Thiourea-Phosphonium Salts From Amino Acids: Cooperative Phase-Transfer Catalysis in Enantioselective aza-Henry Reaction

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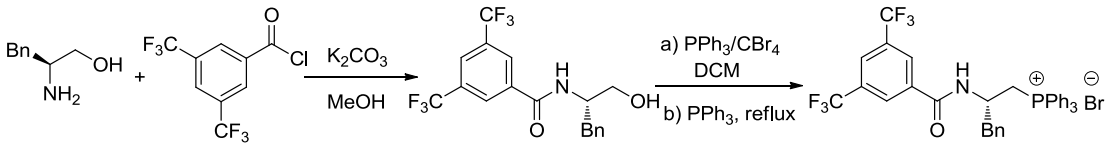
Electronic Supplementary Information

Contents

1. General Information

The ^{1}H NMR spectra were recorded on a Bruker NMR Spectrometer (400 MHz). All chemical shifts (δ) were given in ppm. Data were reported as follows: chemical shift, integration, 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 Waters or Shimadzu using chiral columns. Melting points were determined on a SGW X-4 and were uncorrected. Optical rotations were measured on a *J*ASCO 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 amidosulfones were prepared using reported procedures from corresponding aldehydes.[1] All bifunctional phosphine catalysts were synthesized according to procedures reported previously.[2] Ethyl 4-nitrobutanoate was prepared following reported procedures.[3] All reactions were carried out employing oven-dried glassware. All solvents were used after redistillation according to standard procedures

2. Preparation of catalyst 1a



3,5-Bis(trifluoromethyl)benzoyl chloride (2.8 mmol, 379 mg, 1.1 equiv) was added in one portion to a suspension of (*S*)-2-amino-3-phenylpropan-1-ol (2.5 mmol, 379 mg, 1.0 equiv) and K_2CO_3(415 mg, 1.2 equiv) in MeOH (20 mL). The reaction mixture was stirred at room temperature overnight. The mixture was filtered and the filter cake was washed with MeOH (5 mL). The filtrate was evaporated and the residue was dissolved in water (10 mL) and extracted with dichloromethane (4 × 10 mL). The dichloromethane solution was washed with brine and dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified by chromatography (petroleum ether: ethyl acetate = 2/1). CBr_4 (531 mg, 1.6 mmol, 1 equiv) and PPh_3 (420 mg, 1.6 mmol, 1 equiv) were added to a solution of the acyl

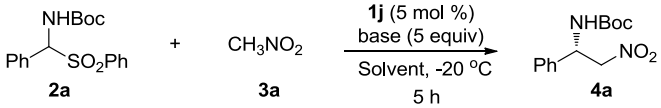
protected amino alcohol (600 mg, 1.6 mmol, 1 equiv) in CH_2Cl_2 (30 mL) and the resulting solution was stirred at room temperature for 48 h. Then the solution was concentrated under reduced pressure. The residue was washed with anhydrous Et_2O (4 × 20 mL), dried under vaccum before being dissolved in anhydrous toluene (15 mL). Then PPh_3 (1.68 g, 6.4 mmol, 4 equiv) was added and the resulting solution was stirred at 110 °C for 48 h. Then the solution was allowed to cool to ambient temperature and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to afford the desired phase transfer catalyst **1a** (CH_2Cl_2/MeOH = 20/1).

3. Preparation of catalysts 1b to 1m

To a solution of the corresponding amino acid-derived bifunctional phosphine[2] (1.0 equiv) in anhydrous toluene was added the corresponding benzylic halide (1.2 equiv), and the resulting mixture was stirred at 110 °C for 8 h. Then the mixture was allowed to cool to ambient temperature and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to afford the desired phase transfer catalyst (CH_2Cl_2/MeOH = 20/1).

4. Optimization of reaction conditions with catalyst 1j (Table S1)

Table S1 Screening of other reaction conditions with **1j**[a]



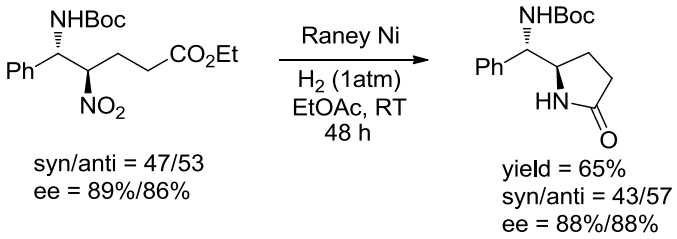
Entry	Solvent	Base	Yield [%][b]	Ee [%][c]
1	$PhCH_3$	KOH	79	96
2	THF	KOH	98	56
3	CH_2Cl_2	KOH	75	92
4	Et_2O	KOH	64	94
5	EtOAc	KOH	90	79
6[d]	$PhCH_3$	K_2CO_3	71	96
7[e]	$PhCH_3$	NaOH	75	96
8[f]	$PhCH_3$	Cs_2CO_3	71	88
9[g]	$PhCH_3$	KOH	68	94
10[h]	$PhCH_3$	KOH	71	96

[a]Unless otherwise noted, reactions were conducted with 0.1 mmol of **2a**, 0.5 mmol of **3a** and 0.5 mmol of base with 5 mol % of **1j** in 1.0 mL of solvent at -20 °C. [b]Isolated yield. [c]Determined by chiral stationary phase HPLC. [d]After 48 h. [e]After 12 h. [f]After 24 h. [g]3 mol% of **1j** was used. [h]At -30 °C. THF = tetrahydrofuran.

5. General procedure for the enantioselective aza-Henry reaction

To a suspension of the corresponding amidosulfone (0.1 mmol) in toluene (1.0 mL) was added nitroalkane (0.5 mmol) and the catalyst (5 mol %) sequentially, and the resulting mixture was stirred at -20 ^{o}C for 10 min. Then freshly grounded KOH (28 mg, 0.5 mmol) was added. The resulting suspension was vigorously stirred at –20 °C for 5 h, before being quenched with 1.0 mL of sat. aq. $NaHCO_3$. The aqueous layer was extracted with EtOAc (4 × 2 mL), and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to afford the corresponding product (petroleum/EtOAc = 4/1).

6. Hydrogenation of the product 4r[4]

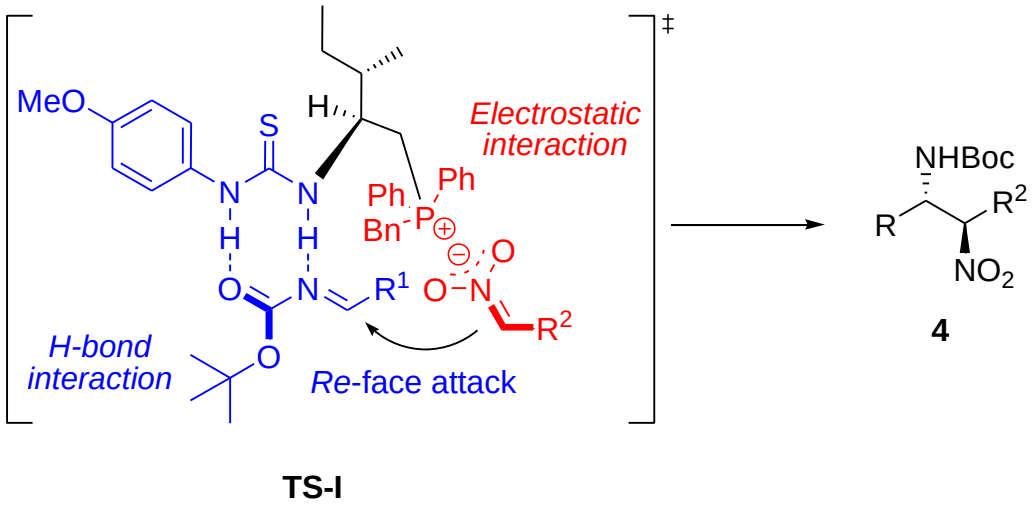


To a solution of **4r** (27 mg) in 2.0 mL of ethyl acetate was added 5 mg of Raney Ni (20 % wt), and the resulting mixture was stirred at RT for 48 h. Then the reaction mixture was filtered and washed with ethyl acetate (3 × 3 mL). The combined solution was concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to afford the desired product **5** (14 mg).(CH_2Cl_2/MeOH = 20/1).

7. A tentative transition state model for the reaction

Based on our experimental results and previous relevant studies, a possible transition state model was proposed to explain the stereochemical results of this reaction (Figure S1). Important assumptions in this model include the activation of the in-situ generated N-Boc imine through dual H-bonding interactions with the thiourea moiety and the electrostatic interaction between the phosphonium centre and the nitro group of the nitroalkanes. Such an assembly would direct the nucleophile to attack from the Re-face of the N-Boc imine. However, other functioning models of the transition state such as H-bonding interactions between thiourea moiety and the nitro group could not be ruled out at present.[5] It is

noteworthy that, under this cooperative catalysis, not only the enantioselectivities in the reaction but also the catalytic efficiency by using catalyst **1j** has been largely improved.

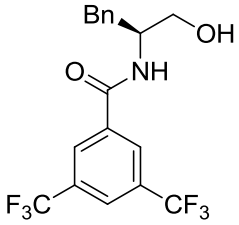


TS-I

Figure 1S A tentative transition state

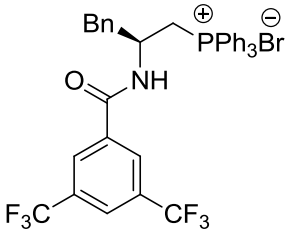
8. Spectral data of the catalysts

(*S*)-*N*-(1-Hydroxy-3-phenylpropan-2-yl)-3,5-bis(trifluoromethyl)benzamide (1a')



Yield: 70%; White solid. m.p.= 134-135 °C; $[\alpha]_D^{23}$ -63.1 (*c* = 0.5, MeOH); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.10 (s, 2H), 7.99 (s, 1H), 7.36-7.25 (m, 5H), 6.55 (d, *J* = 7.2 Hz, 1H), 4.46-4.38 (m, 1H), 3.86-3.81 (m, 1H), 3.78-3.72 (m, 1H), 3.03 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 165.2, 137.3, 136.5 (q, $J_{C\text{-}F}$ = 34.4 Hz), 129.2, 128.9, 127.3, 127.0, 122.9 (q, $J_{C\text{-}F}$ = 273.4 Hz), 125.1, 63.5, 53.5, 36.9; **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.9; **IR (Neat)**: 3308, 3090, 3032, 2934, 1648, 1553, 1281, 1186, 1131, 909, 846, 765, 699, 681; **HRMS (ESI)** ($C_{18}H_{15}F_6NNaO_2$) calcd. for $[M+Na]^+$ requires 414.0905 found 414.0907.

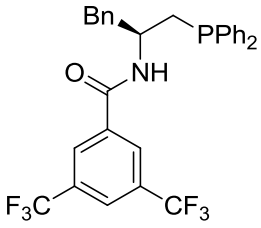
(*S*)-(2-(3,5-Bis(trifluoromethyl)benzamido)-3-phenylpropyl)triphenylphosphonium bromide (1a)



Yield: 55%; White solid. m.p. = 125-127 °C; $[\alpha]_D^{27}$ 6.0 (*c* = 0.2, MeOH); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 10.02 (d, *J* = 8.4 Hz, 1H), 8.34 (s, 2H), 7.90 (s, 1H), 7.68-7.58 (m, 9H), 7.51-7.45 (m, 6H), 7.38-7.31 (m, 1H), 4.92-4.84 (m, 1H), 3.41-3.35 (m, 1H), 3.15 (dd, *J* = 13.2, 11.2 Hz), 2.94 (dd, *J* = 15.4, 13.4 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz); δ 163.0, 137.8, 135.6, 135.1, 134.2 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.6 (q, $J_{C\text{-}F}$ = 33.6 Hz), 130.5 (d, $J_{C\text{-}P}$ = 12.7 Hz), 129.9, 128.7, 128.3, 127.0, 125.3, 123.5 (q, $J_{C\text{-}F}$ = 271.7 Hz), 119.2, 118.3, 79.8, 46.9, 42.6 (d, $J_{C\text{-}P}$ = 15.0 Hz), 31.1, 26.3 (d, $J_{C\text{-}P}$ = 49.8 Hz); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -63.0;

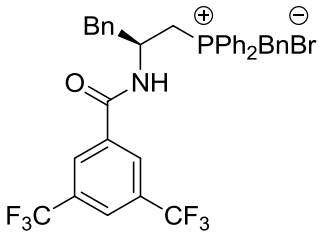
^{31}P NMR ($CDCl_3$, 163 MHz) δ 21.0; **IR (Neat)**: 3177, 3058, 2926, 1662, 1546, 1439, 1280, 1182, 1135, 1111, 908, 746, 696, 681; **HRMS (ESI)**: calcd. For $[M\text{-}Br]^+$($C_{36}H_{29}F_6NOP$) requires 636.1891 found 636.1893.

(*S*)-*N*-(1-(Diphenylphosphino)-3-phenylpropan-2-yl)-3,5-bis(trifluoromethyl)benzamide(1b')[6]



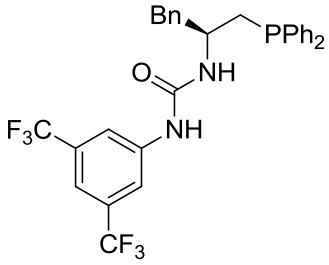
Yield: 72%; White solid. m.p. = 157-159 °C; $[\alpha]_D^{26}$ 14.2 (*c* = 0.8, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.92 (s, 1H), 7.83 (s, 2H), 7.41-7.38 (m, 4H), 7.31-7.21 (m, 11H), 6.06 (m, 1H), 4.62 (m, 1H), 3.14 (d, *J* = 7.0 Hz, 2H), 2.54 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.44 (dd, *J* = 14.1, 7.6 Hz, 1H).

(*S*)-Benzyl(2-(3,5-bis(trifluoromethyl)benzamido)-3-phenylpropyl)diphenylphosphonium bromide(1b)



Yield: 55%; White solid. m.p. = 118-120 °C; $[\alpha]_D^{19}$ -21.2 (*c* = 0.5, $CHCl_3$), **^{1}H NMR** ($CDCl_3$, 400 MHz,) δ 9.67 (d, *J* = 8.4 Hz, 1H), 8.36 (s, 2H), 7.91 (s, 1H), 7.58-7.21 (m, 16H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.77 (d, *J* = 6.8 Hz, 2H), 5.02 (dd, *J* = 26.2 Hz, 11.4 Hz, 1H), 4.79 (m, 1H), 4.47 (t, *J* = 14.8 Hz, 1H), 4.33 (t, *J* = 14.2 Hz, 1H), 3.36 - 3.30 (m, 1H), 3.18-3.12 (m, 1H), 2.60 (t, *J* = 14.2 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 163.7, 137.2, 134.6, 134.4, 133.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.3 (q, $J_{C\text{-}F}$ = 33.9 Hz), 130.2 (d, $J_{C\text{-}P}$ = 4.7 Hz), 129.7, 129.1 (d, $J_{C\text{-}P}$ = 2.4 Hz), 129.0, 128.6 (m), 128.4 (m), 127.2, 126.3 (d, $J_{C\text{-}P}$ = 7.1 Hz) 124.7 (m), 123.1 (q, $J_{C\text{-}F}$ = 270.9 Hz), 118.1 (d, $J_{C\text{-}P}$ = 82.2 Hz), 116.7 (d, $J_{C\text{-}P}$ = 82.1 Hz), 47.2, 42.9 (d, $J_{C\text{-}P}$ = 14.2 Hz), 29.7 (d, $J_{C\text{-}P}$ = 47.4 Hz), 21.9 (d, $J_{C\text{-}P}$ = 52.9 Hz); **^{19}F NMR**($CDCl_3$, 282 MHz) δ -63.3; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ 22.3; **IR (Neat)** 3425, 3193, 3058, 2924, 1660, 1280, 1183, 1136, 744, 700, 681; **HRMS (MALDI)**: calcd. for $[M\text{-}Br]^+$ ($C_{37}H_{31}F_6NOP$) requires 650.2047, found 650.1827.

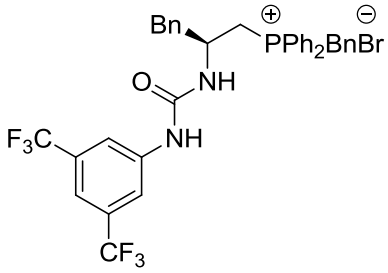
(*S*)-1-(3,5-Bis(trifluoromethyl)phenyl)-3-(1-(diphenylphosphino)-3-phenylpropan-2-yl)urea (1c')



Yield: 67%; White solid. m.p. = 100-102 °C; $[\alpha]_D^{27}$ 6.9 (*c* = 1.0, $CHCl_3$), **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.57 (s, 2 H), .48-7.35 (m, 5H), 7.32-7.28 (m, 8H), 7.17-7.16 (m, 2H), 6.02 (br. s, 1H), 4.83 (br. s, 1H), 3.09-3.07 (m, 2H), 2.54 (dd, *J* = 14.4, 5.2 Hz), 2.30 (dd, *J* = 14.4, 6.8 Hz); **^{13}C NMR**($CDCl_3$,100 MHz) δ 179.2, 138.9, 137.6 (d, $J_{C\text{-}P}$ = 10.3 Hz), 137.2, 136.9 (d, $J_{C\text{-}P}$ = 11.0 Hz), 132.8 (q, $J_{C\text{-}F}$ = 19.0 Hz), 129.4, 129.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.8, 128.7, 127.0, 123.9, 122.9 (q, $J_{C\text{-}F}$ = 271.7 Hz), 119.2, 54.7, 41.1, 33.0; **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.8; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ -24.1; **IR (Neat)** 3333, 3072, 2925, 1655, 1572, 1474, 1435, 1389, 1280, 1184, 1131,

882, 739, 699, 682; **HRMS (ESI)**: calcd. for $[M+H]^+$ ($C_{30}H_{26}F_6N_2OP$) requires 575.1687, found 575.1691.

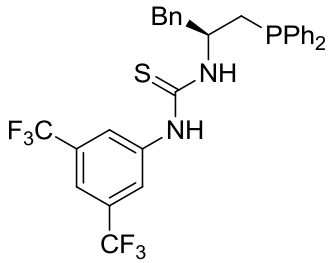
(*S*)-Benzyl(2-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)-3-phenylpropyl)diphenylphosphonium bromide(1c)



Yield: 63%; White solid. m.p. = 108-110 °C; $[\alpha]_D^{22}$ -65.3 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.73 (d, *J* = 5.6 Hz, 1H), 7.93 (br. s, 1H), 7.82 (s, 2H), 7.58-7.19 (m, 17H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.77 (d, *J* = 6.8 Hz, 2H), 4.59 (t, *J* = 14.8 Hz, 1H), 4.39-4.29 (m, 2H), 3.80-3.70 (m, 1H), 3.25-3.21 (m, 1H), 3.00 (dd, *J* = 13.0, 10.2 Hz), 2.62 (t, *J* = 14.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.1, 154.5, 141.3, 140.8, 137.1, 136.8, 134.8 (d, $J_{C\text{-}F}$ = 2.3 Hz), 134.7, 133.3 (t, $J_{C\text{-}P}$ = 8.7 Hz), 131.0 (d, $J_{C\text{-}F}$ = 33.2 Hz), 130.1 (d, $J_{C\text{-}P}$ = 5.5 Hz), 130.0 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.6, 129.2 (d, $J_{C\text{-}P}$ = 2.4 Hz), 129.1, 128.7, 127.2, 126.3 (d, $J_{C\text{-}P}$ = 7.9 Hz), 123.2 (q, $J_{C\text{-}F}$ = 270.9 Hz), 122.8, 118.0, 117.7, 117.3, 116.8, 116.3, 50.5, 42.9 (d, $J_{C\text{-}P}$ = 14.2 Hz), 29.9 (d, $J_{C\text{-}P}$ = 40.3 Hz), 24.7 (d, $J_{C\text{-}P}$ = 51.3 Hz); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.9; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ 23.5; **IR (Neat)**: 3280, 3062, 2927, 1698, 1569, 1456, 1439, 1389, 1278, 1178, 1131, 744, 702, 682; **HRMS (MALDI)**: calcd. for $[M-Br]^+$ ($C_{37}H_{32}F_6N_2OP$) requires 665.2156, found 665.2135.

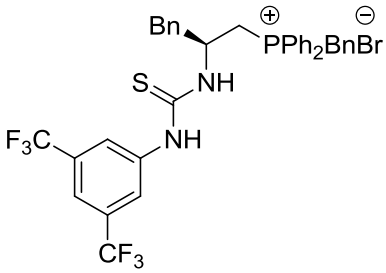
(*S*)-1-(3,5-bis(trifluoromethyl)phenyl)-3-(1-(diphenylphosphino)-3-phenylpropan-2-yl)thiourea(1d')

6



Yield: 70%; White solid, m.p.= 108–110 °C; $[\alpha]_D^{26}$ 8.3 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.73 (br. s, 1H), 7.68 (s, 1H), 7.60 (s, 2H), 7.48-7.35 (m, 4H), 7.35-7.24 (m, 9H), 7.19 (d, *J* = 6.8 Hz, 2H), 6.38 (br. s, 1H), 4.95 (br. s, 1H), 3.28–2.96 (m, 2H), 2.65–2.48 (m, 1H), 2.45–2.26 (m, 1H).

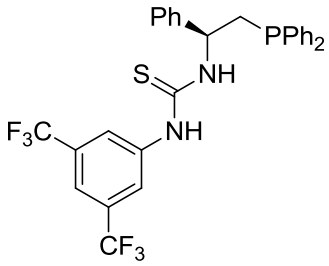
(*S*)-Benzyl(2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-phenylpropyl)diphenylphosphonium bromide(1d)



Yield: 70%; White solid. m.p. = 200-202 °C; $[\alpha]_D^{26}$ -62.6 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.96 (d, *J* = 8.8 Hz, 1H), 9.47 (s, 1H), 8.08 (s, 2H), 7.71-7.64 (m, 2H), 7.55-7.37 (m, 9H), 7.34-7.29 (m, 3H), 7.24-7.20 (m, 3H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 2H), 5.28-5.19 (m, 1H), 4.60 (t, *J* = 14.8 Hz, 1H), 4.36 (t, *J* = 14.4 Hz, 1H),

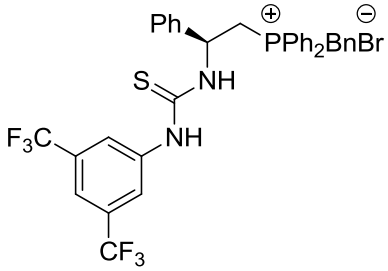
3.75-3.62 (m, 1H), 3.46-3.41 (m, 1H), 2.81 (dd, J = 13.4, 10.6 Hz, 1H), 2.66 (t, J = 14.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.1, 140.8, 136.8, 134.9 (d, J_{C-P} = 2.3 Hz), 134.7 (d, J_{C-P} = 2.4 Hz), 133.3 (d, J_{C-P} = 4.8 Hz), 133.2 (d, J_{C-P} = 4.0 Hz), 131.1 (q, J_{C-F} = 33.2 Hz), 130.1 (d, J_{C-P} = 5.6 Hz), 130.0 (d, J_{C-P} = 12.7 Hz), 129.6, 129.2 (d, J_{C-P} = 3.2 Hz), 129.1, 128.7 (d, J_{C-P} = 3.1 Hz), 127.2, 126.3 (d, J_{C-P} = 8.7 Hz), 123.3 (q, J_{C-F} = 271.7 Hz), 122.7, 117.6, 117.2 (d, J_{C-P} = 3.9 Hz), 117.1, 116.8, 116.3, 50.5 (d, J_{C-P} = 4.0 Hz), 43.0 (d, J_{C-P} = 13.5 Hz), 29.7 (d, J_{C-P} = 45.8 Hz), 24.7 (d, J_{C-P} = 51.3 Hz); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.8; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ 23.0; **IR (neat)** 3212, 3032, 1548, 1386, 1277, 1177, 1132, 742, 700, 681; **HRMS (MALDI)**: calcd. for $[M-Br]^+$ ($C_{37}H_{32}F_6N_2PS$) requires 681.1928, found 681.1900.

(*S*)-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(diphenylphosphino)-1-phenylethyl)thiourea(1e')



Yield: 58%; White solid. m.p. = 123-125 °C; $[\alpha]_D^{27}$ -6.2 (c = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz,) δ 7.64 (br. s, 1H), 7.47-7.41 (m, 4H), 7.36-7.27 (m, 6H), 6.99 (d, J = 8.8 Hz, 2H), 5.78 (d, J = 8.0 Hz, 1H), 4.60 (br. s, 1H), 3.81 (s, 3H), 2.43-2.37 (m, 1H), 2.14 (dd, J = 14.0, 8.6 Hz, 1H), 1.93-1.83 (m, 1H), 1.39-1.29 (m, 1H), 1.03-0.92 (m, 1H), 0.81-0.77 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 179.8, 140.9, 139.1, 137.0 (t, J_{C-P} = 10.7 Hz), 132.9 (d, J_{C-P} = 8.7 Hz), 132.7 (d, J_{C-P} = 8.7 Hz), 132.5, 129.1 (d, J_{C-P} = 7.9 Hz), 128.8 (q, J_{C-F} = 2.3 Hz), 128.6 (d, J_{C-P} = 2.3 Hz), 128.3, 126.4, 123.6, 122.9 (q, J_{C-F} = 271.8 Hz), 119.1 (m), 57.1 (d, J_{C-P} = 16.6 Hz), 36.7 (d, J_{C-P} = 14.2 Hz); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -63.0; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ -23.4; **IR (Neat)** 3252, 3054, 2927, 2854, 1538, 1384, 1278, 1179, 1135, 950, 888, 740, 697, 682; **HRMS (ESI)**: calcd. for $[M+H]^+$ ($C_{29}H_{24}F_6N_2PS$) requires 577.1302, found 577.1298.

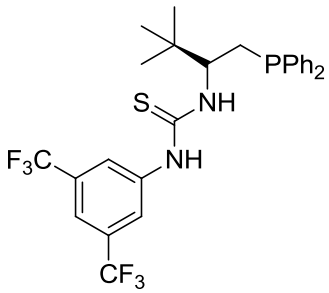
(*S*)-Benzyl(2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-2-phenylethyl)diphenylphosphonium bromide(1e)



Yield: 65%; White solid. m.p. =116-118 °C; $[\alpha]_D^{24}$ -45.7 (c = 0.5, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 10.26 (d, J = 9.2 Hz, 1H), 9.76 (s, 1H), 8.05 (s, 2H), 7.82-7.77 (m, 3H), 7.72-7.49 (m, 10H), 7.38-7.21 (m, 6H), 7.00-6.98 (m, 2H), 6.41 (q, J = 20.8, 14.4 Hz, 1H), 4.79 (t, J = 14.6 Hz, 1H), 4.53 (t, J = 14.8 Hz, 1H), 4.06-3.97 (m, 1H), 2.89 (t, J = 13.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.1, 140.7, 139.8 (d, J_{C-P} = 11.9 Hz), 135.2 (d, J_{C-P} = 23.0 Hz), 133.4 (d, J_{C-P} = 9.5 Hz), 133.2 (d, J_{C-P} = 33.1 Hz), 131.1 (q, J_{C-F} = 33.1 Hz), 130.3 (d, J_{C-P} = 6.3 Hz), 130.2 (d, J_{C-P} = 11.9 Hz), 129.4 (d, J_{C-P} = 2.3 Hz), 129.3, 129.0 (d, J_{C-P} = 3.9 Hz), 128.6, 126.8, 126.4 (d,

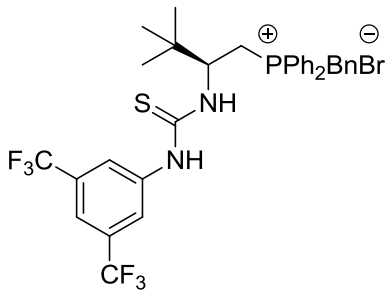
$J_{C\text{-}P}$ = 7.9 Hz), 123.3 (q, $J_{C\text{-}F}$ = 270.9 Hz), 122.7, 117.9 (d, $J_{C\text{-}P}$ = 83.0 Hz), 117.2 (m), 116.6 (d, $J_{C\text{-}P}$ = 82.1 Hz), 51.8, 29.6 (d, $J_{C\text{-}P}$ = 45.0 Hz), 28.8 (d, $J_{C\text{-}P}$ = 47.0 Hz); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -63.2; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ 23.2; **IR (Neat)** 3209, 3034, 2925, 1541, 1386, 1278, 1177, 1132, 955, 743, 699, 681; **HRMS (MALDI)**: calcd. for $[M\text{-}Br]^+$ ($C_{36}H_{30}F_6N_2PS$) requires 667.1772 , found 667.1781.

(*R*)-1-(3,5-bis(trifluoromethyl)phenyl)-3-(1-(diphenylphosphino)-3,3-dimethylbutan-2-yl)thiourea(1f')



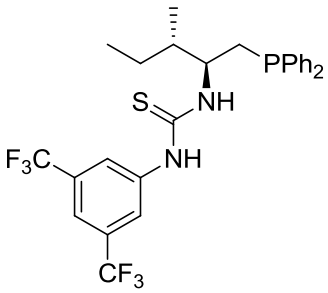
Yield: 60%; White solid. m.p. = 207-209 °C; $[\alpha]_D^{27}$ -12.8 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz,) δ 8.22 (br. s, 1H), 7.62 (s, 1H), 7.58 (s, 2H), 7.41-7.24 (m, 10 H), 6.05 (br. s, 1H), 4.82 (br. s, 1H), 2.55-2.51 (m, 1H), 2.20-2.14 (m, 1H), 0.98 (s, 9H); **^{13}C NMR** ($DMSO_{d\text{-}6}$, 100 MHz) δ 181.5, 142.6, 139.7 (d, $J_{C\text{-}P}$ = 14.2 Hz), 139.5 (d, $J_{C\text{-}P}$ = 15.8 Hz), 133.5 (d, $J_{C\text{-}P}$ = 18.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 18.9 Hz), 130.6 (q, $J_{C\text{-}F}$ = 33.1 Hz), 129.1, 128.7 (d, $J_{C\text{-}P}$ = 6.3 Hz), 128.6, 123.8 (q, $J_{C\text{-}F}$ = 271.0 Hz), 121.8, 115.9 (m), 79.7, 59.3 (d, $J_{C\text{-}P}$ = 14.2 Hz), 36.6 (d, $J_{C\text{-}P}$ = 7.1 Hz), 30.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 26.7; **^{19}F NMR**($CDCl_3$, 282 MHz) δ -63.0; **^{31}P NMR**($CDCl_3$, 163 MHz) δ -22.8; **IR (Neat)** 3263, 3076, 2965, 1540, 1471, 1384, 1341, 1276, 1176, 1136, 954, 886, 710, 695, 681; **HRMS (ESI)**: calcd. for $[M+H]^+$ ($C_{27}H_{28}F_6N_2PS$) requires 557.1615, found 557.1623.

(*S*)-Benzyl(2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3,3-dimethylbutyl)diphenylphosphonium bromide(1f)



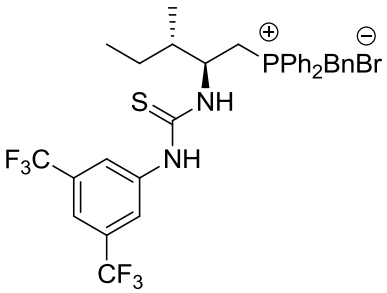
Yield: 65%; White solid. m.p. =131-133 °C; $[\alpha]_D^{30}$ -81.0 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 10.47 (s, 1H), 9.84 (d, *J* = 10.0 Hz, 1H), 8.13 (s, 2H), 7.75-7.70 (m, 3H), 7.55-7.45 (m, 8H), 7.20-7.11 (m, 3H), 6.87 (d, *J* = 6.4 Hz, 2H), 5.09 (q, *J* = 22.4, 11.2 Hz), 4.90 (t, *J* = 14.6 Hz, 1H), 4.46 (t, *J* = 15.0 Hz, 1H), 3.41-3.32 (m, 1H), 2.65 (t, *J* = 14.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 181.2, 141.1, 135.1, 134.5 (d, $J_{C\text{-}P}$ = 2.4 Hz), 133.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.0 (q, $J_{C\text{-}F}$ = 33.1 Hz), 130.3 (d, $J_{C\text{-}P}$ = 5.5 Hz), 130.1 (t, $J_{C\text{-}P}$ = 12.3 Hz), 129.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 129.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 126.6 (d, $J_{C\text{-}P}$ = 7.9 Hz), 123.3 (q, $J_{C\text{-}F}$ = 271.7 Hz), 122.3 (d, $J_{C\text{-}P}$ = 3.1 Hz), 119.3, 118.5, 117.6, 116.8 (m), 55.4 (d, $J_{C\text{-}P}$ = 4.7 Hz), 37.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 29.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 26.2, 23.9 (d, $J_{C\text{-}P}$ = 52.1 Hz); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.8; **^{31}P NMR**($CDCl_3$, 163 MHz) δ 24.3; **IR (Neat)** 3220, 3046, 2964, 1549, 1387, 1277, 1178, 1133, 959, 745, 700, 681; **HRMS (MALDI)**: calcd. for $[M\text{-}Br]^+$($C_{34}H_{34}F_6N_2PS$) requires 647.2085, found 647.2057.

1-(3,5-Bis(trifluoromethyl)phenyl)-3-((2*S*,3*S*)-1-(diphenylphosphino)-3-methylpentan-2-yl)thiourea(1g')



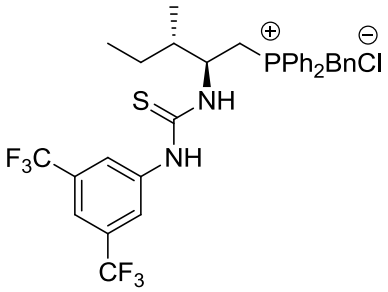
Yield:75%; White solid. m.p. = 163-165 °C; $[\alpha]_D^{27}$ 7.6 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.17 (br. s, 1H), 7.66-7.64 (m, 3H), 7.48-7.37 (m, 4H), 7.31-7.26 (m, 6H), 6.17 (br. s, 1H), 4.67 (br. s, 1H), 2.52-2.47 (m, 1H), 2.23 (dd, *J* = 13.6, 9.6 Hz, 1 H), 1.94 (br. s, 1H), 1.47-1.40 (m, 1H), 1.18-1.07 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR**($CDCl_3$, 100 MHz) δ 179.7, 139.2, 138.0 (d, $J_{C\text{-}P}$ = 10.3 Hz), 137.1 (d, $J_{C\text{-}P}$ = 10.3 Hz), 133.2 (d, $J_{C\text{-}P}$ = 19.8 Hz), 132.9, 132.5 (d, $J_{C\text{-}P}$ = 18.2 Hz), 129.3, 128.9, 128.7 (d, $J_{C\text{-}P}$ = 7.1 Hz), 122.9 (q, $J_{C\text{-}F}$ = 271.0 Hz), 123.1, 118.7, 57.2 (d, $J_{C\text{-}P}$ = 11.1 Hz), 38.7, 30.1, 25.9, 14.8, 11.4; **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -63.0; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ -23.4; **IR (Neat)** 3262, 3087, 2959, 2930, 2879, 1539, 1384, 1276, 1176, 1131, 883, 695, 679; **HRMS (ESI)**: calcd. for $[M+H]^+$ ($C_{27}H_{28}F_6N_2PS$) requires 557.1615, found 557.1633.

Benzyl((2*S*,3*S*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-methylpentyl)diphenylphosphoni um bromide(1g)



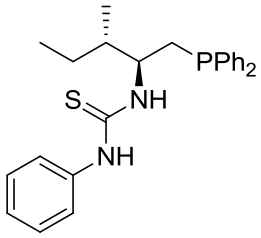
Yield: 68%; White solid. m.p. = 106-109 °C; $[\alpha]_D^{24}$ = -70.9 (*c* = 0.5, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.78 (s, 1H), 9.73 (d, *J* = 9.2 Hz, 1H), 8.10 (s, 2H), 7.79-7.74 (m, 3H), 7.65-7.54 (m, 8H), 7.30-7.28 (m, 1H), 7.20 (t, *J* = 7.6 Hz, 2H), 6.95-6.93 (m, 2H), 5.27-5.17 (m, 1H), 4.80 (t, *J* = 14.8 Hz, 1H), 4.62 (t, *J* = 15.0 Hz, 1H), 3.66-3.57 (m, 1H), 2.55 (t, *J* = 14.2 Hz, 1H), 1.86-1.77 (m, 1H), 1.40-1.30 (m, 1H), 1.24-1.15 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$,100 MHz) δ 180.4, 140.9, 135.0, 134.4, 133.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 133.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.0 (q, $J_{C\text{-}F}$ = 33.1 Hz), 130.2 (d, $J_{C\text{-}P}$ = 4.7 Hz), 130.0 (t, $J_{C\text{-}P}$ = 12.6 Hz), 129.2, 128.8, 126.6 (d, $J_{C\text{-}P}$ = 7.9 Hz), 123.2 (q, $J_{C\text{-}F}$ = 271.0 Hz), 122.3, 118.3 (d, $J_{C\text{-}P}$ = 82.1 Hz), 117.0 (d, $J_{C\text{-}P}$ = 83.0 Hz), 116.8, 51.5 (d, $J_{C\text{-}P}$ = 3.1 Hz), 41.0 (d, $J_{C\text{-}P}$ = 11.9 Hz), 29.3 (d, $J_{C\text{-}P}$ = 45.8 Hz), 25.2, 24.4 (d, $J_{C\text{-}P}$ = 52.1 Hz), 14.8, 11.4; **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.8; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ 24.3; **IR (Neat)** 3151, 3038, 2964, 2930, 2877, 1556, 1388, 1277, 1177, 1133, 746, 700, 681; **HRMS (MALDI)**: calcd. for $[M-Br]^+$ ($C_{34}H_{34}F_6N_2PS$) requires 647.2085, found 647.2081.

Benzyl((2*S*,3*S*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-methylpentyl)diphenylphosphoni um chloride(1h)



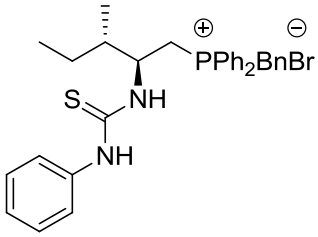
Yield: 73%; White solid. m.p. = 101-104 °C; $[\alpha]_D^{21}$ -67.5 (*c* = 1.0 , $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 10.20 (s, 1H), 10.00 (d, *J* = 3.1 Hz, 1H), 8.12 (s, 2H), 7.78-7.64 (m, 3H), 7.63-7.61 (m, 7H), 7.58-7.56 (m, 2H), 7.54-7.52 (m, 2H), 6.95-6.93 (m, 2H), 5.25-5.16 (m, 1H), 4.83 (t, *J* = 14.6 Hz, 1H), 4.57 (t, *J* = 14.8 Hz, 1H), 3.80-3.51 (m, 1H), 2.56 (t, *J* = 14.2 Hz, 1H), 1.40-1.31 (m, 1H), 1.24-1.15 (m, 1H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.83 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.6, 141.0, 135.1, 134.6, 133.4, 133.3, 133.2, 131.0 (q, $J_{C\text{-}F}$ = 33.2 Hz)， 130.4， 130.3， 130.2，130.1， 129.9, 129.3, 123.3 (q, $J_{C\text{-}F}$ = 270.2 Hz), 122.4, 118.9, 117.8 (d, $J_{C\text{-}P}$ = 49.7 Hz), 116.8 (m), 51.5, 40.9 (d, $J_{C\text{-}P}$ = 11.8 Hz), 29.2 (d, $J_{C\text{-}P}$ = 43.4 Hz), 14.8, 11.4; **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.9; **^{31}P NMR** ($CDCl_3$, 122 MHz) δ 23.5; **IR (Neat)** 3151, 3038, 2964, 2930, 2877, 1556, 1388, 1277, 1177, 1133, 746, 700, 681; **HRMS (MALDI)**: calcd. for $[M\text{-}Cl]^+$ ($C_{34}H_{34}F_6N_2PS$) requires 647.2085, found 647.2081.

1-((2*S*,3*S*)-1-(diphenylphosphino)-3-methylpentan-2-yl)-3-phenylthiourea(1i')



Yield: 70%; colorless oil. $[\alpha]_D^{30}$ = 43.2 (*c* = 1.0, $CHCl_3$), **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.86 (br. s, 1H), 7.47-7.41 (m, 4H), 7.38-7.23 (m, 9H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.00 (d, *J* = 8.0 Hz, 1H), 4.64 (br. s, 1H), 2.43-2.38 (m, 1H), 2.18 (dd, *J* = 14.3, 8.6 Hz, 1 H), 1.96-1.86 (m, 1H), 1.42-1.31 (m, 1H), 1.05-0.94 (m, 1H), 0.83-0.78 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 179.9, 138.6 (d, $J_{C\text{-}P}$ = 11.9 Hz), 138.2 (d, $J_{C\text{-}P}$ = 12.7 Hz), 136.4, 133.1 (d, $J_{C\text{-}P}$ = 19.0 Hz), 132.7 (d, $J_{C\text{-}P}$ = 18.9 Hz), 130.0, 128.8 (d, $J_{C\text{-}P}$ = 19.8 Hz), 128.6 (d, $J_{C\text{-}P}$ = 7.1 Hz), 126.9, 125.1, 57.3 (d, $J_{C\text{-}P}$ = 15.0 Hz), 38.3 (d, $J_{C\text{-}P}$ = 7.9 Hz), 30.5 (d, $J_{C\text{-}P}$ = 14.3 Hz), 25.4, 15.1, 11.6; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ -24.3; **IR (Neat)** 3424, 3216, 3046, 2961, 2929, 2874, 1541, 1497, 1437, 1351, 1255, 1111, 745, 701, 688; **HRMS (ESI)**: calcd. for $[M+Na]^+$ ($C_{25}H_{29}N_2NaPS$) requires 443.1687 , found 443.1687.

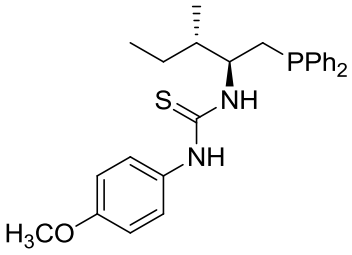
Benzyl((2*S*,3*S*)-3-methyl-2-(3-phenylthioureido)pentyl)diphenylphosphonium bromide(1i)



Yield: 71%; White solid. m.p. = 110-113 °C; $[\alpha]_D^{24}$ -64.7 (*c* = 1.0 , $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.46 (d, *J* = 9.2 Hz, 1H), 9.17 (s, 1H), 7.81-7.62 (m, 9H), 7.57-7.53 (m, 4H), 7.27-7.21 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 5.26-5.17 (m, 1H), 4.81 (d, *J* = 14.8 Hz, 2H), 3.88-3.78 (m, 1H), 2.49 (t, *J* = 14.2 Hz, 1H), 1.36-1.26 (m, 1H), 1.21-1.12 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.4, 139.2, 135.0 (d, $J_{C\text{-}P}$ = 3.1

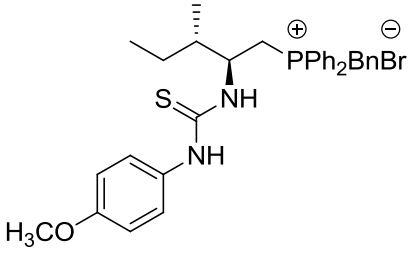
Hz), 134.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 133.4 (t, $J_{C\text{-}P}$ = 9.8 Hz), 130.4 (d, $J_{C\text{-}P}$ = 6.3 Hz), 130.1 (d, $J_{C\text{-}P}$ = 11.9 Hz), 129.9 (d, $J_{C\text{-}P}$ = 11.9 Hz), 129.1 (d, $J_{C\text{-}P}$ = 2.3 Hz), 128.6 (d, $J_{C\text{-}P}$ = 3.1 Hz), 128.1, 127.1 (d, $J_{C\text{-}P}$ = 7.9 Hz), 124.4, 123.4, 118.6, 117.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), 116.8, 51.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 41.0 (d, $J_{C\text{-}P}$ = 11.9 Hz), 28.9 (d, $J_{C\text{-}P}$ = 44.2 Hz), 25.5 (d, $J_{C\text{-}P}$ = 50.5 Hz), 14.8, 11.5; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ 25.6; **IR (Neat)** 3424, 3216, 3046, 2961, 2929, 2874, 1541, 1497, 1437, 1351, 1255, 1111, 745, 701, 688; **HRMS (MALDI)**: calcd. for $[M\text{-}Br]^+$($C_{32}H_{36}N_2PS$) requires 511.2337, found 511.2321.

1-((2*S*,3*S*)-1-(Diphenylphosphino)-3-methylpentan-2-yl)-3-(4-methoxyphenyl)thiourea(1j')



Yield: 67%; White solid. m. p.= 119-121 °C; $[\alpha]_D^{29}$ = 50.3 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64 (br. s, 1H), 7.47-7.41 (m, 4H), 7.36-7.27 (m, 6H), 6.99 (d, *J* = 8.8 Hz, 2H), 5.78 (d, *J* = 8.0 Hz, 1H), 4.60 (br. s, 1H), 3.81 (s, 3H), 2.43-2.37 (m, 1H), 2.14 (dd, *J* = 14.0, 8.6 Hz, 1 H), 1.93-1.83 (m, 1H), 1.39-1.29 (m, 1H), 1.03-0.92 (m, 1H), 0.81-0.77 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.4, 158.7, 138.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 138.3 (d, $J_{C\text{-}P}$ = 12.6 Hz), 133.1 (d, $J_{C\text{-}P}$ = 19.8 Hz), 132.7 (d, $J_{C\text{-}P}$ = 18.9 Hz), 128.8 (d, $J_{C\text{-}P}$ = 20.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 127.6, 115.2, 57.1 (d, $J_{C\text{-}P}$ = 14.2 Hz), 55.5, 38.3 (d, $J_{C\text{-}P}$ = 7.1 Hz), 30.6 (d, $J_{C\text{-}P}$ = 14.2 Hz), 25.4, 15.0, 11.5; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ -24.5; **IR (Neat)** 3380, 3198, 3050, 2960, 2930, 2874, 1509, 1239, 829, 739, 696; **HRMS (ESI)**: calcd. for $[M+H]^+$ ($C_{26}H_{32}N_2OPS$) requires 451.1973, found 451.1987.

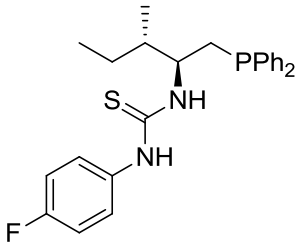
Benzyl((2*S*,3*S*)-2-(3-(4-methoxyphenyl)thioureido)-3-methylpentyl)diphenylphosphonium bromide(1j)



Yield: 60%; White solid. m. p.=125-127 °C; $[\alpha]_D^{29}$ -60.4 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.30 (d, *J* = 7.2 Hz, 1H), 8.94 (s, 1H), 7.81-7.62 (m, 8H), 7.58-7.53 (m, 2H), 7.33-7.31 (m, 2H), 7.21-7.13 (m, 3H), 6.94-6.93 (m, 2H), 6.80-6.78 (m, 2H), 5.25-5.15 (m, 1H), 4.82 (d, *J* = 14.8 Hz, 2H), 3.89-3.82 (m, 1H), 3.77 (s, 3H), 2.50 (t, *J* = 14.2 Hz, 1H), 1.33-1.26 (m, 1H), 1.18-1.11 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 181.1, 156.9, 135.0 (d, $J_{C\text{-}P}$ = 2.4 Hz), 134.6 (d, $J_{C\text{-}P}$ = 3.1 Hz), 133.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 133.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.2, 130.5 (d, $J_{C\text{-}P}$ = 5.5 Hz), 130.1 (d, $J_{C\text{-}P}$ = 11.9 Hz), 129.9 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.1 (d, $J_{C\text{-}P}$ = 2.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 3.2 Hz), 127.2 (d, $J_{C\text{-}P}$ = 8.7 Hz), 125.9, 55.4, 51.8 (d, $J_{C\text{-}P}$ = 4.0 Hz), 41.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 28.9 (d, $J_{C\text{-}P}$ = 44.2 Hz), 25.5 (d, $J_{C\text{-}P}$ = 50.6 Hz), 14.7, 11.5;

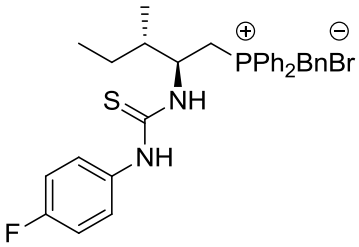
^{31}P NMR ($CDCl_3$, 163 MHz) δ 25.3; **IR (Neat)** 3219, 3050, 2960, 2930, 2875, 1541, 1509, 1437, 1343, 1239, 1181, 1110, 1030, 831, 745, 688; **HRMS (MALDI)**: calcd. for [M-Br]+ ($C_{33}H_{38}N_2OPS$) requires 541.2442, found 541.2428 .

1-((2*S*,3*S*)-1-(Diphenylphosphino)-3-methylpentan-2-yl)-3-(4-fluorophenyl)thiourea(1k')



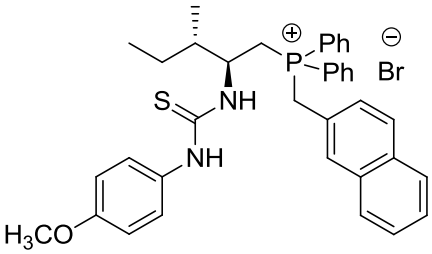
Yield: 65%; White solid. m.p. = 48-50 °C; $[\alpha]_D^{28}$ = 56.0 (*c* = 1.0, $CHCl_3$), **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.51 (br. s, 1H), 7.47-7.40 (m, 4H), 7.36-7.28 (m, 6H), 7.46 (d, *J* = 6.8 Hz, 4H), 5.77 (d, *J* = 8.8 Hz, 1H), 4.60 (br. s, 1H), 2.45-2.40 (m, 1H), 2.15 (dd, *J* = 14.2, 8.6 Hz, 1 H), 1.96-1.85 (m, 1H), 1.41-1.31 (m, 1H), 1.06-0.95 (m, 1H), 0.83-0.79 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.2, 161.2 (d, $J_{C\text{-}F}$ = 247.9 Hz), 138.5 (d, $J_{C\text{-}P}$ = 11.9 Hz), 138.1 (d, $J_{C\text{-}P}$ = 12.7 Hz), 133.1 (d, $J_{C\text{-}P}$ = 19.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 19.1 Hz), 132.3, 128.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 7.2 Hz), 127.5 (d, $J_{C\text{-}P}$ = 8.8 Hz), 116.8 (d, $J_{C\text{-}P}$ = 23.1 Hz), 57.2 (d, $J_{C\text{-}P}$ = 14.3 Hz), 38.3 (d, $J_{C\text{-}P}$ = 7.1 Hz), 30.4 (d, $J_{C\text{-}P}$ = 14.3 Hz), 25.5, 15.0,11.5; **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -113.8; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ -24.5; **IR (Neat)** 3381, 3270, 3052, 2961, 2929, 2874, 1506, 1218, 833, 739, 696; **HRMS (ESI)**: calcd. for $[M+Na]^+$ ($C_{25}H_{28}FN_2NaPS$) requires 461.1593 , found 461.1573.

Benzyl((2*S*,3*S*)-2-(3-(4-fluorophenyl)thioureido)-3-methylpentyl)diphenylphosphonium bromide(1k)



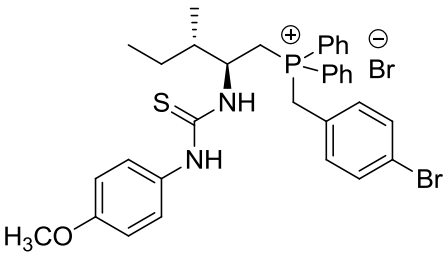
Yield: 72%; White solid. m.p.= 110-113 °C; $[\alpha]_D^{21}$ -34.2 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.47 (d, *J* = 9.6 Hz, 1H), 9.20 (s, 1H), 7.81-7.63 (m, 8H), 7.58-7.54 (m, 2H), 7.47-7.44 (m, 2H), 7.26-7.14 (m, 3H), 6.96-6.92 (m, 4H), 5.23-5.13 (m, 1H), 4.88-4.73 (m, 1H), 3.83-3.74 (m, 1H), 2.49 (t, *J* = 14.2 Hz, 1H), 1.85-1.79 (m, 1H), 1.34-1.24 (m, 1H), 1.19-1.12 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100MHz) δ 180.8, 159.7 (d, $J_{C\text{-}F}$ = 242.5 Hz), 135.2, 135.0, 134.7, 133.4 (t, $J_{C\text{-}P}$ = 8.3 Hz), 130.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 130.1 (d, $J_{C\text{-}P}$ = 10.8 Hz), 130.0 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 3.2 Hz), 128.7 (d, $J_{C\text{-}P}$ = 3.2 Hz), 127.0 (d, $J_{C\text{-}P}$ = 8.7 Hz), 125.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 118.5, 117.7, 116.8, 114.7 (d, $J_{C\text{-}P}$ = 22.2 Hz), 51.7 (d, $J_{C\text{-}P}$ = 3.9 Hz), 41.0 (d, $J_{C\text{-}P}$ = 11.9 Hz), 28.9 (d, $J_{C\text{-}P}$ = 43.4 Hz), 25.5, 24.9 (d, $J_{C\text{-}P}$ = 50.5 Hz), 14.7, 11.5; **^{19}F NMR** ($CDCl_3$, 282 MHz)) δ -118.3; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ 25.7; **IR (Neat)** 3422, 3222, 3050, 2962, 2930, 2875, 1541, 1507, 1437, 1341, 1216, 1111, 835, 744, 688; **HRMS (MALDI)**: calcd. for $[M-Br]^+$ ($C_{32}H_{35}FN_2PS$) requires 529.2243 , found 529.2199.

(2*S*,3*S*)-2-(3-(4-methoxyphenyl)thioureido)-3-methylpentyl)(naphthalen-2-ylmethyl)diphenylphosphonium bromide(1l)



Yield: 52%; White solid. m. p.= 120-123 °C; $[\alpha]_D^{22}$ = -55.9 (*c* = 1.0 , $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (br. s, 1H), 8.96 (s, 1H), 7.77-7.43 (m, 17H), 7.32 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.32-5.22 (m, 1H), 5.00 (d, *J* = 14.8 Hz, 2H), 3.95-3.86 (m, 1H), 3.76(s, 3H), 2.51 (t, *J* = 14.6 Hz, 1H), 1.89-1.80 (m, 1H), 1.34-1.28 (m, 1H), 1.21-1.10 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$,100MHz) δ 181.2, 157.0, 135.0 (d, $J_{C\text{-}P}$ = 31.6 Hz), 133.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 133.0 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.4 Hz), 132.2, 130.2, 130.1, 130.0 (d, $J_{C\text{-}P}$ = 4.8 Hz), 128.9 (d, $J_{C\text{-}P}$ = 2.3 Hz), 127.7, 127.4 (d, $J_{C\text{-}P}$ = 4.8 Hz), 126.9, 126.2, 126.1, 124.4 (d, $J_{C\text{-}P}$ = 8.7 Hz), 118.6, 117.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 117.0, 113.5, 55.4, 52.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 41.0 (d, $J_{C\text{-}P}$ = 11.8 Hz), 29.0 (d, $J_{C\text{-}P}$ = 44.2 Hz), 25.6, 25.2 (d, $J_{C\text{-}P}$ = 50.5 Hz), 14.8, 11.5; **^{31}P NMR** ($CDCl_3$, 163 MHz) δ 26.0; **IR (Neat)** 3216, 3050, 2961, 2929, 1542, 1509, 1463, 1438, 1344, 1240, 1181, 1111, 1033, 903, 829, 738, 688; **HRMS (MALDI)**: calcd. for $[M\text{-}Br]^+$ ($C_{37}H_{40}N_2OPS$) requires 591.2599, found 591.2590.

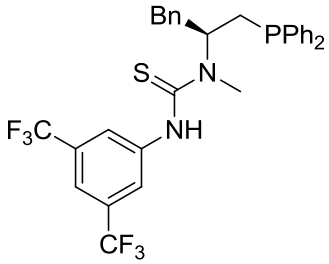
(4-Bromobenzyl)((2*S*,3*S*)-2-(3-(4-methoxyphenyl)thioureido)-3-methylpentyl)diphenylphosphonium bromide(1m)



Yield: 63%; White solid. m. p.=115-118 °C; $[\alpha]_D^{20}$ = -57.5 (*c* = 1.0 , $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.37 (br. s, 1H), 8.93 (s, 1H), 7.86-7.55 (m, 1H), 7.31-7.25 (m, 1H), 6.81 (d, *J* = 8.4 Hz, 4H), 5.19-5.09 (m, 1H), 5.03 (t, *J* = 15.8, 1H), 4.74-4.66 (m, 1H), 4.04-3.95 (m, 1H), 3.77 (s, 3H), 2.45 (t, *J* = 15.0 Hz, 1H), 1.85-1.75 (m, 1H), 1.24-1.20 (m, 1H), 1.12-1.06 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR**($CDCl_3$, 100 MHz) δ 181.2, 157.0, 135.0 (d, $J_{C\text{-}P}$ = 32.4 Hz), 133.5 (d, $J_{C\text{-}P}$ = 8.7 Hz), 133.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 3.2 Hz), 132.1 (d, $J_{C\text{-}P}$ = 5.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 130.0 (d, $J_{C\text{-}P}$ = 11.9 Hz), 126.5 (d, $J_{C\text{-}P}$ = 8.7 Hz), 126.1, 122.8, 117.7 (d, $J_{C\text{-}P}$ = 31.6 Hz), 116.9 (d, $J_{C\text{-}P}$ = 33.2 Hz), 113.5, 55.4, 51.8, 40.9 (d, $J_{C\text{-}P}$ = 11.9 Hz), 30.9, 28.2 (d, $J_{C\text{-}P}$ = 44.2 Hz), 25.6, 14.7, 11.5; **^{31}P NMR**($CDCl_3$, 163 MHz) δ 26.4; **IR (Neat)** 3216, 3042, 2962, 1589, 1542, 1488, 1460, 1438, 1180, 1111,

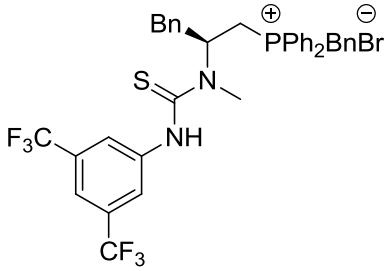
1073, 1033, 1012, 831, 735, 688; **HRMS (MALDI)**: calcd. for $[M-Br]^+$ ($C_{33}H_{37}BrN_2OPS$) requires 619.1548, found 619.1538.

(*S*)-3-(3,5-bis(trifluoromethyl)phenyl)-1-(1-(diphenylphosphino)-3-phenylpropan-2-yl)-1-methylthiourea(1n')



Yield: 65%; White solid. m.p. = 50-52 °C; $[\alpha]_D^{25}$ -1.8 (*c* =0.5, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.50-7.16 (m, 18H), 6.14 (br. s, 1H), 3.14-2.95 (m, 5H), 2.49-2.48 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 207.1, 183.3, 141.4, 137.8, 137.5 (d, J_{C-P} = 13.4 Hz), 136.9, 132.9 (d, J_{C-P} = 19.8 Hz), 131.4 (q, J_{C-F} = 33.2 Hz), 129.2, 129.1, 128.8, 127.4, 123.2 (q, J_{C-F} = 270.9 Hz), 117.5, 60.8, 53.5, 40.2 (d, J_{C-P} = 7.1 Hz), 33.0, 29.7; **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.9; **^{31}P NMR** ($CDCl_3$, 122 MHz) δ -21.8; **IR (neat)** 3346, 3057, 3028, 2927, 1618, 1560, 1474, 1433, 886, 847, 740, 698, 682; **HRMS (MALDI)**: calcd. for $[M+H]^+$ ($C_{31}H_{28}F_6N_2PS$) requires 605.1615, found 605.1619.

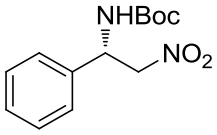
(*S*)-benzyl(2-(3-(3,5-bis(trifluoromethyl)phenyl)-1-methylthioureido)-3-phenylpropyl)diphenylphosphonium bromide(1n)



Yield: 70%; White solid. m.p. = 145-147 °C; $[\alpha]_D^{26}$ -61.0 (*c* = 0.5, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.89 (s, 1H), 7.95 (s, 2H), 7.80-7.67 (m, 4H), 7.61 (s, 1H), 7.57-7.45 (m, 6H), 7.38-7.36 (m, 2H), 7.32-7.27 (m, 2H), 7.16-7.08 (m, 1H), 6.98 (t, *J* = 7.4 Hz), 6.75-6.73 (m, 2H), 6.56-6.47 (m, 1H), 4.99-4.90 (m, 1H), 4.81 (t, *J* = 14.4 Hz), 4.50 (t, *J* = 14.8 Hz), 3.30 (s, 3H), 3.10-3.08 (m, 2H), 2.62 (t, *J* = 14.8 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 206.9, 182.0, 141.5, 136.6, 134.8 (d, J_{C-P} = 11.8 Hz), 133.4 (d, J_{C-P} = 9.5 Hz), 133.0 (d, J_{C-P} = 9.4 Hz), 130.8 (q, J_{C-F} = 33.2 Hz), 130.2 (d, J_{C-P} = 5.5 Hz), 130.1 (d, J_{C-P} = 5.6 Hz), 129.9, 129.7 (m), 129.0, 128.3, 127.2, 126.7 (m), 123.4 (q, J_{C-F} = 171.7 Hz), 118.5 (m), 118.2 (d, J_{C-P} = 35.8 Hz), 117.4 (d, J_{C-P} = 34.0 Hz), 56.9 (d, J_{C-P} = 3.9 Hz), 40.9 (d, J_{C-P} = 14.2 Hz), 34.3, 30.9, 30.3 (d, J_{C-P} = 45.8 Hz), 21.3 (d, J_{C-P} = 48.2 Hz); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -62.8; **^{31}P NMR** ($CDCl_3$, 122 MHz) δ 22.4; **IR (neat)** 2924, 2857, 1536, 1489, 1471, 1455, 1438, 1374, 1331, 1277, 1173, 1133, 982, 885, 743, 699, 681; **HRMS (ESI)**: calcd. for $[M-Br]^+$ ($C_{38}H_{34}F_6N_2PS$) requires 695.2079, found 695.2096.

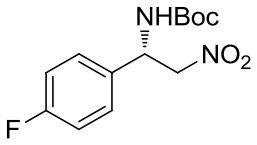
9. Spectral data of the products

***Tert*-butyl [(1*S*)-2-nitro-1-phenylethyl]carbamate (4a)**[7a]



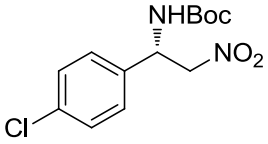
Yield: 79%; white solid. m.p.= 110-112 °C. Enantiomeric excess: 96%; **$[\alpha]_D^{30}$** 20.4 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiral Phenomenex Cellulose-2 column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min; t_{major} = 17.6 min, t_{minor}= 14.9 min, λ = 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.29 (m, 5H), 5.37-5.35 (m, 2H), 4.84 (br. s, 1H), 4.68 (dd, *J* = 12.6 Hz, 5.0 Hz, 1H), 1.44 (s, 9H).

***Tert*-butyl [(1*S*)-1-(4-fluorophenyl)-2-nitroethyl] carbamate(4b)**[7a]



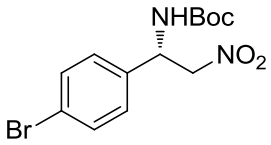
Yield: 77%; white solid. m. p.= 100-102 ℃. Enantiomeric excess: 97%; $[\alpha]_D^{29}$ 18.3 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 16.5 min., t_{minor}= 21.4 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.29 (dd, *J* = 8.8 Hz, 5.2 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.36-5.25 (m, 2H), 4.84 (br. s, 1H), 4.68 (dd, *J* = 8.8 Hz, 5.2Hz, 1H), 1.44 (s, 9H)

***Tert*-butyl [(1*S*)-1-(4-chlorophenyl)-2-nitroethyl] carbamate(4c)**[7b]



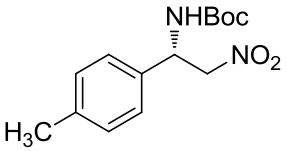
Yield: 80%; white solid. m. p.= 115-117 °C Enantiomeric excess: 97% $[\alpha]_D^{29}$ 18.1 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 20.1 min., t_{minor}= 26.1 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.36 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.34 (br. s, 2H), 4.83 (br. s, 1H), 4.70-4.65 (m, 1H) , 1.44 (s, 9H).

***Tert*-butyl [(1*S*)-1-(4-bromophenyl)-2-nitroethyl] carbamate(4d)**[7d]



Yield: 78%; white solid. m. p.= 140-142 °C. Enantiomeric excess: 97% $[\alpha]_D^{30}$ 18.9 (*c* = 1.0, = $CHCl_3$), determined by HPLC (chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 18.7 min., t_{minor}= 23.8 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.32 (br. s, 2H), 4.82 (br. s, 1H), 4.70-4.65 (m, 1H) , 1.44 (s, 9H).

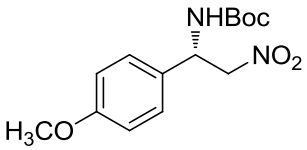
***Tert*-butyl [(1*S*)-1-(4-methylphenyl)-2-nitroethyl] carbamate(4e)**[7c]



Yield: 82%; white solid. m. p.= 110-113 °C; Enantiomeric excess: 98%; $[\alpha]_D^{28}$ 33.8 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak Phenomenex Cellulose-2 column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 16.3 min., t_{minor}= 13.5

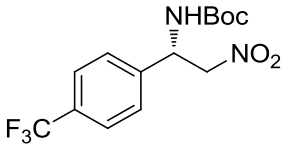
min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (s, 4H), 5.40 - 5.30 (m, 1H), 5.28 (br.s, 1H), 4.90 - 4.78 (m, 1H), 4.68 (dd, *J* = 12.3 Hz, 5.6 Hz, 1H), 2.34 (s, 3H), 1.44 (s, 9H).

***Tert*-butyl [(1*S*)-1-(4-methoxyphenyl)-2-nitroethyl] carbamate(4f)**[7a]



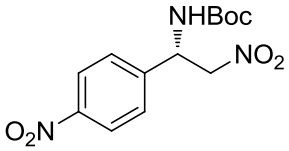
Yield: 81%; white solid. m. p.= 142-144 °C. Enantiomeric excess: 97%; $[\alpha]_D^{28}$ 30.4 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak OD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 37.9 min, t_{minor}= 33.3 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8Hz, 2H), 5.31 (q, *J* = 12.8 Hz, 6.0 Hz, 1H), 5.17 (br. s, 1H), 4.83 (br. s, 1H), 4.66 (dd, *J* =12.4 Hz, 6.0 Hz, 1H), 3.80 (s, 3H), 1.44 (s, 9H).

***Tert*-butyl {(1*S*)-2-nitro-1-[4-(trifluoromethyl)phenyl]ethyl}carbamate(4g)**[7a]



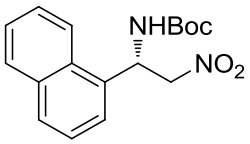
Yield: 84%; white solid. m. p.= 129-131 ℃ Enantiomeric excess: 98%; $[\alpha]_D^{25}$ 8.6 (*c* = 1.0, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 13.8 min., t_{minor}= 27.5 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H) 5.43 (br. s, 2H), 4.88 (br. s, 1H), 4.86 - 4.71 (m, 1H), 1.44 (s, 9H).

***Tert*-butyl [(1*S*)-2-nitro-1-(4-nitrophenyl)ethyl]carbamate(4h)**[7c]



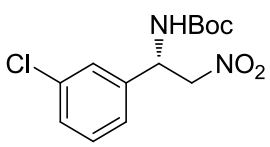
Yield: 68%; white solid. m. p.= 110-111 °C. Enantiomeric excess: 95%; $[\alpha]_D^{28}$ 13.7 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak AD-H column, hexane/*i*-PrOH 4:1, flow rate 0.7 mL/min, t_{major} = 11.8 min, t_{minor}= 23.4 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz 2H), 5.53-5.46 (m, 2H), 4.89 (br. s, 1H), 4.77 (dd, *J* = 13.4 Hz, 4.6 Hz, 1H), 1.44 (s, 9H).

***Tert*-butyl (1*S*)-1-(naphthalen-1-yl)-2-nitroethyl)carbamate(4i)**[7b]



Yield: 92%; white solid. m. p.= 153-154 °C. Enantiomeric excess: 96%; $[\alpha]_D^{27}$ 12.2 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 23.9 min., t_{minor}= 37.6 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.92-7.83 (m, 2H), 7.64-7.55 (m, 2H), 7.47 (d, *J* = 4.4 Hz, 2H), 6.30-6.25 (m, 1H), 5.31 (br. s, 1H), 4.90 (br.s, 1H), 1.44 (s, 9H).

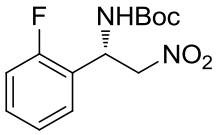
(*S*)-*Tert*-butyl (1-(3-chlorophenyl)-2-nitroethyl)carbamate(4j)[7b]



Yield: 83%; white solid. m. p.= 120-122 °C. Enantiomeric excess: 97%; $[\alpha]_D^{27}$ 15.7 (*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak AD-H column,

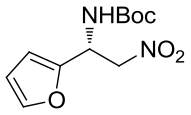
hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 13.6 min., t_{minor}= 17.2 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), 7.18–7.34 (m, 4H), 5.33-5.47 (m, 2H), 4.80 (br s, 1H), 4.65-4.73 (dd, *J* = 12.9, 4.8 Hz, 1H), 1.44 (s, 9H).

(*S*)-*Tert*-butyl (1-(2-fluorophenyl)-2-nitroethyl)carbamate(4k)[7b]



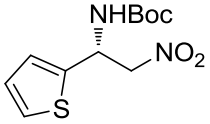
Yield: 95%; white solid. m.p.= 108-110 °C. Enantiomeric excess: 91%; $[\alpha]_D^{25}$ 19.3 (*c* = 1.0, $CHCl_3$), determined by HPLC (Chiralpak AS-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 16.9 min, t_{minor}= 31.6 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.36-7.31 (m, 2H), 7.18-7.08 (m, 2H), 5.59 (br. s, 1H), 5.47 (br. s, 1H), 4.84 (br. s, 1H), 4,72 (dd, *J* = 12.8 Hz, 5.2 Hz, 1H), 1.44 (s, 9H).

(*S*)-*Tert*-butyl (1-(furan-2-yl)-2-nitroethyl)carbamate(4l)[7b]



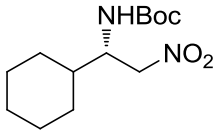
Yield: 98%; white solid. m. p.= 82-84 °C. Enantiomeric excess: 93%; $[\alpha]_D^{27}$ 29.0 (*c* = 1.0, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 14.7 min, t_{minor}= 13.8 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.38 (d, *J* = 0.8 Hz, 1H), 6.36-6.31 (m, 2H), 5.49-5.44 (m, 1H), 5.28 (br. s, 1H), 4.85 (br. s, 1H), 4.74 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H), 1.46 (s, 9H).

(*R*)-*Tert*-butyl (2-nitro-1-(thiophen-2-yl)ethyl)carbamate(4m)[7c]



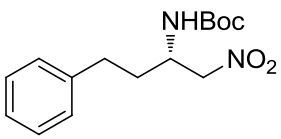
Yield: 92%; white solid. m. p.= 52-54 °C. Enantiomeric excess: 92%; $[\alpha]_D^{26}$ 16.0 (*c* = 1.0, $CHCl_3$), determined by HPLC (Chiralpak Phenomenex Cellulose-2 column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 20.9 min, t_{minor}= 19.0 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.28 (dd, *J* = 5.2 Hz, 1.0 Hz, 1H), 7.01-6.97 (m, 1H), 5.63 (q, *J* =14.0 Hz, 6.6 Hz, 1H), 5.28 (br. s, 1H), 4.90 (br. s, 1H), 4.75 (dd, *J* = 12.8 Hz, 5.2 Hz, 1H), 1.46 (s, 9H).

(*S*)-*Tert*-butyl (1-cyclohexyl-2-nitroethyl)carbamate(4n)[7a]



Yield: 88%; white solid. m. p.= 133-134 °C. Enantiomeric excess: 88%; $[\alpha]_D^{26}$ -21.8 (*c* = 1.0, $CHCl_3$), determined by HPLC(chiralpak Phenomenex Cellulose-2 column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, t_{major} = 15.8 min., t_{minor}= 11.2 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 4.85 (d, *J* = 9.2 Hz, 1H), 4.62-4.50 (m, 2H), 3.95 (br. s, 1H), 1.84-1.66 (m, 5H), 1.54-1.49 (m, 1H), 1.26 - 0.94 (m, 5H), 1.44 (s, 9H).

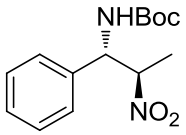
(*S*)-*Tert*-butyl (1-nitro-4-phenylbutan-2-yl)carbamate(4o)[7e]



Yield: 88%; white solid. m. p.= 104-106 °C. Enantiomeric excess: 88% $[\alpha]_D^{26}$ -24.3 (*c* = 1.0, $CHCl_3$), determined by HPLC (Phenomenex Cellulose-2 column,

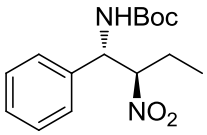
hexane/*i*-PrOH 9:1,flow rate 0.7 mL/min, t_{major} = 17.9 min., t_{minor}= 12.4 min, λ= 214 nm); **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.32 - 7.16 (m, 5H), 4.86 (d, *J* = 5.6 Hz, 2H), 4.54 (br. s, 2H), 4.15 - 4.06 (m, 1H), 2.80-2.66 (m, 1H), 1.98-1.84 (m, 2H), 1.46 (s, 9H).

***Tert*-butyl [(1*S*, 2*R*)-2-nitro-1-phenylpropyl]carbamate(4p)**[7a]



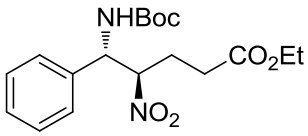
Yield: 99%; white solid. m. p.= 175-176 °C. Enantiomeric excess: 97% $[\alpha]_D^{27}$ 20.8(*c* = 1.0, $CHCl_3$), determined by HPLC (chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, *syn*: ee = 89 %, t_{major} = 21.7 min., t_{minor}= 18.2 min; *anti*: ee = 97 % t_{major} = 13.8 min., t_{minor}= 15.3 min., λ= 214 nm); *dr* was determined by HPLC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 3H, both diastereoisomers), 7.24–7.22 (m, 2H, both diastereoisomers), 5.56 (br. s, 1H, minor), 5.38 (br. s, 1H, major), 5.20 (dd, *J* = 8.8, 5.6 Hz, 1H, both diastereoisomers), 5.09 (br. s, 1H, minor), 4.93 (br. s, 1H, major), 1.53 (d, *J* = 7.0 Hz, 3H, both diastereoisomers), 1.44 (s, 9H, both diastereoisomers).

***Tert*-butyl [(1*S*, 2*R*)-2-nitro-1-phenylbutyl]carbamate(4q)**[7a]



Yield: 99%; white solid. m.p.= 179-180 °C. $[\alpha]_D^{27}$ 26.2 (*c* = 1.0, $CHCl_3$), determined by HPLC(Chiralpak AS-H column, hexane/*i*- PrOH 9:1, flow rate 0.7 mL/min, *syn*: ee = 86 %, t_{major} = 10.2 min., t_{minor}= 11.7 min; *anti*: ee = 96 %, t_{major} = 9.2 min., t_{minor}= 13.1 min., λ= 214 nm); *dr* was determined by HPLC; **^{1}H NMR** (400 MHz, $CDCl_3$), δ 7.38 - 7.31 (m, 3 H), 7.24 - 7.22 (m, 2H, both diastereoisomers), 5.15 (br. s, 2H, both diastereoisomers), 4.73 (br. s, 1H, both diastereoisomers), 2.11-2.00 (m, 1H, both diastereoisomers), 1.93-1.85 (m, 1H, both diastereoisomers), 1.53 (d, *J* = 7.0 Hz, 3H, both diastereoisomers), 1.43 (s, 9H, both diastereoisomers), 0.99 (t, *J* = 7.4 Hz, 3H, both diastereoisomers).

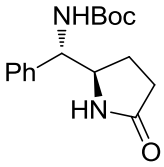
(4*R*,5*S*)-Ethyl 5-((tert-butoxycarbonyl)amino)-4-nitro-5-phenylpentanoate(4r)



Yield: 77%; white solid. m.p.= 112-114 °C. $[\alpha]_D^{26}$ 15.5 (*c* = 1.0, $CHCl_3$), determined by HPLC (Chiralpak AD-H column hexane/*i*-PrOH 9:1, flow rate 0.7 mL/min, *syn*: ee = t_{major} = 17.6min.,t_{minor}= 14.9 min, *anti*: ee = t_{major} = 18.9 min., t_{minor}= 21.2 min λ= 214 nm); *dr* was determined by HPLC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H, both diastereoisomers), 5.65 (br. s, 1H, both diastereoisomers), 5.20 (br. s, 1H, both diastereoisomers), 5.02-4.95 (m, 1H, both diastereoisomers), 4.13 (q, *J* = 7.2 Hz, 2H, both diastereoisomers), 2.46-2.25 (m, 4H, both diastereoisomers), 1.43 (s, 9H, both diastereoisomers), 1.24 (t, *J* = 7.2 Hz, 3H, both diastereoisomers); **^{13}C NMR** ($CDCl_3$,100Hz) δ 172.0, 171.6, 155.0, 137.1, 129.1,

128.8, 126.9, 30.1, 128.5, 126.4, 90.6, 90.3, 60.9, 30.0, 28.3, 26.4, 14.1; **IR (Neat)** 3356, 2979, 2928, 1716, 1556, 1368, 1168, 1029, 756, 702; HRMS(ESI): calcd. for $[M+Na]^+$ ($C_{18}H_{26}N_2O_6Na$) requires 389.1689, Found 389.1688.

***Tert*-butyl ((*S*)-((*R*)-5-oxopyrrolidin-2-yl)(phenyl)methyl)carbamate(5)**



Yield: 65%; white solid. m.p.= 64-65 °C; $[\alpha]_D^{25}$ 20.5 (*c* = 0.45, $CHCl_3$), determined by HPLC (Phenomenex Cellulose-2 column, hexane/*i*-PrOH 4:1, flow rate 0.7 mL/min, *syn*: ee= 88%, t_{major} = 23.9 min.,t_{minor}= 14.8 min, *anti*: ee = 88%, t_{major} = 17.6 min.,t_{minor} = 14.9 min, *anti*: ee = t_{major} = 18.9 min., t_{minor}= 21.2 min λ= 214 nm); *dr* was determined by HPLC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.23 (m, 5H, both diastereoisomers), 6.00-5.91 (m, 1H, both diastereoisomers), 5.22 (br.s, 1H, both diastereoisomers), 4.75-4.65 (m, 1H, both diastereoisomers), 3.98 (br. s, 1H, both diastereoisomers), 2.39-1.96 (m, 4H, both diastereoisomers), 1.43 (s, 9H, minor), 1.42 (s, 9H, major); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 178.1, 155.8, 139.4, 129.0, 128.2, 128.0, 127.3, 126.3, 80.3, 58.2, 30.1, 30.0, 29.5, 28.3, 24.2; **IR (Neat)** 3290, 3070, 2962, 1692, 1529, 1429, 1366, 1261, 1024, 801, 729, 699; **HRMS(ESI)**: calcd. for $[M+Na]^+$ ($C_{16}H_{22}N_2O_3Na$) requires 313.1528, Found 313.1521.

10. References

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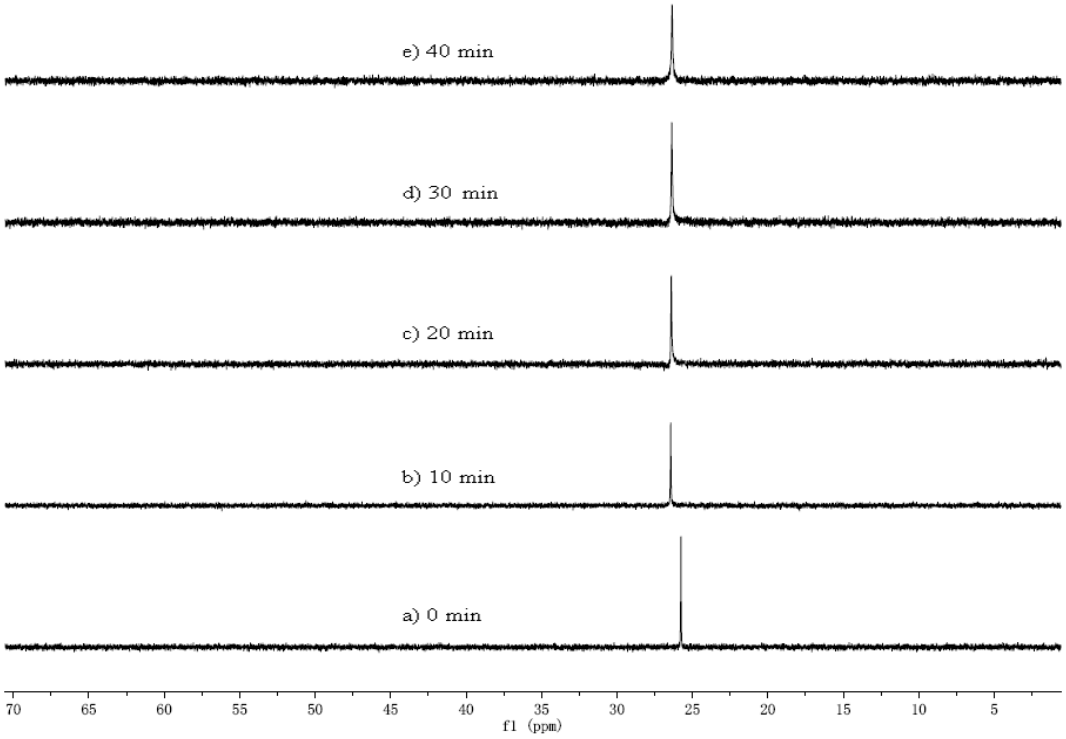
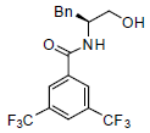
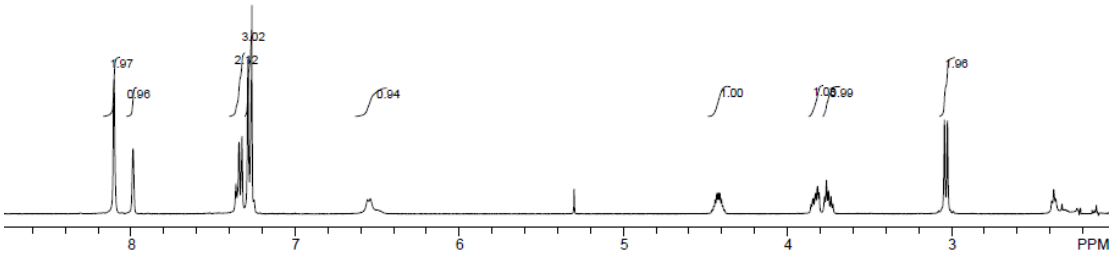
11. ^{31}P NMR monitoring of the catalyst in the reaction

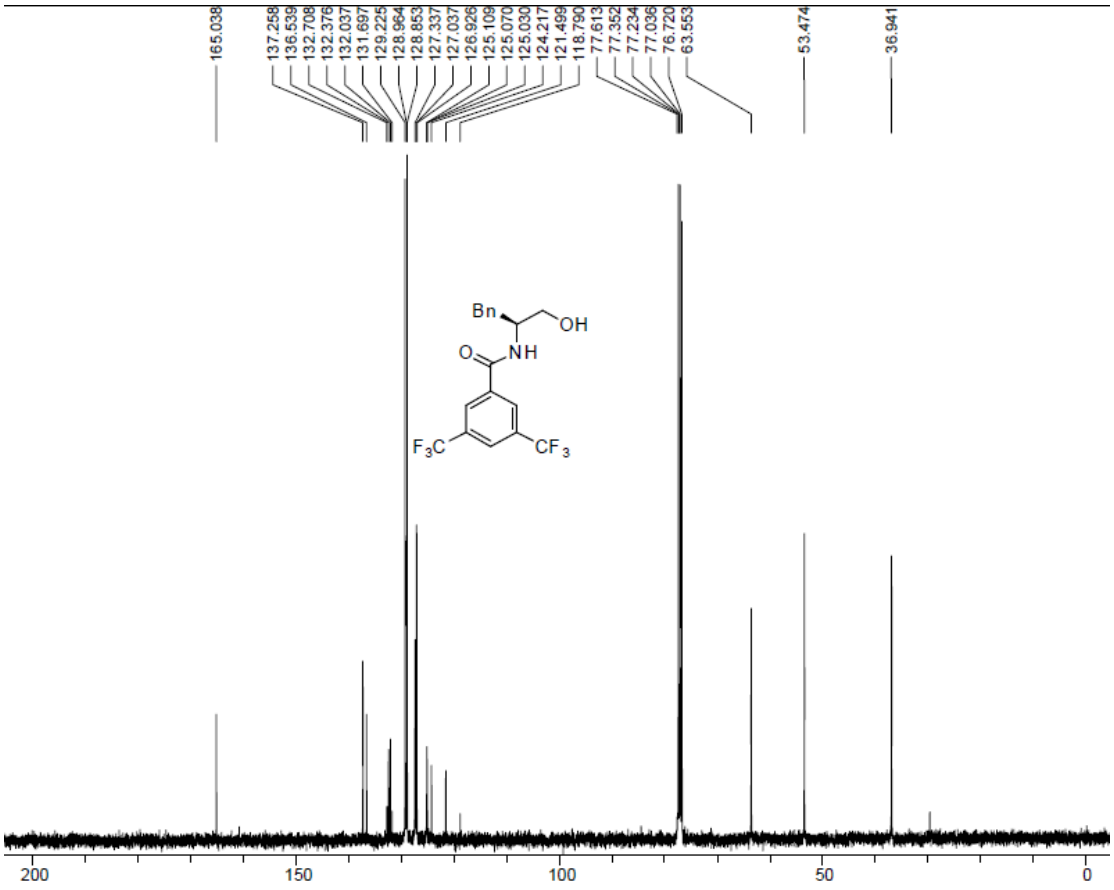
To a solution of amidosulfone **2a** (0.1 mmol) in $CDCl_3$ (1.0 mL) was added nitroalkane **3a** (0.5 mmol) and the catalyst **1j** (5 mol %) sequentially. Then freshly grounded KOH (28 mg, 0.5 mmol) was added. The resulting solution was vigorously stirred at room temperature and ^{31}P NMR analyses were taken at the times indicated below.



12. Copies of NMR spectra and HPLC traces



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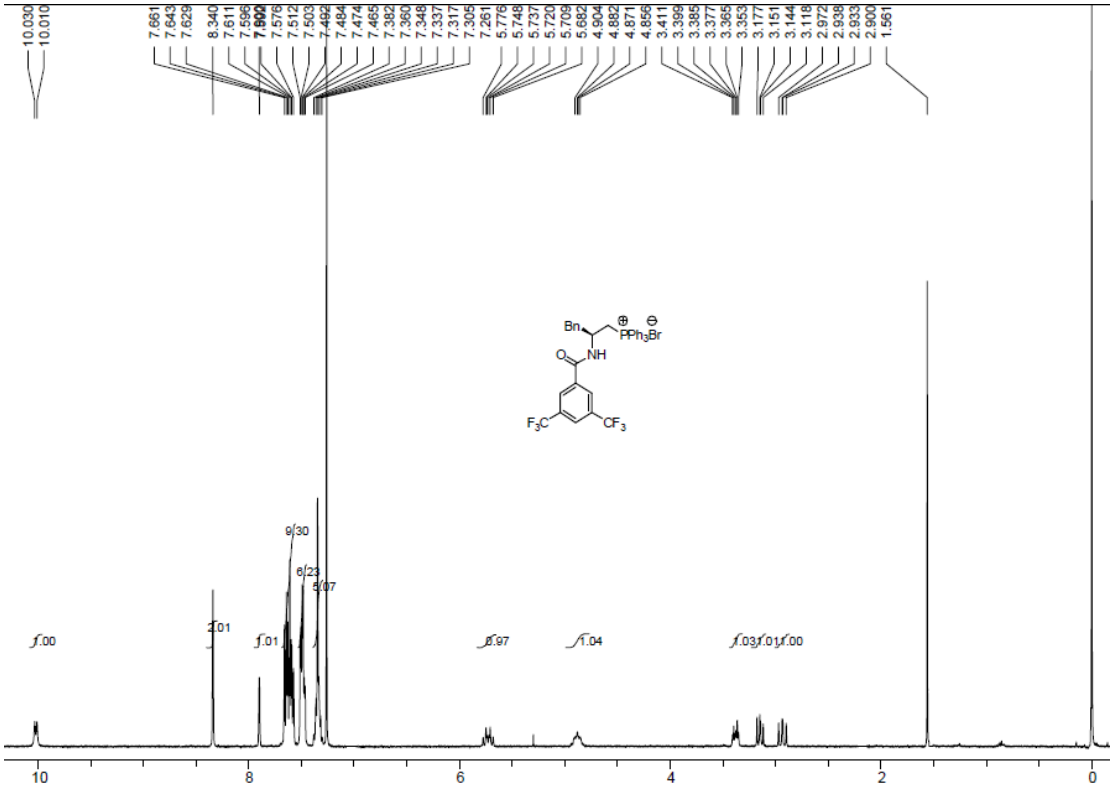
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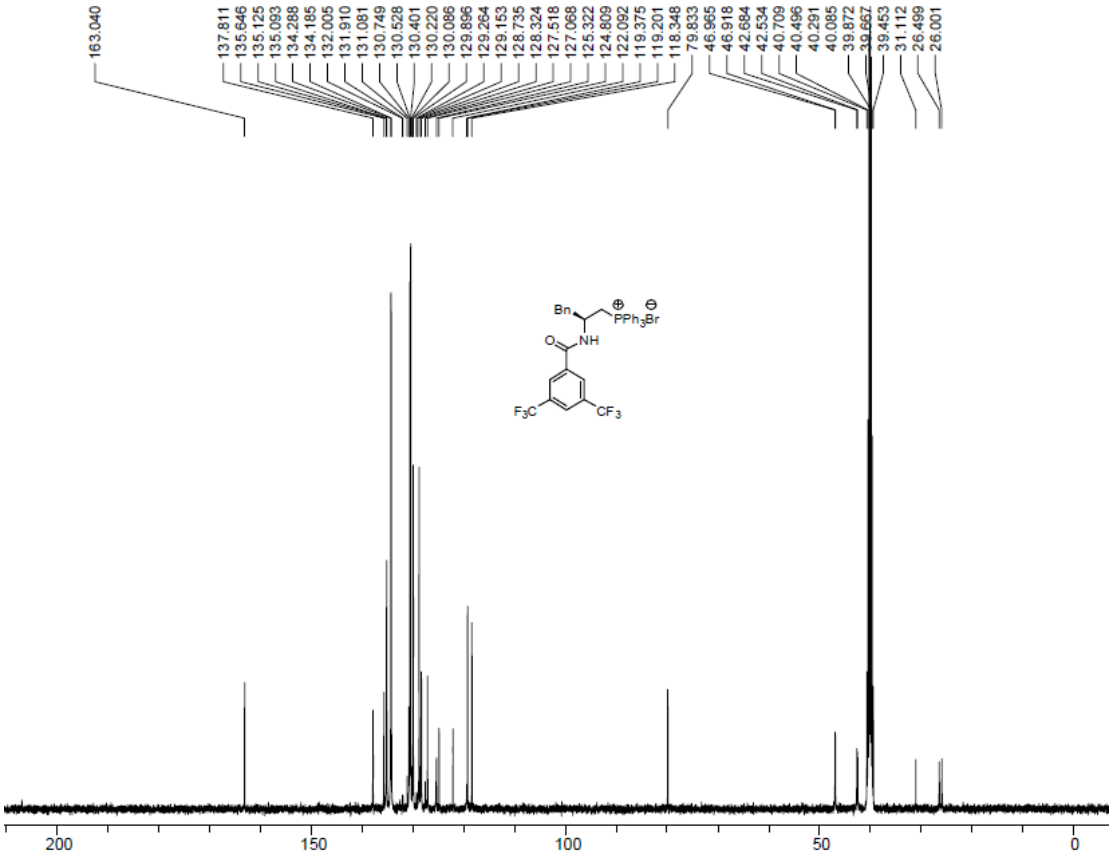

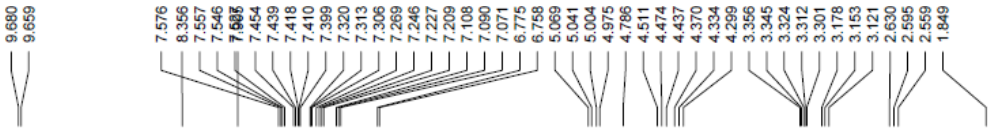

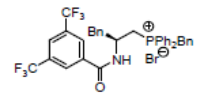

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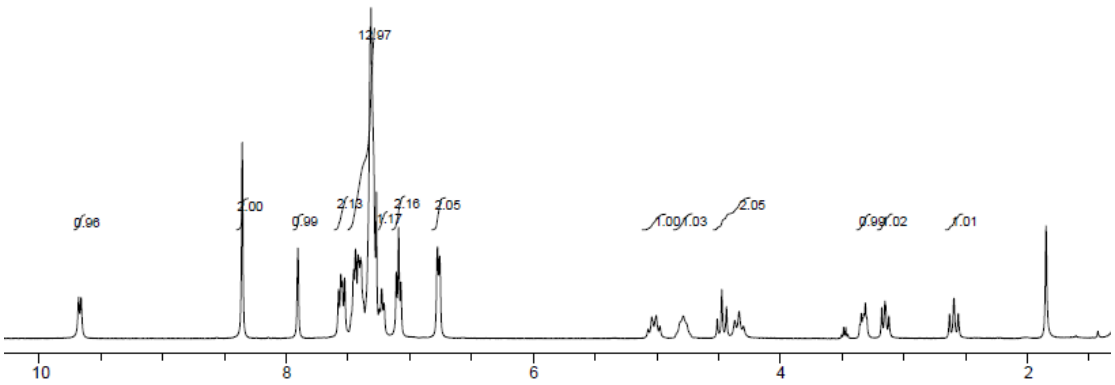

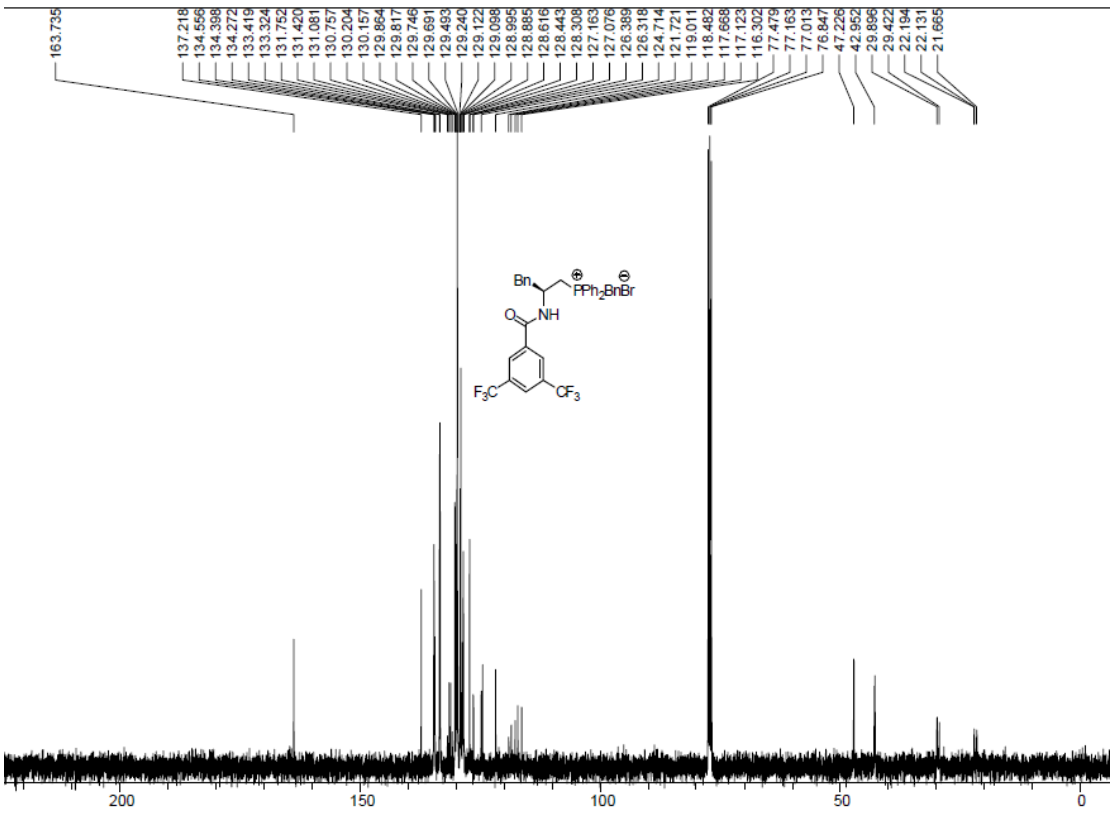
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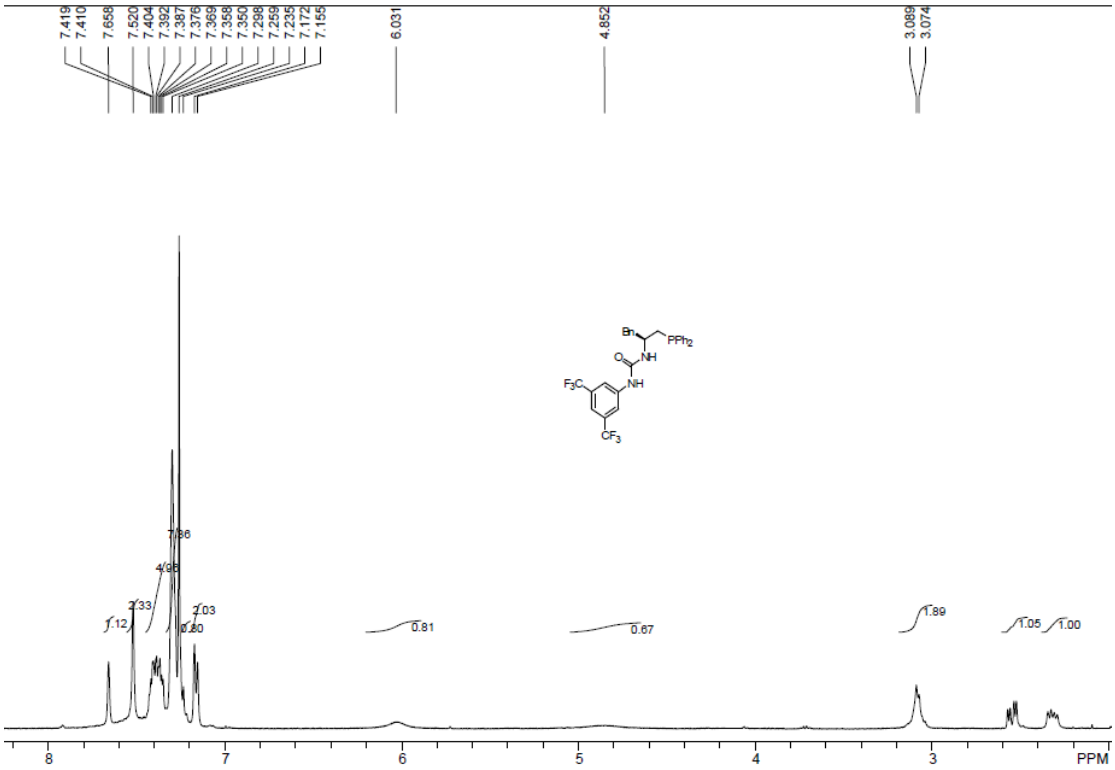
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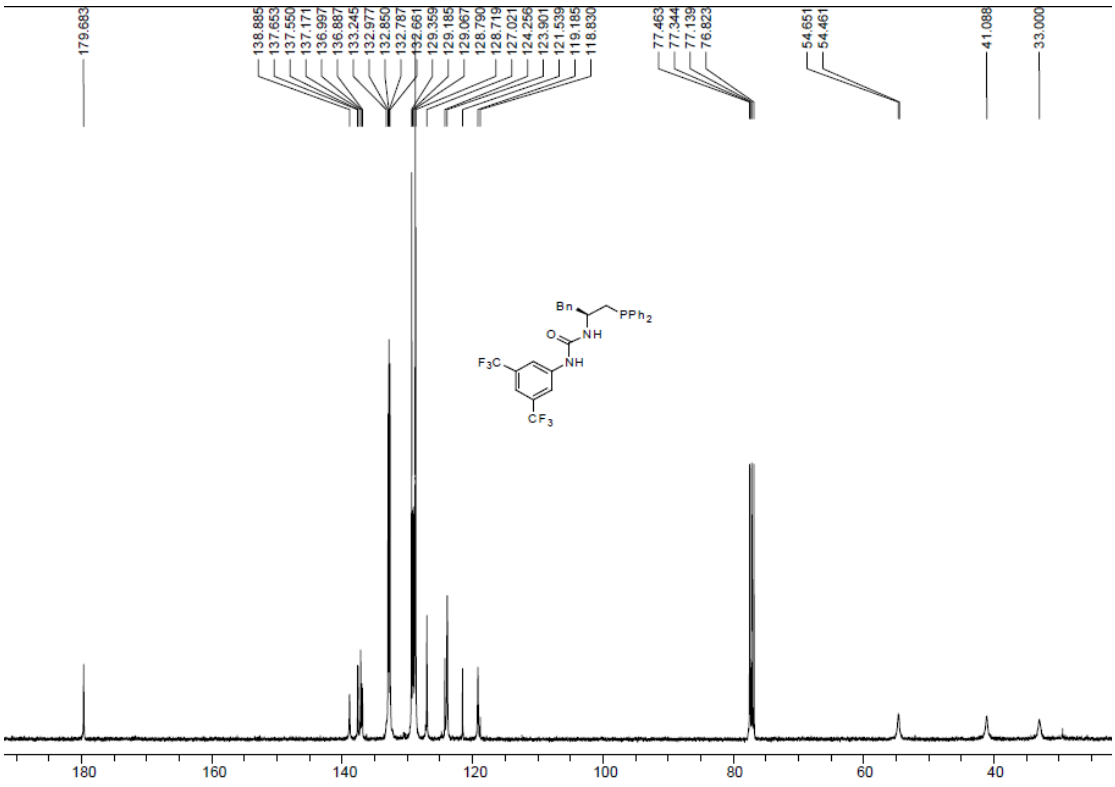
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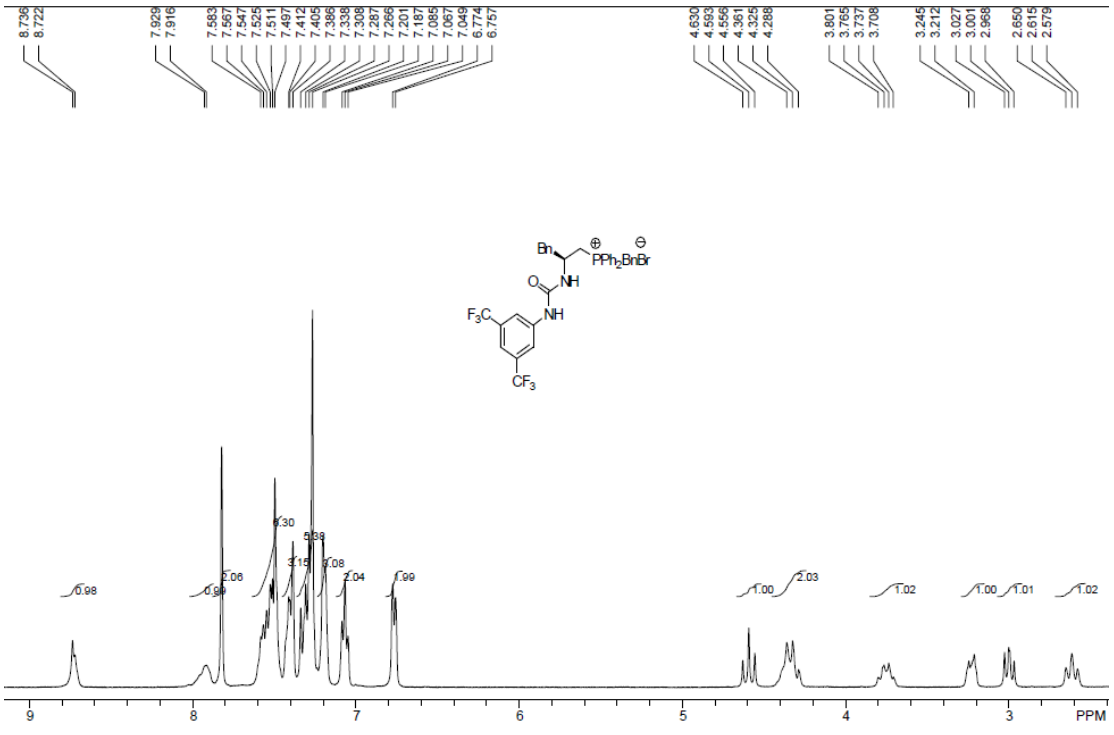
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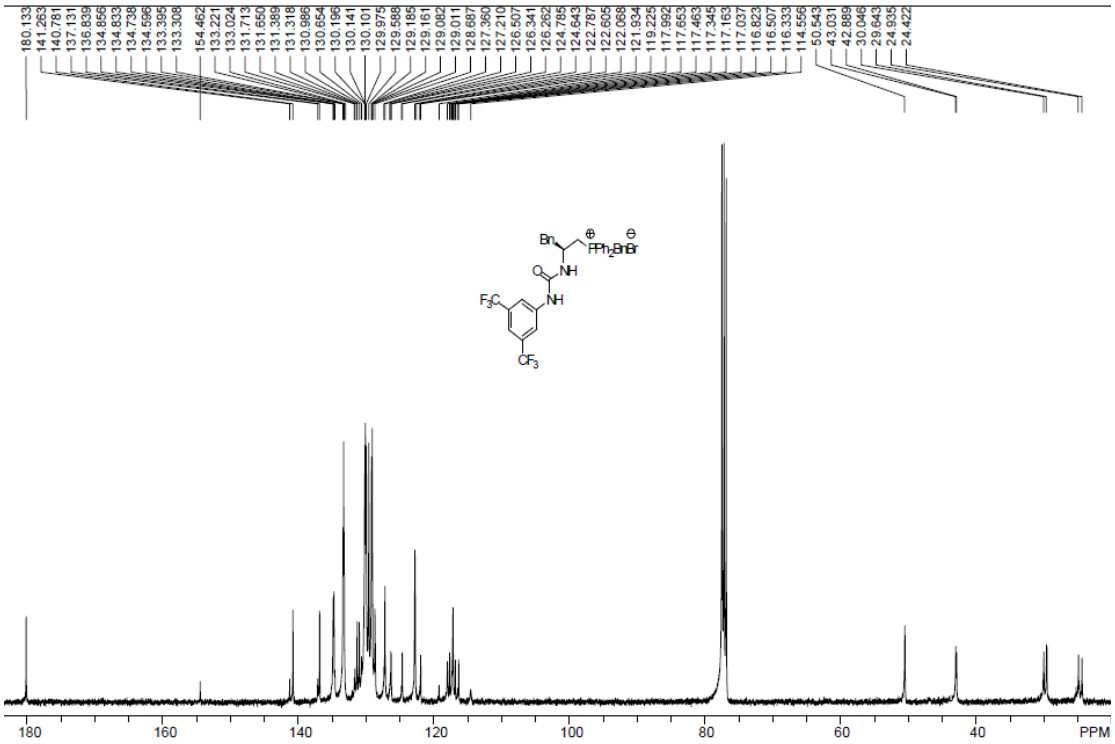
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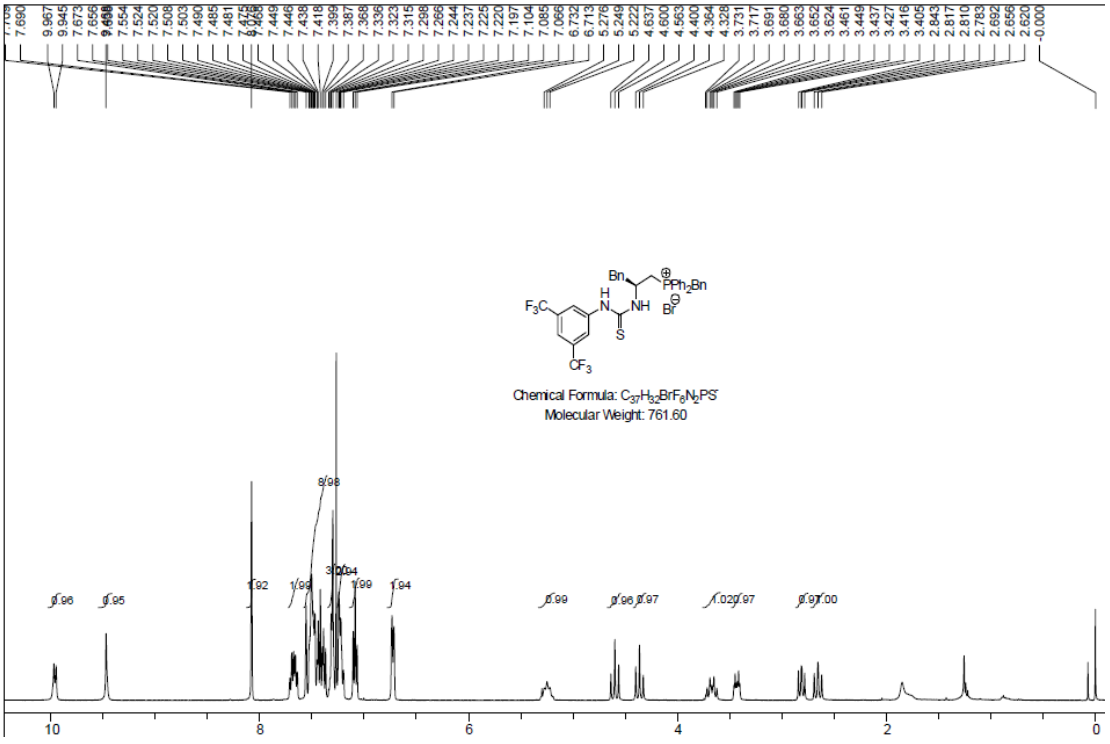
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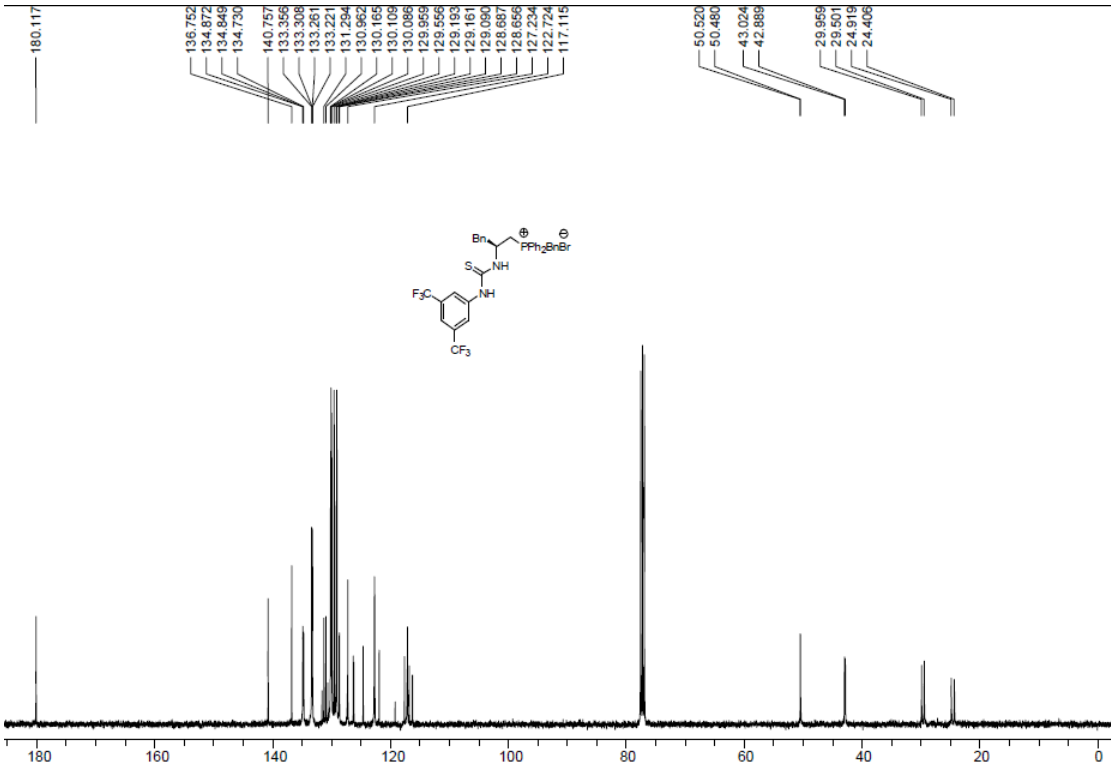
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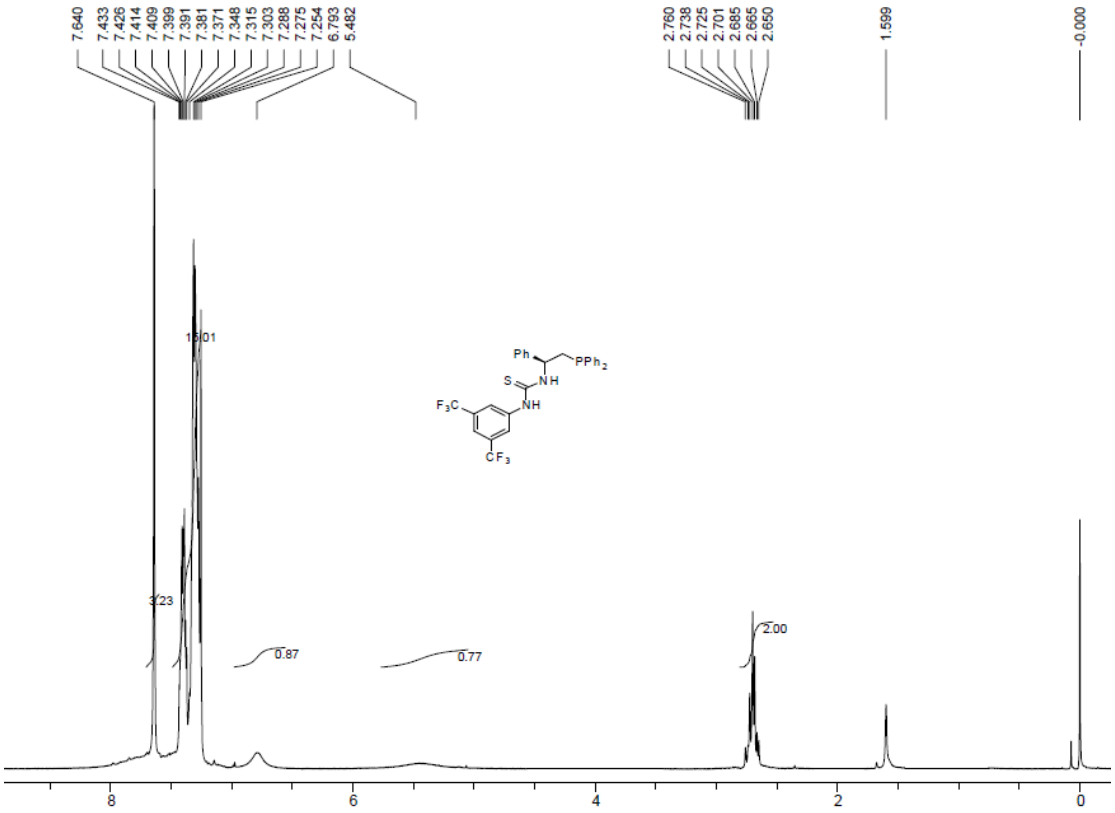
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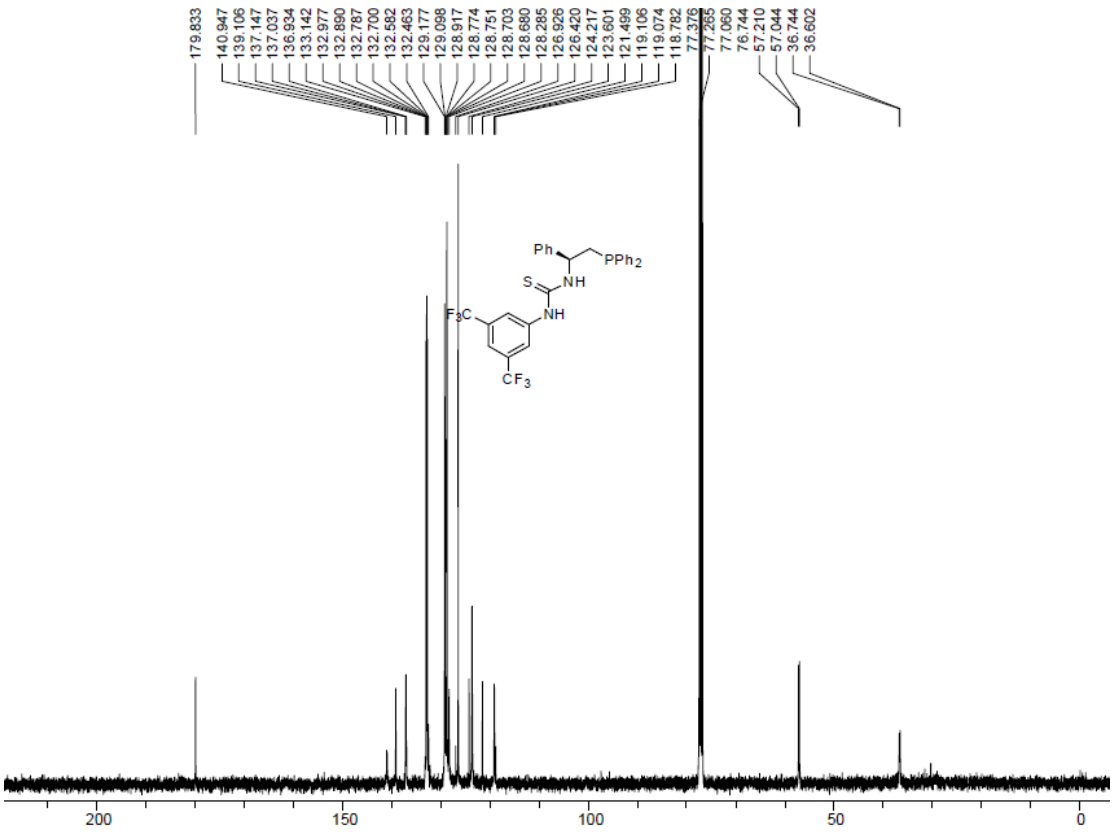
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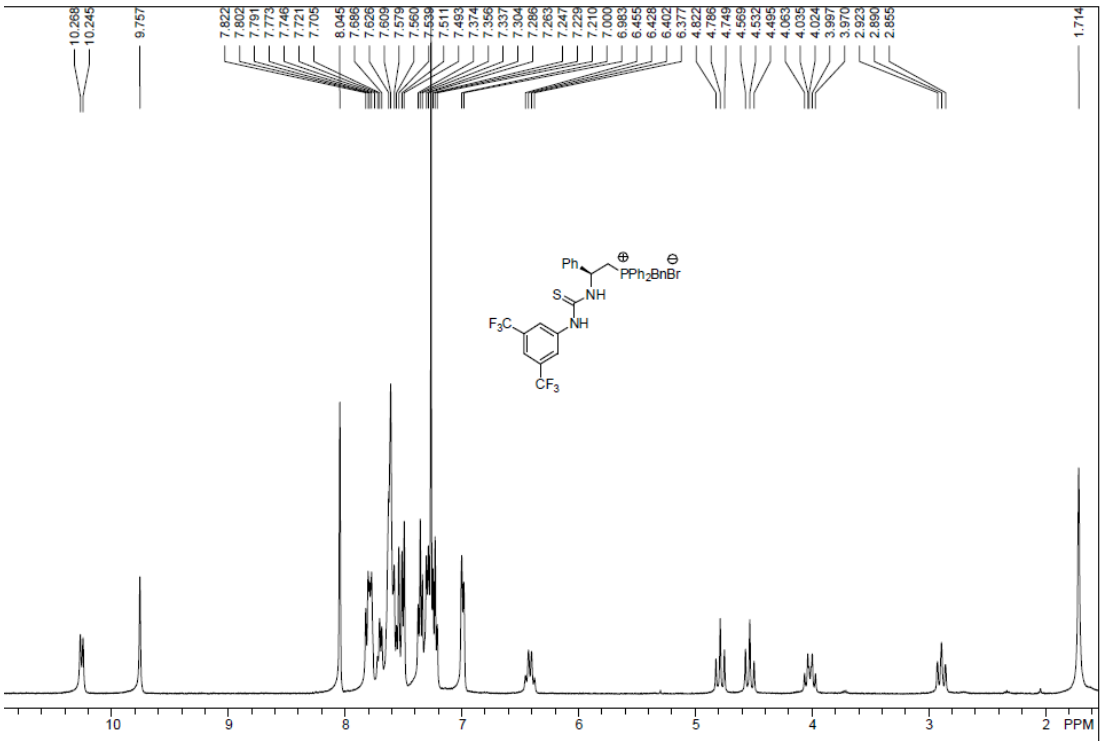
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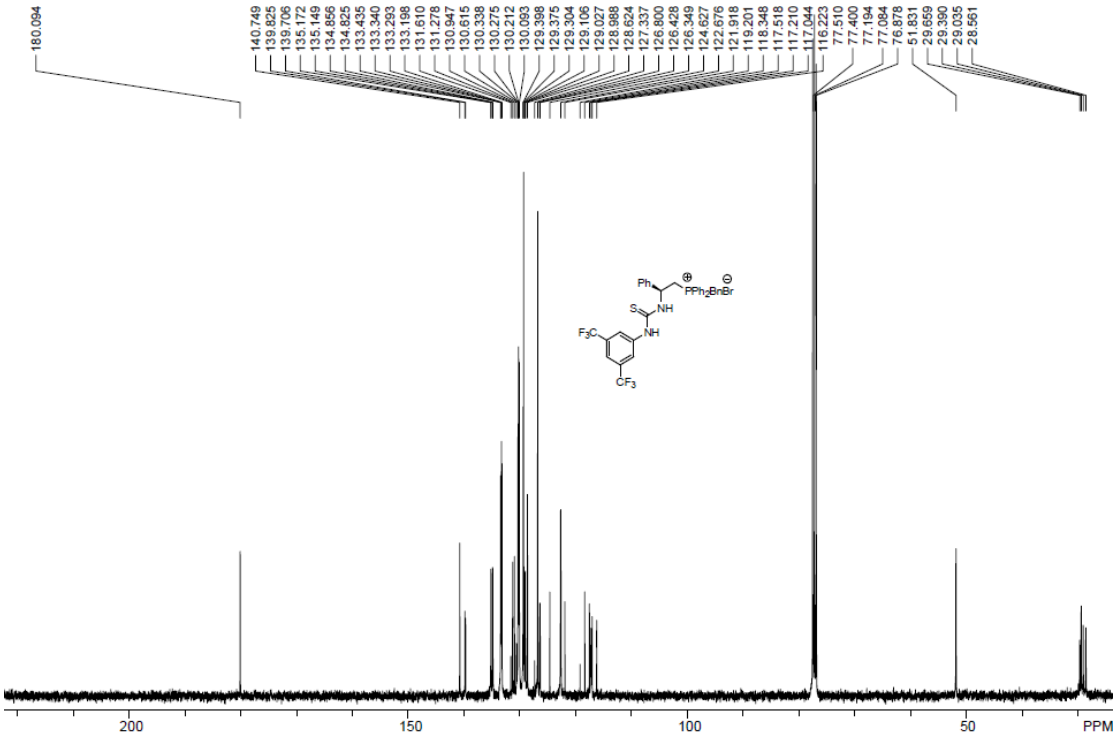
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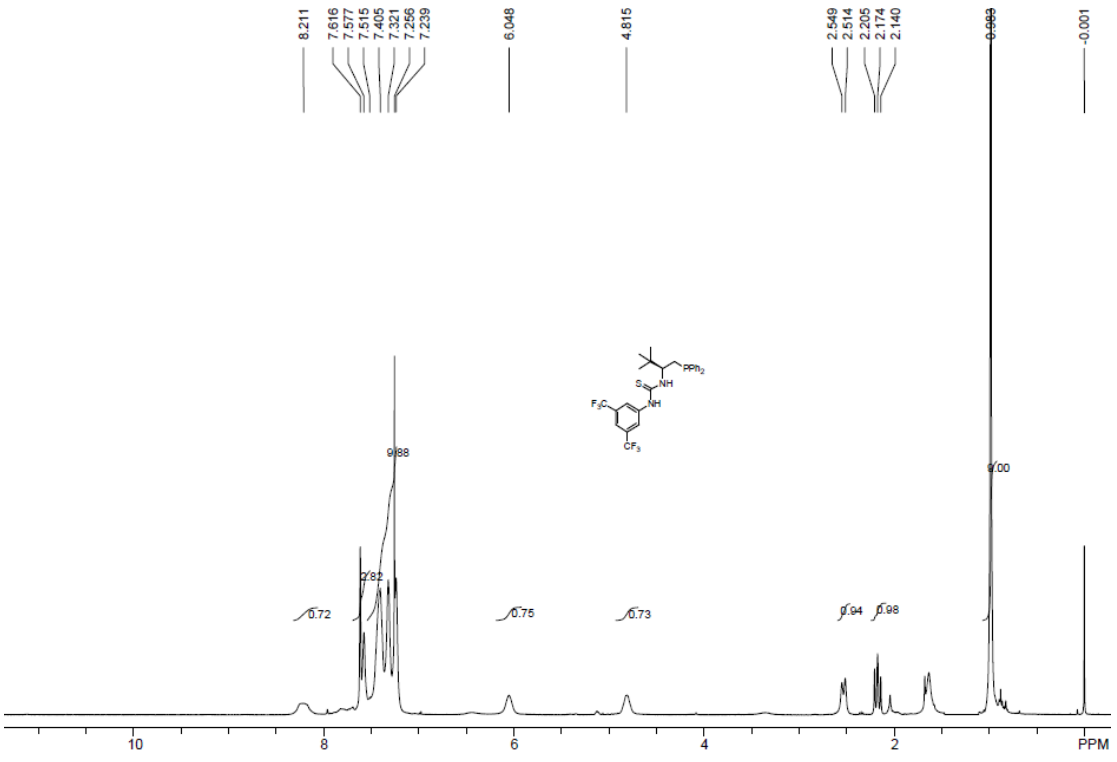
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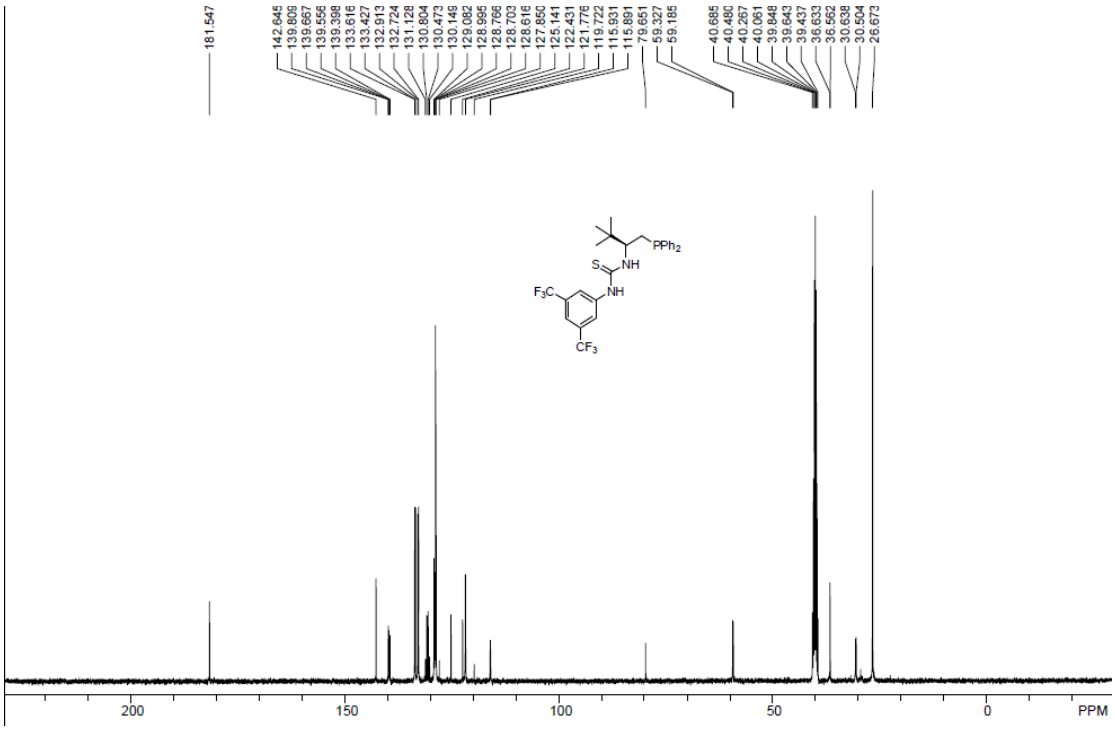
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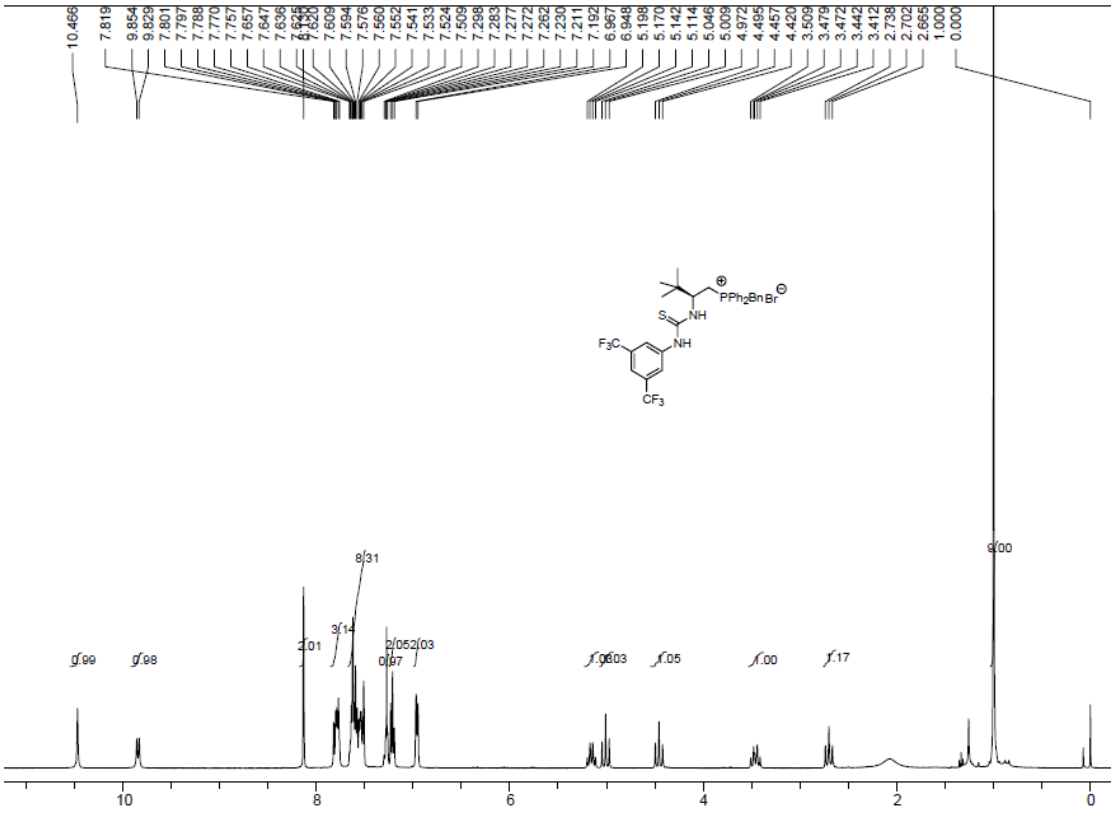
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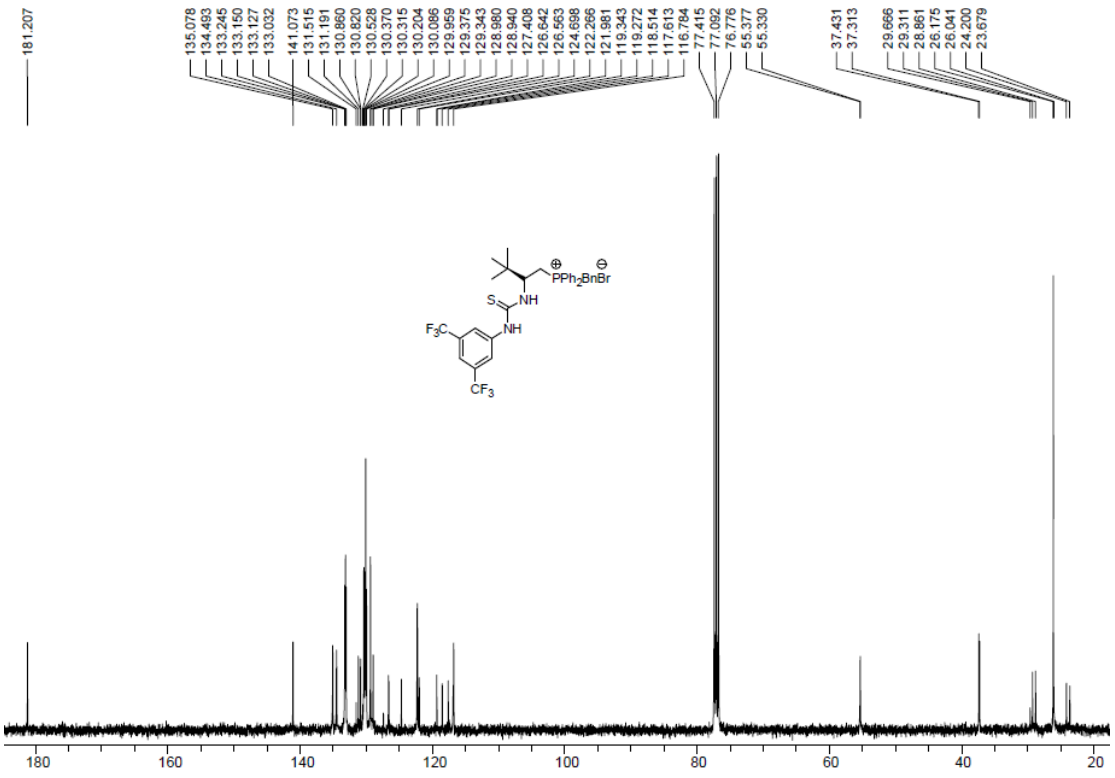
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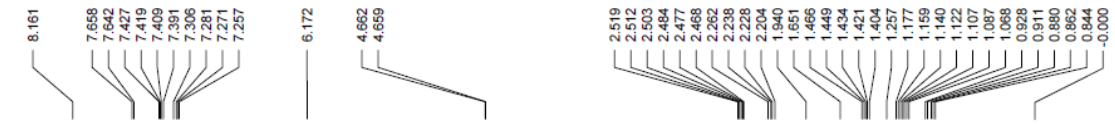
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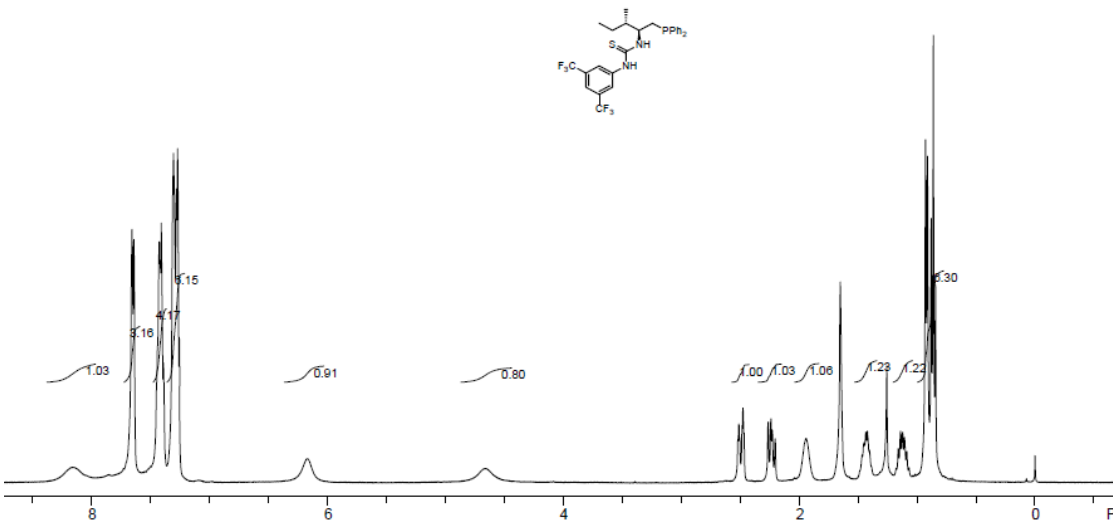
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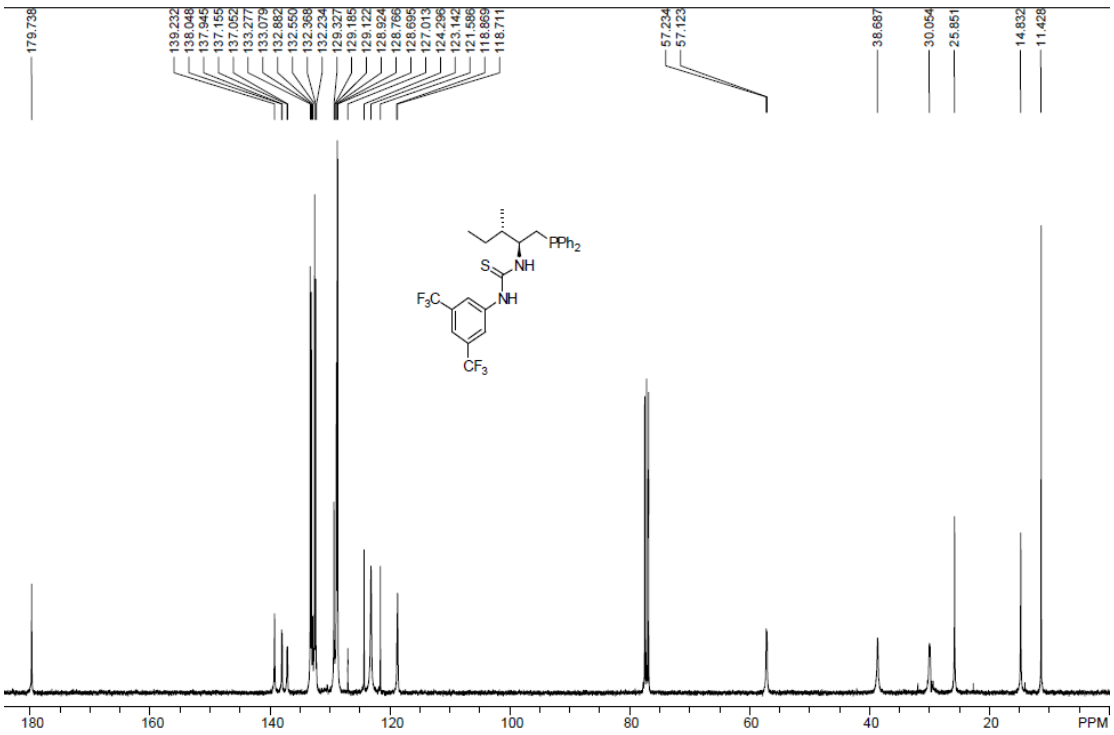
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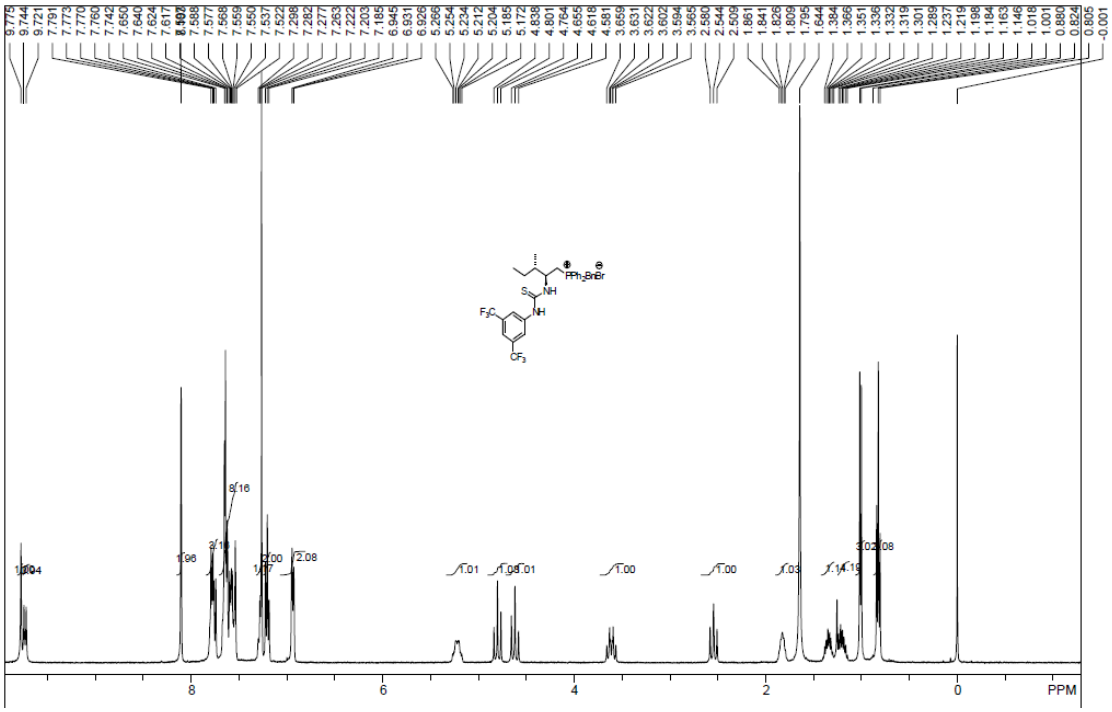
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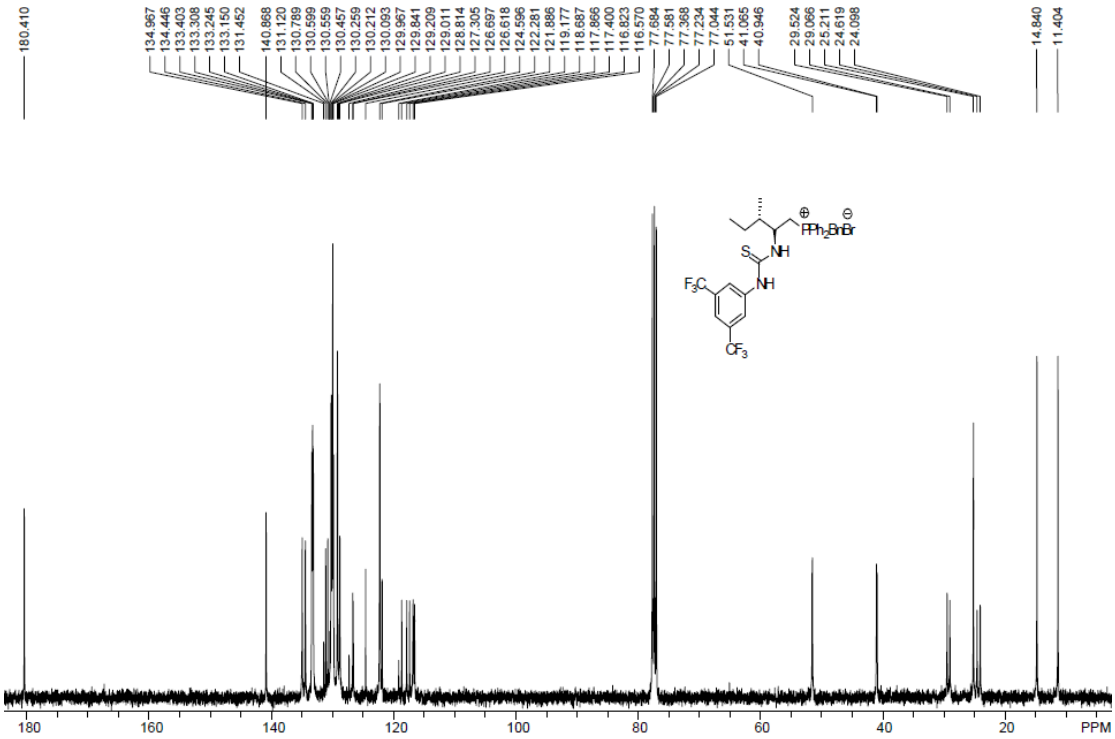
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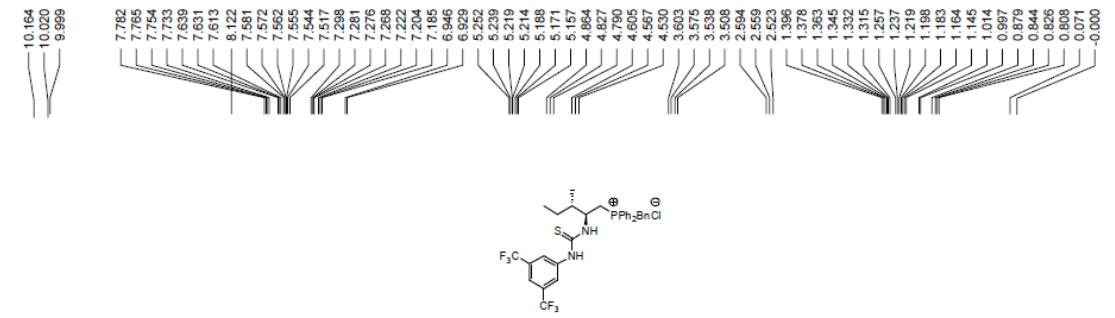
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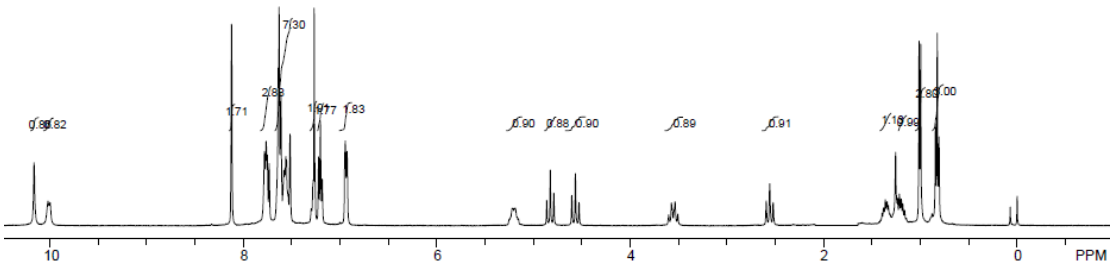
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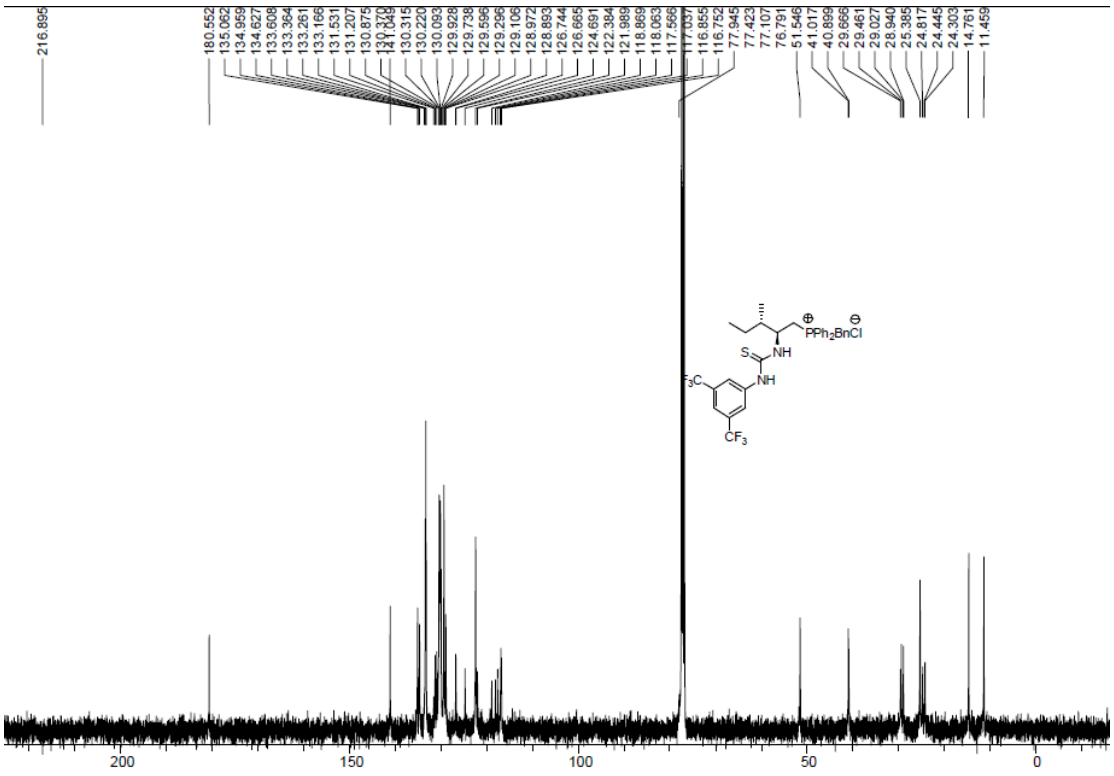
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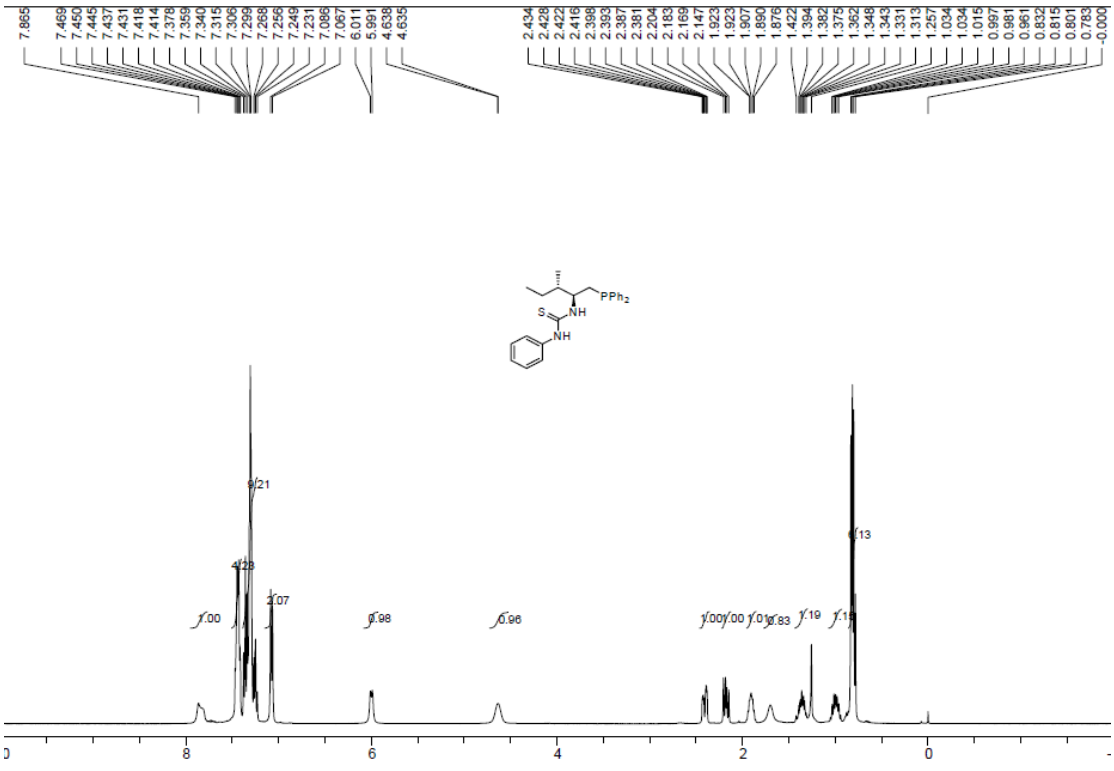
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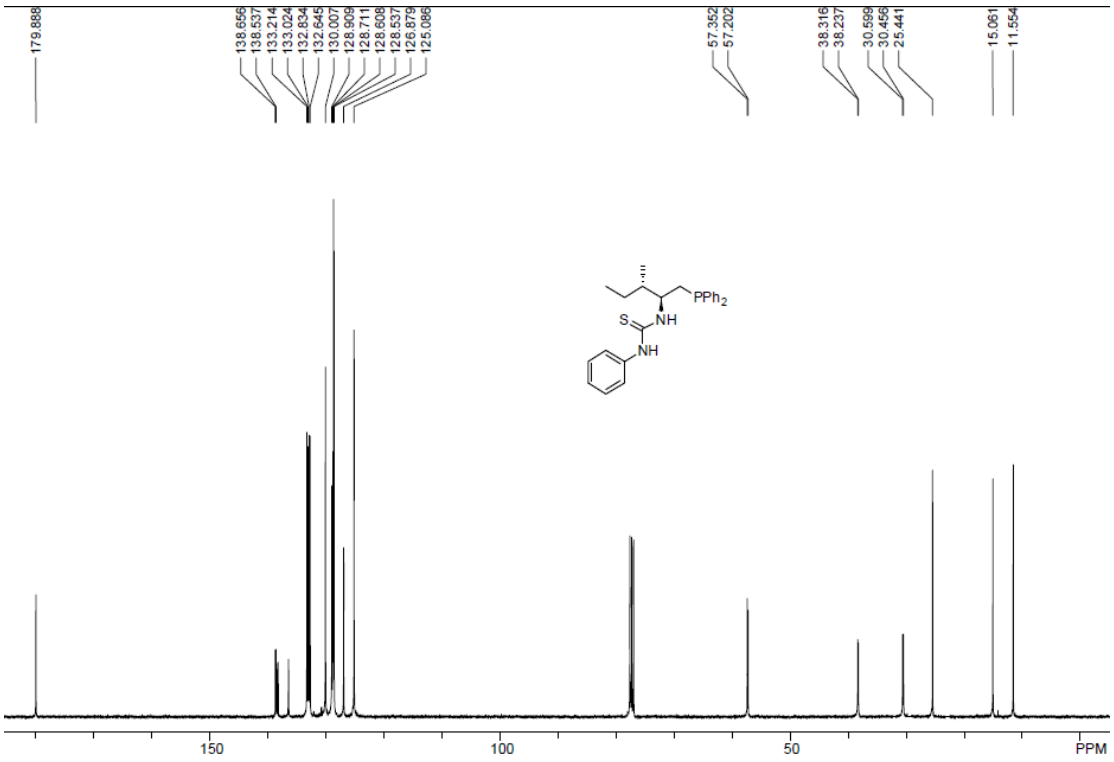
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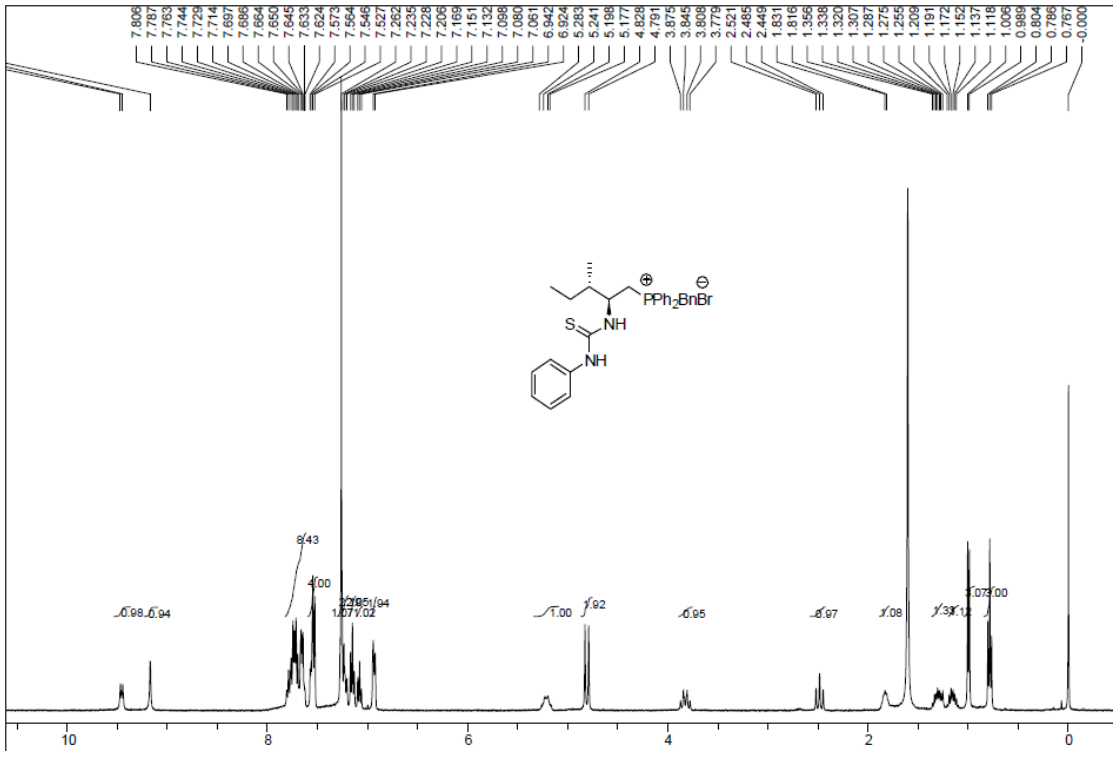
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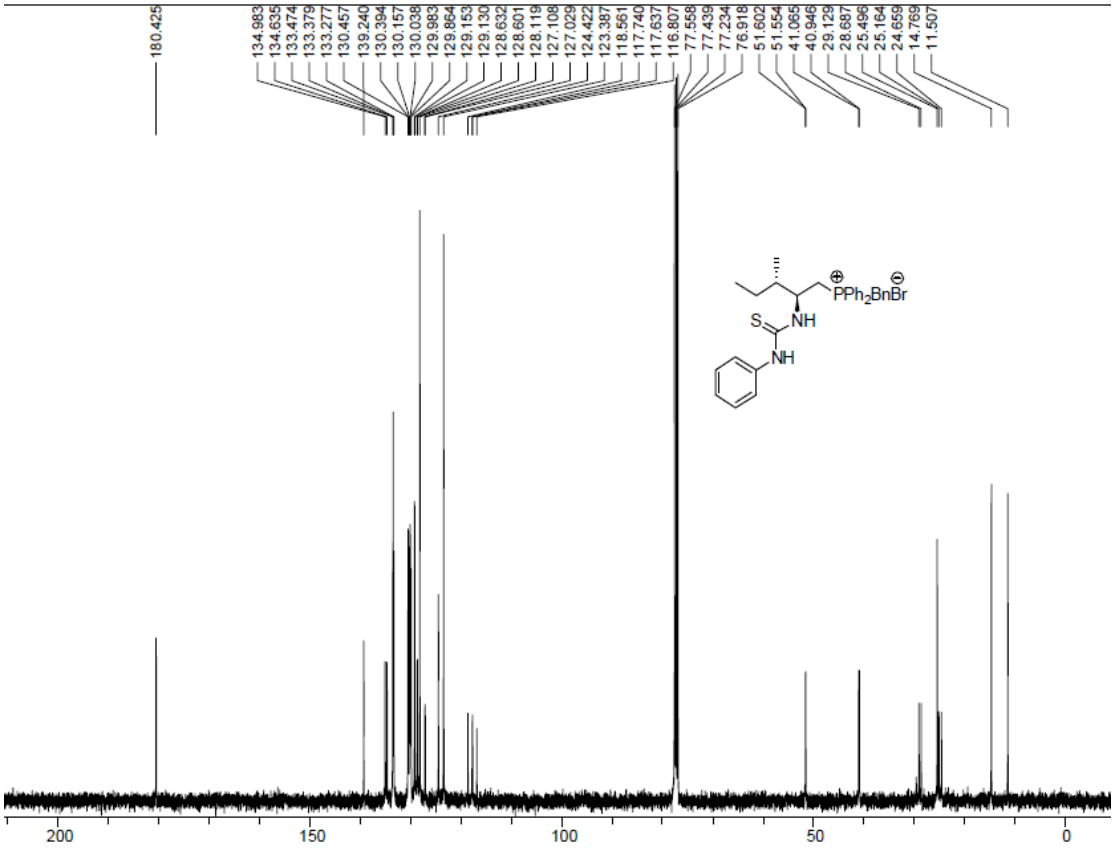
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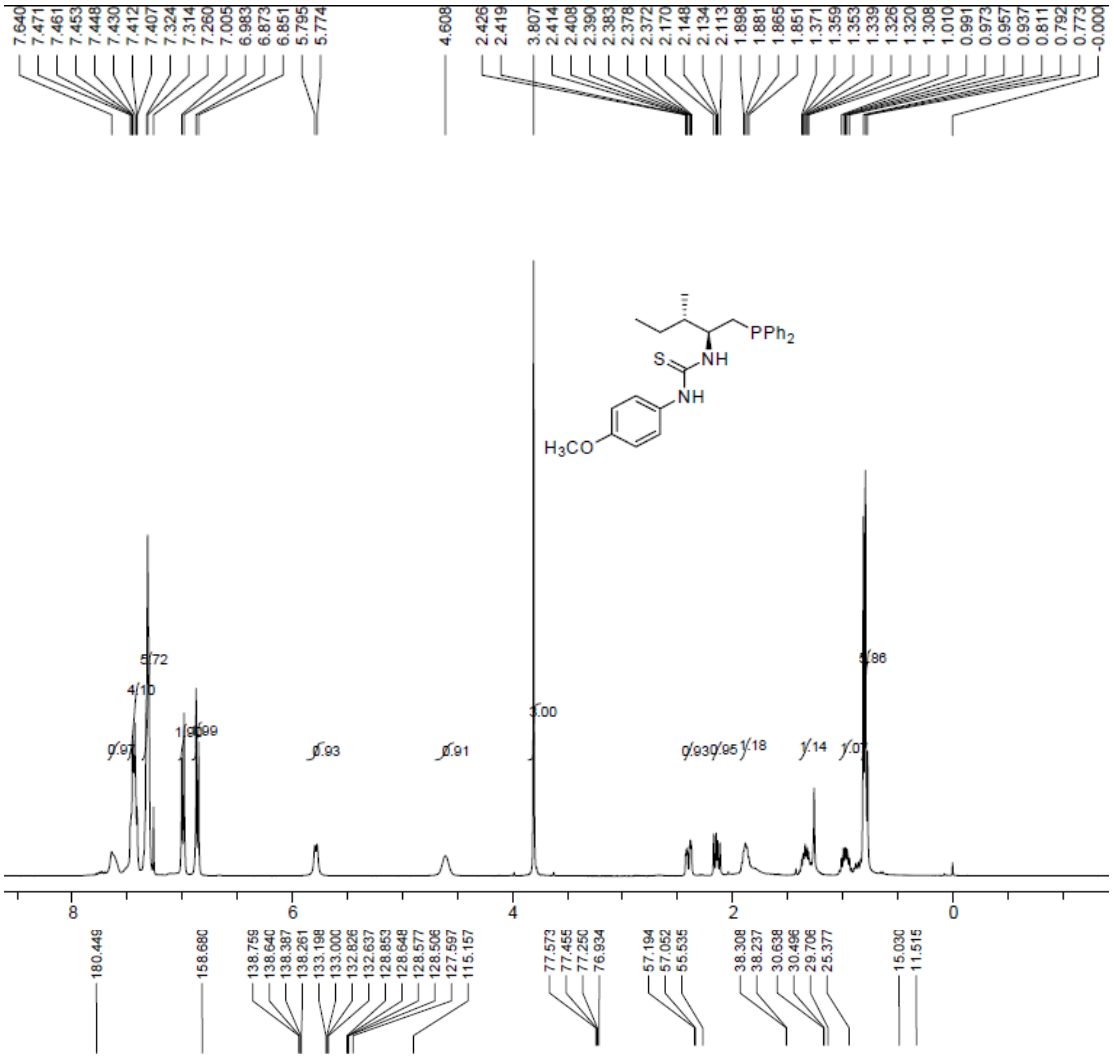
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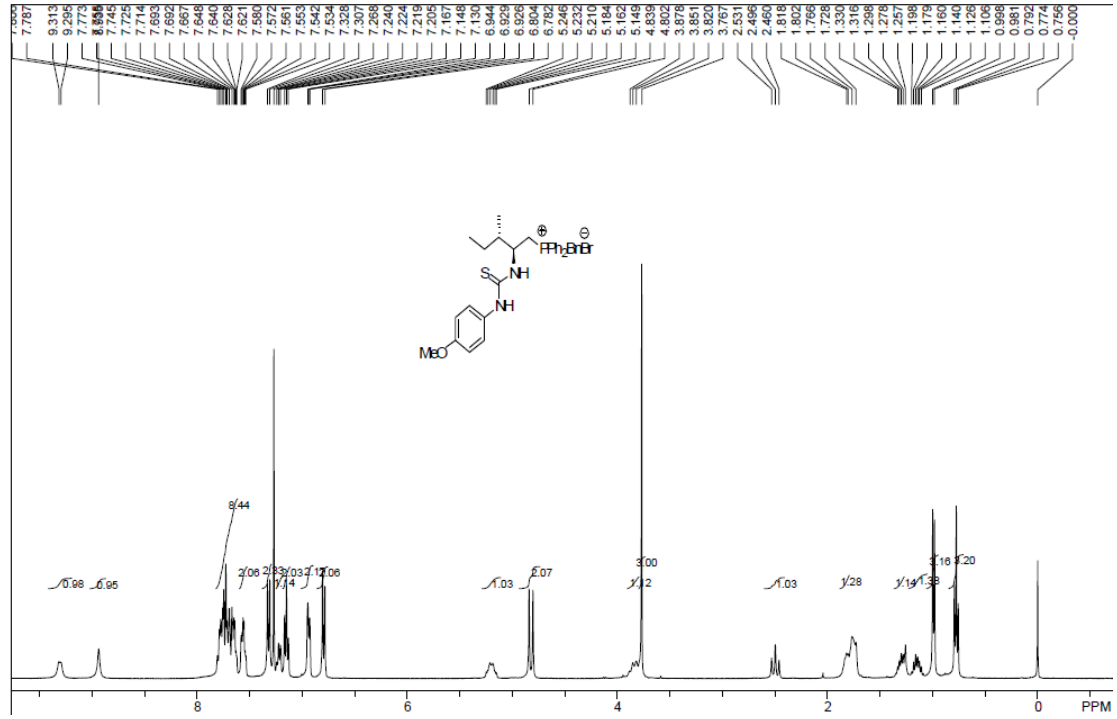
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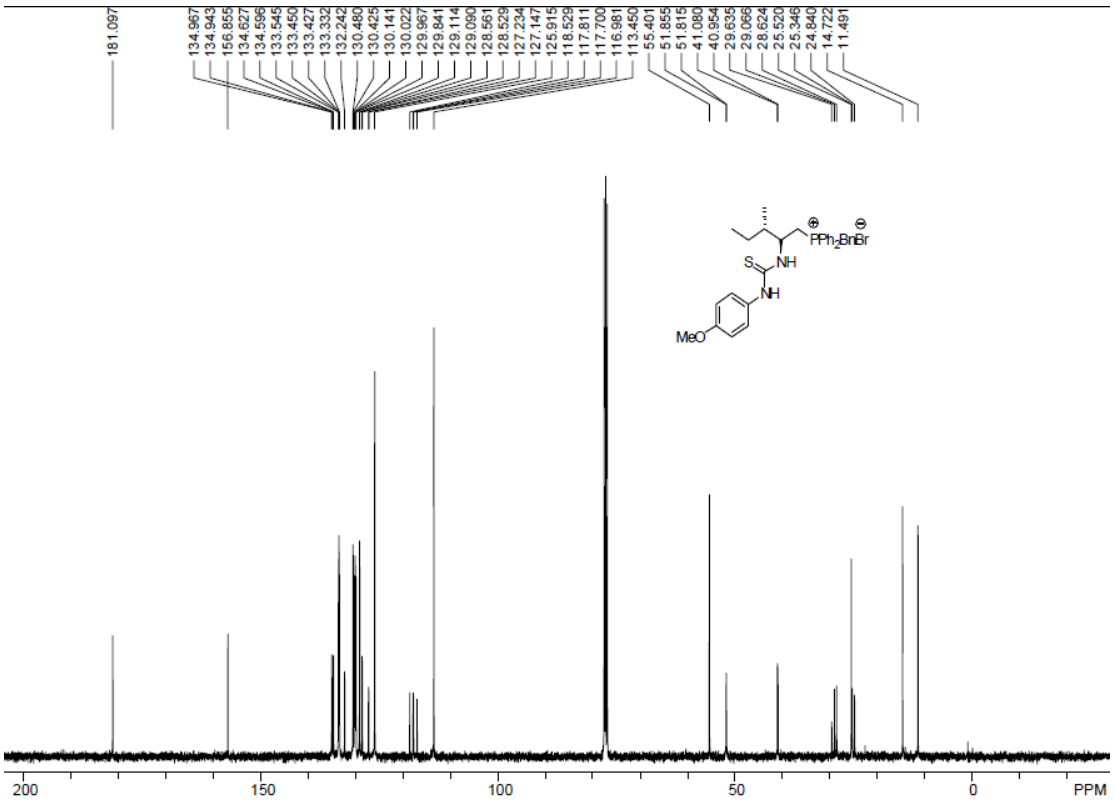
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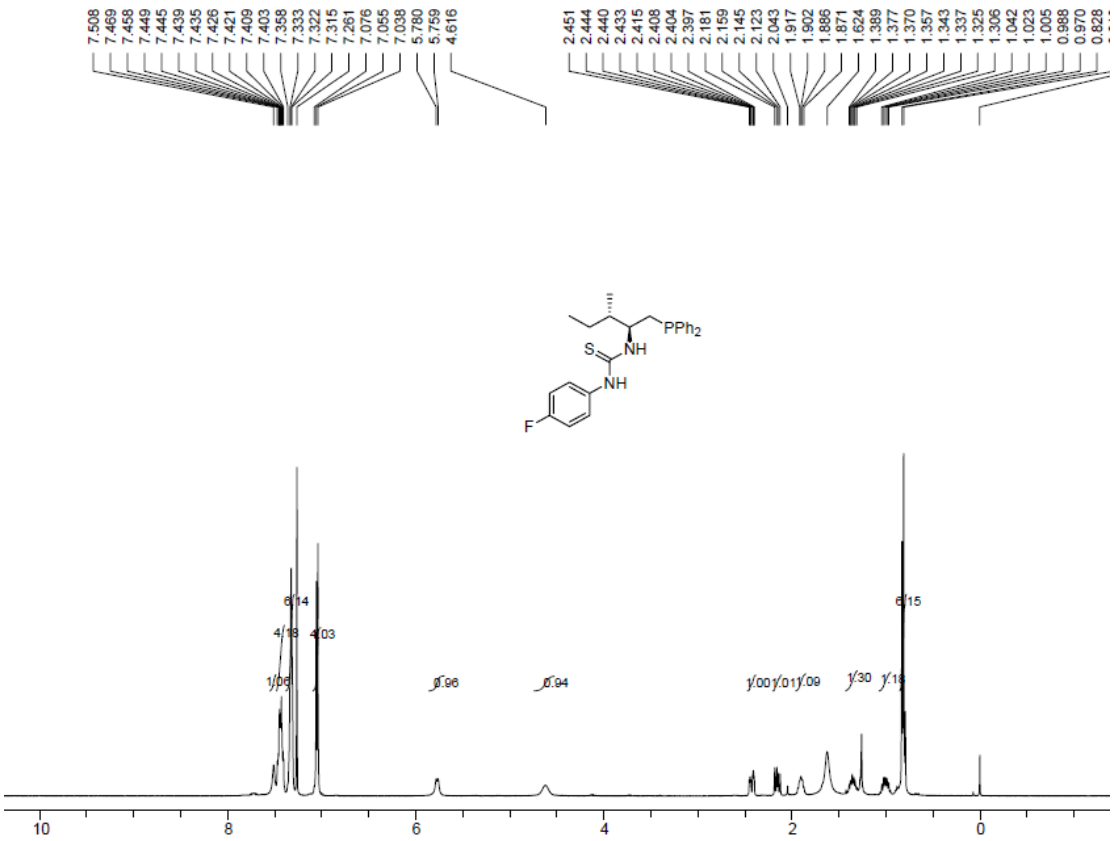
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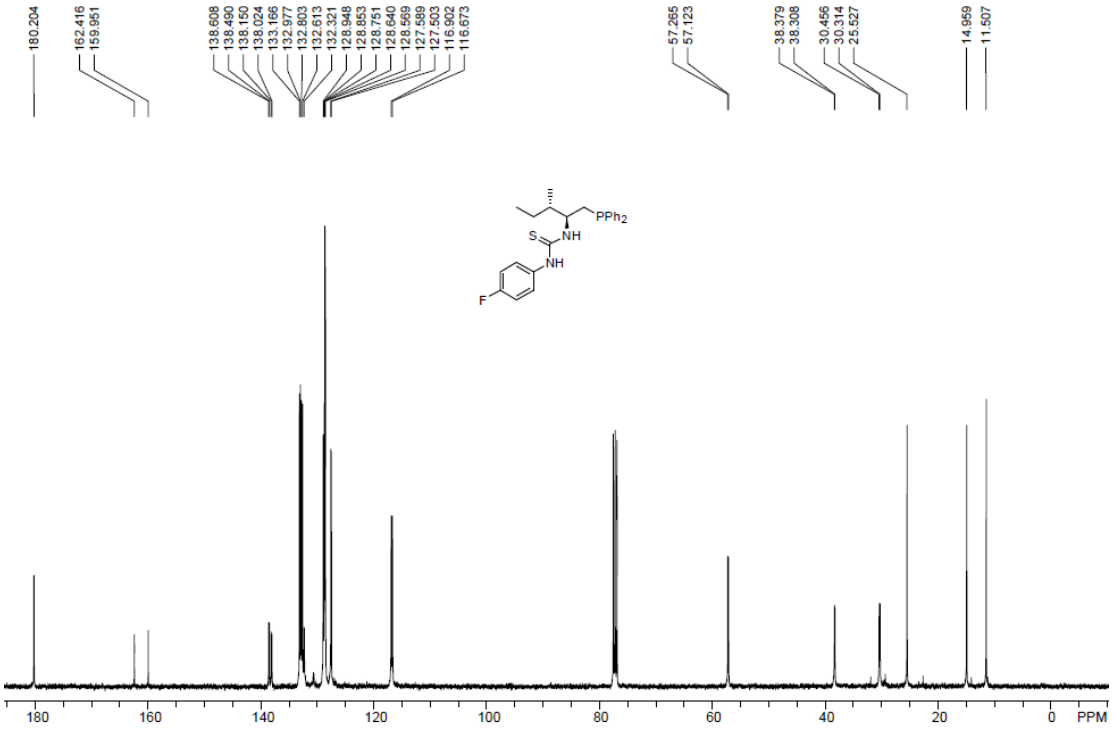
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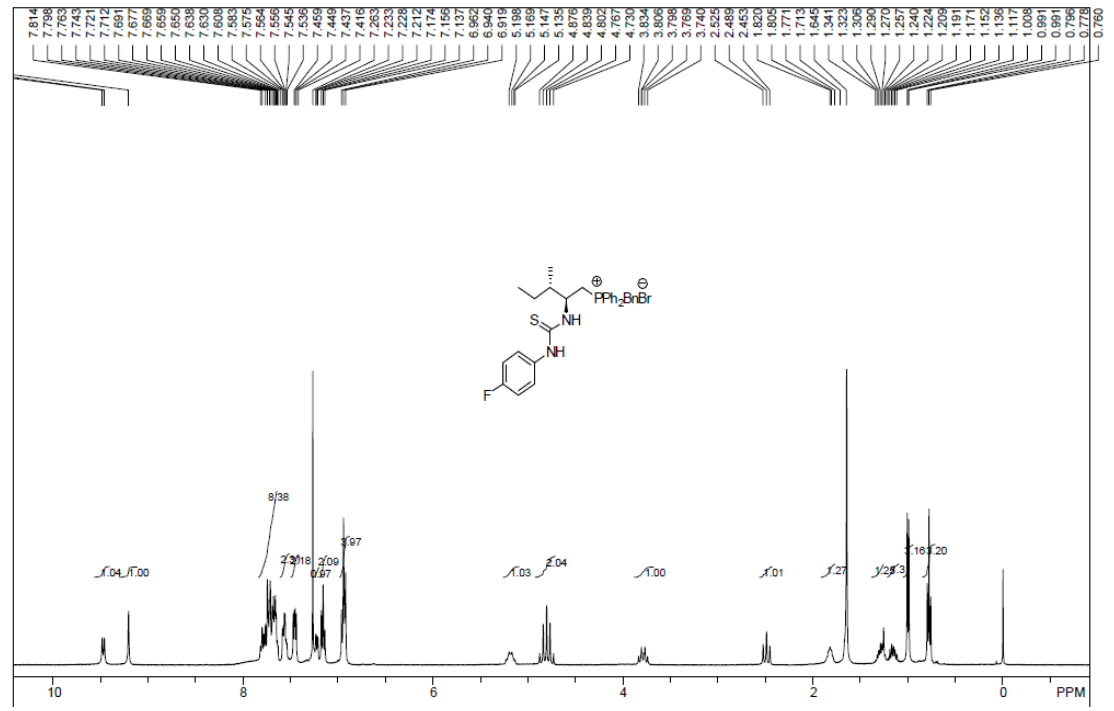
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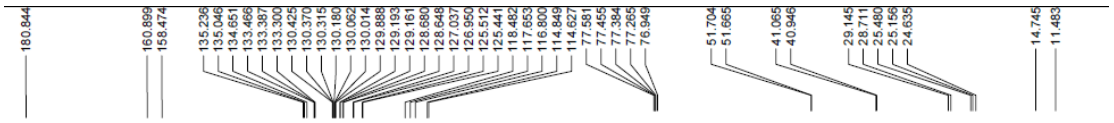

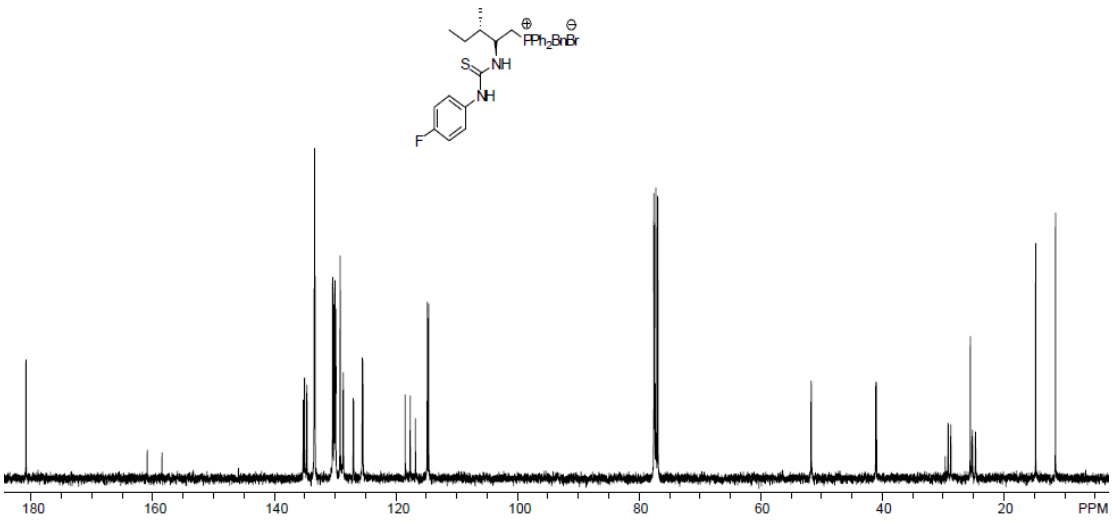
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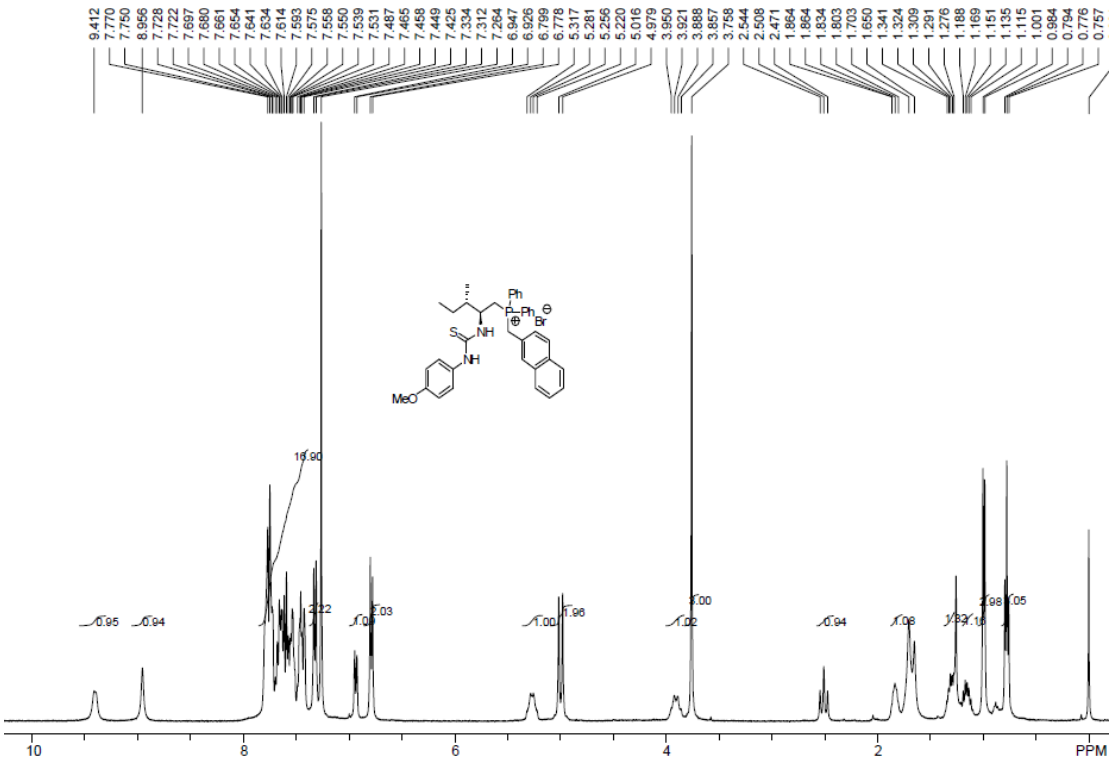
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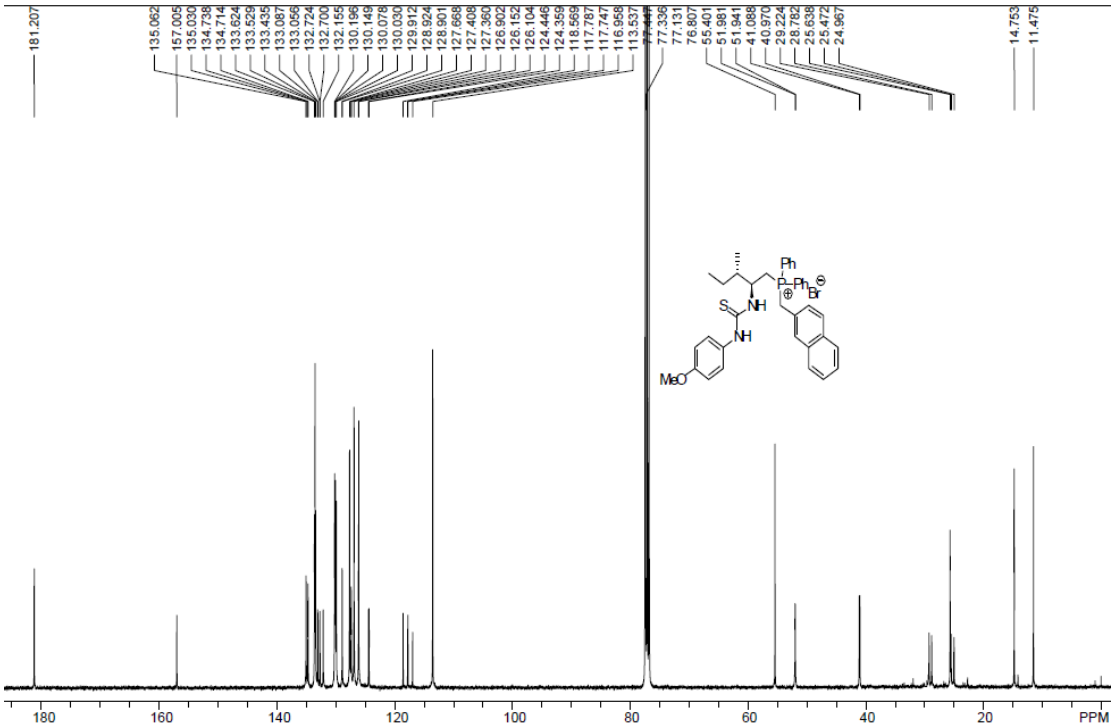
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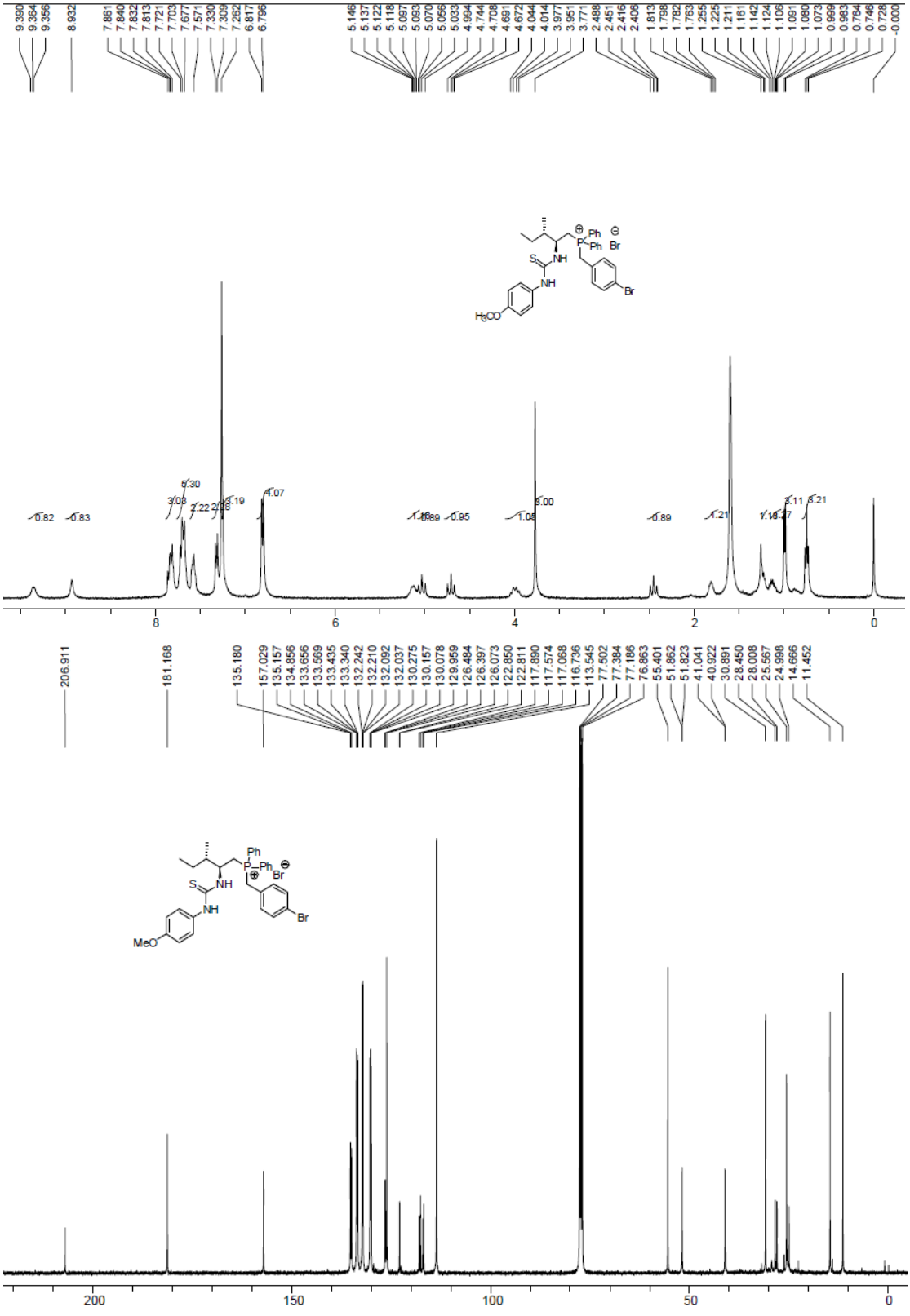
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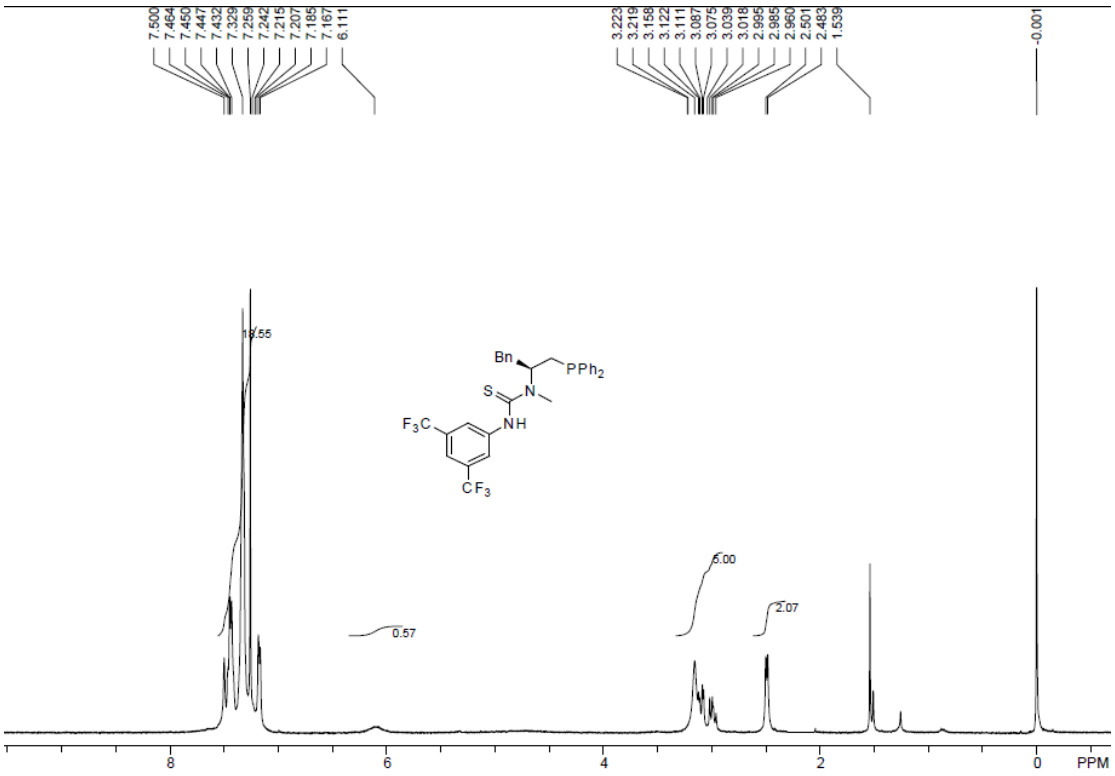
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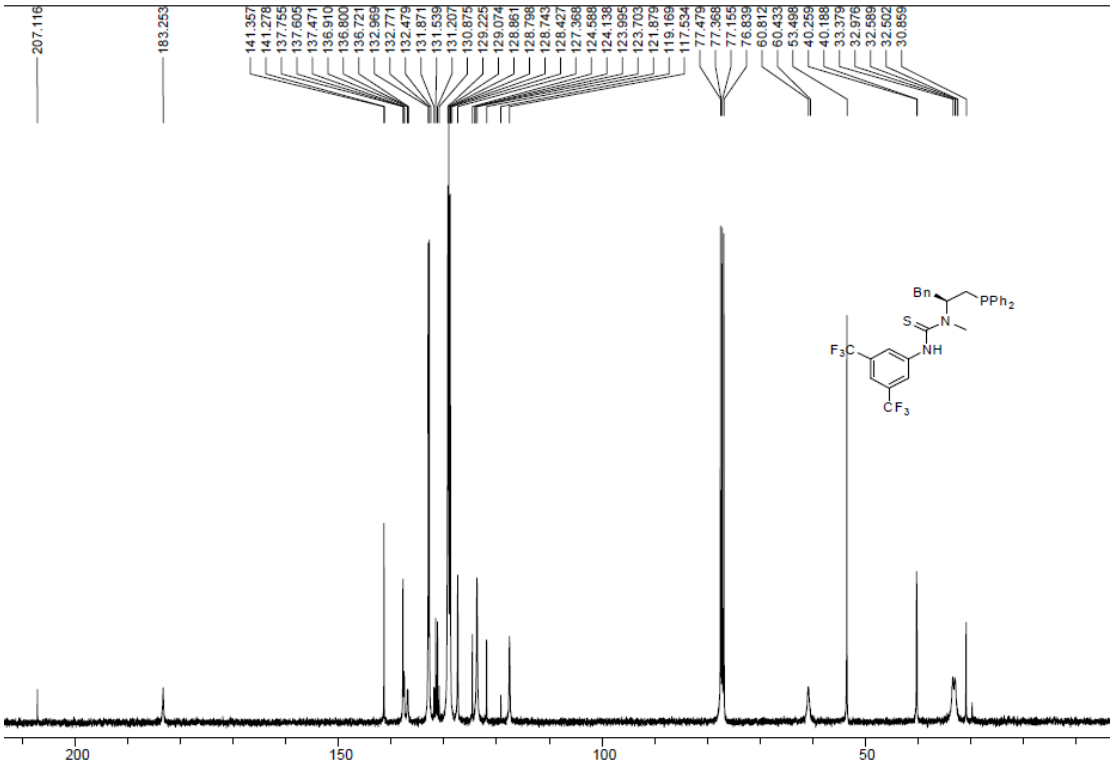
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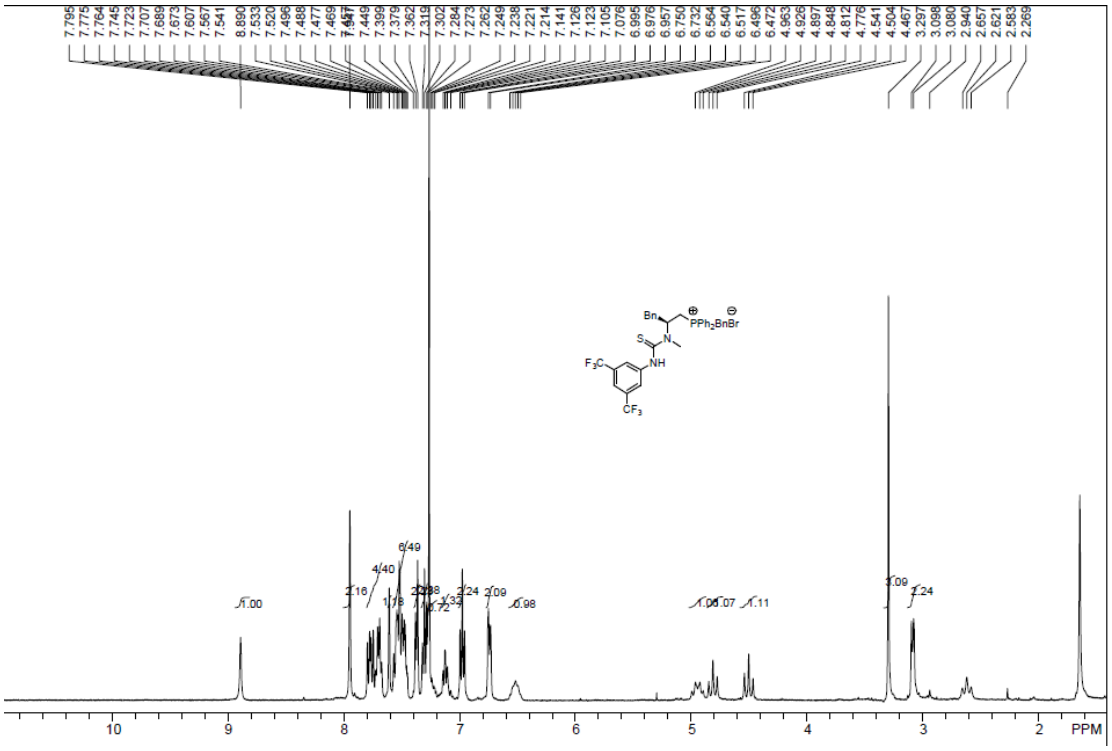
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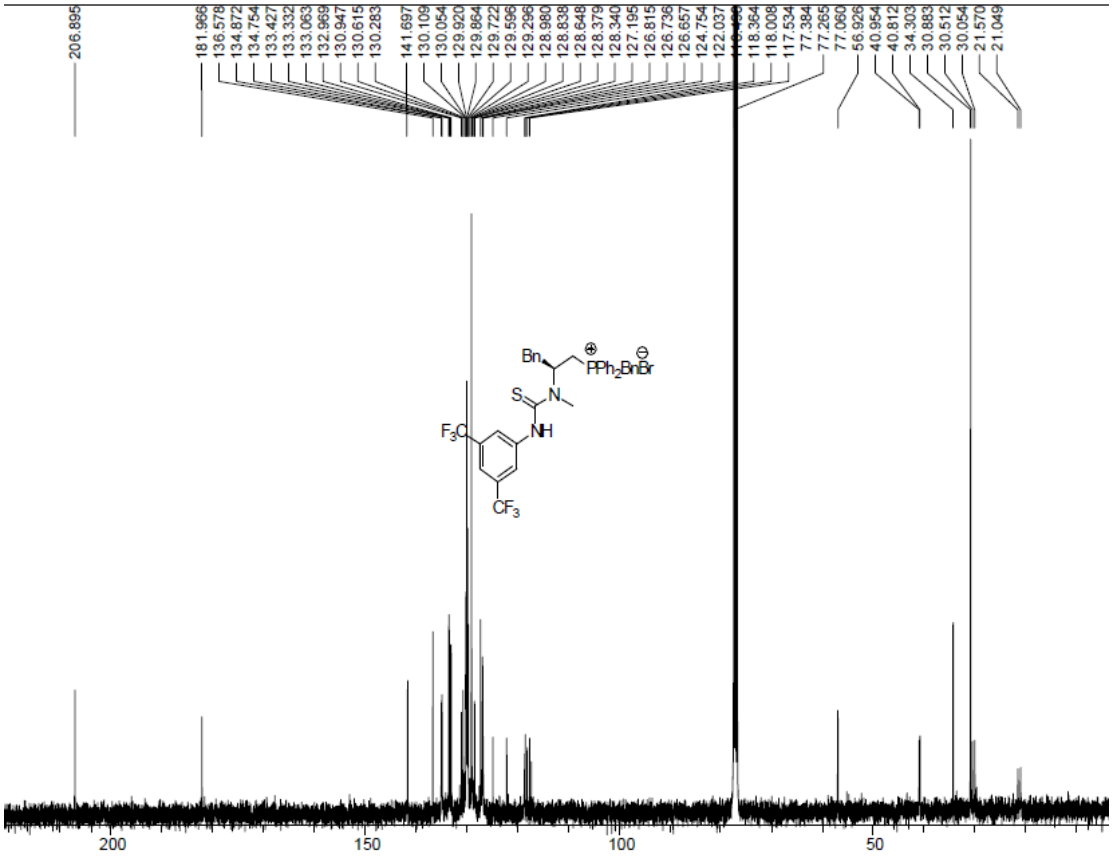
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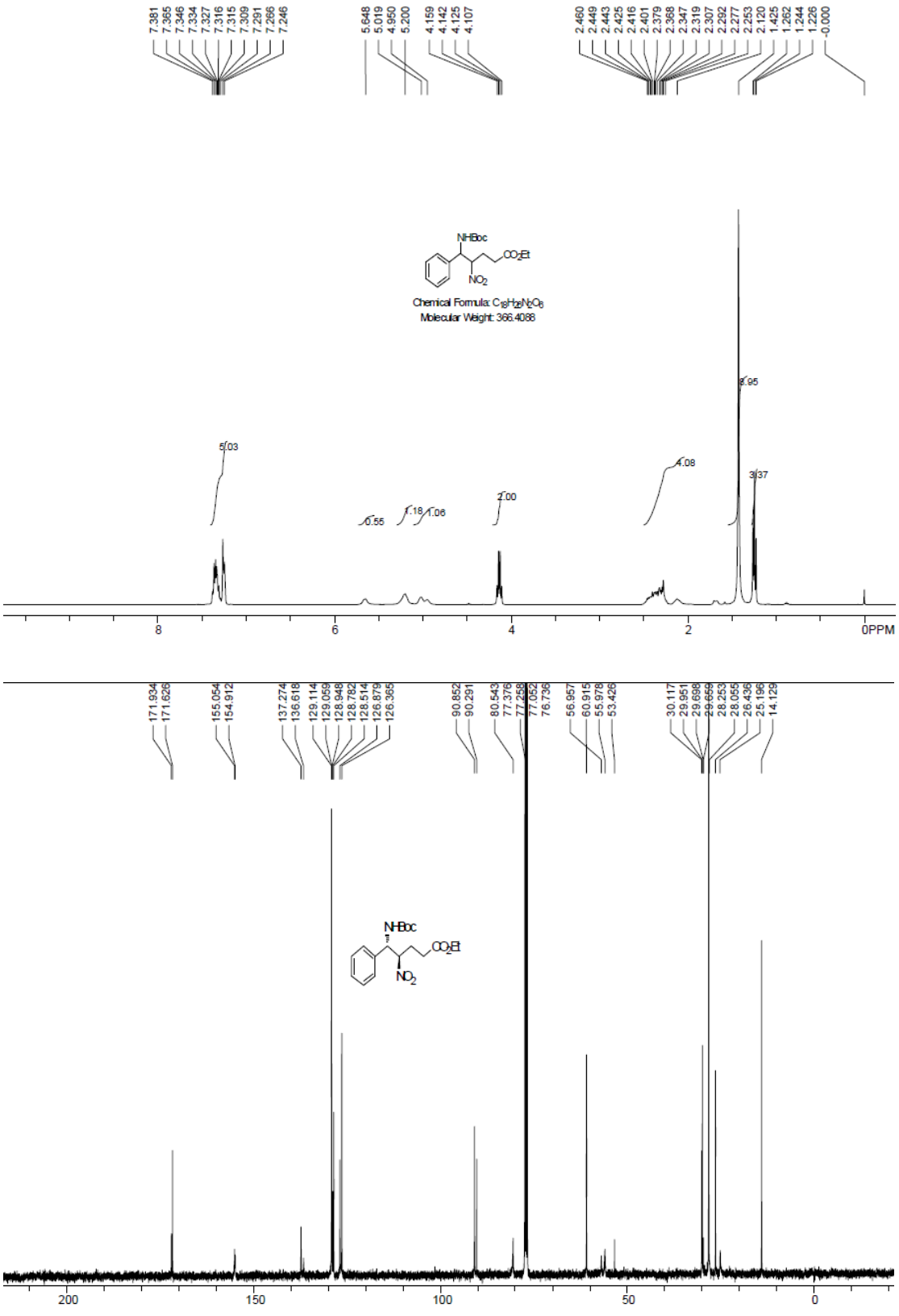
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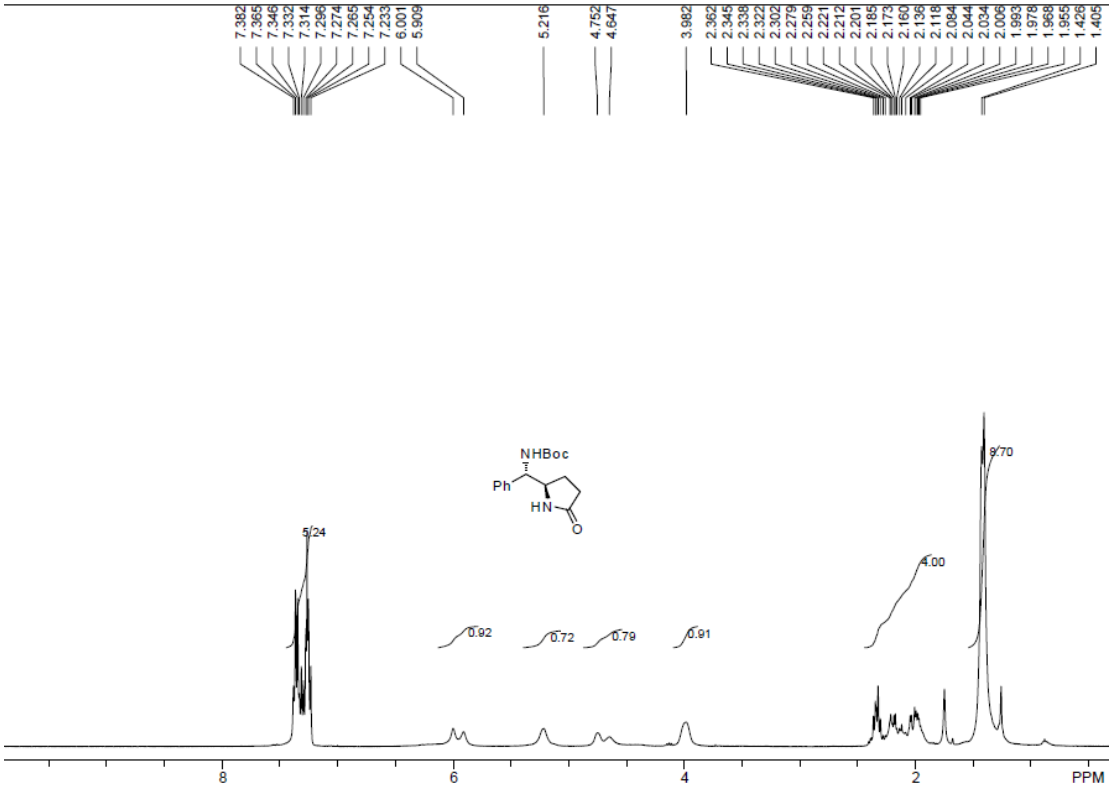
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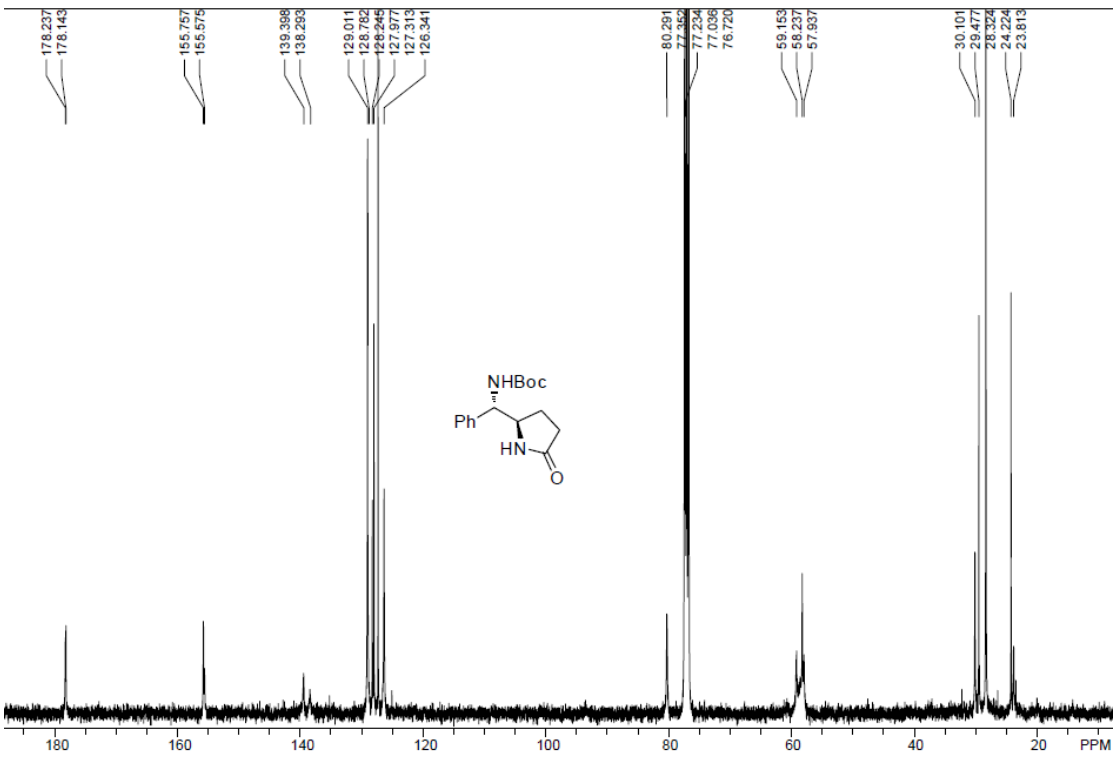
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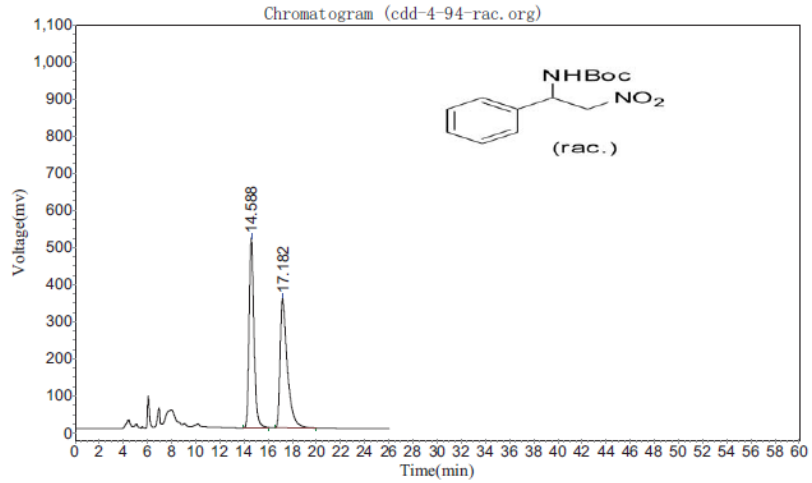
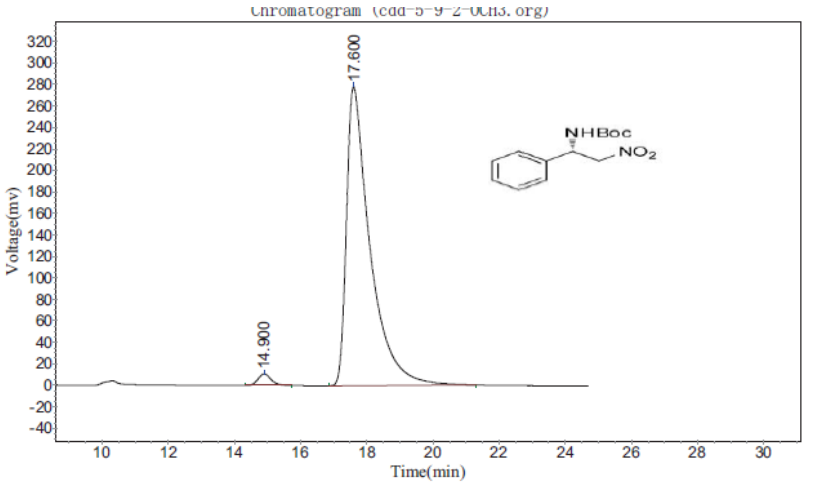


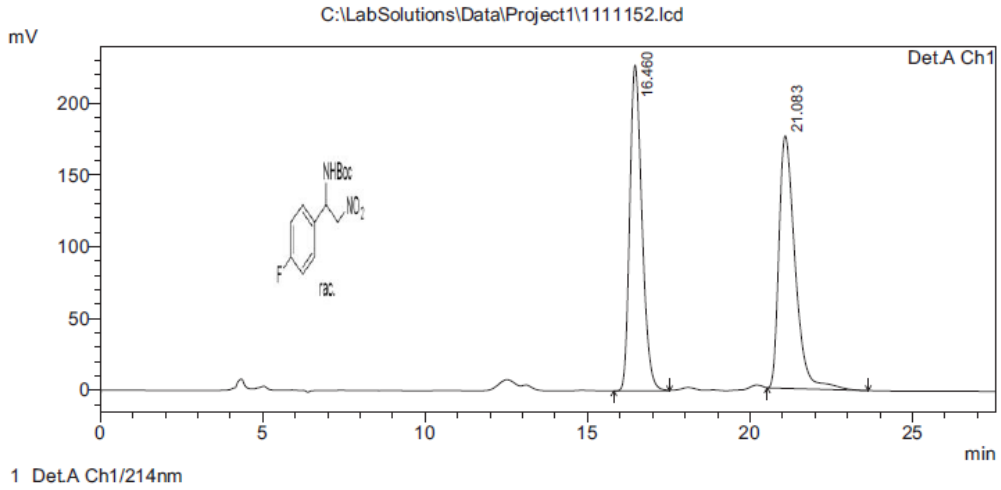
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.588	510756.781	14274351.000	49.6990
2		17.182	348375.969	14447282.000	50.3010
Total			859132.750	28721633.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.900	10821.501	297482.500	2.1236
2		17.600	278075.656	13711201.000	97.8764
Total			288897.157	14008683.500	100.0000

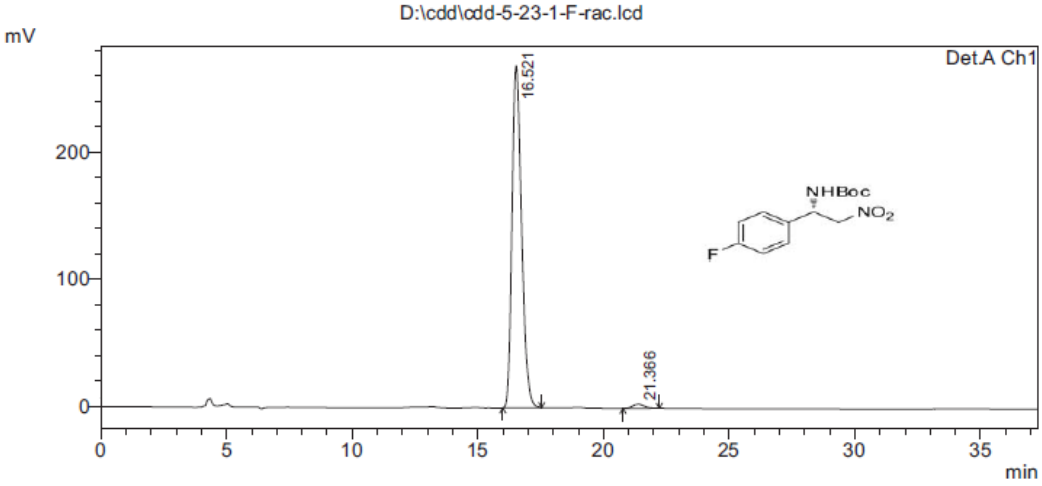


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.460	5932834	227037	49.362	56.326
2	21.083	6086109	176042	50.638	43.674
Total		12018943	403080	100.000	100.000

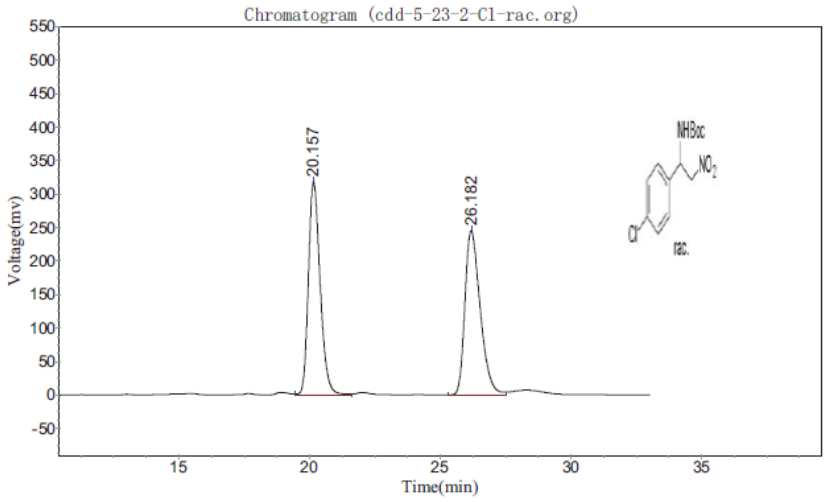


1 Det.A Ch1/214nm

PeakTable

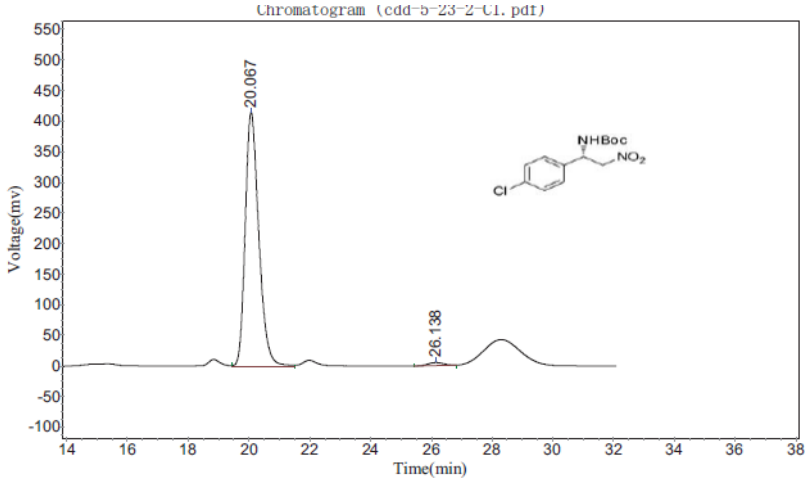
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.521	7104898	268615	98.549	98.783
2	21.366	104580	3308	1.451	1.217
Total		7209478	271923	100.000	100.000



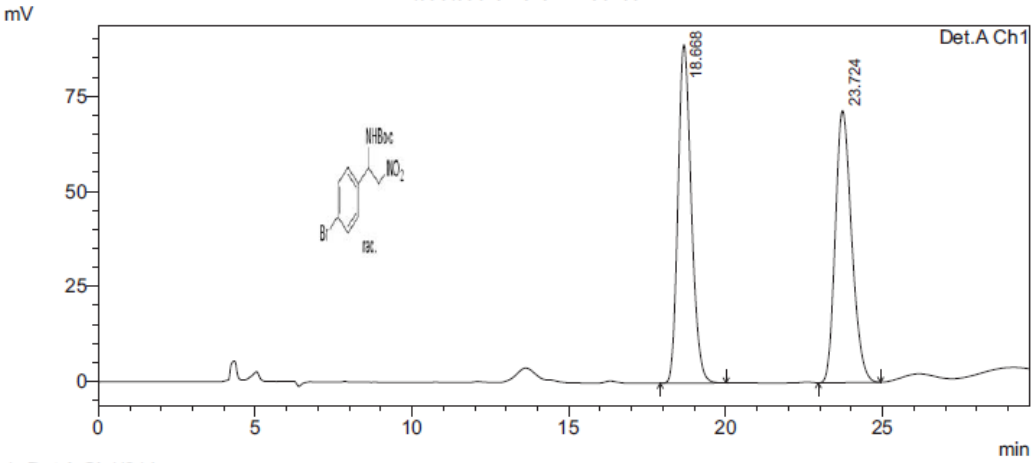
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.157	318868.438	9889219.000	49.9164
2		26.182	245161.094	9922356.000	50.0836
Total			564029.531	19811575.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.067	414771.031	12814074.000	98.6748
2		26.138	5128.383	172087.406	1.3252
Total			419899.415	12986161.406	100.0000

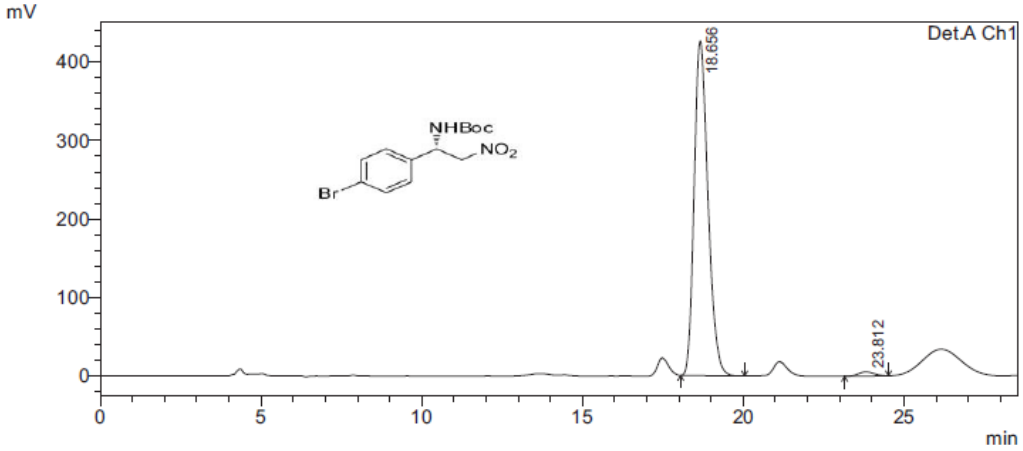


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.668	2632626	88953	50.321	55.439
2	23.724	2599041	71497	49.679	44.561
Total		5231668	160450	100.000	100.000

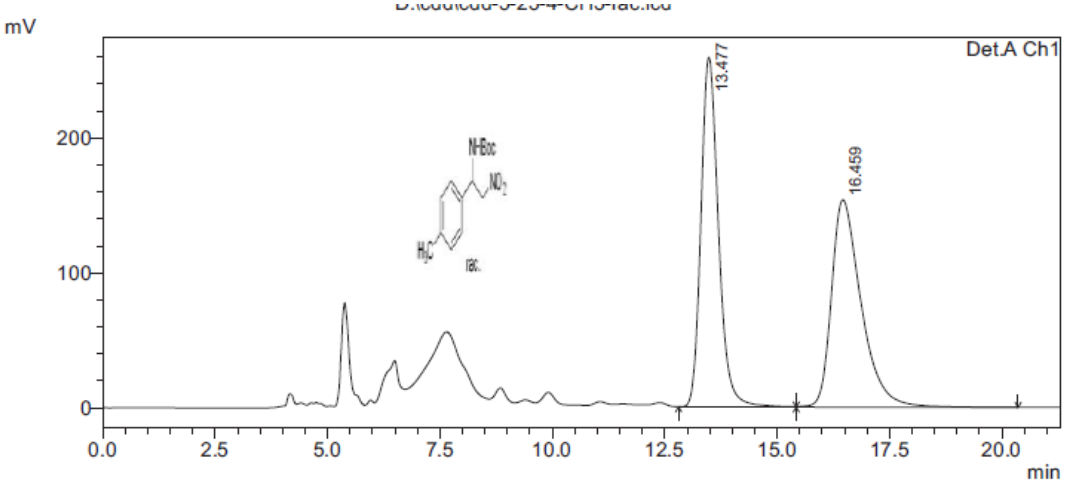


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.656	12767455	426534	98.622	98.770
2	23.812	178364	5311	1.378	1.230
Total		12945818	431845	100.000	100.000

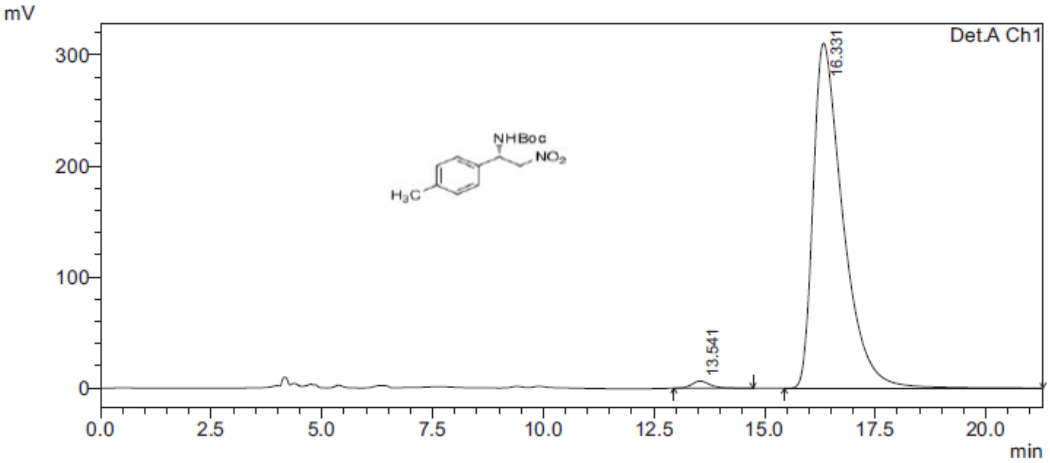


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.477	7023555	259343	49.865	62.771
2	16.459	7061570	153813	50.135	37.229
Total		14085125	413156	100.000	100.000

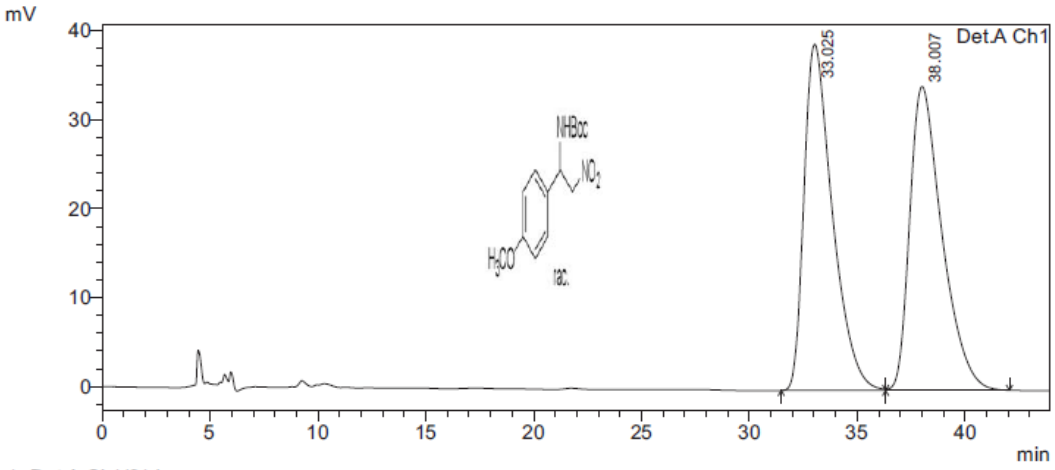


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.541	178671	6324	1.213	1.994
2	16.331	14550398	310855	98.787	98.006
Total		14729069	317179	100.000	100.000

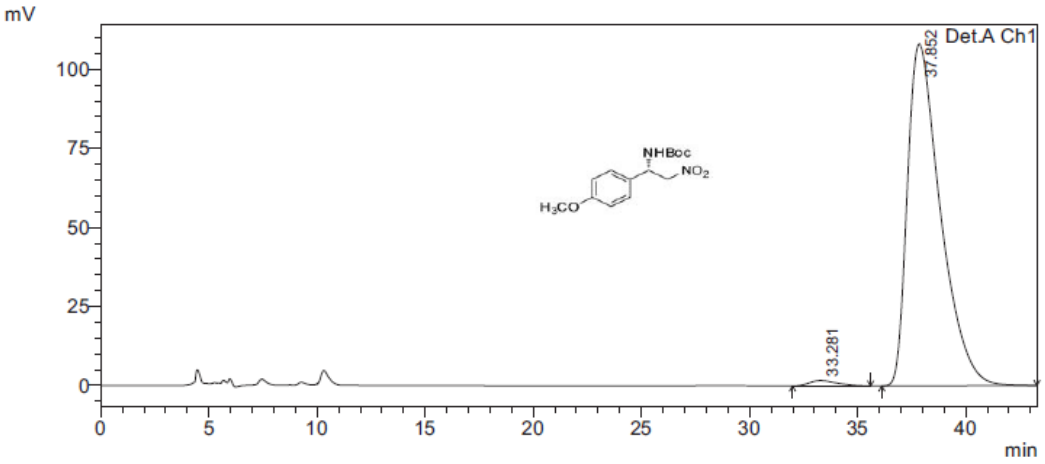


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.025	3569970	38945	50.074	53.261
2	38.007	3559399	34176	49.926	46.739
Total		7129369	73120	100.000	100.000

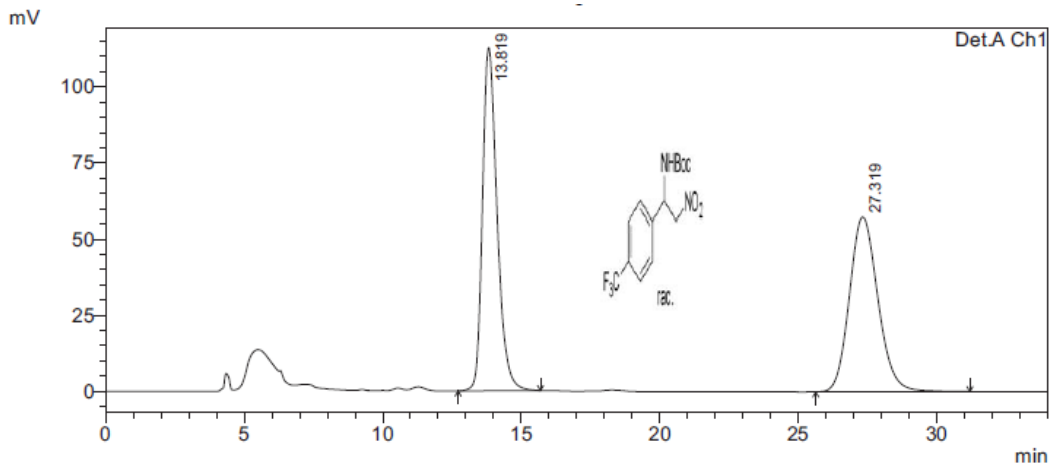


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.281	151370	1708	1.300	1.554
2	37.852	11495529	108196	98.700	98.446
Total		11646900	109904	100.000	100.000

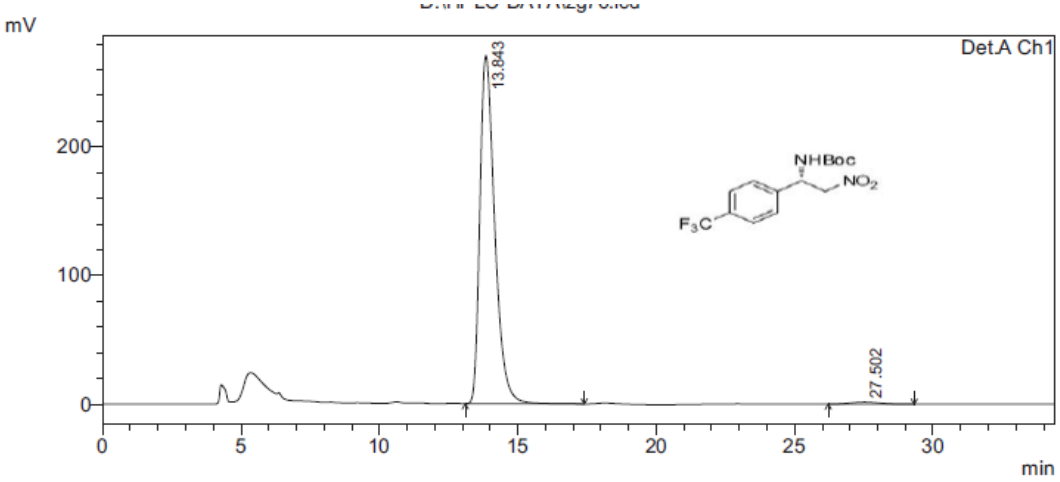


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.819	4136907	112834	50.127	66.238
2	27.319	4115965	57513	49.873	33.762
Total		8252872	170347	100.000	100.000

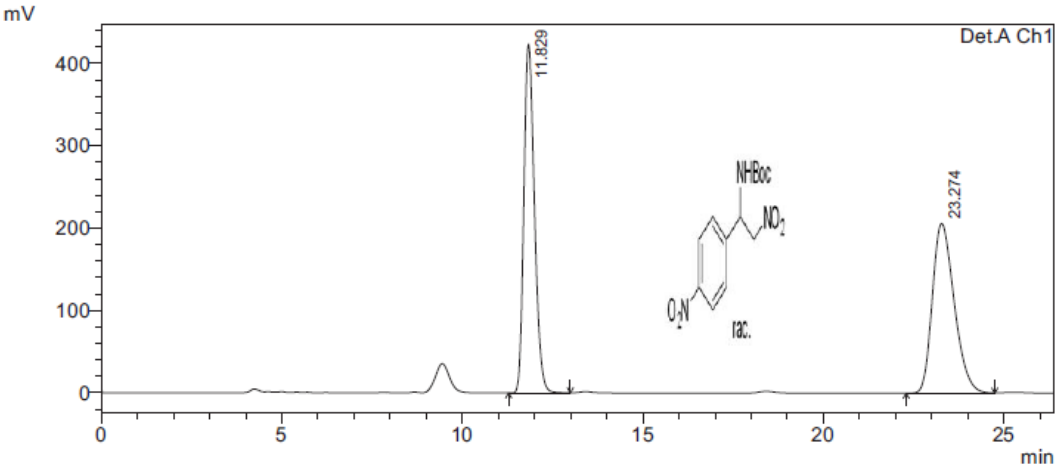


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.843	10092475	270870	98.913	99.422
2	27.502	110955	1575	1.087	0.578
Total		10203430	272445	100.000	100.000

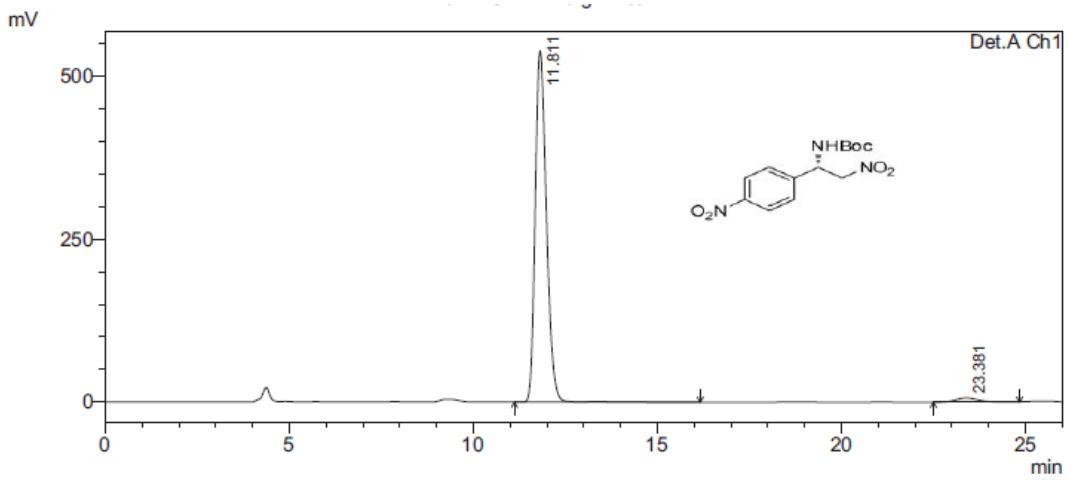


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.829	8652073	423876	49.891	67.278
2	23.274	8689928	206164	50.109	32.722
Total		17342001	630040	100.000	100.000

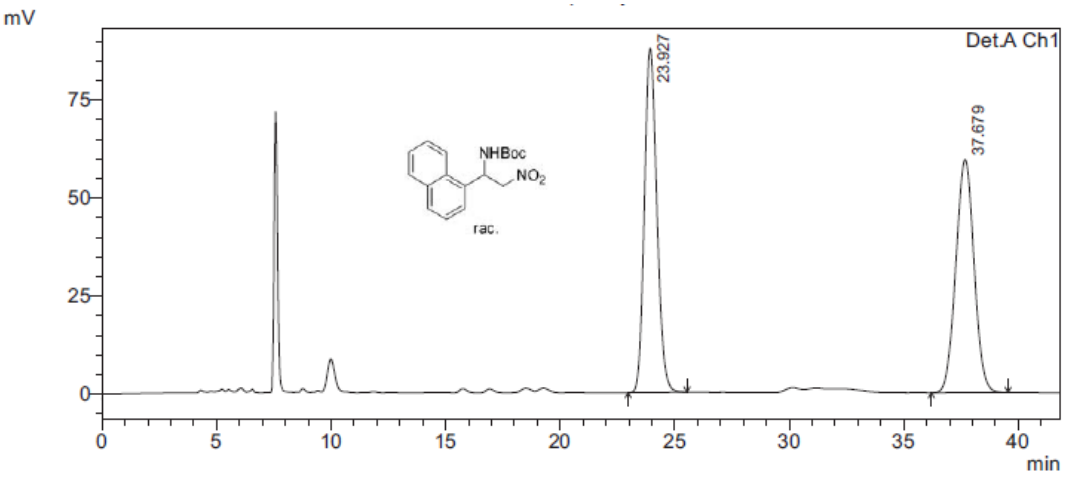


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.811	11402478	539389	97.576	98.778
2	23.381	283263	6674	2.424	1.222
Total		11685741	546063	100.000	100.000

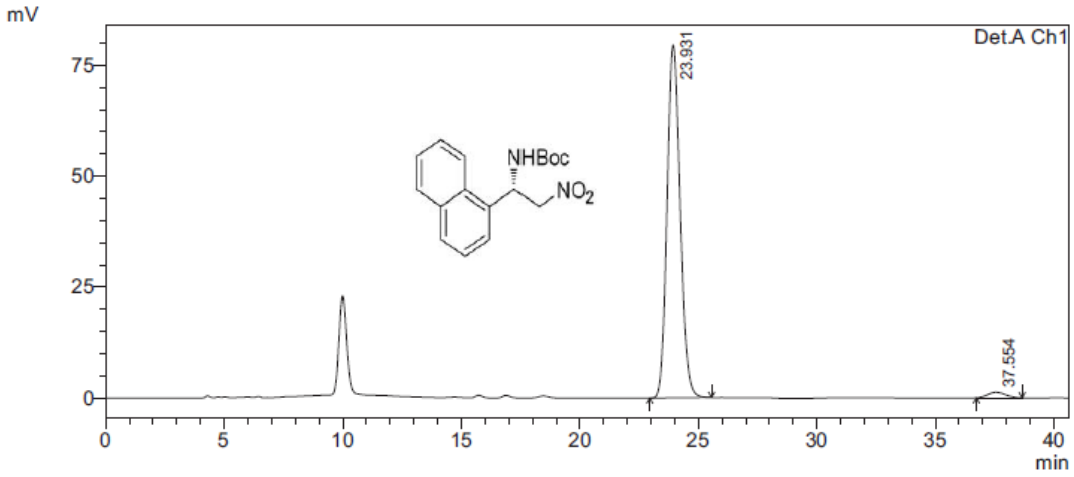


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.927	3324063	87829	50.218	59.619
2	37.679	3295145	59488	49.782	40.381
Total		6619207	147317	100.000	100.000

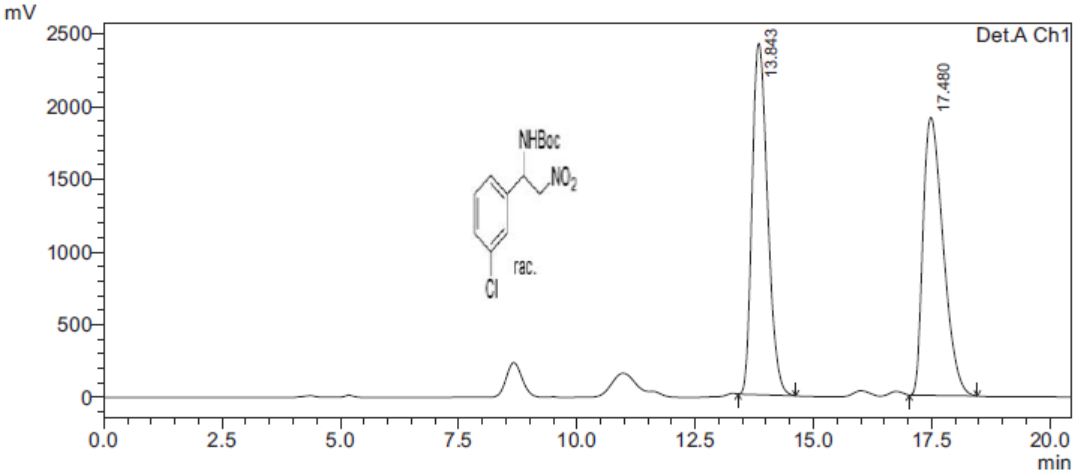


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.931	3042753	79553	97.914	98.445
2	37.554	64810	1257	2.086	1.555
Total		3107563	80810	100.000	100.000

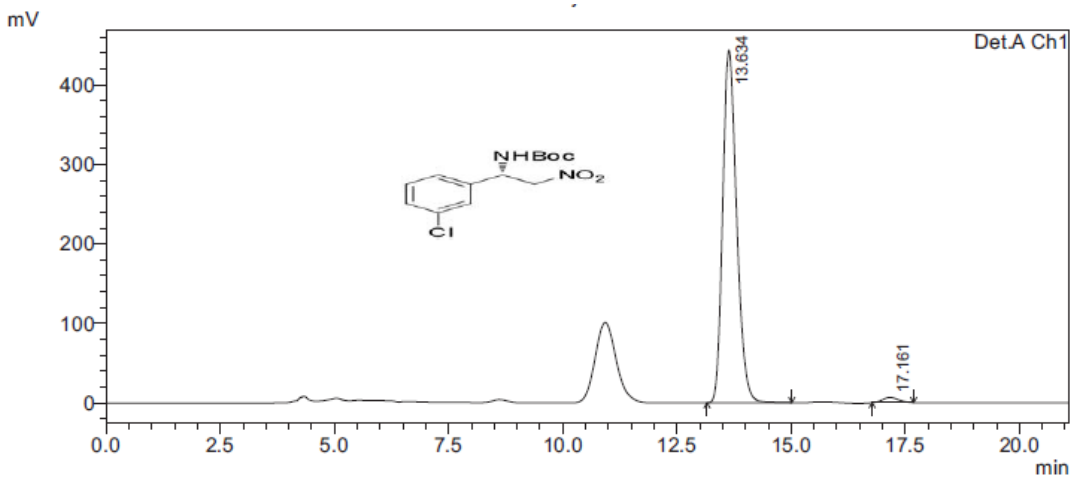


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.843	55156595	2417066	49.296	55.828
2	17.480	56730977	1912410	50.704	44.172
Total		111887572	4329476	100.000	100.000

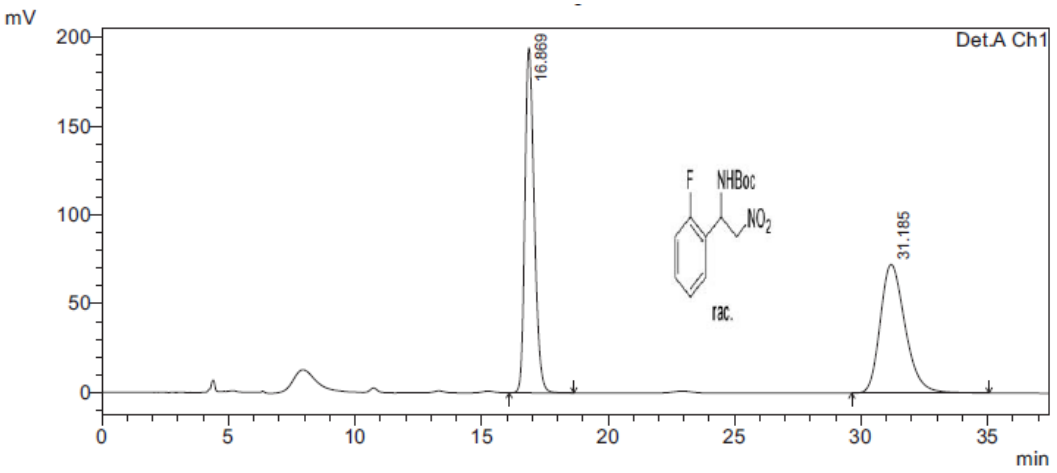


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.634	9428218	443446	98.376	98.554
2	17.161	155596	6508	1.624	1.446
Total		9583814	449954	100.000	100.000

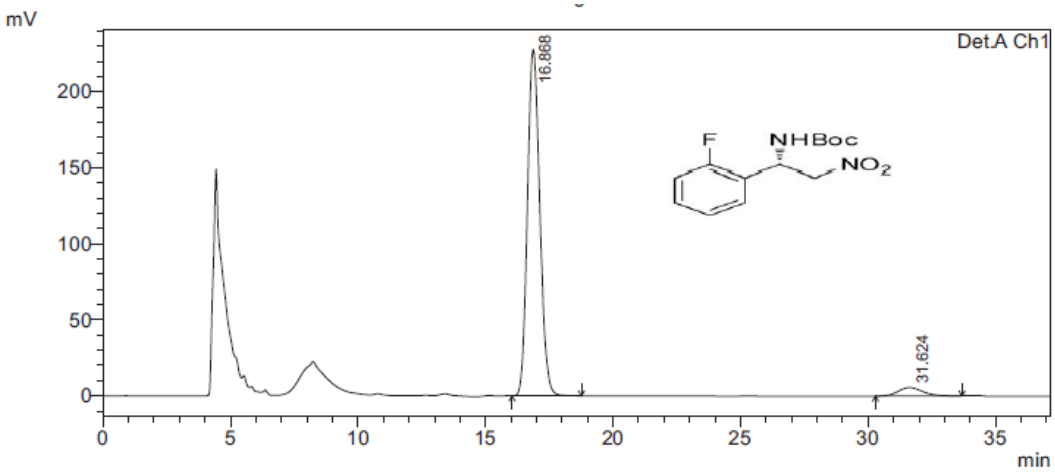


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.869	4998349	194354	50.136	72.832
2	31.185	4971165	72498	49.864	27.168
Total		9969514	266852	100.000	100.000

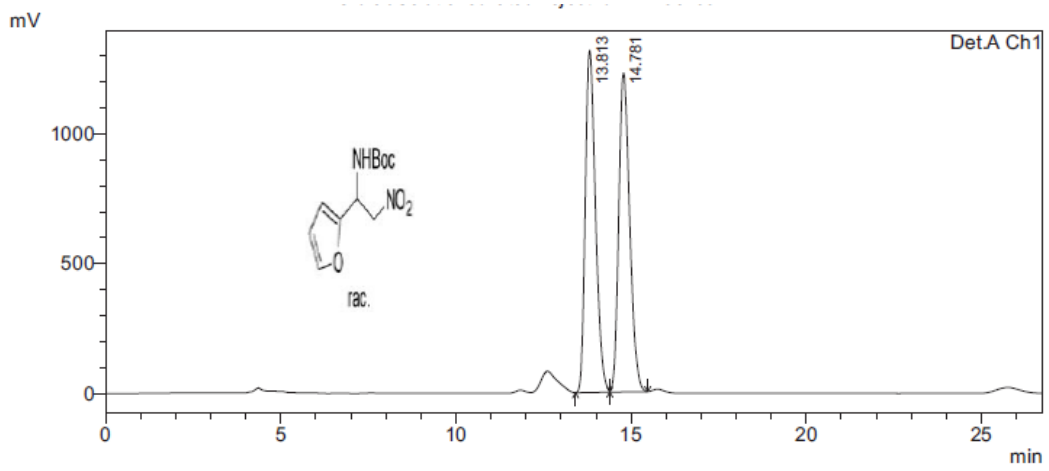


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.868	7668246	228097	95.305	97.613
2	31.624	377783	5579	4.695	2.387
Total		8046029	233676	100.000	100.000

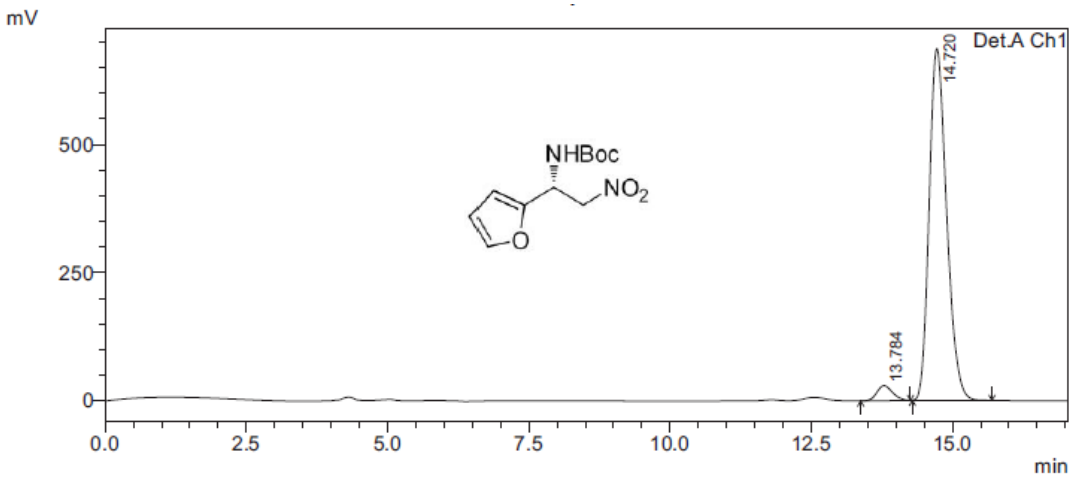


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.813	26722293	1318619	50.068	51.754
2	14.781	26649541	1229233	49.932	48.246
Total		53371834	2547851	100.000	100.000

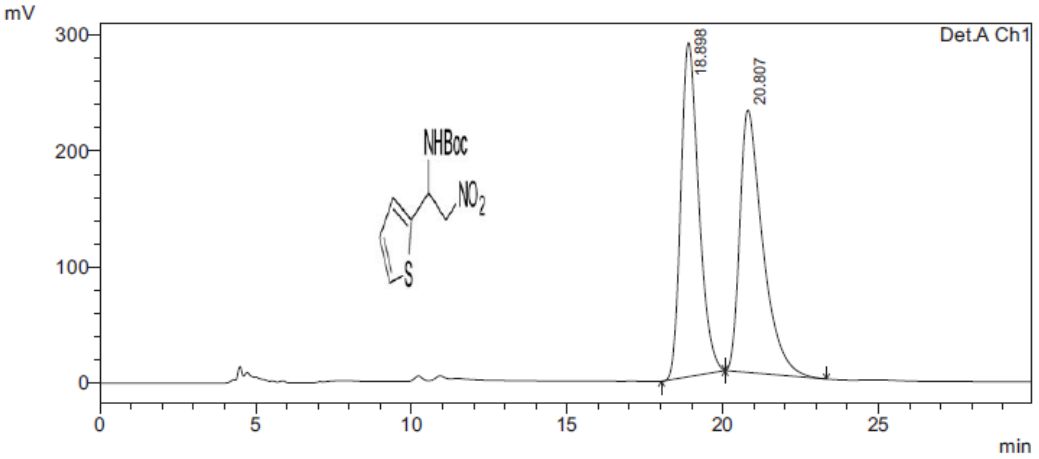


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.784	565415	29280	3.690	4.093
2	14.720	14756476	686151	96.310	95.907
Total		15321891	715431	100.000	100.000

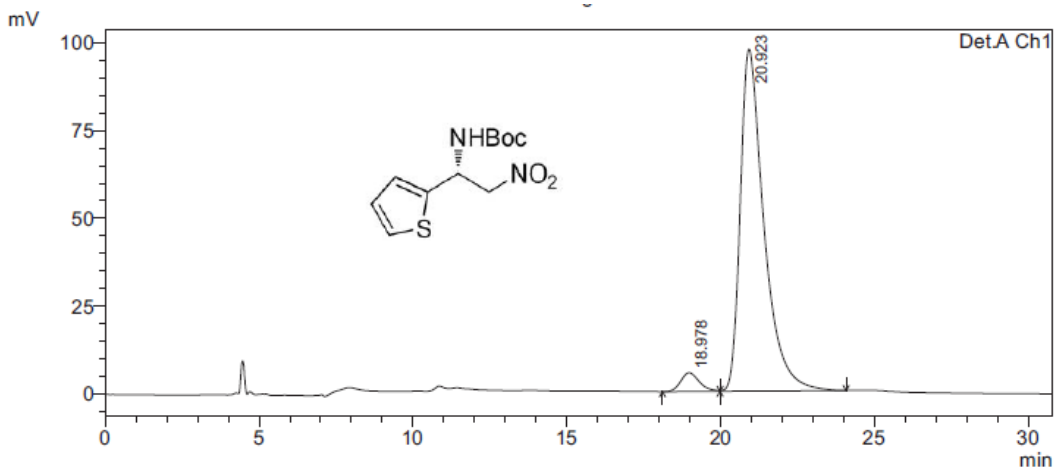


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.898	11523005	288132	49.892	56.010
2	20.807	11573064	226299	50.108	43.990
Total		23096069	514432	100.000	100.000

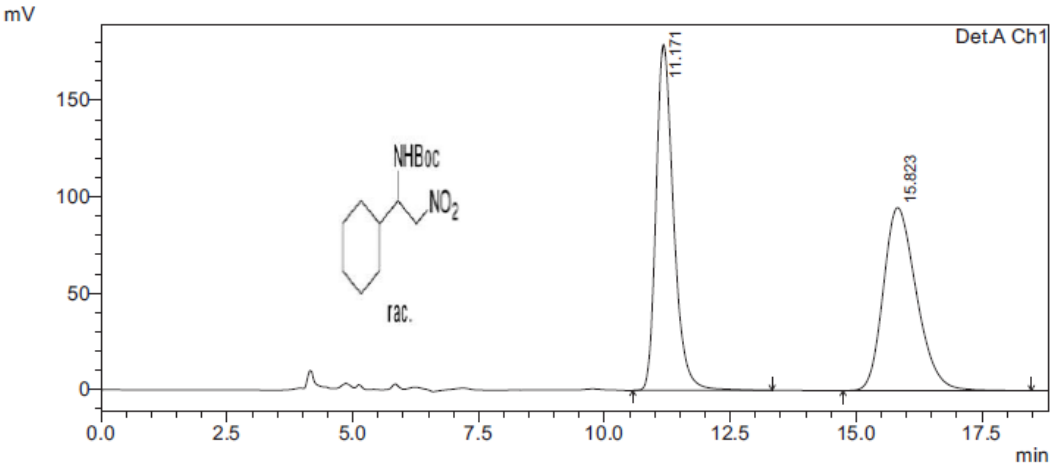


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.978	223604	5326	4.126	5.202
2	20.923	5195204	97059	95.874	94.798
Total		5418807	102385	100.000	100.000

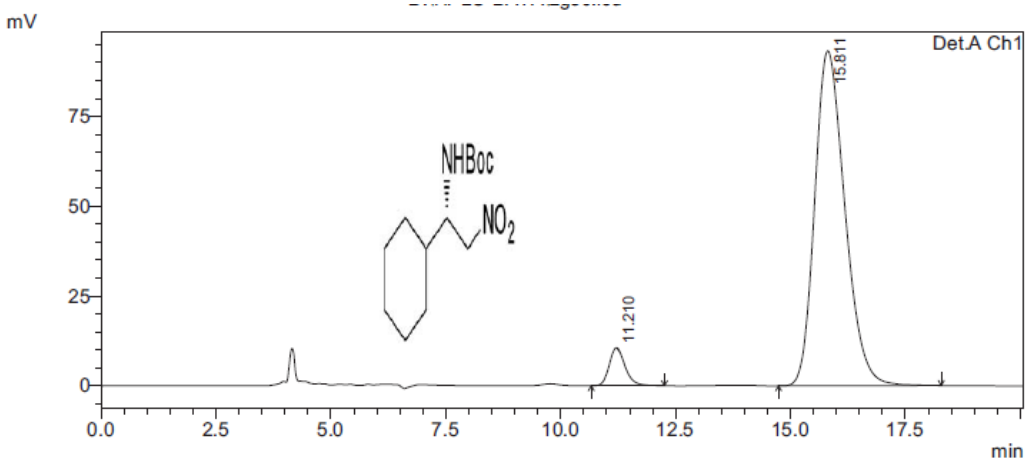


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.171	4348256	179366	49.993	65.413
2	15.823	4349505	94841	50.007	34.587
Total		8697761	274208	100.000	100.000

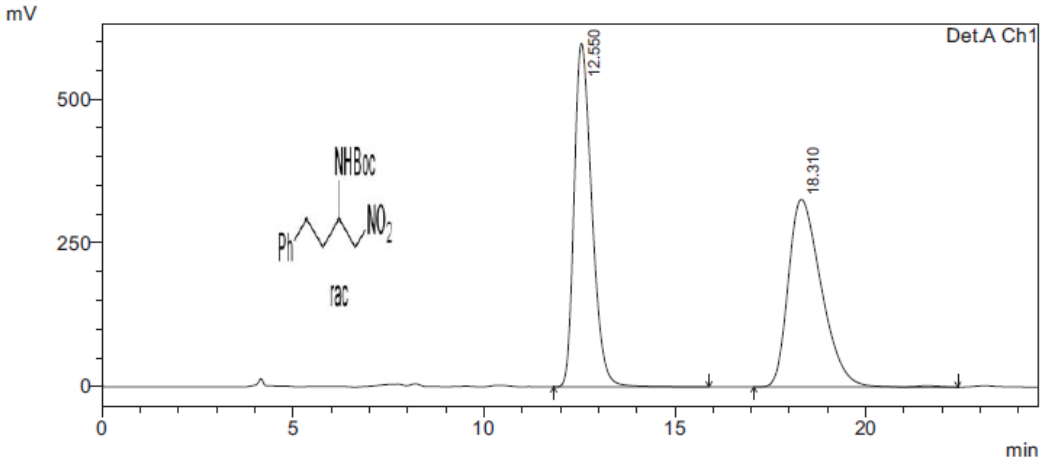


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.210	252942	10587	5.605	10.195
2	15.811	4259770	93259	94.395	89.805
Total		4512712	103846	100.000	100.000

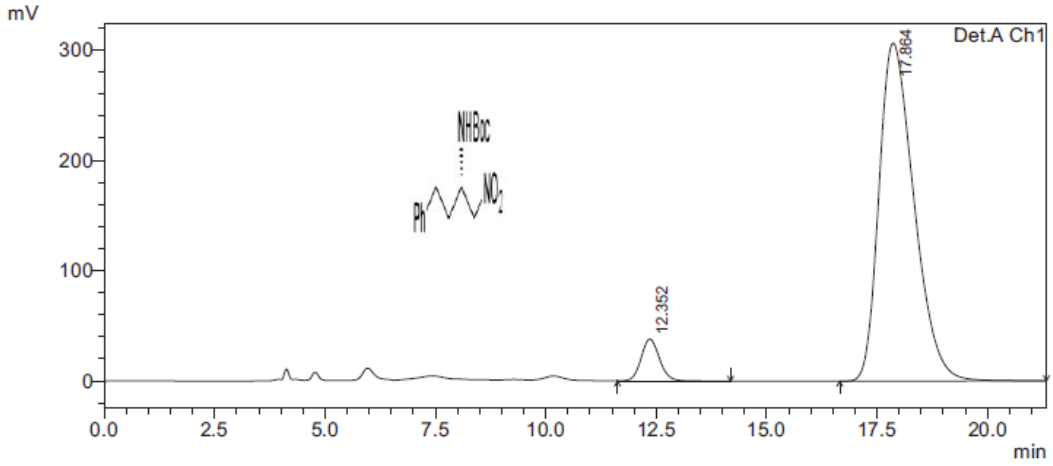


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.550	19305903	597377	49.635	64.666
2	18.310	19590121	326408	50.365	35.334
Total		38896024	923785	100.000	100.000

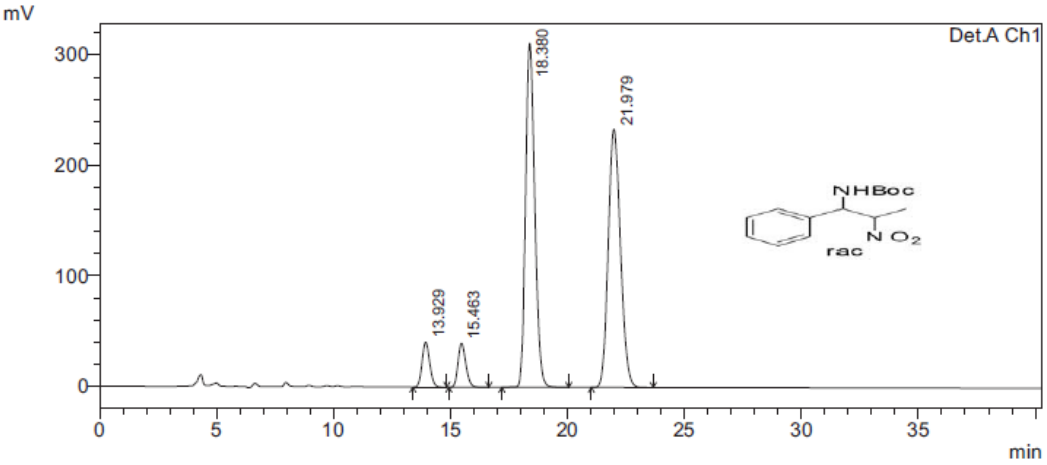


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.352	1111882	38030	6.174	11.037
2	17.864	16898621	306538	93.826	88.963
Total		18010503	344568	100.000	100.000

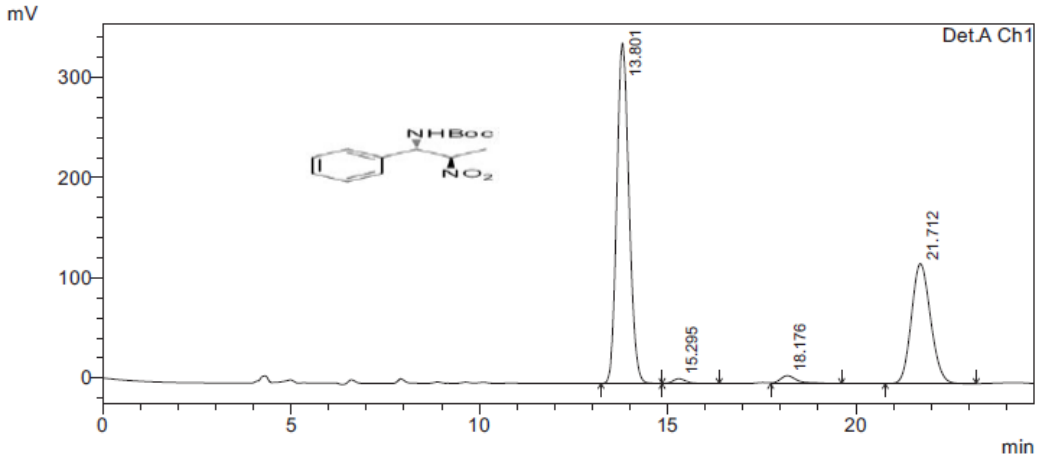


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.929	924791	40751	4.901	6.505
2	15.463	926176	39762	4.909	6.347
3	18.380	8518484	311860	45.148	49.784
4	21.979	8498284	234053	45.041	37.363
Total		18867735	626426	100.000	100.000

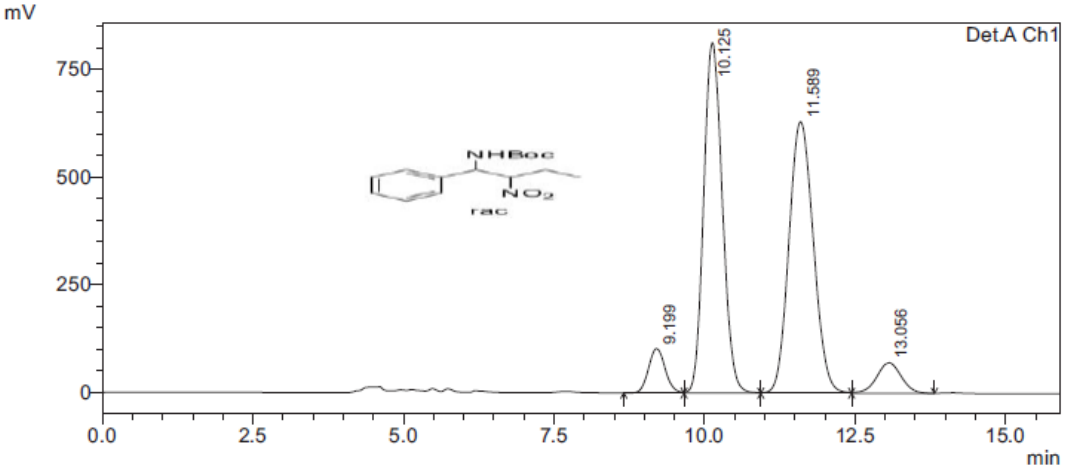


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.801	7671646	339580	62.566	71.967
2	15.295	113512	4813	0.926	1.020
3	18.176	244433	7827	1.993	1.659
4	21.712	4232086	119637	34.515	25.355
Total		12261676	471856	100.000	100.000

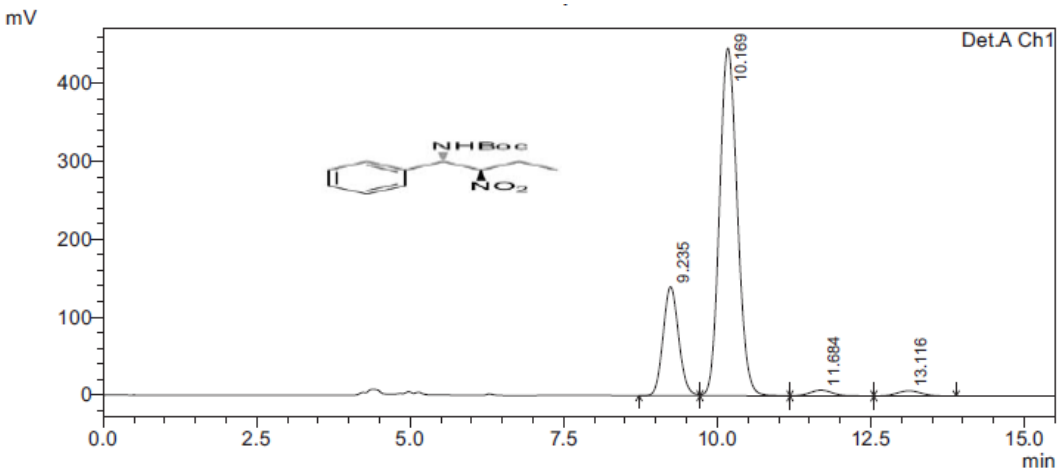


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.199	2000021	103482	5.073	6.384
2	10.125	17563341	814685	44.549	50.256
3	11.589	17840119	631775	45.251	38.973
4	13.056	2021386	71116	5.127	4.387
Total		39424868	1621057	100.000	100.000

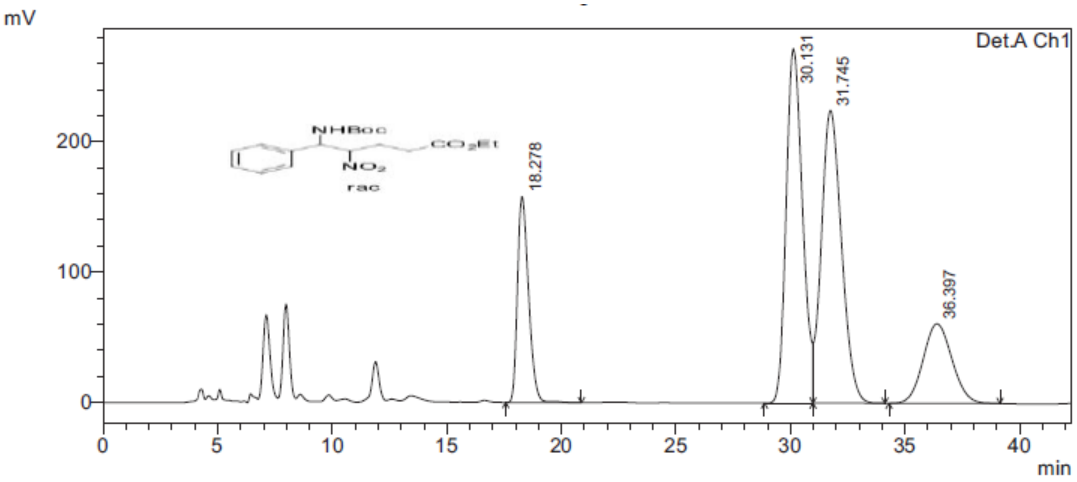


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.235	2470671	139855	20.904	23.300
2	10.169	8984342	446389	76.015	74.368
3	11.684	184100	7343	1.558	1.223
4	13.116	180053	6657	1.523	1.109
Total		11819166	600244	100.000	100.000

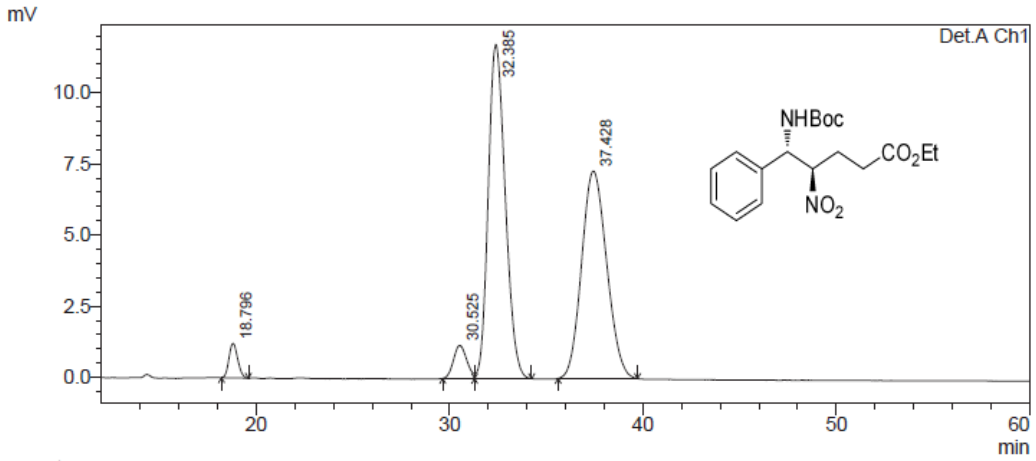


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.278	5331130	157980	14.051	22.094
2	30.131	13481098	271730	35.532	38.003
3	31.745	13802376	224344	36.379	31.376
4	36.397	5326310	60974	14.038	8.527
Total		37940913	715029	100.000	100.000

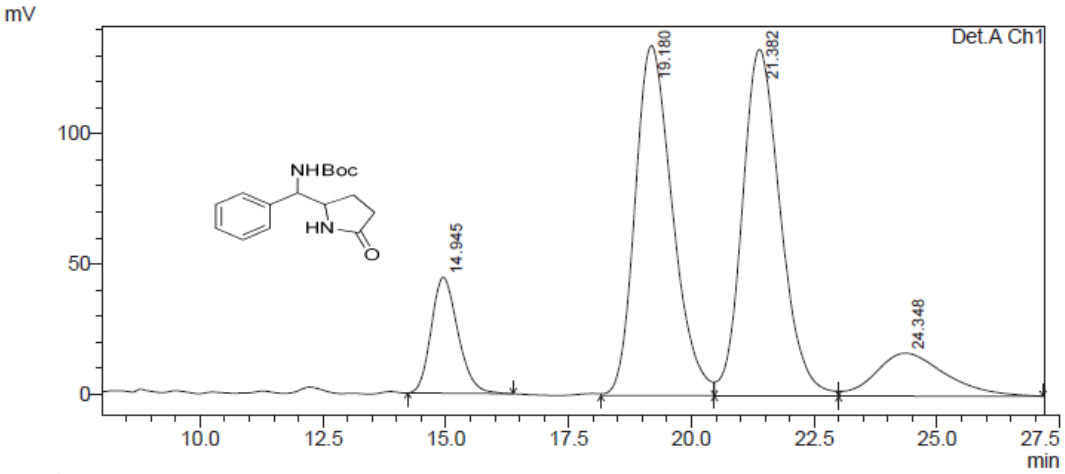


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.796	37980	1212	2.585	5.665
2	30.525	55038	1161	3.746	5.429
3	32.385	718972	11734	48.938	54.855
4	37.428	657156	7284	44.730	34.051
Total		1469146	21391	100.000	100.000

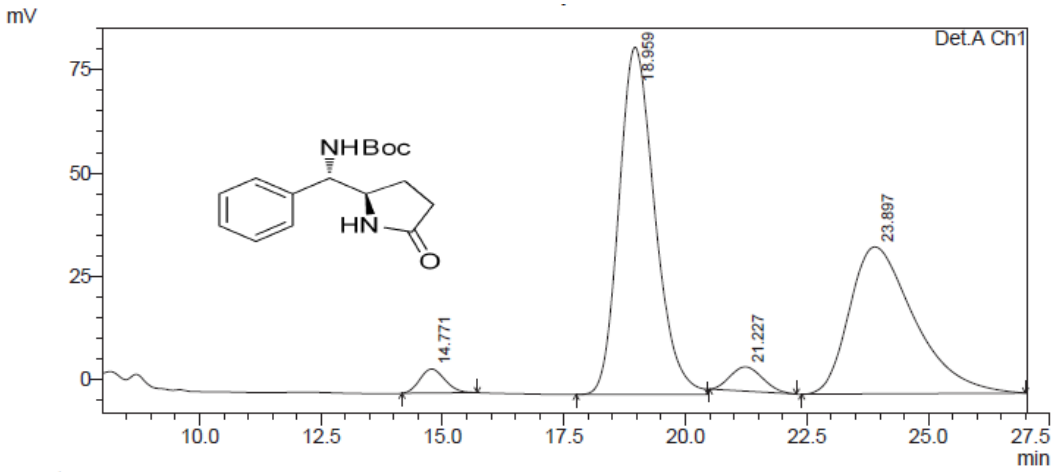


1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.945	1682945	44428	9.568	13.540
2	19.180	7106339	134336	40.403	40.940
3	21.382	7171761	132923	40.775	40.510
4	24.348	1627636	16439	9.254	5.010
Total		17588681	328127	100.000	100.000



1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.771	208476	5818	2.567	4.434
2	18.959	4323169	83994	53.227	64.009
3	21.227	273184	5870	3.363	4.474
4	23.897	3317290	35540	40.843	27.084
Total		8122119	131222	100.000	100.000