Catalytic and Highly Enantioselective Friedel-Crafts Alkylation of Aromatic Ethers with Trifluoropyruvate under Solvent-free Conditions

Jun-Ling Zhao, Li Liu,* Yong Sui, Yu-Liang Liu, Dong Wang,* Yong-Jun Chen*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

Supporting Information

1. General Method

1.1. General method

All reactions were carried out under the protection of argon and all the flasks used were dried in oven. All the ^{1}H and ^{13}C NMR were recorded on Bruker-AV 300 spectrometer and chemical shift reported in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were recorded on a Bruker tensor 27 infrared spectrometer. Elemental analysis was performed on Carlos Flash 1112 Elemental Analysis instrument. Melting points were measured on Beijing-Tiker X-4 apparatus without correction. HRMS spectra were recorded on GCT-Mass Micromass spectrometer. Optical rotation were measured using a 1 mL cell with a 0.5 dm path length on Perkin-Elmer 341 digital polarimeter and reported as follow: $[\alpha]_D$ (*c* in g per 100 mL of solvent). HPLC analysis was performed on Shimadzu CTO-10AS with ChiralPak columns purchased from Daicel Chemical Industries. LTD. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. Common reagents were purchased from commercial sources and were used without further purification.

1.2. Typical experimental procedure for preparation of chiral Lewis acid [L*-Cu(II)]

A dry two neck flask charged with 2,2'-isoprorylidenebis-[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] [(4*R*,5*S*)-**1b**] (17.5mg, 0.036 mmol) and $Cu(OTf)_2$ (10.6mg, 0.03 mmol) was dried under vacuum for 10 min and flushed with argon. Freshly distilled anhydrous CH_2Cl_2 (2 mL) was added, followed by stirring at room temperature for 2 h. Then, the solvent was removed under reduced pressure, and the resulting green powder was dried under vacuum for half an hour, and stored under an argon atmosphere for later use.

2. Experimental Procedures for Enantioselective Friedel-Crafts Alkylation

2.1. Typical experimental procedure for enantionselective Friedel-Crafts reaction in organic solvent

To a solid of pre-prepared chiral Lewis acid catalyst **1b**-$Cu(OTf)_2$ (2.0 mg, 0.002 mmol) in a dry 10 mL test tube freshly distilled anhydrous organic solvent (0.8 mL) was added under the protection of argon at ambient temperature, Ethyl trifluoropyruvate **3** (32 μL, 0.24 mmol, 1.2 eq.) was added and stirred for half an hour. Anisole (**4a**, 0.2 mmol) was added, followed by stirring for 24 h at the same temperature. The mixture was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10 : 1 v/v) to give the product **6a**.

2.2 Typical experimental procedure for enantionselective Friedel-Crafts reaction under solvent-free conditions

To a solid of pre-prepared chiral Lewis acid catalyst (4*R*,5*S*)-**1b**-$Cu(OTf)_2$ (2.0 mg, 0.002 mmol) in a dry 10 mL test tube, ethyl trifluoropyruvate (**3**, 32 μL, 0.24 mmol, 1.2 eq) was added under the protection of argon at 0^oC with ice bath, followed by stirring for 10 min. Anisole (**4a**, 0.2 mmol) was added by syringe. On stirring for 13 h at the same temperature, ethyl acetate (0.5 mL) was added to quench the reaction and the crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10 : 1 v/v) to give a colorless oil **6a**, 50mg (90% yield with 90% ee).

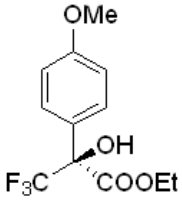
2.3. Typical experimental procedure for solvent-free enantioselective Friedel-Crafts reaction on large scale

To a solid of pre-prepared chiral Lewis acid catalyst (4*R*,5*S*)-**1b**-$Cu(OTf)_2$ (59.6 mg, 0.063 mmol) in a dry 10 mL two-neck flask under the protection of argon, methyl trifluoropyruvate (0.85 mL, 7.56mmol) was added, followed by stirring at -20 ^oC for half an hour. Anisole (**4a**, 0.68g, 6.3 mmol) was added, followed by stirring at the

same temperature for 24 h. Ethyl acetate (1 mL) was added to quench the reaction and the crude product was purified by flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:10 v/v) to give **6a**, 1.30g (78% yield with 90% ee).

2.4. Characterization data of the products

2.4.1. Ethyl (2*S*)-2-hydroxyl-2-(4'-methoxyphenyl)-3,3,3-trifluoro-propanoate (6a):

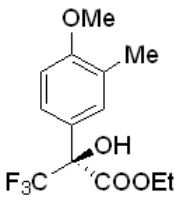


According to the typical procedure, the reaction of anisole **4a** (21.6 mg 0.2 mmol) with ethyl trifluoropyruvate **3** (40.8 mg 0.24 mmol) was carried out at -20^{o}C for 24 h, to afford a colorless oil **6a**,[1] 41.7mg (75% yield with 92% ee).

6a: $[\alpha]_D$ = +19.5 (*c*, 0.41, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.0Hz, 2H), 6.92 (d, *J* = 9.0Hz, 2H), 4.48-4.35 (m, 2H), 4.28 (s, 1H), 3.82 (s, 3H), 1.38 (t, *J* = 14.3Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.1, 160.5, 128.2, 128.1, 123.0 (q, $J_{C\text{-}F}$ = 274.0Hz), 113.7, 77.7 (q, $J_{C\text{-}F}$ = 30.4Hz), 64.3, 55.3, 13.9. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25 ^{o}C): t_S = 13.2 min (major) and t_R = 24.4 min (minor).

(1) Racemic compound: Blay, G.; Fernandez, I.; Marco-Aleixandre, A.; Monje, B.; Prdro, J. R.; Ruiz, R. *Tetrrahedron* **2002**, *58*, 8565

2.4.2. Ethyl (2*S*)-2-hydroxyl-2-(4'-methoxy-3'-methylphenyl)-3,3,3-trifluoro-propanoate (6b):

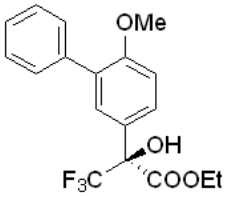


According to the typical procedure, the reaction of 2-methylanisole **4b** (24.4 mg 0.2 mmol) with **3** (40.8 mg 0.24 mmol) was carried out at -20 ^{o}C for 30 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether : ethyl acetate =

10 : 1 v/v), affording a colorless oil **6b**, 46.7 mg (80% yield with 90% ee).

6b: $[\alpha]_D$ = +14.6 (*c*, 0.41, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.56 (m, 2H), 6.84 (m, 1H), 4.48-4.36 (m, 2H), 4.25 (s, 1H), 3.84 (s, 3H), 2.24 (s, 3H), 1.38 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.2, 158.6, 128.9, 126.7, 125.5, 124.3, 123.1 (q, $J_{C\text{-}F}$ = 285.7Hz), 109.5, 77.5 (q, $J_{C\text{-}F}$ = 30.1Hz), 64.1, 55.3, 16.4, 13.9. IR ν_{max} 3485, 2983, 2842, 1739, 1610, 1506, 1465, 1372, 1305, 1255 cm^{-1}. HRMS *m/z* calcd for $C_{13}H_{15}F_3O_4$ [M^+]: 292.0922, found: 292.0920. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25^{o}C): t_S = 11.0 min (major) and t_R = 13.9 min (minor).

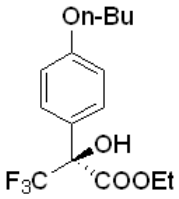
2.4.3. Ethyl (2*S*)-2-hydroxyl-2-(3'-phenyl-4'-methoxylphenyl)-3,3,3-trifluoro-propanote (6c):



According to the typical procedure, the reaction of 2-Phenyl anisole **4c** (36.8 mg, 0.2 mmol) with **3** (40.8 mg, 0.24 mmol) was carried out at -20 ^{o}C for 28 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8 : 1 v/v) to afford a colorless oil **6c**, 38.9 mg (55% yield with 90% ee).

6c: $[\alpha]_D$ = +15.4 (*c*, 0.39, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.54-7.51(m, 2H), 7.45-7.35 (m, 3H), 7.02-6.99 (m, 1H), 4.50-4.38 (m, 2H), 4.31 (s, 1H), 3.84 (s, 3H), 1.39 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.1, 157.4, 138.0, 130.6, 129.5, 129.4, 128.1, 127.2, 123.1 (q, $J_{C\text{-}F}$ = 282.3Hz), 110.9, 77.5 (q, $J_{C\text{-}F}$ = 30.2Hz), 64.3, 55.6, 14.0; IR ν_{max} 3481, 2940, 1739, 1606, 1508, 1490, 1447, 1370, 1266, 1163 cm^{-1}. HRMS *m/z* calcd for $C_{18}H_{17}F_3O_4$ [M^+]: 354.1079, found: 354.1077. E.e. was determined by HPLC (Daicel Chiralpak AS-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.3 mL/min, 5 ^{o}C): t_S = 34.1 min (major) and t_R = 32.2 min (minor).

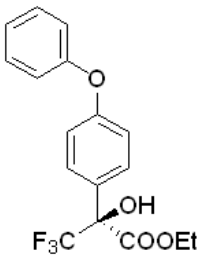
2.4.4. Ethyl (2*S*)-2-(4'-butoxyphenyl)-2-hydroxyl-3,3,3-trifluoro-propanoate (6d):



According to the typical procedure, the reaction of n-butoxy-benzene **4d** (30.0 mg 0.2 mmol) with **3** (40.8 mg 0.24 mmol) was carried out at -20^{o}C for 40 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15 : 1 v/v) to afford a colorless oil **6d**, 56.3 mg (88% yield with 92% ee).

6d: $[\alpha]_D$ = 17.1 (c 0.35 in $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0Hz, 2H), 6.91 (d, *J* = 9.0Hz, 2H), 4.48-4.35 (m, 2H), 4.27 (s, 1H), 3.98 (t, *J* = 6.5Hz, 2H), 1.80-1.73 (m, 2H), 1.53-1.45 (m, 2H), 1.37 (t, *J* = 7.1Hz, 3H), 0.98 (t, *J* = 7.4Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.1, 160.1, 128.1, 124.5, 123.1 (q, $J_{C\text{-}F}$ = 285.7Hz), 114.2, 77.5 (q, $J_{C\text{-}F}$ = 30.2Hz), 67.7, 64.2, 31.2, 19.2, 13.9, 13.8. IR ν_{max} 3486, 2962, 2875, 1739, 1611, 1513, 1471, 1373, 1251, 1170 cm^{-1}. HRMS *m/z* calcd for $C_{15}H_{19}F_3O_4$ [M^+]: 320.1235, found: 320.1238. E.e. determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25^{o}C): t_S = 10.9 min (major) and t_R= 29.8 min (minor).

2.4.5. Ethyl (2*S*)-2-hydroxyl-2-(4'-phenoxyphenyl)-3,3,3-trifluoro-propanoate (6e):

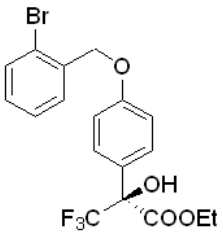


According to the typical procedure, the reaction of diphenyl ether **4e** (34.0 mg 0.2 mmol) with **3** (68.0 mg 0.4 mmol) was carried out at 0^{o}C for 72 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10 : 1 v/v) to afford a light yellow oil **6e**, 42.2 mg (62% yield with 92% ee).

6e: $[\alpha]_D$ = +14.6 (*c*, 0.41, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8Hz, 2H), 7.40-7.33 (m, 2H), 7.18-7.13 (m, 1H), 7.07-6.98 (m, 4H), 4.50-4.36 (m, 2H), 4.34 (s, 1H), 1.38 (t, *J* = 14.3Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.0, 158.7, 156.3, 129.9, 128.4, 127.1, 124.0, 123.0 (q, $J_{C\text{-}F}$ = 285.6Hz), 119.6, 117.9, 77.7 (q, $J_{C\text{-}F}$ =

30.4Hz), 64.4, 13.9. IR ν_{max} 3481, 2986, 2932, 1739, 1590, 1505, 1490, 1370, 1243, 1168 cm^{-1}. HRMS *m/z* calcd for $C_{17}H_{15}F_3O_4$ [M^+]: 340.0922, found: 340.0925. E.e. was determined by HPLC (Daicel Chiralpak AS-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.5 mL/min, 10°C): t_S = 13.0 min (major) and t_R = 14.3 min (minor).

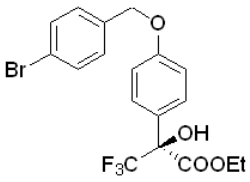
2.4.6. Ethyl (2*S*)-2-hydroxyl-2-[4'-(2'-bromobenzyloxy)phenyl]-3,3,3-trifluoro-propanoate (6f):



According to the typical procedure, the reaction of (2'-bromobenzyloxy)-benzene **4f** (52.6 mg 0.2 mmol) with **3** (102 mg 0.6 mmol) at 15°C for 18 h. The crude product was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 10 : 1 v/v) to afford a colorless oil **6f**, 83.1 mg (96% yield, with 92% ee).

6f: $[\alpha]_D$ = 11.5 (c 0.52 in $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.72 (d, *J* = 9.0Hz, 2H), 7.60-7.51 (m, 2H), 7.35 (td, *J* = 7.0, 1.1Hz, 1H), 7.19 (td, *J* = 7.7, 1.6Hz, 1H), 7.02 (d, *J* = 9.0Hz, 2H), 5.14 (s, 2H), 4.50-4.34 (m, 2H), 4.29 (s, 1H), 1.37 (t, *J* = 7.2Hz, 3H); ^{13}CNMR (75.5MHz, $CDCl_3$) δ 169.1, 159.4, 135.9, 132.7, 129.4, 128.9, 128.3, 127.6, 125.4, 123.1 (q, J_{C-F} = 285.8Hz), 122.3, 114.7, 77.5 (q, J_{C-F} = 30.4Hz), 69.5, 64.3, 13.9. IR ν_{max} 3482, 3069, 2986, 1739, 1609, 1511, 1444, 1374, 1248, 1170 cm^{-1}. HRMS *m/z* calcd for $C_{18}H_{16}BrF_3O_4$ [M^+]: 432.0184, found: 432.0177. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25°C): t_S = 16.3 min (major) and t_R = 25.9 min (minor).

2.4.7. Ethyl (2*S*)-2-hydroxyl-2-[4'-(4'-bromobenzyloxy)-phenyl]-3,3,3-trifluoro-propanoate (6g):

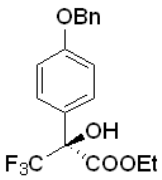


According to the typical procedure, the reaction of

(4-bromobenzyloxy)benzene **4g** (52.6 mg 0.2 mmol) with **3** (40.8 mg 0.24 mmol) in the presence of freshly distilled CH_2Cl_2 (100 μL) was carried out at 25°C for 18 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8 : 1 v/v) to afford a white solid **6g**, 73.6 mg (85% yield with 91% ee).

6g: M.p.: 82-84 °C. $[\alpha]_D$ = +12.9 (*c* 0.31, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.72 (d, *J* = 9.0Hz, 2H), 7.52 (d, *J* = 8.5Hz, 2H), 7.30 (d, *J* = 8.5Hz, 2H), 6.99 (d, *J* = 9.0Hz, 2H), 5.03 (s, 2H), 4.49-4.35 (m, 2H), 4.31 (s, 1H), 1.38 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.0, 159.4, 135.7, 131.8, 129.1, 128.3, 125.3, 123.1 (q, $J_{C\text{-}F}$ = 285.6Hz), 122.0, 114.6, 77.5 (q, $J_{C\text{-}F}$ = 30.3Hz), 69.3, 64.3, 13.9. IR ν_{max} 3480, 2985, 1739, 1609, 1511, 1466, 1373, 1283, 1249, 1169 cm^{-1}. Elemental analysis: calcd for $C_{18}H_{16}BrF_3O_4$: C: 49.90, H: 3.72, found: C: 49.89, H: 3.87. E.e. was determined by HPLC (Daicel Chiralpak OD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25°C): t_S = 29.2 min (major) and t_R = 54.2 min (minor).

2.4.8. Ethyl (2*S*)-2-hydroxyl-2-(4'-benzyloxyphenyl)-3,3,3-trifluoro-propanoate (6h):

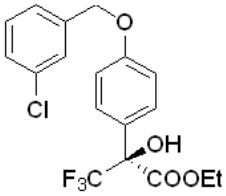


According to the typical procedure, the reaction of benzyloxy-benzene **4h** (36.8 mg 0.2 mmol) with **3** (102 mg 0.6 mmol) was carried out at 15°C for 15 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8 : 1 v/v) to afford a white solid **6h**, 69.4 mg (98% yield with 90% ee).

6h: M.p. 54-55 °C. $[\alpha]_D$ = +17.4 (*c*, 0.46, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.72 (d, *J* = 9.0Hz, 2H), 7.46-7.34 (m, 5H), 7.01 (d, *J* = 9.0Hz, 2H), 5.09 (s, 2H), 4.49-4.36 (m, 2H), 4.30 (s, 1H), 1.38 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.1, 159.7, 136.7, 128.7, 128.2, 128.1, 127.5, 125.1, 123.1 (q, $J_{C\text{-}F}$ = 285.7Hz), 114.6, 77.5 (q, $J_{C\text{-}F}$ = 30.3Hz), 70.1, 64.3, 13.9. IR ν_{max} 3483, 2986, 2939, 1739, 1609, 1511, 1460, 1376, 1248, 1170 cm^{-1}. HRMS *m/z* calcd for $C_{18}H_{17}F_3O_4$ [M^+]: 354.1079, found:

354.1077. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min. 25°C): t_S = 19.1 min (major) and t_R = 45.8 min (minor).

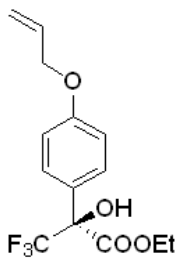
2.4.9. Ethyl (2*S*)-2-hydroxy-2-[4'-(3'-chloro-benzyloxy)phenyl]-3,3,3-trifluoro-propanoate (6i):



According to the typical procedure, the reaction of (3-chlorobenzyloxy)-benzene **4i** (43.7 mg 0.2 mmol) with **3** (40.8 mg 0.24 mmol) was carried out at 0°C for 28 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8 : 1 v/v) to afford a colorless oil **6i**, 60.6 mg (78% yield with 93% ee).

6i: $[\alpha]_D$ = +16.3 (*c*, 0.51, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.73 (d, *J* = 9.0Hz, 2H), 7.44 (s, 1H), 7.32-7.31 (m, 3H), 6.99 (d, *J* = 9.0Hz, 2H), 5.05 (s, 2H), 4.49-4.33 (m, 2H), 4.31 (s, 1H), 1.38 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) 169.0, 159.4, 138.7, 134.6, 129.9, 128.7, 128.3, 128.2, 127.4, 125.4, 123.1 (q, J_{C-F} = 285.8Hz), 114.6, 77.5 (q, J_{C-F} = 30.4Hz), 69.2, 64.4, 13.9; IR ν_{max} 3483, 2987, 2938, 1739, 1609, 1580, 1511, 1471, 1248, 1169 cm^{-1}. HRMS *m/z* calcd for $C_{18}H_{16}ClF_3O_4$ [M^+]: 388.0689, found: 388.0684. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, 0.6 mL/min, 25°C): t_S = 21.0 min (major) and t_R = 52.7 min (minor).

2.4.10. Ethyl (2*S*)-2-hydroxy-2-(4'-allyloxyphenyl)-3,3,3-trifluoro- propanoate (6j):

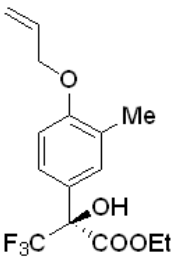


According to the typical procedure, the reaction of allyloxy-benzene **4j** (26.8 mg 0.2 mmol) with **3** (40.8 mg 0.24 mmol) was carried out at -20°C for 30 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl

acetate = 10 : 1 v/v) to afford a colorless oil **6j**, 37.7 mg (62% yield with 93% ee).

6j: $[\alpha]_D$ = +20.7 (*c*, 0.29, $CHCl_3$). ^1H NMR (300MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0Hz, 2H), 6.94 (d, *J* = 9.0Hz, 2H), 6.11-5.99 (m, 1H), 5.45-5.28 (m, 2H), 4.57-4.54 (m, 2H), 4.48-4.35 (m, 2H), 4.28 (s, 1H), 1.37 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.1, 159.5, 133.0, 128.1, 128.1, 123.1 (q, J_{C-F} = 284.6Hz), 117.9, 114.5, 77.5 (q, J_{C-F} = 30.4Hz), 68.8, 64.3, 13.9. IR ν_{max} 3483, 3086, 2988, 1740, 1609, 1511, 1462, 1371, 1246, 1173 cm^{-1}. HRMS *m/z* calcd for $C_{14}H_{15}F_3O_4$ $[M^+]$: 304.0922, found: 304.0919. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25°C): t_S = 12.8 min (major) and t_R = 29.5 min (minor).

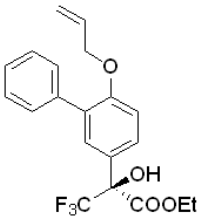
2.4.11. Ethyl (2*S*)-2-hydroxy-2-(4'-allyloxy-3'-methylphenyl)-3,3,3-trifluoro-propanoate (6k):



According to the typical procedure, the reaction of 2-allyloxytoluene **4k** (29.6 mg 0.2 mmol) with **3** (40.8 mg 0.24 mmol) was carried out at -20°C for 30 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10 : 1 v/v) to afford a colorless oil **6k**, 47.7 mg (75% yield with 90% ee).

6k: $[\alpha]_D$ = +12.9 (*c*, 0.31, $CHCl_3$). ^1H NMR (300MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H), 6.83-6.80 (m, 1H), 6.11-6.02 (m, 1H), 5.47-5.27 (m, 2H), 4.58-4.55 (m, 2H), 4.48-4.37 (m, 2H), 4.24 (s, 1H), 2.27 (s, 3H), 1.38 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.2, 157.6, 133.2, 129.0, 127.0, 125.4, 124.4, 123.1 (q, J_{C-F} = 285.6Hz), 117.2, 110.8, 77.5 (q, J_{C-F} = 30.2Hz), 68.7, 64.2, 16.5, 13.9. IR ν_{max} 3486, 2986, 2927, 1739, 1609, 1504, 1459, 1422, 1371, 1305 cm^{-1}. HRMS *m/z* calcd for $C_{15}H_{17}F_3O_4$ $[M^+]$: 318.1079, found: 318.1077. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25°C): t_S = 10.5 min (major), t_R = 14.8 min (minor).

2.4.12. Ethyl (2*S*)-2-hydroxyl-2-(4'-allyloxy-3'-phenylphenyl)-3,3,3-trifluoro-propanoate (6l):

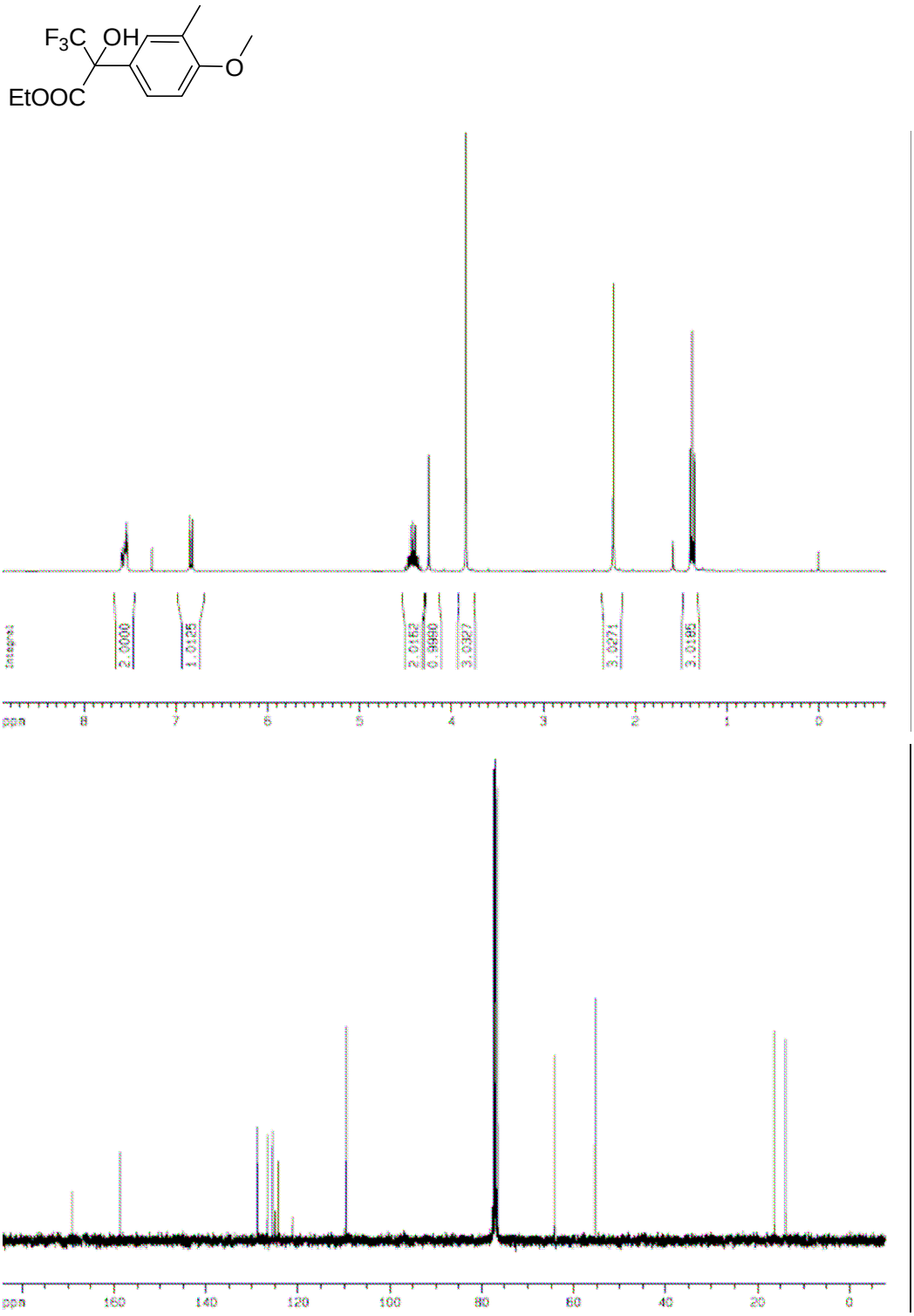


According to the typical procedure, the reaction of 2-allyloxydiphenyl **4l** (42.0 mg 0.2mmol) with **3** (102mg 0.6mmol) was carried out at -20^{o}C for 46 h. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8 : 1 v/v) to afford a colorless oil **6l**, 53.2 mg (70% yield with 93% ee).

6l: $[\alpha]_D$ = +11.8 (c, 0.51, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.78-7.70 (m, 2H), 7.57-7.54 (m, 2H), 7.45-7.34 (m, 3H), 6.99 (d, *J* = 8.7Hz, 1H), 6.04-5.94 (m, 1H), 5.37-5.21 (m, 2H), 4.59-4.56 (m, 2H), 4.49-4.39 (m, 2H), 4.32 (s, 1H), 1.39 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 169.1, 156.4, 138.0, 132.9, 130.9, 129.6, 128.0, 127.2, 127.2, 127.1, 125.2, 123.1 (q, $J_{C\text{-}F}$ = 285.7Hz), 117.1, 112.4, 77.5 (q, $J_{C\text{-}F}$ = 30.4Hz), 69.1, 64.3, 13.9. IR ν_{max} 3482, 2987, 2933, 1739, 1605, 1489, 1451, 1415, 1370, 1234 cm^{-1}. HRMS *m/z* calcd for $C_{20}H_{19}F_3O_4$ [M$^+$]: 380.1235, found: 380.1233. E.e. was determined by HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 9 : 1, flow rate = 0.6 mL/min, 25^{o}C): t_S = 15.6 min (major) and t_R = 14.2 min (minor).

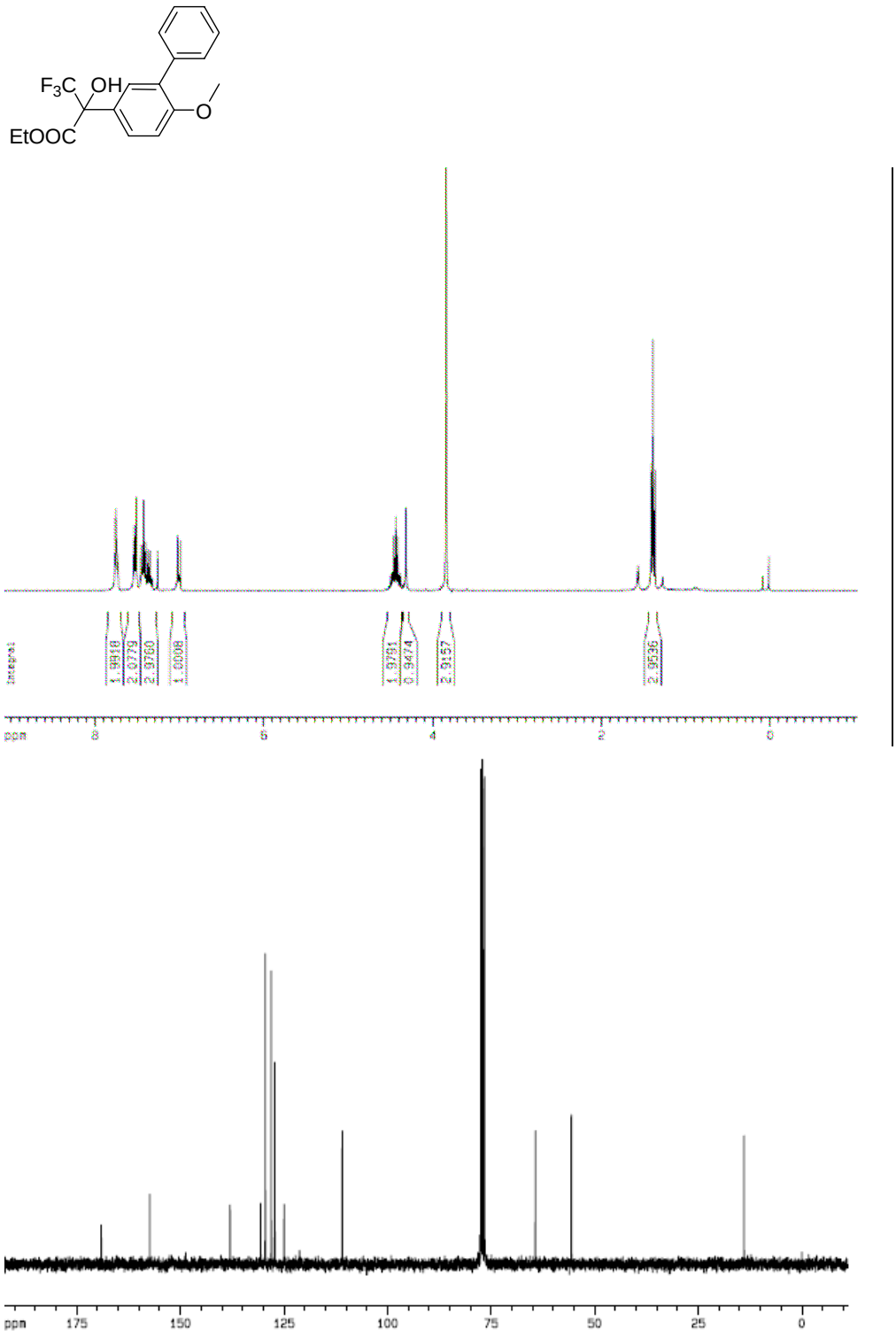
3. ^{1}H and ^{13}C NMR spectra

3.1. Sample 6b



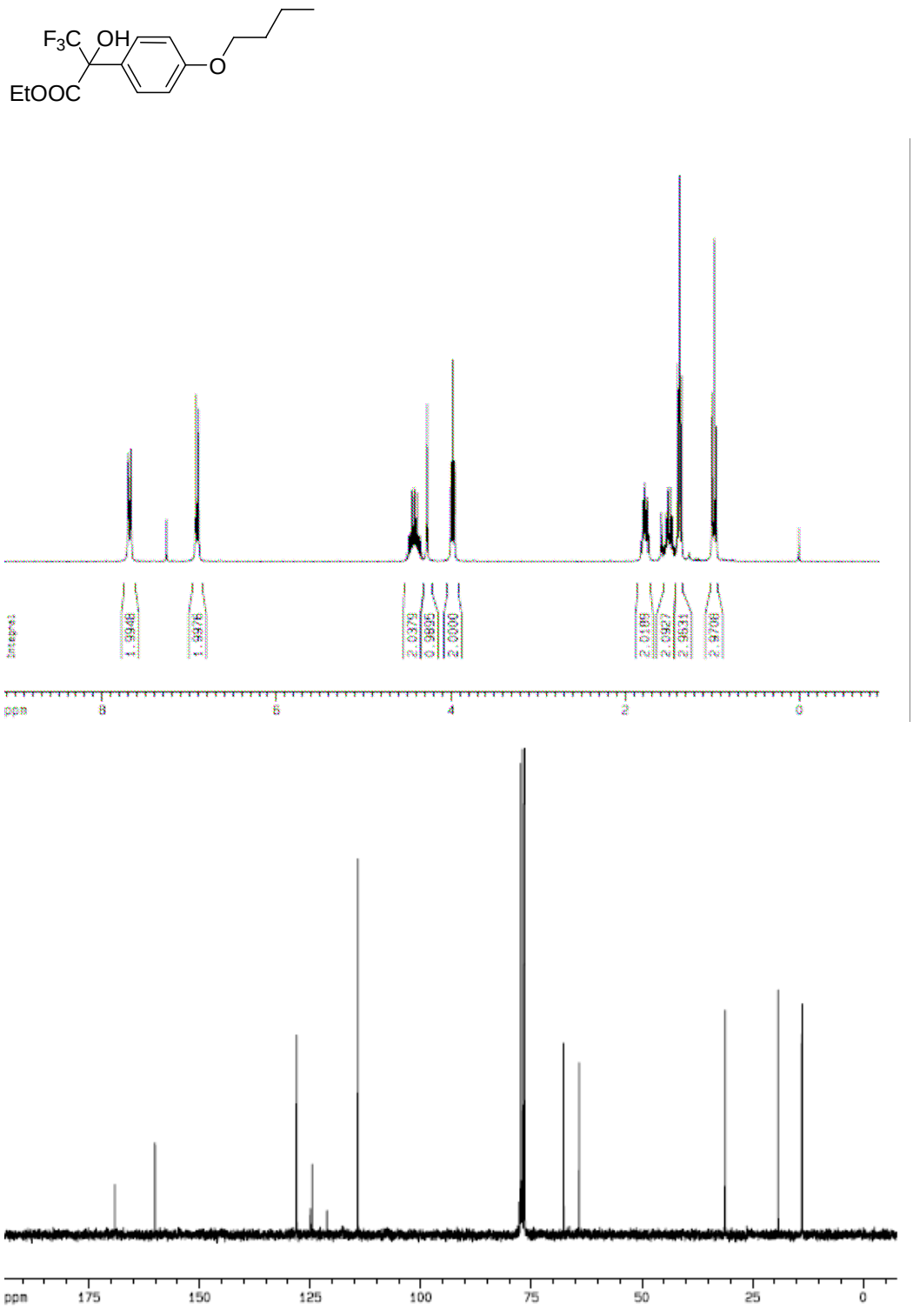
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-(4'-methoxy-3'-methylphenyl)-3,3,3-trifluoro-propanoate (**6b**)

3.2. Sample 6c



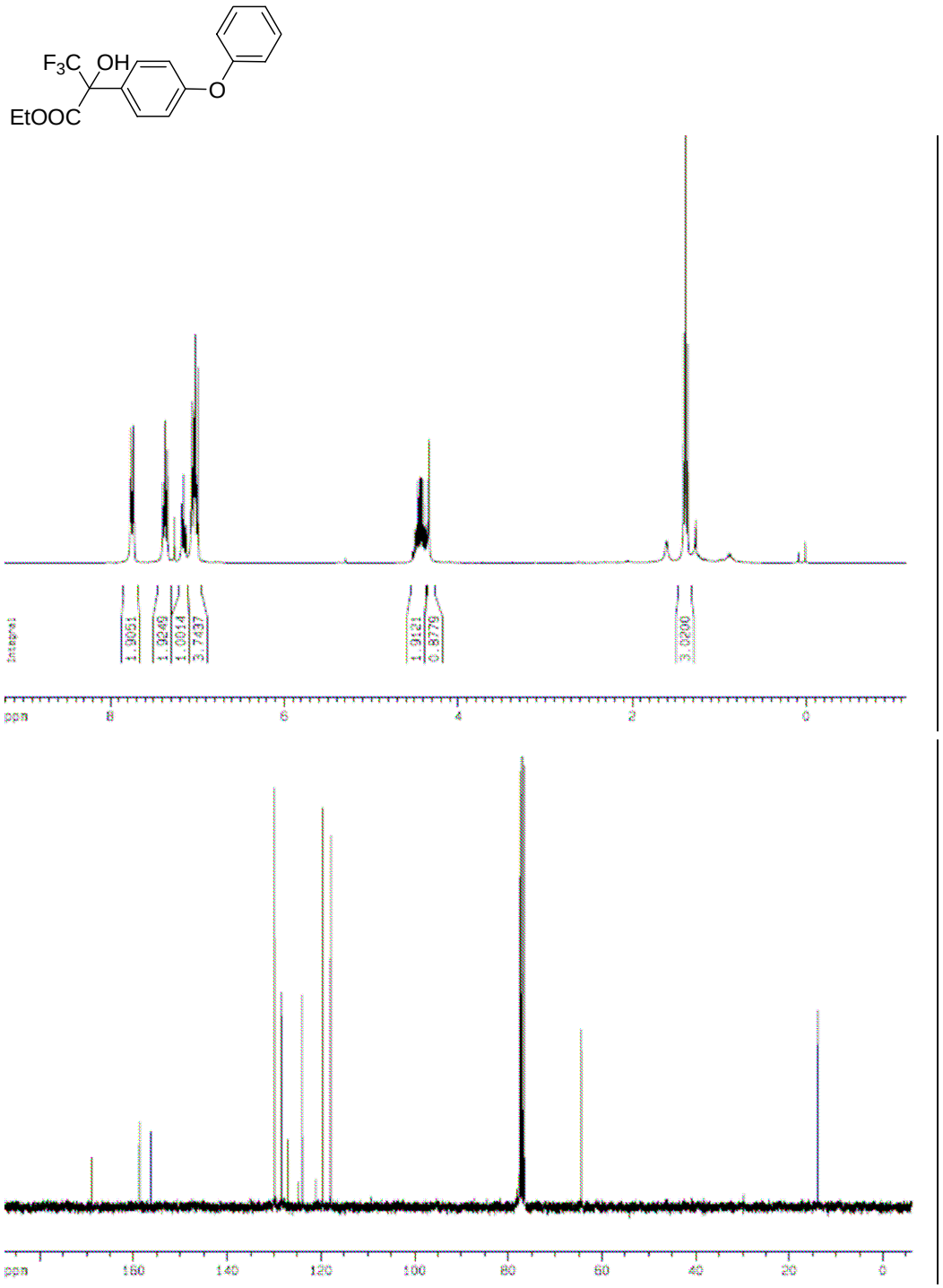
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-(3'-phenyl-4'-methoxyphenyl)-3,3,3-trifluoro-propanote (**6c**)

3.3. Sample 6d



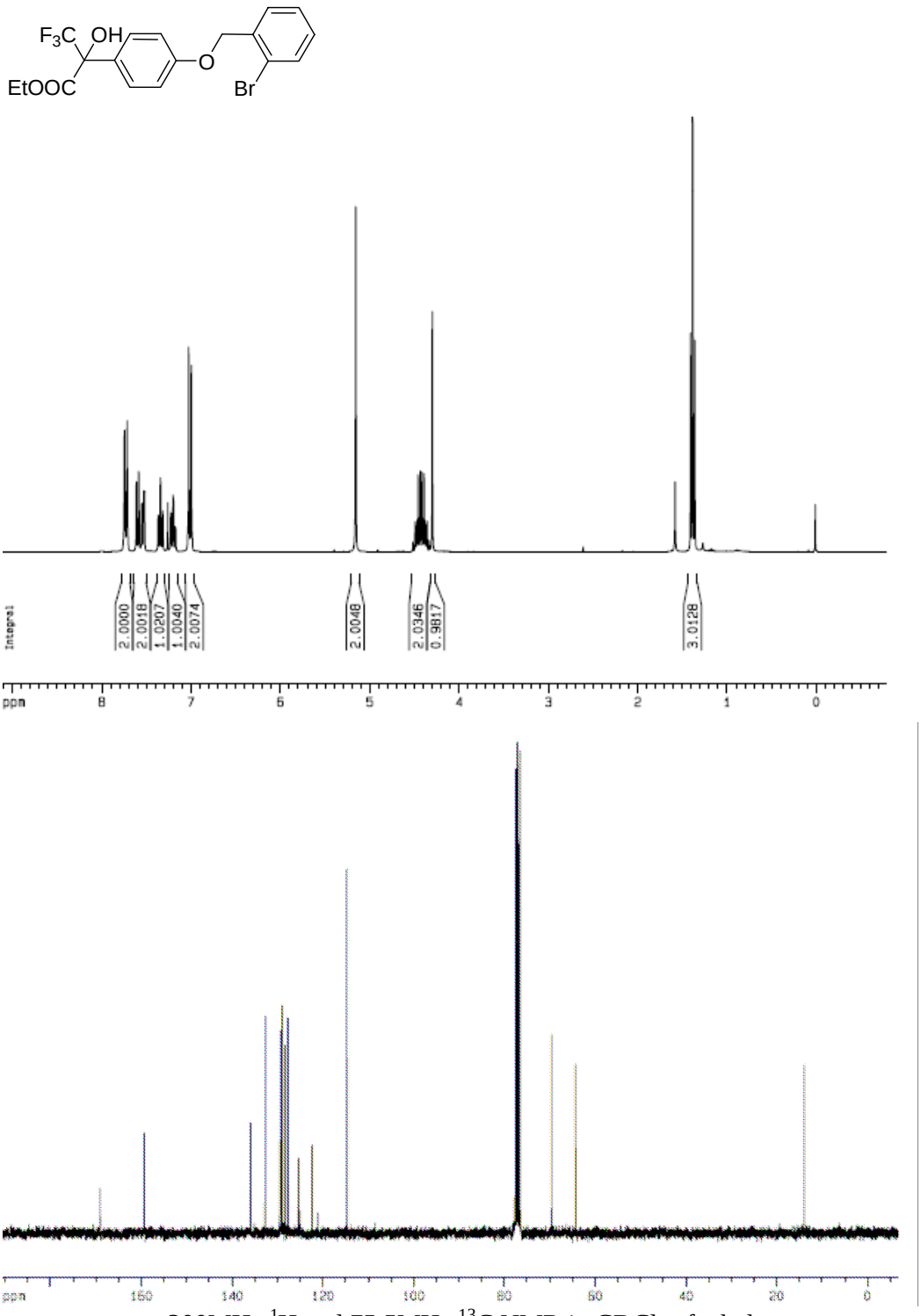
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxyl-2-(4'-butoxyphenyl)-3,3,3-trifluoro-propanoate (**6d**)

3.4. Sample 6e



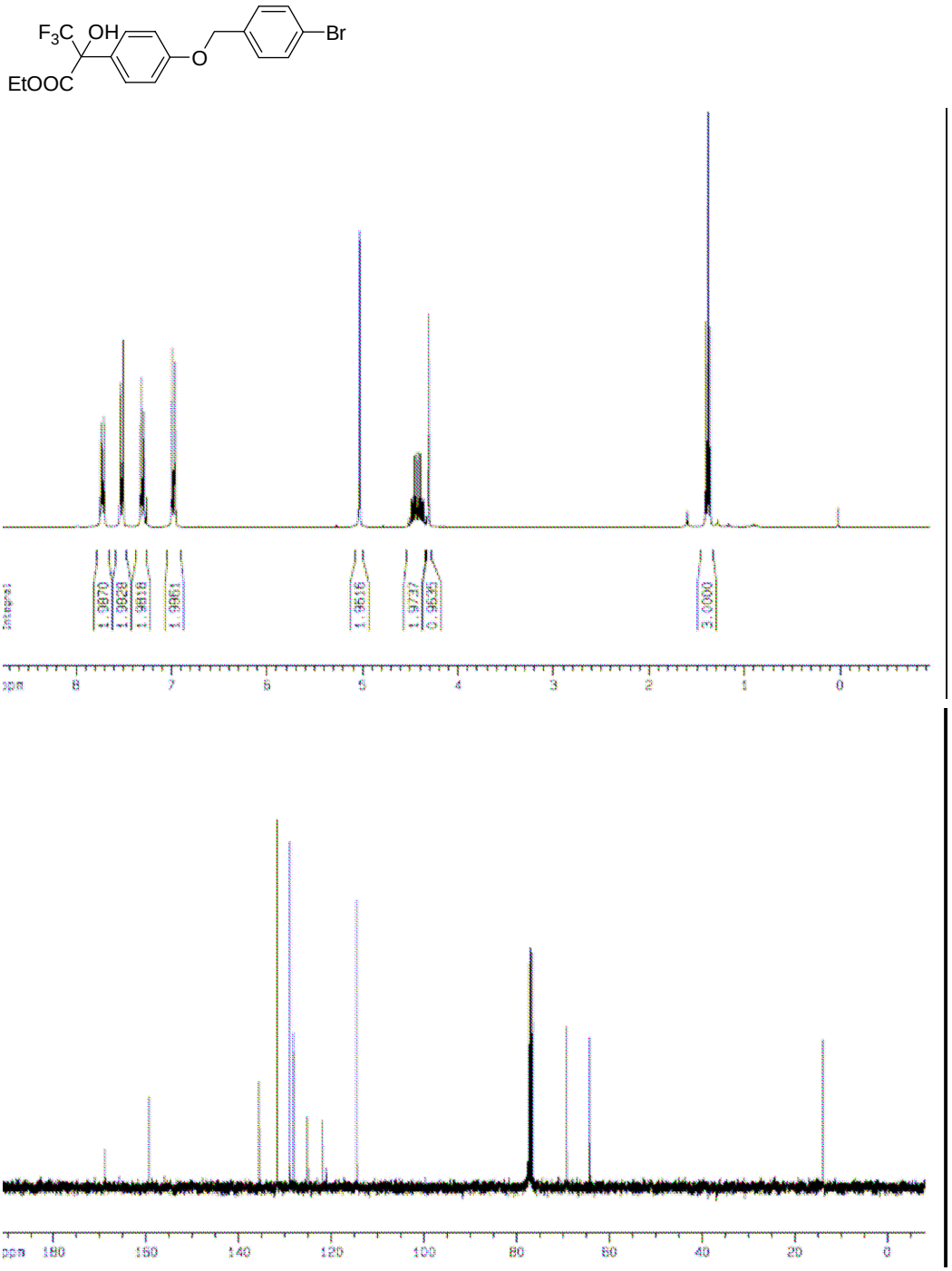
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of (*S*)-ethyl 3,3,3-trifluoro-2-hydroxy-2-(4-phenoxyphenyl)propanoate (**6e**)

3.5. Sample 6f



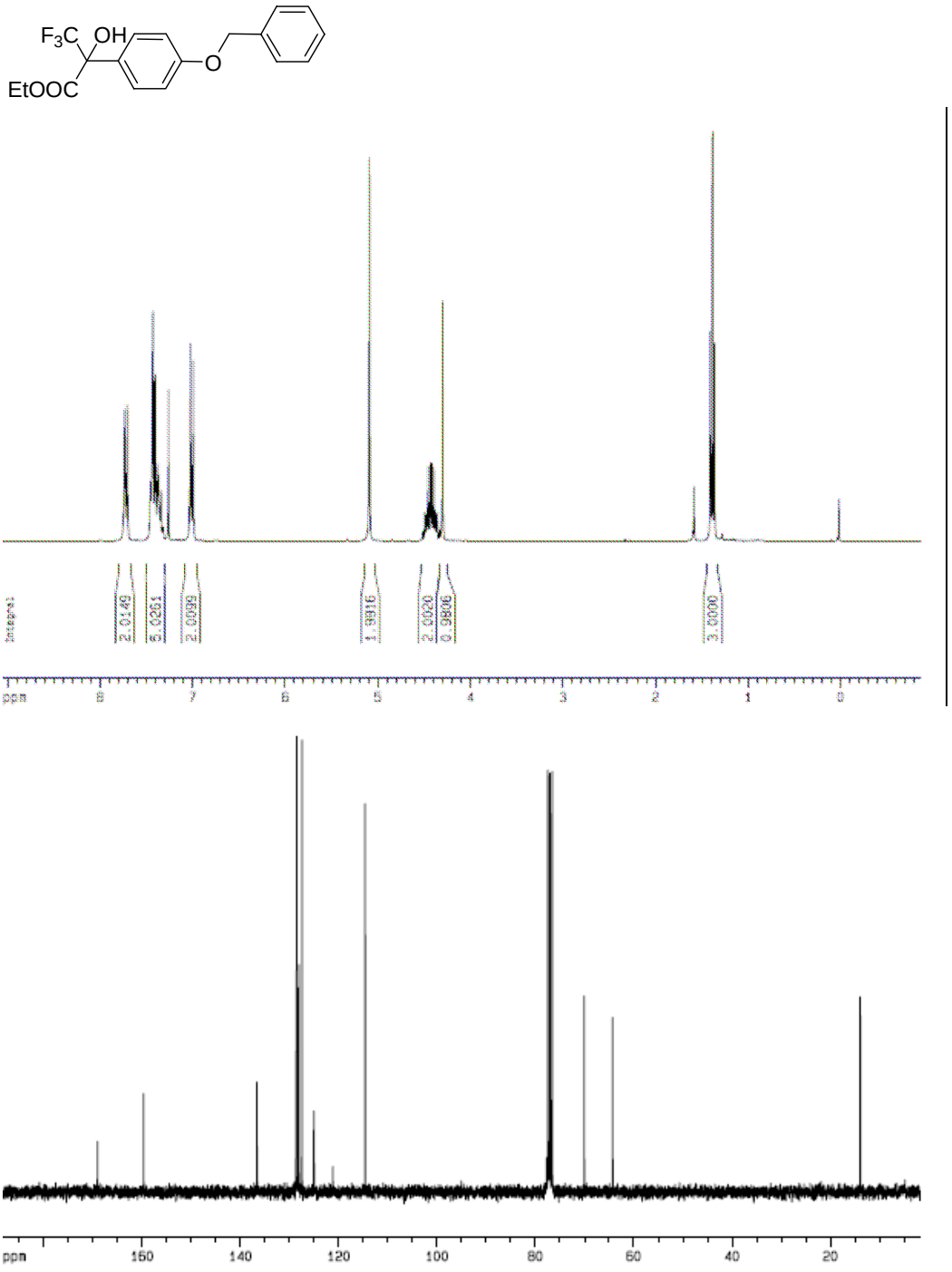
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-[4'-(2'-bromobenzyloxy)-phenyl]-3,3,3-trifluoro-propanoate (**6f**)

3.6. Sample 6g



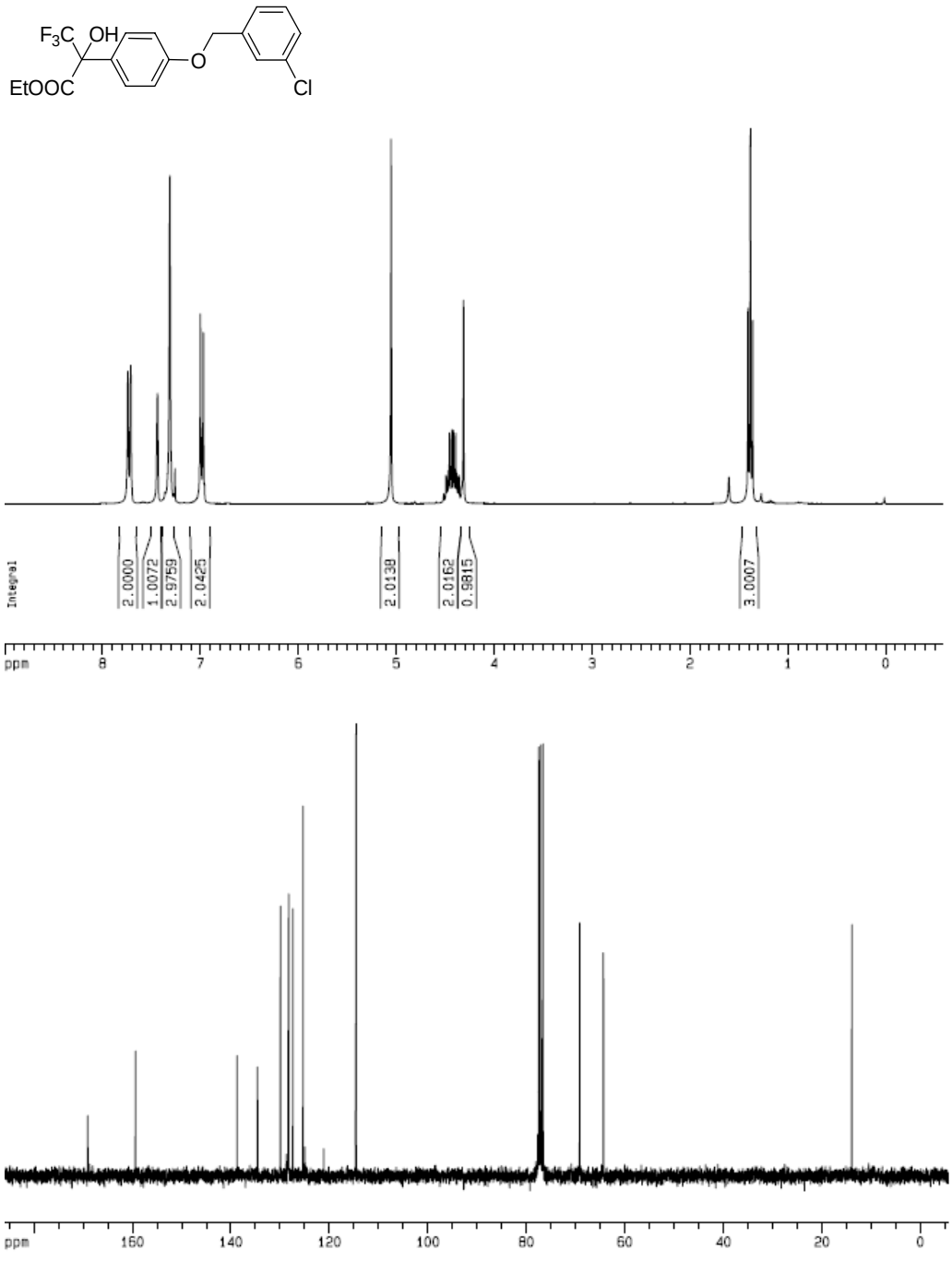
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-[4'-(4'-bromo-benzyloxy)-phenyl]-3,3,3-trifluoro-propanoate (**6g**)

3.7. Sample 6h



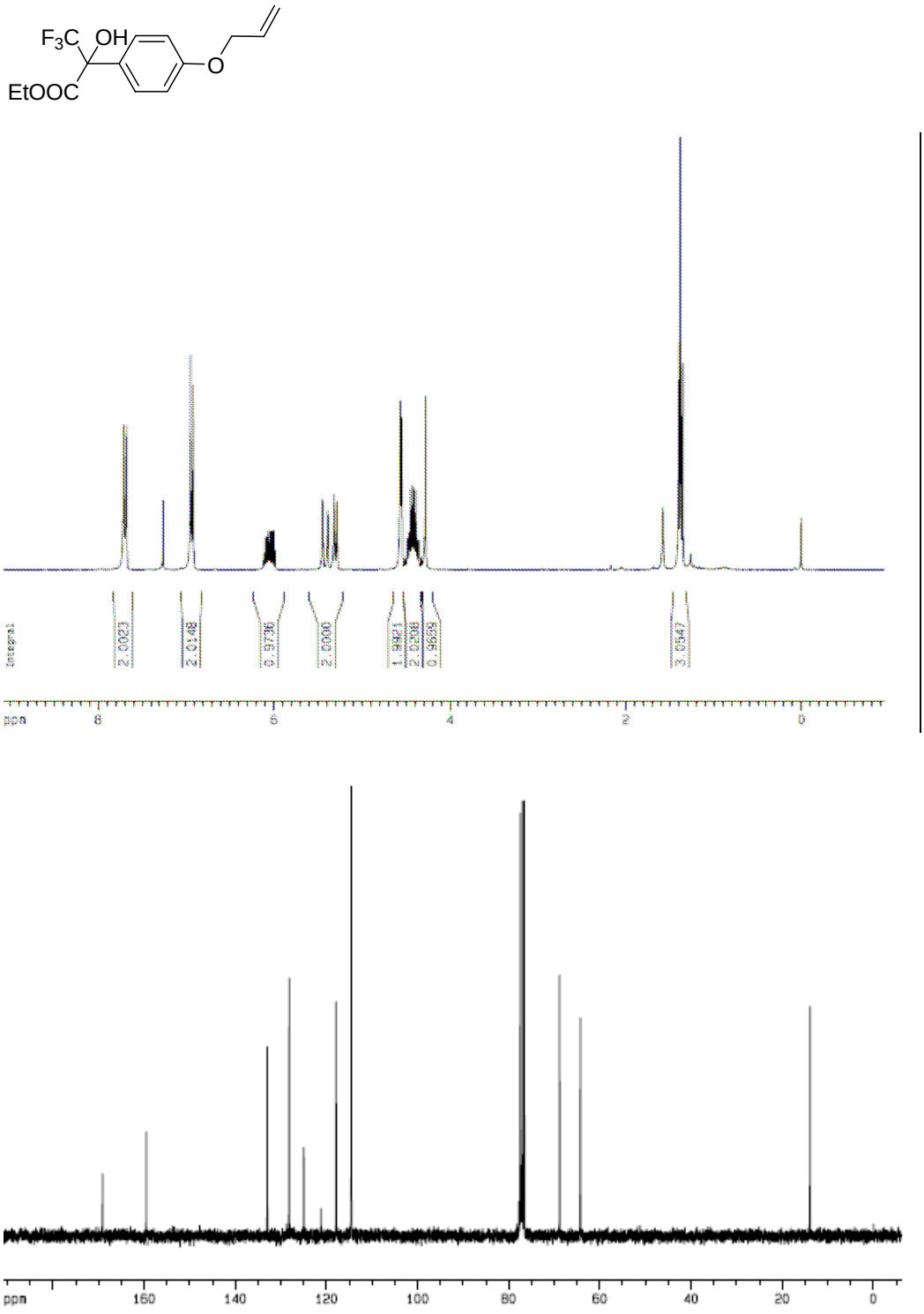
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-(4'-benzyloxyphenyl)-3,3,3-trifluoro-propanoate (**6h**)

3.8. Sample 6i



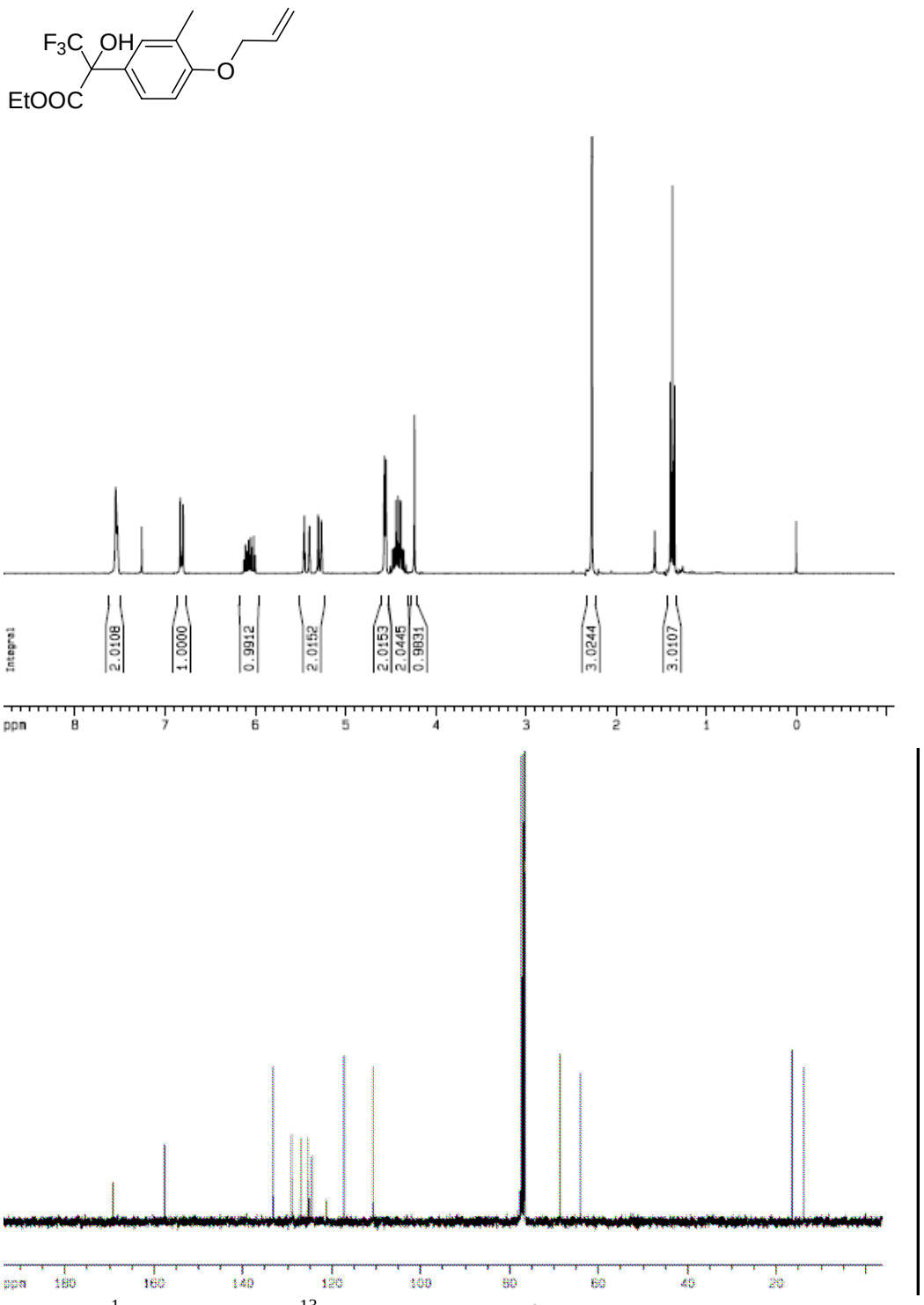
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-[4'-(3'-chlorobenzyloxy)-phenyl]-3,3,3-trifluoro-propanoate (**6i**)

3.9. Sample 6j



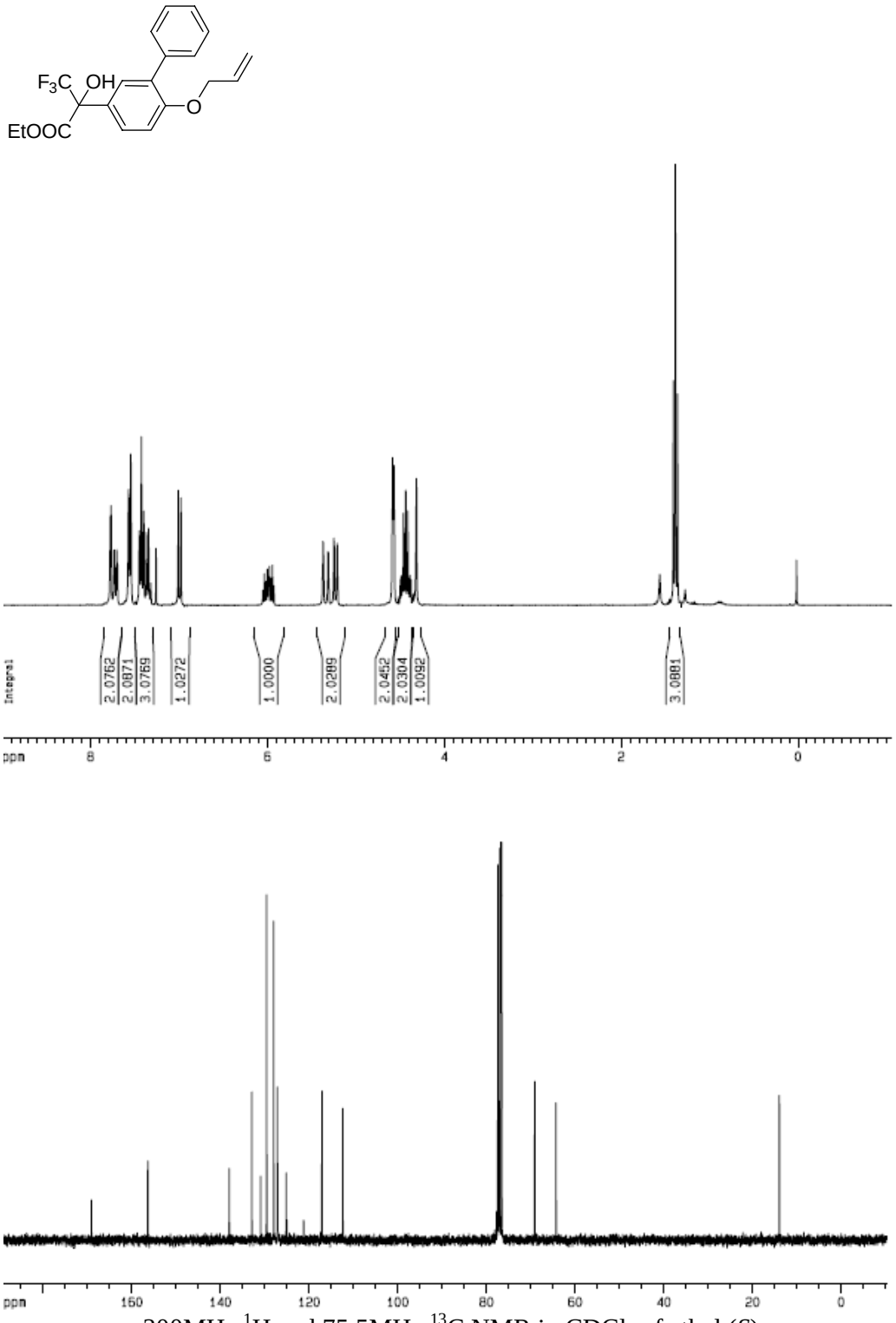
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-(4'-allyloxyphenyl)-3,3,3-trifluoro-propanoate (**6j**)

3.10. Sample 6k



300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-(4'-allyloxy-3'-methylphenyl)-3,3,3-trifluoro-propanoate (**6k**)

3.11. Sample 6l



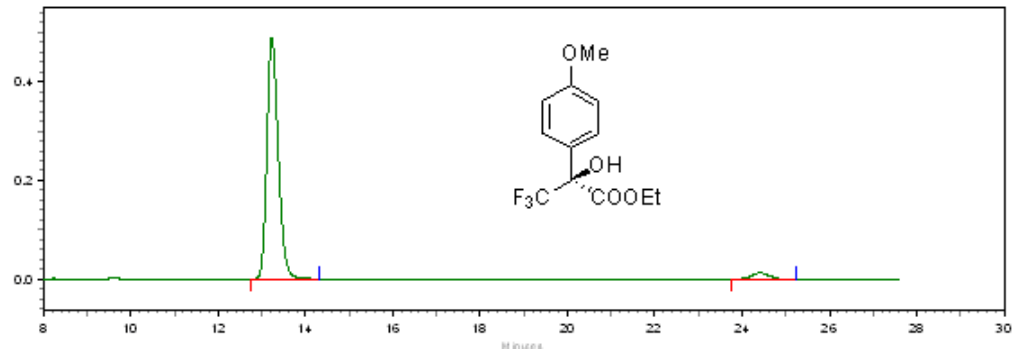
300MHz ^{1}H and 75.5MHz ^{13}C NMR in $CDCl_3$ of ethyl (*S*)-2-hydroxy-2-(4'-allyloxy-3'-phenylphenyl)-3,3,3-trifluoro-propanoate (**6l**)

4. HPLC analysis

4.1. Sample 6a

4.1.1. Chiral product

Sample ID : AD-H/9:1/25/0.6
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060923c-3
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-23 15:25:49

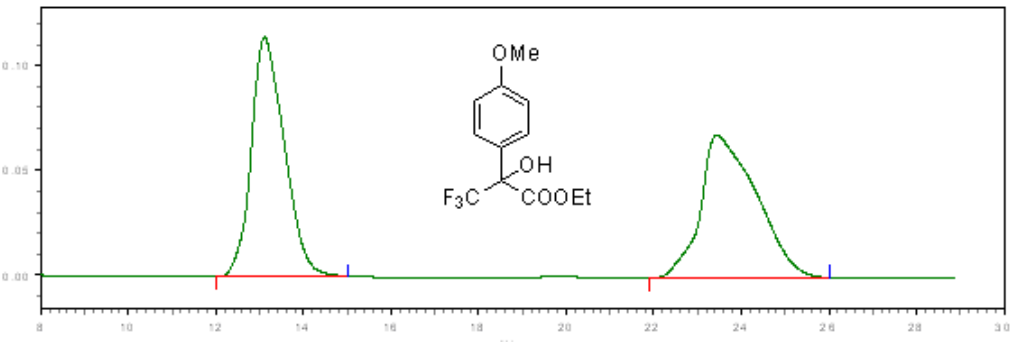


Detector A (254nm)

Retention Time	Area	Area Percent
13.229	8948945	95.91
24.408	381521	4.09

4.1.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060920e
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-20 11:49:53



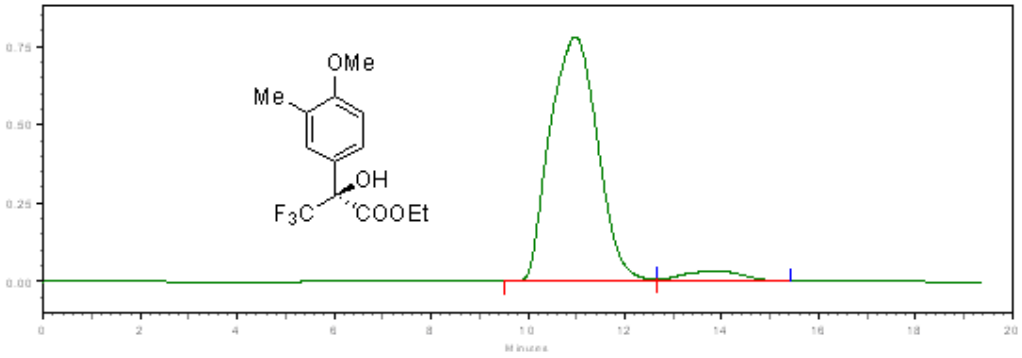
Detector A (254nm)

Retention Time	Area	Area Percent
13.109	6006408	49.70
23.452	6079549	50.30

4.2. Sample 6b

4.2.1. Chiral product

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060317b
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-3-17 10:20:47

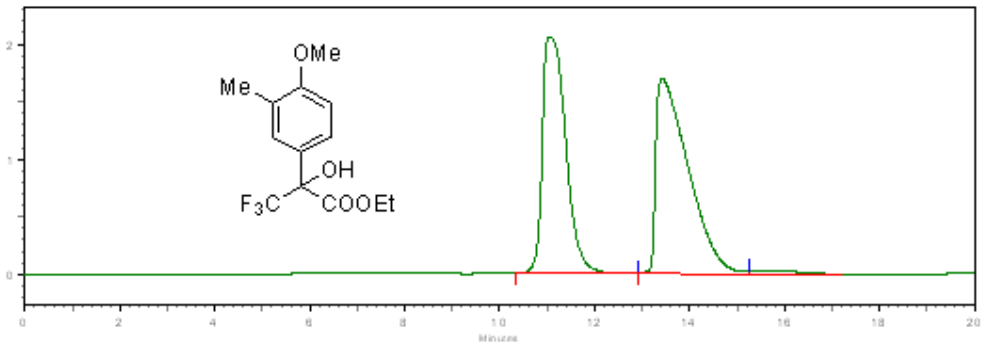


Detector A (254nm)

Retention Time	Area	Area Percent
10.968	53127368	94.95
13.880	2828273	5.05

4.2.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060704c
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-7-4 10:00:13



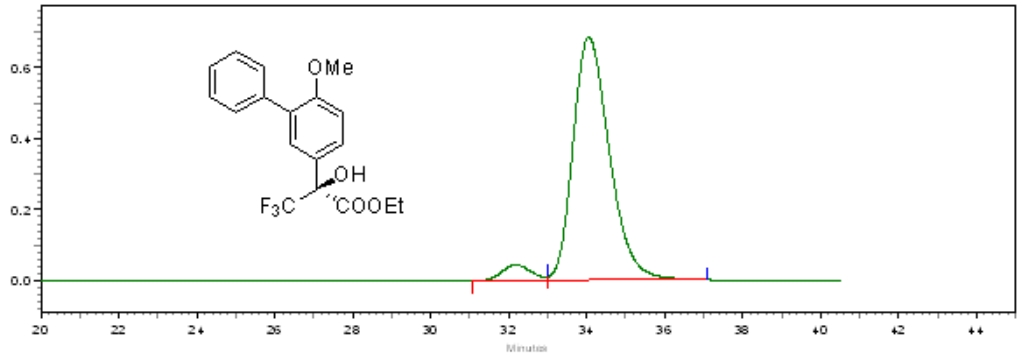
Detector A (254nm)

Retention Time	Area	Area Percent
11.076	70893779	46.83
13.444	80478397	53.17

4.3. Sample 6c

4.3.1. Chiral product

Sample ID : AS-H/9:1/5/0.3
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060414a-3
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-4-14 9:55:43



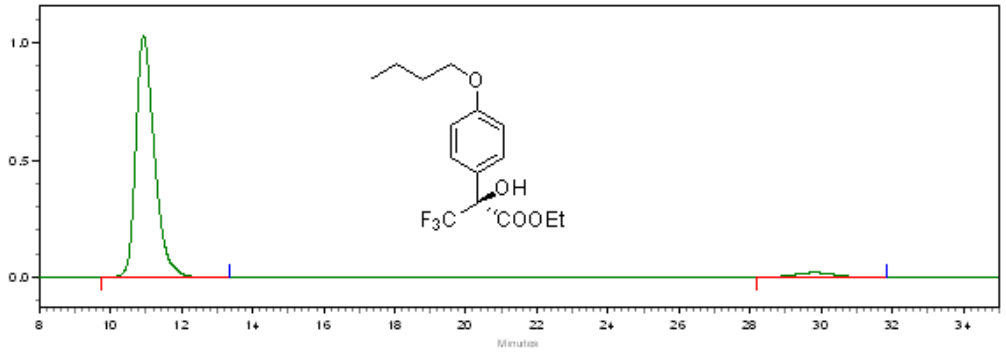
Detector A (254nm)

Retention Time	Area	Area Percent
32.180	2368287	5.04
34.053	44576662	94.96

4.4. Sample 6d

4.4.1. Chiral product

Sample ID : AD-H/25/0.6/9:1
User Name : System
Filename : E:\zhaojunl\asymether\haha\n-Bu-a.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-3-20 12:29:17

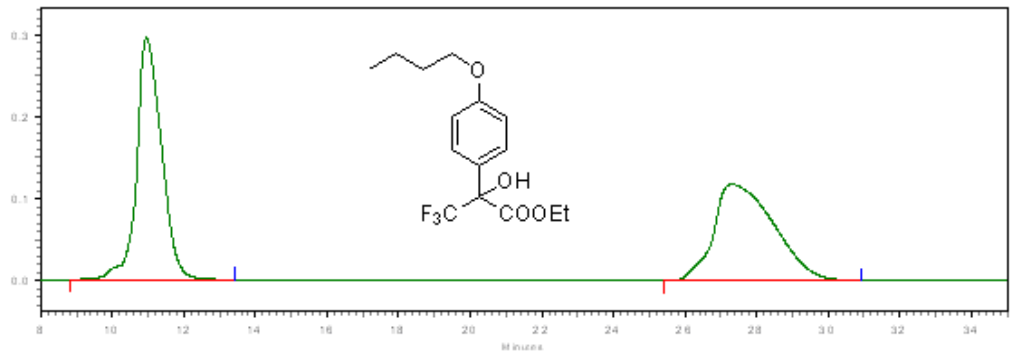


Detector A (254nm)

Retention Time	Area	Area Percent
10.931	37408267	95.97
29.826	1572346	4.03

4.4.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\n-Bu.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-20 13:37:10



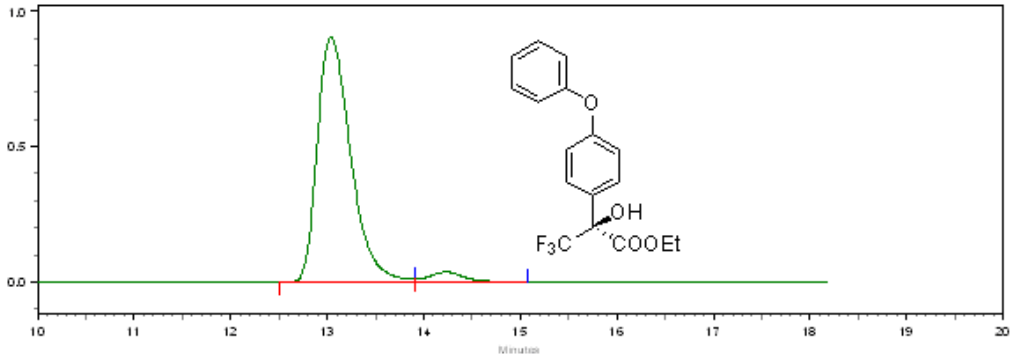
Detector A (254nm)

Retention Time	Area	Area Percent
10.961	14352511	51.21
27.309	13673231	48.79

4.5. Sample 6e

4.5.1. Chiral product

Sample ID : AS-H/9:1/10/0.5
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060923e-4
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-23 18:40:38

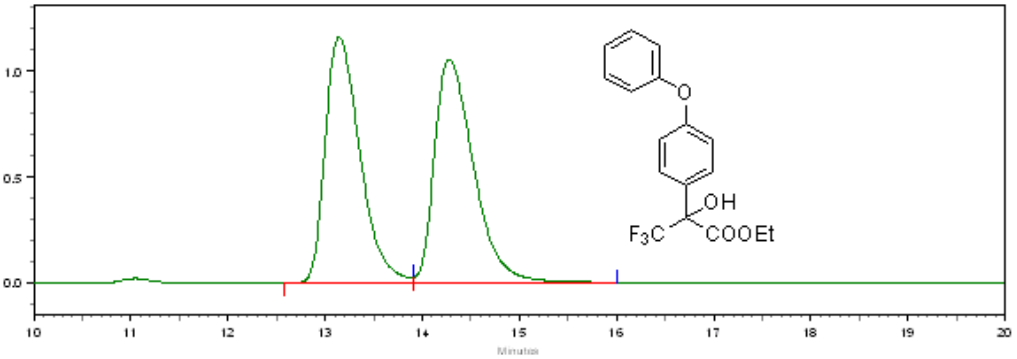


Detector A (254nm)

Retention Time	Area	Area Percent
13.043	21812259	95.86
14.250	940878	4.14

4.5.2 Racemic sample

Sample ID : AS-H/9:1/10/0.5
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060923e-5
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-23 19:00:00



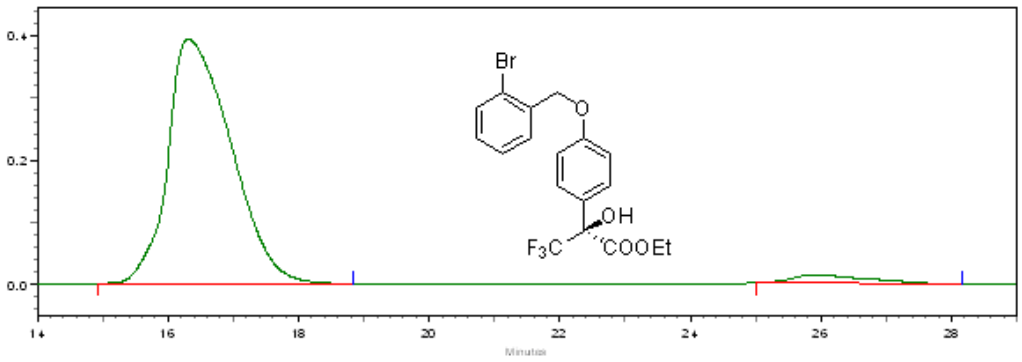
Detector A (254nm)

Retention Time	Area	Area Percent
13.146	28966338	49.55
14.283	29494257	50.45

4.6. Sample 6f

4.6.1. Chiral product

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\2-Br-a.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-20 13:04:11

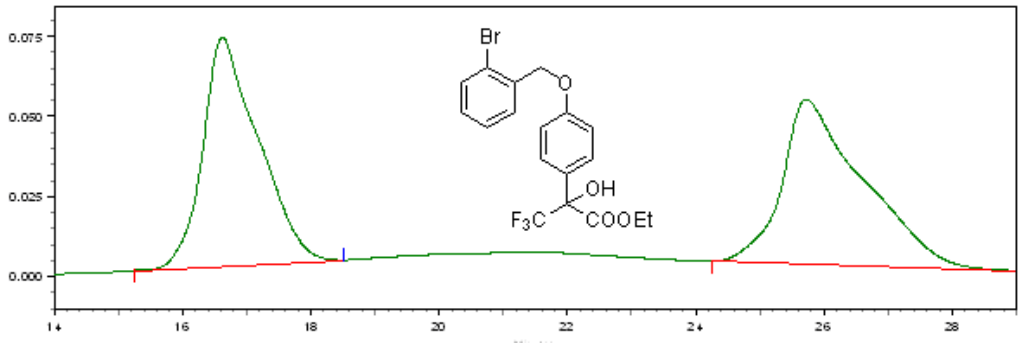


Detector A (254nm)

Retention Time	Area	Area Percent
16.320	26570757	95.97
25.919	1117094	4.03

4.6.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\2-Br.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-21 17:47:39



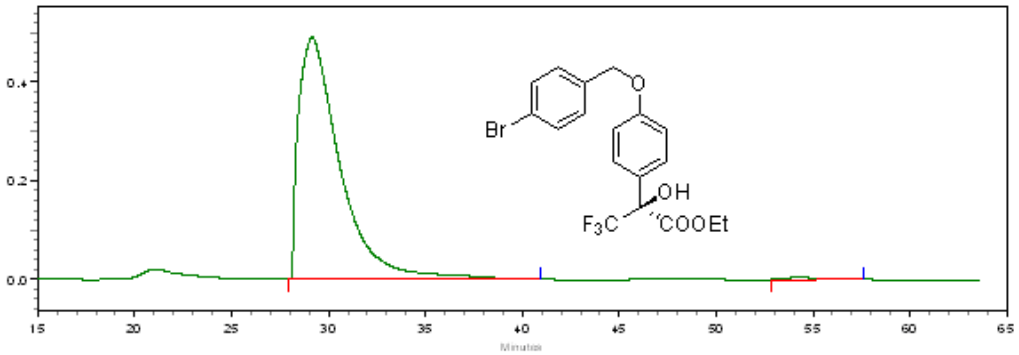
Detector A (254nm)

Retention Time	Area	Area Percent
16.622	4298136	48.57
25.727	4550789	51.43

4.7. Sample 6g

4.7.1. Chiral product (after recrystalization)

Sample ID : AD-H/9:1/25/0.6
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060926
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-27 2:52:25

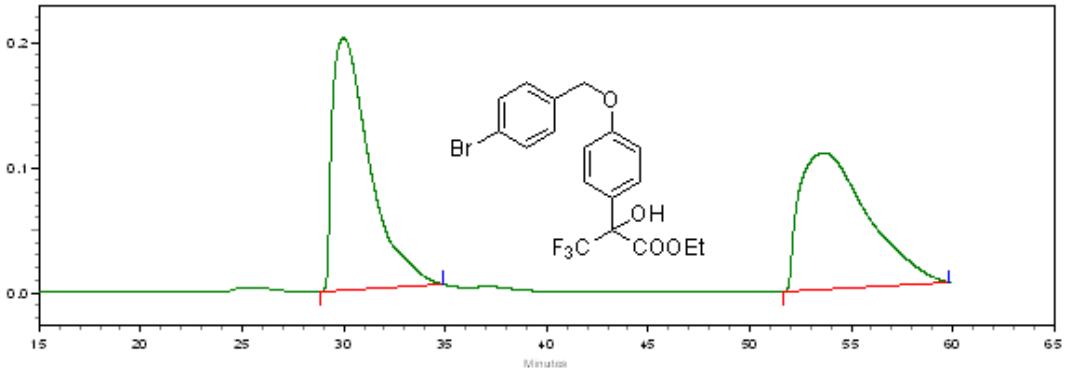


Detector A (254nm)

Retention Time	Area	Area Percent
29.152	73380894	99.26
54.215	561140	0.74

4.7.2. Racemic sample

Sample ID : AD-H/9:1/25/0.6
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060926-1
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-27 3:57:03



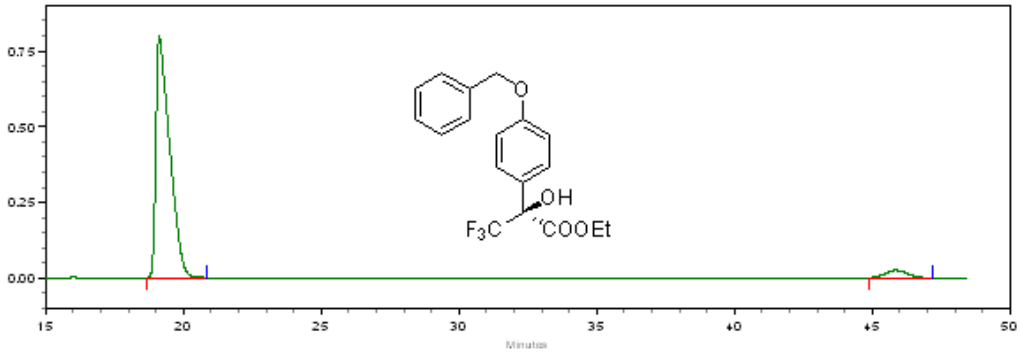
Detector A (254nm)

Retention Time	Area	Area Percent
29.995	25857416	50.14
53.663	25717953	49.86

4.8. Sample 6h

4.8.1. Chiral product

Sample ID : AD-H/9:1/25/0.6
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060923b
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-23 12:44:06

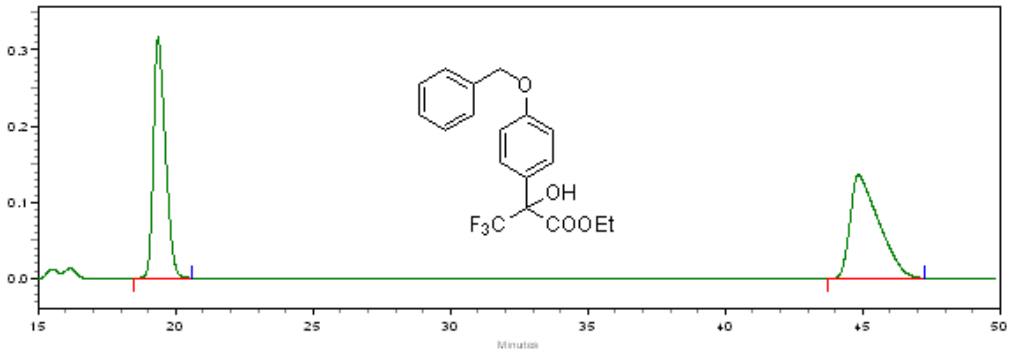


Detector A (254nm)

Retention Time	Area	Area Percent
19.145	27753409	95.04
45.848	1447173	4.96

4.8.2. Racemic sample

Sample ID : AD-H/9:1/25/0.6
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060923b-2
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-23 13:33:58



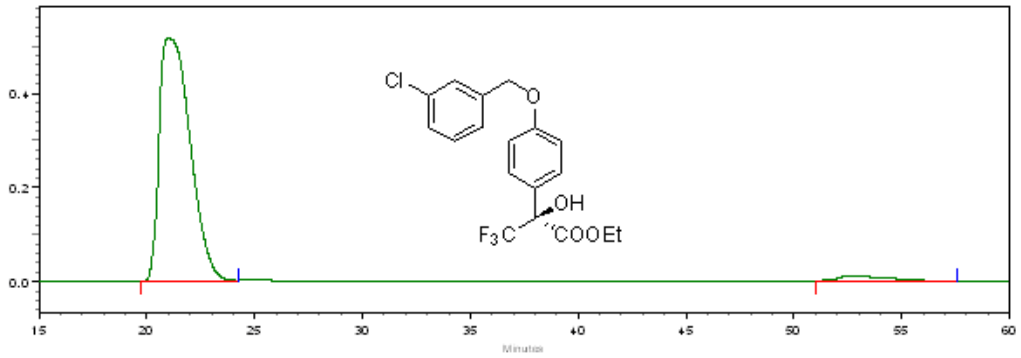
Detector A (254nm)

Retention Time	Area	Area Percent
19.365	9527252	49.08
44.855	9884400	50.92

4.9. Sample 6i

4.9.1. Chiral product

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\3-Cl-a.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-21 19:25:07

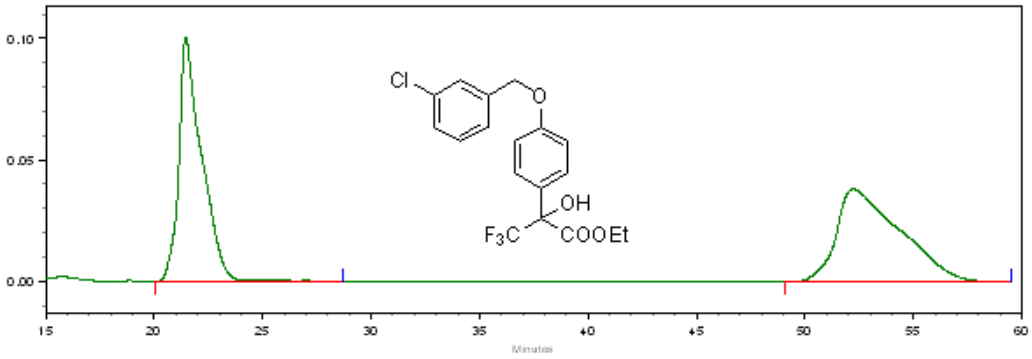


Detector A (254nm)

Retention Time	Area	Area Percent
21.009	51379753	96.36
52.734	1941256	3.64

4.9.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\3-Cl.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-21 18:24:30



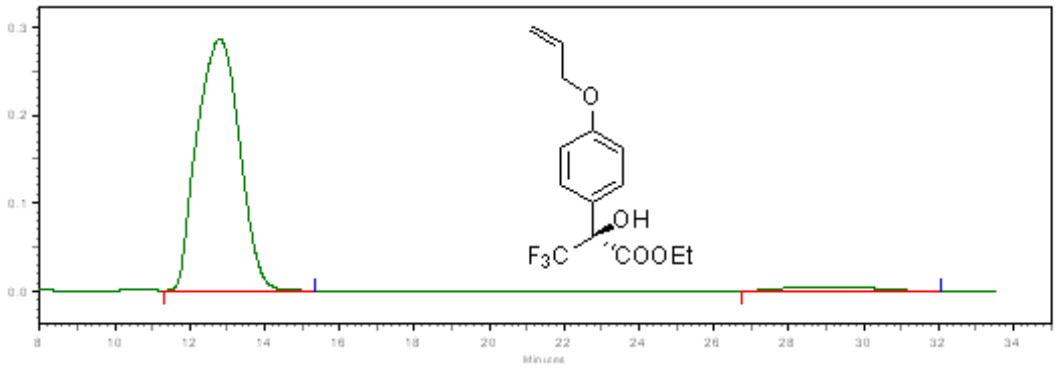
Detector A (254nm)

Retention Time	Area	Area Percent
21.456	7343517	48.56
52.226	7779680	51.44

4.10. Sample 6j

4.10.1. Chiral product

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\allylic-a.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-3-17 10:43:20

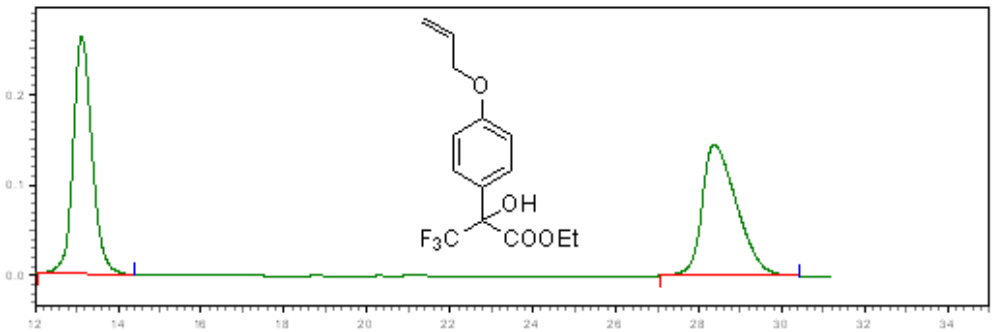


Detector A (254nm)

Retention Time	Area	Area Percent
12.797	22525259	96.45
29.458	829433	3.55

4.10.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\allylic.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-7-4 10:40:53



Detector A (254nm)

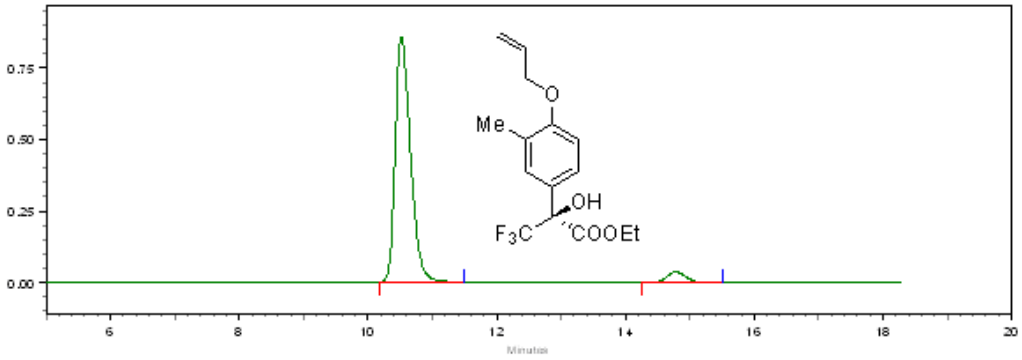
Retention Time	Area	Area Percent

13.123	8272544	49.68
28.375	8379449	50.32

4.11. Sample 6k

4.11.1. Chiral product

Sample ID : AD-H/9:1/25/0.6
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060923d
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-23 15:54:15

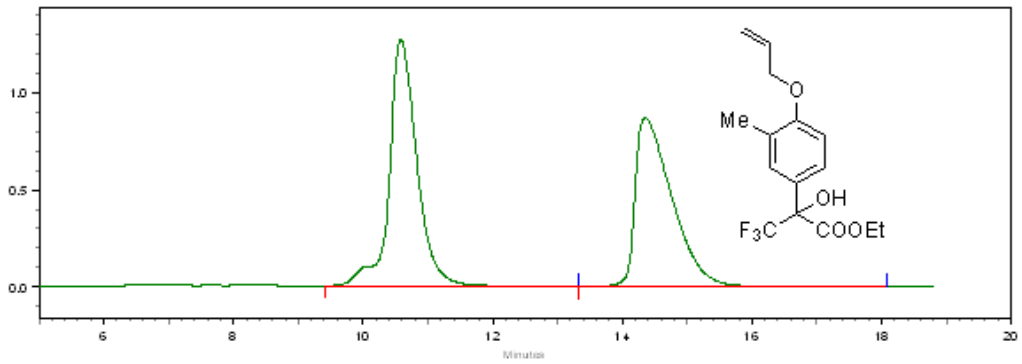


Detector A (254nm)

Retention Time	Area	Area Percent
10.529	14154924	94.94
14.780	754079	5.06

4.11.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\zjl-060704d
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-7-4 10:21:24



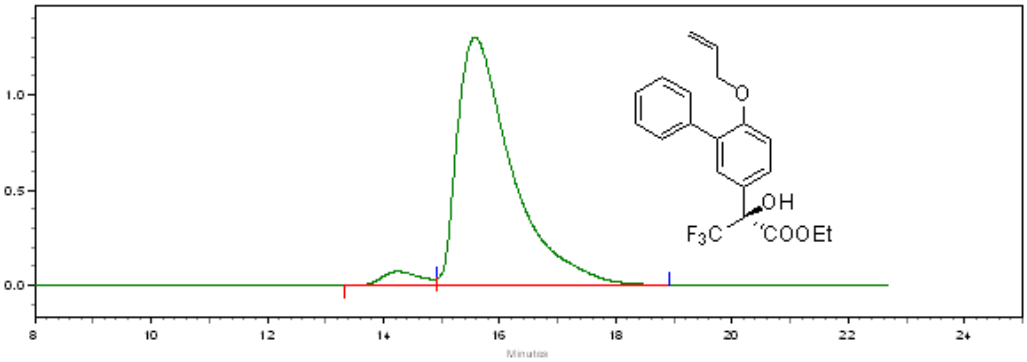
Detector A (254nm)

Retention Time	Area	Area Percent
10.582	37808183	52.55
14.365	34132829	47.45

4.12. Sample 6l

4.12.1. Chiral product

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\2-Ph-al-a.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-4-7 13:33:40

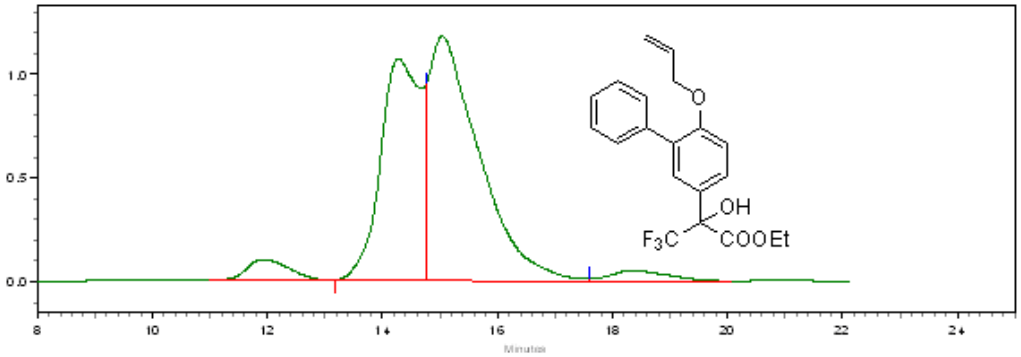


Detector A (254nm)

Retention Time	Area	Area Percent
14.245	3272704	3.74
15.574	84179178	96.26

4.12.2. Racemic sample

Sample ID : AD-H/9:1/0.6/25
User Name : System
Filename : E:\zhaojunl\asymether\haha\2-Ph-al.dat
Method Name : E:\CHENGLIANG\method\1.met
Sequence Name : {Sequence Name}
Run Time : 06-9-20 11:26:41



Detector A (254nm)

Retention Time	Area	Area Percent
14.283	51945822	41.96
15.039	71841308	58.04

5. ORTEP presentation of 6g

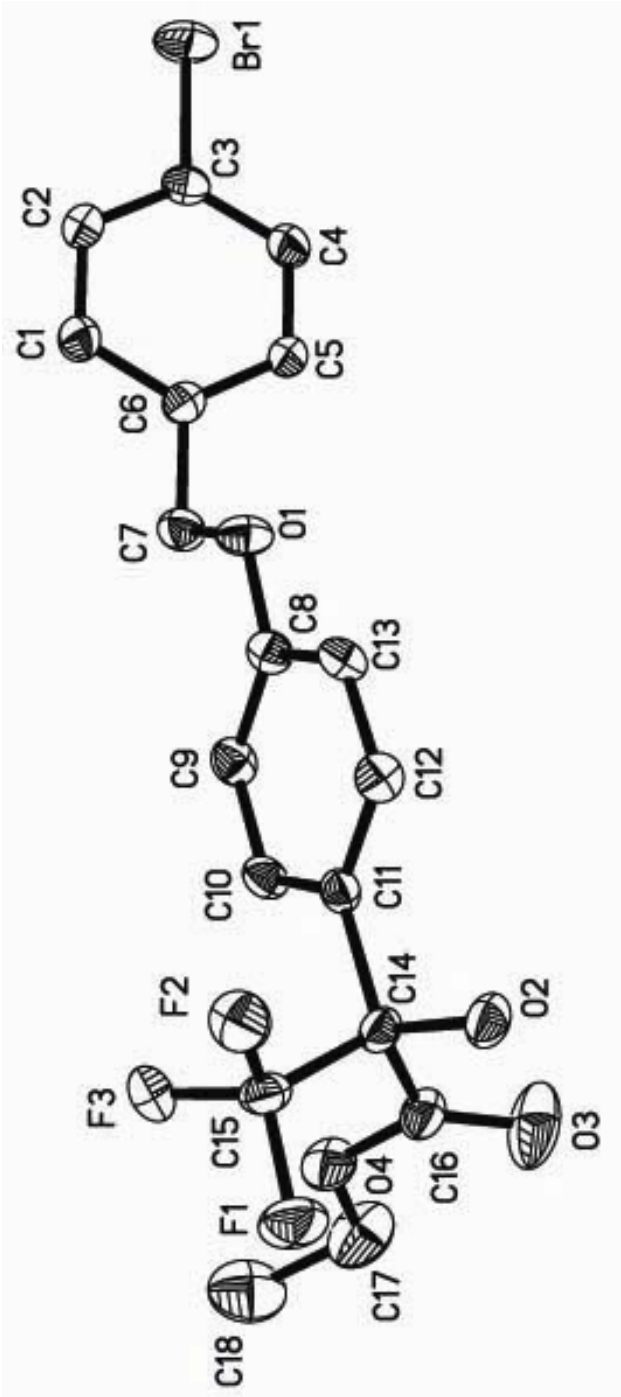


Table 1. Crystal data of **6g** and structure refinement for 60914f.

Compound name: (2*S*)-2-hydroxy-2-[4'-(4'-bromobenzyloxy)-phenyl]-3,3,3-trifluoro-propanoate (**6g**)

Identification code	60914f
Empirical formula	C18 H16 Br F3 O4
Formula weight	433.22
Temperature	294(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 5.9829(11) A alpha = 90 deg. b = 7.2720(14) A beta = 90 deg. c = 41.691(8) A gamma = 90 deg.
Volume	1813.9(6) A^3
Z, Calculated density	4, 1.586 Mg/m^3
Absorption coefficient	2.316 mm^-1
F(000)	872
Crystal size	0.28 x 0.24 x 0.20 mm
Theta range for data collection	1.95 to 26.37 deg.
Limiting indices	-4<=h<=7, -9<=k<=8, -52<=l<=50
Reflections collected / unique	9970 / 2196 [R(int) = 0.0512]
Completeness to theta = 26.37	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6545 and 0.5633
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2196 / 0 / 237
Goodness-of-fit on F^2	1.026

Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1723
R indices (all data)	R1 = 0.0578, wR2 = 0.1776
Absolute structure parameter	0(10)
Largest diff. peak and hole	0.344 and -0.731 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 60914f. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	203(2)	10775(1)	9946(1)	70(1)
F(1)	9122(9)	-4757(6)	8174(1)	70(1)
F(2)	8141(9)	-4220(6)	8663(1)	57(1)
F(3)	5977(7)	-3450(6)	8275(1)	55(1)
O(1)	4656(9)	3497(6)	9137(1)	47(1)
O(2)	11414(7)	-2056(7)	8496(1)	46(1)
O(3)	11458(11)	-298(13)	7943(2)	94(3)
O(4)	7991(9)	-1227(9)	7821(1)	56(1)
C(1)	209(12)	5965(9)	9416(2)	48(2)
C(2)	-359(12)	7388(10)	9629(2)	48(2)
C(3)	1055(12)	8828(8)	9667(2)	40(1)
C(4)	3084(12)	8911(10)	9510(2)	49(2)
C(5)	3661(12)	7487(9)	9300(2)	47(2)
C(6)	2235(11)	6027(9)	9256(1)	39(1)
C(7)	2803(12)	4566(9)	9013(2)	46(2)
C(8)	5644(11)	2273(8)	8932(1)	37(1)
C(9)	4997(12)	1901(8)	8622(2)	43(1)
C(10)	6132(11)	651(9)	8436(2)	40(1)
C(11)	8013(10)	-255(8)	8556(1)	34(1)
C(12)	8665(11)	98(9)	8871(2)	39(1)
C(13)	7502(11)	1327(8)	9054(2)	38(1)
C(14)	9317(10)	-1682(9)	8352(1)	36(1)
C(15)	8128(12)	-3552(10)	8363(2)	43(2)
C(16)	9713(12)	-1009(10)	8014(2)	50(2)
C(17)	8177(18)	-528(18)	7492(2)	80(3)
C(18)	6170(20)	-1164(18)	7312(2)	95(4)

Table 3. Bond lengths [A] and angles [deg] for 60914f.

Br(1)-C(3)	1.902(6)
F(1)-C(15)	1.322(8)
F(2)-C(15)	1.340(8)
F(3)-C(15)	1.341(9)
O(1)-C(8)	1.366(7)
O(1)-C(7)	1.450(8)
O(2)-C(14)	1.418(7)
O(2)-H(2)	0.8200
O(3)-C(16)	1.203(10)
O(4)-C(16)	1.320(9)
O(4)-C(17)	1.465(9)
C(1)-C(6)	1.385(9)
C(1)-C(2)	1.406(9)
C(1)-H(1)	0.9300
C(2)-C(3)	1.355(10)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.380(10)
C(4)-C(5)	1.401(9)
C(4)-H(4)	0.9300
C(5)-C(6)	1.374(9)
C(5)-H(5)	0.9300
C(6)-C(7)	1.508(9)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.378(9)
C(8)-C(13)	1.402(9)
C(9)-C(10)	1.373(9)
C(9)-H(9)	0.9300
C(10)-C(11)	1.397(9)
C(10)-H(10)	0.9300
C(11)-C(12)	1.394(8)
C(11)-C(14)	1.553(8)
C(12)-C(13)	1.364(9)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-C(16)	1.509(9)
C(14)-C(15)	1.535(9)
C(17)-C(18)	1.491(16)

C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600

C(8)-O(1)-C(7)	117.3(5)
C(14)-O(2)-H(2)	109.5
C(16)-O(4)-C(17)	118.1(7)
C(6)-C(1)-C(2)	119.5(6)
C(6)-C(1)-H(1)	120.3
C(2)-C(1)-H(1)	120.3
C(3)-C(2)-C(1)	119.5(6)
C(3)-C(2)-H(2A)	120.3
C(1)-C(2)-H(2A)	120.3
C(2)-C(3)-C(4)	121.8(6)
C(2)-C(3)-Br(1)	118.6(5)
C(4)-C(3)-Br(1)	119.5(5)
C(3)-C(4)-C(5)	118.8(7)
C(3)-C(4)-H(4)	120.6
C(5)-C(4)-H(4)	120.6
C(6)-C(5)-C(4)	120.1(6)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(1)	120.3(6)
C(5)-C(6)-C(7)	119.6(6)
C(1)-C(6)-C(7)	119.9(6)
O(1)-C(7)-C(6)	108.1(5)
O(1)-C(7)-H(7A)	110.1
C(6)-C(7)-H(7A)	110.1
O(1)-C(7)-H(7B)	110.1
C(6)-C(7)-H(7B)	110.1
H(7A)-C(7)-H(7B)	108.4
O(1)-C(8)-C(9)	126.3(6)
O(1)-C(8)-C(13)	116.0(5)
C(9)-C(8)-C(13)	117.7(6)
C(10)-C(9)-C(8)	121.4(6)
C(10)-C(9)-H(9)	119.3
C(8)-C(9)-H(9)	119.3
C(9)-C(10)-C(11)	120.5(6)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	118.5(6)
C(12)-C(11)-C(14)	119.9(5)

C(10)-C(11)-C(14)	121.6(5)
C(13)-C(12)-C(11)	120.2(6)
C(13)-C(12)-H(12)	119.9
C(11)-C(12)-H(12)	119.9
C(12)-C(13)-C(8)	121.6(6)
C(12)-C(13)-H(13)	119.2
C(8)-C(13)-H(13)	119.2
O(2)-C(14)-C(16)	108.6(5)
O(2)-C(14)-C(15)	103.2(5)
C(16)-C(14)-C(15)	112.9(5)
O(2)-C(14)-C(11)	109.9(5)
C(16)-C(14)-C(11)	111.9(5)
C(15)-C(14)-C(11)	110.0(5)
F(1)-C(15)-F(2)	108.3(6)
F(1)-C(15)-F(3)	107.6(6)
F(2)-C(15)-F(3)	106.4(6)
F(1)-C(15)-C(14)	111.1(5)
F(2)-C(15)-C(14)	110.3(5)
F(3)-C(15)-C(14)	112.8(6)
O(3)-C(16)-O(4)	125.3(7)
O(3)-C(16)-C(14)	120.5(7)
O(4)-C(16)-C(14)	114.2(6)
O(4)-C(17)-C(18)	107.5(9)
O(4)-C(17)-H(17A)	110.2
C(18)-C(17)-H(17A)	110.2
O(4)-C(17)-H(17B)	110.2
C(18)-C(17)-H(17B)	110.2
H(17A)-C(17)-H(17B)	108.5
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 60914f. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	90(1)	61(1)	59(1)	-24(1)	1(1)	18(1)
F(1)	81(3)	46(2)	83(3)	-18(2)	22(3)	9(2)
F(2)	71(3)	51(2)	50(2)	9(2)	3(2)	-10(2)
F(3)	49(2)	55(2)	61(2)	-9(2)	-5(2)	-16(2)
O(1)	59(3)	42(2)	39(2)	-8(2)	-2(2)	15(2)
O(2)	30(2)	58(3)	49(2)	1(2)	2(2)	4(2)
O(3)	58(3)	161(8)	64(3)	46(5)	6(3)	-27(5)
O(4)	59(3)	78(4)	30(2)	6(2)	3(2)	-3(3)
C(1)	47(4)	42(3)	54(4)	-6(3)	8(3)	-8(3)
C(2)	40(3)	56(4)	48(3)	-5(3)	7(3)	-4(3)
C(3)	51(4)	31(3)	38(3)	-3(2)	-3(3)	7(3)
C(4)	44(4)	46(4)	56(4)	-14(3)	2(3)	-5(3)
C(5)	38(3)	53(4)	49(4)	-14(3)	9(3)	-7(3)
C(6)	38(3)	43(3)	37(3)	1(3)	1(2)	3(3)
C(7)	48(4)	41(3)	48(3)	-9(3)	0(3)	2(3)
C(8)	43(3)	31(3)	37(3)	1(2)	-2(2)	-1(3)
C(9)	38(3)	42(3)	49(3)	-1(2)	-10(3)	4(3)
C(10)	39(3)	44(3)	37(3)	-6(3)	-10(2)	0(3)
C(11)	31(3)	31(3)	39(3)	-1(2)	-1(2)	-3(2)
C(12)	39(3)	36(3)	41(3)	5(3)	-5(3)	6(3)
C(13)	44(3)	33(3)	36(3)	-4(2)	-10(3)	1(3)
C(14)	27(3)	43(3)	40(3)	-1(3)	3(2)	5(2)
C(15)	50(4)	43(3)	37(3)	-7(3)	11(3)	-1(3)
C(16)	43(3)	52(4)	55(4)	-1(3)	15(3)	-7(4)
C(17)	78(6)	117(8)	45(4)	25(5)	7(4)	14(6)
C(18)	119(9)	106(8)	60(5)	0(6)	-19(6)	16(8)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 60914f.

	x	y	z	U(eq)
H(2)	12244	-1169	8472	68
H(1)	-769	4989	9383	57
H(2A)	-1693	7342	9743	58
H(4)	4051	9894	9544	59
H(5)	5011	7530	9189	56
H(7A)	1520	3777	8976	55
H(7B)	3215	5132	8810	55
H(9)	3766	2508	8536	52
H(10)	5645	407	8229	48
H(12)	9897	-506	8958	46
H(13)	7953	1542	9264	45
H(17A)	9525	-994	7391	96
H(17B)	8244	805	7493	96
H(18A)	4851	-621	7404	142
H(18B)	6061	-2479	7325	142
H(18C)	6291	-801	7091	142

Table 6. Torsion angles [deg] for 60914f.

C(6)-C(1)-C(2)-C(3)	2.1(10)
C(1)-C(2)-C(3)-C(4)	-2.3(10)
C(1)-C(2)-C(3)-Br(1)	177.9(5)
C(2)-C(3)-C(4)-C(5)	1.8(10)
Br(1)-C(3)-C(4)-C(5)	-178.5(5)
C(3)-C(4)-C(5)-C(6)	-1.0(11)
C(4)-C(5)-C(6)-C(1)	0.9(10)
C(4)-C(5)-C(6)-C(7)	176.0(7)
C(2)-C(1)-C(6)-C(5)	-1.4(10)
C(2)-C(1)-C(6)-C(7)	-176.5(6)
C(8)-O(1)-C(7)-C(6)	-170.6(5)
C(5)-C(6)-C(7)-O(1)	71.6(8)
C(1)-C(6)-C(7)-O(1)	-113.2(7)
C(7)-O(1)-C(8)-C(9)	-2.7(10)
C(7)-O(1)-C(8)-C(13)	176.9(6)
O(1)-C(8)-C(9)-C(10)	179.3(6)
C(13)-C(8)-C(9)-C(10)	-0.3(10)

C(8)-C(9)-C(10)-C(11)	-1.2(10)
C(9)-C(10)-C(11)-C(12)	1.9(9)
C(9)-C(10)-C(11)-C(14)	179.6(6)
C(10)-C(11)-C(12)-C(13)	-1.1(9)
C(14)-C(11)-C(12)-C(13)	-178.8(6)
C(11)-C(12)-C(13)-C(8)	-0.4(10)
O(1)-C(8)-C(13)-C(12)	-178.6(6)
C(9)-C(8)-C(13)-C(12)	1.1(10)
C(12)-C(11)-C(14)-O(2)	-16.4(8)
C(10)-C(11)-C(14)-O(2)	165.9(5)
C(12)-C(11)-C(14)-C(16)	-137.1(6)
C(10)-C(11)-C(14)-C(16)	45.2(8)
C(12)-C(11)-C(14)-C(15)	96.6(7)
C(10)-C(11)-C(14)-C(15)	-81.1(7)
O(2)-C(14)-C(15)-F(1)	-67.1(7)
C(16)-C(14)-C(15)-F(1)	49.9(8)
C(11)-C(14)-C(15)-F(1)	175.7(5)
O(2)-C(14)-C(15)-F(2)	53.1(6)
C(16)-C(14)-C(15)-F(2)	170.1(6)
C(11)-C(14)-C(15)-F(2)	-64.1(7)
O(2)-C(14)-C(15)-F(3)	171.9(5)
C(16)-C(14)-C(15)-F(3)	-71.1(7)
C(11)-C(14)-C(15)-F(3)	54.7(7)
C(17)-O(4)-C(16)-O(3)	-1.1(13)
C(17)-O(4)-C(16)-C(14)	176.9(7)
O(2)-C(14)-C(16)-O(3)	-24.6(11)
C(15)-C(14)-C(16)-O(3)	-138.3(9)
C(11)-C(14)-C(16)-O(3)	96.9(9)
O(2)-C(14)-C(16)-O(4)	157.3(6)
C(15)-C(14)-C(16)-O(4)	43.5(8)
C(11)-C(14)-C(16)-O(4)	-81.3(7)
C(16)-O(4)-C(17)-C(18)	172.5(8)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 60914f [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)