Electronic Supplementary Information

Biomimetic Catalytic Enantioselective Decarboxylative Aldol Reaction of β-Ketoacids with Trifluoromethyl Ketones

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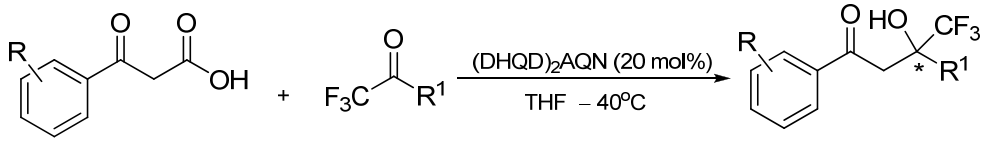
General information: ^{1}H, ^{13}C, ^{19}F NMR were recorded on Varian Mercury Plus 400 instruments at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). LRMS were recorded on a VGZAB-HS spectrometer with the ESI resource. HRMS were recorded on an IonSpec Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS mass spectrometer with ESI resource. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. HPLC analyses were carried out on a Hewlett Packard Model HP 1200instrument.

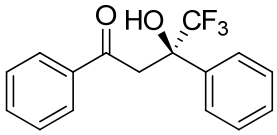
Materials: Tetrahydrofuran (THF) were distilled from sodium/benzophenone; Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200−300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. (+)-Quinidine, Quinine, (+)-Cinchonine, Cinchonidine were bought from Alfa. Aesar Company, Ltd. $(DHQD)_2AQN$, $(DHQ)_2AQN$, $(DHQD)_2PYR$, $(DHQD)_2PHAL$ were bought were bought from Aldrich. Company, Ltd. All the β-ketoacid were prepared according to literatures.[1]

General Procedure for Decarboxylative Aldol Reaction of β-ketoacids with Trifluoromethyl ketones:



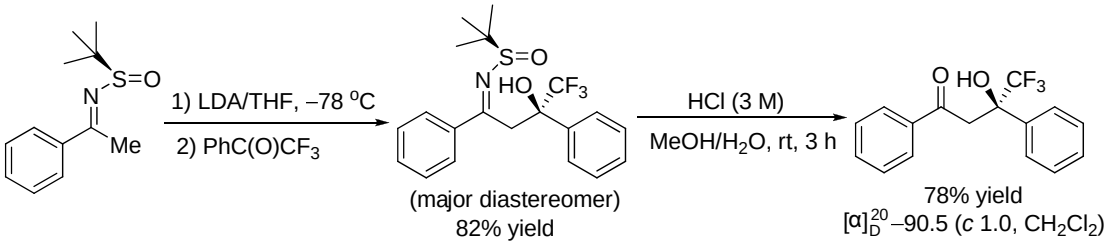
1 **2** **3**

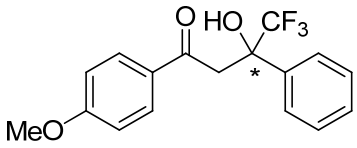
To a solution of trifluoromethyl ketone **2** (0.1 mmol) and $(DHQD)_2AQN$ (18 mg, 20 mol%) in THF (0.2 mL) at −40 °C were added β-ketoacid **1** (0.2 mmol, 2 equiv, in 0.4 ml THF) slowly using a syringe pump. After the addition (4 h), the resulting mixture was further stirred at −40 °C for 24 h. After the solvent was removed under reduced pressure, a crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate: 20/1 to 10/1) to afford the desired product **3**. The catalyst was recovered ($MeOH/CH_2Cl_2$: 1/8 as eluent) in almost quantitative yield.



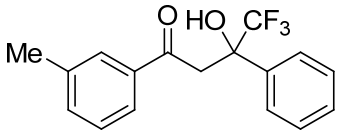
4,4,4-Trifluoro-3-hydroxy-1,3-diphenylbutan-1-one (3a):[2] white solid, mp 42–43 °C, 28 mg, 96% yield; 90% *ee*, [determined by **HPLC** analysis Daicel Chirapak AD, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 10.413 min (major) and t_R = 11.797 min (minor)]; $[\alpha]^{20}_D$ –85.9 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.97 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.1 Hz, 3H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.14 (m, 3H), 5.74 (s, 1H), 4.08 (d, *J* = 17.4 Hz, 1H), 3.69 (d, *J* = 17.4 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.95 (s, 3F).

The absolute configuration of **3a** was determined to be R by comparison with the sign of optical rotation of the deprotected compound reported in the literature:[3]

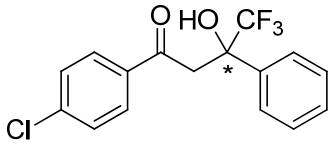




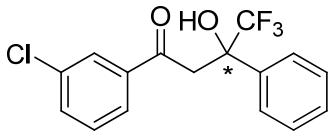
4,4,4-Trifluoro-3-hydroxy-1-(4-methoxyphenyl)-3-phenylbutan-1-one (3b):[2] white solid, mp 90–91 °C, 32 mg, 97% yield; 82% *ee*, [determined by **HPLC** analysis Daicel Chirapak AD, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 17.228 min (major) and t_R = 24.777 min (minor)]; $[\alpha]^{20}_D$ −130.9 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.95 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.34 – 7.40 (m, 3H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.94 (s, 1H), 3.99 (d, *J* = 17.1 Hz, 1H), 3.91 (s, 3H), 3.59 (d, *J* = 17.1 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −80.20 (s, 3F).



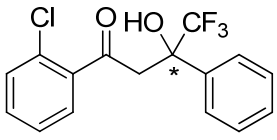
4,4,4-Trifluoro-3-hydroxy-3-phenyl-1-m-tolylbutan-1-one (3c): colorless oil, 29 mg, 93% yield; 80% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 6,790 min (major) and t_R = 7.860 min (minor)]; $[\alpha]^{20}_D$ −106.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.79 (d, *J* = 5.6 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.40 (dd, *J* = 16.6, 8.7 Hz, 4H), 5.85 (s, 1H), 4.09 (d, *J* = 17.4 Hz, 1H), 3.69 (d, *J* = 17.4 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 199.98, 138.93, 137.82, 136.38, 135.29, 128.84, 128.75, 128.70, 128.46, 126.37, 125.54, 124.74 (q, *J* = 283.0 Hz), 76.59 (q, *J* = 28.7 Hz), 40.23, 21.28; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −80.08 (s, 3F); **IR** (neat) ν: 3481, 3037, 1669, 1245, 1163, 699 cm^{-1}; **MS** (ESI) found: m/z 308.1 $[M]^+$; **HRMS** (ESI) found: m/z 308.1027 $[M]^+$; calcd. for $C_{17}H_{15}F_3O_2$ 308.1024.



1-(4-Chlorophenyl)-4,4,4-trifluoro-3-hydroxy-3-phenylbutan-1-one (3d):[2] white solid, mp 75–76 °C, 29 mg, 94% yield; 76% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 10.571 min (major) and t_R = 11.514 min (minor)]; $[\alpha]^{20}_D$ –83.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.89 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.42 – 7.35 (m, 3H), 5.63 (s, 1H), 4.04 (d, *J* = 17.3 Hz, 1H), 3.66 (d, *J* = 17.3 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.06 (s, 3F).

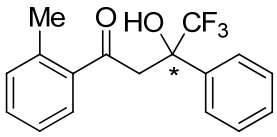


1-(3-Chlorophenyl)-4,4,4-trifluoro-3-hydroxy-3-phenylbutan-1-one (3e): colorless oil, 28 mg, 86% yield; 80% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 8.414 min (major) and t_R = 10.704 min (minor)]; $[\alpha]^{20}_D$ –73.4 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.91 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 6.3 Hz, 3H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.43 – 7.36 (m, 3H), 5.49 (s, 1H), 4.04 (d, *J* = 17.4 Hz, 1H), 3.67 (d, *J* = 17.4 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 198.34, 137.76, 137.44, 135.40, 134.34, 130.29, 128.87, 128.53, 128.25, 126.32, 126.25, 124.55 (q, *J* = 283.0 Hz), 76.49 (q, *J* = 29.0 Hz), 40.62; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.13 (s, 3F); **IR** (neat) ν: 3482, 3069, 1679, 1215, 1168, 700, 675 cm^{-1}; **MS** (ESI) found: m/z 328.1 $[M]^+$; **HRMS** (ESI) found: m/z 328.0475 $[M]^+$; calcd. for $C_{16}H_{12}ClF_3O_2$ 328.0478.

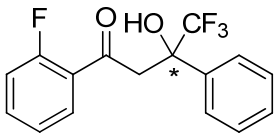


1-(2-Chlorophenyl)-4,4,4-trifluoro-3-hydroxy-3-phenylbutan-1-one (3f): colorless oil, 21 mg, 63% yield; 72% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 90/10, 254 nm UV detector, 1.0 mL/min, t_R = 6.211 min (major) and t_R = 7.611 min (minor)]; $[\alpha]^{20}_D$ –33.0 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$)

δ(ppm): 7.61 (t, *J* = 4.4 2H), 7.45 (d, *J* = 3.9 Hz, 2H), 7.38 (dd, *J* = 5.1, 1.7 Hz, 3H), 7.33 – 7.27 (m, 2H), 5.43 (s, 1H), 4.02 (d, *J* = 17.2 Hz, 1H), 3.77 (d, *J* = 17.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 202.84, 138.35, 137.23, 132.95, 131.22, 130.78, 129.40, 128.85, 128.42, 127.19, 126.43, 124.52 (q, *J* = 283.0 Hz), 76.68 (q, *J* = 28.9 Hz), 45.32; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.06 (s, 3F); **IR** (neat) ν: 3631, 3066, 1682, 1167, 761 cm^{-1}; **MS** (ESI) found: m/z 328.1 $[M]^+$; **HRMS** (ESI) found: m/z 328.0482 $[M]^+$; calcd. for $C_{16}H_{12}ClF_3O_2$ 328.0484.

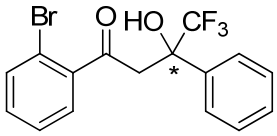


4,4,4-Trifluoro-3-hydroxy-3-phenyl-1-o-tolylbutan-1-one (3g): colorless oil, 25 mg, 80% yield; 74% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 6.400 min (major) and t_R = 8.271 min (minor)]; $[\alpha]^{20}_D$ –57.7 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.70 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.40 (q, *J* = 5.0 Hz, 3H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 5.87 (s, 1H), 3.97 (d, *J* = 16.9 Hz, 1H), 3.66 (d, *J* = 16.9 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 203.85, 138.84, 137.74, 137.22, 132.56, 132.30, 128.76, 128.59, 128.44, 126.43, 126.01, 124.66 (q, *J* = 283.2 Hz), 76.77 (q, *J* = 28.8 Hz), 42.98, 20.93; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm): –80.13 (s, 3F); **IR** (neat) ν: 3449, 3030, 1672, 1169, 1019, 701, 624 cm^{-1}; **MS** (ESI) found: m/z 308.1 $[M]^+$; **HRMS** (ESI) found: m/z 308.1029 $[M]^+$; calcd. for $C_{17}H_{15}F_3O_2$ 308.1024.

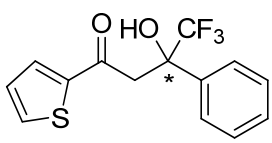


4,4,4-Trifluoro-1-(2-fluorophenyl)-3-hydroxy-3-phenylbutan-1-one (3h): colorless oil, 23 mg, 72% yield; 75% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 7.792 min (major) and

t_R = 9.110 min (minor)]; $[\alpha]^{20}_D$ –82.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.74 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.43 – 7.34 (m, 3H), 7.27 – 7.17 (m, 2H), 5.42 (s, 1H), 4.12 (d, *J* = 18.1 Hz, 1H), 3.76 (d, *J* = 18.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 197.98, 162.09 (d, *J* = 253.9 Hz), 137.69, 135.99 (d, *J* = 9.3 Hz), 130.54 (d, *J* = 2.0 Hz), 128.73, 128.43, 126.38, 125.12 (d, *J* = 11.7 Hz), 124.82 (d, *J* = 3.4 Hz), 124.54 (q, *J* = 282.8 Hz), 116.95 (d, *J* = 23.4 Hz), 76.54 (q, *J* = 28.8 Hz), 45.49; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.29 (s, 3F), –108.72 (s, 1F); **IR** (neat) ν: 3632, 3133, 2923, 1673, 1402, 1169, 617 cm^{-1}; **MS** (ESI) found: m/z 312.1 $[M]^+$; **HRMS** (ESI) found: m/z 312.0771 $[M]^+$; calcd. for $C_{16}H_{12}F_4O_2$ 312.0773.

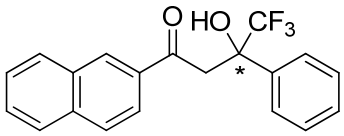


1-(2-Bromophenyl)-4,4,4-trifluoro-3-hydroxy-3-phenylbutan-1-one (3i): colorless oil, 22 mg, 60% yield; 85% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 8.199 min (major) and t_R = 10.539 min (minor)]; $[\alpha]^{20}_D$ –25.4 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.64 (dd, *J* = 5.8, 3.2 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.41 – 7.32 (m, 5H), 7.20 (dd, *J* = 5.7, 3.5 Hz, 1H), 5.38 (s, 1H), 3.98 (d, *J* = 17.1 Hz, 1H), 3.76 (d, *J* = 17.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 203.56, 140.54, 137.12, 133.99, 132.72, 129.06, 128.88, 128.44, 127.63, 126.43, 124.46 (q, *J* = 283.5 Hz), 118.85, 76.62 (q, *J* = 28.7 Hz), 45.12; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.09 (s, 3F); **IR** (neat) ν: 3480, 3166, 1670, 1595,1243, 1170, 755 cm^{-1}; **MS** (ESI) found: m/z 373.0 $[M+H]^+$; **HRMS** (ESI) found: m/z 371.9972 $[M]^+$; calcd. for $C_{16}H_{12}BrF_3O_2$ 371.9973.

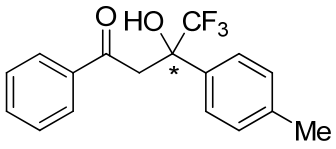


4,4,4-Trifluoro-3-hydroxy-3-phenyl-1-(thiophen-3-yl)butan-1-one (3j): white solid,

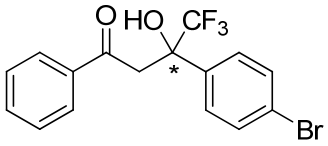
mp 50– 52 °C, 26 mg, 85% yield; 65% *ee*, [determined by **HPLC** analysis Daicel Chirapak AD, hexane/*i*-PrOH = 97/3, 254 nm UV detector, 1.0 mL/min, t_R = 17.107 min (major) and t_R = 18.685 min (minor)]; $[\alpha]^{20}_D$ –95.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 8.18 (s, 1H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 5.6 Hz, 1H), 7.42 – 7.34 (m, 4H), 5.81 (s, 1H), 3.91 (d, *J* = 17.0 Hz, 1H), 3.63 (d, *J* = 17.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 193.50, 141.63, 137.66, 133.99, 128.80, 128.48, 127.22, 126.62, 126.31, 124.65 (q, *J* = 283.0 Hz), 76.49 (q, *J* = 28.8 Hz), 41.49; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.04 (s, 3F); **IR** (KBr) ν: 3462, 3110, 2924, 1651, 1510, 1418, 1235, 1176, 800, 695 cm^{-1}; **MS** (ESI) found: m/z 300.0 $[M]^+$; **HRMS** (ESI) found: m/z 300.0431 $[M]^+$; calcd. for $C_{14}H_{11}F_3O_2S$ 300.0432.



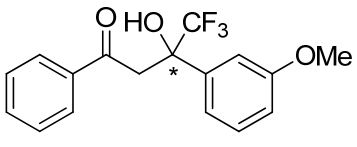
4,4,4-Trifluoro-3-hydroxy-1-(naphthalen-2-yl)-3-phenylbutan-1-one (3k): white solid, mp 100– 102 °C, 34 mg, 98% yield; 65% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 9.564 min (major) and t_R = 14.266 min (minor)]; $[\alpha]^{20}_D$ –138.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 8.52 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.98 – 7.91 (m, 3H), 7.70 – 7.61 (m, 4H), 7.41 – 7.35 (m, 3H), 5.78 (s, 1H), 4.22 (d, *J* = 17.2 Hz, 1H), 3.79 (d, *J* = 17.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 199.60, 137.81, 136.15, 133.67, 132.36, 130.56, 129.83, 129.36, 128.94, 128.80, 128.51, 127.90, 127.27, 126.41, 124.77 (q, *J* = 283.1 Hz), 123.29, 76.69 (q, *J* = 28.5 Hz), 40.25; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.15 (s, 3F); **IR** (KBr) ν:3455, 3056, 2921, 1676, 1235, 1171, 1155, 939, 699 cm^{-1}; **HRMS** (ESI) found: m/z 344.1027 $[M]^+$; calcd. for $C_{20}H_{15}F_3O_2$ 344.1024.



4,4,4-Trifluoro-3-hydroxy-1-phenyl-3-p-tolylbutan-1-one (3l):[2] colorless oil, 30 mg, 97% yield; 64% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 8.563 min (major) and t_R = 9.744 min (minor)]; $[\alpha]^{20}_D$ –69.7 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.97 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (dd, *J* = 7.8, 4.0 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.66 (s, 1H), 4.07 (d, *J* = 17.4 Hz, 1H), 3.65 (d, *J* = 17.4 Hz, 1H), 2.35 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.37 (s, 3F)

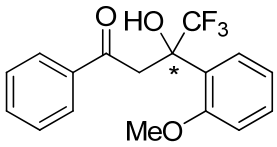


3-(4-Bromo-phenyl)-4,4,4-trifluoro-3-hydroxy-1-phenyl-butan-1-one (3m): white solid, mp 96– 98 °C, 36mg, 95% yield; 78% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 90/10, 254 nm UV detector, 1.0 mL/min, t_R = 8.630 min (major) and t_R = 9.968 min (minor)]; $[\alpha]^{20}_D$ –52.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.96 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 6H), 5.78 (s, 1H), 4.03 (d, *J* = 17.4 Hz, 1H), 3.67 (d, *J* = 17.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 199.54, 136.91, 136.11, 134.68, 131.67, 129.03, 128.27, 128.19, 125.78 (q, *J* = 282.9 Hz), 123.23, 76.51 (q, *J* = 28.9 Hz) 40.01; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –80.21 (s, 3F); **IR** (KBr) ν: 3468, 2927, 1667, 1244, 1166, 759, 618 cm^{-1}; **MS** (ESI) found: m/z 372.0 $[M]^+$; **HRMS** (ESI) found: m/z 371.9971 $[M]^+$; calcd. for $C_{16}H_{12}BrF_3O_2$ 371.9973.

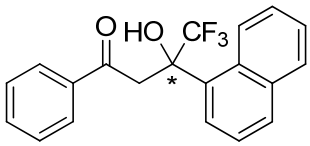


4,4,4-Trifluoro-3-hydroxy-3-(3-methoxyphenyl)-1-phenylbutan-1-one (3n): colorless oil, 30 mg, 92% yield; 72% *ee*, [determined by **HPLC** analysis Daicel Chirapak IB, hexane/*i*-PrOH = 90/10, 254 nm UV detector, 1.0 mL/min, t_R = 7.232 min (major) and t_R = 9.959 min (minor)]; $[\alpha]^{20}_D$ –84.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400

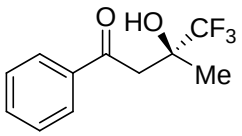
MHz, $CDCl_3$) δ(ppm): 7.96 (d, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.89 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.77 (s, 1H), 4.07 (d, *J* = 17.3 Hz, 1H), 3.80 (s, 3H), 3.65 (d, *J* = 17.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 199.75, 159.71, 139.36, 136.29, 134.47, 129.43, 128.95, 128.25, 124.61 (q, *J* = 282.9 Hz), 118.48, 114.04, 112.72, 76.52 (q, *J* = 28.7 Hz), 55.22, 40.25; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −80.07 (s, 3F); **IR** (neat) ν: 3479, 2925, 1669, 1245, 1164, 1018, 769, 699 cm^{-1}; **MS** (ESI) found: m/z 324.1 $[M]^+$; **HRMS** (ESI) found: m/z 324.0972 $[M]^+$; calcd. for $C_{17}H_{15}F_3O_3$ 324.0973.



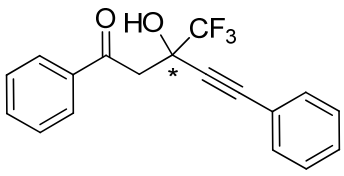
4,4,4-Trifluoro-3-hydroxy-3-(2-methoxyphenyl)-1-phenylbutan-1-one (3o): white solid, mp 87–89 °C, 19 mg, 60% yield; 60% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 9.752 min (major) and t_R = 10.930 min (minor)]; $[\alpha]^{20}_D$ −70.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.99 (d, *J* = 7.3 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 8.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 5.50 (s, 1H), 4.77 (d, *J* = 17.1 Hz, 1H), 3.59 (s, 3H), 3.48 (d, *J* = 17.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 199.20, 156.65, 136.61, 133.81, 130.40, 130.35, 128.72, 128.17, 124.87 (q, *J* = 283.6 Hz), 124.76, 121.06, 111.63, 76.45 (q, *J* = 29.5 Hz), 55.33, 41.27; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −80.62 (s, 3F); **IR** (KBr) ν: 3485, 3014, 2972, 1669, 1235, 1170, 758, 619 cm^{-1}; **MS** (ESI) found: m/z 324.1 $[M]^+$; **HRMS** (ESI) found: m/z 324.0978 $[M]^+$; calcd. for $C_{17}H_{15}F_3O_3$ 324.0973.



4,4,4-Trifluoro-3-hydroxy-3-naphthalen-1-yl-1-phenyl-butan-1-one (3p): white solid, mp 80–82 °C, 21 mg, 60% yield; 62% *ee*, [determined by **HPLC** analysis Daicel Chirapak AD, hexane/*i*-PrOH = 90/10, 254 nm UV detector, 1.0 mL/min, t_R = 7.660 min (major) and t_R = 8.216 min (minor)]; $[\alpha]^{20}_D$ −114.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 9.19 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.87 (t, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.62 – 7.39 (m, 5H), 7.33 (t, *J* = 7.8 Hz, 1H), 6.08 (s, 1H), 4.53 (d, *J* = 17.6 Hz, 1H), 3.77 (d, *J* = 17.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 199.97, 136.45, 135.08, 134.47, 132.76, 132.33, 130.78, 129.02, 128.96, 128.23, 127.65, 126.11, 126.05, 125.72, 125.32 (q, *J* = 284.2 Hz), 124.17, 77.24 (q, *J* = 28.9 Hz), 41.75; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −77.87 (s, 3F); **IR** (KBr) ν: 3408, 3052, 2923, 1665, 1176, 1064, 776, 680 cm^{-1}; **MS** (ESI) found: m/z 344.1 $[M]^+$; **HRMS** (ESI) found: m/z 344.1026 $[M]^+$; calcd. for $C_{20}H_{15}F_3O_2$ 344.1024.

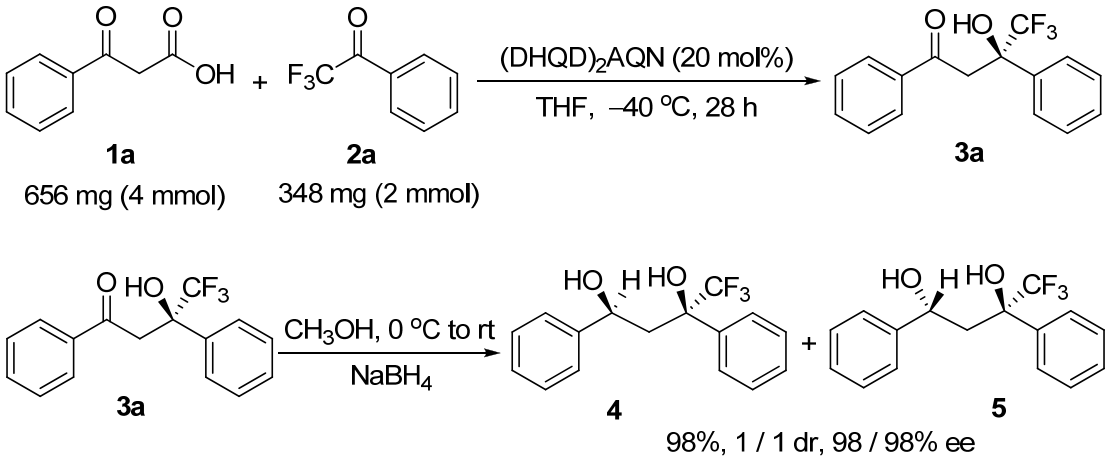


(S)-4,4,4-Trifluoro-3-hydroxy-3-methyl-1-phenyl-butan-1-one (3q):[3] white solid, mp 45–46 °C 22 mg, 94% yield; 64% *ee*, [determined by **HPLC** analysis Daicel Chirapak IC, hexane/*i*-PrOH = 98/2, 254 nm UV detector, 0.6 mL/min, t_R = 12.247 min (major) and t_R = 12.638 min (minor)]; $[\alpha]^{20}_D$ −6.8 (*c* 0.64, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.97 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 5.31 (s, 1H), 3.53 (d, *J* = 17.0 Hz, 1H), 3.12 (d, *J* = 17.0 Hz, 1H), 1.53 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −80.08 (s, 3F); **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −82.68 (s, 3F).



3-Hydroxy-1,5-diphenyl-3-trifluoromethyl-pent-4-yn-1-one (3r): yellow solid, mp 52–54 °C, 31 mg, 98% yield; 61% *ee*, [determined by **HPLC** analysis Daicel Chirapak IC, hexane/*i*-PrOH = 85/15, 254 nm UV detector, 0.8 mL/min, t_R = 5.964 min (major) and t_R = 5.511 min (minor)]; $[\alpha]^{20}_D$ +38.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 8.03 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.27 (m, 2H), 5.47 (s, 1H), 3.83 (d, *J* = 16.7 Hz, 1H), 3.46 (d, *J* = 16.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 198.53, 136.24, 134.50, 132.00, 129.25, 128.98, 128.46, 128.28, 123.32 (q, *J* = 282.2 Hz), 121.08, 86.82, 83.36, 70.58 (q, *J* = 32.3 Hz), 41.67; **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –81.48 (s, 3F); **IR** (KBr) ν: 3484, 3062, 2923, 1676, 1170, 1124, 817, 757 cm^{-1}; **MS** (ESI) found: m/z 319.1 $[M+H]^+$; **HRMS** (ESI) found: m/z 318.0869 $[M]^+$; calcd. for $C_{18}H_{13}F_3O_2$ 318.00868.

A large-scale Aldol reactino and further transformation



To a solution of 2,2,2-Trifluoromethyl-1-phenylethanone **2a** (348 mg, 2 mmol) and $(DHQD)_2AQN$ (360 mg, 20 mol%) in THF (4 mL) at −40 °C were added β-ketoacid **1a** (656 mg, 4 mmol, 2 equiv, in 6 ml THF) slowly using a syringe pump. After the addition (4 h), the resulting mixture was further stirred at −40 °C for 24 h. After the solvent was removed under reduced pressure, a crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate: 20/1 to 10/1) to afford the desired product **3a**. The catalyst was recovered ($MeOH/CH_2Cl_2$: 1/8 as

eluent) (359 mg) in almost quantitative yield. Recrystallization of the product **3a** from CH_2Cl_2/hexane furnished acicular crystal (241 mg), mp 46–46.5 ^oC, 82% yield, 98% ee, $[\alpha]^{20}_D$ –90.1 (*c* 1.0, CH_2Cl_2).

To a solution of **3a** (58.8 mg, 0.2 mmol) in 2 mL of MeOH was added $NaBH_4$ (76 mg, 2.0 mmol) in portions at 0 ^oC. The resultant mixture was stirred over night at room temperature (monitored by TLC). The mixture was evaporated in vacuum, added water (10 mL), and extracted with dichloromethane (10 mL × 3), washed with brine and dried over $MgSO_4$. Concentration and flash chromatography (ethyl acetate/hexane: 1/40 as eluant) afforded 4,4,4-trifluoro-1,3-diphenyl-butane-1,3-diols (**4** and **5**). One diastereomer: colorless oil, 29.1 mg, 49% yield; 98% *ee*, [determined by **HPLC** analysis Daicel Chirapak IA, hexane/*i*-PrOH = 90/10, 220 nm UV detector, 0.8 mL/min, t_R = 8.699 min (major) and t_R = 11.698 min (minor)]; $[\alpha]^{20}_D$ –58.0 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.63 (d, *J* = 7.1 Hz, 2H), 7.50 – 7.26 (m, 8H), 6.06 (s, 1H), 5.38 (d, *J* = 11.2 Hz, 1H), 3.02 (s, 1H), 2.59 (d, *J* = 15.4 Hz, 1H), 2.36 – 2.20 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ(ppm): 143.33, 139.36, 128.87, 128.41, 128.34, 128.31, 126.09 (q, *J* = 285.5 Hz), 125.67, 125.61, 77.02 (q, *J* = 27.8 Hz), 72.75, 44.71; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm): –75.60 (s, 3F); **IR** (neat) ν: 3421, 3272, 3030, 2897, 1456, 1164, 701, 606 cm^{-1}; **MS** (ESI) found: m/z 296.1 $[M]^+$; **HRMS** (ESI) found: m/z 296.1022 $[M]^+$; calcd. for $C_{16}H_{15}F_3O_2$ 296.1024. Another diastereomer:white solid, mp 106–108 ^oC, 29.0 mg, 49% yield; 98% *ee*, [determined by **HPLC** analysis Daicel Chirapak IC, hexane/*i*-PrOH = 85/15, 220 nm UV detector, 1.0 mL/min, t_R = 5.452 min (major) and t_R = 5.172 min (minor)]; $[\alpha]^{20}_D$ –8.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.43 (m, 3H), 7.40 – 7.33 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.41 (s, 1H), 4.67 (d, *J* = 10.2 Hz, 1H), 2.63 – 2.50 (m, 2H), 2.33 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): –81.05 (s, 3F). **IR** (neat) ν: 3421, 3272, 3030, 2897, 1456, 1164, 701, 606 cm^{-1}; **MS** (ESI) found: m/z 296.1 $[M]^+$; **HRMS** (ESI) found: m/z 296.1020 $[M]^+$; calcd. for $C_{16}H_{15}F_3O_2$ 296.1024.

^{19}F NMR spectroscopic analysis of the reaction mixture:

The mixture of 2,2,2-Trifluoromethyl-1-phenylethanone **2a** (17.4 mg, 0.1 mmol), *β*-ketoacid **1a** (32.8 mg, 0.2 mmol), and triethylamine (2 mg, 0.02 mmol) in THF-d_8 (0.5 mL) in NMR tube was stirred at 0 °C. Then the tube was subjected to ^{19}F NMR (376 MHz) spectroscopic analysis every two hours. The relative conversion was determined by the integrated area (Figure 1).

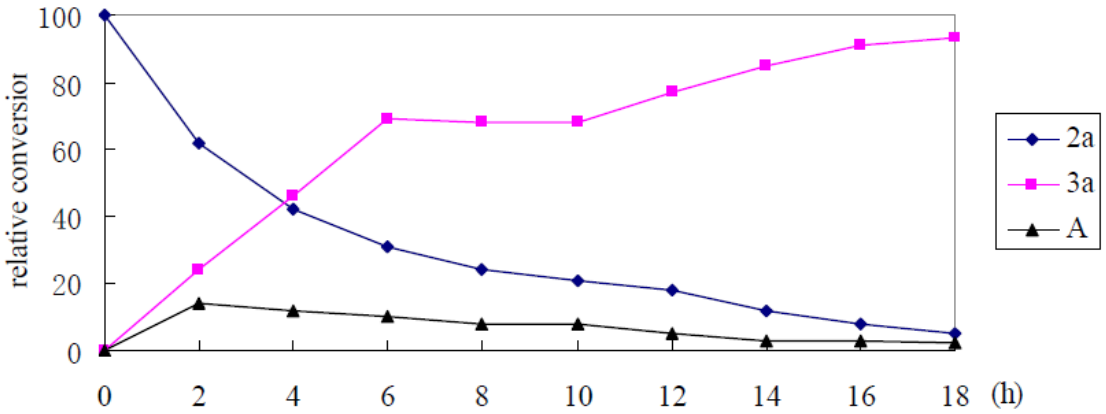
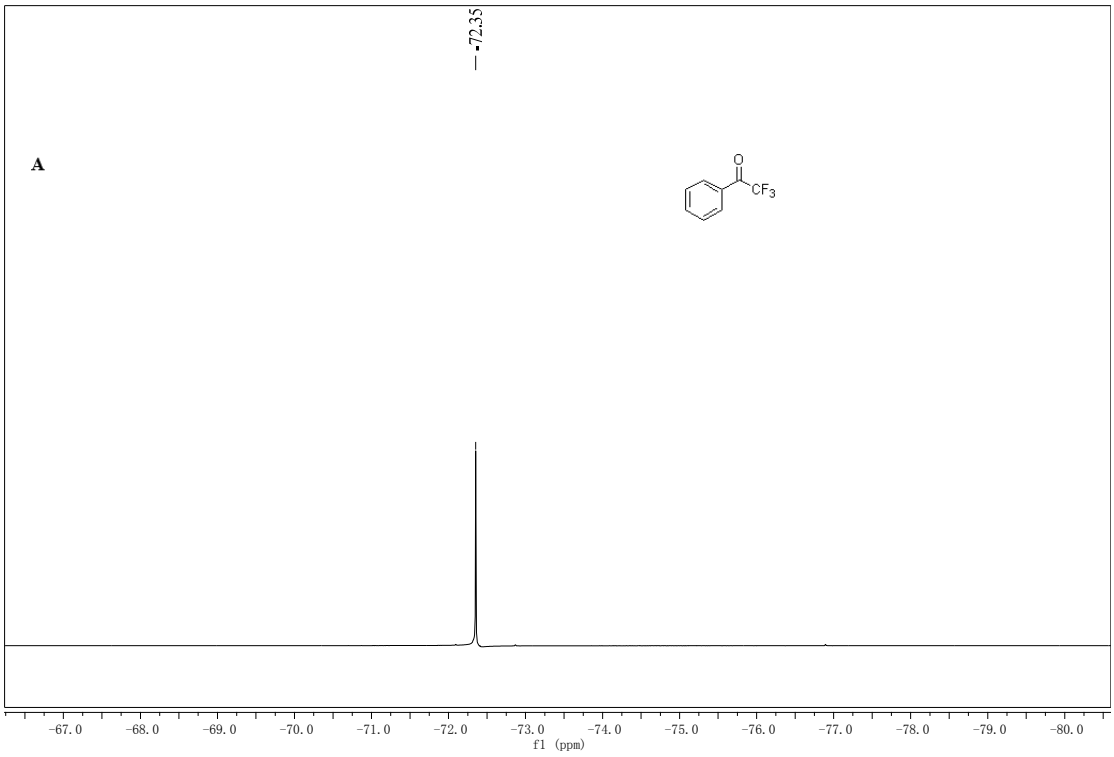
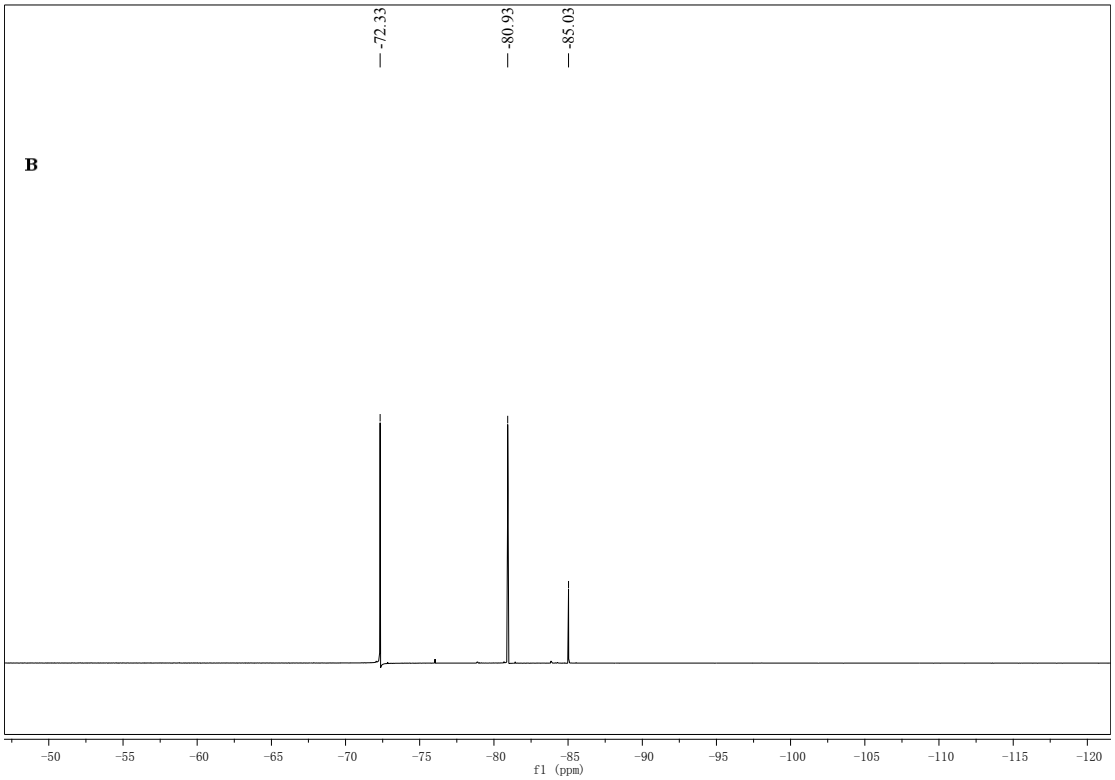
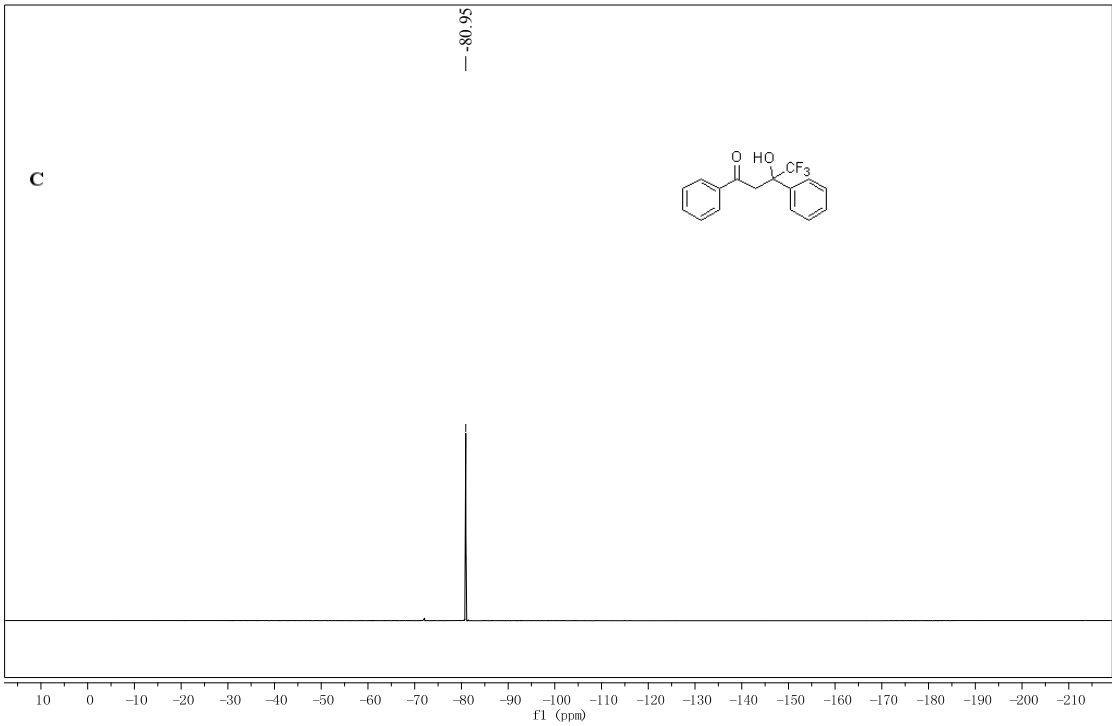


Figure 1 ^{19}F NMR monitoring of the reaction mixture of β-ketoacid **1a**, trifluoromethyl ketone **2a**, and NEt_3 in THF-d_8 as a function of time at 0 ^{o}C.







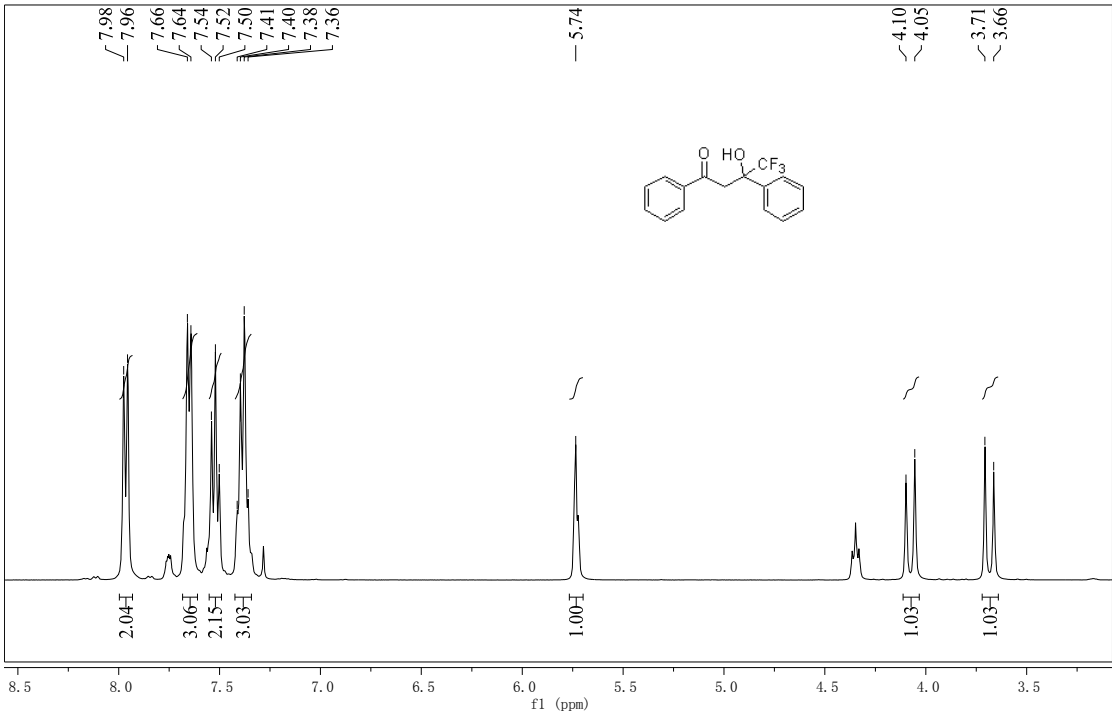
References:

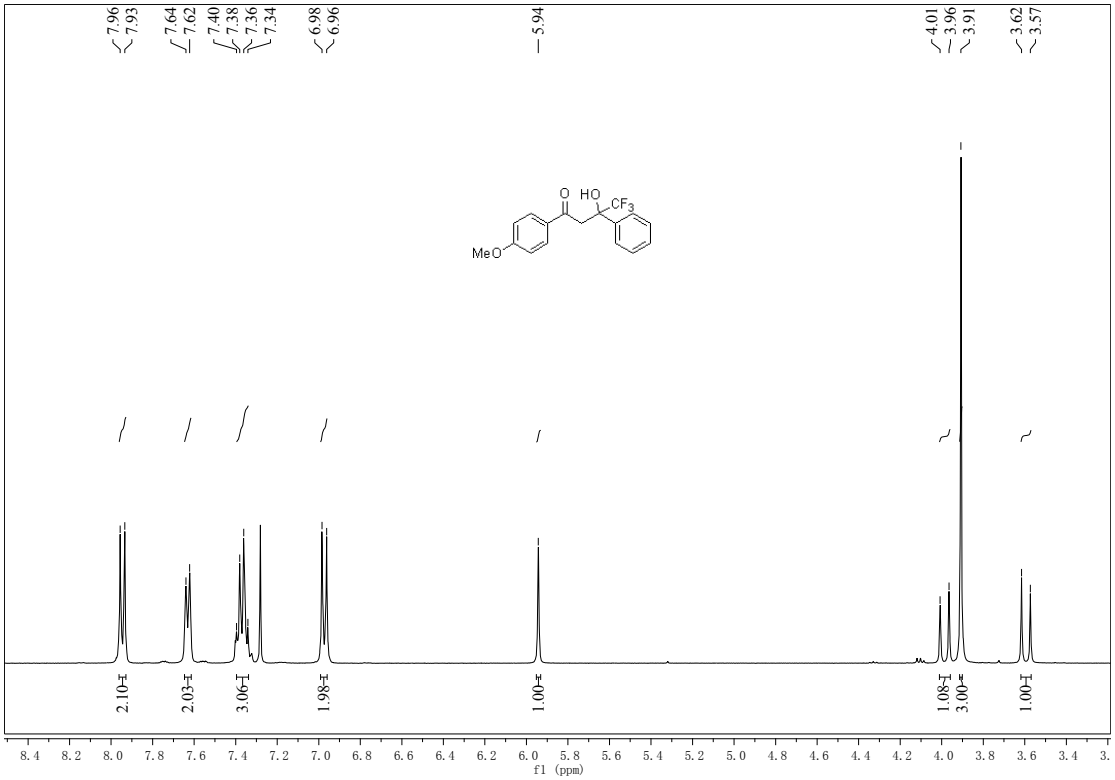
1 D. A. Evans, S. Mito, D. Seidel, *J. Am. Chem. Soc.*, **2007**, *129*, 11583–11592.

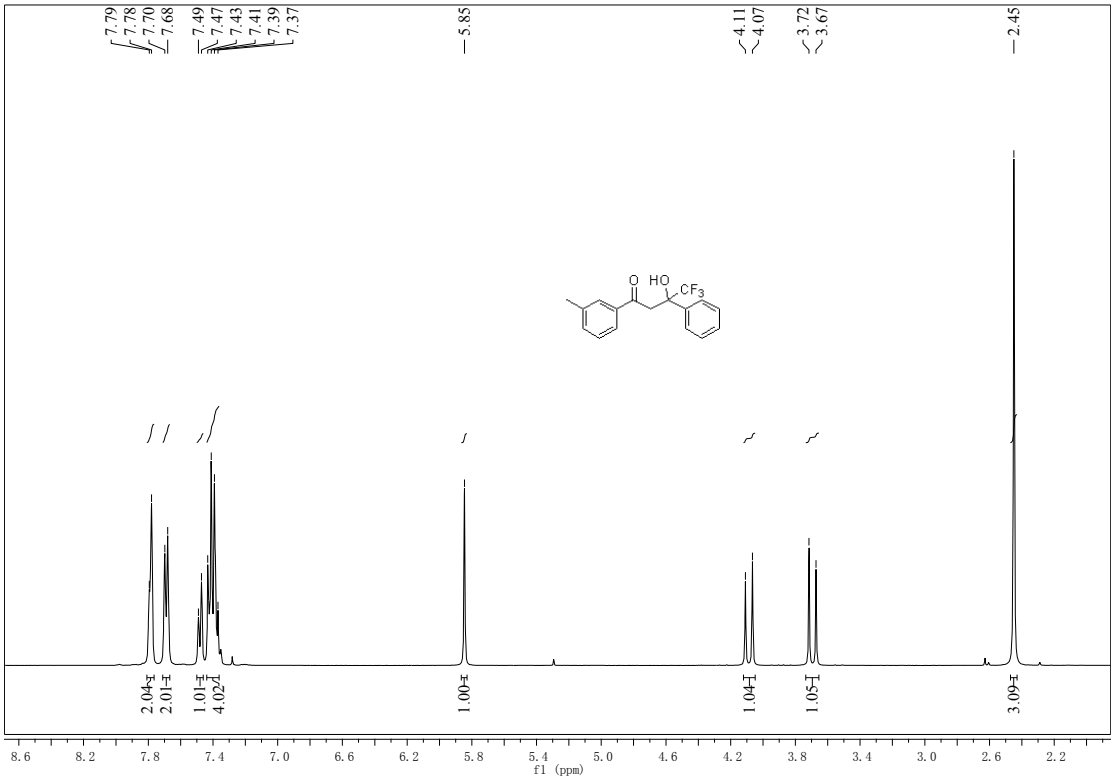
2 S. Sasaki, K. Kikuchi, T. Yamauchi, K. Higashiyama, *Synlett*, **2011**, 10, 1431–1434.

3 Z,-J, Liu, Y,-Q. Mei and J.-T. Liu, *Tetrahedron*, **2007**, *63*, 855–860.

NMR Spectra and HPLC Charts for the Addition Adducts:



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7.41
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3.72
3.67
2.45
O
HO
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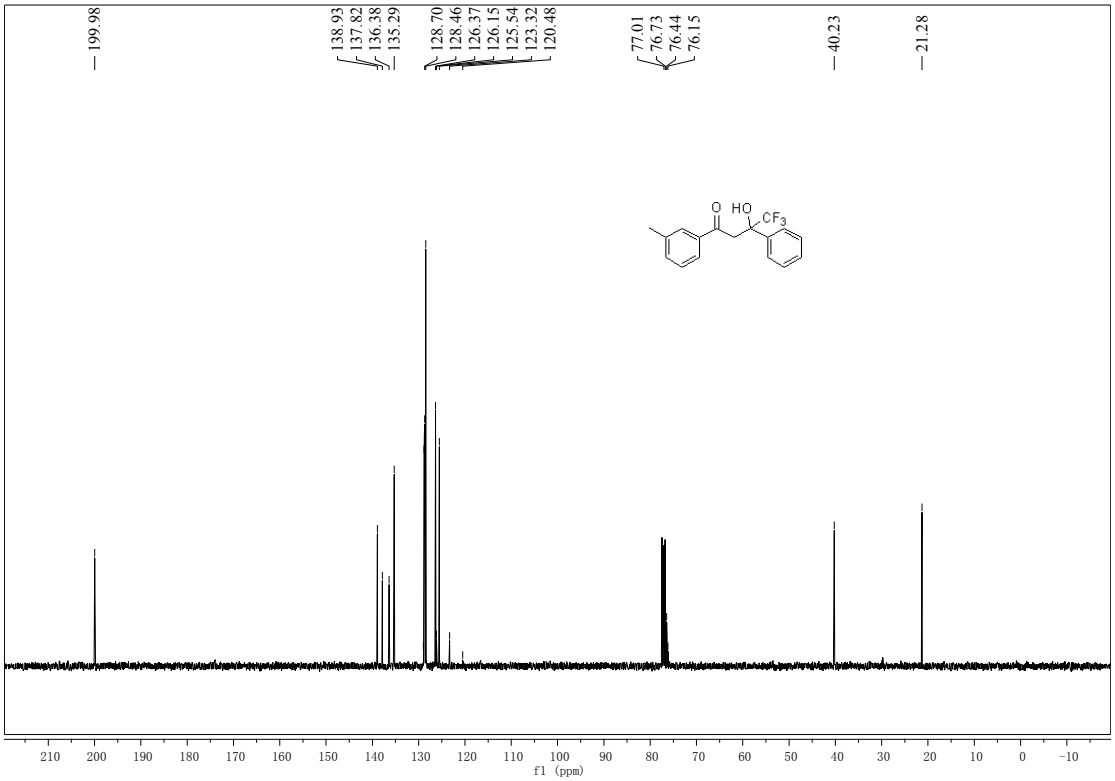
2.01
1.01
4.02
1.00
1.04
1.05
3.09
f1 (ppm)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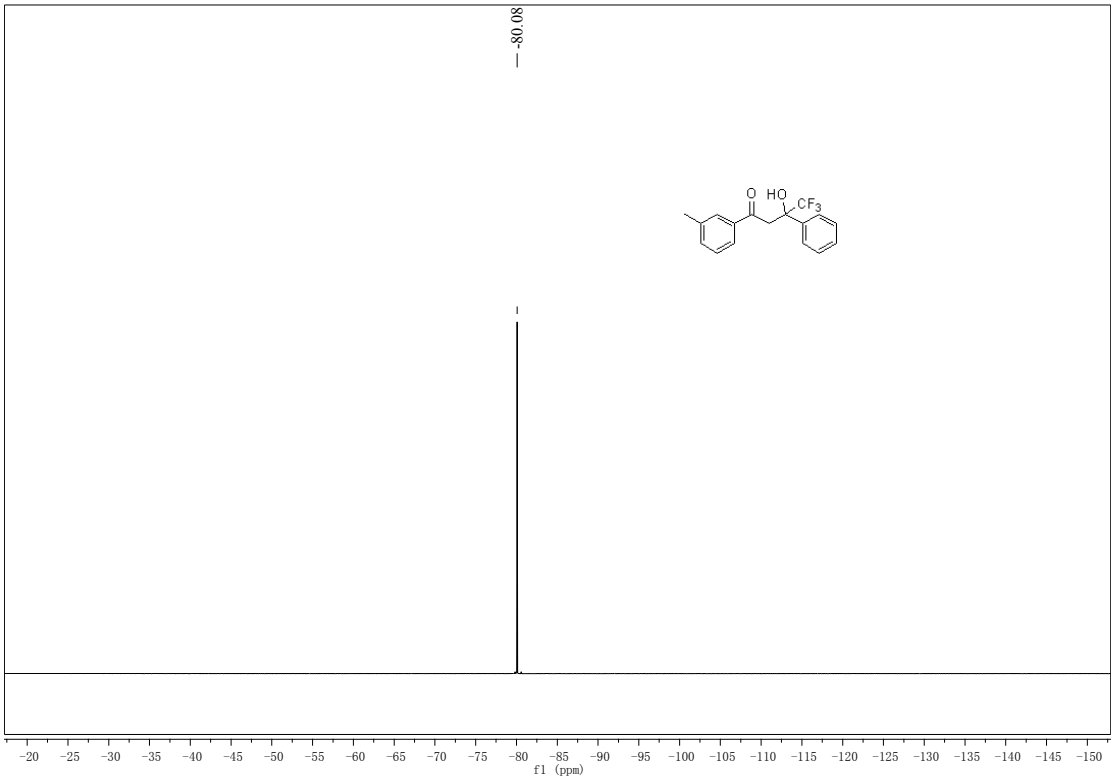
40.23
21.28
O
HO
CF3
f1 (ppm)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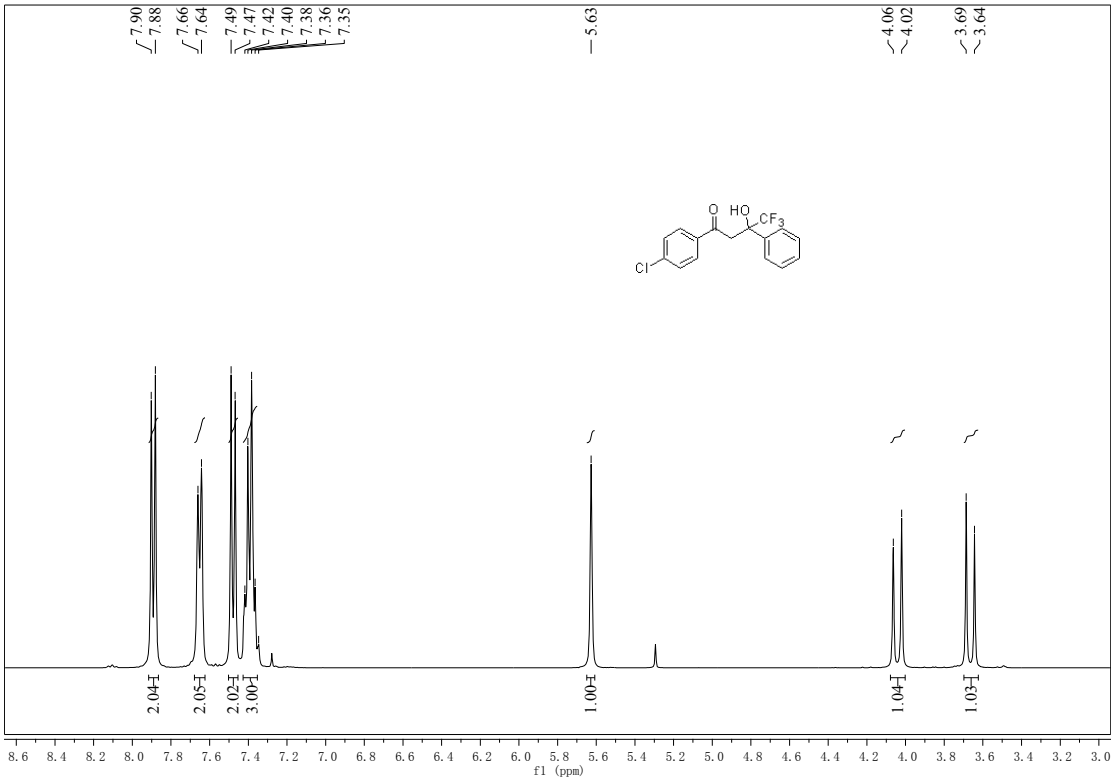
O
HO
CF3
f1 (ppm)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4.02
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Cl
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1.00
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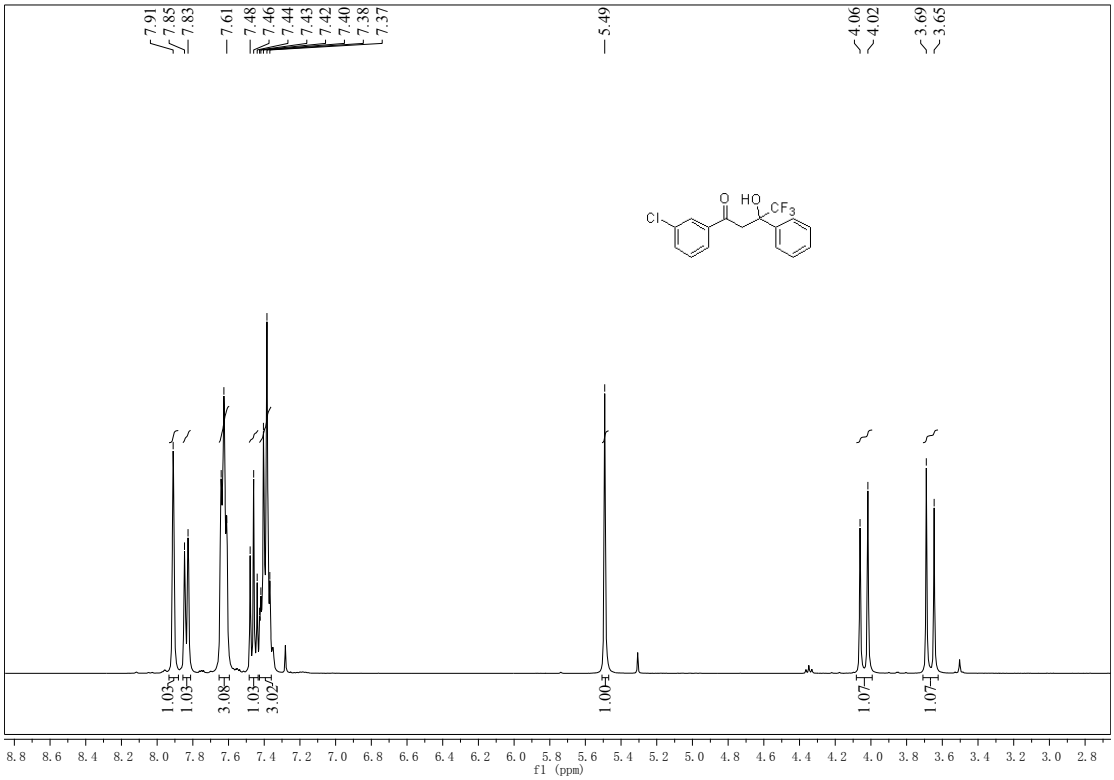
1.03
f1 (ppm)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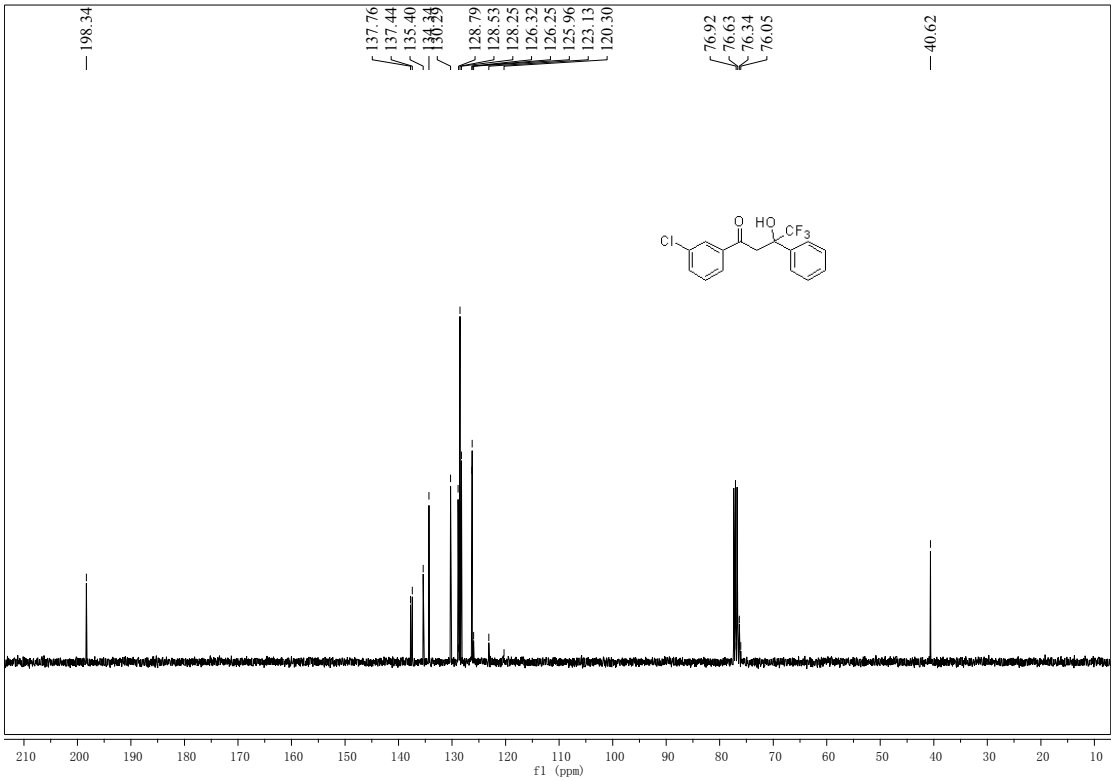
O
HO
CF3
Cl
1.03
1.03
3.08
1.03
3.02
1.00
1.07
1.07
f1 (ppm)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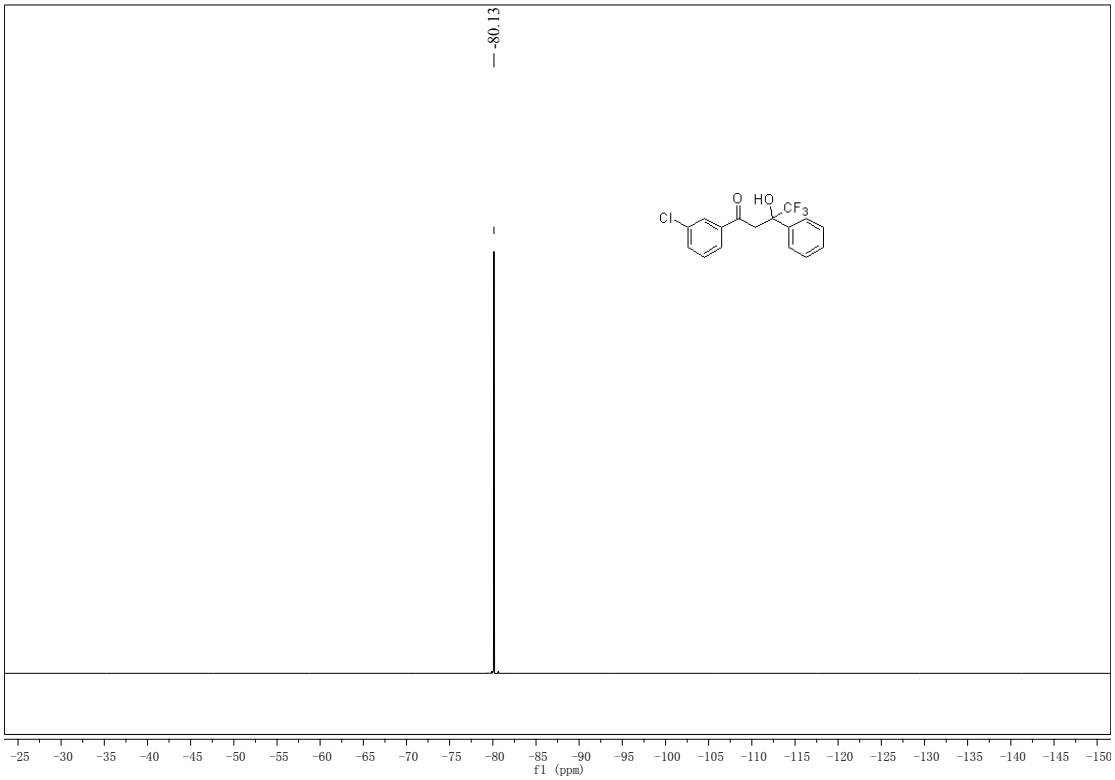
137.76
137.44
135.40
130.29
128.79
128.53
128.25
126.32
126.25
125.96
123.13
120.30
76.92
76.63
76.34
76.05
40.62
O
HO
CF3
Cl
f1 (ppm)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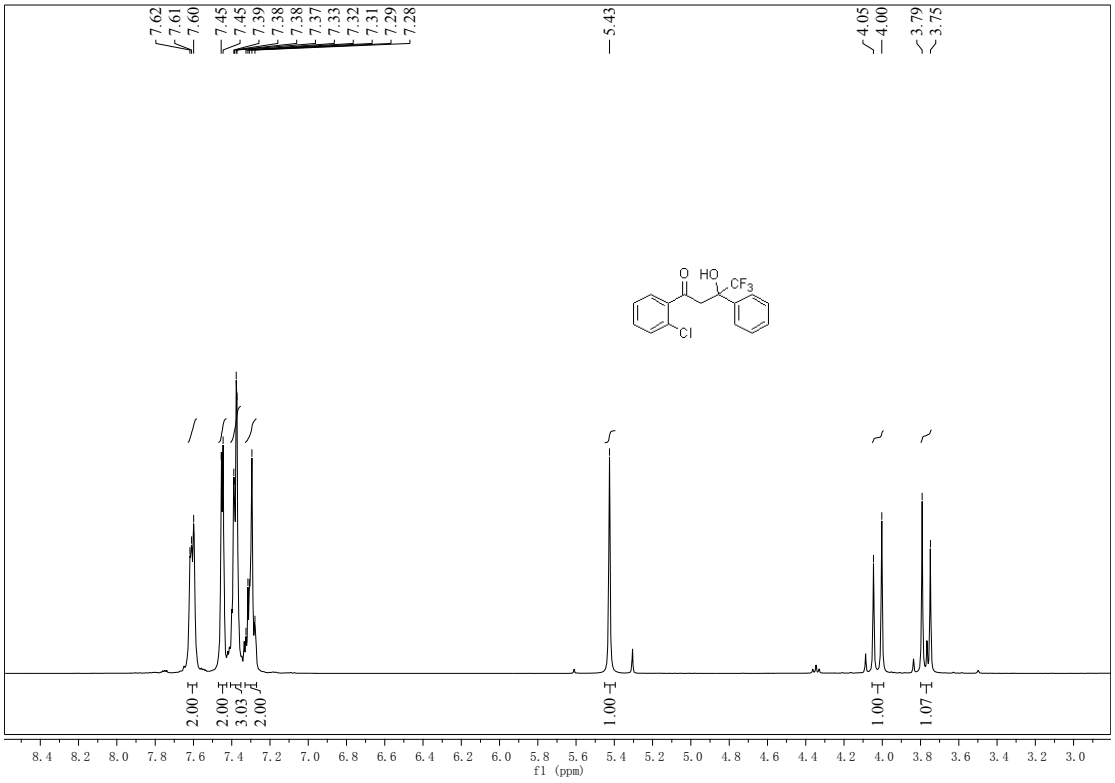
O
HO
CF3
Cl
f1 (ppm)


7.62
7.61
7.60
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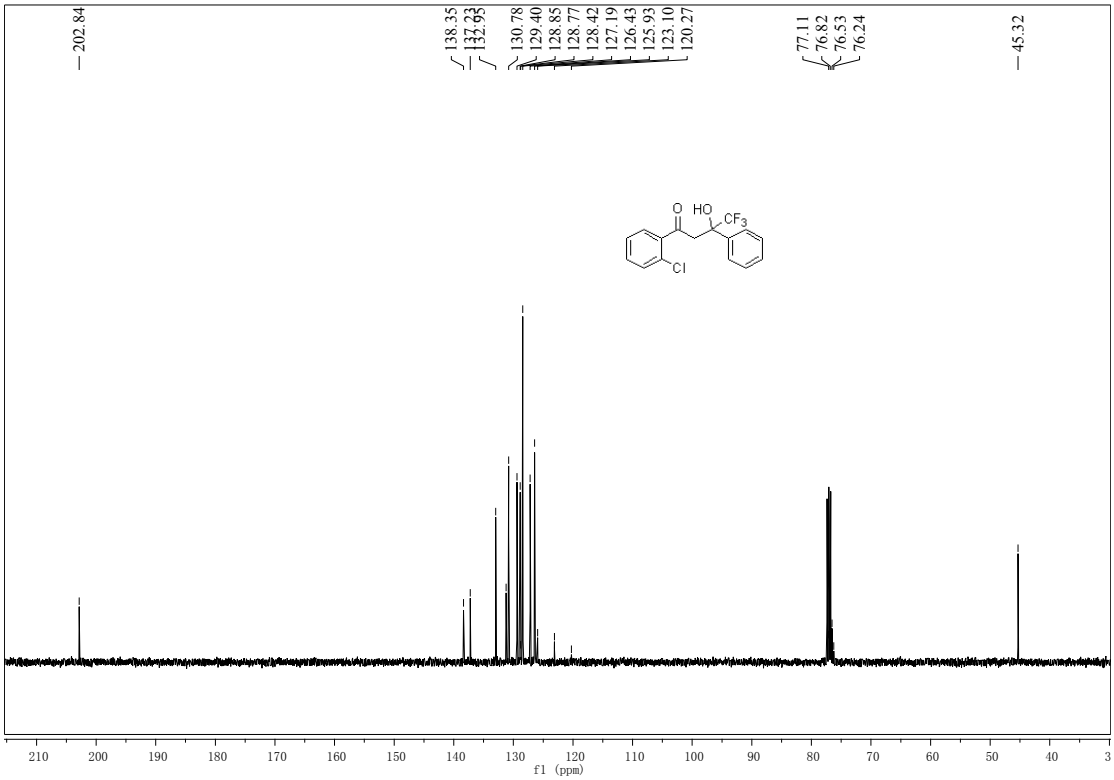
7.45
7.39
7.38
7.38
7.37
7.33
7.32
7.31
7.29
7.28
5.43
4.05
4.00
3.79
3.75
O
HO
CF3
Cl
2.00
2.00
3.03
2.00
1.00
1.00
1.07
f1 (ppm)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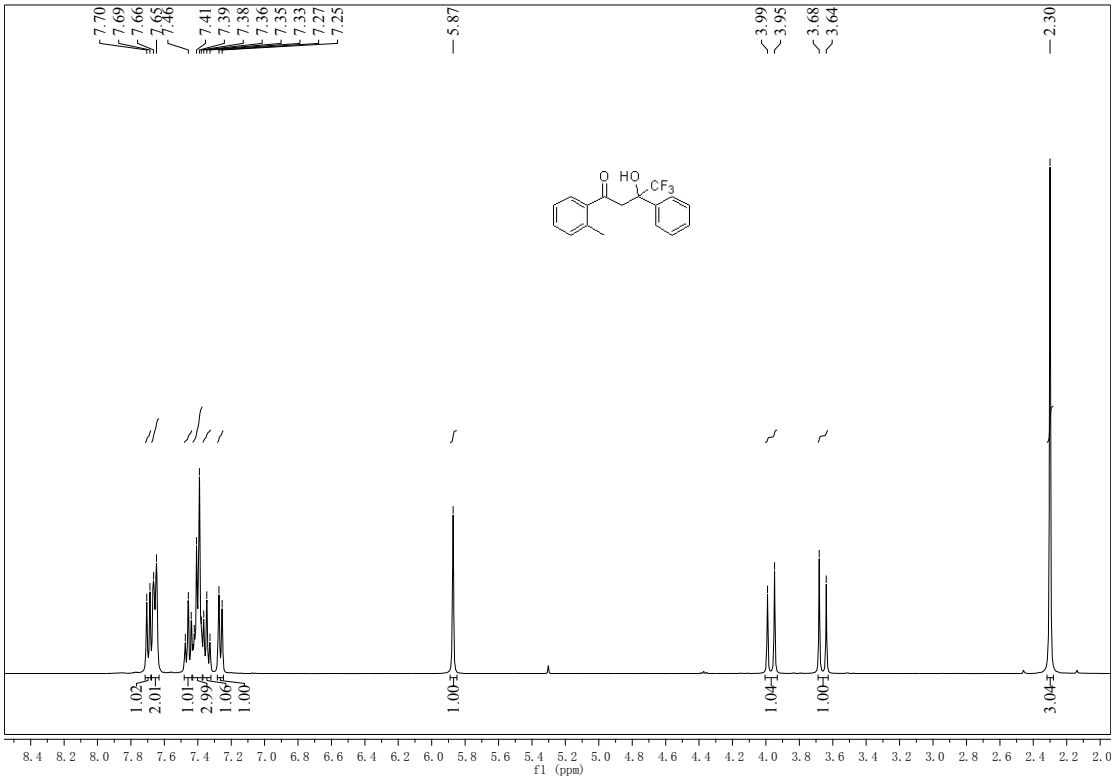
138.35
137.23
132.95
130.78
129.40
128.85
128.77
128.42
127.19
126.43
125.93
123.10
120.27
77.11
76.82
76.53
76.24
45.32
O
HO
CF3
Cl
f1 (ppm)


-80.06
O
HO
CF3
Cl
f1 (ppm)


7.70
7.69
7.66
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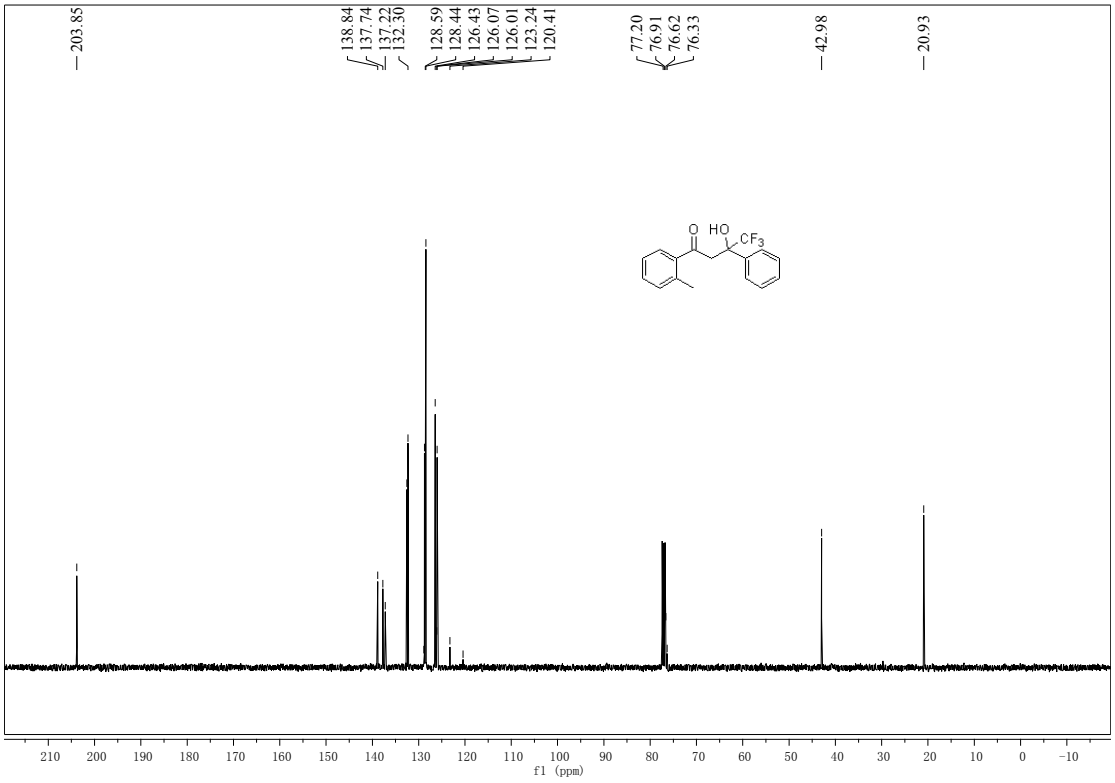
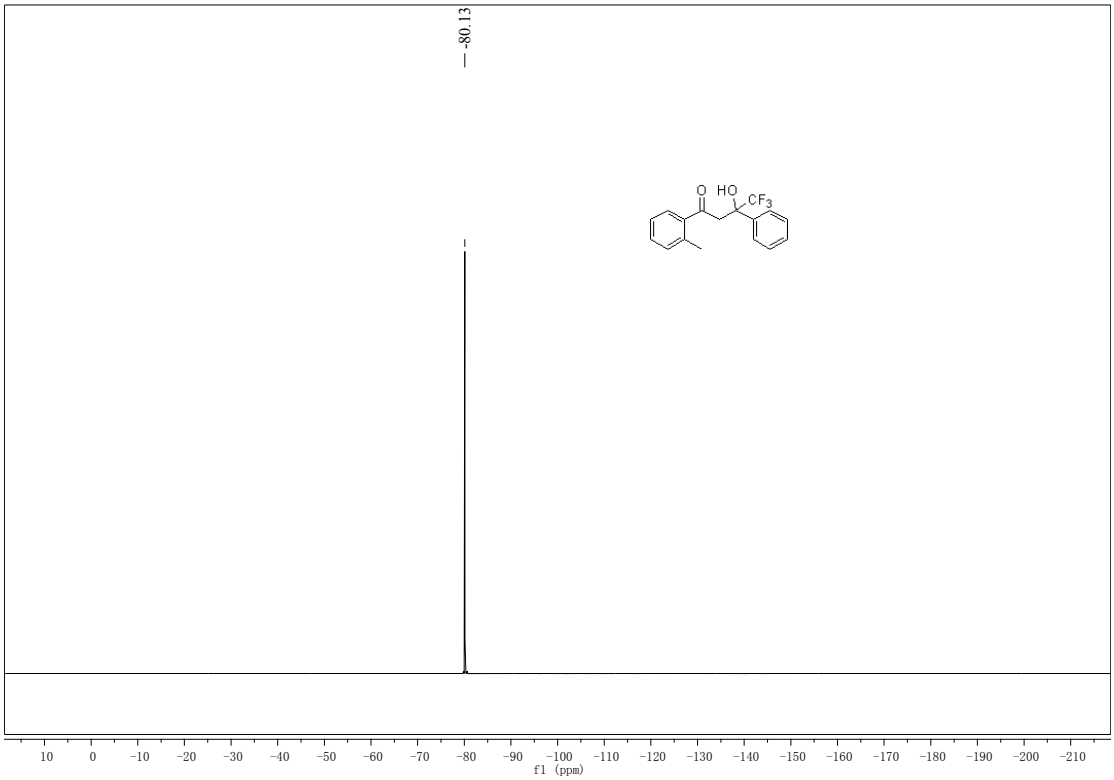
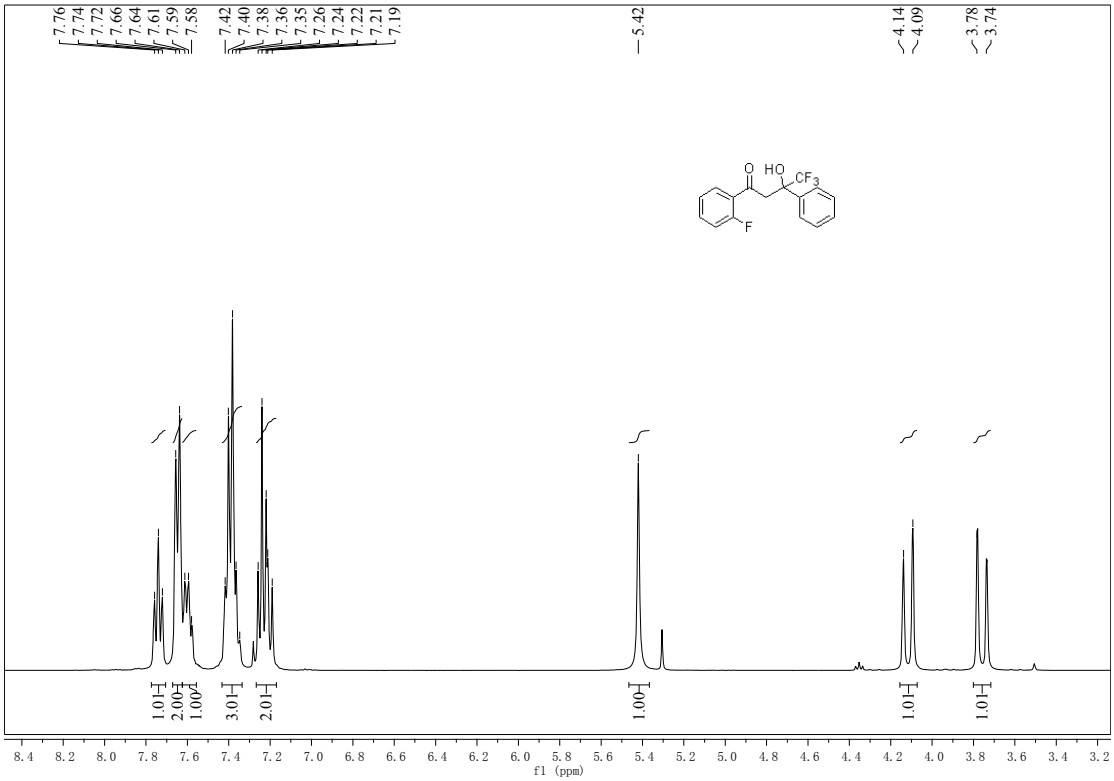
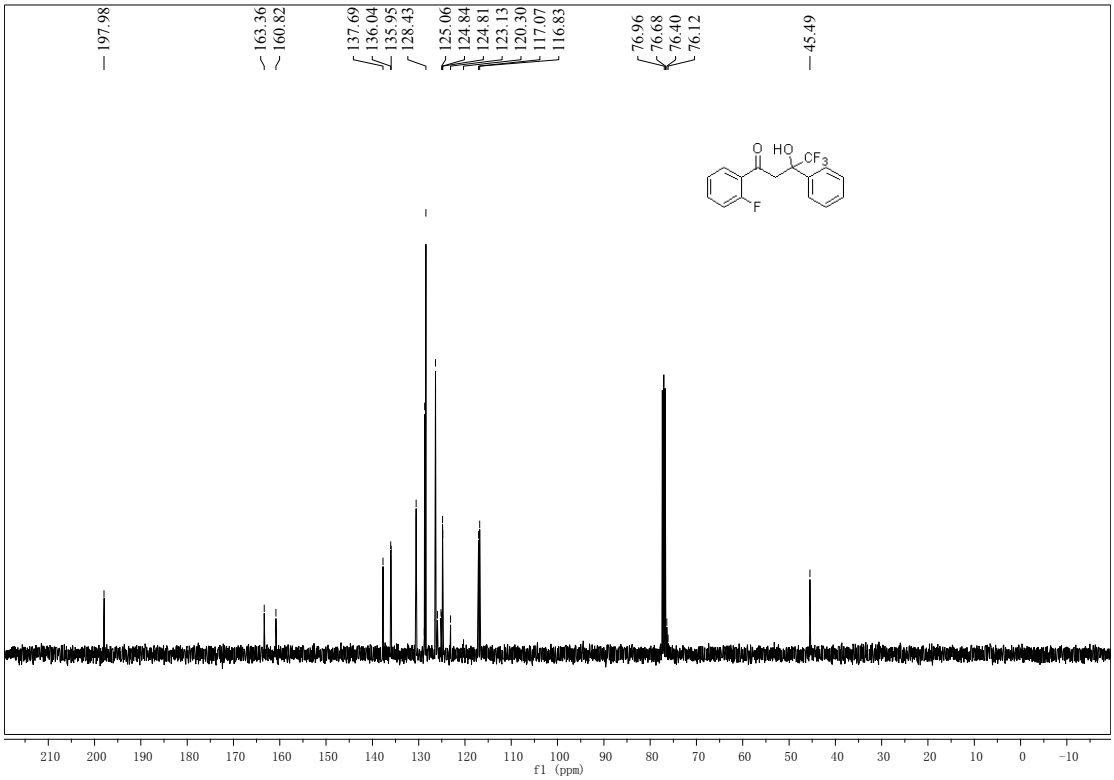
7.46
7.41
7.39
7.38
7.36
7.35
7.33
7.27
7.25
5.87
3.99
3.95
3.68
3.64
2.30
O
HO
CF3
1.02
2.01
1.01
2.99
1.06
1.00
1.00
1.04
1.00
3.04
f1 (ppm)


203.85
138.84
137.74
137.22
132.30
128.59
128.44
126.43
126.07
126.01
123.24
120.41
77.20
76.91
76.62
76.33
42.98
20.93
O
HO
CF3
f1 (ppm)


-80.13
O
HO
CF3
f1 (ppm)


7.76
7.74
7.72
7.66
7.64
7.61
7.59
7.58
7.42
7.40
7.38
7.36
7.35
7.26
7.24
7.22
7.21
7.19
5.42
4.14
4.09
3.78
3.74
O
HO
CF3
F
1.01
2.00
1.00
3.01
2.01
1.00
1.01
1.01
f1 (ppm)


197.98
163.36
160.82
137.69
136.04
135.95
128.43
125.06
124.84
124.81
123.13
120.30
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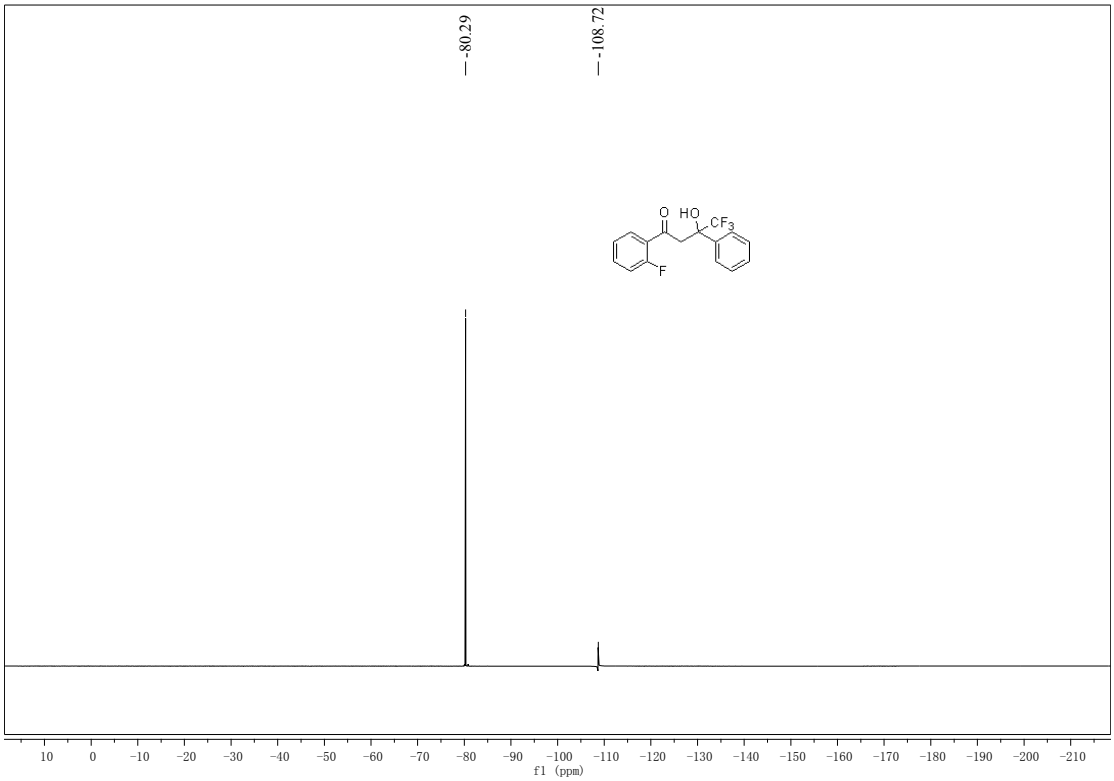
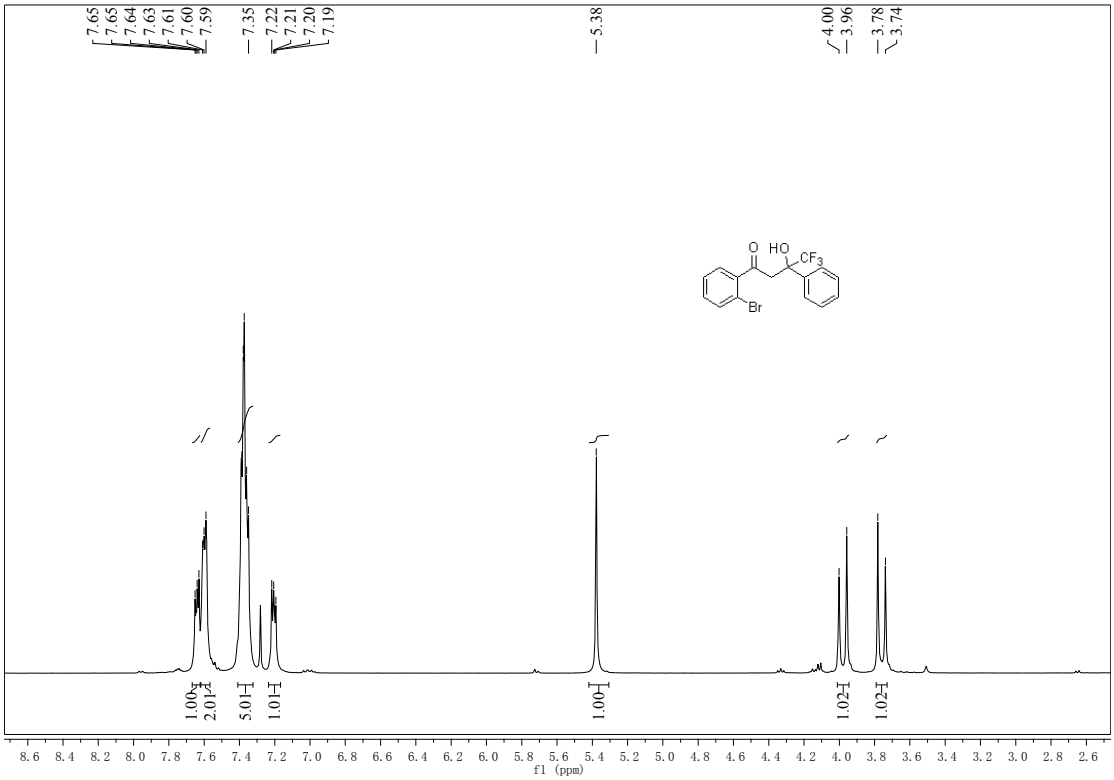
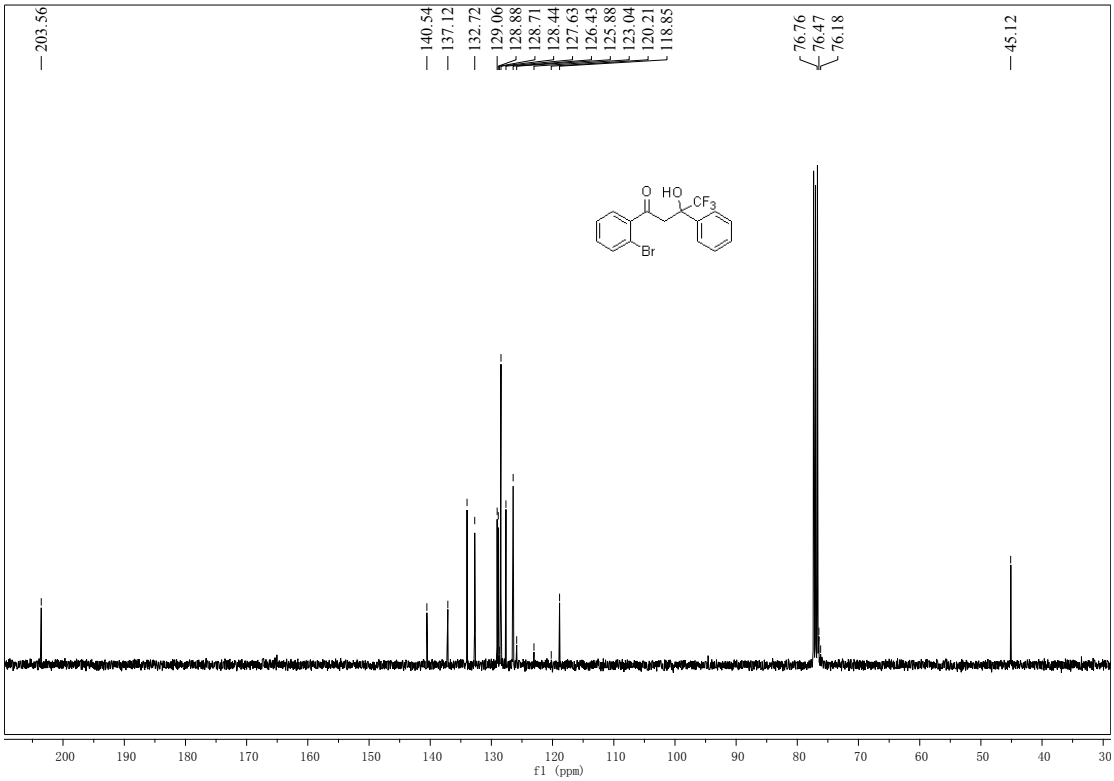
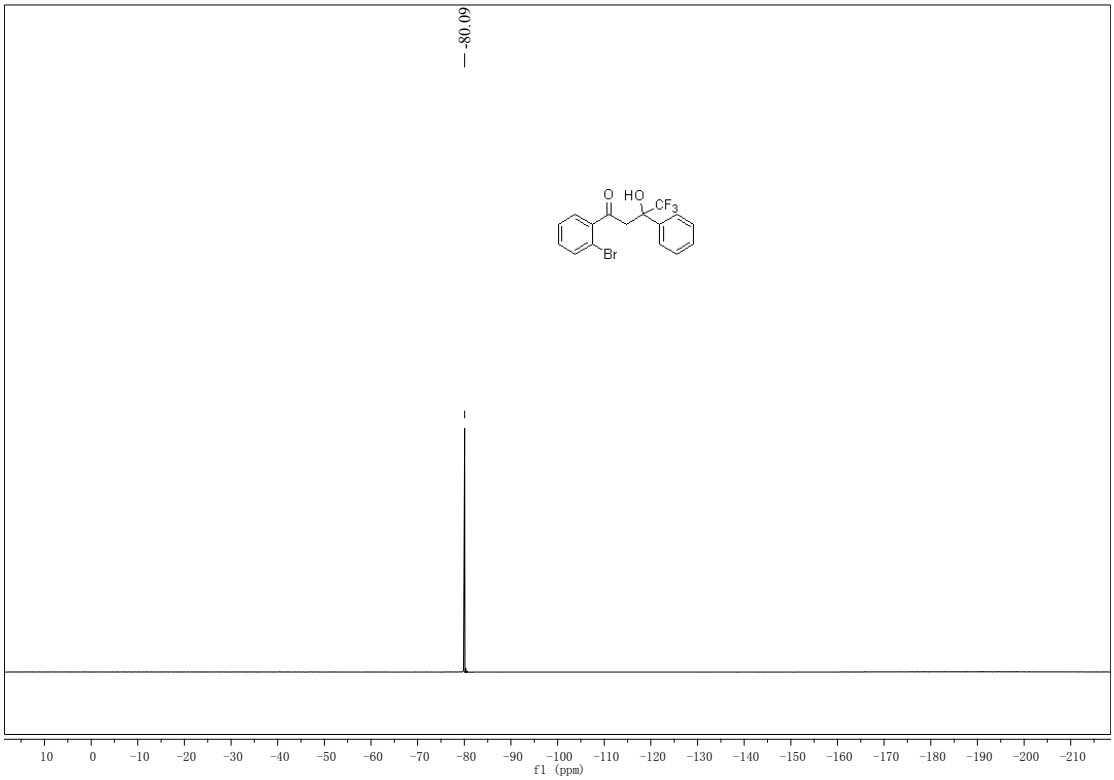
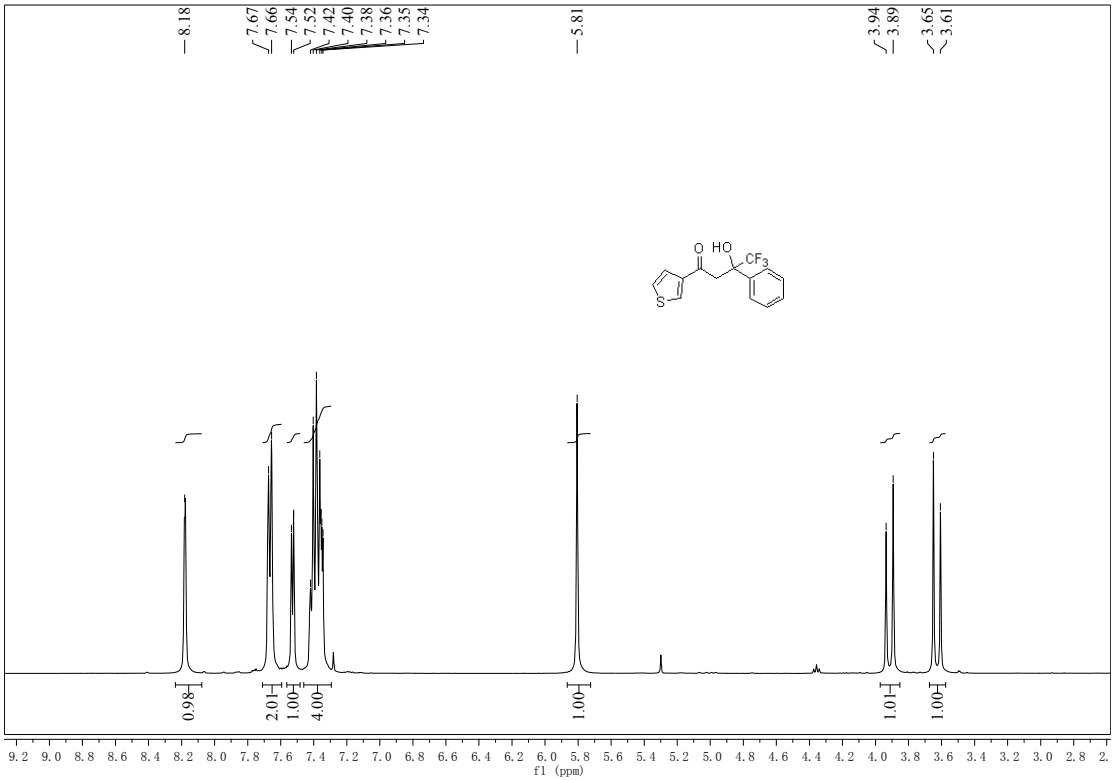
76.12
45.49
O
HO
CF3
F
f1 (ppm)

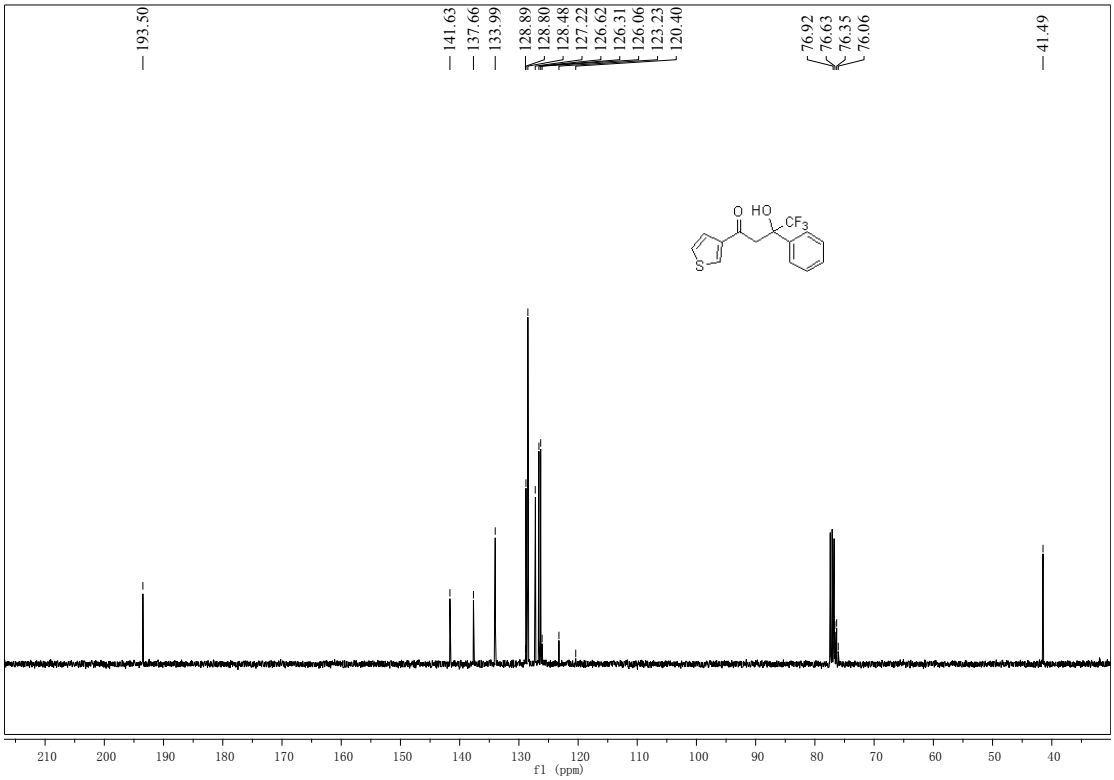

-80.29
-108.72
O
HO
CF3
F
f1 (ppm)

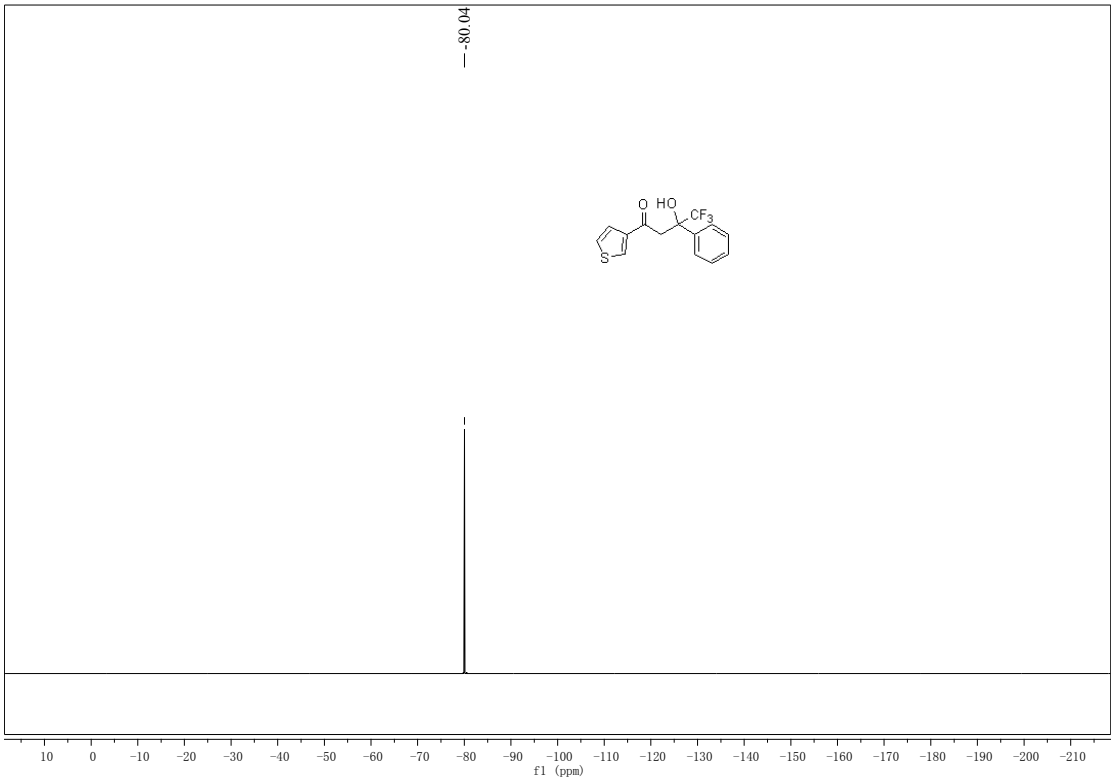

7.65
7.65
7.64
7.63
7.61
7.60
7.59
7.35
7.22
7.21
7.20
7.19
5.38
4.00
3.96
3.78
3.74
O
HO
CF3
Br
1.00
2.01
5.01
1.01
1.00
1.02
1.02
f1 (ppm)

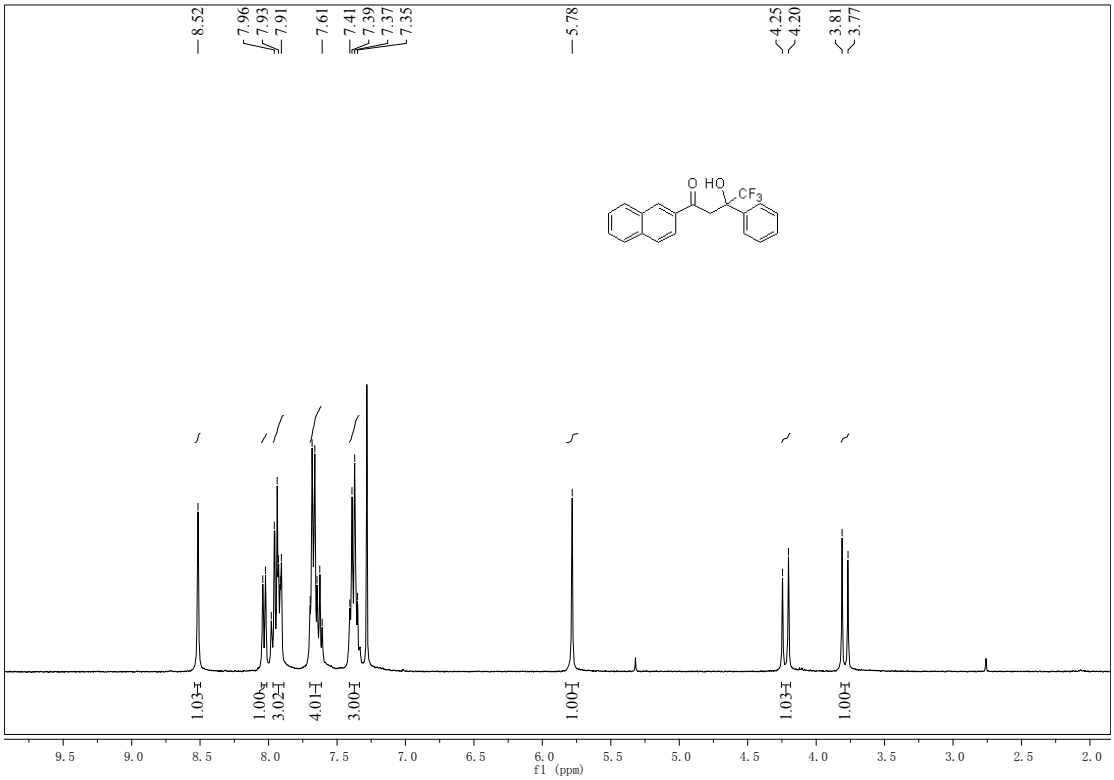

203.56
140.54
137.12
132.72
129.06
128.88
128.71
128.44
127.63
126.43
125.88
123.04
120.21
118.85
76.76
76.47
76.18
45.12
O
HO
CF3
Br
f1 (ppm)

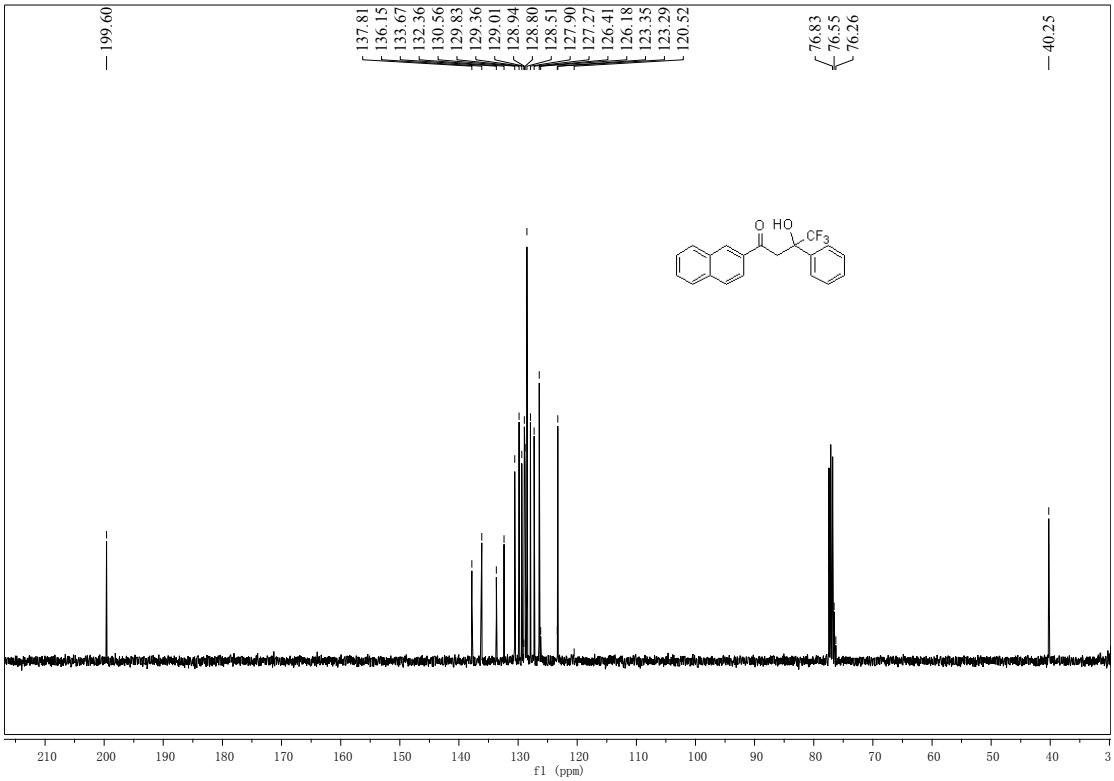

-80.09
O HO CF3
Br
f1 (ppm)

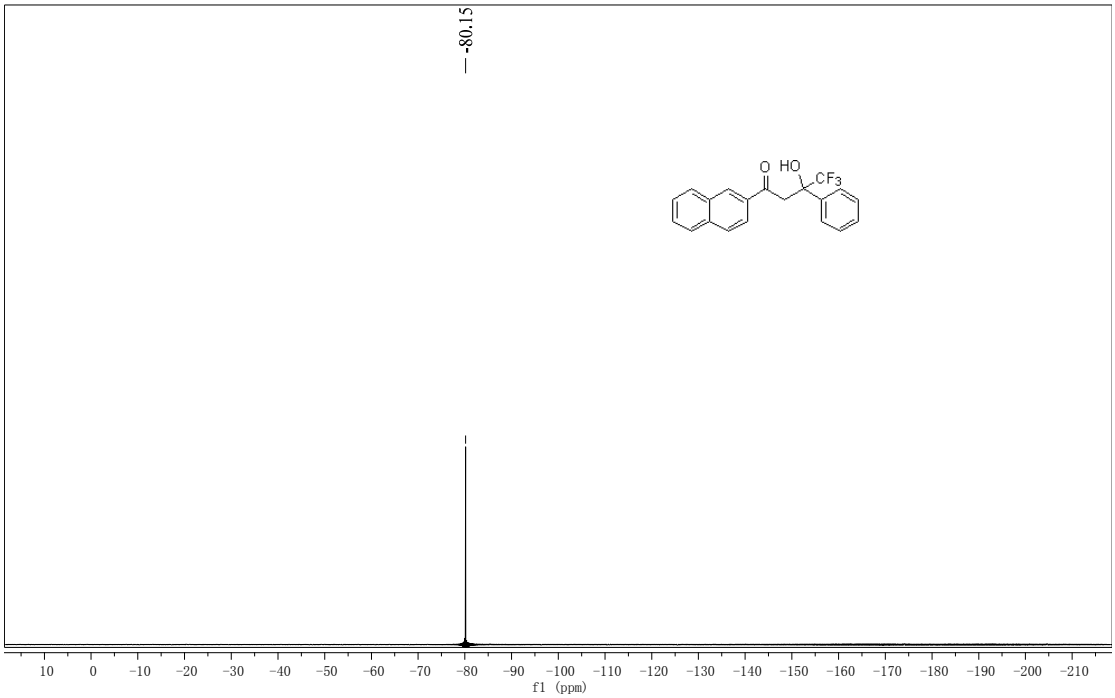

8.18
7.67
7.66
7.54
7.52
7.42
7.40
7.38
7.36
7.35
7.34
5.81
3.94
3.89
3.65
3.61
O HO CF3
S
0.98
2.01
1.00
4.00
1.00
1.01
1.00
f1 (ppm)

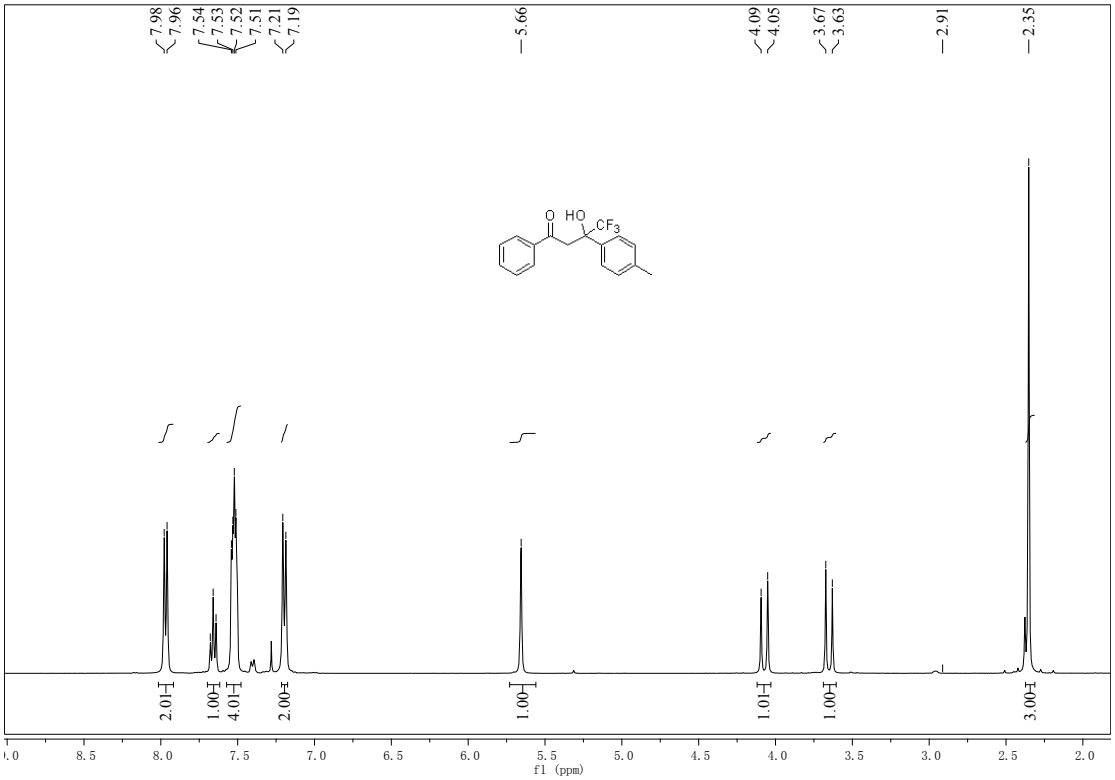

193.50
141.63
137.66
133.99
128.89
128.80
128.48
127.22
126.62
126.31
126.06
123.23
120.40
76.92
76.63
76.35
76.06
41.49
O HO
CF3
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
f1 (ppm)


-80.04
O HO
CF3
S
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.52
7.96
7.93
7.91
7.61
7.41
7.39
7.37
7.35
5.78
4.25
4.20
3.81
3.77
O HO
CF3
1.03
1.00
3.02
4.01
3.00
1.00
1.03
1.00
f1 (ppm)


199.60
137.81
136.15
133.67
132.36
130.56
129.83
129.36
129.01
128.94
128.80
128.51
127.90
127.27
126.41
126.18
123.35
123.29
120.52
76.83
76.55
76.26
40.25
O HO
CF3
f1 (ppm)


-80.15
O HO
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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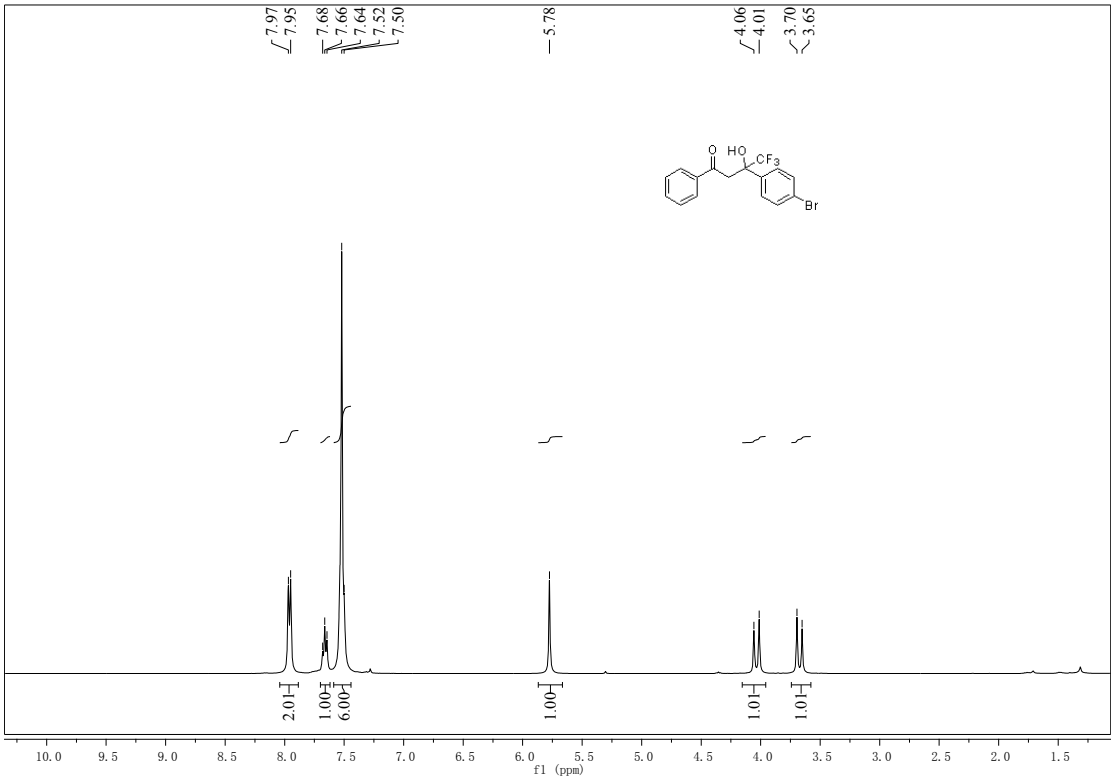
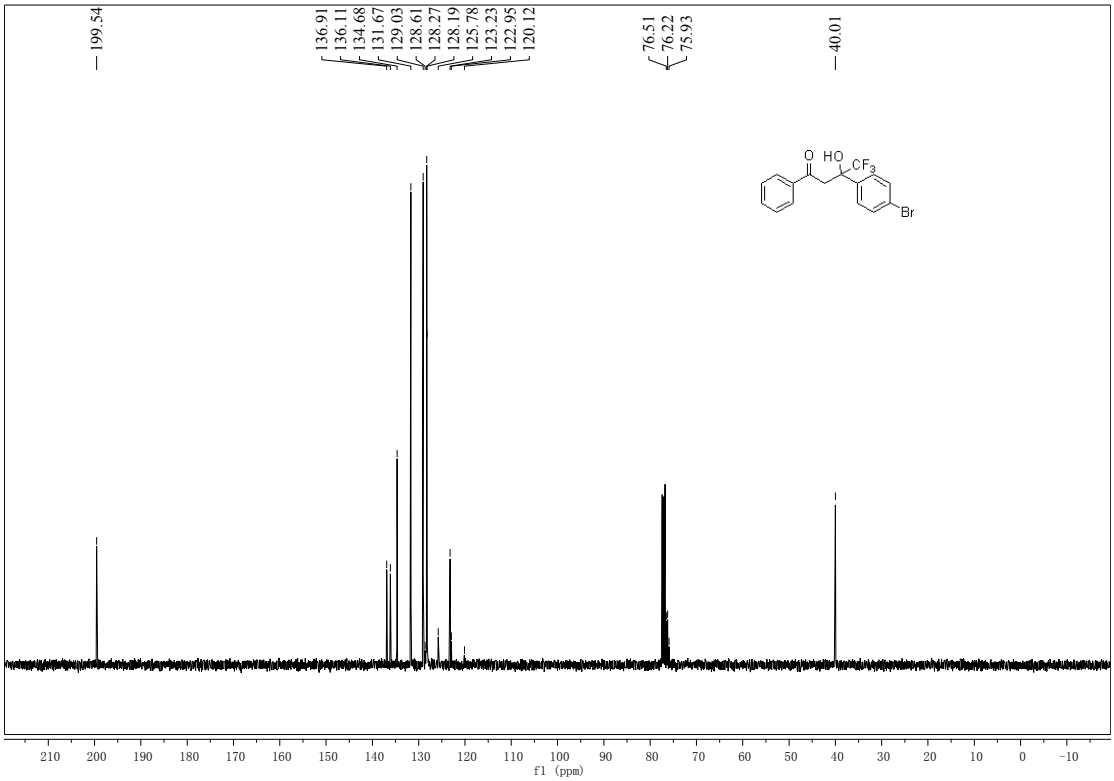
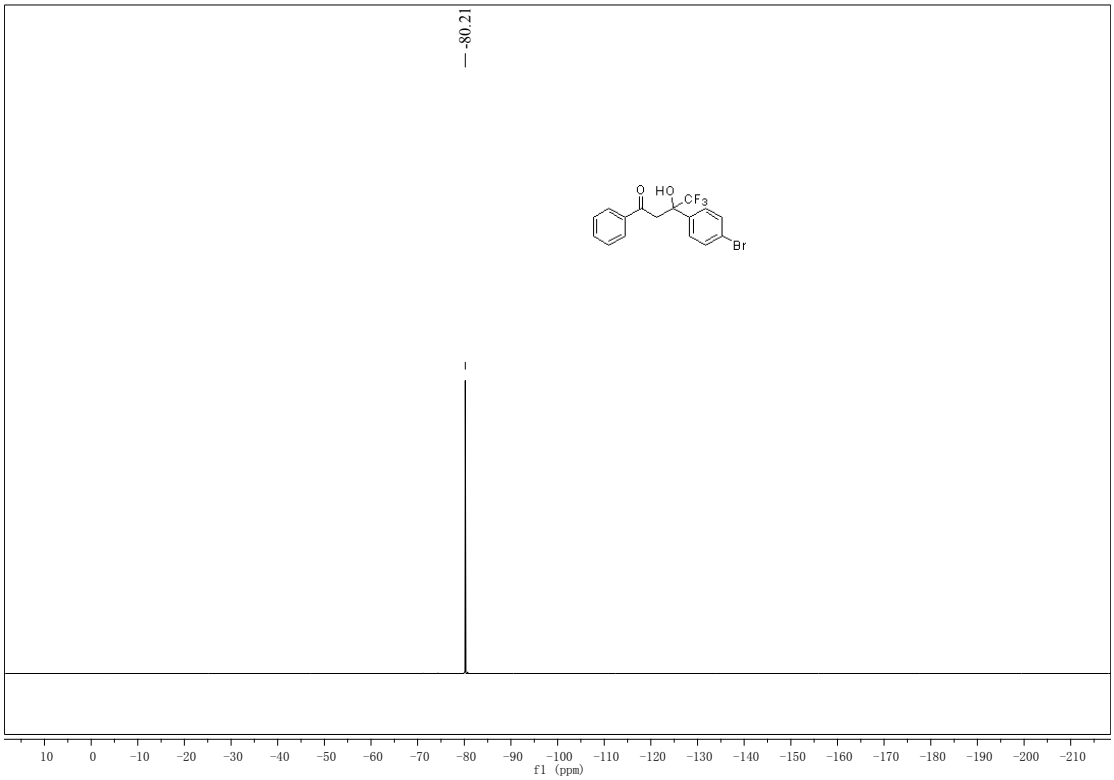
7.96
7.54
7.53
7.52
7.51
7.21
7.19
5.66
4.09
4.05
3.67
3.63
2.91
2.35
O HO
CF3
2.01
1.00
4.01
2.00
1.00
1.01
1.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)


7.97
7.95
7.68
7.66
7.64
7.52
7.50
5.78
4.06
4.01
3.70
3.65
O
HO
CF3
Br
2.01
1.00
6.00
1.00
1.01
1.01
f1 (ppm)


199.54
136.91
136.11
134.68
131.67
129.03
128.61
128.27
128.19
125.78
123.23
122.95
120.12
76.51
76.22
75.93
40.01
O
HO
CF3
Br
f1 (ppm)


-80.21
O
HO
CF3
Br
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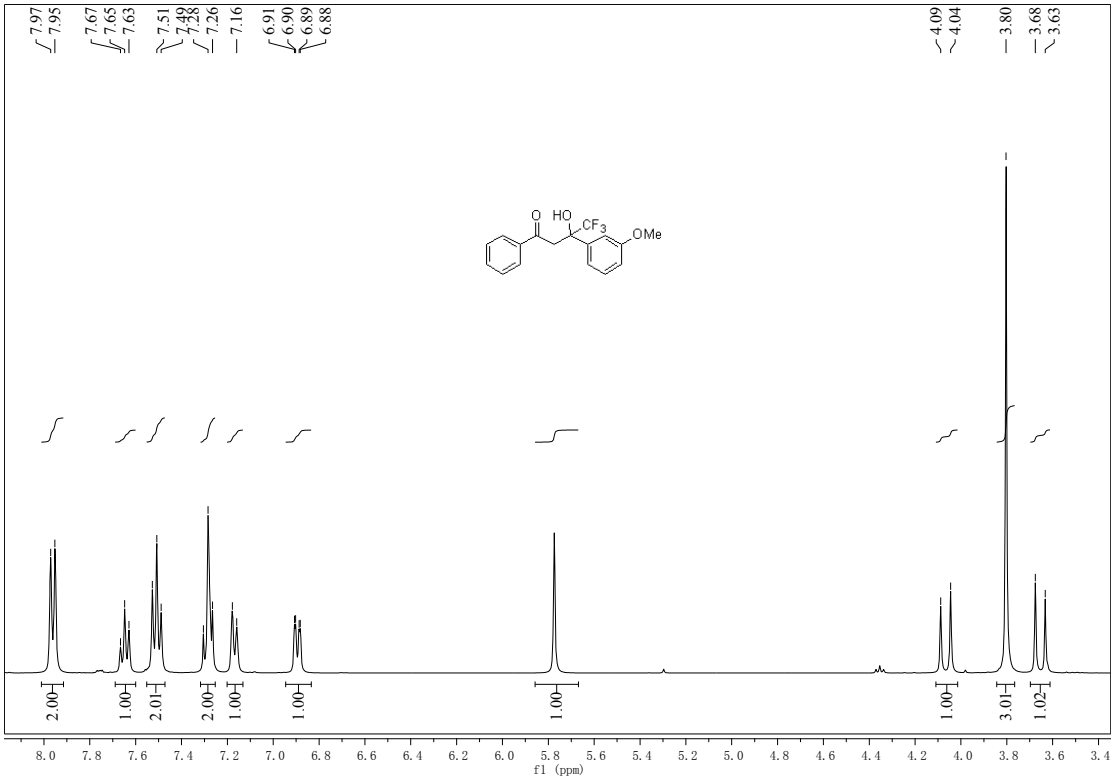
f1 (ppm)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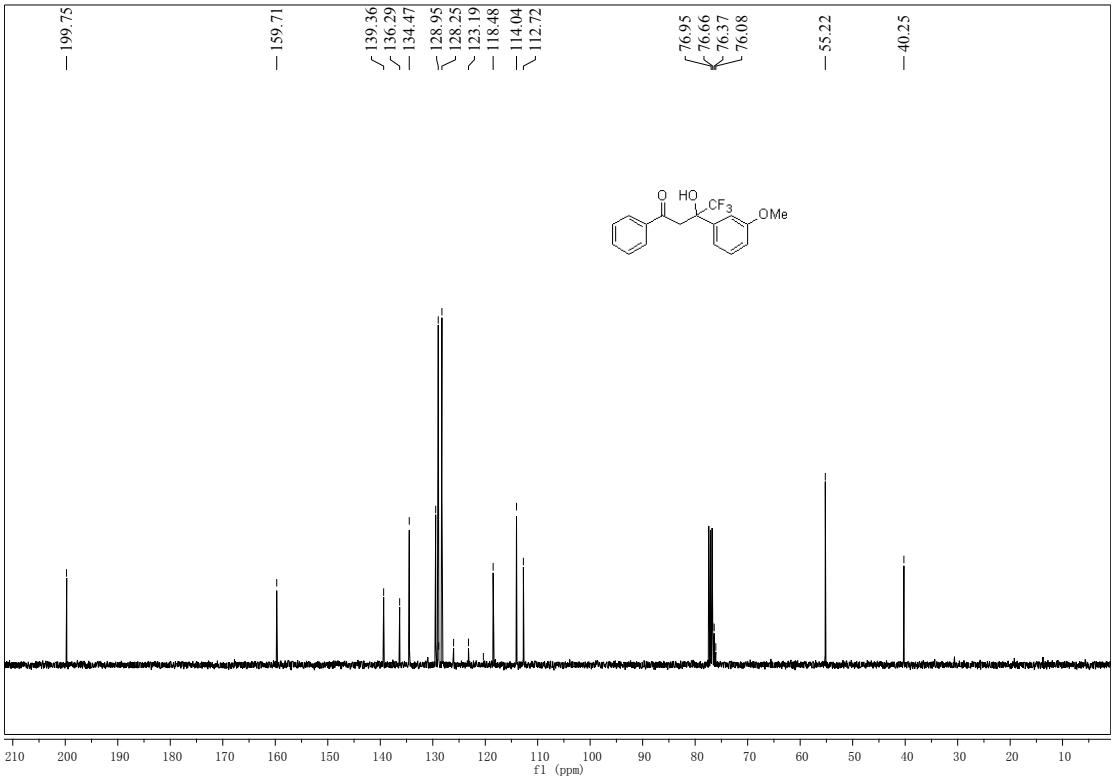
7.51
7.49
7.38
7.26
7.16
6.91
6.90
6.89
6.88
4.09
4.04
3.80
3.68
3.63
O
HO
CF3
OMe
2.00
1.00
2.01
2.00
1.00
1.00
1.00
1.00
3.01
1.02
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
f1 (ppm)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128.25
123.19
118.48
114.04
112.72
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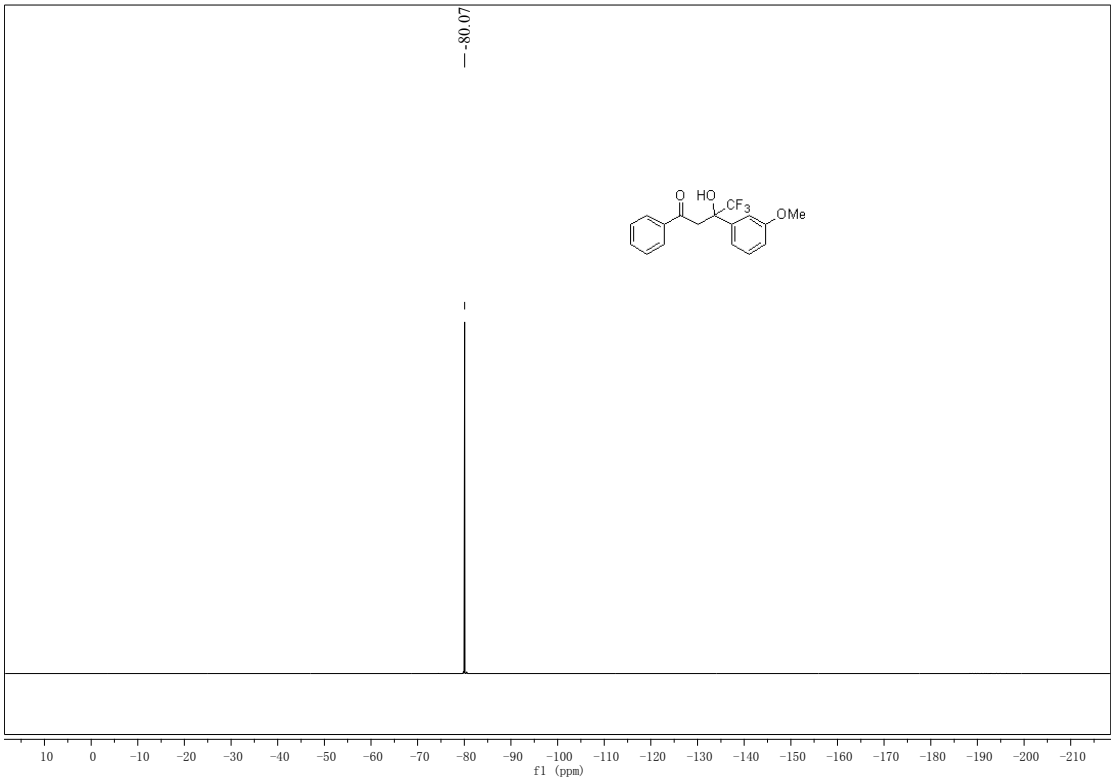
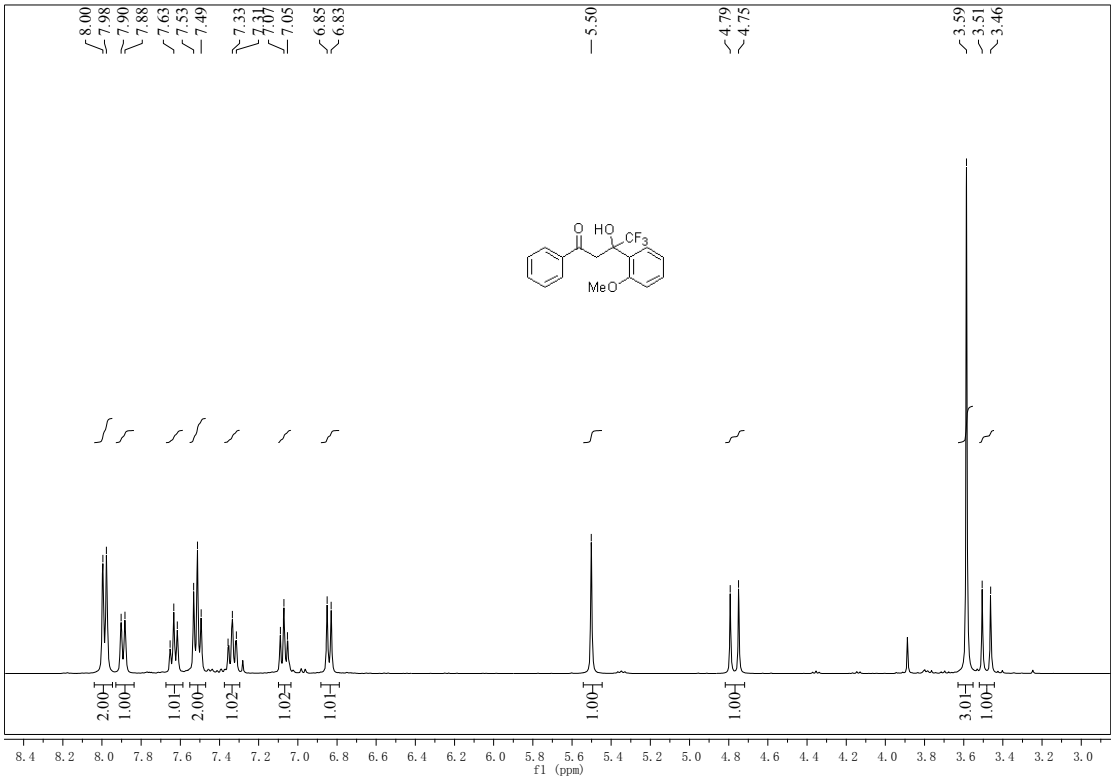
40.25
O
HO
CF3
OMe
f1 (ppm)


-80.07
O
HO
CF3
OMe
f1 (ppm)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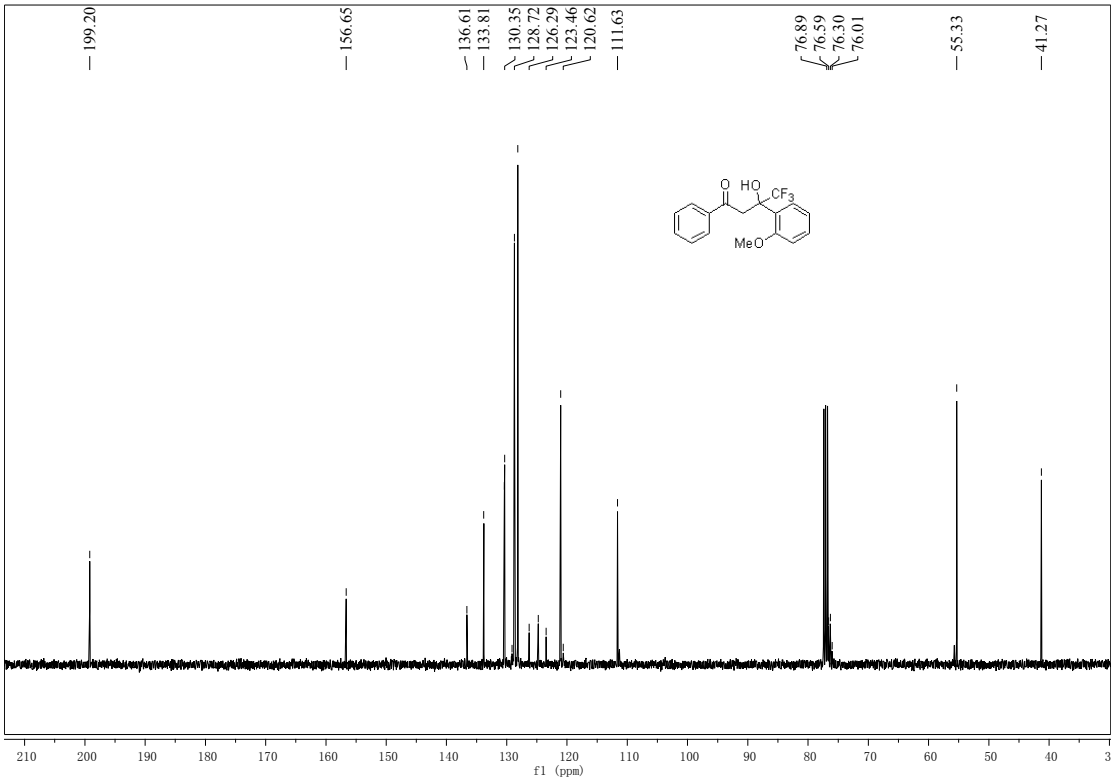
7.90
7.88
7.63
7.53
7.49
7.33
7.31
7.07
7.05
6.85
6.83
5.50
4.79
4.75
3.59
3.51
3.46
O
HO
CF3
MeO
2.00
1.00
1.01
2.00
1.02
1.02
1.01
1.00
1.00
3.01
1.00
f1 (ppm)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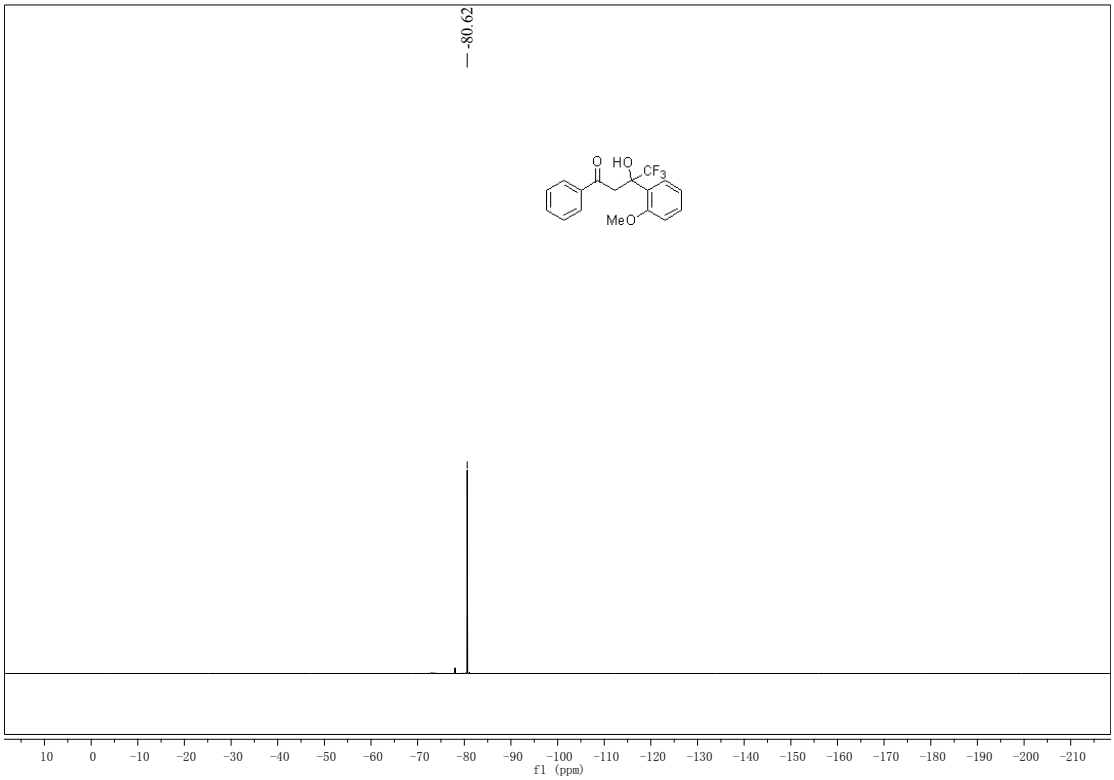
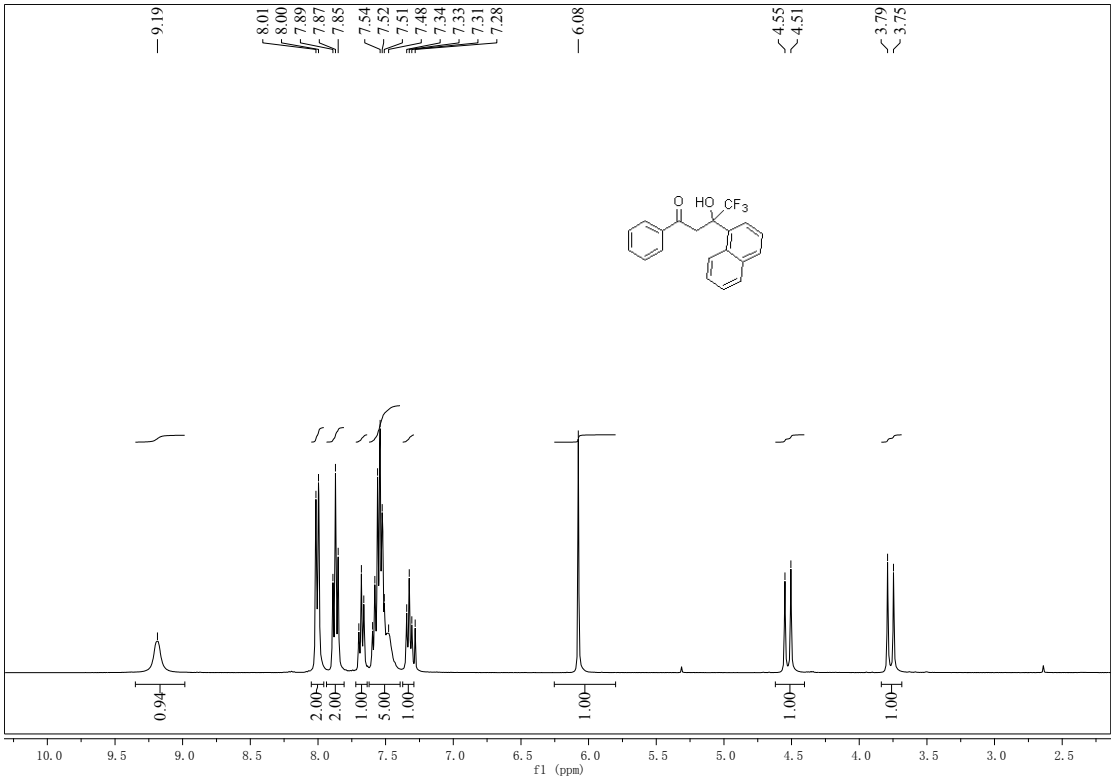
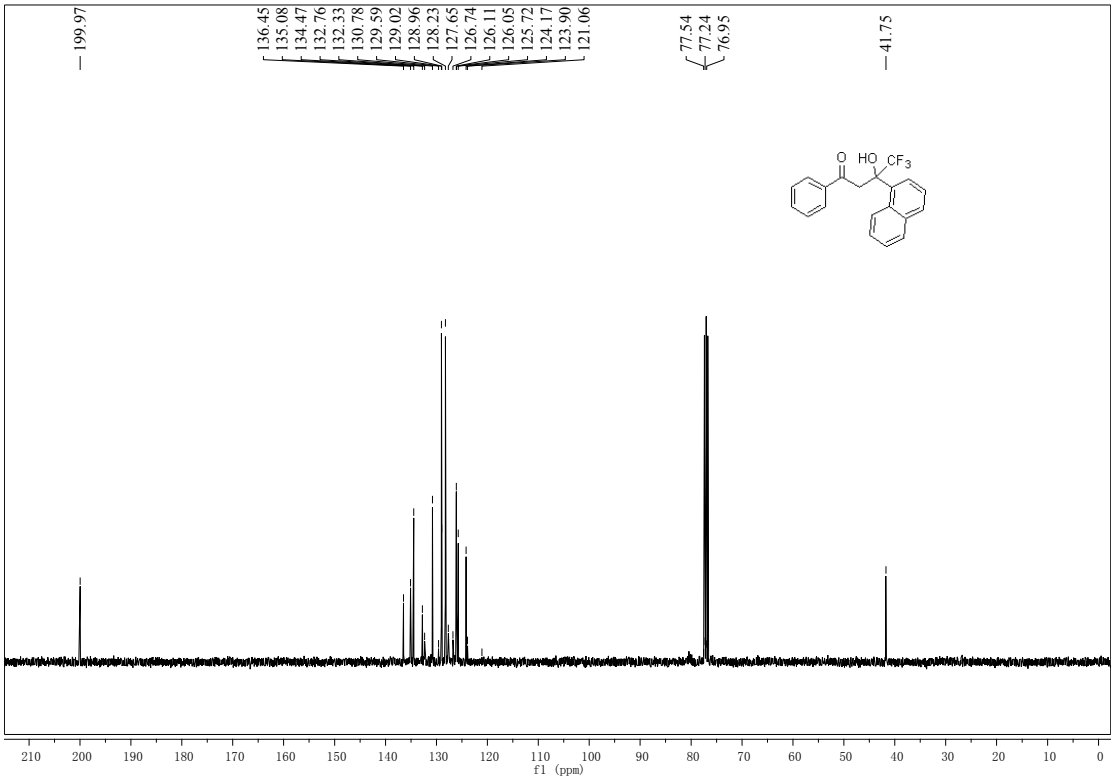
133.81
130.35
128.72
126.29
123.46
120.62
111.63
76.89
76.59
76.30
76.01
55.33
41.27
O
HO
CF3
MeO
f1 (ppm)


-80.62
O
HO
CF3
MeO
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


9.19
8.01
8.00
7.89
7.87
7.85
7.54
7.52
7.51
7.48
7.34
7.33
7.31
7.28
6.08
4.55
4.51
3.79
3.75
O
HO
CF3
0.94
2.00
2.00
1.00
5.00
1.00
1.00
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)


199.97
136.45
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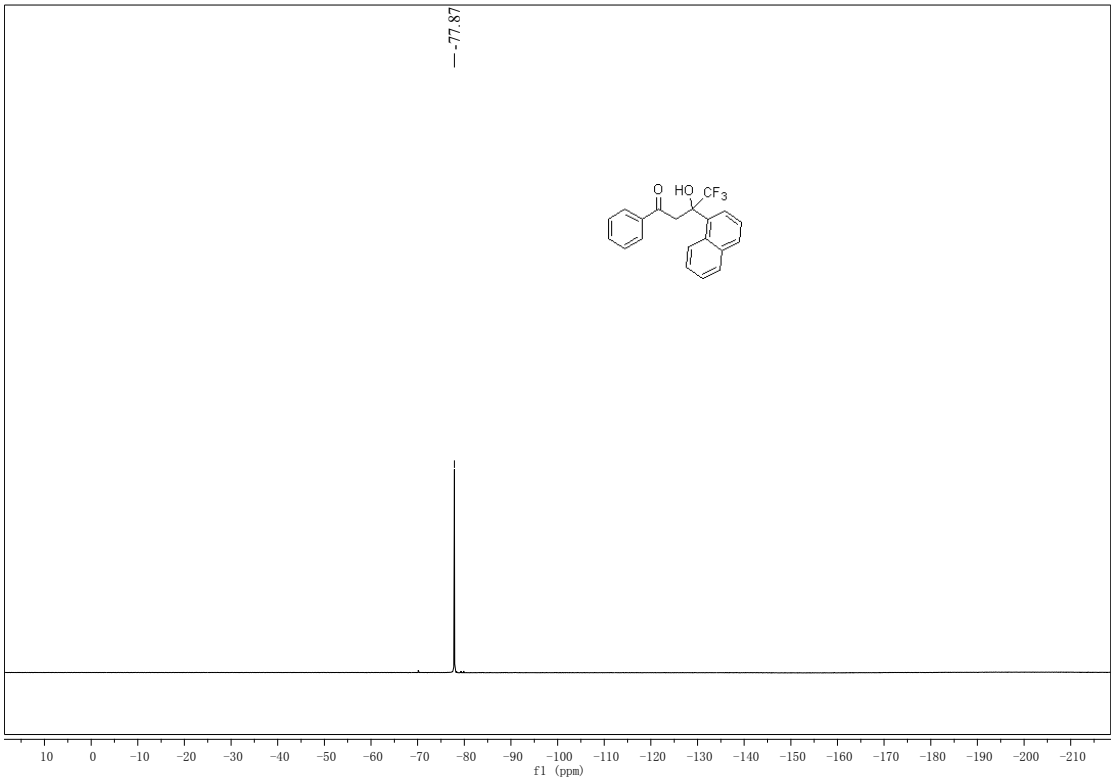
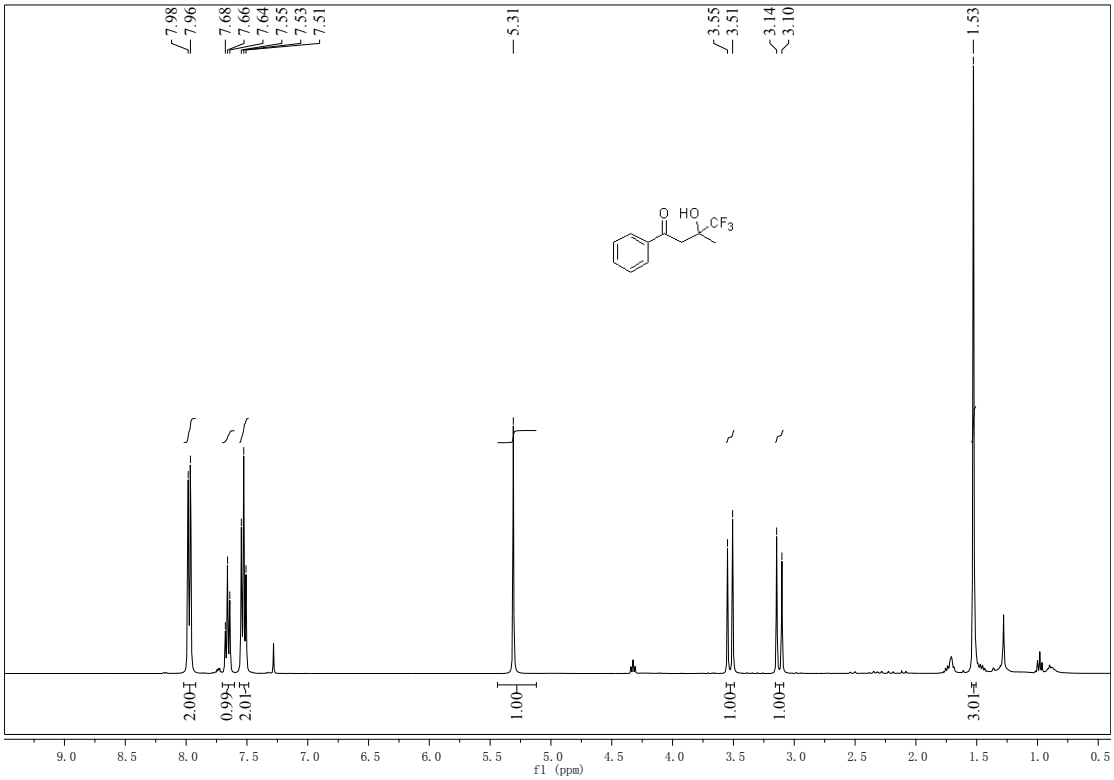
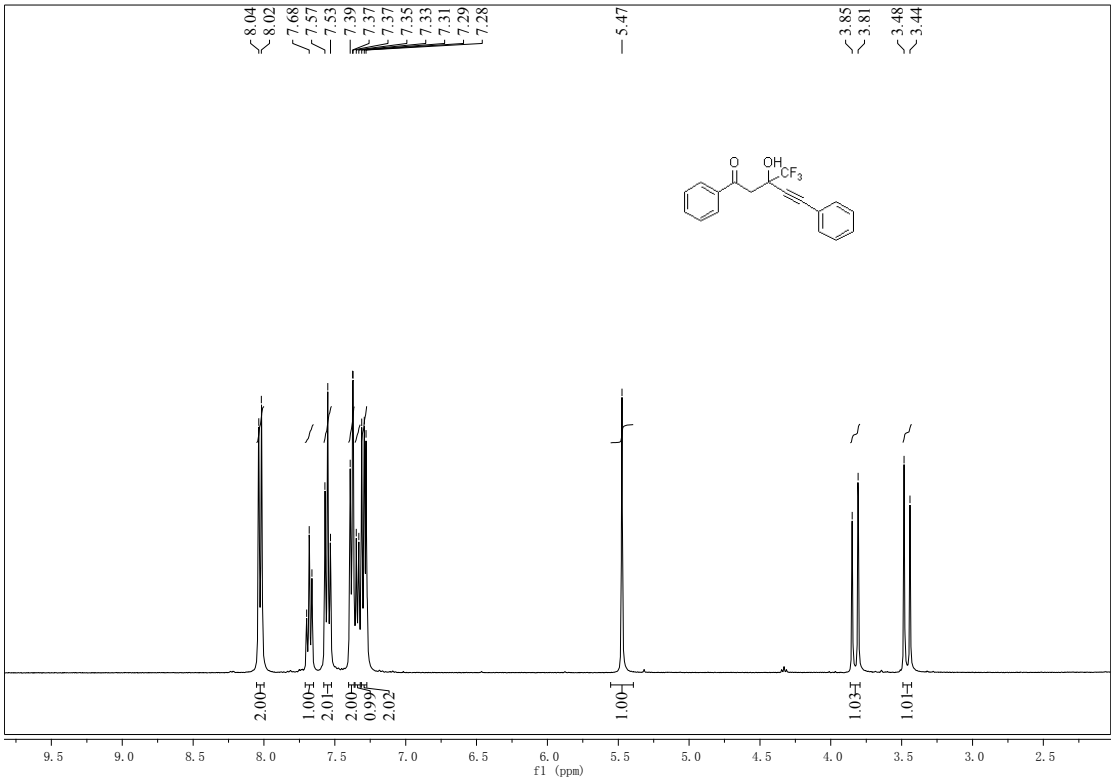
132.76
132.33
130.78
129.59
129.02
128.96
128.23
127.65
126.74
126.11
126.05
125.72
124.17
123.90
121.06
77.54
77.24
76.95
41.75
O
HO
CF3
f1 (ppm)


-77.87
O
HO
CF3
f1 (ppm)


7.98
7.96
7.68
7.66
7.64
7.55
7.53
7.51
5.31
3.55
3.51
3.14
3.10
1.53
O
HO
CF3
2.00
0.99
2.01
1.00
1.00
1.00
3.01
f1 (ppm)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8.02
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7.57
7.53
7.39
7.37
7.37
7.35
7.33
7.31
7.29
7.28
5.47
3.85
3.81
3.48
3.44
O
OH
CF3
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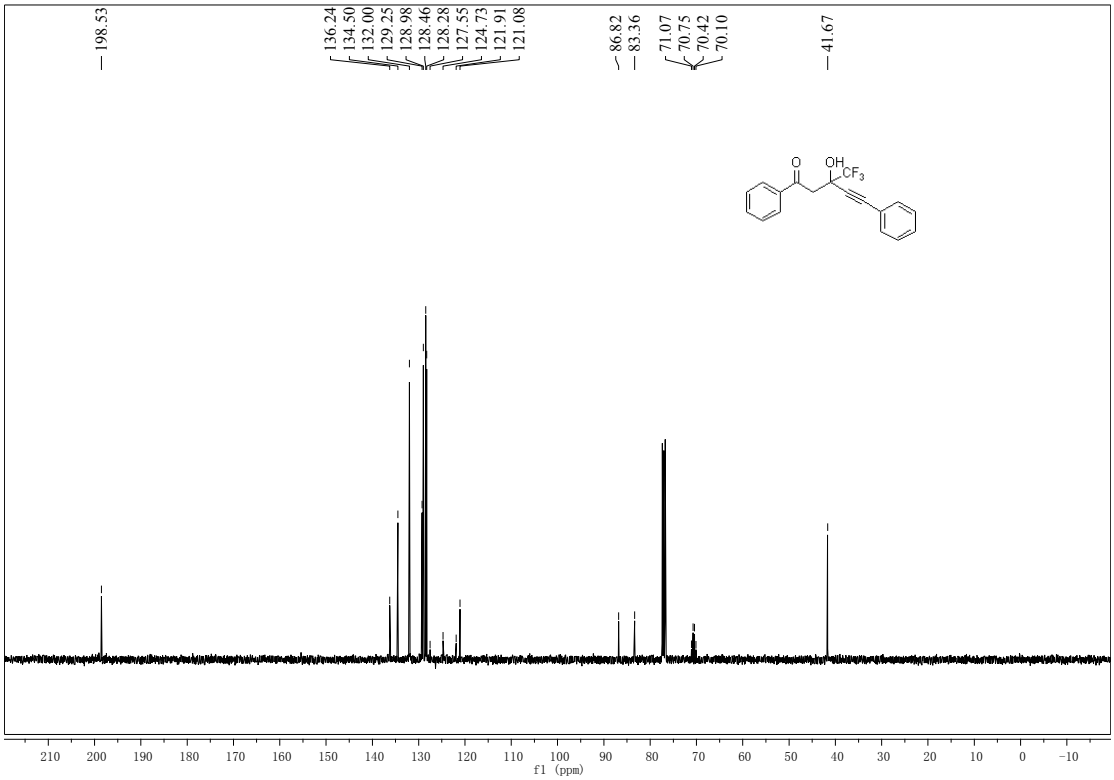
1.00
2.01
2.00
0.99
2.02
1.00
1.03
1.01
f1 (ppm)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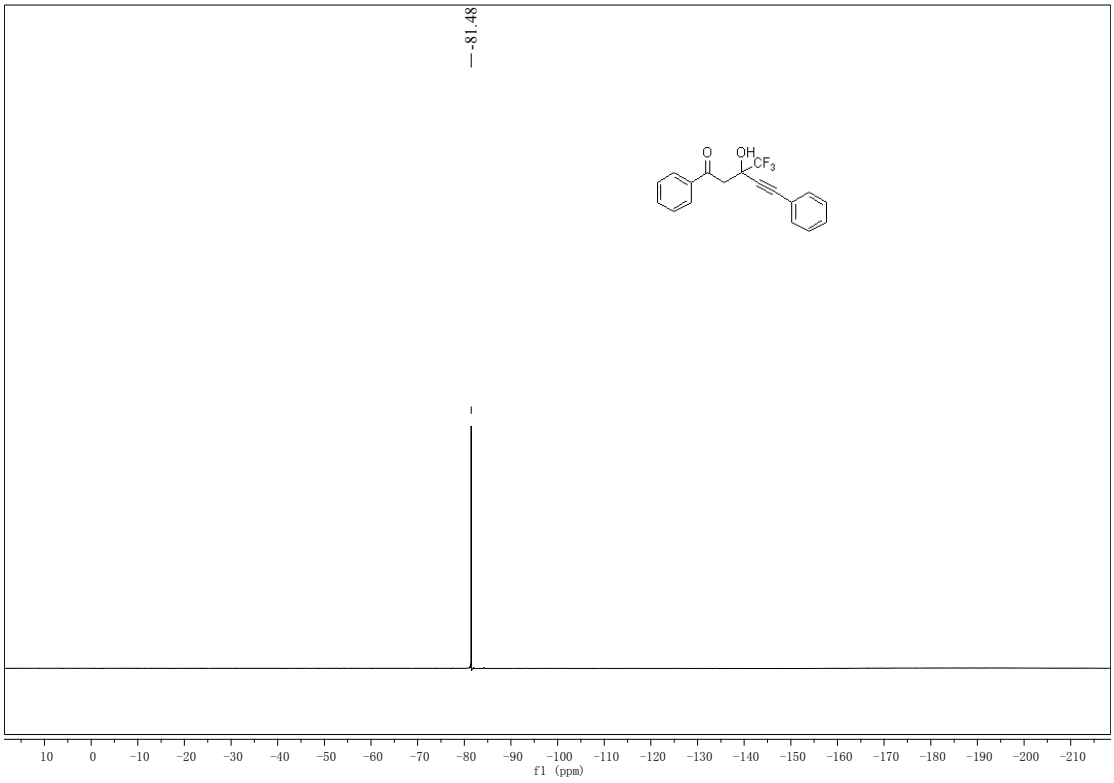
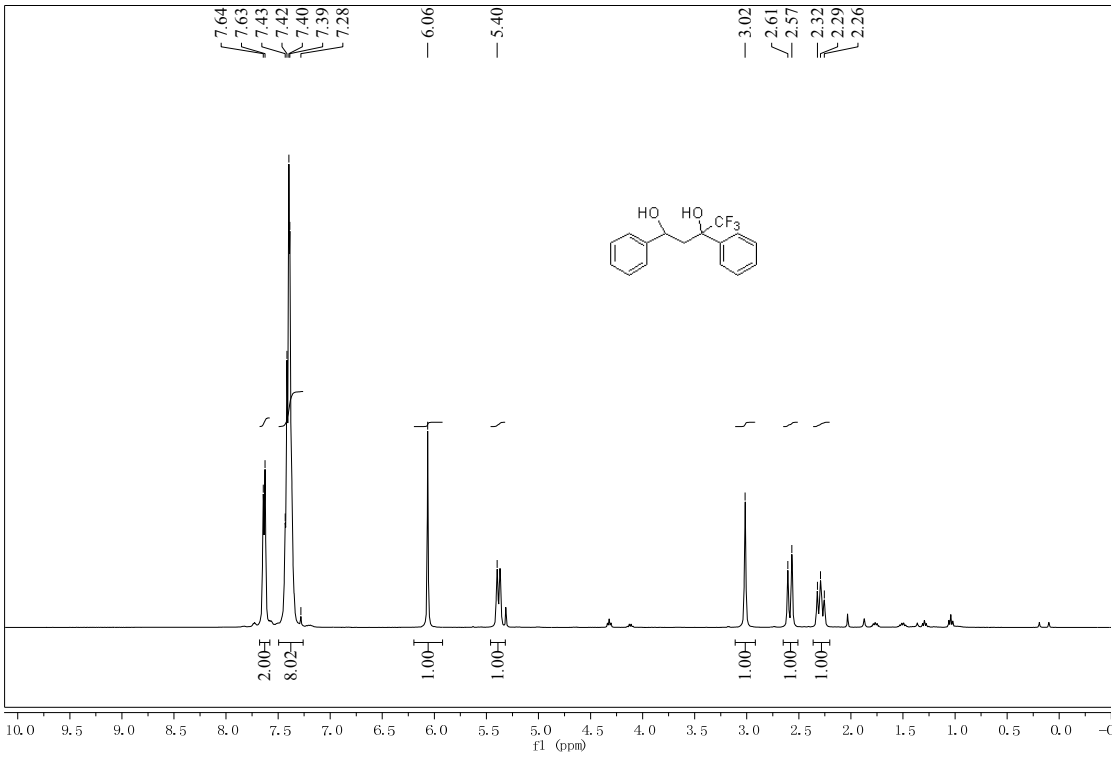
136.24
134.50
132.00
129.25
128.98
128.46
128.28
127.55
124.73
121.91
121.08
86.82
83.36
71.07
70.75
70.42
70.10
41.67
O
OH
CF3
f1 (ppm)


-81.48
O
OH
CF3
f1 (ppm)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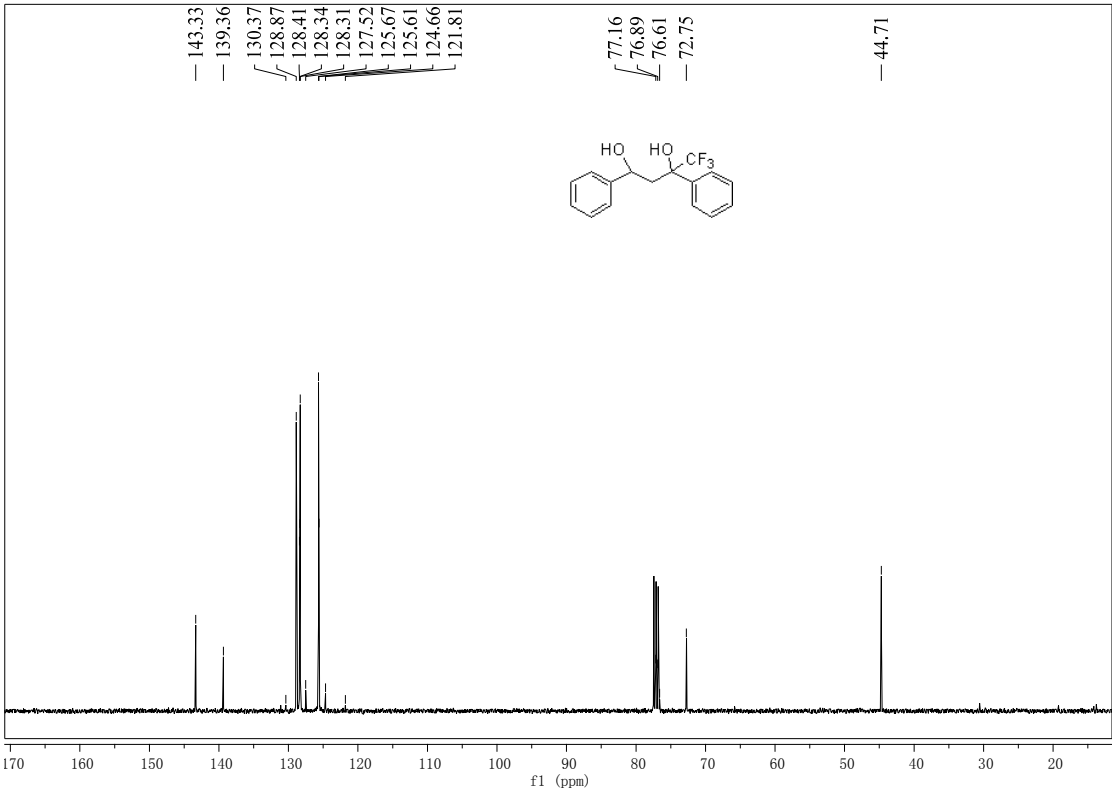
7.63
7.43
7.42
7.40
7.39
7.28
6.06
5.40
3.02
2.61
2.57
2.32
2.29
2.26
HO
HO
CF3
2.00
8.02
1.00
1.00
1.00
1.00
1.00
f1 (ppm)


143.33
139.36
130.37
128.87
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128.34
128.31
127.52
125.67
125.61
124.66
121.81
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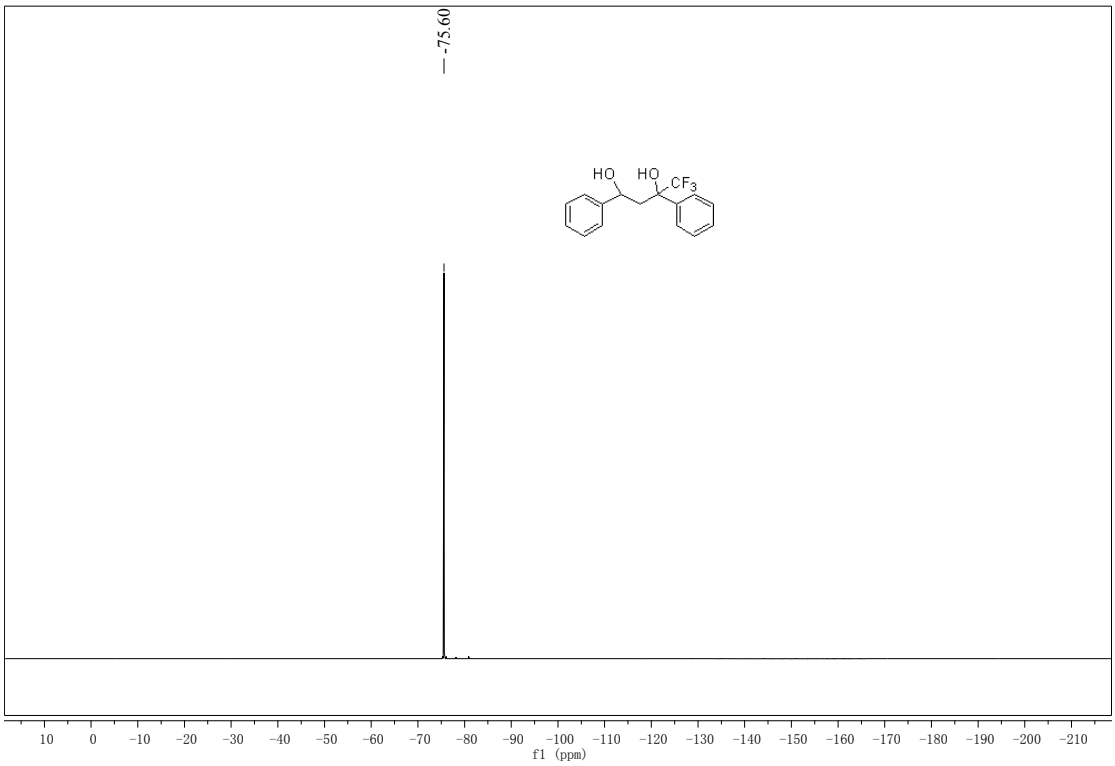
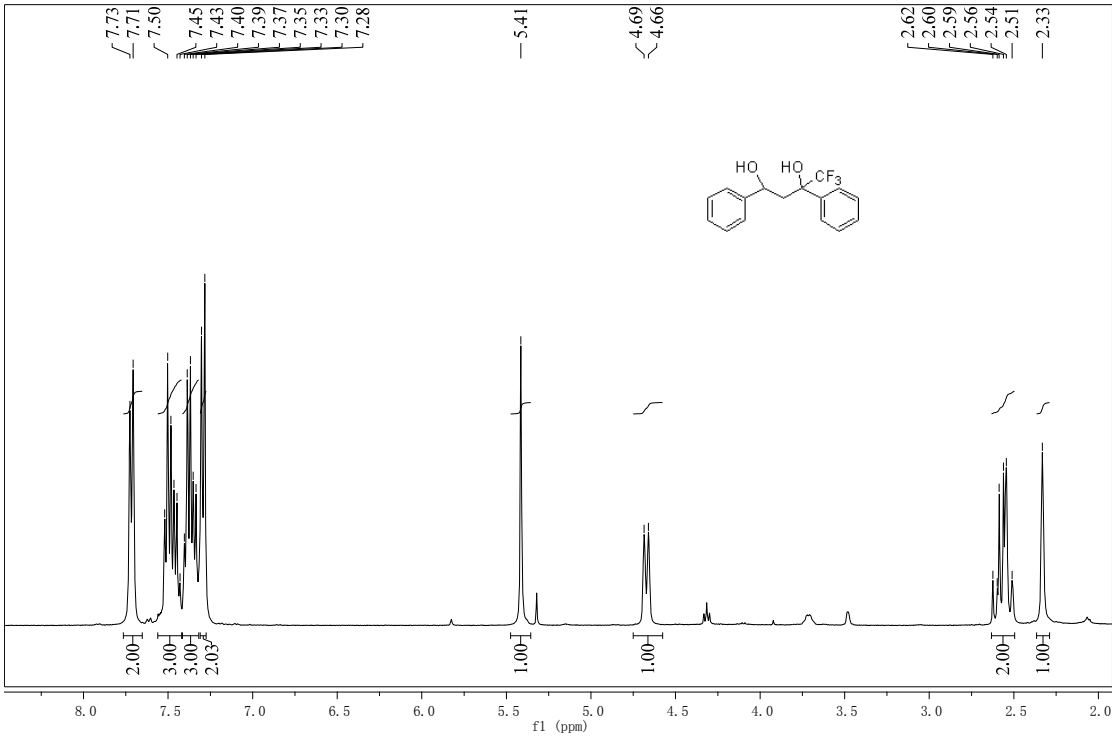
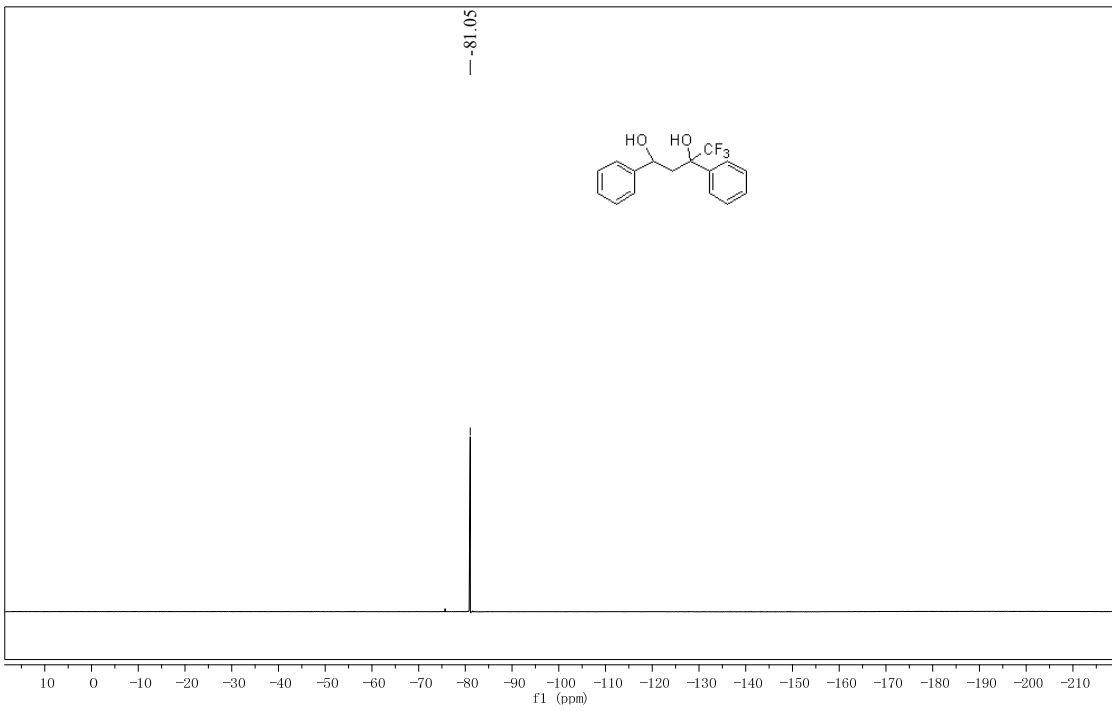
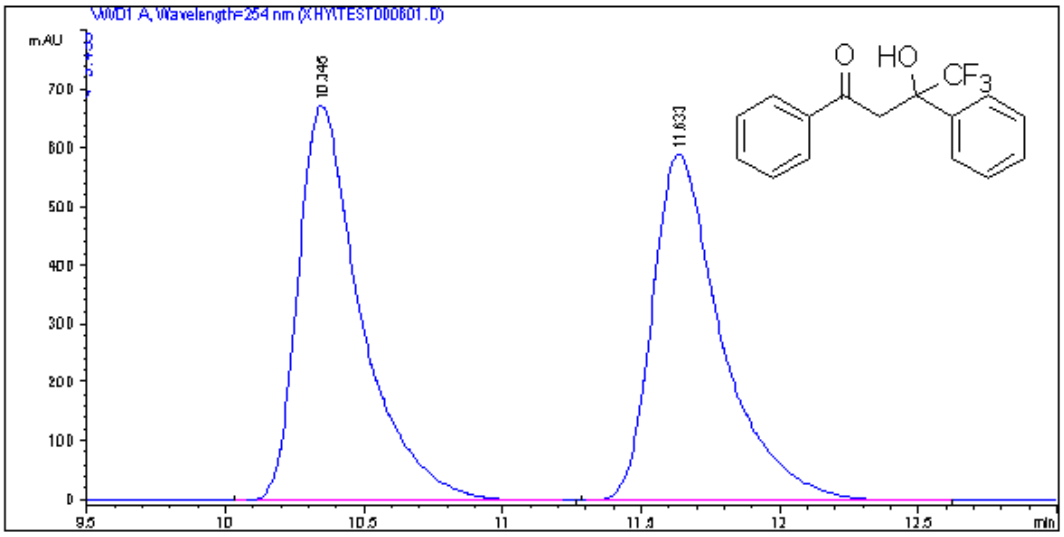
72.75
44.71
HO
HO
CF3
f1 (ppm)


-75.60
HO
HO
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


7.73
7.71
7.50
7.45
7.43
7.40
7.39
7.37
7.35
7.33
7.30
7.28
5.41
4.69
4.66
2.62
2.60
2.59
2.56
2.54
2.51
2.33
HO
HO
CF3
2.00
3.00
3.00
2.03
1.00
1.00
2.00
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)

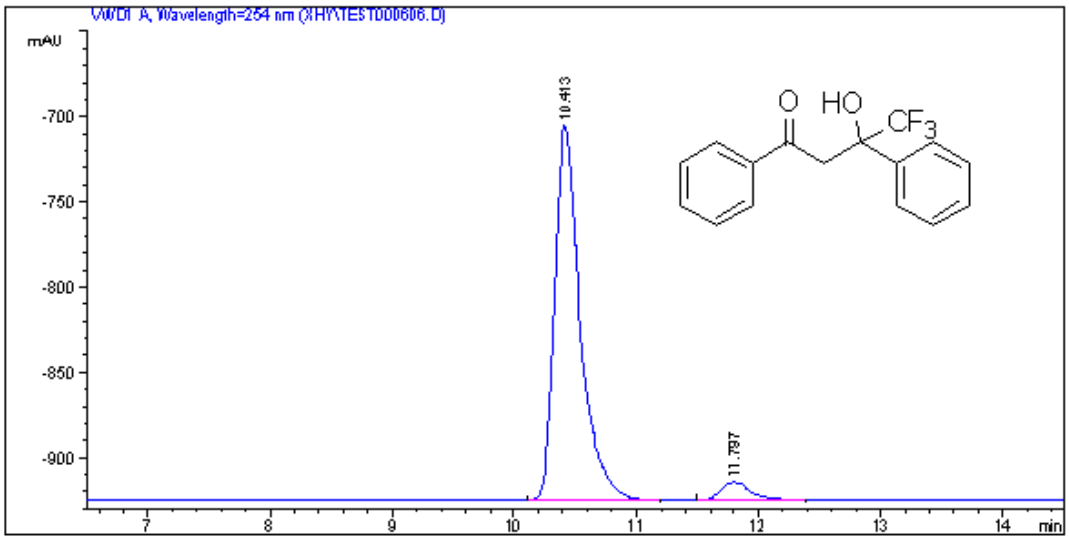

-81.05
HO
HO
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

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



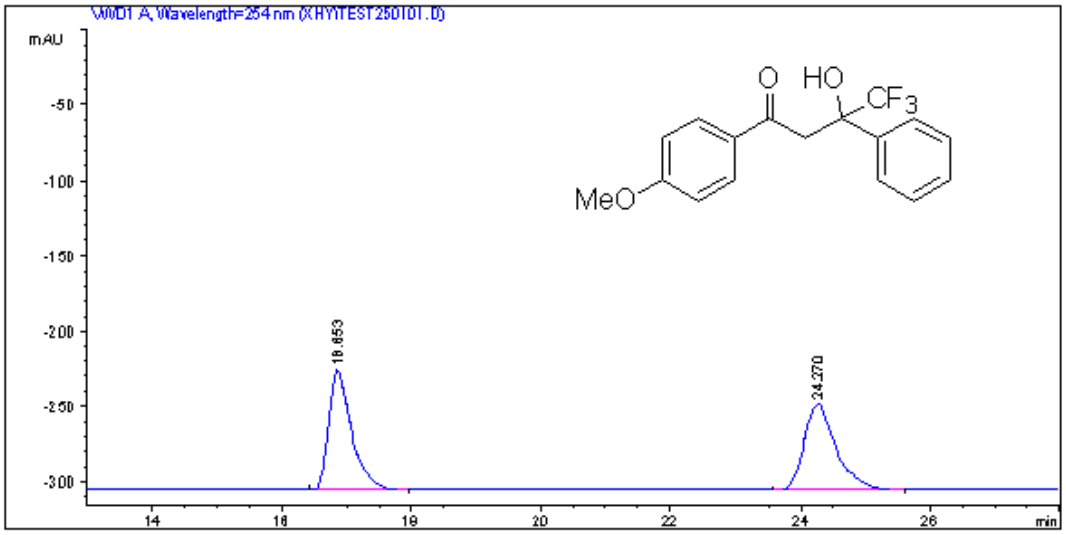
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.345	BB	0.2336	1.06421e4	674.35602	50.9120
2	11.633	BB	0.2579	1.02609e4	591.02728	49.0880

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



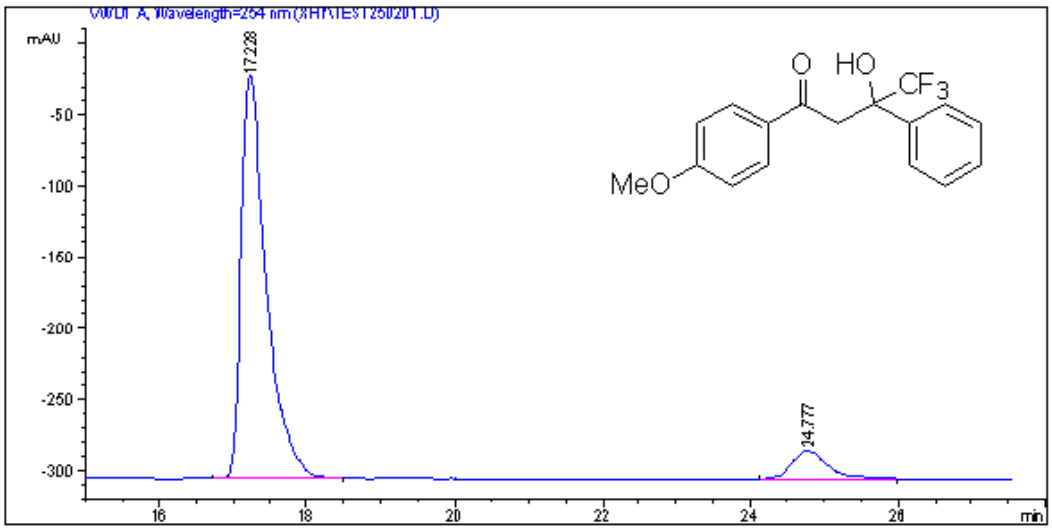
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.413	BB	0.2171	3175.30225	219.08656	94.9599
2	11.797	BB	0.2449	168.53099	10.29410	5.0401

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



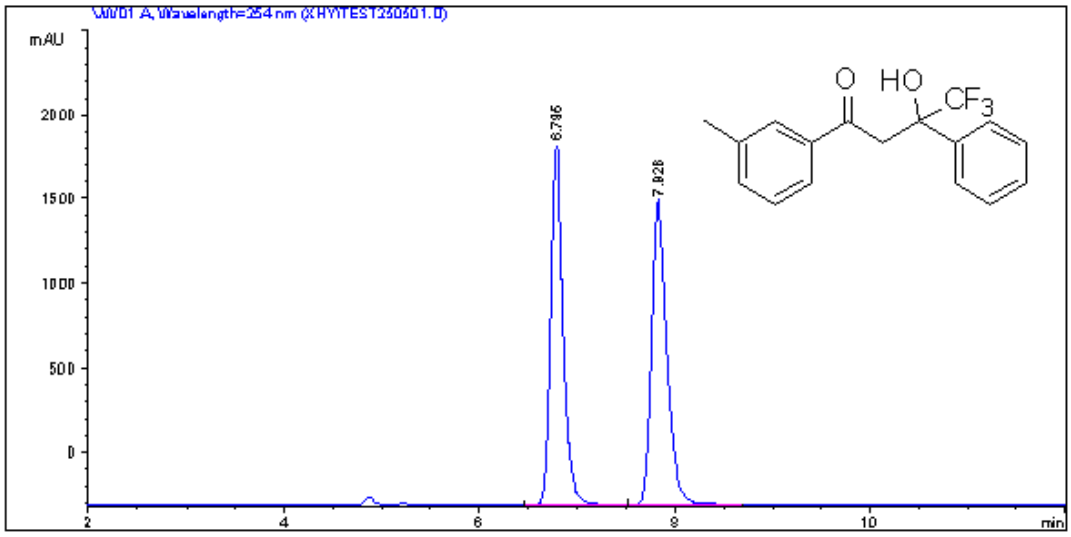
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.853	VB	0.3623	1944.93579	79.99121	49.8302
2	24.270	BB	0.5176	1958.19409	56.75356	50.1698

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



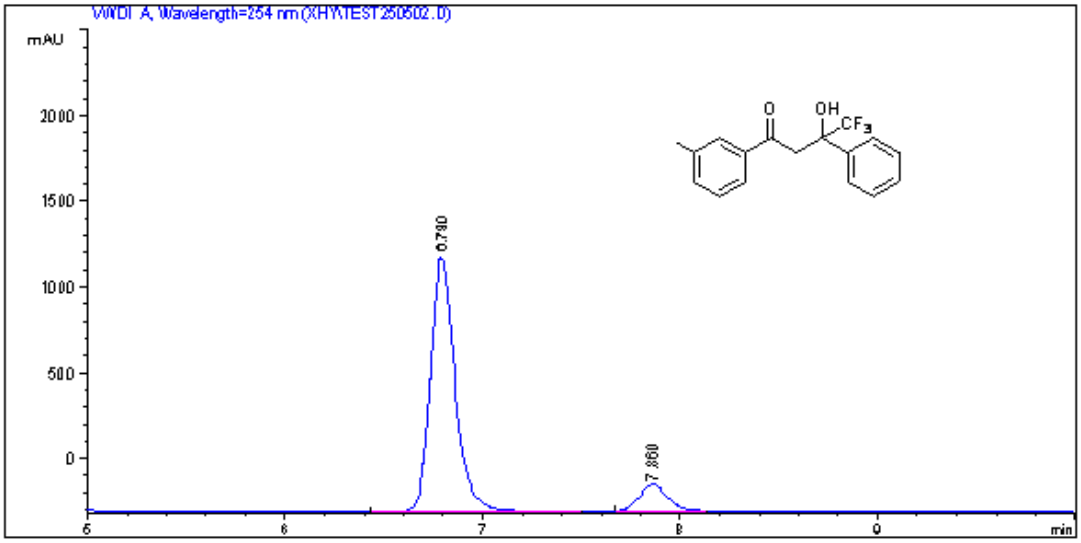
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.228	BB	0.3494	6691.66406	283.72665	90.6676
2	24.777	BB	0.5217	688.76941	19.82883	9.3324

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



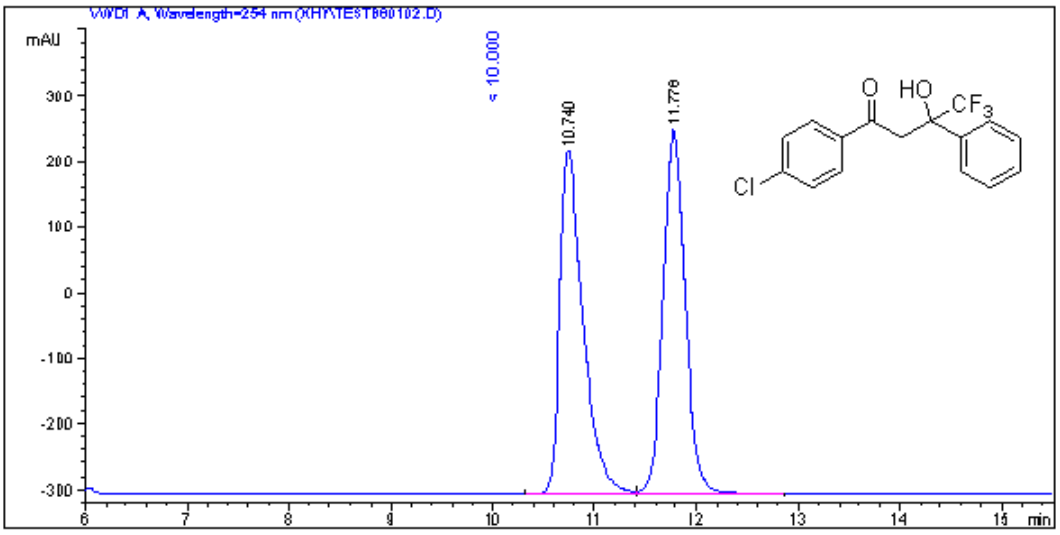
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.785	BV	0.1372	1.88794e4	2124.51978	49.2736
2	7.926	VV	0.1659	1.94361e4	1900.20923	50.7264

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



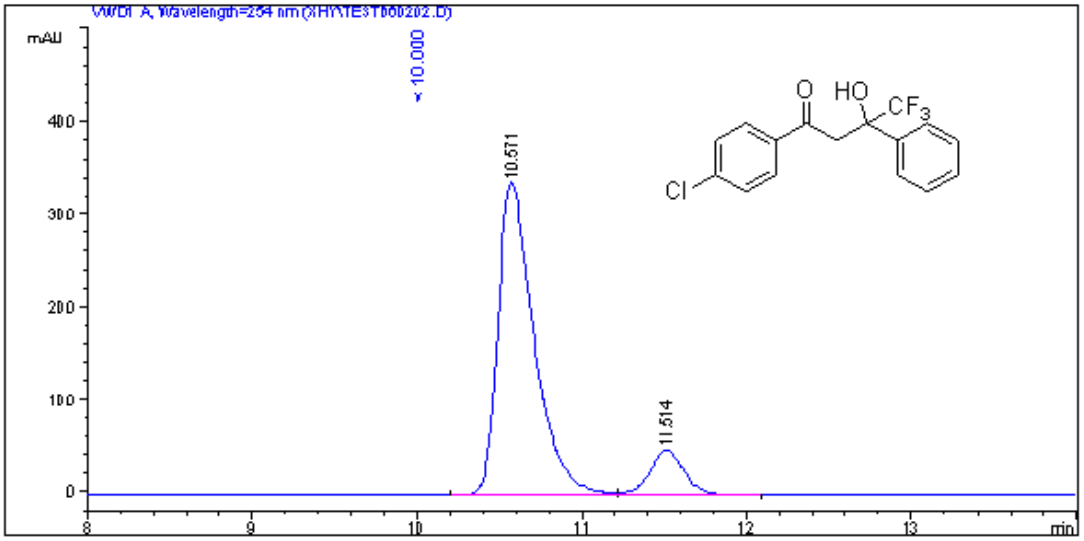
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.790	BBA	0.1306	1.27204e4	1483.53674	89.6054
2	7.860	BBA	0.1505	1475.61328	150.81812	10.3946

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



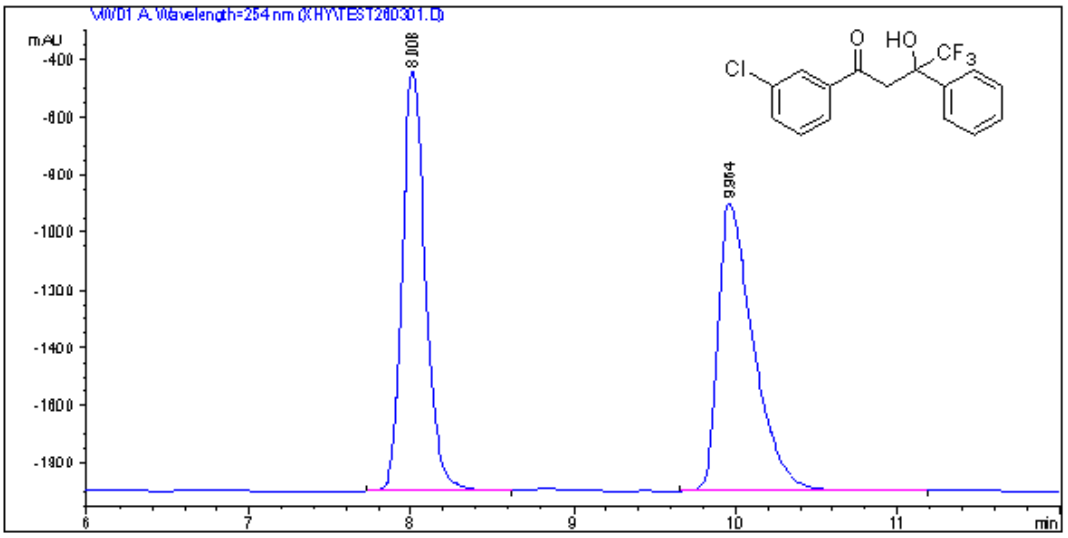
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.740	BV	0.2356	8273.70898	522.66748	49.7915
2	11.776	VB	0.2308	8342.98535	554.70966	50.2085

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



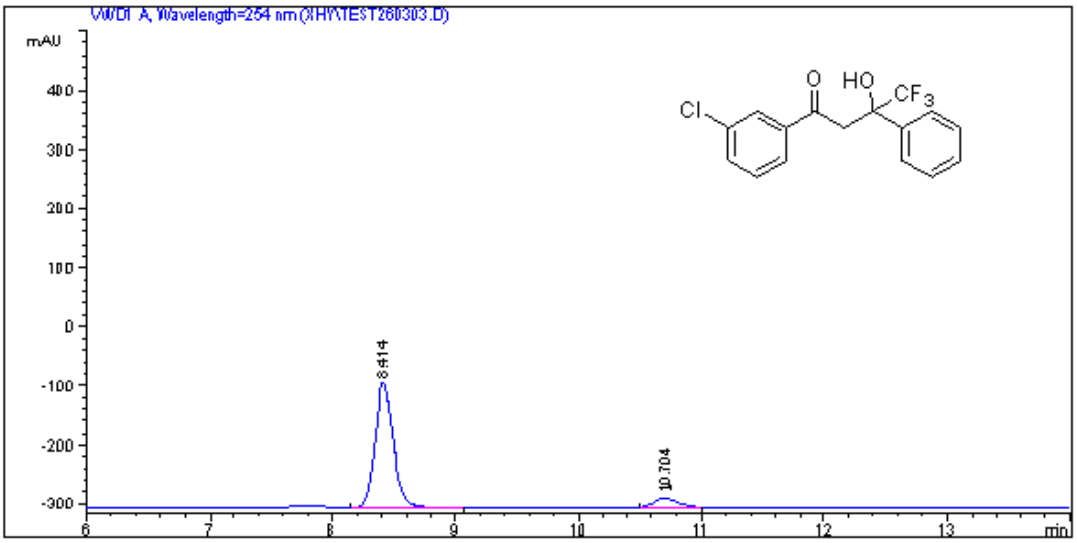
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.571	BV	0.2277	5146.08887	336.85852	88.0498
2	11.514	VB	0.2242	698.43268	47.43889	11.9502

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



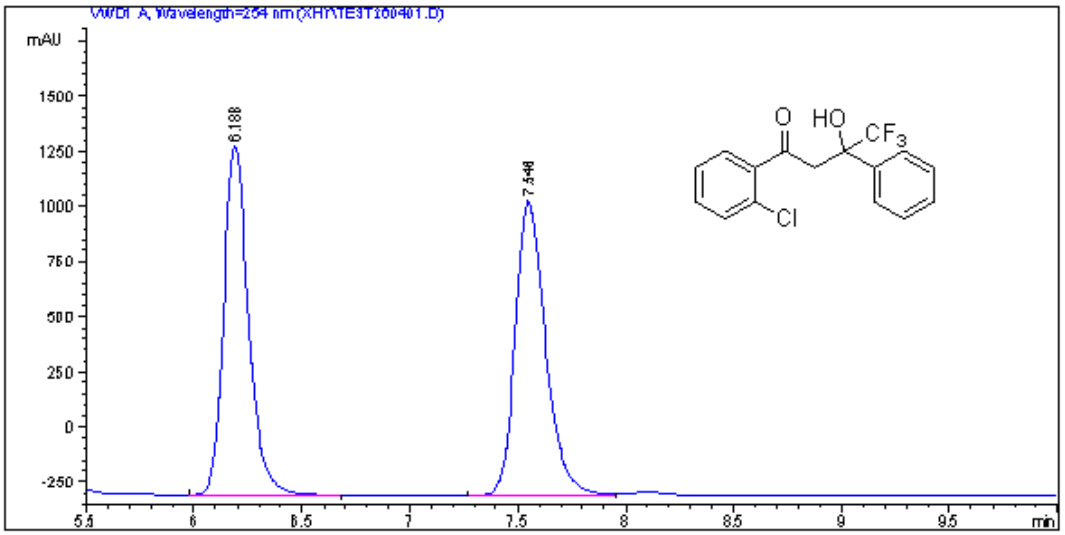
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.008	BV	0.1542	1.45187e4	1456.01428	48.9951
2	9.964	BB	0.2231	1.51142e4	998.77356	51.0049

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



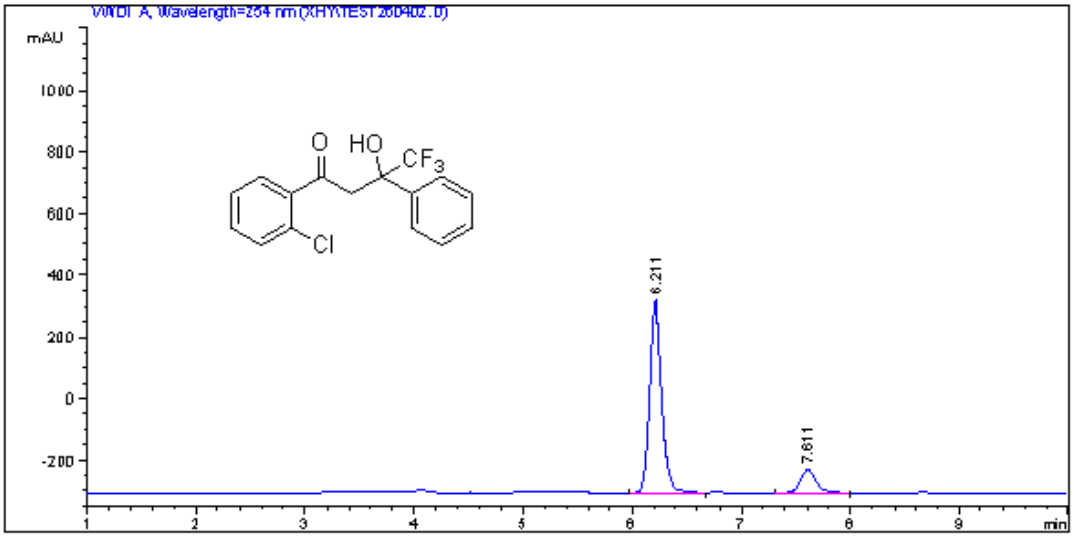
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.414	BB	0.1588	2192.37524	211.45419	90.1092
2	10.704	PM	0.2354	240.64543	17.03605	9.8908

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



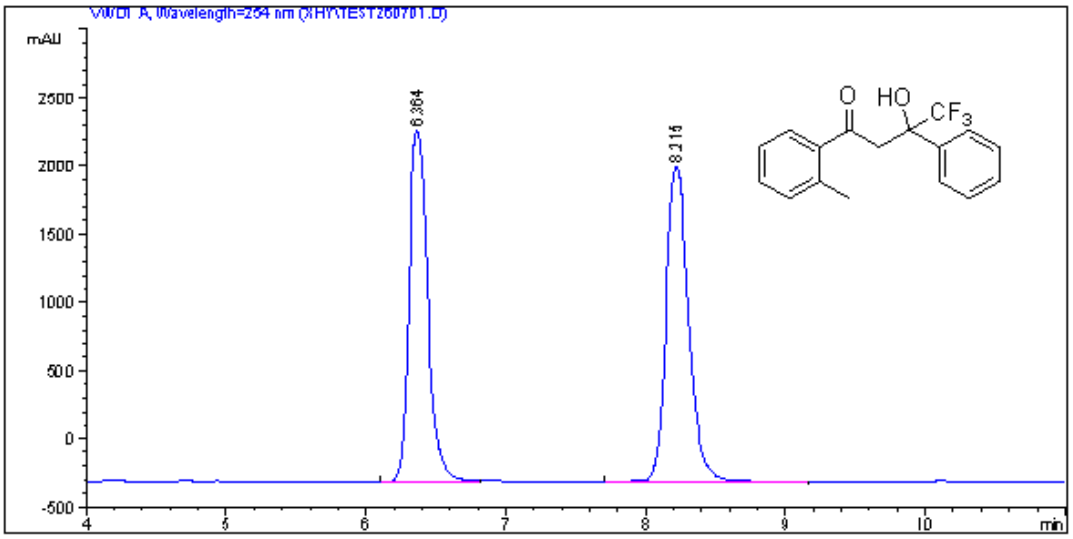
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.188	BV	0.1218	1.25207e4	1576.75220	49.1905
2	7.548	VV	0.1481	1.29328e4	1333.60181	50.8095

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



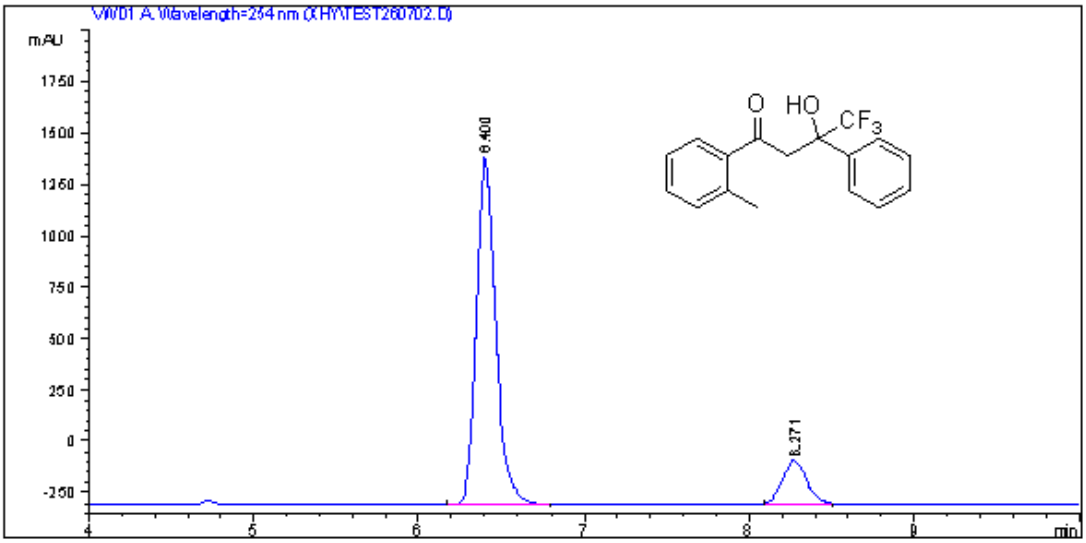
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.211	BV	0.1177	4874.79693	631.37695	86.0187
2	7.611	VV	0.1477	792.32648	80.90234	13.9813

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



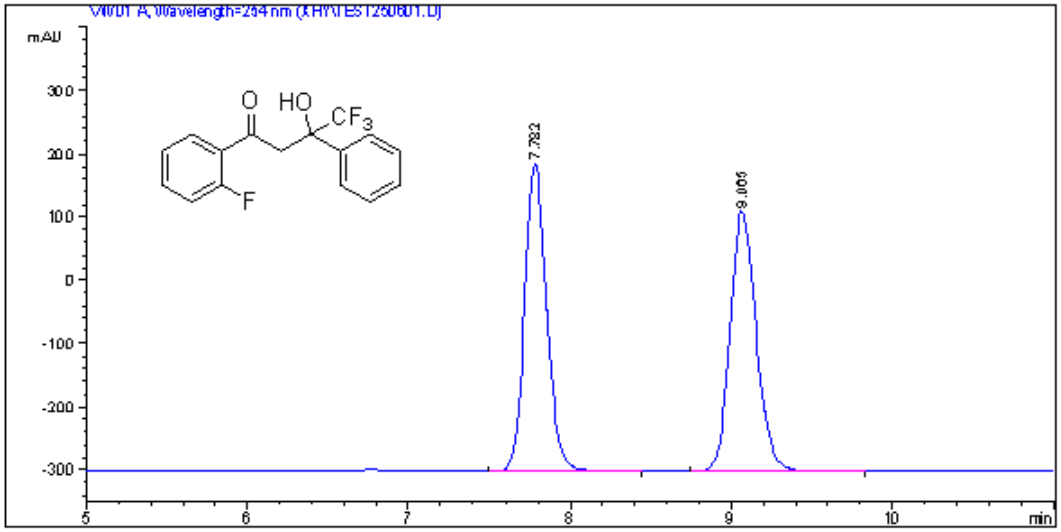
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.364	BV	0.1439	2.36294e4	2565.30005	47.8887
2	8.215	BBA	0.1738	2.57130e4	2304.75610	52.1113

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



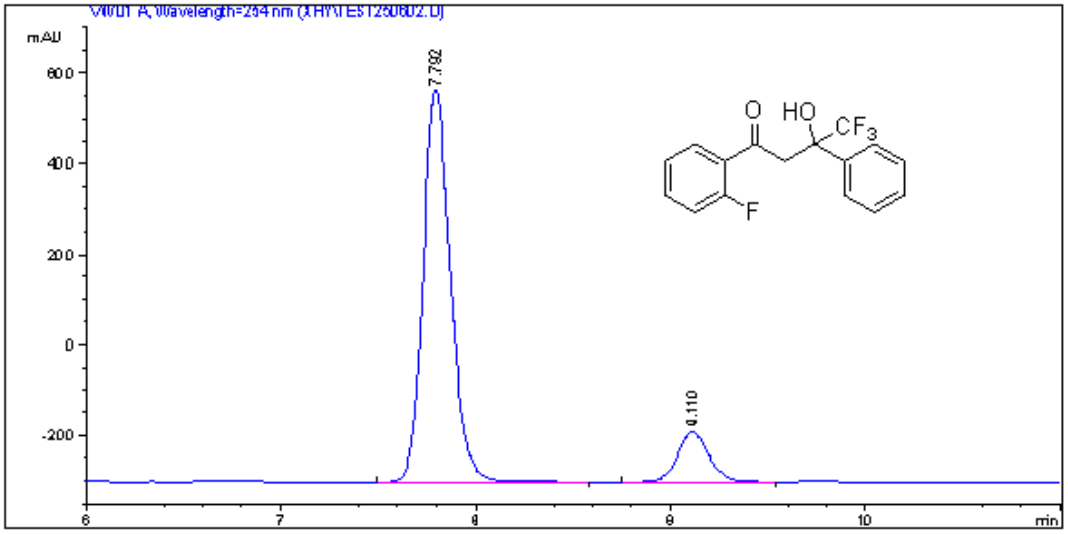
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.400	BV	0.1244	1.37810e4	1688.20178	86.9893
2	8.271	MM	0.1660	2061.17969	206.89876	13.0107

Sample Info : 254nm, IA, 1-PrOH : Hexane =5:95, 1.0 mL/min



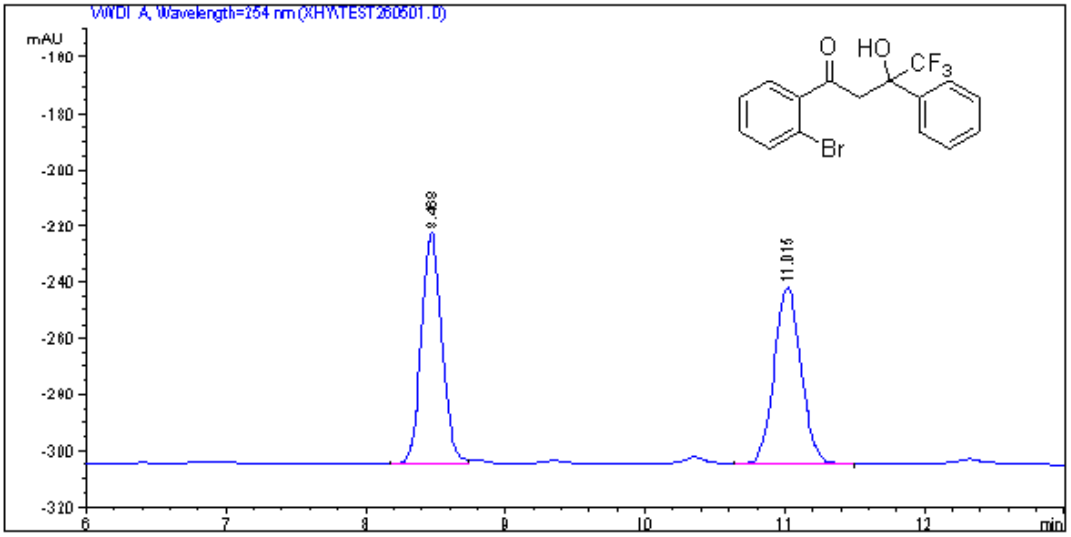
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.782	BB	0.1458	4625.68896	486.91644	49.9450
2	9.065	BB	0.1737	4635.86963	411.46271	50.0550

Sample Info : 254nm, IA, 1-PrOH : Hexane =5:95, 1.0 mL/min



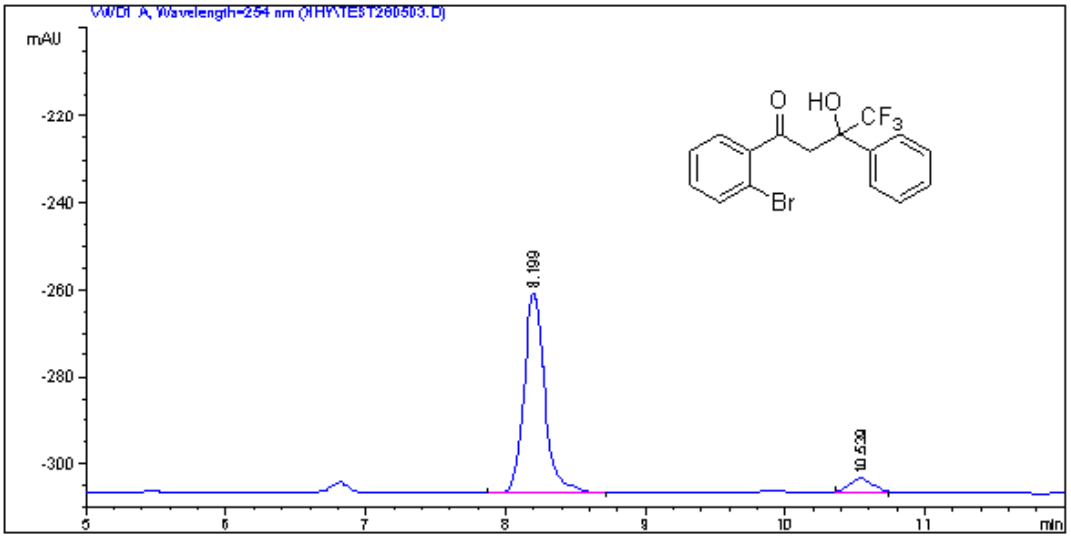
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.792	BB	0.1500	8431.02930	865.69745	87.3241
2	9.110	BB	0.1690	1223.83691	111.30621	12.6759

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



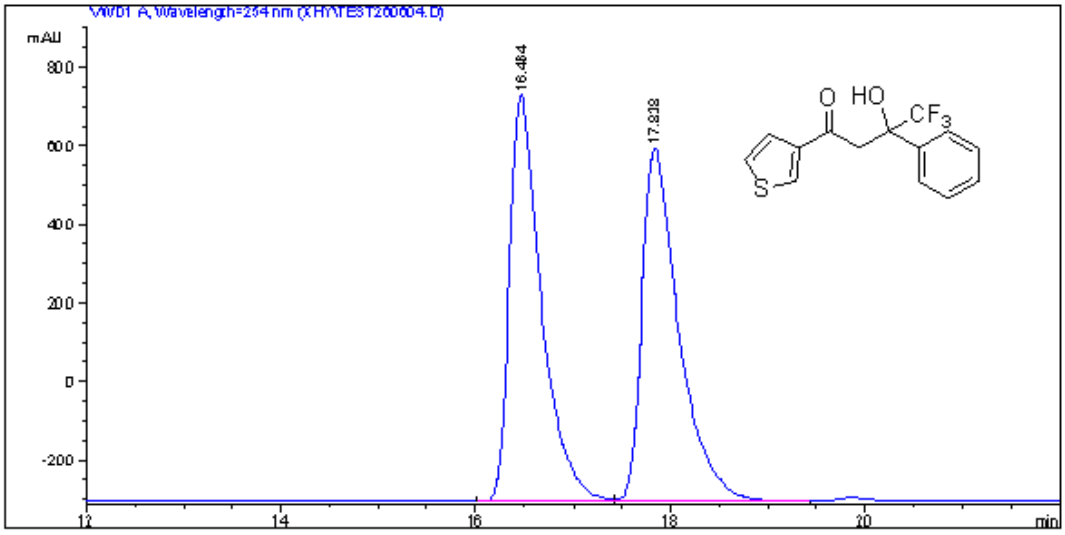
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.468	BV	0.1580	852.30127	82.78377	49.9035
2	11.015	VB	0.2086	855.59894	63.33408	50.0965

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



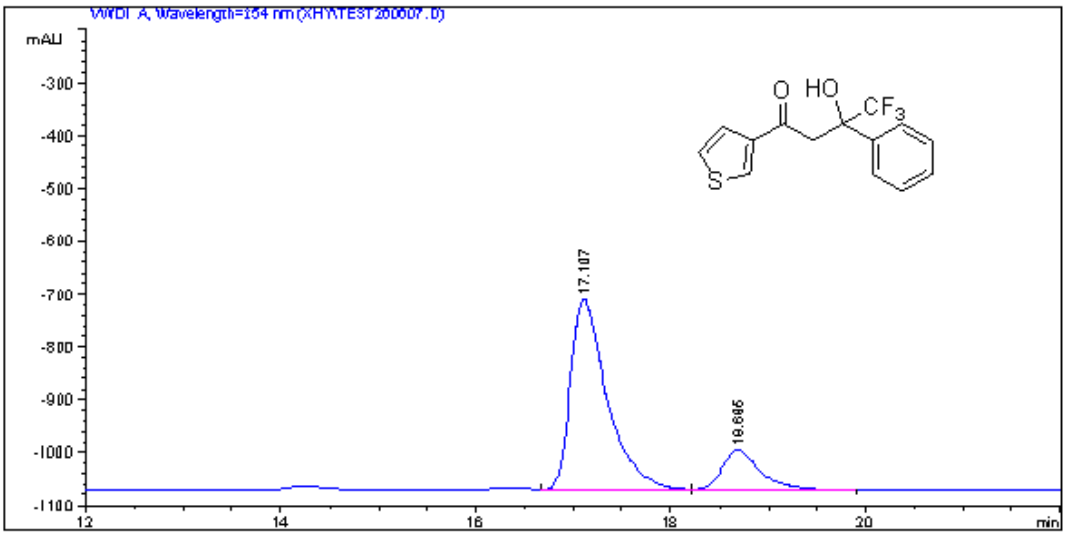
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.199	VB	0.1552	469.58450	46.10499	92.9218
2	10.539	MM	0.1865	35.76990	3.19612	7.0782

Sample Info : 254nm, AD, i-PrOH : Hexane =3:97, 1.0 mL/min



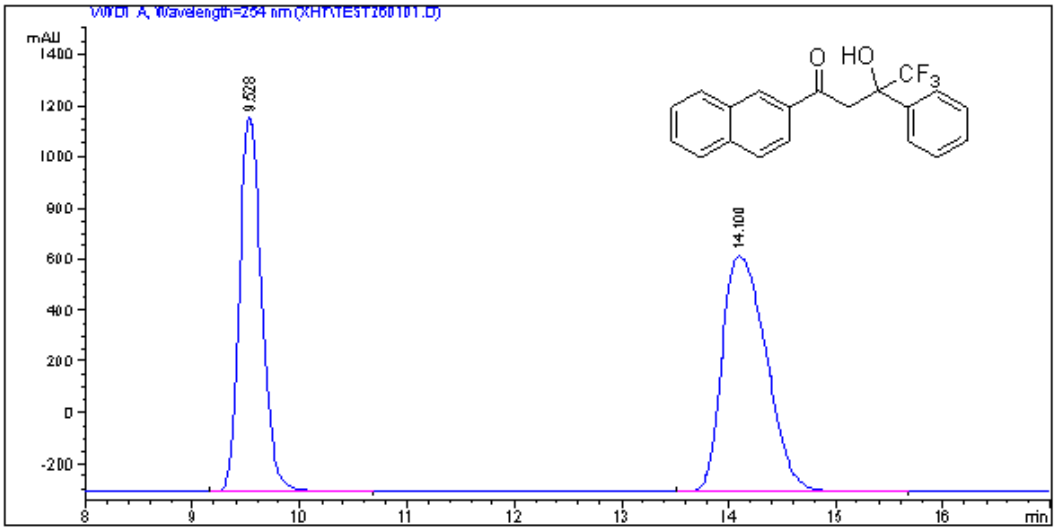
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.464	BV	0.3391	2.36012e4	1034.15247	49.8707
2	17.838	VB	0.3919	2.37236e4	900.22760	50.1293

Sample Info : 254 nm, AD, i-PrOH : Hexane =3:97, 1.0 mL/min



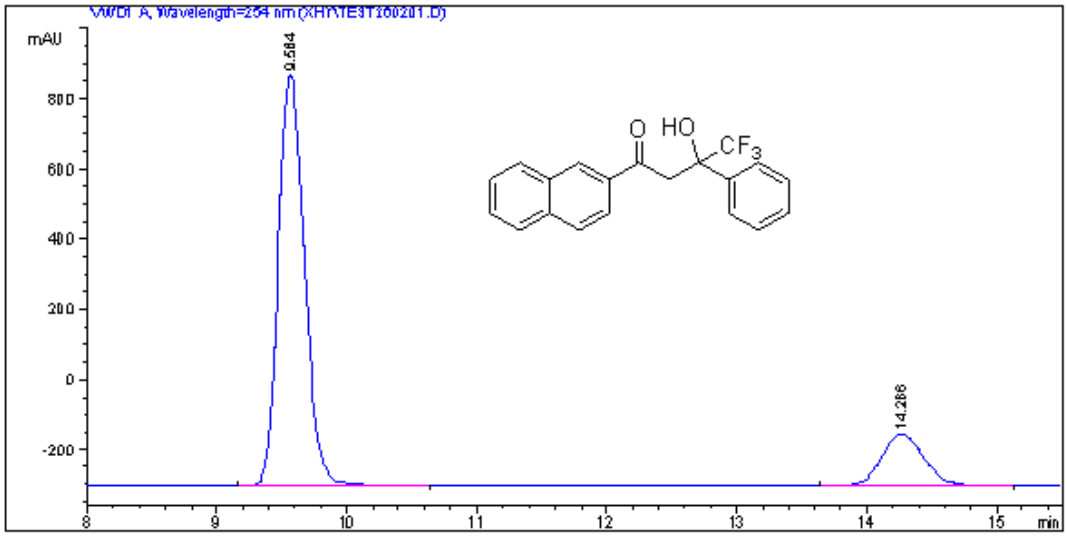
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.107	VV	0.3887	9418.10059	361.19415	82.3357
2	18.685	VB	0.3978	2020.56177	75.59193	17.6643

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



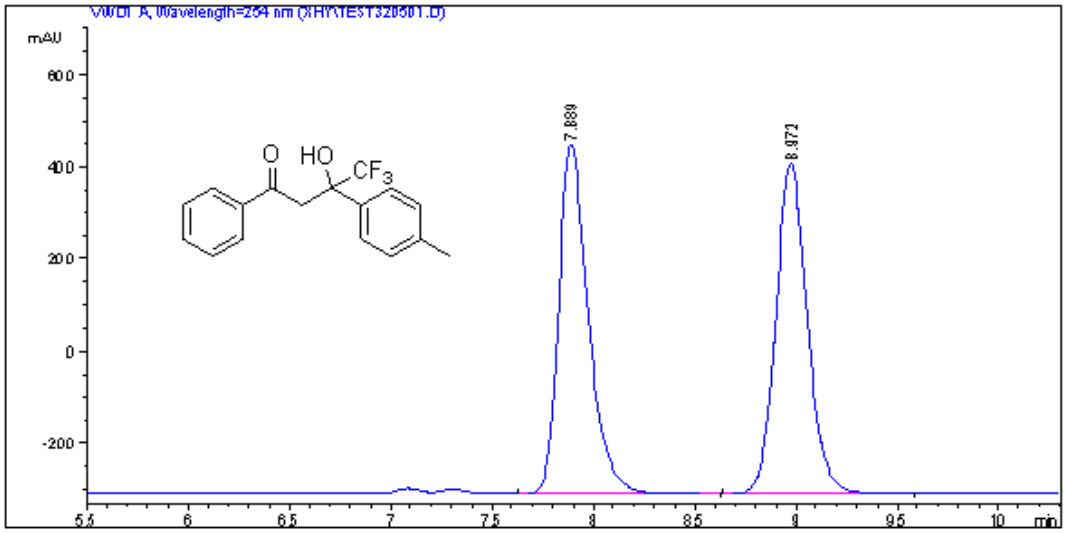
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.528	BB	0.2284	2.11167e4	1460.44385	44.5262
2	14.100	BB	0.4695	2.63087e4	922.60431	55.4738

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



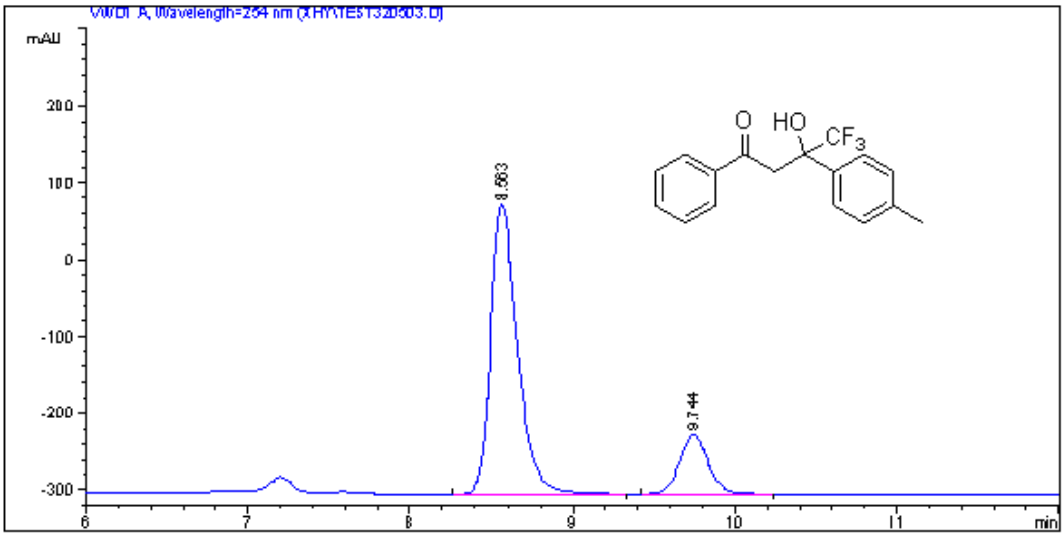
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.564	VB	0.2235	1.65159e4	1176.37122	82.9189
2	14.266	BB	0.3602	3402.24268	148.66226	17.0811

Sample Info : 254nm, IA, 1-PrOH : Hexane =5:95, 1.0 mL/min



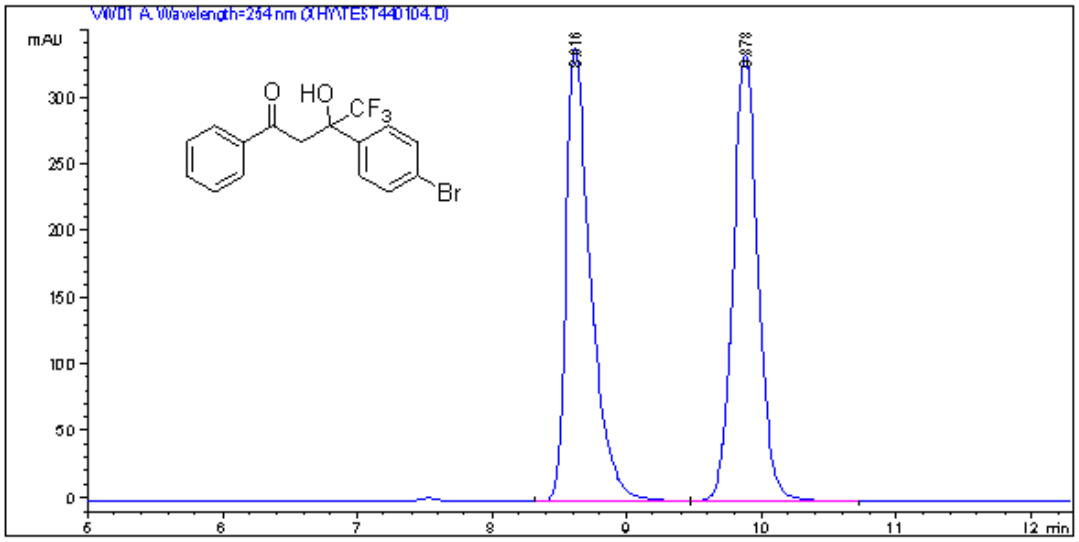
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.889	BB	0.1538	7715.91846	757.29388	49.8968
2	8.972	BB	0.1658	7747.82324	714.84766	50.1032

Sample Info : 254nm, IA, 1-PrOH : Hexane =5:95, 1.0 mL/min



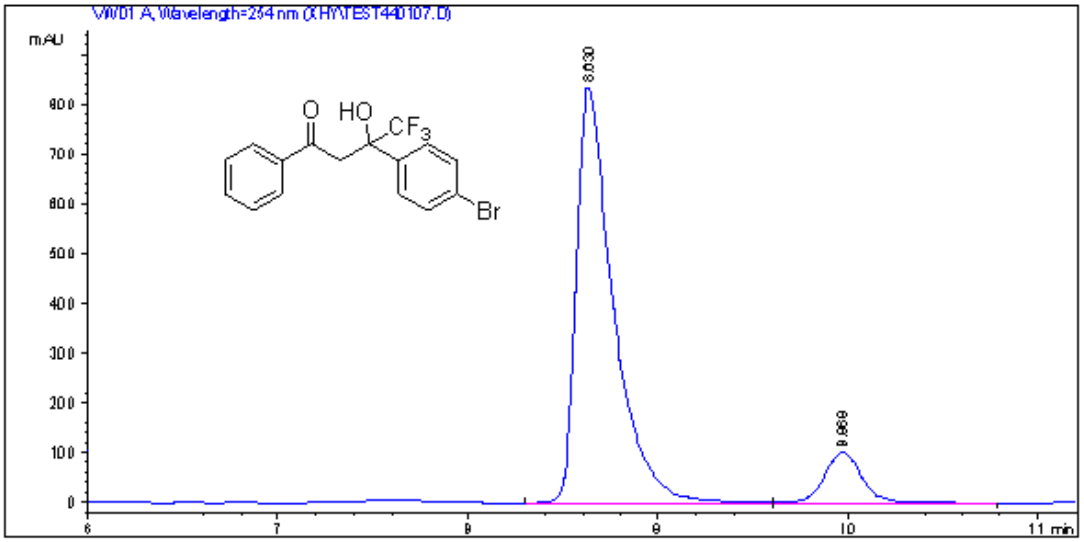
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.563	BB	0.1716	4277.38721	377.26776	82.0345
2	9.744	BB	0.1868	936.74500	77.11848	17.9655

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



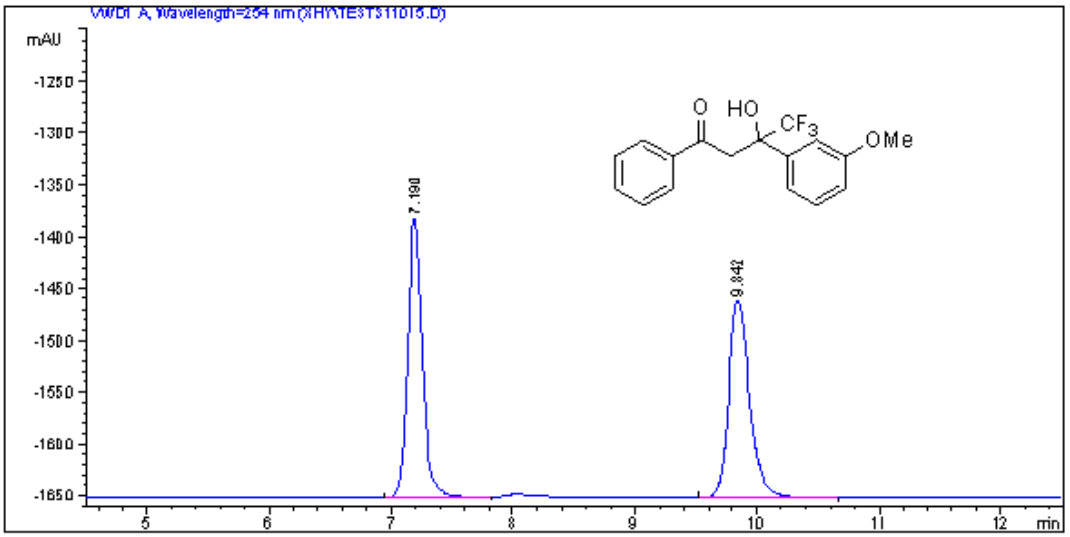
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.616	BV	0.1896	4342.29395	340.29694	50.0388
2	9.878	VB	0.1992	4335.55762	334.56906	49.9612

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



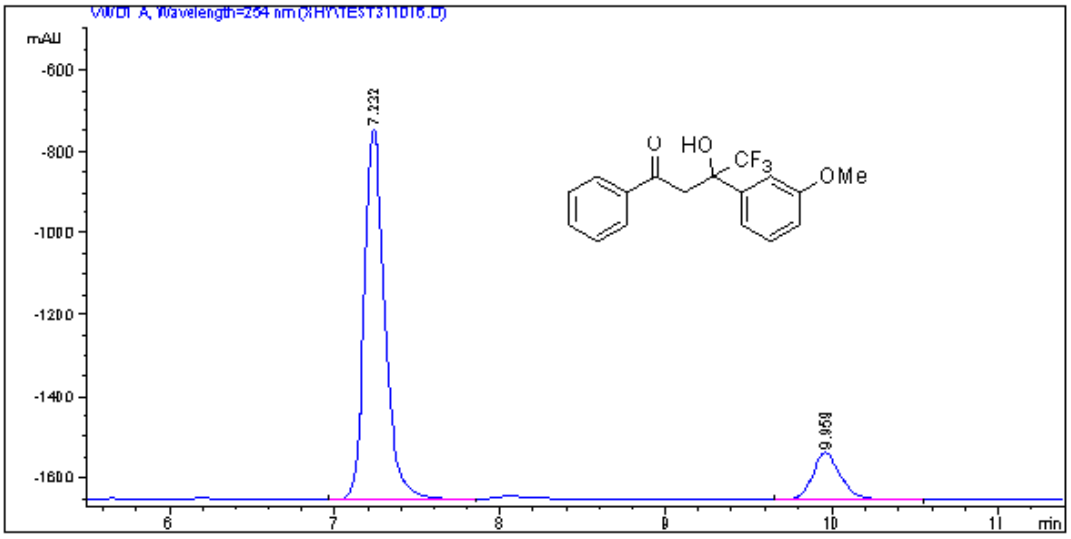
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.630	BV	0.1969	1.13189e4	837.77466	89.0370
2	9.968	VB	0.2066	1393.69177	102.56279	10.9630

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



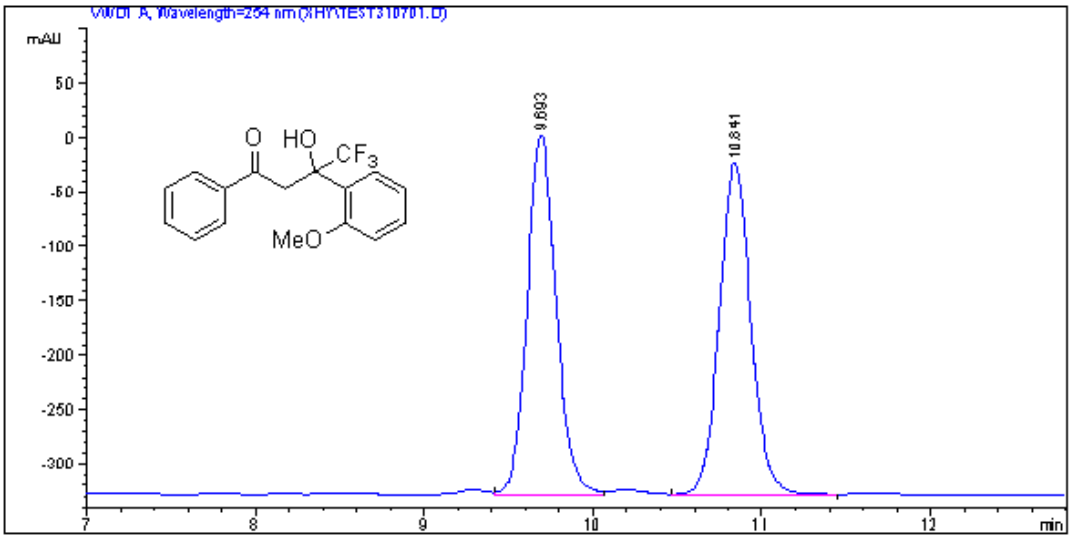
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.190	BV	0.1261	2232.84473	268.65808	50.1161
2	9.842	BB	0.1788	2222.50122	189.80989	49.8839

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



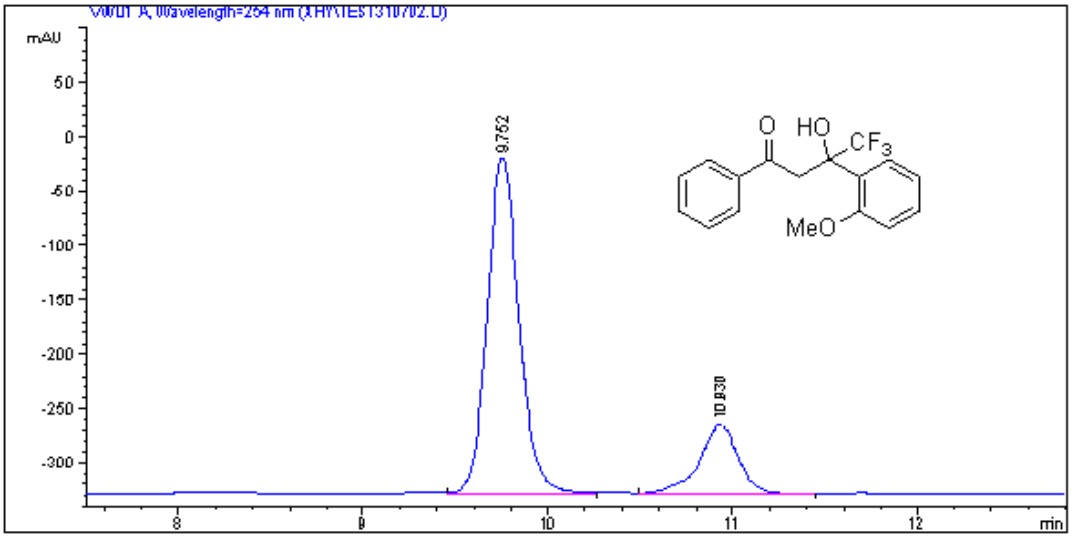
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.232	BV	0.1308	7777.20459	905.66718	85.7037
2	9.959	BB	0.1770	1297.31738	112.31406	14.2963

Sample Info : 254nm, IA, 1-PrOH : Hexane =5:95, 1.0 mL/min



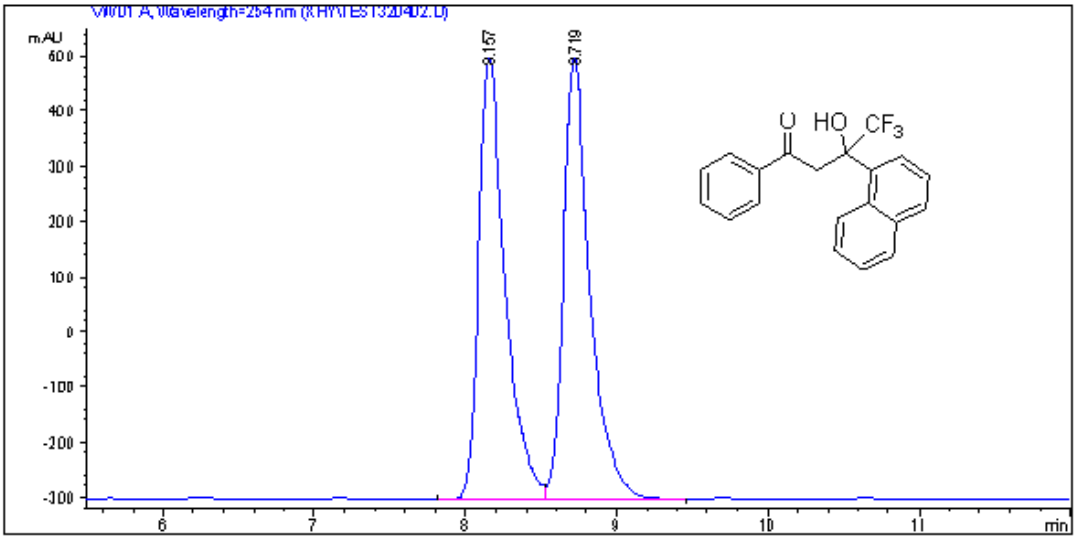
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.693	VV	0.1833	3961.94263	330.96814	50.0428
2	10.841	VB	0.1994	3955.16675	304.91779	49.9572

Sample Info : 254nm, IA, 1-PrOH : Hexane =5:95, 1.0 mL/min



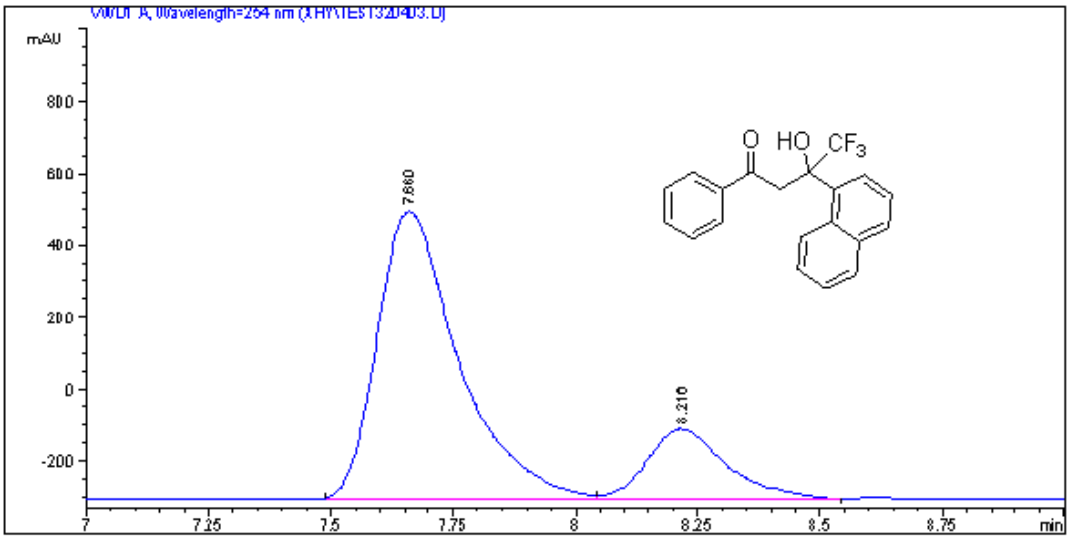
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.752	VB	0.1827	3691.96948	309.75516	79.7340
2	10.930	VB	0.2196	938.38605	63.81752	20.2660

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



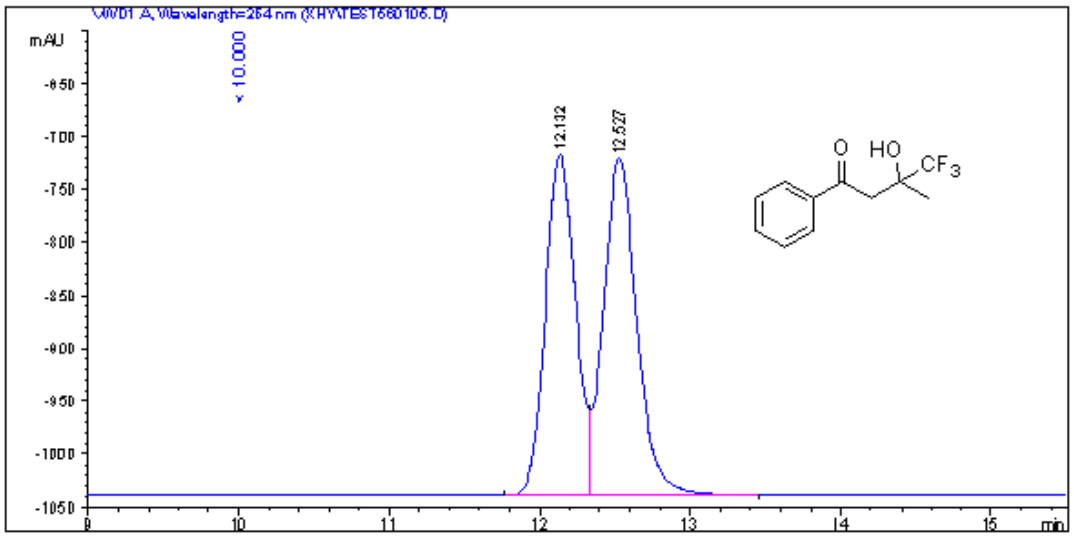
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.157	BV	0.1796	9619.00977	799.89349	49.7752
2	8.719	VB	0.1813	9705.90234	797.73688	50.2248

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



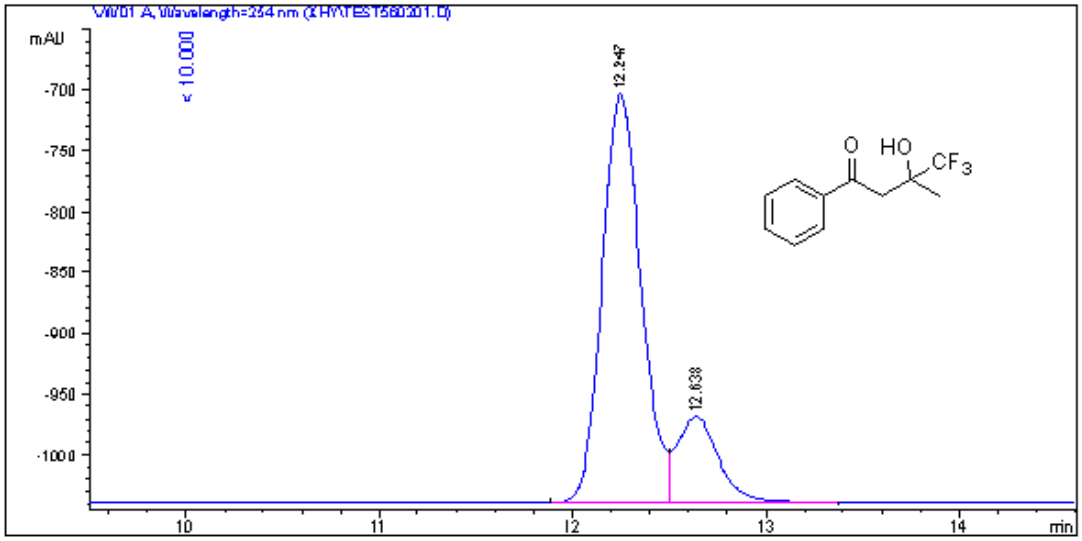
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.660	BV	0.1727	9281.77051	803.13281	80.7759
2	8.216	VBA	0.1691	2209.00171	196.29602	19.2241

Sample Info : 254nm, IC, i-PrOH : Hexane =2:98, 0.6 mL/min



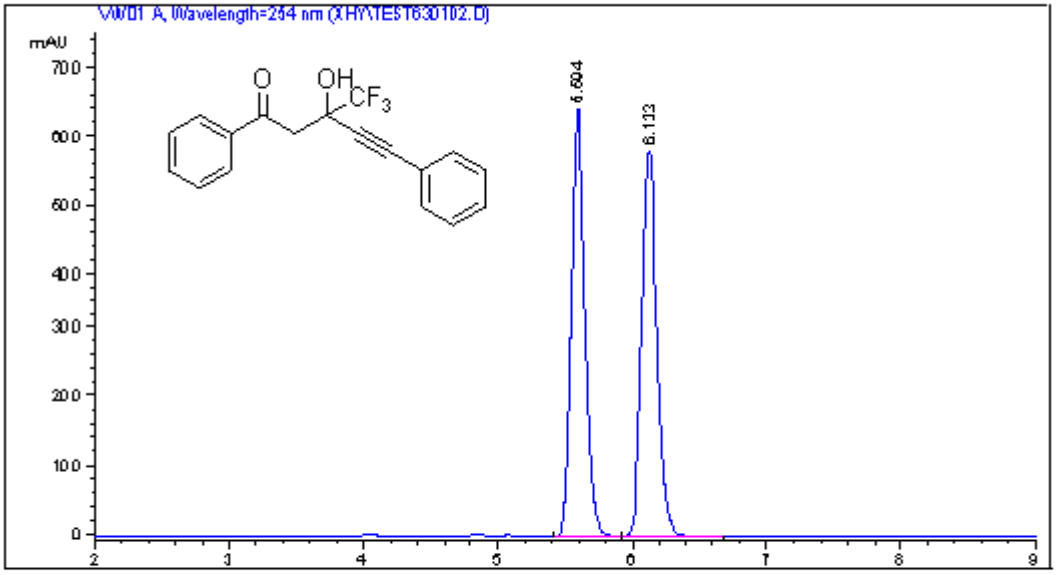
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.132	BV	0.2161	4472.82861	321.70317	47.7784
2	12.527	VB	0.2349	4888.77637	317.66818	52.2216

Sample Info : 254nm, IC, i-PrOH : Hexane =2:98, 0.6 mL/min



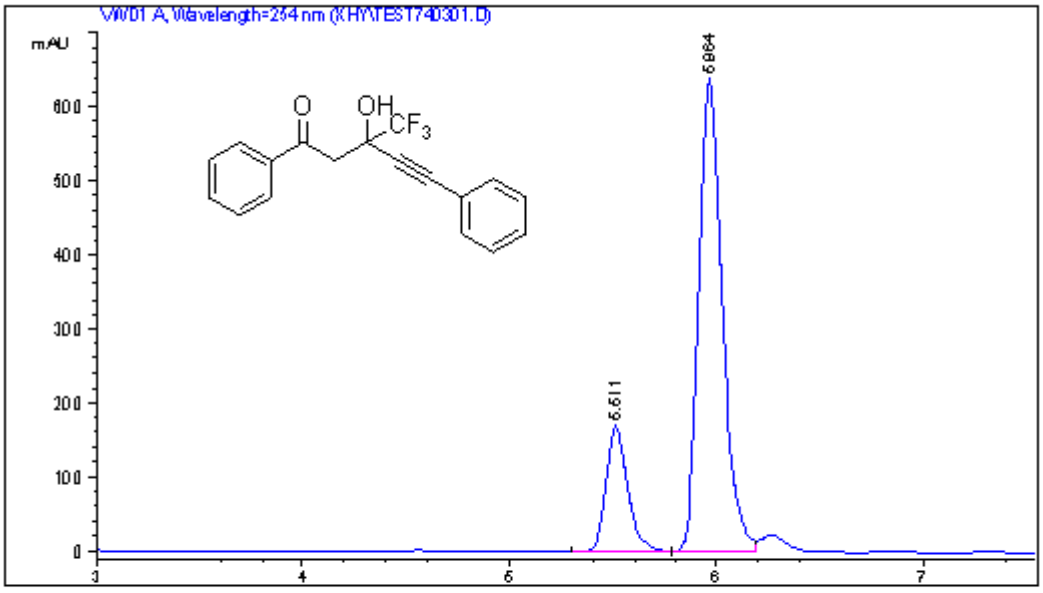
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.247	BV	0.2164	4676.21680	335.74811	81.8495
2	12.638	VB	0.2202	1036.97021	70.25687	18.1505

ple Info : 254nm, IC, i-PrOH : Hexane =15:85, 0.8 ml/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.594	BV	0.1076	4490.53760	648.65814	49.7383
2	6.123	VB	0.1200	4537.79102	582.70569	50.2617

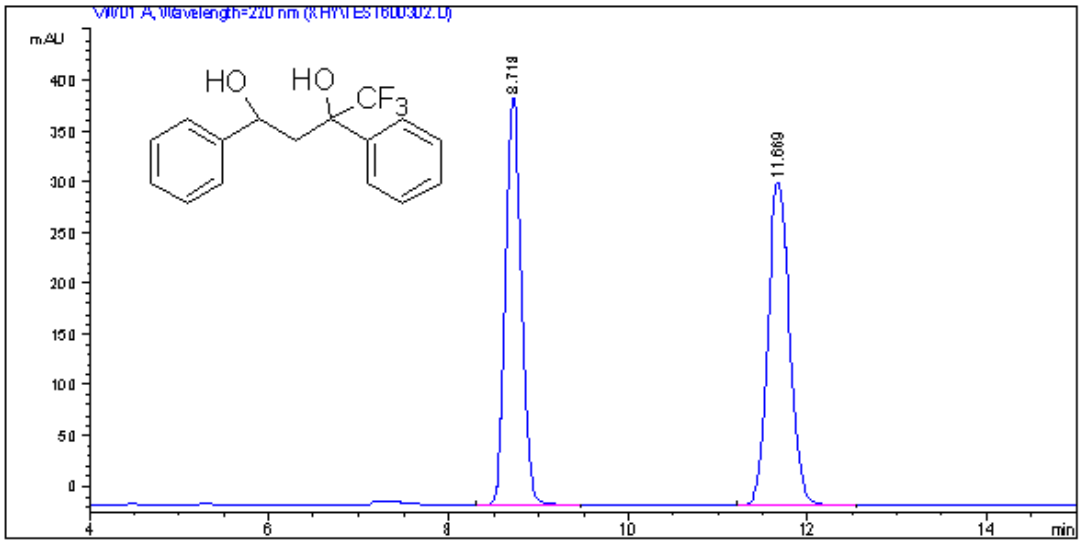
Sample Info : 254 nm, IC, i-PrOH : Hexane =15:85, 0.8mL/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.511	BV	0.1088	1233.62866	171.33815	19.5354
2	5.964	VV	0.1213	5081.21631	642.77081	80.4646

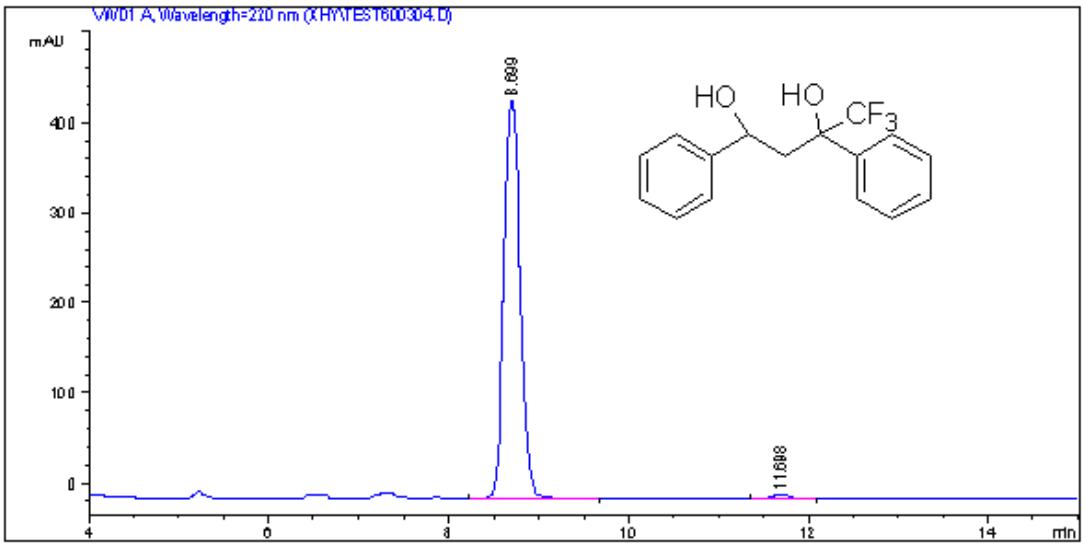
One diastereomer of diol:

Sample Info : 220nm, IA, i-PrOH : Hexane =10:90, 0.8 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.718	BB	0.1946	4328.60742	400.37302	48.1277
2	11.669	BB	0.2638	5312.06982	317.21378	51.8723

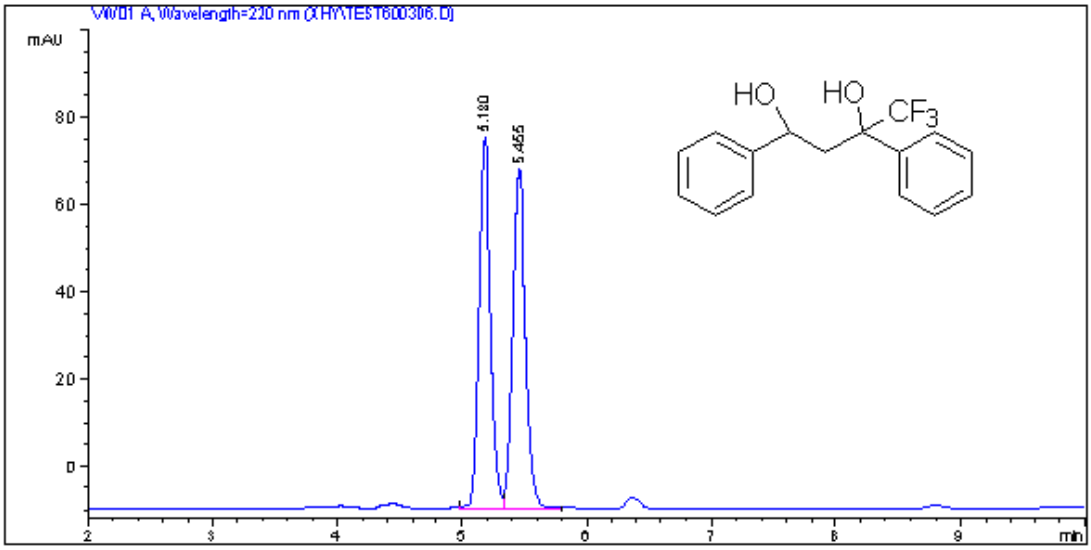
Sample Info : 220nm, IA, i-PrOH : Hexane =10:90, 0.8 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.699	BB	0.1392	5563.01709	442.17465	98.7401
2	11.698	BB	0.2302	70.98238	4.73695	1.2599

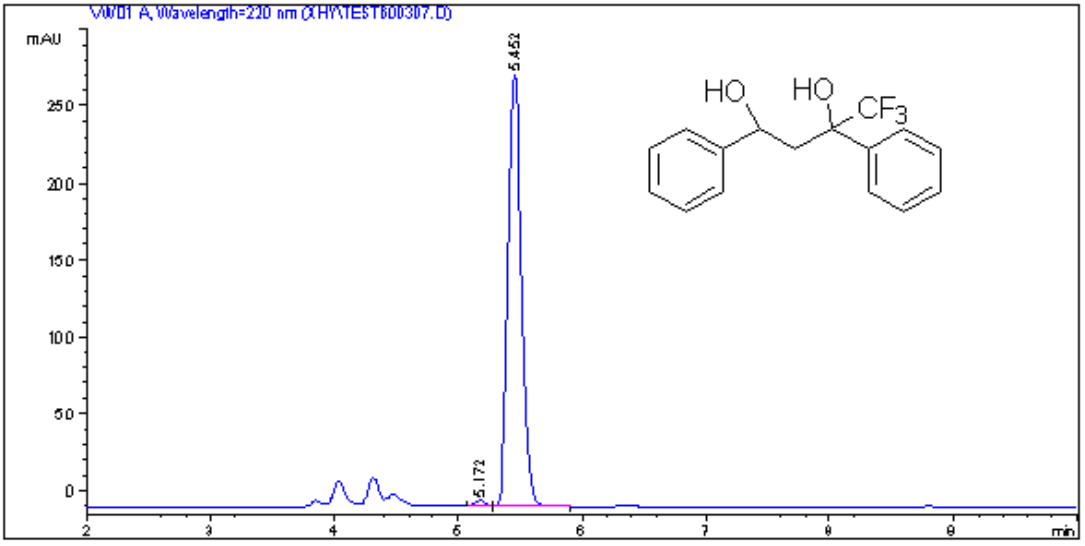
Another diastereomer of diol:

Sample Info : 220nm, IC, i-PrOH : Hexane =15:85, 1.0 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.180	VV	0.0996	548.09601	85.37955	49.8277
2	5.455	VB	0.1101	551.88617	78.08360	50.1723

Sample Info : 220nm, IC, i-PrOH : Hexane =15:85, 1.0 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.172	BV	0.0918	19.62947	3.34138	0.9102
2	5.452	VB	0.1208	2136.91504	280.98108	99.0898