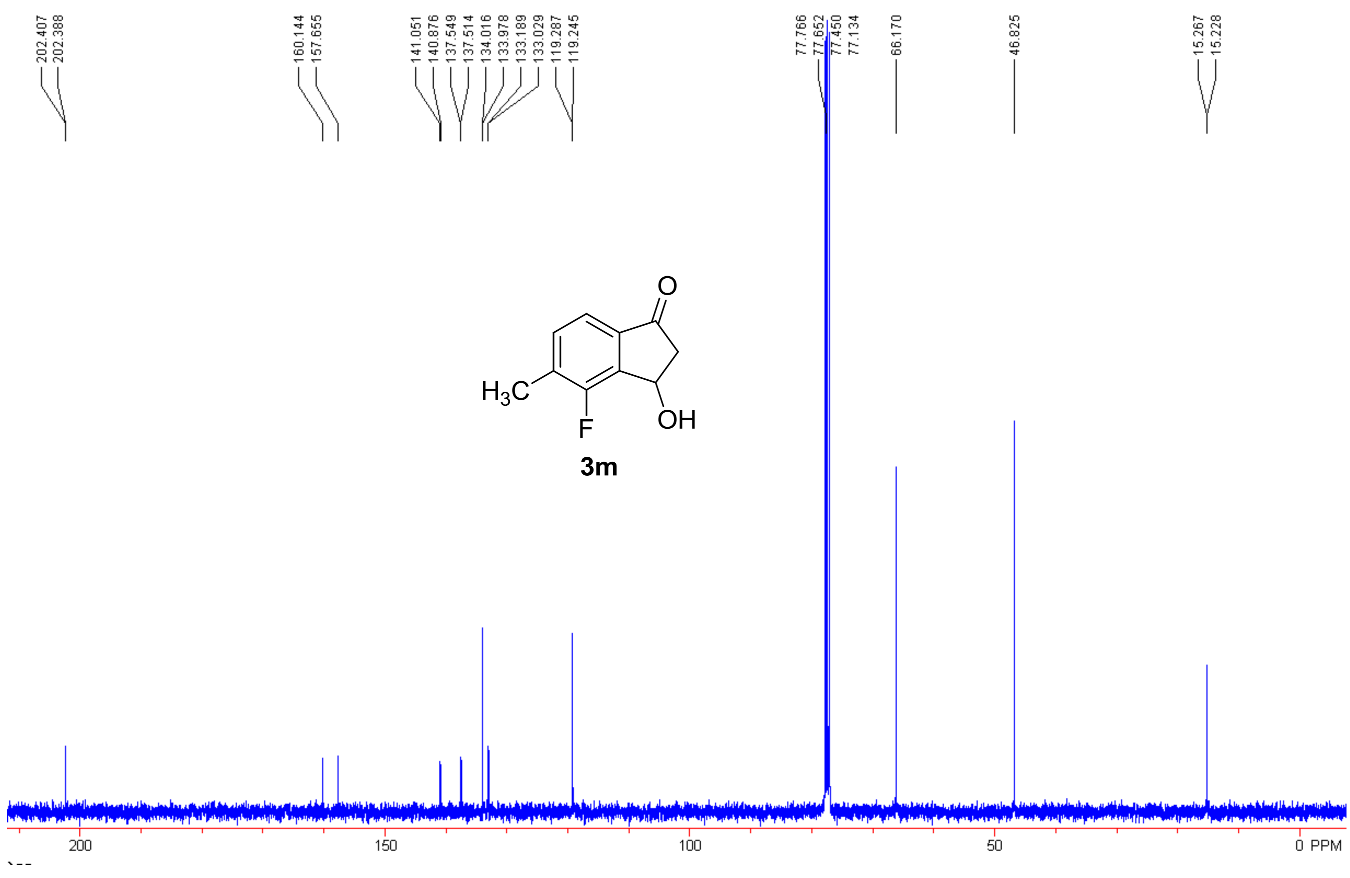
PPM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OH
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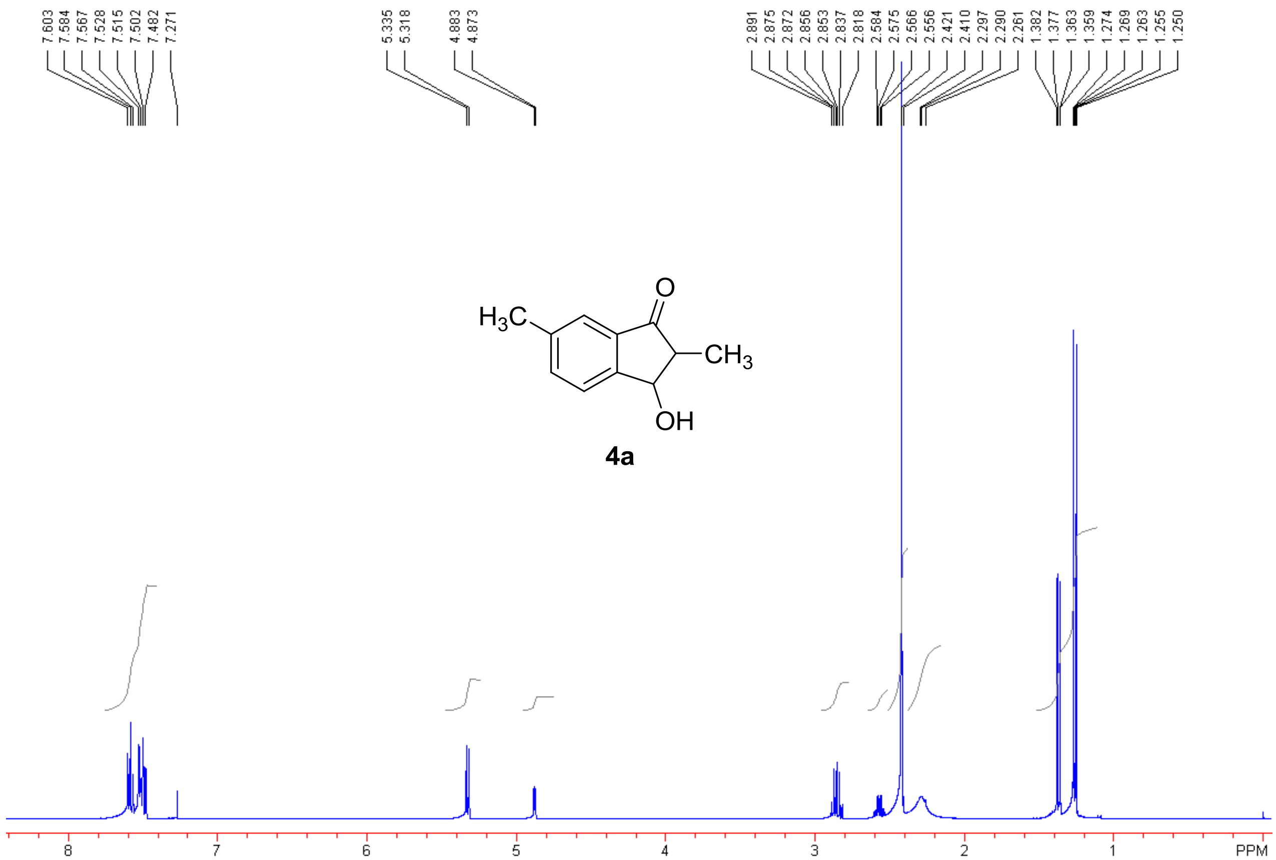
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2.872
2.856
2.853
2.837
2.818
2.584
2.575
2.566
2.556
2.421
2.410
2.297
2.290
2.261
1.382
1.377
1.363
1.359
1.274
1.269
1.263
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H_3C
O
CH_3
OH
4a
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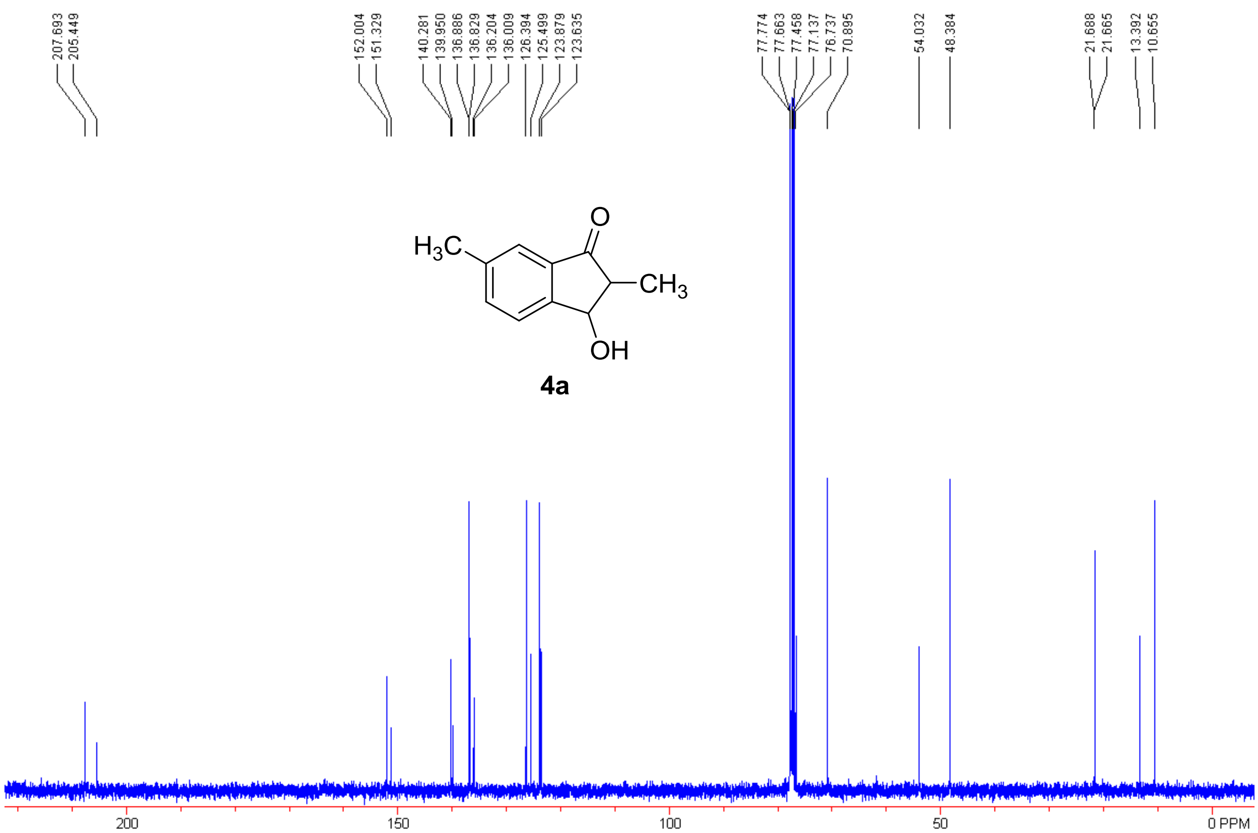
6
5
4
3
2
1
PPM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123.635
77.774
77.663
77.458
77.137
76.737
70.895
54.032
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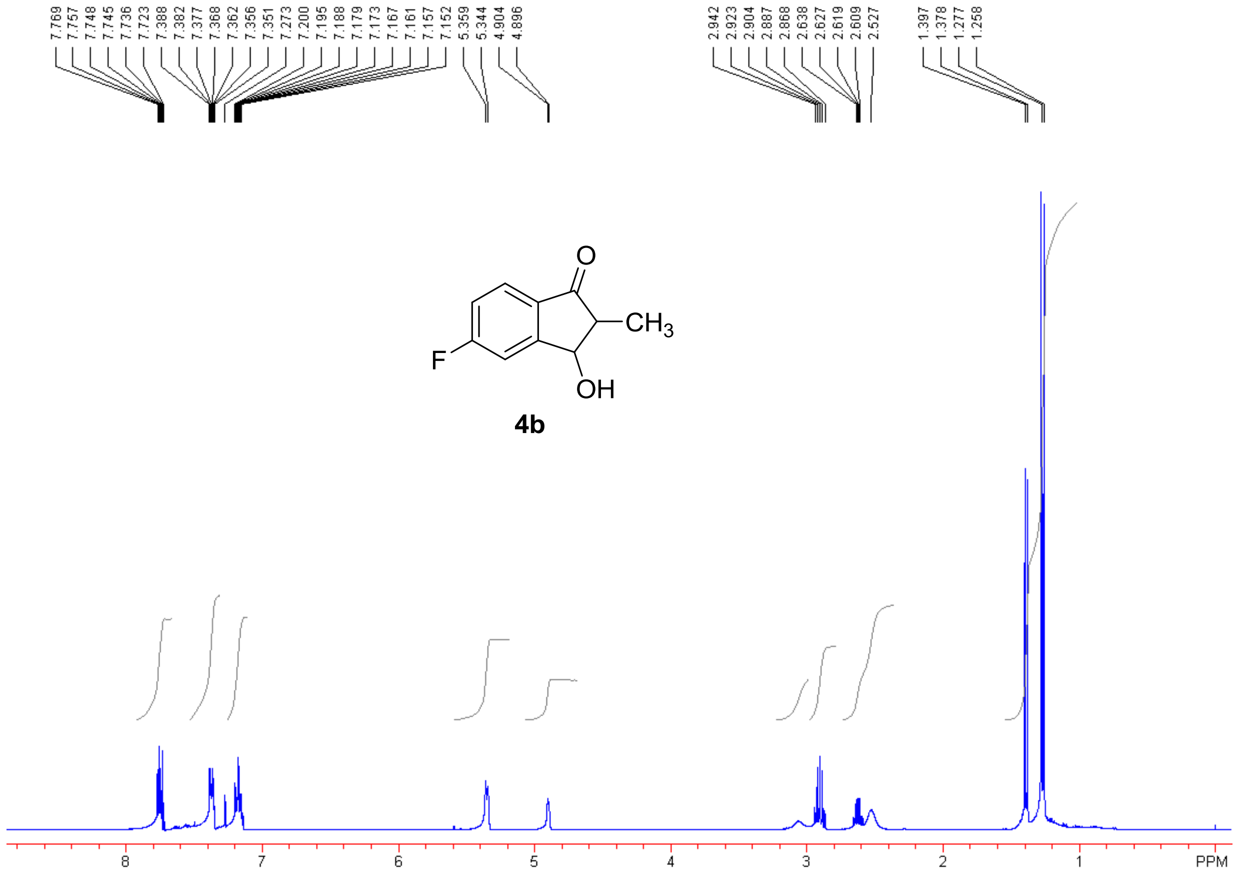
13.392
10.655
H_3C
O
CH_3
OH
4a
200
150
100
50
0 PPM



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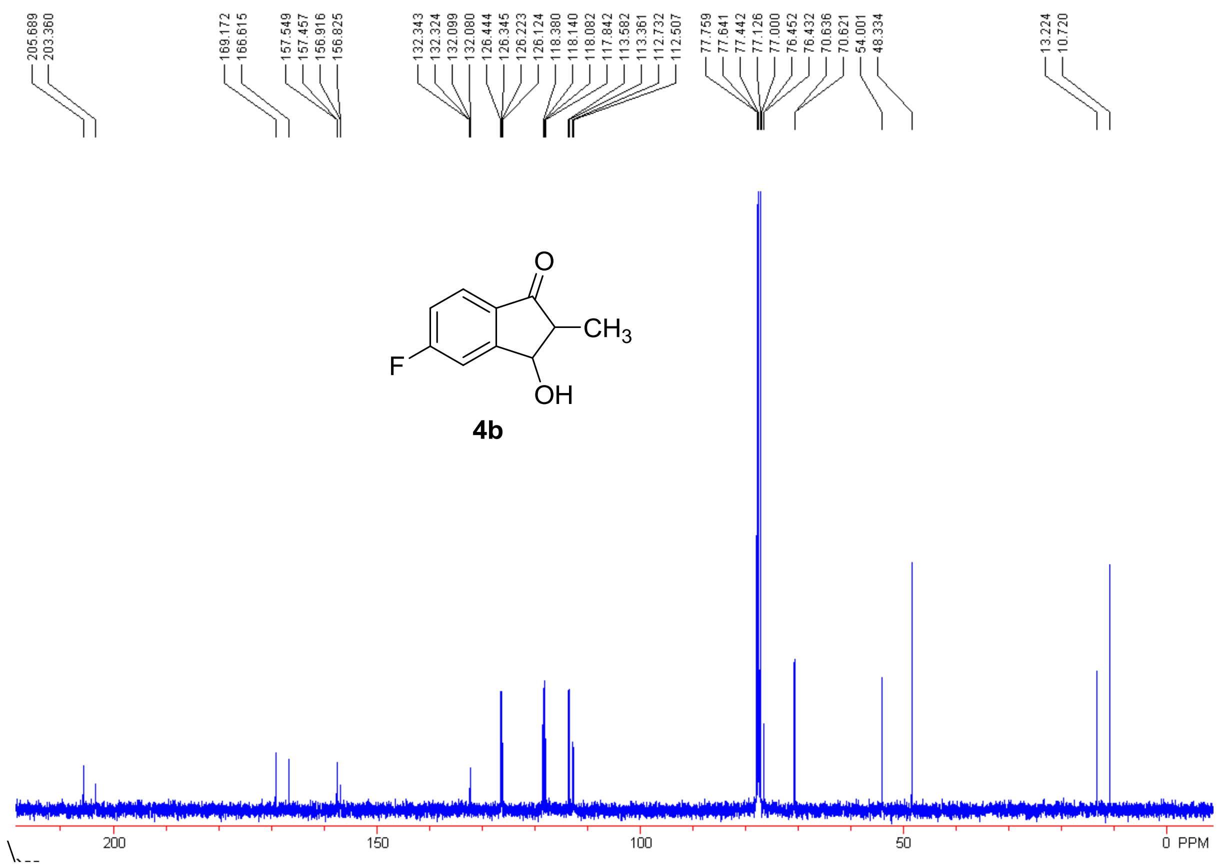

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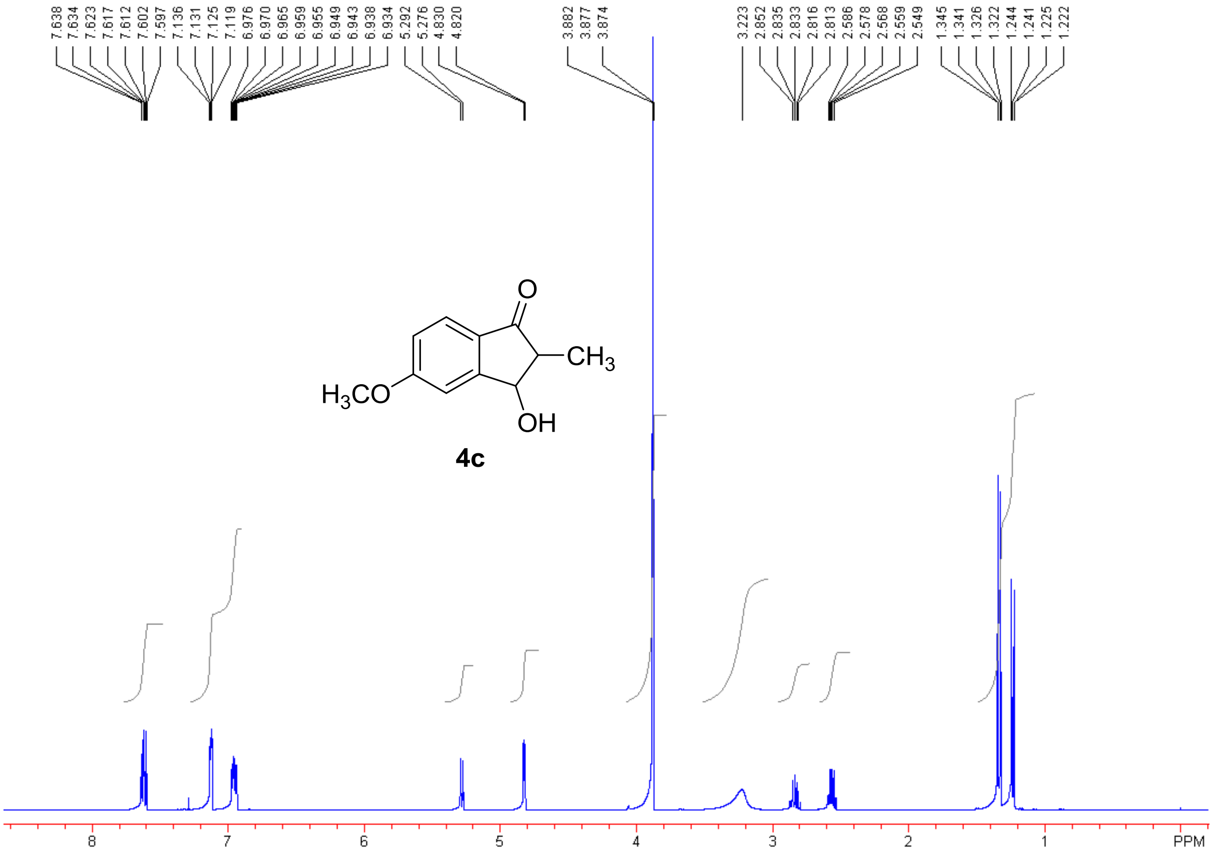
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6.970
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6.959
6.955
6.949
6.943
6.938
6.934
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4.820
3.882
3.877
3.874
3.223
2.852
2.835
2.833
2.816
2.813
2.586
2.578
2.568
2.559
2.549
1.345
1.341
1.326
1.322
1.244
1.241
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O
CH_3
H_3CO
OH
4c
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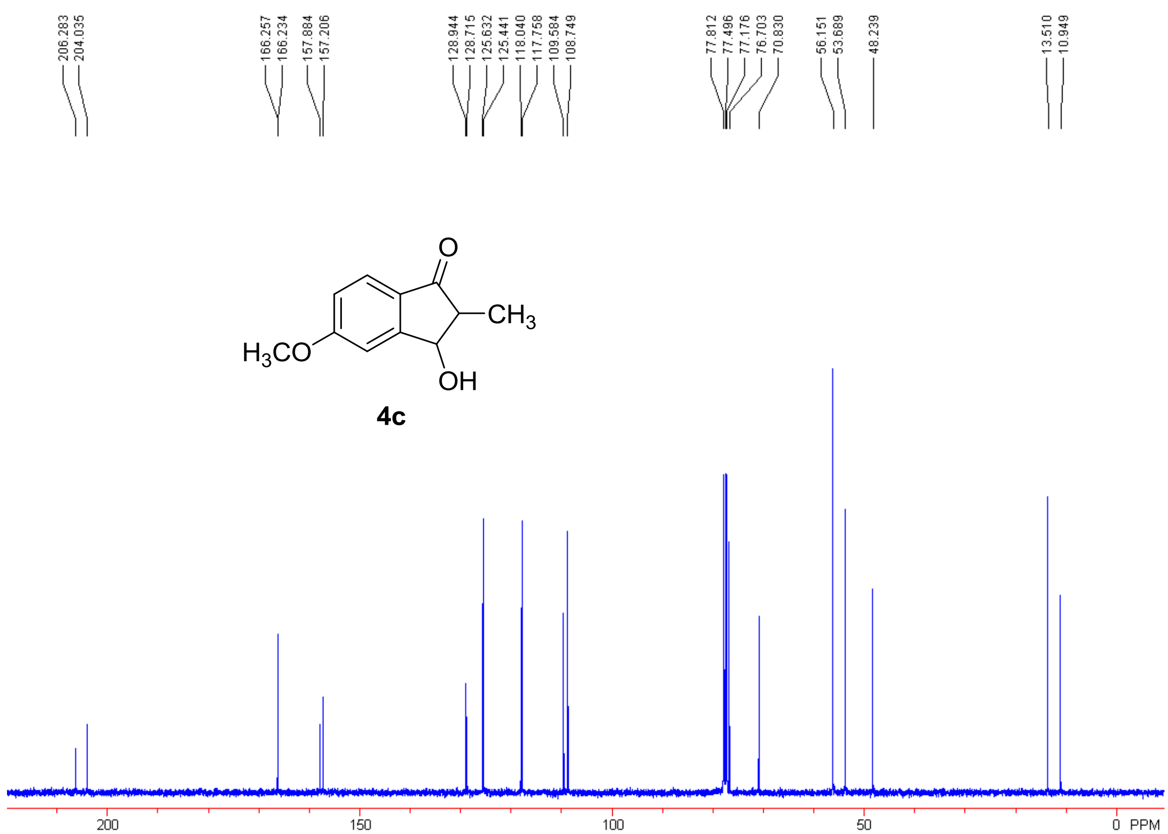
7
6
5
4
3
2
1
PPM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77.812
77.496
77.176
76.703
70.830
56.151
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O
CH_3
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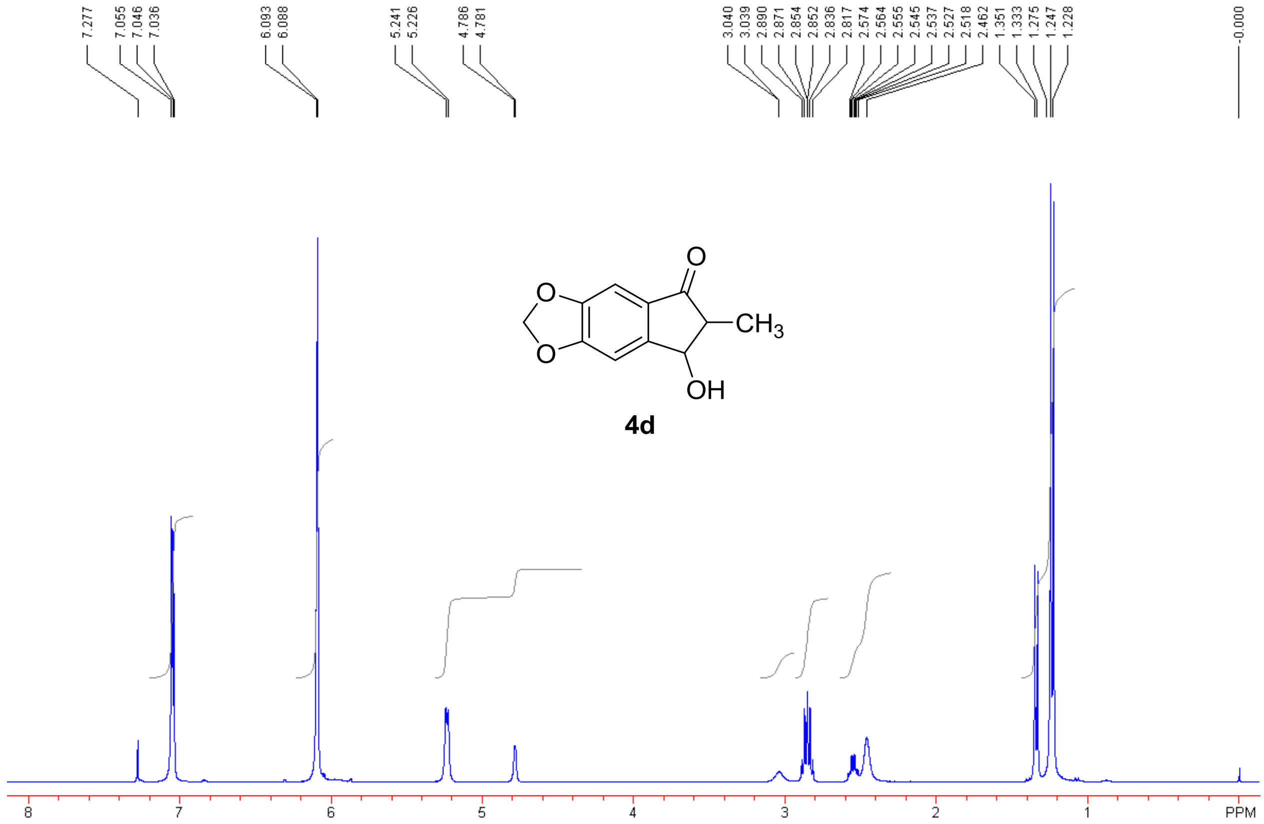
200
150
100
50
0 PPM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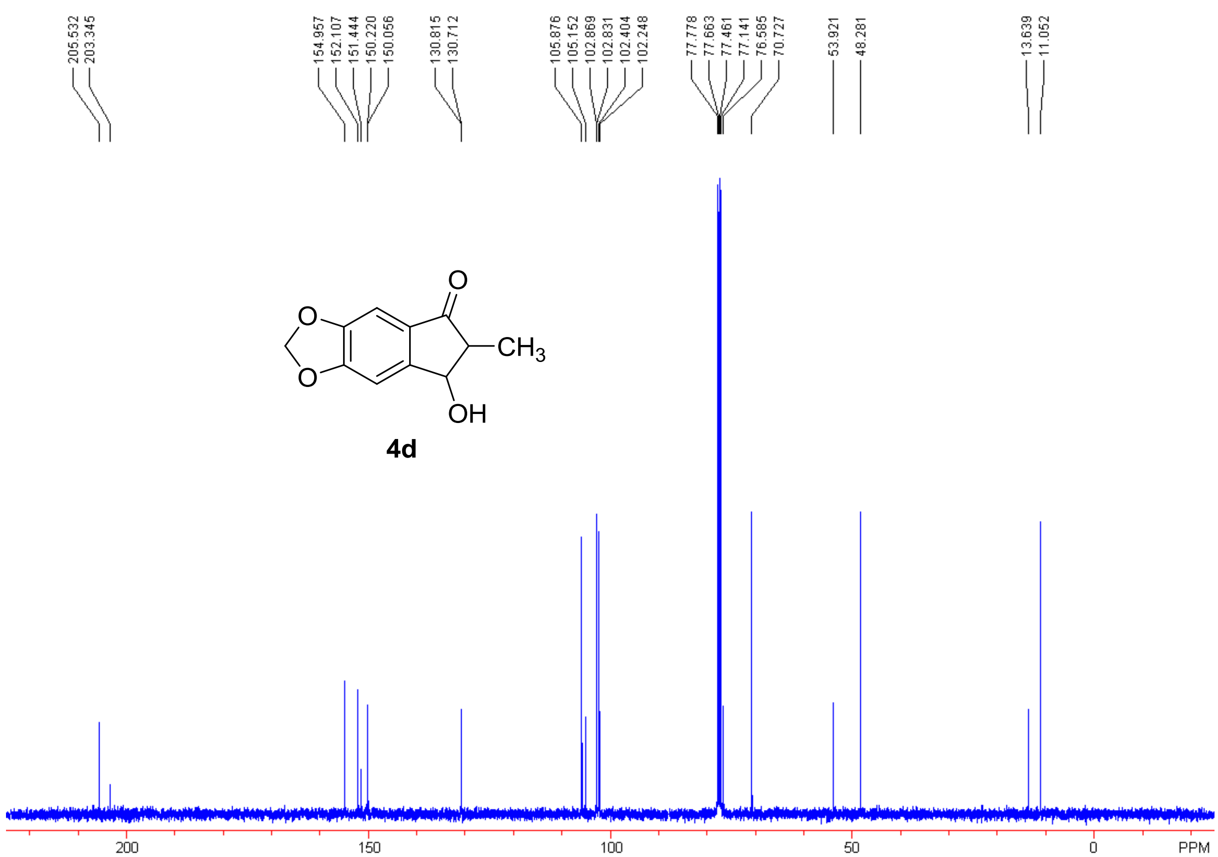
CH3
OH
4d
8 7 6 5 4 3 2 1 PPM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105.876 105.152 102.869 102.831 102.404 102.248
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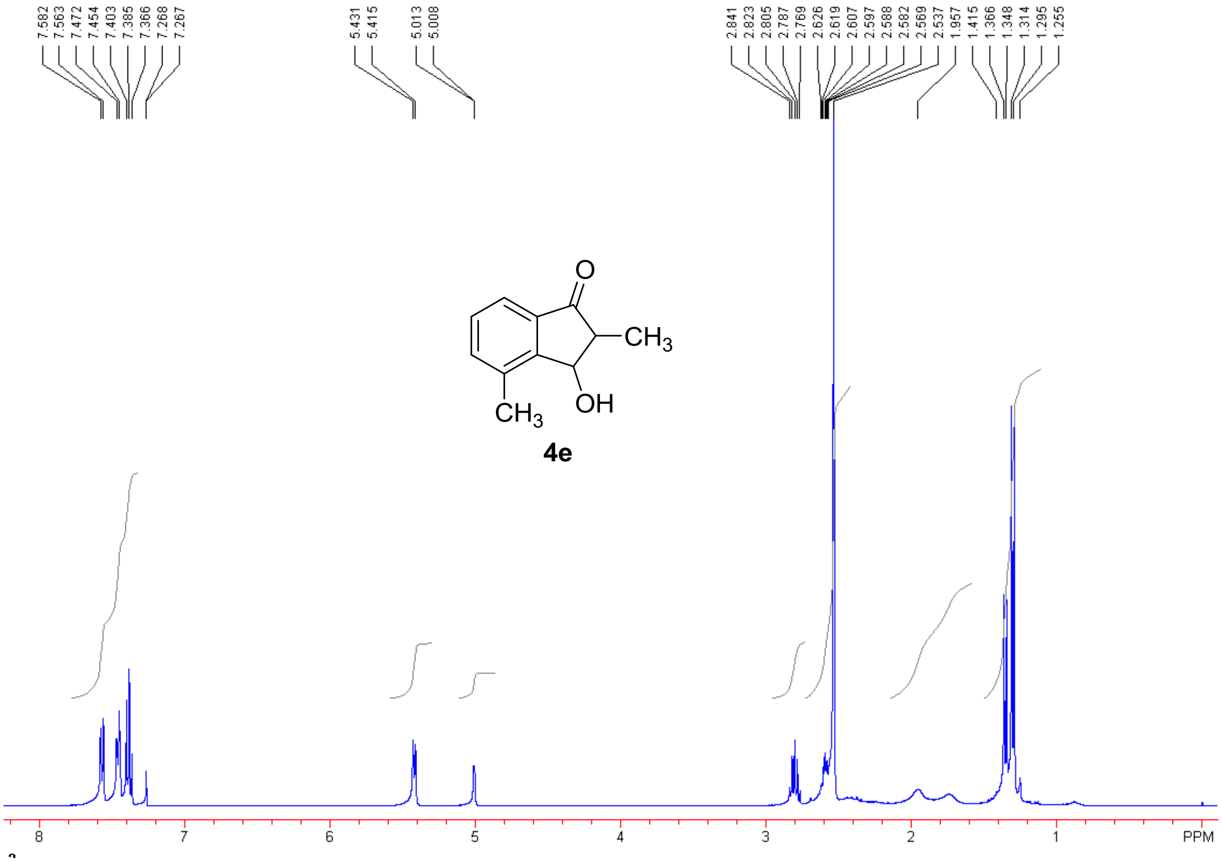
13.639 11.052
O
CH3
OH
4d
200 150 100 50 0 PPM



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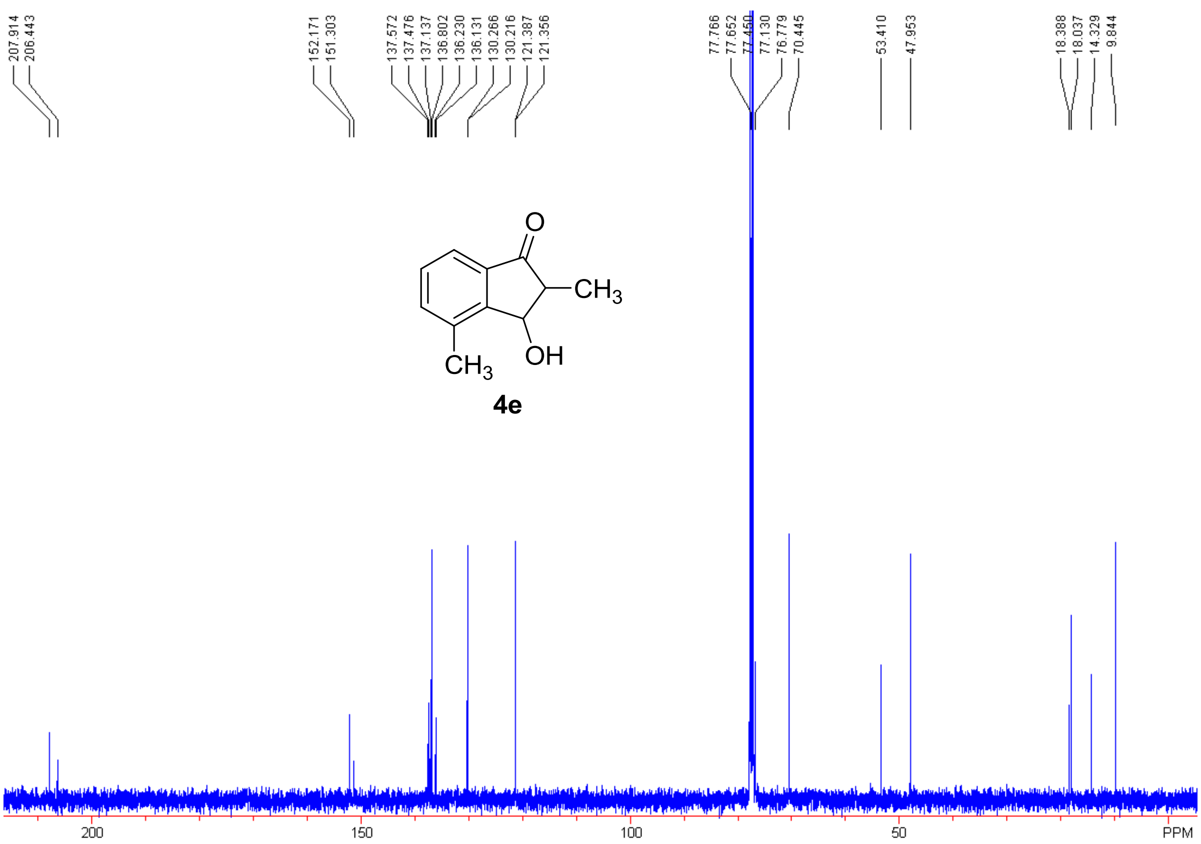

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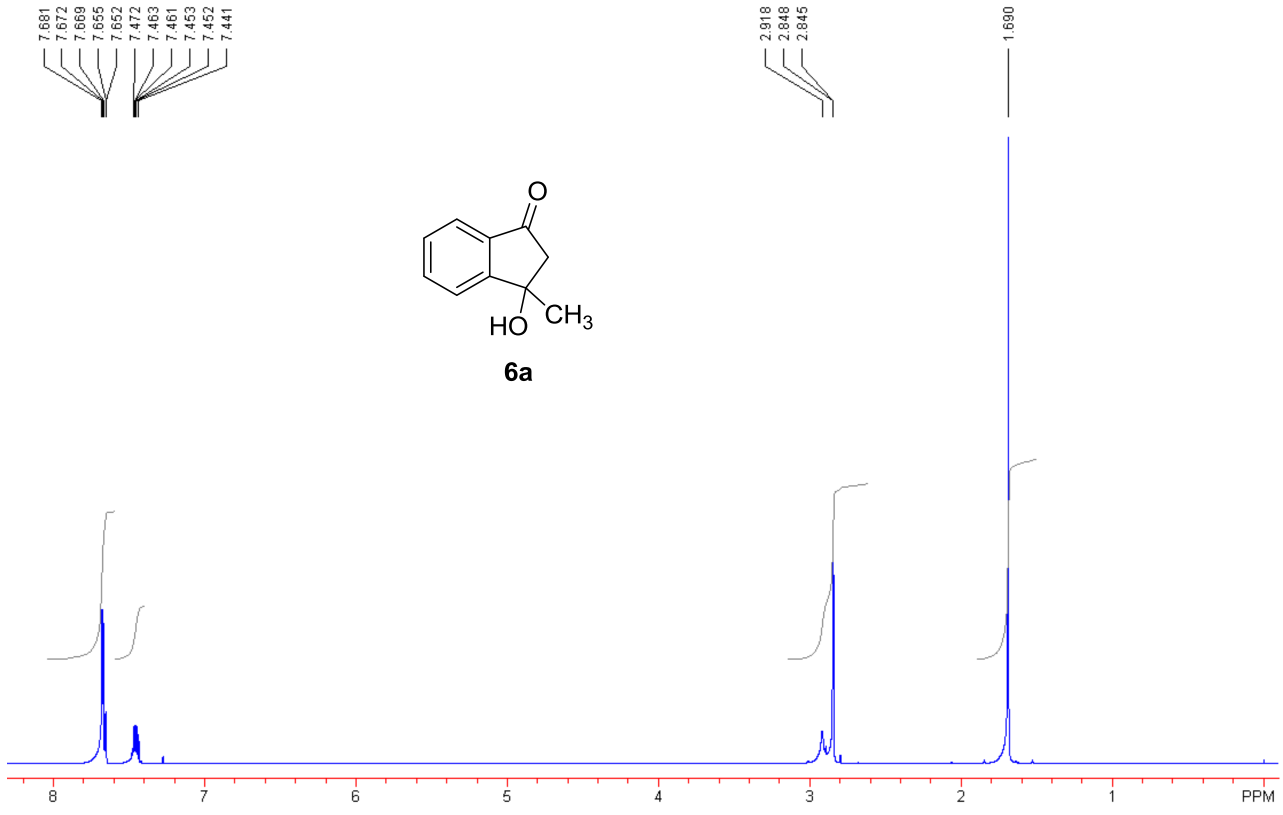
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7
6
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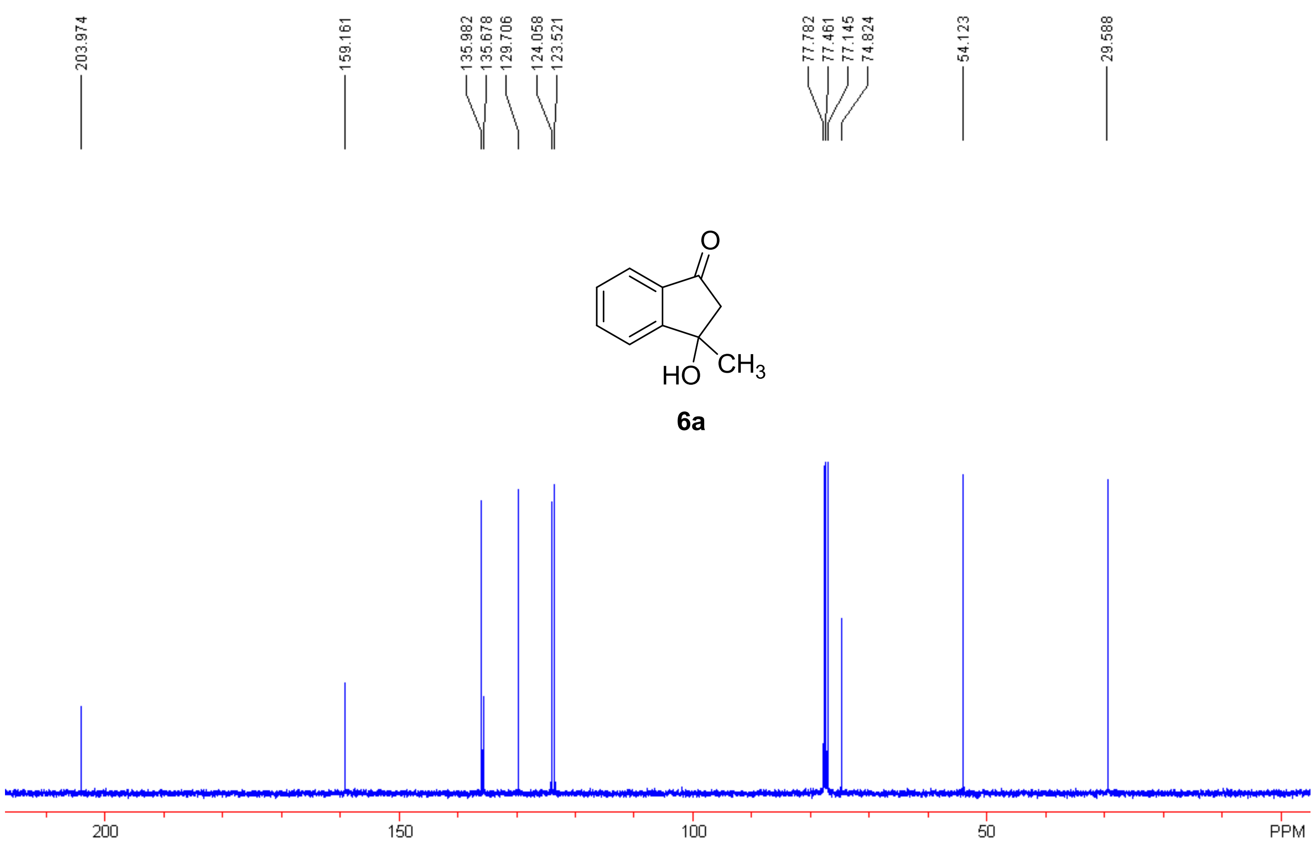
3
2
1
PPM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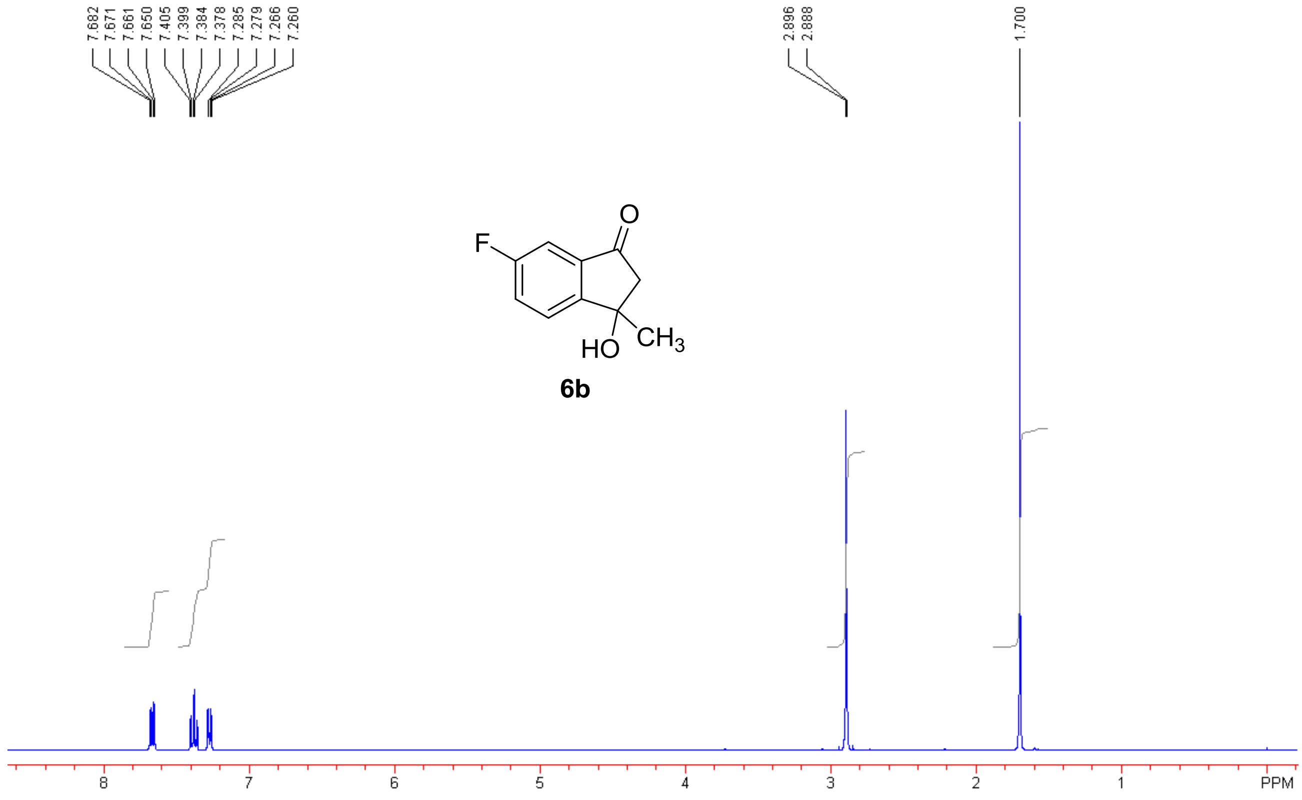
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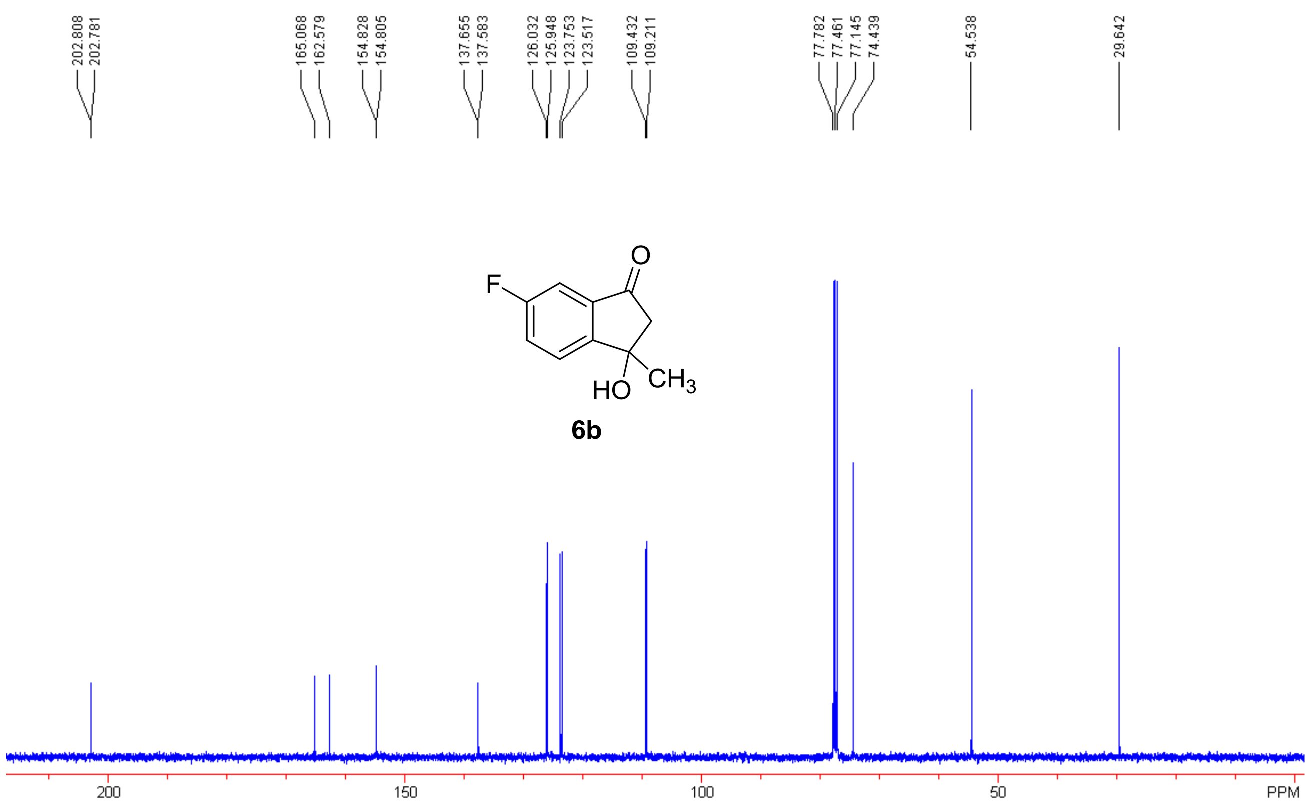
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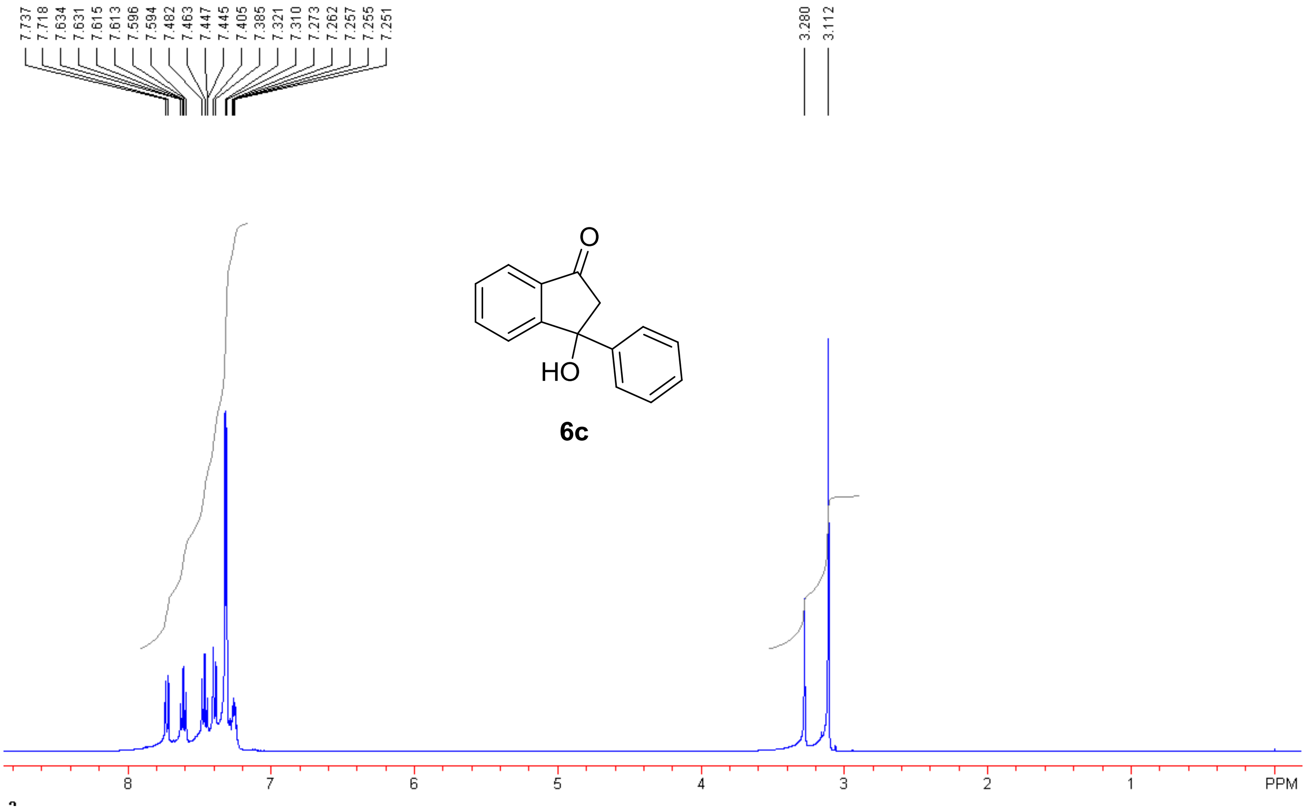
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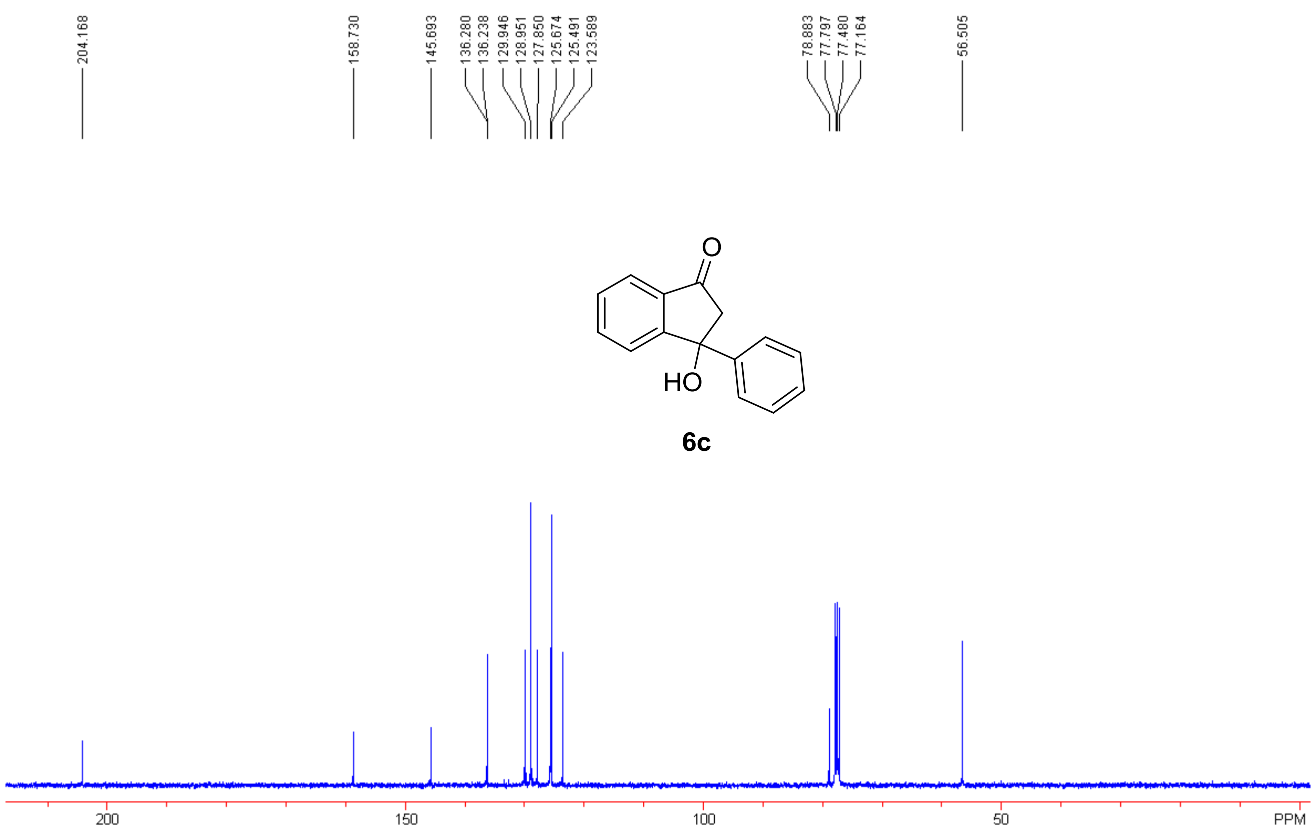
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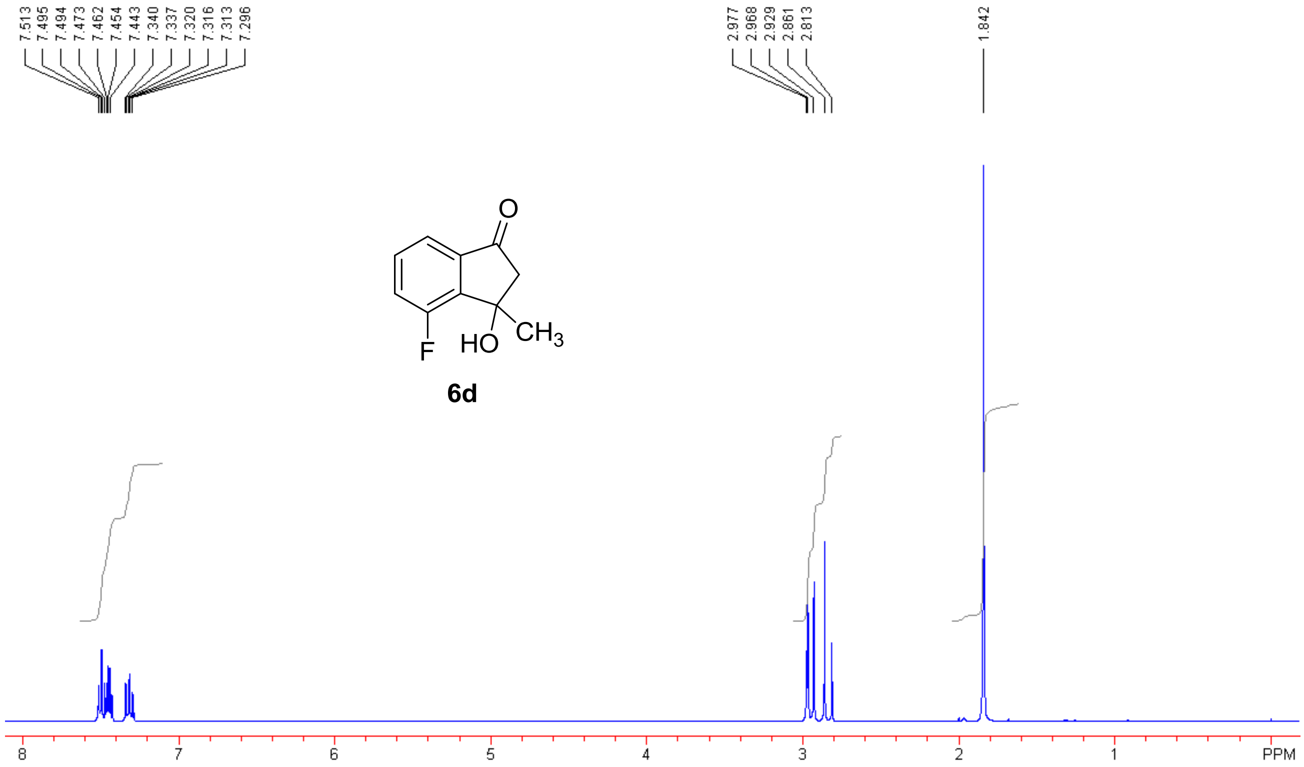

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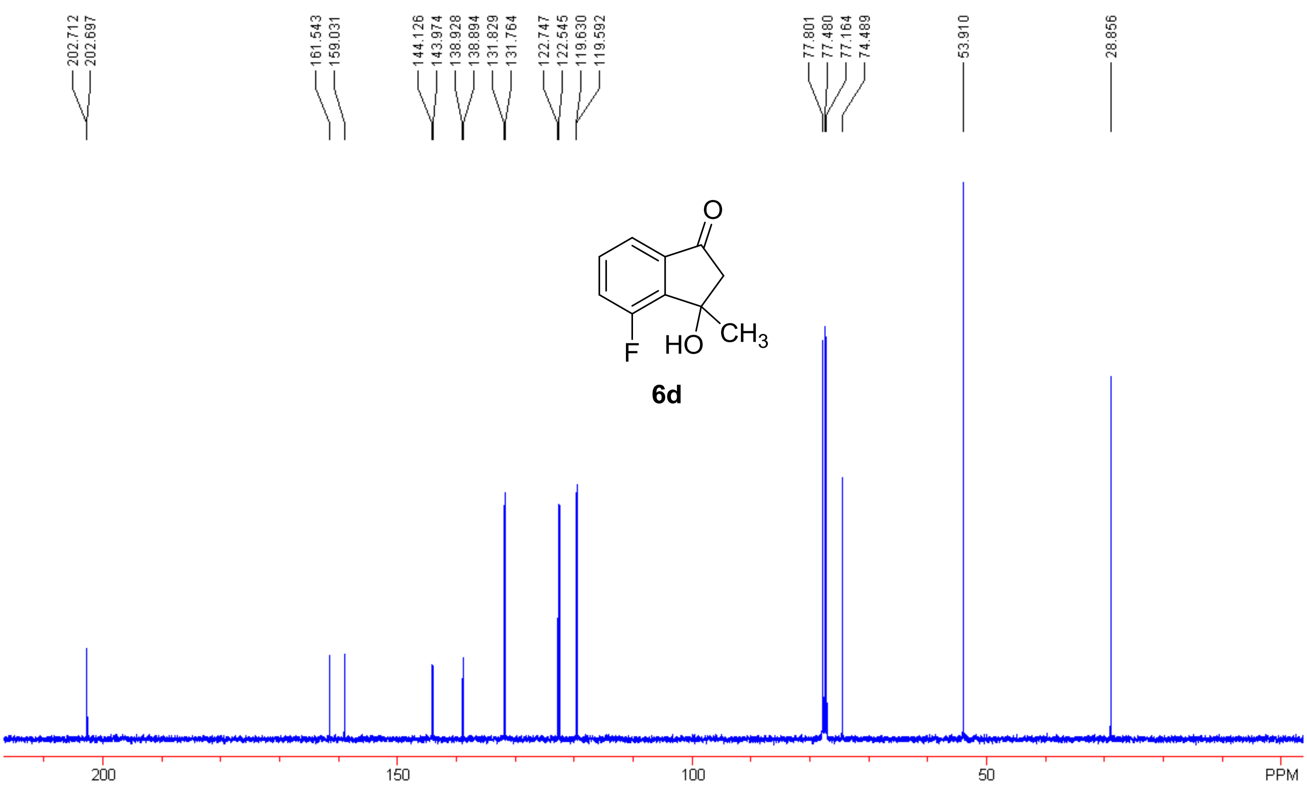

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O
F
HO
CH3
6d
200
150
100
50
PPM