Supporting Information

Enantioselective Addition of Thiols to Imines Catalyzed by Thiourea-quarternary Ammonium Salts

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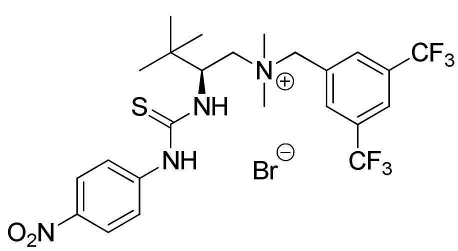
1. General information

The ^{1}H NMR spectra were recorded on a Bruker (400 MHz). All chemical shifts (δ) were given in ppm. Data were reported as follows: chemical shift, intergration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a DPX-400 (400 MHz). Flash column chromatography was performed using H silica gel. For thin-layer chromatography (TLC), silica gel plates (HSGF 254) were used and compounds were visualized by irradiation with UV light. Analytical high performance liquid chromatography (HPLC) was carried out on SHIMADZU equipment using chiral columns. Melting points were determined on a SGW X-4 melting point and were uncorrected. Optical rotations were measured on a JASCO P-1010 Polarimeter at λ =589 nm. IR spectra were recorded on a Perkin-Elmer 983G instrument. Mass spectra analysis was performed on API 200 LC/MS system (Applied Biosystems Co. Ltd.).

All starting amidosulfones and imines were synthesized according to reported methods,[1-6] all thiols were purchased from commercial sources and directly used without purified.

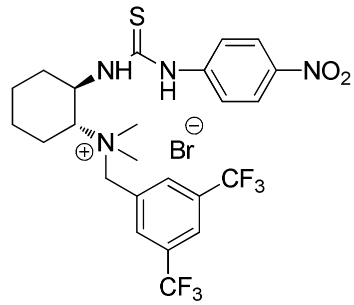
2. Bifunctional Catalysts

These catalysts were prepared according to the previous reported methods.[7]
(*S*)-N-(3,5-bis(trifluoromethyl)benzyl)-2-(3-(4-fluorophenyl)thioureido)-N,N,3,3-tetra methylbutan-1-aminium bromide (**g**)



Yellow solid; mp: 142-144 ^{o}C; $[\alpha]_D^{24.2}$ = -61.8 (*c* 2.0, $CHCl_3$); IR (neat): *v* 3229, 2967, 1577, 1541, 1508, 1334, 1279, 1179, 1138, 1109, 908, 852 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 11.24 (s, 1H), 9.41-9.39 (d, *J* = 8 Hz, 1H), 8.25-8.20 (br, 3H), 8.12-8.10 (br, 4H), 5.27-5.22 (t, *J* = 8 Hz, 1H), 5.00-4.98 (d, *J* = 8 Hz, 2H), 3.88-3.82 (br, 2H), 3.24-3.22 (d, *J* = 8 Hz, 6H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 181.53, 155.94, 151.79, 146.16, 143.05, 140.74, 133.71, 132.48 (q, *J* = 33 Hz), 130.40, 129.35, 127.23 (q, *J* = 271 Hz), 124.14, 122.30, 120.89, 67.19, 66.47, 56.23, 50.06, 37.11, 25.68.
HRMS (ESI): calcd. for $[M-Br]^+$ ($C_{24}H_{29}F_6N_4O_2S$) requires 551.1910, found 551.1913.

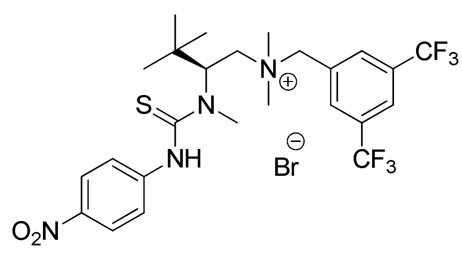
(1R,2R)-N-(3,5-bis(trifluoromethyl)benzyl)-N,N-dimethyl-2-(3-(4-nitrophenyl)thioureido)cyclohexanaminium bromide (**h**)



Yellow solid; mp: 109-111 °C; $[\alpha]_D^{24.0}$ = -126.4 (c 0.75, $CHCl_3$); IR (neat): v 3242, 2944, 2685, 1614, 1578, 1508, 1375, 1278, 1175, 1133, 1108, 1009, 989, 889 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 8.18-8.16 (d, J = 8 Hz, 1H), 8.13-8.11 (d, J = 8 Hz, 2H), 8.02-8.01 (br, 2H), 8.01-8.99 (d, J = 8 Hz, 1H), 7.92 (br, 1H), 6.94-6.92 (br, 2H), 4.76-4.72 (d, J = 16 Hz, 1H), 4.38-4.34 (d, J = 16 Hz, 1H), 4.14 (br, 1H), 3.57-3.52 (m, 1H), 2.76 (s, 6H), 2.12-2.11 (br, 1H), 1.88-1.85 (br, 2H), 1.69-1.67 (br, 1H), 1.47-1.41 (m, 2H), 1.35-1.28 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 180.79, 156.14, 151.42, 146.33, 142.93, 140.85, 131.54 (q, J = 33 Hz), 129.50, 127.55 (q, J = 331 Hz), 124.63, 124.24, 122.64, 121.69, 120.85, 67.23, 66.55, 52.97, 51.87, 39.63, 34.61, 31.97, 23.97, 22.80.

HRMS (ESI): calcd. for $[M-Br]^+$ ($C_{24}H_{27}F_6N_4O_2S$) requires 549.1753, found 549.1759.

(S)-N-(3,5-bis(trifluoromethyl)benzyl)-N,N,3,3-tetramethyl-2-(1-methyl-3-(4-nitrophenyl)thioureido)butan-1-aminium bromide



Yellow solid; mp: 147-151 °C; $[\alpha]_D^{24.8}$ = -2.8 (c 0.75, $CHCl_3$); IR (neat): v 2965, 1652, 1558, 1508, 1372, 1329, 1280, 1180, 1139, 907, 856; ^1H NMR (400 MHz, CD_3CN) δ 8.91 (s, 1H), 8.29 (s, 2H), 8.24 (s, 1H), 8.21-8.17 (m, 2H), 7.77-7.75 (d, J = 8 Hz, 2H), 6.42-6.40 (d, J = 8 Hz, 1H), 5.17-5.14 (d, J = 12 Hz, 1H), 5.06-5.03 (d, J = 12 Hz, 1H), 4.37-4.30 (dd, J = 12 Hz, J = 16 Hz, 1H), 3.39-3.75 (d, J = 16 Hz, 1H), 3.50 (s, 3H), 3.23-3.22 (d, J = 4 Hz, 6H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 183.64, 146.89, 144.17, 133.79, 132.29 (q, J = 33 Hz) 130.83, 127.25 (q, J = 270 Hz), 125.94, 125.17, 124.85, 123.36, 65.31, 63.47, 61.11, 49.24, 37.70, 35.90, 26.77.

HRMS (ESI): calcd. for $[M-Br]^+$ ($C_{25}H_{31}F_6N_4O_2S$) requires 565.2066, found 565.2045.

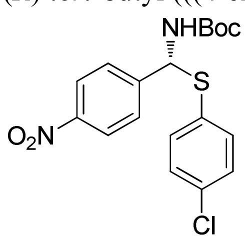
3. General procedure for asymmetric addition of thiols to amidosulfones

To a vial containing catalyst **h** (1 mol%) , thiol (0.1 mmol) and K_2CO_3 (5 equiv) in CH_2Cl_2 (5 mL) was added amidosulfone (0.2 mmol) at -30 ^oC. The mixture was stirred for 5 hours until the reaction was completed (minitored by TLC), and then purified by column chromatography on silica gel to afford the product.

4. General procedure for asymmetric addition of thiols to imines

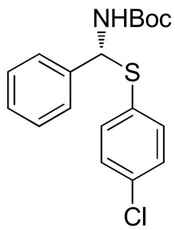
To a vial containing catalyst **h** (1 mol%) , thiol (0.1 mmol) and $PhSO_2Na$ (1 equiv) in CH_2Cl_2 (5 mL) was added imine (0.2 mmol) at -30 ^oC. The mixture was stirred for 5 min until the reaction was completed (minitored by TLC), and then purified by column chromatography on silica gel to afford the product.

(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(4-nitrophenyl)methyl)carbamate (**3j**)



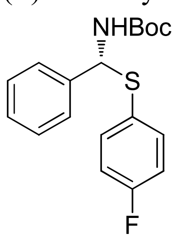
White solid; mp: 159-161 ^oC; $[\alpha]_D^{24.4}$ = -13.7 (*c* 1.0, $CHCl_3$); IR (neat): *v* 3355, 2985, 1687, 1605, 1515, 1365, 1345, 1248, 1013, 889; ^1H NMR (400 MHz, CD_3COCD_3) δ 8.27-8.25 (d, *J* = 8 Hz, 2H), 7.88-7.86 (d, *J* = 8 Hz, 2H), 7.56-7.54 (d, *J* = 8 Hz, 2H), 7.40-7.38 (d, *J* = 8 Hz, 2H), 7.31 (br, 1H), 6.49-6.47 (d, *J* = 8 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.47, 147.54, 146.54, 135.21, 134.00, 131.70, 129.01, 128.11, 123.60, 79.31, 61.17, 27.49.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{19}ClN_2NaO_4S$) requires 417.0652, found 417.0656.
Enantiometric excess: 47%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 18.9 min; t_{minor} = 18.0 min).

(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(phenyl)methyl)carbamate (**4a**)



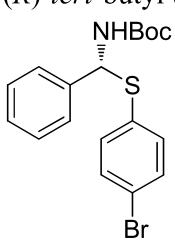
White solid; mp: 119-121 ^{o}C; $[\alpha]_D^{27.3}$ = -23.4 (*c* 0.5, $CHCl_3$); IR (neat): *v* 3351, 1683, 1507, 1474, 1388, 1364, 1247, 1165, 1092, 1014, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.25 (m, 9H), 7.26-7.24 (d, *J* = 8 Hz, 1H), 5.19-5.17 (d, *J* = 8 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.46, 139.50, 134.65, 133.32, 132.88, 128.80, 128.45, 128.03, 126.83, 78.83, 61.68, 27.50.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{20}ClNNaO_2S$) requires 372.0801, found 372.0808.
Enantiometric excess: 94%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 13.8 min; t_{minor} = 8.6 min).

(*R*)-*tert*-butyl (((4-fluorophenyl)thio)(phenyl)methyl)carbamate (**4b**)



White solid; mp: 125-127 ^{o}C; $[\alpha]_D^{23.8}$ = -34.0 (*c* 0.75, $CHCl_3$); IR (neat): *v* 3361, 2970, 1696, 1497, 1473, 1166, 830, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.38-7.29 (m, 5H), 7.01-6.97 (m, 2H), 6.20-6.18 (d, *J* = 8 Hz, 1H), 5.17 (br, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.42, 139.63, 136.27, 136.19, 129.21, 129.18, 128.40, 127.94, 126.82, 115.77, 115.55, 78.73, 62.21, 27.51.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{20}FNNaO_2S$) requires 356.1096, found 356.1074.
Enantiometric excess: 87%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 12.3 min; t_{minor} = 8.4 min).

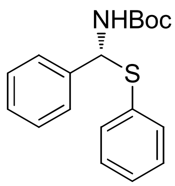
(*R*)-*tert*-butyl (((4-bromophenyl)thio)(phenyl)methyl)carbamate (**4c)**



White solid; mp: = 128-130 ^{o}C; $[\alpha]_D^{27.3}$ = -31.7 (*c* 0.5, $CHCl_3$); IR (neat): *v* 3351, 2981, 1684, 1508, 1164, 1009, 880, 816 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ

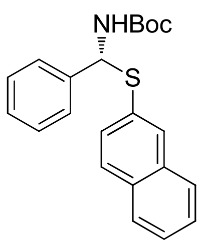
7.42-7.25 (m, 9H), 6.25 (br, 1H), 5.16 (br, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.48, 139.45, 134.77, 133.50, 131.96, 131.91, 131.79, 128.47, 128.06, 126.85, 121.39, 78.88, 61.55, 27.54.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{20}BrNNaO_2S$) requires 416.0296, found 416.0288.
Enantiometric excess: 91%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 14.5 min; t_{minor} = 8.8 min).

(*R*)-*tert*-butyl (phenyl(phenylthio)methyl)carbamate (**4d**)



White solid; mp: 113-115 °C; $[\alpha]_D^{27.3}$ = -30.5 (*c* 0.75, CD_3COCD_3); IR (neat): *v* 3357, 2966, 1684, 1166, 1067, 919, 881, 833, 788 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (d, *J* = 8 Hz, 2H), 7.52-7.50 (d, *J* = 8 Hz, 2H), 7.39-7.29 (m, 6H), 7.02 (br, 1H), 6.36-6.34 (d, *J* = 8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.50, 139.90, 134.13, 132.54, 128.80, 128.40, 127.91, 127.43, 126.83, 109.99, 78.74, 61.33, 27.58.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{21}NNaO_2S$) requires 338.1191, found 338.1178.
Enantiometric excess: 80%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 8.6 min; t_{minor} = 11.9 min).

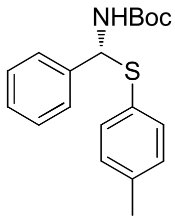
(*R*)-*tert*-butyl ((naphthalen-2-ylthio)(phenyl)methyl)carbamate (**4e**)



White solid; mp = 127-128 °C; $[\alpha]_D^{24.5}$ = -46.5 (*c* 0.5, $CHCl_3$); IR (neat): *v* 3366, 1690, 1507, 1364, 1245, 1166, 1017, 881, 816 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.81-7.76 (m, 3H), 7.53-7.38 (m, 5H), 7.36-7.30 (m, 3H), 6.40-6.38 (d, *J* = 8 Hz, 1H), 5.24-5.22 (d, *J* = 8 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.51, 139.84, 133.77, 132.56, 131.74, 131.11, 129.66, 128.46, 128.23, 127.98, 127.61, 127.45, 126.90, 126.42, 126.20, 78.77, 61.15, 27.47.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{22}H_{23}NNaO_2S$) requires 388.1347, found 388.1343.
Enantiometric excess: 85%, determined by HPLC (Chiralpak AS-H column,

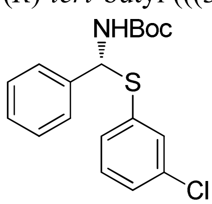
hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 7.4 min; t_{minor} = 8.9 min).

(*R*)-*tert*-butyl (phenyl(*p*-tolylthio)methyl)carbamate (**4f**)



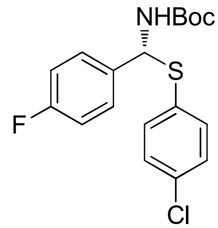
White soild; mp = 110-112 ^{o}C; $[\alpha]_D^{24.1}$ = -16.4 (*c* 0.5, $CHCl_3$); IR (neat): *v* 3355, 2981, 1684, 1508, 1247, 1044, 1020, 879, 812 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$) δ 7.39-7.28 (m, 7H), 7.11-7.09 (m, 2H), 6.20 (br, 1H), 5.16 (br, 1H), 2.32 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.43, 140.05, 137.67, 133.38, 130.33, 129.48, 128.34, 127.81, 126.81, 78.62, 61.77, 27.55, 20.21.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{19}H_{23}NNaO_2S$) requires 352.1347, found 352.1346.
Enantiometric excess: 79%, determined by HPLC (Chiralpak AS-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 12.9 min; t_{minor} = 8.6 min).

(*R*)-*tert*-butyl (((3-chlorophenyl)thio)(phenyl)methyl)carbamate (**4g**)



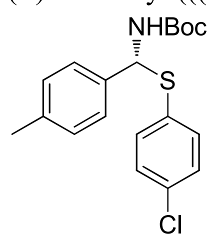
White soild; mp: 118-120 ^{o}C; $[\alpha]_D^{27.3}$ = -37.2 (*c* 0.65, $CHCl_3$); IR (neat): *v* 3354, 2970, 1685, 1508, 1165, 1056, 886, 776 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.34 (m, 7H), 7.24-7.22 (br, 2H), 6.34 (br, 1H), 5.20 (br, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.50, 139.39, 136.54, 133.91, 131.68, 130.62, 130.19, 128.50, 128.12, 127.35, 126.86, 78.94, 61.18, 27.53.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{20}ClNNaO_2S$) requires 372.0801, found 372.0808.
Enantiometric excess: 90%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 13.2 min; t_{minor} = 8.6 min).

(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(4-fluorophenyl)methyl)carbamate (**4h**)



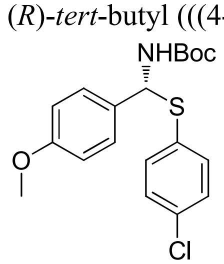
White soild; mp: 131-133 ^{o}C; $[\alpha]_D^{27.3}$ = -23.9 (*c* 0.5, $CHCl_3$); IR (neat): *v* 3349, 2982, 1683, 1505, 1166, 882, 844, 826, 797 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 4H), 7.28 (br, 2H), 7.06-7.01 (m, 2H), 6.22 (br, 1H), 5.11 (br, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 163.49, 161.05, 154.42, 135.73, 134.78, 132.61, 128.99, 128.91, 128.84, 115.25, 115.03, 78.91, 60.97, 27.48.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{19}ClFNNaO_2S$) requires 390.0707, found 390.0720.
Enantiometric excess: 95%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 12.4 min; t_{minor} = 9.2 min).

(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(*p*-tolyl)methyl)carbamate (**4i**)



White soild; mp: 140-143 ^{o}C; $[\alpha]_D^{24.6}$ = -28.2 (*c* 0.75, $CHCl_3$); IR (neat): *v* 3345, 2979, 1670, 1508, 1288, 1011, 876, 821, 811 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (d, *J* = 8 Hz, 2H), 7.28-7.26 (m, 4H), 7.16-7.14 (d, *J* = 8 Hz, 2H), 6.22 (br, 1H), 5.13 (br, 1H), 2.34 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.52, 140.01, 137.73, 134.57, 133.41, 129.49, 129.04, 128.78, 128.36, 127.83, 126.81, 78.68, 61.78, 27.56, 20.25.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{19}H_{22}ClNNaO_2S$) requires 386.0957, found 386.0938.
Enantiometric excess: 86%, determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 13.1 min; t_{minor} = 9.0 min).

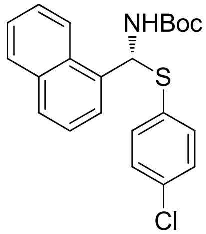
(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(4-methoxyphenyl)methyl)carbamate (**4j**)



White soild; mp: 135-137 ^{o}C; $[\alpha]_D^{27.3}$ = -12.0 (*c* 0.75, CD_3COCD_3); IR (neat): *v* 3341,

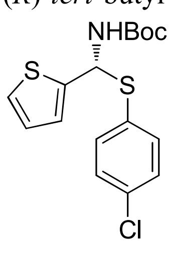
1682, 1507, 1359, 1300, 1246, 1166, 880, 823 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (br, 4H), 7.24-7.20 (br, 2H), 6.91-6.89 (br, 1H), 6.80-6.78 (d, J = 8 Hz, 2H), 6.20-6.18 (d, J = 8 Hz, 1H), 3.66 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 159.55, 154.41, 134.51, 133.15, 131.78, 131.52, 129.37, 129.36, 128.75, 128.10, 113.74, 78.75, 61.18, 54.70, 27.52.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{19}H_{22}ClNNaO_3S$) requires 402.0907, found 402.0917.
Enantiometric excess: 86%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 19.6 min; t_{minor} = 12.2 min).

(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(naphthalen-1-yl)methyl)carbamate (**4k**)



White soild; mp: 163-166 °C; $[\alpha]_D^{27.3}$ = -45.0 (c 0.5, CD_3COCD_3); IR (neat): v 3335, 2977, 1792, 1653, 1521, 1507, 1363, 1091, 1052, 885, 830 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39-8.37 (d, J = 8 Hz, 1H), 7.98-7.96 (d, J = 8 Hz, 1H), 7.93-7.89 (m, 2H), 7.67-7.51 (m, 5H), 7.41-7.39 (m, 2H), 7.34 (br, 1H), 7.12-7.10 (d, J = 8 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.63, 136.82, 135.09, 134.53, 133.85, 133.45, 133.02, 129.84, 128.93, 128.88, 128.78, 126.57, 125.94, 125.28, 124.77, 123.21, 78.99, 58.22, 27.52.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{22}H_{22}ClNNaO_2S$) requires 422.0957, found 490.0966.
Enantiometric excess: 78%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 13.0 min; t_{minor} = 11.2 min).

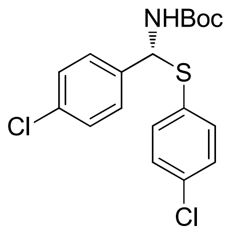
(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(thiophen-2-yl)methyl)carbamate (**4l**)



White soild; mp: 105-107 °C; $[\alpha]_D^{27.3}$ = -20.3 (c 0.75, CD_3COCD_3); IR (neat): v 3343, 2976, 1654, 1508, 1161, 1014, 819, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (d, J = 8 Hz, 2H), 7.43-7.41 (d, J = 8 Hz, 1H), 7.39-7.37 (d, J = 8 Hz, 2H), 7.22-7.20 (d, J = 8 Hz, 2H), 7.14 (br, 1H), 7.00-6.98 (m, 1H), 6.56-6.54 (d, J = 8 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.34, 143.03, 135.04,

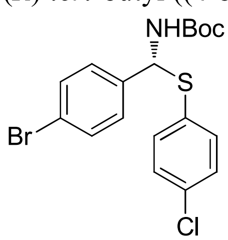
132.23, 129.37, 128.89, 126.78, 125.56, 125.52, 79.12, 57.82, 27.50.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{16}H_{18}ClNNaO_2S_2$) requires 378.0365, found 378.0346.
Enantiometric excess: 89%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 12.1 min; t_{minor} = 8.9 min).

(*R*)-*tert*-butyl ((4-chlorophenyl)((4-chlorophenyl)thio)methyl)carbamate (**4m**)



White soild; mp: 145-147 °C; $[\alpha]_D^{27.3}$ = -33.8 (*c* 0.75, $CHCl_3$); IR (neat): *v* 3296, 1670, 1521, 1489, 1389, 1367, 1281, 1248, 1159, 1093, 1011, 873 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (d, *J* = 8 Hz, 2H), 7.32 (br, 4H), 7.28-7.26 (d, *J* = 8 Hz, 2H), 6.20 (br, 1H), 5.11 (br, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.43, 138.84, 134.84, 133.30, 132.42, 128.88, 128.63, 128.50, 79.03, 61.07, 27.50.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{19}Cl_2NNaO_2S$) requires 406.0411, found 406.0392.
Enantiometric excess: 86%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 13.1 min; t_{minor} = 9.8 min).

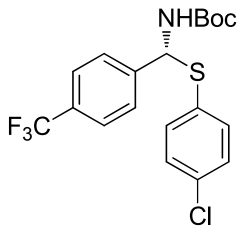
(*R*)-*tert*-butyl ((4-bromophenyl)((4-chlorophenyl)thio)methyl)carbamate (**4n**)



White soild; mp: 150-152 °C; $[\alpha]_D^{27.3}$ = -20.8 (*c* 0.75, $CHCl_3$); IR (neat): *v* 3326, 2973, 1685, 1489, 1163, 1072, 883, 830, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (d, *J* = 8 Hz, 2H), 7.39-7.37 (d, *J* = 8 Hz, 2H), 7.28-7.26 (m, 4H), 6.18 (br, 1H), 5.11 (br, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.47, 139.02, 134.92, 133.66, 132.46, 131.54, 129.41, 128.97, 128.92, 121.49, 79.08, 61.24, 27.52.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{19}BrClNNaO_2S$) requires 449.9906, found 449.9901.
Enantiometric excess: 85%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 14.9 min; t_{minor} = 10.6 min).

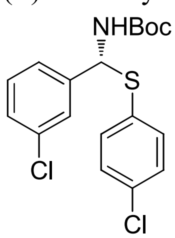
(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(4-(trifluoromethyl)phenyl)methyl)carbamate

(**4o**)



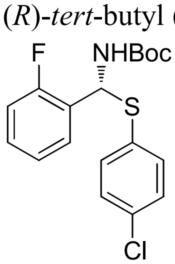
White soild; mp: 149-152 °C; $[\alpha]_D^{27.3}$ = -24.1 (*c* 0.75, $CHCl_3$); IR (neat): *v* 3347, 2977, 1654, 1328, 1128, 1067, 1015, 850, 824 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (d, *J* = 8 Hz, 2H), 7.52-7.50 (d, *J* = 8 Hz, 2H), 7.40-7.38 (d, *J* = 8 Hz, 2H), 7.29-7.27 (d, *J* = Hz, 2H), 6.26 (s, 1H), 5.15 (s, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.54, 143.98, 135.05, 133.85, 132.18, 129.61 (q, *J* = 30 Hz), 128.98, 127.68, 125.44 (q, *J* = 4 Hz), 124.32 (q, *J* = 270 Hz), 79.34, 61.35, 27.69.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C_{19}H_{19}ClF_3NNaO_2S$) requires 440.0675, found 440.0681.
Enantiometric excess: 77%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 10.3 min; t_{minor} = 8.5 min).

(*R*)-*tert*-butyl ((3-chlorophenyl)((4-chlorophenyl)thio)methyl)carbamate (**4p**)



White soild; mp: 115-117 °C; $[\alpha]_D^{27.3}$ = -36.5 (*c* 1.00, CD_3COCD_3); IR (neat): *v* 3329, 1679, 1517, 1366, 1247, 1160, 1055, 1012, 870, 810 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.54-7.52 (m, 3H), 7.43-7.34 (m, 4H), 7.19 (br, 1H), 6.37-6.35 (d, *J* = 8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 154.47, 141.90, 134.99, 133.89, 133.78, 130.20, 128.95, 128.03, 126.94, 125.50, 79.15, 61.20, 27.55.
HRMS (ESI): calcd. for $[M+Na]^+$ ($C1_8H_{19}Cl_2NNaO_2S$) requires 406.0411, found 406.0392.
Enantiometric excess: 85%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 9.6 min; t_{minor} = 7.4 min).

(*R*)-*tert*-butyl (((4-chlorophenyl)thio)(2-fluorophenyl)methyl)carbamate (**4q**)



White soild; mp: 105-107 ^{o}C; $[\alpha]_D^{26.3}$ = -28.9 (*c* 0.5, $CHCl_3$); IR (neat): *v* 3342, 2974, 1654, 1474, 1251, 1164, 1014, 825, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (d, *J* = 8 Hz, 2H), 7.31-7.22 (m, 4H), 7.12-7.04 (m, 2H), 6.36-6.34 (d, *J* = 8 Hz, 1H), 5.46 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 158.94 (d, J = 244 Hz), 154.39, 135.10, 133.87, 132.29, 130.20 (d, *J* = 8 Hz), 128.99, 128.54, 126.90 (d, *J* = 13 Hz), 124.60 (d, *J* = 4 Hz), 115.50 (d, *J* = 21 Hz), 79.22, 55.47, 27.56.

HRMS (ESI): calcd. for $[M+Na]^+$ ($C1_8H_{19}ClFNNaO_2S$) requires 390.0707, found 390.0720.

Enantiometric excess: 75%, determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 90:10, λ=254 nm, flow rate 0.7 mL/min; t_{major} = 10.6 min; t_{minor} = 8.2 min).

5. References

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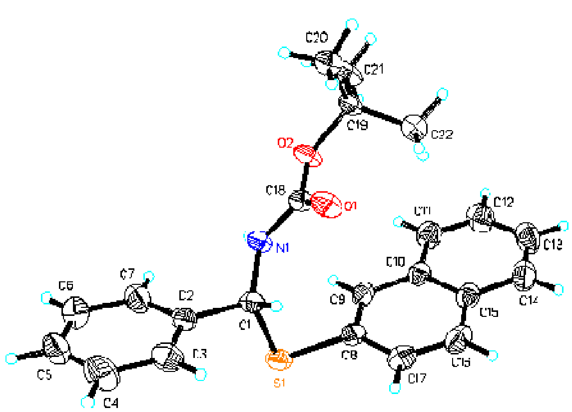
6. Crystal data and structure of 4e



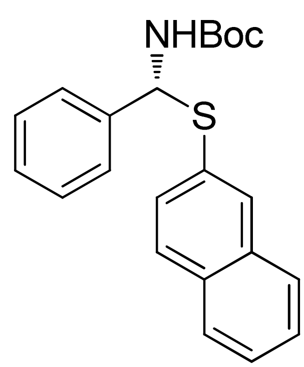


Table S1. Crystal data and structure refinement for cd213265.

Identification code	cd213265
Empirical formula	C22 H23 N O2 S
Formula weight	365.47
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 5.3645(4) A alpha = 90 deg.
b = 19.0869(14) A beta = 90 deg.	
c = 19.4095(15) A gamma = 90 deg.	
Volume	1987.4(3) A^3
Z, Calculated density	4, 1.221 Mg/m^3
Absorption coefficient	0.178 mm^-1
F(000)	776
Crystal size	0.212 x 0.158 x 0.112 mm
Theta range for data collection	2.10 to 26.00 deg.
Limiting indices	-6<=h<=6, -23<=k<=23, -16<=l<=23
Reflections collected / unique	12072 / 3906 [R(int) = 0.0289]
Completeness to theta = 26.00	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.66097
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3906 / 0 / 242
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0907
R indices (all data)	R1 = 0.0423, wR2 = 0.0942
Absolute structure parameter	-0.03(7)
Largest diff. peak and hole	0.192 and -0.158 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd213265.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	3775(1)	8055(1)	2404(1)	55(1)
N(1)	2573(3)	6882(1)	3132(1)	45(1)
O(1)	-1494(2)	6570(1)	2998(1)	60(1)
O(2)	1669(2)	5782(1)	2900(1)	55(1)
C(1)	2114(4)	7625(1)	3126(1)	45(1)
C(2)	2924(4)	8002(1)	3775(1)	50(1)
C(3)	1498(5)	8545(1)	4025(1)	74(1)
C(4)	2175(7)	8884(1)	4633(1)	99(1)

C(5)	4239(7)	8676(1)	4985(1)	90(1)
C(6)	5696(6)	8146(1)	4738(1)	85(1)
C(7)	5055(4)	7813(1)	4129(1)	67(1)
C(8)	2528(4)	7566(1)	1698(1)	50(1)
C(9)	3684(4)	6966(1)	1490(1)	50(1)
C(10)	2730(4)	6564(1)	938(1)	50(1)
C(11)	3851(5)	5932(1)	714(1)	67(1)
C(12)	2885(5)	5561(1)	179(1)	81(1)
C(13)	768(6)	5798(2)	-162(1)	83(1)
C(14)	-372(5)	6397(1)	36(1)	75(1)
C(15)	549(4)	6802(1)	595(1)	55(1)
C(16)	-577(4)	7428(1)	824(1)	68(1)
C(17)	364(4)	7796(1)	1363(1)	61(1)
C(18)	698(3)	6423(1)	3003(1)	45(1)
C(19)	42(3)	5177(1)	2742(1)	47(1)
C(20)	-1567(4)	5012(1)	3364(1)	63(1)
C(21)	1908(4)	4593(1)	2615(1)	75(1)
C(22)	-1486(4)	5313(1)	2103(1)	63(1)

Table S3. Bond lengths [A] and angles [deg] for cd213265.

S(1)-C(8)	1.7875(18)
S(1)-C(1)	1.8510(16)
N(1)-C(18)	1.358(2)
N(1)-C(1)	1.440(2)
N(1)-H(1A)	0.88(2)
O(1)-C(18)	1.209(2)
O(2)-C(18)	1.345(2)
O(2)-C(19)	1.4796(19)
C(1)-C(2)	1.514(2)
C(1)-H(1)	0.9800
C(2)-C(3)	1.378(3)
C(2)-C(7)	1.382(3)
C(3)-C(4)	1.393(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.360(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.366(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.386(3)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-C(9)	1.364(2)

C(8)-C(17)	1.401(3)
C(9)-C(10)	1.413(2)
C(9)-H(9)	0.9300
C(10)-C(11)	1.417(3)
C(10)-C(15)	1.421(3)
C(11)-C(12)	1.360(3)
C(11)-H(11)	0.9300
C(12)-C(13)	1.389(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.353(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.421(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.410(3)
C(16)-C(17)	1.358(3)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(19)-C(22)	1.510(3)
C(19)-C(20)	1.516(3)
C(19)-C(21)	1.518(2)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(8)-S(1)-C(1)	99.71(7)
C(18)-N(1)-C(1)	120.49(16)
C(18)-N(1)-H(1A)	118.4(13)
C(1)-N(1)-H(1A)	117.9(13)
C(18)-O(2)-C(19)	120.81(13)
N(1)-C(1)-C(2)	114.27(13)
N(1)-C(1)-S(1)	111.13(11)
C(2)-C(1)-S(1)	106.32(11)
N(1)-C(1)-H(1)	108.3
C(2)-C(1)-H(1)	108.3
S(1)-C(1)-H(1)	108.3
C(3)-C(2)-C(7)	118.68(18)
C(3)-C(2)-C(1)	119.46(18)
C(7)-C(2)-C(1)	121.85(16)

C(2)-C(3)-C(4)	120.2(2)
C(2)-C(3)-H(3)	119.9
C(4)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	120.2(2)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(4)-C(5)-C(6)	120.4(2)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(5)-C(6)-C(7)	119.8(3)
C(5)-C(6)-H(6)	120.1
C(7)-C(6)-H(6)	120.1
C(2)-C(7)-C(6)	120.7(2)
C(2)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(9)-C(8)-C(17)	120.14(17)
C(9)-C(8)-S(1)	119.72(14)
C(17)-C(8)-S(1)	120.14(14)
C(8)-C(9)-C(10)	121.03(16)
C(8)-C(9)-H(9)	119.5
C(10)-C(9)-H(9)	119.5
C(9)-C(10)-C(11)	122.73(18)
C(9)-C(10)-C(15)	118.71(16)
C(11)-C(10)-C(15)	118.56(18)
C(12)-C(11)-C(10)	121.1(2)
C(12)-C(11)-H(11)	119.5
C(10)-C(11)-H(11)	119.5
C(11)-C(12)-C(13)	120.3(2)
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	120.7(2)
C(14)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	121.3(2)
C(13)-C(14)-H(14)	119.4
C(15)-C(14)-H(14)	119.4
C(16)-C(15)-C(14)	123.5(2)
C(16)-C(15)-C(10)	118.43(17)
C(14)-C(15)-C(10)	118.0(2)
C(17)-C(16)-C(15)	121.39(19)
C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(16)-C(17)-C(8)	120.28(18)
C(16)-C(17)-H(17)	119.9

C(8)-C(17)-H(17)	119.9
O(1)-C(18)-O(2)	125.92(15)
O(1)-C(18)-N(1)	124.93(16)
O(2)-C(18)-N(1)	109.13(15)
O(2)-C(19)-C(22)	110.80(14)
O(2)-C(19)-C(20)	109.45(13)
C(22)-C(19)-C(20)	112.36(16)
O(2)-C(19)-C(21)	102.58(13)
C(22)-C(19)-C(21)	110.59(16)
C(20)-C(19)-C(21)	110.64(16)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for cd213265.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	71(1)	39(1)	55(1)	4(1)	5(1)	-12(1)
N(1)	45(1)	31(1)	58(1)	-1(1)	-1(1)	-3(1)
O(1)	46(1)	44(1)	91(1)	-7(1)	3(1)	0(1)
O(2)	41(1)	32(1)	90(1)	-4(1)	-6(1)	-4(1)
C(1)	52(1)	34(1)	50(1)	2(1)	4(1)	-1(1)

C(2)	64(1)	37(1)	49(1)	1(1)	6(1)	-7(1)
C(3)	91(2)	50(1)	80(1)	-14(1)	0(1)	13(1)
C(4)	137(3)	70(1)	90(2)	-33(1)	11(2)	14(2)
C(5)	141(3)	69(1)	62(1)	-16(1)	-3(2)	-23(2)
C(6)	103(2)	83(2)	69(1)	-4(1)	-21(1)	-14(2)
C(7)	74(2)	60(1)	66(1)	-11(1)	-6(1)	0(1)
C(8)	56(1)	47(1)	47(1)	8(1)	3(1)	-5(1)
C(9)	48(1)	55(1)	47(1)	8(1)	-2(1)	-1(1)
C(10)	53(1)	55(1)	42(1)	6(1)	4(1)	-2(1)
C(11)	73(1)	71(1)	56(1)	-7(1)	-1(1)	6(1)
C(12)	97(2)	80(2)	64(1)	-17(1)	8(1)	-4(1)
C(13)	97(2)	98(2)	54(1)	-13(1)	-3(1)	-28(2)
C(14)	69(1)	99(2)	56(1)	8(1)	-10(1)	-21(1)
C(15)	52(1)	69(1)	45(1)	13(1)	0(1)	-10(1)
C(16)	56(1)	81(1)	68(1)	20(1)	-8(1)	7(1)
C(17)	62(1)	57(1)	65(1)	9(1)	2(1)	11(1)
C(18)	45(1)	37(1)	52(1)	2(1)	2(1)	-3(1)
C(19)	44(1)	31(1)	66(1)	-2(1)	-4(1)	-6(1)
C(20)	71(1)	54(1)	64(1)	3(1)	-1(1)	-14(1)
C(21)	56(1)	39(1)	130(2)	-13(1)	-4(1)	-1(1)
C(22)	68(1)	57(1)	63(1)	-1(1)	-5(1)	-6(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd213265.

	x	y	z	U(eq)
H(1)	321	7701	3063	55
H(3)	77	8686	3788	88
H(4)	1213	9252	4798	119
H(5)	4662	8897	5396	108
H(6)	7113	8008	4979	102
H(7)	6070	7459	3957	80
H(9)	5124	6818	1714	60
H(11)	5270	5767	937	80
H(12)	3646	5146	39	97
H(13)	128	5541	-529	100
H(14)	-1786	6547	-199	89
H(16)	-1995	7592	600	82
H(17)	-431	8202	1511	74
H(20A)	-536	4981	3767	94
H(20B)	-2407	4574	3293	94
H(20C)	-2776	5378	3425	94

H(21A)	2948	4713	2231	112
H(21B)	1032	4165	2517	112
H(21C)	2922	4530	3018	112
H(22A)	-2706	5668	2199	94
H(22B)	-2314	4890	1966	94
H(22C)	-412	5469	1738	94
H(1A)	4120(40)	6739(10)	3078(10)	52(6)

Table S6. Torsion angles [deg] for cd213265.

C(18)-N(1)-C(1)-C(2)	126.28(17)
C(18)-N(1)-C(1)-S(1)	-113.41(16)
C(8)-S(1)-C(1)-N(1)	56.74(14)
C(8)-S(1)-C(1)-C(2)	-178.34(13)
N(1)-C(1)-C(2)-C(3)	-142.69(18)
S(1)-C(1)-C(2)-C(3)	94.35(19)
N(1)-C(1)-C(2)-C(7)	36.8(2)
S(1)-C(1)-C(2)-C(7)	-86.16(17)
C(7)-C(2)-C(3)-C(4)	-1.4(3)
C(1)-C(2)-C(3)-C(4)	178.1(2)
C(2)-C(3)-C(4)-C(5)	-0.5(4)
C(3)-C(4)-C(5)-C(6)	1.4(4)
C(4)-C(5)-C(6)-C(7)	-0.5(4)
C(3)-C(2)-C(7)-C(6)	2.4(3)
C(1)-C(2)-C(7)-C(6)	-177.11(19)
C(5)-C(6)-C(7)-C(2)	-1.5(4)
C(1)-S(1)-C(8)-C(9)	-89.22(15)
C(1)-S(1)-C(8)-C(17)	90.43(15)
C(17)-C(8)-C(9)-C(10)	-0.3(3)
S(1)-C(8)-C(9)-C(10)	179.36(13)
C(8)-C(9)-C(10)-C(11)	-178.83(18)
C(8)-C(9)-C(10)-C(15)	0.9(3)
C(9)-C(10)-C(11)-C(12)	-179.7(2)
C(15)-C(10)-C(11)-C(12)	0.6(3)
C(10)-C(11)-C(12)-C(13)	0.1(3)
C(11)-C(12)-C(13)-C(14)	-0.3(4)
C(12)-C(13)-C(14)-C(15)	-0.1(4)
C(13)-C(14)-C(15)-C(16)	-179.6(2)
C(13)-C(14)-C(15)-C(10)	0.7(3)
C(9)-C(10)-C(15)-C(16)	-0.4(2)
C(11)-C(10)-C(15)-C(16)	179.32(18)
C(9)-C(10)-C(15)-C(14)	179.30(17)
C(11)-C(10)-C(15)-C(14)	-1.0(3)

C(14)-C(15)-C(16)-C(17)	179.62(19)
C(10)-C(15)-C(16)-C(17)	-0.7(3)
C(15)-C(16)-C(17)-C(8)	1.3(3)
C(9)-C(8)-C(17)-C(16)	-0.8(3)
S(1)-C(8)-C(17)-C(16)	179.52(15)
C(19)-O(2)-C(18)-O(1)	2.1(3)
C(19)-O(2)-C(18)-N(1)	-179.58(14)
C(1)-N(1)-C(18)-O(1)	-14.0(3)
C(1)-N(1)-C(18)-O(2)	167.58(13)
C(18)-O(2)-C(19)-C(22)	57.8(2)
C(18)-O(2)-C(19)-C(20)	-66.63(19)
C(18)-O(2)-C(19)-C(21)	175.87(17)

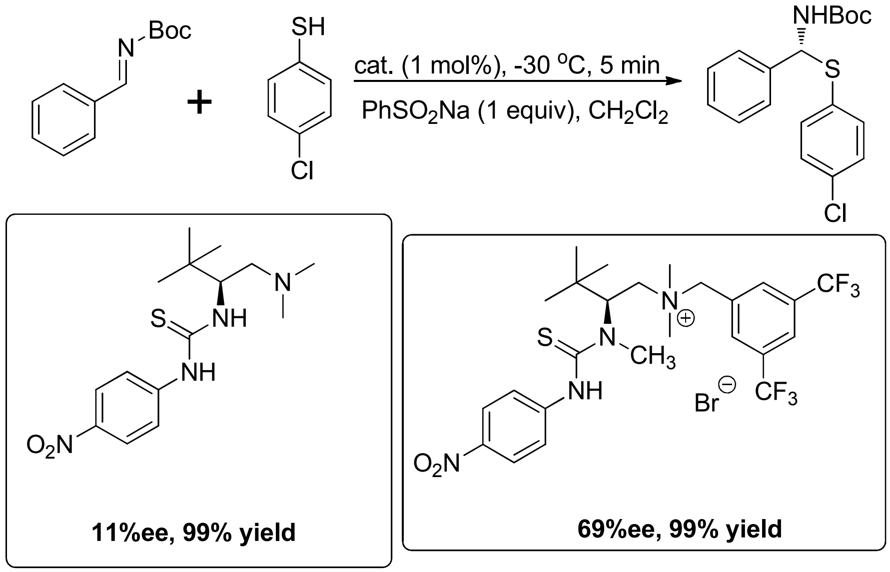
Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for cd213265 [A and deg.].

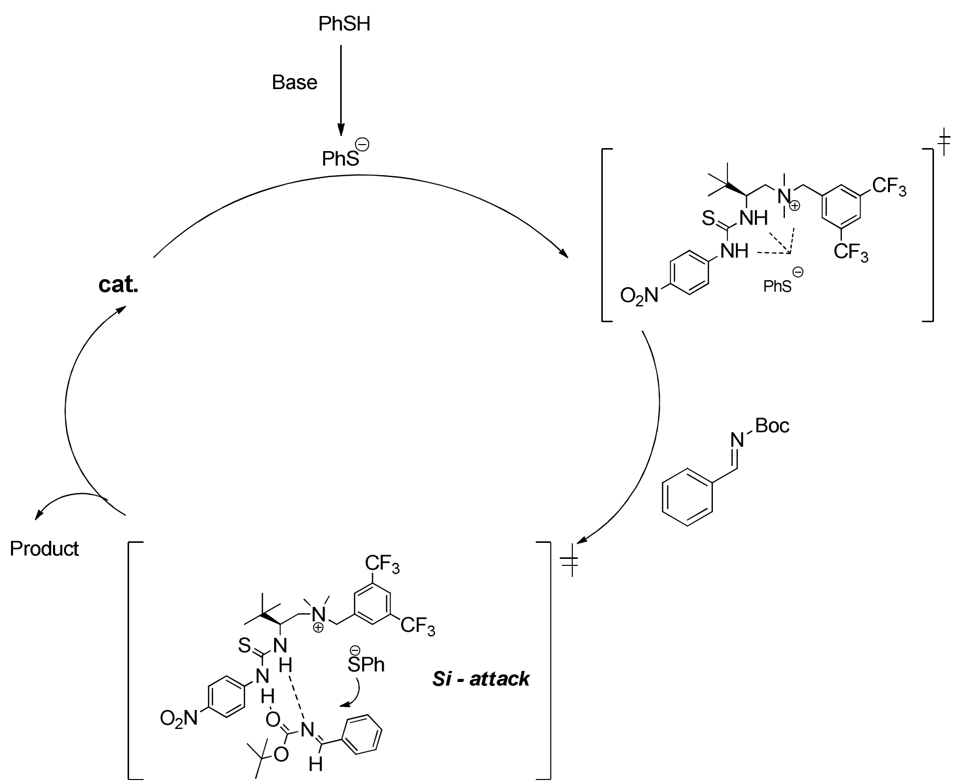
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)#1	0.88(2)	2.38(2)	3.248(2)	169.1(17)

Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z

7.Control experiments



8.The possible catalytic cycle and transition state



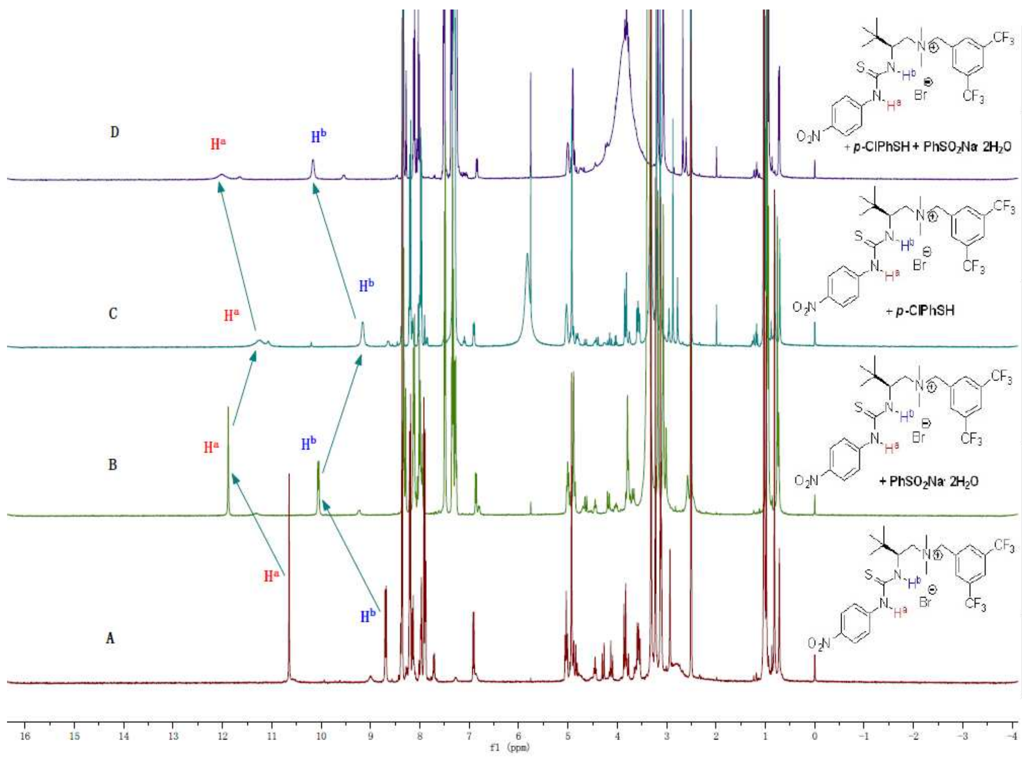
9.NMR binding studies

A ： The ^{1}H NMR spectra of **g** in $(CD_3)_2SO$

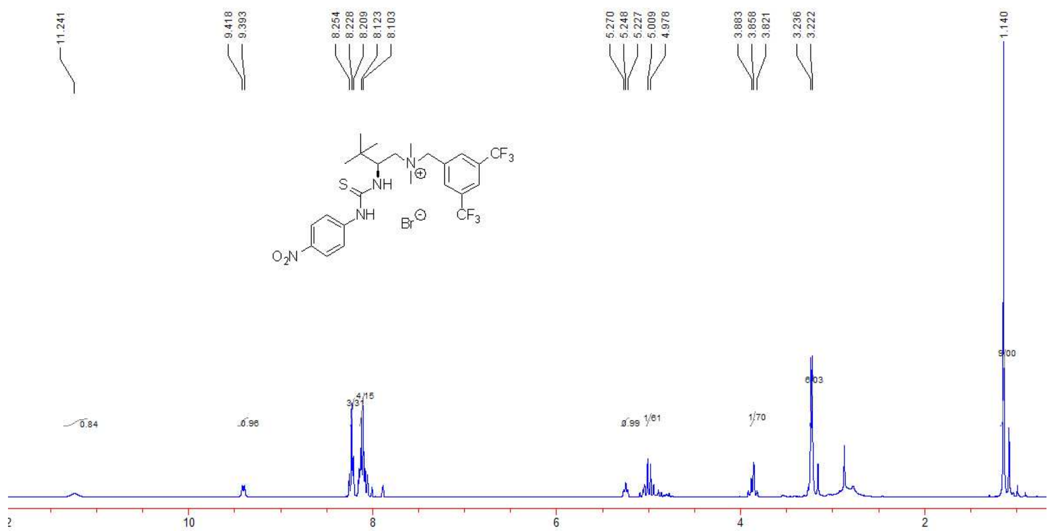
B： The ^{1}H NMR spectra of **g** and $PhSO_2Na{\cdot}2H_2O$ (1:1) in $(CD_3)_2SO$

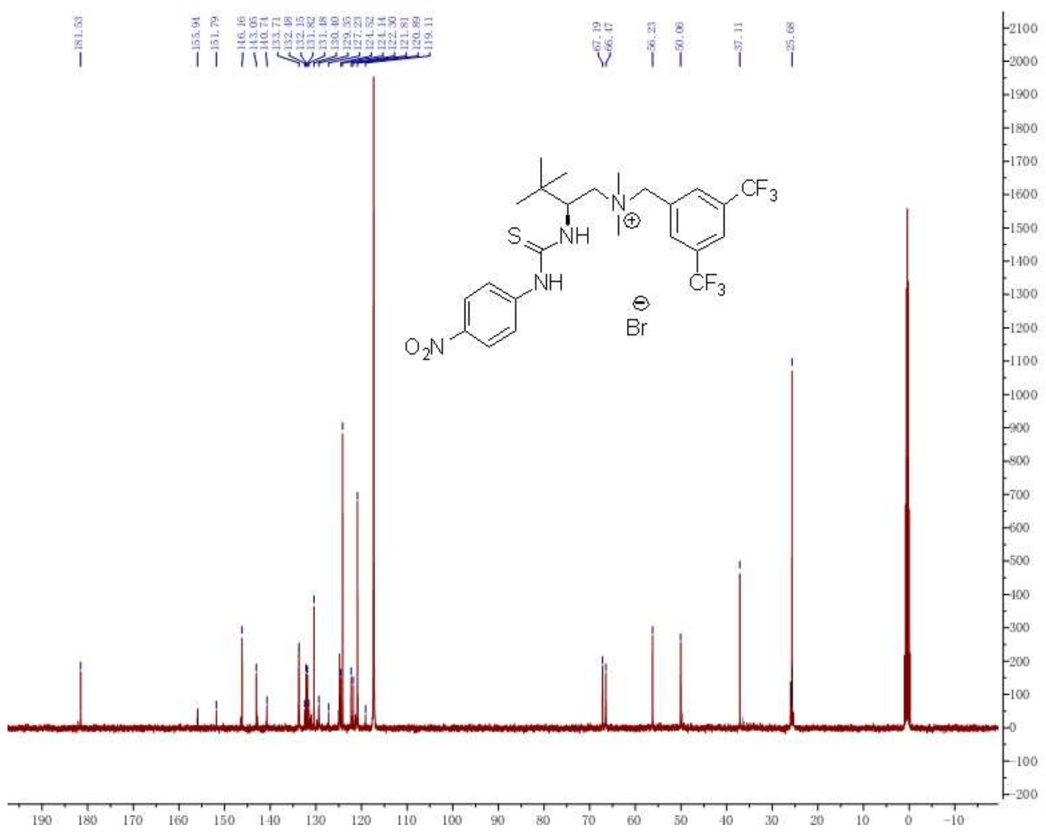
C： The ^{1}H NMR spectra of **g** and *p*-ClC_6H_4SH (1:1) in $(CD_3)_2SO$

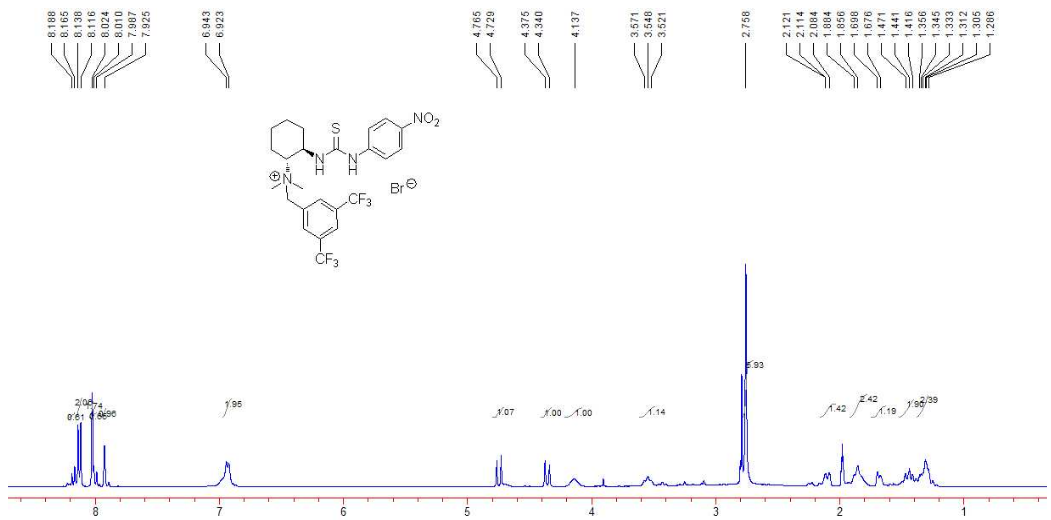
D： The ^{1}H NMR spectra of **g**, $PhSO_2Na{\cdot}2H_2O$ and *p*-ClC_6H_4SH(1:1:1) in $(CD_3)_2SO$

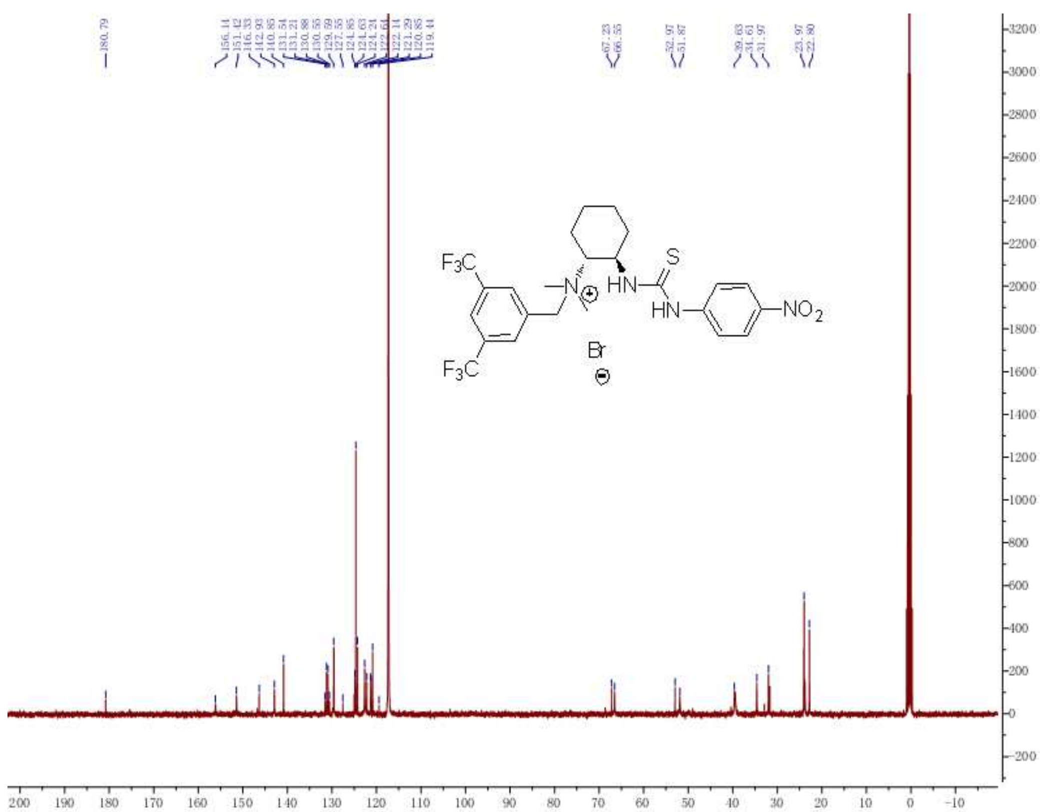


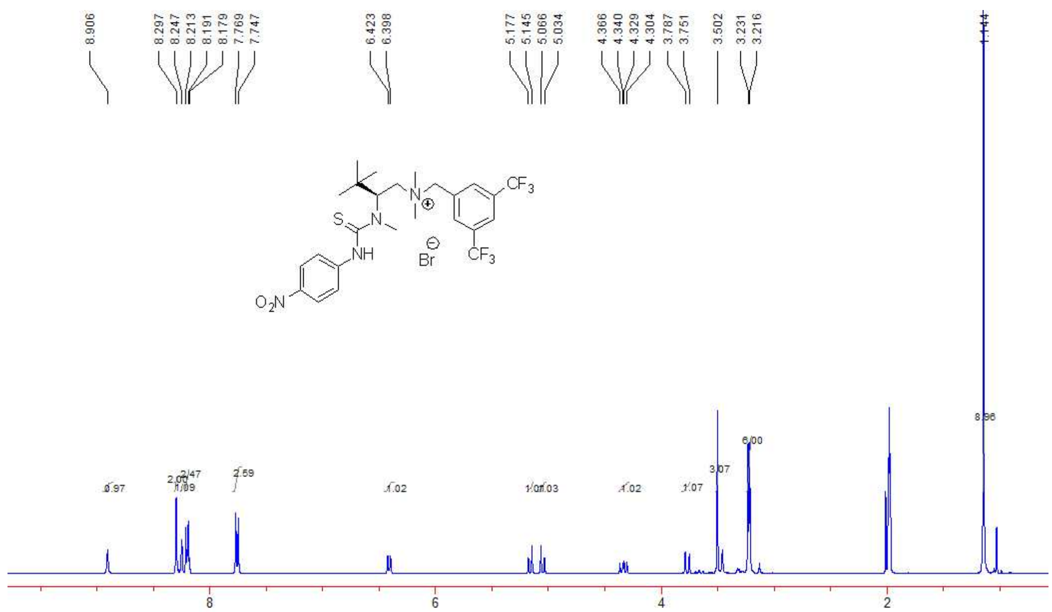
10. NMR and HPLC spectra

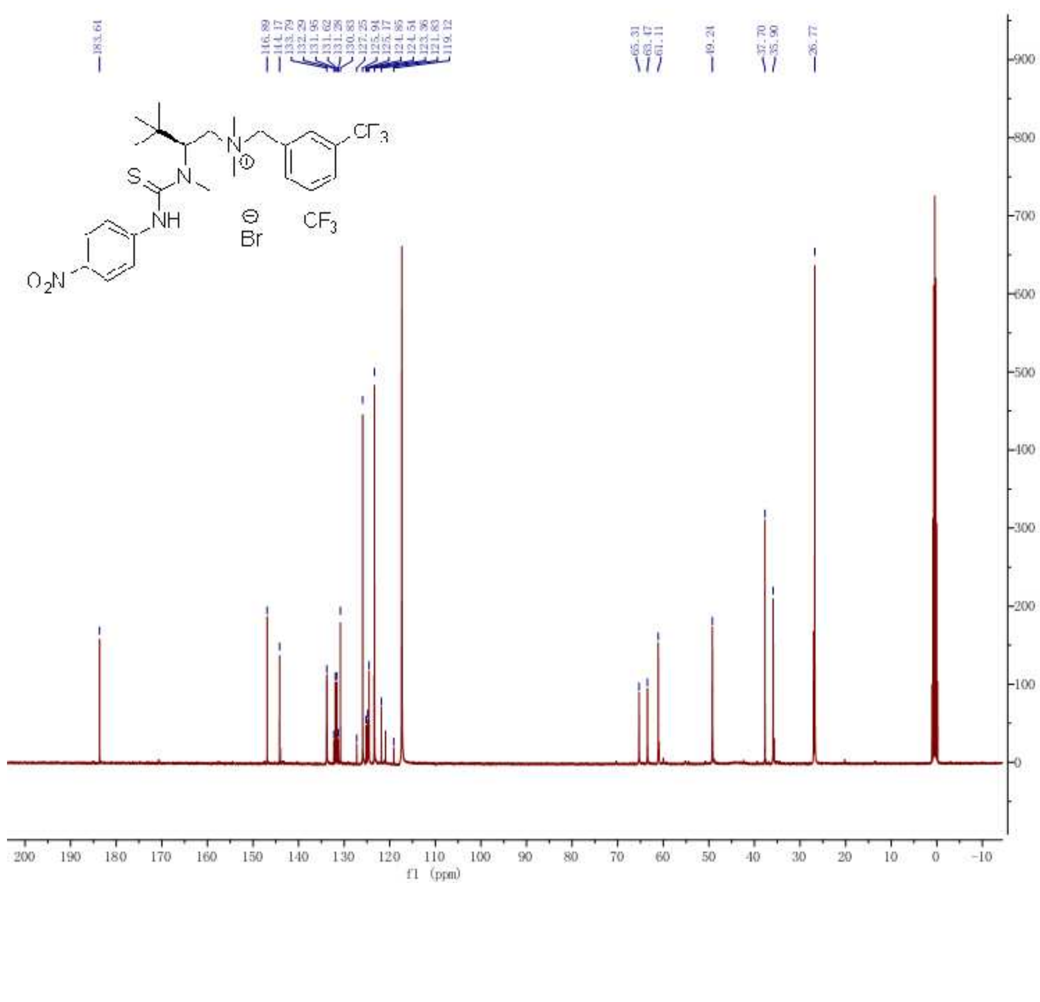


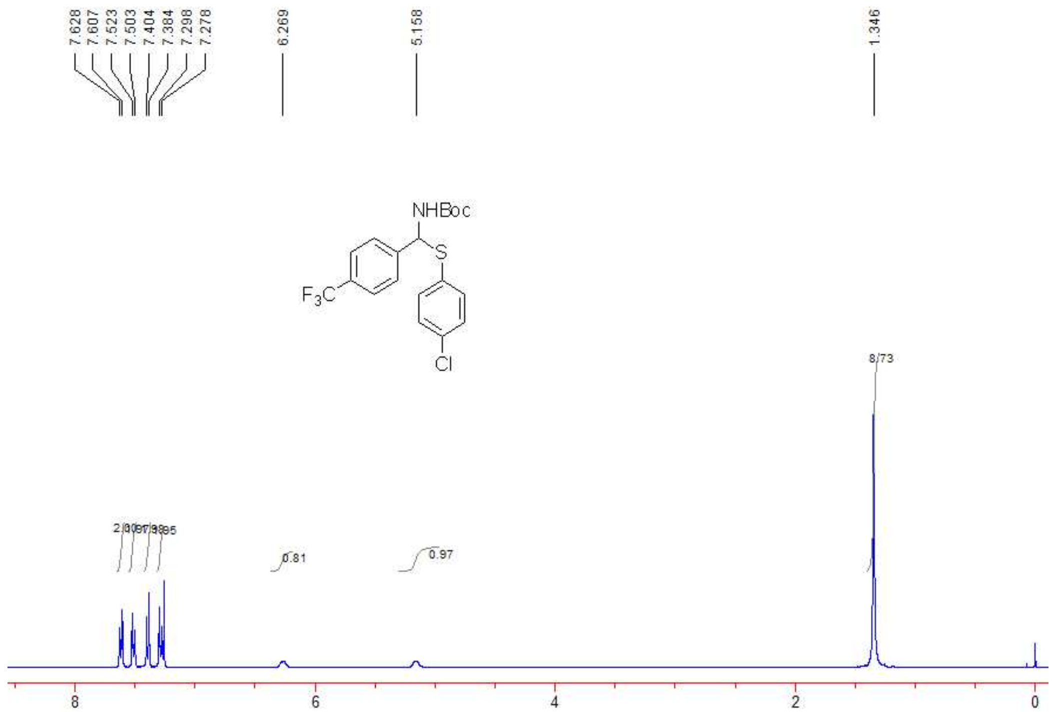


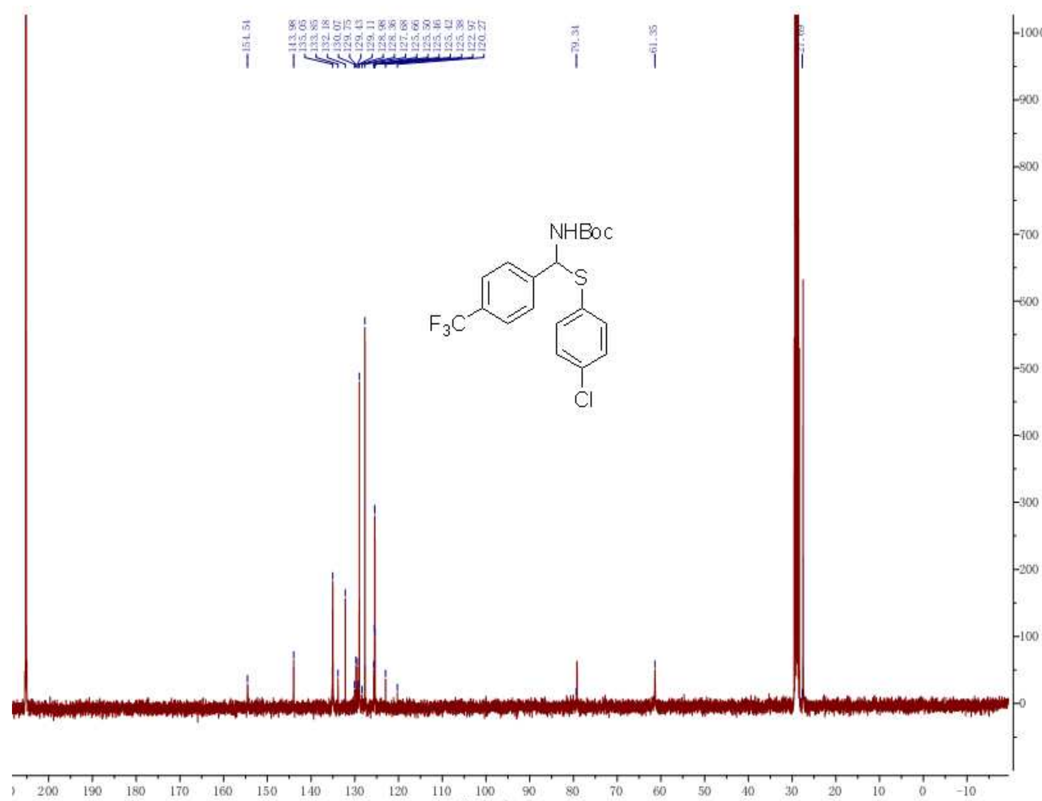


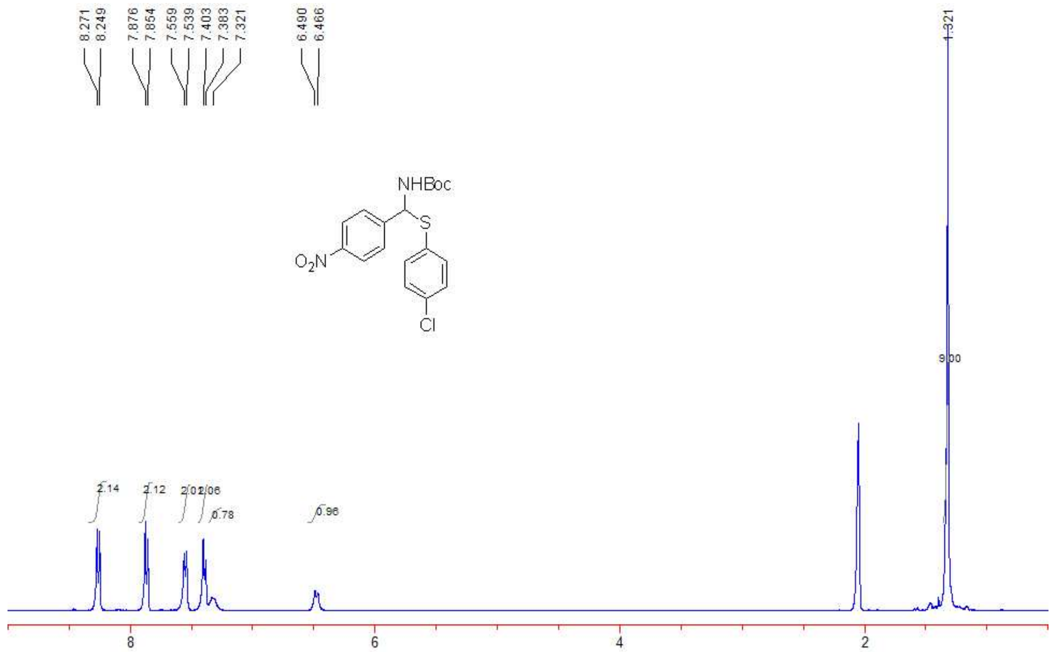








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7.559
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7.403
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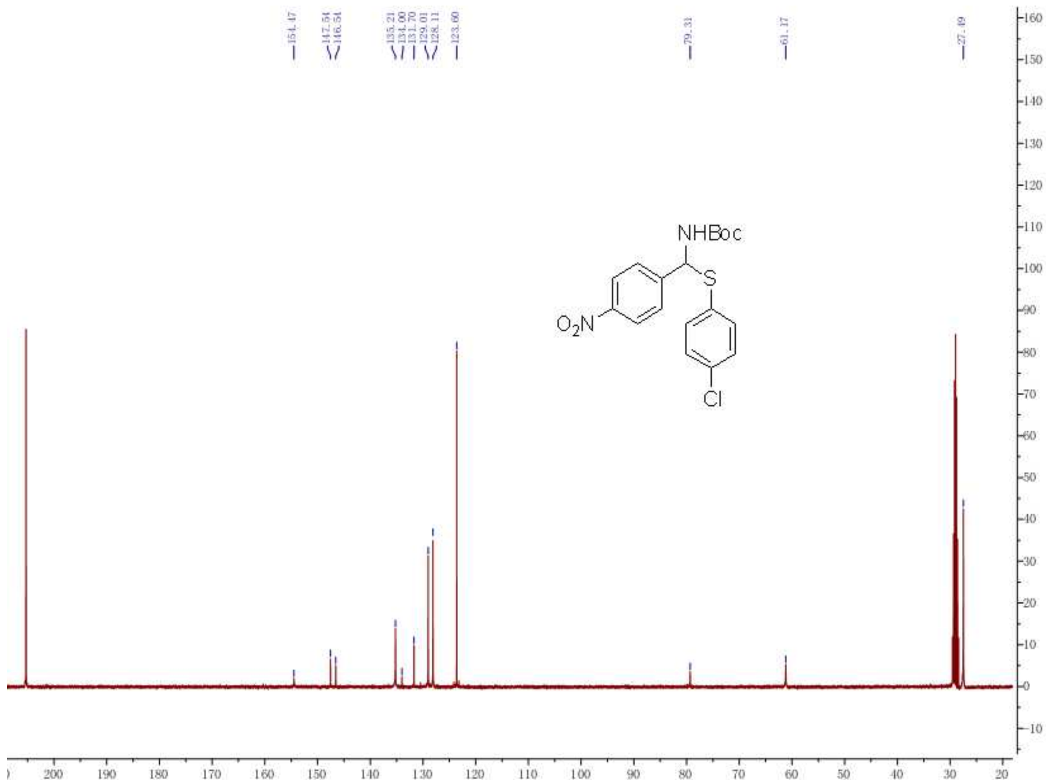
1.321
NHBoc
S
O_2N
Cl
9.00
2.14
2.12
2.01
2.06
0.78
0.96
8
6
4
2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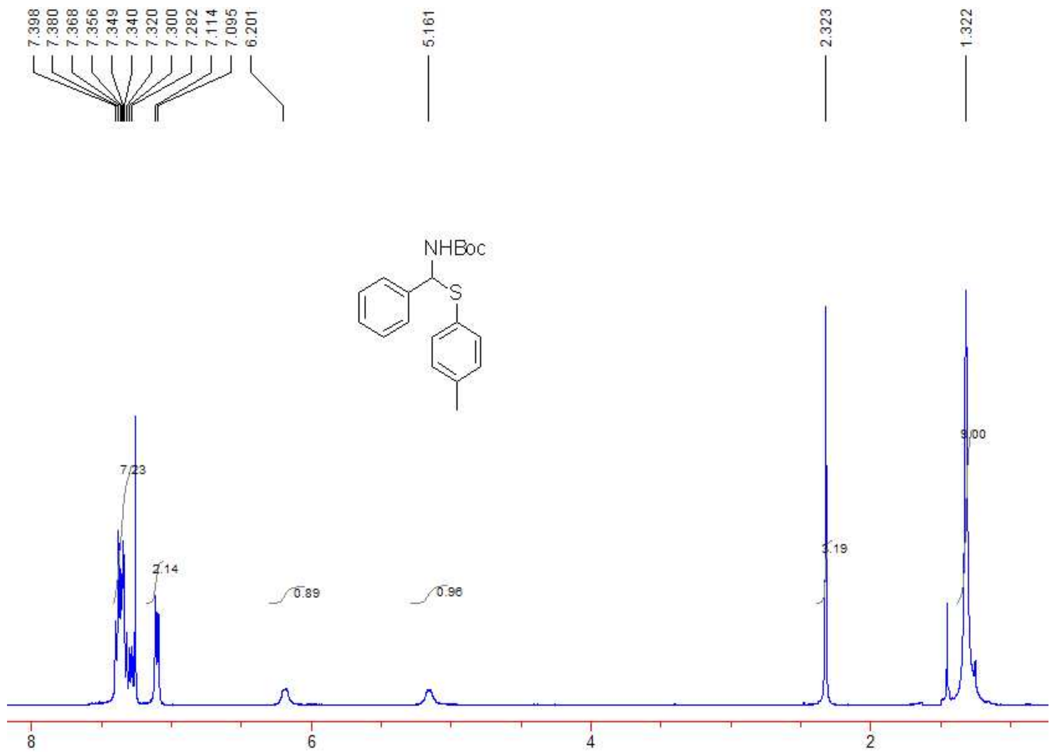
S
O_2N
Cl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5.161
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S
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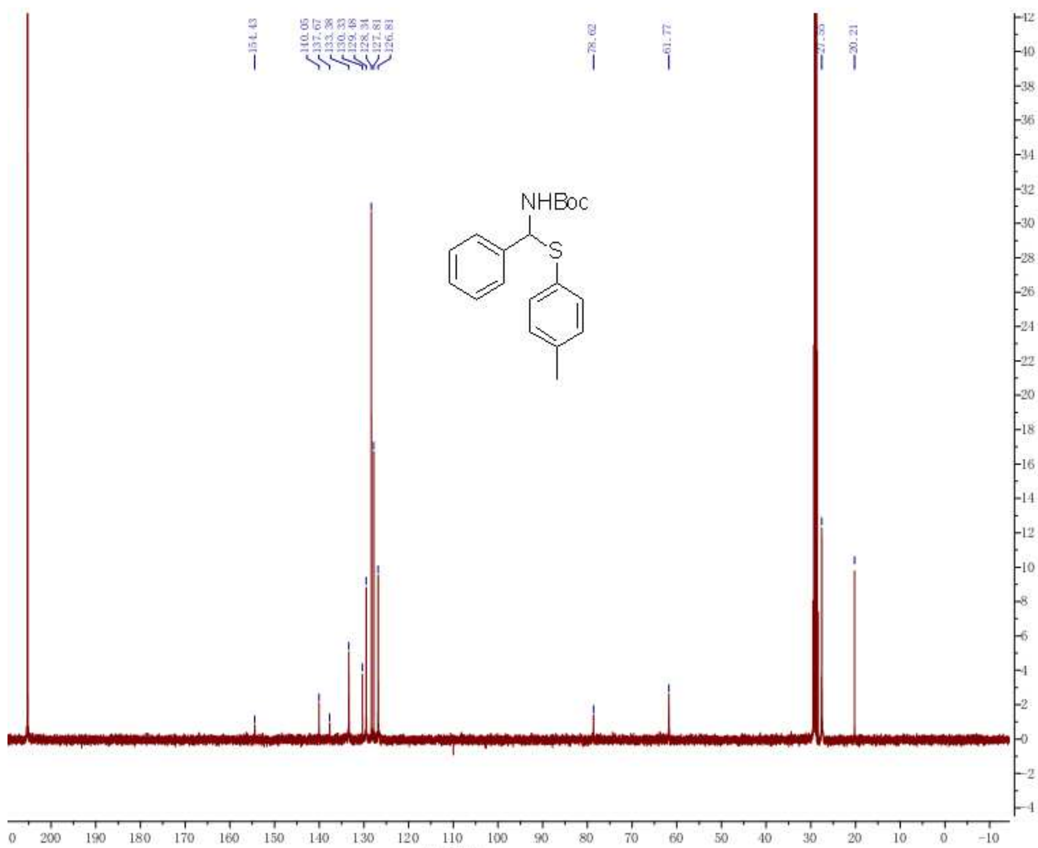
0.96
3.19
9.00
8
6
4
2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78.62
61.77
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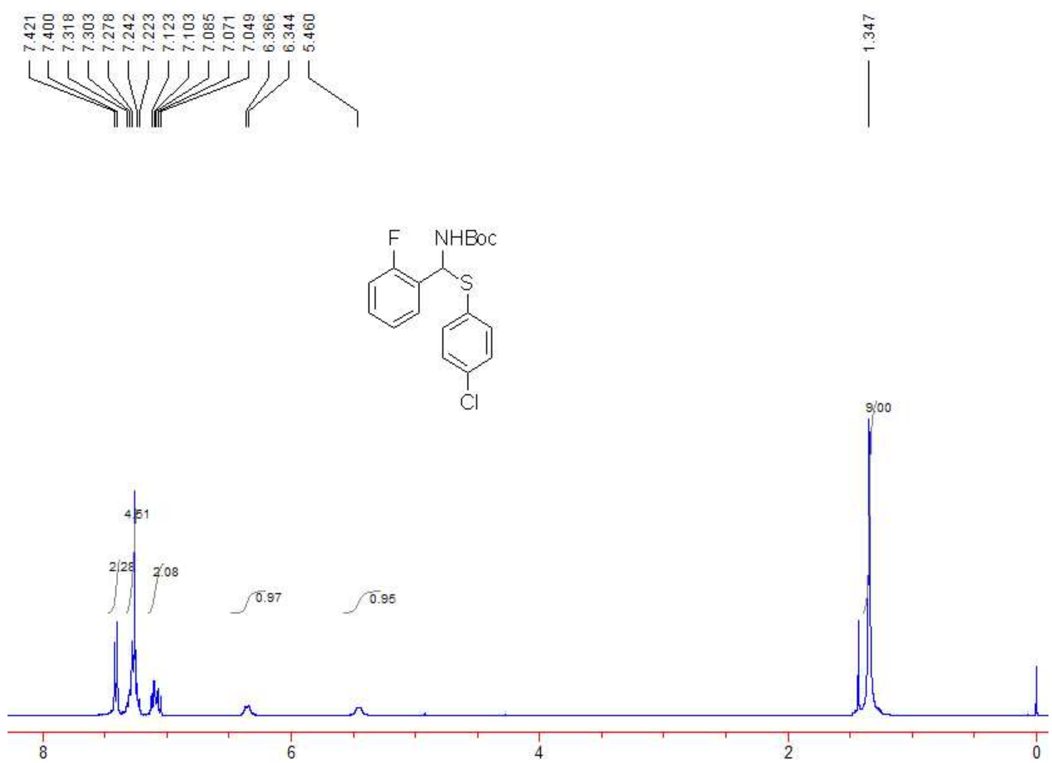
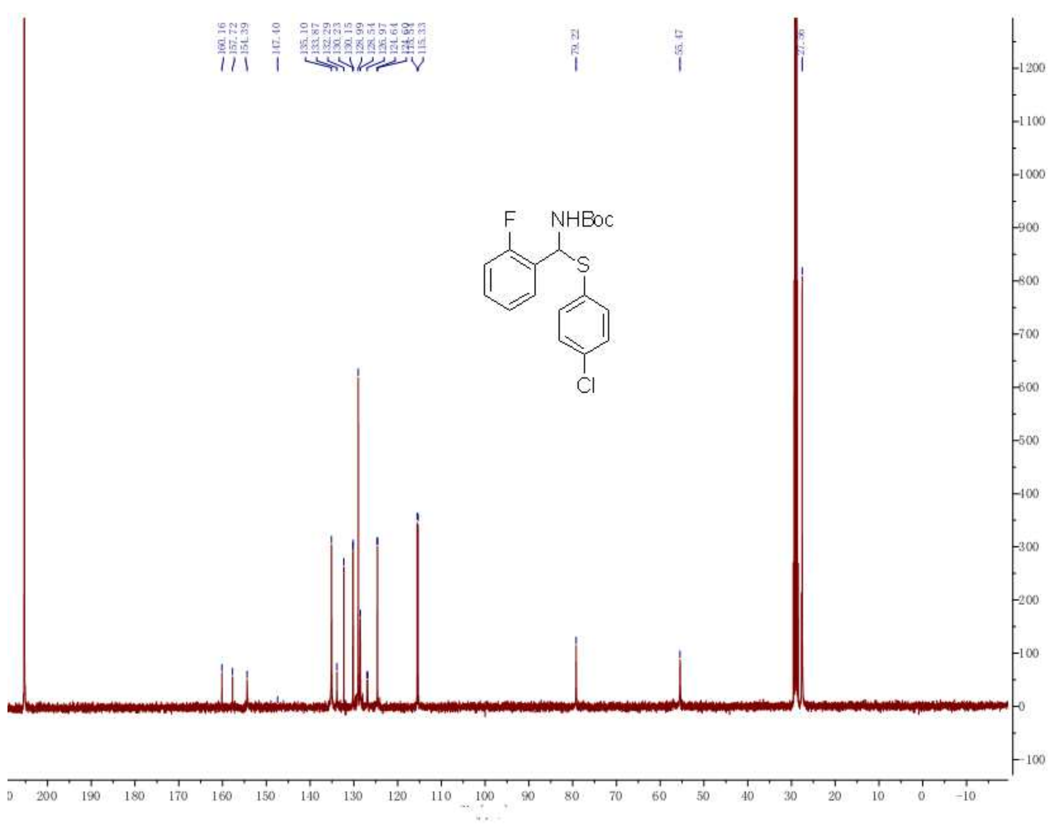
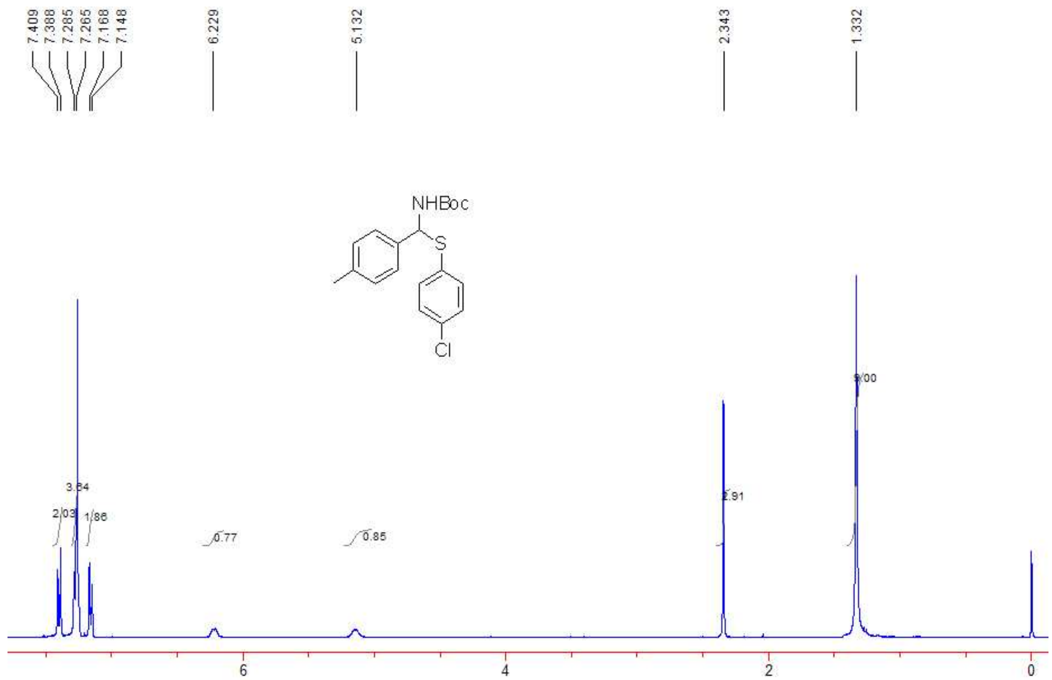
NHBoc
S
f1 (ppm)



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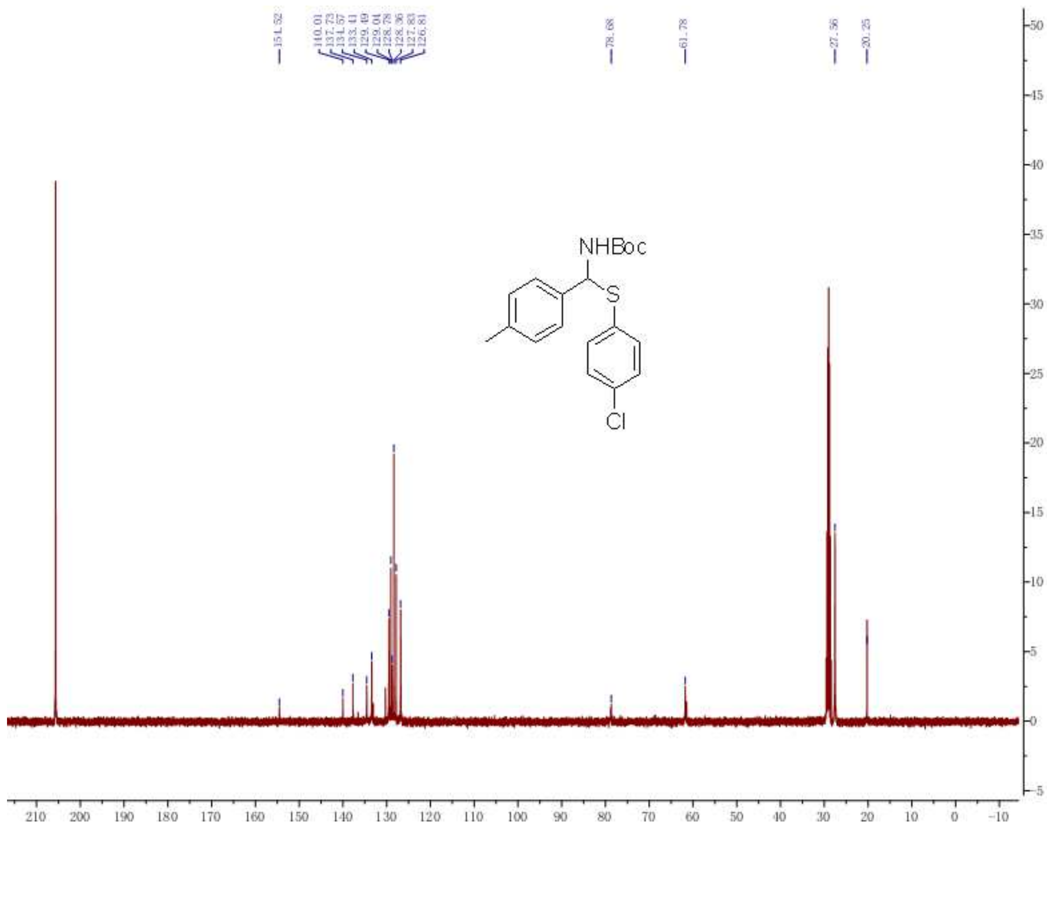
9.00
6
4
2
0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S
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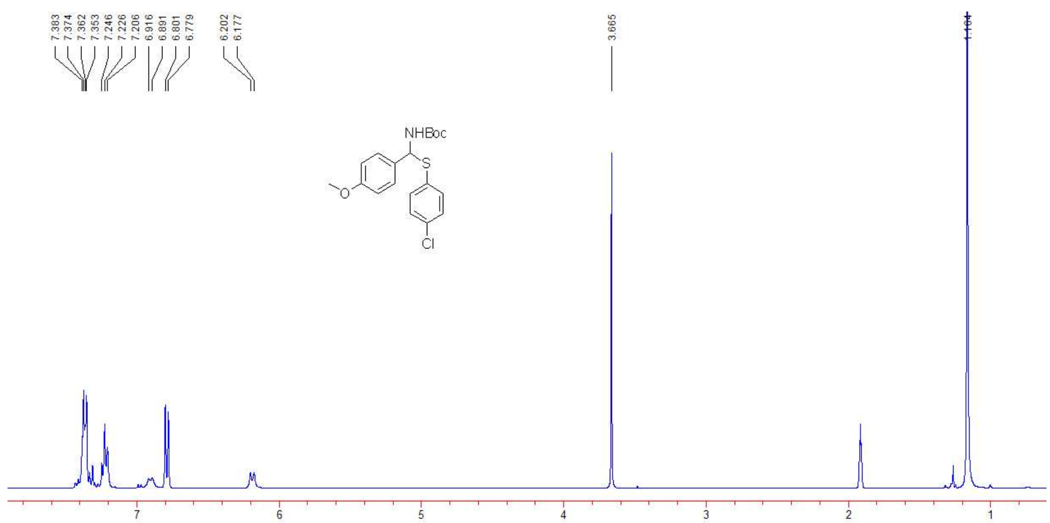

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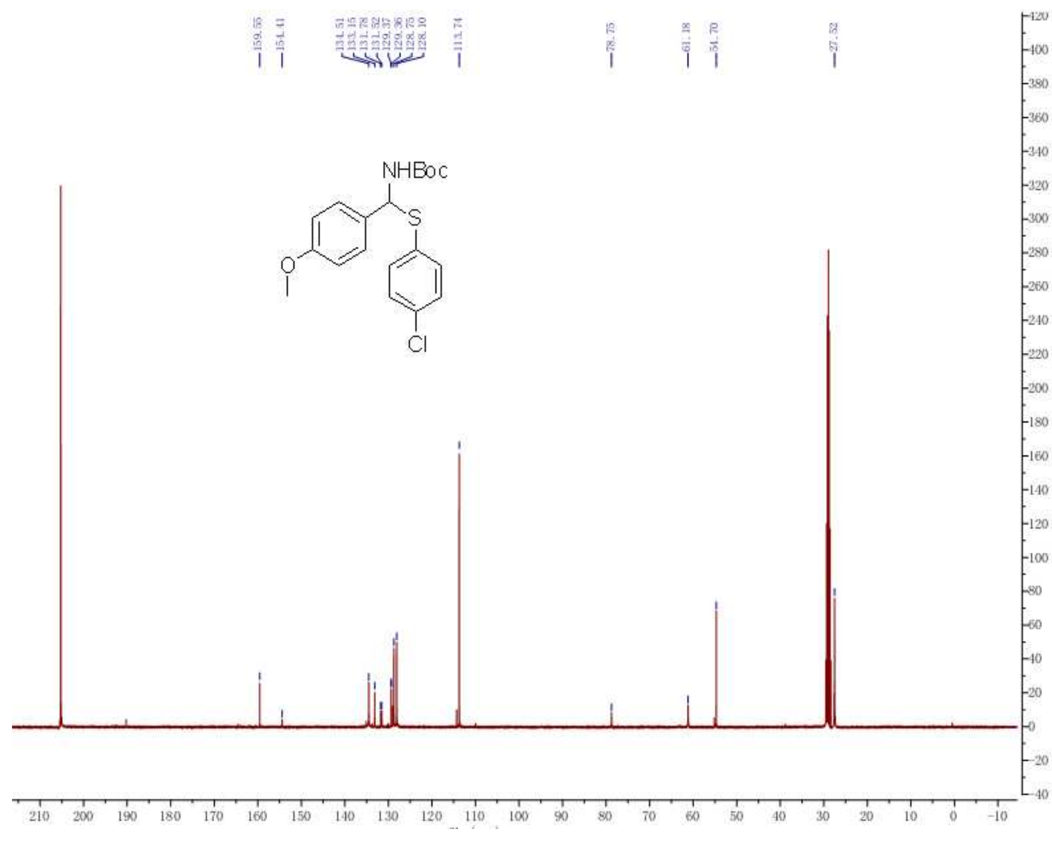
S
O
Cl



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131.52
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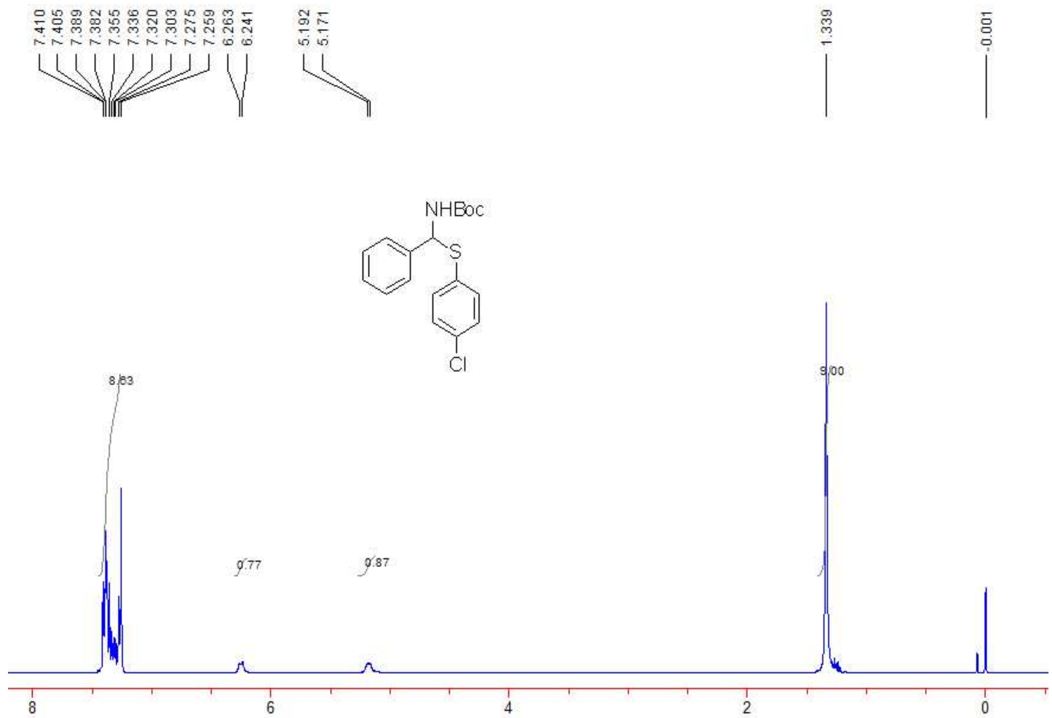
54.70
27.52
NHBoc
S
O
Cl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5.192
5.171
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NHBoc
S
Cl
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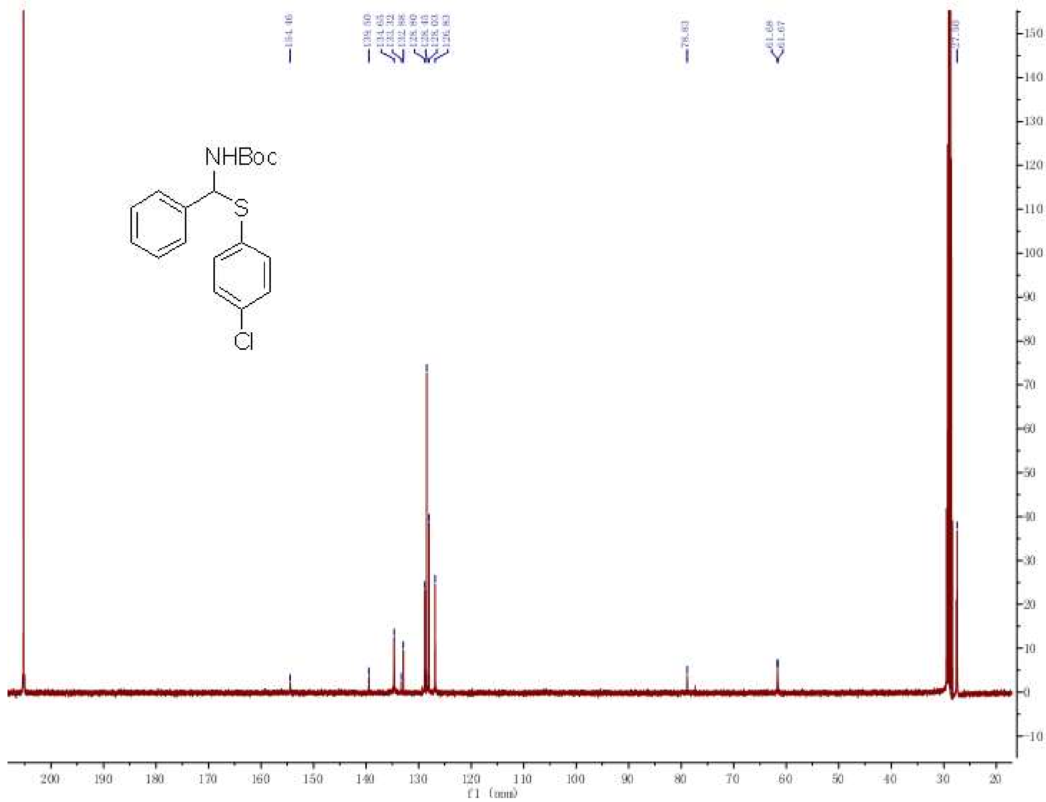
0.87
9.00
8
6
4
2
0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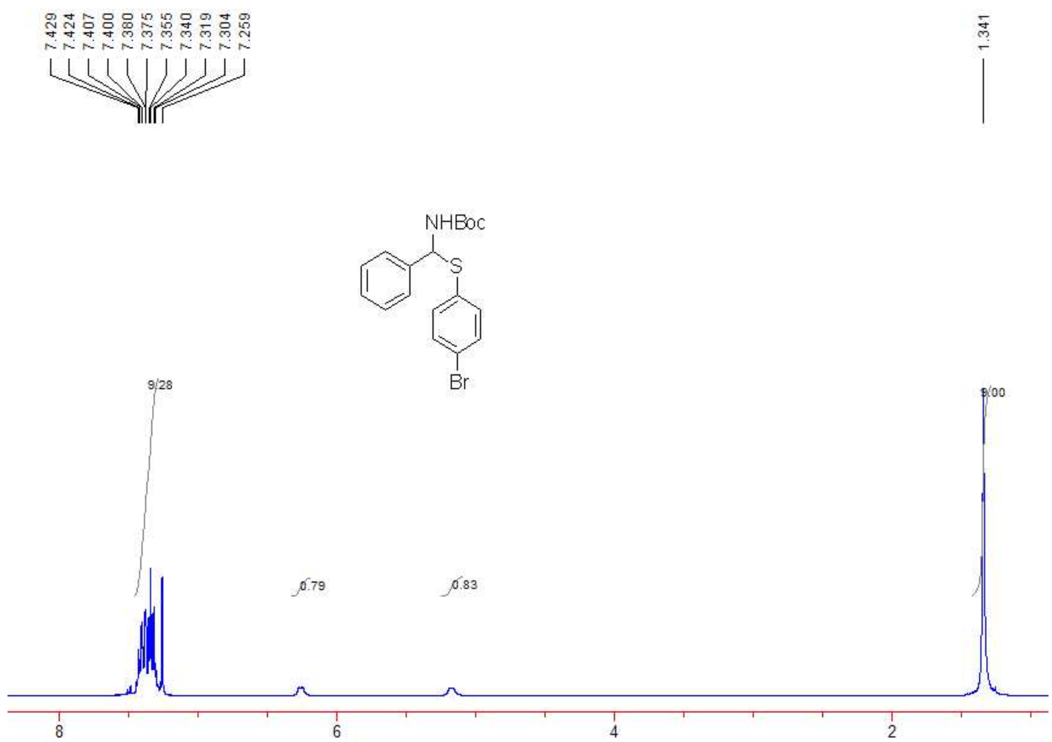
NHBoc
S
Cl
f1 (ppm)



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7.340
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Br
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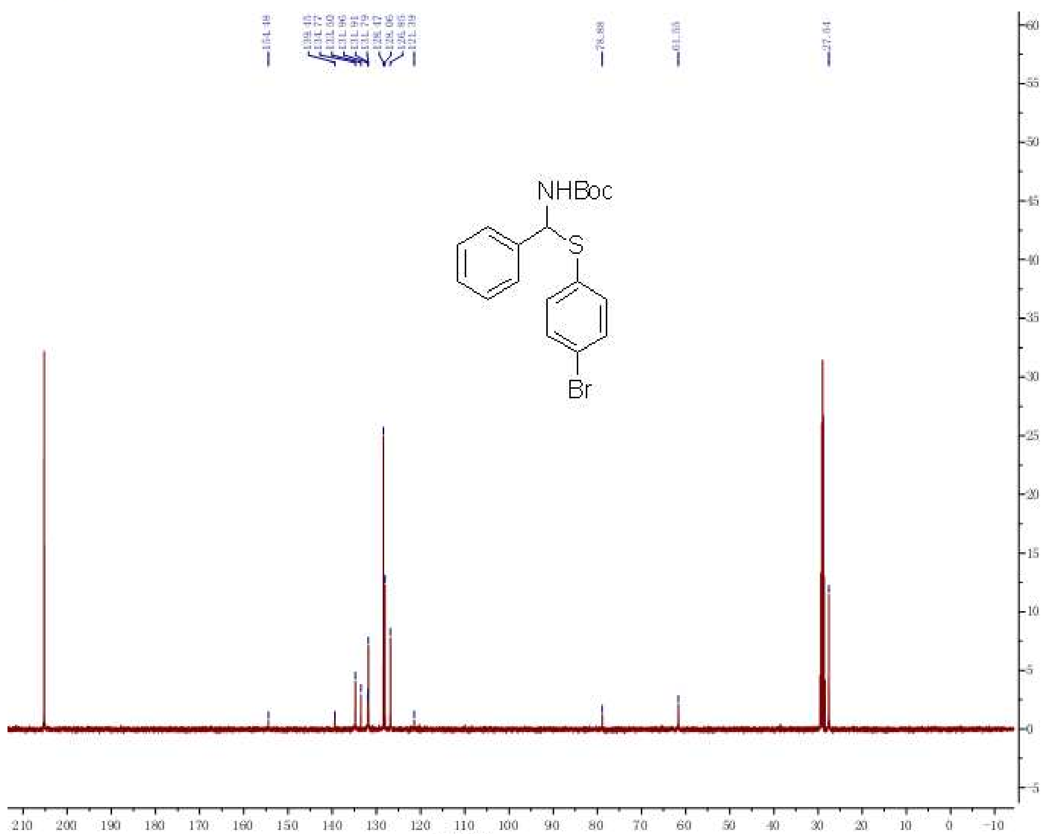
0.83
9.00
8
6
4
2



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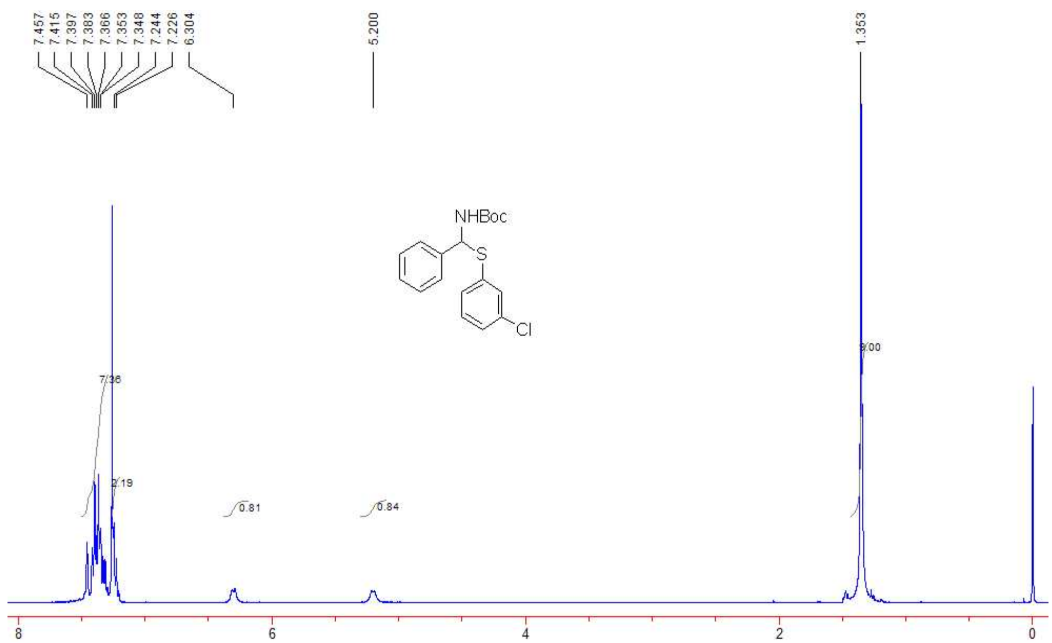
NHBoc
S
Br
f1 (ppm)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Cl
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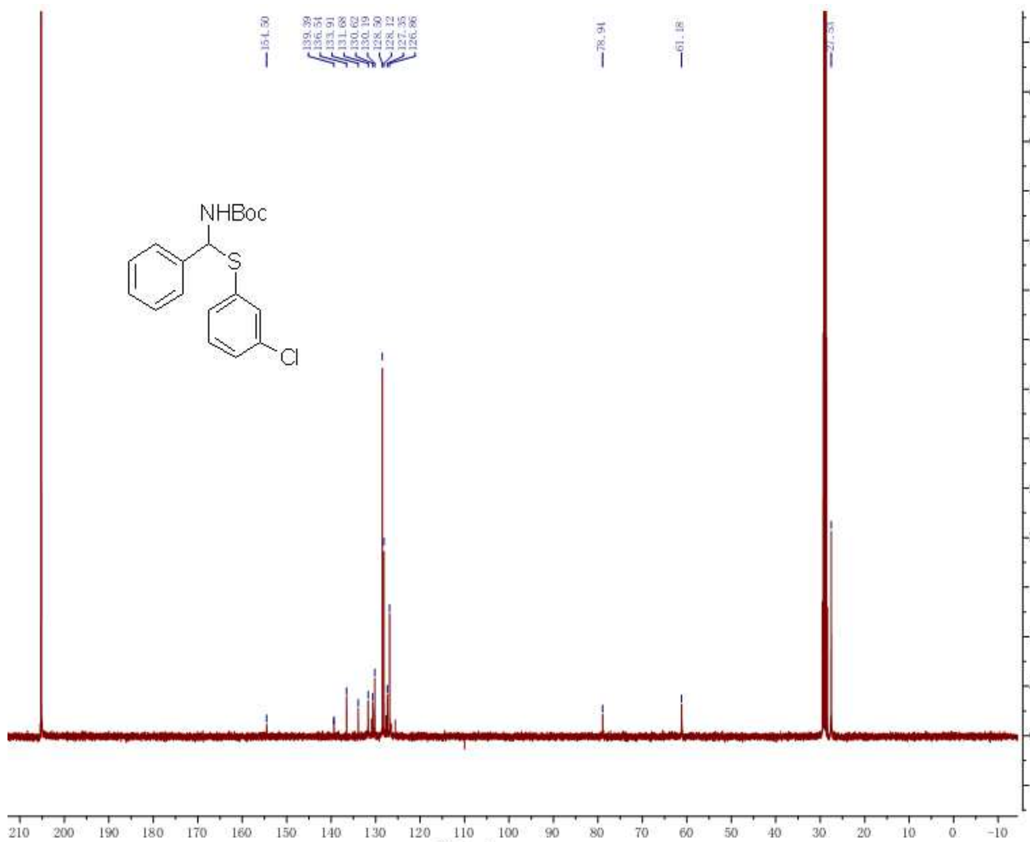
4
2
0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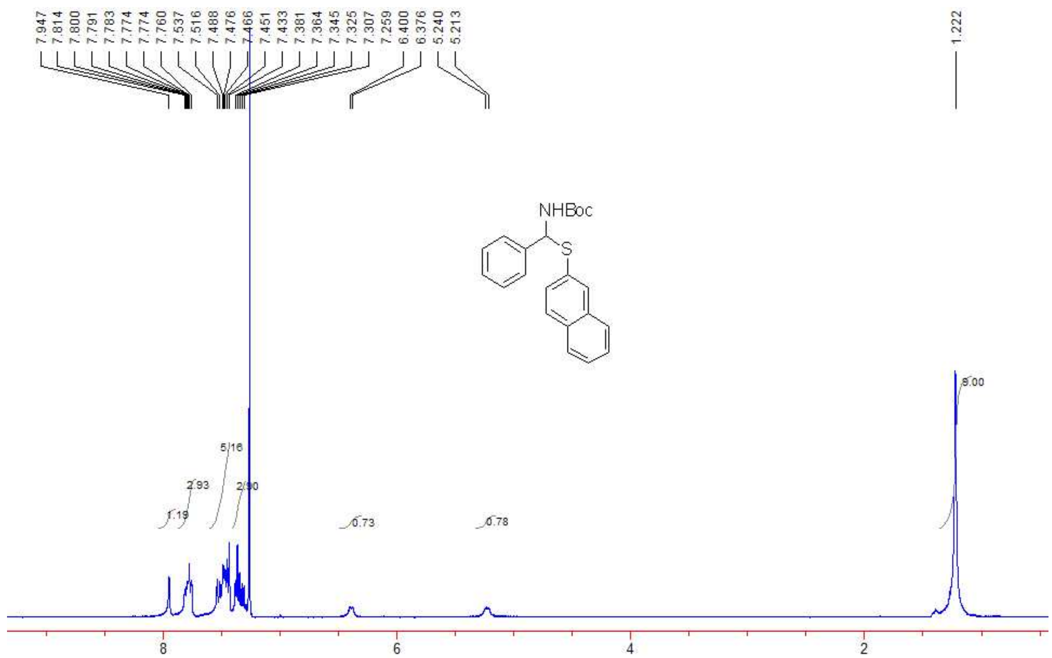
NHBoc
S
Cl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7.451
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7.381
7.364
7.345
7.325
7.307
7.259
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6.376
5.240
5.213
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NHBoc
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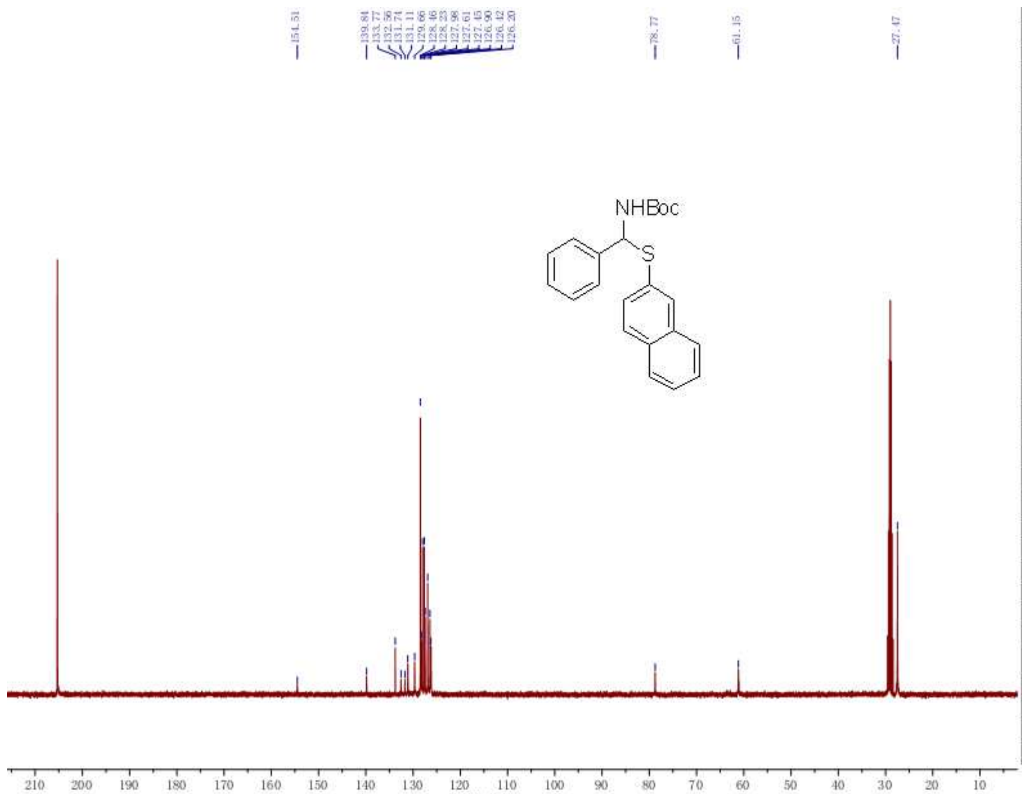
0.78
9.00
8
6
4
2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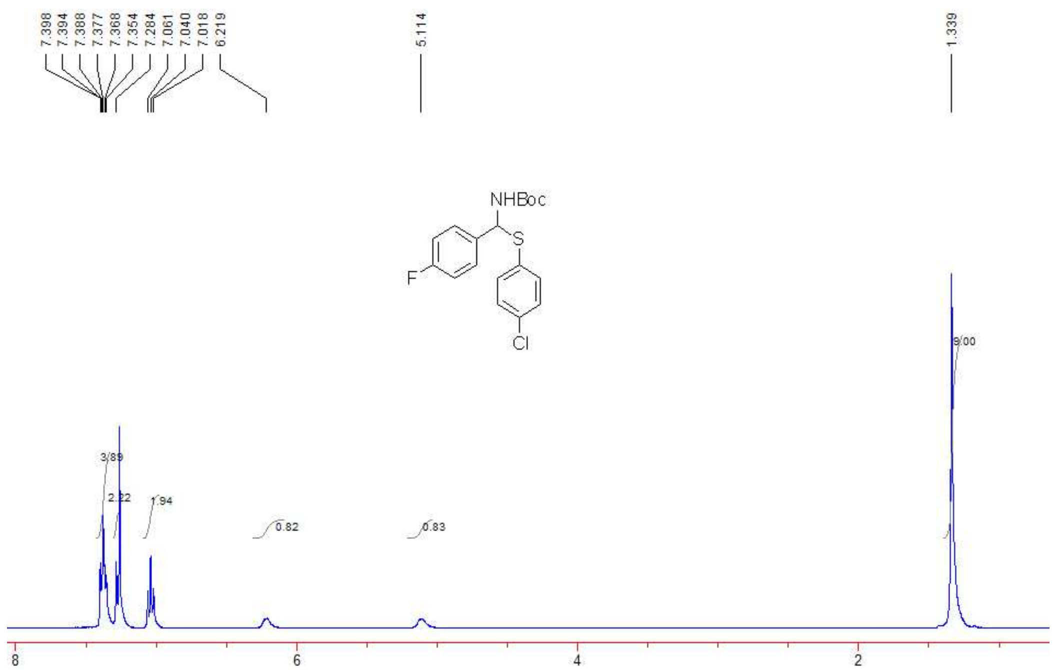
61.15
27.47
NHBoc
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10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Cl
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8
6
4
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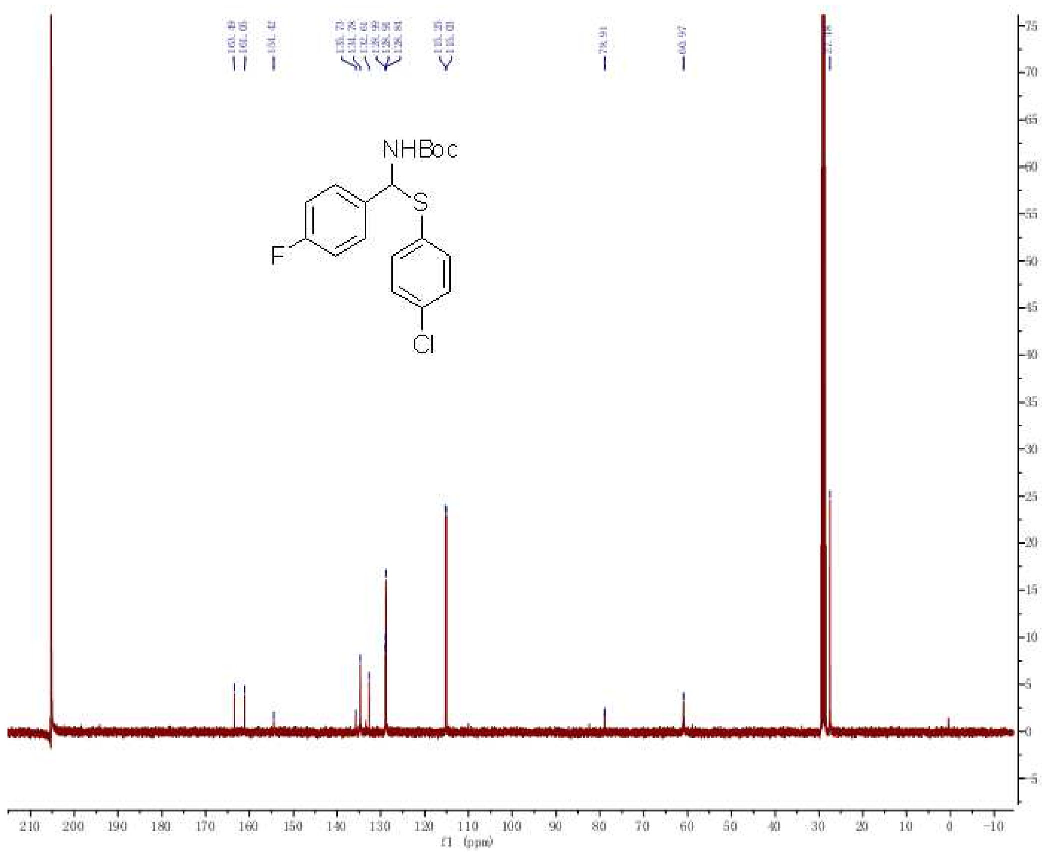
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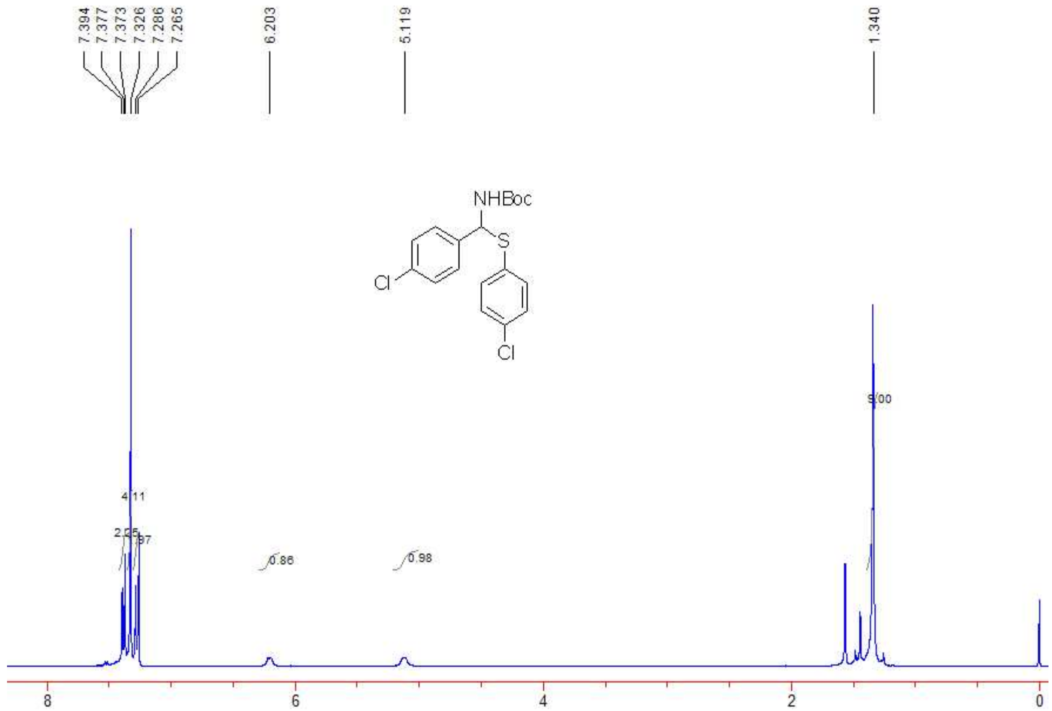
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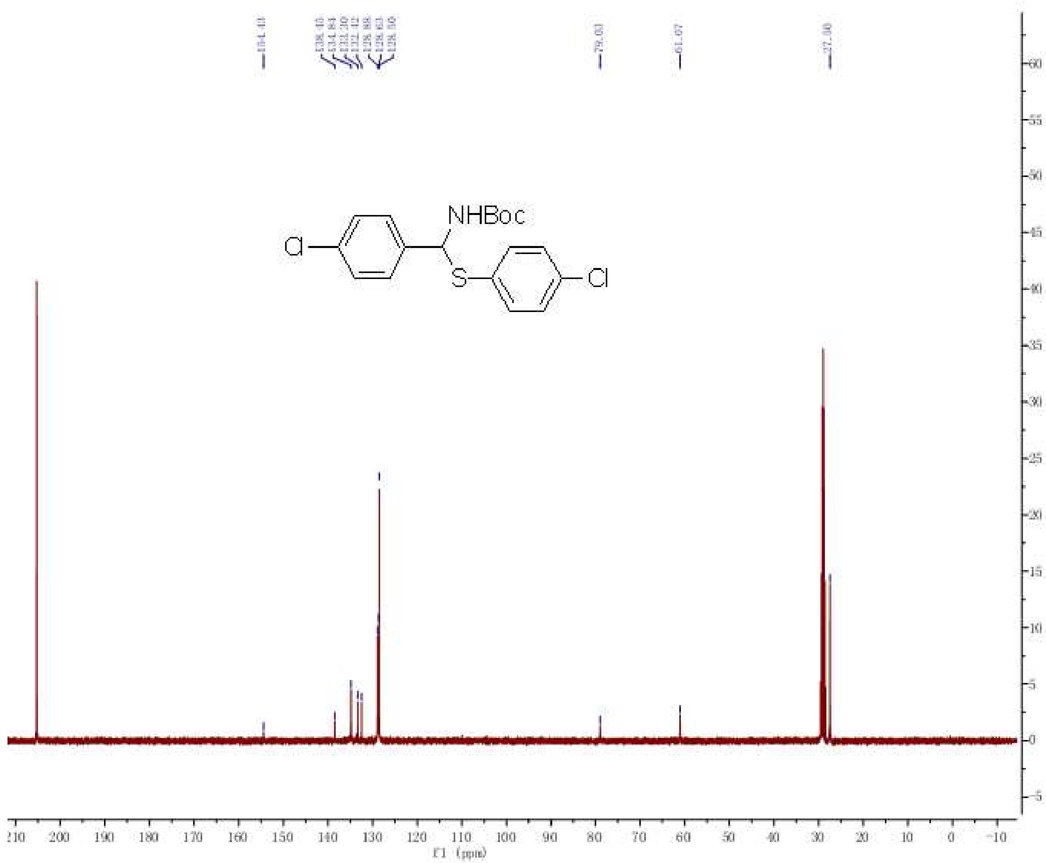
4.11
2.25
1.97
0.86
0.98
8
6
4
2
0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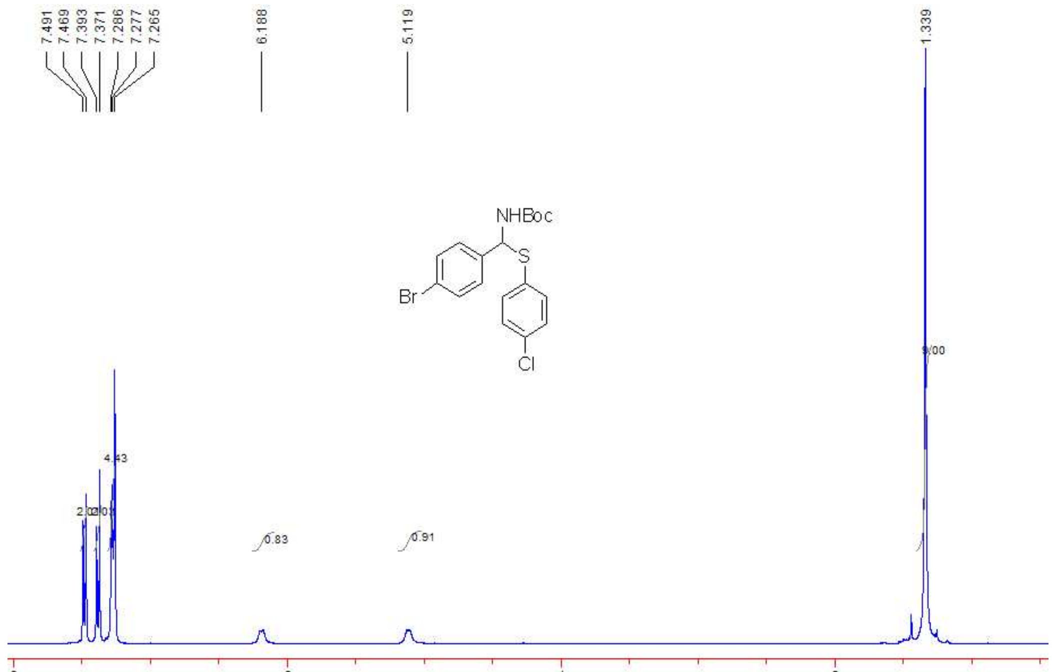
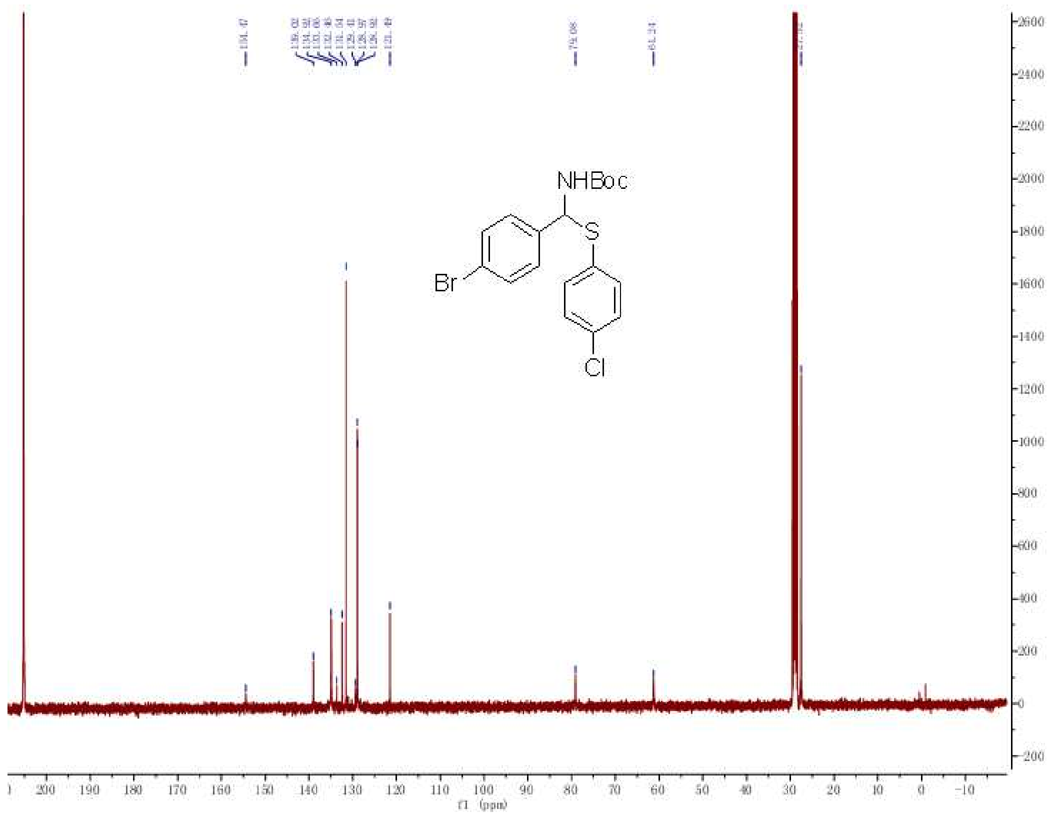
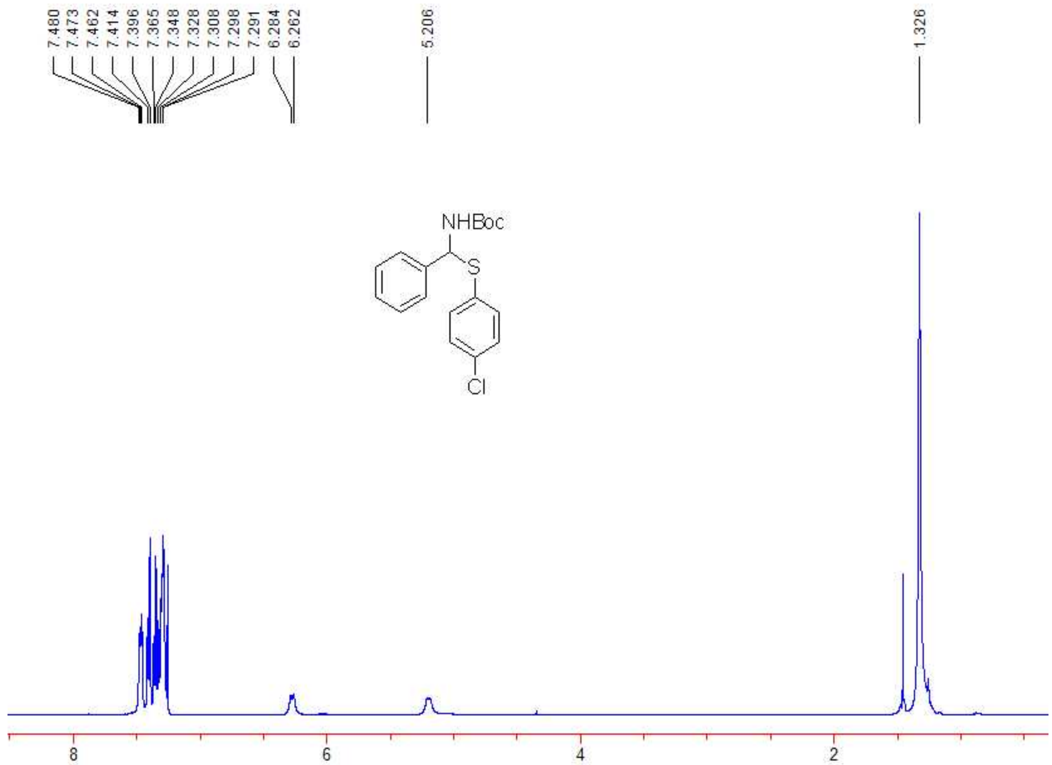
Cl
S
Cl
f1 (ppm)



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NHBoc
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4
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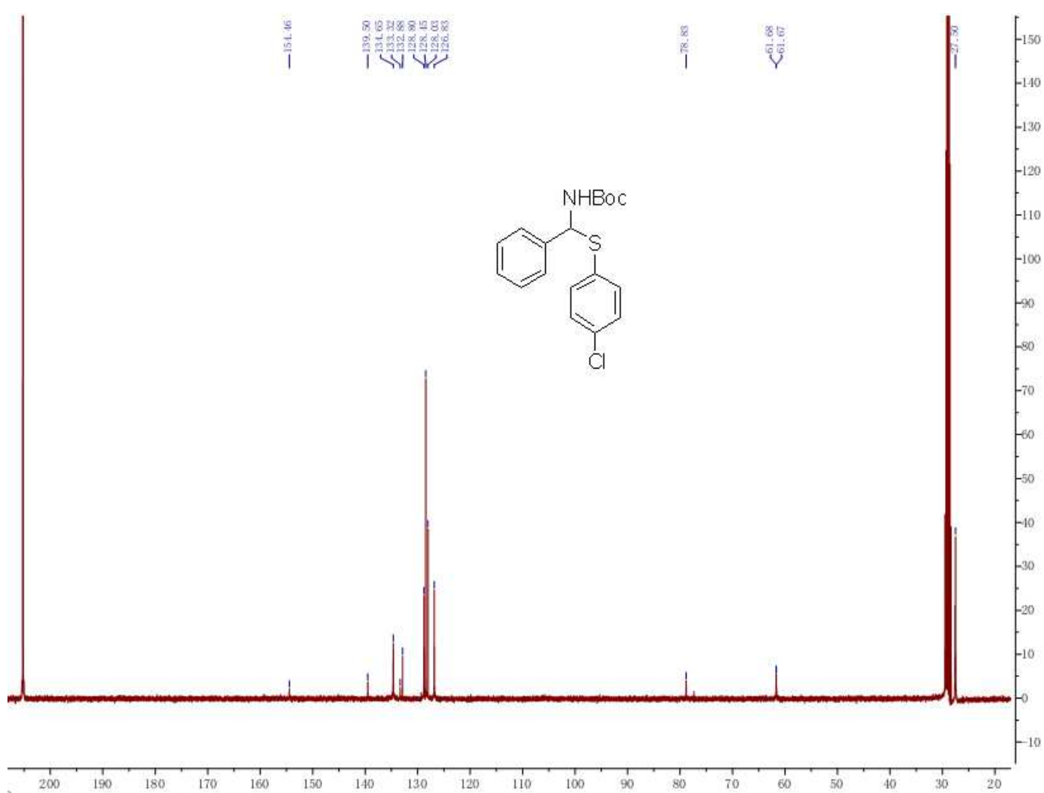
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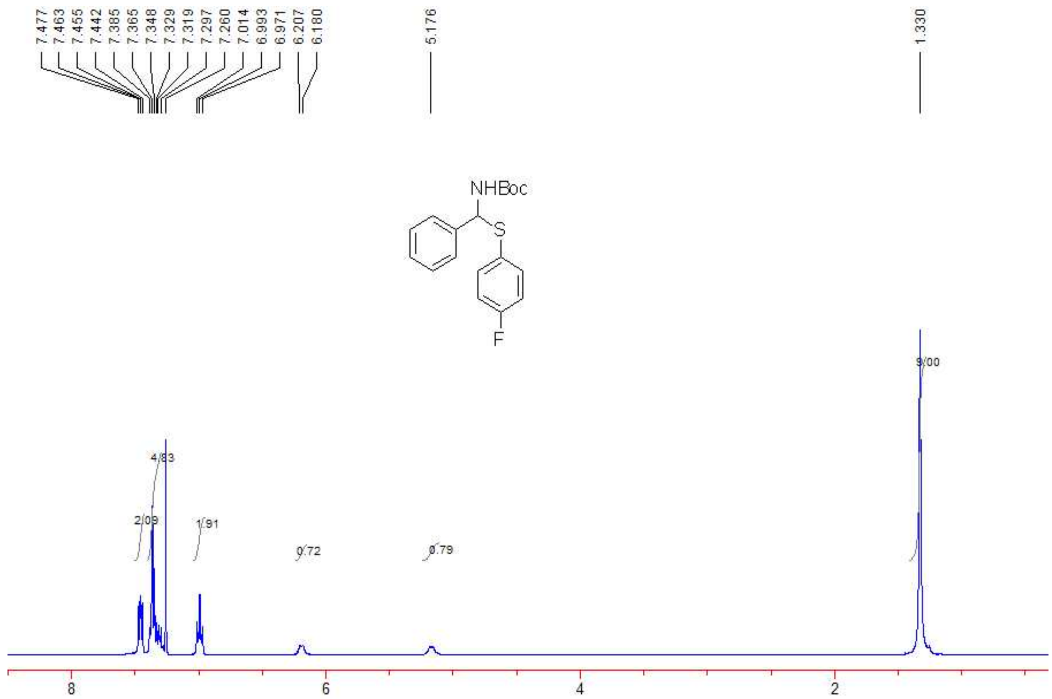

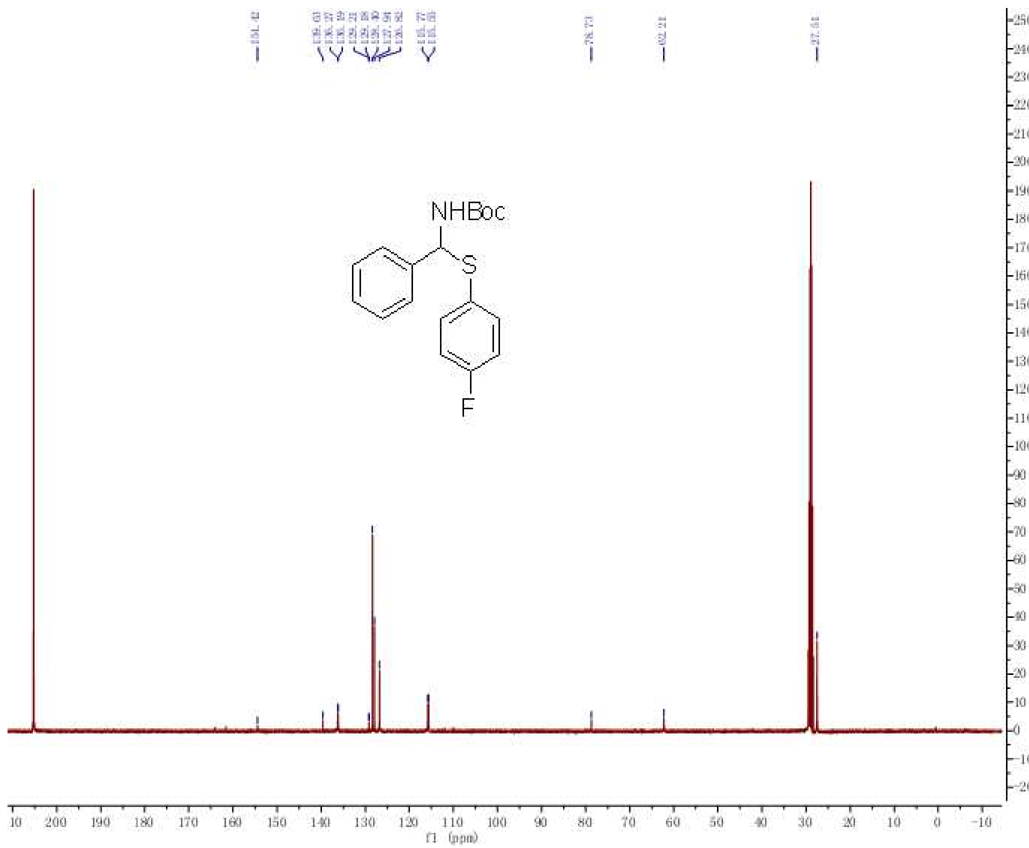

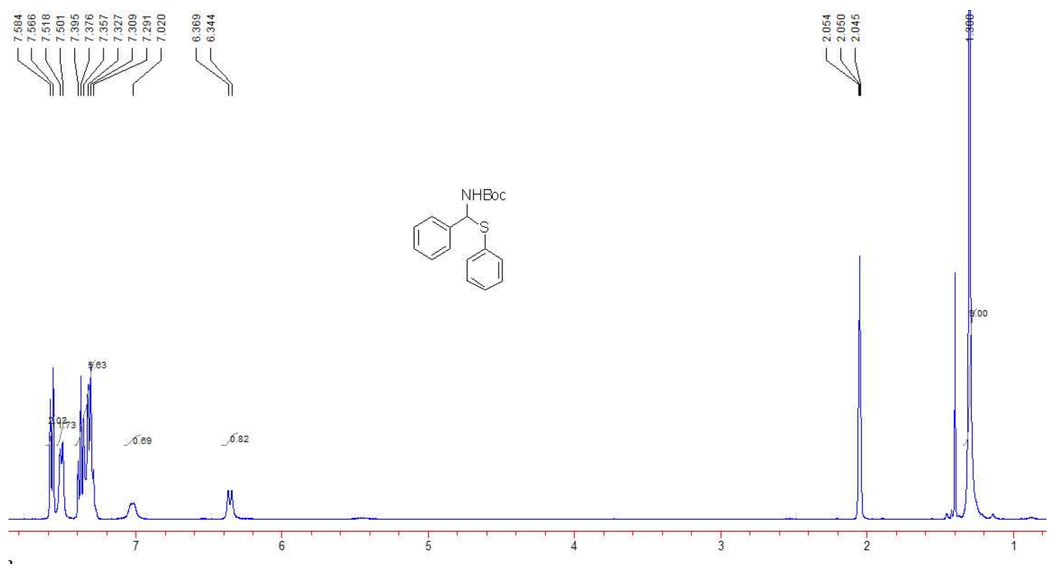
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2
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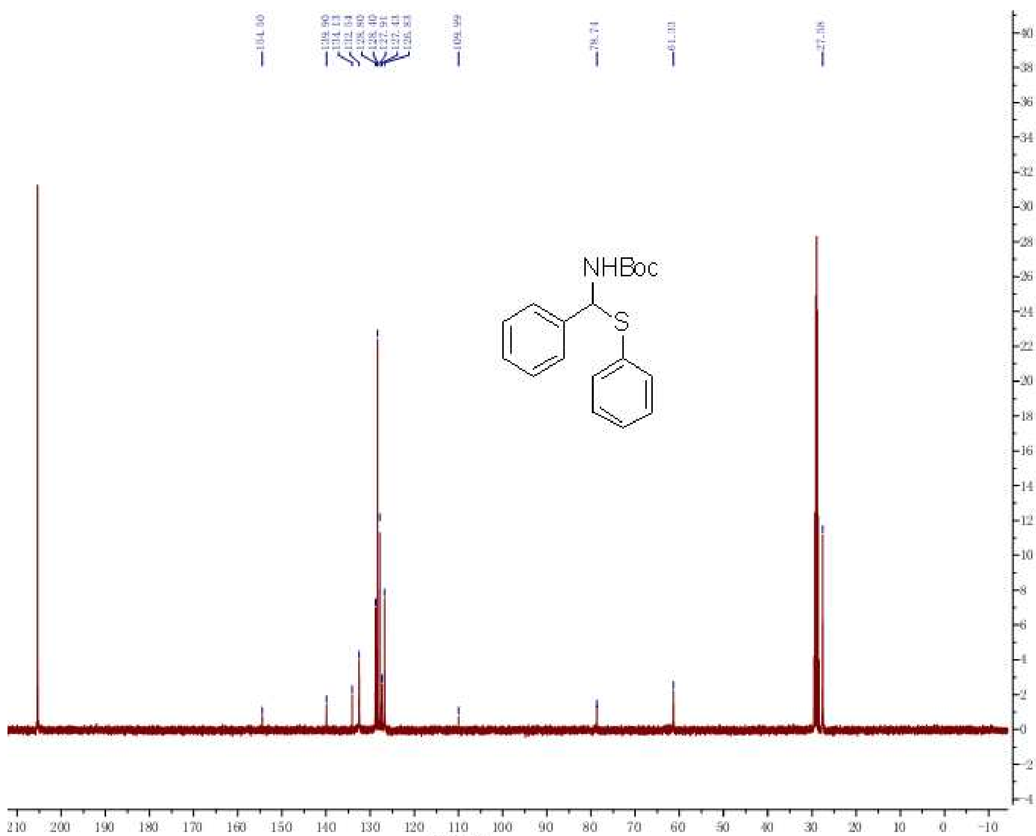
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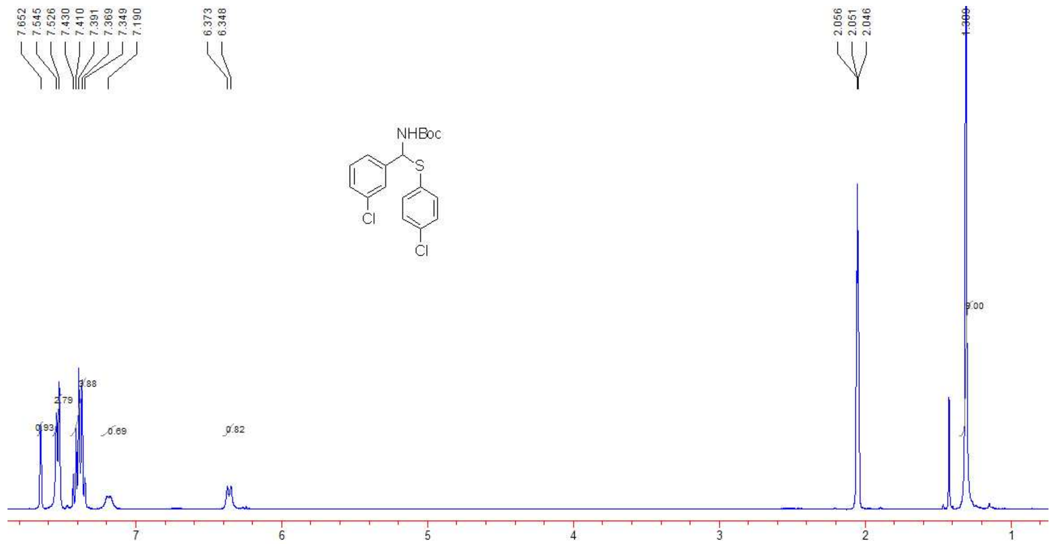
NHBoc
S
f1 (ppm)



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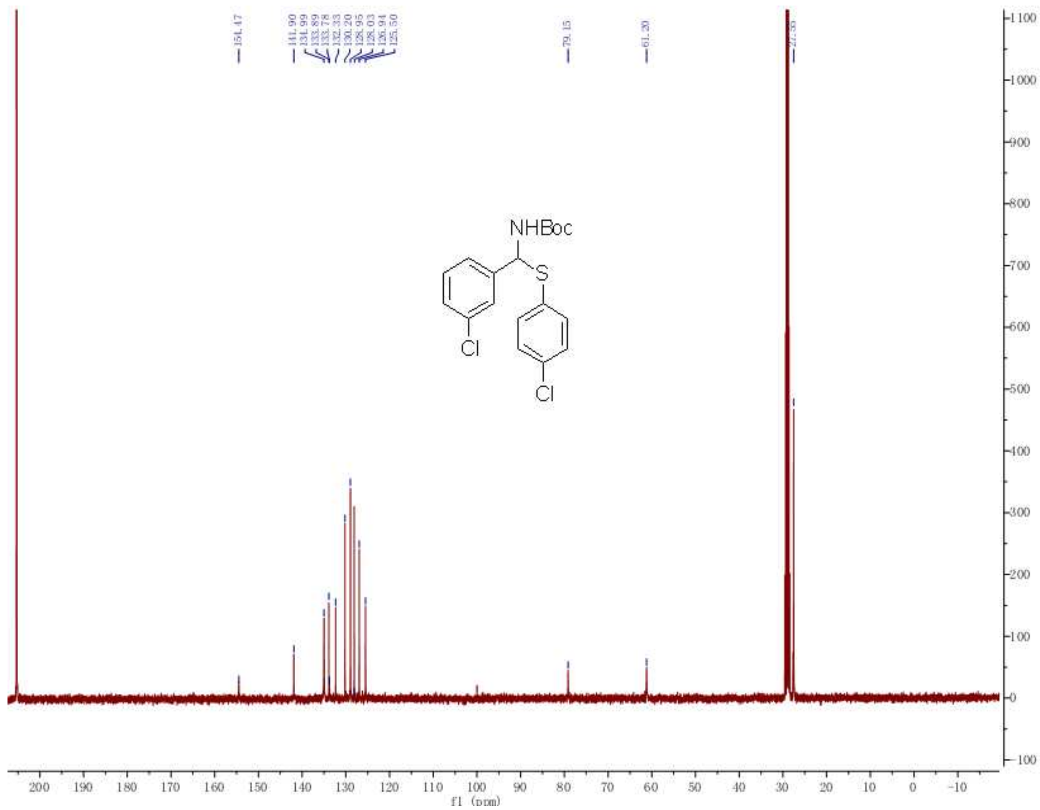
NHBoc
S
Cl
Cl



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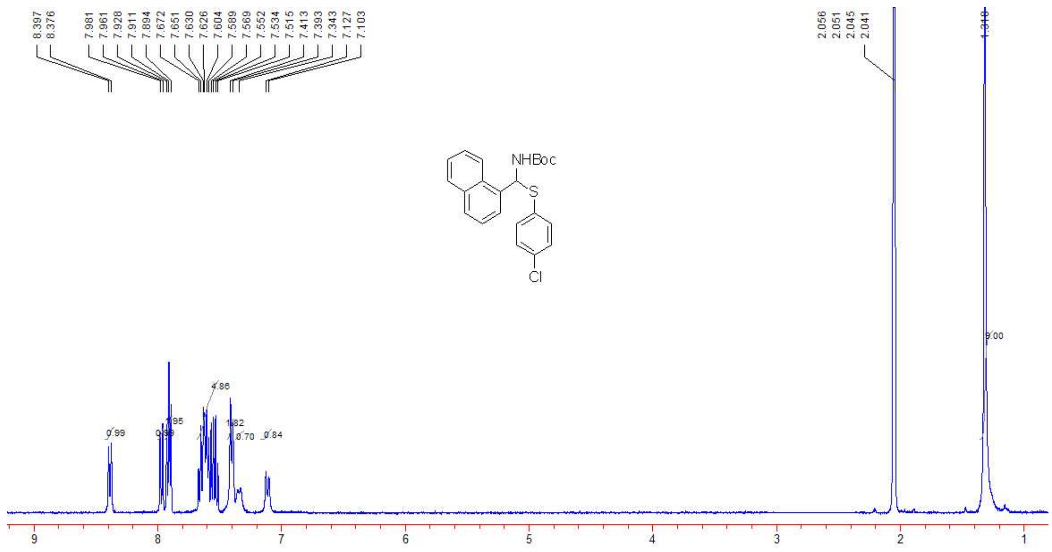
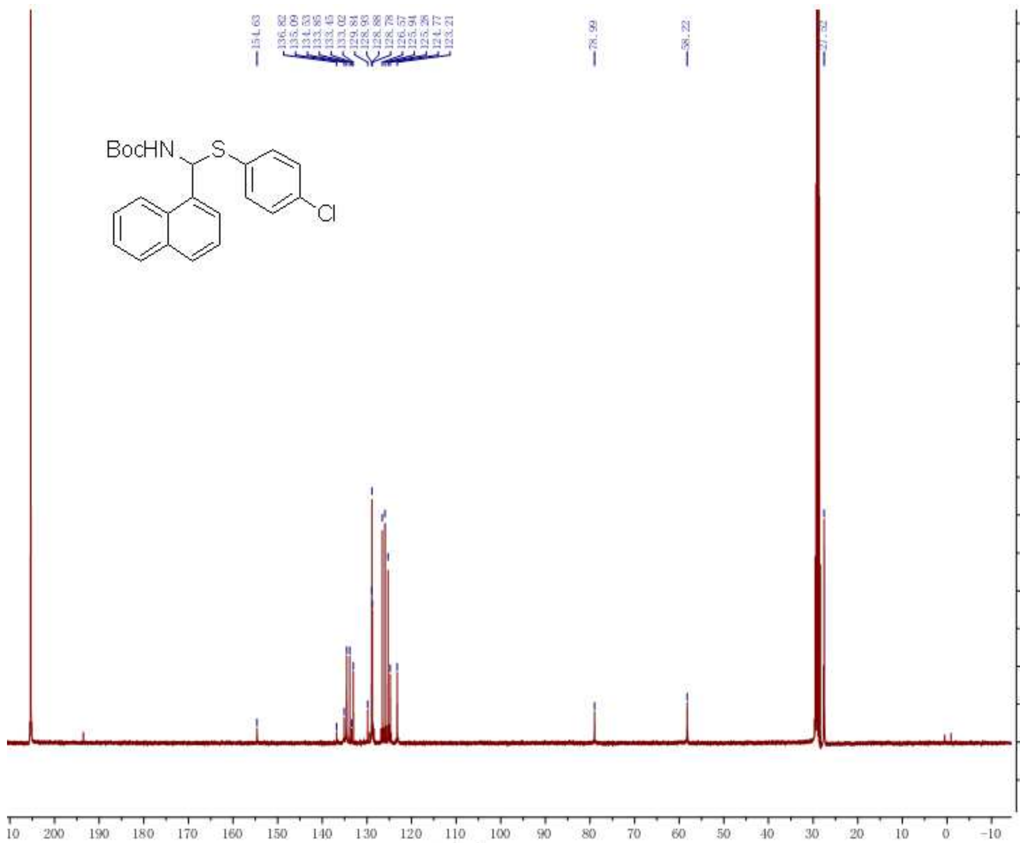
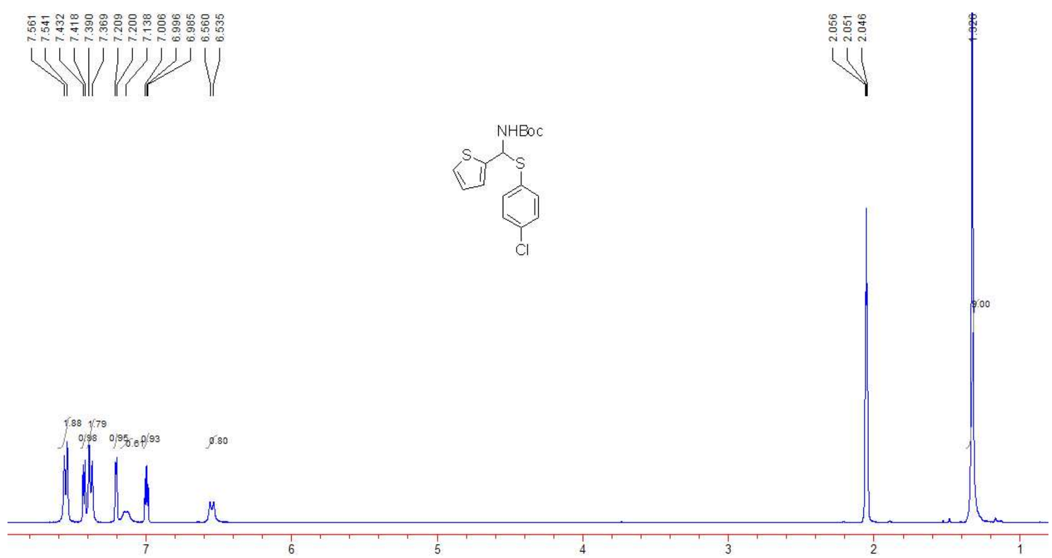
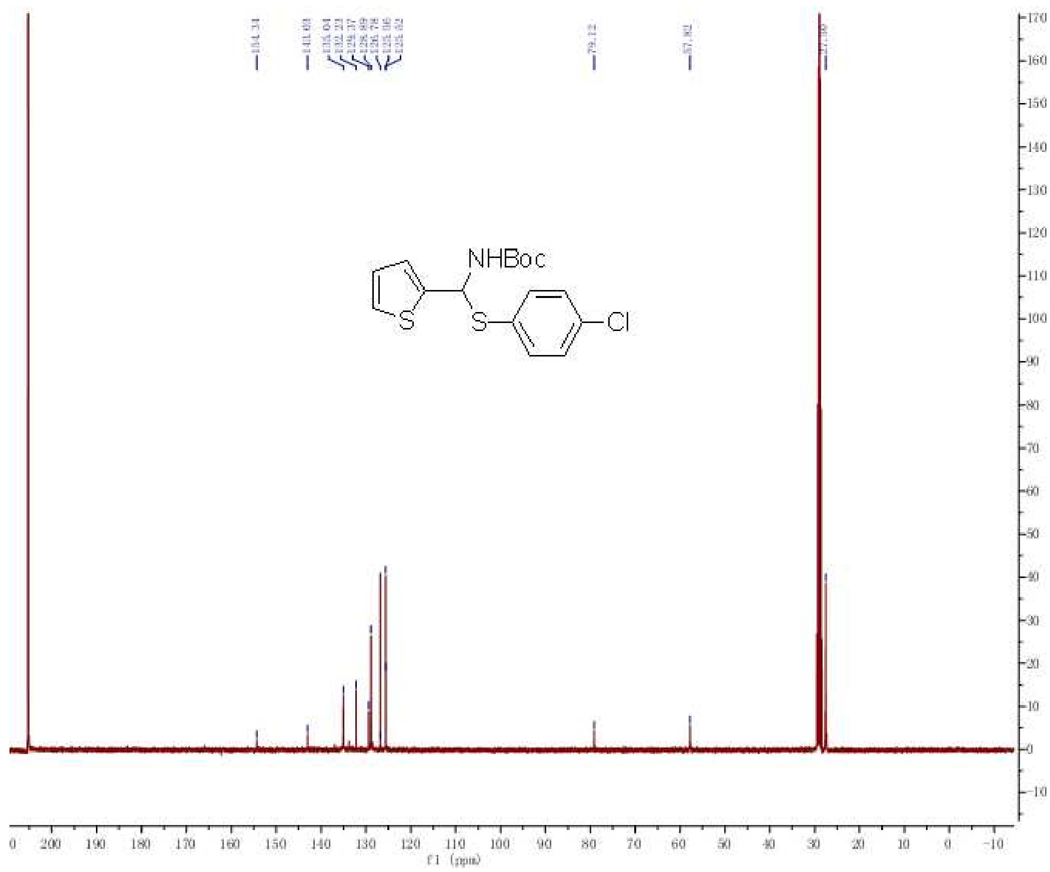
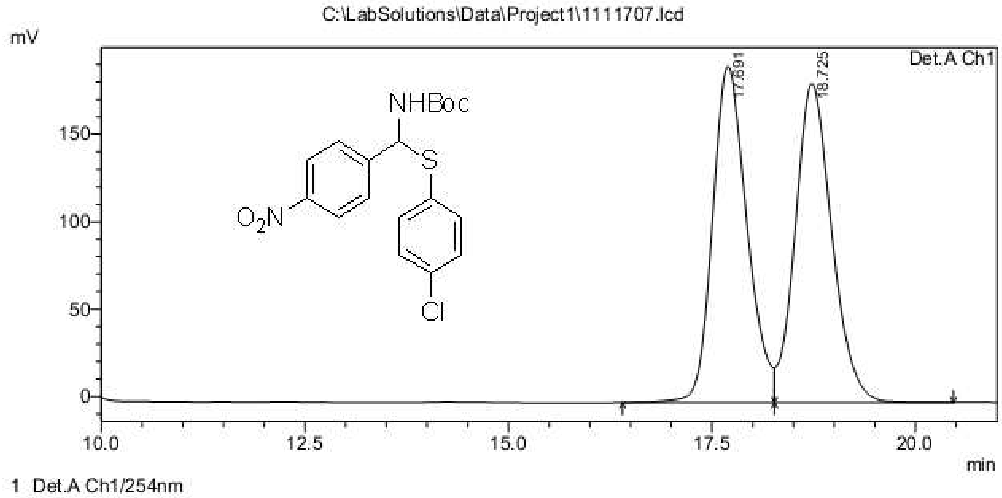
Cl
Cl
f1 (ppm)







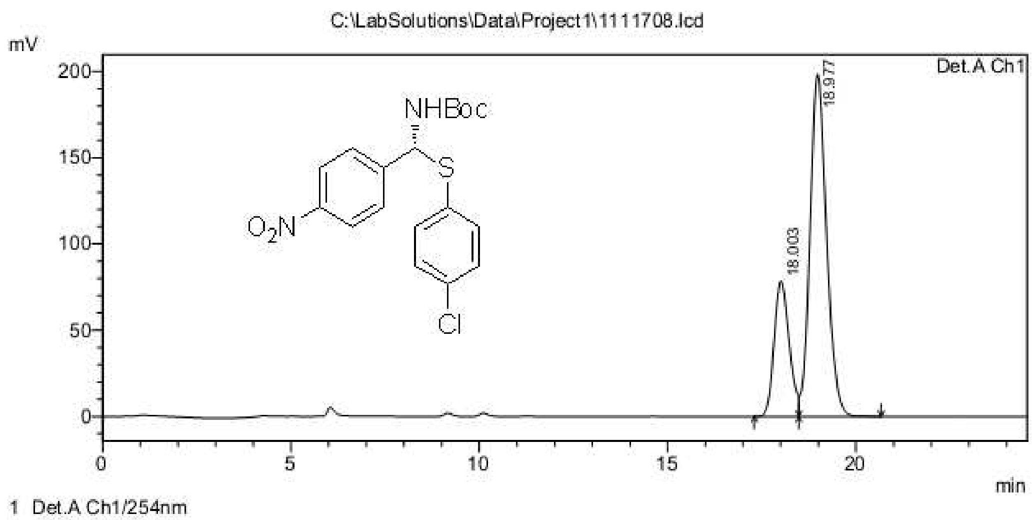




PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.691	5659198	192507	49.729	51.338
2	18.725	5720807	182476	50.271	48.662
Total		11380005	374983	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.003	2181418	78622	26.492	28.375
2	18.977	6052911	198465	73.508	71.625
Total		8234329	277087	100.000	100.000

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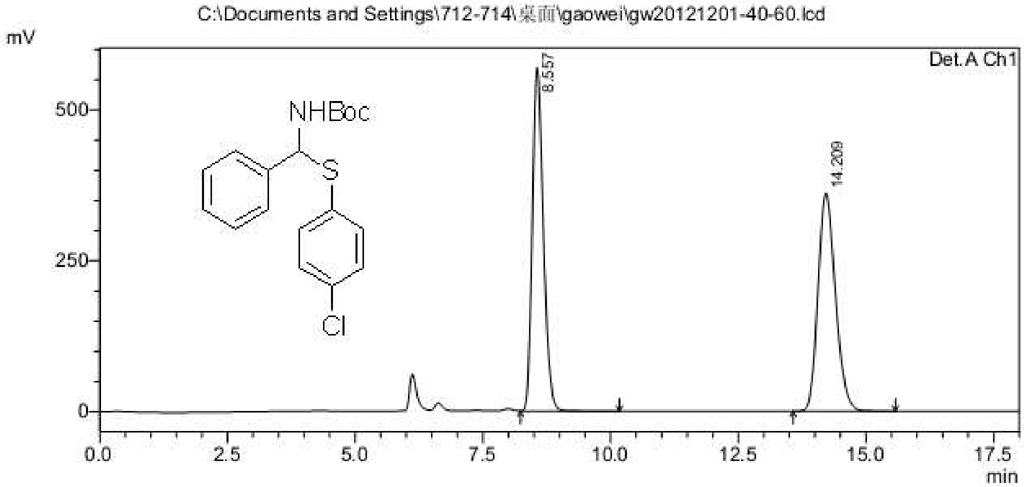

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.557	8546837	570119	49.942	61.210
2	14.209	8566688	361291	50.058	38.790
Total		17113525	931411	100.000	100.000

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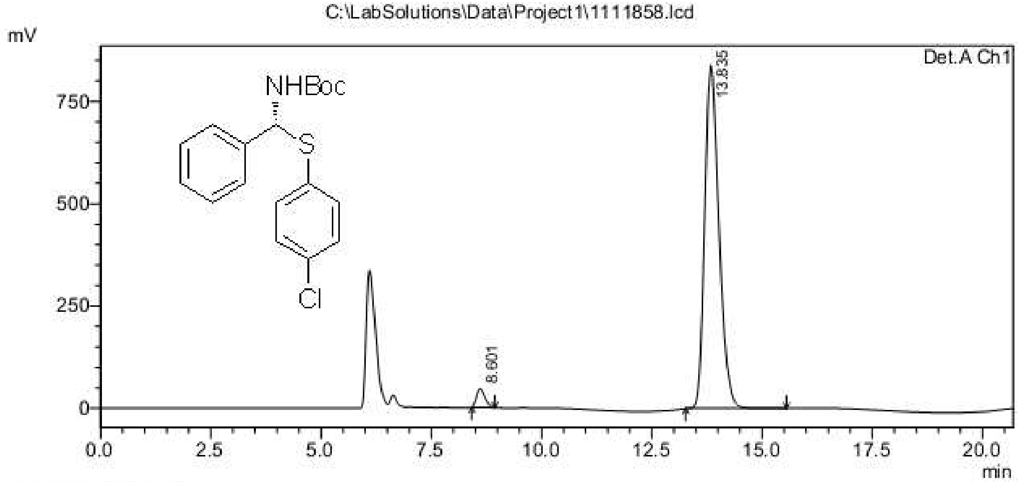

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.601	603160	46162	3.122	5.217
2	13.835	18715568	838714	96.878	94.783
Total		19318727	884876	100.000	100.000

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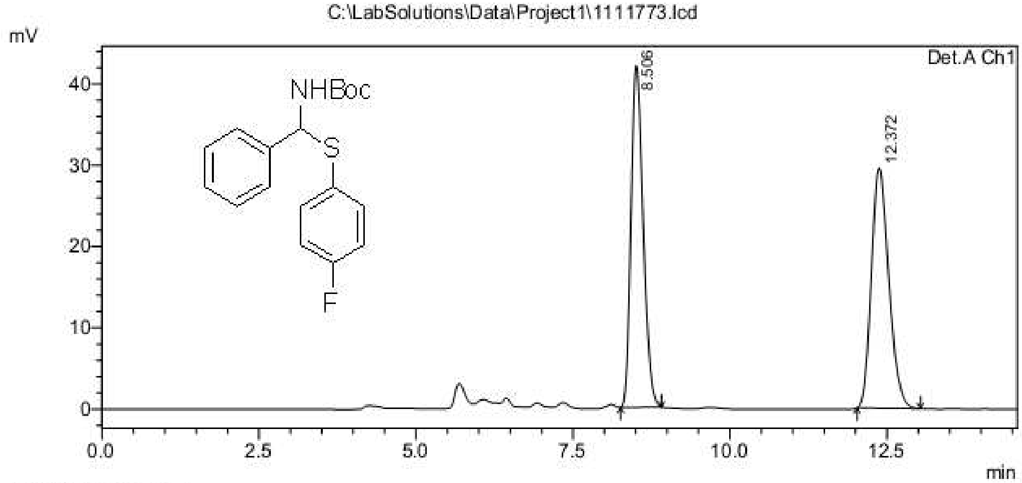

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.506	562445	42047	49.651	58.723
2	12.372	570344	29555	50.349	41.277
Total		1132789	71602	100.000	100.000

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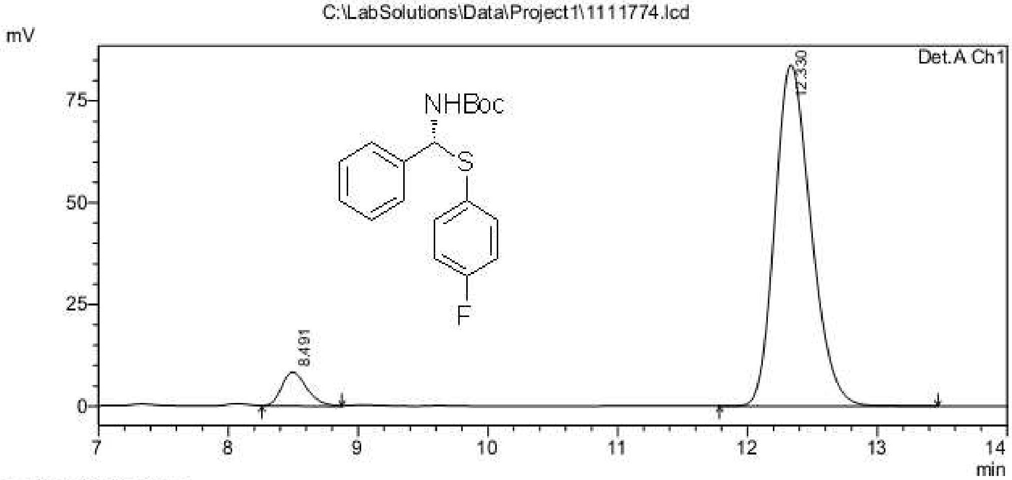
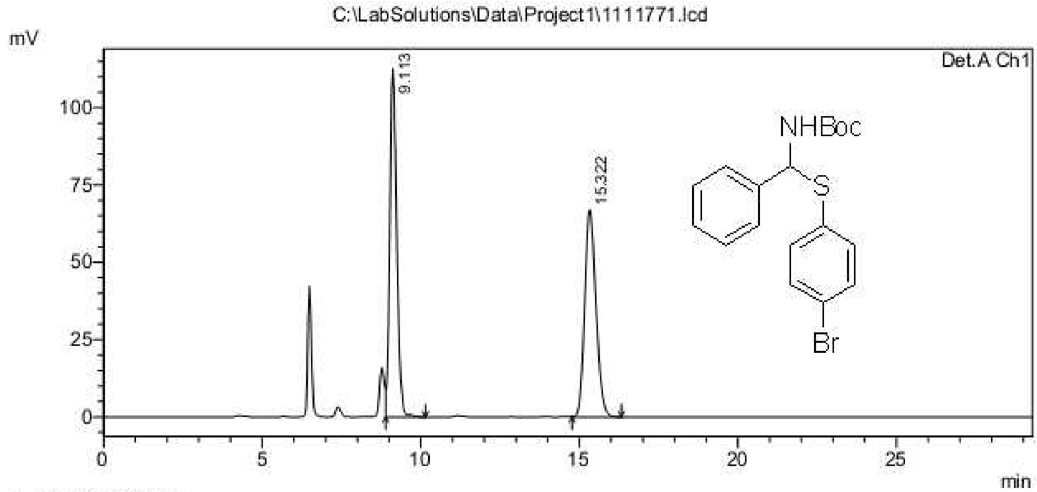


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.491	112794	8356	6.518	9.064
2	12.330	1617676	83830	93.482	90.936
Total		1730471	92186	100.000	100.000

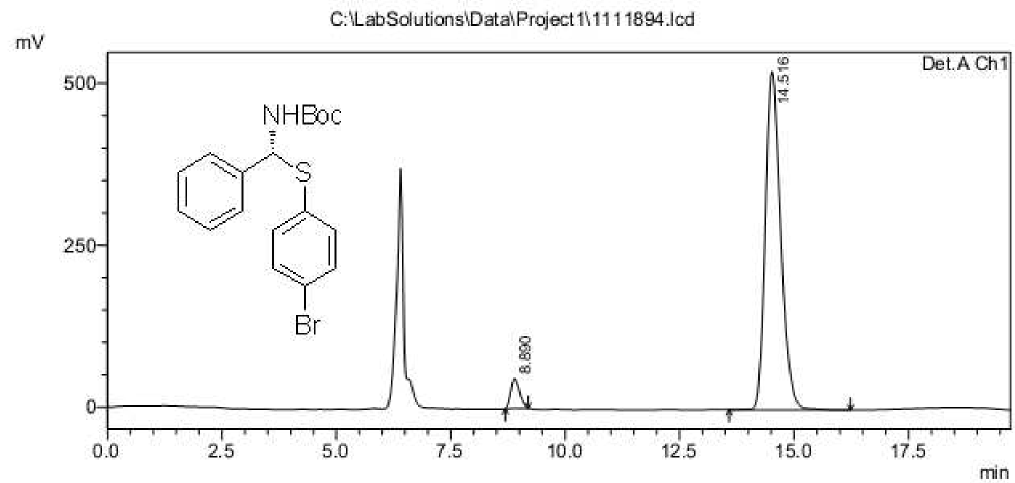


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.113	1684757	112739	50.465	62.731
2	15.322	1653700	66978	49.535	37.269
Total		3338457	179717	100.000	100.000

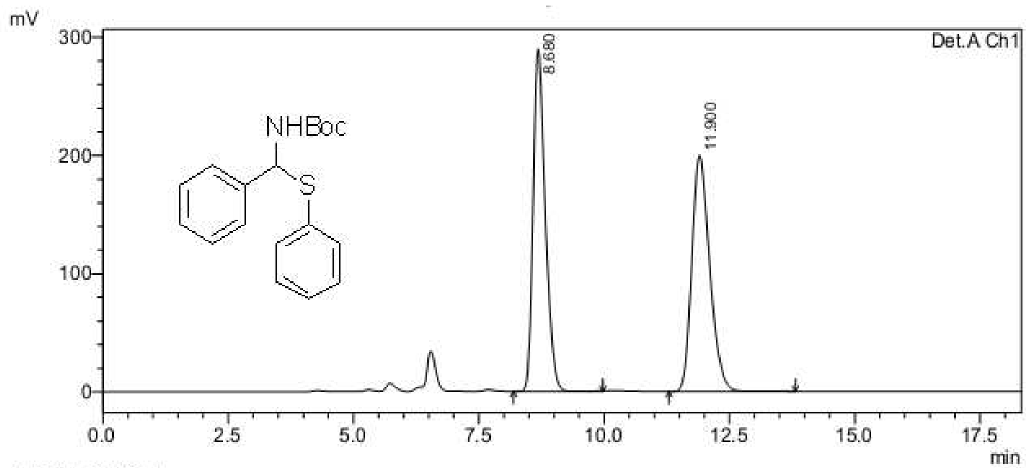


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.890	611528	46204	4.772	8.124
2	14.516	12203344	522541	95.228	91.876
Total		12814872	568746	100.000	100.000

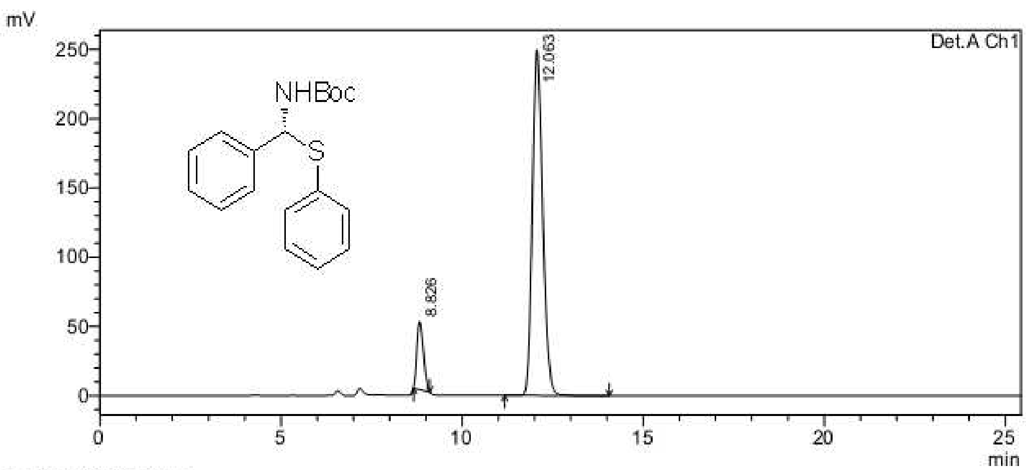


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.680	4882143	289766	49.771	59.244
2	11.900	4927096	199338	50.229	40.756
Total		9809239	489104	100.000	100.000

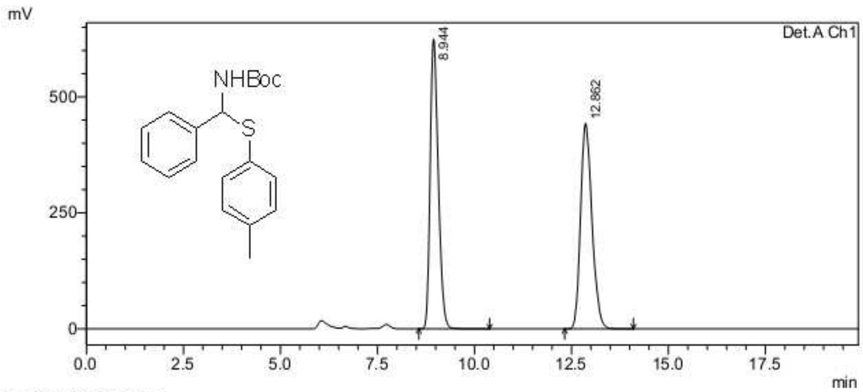


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.826	610735	48932	10.985	16.378
2	12.063	4949134	249838	89.015	83.622
Total		5559869	298770	100.000	100.000

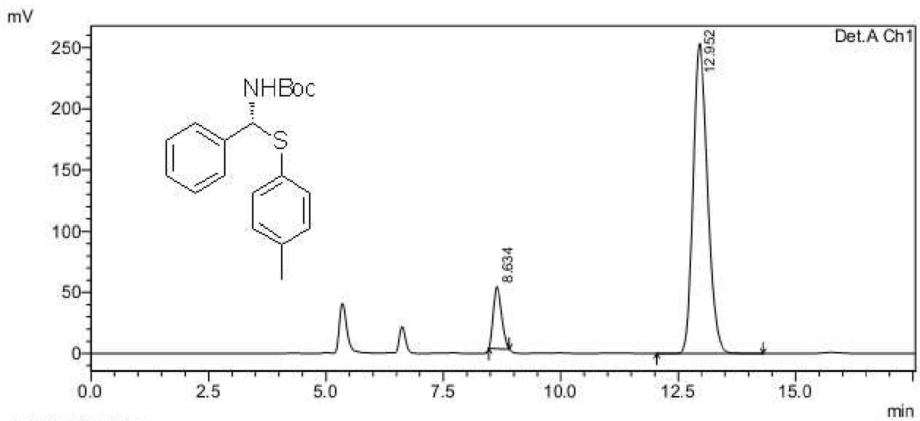


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.944	9056526	624604	49.988	58.503
2	12.862	9060697	443049	50.012	41.497
Total		18117222	1067654	100.000	100.000

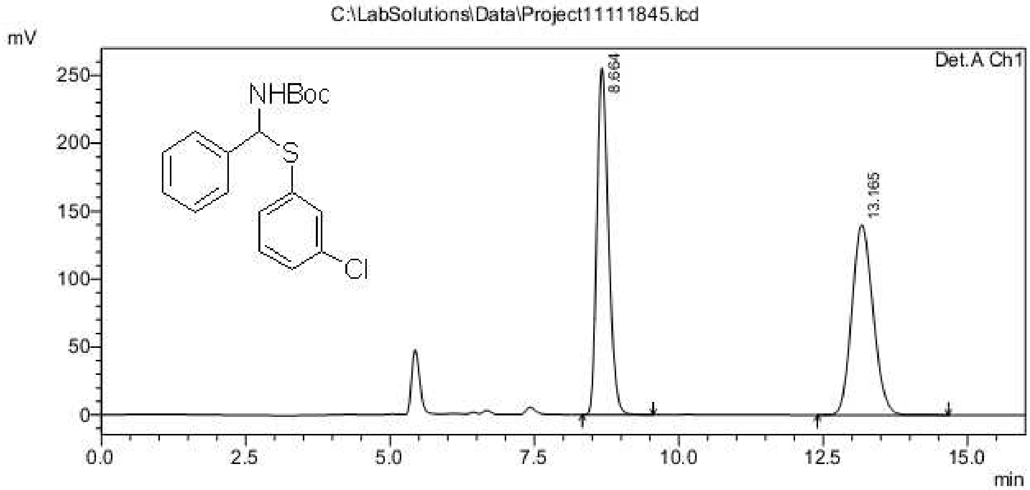


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.634	632494	50854	10.479	16.709
2	12.952	5403218	253503	89.521	83.291
Total		6035713	304358	100.000	100.000

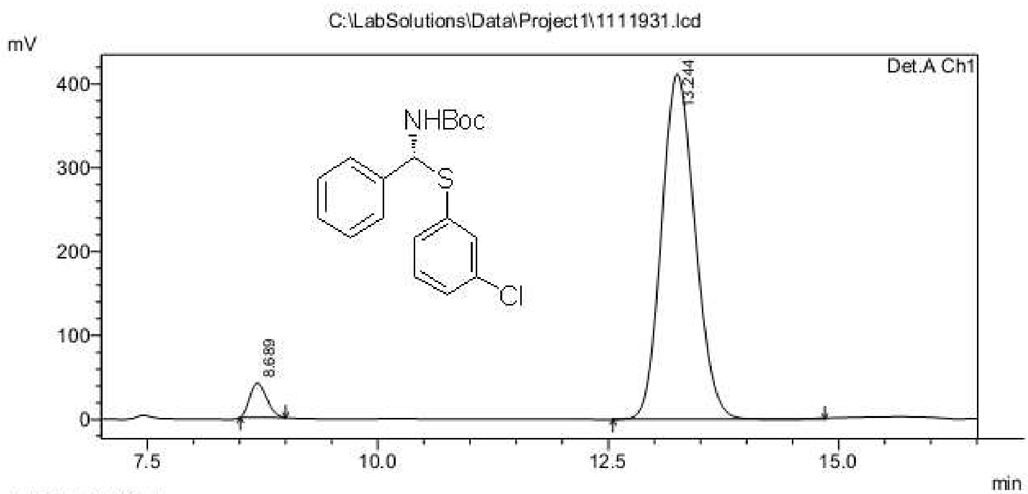


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.664	3561999	255467	49.913	64.631
2	13.165	3574480	139803	50.087	35.369
Total		7136479	395270	100.000	100.000

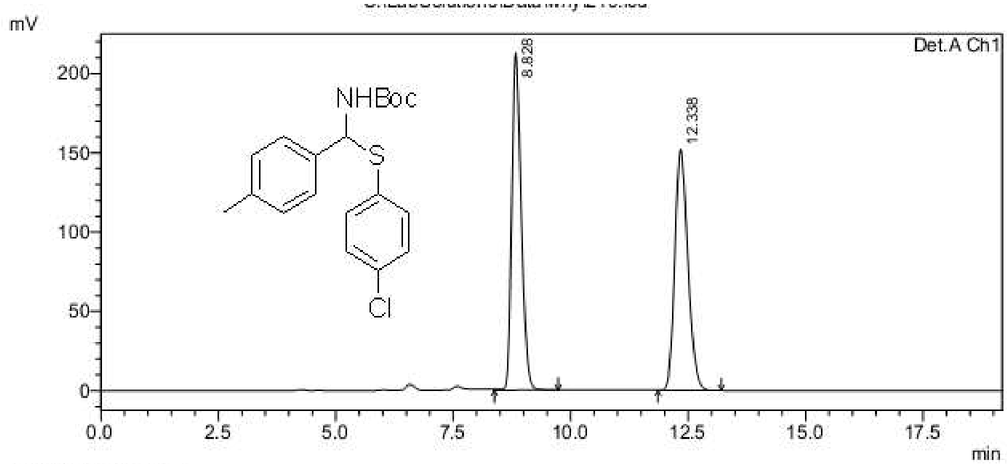


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.689	524900	41002	4.790	9.056
2	13.244	10434412	411765	95.210	90.944
Total		10959312	452768	100.000	100.000



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.828	2958607	212680	50.197	58.310
2	12.338	2935404	152063	49.803	41.690
Total		5894011	364743	100.000	100.000

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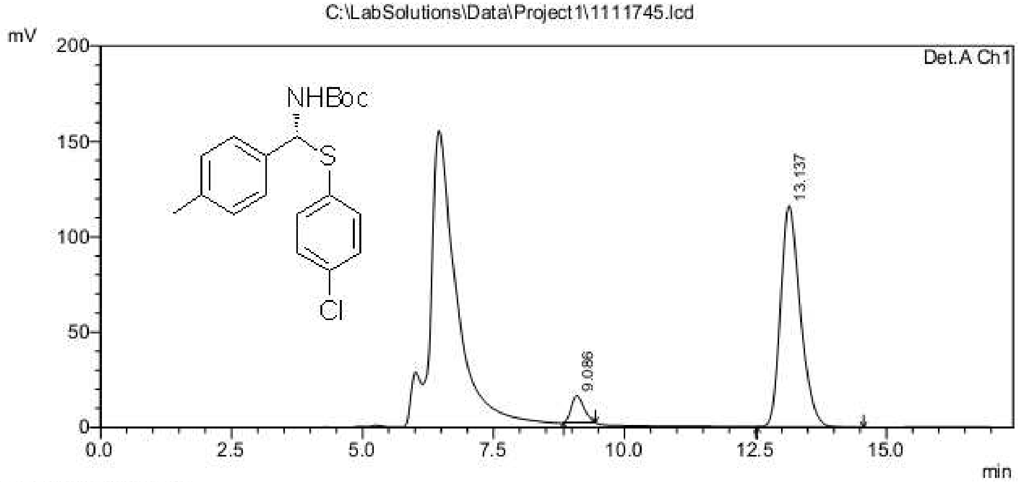
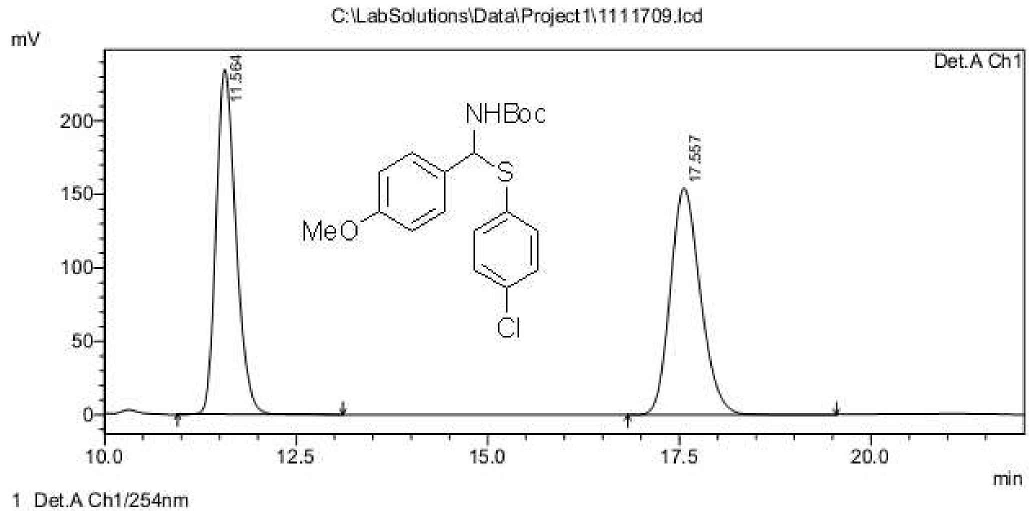


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

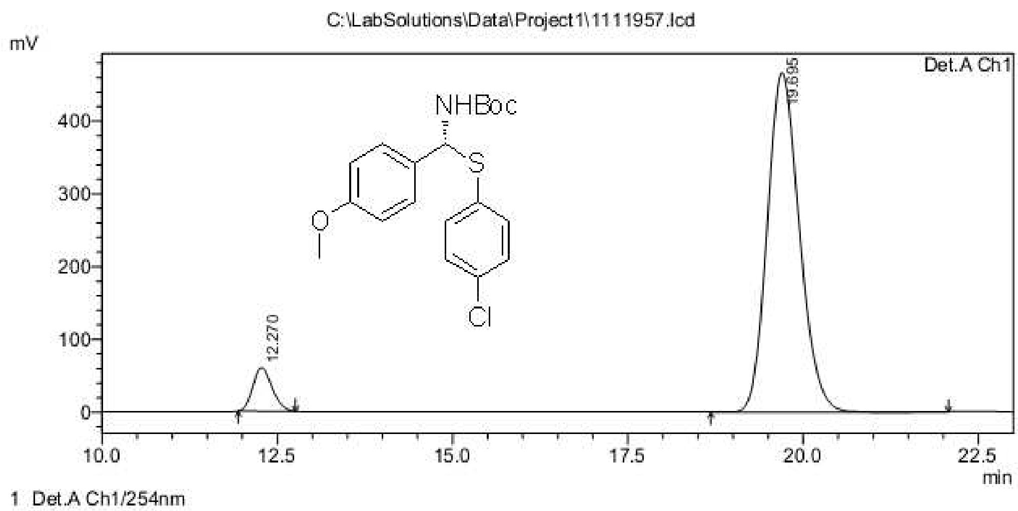
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.086	234292	14154	7.144	10.868
2	13.137	3045173	116083	92.856	89.132
Total		3279466	130237	100.000	100.000



PeakTable

Detector A Ch1 254nm

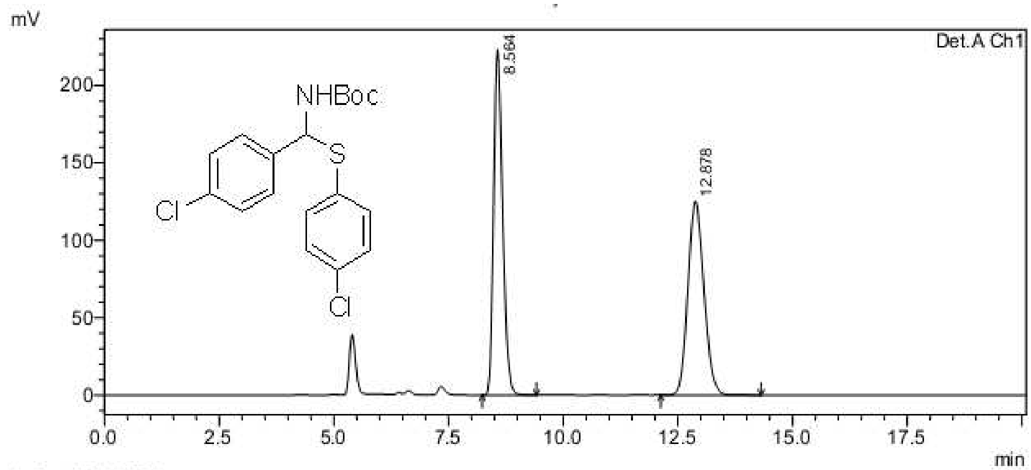
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.564	4206491	234899	49.931	60.341
2	17.557	4218151	154384	50.069	39.659
Total		8424642	389284	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.270	1145334	59859	7.155	11.378
2	19.695	14862052	466224	92.845	88.622
Total		16007386	526083	100.000	100.000

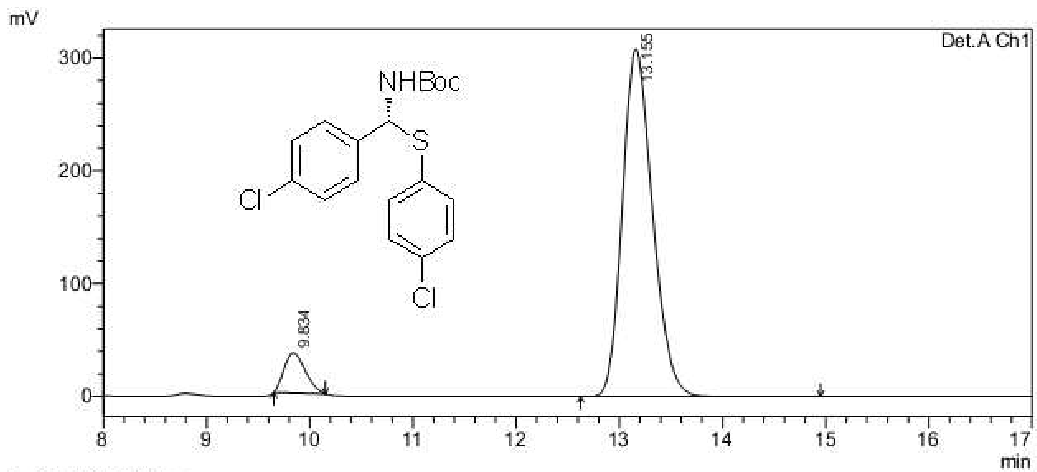


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.564	3049513	223483	49.966	64.064
2	12.878	3053654	125360	50.034	35.936
Total		6103167	348843	100.000	100.000

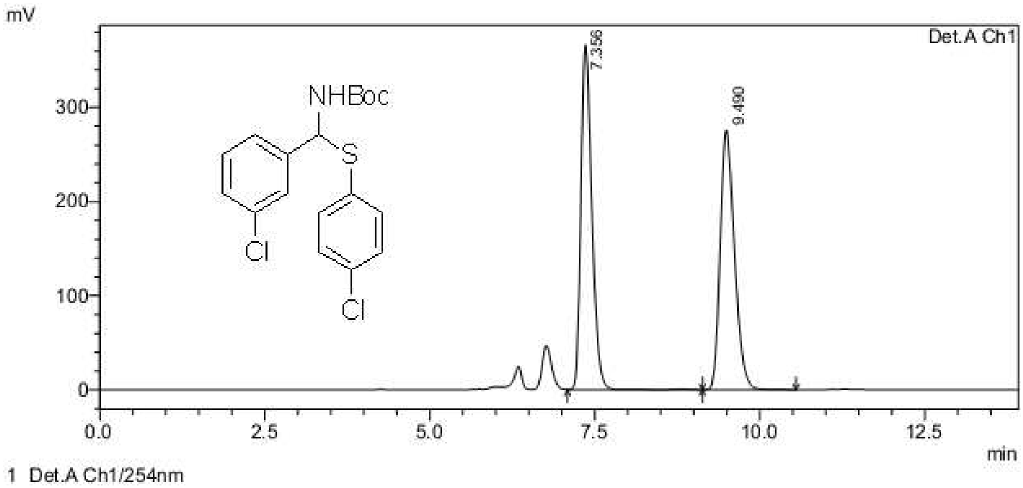


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

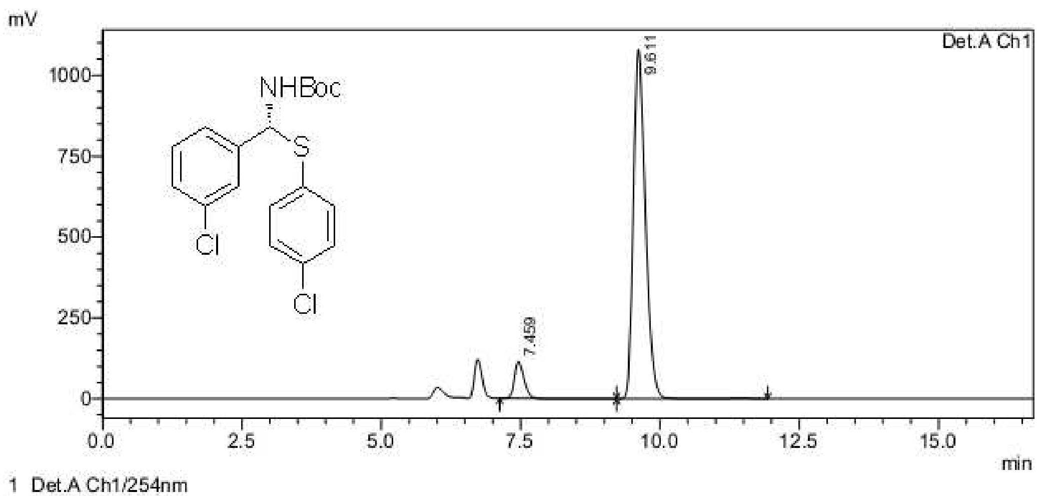
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.834	505495	35438	7.471	10.306
2	13.155	6261039	308433	92.529	89.694
Total		6766534	343871	100.000	100.000



PeakTable

Detector A Ch1 254nm

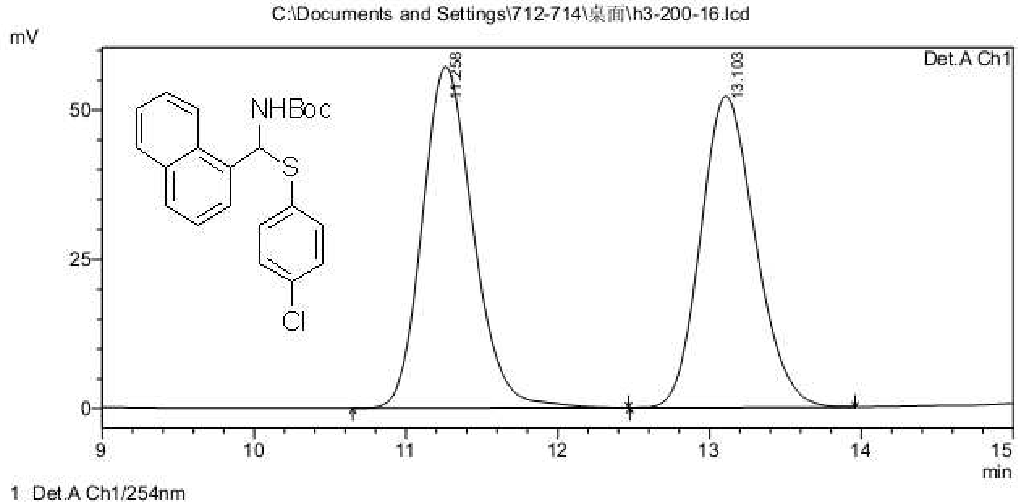
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.356	4190168	366682	50.217	57.078
2	9.490	4153897	275747	49.783	42.922
Total		8344065	642429	100.000	100.000



PeakTable

Detector A Ch1 254nm

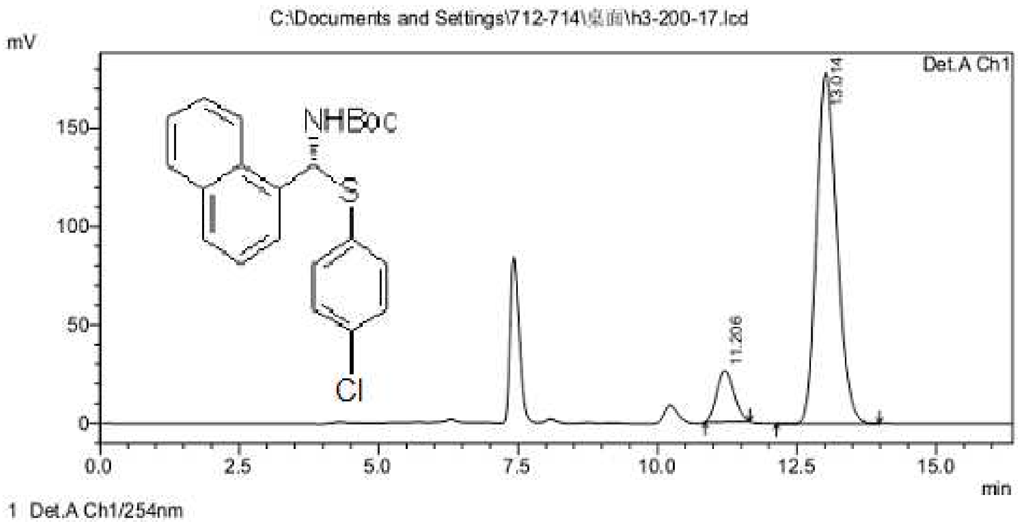
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.459	1338337	114192	7.639	9.561
2	9.611	16181604	1080192	92.361	90.439
Total		17519941	1194384	100.000	100.000



PeakTable

Detector A Ch1 254nm

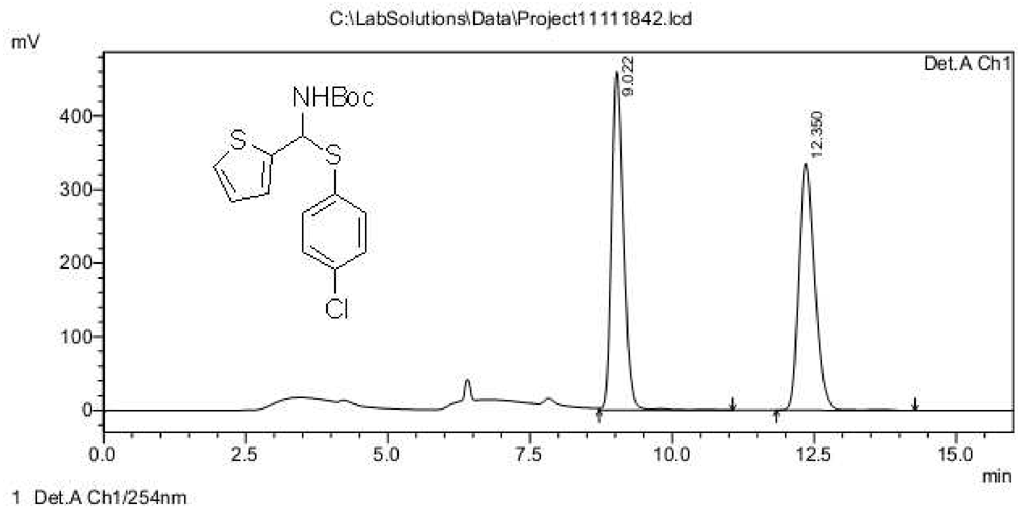
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.258	1332105	57161	50.452	52.297
2	13.103	1308248	52140	49.548	47.703
Total		2640353	109302	100.000	100.000



PeakTable

Detector A Ch1 254nm

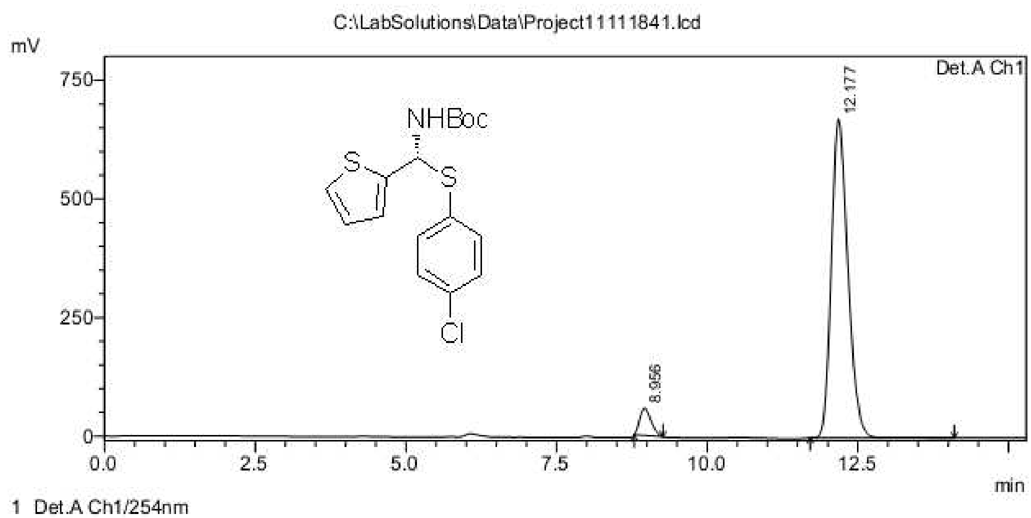
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.206	554953	25960	10.900	12.695
2	13.014	4536185	178519	89.100	87.305
Total		5091139	204479	100.000	100.000



PeakTable

Detector A Ch1 254nm

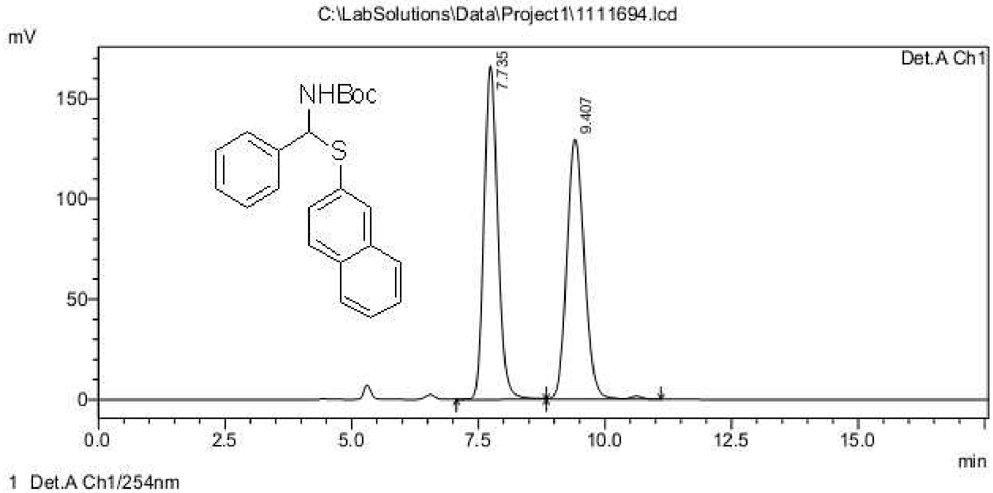
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.022	6659987	460151	50.591	57.841
2	12.350	6504370	335391	49.409	42.159
Total		13164357	795542	100.000	100.000



PeakTable

Detector A Ch1 254nm

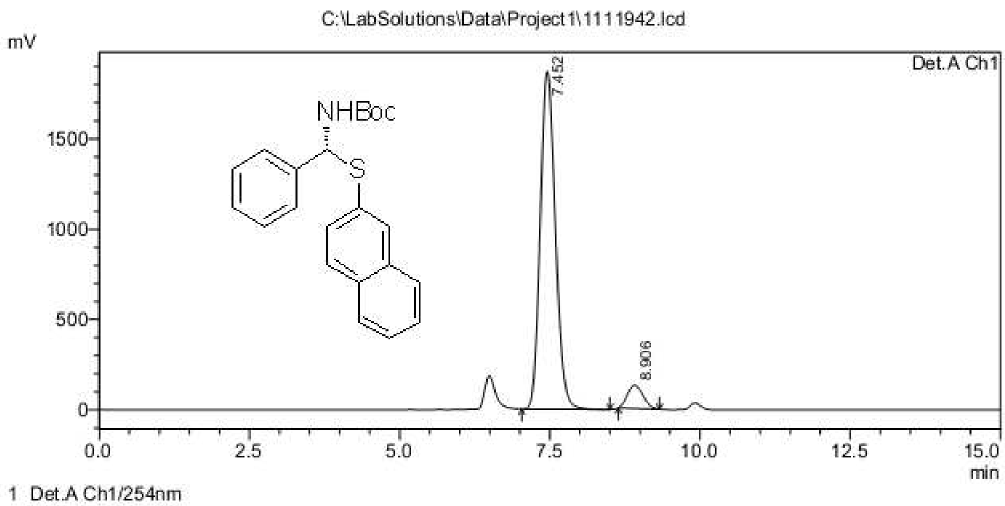
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.956	745012	57641	5.509	7.902
2	12.177	12779281	671812	94.491	92.098
Total		13524293	729453	100.000	100.000



PeakTable

Detector A Ch1 254nm

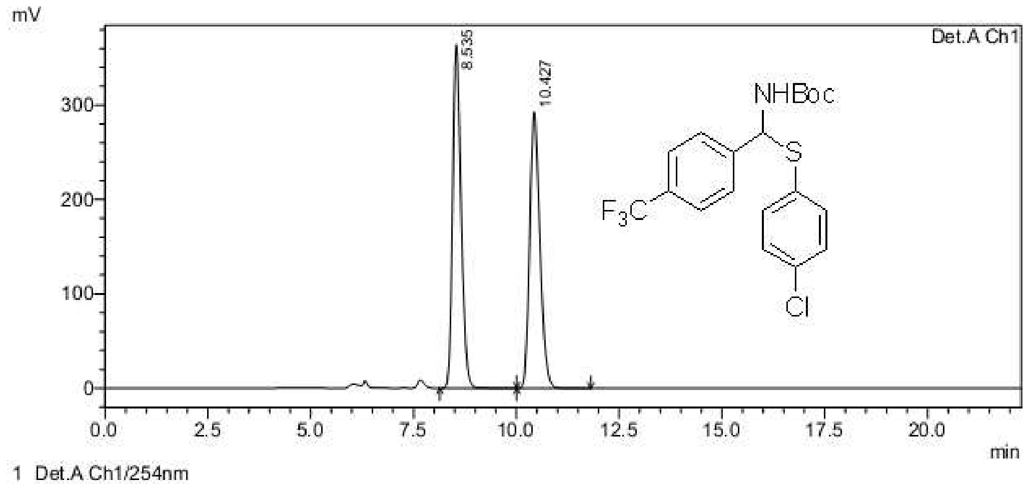
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.735	3126425	166320	50.182	56.193
2	9.407	3103795	129663	49.818	43.807
Total		6230221	295983	100.000	100.000



PeakTable

Detector A Ch1 254nm

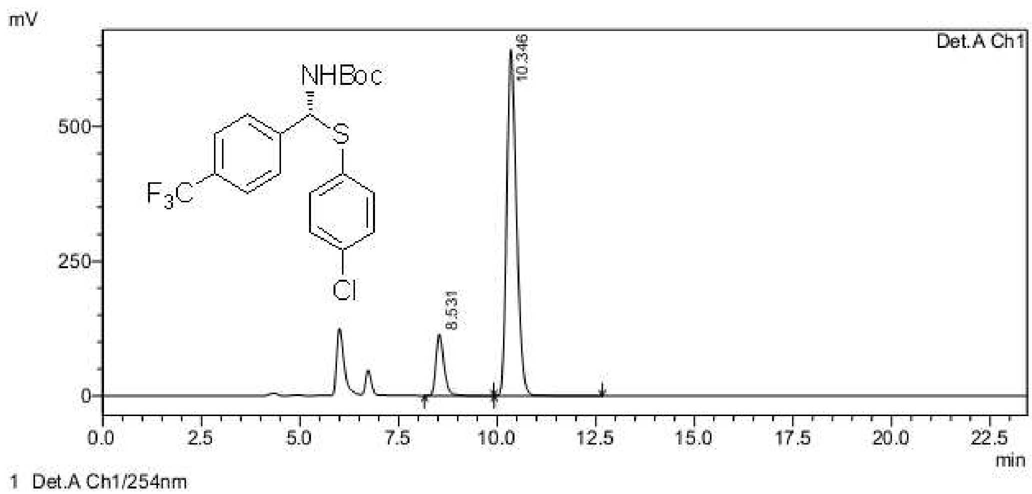
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.452	32682332	1869961	93.299	93.490
2	8.906	2347268	130203	6.701	6.510
Total		35029599	2000164	100.000	100.000



PeakTable

Detector A Ch1 254nm

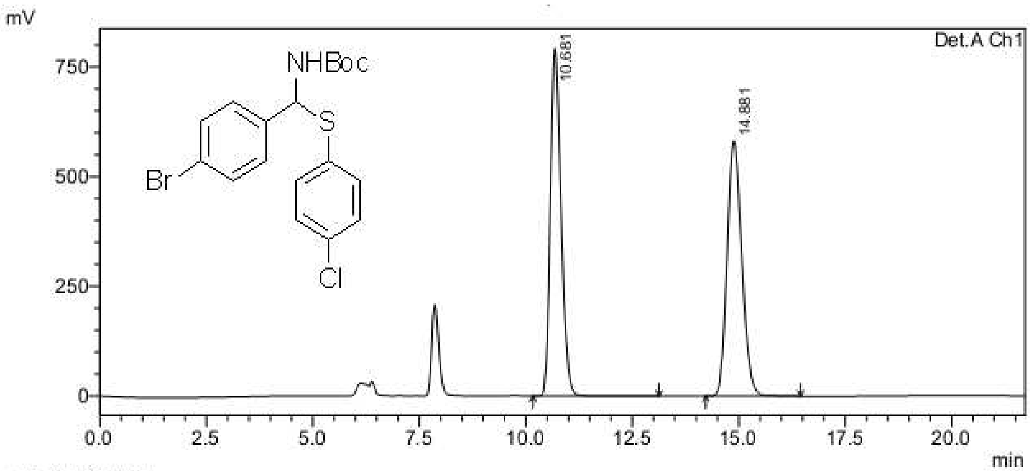
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.535	5162037	364149	50.433	55.423
2	10.427	5073490	292882	49.567	44.577
Total		10235527	657031	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.531	1611122	113886	12.730	15.039
2	10.346	11045200	643371	87.270	84.961
Total		12656323	757257	100.000	100.000

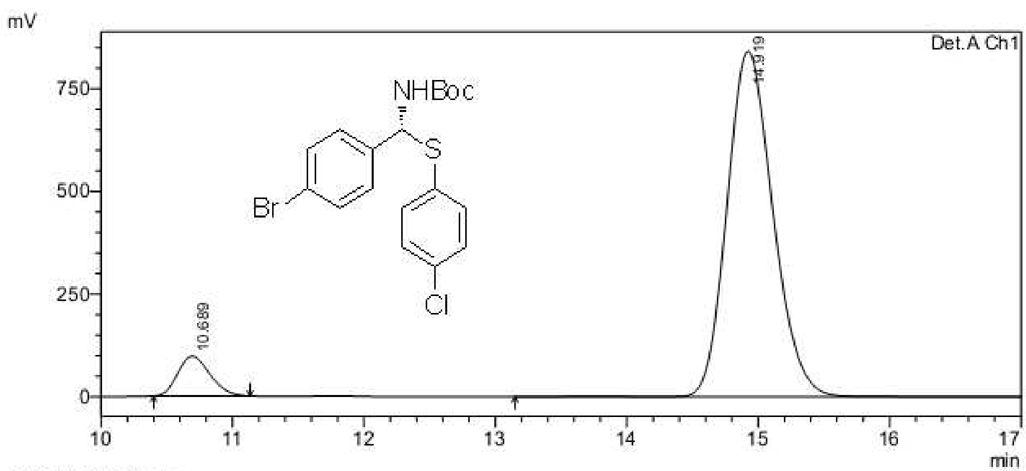


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.681	13780934	792472	49.953	57.717
2	14.881	13806626	580561	50.047	42.283
Total		27587560	1373033	100.000	100.000

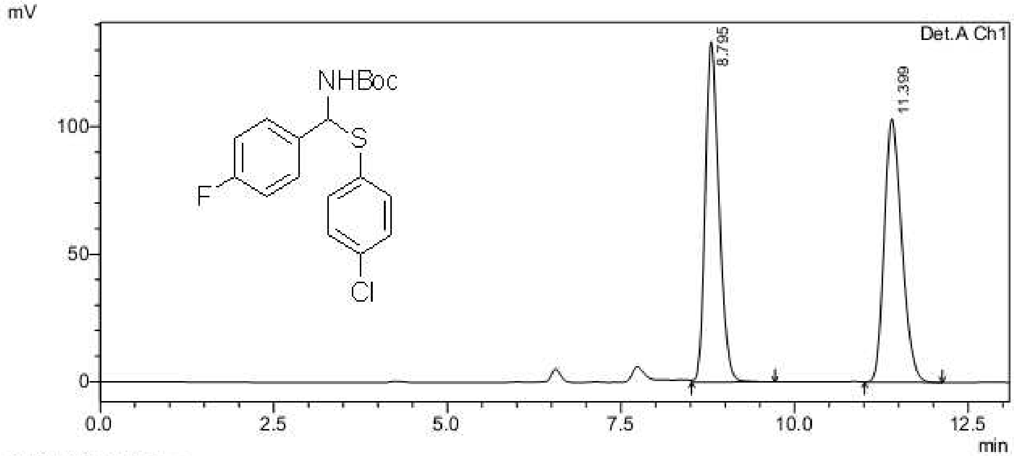


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.689	1655311	97559	7.512	10.393
2	14.919	20380546	841120	92.488	89.607
Total		22035857	938679	100.000	100.000

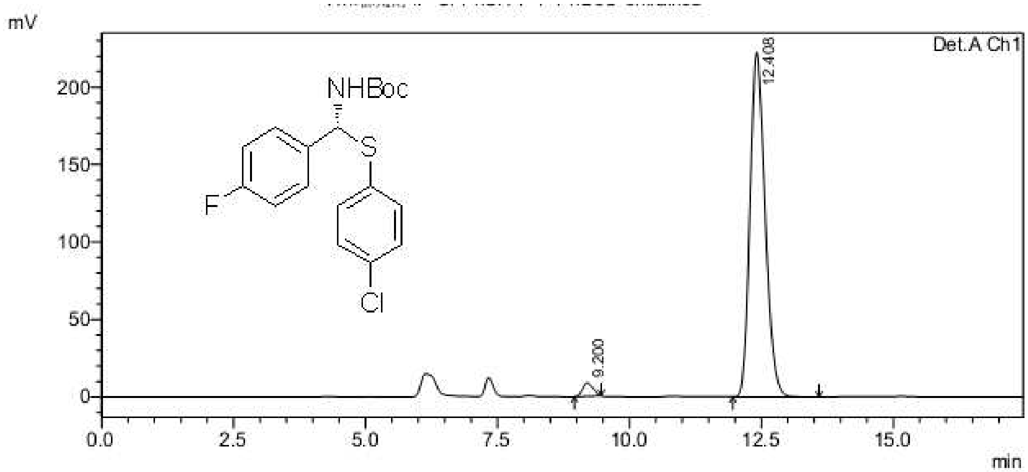


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.795	1838631	133541	50.229	56.412
2	11.399	1821868	103184	49.771	43.588
Total		3660499	236725	100.000	100.000

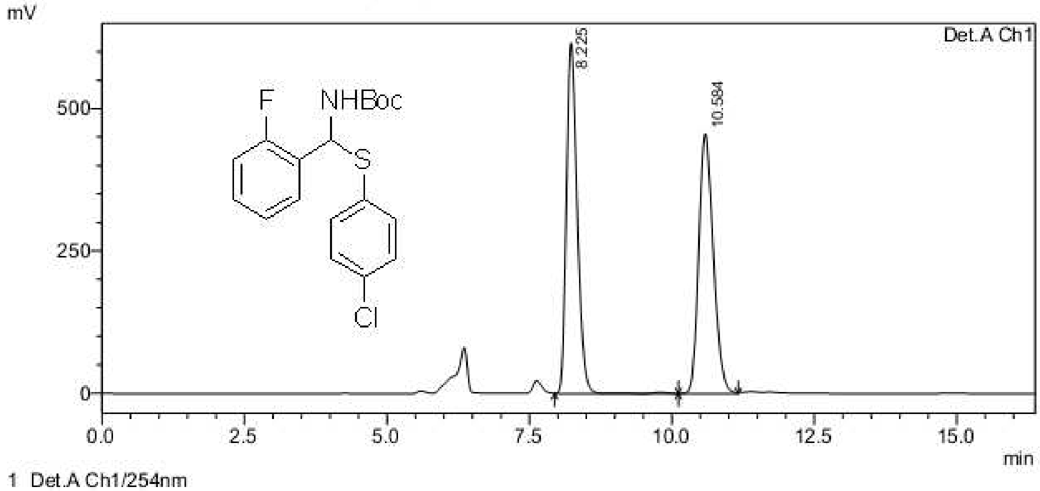


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.200	120140	8691	2.636	3.760
2	12.408	4437258	222430	97.364	96.240
Total		4557398	231121	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.225	8120994	615204	50.055	57.436
2	10.584	8103011	455916	49.945	42.564
Total		16224004	1071120	100.000	100.000

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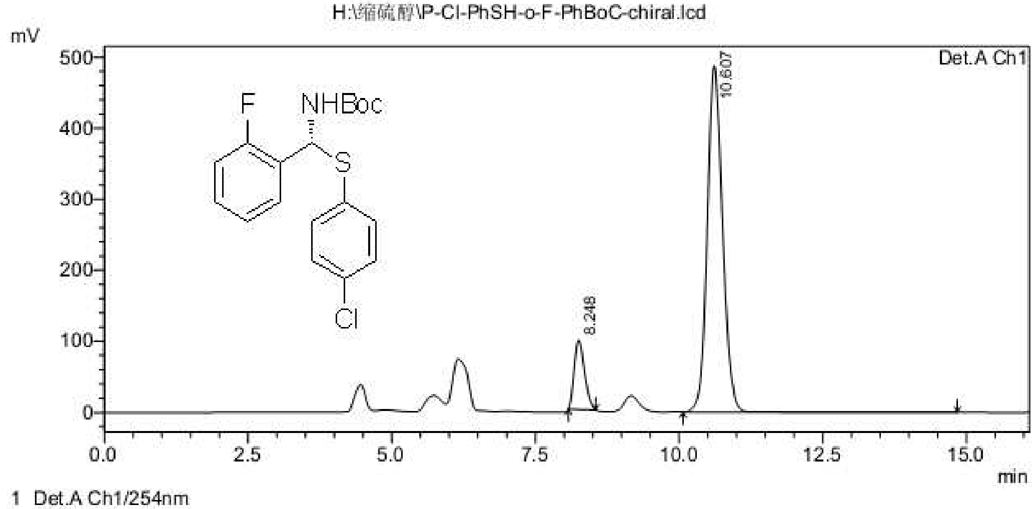

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.248	1218694	97879	11.972	16.725
2	10.607	8960419	487331	88.028	83.275
Total		10179113	585210	100.000	100.000