

Electronic Supplementary Information

A highly enantioselective approach towards 2-substituted 3-bromopyrrolidines

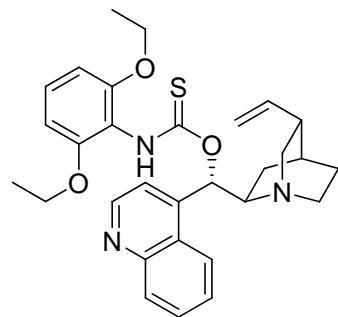
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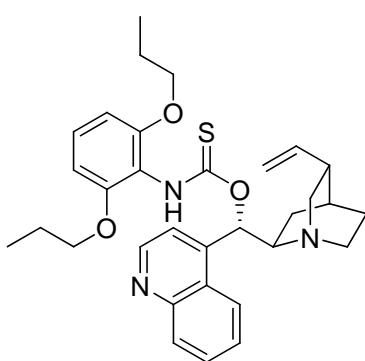
General. All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a BIO-RAD FTS 165 FT-IR spectrophotometer and reported in wave numbers (cm^{-1}). Melting points were determined on a BÜCHI B-540b melting point apparatus. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz), Bruker DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^1H NMR and to chloroform (δ 77.0) for the ^{13}C NMR measurements. Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode. High resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Enantiomeric excesses were determined by HPLC analysis on Shimadzu HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Daicel Chiralpak IA, IB or IC. Optical rotations were recorded on a Jasco DIP-1000 polarimeter. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

Catalysts were synthesized according to the report procedure.¹



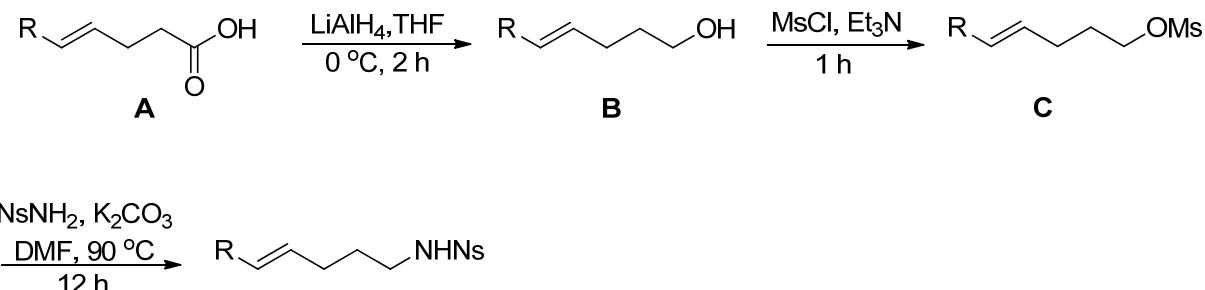
Amino-thiocabamate 9h

71%; light yellow solid, $[\alpha]_D^{28} +35.9$ (c 1.6, CH_2Cl_2); IR (KBr): 2934, 1591, 1463, 1257, 1181, 1090 cm^{-1} ; ^1H NMR (the compound existed as a mixture of rotamers and the major rotamer was assigned) (400 MHz, CDCl_3): δ 8.84 (d, J = 3.1 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.97-7.94 (m, 1H), 7.69-7.67 (m, 2H), 7.49-7.35 (m, 2H), 7.25-7.20 (m, 2H), 6.53 (d, J = 8.3 Hz, 2H), 5.88-5.80 (m, 1H), 5.18-5.02 (m, 2H), 3.90-3.69 (m, 4H), 3.23 (d, J = 8.4 Hz, 1H), 2.95-2.82 (m, 2H), 2.64-2.59 (m, 2H), 2.21-2.06 (m, 2H), 1.90-1.77 (m, 1H), 1.55-1.24 (m, 3H), 1.15-1.10 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.3, 155.4, 149.7, 148.6, 145.2, 140.5, 130.1, 128.9, 128.7, 126.3, 126.1, 124.4, 120.2, 114.8, 104.7, 81.4, 64.1, 60.2, 49.5, 49.0, 40.7, 28.2, 26.3, 23.5, 14.5; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{36}\text{N}_3\text{O}_3\text{S}$ m/z [M + H] $^+$: 518.2472; found: 518.2495.



Amino-thiocabamate 9i

77%; White solid, $[\alpha]_D^{28} +60.5$ (c 3.0, CH_2Cl_2); IR (KBr): 2936, 1594, 1522, 1461, 1258, 1178, 1113 cm^{-1} ; ^1H NMR (the compound existed as a mixture of rotamers and the major rotamer was assigned) (400 MHz, CDCl_3): δ 8.80 (d, J = 4.2 Hz, 1H), 8.08 (d, J = 8.2 Hz, 1H), 7.89-7.79 (m, 2H), 7.65-7.61 (m, 1H), 7.45-7.28 (m, 2H), 7.25-7.14 (m, 2H), 6.49 (d, J = 7.9 Hz, 2H), 5.89-5.81 (m, 1H), 5.14-5.00 (m, 2H), 3.92-3.72 (m, 3H), 3.50-3.34 (m, 2H), 3.24-3.20 (m, 1H), 2.94-2.75 (m, 2H), 2.62-2.54 (m, 1H), 2.26-2.12 (m, 1H), 1.86-1.73 (m, 1H), 1.60-1.30 (m, 8H), 0.82-0.75 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.3, 155.6, 149.6, 148.6, 145.1, 140.4, 130.0, 128.9, 128.6, 126.2, 126.1, 124.5, 120.3, 114.7, 114.1, 104.7, 81.3, 69.9, 60.2, 49.3, 48.8, 40.6, 28.2, 26.2, 23.6, 22.2, 10.3; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{40}\text{N}_3\text{O}_3\text{S}$ m/z [M + H] $^+$: 546.2785; found: 546.2772.



7

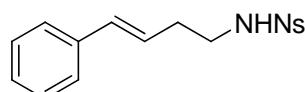
General Procedure for the Preparation of amide 7

To a solution of ester **A** (1.0 mmol, 1.0 eq) in THF (10 mL) was added LiAlH_4 (76 mg, 2.0 mmol, 2.0 eq) at 0°C under N_2 . The resulting mixture was stirred at 0°C for 10 min and then was warmed to 25°C and stirred for another 3 h. After TLC revealed the absence of the starting material, the reaction was quenched with crushed ice. The mixture was filtered through a thin pad of silica gel and eluted with EtOAc (20 mL). The filtrate was concentrated *in vacuo*, which was used directly without further purification, or purified by a short column (hexane/ EtOAc 3:1) to give alcohol **B**.

To a solution of alcohol **B** (1.0 mmol, 1.0 eq) and triethylamine (418 μL , 3.0 mmol, 3.0 eq) in DCM (5

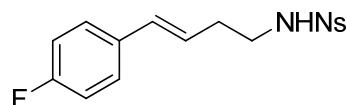
mL) was added MsCl (116 μ L, 1.5 mmol, 1.5 eq) at 0 °C. The resulting mixture was stirred at 0 °C for 10 min and then was warmed to 25 °C and stirred for another 2 h. After TLC revealed the absence of the starting material, the reaction was quenched with water (4 mL) and extracted with DCM (3×5 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc 3:1) to give the compound **C**.

A modified literature² procedure was used for the direct conversion of Ms-activated alcohols to the corresponding 4-nitrobenzenesulfonamides. A solution of compound **C** (1.0 mmol, 1.0 eq), NsNH₂ (404 mg, 2.0 mmol, 2.0 eq) and K₂CO₃ (276 mg, 2.0 mmol, 2.0 eq) in DMF (5 mL) was stirred at 90 °C for 12 h. The reaction mixture was diluted with water (10 mL) and extracted with Et₂O (3×15 mL). The combined organic extracts were washed with water (3×10 mL) and brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash column chromatography (DCM/hexane 2:1 to pure DCM) to give the product **7**.



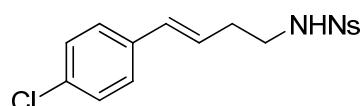
(E)-4-Nitro-N-(phenylbut-3-enyl)benzenesulfonamide (7a)

yellow solid, IR (KBr): 3263, 1530, 1351, 1226, 1162, 1091 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.8-7.20 (m, 5H), 6.34 (d, *J* = 15.9 Hz, 1H), 5.92 (dt, *J* = 15.7, 7.2 Hz, 1H), 4.90 (t, *J* = 6.0 Hz, 1H), 3.18 (dt, *J* = 6.3 Hz, 2H), 2.38 (dt, *J* = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 145.9, 136.5, 133.6, 128.6, 128.2, 127.7, 126.0, 124.9, 124.3, 42.7, 33.1; HRMS (ESI) calcd for C₁₆H₁₅N₂O₄S *m/z* [M - H]⁻: 331.0758; found: 331.0749.



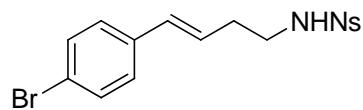
(E)-N-[4-(4-Fluorophenyl)but-3-enyl]-4-Nitrobenzenesulfonamide (7b)

yellow solid, IR (KBr): 3264, 1529, 1350, 1229, 1161, 1090 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.02(d, *J* = 8.8 Hz, 2H), 7.19 (dd, *J* = 8.8, 1.9 Hz, 2H), 6.84 (dd, *J* = 8.9 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.32 (dt, *J* = 15.8, 7.0 Hz, 1H), 5.16 (t, *J* = 6.3 Hz, 1H), 3.16 (dt, *J* = 6.3 Hz, 2H), 2.38 (dt, *J* = 6.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 162.2 (d, *J* = 246.0 Hz), 149.9, 145.8, 132.7 (d, *J* = 2.7 Hz), 132.2, 128.2, 127.5 (d, *J* = 8.2 Hz), 124.8 (d, *J* = 1.8 Hz), 124.3, 115.4 (d, *J* = 21.9 Hz), 42.7, 33.0; HRMS (ESI) calcd for C₁₆H₁₄FN₂O₄S *m/z* [M - H]⁻: 349.0664; found: 349.0664.



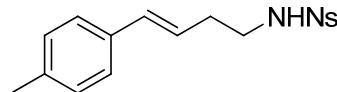
(E)-N-[4-(4-Chlorophenyl)but-3-enyl]-4-Nitrobenzenesulfonamide (7c)

Yellow solid, IR (KBr): 3269, 1530, 1426, 1350, 1161, 1091 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 8.29 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 5.96 (dt, *J* = 15.7, 7.2 Hz, 1H), 4.99 (t, *J* = 5.8 Hz, 1H), 3.17 (dt, *J* = 6.4 Hz, 2H), 2.39 (dt, *J* = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 150.0, 145.8, 135.0, 133.3, 132.3, 128.7, 128.2, 127.3, 125.7, 124.3, 42.6, 33.1; HRMS (ESI) calcd for C₁₆H₁₄ClN₂O₄S *m/z* [M - H]⁻: 365.0368; found: 365.0368.



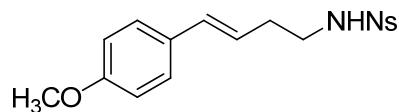
(E)-N-[4-(4-Bromophenyl)but-3-enyl]-4-Nitrobenzenesulfonamide (7d)

yellow solid; IR (neat): 3270, 3100, 1528, 1346, 1162, 1089 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 8.32 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.96 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.73 (brs, 1H), 3.19 (dt, *J* = 6.5 Hz, 2H), 2.40 (ddt, *J* = 6.4, 1.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 145.9, 135.4, 132.5, 131.7, 128.2, 127.6, 125.8, 124.4, 121.5, 42.6, 33.2; HRMS (ESI) calcd for C₁₆H₁₄BrN₂O₄S *m/z* [M - H]⁻: 408.9863; found: 408.9857.



(E)-4-Nitro-N-(4-p-tolylbut-3-enyl)benzenesulfonamide (7e)

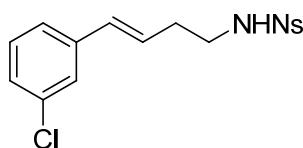
Yellow solid; IR (neat): 3246, 1528, 1348, 1312, 1163, 1092 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 8.22 (d, *J* = 8.9 Hz, 2H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 5.86 (dt, *J* = 15.7, 7.2 Hz, 1H), 5.10 (t, *J* = 5.9 Hz, 1H), 3.17 (dt, *J* = 6.3 Hz, 2H), 2.37 (ddt, *J* = 6.5, 1.1 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.8, 145.8, 137.5, 133.7, 133.3, 129.2, 128.1, 125.9, 124.3, 123.9, 42.8, 33.0, 21.1; HRMS (ESI) calcd for C₁₇H₁₇N₂O₄S *m/z* [M - H]⁻: 345.0915; found: 345.0904.



(E)-N-[4-(4-methoxyphenyl)but-3-enyl]-4-nitrobenzenesulfonamide (7f)

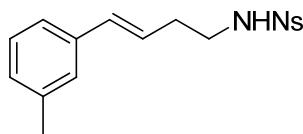
Yellow solid; IR (KBr): 3244, 1605, 1530, 1351, 1232, 1160 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 8.23 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 5.76 (dt, *J* = 15.8, 7.3 Hz, 1H), 5.09 (t, *J* = 5.9 Hz, 1H), 3.79 (s, 3H), 3.16 (dt, *J* = 6.3 Hz, 2H), 2.35 (dt, *J* = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 149.8, 145.8, 132.8, 129.3, 128.2, 127.1, 124.2, 122.7, 113.9, 55.2, 42.8, 33.0; HRMS (ESI) calcd for C₁₇H₁₇N₂O₅S *m/z* [M - H]⁻: 361.0864;

found: 361.0862.



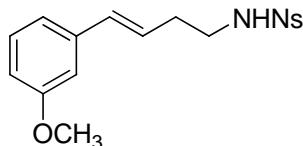
(E)-N-[4-(3-Chlorophenyl)but-3-enyl]-4-Nitrobenzenesulfonamide (7g)

Yellow solid, IR (KBr): 3239, 1529, 1422, 1348, 1310, 1162, 1092 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 8.27 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.20-7.08 (m, 4H), 6.29 (d, *J* = 16.0 Hz, 1H), 5.98 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.18 (t, *J* = 5.9 Hz, 1H), 3.16 (dt, *J* = 6.5 Hz, 2H), 2.35 (ddt, *J* = 6.4, 1.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 145.7, 138.4, 134.4, 132.1, 129.8, 127.5, 126.7, 125.9, 124.32, 124.28, 42.6, 33.0; HRMS (ESI) calcd for C₁₆H₁₄ClN₂O₄S *m/z* [M - H]⁻: 365.0368; found: 365.0366.



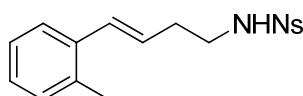
(E)-4-Nitro-N-(4-m-tolylbut-3-enyl)benzenesulfonamide (7h)

Yellow solid, IR (KBr): 3279, 1607, 1529, 1350, 1161, 1090 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): 8.21 (dd, *J* = 8.9 Hz, 2H), 8.01 (d, *J* = 9.0 Hz, 2H), 8.01 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.03-7.00 (m, 3H), 6.30 (d, *J* = 15.9 Hz, 1H), 5.94 (dt, *J* = 15.8, 7.1 Hz, 1H), 5.40 (t, *J* = 5.9 Hz, 1H), 3.17 (dt, *J* = 6.4 Hz, 2H), 2.38 (dt, *J* = 6.6 Hz, 2H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.7, 145.6, 138.0, 136.4, 133.2, 128.29, 128.25, 128.1, 126.6, 124.9, 124.1, 123.0, 42.7, 32.9, 21.1; HRMS (ESI) calcd for C₁₇H₁₇N₂O₄S *m/z* [M - H]⁻: 345.0915; found: 345.0911.



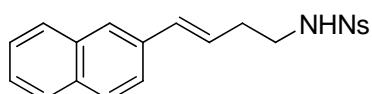
(E)-N-[4-(3-methoxyphenyl)but-3-enyl]-4-nitrobenzenesulfonamide (7i)

Yellow solid, IR (KBr): 3258, 1606, 1528, 1350, 1162, 1050 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.26 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 1H), 6.83-6.74 (m, 3H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.92 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.02 (t, *J* = 5.9 Hz, 1H), 3.79 (s, 3H), 3.18 (dt, *J* = 6.2 Hz, 2H), 2.38 (dt, *J* = 6.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 159.7, 149.9, 145.8, 137.9, 133.4, 129.6, 128.2, 125.4, 124.3, 119.7, 112.9, 111.7, 55.2, 42.7, 33.0; HRMS (ESI) calcd for C₁₇H₁₇N₂O₅S *m/z* [M - H]⁻: 361.0864; found: 361.0862.



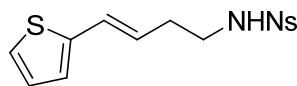
(E)-4-Nitro-N-(4-o-tolylbut-3-enyl)benzenesulfonamide (7j)

Light yellow solid, IR (KBr): 3254, 1609, 1530, 1349, 1155, 1057 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 8.26 (d, $J = 8.9$ Hz, 2H), 8.04 (d, $J = 8.9$ Hz, 2H), 7.29 (dd, $J = 7.6, 2.0$ Hz, 1H), 7.17-7.10 (m, 3H), 6.30 (d, $J = 15.7$ Hz, 1H), 5.86 (dt, $J = 15.6, 7.0$ Hz, 1H), 5.26 (t, $J = 5.9$ Hz, 1H), 3.21 (dt, $J = 6.4$ Hz, 2H), 2.38 (dt, $J = 6.8, 1.2$ Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 145.7, 135.5, 134.9, 131.1, 130.2, 128.1, 127.5, 126.3, 126.0, 125.2, 124.2, 42.8, 33.3, 19.6; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_4\text{S}$ m/z [M - H] $^-$: 345.0915; found: 345.0913.



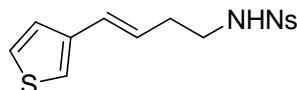
(E)-N-[4-(naphthalene-2-yl)but-3-enyl]-4-nitrobenzenesulfonamide (7k)

Yellow solid, IR (KBr): 3248, 1531, 1348, 1305, 1155, 1061 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): 8.31-8.21 (m, 2H), 7.99 (d, $J = 8.9$ Hz, 2H), 7.80-7.72 (m, 3H), 7.58 (s, 1H), 7.49-7.41 (m, 3H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.06 (dt, $J = 15.6, 7.1$ Hz, 1H), 4.94 (t, $J = 5.9$ Hz, 1H), 3.21 (dt, $J = 6.2$ Hz, 2H), 2.44 (dt, $J = 6.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 163.4, 149.9, 145.8, 133.9, 133.7, 133.5, 132.9, 128.3, 128.2, 127.9, 127.6, 126.4, 126.0, 125.3, 124.3, 123.1, 42.7, 33.2; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_4\text{S}$ m/z [M - H] $^-$: 381.0915; found: 381.0917.



(E)-4-Nitro-N-[4-(thiophen-2-yl)but-3-enyl]benzenesulfonamide (7l)

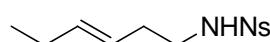
Yellow solid, IR (KBr): 3271, 1523, 1422, 1350, 1167, 1072 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 8.30 (d, $J = 8.9$ Hz, 2H), 8.03 (d, $J = 8.9$ Hz, 2H), 7.11 (d, $J = 5.1$ Hz, 1H), 6.92 (dd, $J = 5.1, 3.6$ Hz, 1H), 6.84 (d, $J = 3.3$ Hz, 1H), 6.48 (d, $J = 15.6$ Hz, 1H), 5.86 (dt, $J = 15.6, 7.2$ Hz, 1H), 4.90 (t, $J = 5.9$ Hz, 1H), 3.17 (dt, $J = 6.2$ Hz, 2H), 2.38 (dt, $J = 6.3, 1.0$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 149.9, 145.8, 141.5, 128.2, 127.4, 126.7, 125.5, 124.6, 124.4, 124.1, 42.6, 33.0; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4\text{S}_2$ m/z [M - H] $^-$: 337.0322; found: 337.0310.



(E)-4-Nitro-N-[4-(thiophen-2-yl)but-3-enyl]benzenesulfonamide (7m)

Yellow solid, IR (KBr): 3259, 1525, 1423, 1350, 1167, 1091 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.31 (d,

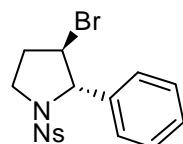
$J = 8.6$ Hz, 2H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 4.6$ Hz, 1H), 7.07 (d, $J = 5.2$ Hz, 2H), 6.38 (d, $J = 15.8$ Hz, 1H), 5.79 (dt, $J = 15.1, 7.3$ Hz, 1H), 4.73 (t, $J = 5.8$ Hz, 1H), 3.17 (dt, $J = 6.2$ Hz, 2H), 2.37 (dt, $J = 6.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 150.0, 146.0, 139.1, 128.3, 128.0, 126.3, 124.7, 124.6, 124.4, 121.9, 42.7, 33.1; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4\text{S}_2$ m/z [M – H] $^-$: 337.0322; found: 337.0319.



(E)-N-(Hex-3-enyl)-4-nitrobenzenesulfonamide (7n)

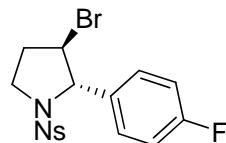
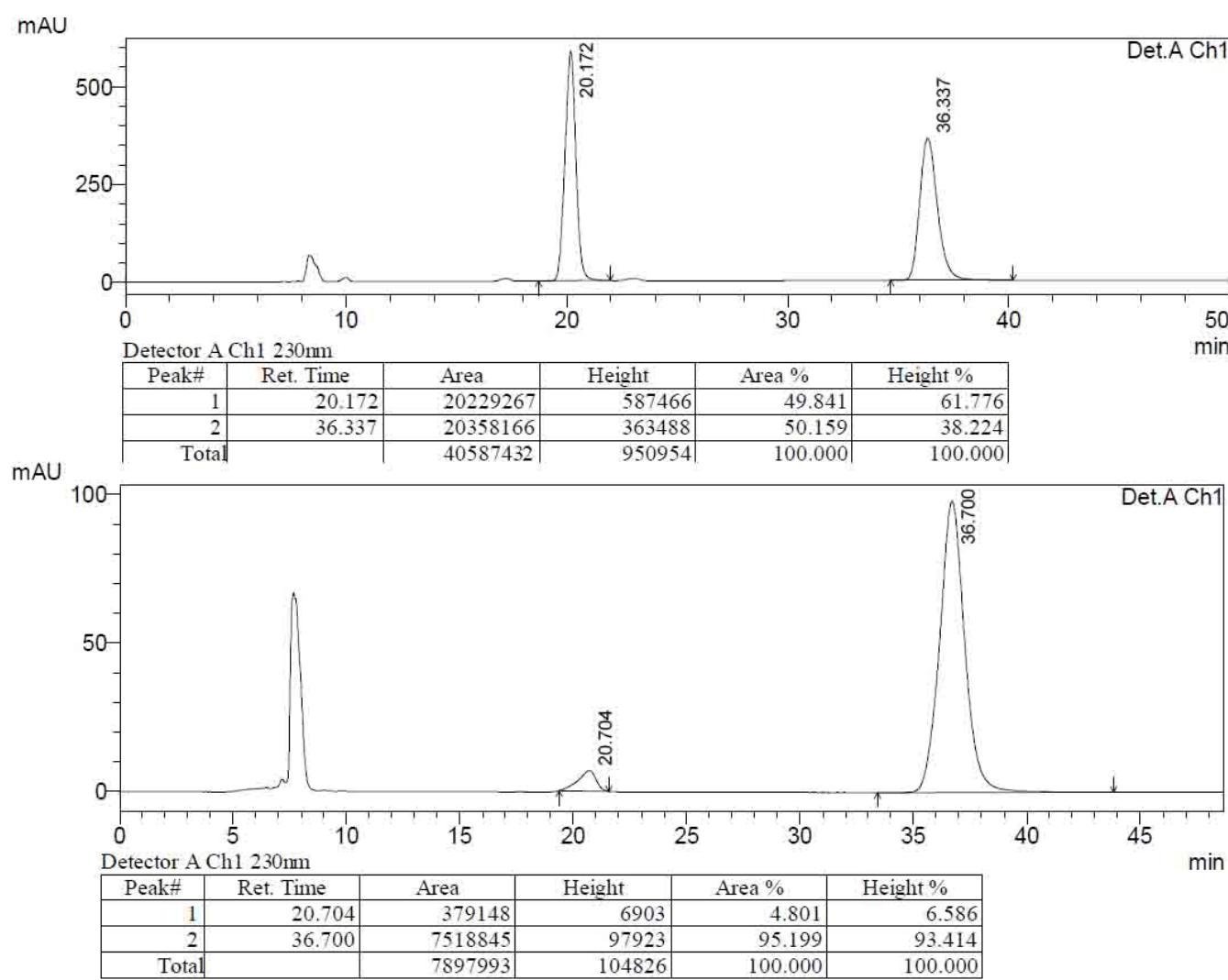
yellow solid, IR (KBr): 3278, 2962, 1531, 1350, 1161, 1091 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, $J = 9.0$ Hz, 2H), 8.04 (d, $J = 8.9$ Hz, 2H), 5.46–5.39 (m, 1H), 5.31 (t, $J = 5.9$ Hz, 1H), 5.20–5.12 (m, 1H), 3.00 (dt, $J = 6.8$ Hz, 2H), 2.12 (dt, $J = 6.8, 1.0$ Hz, 2H), 1.88 (ddt, $J = 7.4, 1.1$ Hz, 2H), 0.85 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 145.8, 135.8, 128.1, 124.2, 123.8, 42.8, 32.3, 25.2, 13.2; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_4\text{S}$ m/z [M – H] $^-$: 283.0758; found: 283.0760.

General Procedure for the Bromoamidation. To a solution of amide **7** (0.1 mmol, 1.0 equiv), catalyst **9h** (0.01 mmol, 0.1 equiv) in the corresponding solvent (0.02 M) at corresponding temperature in dark under N_2 was added brominating source (0.12 mmol, 1.2 equiv). The resulting mixture was stirred at that temperature and monitored by TLC. The reaction was quenched with saturated Na_2SO_3 (2.0 mL) and then was warmed to 25 °C. The solution was diluted with water (3.0 mL) and extracted with CH_2Cl_2 (3×5 mL). The combined extracts were washed with brine (5.0 mL), dried (MgSO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 2:1) to yield the corresponding pyrrolidine **8**.



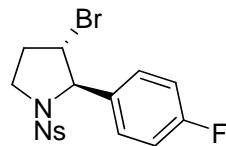
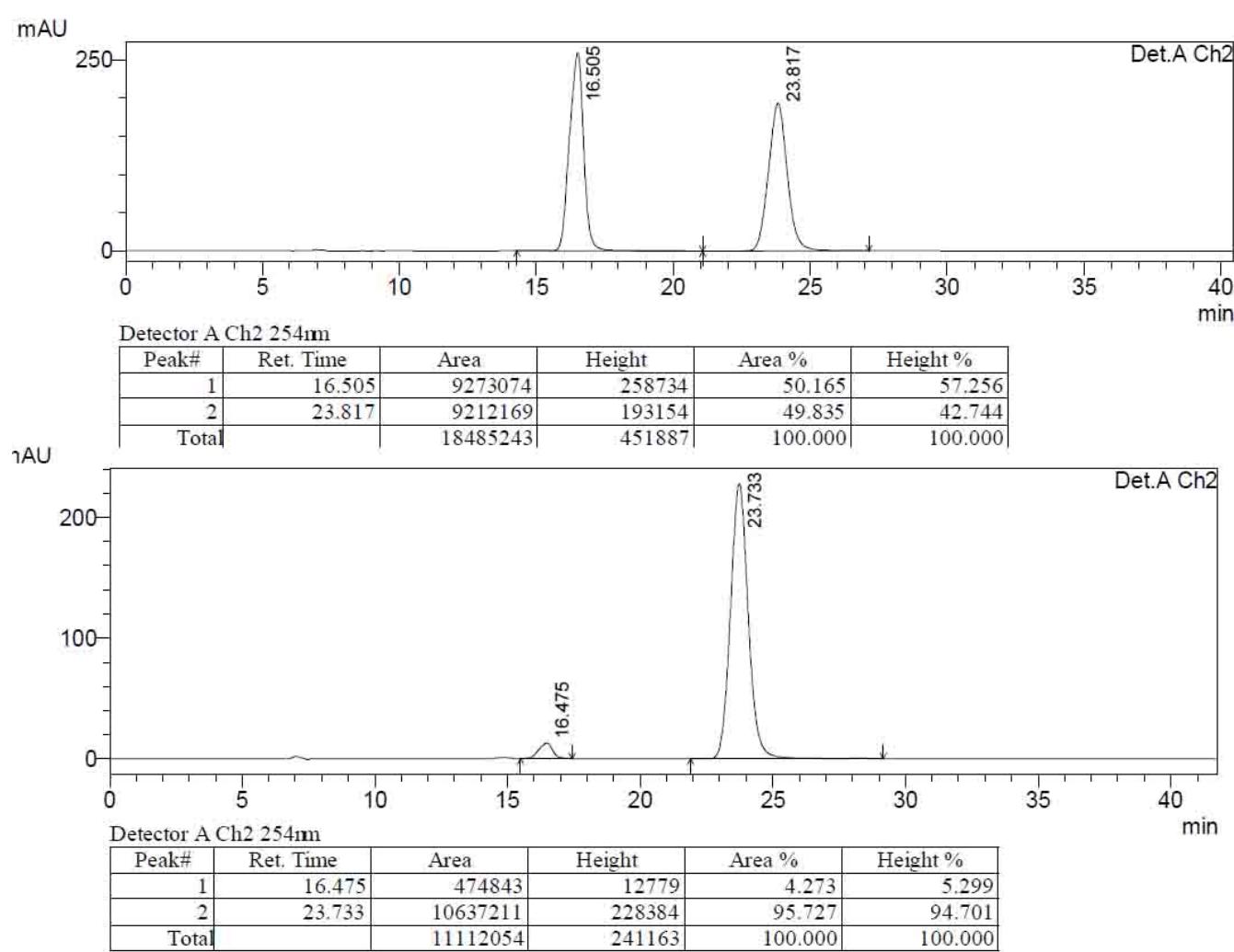
(2*S*,3*R*)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-phenylpyrrolidine (8a)

White solid, $[\alpha]_D^{26} +104.4$ (c 0.3, CH_2Cl_2 , 90% ee); IR (KBr): 2936, 1527, 1349, 1166, 1095, 1019 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2): δ 8.35 (d, $J = 8.9$ Hz, 2H), 8.03 (d, $J = 8.9$ Hz, 2H), 7.38–7.32 (m, 5H), 5.08 (s, 1H), 4.26 (d, $J = 4.4$ Hz, 1H), 3.88 (ddd, $J = 9.4, 8.2, 1.2$ Hz, 1H), 3.63 (ddd, $J = 16.4, 10.1, 7.0$ Hz, 1H), 2.46–2.39 (m, 1H), 2.09 (ddd, $J = 14.5, 6.3, 1.2$ Hz); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 150.7, 142.9, 140.2, 129.3, 129.1, 128.6, 126.3, 124.5, 73.4, 54.6, 47.5, 33.4; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{BrN}_2\text{O}_4\text{S}$ m/z [M] $^+$: 409.9930; found: 409.9929. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.42 mL/min, 230 nm) $t_1 = 20.7$ min (minor), $t_2 = 36.7$ min (major).



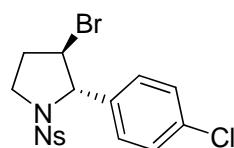
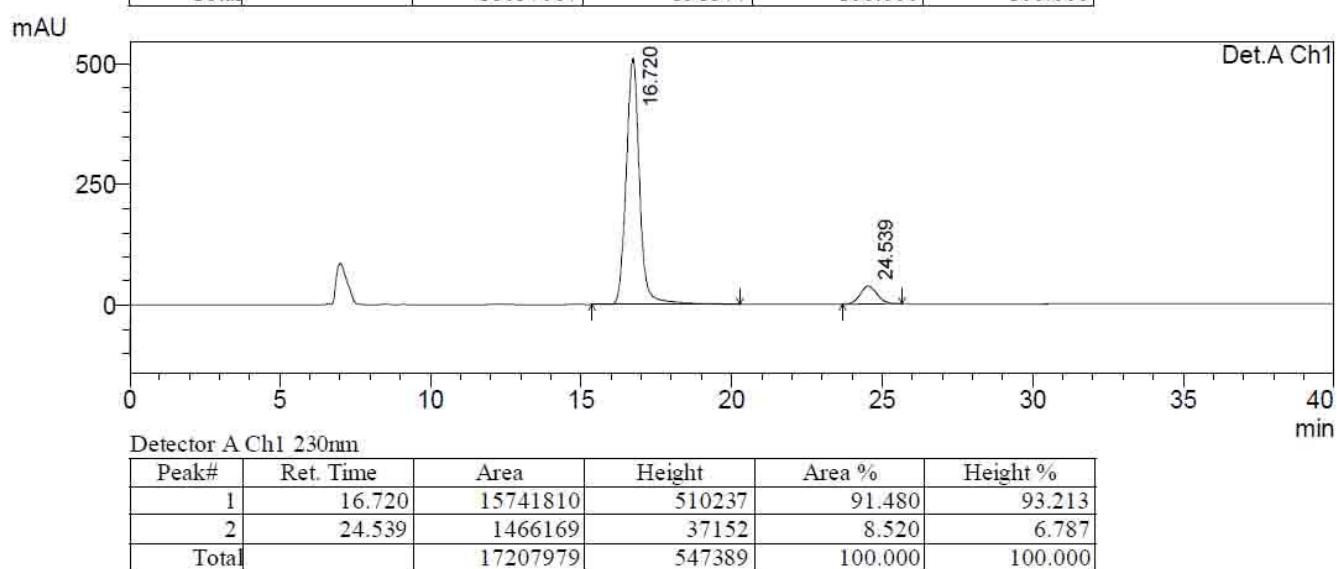
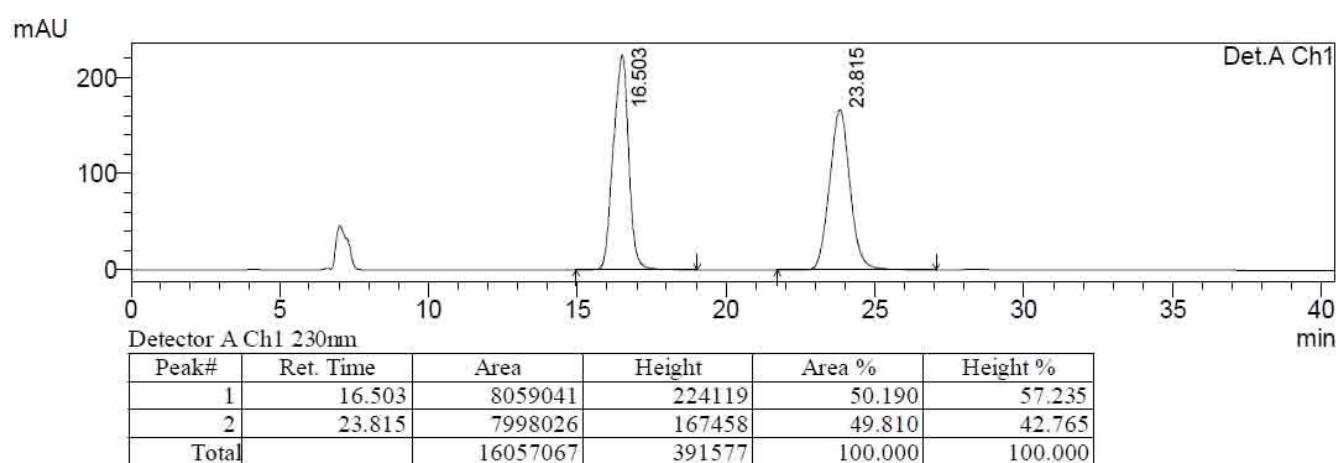
(2S,3R)-3-Bromo-2-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine (8b)

White solid, $[\alpha]_D^{28} +62.5$ (c 0.2, CH_2Cl_2 , 91% ee); IR (KBr): 3109, 1526, 1351, 1169, 1095, 1019 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, J = 9.0 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H), 7.34 (dd, J = 8.3, 5.1 Hz, 2H), 7.07 (dd, J = 8.6 Hz, 2H), 5.09 (s, 1H), 4.23 (d, J = 4.2 Hz, 1H), 3.92 (ddd, J = 9.3, 8.0, 1.3 Hz, 1H), 3.63 (ddd, J = 15.8, 9.5, 6.4 Hz, 1H), 2.44-2.37 (m, 1H), 2.11 (ddd, J = 14.5, 6.4, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.6 (d, J = 246.4 Hz), 150.4, 142.4, 135.5 (d, J = 2.9 Hz), 129.0, 127.7 (d, J = 8.0 Hz), 124.2, 115.9 (d, J = 21.1 Hz), 72.6, 53.9, 47.1, 32.9; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{FBrN}_2\text{O}_4\text{S}$ m/z [M] $^+$: 427.9836; found: 427.9826. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 40/60, 0.5 mL/min, 254 nm), t_1 = 16.5 min (minor), t_2 = 23.7 min (major).



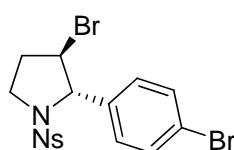
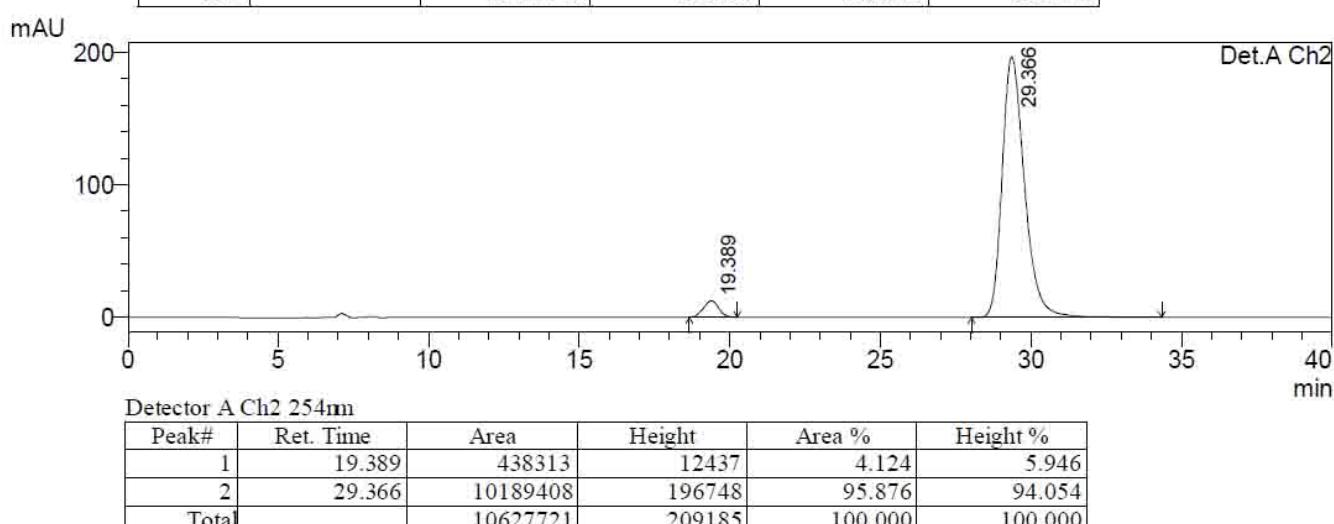
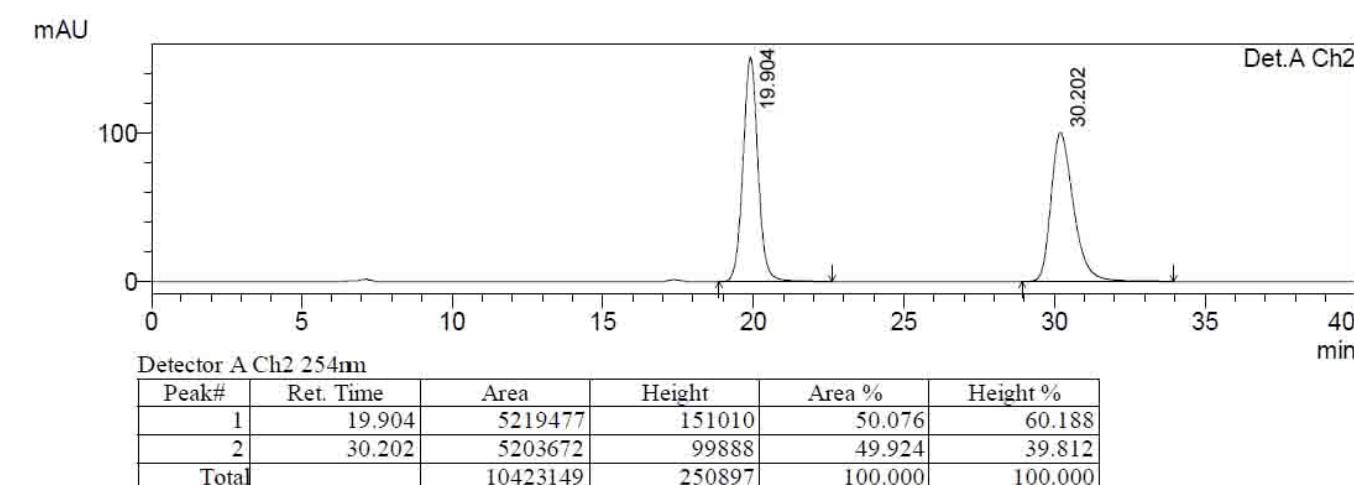
(2*R*,3*S*)-3-Bromo-2-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine (ent-8b)

$[\alpha]_D^{28} -56.7$ (*c* 0.3, CH₂Cl₂, 83% ee); HPLC (Daicel Chiraldak IA, *i*-PrOH/hexane = 40/60, 0.5 mL/min, 254 nm), t₁ = 16.7 min (major), t₂ = 23.5 min (minor).



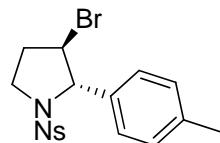
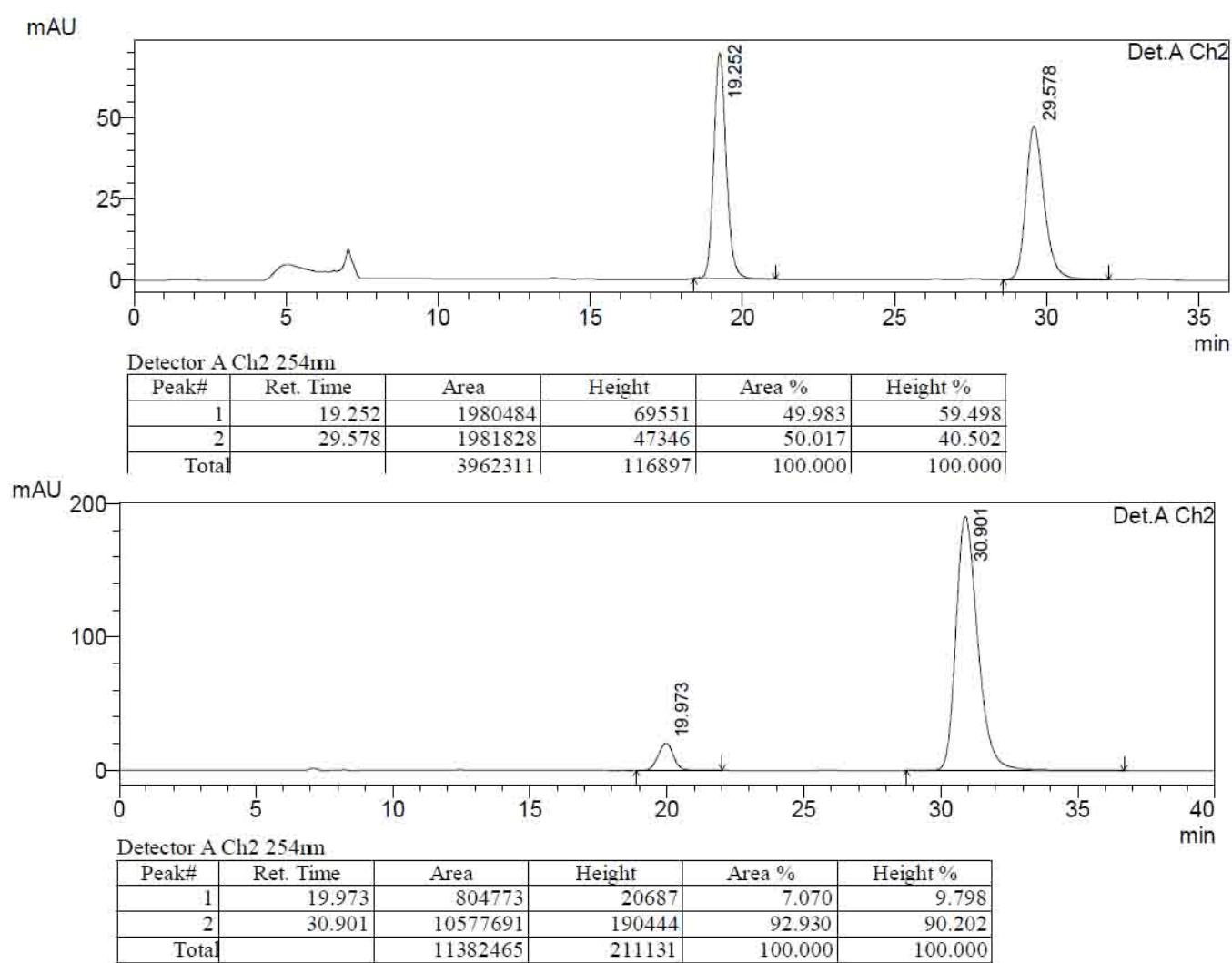
(2*S*,3*R*)-3-Bromo-2-(4-chlorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine (8c)

White solid, $[\alpha]_D^{25} +34.5$ (c 0.2, CH_2Cl_2 , 92% ee); IR (KBr): 2943, 1526, 1347, 1165, 1094, 1012 cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2): δ 8.37 (d, J = 8.8 Hz, 2H), 8.04 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 5.04 (s, 1H), 4.22 (d, J = 4.1 Hz, 1H), 3.88 (ddd, J = 9.3, 7.9, 1.4 Hz, 1H), 3.60 (ddd, J = 16.0, 9.5, 6.4 Hz, 1H), 2.42-2.33 (m, 1H), 2.10 (ddd, J = 14.5, 6.4, 1.2 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.8, 142.6, 139.0, 134.5, 129.42, 129.35, 127.9, 124.7, 72.9, 53.8, 47.6, 33.4; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{ClBrN}_2\text{O}_4\text{S}$ m/z [M] $^+$: 443.9541; found: 443.9553. HPLC (Daicel Chiraldak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 254 nm) t_1 = 19.4 min (minor), t_2 = 29.4 min (major).



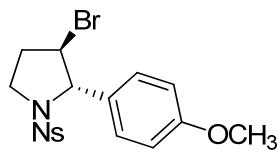
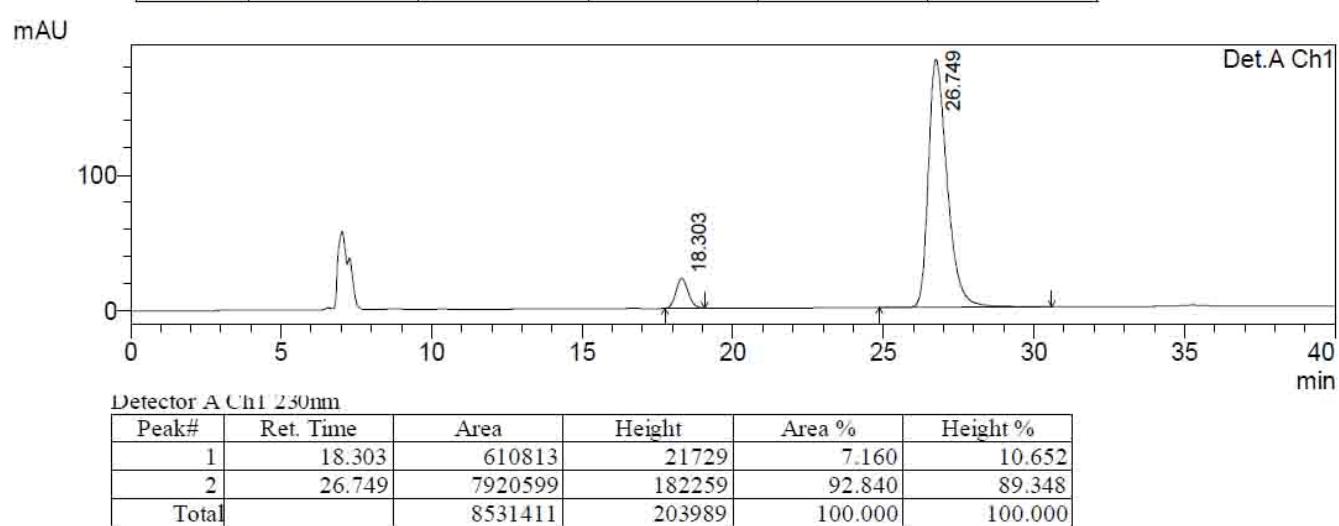
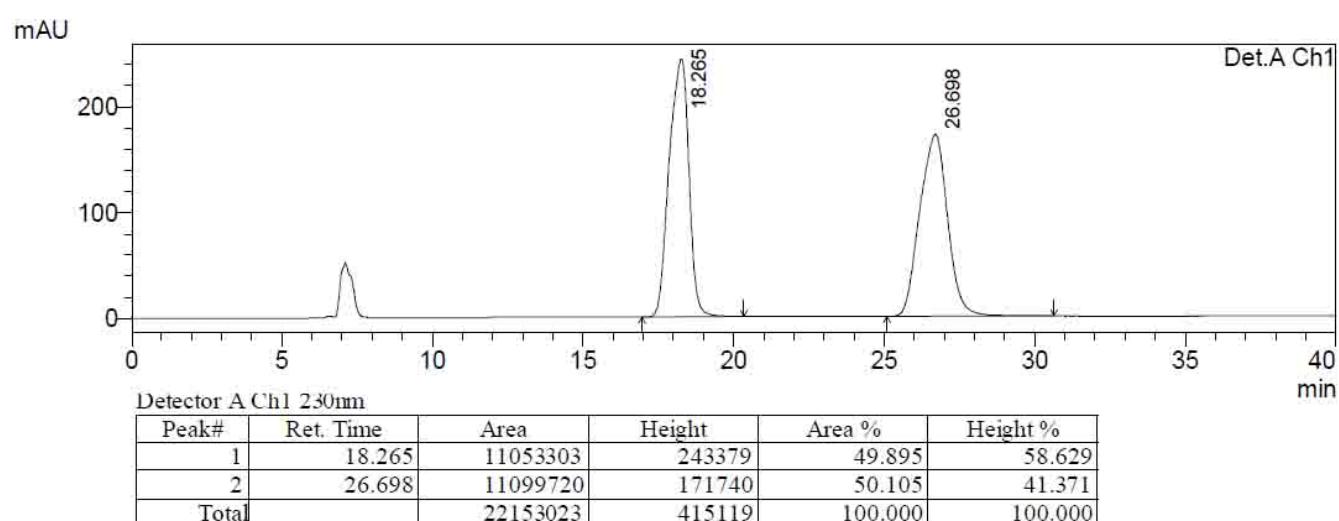
(2S,3R)-3-Bromo-2-(4-bromophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine (8d)

White solid, $[\alpha]_D^{25} +92.0$ (c 0.2, CH_2Cl_2 , 86% ee); IR (KBr): 2925, 1528, 1350, 1165, 1094, 1018 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.40 (d, J = 9.0 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 5.05 (s, 1H), 4.22 (d, J = 4.3 Hz, 1H), 3.92 (ddd, J = 9.4, 8.2, 1.2 Hz, 1H), 3.62 (ddd, J = 15.8, 9.5, 6.4 Hz, 1H), 2.44-2.35 (m, 1H), 2.11 (ddd, J = 14.4, 6.4, 1.2 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 150.4, 142.3, 138.8, 132.1, 129.0, 127.6, 124.3, 122.5, 72.7, 53.5, 47.1, 33.0; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_4\text{S}$ m/z [M] $^+$: 487.9036; found: 487.9043. HPLC (Daicel Chiraldak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 254 nm) t_1 = 20.0 min (minor), t_2 = 30.9 min (major).



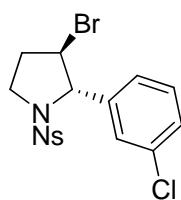
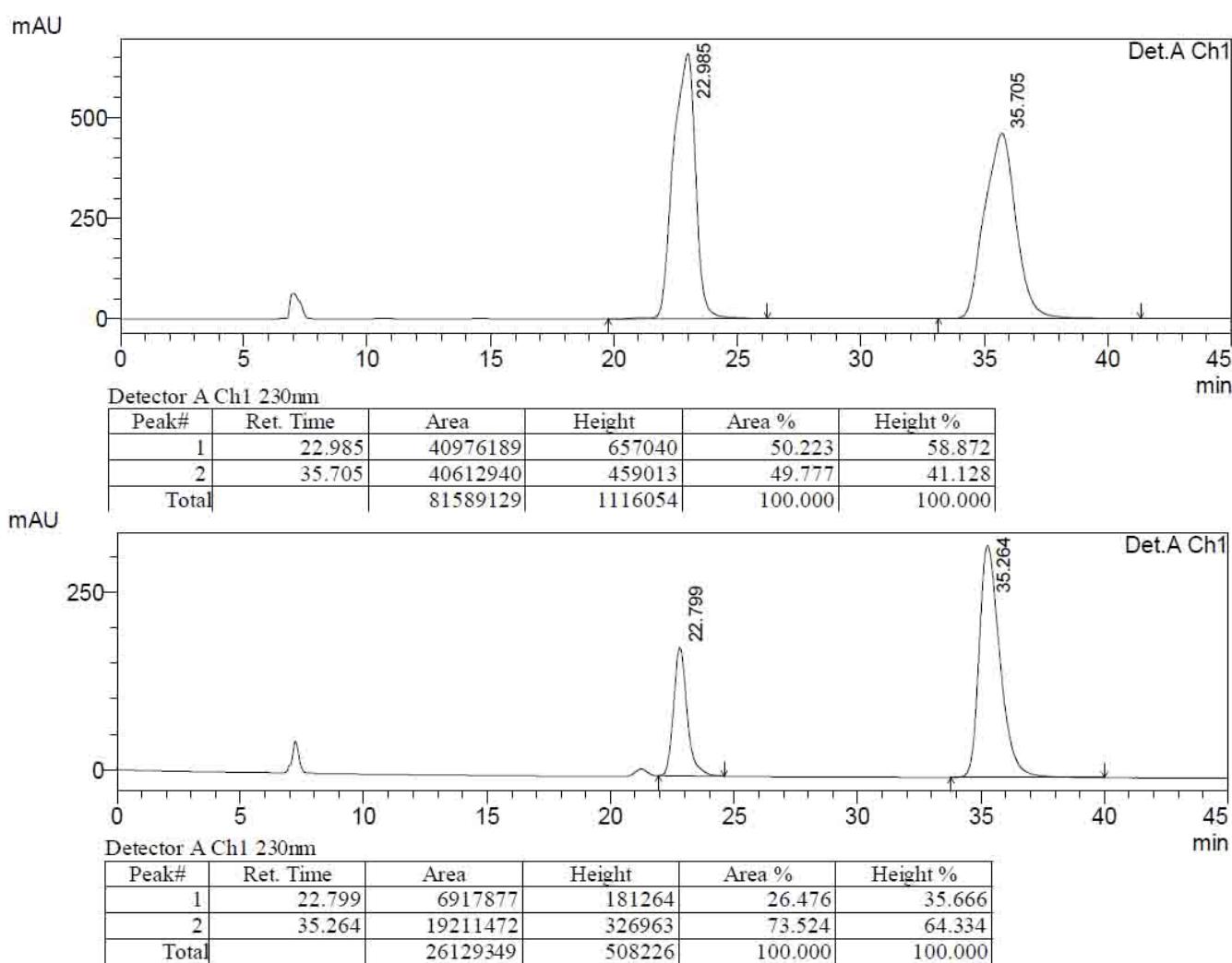
(2S,3R)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-p-tolylpyrrolidine (8e)

White solid, $[\alpha]_D^{25} +78.4$ (*c* 0.3, CH₂Cl₂, 86% ee); IR (KBr): 3110, 1523, 1346, 1165, 1093, 1018 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.36 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.09 (s, 1H), 4.25 (d, *J* = 4.2 Hz, 1H), 3.90 (ddd, *J* = 9.4, 8.1, 1.3 Hz, 1H), 3.54 (ddd, *J* = 15.8, 9.4, 6.4 Hz, 1H), 2.49-2.40 (m, 1H), 2.34 (s, 3H), 2.10 (ddd, *J* = 14.5, 6.4, 1.3 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 150.2, 142.8, 138.3, 136.7, 1219.6, 129.0, 125.8, 124.1, 73.0, 54.3, 47.1, 33.0, 21.1; HRMS (EI) calcd for C₁₇H₁₇BrN₂O₄S *m/z* [M]⁺: 424.0087; found: 424.0075. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 230 nm) t₁ = 18.3 min (minor), t₂ = 26.7 min (major).



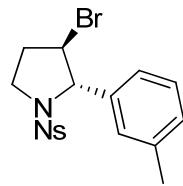
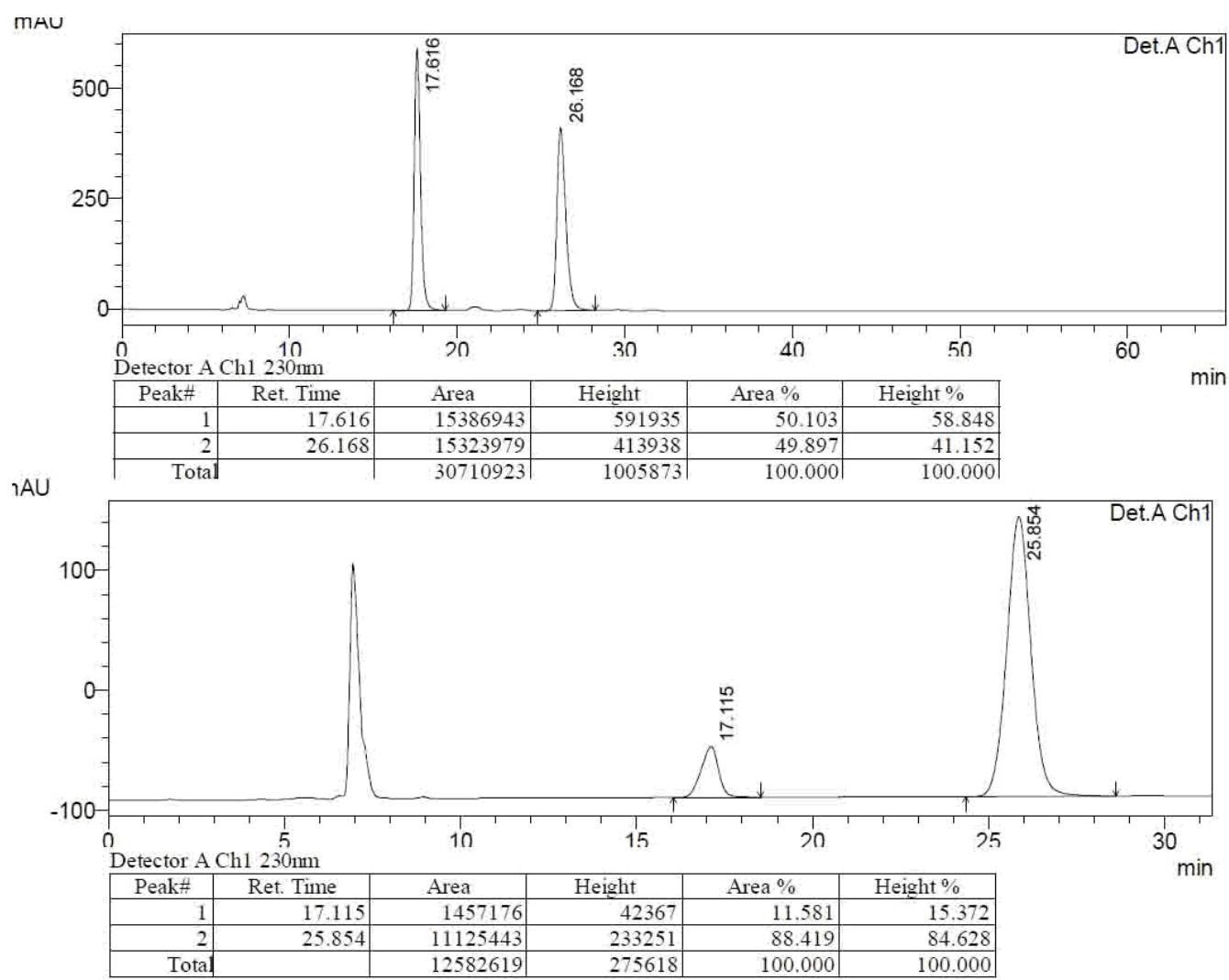
(2S,3R)-3-Bromo-2-(4-methoxyphenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine (8f)

White solid, $[\alpha]_D^{26} +19.1$ (*c* 0.4, CH₂Cl₂, 47% ee); IR (KBr): 2956, 1526, 1345, 1253, 1166, 1092 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.37 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.08 (s, 1H), 4.23 (d, *J* = 4.2 Hz, 1H), 3.89 (ddd, *J* = 9.3, 8.2, 1.2 Hz, 1H), 3.81 (s, 3H), 3.64 (ddd, *J* = 15.8, 9.4, 6.4 Hz, 1H), 2.49-2.40 (m, 1H), 2.10 (ddd, *J* = 14.5, 6.4, 1.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 159.6, 150.2, 142.8, 131.7, 129.0, 127.2, 124.1, 114.3, 72.7, 55.4, 54.3, 47.1, 33.0; HRMS (EI) calcd for C₁₇H₁₇BrN₂O₅S *m/z* [M]⁺: 440.0036; found: 440.0039. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 230 nm) t₁ = 22.8 min (minor), t₂ = 35.3 min (major).



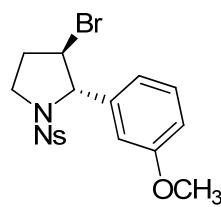
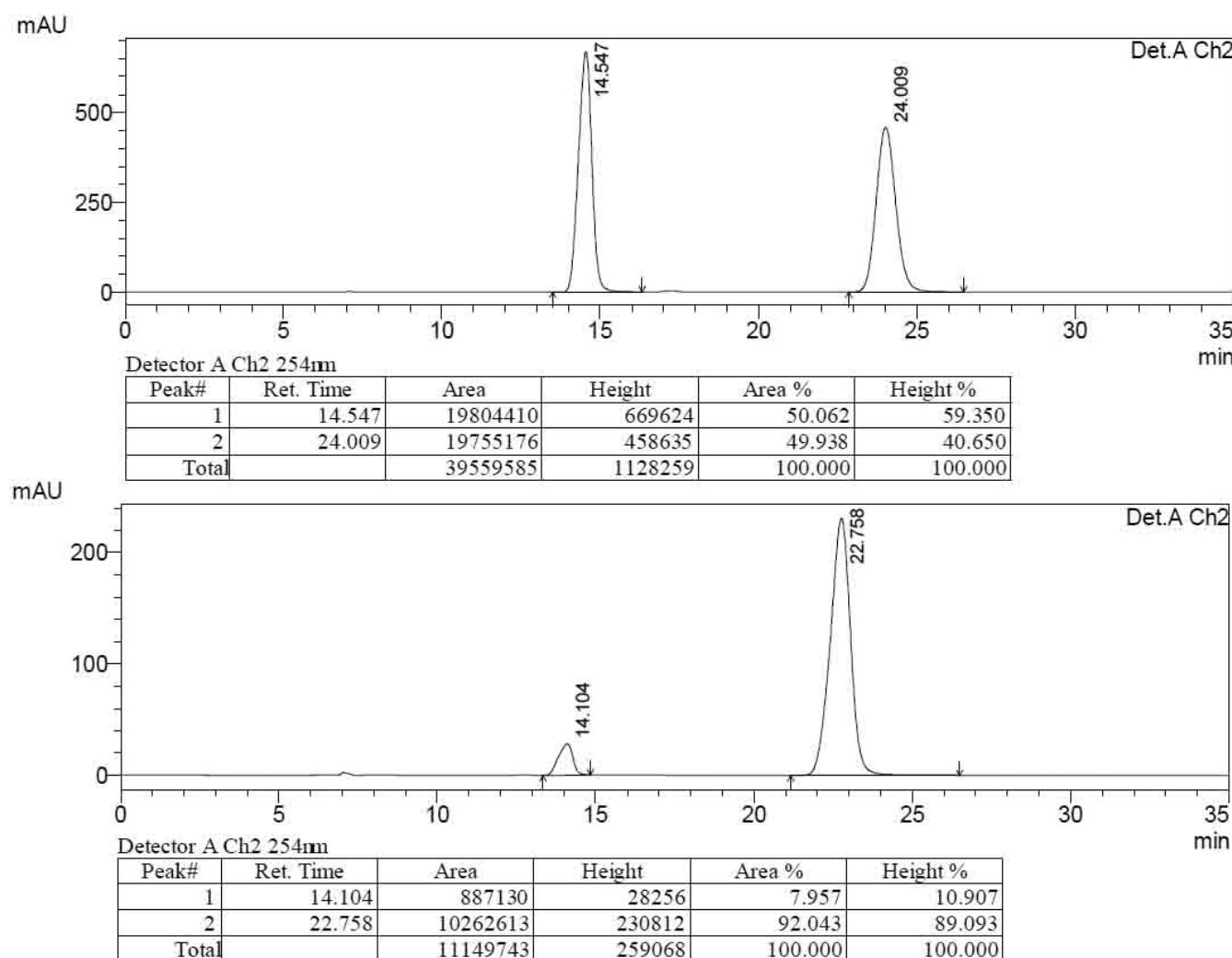
(2S,3R)-3-Bromo-2-(3-chlorophenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine (8g)

White solid, $[\alpha]_D^{26} +34.6$ (c 0.3, CH_2Cl_2 , 77% ee); IR (KBr): 2941, 1528, 1350, 1162, 1095, 1011 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.9 Hz, 2H), 7.31-7.25 (m, 4H), 5.07 (s, 1H), 4.24 (d, J = 4.3 Hz, 1H), 3.92 (ddd, J = 9.3, 8.2, 1.2 Hz, 1H), 3.64 (ddd, J = 15.9, 9.5, 6.4 Hz, 1H), 2.47-2.38 (m, 1H), 2.12 (ddd, J = 14.3, 6.3, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 150.4, 142.4, 141.6, 135.0, 130.2, 129.0, 128.7, 124.2, 72.5, 53.5, 47.2, 33.1; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{ClBrN}_2\text{O}_4\text{S}$ m/z [M] $^+$: 443.9541; found: 443.9550. HPLC (Daicel Chiraldak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 230 nm) t_1 = 17.1 min (minor), t_2 = 25.9 min (major).



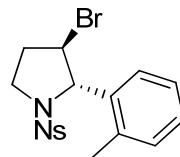
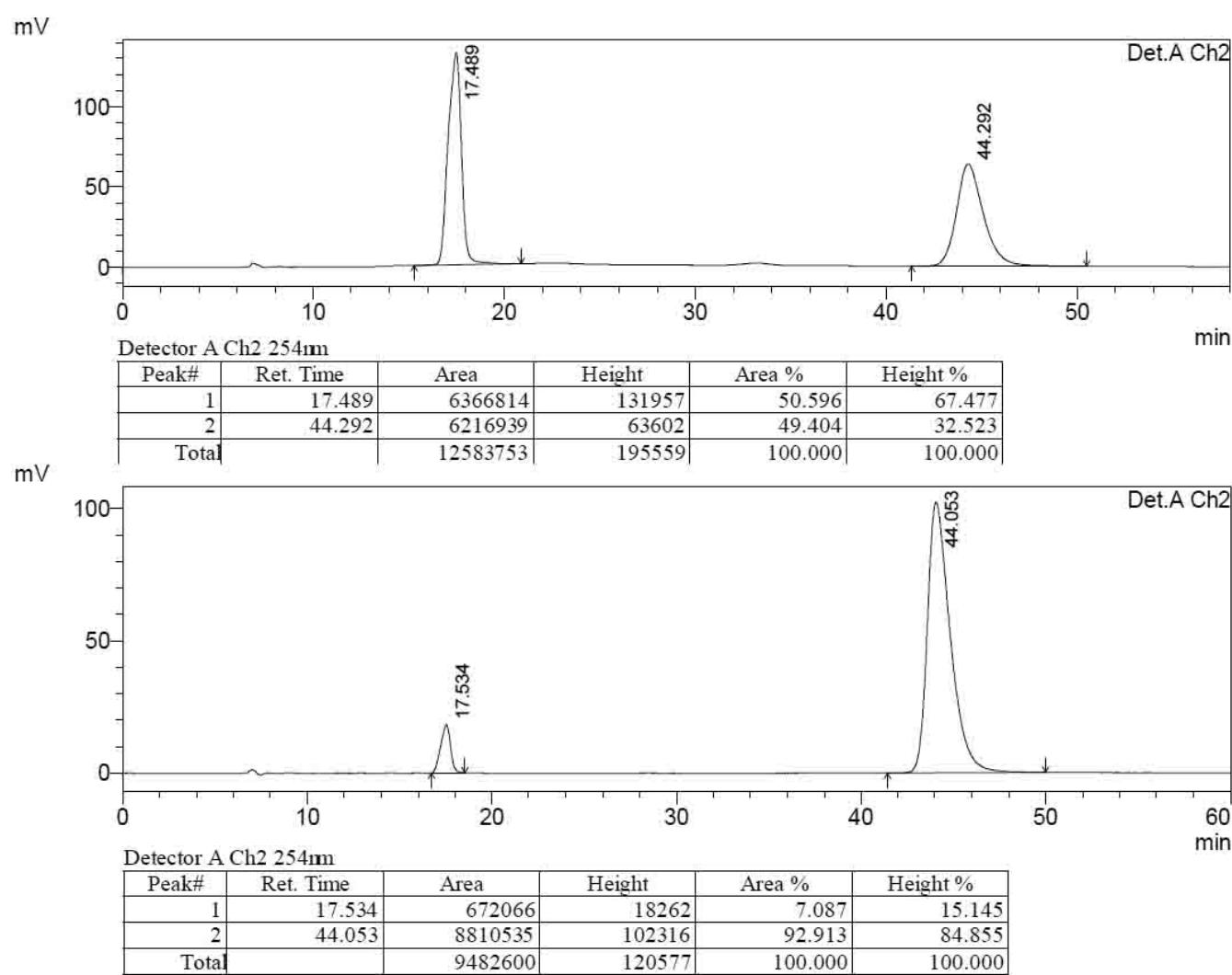
(2S,3R)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-m-tolylpyrrolidine (8h)

White solid, $[\alpha]_D^{26} +52.8$ (c 1.0, CH_2Cl_2 , 84% ee); IR (KBr): 2930, 1527, 1348, 1310, 1165, 1094 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.36 (d, $J = 8.8$ Hz, 2H), 8.04 (d, $J = 8.9$ Hz, 2H), 7.24 (d, $J = 7.6$ Hz, 1H), 7.11 (dd, $J = 7.9$ Hz, 3H), 5.09 (s, 1H), 4.26 (d, $J = 3.8$ Hz, 1H), 3.91 (dt, $J = 9.5, 1.3$ Hz, 1H), 3.64 (ddd, $J = 15.8, 9.3, 6.4$ Hz, 1H), 2.49-2.34 (m, 1H), 2.34 (s, 3H), 2.11 (ddd, $J = 14.5, 6.3, 1.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 150.2, 142.7, 139.5, 138.7, 129.1, 128.9, 128.8, 126.5, 124.1, 123.0, 73.1, 54.2, 33.0, 21.4; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{17}\text{BrN}_2\text{O}_4\text{S}$ m/z [M] $^+$: 424.0087; found: 424.0086. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 254 nm) $t_1 = 14.1$ min (minor), $t_2 = 22.8$ min (major).



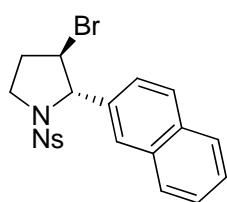
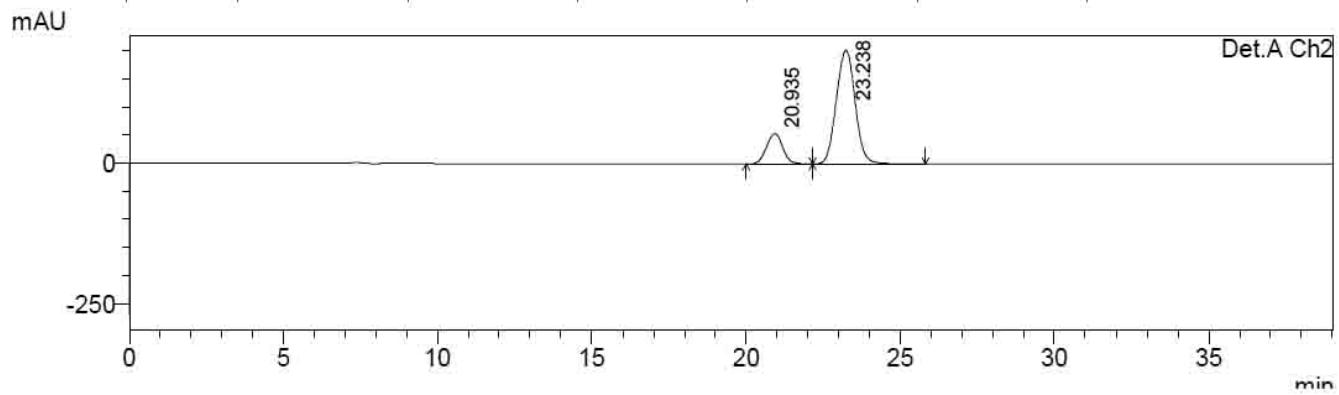
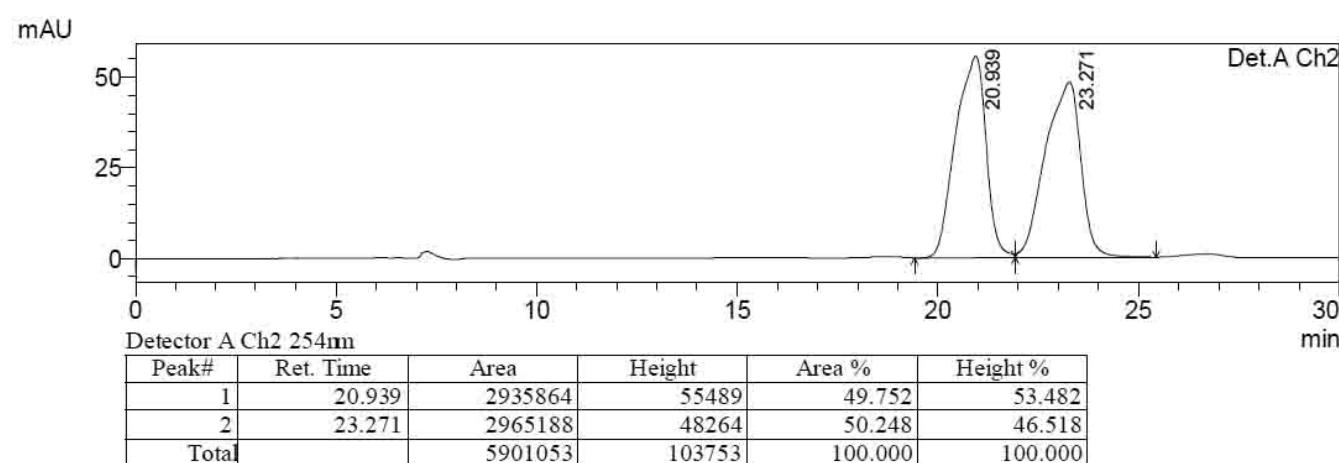
(2S,3R)-3-Bromo-2-(3-methoxyphenyl)-1-(4-nitrophenylsulfonyl)pyrrolidine (8i)

White solid, $[\alpha]_D^{26} +67.1$ (c 0.6, CH_2Cl_2 , 86% ee); IR (KBr): 2971, 1606, 1529, 1353, 1164, 1092 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.37 (d, J = 9.0 Hz, 2H), 8.05 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.85-6.83 (m, 2H), 5.10 (s, 1H), 4.27 (d, J = 3.8 Hz, 1H), 3.90 (dt, J = 9.5, 1.0 Hz, 1H), 3.81 (s, 3H), 3.66 (ddd, J = 15.8, 9.4, 6.3 Hz, 1H), 2.49-2.42 (m, 1H), 2.11 (ddd, J = 14.5, 6.3, 1.3 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 160.0, 150.2, 142.7, 141.2, 130.0, 129.0, 124.1, 118.2, 113.3, 112.1, 55.3, 54.0, 47.1, 33.1; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{17}\text{BrN}_2\text{O}_5\text{S}$ m/z [M] $^+$: 440.0036; found: 440.0044. HPLC (Daicel Chiralpak IA, $i\text{-PrOH}/\text{hexane} = 50/50$, 0.5 mL/min, 254 nm) $t_1 = 17.5$ min (minor), $t_2 = 44.1$ min (major).



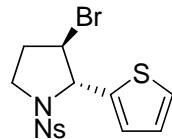
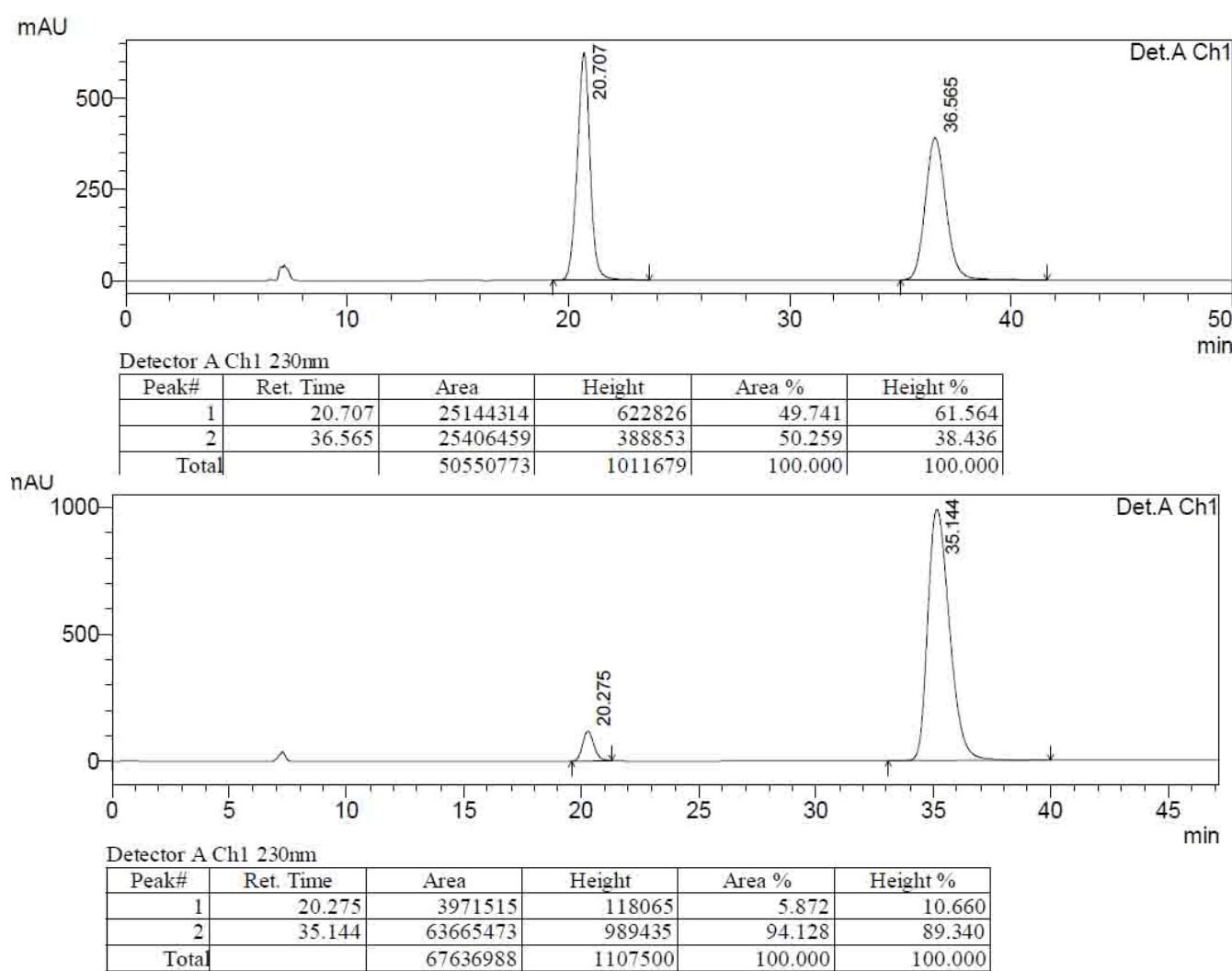
(2S,3R)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-o-tolylpyrrolidine (8j)

White solid, $[\alpha]_D^{26} +30.0$ (*c* 0.5, CH₂Cl₂, 62% ee); IR (KBr): 2974, 1526, 1354, 1159, 1093, 1009 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.39 (d, *J* = 8.9 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.33 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.23-7.18 (m, 3H), 5.22 (s, 1H), 4.13 (d, *J* = 4.1 Hz, 1H), 3.96 (dd, *J* = 8.2 Hz, 1H), 3.68 (ddd, *J* = 15.4, 9.2, 6.2 Hz, 1H), 2.52-2.42 (m, 1H), 2.39 (s, 3H), 2.13 (ddd, *J* = 14.4, 6.3, 1.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 150.3, 142.6, 138.0, 134.4, 130.8, 129.0, 128.3, 126.5, 125.6, 124.2, 71.2, 53.0, 47.3, 32.8, 19.5; HRMS (EI) calcd for C₁₇H₁₇BrN₂O₄S *m/z* [M]⁺: 424.0087; found: 424.0085. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 20/80, 0.5 mL/min, 254 nm) t₁ = 20.9 min (minor), t₂ = 23.2 min (major).



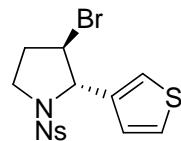
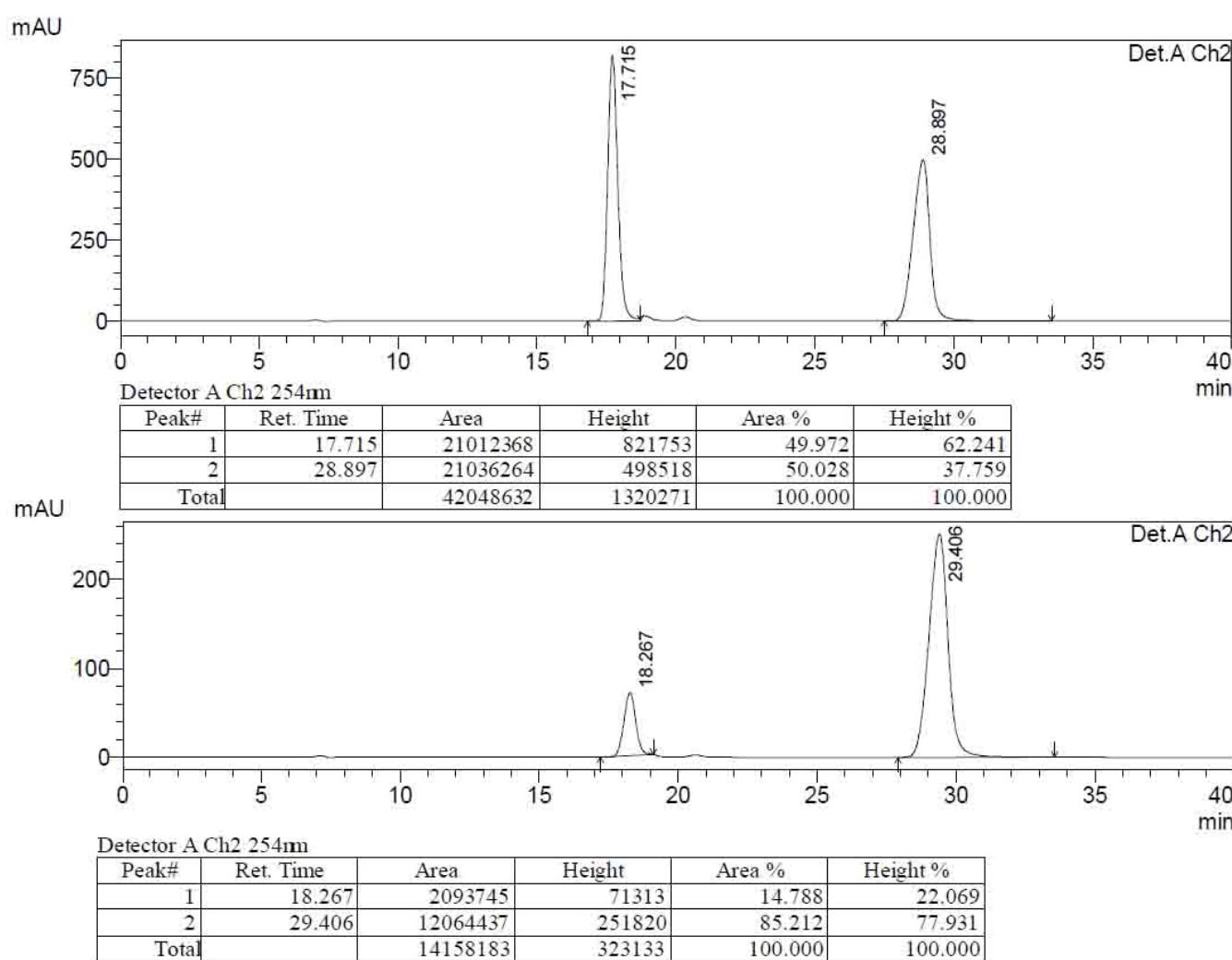
(2S,3R)-3-Bromo-2-(naphthalene-2-yl)-1-(4-nitrophenylsulfonyl)pyrrolidine (8k)

White solid, $[\alpha]_D^{26} +119.6$ (c 0.2, CH_2Cl_2 , 88% ee); IR (KBr): 3106, 1604, 1526, 1343, 1163, 1093 cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2): δ 8.34 (d, $J = 8.9$ Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 2H), 7.86-7.83 (m, 3H), 7.81 (s, 1H), 7.52-7.50 (m, 2H), 7.39 (dd, $J = 8.7, 1.9$ Hz, 1H), 5.24 (s, 1H), 4.36 (d, $J = 4.2$ Hz, 1H), 3.97 (ddd, $J = 9.4, 8.0, 1.4$ Hz, 1H), 3.70 (ddd, $J = 16.0, 9.7, 6.4$ Hz, 1H), 2.53-2.43 (m, 1H), 2.12 (ddd, $J = 14.3, 6.4, 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.4, 142.7, 137.3, 133.2, 129.1, 128.8, 127.7, 126.8, 126.6, 125.3, 124.3, 123.7, 73.3, 54.1, 47.5, 33.2; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{17}\text{BrN}_2\text{O}_4\text{S} m/z [M]^+$: 460.0087; found: 460.0091. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 230 nm) $t_1 = 20.2$ min (minor), $t_2 = 35.1$ min (major).



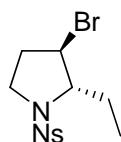
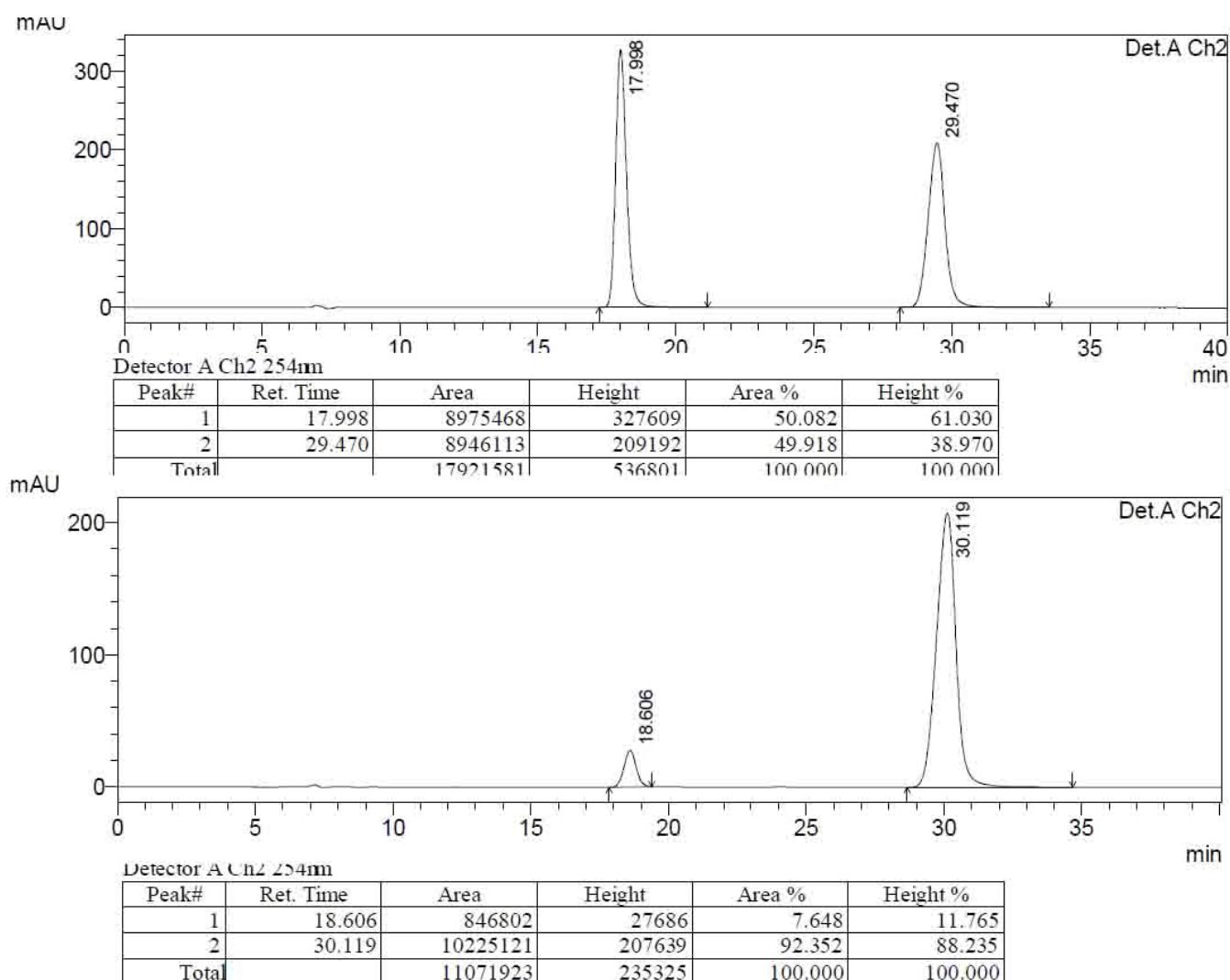
(2S,3R)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-(thiophen-2-yl)pyrrolidine (8l)

White solid, $[\alpha]_D^{26} +39.8$ (*c* 0.5, CH_2Cl_2 , 70% ee); IR (KBr): 3110, 1527, 1350, 1311, 1166, 1094 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.01 (d, *J* = 8.9 Hz, 2H), 7.26-7.24 (m, 1H), 7.04 (ddd, *J* = 3.5, 1.0 Hz, 1H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 5.35 (s, 1H), 4.34 (d, *J* = 4.4 Hz, 1H), 3.82 (ddd, *J* = 9.4, 8.0, 1.3 Hz, 1H), 3.66 (ddd, *J* = 15.8, 9.4, 6.4 Hz, 1H), 2.67-2.60 (m, 1H), 2.21 (ddd, *J* = 14.3, 6.4, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 150.2, 143.5, 142.9, 128.9, 127.3, 125.7, 125.6, 124.1, 69.1, 53.4, 46.6, 33.8; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{13}\text{BrN}_2\text{O}_4\text{S}_2$ *m/z* [M] $^+$: 415.9495; found: 415.9495. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 254 nm) t_1 = 18.3 min (minor), t_2 = 29.4 min (major).



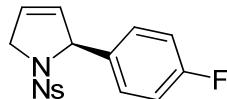
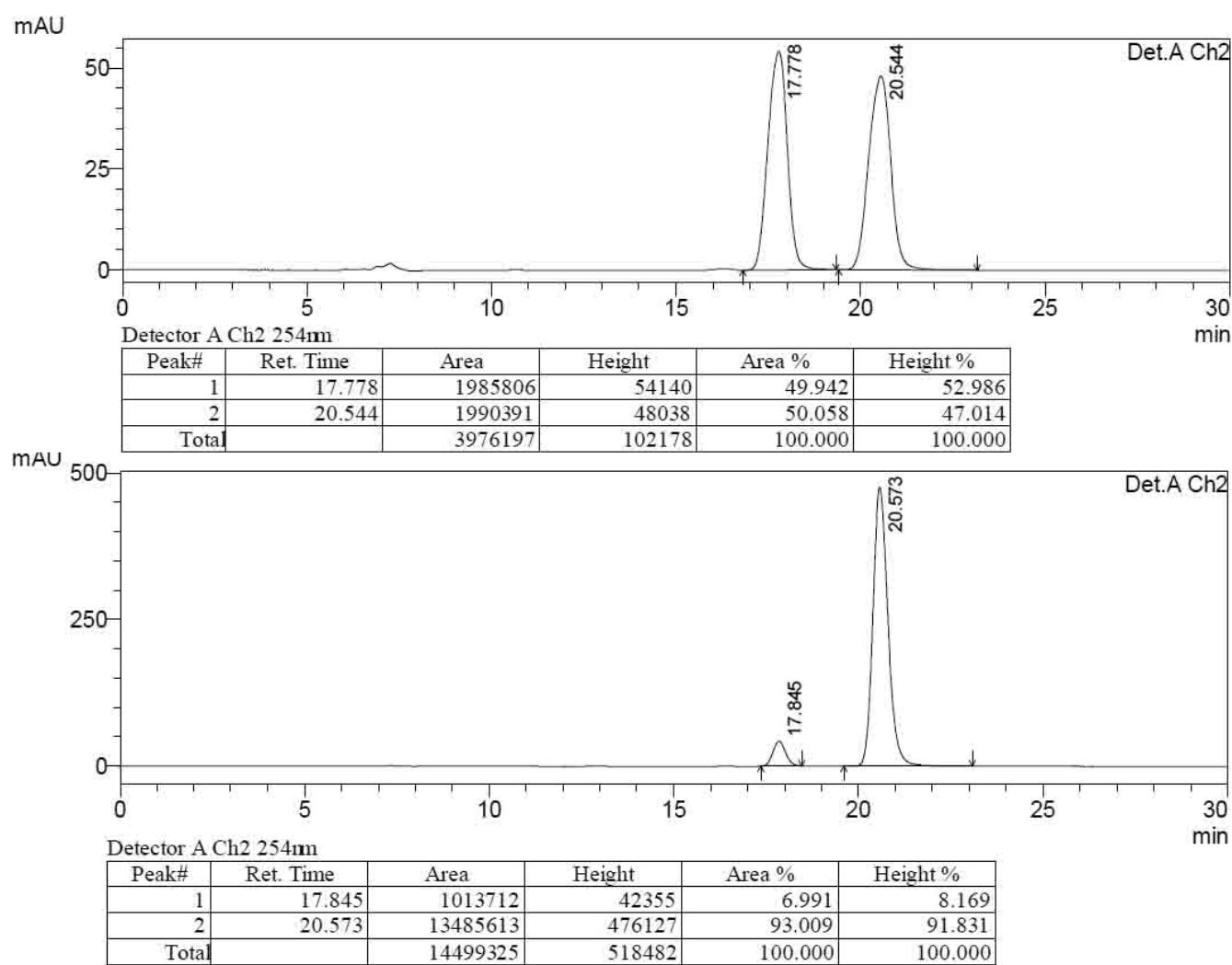
(2*S*,3*R*)-3-Bromo-1-(4-nitrophenylsulfonyl)-2-(thiophen-3-yl)pyrrolidine (8m)

White solid, $[\alpha]_D^{26} +66.4$ (*c* 0.5, CH₂Cl₂, 84% ee); IR (KBr): 2925, 1528, 1465, 1349, 1167, 1096 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 9.3 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.32 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.30-7.28 (m, 1H), 6.96 (dd, *J* = 4.9, 1.2 Hz, 1H), 5.15 (s, 1H), 4.32 (d, *J* = 4.3 Hz, 1H), 3.85 (ddd, *J* = 10.4, 8.2, 1.3 Hz, 1H), 3.63 (ddd, *J* = 16.3, 9.3, 6.4 Hz, 1H), 2.53-2.43 (m, 1H), 2.15 (ddd, *J* = 14.3, 6.4, 1.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 150.2, 142.7, 141.0, 129.0, 127.3, 125.2, 124.1, 122.8, 69.7, 52.9, 46.7, 33.6; HRMS (EI) calcd for C₁₄H₁₃BrN₂O₄S₂ *m/z* [M]⁺: 415.9495; found: 415.9497. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 254 nm) t₁ = 18.6 min (minor), t₂ = 30.1 min (major).



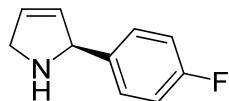
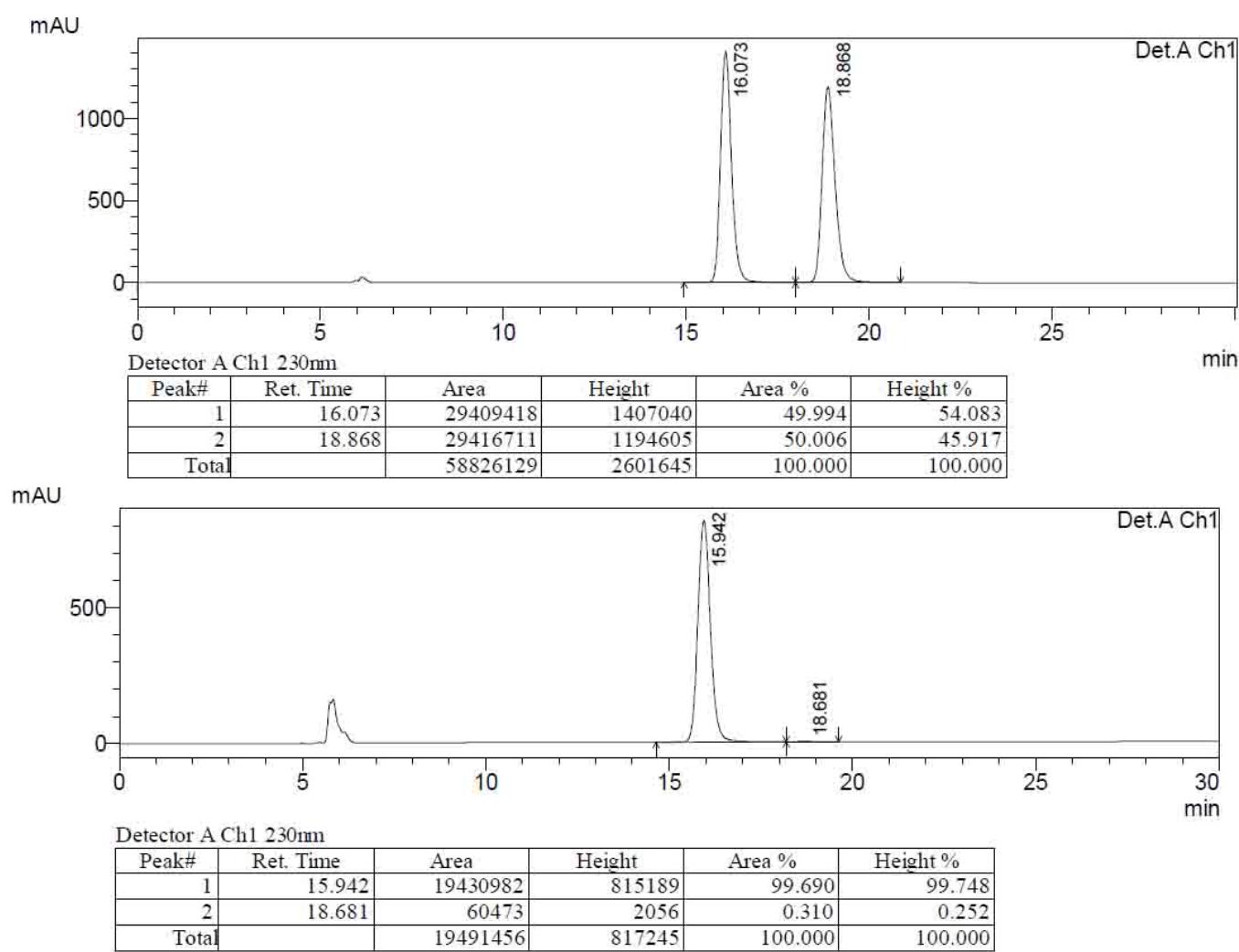
(2*S*,3*R*)-3-Bromo-2-ethyl-1-(4-nitrophenylsulfonyl)pyrrolidine (8n)

White solid, $[\alpha]_D^{26} +29.5$ (*c* 0.6, CH₂Cl₂, 86% ee); IR (KBr): 2974, 1529, 1351, 1163, 1092, 1000 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.39 (d, *J* = 9.0 Hz, 2H), 8.07 (d, *J* = 9.0 Hz, 2H), 4.22 (d, *J* = 4.4 Hz, 1H), 3.82 (dd, *J* = 9.8, 4.5 Hz, 1H), 3.70 (ddd, *J* = 9.2, 8.0, 1.0 Hz, 1H), 3.38 (ddd, *J* = 15.7, 9.4, 6.3 Hz, 1H), 2.47-2.41 (m, 1H), 2.11 (ddd, *J* = 14.3, 6.3, 1.0 Hz, 1H), 1.95-1.87 (m, 1H), 1.53-1.46 (m, 1H), 1.01 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 150.3, 142.1, 129.1, 124.1, 72.5, 50.4, 46.6, 34.0, 30.2, 10.6; HRMS (EI) calcd for C₁₂H₁₅BrN₂O₄S *m/z* [M]⁺: 361.9930; found: 361.9927. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 35/65, 0.5 mL/min, 254 nm) t₁ = 17.8 min (minor), t₂ = 20.6 min (major).



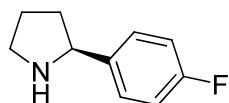
(S)-2-(4-fluorophenyl)-1-(4-nitrophenylsulfonyl)-2,5-dihydro-1H-pyrrole (10)

White solid, $[\alpha]_D^{26} -219.6$ (c 1.0, CH_2Cl_2 , 99% ee); ^1H NMR (400 MHz, CDCl_3): δ 8.18 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.14 (dd, J = 8.6, 5.3 Hz, 2H), 6.93 (dd, J = 8.6 Hz, 2H), 5.90 (ddd, J = 6.0, 3.9, 1.9 Hz, 1H), 5.69 (ddd, J = 6.4, 4.4, 2.1 Hz, 1H), 5.60 (ddd, J = 6.0, 4.3, 2.0 Hz, 1H), 4.45 (ddd, J = 14.3, 4.5, 2.2 Hz, 1H), 4.25 (dddd, J = 14.3, 5.7, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.6 (d, J = 246.4 Hz), 149.7, 144.8, 135.0 (d, J = 2.9 Hz), 130.2, 129.4 (d, J = 8.8 Hz), 128.0, 124.7, 123.9, 115.4 (d, J = 21.2 Hz), 69.6, 55.2; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{13}\text{FN}_2\text{O}_4\text{S}$ m/z [M] $^+$: 348.0575; found: 348.0575. HPLC (Daicel Chiralpak IA, *i*-PrOH/hexane = 25/75, 0.6 mL/min, 230 nm) t_1 = 15.9 min (major), t_2 = 18.7 min (minor).



(S)-2-(4-Fluorophenyl)-2,5-dihydro-1*H*-pyrrole (11)

White solid, $[\alpha]_D^{26} -236.5$ (*c* 1.0, CH_2Cl_2 , 99% ee); IR (KBr): 3415, 1604, 1508, 1404, 1223 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.26 (dd, *J* = 8.6, 5.7 Hz, 2H), 7.00 (dd, *J* = 8.7 Hz, 2H), 6.02 (ddd, *J* = 5.9, 4.0, 2.0 Hz, 1H), 5.82 (ddd, *J* = 5.7, 4.4, 1.9 Hz, 1H), 5.07-5.04 (m, 1H), 3.95 (dddd, *J* = 14.7, 4.8, 2.1 Hz, 1H), 3.84 (dddd, *J* = 14.7, 4.0, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 162.1 (d, *J* = 243.2 Hz), 140.0 (d, *J* = 3.7 Hz), 131.8, 129.1, 128.5 (d, *J* = 8.2 Hz), 115.3 (d, *J* = 21.0 Hz), 68.3, 54.0; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{FN}$ *m/z* [M + H] $^+$: 164.0870; found: 164.0867.



(S)-2-(4-fluorophenyl)pyrrolidine (12)

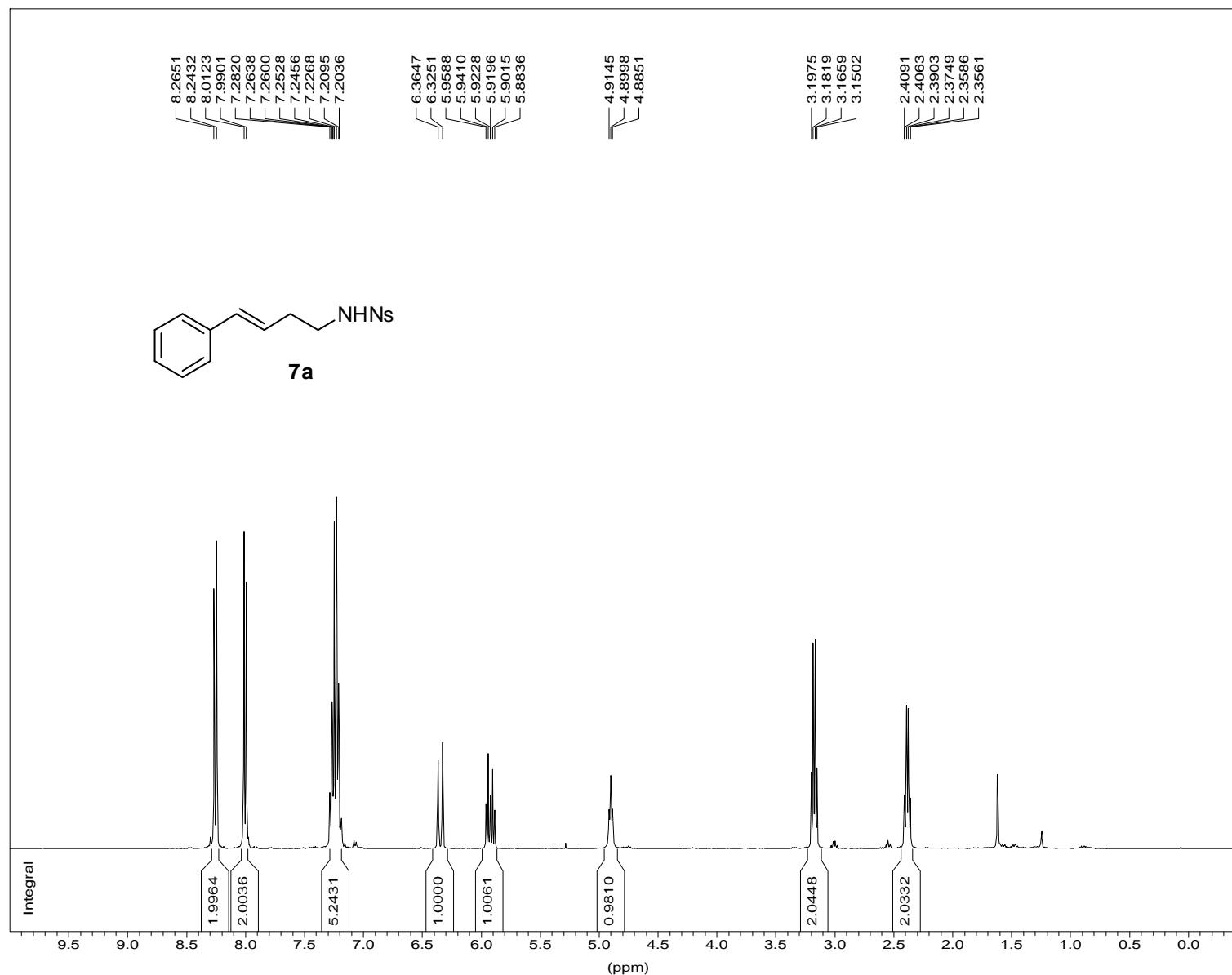
White solid, $[\alpha]_D^{26} -57.0$ (*c* 0.8, CH_2Cl_2 , 99% ee); IR (KBr): 3413, 2966, 1605, 1510, 1408, 1224 cm^{-1} ;

¹H NMR (300 MHz, CDCl₃): δ 7.32 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.00 (dd, *J* = 8.7 Hz, 2H), 4.10 (t, *J* = 7.6 Hz, 1H), 3.19 (ddd, *J* = 13.1, 7.7, 5.5 Hz, 1H), 3.01 (dd, *J* = 13.2, 7.7 Hz, 1H), 2.29 (brs, 1H), 2.17 (dddd, *J* = 12.2, 7.5, 4.9 Hz, 1H), 2.00-1.78 (m, 2H), 1.70-1.58 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 161.8 (d, *J* = 242.7 Hz), 140.0, 128.0 (d, *J* = 7.6 Hz), 115.1 (d, *J* = 21.3 Hz), 61.9, 46.8, 34.3, 25.4; MS (ESI) *m/z* [M + H]⁺: 166.0.

References

- (1) Zhou, L.; Tan, C. K.; Jiang, X.; Chen, F.; Yeung, Y. -Y. *J. Am. Chem. Soc.* **2010**, *132*, 15474-15476.
- (2) Zhou, L.; Chen, J.; Tan, C. K.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2011**, *133*, 9164-9167.

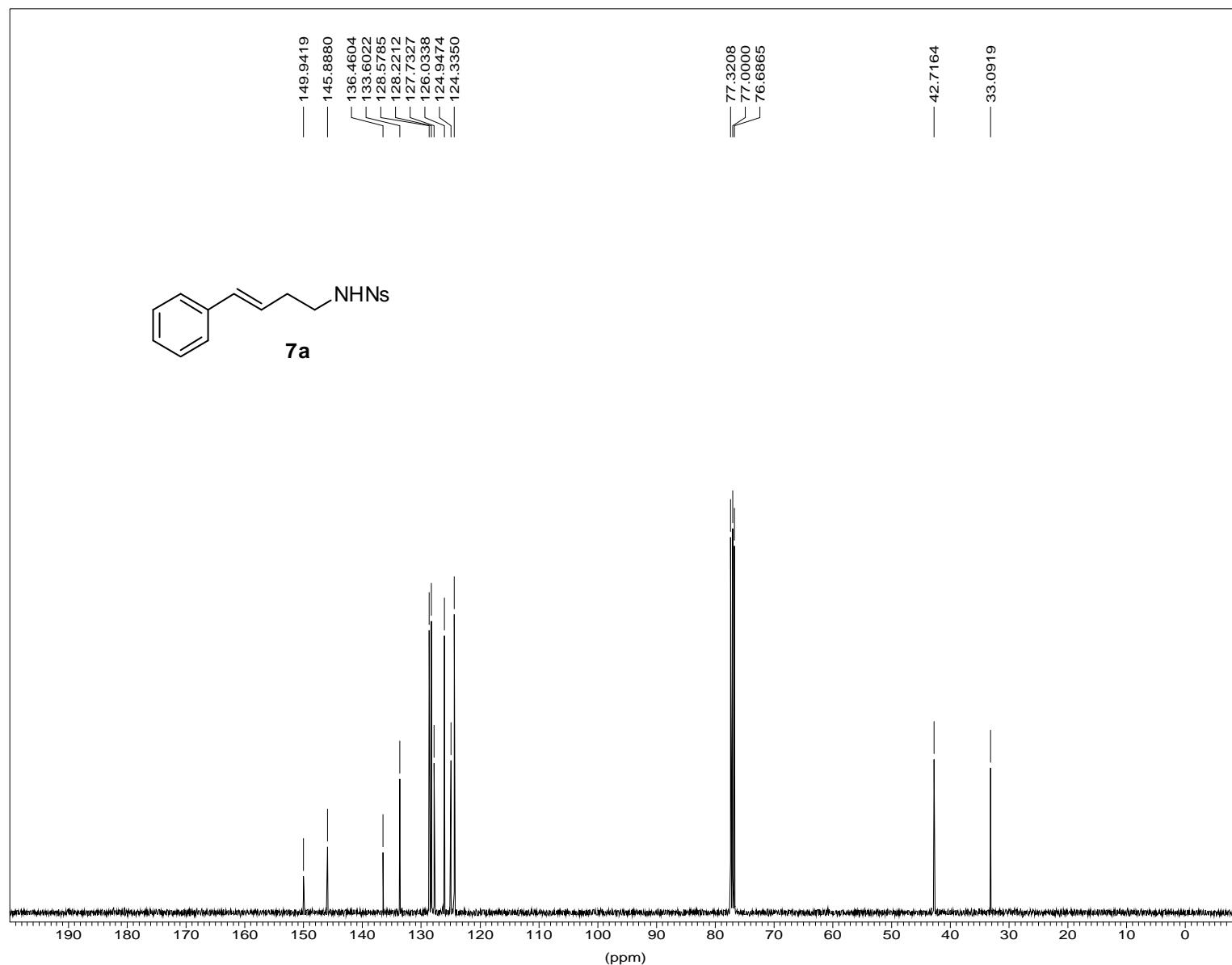
cj1196



*** Current Data Parameters ***

NAME	:	dec08cj
EXPNO	:	1
PROCNO	:	1
*** Acquisition Parameters ***		
BF1	:	400.130000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	2470.97 Hz
PULPROG	:	zg30
SFO1	:	400.1324710 MHz
SOLVENT	:	CDCl3
SW	:	20.5524 ppm
*** Processing Parameters ***		
LB	:	0.30 Hz
PHC0	:	-41.504 degree
PHC1	:	-18.762 degree

cj1196



*** Current Data Parameters ***

NAME : dec08cj
EXPNO : 2
PROCNO : 1

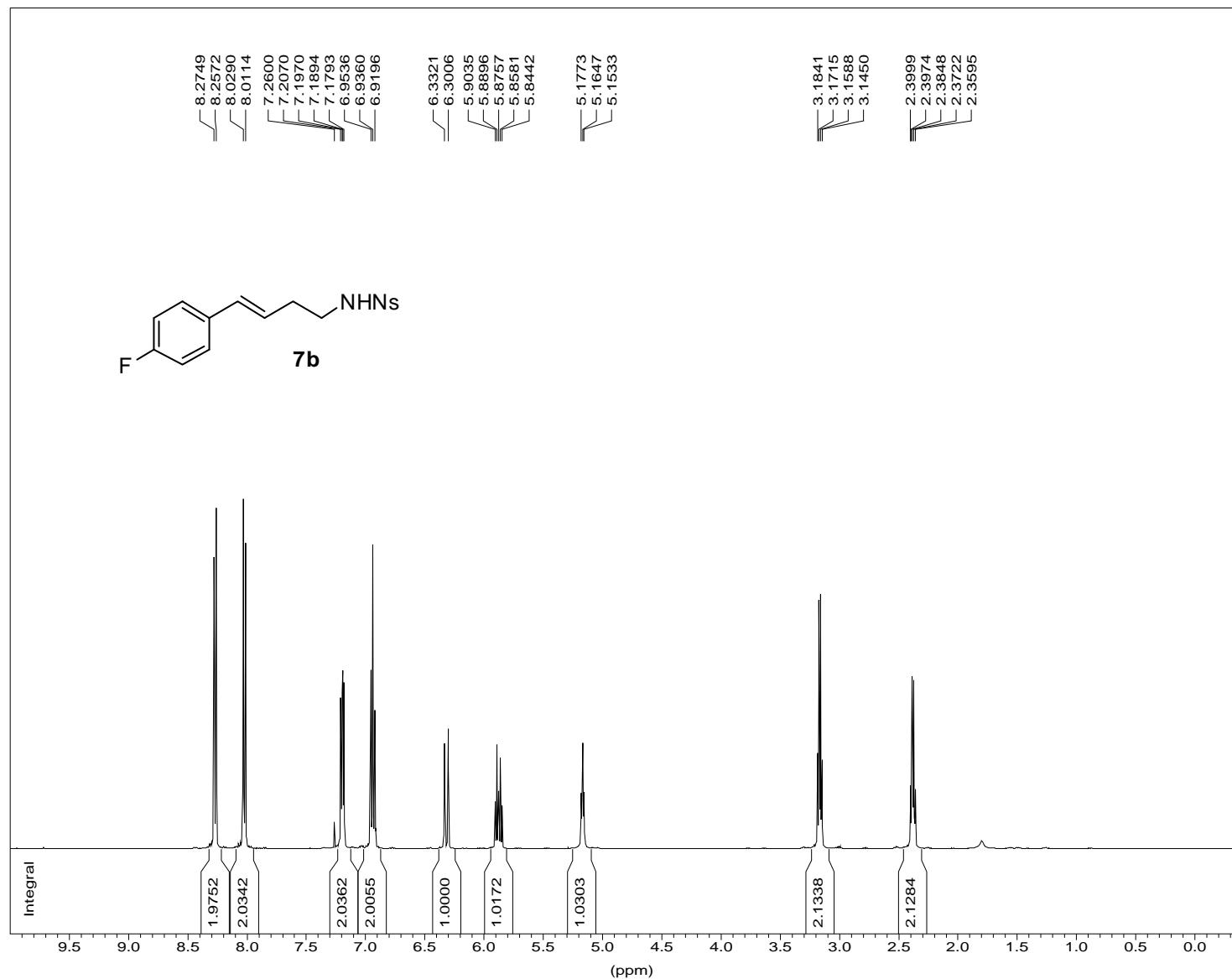
*** Acquisition Parameters ***

BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 500
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 91.612 degree
PHC1 : -52.299 degree

1H AMX500 cj2046b



*** Current Data Parameters ***

NAME : ck0923
EXPNO : 1
PROCNO : 1

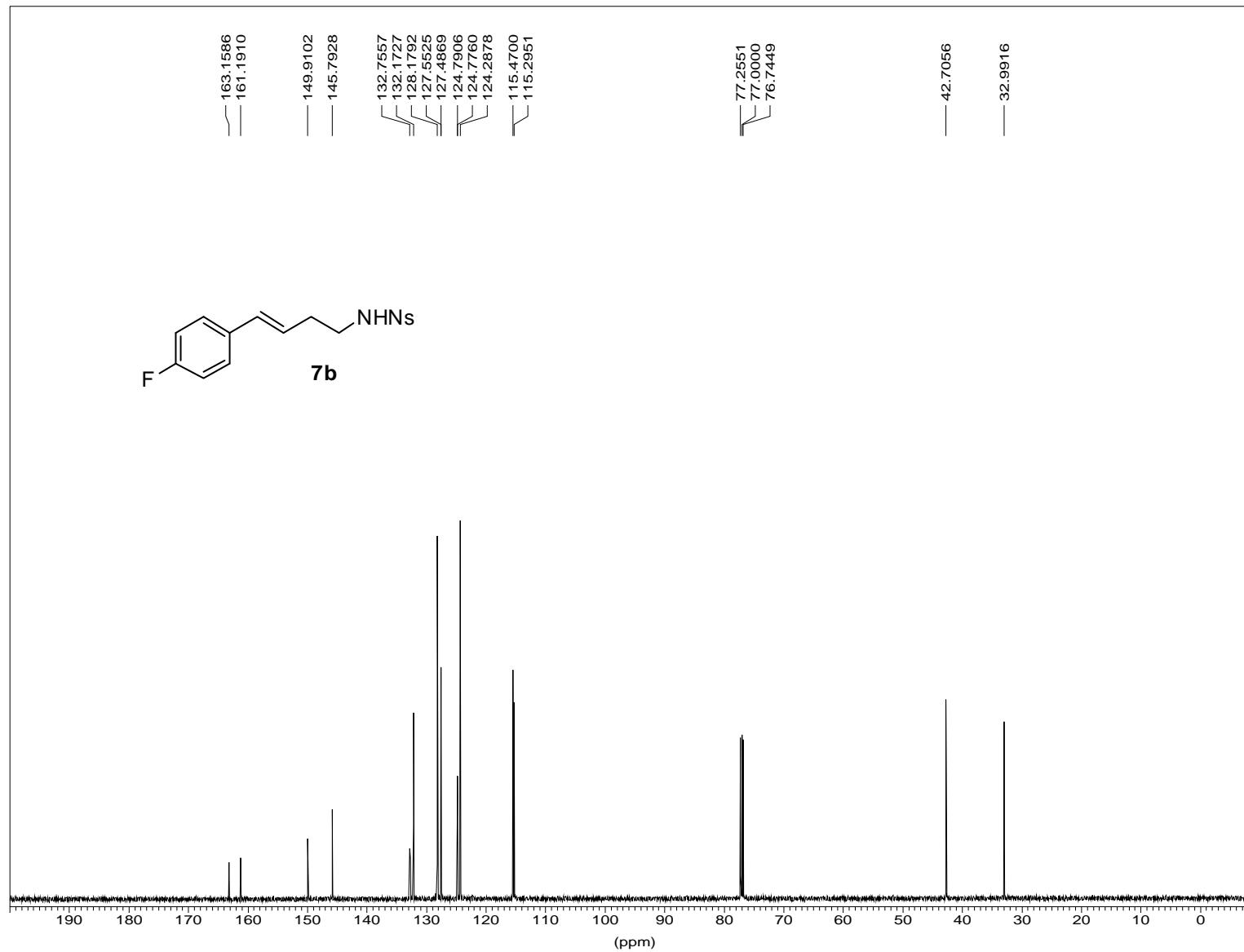
*** Acquisition Parameters ***

BF1 : 500.1300000 MHz
LOCMUC : 2H
NS : 8
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : 164.298 degree
PHC1 : -0.182 degree

13C AMX500 cj2046b



*** Current Data Parameters ***

NAME : ck0923

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 125.7577890

LOCNUC : 2H

NS : 200

01 : 13204.57

PULPROG : zgpg30

SF01 : 125.7709936

SOLVENT : CDCl₃

SW : 238.7675

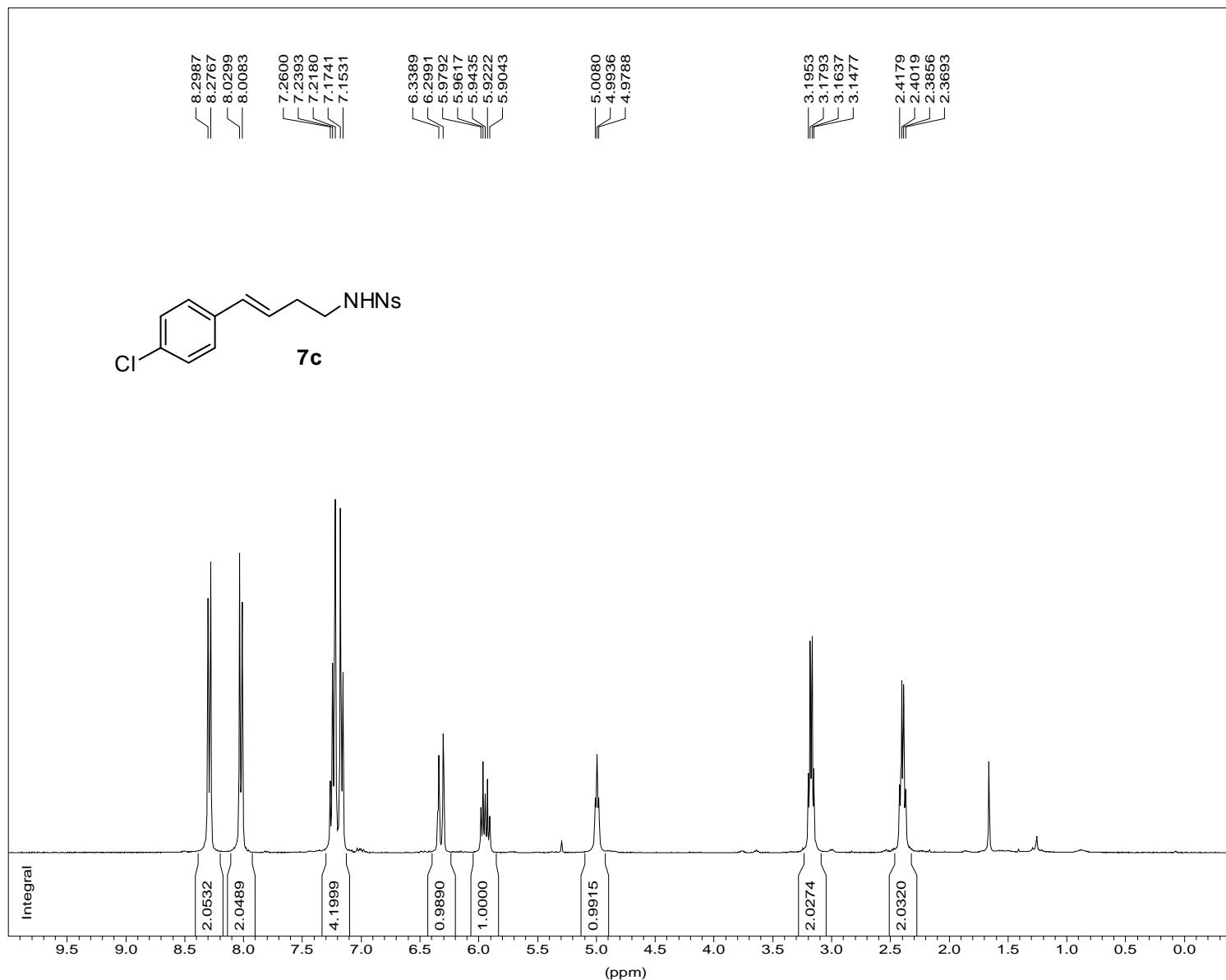
Processing Parameters

LB . 1.00

PHQ0 . 312.55

11101 : 54.450

cj1281



*** Current Data Parameters ***

NAME : aug02cj
EXPNO : 5
PROCNO : 1

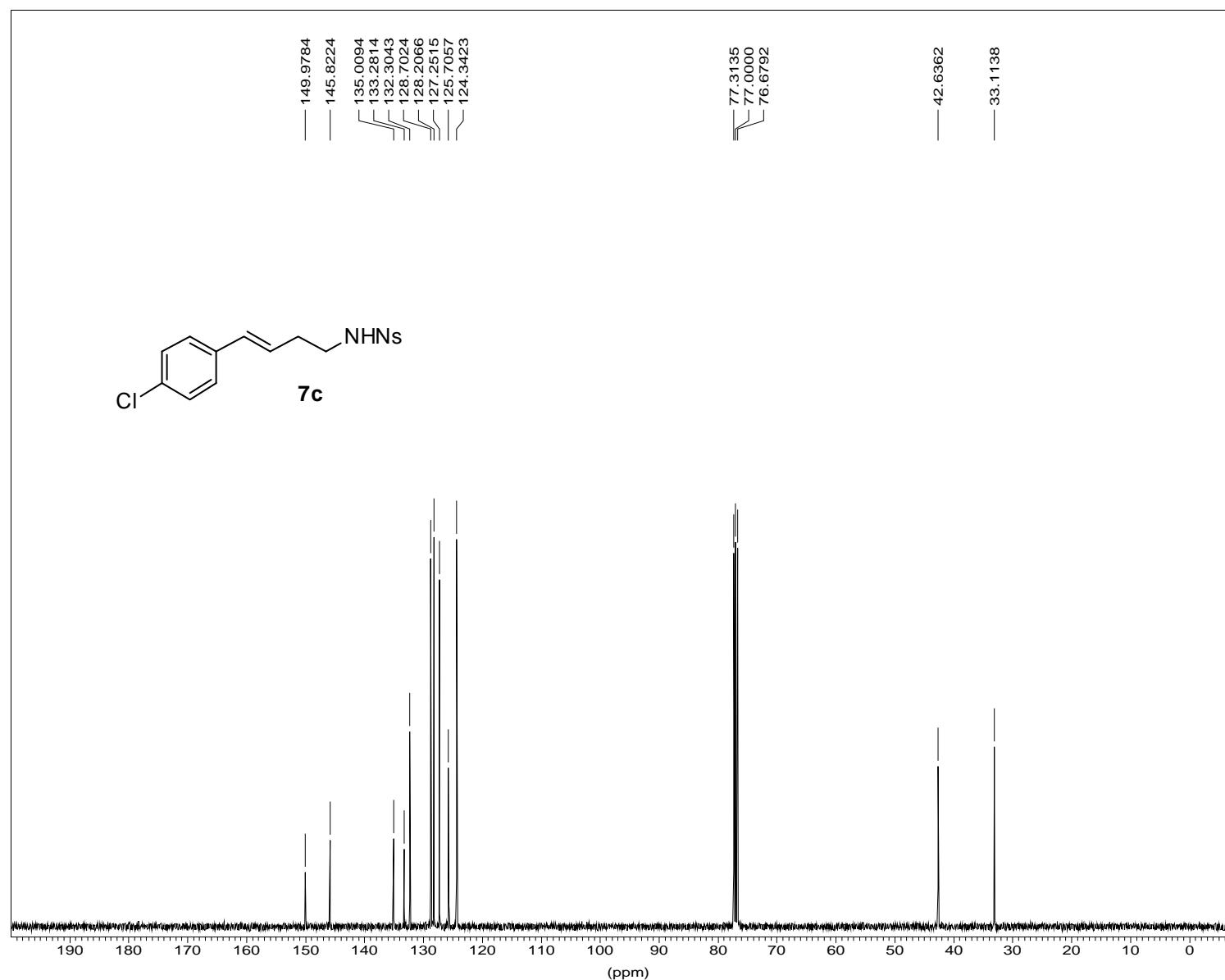
*** Acquisition Parameters ***

BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.5524 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -45.794 degree
PHC1 : -13.950 degree

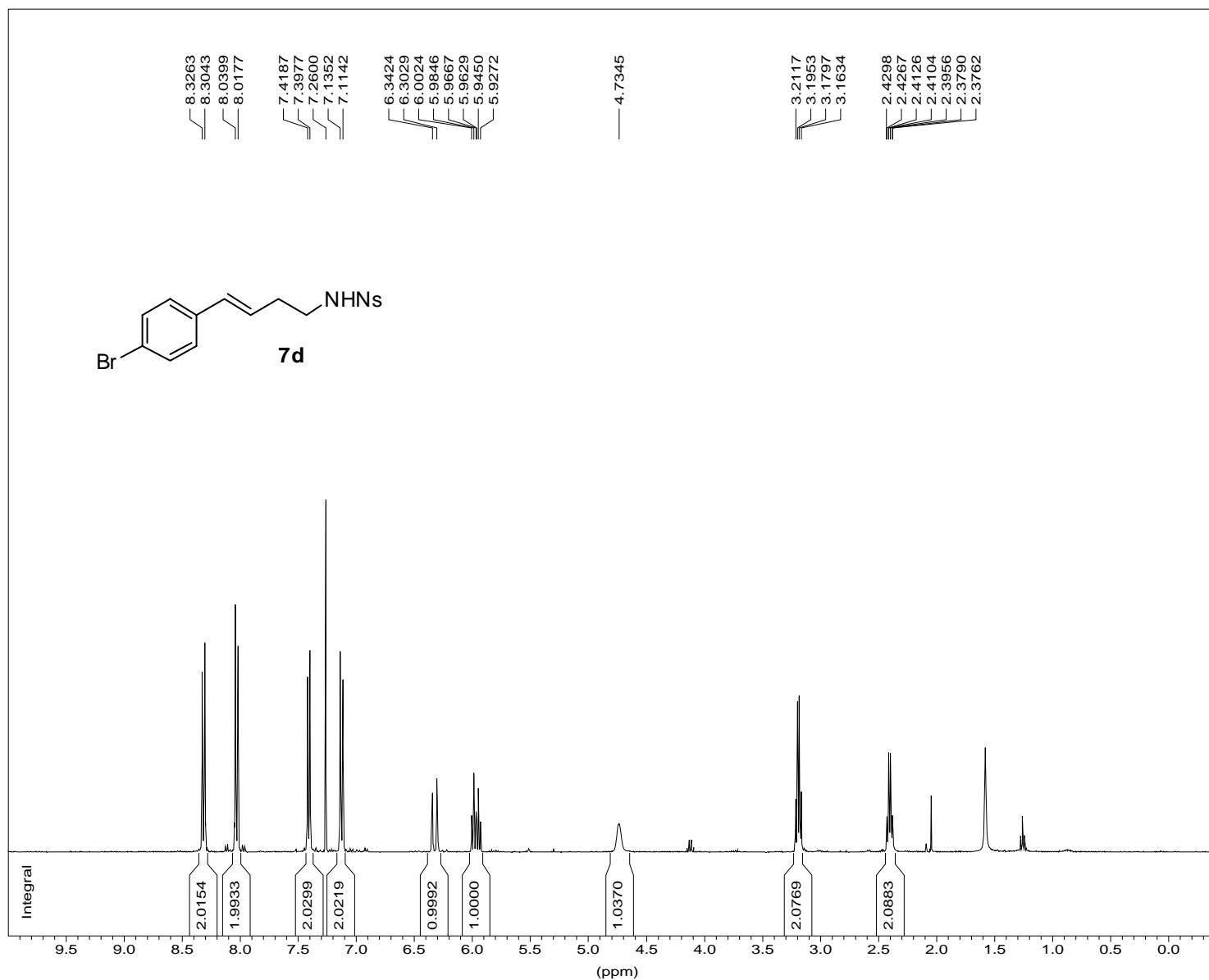
cj1281



*** Current Data Parameters ***

NAME : aug02cj
EXPNO : 6
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 500
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 94.386 degree
PHC1 : -67.881 degree

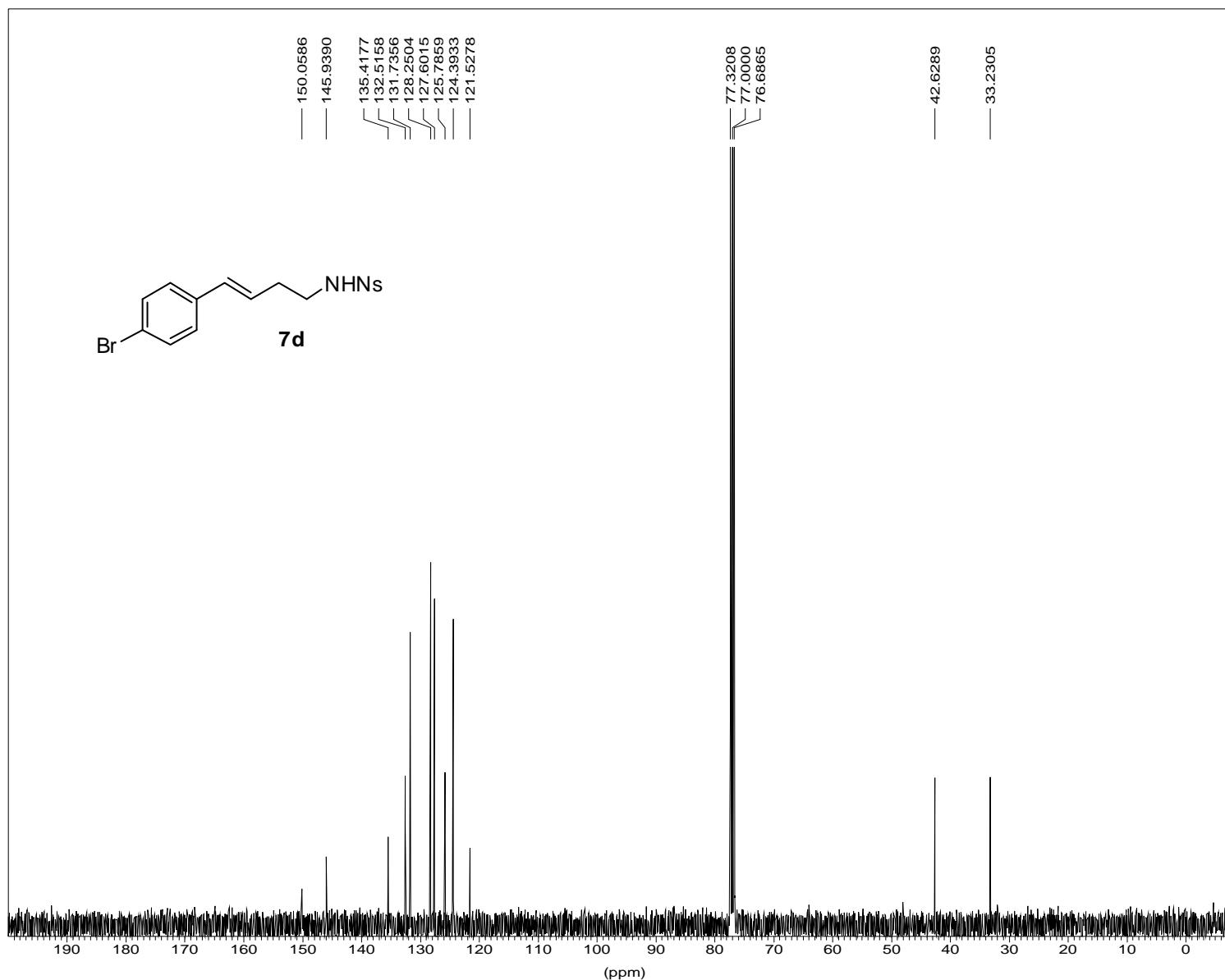
cj1255C



*** Current Data Parameters ***

NAME : oct22cj
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.5524 ppm
*** Processing Parameters ***
LB : 0.30 Hz
PHC0 : -44.832 degree
PHC1 : -11.768 degree

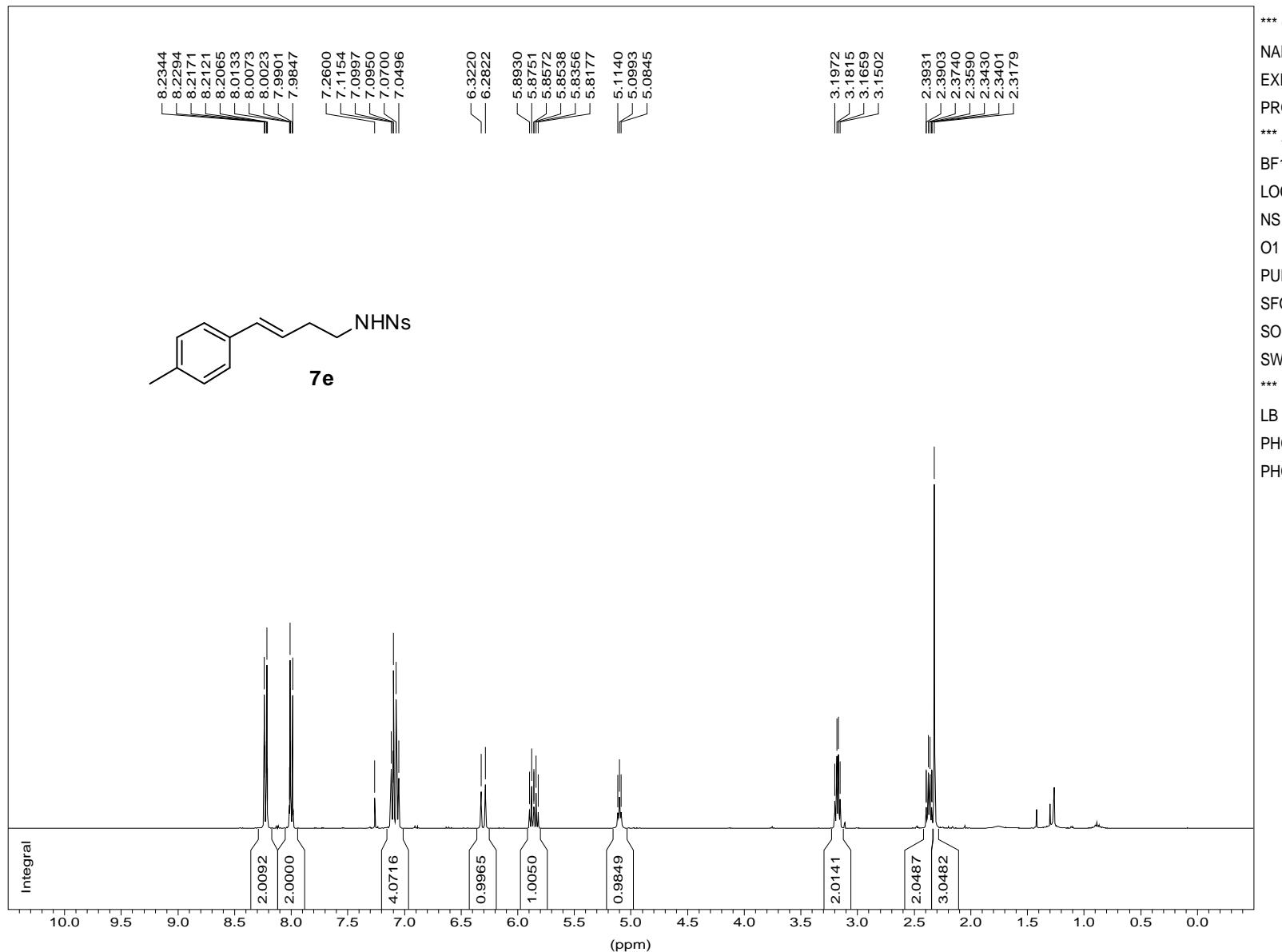
cj1255C



*** Current Data Parameters ***

NAME : oct22cj
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
RF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 300
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 110.320 degree
PHC1 : -31.047 degree

cj2034



*** Current Data Parameters ***

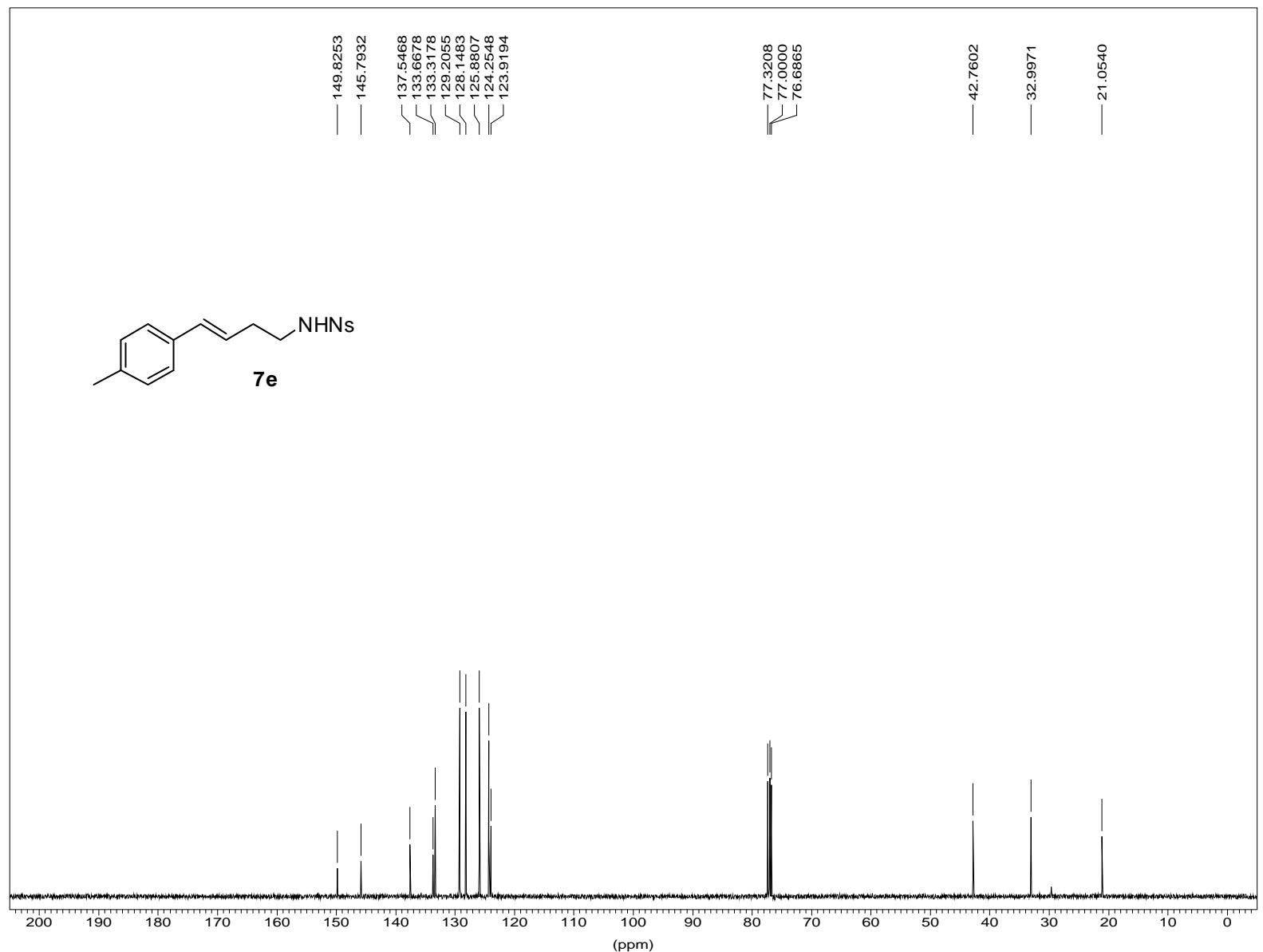
NAME : aug31zl
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***

BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl₃
SW : 20.5524 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -48.869 degree
PHC1 : -17.207 degree

cj2034



*** Current Data Parameters ***

NAME : aug31z1

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 100.6127690 MHz

LOCNUC : 2H

NS : 97

O1 : 11067.40 Hz

PULPROG : zgpg30

SFO1 : 100.6238364 MHz

SOLVENT : CDCl₃

SW : 238.8943 ppm

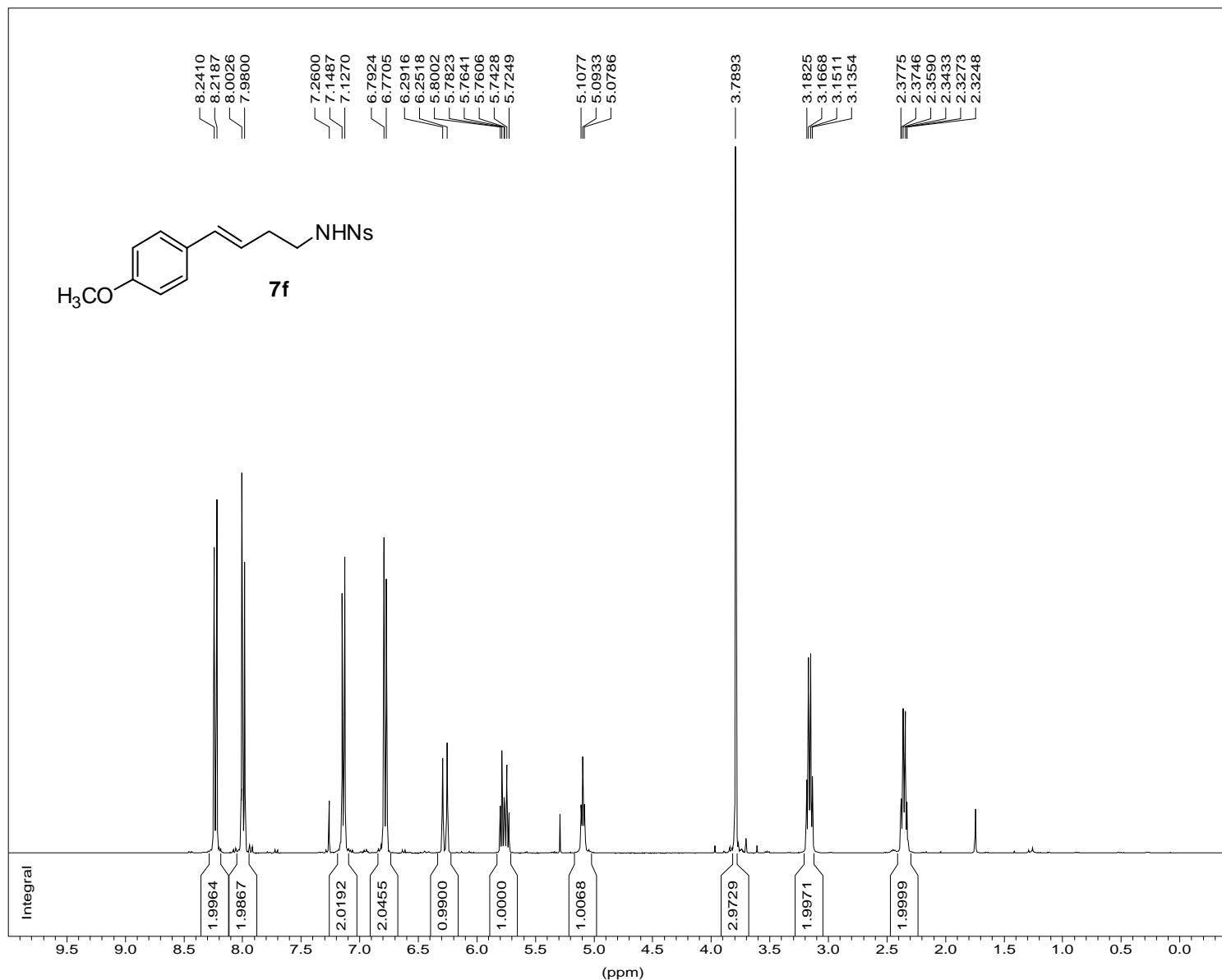
*** Processing Parameters ***

LB : 1.00 Hz

PHC0 : 95.060 degree

PHC1 : -67.724 degree

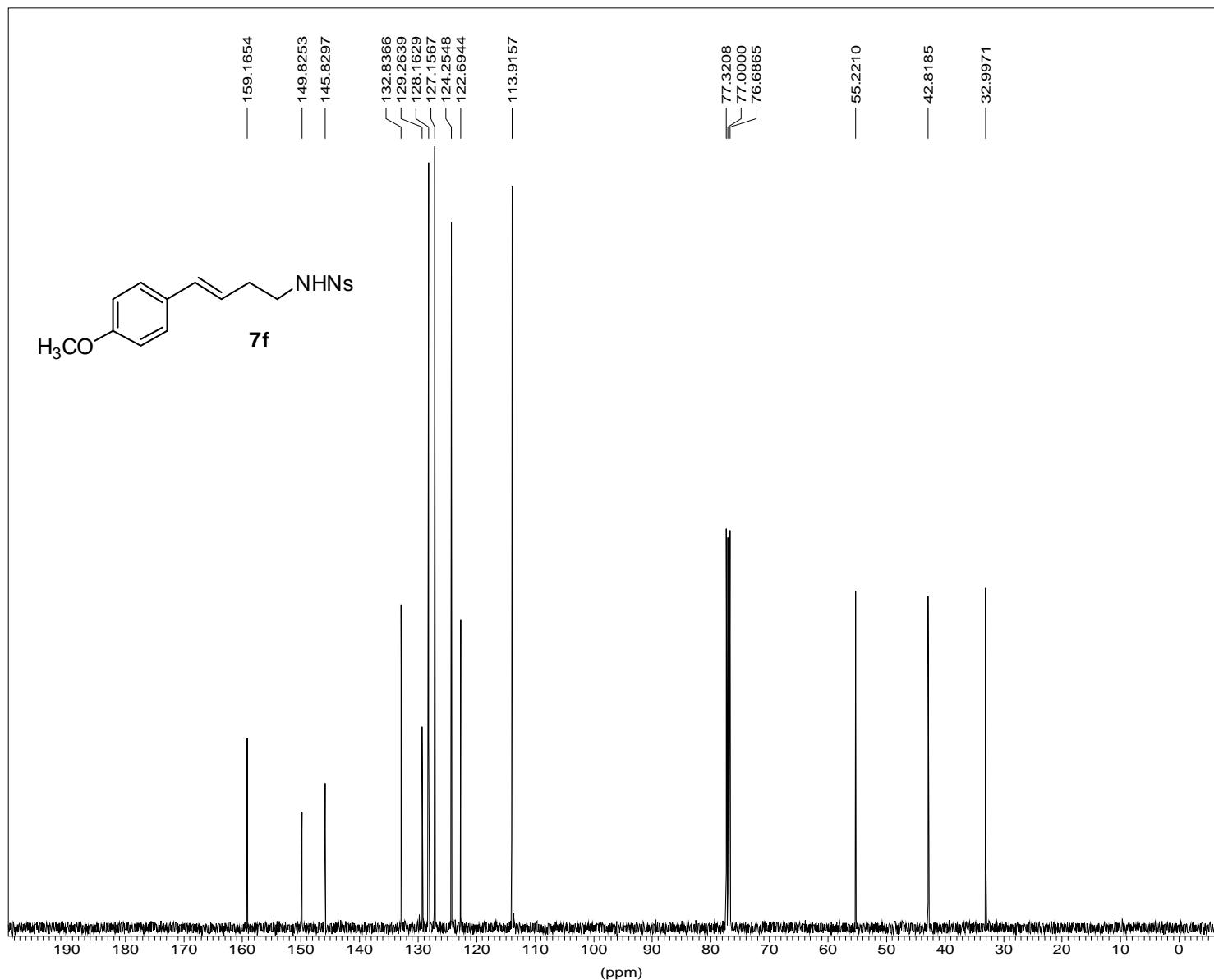
cj1289-1



*** Current Data Parameters ***

NAME : dec03cj
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.5524 ppm
*** Processing Parameters ***
LB : 0.30 Hz
PHC0 : -54.560 degree
PHC1 : -18.735 degree

cj1289-1



*** Current Data Parameters ***

NAME : dec03cj
EXPNO : 2
PROCNO : 1

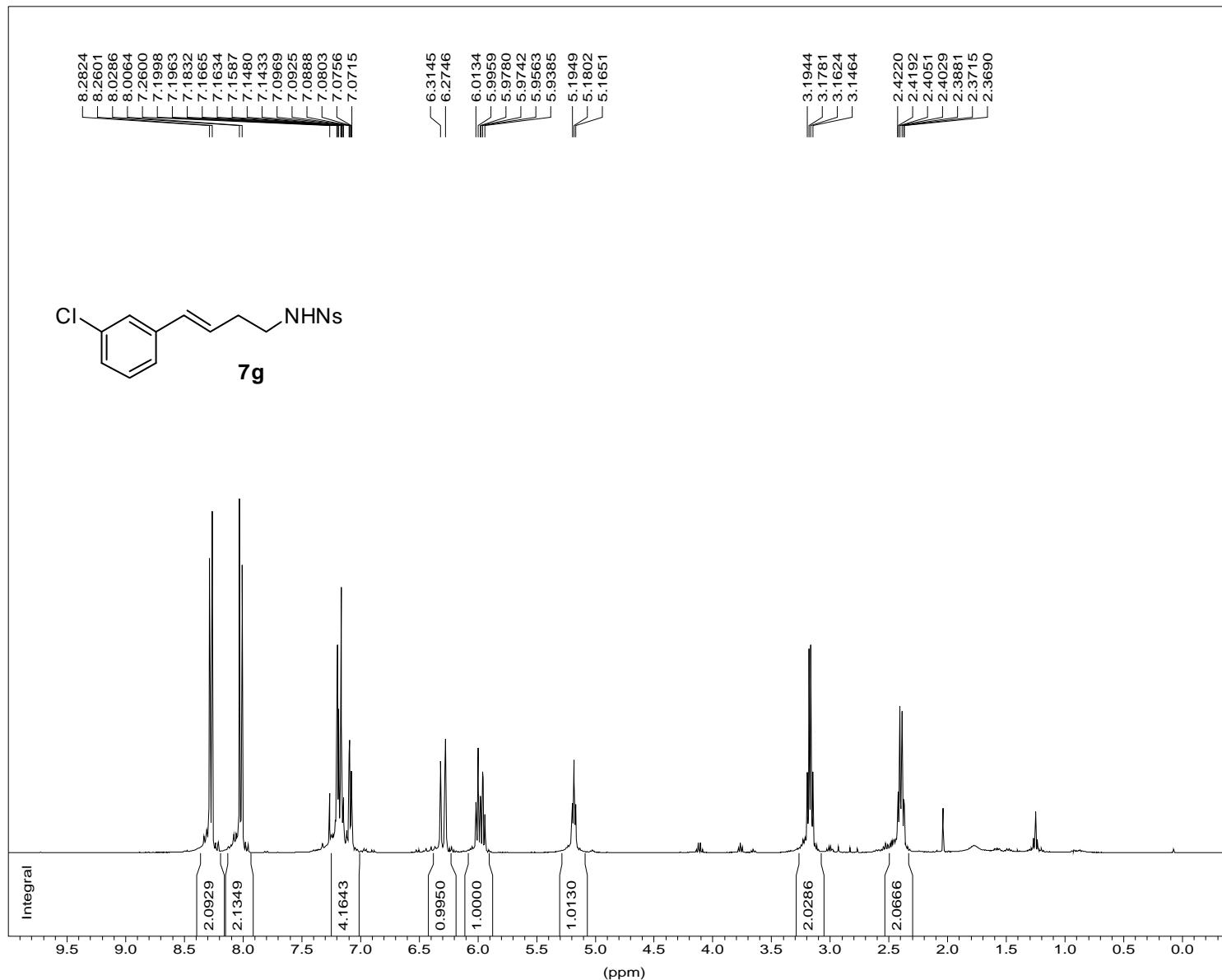
*** Acquisition Parameters ***

BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 200
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 91.600 degree
PHC1 : -58.119 degree

cj1254B



*** Current Data Parameters ***

NAME : jul05zl

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 400.1300000 MHz

LOCNUC : 2H

NS : 8

O1 : 2470.97 Hz

PULPROG : zg30

SFO1 : 400.1324710 MHz

SOLVENT : CDCl₃

SW : 20.5524 ppm

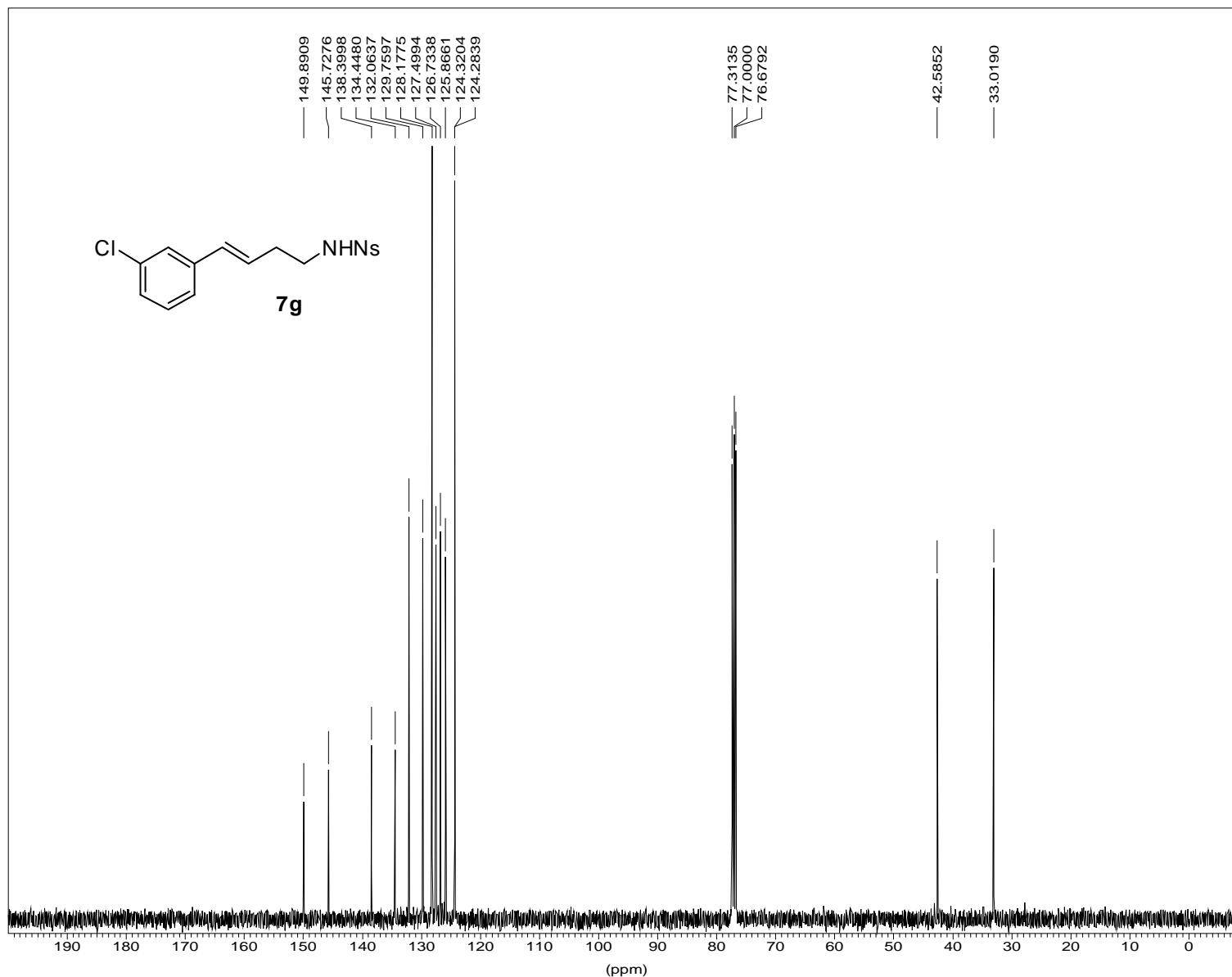
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : -50.271 degree

PHC1 : -12.560 degree

cj1254B



*** Current Data Parameters ***

NAME : jul05zl

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 100.6127690 MHz

LOCNUC : 2H

NS : 115

O1 : 11067.40 Hz

PULPROG : zgpg30

SFO1 : 100.6238364 MHz

SOLVENT : CDCl₃

SW : 238.8943 ppm

*** Processing Parameters ***

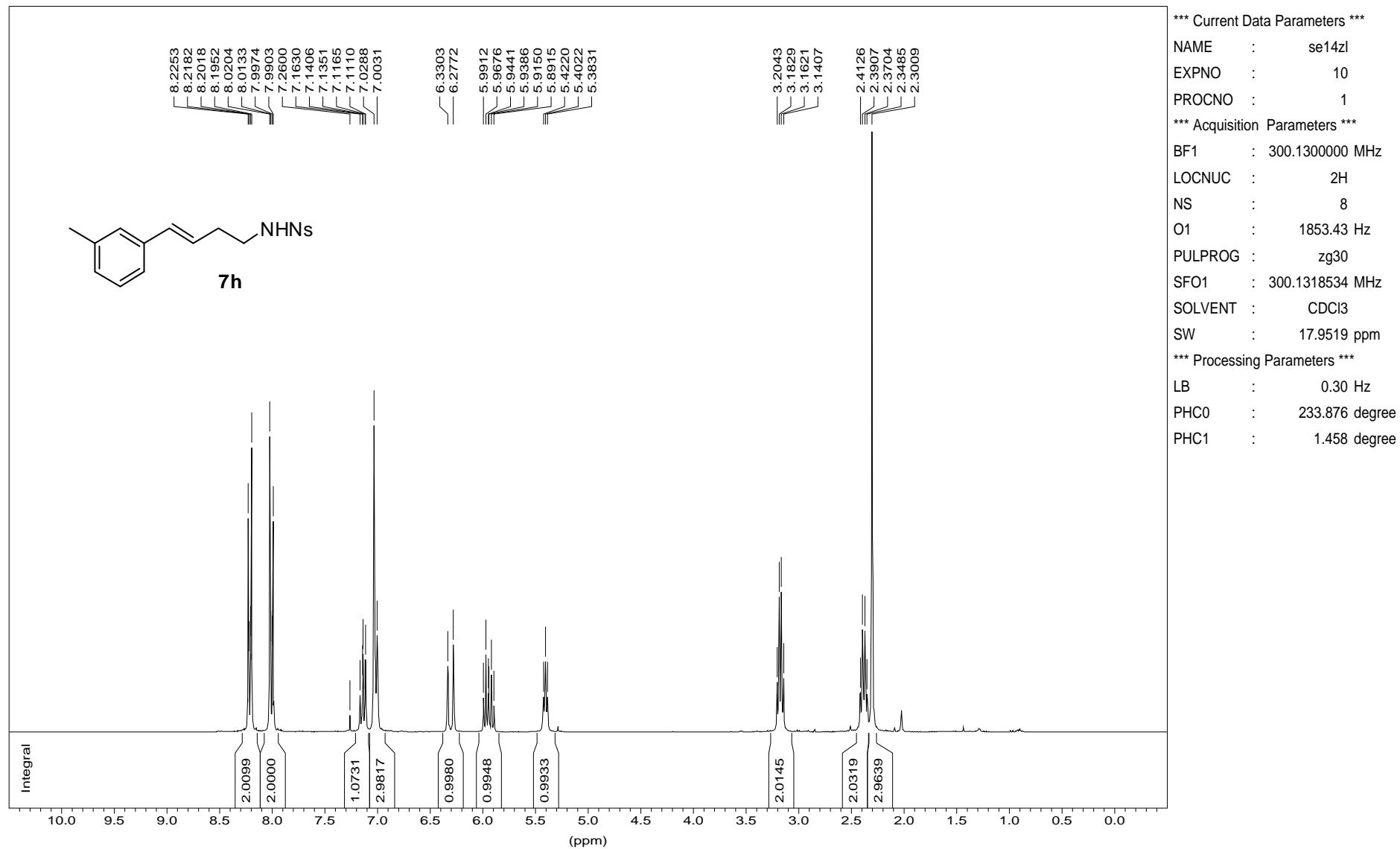
LB : 1.00 Hz

PHC0 : 97.316 degree

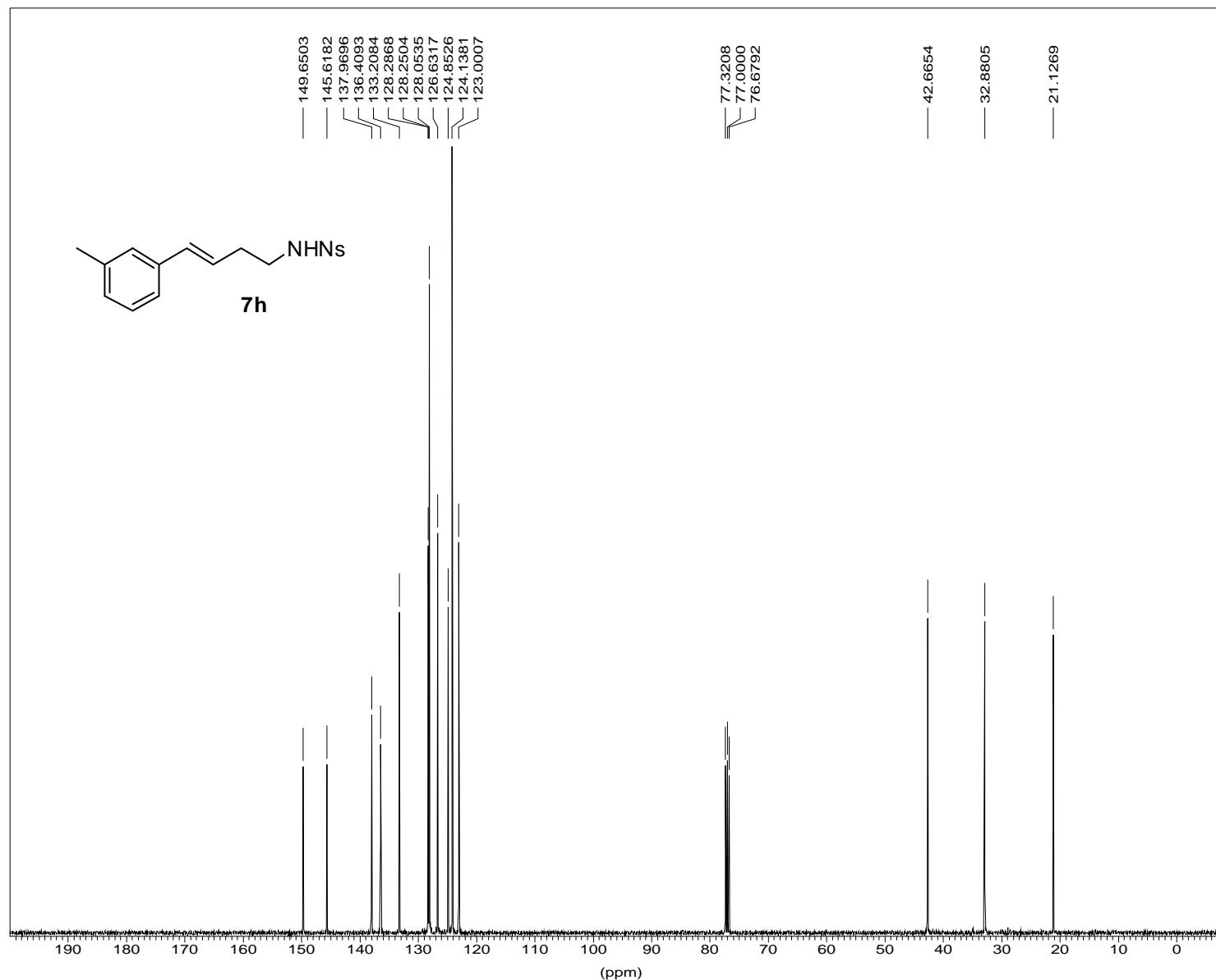
PHC1 : -51.237 degree

1H normal range AC300

2043B



2043B



*** Current Data Parameters ***

NAME : sep14zl
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

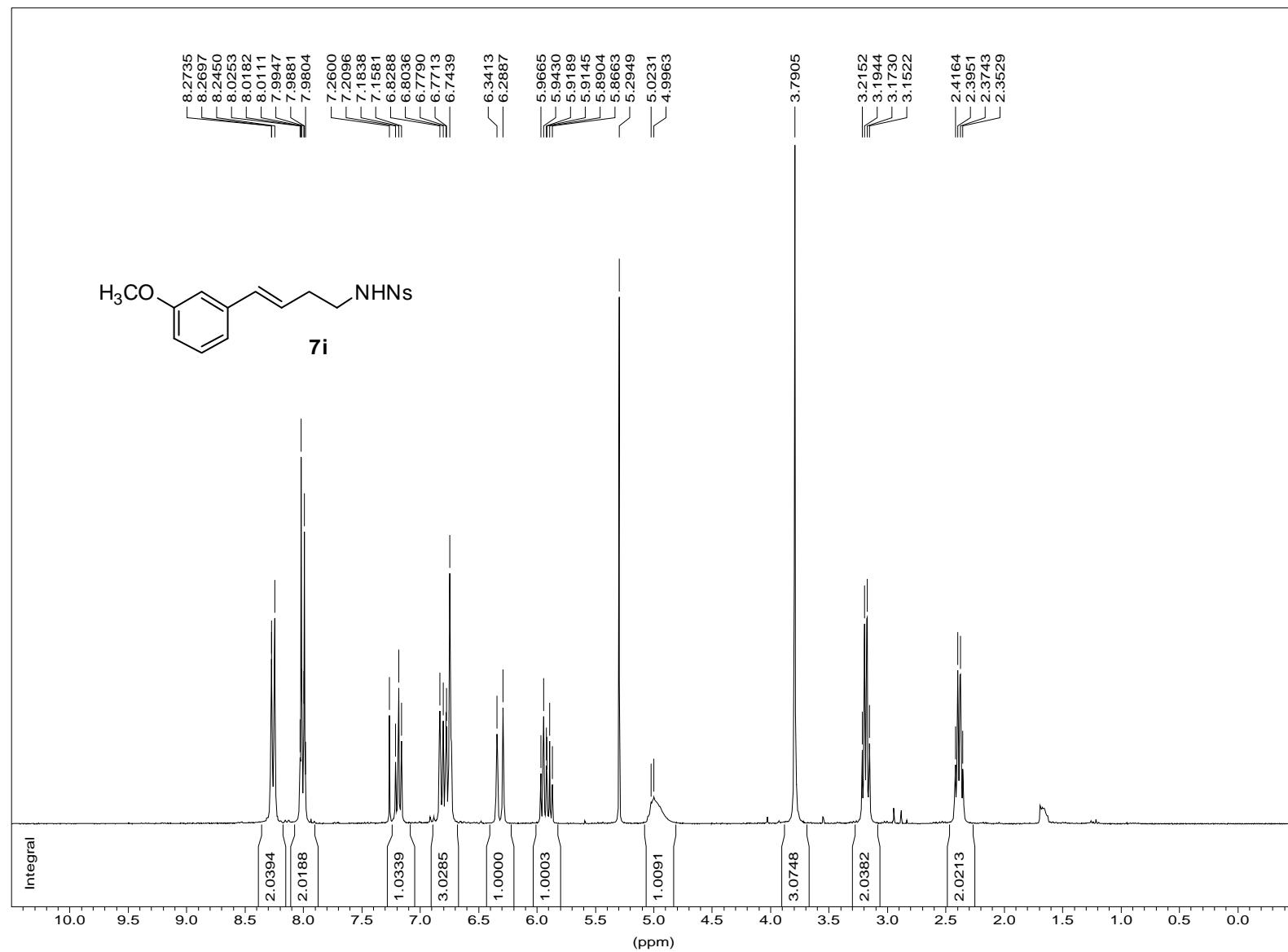
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 266
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 85.997 degree
PHC1 : -57.951 degree

1H normal range AC300

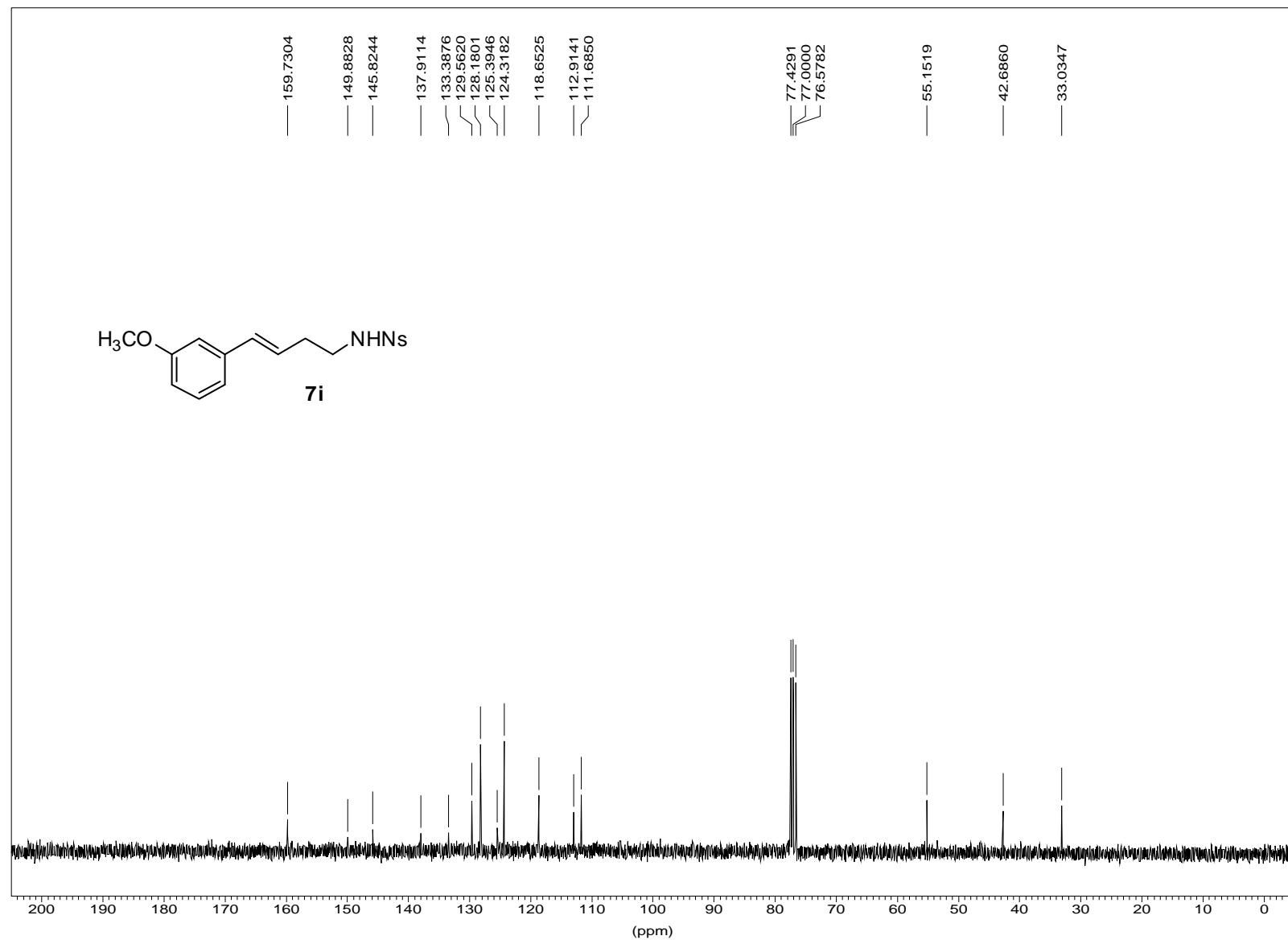
2043A



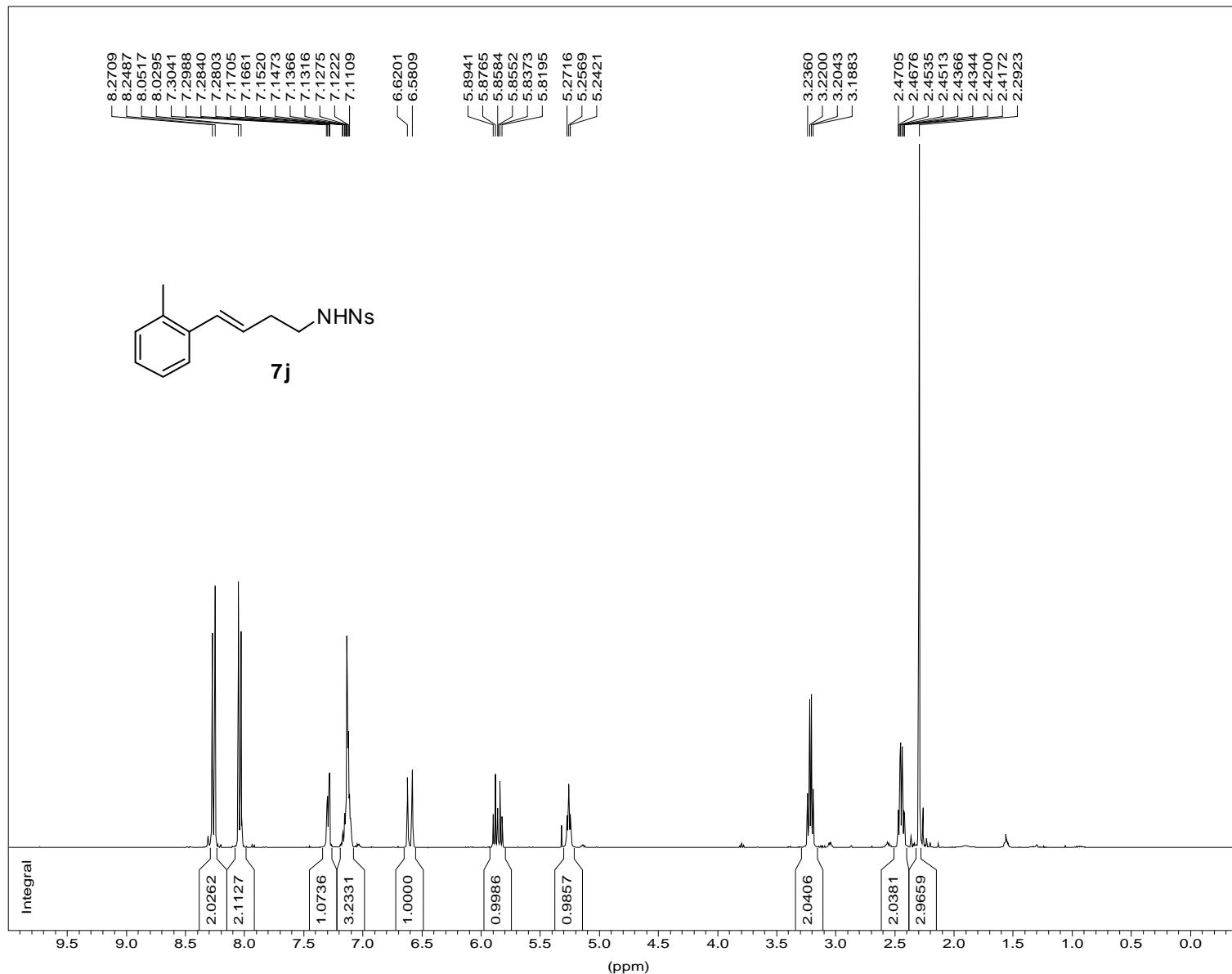
*** Current Data Parameters ***

NAME	:	se14zl
EXPNO	:	8
PROCNO	:	1
*** Acquisition Parameters ***		
BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl ₃
SW	:	17.9519 ppm
*** Processing Parameters ***		
LB	:	0.30 Hz
PHC0	:	19.308 degre
PHC1	:	4.868 degre

¹³C Standard AC300
2043A



cj2047A



*** Current Data Parameters ***

NAME : sep29cj
EXPNO : 1
PROCNO : 1

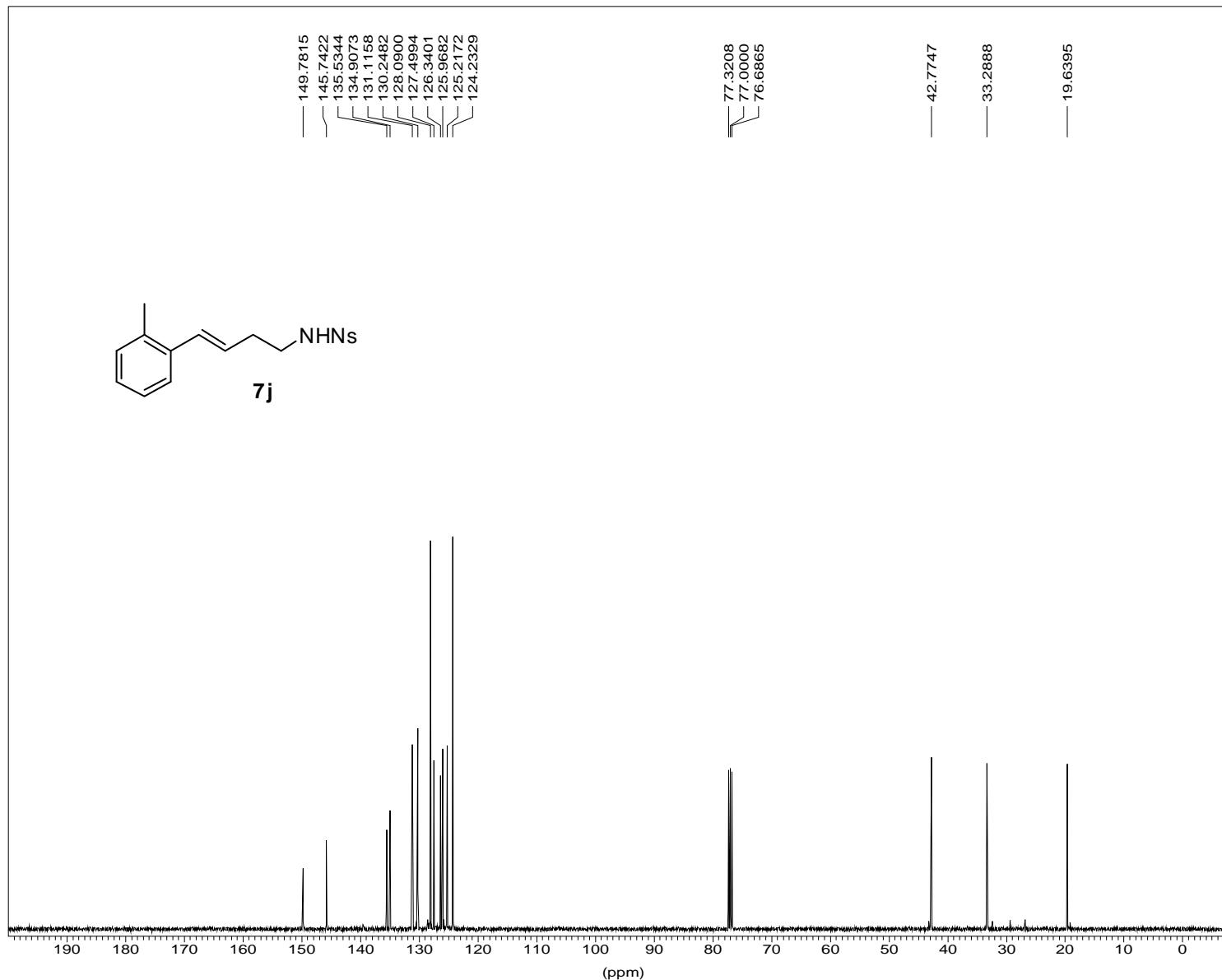
*** Acquisition Parameters ***

BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl₃
SW : 20.5524 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -53.217 degree
PHC1 : -19.041 degree

cj2047A



*** Current Data Parameters ***

NAME : sep29cj
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

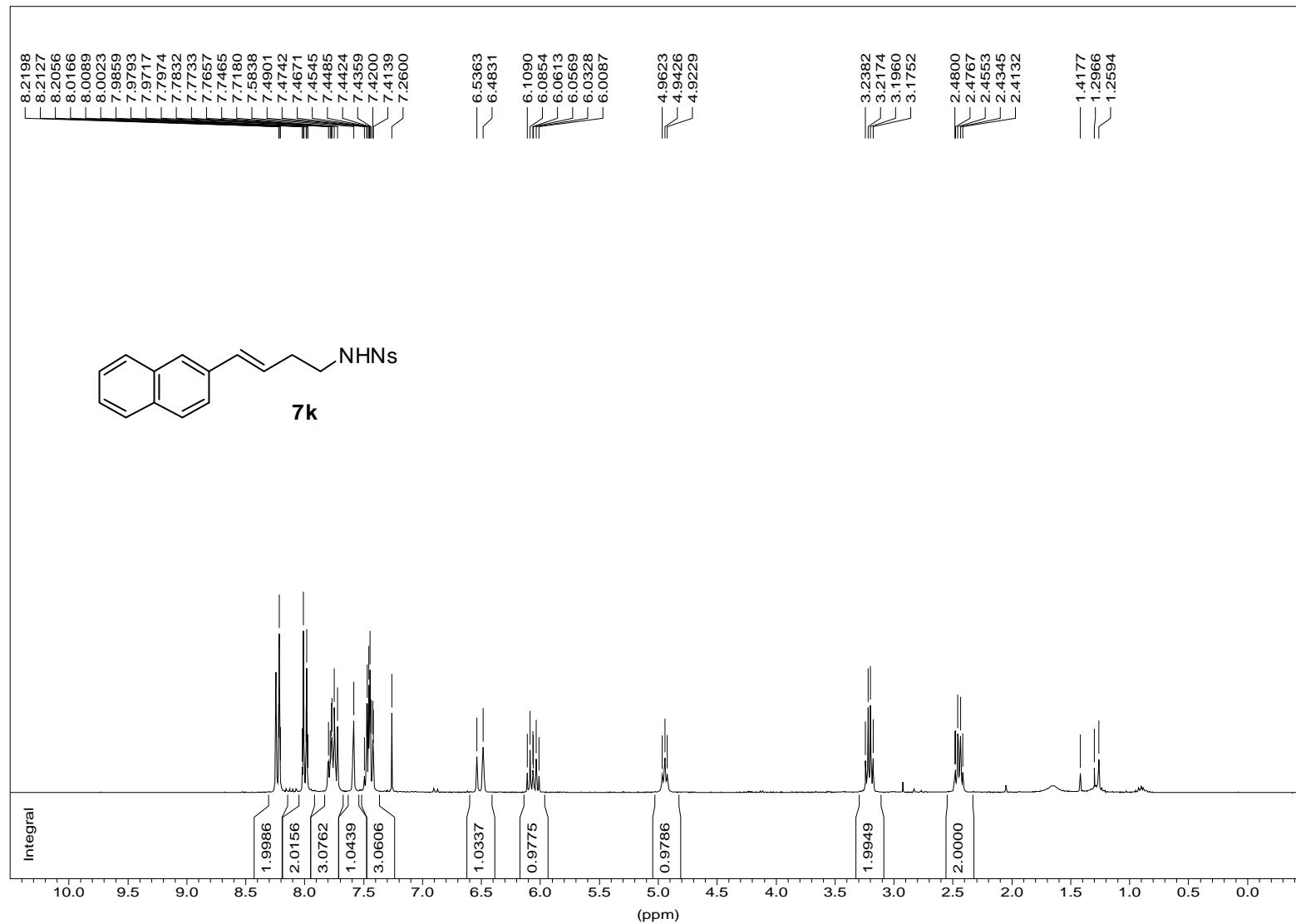
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 180
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 93.109 degree
PHC1 : -54.886 degree

1H normal range AC300

1286b



*** Current Data Parameters ***

NAME : j22zl

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 300.1300000 MHz

LOCNUC : 2H

NS : 8

O1 : 1853.43 Hz

PULPROG : zg30

SFO1 : 300.1318534 MHz

SOLVENT : CDCl₃

SW : 17.9519 ppm

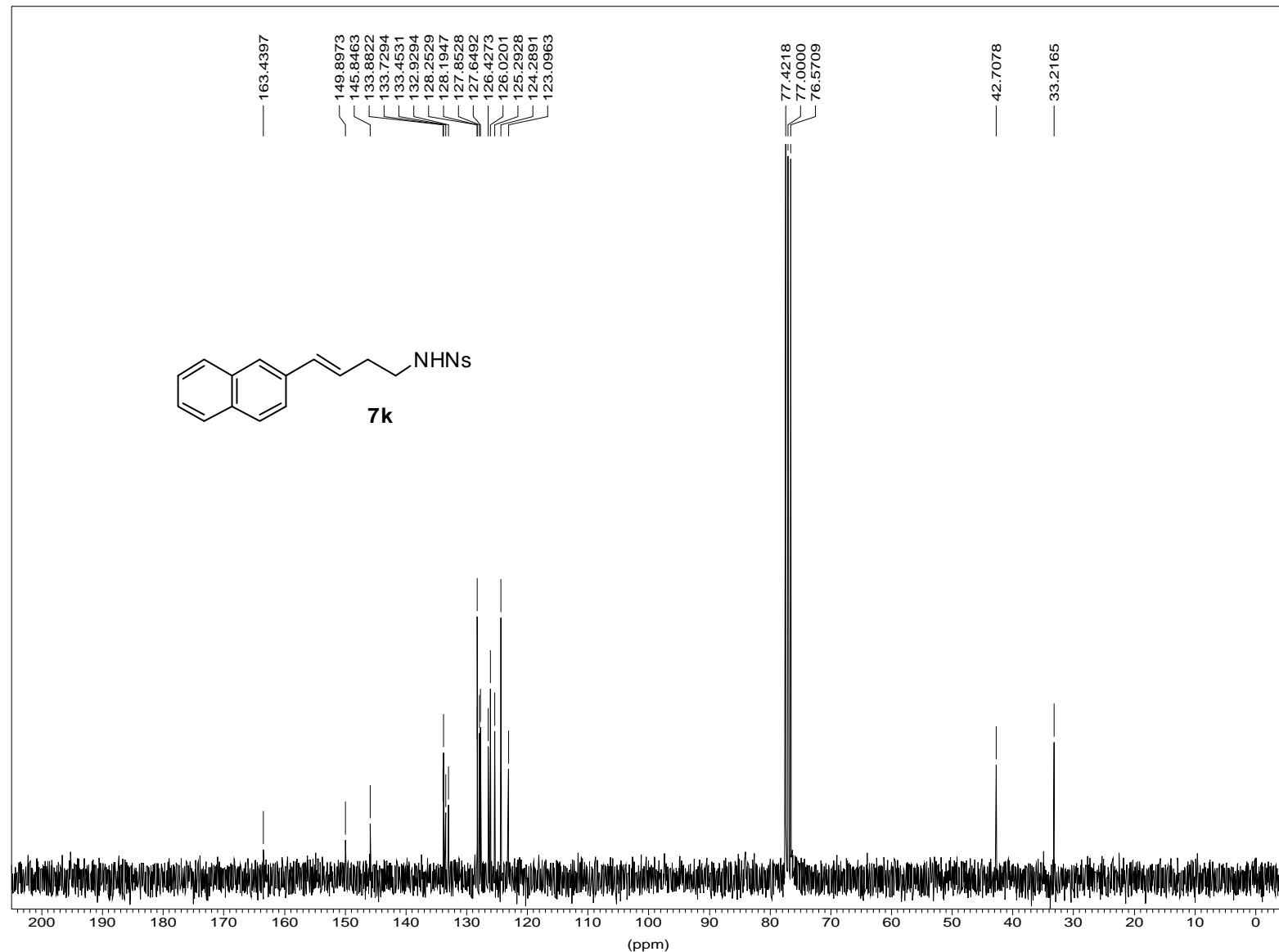
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : 28.377 degree

PHC1 : -8.852 degree

¹³C Standard AC300
1286b

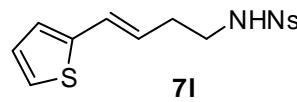
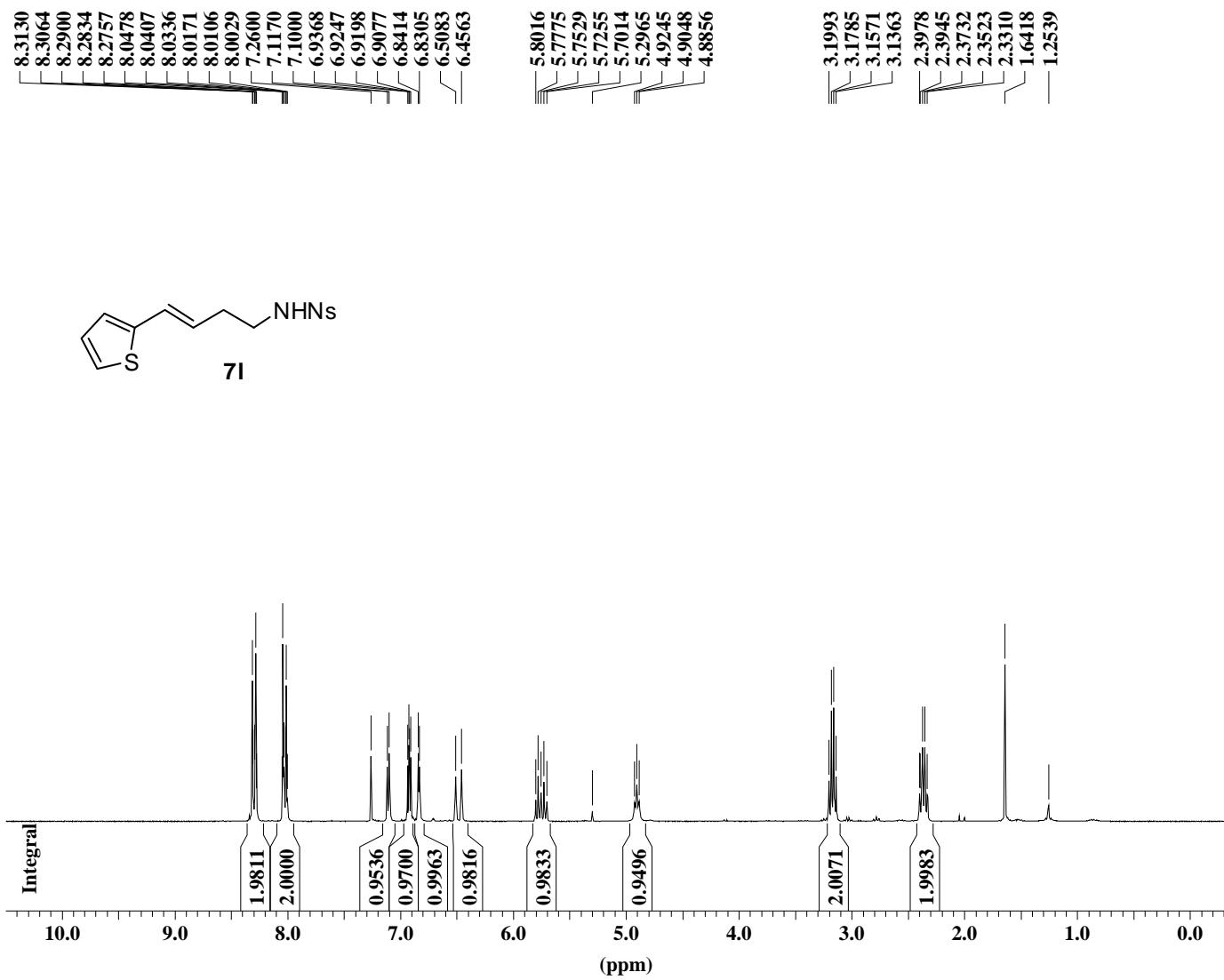


*** Current Data Parameters ***

NAME : j122zl
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 75.4677490 MHz
LOCNUC : 2H
NS : 408
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl₃
SW : 238.2968 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : -14.077 degree
PHC1 : 42.883 degree

1H normal range AC300

2059A



*** Current Data Parameters ***

NAME : oc15zl
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 8
NUCLEUS : off
O1 : 1853.43 Hz
PULPROG : zg30
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
SW : 17.9519 ppm
TD : 32768
TE : 296.8 K

*** Processing Parameters ***

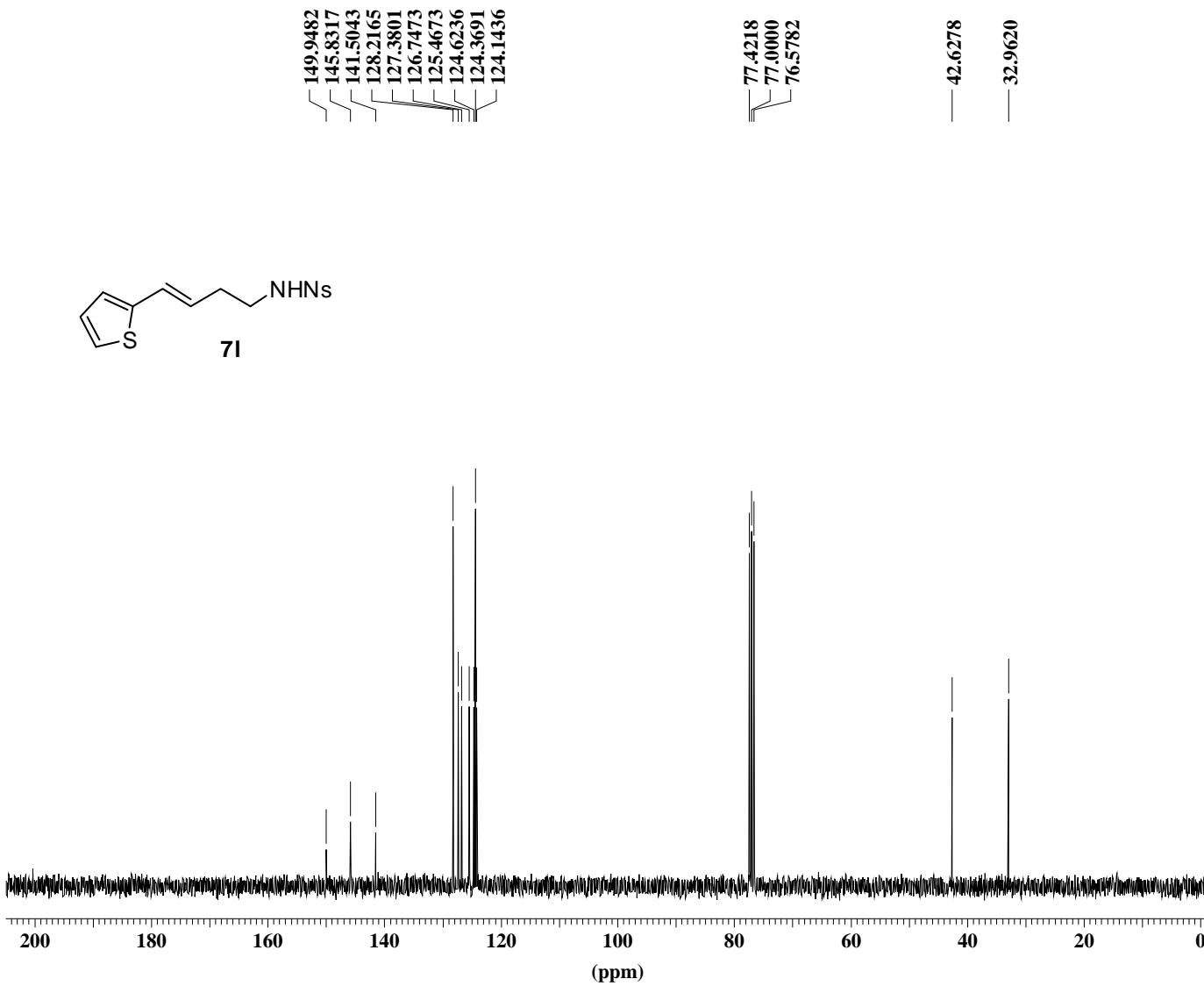
LB : 0.30 Hz
SF : 300.1300120 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

13C Standard AC300

2059A



*** Current Data Parameters ***

NAME : oc15zl
EXPNO : 6
PROCNO : 1
LOCMNUC : 2H
NS : 326
NUCLEUS : off
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl₃
SW : 238.2968 ppm
TD : 32768
TE : 297.0 K

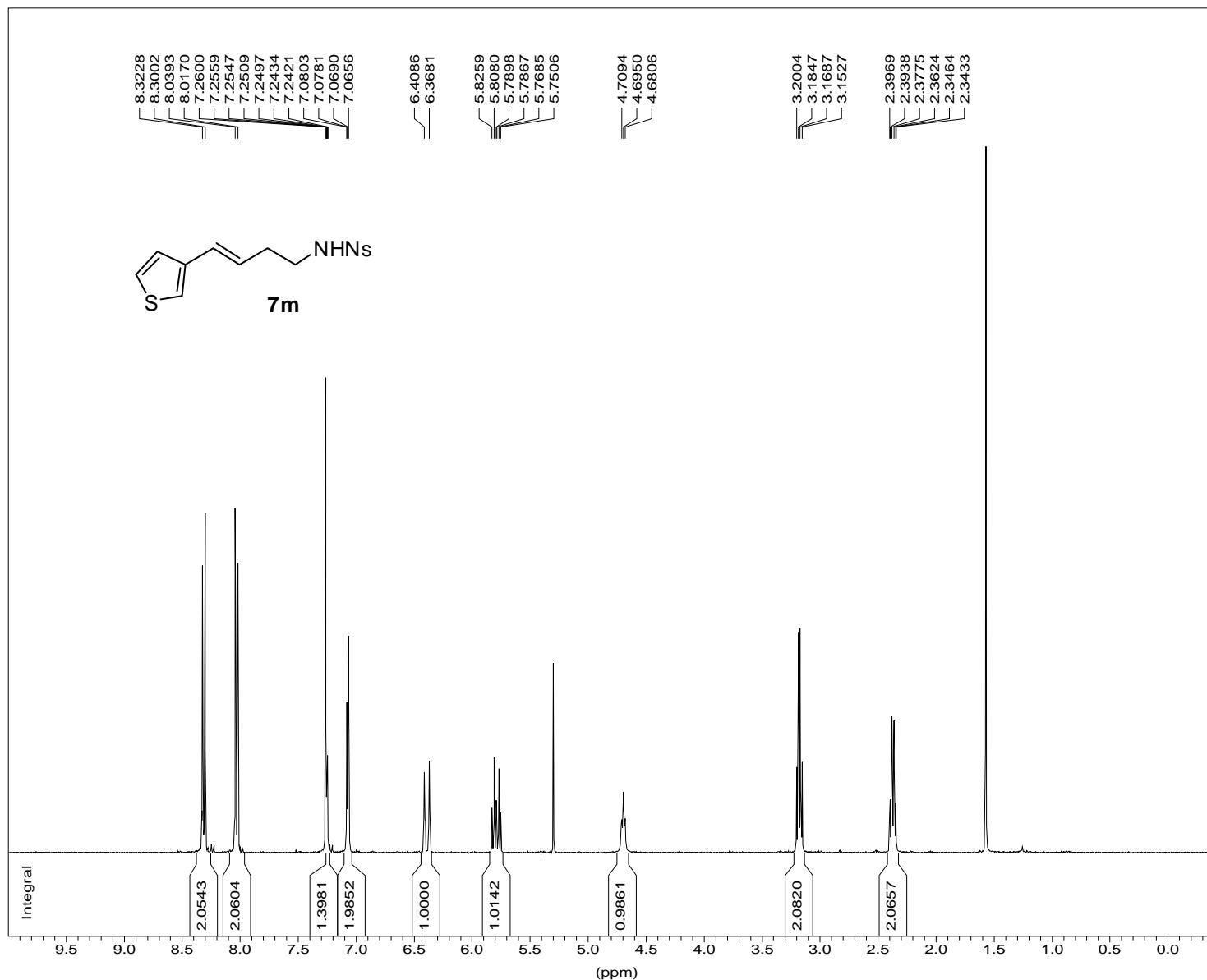
*** Processing Parameters ***

LB : 1.00 Hz
SF : 75.4677540 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

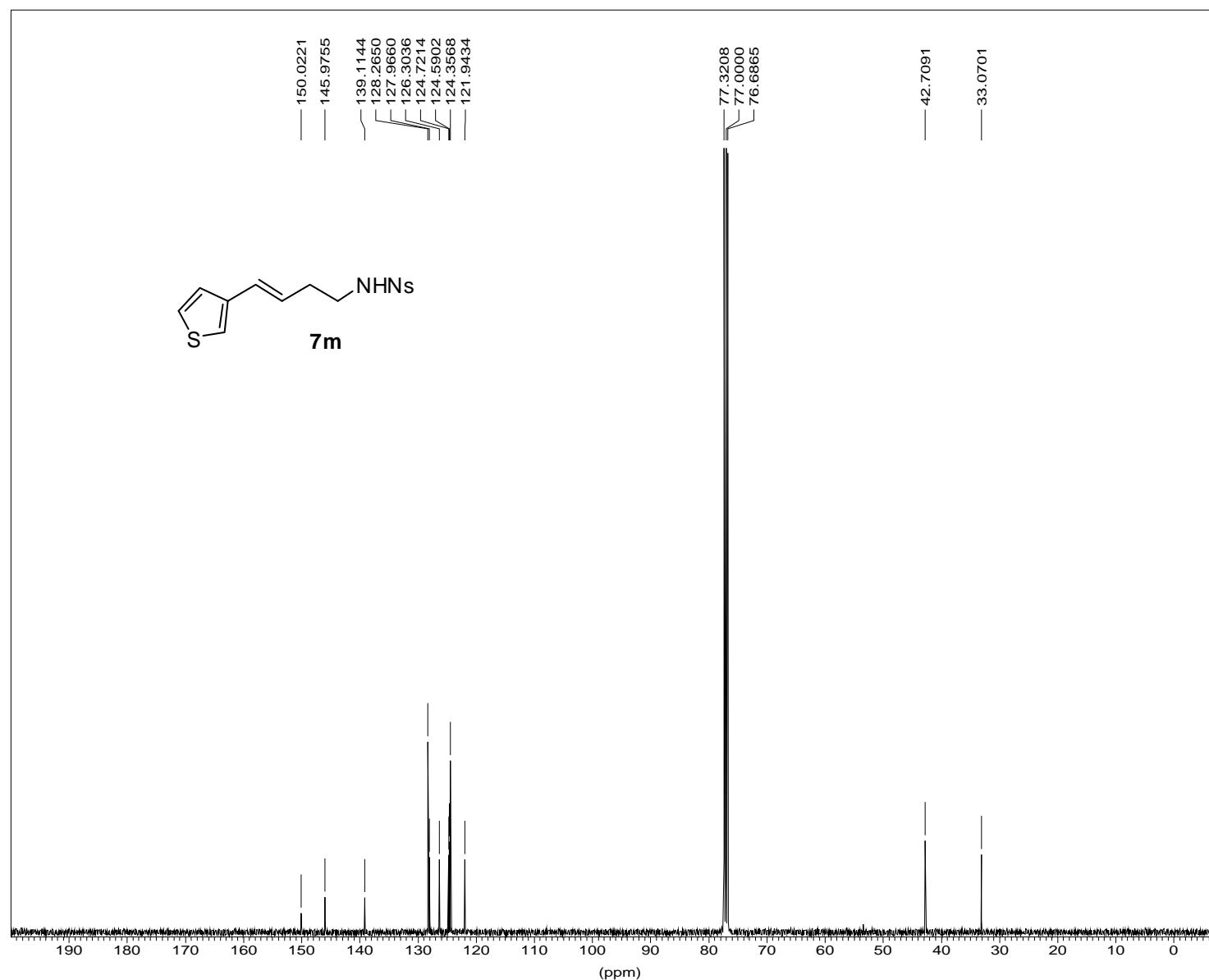
cj2059B



*** Current Data Parameters ***

NAME : oct15cj
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.5524 ppm
*** Processing Parameters ***
LB : 0.30 Hz
PHC0 : -48.305 degree
PHC1 : -15.608 degree

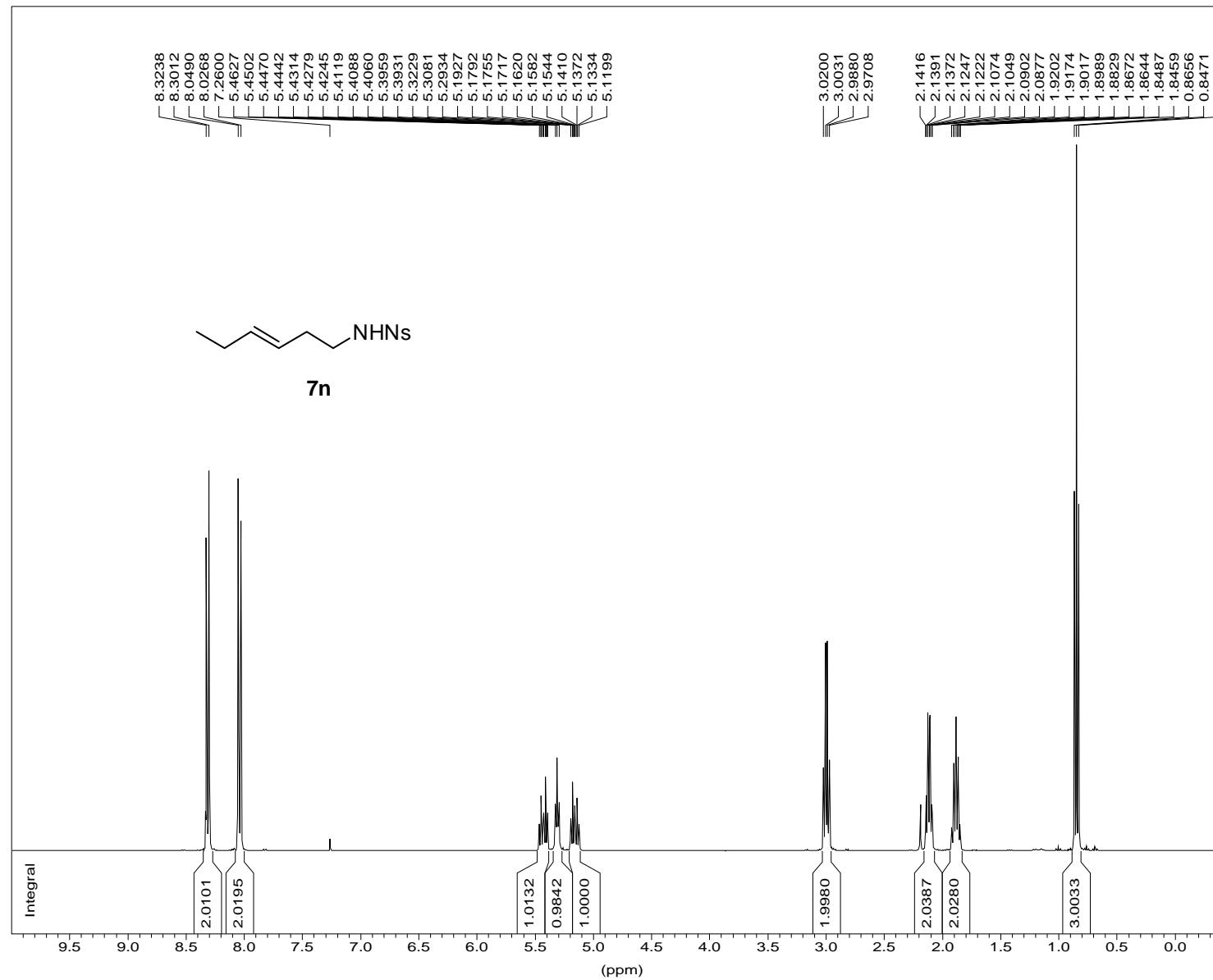
cj2059B



*** Current Data Parameters ***

NAME : oct15cj
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 2000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 102.419 degree
PHC1 : -77.459 degree

cj2055C



*** Current Data Parameters ***

NAME : oct22cj

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 400.1300000 MHz

LOCNUC : 2H

NS : 8

O1 : 2470.97 Hz

PULPROG : zg30

SFO1 : 400.1324710 MHz

SOLVENT : CDCl₃

SW : 20.5524 ppm

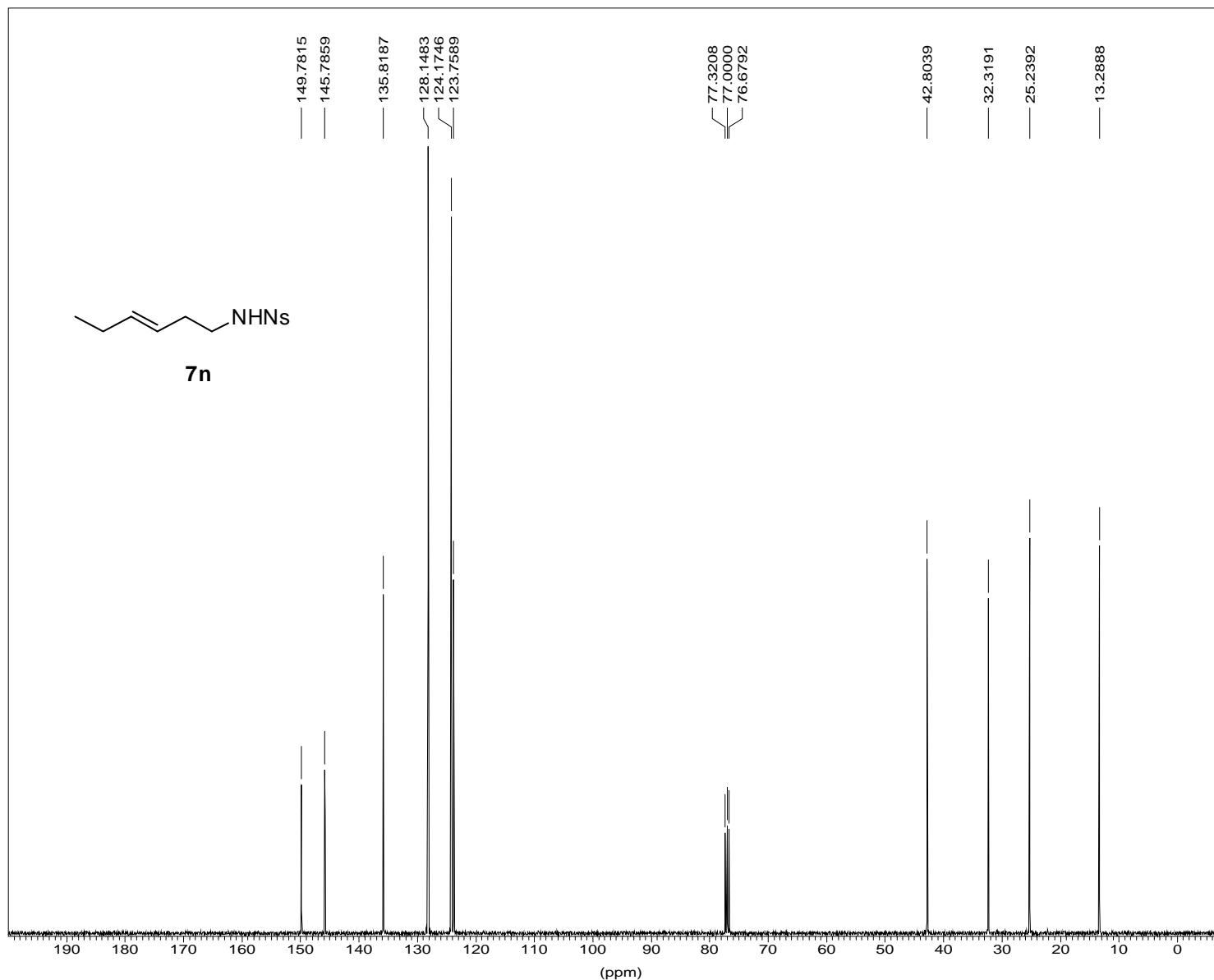
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : -44.638 degree

PHC1 : -22.899 degree

cj2055C

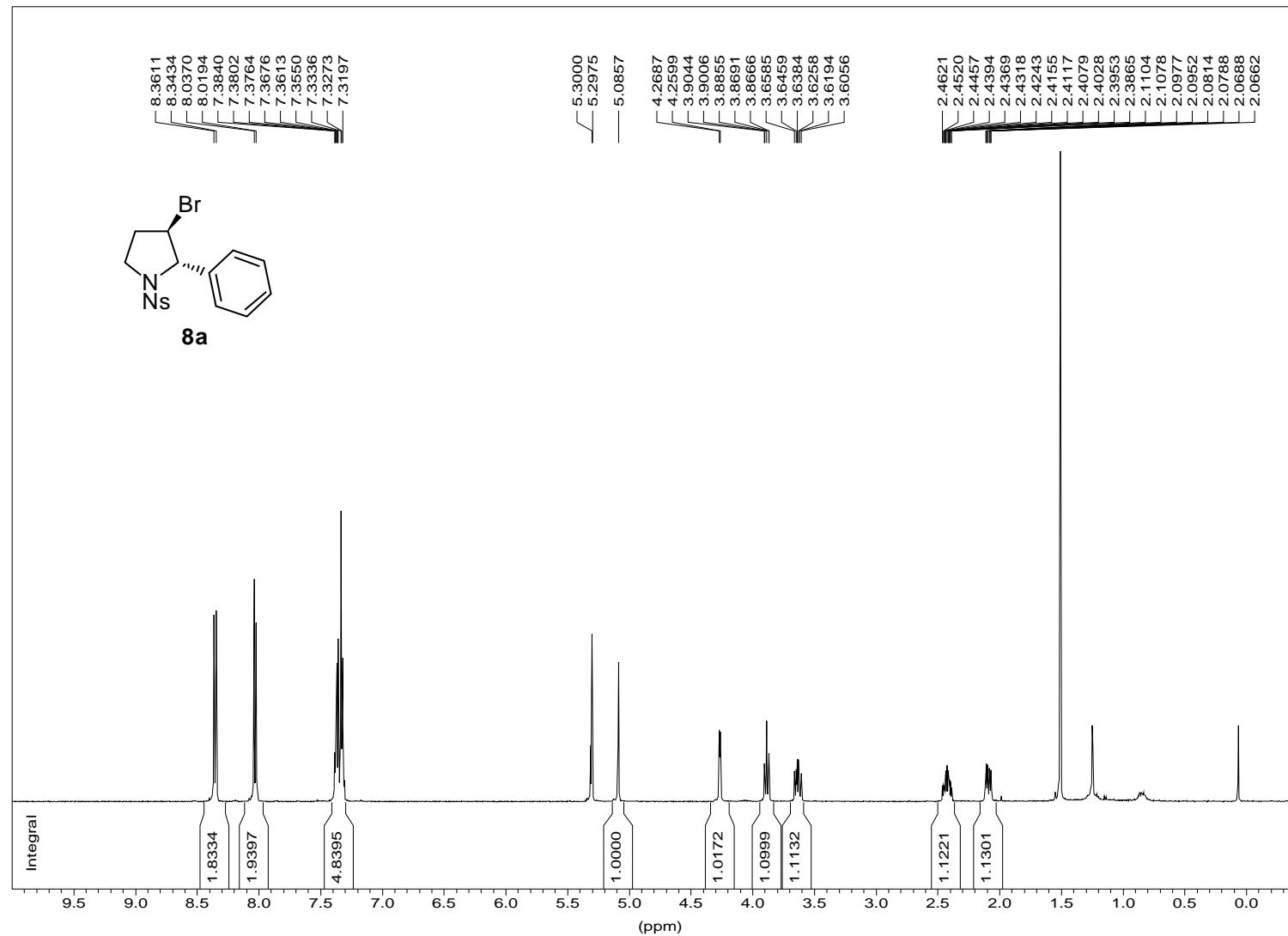


*** Current Data Parameters ***

NAME : oct22cj
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 100
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl3
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 101.482 degree
PHC1 : -60.621 degree

1H AMX500

cj1231A



*** Current Data Parameters ***

NAME : zl0512

EXPNO : 4

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 500.1300000 MHz

LOCNUC : 2H

NS : 8

O1 : 3088.51 Hz

PULPROG : zg30

SFO1 : 500.1330885 MHz

SOLVENT : CD2Cl2

SW : 20.6557 ppm

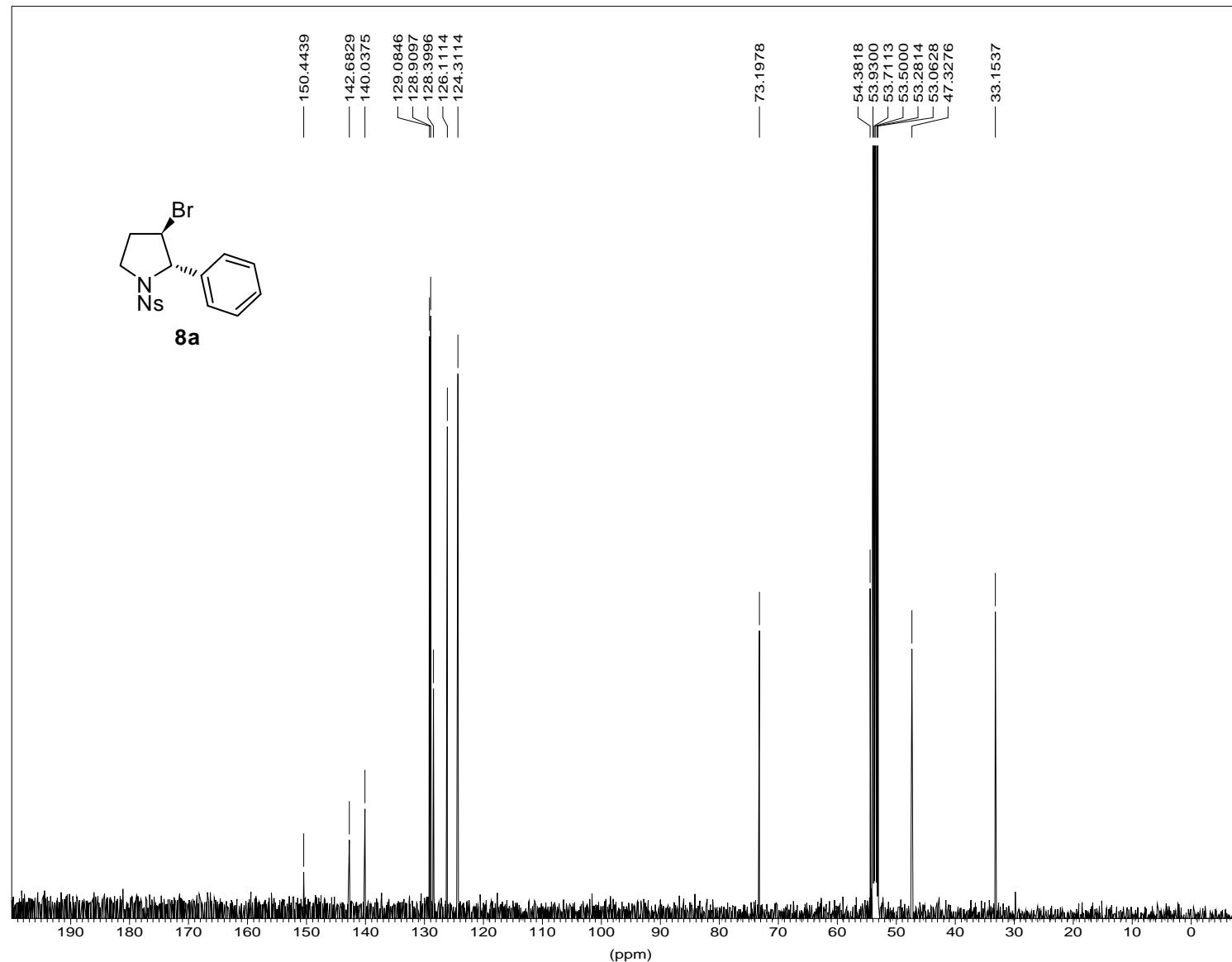
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : 175.676 degree

PHC1 : 6.634 degree

13C AMX500
cj1231A



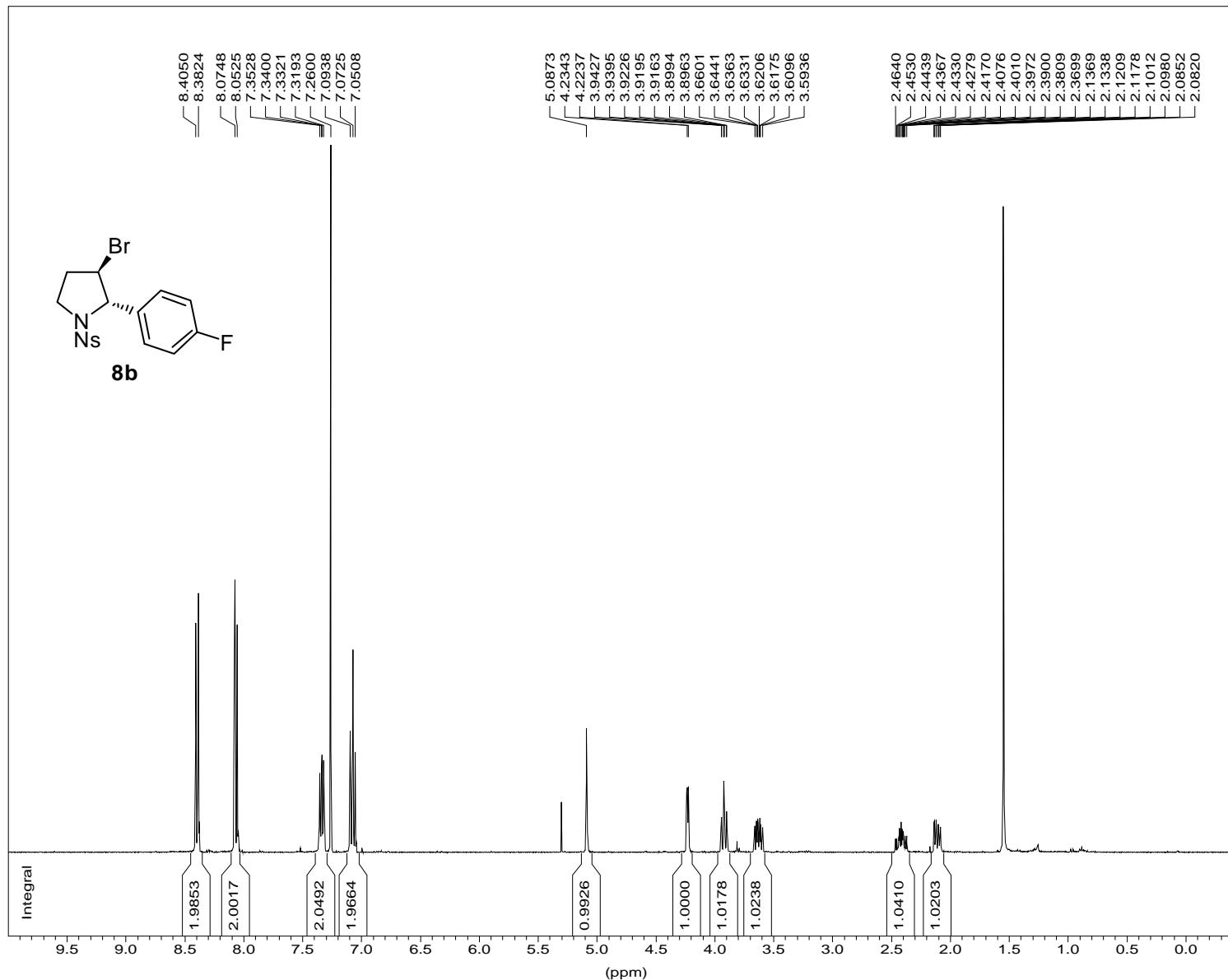
*** Current Data Parameters ***

NAME : zl0512
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
LOCNUC : 2H
NS : 791
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 198.124 degree
PHC1 : 47.451 degree

cj2052A



*** Current Data Parameters ***

NAME : oct01cj

EXPNO : 6

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 400.130000 MHz

LOCNUC : 2H

NS : 16

O1 : 2470.97 Hz

PULPROG : zg30

SFO1 : 400.1324710 MHz

SOLVENT : CDCl₃

SW : 20.5524 ppm

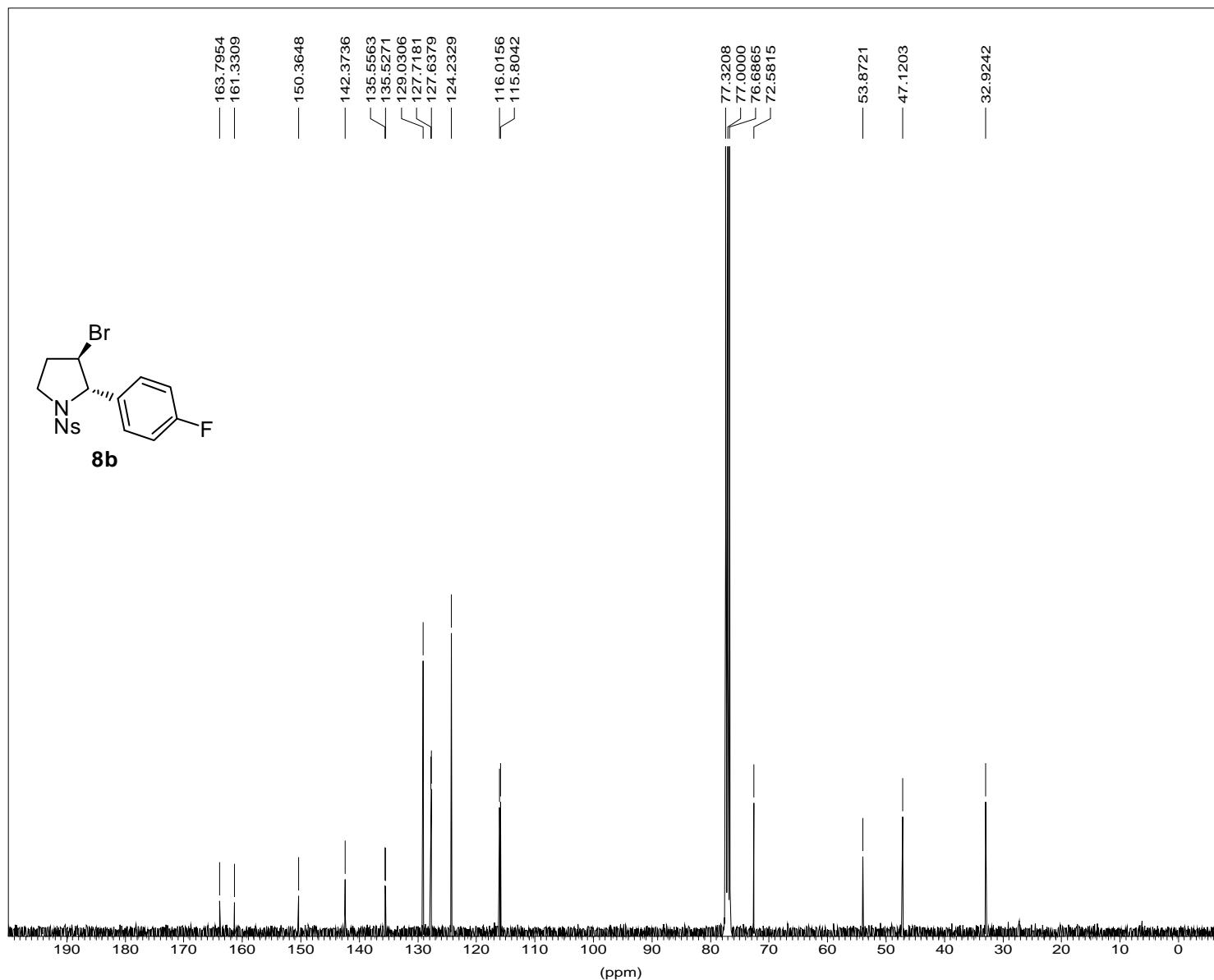
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : -48.854 degree

PHC1 : -9.841 degree

cj2052A

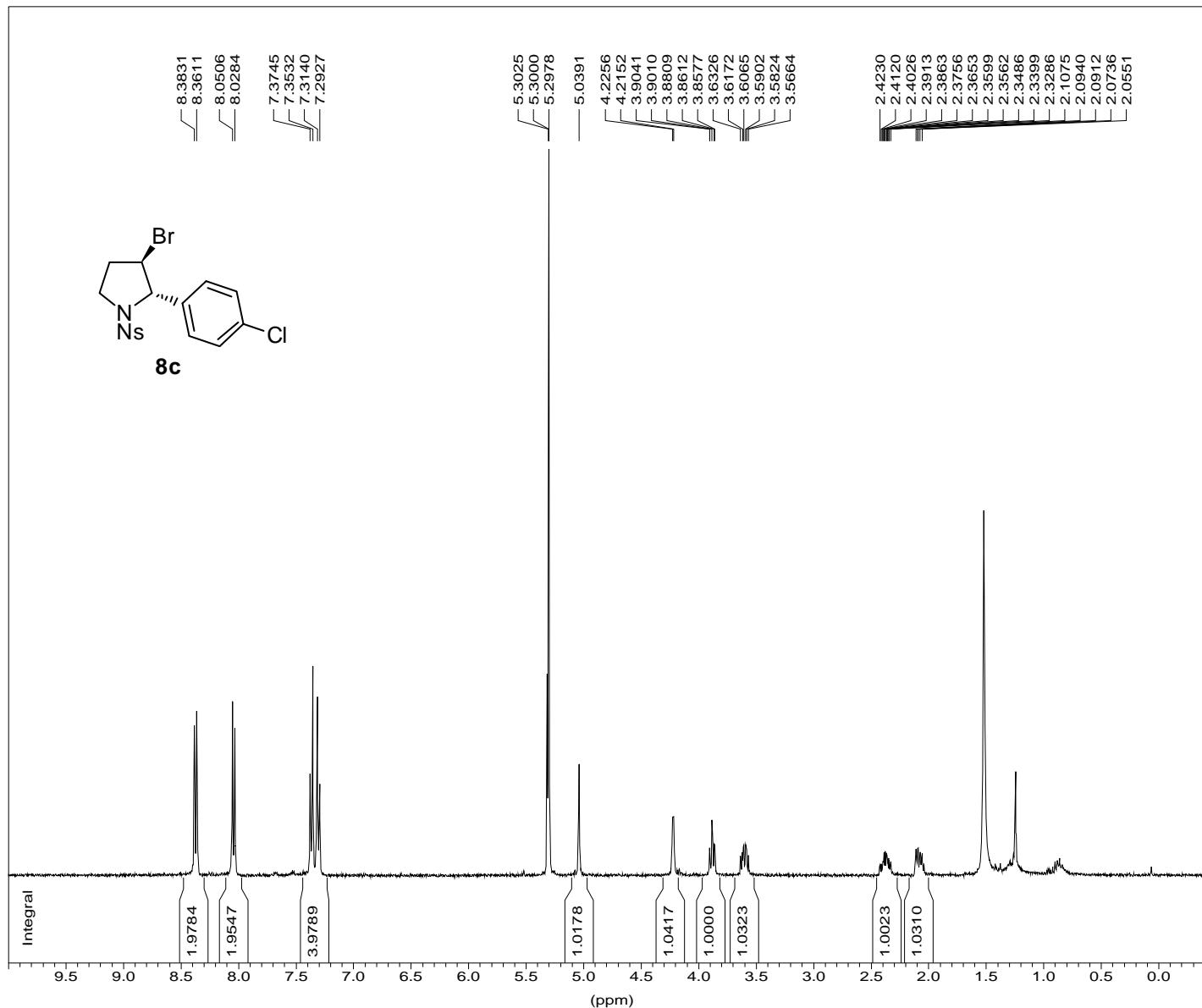


*** Current Data Parameters ***

NAME : oct01cj
EXPNO : 7
PROCNO : 1
*** Acquisition Parameters ***

BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 5000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 92.764 degree
PHC1 : -54.021 degree

cj1217B



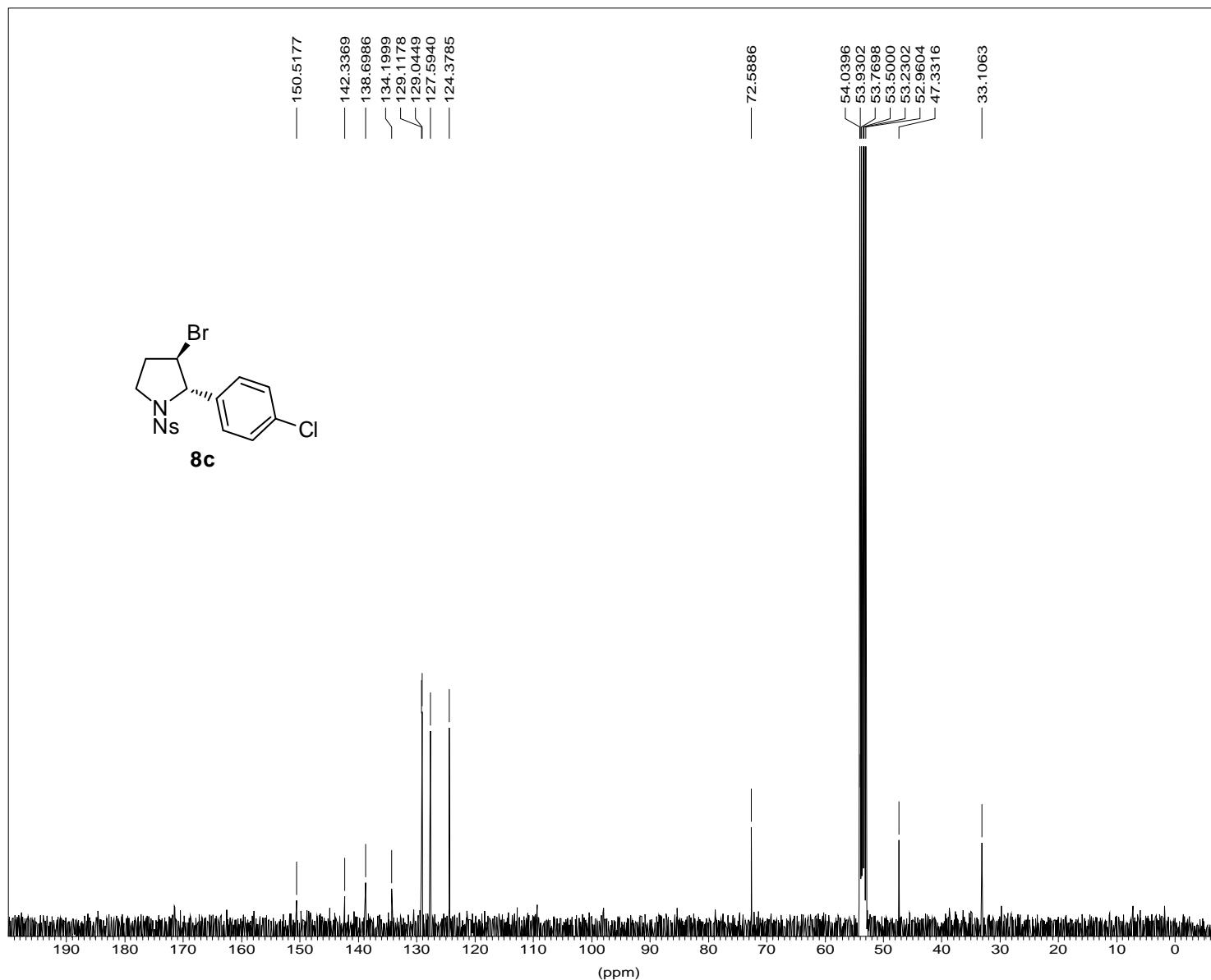
*** Current Data Parameters ***

NAME : aug02cj
EXPNO : 9
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.130000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CD₂Cl₂
SW : 20.5524 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -58.661 degree
PHC1 : 1.997 degree

cj1217B



*** Current Data Parameters ***

NAME : aug02cj
EXPNO : 10
PROCNO : 1

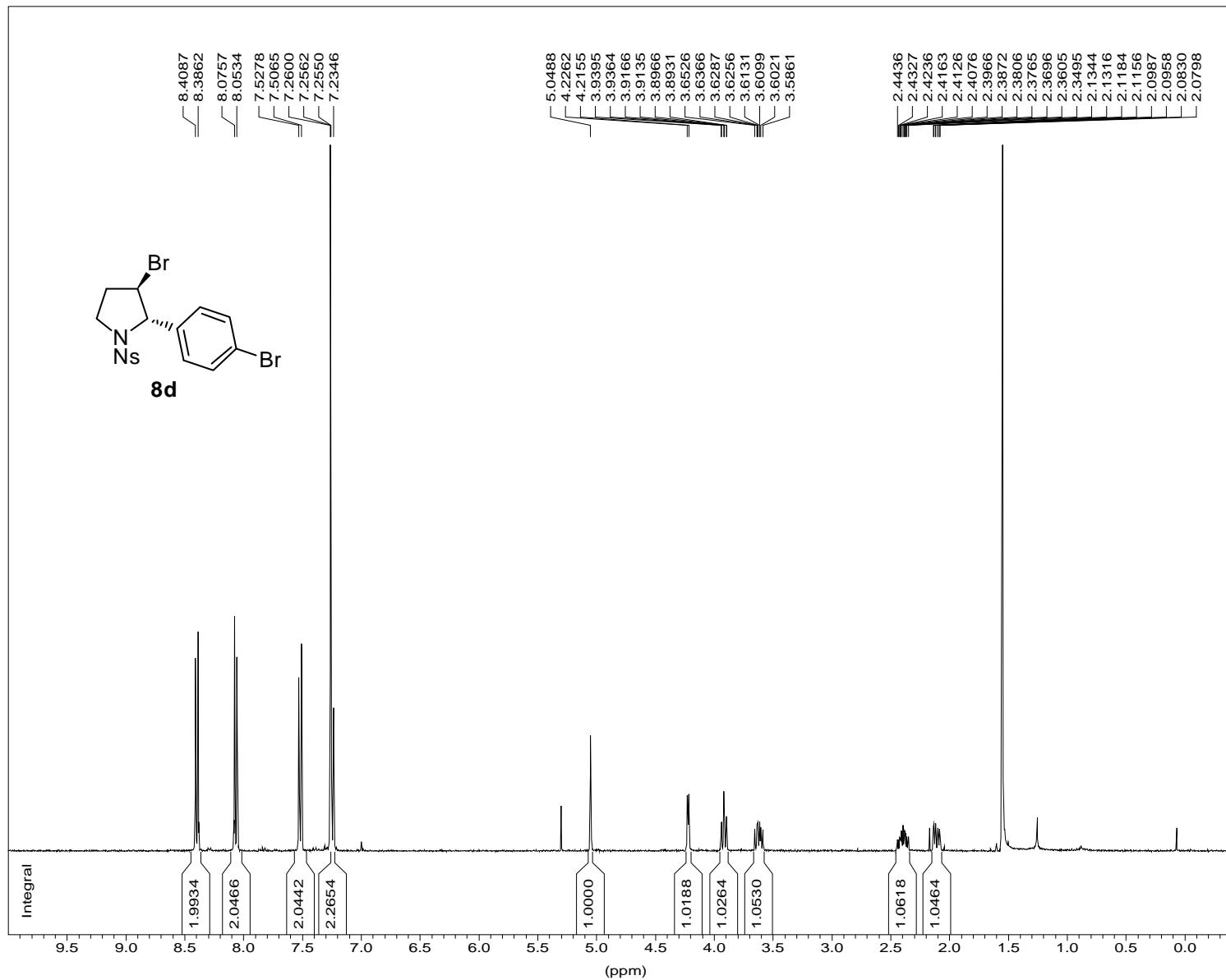
*** Acquisition Parameters ***

BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 2000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CD2Cl₂
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 99.218 degree
PHC1 : -40.416 degree

cj2057D



S60

*** Current Data Parameters ***

NAME : oct25cj

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 400.1300000 MHz

LOCNUC : 2H

NS : 32

O1 : 2470.97 Hz

PULPROG : zg30

SFO1 : 400.1324710 MHz

SOLVENT : CDCl₃

SW : 20.5524 ppm

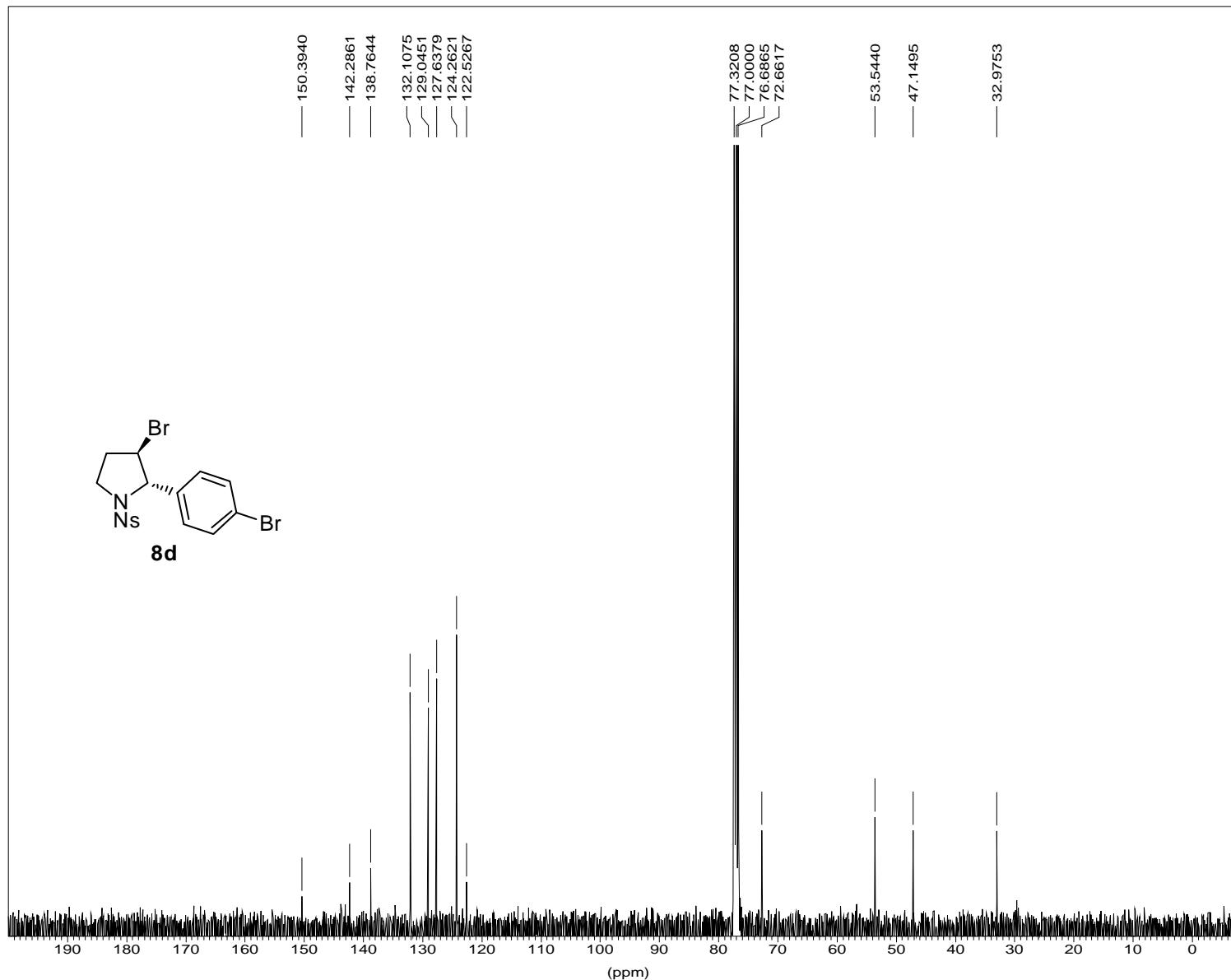
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : -45.655 degree

PHC1 : -13.262 degree

cj2057D



*** Current Data Parameters ***

NAME : oct25cj
EXPNO : 2
PROCNO : 1

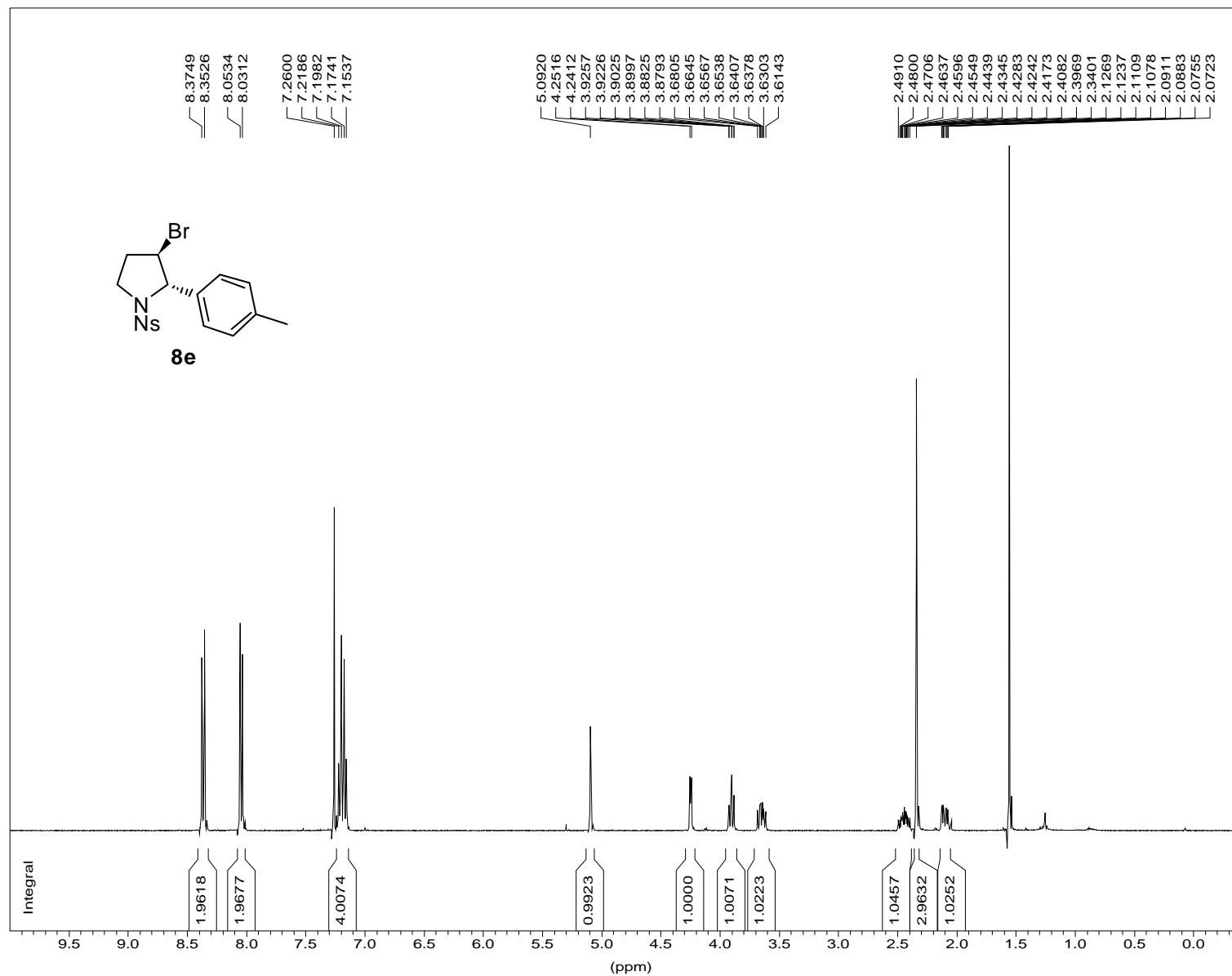
*** Acquisition Parameters ***

BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 4150
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl3
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 83.205 degree
PHC1 : -32.057 degree

cj2042D



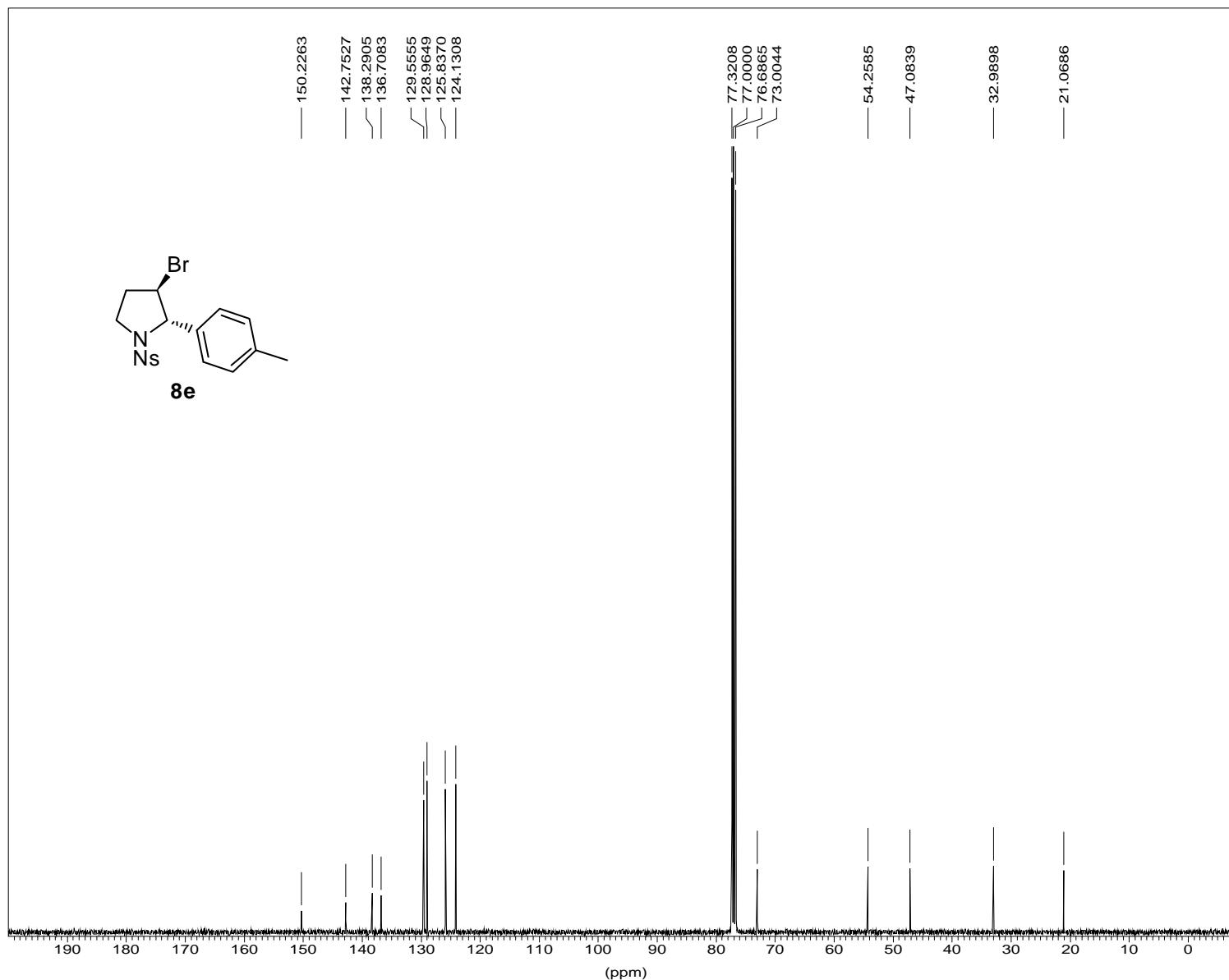
*** Current Data Parameters ***

NAME : sep08cj
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***

BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl₃
SW : 20.5524 ppm
*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -46.846 degree
PHC1 : -18.381 degree

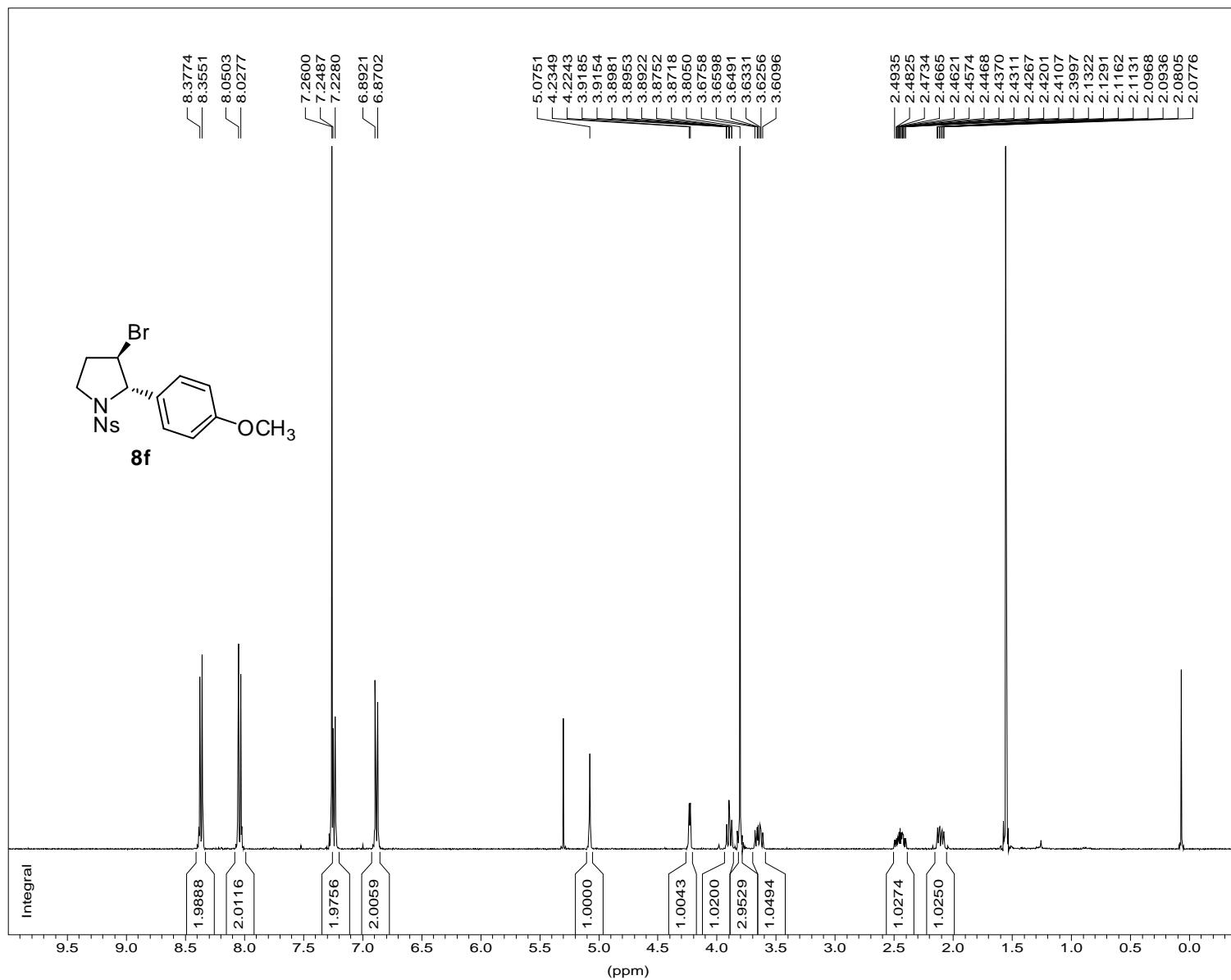
cj2042D



*** Current Data Parameters ***

NAME : sep08cj
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 3000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 99.903 degree
PHC1 : -51.719 degree

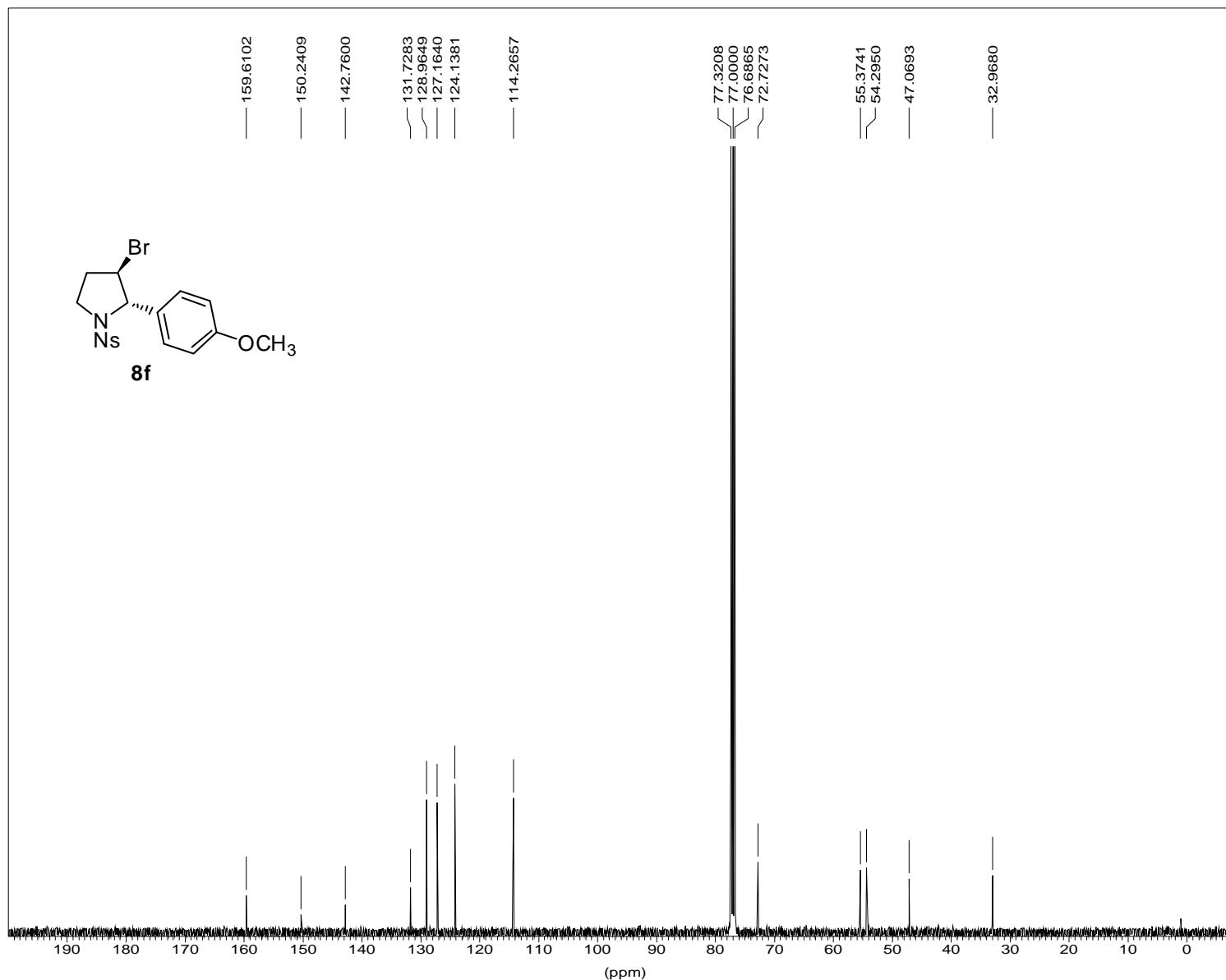
cj2042C



*** Current Data Parameters ***

NAME : sep08cj
EXPNO : 20
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl₃
SW : 20.5524 ppm
*** Processing Parameters ***
LB : 0.30 Hz
PHC0 : -49.424 degree
PHC1 : -19.603 degree

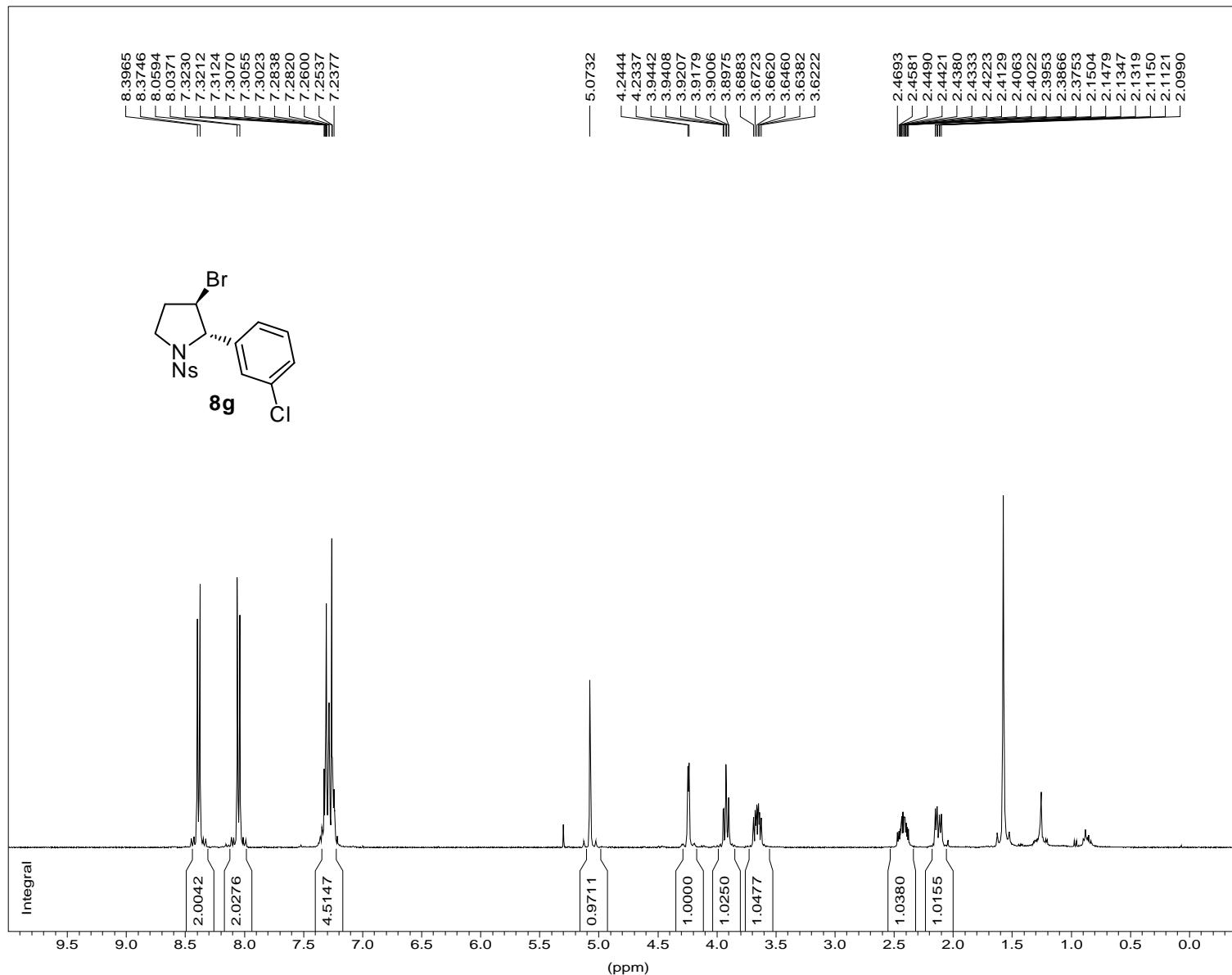
cj2042C



*** Current Data Parameters ***

NAME : sep08cj
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
RF1 : 100.6127690 MHz
LOCMNUC : 2H
NS : 3000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl3
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 86.461 degree
PHC1 : -42.460 degree

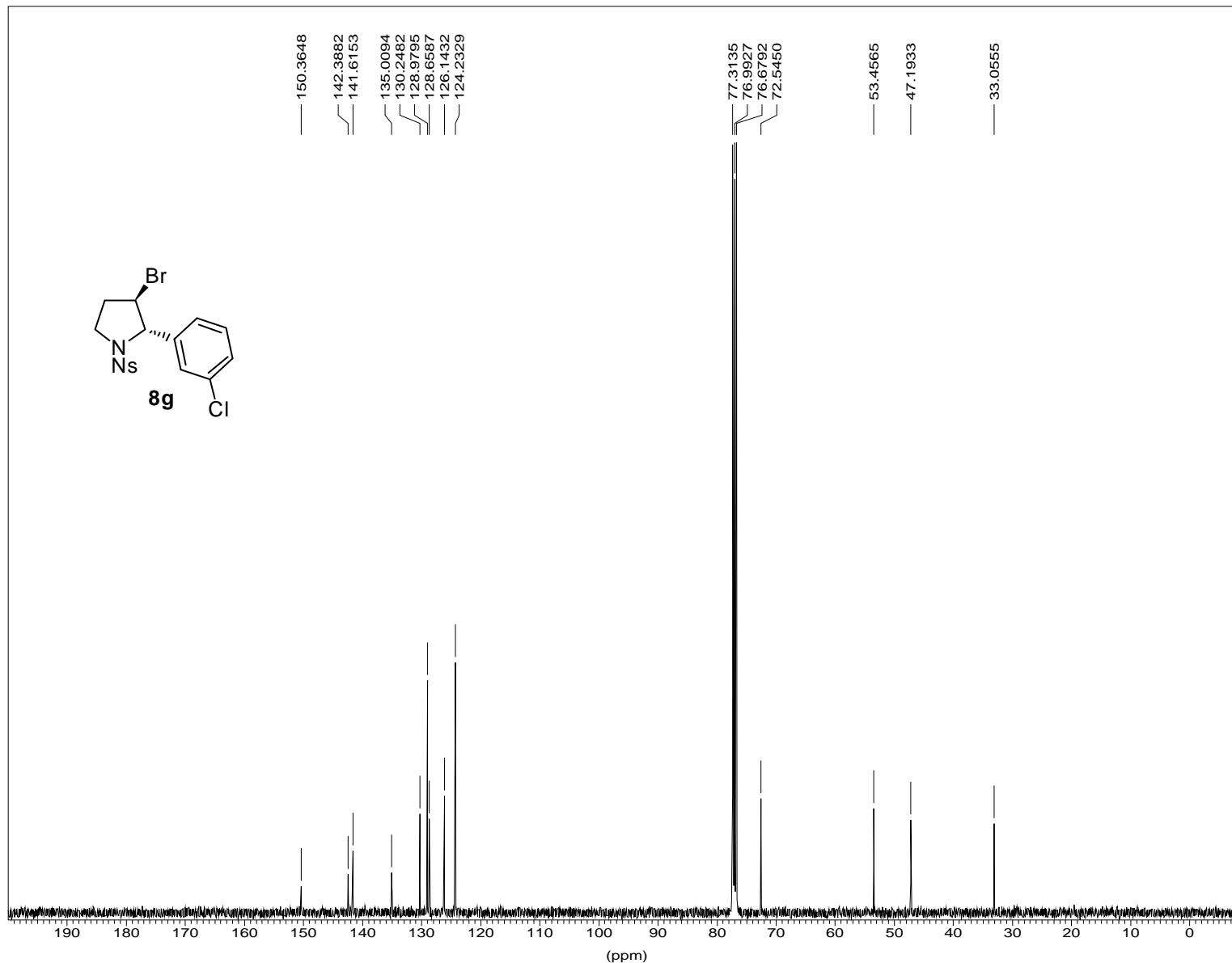
cj1273A



*** Current Data Parameters ***

NAME : cj1jul13
EXPNO : 6
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl3
SW : 20.5524 ppm
*** Processing Parameters ***
LB : 0.30 Hz
PHC0 : -54.018 degree
PHC1 : -13.790 degree

cj1273A



*** Current Data Parameters ***

NAME : cijul13
EXPNO : 7
PROCNO : 1

*** Acquisition Parameters ***

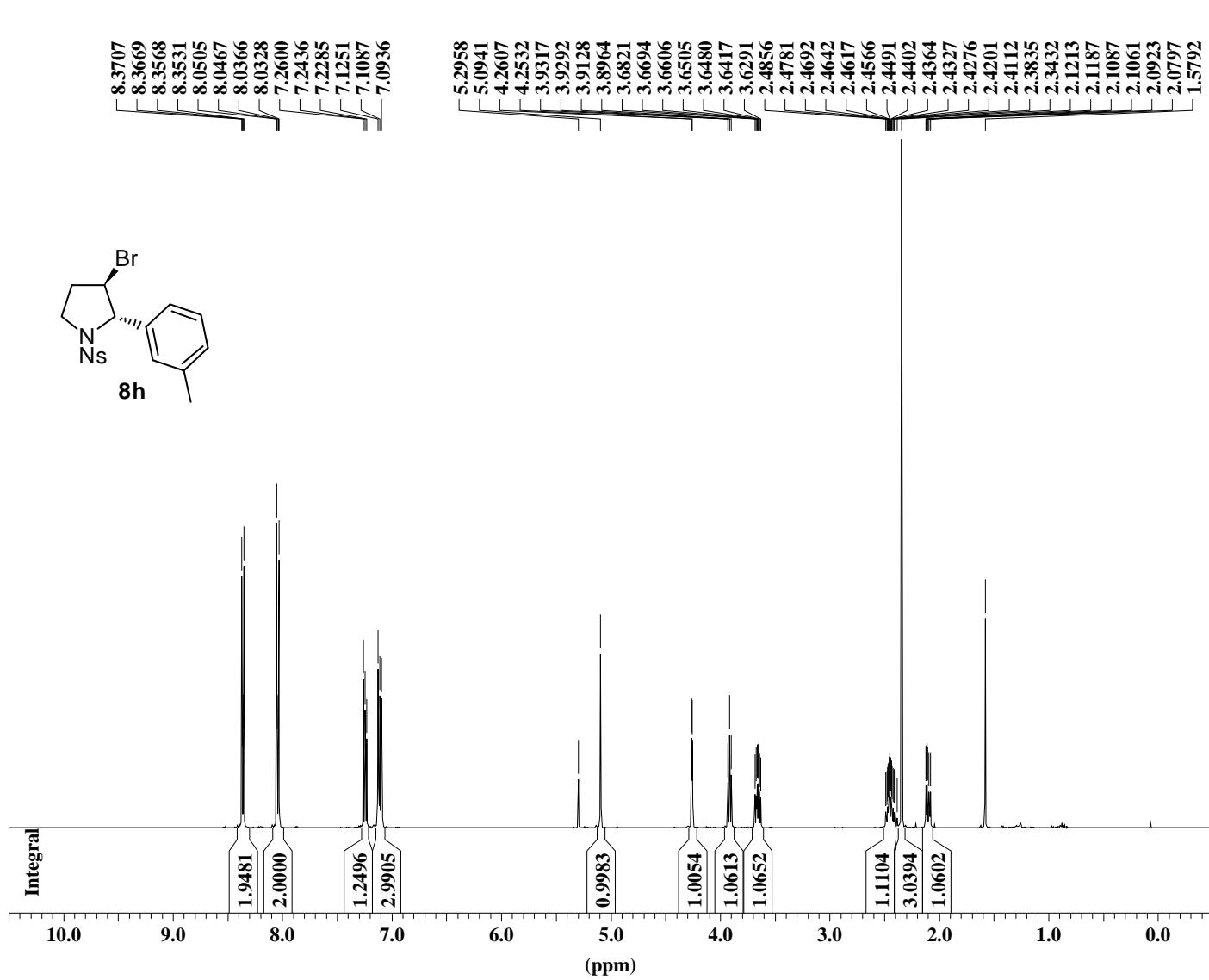
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 1024
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 95.922 degree
PHC1 : -58.875 degree

1H AMX500

cj2044E



*** Current Data Parameters ***

NAME : zl0916
EXPNO : 6
PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H
NS : 8
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm
TD : 32768
TE : 295.6 K

*** Processing Parameters ***

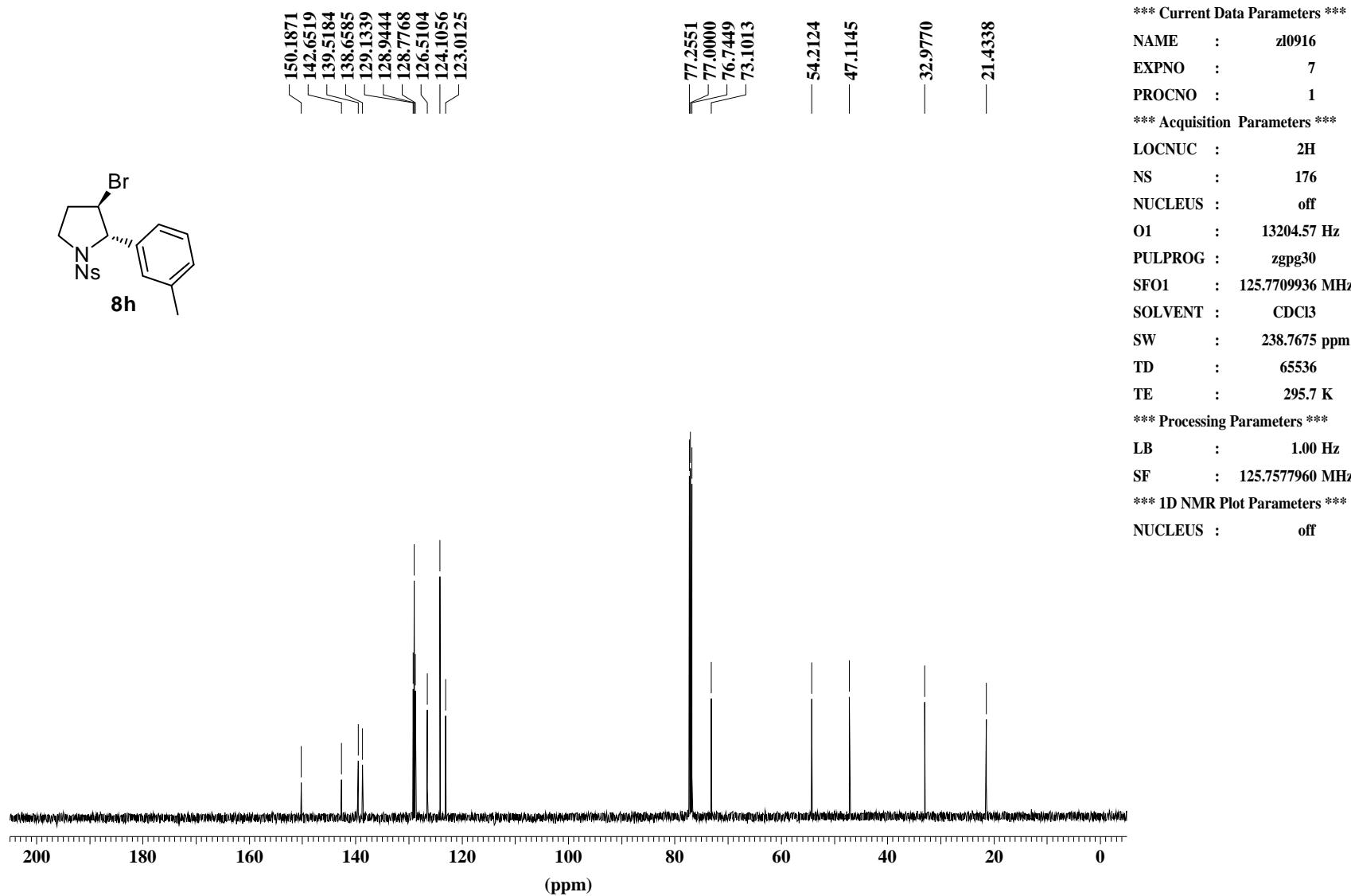
LB : 0.30 Hz
SF : 500.1300140 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

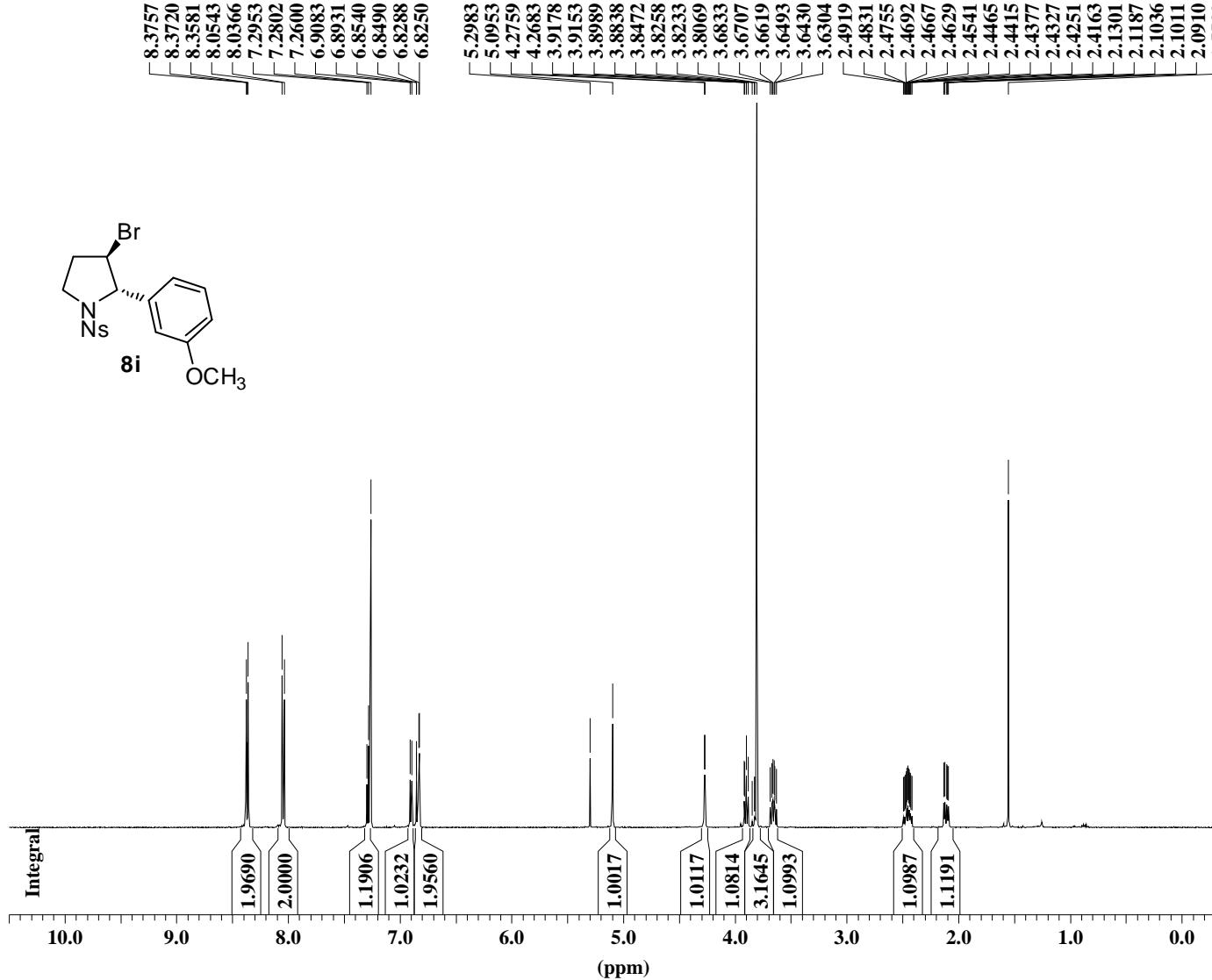
13C AMX500

cj2044E



1H AMX500

cj2044D



*** Current Data Parameters ***

NAME : zl0916
EXPNO : 5
PROCNO : 1
LOCMNUC : 2H
NS : 8
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm
TD : 32768
TE : 295.6 K

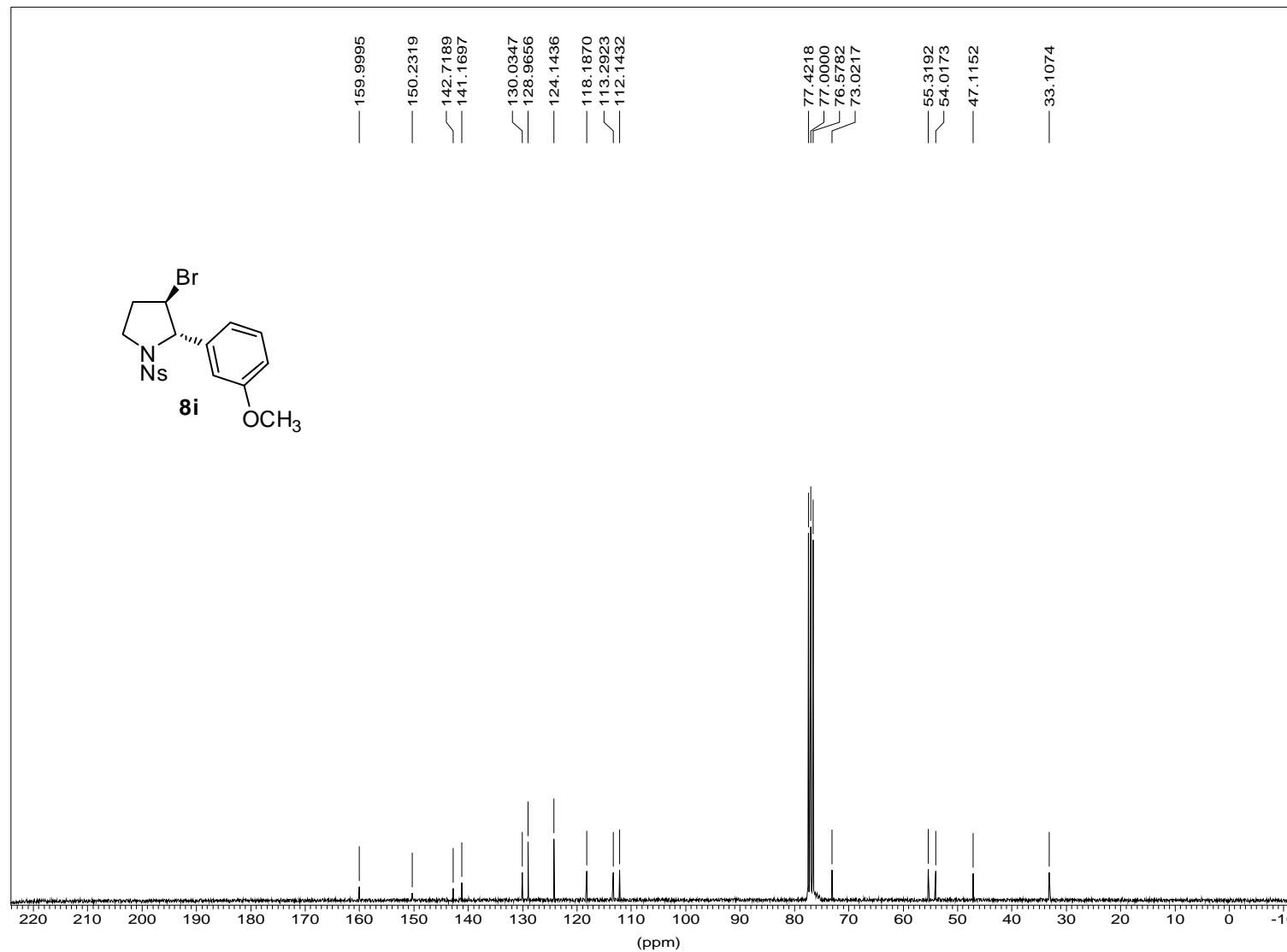
*** Processing Parameters ***

LB : 0.30 Hz
SF : 500.1300140 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹³C Standard AC300
cj2044D



*** Current Data Parameters ***

NAME : se16zl
EXPNO : 5
PROCNO : 1

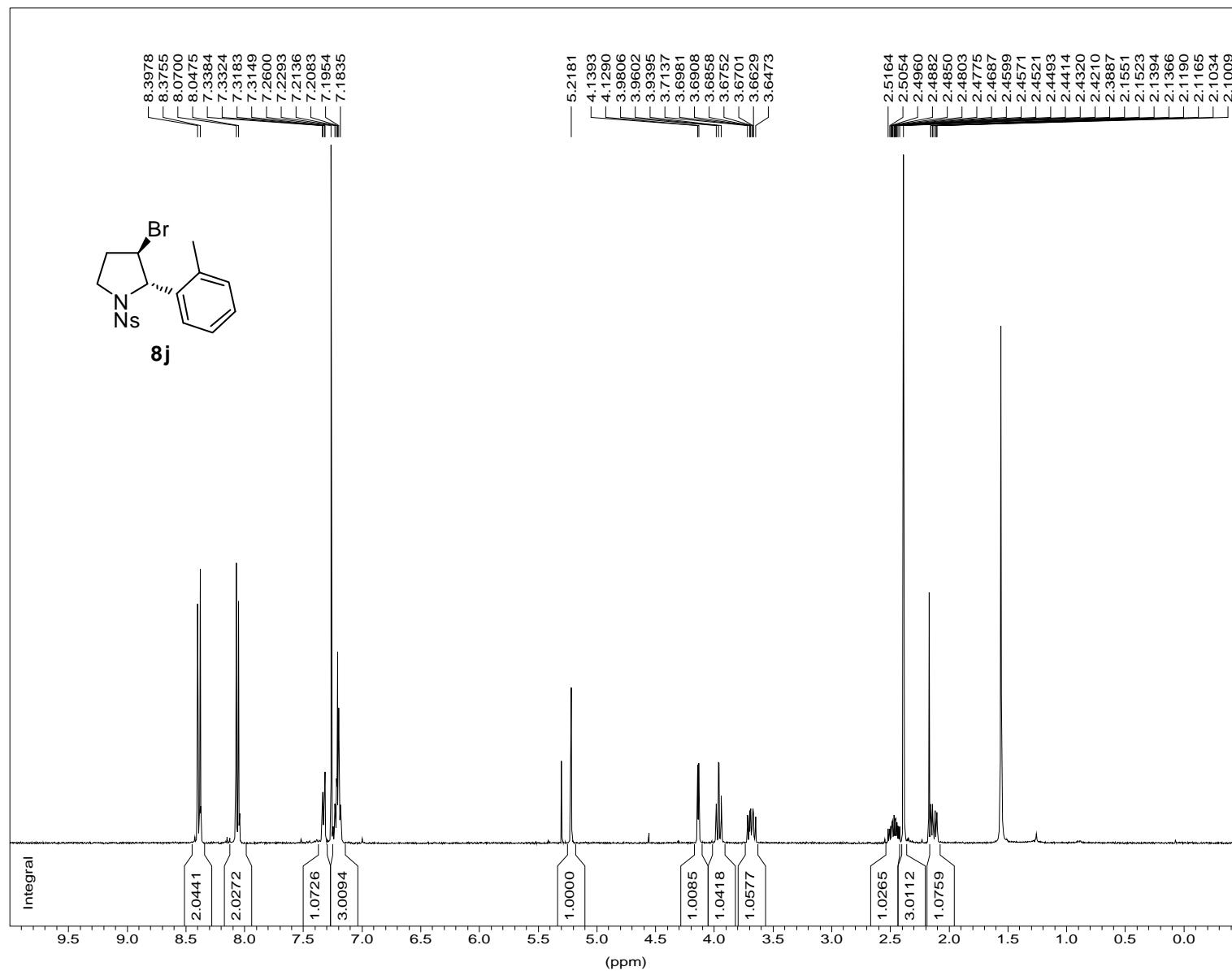
*** Acquisition Parameters ***

BF1 : 75.4677490 MHz
LOCNUC : 2H
NS : 15360
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl₃
SW : 238.2968 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 45.551 degree
PHC1 : 6.960 degree

cj2052B



*** Current Data Parameters ***

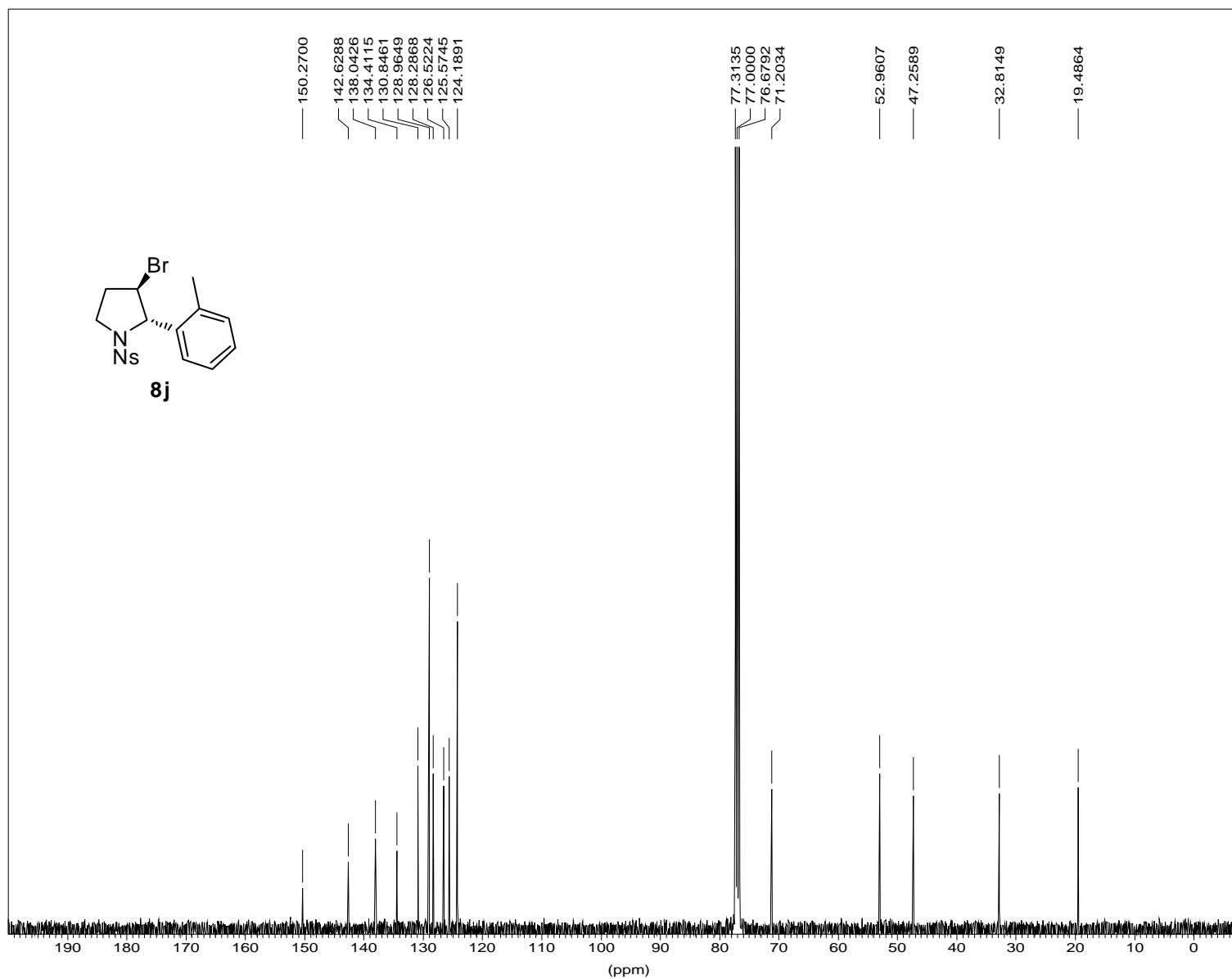
NAME : oct01cj
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***

BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 8
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl₃
SW : 20.5524 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -43.690 degree
PHC1 : -13.311 degree

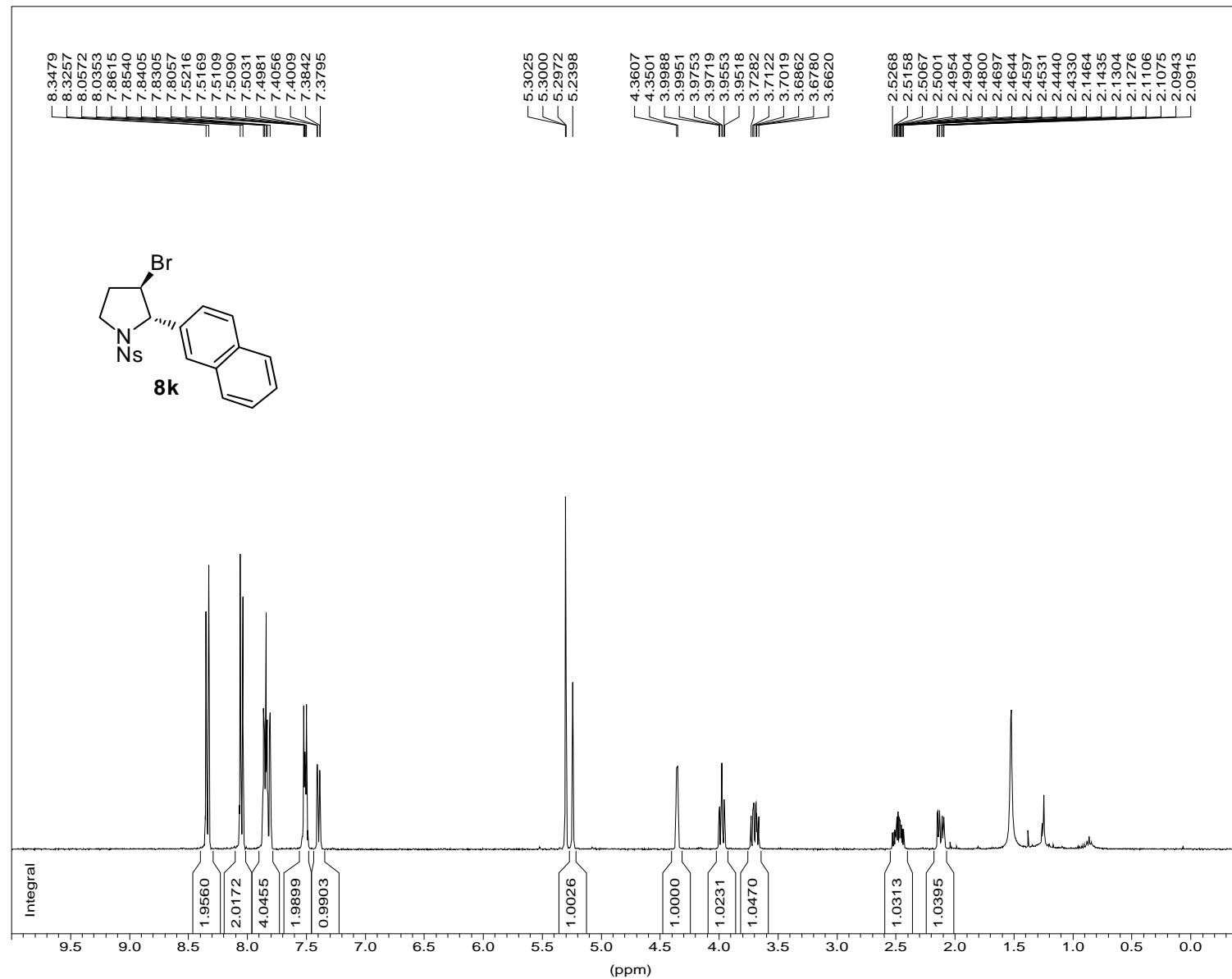
cj2052B



*** Current Data Parameters ***

NAME : oct01cj
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
RF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 3000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl3
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 82.952 degree
PHC1 : -35.813 degree

cj2017A



*** Current Data Parameters ***

NAME : aug02cj

EXPNO : 7

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 400.1300000 MHz

LOCNUC : 2H

NS : 16

O1 : 2470.97 Hz

PULPROG : zg30

SFO1 : 400.1324710 MHz

SOLVENT : CD₂Cl₂

SW : 20.5524 ppm

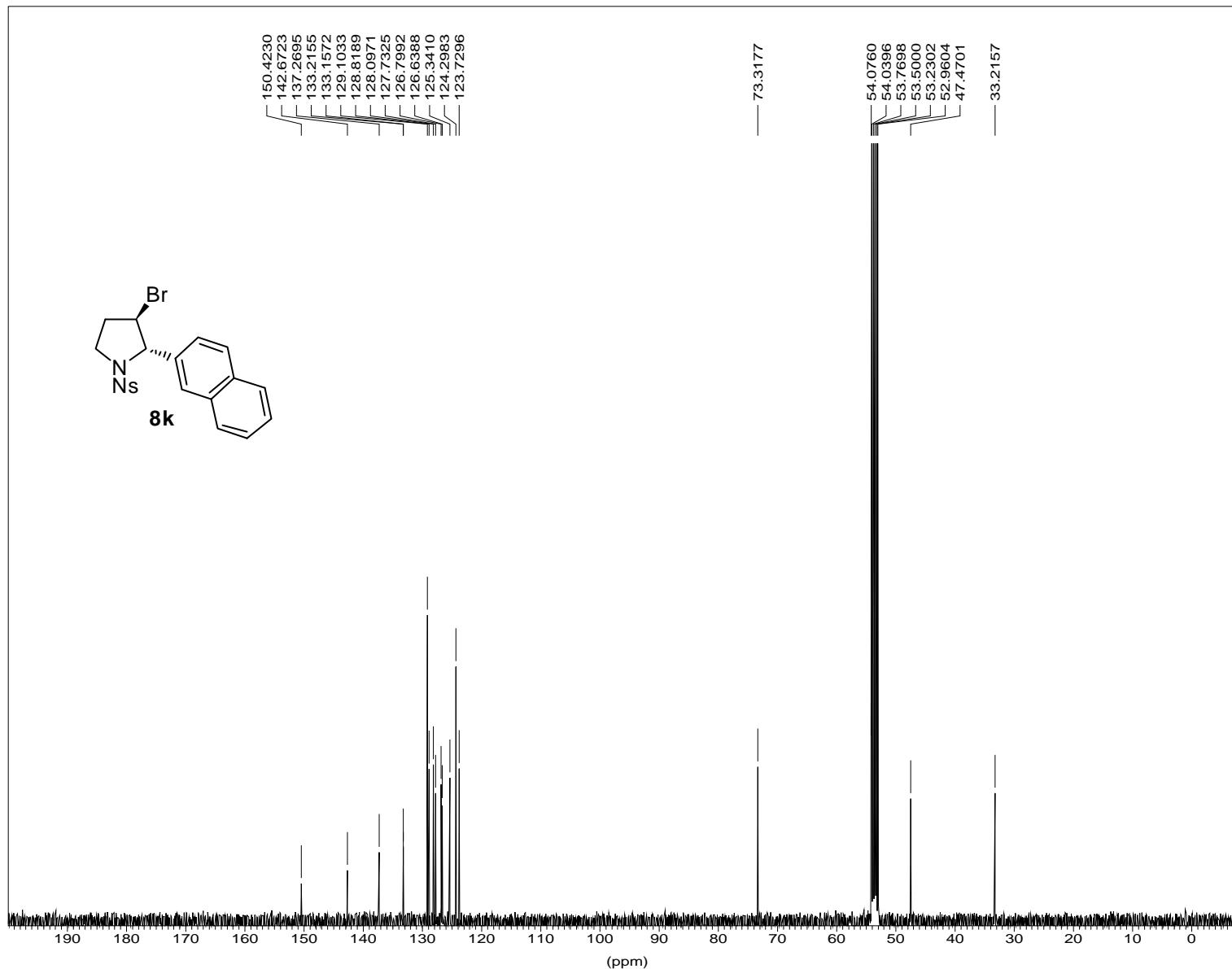
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : -53.830 degree

PHC1 : -8.509 degree

cj2017A



*** Current Data Parameters ***

NAME : aug02cj
EXPNO : 8
PROCNO : 1

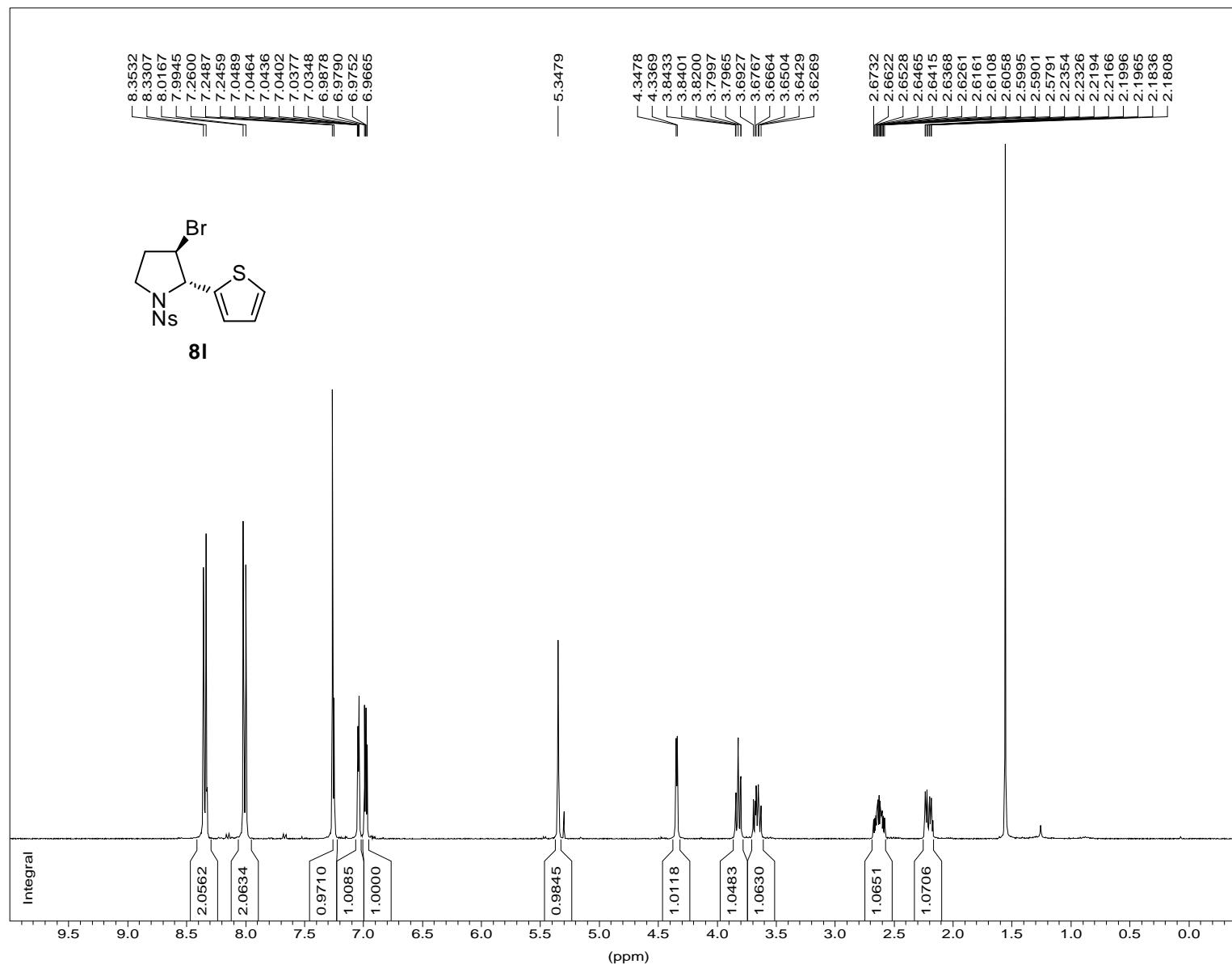
*** Acquisition Parameters ***

BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 2000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CD2Cl2
SW : 238.8943 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 100.684 degree
PHC1 : -50.812 degree

cj2060B



*** Current Data Parameters ***

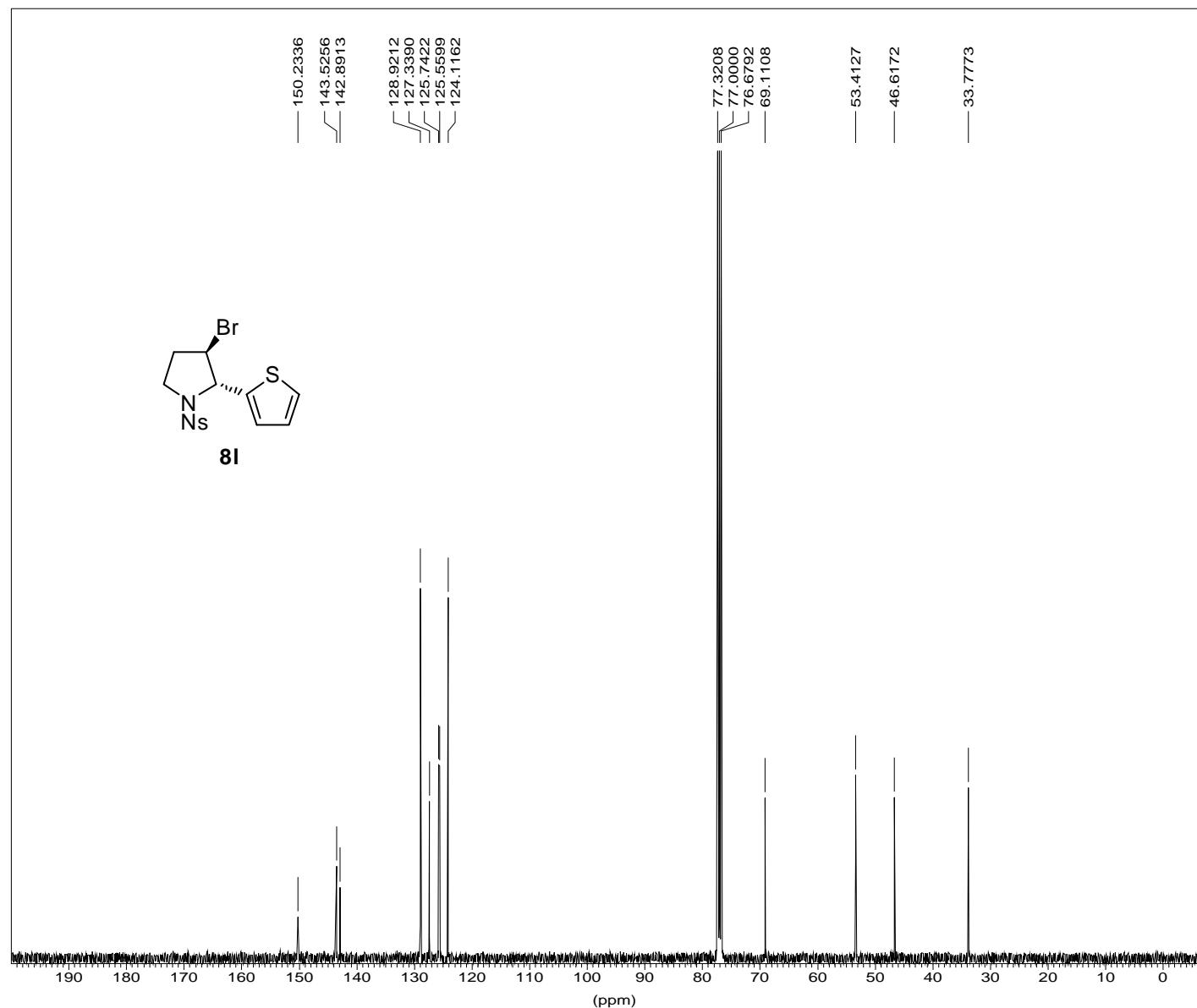
NAME : oct22cj
EXPNO : 15
PROCNO : 1
*** Acquisition Parameters ***

BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 16
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl₃
SW : 20.5524 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -46.229 degree
PHC1 : -13.360 degree

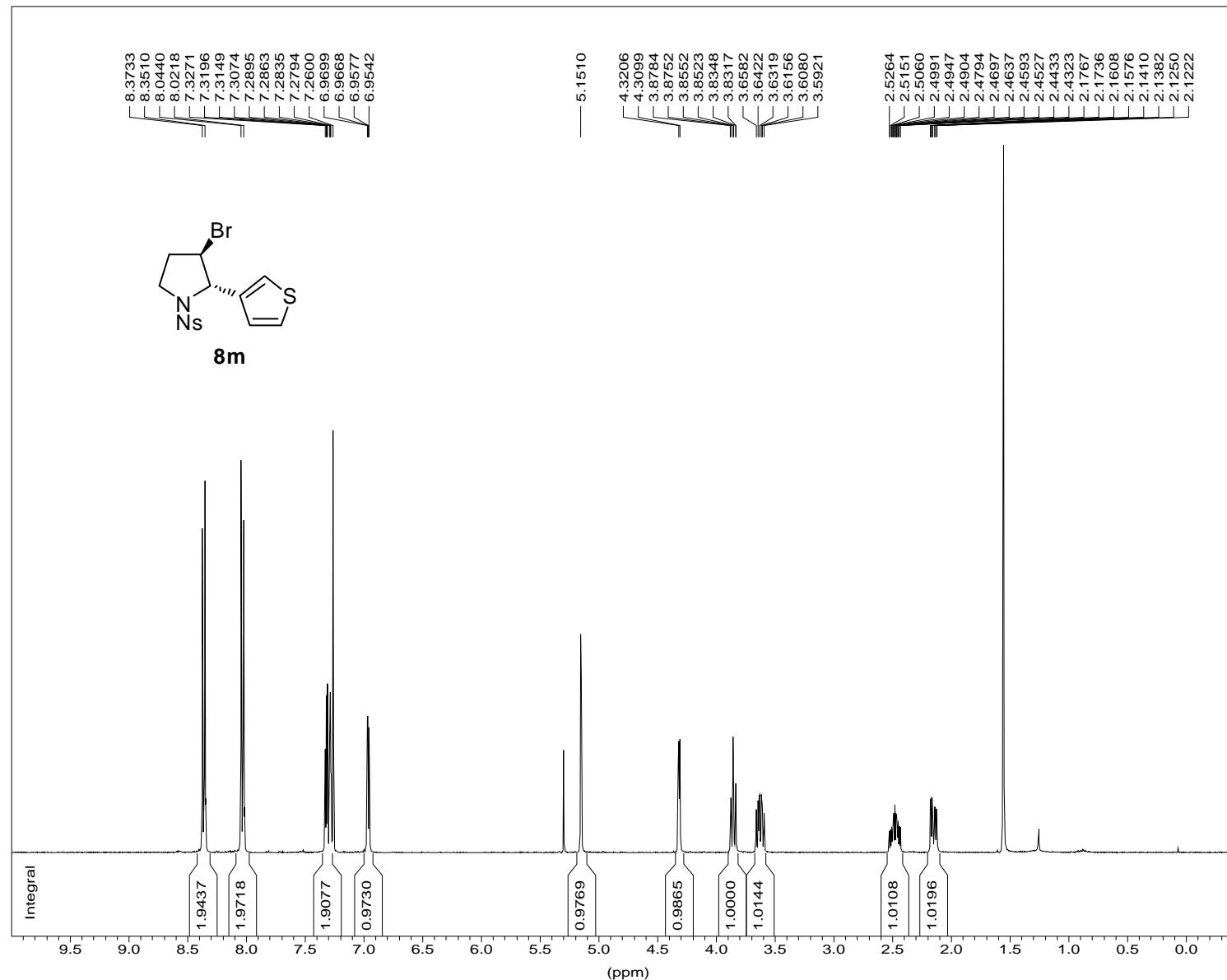
cj2060B



*** Current Data Parameters ***

NAME : oct22cj
EXPNO : 16
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 3000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 101.857 degree
PHC1 : -33.974 degree

cj2060C



*** Current Data Parameters ***

NAME : oct22cj

EXPNO : 13

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 400.1300000 MHz

LOCNUC : 2H

NS : 16

O1 : 2470.97 Hz

PULPROG : zg30

SFO1 : 400.1324710 MHz

SOLVENT : CDCl₃

SW : 20.5524 ppm

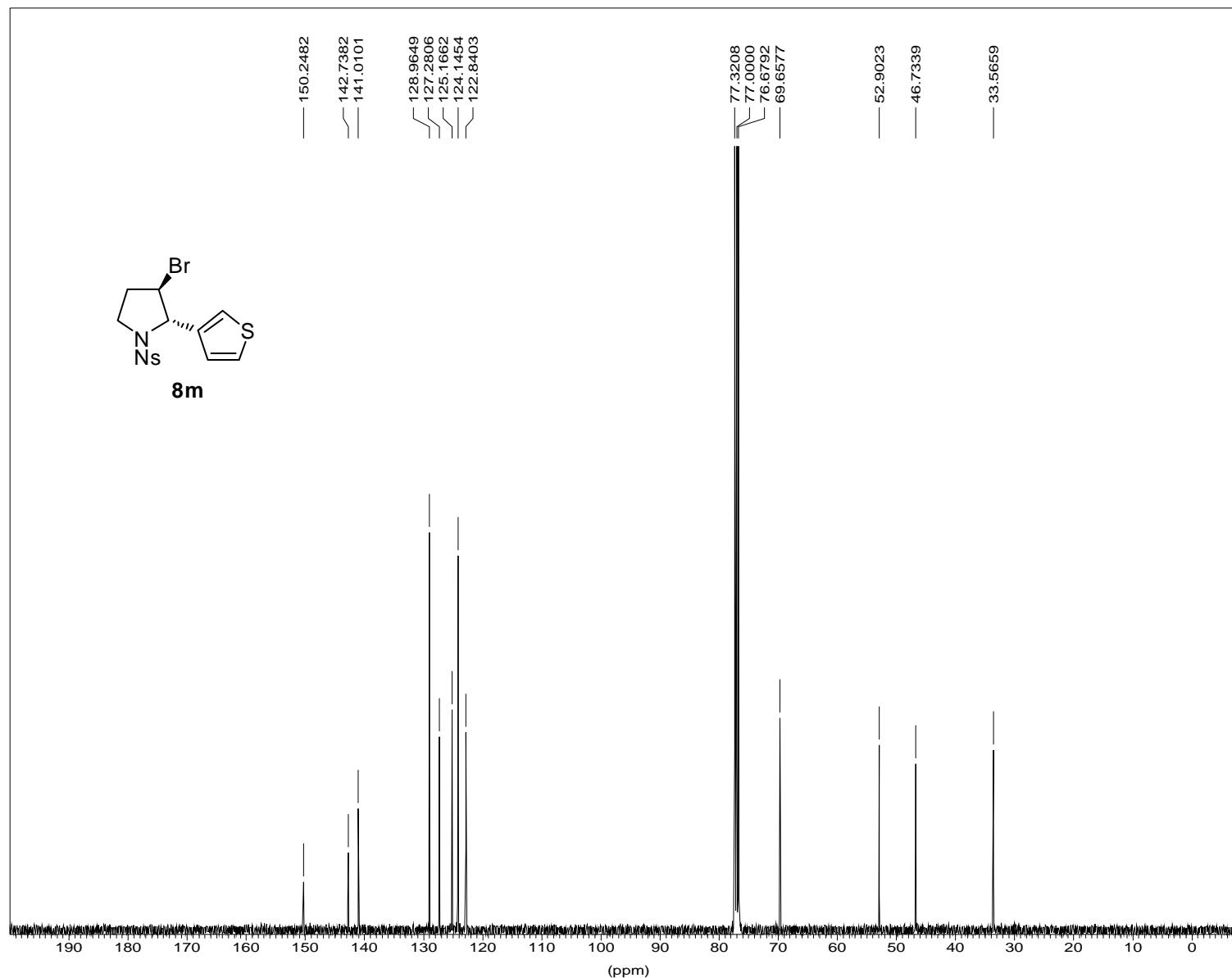
*** Processing Parameters ***

LB : 0.30 Hz

PHC0 : -42.965 degree

PHC1 : -14.317 degree

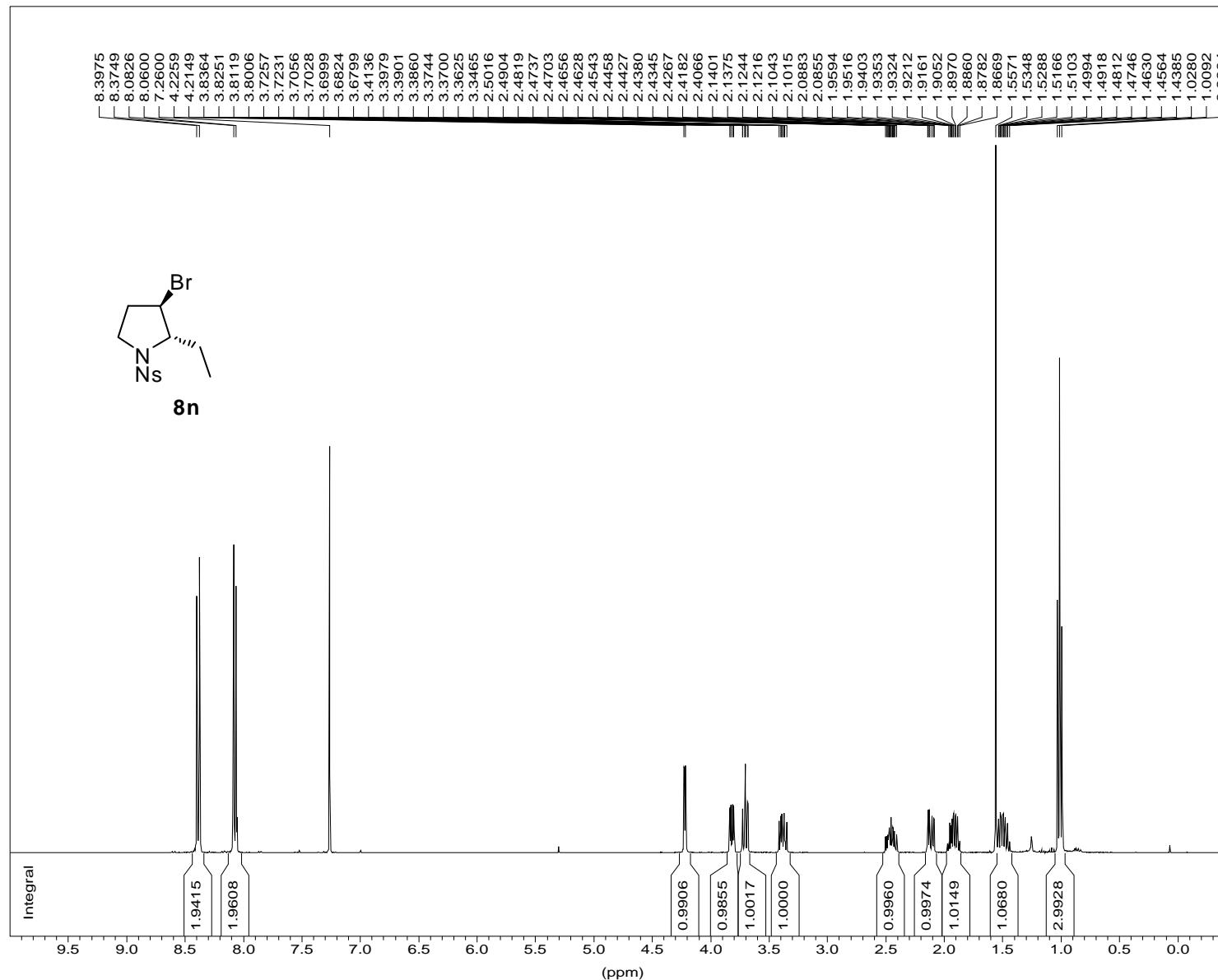
cj2060C



*** Current Data Parameters ***

NAME : oct22cj
EXPNO : 14
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 3000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 113.188 degree
PHC1 : -34.717 degree

cj2057C



*** Current Data Parameters ***

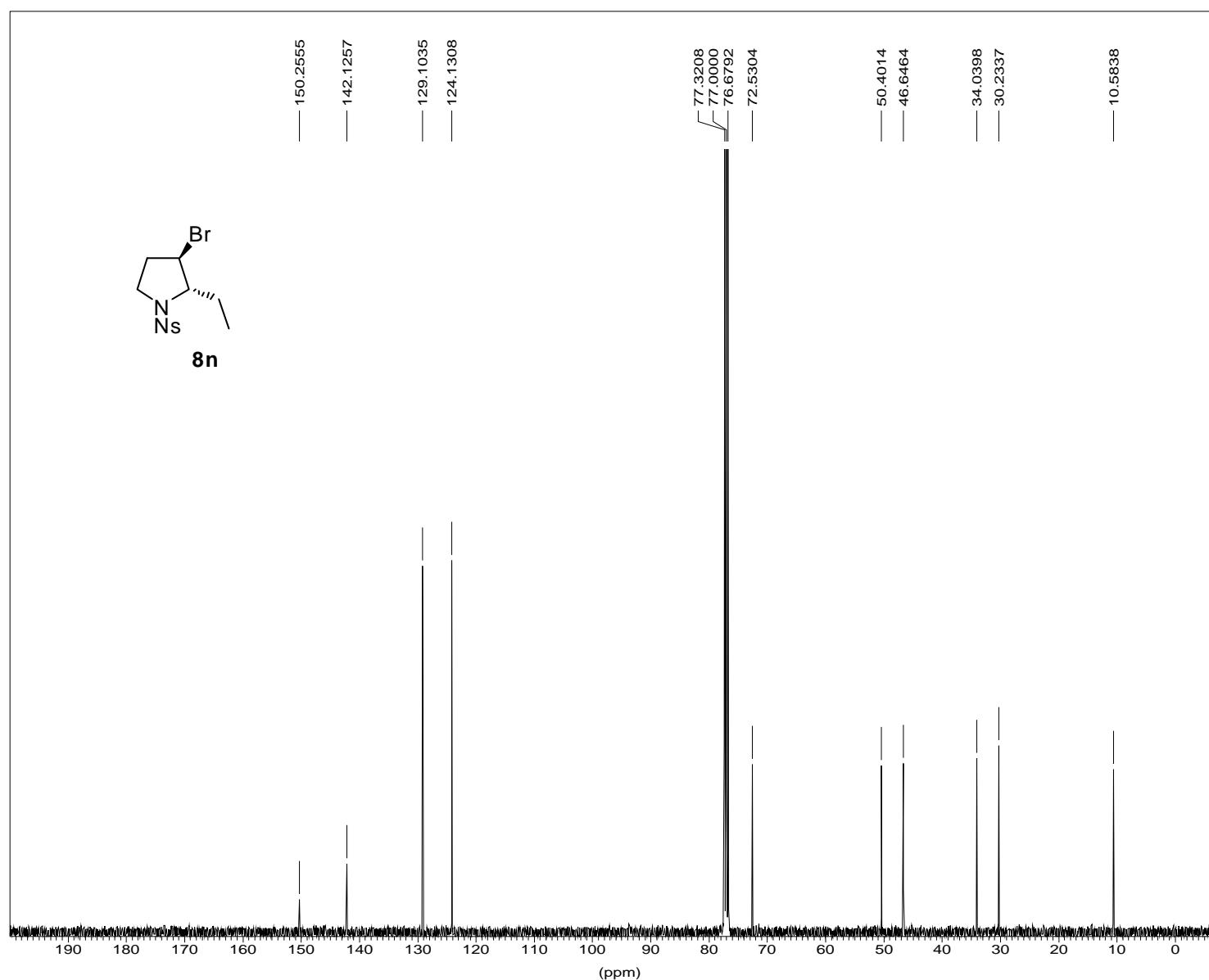
NAME : oct15cj
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***

BF1 : 400.1300000 MHz
LOCNUC : 2H
NS : 16
O1 : 2470.97 Hz
PULPROG : zg30
SFO1 : 400.1324710 MHz
SOLVENT : CDCl₃
SW : 20.5524 ppm

*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : -45.656 degree
PHC1 : -17.365 degree

cj2057C



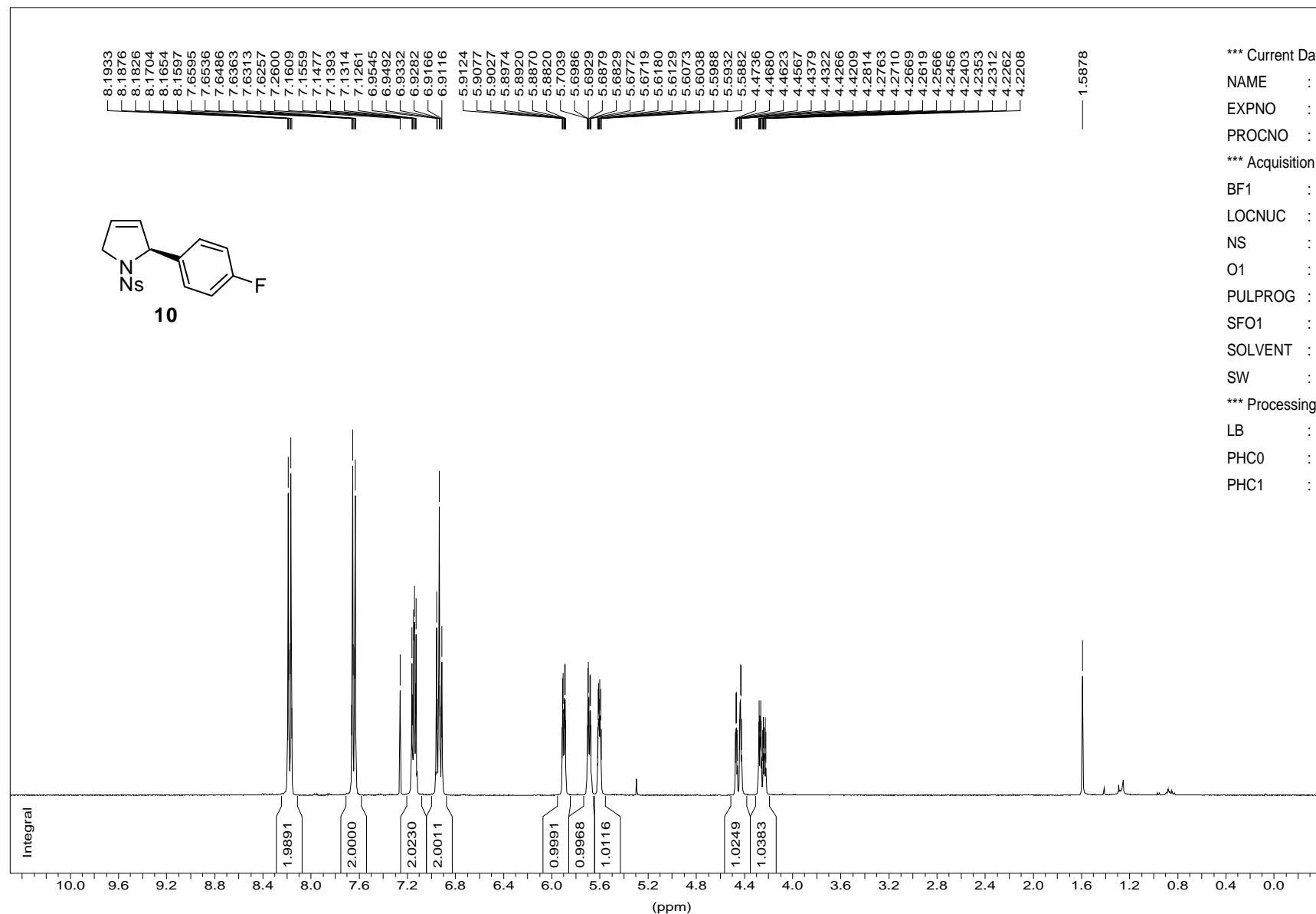
*** Current Data Parameters ***

NAME : oct15cj
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
LOCNUC : 2H
NS : 2000
O1 : 11067.40 Hz
PULPROG : zgpg30
SFO1 : 100.6238364 MHz
SOLVENT : CDCl₃
SW : 238.8943 ppm

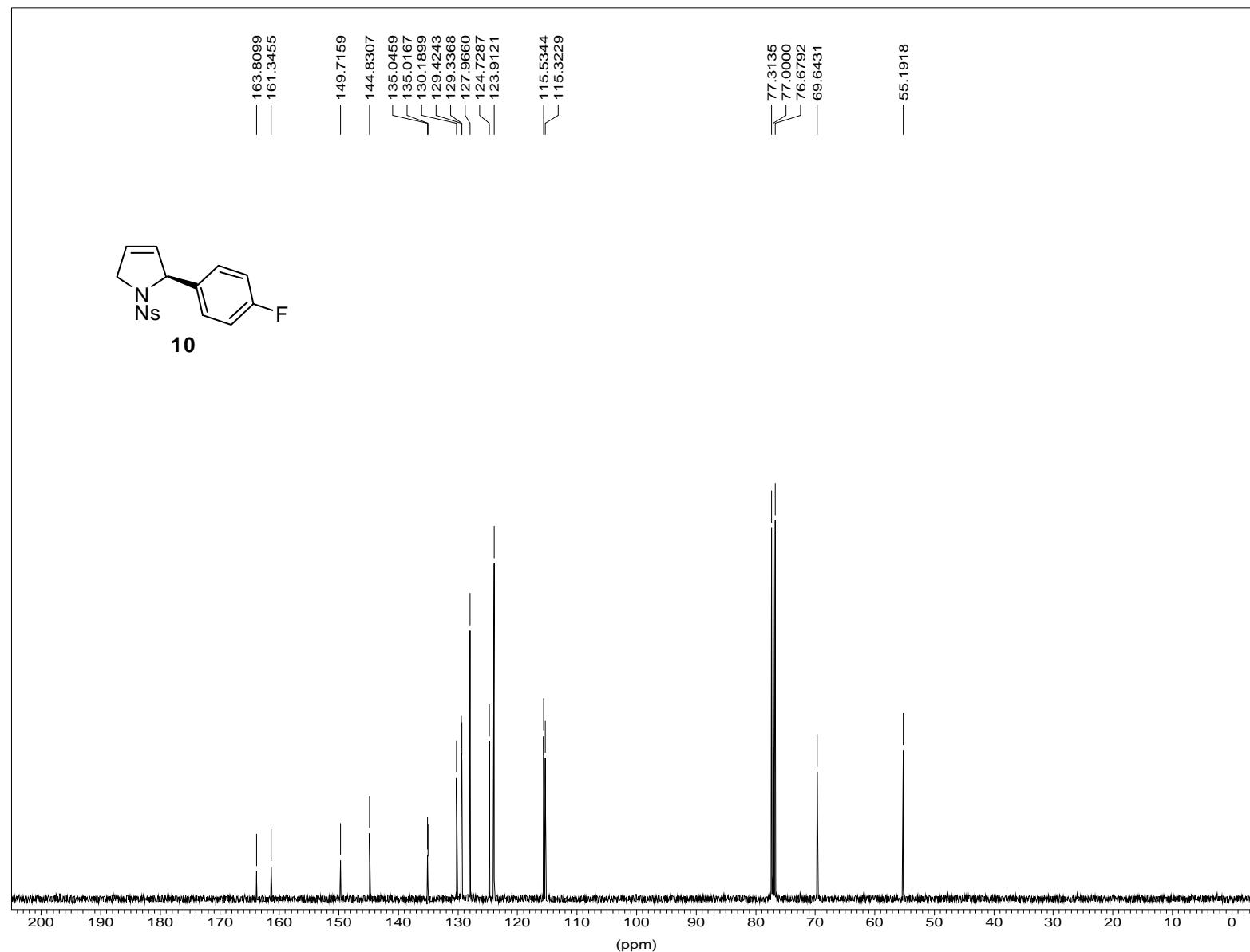
*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 97.657 degree
PHC1 : -62.248 degree

4-F-DBU



4-F-DBU



*** Current Data Parameters ***

NAME : nov24zl

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 100.6127690 MHz

LOCNUC : 2H

NS : 362

O1 : 11067.40 Hz

PULPROG : zgpg30

SFO1 : 100.6238364 MHz

SOLVENT : CDCl₃

SW : 238.8943 ppm

*** Processing Parameters ***

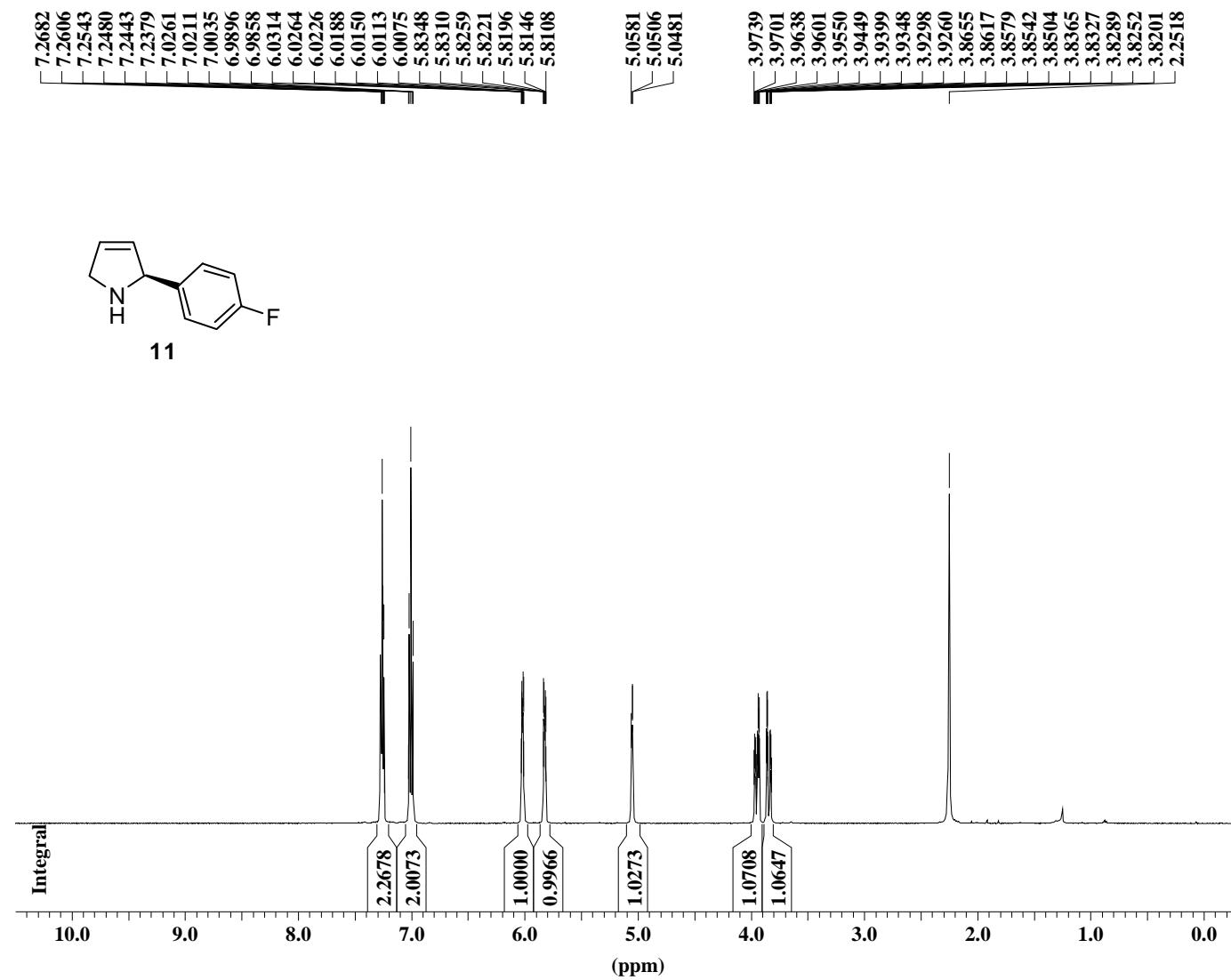
LB : 1.00 Hz

PHC0 : 92.484 degree

PHC1 : -60.947 degree

1H AMX500

3241B



*** Current Data Parameters ***

NAME : z1125
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

LOCMNUC : 2H
NS : 8
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm
TD : 32768
TE : 295.6 K

*** Processing Parameters ***

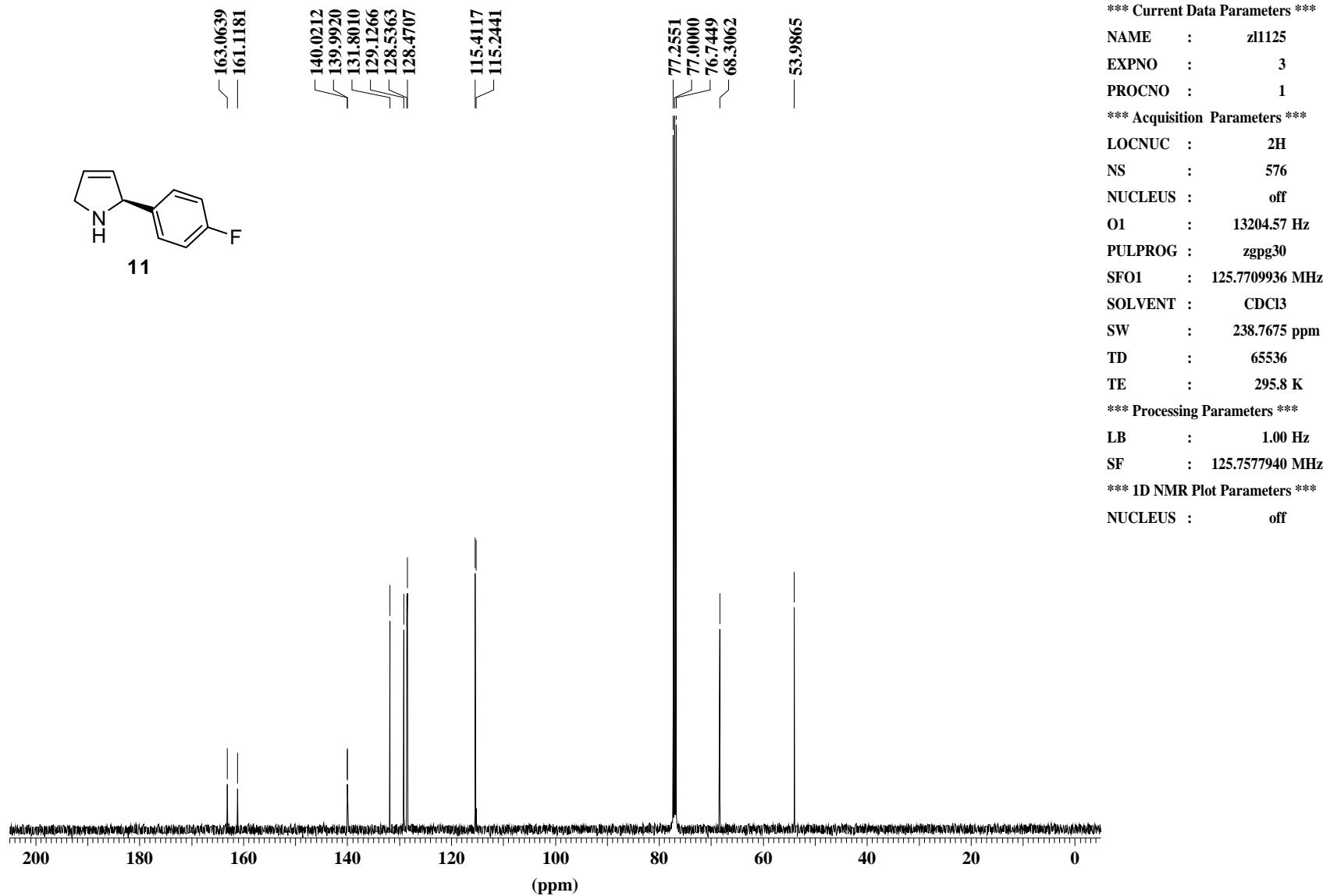
LB : 0.30 Hz
SF : 500.1300140 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

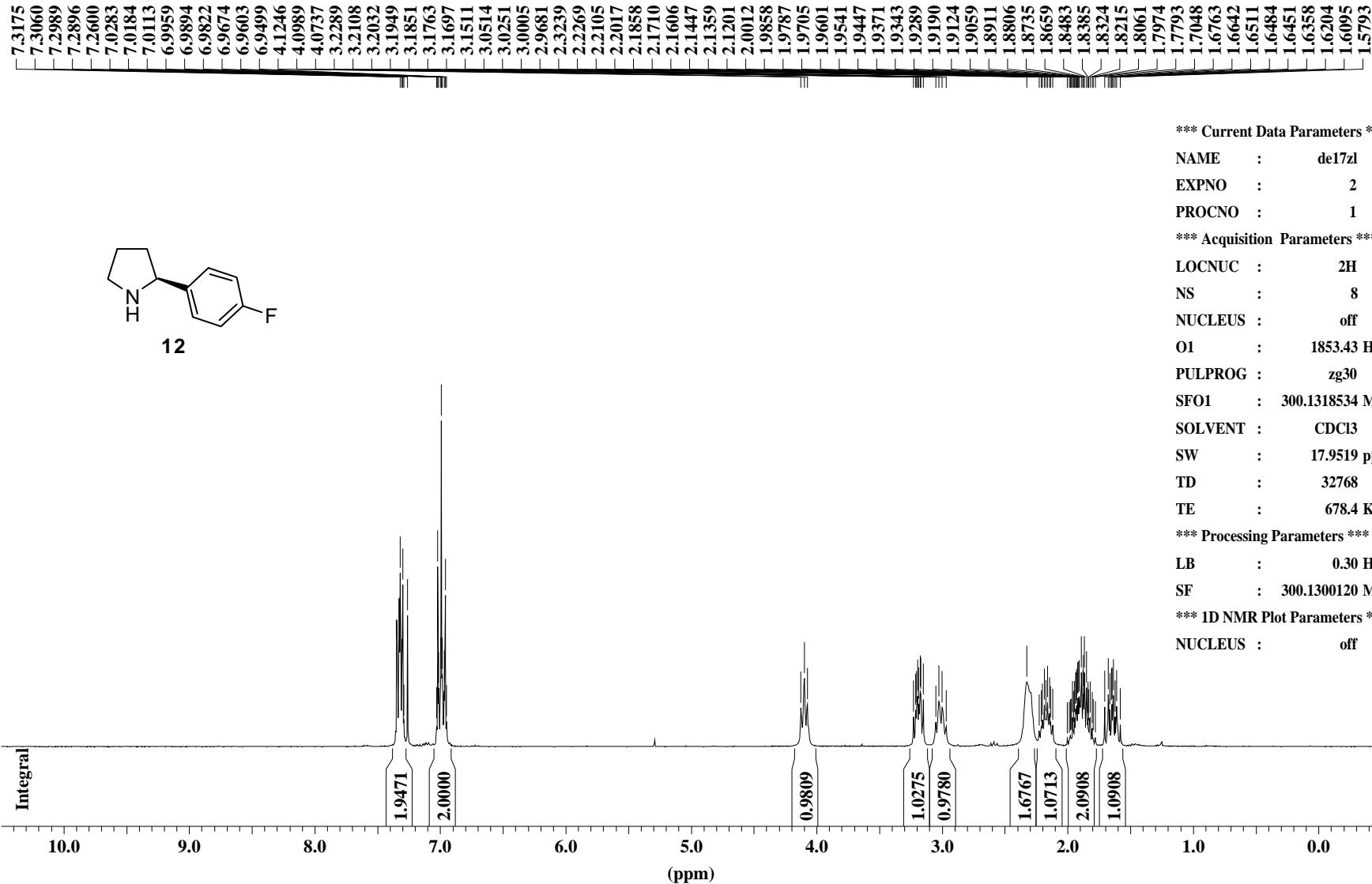
13C AMX500

3241B



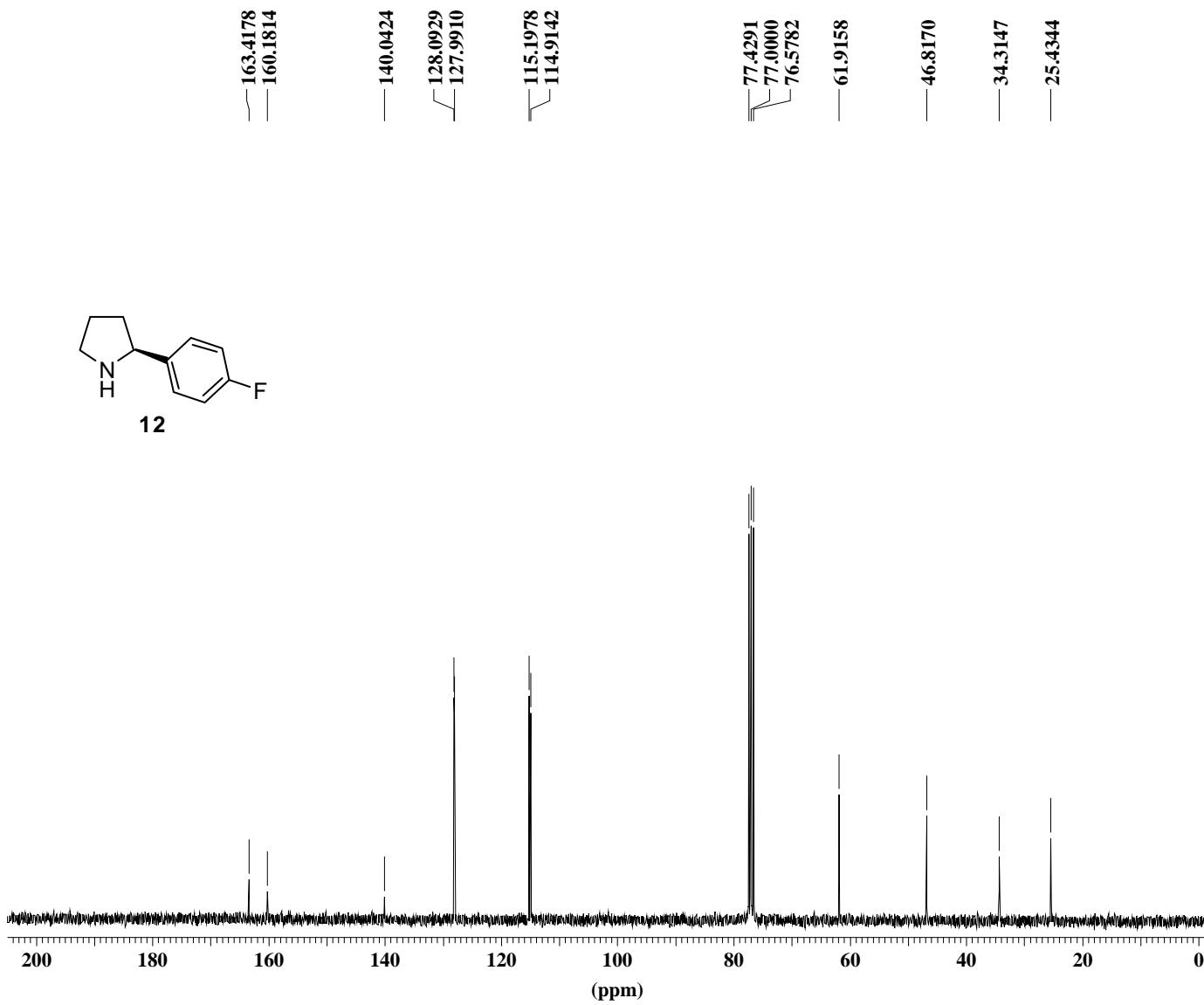
1H normal range AC300

3255A



¹³C Standard AC300

3255A



*** Current Data Parameters ***

NAME : de17zl
EXPNO : 3
PROCNO : 1
LOCMUC : 2H
NS : 1426
NUCLEUS : off
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl₃
SW : 238.2968 ppm
TD : 32768
TE : 678.3 K

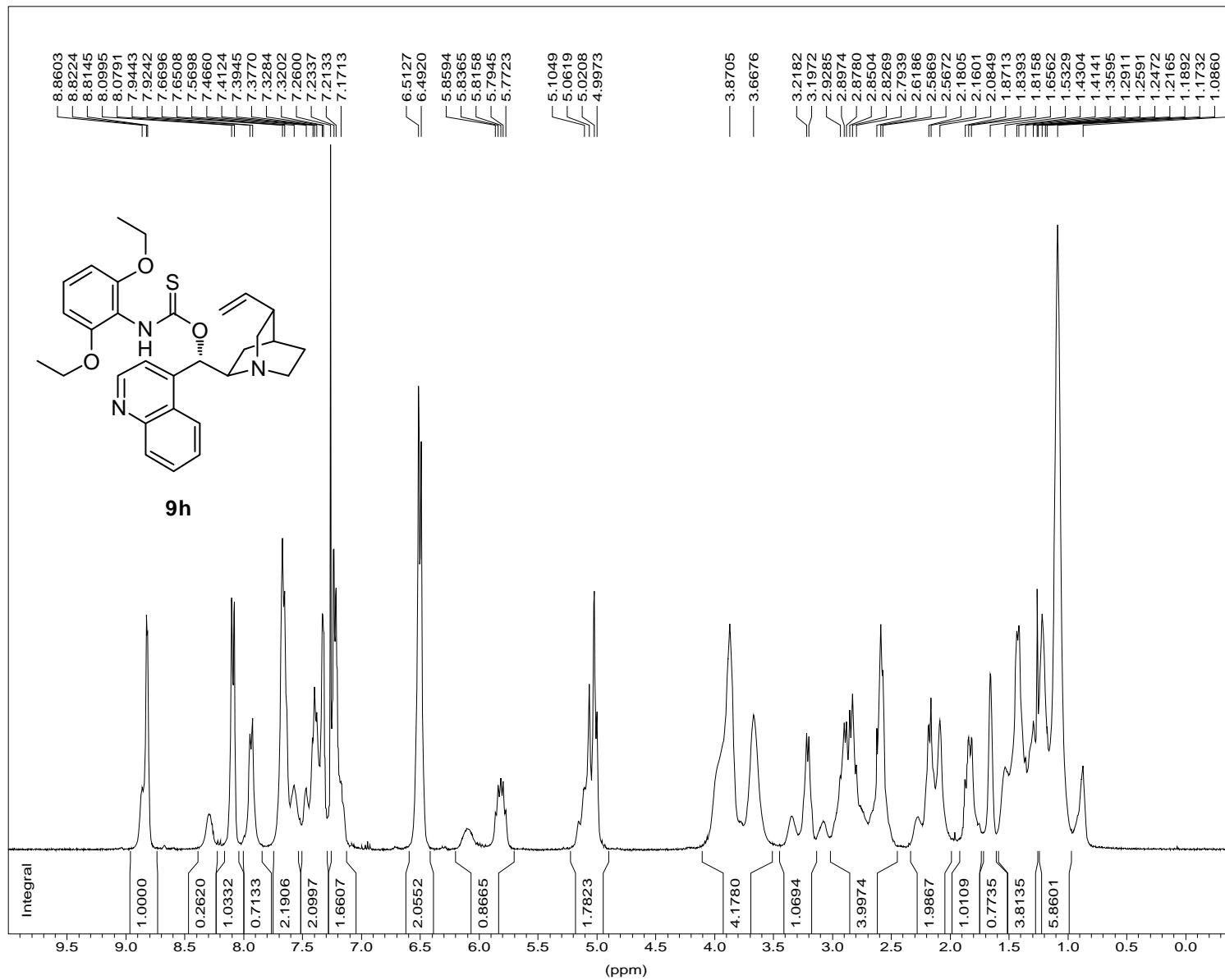
*** Processing Parameters ***

LB : 1.00 Hz
SF : 75.4677520 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

cj2,6-OEt-cinchonine



*** Current Data Parameters ***

NAME : dec03cj

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 400.1300000

LOCNUC : 2H

NS : 8

O1 : 2470.97 Hz

PULL PROG : za30

SEQ1 : 400 1324710 MH

SOLVENT : CDCl₃

SW : 20.5524 ppm

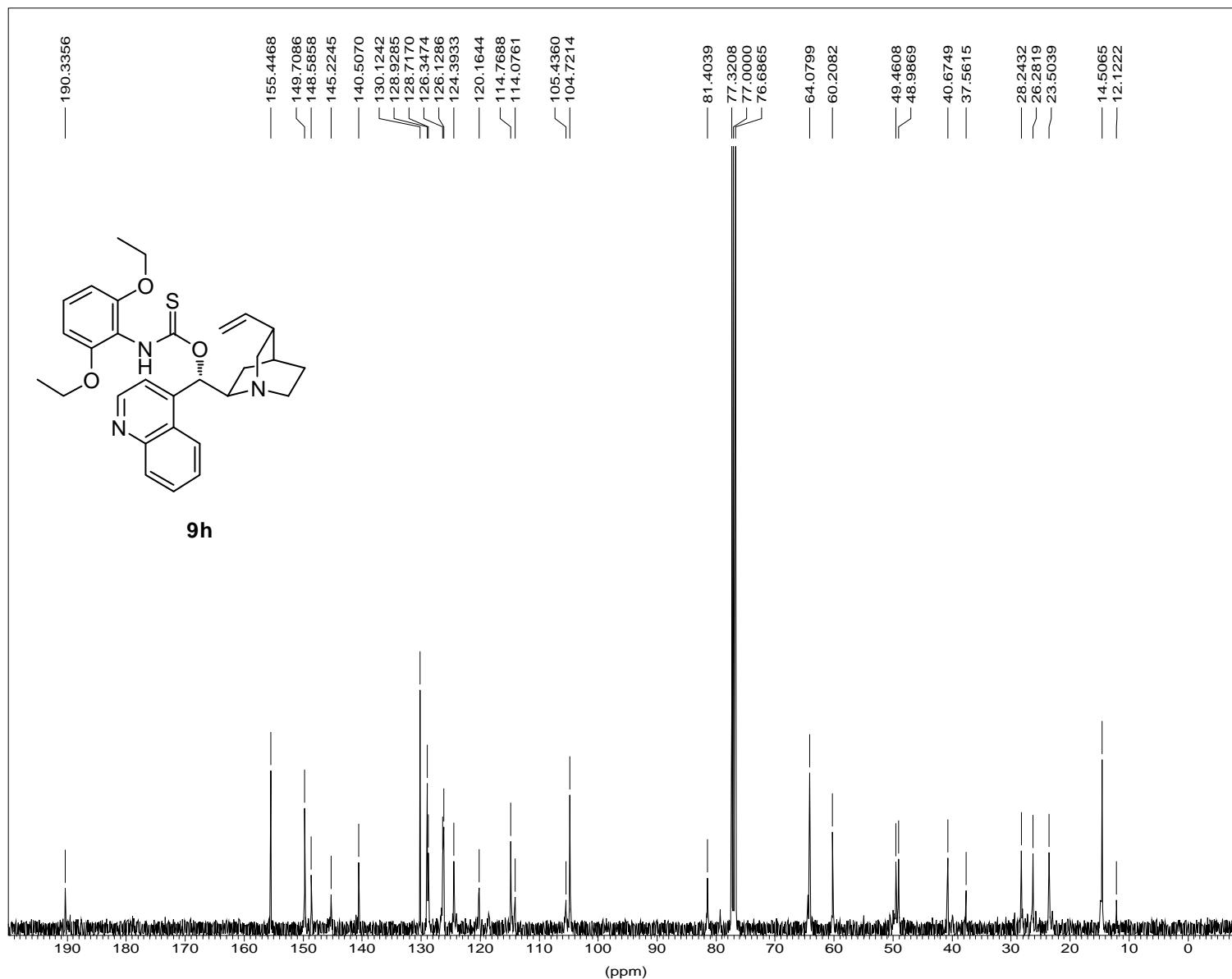
*** Processing Parameters ***

Processing Parameters

BH02 . 54.181 km

FHC0 : -34.161 degree
FHC1 : 62.666 degree

cj2,6-OEt-cinchonine



*** Current Data Parameters ***

NAME : dec03cj

EXPNO : 6

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 100.6127690 MHz

LOCNUC : 2H

NS : 1024

O1 : 11067.40 Hz

PULPROG : zgpg30

SFO1 : 100.6238364 MHz

SOLVENT : CDCl₃

SW : 238.8943 ppm

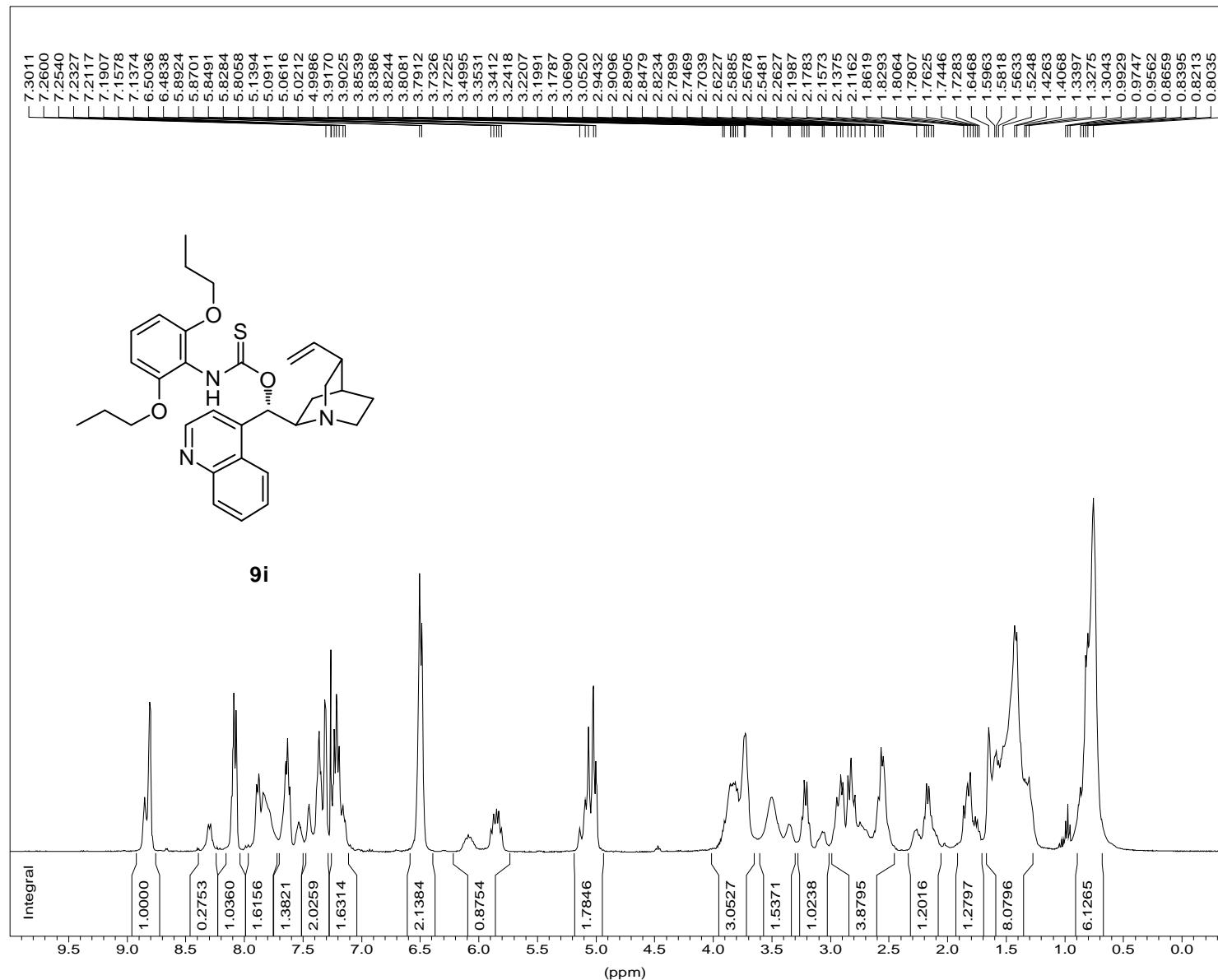
*** Processing Parameters ***

LB : 1.00 Hz

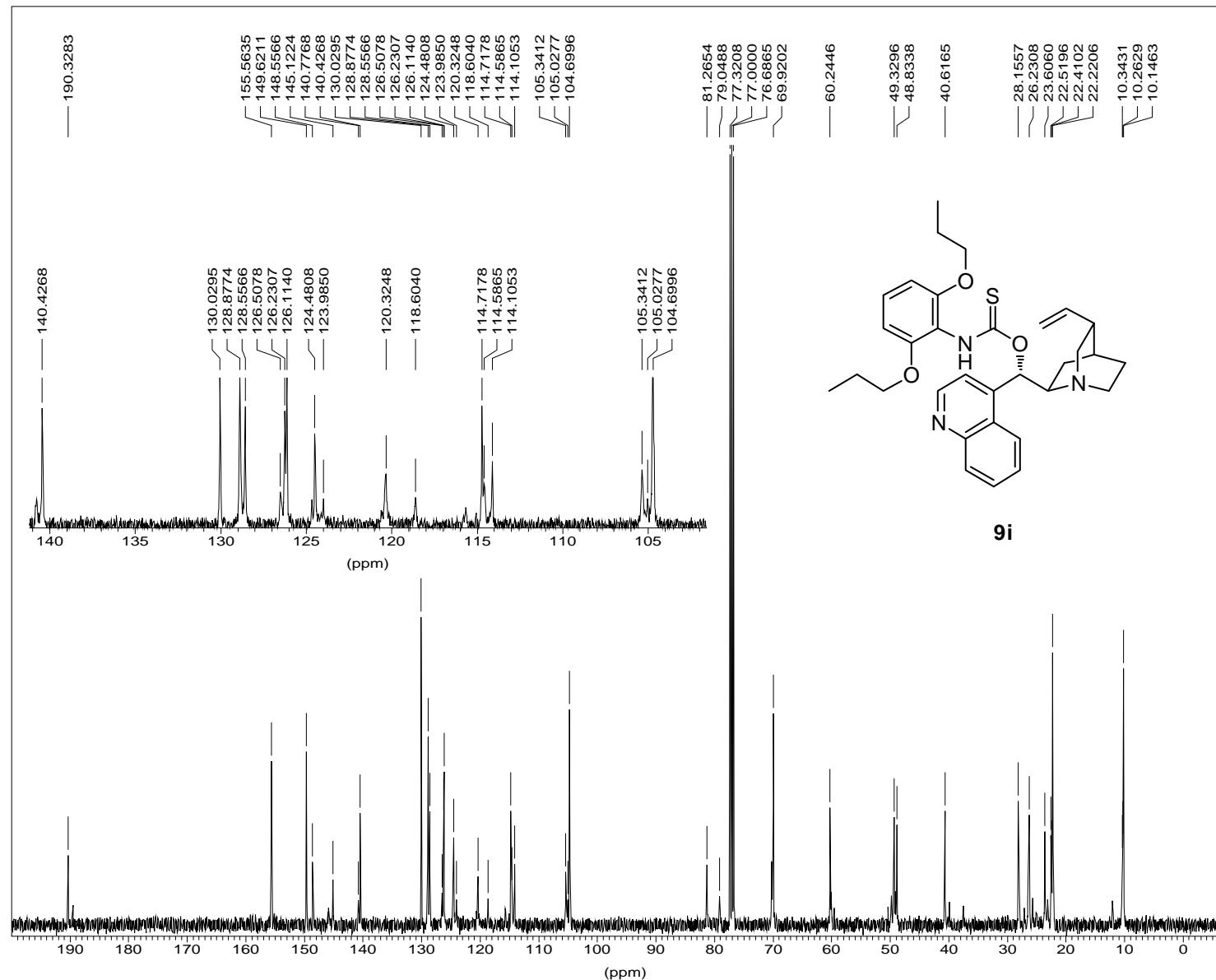
PHC0 : 89.476 degree

PHC1 : -59.519 degree

cj2,6-Opropyl-cinchonine



cj2,6-Opropyl-cinchonine



*** Current Data Parameters ***

NAME : dec03cj

EXPNO : 8

PROCNO : 1

*** Acquisition Parameters ***

BF1 : 100.6127690 MHz

LOCNUC : 2H

NS : 500

O1 : 11067.40 Hz

PULPROG : zgpg30

SFO1 : 100.6238364 MHz

SOLVENT : CDCl₃

SW : 238.8943 ppm

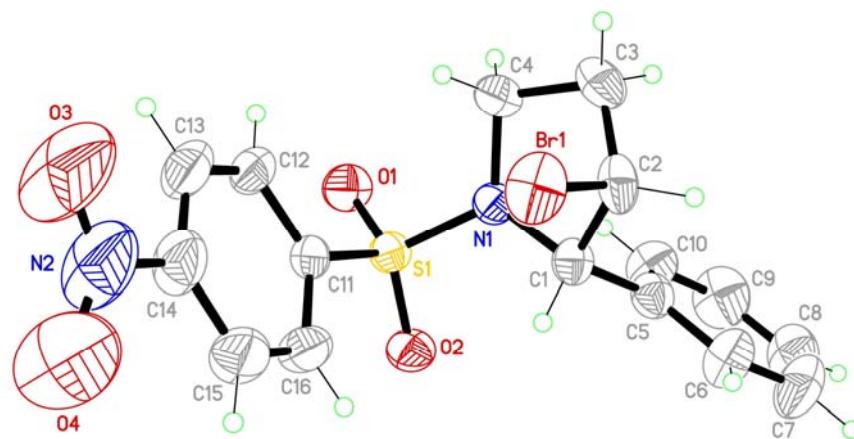
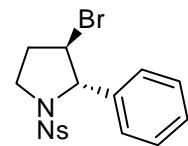
*** Processing Parameters ***

LB : 1.00 Hz

PHC0 : 94.604 degree

PHC1 : -60.082 degree

Figure S1. X-ray structure of **8a** (CCDC 859894)



Empirical formula	C ₁₆ H ₁₅ BrN ₂ O ₄ S		
Formula weight	411.27		
Temperature	223(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	P2(1)2(1)2(1)		
Unit cell dimensions	a = 7.5614(5) Å	α = 90°.	
	b = 11.1691(7) Å	β = 90°.	
	c = 20.0521(13) Å	γ = 90°.	

Volume	1693.48(19) Å ³
Z	4
Density (calculated)	1.613 Mg/m ³
Absorption coefficient	2.573 mm ⁻¹
F(000)	832
Crystal size	0.60 x 0.60 x 0.34 mm ³
Theta range for data collection	2.03 to 27.49°.
Index ranges	-9<=h<=9, -11<=k<=14, -25<=l<=25
Reflections collected	11943
Independent reflections	3889 [R(int) = 0.0438]
Completeness to theta = 27.49°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4749 and 0.3074
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3889 / 0 / 217
Goodness-of-fit on F ²	0.954
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0726
R indices (all data)	R1 = 0.0484, wR2 = 0.0764
Absolute structure parameter	0.009(9)
Largest diff. peak and hole	0.484 and -0.273 e.Å ⁻³

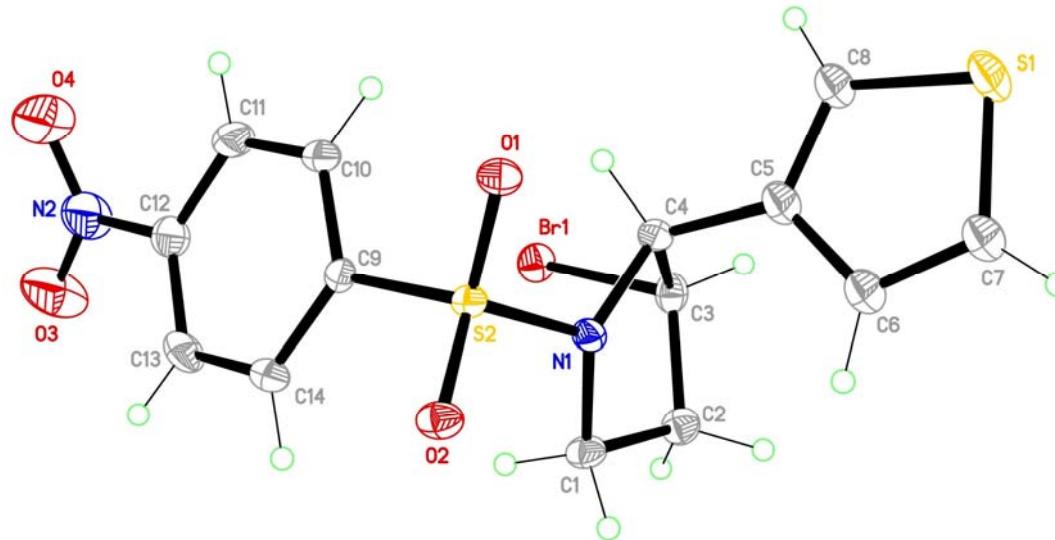
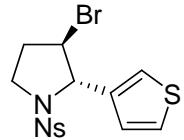
Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³)

for B668. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	10035(1)	7137(1)	1991(1)	57(1)

S(1)	4973(1)	6299(1)	2857(1)	33(1)
O(1)	4258(2)	5161(2)	3039(1)	45(1)
O(2)	4101(2)	7379(2)	3059(1)	44(1)
O(3)	6653(7)	5553(3)	-349(1)	130(2)
O(4)	5330(8)	7235(3)	-392(1)	163(2)
N(1)	6962(3)	6346(2)	3152(1)	34(1)
N(2)	5892(6)	6385(4)	-93(2)	97(1)
C(1)	7962(3)	7484(2)	3172(1)	34(1)
C(2)	9824(4)	7088(2)	2968(1)	43(1)
C(3)	9938(4)	5805(2)	3222(1)	48(1)
C(4)	8133(3)	5298(2)	3074(1)	41(1)
C(5)	7984(3)	8037(2)	3867(1)	38(1)
C(6)	8764(5)	9148(3)	3947(2)	57(1)
C(7)	8851(6)	9686(3)	4565(2)	72(1)
C(8)	8164(5)	9139(4)	5113(2)	70(1)
C(9)	7374(5)	8047(4)	5042(2)	67(1)
C(10)	7284(4)	7490(3)	4421(2)	50(1)
C(11)	5162(4)	6317(2)	1978(1)	34(1)
C(12)	5486(4)	5258(2)	1639(1)	44(1)
C(13)	5746(5)	5288(3)	961(2)	58(1)
C(14)	5634(5)	6361(3)	636(2)	59(1)
C(15)	5274(5)	7424(3)	964(2)	62(1)
C(16)	5045(5)	7399(2)	1640(1)	47(1)

Figure S2. X-ray structure of **8m** (CCDC 859895)



Empirical formula	C ₁₄ H ₁₃ BrN ₂ O ₄ S ₂
Formula weight	417.29
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.4711(7) Å α = 90°. b = 11.1765(10) Å β = 90°. c = 19.4619(17) Å γ = 90°.
Volume	1625.1(3) Å ³
Z	4

Density (calculated)	1.706 Mg/m ³
Absorption coefficient	2.807 mm ⁻¹
F(000)	840
Crystal size	0.60 x 0.30 x 0.04 mm ³
Theta range for data collection	2.09 to 27.50°.
Index ranges	-9<=h<=9, -12<=k<=14, -23<=l<=25
Reflections collected	11487
Independent reflections	3714 [R(int) = 0.0302]
Completeness to theta = 27.50°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5086
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3714 / 172 / 273
Goodness-of-fit on F ²	0.833
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0646
R indices (all data)	R1 = 0.0292, wR2 = 0.0656
Absolute structure parameter	0.028(7)
Largest diff. peak and hole	0.641 and -0.314 e.Å ⁻³

Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³)

. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(3)	6670(100)	3930(20)	10483(11)	51(4)
O(4)	5630(30)	2131(10)	10390(8)	45(2)
S(1)	8630(1)	777(1)	4959(1)	30(1)
C(5)	8325(4)	2137(3)	6004(1)	22(1)
C(6)	8109(4)	2881(3)	5416(1)	23(1)
C(7)	8224(4)	2267(3)	4816(2)	25(1)
C(8)	8622(4)	972(3)	5830(2)	24(1)
O(3A)	6430(50)	4017(10)	10445(6)	52(4)
O(4A)	6360(20)	2081(4)	10404(4)	45(2)
S(1A)	8220(30)	1620(20)	4789(8)	27(1)
C(5A)	8430(60)	2060(50)	6052(12)	23(1)
C(6A)	9360(60)	1000(40)	5957(13)	24(1)
C(7A)	9420(60)	580(30)	5294(17)	26(1)
C(8A)	7680(60)	2570(40)	5489(19)	23(1)
Br(1)	10376(1)	2969(1)	7960(1)	20(1)
S(2)	5078(1)	3428(1)	7118(1)	13(1)
O(1)	4447(2)	2286(1)	6880(1)	17(1)
O(2)	4093(2)	4495(2)	6964(1)	18(1)
N(1)	7072(3)	3612(2)	6812(1)	14(1)
N(2)	6175(4)	3074(2)	10141(1)	38(1)
C(1)	8023(3)	4748(2)	6944(1)	16(1)
C(2)	9954(3)	4430(2)	6762(1)	18(1)

C(3)	10099(3)	3114(2)	6960(1)	18(1)
C(4)	8296(3)	2576(2)	6739(1)	15(1)
C(9)	5307(3)	3344(2)	8020(1)	14(1)
C(10)	5551(4)	2226(2)	8314(1)	19(1)
C(11)	5816(4)	2142(3)	9013(1)	24(1)
C(12)	5864(4)	3182(2)	9394(1)	24(1)
C(13)	5615(4)	4301(2)	9112(1)	25(1)
C(14)	5322(4)	4385(2)	8410(1)	19(1)