Supplementary Material for Organic & Biomolecular Chemistry

Supporting Information

New Catalytic System for Aminohalogenation of β-Methyl-β-nitrostyrenes to Give Opposite Regiochemistry

San-Jun Zhi,[a,b] Hao Sun,[a] Guangqian Zhang,[a] Guigen Li,*[d] and Yi Pan *[a,c]

[a] School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China;
[b] Department of Chemistry, Huaiyin Normal University, Huaian 221003, PR China;
[c] State Key Lab of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China;
[d] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061;

Table of Contents：

I. General Experimental Procedures

General Information

All moisture-sensitive reactions were performed under nitrogen in glassware that had been flame-dried. Solvents were dried and distilled prior to use. Flash chromatography was performed on silica gel 60 (F-254) TCL plates (20cm × 20cm). Melting points are uncorrected. IR spectra were collected with a Bruker Vector 22 instrument (KBr pellets). NMR spectra were recorded in in deuterated dimethylsulfoxide (CD_3SOCD_3), deuterated acetone (CD_3COCD_3) and deuterated chloroform ($CDCl_3$) with TMS for ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) as internal reference. Elemental analyses were performed with a Perkin-Elmer 240 elemental analysis instrument. Mass spectra of new compounds were measured with a Finnigan LCQ Electrospray Mass Spectrometer.

II. Synthesis of 1-aryl-2-nitropropenes

1-Aryl-2-nitropropenes **(1a-1h)** were synthesized according to literature procedures.[1]

III. General Procedure for Electrophilic Aminochloronation

Into a dry vial was added 1-aryl-2-nitropropene (1.0 mmol), $TsNH_2$ (340 mg, 2.0 mmol), catalyst (0.20 mmol, 0.20 equiv), 4 Å molecular sieves (500 mg, predried in the oven at 200 °C overnight), and freshly distilled dichloromethane (5.0 mL) with nitrogen atmosphere. The mixture was stirred at room temperature for 10 min before $TsNCl_2$ (480 mg, 2 mmol) was added. The resulting mixture was stirred at room temperature for 48h in the capped vial nitrogen atmosphere protection and the reaction was then quenched with saturated aqueous Na_2SO_3 (5.0 mL) solution. The 4 Å molecular sieves and other solid precipitates were filtered off and washed with EtOAc (3×10 mL). The combined organic phases were washed with brine and dried with anhydrous sodium sulfate. The organic solution was concentrated and purified via flash chromatography with EtOAc and petroleum ether (v/v=1:4) as the eluent to give the pure products.

References

1 (a) E. Dumez, R. Faure, J. P. Dulcere, *Eur. J. Org. Chem.,* 2001, **13**, 2577. (b) A. S. Abdallah, F. Texier-Boullet, J. Hamelin, *Synthesis,* 1994, **3**, 258. (c) P. Alain, S. L. Dewey, J. S. Fowler, M. Guillaume,; A. P. Wolf, *Journal of Medicinal Chemistry,* 1990, **33**, 2015. (d) B. P. Bandgar, L. S. Uppalla, V. S. Sadavarte, *Monatshefte fuer Chemie,* 2000, **131**, 949. (e) R. Ballini, F. Bigi, E. Gogni, R. Maggi, G. Sartori, *Journal of Catalysis,* 2000, **191**, 348.

IV. NMR Data for Compound 4a-4h

4a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49-7.47 (d, J = 8.4 Hz, 2 H), 7.20-7.10 (m, 3 H), 7.05-6.98 (m, 4 H), 5.78 (d, J = 10.8 Hz, 1 H), 5.18 (d, J = 10.8 Hz, 1H), 2.30 (s, 3 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 143.2, 137.6, 133.1, 129.1, 128.9, 128.5, 127.9, 12.6.8, 106.7, 64.8, 26.2, 20.4 ppm.

4b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.47 (d, J = 8.4 Hz, 2 H), 7.06-7.03 (d, J = 8.4 Hz, 2 H), 6.93-6.86 (m, 4 H), 5.88 (d, J = 10.5 Hz, 1 H), 5.14 (d, J = 10.5 Hz, 1H), 2.31 (s, 3 H) , 2.25 (s, 3 H) , 2.24 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 143.1, 138.4, 137.6, 130.1, 129.0, 128.9, 128.6, 128.5, 126.8, 106.8, 64.7, 26.1, 20.4, 20.1 ppm.

4c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.48 (d, J = 8.4 Hz, 2 H), 7.07-7.05 (d, J = 8.4 Hz, 2 H), 6.94-6.91 (d, J = 8.7 Hz, 2H), 6.64-6.61 (d, J = 8.7 Hz, 2H), 5.82 (d, J = 10.5 Hz, 1 H), 5.14 (d, J = 10.5 Hz, 1H), 3.73 (s, 3 H) ,2.32 (s, 3 H) , 2.24 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ = 159.7, 143.0, 137.6, 130.7, 129.5, 126.8, 125.1, 113.6, 106.4, 64.6, 55.5, 25.2, 21.2 ppm.

4d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.47 (d, J = 8.7 Hz, 2 H), 7.10-7.07 (m, 4 H), 6.96-6.93 (m, 2 H), 5.95 (d, J = 10.8 Hz, 1 H), 5.18 (d, J = 10.8 Hz, 1 H), 2.35 (s, 3 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3): δ= 143.4, 137.4, 134.2, 131.9, 130.7, 129.2, 128.0, 126.9, 106.5, 64.2, 26.4, 20.4 ppm.

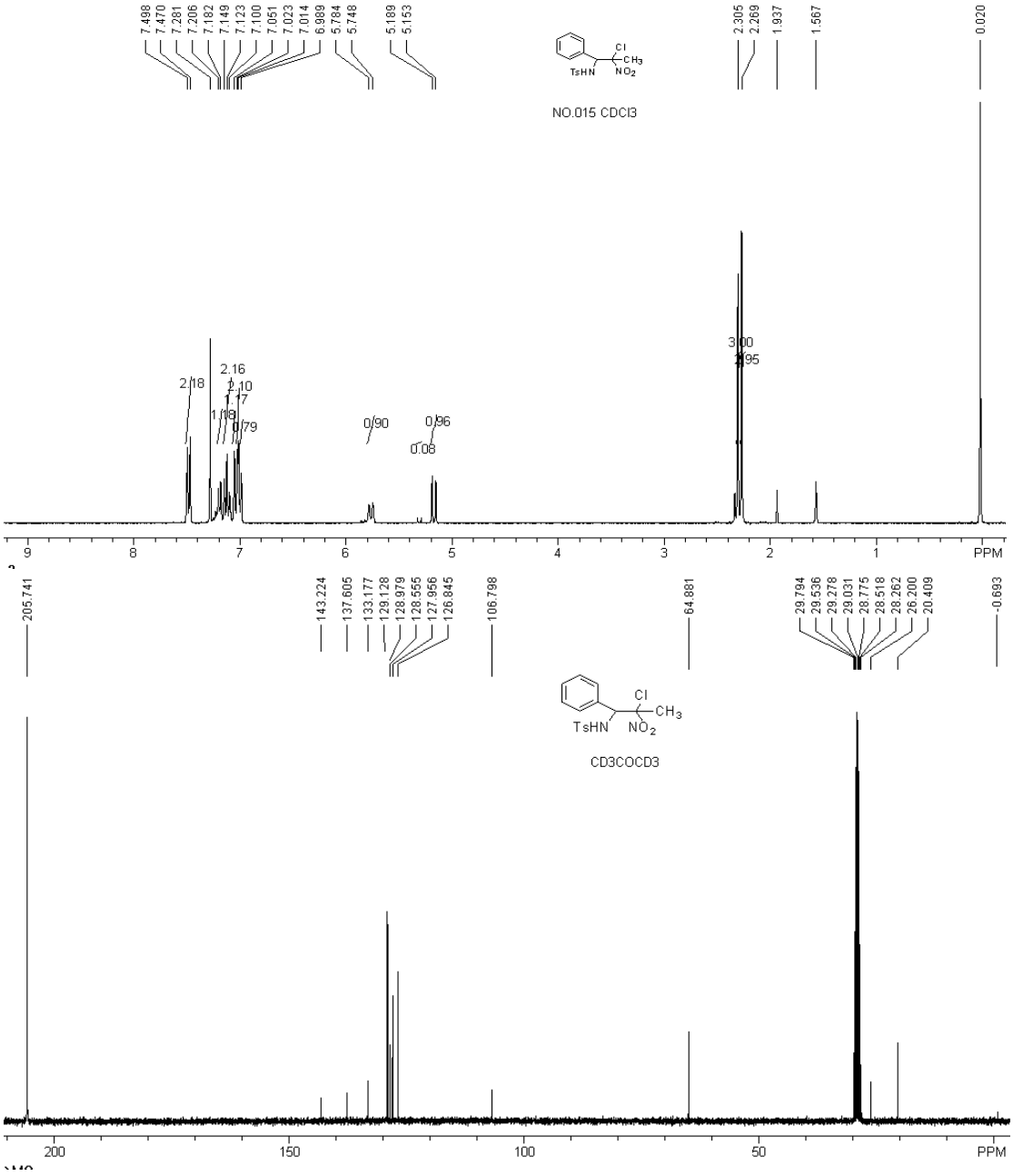
4e: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.47 (d, J = 8.1 Hz, 2 H), 7.09-7.07 (m, 3 H), 7.02-6.79 (m, 4 H), 5.70 (d, J = 10.5 Hz, 1 H), 5.19 (d, J = 10.5 Hz, 1 H), 2.32 (s, 3 H), 2.27 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 164.3, 161.1, 143.2, 137.6, 131.2, 131.0, 129.3, 129.1, 126.9, 114.8, 114.6, 106.8, 64.1, 26.2, 20.3 ppm.

4f: ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.58-7.56 (d, J = 7.8 Hz, 2 H), 7.22-7.06 (m, 6 H), 6.46 (d, J = 10.8 Hz, 1 H), 5.81 (d, J = 10.8 Hz, 1 H), 2.31 (s, 3 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ = 161.6, 158.3, 143.4, 136.9, 131.3, 129.6, 126.6, 124.7, 121.0, 115.1, 104.7, 57.0, 24.3, 20.9 ppm.

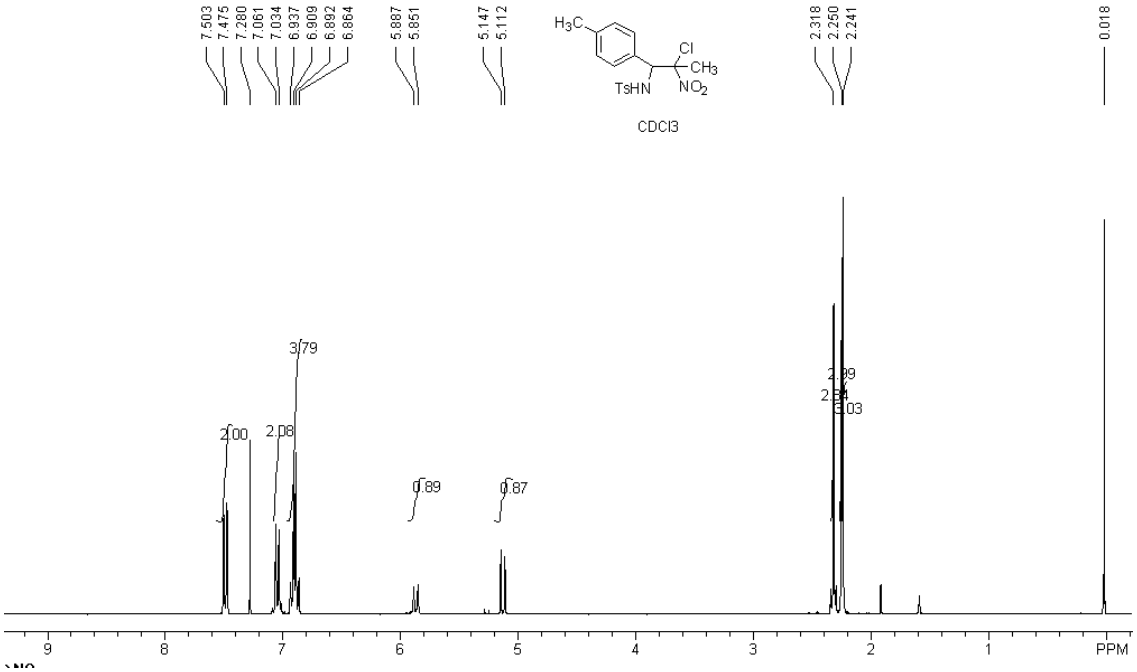
4g: ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.01-7.98 (d, J = 9.0 Hz, 2 H), 7.52-7.49 (d, J = 8.4 Hz, 2 H), 7.24-7.22 (d, J = 9.0 Hz, 2 H), 7.10-7.07 (d, J = 8.4 Hz, 2 H), 5.71 (d, J = 10.8 Hz, 1 H), 5.34 (d, J = 10.8 Hz, 1H), 2.32 (s, 3 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ = 147.7, 143.5, 140.4, 137.1, 131.1, 129.6, 127.0, 123.2, 105.2, 64.2, 25.1, 21.1 ppm.

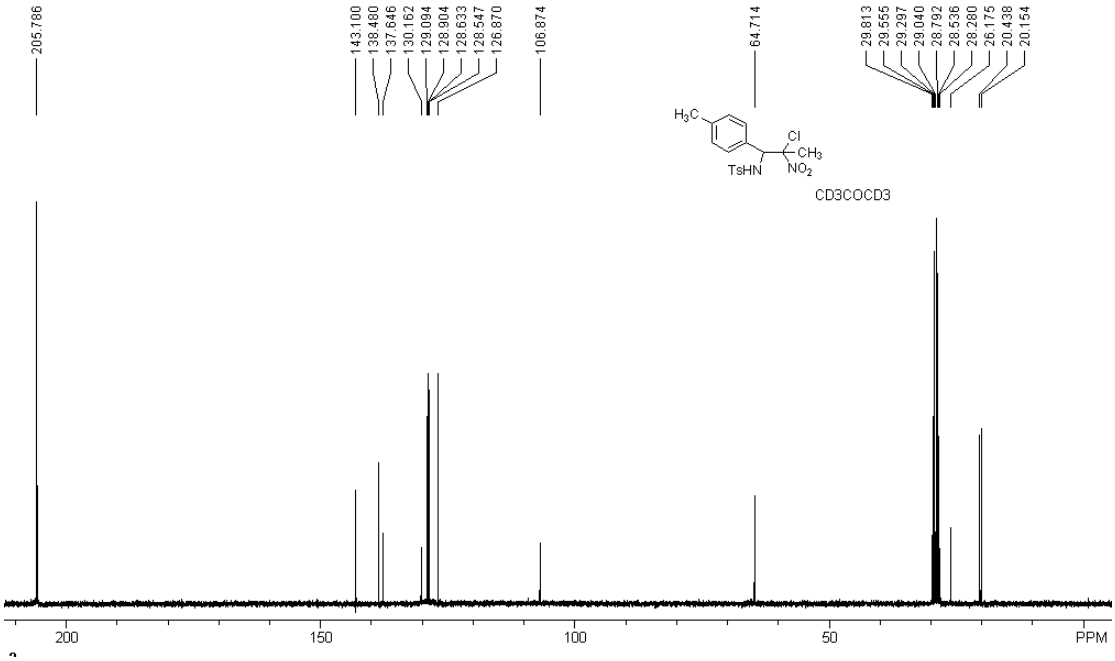
4h: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.52 (d, J = 8.1 Hz, 2 H), 7.24-6.80 (m, 6 H), 6.01 (d, J = 10.8 Hz, 1 H), 5.45 (d, J = 10.8 Hz, 1H), 2.30 (s, 3 H), 2.20 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ = 143.3, 137.0, 136.9, 134.6, 131.6, 131.5, 130.6, 130.1, 129.7, 129.5, 127.5, 126.6, 104.6, 59.7, 23.9, 21.2 ppm.

IV. 1H NMR and 13C NMR Spectra for Compound 4a-4h

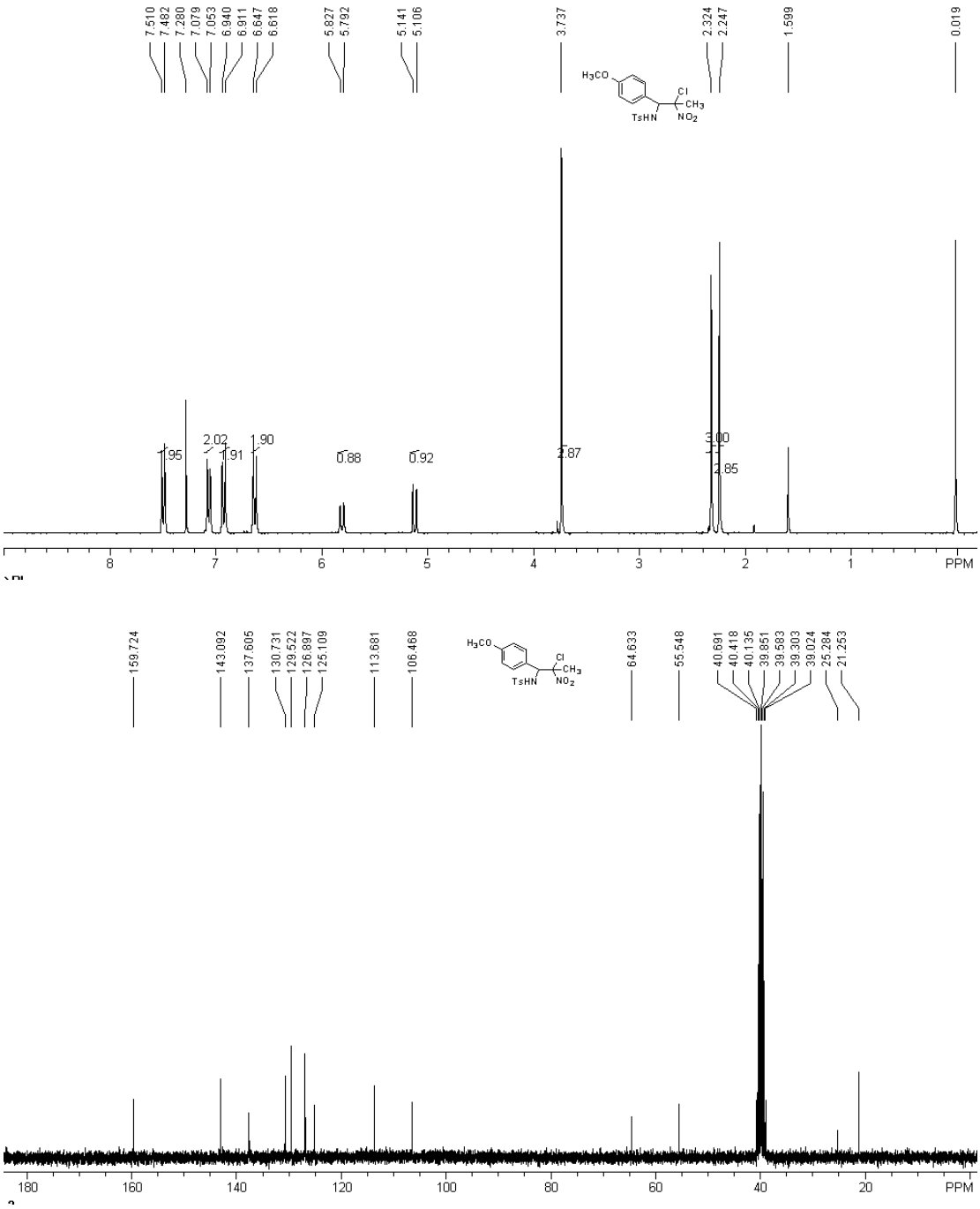


^{1}H and ^{13}C NMR spectra of 4a

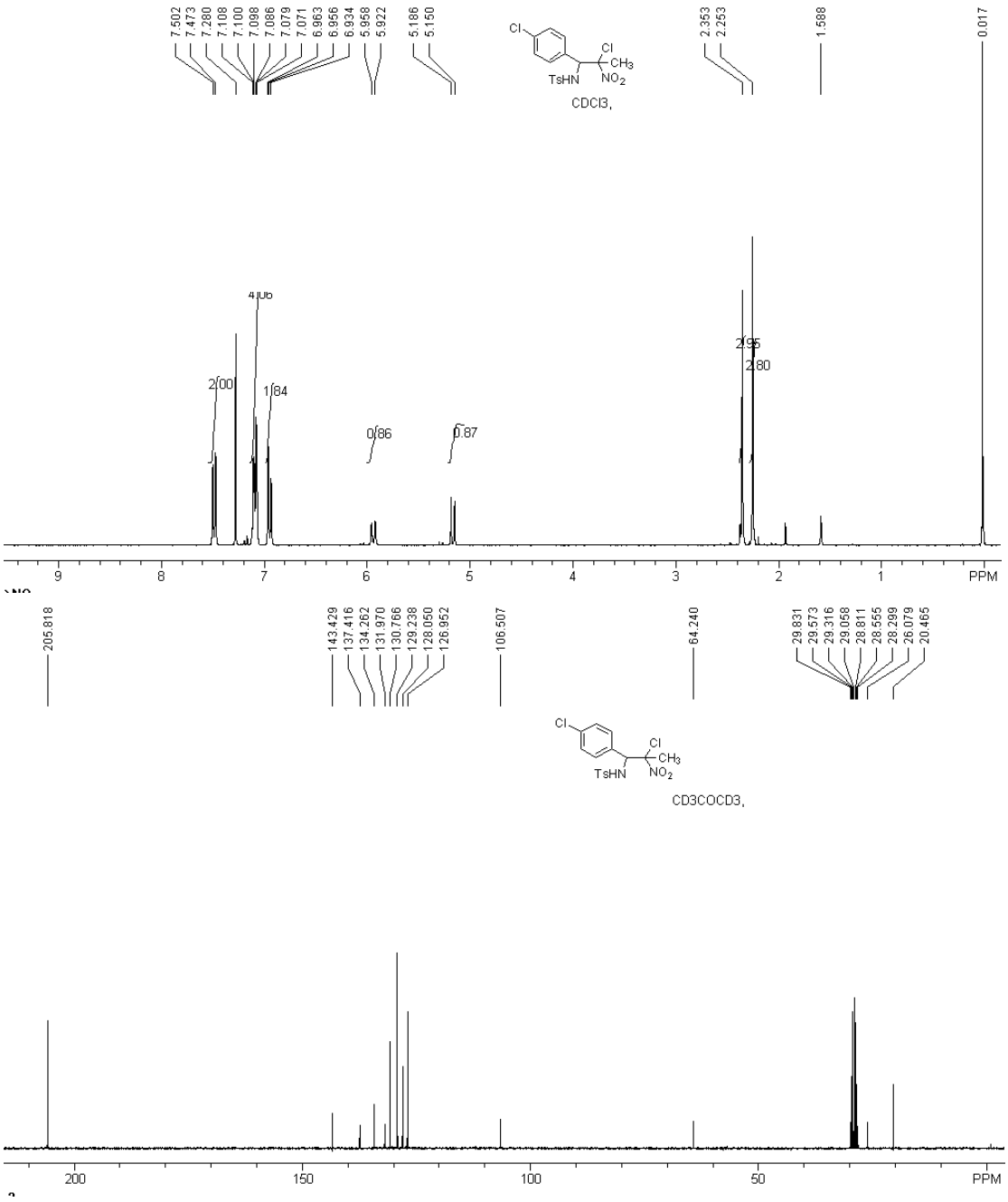




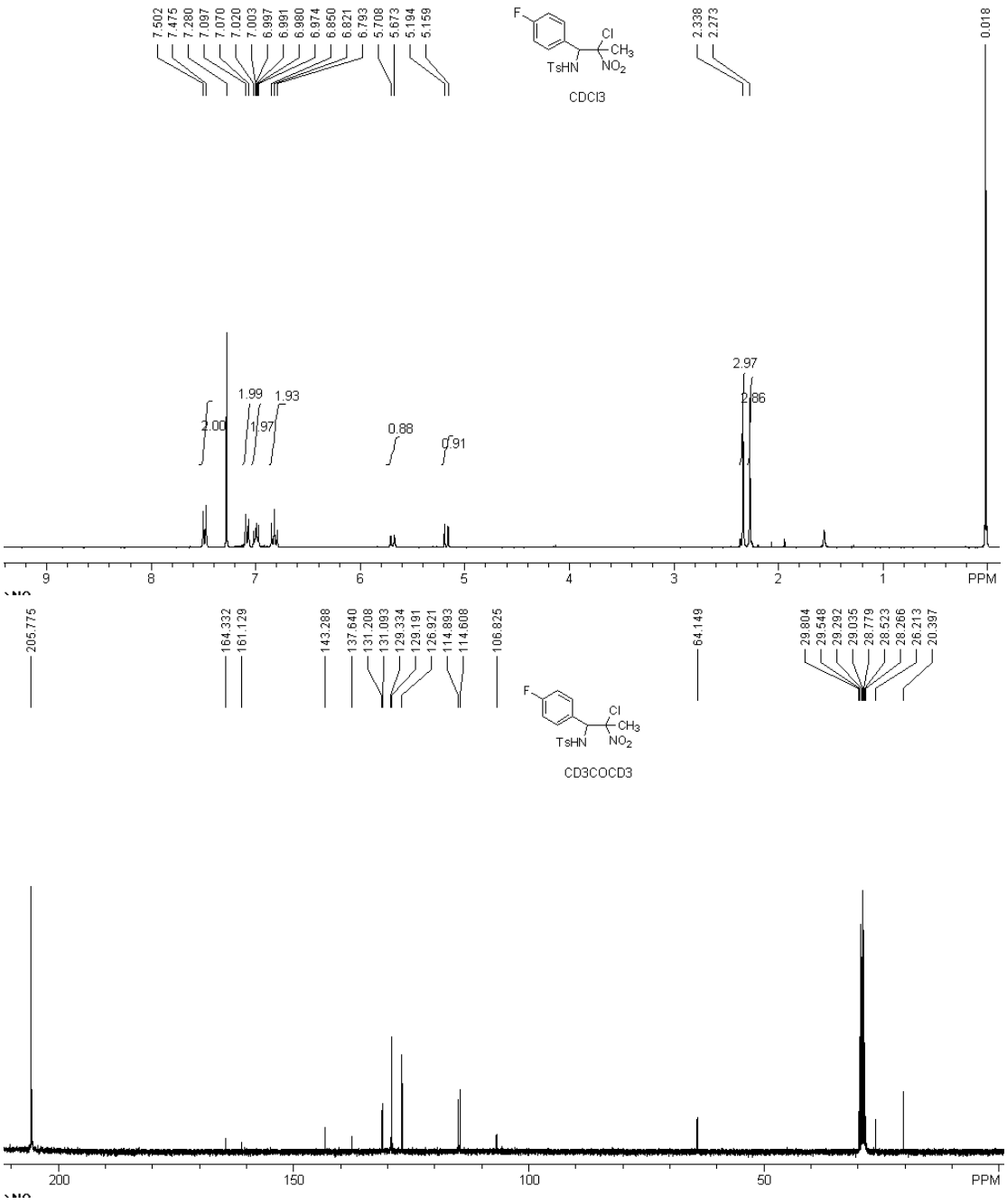
^{1}H and ^{13}C NMR spectra of 4b



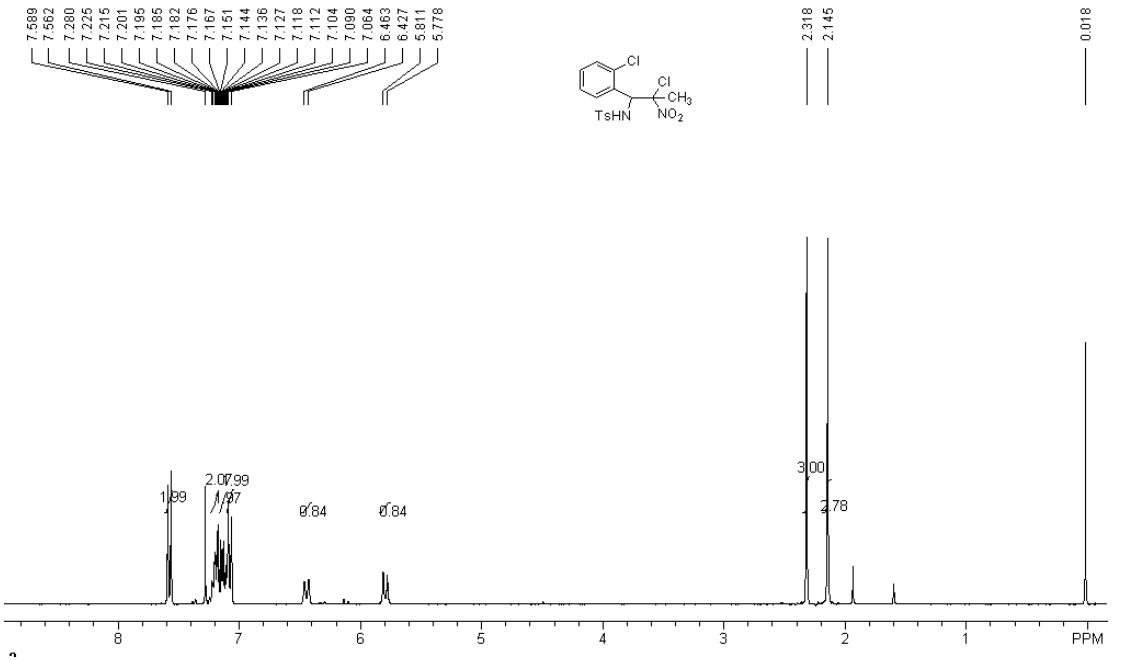
^{1}H and ^{13}C NMR spectra of 4c

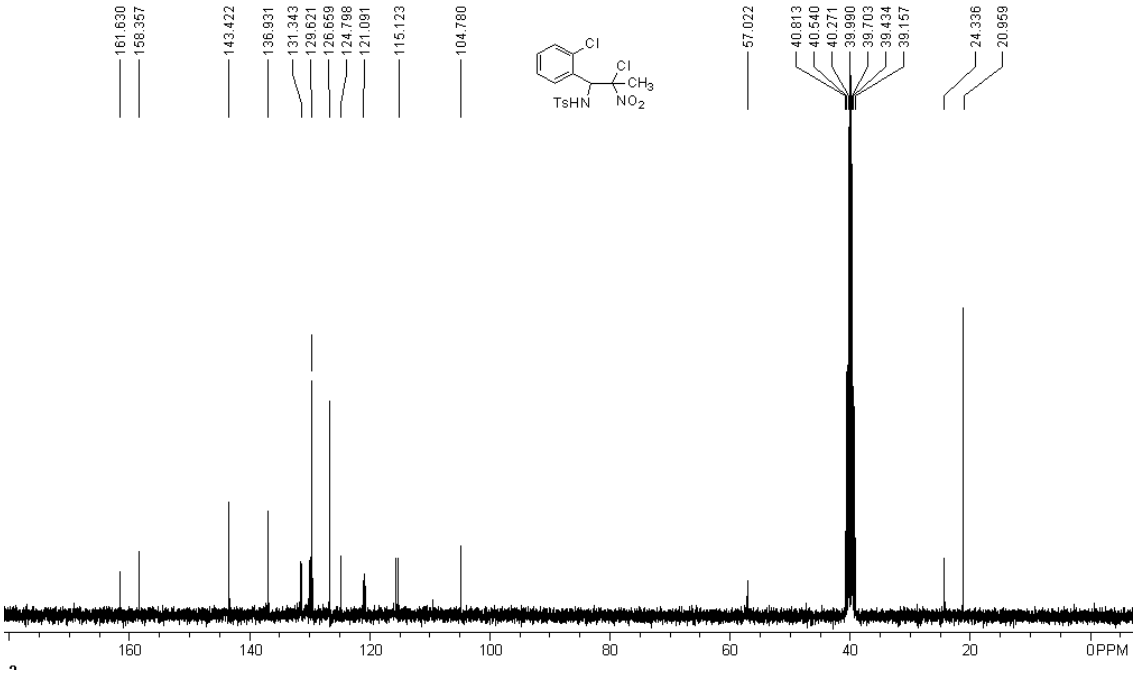


^{1}H and ^{13}C NMR spectra of 4d

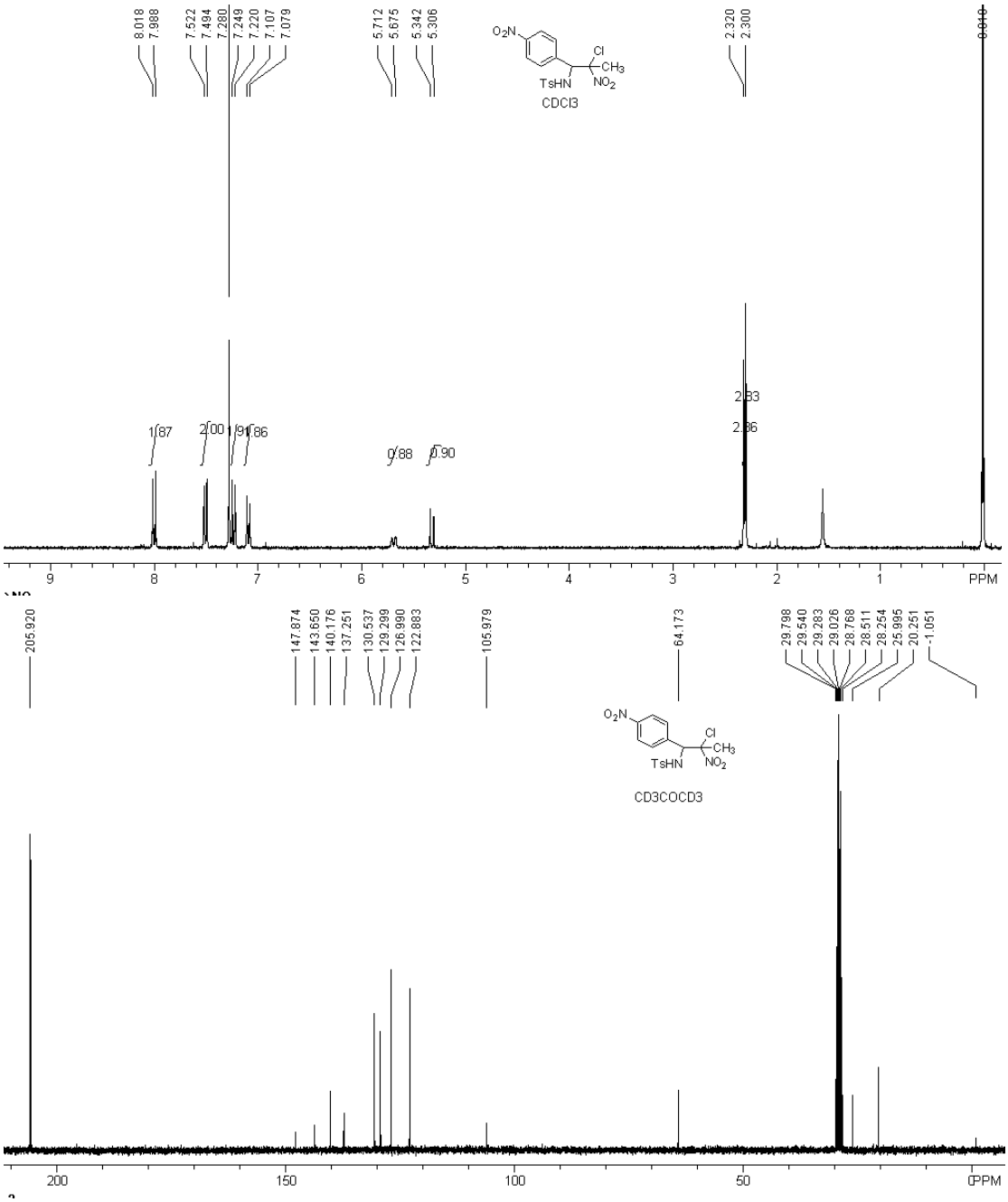


^{1}H and ^{13}C NMR spectra of 4e

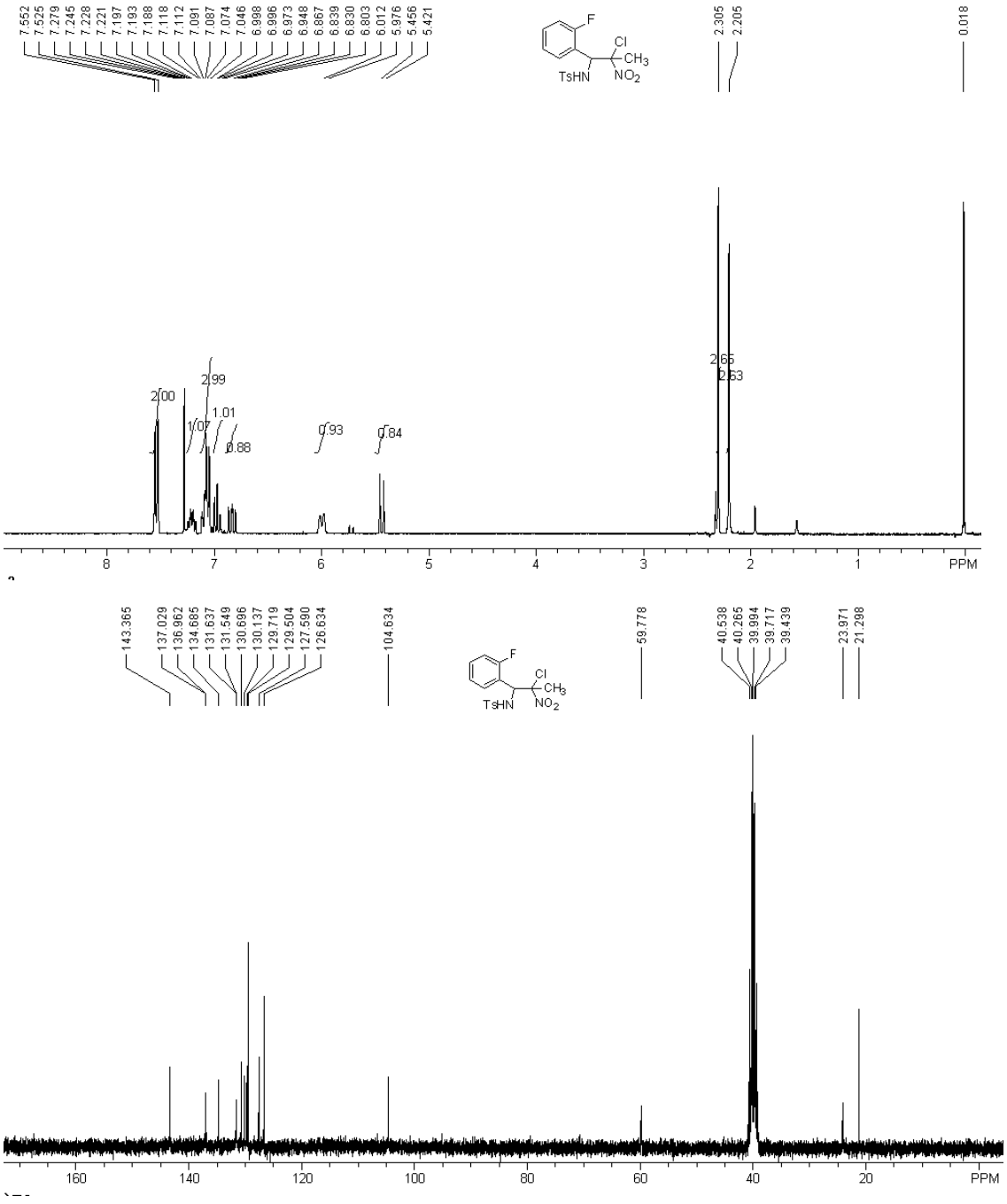




^{1}H and ^{13}C NMR spectra of 4f



^{1}H and ^{13}C NMR spectra of 4g



^{1}H and ^{13}C NMR spectra of 4h