Enantioselective *N*-heterocyclic carbene-catalysed intermolecular crossed benzoin condensations: improved catalyst design and the role of *in situ* racemisation

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Supporting Information

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1 General Methods

Unless otherwise noted, all commercially available compounds were used as provided without further purification.

Melting points were determined using a standard melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a Bruker Avance III 400 MHz (400.23 MHz) spectrometer using the solvent peak as internal reference (CDCl3: δ H 7.26; δ C 77.0 and DMSO-d6: δ H 2.51; δ C 39.5). Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). Carbon NMR were recorded on the previously mentioned instrument (100.61 Hz) with total proton decoupling. Mass spectra (MS-ESI) were recorded using a Finnigan MAT 95 or Varian MAT 311A. Electron Impact mass spectra were recorded on the same machine in EI mode. TLC analysis was performed on precoated $60F_{254}$ slides, and visualised under a UV lamp. Flash chromatography was carried out using silica gel, particle size 0.2-0.063 mm and using the indicated mobile phase as correlated with TLC analysis. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR sampling accessory. Optical rotation measurements were made on a Rudolph Research Analytical Autopol IV instrument and are quoted in units of 10^{-1} deg cm^2 g^{-1} with concentration units in mol L^{-1}. Analytical CSP-HPLC was performed on a Daicel CHIRALCEL OD-H (4.6 mm x 25 mm) in isocratic mode (*n*-hexane/IPA, 9/1) at a flow speed of 1.0 mL min^{-1}. RT UV detection was collected at 254 nm. Tetrahydrofuran was distilled from sodium/benzophenone under argon. Liquid aldehydes were distilled under vacuum prior to use. Solid aldehydes were washed acid-free with 10% aq. K_2CO_3-solution prior to use.

2 General Procedures

General Procedure 1 (Synthesis of Arylhydrazine Precursors to Triazolium Ion Precatalysts)

To a 500 mL round-bottom flask equipped with a magnetic stirring bar was charged the relevant aniline precursor. Glacial acetic acid was added to create a 0.8 M solution which was stirred gently at room temperature for 2 minutes. A 1.7 M solution of sodium nitrite (1.09 equiv.) in sulfuric acid was then added dropwise, ensuring that the temperature did not exceed 40 °C. A red or yellow colour was observed upon formation of the diazonium species *in situ*. The solution was then cooled to 0 °C and stirred for 15 minutes before rapid addition of a 3.86 M solution of stannous chloride dihydrate (3.34 equiv.) in hydrochloric acid (note: a thick white slurry results that can cause stirring to halt; it is recommended that the rate of stirring is increased prior to addition or use of an overhead stirrer is employed). Stirring was continued at 0 °C for 15 minutes before allowing the solution to warm to room temperature and stir for a further 1 hour. It was then filtered and the resulting white solid dried *via* suction filtration for 2 hours. This solid was charged to a 250 mL Erlenmeyer flask equipped with a magnetic stirring bar and 2 M NaOH (30 mL) added. The suspension was stirred at room temperature for 15 minutes before extracting with Et_2O (3 x

100 mL). The combined organic extracts were washed with H_2O (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Recrystallisation of the resulting solid from hexane yields the desired arylhydrazine.

General Procedure 2 (Synthesis of Triazolium Ion Precatalysts)

5-(Diphenyl-trimethylsilanyloxy-methyl)-pyrrolidin-2-one (**16** below, 1.00 equiv.) was charged to 250 mL round-bottom flask, equipped with a magnetic stirring bar, the vessel flushed with argon and fitted with a rubber septum. CH_2Cl_2 was added *via* syringe, followed quickly by trimethyloxonium tetrafluoroborate (Meerwein salt, 1.00 equiv.) in one portion. The solution was stirred under argon for 18 h at room temperature before the addition of the relevant arylhydrazine (1.00 equiv.) and stirring continued for a further 24 h. The solution was then concentrated *in vacuo* to yield the hydrazone intermediate as a white fluffy solid. This was dissolved in chlorobenzene and the vessel set up for reflux under argon. Triethyl orthoformate (4.3 equiv.) was added *via* syringe and the solution refluxed at 120 °C for 24 h. A further aliquot of triethyl orthoformate (4.3 equiv.) was added and refluxing continued for a further 48 h. Upon cooling, the dark brown solution was concentrated *in vacuo* and the oily residue dissolved in MeOH. The vessel was again flushed with argon and fitted with a rubber septum. Bromotrimethylsilane (TMS-Br, 3.5 equiv. as a 10% v/v solution in MeOH) was added *via* syringe and the solution stirred under argon for 24 h at room temperature. Upon concentration, the dark brown residue was subjected to flash chromatography as outlined below to obtain the final compound.

An important note is that the ^{19}F NMR spectra of catalysts of general type **20** are silent, so full or partial anion exchange (most likely with bromide derived from the last step) may occur.

General Procedure 3 (Asymmetric NHC-Catalysed Crossed Aromatic-Aromatic Benzoin Condensation Between Two Non-identical Aromatic Aldehydes)

A flame-dried 5 mL round-bottom flask containing a magnetic stirring bar was charged with the relevant chiral triazolium ion precatalyst (0.066 mmol, 6 mol%), flushed with argon gas and sealed with a rubber septum under an inert atmosphere. Toluene and THF (7.5:1, 1.1 M) and DIPEA (11.5 µL, 0.066 mmol, 6 mol%) were added *via* syringe and the suspension stirred for 5 minutes. A colour charge from orange to red is usually observed upon formation of the carbene species *in situ*. The relevant *ortho*-substituted aromatic benzaldehyde was then added *via* syringe, followed by the relevant aldehyde coupling partner (1.1 mmol, 1.00 equiv.). The septum was replaced with a glass stopper under a gentle flow of argon and the vessel sealed to the external atmosphere using parafilm. The reaction was stirred at room temperature for 20 hours before quenching with H_2O (5 mL) and extracting with CH_2Cl_2 (2 x 10 mL). The combined

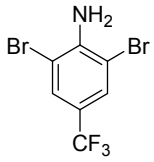
organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified *via* flash chromatography.

Hydrodebromination of Crossed-Benzoin **30**

To a flame-dried 50 mL round-bottom flask equipped with a magnetic stirring bar was charged **30** (116 mg, 0.34 mmol, 1.00 equiv.), MeOH (10 mL), palladium on activated charcoal (10% Pd basis, 25 wt%) and ammonium formate (100 mg, 1.6 mmol, 5.00 equiv.). After fitting the flask with a reflux condenser, the mixture was refluxed and the progress of the reaction monitored *via* TLC. Upon consumption of the starting material, the reaction was allowed to cool and filtered to remove the Pd/C. The filtrate was concentrated *in vacuo* before adding CH_2Cl_2 (10 mL) and H_2O (5 mL). The layers were separated and the aqueous layer extracted once further with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* once more to yield **6** (83 mg, 93%).

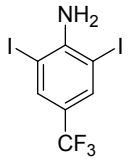
3 Synthesis

2,6-Dibromo-4-(trifluoromethyl)aniline (S1)[1]



To a 250 mL round-bottom flask equipped with a magnetic stirring bar was charged 4-(trifluoromethyl)aniline (2.3 mL/3 g, 18.6 mmol, 1.00 equiv.), iron filings (190 mg) and ethyl acetate (20 mL). Br_2 (1.92 mL, 37.2 mmol, 2.00 equiv.) was added dropwise at 30 – 50 °C. The solution was then heated at reflux for 1 hour before being concentrated *in vacuo*, redissolved in Et_2O and basefied to pH 14 with 2 M NaOH. The organic layer was separated and the aqueous layer washed with Et_2O (2 x 50 mL). The organic extracts were then combined, washed with H_2O (2 x 50 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give the crude product as a pale yellow oil. Purification *via* flash chromatography (100% hexane) yielded a colourless oil. Scratching the bottom of the vessel with a glass pipette caused solidification, producing the title compound as a white solid (3.00 g, 50%). M.p. 37 °C (lit. 37-39 °C). δ_H (400 MHz, $CDCl_3$): 4.78 (s, 2H), 7.62 (s, 2H).

2,6-Diiodo-4-(trifluoromethyl)aniline (S2)[2]

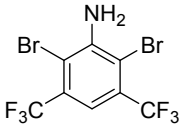


To a 250 mL round-bottom flask equipped with a magnetic stirring bar was charged 4-(trifluoromethyl)aniline (1.54 mL/2 g, 12 mmol, 1.00 equiv.) and acetic acid (12.5 mL). A solution of iodine monochloride (4.5 g, 27 mmol, 2.27 equiv.) in acetic acid (15 mL) was added dropwise followed by immediate addition of H_2O (50 mL). The resulting suspension was heated gradually to 80 °C, stirred at this temperature for 3 hours and, upon cooling, basefied with a 40% NaOH solution to pH 11. The product was then extracted with EtOAc (2 x 100 mL). The combined organic extracts were washed with a saturated aqueous sodium thiosulfate solution, dried over $MgSO_4$ and concentrated *in vacuo* to give the crude product as a light brown solid. Trituration with cold hexane provided the title compound as a white solid (4.28 g, 86%). M.p. 97 °C (lit. 96 °C). δ_H (400 MHz, $CDCl_3$): 4.95 (s, 2H), 7.84 (s, 2H).

2,6-Dibromo-3,5-bis(trifluoromethyl)phenylamine (S3)[3]

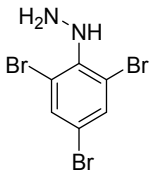
[1] "5-Acylamino-4-cyano-1-phenylpyrazole derivatives and use as herbicides", Mayr & Baker Ltd, Patent US4459150 A1, 1984.

[2] D. M. Lindsay, W. Dohle, A. E. Jensen, F. Kopp, P. Knochel, *Org. Lett.*, 2002, **4**, 1819.



To a mixture of 3,5-bis(trifluoromethyl)aniline (2.04 mL/3.00 g, 13.2 mmol, 1.00 equiv.), K_2CO_3 (2.32 g, 16.7 mmol) and iron filings (384 mg) in a 500 mL round-bottom flask, equipped with a magnetic stirring bar, was added CH_2Cl_2 (300 mL). A solution of Br_2 (3 mL, 41.3 mmol, 3.13 equiv.) in CH_2Cl_2 (30 mL) was added dropwise with stirring and the mixture heated at reflux for 3 days. Upon cooling, a saturated aqueous Na_2CO_3 solution (200 mL) was added the organic layer extracted with Et_2O (2 x 100 mL). After drying over $MgSO_4$ and filtering, the organic extracts were concentrated *in vacuo* to give the crude product as a red solid which was purified *via* flash chromatography (100% hexane). The title compound was obtained as a white solid (2.45 g, 48%). M.p. 76 °C (lit. 75 – 76 °C).

(2,4,6-tribromophenyl)hydrazine (S4)[4]

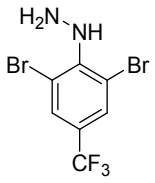


Commercially available 1,3,5-tribromoaniline (3.0 g, 9.1 mmol, 1.00 equiv.) was charged to a 250 mL round-bottom flask equipped with a large magnetic stirring bar and cooled to -25 °C. Hydrochloric acid (36.5%, 12 mL) was added before a 3.2 M aqueous solution of $NaNO_2$ (0.66 g, 9.57 mmol, 1.05 equiv.) was added dropwise with stirring and the solution turned yellow. Stirring was continued for 15 minutes before rapid addition of a 3.6 M solution of $SnCl_2.2H_2O$ (4.926 g, 21.83 mmol, 2.40 equiv.) in hydrochloric acid (36.5%, 6 mL). A thick white slurry developed which required swirling by hand for 5 minutes. Follwing this, the solution was warmed to 0 °C and stirred vigourously for 1 hour. The white solid was filtered, washed with water and dried extensively in air before being collected and transferred to an Erlenmeyer flask. A magnetic stirring bar was charged to the flask followed by a 40% aqeous solution of NaOH (30 mL). The mixture was stirred at ambient temperature for 1 hour before filtering the obtained solid again and drying further in air. Recrystallisation from hot EtOH yielded the titled compound as tan needle-like crystals (1.41 g, 45%). M.p. 143 °C. δ_H (400 MHz, DMSO-d_6): 4.33 (s, 2H), 5.78 (s, 1H), 7.74 (s, 2H).

[3] D. E. Grocock, T. K. Jones, G. Hallas, J. D. Hepworth, *J. Chem. Soc. C*, 1971, 3305.

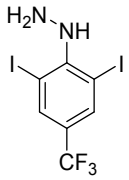
[4] M. Soroka, W. Goldemann, P. Malysa, M. Stochaj, *Syntheis*, 2003, **15**, 2341.

(2,6-Dibromo-4-trifluoromethyl-phenyl)hydrazine (S5)[1]



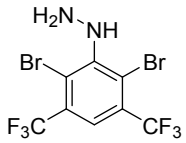
Prepared according to **general procedure 1** using **S1** (3.32 g, 10.4 mmol) as white needle-like crystals (0.973 g, 28%). M.p. 65-66 °C. (lit. 65-67 °C). δ_H (400 MHz, $CDCl_3$): 4.03 (s, 2H), 5.78 (s, 1H) 7.71 (s, 2H). HRMS (*m/z*-ESI$^+$): Found 332.8848 ($[M + H]^+$, $C_7H_6Br_2F_3N_2$ requires 332.8844).

(2,6-Diiodo-4-(trifluoromethyl)-phenyl)hydrazine (S6)



Prepared according to **general procedure 1** using **S2** (2.42 g, 5.8 mmol) as white needle-like crystals (0.81 g, 32%). M.p. 94-95 °C. R_f = 0.17 (9:1, hexanes:EtOAc). δ_H (400 MHz, $CDCl_3$): 3.96 (s, 2H), 5.52 (s, 1H), 7.99 (s, 2H). δ_C (100 MHz, $CDCl_3$): 79.5, 118.2 (quart., J_{CF} 273.6), 122.0 (quart., J_{CF} 33.8), 136.3 (quart., J_{CF} 3.7), 148.9. δ_F (376 MHz, $CDCl_3$): -61.40. ν_{max} (neat)/cm^{-1} 3410, 3323, 3088, 1784, 1604, 1545, 1464, 1387, 1307, 1110, 1088, 933, 886, 739, 700, 655, 619. HRMS (*m/z*-ESI$^+$): Found 428.8572 ($[M + H]^+$, $C_7H_6I_2F_3N_2$ requires 428.8567).

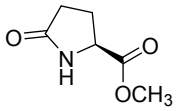
(2,6-Dibromo-3,5-bis(trifluoromethyl)phenyl)hydrazine (S6)



Prepared according **general procedure 1** using **S3** (2.45 g, 6.33 mmol, 1.00 equiv.) as white needle-like crystals (1.27 g, 50%). M.p. 122 °C. R_f = 0.13 (9:1, hexanes:EtOAc). δ_H (400 MHz, $CDCl_3$): 4.02 (s, 2H), 5.90 (s, 1H), 7.69 (s, 1H). δ_C (100 MHz, $CDCl_3$): 118.0 (quart., J_{CF} 273.8), 119.8, 120.8 (quart., J_{CF} 5.8), 130.5 (quart., J_{CF} 32.5), 150.2. δ_F (376 MHz, $CDCl_3$): -62.19, -62.16. ν_{max} (neat)/cm^{-1} 3369, 3268, 3103, 1586, 1497, 1413, 1350, 1279, 1176, 1113, 1053, 937, 900, 799, 725, 661. HRMS (*m/z*-ESI$^+$): Found 400.8728 ($[M + H]^+$, $C_8H_5Br_2F_6N_2$ requires 400.8718).

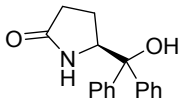
3.1 Experimental Data for Triazolium Salt Precatalysts

(5*S*)-oxopyrrolidine-2-carboxylic acid methyl ester (14)[5]



To an oven-dried 250 mL Schlenk flask was charged *L*-pyroglutamic acid (10.00 g, 77.447 mmol) and Dowex-50W (X8-200) resin (5.00 g). The flask was evacuated and back-flushed with Argon x 3. Methanol (HPLC grade) was added to the flask, which was then equipped with a reflux condenser. The reaction was heated under reflux at for 72 h. The solution was filtered to remove the solid resin and concentration of the filtrate *in vacuo* yielded the title product as a pale yellow oil (11.08 g, 100%). δ_H (600 MHz, $CDCl_3$): 2.13-2.21 (m, 1H), 2.25-2.48 (m, 3H), 3.73 (s, 3H), 4.22 (dd, *J* 8.8, 5.0, 1H), 7.35 (br. s, 1H). δ_C (150 MHz, $CDCl_3$): 24.8, 29.3, 52.5, 55.5, 172.7, 178.5. HRMS (*m/z*-ESI$^+$): Found 166.0477 ($[M^+ + Na]^+$ $C_6H_9NO_3Na$ requires 166.0480).

(5*S*)-(Hydroxy-diphenyl-methyl)-pyrrolidin-2-one (15)[6,7]



An oven-dried 500 mL round bottomed flask equipped with a magnetic stirrer was charged with magnesium (3.28 g, 0.175 mol, 3.00 equiv.) and THF (15 mL) was added. Bromobenzene (15.12 mL 0.175 mol, 3.00 equiv.) was added slowly over 5 minutes in 1 mL aliquots with stirring. Gentle heating was provided by holding the flask with one hand and once 3.0 mL of bromobenzene had been added, formation of the Grignard reagent was observed *in situ* as the solution turned dark brown. Bromobenzene was continually added in 1 mL aliquots. Once 7 mL of bromobenzene had been added, a further 15 mL THF was syringed into the reaction mixture and the remaining bromobenzene was added in 1 mL aliquots. The reaction was then heated to 80 °C for 1 hour to ensure complete formation of the Grignard reagent. Upon cooling, **14** (4.7 g, 36.0 mmol, 1.00 equiv.) was charged to a pressure-equalised dropping funnel and dissolved in THF (150 mL). This solution was added in a dropwise manner over the course of 30

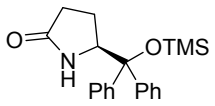
[5] K. Drauz, A. Kleemann, J. Martens and P. Scherberich, *J. Org. Chem.*, 1986, **51**, 3494.

[6] M. Ostendorf, J. Dijkink, F. P. J. T. Rutjes and H. Hiemstra, *Eur. J. Org. Chem.*, 2000, 115.

[7] W.-B. Liu, H.-F. Jiang, and C.-L. Qiao, *Tetrahedron*, 2009, **65**, 2110.

minutes. The reaction was allowed to stir at room temperature for 2 hours before it was cooled to 0 °C and excess phenylmagnesium bromide quenched with 5% (*v/v*) HCl (30 mL). The aqueous layer was extracted with CH_2Cl_2 (5 x 100 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated *in vacuo* to give an off-white solid. Recrystallisation from CH_2Cl_2 and Et_2O gave the title compound as a white solid (5.37 g, 76%). M.p. 192-194 °C (lit. 191-192 °C). (600 MHz, $CDCl_3$): 1.94-2.01 (m, 1H), 2.11-2.17 (m, 1H), 2.24-2.30 (m, 1H), 2.33-2.39 (m, 1H), 2.74 (br. s, 1H), 4.74 (dd, *J* 8.3, 5.0, 1H), 5.47 (br. s, 1H), 7.23 (t, *J* 7.3, 1H), 7.26 (t, *J* 7.3, 1H), 7.33 (app. t, 2H), 7.37 (app. t, 2H), 7.46 (d, *J* 7.5, 2H), 7.50 (d, *J* 8.3, 2H). δ_C (150 MHz, $CDCl_3$): 21.5, 30.1, 60.5, 78.6, 125.5, 125.7, 127.0, 127.4, 128.2, 128.7, 143.0, 145.1, 179.1.

(5*S*)-(Diphenyl-trimethylsilanyloxy-methyl)-pyrrolidin-2-one (16)[8,9]



An oven-dried 25 mL Schlenk flask equipped with a magnetic stirrer was charged with **15** (0.470 g, 1.750 mmol, 1.00 equiv.) and dimethylaminopyridine (22.0 mg, 0.175 mmol, 0.10 equiv.). The flask was evacuated and back-flushed with Argon x 3. CH_2Cl_2 (18.0 mL) was added *via* a syringe and the reaction cooled to 0 ^oC. Triethylamine (1.0 mL, 3.06 mmol, 9.00 equiv.) was charged and the reaction stirred for 20 min. Trimethylsilane chloride (1.10 mL, 8.5 mmol, 18.0 equiv.) was added to the reaction slowly over 30 min. The reaction was stirred overnight at ambient temperature and quenched *via* slow addition of deionised water (10 mL). The organic layer was removed and the aqueous layer was washed with CH_2Cl_2 (4 x 10 mL aliquots). The organic layers were combined, dried ($MgSO_4$) and solvent removed under reduced pressure to give a brown residue. Purification by column chromatography (3:2 EtOAc:hexane, R_f 0.4) yielded the title compound as a white solid (0.285 g, 96%). M.p. 120-121 °C (lit. 120-122 °C). δ_H (400 MHz, $CDCl_3$): -0.10 (s, 9H) 1.28-1.38 (m, 1H), 1.94-2.02 (m, 1H), 2.07-2.16 (m, 2H), 4.64 (dd, *J* 7.8, 4.3, 1H), 5.89 (bs, 1H), 7.32-7.37 (m, 10H). δ_C (100 MHz, $CDCl_3$): 1.9, 22.3, 29.2, 60.3, 82.7, 127.8, 128.0, 128.1, 128.2, 142.9, 143.1, 178.7.

Precatalysts **12** and **21** were prepared according to previous literature.[10,11]

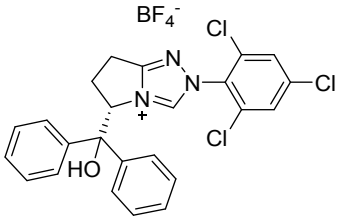
[8] Y.-R. Zhang, L. He, X. Wu, P. -L. Shao and S. Ye, *Org. Lett.*, 2008, **10**, 2, 277.

[9] a) C. B. Cui, H. Kakeya, H. Osada, *Tetrahedron* 1996, **52**, 12651. b) C. B. Cui, H. Kakeya and H. Osada, *J. Antibiot*., 1996, **49**, 832.

[10] D. Enders and J. Han, Tetrahedron: Asymmetry, 2008, 19, 1367.

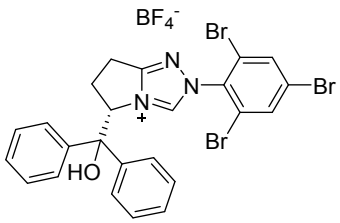
[11] S. E. O'Toole, S. J. Connon, *Org. Biomol. Chem.*, 2009, **7**, 3584.

(*S*)-5-(Hydroxy-diphenyl-methyl)-2-(2,4,6-trichloro-phenyl)-2,5,6,7-tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium tetrafluoroboride (22)



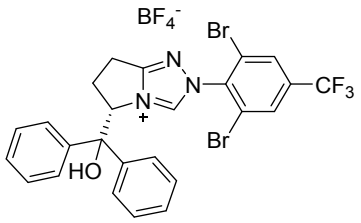
Prepared according to **general procedure 2** using **16** (1.27 g, 3.7 mmol, 1.00 equiv.), Meerwein salt (0.71 g, 3.7 mmol, 1.00 equiv.), CH_2Cl_2 (30 mL), 2,4,6-trichlorophenyl hydrazine (0.79 g, 3.7 mmol, 1.00 equiv.), chlorobenzene (35 mL), triethyl orthoformate (2 x 2.7 mL, 26 mmol, 8.6 equiv.), TMS-Br (1.7 mL, 13.1 mmol, 3.5 equiv.) and MeOH (100 mL). Purified *via* flash chromatography using a solvent gradient of EtOAc:hexanes (9:1) to EtOAc:MeOH (9:1). Concentration *in vacuo* yielded a tan residue that was redissolved in CH_2Cl_2 and re-concentrated to produce a yellow crystalline solid (854 mg, 41 %). M.p. 182-184 °C. R_f = 0.4 (9:1, EtOAc:MeOH). $[\alpha]_D^{20}$ = -168 (*c* 1.40 in $CHCl_3$), for *S* enantiomer with 100% *ee*. δ_H (400 MHz, DMSO-d_6): 2.64-2.74 (m, 1H), 2.82-2.86 (m, 1H), 3.08-3.21 (m, 2H), 6.16 (d, *J* 7.3, 1H), 6.79 (s, 1H), 7.28-7.31 (m, 2H), 7.35-7.41 (m, 6H), 7.44 (d, *J* 7.6, 2H), 8.11 (s, 2H), 9.45 (s, 1H). δ_C (100 MHz, DMSO-d_6): 21.9, 30.3, 68.5, 79.3, 126.6, 126.8, 128.2, 128.4, 128.9, 129.2, 129.7, 130.7, 134.0, 138.6, 143.3, 143.5, 164.8. ν_{max} (neat)/cm^{-1} 3187, 2951, 1729, 1671, 1593, 1572, 1559, 1448, 1413, 1374, 1245, 1192, 1152, 959, 855, 823, 768, 700. HRMS (*m/z*-ESI$^+$): Found 470.0574 (M^+, $C_{24}H_{19}Cl_3N_3O$ requires 470.0594).

(*S*)-5-(Hydroxy-diphenyl-methyl)-2-(2,4,6-tribromo-phenyl)-2,5,6,7-tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium tetrafluoroboride (23)



Prepared according to **general procedure 2** using **16** (1.42 g, 4.2 mmol, 1.00 equiv.), Meerwein salt (0.80 g, 4.2 mmol, 1.00 equiv.), CH_2Cl_2 (60 mL), 2,4,6-tribromophenyl hydrazine (1.44 g, 4.2 mmol, 1.00 equiv.), chlorobenzene (40 mL), triethyl orthoformate (2 x 3 mL, 29 mmol, 8.60 eq), TMS-Br (1.90 mL, 14.7 mmol, 3.50 equiv.) and MeOH (120 mL). Purified twice *via* flash chromatography using 1) 100 % EtOAc to EtOAc:MeOH (9:1) and 2) EtOAc:MeOH (9:1). Concentration *in vacuo* yielded a tan residue that was redissolved in CH_2Cl_2 and re-concentrated to produce a light tan crystalline solid (913 mg, 31 %). M.p. 190 – 192 °C. R_f = 0.34 (9:1, EtOAc:MeOH). $[\alpha]_D^{20}$ = -175 (*c* 1.40 in $CHCl_3$), for *S* enantiomer with 100% *ee*. δ_H (400 MHz, DMSO-d_6): 2.68-2.73 (m, 2H), 3.08-3.23 (m, 2H), 6.24 (d, *J* 8.0, 1H), 6.76 (s, 1H), 7.26-7.31 (m, 2H), 7.34-7.43 (m, 6H, H-4), 7.45 (d, *J* 7.51, 2H), 8.30 (s, 1H), 8.32 (s, 1H), 9.39 (s, 1H). δ_C (100 MHz, DMSO-d_6): 21.9, 30.4, 68.6, 79.3, 123.6, 123.9, 126.6, 126.8, 127.4, 128.2, 128.4, 129.0, 129.2, 133.8, 135.6, 142.8, 143.4, 143.5, 164.6. ν_{max} (neat)/cm^{-1} 3243, 1668, 1592, 1553, 1494, 1445, 1405, 1371, 1250, 1190, 1066, 1012, 963, 856, 750, 699, 654, 627. HRMS (*m/z*-ESI$^+$): Found 601.9080 (M^+, $C_{24}H_{19}Br_3N_3O$ requires 601.9073).

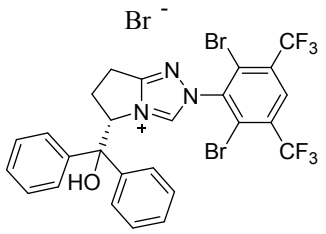
(*S*)-2-(2,6-Dibromo-4-trifluoromethyl-phenyl)-5-(hydroxy-diphenyl-methyl)-2,5,6,7-tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium tetrafluoroboride (24)



Prepared according to **general procedure 2** using **16** (0.99 g, 2.9 mmol, 1.00 equiv.), Meerwein salt (0.43 g, 2.9 mmol, 1.00 equiv.), CH_2Cl_2 (25 mL), 2,6-dibromo-4-(trifluoromethyl)phenyl hydrazine (0.97 g, 2.9 mmol, 1.00 equiv.), chlorobenzene (35 mL), triethyl orthoformate (2 x 2.1 mL, 25 mmol. 8.60 equiv.), TMS-Br (1.34 mL, 10.2 mmol, 3.50 equiv.) and MeOH (90 mL). Purified twice *via* flash chromatography using 1) 100 % EtOAc to EtOAc:MeOH (9:1) and 2) EtOAc:MeOH (9:1). Concentration *in vacuo* yielded a tan residue that was redissolved in CH_2Cl_2 and re-concentrated to produce a light tan crystalline solid in 577 mg (29 %) yield. M.p. 187 °C. R_f = 0.38 (9:1, EtOAc:MeOH). $[\alpha]_D^{20}$ = -189 (*c* 1.40 in $CHCl_3$), for *S* enantiomer with 100% *ee*. δ_H (400 MHz, DMSO-d_6): 2.70 (t, *J* 10.8, 1H), 2.92-2.98 (m, 1H), 3.12 (m, 2H), 6.27 (d, *J* 7.3, 1H), 6.79 (s, 1H), 7.26-7.32 (m, 2H), 7.34 (t, *J* 7.8, 2H), 7.37 (app. t, 2H), 7.43 (d, *J* 7.6, 2H), 7.47 (d, *J* 7.6, 2H), 8.44 (s, 1H), 8.46 (s, 1H), 9.37 (s, 1H). δ_C (100 MHz, DMSO-d_6): 21.9, 30.5, 63.2, 68.7, 79.4, 118.1 (quart., J_{CF} 272.8), 124.1, 124.3, 126.6, 126.8, 128.2, 128.4, 129.0, 129.2, 130.5 (quart., J_{CF} 3.9), 134.2 (quart., J_{CF} 33.6), 137.8 (d, J_{CF} 1.2), 142.8, 143.4, 143.5, 164.8. δ_F (376 MHz, DMSO-d_6): -61.52. ν_{max} (neat)/cm^{-1} 3215, 3060, 2972, 1668, 1593, 1493, 1449, 1389, 1307, 1136, 1100,

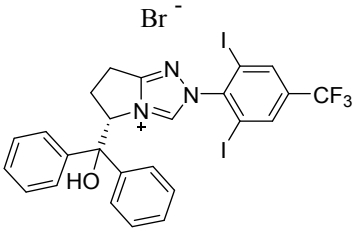
962, 881, 751, 700, 656, 623. HRMS (*m/z*-ESI$^+$): Found 591.9859 (M^+, $C_{25}H_{19}Br_2F_3N_3O$ requires 591.9841).

(*S*)-2-(2,6-Dibromo-3,5-bis-trifluoromethyl-phenyl)-5-(hydroxy-diphenyl-methyl)-2,5,6,7-tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium bromide (25)



Prepared according to **general procedure 2** using **16** (0.93 g, 2.7 mmol, 1.00 equiv.), Meerwein salt (0.40 g, 2.7 mmol, 1.00 equiv.), CH_2Cl_2 (25 mL), 2,6-dibromo-3,5-*bis*(trifluoromethyl)phenyl hydrazine (1.1 g, 2.7 mmol, 1.00 equiv.), chlorobenzene (40 mL), triethyl orthoformate (2 x 1.93 mL, 23 mmol, 8.60 equiv.), TMS-Br (1.25 mL, 9.5 mmol, 3.50 equiv.) and MeOH (100 mL). Purified *via* flash chromatography using a solvent gradient of 100 % EtOAc to EtOAc:MeOH (97:3). Concentration *in vacuo* yielded a tan residue that was redissolved in CH_2Cl_2 and re-concentrated to produce a light tan crystalline solid (568 mg, 28 %). M.p. 147 °C. R_f = 0.35 (9:1, EtOAc:MeOH). $[\alpha]_D^{20}$ = -194 (*c* 1.40 in $CHCl_3$), for *S* enantiomer with 100% *ee*. δ_H (400 MHz, DMSO-d_6): 2.74 (app. t, 1H), 2.97-3.20 (m, 3H), 6.32 (d, *J* 7.6, 1H), 6.79 (s, 1H), 7.28-7.38 (m, 4H), 7.39 (app. t, 2H), 7.46 (d, *J* 7.9, 2H), 7.49 (d, *J* 7.9, 1H), 8.37 (s, 1H), 9.24 (s, 1H). δ_C (100 MHz, DMSO-d_6): 22.1, 30.5, 63.2, 68.9, 79.5, 122.0 (quart., J_{CF} 272.9), 126.6, 126.8, 127.1, 127.6, 128.2, 128.4, 128.8 (quart., J_{CF} 30.7) 129.1, 129.2, 129.9 (quart., J_{CF} 30.7), 138.9, 143.3, 143.3, 143.7, 165.1. δ_F (376 MHz, DMSO-d_6): -61.91, -62.04. ν_{max} (neat)/cm^{-1} 3283, 2936, 1596, 1333, 1282, 1260, 1190, 1145, 1040, 701. HRMS (*m/z*-ESI$^+$): Found 659.9717 (M^+, $C_{25}H_{19}F_3I_2N_3O$ requires 659.9721).

(*S*)-2-(2,6-Diiodo-4-trifluoromethyl-phenyl)-5-(hydroxy-diphenyl-methyl)-2,5,6,7-tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium bromide (26)

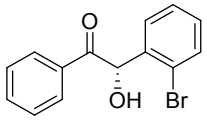


Prepared according to **general procedure 2** using **16** (1.11 g, 3.3 mmol, 1.00 equiv.), Meerwein salt (0.48 g, 3.3 mmol, 1.00 equiv.), CH_2Cl_2 (30 mL), 2,6-diiodo-4-(trifluoromethyl)phenyl hydrazine (1.4 g, 3.3

mmol, 1.00 equiv.), chlorobenzene (40 mL), triethyl orthoformate (2 x 2.33 mL, 28 mmol, 8.60 equiv.), TMS-Br (1.51 mL, 11.5 mmol, 3.50 equiv.) and MeOH (100 mL). Purified twice *via* flash chromatography using 1) 100 % EtOAc to EtOAc:MeOH (9:1) and 2) EtOAc:MeOH (9:1). Concentration *in vacuo* yielded a tan residue that was redissolved in CH_2Cl_2 and re-concentrated to produce a light tan crystalline solid (948 mg, 37 %). M.p. 196 °C. R_f = 0.47 (9:1, EtOAc:MeOH). $[\alpha]_D^{20}$ = -162 (*c* 1.40 in $CHCl_3$), for *S* enantiomer with 100% *ee*. δ_H (400 MHz, DMSO-d_6): 2.71 (t, *J* 10.8, 1H), 2.97-3.01 (m, 1H), 3.03-3.14 (m, 1H), 3.23 (obscured, 1H), 6.37 (d, *J* 8.1, 1H), 6.75 (s, 1H), 7.27-7.32 (m, 2H), 7.34 (app. t, 2H), 7.38 (app. t, 2H), 7.46 (d, *J* 7.7, 2H), 7.51 (d, *J* 7.7, 2H), 8.41 (s, 1H), 8.44 (s, 1H), 9.38 (s, 1H). δ_C (100 MHz, DMSO-d_6): 21.8, 30.6, 68.6, 79.4, 100.3, 101.2, 121.8 (quart., J_{CF} 271.4), 126.7, 126.9, 128.1, 128.3, 129.1, 129.2, 134.1 (quart., J_{CF} 32.7), 136.4 (quart., J_{CF} 7.7), 142.1, 143.3, 144.8, 144.1, 164.5. δ_F (376 MHz, DMSO-d_6): -61.92, -62.05. ν_{max} (neat)/cm^{-1} 3255, 3057, 2974, 1587, 1497, 1448, 1383, 1306, 1133, 1077, 963, 884, 757, 700, 653, 629. HRMS (*m/z*-ESI$^+$): Found 687.9565 (M^+, $C_{25}H_{19}F_3I_2N_3O$ requires 687.9564).

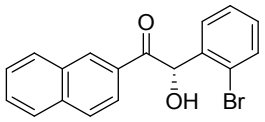
4 Experimental data for cross-benzoin products

(*S*)-2-(2-bromophenyl)-2-hydroxy-1-phenylethan-1-one (30)



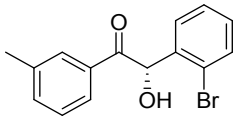
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and benzaldehyde (112 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid in 202 mg (63%) yield following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.27. M.p. 74 – 76 °C. δ_H (400 MHz, $CDCl_3$): 4.51 (d, *J* 5.6, 1H), 6.34 (d, *J* 5.6, 1H), 7.04 (dd, *J* 7.7, 1.8, 1H), 7.10 (td, *J* 7.7, 1.8, 1H), 7.17 (td, *J* 7.5, 1.2, 1H), 7.37 (app. t, 2H), 7.50 (t, *J* 7.5, 1H), 7.59 (dd, *J* 8.0, 1.2, 1H), 7.89 (dd, *J* 7.3, 1.2, 2H). δ_C (100 MHz, $CDCl_3$): 75.3, 124.2, 128.3, 128.8, 129.0, 129.2, 130.2, 133.1, 133.6, 134.1, 138.4, 198.7. ν_{max} (neat)/cm^{-1}: 3479, 2924, 1669, 1595, 1446, 1245, 1193, 1083, 969, 760, 703, 681. HRMS (*m/z*-ESI$^-$): Found 288.9878 ($C_{14}H_{10}BrO_2$ requires 288.9864). $[\alpha]_D^{27}$ = + 2 (*c* 0.3, $CHCl_3$) for 75% *ee*. CSP-HPLC analysis: 12.9 min (major enantiomer) and 30.1 min (minor enantiomer).

(*S*)-2-(2-bromophenyl)-2-hydroxy-1-(naphthalen-2-yl)ethan-1-one (40)



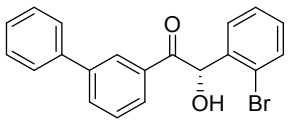
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 2-naphthaldehyde (172 mg, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (233 mg, 62%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.23. M.p. 128 – 130 °C. δ_H (600 MHz, $CDCl_3$): 4.61 (d, *J* 5.7, 1H), 6.51 (d, *J* 5.7, 1H), 7.08-7.12 (m, 2H), 7.16-7.20 (m, 1H), 7.49-7.54 (m, 1H), 7.56-7.62 (m, 2H), 7.80 (app. t, 2H), 7.89 (d, *J* 8.2, 1H), 7.94 (dd, *J* 1.7, 8.7, 1H), 8.50 (s, 1H). δ_C (150 MHz, $CDCl_3$): 75.3, 124.0, 124.2, 127.0, 127.7, 128.4, 128.7, 129.1, 129.2, 129.2, 129.8, 130.2, 130.3, 131.3, 132.2, 133.7, 135.9, 138.6, 198.7. ν_{max} (neat)/cm^{-1}: 3448, 3057, 2925, 1665, 1621, 1598, 1584, 1470, 1440, 1380, 1350, 1279, 1229, 1182, 1127, 1117, 1071, 1022, 981, 937, 865, 803, 760, 744. HRMS (*m/z*-ESI$^+$): Found 362.9997 (M^+ + Na. $C_{18}H_{13}BrO_2Na$ requires 362.9997). $[\alpha]_D^{28}$ = + 1 (*c* 0.15, $CHCl_3$) for 84% *ee*. CSP-HPLC analysis: 17.5 min (major enantiomer) and 46.2 min (minor enantiomer).

(*S*)-2-(2-Bromophenyl)-2-hydroxy-1-(3-tolyl)ethan-1-one (42)



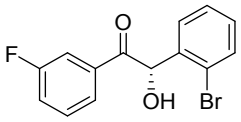
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 3-tolualdehyde (130 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (222 mg, 66%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.26. M.p. 86 °C. δ_H (400 MHz, $CDCl_3$): 2.34 (s, 3H), 4.53 (d, *J* 5.6, 1H), 6.34 (d, *J* 5.6, 1H), 7.04 (dd, *J* 1.7, 7.7, 1H), 7.10-7.14, (m, 1H), 7.17 (td, *J* 1.2, 7.7, 1H), 7.26 (obscured, 1H), 7.31 (d, *J* 7.6, 1H), 7.59 (dd, *J* 1.3, 7.9, 1H), 7.66 (d, *J* 7.6, 1H), 7.78 (s, 1H). δ_C (100 MHz, $CDCl_3$): 21.2, 75.2, 124.2, 126.2, 128.3, 128.6, 129.2, 129.4, 130.2, 133.1, 133.6, 135.0, 138.5, 138.7, 198.9. ν_{max} (neat)/cm^{-1}: 3431, 2921, 1665, 1582, 1468, 1432, 1372, 1272, 1186, 1114, 1073, 1022, 975, 890. 816, 786, 757, 706, 680. HRMS (*m/z*-ESI$^-$): Found 303.0034 ($C_{15}H_{12}BrO_2$ requires 303.0021). $[\alpha]_D^{28}$ = + 3 (*c* 0.79, $CHCl_3$) for 83% *ee*. CSP-HPLC analysis: 13.0 min (major enantiomer) and 30.0 min (minor enantiomer).

(*S*)-1-([1,1'-Biphenyl]-3-yl)-2-(2-bromophenyl)-2-hydroxyethan-1-one (44)



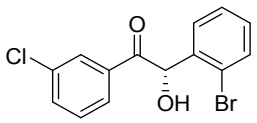
Prepared according to **general procedure 3** using 22 (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and biphenyl-3-carbaldehyde (179 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (230 mg, 57%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.23. M.p. 72 °C. δ_H (600 MHz, $CDCl_3$): 4.59 (d, *J* 5.3, 1H), 6.45 (d, *J* 5.3, 1H), 7.14 (d, *J* 7.6, 1H), 7.17 (app. t, 1H), 7.25 (t, *J* 7.5, 1H), 7.40 (t, *J* 7.3, 1H), 7.47-7.52 (m, 3H), 7.56 (d, *J* 8.3, 2H), 7.67 (d, *J* 7.9, 1H), 7.78 (d, *J* 7.7, 1H), 7.91 (d, *J* 7.9, 1H), 8.20 (d, *J* 1.2, 1H). δ_C (150 MHz, $CDCl_3$): 75.5, 124.2, 127.1, 127.6, 127.7, 128.0, 128.4, 129.3, 129.3, 130.3, 132.7, 133.6, 133.7, 138.5, 139.6, 141.9, 198.7. ν_{max} (neat)/cm^{-1}: 3471, 2912, 1674, 1622, 1579, 1474, 1291, 1227, 1187, 1090, 1021, 978, 756, 688. HRMS (*m/z*-ESI$^+$): Found 389.0144 ($C_{20}H_{16}BrO_2$ requires 389.0148). $[\alpha]_D^{28}$ = + 2 (*c* 0.3, $CHCl_3$) for 77% *ee*. CSP-HPLC analysis: 20.4 min (major enantiomer) and 58.3 min (minor enantiomer).

(*S*)-2-(2-Bromophenyl)-1-(3-fluorophenyl)-2-hydroxyethan-1-one (46)



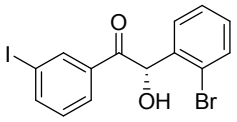
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 3-fluorobenzaldehyde (117 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a yellow oil (160 mg, 47%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.25. δ_H (400 MHz, $CDCl_3$): 4.40 (d, *J* 5.6, 1H), 6.31 (d, *J* 5.6, 1H), 7.04 (dd, *J* 7.7, 1.7, 1H), 7.12-7.17 (m, 1H), 7.20-7.24 (m, 2H), 7.34-7.39 (m, 1H), 7.60-7.67 (m, 3H). δ_C (100 MHz, $CDCl_3$): 75.6, 115.6 (d, J_{CF} 22.8), 121.2 (d, J_{CF} 21.8), 124.2, 124.7 (d, J_{CF} 3.1), 128.4, 129.2, 130.4, 130.5 (d, J_{CF} 7.7), 133.8, 135.2 (d, J_{CF} 6.5), 137.9, 162.7 (d, J_{CF} 249.3), 197.8 (d, J_{CF} 2.3). δ_F (376 MHz, $CDCl_3$): -110.88 (dt, J_{HF} 8.8, 3.2). ν_{max} (neat)/cm^{-1}; 3450, 3072, 2925, 1683, 1587, 1440, 1258, 1079, 1015, 889, 785, 755. HRMS (*m/z*-ESI^-): Found 306.9776 ($C_{14}H_9BrFO_2$ requires 306.9770). $[\alpha]_D^{28}$ = + 2 (*c* 0.29, $CHCl_3$) for 66% *ee*. CSP-HPLC analysis: 14.5 min (major enantiomer) and 44.9 min (minor enantiomer).

(*S*)-2-(2-Bromophenyl)-1-(3-chlorophenyl)-2-hydroxyethan-1-one (48)



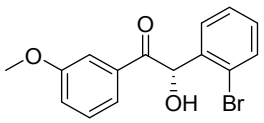
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 3-chlorobenzaldehyde (124 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a pale yellow solid (172 mg, 48%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.24. Upon standing for several hours, this oil gradually solidified to a pale yellow solid. M.p. 93 °C. δ_H (400 MHz, $CDCl_3$): 4.39 (d, *J* 5.7, 1H), 6.31 (d, *J* 5.7, 1H), 7.03 (dd, *J* 7.7, 1.8, 1H), 7.12 (td, *J* 7.8, 1.6, 1H), 7.20 (obscured, 1H), 7.30 (t, *J* 7.9, 1H), 7.47 (d, *J* 7.9, 1H), 7.60 (d, *J* 7.9, 1H), 7.72 (d, *J* 7.8, 1H), 7.94 (s, 1H). δ_C (100 MHz, $CDCl_3$): 75.7, 124.1, 126.9, 128.4, 128.9, 129.2, 130.1, 130.5, 133.8, 134.0, 134.7, 135.2, 137.8, 197.8. ν_{max} (neat)/cm^{-1}: 3492, 3069, 2904, 1677, 1565, 1469, 1419, 1353, 1285, 1234, 1185, 1118, 1086, 1021, 975, 871, 798, 750, 708, 672. HRMS (*m/z*-ESI^-): Found 322.9468 ($C_{14}H_9BrClO_2$ requires 322.9474). $[\alpha]_D^{28}$ = + 1 (*c* 0.25, $CHCl_3$) for 45% *ee*. CSP-HPLC analysis: 14.9 min (major enantiomer) and 48.3 min (minor enantiomer).

(*S*)-2-(2-bromophenyl)-1-(3-iodophenyl)-2-hydroxyethan-1-one (50)



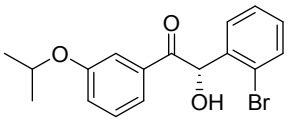
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 3-iodobenzaldehyde (272 mg, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (172 mg, 48%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.26. M.p. 86 °C. δ_H (400 MHz, $CDCl_3$): 4.41 (d, *J* 5.6, 1H, OH), 6.31 (d, *J* 5.6, 1H), 7.05 (dd, *J* 7.6, 1.5, 1H), 7.11-717 (m, 2H), 7.21 (obscured, 1H), 7.61 (d, *J* 7.9, 1H), 7.81-7.85 (m, 2H), 8.32 (s, 1H). δ_C (100 MHz, $CDCl_3$): 75.3, 94.4, 124.1, 127.9, 128.4, 129.2, 130.4, 130.5, 133.8, 134.8, 137.7, 137.8, 142.8, 197.6. ν_{max} (neat)/cm^{-1}: 3492, 3067, 2905, 1674, 1583, 1557, 1354, 1284, 1233, 1183, 1087, 1019, 971, 862, 795, 756, 726, 693, 672, 639. HRMS (*m/z*-ESI^-): Found 414.8841 ($C_{14}H_9BrIO_2$ requires 414.8836). $[\alpha]_D^{28}$ = + 1 (*c* 0.35, $CHCl_3$) for 52% *ee*. CSP-HPLC analysis: 15.2 min (major enantiomer) and 50.7 min (minor enantiomer).

(*S*)-2-(2-Bromophenyl)-1-(3-methoxyphenyl)-2-hydroxyethan-1-one (52)



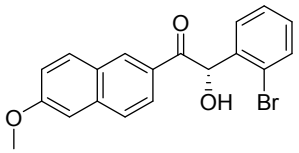
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 3-anisaldehyde (134 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as white solid (170 mg, 48%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.26. M.p. 67 – 68 °C. δ_H (400 MHz, $CDCl_3$): 3.79 (s, 3H), 4.50 (d, *J* 5.7, 1H), 6.34 (d, *J* 5.7, 1H), 7.04-7.07 (m, 2H, H-2), 7.10 (td, *J* 7.7, 1.3, 1H), 7.18 (t, *J* 7.5, 1H), 7.26 (t, *J* 7.9, 1H), 7.43 (s, 1H), 7.47 (d, *J* 7.6, 1H), 7.60 (d, *J* 7.9, 1H). δ_C (100 MHz, $CDCl_3$): 55.5, 75.4, 112.7, 121.1, 121.6, 124.2, 128.4, 129.2, 129.8, 130.2, 133.6, 134.3, 138.5, 159.7, 198.5. ν_{max} (neat)/cm^{-1}: 3430, 2943, 1675, 1593, 1463, 1427, 1389, 1336, 1259, 1176, 1117, 1082, 1009, 875, 763, 719, 675. HRMS (*m/z*-ESI^-): Found 318.9974 ($C_{15}H_{14}BrO_3$ requires 318.9970). $[\alpha]_D^{28}$ = + 2 (*c* 0.5, $CHCl_3$) for 83% *ee*. CSP-HPLC analysis: 16.8 min (major enantiomer) and 38.2 min (minor enantiomer).

(*S*)-2-(2-Bromophenyl)-1-(3-*iso*propoxyphenyl)-2-hydroxyethan-1-one (54)



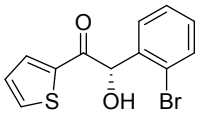
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 3-*iso*propoxybenzaldehyde (187 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (161 mg, 42%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.28. M.p. 66 - 67 °C. δ_H (400 MHz, $CDCl_3$): 1.22 (d, *J* 6.0, 3H), 1.30 (d, *J* 6.0, 3H), 4.49-4.58 (m, 2H), 6.31 (d, *J* 5.5, 1H), 7.01-7.05 (m, 2H), 7.10-7.14 (m, 1H), 7.18 (app. t, 1H), 7.24 (app. t, *J* 7.9, 1H), 7.38 (s, 1H), 7.44 (d, *J* 7.6, 1H), 7.59 (d, *J* = 7.5, 1H). δ_C (100 MHz, $CDCl_3$): 21.7, 22.0, 70.2, 75.4, 114.5, 121.3, 122.9, 124.2, 128.4, 129.2, 129.8, 130.2, 133.6, 134.2, 138.6, 158.1, 198.5. ν_{max} (neat)/cm^{-1}: 3423, 2984, 2937, 1675, 1575, 1469, 1434, 1378, 1273, 1194, 1108, 1067, 1019, 953, 874, 761, 719, 674. HRMS (*m/z*-ESI$^-$): Found 347.0269 ($C_{17}H_{16}BrO_3$ requires 347.0283). $[\alpha]_D^{29}$ = + 2 (*c* 0.6, $CHCl_3$) for 76% *ee*. CSP-HPLC analysis: 12.8 min (major enantiomer) and 34.8 min (minor enantiomer).

(*S*)-2-(2-Bromophenyl)-2-hydroxy-1-(6-methoxynaphthalen-2-yl)ethan-1-one (56)



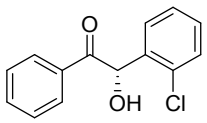
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 6-methoxynaphthaldehyde (205 mg, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (229 mg, 56%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.18. M.p. 84 °C. δ_H (600 MHz, $CDCl_3$): 4.61 (d, *J* 5.6, 1H), 6.51 (d, *J* 5.6, 1H), 7.11-7.16 (m, 3H), 7.19-7.23 (m, 2H), 7.65 (d, *J* 7.9, 1H), 7.73 (d, *J* 8.7, 1H), 7.81 (d, *J* 8.7, 1H), 7.96 (d, *J* 8.7, 1H), 8.46 (s, 1H). δ_C (150 MHz, $CDCl_3$): 55.5, 75.1, 105.7, 120.0, 124.1, 124.8, 127.3, 127.6, 128.3, 128.4, 129.2, 130.2, 131.2, 131.5, 133.6, 137.8, 138.9, 160.3, 198.2. ν_{max} (neat)/cm^{-1}: 3459, 2937, 1673, 1622, 1476, 1396, 1275, 1171, 1083, 1025, 984, 853, 760, 704. HRMS (*m/z*-ESI$^+$): Found 393.0090 (M^+ + Na. $C_{19}H_{15}BrO_3Na$ requires 393.0097). $[\alpha]_D^{29}$ = + 1 (*c* 0.23, $CHCl_3$) for 67% *ee*. CSP-HPLC analysis: 22.7 min (major enantiomer) and 51.4 min (minor enantiomer).

(*S*)-2-(2-Bromophenyl)-2-hydroxy-1-(thiophen-2-yl)ethan-1-one (58)



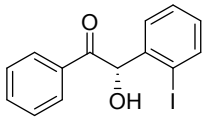
Prepared according to **general procedure 3** using **22** (36 mg), 2-bromobenzaldehyde (160 μL, 1.38 mmol, 1.25 equiv.) and 2-thiophenecarbaldehyde (103 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a yellow solid (248 mg, 76%) following flash chromatography (9:1, hexanes:EtOAc). R_f = 0.29. M.p. 87 °C. δ_H (400 MHz, $CDCl_3$): 4.41 (d, *J* 5.5, 1H), 6.18 (d, *J* 5.5, 1H), 7.03 (app. t, 1H), 7.14-7.19 (m, 2H), 7.26 (app. t, 1H), 7.61-7.67 (m, 3H). δ_C (100 MHz, $CDCl_3$): 75.8, 124.2, 128.4, 128.5, 129.5, 130.4, 133.6, 133.9, 135.2, 138.7, 139.4, 191.2. ν_{max} (neat)/cm^{-1}: 3413, 3096, 3084, 2901, 1638, 1471, 1407, 1244, 1189, 1051, 1018, 934, 864, 815, 743, 662. HRMS (*m/z*-ESI^+): Found 296.9586 ($C_{12}H_{10}BrO_2S$ requires 296.9579). $[\alpha]_D^{28}$ = + 3 (*c* 0.68, $CHCl_3$) for 71% *ee*. CSP-HPLC analysis: 16.5 min (major enantiomer) and 33.8 min (minor enantiomer).

(*S*)-2-(2-Chlorophenyl)-2-hydroxy-1-phenylethan-1-one (37)



Prepared according to **general procedure 3** (in THF exclusively) using **23** (45 mg), 2-chlorobenzaldehyde (124 μL, 1.1 mmol, 1.25 equiv.) and benzaldehyde (112 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (76 mg, 28%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.27. M.p. 70 – 72 °C. δ_H (400 MHz, $CDCl_3$): 4.53 (d, *J* 5.8, 1H), 6.35 (d, *J* 5.8, 1H), 7.09 (d, *J* 7.4, 1H), 7.14-7.22 (m, 2H), 7.36-7.41 (m, 3H), 7.49 (t, *J* 7.4, 1H), 7.89 (d, *J* 7.6, 2H). δ_C (100 MHz, $CDCl_3$): 72.8, 127.7, 128.8, 128.9, 129.2, 130.0, 130.3, 133.1, 133.6, 134.1, 136.7, 198.7. ν_{max} (neat)/cm^{-1}: 3479, 2958, 2913, 1669, 1595, 1445, 1392, 1358, 1314, 1240, 1178, 1089, 1035, 970, 851, 759, 713, 678, 628. HRMS (*m/z*-ESI^-): Found 244.0291 ($C_{14}H_9ClO_2$ requires 244.0297). $[\alpha]_D^{20}$ = + 2 (*c* 0.3, $CHCl_3$) for 53% *ee*. CSP-HPLC analysis: 12.8 min (major enantiomer) and 22.2 min (minor enantiomer)

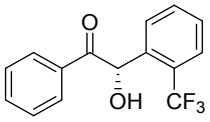
(*S*)-2-(2-Iodophenyl)-2-hydroxy-1-phenylethan-1-one (38)



Prepared according to **general procedure 3** (in THF exclusively) using **23** (45 mg), 2-iodobenzaldehyde (272 mg, 1.1 mmol, 1.0 equiv.) and benzaldehyde (112 μL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (91 mg, 27%) following flash chromatography (9:1, hexanes:EtOAc). R_f = 0.27. M.p. 104 °C. δ_H (400 MHz, $CDCl_3$): 4.47 (d, *J* 5.5, 1H), 6.21 (d, *J* 5.5, 1H), 6.93-6.99 (m, 2H, H-5), 7.19

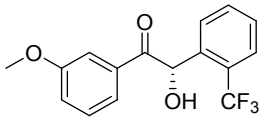
(app. t, 1H), 7.37 (t, *J* 7.7, 2H), 7.50 (t, *J* 7.4, 1H), 7.87-7.91 (m, 3H). δ_C (100 MHz, $CDCl_3$): 75.3, 124.1, 122.9, 128.4, 129.2, 130.4, 130.5, 133.8, 134.8, 137.7, 137.8, 142.8, 197.6. ν_{max} (neat)/cm^{-1}: 3479, 3057, 2912, 1669, 1579, 1447, 1363, 1311, 1244, 1186, 1084, 1007, 970, 844, 759, 724, 695, 674. HRMS (*m/z*-ESI$^+$): 360.9695 (M^+ + Na. $C_{14}H_{11}IO_2Na$ requires 360.9696). $[\alpha]_D^{20}$ = + 3 (*c* 0.3, $CHCl_3$) for 74% *ee*. CSP-HPLC analysis: 14.3 min (major enantiomer) and 47.4 min (minor enantiomer).

(*S*)-2-Hydroxy-1-phenyl-2-(2-(trifluoromethyl)phenyl)ethan-1-one (62)



Prepared according to **general procedure 3** using **22** (36 mg), 2-(trifluoro)benzaldehyde (145 µL, 1.1 mmol, 1.0 equiv.) and benzaldehyde (112 µL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (105 mg, 34%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.25. M.p. 83 – 84 °C. δ_H (400 MHz, $CDCl_3$): 4.49 (d, *J* 5.5, 1H), 6.23 (d, *J* 5.5, 1H), 7.05-7.08 (m, 1H), 7.35-7.42 (m, 4H), 7.48 (t, *J* 7.4, 1H), 7.74-7.77 (m, 1H), 7.83-7.85 (m, 2H). δ_C (100 MHz, $CDCl_3$): 71.8 (quart., J_{CF} 1.5), 124.3 (quart., J_{CF} 275.2), 126.7 (quart., J_{CF} 5.7), 128.7 (quart., J_{CF} 36.6,), 128.8, 129.1, 129.2, 132.8, 133.1, 134.1, 137.3 (quart., J_{CF} 1.6), 198.6. δ_F (376 MHz, $CDCl_3$): -57.68. ν_{max} (neat)/cm^{-1}: 3483, 2939, 1673, 1582, 1451, 1369, 1304, 1241, 1158, 1117, 1058, 1033, 969, 852, 768, 693, 670. HRMS (*m/z*-ESI$^+$): Found 303.0609 ($C_{15}H_{12}F_3O_2$ requires 303.0603). $[\alpha]_D^{24}$ = + 1 (*c* 0.15, $CHCl_3$) for 92% *ee*. CSP-HPLC analysis: 7.9 min (major enantiomer) and 13.3 min (minor enantiomer).

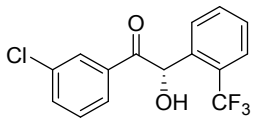
(*S*)-2-hydroxy-1-(3-methoxyphenyl)-2-(2-(trifluoromethyl)phenyl)ethan-1-one (63)



Prepared according to **general procedure 3** using **22** (36 mg), 2-(trifluoromethyl)benzaldehyde (145 µL, 1.1 mmol, 1.25 equiv.) and 3-anisaldehyde (134 µL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (21 mg, 6%) following flash chromatography (9:1, hexanes:EtOAc), R_f = 0.18. M.p. 78 °C. δ_H (400 MHz, $CDCl_3$): 3.74 (s, 3H), 4.47 (d, *J* 5.4, 1H), 6.21 (d, *J* 5.4, 1H), 7.03-7.06 (m, 2H), 7.27 (obscured, 1H), 7.37-7.44 (m, 4H), 7.75 (d, *J* 6.8, 1H). δ_C (100 MHz, $CDCl_3$): 55.3, 71.9 (quart., J_{CF} 1.8), 120.2 (quart., J_{CF} 274.3), 121.1, 121.7 (d, J_{CF} 0.7), 126.6 (quart., J_{CF} 5.8), 128.8, 129.1, 129.8, 132.8 (d, J_{CF} 0.8), 134.3, 137.4, 159.8, 198.4. ν_{max} (neat)/cm^{-1} 3470, 3080, 2967, 2840, 1685, 1599, 1458, 1306,

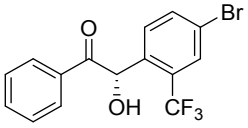
1261, 1153, 1109, 1035, 1011, 875, 804, 778, 705, 674, 608. HRMS (*m/z*-ESI$^-$): Found 308.0750 ($C_{16}H_{13}F_3O_3$ requires 309.0739). $[\alpha]_D^{24}$ = + 2 (*c* 0.01, $CHCl_3$) for 90% *ee*. CSP-HPLC analysis: 9.2 min (major enantiomer) and 15.8 min (minor enantiomer).

(*S*)-1-(3-chlorophenyl)-2-hydroxy-2-(2-(trifluoromethyl)phenyl)ethan-1-one (64)



Prepared according to **general procedure 3** using **22** (36 mg), 2-(trifluoromethyl)benzaldehyde (145 µL, 1.1 mmol, 1.25 equiv.) and 3-chlorobenzaldehyde (124 µL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a white solid (42 mg, 12%) following flash chromatography (9:1, hexanes:EtOAc), R_f= 0.24. M.p. 78-80 °C. δ_H (400 MHz, $CDCl_3$): 4.35 (d, *J* 5.5, 1H), 6.19 (d, *J* 5.5, 1H), 7.04 (app. t, 1H), 7.27 (app. t, 1H), 7.42 (m, 3H, H-3), 7.63 (d, *J* 7.8, 1H), 7.76 (app. t, 1H), 7.88 (s, 1H). δ_C (100 MHz, $CDCl_3$): 71.9 (quart., J_{CF} 1.6), 120.1 (quart., J_{CF} 274.2), 126.8 (quart., J_{CF}, 5.8), 127.0 (d, J_{CF} 1.1), 129.0, 129.1, 129.1, 130.1, 132.9 (quart., J_{CF} 0.8), 134.7, 135.3, 136.7 (quart., J_{CF} 1.3), 197.6. ν_{max} (neat)/cm^{-1} 3481, 3073, 2964, 1684, 1572, 1427, 1396, 1309, 1259, 1144, 1110, 1034, 997, 903, 869, 766, 702, 671, 642, 604. HRMS (*m/z*-ESI$^-$): Found 313.024883 ($C_{15}H_{10}ClF_3O_2$ requires 313.024865). $[\alpha]_D^{24}$ = + 0.36 (*c* 0.1, $CHCl_3$) for 80% *ee*. CSP-HPLC analysis: 7.5 min (major enantiomer) and 16.2 min (minor enantiomer).

(*S*)-1-(3-Chloro-phenyl)-2-hydroxy-2-(2-trifluoromethyl-phenyl)-ethanone (66)

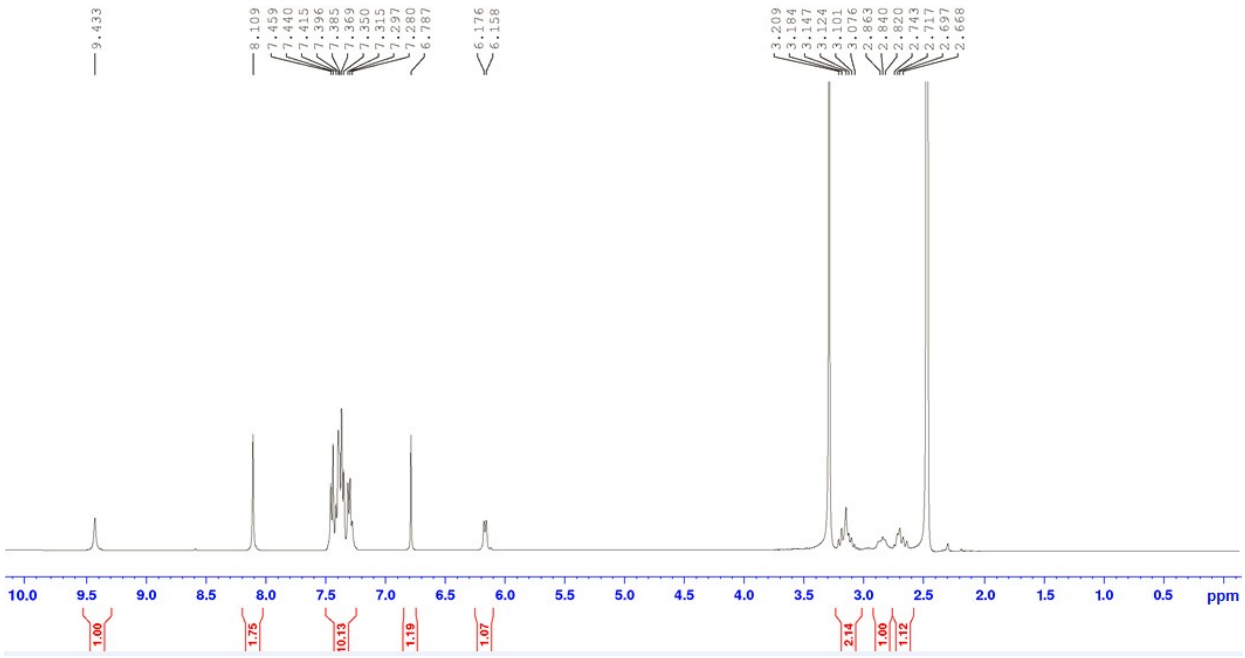


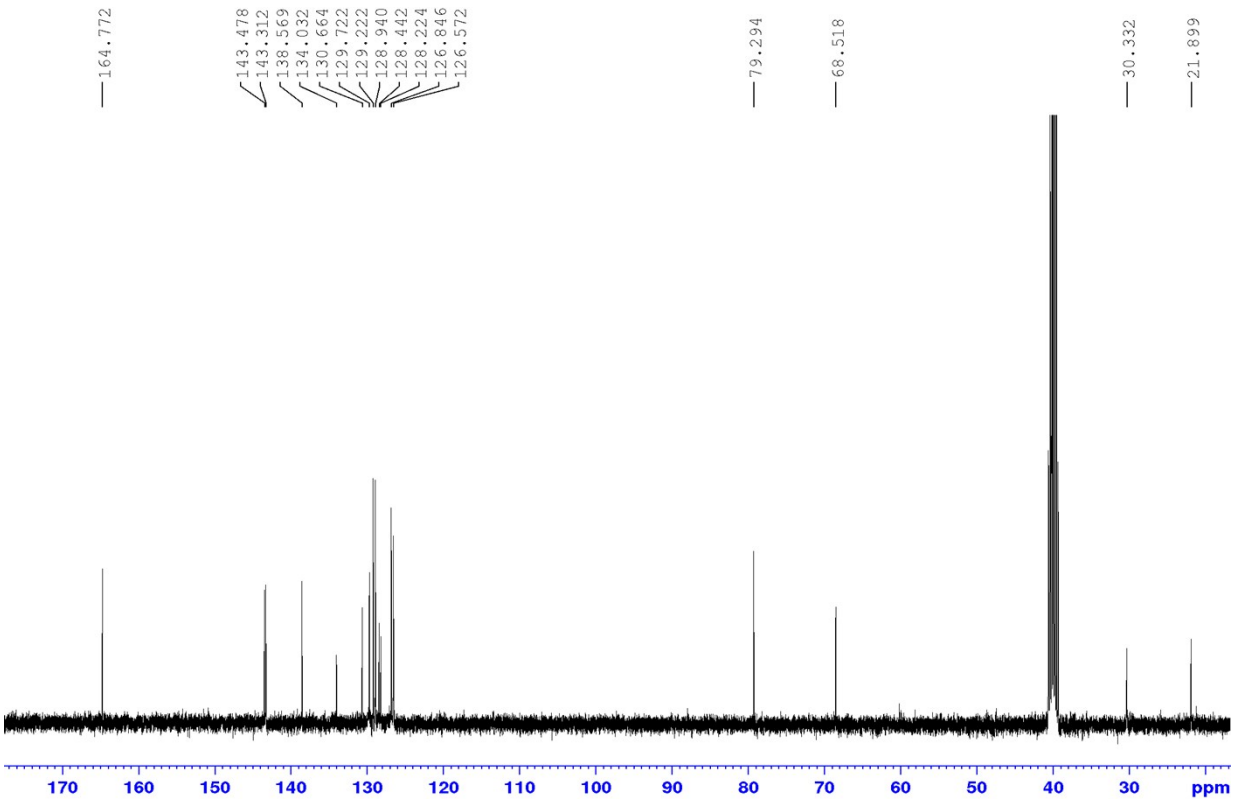
Prepared according to **general procedure 3** using **22** (36 mg), 4-bromo-2-(trifluoromethyl)benzaldehyde (278 µL, 1.1 mmol, 1.00 equiv.) and benzaldehyde (112 µL, 1.1 mmol, 1.00 equiv.). The title product was obtained as a pale yellow oil (41 mg, 12%) following flash chromatography (95:5, hexanes:EtOAc). δ_H (400 MHz, $CDCl_3$): 4.47 (d, *J* 5.4, 1H), 6.17 (d, *J* 5.4, 1H), 6.92 (d, *J* 8.4, 1H), 7.37 (app. t, 2H), 7.50-7.55 (m, 2H), 7.81 (dd, *J* 8.5, 1.1, 2H), 7.88 (s, 1H). δ_C (100 MHz, $CDCl_3$): 71.2 (quart., J_{CF} 1.8), 122.9, 123.3 (quart., J_{CF} 275.2), 128.9, 129.0, 130.0 (quart., J_{CF} 6.0), 130.3 (quart., J_{CF} 31.4), 130.8, 132.8, 134.4, 135.9 (quart., J_{CF} 1.0), 136.4 (quart., J_{CF} 1.1), 198.1. δ_F (376 MHz, $CDCl_3$): -58.07. ν_{max} (neat)/cm^{-1}: 3444, 3072, 2959, 1683, 1596, 1403, 1300, 1162, 1121, 1046, 973, 832, 706, 682. HRMS (*m/z*-ESI$^-$): Found 356.9741

($C_{15}H_9BrF_3O$ requires 356.9744). $[\alpha]_D^{24}$ = - 2 (*c* 0.01, $CHCl_3$) for 50% *ee*. CSP-HPLC analysis: 35.7 min (major enantiomer) and 38.5 min (minor enantiomer).

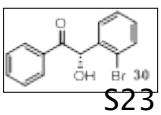
5 NMR spectral data

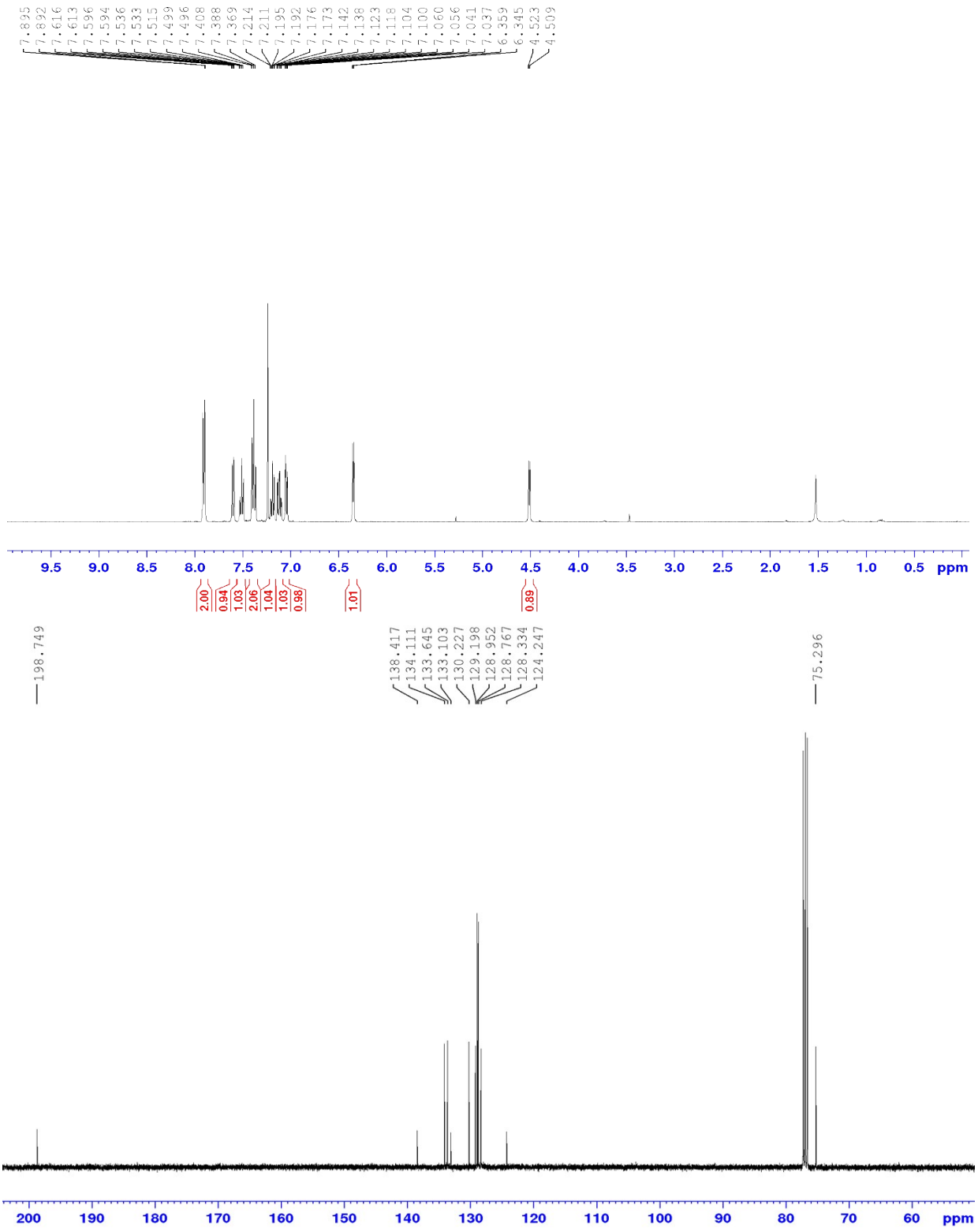
5.1 NMR spectral data for triazolium precatalyst 22





5.2 NMR spectral data for cross-benzoin products

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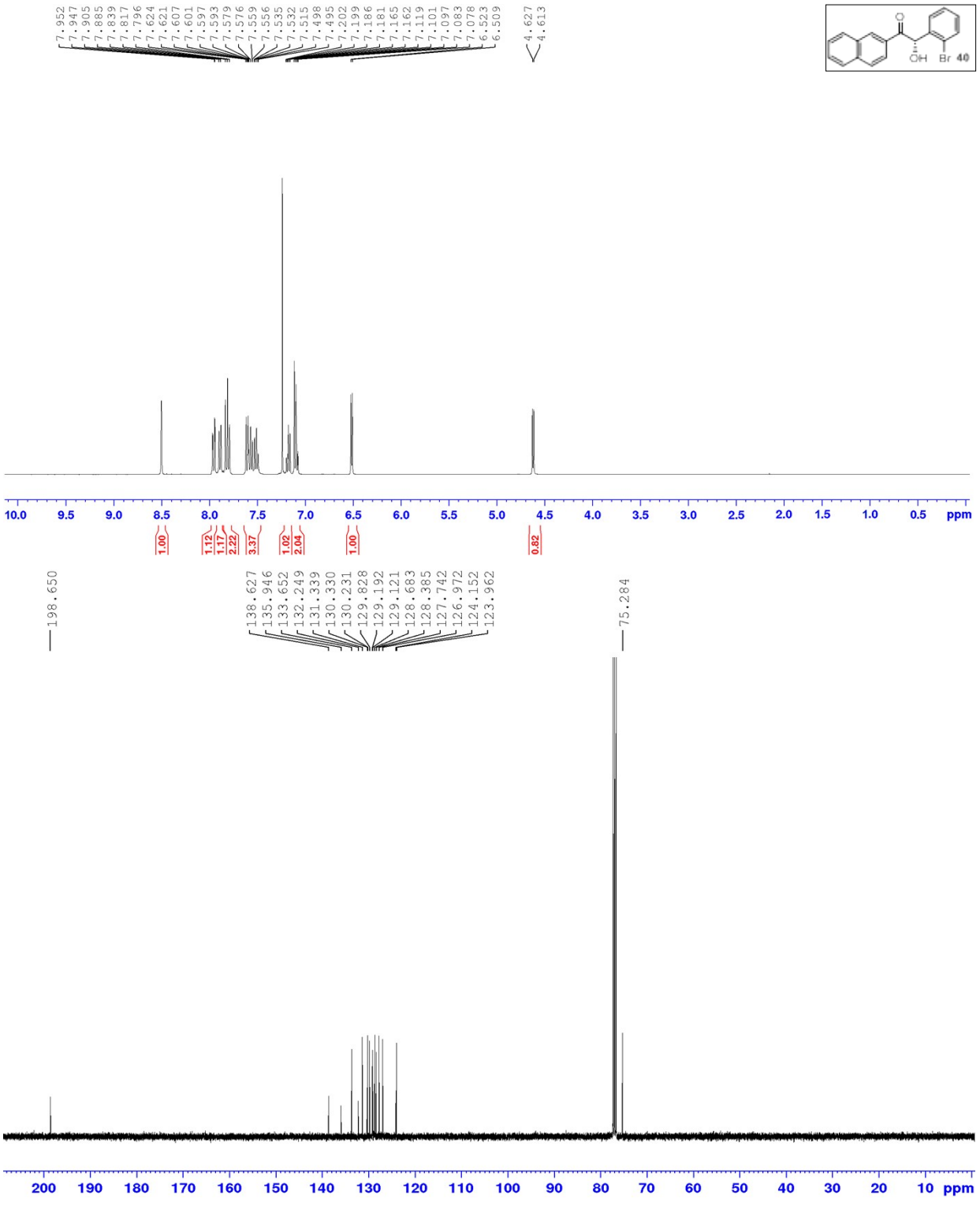
7.616
7.613
7.596
7.594
7.536
7.533
7.515
7.499
7.496
7.408
7.388
7.369
7.214
7.211
7.195
7.192
7.176
7.173
7.142
7.136
7.123
7.118
7.104
7.100
7.060
7.056
7.041
7.037
6.359
6.345
4.523
4.509
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
0.94
1.03
2.06
1.04
1.03
0.98
1.01
0.89
198.749
138.417
134.111
133.645
133.103
130.227
129.198
128.952
128.767
128.334
124.247
75.296
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 ppm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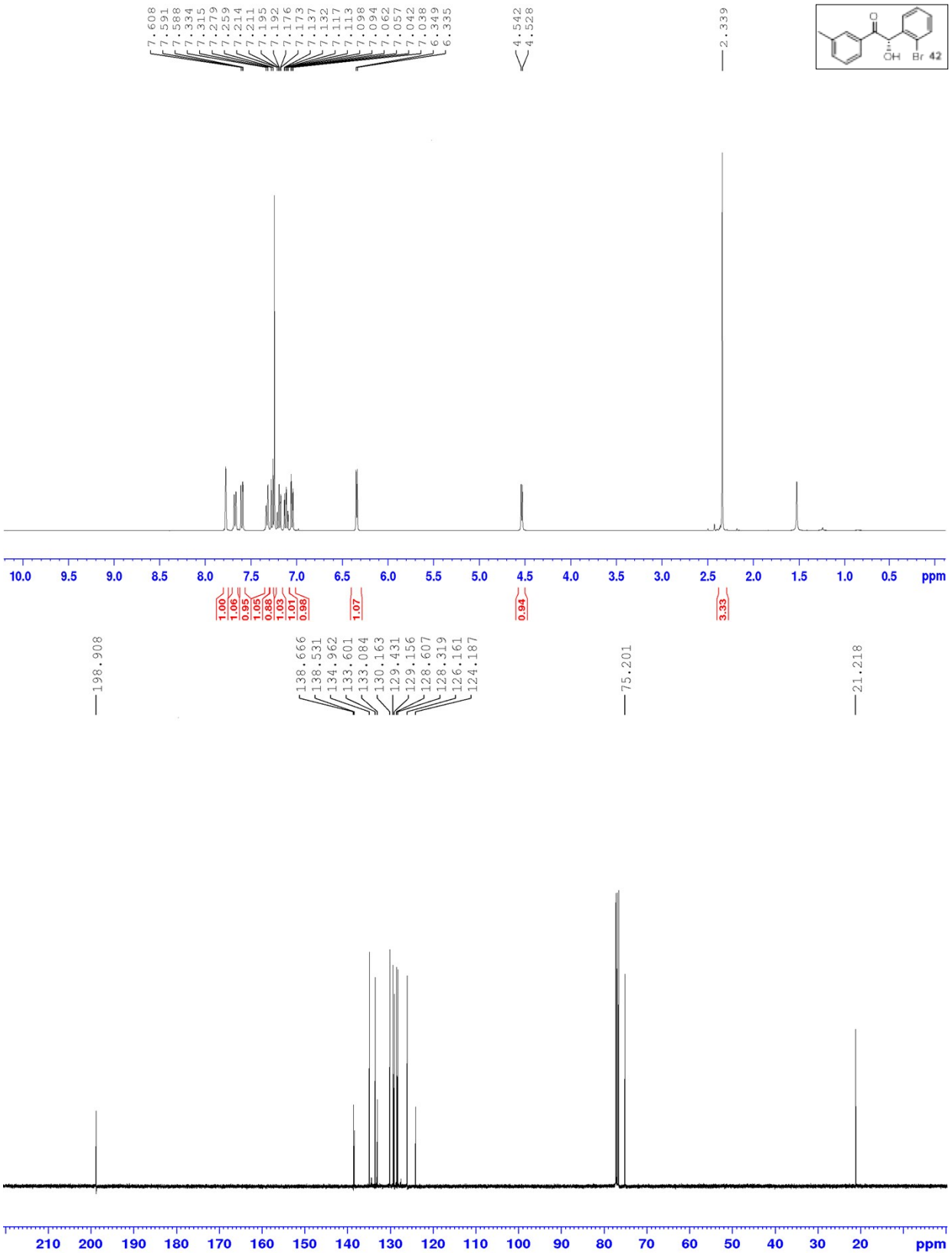
7.947
7.905
7.885
7.839
7.817
7.796
7.624
7.621
7.607
7.601
7.597
7.593
7.579
7.576
7.559
7.556
7.535
7.532
7.515
7.498
7.495
7.202
7.199
7.186
7.181
7.165
7.162
7.119
7.101
7.097
7.083
7.078
6.523
6.509
4.627
4.613
OH
Br
40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.12
1.17
2.22
3.37
1.02
2.04
1.00
0.82
198.650
138.627
135.946
133.652
132.249
131.339
130.330
130.231
129.828
129.192
129.121
128.683
128.385
127.742
126.972
124.152
123.962
75.284
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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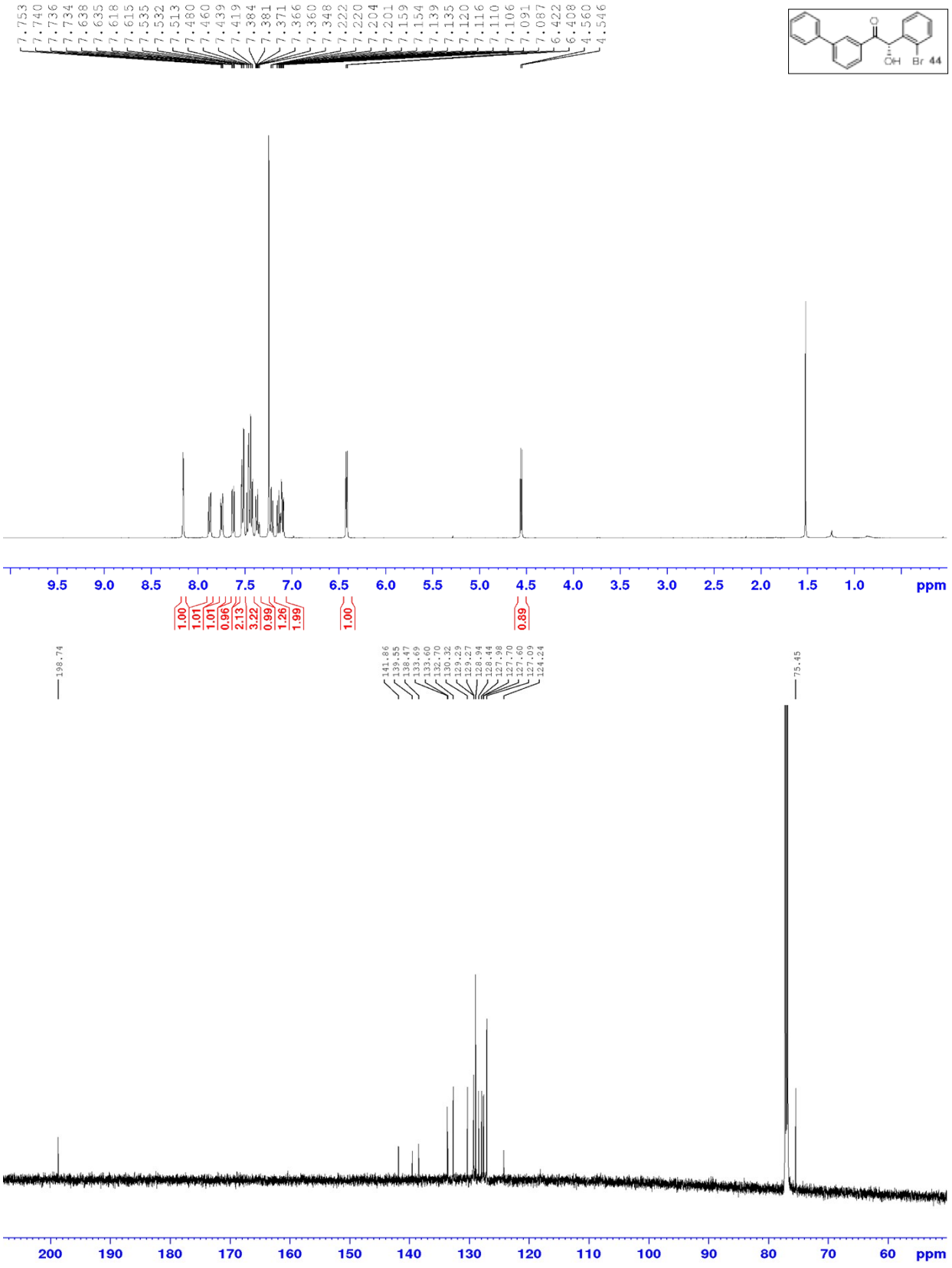
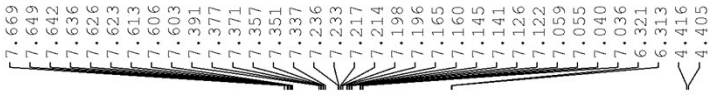
7.591
7.588
7.334
7.315
7.279
7.259
7.214
7.211
7.195
7.192
7.176
7.173
7.137
7.132
7.117
7.113
7.098
7.094
7.062
7.057
7.042
7.038
6.349
6.335
4.542
4.528
2.339
OH
Br
42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.06
0.95
1.05
0.88
1.03
1.01
0.98
1.07
0.94
3.33
198.908
138.666
138.531
134.962
133.601
133.084
130.163
129.431
129.156
128.607
128.319
126.161
124.187
75.201
21.218
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.753
7.740
7.736
7.734
7.638
7.635
7.618
7.615
7.535
7.532
7.513
7.480
7.460
7.439
7.419
7.384
7.381
7.371
7.366
7.360
7.348
7.222
7.220
7.204
7.201
7.159
7.154
7.139
7.135
7.120
7.116
7.110
7.106
7.091
7.087
6.422
6.408
4.560
4.546
OH
Br
44
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 2.0 1.5 1.0 ppm
1.00 1.01 1.01 0.96 2.13 3.22 0.99 1.26 1.99 1.00 0.89
198.74
141.86
139.55
138.47
133.69
133.60
130.70
130.32
129.28
129.27
128.94
128.44
127.98
127.70
127.60
127.09
124.24
75.45
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 ppm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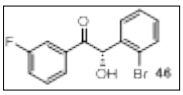
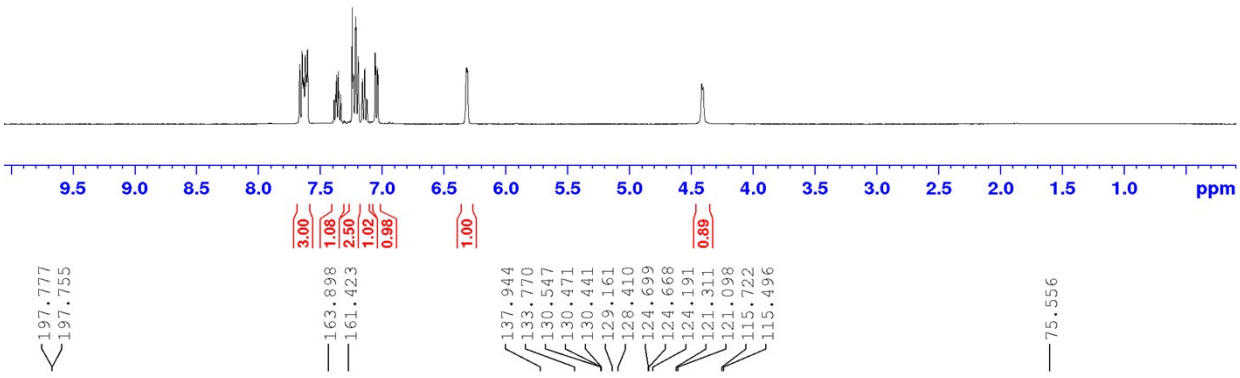
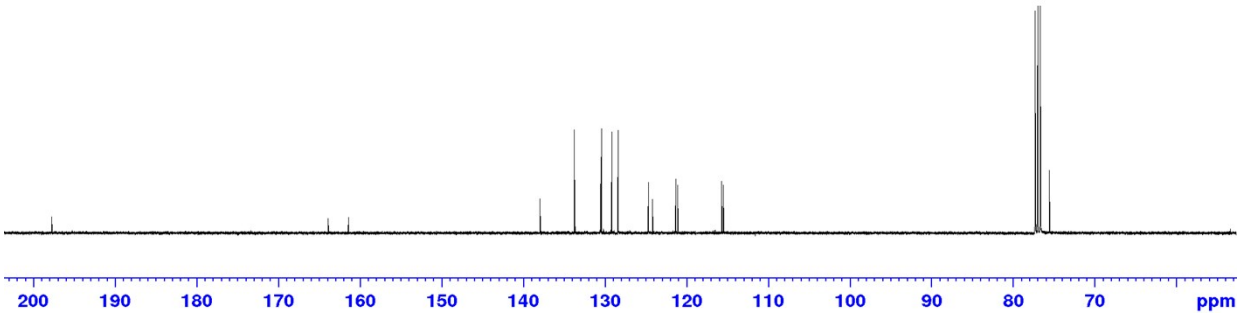
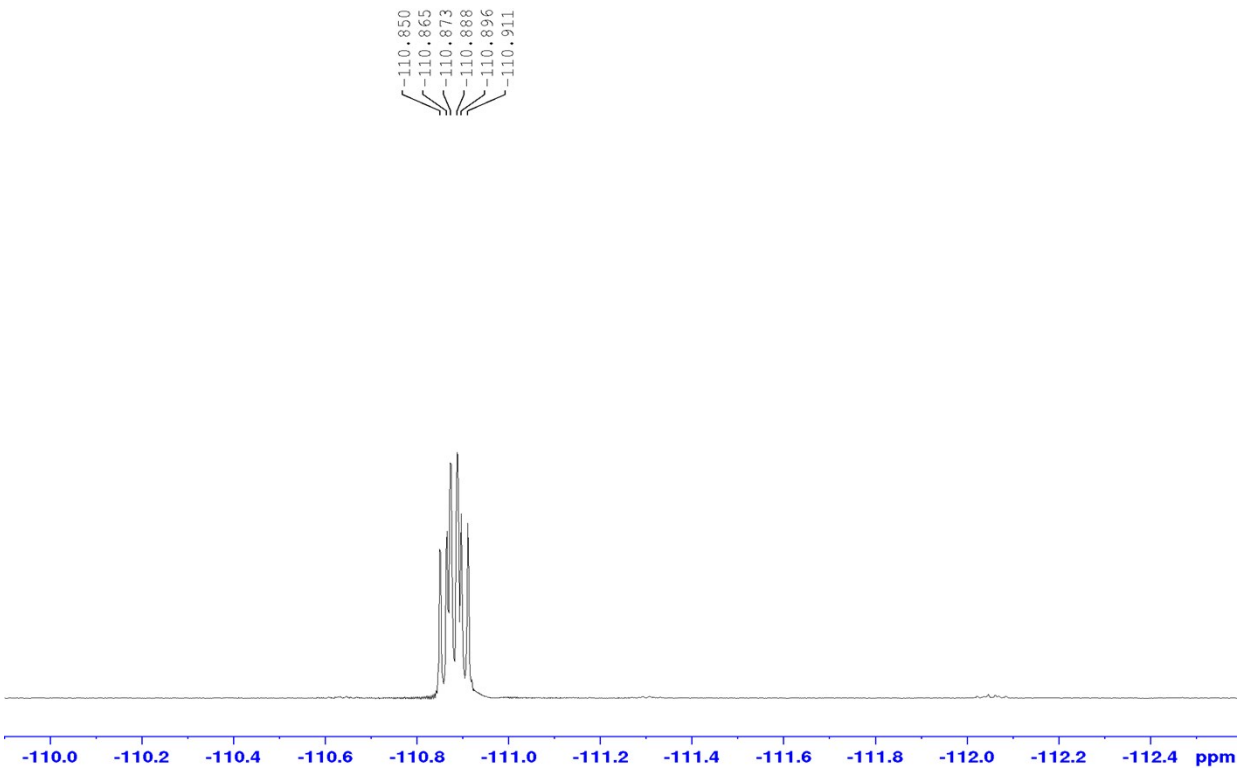
7.649
7.642
7.636
7.626
7.623
7.613
7.606
7.603
7.391
7.377
7.371
7.357
7.351
7.337
7.236
7.233
7.217
7.214
7.198
7.196
7.165
7.160
7.145
7.141
7.126
7.122
7.059
7.055
7.040
7.036
6.321
6.313
4.416
4.405

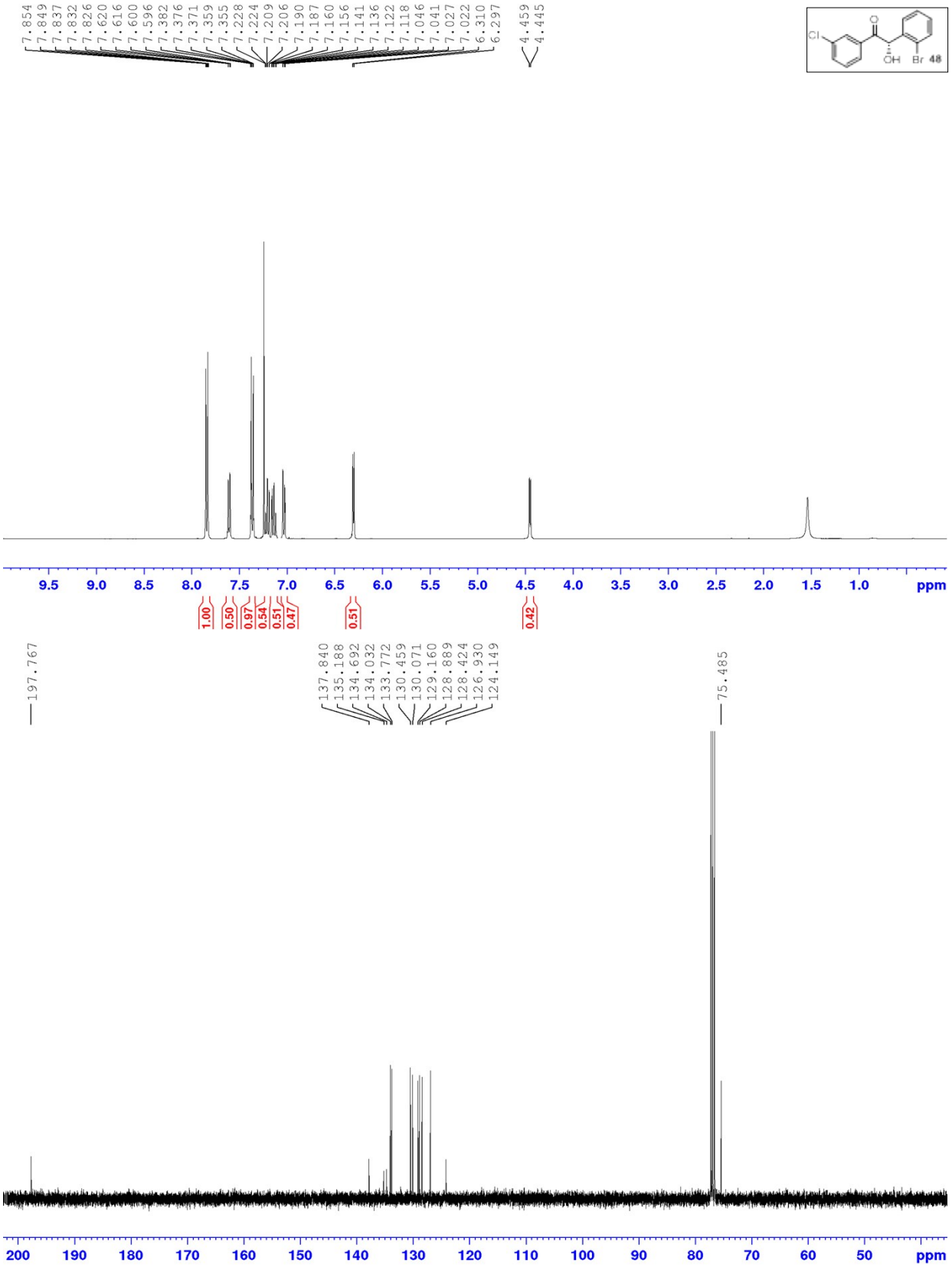

F
OH
Br
46


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
2.0
1.5
1.0
ppm
3.00
1.08
2.50
1.02
0.98
1.00
0.89

197.777
197.755
163.898
161.423
137.944
133.770
130.547
130.471
130.441
129.161
128.410
124.699
124.668
124.191
121.311
121.098
115.722
115.496
75.556


200
190
180
170
160
150
140
130
120
110
100
90
80
70
ppm


-110.850
-110.865
-110.873
-110.888
-110.896
-110.911
-110.0
-110.2
-110.4
-110.6
-110.8
-111.0
-111.2
-111.4
-111.6
-111.8
-112.0
-112.2
-112.4
ppm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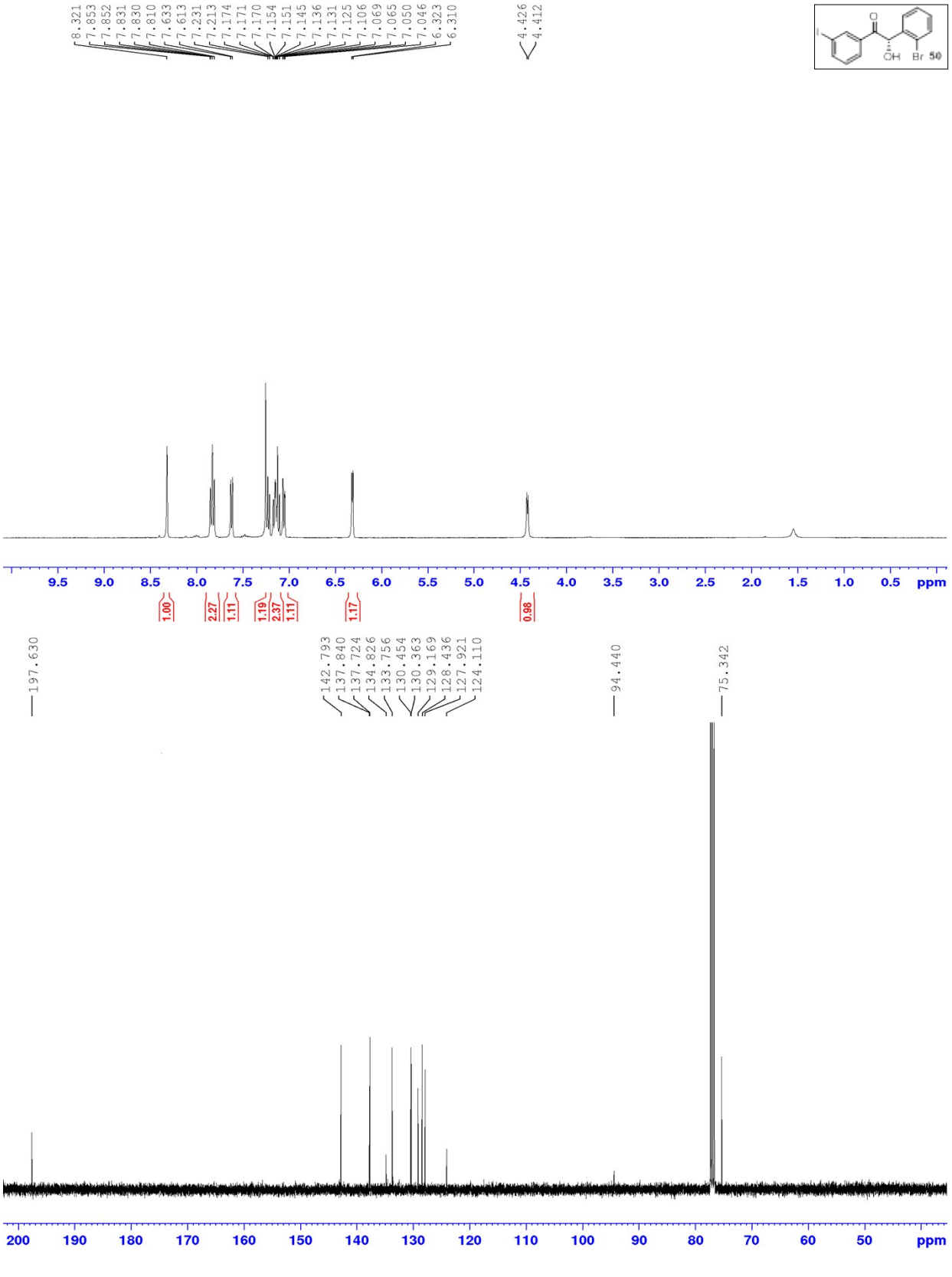
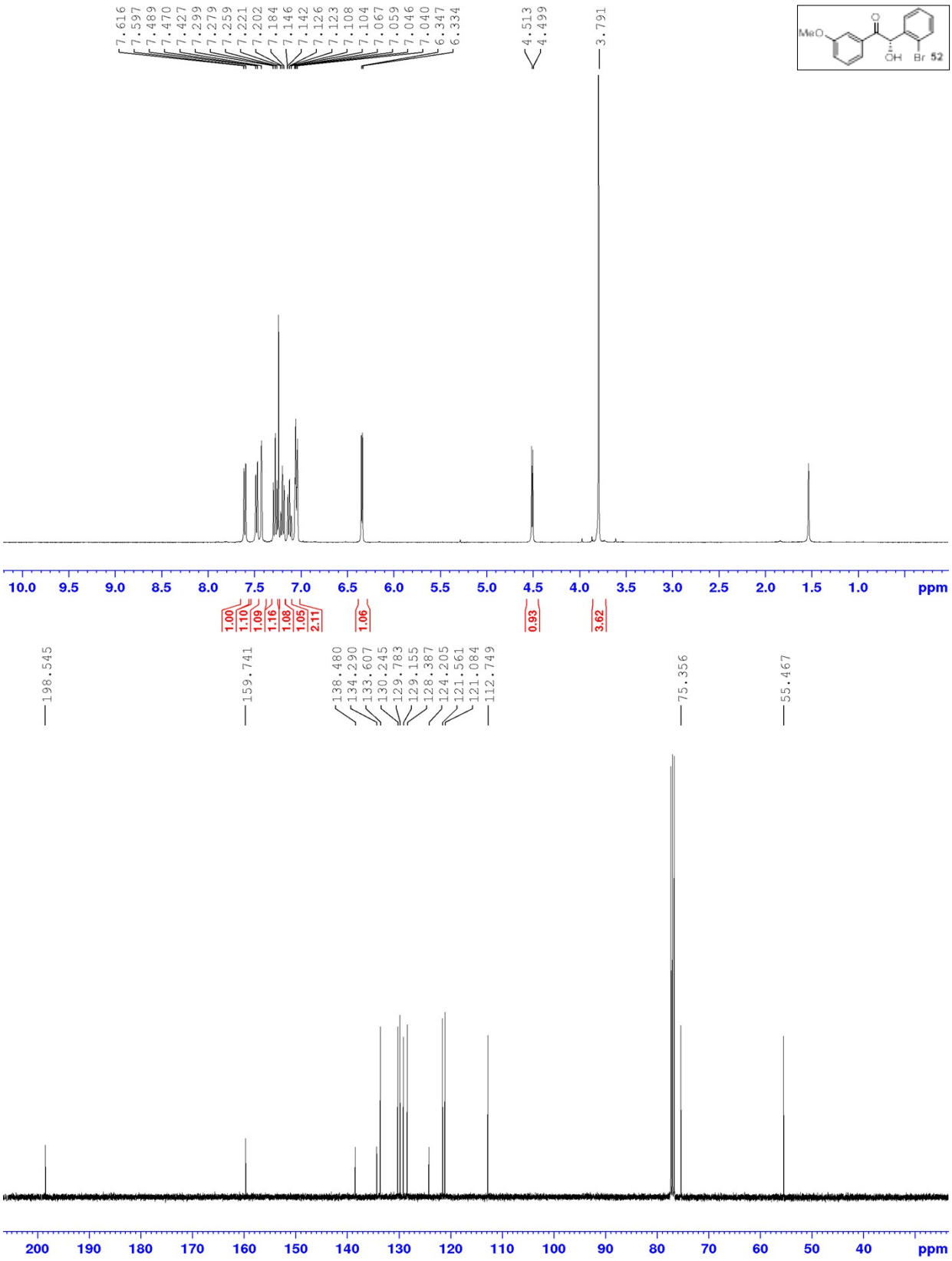
7.849
7.837
7.832
7.826
7.620
7.616
7.600
7.596
7.382
7.376
7.371
7.359
7.355
7.228
7.224
7.209
7.206
7.190
7.187
7.160
7.156
7.141
7.136
7.122
7.118
7.046
7.041
7.027
7.022
6.310
6.297
4.459
4.445
Cl
O
OH
Br 48
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
0.50
0.97
0.54
0.51
0.47
0.51
0.42
197.767
137.840
135.188
134.692
134.032
133.772
130.459
130.071
129.160
128.889
128.424
126.930
124.149
75.485
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 ppm


8.321
7.853
7.852
7.831
7.830
7.810
7.633
7.613
7.231
7.213
7.174
7.171
7.170
7.154
7.151
7.145
7.136
7.131
7.125
7.106
7.069
7.065
7.050
7.046
6.323
6.310
4.426
4.412
OH
Br
50
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 2.0 1.5 1.0 0.5 ppm
1.00
2.27
1.11
1.19
2.37
1.11
1.17
0.98
197.630
142.793
137.840
137.724
134.826
133.756
130.454
130.363
129.169
128.436
127.921
124.110
94.440
75.342
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 ppm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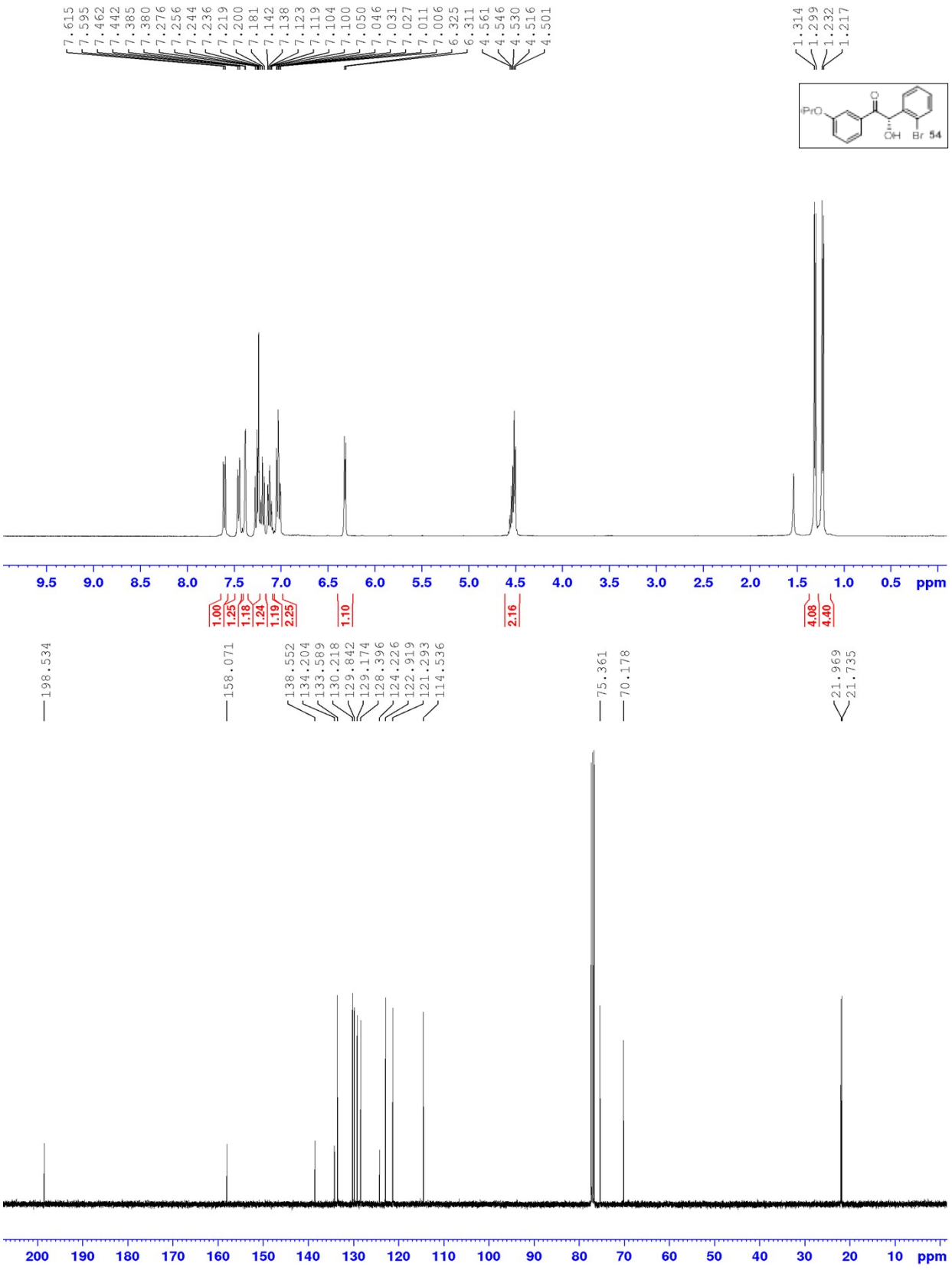
7.597
7.489
7.470
7.427
7.299
7.279
7.259
7.221
7.202
7.184
7.146
7.142
7.126
7.123
7.108
7.104
7.067
7.059
7.046
7.040
6.347
6.334
4.513
4.499
3.791
MeO
OH
Br
52
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 1.10 1.09 1.16 1.08 1.05 2.11 1.06 0.93 3.62
198.545
159.741
138.480
134.290
133.607
130.245
129.783
129.155
128.387
124.205
121.561
121.084
112.749
75.356
55.467
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm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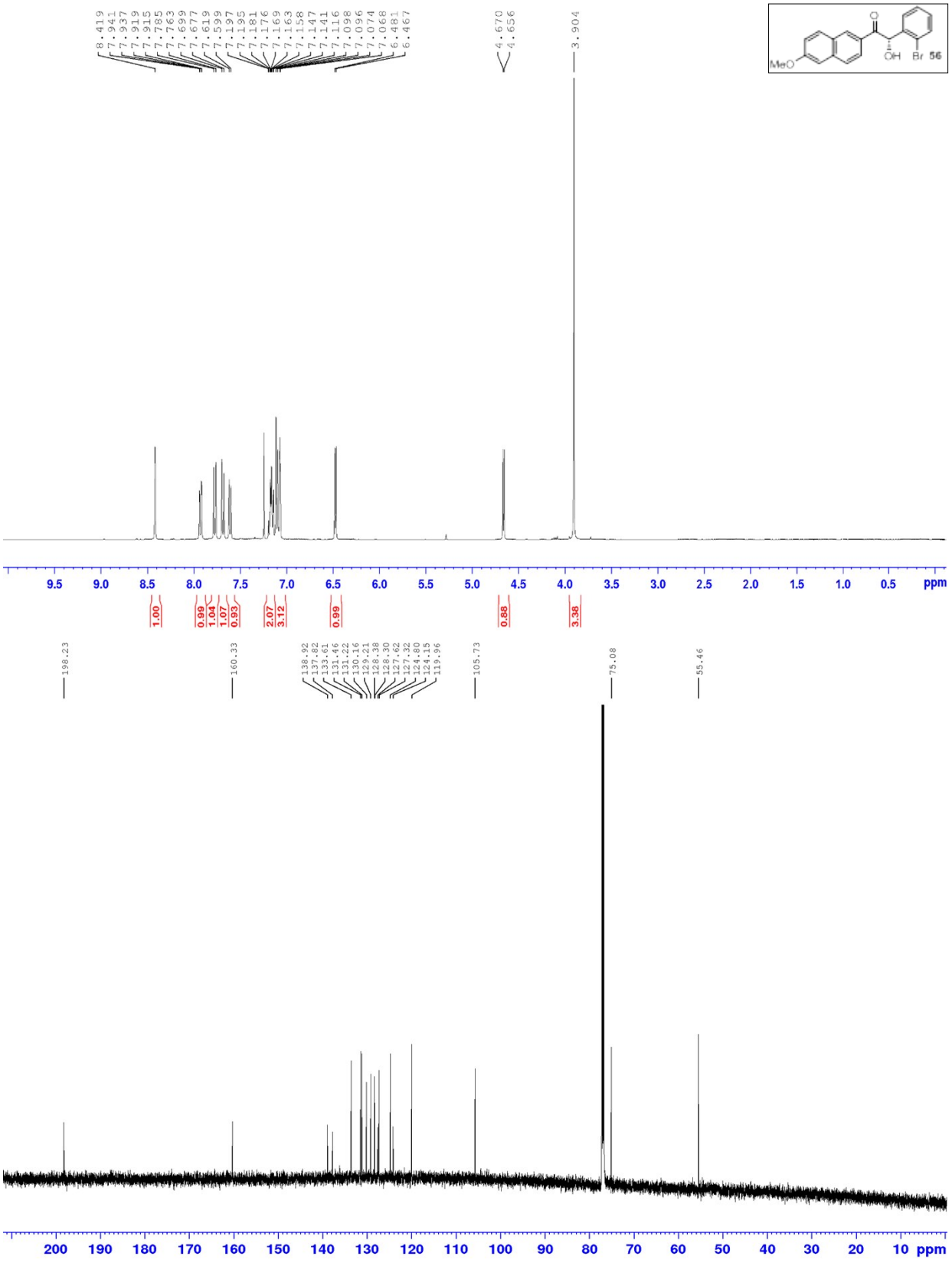
7.442
7.385
7.380
7.276
7.256
7.244
7.236
7.219
7.200
7.181
7.142
7.138
7.123
7.119
7.104
7.100
7.050
7.046
7.031
7.027
7.011
7.006
6.325
6.311
4.561
4.546
4.530
4.516
4.501
1.314
1.299
1.232
1.217
iPrO
O
OH
Br
54
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.25
1.18
1.24
1.19
2.25
1.10
2.16
4.08
4.40
198.534
158.071
138.552
134.204
133.589
130.218
129.842
129.174
128.396
124.226
122.919
121.293
114.536
75.361
70.178
21.969
21.735
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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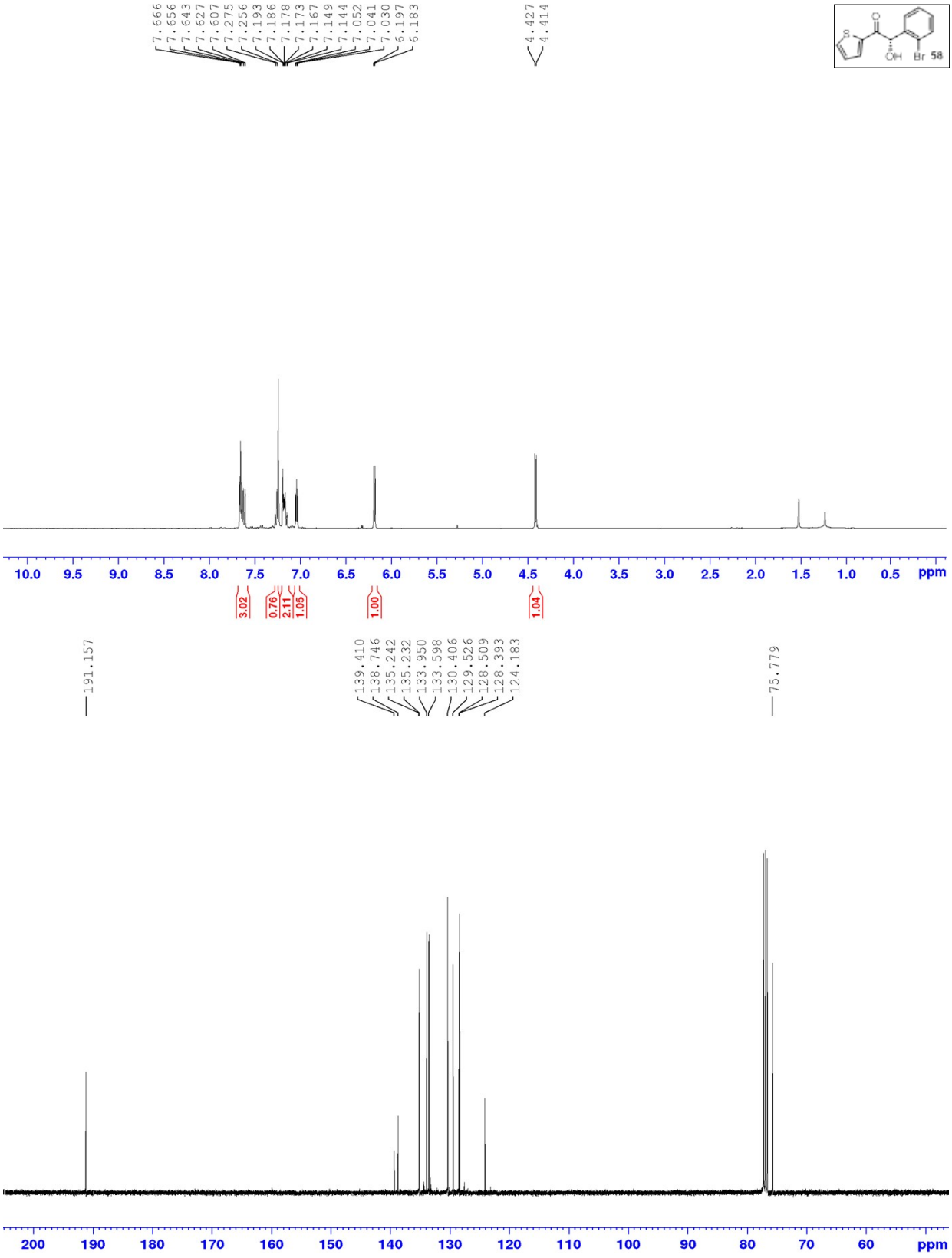
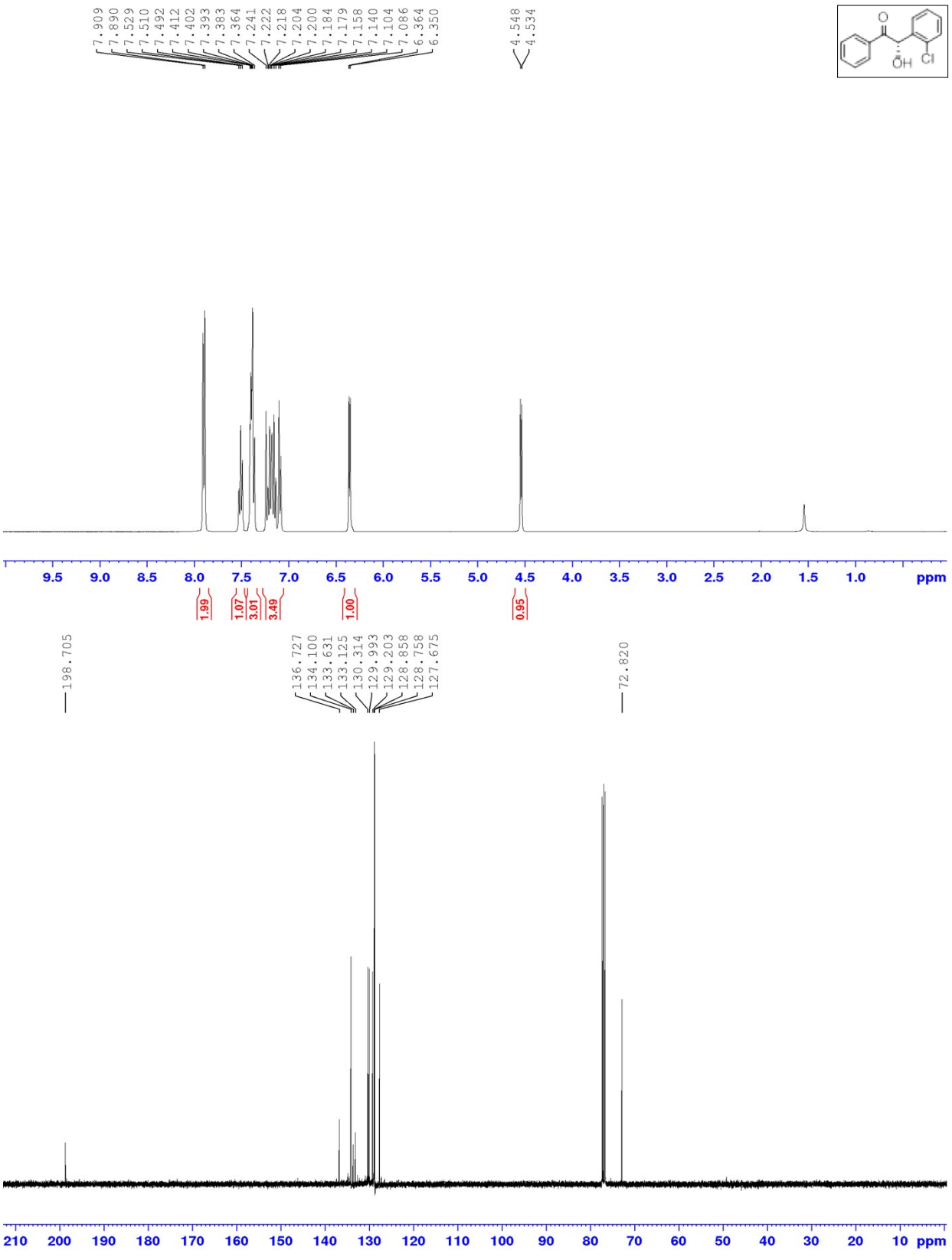
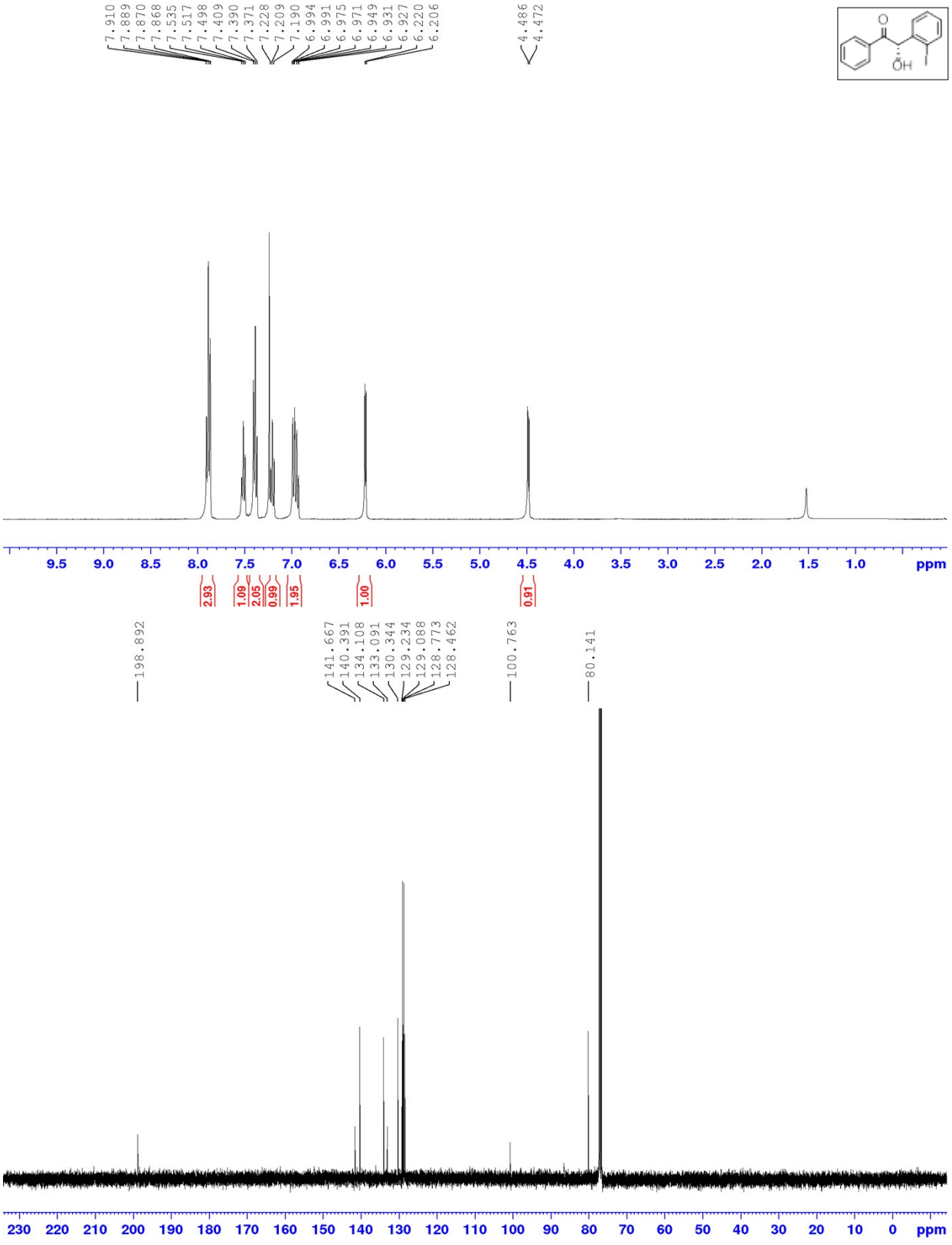
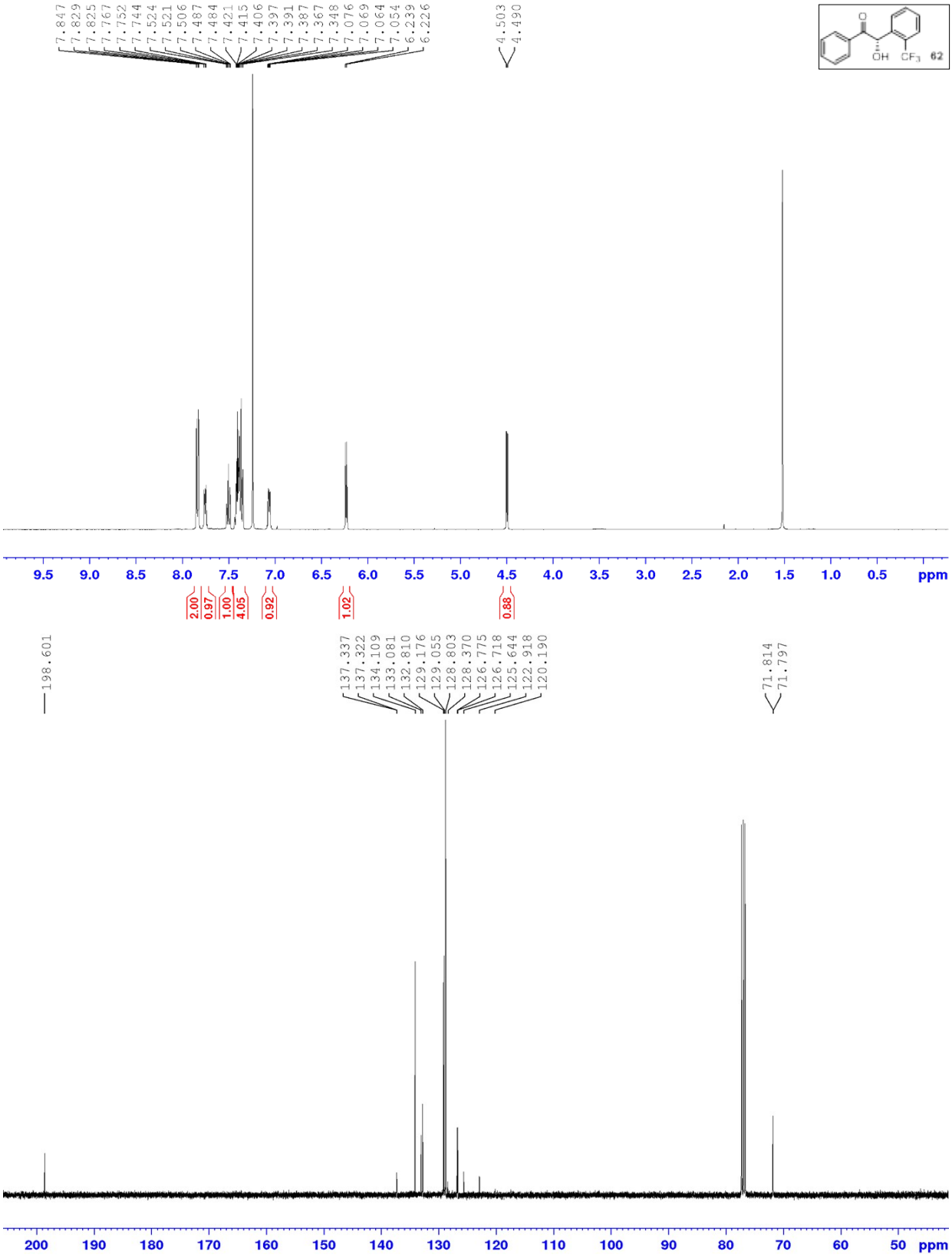
7.937
7.919
7.915
7.785
7.763
7.699
7.677
7.619
7.599
7.197
7.195
7.181
7.176
7.169
7.163
7.158
7.147
7.141
7.116
7.098
7.096
7.074
7.068
6.481
6.467
4.670
4.656
3.904
MeO
OH
Br
56
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.99
1.04
1.07
0.93
2.07
3.12
0.99
0.88
3.38
198.23
160.33
138.92
137.82
133.61
131.46
131.22
130.16
129.21
128.38
128.30
127.62
127.32
124.80
124.15
119.96
105.73
75.08
55.46
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.666
7.656
7.643
7.627
7.607
7.275
7.256
7.193
7.186
7.178
7.173
7.167
7.149
7.144
7.052
7.041
7.030
6.197
6.183
4.427
4.414
OH
Br
58
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 2.0 1.5 1.0 0.5 ppm
3.02
0.76
2.11
1.05
1.00
1.04
191.157
139.410
138.746
135.242
135.232
133.950
133.598
130.406
129.526
128.509
128.393
124.183
75.779
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 ppm


7.909
7.890
7.529
7.510
7.492
7.412
7.402
7.393
7.383
7.364
7.241
7.222
7.218
7.204
7.200
7.184
7.179
7.158
7.140
7.104
7.086
6.364
6.350
4.548
4.534
O
OH
Cl
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 2.0 1.5 1.0 ppm
1.99
1.07
3.01
3.49
1.00
0.95
198.705
136.727
134.100
133.631
133.125
130.314
129.993
129.203
128.858
128.758
127.675
72.820
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.910
7.889
7.870
7.868
7.535
7.517
7.498
7.409
7.390
7.371
7.228
7.209
7.190
6.994
6.991
6.975
6.971
6.949
6.931
6.927
6.220
6.206
4.486
4.472
O
OH
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 2.0 1.5 1.0 ppm
2.93
1.09
2.05
0.99
1.95
1.00
0.91
198.892
141.667
140.391
134.108
133.091
130.344
129.234
129.088
128.773
128.462
100.763
80.141
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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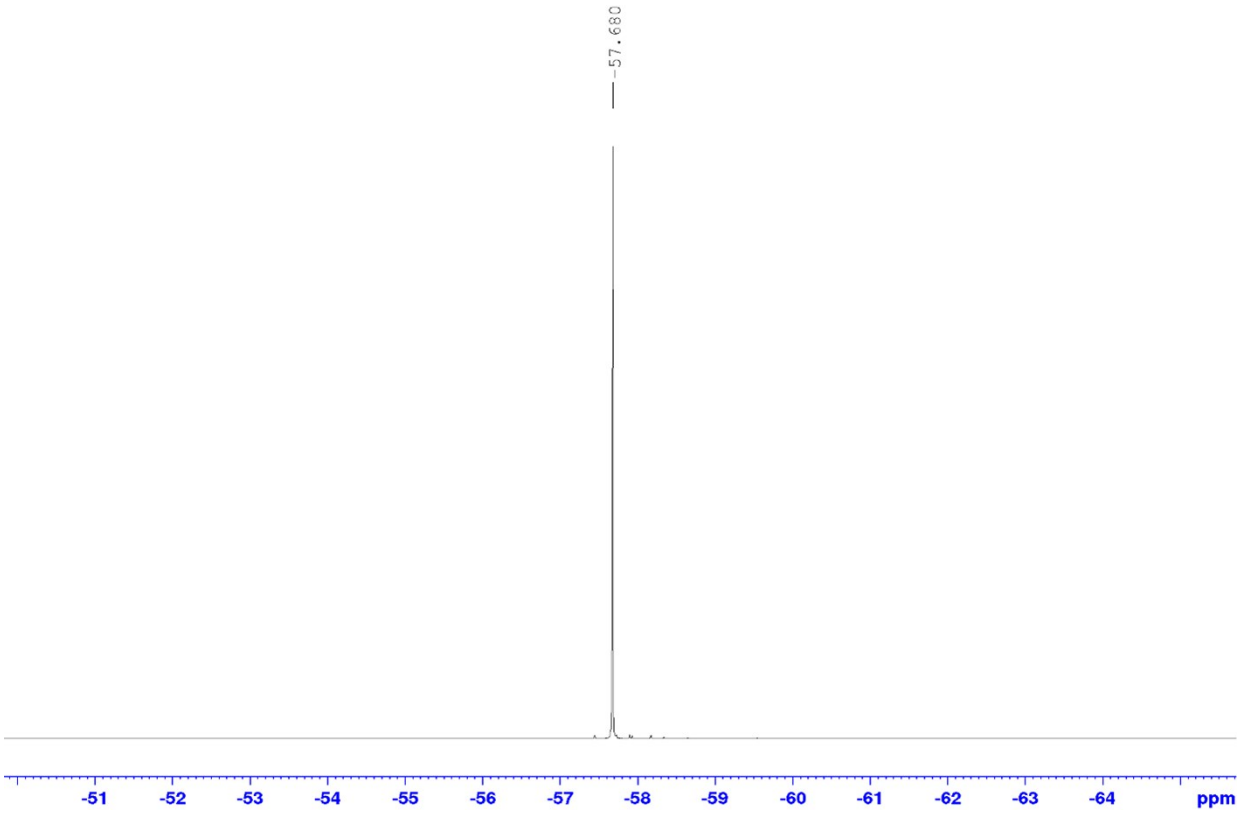
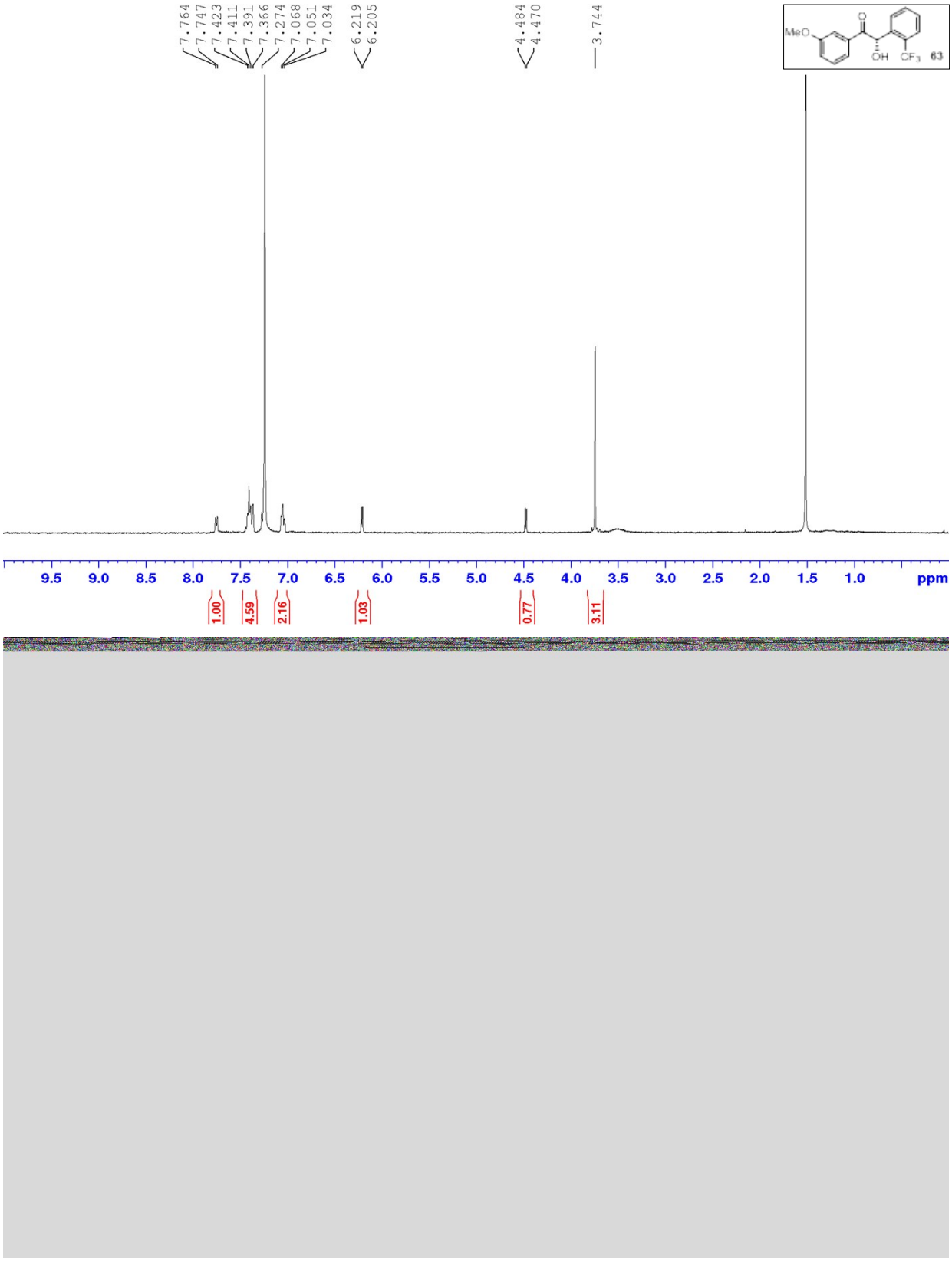
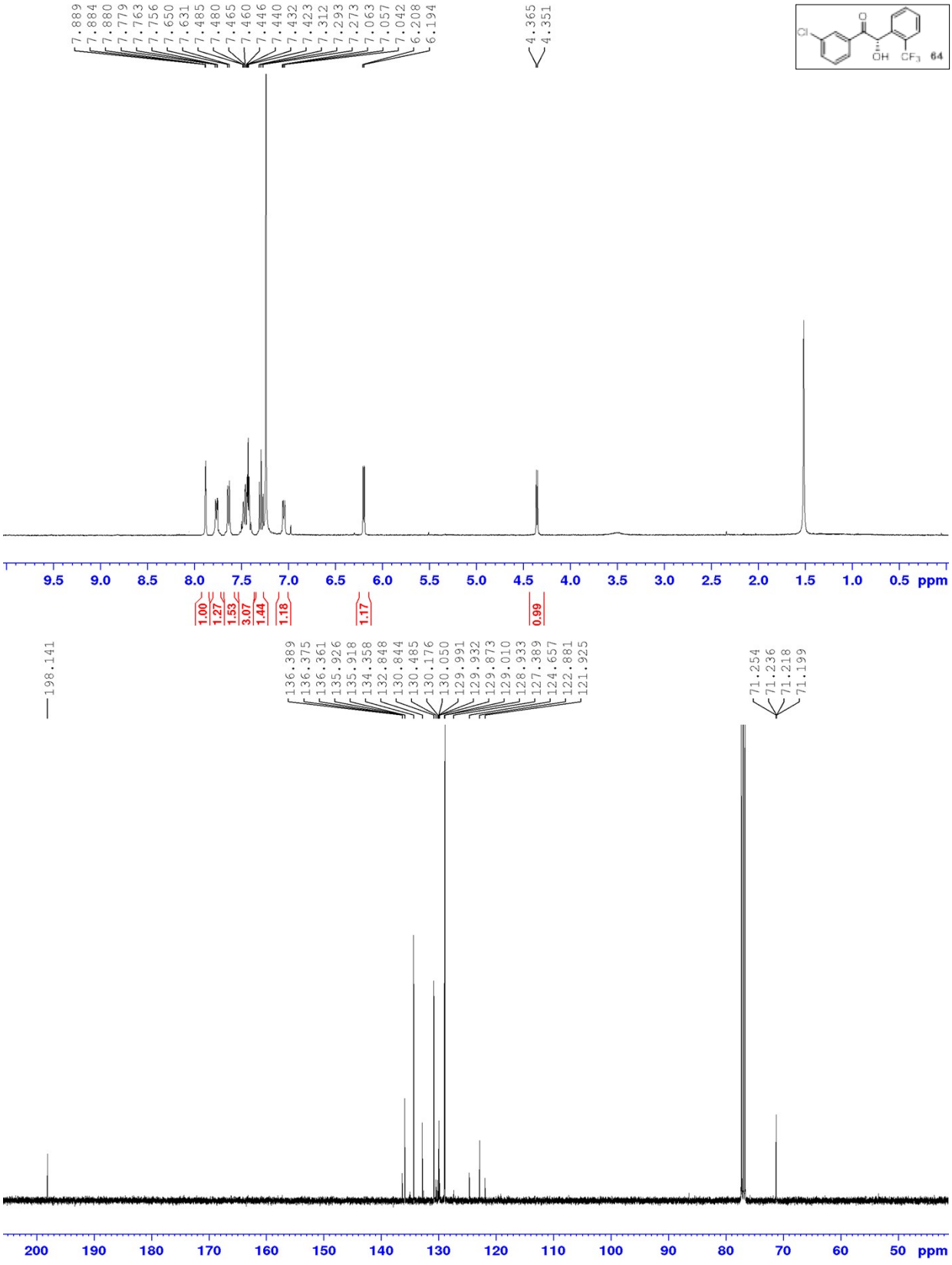
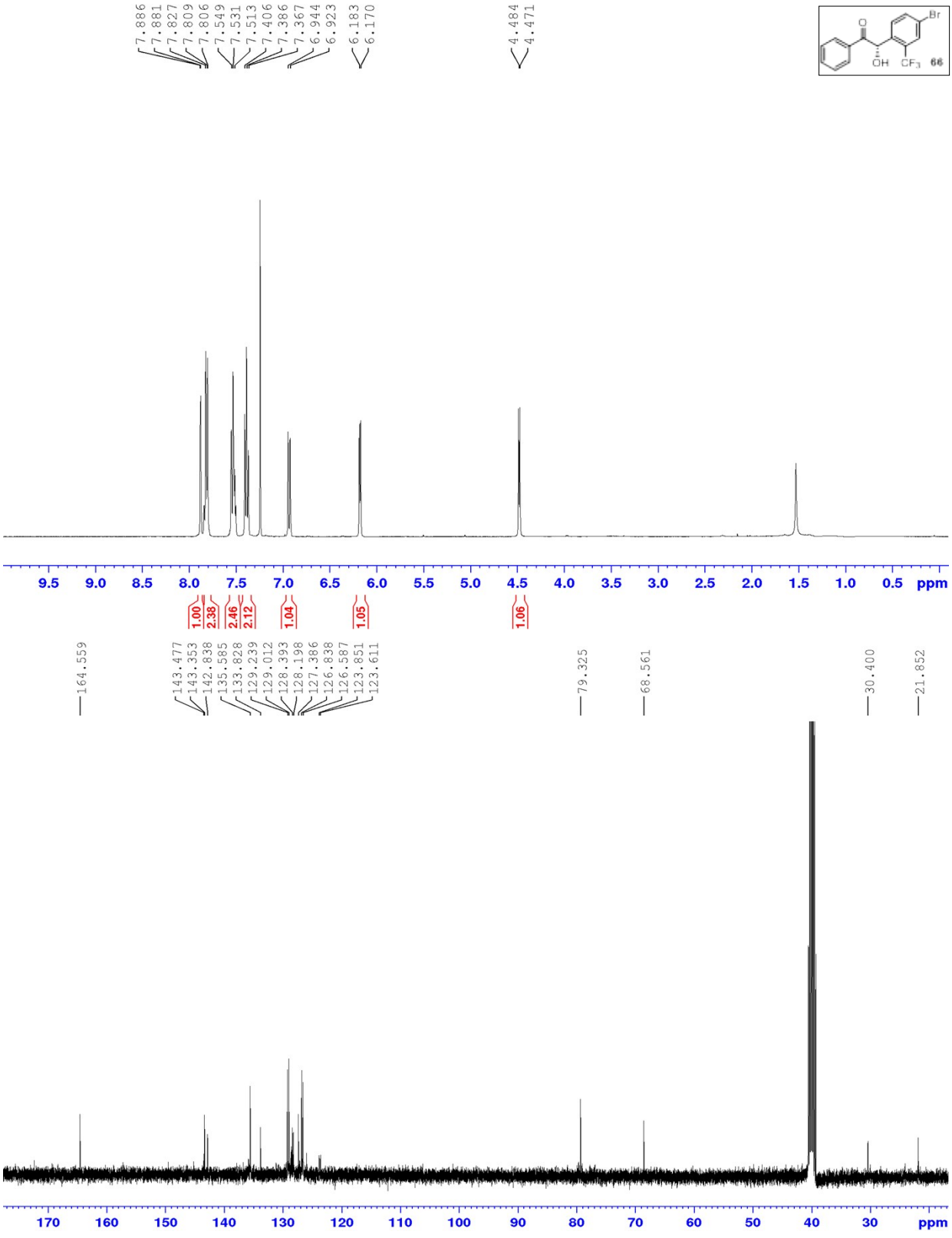
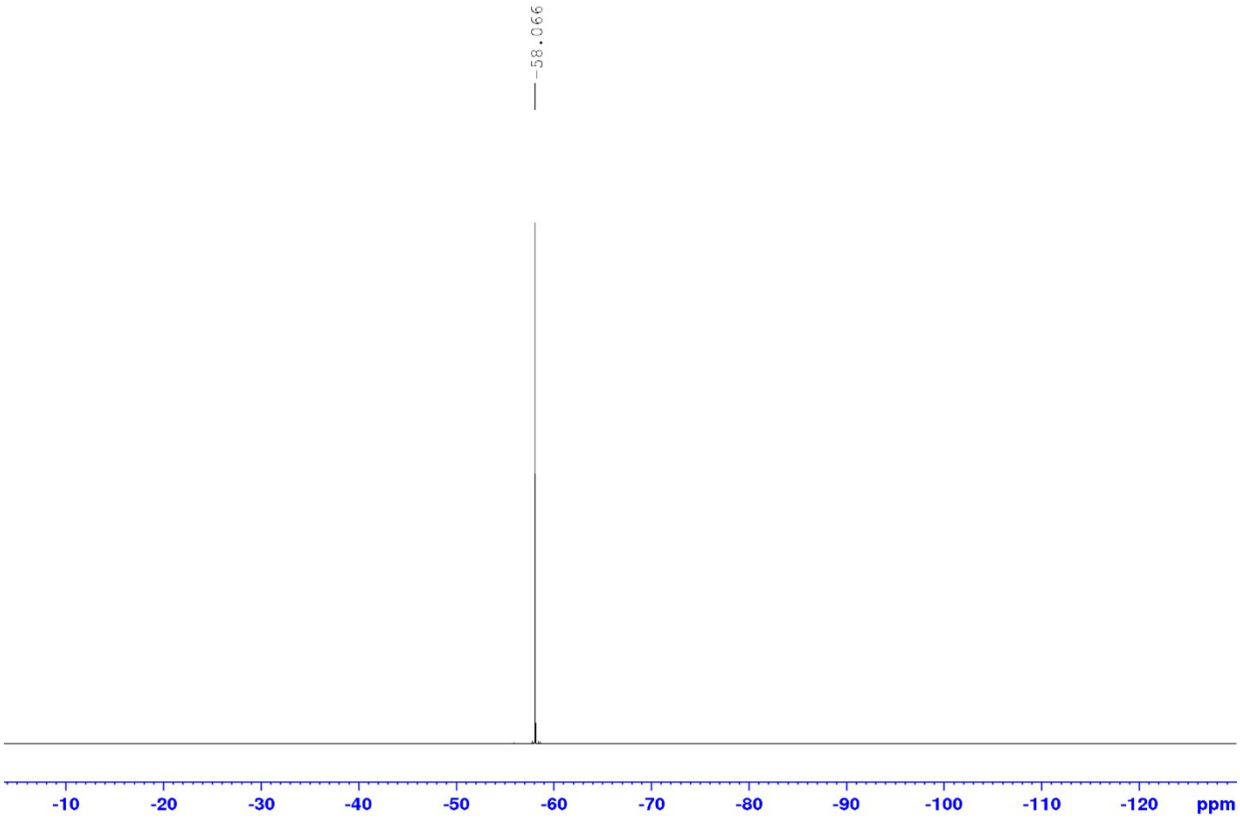
7.825
7.767
7.752
7.744
7.524
7.521
7.506
7.487
7.484
7.421
7.415
7.406
7.397
7.391
7.387
7.367
7.348
7.076
7.069
7.064
7.054
6.239
6.226
4.503
4.490
OH
CF3
62
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
0.97
1.00
4.05
0.92
1.02
0.88
198.601
137.337
137.322
134.109
133.081
132.810
129.176
129.055
128.803
128.370
126.775
126.718
125.644
122.918
120.190
71.814
71.797
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 ppm


-57.680
-51
-52
-53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
ppm

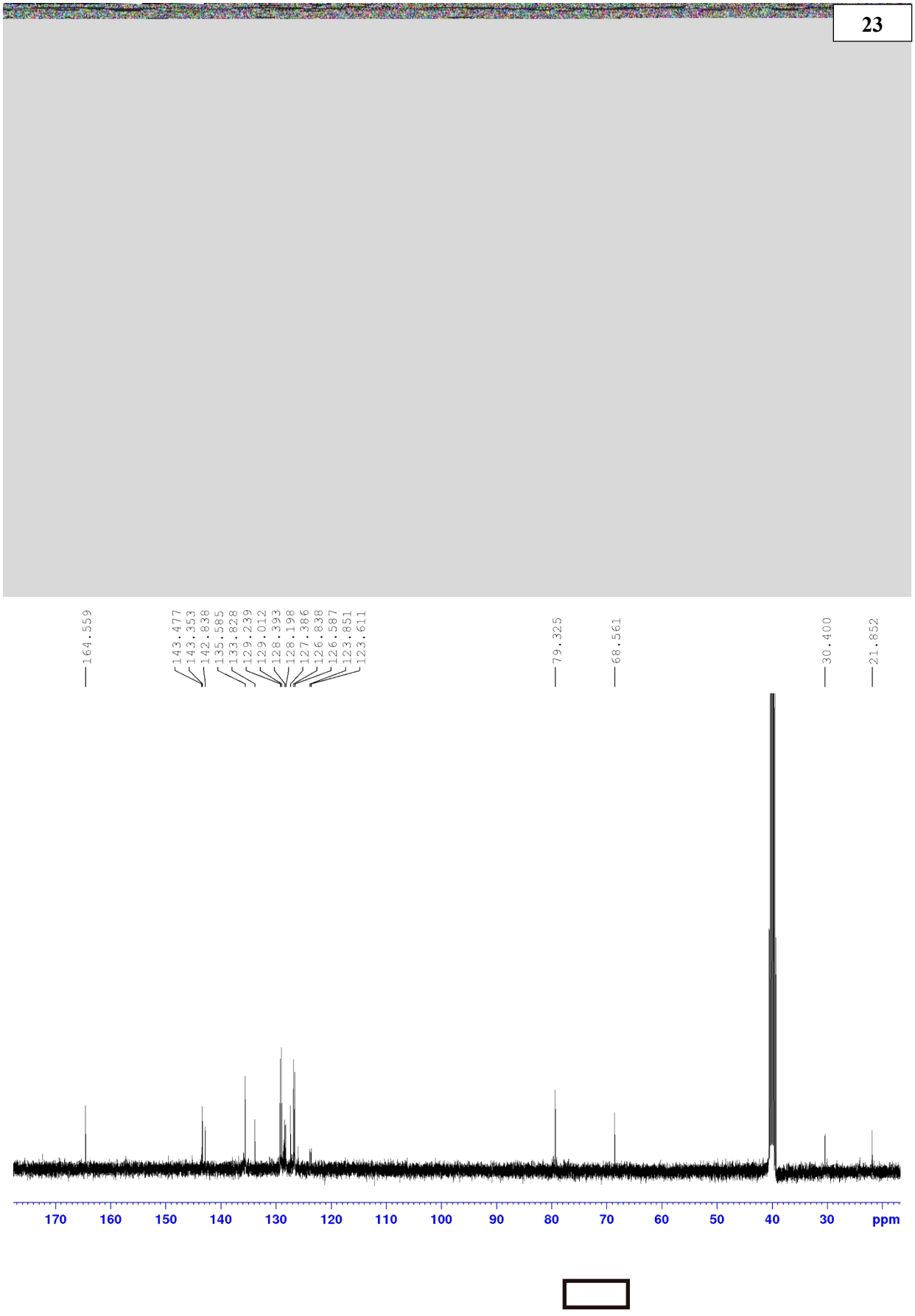

7.764
7.747
7.423
7.411
7.391
7.366
7.274
7.068
7.051
7.034
6.219
6.205
4.484
4.470
3.744
MeO
OH
CF3
63
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
4.59
2.16
1.03
0.77
3.11


7.889
7.884
7.880
7.779
7.763
7.756
7.650
7.631
7.485
7.480
7.465
7.460
7.446
7.440
7.432
7.423
7.312
7.293
7.273
7.063
7.057
7.042
6.208
6.194
4.365
4.351
Cl
OH
CF3
64
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 2.0 1.5 1.0 0.5 ppm
1.00
1.27
1.53
3.07
1.44
1.18
1.17
0.99
198.141
136.389
136.375
136.361
135.926
135.918
134.358
132.848
130.844
130.485
130.176
130.050
129.991
129.932
129.873
129.010
128.933
127.389
124.657
122.881
121.925
71.254
71.236
71.218
71.199
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 ppm

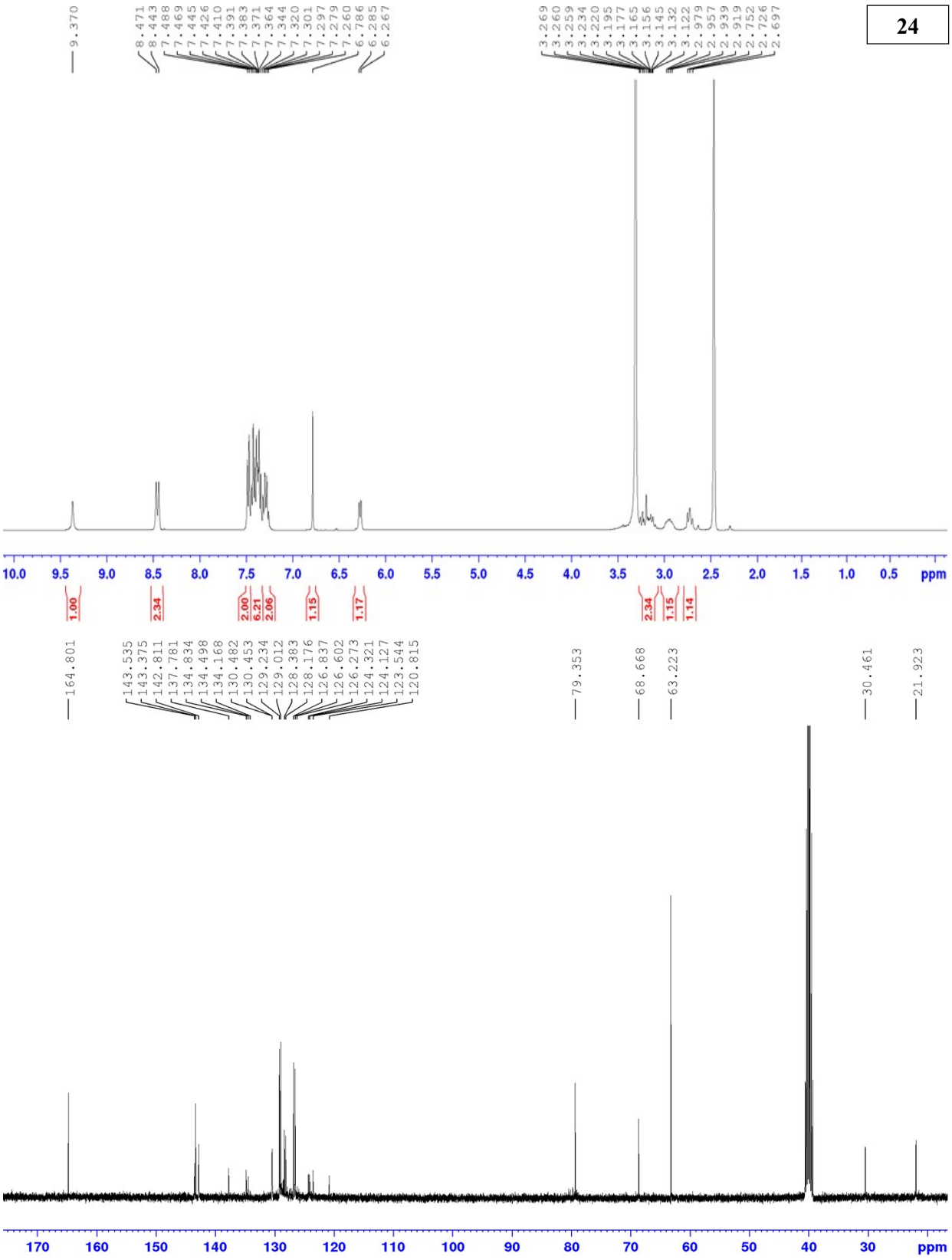

7.886
7.881
7.827
7.809
7.806
7.549
7.531
7.513
7.406
7.386
7.367
6.944
6.923
6.183
6.170
4.484
4.471
Br
O
OH
CF3
66
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.38
2.46
2.12
1.04
1.05
1.06
164.559
143.477
143.353
142.838
135.585
133.828
129.239
129.012
128.393
128.198
127.386
126.838
126.587
123.851
123.611
79.325
68.561
30.400
21.852
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


-58.066
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
ppm

5.3 NMR spectral data for triazolium precatalysts



24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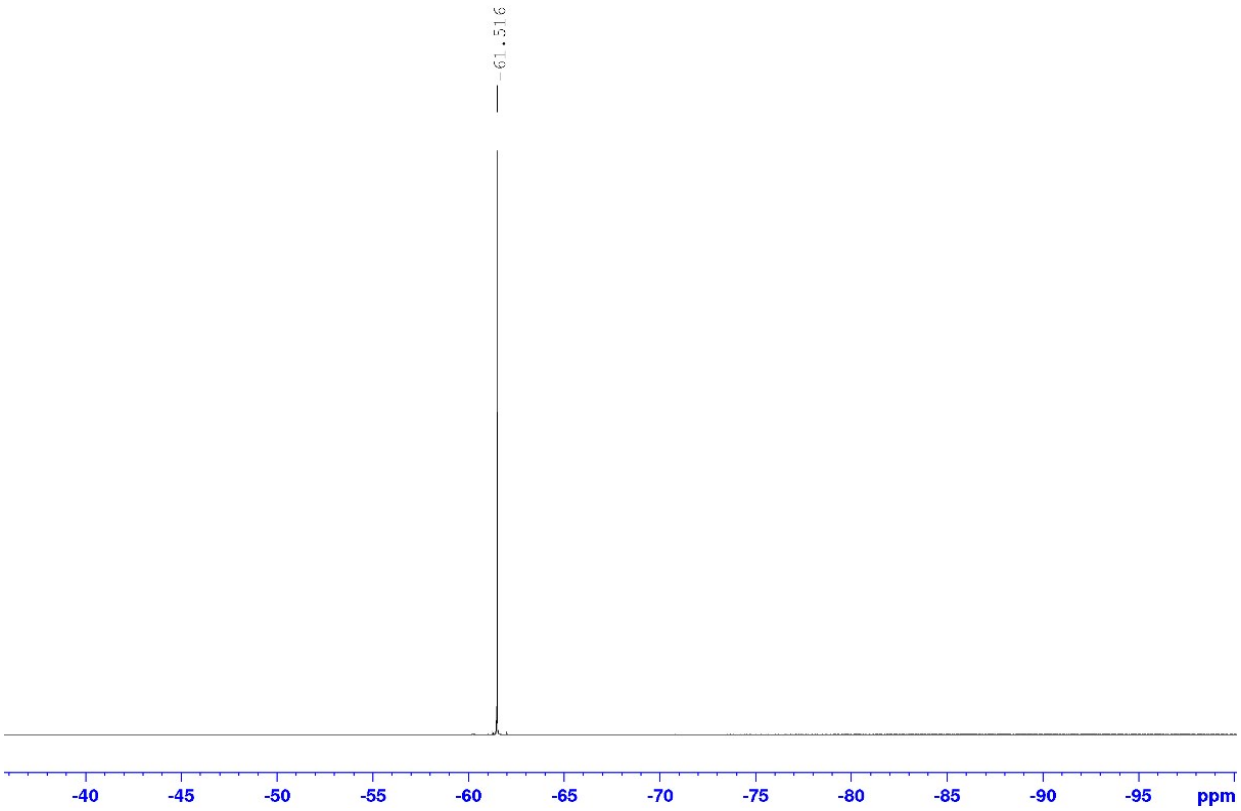
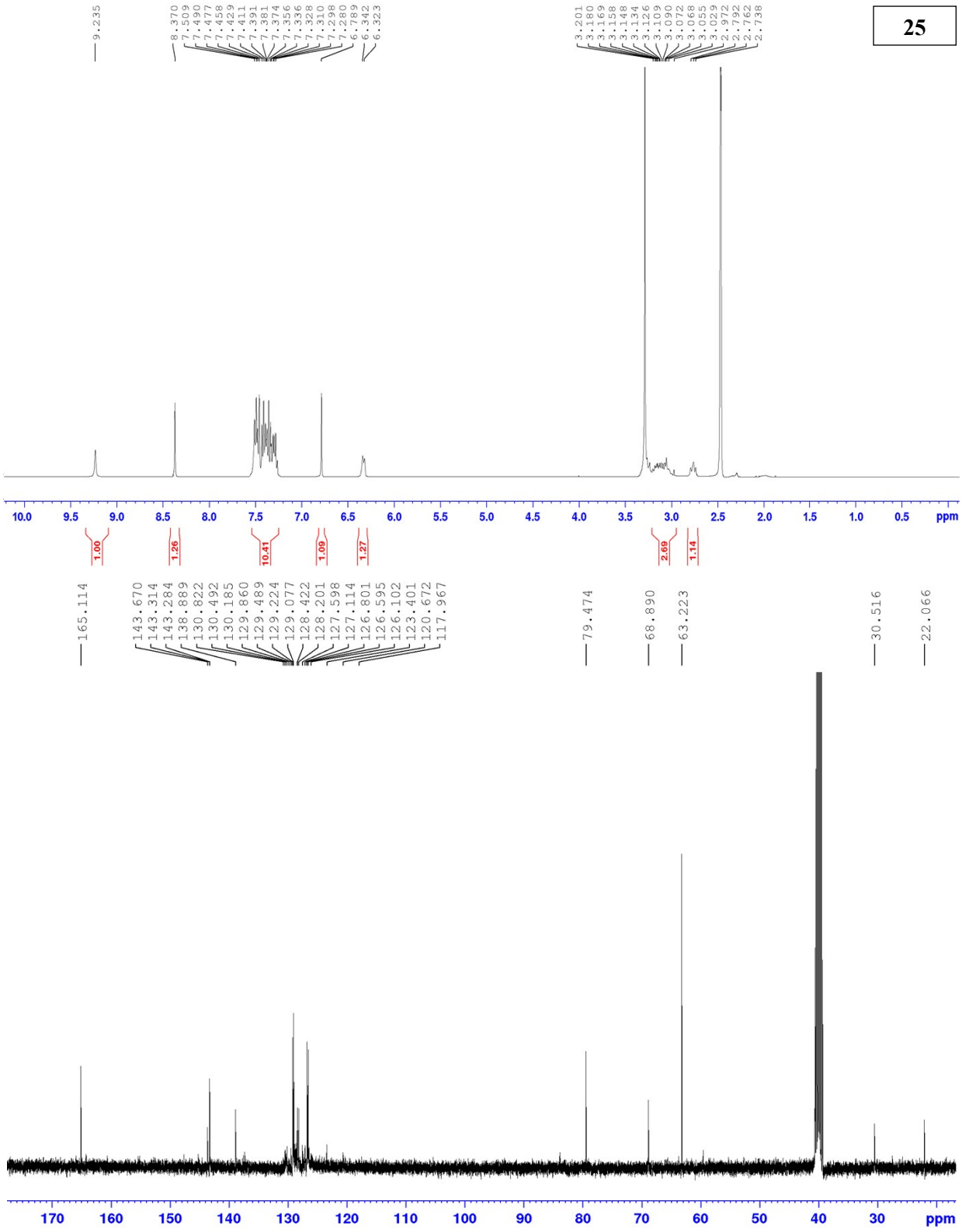
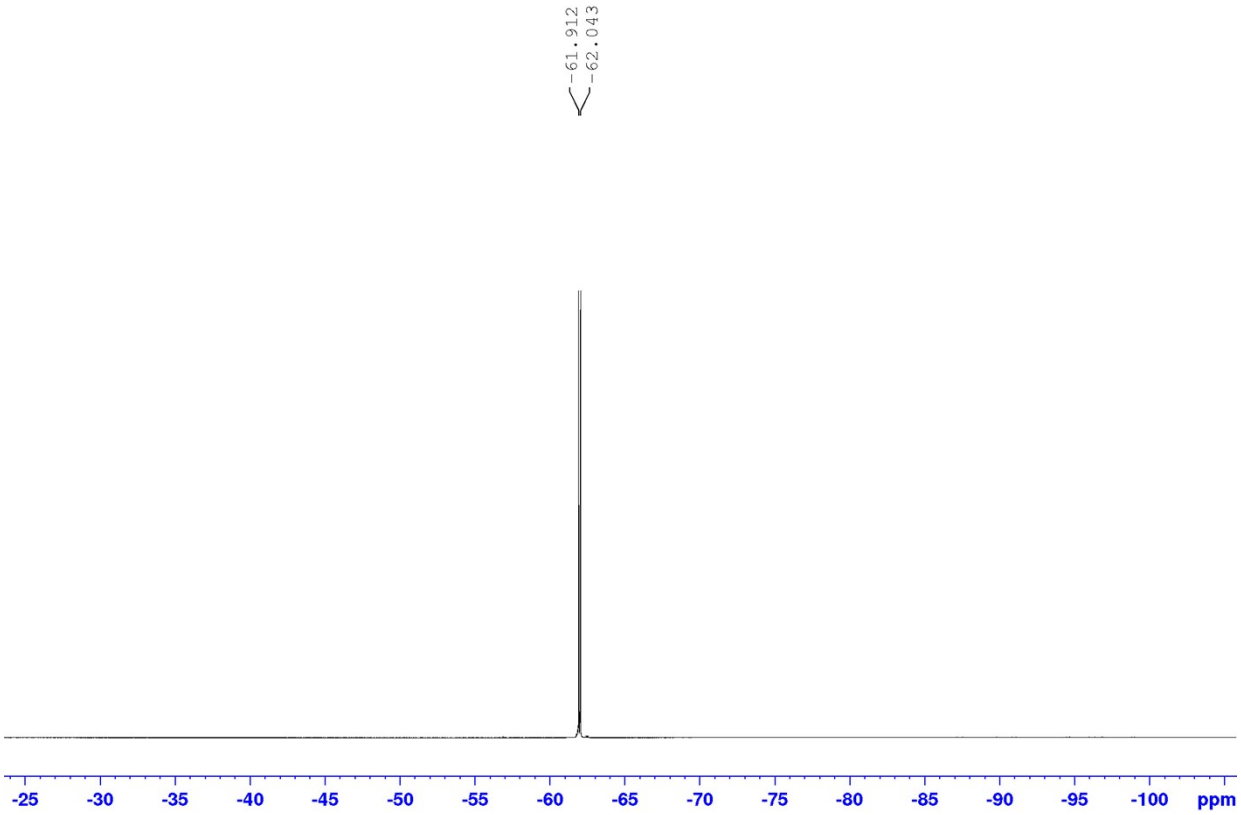
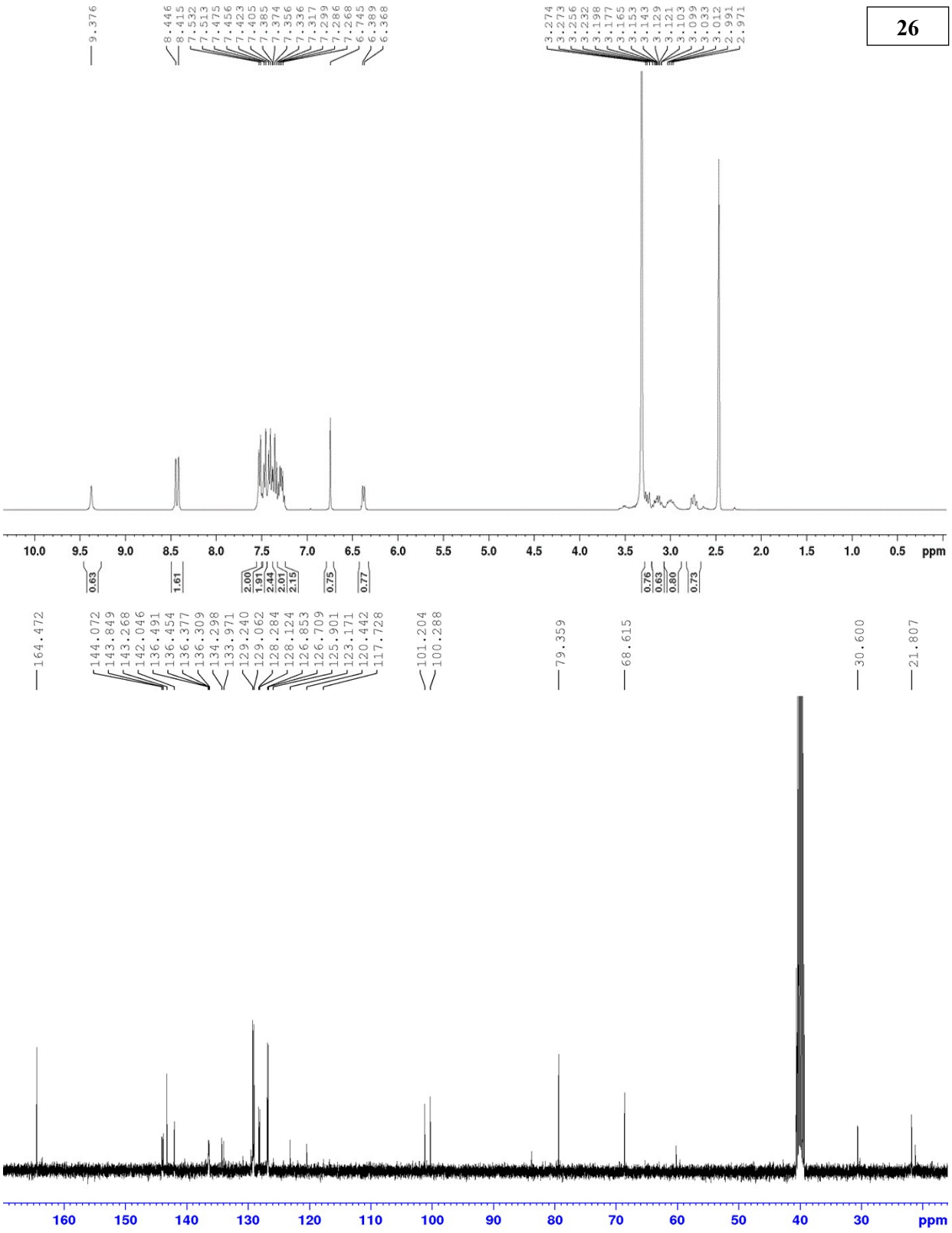
8.471
8.443
7.488
7.469
7.445
7.426
7.410
7.391
7.383
7.371
7.364
7.344
7.320
7.301
7.297
7.279
7.260
6.786
6.285
6.267
3.269
3.260
3.259
3.234
3.220
3.195
3.177
3.165
3.156
3.145
3.132
3.122
2.979
2.957
2.939
2.919
2.752
2.726
2.697
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.34
2.00
6.21
2.06
1.15
1.17
2.34
1.15
1.14
164.801
143.535
143.375
142.811
137.781
134.834
134.498
134.168
130.482
130.453
129.234
129.012
128.383
128.176
126.837
126.602
126.273
124.321
124.127
123.544
120.815
79.353
68.668
63.223
30.461
21.923
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


-61.516
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm


25
9.235
8.370
7.509
7.490
7.477
7.458
7.429
7.411
7.391
7.381
7.374
7.356
7.336
7.328
7.310
7.298
7.280
6.789
6.342
6.323
3.201
3.180
3.169
3.158
3.148
3.134
3.126
3.109
3.090
3.072
3.068
3.055
3.029
2.972
2.792
2.762
2.738
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 2.0 1.5 1.0 0.5 ppm
1.00
1.26
10.41
1.09
1.27
2.69
1.14
165.114
143.670
143.314
143.284
138.889
130.822
130.492
130.185
129.860
129.489
129.224
129.077
128.422
128.201
127.598
127.114
126.801
126.595
126.102
123.401
120.672
117.967
79.474
68.890
63.223
30.516
22.066
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


61.912
62.043
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
ppm

26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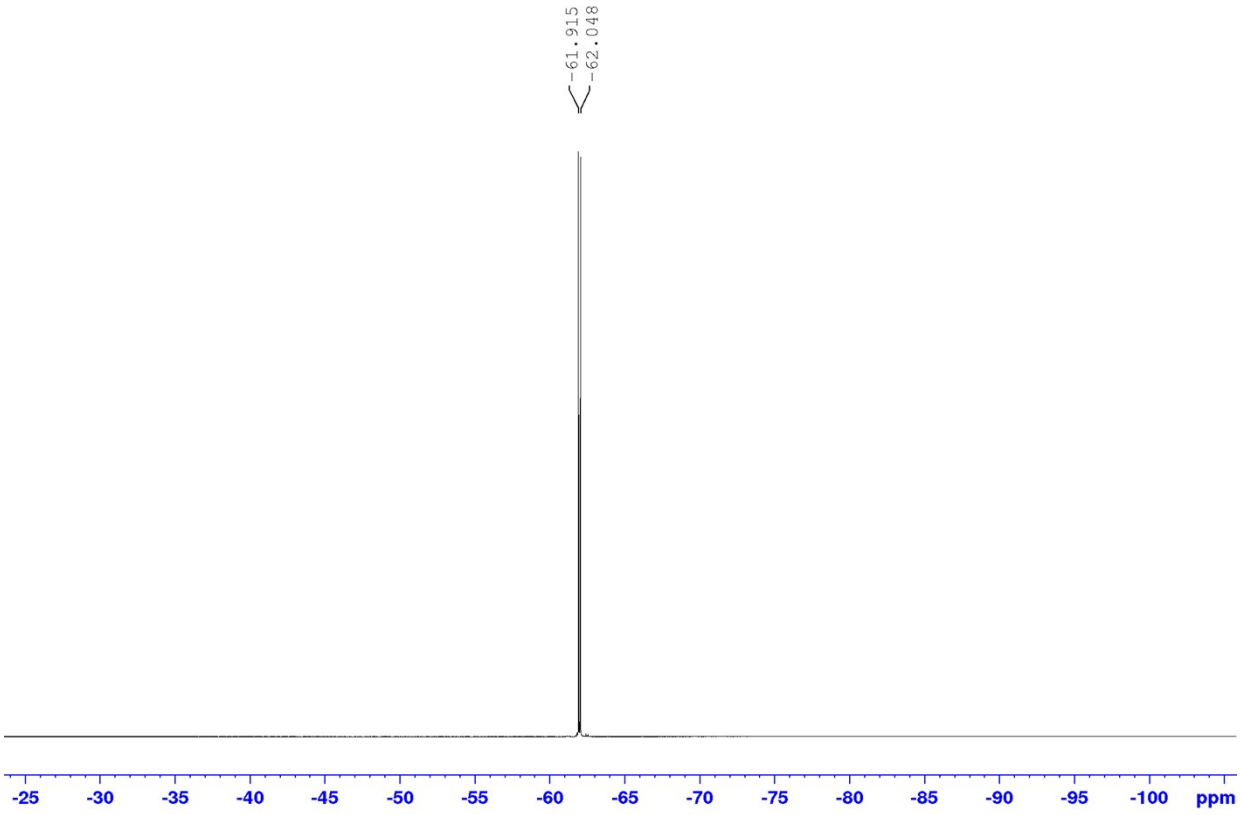
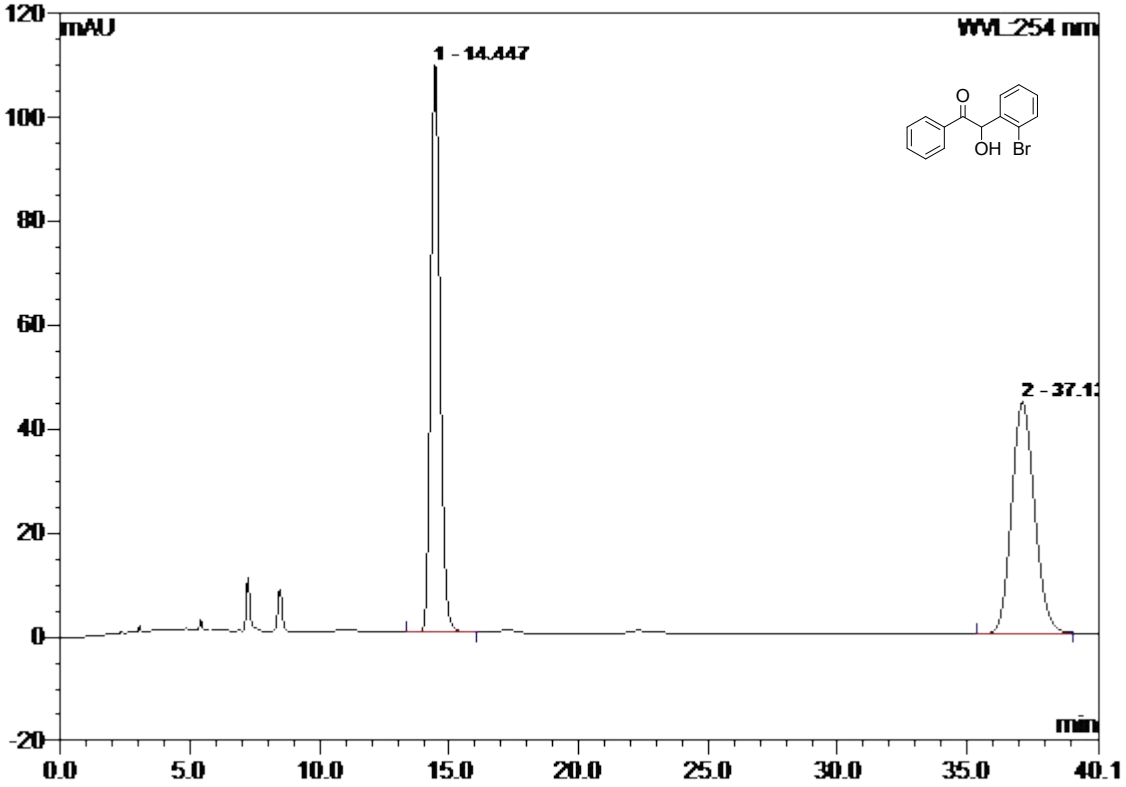
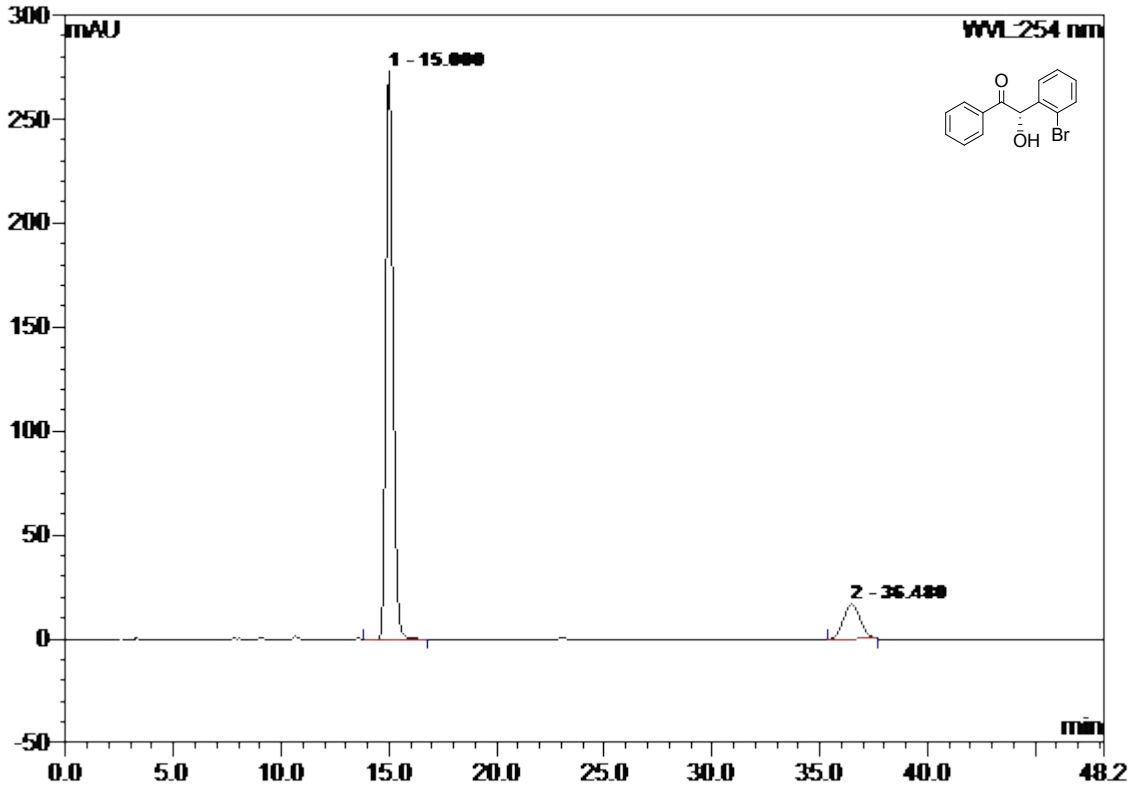
8.446
8.415
7.532
7.513
7.475
7.456
7.423
7.405
7.385
7.374
7.356
7.336
7.317
7.299
7.286
7.268
6.745
6.389
6.368
3.274
3.273
3.256
3.232
3.198
3.177
3.165
3.153
3.143
3.129
3.121
3.103
3.099
3.033
3.012
2.991
2.971
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.63
1.61
2.00
1.91
2.44
2.01
2.15
0.75
0.77
0.76
0.63
0.80
0.73
164.472
144.072
143.849
143.268
142.046
136.491
136.454
136.377
136.309
134.298
133.971
129.240
129.062
128.284
128.124
126.853
126.709
125.901
123.171
120.442
117.728
101.204
100.288
79.359
68.615
30.600
21.807
160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


-61.915
-62.048
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
ppm

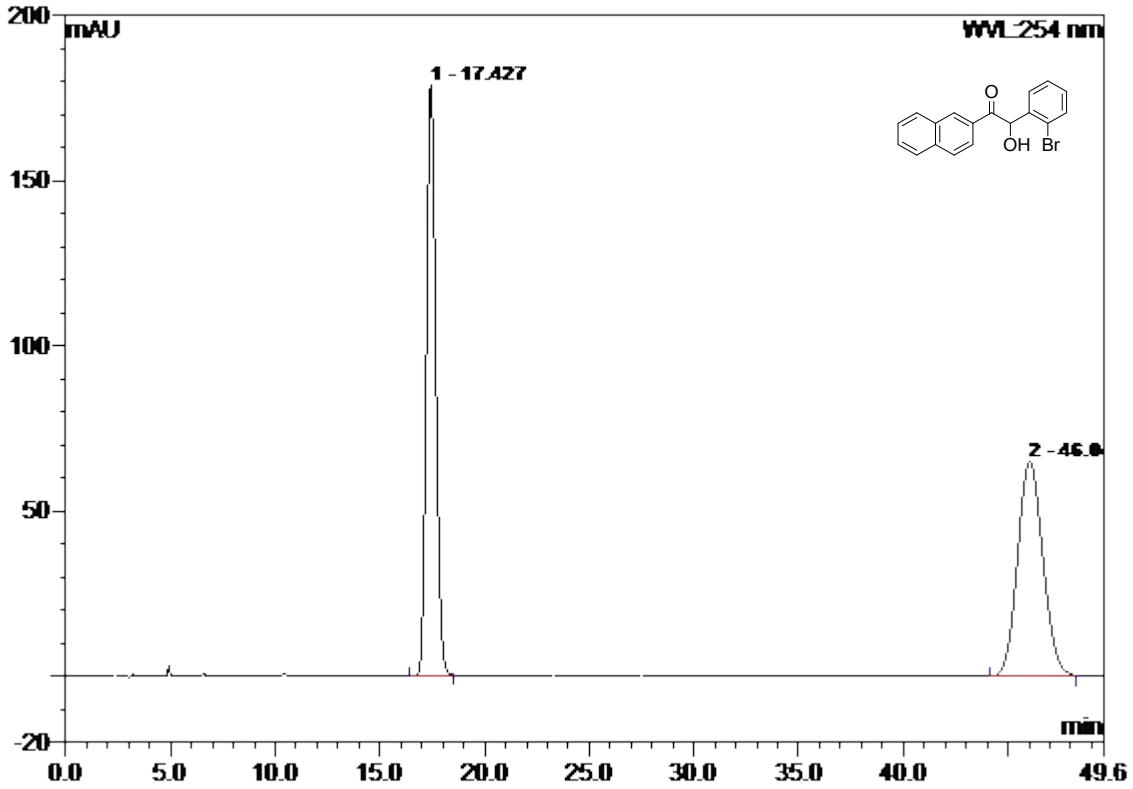
6 HPLC chromatograph data for cross-benzoin products



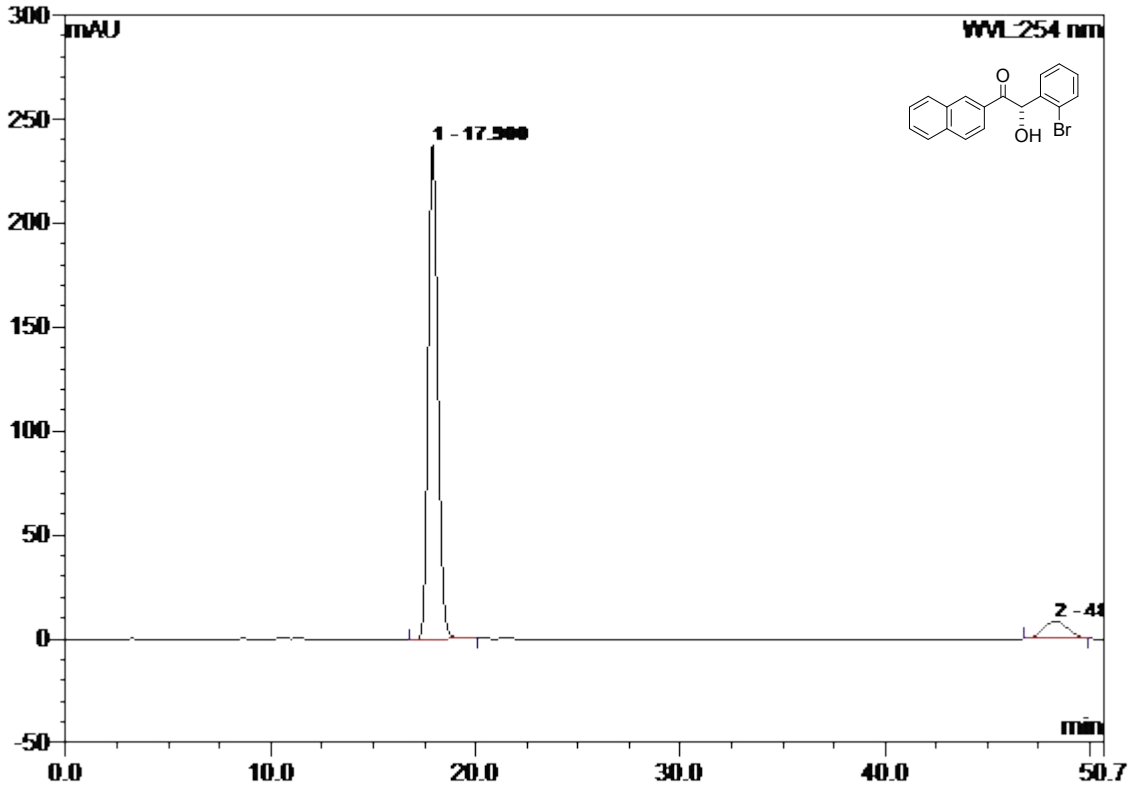
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.45	*S*-enantiomer	109.137	46.092	50.27	n.a.	BMB*
2	37.13	*R*-enantiomer	44.446	45.606	49.73	n.a.	BMB*
Total:			153.582	91.698	100.00	0.000	



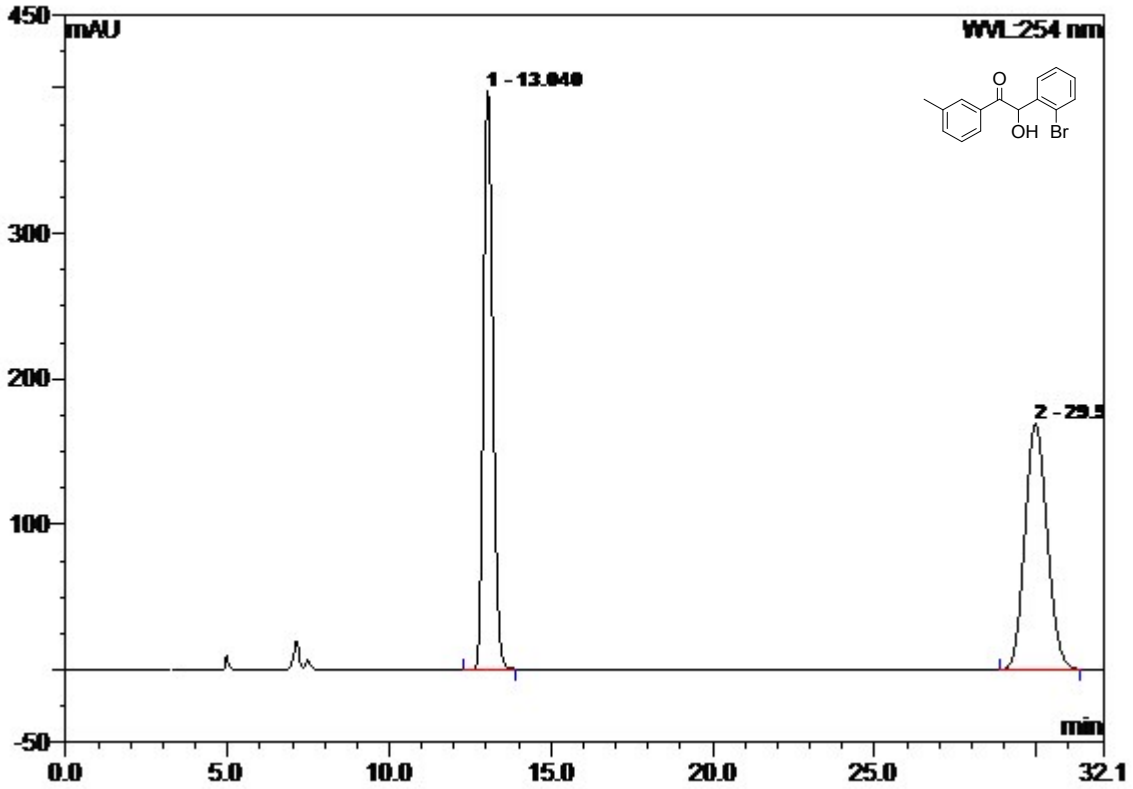
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.00	*S*-enantiomer	273.770	106.501	87.57	n.a.	BMB*
2	36.48	*R*-enantiomer	16.546	15.123	12.43	n.a.	BMB*
Total:			290.316	121.624	100.00	0.000	



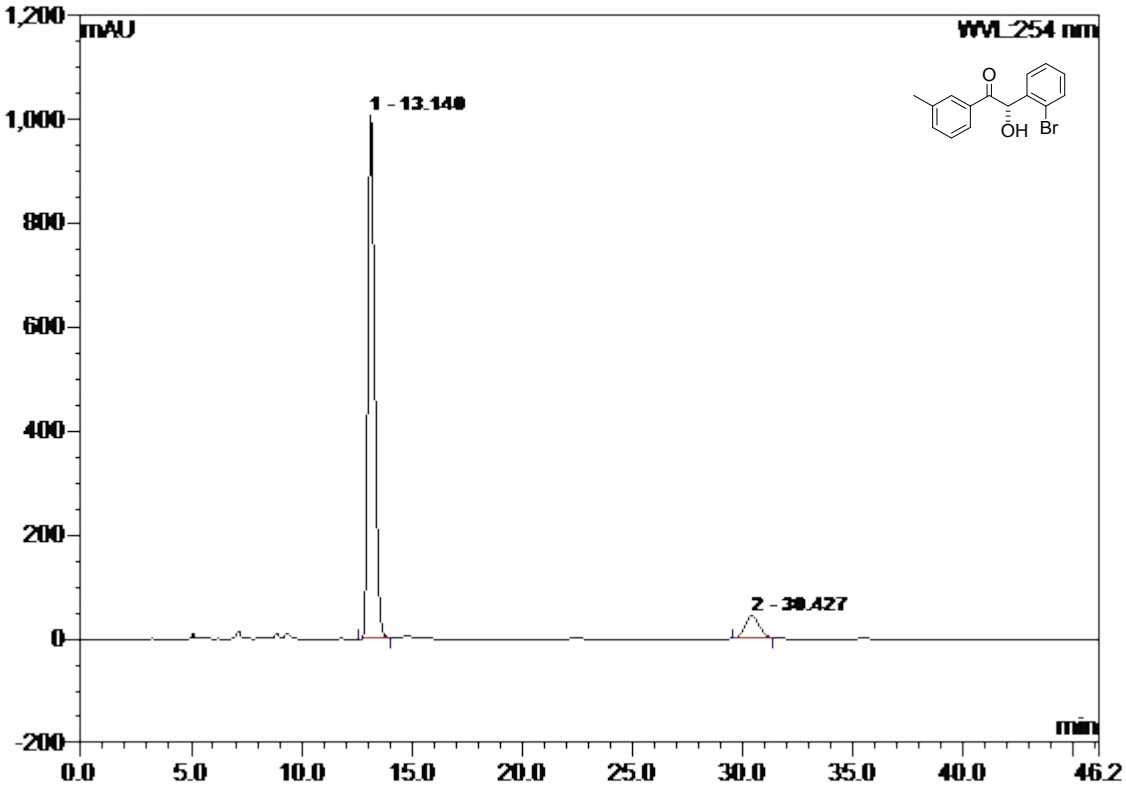
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.43	Enantiomer 1	178.904	92.798	50.52	n.a.	BMB*
2	46.04	Enantiomer 2	64.923	90.897	49.48	n.a.	BMB*
Total:			243.827	183.694	100.00	0.000	



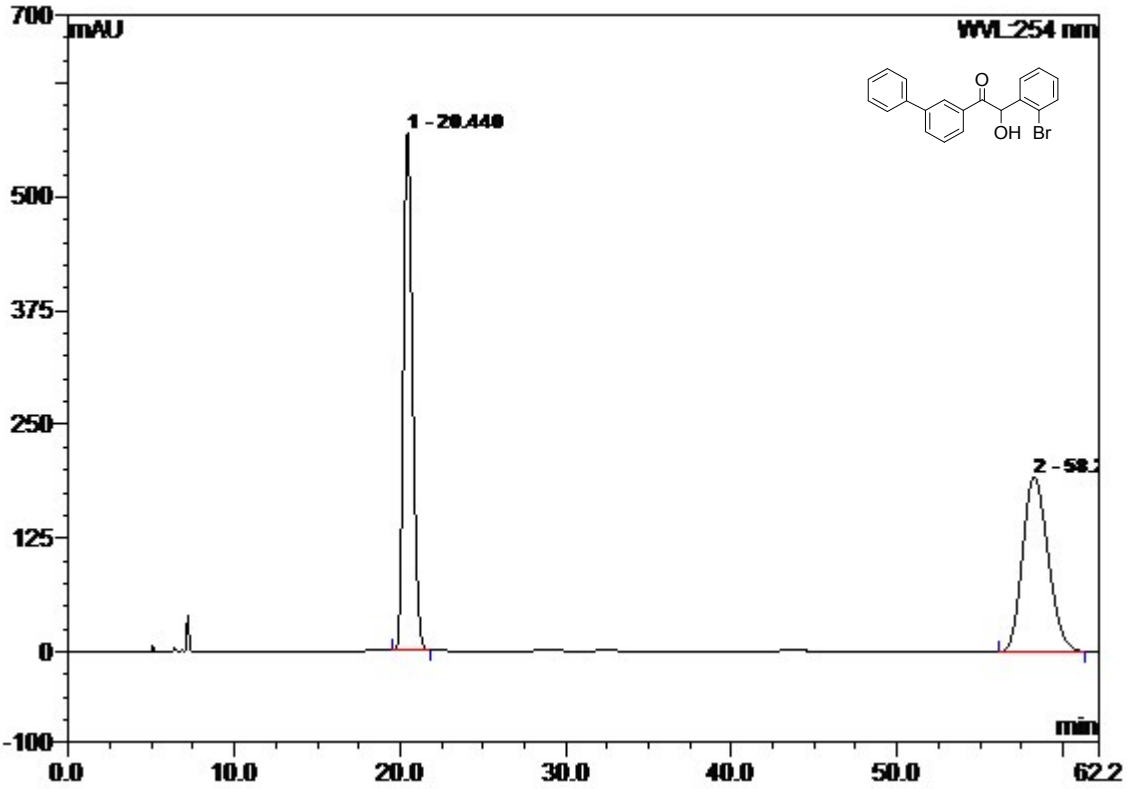
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.90	Enantiomer 1	237.631	130.274	91.89	n.a.	BMB*
2	48.30	Enantiomer 2	8.207	11.490	8.11	n.a.	BMB*
Total:			245.838	141.764	100.00	0.000	



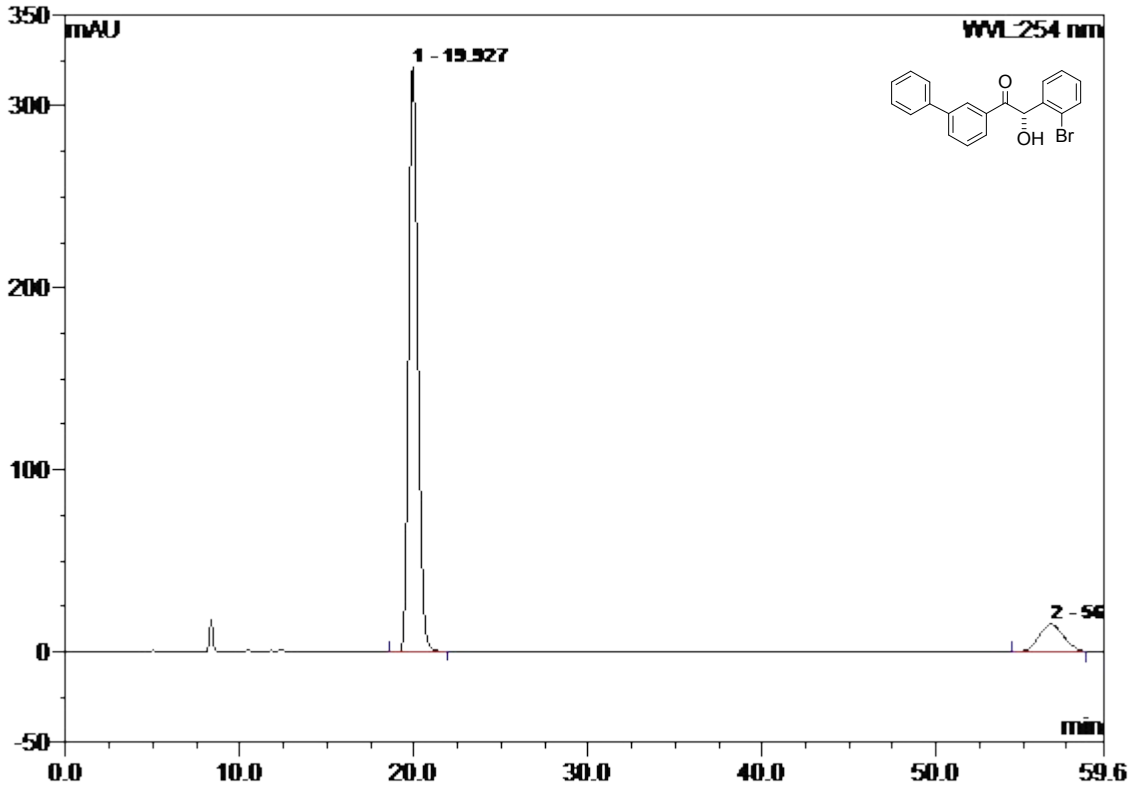
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.04	Enantiomer 1	397.206	133.979	49.77	n.a.	BMB*
2	29.98	Enantiomer 2	168.735	135.215	50.23	n.a.	BMB*
Total:			565.941	269.194	100.00	0.000	



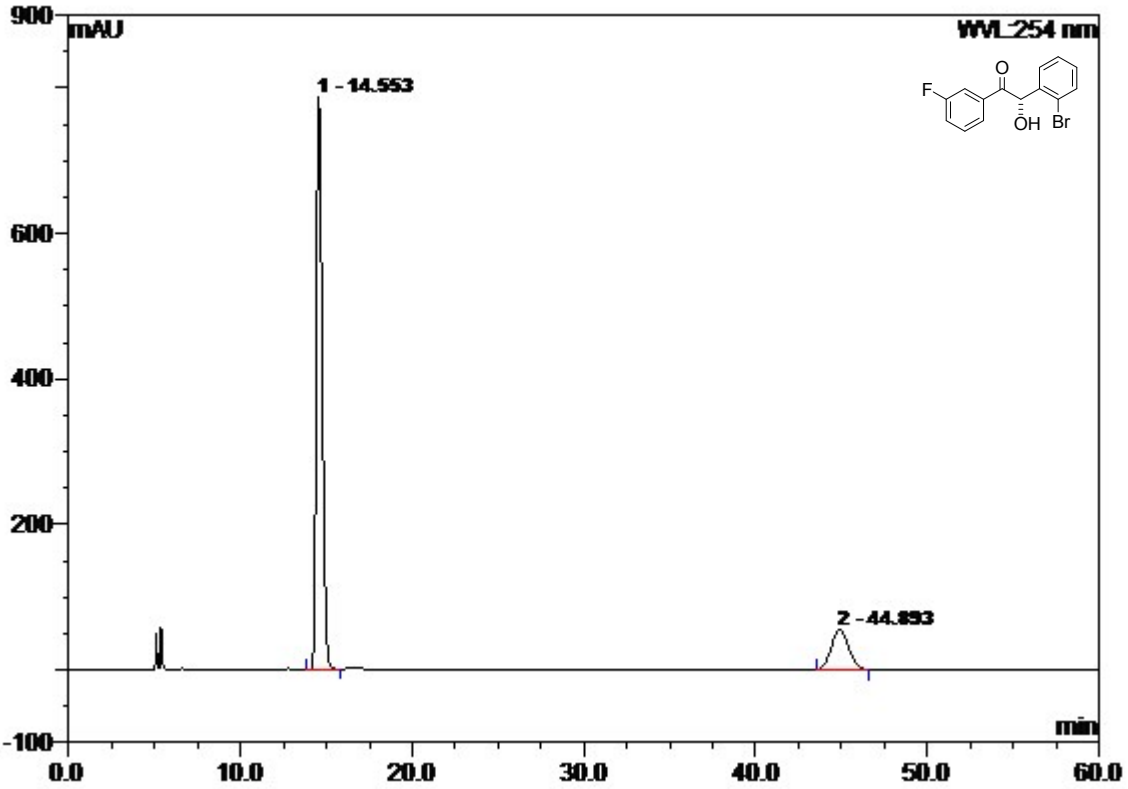
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.14	Enantiomer 1	1006.781	359.280	91.51	n.a.	BMB*
2	30.43	Enantiomer 2	42.886	33.324	8.49	n.a.	BMB*
Total:			1049.667	392.604	100.00	0.000	



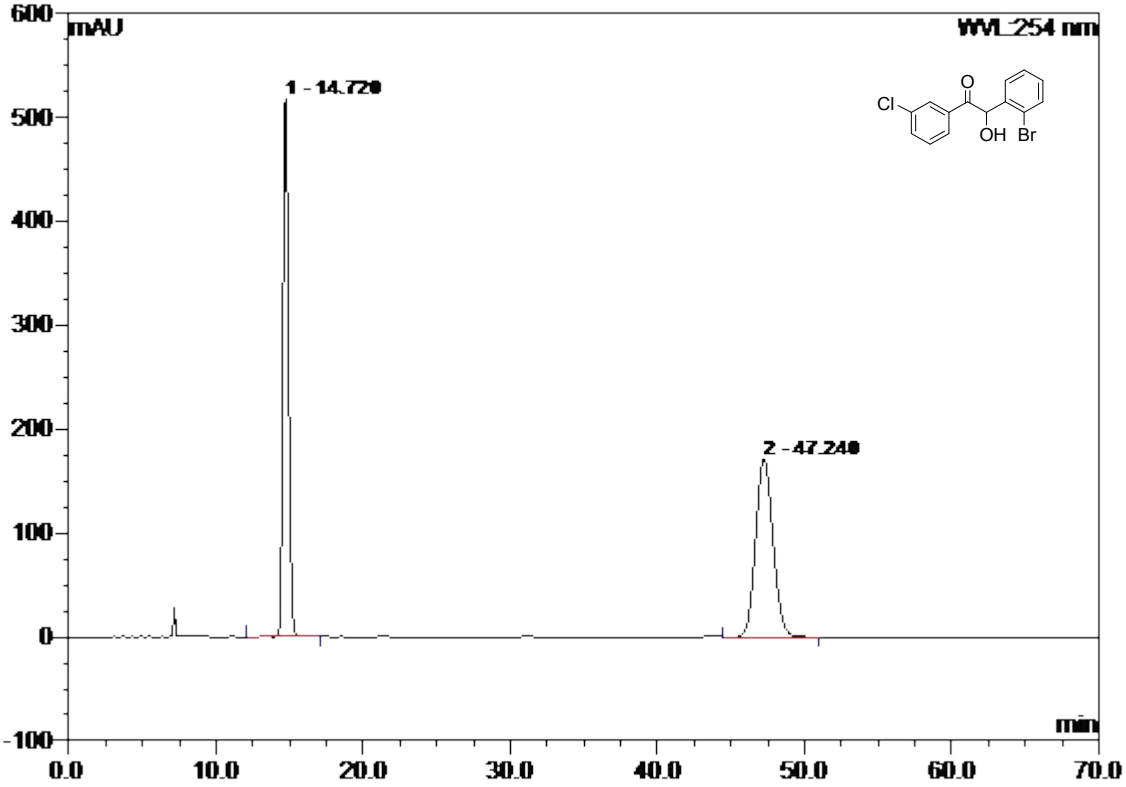
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.44	Enantiomer 1	568.749	363.773	51.40	n.a.	BMB*
2	58.27	Enantiomer 2	191.953	343.967	48.60	n.a.	BMB*
Total:			760.702	707.740	100.00	0.000	



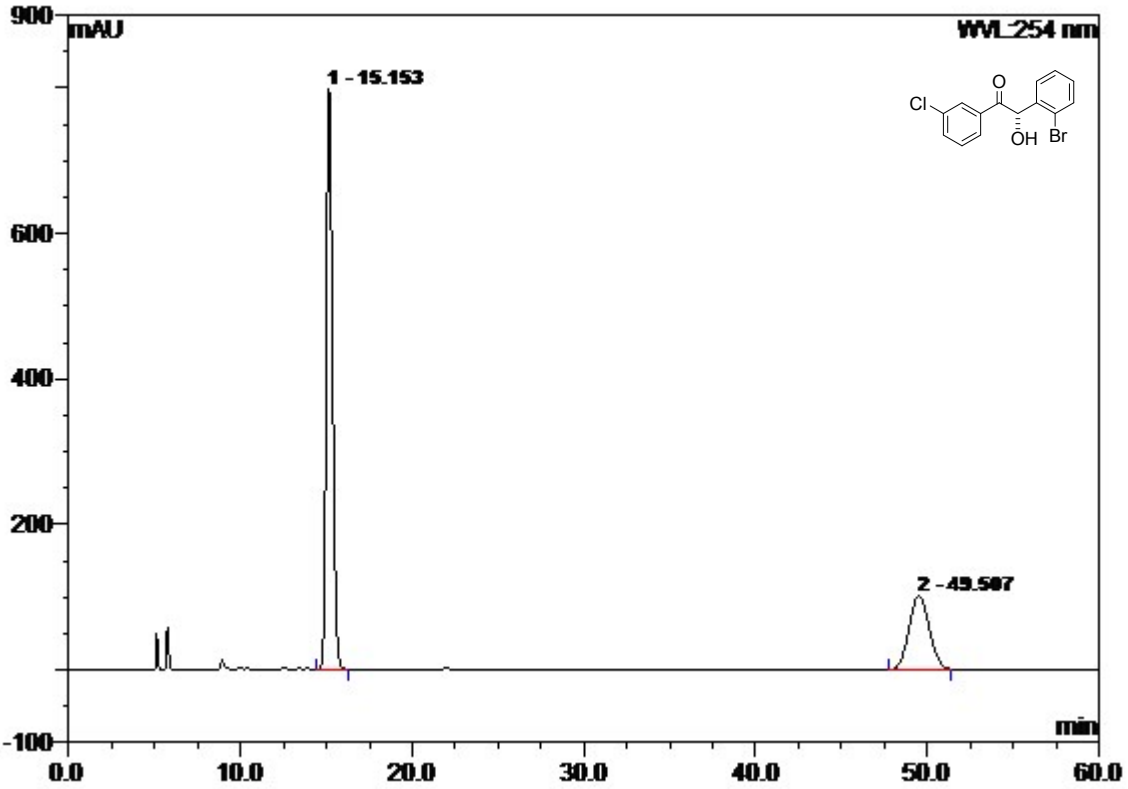
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.93	Enantiomer 1	321.220	196.321	88.68	n.a.	BMB*
2	56.59	Enantiomer 2	15.047	25.061	11.32	n.a.	BMB*
Total:			336.267	221.382	100.00	0.000	



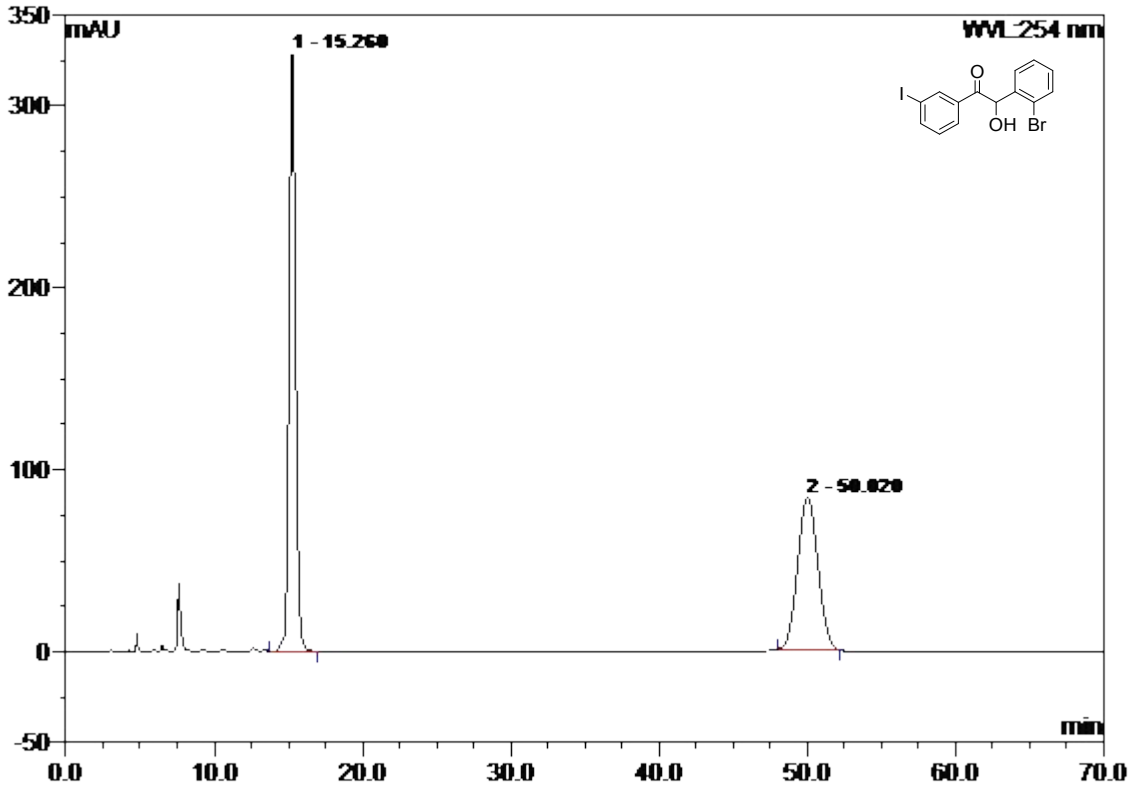
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.55	Enantiomer 1	788.302	315.424	83.05	n.a.	BMB*
2	44.89	Enantiomer 2	54.320	64.358	16.95	n.a.	BMB*
Total:			842.621	379.782	100.00	0.000	



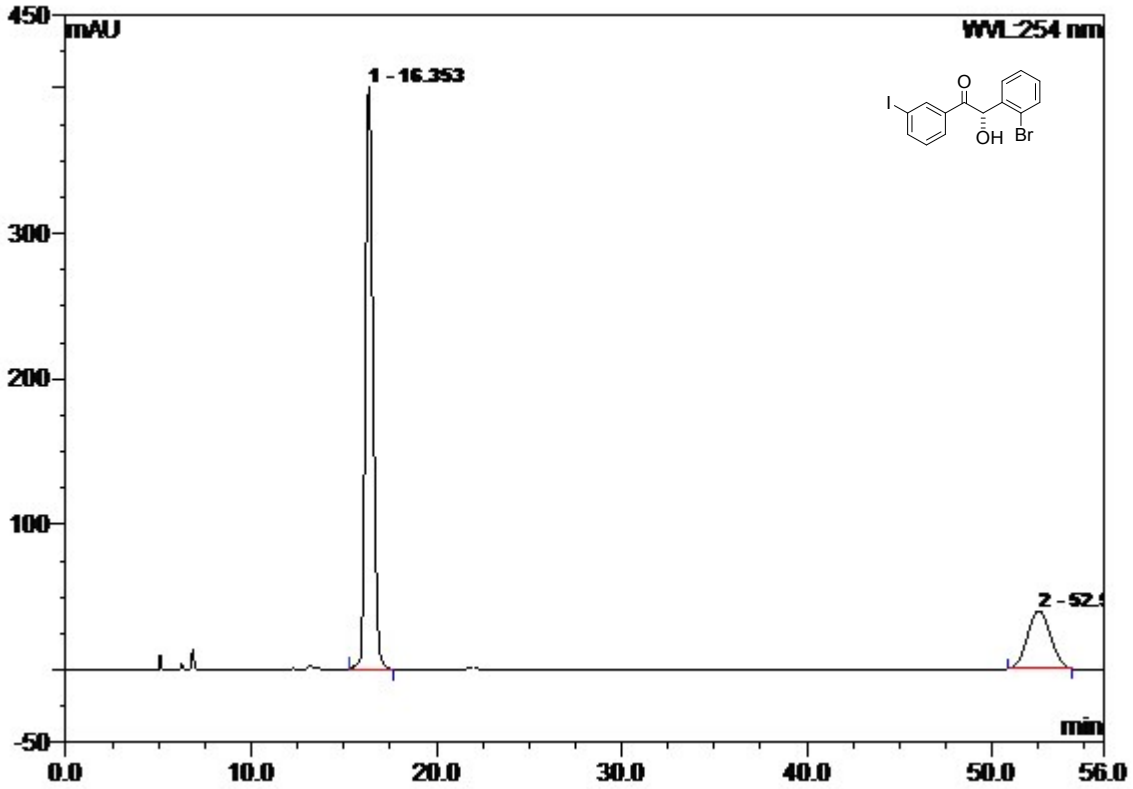
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.72	Enantiomer 1	517.586	227.314	49.35	n.a.	BMB*
2	47.24	Enantiomer 2	171.000	233.285	50.65	n.a.	BMB*
Total:			688.586	460.599	100.00	0.000	



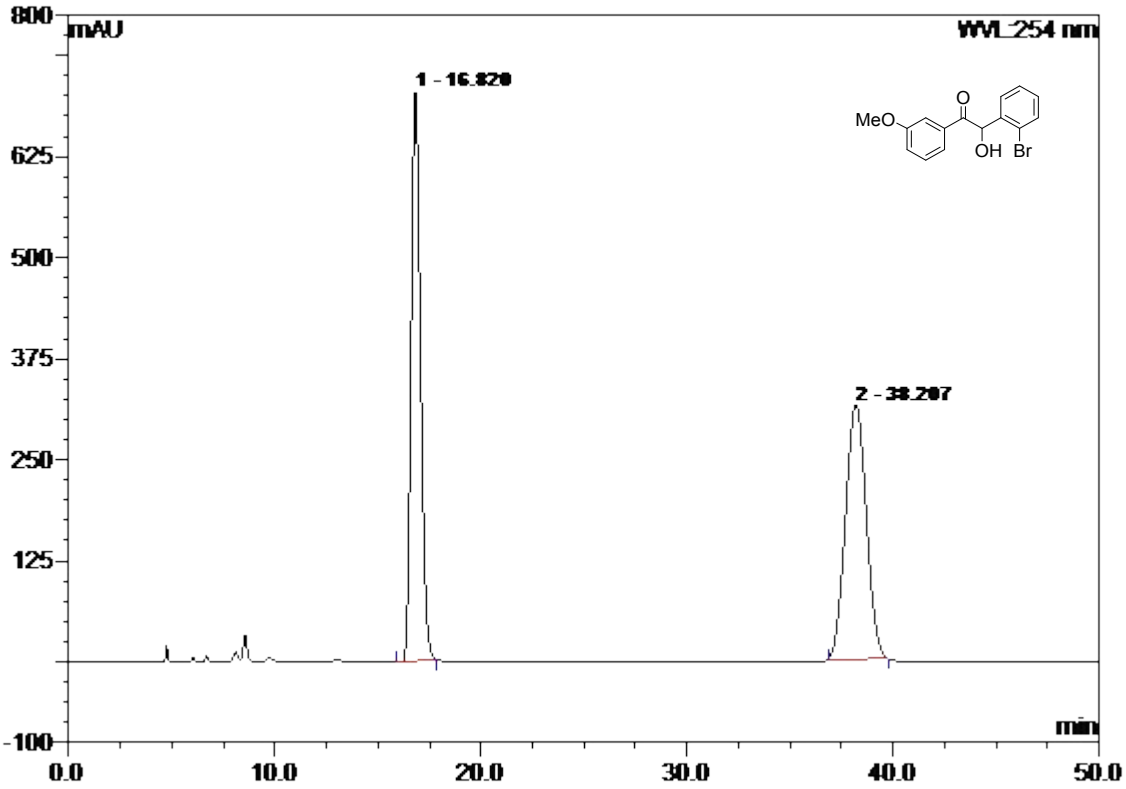
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.15	Enantiomer 1	797.777	336.670	70.74	n.a.	BMB*
2	49.51	Enantiomer 2	101.722	139.225	29.26	n.a.	BMB*
Total:			899.499	475.895	100.00	0.000	



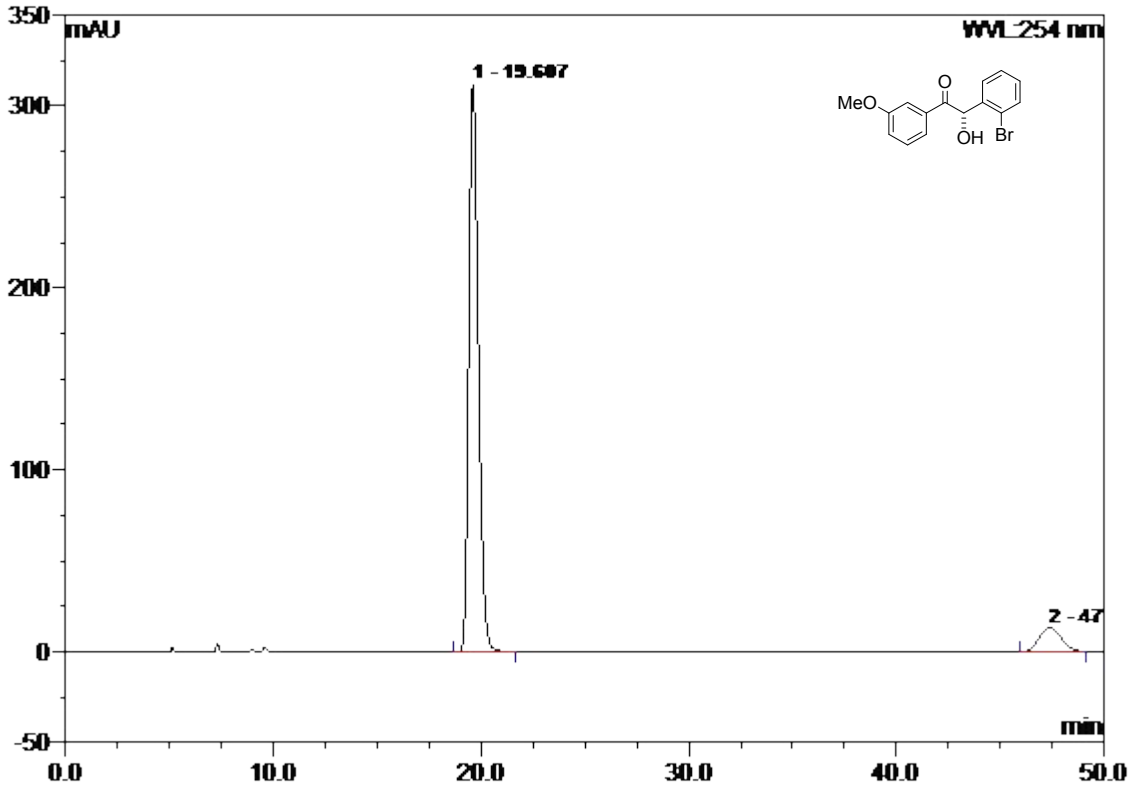
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.26	Enantiomer 1	328.386	150.780	50.07	n.a.	BMB*
2	50.02	Enantiomer 2	83.329	150.337	49.93	n.a.	BMB*
Total:			411.716	301.117	100.00	0.000	



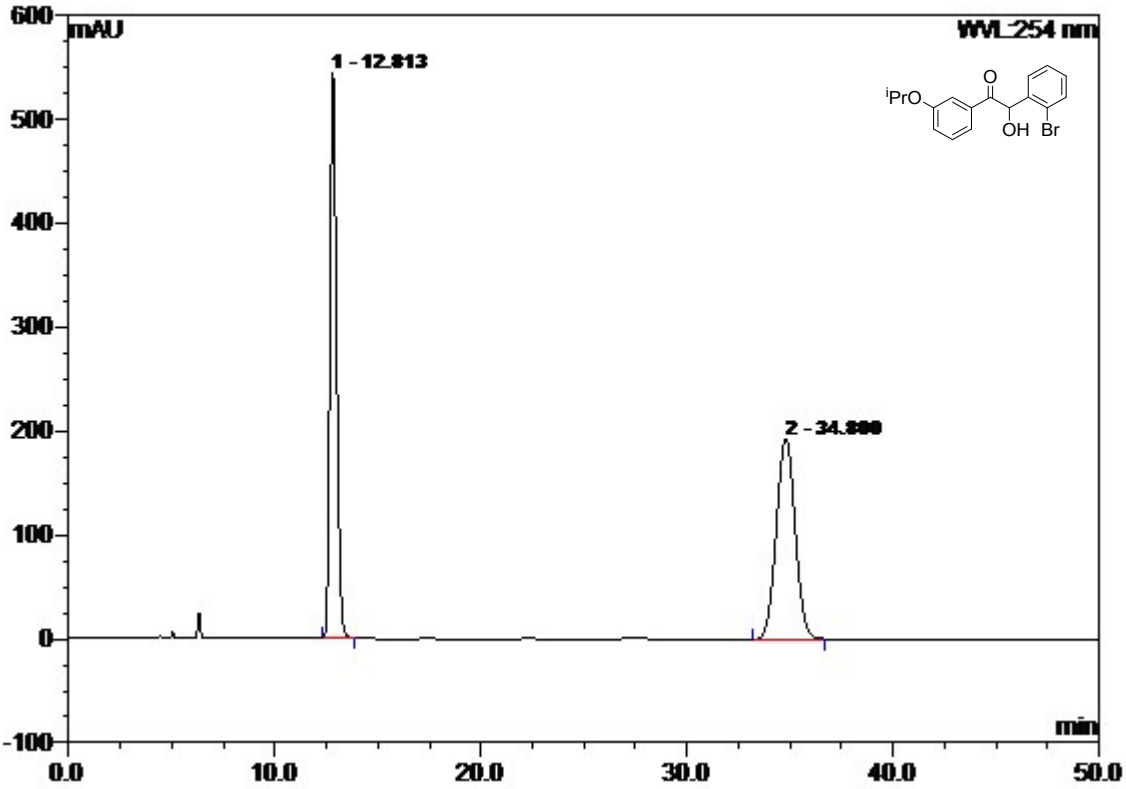
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.35	Enantiomer 1	396.703	184.203	76.11	n.a.	BMB*
2	52.52	Enantiomer 2	39.909	57.835	23.89	n.a.	BMB*
Total:			436.613	242.038	100.00	0.000	



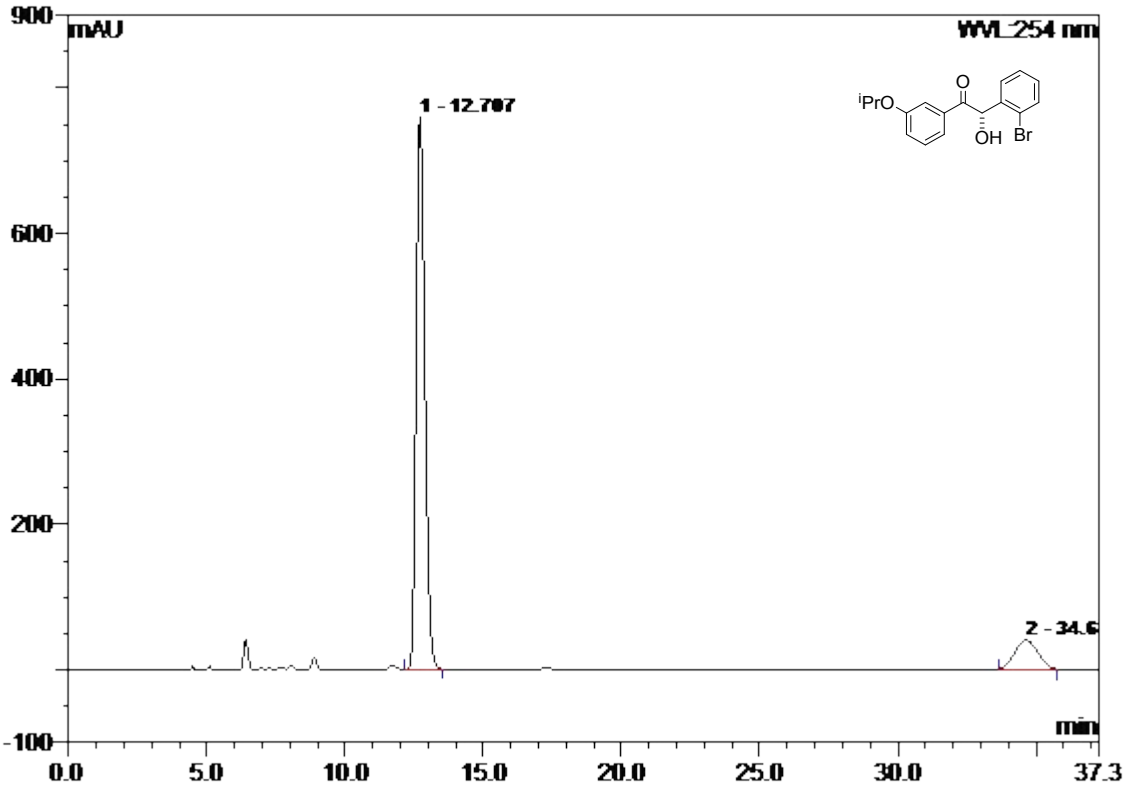
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.82	Enantiomer 1	704.129	373.650	50.38	n.a.	BMB*
2	38.21	Enantiomer 2	313.999	368.015	49.62	n.a.	BMB*
Total:			1018.128	741.665	100.00	0.000	



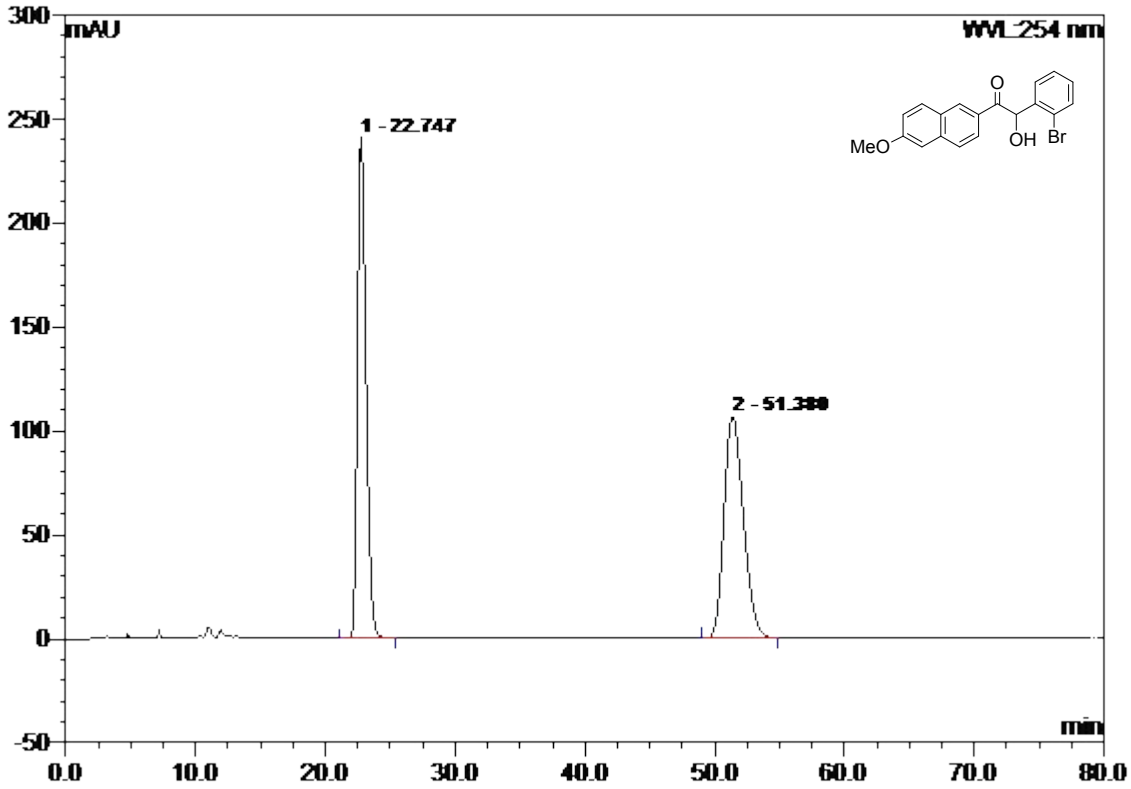
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.61	Enantiomer 1	312.329	168.281	90.89	n.a.	BMB*
2	47.39	Enantiomer 2	13.283	16.859	9.11	n.a.	BMB*
Total:			325.612	185.140	100.00	0.000	



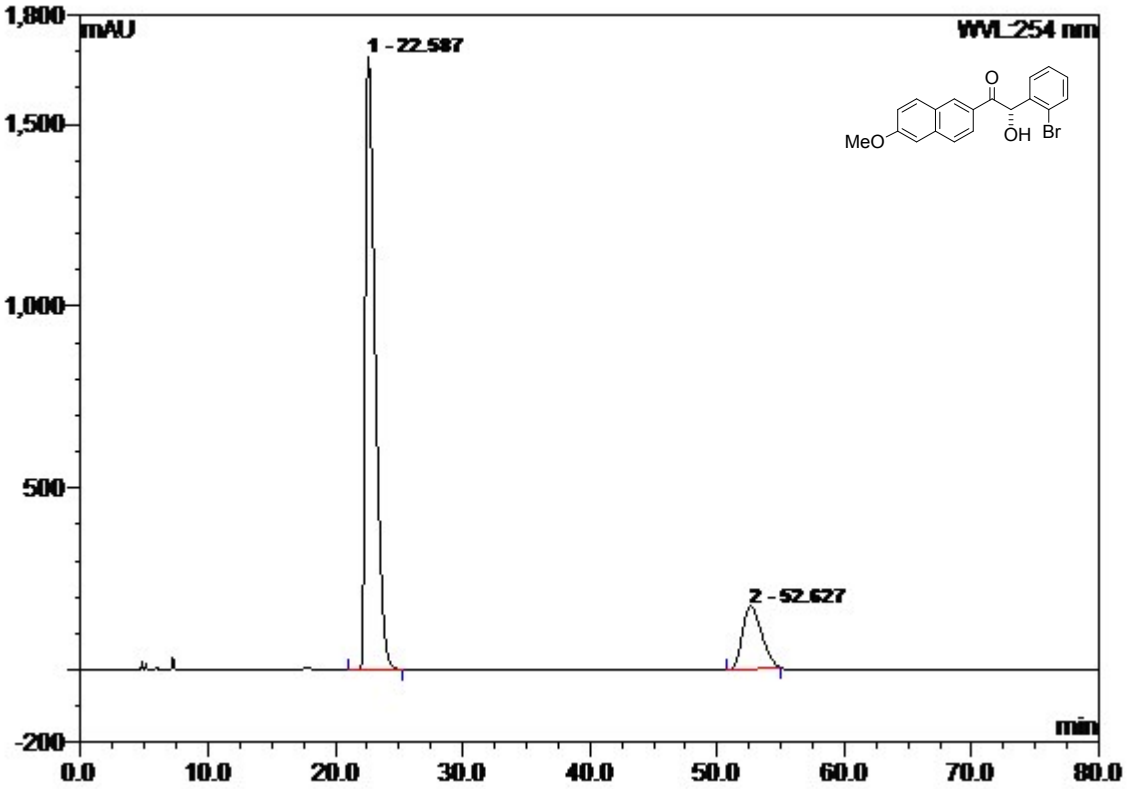
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.81	Enantiomer 1	542.668	202.005	49.72	n.a.	BMB*
2	34.80	Enantiomer 2	192.900	204.309	50.28	n.a.	BMB*
Total:			735.568	406.315	100.00	0.000	



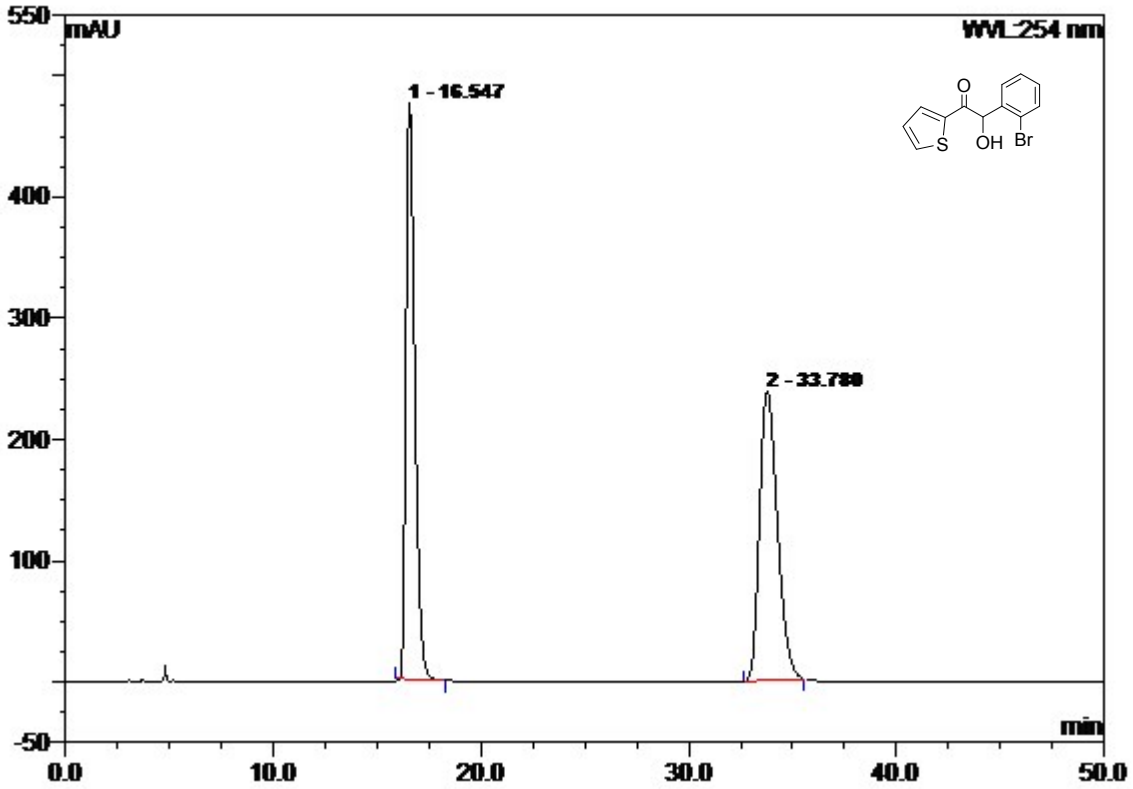
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.71	Enantiomer 1	759.845	277.649	87.90	n.a.	BMB*
2	34.64	Enantiomer 2	39.582	38.235	12.10	n.a.	BMB*
Total:			799.426	315.884	100.00	0.000	



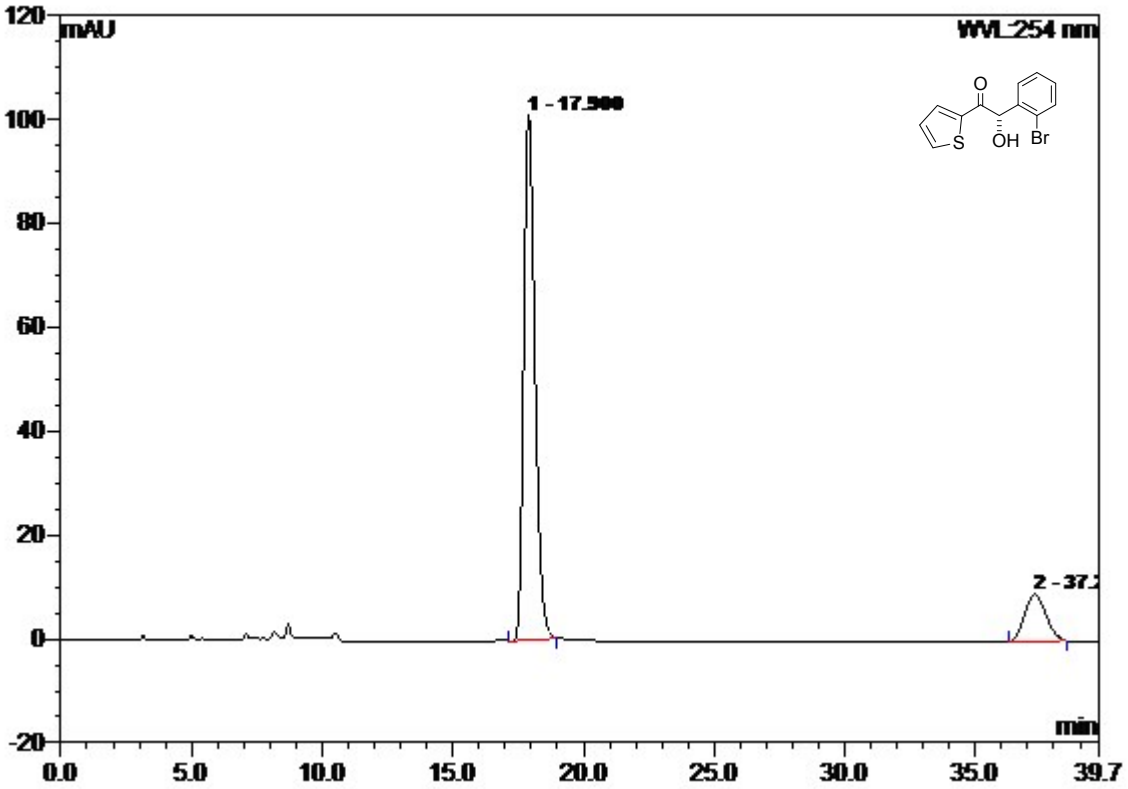
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.75	Enantiomer 1	240.729	185.198	49.99	n.a.	BMB*
2	51.38	Enantiomer 2	107.060	185.257	50.01	n.a.	BMB*
Total:			347.789	370.456	100.00	0.000	



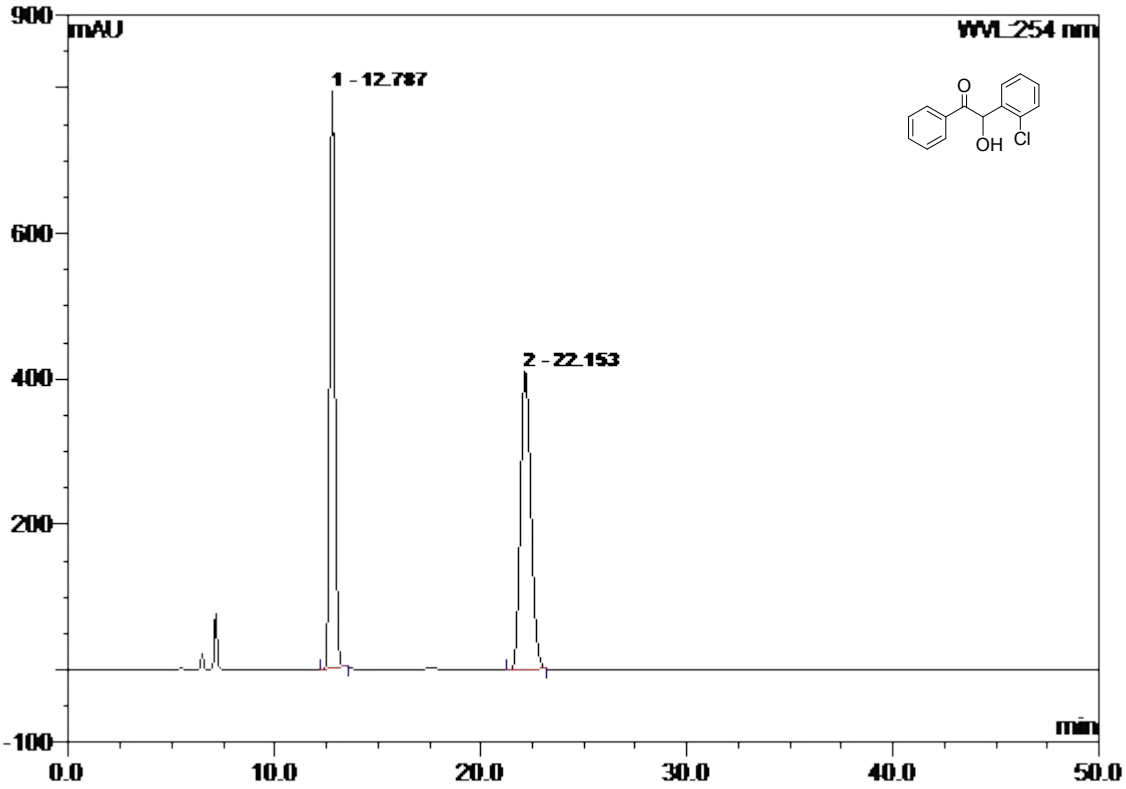
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.59	Enantiomer 1	1684.957	1513.178	83.32	n.a.	BMB*
2	52.63	Enantiomer 2	171.662	302.835	16.68	n.a.	BMB*
Total:			1856.620	1816.012	100.00	0.000	



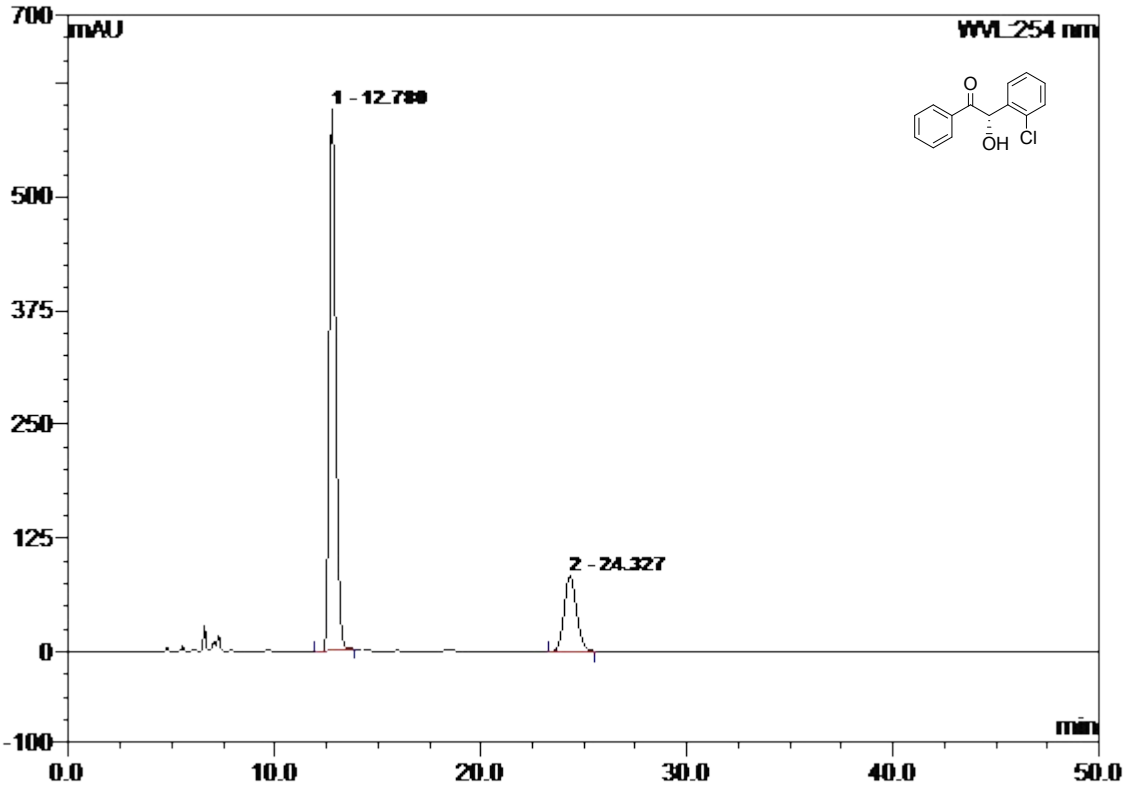
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.55	Enantiomer 1	475.198	236.512	49.86	n.a.	BMB*
2	33.78	Enantiomer 2	238.872	237.794	50.14	n.a.	BMB*
Total:			714.069	474.305	100.00	0.000	



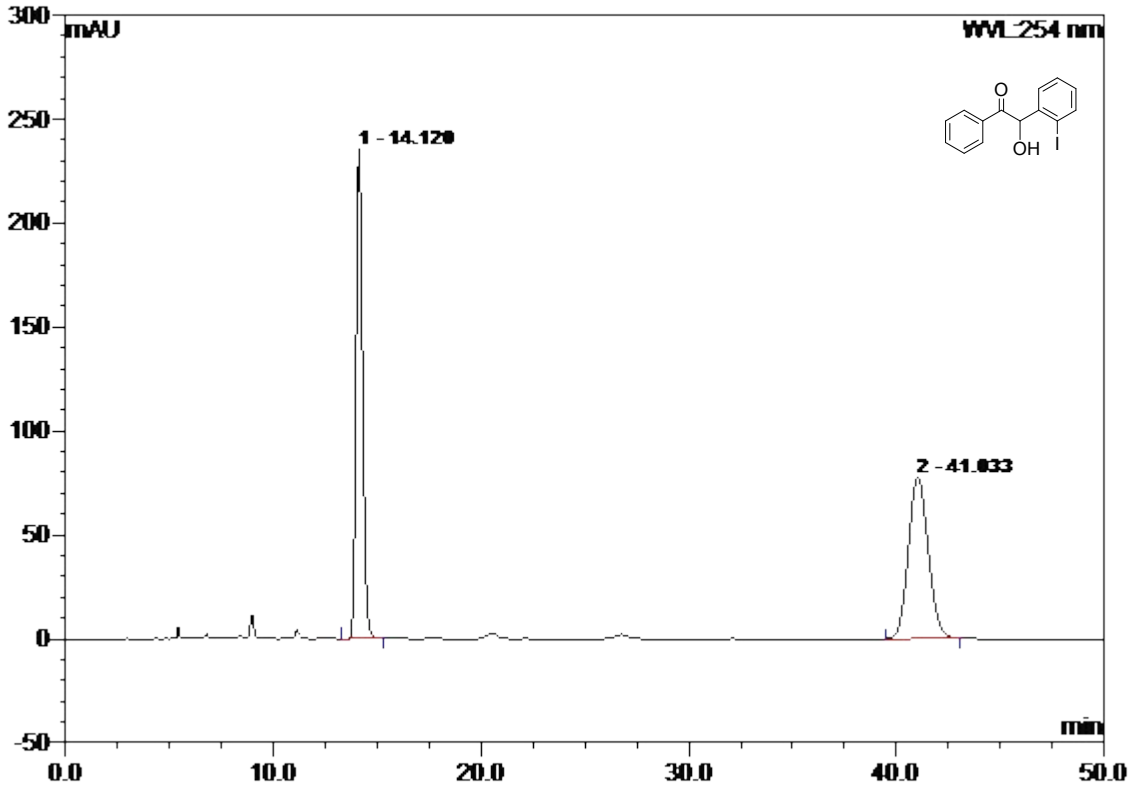
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.90	Enantiomer 1	100.991	50.152	85.37	n.a.	BMB*
2	37.27	Enantiomer 2	9.011	8.596	14.63	n.a.	BMB*
Total:			110.002	58.748	100.00	0.000	



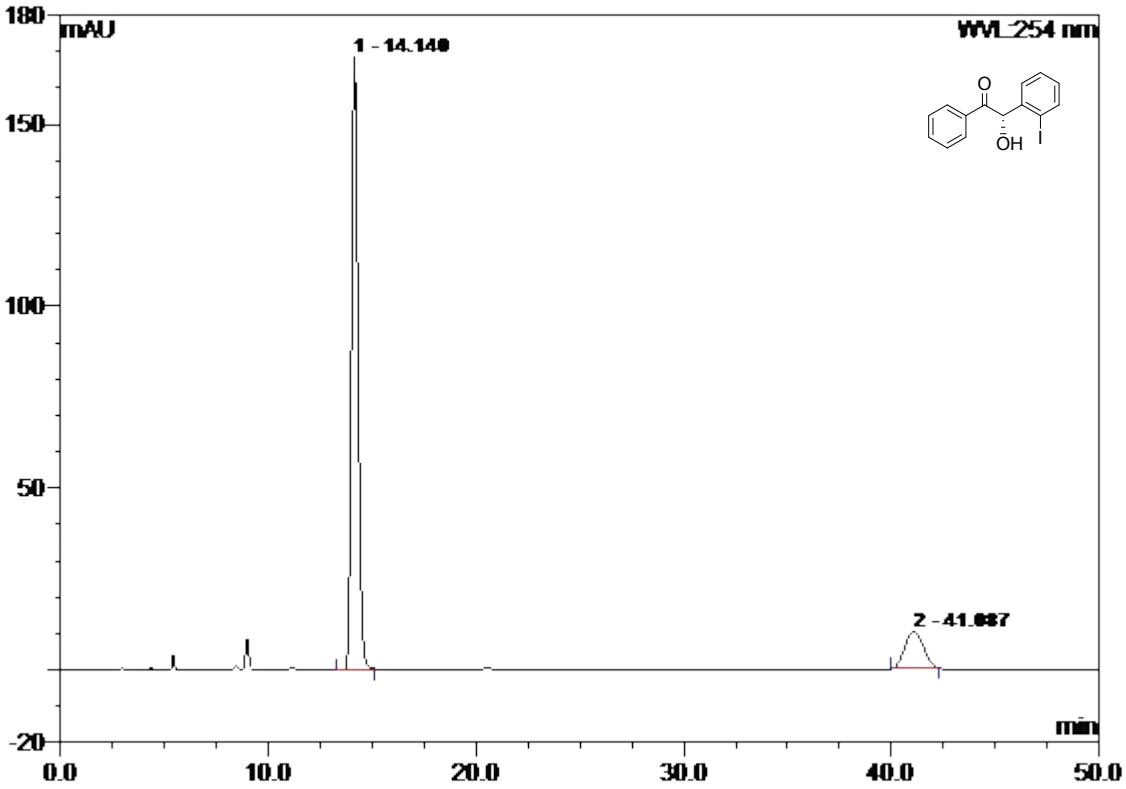
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.79	*S*-enantiomer	793.490	236.600	49.38	n.a.	BMB*
2	22.15	*R*-enantiomer	409.227	242.499	50.62	n.a.	BMB*
Total:			1202.718	479.099	100.00	0.000	



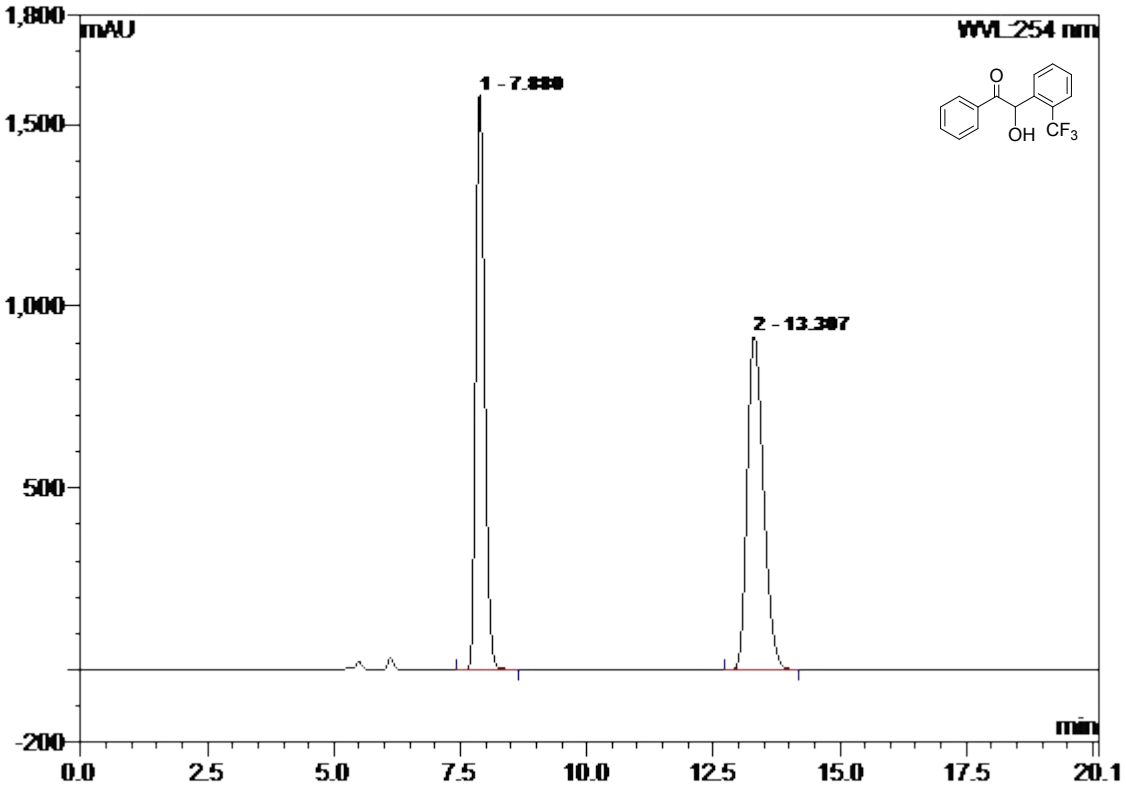
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.78	*S*-enantiomer	595.633	220.923	79.24	n.a.	BMB*
2	24.33	*R*-enantiomer	83.432	57.897	20.76	n.a.	BMB*
Total:			679.065	278.820	100.00	0.000	



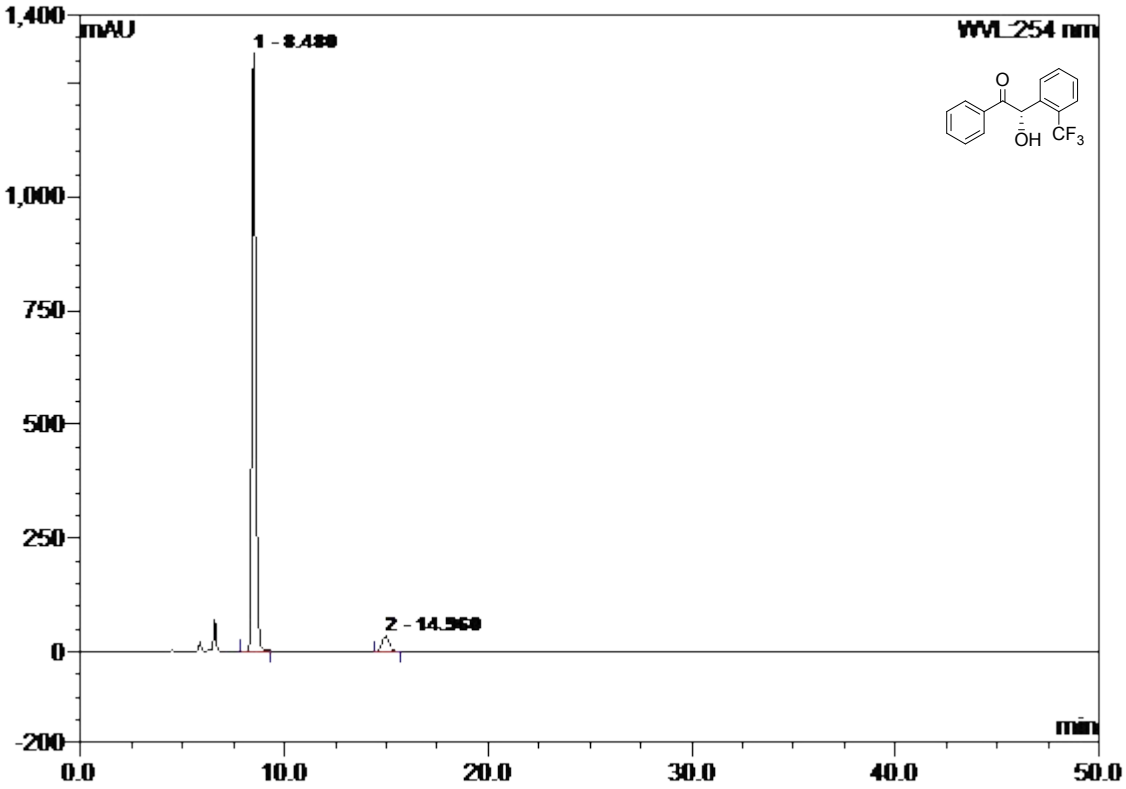
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.12	*S*-enantiomer	235.351	86.060	49.90	n.a.	BMB*
2	41.03	*R*-enantiomer	77.822	86.390	50.10	n.a.	BMB*
Total:			313.172	172.450	100.00	0.000	



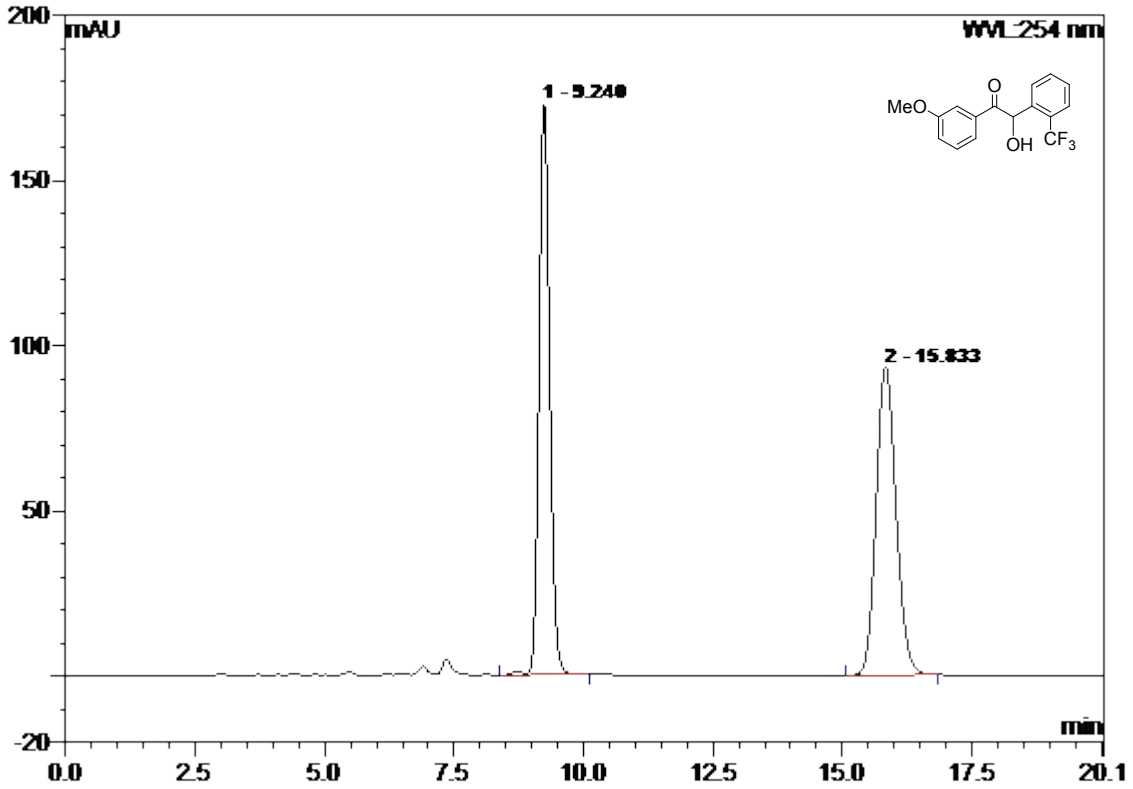
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.14	*S*-enantiomer	168.566	61.216	85.12	n.a.	BMB*
2	41.09	*R*-enantiomer	10.261	10.700	14.88	n.a.	BMB*
Total:			178.827	71.917	100.00	0.000	



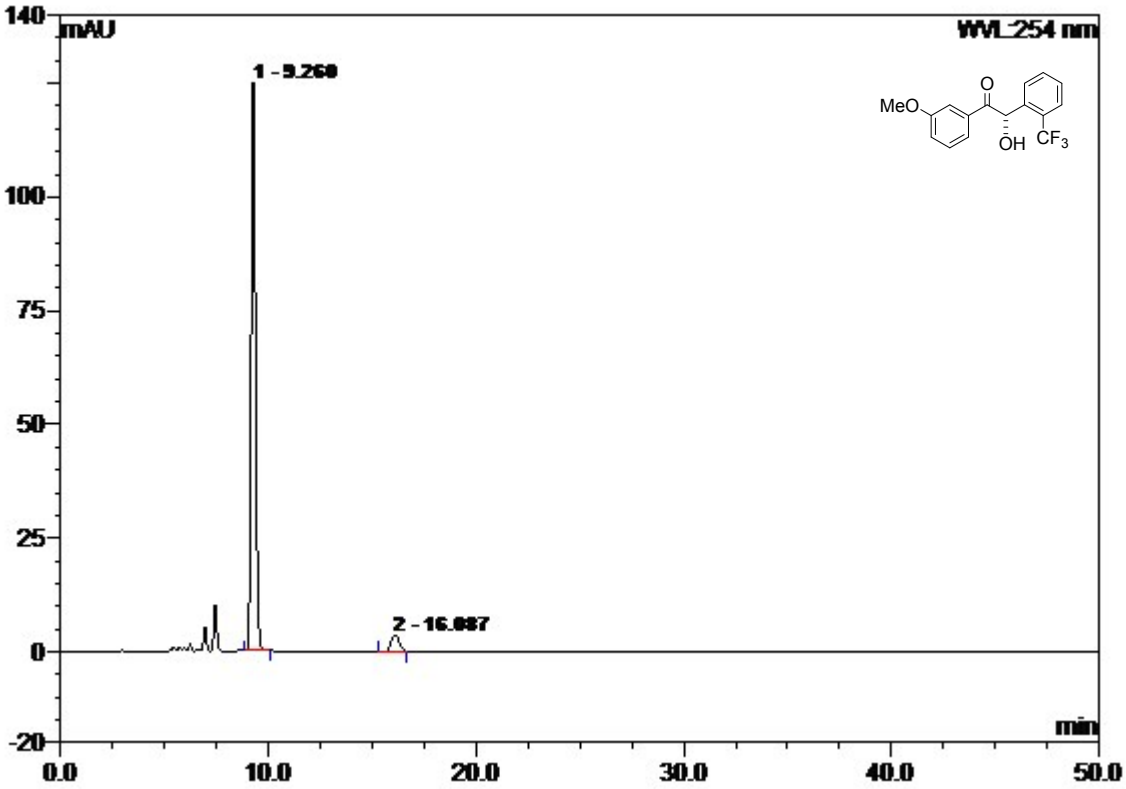
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.88	Enantiomer 1	1581.174	323.235	48.50	n.a.	BMB*
2	13.31	Enantiomer 2	917.204	343.284	51.50	n.a.	BMB*
Total:			2498.378	666.519	100.00	0.000	



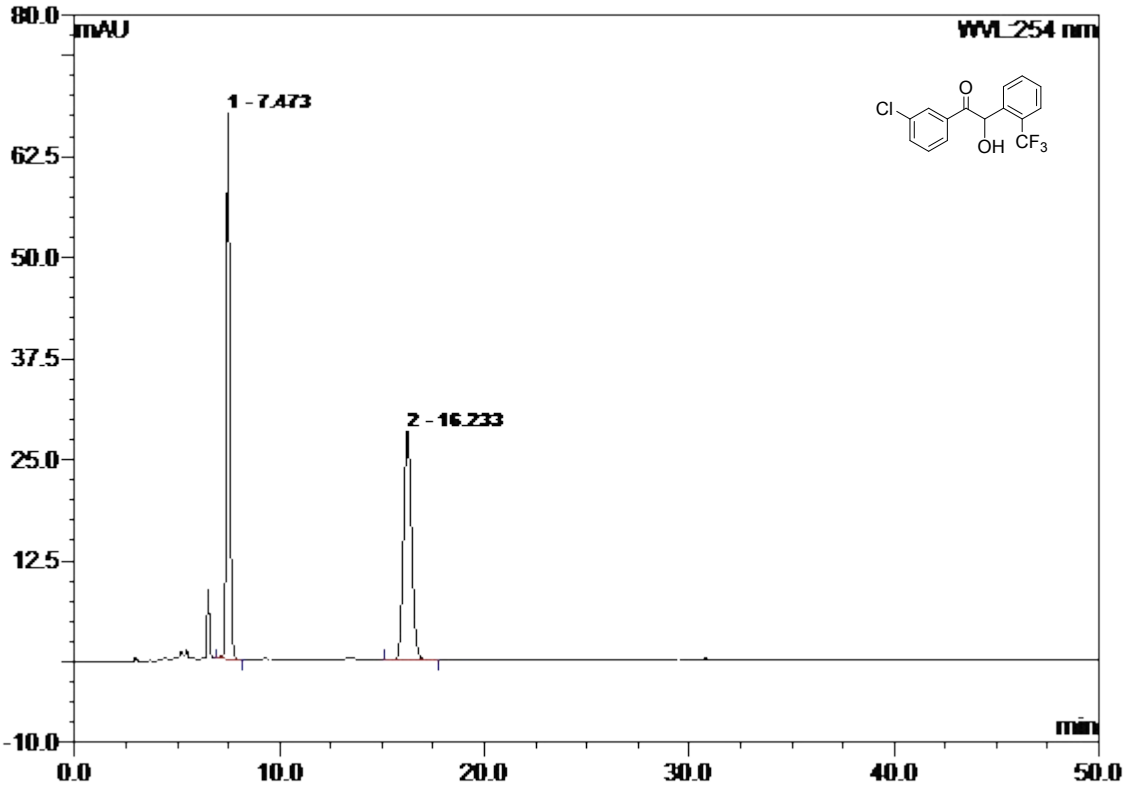
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.48	Enantiomer 1	1316.225	289.638	96.02	n.a.	BMB*
2	14.96	Enantiomer 2	33.120	12.951	3.98	n.a.	BMB*
Total:			1349.345	301.643	100.00	0.000	



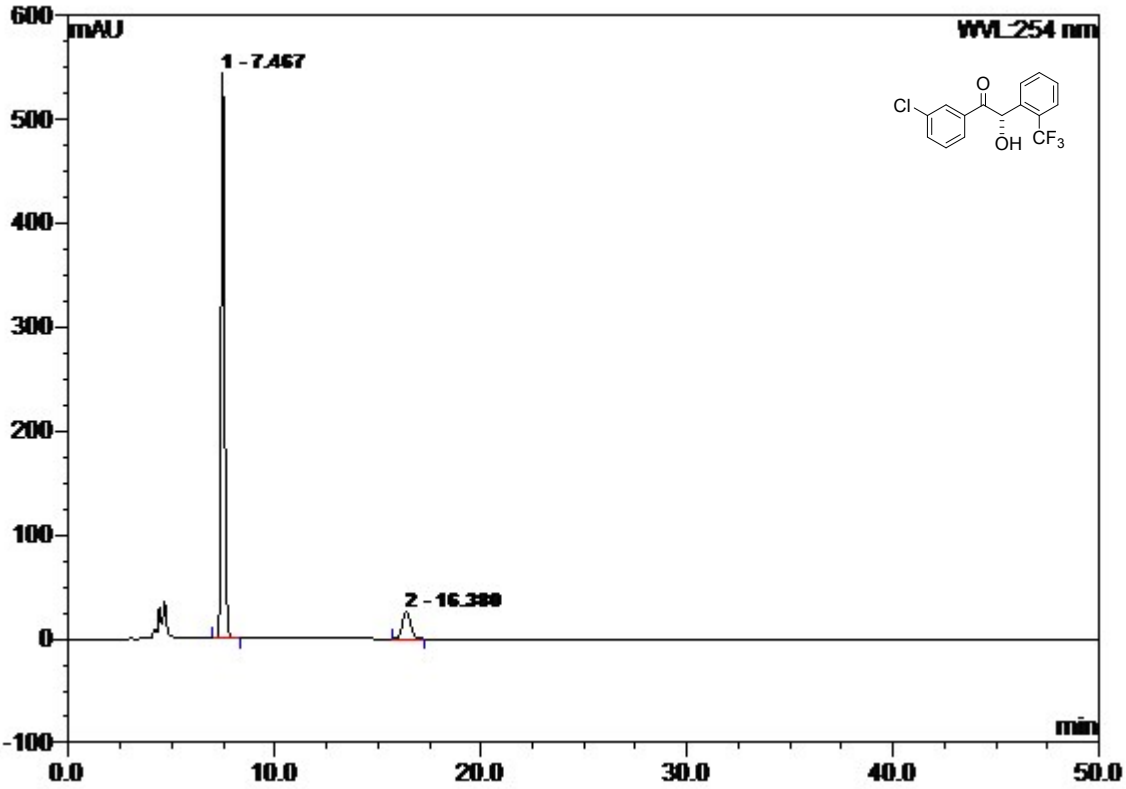
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.24	Enantiomer 1	172.568	41.535	50.01	n.a.	BMB*
2	15.83	Enantiomer 2	93.283	41.527	49.99	n.a.	BMB*
Total:			265.851	83.062	100.00	0.000	



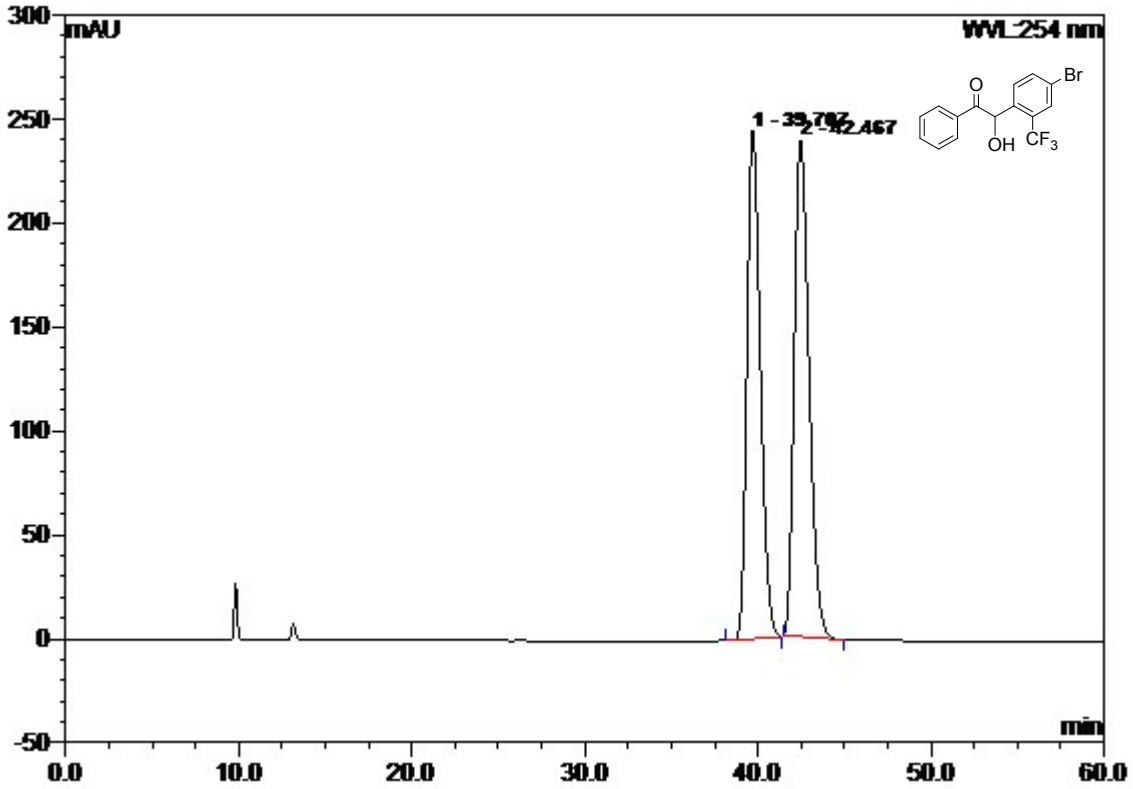
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.26	Enantiomer 1	124.983	29.845	94.83	n.a.	BMB*
2	16.09	Enantiomer 2	3.726	1.626	5.17	n.a.	BMB*
Total:			128.709	31.471	100.00	0.000	



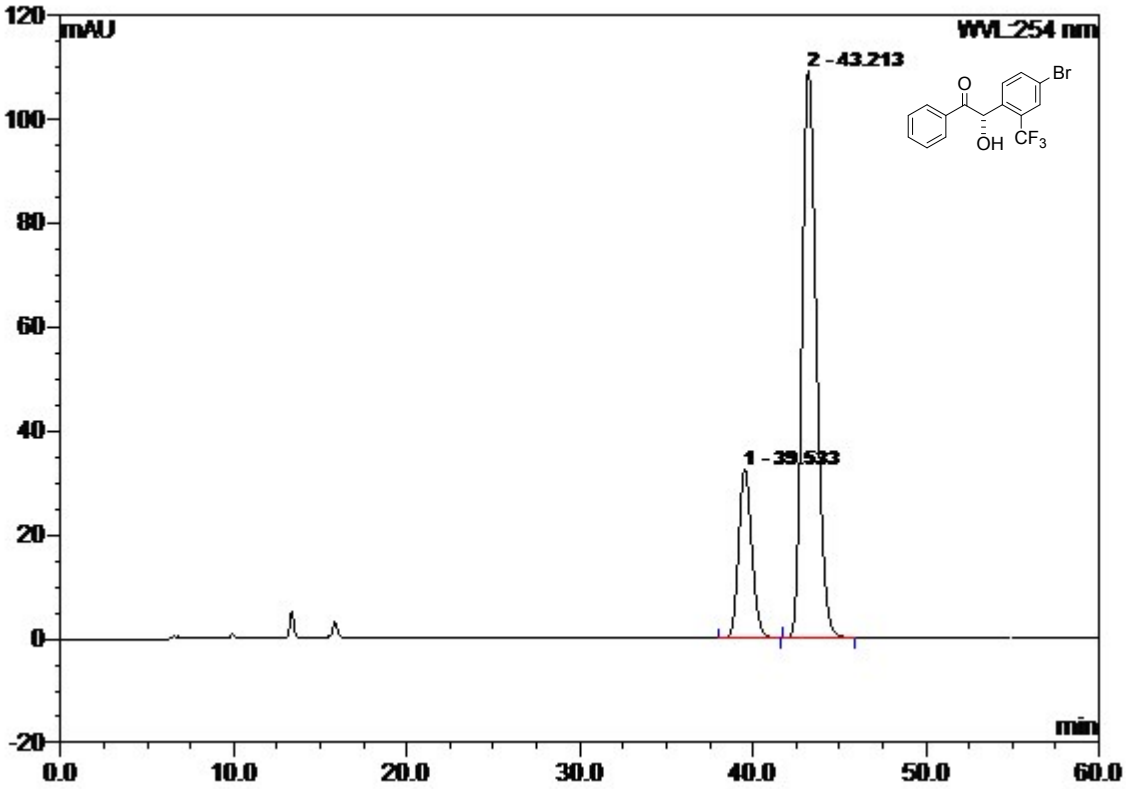
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.47	Enantiomer 1	67.512	13.089	50.16	n.a.	BMB*
2	16.23	Enantiomer 2	28.275	13.006	49.84	n.a.	BMB*
Total:			95.787	26.095	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.47	Enantiomer 1	543.422	105.119	89.76	n.a.	BMB*
2	16.38	Enantiomer 2	26.008	11.988	10.24	n.a.	BMB*
Total:			569.430	117.106	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	39.71	Enantiomer 1	244.481	218.882	48.11	n.a.	BMB*
2	42.47	Enantiomer 2	238.894	236.049	51.89	n.a.	BMB*
Total:			483.375	454.932	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	39.53	Enantiomer 1	32.635	29.047	21.68	n.a.	BM *
2	43.21	Enantiomer 2	109.183	104.934	78.32	n.a.	BMB*
Total:			141.817	133.981	100.00	0.000	