Supporting Information

Highly Enantioselective Aza-Henry Reaction of Ketoimines Catalyzed by Chiral *N,N'*-Dioxide-Copper(I) Complexes

Cheng Tan,[†] Xiaohua Liu,[†] Liwei Wang,[†] Jun Wang,[†] and Xiaoming Feng[*,†,‡]

[†]*Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China*
[‡]*State Key Laboratory of Biotherapy, Sichuan University, Chengdu 610041, P. R. China*

xmfeng@scu.edu.cn

Contents

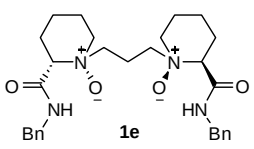
1. General

^{1}H NMR spectra were recorded on commercial instruments (400 or 600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 or 150 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). HRMS spectra were recorded on a commercial apparatus (ESI Source). Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral columns as stated in the experimental procedures at 23 °C with UV detector at 215 nm. Optical rotations were measured on a commercial polarimeter and reported as follows: $[\alpha]_D^T$ (*c* = g/100 mL, solvent).

N-tosyl imines **2a-p** were prepared according to the literature procedure.[1] $(CuOTf)_2{\cdot}C_7H_8$ was purchased from Fluka and used without further purification. 4 Å MS was purchased from Acros powdered <50 μm and used directly. CH_3NO_2 and PhOEt were commercially available and distilled before use. Racemic samples were prepared according to the literature procedure.[2]

2. General Procedure for the Preparation of Chiral *N,N'*-Dioxide Ligands

Chiral *N,N'*-dioxide ligands **1a-e** were prepared according to the literature procedures.[3] For the characterization of the ligands **1a**,[3b] **1b**,[3c] **1c**,[3d] and **1d**,[3d] see literatures.



1e

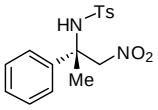
white solid; $[\alpha]_D^{22}$ -51.0 (*c* 0.202, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35-1.39 (m, 2H), 1.58 (d, *J* = 14.0 Hz, 2H), 1.83 (d, *J* = 13.2 Hz, 2H), 1.97 (d, *J* = 10.8 Hz, 2H), 2.27-2.42 (m, 6H), 2.68-2.75 (m, 2H), 2.88-2.97 (m, 4H), 3.30-3.41 (m, 4H), 4.32-4.37 (m, 2H), 4.47-4.53 (m, 2H), 7.27-7.34 (m, 10H), 10.82 (t, *J* = 6.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 168.6, 138.5, 77.6, 77.3, 77.0, 75.9, 65.7, 64.4, 42.5, 26.2, 22.2, 20.0, 15.6 ppm; HRMS (ESI): calcd for $C_{29}H_{41}N_4O_4$ [M + H$^+$] 509.3122, found 509.3130.

(1) Huang, X.; Huang, J. L.; Wen, Y. H.; Feng, X. M. *Adv. Synth. Catal.* **2006**, *348*, 2579.
(2) Wang, L. W.; Tan, C.; Liu, X. H.; Feng, X. M. *Synlett* **2008**, 2075.
(3) (a) Wen, Y. H.; Huang, X.; Huang, J. L.; Xiong, Y.; Qin, B.; Feng, X. M. *Synlett* **2005**, 2445. (b) Yu, Z. P.; Liu, X. H.; Dong, Z. H.; Xie, M. S.; Feng, X. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 1308. (c) Zheng, K.; Qin, B.; Liu, X. H.; Feng, X. M. *J. Org. Chem.* **2007**, *72*, 8478. (d) Zhang, X.; Chen, D. H.; Liu, X. H.; Feng, X. M. *J. Org. Chem.* **2007**, *72*, 5227.

3. General Procedure for the Enantioselective Aza-Henry Reaction of Ketoimines

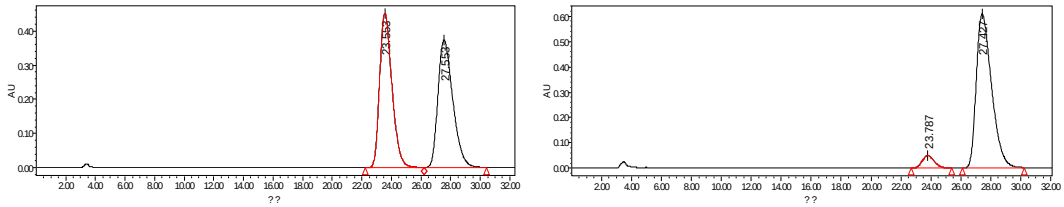
Ligand **1e** (10.2 mg, 0.02 mmol) and $(CuOTf)_2 \cdot C_7H_8$ (5.3 mg, 0.01 mmol) were stirred in CH_2Cl_2 (0.4 mL) at 25 °C under air atmosphere for 30 min and the resulting mixture became green. After the solvent was removed in vacuo, ketoimine (0.1 mmol), 4 Å molecular sieves (20 mg) and PhOEt (0.5 mL) were added. The reaction mixture was cooled to 0 °C and nitromethane (0.1 mL) was added under stirring. The mixture was stirred for 10 days at 0 °C and directly purified by column chromatography on silica gel (petroleum ether/EtOAc 5/1 or 10/1 as eluent) to afford the desired product.

(*S*)-*N*-Tosyl-2-nitro-1-phenyl-1-methylethanamine (3a)[2]

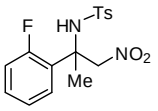


3a

white solid; 64% yield, 88% *ee*. $[\alpha]_D^{22}$ +34.1 (*c* 0.208, CH_2Cl_2); HPLC (Chiralpak OD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 23.8 min, t_r (major) = 27.4 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3H), 2.42 (s, 3H), 4.81 (d, *J* = 12.8 Hz, 1H), 4.94 (d, *J* = 12.8 Hz, 1H), 5.93 (s, 1H), 7.22-7.33 (m, 7H), 7.63 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 143.6, 139.7, 139.2, 129.6, 128.9, 128.4, 127.0, 125.3, 82.9, 60.1, 24.7, 21.5 ppm; HRMS (ESI): calcd for $C_{16}H_{18}N_2NaO_4S$ [M + Na^+] 357.0879, found 357.0882.

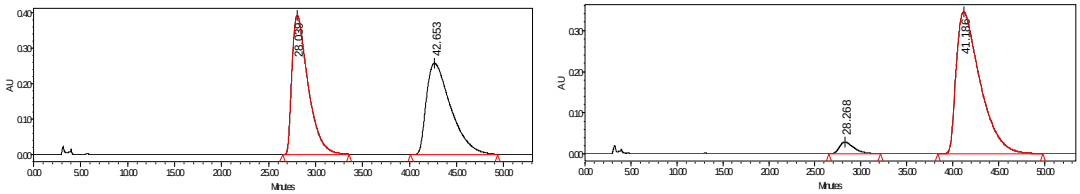


N-Tosyl-2-nitro-1-(2'-fluorophenyl)-1-methylethanamine (3b)[2]

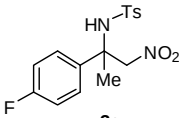


3b

white solid; 80% yield, 90% *ee*. $[\alpha]_D^{23}$ +40.8 (*c* 0.206, CH_2Cl_2); HPLC (Chiralpak OJ-H, 2-propanol/*n*-hexane = 25/75, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 28.3 min, t_r (major) = 41.2 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 3H), 2.40 (s, 3H), 4.77 (d, *J* = 12.8 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 5.92 (s, 1H), 6.86-6.92 (m, 1H), 7.13-7.30 (m, 4H), 7.46-7.51 (m, 1H), 7.64 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 159.8 (d, *J* = 245.0 Hz), 143.6, 138.8, 130.7 (d, *J* = 10.0 Hz), 129.5, 128.3 (d, *J* = 4.0 Hz), 127.0, 126.4 (d, *J* = 10.0 Hz), 124.7 (d, *J* = 3.0 Hz), 116.6 (d, *J* = 24.0 Hz), 82.3 (d, *J* = 7.0 Hz), 59.0 (d, *J* = 3.0 Hz), 22.6 (d, *J* = 3.0 Hz), 21.5 ppm; HRMS (ESI): calcd for $C_{16}H_{21}FN_3O_4S$ [M + NH_4^+] 370.1231, found 370.1237.

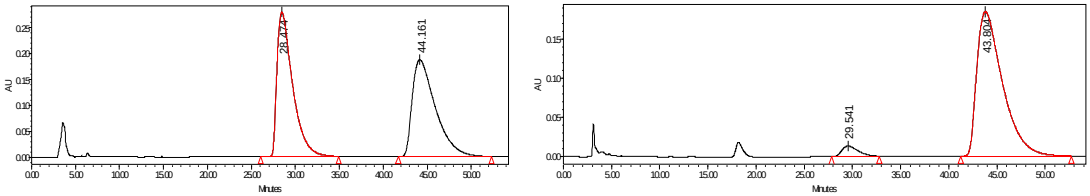


N-Tosyl-2-nitro-1-(4'-fluorophenyl)-1-methylethanamine (3c)[2]

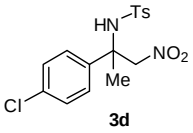


3c

white solid; 75% yield, 91% *ee*. $[\alpha]_D^{24}$ +28.8 (*c* 0.208, CH_2Cl_2); HPLC (Chiralpak OJ-H, 2-propanol/*n*-hexane = 25/75, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 29.5 min, t_r (major) = 43.8 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (s, 3H), 2.42 (s, 3H), 4.76 (d, *J* = 12.8 Hz, 1H), 4.90 (d, *J* = 12.8 Hz, 1H), 5.94 (s, 1H), 6.92-6.97 (m, 2H), 7.23-7.30 (m, 4H), 7.59-7.61 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): 161.4 (d, *J* = 247.5 Hz), 142.7, 138.0, 134.3, 128.6, 126.4 (d, *J* = 9.0 Hz), 126.0, 114.7 (d, *J* = 22.5 Hz), 82.0, 58.6, 23.7, 20.5 ppm; HRMS (ESI): calcd for $C_{16}H_{21}FN_3O_4S$ [M + NH_4^+] 370.1231, found 370.1227.

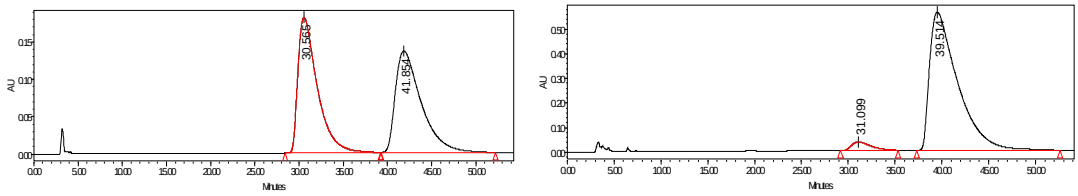


***N*-Tosyl-2-nitro-1-(4'-chlorophenyl)-1-methylethanamine (3d)**[2]

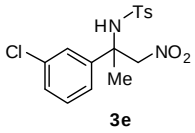


3d

white solid; 81% yield, 92% *ee*. $[\alpha]_D^{23}$ +50.5 (*c* 0.208, CH_2Cl_2); HPLC (Chiralpak OJ-H, 2-propanol/*n*-hexane = 25/75, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 31.1 min, t_r (major) = 39.5 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3H), 2.43 (s, 3H), 4.76 (d, *J* = 13.2 Hz, 1H), 4.90 (d, *J* = 12.8 Hz, 1H), 5.92 (s, 1H), 7.22-7.25 (m, 6H), 7.59 (d, *J* = 8.4Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 143.8, 138.8, 137.9, 134.5, 129.6, 128.9, 127.1, 127.0, 82.8, 59.6, 24.6, 21.5 ppm; HRMS (ESI): calcd for $C_{16}H_{21}ClN_3O_4S$ [M + NH_4^+] 386.0936, found 386.0933.

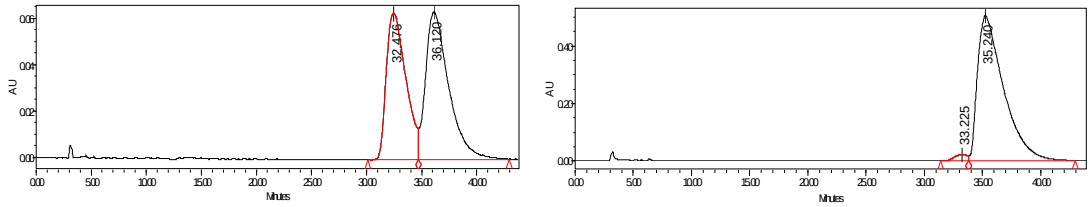


***N*-Tosyl-2-nitro-1-(3'-chlorophenyl)-1-methylethanamine (3e)**[2]

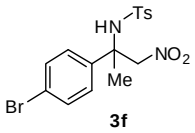


3e

white soild; 80% yield, 96% *ee*. $[\alpha]_D^{24}$ +33.9 (*c* 0.218, CH_2Cl_2); HPLC (Chiralpak OJ-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 33.2 min, t_r (major) = 35.2 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.71 (s, 3H), 2.42 (s, 3H), 4.76 (d, *J* = 13.2 Hz, 1H), 4.91 (d, *J* = 12.6 Hz, 1H), 5.95 (s, 1H), 7.20-7.24 (m, 6H), 7.58 (d, *J* = 8.4Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): 142.8, 140.3, 137.7, 133.8, 129.0, 128.6, 127.6, 125.9, 125.3, 122.6, 81.7, 58.5, 23.7, 20.5 ppm; HRMS (ESI): calcd for $C_{16}H_{21}ClN_3O_4S$ [M + NH_4^+] 386.0936, found 386.0933.

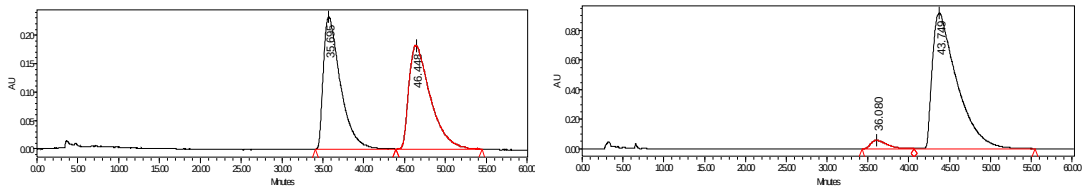


***N*-Tosyl-2-nitro-1-(4'-bromophenyl)-1-methylethanamine (3f)**[2]

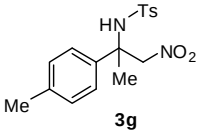


3f

white solid; 83% yield, 92% *ee*. $[\alpha]_D^{23}$ +47.2 (*c* 0.212, CH_2Cl_2); HPLC (Chiralpak OJ-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 36.1 min, t_r (major) = 43.7 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 3H), 2.45 (s, 3H), 4.78 (d, *J* = 13.2 Hz, 1H), 4.92 (d, *J* = 13.2 Hz, 1H), 5.94 (s, 1H), 7.17-7.27 (m, 4H), 7.38-7.40 (m, 2H), 7.59-7.61 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 143.8, 138.8, 138.4, 131.8, 129.6, 127.3, 127.0, 122.7, 82.7, 59.6, 24.6, 21.6 ppm; HRMS (ESI): calcd for $C_{16}H_{21}BrN_3O_4S$ [M + NH_4^+] 430.0431, found 430.0438.

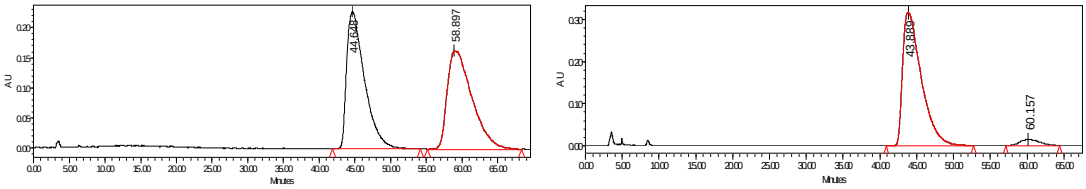


***N*-Tosyl-2-nitro-1-(4'-methylphenyl)-1-methylethanamine (3g)**[2]

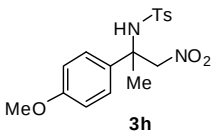


3g

white solid; 42% yield, 90% *ee*. $[\alpha]_D^{24}$ +43.3 (*c* 0.208, CH_2Cl_2); HPLC (Chiralpak AS-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (major) = 43.9 min, t_r (minor) = 60.2 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (s, 3H), 2.31 (s, 3H), 2.42 (s, 3H), 4.78 (d, *J* = 13.2 Hz, 1H), 4.92 (d, *J* = 13.2 Hz, 1H), 5.89 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.17-7.24 (m, 4H), 7.63 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): 143.4, 139.2, 138.3, 136.6, 129.5, 129.4, 127.0, 125.3, 83.0, 59.8, 24.6, 21.5, 20.9 ppm; HRMS (ESI): calcd for $C_{17}H_{24}N_3O_4S$ [M + NH_4^+] 366.1482, found 366.1481.

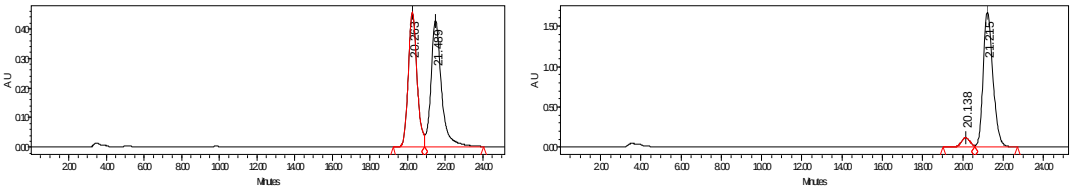


_N_-Tosyl-2-nitro-1-(4'-methoxyphenyl)-1-methylethanamine (3h)[2]

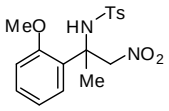


3h

white solid; 30% yield, 88% *ee*. $[\alpha]_D^{24}$ +40.9 (*c* 0.208, CH_2Cl_2); HPLC (Chiralpak AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 20.1 min, t_r (major) = 21.2 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3H), 2.41 (s, 3H), 3.78 (s, 3H), 4.75 (d, *J* = 12.8 Hz, 1H), 4.91 (d, *J* = 12.8 Hz, 1H), 5.84 (s, 1H), 6.75-6.77 (m, 2H), 7.19-7.23 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 159.4, 143.4, 139.2, 131.3, 129.5, 127.1, 126.8, 114.0, 83.2, 59.7, 55.3, 24.6, 21.5 ppm; HRMS (ESI): calcd for $C_{17}H_{20}N_2NaO_5S$ [M + Na^+] 387.0985, found 387.0987.

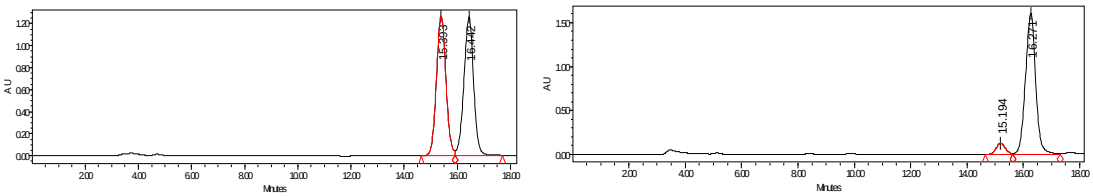


_N_-Tosyl-2-nitro-1-(2'-methoxyphenyl)-1-methylethanamine (3i)

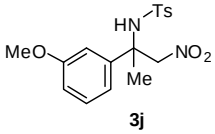


3i

white solid; 44% yield, 87% *ee*. $[\alpha]_D^{23}$ +21.2 (*c* 0.222, CH_2Cl_2); HPLC (Chiralpak AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 15.2 min, t_r (major) = 16.3 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 2.35 (s, 3H), 3.85 (s, 3H), 4.85 (d, *J* = 11.2 Hz, 1H), 5.08 (d, *J* = 11.2 Hz, 1H), 6.33 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 8.0 Hz, 1H), 7.11-7.27 (m, 4H), 7.55 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 143.3, 138.6, 130.2, 129.3, 127.8, 127.1, 126.1, 121.2, 111.6, 82.8, 59.6, 55.5, 21.9, 21.5 ppm; HRMS (ESI): calcd for $C_{17}H_{21}N_2O_5S$ [M + H^+] 365.1166, found 365.1175.

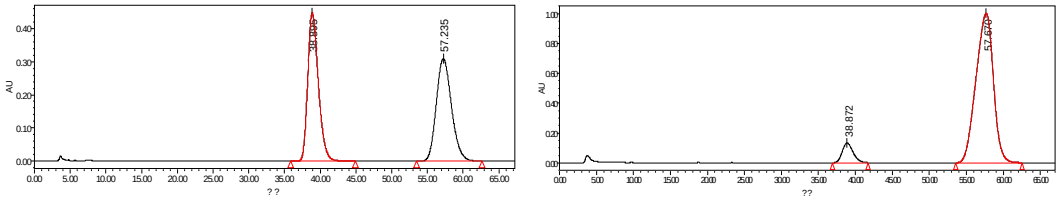


_N_-Tosyl-2-nitro-1-(3'-methoxyphenyl)-1-methylethanamine (3j)[2]

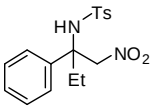


3j

white solid; 49% yield, 85% *ee*. $[\alpha]_D^{21}$ +32.2 (*c* 0.174, CH_2Cl_2); HPLC (Chiralpak OD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 38.9 min, t_r (major) = 57.7 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.67 (s, 3H), 2.41 (s, 3H), 3.72 (s, 3H), 4.80 (d, *J* = 13.2 Hz, 1H), 4.92 (d, *J* = 13.2 Hz, 1H), 5.91 (s, 1H), 6.79-6.89 (m, 3H), 7.20-7.24 (m, 3H), 7.63 (d, *J* = 7.8 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): 158.8, 142.5, 140.3, 138.1, 128.9, 128.5, 126.0, 116.3, 112.4, 110.9, 81.8, 58.9, 54.1, 23.7, 20.5 ppm; HRMS (ESI): calcd for $C_{17}H_{20}N_2NaO_5S$ [M + Na^+] 387.0985, found 387.0979.

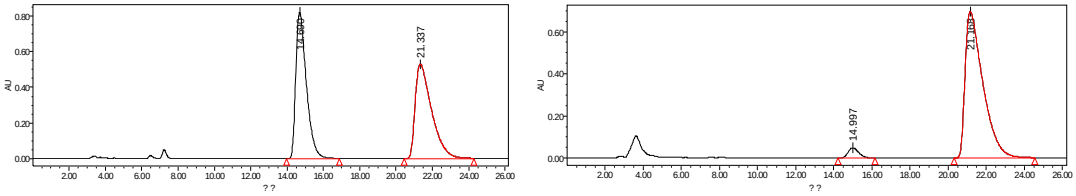


***N*-Tosyl-1-nitro-2-phenylbutan-2-amine (3k)**

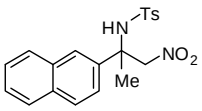


3k

white solid; 36% yield, 92% *ee*. $[\alpha]_D^{23}$ +17.6 (*c* 0.216, CH_2Cl_2); HPLC (Chiralpak OD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 15.0 min, t_r (major) = 21.2 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.54 (t, *J* = 7.6 Hz, 3H), 1.89-1.97 (m, 1H), 2.05-2.12 (m, 1H), 2.40 (s, 3H), 5.14 (d, *J* = 13.2 Hz, 1H), 5.33 (d, *J* = 13.6 Hz, 1H), 5.62 (s, 1H), 7.12-7.23 (m, 7H), 7.55 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 139.0, 137.3, 129.5, 128.7, 128.2, 127.2, 126.0, 79.1, 63.7, 31.2, 21.6, 8.0 ppm; HRMS (ESI): calcd for $C_{17}H_{24}N_3O_4S$ [M + NH_4^+] 366.1482, found 366.1488.

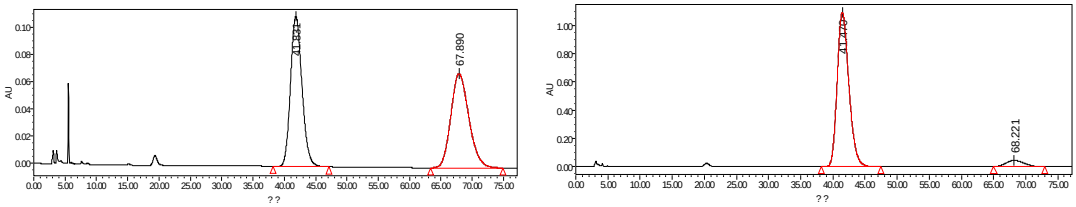


***N*-Tosyl-2-nitro-1-(2-naphthyl)-1-methylethanamine (3l)**[2]

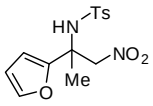


3l

white solid; 47% yield, 88% *ee*. $[\alpha]_D^{22}$ +64.1 (*c* 0.248, CH_2Cl_2); HPLC (Chiralpak OD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (major) = 41.5 min, t_r (minor) = 68.2 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.82 (s, 3H), 2.33 (s, 3H), 4.86 (d, *J* = 12.6Hz, 1H), 5.09 (d, *J* = 13.2 Hz, 1H), 6.02 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.33-7.35 (m, 1H), 7.49-7.55 (m, 4H), 7.69-7.79 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): 143.5, 138.9, 136.4, 132.8, 132.8, 129.4, 128.7, 128.4, 127.4, 127.0, 126.9, 126.6, 125.1, 122.9, 83.0, 60.0, 24.7, 21.4 ppm; HRMS (ESI): calcd for $C_{20}H_{24}N_3O_4S$ [M + NH_4^+] 402.1482, found 402.1480.

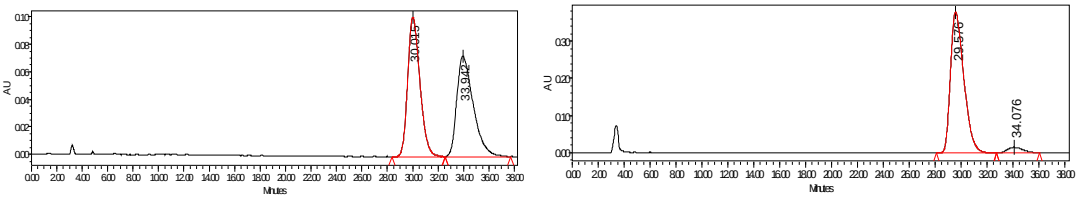


***N*-Tosyl-2-nitro-1-(2-furyl) -1-methylethanamine (3m)**[2]

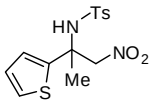


3m

white solid; 82% yield, 91% *ee*. $[\alpha]_D^{22}$ +20.8 (*c* 0.202, CH_2Cl_2); HPLC (Chiralpak AS-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (major) = 29.6 min, t_r (minor) = 34.1 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (s, 3H), 2.40 (s, 3H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 5.75 (s, 1H), 6.22-6.27 (m, 2H), 7.12-7.23 (m, 3H), 7.59-7.61 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): 150.8, 143.4, 142.9, 138.3, 129.5, 127.1, 110.5, 108.5, 81.6, 56.2, 22.4, 21.5 ppm; HRMS (ESI): calcd for $C_{14}H_{16}N_2NaO_5S$ [M + Na^+] 347.0672, found 347.0672.

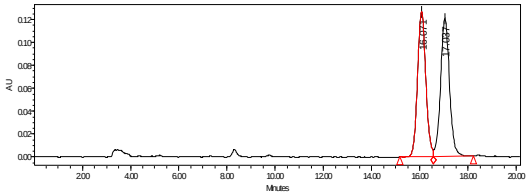


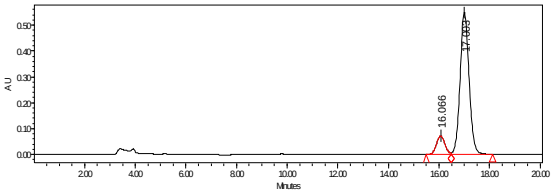
***N*-Tosyl-2-nitro-1-(2-thienyl) -1-methylethanamine (3n)**[2]



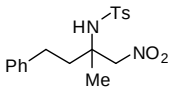
3n

white solid; 43% yield, 78% *ee*. $[\alpha]_D^{22}$ +17.3 (*c* 0.202, CH_2Cl_2); HPLC (Chiralpak AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 16.1 min, t_r (major) = 17.0 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3H), 2.41 (s, 3H), 4.89 (d, *J* = 12.8 Hz, 1H), 4.98 (d, *J* = 12.8 Hz, 1H), 5.90 (s, 1H), 6.87-6.94 (m, 2H), 7.19-7.24 (m, 3H), 7.63-7.65 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 144.0, 143.6, 138.9, 129.6, 127.1, 125.9, 125.1, 83.1, 58.3, 26.1, 21.5 ppm; HRMS (ESI): calcd for $C_{14}H_{16}N_2NaO_4S_2$ [M + Na^+] 363.0444, found 363.0446.



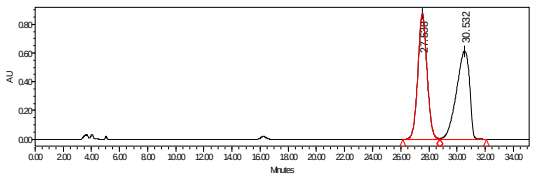


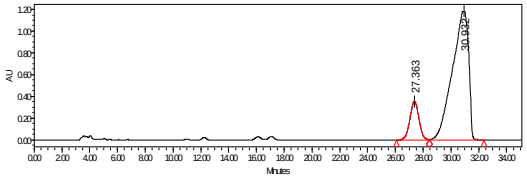
_N_-Tosyl-1-nitro-4-phenyl-2-methylbutan-2-amine (3o)[2]



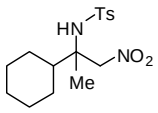
3o

colorless oil; 76% yield, 71% *ee*. $[\alpha]_D^{23}$ +24.0 (*c* 0.204, CH_2Cl_2); HPLC (Chiralpak AD-H, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 27.4 min, t_r (major) = 30.9 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 3H), 1.90-1.96 (m, 2H), 2.43 (s, 3H), 2.60-2.65 (m, 2H), 4.56 (d, *J* = 12.0Hz, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 5.14 (s, 1H), 7.07-7.09 (m, 2H), 7.18-7.32 (m, 5H), 7.79-7.81 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 143.9, 140.2, 139.4, 129.9, 128.6, 128.3, 127.1, 126.3, 82.4, 58.0, 40.4, 29.5, 21.8, 21.6 ppm; HRMS (ESI): calcd for $C_{18}H_{26}N_3O_4S$ [M + NH_4^+] 380.1639, found 380.1645.



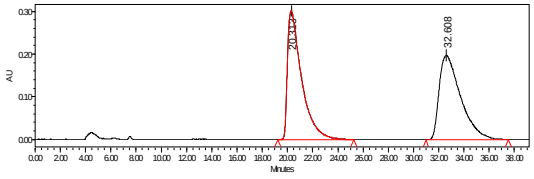


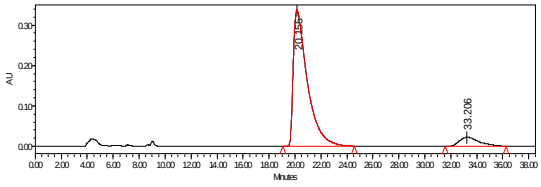
_N_-Tosyl-2-nitro-1-cyclohexyl-1-methylethanamine (3p)[2]



3p

white solid; 35% yield, 83% *ee*. $[\alpha]_D^{22}$ -12.4 (*c* 0.170, CH_2Cl_2); HPLC (Chiralpak AS-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (major) = 20.2 min, t_r (minor) = 33.2 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89-1.27 (m, 9H), 1.66-1.88 (m, 5H), 2.44 (s, 3H), 4.52 (d, *J* = 12.4Hz, 1H), 4.67 (d, *J* = 12.4 Hz, 1H), 5.07 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 139.7, 129.8, 127.2, 80.5, 61.1, 44.8, 27.1, 27.0, 26.4, 26.3, 26.2, 21.7, 17.7 ppm; HRMS (ESI): calcd for $C_{18}H_{28}N_3O_4S$ [M + NH_4^+] 358.1795, found 358.1796.

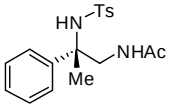




4. Conversion of product 3a to diamine 4a

To a suspension of **3a** (88% *ee*, 33.4 mg, 0.10 mmol) in EtOH (2 mL) was added 1 N HCl (1 mL), then zinc dust (130.8 mg, 2 mmol) was added in small portions and the mixture was stirred for 4 h at room temperature. The resulting suspension was quenched with saturated aqueous $NaHCO_3$, filtered through a short pad of celite and washed with CH_2Cl_2 (10 mL). The filtrate was further extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 mL), then Ac_2O (19 μL, 0.20 mmol) and Et_3N (28 μL, 0.20 mmol) were added. After stirring for 1 h at room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 1/5 as eluent) to afford the product **4a** as a white solid (33.8 mg, 97% yield and 90% *ee*).

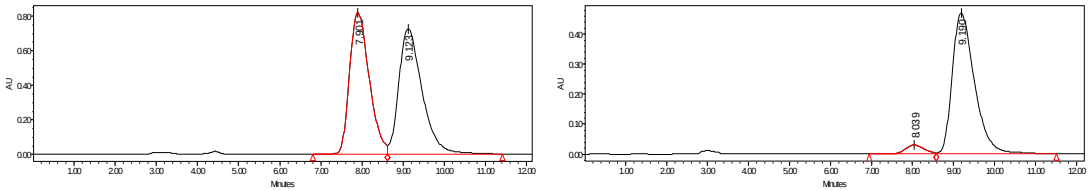
(*S*)-*N*-Tosyl-2-acetylamino-1-phenyl-1-methylethanamine (4a)



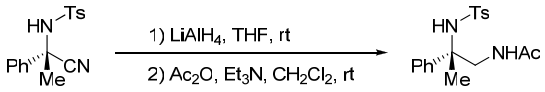
4a

white solid; 97% yield, 90% *ee*. $[\alpha]_D^{29}$ +133.3 (*c* 0.246, CH_2Cl_2); HPLC (Chiralpak OD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 8.0 min, t_r (major) = 9.2 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 3H), 1.97 (d, *J* = 2.4 Hz, 3H), 2.38 (s, 3H), 3.54-3.65 (m, 2H), 6.02-6.15 (m, 2H), 7.14-7.31 (m, 7H), 7.56 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 142.9, 142.4,

139.8, 129.5, 128.4, 127.4, 126.9, 126.0, 62.5, 50.1, 24.3, 23.3, 21.6 ppm; HRMS (ESI): calcd for $C_{18}H_{23}N_2O_3S$ [M + H^+] 347.1424, found 347.1430.

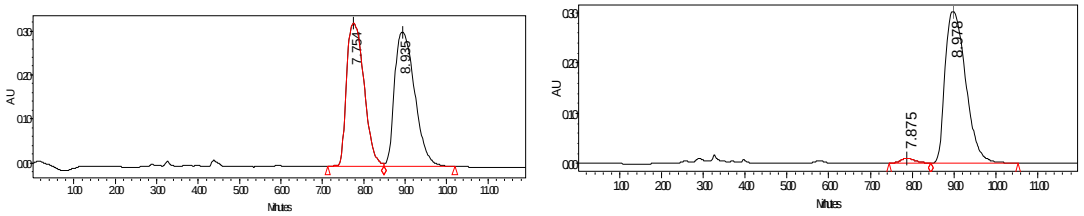


5. Determination of the Absolute Configuration of 3a



5 **4a'**

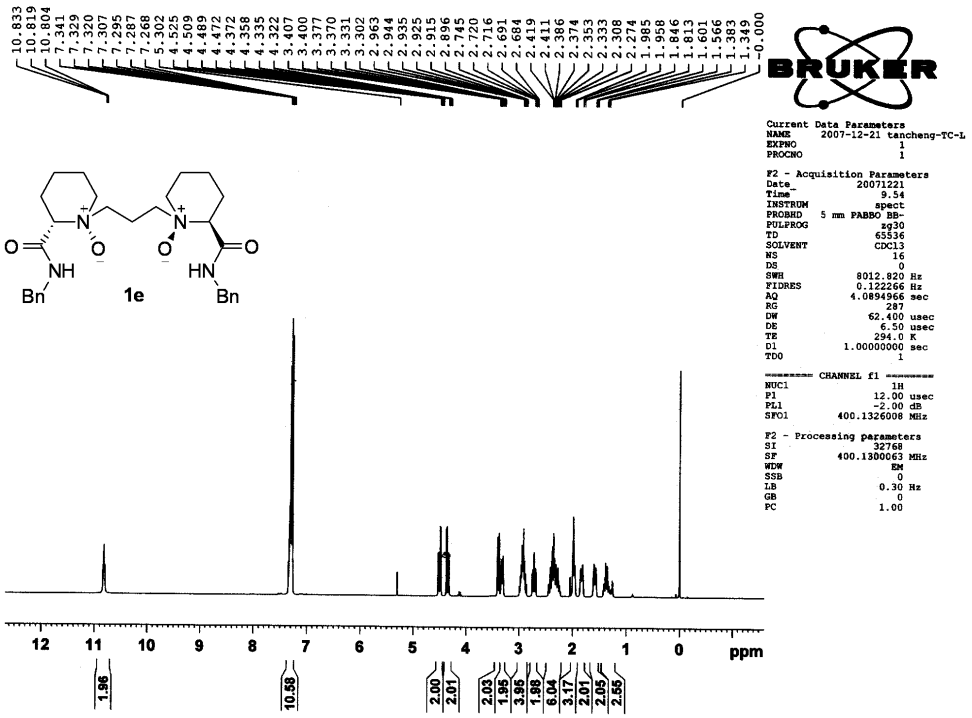
(*S*)-**5** was prepared according to the literature procedure.[4] To a solution of **5** (99% *ee*, 89.4 mg, 0.3 mmol) in dry THF (10 mL) was added $LiAlH_4$ (45.5 mg, 1.2 mmol), and the mixture was stirred at room temperature for 24 h. Then H_2O (0.2 mL), 2 N aqueous NaOH (0.2 mL) and H_2O (0.4 mL) were added sequentially. The precipitate was removed by filtration through celite, and the filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc as eluent) to afford a light yellow liquid. Further acetylation was the same as that of **3a** to give the identical *N*-protected diamine **4a'** as a white solid (7.4 mg, 96% *ee*). $[\alpha]_D^{28}$ +120.2 (*c* 0.114, CH_2Cl_2); HPLC (Chiralpak OD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 215 nm): t_r (minor) = 7.9 min, t_r (major) = 9.0 min. The absolute configuration of **4a'** was *S* according to **5**.

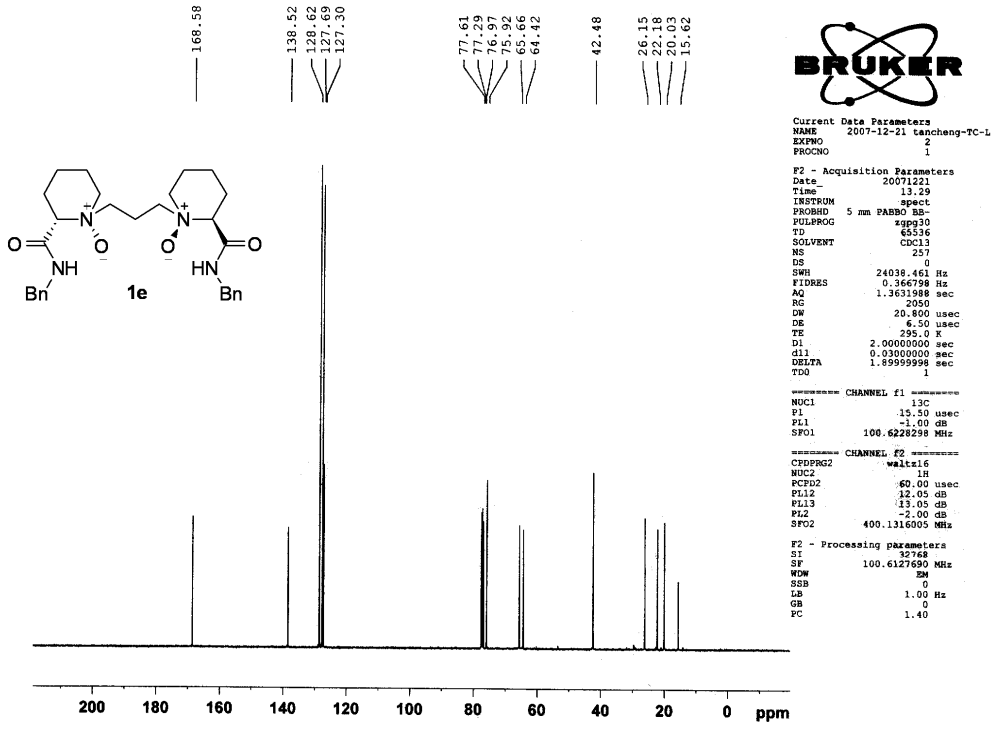


The absolute configuration of **4a** was determined to be *S* by comparison of optical rotation and HPLC date with **4a'**. Thus the absolute configuration of **3a** was *S* according to **4a**.

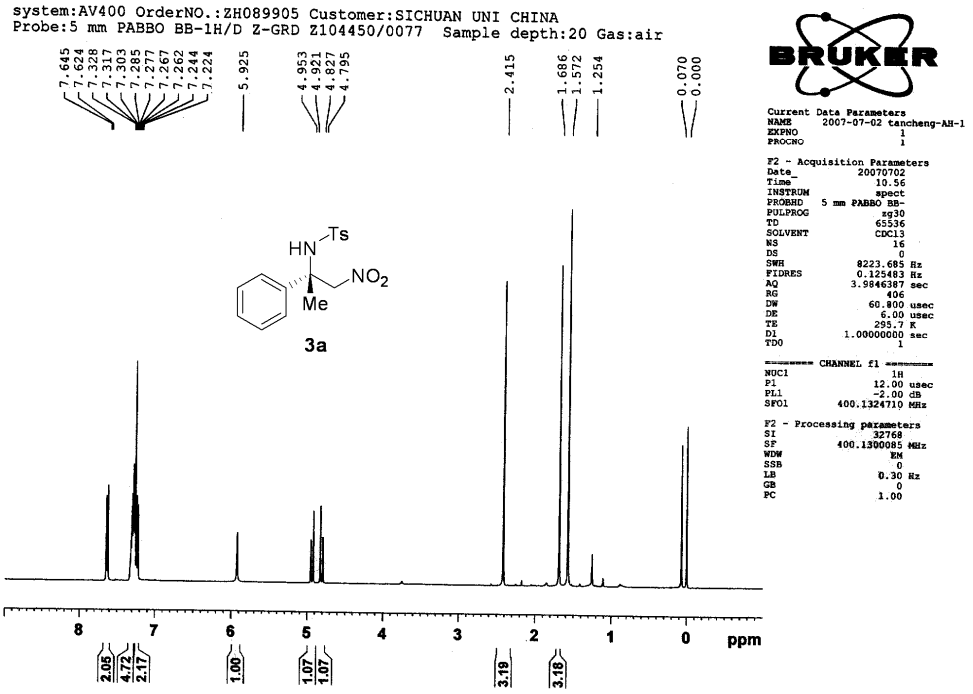
(4) Wang, J.; Hu, X. L.; Jiang, J.; Gou, S. H.; Huang, X.; Liu, X. H.; Feng, X. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8468.

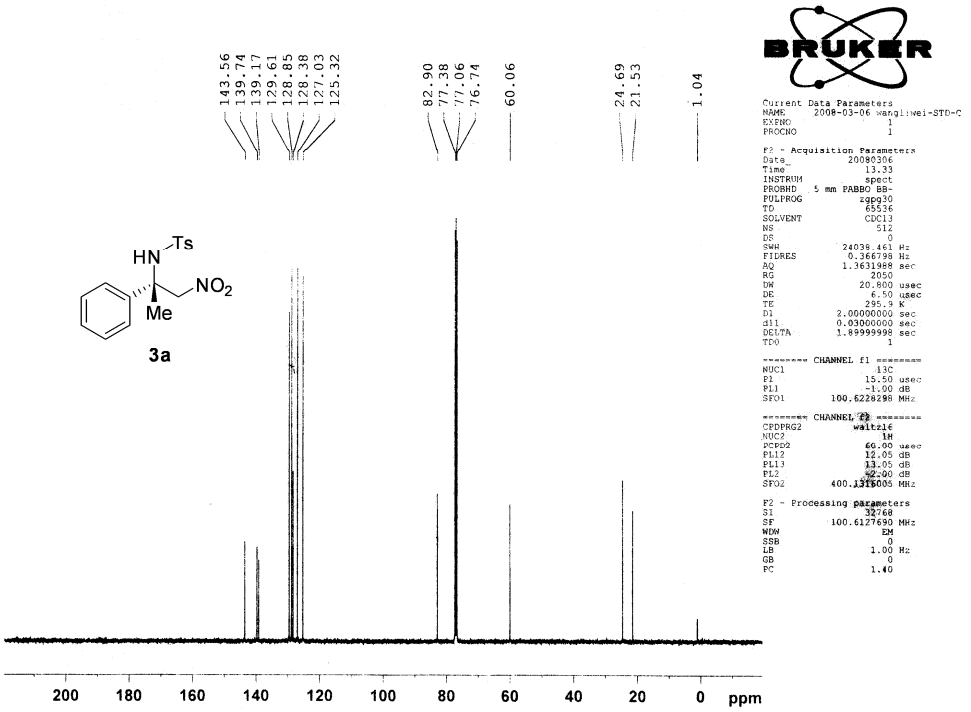
6. Copy of NMR Spectra for *N,N'*-Dioxide Ligand 1e

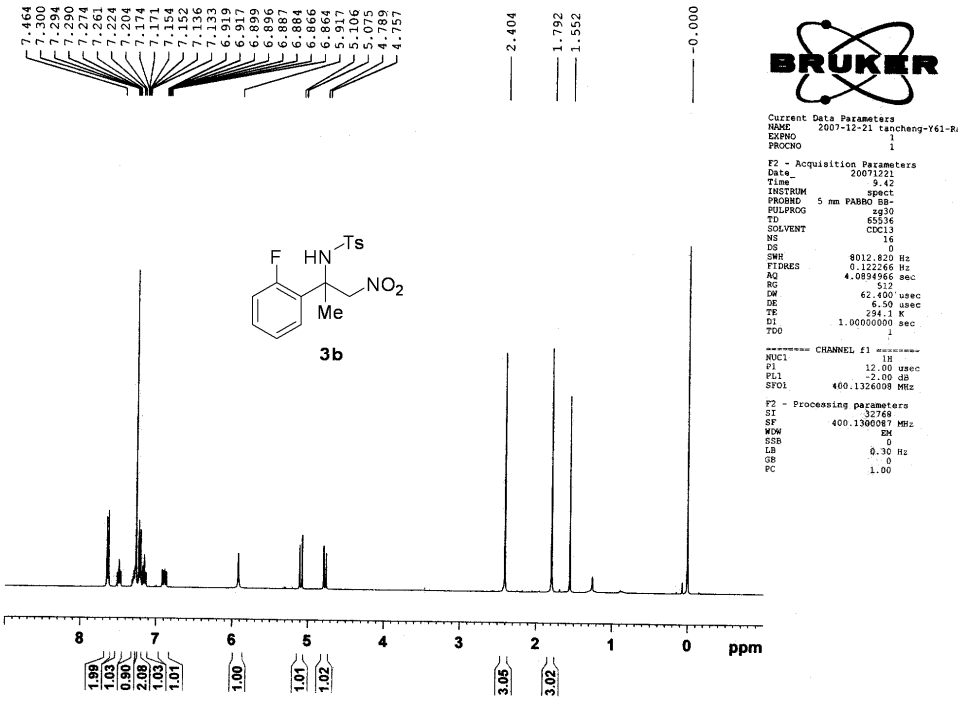




7. Copy of NMR Spectra for the Products







BRUKER

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PROCNO 1

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DE 6.50 usec
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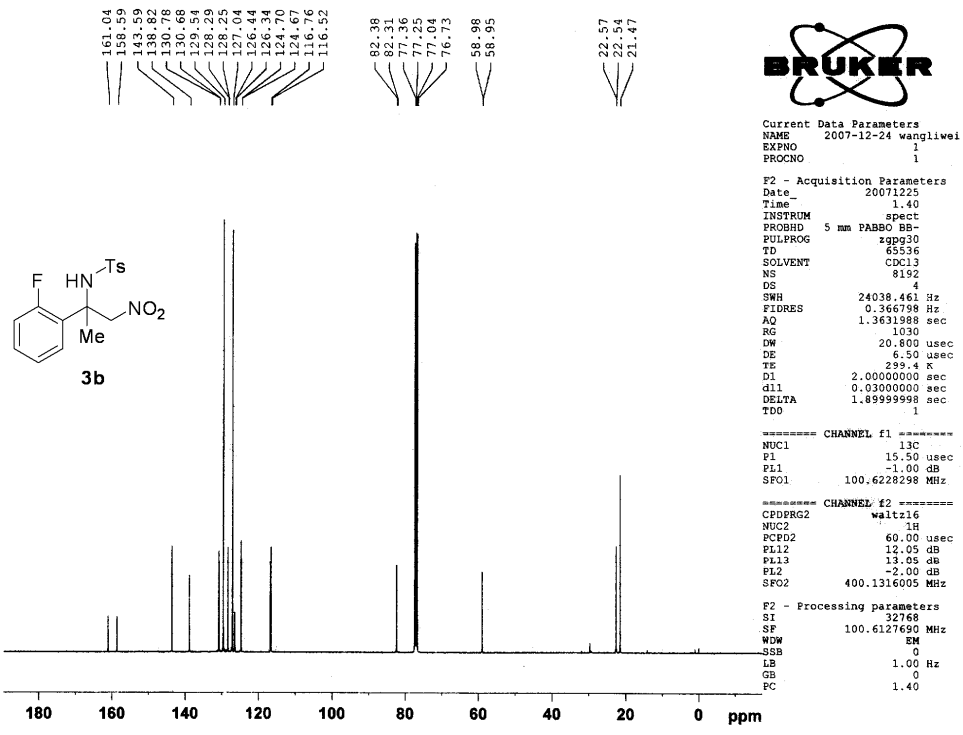

BRUKER

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PL13 13.05 dB
PL2 -2.00 dB
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F2 - Processing parameters
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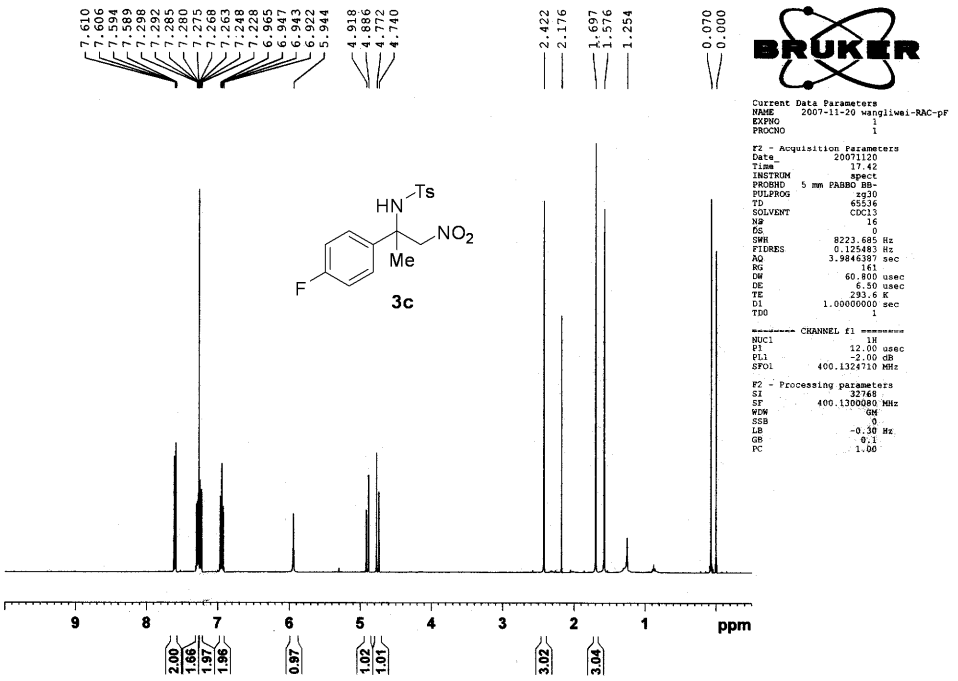
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1.697
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BRUKER
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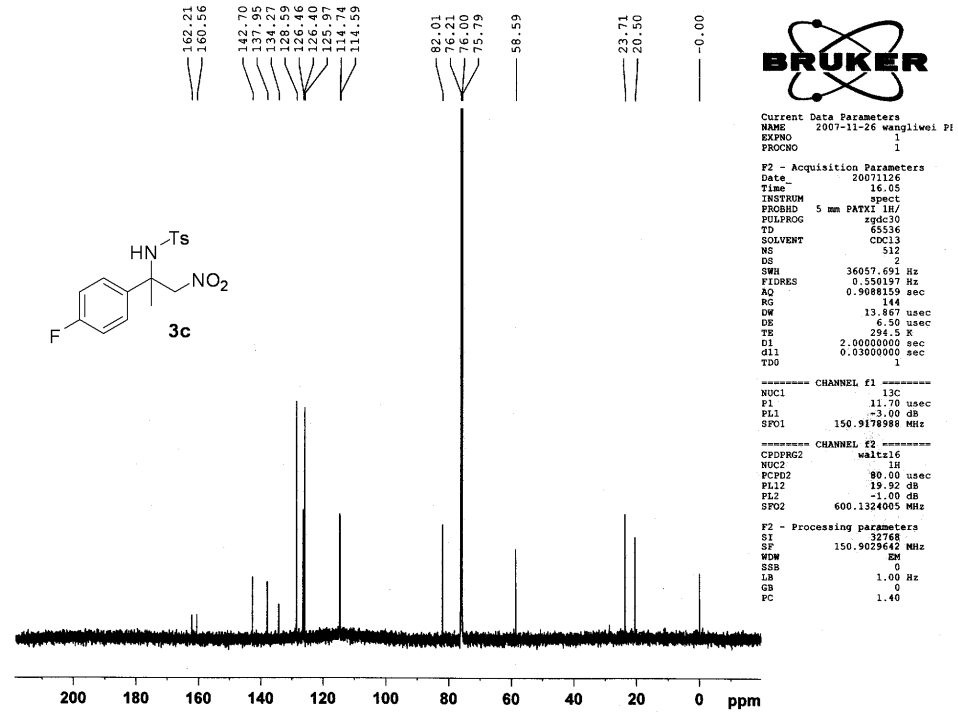
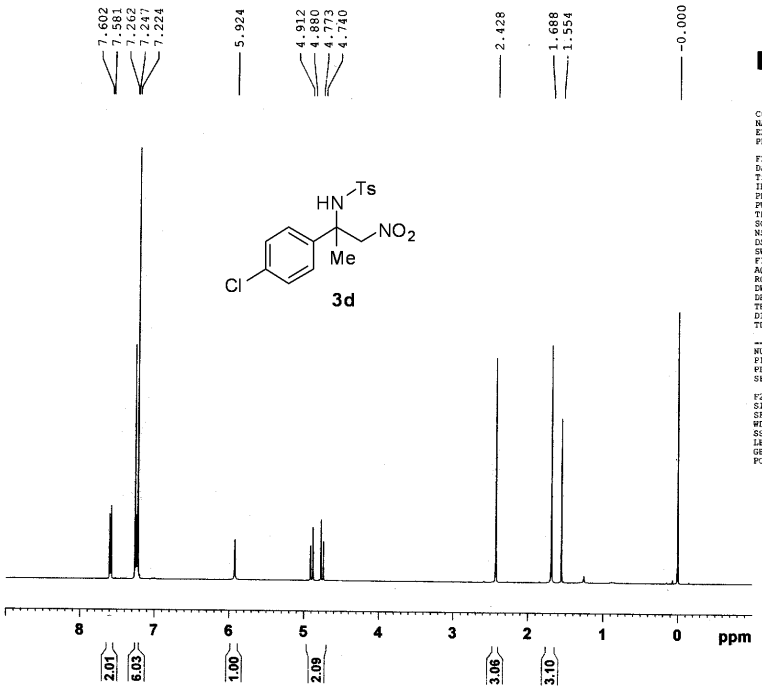
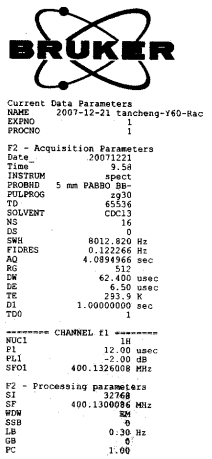
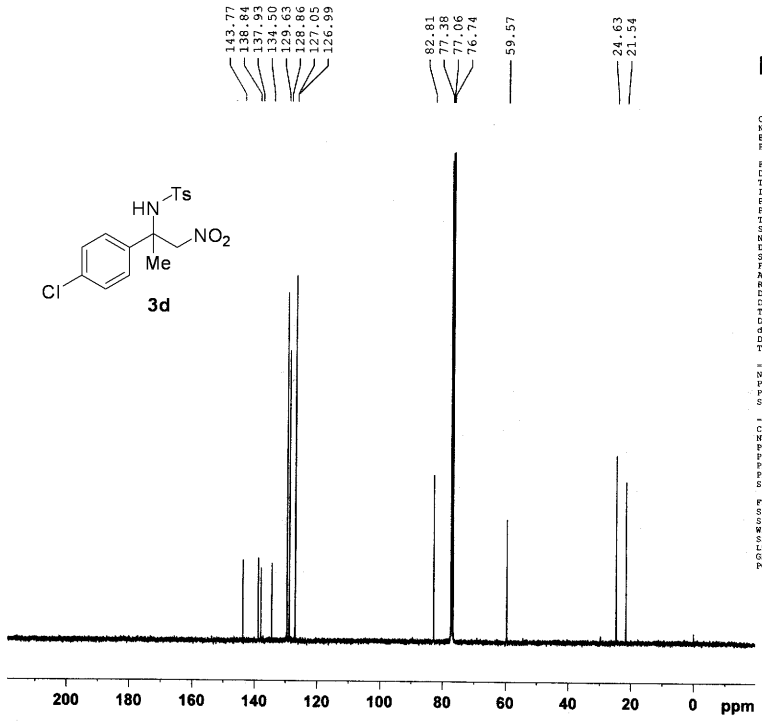
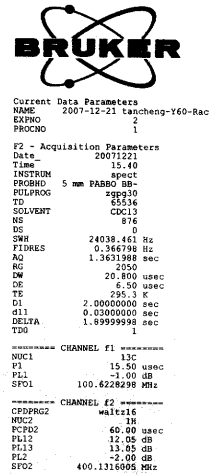
LB -0.30 Hz
GB 0.1
PC 1.00

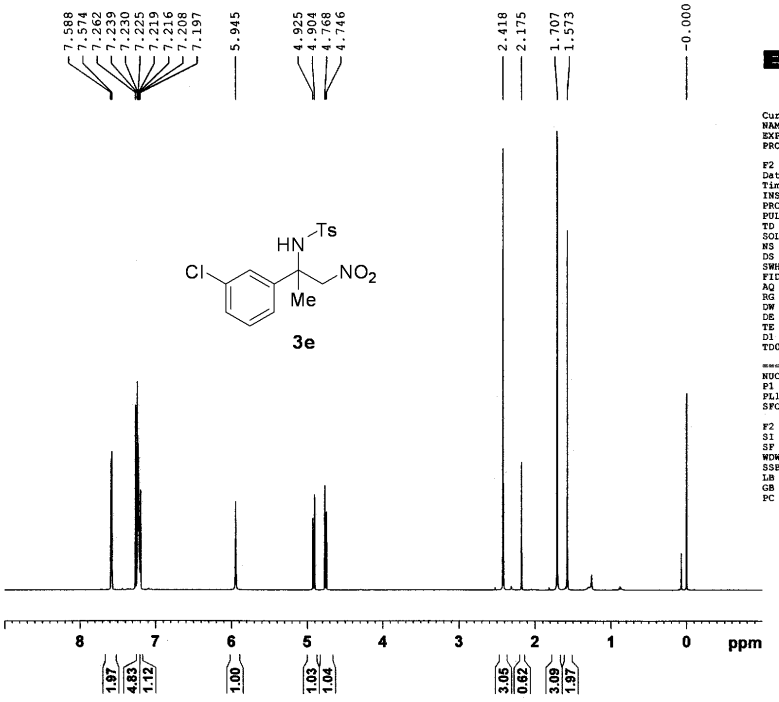

162.21
160.56
142.70
137.95
134.27
128.59
126.46
126.40
125.97
114.74
114.59
82.01
76.21
76.00
75.79
58.59
23.71
20.50
-0.00
HN
Ts
NO2
F
3c
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME 2007-11-26 wangliwei PI
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071126
Time_ 16.05
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 144
DW 13.867 usec
DE 6.50 usec
TE 294.5 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.70 usec
PL1 -3.00 dB
SFO1 150.9178988 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 19.92 dB
PL2 -1.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9029642 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.602
7.581
7.262
7.247
7.224
5.924
4.912
4.880
4.773
4.740
2.428
1.688
1.554
-0.000
HN
Ts
NO2
Me
Cl
3d
8
7
6
5
4
3
2
1
0
ppm
2.01
6.03
1.00
2.09
3.06
3.10

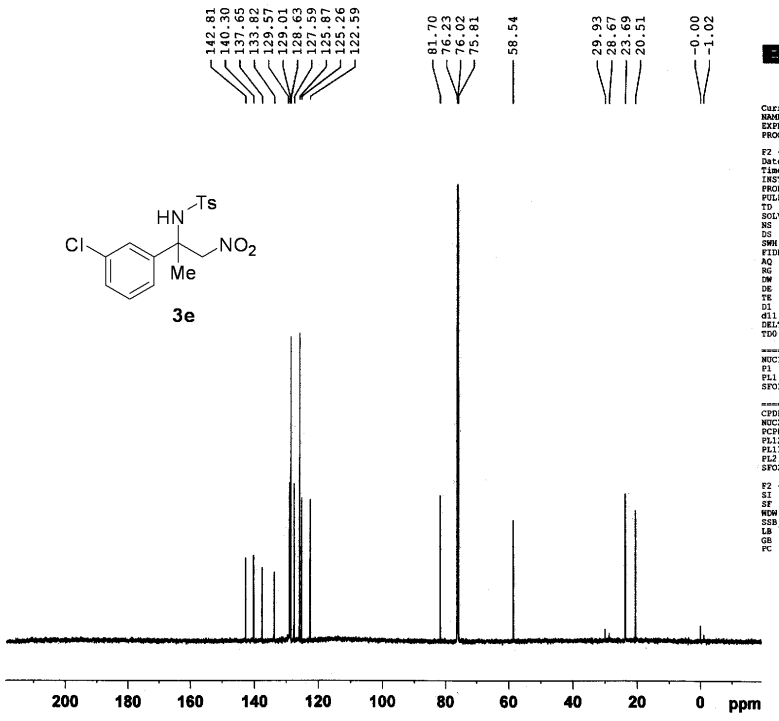

BRUKER
Current Data Parameters
NAME 2007-12-21 tancheng-Y60-Rac
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071221
Time 9.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 512
DW 62.400 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


143.77
138.84
137.93
134.50
129.63
128.86
127.05
126.99
82.81
77.38
77.06
76.74
59.57
24.63
21.54
HN
Ts
NO2
Me
Cl
3d
200
180
160
140
120
100
80
60
40
20
0
ppm

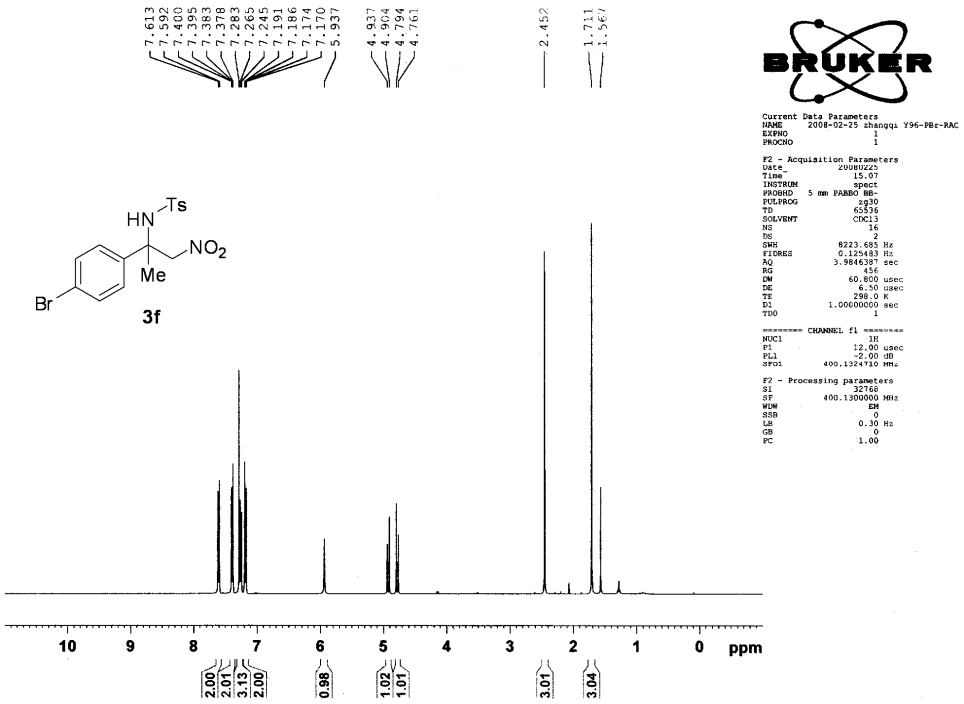

BRUKER
Current Data Parameters
NAME 2007-12-21 tancheng-Y60-Rac
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071221
Time 15.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 876
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 295.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 15.50 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 12.05 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



```
Current Data Parameters
NAME      2007-11-26 wangliwei mcl
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20071126
Time               15.39
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH           12335.526 Hz
FIDRES        0.188225 Hz
AQ            2.6564426 sec
RG                  322
DW             40.533 usec
DE              6.50 usec
TE               294.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1              7.20 usec
PL1             -1.00 dB
SFO1        600.1337060 MHz

F2 - Processing parameters
SI                32768
SF          600.1300082 MHz
WDW                  EM
SSB                   0
LB             0.30 Hz
GB                    0
PC                 1.00
```



```
Current Data Parameters
NAME      2007-11-28 wangliwei RAC-mcl
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20071128
Time               11.29
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    0
SWH           36057.691 Hz
FIDRES        0.550197 Hz
AQ            0.9088159 sec
RG                 71.8
DW             13.867 usec
DE              6.50 usec
TE               293.4 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1             11.70 usec
PL1             -3.00 dB
SFO1        150.9176988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2          80.00 usec
PL12            19.92 dB
PL13            19.50 dB
PL2             -1.00 dB
SFO2        600.1324005 MHz

F2 - Processing parameters
SI                32768
SF          150.9029653 MHz
WDW                  EM
SSB                   0
LB             2.00 Hz
GB                    0
PC                 1.40
```

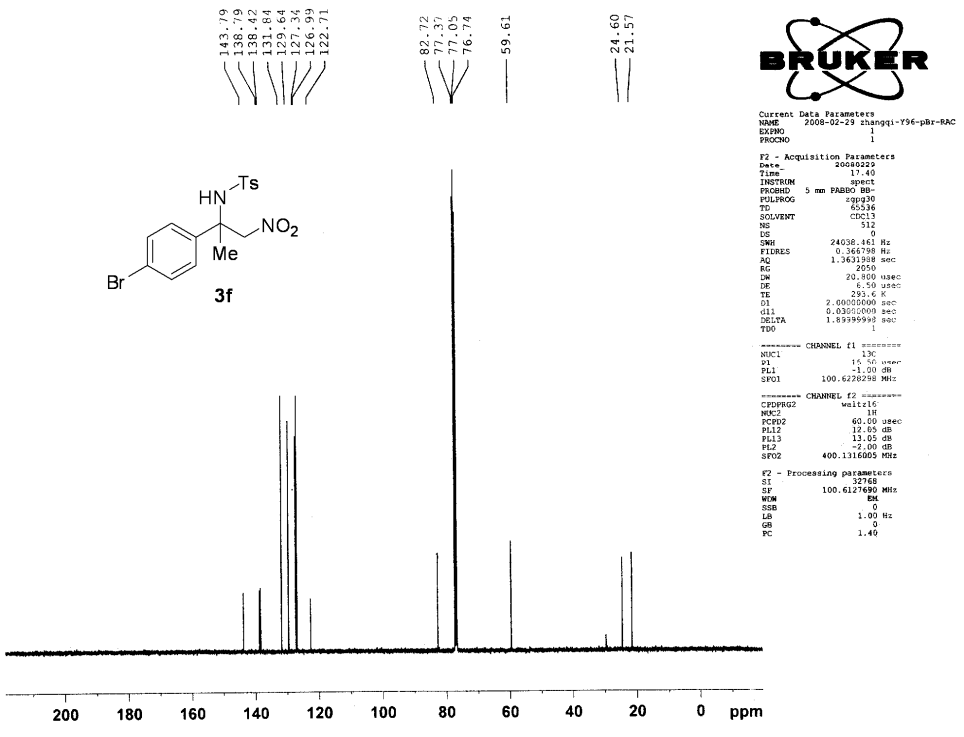


Current Data Parameters
NAME 2008-02-25 zhangqi Y96-PBr-RAC
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080225
Time 15.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 456
DW 60.800 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



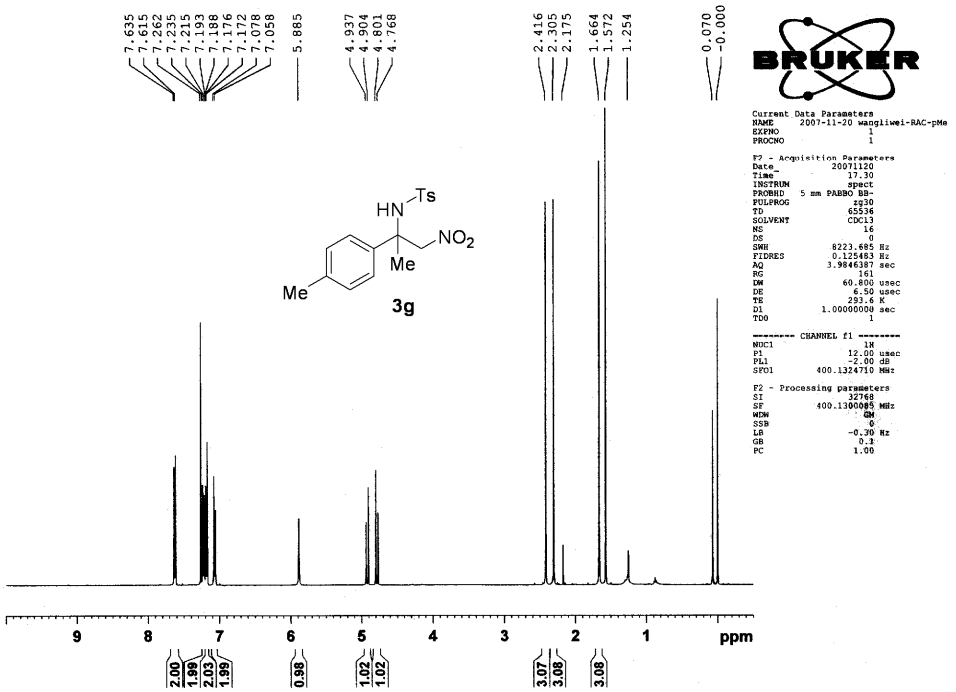
Current Data Parameters
NAME 2008-02-29 zhangqi-Y96-pBr-RAC
EXPNO 1
PROCNO 1

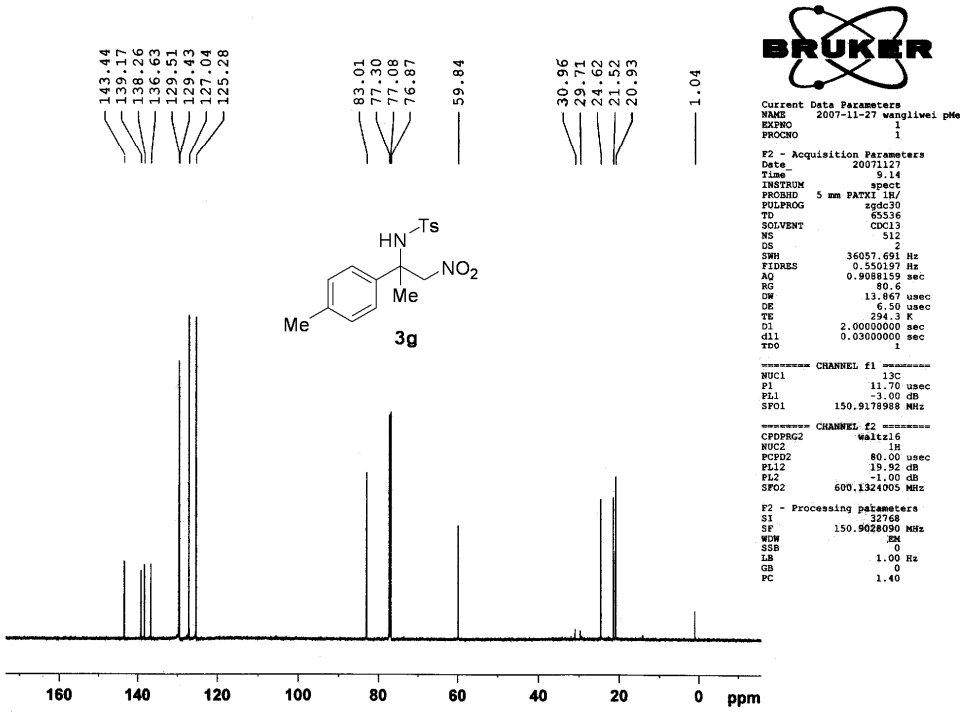
F2 - Acquisition Parameters
Date_ 20080229
Time 17.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

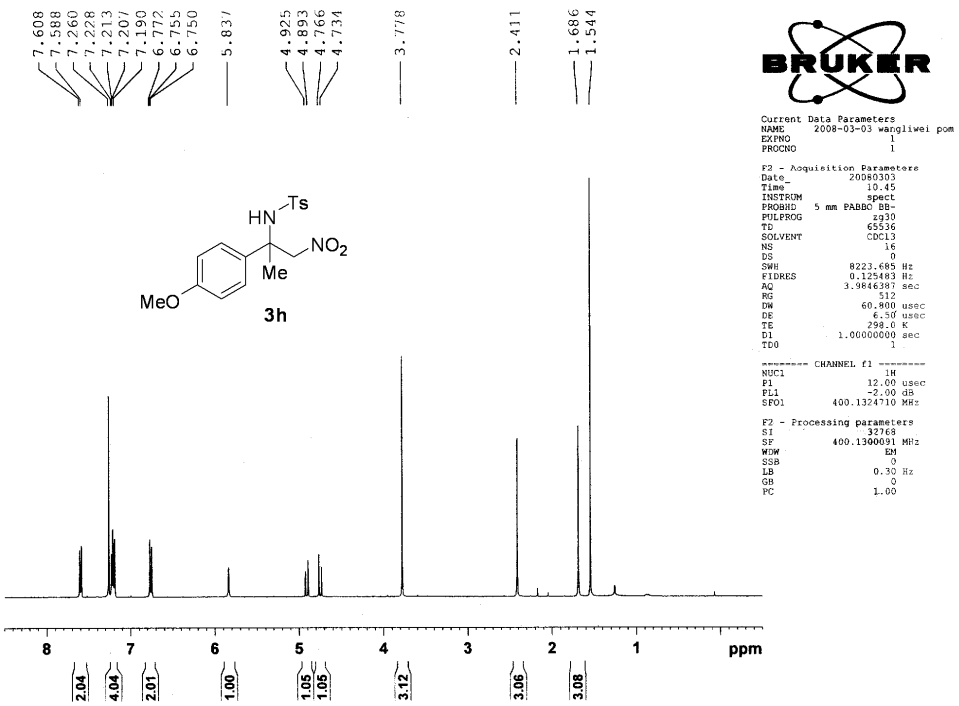
======== CHANNEL f1 ========
NUC1 13C
P1 14.50 usec
PL1 -1.00 dB
SFO1 100.6278298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 12.05 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz

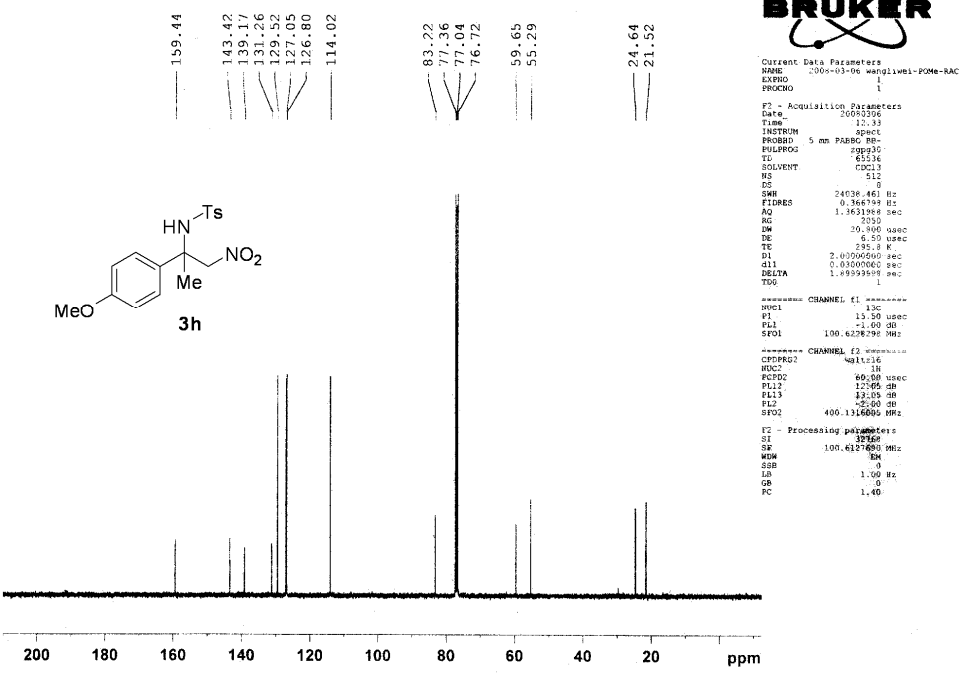
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.49


7.635
7.615
7.262
7.235
7.215
7.193
7.188
7.176
7.172
7.078
7.058
5.885
4.937
4.904
4.801
4.768
2.416
2.305
2.175
1.664
1.572
1.254
0.070
-0.000
HN
Ts
NO2
Me
Me
3g
9
8
7
6
5
4
3
2
1
ppm
2.00
1.99
2.03
1.99
0.98
1.02
1.02
3.07
3.08
3.08
BRUKER
Current Data Parameters
NAME 2007-11-20 wangliwei-RAC-pMe
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071120
Time 17.30
INSTRUM spect
PROBHD 5 mm PABBO BA-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 161
DW 60.800 usec
DE 6.50 usec
TE 293.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB -0.70 Hz
GB 0.3
PC 1.00

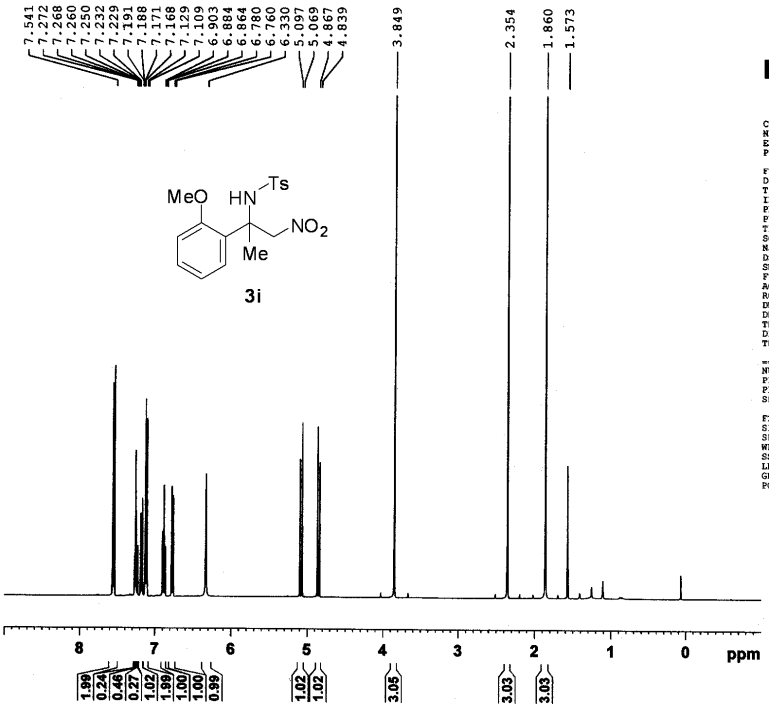

143.44
139.17
138.26
136.63
129.51
129.43
127.04
125.28
83.01
77.30
77.08
76.87
59.84
30.96
29.71
24.62
21.52
20.93
1.04
HN
Ts
NO2
Me
Me
3g
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME 2007-11-27 wangliwei pMe
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071127
Time 9.14
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 80.6
DW 13.867 usec
DE 6.50 usec
TE 294.3 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.70 usec
PL1 -3.00 dB
SFO1 150.9178988 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 19.92 dB
PL2 -1.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9028090 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

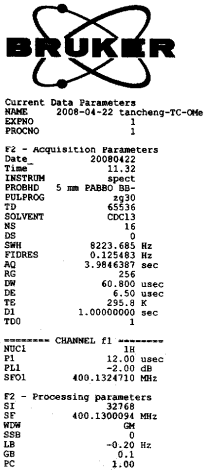



```
Current Data Parameters
NAME      2008-03-03 wangliwei pom
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_             20080303
Time                10.45
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   512
DW                60.800 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300091 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

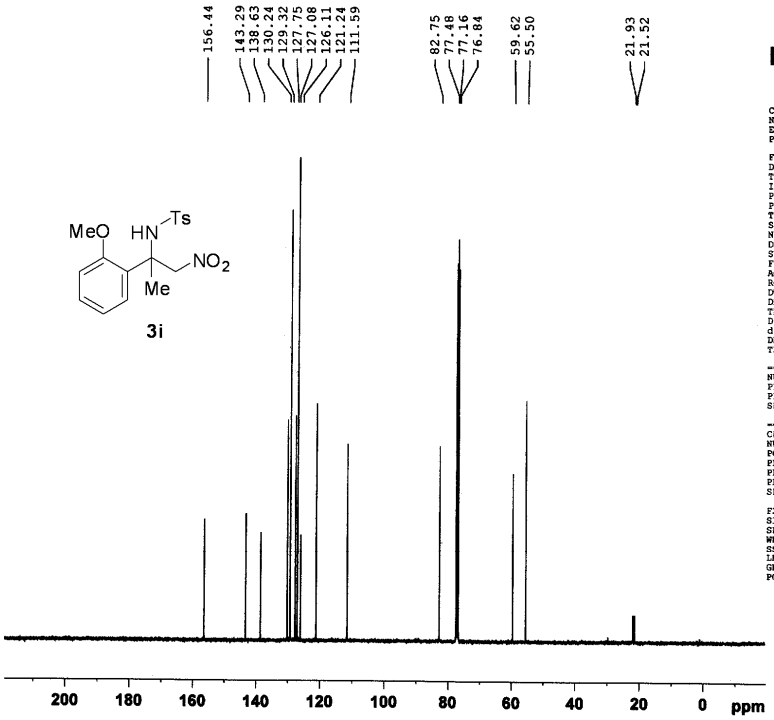


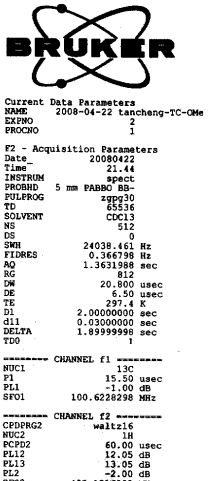

```
Current Data Parameters
NAME      2008-03-06 wangliwei-POMe-RAC
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_             20080306
Time                12.33
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     0
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                295.8 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89993598 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 15.50 usec
PL1                -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               12.05 dB
PL13               12.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



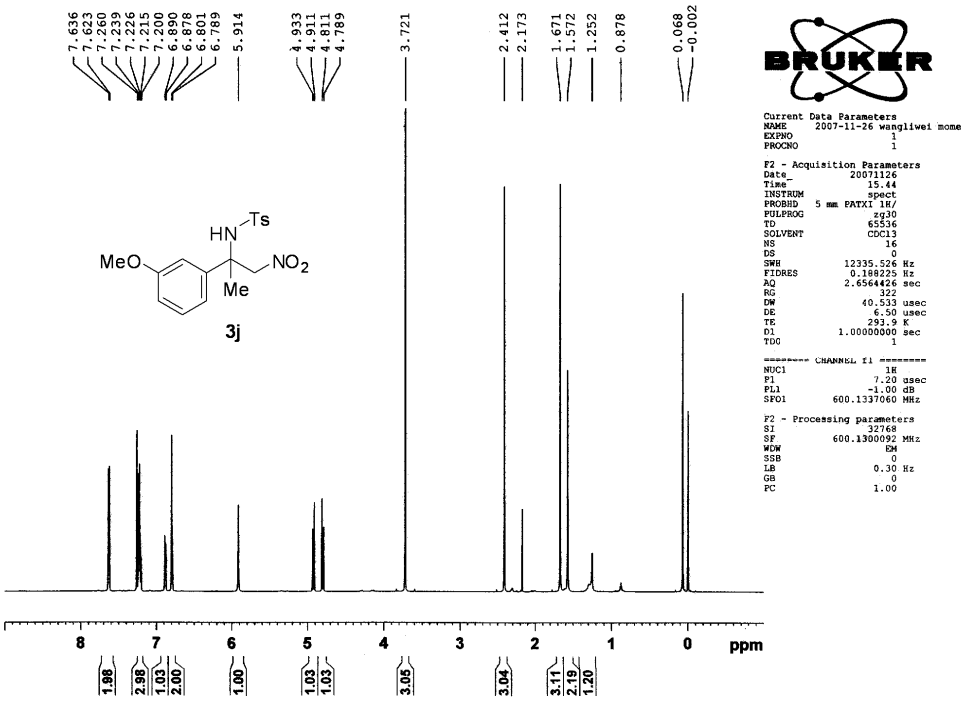



```
Current Data Parameters
NAME      2008-04-22 tancheng-TC-OMe
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_              20080422
Time                 11.32
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     256
DW                  60.800 usec
DE                   6.50 usec
TE                  295.8 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300094 MHz
WDW                     EM
SSB                      0
LB                   -0.20 Hz
GB                      0.1
PC                     1.00
```






```
Current Data Parameters
NAME      2008-04-22 tancheng-TC-OMe
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_              20080422
Time                 21.44
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              CDCl3
NS                     512
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                     812
DW                  20.800 usec
DE                   6.50 usec
TE                  297.4 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   15.50 usec
PL1                  -1.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                60.00 usec
PL12                 12.05 dB
PL13                 13.05 dB
PL2                  -2.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127619 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                     1.40
```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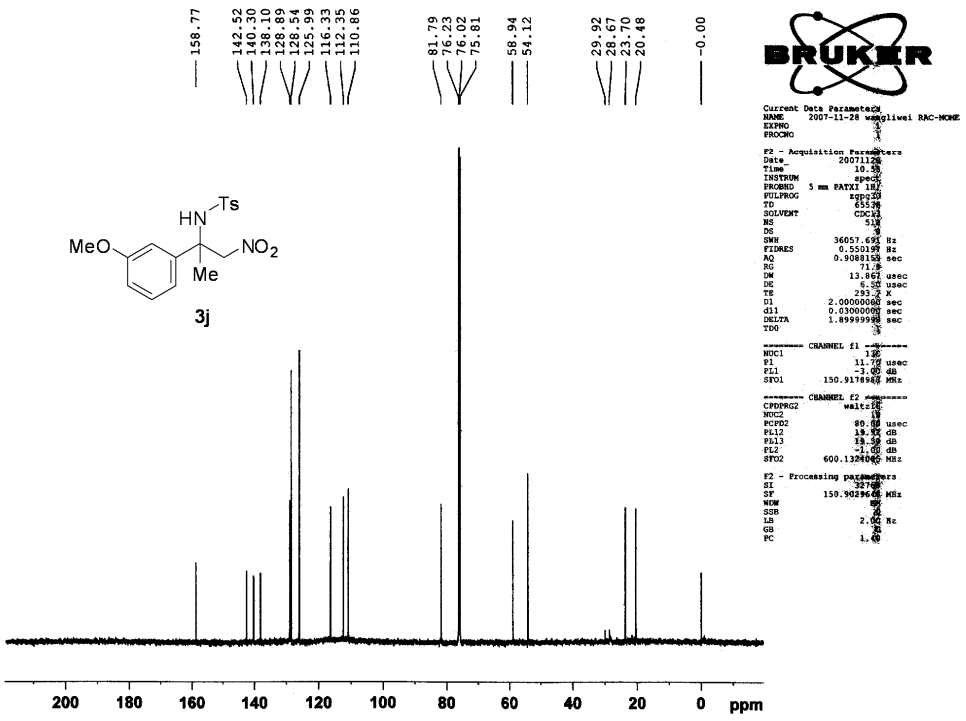
7.239
7.226
7.215
7.200
6.890
6.878
6.801
6.789
5.914
4.933
4.911
4.811
4.789
3.721
2.412
2.173
1.671
1.572
1.252
0.878
0.068
-0.002
HN
Ts
MeO
NO2
Me
3j
8
7
6
5
4
3
2
1
0
ppm
1.98
2.98
1.03
2.00
1.00
1.03
1.03
3.05
3.04
3.11
2.19
1.20
BRUKER
Current Data Parameters
NAME 2007-11-26 wangliwei mome
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071126
Time 15.44
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 322
DW 40.533 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.20 usec
PL1 -1.00 dB
SFO1 600.1337060 MHz
F2 - Processing parameters
SI 32768
SF 600.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


158.77
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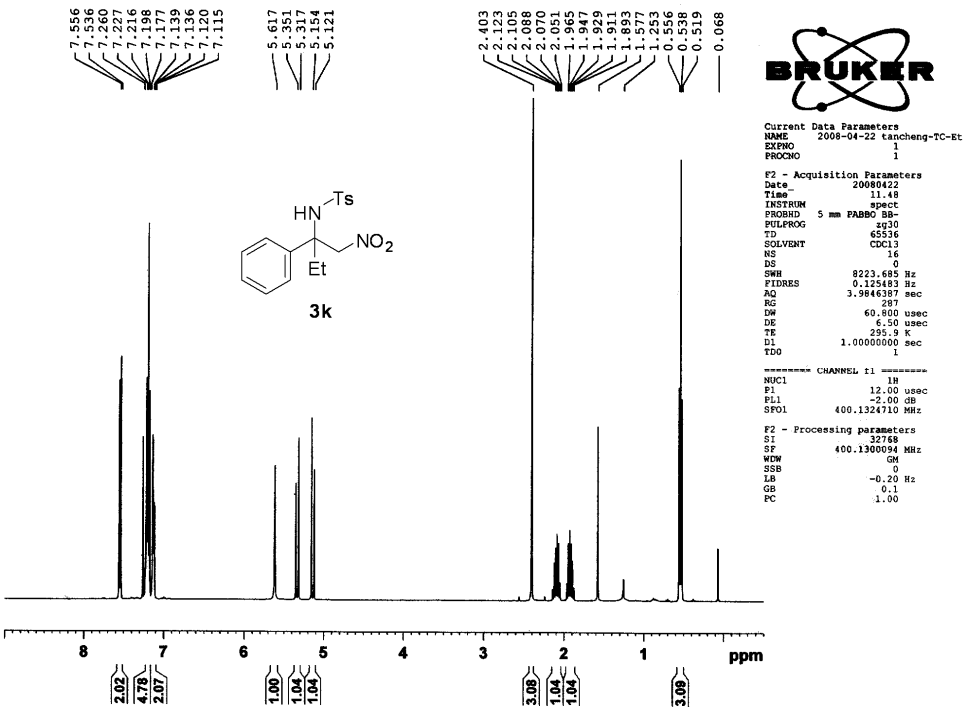
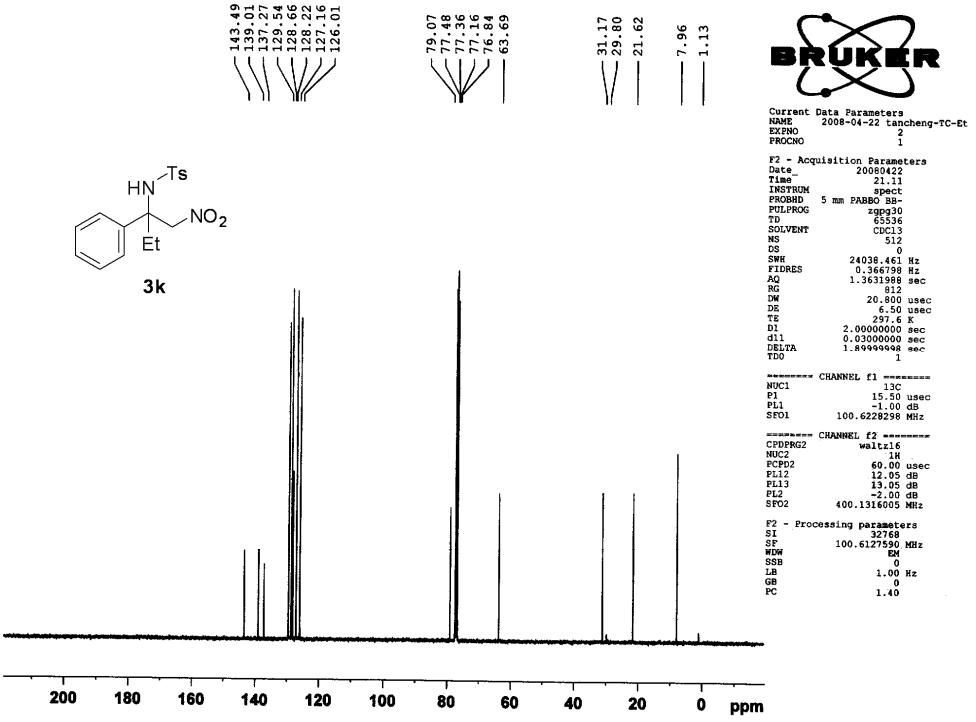
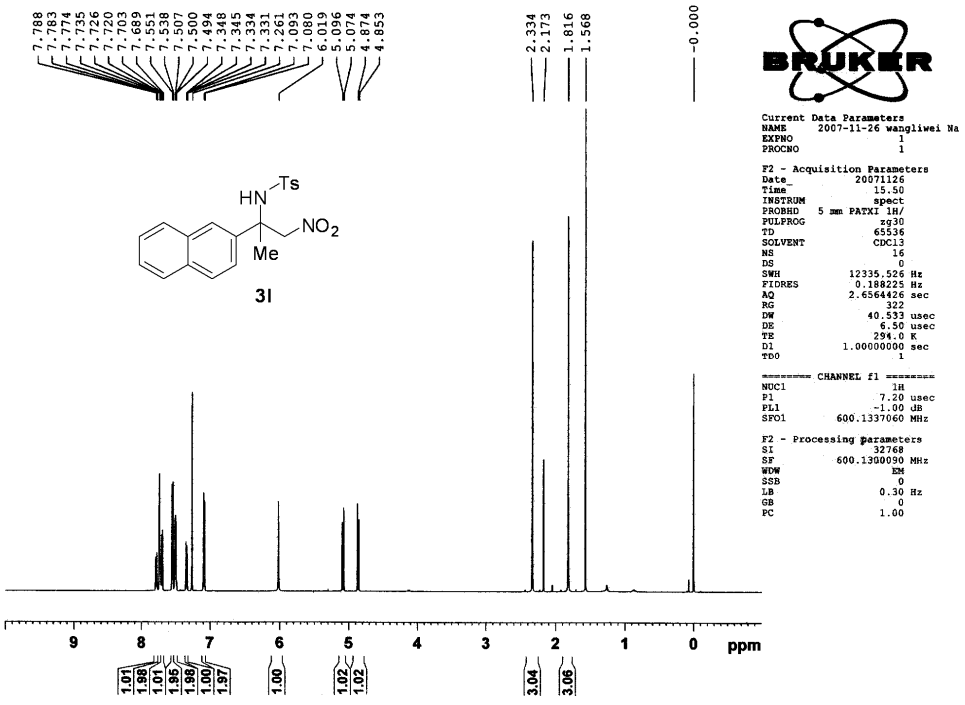
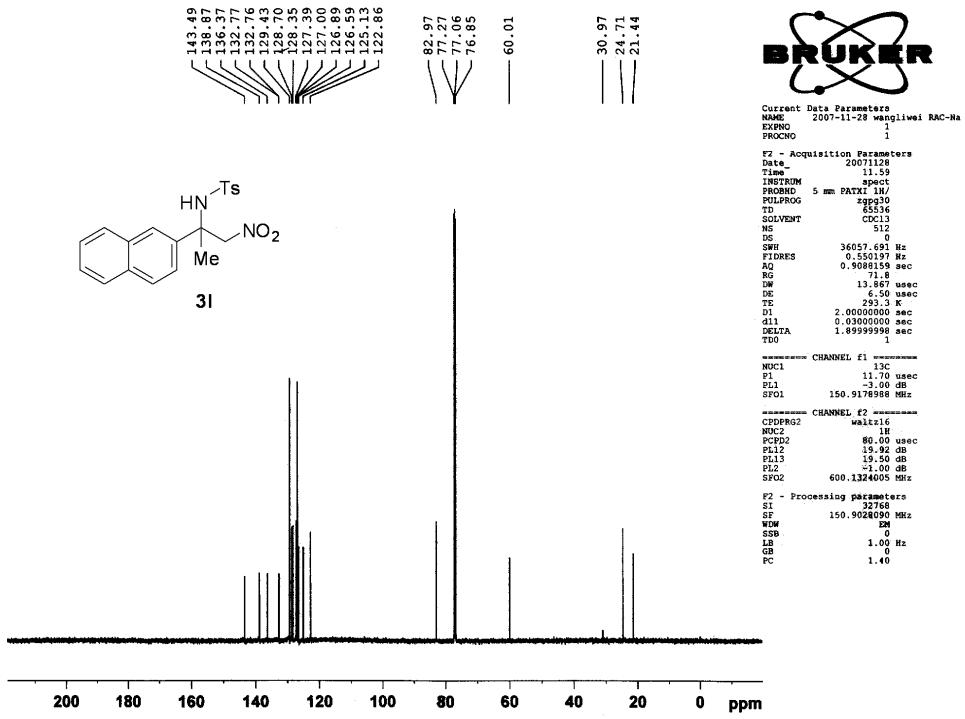
128.89
128.54
125.99
116.33
112.35
110.86
81.79
76.23
76.02
75.81
58.94
54.12
29.92
28.67
23.70
20.48
-0.00
HN
Ts
MeO
NO2
Me
3j
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME 2007-11-28 wangliwei RAC-MOME
EXPNO
PROCNO
F2 - Acquisition Parameters
Date_ 20071128
Time 10.55
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088153 sec
RG 71.6
DW 13.867 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.70 usec
PL1 -3.00 dB
SFO1 150.9178987 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 18.50 dB
PL13 18.50 dB
PL2 -1.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9029683 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40


7.556
7.536
7.260
7.227
7.216
7.198
7.177
7.139
7.136
7.120
7.115
5.617
5.351
5.317
5.154
5.121
2.403
2.123
2.105
2.088
2.070
2.051
1.965
1.947
1.929
1.911
1.893
1.577
1.253
0.556
0.538
0.519
0.068
HN
Ts
NO2
Et
3k
8
7
6
5
4
3
2
1
ppm
2.02
4.78
2.07
1.00
1.04
1.04
3.08
1.04
1.04
3.09
BRUKER
Current Data Parameters
NAME 2008-04-22 tancheng-TC-Et
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080422
Time 11.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
DW 60.800 usec
DE 6.50 usec
TE 295.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW GM
SSB 0
LB -0.20 Hz
GB 0.1
PC 1.00

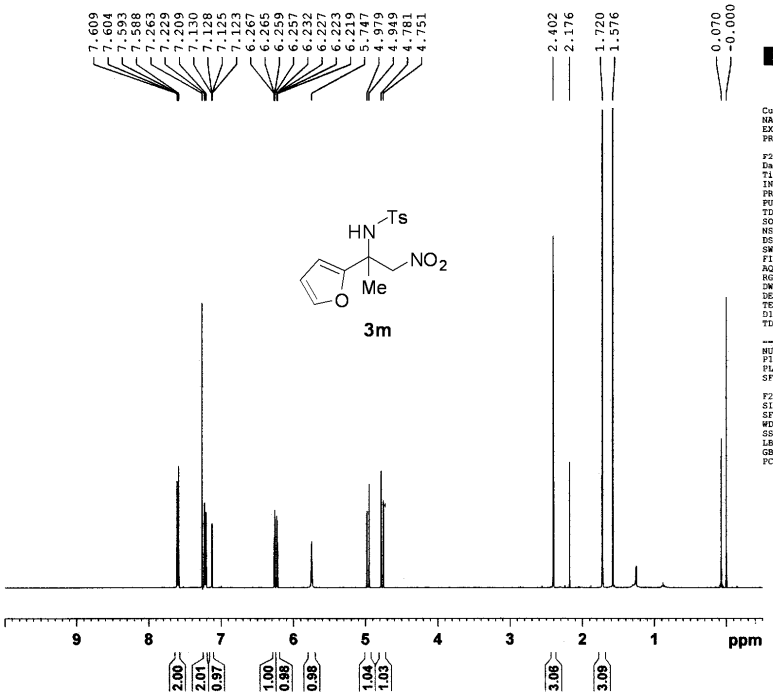

143.49
139.01
137.27
129.54
128.66
128.22
127.16
126.01
79.07
77.48
77.36
77.16
76.84
63.69
31.17
29.80
21.62
7.96
1.13
HN
Ts
NO2
Et
3k
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME 2008-04-22 tancheng-TC-Et
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080422
Time 21.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 812
DW 20.800 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 15.50 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 12.05 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127590 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



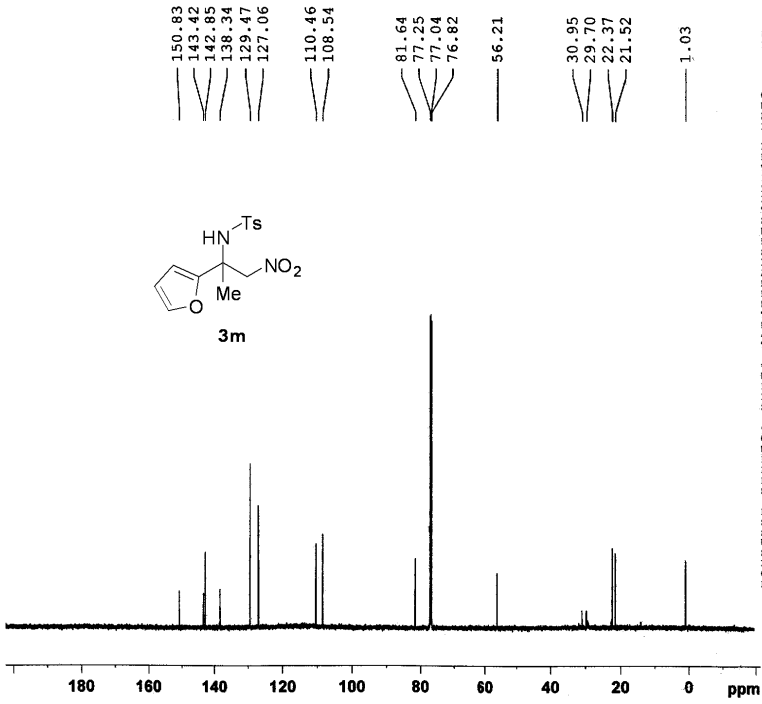

```
Current Data Parameters
NAME      2007-11-26 wangliwei Na
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20071126
Time                        15.50
INSTRUM                     spect
PROBHD    5 mm PATXI 1H/
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                             16
DS                              0
SWH                     12335.526 Hz
FIDRES                   0.188225 Hz
AQ                       2.6564426 sec
RG                            322
DW                         40.533 usec
DE                          6.50 usec
TE                           294.0 K
D1                    1.00000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                           1H
P1                           7.20 usec
PL1                         -1.00 dB
SFO1                600.1337060 MHz

F2 - Processing parameters
SI                             32768
SF                  600.1300090 MHz
WDW                               EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```



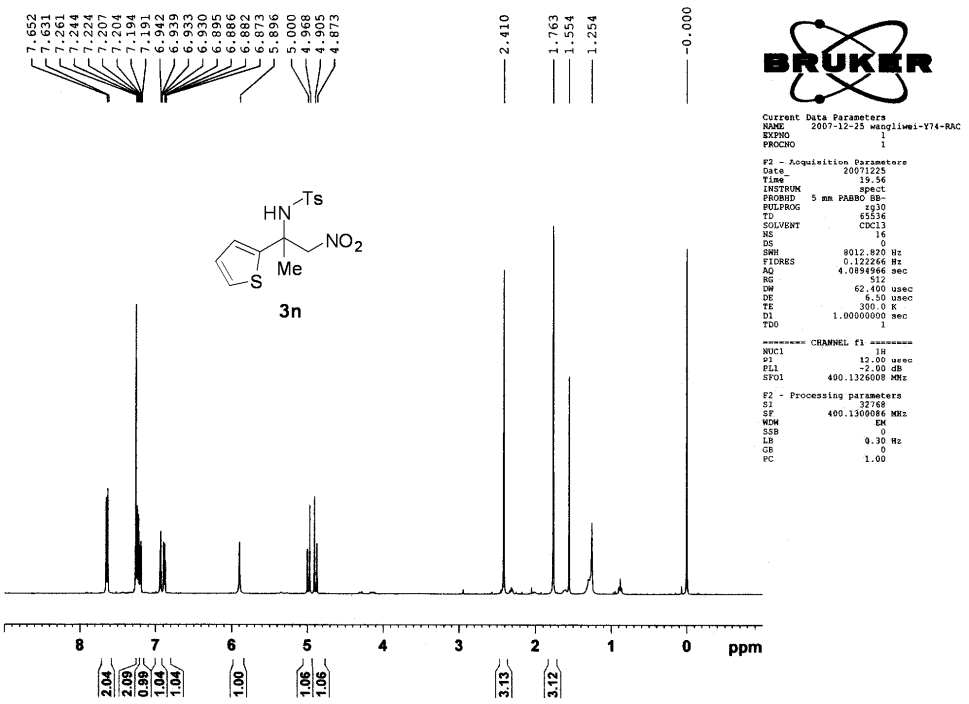

```
Current Data Parameters
NAME      2007-11-28 wangliwei RAC-Na
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20071128
Time                        11.59
INSTRUM                     spect
PROBHD    5 mm PATXI 1H/
PULPROG                   zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                            512
DS                              0
SWH                     36057.691 Hz
FIDRES                   0.550197 Hz
AQ                       0.9088159 sec
RG                             71.8
DW                         13.867 usec
DE                          6.50 usec
TE                           293.3 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                           13C
P1                          11.70 usec
PL1                          -3.00 dB
SFO1                150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                           1H
PCPD2                       80.00 usec
PL12                        19.92 dB
PL13                        19.50 dB
PL2                         -1.00 dB
SFO2                600.1324005 MHz

F2 - Processing parameters
SI                             32768
SF                  150.9028090 MHz
WDW                               EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```



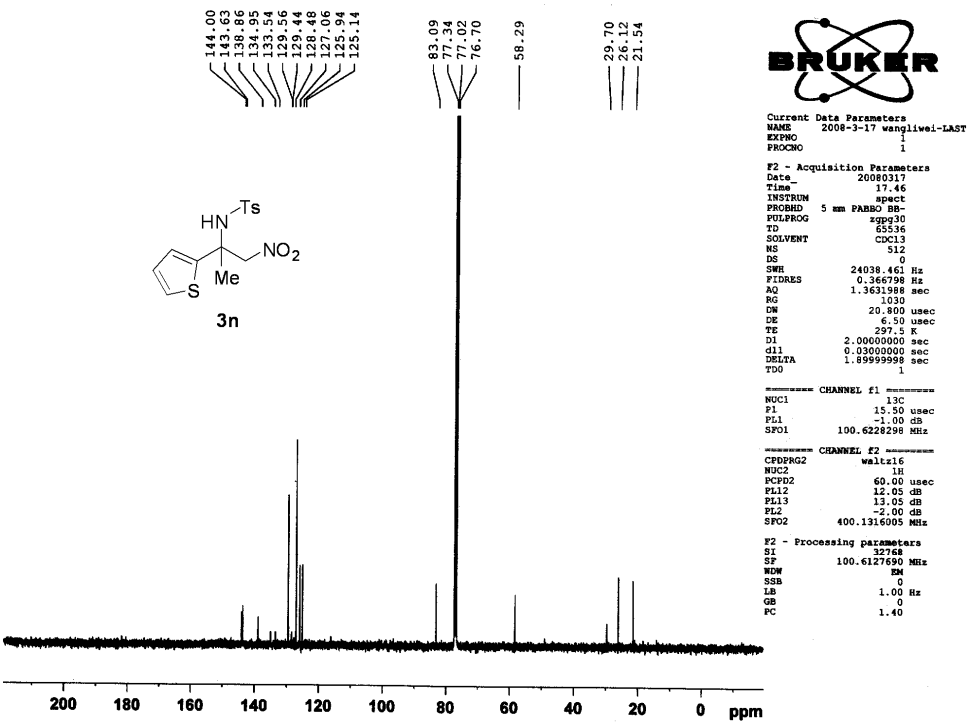
```
Current Data Parameters
NAME      2007-11-20 wangliwei-RAC-Fu
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20071120
Time              17.36
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                  161
DW               60.800 usec
DE                6.50 usec
TE                293.7 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300081 MHz
WDW                  EM
SSB                   0
LB                -0.30 Hz
GB                   0.1
PC                  1.00
```



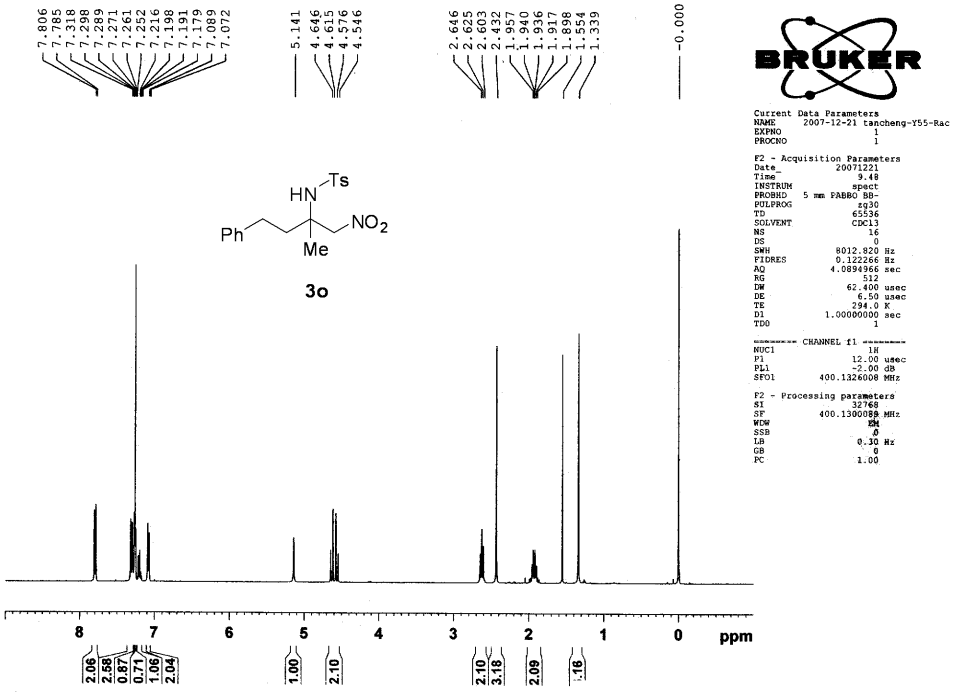
```
Current Data Parameters
NAME      2007-11-27 wangliwei Fu
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20071127
Time              8.43
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG          zgdc30
TD               65536
SOLVENT           CDCl3
NS                  512
DS                    2
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9088159 sec
RG                 80.6
DW               13.867 usec
DE                6.50 usec
TE                294.0 K
D1           2.00000000 sec
d11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                11.70 usec
PL1               -3.00 dB
SFO1         150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL12              19.92 dB
PL2               -1.00 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                32768
SF          150.9028890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                  1.40
```



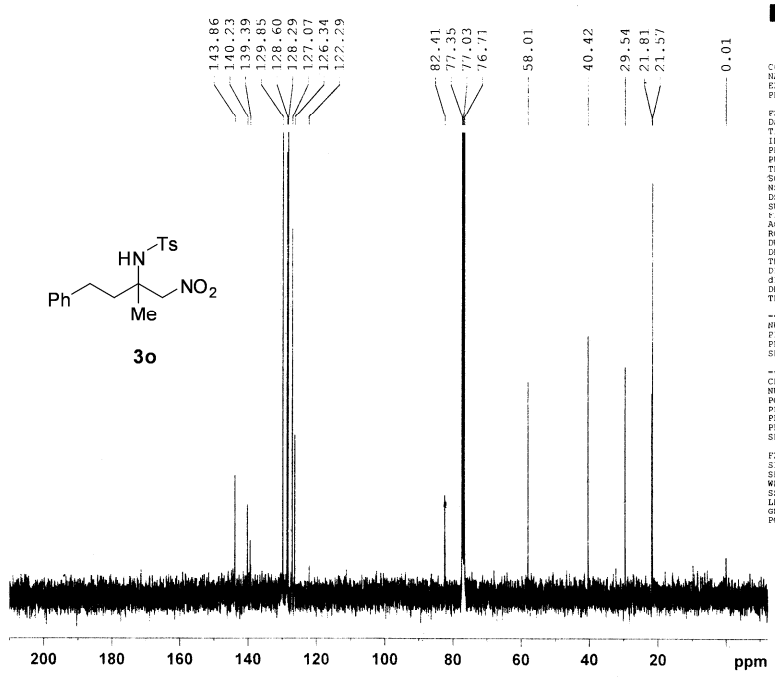

```
Current Data Parameters
NAME      2007-12-25 wangliwei-Y74-RAC
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20071225
Time              19.56
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   0
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894966 sec
RG                 512
DW              62.400 usec
DE               6.50 usec
TE              300.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -2.00 dB
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                32768
SF          400.1300086 MHz
WDW                  EM
SSB                   0
LB               0.30 Hz
GB                    0
PC                 1.00
```

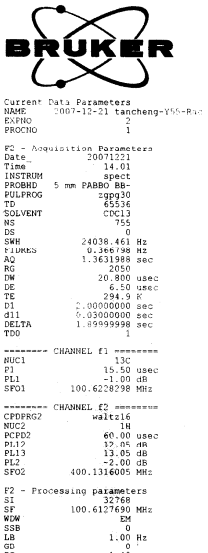


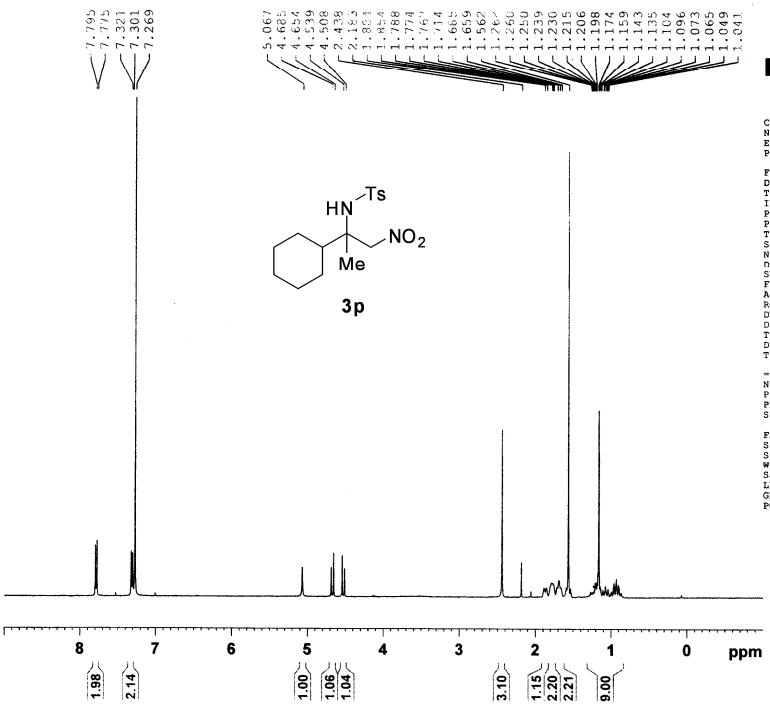

```
Current Data Parameters
NAME      2008-3-17 wangliwei-LAST
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20080317
Time              17.46
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 512
DS                   0
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                1030
DW              20.800 usec
DE               6.50 usec
TE              297.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1               15.50 usec
PL1              -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            60.00 usec
PL12             12.05 dB
PL13             13.05 dB
PL2              -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB               1.00 Hz
GB                    0
PC                 1.40
```


7.806
7.785
7.318
7.298
7.289
7.271
7.261
7.252
7.216
7.198
7.191
7.179
7.089
7.072
5.141
4.646
4.615
4.576
4.546
2.646
2.625
2.603
2.432
1.957
1.940
1.936
1.917
1.898
1.554
1.339
0.000
HN
Ts
Ph
NO2
Me
3o
8
7
6
5
4
3
2
1
0
ppm
2.06
2.58
0.87
0.71
1.06
2.04
1.00
2.10
2.10
3.18
2.09
1.16

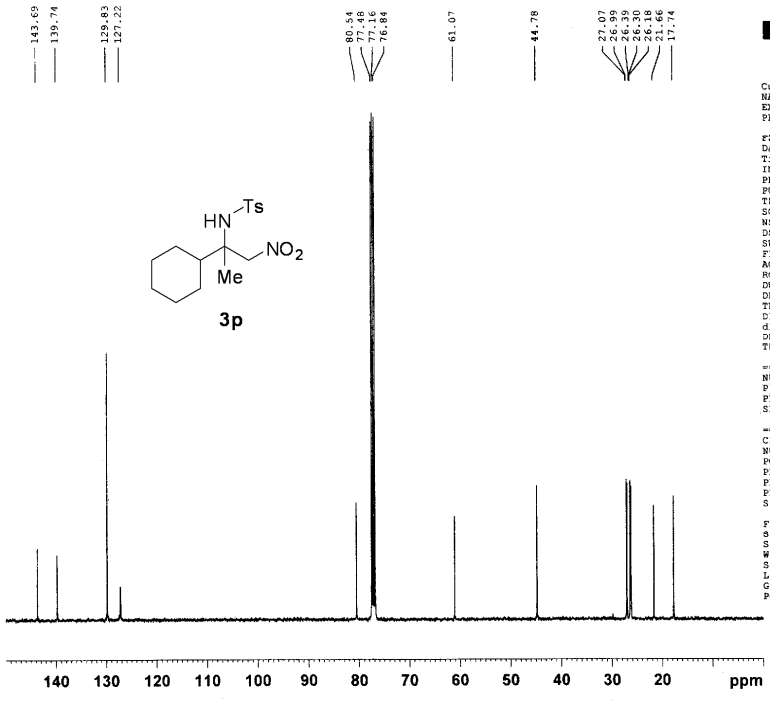
BRUKER
Current Data Parameters
NAME 2007-12-21 tancheng-Y55-Rac
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071221
Time 9.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 512
DW 62.400 usec
DE 6.50 usec
TE 294.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -2.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


143.86
140.23
139.39
129.85
128.60
128.29
127.07
126.34
122.29
82.41
77.35
77.03
76.71
58.01
40.42
29.54
21.81
21.57
0.01
HN
Ts
Ph
NO2
Me
3o
200
180
160
140
120
100
80
60
40
20
ppm


BRUKER
Current Data Parameters
NAME 2007-12-21 tancheng-Y55-Rac
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071221
Time 14.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 755
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 15.50 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 12.05 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
Current Data Parameters
NAME        2008-02-29 wangliwei-RAC
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_            20080229
Time               15.04
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                  406
DW               60.800 usec
DE                6.50 usec
TE               292.1 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF           400.1300057 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




```
Current Data Parameters
NAME        2008-03-03 wangliwei AC
EXPNO                1
PROCNO               1

f2 - Acquisition Parameters
Date_            20080303
Time               11.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               297.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
PL1               -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             60.00 usec
PL12              12.05 dB
PL13              13.05 dB
PL2               -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127565 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.40
```

8. Copy of NMR Spectra for Diamine 4a