Electronic Supporting Information

Perfectly Double Roles of CF_3 Group in Activating Substrates and Stabilizing Adducts: Chiral Brønsted Acid-Catalyzed Direct Arylation of Simple Trifluoromethyl Ketones

Jing Nie,[a] Guang-Wu Zhang,[a] Lian Wang,[a] Aiping Fu,[c] Yan Zheng,[a] Jun-An Ma[*a, b]

[a] Department of Chemistry, Tianjin University, Tianjin 300072, China. [b] State Key Laboratory of Elemento-Organic Chemistry, Tianjin 300071, China.[c] Instituted for Computational Science and Engineering, Qingdao University, Shandong, Qingdao 266071, China

General information

NMR were recorded on Varian Mercury Plus 500 and 400 instruments at 500 MHz or 400 MHz (^{1}H NMR), 125 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CF_3COOH, respectively. MS were recorded on a VG-7070E or HP 5988A spectrometer using the EI method. HPLC analyses were carried out on a Hewlett Packard Model HP 1200 instrument.

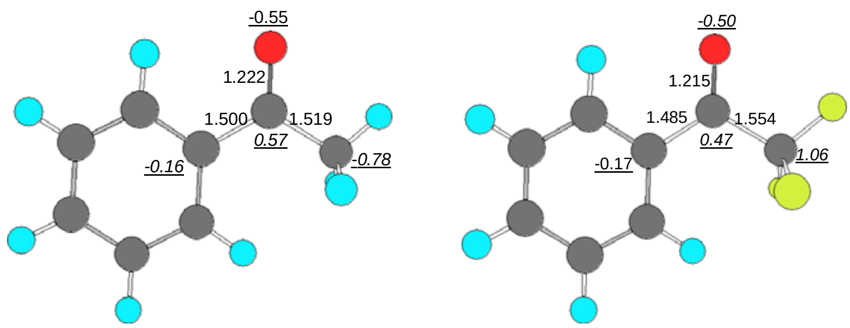
Experimental section

Unless otherwise noted, all commercially available compounds and solvents were used as provided without further purification. All trifluoroacetophenone substrares were prepared by previous method.[1] The chiral phosphoric acids[2] and N-triflyl phosphoramides[3] were synthesized according to the literatures.

Theoretical study

Calculations were performed using the Gaussian 03 Program.[4] Geometries were optimized by the B3LYP[5] method with the 6-31G** basis set. Population analyses were performed by the natural bond orbital method at the same level.

Figure SI. The 3D structures of acetophenone and trifluoroacetophenone. Bond lengths are in Å and NPA charges are also listed with underline and in italic type.



LUMO (π* $_{C=O}$) **-1.48 *eV*** ***-2.25 eV***

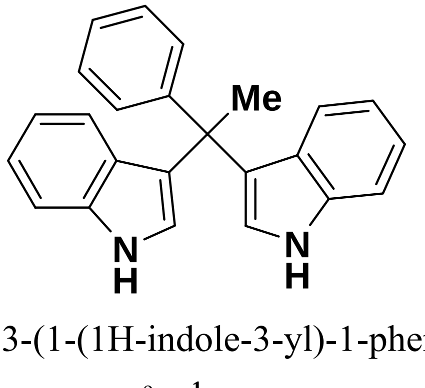
Note: Figure SI shows the significant changes of the carbonyl functionality resulting from the F-substitute: (i) the C1-O bond length decreases (ii) the charges on the carbon and oxygen atoms in the carbonyl group are changed from 0.57 (C) and –0.55 (O), to 0.47 (C) and –0.55 (O), respectively. (iii) the energy of the LUMO ($\pi^*_{C=O}$) is lowered from -1.48 *eV to -2.25 eV,* which might indicate that trifluoroacetophenone can be more reactive than acetophenone.

Brønsted Acid-catalyzed diarylation of acetophenone:

To a flame-dried reaction tube was added indole (30.4 mg, 0.26 mmol), acetophenone (37.0 mg, 0.31 mmol), chiral phosphoric acid (9.7 mg, 0.013 mmol), and solvent (CH_2Cl_2, 0.3 mL). After the solution was stirred for 168 h at room temperature (25 ^oC), the crude product was purified directly by flash column chromatography with ethyl acetate/petroleum ether (1:10 to 1:5) to afford the bisindole product (42.3 mg, 96.8% yield). (Notes: no any product was observed at 0 ^oC for 168 h).

Brønsted Acid-catalyzed arylation of 1-(1H-indole-3-yl)-1-phenylethanol:

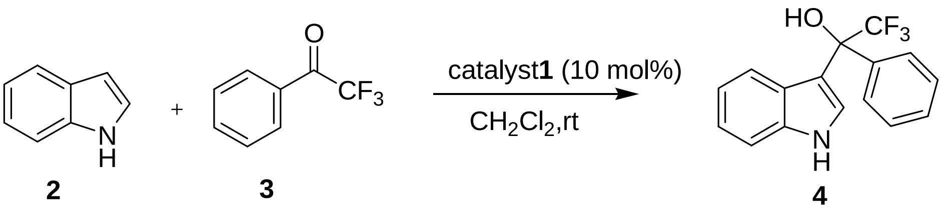
To a flame-dried reaction tube was added indole (20.0 mg, 0.17 mmol), 1-(1H-indole-3-yl)-1-phenylethanol [6] (40.3 mg, 0.17 mmol), chiral phosphoric acid **1** or N-triflyl phosphoramide (0.0085 mmol), and solvent (CH_2Cl_2, 0.3mL). After the solution was stirred for 10 min, the reaction was complete. The crude product was purified directly by flash column chromatography with ethyl acetate/petroleum ether (1:10 to 1:5) to afford the bisindole product in quantitative yield (57.1 mg).

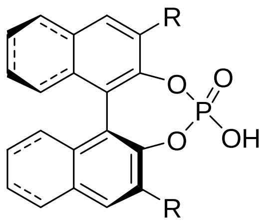


3-(1-(1H-indole-3-yl)-1-phenylyl)-1H-indole

mp: 82-84 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] 7.90 (br, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.34 (dd, *J* = 8.0, 5.5 Hz, 4H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.65 (d, *J* = 2.5 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 148.3, 137.3, 128.3, 128.0, 126.7, 126.1, 124.9, 123.6, 122.3, 121.7, 119.1, 111.4, 44.0, 29.0; **IR** (KBr) ν (cm^{-1}) 3412, 3053, 2918, 2849, 1597, 1456, 1415, 1338, 1245, 1100, 1011, 909, 741, 701 cm^{-1}; **MS (ESI)** m/z 335.6 $[M-H]^-$ (100%).

Screening of catalysts for the model reaction





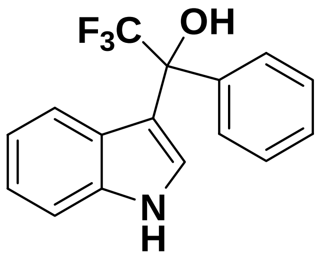
1a: R = Ph
1b: R = $SiPh_3$
1c: R = 3,5-$(CF_3)_2C_6H_3$
1d: R = 9-Anthracenyl
1e: R = 9-Phenanthryl
1f : R = 4-Biphenyl
1g: R = 2-Naphthyl
1h: R = 2,4,6-(i-Pr)$_3C_6H_2$
1i : R = 4-adamantyl, 2,6-(i-Pr)$_2C_6H_2$
1j : R = Ph[H_8]
1k: R = 3,5-$(CF_3)_2C_6H_3$[H_8]

Entry[a]	Catalyst	Time (h)	Yield [%][b]	ee [%][c]
1	**1a**	240	19	33
2	**1b**	240	19	15
3	**1c**	240	19	9
4	**1d**	144	41	46
5	**1e**	144	37	36
6	**1f**	144	40	26
7	**1g**	144	48	28
8	**1h**	48	99	92
9	**1i**	96	86	83
10	**1j**	240	29	27
11	**1k**	240	16	12

[a] The reaction employed a molar ratio of **2**:**3 = 1:1.2** (equiv), with a concentration of **2** being 0.56 M. [b] Isolated yield. [c] Enantiometric excess was determined by chiral HPLC analysis

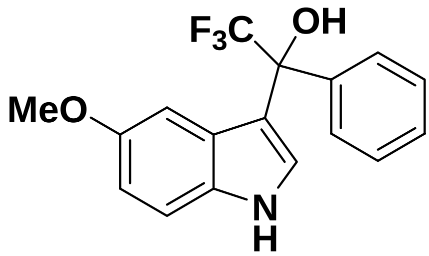
General Procedure for the Catalytic Asymmetric Arylation Reaction of Indoles with Trifluoromethyl ketones

To a flame-dried reaction tube was added indole (0.17 mmol), trifluoroacetophenone (0.21 mmol), chiral phosphoric acid **1** (0.0085 mmol), and solvent (CH_2Cl_2, 0.3mL). After the solution was stirred for the stated time, the crude product was purified directly by flash column chromatography with ethyl acetate/petroleum ether (1:10 to 1:5) to afford the desired product.



2,2,2-trifluoro-1-(1H-indole-3-yl)-1-phenylethanol

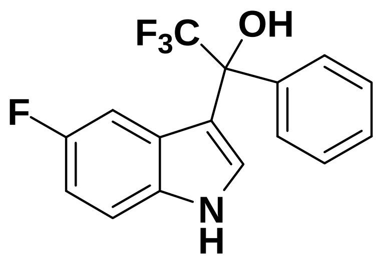
> 99% yield, mp: 82-84 ^oC; $[\alpha]_D^{20}$ = +78.2 (c 1.0, CH_2Cl_2); 92% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t (major) = 8.149 min, t (minor) = 10.826 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.1 (s, 3F); **^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] 8.26 (br, 1H), 7.61-7.59 (m, 2H), 7.49-7.48 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.37-7.34 (m, 3H), 7.20-7.15 (m, 2H), 6.97-6.94 (m, 1H), 2.86 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 137.9, 136.5, 128.8, 128.2, 127.9 (d, $^3J_{C\text{-}F}$ = 0.9 Hz), 125.6 (q, $^1J_{C\text{-}F}$ = 284.6 Hz), 125.4, 123.5 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 123.0, 121.2, 120.5, 114.3, 111.5, 77.3 (q, $^2J_{C\text{-}F}$ = 29.5 Hz); **IR** (KBr) ν (cm^{-1}) 3535, 3503, 3402, 1544, 1461, 1449, 1273, 1164, 1042, 937, 752 cm^{-1}; **MS (ESI)** m/z 290.05 $[M\text{-}H]^-$ (100%).



2,2,2-trifluoro-1-(5-methoxy-1H-indole-3-yl)-1-phenylethanol

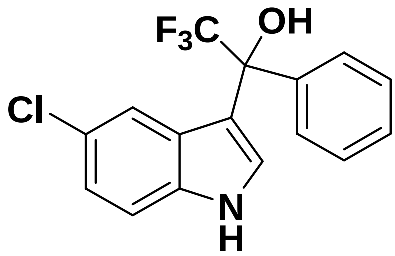
> 99% yield, mp: 120-121 ^oC; $[\alpha]_D^{20}$ = +14.5 (c 1.0, CH_2Cl_2); 92% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t (major) = 8.990 min,

t (minor) = 10.963 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.2 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.16 (br, 1H), 7.61-7.59 (m, 2H), 7.45-7.44 (m, 1H), 7.36-7.34 (m, 3H), 7.26 (d, *J* = 9.0 Hz, 1H), 6.82 (dd, *J* = 6.5, 2.5 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 3.57 (s, 3H), 2.84 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 154.2, 137.9, 131.5, 128.7, 128.2, 127.9 (d, $^3J_{C\text{-}F}$ = 0.9 Hz), 126.0, 125.6 (q, $^1J_{C\text{-}F}$ = 284.6 Hz), 124.0 (q, $^3J_{C\text{-}F}$ = 2.9 Hz), 114.0, 113.3, 112.1, 102.7, 77.2 (q, $^2J_{C\text{-}F}$ = 28.3 Hz), 55.8; **IR** (KBr) ν (cm^{-1}) 3429, 2962, 1589, 1488, 1455, 1299, 1212, 1172, 921, 808, 724, 477 cm^{-1}; **MS (ESI)** m/z 320.04 $[M-H]^-$ (100%).



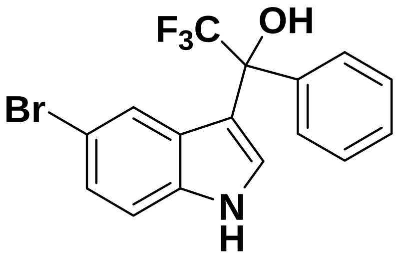
2,2,2-trifluoro-1-(5-fluoro-1H-indole-3-yl)-1-phenylethanol

> 99% yield, mp: 90-91 ^oC; $[\alpha]_D^{20}$ = +45.2 (c 1.0, CH_2Cl_2); 92% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 98/2, 1.0 mL/min, 254 nm; t (minor) = 94.915 min, t (major) = 102.483 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.2 (s, 3F), -123.3 ~ -123.4 (m, 1F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.30 (br, 1H), 7.58-7.56 (m, 2H), 7.51-7.50 (m, 1H), 7.37-7.35 (m, 3H), 7.31-7.28 (m, 1H), 6.94-6.90 (m, 1H), 6.81 (dd, *J* = 7.5, 2.5 Hz, 1H), 2.86 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 157.9 (d, $^1J_{C\text{-}F}$ = 234.4 Hz), 137.5, 133.0, 128.9, 128.3, 127.7 (d, $^3J_{C\text{-}F}$ = 1.0 Hz), 125.9 (q, $^3J_{C\text{-}F}$ = 10.5 Hz), 125.5 (q, $^1J_{C\text{-}F}$ = 284.5 Hz), 125.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 114.6 (d, $^4J_{C\text{-}F}$ = 4.8 Hz), 112.2 (d, $^3J_{C\text{-}F}$ = 9.6 Hz), 111.6 (d, $^2J_{C\text{-}F}$ = 26.5 Hz), 106.2 (d, $^2J_{C\text{-}F}$ = 24.4 Hz), 77.1 (q, $^2J_{C\text{-}F}$ = 29.4 Hz); **IR** (KBr) ν (cm^{-1}) 3465, 2924, 1584, 1486, 1167, 1028, 804, 719 cm^{-1}; **MS (ESI)** m/z 308.06 $[M-H]^-$ (100%).



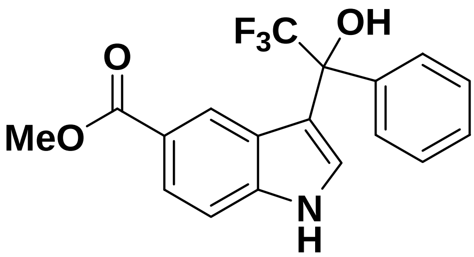
1-(5-chloro-1H-indole-3-yl)-2,2,2-trifluoro-1-phenylethanol

> 99% yield, mp: 104-106 °C; $[\alpha]_D^{20}$ = -7.8 (c 1.0, CH_2Cl_2); 90% ee, [Daicel Chiralcel AD-H, Hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t (major) = 49.317 min, t (minor) = 55.342 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -75.3 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.35 (br, 1H), 7.58-7.57 (m, 2H), 7.46 (s, 1H), 7.38-7.36 (m, 3H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.18-7.17 (m, 1H), 7.13-7.11 (m, 1H), 2.96 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ [ppm] 140.5, 135.1, 134.8, 128.9, 128.5, 127.9 (q, $^{3}J_{C-F}$ = 1.9 Hz), 127.8, 126.2 (q, $^{1}J_{C-F}$ = 284.5 Hz), 121.5, 121.1 (q, $^{3}J_{C-F}$ = 1.4 Hz), 120.1, 110.3, 109.9, 78.9 (q, $^{2}J_{C-F}$ = 30.0 Hz); **IR** (KBr) ν (cm^{-1}) 3478, 3404, 1464, 1290, 1182, 1054, 812, 701 cm^{-1}; **MS (ESI)** m/z 324.10 $[M-H]^-$ (100%), 359.78.



1-(5-bromo-1H-indole-3-yl)-2,2,2-trifluoro-1-phenylethanol

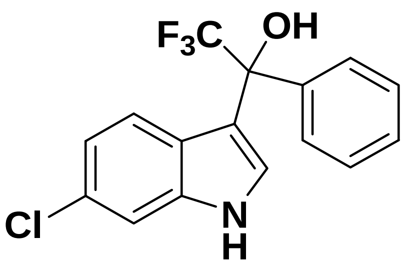
> 52% yield, mp: 108-110 °C; $[\alpha]_D^{20}$ = -12.8 (c 1.0, CH_2Cl_2); 92% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 98/2, 1.0 mL/min, 254 nm; t (major) = 118.983 min, t (minor) = 136.938 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.2 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.33 (br, 1H), 7.57-7.55 (m, 2H), 7.46 (s, 1H), 7.37-7.34 (m, 4H), 7.26 (s, 2H), 2.87 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 137.4, 135.1, 129.0, 128.3, 127.7 (d, $^{3}J_{C-F}$ = 0.9 Hz), 127.2, 126.0, 125.5 (q, $^{1}J_{C-F}$ = 284.6 Hz), 124.5 (q, $^{3}J_{C-F}$ = 2.9 Hz), 123.8, 114.2, 113.8, 112.9, 77.4 (q, $^{2}J_{C-F}$ = 30.0 Hz); **IR** (KBr) ν (cm^{-1}) 3482, 3379, 3067, 2924, 1467, 1288, 1180, 1046, 809, 727 cm^{-1}; **MS (ESI)** m/z 738.47 $[2M-H]^-$ (100%), 370.12 $[M-H]^-$ (82%).



Methyl 3-(2,2,2-trifluoro-1-hydroxy-1-phenylethyl)-1H-indole-5-carboxylate

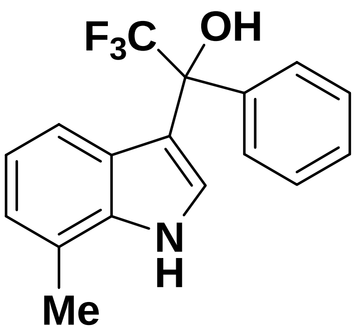
93% yield, mp: 173-175 °C; $[\alpha]_D^{20}$ = +23.2 (c 1.0, CH_2Cl_2); 90% ee, [Daicel Chiralcel

AD-H, Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t (major) = 21.241 min, t (minor) = 32.922 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.1 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.47 (br, 1H), 7.97 (s, 1H), 7.88 (dd, J = 7.0, 2.0 Hz, 1H), 7.60-7.58 (m, 2H), 7.51 (s, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.37-7.35 (m, 3H), 3.82 (s, 3H), 2.94 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ [ppm] 168.2, 139.2, 137.8, 128.9, 128.6, 128.3, 127.7, 125.6 (q, $^1J_{C-F}$ = 284.6 Hz), 125.1, 124.9 (q, $^3J_{C-F}$ = 2.8 Hz), 124.2, 122.4, 115.6, 111.3, 77.2 (q, $^3J_{C-F}$ = 30.0 Hz); **IR** (KBr) ν (cm^{-1}) 3526, 3354, 1699, 1620, 1435, 1279, 1182, 1157, 1044, 749 cm^{-1}; **MS (ESI)** m/z 348.23 $[M-H]^-$ (100%).



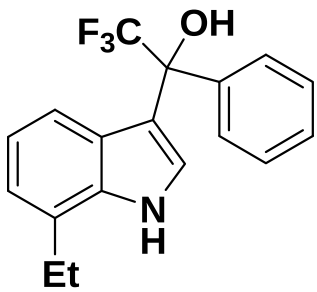
1-(6-chloro-1H-indole-3-yl)-2,2,2-trifluoro-1-phenylethanol

96% yield, mp: 110-111 °C; $[\alpha]_D^{20}$ = +55.4 (c 1.0, CH_2Cl_2); ee 92 %, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 98/2, 1.0 mL/min, 254 nm; t (minor) = 83.007 min, t (major) = 86.323 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.3 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.28 (br, 1H), 7.56-7.54 (m, 2H), 7.47-7.46 (m, 1H), 7.38-7.34(m, 4H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.92-6.90 (m, 1H), 2.85 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 137.6, 136.9, 129.0, 128.9, 128.3, 127.8 (d, $^3J_{C-F}$ = 1.0 Hz), 125.5 (q, $^1J_{C-F}$ = 284.6 Hz), 124.1, 124.0 (q, $^3J_{C-F}$ = 3.0 Hz), 122.1, 121.3, 114.6, 111.4, 77.1 (q, $^2J_{C-F}$ = 30.0 Hz); **IR** (KBr) ν (cm^{-1}) 3504, 3391, 3134, 2923, 1543, 1451, 1269, 1168, 1040, 886, 730 cm^{-1}; **MS (ESI)** m/z 324.14 $[M-H]^-$ (100%).



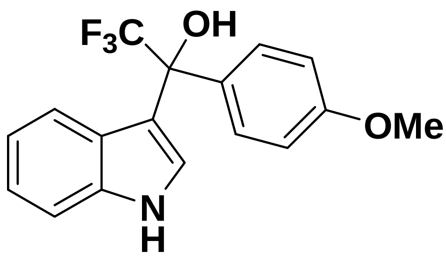
2,2,2-trifluoro-1-(7-methyl-1H-indole-3-yl)-1-phenylethanol

> 99% yield, mp: 89-90 °C; $[\alpha]_D^{20}$ = +75.5 (c 1.0, CH_2Cl_2); 95% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t (major) = 6.335 min, t (minor) = 10.299 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.1 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.20 (br, 1H), 7.62-7.61 (m, 2H), 7.47 (s, 1H), 7.37-7.36 (m, 3H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 8.0 Hz, 1H), 2.92 (s, 1H), 2.51 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 138.0, 136.1, 128.7, 128.2, 127.9 (d, $^3J_{C-F}$ = 0.9 Hz), 125.6 (q, $^1J_{C-F}$ = 284.6 Hz), 124.9, 123.5, 123.2 (q, $^3J_{C-F}$ = 3.0 Hz), 120.7, 118.9, 114.8, 77.3 (q, $^2J_{C-F}$ = 29.5 Hz), 16.8; **IR** (KBr) ν (cm^{-1}) 3419, 3059, 2924, 1618, 1547, 1496, 1271, 1159, 1045, 885, 753, 725, 518 cm^{-1}; **MS (ESI)** m/z 304.24 $[M-H]^-$ (100%).



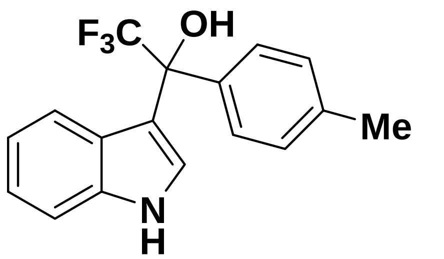
2,2,2-trifluoro-1-(7-ethyl-1H-indole-3-yl)-1-phenylethanol

> 99% yield, mp: 80-81 °C; $[\alpha]_D^{20}$ = +89.2 (c 1.0, CH_2Cl_2); 98% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t (major) = 8.493 min, t (minor) = 14.094 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.1 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.23 (br, 1H), 7.61-7.59 (m, 2H), 7.49-7.48 (m, 1H), 7.35-7.34 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 2.90-2.86 (m, 3H), 1.38 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 138.0, 135.4, 128.7, 128.2, 127.9, 126.9, 125.6 (q, $^1J_{C-F}$ = 284.6 Hz), 125.1, 123.1 (q, $^3J_{C-F}$ = 2.9 Hz), 121.5, 120.8, 118.9, 114.7, 77.3 (q, $^2J_{C-F}$ = 29.3 Hz), 24.1, 14.0; **IR** (KBr) ν (cm^{-1}) 3425, 3060, 2967, 1547, 1495, 1455, 1270, 1157, 1036, 884, 725 cm^{-1}; **MS (ESI)** m/z 318.31 $[M-H]^-$ (100%).



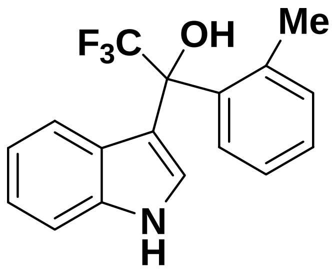
2,2,2-trifluoro-1-(1H-indole-3-yl)-1-(4-methoxyphenyl)ethanol

>99% yield, mp: 49-50 ^oC; $[\alpha]_D^{20}$ = +46.6 (c 1.0, CH_2Cl_2); 87% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; t (major) = 20.341 min, t (minor) = 25.808 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.3 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.26 (br, 1H), 7.50-7.46 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.20-7.17 (m, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 2.83 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 159.8, 136.5, 130.1, 129.2, 125.7 (q, $^1J_{C-F}$ = 284.4 Hz), 125.5, 123.5 (q, $^3J_{C-F}$ = 3.0 Hz), 122.9, 121.3, 120.4, 114.3, 113.5, 111.5, 77.0 (q, $^2J_{C-F}$ = 29.5 Hz), 55.4; **IR** (KBr) ν (cm^{-1}) 3416, 2919, 2851, 1611, 1513, 1459, 1253, 1159, 1038, 829, 745, 593 cm^{-1}; **MS (ESI)** m/z 320.4 $[M-H]^-$ (100%).



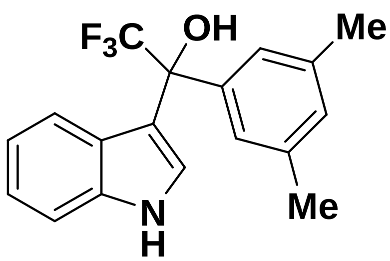
2,2,2-trifluoro-1-(1H-indole-3-yl)-1-*p*-tolylethanol

> 99% yield, mp: 102-103 ^oC; $[\alpha]_D^{20}$ = +56.8 (c 1.0, CH_2Cl_2); 91% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t (major) = 11.763 min, t (minor) = 14.055 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.3 (s, 3F); **^{1}H NMR** (400MHz, $CDCl_3$) δ [ppm] 8.27 (br, 1H), 7.48-7.46 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.19-7.14 (m, 4H), 6.96 (t, *J* = 7.2 Hz, 1H), 2.88 (s, 1H), 2.35 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 138.5, 136.5, 135.0, 128.9, 127.7 (d, $^3J_{C-F}$ = 0.9 Hz), 125.6 (q, $^1J_{C-F}$ = 284.5 Hz), 125.5, 123.4 (q, $^3J_{C-F}$ = 3.0 Hz), 122.9, 121.3, 120.5, 114.4, 111.4, 77.2 (q, $^2J_{C-F}$ = 29.2 Hz), 21.4; **IR** (KBr) ν (cm^{-1}) 3587, 3415, 3142, 2924, 1547, 1456, 1279, 1152, 1038, 922, 812, 749, 588 cm^{-1}; **MS (ESI)** m/z 304.4 $[M-H]^-$ (100%).



2,2,2-trifluoro-1-(1H-indole-3-yl)-1-*o*-tolylethanol

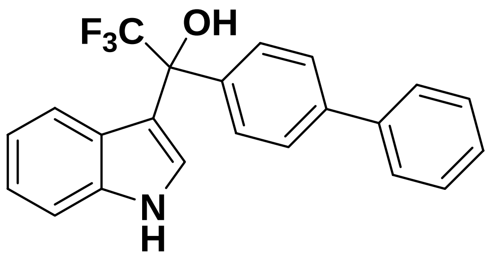
81% yield, mp: 136-139 ^{o}C; $[\alpha]_D^{20}$ = +26.6 ^{o} (c 1.0, CH_2Cl_2); 86% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t (major) = 9.837 min, t (minor) = 11.713 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -76.0 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.26 (br, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.35-7.34 (m, 1H), 7.29-7.26 (m, 1H), 7.25-7.22 (m, 1H), 7.19-7.16 (m, 1H), 7.14-7.09 (m, 2H), 6.96-6.93 (m, 1H), 2.77 (s, 1H), 2.13 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 138.7, 136.4, 135.6, 133.0, 129.0, 128.8 (d, $^{3}J_{C-F}$ = 1.0 Hz), 126.0 (q, $^{1}J_{C-F}$ = 285.1 Hz), 125.7, 125.6, 123.6 (q, $^{3}J_{C-F}$ = 2.4 Hz), 122.9, 120.9, 120.5, 114.9, 111.4, 78.2 (q, $^{2}J_{C-F}$ = 29.3 Hz), 21.8; **IR** (KBr) ν (cm^{-1}) 3502, 3415, 3141, 2926, 1548, 1459, 1271, 1171, 1022, 922, 748, 585 cm^{-1}; **MS (ESI)** m/z 304.4 $[M-H]^-$ (100%).



2,2,2-trifluoro-1-(1H-indole-3-yl)-1-(3,5-dimethylphenyl)ethanol

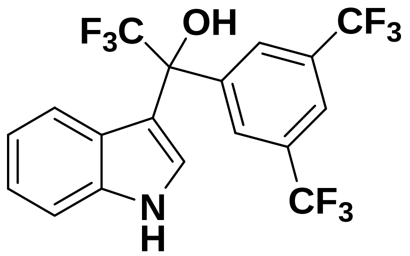
> 99% yield, mp: 158-159 ^{o}C; $[\alpha]_D^{20}$ = +55.7 (c 1.0, CH_2Cl_2); 85% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; t (major) = 11.068 min, t (minor) = 12.268 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.1 (s, 3F); **^{1}H NMR** (400MHz, $CDCl_3$) δ [ppm] 8.25 (br, 1H), 7.44-7.43 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.24-7.16 (m, 4H), 6.99-6.96 (m, 2H), 2.86 (s, 1H), 2.29 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 137.7, 137.6, 136.5, 130.5, 125.7 (q, $^{1}J_{C-F}$ = 284.5 Hz), 125.5, 123.4 (q, $^{3}J_{C-F}$ = 2.9 Hz), 121.4, 120.5, 114.5, 111.4, 77.3 (q, $^{2}J_{C-F}$ = 29.3 Hz). 30.0, 21.7; **IR** (KBr) ν (cm^{-1}) 3526, 3342, 2923, 2856, 1539, 1461, 1245, 1180, 1042,

847, 758 cm^{-1}; **MS (ESI)** m/z 318.4 $[M-H]^-$ (100%).



2,2,2-trifluoro-1-(1H-indole-3-yl)-1-biphenylethanol

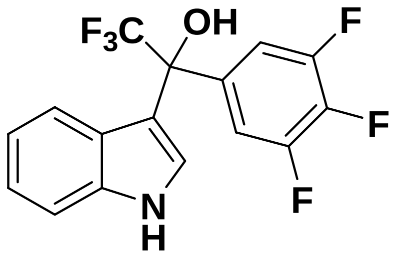
> 99% yield, mp: 177-178 °C; $[\alpha]_D^{20}$ = +23.5 (c 1.0, CH_2Cl_2); 90% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t (major) = 17.174 min, t (minor) = 20.818 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.1 (s, 3F); **^{1}H NMR** (400MHz, $CDCl_3$) δ [ppm] 8.27 (br, 1H), 7.67-7.57 (m, 6H), 7.50-7.34 (m, 5H), 7.26-7.18 (m, 2H), 6.98 (t, J = 8.0 Hz, 1H), 2.93 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 141.4, 140.7, 136.9, 136.5, 129.0, 128.3, 127.7, 127.4, 126.9, 125.6 (q, $^1J_{C-F}$ = 284.6 Hz), 125.4, 123.5 (q, $^3J_{C-F}$ = 2.9 Hz), 123.1, 121.3, 120.6, 114.2, 111.5, 77.2 (q, $^2J_{C-F}$ = 29.5 Hz); **IR** (KBr) ν (cm^{-1}) 3521, 3452, 1549, 1458, 1273, 1166, 1045, 832, 751 cm^{-1}; **MS (ESI)** m/z 366.4 $[M-H]^-$ (100%).



(3,5-bis(trifluoromethyl)phenyl)-2,2,2-trifluoro-1-(1H-indole-3-yl)-1-ethanol

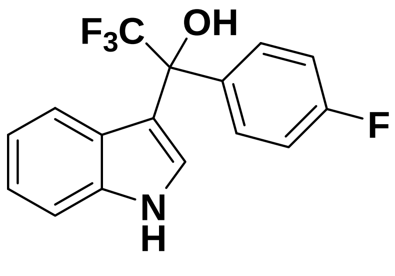
> 99% yield, mp: 144-146 °C; $[\alpha]_D^{20}$ = +52.4 (c 1.0, CH_2Cl_2); 90% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; t (major) = 7.053 min, t (minor) = 7.828 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -63.1 (s, 6F), -77.4 (s, 3F); **^{1}H NMR** (400MHz, $CDCl_3$) δ [ppm] 8.43 (br, 1H), 8.07 (s, 2H), 7.89 (s, 1H), 7.55 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.08-6.97 (m, 2H), 3.13 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 140.8, 136.5, 131.7 (q, $^2J_{C-F}$ = 33.3 Hz), 128.3, 124.9 (q, $^1J_{C-F}$ = 284.8 Hz), 124.6, 123.6 (q, $^3J_{C-F}$ = 3.0 Hz), 123.5, 123.4 (q, $^1J_{C-F}$ = 271.3 Hz), 123.0 (q, $^3J_{C-F}$ = 3.8 Hz), 121.0, 120.4, 112.4, 111.8, 76.8 (q, $^2J_{C-F}$ = 29.9 Hz); **IR** (KBr) ν (cm^{-1}) 3457, 3403, 3114, 2923, 1543, 1462, 1280,

1181, 1130, 887, 753 cm^{-1}; **MS (ESI)** m/z 426.3 $[M-H]^-$ (100%).



2,2,2-trifluoro-1-(1H-indole-3-yl)-1-3,4,5-trifluorophenylethanol

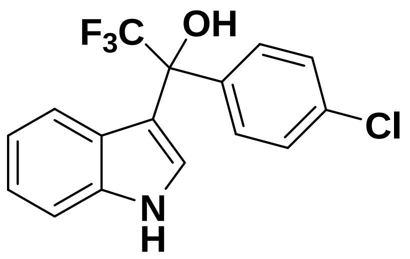
91% yield, mp: 134-135 °C; $[\alpha]_D^{20}$ = + 53.3 (c 1.0, CH_2Cl_2); 85% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; t (major) = 9.997 min, t (minor) = 18.606 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.5 (s, 3F), -134.4 ~ -134.5 (m, 2F), -160.3 ~ -160.4 (m, 1F). **^{1}H NMR** (400MHz, $CDCl_3$) δ [ppm] 8.36 (br, 1H), 7.49 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.23 (q, *J* = 7.0 Hz, 3H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 3.00 (br, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 151.0 (dq, J_{C-F} = 248.1, 6.1, 3.9 Hz), 140.0 (dt, J_{C-F} = 251.6, 15.0 Hz), 136.5, 134.3 (dt, J_{C-F} = 9.1, 4.6 Hz), 128.9, 128.5, 124.9 (q, $^1J_{C-F}$ = 285.1 Hz), 124.8, 123.5, 123.4 (q, $^3J_{C-F}$ = 3.1 Hz), 122.2, 120.8 (d, $^2J_{C-F}$ = 40.4 Hz), 120.2, 119.5, 111.8, 76.4 (q, $^2J_{C-F}$ = 30.1 Hz); **IR** (KBr) ν (cm^{-1}) 3525, 3452, 3071, 2925, 1623, 1532, 1493, 1443, 1421, 1362, 1340, 1270, 1210, 1171, 1110, 1035, 904, 858, 758, 717 cm^{-1}; **MS (ESI)** m/z 344.3 $[M-H]^-$ (100%).



2,2,2-trifluoro-1-(4-fluorophenyl)-1-(1H-indole-3-yl)ethanol

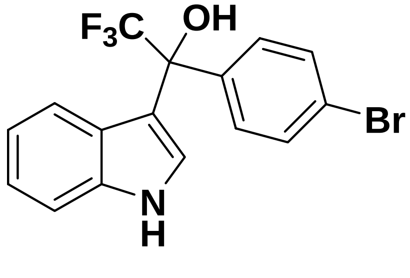
> 99% yield, mp: 130-131 °C; $[\alpha]_D^{20}$ = +83.5 (c 1.0, CH_2Cl_2); 89% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t (major) = 7.297 min, t (minor) = 11.306 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.6 (s, 3F), -114.2 ~ -114.3 (m, 1F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.29 (br, 1H), 7.57-7.54 (m, 2H),

7.49-7.48 (m, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.21-7.18 (m, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.04-6.95 (m, 3H), 2.86 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 163.1(d, $^1J_{C-F}$ = 245.9 Hz), 136.5, 133.7 (d, $^4J_{C-F}$ = 3.1 Hz), 129.9 (d, $^3J_{C-F}$ = 8.4 Hz), 125.4 (q, $^1J_{C-F}$ = 284.4 Hz), 125.2, 123.4 (q, $^3J_{C-F}$ = 3.1 Hz), 123.1, 121.1, 120.6, 115.1 (d, $^2J_{C-F}$ = 21.5 Hz), 114.0, 111.6, 76.9 (q, $^2J_{C-F}$ = 29.8 Hz); **IR** (KBr) ν (cm^{-1}) 3544, 3482, 3409, 3326, 1509, 1459, 1276, 1189, 830, 746 cm^{-1}; **MS (ESI)** m/z 308.51 $[M-H]^-$ (100%).



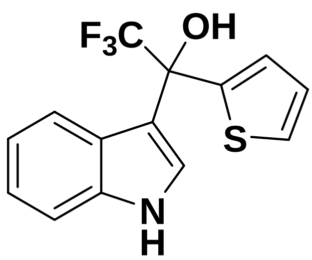
1-(4-chlorophenyl)-2,2,2-trifluoro-1-(1H-indole-3-yl)ethanol

> 99% yield, mp: 112-113 °C; $[\alpha]_D^{20}$ = +52.6 (c 1.0, CH_2Cl_2); 99% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t (major) = 6.531 min, t (minor) = 9.856 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.3 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.34 (br, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.46 (s, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.22 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 3.09 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 136.6, 136.5, 134.9, 129.5, 128.5, 125.4 (q, $^1J_{C-F}$ = 284.6 Hz), 125.2, 123.5 (q, $^3J_{C-F}$ = 2.9 Hz), 123.2, 121.0, 120.7, 113.6, 111.7, 77.0 (q, $^2J_{C-F}$ = 30.0 Hz); **IR** (KBr) ν (cm^{-1}) 3412, 3059, 2925, 1544, 1492, 1272, 1161, 820, 741 cm^{-1}; **MS (ESI)** m/z 324.08 $[M-H]^-$ (100%).



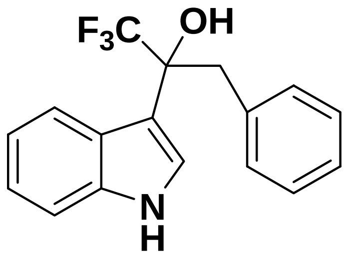
1-(4-bromophenyl)-2,2,2-trifluoro-1-(1H-indole-3-yl)ethanol

> 99% yield; $[\alpha]_D^{20}$ = +45.7 (c 1.0, CH_2Cl_2); 87% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t (major) = 11.324 min, t (minor) = 17.834 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.3 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.32 (br, 1H), 7.47 (s, 5H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 2.98 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ [ppm] 137.0, 136.5, 131.4, 129.8, 125.3 (q, $^1J_{C\text{-}F}$ = 284.6 Hz), 125.2, 123.4 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 123.2, 121.0, 120.7, 113.6, 111.6, 77.0 (q, $^2J_{C\text{-}F}$ = 29.8 Hz); **IR** (KBr) ν (cm^{-1}) 3407, 3063, 2922, 1542, 1488, 1268, 1164, 1011, 924, 817, 746 cm^{-1}; **MS (ESI)** m/z 368.3 $[M\text{-}H]^-$ (100%).



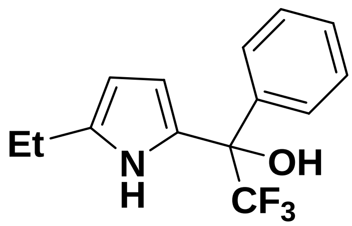
2,2,2-trifluoro-1-(1H-indole-3-yl)-1-(thiophene-2-yl)ethanol

84% yield; $[\alpha]_D^{20}$ = + 44.2 (c1.0, CH_2Cl_2); 86% ee, [Daicel Chiralcel AD-H, Hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t (minor) = 56.598 min, t (major) = 58.990 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.9 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.29 (br, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.41-7.36 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.00-6.98 (m, 1H), 3.14 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ [ppm] 142.3, 136.5, 127.6 (q, $^3J_{C\text{-}F}$ = 1.3 Hz), 127.0, 126.9, 125.5, 125.2 (q, $^1J_{C\text{-}F}$ = 284.4 Hz), 123.8 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 123.0, 121.2, 120.7, 76.3 (q, $^2J_{C\text{-}F}$ = 31.3 Hz); **IR** (KBr) ν (cm^{-1}) 3421, 3063, 2925, 1619, 1544, 1459, 1423, 1275, 1156, 1089, 1027, 900, 836, 747, 714, 631 cm^{-1}; **MS (ESI)** m/z 296.4 $[M\text{-}H]^-$ (100%).



1,1,1-trifluoro-2-(1H-indole-3-yl)-3-phenylpropan-2-ol

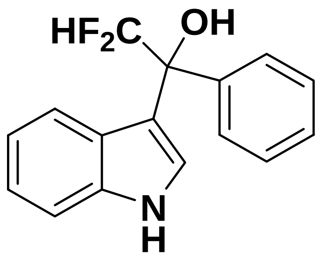
86% yield; $[\alpha]_D^{20}$ = +55.3 (c 1.0, CH_2Cl_2); 76% ee, [Daicel Chiralcel AD-H, Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t (major) = 16.491 min, t (minor) = 18.895 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -78.9 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.18 (br, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.0 Hz, 1H), 7.21-7.15 (m, 5H), 6.99 (d, *J* = 7.0 Hz, 2H), 3.51 (dd, *J* = 13.5, 97.5 Hz, 2H), 2.54 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ [ppm] 136.9, 133.9, 131.0, 128.5, 127.5, 126.5, 126.1 (q, $^{1}J_{C-F}$ = 284.3 Hz), 125.4, 124.3, 122.6, 122.1, 121.3 (d, $^{3}J_{C-F}$ = 2.0 Hz), 120.6, 119.8, 111.8, 76.5 (q, $^{2}J_{C-F}$ = 29.1 Hz); **IR** (KBr) ν (cm^{-1}) 3417，3061, 3032, 2924, 1546, 1496, 1458, 1424, 1339, 1272, 1166, 1105, 1017, 982, 948 cm^{-1}; **MS (ESI)** m/z 304.4 $[M-H]^-$ (100%).



1-(5-ethyl-1H-prrol-2-yl)-2,2,2-trifluoro-1-phenylethanol

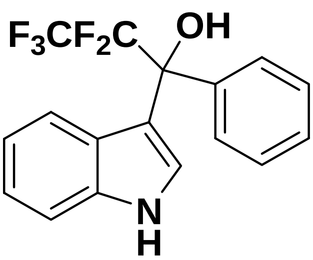
> 99% yield; mp: 55-57 °C; $[\alpha]_D^{20}$ = +44.2 (c 1.0, CH_2Cl_2); 65% ee, [Daicel Chiralcel AD-H, Hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t (minor) = 56.598 min, t (major) = 58.990 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.9 (s, 3F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.29 (br, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.41-7.36 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.00-6.98 (m, 1H), 3.14 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ [ppm] 142.3, 136.5, 127.6 (q, $^{3}J_{C-F}$ = 1.3 Hz), 127.0, 126.9, 125.5, 125.2 (q, $^{1}J_{C-F}$ = 284.4 Hz), 123.8 (q, $^{3}J_{C-F}$ = 2.6 Hz), 123.0,

121.2, 120.7, 76.3 (q, $^{2}J_{C\text{-}F}$ = 31.3 Hz); **IR** (KBr) ν (cm^{-1}) 3421, 3063, 2925, 1619, 1544, 1459, 1423, 1275, 1156, 1089, 1027, 900, 836, 747, 714, 631 cm^{-1}; **MS (ESI)** m/z 296.4 $[M-H]^{-}$ (100%)



2,2-difluoro-1-(1H-indole-3-yl)-1-phenylethanol

92% yield, mp: 96-98 °C; $[\alpha]_D^{20}$ = +54.1 (c 1.0, CH_2Cl_2); 90% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 0.9 mL/min, 254 nm; t (major) = 21.961 min, t (minor) = 40.352 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -126.9 (dd, *J* = 273.0, 21.1 Hz, 2F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.25 (br, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 1H), 7.40-7.34 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.10 (t, *J* = 56.0 Hz, 1H), 2.76 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 139.6, 136.6, 128.4, 127.4, 125.8, 123.3, 122.8, 122.2, 121.3, 120.3, 119.8 (t, $^{1}J_{C\text{-}F}$ = 244.6 Hz), 119.5 (t, $^{3}J_{C\text{-}F}$ = 5.0 Hz), 117.4, 114.9, 111.4, 76.4 (q, $^{2}J_{C\text{-}F}$ = 21.8 Hz); **IR** (KBr) ν (cm^{-1}) 3450, 3424, 3151, 3060, 1617, 1546, 1457, 1334, 1172, 1069, 1037, 906, 829, 750, 698, 683, 606 cm^{-1}; **MS (ESI)** m/z 272.2 $[M-H]^{-}$ (100%).

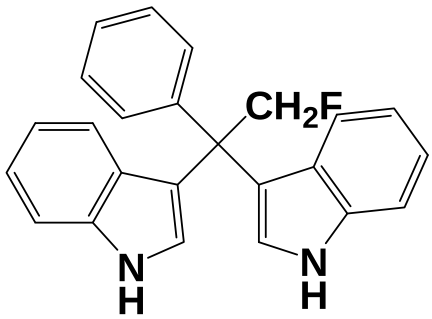


2,2,3,3,3-pentafluoro-1-(1H-indole-3-yl)-1-phenylpropan-1-ol

78% yield, mp: 140-141 °C; $[\alpha]_D^{20}$ = +62.5 (c 1.0, CH_2Cl_2); 97% ee, [Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 90/10, 0.9 mL/min, 254 nm; t (major) = 11.769 min, t (minor) = 18.502 min]; **^{19}F NMR** (376 MHz, $CDCl_3$) δ [ppm] -77.1 (s, 3F), -118.2

(dd, J = 308.7, 273.7 Hz, 2F); **^{1}H NMR** (500MHz, $CDCl_3$) δ [ppm] 8.25 (br, 1H), 7.65-7.64 (m, 2H), 7.54 (s, 1H), 7.37-7.34 (m, 4H), 7.19-7.15 (m, 2H), 6.94 (t, J = 8.0 Hz, 1H), 2.97 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 137.9, 136.3, 128.6, 128.1, 127.6, 125.3, 123.1 (q, $^{3}J_{C\text{-}F}$ = 4.5 Hz), 122.9, 121.1, 120.4, 115.0, 111.4, 77.2 (q, $^{2}J_{C\text{-}F}$ = 28.0 Hz); **IR** (KBr) ν (cm^{-1}) 3474, 3410, 3148, 3062, 1551, 1455, 1348, 1220, 1181, 1134, 1052, 1024, 911, 833, 728, 698 cm^{-1}; **MS (ESI)** m/z 340.2 $[M-H]^-$ (100%).

Brønsted Acid-catalyzed diarylation of 2-fluoroacetophenone:



3-(2-fluoro-1-(1H-indole-3-yl)-1-phenylyl)-1H-indole

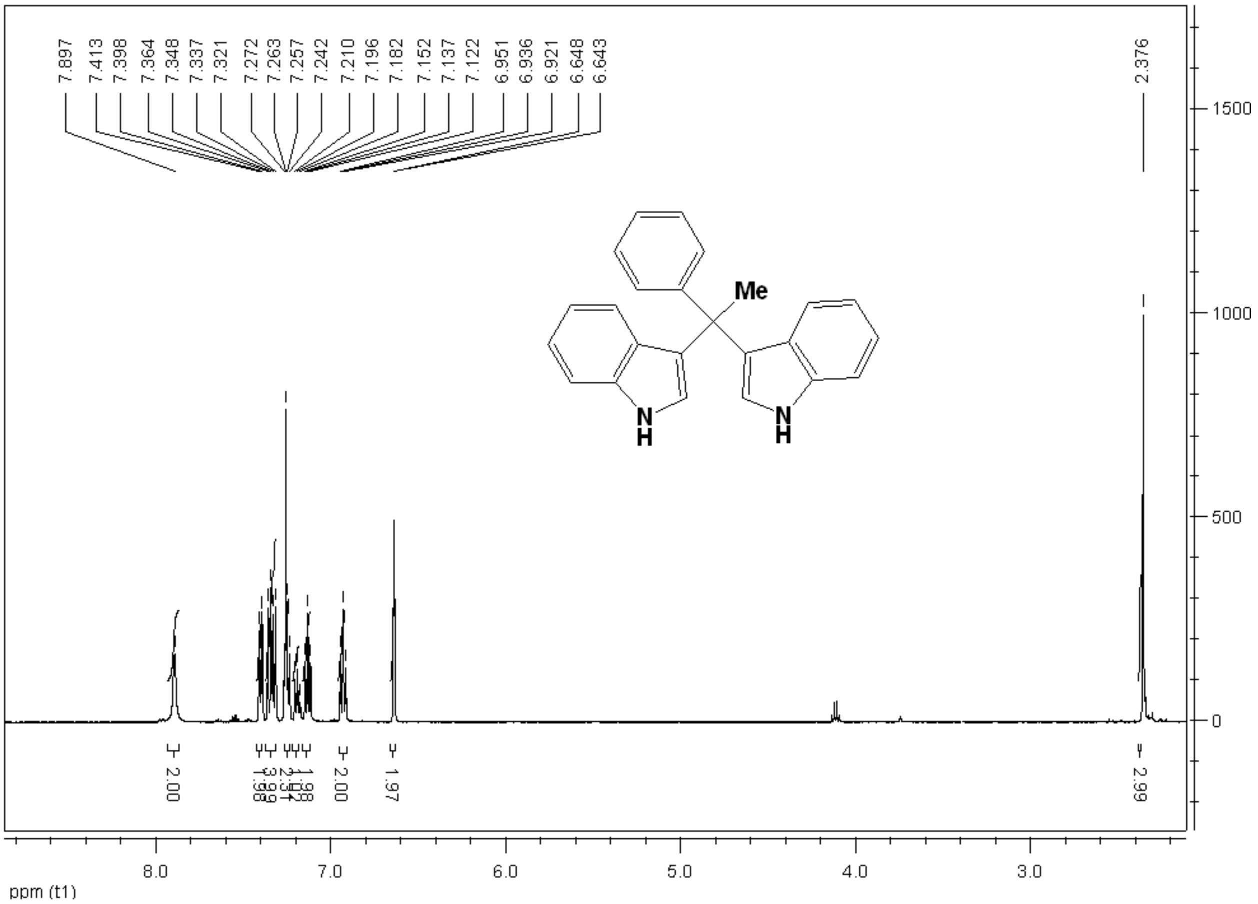
74% yield, mp: 72-74 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ [ppm] 8.03 (br, 2H), 7.47 (d, J = 6.8 Hz, 2H), 7.37 (d, J = 8.0, 2H), 7.32-7.26 (m, 3H), 7.21 (d, J = 8.4 Hz, 2H), 7.15 (t, J = 8.0 Hz, 2H), 6.95-6.90 (m, 4H), 5.51 (d, J = 48.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ [ppm] 143.4 (d, $^{3}J_{C\text{-}F}$ = 1.5 Hz), 137.0, 129.0 (d, $^{3}J_{C\text{-}F}$ = 2.1 Hz), 128.3, 126.9, 126.7, 125.1 (d, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 122.0, 121.9, 119.5, 119.4 (d, $^{3}J_{C\text{-}F}$ =3.6 Hz), 111.5, 88.2 (d, $^{1}J_{C\text{-}F}$ = 182.1 Hz), 49.9 (d, $^{2}J_{C\text{-}F}$ =18.6 Hz) ; **IR** (KBr) ν (cm^{-1}) 3412, 3053, 2918, 2849, 1597, 1456, 1415, 1338, 1245, 1100, 1011, 909, 741, 701 cm^{-1}; **MS (ESI)** m/z 353.16 $[M-H]^-$ (100%).

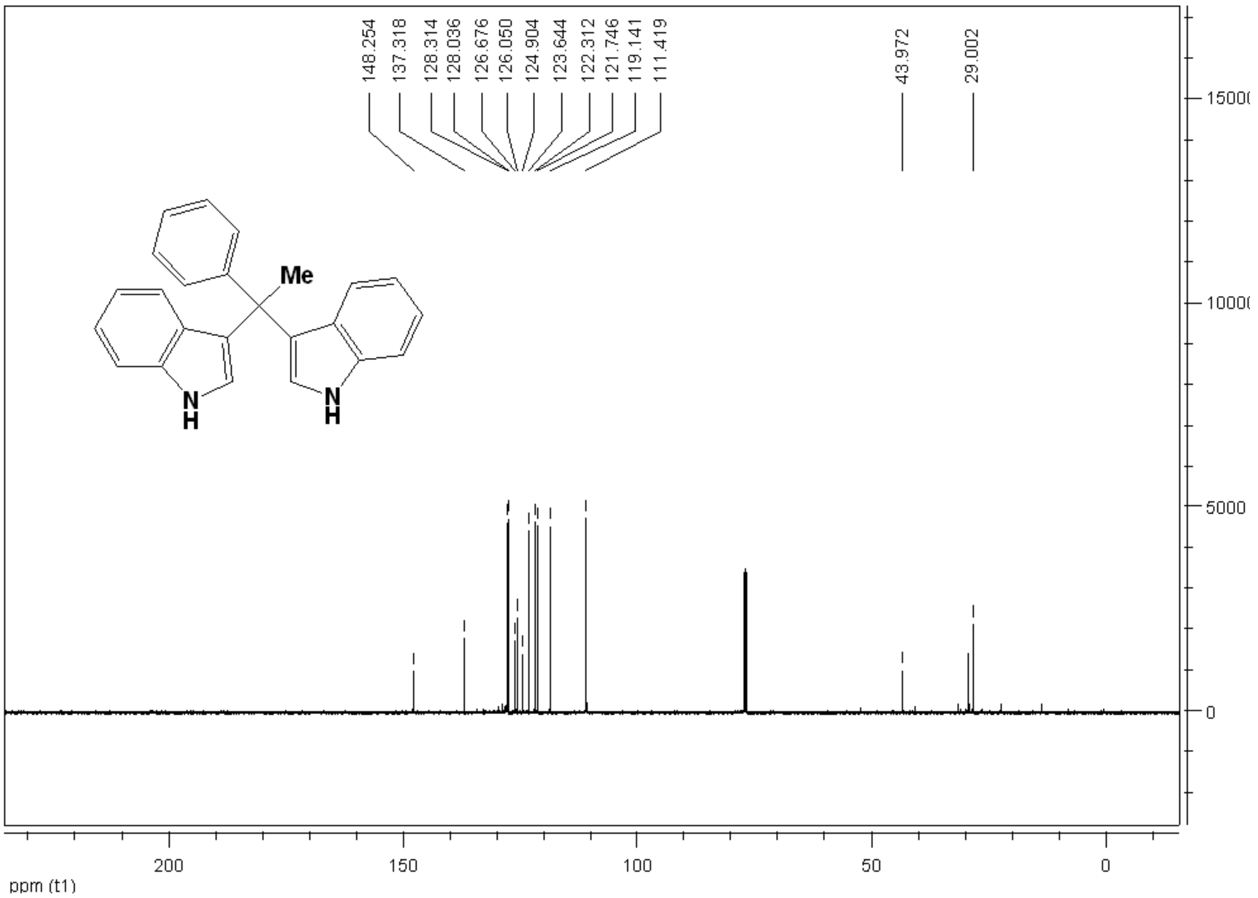
References:

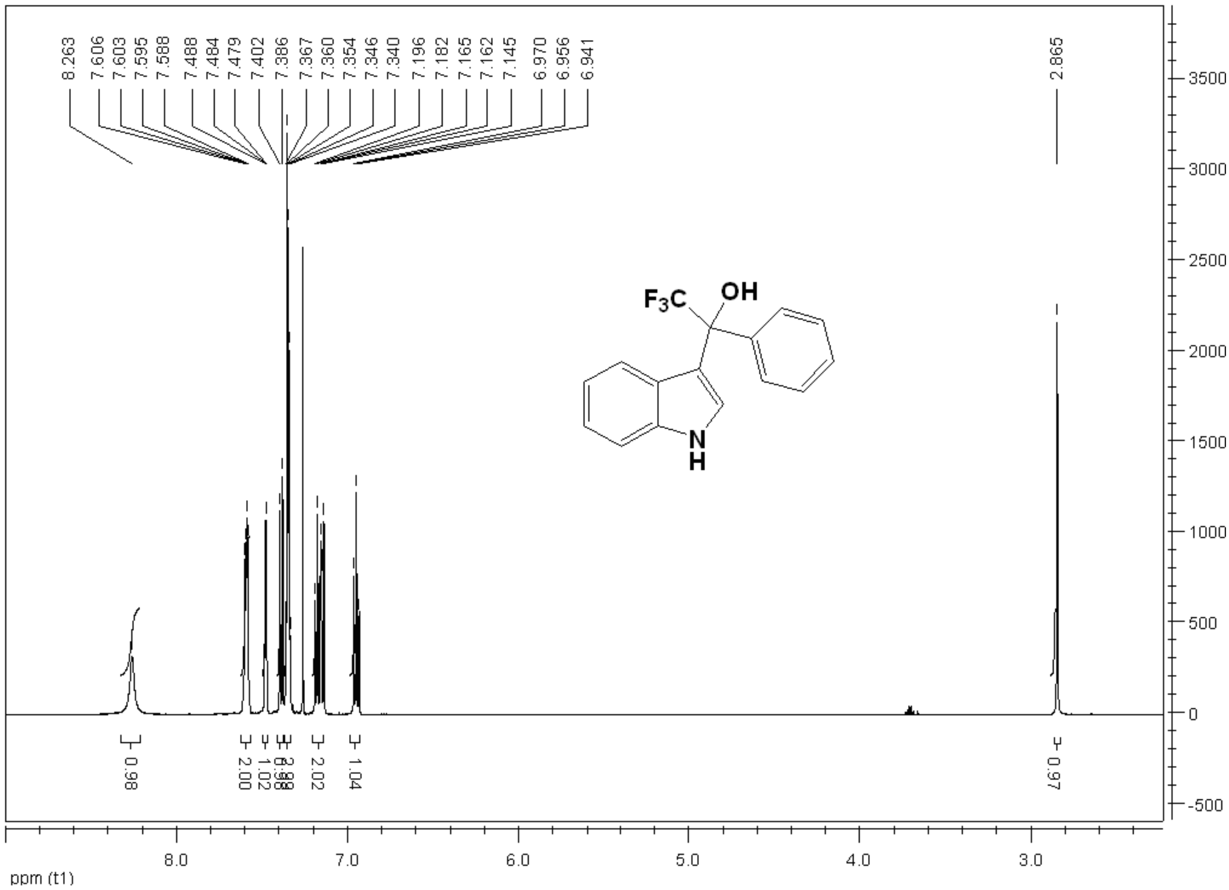
1. a) X. Creary, *J. Org. Chem.* **1987**, 52, 5026; b) J. M. Chong, E. K. Mar, *J. Org. Chem.* **1991**, 56, 893.
2. a) T. Akiyama, J. Itoh, K. Yokota, K. Fuchibe, *Angew. Chem.* **2004**, 116, 1592; b) D. Uraguchi, M. Terada, *J. Am. Chem. Soc.* **2004**, 126, 5356; c) S. Hoffmann, A. Seayad, B. List, *Angew. Chem.* **2005**, 117, 7590; d) R. I. Storer, D. E. Carrera, Y.

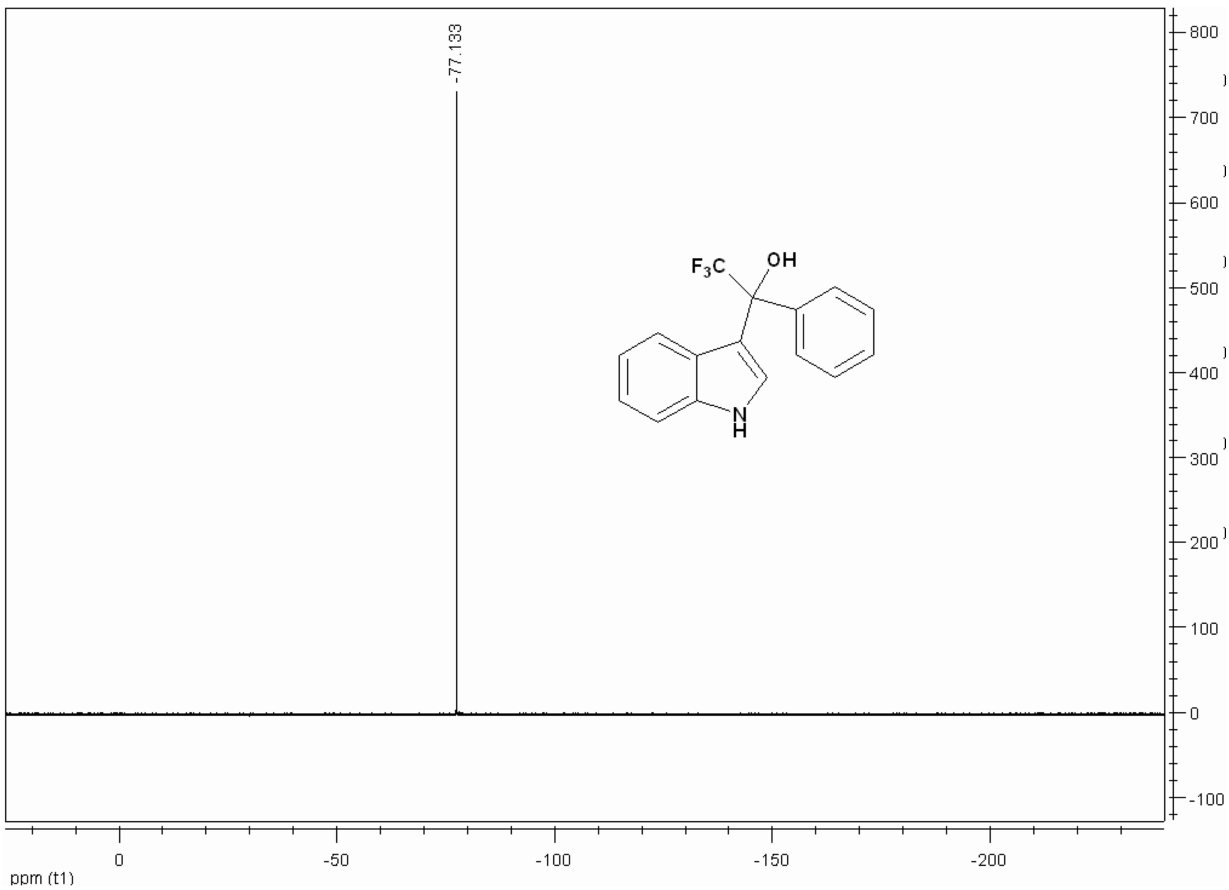
Ni, D. W. C. MacMillan, *J. Am. Chem. Soc*. **2006**, 128, 84.

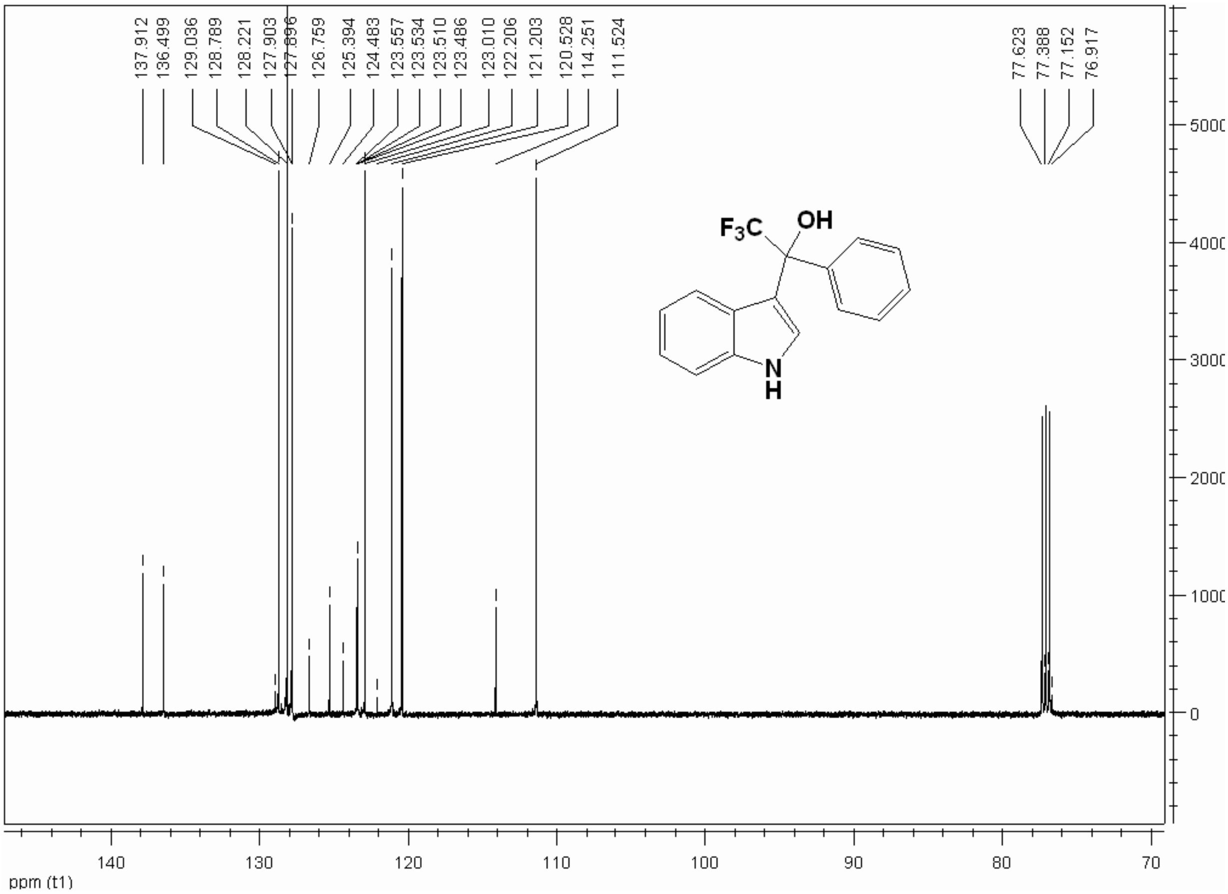
3. Nakashima, D.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 9626.
4. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A.D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, I. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzales, C.; Pople, J. A. Gaussian03, Revision D.01; Gaussian, Inc.; Wallingford CT, 2004.
5. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372-1377. (b) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648-5652. (c) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
6. Somei, M.; Kobayashi, T. *Heterocycles*, **1992**, *34*, 1295.

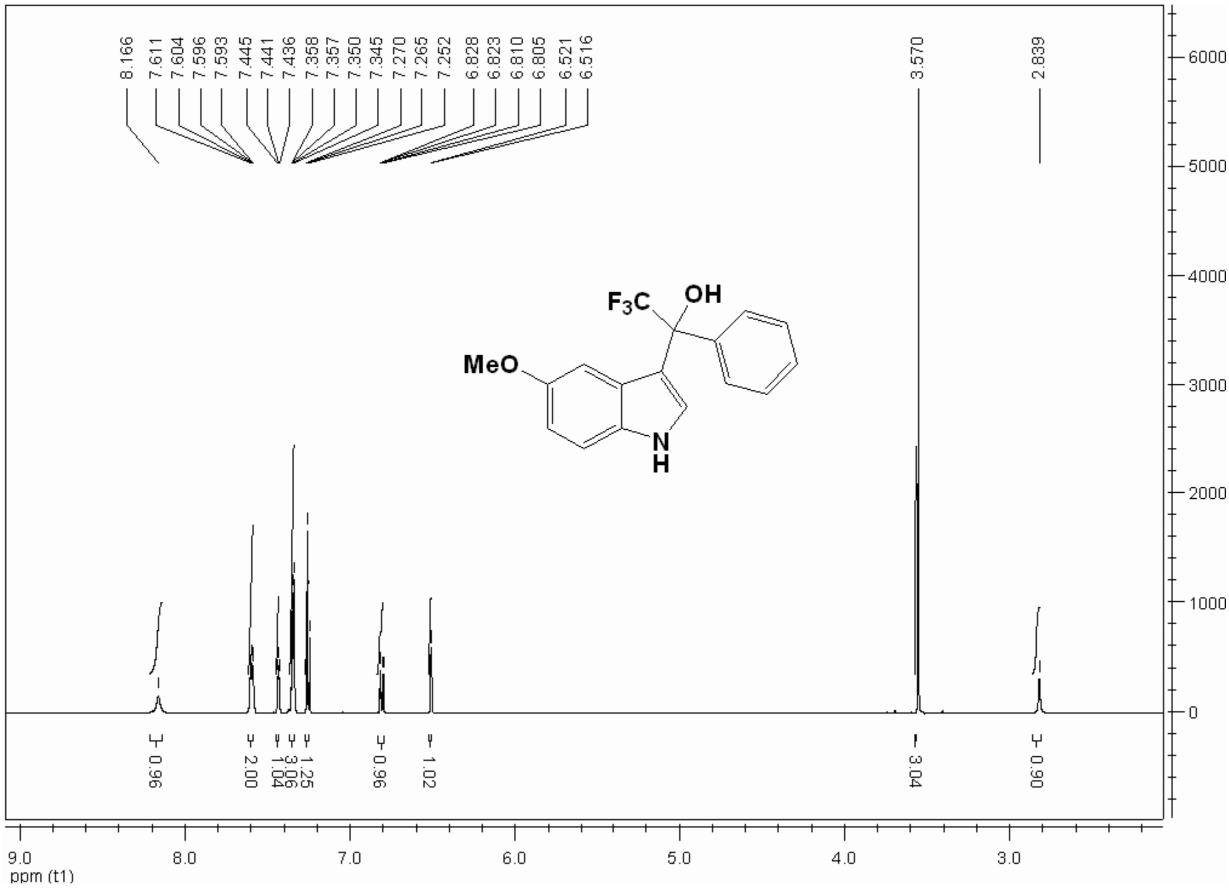

7.897
7.413
7.398
7.364
7.348
7.337
7.321
7.272
7.263
7.257
7.242
7.210
7.196
7.182
7.152
7.137
7.122
6.951
6.936
6.921
6.648
6.643
2.376
Me
N
H
N
H
2.00
2.00
1.97
2.99
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

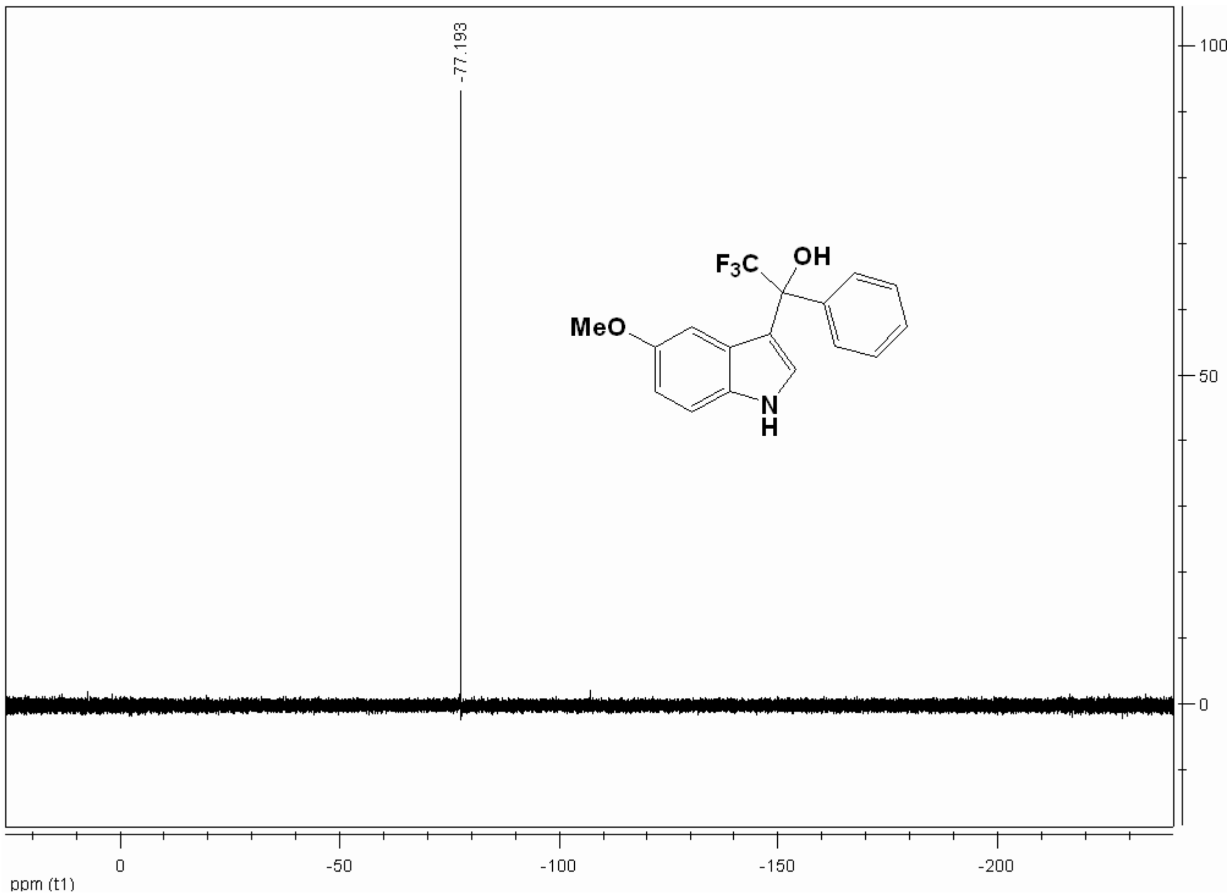

148.254
137.318
128.314
128.036
126.676
126.050
124.904
123.644
122.312
121.746
119.141
111.419
43.972
29.002
Me
N
H
N
H
200
150
100
50
0
ppm (t1)

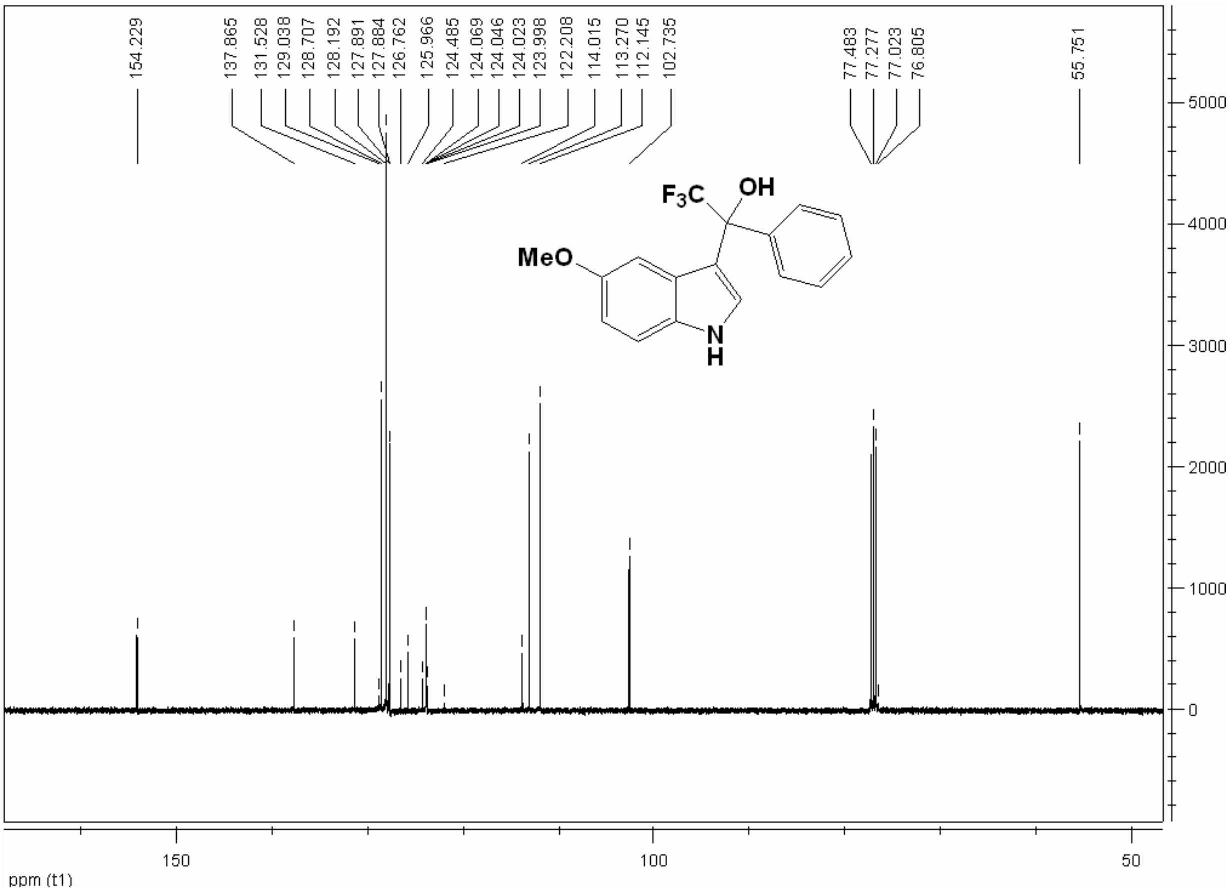

8.263
7.606
7.603
7.595
7.588
7.488
7.484
7.479
7.402
7.386
7.367
7.360
7.354
7.346
7.340
7.196
7.182
7.165
7.162
7.145
6.970
6.956
6.941
2.865
F_3C
OH
N
H
0.98
2.00
1.02
2.98
2.02
1.04
0.97
ppm (t1)

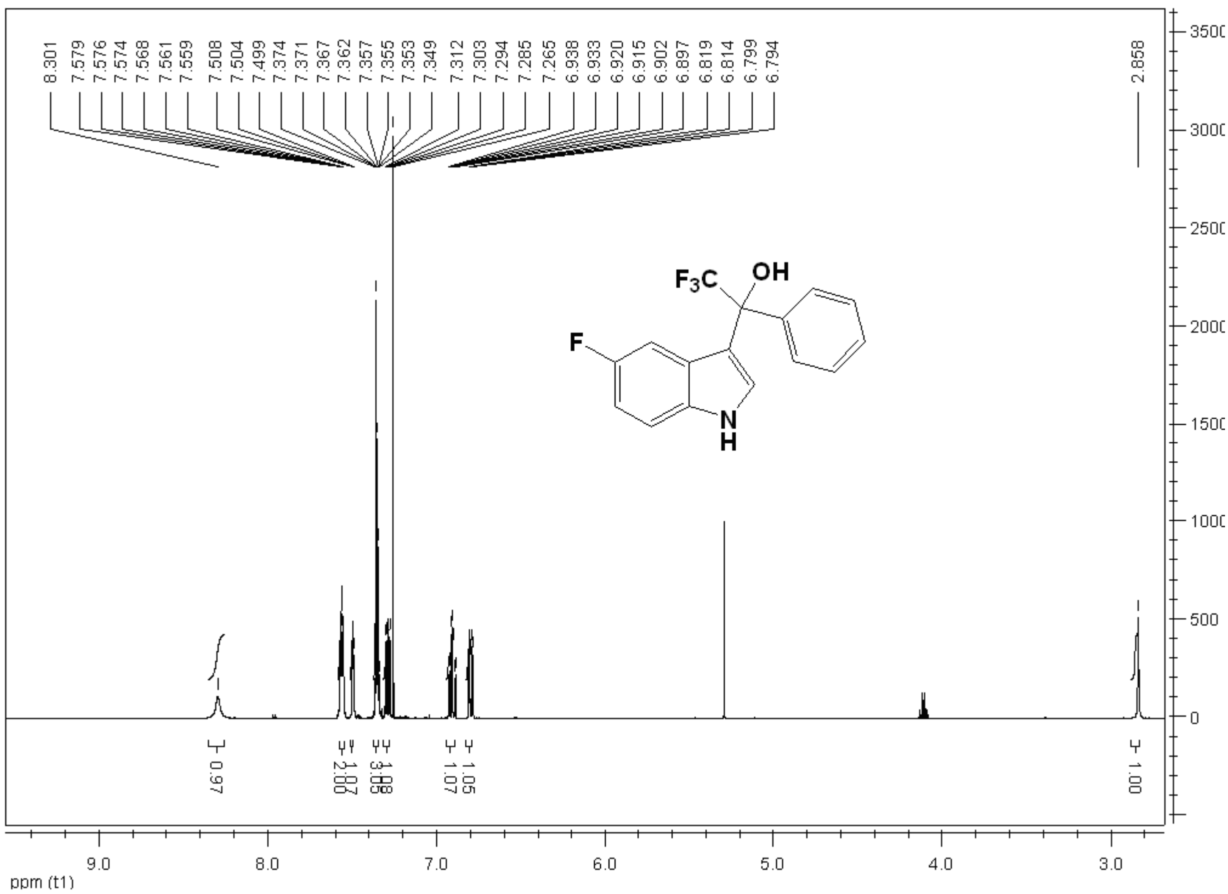

-77.133
F_3C
OH
N
H
ppm (t1)

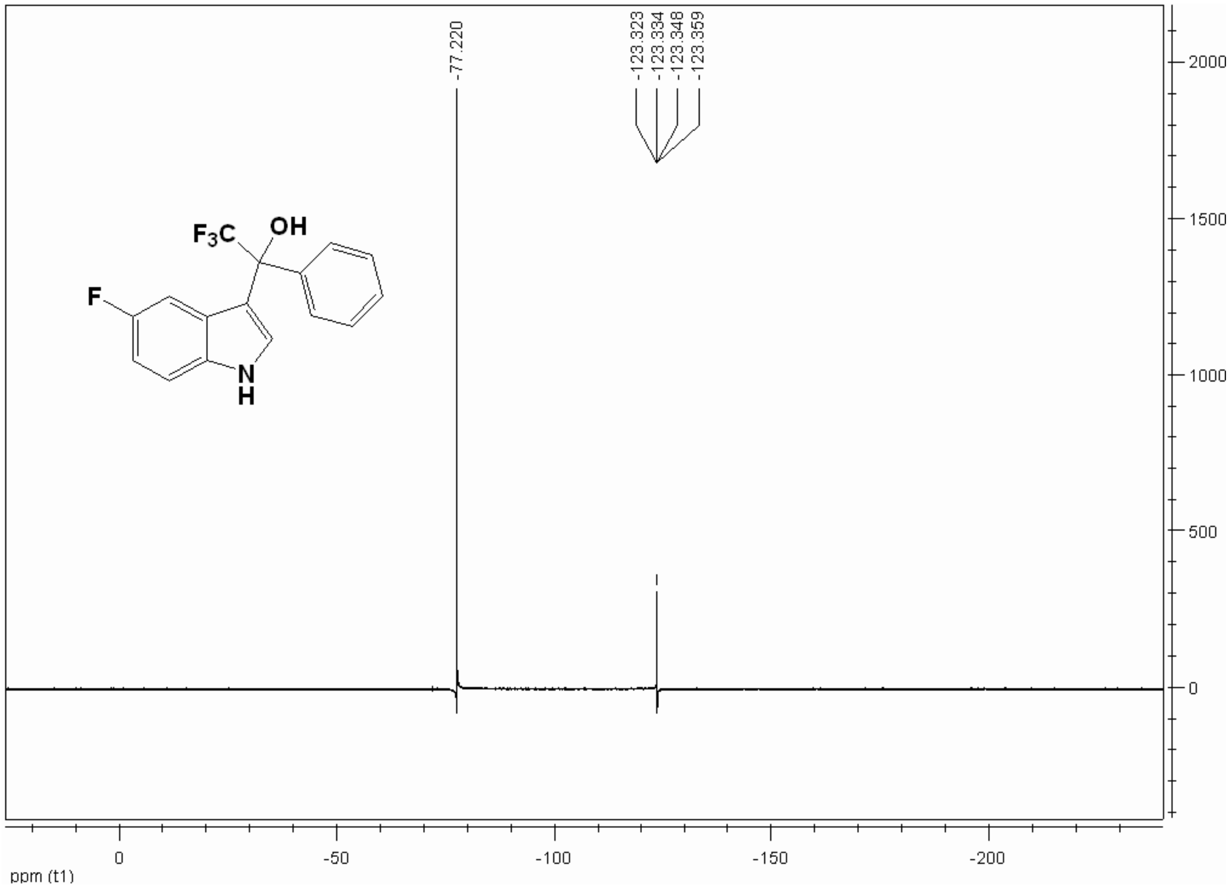

137.912
136.499
129.036
128.789
128.221
127.903
127.896
126.759
125.394
124.483
123.557
123.534
123.510
123.486
123.010
122.206
121.203
120.528
114.251
111.524
77.623
77.388
77.152
76.917
F_3C
OH
N
H
5000
4000
3000
2000
1000
0
140
130
120
110
100
90
80
70
ppm (t1)

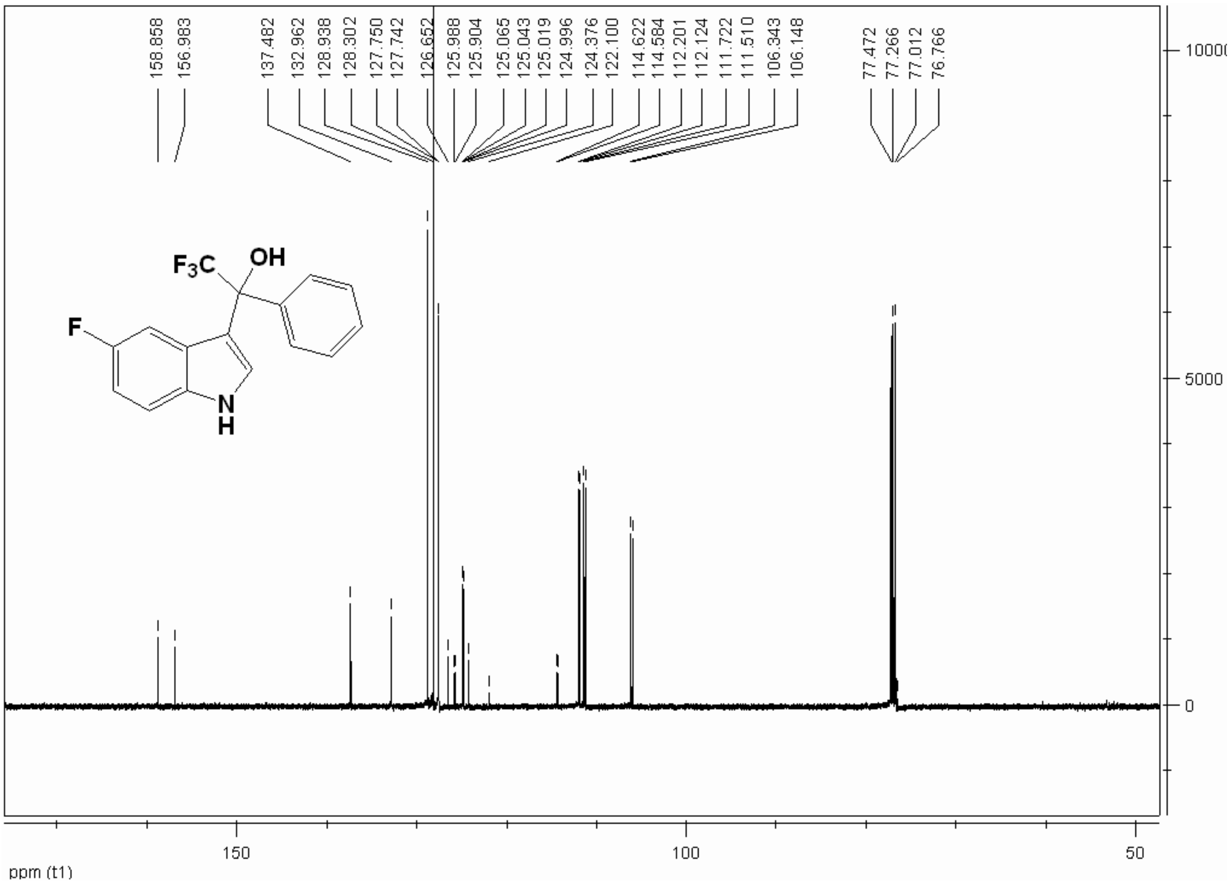

8.166
7.611
7.604
7.596
7.593
7.445
7.441
7.436
7.358
7.357
7.350
7.345
7.270
7.265
7.252
6.828
6.823
6.810
6.805
6.521
6.516
3.570
2.839
F3C
OH
MeO
N
H
0.96
2.00
1.04
3.06
1.25
0.96
1.02
3.04
0.90
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)
6000
5000
4000
3000
2000
1000
0

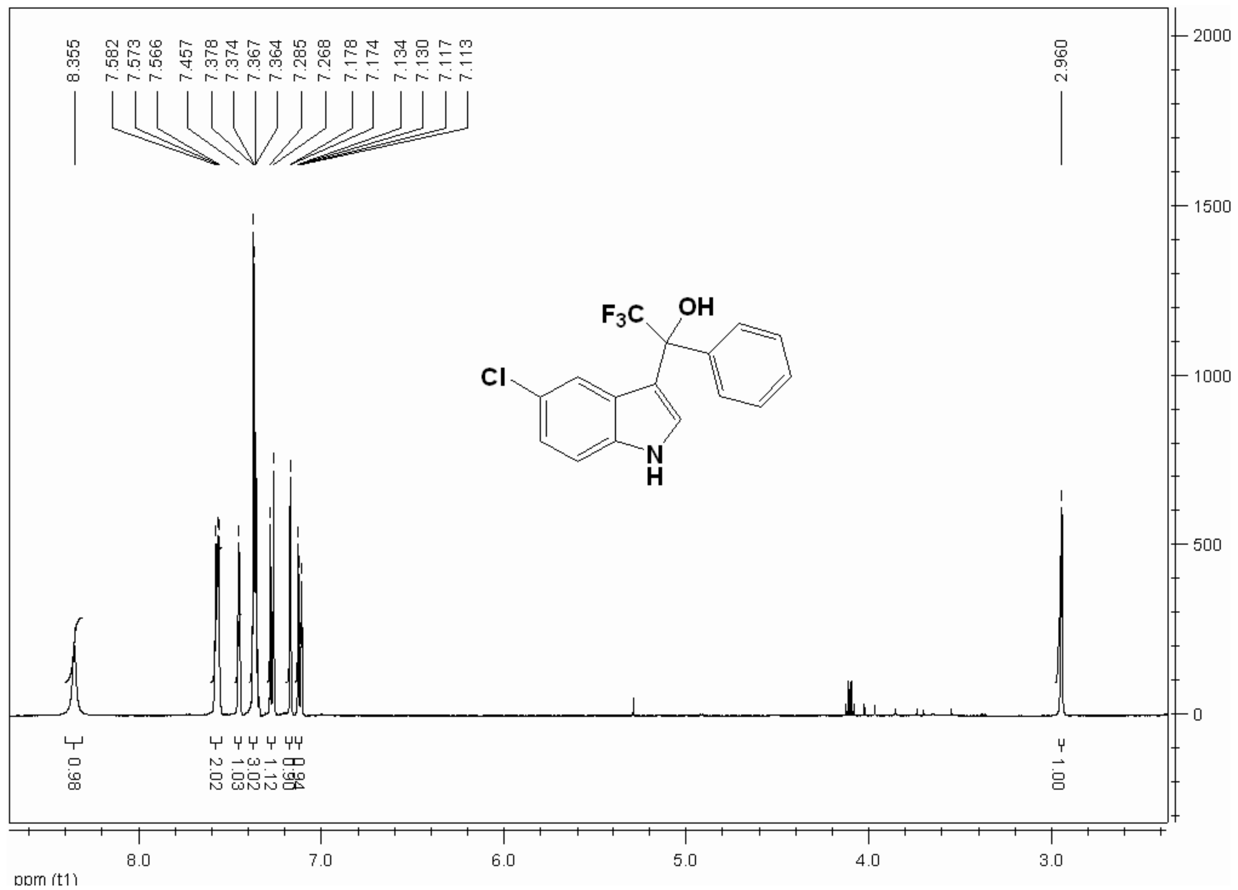

-77.193
F3C
OH
MeO
N
H
0
-50
-100
-150
-200
ppm (t1)
100
50
0

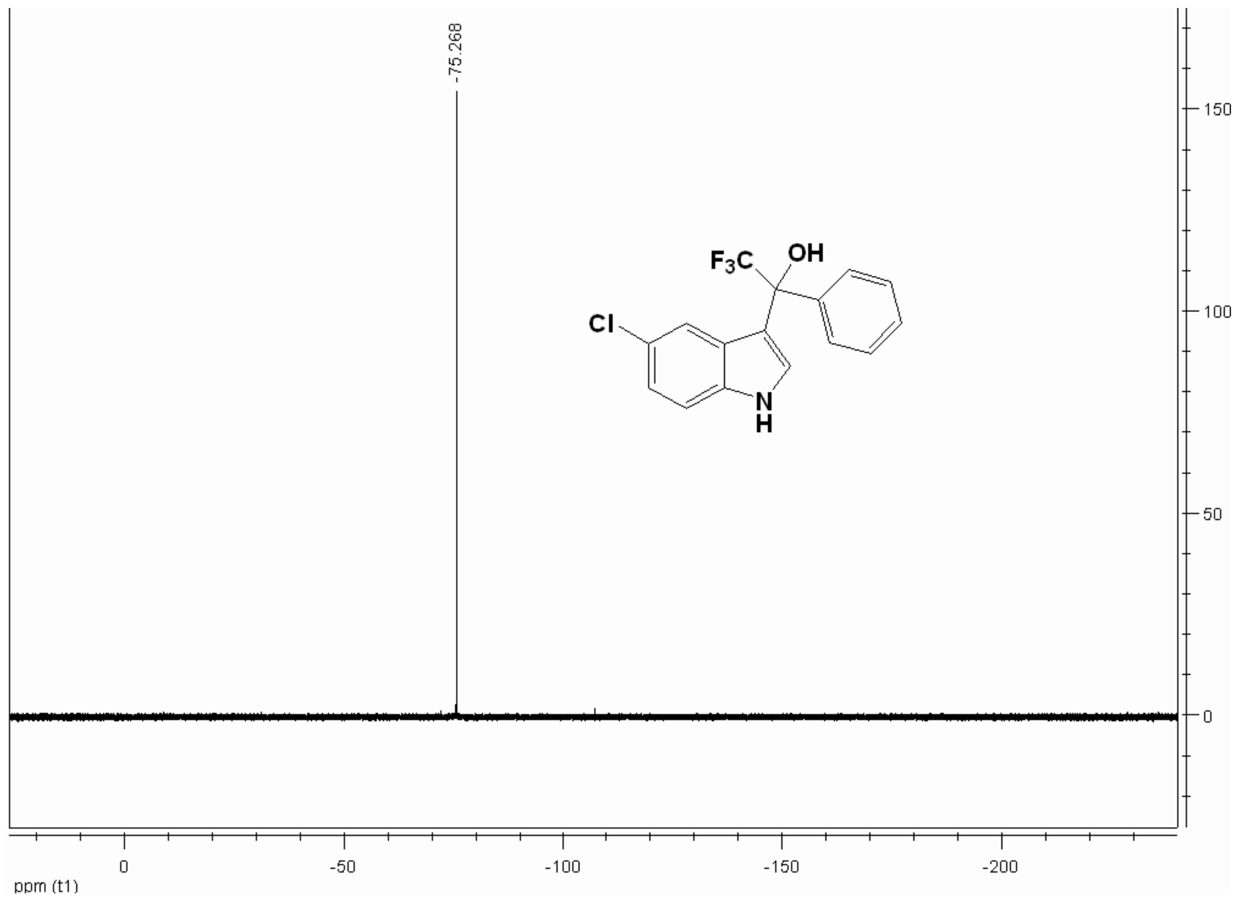

154.229
137.865
131.528
129.038
128.707
128.192
127.891
127.884
126.762
125.966
124.485
124.069
124.046
124.023
123.998
122.208
114.015
113.270
112.145
102.735
77.483
77.277
77.023
76.805
55.751
F3C
OH
MeO
N
H
150
100
50
ppm (t1)

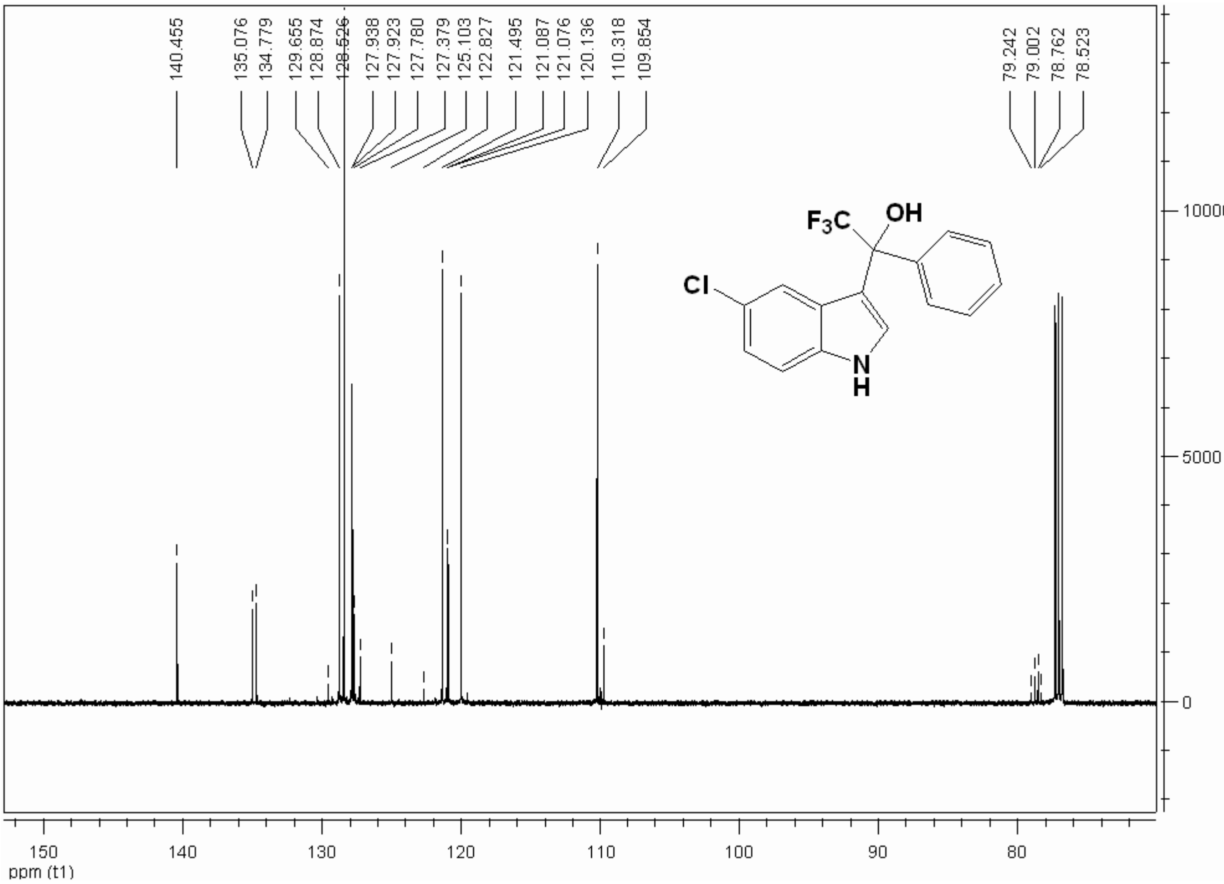

8.301
7.579
7.576
7.574
7.568
7.561
7.559
7.508
7.504
7.499
7.374
7.371
7.367
7.362
7.357
7.355
7.353
7.349
7.312
7.303
7.294
7.285
7.265
6.938
6.933
6.920
6.915
6.902
6.897
6.819
6.814
6.799
6.794
2.858
F3C
OH
F
N
H
0.97
2.07
2.00
3.08
1.05
1.07
1.05
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

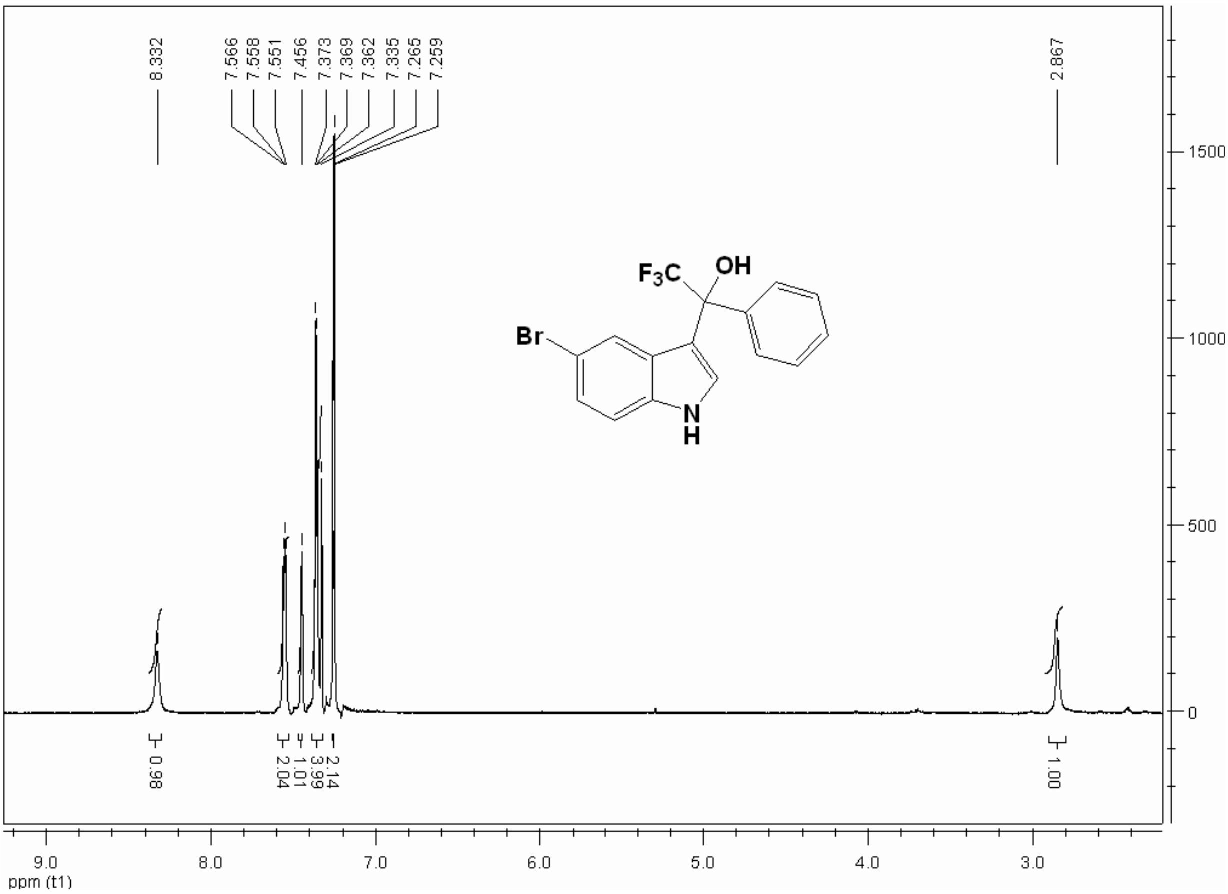

-77.220
-123.323
-123.334
-123.348
-123.359
F3C
OH
F
N
H
2000
1500
1000
500
0
0
-50
-100
-150
-200
ppm (t1)

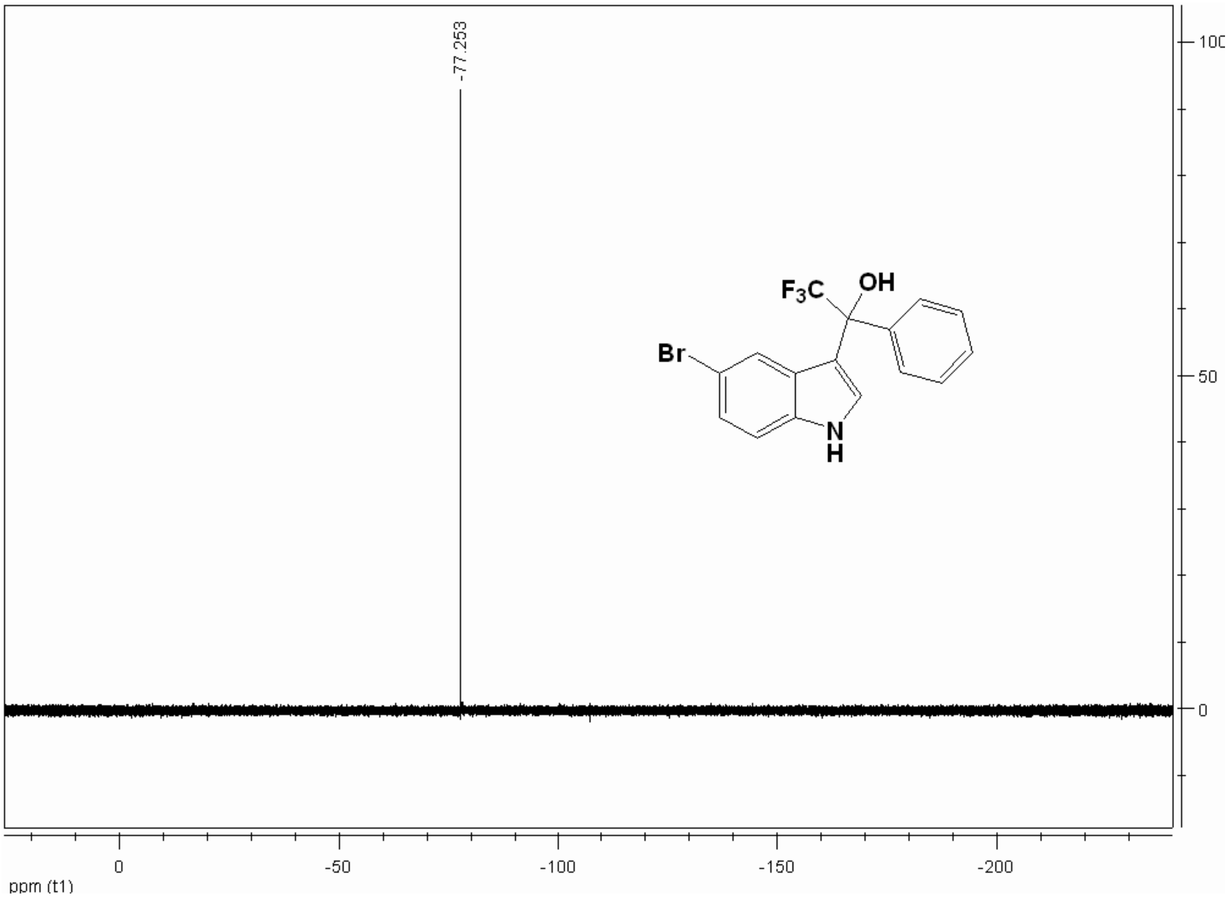

158.858
156.983
137.482
132.962
128.938
128.302
127.750
127.742
126.652
125.988
125.904
125.065
125.043
125.019
124.996
124.376
122.100
114.622
114.584
112.201
112.124
111.722
111.510
106.343
106.148
77.472
77.266
77.012
76.766
F3C
OH
F
N
H
10000
5000
0
150
100
50
ppm (t1)

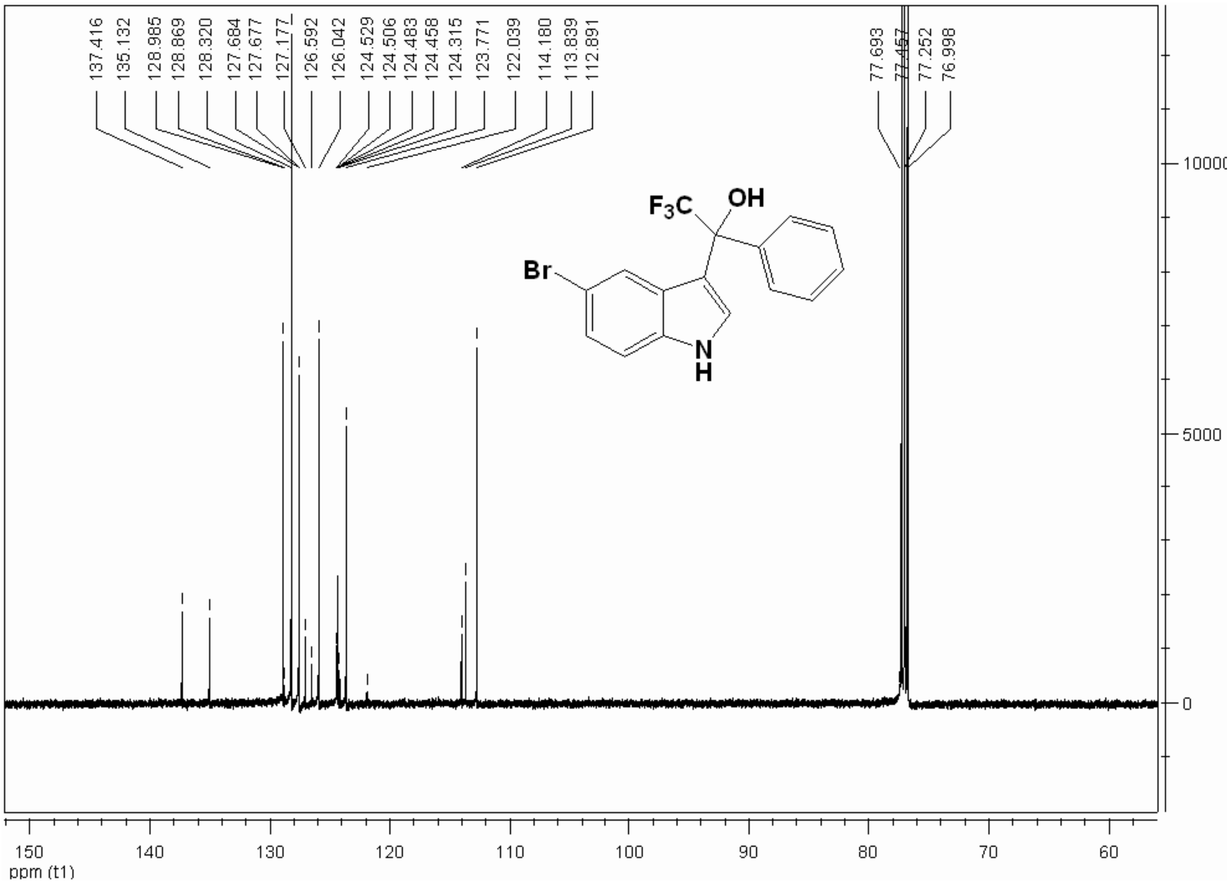


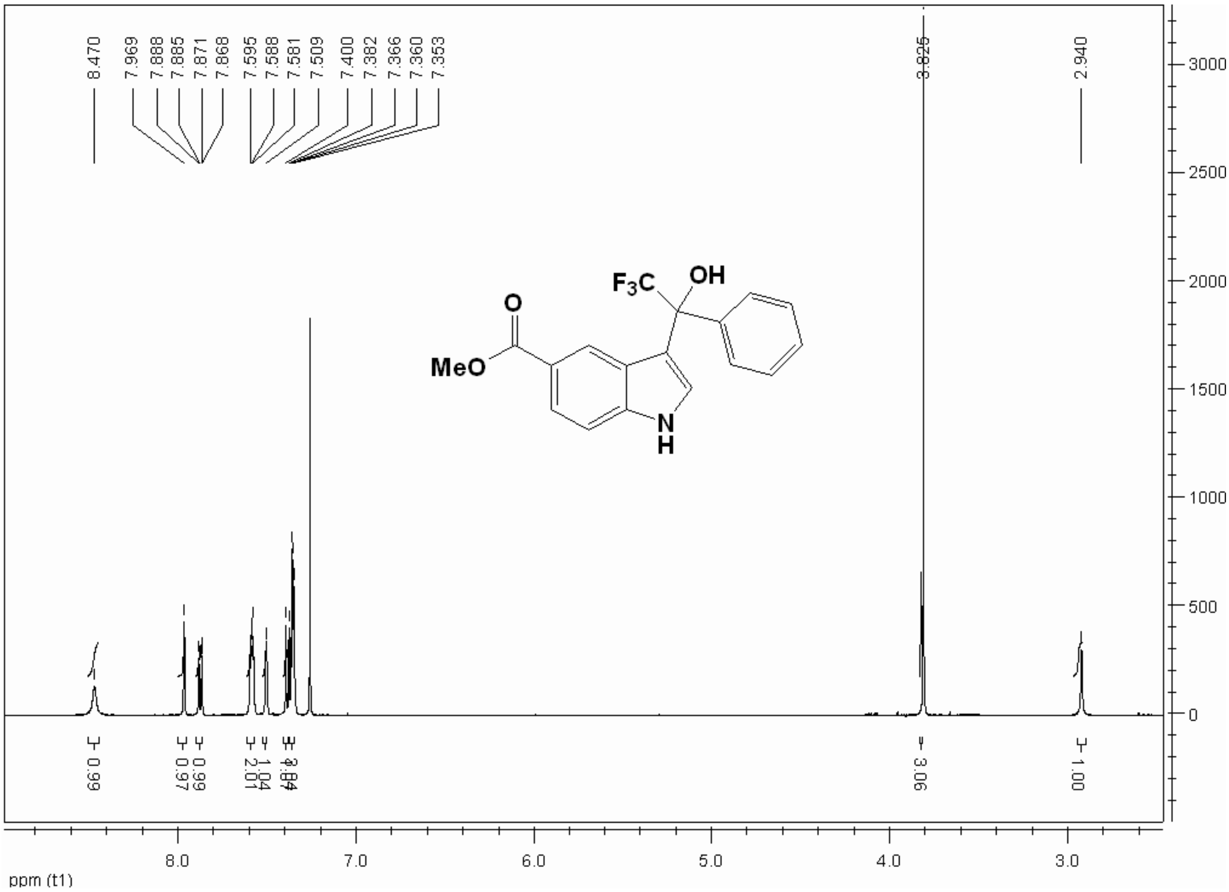


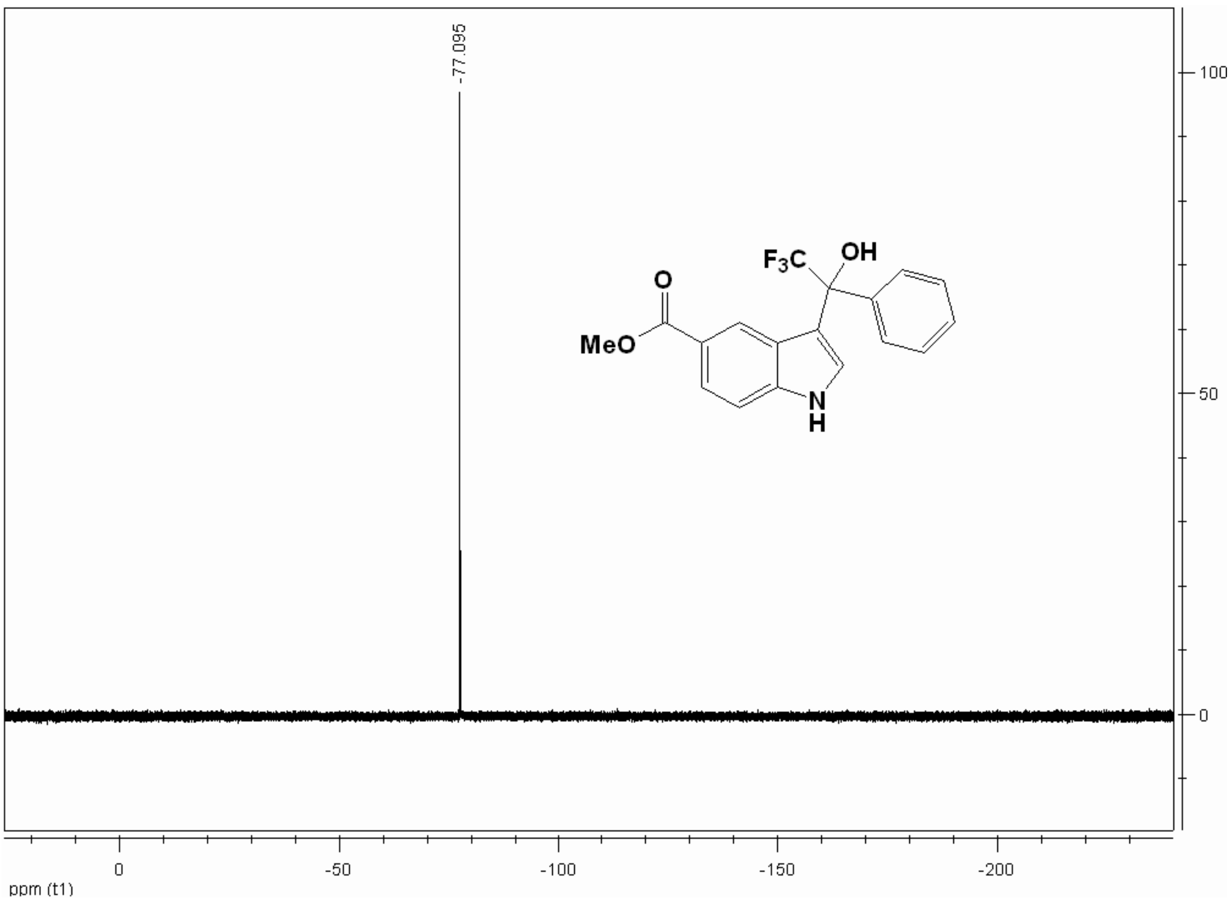

140.455
135.076
134.779
129.655
128.874
128.526
127.938
127.923
127.780
127.379
125.103
122.827
121.495
121.087
121.076
120.136
110.318
109.854
79.242
79.002
78.762
78.523
F3C
OH
Cl
N
H
10000
5000
0
150
140
130
120
110
100
90
80
ppm (t1)

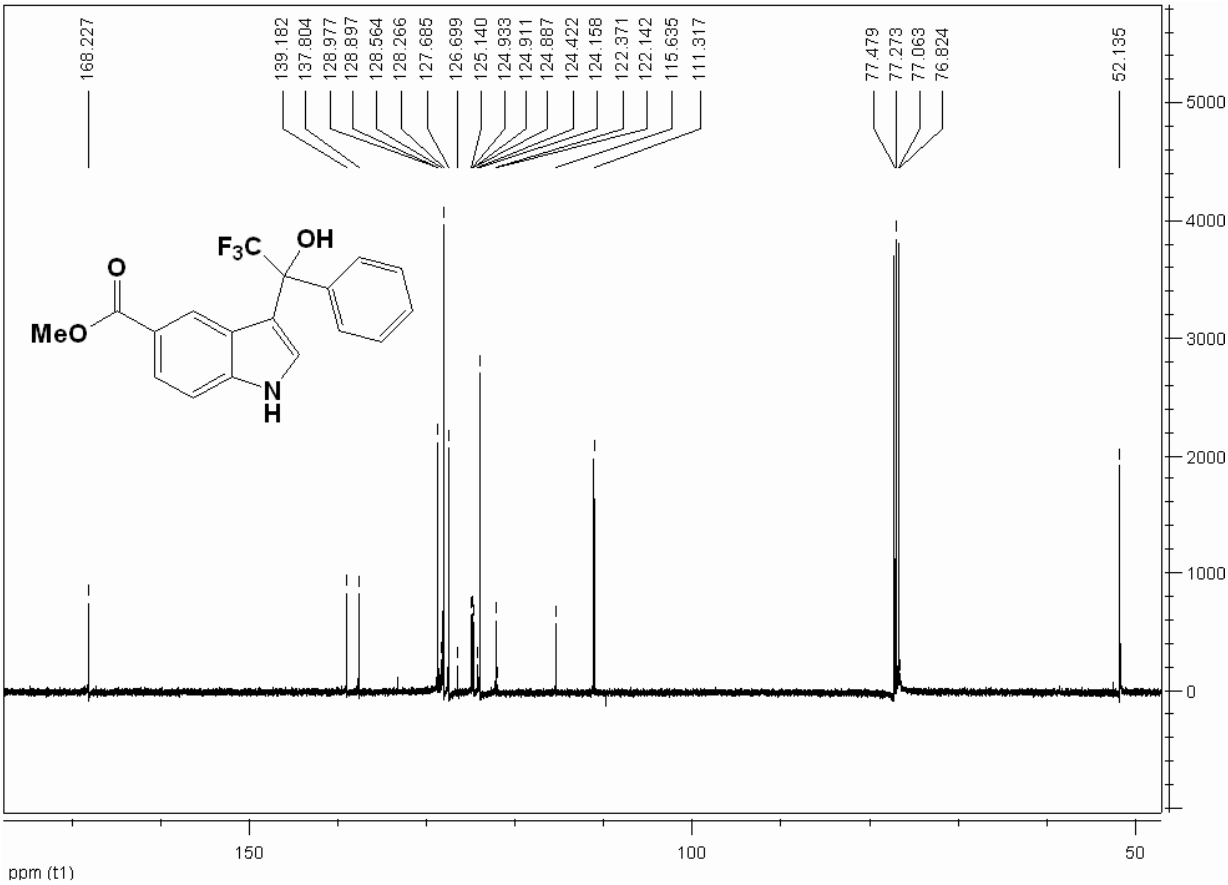

8.332
7.566
7.558
7.551
7.456
7.373
7.369
7.362
7.335
7.265
7.259
2.867
F3C
OH
Br
N
H
1500
1000
500
0
0.98
2.04
1.01
3.99
2.14
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

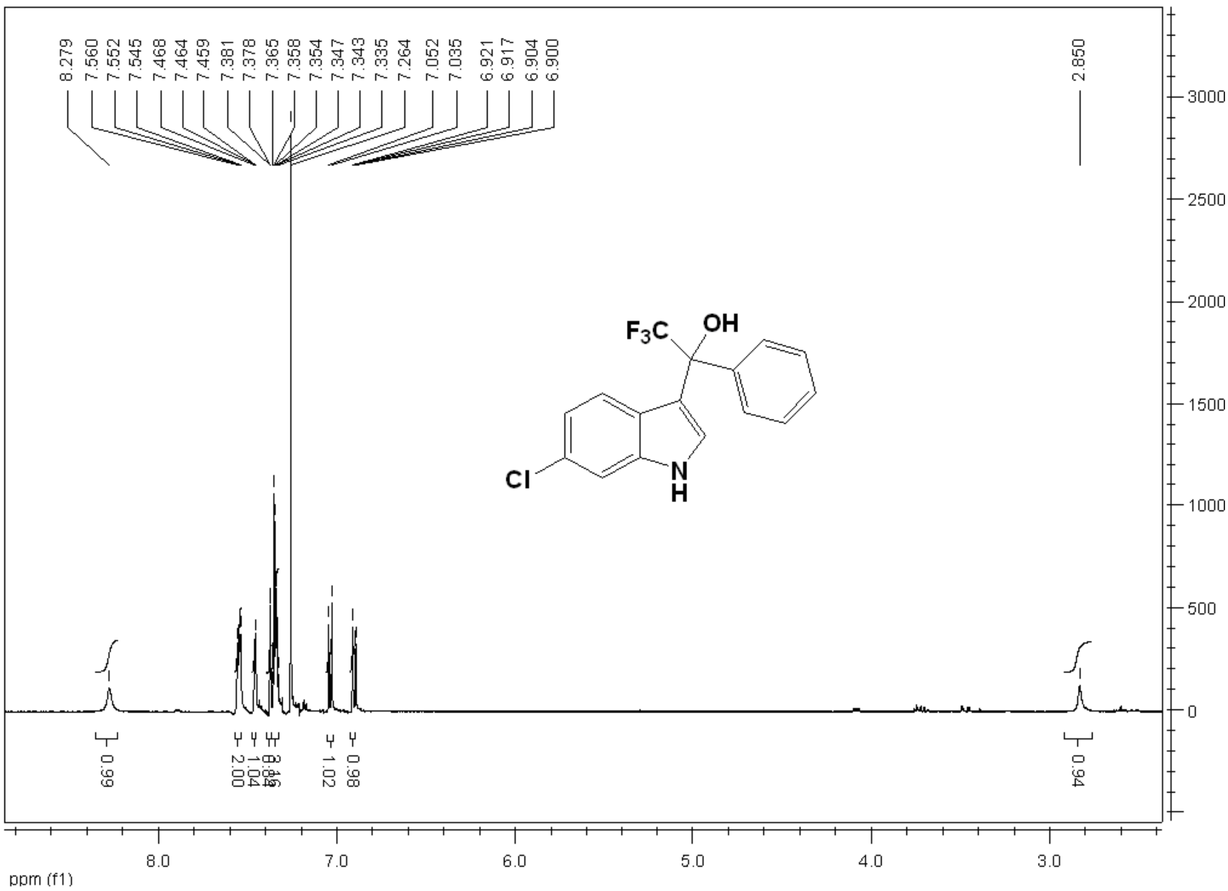

-77.253
F3C
OH
Br
N
H
100
50
0
0
-50
-100
-150
-200
ppm (t1)

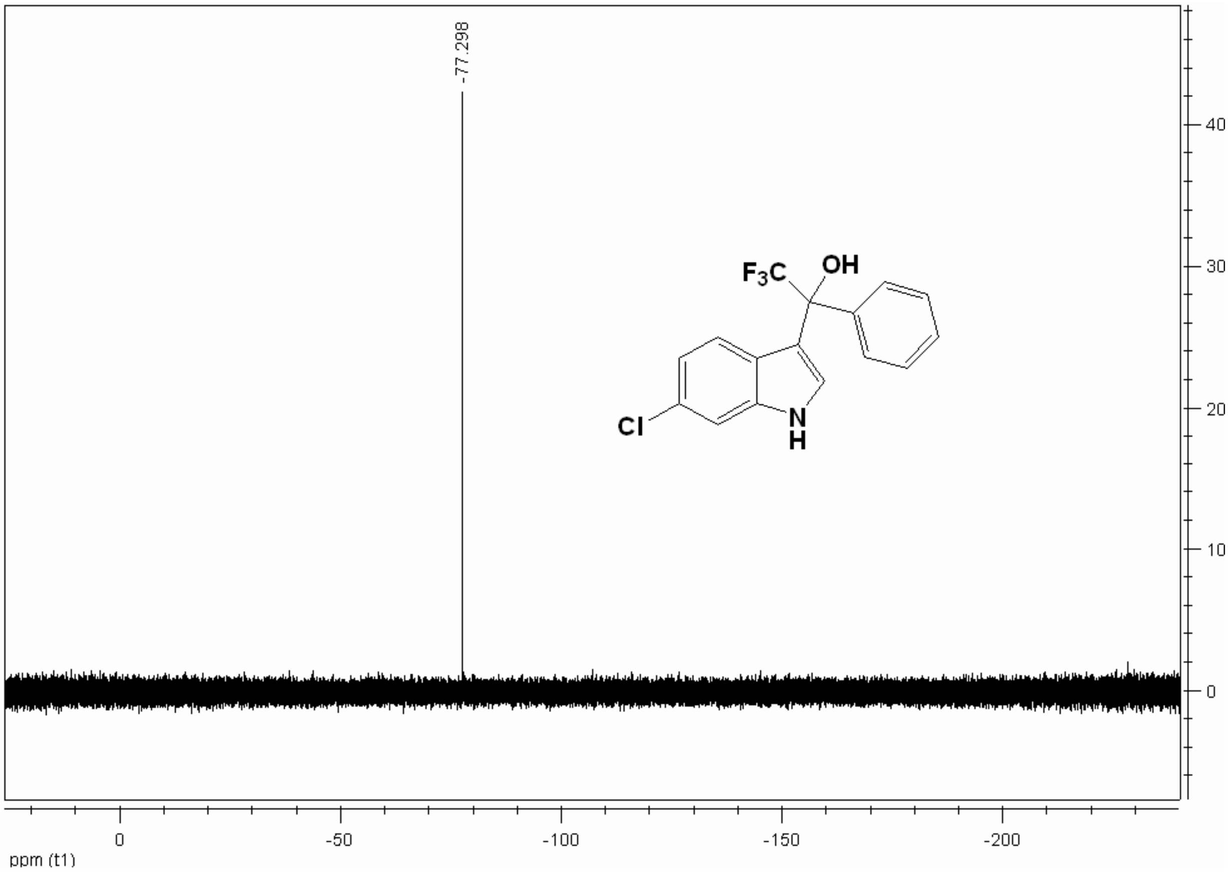

137.416
135.132
128.985
128.869
128.320
127.684
127.677
127.177
126.592
126.042
124.529
124.506
124.483
124.458
124.315
123.771
122.039
114.180
113.839
112.891
77.693
77.457
77.252
76.998
F3C
OH
Br
N
H
10000
5000
0
150
140
130
120
110
100
90
80
70
60
ppm (t1)

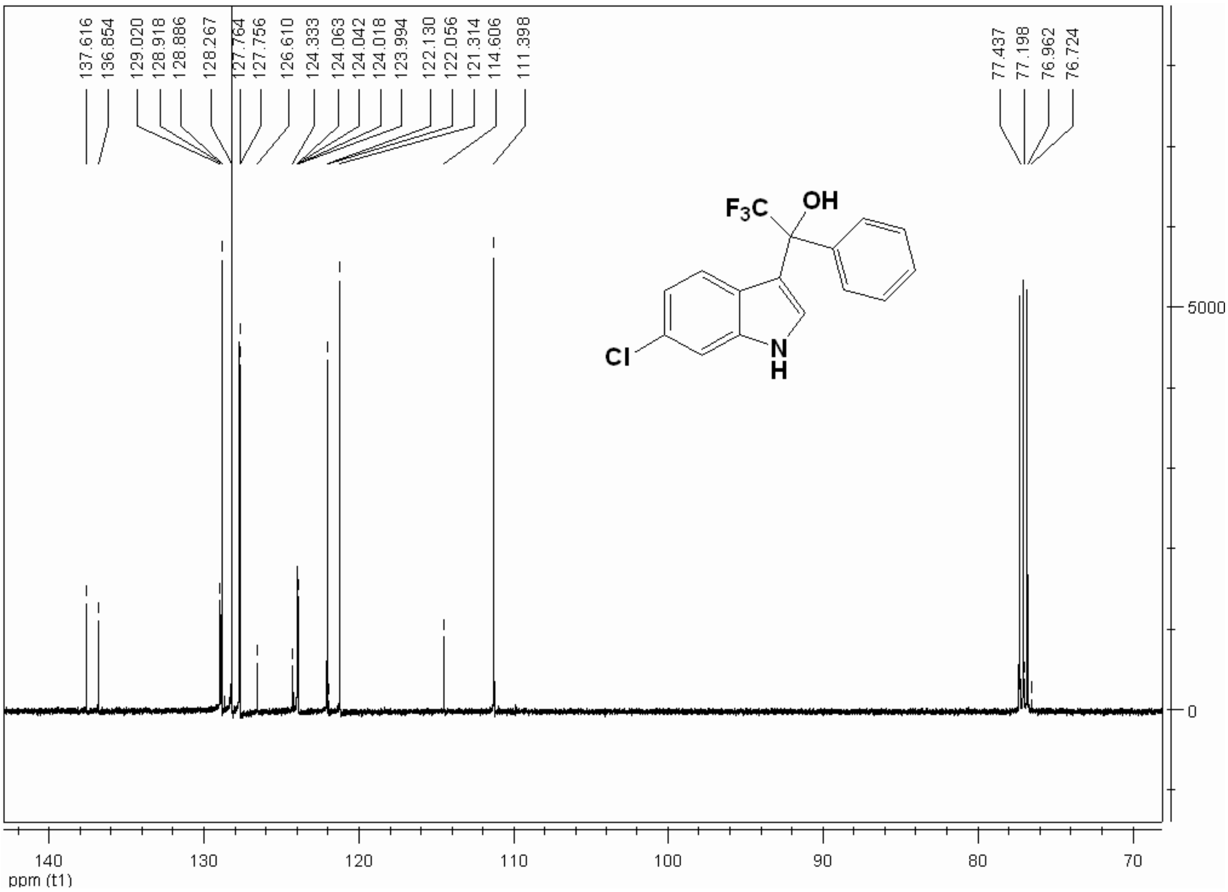

8.470
7.969
7.888
7.885
7.871
7.868
7.595
7.588
7.581
7.509
7.400
7.382
7.366
7.360
7.353
3.825
2.940
F3C
OH
O
MeO
N
H
0.99
0.97
0.99
2.01
1.04
3.06
1.00
3000
2500
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

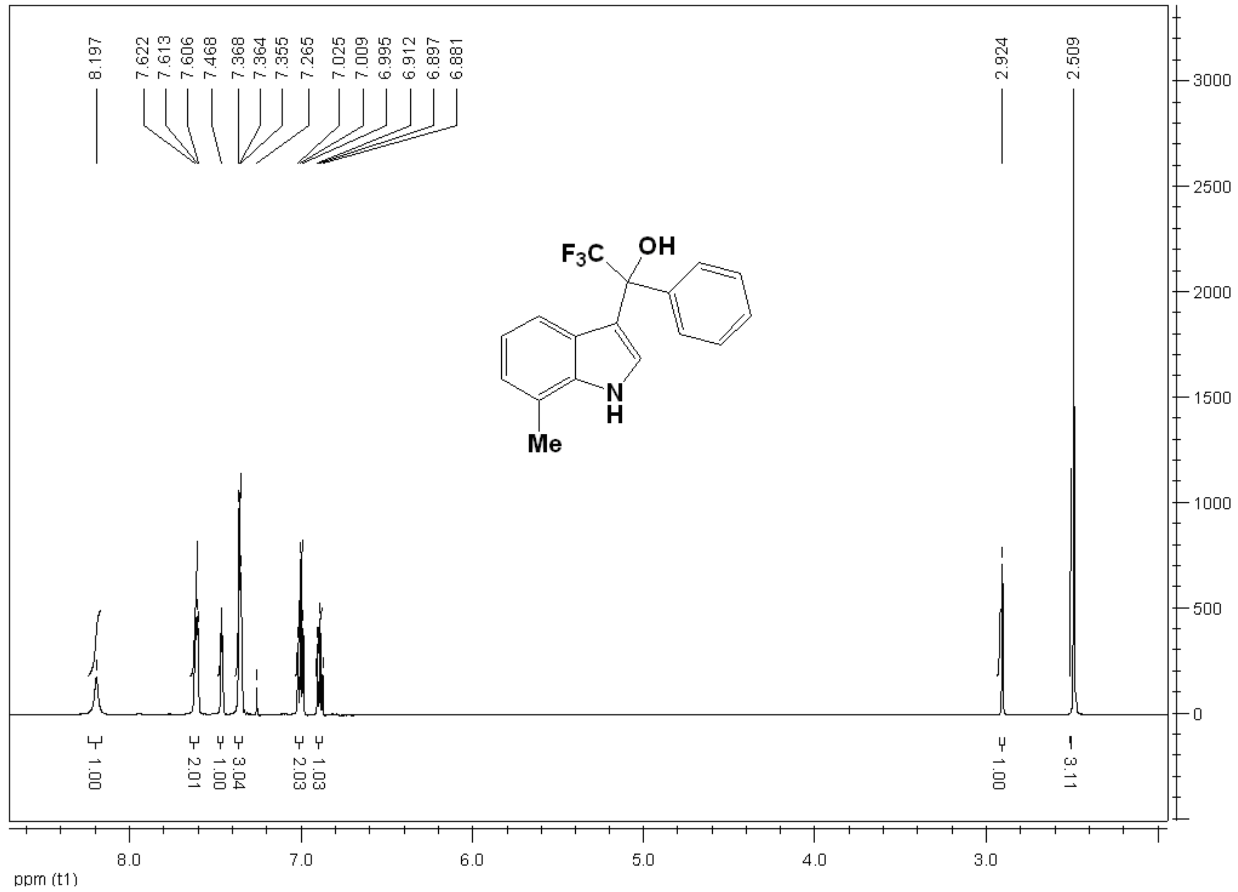

-77.095
F3C
OH
O
MeO
N
H
100
50
0
0
-50
-100
-150
-200
ppm (t1)

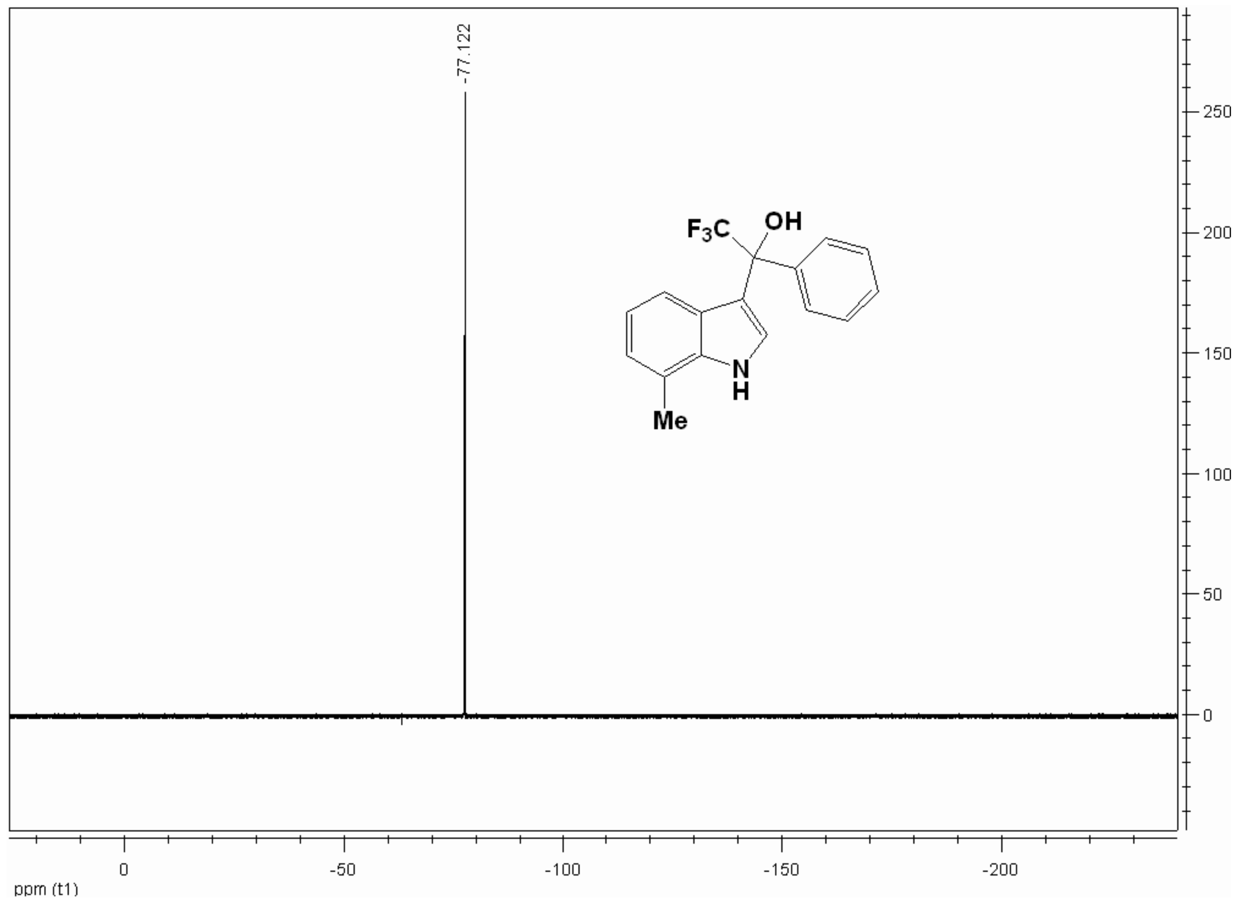

168.227
139.182
137.804
128.977
128.897
128.564
128.266
127.685
126.699
125.140
124.933
124.911
124.887
124.422
124.158
122.371
122.142
115.635
111.317
77.479
77.273
77.063
76.824
52.135
F3C
OH
O
MeO
N
H
5000
4000
3000
2000
1000
0
150
100
50
ppm (t1)

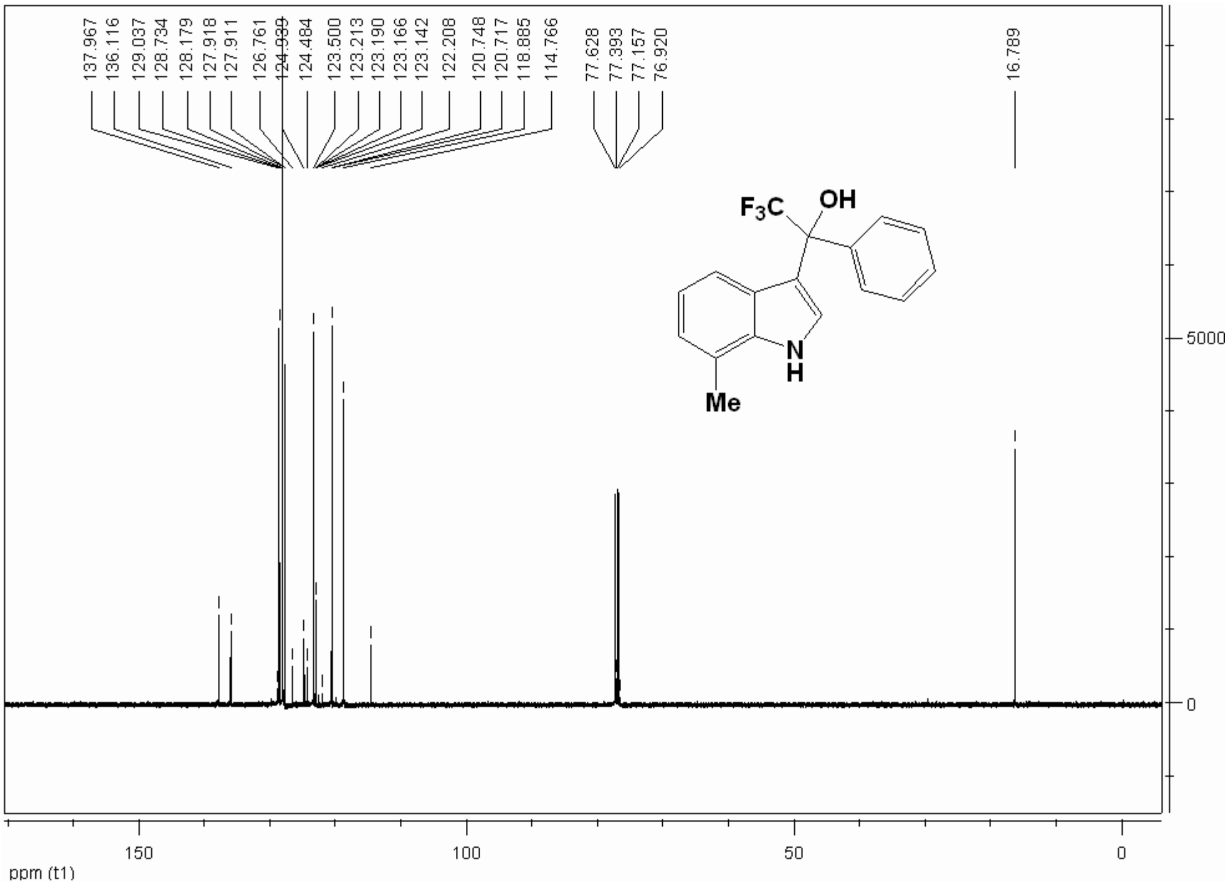

8.279
7.560
7.552
7.545
7.468
7.464
7.459
7.381
7.378
7.365
7.358
7.354
7.347
7.343
7.335
7.264
7.052
7.035
6.921
6.917
6.904
6.900
2.850
F3C
OH
Cl
N
H
3000
2500
2000
1500
1000
500
0
0.99
2.00
1.04
1.02
0.98
0.94
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

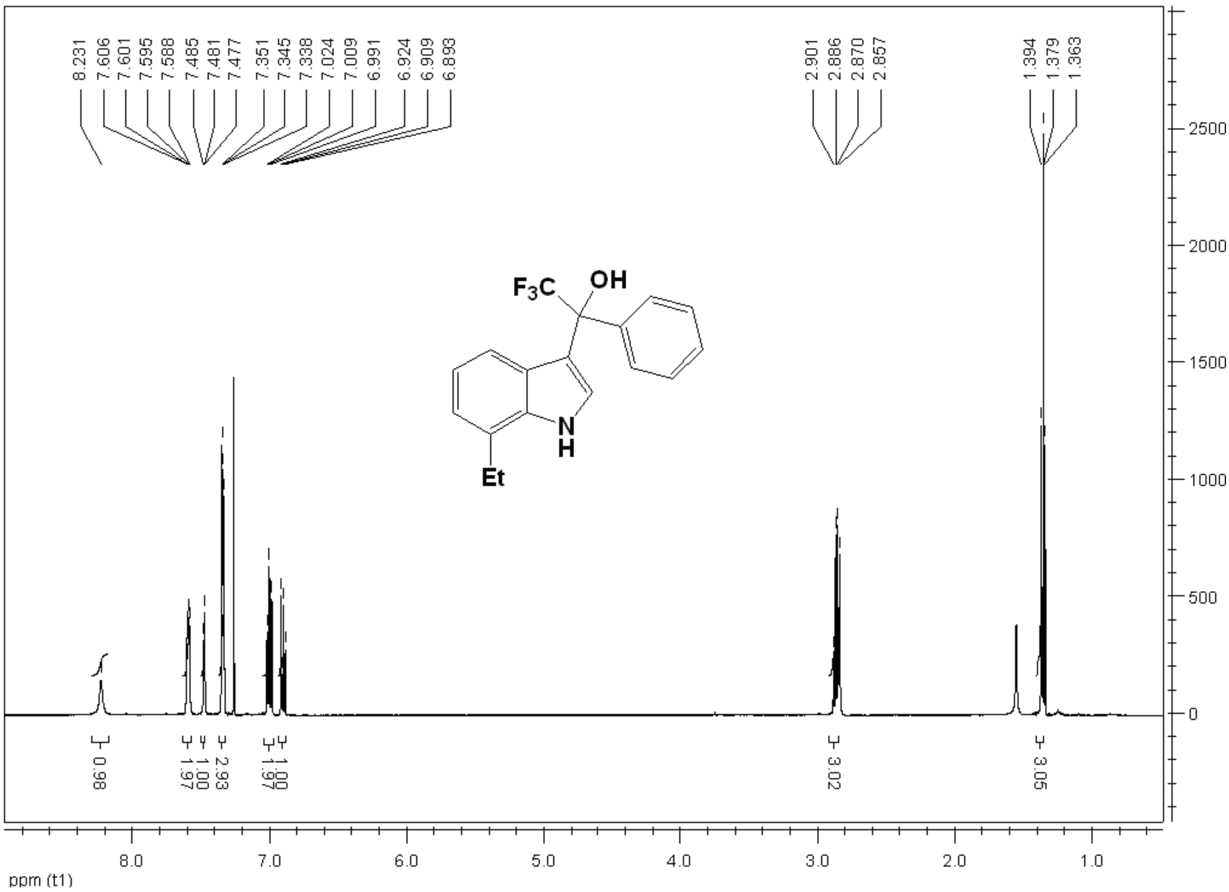

-77.298
40
30
20
10
0
0
-50
-100
-150
-200
ppm (t1)
F3C
OH
Cl
N
H

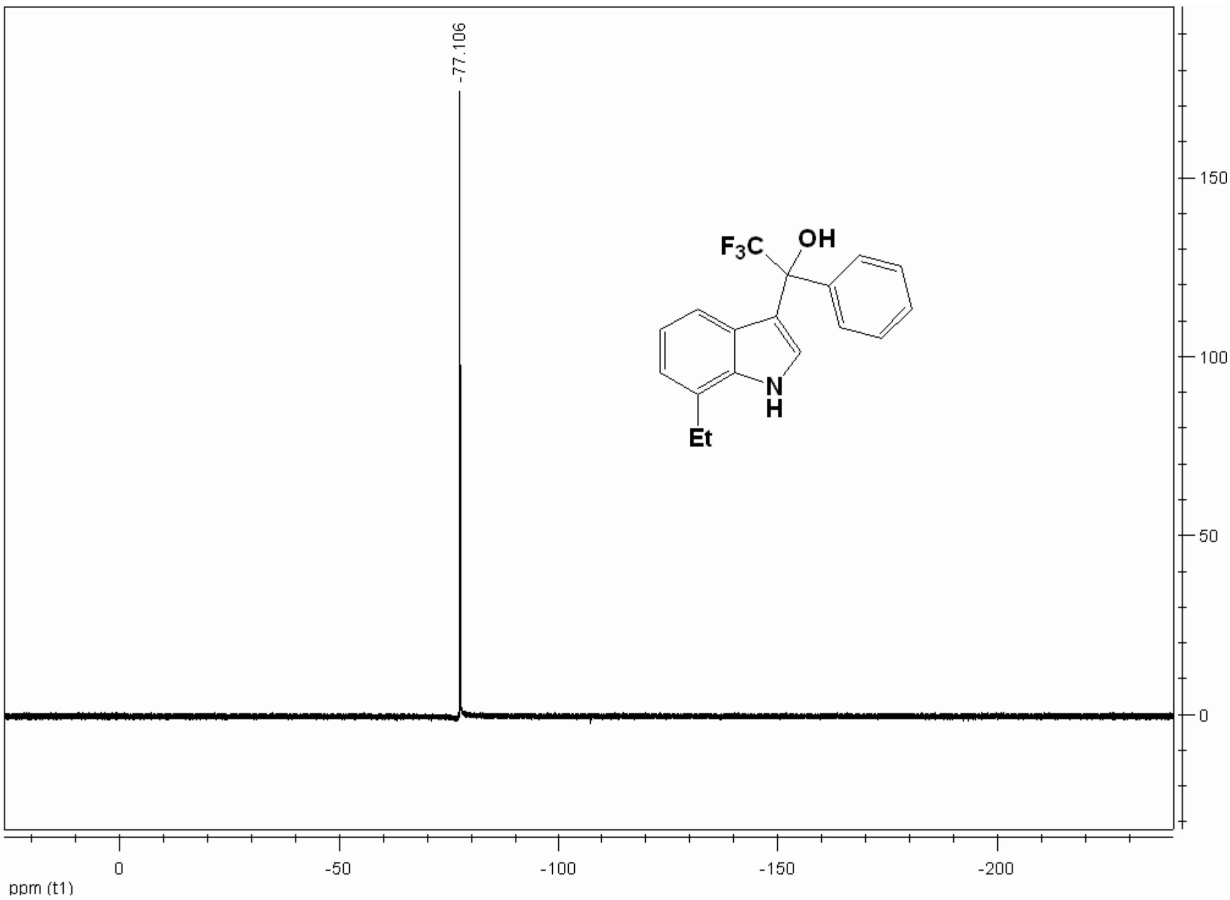

137.616
136.854
129.020
128.918
128.886
128.267
127.764
127.756
126.610
124.333
124.063
124.042
124.018
123.994
122.130
122.056
121.314
114.606
111.398
77.437
77.198
76.962
76.724
5000
0
140
130
120
110
100
90
80
70
ppm (t1)
F3C
OH
Cl
N
H

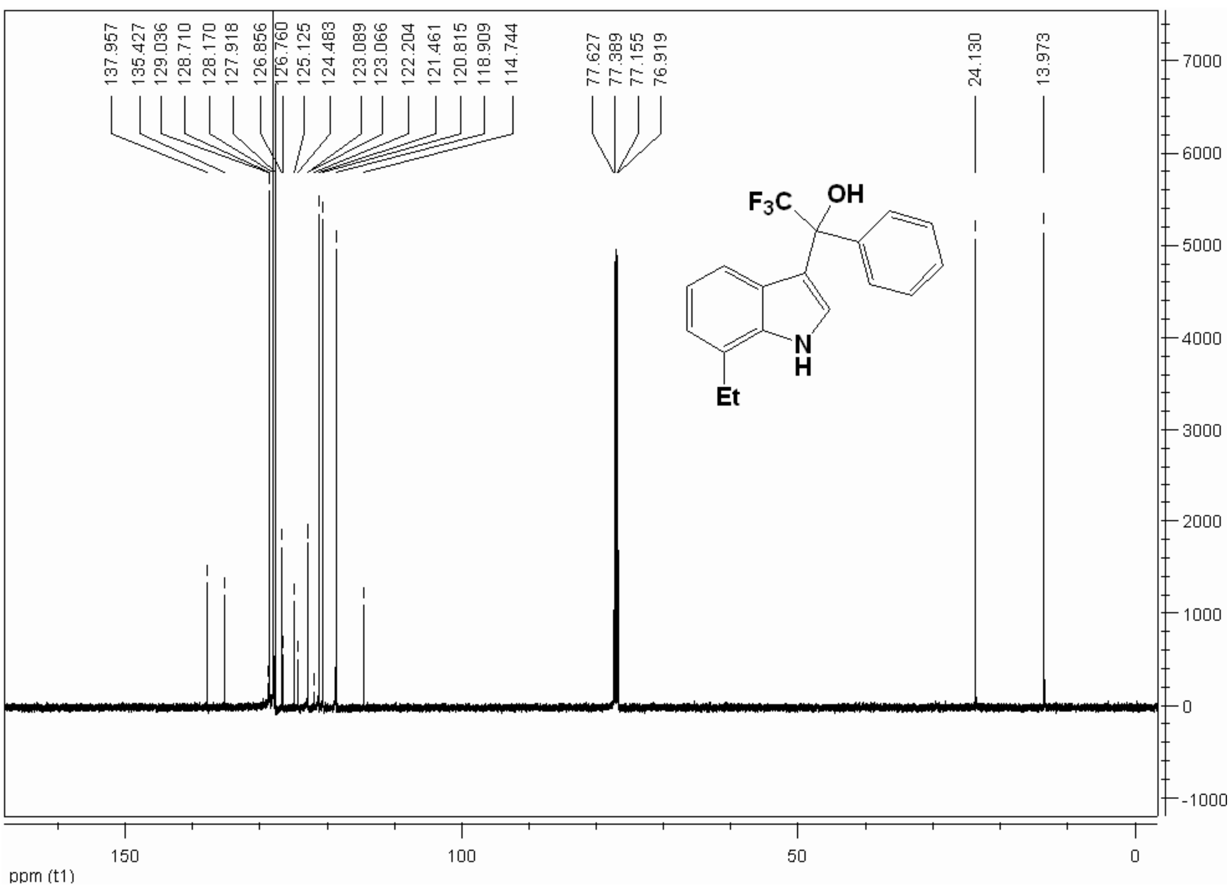

8.197
7.622
7.613
7.606
7.468
7.368
7.364
7.355
7.265
7.025
7.009
6.995
6.912
6.897
6.881
2.924
2.509
F3C
OH
N
H
Me
1.00
2.01
1.00
3.04
2.03
1.03
1.00
3.11
ppm (t1)

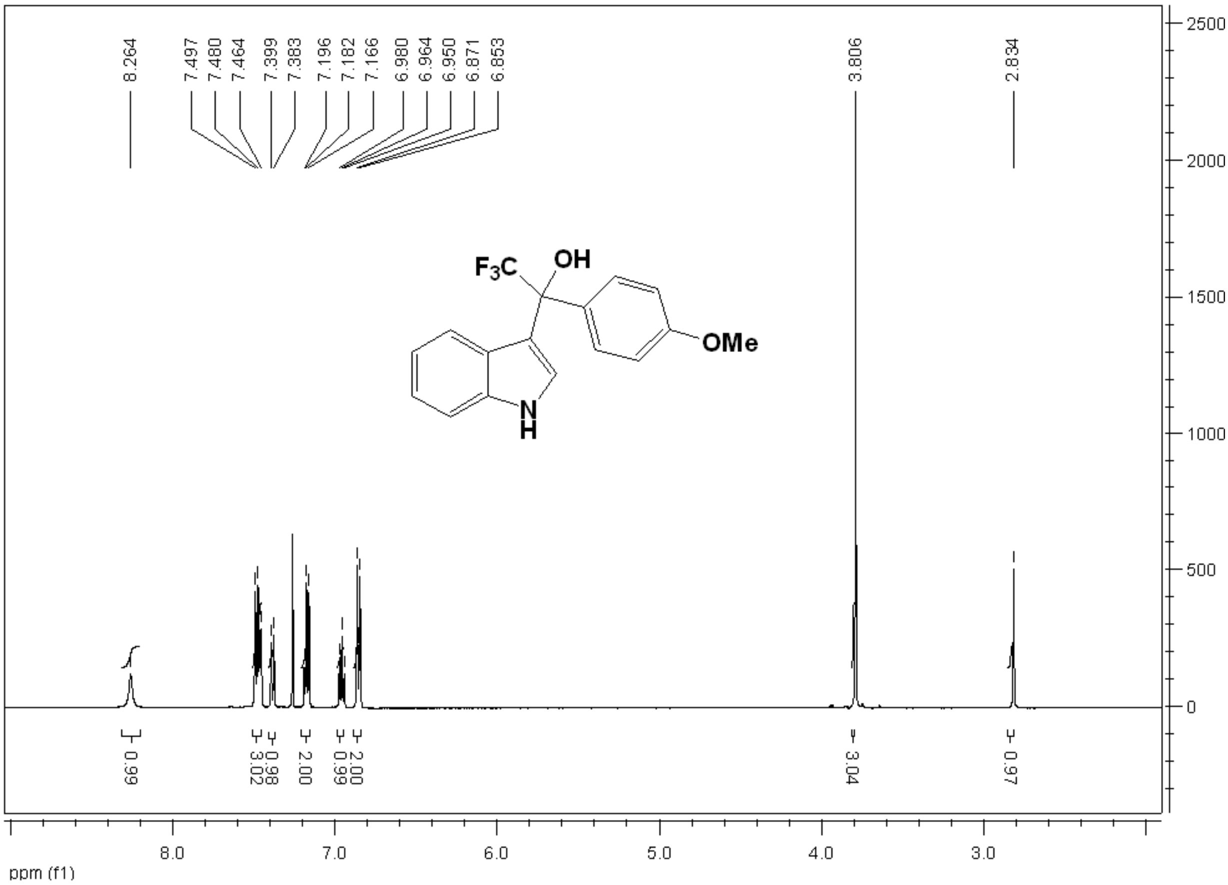

-77.122
F3C
OH
N
H
Me
ppm (t1)

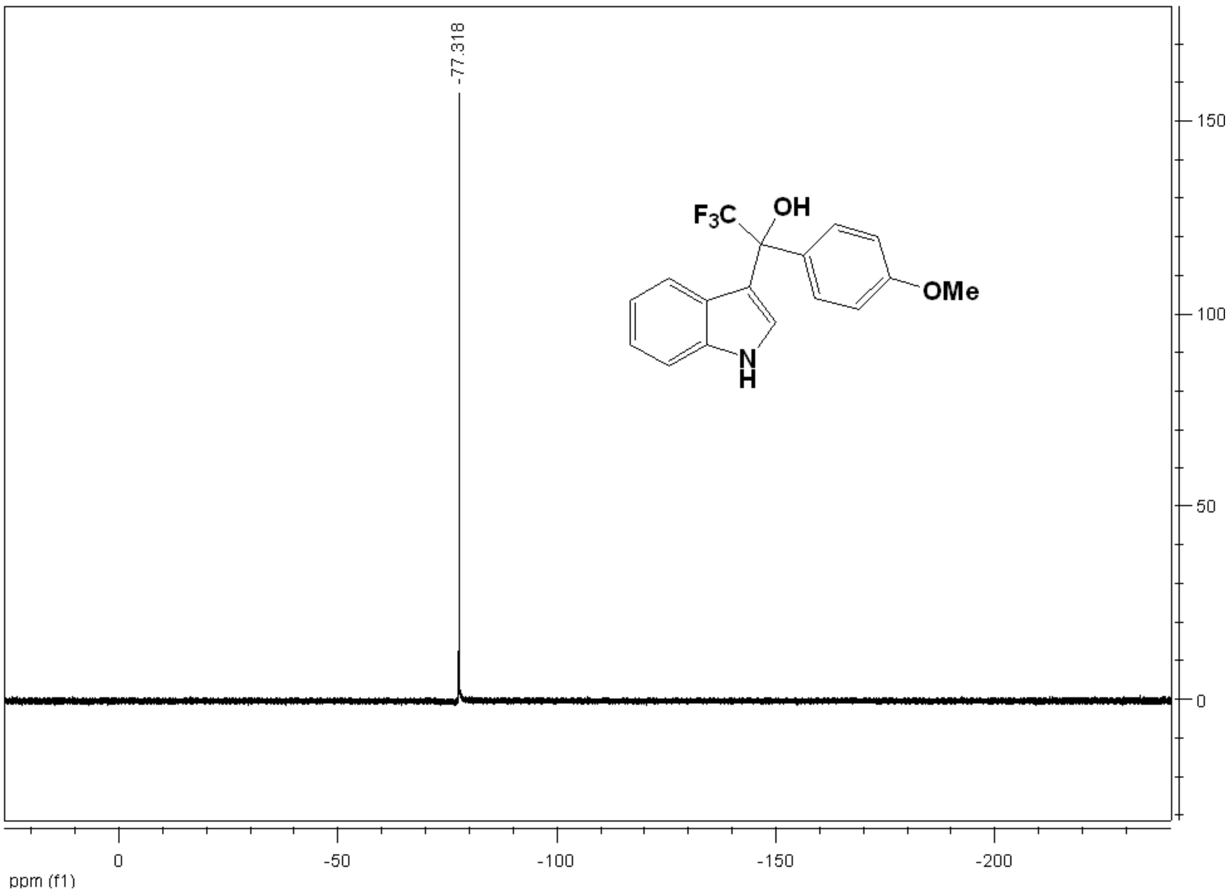


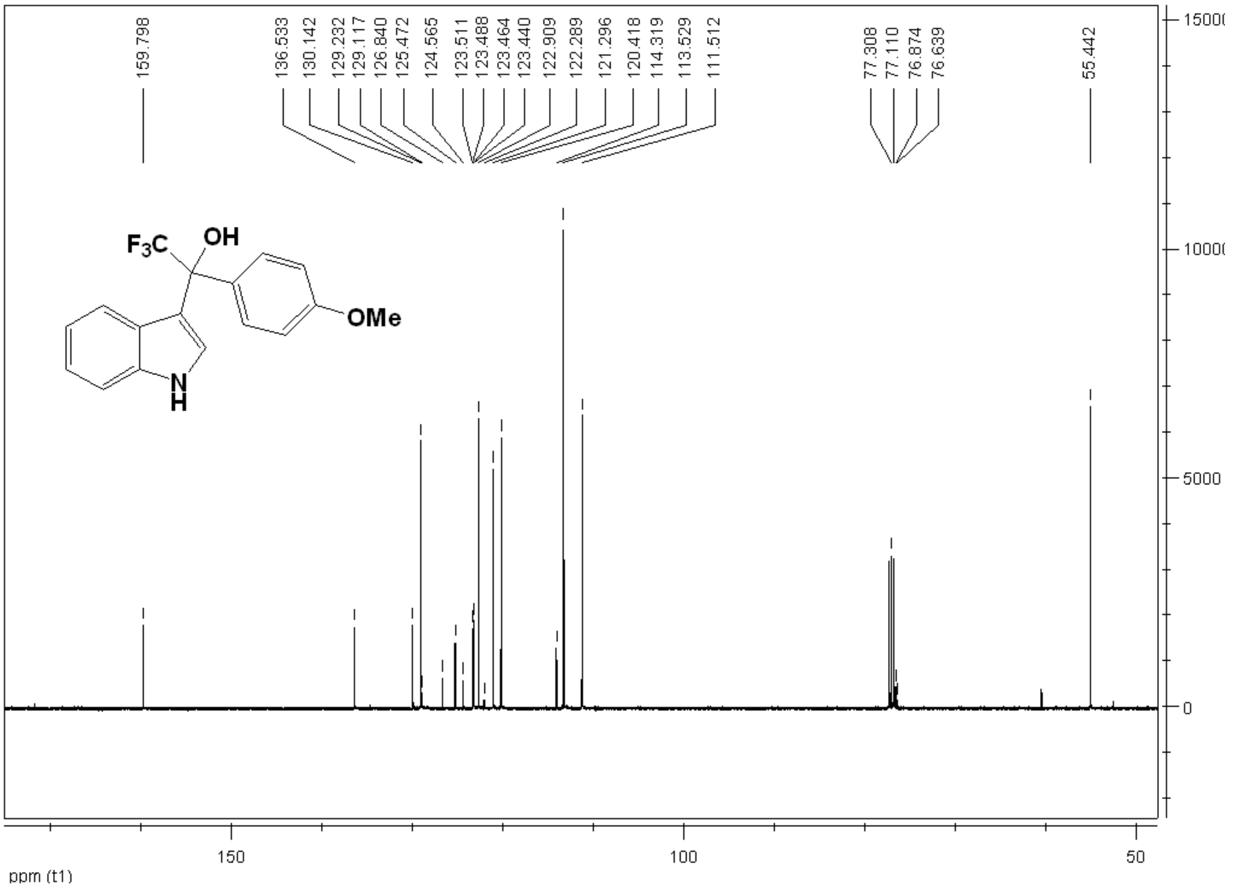


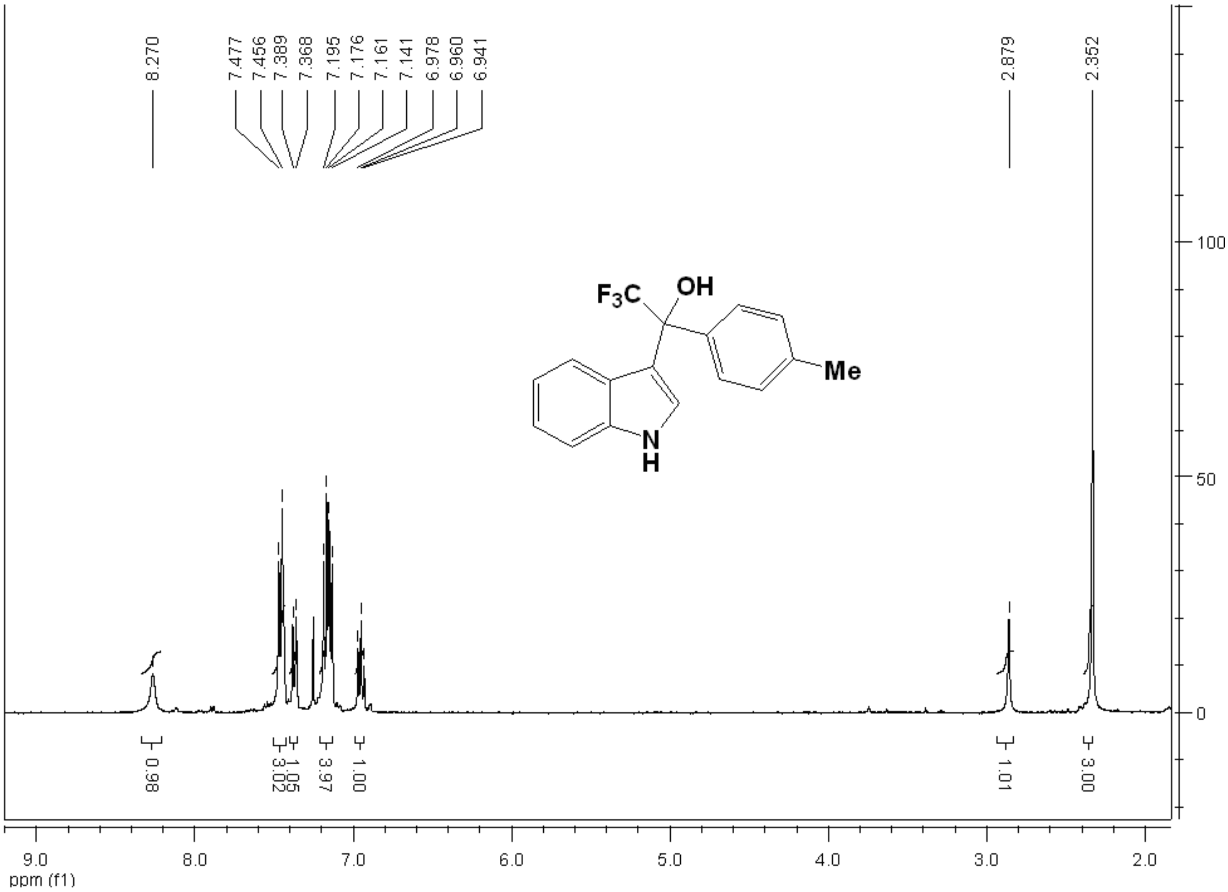

-77.106
F3C
OH
N
H
Et
150
100
50
0
0
-50
-100
-150
-200
ppm (t1)

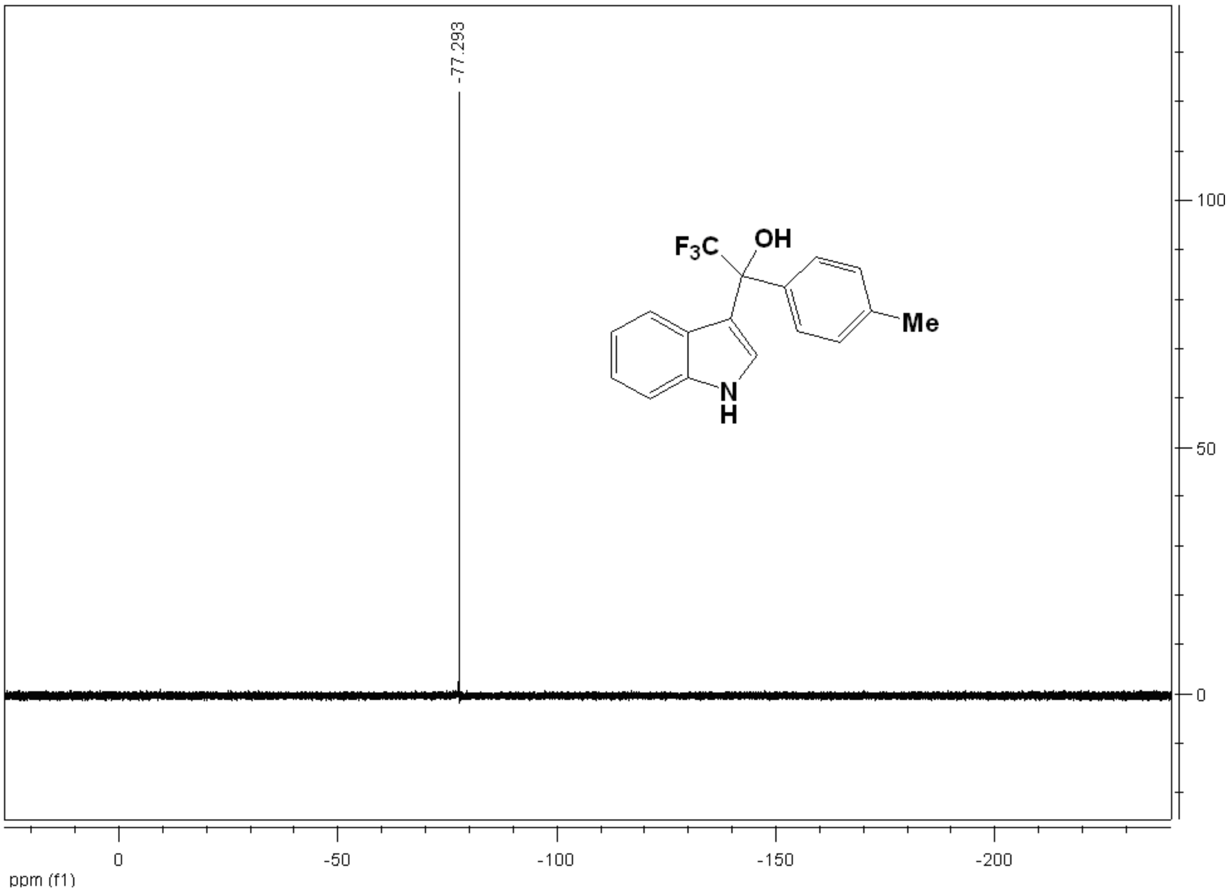

137.957
135.427
129.036
128.710
128.170
127.918
126.856
126.760
125.125
124.483
123.089
123.066
122.204
121.461
120.815
118.909
114.744
77.627
77.389
77.155
76.919
24.130
13.973
F3C
OH
N
H
Et
7000
6000
5000
4000
3000
2000
1000
0
-1000
150
100
50
0
ppm (t1)

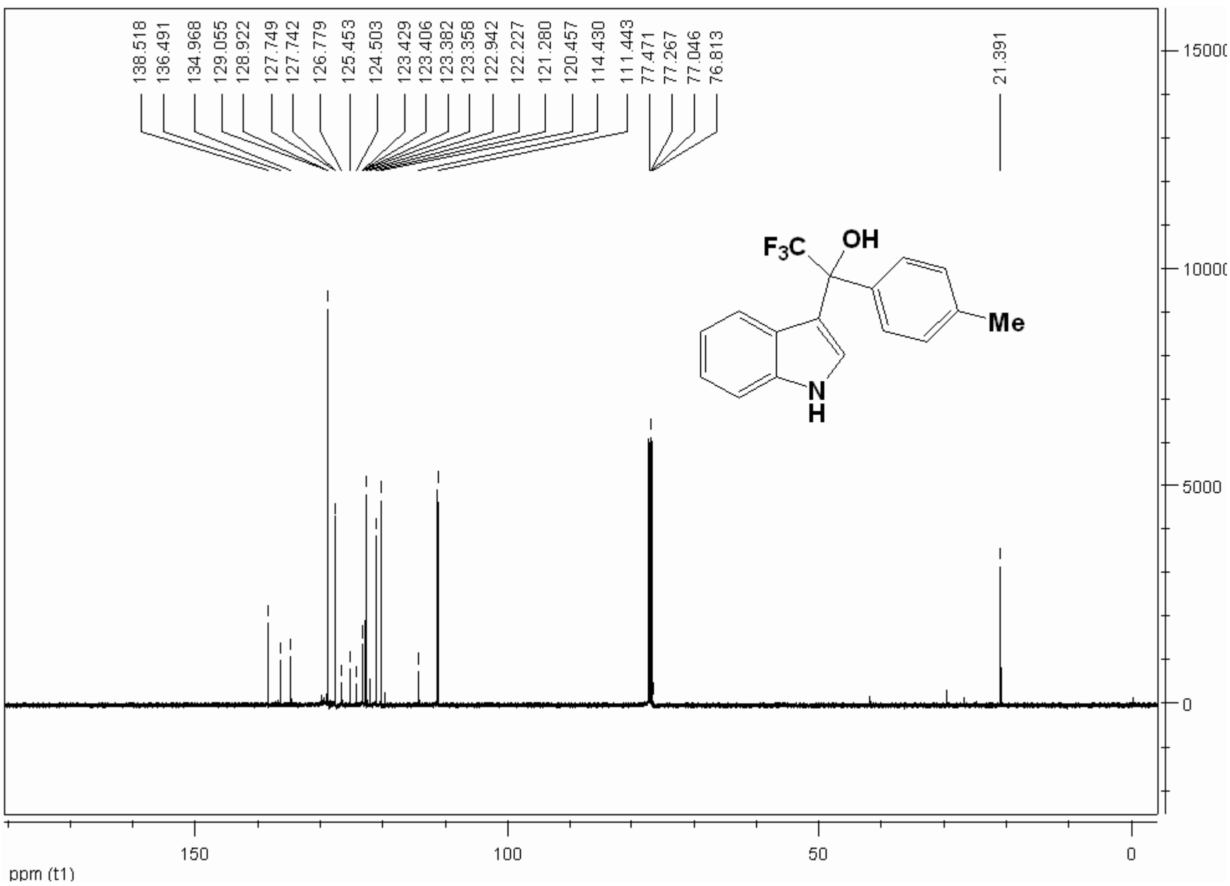

8.264
7.497
7.480
7.464
7.399
7.383
7.196
7.182
7.166
6.980
6.964
6.950
6.871
6.853
3.806
2.834
F3C
OH
OMe
N
H
0.99
3.02
0.98
2.00
0.99
2.00
3.04
0.97
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)
2500
2000
1500
1000
500
0

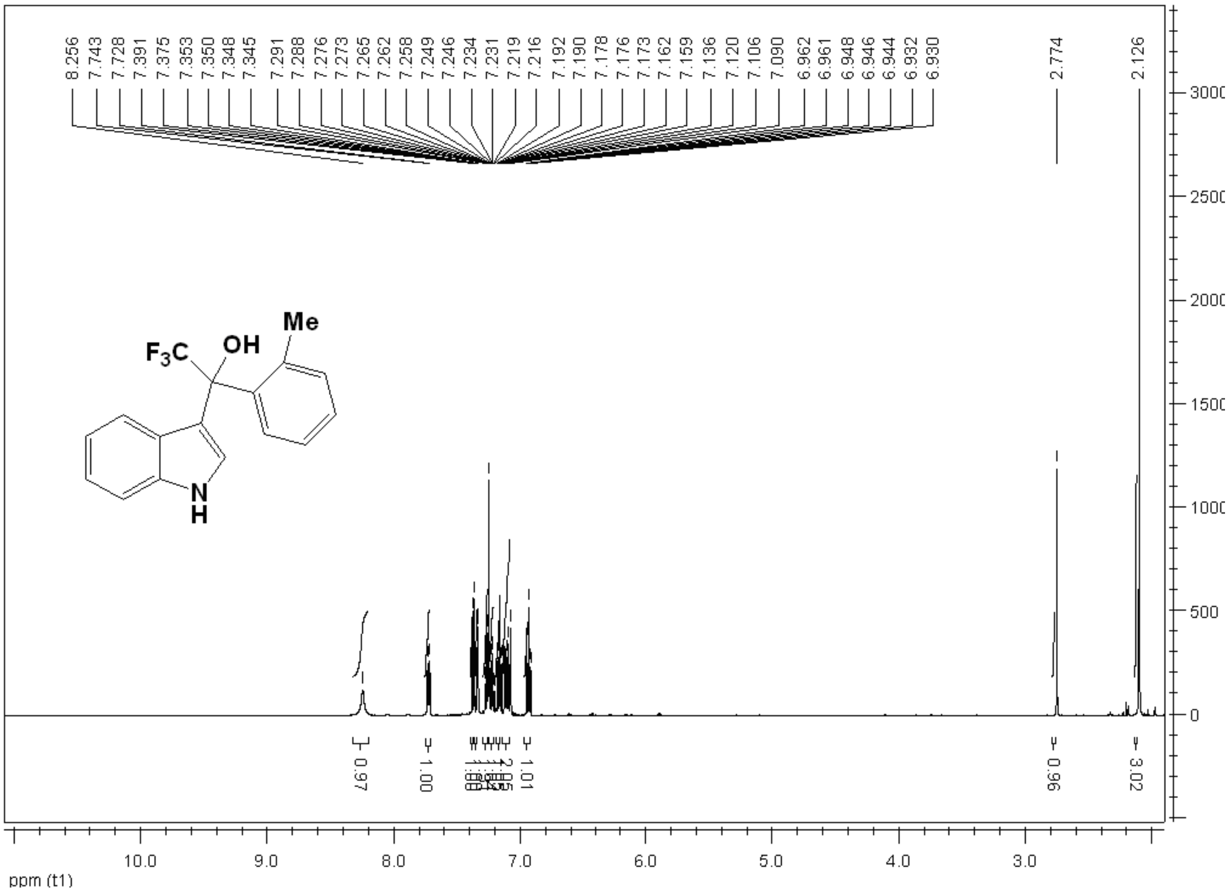

-77.318
F3C
OH
OMe
N
H
0
-50
-100
-150
-200
ppm (f1)
150
100
50
0

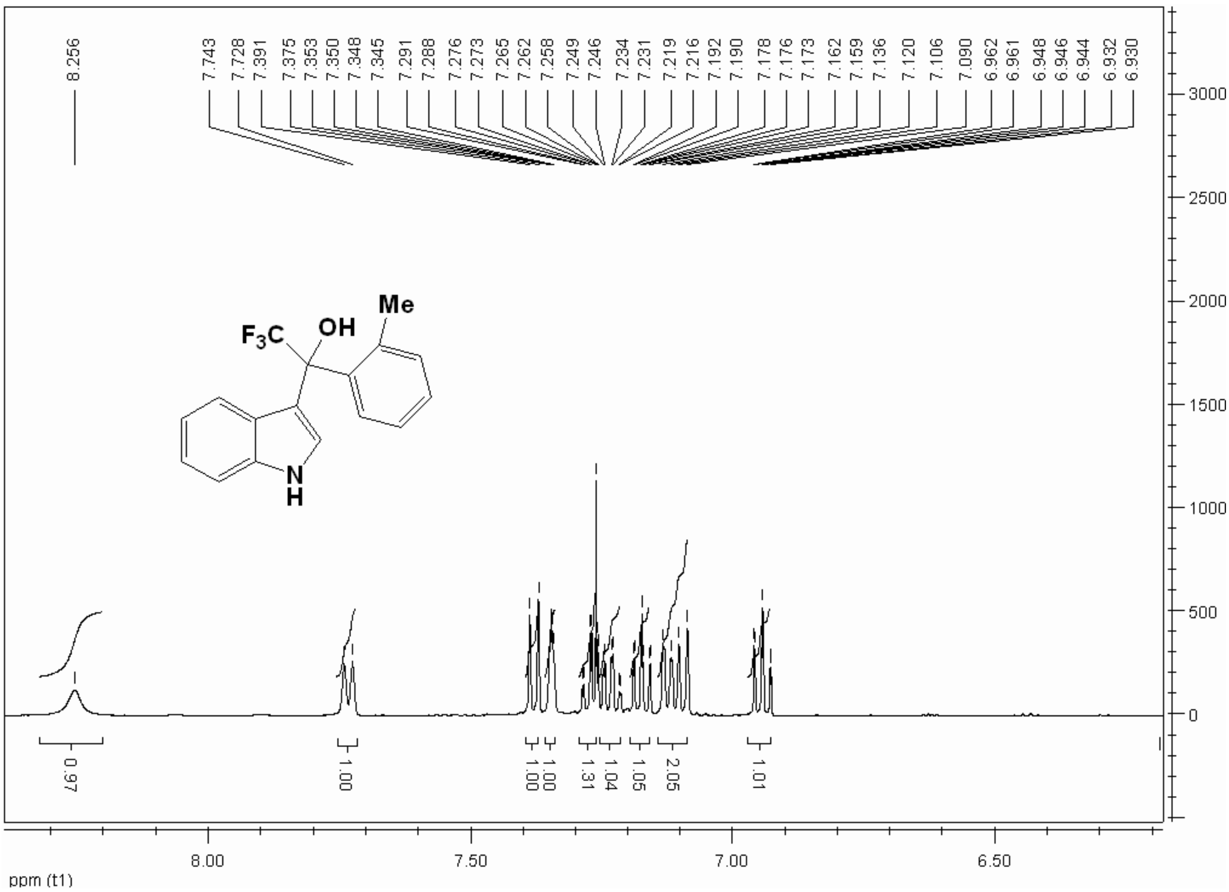

159.798
136.533
130.142
129.232
129.117
126.840
125.472
124.565
123.511
123.488
123.464
123.440
122.909
122.289
121.296
120.418
114.319
113.529
111.512
77.308
77.110
76.874
76.639
55.442
F3C
OH
OMe
N
H
150
100
50
ppm (t1)
5000
0

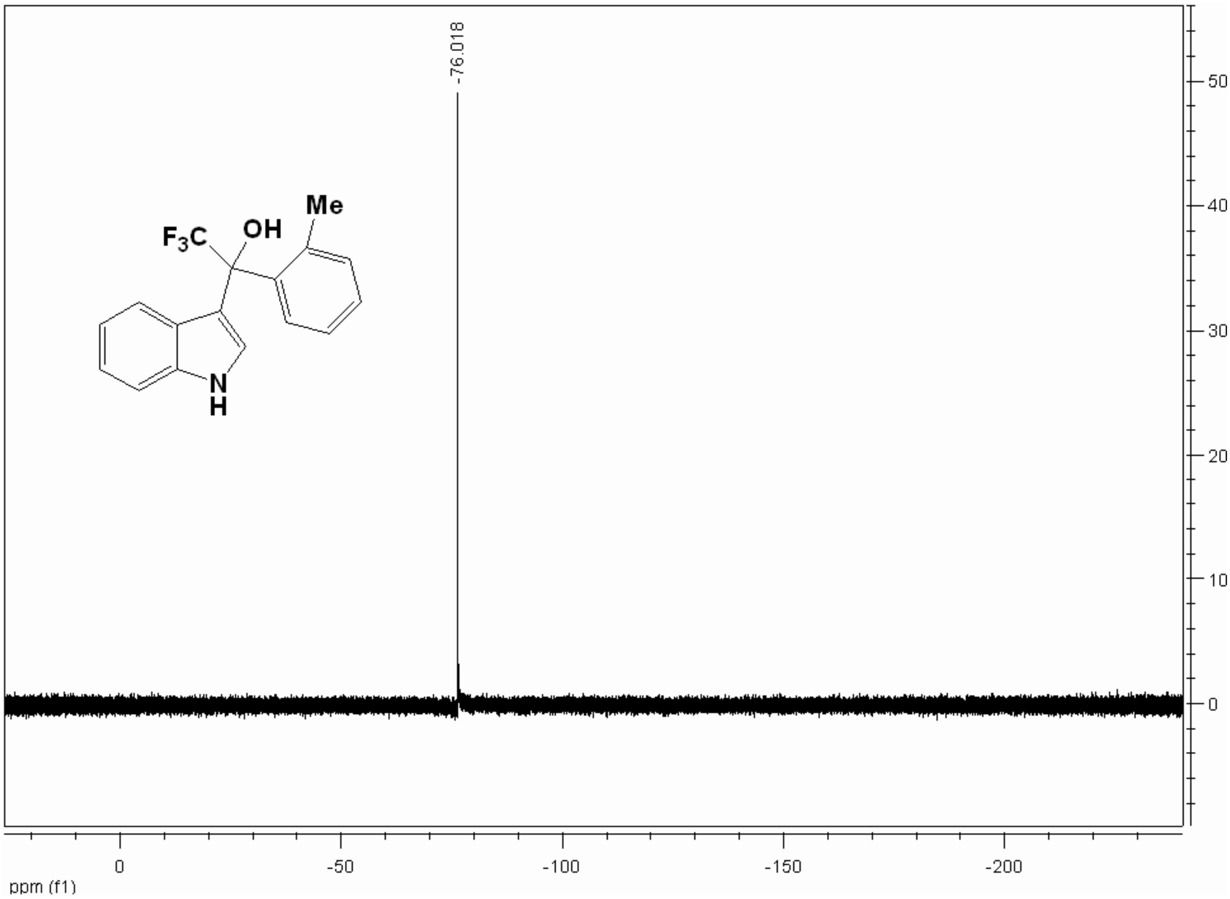

8.270
7.477
7.456
7.389
7.368
7.195
7.176
7.161
7.141
6.978
6.960
6.941
2.879
2.352
F3C
OH
Me
N
H
100
50
0
0.98
3.02
1.05
3.97
1.00
1.01
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

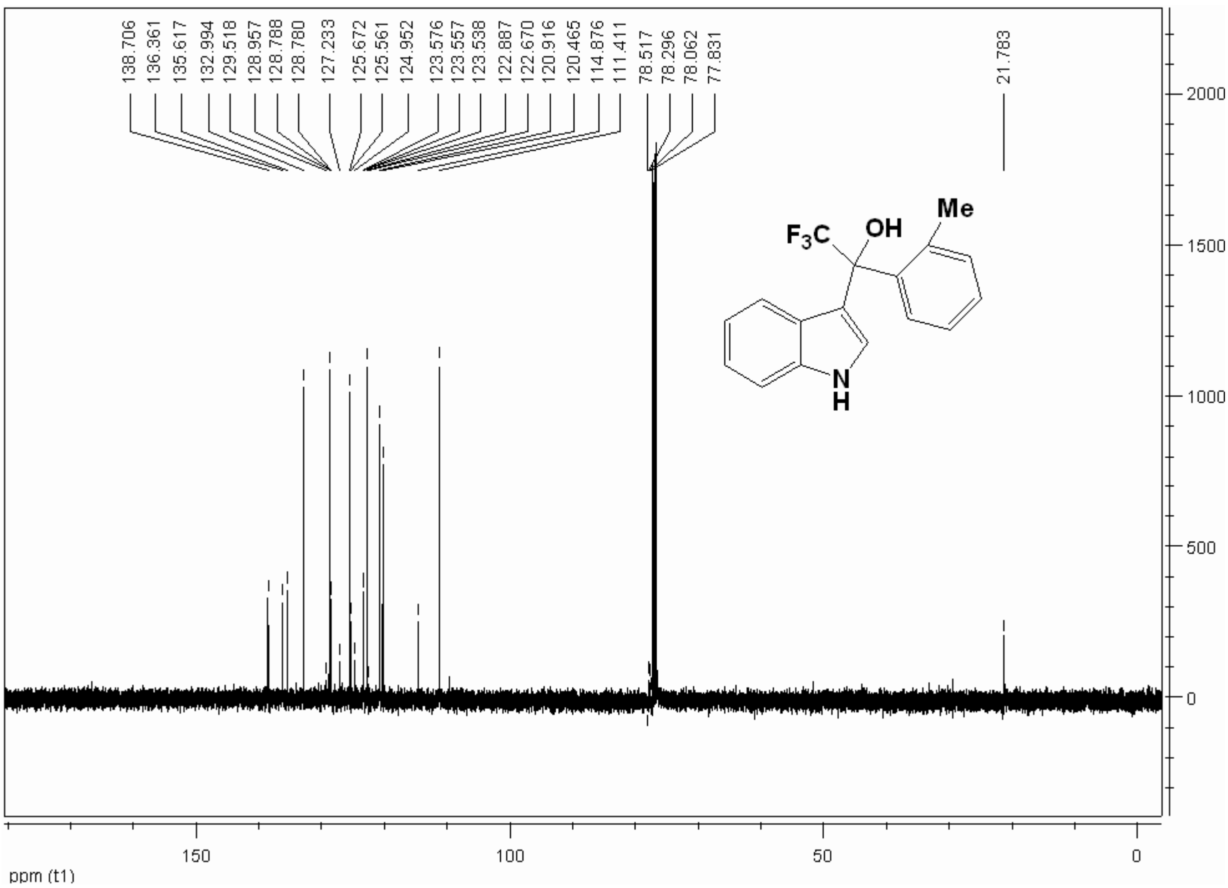

-77.293
F3C OH
Me
N
H
100
50
0
0
-50
-100
-150
-200
ppm (f1)

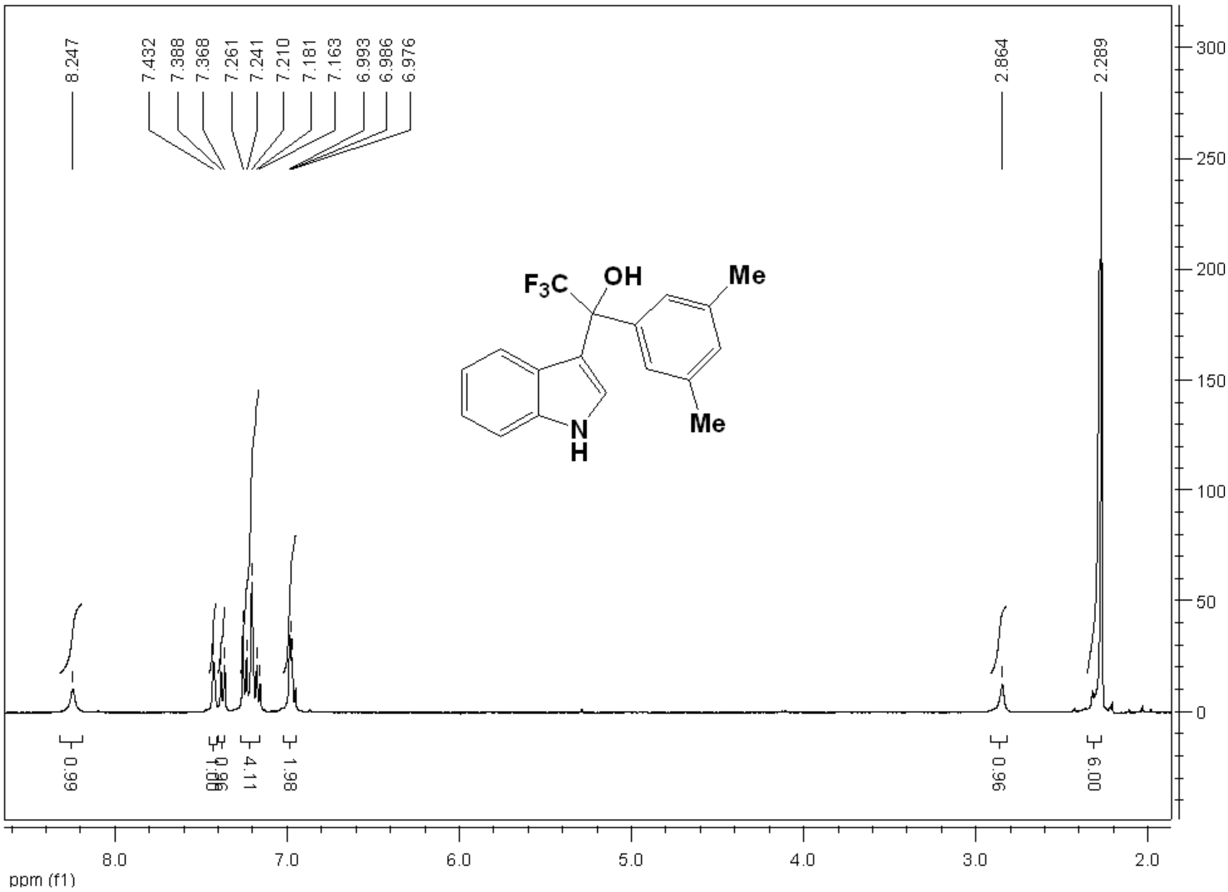

138.518
136.491
134.968
129.055
128.922
127.749
127.742
126.779
125.453
124.503
123.429
123.406
123.382
123.358
122.942
122.227
121.280
120.457
114.430
111.443
77.471
77.267
77.046
76.813
21.391
F3C OH
Me
N
H
15000
10000
5000
0
150
100
50
0
ppm (t1)

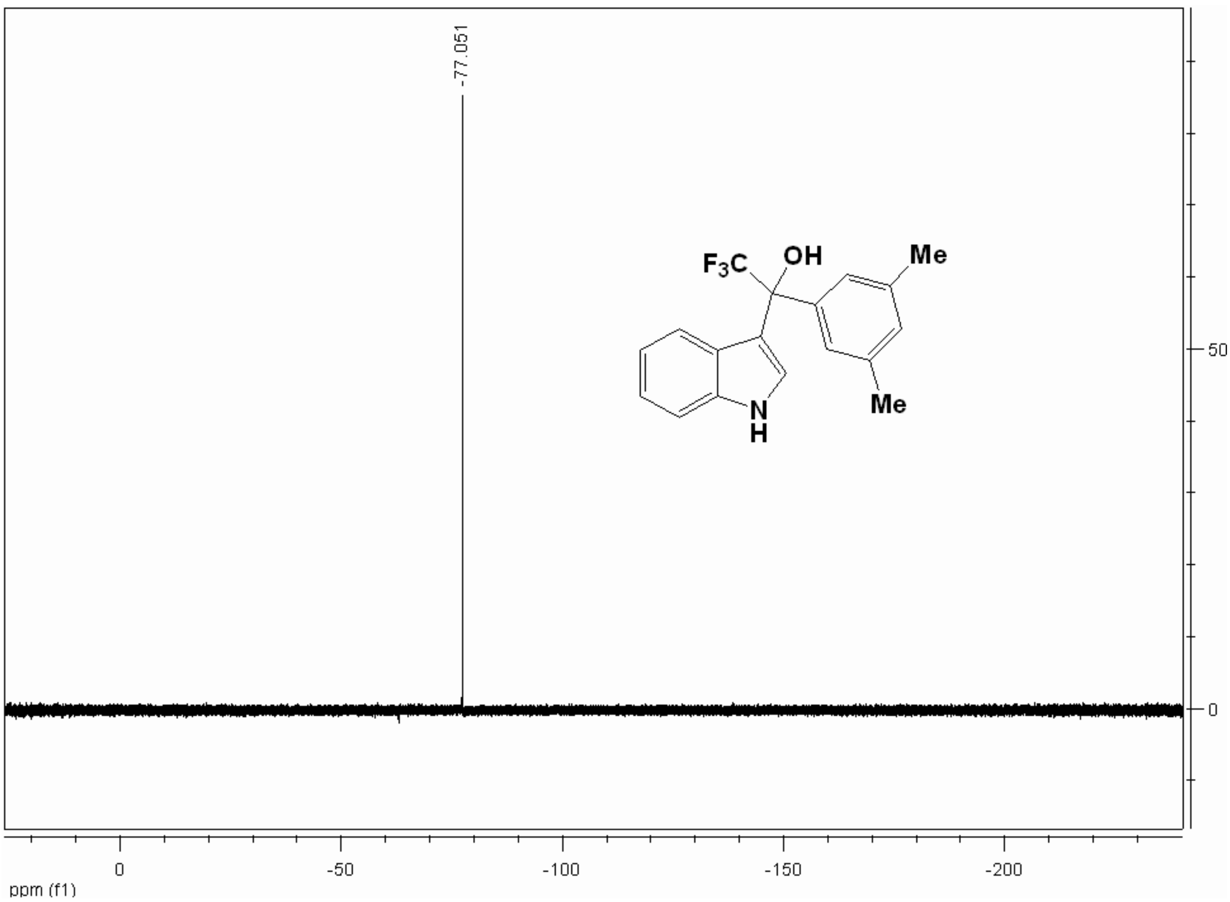


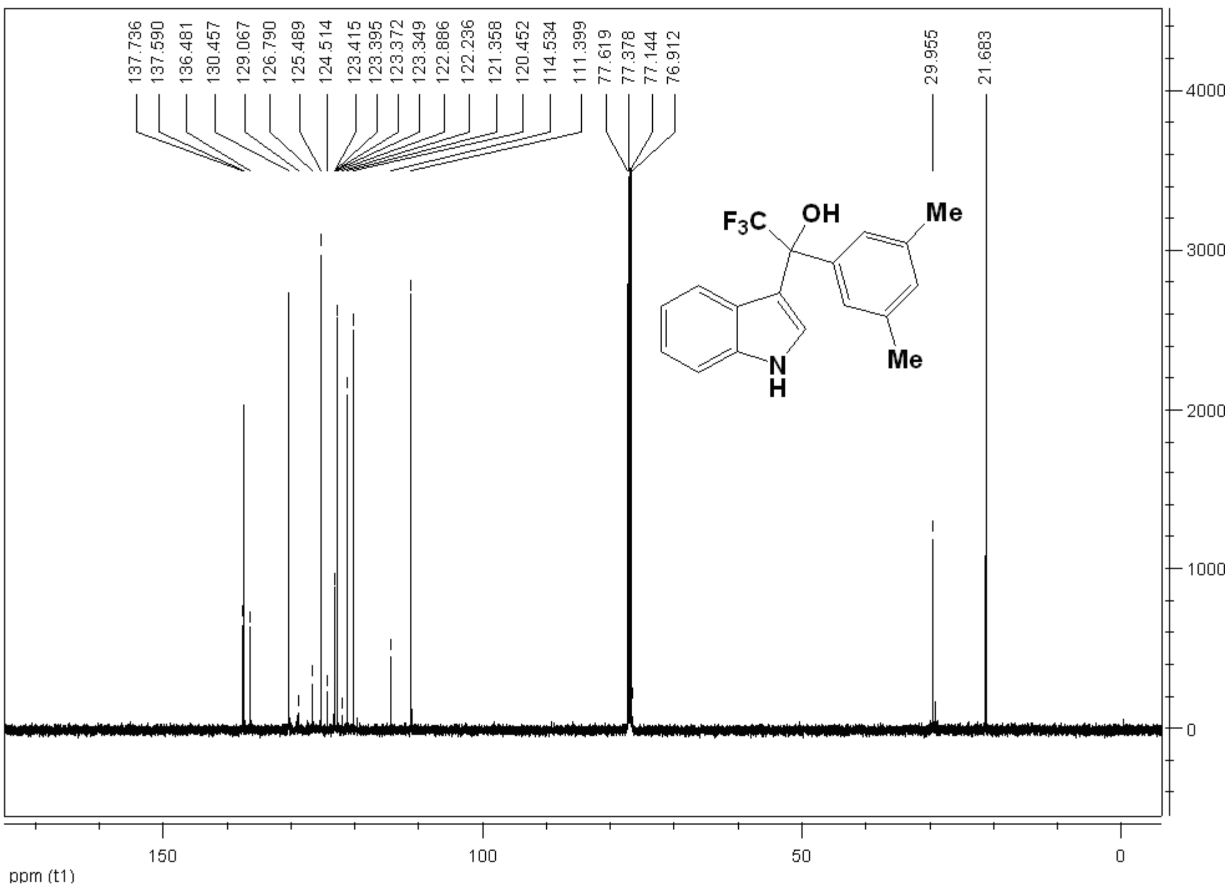


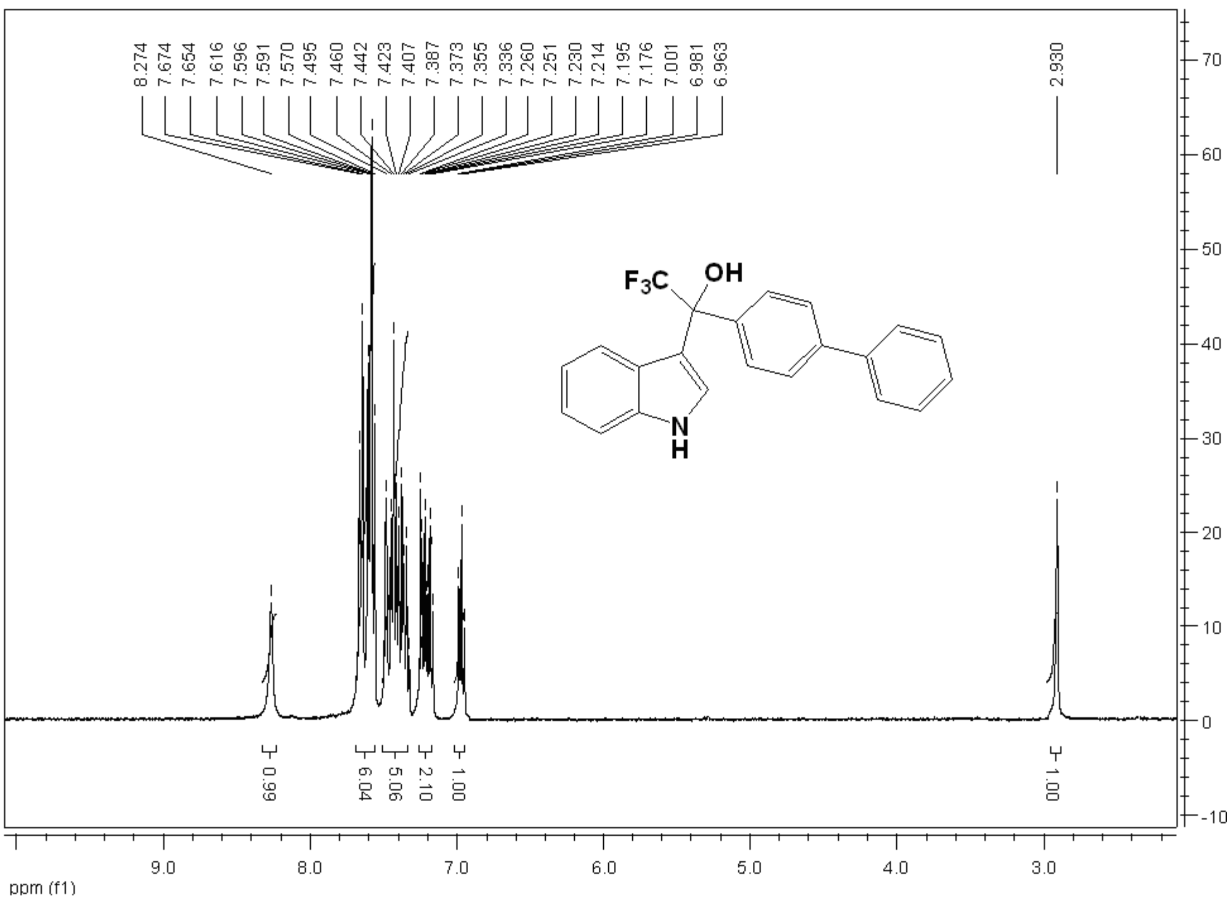

-76.018
Me
F3C
OH
N
H
50
40
30
20
10
0
0
-50
-100
-150
-200
ppm (f1)

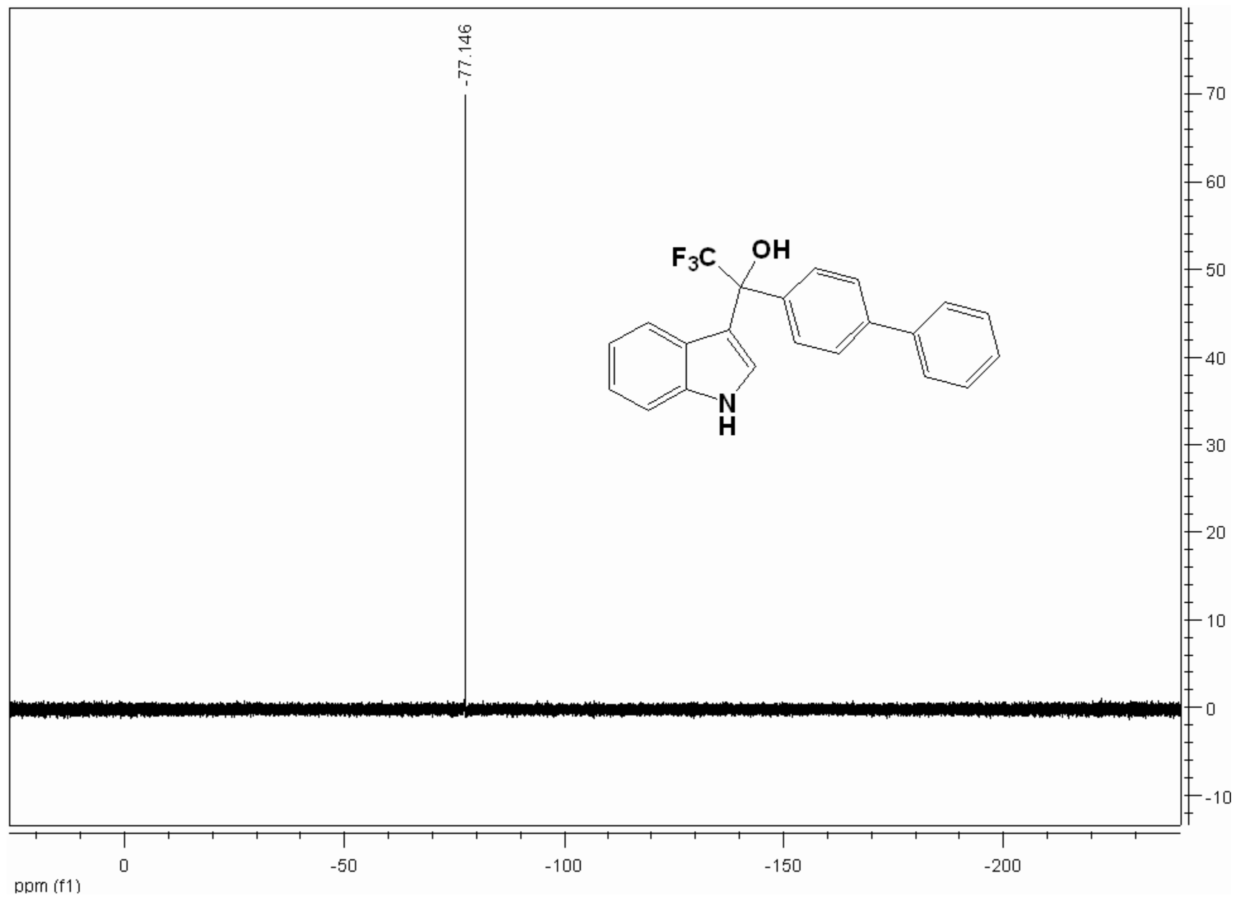

138.706
136.361
135.617
132.994
129.518
128.957
128.788
128.780
127.233
125.672
125.561
124.952
123.576
123.557
123.538
122.887
122.670
120.916
120.465
114.876
111.411
78.517
78.296
78.062
77.831
21.783
Me
F3C
OH
N
H
2000
1500
1000
500
0
150
100
50
0
ppm (t1)

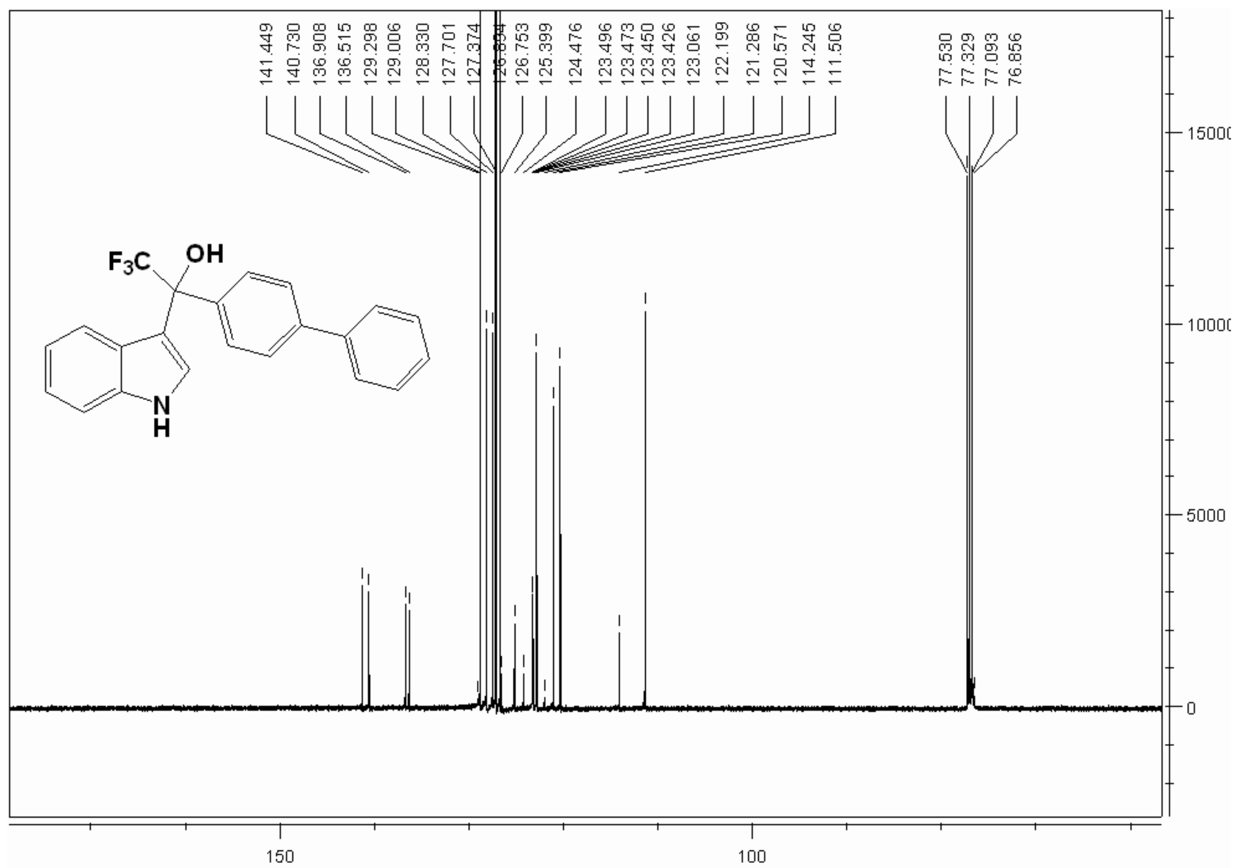

8.247
7.432
7.388
7.368
7.261
7.241
7.210
7.181
7.163
6.993
6.986
6.976
2.864
2.289
F3C
OH
Me
Me
N
H
0.99
1.00
0.96
4.11
1.98
0.96
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

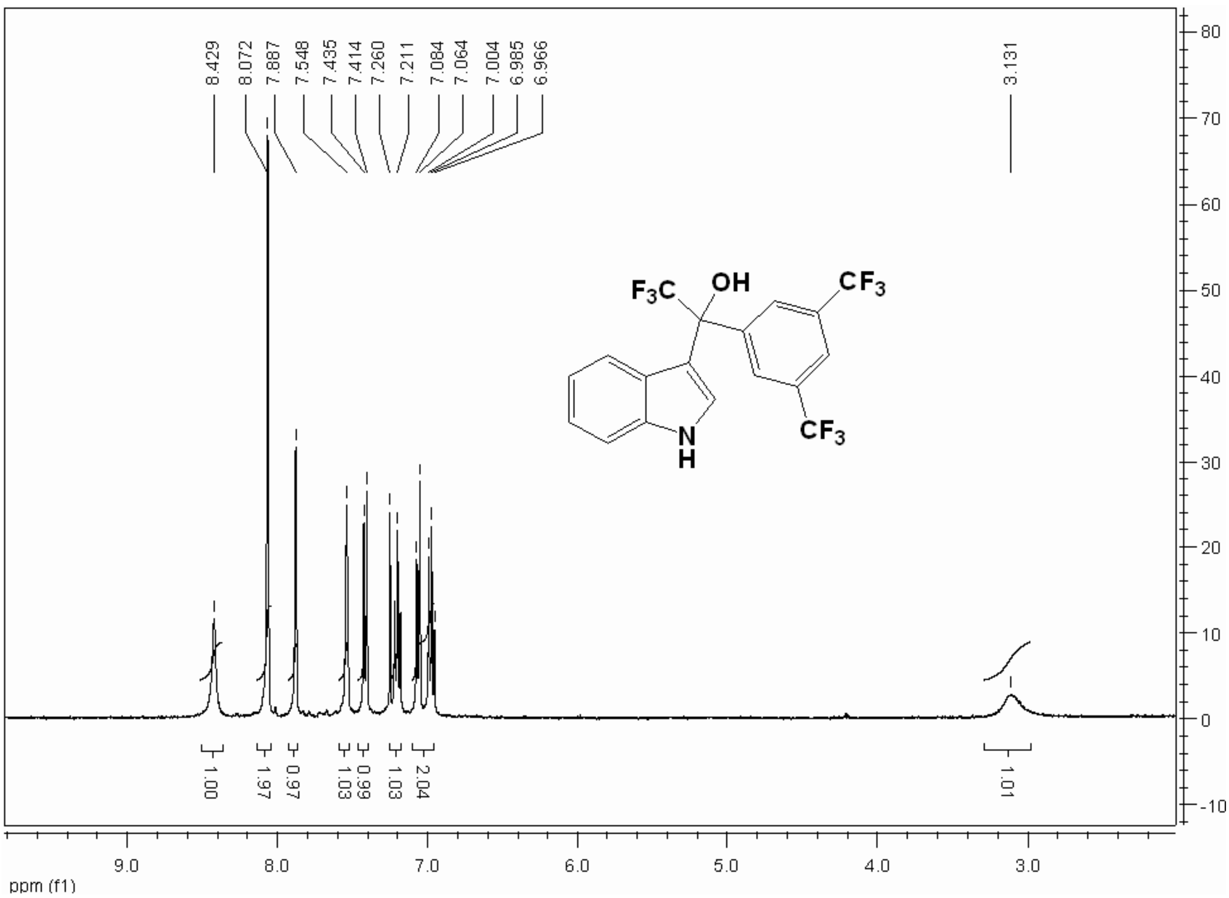

-77.051
F3C
OH
Me
Me
N
H
0
-50
-100
-150
-200
ppm (f1)

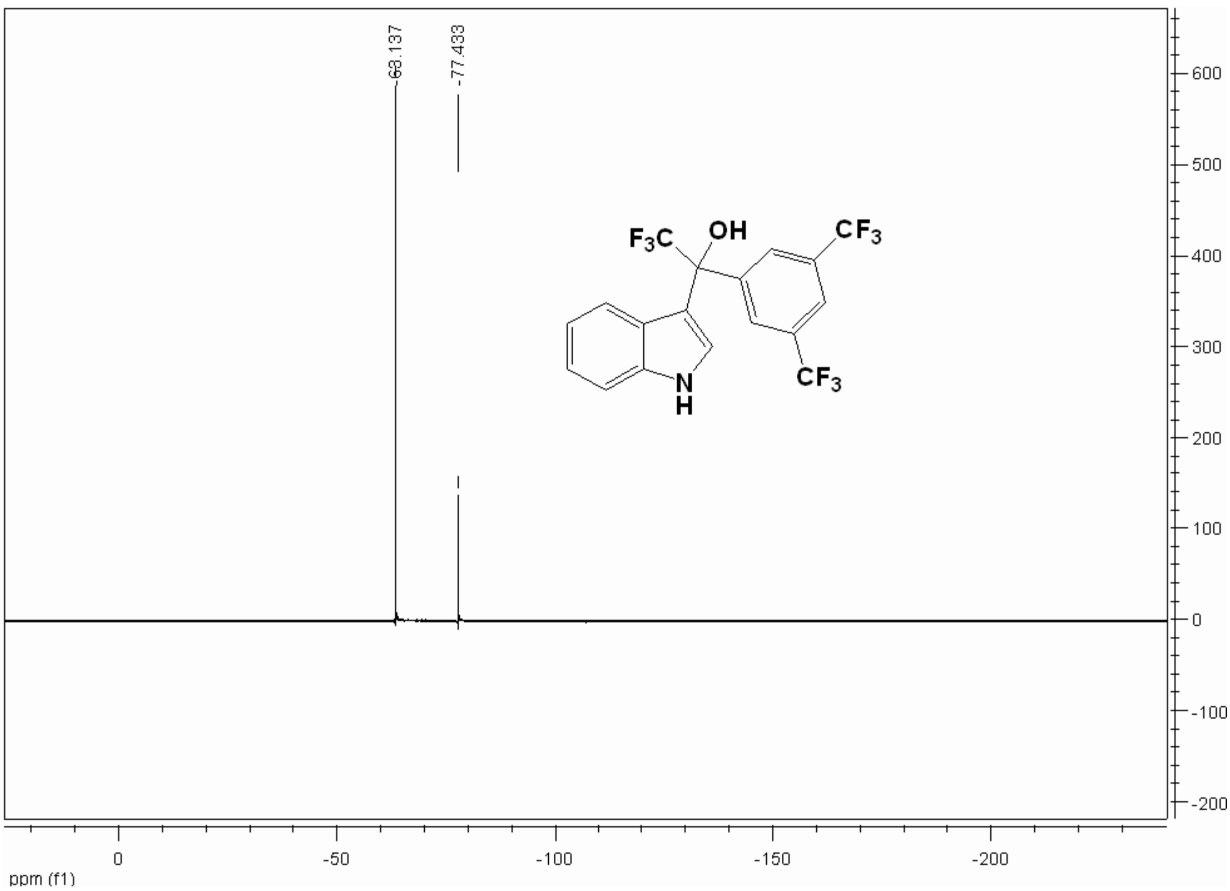

137.736
137.590
136.481
130.457
129.067
126.790
125.489
124.514
123.415
123.395
123.372
123.349
122.886
122.236
121.358
120.452
114.534
111.399
77.619
77.378
77.144
76.912
29.955
21.683
F3C
OH
Me
Me
N
H
4000
3000
2000
1000
0
150
100
50
0
ppm (t1)

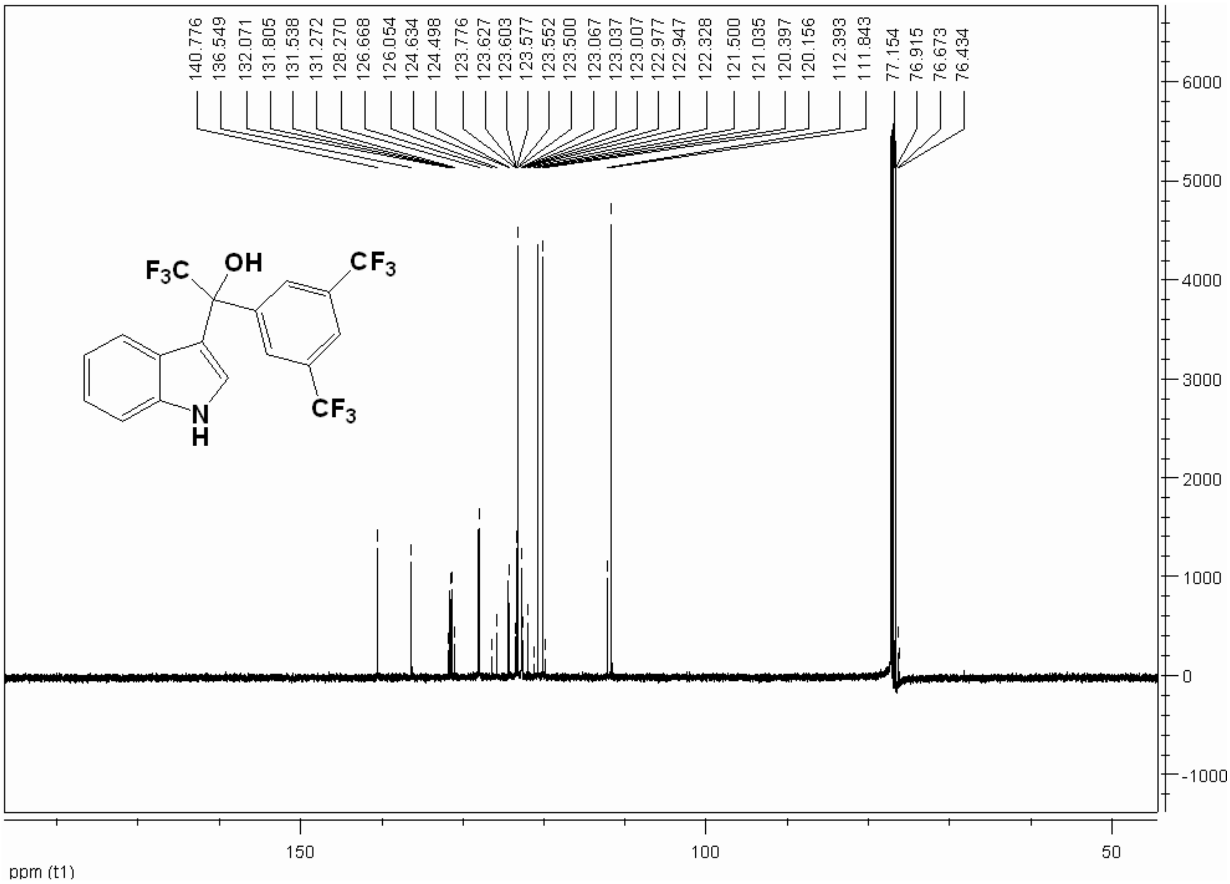

8.274
7.674
7.654
7.616
7.596
7.591
7.570
7.495
7.460
7.442
7.423
7.407
7.387
7.373
7.355
7.336
7.260
7.251
7.230
7.214
7.195
7.176
7.001
6.981
6.963
2.930
F3C
OH
N
H
70
60
50
40
30
20
10
0
-10
0.99
6.04
5.06
2.10
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

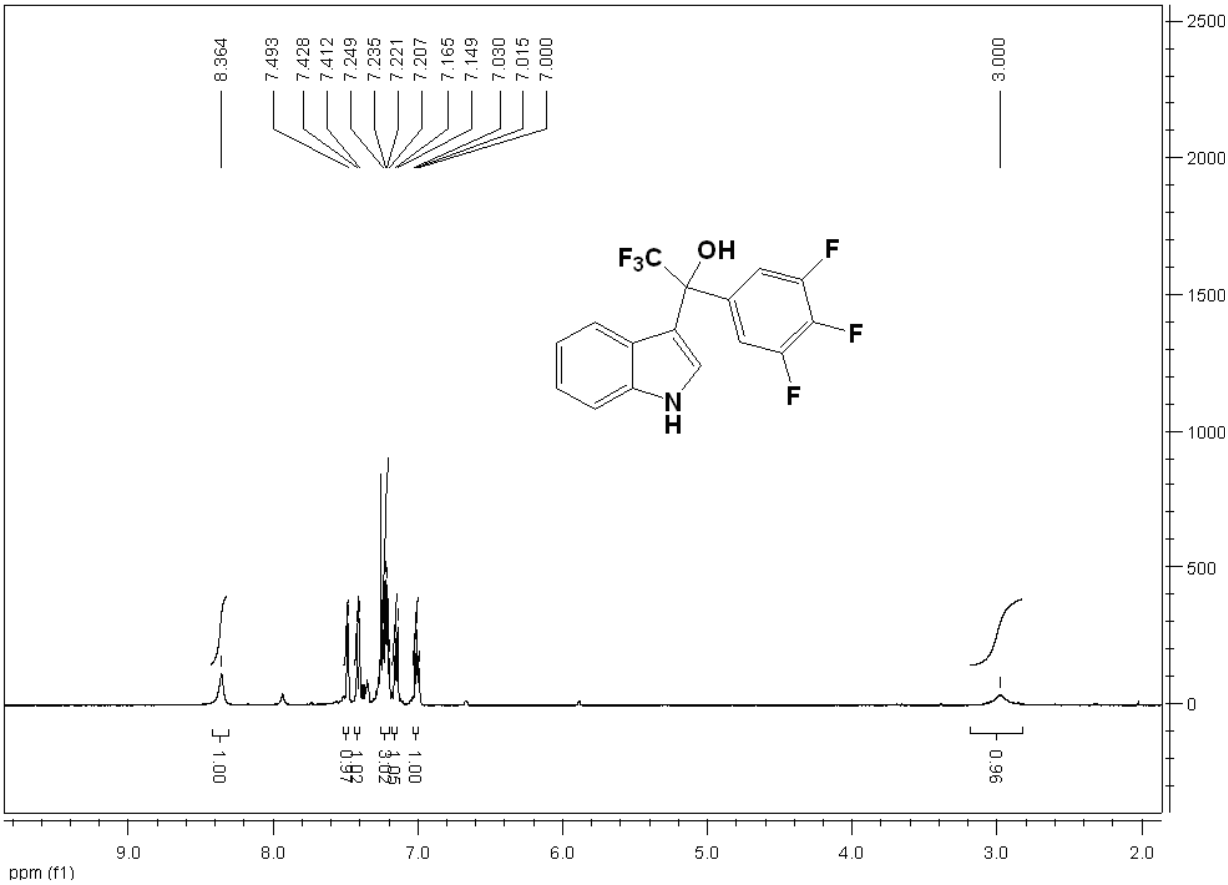

-77.146
F3C
OH
N
H
ppm (f1)

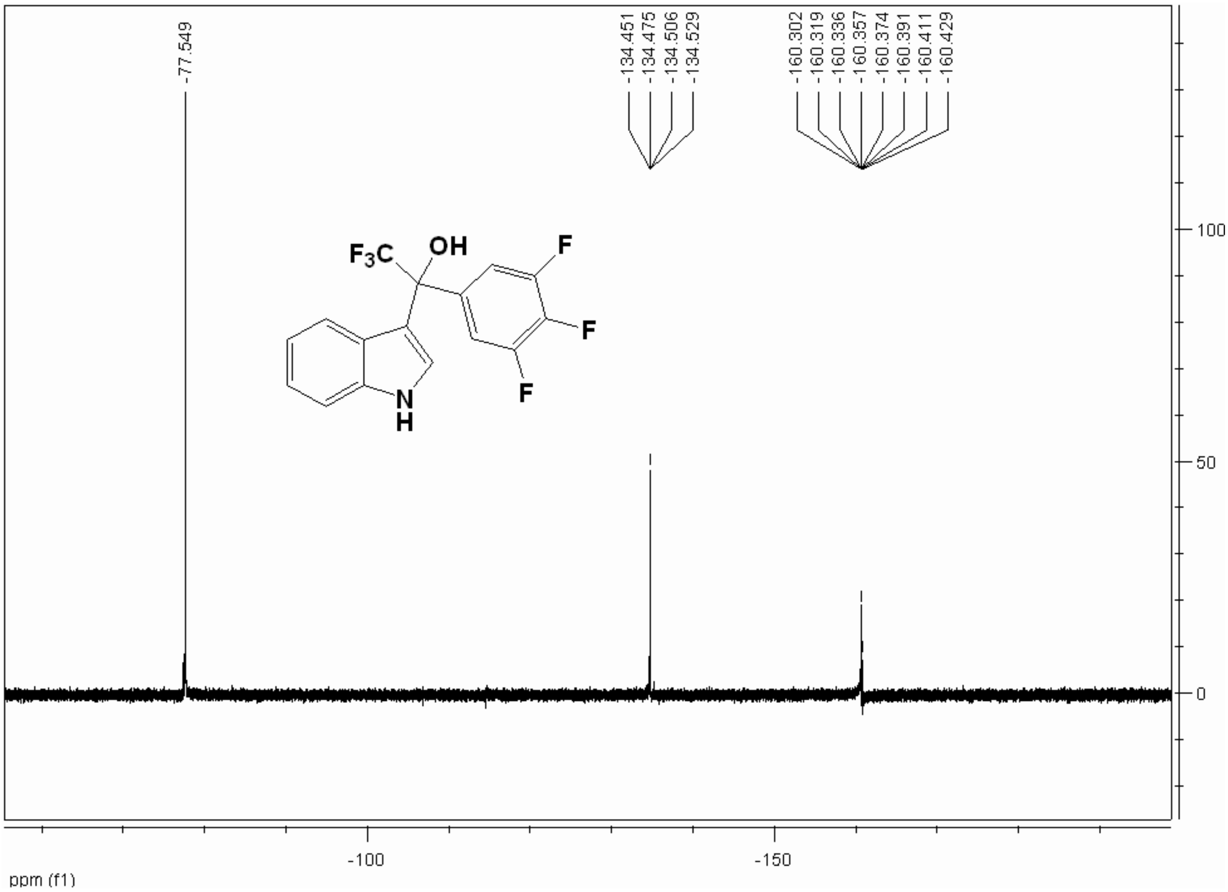

141.449
140.730
136.908
136.515
129.298
129.006
128.330
127.701
127.374
126.834
126.753
125.399
124.476
123.496
123.473
123.450
123.426
123.061
122.199
121.286
120.571
114.245
111.506
77.530
77.329
77.093
76.856
F3C
OH
N
H
ppm (t1)

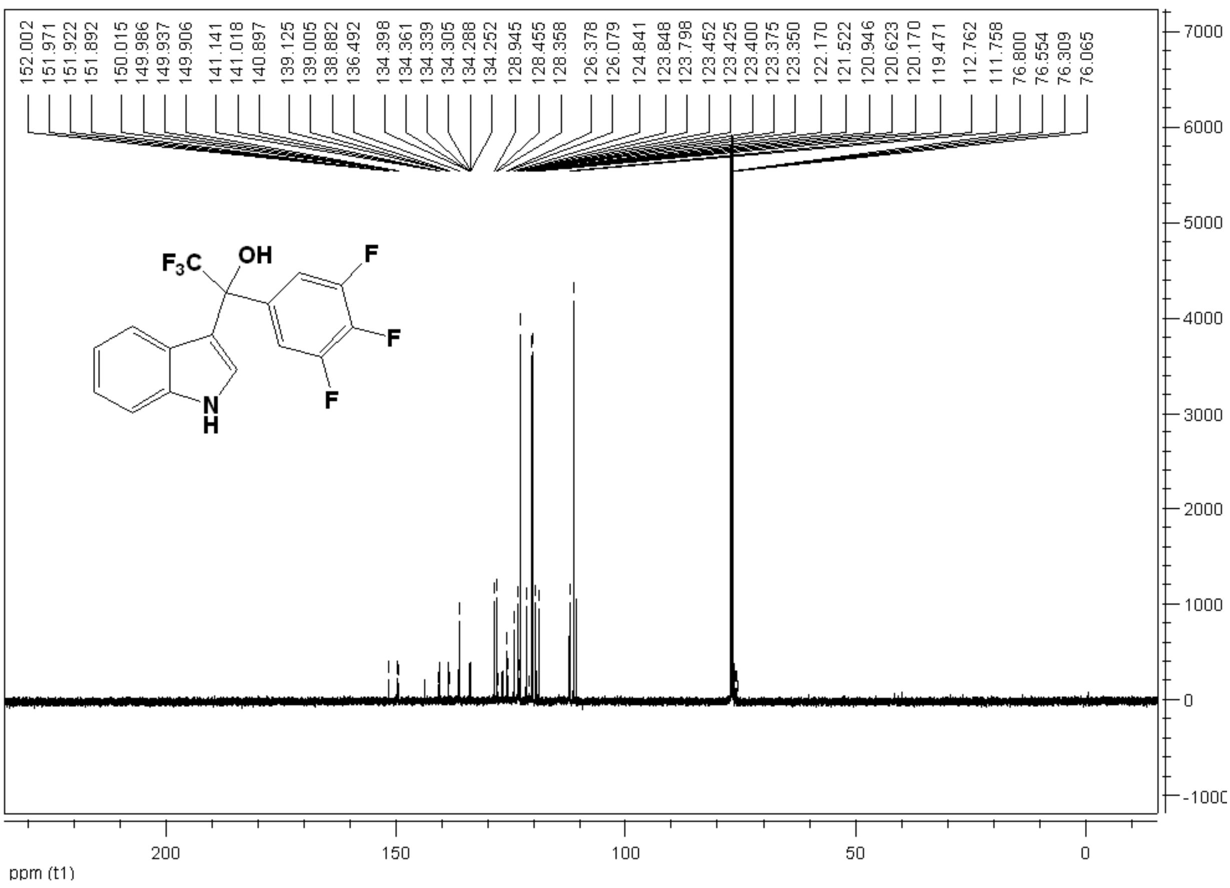

8.429
8.072
7.887
7.548
7.435
7.414
7.260
7.211
7.084
7.064
7.004
6.985
6.966
3.131
1.00
1.97
0.97
1.03
0.99
1.03
2.04
1.01
F3C
OH
CF3
N
H
CF3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

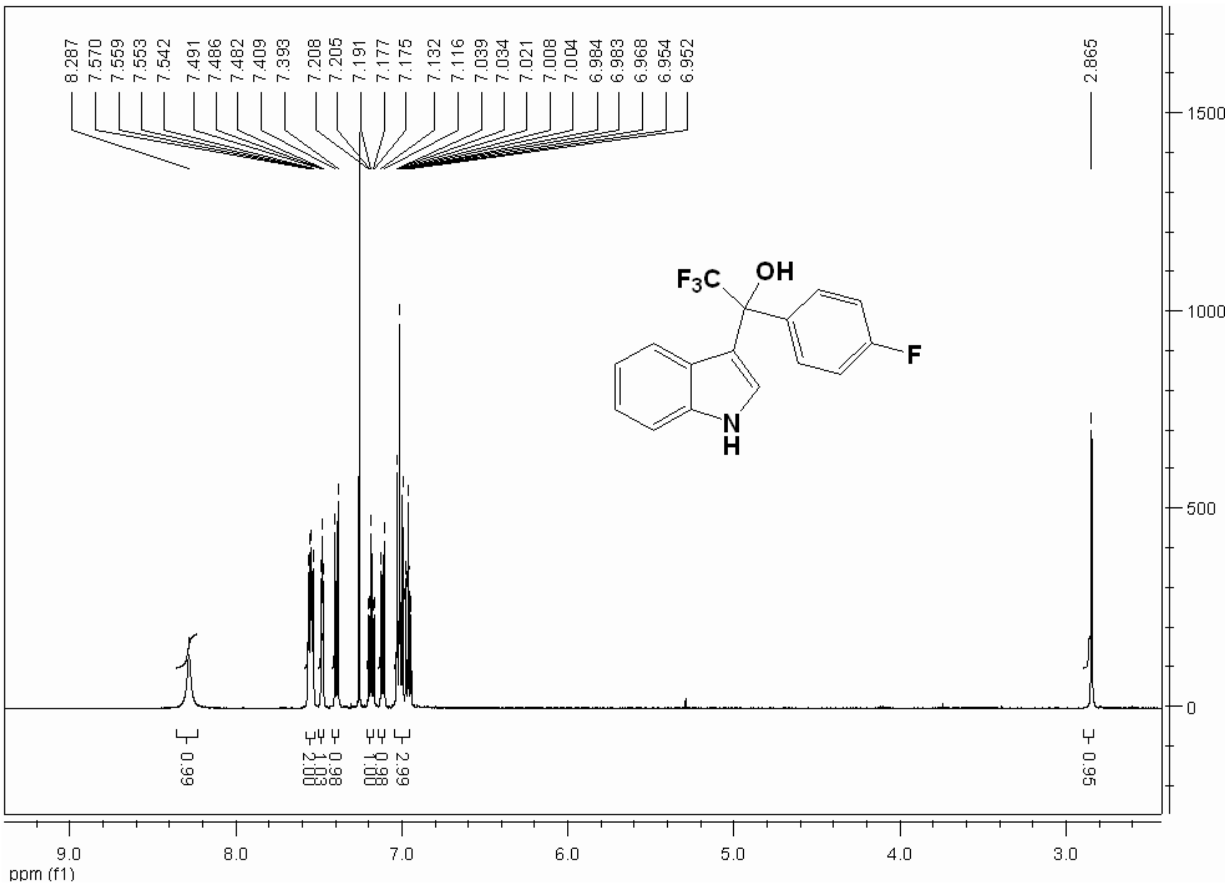

-63.137
-77.433
F3C
OH
CF3
N
H
CF3
0
-50
-100
-150
-200
ppm (f1)

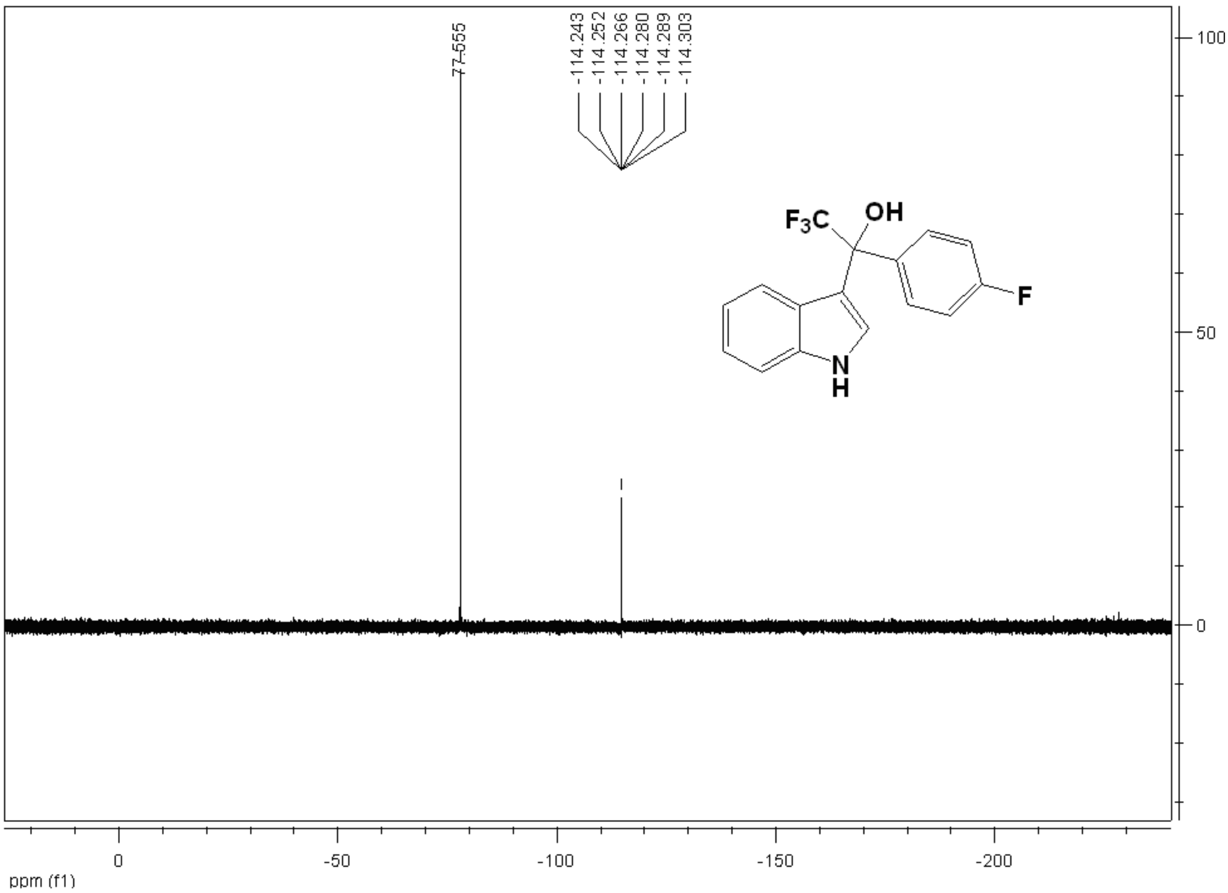

140.776
136.549
132.071
131.805
131.538
131.272
128.270
126.668
126.054
124.634
124.498
123.776
123.627
123.603
123.577
123.552
123.500
123.067
123.037
123.007
122.977
122.947
122.328
121.500
121.035
120.397
120.156
112.393
111.843
77.154
76.915
76.673
76.434
F3C OH CF3
N H
CF3
6000
5000
4000
3000
2000
1000
0
-1000
150
100
50
ppm (t1)

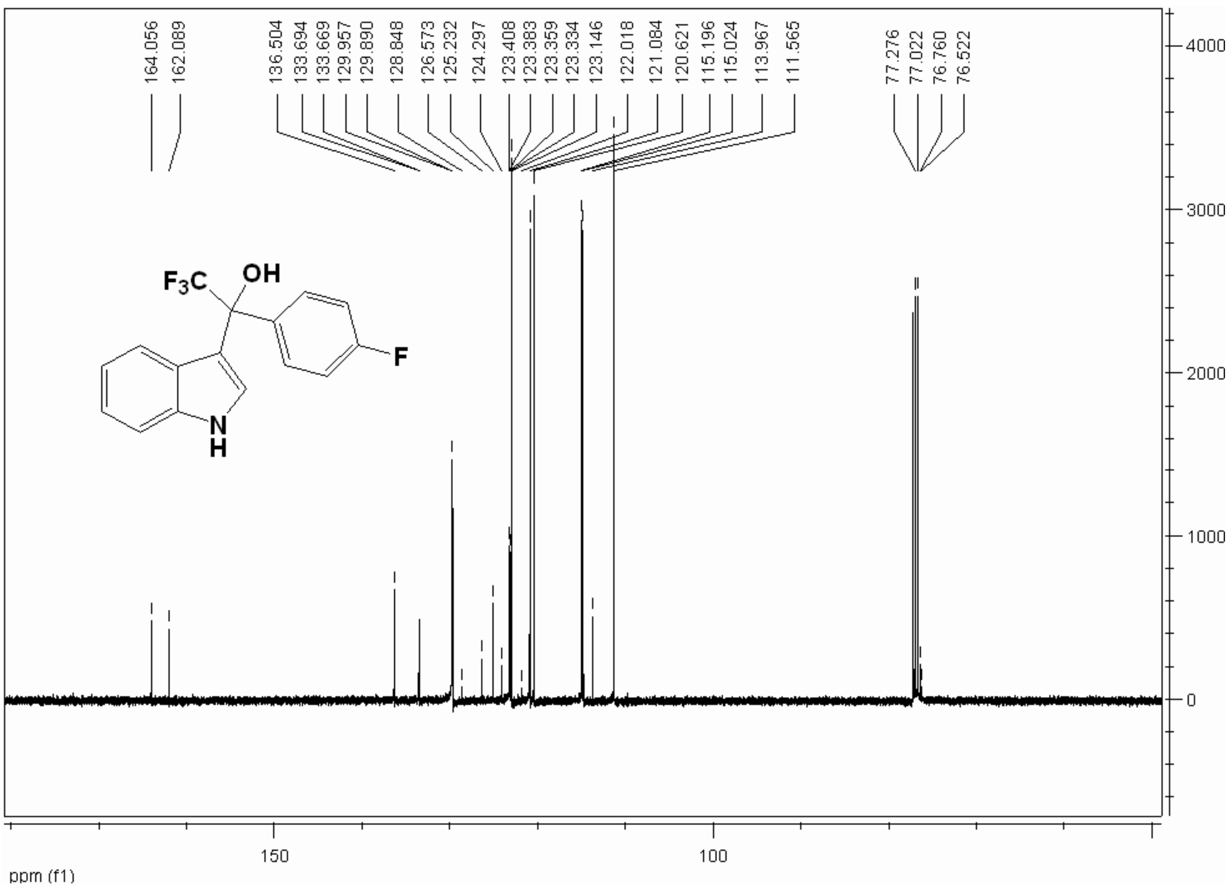

8.364
7.493
7.428
7.412
7.249
7.235
7.221
7.207
7.165
7.149
7.030
7.015
7.000
3.000
F3C OH F
F
F
N H
2500
2000
1500
1000
500
0
1.00
0.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

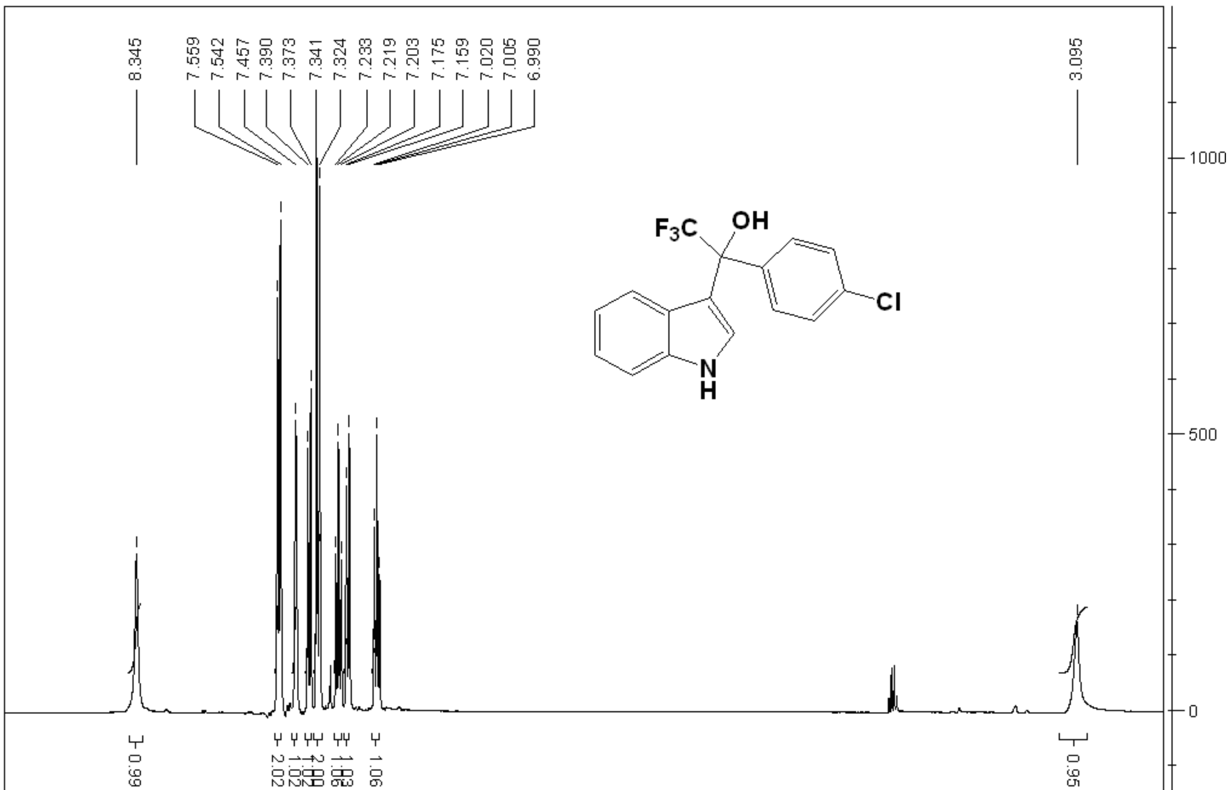

-77.549
-134.451
-134.475
-134.506
-134.529
-160.302
-160.319
-160.336
-160.357
-160.374
-160.391
-160.411
-160.429
F_3C
OH
F
F
F
N
H
100
50
0
-100
-150
ppm (f1)

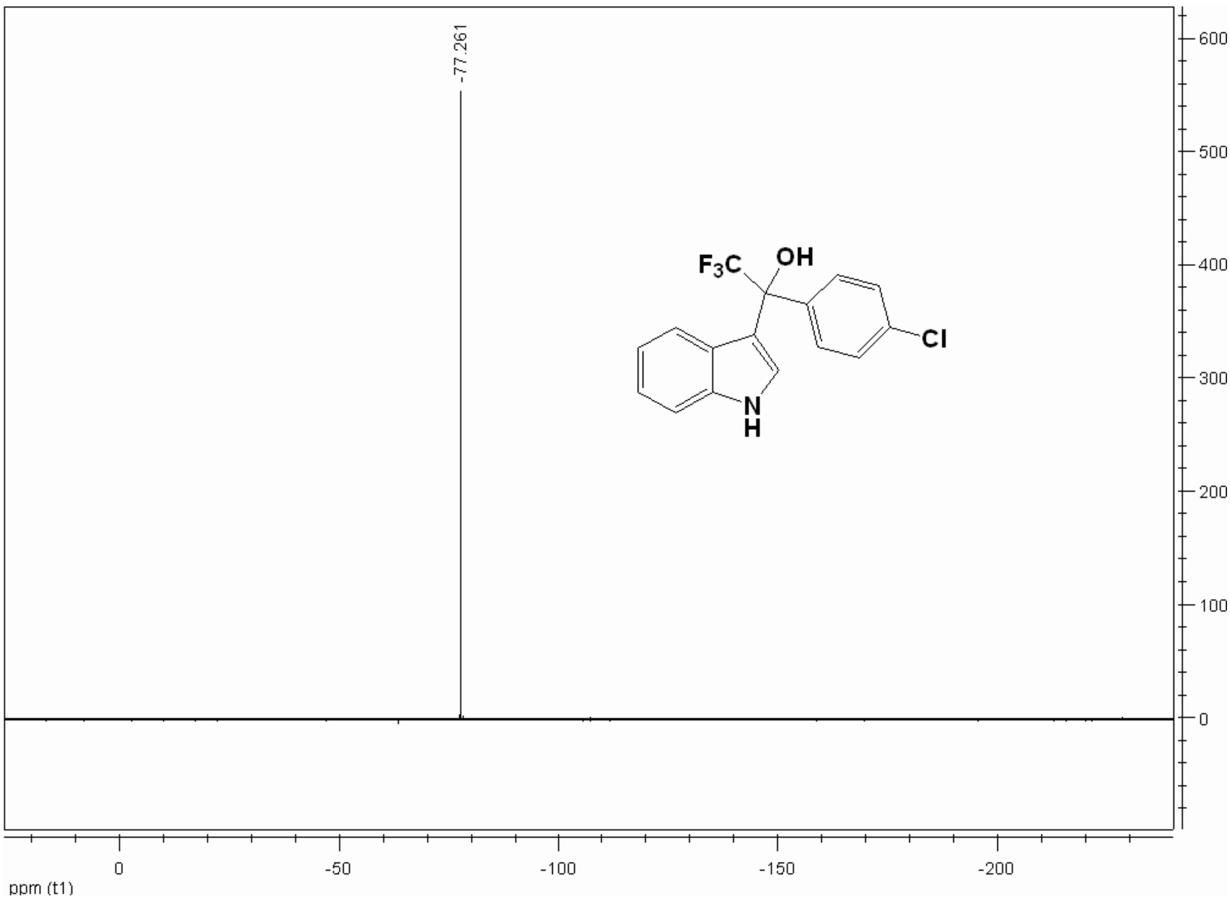

152.002
151.971
151.922
151.892
150.015
149.986
149.937
149.906
141.141
141.018
140.897
139.125
139.005
138.882
136.492
134.398
134.361
134.339
134.305
134.288
134.252
128.945
128.455
128.358
126.378
126.079
124.841
123.848
123.798
123.452
123.425
123.400
123.375
123.350
122.170
121.522
120.946
120.623
120.170
119.471
112.762
111.758
76.800
76.554
76.309
76.065
F_3C
OH
F
F
F
N
H
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
150
100
50
0
ppm (t1)

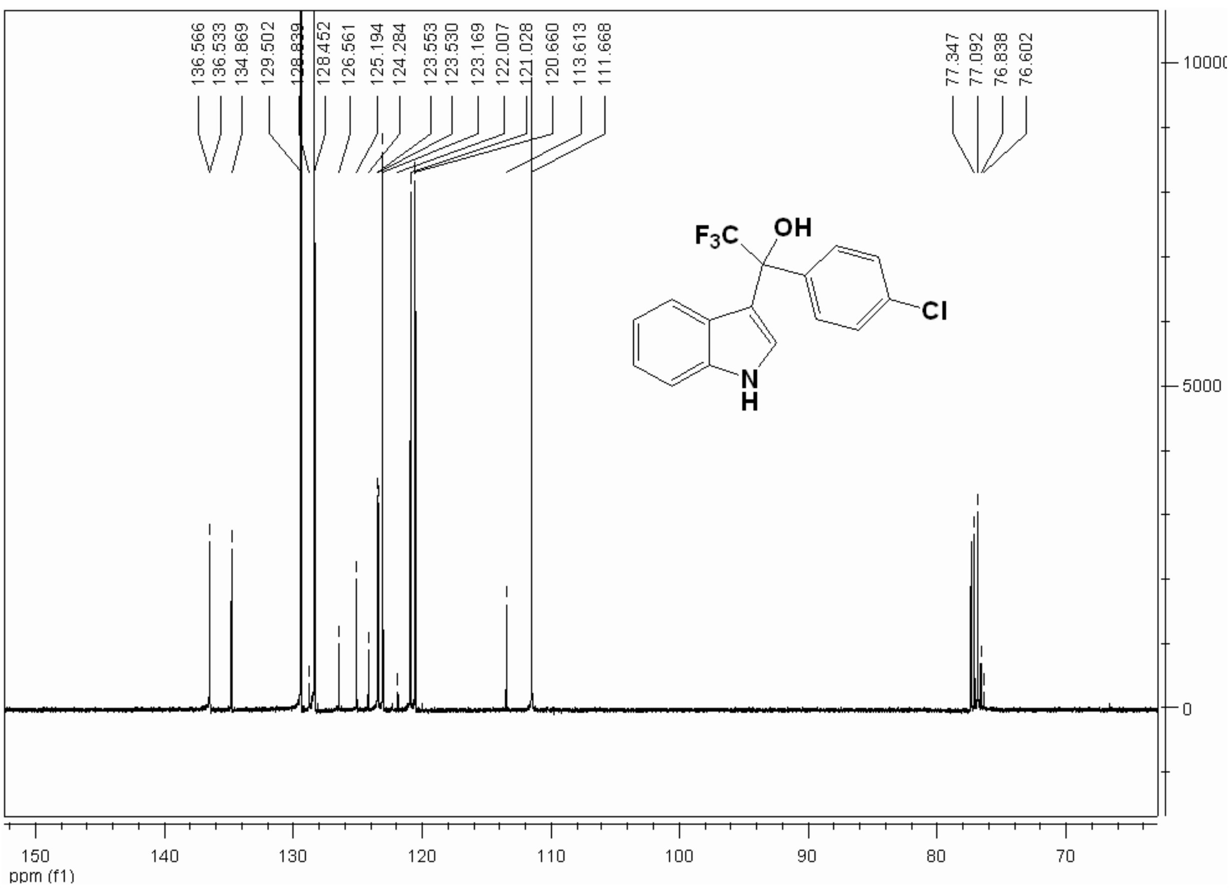


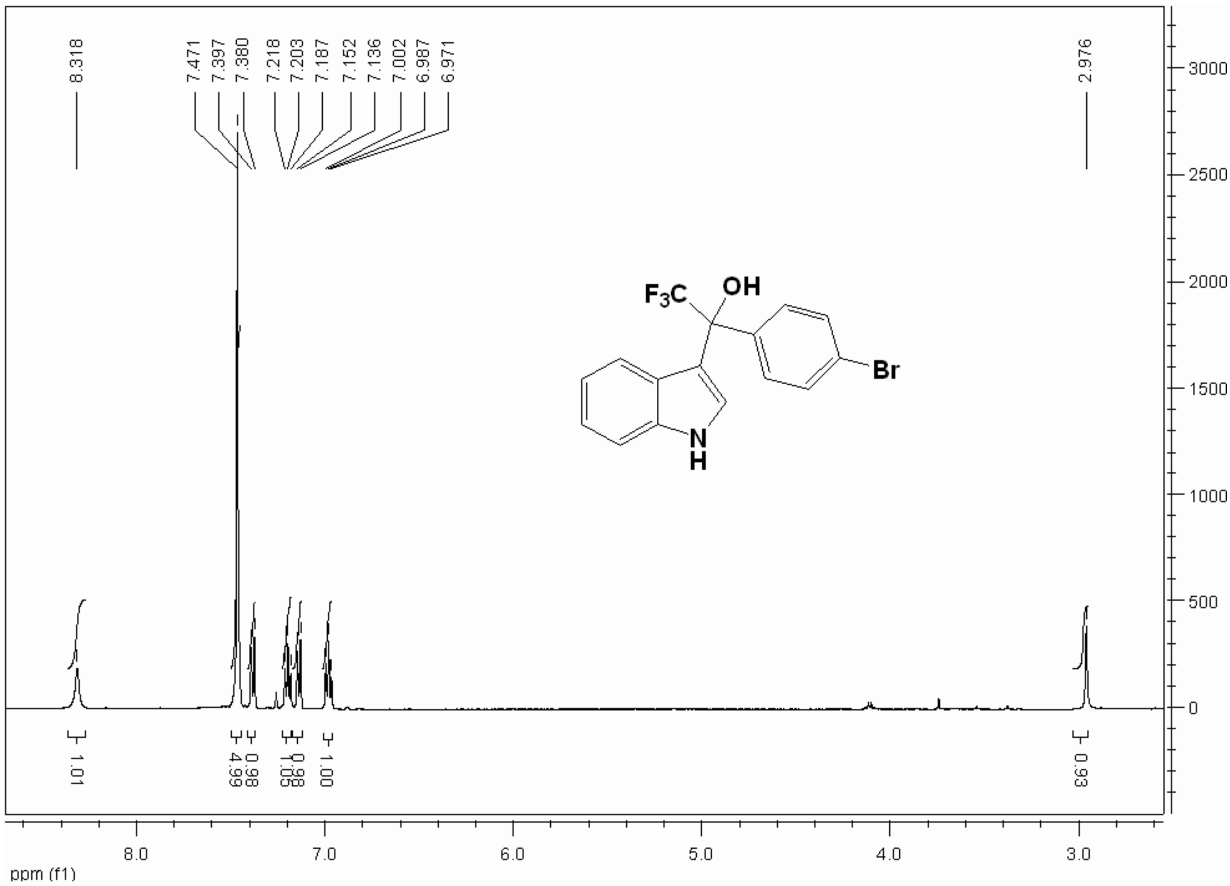


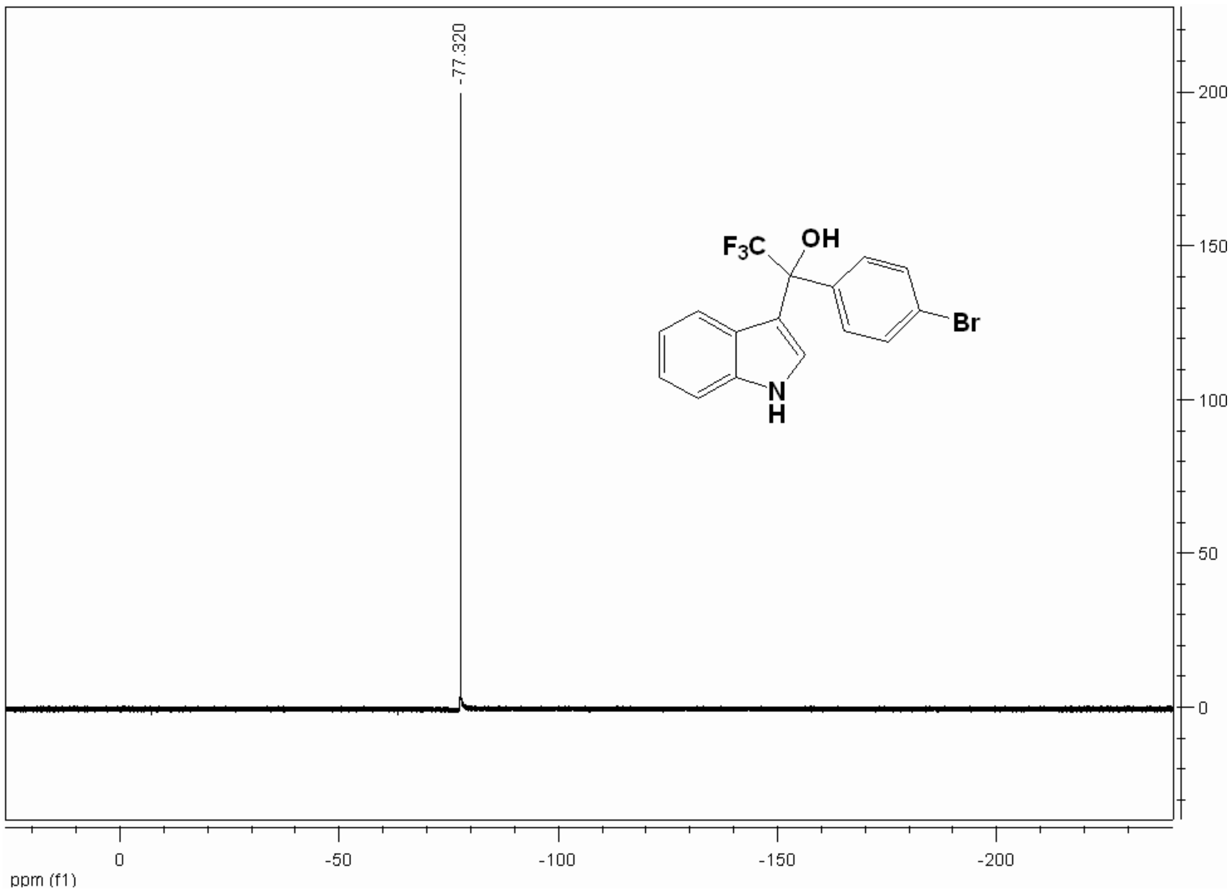

164.056
162.089
136.504
133.694
133.669
129.957
129.890
128.848
126.573
125.232
124.297
123.408
123.383
123.359
123.334
123.146
122.018
121.084
120.621
115.196
115.024
113.967
111.565
77.276
77.022
76.760
76.522
F3C
OH
F
N
H
4000
3000
2000
1000
0
150
100
ppm (f1)

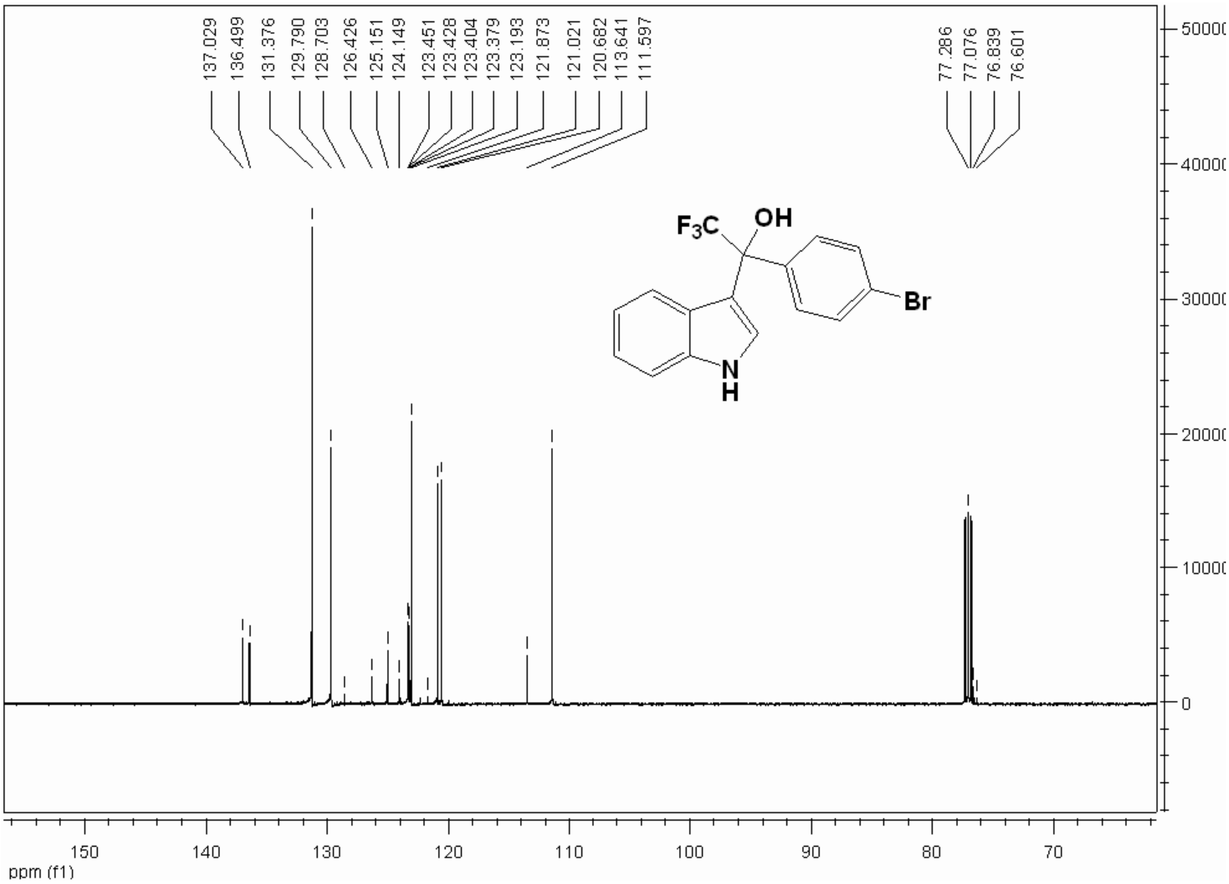

8.345
7.559
7.542
7.457
7.390
7.373
7.341
7.324
7.233
7.219
7.203
7.175
7.159
7.020
7.005
6.990
3.095
F3C
OH
Cl
N
H
1000
500
0
0.99
2.02
1.02
1.06
0.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

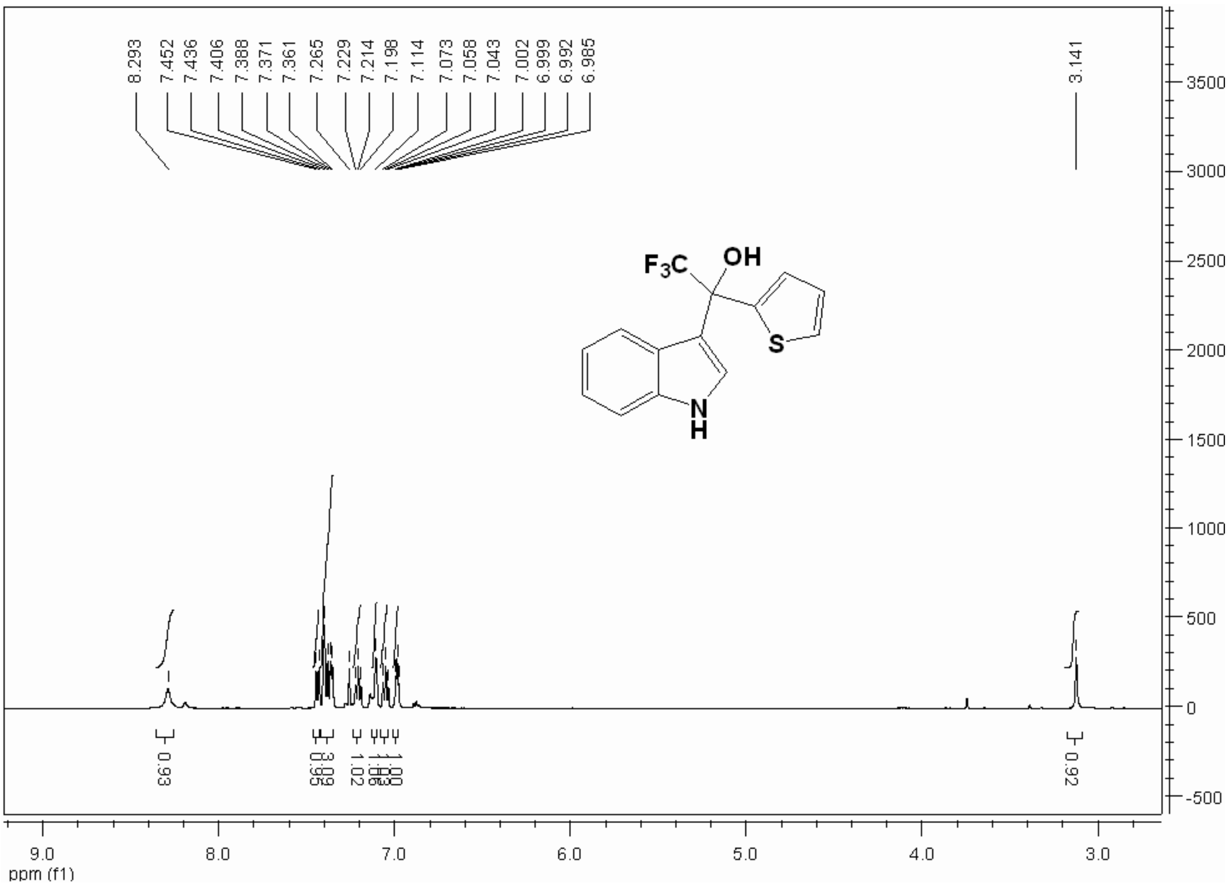

-77.261
F3C
OH
Cl
N
H
600
500
400
300
200
100
0
0
-50
-100
-150
-200
ppm (t1)

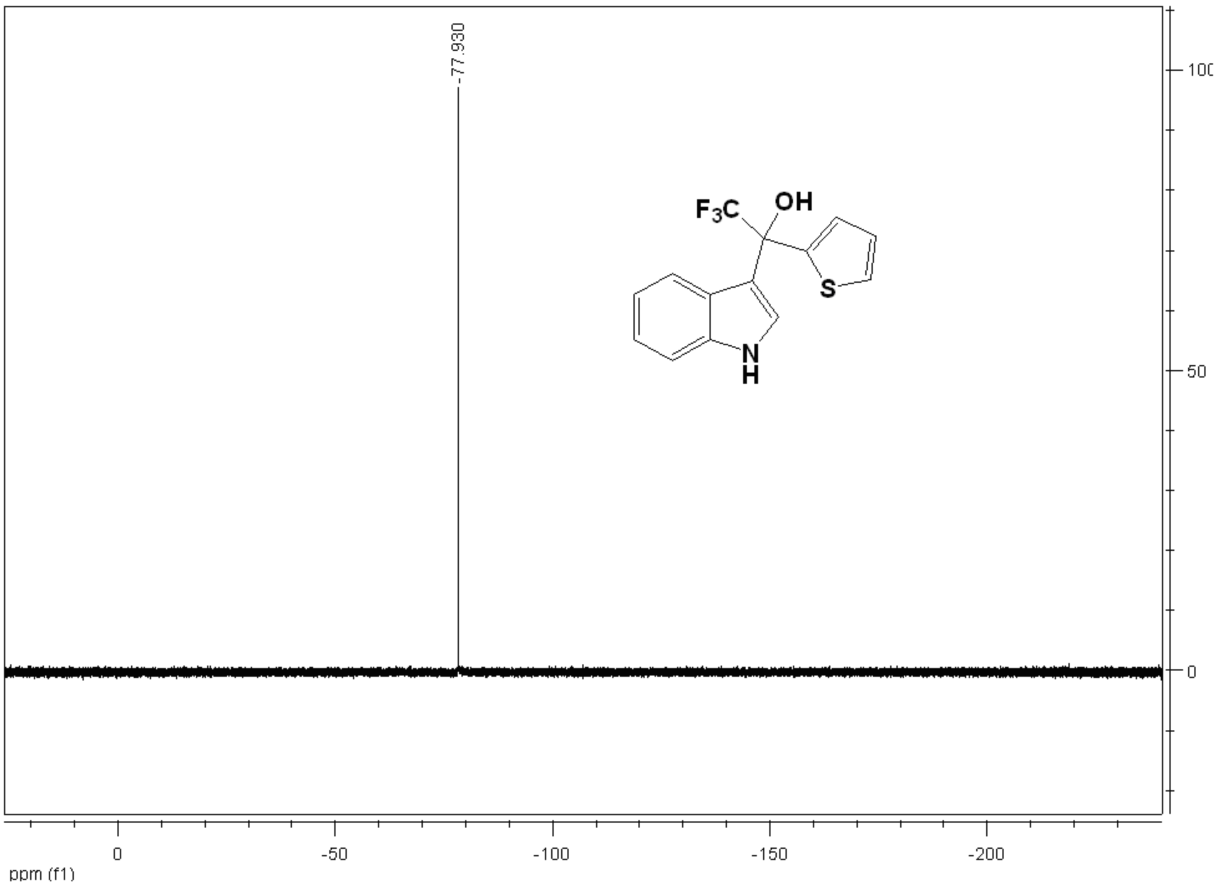

136.566
136.533
134.869
129.502
128.839
128.452
126.561
125.194
124.284
123.553
123.530
123.169
122.007
121.028
120.660
113.613
111.668
77.347
77.092
76.838
76.602
F3C
OH
Cl
N
H
10000
5000
0
150
140
130
120
110
100
90
80
70
ppm (f1)

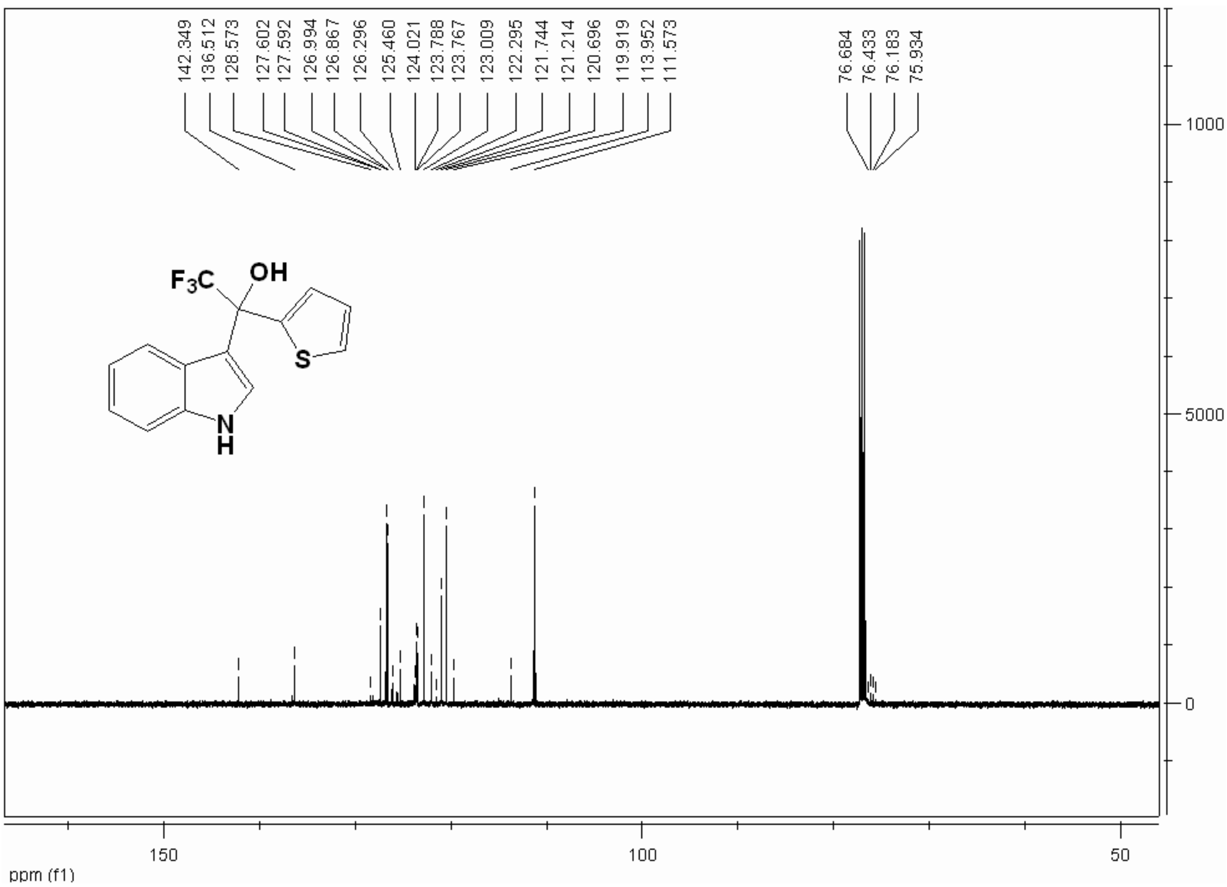

8.318
7.471
7.397
7.380
7.218
7.203
7.187
7.152
7.136
7.002
6.987
6.971
2.976
F3C
OH
Br
N
H
1.01
4.99
0.98
1.05
0.98
1.00
0.93
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)
3000
2500
2000
1500
1000
500
0

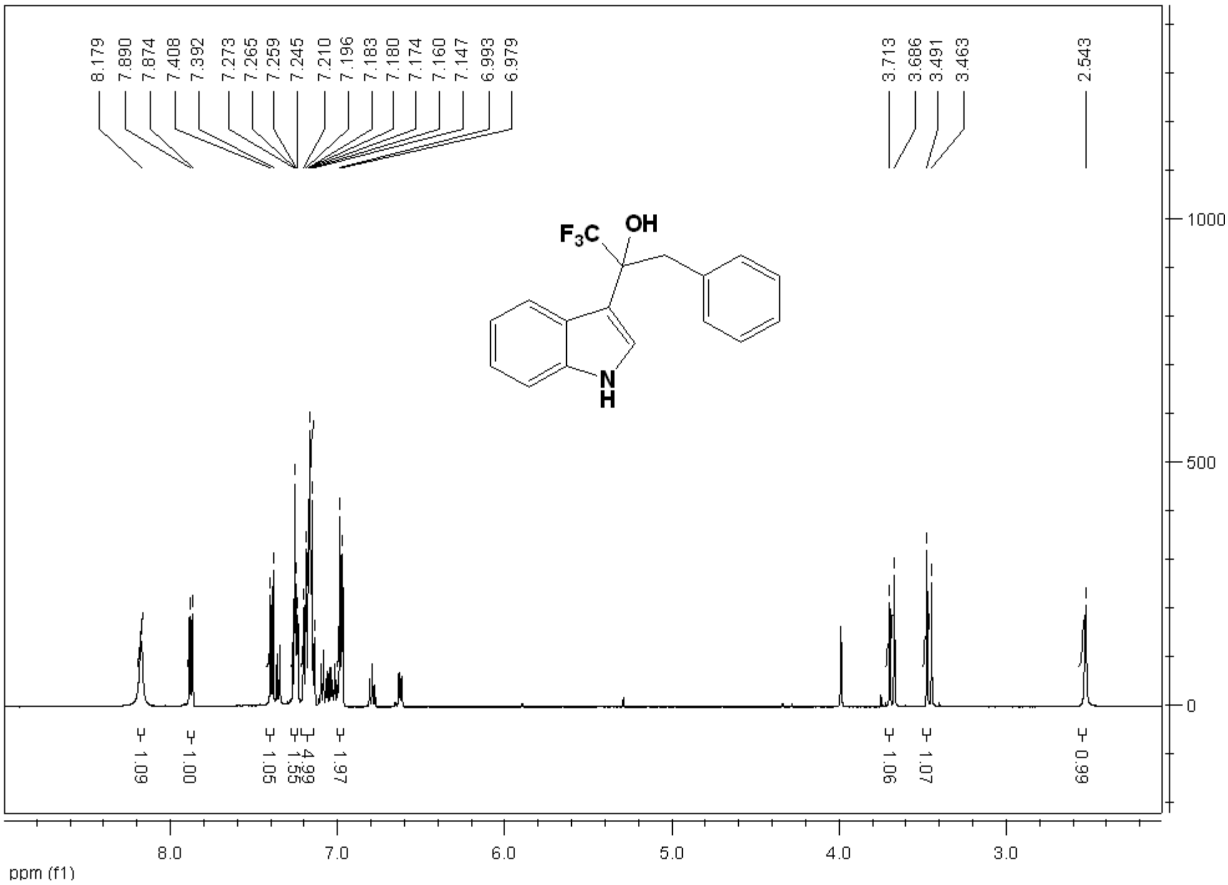

-77.320
F3C
OH
Br
N
H
0
-50
-100
-150
-200
ppm (f1)
200
150
100
50
0

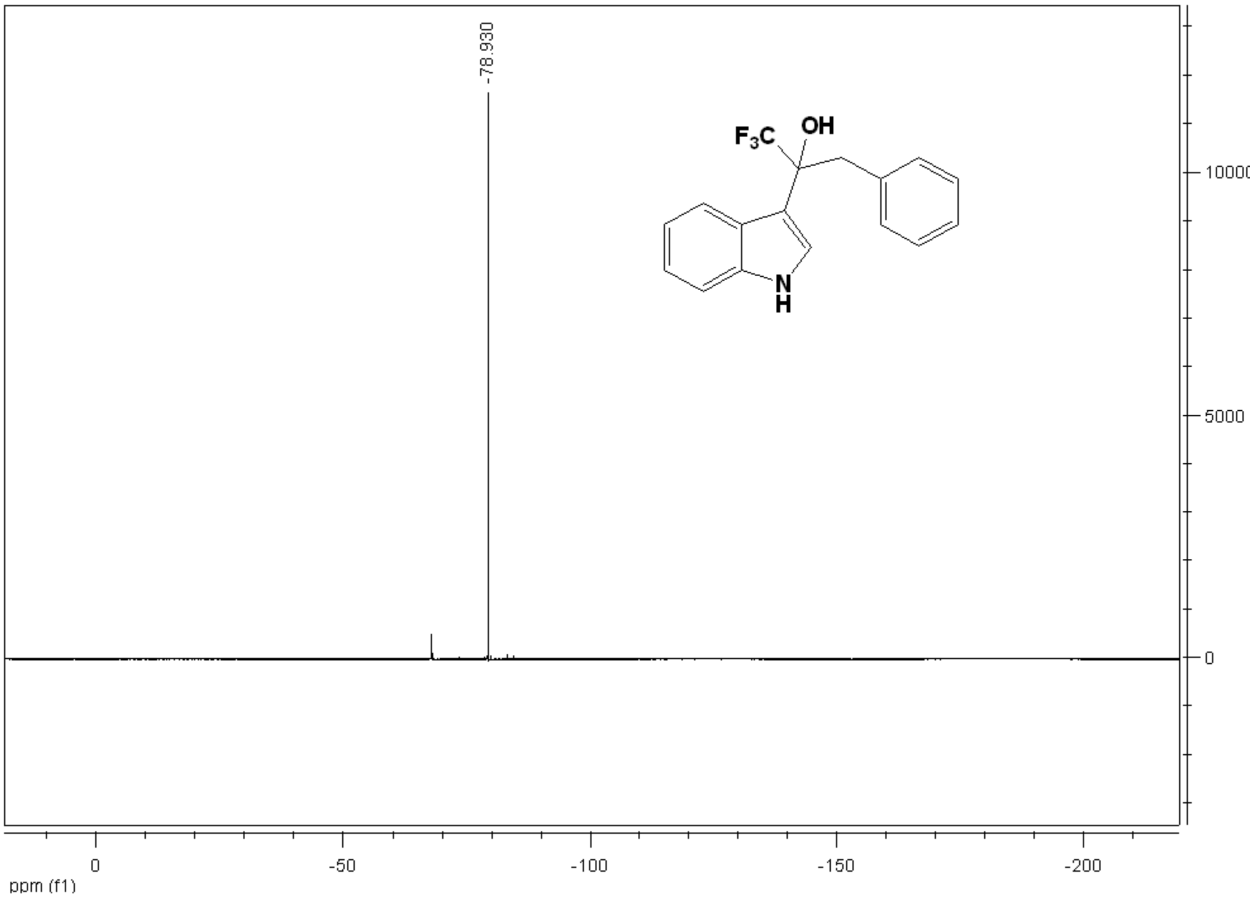

137.029
136.499
131.376
129.790
128.703
126.426
125.151
124.149
123.451
123.428
123.404
123.379
123.193
121.873
121.021
120.682
113.641
111.597
77.286
77.076
76.839
76.601
F3C
OH
Br
N
H
50000
40000
30000
20000
10000
0
150
140
130
120
110
100
90
80
70
ppm (f1)

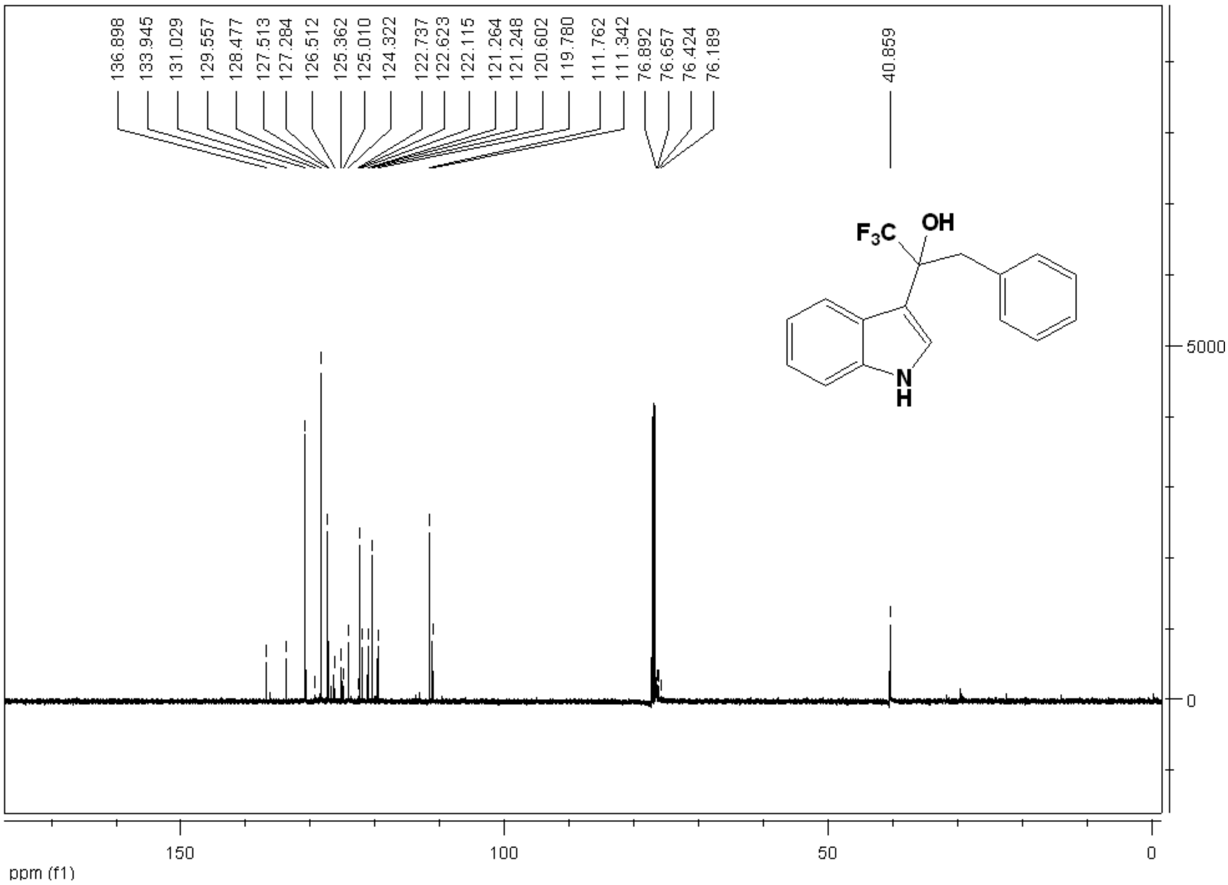

8.293
7.452
7.436
7.406
7.388
7.371
7.361
7.265
7.229
7.214
7.198
7.114
7.073
7.058
7.043
7.002
6.999
6.992
6.985
3.141
F3C
OH
S
N
H
0.93
1.02
0.92
3500
3000
2500
2000
1500
1000
500
0
-500
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

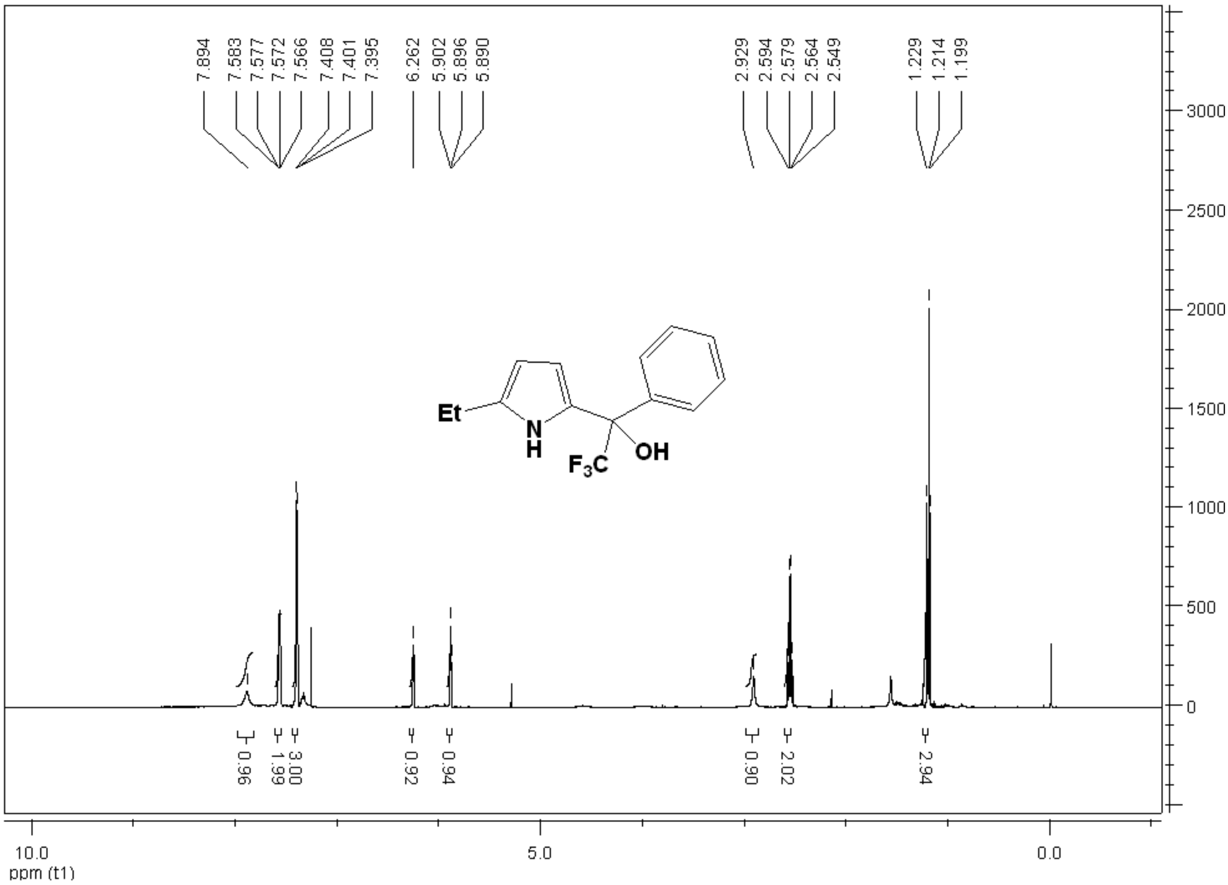

-77.930
F_3C
OH
S
N
H
100
50
0
0
-50
-100
-150
-200
ppm (f1)

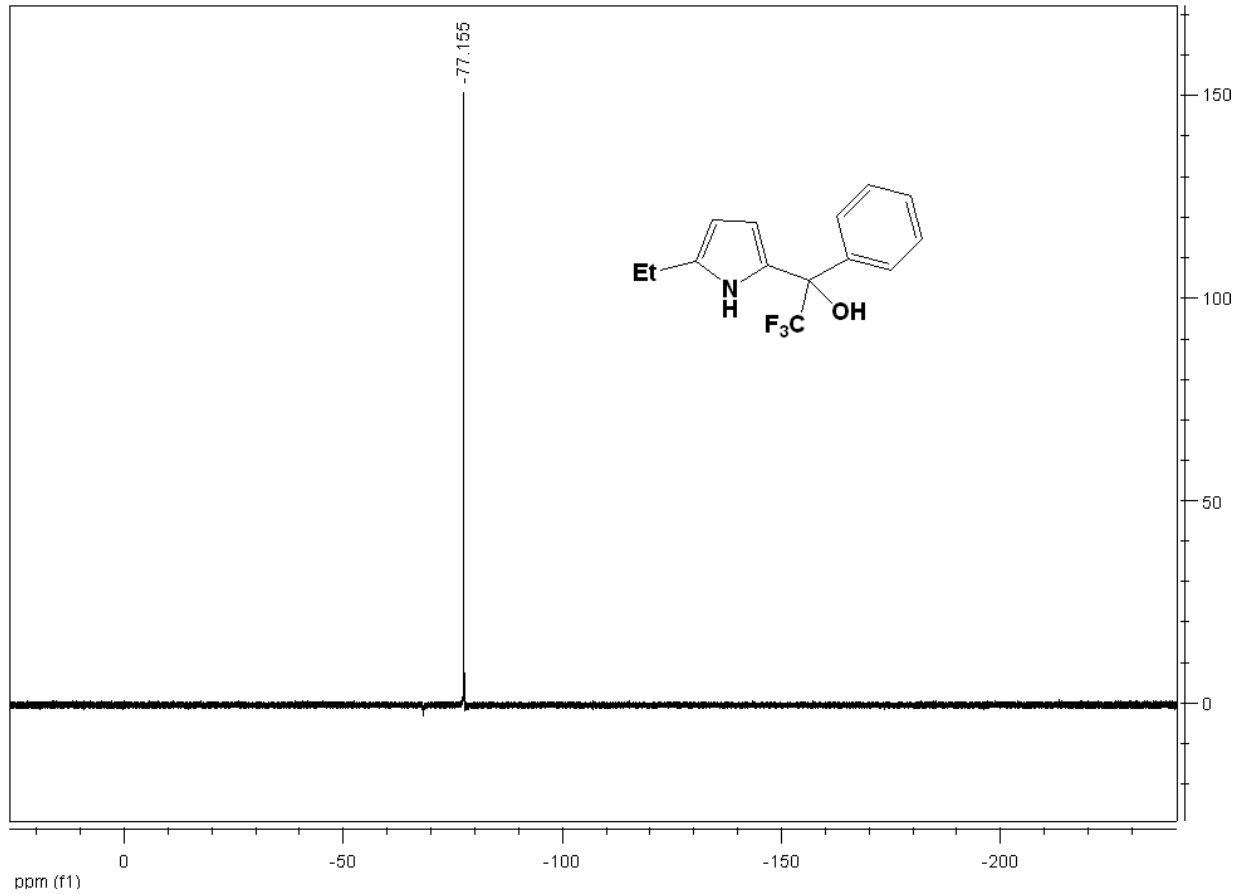

142.349
136.512
128.573
127.602
127.592
126.994
126.867
126.296
125.460
124.021
123.788
123.767
123.009
122.295
121.744
121.214
120.696
119.919
113.952
111.573
76.684
76.433
76.183
75.934
F_3C
OH
S
N
H
1000
5000
0
150
100
50
ppm (f1)

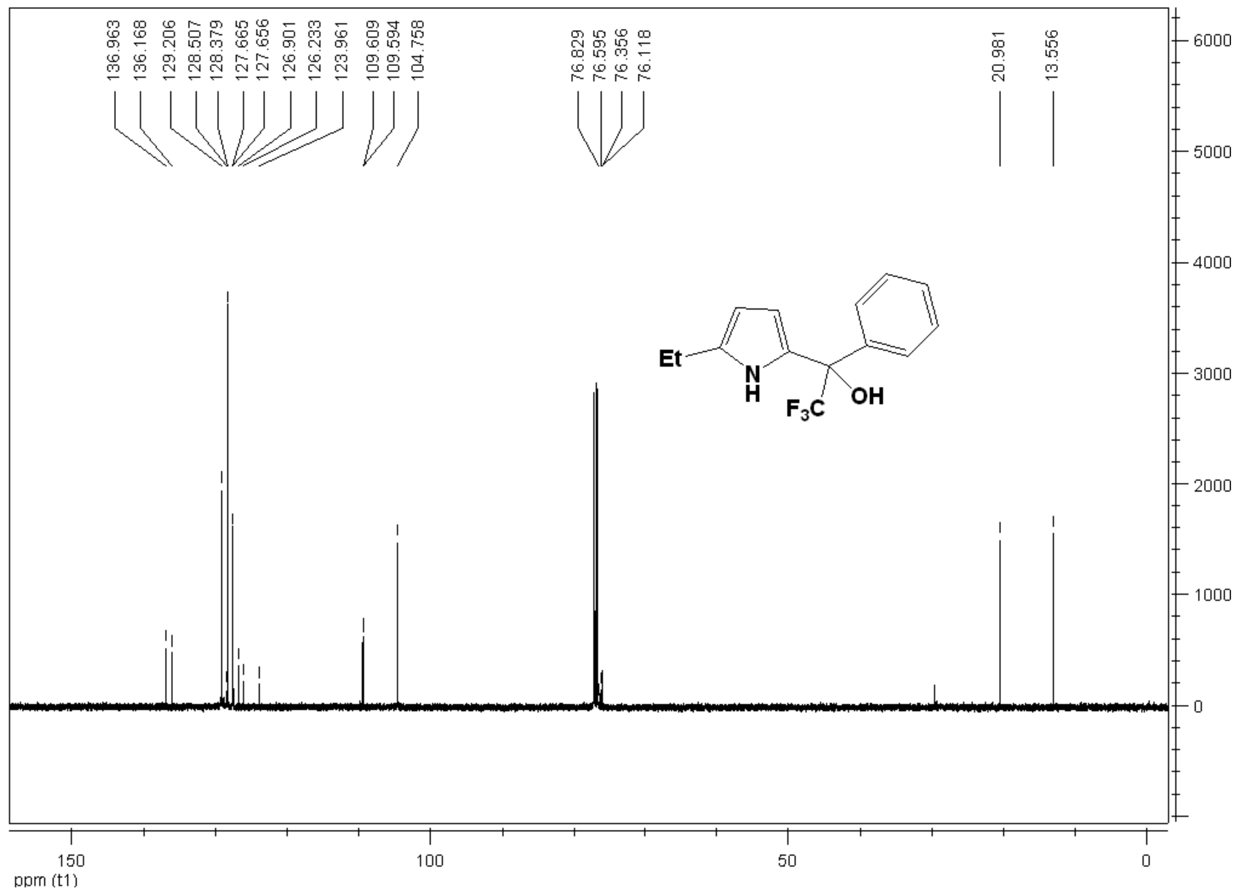

8.179
7.890
7.874
7.408
7.392
7.273
7.265
7.259
7.245
7.210
7.196
7.183
7.180
7.174
7.160
7.147
6.993
6.979
3.713
3.686
3.491
3.463
2.543
F3C
OH
N
H
1000
500
0
1.09
1.00
1.05
1.55
4.99
1.97
1.06
1.07
0.99
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

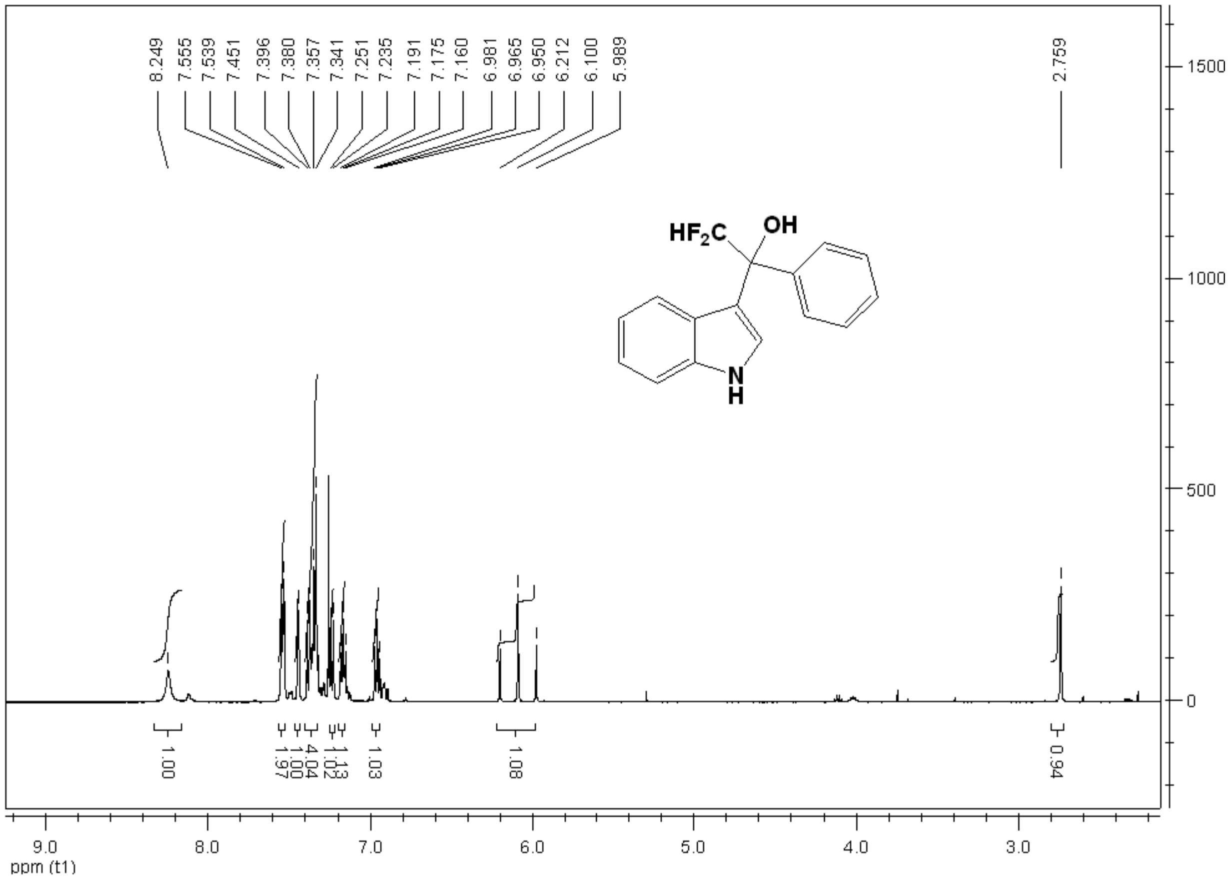

-78.930
F3C
OH
N
H
10000
5000
0
0
-50
-100
-150
-200
ppm (f1)

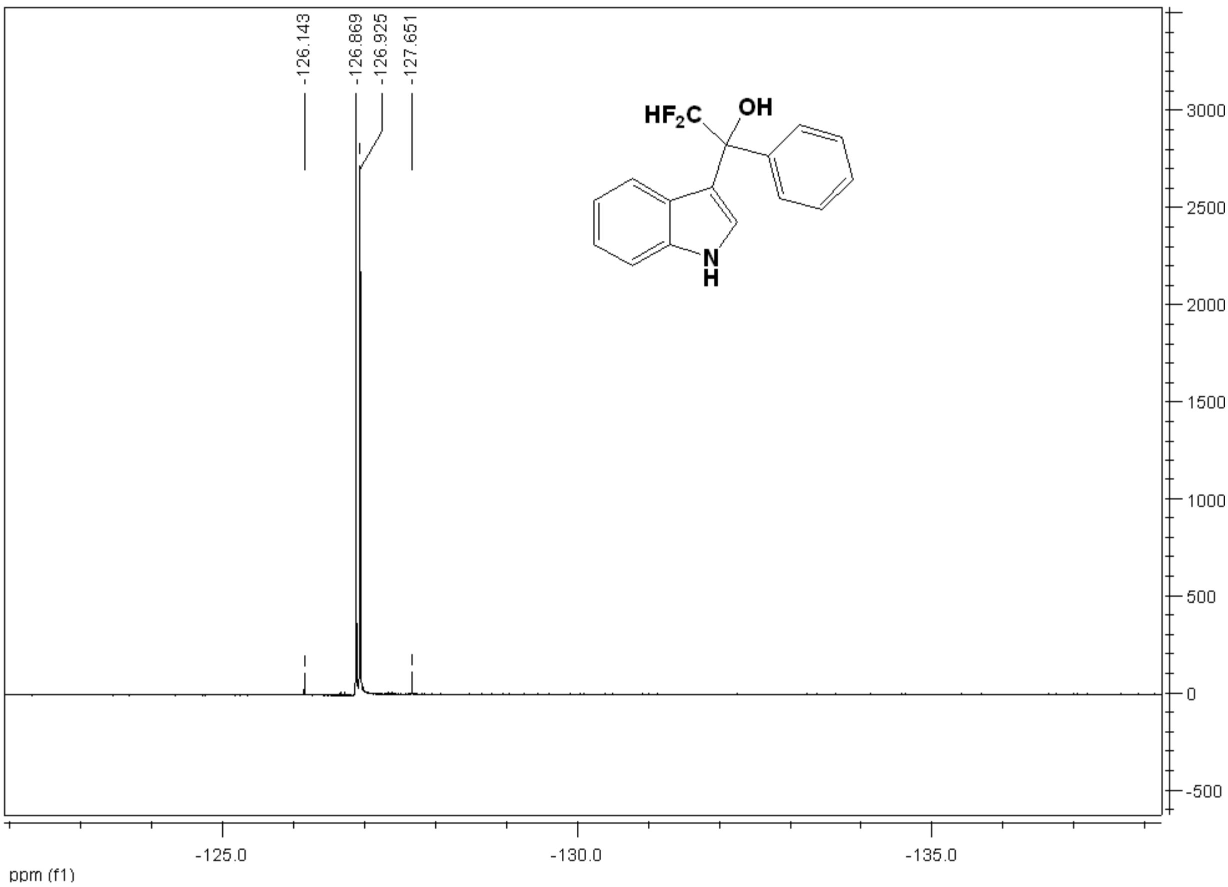

136.898
133.945
131.029
129.557
128.477
127.513
127.284
126.512
125.362
125.010
124.322
122.737
122.623
122.115
121.264
121.248
120.602
119.780
111.762
111.342
76.892
76.657
76.424
76.189
40.859
F3C
OH
N
H
5000
0
150
100
50
0
ppm (f1)

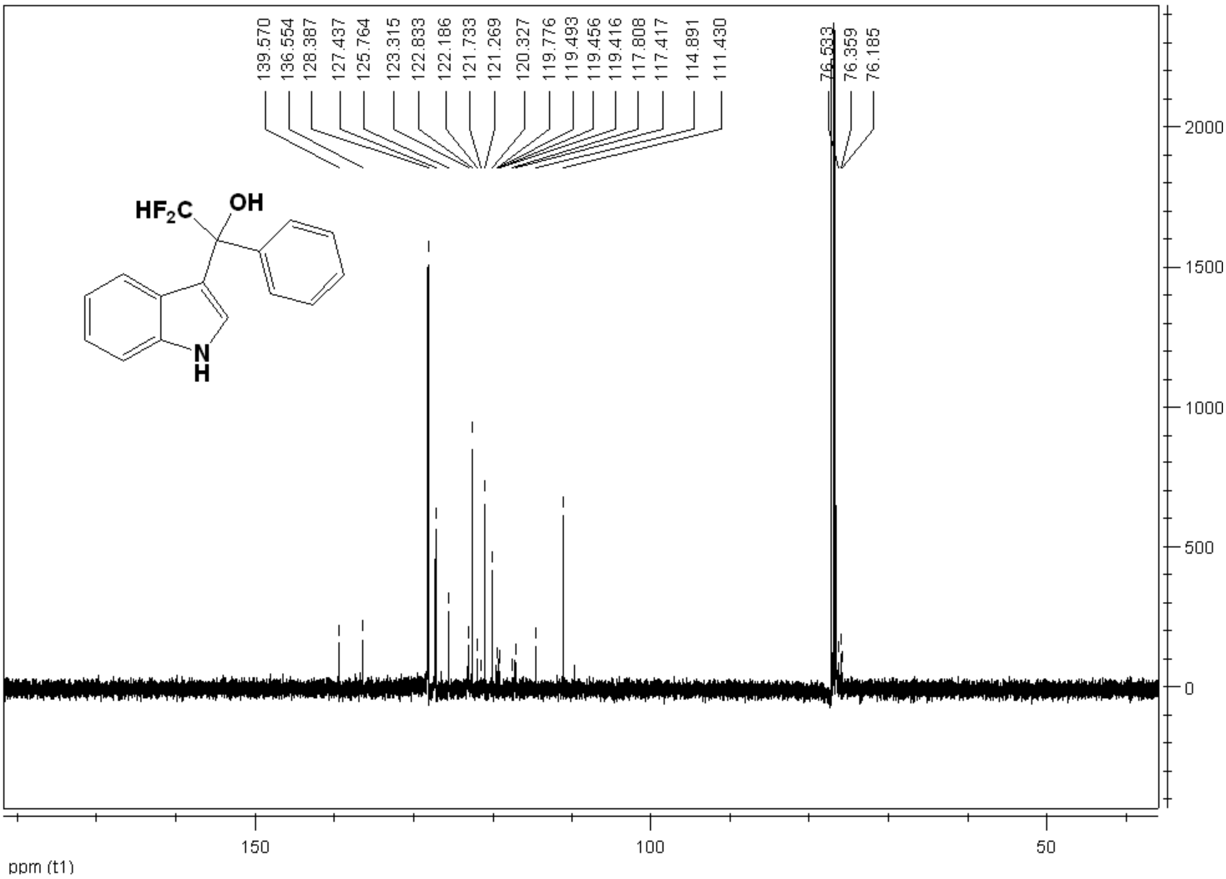

7.894
7.583
7.577
7.572
7.566
7.408
7.401
7.395
6.262
5.902
5.896
5.890
2.929
2.594
2.579
2.564
2.549
1.229
1.214
1.199
Et
N
H
F3C
OH
3000
2500
2000
1500
1000
500
0
0.96
1.99
3.00
0.92
0.94
0.90
2.02
2.94
10.0
5.0
0.0
ppm (t1)

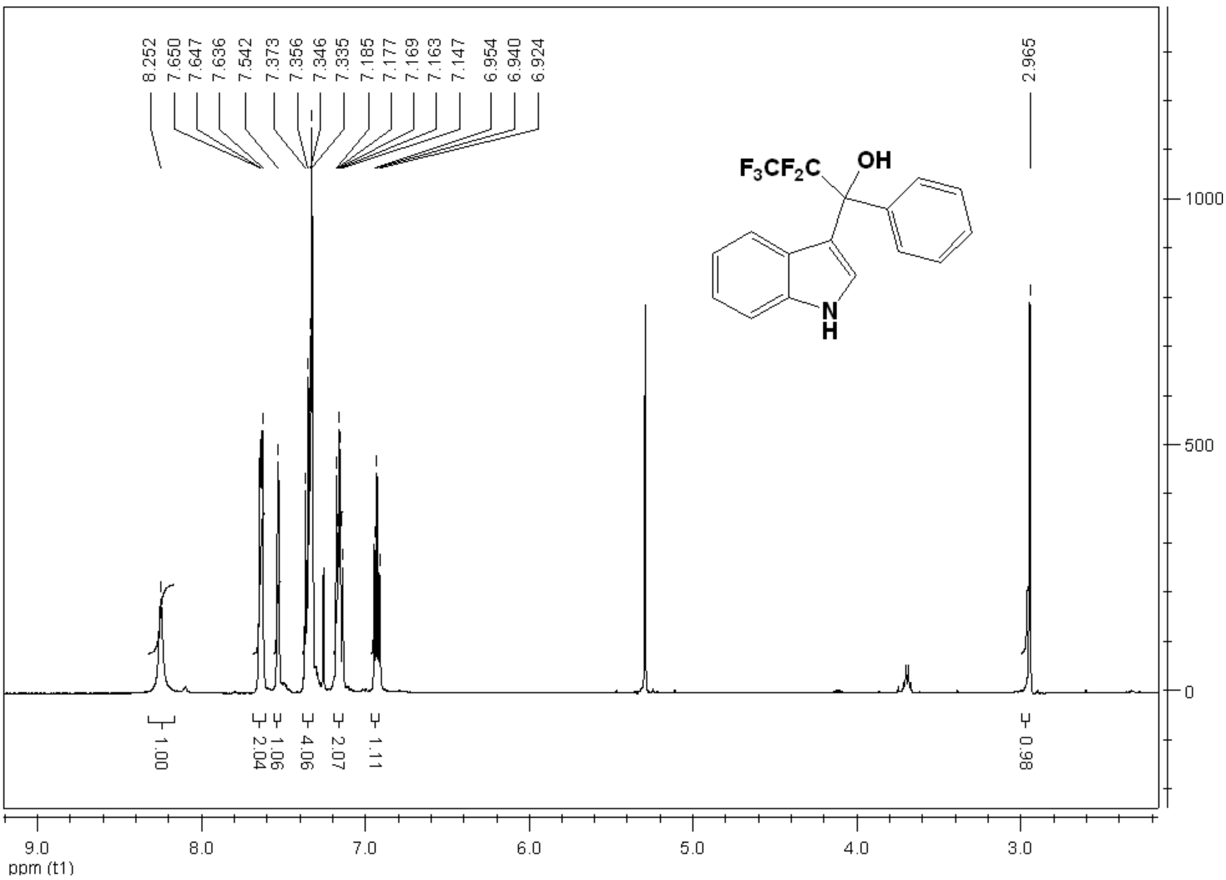

-77.155
Et
N
H
F3C
OH
150
100
50
0
0
-50
-100
-150
-200
ppm (f1)

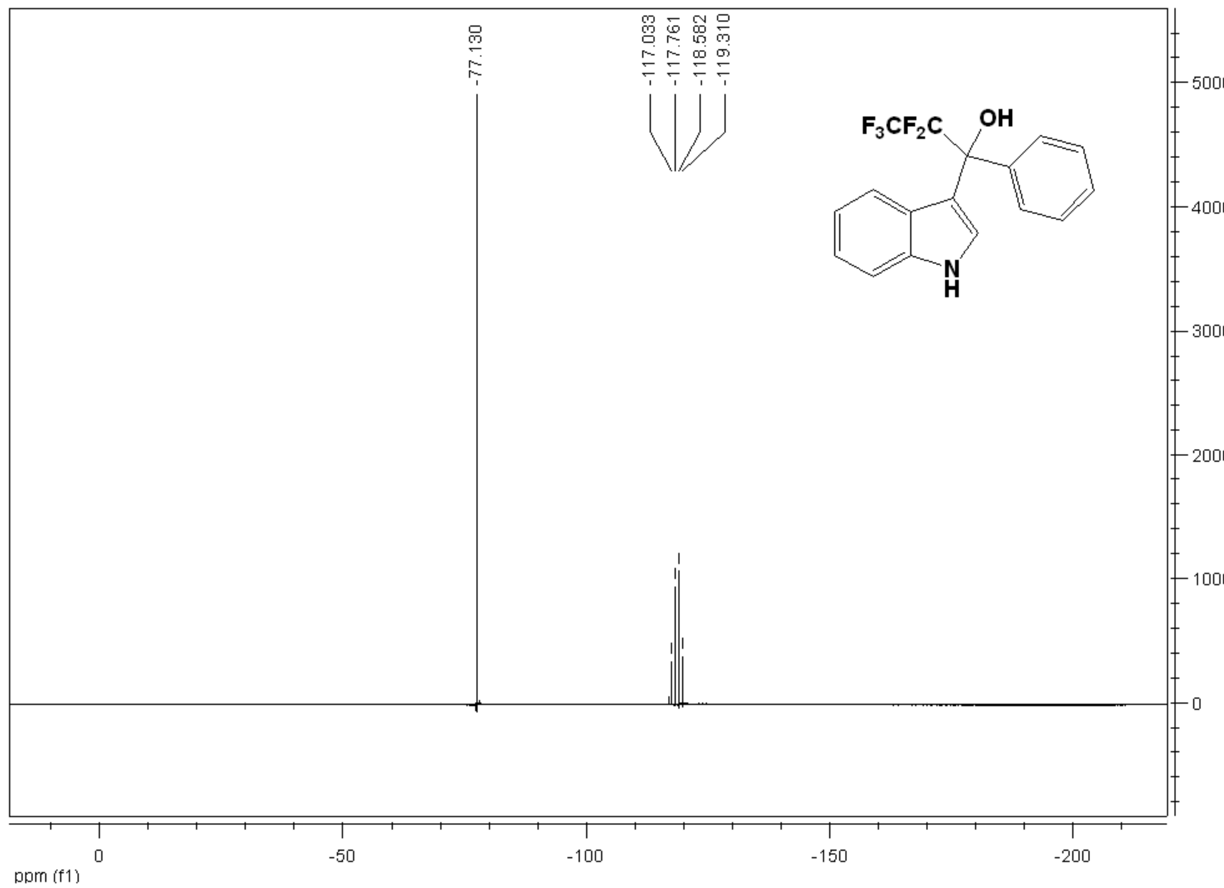

136.963
136.168
129.206
128.507
128.379
127.665
127.656
126.901
126.233
123.961
109.609
109.594
104.758
76.829
76.595
76.356
76.118
20.981
13.556
Et
N
H
F3C
OH
6000
5000
4000
3000
2000
1000
0
150
100
50
0
ppm (t1)

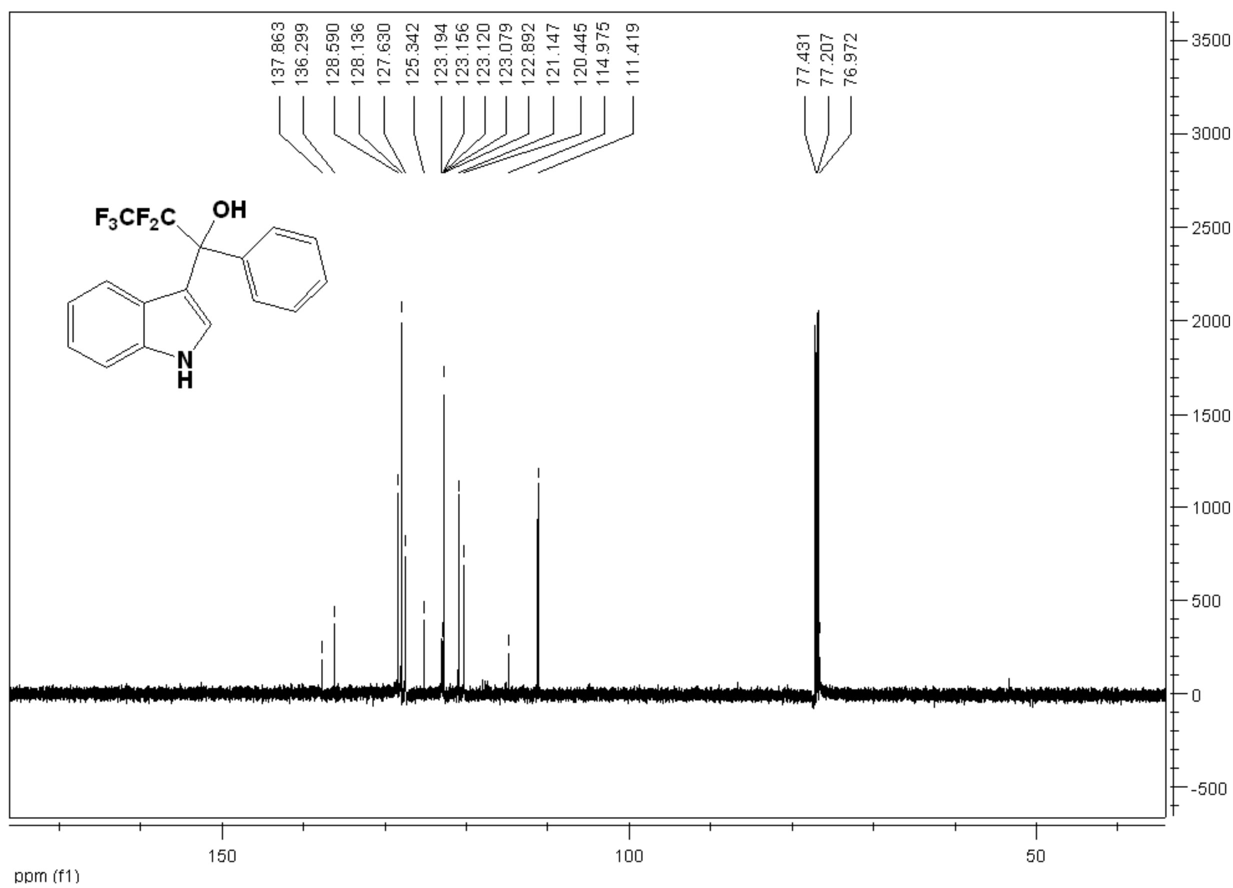

8.249
7.555
7.539
7.451
7.396
7.380
7.357
7.341
7.251
7.235
7.191
7.175
7.160
6.981
6.965
6.950
6.212
6.100
5.989
2.759
HF2C
OH
N
H
1500
1000
500
0
1.00
1.97
1.00
4.04
1.02
1.13
1.03
1.08
0.94
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

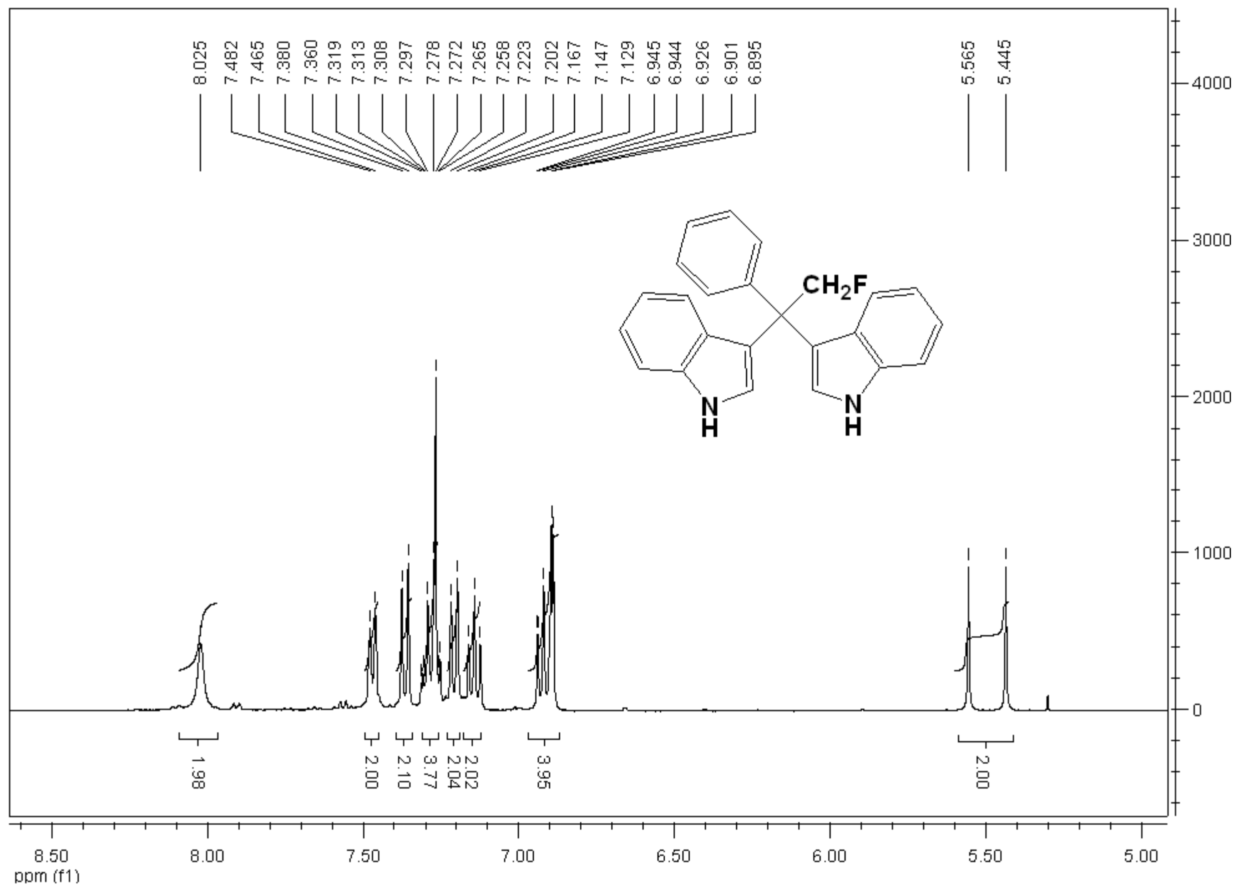

-126.143
-126.869
-126.925
-127.651
HF2C
OH
N
H
3000
2500
2000
1500
1000
500
0
-500
-125.0
-130.0
-135.0
ppm (f1)

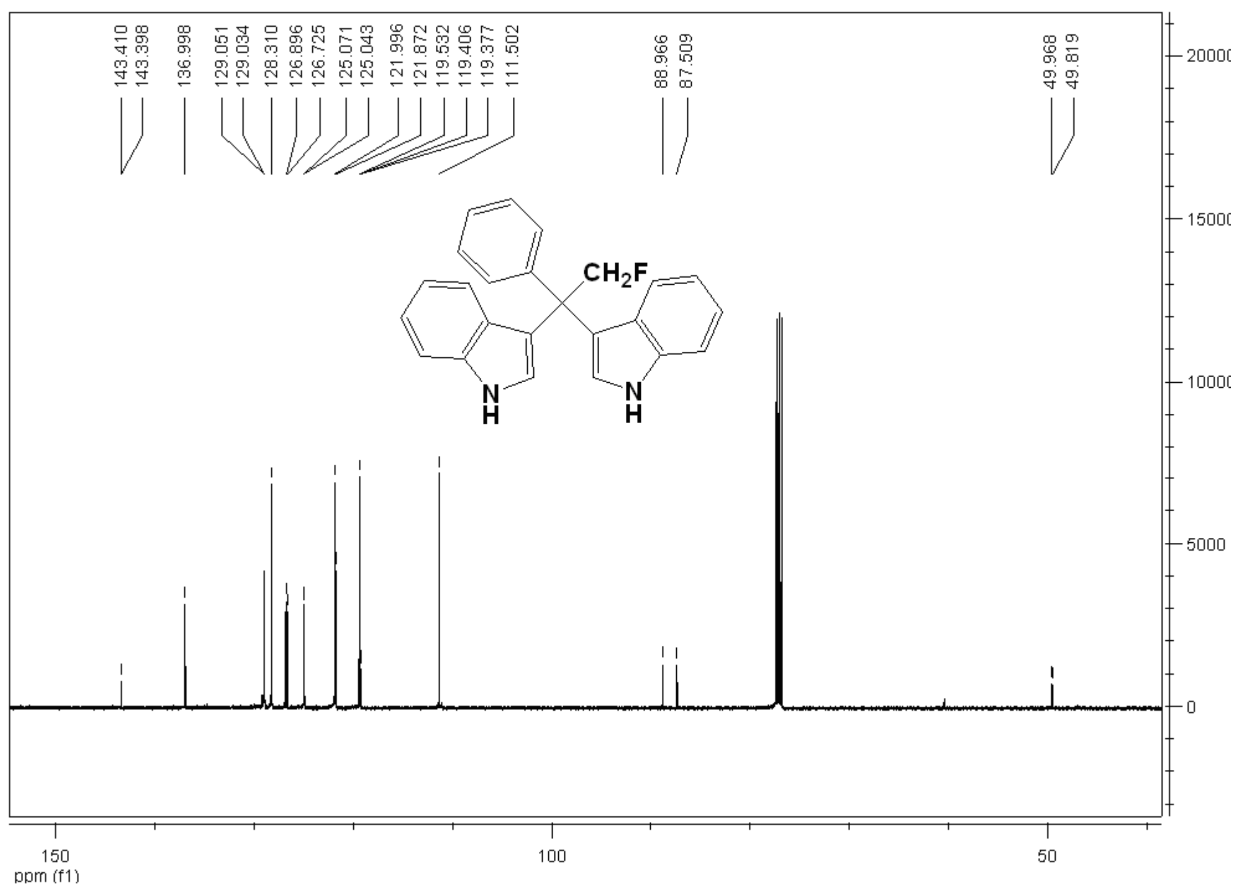

139.570
136.554
128.387
127.437
125.764
123.315
122.833
122.186
121.733
121.269
120.327
119.776
119.493
119.456
119.416
117.808
117.417
114.891
111.430
76.533
76.359
76.185
HF2C
OH
N
H
2000
1500
1000
500
0
150
100
50
ppm (t1)


8.252
7.650
7.647
7.636
7.542
7.373
7.356
7.346
7.335
7.185
7.177
7.169
7.163
7.147
6.954
6.940
6.924
2.965
F3CF2C
OH
N
H
1000
500
0
1.00
2.04
1.06
4.06
2.07
1.11
0.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

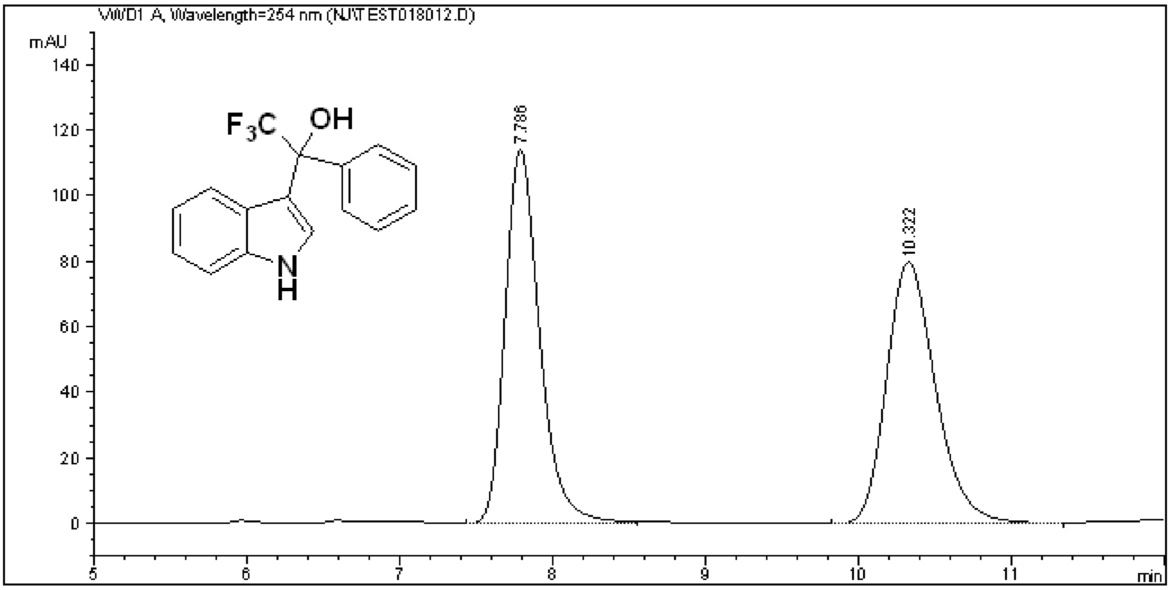

-77.130
-117.033
-117.761
-118.582
-119.310
F_3CF_2C
OH
N
H
5000
4000
3000
2000
1000
0
0
-50
-100
-150
-200
ppm (f1)


137.863
136.299
128.590
128.136
127.630
125.342
123.194
123.156
123.120
123.079
122.892
121.147
120.445
114.975
111.419
77.431
77.207
76.972
F_3CF_2C
OH
N
H
3500
3000
2500
2000
1500
1000
500
0
-500
150
100
50
ppm (f1)


8.025
7.482
7.465
7.380
7.360
7.319
7.313
7.308
7.297
7.278
7.272
7.265
7.258
7.223
7.202
7.167
7.147
7.129
6.945
6.944
6.926
6.901
6.895
5.565
5.445
CH2F
N
H
1.98
2.00
2.10
3.77
2.04
2.02
3.95
2.00
ppm (f1)

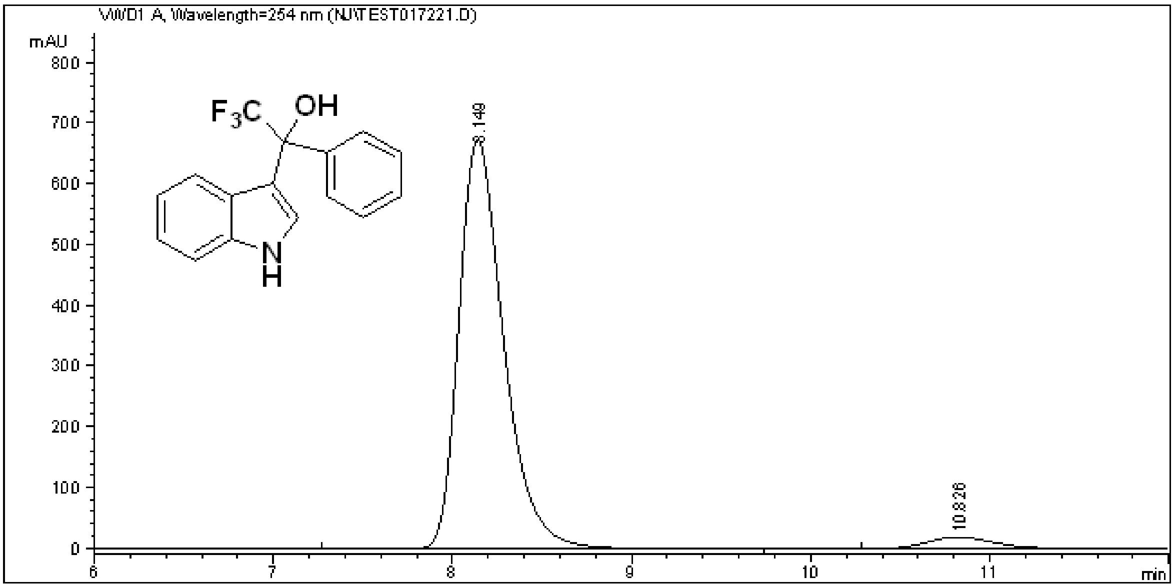

143.410
143.398
136.998
129.051
129.034
128.310
126.896
126.725
125.071
125.043
121.996
121.872
119.532
119.406
119.377
111.502
88.966
87.509
49.968
49.819
CH2F
N
H
ppm (f1)

Sample Info : 254nm,OD-H,i-PrOH:Hexane=20:80,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

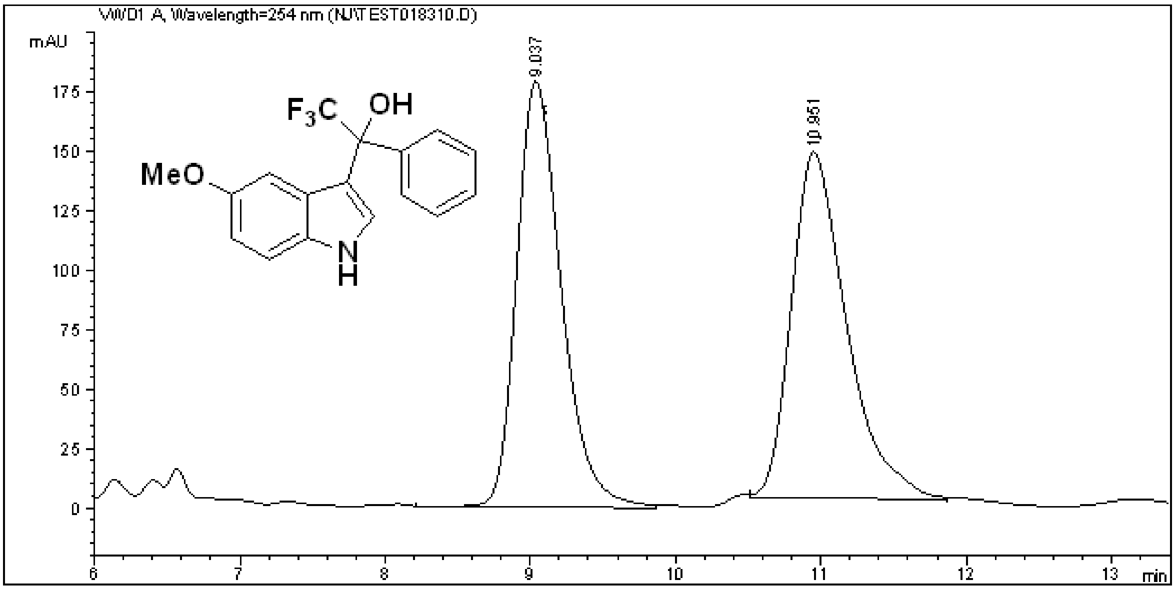
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.786	VV	0.2428	1810.39587	114.44141	50.1359
2	10.322	VV	0.3470	1800.57776	80.01328	49.8641
Totals :				3610.97363	194.45468	



Signal 1: VWD1 A, Wavelength=254 nm

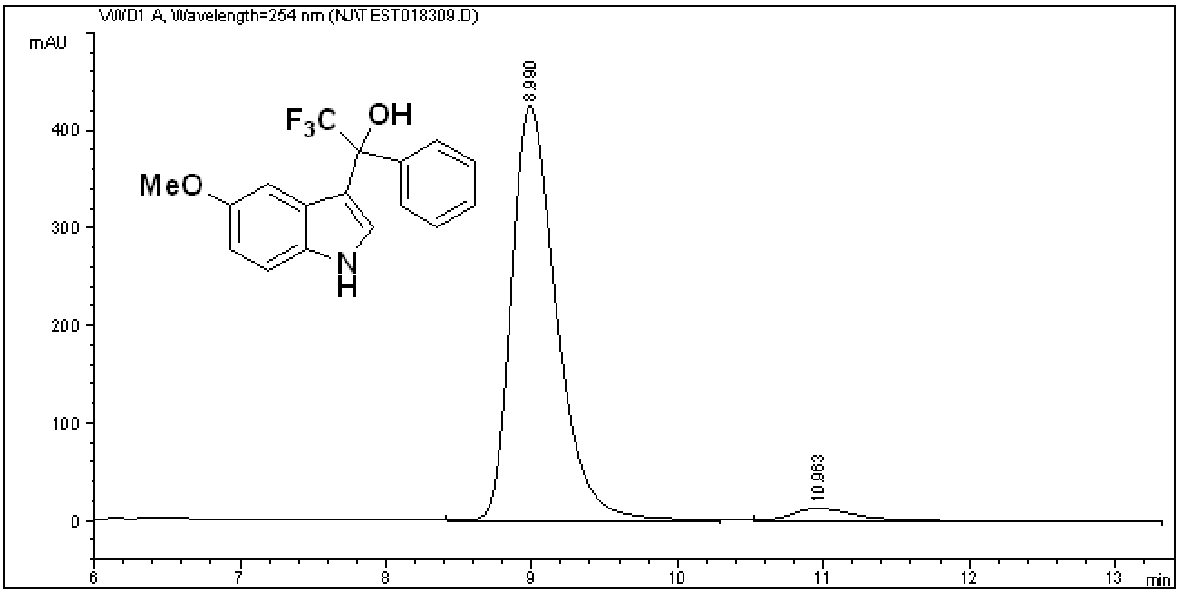
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.149	VB	0.3006	1.17232e4	659.35413	95.8072
2	10.826	BB	0.4322	513.03882	18.95854	4.1928
Totals :				1.22363e4	678.31267	

```
Sample Info      : 254nm,OD-H,i-PrOH:Hexane=20:80,0.8mL/min
```



Signal 1: VWD1 A, Wavelength=254 nm

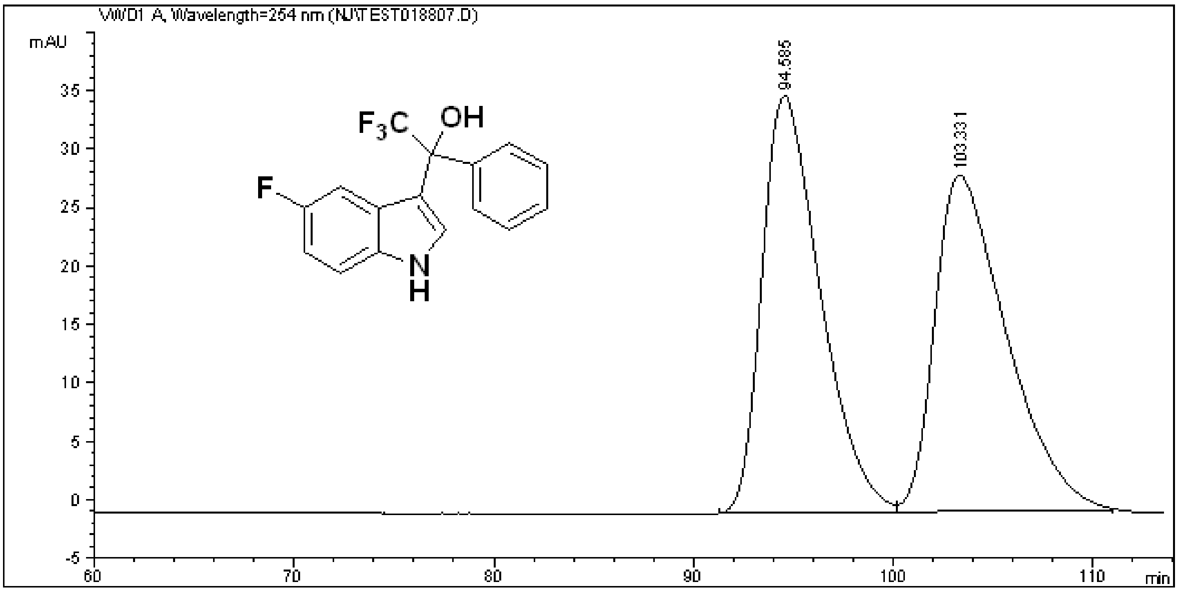
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.037	MM	0.3555	3815.95581	178.91862	49.7937
2	10.951	MM	0.4407	3847.57178	145.51312	50.2063
Totals :				7663.52759	324.43175	



Signal 1: VWD1 A, Wavelength=254 nm

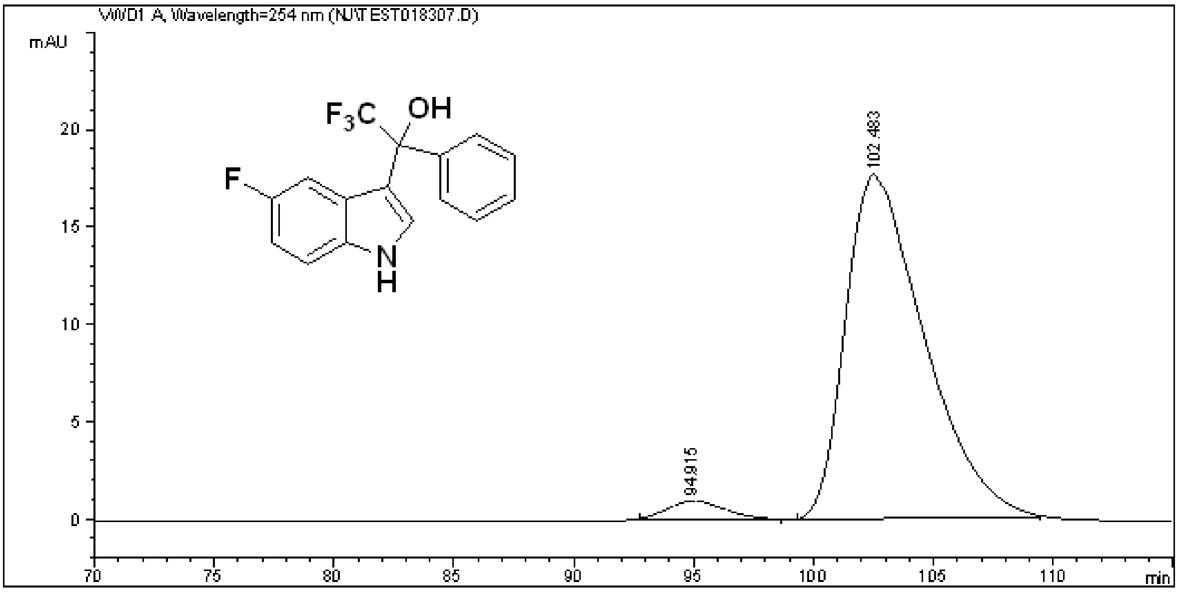
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.990	VV	0.3335	9164.09375	424.37775	95.7187
2	10.963	VBA	0.4885	409.88623	12.65743	4.2813
Totals :				9573.97998	437.03518	

```
Sample Info      : 254nm,OD-H,i-PrOH:Hexane=2:98,1.0mL/min
```



Signal 1: VWD1 A, Wavelength=254 nm

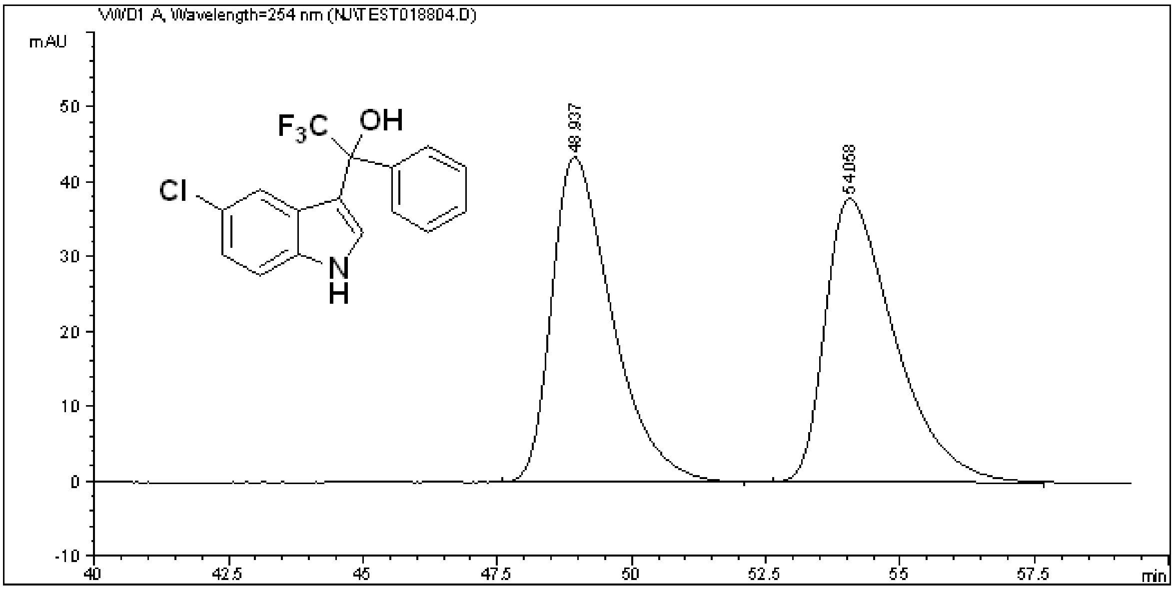
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	94.585	BB	2.8646	7259.76318	35.74360	50.1971
2	103.331	BB	3.3302	7202.76123	28.75344	49.8029
Totals :				1.44625e4	64.49703	



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	94.915	BB	1.9876	158.11581	9.39091e-1	3.7600
2	102.483	BB	2.8178	4047.04053	17.70761	96.2400
Totals :				4205.15634	18.64670	

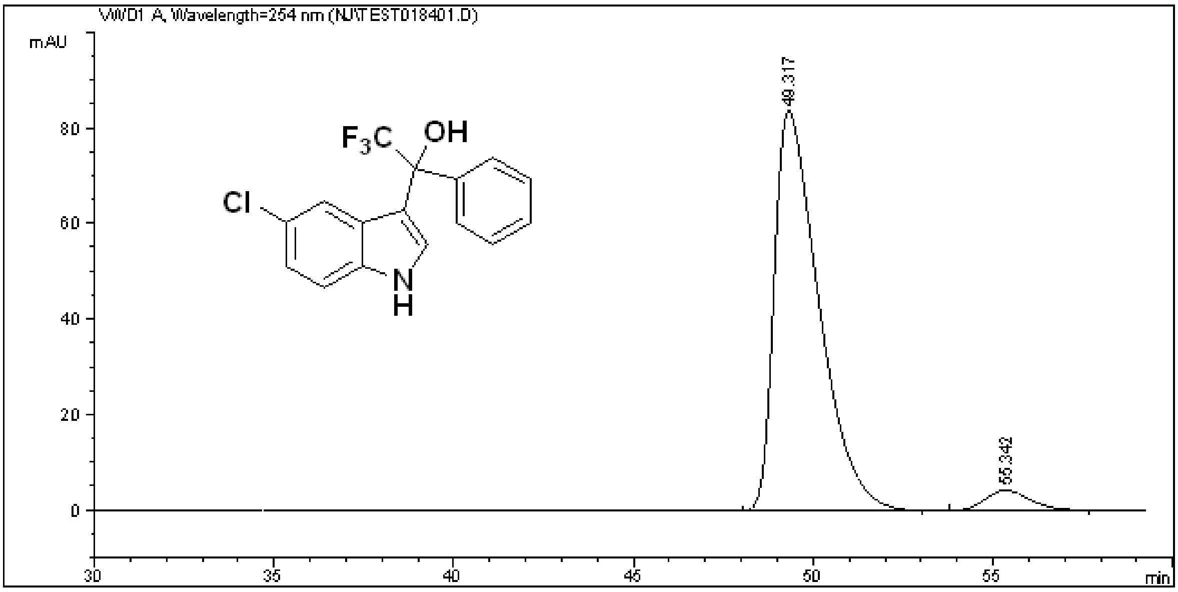
Sample Info : 254nm,AD-H,i-PrOH:Hexane=5:95,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.937	BB	1.1865	3400.85571	43.46859	49.8551
2	54.058	BB	1.3614	3420.62476	37.90794	50.1449

Totals : 6821.48047 81.37653

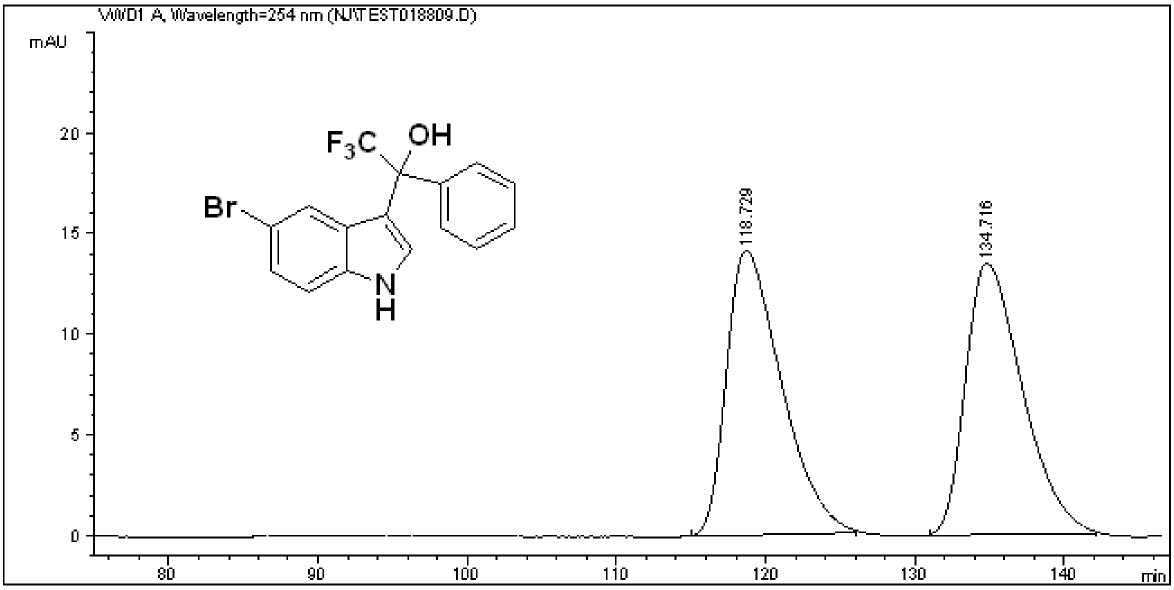


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.317	BB	1.2895	7227.47314	83.73340	95.0381
2	55.342	BB	1.2746	377.34332	4.28636	4.9619

Totals : 7604.81647 88.01976

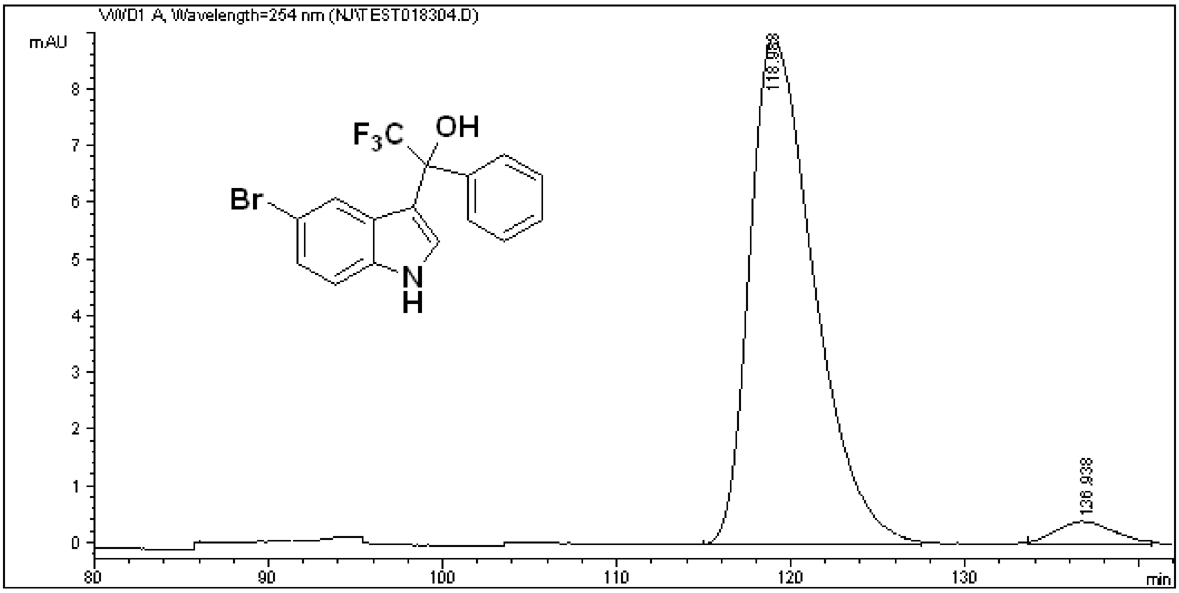
Sample Info : 254nm,OD-H,i-PrOH:Hexane=2:98,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	118.729	BB	3.1485	3635.73804	14.09794	50.3694
2	134.716	BB	3.2216	3582.40942	13.46014	49.6306

Totals : 7218.14746 27.55807

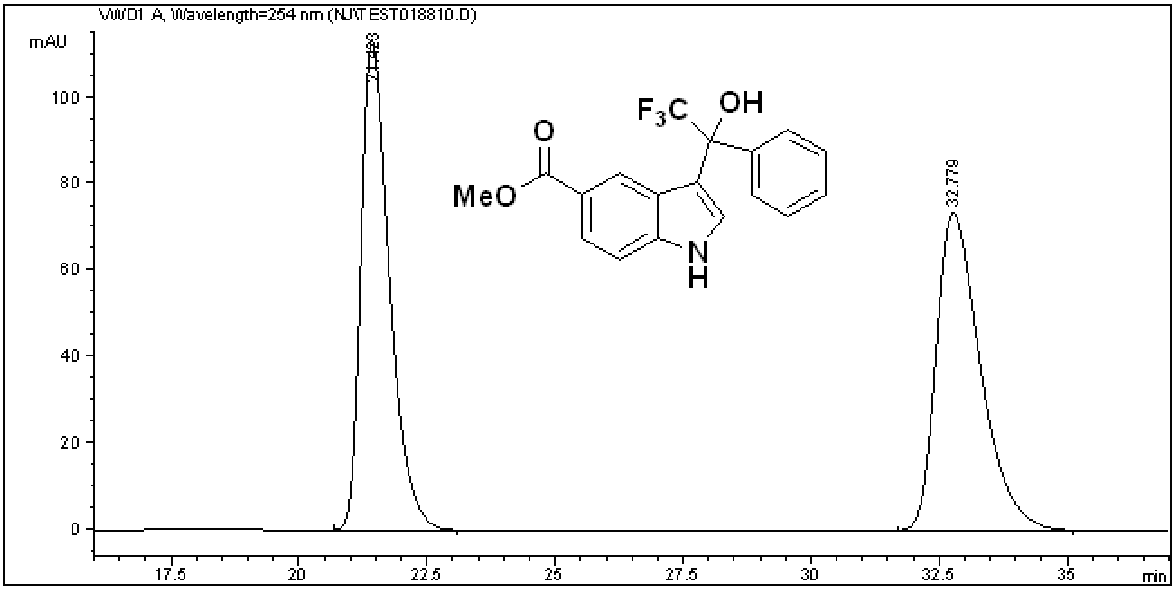


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	118.983	MM	4.2706	2289.06714	8.93337	96.0350
2	136.938	MM	3.8482	94.50867	4.09322e-1	3.9650

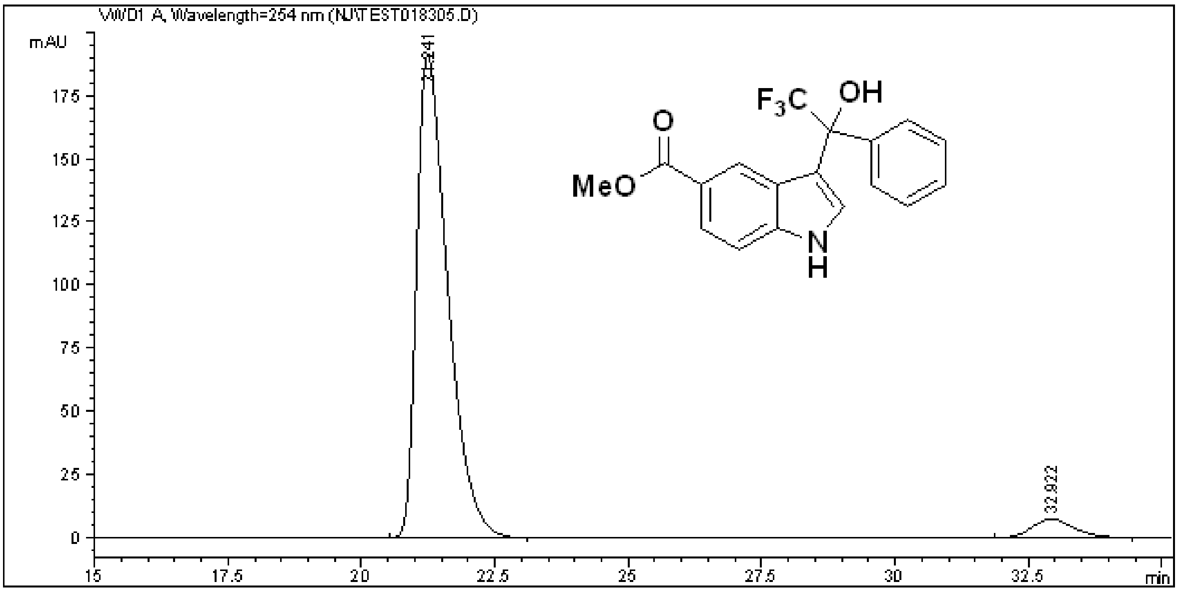
Totals : 2383.57581 9.34269

Sample Info : 254nm,AD-H,i-PrOH:Hexane=10:90,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

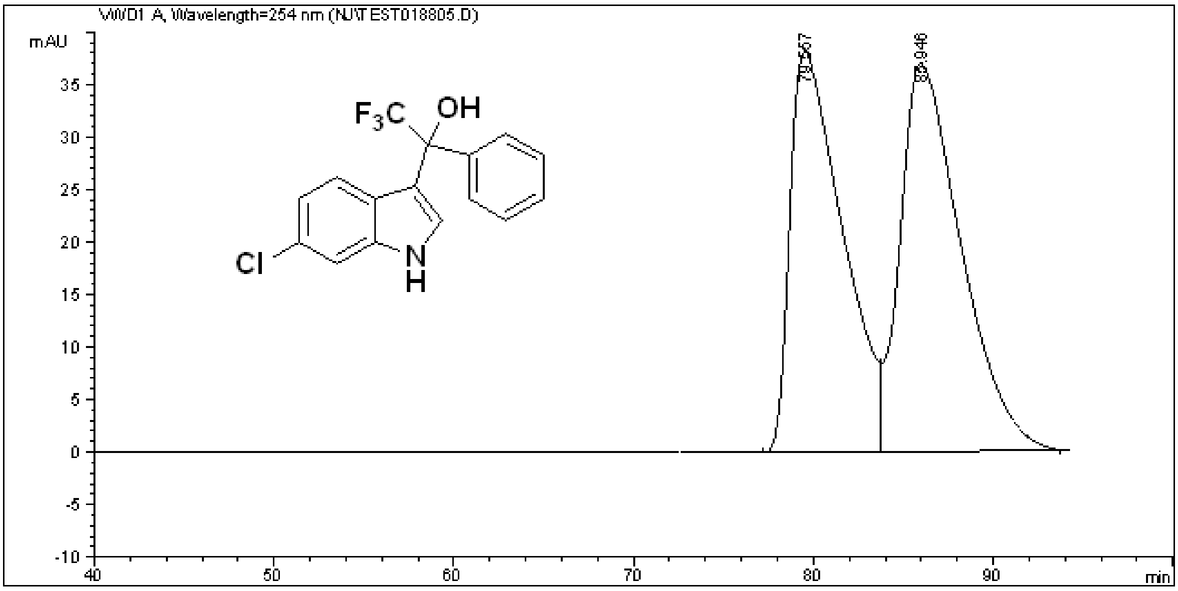
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.423	BB	0.5898	4402.53662	113.40026	49.9024
2	32.779	BB	0.9184	4419.75098	73.50591	50.0976
Totals :				8822.28760	186.90617	



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.241	BB	0.6188	7748.64600	191.05151	94.8510
2	32.922	BB	0.8787	420.63800	7.39954	5.1490
Totals :				8169.28400	198.45105	

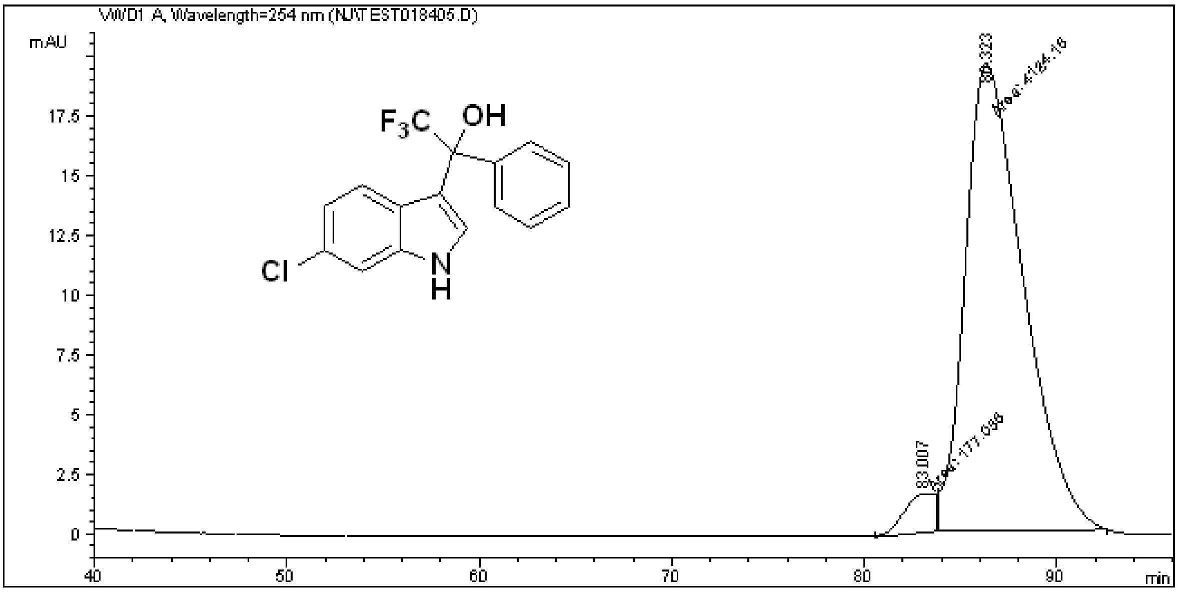
Sample Info : 254nm,OD-H,i-PrOH:Hexane=2:98,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	79.557	BV	2.7452	7778.99170	38.25350	47.1074
2	85.946	VB	3.1886	8734.32227	36.99137	52.8926

Totals : 1.65133e4 75.24488

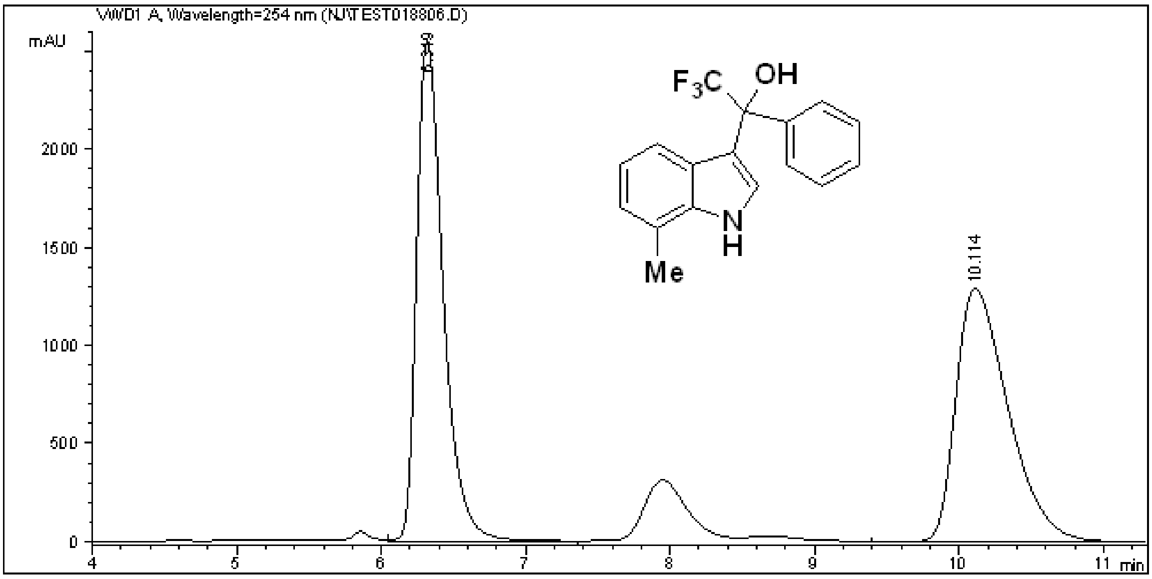


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	83.007	MM T	1.8259	177.03844	1.61596	4.1160
2	86.323	MP	3.5138	4124.16455	19.56188	95.8840

Totals : 4301.20299 21.17783

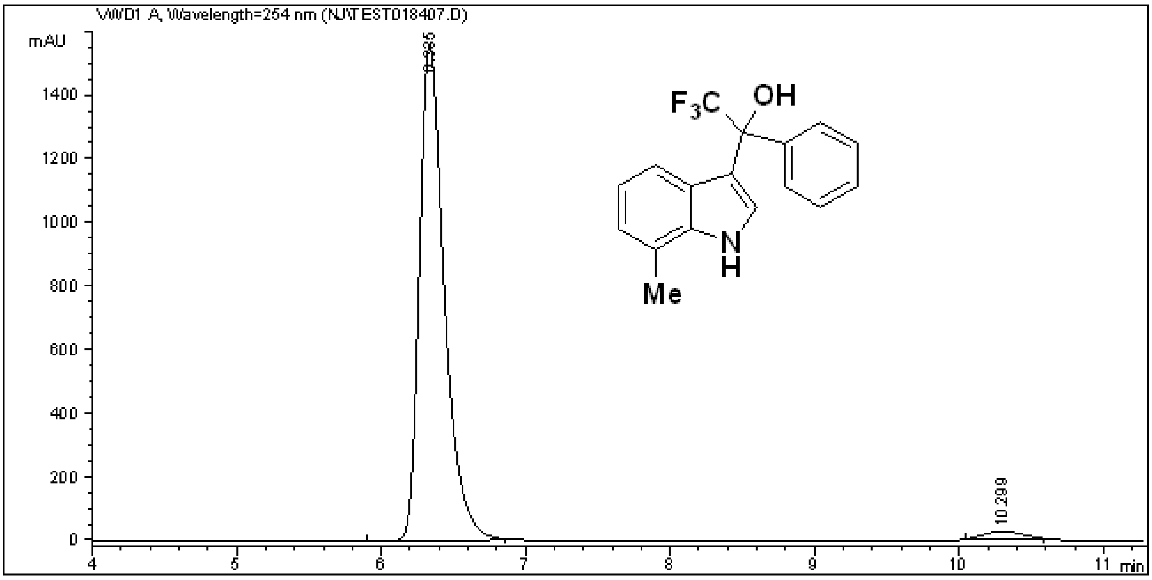
Sample Info : 254nm,OD-H,i-PrOH:Hexane=20:80,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.319	VV	0.1970	3.28824e4	2550.74121	50.2815
2	10.114	VBA	0.3870	3.25142e4	1291.09583	49.7185

Totals : 6.53965e4 3841.83704

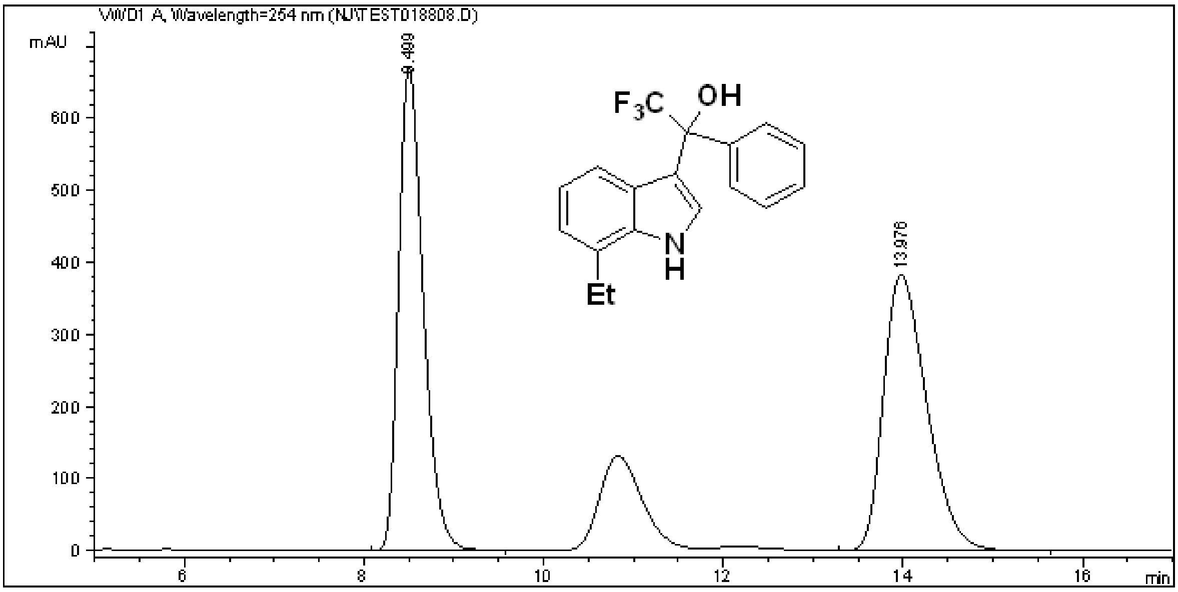


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.335	MM	0.1993	1.87806e4	1570.64319	97.2837
2	10.299	MM	0.3329	524.37408	26.25392	2.7163

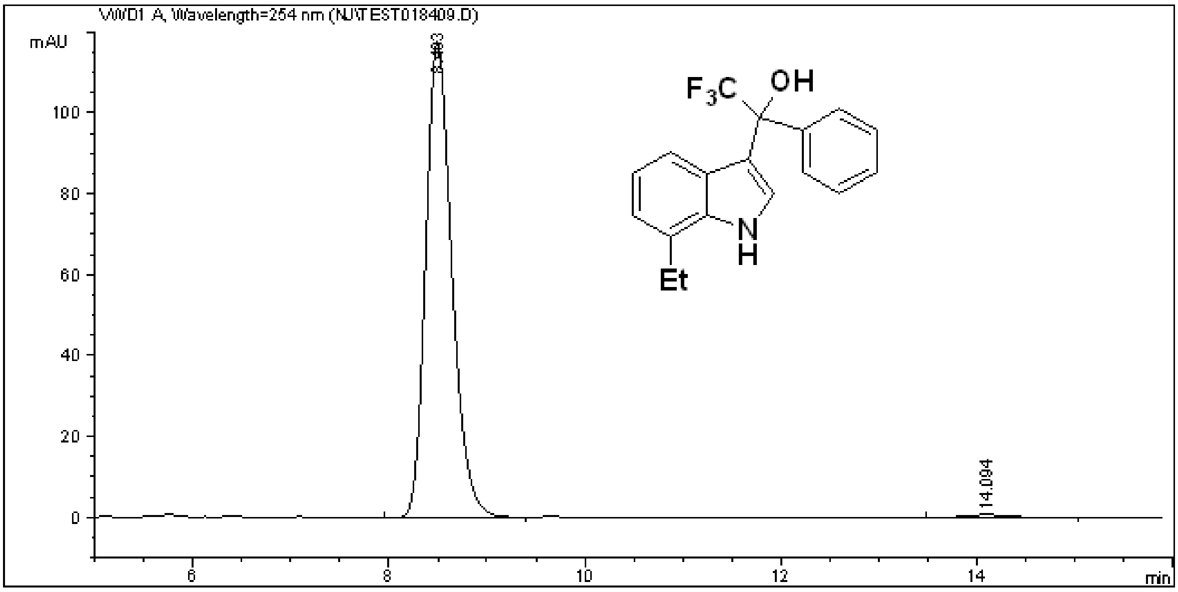
Totals : 1.93050e4 1596.89711

Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

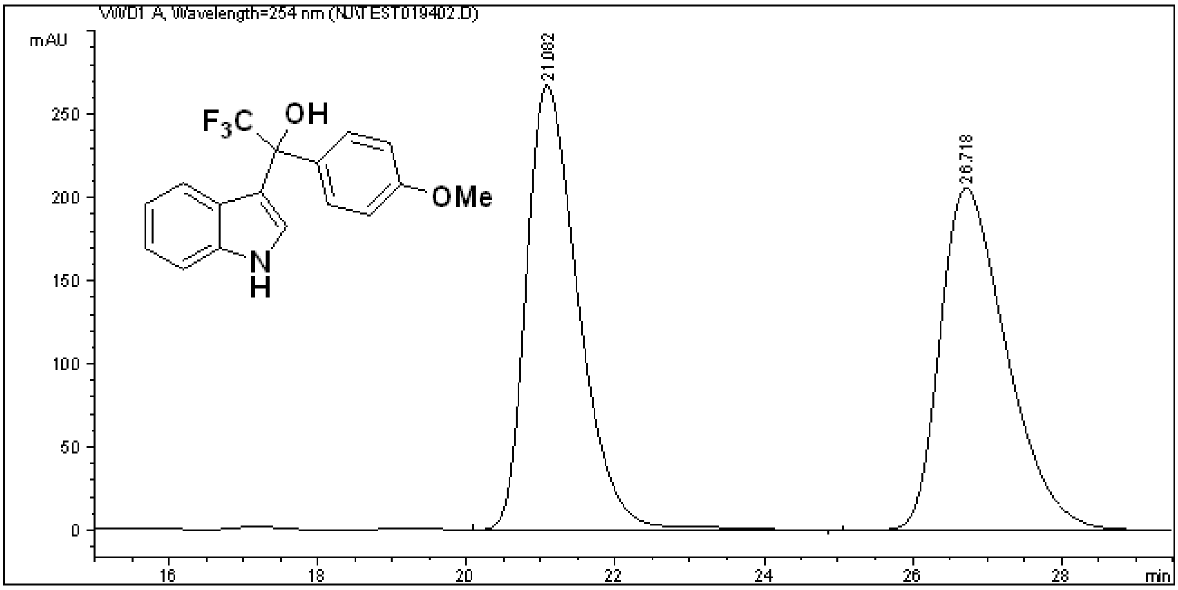
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.499	BV	0.2924	1.28247e4	672.56567	50.0122
2	13.976	VB	0.5187	1.28184e4	382.94171	49.9878
Totals :				2.56430e4	1055.50739	



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.493	VV	0.2847	2181.36572	117.64856	98.9767
2	14.094	BB	0.4881	22.55185	6.97106e-1	1.0233
Totals :				2203.91757	118.34567	

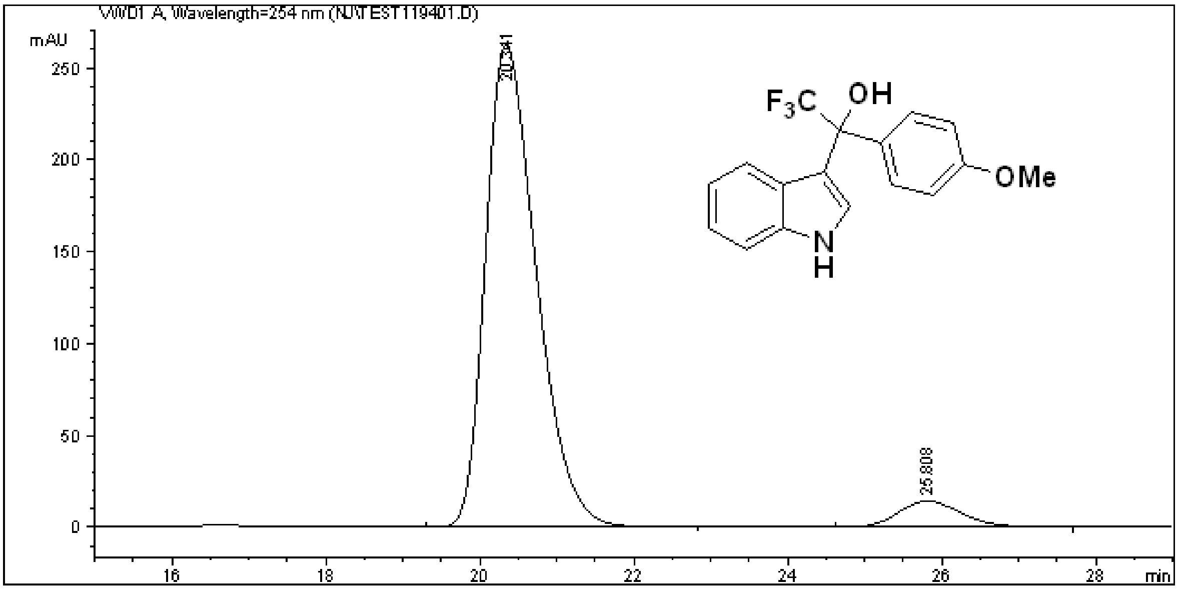
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.082	VB	0.7441	1.29962e4	267.67911	50.4822
2	26.718	BBA	0.9535	1.27479e4	205.58960	49.5178

Totals : 2.57441e4 473.26871

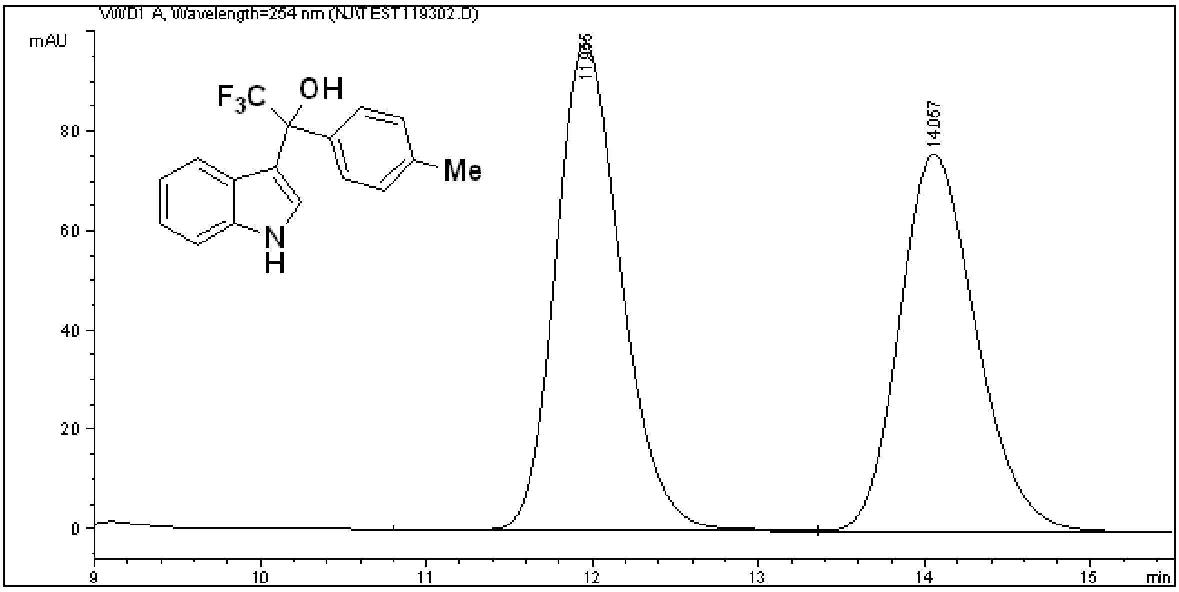


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.341	VB	0.7065	1.20400e4	262.69604	93.6905
2	25.808	BB	0.8700	810.81628	14.26214	6.3095

Totals : 1.28508e4 276.95818

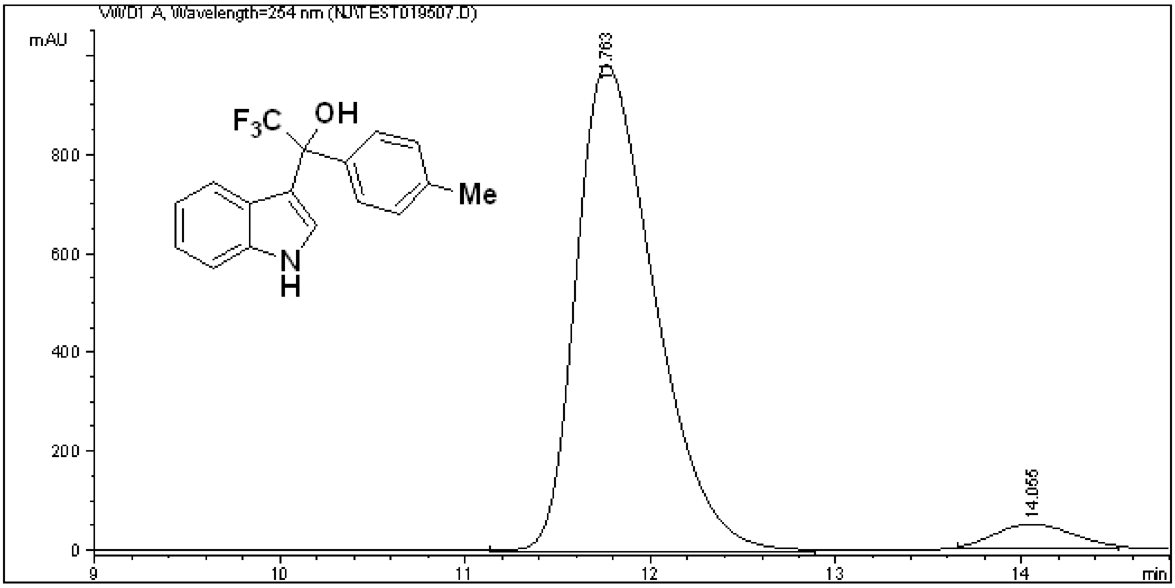
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.955	VV	0.4242	2687.52661	98.18417	52.4450
2	14.057	VB	0.4969	2436.93970	75.90729	47.5550

Totals : 5124.46631 174.09146

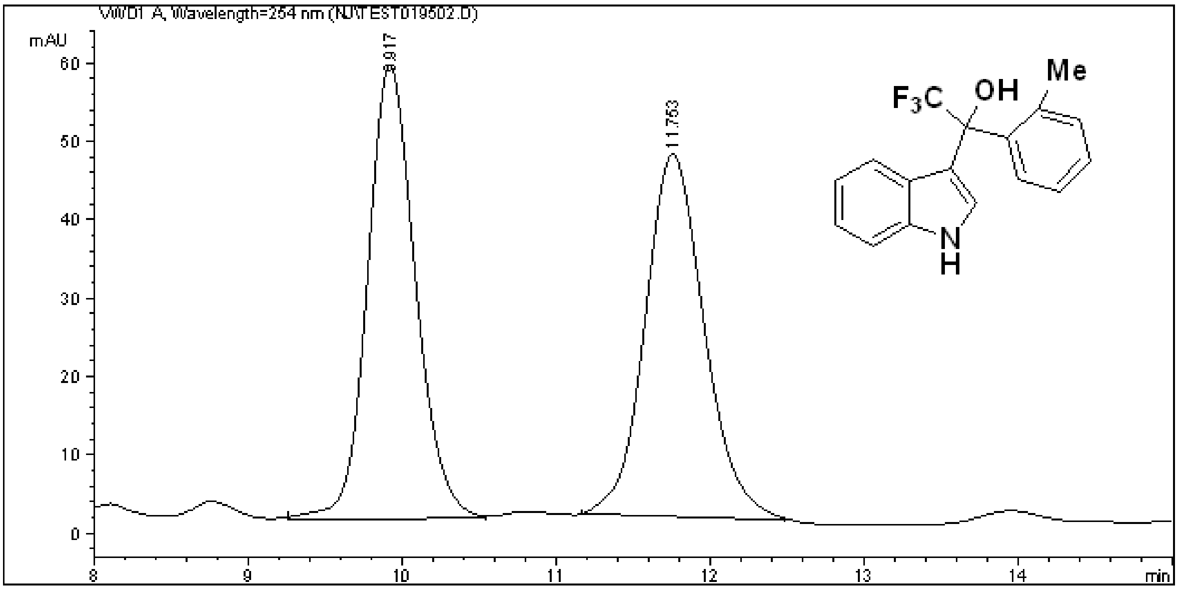


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.763	MM	0.4927	2.91500e4	985.97650	95.4076
2	14.055	MM	0.4839	1403.12378	48.32924	4.5924

Totals : 3.05531e4 1034.30574

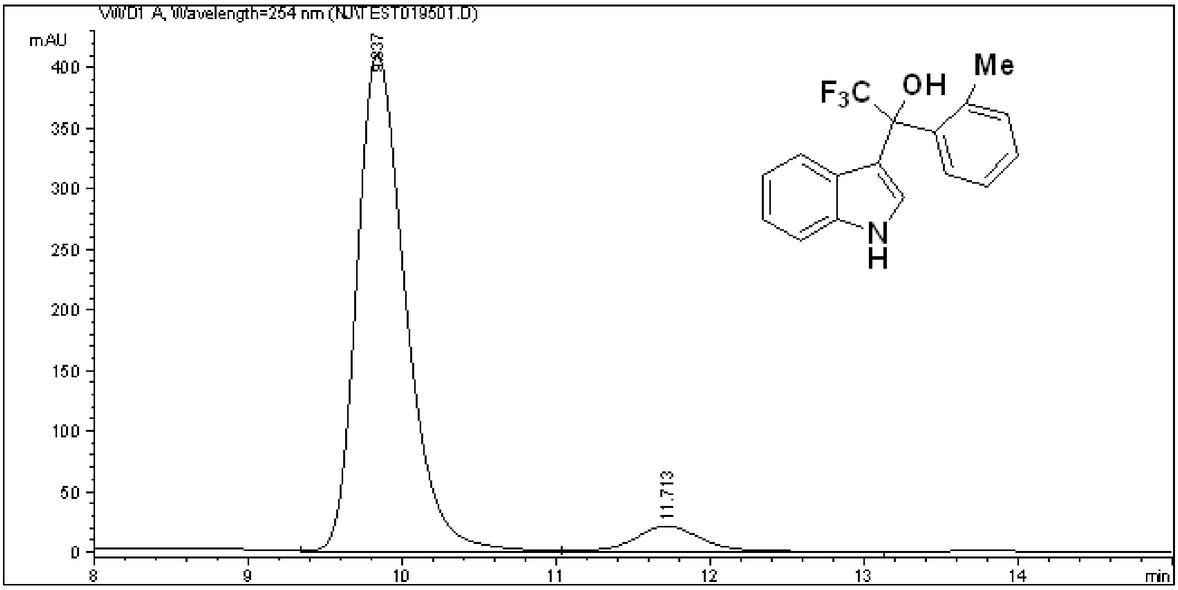
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.917	MM	0.3610	1253.81824	57.87966	50.3713
2	11.753	MM	0.4454	1235.33240	46.22379	49.6287

Totals : 2489.15063 104.10345

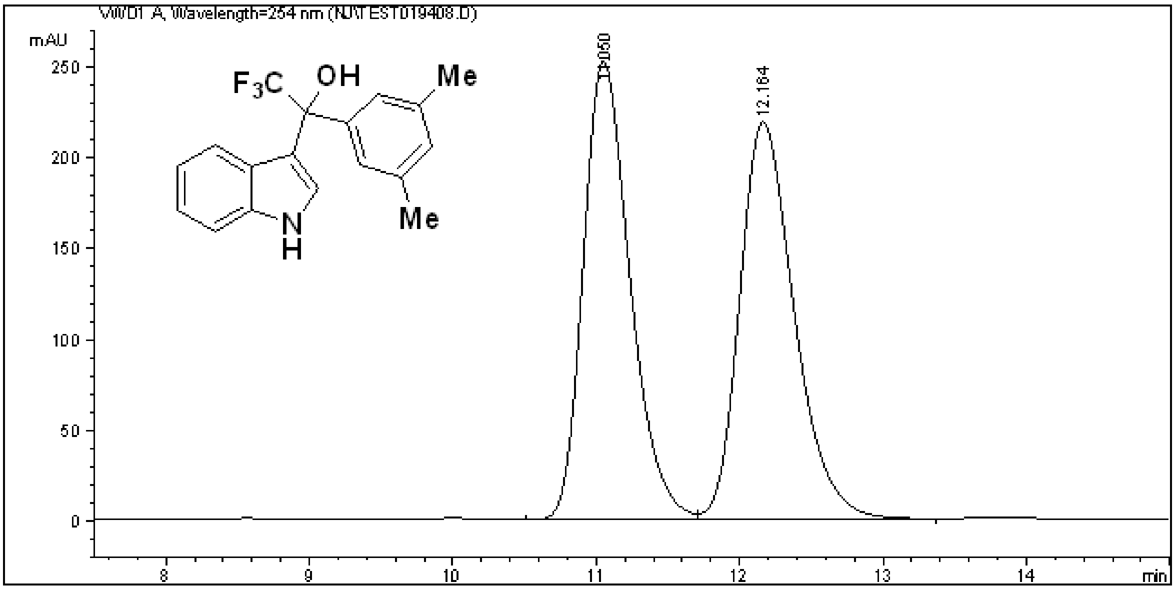


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.837	VV	0.3378	9033.61523	411.22504	93.0366
2	11.713	VV	0.4722	676.13019	21.47260	6.9634

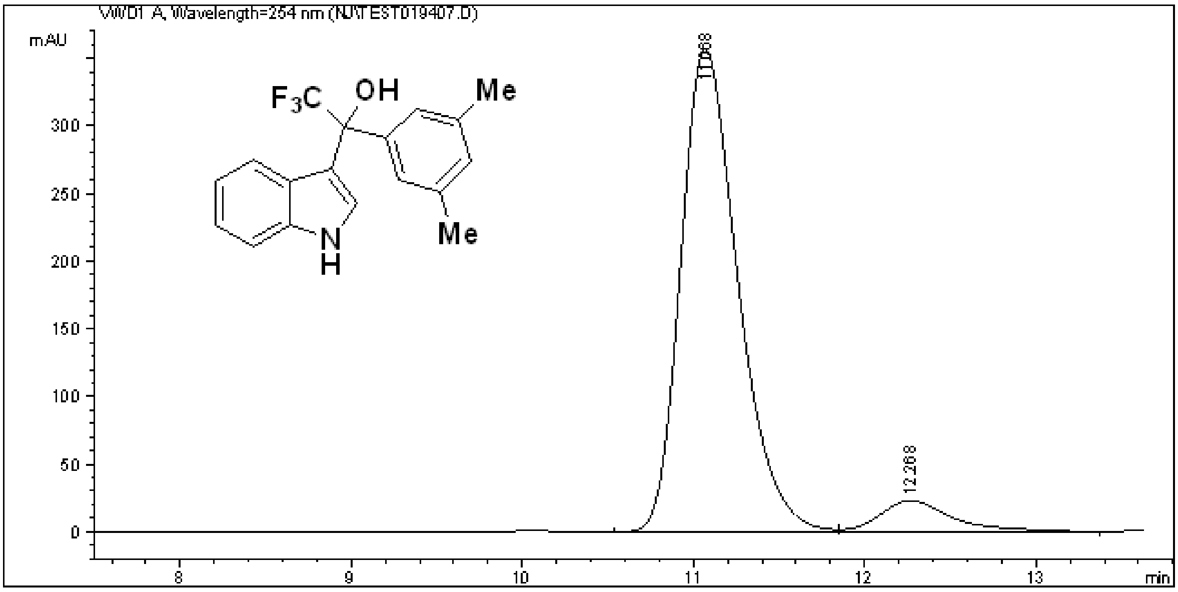
Totals : 9709.74542 432.69764

Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

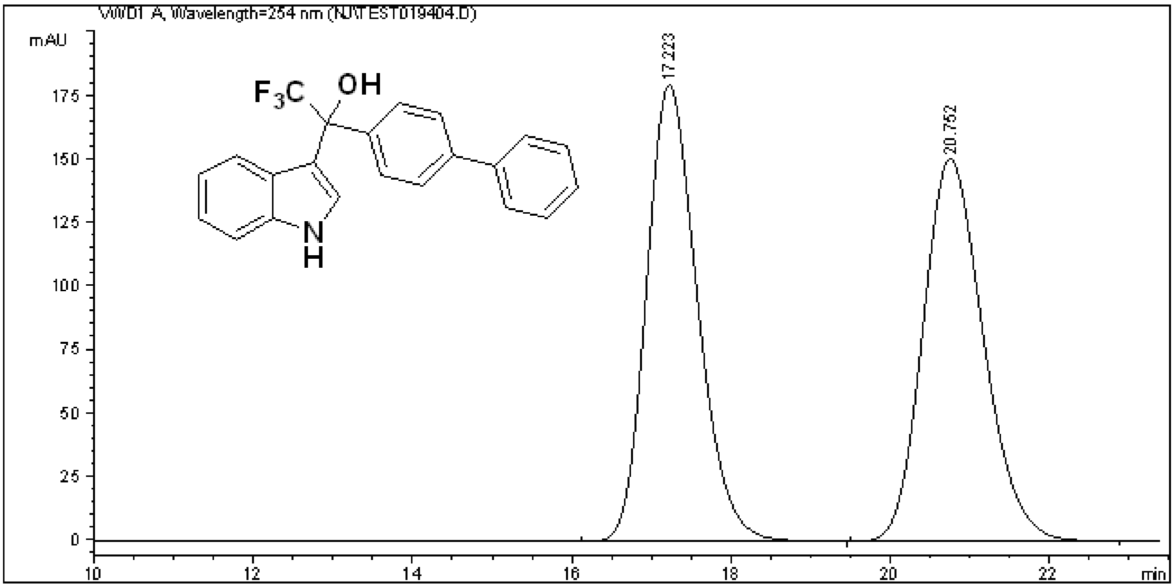
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.050	VV	0.3498	5765.49951	253.45621	49.6180
2	12.164	VV	0.4068	5854.27344	219.85269	50.3820
Totals :				1.16198e4	473.30890	



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.068	VV	0.3541	8253.09570	357.09744	92.4921
2	12.268	VV	0.4390	669.92804	22.98512	7.5079
Totals :				8923.02374	380.08257	

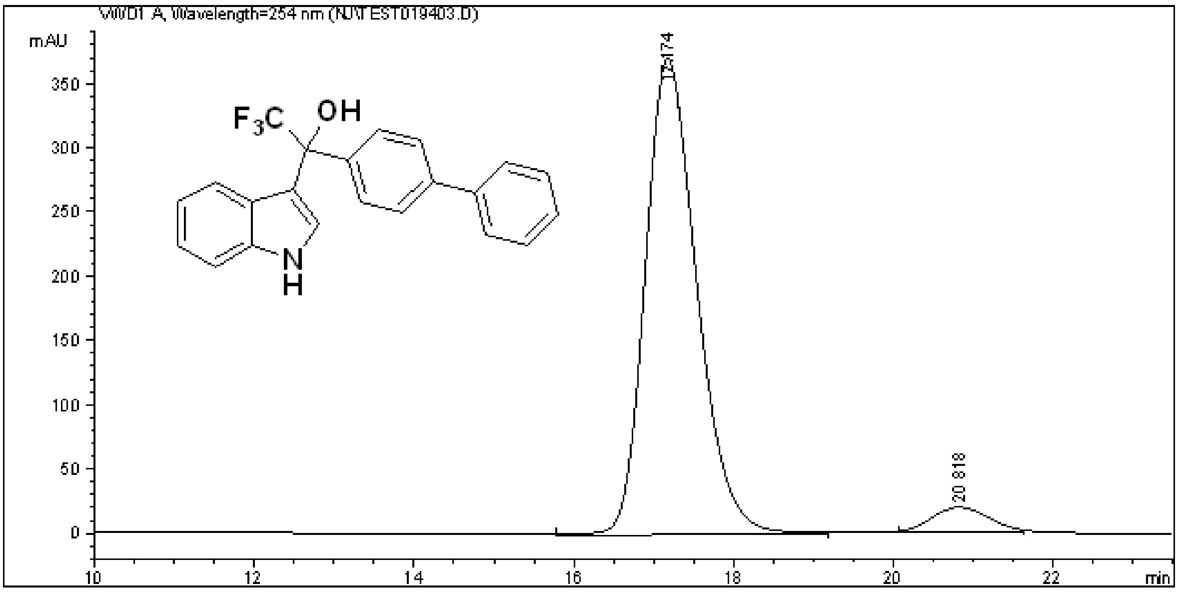
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.223	VB	0.6882	7994.50439	179.59659	50.1885
2	20.752	BB	0.8078	7934.44727	150.37811	49.8115

Totals : 1.59290e4 329.97470

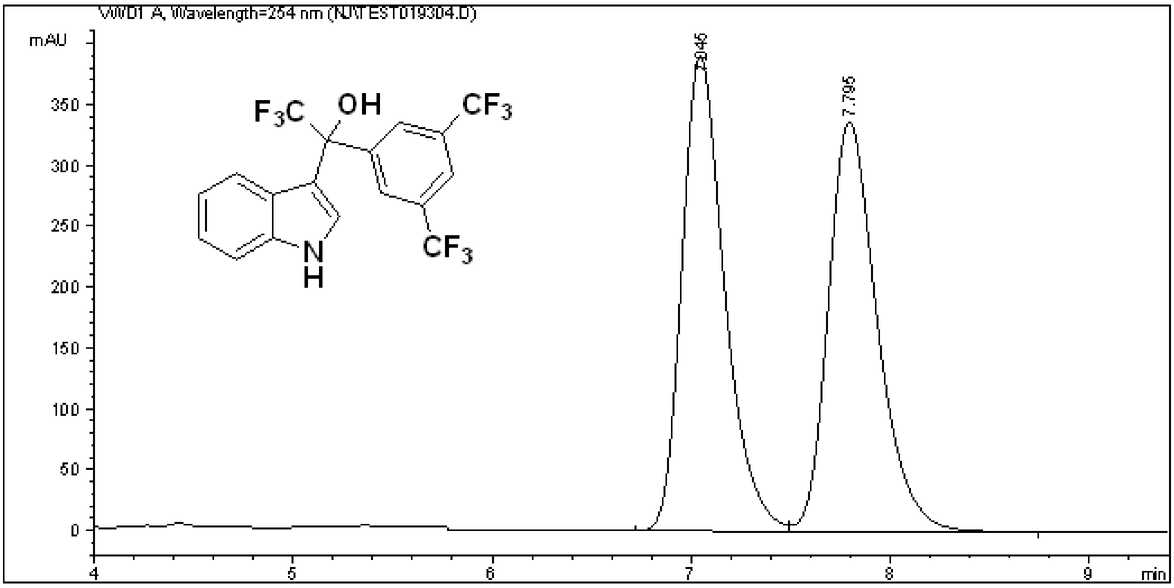


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.174	MM	0.7481	1.66279e4	370.46442	94.8972
2	20.818	PM	0.7975	894.11829	18.68536	5.1028

Totals : 1.75220e4 389.14977

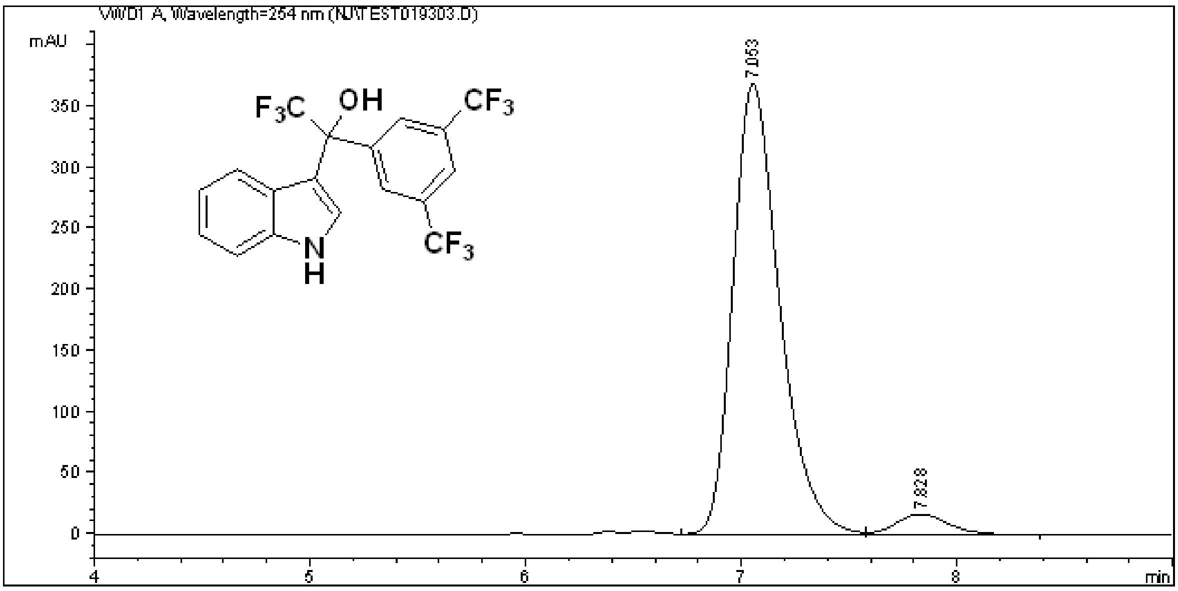
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.045	VV	0.2265	5815.16064	389.61426	50.2622
2	7.795	VV	0.2606	5754.48730	336.63477	49.7378

Totals : 1.15696e4 726.24902

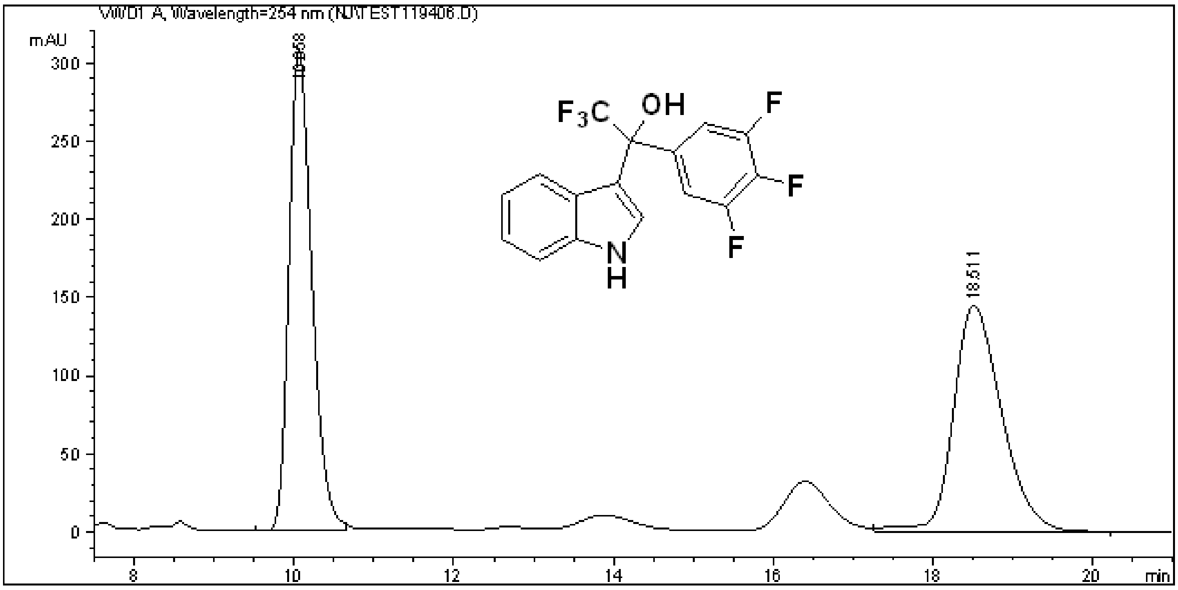


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.053	VV	0.2291	5590.82617	369.19833	94.7892
2	7.828	VV	0.2724	307.34070	17.21092	5.2108

Totals : 5898.16687 386.40925

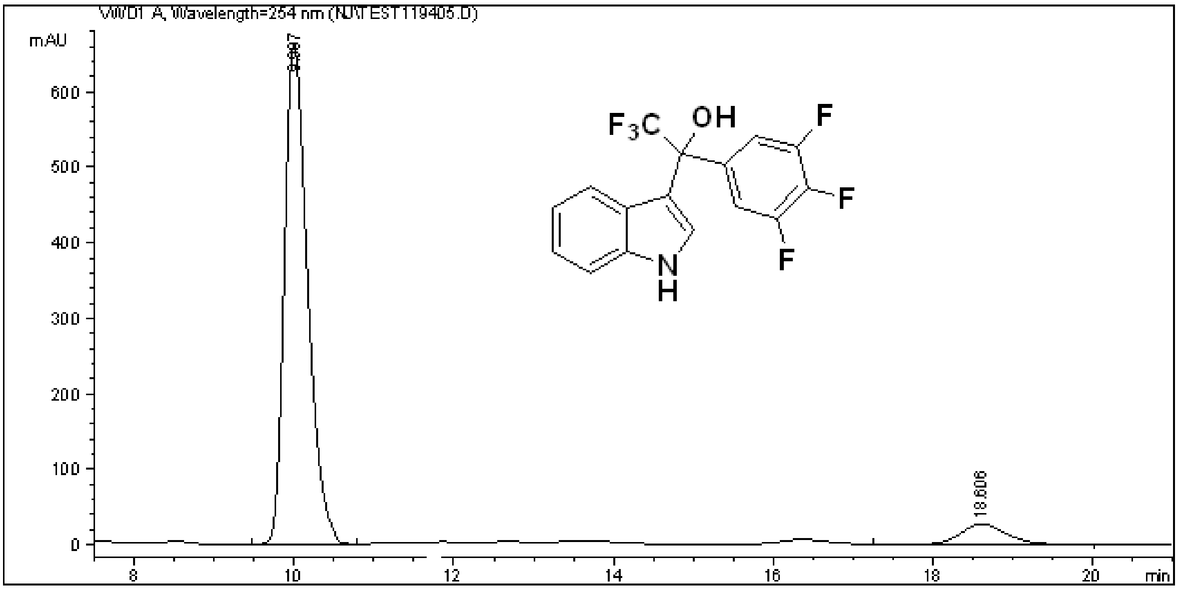
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.058	VV	0.3059	6150.31006	307.80887	50.4946
2	18.511	VB	0.6413	6029.81934	144.46465	49.5054

Totals : 1.21801e4 452.27351

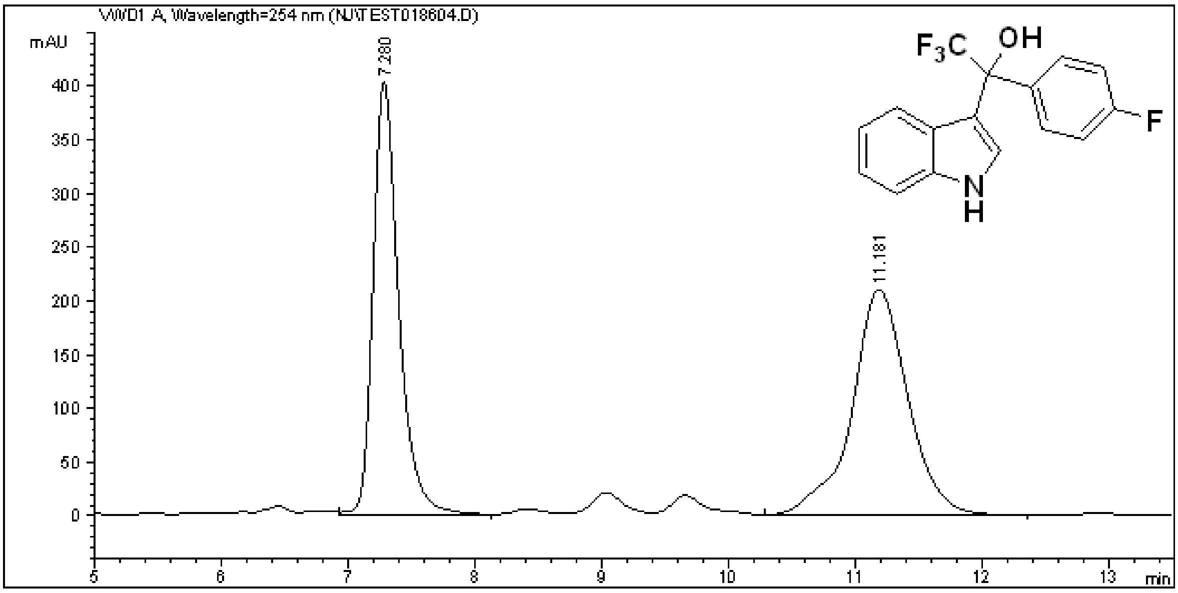


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.997	VBA	0.3081	1.33820e4	663.61560	92.4960
2	18.606	VB	0.6296	1085.64880	26.64857	7.5040

Totals : 1.44676e4 690.26417

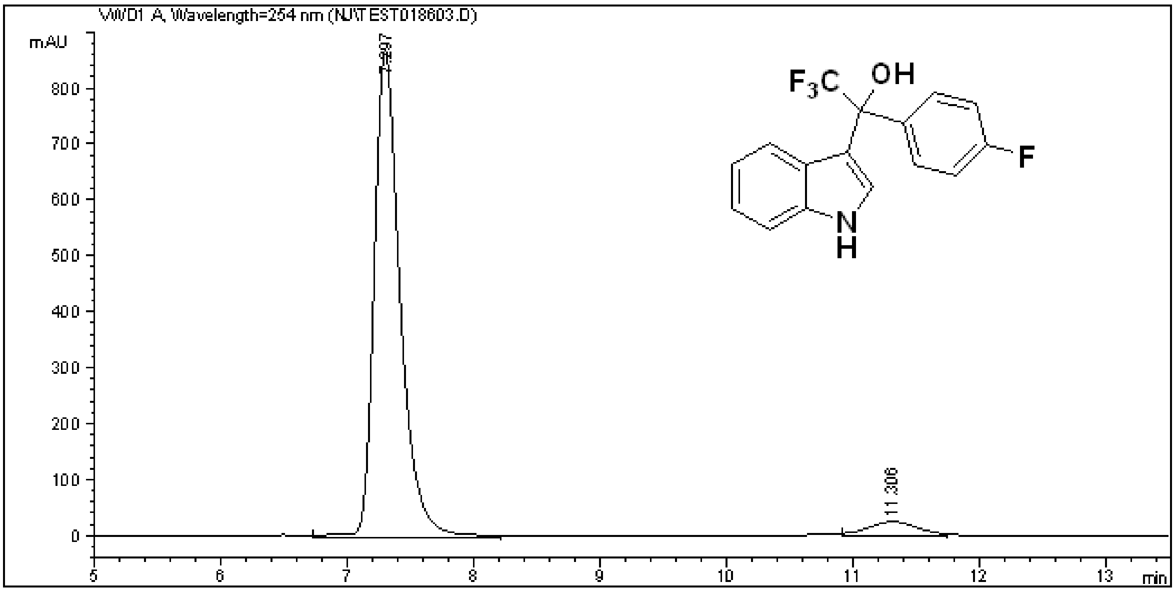
Sample Info : 254nm,OD-H,i-PrOH:Hexane=20:80,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.280	VV	0.2153	5745.09717	404.25415	46.6568
2	11.181	VB	0.4681	6568.43115	210.96999	53.3432

Totals : 1.23135e4 615.22414

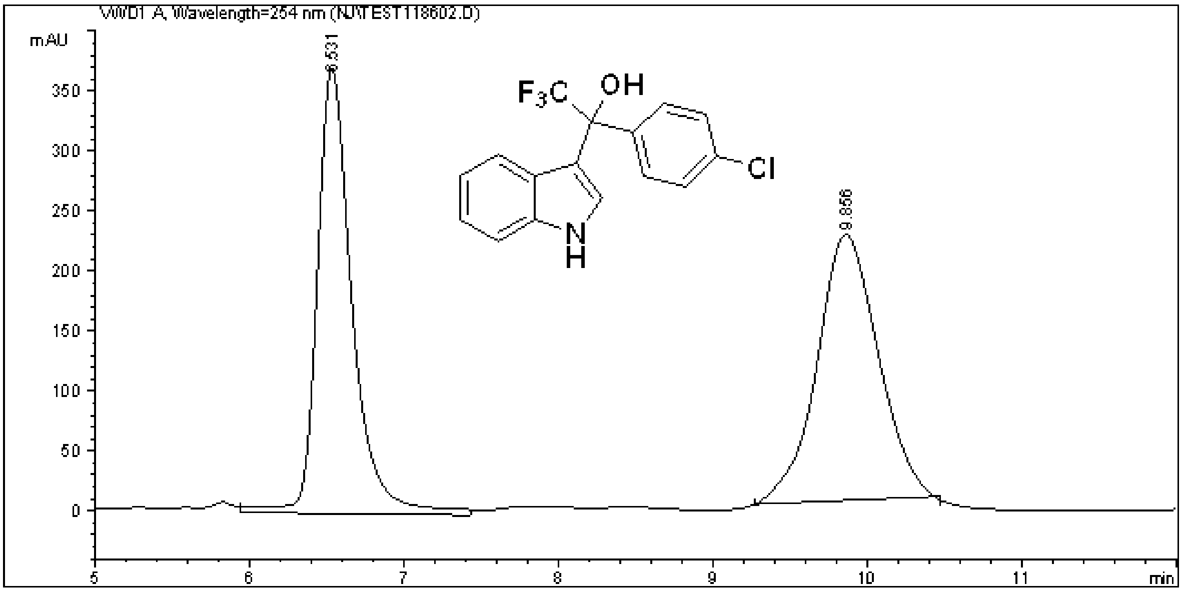


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.297	MM	0.2417	1.26761e4	874.12439	94.4796
2	11.306	MM	0.4731	740.65753	26.09104	5.5204

Totals : 1.34167e4 900.21543

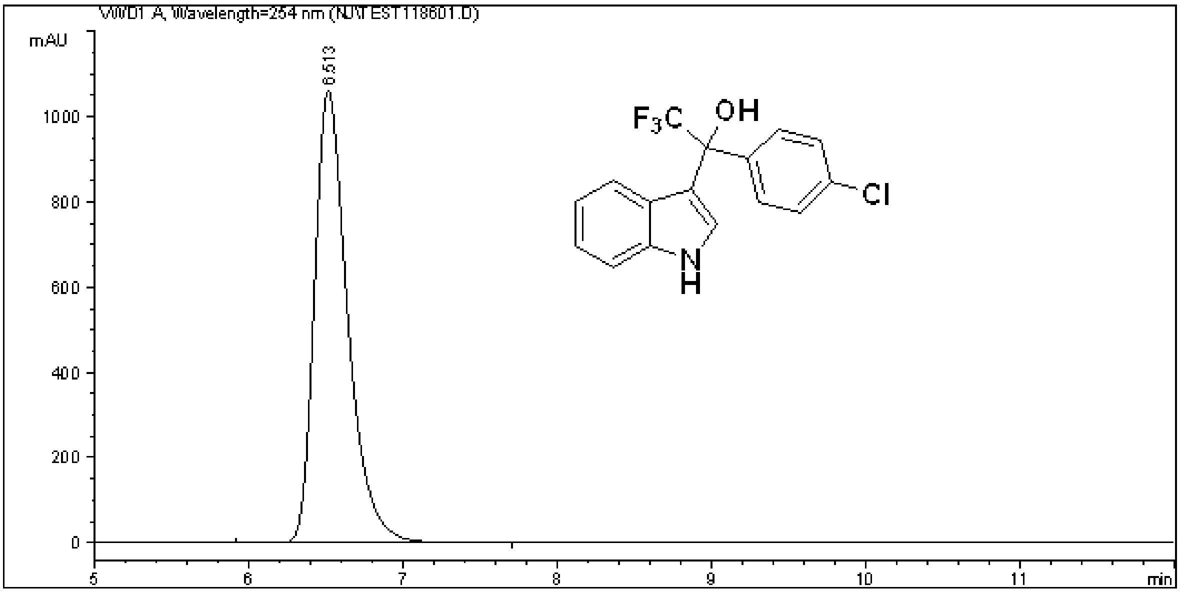
Sample Info : 254nm,OD-H,i-PrOH:Hexane=20:80,0.8mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.531	MM	0.2636	5878.44580	371.71259	49.0932
2	9.856	MM	0.4583	6095.60156	221.68637	50.9068

Totals : 1.19740e4 593.39896

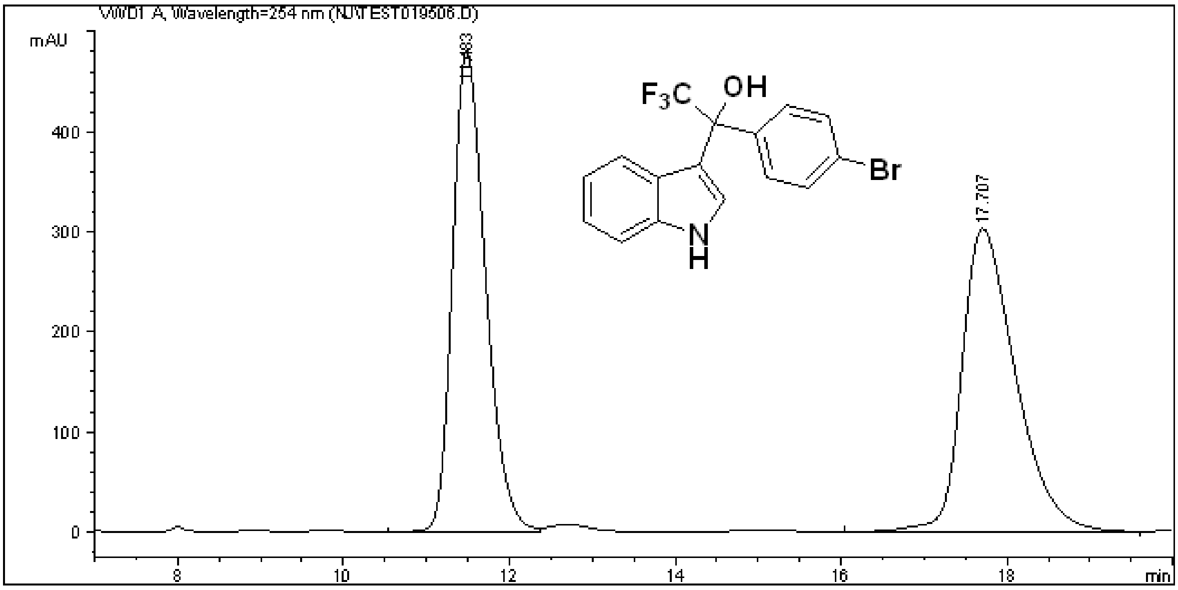


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.513	VB	0.2273	1.58972e4	1060.72620	100.0000

Totals : 1.58972e4 1060.72620

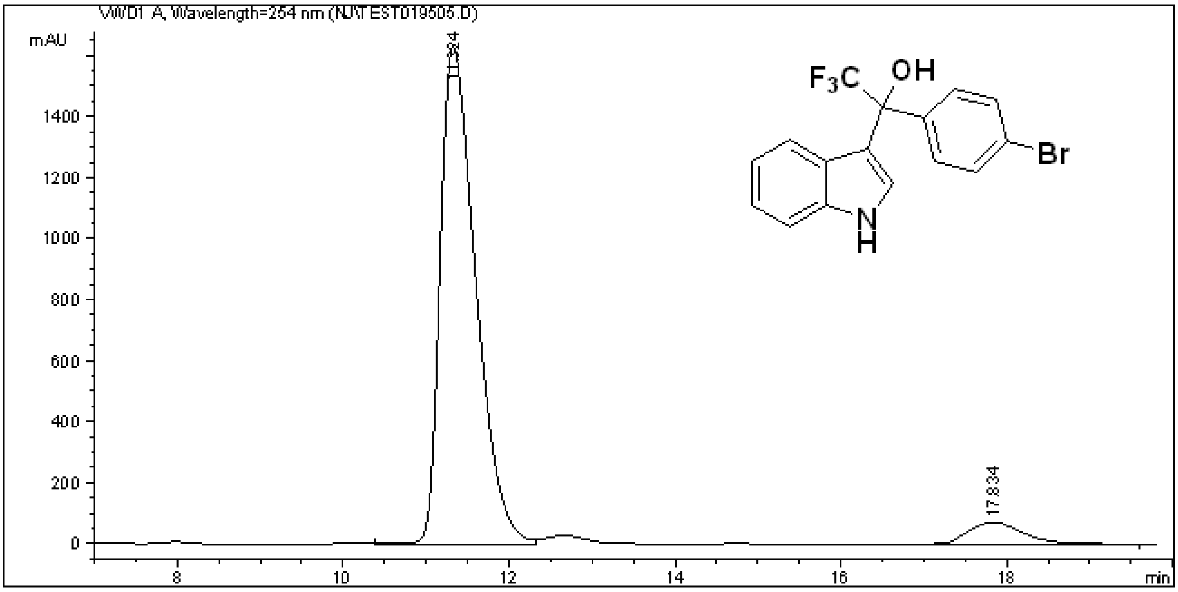
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.483	VV	0.4277	1.32993e4	480.63654	49.2703
2	17.707	VV	0.6843	1.36932e4	303.10638	50.7297

Totals : 2.69925e4 783.74292

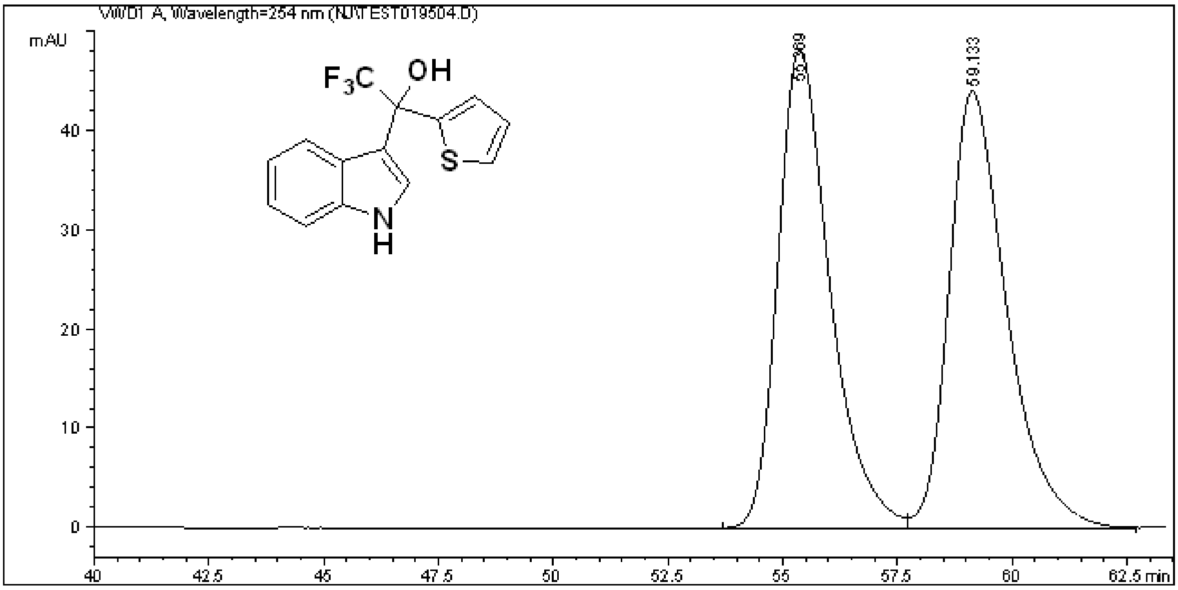


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.324	VV	0.4574	4.84758e4	1630.94202	93.5435
2	17.834	VV	0.6970	3345.83838	71.17182	6.4565

Totals : 5.18216e4 1702.11384

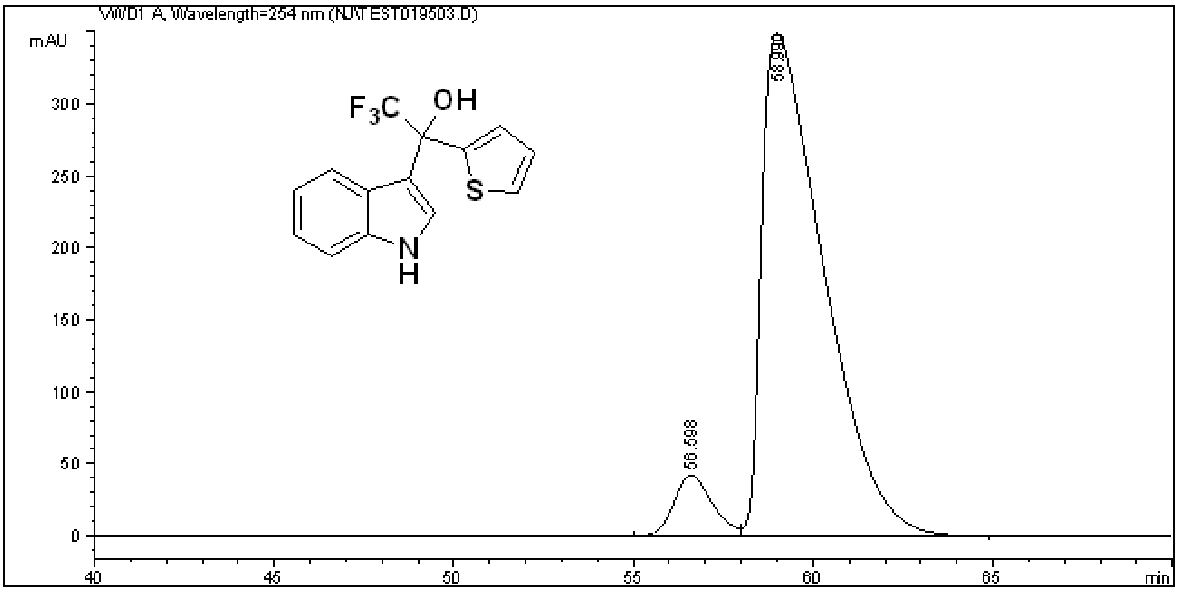
Sample Info : 254nm,AD-H,i-PrOH:Hexane=5:95,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	55.369	BV	1.2099	3819.26416	48.19700	49.7189
2	59.133	VB	1.3385	3862.45703	44.12909	50.2811

Totals : 7681.72119 92.32609

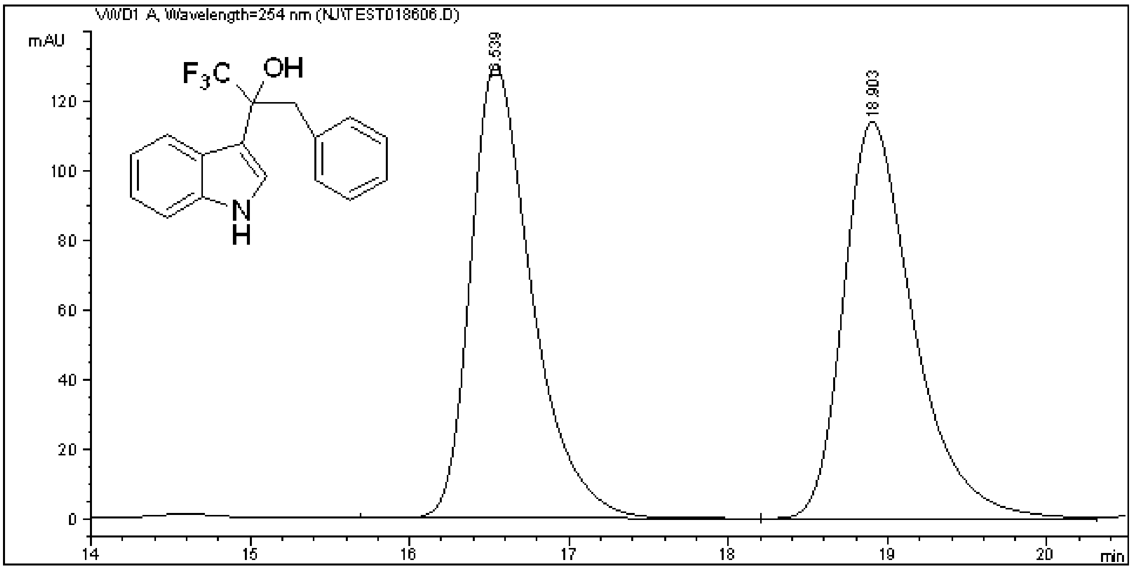


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	56.598	BV	1.1263	3099.97705	42.13010	6.9096
2	58.990	VB	1.7081	4.17651e4	348.91254	93.0904

Totals : 4.48650e4 391.04263

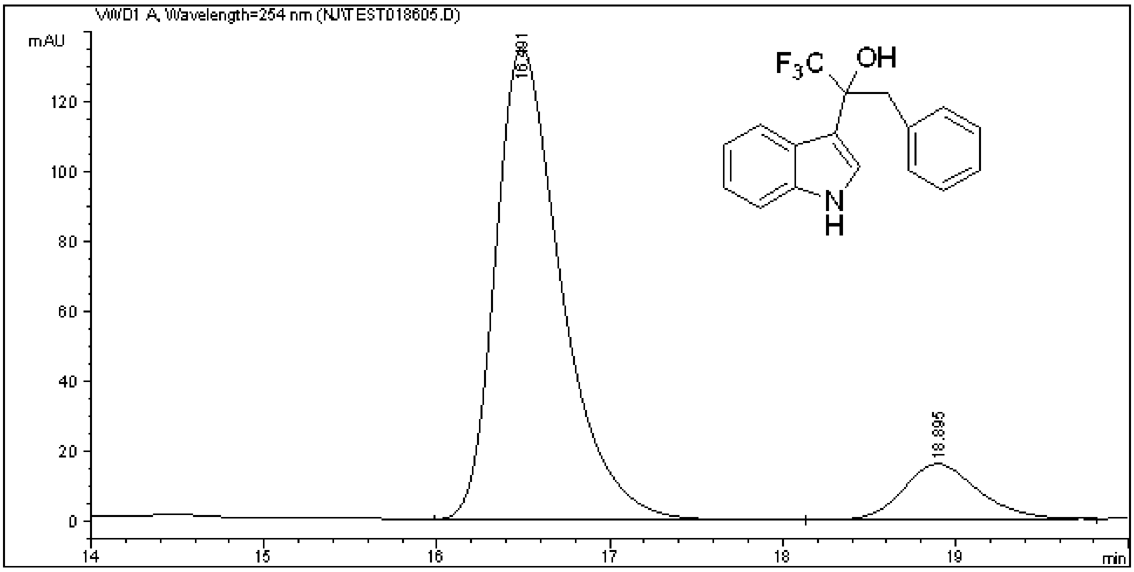
Sample Info : 254nm,AD-H,i-PrOH:Hexane=10:90,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.539	BV	0.4045	3465.19019	129.86356	49.9032
2	18.903	VV	0.4619	3478.63452	113.66528	50.0968

Totals : 6943.82471 243.52884

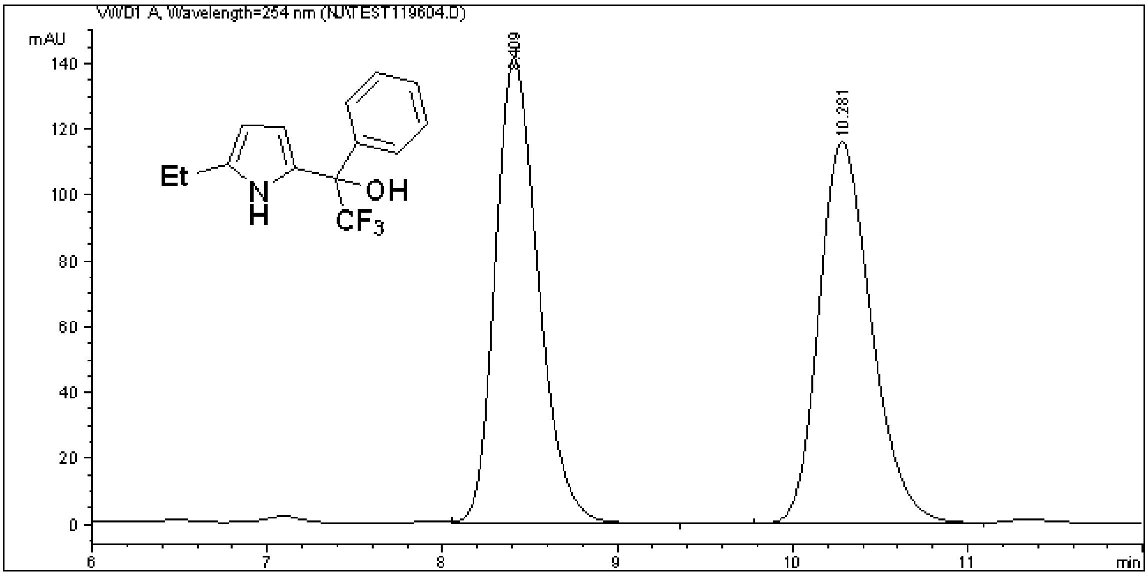


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.491	BV	0.4023	3569.87231	134.74466	88.1126
2	18.895	VV	0.4588	481.61505	15.87487	11.8874

Totals : 4051.48737 150.61953

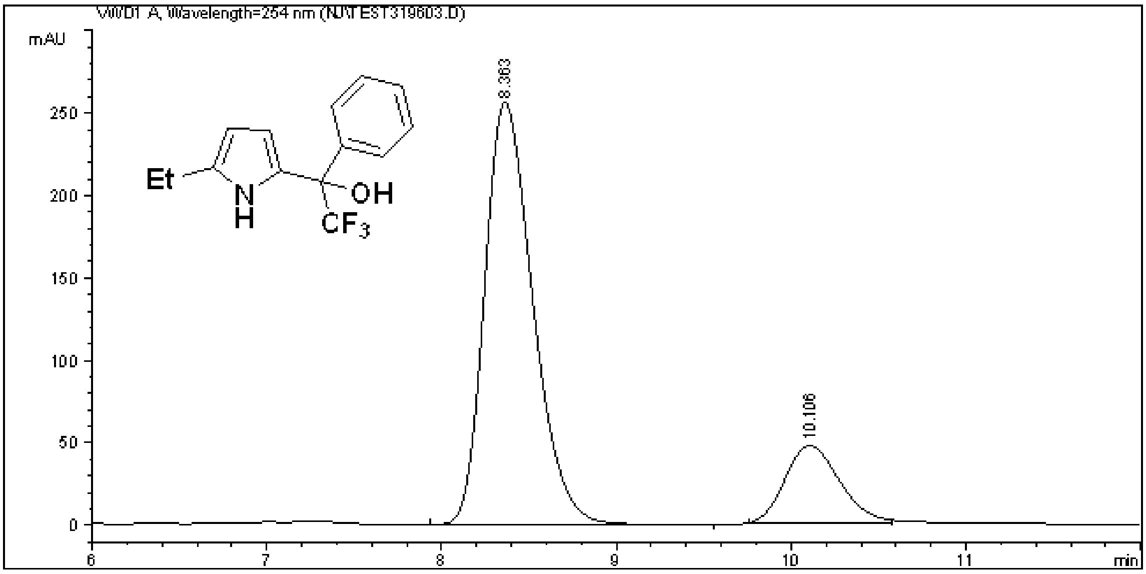
Sample Info : 254nm,OD-H,i-PrOH:Hexane=2:98,1.0mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.409	VB	0.2646	2428.48828	141.30510	50.0127
2	10.281	BV	0.3225	2427.25659	116.11211	49.9873

Totals : 4855.74487 257.41721

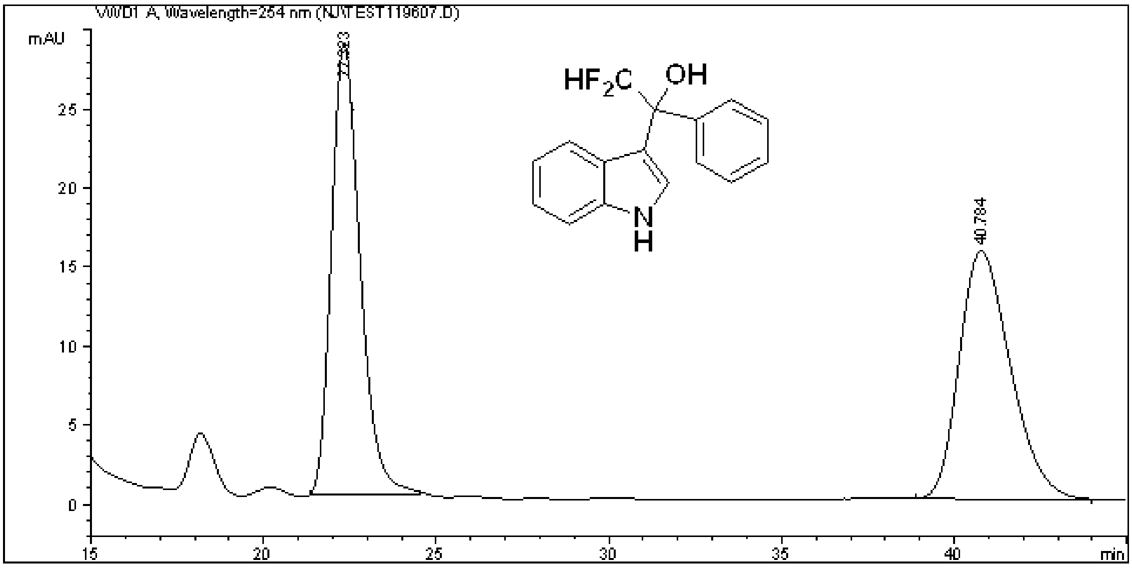


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.363	VB	0.2967	4915.94141	256.15021	82.6345
2	10.106	MM	0.3635	1033.07678	47.36842	17.3655

Totals : 5949.01819 303.51863

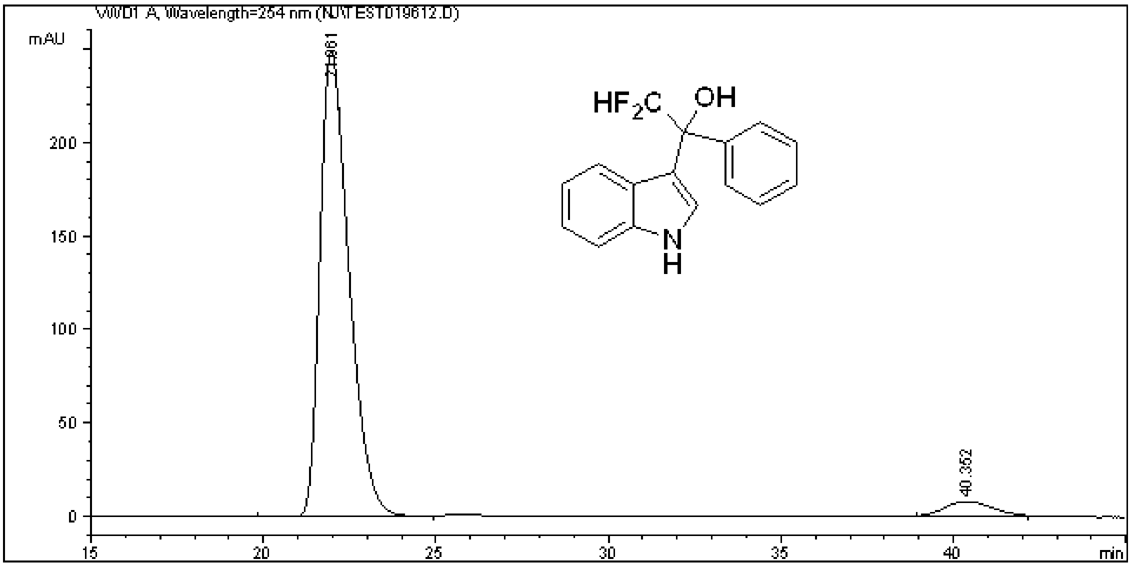
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,0.9mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.323	PM	0.9632	1647.94971	28.51564	50.3624
2	40.784	PM	1.7193	1624.23352	15.74555	49.6376

Totals : 3272.18323 44.26118

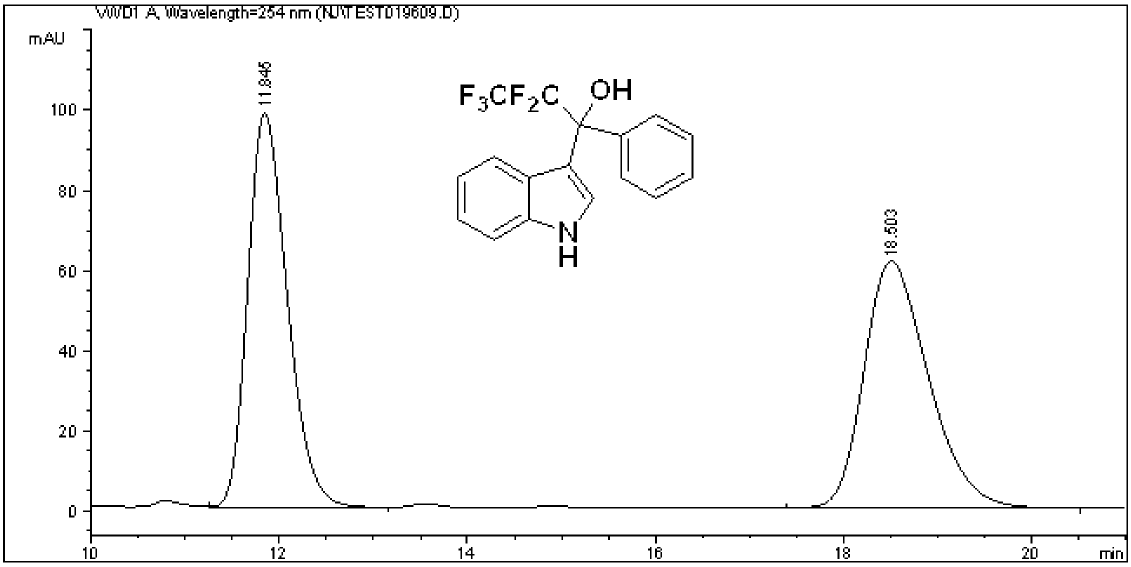


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.961	MM	0.9755	1.46063e4	249.55125	94.8738
2	40.352	MM	1.6338	789.20020	8.05054	5.1262

Totals : 1.53955e4 257.60179

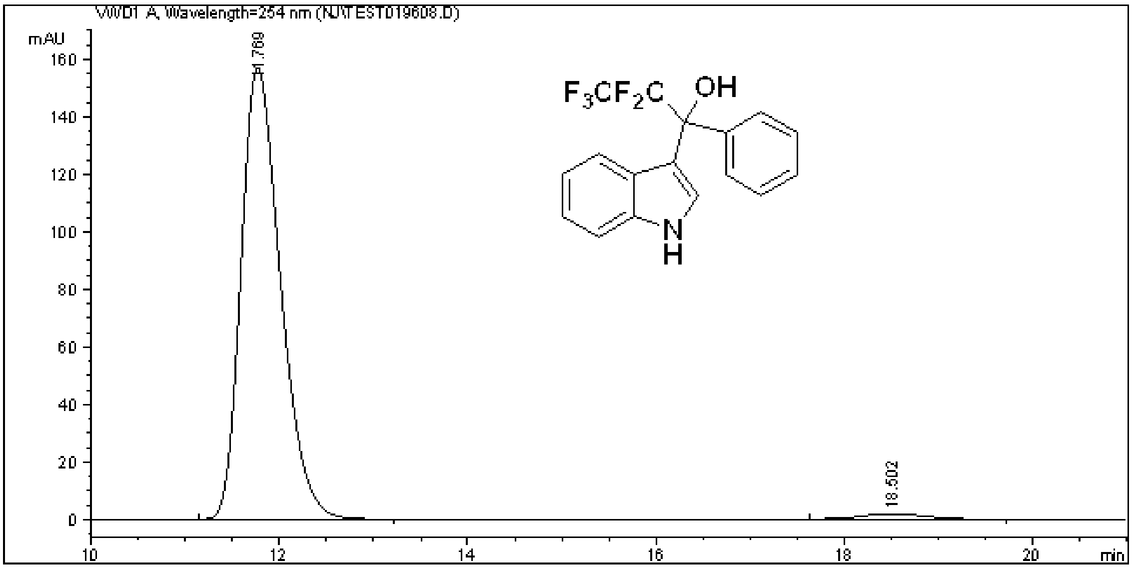
Sample Info : 254nm,OD-H,i-PrOH:Hexane=10:90,0.9mL/min



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.845	VV	0.4522	2879.89771	98.38171	49.4583
2	18.503	BB	0.7374	2942.97998	61.66174	50.5417

Totals : 5822.87769 160.04345



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.769	BB	0.4463	4559.21582	157.12010	98.0809
2	18.502	BB	0.6862	89.20952	1.93583	1.9191

Totals : 4648.42534 159.05593