Aminative Umpolung Cyclization for Synthesis of Chiral Exocyclic Vicinal Diamines

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Supporting Information

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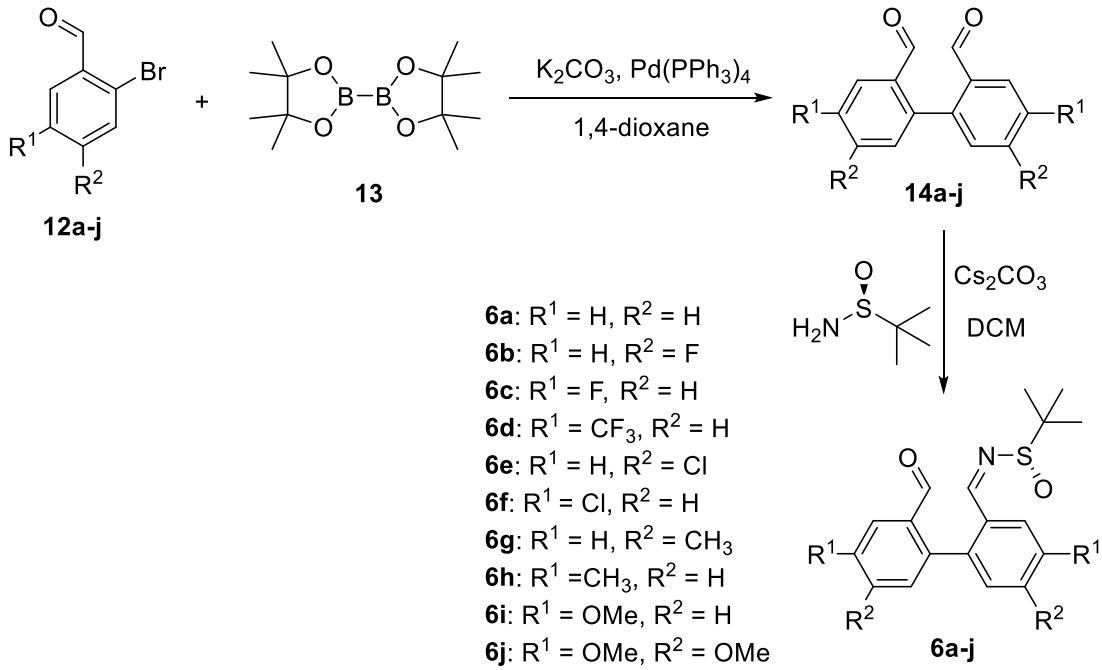
General Methods

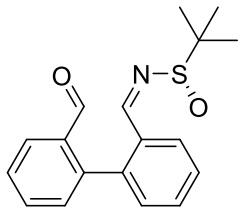
All commercially available reagents were used without further purification unless otherwise stated. Dichloromethane was freshly distilled from CaH_2. Column chromatography was performed on silica gel (200-300 mesh). ^1H NMR spectra were recorded on a 400 or 600 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. ^1H shifts were referenced to $CDCl_3$ at 7.26 ppm, ^{13}C shifts were referenced to $CDCl_3$ at 77.16 ppm. IR spectra were recorded on a FT-IR spectrometer.

General Procedure for the Synthesis of Compounds 6a-j (Tables 1 and 2)



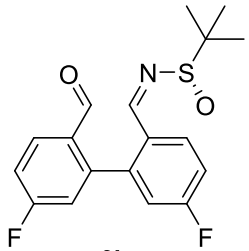
A mixture of 2-bromobenzaldehyde **12** (10 mmol), bis(pinacolato)diboron **13** (1.32 g, 5.2 mmol), K_2CO_3 (2.07 g, 15 mmol), and $Pd(PPh_3)_4$ (0.347 g, 0.30 mmol) in 1,4-dioxane (25 mL) was stirred under N_2 atmosphere at room temperature for 20 min and then at 80 ^oC for 24 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure to remove most of the solvent. Water (15 mL)

was added. The resulting suspend was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash column chromatography (petroleum ether / ethyl acetate = 30:1) to give the coupling product **14** (32-86% yield). To a solution of dialdehyde **14** (5.0 mmol) in anhydrous DCM (12 mL) was added (*S*)-*tert*-butylsulfinamide (0.61 g, 5.0 mmol) and Cs_2CO_3 (2.45 g, 7.5 mmol). The reaction mixture was stirred at 50 ^oC for 12 h. Then the reaction mixture was cooled to room temperature, filtered, concentrated under reduced pressure, and purified by flash column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product **6** (29-90% yield based on **14**).



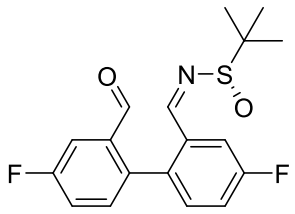
6a

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1 H), 8.40 (s, 0.45 H for minor isomer), 8.38 (s, 0.55 H for major isomer), 8.16-8.10 (m, 1 H), 8.03 (d, *J* = 7.6 Hz, 1 H), 7.64 (t, *J* = 7.2 Hz, 1 H), 7.60-7.50 (m, 3 H), 7.36-7.27 (m, 2 H), 1.17 (s, 4.1 H for minor isomer), 1.11 (s, 4.9 H for major isomer).



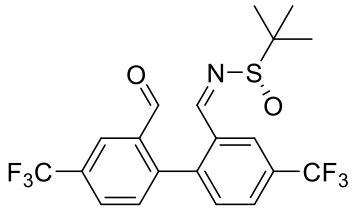
6b

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 0.44 H for minor isomer), 9.70 (s, 0.56 H for major isomer), 8.294 (s, 0.44 H for minor isomer), 8.285 (s, 0.56 H for major isomer), 8.16-8.10 (m, 1 H), 8.09-8.02 (m, 1 H), 7.33-7.24 (m, 2 H), 7.08-6.95 (m, 2 H), 1.15 (s, 4.0 H for minor isomer), 1.10 (s, 5.0 H for major isomer); HRMS *m/z* Calcd. For $C_{18}H_{17}F_2NO_2SNa$ ($M + Na^+$): 372.0846; Found: 372.0842.



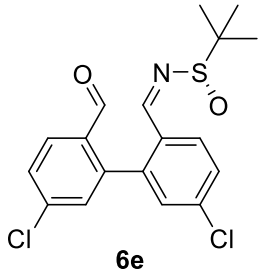
6c

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (d, *J* = 2.8 Hz, 0.44 H for minor isomer), 9.70 (d, *J* = 2.8 Hz, 0.56 H for major isomer), 8.31 (d, *J* = 2.0 Hz, 0.44 H for minor isomer), 8.29 (d, *J* = 2.0 Hz, 0.56 H for major isomer), 7.86-7.84 (m, 0.44 H for minor isomer), 7.83-7.82 (m, 0.56 H for major isomer), 7.72 (t, *J* = 2.4 Hz, 0.44 H for minor isomer), 7.70 (t, *J* = 2.4 Hz, 0.56 H for major isomer), 7.39-7.32 (m, 1 H), 7.32-7.27 (m, 3 H), 1.20 (s, 4.0 H for minor isomer), 1.15 (s, 5.0 H for major isomer); HRMS *m/z* Calcd. For $C_{18}H_{18}F_2NO_2S$ ($M + H^+$): 350.1026; Found: 350.1019.



6d

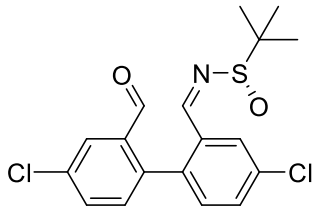
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1 H), 8.39 (s, 0.42 H for minor isomer), 8.38 (s, 0.42 H for minor isomer), 8.37 (s, 0.58 H for major isomer), 8.36 (s, 0.58 H for major isomer), 8.31 (s, 0.42 H for minor isomer), 8.30 (s, 0.58 H for major isomer), 7.96-7.90 (m, 1 H), 7.88-7.82 (m, 1 H), 7.48-7.45 (m, 2 H), 1.16 (s, 3.8 H for minor isomer), 1.09 (s, 5.2 H for major isomer); HRMS *m/z* Calcd. For $C_{20}H_{18}F_6NO_2S$ ($M + H^+$): 450.0962; Found: 450.0962.



6e

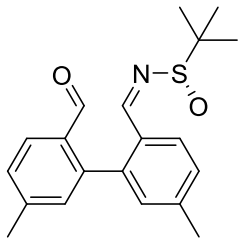
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 0.42 H for minor isomer), 9.71 (s, 0.58 H for major isomer), 8.29 (s, 1 H), 8.03 (d, *J* = 8.4 Hz, 0.42 H for minor isomer),

8.02 (d, *J* = 8.4 Hz, 0.58 H for major isomer), 7.96 (d, *J* = 8.4 Hz, 0.42 H for minor isomer), 7.95 (d, *J* = 8.4 Hz, 0.58 H for major isomer), 7.56-7.55 (m, 1 H), 7.54-7.53 (m, 1 H), 7.32 (d, *J* = 2.0 Hz, 1 H), 7.30 (d, *J* = 2.0 Hz, 0.58 H for major isomer), 7.28 (d, *J* = 2.0 Hz, 0.42 H for minor isomer), 1.15 (s, 3.8 H for minor isomer), 1.08 (s, 5.2 H for major isomer); HRMS *m/z* Calcd. for $C_{18}H_{18}Cl_2NO_2S$ ($M + H^+$): 382.0435; Found: 382.0429.



6f

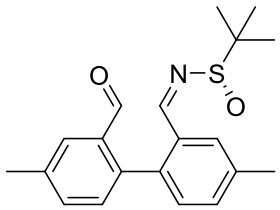
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 0.45 H for minor isomer), 9.72 (s, 0.55 H for major isomer), 8.31 (s, 0.45 H for minor isomer), 8.28 (s, 0.55 H for major isomer), 8.13-8.09 (m, 1 H), 8.01-7.98 (m, 1 H), 7.65-7.59 (m, 1 H), 7.57-7.53 (m, 1 H), 7.25-7.20 (m, 2 H), 1.20 (s, 4.1 H for minor isomer), 1.14 (s, 4.9 H for major isomer); HRMS *m/z* Calcd. for $C_{18}H_{17}Cl_2NO_2SNa$ ($M + Na^+$): 404.0255; Found: 404.0253.



6g

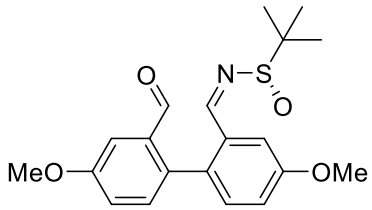
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 0.45 H for minor isomer), 9.70 (s, 0.55 H for major isomer), 8.34 (s, 0.45 H for minor isomer), 8.33 (s, 0.55 H for major isomer), 8.01 (d, *J* = 8.0 Hz, 0.45 H for minor isomer), 8.00 (d, *J* = 8.0 Hz, 0.55 H for major isomer), 7.92 (d, *J* = 8.0 Hz, 0.45 H for minor isomer), 7.91 (d, *J* = 8.0 Hz, 0.55 H for major isomer), 7.36-7.30 (m, 2 H), 7.11 (s, 1 H), 7.08 (s, 0.55 H for major isomer), 7.07 (s, 0.45 H for minor isomer), 2.45-2.41 (m, 6 H), 1.17 (s, 4.1 H for minor isomer), 1.10 (s, 4.9 H for major isomer); HRMS *m/z* Calcd. for $C_{20}H_{24}NO_2S$

(M + H^+): 342.1528; Found: 342.1532.



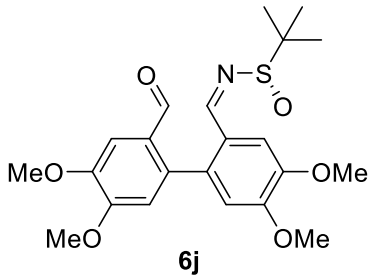
6h

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 0.45 H for minor isomer), 9.76 (s, 0.55 H for major isomer), 8.39 (s, 0.45 H for minor isomer)), 8.36 (s, 0.55 H for major isomer), 7.95 (s, 0.45 H for minor isomer), 7.93 (s, 0.55 H for major isomer), 7.82 (s, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.22-7.13 (m, 2 H), 2.48 (s, 3 H), 2.45 (s, 3 H), 1.20 (s, 4.1 H for minor isomer), 1.14 (s, 4.9 H for major isomer); HRMS *m/z* Calcd. for $C_{20}H_{23}NO_2SNa$ (M + Na^+): 364.1347; Found: 364.1341.



6i

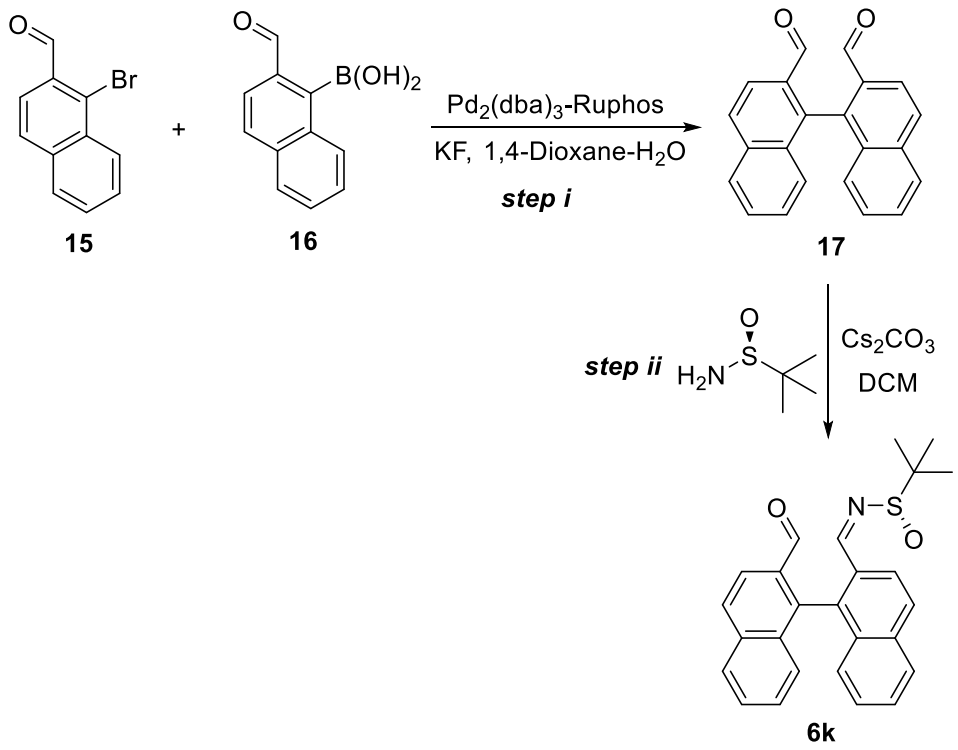
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 0.46 H for minor isomer), 9.72 (s, 0.54 H for major isomer), 8.38 (s, 0.46 H for minor isomer), 8.35 (s, 0.54 H for major isomer), 7.66-7.63 (m, 1 H), 7.501 (s, 0.54 H for major isomer), 7.497 (s, 0.46 H for minor isomer), 7.25-7.15 (m, 3 H), 7.13-7.08 (m, 1 H), 3.92 (s, 3 H), 3.90 (s, 3 H), 1.21 (s, 4.1 H for minor isomer), 1.16 (s, 4.9 H for major isomer); HRMS *m/z* Calcd. for $C_{20}H_{24}NO_4S$ (M + H^+): 374.1426; Found: 374.1418.



6j

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 0.45 H for minor isomer), 9.57 (s, 0.55 H for major isomer), 8.31 (s, 0.45 H for minor isomer), 8.28 (s, 0.55 H for major isomer), 7.65 (s, 1 H), 7.52 (s, 0.45 H for minor isomer), 7.51 (s, 0.55 H for major isomer), 6.79 (s, 0.55 H for major isomer), 6.77 (s, 0.45 H for minor isomer), 6.74 (s, 0.55 H for major isomer), 6.70 (s, 0.45 H for minor isomer), 4.01 (s, 3 H), 3.99 (s, 1.3 H for minor isomer), 3.98 (s, 1.7 H for major isomer), 3.94 (s, 3 H), 3.93 (s, 1.3 H for minor isomer), 3.91 (s, 1.7 H for major isomer), 1.20 (s, 4.1 H for minor isomer), 1.17 (s, 4.9 H for major isomer); HRMS *m/z* Calcd. for $C_{22}H_{27}NO_6SNa$ (M + Na^+): 456.1457; Found: 456.1453.

Procedure for Synthesis of Compound 6k (Table 2)



Step i. **Synthesis of dialdehyde 17**

A mixture of 1-bromo-2-naphthaldehyde **15** (1.0 g, 4.26 mmol), (2-formylnaphthalen-1-yl)boronic acid **16** (1.28 g, 6.38 mmol), $Pd_2(dba)_3$ (0.10 g, 0.109 mmol), KF (0.74 g, 12.78 mmol) and

2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (RuPhos) (0.10 g, 0.215 mmol) in 1,4-dioxane (5.0 mL) and H_2O (4 mL) was vigorously stirred under N_2 atmosphere at room temperature for 20 min and then at 100 °C for 21 hours. The reaction mixture was cooled to room temperature and extracted with EtOAc (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, concentrated under reduced pressureand, and purified by column chromatography (petroleum ether / ethyl acetate = 30:1) to give the product **17** as a yellow solid (0.687 g, 52% yield).

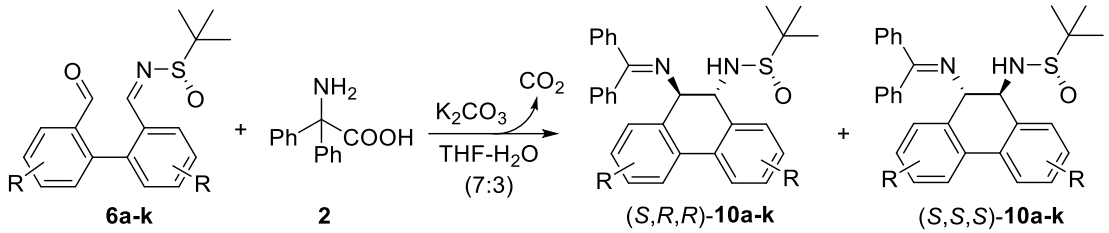
17: Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 2 H), 8.21 (d, *J* = 8.4 Hz, 2 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 8.4, 6.6 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H).

***Step ii.* Synthesis of dialdehyde 6k**

A mixture of compound **17** (0.476 g, 1.526 mmol)，(*S*)-*tert*-butylsulfinamide (0.185 g, 1.526 mmol) and Cs_2CO_3 (0.746 g, 2.289 mmol) in anhydrous DCM (10 mL) was stirred at 50 °C for 36 h. The reaction mixture was cooled to room temperature, filtered, concentrated under reduced pressure, and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product **6k** as a yellow solid (0.274 g, 43%).

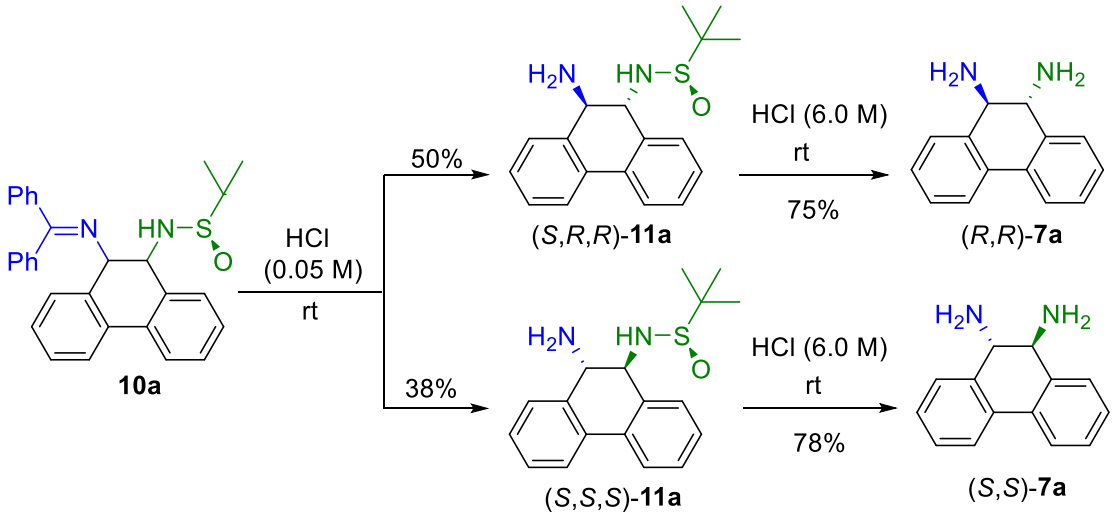
6k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 0.50 H), 9.59 (s, 0.50 H), 8.32 (d, *J* = 8.4 Hz, 0.50 H), 8.29 (d, *J* = 8.4 Hz, 0.50 H), 8.21-8.15 (m, 2 H), 8.12-8.06 (m, 2 H), 7.99 (d, *J* = 8.0 Hz, 2 H), 7.63-7.55 (m, 2 H), 7.36-7.27 (m, 2 H), 7.23-7.16 (m, 1 H), 7.15-7.08 (m, 1 H), 1.05 (s, 4.5 H), 1.04 (s, 4.5 H); HRMS *m/z* Calcd. for $C_{26}H_{24}NO_2S$ ($M + H^+$): 414.1528; Found: 414.1529.

General Procedure for Aminative Umpolung Cyclization of 6 to Diamines 10 (Table 2)



A mixture of compound **6** (0.20 mmol), 2,2-diphenylglycine **2** (0.045 g, 0.20 mmol) and K_2CO_3 (0.0055 g, 0.040 mmol) in THF-H_2O (7:3) (1.2 mL) was stirred at 40 °C for 48 h. After removal of the solvent via rotary evaporation under reduced pressure, the residue was submitted to flash column chromatography on silica gel (petroleum ether / ethyl acetate = 3:1) to give the product **10**.

Deprotection of 10a to 11a and 7a (Scheme 3)



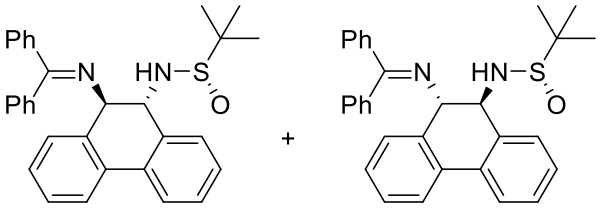
A mixture of **10a** (0.50 g, 1.046 mmol), HCl aqueous solution (0.05 M) (60 mL), and THF (15 mL) was stirred at room temperature. The reaction was monitored by TLC analysis. Upon completion, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ until pH 7~8, then extracted with EtOAc (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography (ethyl acetate / methanol = 20:1) to give the product (*S*,*R*,*R*)-**11a** (0.165 g, 50% yield) and (*S*,*S*,*S*)-**11a** (0.125g, 38% yield).

To a stirred solution of (*S*,*R*,*R*)-**11a** (0.075 g, 0.239 mmol) in THF (0.30 mL) was added HCl aqueous solution (6.0 M, 0.30 mL). The mixture was stirred at room temperature for 30 min. Upon completion, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ until pH 7~8, then extracted with DCM (10 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography (DCM / 2.9 M ammonia solution in ethanol = 8:1) to give the product (*R*,*R*)-**7a** (0.038 g, 75% yield) as a blue solid.

Compound (*S*,*S*)-**7a** was also obtained in 78% yield as a blue solid from (*S*,*S*,*S*)-**11a** following a similar procedure.

Characterization Data

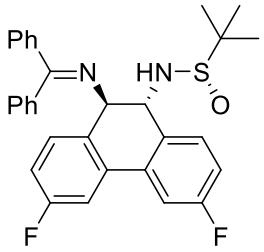
Table 2, Compounds (*S*,*S*,*S*)-10a and (*S*,*R*,*R*)-10a



(*S*,*R*,*R*)-**10a** (major) (*S*,*S*,*S*)-**10a** (minor)

White solid; IR (KBr) 3189, 3059, 1626, 1484, 1446, 1285, 1266, 1054 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.85 (m, 3 H), 7.68 (d, *J* = 7.6 Hz, 1 H), 7.67-7.25 (m, 13 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 4.89 (t, *J* = 8.0 Hz, 0.56 H), 4.82 (d, *J* = 7.2 Hz, 0.44 H), 4.73-4.77 (m, 1 H), 3.40 (d, *J* = 8.0 Hz, 0.56 H), 3.13 (d, *J* = 7.6 Hz, 0.44 H), 1.13 (s, 5.0 H), 1.12 (s, 4.0 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.3, 139.7, 139.3, 136.6, 136.44, 136.40, 135.7, 135.6, 135.4, 133.8, 133.7, 133.33, 133.29, 130.34, 130.2, 129.0, 128.9, 128.78, 128.76, 128.6, 128.49, 128.45, 128.3, 128.19, 128.15, 128.1, 128.00, 127.96, 127.9, 127.74, 127.66, 127.4, 124.1, 124.03, 124.01, 123.9, 66.5, 66.2, 61.4, 59.9, 56.3, 56.1, 22.8, 22.4; HRMS *m/z* Calcd. for $C_{31}H_{31}N_2OS$ ($M + H^+$): 479.2157; Found: 479.2154.

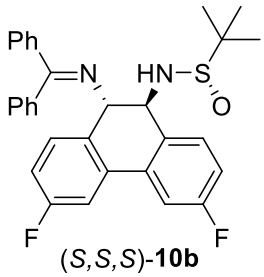
Table 2, Compound (*S,R,R*)-10b



(*S,R,R*)-**10b**

White solid; IR (KBr) 3440, 3183, 1613, 1579, 1501, 1428, 1287, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.4, 5.6 Hz, 1 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.53-7.45 (m, 3 H), 7.43-7.34 (m, 3 H), 7.29 (t, *J* = 7.6 Hz, 2 H), 7.24 (d, *J* = 7.2 Hz, 2 H), 7.04 (td, *J* = 8.4, 2.8 Hz, 1 H), 6.96 (d, *J* = 7.2 Hz, 2 H), 4.76-4.66 (m, 2 H), 3.31-3.24 (m, 1 H), 1.06 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 164.5, 164.3, 162.1, 161.8, 139.1, 136.4, 134.95, 134.93, 134.87, 134.85, 134.61, 134.59, 134.53, 134.51, 132.13, 132.10, 131.38, 131.36, 130.7, 130.6, 130.5, 130.0, 129.9, 128.95, 128.91, 128.1, 127.4, 115.8, 115.5, 115.3, 115.1, 111.4, 111.2, 110.9, 65.6, 60.5, 56.2, 22.7; HRMS *m/z* Calcd. for $C_{31}H_{29}F_2N_2OS$ ($M + H^+$): 515.1969; Found: 515.1955.

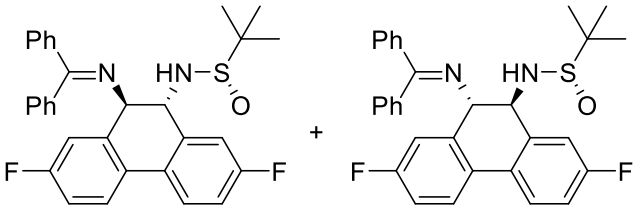
Table 2, Compound (*S,S,S*)-10b



(*S,S,S*)-**10b**

White solid; IR (KBr) 3446, 1615, 1579, 1501, 1429, 1172, 1073 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.38 (m, 8 H), 7.36-7.30 (m, 1 H), 7.29-7.22 (m, 4 H), 7.06 (td, *J* = 8.4, 2.4 Hz, 1 H), 6.95 (d, *J* = 1.2 Hz, 1 H), 6.93 (d, *J* = 1.2 Hz, 1 H), 4.78 (d, *J* = 5.6 Hz, 1 H), 4.58 (dd, *J* = 7.2, 5.6 Hz, 1 H), 3.05 (d, *J* = 7.2 Hz, 1 H), 1.03 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 164.4, 164.3, 162.0, 161.9, 139.5, 136.51, 134.99, 134.96, 134.90, 134.88, 134.74, 134.72, 134.67, 134.64, 131.32, 131.29, 131.04, 131.01, 130.84, 130.76, 130.68, 130.5, 129.0, 128.9, 128.1, 127.7, 115.5, 115.32, 115.26, 115.1, 111.4, 111.3, 111.13, 111.11, 65.8, 59.1, 56.3, 22.4; HRMS *m/z* Calcd. for $C_{31}H_{29}F_2N_2OS$ ($M + H^+$): 515.1969; Found: 515.1964.

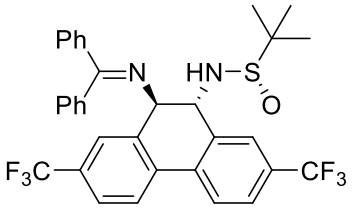
Table 2, Compound (*S*,*S*,*S*)-10c and (*S*,*R*,*R*)-10c



(*S*,*R*,*R*)-**10c** (major) (*S*,*S*,*S*)-**10c** (minor)

White solid; IR (KBr) 3177, 1626, 1597, 1481, 1446, 1431, 1266, 1043 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.56 (m, 5 H), 7.52-7.26 (m, 7 H), 7.25-7.20 (m, 1 H), 7.11-7.02 (m, 2 H), 6.82-6.76 (m, 1 H), 4.83 (t, *J* = 8.6 Hz, 0.60 H), 4.74-4.68 (m, 0.80 H), 4.65 (d, *J* = 8.8 Hz, 0.60 H), 3.33 (d, *J* = 8.0 Hz, 0.60 H), 3.04 (d, *J* = 6.4 Hz, 0.40 H), 1.14 (s, 3.6 H), 1.13 (s, 5.4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.3, 163.9, 163.75, 163.70, 163.6, 161.5, 161.3, 161.2, 161.1, 139.4, 139.0, 138.7, 138.6, 138.0, 137.9, 137.8, 137.7, 137.6, 137.5, 136.3, 136.1, 130.7, 130.6, 129.25, 129.21, 129.17, 129.13, 129.07, 129.02, 128.99, 128.95, 128.94, 128.12, 128.09, 127.5, 127.3, 125.8, 125.72, 125.71, 125.63, 125.61, 125.54, 125.52, 115.62, 115.56, 115.44, 115.40, 115.3, 115.2, 115.1, 115.0, 114.9, 114.8, 114.7, 114.6, 66.13, 66.11, 65.83, 65.82, 61.4, 59.59, 59.58, 56.6, 56.3, 22.7, 22.5; HRMS *m/z* Calcd. for $C_{31}H_{29}F_2N_2OS$ ($M + H^+$): 515.1969; Found: 515.1959.

Table 2, Compound (*S*,*R*,*R*)-10d

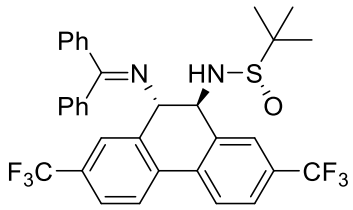


(*S*,*R*,*R*)-**10d**

White solid; IR (KBr) 3192, 1631, 1330, 1318, 1265, 1172, 1123, 1086 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.93 (d, *J* = 8.8 Hz, 1 H), 7.72 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.65 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.58-7.46 (m, 5 H), 7.41-7.34 (m, 1 H), 7.29 (d, *J* = 7.6 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.16 (s, 1 H), 4.88-4.78 (m, 2 H), 3.21 (d, *J* = 5.6 Hz, 1 H), 1.02 (s, 9 H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 170.7, 138.9, 137.3, 136.8, 136.3, 136.0, 135.6, 131.39 (q, *J* = 32.6 Hz), 130.86 (q, *J* = 32.4 Hz), 130.8, 129.2, 128.9, 128.2, 127.4, 126.22 (q, *J* = 3.6 Hz), 126.05 (q, *J* = 3.6 Hz), 125.61 (q, *J* = 3.5 Hz), 125.46 (q, *J* = 3.7 Hz), 125.1, 124.9, 124.00 (q, *J* = 270.9 Hz), 123.99 (q, *J* = 270.3 Hz), 65.2, 59.9, 56.3, 22.5; HRMS *m/z* Calcd. for $C_{33}H_{29}F_6N_2OS$ ($M + H^+$): 615.1905; Found: 615.1907.

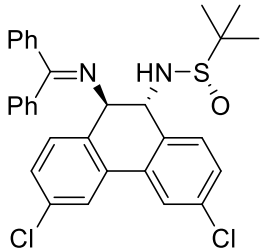
Table 2, Compound (*S,S,S*)-10d



(*S,S,S*)-**10d**

White solid; IR (KBr) 3208, 3061, 1622, 1324, 1264, 1171, 1124, 1082 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.83 (s, 1 H), 7.71 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.65 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.56-7.46 (m, 5 H), 7.40-7.32 (m, 2 H), 7.31-7.24 (m, 3 H), 7.21 (s, 1 H), 4.87 (d, *J* = 6.4 Hz, 1 H), 4.77 (t, *J* = 6.8 Hz, 1 H), 3.20 (dd, *J* = 6.4, 2.8 Hz, 1 H), 1.07 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 139.2, 137.1, 136.6, 136.3, 135.8, 135.6, 131.01 (q, *J* = 32.2 Hz), 130.88 (q, *J* = 32.5 Hz), 130.8, 129.3, 129.2, 129.1, 128.2, 127.6, 126.9, 125.91 (q, *J* = 3.3 Hz), 125.80 (q, *J* = 3.8 Hz), 125.70 (q, *J* = 3.7 Hz), 125.59 (q, *J* = 3.7 Hz), 125.0, 124.10 (q, *J* = 270.5 Hz), 123.96 (q, *J* = 270.7 Hz), 65.7, 59.2, 56.6, 22.5; HRMS *m/z* Calcd. for $C_{33}H_{29}F_6N_2OS$ ($M + H^+$): 615.1905; Found: 615.1907.

Table 2, Compound (*S,R,R*)-10e

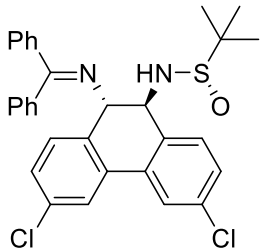


(*S,R,R*)-**10e**

White solid; IR (KBr) 3213, 1625, 1598, 1557, 1446, 1401, 1064 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73-7.65 (m, 3 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.54-7.44 (m, 3 H),

7.42-7.35 (m, 1 H), 7.32-7.27 (m, 3 H), 7.24-7.18 (m, 3 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 4.74 (t, *J* = 7.4 Hz, 1 H), 4.67 (d, *J* = 8.0 Hz, 1 H), 3.25-3.28 (m, 1 H), 1.07 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.0, 136.3, 134.84, 134.81, 134.4, 134.2, 134.1, 133.9, 130.6, 130.2, 129.6, 129.00, 128.98, 128.93, 128.5, 128.1, 127.4, 124.4, 124.1, 65.5, 60.6, 56.3, 22.7; HRMS *m/z* Calcd. for $C_{31}H_{29}Cl_2N_2OS$ (M + H^+): 547.1378; Found: 547.1381.

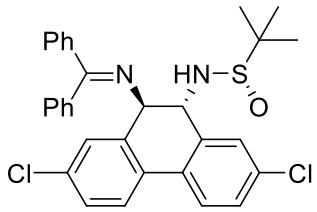
Table 2, Compound (*S*,*S*,*S*)-10e



(*S*,*S*,*S*)-**10e**

White solid; IR (KBr) 3321, 1622, 1598, 1558, 1485, 1446, 1401, 1074 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.4 Hz, 1 H), 7.72 (d, *J* = 2.0 Hz, 1 H), 7.55-7.45 (m, 5 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.37-7.30 (m, 2 H), 7.28-7.23 (m, 4 H), 7.21 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 4.76 (d, *J* = 6.0 Hz, 1 H), 4.59 (dd, *J* = 7.2, 6.0 Hz, 1 H), 3.04 (d, *J* = 7.2 Hz, 1 H), 1.04 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 139.4, 136.4, 134.7, 134.6, 134.3, 134.09, 134.07, 133.7, 130.5, 130.4, 130.3, 129.1, 129.03, 128.98, 128.6, 128.5, 128.1, 127.7, 124.3, 65.7, 59.1, 56.4, 22.5; HRMS *m/z* Calcd. for $C_{31}H_{29}Cl_2N_2OS$ (M + H^+): 547.1378; Found: 547.1381.

Table 2, Compound (*S*,*R*,*R*)-10f

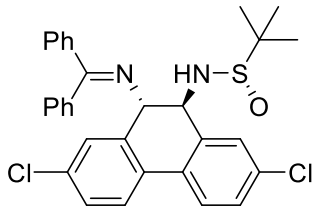


(*S*,*R*,*R*)-**10f**

White solid; IR (KBr) 3162, 2961, 1629, 1468, 1446, 1279, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 1.6 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 8.0

Hz, 2 H), 7.53-7.27 (m, 8 H), 7.23 (dd, *J* = 8.0, 1.6 Hz, 2 H), 6.96 (d, *J* = 2.0 Hz, 1 H), 4.75 (dd, *J* = 7.6, 7.2 Hz, 1 H), 4.66 (d, *J* = 7.6 Hz, 1 H), 3.26 (d, *J* = 7.2 Hz, 1 H), 1.08 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 138.9, 137.9, 137.2, 136.2, 134.5, 134.0, 132.5, 131.3, 131.1, 130.7, 130.1, 129.01, 128.96, 128.7, 128.5, 128.3, 128.1, 127.3, 125.5, 125.3, 65.5, 60.7, 56.3, 22.7; HRMS *m/z* Calcd. for $C_{31}H_{29}Cl_2N_2OS$ (M + H^+): 547.1378; Found: 547.1384.

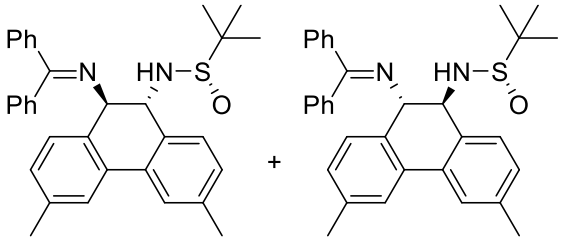
Table 2, Compound (*S,S,S*)-10f



(*S,S,S*)-**10f**

White solid; IR (KBr) 3445, 2958, 1622, 1598, 1470, 1446, 1180, 1095 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 7.53-7.45 (m, 4 H), 7.40-7.26 (m, 7 H), 6.95 (d, *J* = 2.4 Hz, 1 H), 4.73 (d, *J* = 7.2 Hz, 1 H), 4.64 (t, *J* = 7.2 Hz, 1 H), 3.11 (d, *J* = 7.2 Hz, 1 H), 1.10 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.3, 137.4, 137.0, 136.3, 134.2, 133.9, 131.4, 131.1, 130.6, 130.1, 129.11, 129.08, 129.03, 128.74, 128.65, 128.5, 128.1, 127.6, 125.4, 125.3, 65.9, 59.4, 56.6, 22.5; HRMS *m/z* Calcd. for $C_{31}H_{29}Cl_2N_2OS$ (M + H^+): 547.1378; Found: 547.1383.

Table 2, Compounds (*S,S,S*)-10g and (*S,R,R*)-10g

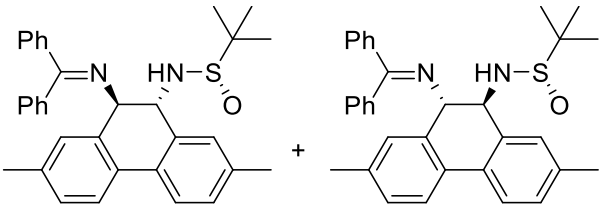


(*S,R,R*)-**10g** (major) (*S,S,S*)-**10g** (minor)

White solid; IR (KBr) 2957, 2922, 1621, 1446, 1266, 1070 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.62 (m, 5 H), 7.52-7.25 (m, 8 H), 7.22-7.14 (m, 1 H), 7.12-7.06 (m, 1

H), 6.98 (d, *J* = 7.6 Hz, 1 H), 4.83 (t, *J* = 8.0 Hz, 0.55 H for major isomer), 4.77 (d, *J* = 7.2 Hz, 0.45 H for minor isomer), 4.71-4.67 (m, 1 H), 3.35 (d, *J* = 8.0 Hz, 0.55 H for major isomer), 3.09 (d, *J* = 8.0 Hz, 0.45 H for minor isomer), 2.46 (s, 1.35 H for minor isomer), 2.444 (s, 1.65 H for major isomer), 2.436 (s, 1.65 H for major isomer), 2.431 (s, 1.35 H for minor isomer), 1.13 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.0, 139.8, 139.3, 138.1, 137.9, 137.7, 137.6, 136.7, 136.5, 133.7, 133.62, 133.56, 133.12, 133.10, 133.0, 132.8, 132.5, 132.4, 130.2, 130.1, 130.0, 129.03, 128.97, 128.9, 128.71, 128.68, 128.66, 128.6, 128.5, 128.4, 128.3, 128.0, 127.94, 127.89, 127.6, 127.4, 124.7, 124.62, 124.58, 124.5, 66.5, 66.2, 61.4, 59.9, 56.3, 56.1, 22.7, 22.4, 21.5, 21.43, 21.39; HRMS *m/z* Calcd. for $C_{33}H_{35}N_2OS$ ($M + H^+$): 507.2470; Found: 507.2466.

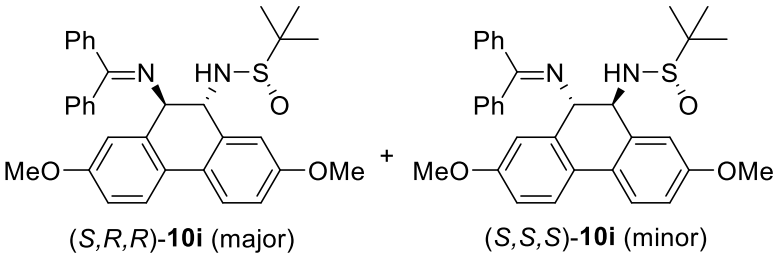
Table 2, Compounds (*S,S,S*)-10h and (*S,R,R*)-10h



(*S,R,R*)-**10h** (major) (*S,S,S*)-**10h** (minor)

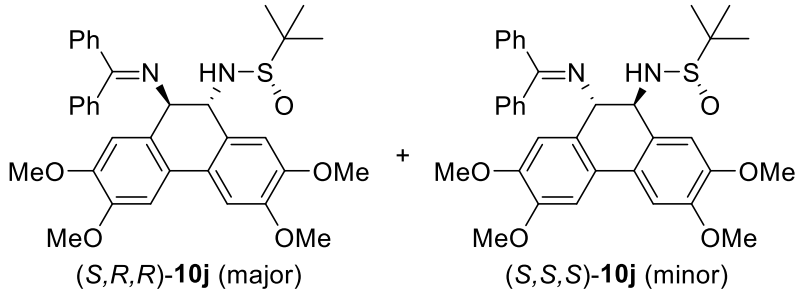
White solid; IR (KBr) 3055, 3025, 1625, 1487, 1446, 1284, 1072 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.60 (m, 5 H), 7.52-7.44 (m, 3 H), 7.38-7.27 (m, 5 H), 7.23-7.17 (m, 2 H), 6.84 (s, 1 H), 4.83-4.78 (m, 1 H), 4.73-4.66 (m, 1 H), 3.32 (d, *J* = 7.6 Hz, 0.58 H for major isomer), 3.08 (d, *J* = 8.0 Hz, 0.42 H for minor isomer), 2.42 (s, 1.74 H for major isomer), 2.41 (s, 1.26 H for minor isomer), 2.35 (s, 1.74 H for major isomer), 2.33 (s, 1.26 H for minor isomer), 1.14 (s, 3.8 H for minor isomer), 1.12 (s, 5.2 H for major isomr); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.1, 139.8, 139.3, 137.9, 137.5, 137.3, 137.2, 136.7, 136.5, 135.9, 135.3, 135.2, 134.9, 131.09, 131.05, 130.64, 130.62, 130.3, 130.2, 130.1, 129.3, 129.1, 129.04, 129.00, 128.95, 128.9, 128.8, 128.7, 128.6, 128.4, 128.0, 127.9, 127.7, 127.5, 123.8, 123.65, 123.62, 123.5, 66.6, 66.3, 61.4, 60.1, 56.4, 56.1, 22.7, 22.5, 21.5, 21.44, 21.39; HRMS *m/z* Calcd. for $C_{33}H_{35}N_2OS$ ($M + H^+$): 507.2470; Found: 507.2463.

Table 2, Compounds (*S,S,S*)-10i and (*S,R,R*)-10i



White solid; IR (KBr) 2958, 2835, 1614, 1487, 1464, 1431, 1281, 1248, 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72-7.58 (m, 4 H), 7.50-7.22 (m, 8.43 H), 7.11 (d, *J* = 2.4 Hz, 0.57 H for major isomer), 6.94-6.85 (m, 2 H), 6.65-6.60 (m, 1 H), 4.84 (dd, *J* = 8.8, 8.4 Hz, 0.57 H for major isomer), 4.75-4.64 (m, 1.43 H), 3.86 (s, 1.7 H for major isomer), 3.83 (s, 1.3 H for minor isomer), 3.78 (s, 1.7 H for major isomer), 3.77 (s, 1.3 H for minor isomer), 3.34 (d, *J* = 8.4 Hz, 0.57 H for major isomer), 3.09 (d, *J* = 7.2 Hz, 0.43 H for minor isomer), 1.15 (s, 3.9 H for minor isomer), 1.13 (s, 5.1 H for major isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.5, 159.4, 159.0, 158.84, 158.81, 139.7, 139.2, 137.3, 136.7, 136.6, 136.43, 136.38, 136.2, 130.4, 130.2, 129.0, 128.9, 128.79, 128.77, 128.02, 127.97, 127.7, 127.4, 126.6, 126.4, 126.3, 126.2, 124.7, 124.6, 115.0, 114.1, 113.9, 113.7, 113.3, 113.1, 112.7, 112.6, 66.7, 66.3, 62.1, 60.3, 56.5, 56.2, 55.5, 55.4, 55.31, 55.30, 22.7, 22.5; HRMS *m/z* Calcd. for $C_{33}H_{35}N_2O_3S$ ($M + H^+$): 539.2368; Found: 539.2363.

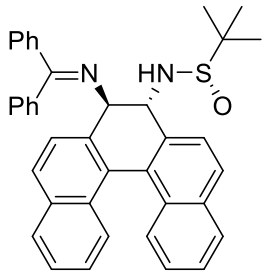
Table 2, Compounds (*S,S,S*)-10j and (*S,R,R*)-10j



White solid; IR (KBr) 2932, 1607, 1508, 1464, 1447, 1263, 1134, 1116, 1044 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.59 (m, 1 H), 7.64-7.15 (m, 11.63 H), 7.00 (s, 0.37 H for minor isomer), 6.48 (s, 0.63 H for major isomer), 6.39 (s, 0.37 H for minor isomer), 4.76 (d, *J* = 5.6 Hz, 0.37 H for minor isomer), 4.71 (dd, *J* = 8.0, 7.6 Hz, 0.63

H for major isomer), 4.62 (d, *J* = 8.0 Hz, 0.63 H for major isomer), 4.52 (dd, *J* = 8.4, 5.6 Hz, 0.37 H for minor isomer), 4.00 (s, 1.1 H for minor isomer), 3.97 (s, 1.9 H for major isomer), 3.96 (s, 1.9 H for major isomer), 3.95 (s, 1.1 H for minor isomer), 3.94 (s, 1.9 H for major isomer), 3.91 (s, 1.1 H for minor isomer), 3.78 (s, 1.9 H for major isomer), 3.76 (s, 1.1 H for minor isomer), 3.21 (d, *J* = 7.6 Hz, 0.63 H for major isomer), 3.16 (d, *J* = 8.4 Hz, 0.37 H for minor isomer), 1.08 (s, 5.7 H for major isomer), 1.06 (s, 3.3 H for minor isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.1, 149.08, 149.05, 149.03, 149.00, 148.9, 148.5, 148.4, 148.3, 139.7, 139.3, 136.8, 136.6, 132.4, 130.3, 130.1, 130.0, 128.81, 128.78, 128.76, 128.3, 128.0, 127.9, 127.8, 127.7, 127.5, 127.2, 126.3, 126.24, 126.18, 112.5, 112.1, 111.6, 107.4, 107.3, 107.04, 107.01, 66.2, 66.0, 61.5, 60.1, 56.33, 56.31, 56.25, 56.2, 56.10, 56.05, 56.0, 55.9, 22.6, 22.5; HRMS *m/z* Calcd. for $C_{35}H_{39}N_2O_5S$ ($M + H^+$): 599.2580; Found: 599.2576.

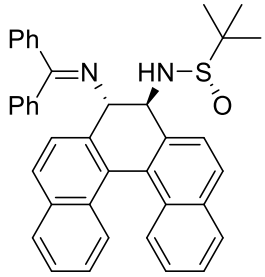
Table 2, Compound (*S*,*R*,*R*)-10k



(*S*,*R*,*R*)-**10k**

White solid; IR (KBr) 3056, 2959, 1625, 1596, 1446, 1079 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.88 (m, 7 H), 7.60-7.52 (m, 3 H), 7.50-7.42 (m, 5 H), 7.38-7.22 (m, 7 H), 5.05 (dd, *J* = 11.2, 7.6 Hz, 1 H), 4.65 (d, *J* = 11.2 Hz, 1 H), 3.10 (d, *J* = 7.6 Hz, 1 H), 1.36 (s, 9 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 139.8, 137.0, 136.8, 136.5, 133.7, 133.4, 130.6, 130.4, 130.3, 130.2, 129.4, 129.2, 128.9, 128.8, 128.7, 128.4, 128.39, 128.32, 128.2, 127.8, 127.6, 125.6, 125.5, 125.29, 125.25, 124.0, 122.4, 67.8, 60.8, 57.0, 22.7; HRMS *m/z* Calcd. for $C_{39}H_{35}N_2OS$ ($M + H^+$): 579.2470; Found: 579.2472.

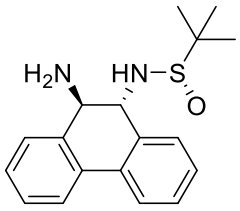
Table 2, Compound (*S,S,S*)-10k



(*S,S,S*)-**10k**

White solid; IR (KBr) 3208, 3055, 1627, 1446, 1120, 1047, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 7.95-7.88 (m, 3 H), 7.30 (d, *J* = 7.6 Hz, 2 H), 7.54-7.21 (m, 15 H), 5.14 (t, *J* = 10.8 Hz, 1 H), 4.67 (d, *J* = 11.2 Hz, 1 H), 3.61 (d, *J* = 10.4 Hz, 1 H), 1.27 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 139.3, 137.4, 136.3, 136.2, 133.6, 133.5, 130.6, 130.4, 130.14, 130.09, 129.4, 129.1, 128.91, 128.88, 128.6, 128.22, 128.19, 128.17, 127.7, 127.6, 127.2, 125.6, 125.5, 125.3, 125.2, 123.8, 123.7, 67.4, 64.3, 56.7, 23.1; HRMS *m/z* Calcd. for $C_{39}H_{35}N_2OS$ ($M + H^+$): 579.2470; Found: 579.2463.

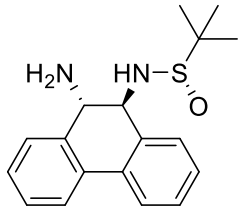
Scheme 3, Compound (*S,R,R*)-11a



(*S,R,R*)-**11a**

White solid; IR (KBr) 3365, 3212, 2958, 1484,1451, 1363, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.53 (m, 2 H), 7.38 (d, *J* = 7.6 Hz, 1 H), 7.25-7.06 (m, 5 H), 4.32-4.22 (m, 1 H), 3.95-3.86 (m, 1 H), 3.62-3.50 (m, 1 H), 1.93 (br, 2 H), 0.90 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 134.0, 132.8, 131.7, 129.5, 128.9, 128.2, 128.1, 128.0, 123.8, 123.7, 60.5, 55.8, 54.7, 22.3; HRMS *m/z* Calcd. for $C_{18}H_{23}N_2OS$ ($M + H^+$): 315.1531; Found: 315.1523.

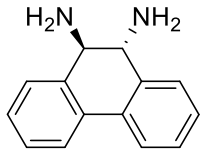
Scheme 3, Compound (*S*,*S*,*S*)-11a



(*S*,*S*,*S*)-**11a**

White solid; IR (KBr) 3362, 3192, 2979, 2958, 1481, 1452, 1363, 1047 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 6.8 Hz, 2 H), 7.28-7.14 (m, 4 H), 4.26 (dd, *J* = 6.8, 6.4 Hz, 1 H), 4.02-3.92 (m, 2 H), 2.56 (br, 2 H), 0.96 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.1, 132.9, 132.1, 129.2, 128.7, 128.4, 128.2, 128.1, 128.0, 124.0, 123.7, 61.2, 56.0, 55.3, 22.5; HRMS *m/z* Calcd. for $C_{18}H_{23}N_2OS$ ($M + H^+$): 315.1531; Found: 315.1524.

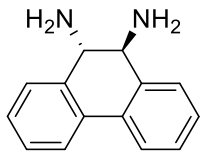
Scheme 3, Compound (*R*,*R*)-7a



(*R*,*R*)-**7a**

Blue solid; m.p. 100-103 ºC ; $[\alpha]_D^{25}$ = -180.1 (*c* = 0.5, $CHCl_3$); IR (KBr) 3349, 2924, 1577, 1482, 1450 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2 H), 7.48 (d, *J* = 7.2 Hz, 2 H), 7.42-7.30 (m, 4 H), 3.85 (s, 2 H), 1.61 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 132.4, 128.4, 128.2, 127.9, 124.1, 57.2; HRMS *m/z* Calcd. for $C_{14}H_{15}N_2$ ($M + H^+$): 211.1230; Found: 211.1230.

Scheme 3, Compound (*S*,*S*)-7a

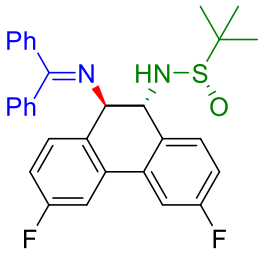


(*S*,*S*)-**7a**

Blue solid; m.p. 100-103 ºC ; $[\alpha]_D^{25}$ = 190.8 (*c* = 0.5, $CHCl_3$); IR (KBr) 3356, 2924, 1560, 1512, 1450 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.42-7.30 (m, 4 H), 3.85 (s, 2 H), 1.61 (s, 4 H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 138.6, 132.4, 128.4, 128.2, 127.9, 124.1, 57.2; HRMS *m/z* Calcd. for $C_{14}H_{15}N_2$ ($M + H^+$): 211.1230; Found: 211.1230.

X-ray structure of compound (*S*,*R*,*R*)-10b (CCDC 1862252)



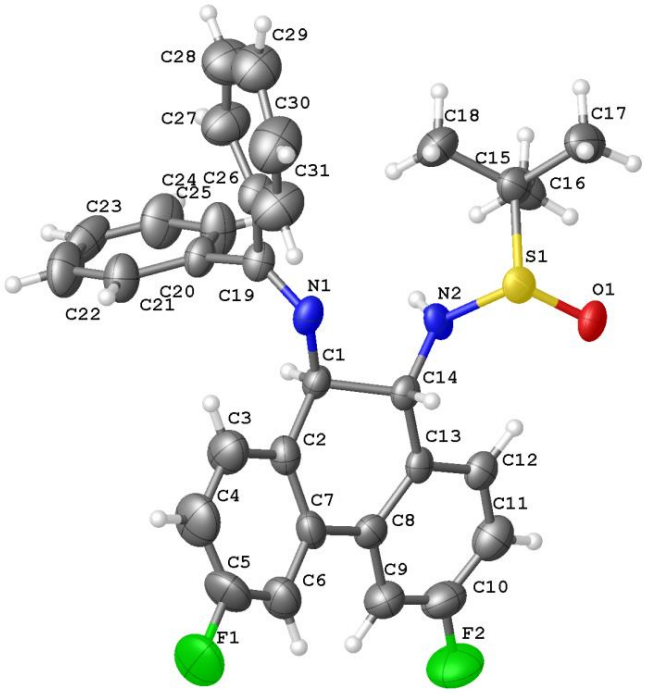
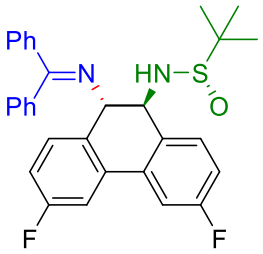


Table 1. Crystal data and structure refinement for (*S*,*R*,*R*)-10b (mo_dm17172_0m) (CCDC 1862252)

Identification code	mo_dm17172_0m	
Empirical formula	C31 H28 F2 N2 O S	
Formula weight	514.61	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.0912(17) Å	α= 90°.
	b = 17.553(3) Å	β= 90°.
	c = 20.148(4) Å	γ = 90°.
Volume	3215.1(10) $Å^3$	
Z	4	
Density (calculated)	1.063 Mg/m^3	
Absorption coefficient	0.134 mm^{-1}	
F(000)	1080	
Crystal size	0.2 x 0.18 x 0.15 mm^3	
Theta range for data collection	2.022 to 27.518°.	
Index ranges	-11<=h<=11, -22<=k<=20, -26<=l<=26	
Reflections collected	25952	
Independent reflections	7376 [R(int) = 0.0773]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6151	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7376 / 36 / 337	
Goodness-of-fit on F^2	0.998	
Final R indices [I>2sigma(I)]	R1 = 0.0670, wR2 = 0.1780	
R indices (all data)	R1 = 0.1577, wR2 = 0.2264	
Absolute structure parameter	0.09(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.437 and -0.274 $e.Å^{-3}$	

X-ray structure of compound (*S*,*S*,*S*)-10b (CCDC 1862253)



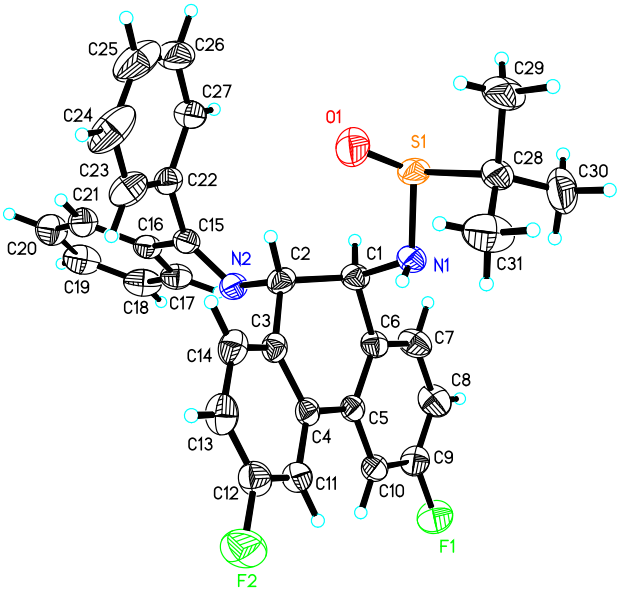
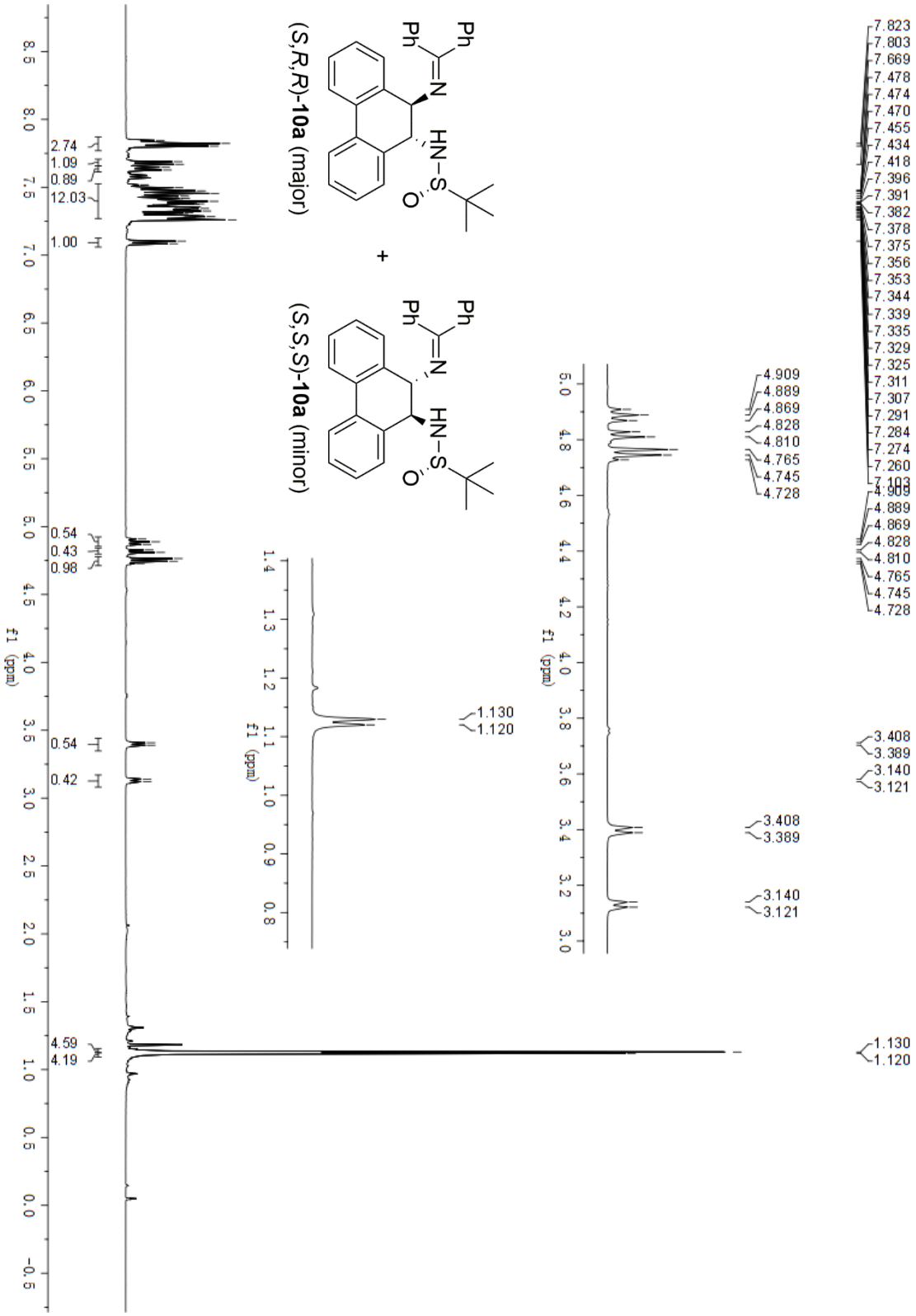


Table 1. Crystal data and structure refinement for (*S*,*S*,*S*)-10b (cd17233) (CCDC 1862253)

Identification code	cd17233	
Empirical formula	C31 H28 F2 N2 O S	
Formula weight	514.61	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.2418(17) Å	α= 98.339(3)°.
	b = 11.3491(16) Å	β= 114.149(3)°.
	c = 11.7184(18) Å	γ = 93.521(3)°.
Volume	1337.7(3) $Å^3$	
Z	2	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	540	
Crystal size	0.200 x 0.140 x 0.100 mm^3	
Theta range for data collection	1.830 to 24.997°.	
Index ranges	-13<=h<=13, -13<=k<=11, -13<=l<=13	
Reflections collected	7414	
Independent reflections	4701 [R(int) = 0.0232]	
Completeness to theta = 25.242°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6315	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4701 / 0 / 350	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0588, wR2 = 0.1384	
R indices (all data)	R1 = 0.0755, wR2 = 0.1492	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.499 and -0.331 $e.Å^{-3}$	


(S,R,R)-10a (major)
+
(S,S,S)-10a (minor)
Ph
Ph
N
HN
S
O
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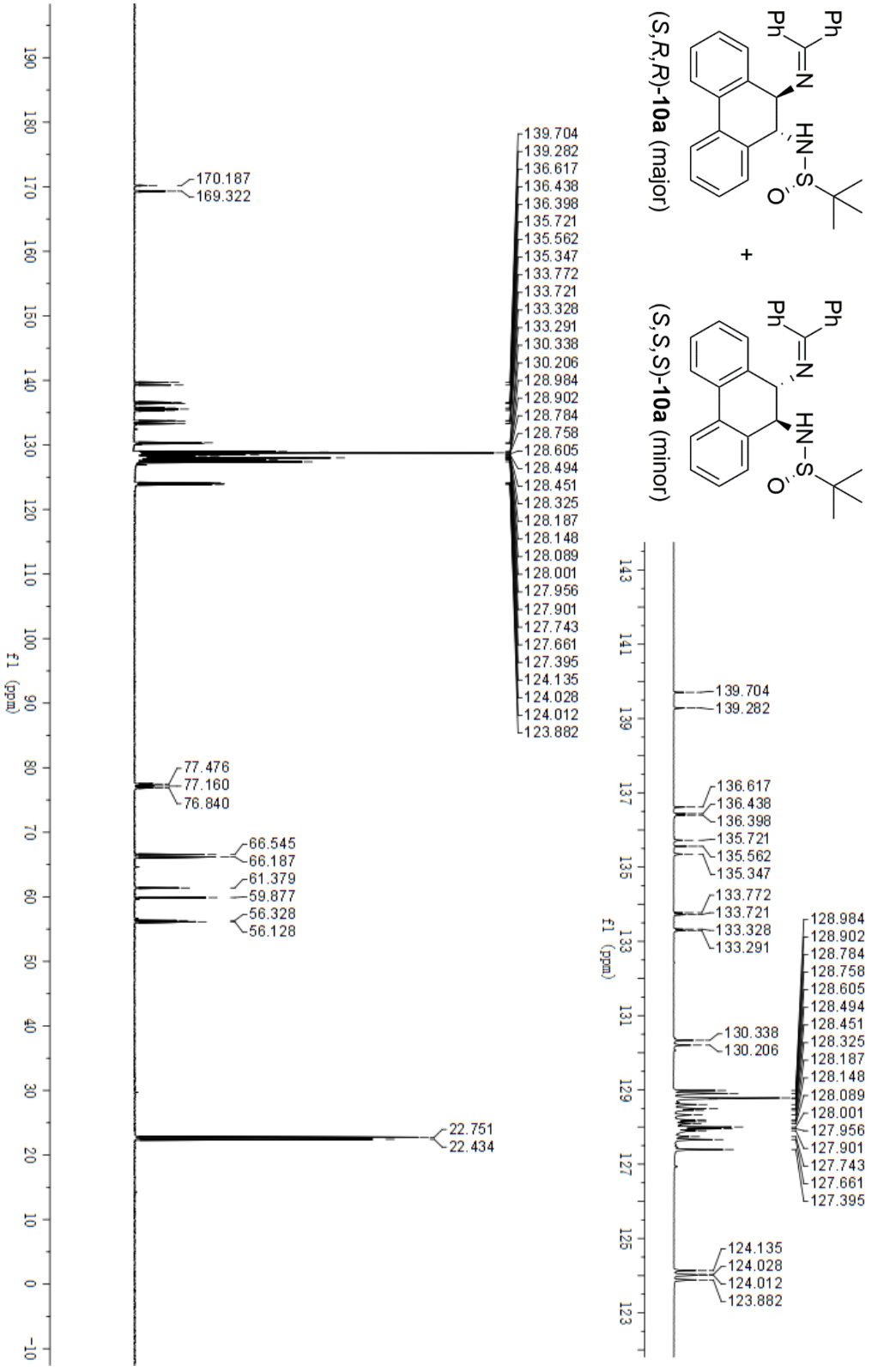
7.803
7.669
7.478
7.474
7.470
7.455
7.434
7.418
7.396
7.391
7.382
7.378
7.375
7.356
7.353
7.344
7.339
7.335
7.329
7.325
7.311
7.307
7.291
7.284
7.274
7.260
7.103
4.909
4.889
4.869
4.828
4.810
4.765
4.745
4.728
3.408
3.389
3.140
3.121
1.130
1.120
2.74
1.09
0.89
12.03
1.00
0.54
0.43
0.98
0.54
0.42
4.59
4.19
f1 (ppm)


(S,R,R)-10a (major)
+
(S,S,S)-10a (minor)
Ph
Ph
N
HN
S
O
f1 (ppm)
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169.322
139.704
139.282
136.617
136.438
136.398
135.721
135.562
135.347
133.772
133.721
133.328
133.291
130.338
130.206
128.984
128.902
128.784
128.758
128.605
128.494
128.451
128.325
128.187
128.148
128.089
128.001
127.956
127.901
127.743
127.661
127.395
124.135
124.028
124.012
123.882
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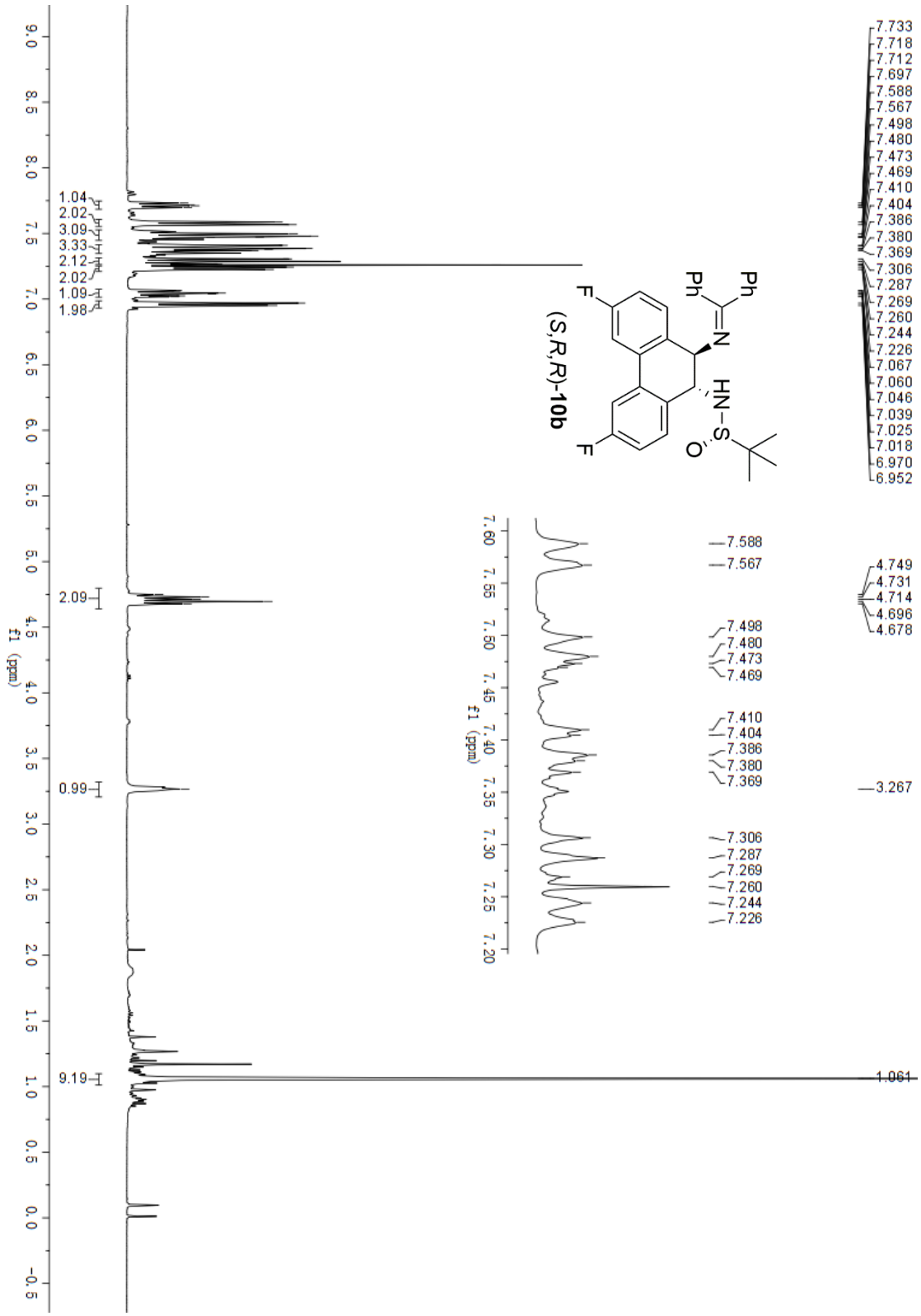
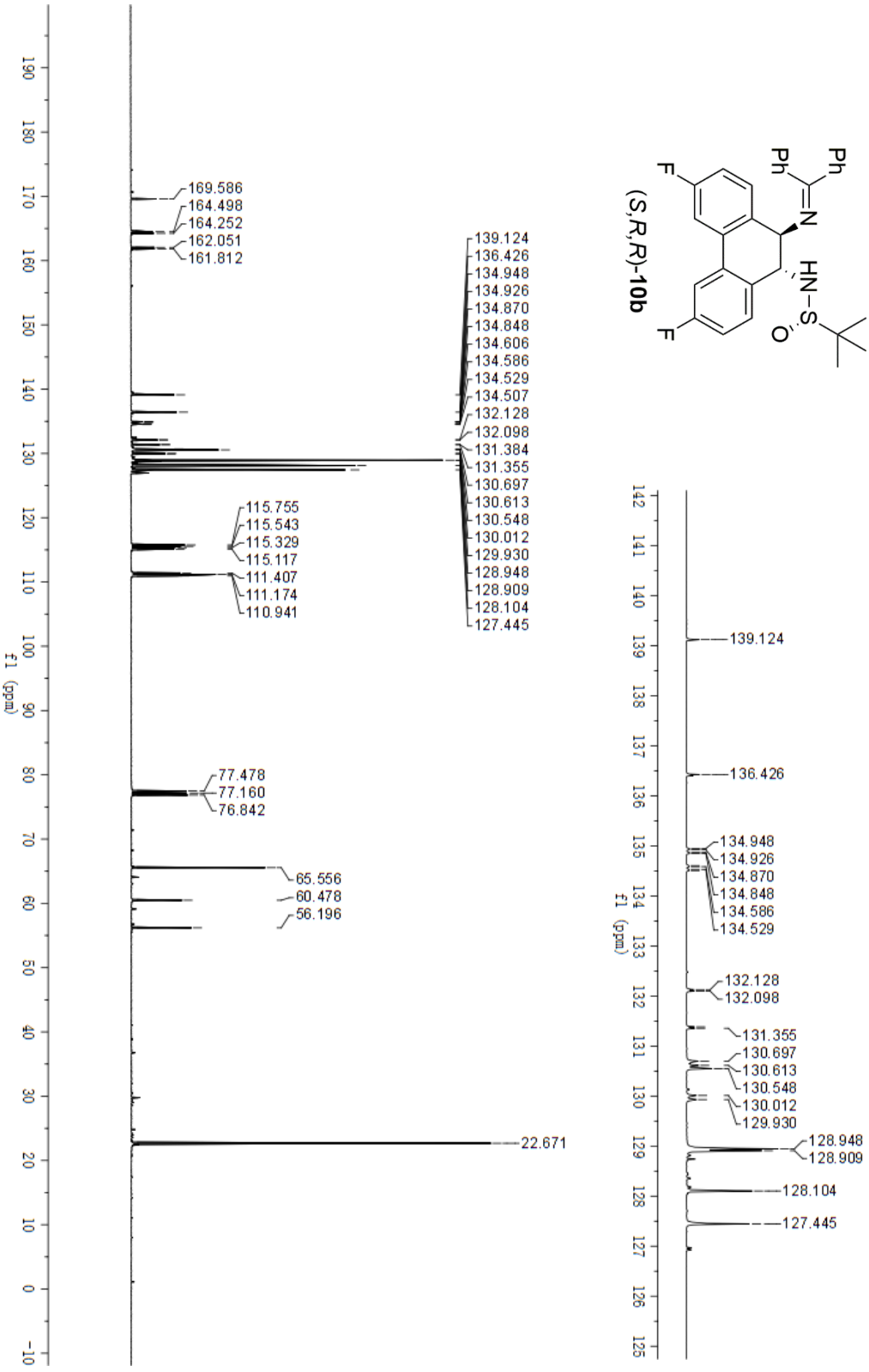
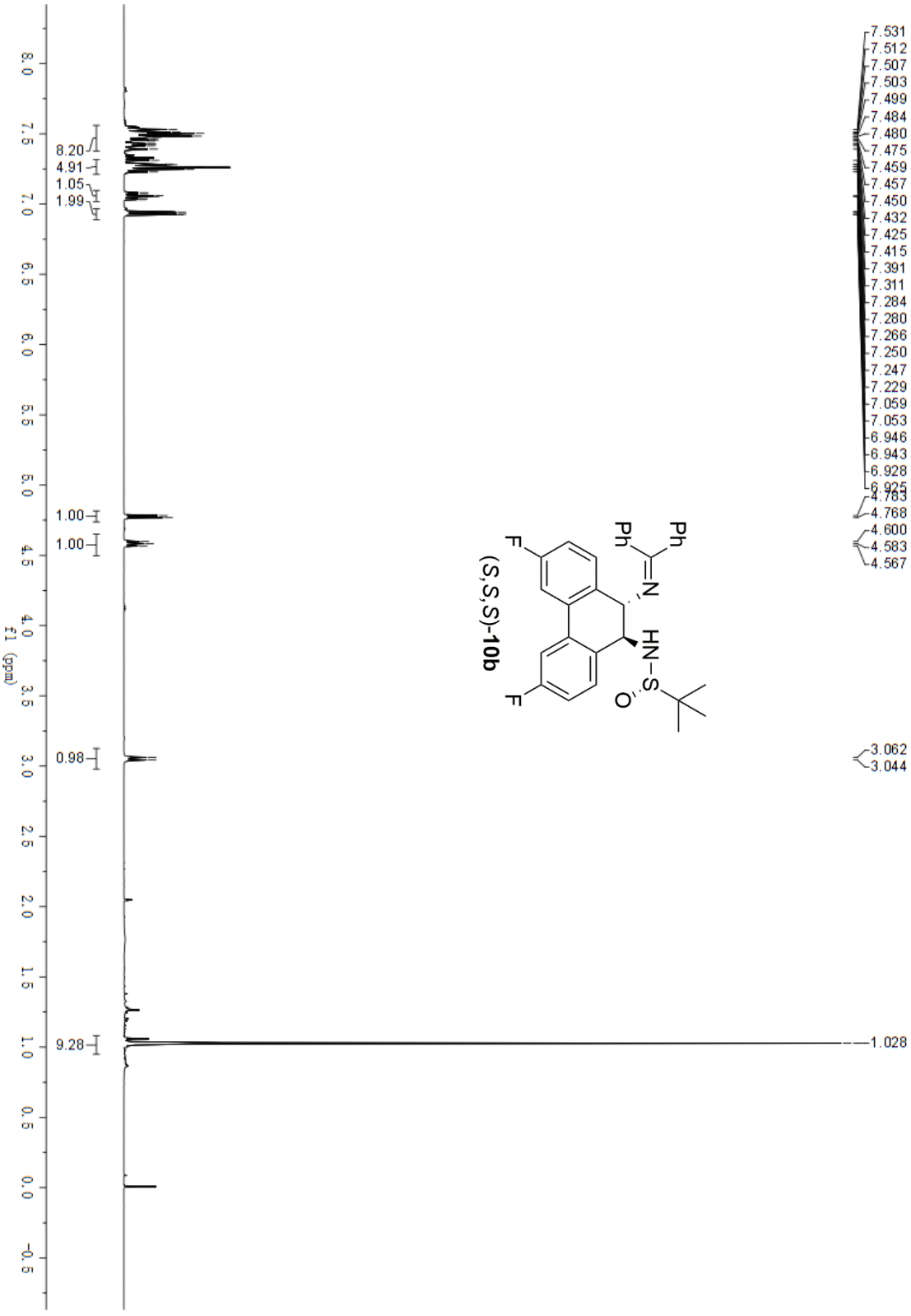
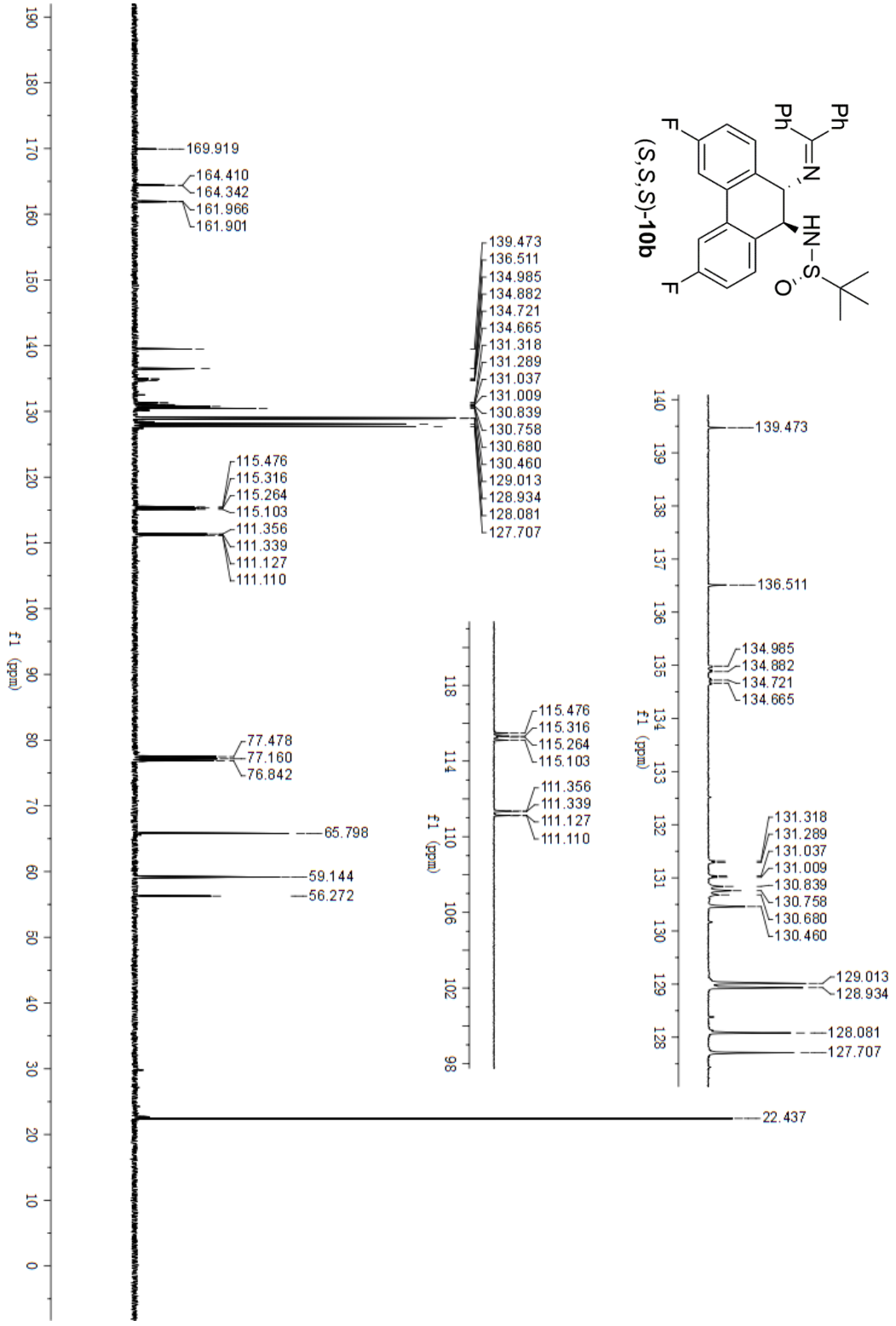
77.160
76.840
66.545
66.187
61.379
59.877
56.328
56.128
22.751
22.434


(S,R,R)-10b
F
F
Ph
Ph
N
HN
S
O
1.04
2.02
3.09
3.33
2.12
2.02
1.09
1.98
2.09
0.99
9.19
7.733
7.718
7.712
7.697
7.588
7.567
7.498
7.480
7.473
7.469
7.410
7.404
7.386
7.380
7.369
7.306
7.287
7.269
7.260
7.244
7.226
7.067
7.060
7.046
7.039
7.025
7.018
6.970
6.952
4.749
4.731
4.714
4.696
4.678
3.267
1.061
f1 (ppm)


(S,R,R)-10b
F
Ph
Ph
N
HN
S
O
F
169.586
164.498
164.252
162.051
161.812
139.124
136.426
134.948
134.926
134.870
134.848
134.606
134.586
134.529
134.507
132.128
132.098
131.384
131.355
130.697
130.613
130.548
130.012
129.930
128.948
128.909
128.104
127.445
115.755
115.543
115.329
115.117
111.407
111.174
110.941
77.478
77.160
76.842
65.556
60.478
56.196
22.671
f1 (ppm)
139.124
136.426
134.948
134.926
134.870
134.848
134.586
134.529
132.128
132.098
131.355
130.697
130.613
130.548
130.012
129.930
128.948
128.909
128.104
127.445
f1 (ppm)


7.531
7.512
7.507
7.503
7.499
7.484
7.480
7.475
7.459
7.457
7.450
7.432
7.425
7.415
7.391
7.311
7.284
7.280
7.266
7.250
7.247
7.229
7.059
7.053
6.946
6.943
6.928
6.925
4.783
4.768
4.600
4.583
4.567
3.062
3.044
1.028
8.20
4.91
1.05
1.99
1.00
1.00
0.98
9.28
f1 (ppm)
(S,S,S)-10b
Ph
Ph
N
HN
S
O
F
F


(S,S,S)-10b
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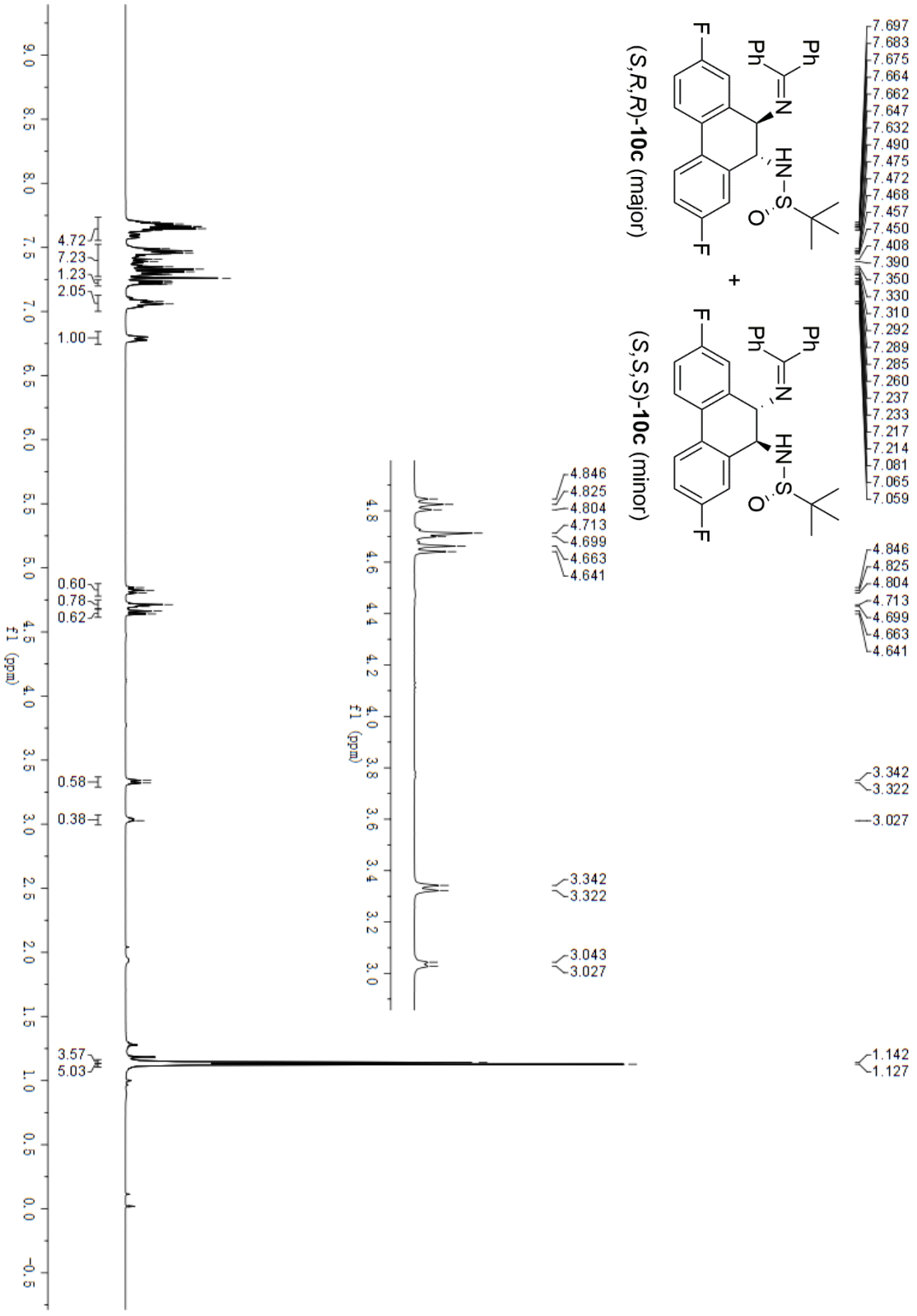
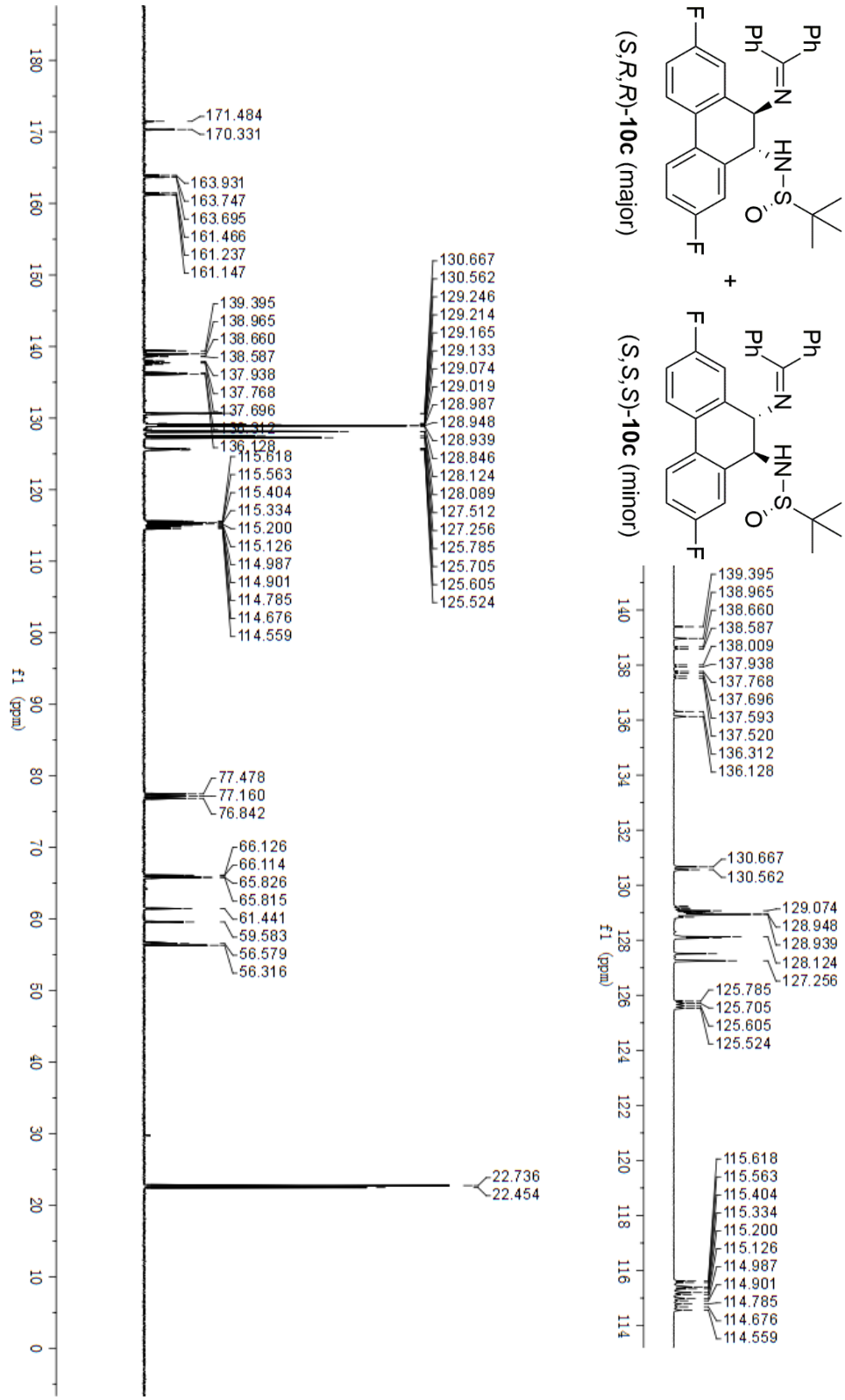
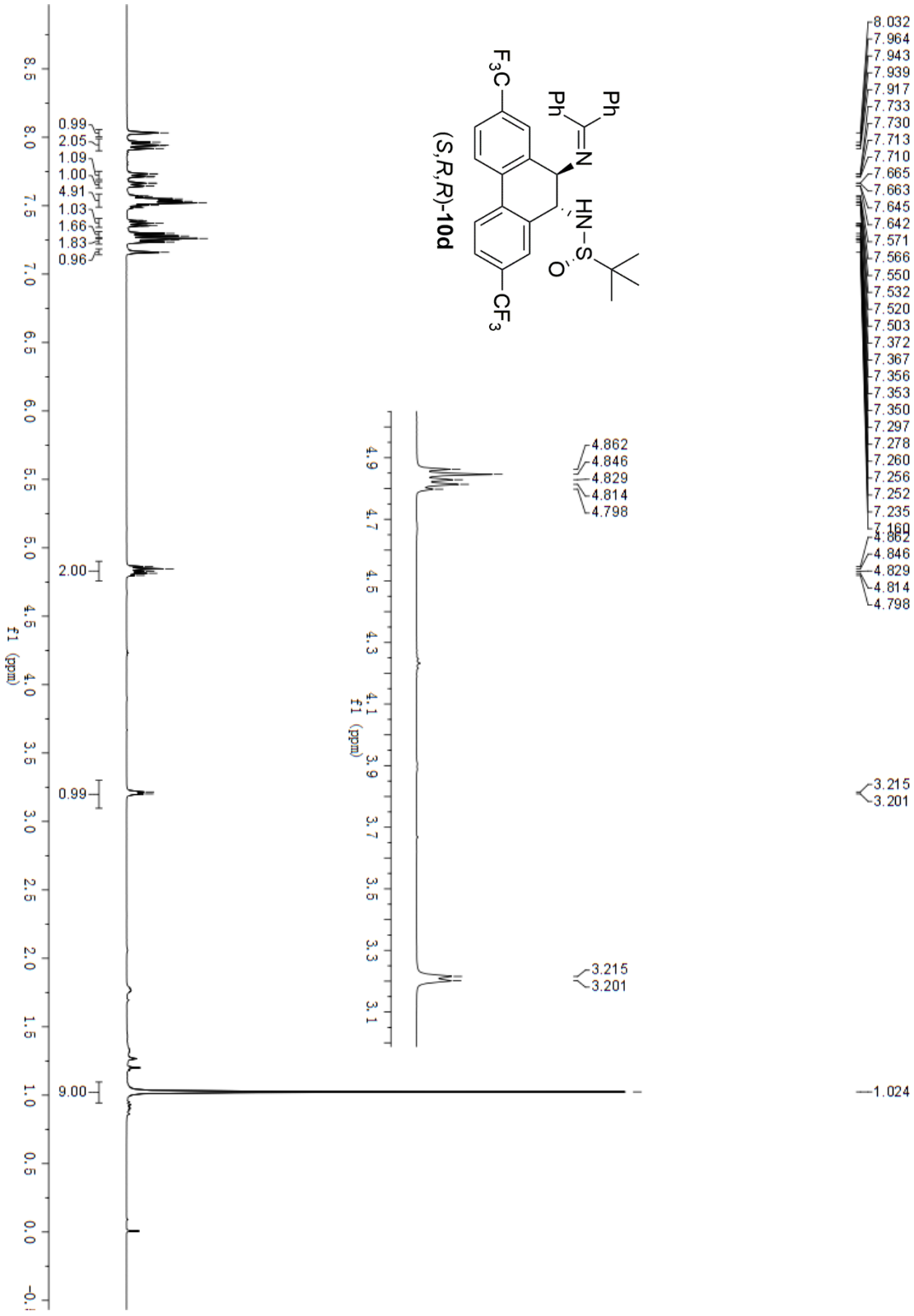
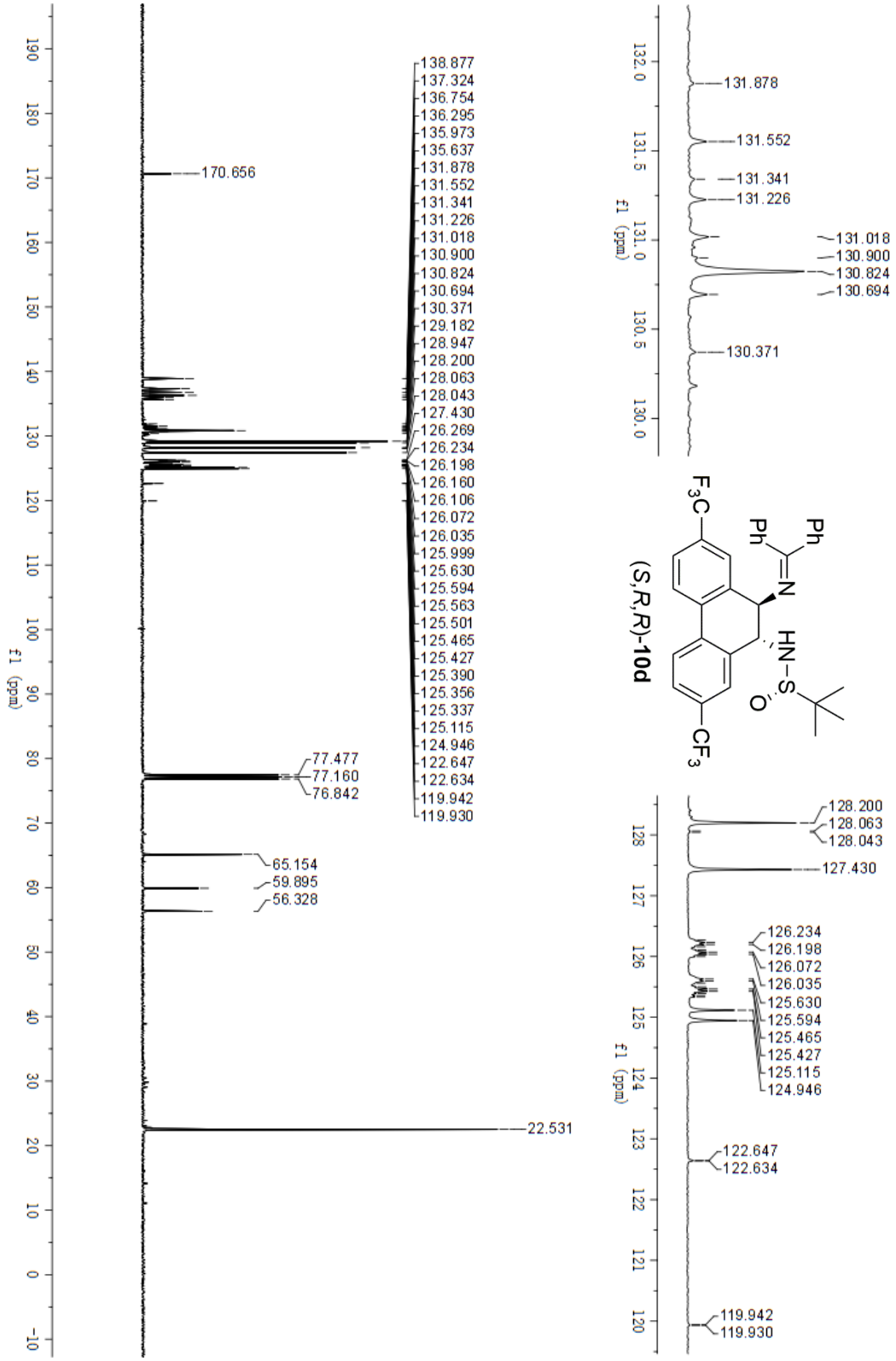
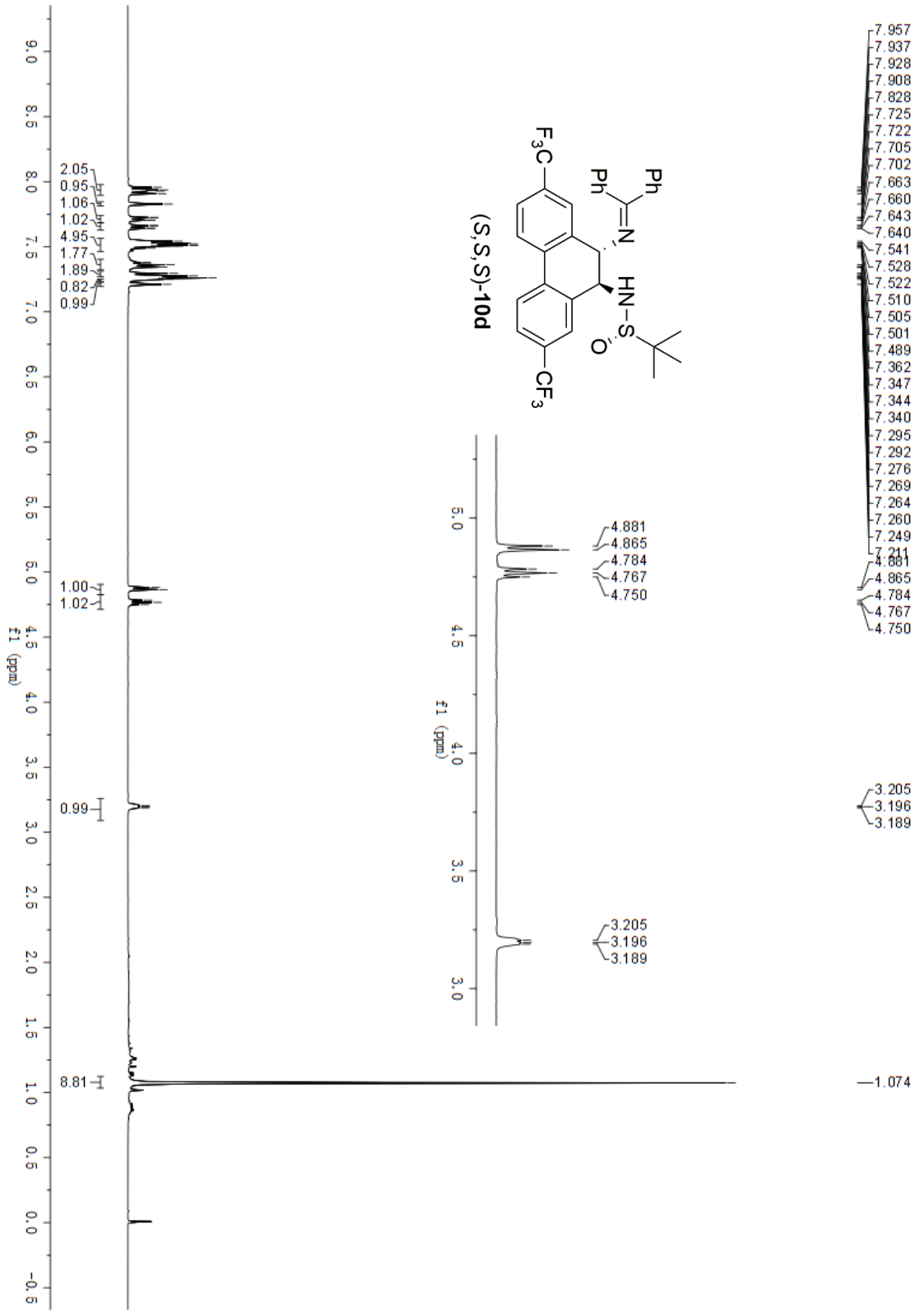
164.342
161.966
161.901
139.473
136.511
134.985
134.882
134.721
134.665
131.318
131.289
131.037
131.009
130.839
130.758
130.680
130.460
129.013
128.934
128.081
127.707
115.476
115.316
115.264
115.103
111.356
111.339
111.127
111.110
77.478
77.160
76.842
65.798
59.144
56.272
22.437
f1 (ppm)

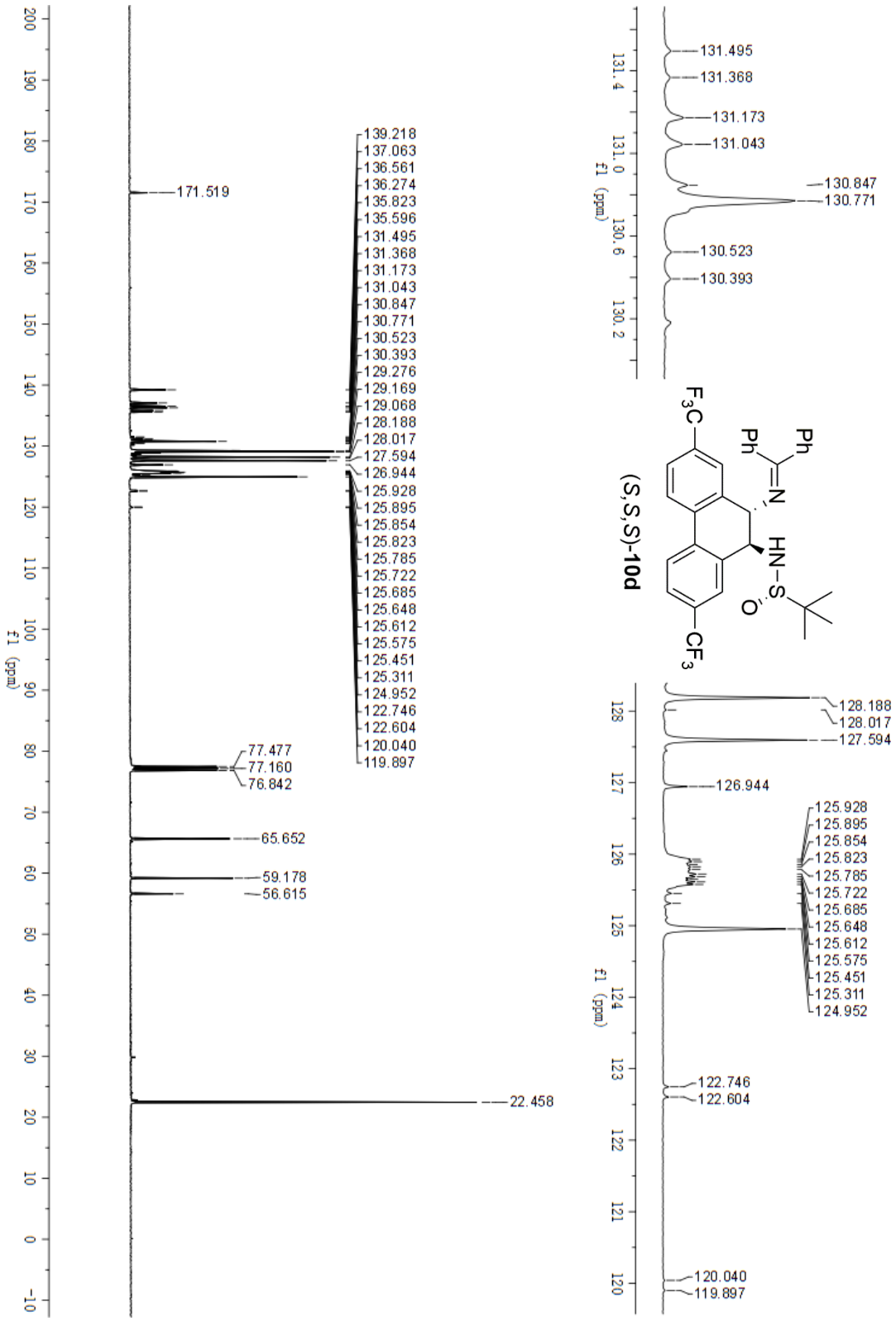

(S,R,R)-10c (major)
(S,S,S)-10c (minor)
F
Ph
Ph
N
HN
S
O
F
+
7.697
7.683
7.675
7.664
7.662
7.647
7.632
7.490
7.475
7.472
7.468
7.457
7.450
7.408
7.390
7.350
7.330
7.310
7.292
7.289
7.285
7.260
7.237
7.233
7.217
7.214
7.081
7.065
7.059
4.846
4.825
4.804
4.713
4.699
4.663
4.641
3.342
3.322
3.027
1.142
1.127
4.72
7.23
1.23
2.05
1.00
0.60
0.78
0.62
0.58
0.38
3.57
5.03
f1 (ppm)

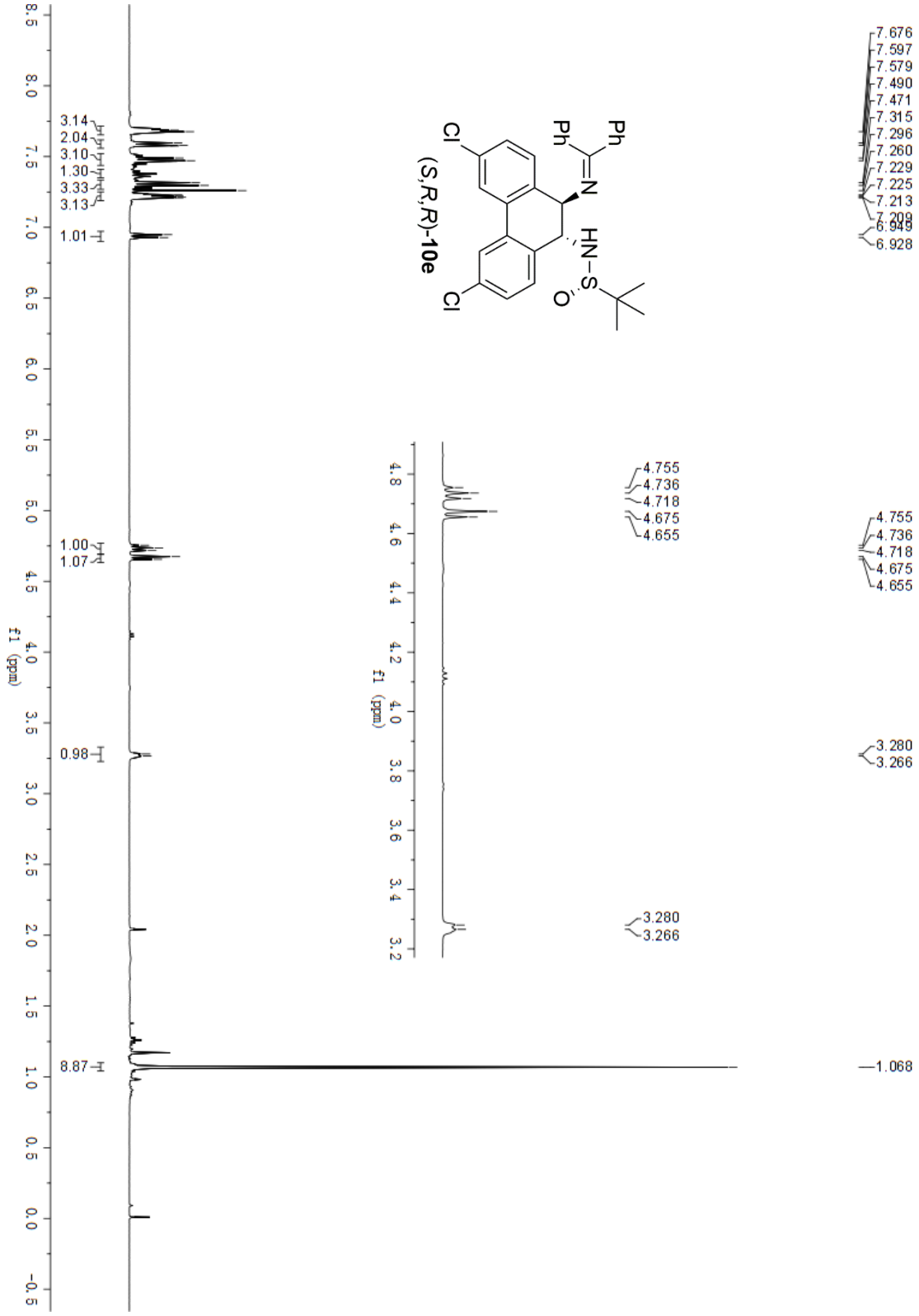

(S,R,R)-10c (major)
+
(S,S,S)-10c (minor)
F
Ph
Ph
N
HN
S
O
F
f1 (ppm)
171.484
170.331
163.931
163.747
163.695
161.466
161.237
161.147
139.395
138.965
138.660
138.587
137.938
137.768
137.696
136.128
130.667
130.562
129.246
129.214
129.165
129.133
129.074
129.019
128.987
128.948
128.939
128.846
128.124
128.089
127.512
127.256
125.785
125.705
125.605
125.524
115.618
115.563
115.404
115.334
115.200
115.126
114.987
114.901
114.785
114.676
114.559
77.478
77.160
76.842
66.126
66.114
65.826
65.815
61.441
59.583
56.579
56.316
22.736
22.454

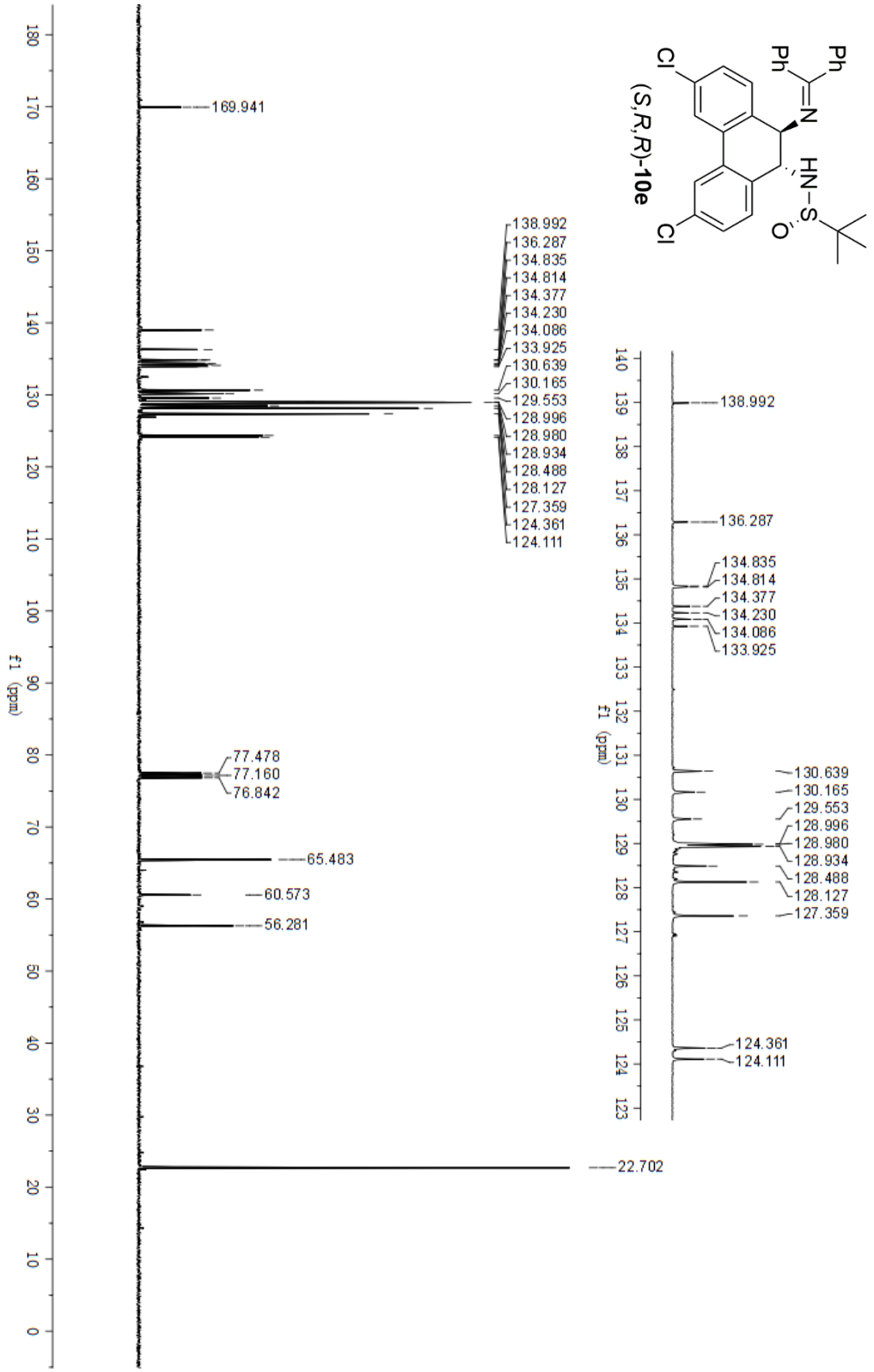

(S,R,R)-10d
F3C
CF3
Ph
Ph
N
HN
S
O
0.99
2.05
1.09
1.00
4.91
1.03
1.66
1.83
0.96
2.00
0.99
9.00
f1 (ppm)
4.862
4.846
4.829
4.814
4.798
3.215
3.201
8.032
7.964
7.943
7.939
7.917
7.733
7.730
7.713
7.710
7.665
7.663
7.645
7.642
7.571
7.566
7.550
7.532
7.520
7.503
7.372
7.367
7.356
7.353
7.350
7.297
7.278
7.260
7.256
7.252
7.235
7.160
1.024

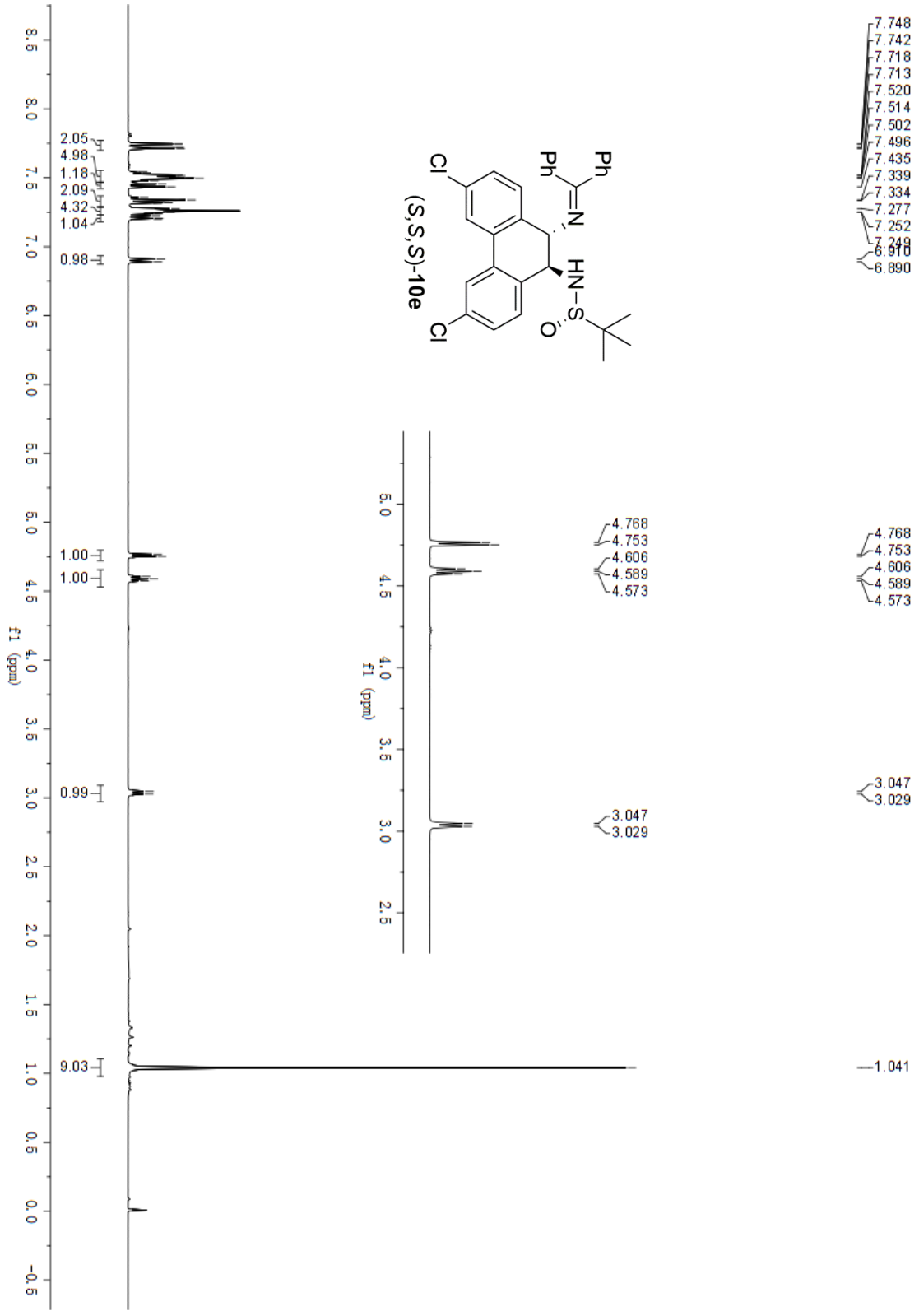

138.877
137.324
136.754
136.295
135.973
135.637
131.878
131.552
131.341
131.226
131.018
130.900
130.824
130.694
130.371
129.182
128.947
128.200
128.063
128.043
127.430
126.269
126.234
126.198
126.160
126.106
126.072
126.035
125.999
125.630
125.594
125.563
125.501
125.465
125.427
125.390
125.356
125.337
125.115
124.946
122.647
122.634
119.942
119.930
170.656
77.477
77.160
76.842
65.154
59.895
56.328
22.531
f1 (ppm)
131.878
131.552
131.341
131.226
131.018
130.900
130.824
130.694
130.371
f1 (ppm)
F3C
Ph
Ph
N
HN
S
O
CF3
(S,R,R)-10d
128.200
128.063
128.043
127.430
126.234
126.198
126.072
126.035
125.630
125.594
125.465
125.427
125.115
124.946
122.647
122.634
119.942
119.930
f1 (ppm)

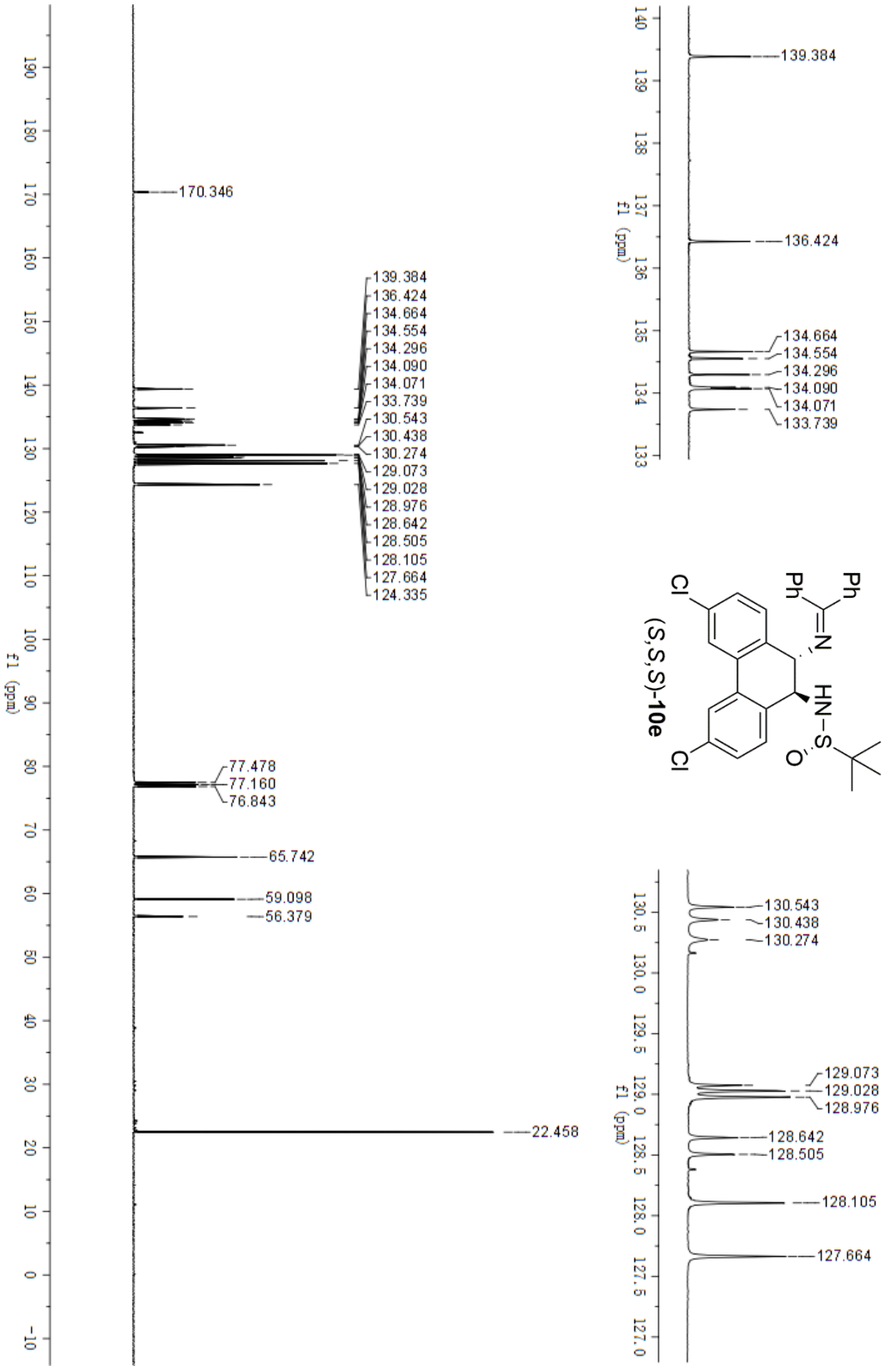

(S,S,S)-10d
F3C
CF3
Ph
Ph
N
HN
S
O
f1 (ppm)
2.05
0.95
1.06
1.02
4.95
1.77
1.89
0.82
0.99
1.00
1.02
0.99
8.81
4.881
4.865
4.784
4.767
4.750
3.205
3.196
3.189
7.957
7.937
7.928
7.908
7.828
7.725
7.722
7.705
7.702
7.663
7.660
7.643
7.640
7.541
7.528
7.522
7.510
7.505
7.501
7.489
7.362
7.347
7.344
7.340
7.295
7.292
7.276
7.269
7.264
7.260
7.249
7.211
1.074

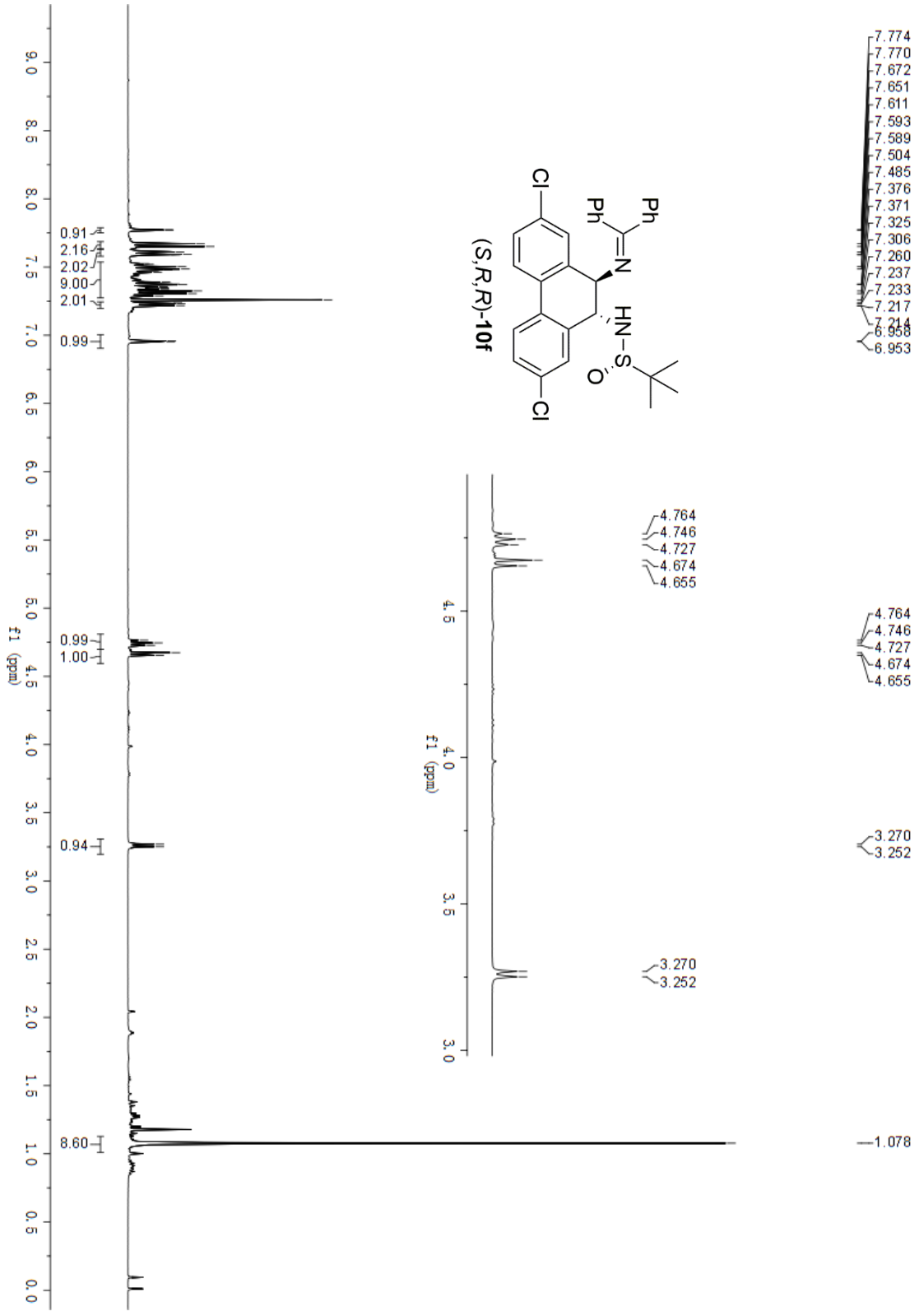

(S,S,S)-10d
F3C
CF3
Ph
Ph
N
HN
S
O
f1 (ppm)
171.519
139.218
137.063
136.561
136.274
135.823
135.596
131.495
131.368
131.173
131.043
130.847
130.771
130.523
130.393
129.276
129.169
129.068
128.188
128.017
127.594
126.944
125.928
125.895
125.854
125.823
125.785
125.722
125.685
125.648
125.612
125.575
125.451
125.311
124.952
122.746
122.604
120.040
119.897
77.477
77.160
76.842
65.652
59.178
56.615
22.458

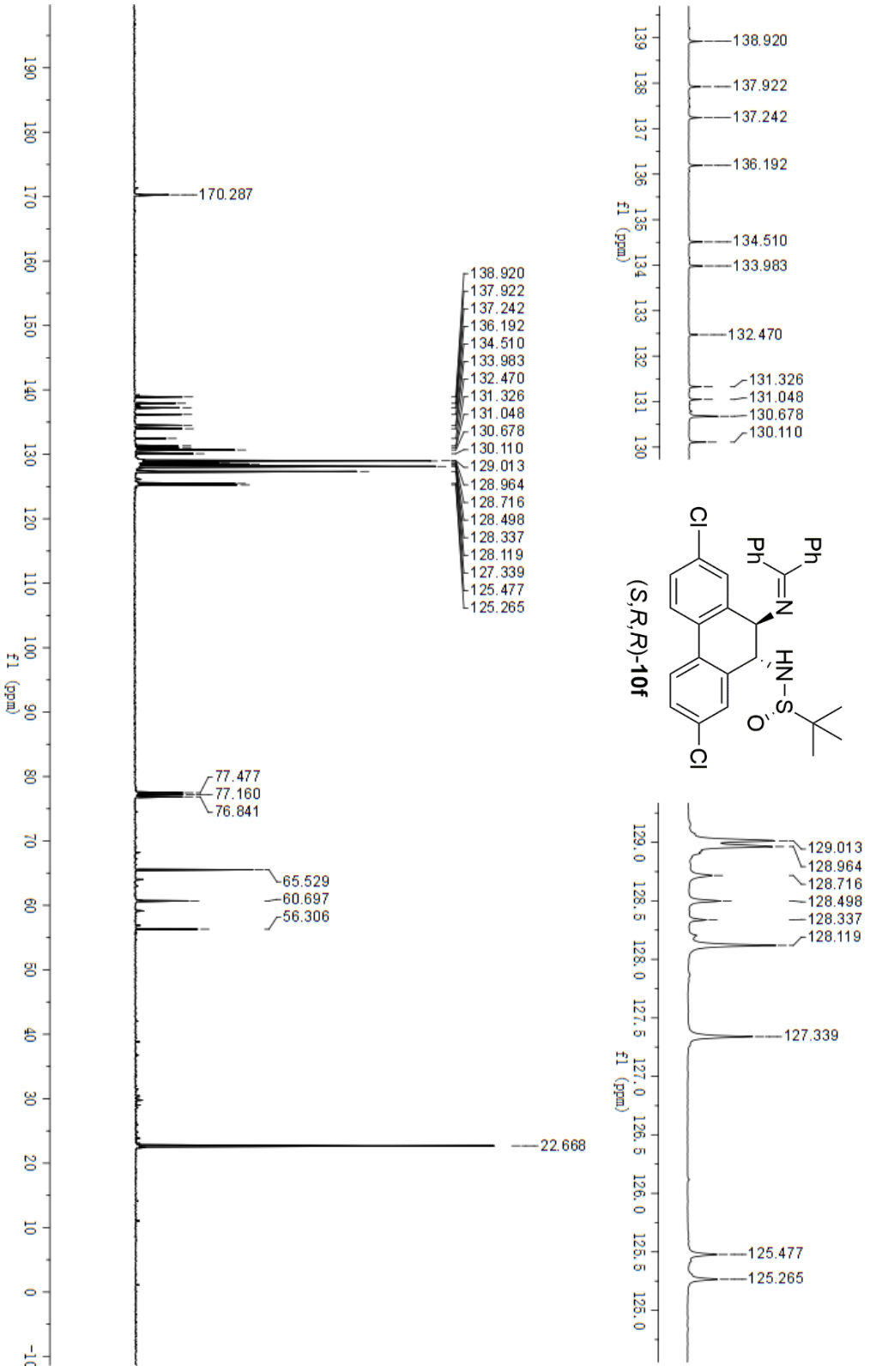

(S,R,R)-10e
Cl
Cl
Ph
Ph
N
HN
S
O
f1 (ppm)
3.14
2.04
3.10
1.30
3.33
3.13
1.01
1.00
1.07
0.98
8.87
7.676
7.597
7.579
7.490
7.471
7.315
7.296
7.260
7.229
7.225
7.213
7.209
6.949
6.928
4.755
4.736
4.718
4.675
4.655
3.280
3.266
1.068

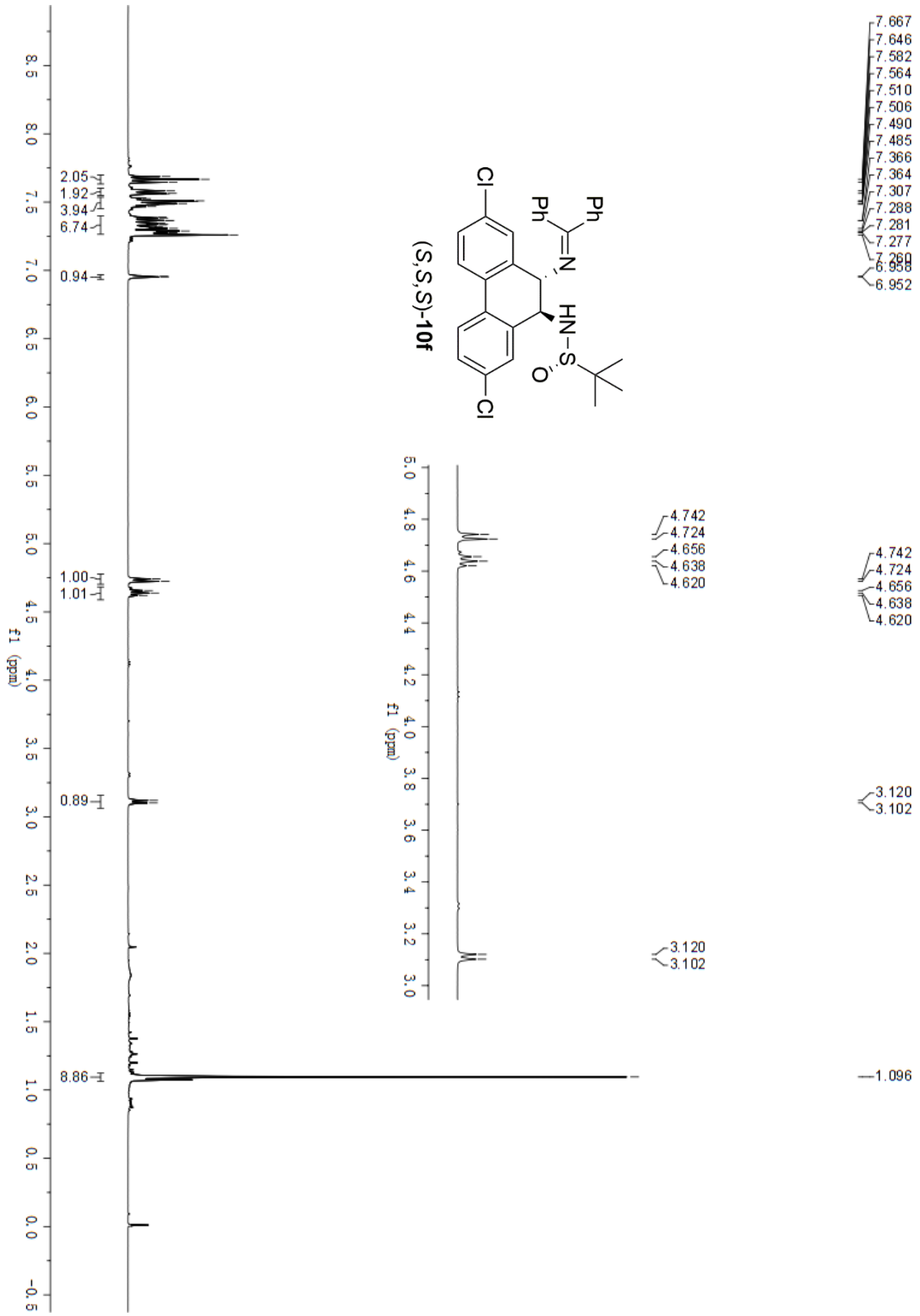

(S,R,R)-10e
Cl
Ph
Ph
N
HN
S
O
Cl
169.941
138.992
136.287
134.835
134.814
134.377
134.230
134.086
133.925
130.639
130.165
129.553
128.996
128.980
128.934
128.488
128.127
127.359
124.361
124.111
77.478
77.160
76.842
65.483
60.573
56.281
22.702
f1 (ppm)

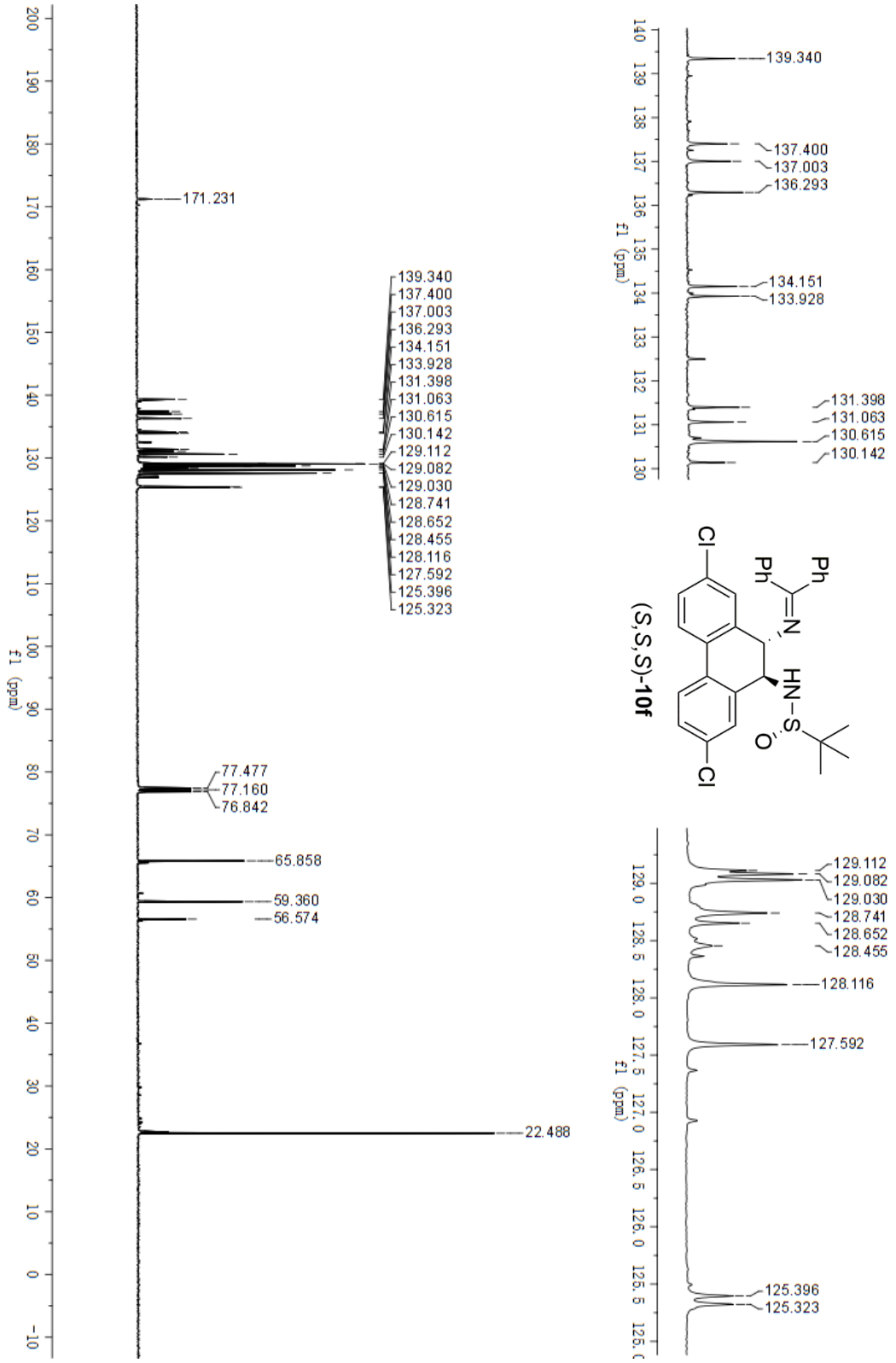

(S,S,S)-10e
Cl
Cl
Ph
Ph
N
HN
S
O
2.05
4.98
1.18
2.09
4.32
1.04
0.98
1.00
1.00
0.99
9.03
7.748
7.742
7.718
7.713
7.520
7.514
7.502
7.496
7.435
7.339
7.334
7.277
7.252
7.249
6.910
6.890
4.768
4.753
4.606
4.589
4.573
3.047
3.029
1.041
f1 (ppm)

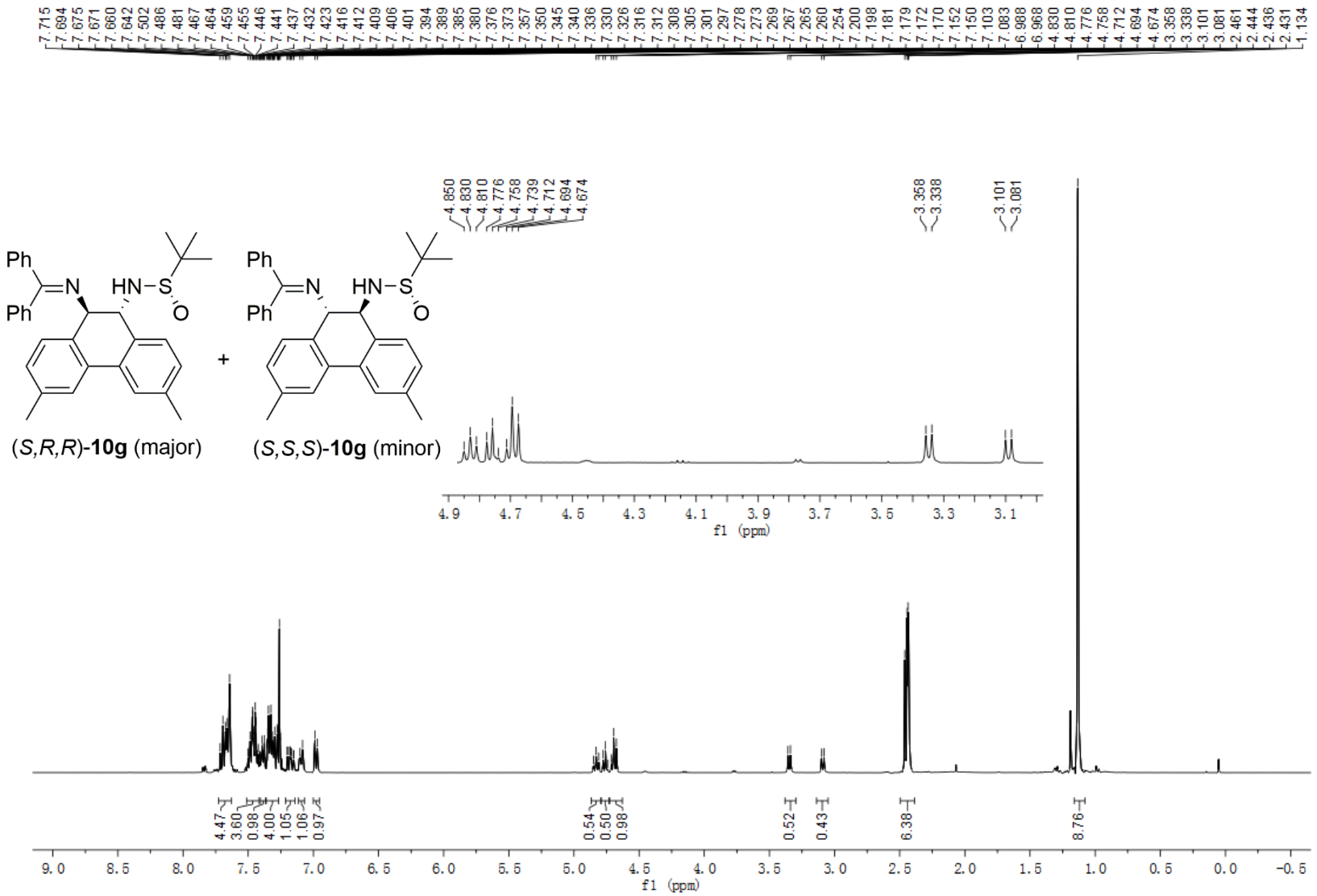

170.346
139.384
136.424
134.664
134.554
134.296
134.090
134.071
133.739
130.543
130.438
130.274
129.073
129.028
128.976
128.642
128.505
128.105
127.664
124.335
77.478
77.160
76.843
65.742
59.098
56.379
22.458
f1 (ppm)
(S,S,S)-10e
Cl
Ph
N
HN
S
O
Cl
Ph

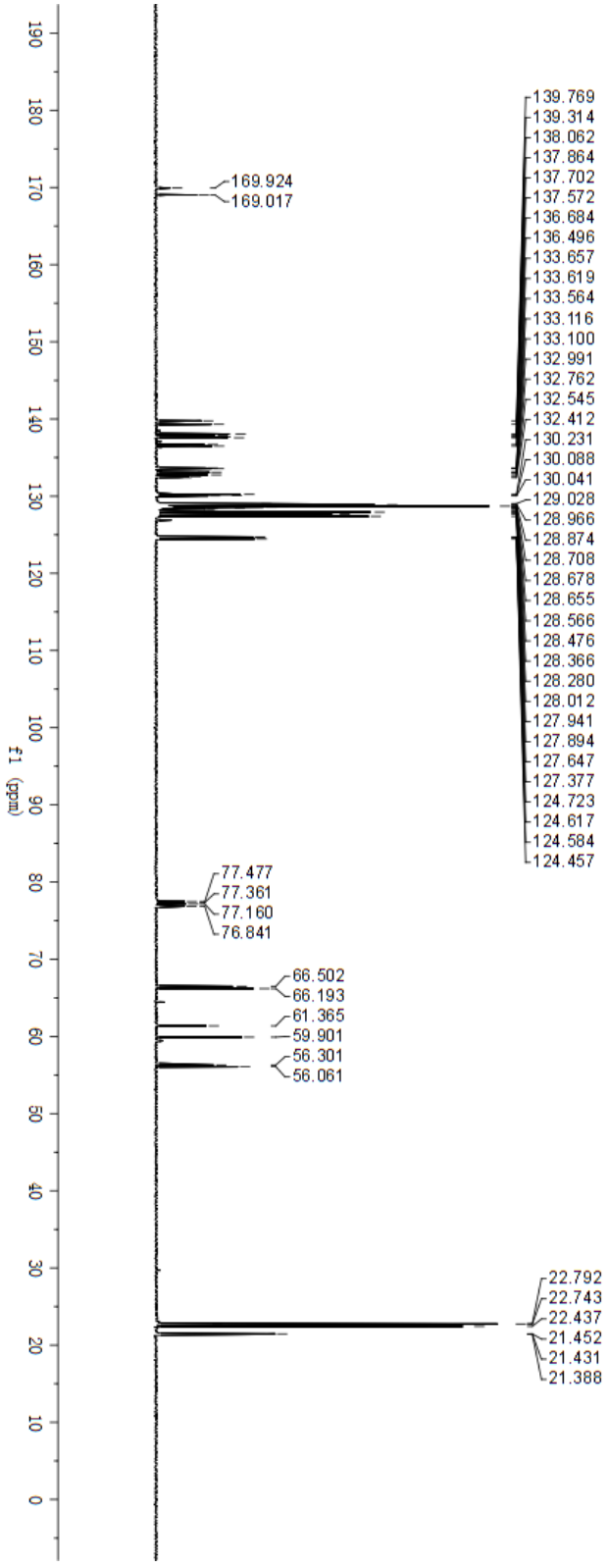

(S,R,R)-10f
Cl
Ph
Ph
N
HN
S
O
Cl
7.774
7.770
7.672
7.651
7.611
7.593
7.589
7.504
7.485
7.376
7.371
7.325
7.306
7.260
7.237
7.233
7.217
7.214
6.958
6.953
4.764
4.746
4.727
4.674
4.655
3.270
3.252
1.078
0.91
2.16
2.02
9.00
2.01
0.99
0.99
1.00
0.94
8.60
f1 (ppm)

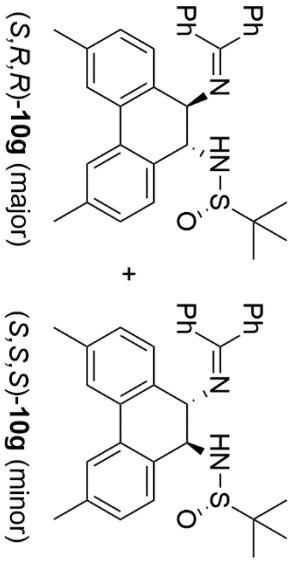

170.287
138.920
137.922
137.242
136.192
134.510
133.983
132.470
131.326
131.048
130.678
130.110
129.013
128.964
128.716
128.498
128.337
128.119
127.339
125.477
125.265
77.477
77.160
76.841
65.529
60.697
56.306
22.668
f1 (ppm)
(S,R,R)-10f
Cl
Ph
Ph
N
HN
S
O
Cl

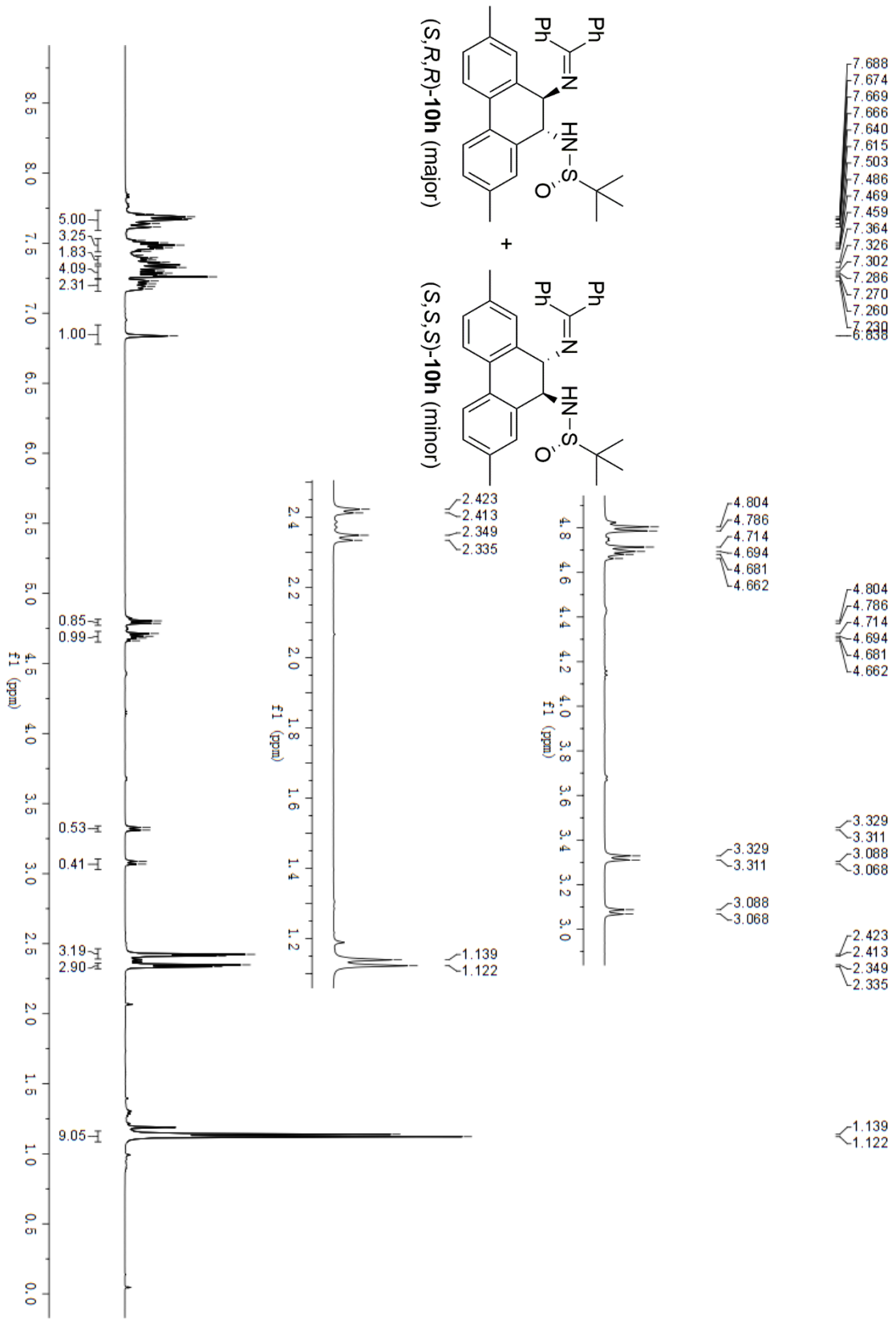

(S,S,S)-10f
Cl
Cl
Ph
Ph
N
HN
S
O
7.667
7.646
7.582
7.564
7.510
7.506
7.490
7.485
7.366
7.364
7.307
7.288
7.281
7.277
7.260
6.958
6.952
4.742
4.724
4.656
4.638
4.620
3.120
3.102
1.096
2.05
1.92
3.94
6.74
0.94
1.00
1.01
0.89
8.86
f1 (ppm)

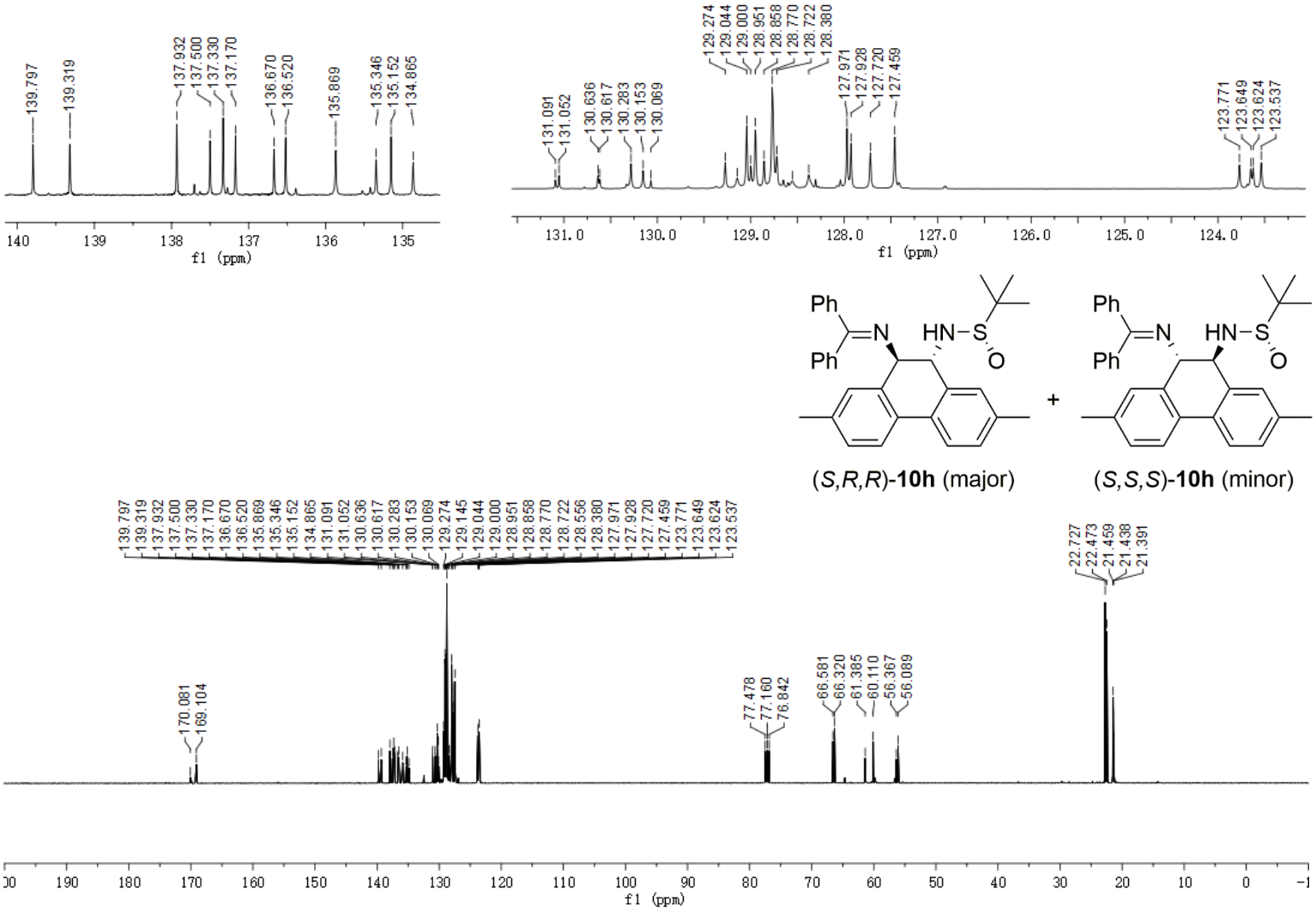

171.231
139.340
137.400
137.003
136.293
134.151
133.928
131.398
131.063
130.615
130.142
129.112
129.082
129.030
128.741
128.652
128.455
128.116
127.592
125.396
125.323
77.477
77.160
76.842
65.858
59.360
56.574
22.488
f1 (ppm)
(S,S,S)-10f
Cl
Ph
Ph
N
HN
S
O
Cl

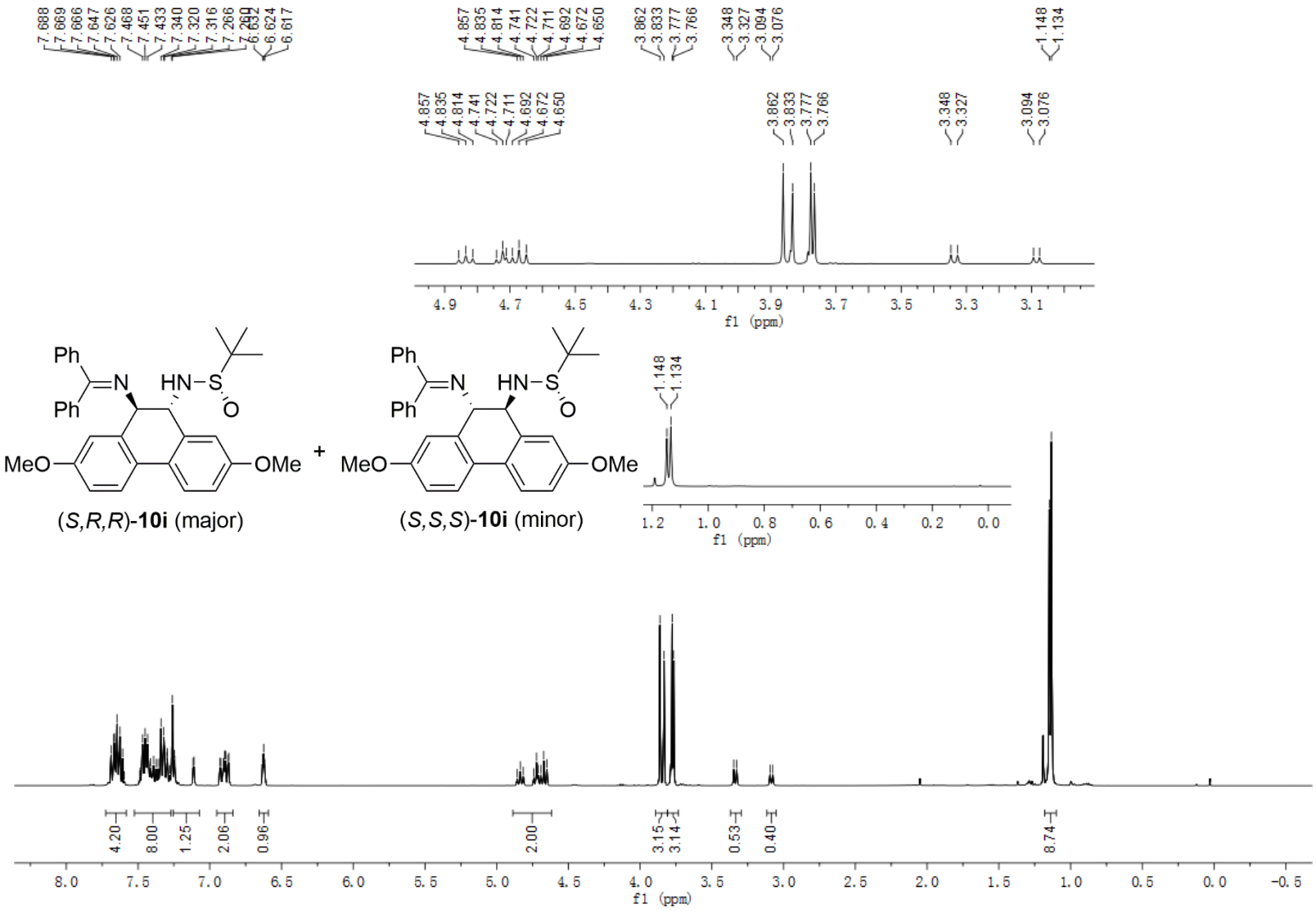

(S,R,R)-10g (major)
(S,S,S)-10g (minor)
f1 (ppm)
f1 (ppm)

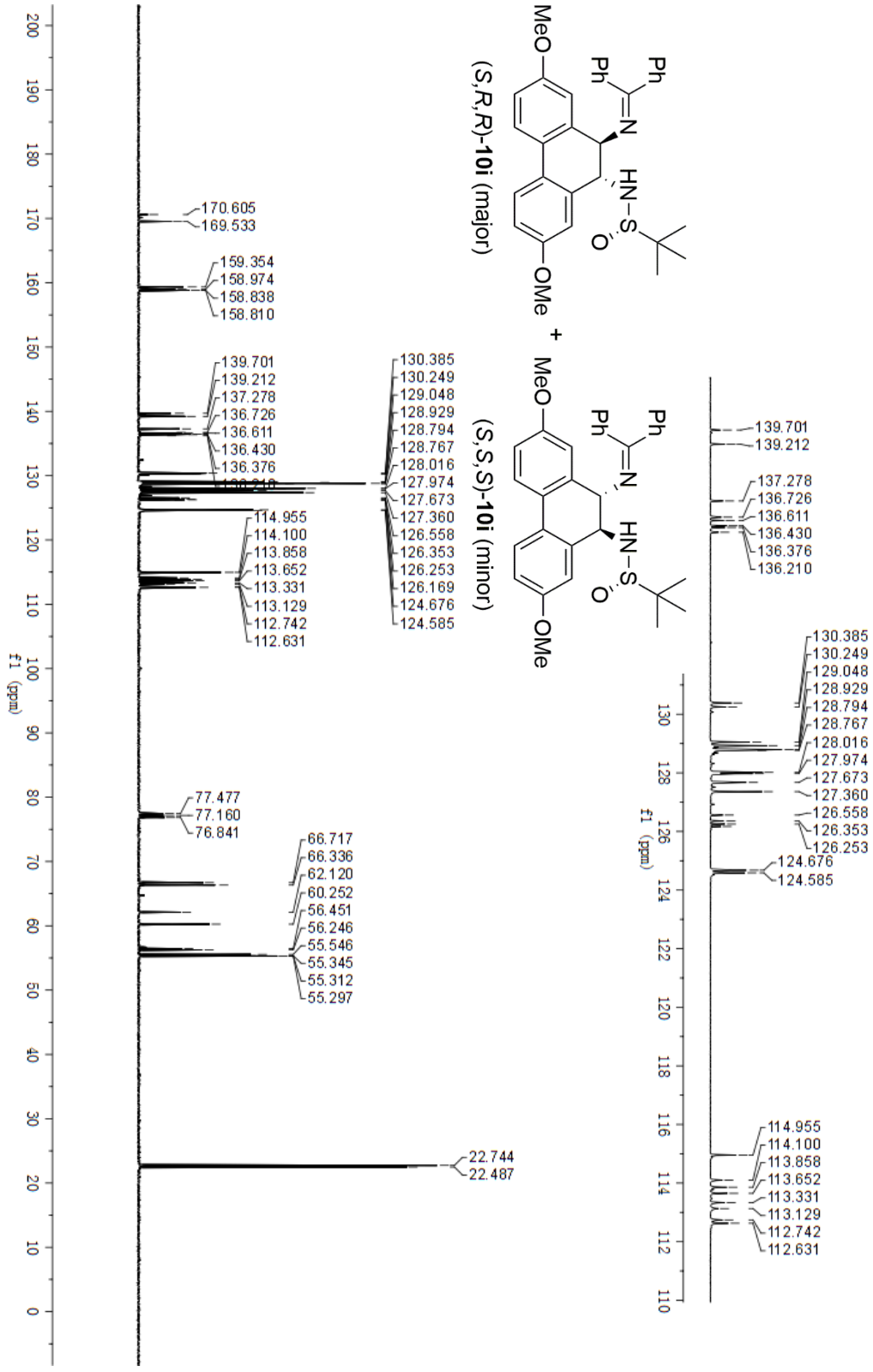

f1 (ppm)
169.924
169.017
139.769
139.314
138.062
137.864
137.702
137.572
136.684
136.496
133.657
133.619
133.564
133.116
133.100
132.991
132.762
132.545
132.412
130.231
130.088
130.041
129.028
128.966
128.874
128.708
128.678
128.655
128.566
128.476
128.366
128.280
128.012
127.941
127.894
127.647
127.377
124.723
124.617
124.584
124.457
77.477
77.361
77.160
76.841
66.502
66.193
61.365
59.901
56.301
56.061
22.792
22.743
22.437
21.452
21.431
21.388

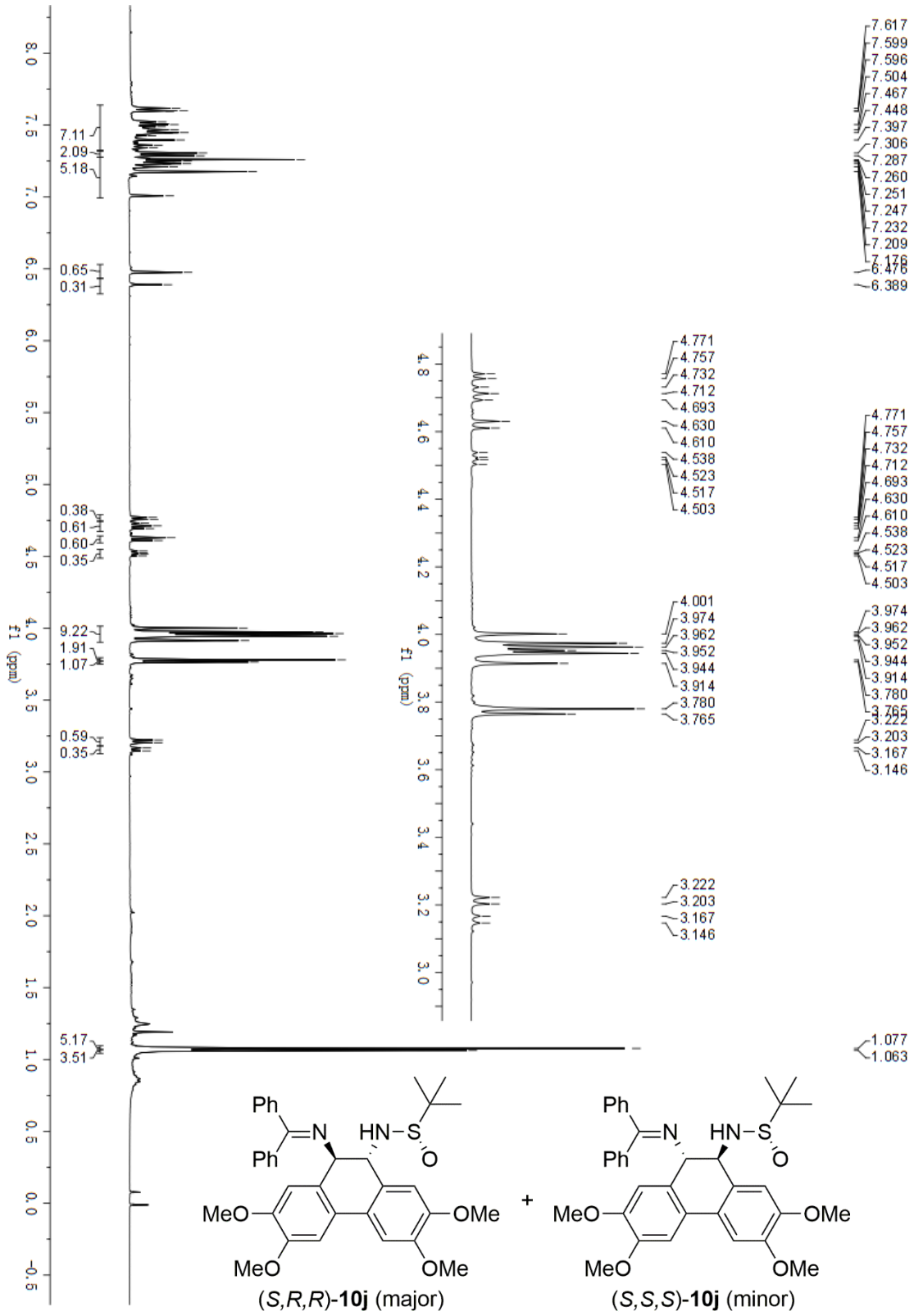

(S,R,R)-10g (major)
+
(S,S,S)-10g (minor)
Ph
Ph
N
HN
S
O

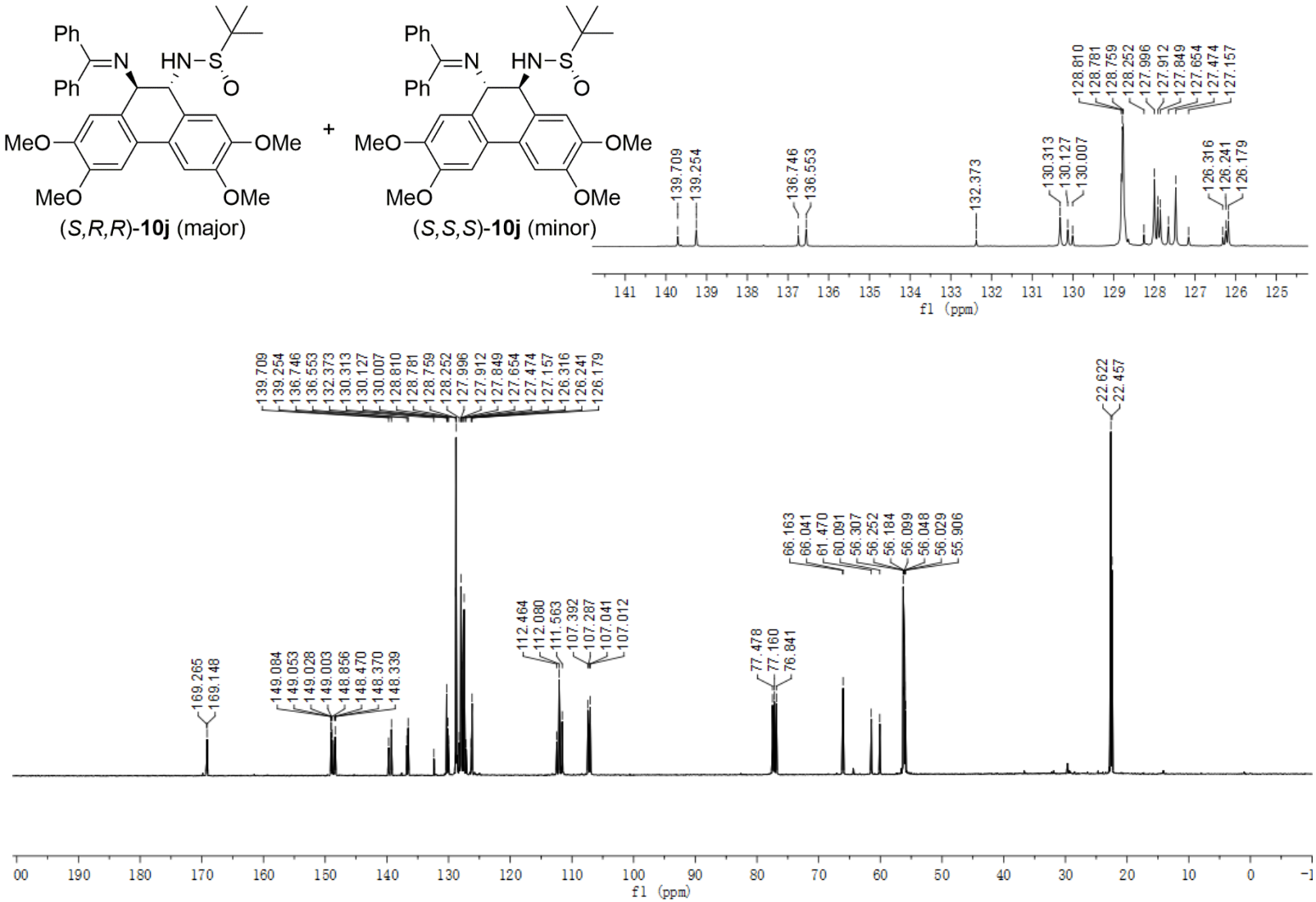

(S,R,R)-10h (major)
+
(S,S,S)-10h (minor)
Ph
Ph
N
HN
S
O
5.00
3.25
1.83
4.09
2.31
1.00
0.85
0.99
0.53
0.41
3.19
2.90
9.05
f1 (ppm)
7.688
7.674
7.669
7.666
7.640
7.615
7.503
7.486
7.469
7.459
7.364
7.326
7.302
7.286
7.270
7.260
6.638
4.804
4.786
4.714
4.694
4.681
4.662
3.329
3.311
3.088
3.068
2.423
2.413
2.349
2.335
1.139
1.122

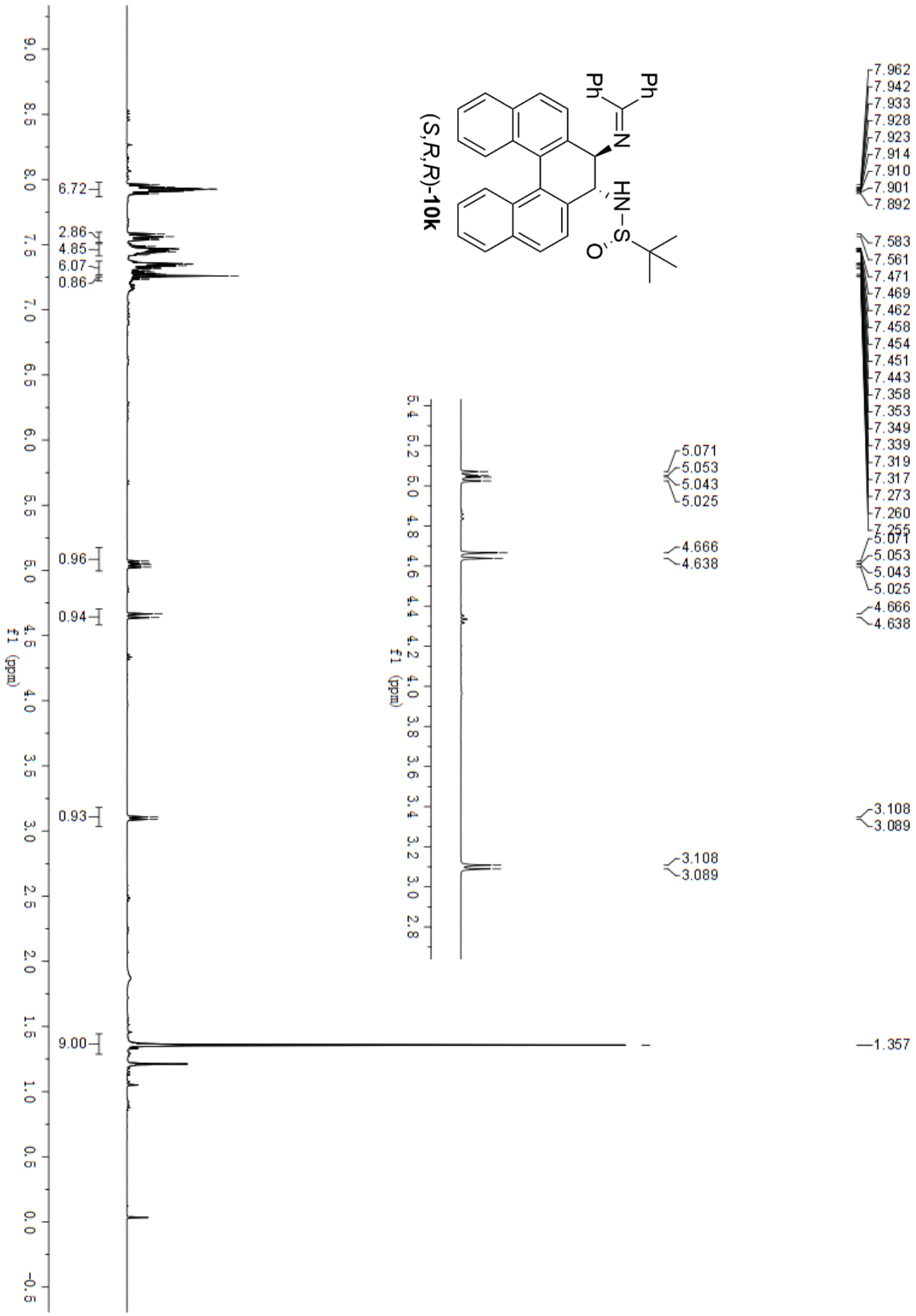

139.797
139.319
137.932
137.500
137.330
137.170
136.670
136.520
135.869
135.346
135.152
134.865
f1 (ppm)
131.091
131.052
130.636
130.617
130.283
130.153
130.069
129.274
129.044
129.000
128.951
128.858
128.770
128.722
128.380
127.971
127.928
127.720
127.459
123.771
123.649
123.624
123.537
Ph
N
HN−S
O
Ph
+
(S,R,R)-10h (major)
(S,S,S)-10h (minor)
170.081
169.104
77.478
77.160
76.842
66.581
66.320
61.385
60.110
56.367
56.089
22.727
22.473
21.459
21.438
21.391

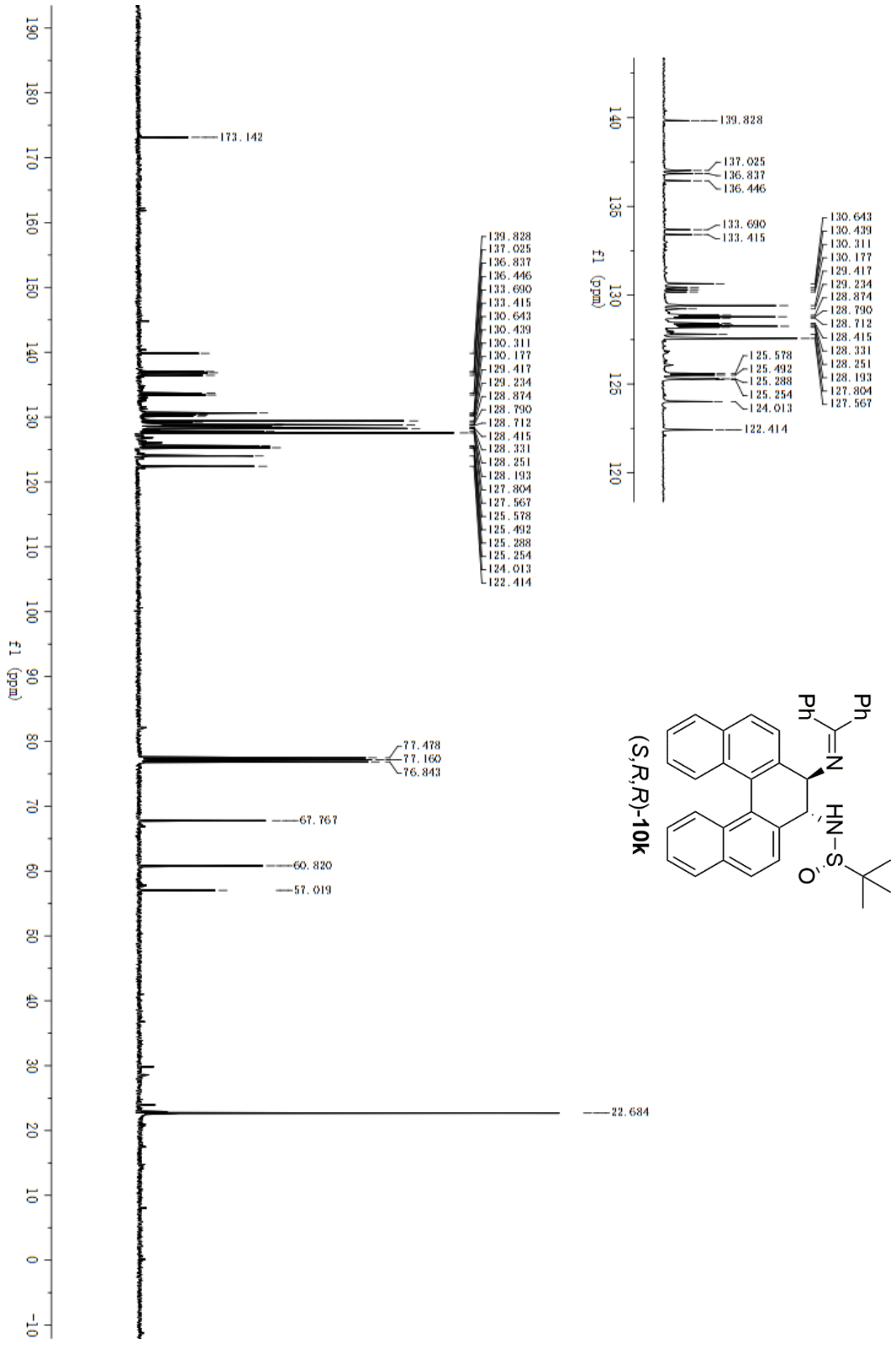

(S,R,R)-10i (major)
(S,S,S)-10i (minor)
f1 (ppm)


(S,R,R)-10i (major)
(S,S,S)-10i (minor)
MeO
OMe
Ph
Ph
N
HN
S
O
f1 (ppm)
170.605
169.533
159.354
158.974
158.838
158.810
139.701
139.212
137.278
136.726
136.611
136.430
136.376
130.385
130.249
129.048
128.929
128.794
128.767
128.016
127.974
127.673
127.360
126.558
126.353
126.253
126.169
124.676
124.585
114.955
114.100
113.858
113.652
113.331
113.129
112.742
112.631
77.477
77.160
76.841
66.717
66.336
62.120
60.252
56.451
56.246
55.546
55.345
55.312
55.297
22.744
22.487

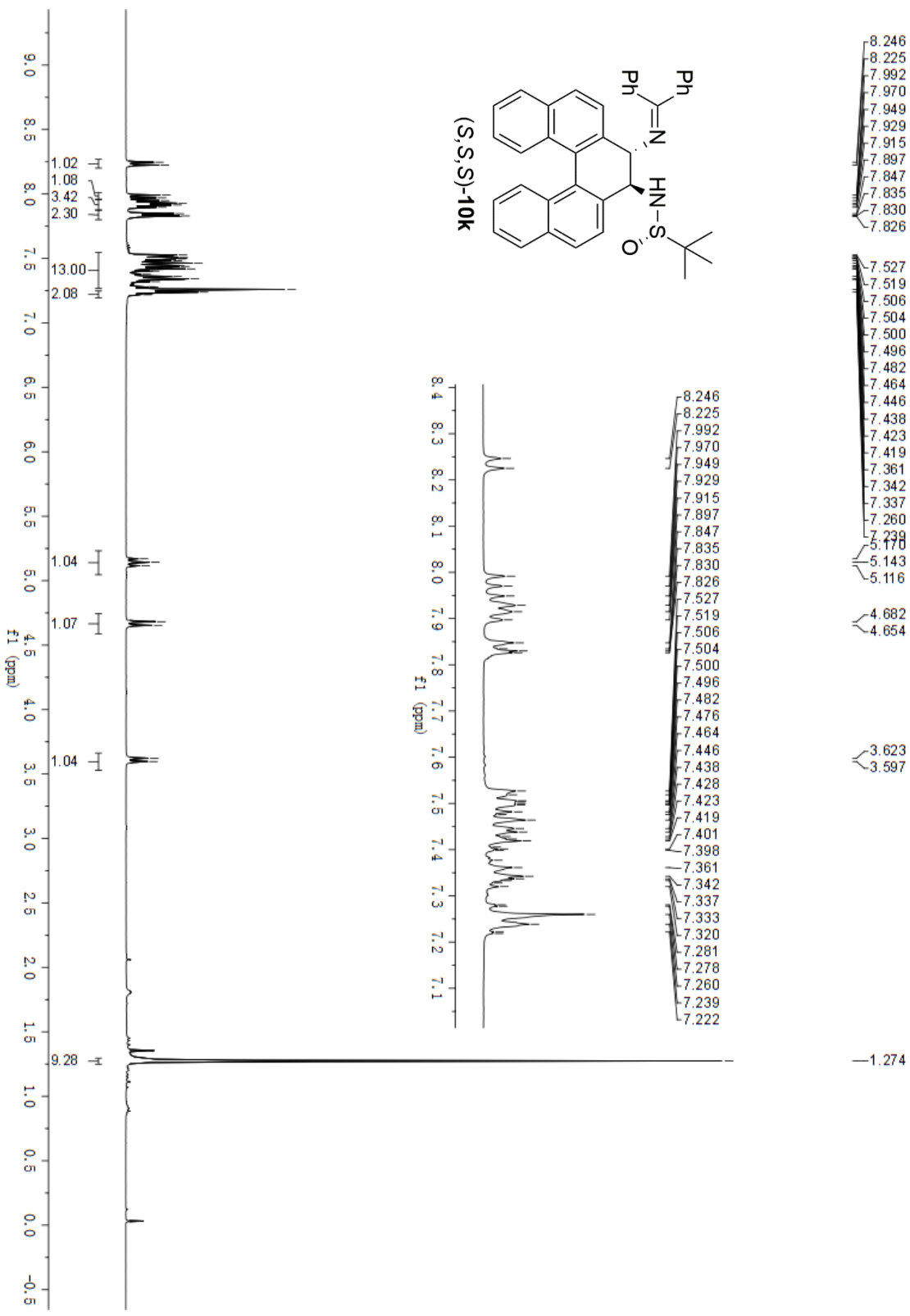

7.617
7.599
7.596
7.504
7.467
7.448
7.397
7.306
7.287
7.260
7.251
7.247
7.232
7.209
7.176
6.476
6.389
4.771
4.757
4.732
4.712
4.693
4.630
4.610
4.538
4.523
4.517
4.503
4.001
3.974
3.962
3.952
3.944
3.914
3.780
3.765
3.222
3.203
3.167
3.146
1.077
1.063
7.11
2.09
5.18
0.65
0.31
0.38
0.61
0.60
0.35
9.22
1.91
1.07
0.59
0.35
5.17
3.51
f1 (ppm)
Ph
N
HN
S
O
Ph
MeO
OMe
MeO
OMe
+
(S,R,R)-10j (major)
(S,S,S)-10j (minor)

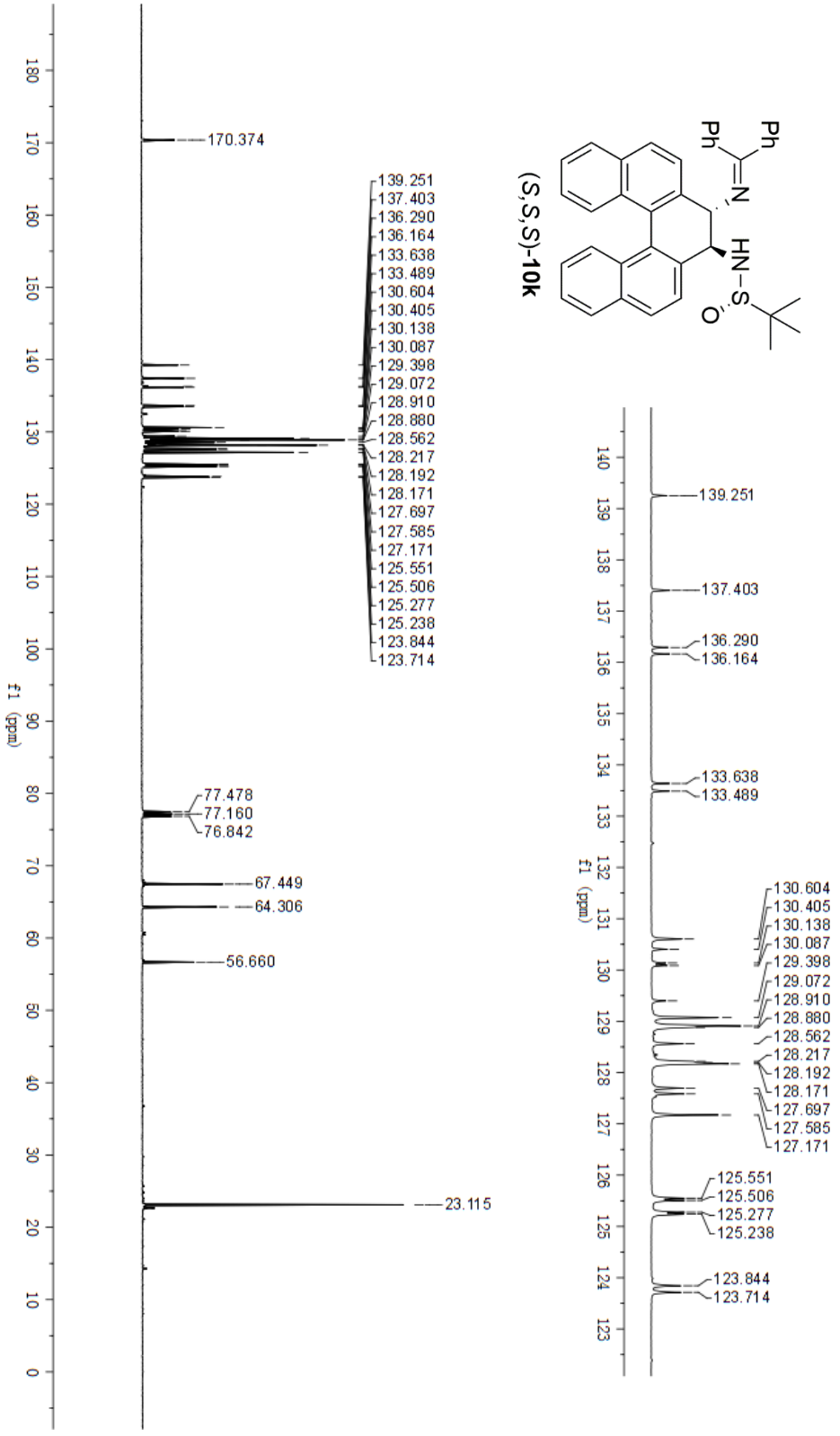

Ph
N
HN−S
O
Ph
MeO
OMe
MeO
OMe
(S,R,R)-10j (major)
+
(S,S,S)-10j (minor)
139.709
139.254
136.746
136.553
132.373
130.313
130.127
130.007
128.810
128.781
128.759
128.252
127.996
127.912
127.849
127.654
127.474
127.157
126.316
126.241
126.179
f1 (ppm)
22.622
22.457
66.163
66.041
61.470
60.091
56.307
56.252
56.184
56.099
56.048
56.029
55.906
77.478
77.160
76.841
112.464
112.080
111.563
107.392
107.287
107.041
107.012
169.265
169.148
149.084
149.053
149.028
149.003
148.856
148.470
148.370
148.339
f1 (ppm)

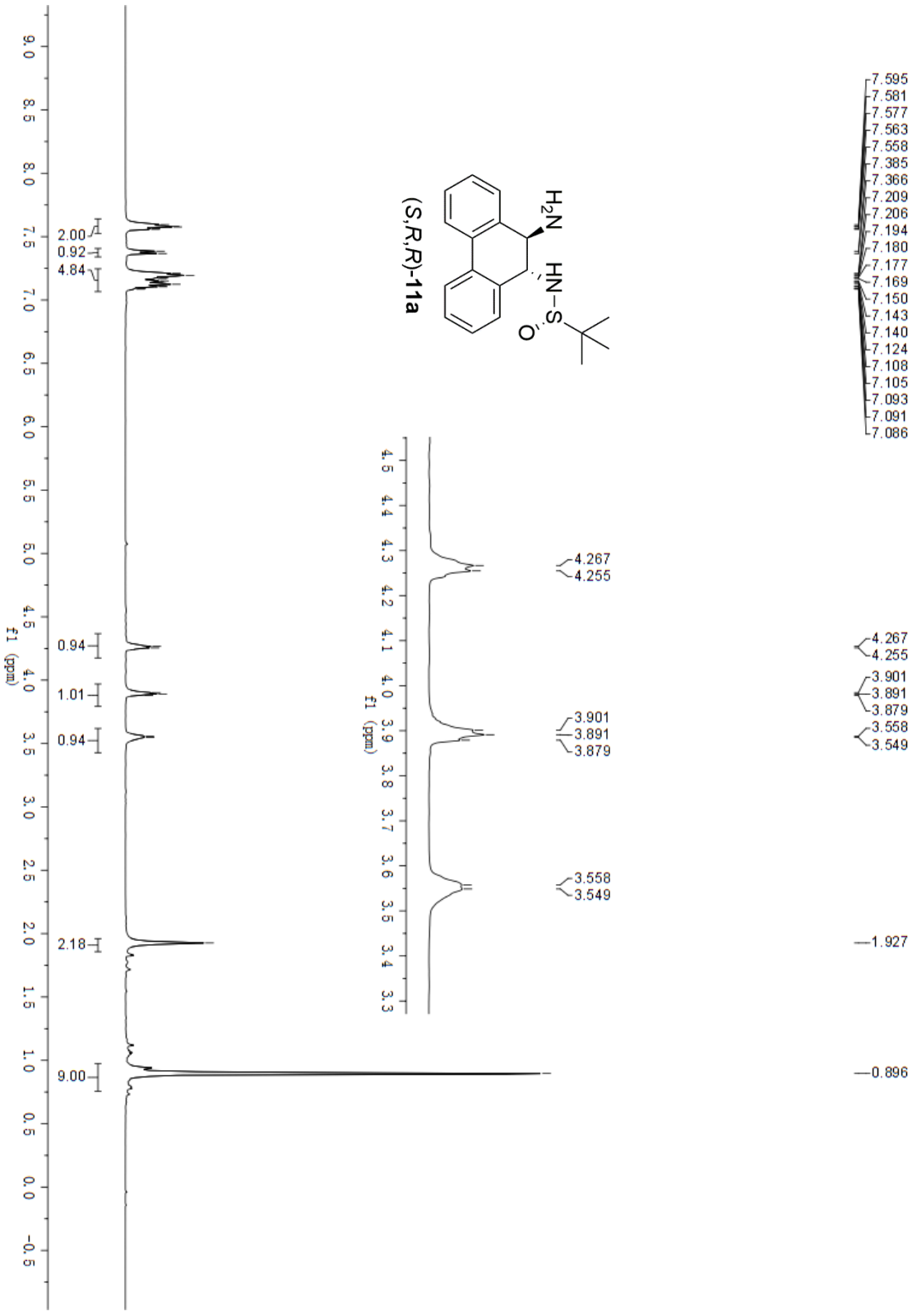

(S,R,R)-10k
Ph
Ph
N
HN
S
O
6.72
2.86
4.85
6.07
0.86
0.96
0.94
0.93
9.00
f1 (ppm)
7.962
7.942
7.933
7.928
7.923
7.914
7.910
7.901
7.892
7.583
7.561
7.471
7.469
7.462
7.458
7.454
7.451
7.443
7.358
7.353
7.349
7.339
7.319
7.317
7.273
7.260
7.255
5.071
5.053
5.043
5.025
4.666
4.638
3.108
3.089
1.357

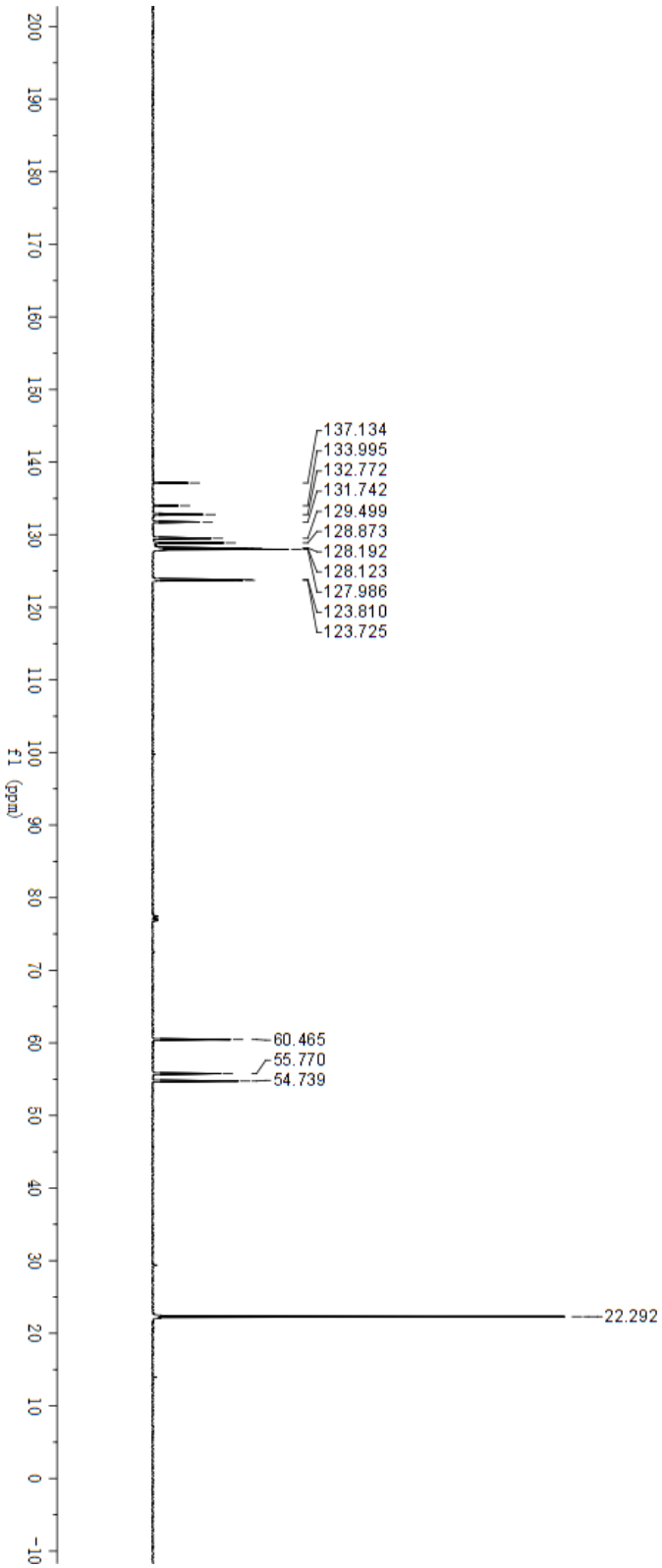

f1 (ppm)
173.142
139.828
137.025
136.837
136.446
133.690
133.415
130.643
130.439
130.311
130.177
129.417
129.234
128.874
128.790
128.712
128.415
128.331
128.251
128.193
127.804
127.567
125.578
125.492
125.288
125.254
124.013
122.414
77.478
77.160
76.843
67.767
60.820
57.019
22.684
Ph
Ph
N
HN
S
O

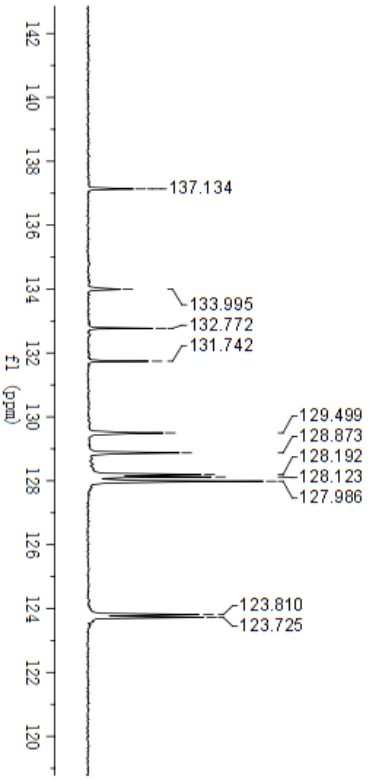
(*S*,*R*,*R*)-**10k**

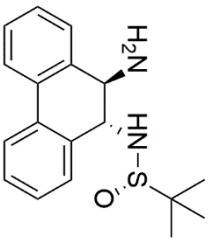

(S,S,S)-10k
Ph
Ph
N
HN
S
O
f1 (ppm)
1.02
1.08
3.42
2.30
13.00
2.08
1.04
1.07
1.04
9.28
8.246
8.225
7.992
7.970
7.949
7.929
7.915
7.897
7.847
7.835
7.830
7.826
7.527
7.519
7.506
7.504
7.500
7.496
7.482
7.476
7.464
7.446
7.438
7.428
7.423
7.419
7.401
7.398
7.361
7.342
7.337
7.333
7.320
7.281
7.278
7.260
7.239
7.222
5.170
5.143
5.116
4.682
4.654
3.623
3.597
1.274


(S,S,S)-10k
Ph
Ph
N
HN
S
O
f1 (ppm)
170.374
139.251
137.403
136.290
136.164
133.638
133.489
130.604
130.405
130.138
130.087
129.398
129.072
128.910
128.880
128.562
128.217
128.192
128.171
127.697
127.585
127.171
125.551
125.506
125.277
125.238
123.844
123.714
77.478
77.160
76.842
67.449
64.306
56.660
23.115

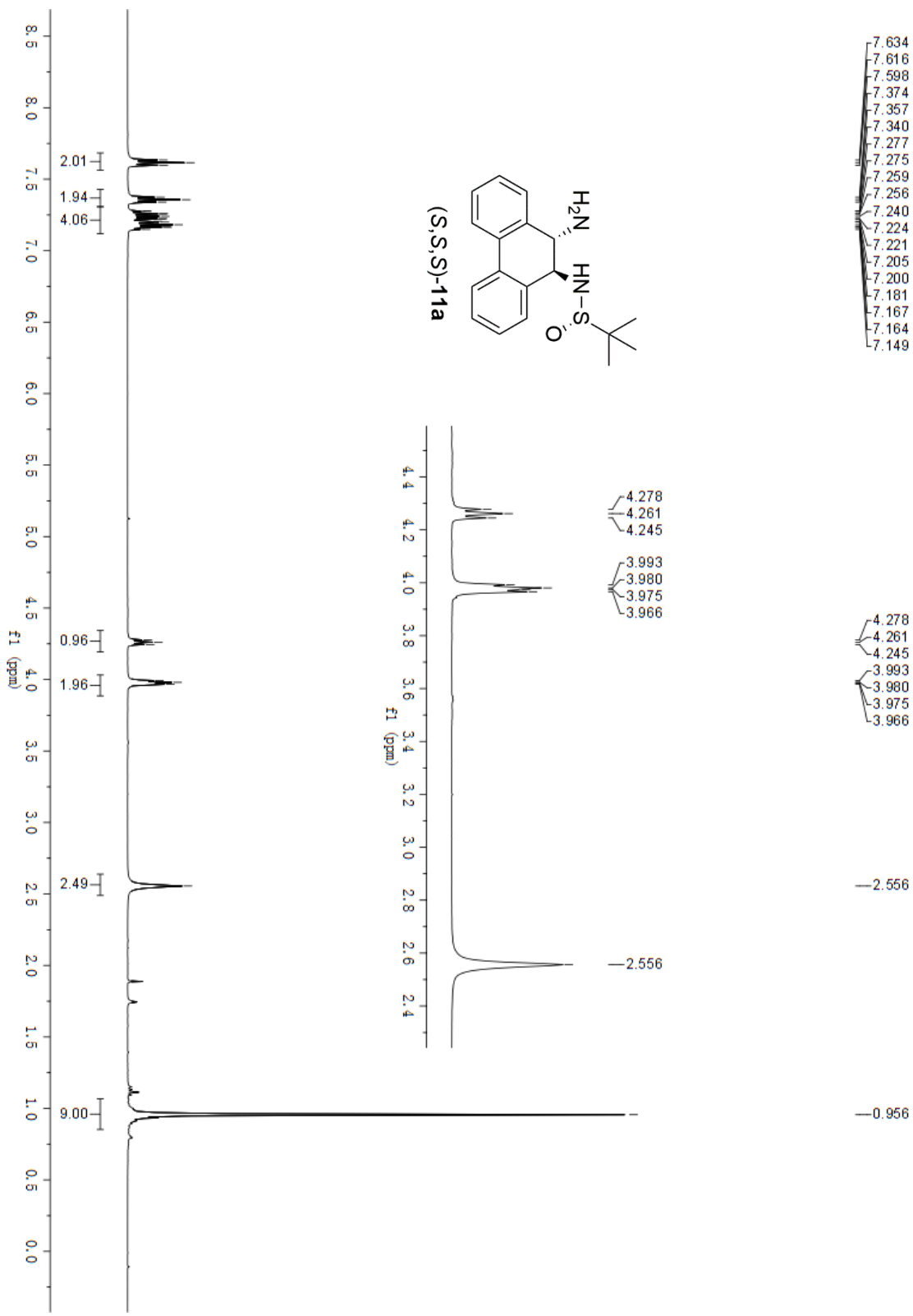

(S,R,R)-11a
H2N
HN
S
O
2.00
0.92
4.84
0.94
1.01
0.94
2.18
9.00
f1 (ppm)
7.595
7.581
7.577
7.563
7.558
7.385
7.366
7.209
7.206
7.194
7.180
7.177
7.169
7.150
7.143
7.140
7.124
7.108
7.105
7.093
7.091
7.086
4.267
4.255
3.901
3.891
3.879
3.558
3.549
1.927
0.896

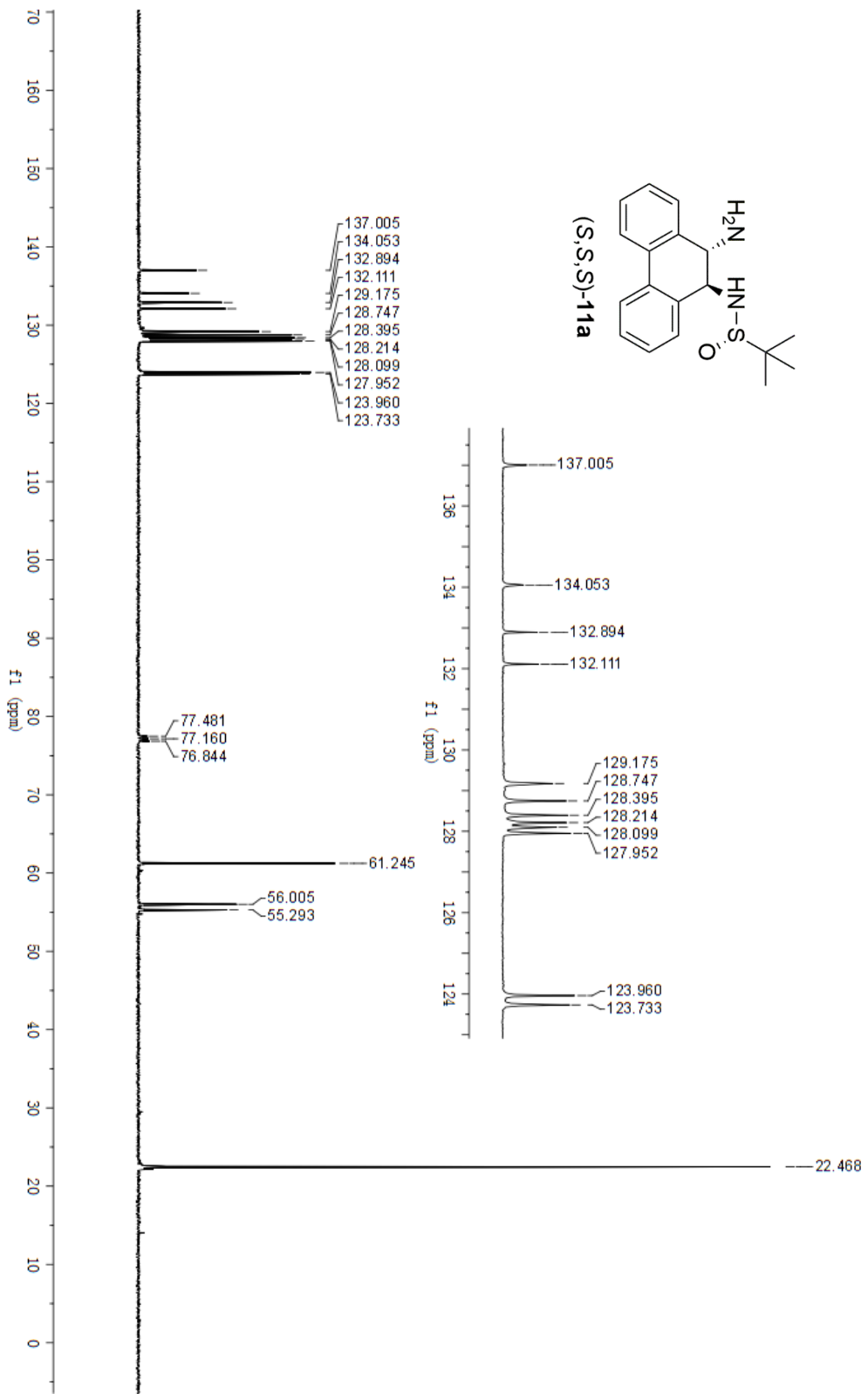

137.134
133.995
132.772
131.742
129.499
128.873
128.192
128.123
127.986
123.810
123.725
60.465
55.770
54.739
22.292
f1 (ppm)

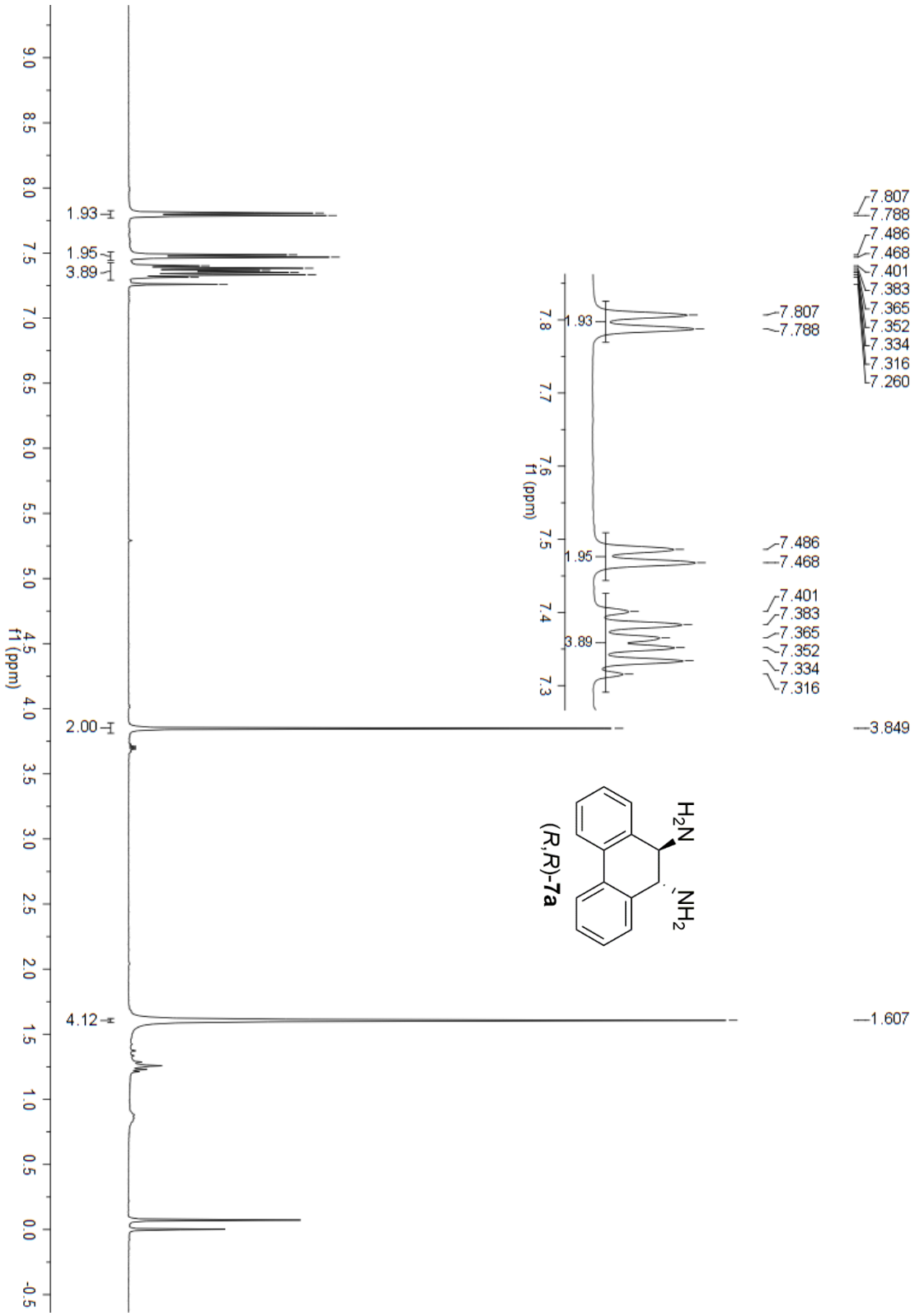

137.134
133.995
132.772
131.742
129.499
128.873
128.192
128.123
127.986
123.810
123.725
f1 (ppm)

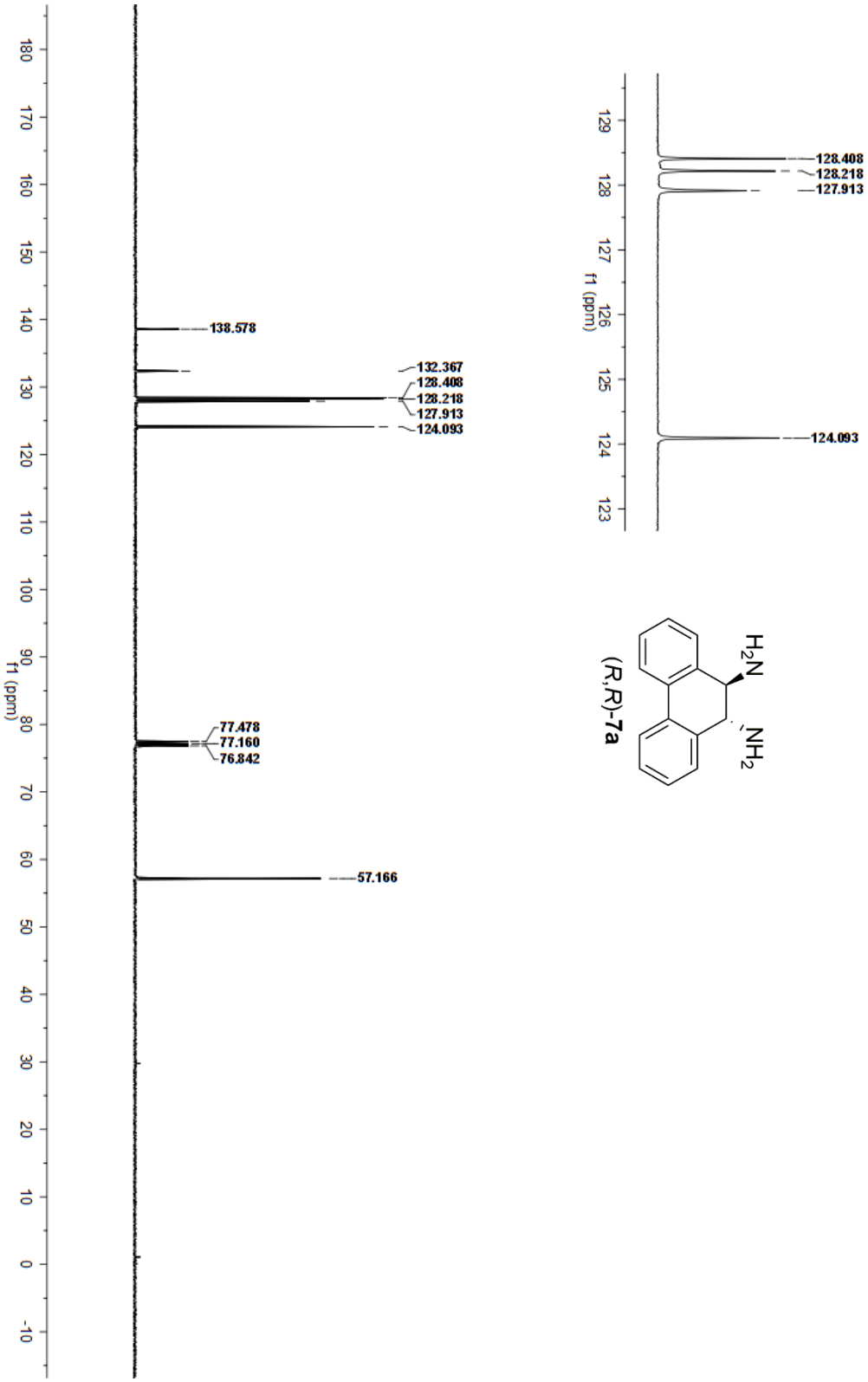

H2N
HN
S
O

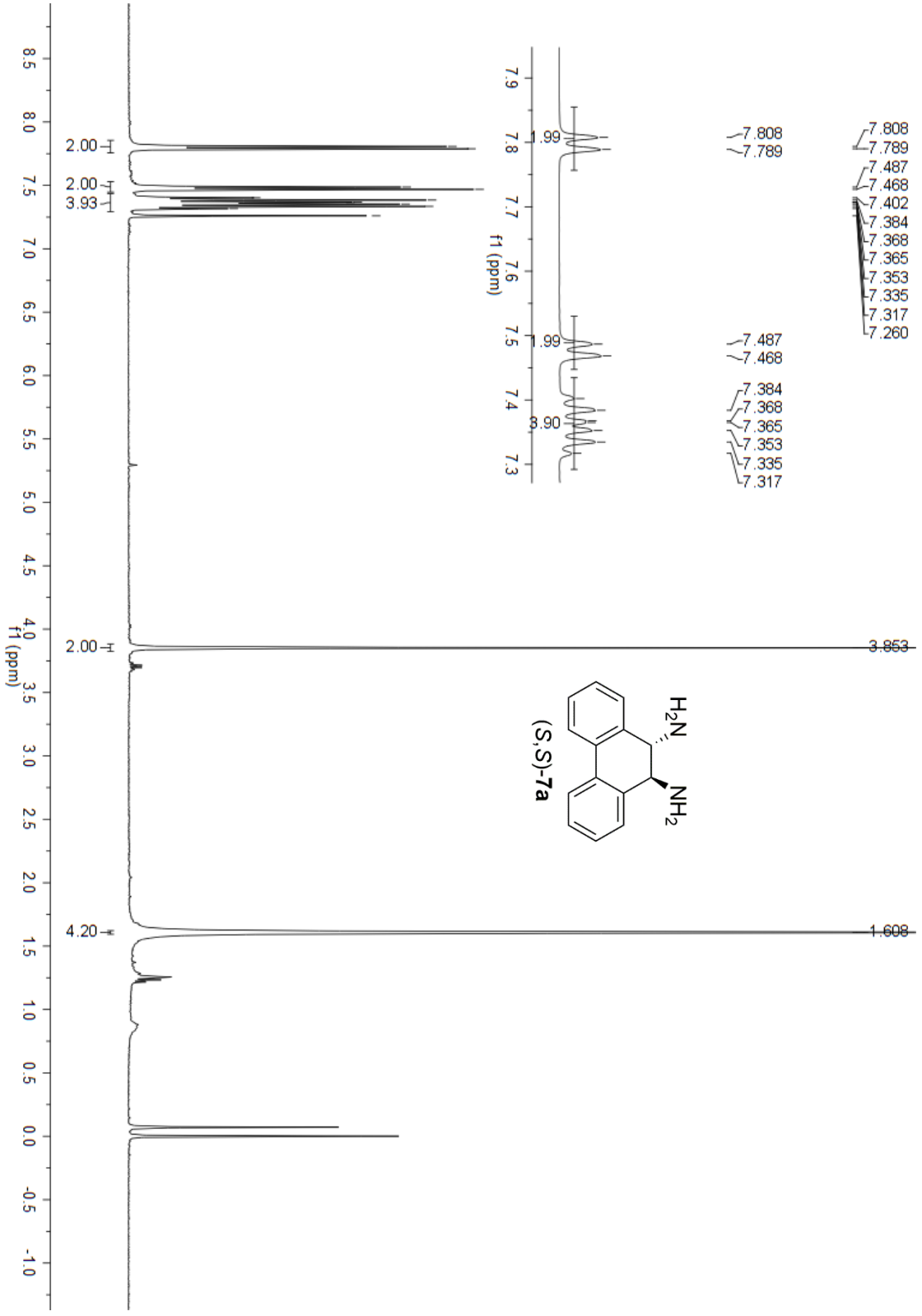
(*S*,*R*,*R*)-**11a**

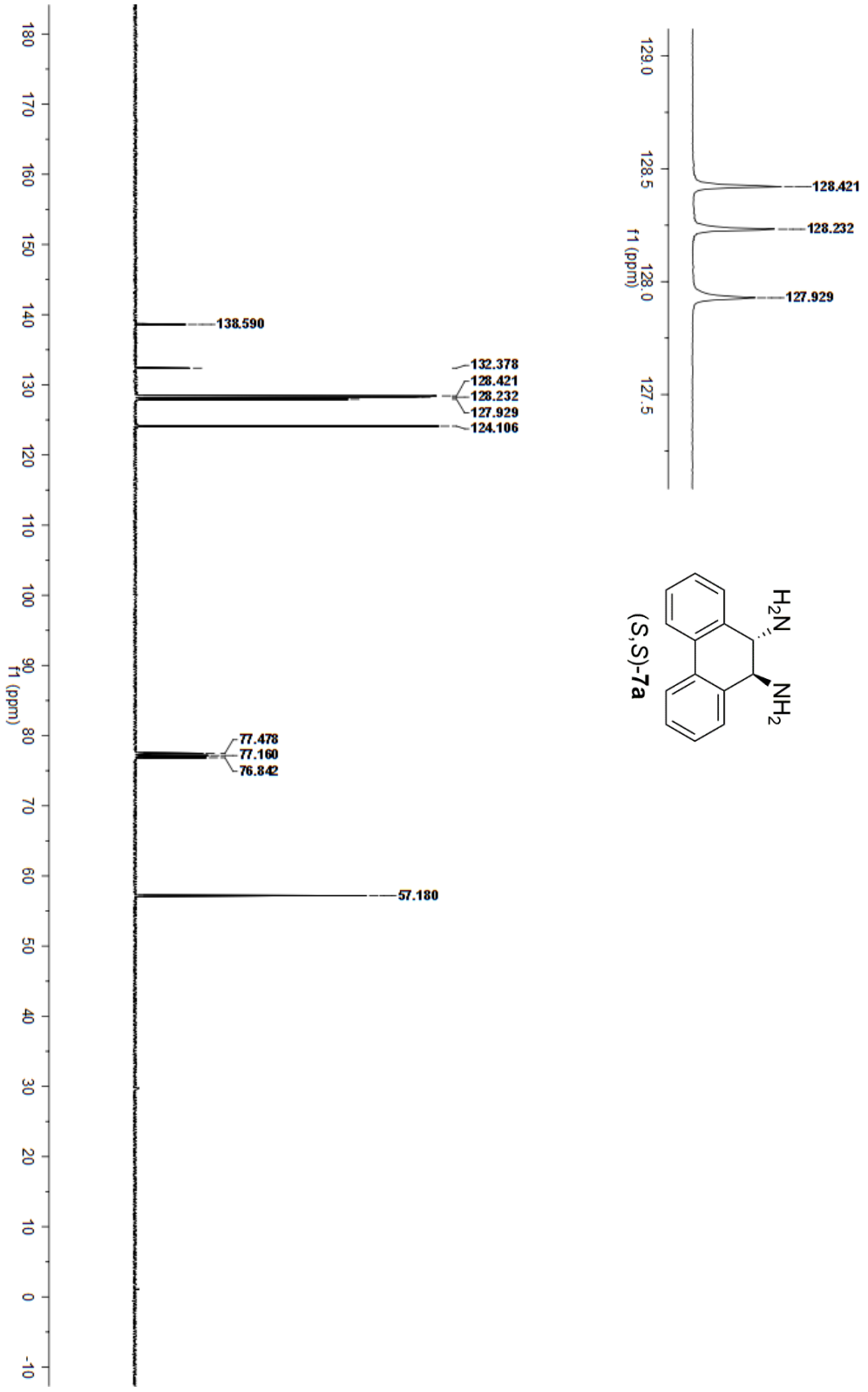

(S,S,S)-11a
H2N
HN–S
O
7.634
7.616
7.598
7.374
7.357
7.340
7.277
7.275
7.259
7.256
7.240
7.224
7.221
7.205
7.200
7.181
7.167
7.164
7.149
4.278
4.261
4.245
3.993
3.980
3.975
3.966
2.556
0.956
2.01
1.94
4.06
0.96
1.96
2.49
9.00
f1 (ppm)


(S,S,S)-11a
H2N
HN–S
O
137.005
134.053
132.894
132.111
129.175
128.747
128.395
128.214
128.099
127.952
123.960
123.733
77.481
77.160
76.844
61.245
56.005
55.293
22.468
f1 (ppm)


1.93
1.95
3.89
2.00
4.12
f1 (ppm)
7.807
7.788
7.486
7.468
7.401
7.383
7.365
7.352
7.334
7.316
7.260
3.849
1.607
(R,R)-7a
H2N
NH2


138.578
132.367
128.408
128.218
127.913
124.093
77.478
77.160
76.842
57.166
f1 (ppm)
128.408
128.218
127.913
124.093
f1 (ppm)
H2N
NH2
(R,R)-7a


2.00
2.00
3.93
2.00
4.20
3.853
1.608
1.99
1.99
3.90
7.808
7.789
7.487
7.468
7.384
7.368
7.365
7.353
7.335
7.317
7.808
7.789
7.487
7.468
7.402
7.384
7.368
7.365
7.353
7.335
7.317
7.260
f1 (ppm)
f1 (ppm)
(S,S)-7a
H2N
NH2


138.590
132.378
128.421
128.232
127.929
124.106
77.478
77.160
76.842
57.180
f1 (ppm)
128.421
128.232
127.929
f1 (ppm)
(S,S)-7a
H2N
NH2