

Supporting Information

Pd-Catalyzed Regioselective Intramolecular Allylic C-H Amination of 1,1-Disubstituted Alkenyl Amines

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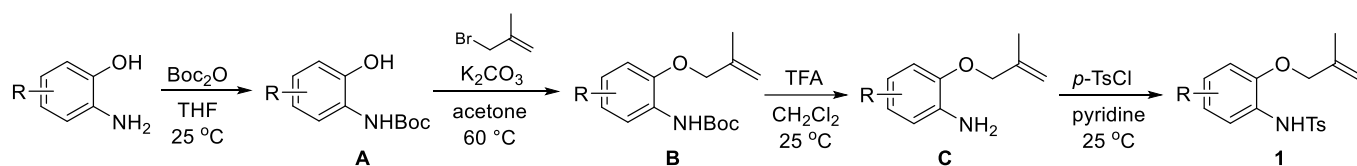
General Information

Nuclear Magnetic Resonance spectra were recorded on 400 MHz instruments. Spectra were recorded in CDCl₃ solutions referenced to TMS or solvent residual peaks. High Resolution Mass Spectra (HRMS) were measured using EI at 70 eV and mass analyzer type was TOF. GC-MS spectra were recorded on a Perkin Elmer's Clarus 600S GC-system with Turbo mass ver. 5.4.2 inert Mass Selective Detector (EI) and Elite-1 column (0.25 mm x 30 m, Film: 0.25 μm). For control of the conversion and characterization of the products, the following method was used: The method starts with the injection temperature T₀ (50 °C), after holding this temperature for 5 min, the column is heated to the temperature T₁ (ramp, 300 °C, 10 °C/min) and hold for additional 10 min.

The determination of e.e. was performed via chiral HPLC analysis using Young Lin YL9100 HPLC workstation. Chiralcel OD-H, OJ-H, Chiralpak AD-H columns were purchased from Daicel Chemical Industries, LTD. Optical rotations were measured using a 1 mL cell with a 0.5 dm path length on a Jasco P-1020 polarimeter and are reported as follows: [α]_D²⁰ (c in g per 100 mL solvent).

Flash chromatography was performed on silica gel 230-400 mesh. All commercially available catalysts and ligands were purchased from Sigma-Aldrich or Strem and used as received. Unless otherwise noted, all commercially obtained reagents and solvents were used as received. Anhydrous toluene, ClCH₂CH₂Cl, DMF, and 1,4-dioxane were purchased from Sigma-Aldrich in a SureSeal™ bottle and used as received. THF and Et₂O were distilled from sodium benzophenone ketyl immediately prior to use. MeOH, EtOH, CH₂Cl₂, EtOAc, and MeCN were distilled from CaH₂ immediately prior to use. Thin layer chromatograms (TLC) was visualized via UV. Oil bath and IKA reaction block were used for reactions that require heating.

General Procedure for the Preparation of *N*-Ts-2-Methallyloxyaniline Derivatives **1**¹



Method A: To a solution of 2-aminophenol (0.927~18.2 mmol, 1.0 equiv) in THF (1.5~30.3 mL, 0.6 M) was added Boc₂O (0.927~18.2 mmol, 1.0 equiv) at 0 °C. After being stirred at room temperature for 5~12 h, the reaction mixture was poured into water and then the product was extracted with CH₂Cl₂ (three times). The combined organic layer was washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:6 ~ 1:7) to give **A** in 92-98% yields.

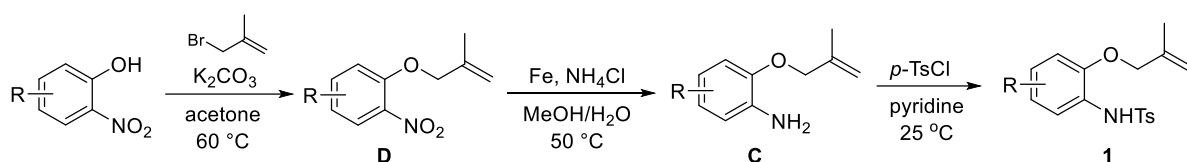
To a solution of **A** (0.857~17.9 mmol, 1.0 equiv) in acetone (0.6~12.8 mL, 1.4 M) were added K₂CO₃ (1.03~21.4 mmol, 1.2 equiv) and then methallyl bromide (0.857~17.9 mmol, 1.0 equiv) dropwise at 0 °C. After being stirred at 60 °C for 3~12 h, the reaction mixture was cooled to room temperature and diluted

¹ (a) Carmona, R. C.; Köster, O. D.; Correia, C. R. D. *Angew. Chem. Int. Ed.* **2018**, *57*, 12067. (b) Sen, A.; Takenaka, K.; Sasai, H. *Org. Lett.* **2018**, *20*, 6827. (c) Hartmann, M.; Studer, A.; *Angew. Chem. Int. Ed.* **2014**, *53*, 8180.

with Et₂O, washed with H₂O, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:10 ~ 1:20) to give **B** in 82-98% yields.

To a solution of **B** (0.703~17.5 mmol, 1.0 equiv) in CH₂Cl₂ (2.3~58.4 mL, 0.3 M) was added CF₃CO₂H (3.52~87.6 mmol, 5.0 equiv) at 25 °C. After being stirred at room temperature for 3~5 h, the reaction mixture was neutralized (pH 7~8) with aq. NaHCO₃, extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5 ~ 1:10) to give **C** in 85-91% yields.

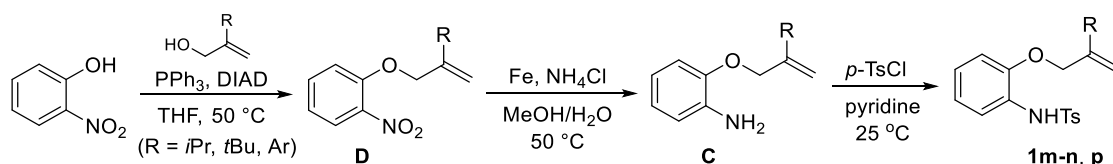
To a solution of **C** (0.599~15.9 mmol, 1.0 equiv) in pyridine (2.9~79.6 mL, 0.2 M) was added *p*-TsCl (0.719~19.1 mmol, 1.2 equiv) at 0 °C. After being stirred at room temperature for 5~12 h, pyridine was removed by rotary evaporator and the reaction mixture was poured into water. The product was extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3 ~ 1:5) to give **1** in 65-90% yields.



Method B: To a solution of 2-nitrophenol (0.956-3.15 mmol, 1.0 equiv) in acetone (0.7-2.2 mL, 1.4 M) were added K₂CO₃ (1.15-3.78 mmol, 1.2 equiv) and then methallyl bromide (0.956-3.15 mmol, 1.0 equiv) dropwise at 0 °C. After being stirred at 60 °C for 5-48 h, the reaction mixture was cooled to room temperature and diluted with Et₂O, washed with H₂O, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3 ~ 1:5) to give **D** in 35-99% yields.

To a solution of **D** (0.335-2.65 mmol, 1.0 equiv) in MeOH/H₂O (3:1, 4.5-35.3 mL, 0.075 M) were added Fe powder (3.35-26.5 mmol, 10.0 equiv) and NH₄Cl (1.34-10.6 mmol, 4.0 equiv). After being stirred at 50 °C for 5-24 h, the reaction mixture was extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3 ~ 1:8) to give **C** in 67-99%.

N-Tosylation of **C** was performed as described above in Method A to give **1** in 57-99% yields.



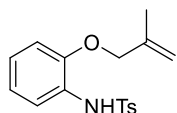
Method C: To a solution of 2-nitrophenol (0.448-3.66 mmol, 1.0 equiv), allyl alcohol² (0.448-3.66 mmol, 1.0 equiv), and PPh₃ (0.537-4.40 mmol, 1.2 equiv) in THF (0.7-5.5 mL, 0.66 M) was added diisopropyl azodicarboxylate (DIAD, 0.537-4.40 mmol, 1.2 equiv) dropwise at 0 °C. After being stirred at 50 °C for 6-

² (a) Ma, W.; Ren, F. J.; Wang, Z. *Org. Lett.* **2015**, *17*, 4180. (b) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *J. Org. Chem.* **1992**, *57*, 3558.

18 h, the reaction mixture was quenched with H₂O, extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5 ~ 1:10) to give **D** in 47-82% yields.

Following nitro reduction of **D** and *N*-tosylation of **C** were performed as described above in Method B to give **1** in 70-80% yields.

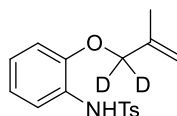
N-Ts-2-(Methallyloxy)aniline (**1a**)



Following the Method A: 4.53 g, a white solid (EtOAc : *n*-Hexane = 1:5), mp 80-82 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.63 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.00 (td, *J* = 7.9, 1.6 Hz, 1H), 6.99 (br s, 1H), 6.90 (td, *J* = 7.8, 1.2 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.93 (s, 1H), 4.84 (s, 1H), 4.25 (s, 2H), 2.35 (s, 3H), 1.69 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 148.6, 143.6, 139.9, 136.3, 129.4, 127.2, 126.1, 125.2, 121.4, 121.2, 113.2, 111.8, 72.2, 21.5, 19.2. EIMS *m/z* 317 (M⁺), 252, 219, 162, 91.

N-Ts-2-(Methallyloxy)aniline (**1a-d₂(allyl)**)



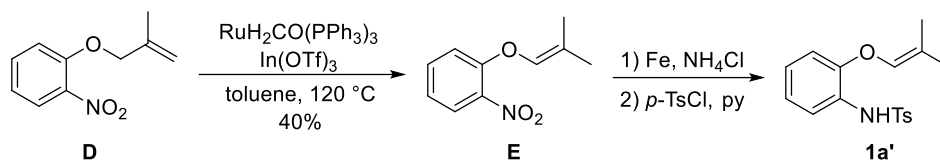
1,1-*d*₂-Methallyl alcohol was prepared according to literature procedure reported by Trost and Tanaka.³ To a solution of NaH (82.4 mg, 2.061 mmol, 2.3 equiv) in THF (1.7 mL, 0.54 M) was added 1,1-*d*₂-methallyl alcohol (79.7 mg, 1.075 mmol, 1.2 equiv) dropwise at 0 °C. After 15 min, 1-fluoro-2-nitrobenzene (95 μ L, 0.897 mmol, 1.0 equiv) was added to the reaction mixture. After being stirred at room temperature for 20 h, the reaction mixture was quenched with sat. aq. NH₄Cl, extracted with EtOAc, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:10) to give the corresponding **D** (97.5 mg, 56%) as a colorless oil.

Following nitro reduction of **D** and *N*-tosylation were performed as described above in Method B to give **1a-d₂(allyl)** (108.0 mg, 81%, EtOAc : *n*-Hexane = 1:5) as a white solid (mp 84-86 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.996 (td, *J* = 7.8, 1.6 Hz, 1H), 7.00 (br s, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.71 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.93 (s, 1H), 4.84 (s, 1H), 2.34 (s, 3H), 1.68 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 148.6, 143.6, 139.8, 136.2, 129.4, 127.2, 126.0, 125.2, 121.3, 121.2, 113.3, 111.8, 21.4, 19.1. EIMS *m/z* 319 (M⁺), 253, 252, 235, 164, 163, 91, 65.

³ (a) Trost, B. M.; King, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 408. (b) Okamoto, R.; Tanaka, K. *Org. Lett.* **2013**, *15*, 2112.

N-Ts-2-((Methylprop-1-en-1-yl)oxy)aniline (**1a'**)

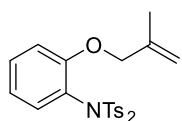


D (124.0 mg, 0.642 mmol, 1.0 equiv), $\text{RuH}_2\text{CO}(\text{PPh}_3)_3$ (3.0 mg, 0.00321 mmol, 0.5 mol%), and $\text{In}(\text{OTf})_3$ (3.6 mg, 0.00642 mmol, 1 mol%) were dissolved in toluene (1.6 ml, 0.4 M).⁴ After being stirred at 120°C for 48 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **E** (49.9 mg, 40%) as a xx solid.

Following nitro reduction of **E** and *N*-tosylation were performed as described above in Method B to give **1a'** (36.0 mg, 55%, EtOAc : *n*-Hexane = 1:5) as a white solid (mp $78\text{--}80^\circ\text{C}$).

^1H NMR (CDCl_3 , 400 MHz) δ 7.62 (d, $J = 8.0$ Hz, 2H), 7.57 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.01 (td, $J = 7.7, 2.0$ Hz, 1H), 6.98 (br s, 1H), 6.95 (td, $J = 7.8, 1.2$ Hz, 1H), 6.76 (dd, $J = 8.0, 1.6$ Hz, 1H), 5.763–5.756 (m, 1H), 2.34 (s, 3H), 1.62 (s, 3H), 1.53 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 148.0, 143.6, 136.1, 134.3, 129.4, 127.1, 126.1, 125.5, 122.4, 122.0, 119.3, 114.2, 21.4, 19.2, 15.0. EIMS m/z 317 (M^+), 252, 162, 147, 91, 65.

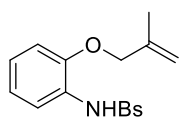
N,N-BisTs-2-(Methallyloxy)aniline (**1a''**)



To a solution of **1a** (188.4 mg, 0.594 mmol, 1.0 equiv) in CH_2Cl_2 (3.0 mL, 0.2 M) were added DMAP (14.7 mg, 0.119 mmol, 20 mol%), *p*-TsCl (137.2 mg, 0.712 mmol, 1.2 equiv), and Et_3N (259 μL , 1.840 mmol, 3.1 equiv) at 0°C . After being stirred at reflux for 2 h, the reaction mixture was cooled to room temperature and poured into 1 M HCl. The product was extracted with CH_2Cl_2 , dried over MgSO_4 , and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:4) to give **1a''** (171.2 mg, 61%, EtOAc : *n*-Hexane = 1:4) as a white solid (mp $132\text{--}134^\circ\text{C}$).

^1H NMR (CDCl_3 , 400 MHz) δ 7.85 (d, $J = 8.4$ Hz, 4H), 7.37 (ddd, $J = 8.4, 7.6, 1.6$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 4H), 7.06 (dd, $J = 7.8, 1.8$ Hz, 1H), 6.92 (td, $J = 7.6, 1.2$ Hz, 1H), 6.86 (dd, $J = 8.4, 1.2$ Hz, 1H), 4.87 (s, 1H), 4.84 (s, 1H), 4.13 (s, 2H), 2.44 (s, 6H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 156.9, 144.4, 139.9, 137.2, 133.0, 131.7, 129.1, 128.6, 122.8, 120.4, 112.8, 112.5, 71.8, 21.5, 19.1. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{24}\text{H}_{25}\text{NNaO}_5\text{S}_2$ 494.1066, found 494.1069.

N-Bs-2-(Methallyloxy)aniline (**1b**)

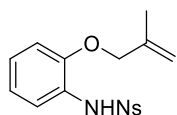


Following the Method A using BsCl instead of *p*-TsCl: 53.2 mg, 94%, a white solid (EtOAc : *n*-Hexane = 1:5), mp $75\text{--}77^\circ\text{C}$.

⁴ Wang, H.; Liu, S.; Sun, T.; Lv, Z.; Zhan, Z.; Yin, G.; Chen, Z. *Mol. Catal.* **2019**, 469, 10.

^1H NMR (CDCl_3 , 400 MHz) δ 7.74 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.58 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.01 (td, $J = 7.8, 1.6$ Hz, 1H), 7.01 (br s, 1H), 6.91 (td, $J = 7.7, 1.2$ Hz, 1H), 6.71 (dd, $J = 8.4, 1.2$ Hz, 1H), 4.93 (s, 1H), 4.84 (s, 1H), 4.22 (s, 2H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 148.7, 139.8, 139.2, 132.8, 128.7, 127.1, 125.8, 125.5, 121.7, 121.2, 113.3, 111.8, 72.2, 19.2. EIMS m/z 303 (M^+), 252, 219, 162, 77, 51.

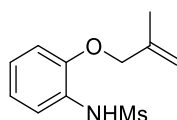
***N*-Ns-2-(Methallyloxy)aniline (1c)**



Following the Method A using NsCl instead of *p*-TsCl: 51.1 mg, 99%, a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 69-71 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 8.21 (dt, $J = 9.2, 2.2$ Hz, 2H), 7.89 (dt, $J = 9.2, 2.2$ Hz, 2H), 7.59 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.08 (ddd, $J = 8.4, 7.6, 1.6$ Hz, 1H), 7.02 (br s, 1H), 6.95 (td, $J = 7.6, 1.2$ Hz, 1H), 6.73 (dd, $J = 8.0, 1.2$ Hz, 1H), 4.93 (s, 1H), 4.79 (s, 1H), 4.22 (s, 2H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 150.1, 149.1, 144.8, 139.6, 128.5, 126.6, 124.6, 124.0, 122.7, 121.4, 113.4, 111.9, 72.1, 19.2. EIMS m/z 348 (M^+), 252, 235, 219, 162.

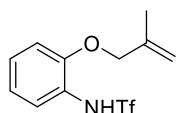
***N*-Ms-2-(Methallyloxy)aniline (1d)**



Following the Method A using MsCl instead of *p*-TsCl: 81.8 mg, 89%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 90-92 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.54 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.11 (td, $J = 8.0, 1.6$ Hz, 1H), 6.97 (td, $J = 7.8, 1.2$ Hz, 1H), 6.91 (dd, $J = 8.4, 1.2$ Hz, 1H), 6.79 (br s, 1H), 5.06 (s, 1H), 5.04 (s, 1H), 4.50 (s, 2H), 2.96 (s, 3H), 1.83 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 148.6, 139.9, 126.1, 125.5, 121.5, 121.1, 113.7, 112.0, 72.4, 39.1, 19.4. EIMS m/z 241 (M^+), 186, 162, 108, 80.

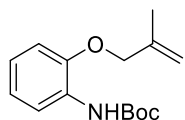
***N*-Tf-2-(Methallyloxy)aniline**



Following the Method A using TfCl instead of *p*-TsCl: 44.8 mg, 45%, a brown solid (EtOAc : *n*-Hexane = 1:5), mp 66-68 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.52 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.19 (td, $J = 8.0, 1.2$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.08 (s, 1H), 5.05 (d, $J = 0.8$ Hz, 1H), 4.52 (s, 2H), 1.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 149.4, 139.7, 127.2, 123.5, 122.1, 121.3, 119.8 (q, $J = 322$ Hz), 113.7, 112.1, 72.6, 19.2. EIMS m/z 295 (M^+), 252, 235, 162, 147, 120.

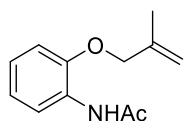
N-Boc-2-(Methallyloxy)aniline (**B** with R = H)



Following the Method A: 4.62 g, 98%, a pale yellow oil (EtOAc : *n*-Hexane = 1:20).

^1H NMR (CDCl_3 , 400 MHz) δ 8.11 (br s, 1H), 7.12 (br s, 1H), 6.98-6.91 (m, 2H), 6.86-6.83 (m, 1H), 5.08 (s, 1H), 5.03 (s, 1H), 4.49 (s, 2H), 1.85 (s, 3H), 1.55 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 152.8, 146.6, 140.5, 128.3, 122.2, 121.2, 118.2, 112.9, 111.4, 80.3, 72.3, 28.3, 19.4. EIMS m/z 263 (M^+), 252, 207, 163, 108, 80, 57.

N-Ac-2-(Methallyloxy)aniline

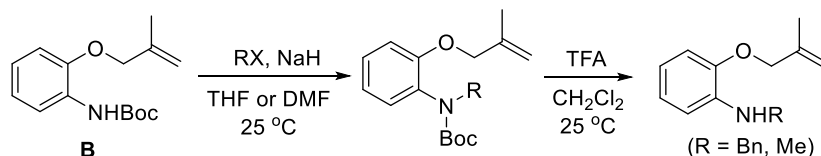


Following the Method A using AcCl instead of *p*-TsCl: 2.54 g, 95%, a white solid (EtOAc : *n*-Hexane = 1:3), mp 143-145 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 8.35 (dd, J = 8.0, 1.6 Hz, 1H), 7.79 (br s, 1H), 7.00 (td, J = 7.6, 1.6 Hz, 1H), 6.95 (td, J = 7.7, 2.0 Hz, 1H), 6.86 (dd, J = 7.8, 1.4 Hz, 1H), 5.08 (s, 1H), 5.03 (s, 1H), 4.50 (s, 2H), 2.20 (s, 3H), 1.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 168.0, 146.8, 140.3, 127.9, 123.5, 121.3, 119.9, 113.1, 111.4, 72.3, 24.9, 19.4. EIMS m/z 205 (M^+), 163, 108, 80.

Spectral data were consistent with data reported in the literature.^{1a}

N-Bn-2-(Methallyloxy)aniline

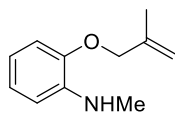


To a solution of NaH (25.1 mg, 0.627 mmol, 1.2 equiv) in DMF (1.3 mL, 0.4 M) was added **B** (137.6 mg, 0.523 mmol, 1.0 equiv) in DMF (1.3 mL, 0.4 M) at 0 °C. After 30 min, BnBr (68 μL , 0.575 mmol, 1.1 equiv) was added to the reaction mixture slowly. After being stirred at room temperature for 14 h, the reaction mixture was quenched with H_2O , extracted with EtOAc, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give *N*-Bn-**B** (184.4 mg, 99%) as a pale yellow solid.

Following removal of *N*-Boc group was performed as described above in Method A to give *N*-Bn-2-(methallyloxy)aniline (131.0 mg, 99%, EtOAc : *n*-Hexane = 1:8) as a yellow oil.

^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.33 (m, 4H), 7.29-7.25 (m, 1H), 6.83 (td, J = 7.6, 1.2 Hz, 1H), 6.79 (dd, J = 8.0, 1.2 Hz, 1H), 6.65 (td, J = 7.7, 1.6 Hz, 1H), 6.60 (dd, J = 7.8, 1.4 Hz, 1H), 5.09 (s, 1H), 4.99 (s, 1H), 4.72 (br s, 1H), 4.49 (s, 2H), 4.39 (s, 2H), 1.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 145.8, 141.0, 139.7, 138.3, 128.6, 127.3, 127.0, 121.5, 116.5, 112.6, 111.0, 110.3, 72.1, 48.0, 19.5. EIMS m/z 253 (M^+), 235, 217, 162, 117, 91.

***N*-Me-2-(Methallyloxy)aniline**

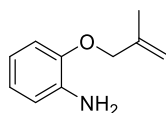


To a solution of **B** (218.5 mg, 0.830 mmol, 1.0 equiv) in THF (0.7 mL, 1.2 M) were added NaH (39.8 mg, 0.996 mmol, 1.2 equiv) and MeI (63 μ L, 0.996 mmol, 1.2 equiv) at 0 °C. After being stirred at room temperature for 14 h, the reaction mixture was quenched with H₂O, extracted with EtOAc, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:8) to give *N*-Me-**B** (227.7 mg, 99%) as a pale yellow solid.

Following removal of *N*-Boc group was performed as described above in Method A to give *N*-Me-2-(methallyloxy)aniline (138.5 mg, 95%, EtOAc : *n*-Hexane = 1:10) as a pale yellow oil.

¹H NMR (CDCl₃, 400 MHz) δ 6.95 (td, J = 7.6, 1.2 Hz, 1H), 6.81 (dd, J = 7.8, 1.0 Hz, 1H), 6.69 (td, J = 7.6, 1.6 Hz, 1H), 6.66 (dd, J = 7.4, 1.4 Hz, 1H), 5.14 (s, 1H), 5.04 (s, 1H), 4.49 (s, 2H), 4.31 (br s, 1H), 2.92 (s, 3H), 1.89 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 145.9, 141.0, 139.5, 121.5, 116.1, 112.5, 110.7, 109.4, 72.0 30.3, 19.5. EIMS m/z 177 (M⁺), 122, 94, 77, 65.

2-(Methallyloxy)aniline (C with R = H)

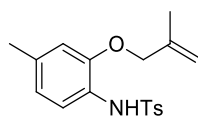


Following the Method A: 2.60 g, a pale yellow oil (EtOAc : *n*-Hexane = 1:10).

¹H NMR (CDCl₃, 400 MHz) δ 6.82-6.78 (m, 2H), 6.75-6.68 (m, 2H), 5.10 (s, 1H), 5.00 (s, 1H), 4.47 (s, 2H), 3.82 (br s, 2H), 1.85 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 146.3, 141.0, 136.4, 121.3, 118.4, 115.2, 112.5, 112.0, 72.0, 19.5. EIMS m/z 163 (M⁺), 108, 80, 53.

Spectral data were consistent with data reported in the literature.^{1a, 1c}

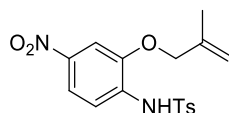
***N*-Ts-2-(Methallyloxy)-4-methylaniline (1e)**



Following the Method A: 1.01 g, a white solid (EtOAc : *n*-Hexane = 1:5), mp 94-96 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.60 (dd, J = 6.6, 1.8 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 7.6 Hz, 2H), 6.86 (br s, 1H), 6.71 (dd, J = 8.2, 0.6 Hz, 1H), 6.52 (d, J = 1.2 Hz, 1H), 4.92 (s, 1H), 4.83 (s, 1H), 4.19 (s, 2H), 2.34 (s, 3H), 2.25 (s, 3H), 1.67 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 148.8, 143.4, 140.0, 136.3, 135.6, 129.3, 127.2, 123.3, 121.9, 121.6, 113.0, 112.6, 72.1, 21.4, 21.3, 19.2. EIMS m/z 331 (M⁺), 252, 235, 176, 161, 91.

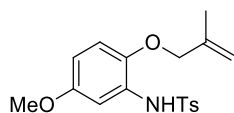
***N*-Ts-2-(Methallyloxy)-4-nitroaniline (1f)**



Following the Method A: 750.0 mg, a pale yellow solid (EtOAc : *n*-Hexane = 1:4), mp 108-110 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.82 (dd, J = 8.8, 2.4 Hz, 1H), 7.73 (dd, J = 6.6, 1.8 Hz, 2H), 7.64 (d, J = 6.4 Hz, 1H), 7.63 (s, 1H), 7.39 (br s, 1H), 7.26 (d, J = 8.0 Hz, 2H), 5.05 (s, 1H), 4.98 (s, 1H), 4.50 (s, 2H), 2.39 (s, 3H), 1.75 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 146.9, 144.7, 143.8, 138.6, 135.7, 132.6, 129.9, 127.2, 117.5, 117.4, 114.8, 107.2, 73.1, 21.6, 19.2. EIMS m/z 362 (M^+), 345, 252, 207, 190, 161, 149, 117, 91, 65.

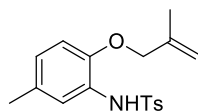
***N*-Ts-2-(Methallyloxy)-5-methoxyaniline (1g)**



Following the Method A: 693.1 mg, a white solid (EtOAc : *n*-Hexane = 1:5), mp 73-75 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.65 (d, J = 8.4 Hz, 2H), 7.183 (d, J = 8.0 Hz, 2H), 7.182 (d, J = 3.2 Hz, 1H), 7.03 (br s, 1H), 6.65 (d, J = 8.8 Hz, 1H), 6.51 (dd, J = 8.8, 2.8 Hz, 1H), 4.92 (s, 1H), 4.86 (s, 1H), 4.19 (s, 2H), 3.74 (s, 3H), 2.35 (s, 3H), 1.68 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 154.0, 143.7, 142.5, 140.2, 136.2, 129.4, 127.2, 126.9, 113.1, 112.9, 109.8, 107.0, 72.9, 55.7, 21.5, 19.2. EIMS m/z 347 (M^+), 252, 235, 219, 193, 176, 150, 91.

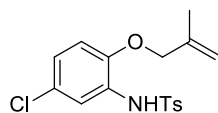
***N*-Ts-2-(Methallyloxy)-5-methylaniline (1h)**



Following the Method A: 287.0 mg, a pale yellow solid (EtOAc : *n*-Hexane = 1:5), mp 111-113 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.62 (d, J = 8.0 Hz, 2H), 7.39 (s, 1H), 7.17 (d, J = 7.6 Hz, 2H), 6.94 (br s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 4.91 (s, 1H), 4.83 (s, 1H), 4.20 (s, 2H), 2.35 (s, 3H), 2.26 (s, 3H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 146.5, 143.5, 140.1, 136.3, 130.8, 129.4, 127.2, 125.7, 125.6, 122.1, 113.0, 111.7, 72.3, 21.5, 20.8, 19.2. EIMS m/z 331 (M^+), 313, 252, 219, 176, 161, 131, 91.

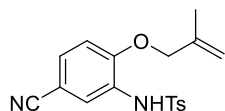
***N*-Ts-5-Chloro-2-(methallyloxy)aniline (1i)**



Following the Method A: 292.3 mg, a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 90-92 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 2.4 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.02 (br s, 1H), 6.94 (dd, J = 8.8, 2.8 Hz, 1H), 6.64 (d, J = 8.8 Hz, 1H), 4.94 (s, 1H), 4.84 (s, 1H), 4.27 (s, 2H), 2.37 (s, 3H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 146.8, 144.0, 139.5, 136.0, 129.6, 127.20, 127.17, 126.2, 124.6, 120.7, 113.6, 112.7, 72.6, 21.5, 19.1. EIMS m/z 351 (M^+), 252, 235, 196, 161, 91, 65.

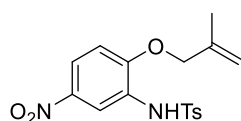
***N*-Ts-5-Cyano-2-(methallyloxy)aniline (1j)**



Following the Method B: 65.4 mg, a white solid (EtOAc : *n*-Hexane = 1:2), mp 124-126 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.80 (d, J = 2.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.28 (dd, J = 8.6, 1.8 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.18 (br s, 1H), 6.78 (d, J = 8.8 Hz, 1H), 4.97 (s, 1H), 4.84 (s, 1H), 4.39 (s, 2H), 2.36 (s, 3H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 151.4, 144.3, 138.6, 135.7, 129.7, 129.6, 127.1, 123.4, 118.5, 114.2, 112.2, 104.5, 72.6, 21.4, 19.0 (1 carbon is missing due to overlapping). EIMS m/z 342 (M^+), 252, 235, 187, 159, 131, 91, 65.

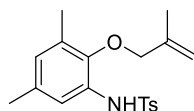
***N*-Ts-2-(Methallyloxy)-5-nitroaniline (1k)**



Following the Method A: 338.3 mg, a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 115-117 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 8.41 (d, J = 2.8 Hz, 1H), 7.90 (dd, J = 9.0, 2.6 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.19 (br s, 1H), 6.81 (d, J = 9.2 Hz, 1H), 5.01 (s, 1H), 4.89 (s, 1H), 4.47 (s, 2H), 2.37 (s, 3H), 1.71 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 152.6, 144.5, 141.6, 138.6, 135.7, 129.8, 127.3, 126.8, 120.7, 115.2, 114.6, 111.1, 73.1, 21.5, 19.1. EIMS m/z 362 (M^+), 252, 235, 207, 161, 91, 65.

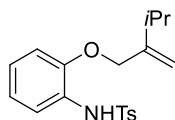
***N*-Ts-2-(Methallyloxy)-3,5-dimethylaniline (1l)**



Following the Method A: 128.5 mg, a yellow solid (EtOAc : *n*-Hexane = 1:3), mp 67-69 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.70 (d, J = 8.4 Hz, 2H), 7.26 (s, 1H), 7.23 (d, J = 8.0 Hz, 2H), 6.98 (br s, 1H), 6.67 (s, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 3.77 (s, 2H), 2.37 (s, 3H), 2.24 (s, 3H), 2.15 (s, 3H), 1.78 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 144.8, 143.8, 140.8, 136.5, 134.1, 130.6, 129.9, 129.6, 127.4, 127.1, 117.8, 112.4, 76.2, 21.5, 21.1, 19.4, 16.0. EIMS m/z 345 (M^+), 290, 252, 219, 190, 155, 148, 136, 91, 65.

***N*-Ts-2-(3-Methyl-2-methylenebutoxy)aniline (1m)**

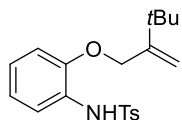


Following the Method C: 318.0 mg, a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 60-62 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.60 (d, J = 8.4 Hz, 2H), 7.58 (dd, J = 8.0, 1.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 2H), 7.07 (br s, 1H), 6.98 (td, J = 7.1, 1.4 Hz, 1H), 6.86 (t, J = 7.8 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 4.93 (s, 1H), 4.83 (s, 1H), 4.30 (s, 2H), 2.29 (s, 3H), 2.20 (septet, J = 6.9 Hz, 1H), 1.03 (d, J = 6.8 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 149.5, 148.6, 143.3, 136.0, 129.1, 126.9, 125.7, 125.2, 121.3, 120.8,

111.6, 110.0, 70.2, 30.5, 21.3, 21.2. EIMS m/z 345 (M^+), 275, 252, 235, 190, 173, 148, 134, 122, 91, 65.

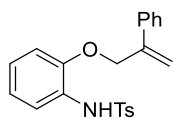
***N*-Ts-2-(3,3-Dimethyl-2-methylenebutoxy)aniline (1n)**



Following the Method C: 260.5 mg, a white solid (EtOAc : *n*-Hexane = 1:5), mp 61-63 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.62 (dd, J = 7.0, 1.8 Hz, 2H), 7.58 (dd, J = 8.0, 1.6 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.01 (td, J = 7.8, 1.6 Hz 1H), 7.00 (br s, 1H), 6.90 (td, J = 7.8, 1.2 Hz, 1H), 6.71 (dd, J = 8.0, 1.2 Hz, 1H), 5.02 (s, 1H), 4.79 (s, 1H), 4.37 (s, 2H), 2.34 (s, 3H), 1.10 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 151.2, 148.7, 143.5, 136.2, 129.3, 127.1, 126.0, 125.2, 121.2, 121.1, 111.7, 110.1, 68.9, 34.9, 29.2, 21.4. EIMS m/z 359 (M^+), 302, 252, 204, 148, 91, 57.

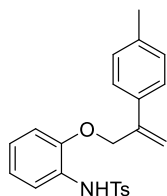
***N*-Ts-2-(2-Phenylallyloxy)aniline (1o)**



Following the Method B using 2-phenylallyl bromide⁵ instead of methallyl bromide: 554.0 mg, a white solid (EtOAc : *n*-Hexane = 1:5), mp 87-89 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (dd, J = 8.4, 1.6 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.39-7.37 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 7.02 (td, J = 7.8, 1.6 Hz, 1H), 6.92 (td, J = 7.8, 1.2 Hz, 1H), 6.88 (br s, 1H), 6.81 (dd, J = 8.0, 1.2 Hz, 1H), 5.53 (s, 1H), 5.17 (s, 1H), 4.72 (s, 2H), 2.34 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 148.4, 143.5, 142.4, 137.8, 136.2, 129.4, 128.6, 128.3, 127.2, 126.3, 125.9, 125.2, 121.5, 121.3, 115.1, 112.2, 70.5, 21.5. EIMS m/z 379 (M^+), 281, 252, 224, 207, 180, 165, 103, 91, 64.

***N*-Ts-2-(2-(*p*-Tolyl)allyloxy)aniline (1p)**

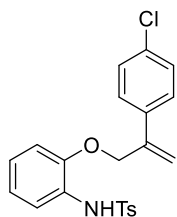


Following the Method C: 661.7 mg, a white solid (EtOAc : *n*-Hexane = 1:5), mp 94-96 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (dd, J = 8.0, 1.6 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.28 (dd, J = 6.6, 1.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.02 (td, J = 7.8, 1.6 Hz, 1H), 6.91 (td, J = 7.7, 1.6 Hz, 1H), 6.90 (br s, 1H), 6.81 (dd, J = 8.0, 1.2 Hz, 1H), 5.50 (s, 1H), 5.11 (s, 1H), 4.70 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 148.5, 143.5, 142.2, 138.2, 136.2, 134.9, 129.34, 129.32, 127.2, 126.3, 125.7, 125.2, 121.5, 121.3, 114.2, 112.2, 70.5, 21.5, 21.2. EIMS m/z 393 (M^+), 281, 252, 238, 207, 193, 165, 117, 105, 91, 65.

⁵ Budai, B.; Leclair, A.; Wang, Q.; Zhu, J. *Angew. Chem. Int. Ed.* **2019**, *58*, 10305.

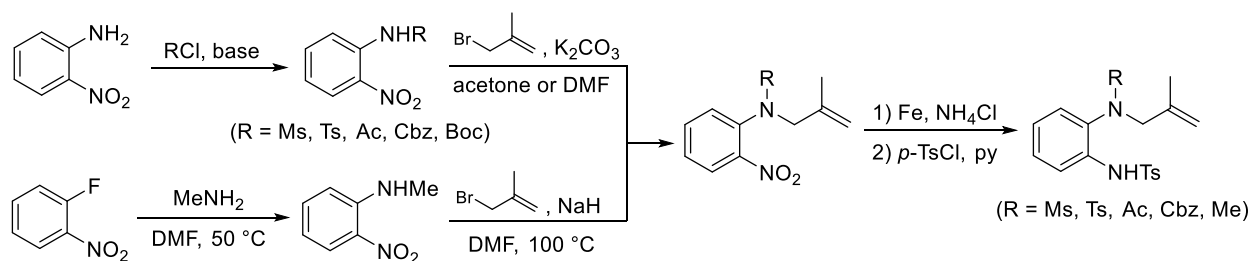
***N*-Ts-2-(2-(4-Chlorophenyl)allyloxy)aniline (1q)**



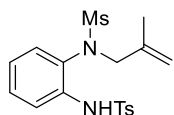
To a solution of NaH (193.2 mg, 4.830 mmol, 2.3 equiv) in THF (3.9 mL, 0.54 M) was added 2-(4-chlorophenyl)allyl alcohol^{2b} (424.9 mg, 2.520 mmol, 1.2 equiv) dropwise at 0 °C. After 15 min, 1-fluoro-2-nitrobenzene (224 µL, 2.100 mmol, 1.0 equiv) was added to the reaction mixture. After being stirred at room temperature for 6 h, the reaction mixture was quenched with sat. aq. NH₄Cl, extracted with EtOAc, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give the corresponding **D** (374.0 mg, 61%) as a yellow oil.

Following nitro reduction of **D** and *N*-tosylation were performed as described above in Method B to give **1q** (393.3 mg, 86%, EtOAc : *n*-Hexane = 1:5) as a white solid (mp 99-101 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.57 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 9.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.02 (td, *J* = 7.8, 1.6 Hz, 1H), 6.93 (br s, 1H), 6.92 (td, *J* = 7.8, 1.2 Hz, 1H), 6.81 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.54 (s, 1H), 5.22 (s, 1H), 4.69 (s, 2H), 2.34 (s, 3H).
¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 148.2, 143.6, 141.3, 136.14, 136.11, 134.0, 129.3, 128.7, 127.13, 127.06, 126.2, 125.1, 121.6, 121.1, 115.9, 112.0, 70.2, 21.4. EIMS *m/z* 413 (M⁺), 281, 252, 207, 91.



***N*¹-Ms-*N*²-Ts-*N*¹-Methallylbenzene-1,2-diamine (1r)**



To a solution of 2-nitroaniline (456.8 mg, 3.556 mmol, 1.0 equiv) in CH₂Cl₂ (8.9 mL, 0.4 M) were added Et₃N (1.5 mL, 10.668 mmol, 3.0 equiv) and MsCl (883 µL, 10.668 mmol, 3.0 equiv) at 0 °C. After being stirred at room temperature for 5 h, the reaction mixture was poured into 1 M HCl, extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:1) to give *N,N*-bisMs-2-nitroaniline (783.6 mg, 75%) as a yellow solid.

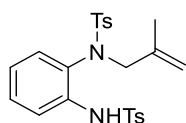
To a solution of *N,N*-bisMs-2-nitroaniline (783.6 mg, 2.663 mmol, 1.0 equiv) in THF (26.6 mL, 0.1 M) was added *n*Bu₄NF (TBAF, 1.0 M solution in THF, 0.5 mL, 2.929 mmol, 1.1 equiv) dropwise. Two further aliquots of TBAF solution were added every 1 h. After being stirred at room temperature for 4 h, the reaction mixture was extracted with EtOAc, washed with H₂O, dried over MgSO₄, and concentrated in vacuo. The

residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:1) to give *N*-Ms-2-nitroaniline (435.3 mg, 76%) as a yellow solid.

Following allylation, nitro reduction, and *N*-tosylation were performed as described above in Method B to give **1r** (214.4 mg, 51%, EtOAc : *n*-Hexane = 1:1) as a white solid (mp 87-89 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.79 (br s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.04 (td, *J* = 7.7, 1.2 Hz, 1H), 4.74 (s, 1H), 4.61 (s, 1H), 4.02 (br s, 2H), 2.90 (s, 3H), 2.37 (s, 3H), 1.77 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 144.0, 138.7, 137.1, 136.6, 129.6, 128.0, 127.9, 127.4, 123.8, 118.7, 116.9, 58.2, 36.3, 21.5, 20.3 (1 carbon is missing due to overlapping). EIMS *m/z* 394 (M⁺), 315, 252, 235, 207, 159, 119, 91, 65.

*N*¹,*N*²-BisTs-*N*¹-Methallylbenzene-1,2-diamine

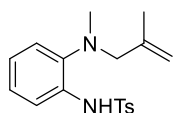


To a solution of 2-nitroaniline (278.8 mg, 1.877 mmol, 1.0 equiv) in CH₂Cl₂ (4.7 mL, 0.4 M) were added Et₃N (458 μL, 5.631 mmol, 3.0 equiv) and *p*-TsCl (1.10 g, 5.631 mmol, 3.0 equiv) at 0 °C. After being stirred at room temperature for 24 h, the reaction mixture was poured into 1 M HCl, extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give *N*-Ts-2-nitroaniline (449.3 mg, 82%) as a yellow solid.

Following allylation, nitro reduction, and *N*-tosylation were performed as described above in Method B to give *N*¹,*N*²-bisTs-*N*¹-Methallylbenzene-1,2-diamine (346.8 mg, 81%, EtOAc : *n*-Hexane = 1:3) as a yellow solid (mp 124-126 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.89 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.85 (br s, 1H), 7.46 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.43 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.13 (td, *J* = 7.9, 1.4 Hz, 1H), 6.77 (td, *J* = 7.8, 1.6 Hz, 1H), 6.30 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.66 (t, *J* = 1.4 Hz, 1H), 4.50 (s, 1H), 4.33 (d, *J* = 12.8 Hz, 1H), 3.58 (d, *J* = 12.4 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 1.76 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 144.4, 143.9, 138.6, 137.3, 136.9, 133.2, 129.59, 129.55, 129.2, 128.2, 127.9, 127.8, 127.5, 122.9, 117.9, 116.7, 58.6, 21.6, 21.5, 20.3. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₂₄H₂₆N₂NaO₄S₂ 493.1226, found 493.1229.

*N*²-Ts-*N*¹-Methallyl-*N*¹-methylbenzene-1,2-diamine⁶



To a solution of 1-fluoro-2-nitrobenzene (1.15 g, 8.18 mmol, 1.0 equiv) in DMF (8.2 mL, 1.0 M) was added MeNH₂ (33% in EtOH, 2.0 mL, 16.4 mmol, 2.0 equiv). After being stirred at 50 °C for 24 h, the reaction mixture was concentrated in vacuo to afford crude *N*-methyl-2-nitroaniline. To a solution of *N*-methyl-2-nitroaniline in DMF (8.2 mL, 1.0 M) was added NaH (359.9 mg, 9.00 mmol, 1.1 equiv) slowly at 0 °C. After 30 min, methallyl bromide (1.3 mL, 12.27 mmol, 1.5 equiv) was added dropwise. After being stirred

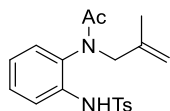
⁶ Hopkins, B. A.; Wolfe, J. P. *Chem. Sci.* **2014**, *5*, 4840.

at 100 °C for 12 h, the reaction mixture was cooled to room temperature and poured into sat. aq. NH₄Cl. The product was extracted with EtOAc, washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give *N*-methallyl-*N*-methyl-2-nitroaniline (800.1 mg, 55%) as a yellow oil.

Following nitro reduction and *N*-tosylation were performed as described above in Method B to give *N*²-Ts-*N*¹-methallyl-*N*¹-methylbenzene-1,2-diamine (186.0 mg, 88%, EtOAc : *n*-Hexane = 1:10) as a pale yellow oil.

¹H NMR (CDCl₃, 400 MHz) δ 8.04 (br s, 1H), 7.72 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.59 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.09-7.04 (m, 2H), 6.99 (td, *J* = 7.6, 1.6 Hz, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 3.09 (s, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 1.73 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 143.7, 142.4, 141.6, 136.6, 133.2, 129.5, 127.0, 125.5, 123.8, 122.0, 117.6, 113.4, 63.7, 41.7, 21.4, 20.5. EIMS *m/z* 330 (M⁺), 252, 175, 133, 119, 91.

*N*¹-Ac-*N*²-Ts-*N*¹-Methallylbenzene-1,2-diamine⁷



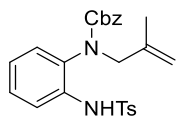
To a solution of 2-nitroaniline (201.2 mg, 1.355 mmol, 1.0 equiv), DMAP (2.0 mg), and Et₃N (38 μL, 0.271 mmol, 0.2 equiv) in CH₂Cl₂ (6.8 mL, 0.2 M) was added AcCl (0.2 mL, 2.709 mmol, 2.0 equiv) dropwise at room temperature. After being stirred at room temperature for 20 h, the reaction mixture was poured into sat. NaHCO₃, extracted in CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give *N*-Ac-2-nitroaniline (240.6 mg, 99%) as a yellow solid.

To a solution of *N*-Ac-2-nitroaniline (225.6 mg, 1.252 mmol, 1.0 equiv) in acetone (5.0 mL, 0.25 M) were added KOH (302.2 mg, 5.009 mmol, 4.0 equiv) and methallyl bromide (0.2 mL, 1.377 mmol, 1.1 equiv) dropwise. After being stirred at reflux for 3 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residue (318.7 mg, ~99%) was used in the next step without further purification. Following nitro reduction and *N*-tosylation were performed as described above in Method B to give *N*¹-Ac-*N*²-Ts-*N*¹-methallylbenzene-1,2-diamine (106.0 mg, 62%, EtOAc : *n*-Hexane = 1:1) as a pale yellow solid (mp 143-145 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.76 (br s, 1H), 7.74 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.30 (td, *J* = 7.8, 1.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.04 (td, *J* = 7.6, 1.2 Hz, 1H), 6.94 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.77 (s, 1H), 4.59 (d, *J* = 14.4 Hz, 1H), 4.40 (s, 1H), 3.08 (d, *J* = 14.4 Hz, 1H), 2.37 (s, 3H), 1.70 (s, 3H), 1.65 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 171.3, 143.9, 140.1, 137.0, 134.2, 131.6, 129.9, 129.6, 129.3, 127.0, 124.3, 120.3, 114.6, 53.3, 22.3, 21.3, 20.5. EIMS *m/z* 358 (M⁺), 252, 203, 161, 119, 91.

⁷ (a) Guan, Q. Sun, Q.; Wen, L.; Zha, Z.; Yang, Y.; Wang, Z. *Org. Biomol. Chem.* **2018**, *16*, 2088. (b) Beckwith, A. L. J.; Meijjs, G. F. J. *Org. Chem.* **1987**, *52*, 1922.

*N*¹-Cbz-*N*²-Ts-*N*¹-Methallylbenzene-1,2-diamine

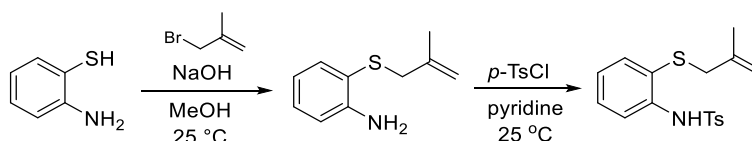


To a solution of 2-nitroaniline (200.8 mg, 1.352 mmol, 1.0 equiv) in THF (2.7 mL, 0.5 M) were added NaHCO₃ (229.4 mg, 2.704 mmol, 2.0 equiv) and benzyl chloroformate (0.2 mL, 1.622 mmol, 1.2 equiv) dropwise at 0 °C. After being stirred at room temperature for 48 h, the reaction mixture was poured into H₂O, extracted in EtOAc, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give *N*-Cbz-2-nitroaniline (178.5 mg, 48%) as a yellow solid.

Following allylation (in DMF instead of acetone), nitro reduction, and *N*-tosylation were performed as described above in Method B to give *N*¹-Cbz-*N*²-Ts-*N*¹-methallylbenzene-1,2-diamine (165.8 mg, 87%, EtOAc : *n*-Hexane = 1:5) as a pale yellow solid (mp 114-116 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 3H), 7.16-7.10 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.99-6.95 (m, 2H), 6.86 (br s, 1H), 5.03 (s, 2H), 4.74 (s, 1H), 4.52 (s, 1H), 2.24 (s, 3H), 1.58 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 155.5, 143.7, 140.7, 137.4, 136.1, 133.2, 129.6, 128.5, 128.24, 128.18, 127.8, 127.1, 125.5, 113.2, 67.9, 56.1, 21.3, 20.2 (3 carbons are missing due to overlapping). EIMS *m/z* 450 (M⁺), 342, 252, 187, 159, 119, 91.

N-Ts-2-(Methallylthio)aniline⁸



To a solution of NaOH (74.0 mg, 1.813 mmol, 1.0 equiv) in MeOH (9.1 mL, 0.2 M) was added 2-aminobenzenethiol (196 μ L, 1.813 mmol, 1.0 equiv) at 0 °C. After 15 min, methallyl bromide (195 μ L, 1.813 mmol, 1.0 equiv) was added. After being stirred at room temperature for 16 h, the reaction mixture was diluted with CH₂Cl₂, washed with H₂O, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give 2-(methallylthio)aniline (319.1 mg, 98%) as a yellow oil.

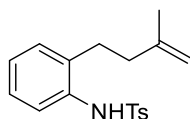
Following *N*-tosylation was performed as described above in Method B to give **1t** (464.9 mg, 78%, EtOAc : *n*-Hexane = 1:5) as a yellow solid (mp 51-53 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.84 (br s, 1H), 7.70 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.63 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.25 (td, *J* = 7.4, 1.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.98 (td, *J* = 7.6, 1.2 Hz, 1H), 4.66 (quintet, *J* = 1.5 Hz, 1H), 4.34 (q, *J* = 0.8 Hz, 1H), 3.05 (s, 2H), 2.36 (s, 3H), 1.79 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 144.0, 139.7, 138.7, 136.2, 136.0, 129.8, 129.6, 127.2, 124.3, 124.0,

⁸ (a) Erden, I.; Xu, F.-P.; Sadoun, A.; Smith, W.; Sheff, G.; Ossun, M. *J. Org. Chem.* **1995**, *60*, 813. (b) Morgans, G. L.; Yadav, D. B.; Fernandes, M. A.; de Koning, C. B.; Michael, J. P.; van Otterlo, W. A. L. *Tetrahedron Lett.* **2012**, *53*, 2384. (c) Morgans, G. L.; Ngidi, E. L.; Madeley, L. G.; Khanye, S. D.; Michael, J. P.; de Koning, C. B.; van Otterlo, W. A. L. *Tetrahedron* **2009**, *65*, 10650.

119.2, 114.9, 44.0, 21.5, 20.8. EIMS m/z 333 (M^+), 252, 199, 178, 144, 91.

N-Ts-2-(3-Methylbut-3-en-1-yl)aniline (1s)

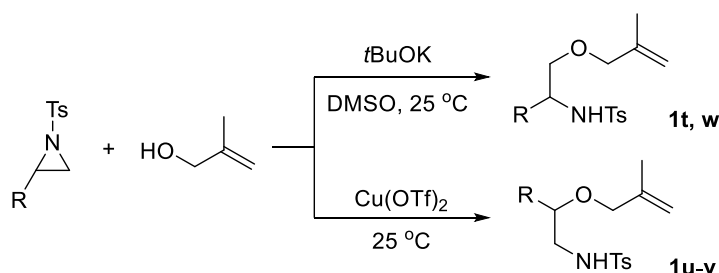


Prepared following the method reported by Douglas and co-workers.⁹

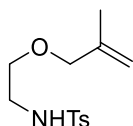
326.3 mg, 84% (EtOAc : *n*-Hexane = 1:5), a pale yellow solid (mp 89-91 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.64 (d, J = 8.0 Hz, 2H), 7.33-7.30 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.15-7.10 (m, 3H), 6.88 (br s, 1H), 4.72 (s, 1H), 4.59 (s, 1H), 2.51 (t, J = 7.8 Hz, 2H), 2.38 (s, 3H), 2.06 (t, J = 8.0 Hz, 2H), 1.68 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 144.7, 143.6, 136.6, 135.9, 133.8, 129.50, 129.49, 127.1, 126.7, 126.3, 125.0, 110.5, 37.6, 28.8, 22.5, 21.4. EIMS m/z 315 (M^+), 313, 252, 196, 180, 160, 144, 91, 65.

Spectral data were consistent with data reported in the literature.⁹



N-Ts-2-(Methallyloxy)ethanamine (1t)¹⁰



To a solution of *N*-Ts-aziridine¹¹ (343.9 mg, 1.743 mmol, 1.0 equiv) in DMSO (7.0 mL, 0.25 M) was added methallyl alcohol (0.2 mL, 2.092 mmol, 1.2 equiv). After 5 min, *t*-BuOK (308.9 mg, 2.615 mmol, 1.5 equiv) was added. After being stirred at room temperature for 5 h, the reaction mixture was quenched by H₂O, extracted with Et₂O, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **1t** (212.5 mg, 45%) as a pale yellow oil.

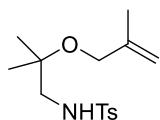
¹H NMR (CDCl₃, 400 MHz) δ 7.73 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.98 (br s, 1H), 4.86-4.85 (m, 2H), 3.77 (s, 2H), 3.40 (td, J = 5.2, 0.8 Hz, 2H), 3.11 (q, J = 5.7 Hz, 2H), 2.40 (s, 3H), 1.66 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 143.3, 141.5, 136.8, 129.6, 127.0, 112.5, 74.9, 67.9, 42.9, 21.4, 19.3. HRMS (EI) [$M+Na$]⁺ m/z calcd for C₁₃H₁₉NNaO₃S 292.0978, found 292.0980.

⁹ Pan, Z.; Pound, S. M.; Rondla, N. R.; Douglas, C. J. *Angew. Chem. Int. Ed.* **2014**, 53, 5170.

¹⁰ Wang, L.; Liu, Q.-B.; Wang, D.-S.; Li, X.; Han, X.-W.; Xiao, W.-J.; Zhou, Y.-G. *Org. Lett.* **2009**, 11, 1119.

¹¹ Bieber, L. W.; de Araújo, M. C. F. *Molecules* **2002**, 7, 902.

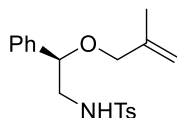
***N*-Ts-2-(Methallyloxy)-2-methylpropanamine (**1u**)**¹²



To a solution of *N*-Ts-2,2-Me₂-aziridine¹¹ (202.5 mg, 0.899 mmol, 1.0 equiv) in methallyl alcohol (8.9 mL, 0.1 M) was added Cu(OTf)₂ (331.7 mg, 0.899 mmol, 1.0 equiv). After being stirred at room temperature for 1 h, the reaction mixture was poured into sat. aq. NaHCO₃, extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:7) to give **1u** (230.0 mg, 86%) as a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.88 (s, 1H), 4.81 (s, 1H), 4.73 (br s, 1H), 3.64 (s, 2H), 2.88 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.67 (s, 3H), 1.18 (s, 6H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 143.2, 142.5, 136.7, 129.6, 127.0, 111.1, 74.0, 65.4, 51.7, 22.9, 21.4, 19.6. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₅H₂₃NNaO₃S 320.1291, found 320.1289.

(*R*)-*N*-Ts-2-(Methallyloxy)-2-phenylethylamine (1v**)**

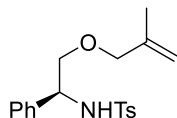


Prepared from (*S*)-*N*-Ts-2-phenylaziridine¹³ following the method for **1u**.

213.3 mg, 76% (EtOAc : *n*-Hexane = 1:5), 91:9 er (82% ee), a white solid (mp 51-53 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.72 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.35-7.28 (m, 5H), 7.21 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.92 (br d, *J* = 3.2 Hz, 1H), 4.87 (s, 2H), 4.36 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.76 (d, *J* = 12.4 Hz, 1H), 3.60 (d, *J* = 12.0 Hz, 1H), 3.22 (ddd, *J* = 13.0, 9.2, 4.0 Hz, 1H), 3.03 (ddd, *J* = 13.0, 9.2, 3.6 Hz, 1H), 2.42 (s, 3H), 1.70 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 143.4, 141.5, 138.5, 137.0, 129.7, 128.7, 128.4, 127.1, 126.7, 112.6, 79.5, 72.5, 49.3, 21.5, 19.7. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₉H₂₃NNaO₃S 368.1291, found 368.1291. HPLC analysis (Daicel Chiralcel OJ-H column, *n*-Hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm): *t*_{minor} = 15.0 min, *t*_{major} = 18.1 min.

(*S*)-*N*-Ts-2-(Methallyloxy)-1-phenylethylamine (1w**)**



Prepared from (*S*)-*N*-Ts-2-phenylaziridine¹³ following the method for **1t**.

85.2 mg, 57% (EtOAc : *n*-Hexane = 1:5), 96:4 er (92% ee), a white solid (mp 58-60 °C).

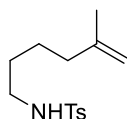
¹H NMR (CDCl₃, 400 MHz) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.20-7.14 (m, 7H), 5.43 (br s, 1H), 4.84 (s, 1H), 4.82 (s, 1H), 4.46 (q, *J* = 5.6 Hz, 1H), 3.76 (s, 2H), 3.51-3.44 (m, 2H), 2.37 (s, 3H), 1.61 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 143.0, 141.3, 138.0, 137.2, 129.3, 128.2, 127.6, 127.2, 127.1, 112.5, 74.8, 72.6, 57.3, 21.4, 19.2. EIMS *m/z* 345 (M⁺), 302, 260, 155, 91. HPLC analysis (Daicel Chiralcel OD-H column,

¹² Ghorai, M. K.; Das, K.; Shukla, D. *J. Org. Chem.* **2007**, 72, 5859.

¹³ Li, K.; Weber, A. E.; Tseng, L.; Malcolmson, S. *J. Org. Lett.* **2017**, 19, 4239.

n-Hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} = 14.4 min, t_{minor} = 17.2 min.

N-Ts-5-Methylhex-5-en-1-amine (1x)



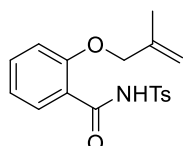
Prepared following the method reported by Xu and co-workers.¹⁴

104.2 mg, 85% (EtOAc : *n*-Hexane = 1:5), a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.75 (dd, J = 6.8, 1.6 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 4.66 (t, J = 0.6 Hz, 1H), 4.66 (br s, 1H), 4.58 (t, J = 0.6 Hz, 1H), 2.93 (q, J = 6.5 Hz, 2H), 2.42 (s, 3H), 1.93 (t, J = 7.0 Hz, 2H), 1.64 (s, 3H), 1.48-1.34 (m, 4H). ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 145.1, 143.3, 136.9, 129.7, 127.1, 110.2, 43.0, 37.0, 29.1, 24.3, 22.2, 21.5. EIMS m/z 267 (M⁺), 226, 198, 155, 91, 55.

Spectral data were consistent with data reported in the literature.¹⁴

N-Ts-2-(Methallyloxy)benzamide (1y)

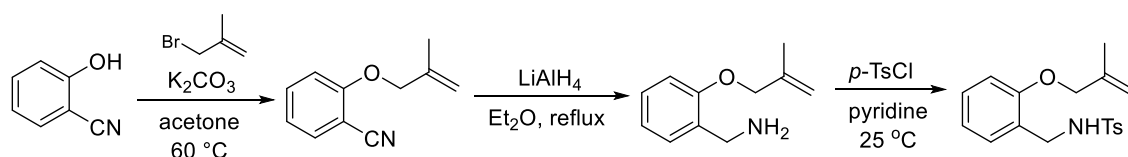


Prepared following the method reported by Porcel and co-workers.¹⁵

287.1 mg, a white solid (EtOAc : *n*-Hexane = 1:3), mp 66-68 °C.

¹H NMR (CDCl₃, 400 MHz) δ 10.50 (br s, 1H), 8.07 (dd, J = 7.8, 1.8 Hz, 1H), 8.02 (dd, J = 6.6, 1.8 Hz, 2H), 7.48 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.04 (td, J = 7.6, 0.8 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 5.18 (s, 2H), 4.64 (s, 2H), 2.42 (s, 3H), 1.95 (s, 3H). ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 162.2, 157.0, 144.7, 138.7, 136.0, 134.9, 132.6, 129.4, 128.6, 121.8, 119.0, 115.4, 112.8, 73.5, 21.6, 19.5. EIMS m/z 345 (M⁺), 281, 252, 207, 91, 73.

N-Ts-(2-Methallyloxy)benzylamine (1z)



Alkylation was performed as described above in Method B using 2-hydroxybenzonitrile to give 2-(methallyloxy)benzonitrile (132.8 mg, 87%, EtOAc : *n*-Hexane = 1:5) as a colorless oil.

To a solution of 2-(methallyloxy)benzonitrile (132.8 mg, 0.767 mmol, 1.0 equiv) in Et₂O (0.7 mL, 1.0 M) was added LiAlH₄ (45.9 mg, 1.150 mmol, 1.5 equiv) portion wise at 0 °C. After being stirred at reflux for 2.5 h, the resulting mixture was cooled and quenched with H₂O at 0 °C. 15% aq. NaOH was added to the reaction mixture, extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue (129.1

¹⁴ Zhou, Y.; Xu, X.; Sun, H.; Tao, G.; Chang, X. -Y.; Xing, X.; Chen, B.; Xu, C. *Nature Commun.* **2021**, *12*, 1953.

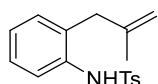
¹⁵ Carrillo-Arcos, U. A.; Rojas-Ocampo, J.; Porcel, S. *Dalton Trans.* **2016**, *45*, 479.

mg, ~95%) was used in the next step without further purification.

Following *N*-tosylation was performed as described above in Method B to give **1z** (137.1 mg, 57%, EtOAc : *n*-Hexane = 1:5) as a pale yellow oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.16 (td, *J* = 8.0, 1.2 Hz, 1H), 7.10 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.14 (br s, 1H), 4.98 (s, 1H), 4.95 (s, 1H), 4.34 (s, 2H), 4.16 (d, *J* = 6.4 Hz, 2H), 2.38 (s, 3H), 1.75 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 156.2, 143.0, 140.2, 137.0, 129.8, 129.3, 129.0, 127.0, 124.4, 120.6, 112.7, 111.3, 71.4, 43.8, 21.4, 19.3. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₈H₂₁NNaO₃S 354.1134, found 354.1133.

N-Ts-2-Methallylaniline (**1aa**)



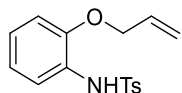
Prepared following the method reported by Xu and co-workers.¹⁴

113.2 mg, 97% (EtOAc : *n*-Hexane = 1:10), a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.20 (td, *J* = 7.8, 1.6 Hz, 1H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 7.03 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.71 (br s, 1H), 4.88 (s, 1H), 4.61 (s, 1H), 2.93 (s, 2H), 2.38 (s, 3H), 1.57 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 143.7, 143.6, 136.9, 135.5, 131.2, 130.9, 129.6, 127.7, 127.0, 125.9, 124.0, 112.9, 40.9, 22.1, 21.5. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₇H₁₉NNaO₂S 324.1029, found 324.1029.

Spectral data were consistent with data reported in the literature.^{9, 14}

N-Ts-2-Allyloxyaniline

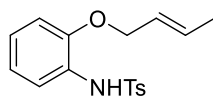


Following the Method B using allyl bromide instead of methallyl bromide: 207.6 mg, a white solid (EtOAc : *n*-Hexane = 1:5), mp 101-103 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.62 (dt, *J* = 8.6, 1.9 Hz, 2H), 7.55 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.01 (td, *J* = 8.0, 1.6 Hz, 1H), 7.00 (br s, 1H), 6.90 (td, *J* = 7.6, 1.2 Hz, 1H), 6.71 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.88-5.78 (m, 1H), 5.25-5.17 (m, 2H), 4.34 (dt, *J* = 5.6, 1.4 Hz, 2H), 2.35 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 148.5, 143.6, 136.3, 132.4, 129.3, 127.2, 126.1, 125.3, 121.6, 121.3, 118.2, 111.8, 69.3, 21.5. EIMS *m/z* 303 (M⁺), 252, 235, 148, 120, 91.

Spectral data were consistent with data reported in the literature.¹⁶

N-Ts-2-(But-2-en-1-yloxy)aniline



¹⁶ Foschi, F.; Loro, C.; Sala, R.; Oble, J.; Presti, L.L.; Beccalli, E. M.; Poli, G.; Broggini, G. *Org. Lett.* **2020**, 22, 1402.

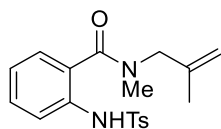
Prepared following the method reported by Stahl and co-workers.¹⁷

223.7 mg (*E:Z* = 5:1), a white solid (EtOAc : *n*-Hexane = 1:5), mp 102-104 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.03 (br s, 1H), 7.00 (td, *J* = 7.8, 1.6 Hz, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.71 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.71-5.64 (m, 1H), 5.52-5.41 (m, 1H), 4.25 (dt, *J* = 6.2, 1.1 Hz, 2H), 2.352 (s, 3H), 1.74 (dq, *J* = 6.4, 1.2 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 148.6, 143.5, 136.29, 131.1, 129.3, 127.24, 126.13, 125.3, 125.19, 121.26, 120.99, 111.7, 69.2, 21.5, 17.8. Representative signals corresponding to (*Z*)-isomer: ¹H NMR (CDCl₃, 400 MHz) δ 7.54 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.89 (td, *J* = 7.8, 1.4 Hz, 1H), 6.73 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.40 (d, *J* = 6.4 Hz, 2H), 2.345 (s, 3H), 1.66 (dq, *J* = 6.8, 0.8 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 136.27, 129.1, 127.22, 126.16, 125.22, 124.7, 121.32, 121.07, 111.6, 64.2, 13.3. EIMS *m/z* 317 (*M*⁺), 252, 235, 162, 117, 91.

Spectral data were consistent with data reported in the literature.¹⁷

N-Methyl-*N*-methallyl-2-tosylaminobenzamide

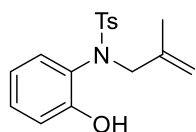


Prepared following the method reported by Broggini and co-workers.¹⁸

510.9 mg, a white solid (EtOAc : *n*-Hexane = 1:1), mp 61-63 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.42 (br s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.34 (td, *J* = 7.8, 1.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 4.98 (s, 1H), 4.83 (s, 1H), 3.93 (br s, 1H), 3.34 (br s, 1H), 2.77 (br s, 3H), 2.37 (s, 3H), 1.64 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 170.0, 143.5, 140.0, 137.4, 136.2, 130.9, 129.5, 127.3, 127.0, 126.2, 123.8, 123.4, 112.4, 57.1, 53.1, 21.4, 19.9. EIMS *m/z* 358 (*M*⁺), 315, 274, 252, 203, 155, 120, 91, 65.

N-Ts-*N*-Methallyl-2-aminophenol (3a)



Prepared following the method reported by Saikia and co-workers.¹⁹

308.9 mg, a white solid (EtOAc : *n*-Hexane = 1:5), mp 88-90 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.16 (td, *J* = 7.8, 1.6 Hz, 1H), 7.03 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.76 (s, 1H), 6.68 (td, *J* = 7.7, 1.2 Hz, 1H), 6.33 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.74 (s, 1H), 4.68 (s, 1H), 4.08 (br s, 2H), 2.44 (s, 3H), 1.77 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 154.6, 144.3, 139.1, 133.2, 129.6, 129.5, 128.0, 127.1, 125.8, 120.4, 118.0, 115.7, 57.9, 21.6, 19.9. EIMS

¹⁷ Zhan, L.; Stahl, S. S. *Org. Lett.* **2012**, *14*, 1234.

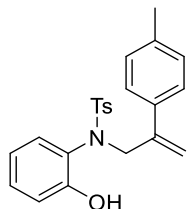
¹⁸ (a) Beccalli, E. M.; Broggini, G.; Paladino, G.; Penoni, A.; Zoni, C. *J. Org. Chem.* **2004**, *69*, 5627. (b) Borelli, T.; Brenna, S.; Broggini, G.; Obler, J.; Poli, G. *Adv. Synth. Catal.* **2017**, *359*, 623.

¹⁹ Deka, M. J.; Indukuri, K.; Sultana, S.; Borah, M.; Saikia, A. K. *J. Org. Chem.* **2015**, *80*, 4349.

m/z 317 (M^+), 252, 235, 162, 134, 91.

The chemical structure was assigned based on spectral correlation with its Ph-substituted (instead of methyl-substituted alkene) congener.¹⁹

N-Ts-*N*-(2-(*p*-Tolyl)allyl)-2-aminophenol (**3p**)



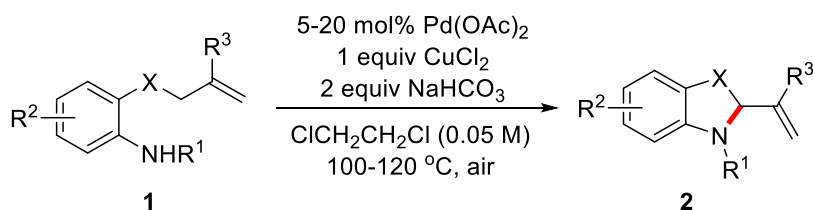
Prepared following the method reported by Saikia and co-workers.¹⁹

167.6 mg, a pale yellow solid (EtOAc : *n*-Hexane = 1:3), mp 152-154 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.13 (td, $J = 7.7$, 1.4 Hz, 1H), 6.87 (dd, $J = 8.2$, 1.4 Hz, 1H), 6.65 (td, $J = 7.7$, 1.2 Hz, 1H), 6.33 (dd, $J = 8.0$, 1.6 Hz, 1H), 5.67 (s, 1H), 5.23 (s, 1H), 4.87 (s, 1H), 2.46 (s, 3H), 2.37 (s, 3H) (OH and 1H of allylic protons are missing due to broadening). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 155.1, 144.3, 141.6, 138.2, 134.5, 133.5, 129.8, 129.6, 129.4, 128.3, 127.2, 126.4, 124.7, 119.9, 117.0, 116.8, 55.5, 21.6, 21.2. EIMS m/z 393 (M^+), 281, 252, 238, 207, 120, 91.

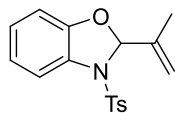
The chemical structure was assigned based on spectral correlation with its Ph-substituted (instead of *p*-tolyl-substituted alkene) congener.¹⁹

General Procedure for the Pd-Catalyzed Intramolecular Allylic C-H Amination of **1**



Substrate **1** (0.0630~1.001 mmol, 1 equiv), $\text{Pd}(\text{OAc})_2$ (5~20 mol%), CuCl_2 (0.0630~1.001 mmol, 1.0 equiv), and NaHCO_3 (0.126~2.003 mmol, 2.0 equiv) were dissolved in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1.3~20.0 ml, 0.05 M). The resulting mixture was stirred at 100~120 °C for the reported time under aerobic conditions (in a closed vial with a screw cap). After the reaction was completed, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product **2**. All reactions were carried out 2-3 times repetitively and the average values of yields are given. In most reactions, the corresponding **2'** was not formed, while some cases gave at most $\leq 5\%$ ^1H NMR yields of **2'** as a byproduct.

***N*-Ts-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2a)**



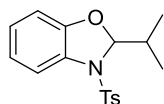
15.5 mg, 78%, using 5 mol% Pd(OAc)₂ at 100 °C for 12 h.

221.7 mg, 70%, using 1.0 mmol of **1a** and 10 mol% Pd(OAc)₂ at 100 °C for 24 h.

a white solid (EtOAc : *n*-Hexane = 1:5), mp 156-158 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.56 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.01 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (td, *J* = 7.6, 0.8 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.16 (s, 1H), 5.28 (s, 1H), 5.03 (s, 1H), 2.36 (s, 3H), 1.79 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 151.7, 144.7, 140.2, 132.9, 129.6, 128.9, 127.5, 126.6, 121.5, 117.9, 115.4, 109.3, 96.7, 21.5, 16.5. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₇H₁₇NNaO₃S 338.0821, found 338.0822.

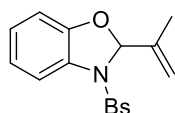
***N*-Ts-2-Isopropyl-2,3-dihydrobenzo[*d*]oxazole (2a')**



a white solid (EtOAc : *n*-Hexane = 1:5), mp 140-142 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.00 (td, *J* = 7.7, 1.2 Hz, 1H), 6.90 (td, *J* = 7.7, 1.2 Hz, 1H), 6.61 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.61 (d, *J* = 6.0 Hz, 1H), 2.34 (s, 3H), 2.01 (octet, *J* = 6.8 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 152.2, 144.5, 132.9, 129.6, 129.4, 127.5, 126.7, 121.2, 118.2, 109.2, 100.3, 34.1, 21.6, 17.1, 16.1. HRMS (EI) [M+H]⁺ *m/z* calcd for C₁₇H₂₀NO₃S 318.1158, found 318.1168.

***N*-Bs-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2b)**

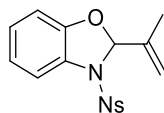


12.0 mg, 57%, using 5 mol% Pd(OAc)₂ at 100 °C for 12 h under Ar.

a pale yellow solid (EtOAc : *n*-Hexane = 1:5), mp 95-97 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.57 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.01 (td, *J* = 7.7, 0.8 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.18 (s, 1H), 5.29 (s, 1H), 5.04 (s, 1H), 1.79 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 151.7, 140.2, 135.9, 133.7, 129.0, 128.8, 127.5, 126.8, 121.6, 118.0, 115.5, 109.4, 96.8, 16.6. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₆H₁₅NNaO₃S 324.0665, found 324.0667.

***N*-Ns-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2c)**

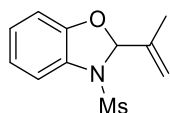


11.2 mg, 43%, using 5 mol% Pd(OAc)₂ at 100 °C for 12 h under Ar.

a yellow solid (EtOAc : *n*-Hexane = 1:6), mp 128-130 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 8.22 (dd, $J = 7.2, 1.6$ Hz, 2H), 7.78 (dd, $J = 7.2, 1.6$ Hz, 2H), 7.57 (dt, $J = 8.0, 0.6$ Hz, 1H), 7.07 (td, $J = 7.8, 0.8$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 1H), 6.69 (d, $J = 7.6$ Hz, 1H), 6.18 (s, 1H), 5.29 (s, 1H), 5.07 (s, 1H), 1.79 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 151.7, 141.5, 139.5, 128.8, 127.9, 127.6, 124.2, 121.9, 118.1, 115.9, 109.9, 96.7, 16.6 (1 carbon is missing due to overlapping). HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{NaO}_5\text{S}$ 369.0516, found 369.0518.

***N*-Ms-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2d)**

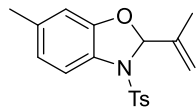


9.7 mg, 41%, using 5 mol% $\text{Pd}(\text{OAc})_2$ at 100 °C for 12 h under Ar.

a white solid (EtOAc : *n*-Hexane = 1:5), mp 75-77 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.39 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.11 (td, $J = 7.8, 1.2$ Hz, 1H), 6.95 (td, $J = 7.8, 0.8$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.28 (s, 1H), 5.30 (d, $J = 0.8$ Hz, 1H), 5.05 (s, 1H), 2.79 (s, 3H), 1.79 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 151.5, 140.1, 128.8, 126.9, 122.0, 117.4, 115.7, 109.8, 97.0, 35.3, 16.4. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{11}\text{H}_{13}\text{NNaO}_3\text{S}$ 262.0508, found 262.0509.

***N*-Ts-6-Methyl-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2e)**

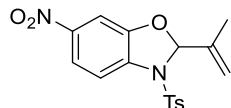


20.6 mg, 50% (Obtained as an inseparable mixture with a trace amount of **2e'**), using 10 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 24 h.

a yellow solid (EtOAc : *n*-Hexane = 1:8), mp 121-123 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.47 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.73 (dd, $J = 8.0, 0.8$ Hz, 1H), 6.48 (s, 1H), 6.13 (s, 1H), 5.27 (d, $J = 0.8$ Hz, 1H), 5.02 (d, $J = 0.4$ Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H), 1.78 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 151.9, 144.6, 140.3, 137.1, 133.0, 129.6, 127.6, 126.4, 122.0, 117.6, 115.2, 110.1, 96.8, 21.6, 21.4, 16.7. Representative signals corresponding to **2e'**: ^1H NMR (CDCl_3 , 400 MHz) δ 5.57 (d, $J = 6.0$ Hz, 1H), 1.02 (d, $J = 6.8$ Hz, 3H), 0.96 (d, $J = 6.8$ Hz, 3H). HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{18}\text{H}_{19}\text{NNaO}_3\text{S}$ 352.0978, found 352.0981.

***N*-Ts-6-Nitro-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2f)**



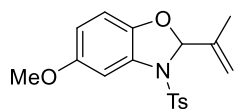
22.1 mg, 54%, using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 8 h.

a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 76-78 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.90 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.61 (d, $J = 8.8$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 2.0$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 6.29 (s, 1H), 5.34 (d, $J = 0.8$ Hz, 1H), 5.14 (s, 1H), 2.40 (s, 3H), 1.76 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 151.7, 145.8, 145.7, 139.5, 135.4, 132.9,

130.2, 127.4, 118.5, 117.3, 115.3, 104.9, 99.1, 21.6, 15.9. HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{17}H_{16}N_2NaO_5S$ 383.0672, found 383.0674.

***N*-Ts-5-Methoxy-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2g)**

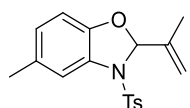


18.1 mg, 49% (Obtained as an inseparable mixture with a trace amount of **2g'**), using 20 mol% $Pd(OAc)_2$ at 120 °C for 6 h.

a yellow solid (EtOAc : *n*-Hexane = 1:8), mp 151-153 °C.

1H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, J = 8.4 Hz, 2H), 7.191 (d, J = 8.4 Hz, 2H), 7.186 (s, 1H), 6.57-6.52 (m, 2H), 6.13 (s, 1H), 5.27 (d, J = 0.8 Hz, 1H), 5.03 (s, 1H), 3.80 (s, 3H), 2.37 (s, 3H), 1.79 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 154.8, 145.8, 144.8, 140.4, 133.1, 129.7, 129.6, 127.5, 115.4, 111.5, 109.2, 104.6, 97.3, 56.1, 21.6, 16.6. Representative signals corresponding to **2g'**: 1H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, J = 8.4 Hz, 2H), 5.58 (d, J = 6.0 Hz, 1H), 2.35 (s, 3H), 1.03 (d, J = 7.2 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H). HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{18}H_{19}NNaO_4S$ 368.0927, found 368.0923.

***N*-Ts-5-Methyl-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2h)**

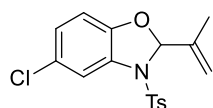


25.3 mg, 56% (Obtained as an inseparable mixture with a trace amount of **2h'**), using 20 mol% $Pd(OAc)_2$ at 120 °C for 8 h.

a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 108-110 °C.

1H NMR ($CDCl_3$, 400 MHz) δ 7.48 (dd, J = 8.4, 1.6 Hz, 2H), 7.39 (d, J = 1.2 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 6.80 (dt, J = 8.2, 0.9 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.12 (s, 1H), 5.27 (d, J = 0.8 Hz, 1H), 5.02 (s, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 1.78 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 149.7, 144.6, 140.4, 133.1, 131.2, 129.6, 128.8, 127.5, 126.9, 118.5, 115.3, 108.8, 96.8, 21.6, 21.1, 16.6. Representative signals corresponding to **2h'**: 1H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 8.0 Hz, 1H), 5.57 (d, J = 6.0 Hz, 1H), 1.02 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H). HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{18}H_{19}NNaO_3S$ 352.0978, found 352.0980.

***N*-Ts-5-Chloro-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2i)**



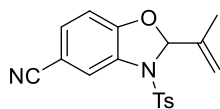
24.9 mg, 87% (Obtained as an inseparable mixture with a trace amount of **2i'**), using 20 mol% $Pd(OAc)_2$ at 120 °C for 8 h.

a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 116-118 °C.

1H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.96 (dd, J = 8.4, 2.0 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 6.16 (s, 1H), 5.28 (d, J = 0.8 Hz, 1H), 5.06 (s, 1H),

2.38 (s, 3H), 1.77 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 150.4, 145.1, 140.0, 132.9, 130.3, 129.9, 127.5, 126.3, 126.2, 117.9, 116.0, 109.9, 97.8, 21.6, 16.4. Representative signals corresponding to **2i'**: ^1H NMR (CDCl_3 , 400 MHz) δ 5.64 (d, J = 5.6 Hz, 1H), 1.02 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H). HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{17}\text{H}_{16}\text{ClNNaO}_3\text{S}$ 372.0432, found 372.0432.

***N*-Ts-5-Cyano-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2j)**

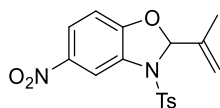


26.9 mg, 66%, using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 10 h.

a pale yellow solid (EtOAc : *n*-Hexane = 1:5), mp 188-190 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.78 (d, J = 1.6 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.34 (dd, J = 8.0, 1.6 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.25 (s, 1H), 5.30 (d, J = 0.8 Hz, 1H), 5.10 (s, 1H), 2.39 (s, 3H), 1.76 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 154.9, 145.5, 139.4, 132.6, 131.8, 130.4, 130.0, 127.5, 120.2, 118.6, 116.8, 110.1, 105.1, 98.4, 21.6, 16.2. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{NaO}_3\text{S}$ 363.0774, found 363.0775.

***N*-Ts-5-Nitro-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2k)**

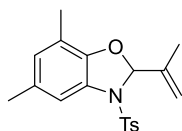


17.5 mg, 61%, using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 18 h.

a yellow solid (EtOAc : *n*-Hexane = 1:3), mp 139-141 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 8.37 (d, J = 2.4 Hz, 1H), 8.00 (dd, J = 8.8, 2.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.8 Hz, 1H), 6.33 (s, 1H), 5.33 (d, J = 0.8 Hz, 1H), 5.13 (s, 1H), 2.39 (s, 3H), 1.77 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 156.4, 145.6, 142.7, 139.4, 132.7, 130.5, 130.1, 127.5, 123.6, 117.1, 112.8, 108.7, 99.4, 21.6, 16.2. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{NaO}_5\text{S}$ 383.0672, found 383.0675.

***N*-Ts-5,7-Dimethyl-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[d]oxazole (2l)**



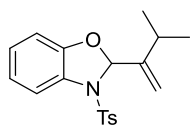
26.9 mg, 74% (Obtained as an inseparable mixture with a trace amount of **2l'**), using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 6 h.

a pale yellow solid (EtOAc : *n*-Hexane = 1:6), mp 132-134 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.50 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 0.4 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 6.12 (s, 1H), 5.26 (s, 1H), 5.01 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.01 (s, 3H), 1.78 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 148.0, 144.5, 140.5, 133.3, 130.9, 129.6, 128.5, 128.1, 127.5, 119.0, 115.8, 115.0, 96.6, 21.5, 21.0, 16.6, 14.5. Representative signals corresponding to **2l'**: ^1H NMR (CDCl_3 , 400 MHz) δ 7.44 (d, J = 8.4 Hz, 2H), 5.57 (d, J = 6.0 Hz, 1H), 2.34 (s, 3H), 1.98 (s, 3H), 1.03 (d, J = 6.8

Hz, 3H), 0.95 (d, $J = 6.8$ Hz, 3H). HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{19}H_{21}NNaO_3S$ 366.1134, found 366.1132.

***N*-Ts-2-(3-Methylbut-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2m)**

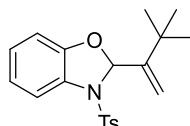


15.6 mg, 53%, using 20 mol% $Pd(OAc)_2$ at 120 °C for 10 h.

a pale yellow solid (EtOAc : *n*-Hexane = 1:8), mp 105-107 °C.

1H NMR ($CDCl_3$, 400 MHz) δ 7.56 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.45 (dd, $J = 8.4, 1.6$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.02 (td, $J = 7.8, 1.2$ Hz, 1H), 6.93 (td, $J = 7.7, 1.2$ Hz, 1H), 6.64 (dd, $J = 7.6, 0.8$ Hz, 1H), 6.28 (s, 1H), 5.34 (d, $J = 0.4$ Hz, 1H), 5.07 (s, 1H), 2.56 (septet, $J = 6.8$ Hz, 1H), 2.35 (s, 3H), 1.13 (d, $J = 6.8$ Hz, 3H), 1.10 (d, $J = 6.8$ Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 151.8, 150.3, 144.7, 133.0, 129.6, 128.9, 127.6, 126.9, 121.5, 118.5, 112.0, 109.5, 95.7, 28.1, 22.4, 21.6. HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{19}H_{21}NNaO_3S$ 366.1134, found 366.1132.

***N*-Ts-2-(3,3-Dimethylbut-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2n)**

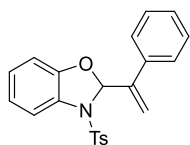


28.4 mg, 76%, using 20 mol% $Pd(OAc)_2$ at 120 °C for 4 h.

a pale yellow solid (EtOAc : *n*-Hexane = 1:8), mp 109-111 °C.

1H NMR ($CDCl_3$, 400 MHz) δ 7.58 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.00 (td, $J = 7.8, 1.2$ Hz, 1H), 6.92 (td, $J = 7.7, 1.2$ Hz, 1H), 6.61 (dd, $J = 8.0, 0.8$ Hz, 1H), 6.44 (s, 1H), 5.54 (d, $J = 0.4$ Hz, 1H), 5.23 (s, 1H), 2.36 (s, 3H), 1.20 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 151.6, 150.7, 144.6, 133.2, 129.7, 129.5, 127.5, 126.6, 121.3, 117.7, 113.7, 109.7, 94.2, 34.7, 29.8, 21.6. HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{20}H_{23}NNaO_3S$ 380.1291, found 380.1292.

***N*-Ts-2-(1-Phenylvinyl)-2,3-dihydrobenzo[*d*]oxazole (2o)**



21.1 mg, 67%, using 20 mol% $Pd(OAc)_2$ at 120 °C for 6 h.

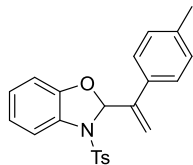
a yellow solid (EtOAc : *n*-Hexane = 1:2), mp 123-125 °C.

Recrystallization from EtOAc was undertaken for X-ray analysis.

1H NMR ($CDCl_3$, 400 MHz) δ 7.58 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.45 (dd, $J = 7.8, 1.8$ Hz, 2H), 7.36-7.30 (m, 3H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.00 (td, $J = 7.7, 1.2$ Hz, 1H), 6.93 (td, $J = 7.6, 1.2$ Hz, 1H), 6.70 (s, 1H), 6.61 (dd, $J = 7.6, 0.8$ Hz, 1H), 5.76 (s, 1H), 5.56 (s, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 151.1, 144.8, 143.4, 137.1, 133.0, 129.7, 129.2, 128.3, 128.1, 127.6, 127.3, 126.8, 121.6, 118.0, 117.9, 109.8, 95.1, 21.6. HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{22}H_{19}NNaO_3S$ 400.0978,

found 400.0977.

***N*-Ts-2-(1-(*p*-Tolyl)vinyl)-2,3-dihydrobenzo[*d*]oxazole (2p)**

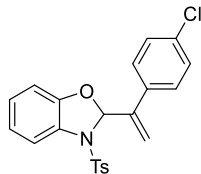


26.0 mg, 72%, using 20 mol% Pd(OAc)₂ at 120 °C for 6 h.

a pale yellow solid (EtOAc : *n*-Hexane = 1:3), mp 132-134 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.58 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.00 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (td, *J* = 7.6, 1.2 Hz, 1H), 6.68 (s, 1H), 6.61 (dd, *J* = 7.6, 0.8 Hz, 1H), 5.71 (s, 1H), 5.53 (s, 1H), 2.36 (s, 3H), 2.34 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 151.1, 144.8, 143.2, 137.9, 134.2, 133.0, 129.7, 129.2, 129.0, 127.6, 127.1, 126.8, 121.5, 118.0, 117.2, 109.8, 95.1, 21.6, 21.1. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₂₃H₂₁NNaO₃S 414.1134, found 414.1138.

***N*-Ts-2-(1-(4-Chlorophenyl)vinyl)-2,3-dihydrobenzo[*d*]oxazole (2q)**

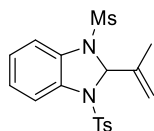


28.2 mg, 73%, using 20 mol% Pd(OAc)₂ at 120 °C for 8 h.

a pale yellow solid (EtOAc : *n*-Hexane = 1:4), mp 94-96 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.57 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.49 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.37 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.29 (dt, *J* = 8.8, 2.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.00 (td, *J* = 7.8, 1.6 Hz, 1H), 6.93 (td, *J* = 7.8, 1.2 Hz, 1H), 6.63 (s, 1H), 6.61 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.76 (s, 1H), 5.53 (s, 1H), 2.36 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 151.0, 144.9, 142.6, 135.5, 134.0, 132.9, 129.7, 129.0, 128.7, 128.4, 127.5, 126.9, 121.7, 118.6, 118.0, 109.8, 95.0, 21.6. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₂₂H₁₈ClNNaO₃S 434.0588, found 434.0591.

***N*-Ts-*N'*-Ms-2-(Prop-1-en-2-yl)-2,3-dihydro-1*H*-benzo[*d*]imidazole (2r)**



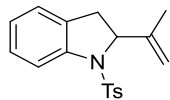
19.1 mg, 50% (Obtained as an inseparable mixture with ~10% of **2r'**), using 20 mol% Pd(OAc)₂ at 120 °C for 4 h.

a yellow solid (EtOAc : *n*-Hexane = 1:3), mp 141-143 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.66-7.58 (m, 3H), 7.26-7.22 (m, 3H), 7.15 (td *J* = 7.6, 1.6 Hz, 1H), 7.11 (td, *J* = 7.6, 1.6 Hz, 1H), 6.04 (s, 1H), 5.24 (d *J* = 0.4 Hz, 1H), 4.99 (s, 1H), 2.36 (s, 3H), 2.11 (s, 3H), 1.71 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 145.3, 140.7, 133.9, 133.1, 132.7, 130.1, 127.7, 126.2, 125.6,

117.8, 115.8, 115.5, 81.6, 36.0, 21.6, 16.5. Representative signals corresponding to **2r'**: ^1H NMR (CDCl_3 , 400 MHz) δ 5.54 (d, $J = 4.0$ Hz, 1H), 2.34 (s, 3H), 1.83 (s, 3H), 0.94 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.8$ Hz, 3H). HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}_2$ 415.0757, found 415.0758.

***N*-Ts-2-(Prop-1-en-2-yl)indoline (2s)**



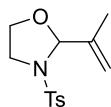
23.7 mg, 71%, using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 5 h.

a yellow solid (EtOAc : *n*-Hexane = 1:8), mp 74-76 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.67 (d, $J = 8.4$ Hz, 1H), 7.60 (dd, $J = 8.4, 1.6$ Hz, 2H), 7.20 (tt, $J = 8.0, 0.8$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.03 (dd, $J = 7.2, 0.8$ Hz, 1H), 6.99 (td, $J = 7.2, 0.8$ Hz, 1H), 5.07 (s, 1H), 4.86 (t, $J = 1.4$ Hz, 1H), 4.66 (dd, $J = 10.2, 3.8$ Hz, 1H), 2.98 (dd, $J = 16.2, 10.2$ Hz, 1H), 2.69 (dd, $J = 16.2, 3.8$ Hz, 1H), 2.36 (s, 3H), 1.70 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 144.4, 143.8, 142.0, 135.1, 131.4, 129.5, 127.8, 127.1, 124.8, 124.3, 116.4, 112.2, 66.8, 34.3, 21.5, 17.7. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{18}\text{H}_{19}\text{NNaO}_2\text{S}$ 336.1029, found 336.1031.

Spectral data were consistent with data reported in the literature.²⁰

***N*-Ts-2-(prop-1-en-2-yl)oxazolidine (2t)**

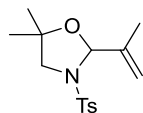


15.5 mg, 54% (Obtained as an inseparable mixture with ~10% of **2t'**), using 10 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 2 h.

a colorless oil (EtOAc : *n*-Hexane = 1:5).

^1H NMR (CDCl_3 , 400 MHz) δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 5.49 (s, 1H), 5.21 (s, 1H), 5.03 (dd, $J = 2.4, 1.6$ Hz, 1H), 3.85-3.79 (m, 1H), 3.61-3.55 (m, 1H), 3.43-3.35 (m, 2H), 2.44 (s, 3H), 1.76 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 144.1, 141.4, 134.7, 129.9, 127.8, 114.8, 92.6, 65.2, 46.2, 21.6, 17.3. Representative signals corresponding to **2v'**: ^1H NMR (CDCl_3 , 400 MHz) δ 4.92 (d, $J = 5.6$ Hz, 1H), 1.01 (d, $J = 6.8$ Hz, 3H), 0.95 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 127.8, 95.8, 46.8, 33.0, 18.2, 16.3. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{13}\text{H}_{17}\text{NNaO}_3\text{S}$ 290.0821, found 290.0823.

***N*-Ts-5,5-Dimethyl-2-(prop-1-en-2-yl)oxazolidine (2u)**



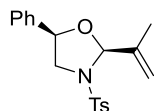
19.1 mg, 52%, using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 3 h.

a pale yellow solid (EtOAc : *n*-Hexane = 1:5), mp 68-70 °C.

²⁰ (a) Rogers, M. M.; Wendlandt, J. E.; Guzei, I. A.; Stahl, S. S. *Org. Lett.* **2006**, 8, 2257. (b) Aebly, A. H.; Rainey, T. J. *Tetrahedron Lett.* **2017**, 58, 3795.

^1H NMR (CDCl_3 , 400 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.28 (s, 1H), 5.21 (s, 1H), 5.06 (t, J = 1.4 Hz, 1H), 3.48 (d, J = 10.0 Hz, 1H), 3.20 (d, J = 10.4 Hz, 1H), 2.43 (s, 3H), 1.65 (s, 3H), 1.32 (s, 3H), 0.92 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 143.8, 142.3, 135.6, 129.6, 127.5, 116.8, 92.7, 79.9, 57.7, 26.2, 24.6, 21.5, 15.5. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{15}\text{H}_{21}\text{NNaO}_3\text{S}$ 318.1134, found 318.1136.

(2*S*,5*R*)-*N*-Ts-5-Phenyl-2-(prop-1-en-2-yl)oxazolidine (2v)

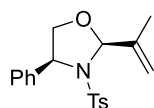


17.1 mg, 66% (dr = *cis* : *trans* = 1.5:1, obtained as an inseparable mixture with a trace amount of **2v'**), using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 4 h.

a colorless oil (EtOAc : *n*-Hexane = 1:5).

^1H NMR (CDCl_3 , 400 MHz) δ 7.81 (dd, J = 8.0, 1.6 Hz, 2H, *cis*), 7.72 (d, J = 8.4 Hz, 2H, *trans*), 7.38 (d, J = 8.0 Hz, 2H, *cis*), 7.33-7.30 (m, each 3H, *cis* & *trans*), 7.24-7.16 (m, each 2H, *cis* & *trans*), 6.82 (dd, J = 8.8, 2.0 Hz, 2H, *trans*), 5.74 (s, 1H, *trans*), 5.57 (s, 1H, *cis*), 5.39 (d, J = 0.8 Hz, 1H, *trans*), 5.30 (s, 1H, *cis*), 5.14 (q, J = 1.3 Hz, 1H, *trans*), 5.10 (t, J = 1.4 Hz, 1H, *cis*), 5.02 (t, J = 7.4 Hz, 1H, *trans*), 4.33 (dd, J = 10.0, 5.6 Hz, 1H, *cis*), 4.04 (dd, J = 12.0, 5.6 Hz, 1H, *cis*), 3.83 (dd, J = 10.4, 6.8 Hz, 1H, *trans*), 3.25-3.19 (m, each 1H, *cis* & *trans*), 2.47 (s, each 3H, *cis* & *trans*), 1.85 (s, 3H, *trans*), 1.83 (s, 3H, *cis*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 144.3, 144.1, 142.0, 141.2, 137.9, 136.7, 135.4, 133.8, 130.0, 129.9, 128.59, 128.56, 128.4, 128.2, 128.1, 127.7, 126.2, 125.8, 116.3, 115.1, 93.7, 93.0, 79.0, 77.8, 53.9, 53.6, 21.59, 21.55, 18.0, 16.6. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}_3\text{S}$ 366.1134, found 366.1137.

(2*S*,4*S*)-*N*-Ts-4-Phenyl-2-(prop-1-en-2-yl)oxazolidine (2w)

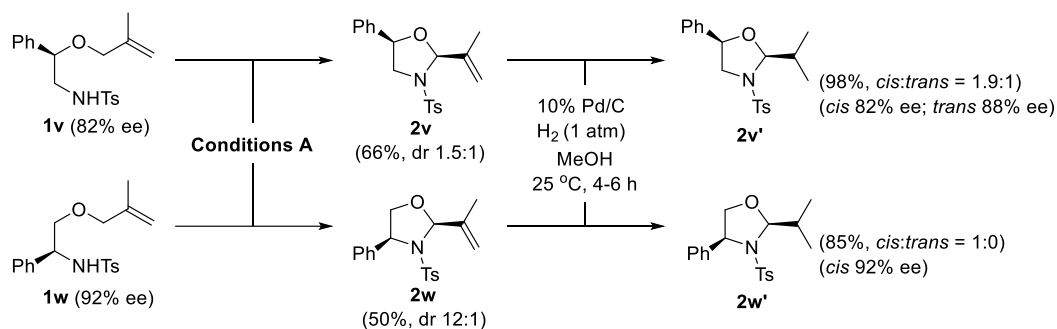


11.5 mg, 50% (dr = *cis* : *trans* = 12:1, obtained as an inseparable mixture with a trace amount of **2w'**), using 20 mol% $\text{Pd}(\text{OAc})_2$ at 120 °C for 3 h.

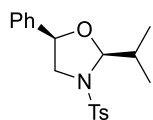
a colorless oil (EtOAc : *n*-Hexane = 1:5).

^1H NMR (CDCl_3 , 400 MHz) δ 7.68 (dd, J = 8.4, 1.8 Hz, 2H), 7.40-7.28 (m, 7H), 5.58 (s, 1H), 5.34 (d, J = 0.4 Hz, 1H), 5.12 (q, J = 1.3 Hz, 1H), 4.77 (t, J = 6.8 Hz, 1H), 4.04 (dd, J = 8.8, 7.2 Hz, 1H), 3.94 (dd, J = 8.8, 6.4 Hz, 1H), 2.43 (s, 3H), 1.80 (s, 3H). Representative signals corresponding to *trans* isomer: ^1H NMR (CDCl_3 , 400 MHz) δ 7.73 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 5.50 (s, 1H), 5.31 (s, 1H), 5.19 (t, J = 1.4 Hz, 1H), 5.01 (dd, J = 6.0, 1.6 Hz, 1H), 4.44-4.39 (m, 1H), 2.32 (s, 3H), 1.85 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 144.1, 141.3, 138.8, 134.3, 129.7, 128.5, 128.1, 127.9, 127.2, 116.2, 94.1, 72.5, 62.7, 21.6, 17.9. Representative signals corresponding to **2w'**: ^1H NMR (CDCl_3 , 400 MHz) δ 1.14 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H). HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}_3\text{S}$ 366.1134, found 366.1135.

Stereochemistry of **2v** and **2w** was determined after their hydrogenation to give **2v'** and **2w'**, respectively. Spectral data of both *cis*- and *trans*-**2v'** have been reported in the literature.²¹ Therefore, we could confirm the relative stereochemistry by comparison of our own data with those in the literature. The relative stereochemistry of **2w'** was determined by ¹H NMR and NOESY experiments, confirming the major diastereomer to be *cis*. Chiral HPLC analysis indicated the retention of enantiomeric purities of **1v** (82% ee) and **1w** (92% ee) during their conversion to **2v/2v'** and **2w/2w'**, respectively.



(2*S*,5*R*)-*N*-Ts-2-Isopropyl-5-phenyloxazolidine (**2v'**)

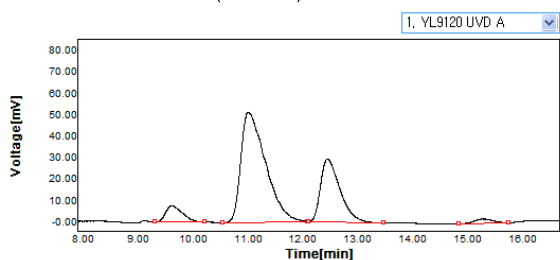
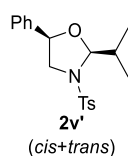


A solution of **2v** (17.1 mg, 0.0498 mmol, 1.0 equiv) and 10 % Pd/C (1.7 mg, 10 wt % of **2v**) in MeOH (0.8 mL, 0.06 M) was stirred at room temperature under H₂ (balloon) for 6 h. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **2v'** (16.9 mg, 98%, *cis* : *trans* = 1.9:1) as a colorless oil.

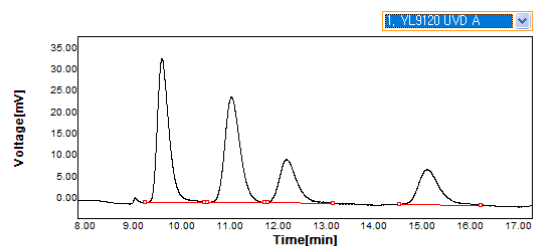
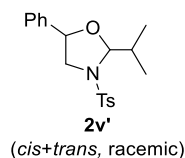
¹H NMR (CDCl₃, 400 MHz) δ 7.83 (d, *J* = 8.4 Hz, 2H, *cis*), 7.67 (d, *J* = 8.4 Hz, 2H, *trans*), 7.39 (d, *J* = 8.0 Hz, 2H, *cis*), 7.34-7.25 (m, 3H of *cis* & 2H of *trans*), 7.27-7.25 (m, 2H of *cis* & 1H of *trans*), 7.12 (td, *J* = 7.2, 1.4 Hz, 2H, *trans*), 6.71 (d, *J* = 7.2 Hz, 2H, *trans*), 5.14 (d, *J* = 7.2 Hz, 1H, *trans*), 5.12 (d, *J* = 4.8 Hz, 1H, *cis*), 5.08 (d, *J* = 7.2 Hz, 1H, *trans*), 4.07 (dd, *J* = 10.2, 5.4 Hz, 1H, *cis*), 3.95 (dd, *J* = 12.2, 5.4 Hz, 1H, *cis*), 3.85 (dd, *J* = 10.8, 7.2 Hz, 1H, *trans*), 3.24 (dd, *J* = 10.8, 7.2 Hz, 1H, *trans*), 3.10 (dd, *J* = 12.2, 10.2 Hz, 1H, *cis*), 2.47 (s, 3H, *cis*), 2.45 (s, 3H, *trans*), 2.16-2.07 (m, each 1H, *cis* & *trans*), 1.12 (d, *J* = 6.8 Hz, 3H, *trans*), 1.0845 (d, *J* = 6.8 Hz, 3H, *cis*), 1.082 (d, *J* = 6.8 Hz, 3H, *cis*), 1.03 (d, *J* = 6.8 Hz, 3H, *trans*).
¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 144.3, 143.9, 138.8, 137.2, 135.2, 133.8, 130.0, 129.8, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 125.9, 125.5, 97.1, 95.7, 78.3, 78.0, 54.1, 53.7, 34.0, 32.5, 21.6, 21.5, 18.5, 18.2, 17.0, 16.0. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₉H₂₃NNaO₃S 368.1291, found 368.1294.

Spectral data of both *cis*- and *trans*-**2v'** were consistent with data reported in the literature.²¹ *cis* (82% ee, 91:9 er), *trans* (88% ee, 94:6 er). HPLC analysis (Daicel Chiralcel OJ-H column, *n*-Hexane/*i*-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 254 nm): *t*_{minor} (*cis*) = 9.6 min, *t*_{major} (*cis*) = 11.0 min, *t*_{major} (*trans*) = 12.4 min, *t*_{minor} (*trans*) = 15.3 min.

²¹ Aldmairi, A. H.; Knight, D. W.; Wirth, T. *Synlett* **2017**, 28, 2976.

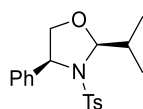


#	Name	RT[min]	Area[mV*sec]	Area%
1		9.5917	162,5554	6.4
2		10.9850	1607,8998	63.2
3		12.4333	724,2745	28.5
4		15.2667	49,4410	1.9
Sum			2544,1707	



#	Name	RT[min]	Area[mV*sec]	Area%
1		9.5733	565,5387	35.0
2		11.0183	540,0538	33.5
3		12.1717	257,2557	15.9
4		15.0800	251,0973	15.6
Sum			1613,9455	

(2*S*,4*S*)-*N*-Ts-2-Isopropyl-4-phenyloxazolidine (**2w'**)

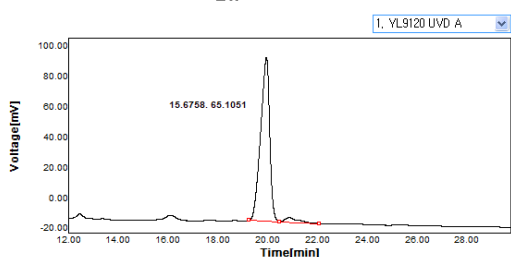
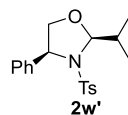


A solution of **2w** (18.7 mg, 0.0544 mmol, 1.0 equiv) and 10 % Pd/C (1.9 mg, 10 wt % of **2w**) in MeOH (0.9 mL, 0.06 M) was stirred at room temperature under H₂ (balloon) for 4 h. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **2w'** (16.0 mg, 85%, *cis* : *trans* = 1:0) as a colorless oil.

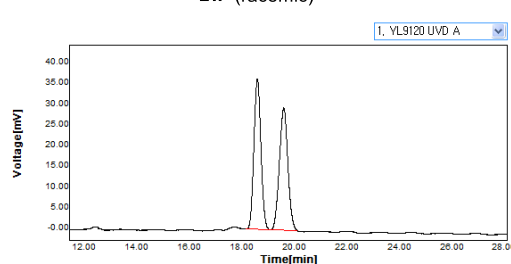
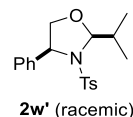
¹H NMR (CDCl₃, 400 MHz) δ 7.73 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.39-7.27 (m, 7H), 4.99 (d, *J* = 7.6 Hz, 1H), 4.78 (t, *J* = 6.8 Hz, 1H), 3.96 (dd, *J* = 8.8, 7.6 Hz, 1H), 3.87 (dd, *J* = 8.8, 6.0 Hz, 1H), 2.44 (s, 3H), 1.94 (octet, *J* = 6.8 Hz, 1H), 1.14 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 144.1, 139.4, 134.3, 129.8, 128.5, 128.1, 127.7, 126.4, 97.8, 71.6, 61.9, 31.8, 21.6, 18.6, 17.3. HRMS (EI) [M+Na]⁺ *m/z* calcd for C₁₉H₂₃NNaO₃S 368.1291, found 368.1296.

The relative stereochemistry was determined by ¹H NMR and NOESY experiments, confirming the major diastereomer to be *cis*.

Only *cis* (92% ee, 96:4 er). HPLC analysis (Daicel Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm): *t*_{major} = 19.9 min, *t*_{minor} = 20.8 min.

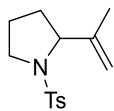


#	Name	RT[min]	Area[mV*sec]	Area%
1		19.9200	2733,3539	96.1
2		20.8267	110,1701	3.9
Sum			2843,5240	



#	Name	RT[min]	Area[mV*sec]	Area%
1		18.5733	676,2237	50.3
2		19.5783	668,3509	49.7
Sum			1344,5746	

***N*-Ts-2-(Prop-1-en-2-yl)pyrrolidine (2x)**



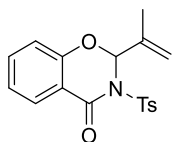
7.6 mg, 42%, using 20 mol% Pd(OAc)₂ at 120 °C for 10 h.

a colorless oil (EtOAc : *n*-Hexane = 1:5).

¹H NMR (CDCl₃, 400 MHz) δ 7.72 (dd, J = 8.4, 1.8 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.00 (d, J = 0.8 Hz, 1H), 4.86 (d, J = 1.2 Hz, 1H), 4.04 (t, J = 6.2 Hz, 1H), 3.49-3.43 (m, 1H), 3.31-3.25 (m, 1H), 2.43 (s, 3H), 1.85-1.76 (m, 1H), 1.73 (s, 3H), 1.72-1.66 (m, 2H), 1.59-1.52 (m, 1H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 145.0, 143.2, 135.0, 129.5, 127.5, 111.7, 64.9, 49.2, 31.4, 24.0, 21.5, 18.6. EIMS m/z 265 (M⁺), 224, 155, 110, 91, 65.

Spectral data were consistent with data reported in the literature.²²

***N*-Ts-2-(Prop-1-en-2-yl)-2,3-dihydro-4*H*-benzo[*e*][1,3]oxazin-4-one (2y)**

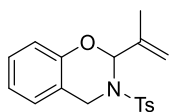


10.0 mg, 41%, using 10 mol% Pd(OAc)₂ at 120 °C for 20 h.

a white solid (EtOAc : *n*-Hexane = 1:5), mp 116-118 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.00 (dd, J = 8.4, 1.6 Hz, 2H), 7.81 (dd, J = 7.8, 1.4 Hz, 1H), 7.47 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.50 (td, J = 7.6, 1.2 Hz, 1H), 6.96 (dd, J = 8.2, 0.6 Hz, 1H), 6.73 (d, J = 0.8 Hz, 1H), 5.13 (t, J = 1.4 Hz, 1H), 5.09 (t, J = 0.8 Hz, 1H), 2.42 (s, 3H), 1.79 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 159.5, 155.1, 145.3, 139.7, 135.8, 135.2, 129.5, 129.2, 128.4, 123.0, 118.3, 118.1, 117.3, 87.1, 21.7, 19.2. HRMS (EI) [M+Na]⁺ m/z calcd for C₁₈H₁₇NNaO₄S 366.0770, found 366.0772.

***N*-Ts-2-(Prop-1-en-2-yl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine (2z)**



13.8 mg, 50% (Obtained as an inseparable mixture with ~10% **2z'**), using 10 mol% Pd(OAc)₂ at 120 °C for 14 h.

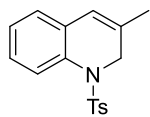
a white solid (EtOAc : *n*-Hexane = 1:10), mp 72-74 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.60 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.93 (td, J = 7.6, 2.0 Hz, 1H), 6.77-6.70 (m, 2H), 6.48 (d, J = 8.4 Hz, 1H), 6.23 (s, 1H), 5.06 (d, J = 1.2 Hz, 1H), 5.04 (d, J = 0.8 Hz, 1H), 4.58 (d, J = 17.2 Hz, 1H), 4.32 (d, J = 17.6 Hz, 1H), 2.25 (s, 3H), 1.82 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 150.9, 143.6, 139.1, 135.7, 129.0, 128.0, 127.6, 126.0, 120.7, 117.4, 116.3, 115.5, 84.1, 40.8, 21.3, 18.0. Representative signals corresponding to **2z'**: ¹H NMR (CDCl₃, 400 MHz) δ 7.62 (d, J = 8.4 Hz, 2H), 5.37 (d, J = 9.6 Hz, 1H), 4.66 (d, J = 18.0 Hz, 1H), 4.43 (d, J = 18.0 Hz, 1H), 2.10-2.01 (m, 1H), 1.05 (d, J = 6.0 Hz, 3H), 1.03 (d, J = 6.4 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 88.2, 29.6, 18.7, 17.7.

²² Xu, H.-C.; Moeller, K. D. *J. Am. Chem. Soc.* **2008**, *130*, 13542.

HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{18}H_{19}NNaO_3S$ 352.0978, found 352.0971.

***N*-Ts-3-Methyl-1,2-dihydroquinoline (2aa)**



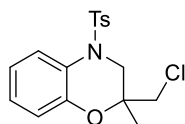
10.4 mg, 43%, using 10 mol% $Pd(OAc)_2$ at 120 °C for 8 h.

a white solid (EtOAc : *n*-Hexane = 1:5), mp 132-134 °C.

1H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.22 (td, J = 7.6, 1.6 Hz, 1H), 7.15 (td, J = 7.5, 1.2 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 6.86 (dd, J = 7.6, 1.6 Hz, 1H), 5.72 (s, 1H), 4.26 (s, 2H), 2.34 (s, 3H), 1.66 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 143.4, 135.9, 133.7, 133.5, 130.5, 128.9, 126.9, 126.82, 126.77, 126.7, 125.6, 120.9, 49.3, 21.5, 20.7. EIMS m/z 299 (M^+), 252, 235, 144, 115, 91.

Spectral data were consistent with data reported in the literature.²³

***N*-Ts-2-(Chloromethyl)-2-methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (4a-Cl)**

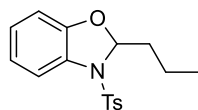


10.1 mg, 28%, using **3a** and 5 mol% $Pd(OAc)_2$ at 100 °C for 12 h.

a yellow solid (EtOAc : *n*-Hexane = 1:8), mp 67-69 °C.

1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.4 Hz, 2H), 7.59 (dd, J = 8.4, 1.2 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.96 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 6.87-6.82 (m, 2H), 4.09 (d, J = 12.8 Hz, 1H), 3.72 (d, J = 13.2 Hz, 1H), 3.56 (s, 2H), 2.42 (s, 3H), 1.47 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 144.3, 143.8, 136.8, 129.9, 127.1, 124.6, 124.0, 121.0, 119.1, 118.1, 75.3, 49.6, 47.2, 21.6, 21.5. HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{17}H_{18}ClNNaO_3S$ 374.0588, found 374.0593.

***N*-Ts-2-Propyl-2,3-dihydrobenzo[*d*]oxazole**



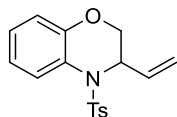
7.4 mg, 23%, using *N*-Ts-2-(but-2-en-1-yloxy)aniline and 5 mol% $Pd(OAc)_2$ at 100 °C for 24 h.

a colorless oil (EtOAc : *n*-Hexane = 1:10).

1H NMR ($CDCl_3$, 400 MHz) δ 7.55 (dd, J = 7.9, 1.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.00 (td, J = 7.8, 1.2 Hz, 1H), 6.92 (td, J = 7.8, 1.2 Hz, 1H), 6.62 (dd, J = 8.0, 0.8 Hz, 1H), 5.89 (t, J = 5.8 Hz, 1H), 2.34 (s, 3H), 1.82-1.77 (m, 2H), 1.55-1.48 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 151.7, 144.6, 133.0, 129.6, 128.8, 127.5, 126.6, 121.3, 118.3, 109.6, 96.3, 38.0, 21.6, 16.7, 13.6. HRMS (EI) $[M+Na]^+$ m/z calcd for $C_{17}H_{19}NNaO_3S$ 340.0978, found 340.0979.

²³ (a) Zhang, Y.; Sim, J. H.; MacMillan, S. N.; Lambert, T. H. *Org. Lett.* **2020**, 22, 15, 6026. (b) Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* **1996**, 61, 3584.

***N*-Ts-3-Vinyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine**

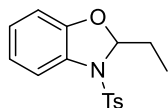


8.0 mg, 25%, using *N*-Ts-2-(but-2-en-1-yloxy)aniline and 5 mol% Pd(OAc)₂ at 100 °C for 24 h.
a colorless oil (EtOAc : *n*-Hexane = 1:5).

¹H NMR (CDCl₃, 400 MHz) δ 7.88 (dd, J = 8.4, 1.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.05 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 6.94 (ddd, J = 8.8, 7.6, 1.6 Hz, 1H), 6.78 (dd, J = 8.4, 1.6 Hz, 1H), 5.73 (ddd, J = 16.8, 10.4, 4.4 Hz, 1H), 5.35 (ddd, J = 17.2, 1.6, 0.8 Hz, 1H), 5.21 (ddd, J = 10.4, 2.0, 0.8 Hz, 1H), 4.90-4.87 (m, 1H), 4.09 (dd, J = 11.2, 1.6 Hz, 1H), 3.35 (dd, J = 11.0, 3.0 Hz, 1H), 2.39 (s, 3H).
¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 146.2, 144.2, 135.5, 132.7, 129.9, 127.2, 126.1, 125.3, 122.4, 121.2, 118.7, 117.2, 64.9, 54.2, 21.6. EIMS m/z 315 (M⁺), 160, 132, 91, 65.

Spectral data were consistent with data reported in the literature.^{17, 24}

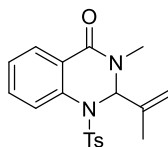
***N*-Ts-2-Ethyl-2,3-dihydrobenzo[*d*]oxazole**



10.4 mg, 21%, using *N*-Ts-2-allyloxylaniline and 5 mol% Pd(OAc)₂ at 100 °C for 6 h.
a colorless oil (EtOAc : *n*-Hexane = 1:6).

¹H NMR (CDCl₃, 400 MHz) δ 7.55 (dd, J = 7.6, 1.2 Hz, 1H), 7.45 (dd, J = 8.0, 1.6 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.00 (td, J = 7.8, 1.2 Hz, 1H), 6.91 (td, J = 7.8, 1.2 Hz, 1H), 6.62 (dd, J = 7.8, 1.0 Hz, 1H), 5.88 (t, J = 5.6 Hz, 1H), 2.34 (s, 3H), 1.85 (quintet, J = 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 151.7, 144.6, 133.0, 129.6, 128.9, 127.5, 126.6, 121.3, 118.1, 109.5, 97.3, 29.2, 21.6, 7.7. HRMS (EI) [M+Na]⁺ m/z calcd for C₁₆H₁₇NNaO₃S 326.0821, found 326.0818.

***N*-Ts-3-Methyl-2-(prop-1-en-2-yl)-2,3-dihydroquinazolin-4(1*H*)-one**



18.5 mg, 49%, using *N*-methyl-*N*-methallyl-2-tosylaminobenzamide and 20 mol% Pd(OAc)₂ at 120 °C for 10 h.

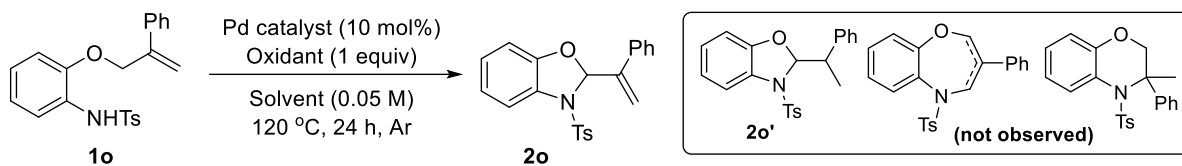
a white solid (EtOAc : *n*-Hexane = 1:1), mp 150-152 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.84 (dd, J = 7.6, 1.2 Hz, 1H), 7.70 (dd, J = 8.2, 0.6 Hz, 1H), 7.54 (td, J = 7.8, 1.2 Hz, 1H), 7.34 (td, J = 7.6, 0.8 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.75 (s, 1H), 4.91 (d, J = 1.2 Hz, 1H), 4.61 (s, 1H), 2.80 (s, 3H), 2.34 (s, 3H), 1.81 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 161.2, 144.7, 138.5, 135.4, 134.2, 132.6, 129.6, 127.6, 127.3, 126.9, 126.7, 125.1, 115.0, 75.4, 33.7, 21.6, 19.0. HRMS (EI) [M+Na]⁺ m/z calcd for C₁₉H₂₀N₂NaO₃S 379.1087, found 379.1083.

²⁴ Wen, K.; Wu, Z.; Huang, B.; Ling Z.; Gridnev, I. D.; Zhang, W. *Org. Lett.* **2018**, *20*, 1608.

Full Data of Optimization Studies

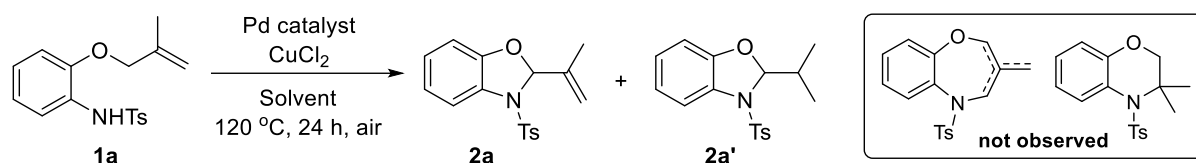
1. Screening of Pd Catalysts, Oxidants, and Solvents Using **1o**



Entry	Pd Catalyst	Oxidant	Solvent	1o (%) ^a	2o (%) ^a
1	Pd(OAc)₂	O ₂ (1 atm)	ClCH₂CH₂Cl	78	7
2		CuCl₂		24; - ^b ; - ^c	46 (45); (42) ^b ; 37 ^c
3		CuBr ₂		-	9
4		Cu(OAc) ₂		56	6
5		Cu(OTf) ₂		-	-
6		CuCl		61	8
7		AgOAc, Ag ₂ O, or Ag ₂ CO ₃		8-48	9-12
8		BQ		83	2
9		Other oxidants ^d		8-61	0-17
10	Pd(O ₂ CCF ₃) ₂	CuCl ₂	ClCH ₂ CH ₂ Cl	26	(46)
11	PdCl ₂			30	32
12	[Pd(allyl)Cl] ₂			24	36
13	PdCl ₂ (MeCN) ₂			24	(44)
14	PdCl ₂ (PhCN) ₂			19	(44)
15	PdCl ₂ (PPh ₃) ₂			44	21
16	PdCl ₂ (dppf)			47	-
17	Pd ₂ (dba) ₃			28	37
18	Pd(PPh ₃) ₄			55	-
19	Pd(OAc) ₂	CuCl ₂	toluene	17	23
20			1,4-dioxane	36	11
21			EtOAc	26	31
22			EtOH	40	-
23			AcOH	-	trace
24			MeCN	46	5
25			DMF	52	-
26			DMSO	60	-

^a Yields were determined by ¹H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. ^b Under aerobic condition. ^c Using 5 mol% Pd(OAc)₂ and 2 equiv CuCl₂ at 150 °C. ^d Other oxidants: 2-MeBQ, 2-*t*BuBQ, 2,5-Me₂BQ, 2,6-Me₂BQ, 2,5-*t*Bu₂BQ, 1,4-naphthoquinone, 9,10-phenanthrenequinone, DDQ, K₂S₂O₈, Oxone, PhI(OAc)₂, I₂, NIS, Selectfluor, NFSI, *t*BuOOH, BzOOH, (*t*BuO)₂.

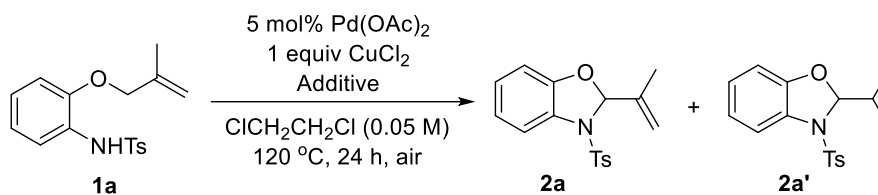
2. Screening of Pd Catalysts, Solvents, Oxidant Amount, and Concentration Using 1a



Entry	Pd Catalyst (mol%)	CuCl ₂ (equiv)	Solvent (M)	1a (%) ^a	2a (%) ^a	2a' (%) ^a
1	Pd(OAc) ₂ (2)	1	ClCH ₂ CH ₂ Cl (0.05)	38	39	6
2	Pd(OAc)₂ (5)	1	ClCH₂CH₂Cl (0.05)	(33); (37) ^b	(64); (53) ^b	-; - ^b
3	Pd(OAc) ₂ (5)	1	ClCH ₂ CH ₂ Cl (0.1)	21	39	10
4	Pd(OAc) ₂ (5)	0.5	ClCH ₂ CH ₂ Cl (0.05)	53	40	-
5	Pd(OAc) ₂ (5)	2	ClCH ₂ CH ₂ Cl (0.05)	trace	39	6
6	Pd(OAc) ₂ (10)	1	ClCH ₂ CH ₂ Cl (0.05)	6	60 (57)	7
7	Pd(O ₂ CCF ₃) ₂ (5)	1	ClCH ₂ CH ₂ Cl (0.05)	25	29	10
8 ^c	White catalyst (5)			48	25	-
9	PdCl ₂ (5)			30	24	10
10	[Pd(allyl)Cl] ₂ (5)			16	15	18
11	PdCl ₂ (MeCN) ₂ (5)			30	35	9
12	PdCl ₂ (PhCN) ₂ (5)			15	23	16
13	PdCl ₂ (PPh ₃) ₂ (5)			49	10	7
14	Pd(acac) ₂ (5)			21	15	16
15	Pd ₂ (dba) ₃ (5)			31	16	12
16	Pd(OAc) ₂ (5)	1	toluene (0.05)	6	18	10
17			PhCN (0.05)	13	24	-
18			1,4-dioxane (0.05)	19	13	19
19			EtOAc (0.05)	3	2	22
20			EtOH (0.05)	36	-	-
21			<i>t</i> BuOH (0.05)	61	-	-
22			CF ₃ CH ₂ OH (0.05)	3	-	11
23			(CF ₃) ₂ CHOH (0.05)	-	-	53
24			DME (0.05)	33	-	-
25			MeNO ₂ (0.05)	-	-	25
26			MeCN (0.05)	50	24	-
27			DMF (0.05)	38	20	-
28			DMSO (0.05)	69	-	-

^a Yields were determined by ¹H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. ^b Under argon instead of air. ^c In the presence of 2 equiv NaHCO₃ at 100 °C.

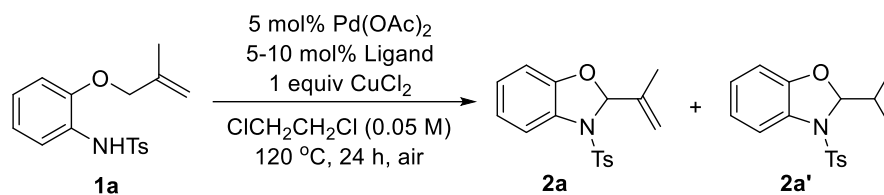
3. Screening of Additives



Entry	Additive (equiv)	1a (%) ^a	2a (%) ^a	2a' (%) ^a
1	-	(33)	(64)	-
2	Li ₂ CO ₃ (1)	36	57 (54)	2
3	Na ₂ CO ₃ (1)	33	36	4
4	K ₂ CO ₃ (1)	20	30	-
5	Cs ₂ CO ₃ (1)	33	-	-
6	NaHCO ₃ (1)	16	(63)	3
7	NaHCO ₃ (2)	12	(70)	1
8 ^b	NaHCO ₃ (2)	11	(78)	5
9 ^c	NaHCO ₃ (2)	48	25	-
10 ^d	NaHCO ₃ (2)	(9)	(63)	-
11	NaHCO ₃ (3)	18	(60)	1
12	KHCO ₃ (1)	23	50 (48)	2
13	LiOAc (1)	34	(59)	4
14	LiOAc (2)	14	(55)	4
15	NaOAc (1)	47	37	-
16	KOAc (1)	83	6	-
17	CsOAc (1)	46	22	3
18	K ₃ PO ₄ (1)	43	-	-
19	Na ₂ HPO ₄ (1)	37	37	2
20	LiH ₂ PO ₄ (1)	27	52	7
21	NaH ₂ PO ₄ (1)	26	62	4
22	NaH ₂ PO ₄ (2)	(21)	(61)	-
23	KH ₂ PO ₄ (1)	46	39	3
24	NaOMe (1)	75	14	-
25	NaOtBu (1)	13	4	-
26 ^b	pyridine (2)	86	8	-
27	DMSO (0.2)	(87)	(13)	-
28 ^e	LiCl (2)	44	28	5

^a Yields were determined by ¹H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. ^b At 100 °C for 12 h. ^c Using 5 mol% White catalyst instead of Pd(OAc)₂ at 100 °C for 24 h. ^d At 140 °C for 7 h. ^e At 100 °C for 24 h.

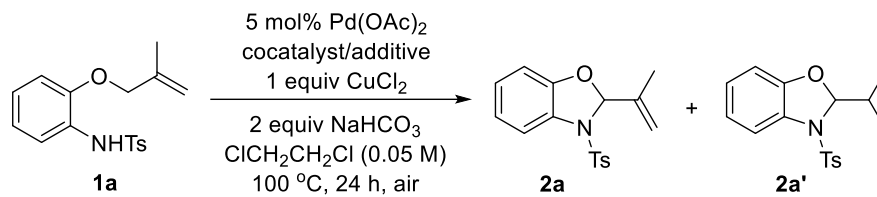
4. Screening of Ligands



Entry	Ligand	1a (%) ^a	2a (%) ^a	2a' (%) ^a
1	-	(33) ^b	(64) ^b	0
2	PPh ₃ , P(oTol) ₃ , P(1-naphthyl) ₃ , P(OEt) ₃ , dppp, dppb, BIPHEP (R = H, Ph)	23-60	35-46	0-9
3	P(C ₆ F ₅) ₃ , P(2-furyl) ₃ , dppe, dppf, SPhos Xantphos, DPEphos, <i>rac</i> -BINAP	45-92	0-26	0-12
4	 (R = H, 2-Me, 3-Me, 2,6-Me ₂) (R = H, 3-Me, 5-Cl, 4,6-Me ₂) (R ¹ = H, R ² = H, Me, Ph, OMe) (R ¹ = Me, R ² = H) (R = H, Ph) TMEDA (R = H, Me)	21-95	0-28	0-34
5	 (R ¹ = H, R ² = Ph, cHex) (R ¹ = R ² = Ph) (R ¹ = Cl, R ² = OMe) (R ¹ , R ² = OCH ₂ O, (CH) ₄)	30-84	17-33 (0-16% ee) ^c	0-trace

^a Determined by ¹H NMR using trichloroethylene as an internal standard. ^b Isolated yields. ^c Determined by chiral HPLC.

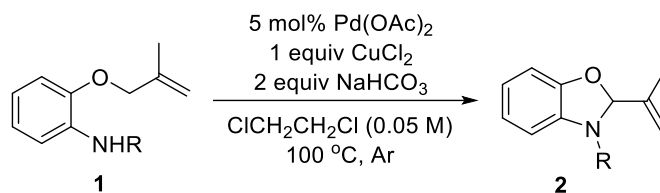
5. Screening of Cocatalysts/Additive



Entry	Cocatalyst/Additive (mol%)	1a (%) ^a	2a (%) ^a	2a' (%) ^a
1 ^b	-	11	(78)	5
2 ^c	AgOTf (2)	25	33	31
3 ^{c-d}	AgOTf (5)	-	-	84
4	White cat. (5)	4	34	5
5 ^b	PdCl ₂ (5)	-	20	4
6 ^b	PdCl ₂ (MeCN) ₂ (5)	-	31	8
7	PdCl ₂ (MeCN) ₂ (5)	26	36	-
8	[Pd(allyl)Cl] ₂ (5)	25	58	-
9	RuH ₂ (CO)(PPh ₃) ₃ (5)	51	21	-
10	[Ru(<i>p</i> -cymene)Cl ₂] ₂ (5)	24	16	-
11	RuCl ₃ (5)	44	56	-
12	Ni(cod) ₂ (5)	32	26	-
13	NiCl ₂ (5)	33	32	-
14	NiBr ₂ (5)	33	30	-
15	Co(acac) ₃ (5)	38	17	-
16	CoCl ₂ (5)	30	27	-
17	Co(OAc) ₂ (5)	17	47	-
18	Fe ₂ (CO) ₉ (5)	38	26	-
19	Fe(acac) ₃	30	18	-
20	FeCl ₂ (5)	36	12	-
21	FeCl ₃ (5)	9 (trace)	-	6 (5)
22	[(COD)IrCl] ₂ (5)	38	28	-
23	IrH(CO)(PPh ₃) ₃ (5)	40	31	-
24	DMSO (20)	(57)	(33)	-
25 ^b	pyridine (20)	54	9	-
26 ^b	pyridine (200)	30	19	-
27	NCS (100)	24	24	-

^a Yields were determined by ¹H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. ^b For 12 h. ^c Under argon instead of air. ^d For 3 h.

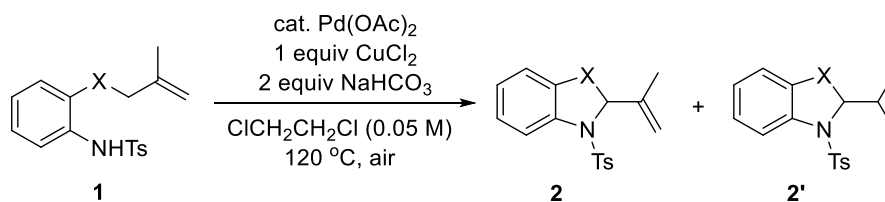
6. Screening of *N*-Protecting Groups



Entry	R	<i>t</i> (h)	1 (%) ^a	2 (%) ^a	Entry	R	<i>t</i> (h)	1 (%) ^a	2 (%) ^a
1	Ts (1a)	12	(20)	(73) (2a)	6	Boc	12	(54)	-
2	Bs (1b)	12	(38)	(57) (2b)	7	Ac	24	(25)	-
3	Ns (1c)	12	(42)	(43) (2c)	8	Bn	12	(27)	-
4	Ms (1d)	12	(44)	(41) (2d)	9	Me	12	-	-
5	Tf	12	(48)	-	10	H	12	24	-

^a Yields were determined by ¹H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields.

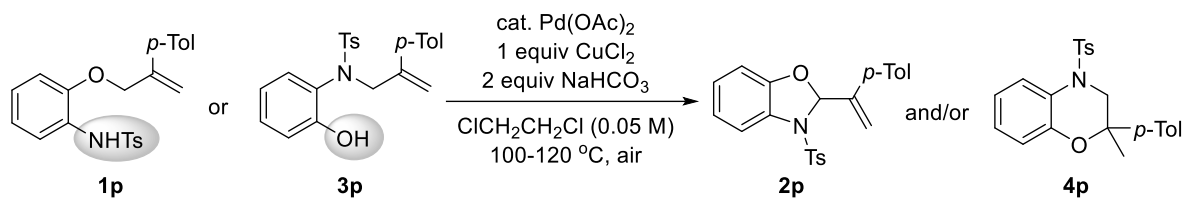
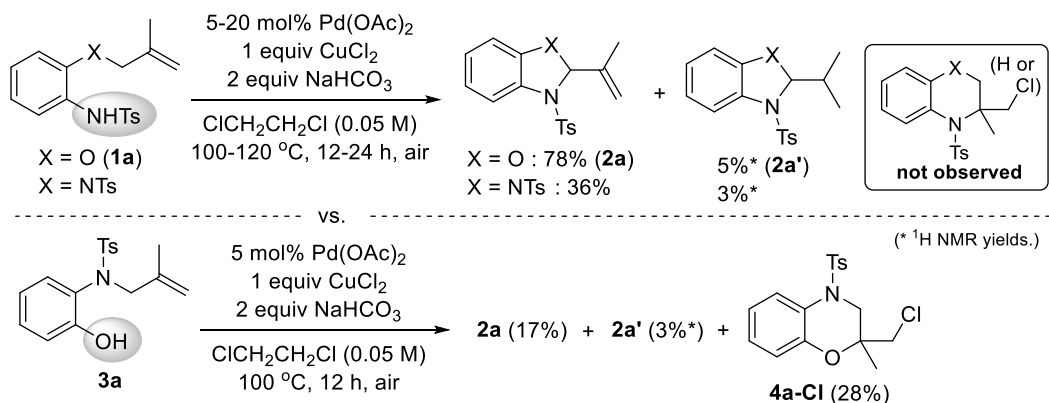
7. Screening of Tethering Moiety



Entry	X	[Pd] (mol%)	<i>t</i> (h)	1 (%) ^a	2 (%) ^a	2' (%) ^a
1	O (1a)	5	24	12 ^b	70 (2a)	1 ^b (2a')
2 ^c	NMs (1r)	5	24	31	44 ^d (2r)	4 ^d (2r')
3	NMs (1r)	20	4	40	50 ^d (2r)	5 ^d (2r')
4	NTs	10	24	30	29 ^d	3 ^d
5	NTs	20	24	trace	36 ^d	3 ^d
6 ^c	NMe	5	12	-	-	-
7 ^c	NAc	5	24	-	15 ^b	-
8 ^c	NCbz	5	24	33	25	-
9	S	10	24	12 ^b	19 ^b	-
10	S	20	16	-	13 ^b	-
11	CH ₂ (1s)	20	5	-	71 (2s)	-
12 ^e	CONMe	5	24	43	45	-
13	CONMe	20	10	-	49	-

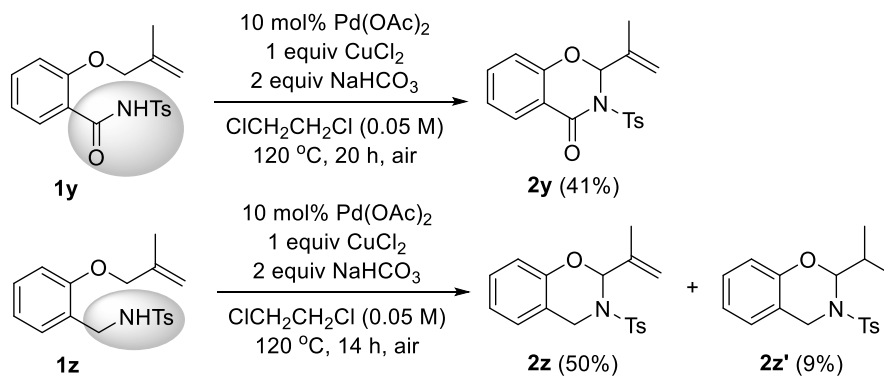
^a Isolated yields. ^b Determined by ¹H NMR. ^c In the absence of NaHCO₃. ^d Obtained as an inseparable mixture. ^e At 100 °C.

8. Screening of Tethering Nucleophiles

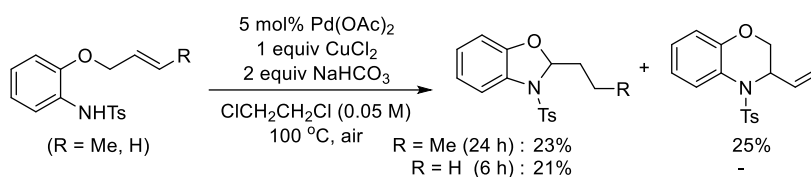
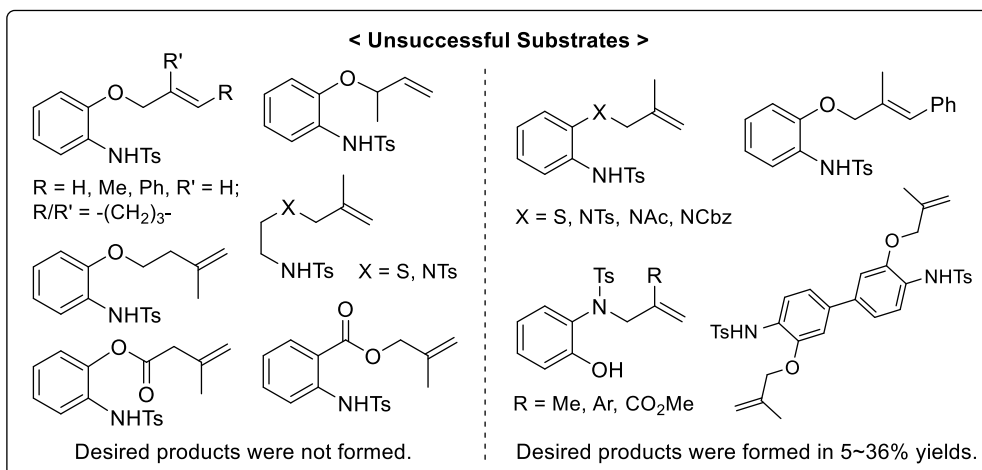


Entry	Substrate	[Pd] (mol%)	Temp. (°C)	t (h)	1p or 3p (%) ^a	2p (%) ^b	4p (%) ^b
1	1p	5	100	24	21 (1p)	40 ^a	-
2	1p	20	120	6	-	72	-
3	3p	5	100	24	-	26 ^c	18 ^c

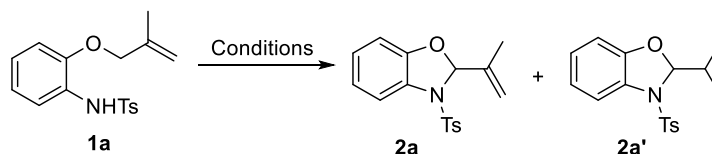
^a Determined by ¹H NMR. ^b Isolated yields. ^c Obtained as an inseparable mixture.



Limitations



Reactions Under the Conditions Reported in the Related Works or Their Modified Conditions



< Conditions >

* G. Brogini *et al. J. Org. Chem.* **2004**, 69, 5627.

- : 10 mol% Pd(OAc)₂, 1 equiv NaOAc in DMSO at 100 °C, 24 h, air ⇒ **1a** (28%)
- : 10 mol% Pd(OAc)₂, 0.2 equiv pyridine in xylene at 100 °C, 48 h, air ⇒ **1a** (78%)
- : 5 mol% Pd(OAc)₂, 1 equiv CuCl₂, 2 equiv NaHCO₃ in DCE/H₂O (10/1) at 100 °C, 12 h, air ⇒ **1a** (30%), **2a** (3%)

* R. Jana *et al. Org. Lett.* **2020**, 22, 7443.

- : 10 mol% White catalyst, 10 mol% AgOTf, 3 equiv BQ in toluene at 45 °C, 24 h, Ar ⇒ **1a** (70%), **2a** (14%)
- : 5 mol% Pd(OAc)₂, 2 mol% AgOTf, 1 equiv CuCl₂, 2 equiv NaHCO₃ in DCE at 100 °C, 24 h, Ar ⇒ **1a** (25%), **2a** (33%), **2a'** (31%)
- : 5 mol% Pd(OAc)₂, 5 mol% AgOTf, 1 equiv CuCl₂, 2 equiv NaHCO₃ in DCE at 100 or 80 °C, 3 or 8 h, Ar ⇒ **2a'** (84% or 78%)
- : 10 mol% Pd(OAc)₂, 5 mol% AgOTf, 1 equiv CuCl₂, 2 equiv NaHCO₃ in DCE at 60 °C, 24 h, Ar ⇒ **1a** (32%), **2a** (33%), **2a'** (5%)
- : 5 mol% White catalyst, 1 equiv CuCl₂, 2 equiv NaHCO₃ in DCE at 100 °C, 24 h, air ⇒ **1a** (48%), **2a** (25%)

* Z. Wang *et al. Org. Biomol. Chem.* **2009**, 7, 3168.

- : 10 mol% PdCl₂, 10 mol% FeCl₃ in DCE at 50 °C, 3 h, air ⇒ **1a** (9%), **2a'** (43%)
- : 10 mol% PdCl₂, 10 mol% FeCl₃, 1 equiv CuCl₂, 2 equiv NaHCO₃ in DCE at 50 °C, 24 h, air ⇒ **1a** (81%), **2a'** (2%)
- : 1) 10 mol% PdCl₂(MeCN)₂, 10 mol% FeCl₃ in DCE at 40 °C, 0.5 h, air; 2) 1 equiv CuCl₂, 2 equiv NaHCO₃ in DCE at 100 °C, 12 h, air ⇒ **1a** (14%), **2a'** (19%)

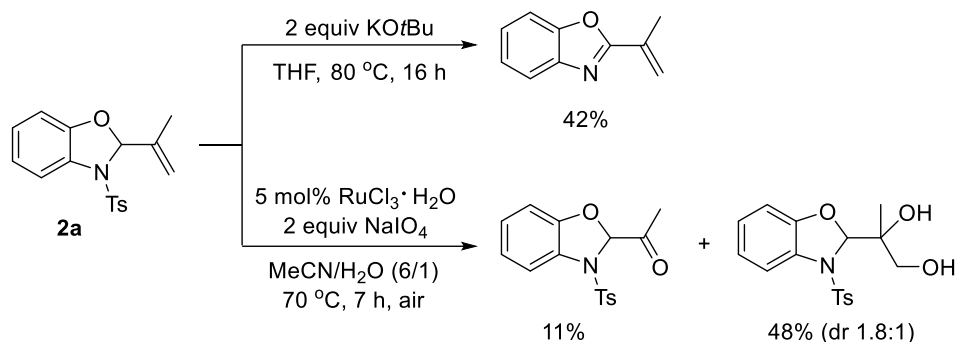
* G. Poli *et al. Adv. Synth. Catal.* **2017**, 359, 623.

- : 5 mol% Pd(OAc)₂, 2 equiv PhI(O₂CCF₃)₂, 1 equiv *n*Bu₄NHSO₄, 1 equiv NaOAc in CH₂Cl₂ or DCE at rt or reflux, 1-2 h, Ar ⇒ decomposed
- : 5 mol% Pd(OAc)₂, 2 equiv PhI(OAc)₂, 1 equiv *n*Bu₄NHSO₄, 1 equiv NaOAc in CH₂Cl₂ or DCE at rt or reflux, 1 h or 2 h, Ar ⇒ **1a** (69% or 30%)

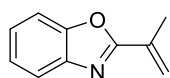
* M. Jeganmohan *et al. J. Org. Chem.* **2019**, 84, 13053.

- : 2.5 mol% [Cp*IrCl₂]₂, 10 mol% AgBF₄, 2.2 equiv AgOAc in DCE at 65 °C, 24 h, Ar ⇒ **1a** (71%), **2a** (14%)

Synthetic Transformation



2-(Prop-1-en-2-yl)benzo[d]oxazole

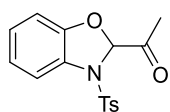


To a solution of **2a** (42.1 mg, 0.133 mmol, 1 equiv) in THF (0.7 mL, 0.2 M) was added KO^tBu (31.5 mg, 0.267 mmol, 2 equiv). After being stirred at reflux for 16 h, the reaction mixture was quenched with sat. aq. NH₄Cl (100 mg/mL) and then the product was extracted with EtOAc (three times). The combined organic layer was washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:8) to give the product (9.2 mg, 42%) as a colorless solid (mp 41-43 °C).

¹H NMR (CDCl₃, 400 MHz) δ 7.76-7.71 (m, 1H), 7.53-7.49 (m, 1H), 7.36-7.29 (m, 2H), 6.24 (t, *J* = 1.0 Hz, 1H), 5.61 (quintet, *J* = 1.6 Hz, 1H), 2.29 (dd, *J* = 1.6, 1.2 Hz, 3H). ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 163.8, 150.5, 141.9, 131.9, 125.3, 124.3, 121.4, 120.1, 110.4, 19.1. EIMS *m/z* 159 (M⁺), 133, 91, 63.

Spectral data were consistent with data reported in the literature.²⁵

N-Ts-2-Acetyl-2,3-dihydrobenzo[d]oxazole²⁴



A solution of **2a** (63.6 mg, 0.202 mmol, 1 equiv) and RuCl₃·xH₂O (2.1 mg, 0.0101 mmol, 5 mol%) in MeCN/H₂O (6:1, 6.7 mL, 0.03 M) was stirred at room temperature. After 0.5 h, NaIO₄ (86.3 mg, 0.403 mmol, 2 equiv) was added and then stirred at 70 °C for 7 h. The reaction mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel to give the corresponding products, *N*-Ts-2-acetyl-2,3-dihydrobenzo[d]oxazole and *N*-Ts-2-(1,2-dihydroxypropan-2-yl)-2,3-dihydrobenzo[d]oxazole.

N-Ts-2-Acetyl-2,3-dihydrobenzo[d]oxazole

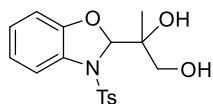
11.0 mg, 11%, a white solid (EtOAc : *n*-Hexane = 1:10), mp 141-143 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz,

²⁵ Yao, Y.-X.; Fang, D.-M.; Gao, F.; Liang, X.-X. *Tetrahedron Lett.* **2019**, 60, 68.

2H), 7.06 (td, $J = 7.8, 1.2$ Hz, 1H), 6.98 (td, $J = 7.6, 1.2$ Hz, 1H), 6.75 (dd, $J = 8.0, 0.8$ Hz, 1H), 5.96 (s, 1H), 2.36 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 199.3, 151.7, 145.4, 132.0, 129.8, 128.0, 127.7, 127.5, 122.3, 118.4, 110.0, 93.4, 24.5, 21.6. EIMS m/z 317 (M^+), 274, 235, 219, 155, 119, 91, 63. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{16}\text{H}_{15}\text{NNaO}_4\text{S}$ 340.0614, found 340.0612.

***N*-Ts-2-(1,2-Dihydroxypropan-2-yl)-2,3-dihydrobenzo[*d*]oxazole**



The relative stereochemistry could not be determined and two diastereomers were obtained with a 1.8:1 (= **A** : **B**) ratio.

A isomer: 21.7 mg, 31%, a white solid (EtOAc : *n*-Hexane = 1:1), mp 172-174 °C.

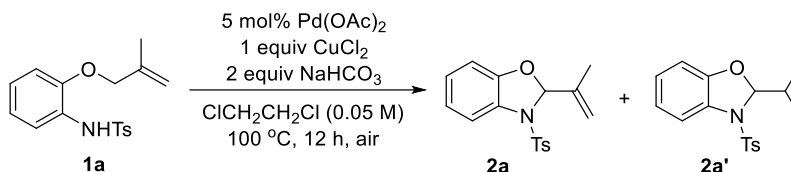
^1H NMR (CDCl_3 , 400 MHz) δ 7.59 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.03 (td, $J = 7.8, 1.6$ Hz, 1H), 6.94 (td, $J = 7.8, 1.2$ Hz, 1H), 6.65 (dd, $J = 8.0, 0.8$ Hz, 1H), 5.87 (s, 1H), 3.65 (d, $J = 5.2$ Hz, 2H), 2.78 (br d, $J = 5.2$ Hz, 1H), 2.49 (br s, 1H), 2.35 (s, 3H), 1.09 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 152.4, 145.3, 131.8, 129.9, 129.4, 127.7, 127.1, 121.6, 118.1, 109.2, 96.5, 74.7, 66.0, 21.6, 18.5. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{17}\text{H}_{19}\text{NNaO}_5\text{S}$ 372.0876, found 372.0879.

B isomer: 11.8 mg, 17%, a white solid (EtOAc : *n*-Hexane = 1:1), mp 162-164 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 7.04 (td, $J = 7.8, 1.2$ Hz, 1H), 6.94 (td, $J = 7.6, 1.2$ Hz, 1H), 6.68 (d, $J = 8.0$ Hz, 1H), 5.88 (s, 1H), 4.09 (dd, $J = 12.2, 3.8$ Hz, 1H), 3.44 (dd, $J = 12.2, 7.8$ Hz, 1H), 2.79 (br s, 1H), 2.75 (br s, 1H), 2.35 (s, 3H), 0.97 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 152.7, 145.4, 131.6, 129.8, 129.3, 127.7, 127.5, 121.6, 118.4, 109.3, 97.0, 75.6, 65.4, 21.6, 17.1. EIMS m/z 349 (M^+), 274, 252, 235, 219, 155, 119, 91, 63. HRMS (EI) $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{17}\text{H}_{19}\text{NNaO}_5\text{S}$ 372.0876, found 372.0874.

Mechanistic Studies

1) Control Experiments

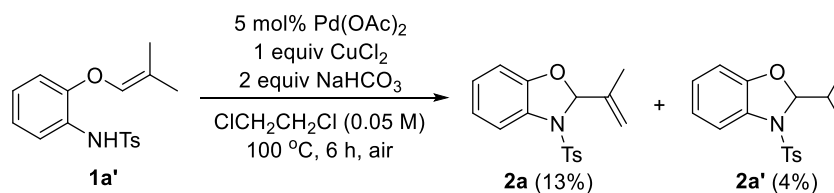


Entry	Variation from the standard conditions	1a (%) ^a	2a (%) ^a	2a' (%) ^a
1	-	11	(78)	5
2	Without Pd(OAc) ₂	100	-	-
3	Without CuCl ₂	93	4	-
4	Without NaHCO ₃	27	53	6
5	Under Ar atmosphere	(20)	(73)	3
6	Under O ₂ (1 atm)	20	(70)	3
7	Various Ru, Rh, Ni, Co, Fe catalysts ^b instead of Pd(OAc) ₂	0-100	0-24	0-15

^a Yields were determined by ¹H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. ^b RuCl₃, RuCl₂(CO)₂(PPh₃)₂, RuH₂(CO)(PPh₃)₃, [RuCl₂(*p*-cymene)]₂, RhCl(PPh₃)₃, [Cp*RhCl]₂, RhCl(CO)(PPh₃)₂, RhH(CO)(PPh₃)₃, Ni(cod)₂, NiCl₂, Ni(acac)₂, Ni(OAc)₂ · 4H₂O, NiCl₂(PPh₃)₂, NiCl₂(dppe), Co(acac)₃, CoCl₂(dppe), CoCl₂, Co(OAc)₂, Fe₂(CO)₉, Fe(acac)₃, FeCl₂, FeCl₃, FeSO₄ · 7H₂O.

Control experiments indicated that both Pd(OAc)₂ and CuCl₂ are essential for the reaction to occur, while the reaction still worked in the absence of NaHCO₃, albeit with a lower yield (entries 1-4). The reaction could be performed without strict exclusion of air, giving a bit better result than those under argon or O₂ atmosphere (entries 1 vs 5-6).

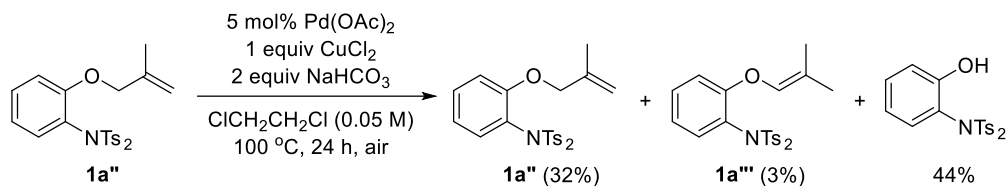
2) Reaction of a Possible Intermediate



Given the well-known Pd-catalyzed²⁶ olefin isomerization, although such intermediates were not observed during the reaction progress (as monitored by TLC and ¹H NMR), a probable intermediate **1a'** was prepared and subjected to the standard conditions. Only low conversion of **1a'** into **2a** and **2a'** was observed in this reaction.

²⁶ (a) Davies, N. R. *Aust. J. Chem.* **1964**, *17*, 212. (b) Bingham, D.; Hudson, B.; Webster, D.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1521. (c) Fan, J.; Wan, C.; Wang, Q.; Gao, L.; Zheng, X.; Wang, Z. *Org. Biomol. Chem.* **2009**, *7*, 3168. (d) Ning, X.-S.; Wang, M.-M.; Qu, J.-P.; Kang, Y.-B. *J. Org. Chem.* **2018**, *83*, 13523.

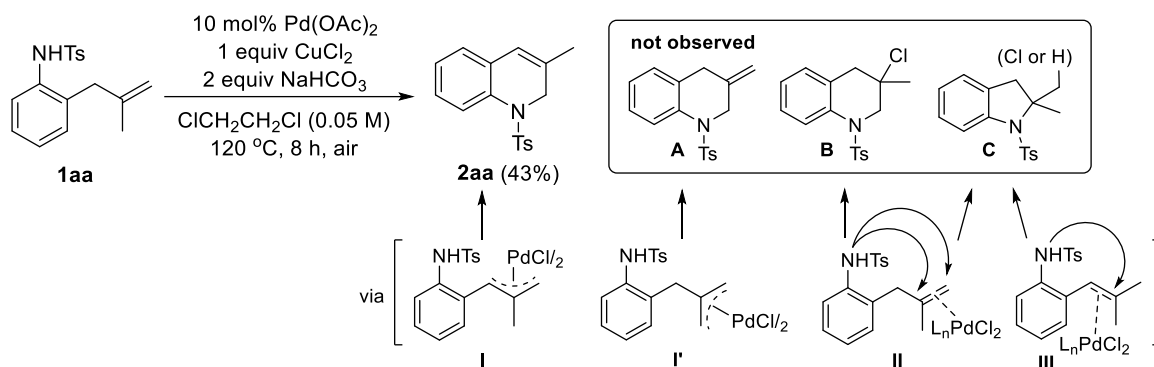
3) Olefin Isomerization under the Standard Reaction Conditions



Reaction of tertiary sulfonamide **1a''** under the standard conditions furnished mostly deallylation products and remaining **1a''** along with very small amount of olefin isomerized compound **1a'''**.

All these outcomes indicate that the olefin isomerization/cyclization pathway is possible but not dominant in Pd protocol.

4) Allylic C-H Activation vs. Aminopalladation

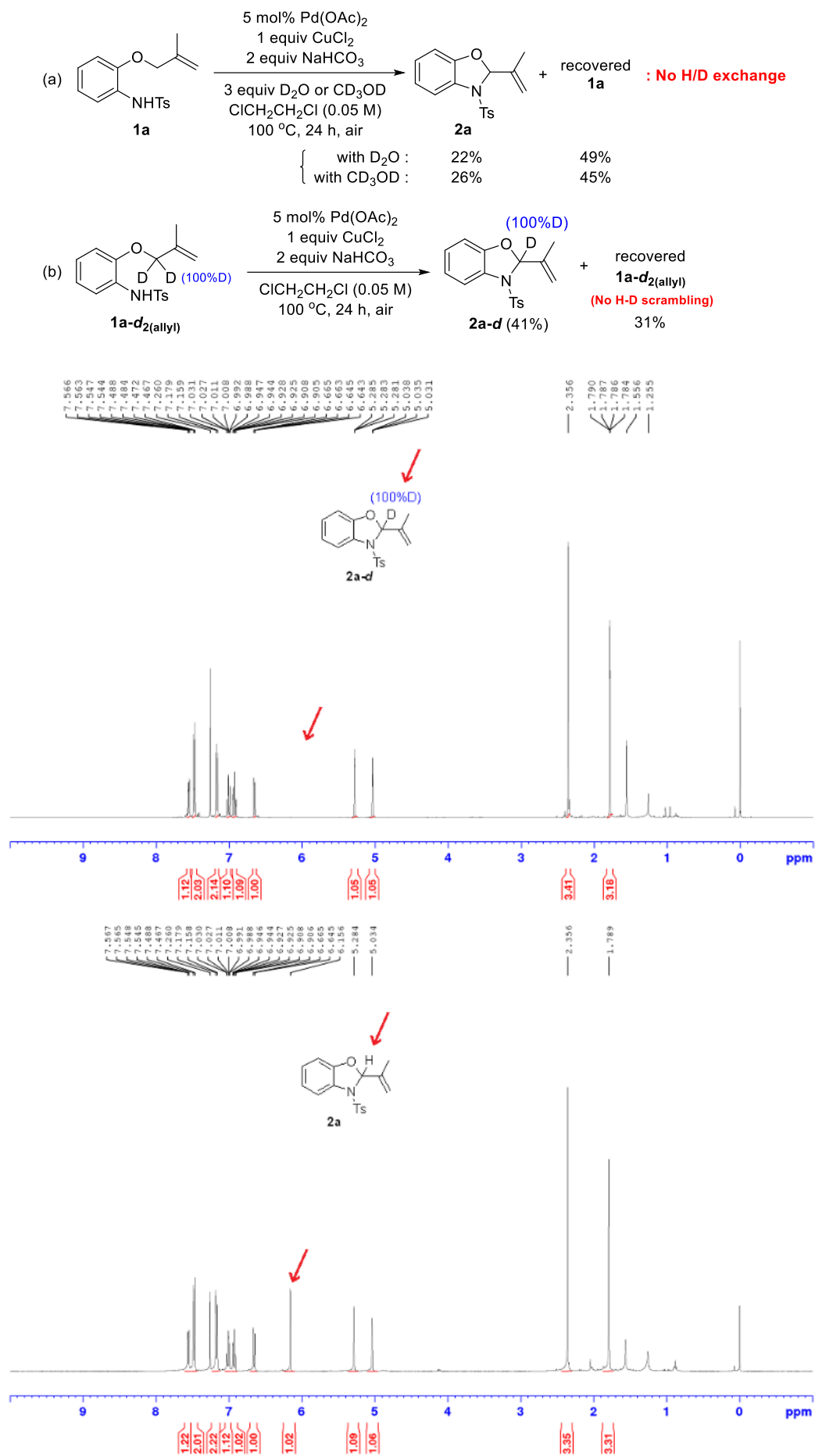


1,2-Dihydroquinoline **2aa** was formed in the Pd-catalyzed reaction of **1a** with a one-carbon-shorter linker, which has previously provided indolines (**C**) and/or 3-halotetrahydroquinolines (**B**) under similar conditions,²⁷ suggesting that allylic C–H cleavage/ π -allylpalladium formation²⁸ is more likely than either direct aminopalladation (**II**) or initial olefin isomerization (**III**). In addition, the formation of π -allylpalladium intermediates occurred through preferential allylic C–H activation at the internal methylene moiety (**I**) over the terminal methyl group (**I'**).

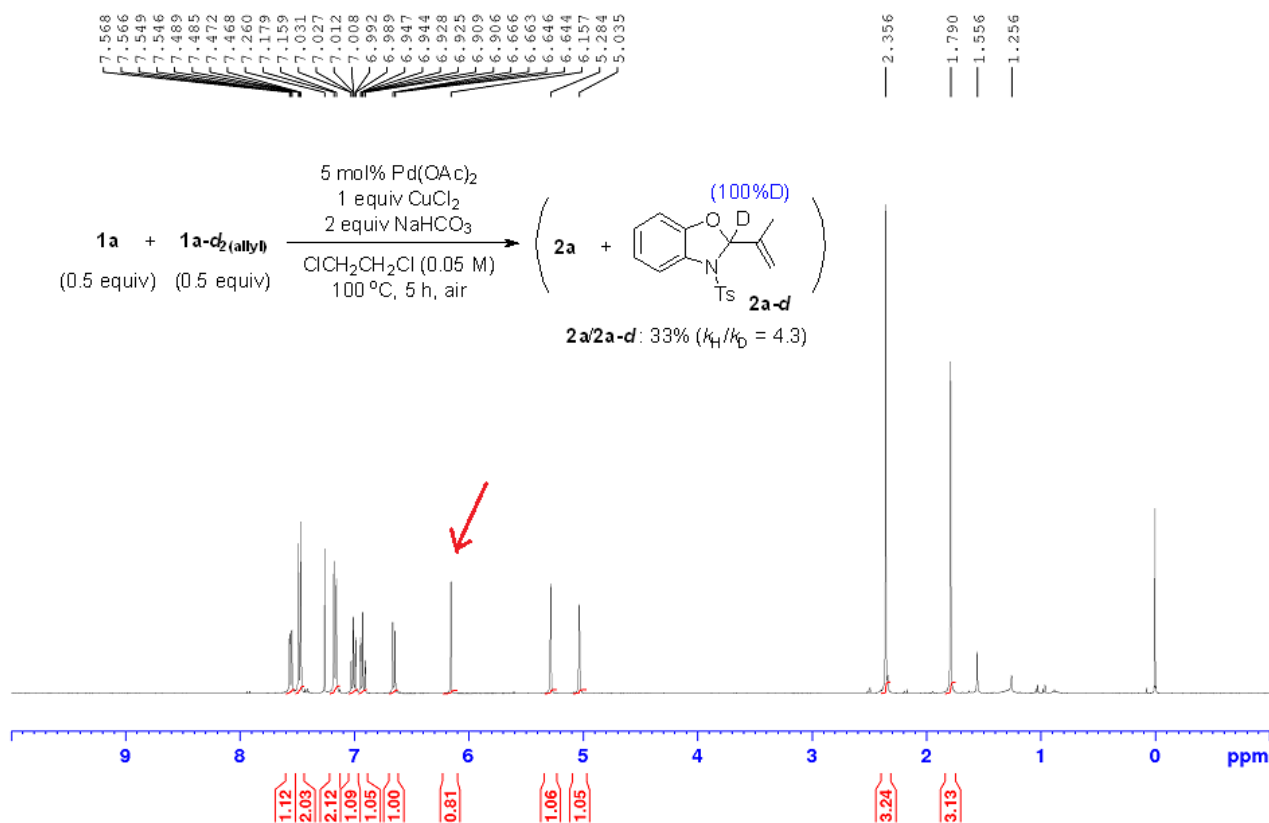
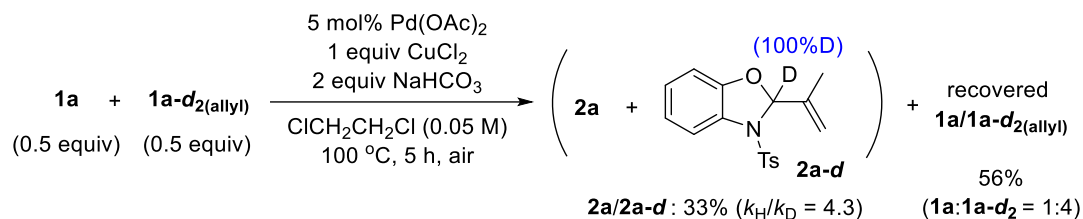
²⁷ (a) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 2674. (b) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800. (c) Manzoni, M. R.; Zabawa, T. P.; Kasi, D.; Chemler, S. R. *Organometallics* **2004**, *23*, 5618.

²⁸ (a) van der Schaaf, P. A.; Sutter, J.-P.; Grellier, M.; van Mier, G. P. M.; Spek, A. L.; van Koten, G.; Pfeffer, M. *J. Am. Chem. Soc.* **1994**, *116*, 5134. (b) Heathcock, C. H.; Stafford, J. A.; Clark, D. L. *J. Org. Chem.* **1992**, *57*, 2575. (c) Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* **1996**, *61*, 3584.

5) H/D Exchange Experiments

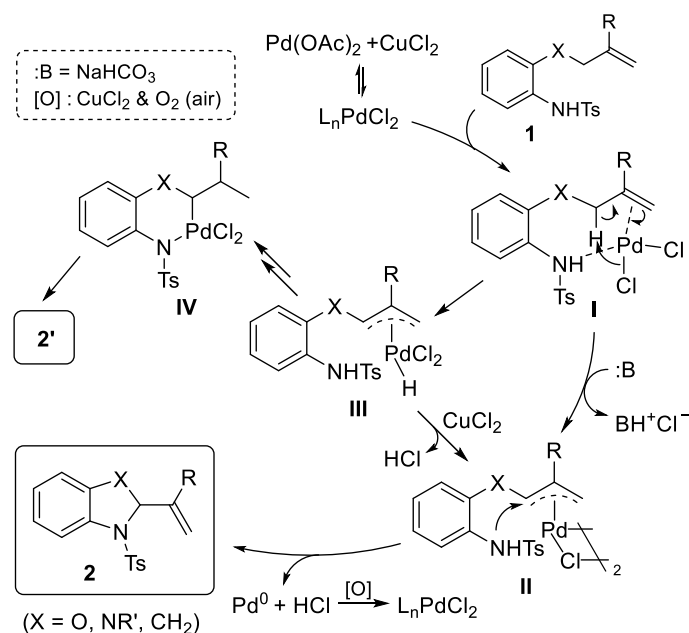


6) Intermolecular Kinetic Isotope Effect



No H/D scrambling in the substrate and product, the lower conversion of **1a-d**_{2(allyl)}, and the large primary kinetic isotopic effect (KIE) value ($k_{\text{H}}/k_{\text{D}} = 4.3$) suggest allylic C-H amination involving irreversible allylic C-H cleavage, presumably as a rate-determining step, to form π -allylpalladium intermediate.

Proposed Mechanism



Based on the mechanisms established for the related processes and on the basis of our experimental findings, a plausible mechanism is proposed as above.

Upon initial coordination (**I**) of the olefin and NHTs groups to Pd^{II} ,²⁹ a π -allylpalladium intermediate **II** could be invoked through intramolecular abstraction of an allylic methylene proton by the chloride ligand³⁰⁻³¹ or via the intermediacy of π -allylpalladium hydride species **III** generated by inserting Pd into the C-H bond. Our attempts to form and isolate π -allylpalladium species like **II** failed due to easy deallylation. Previous studies in the literature³¹ have demonstrated that CuCl_2 facilitates the formation of a halo-bridged dimeric complex (e.g., **II**) through oxidative conversion of a hydridopalladium species (e.g., **III**). Having uncovered that CuCl_2 is essential for the reaction to take place in our protocol, CuCl_2 appears to serve as an effective oxidant as well as a source of chloride ligand in this transformation.

Considering the much lower catalytic activity of *preformed* PdCl_2 compared to the *in situ*-mixture of $\text{Pd}(\text{OAc})_2$ and CuCl_2 , another conceivable mechanism involves the formation of an *in situ* heteroleptic Pd-Cu complex with Cl and OAc bridged ligands rather than a simple L_nPdCl_2 as the key metallic intermediate.³²

Subsequent intramolecular nucleophilic attack by the sulfonamide onto the proximal position of the π -allyl system in **II** produces 5-membered ring product **2**. Lastly, Pd^0 is reoxidized to the catalytically active Pd^{II} species by CuCl_2 and O_2 in air to complete the catalytic cycle. We supposed that the base would promote

²⁹ (a) Fan, J.; Wan, C.; Wang, Q.; Gao, L.; Zheng, X.; Wang, Z. *Org. Biomol. Chem.* **2009**, 7, 3168. (b) Ning, X.-S.; Wang, M.-M.; Qu, J.-P.; Kang, Y.-B. *J. Org. Chem.* **2018**, 83, 13523.

³⁰ (a) Lukas, J.; Coren, S.; Blom, J. E. *J. Chem. Soc., Chem. Commun.* **1969**, 1303. (b) Harvie, I. J.; McQuillin, F. *J. Chem. Soc., Chem. Commun.* **1978**, 747.

³¹ (a) Trost, B. M.; Strege, P. E. *Tetrahedron Lett.* **1974**, 2603. (b) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. *J. Am. Chem. Soc.* **1978**, 100, 3407. (c) Chrisope, D. R.; Beak, P. *J. Am. Chem. Soc.* **1986**, 108, 334. (d) Chrisope, D. R.; Beak, P.; Saunders, W. H. *J. Am. Chem. Soc.* **1988**, 110, 230.

³² Authors highly appreciate the reviewer's insightful and valuable comments on the mechanism.

the formation of **II** and/or the cyclization through deprotonation of the allylic moiety and/or the NHTs nucleophile, respectively. Although more detailed mechanistic studies remain to be needed, we speculated that the formation of a small amount of **2'** can be attributed to hydride/proton transfer of **III** followed by the reductive elimination of the resulting **IV**.

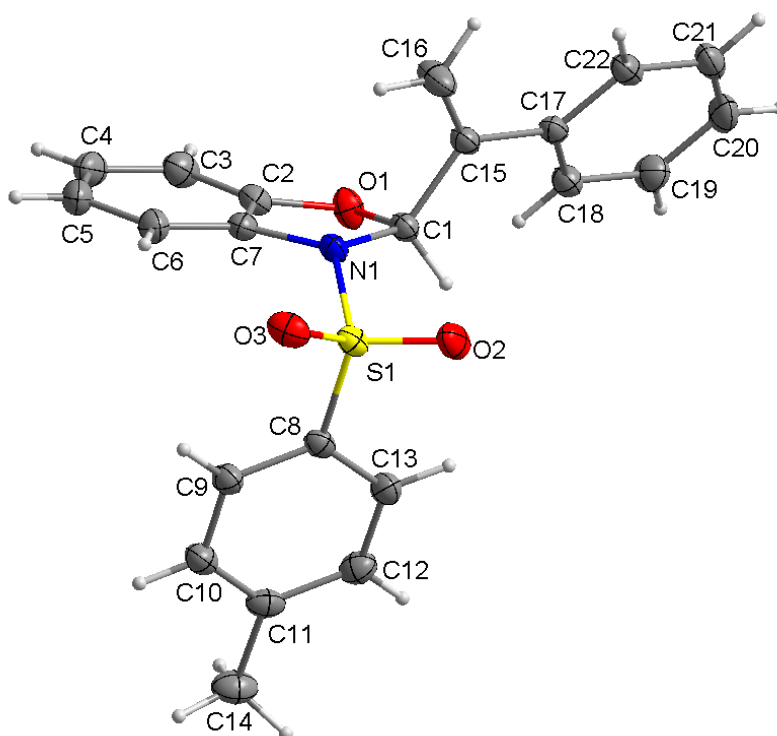
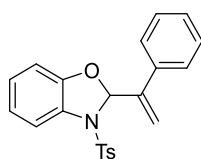
X-Ray Crystallographic Analysis

Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX2 ULTRA and an APEX II CCD area detector with a multilayer-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2.³³ All of the calculations for the structure determination were carried out using the SHELXTL package.³⁴ All non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms.

X-Ray Crystallographic Data of 2o

Recrystallization of **2o** from EtOAc was undertaken for X-ray analysis.

Thermal ellipsoids are shown at the 50% probability level.



CCDC 2128320 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

³³ APEX2 (Version 2009.1–0) Data Collection and Processing Software; Bruker AXS Inc.: Madison, Wisconsin, U.S.A., 2008.

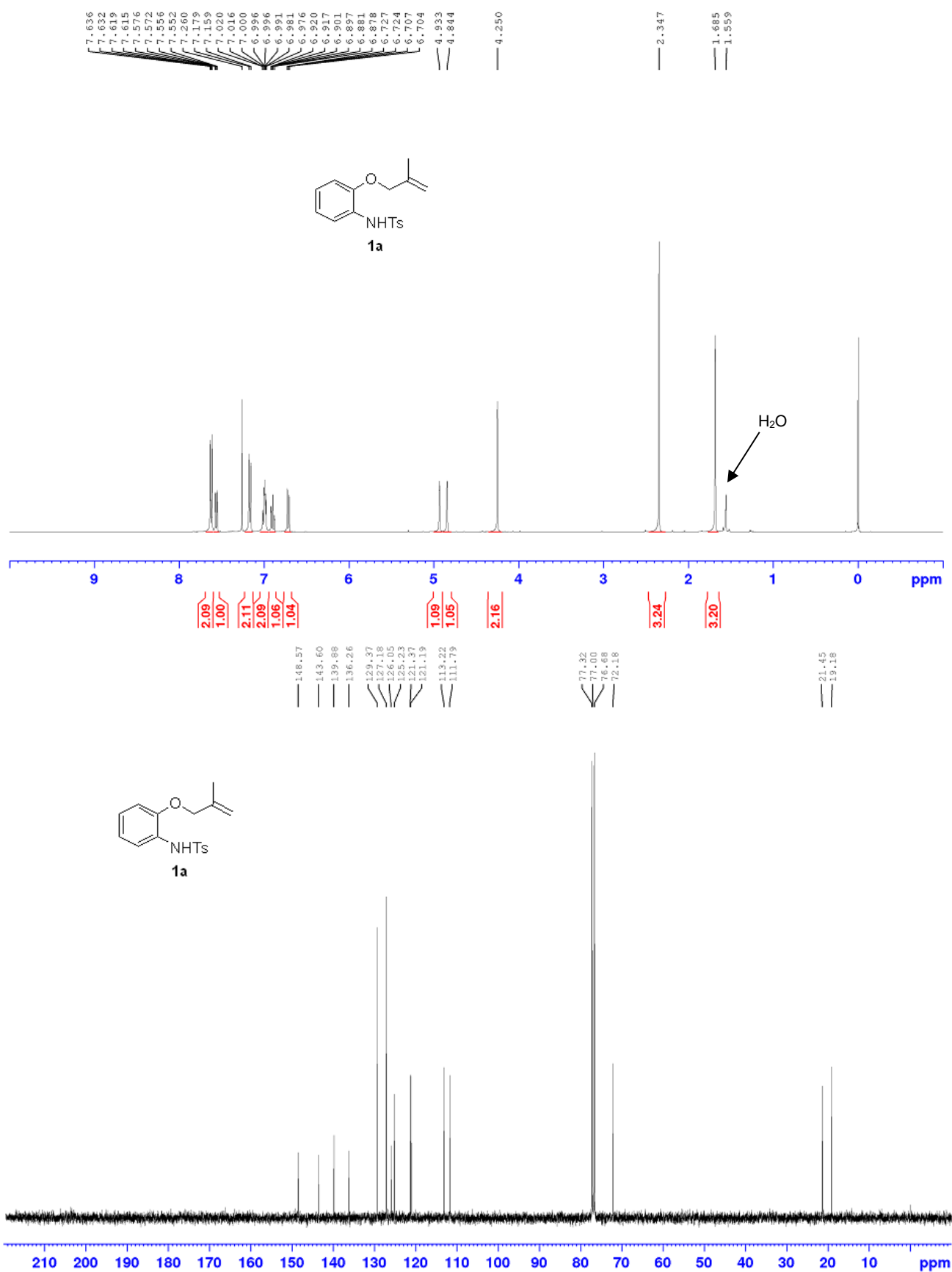
³⁴ SHELXTL-PC (Version 6.22) Program for Solution and Refinement of Crystal Structures; Bruker AXS Inc.: Madison, Wisconsin, U.S.A., 2001.

Table S1. Crystal data and structure refinement for **2o**.

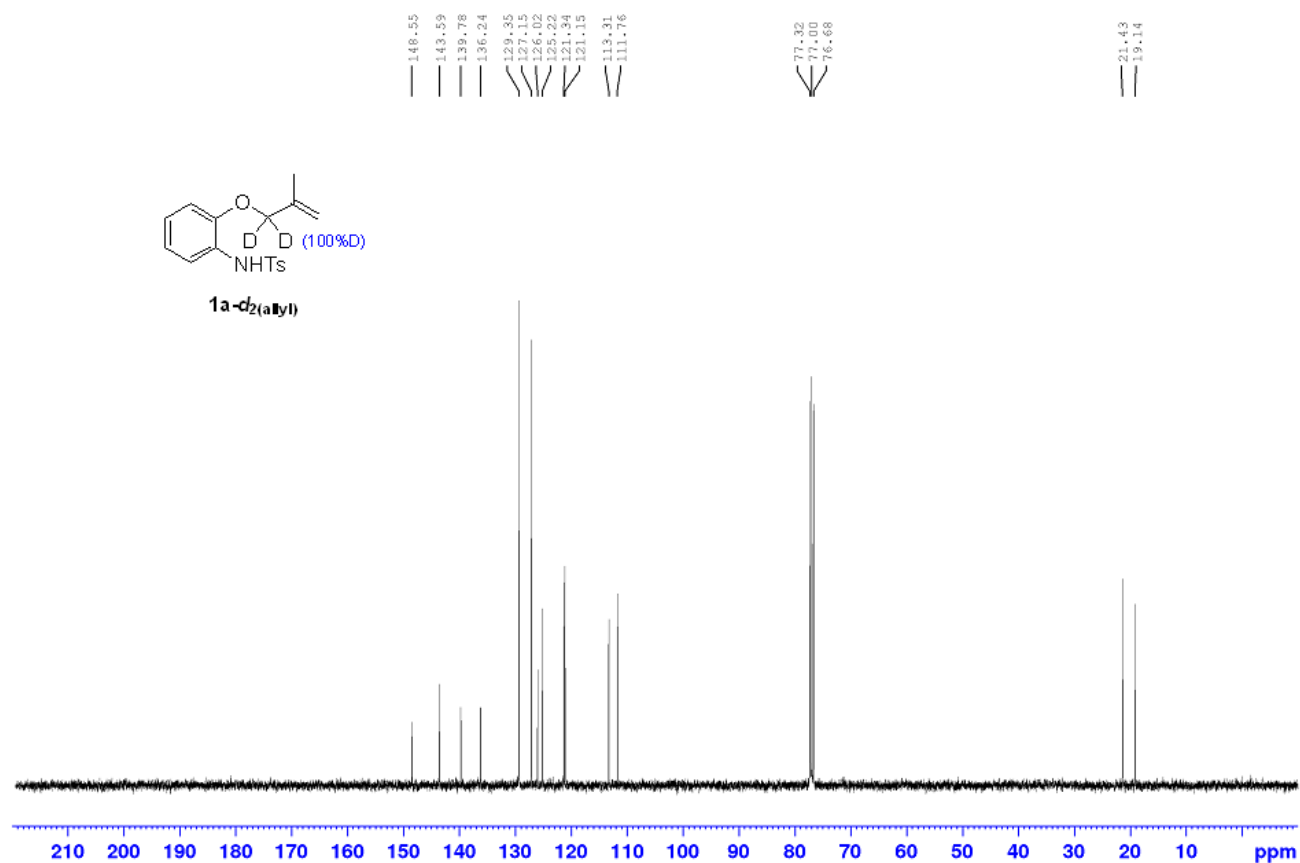
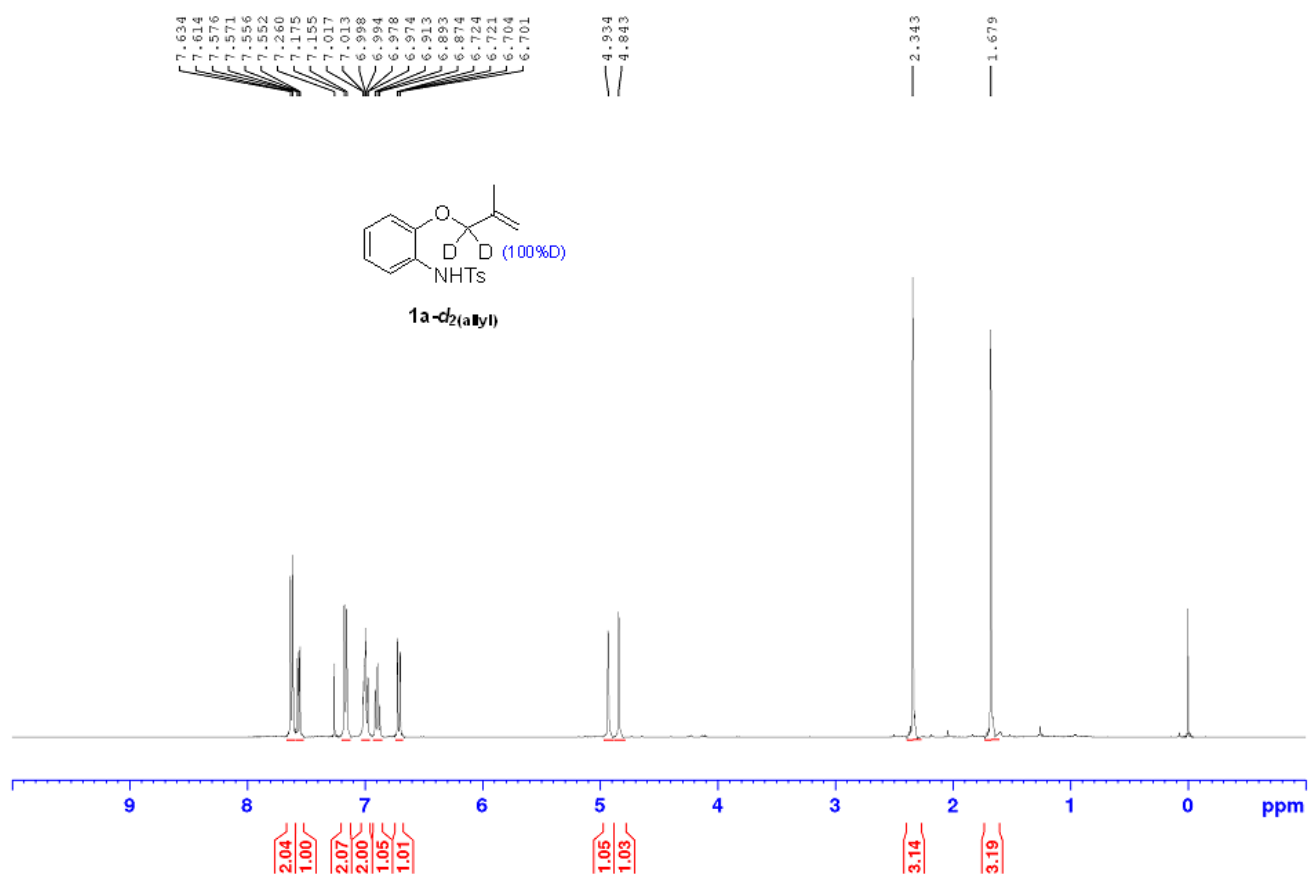
Identification code	2o	
Empirical formula	C ₂₂ H ₁₉ N O ₃ S	
Formula weight	377.44	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.8166(2) Å b = 8.4459(2) Å c = 14.4040(3) Å	a = 98.1198(10)°. b = 90.3030(9)°. g = 105.9760(9)°.
Volume	904.06(4) Å ³	
Z	2	
Density (calculated)	1.387 Mg/m ³	
Absorption coefficient	0.202 mm ⁻¹	
F(000)	396	
Crystal size	0.419 x 0.382 x 0.248 mm ³	
Theta range for data collection	1.430 to 28.316°.	
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19	
Reflections collected	16753	
Independent reflections	4494 [R(int) = 0.0247]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7457 and 0.7004	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4494 / 0 / 246	
Goodness-of-fit on F ²	1.038	
Final R indices [I > 2σ(I)]	R1 = 0.0351, wR2 = 0.0951	
R indices (all data)	R1 = 0.0383, wR2 = 0.0979	
Extinction coefficient	0.031(3)	
Largest diff. peak and hole	0.318 and -0.322 e.Å ⁻³	

Copies of NMR Spectra

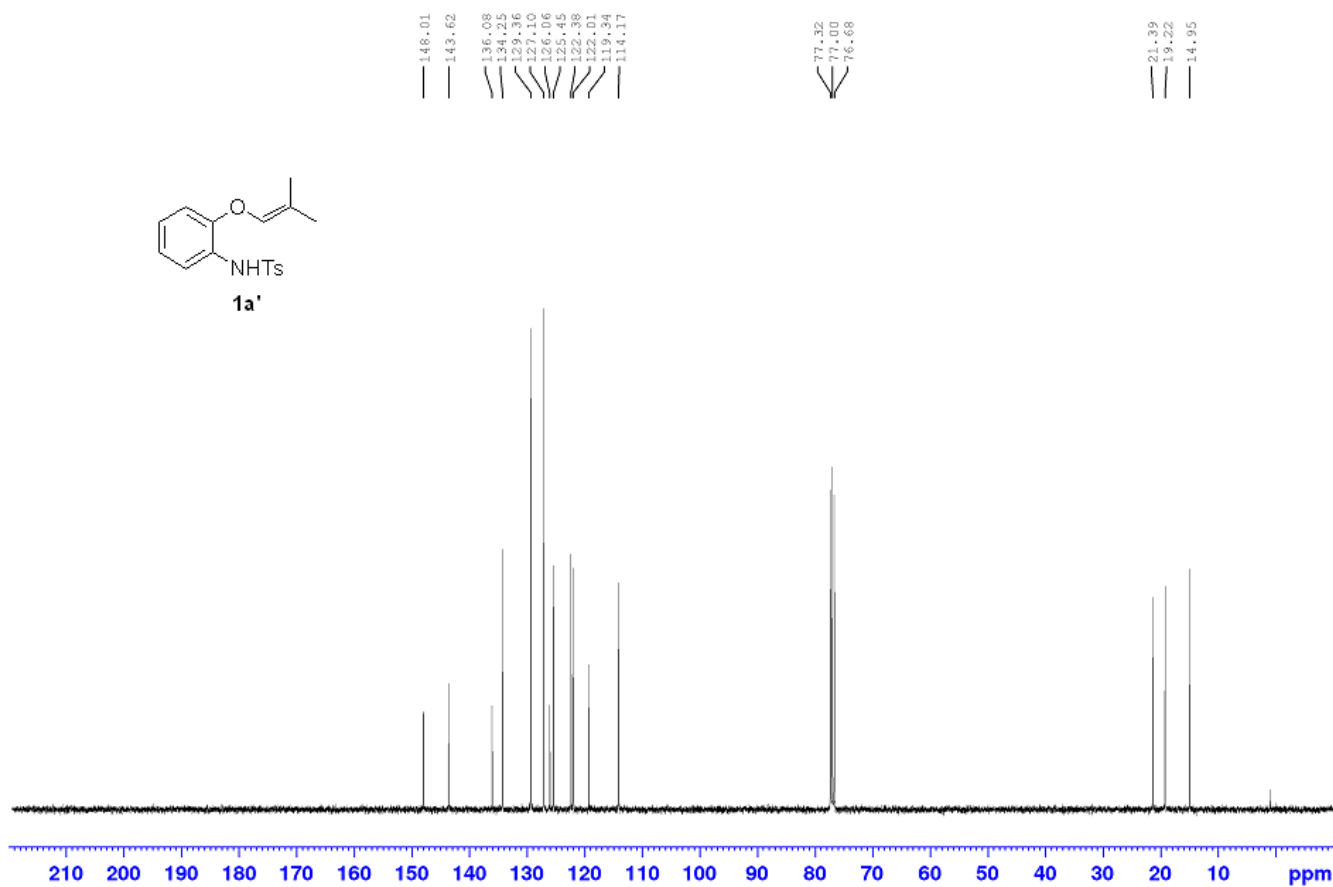
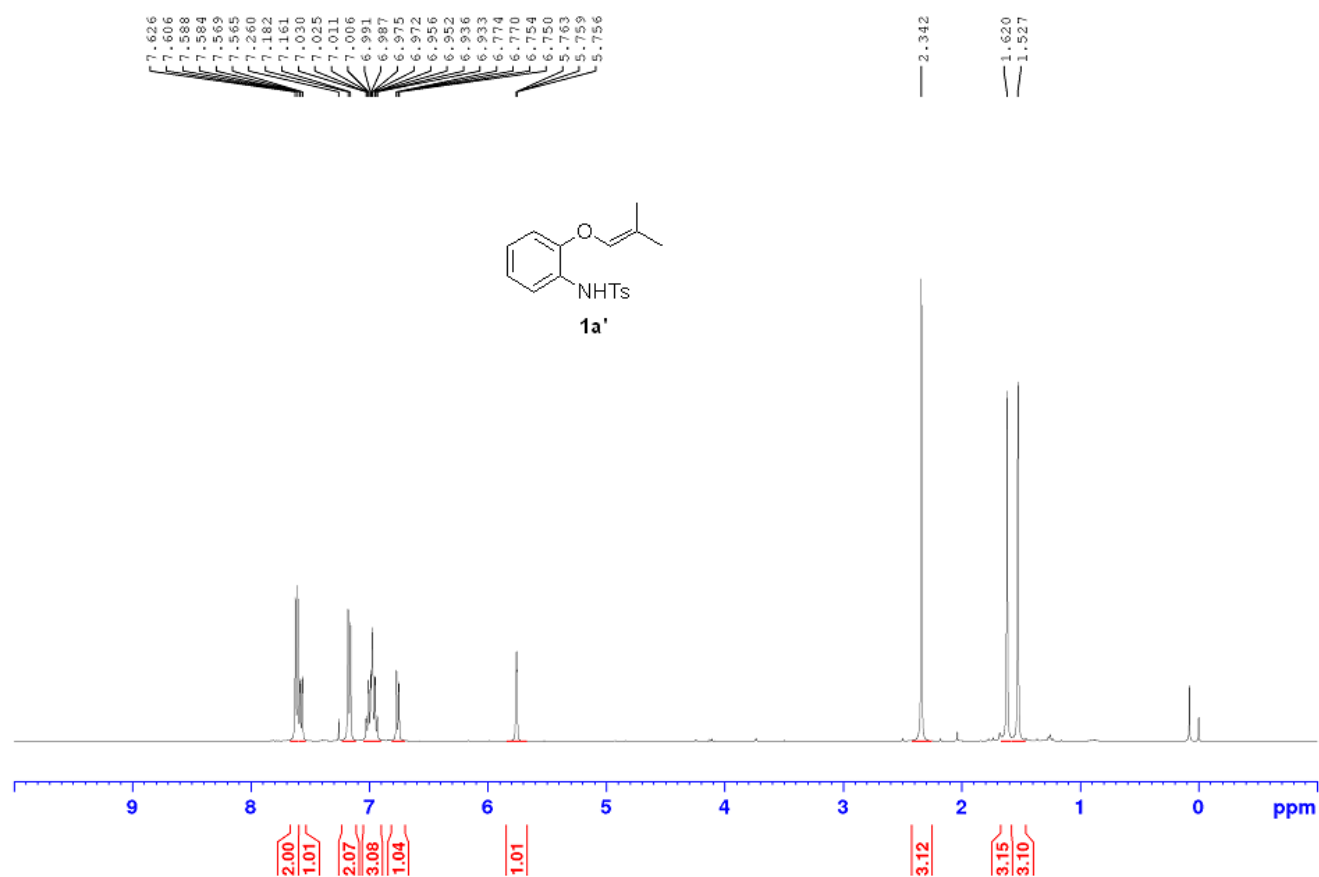
N-Ts-2-(Methallyloxy)aniline (**1a**) (in CDCl₃)



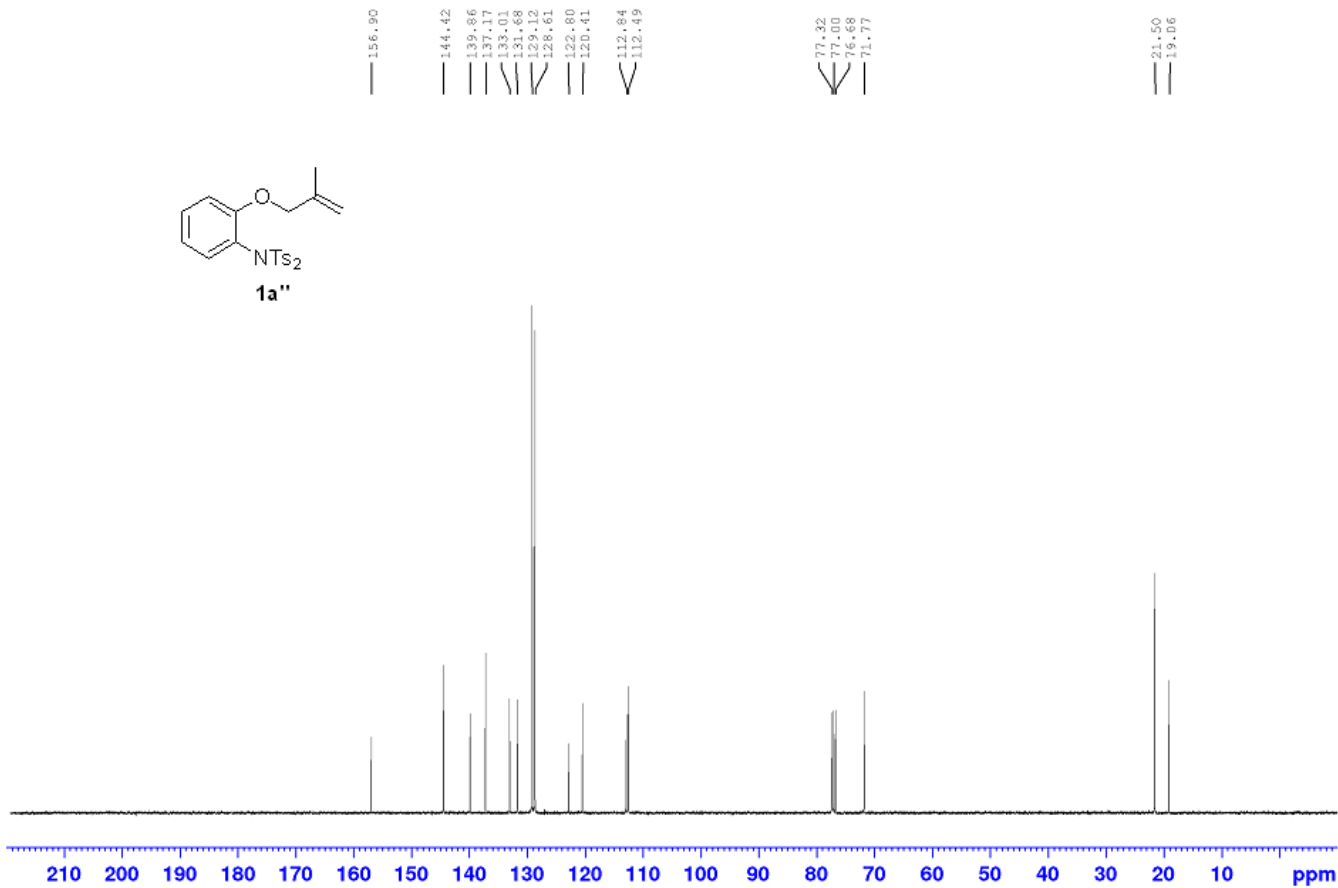
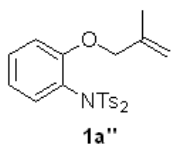
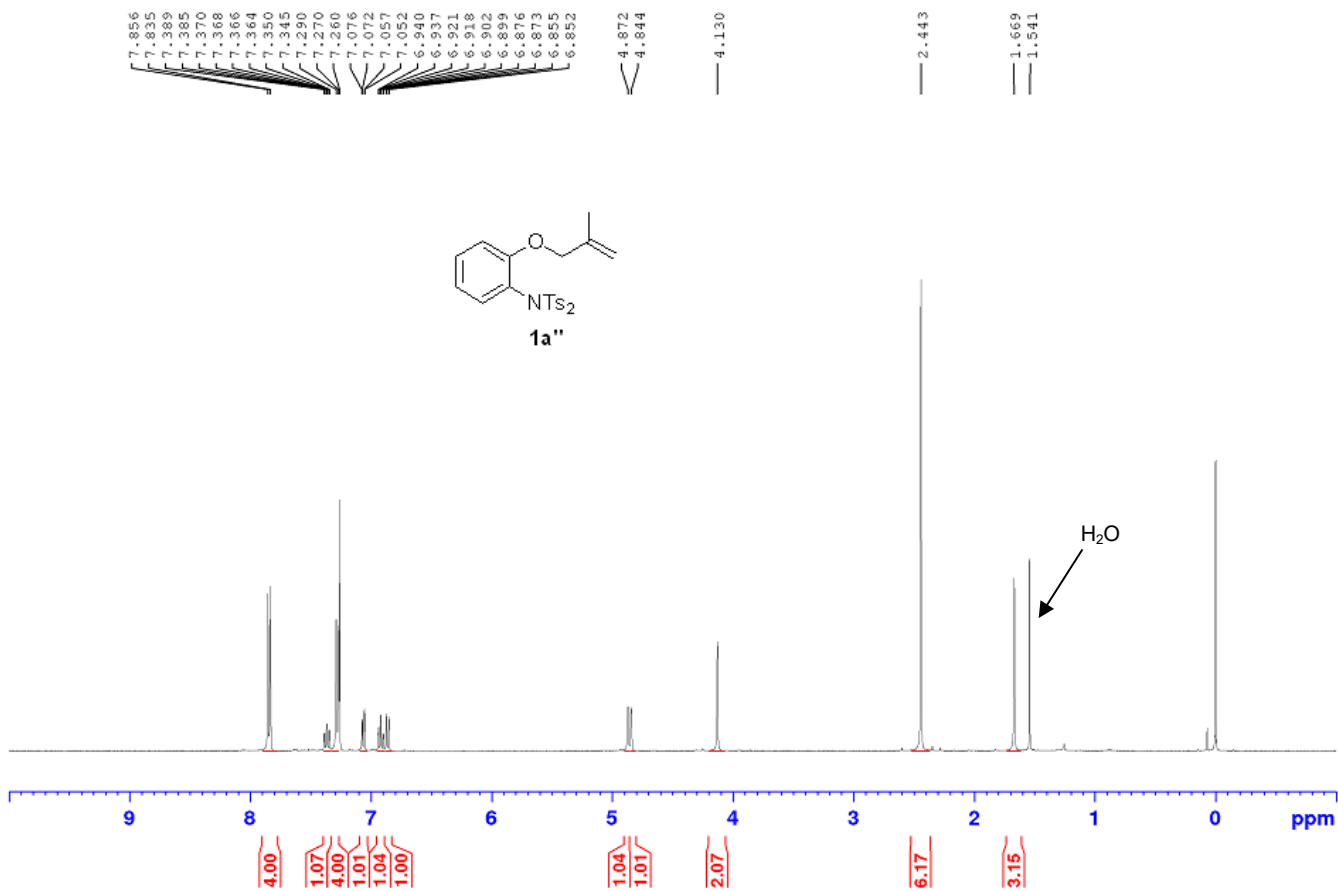
***N*-Ts-2-(Methallyloxy)aniline (**1a-d₂(allyl)**) (in CDCl₃)**



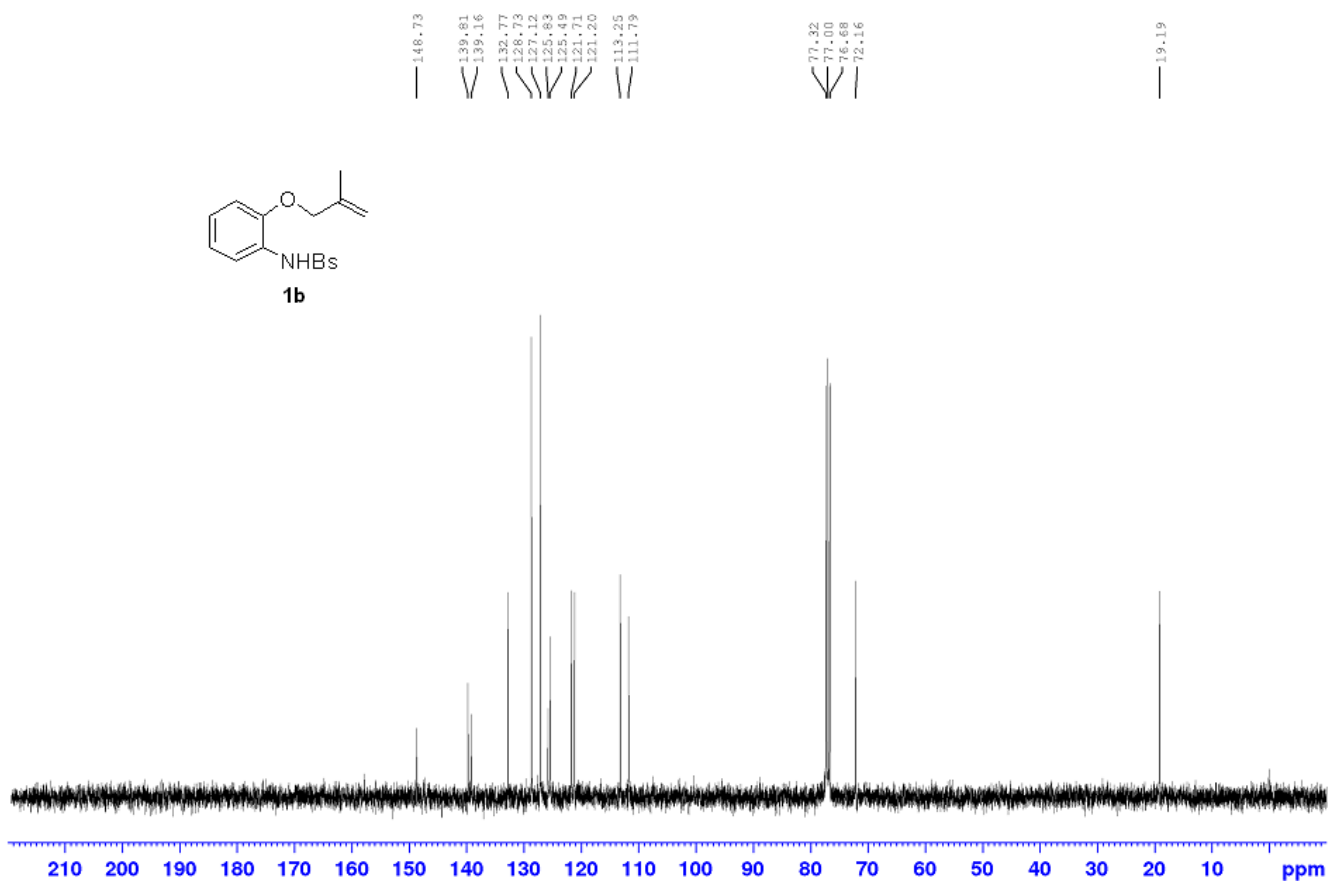
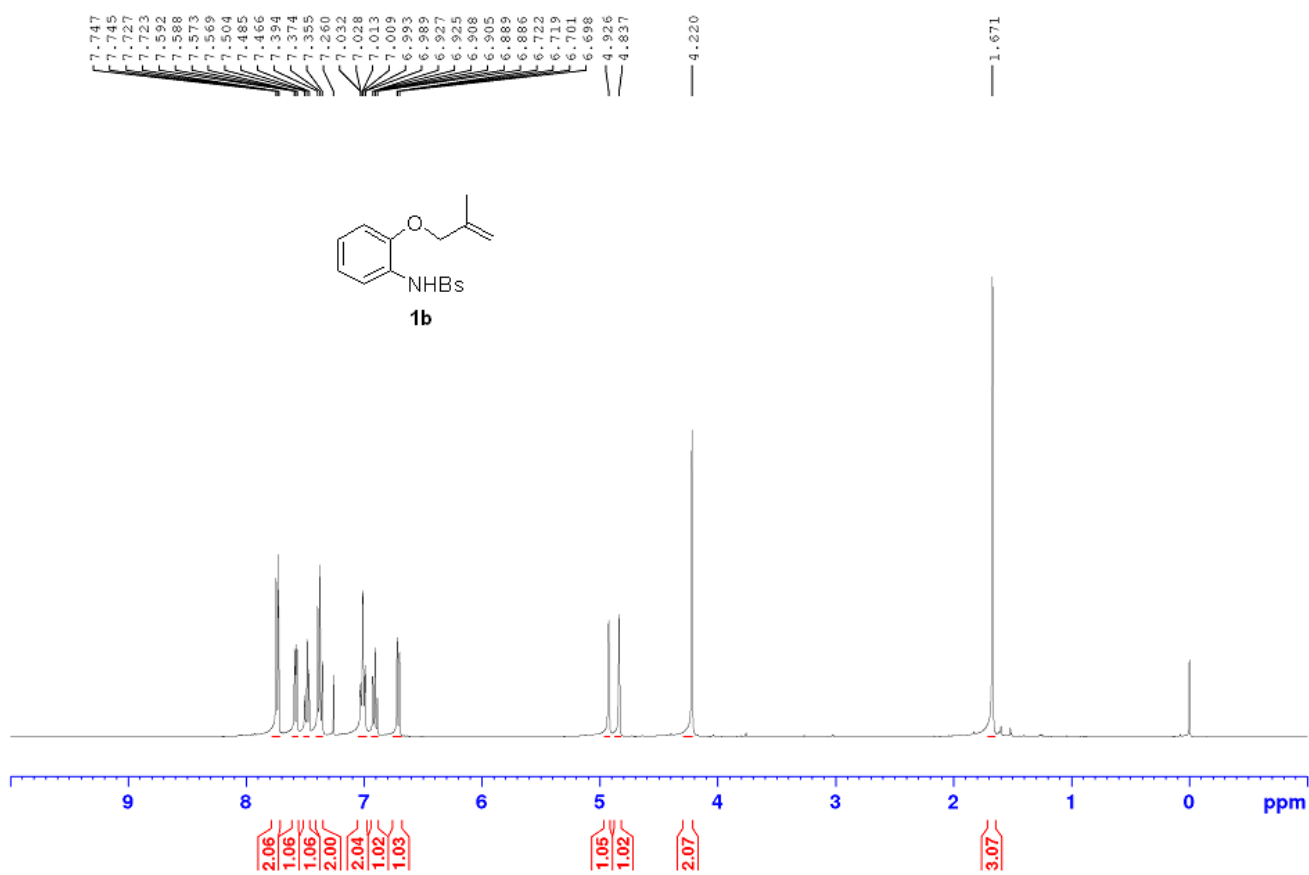
***N*-Ts-2-((Methylprop-1-en-1-yl)oxy)aniline (**1a'**) (in CDCl₃)**



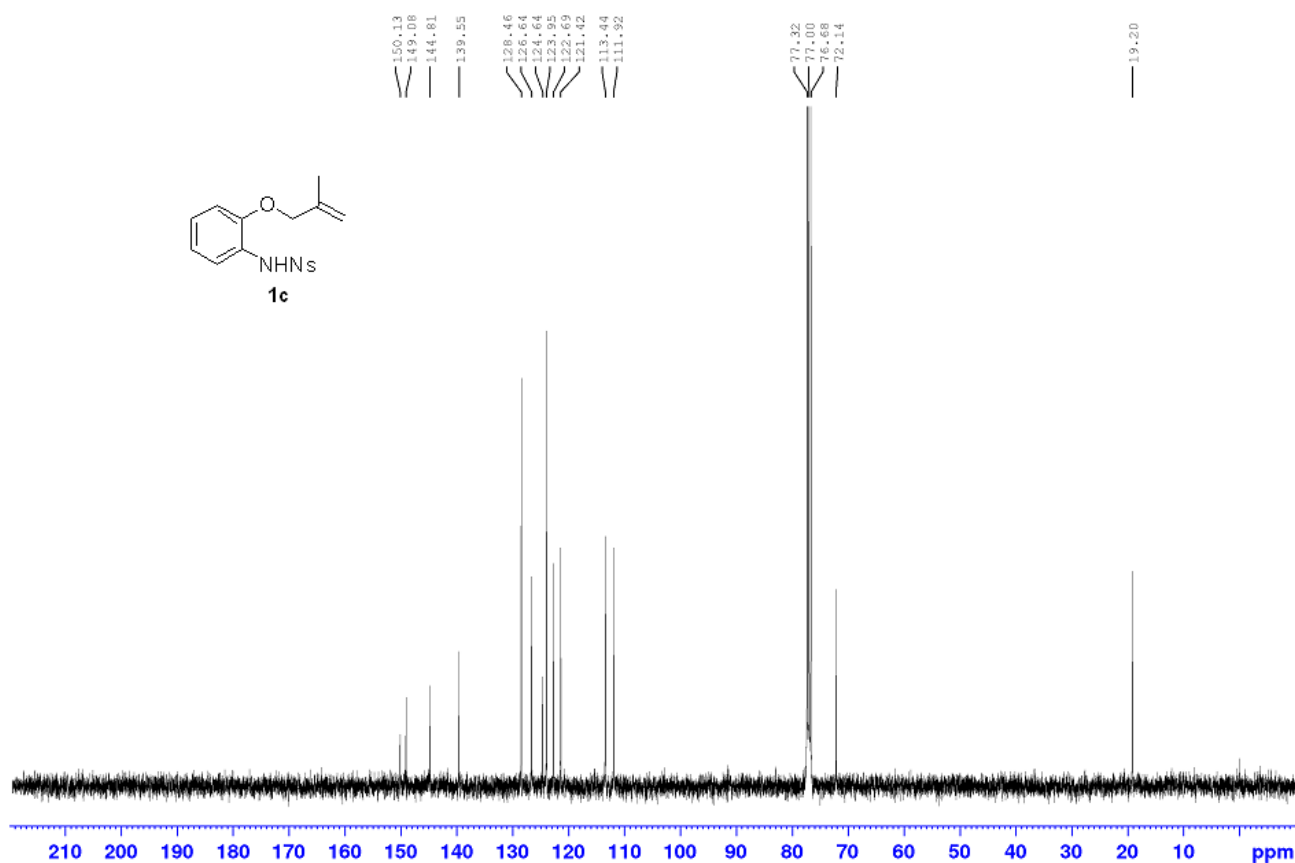
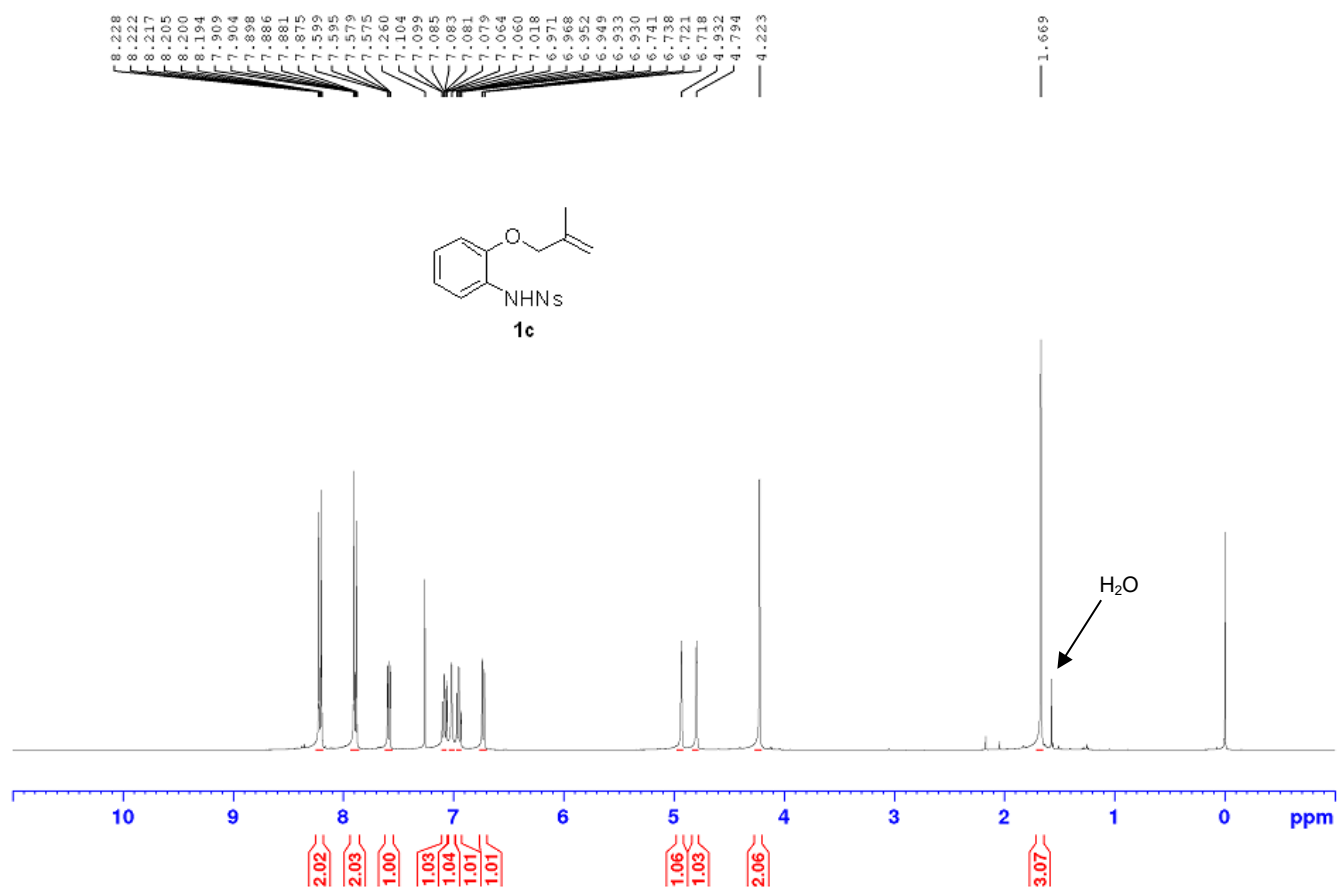
***N,N*-BisTs-2-(Methallyloxy)aniline (1a'')** (in CDCl₃)



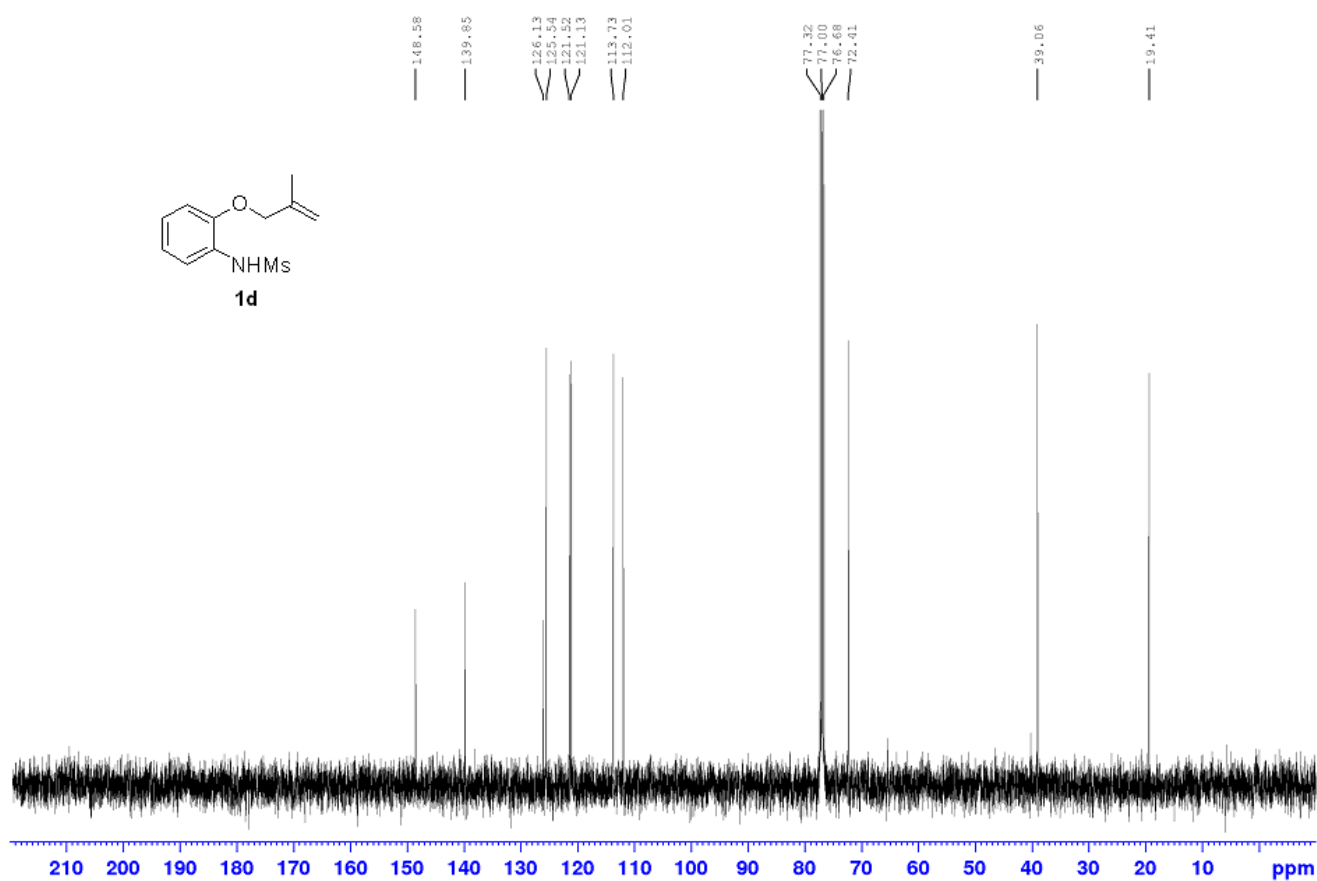
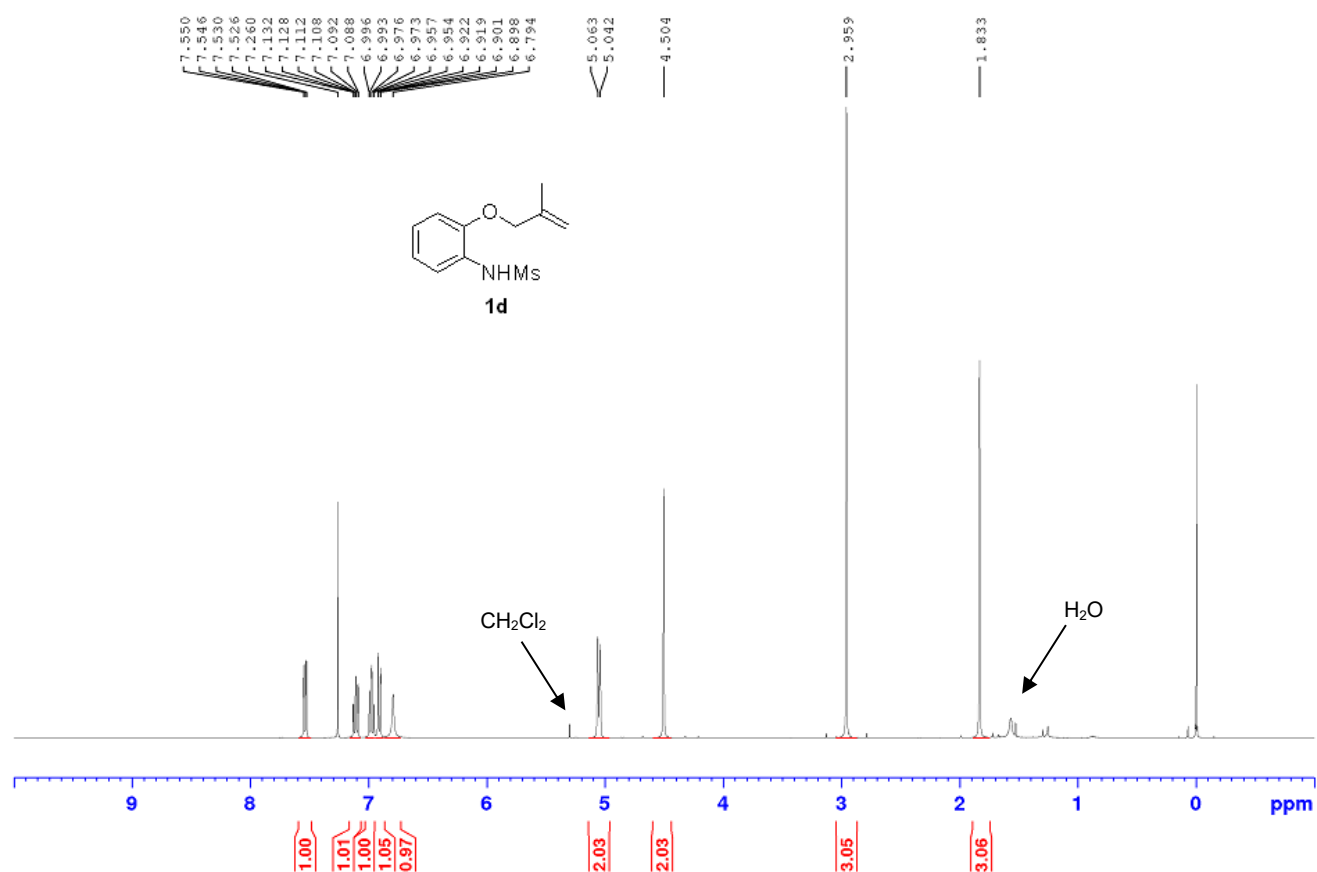
***N*-Bs-2-(Methallyloxy)aniline (**1b**) (in CDCl₃)**



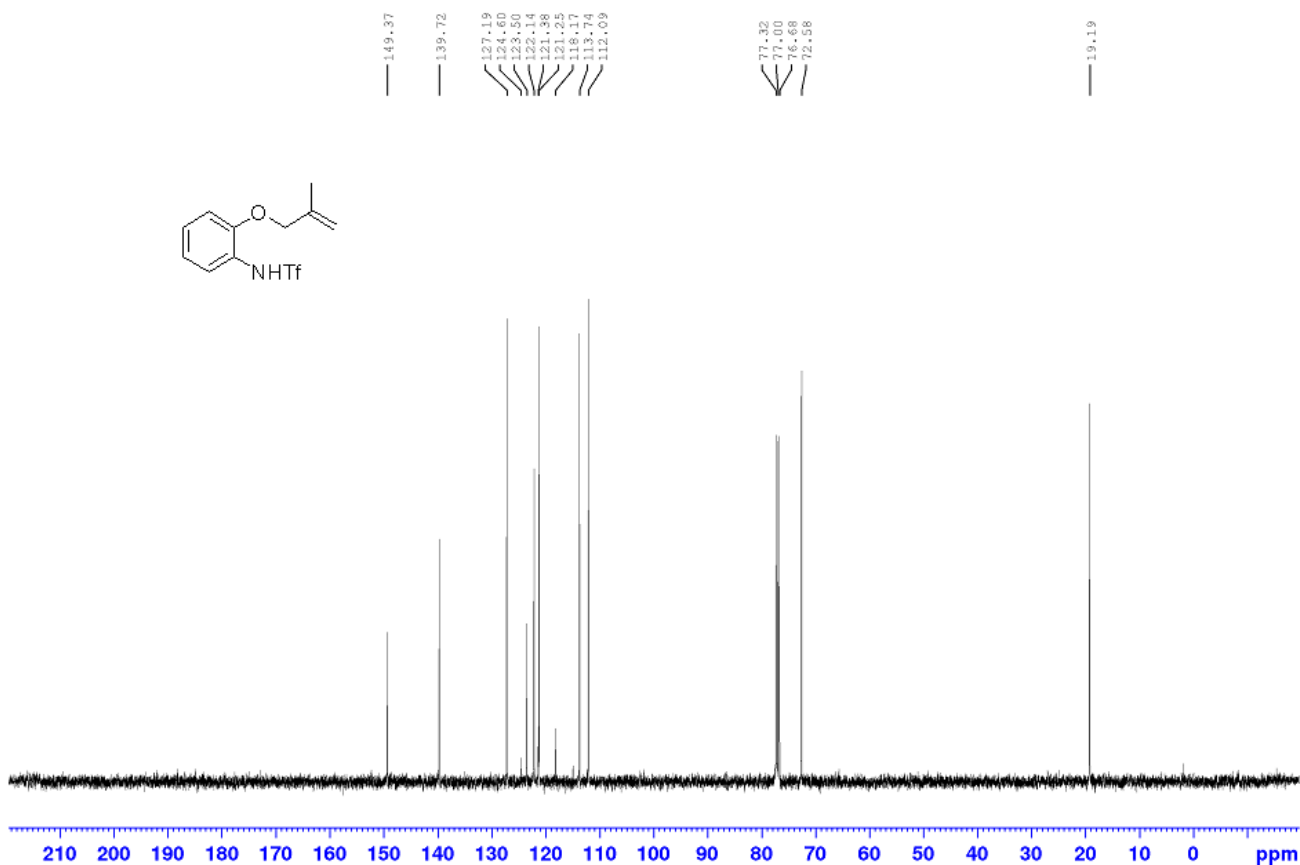
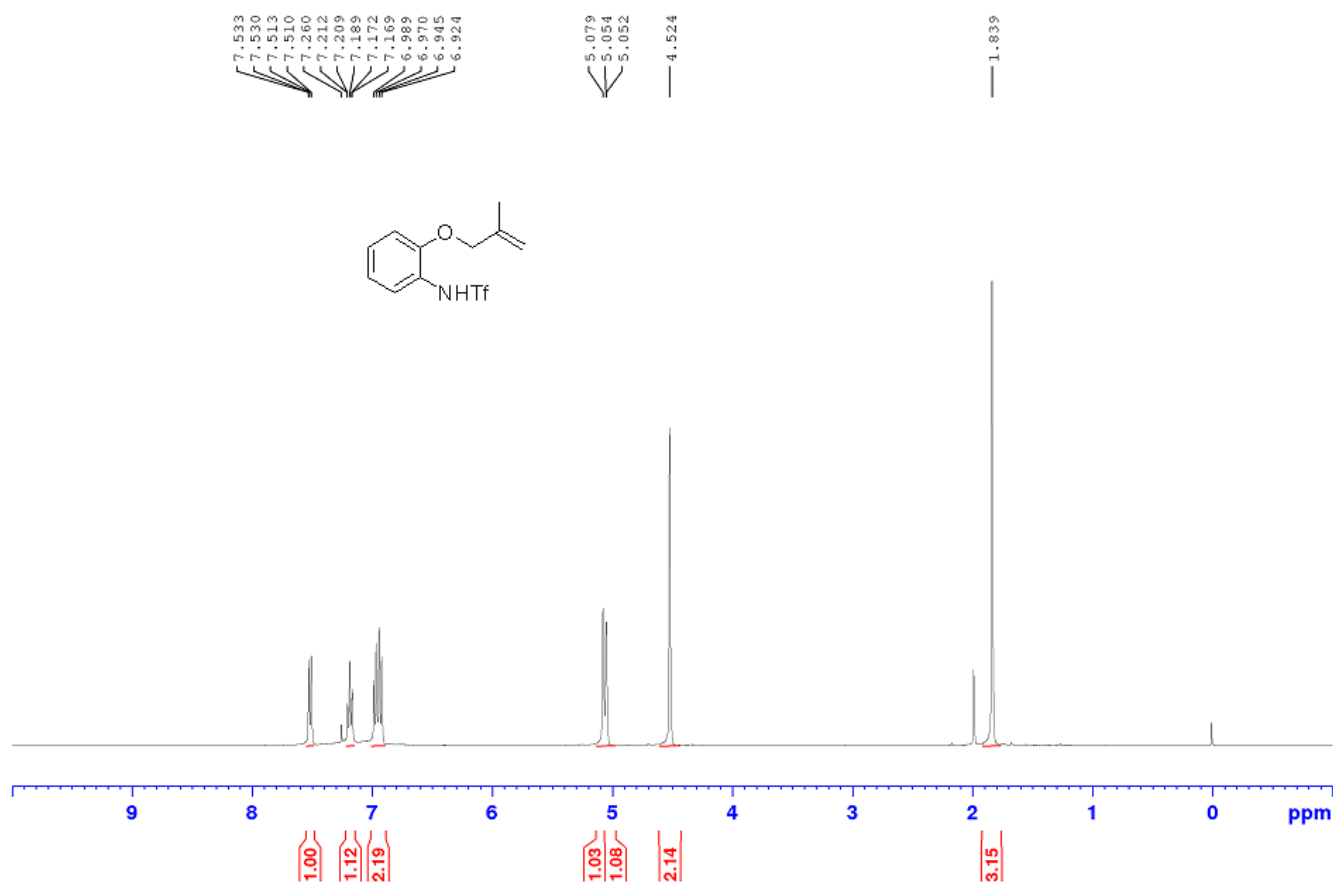
***N*-Ns-2-(Methallyloxy)aniline (1c) (in CDCl₃)**



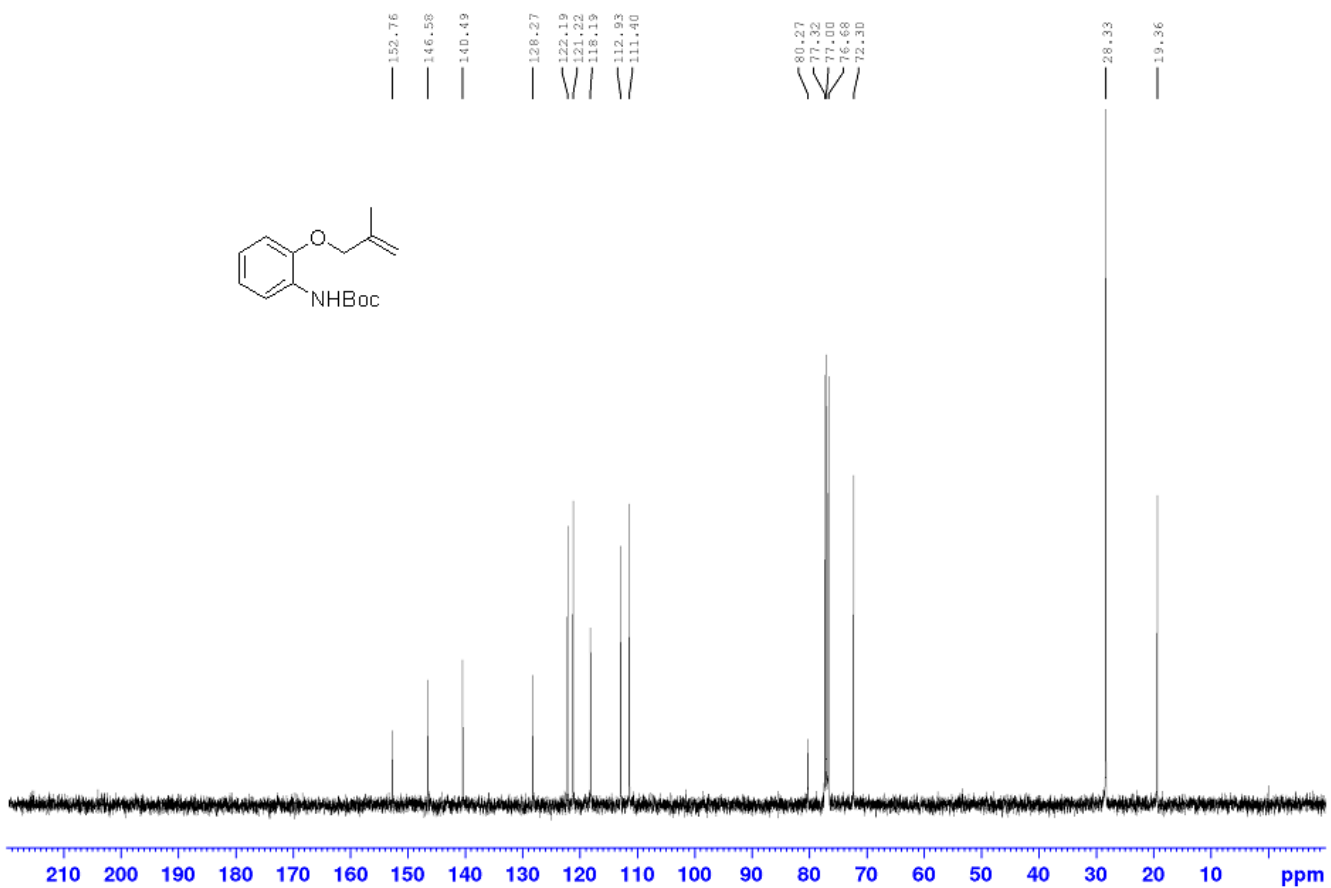
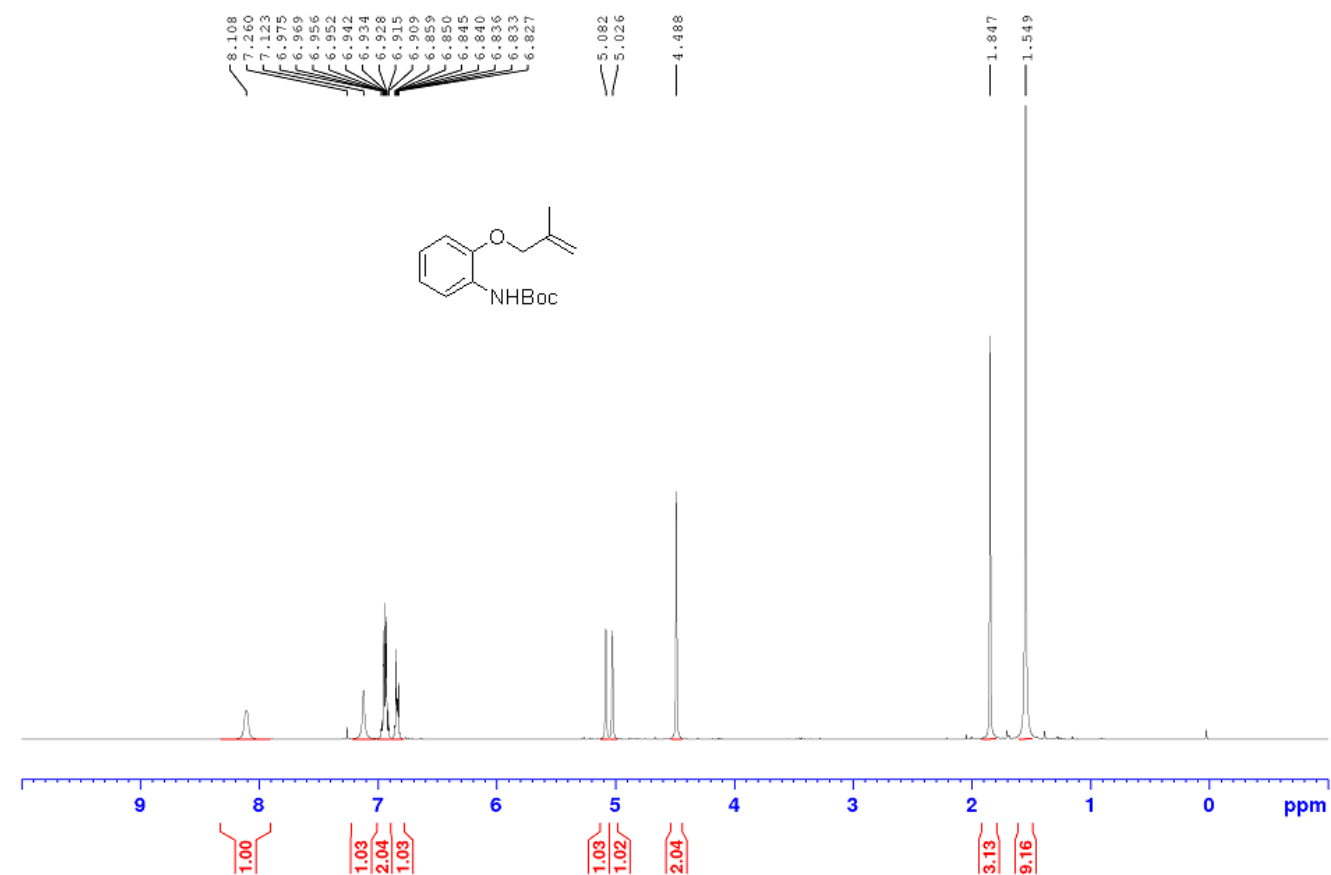
***N*-Ms-2-(Methallyloxy)aniline (**1d**) (in CDCl₃)**



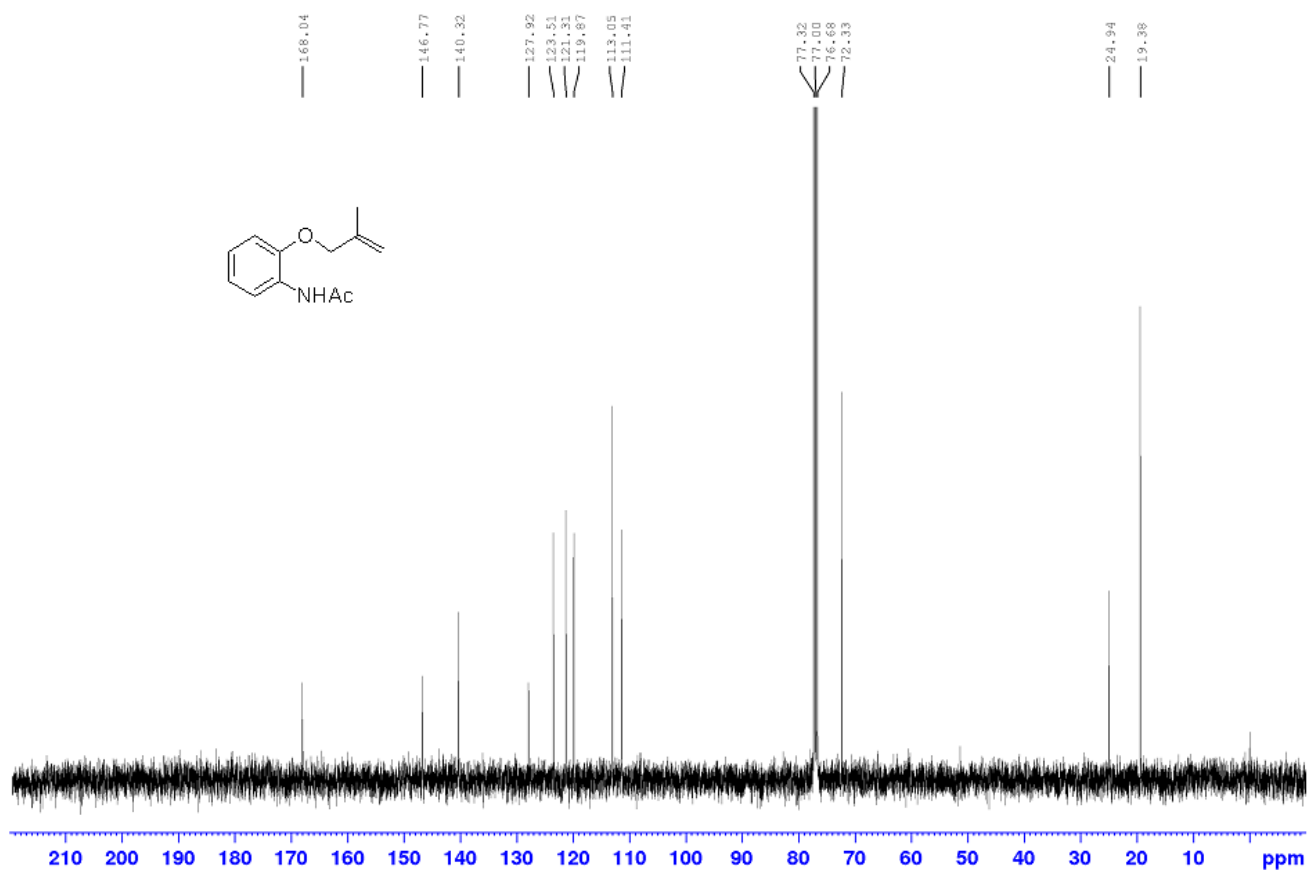
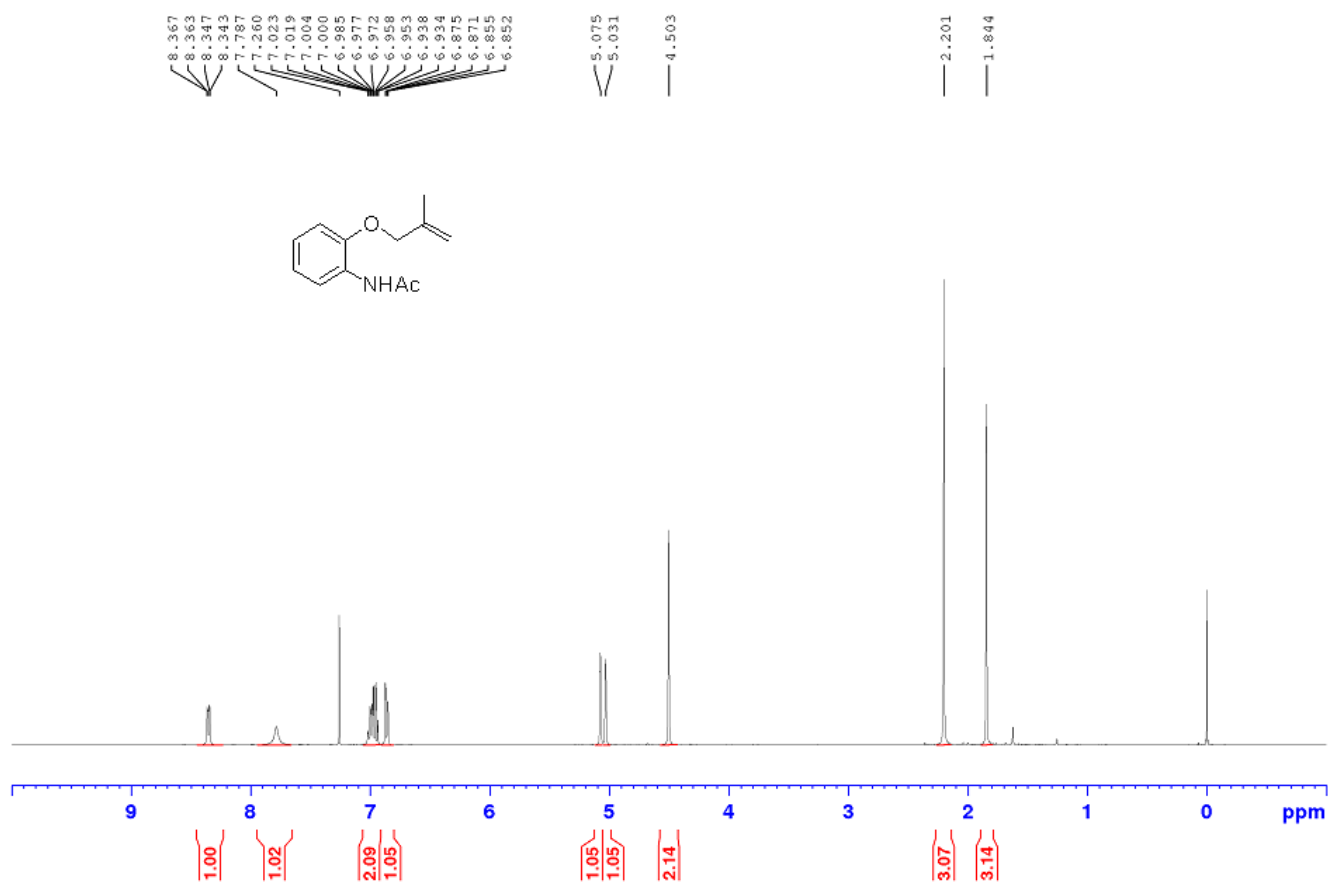
***N*-Tf-2-(Methallyloxy)aniline (in CDCl₃)**



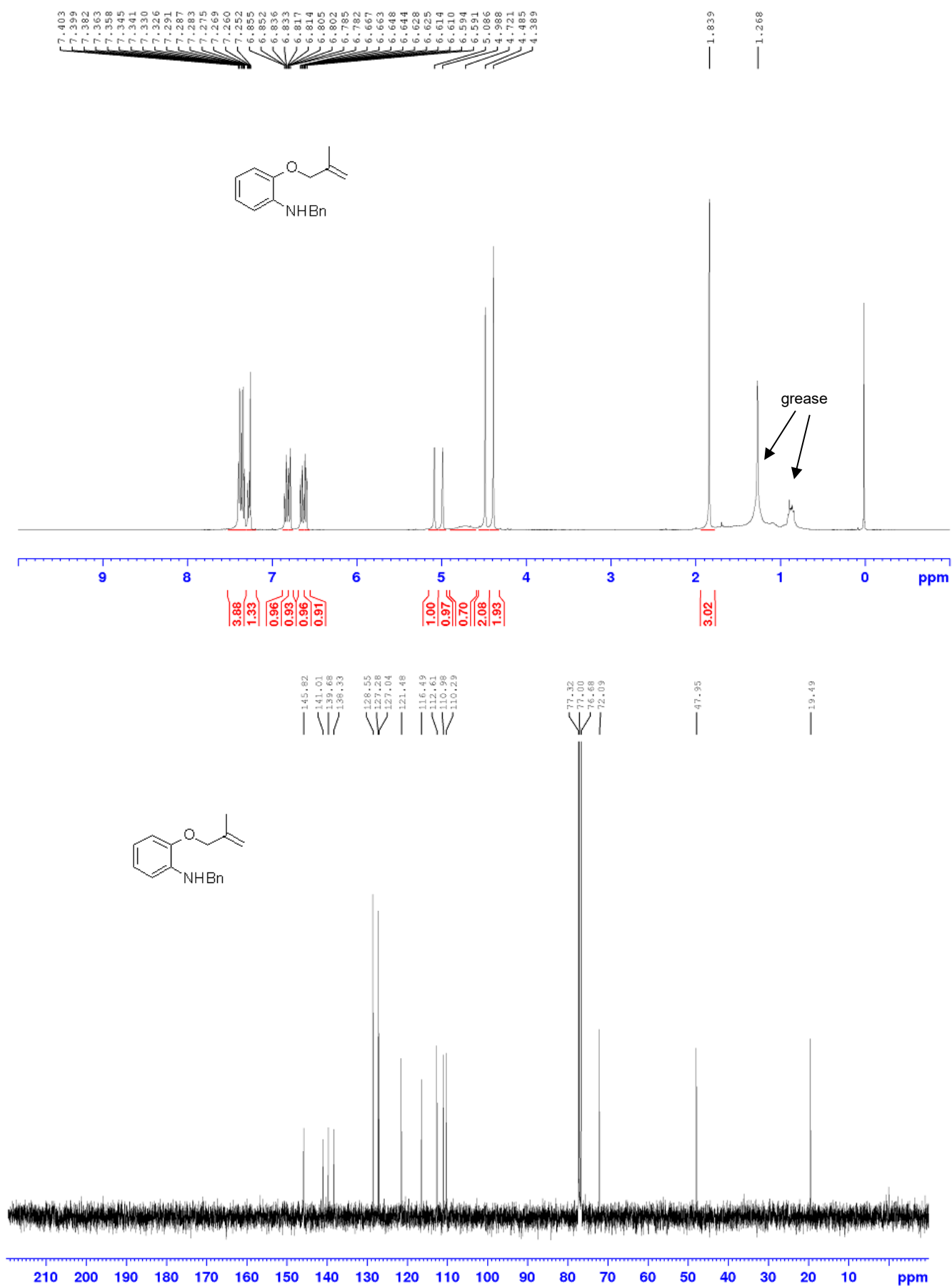
***N*-Boc-2-(Methallyloxy)aniline (in CDCl₃)**



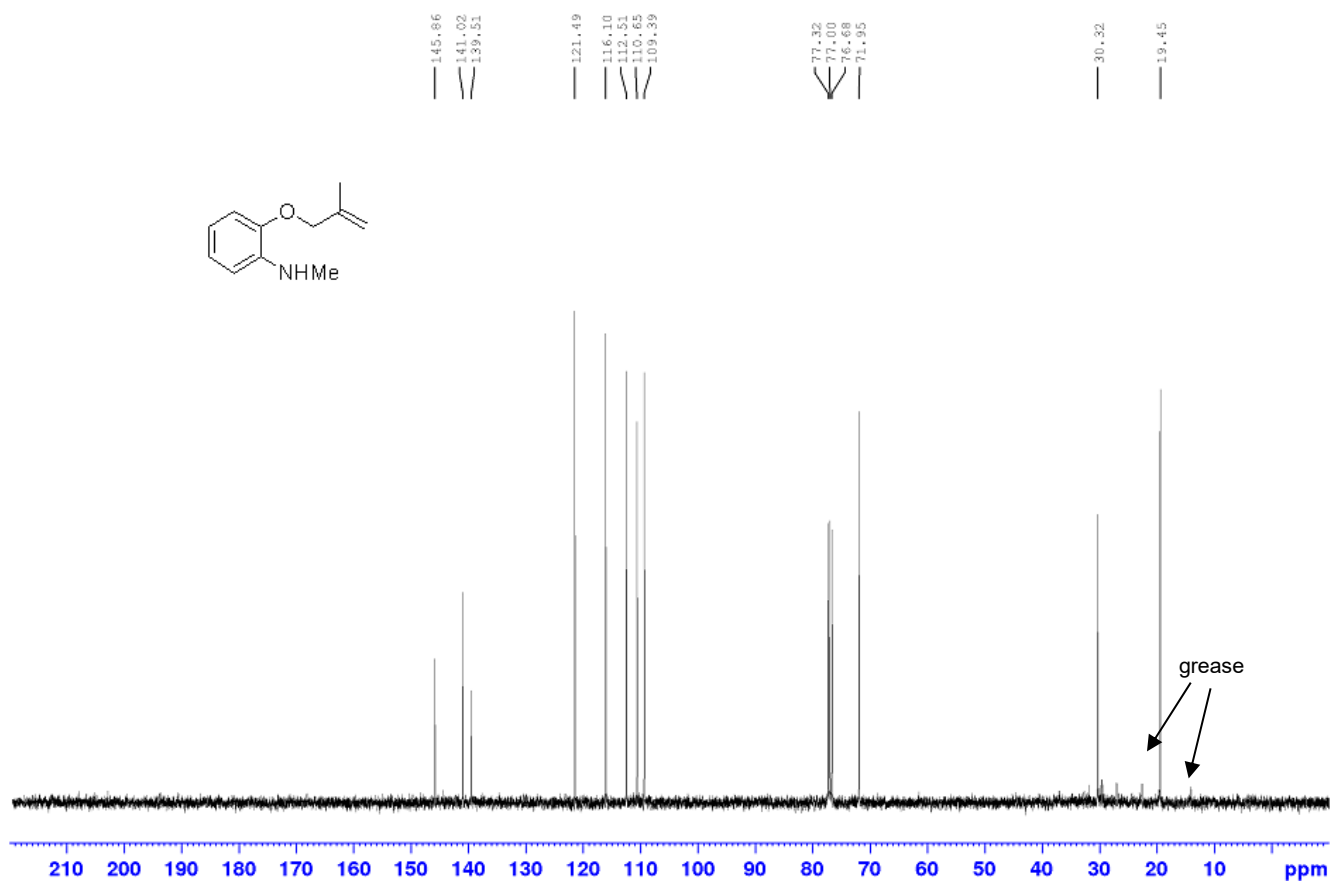
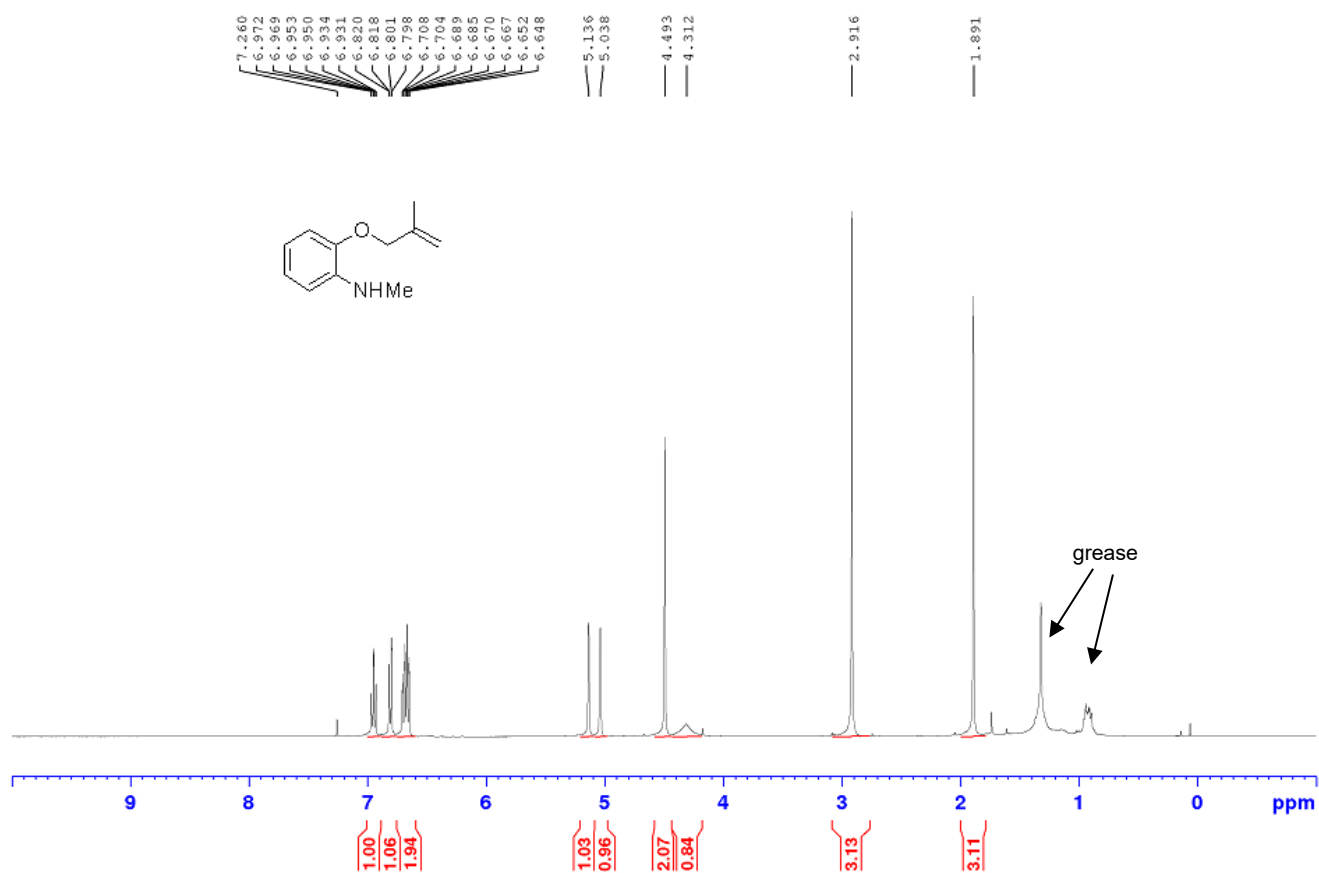
***N*-Ac-2-(Methallyloxy)aniline (in CDCl₃)**



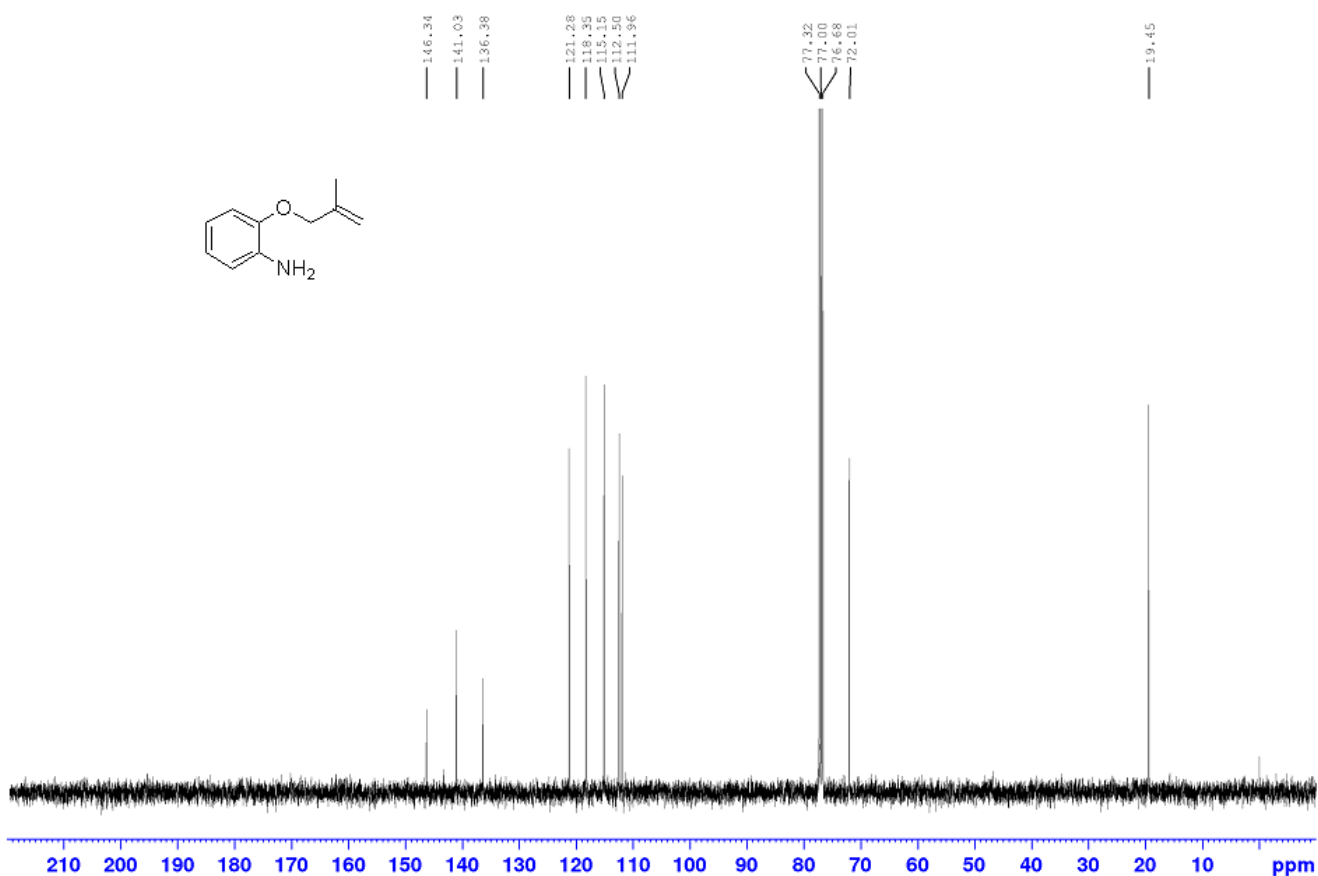
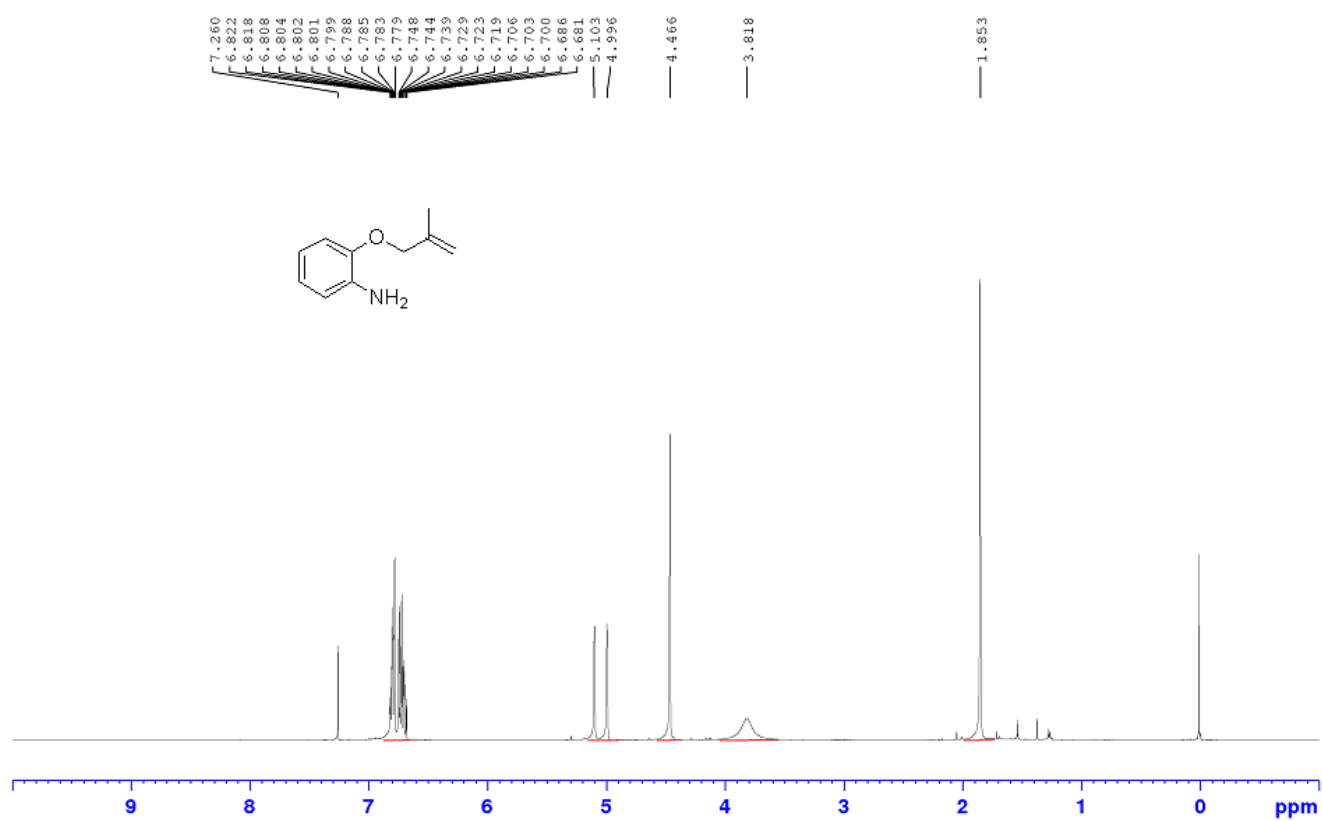
***N*-Bn-2-(Methallyloxy)aniline (in CDCl₃)**



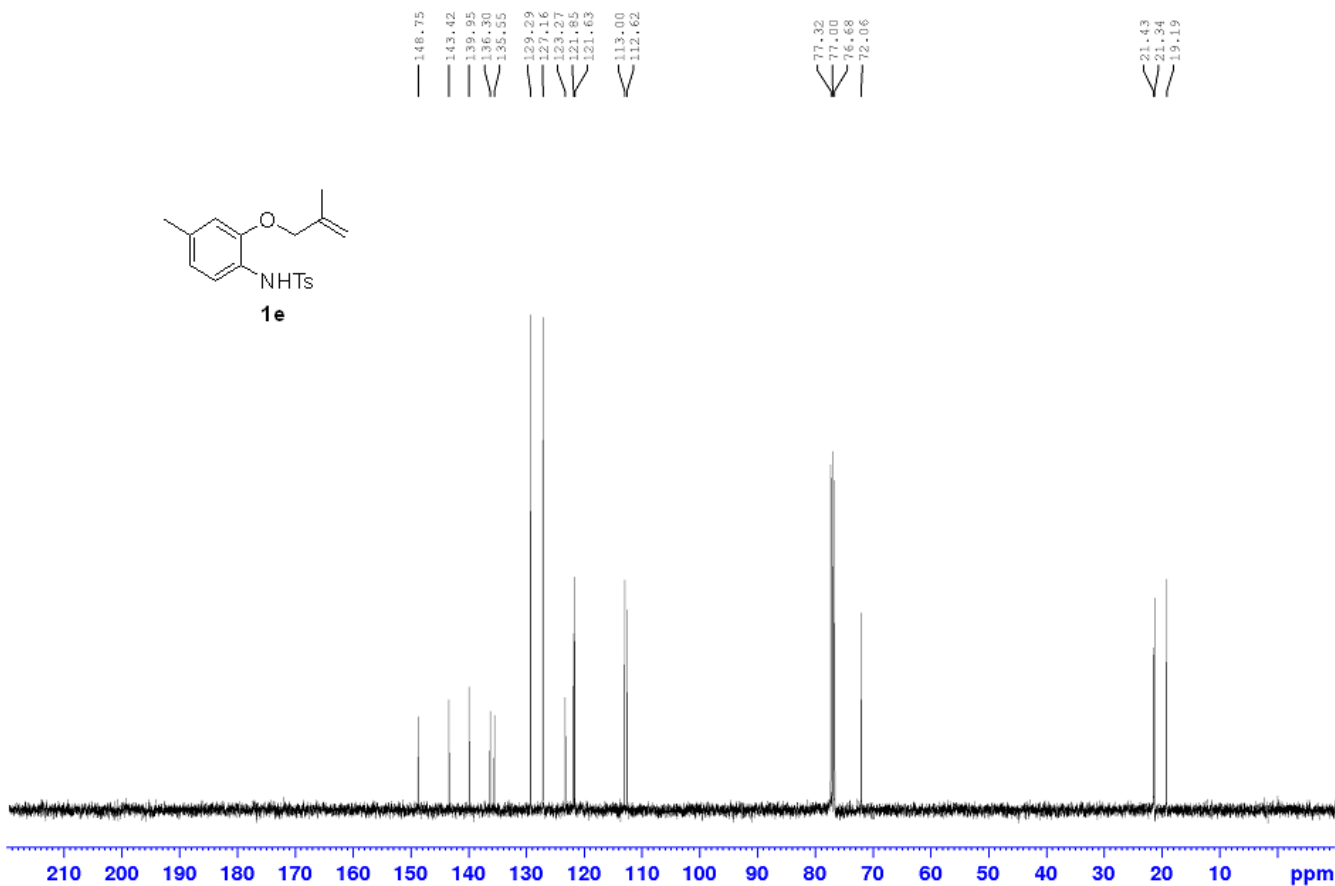
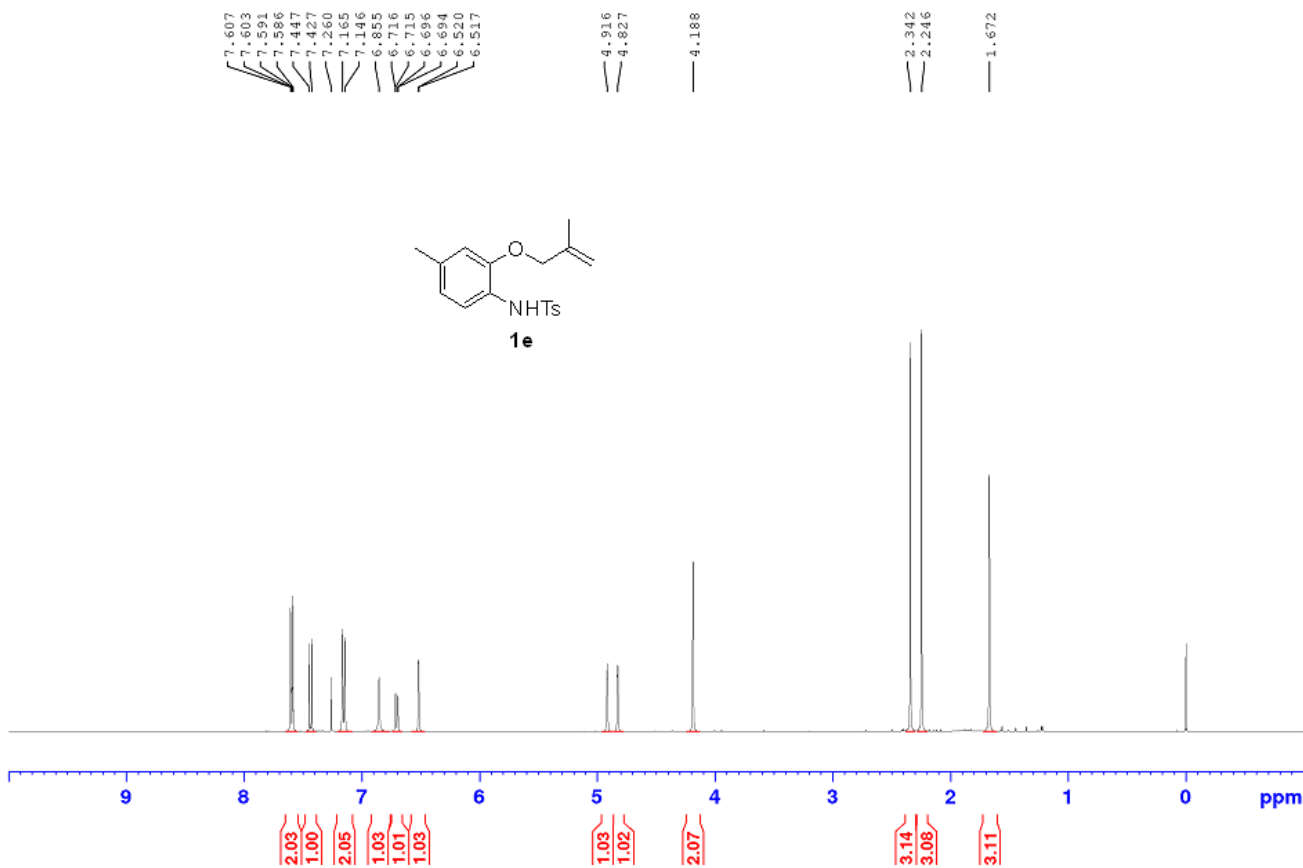
***N*-Me-2-(Methallyloxy)aniline (in CDCl₃)**



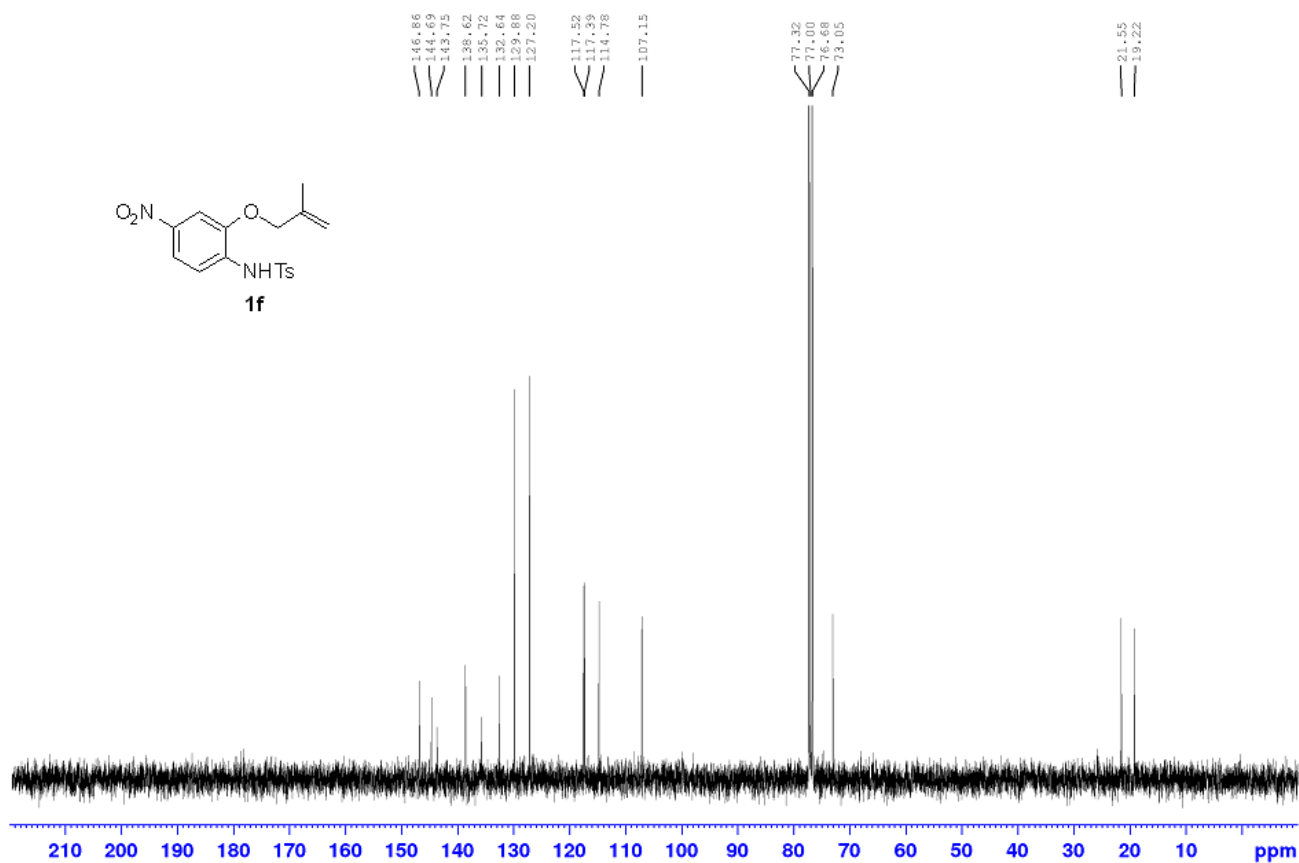
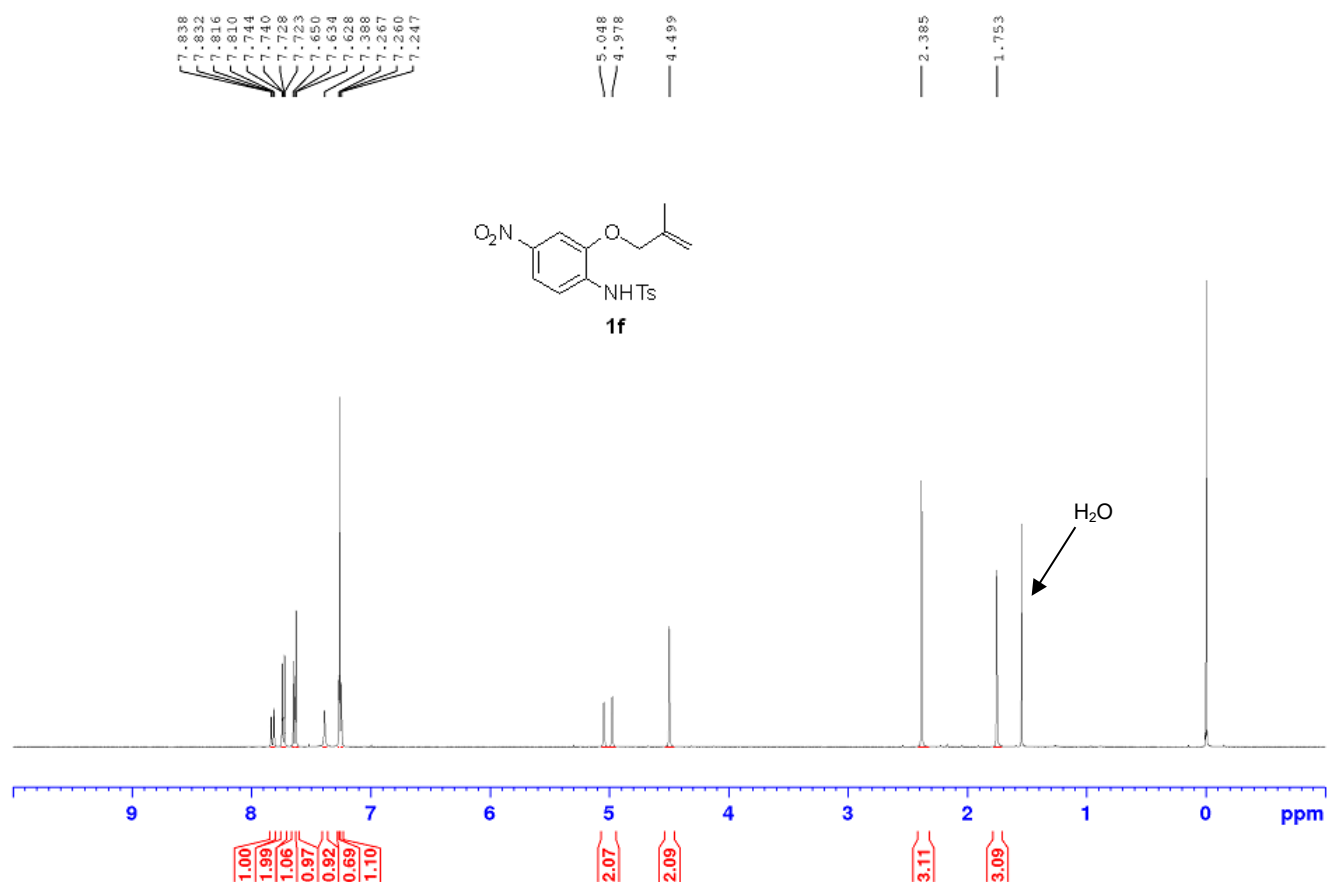
2-(Methallyloxy)aniline (in CDCl₃)



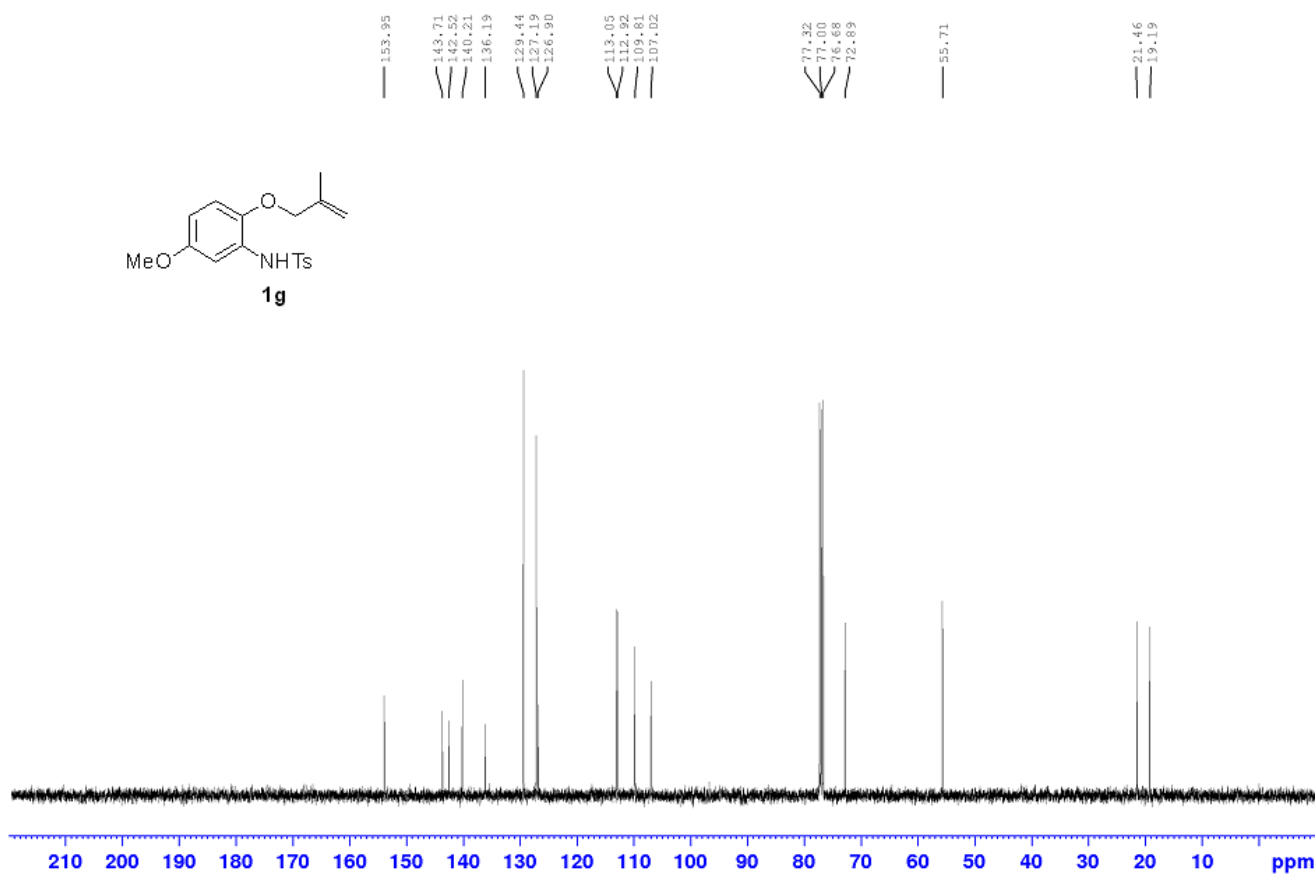
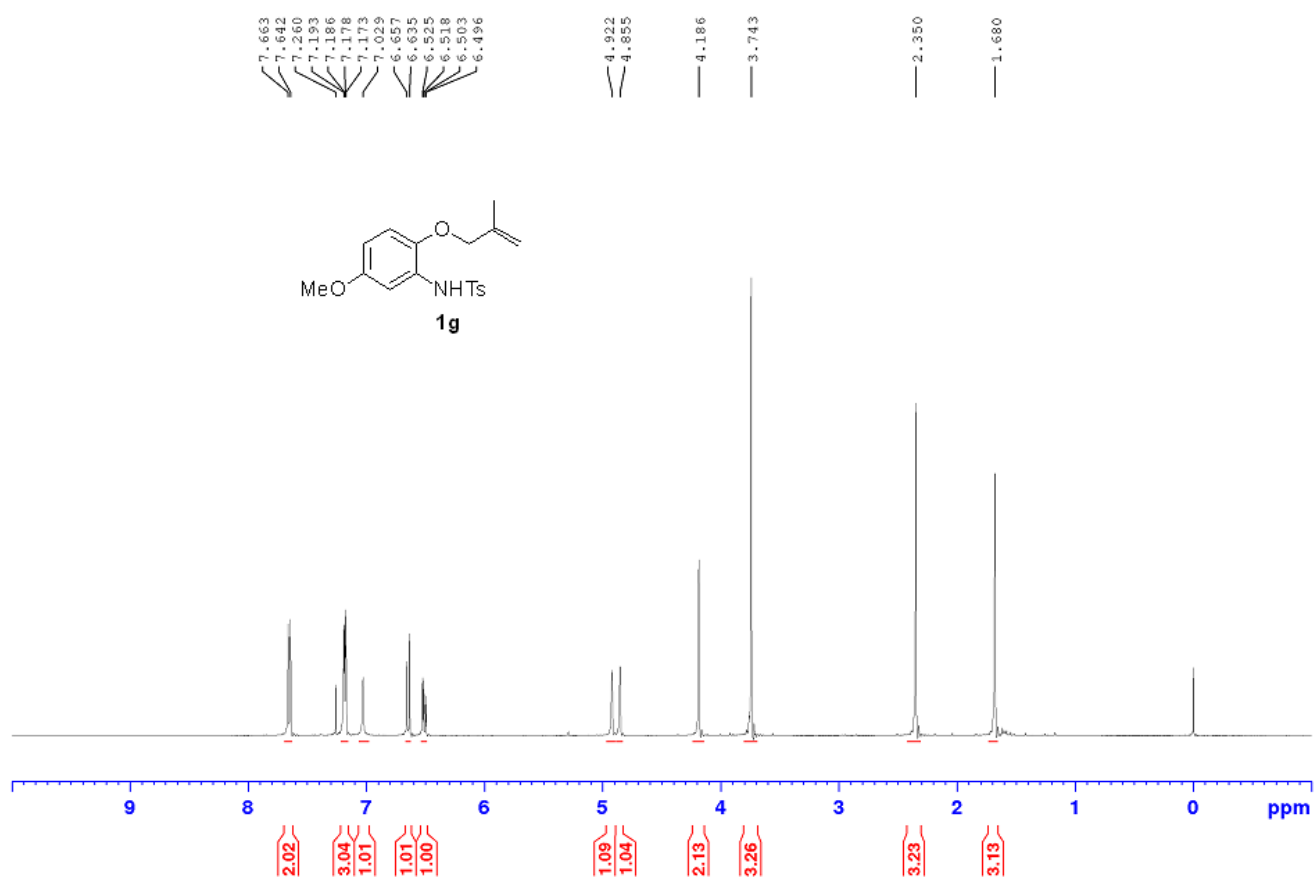
***N*-Ts-2-(Methallyloxy)-4-methylaniline (1e)** (in CDCl₃)



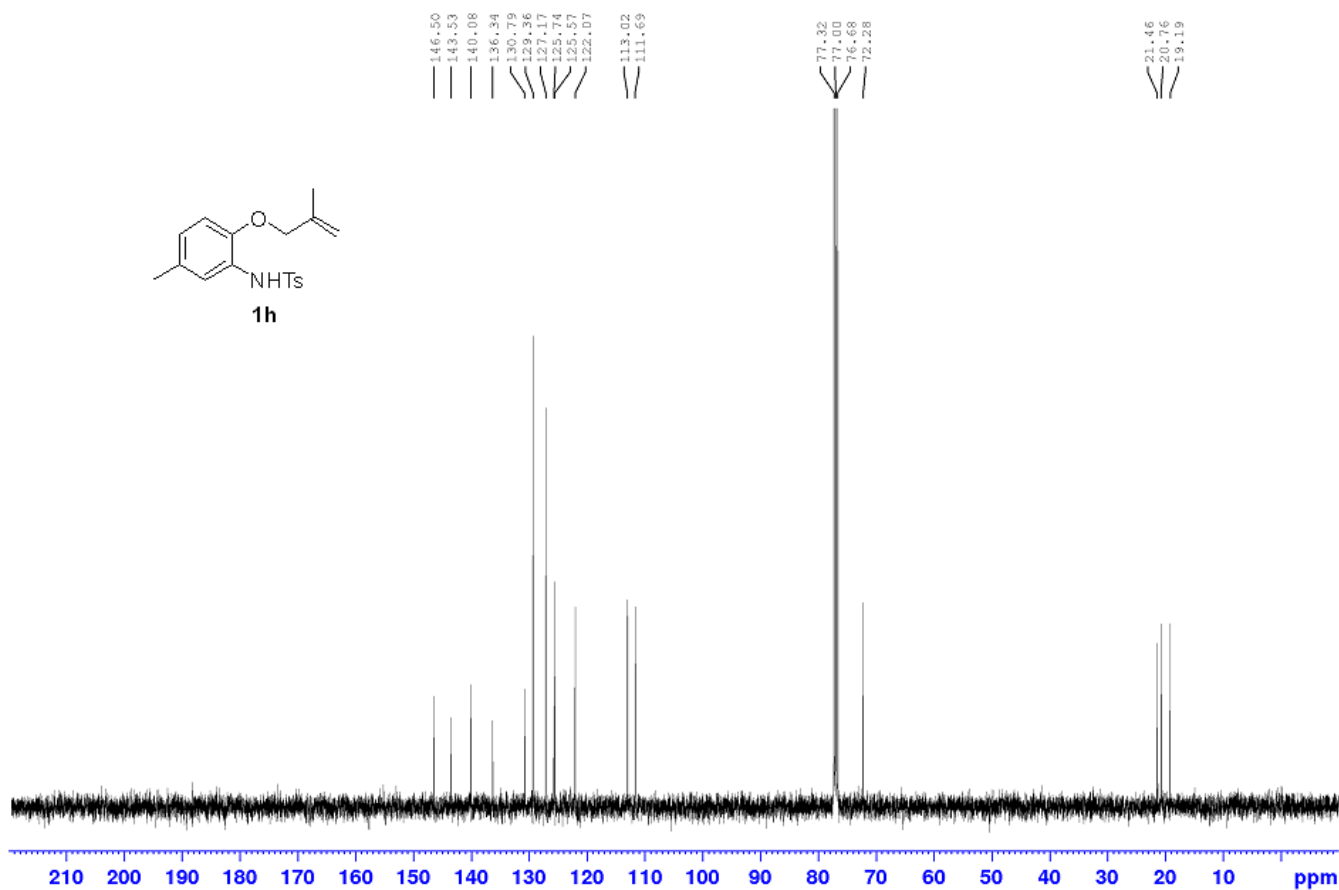
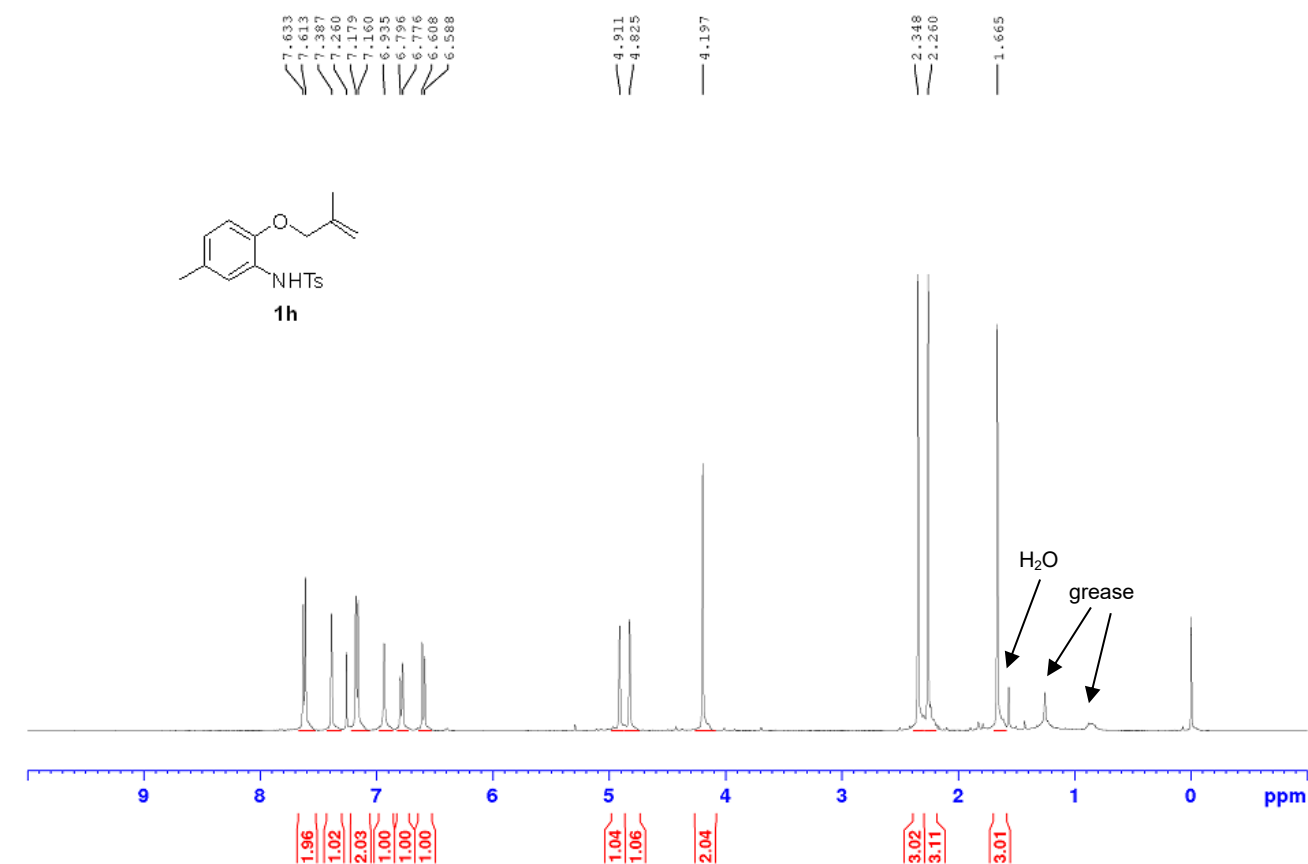
***N*-Ts-2-(Methallyloxy)-4-nitroaniline (**1f**) (in CDCl₃)**



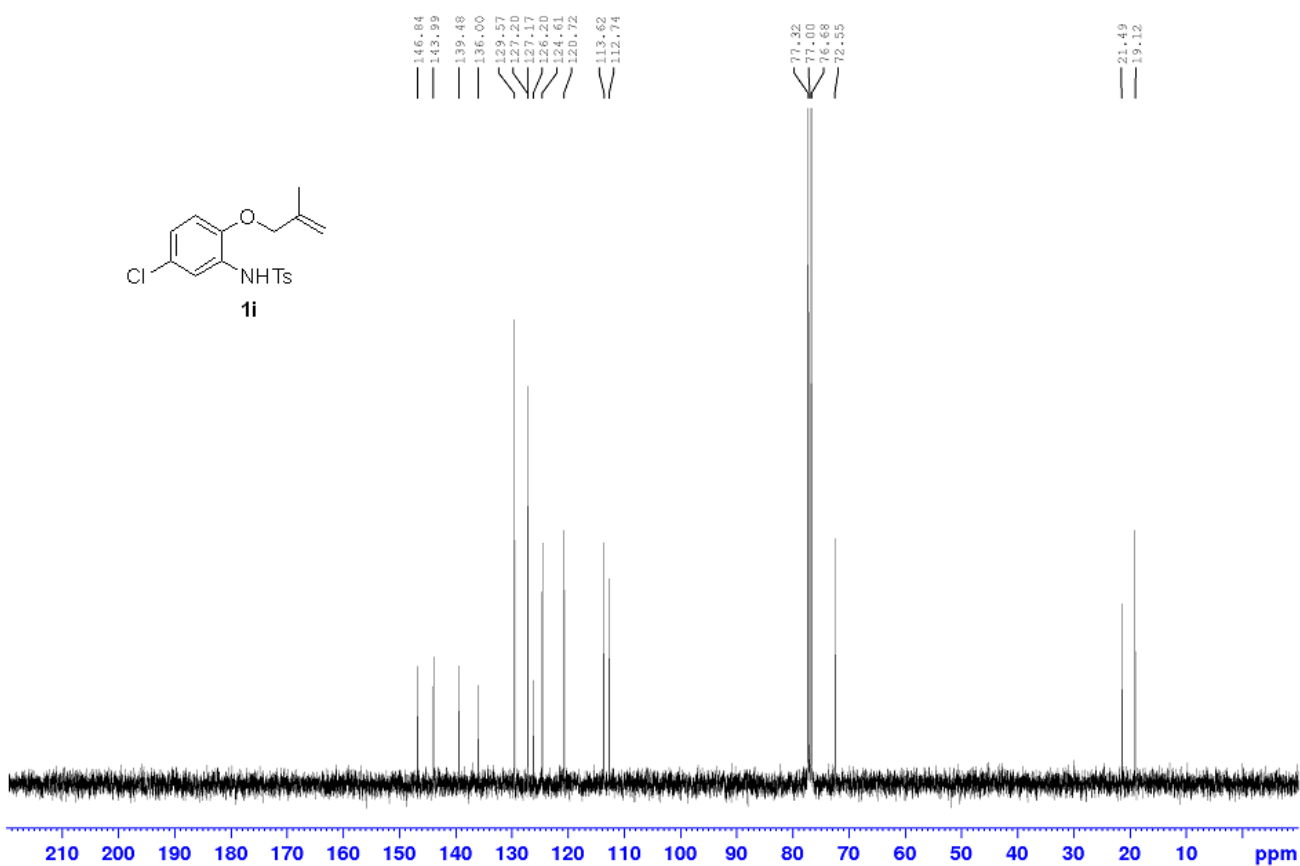
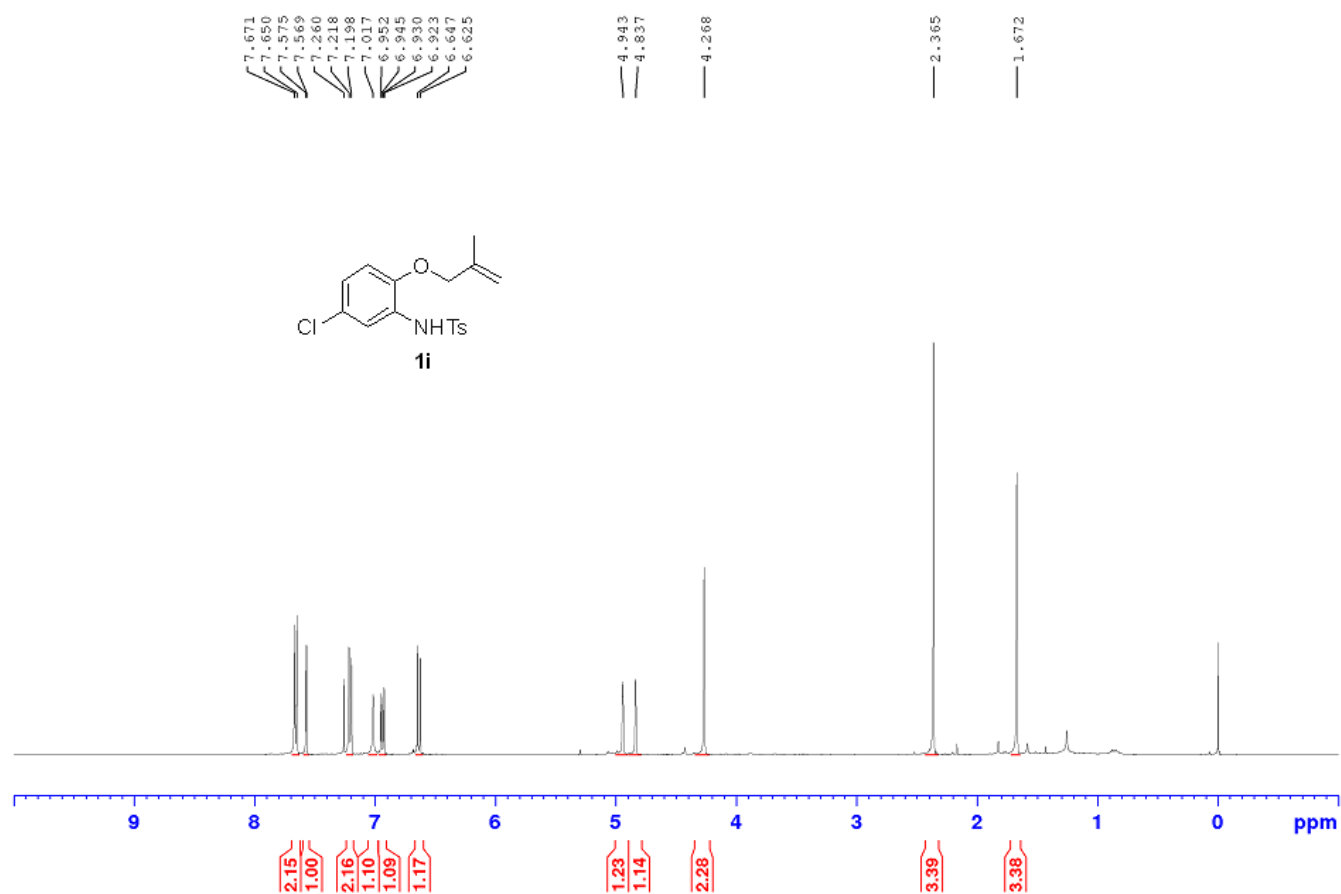
***N*-Ts-2-(Methallyloxy)-5-methoxyaniline (**1g**) (in CDCl₃)**



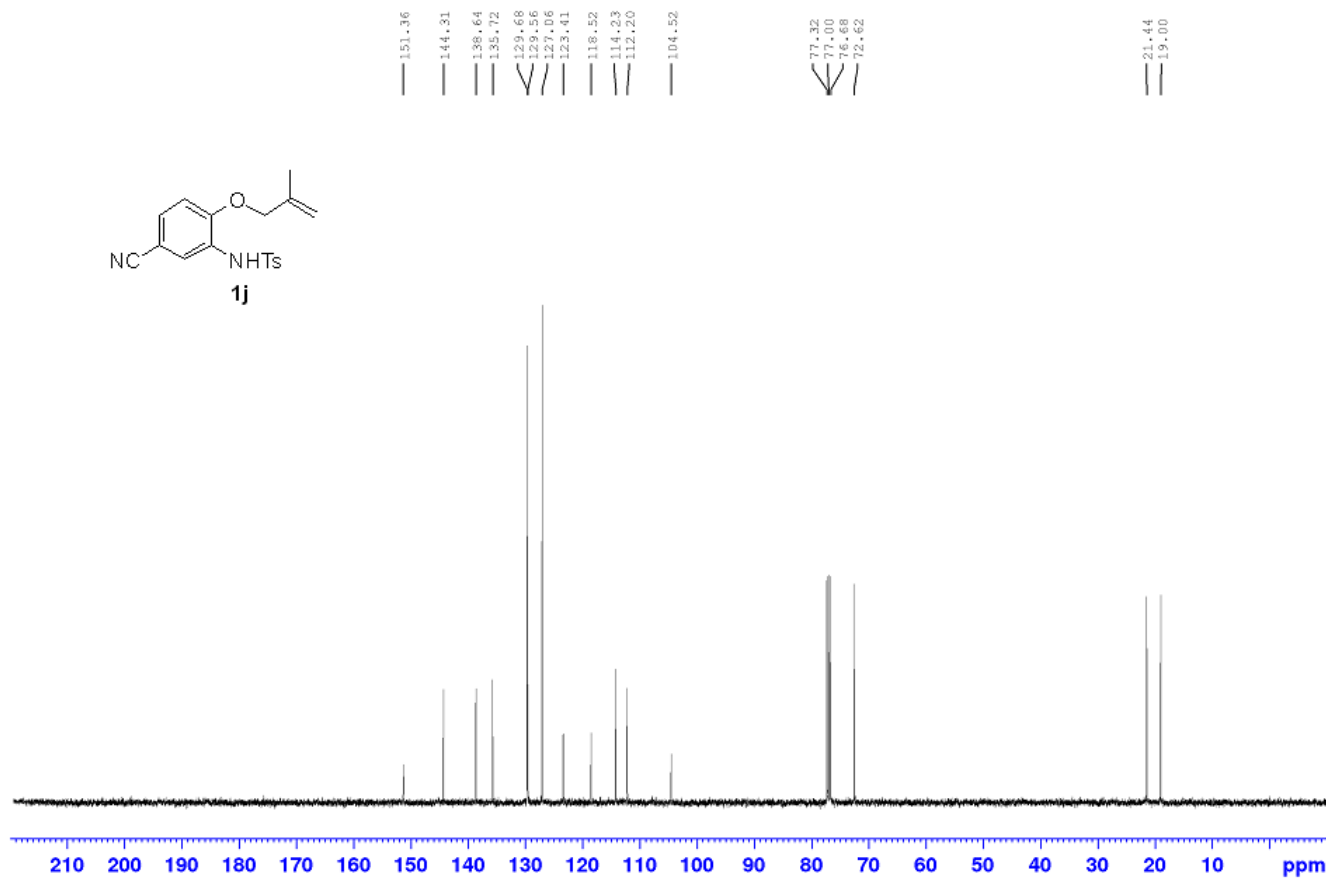
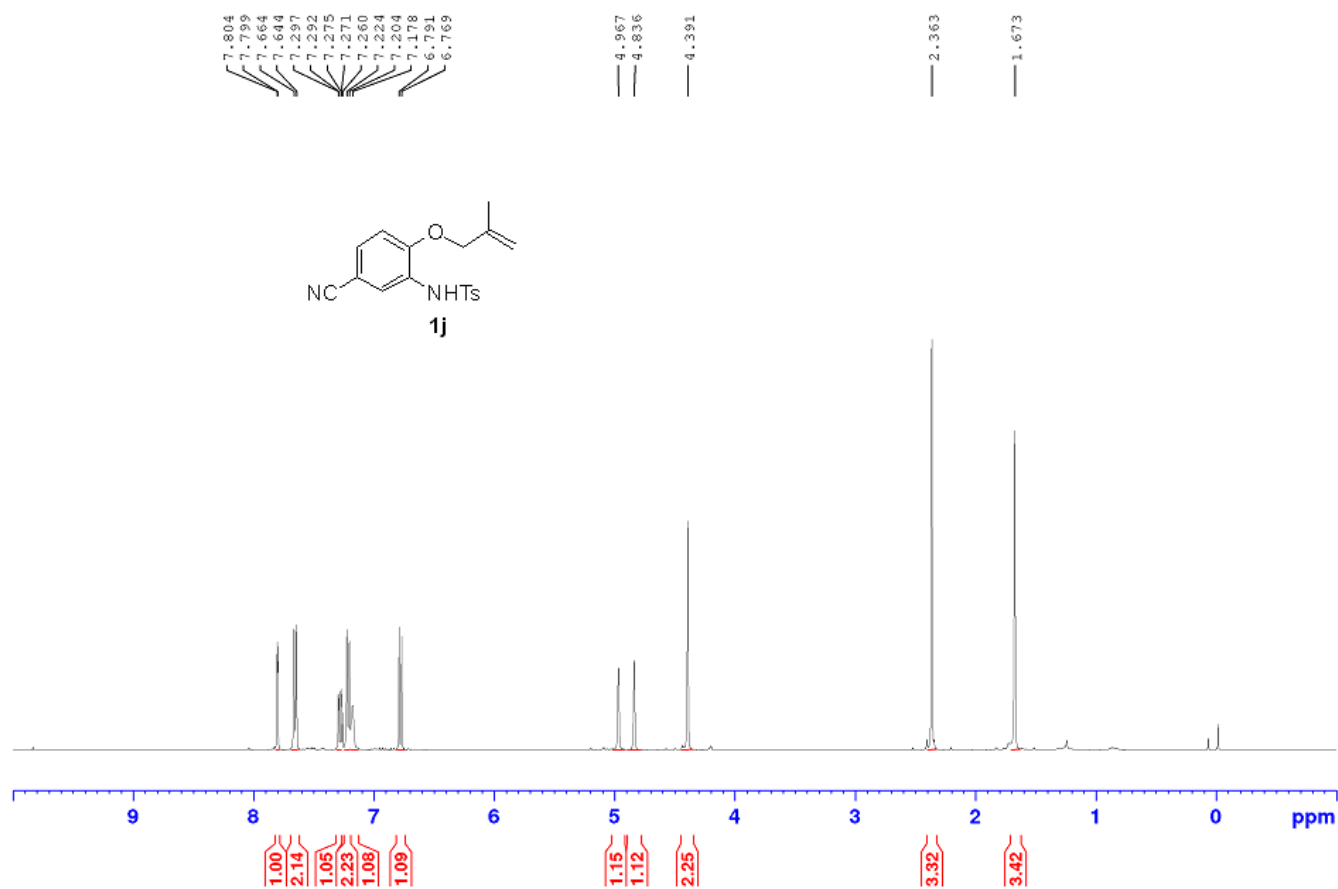
***N*-Ts-2-(Methallyloxy)-5-methylaniline (**1h**) (in CDCl₃)**



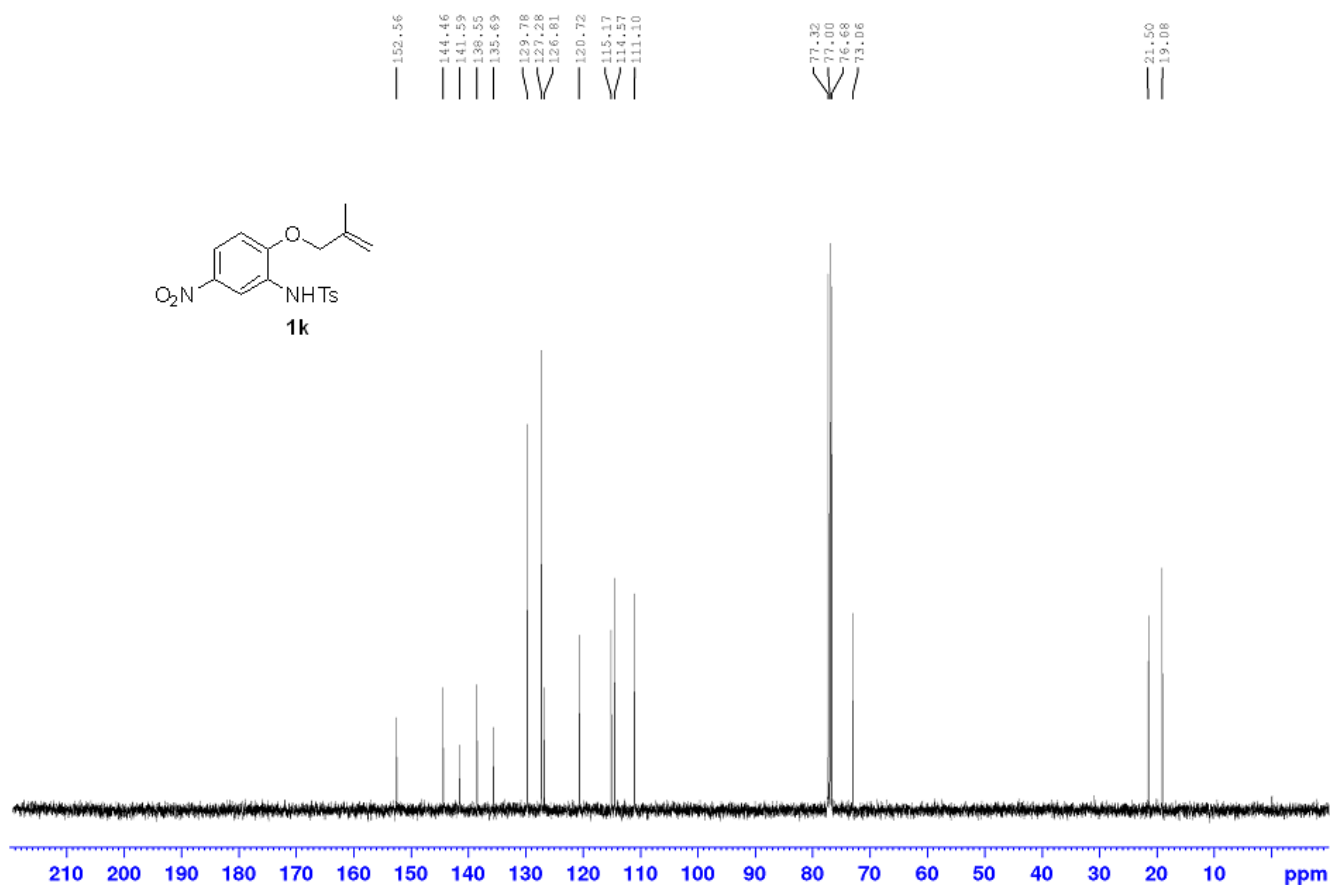
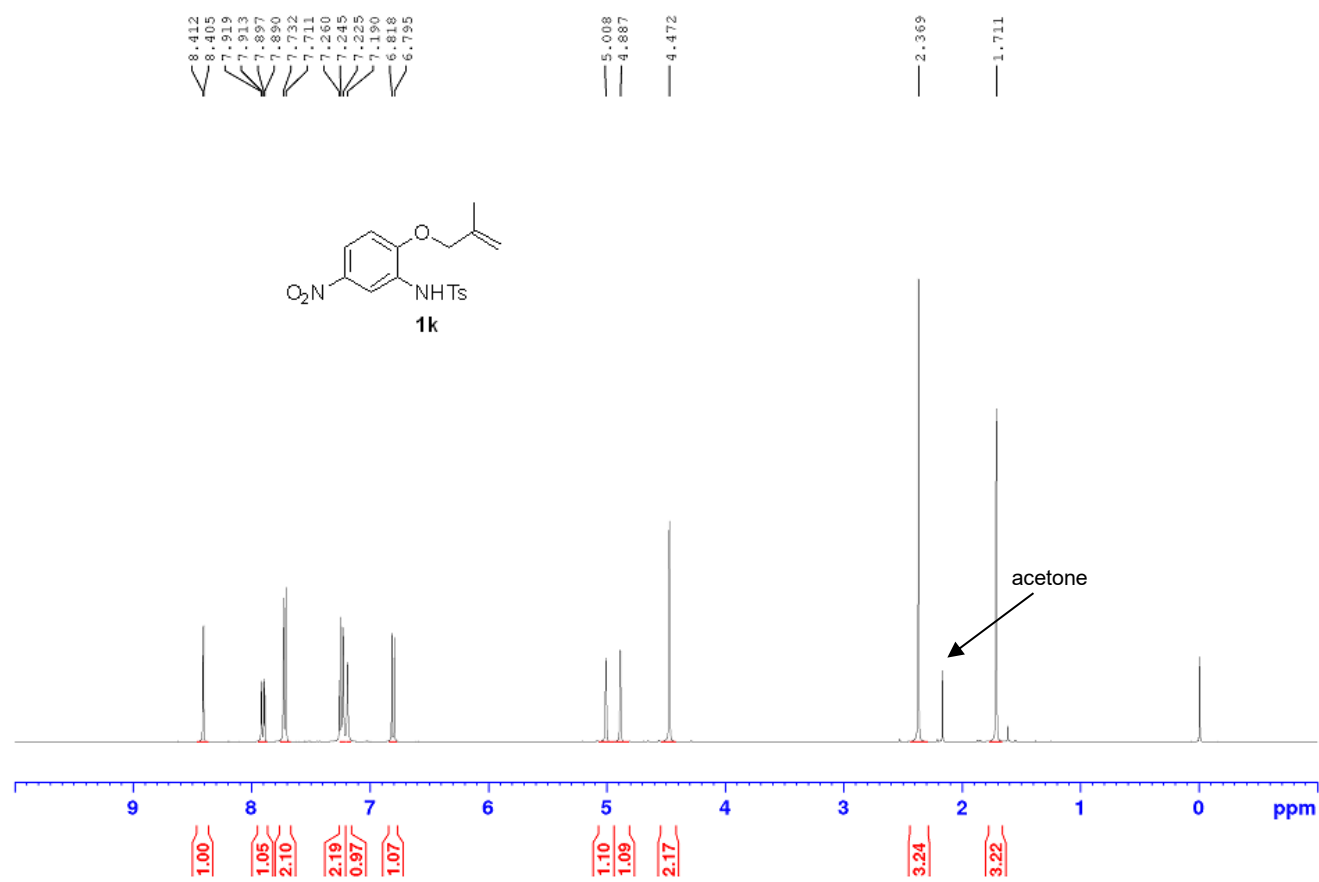
***N*-Ts-5-Chloro-2-(methallyloxy)aniline (**1i**) (in CDCl₃)**



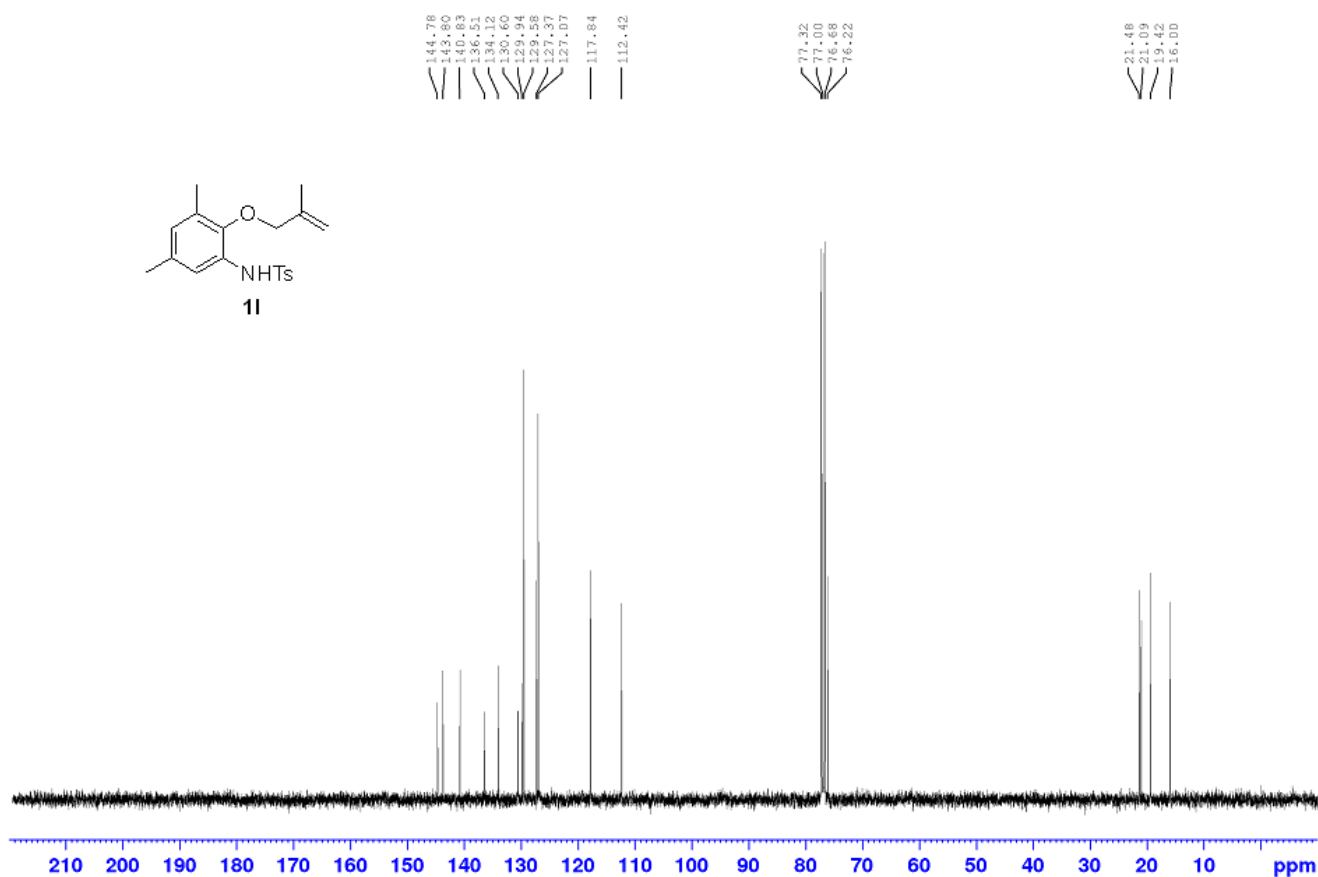
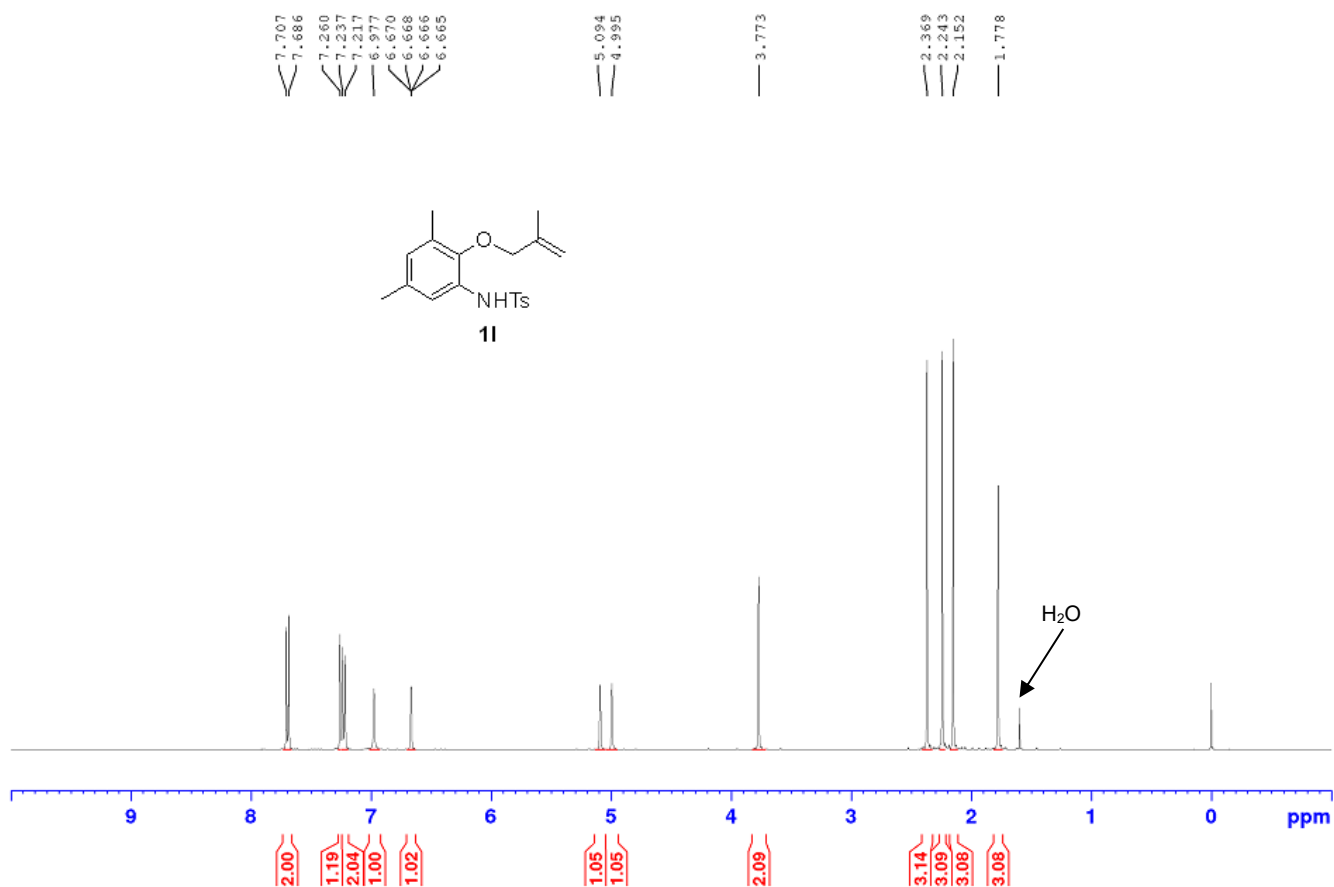
***N*-Ts-5-Cyano-2-(methallyloxy)aniline (**1j**) (in CDCl₃)**



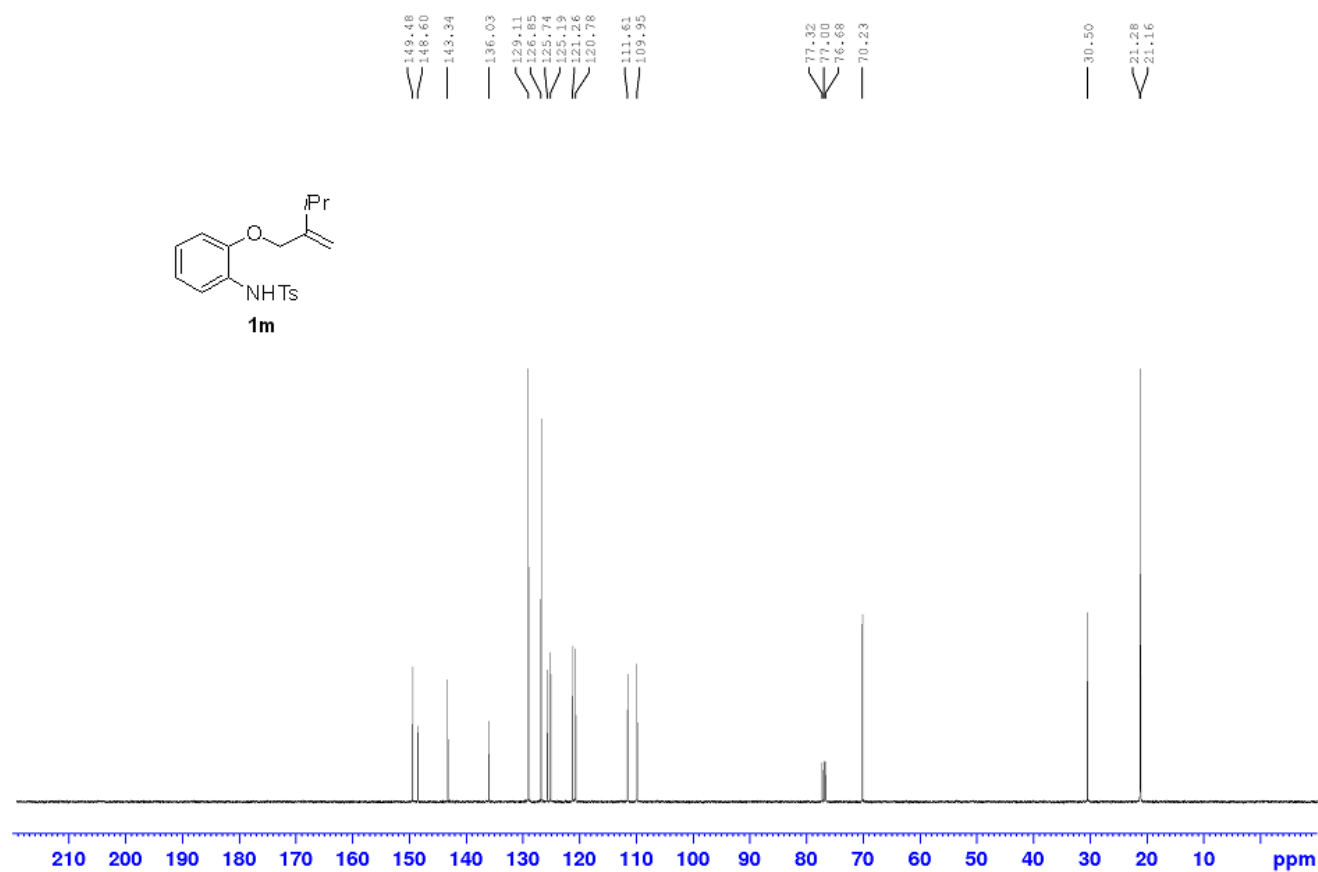
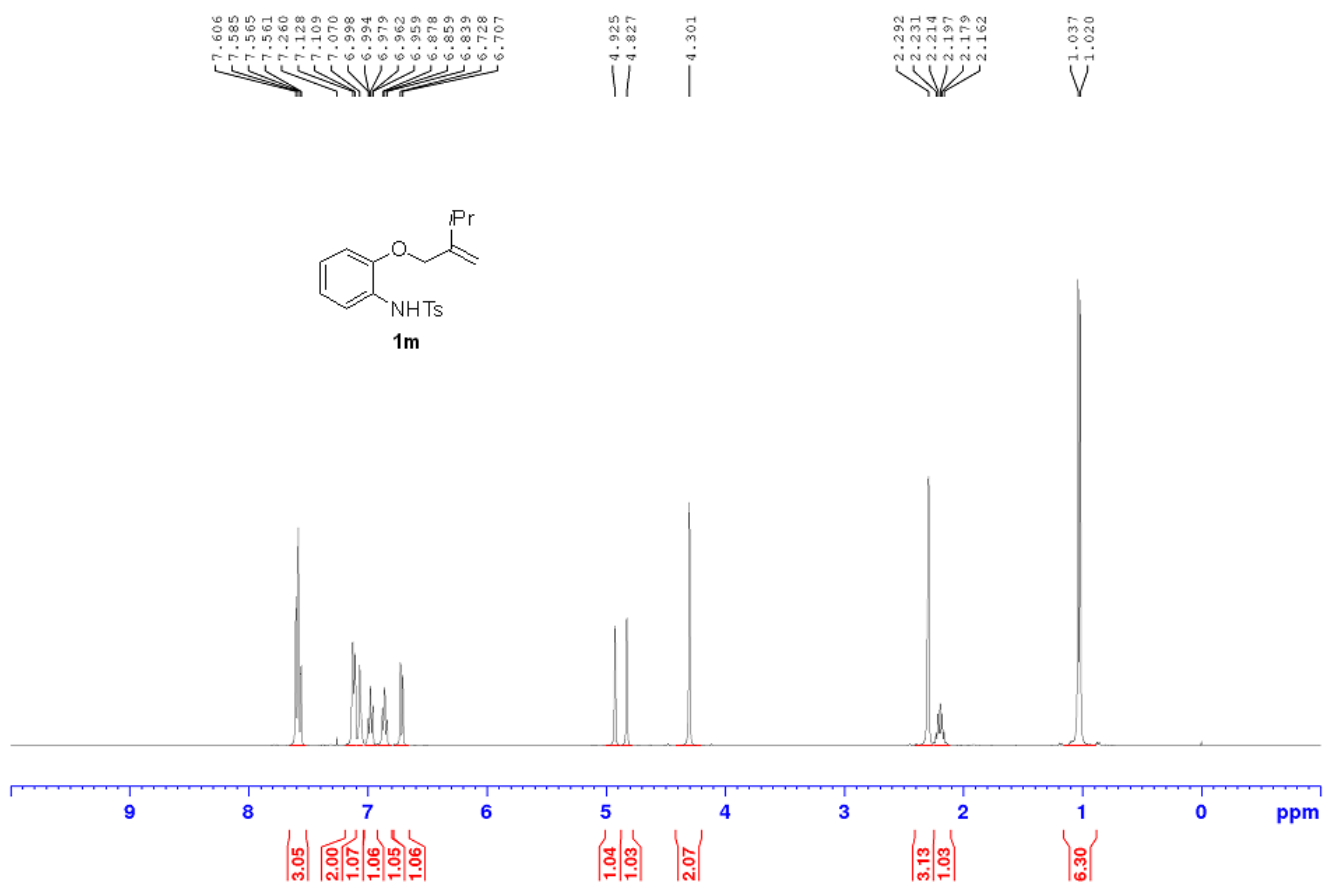
***N*-Ts-2-(Methallyloxy)-5-nitroaniline (**1k**) (in CDCl₃)**



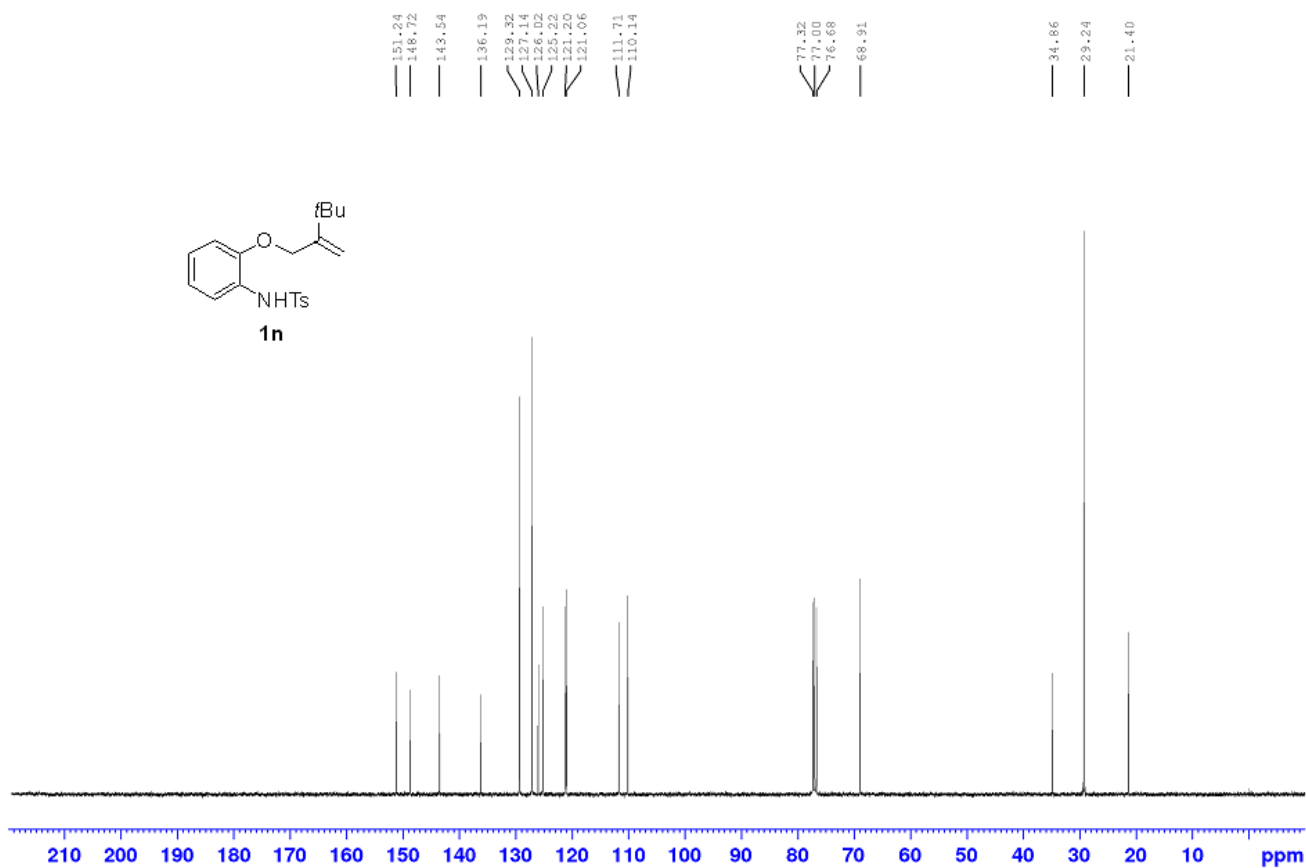
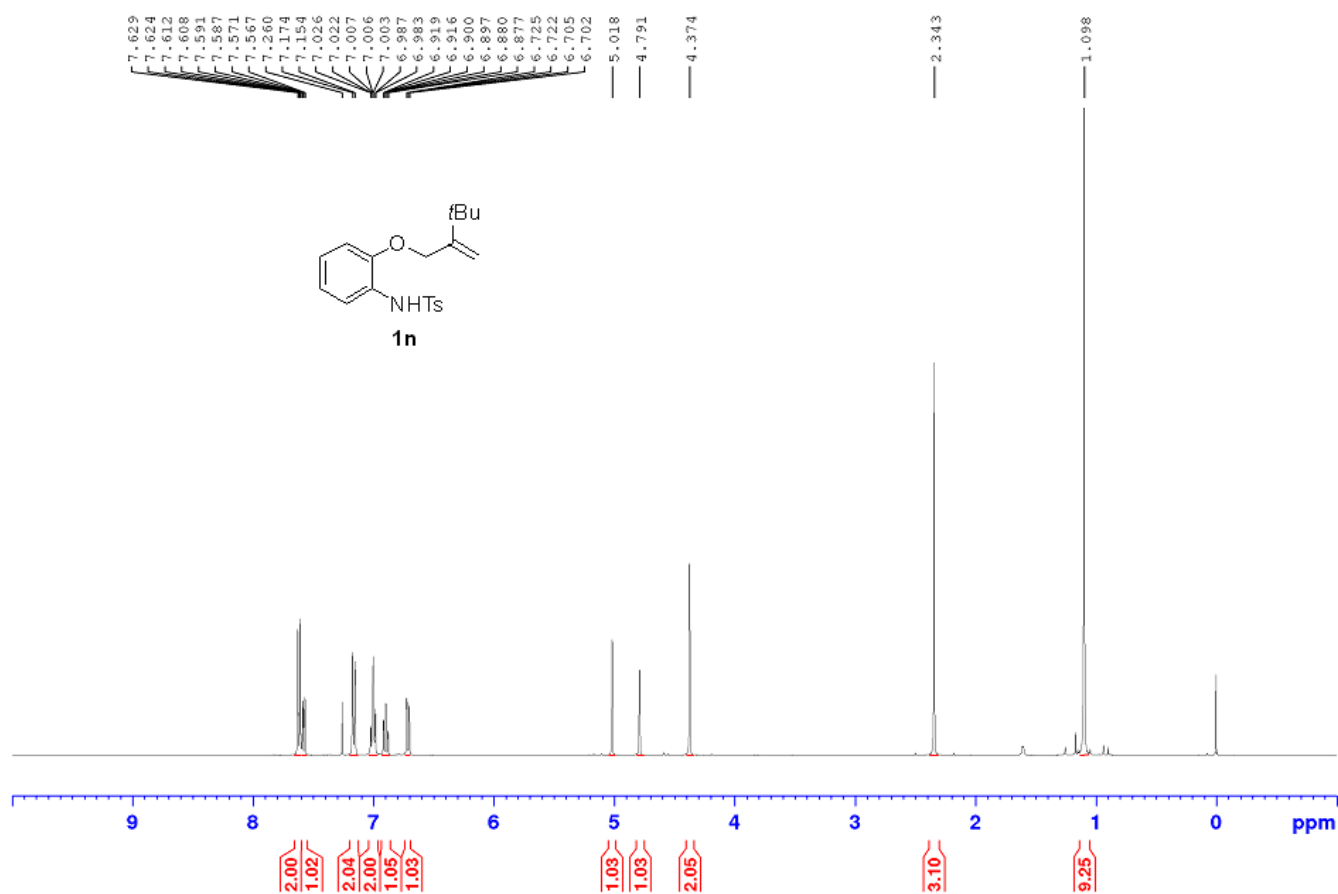
***N*-Ts-2-(Methallyloxy)-3,5-dimethylaniline (**11**) (in CDCl₃)**



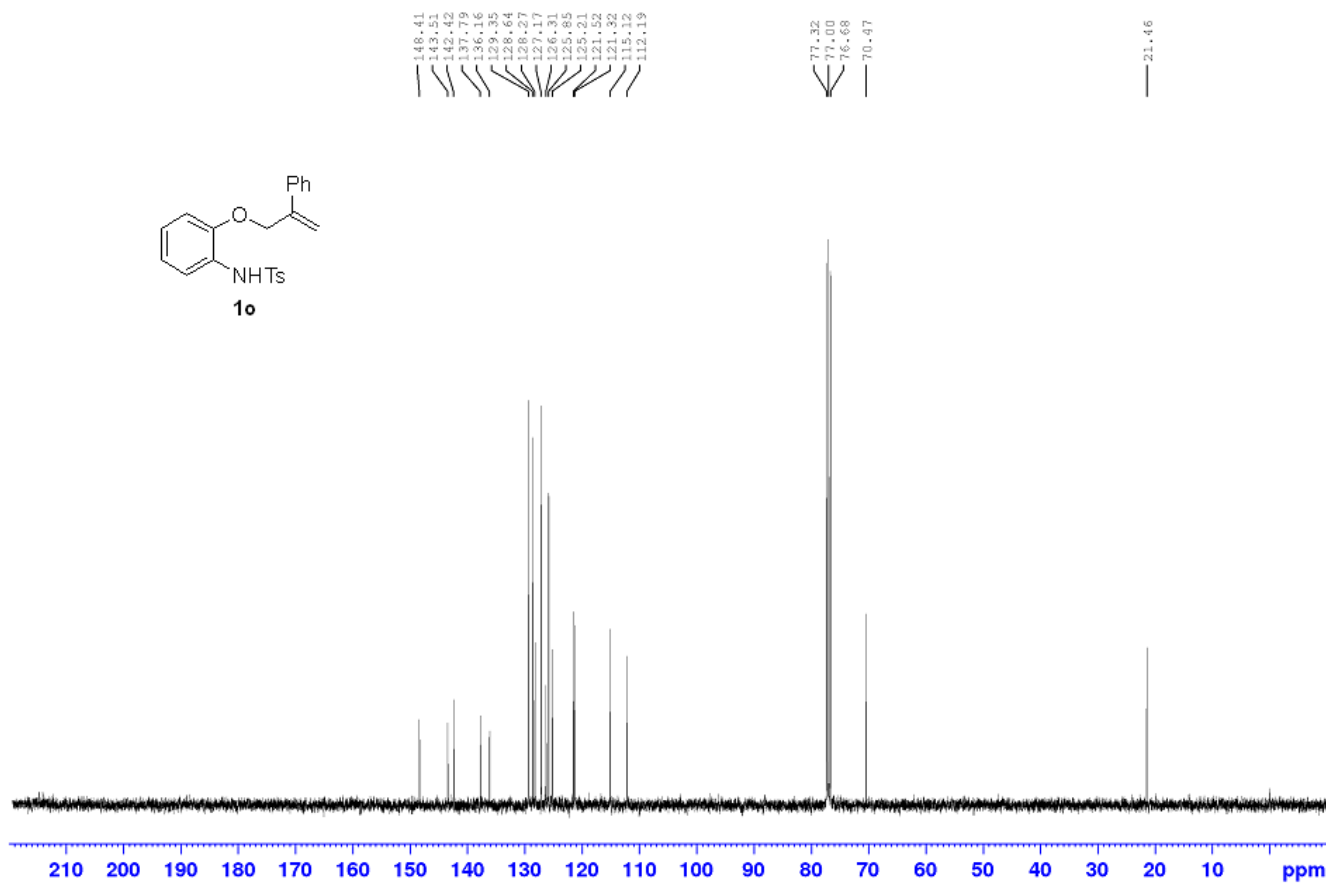
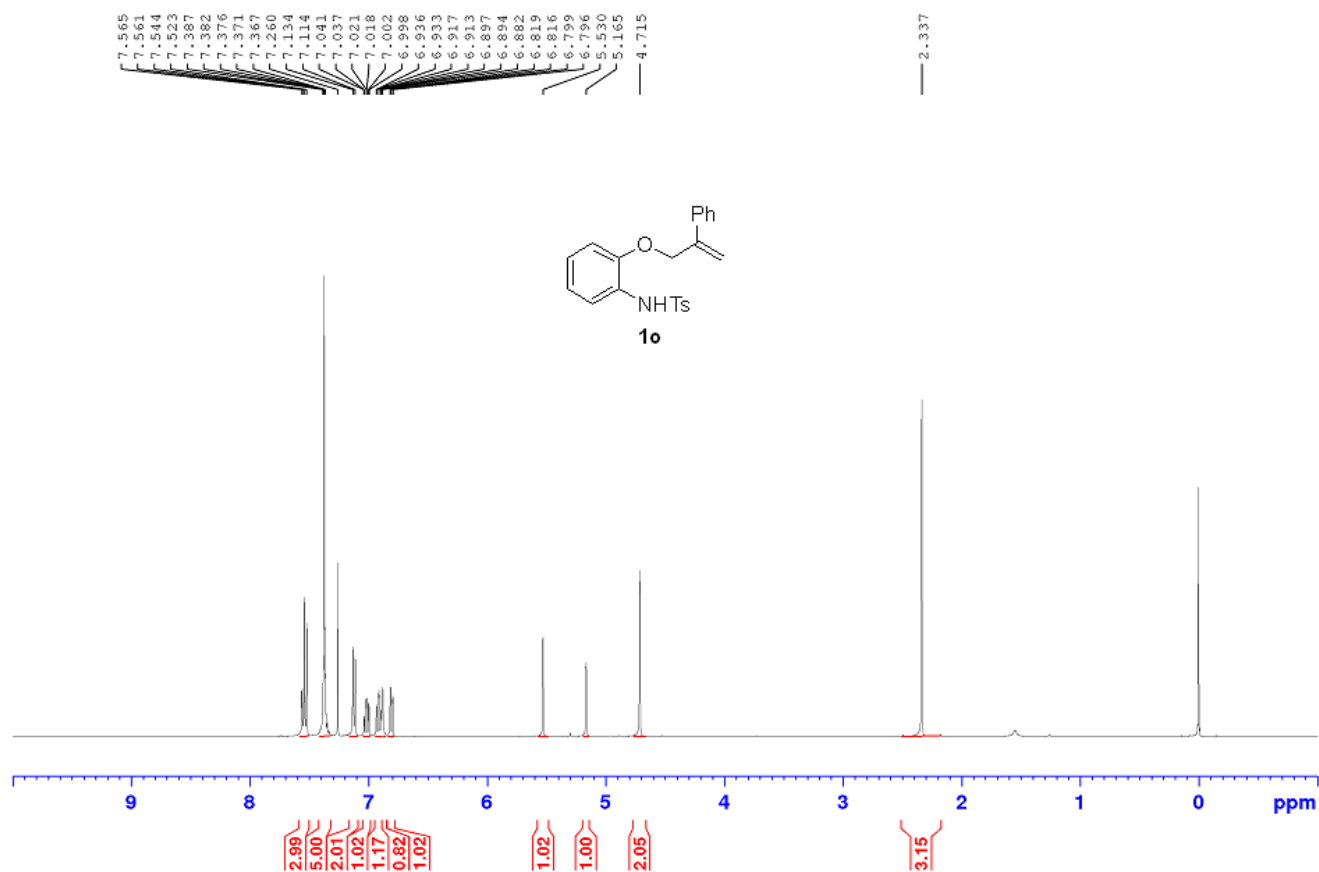
***N*-Ts-2-(3-Methyl-2-methylenebutoxy)aniline (1m) (in CDCl₃)**



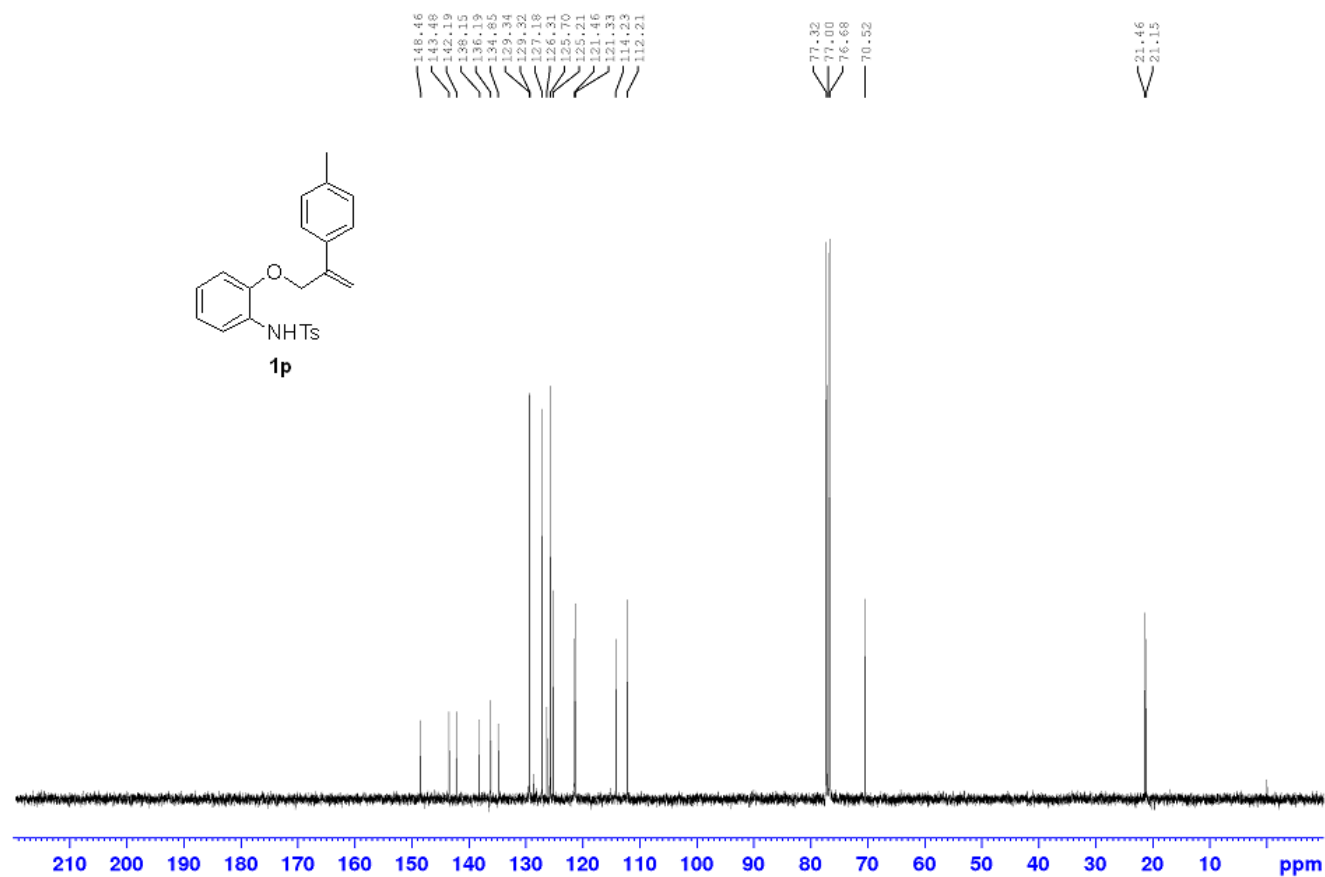
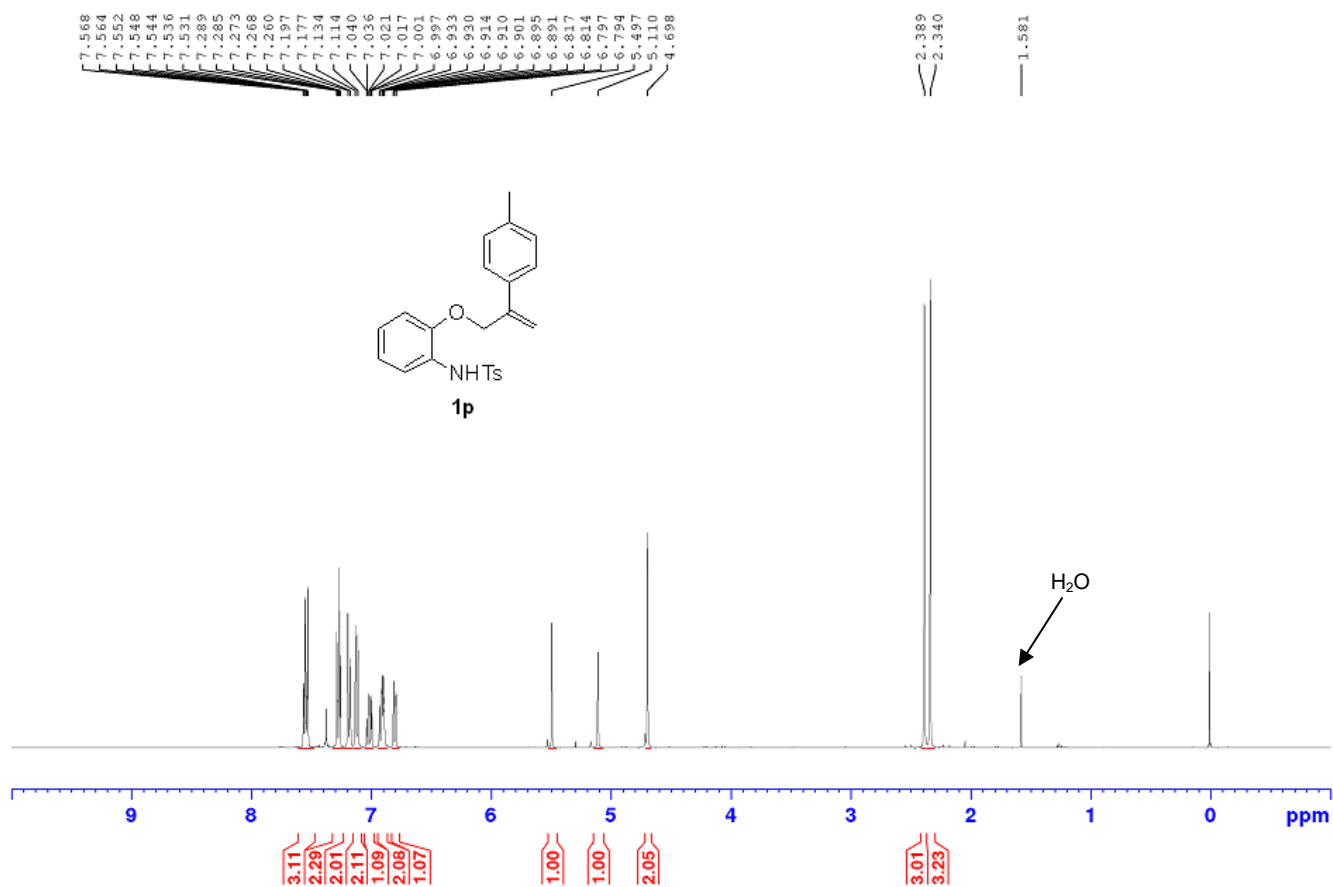
***N*-Ts-2-(3,3-Dimethyl-2-methylenebutoxy)aniline (1n) (in CDCl₃)**



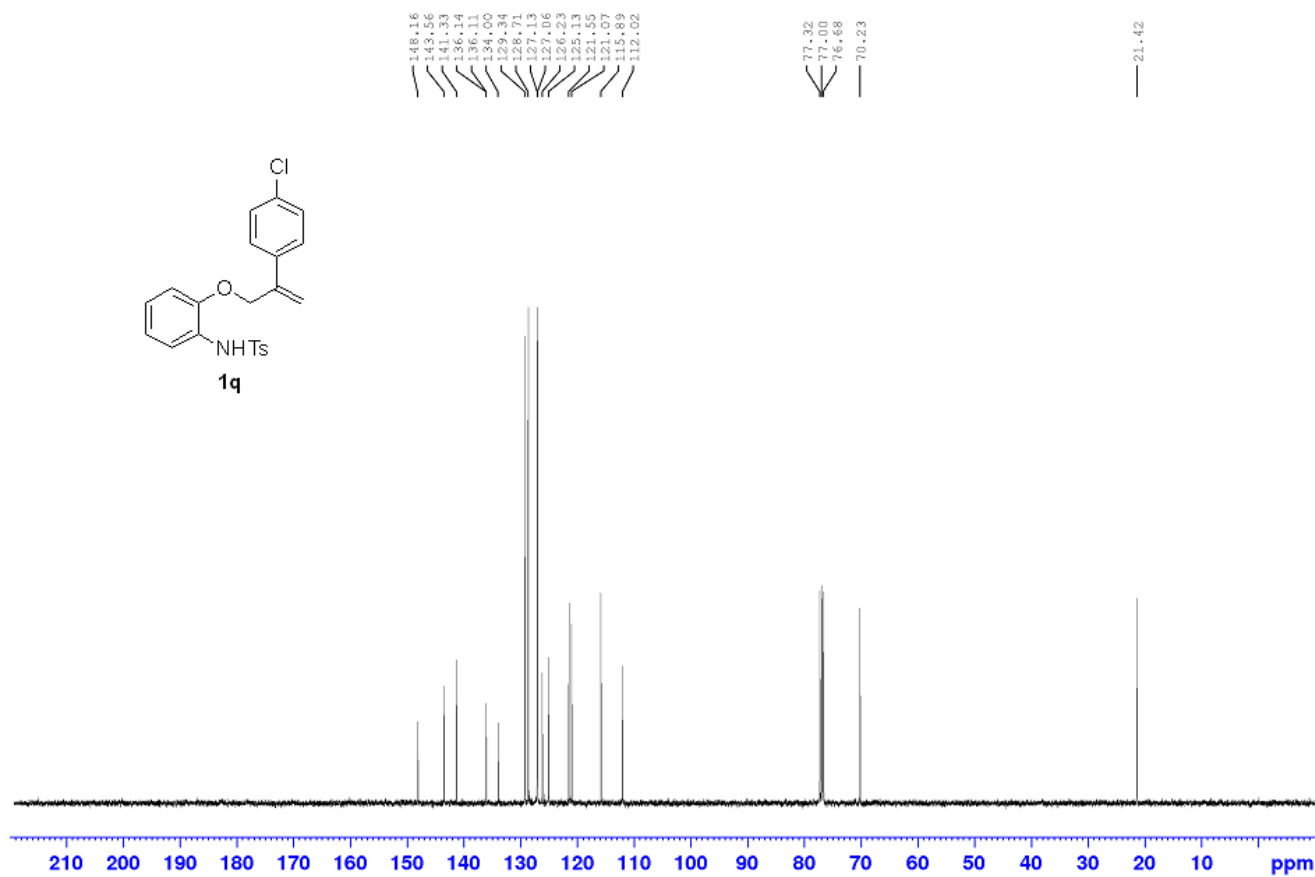
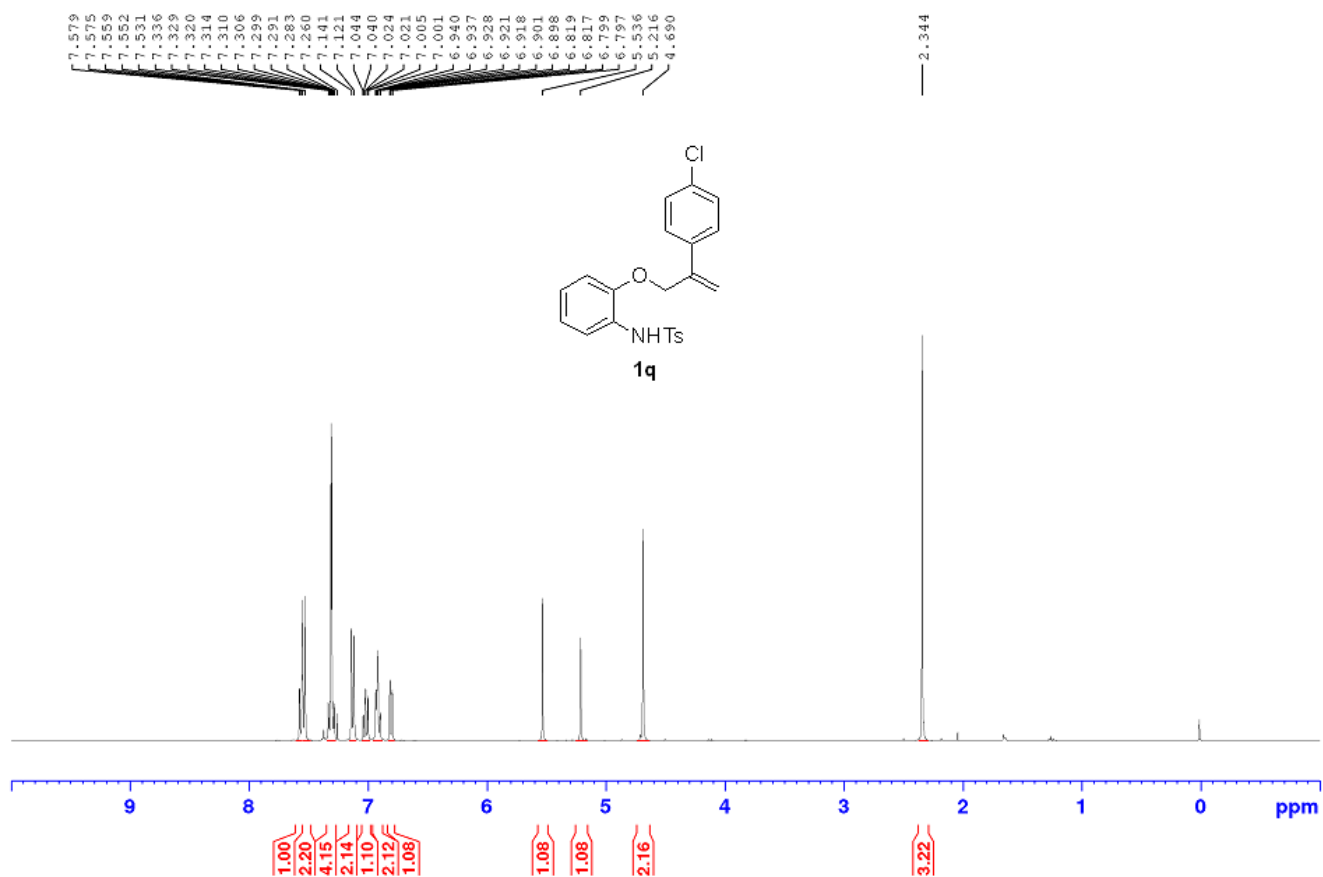
***N*-Ts-2-(2-Phenylallyloxy)aniline (1o)** (in CDCl₃)



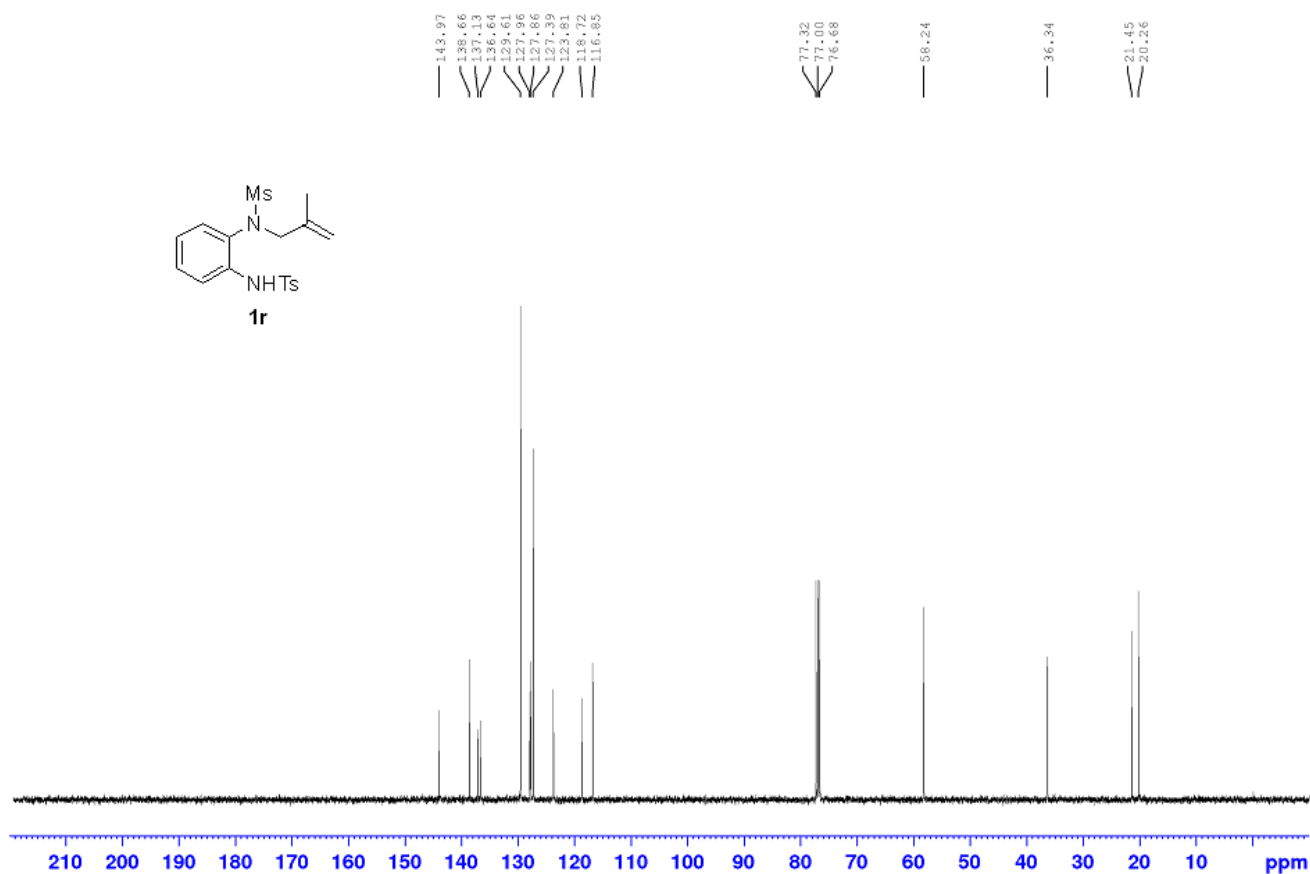
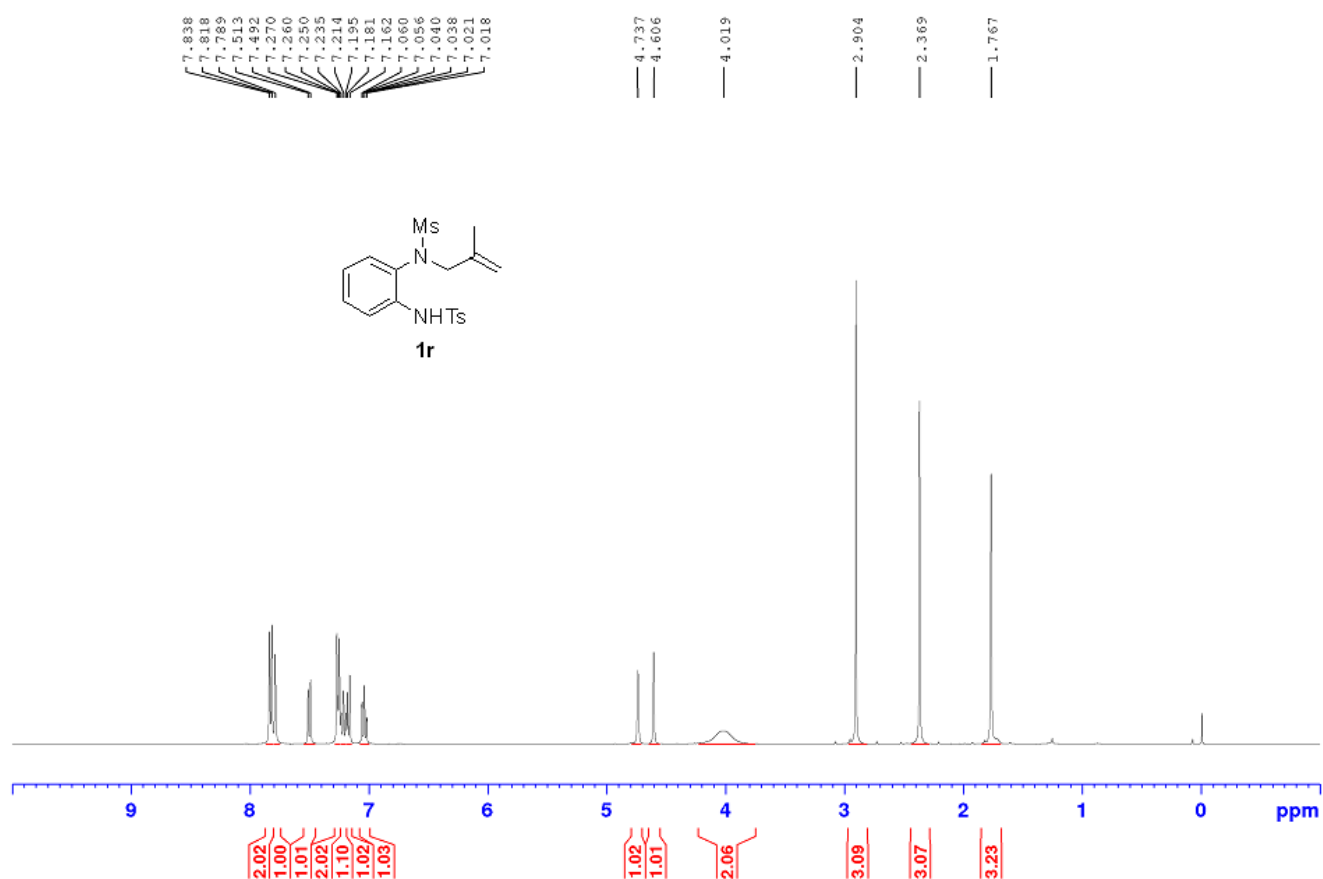
***N*-Ts-2-(2-(*p*-Tolyl)allyloxy)aniline (**1p**) (in CDCl₃)**



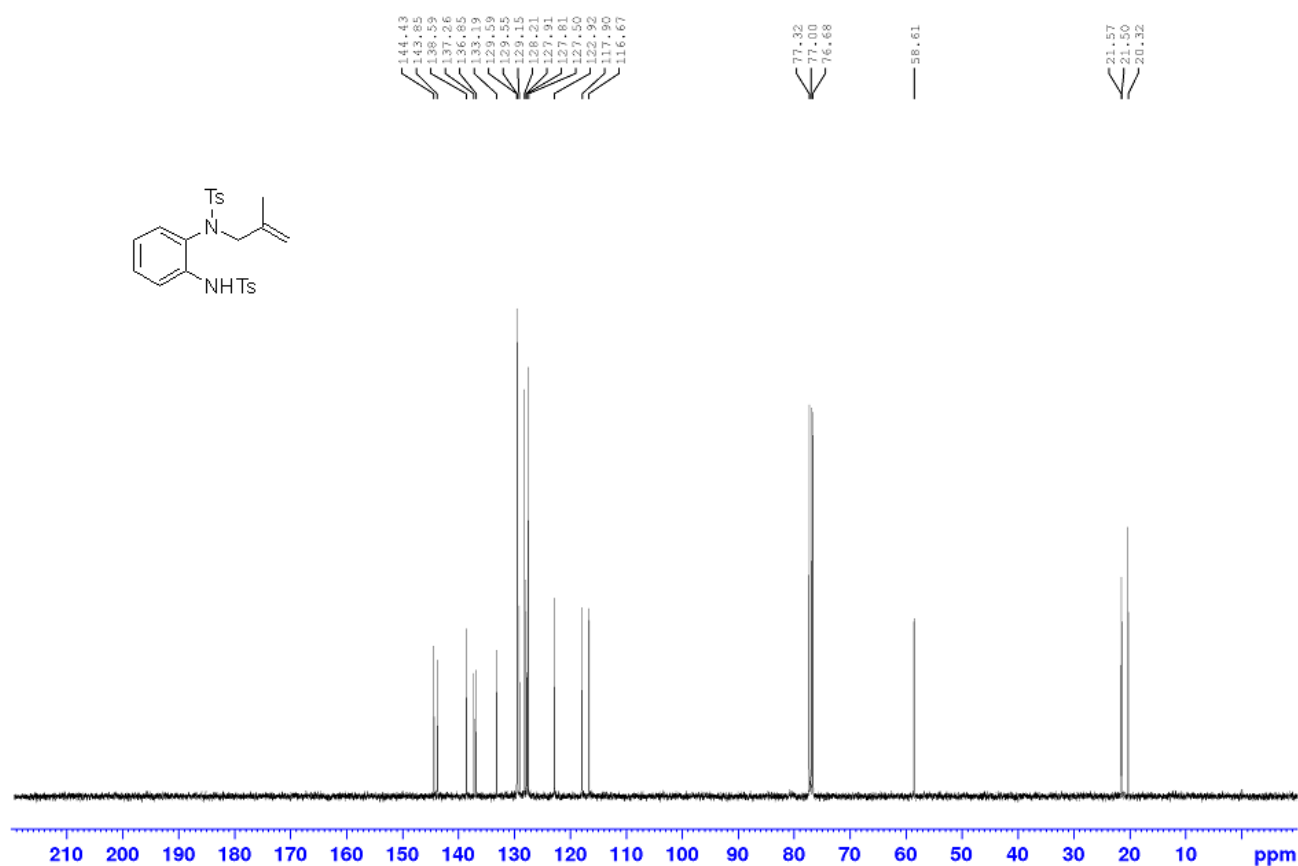
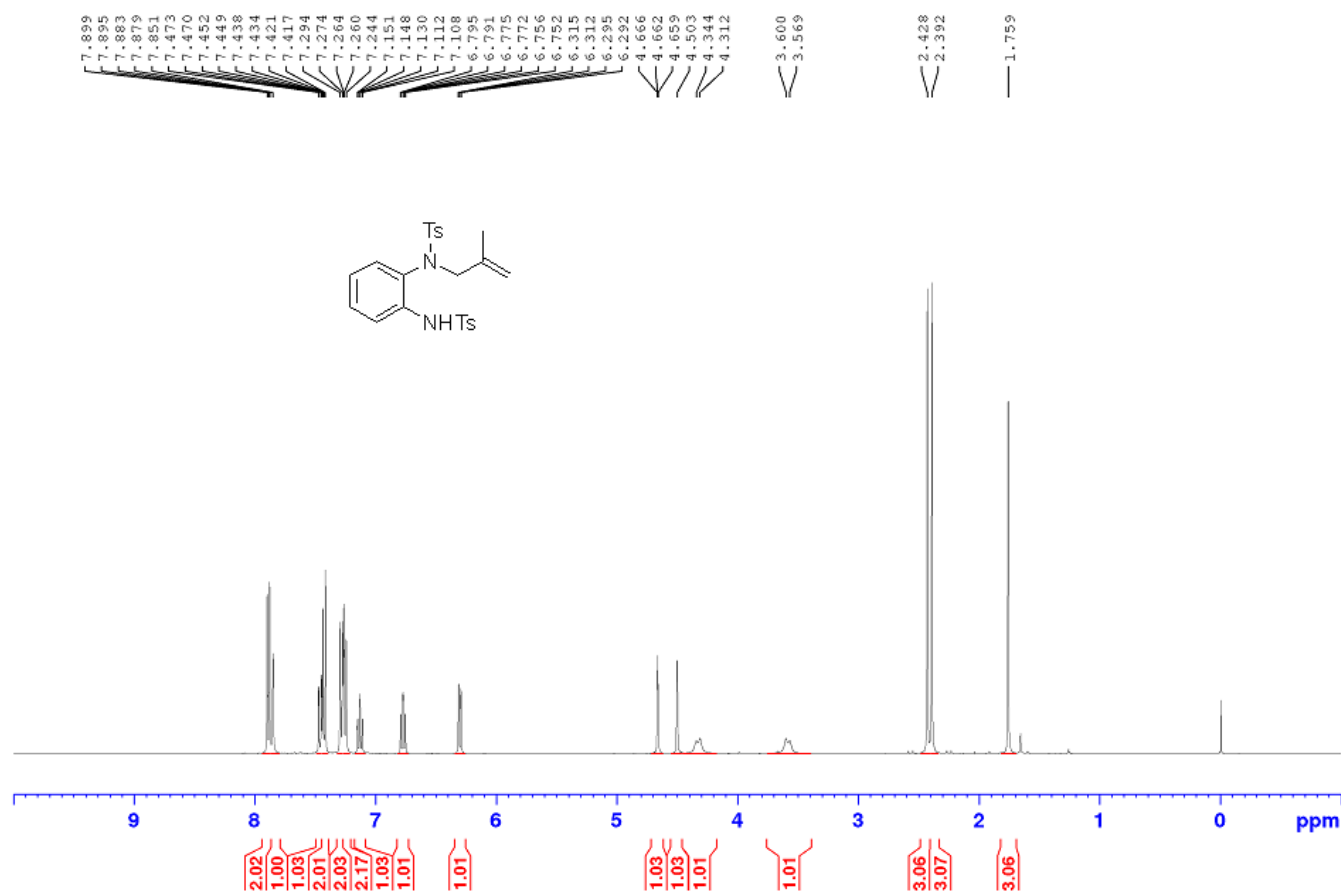
***N*-Ts-2-(2-(4-Chlorophenyl)allyloxy)aniline (**1q**) (in CDCl₃)**



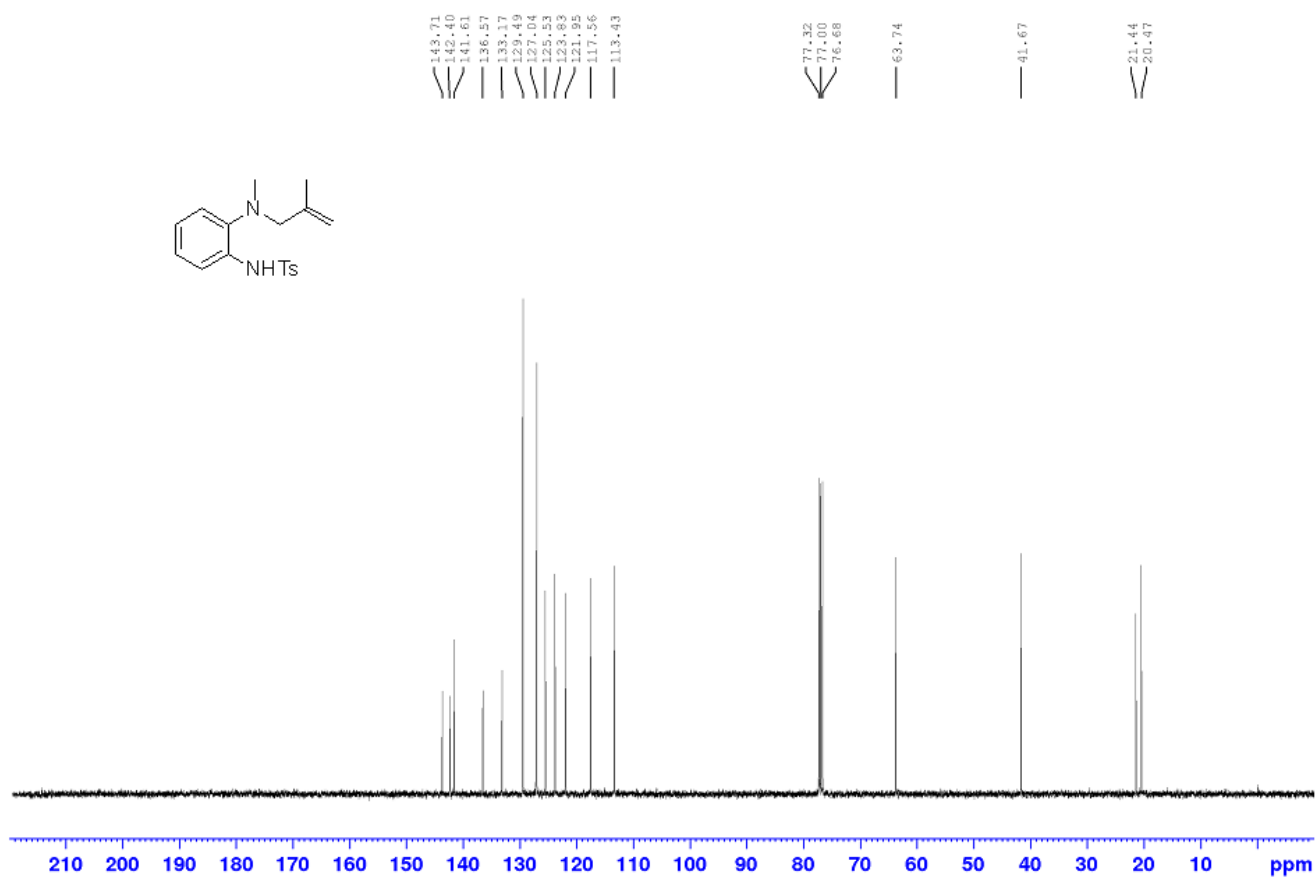
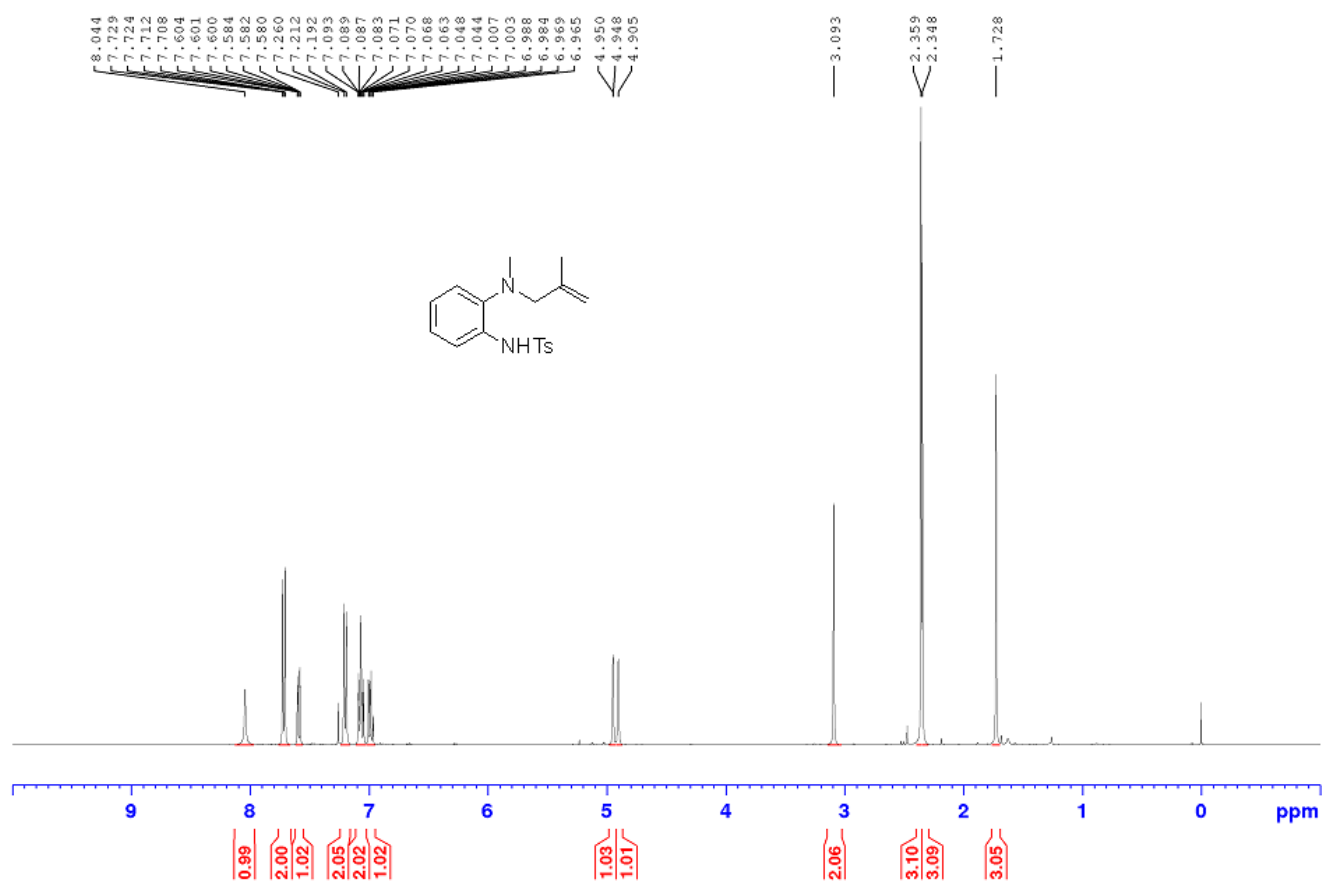
***N*¹-Ms-*N*²-Ts-*N*¹-Methallylbenzene-1,2-diamine (1r) (in CDCl₃)**



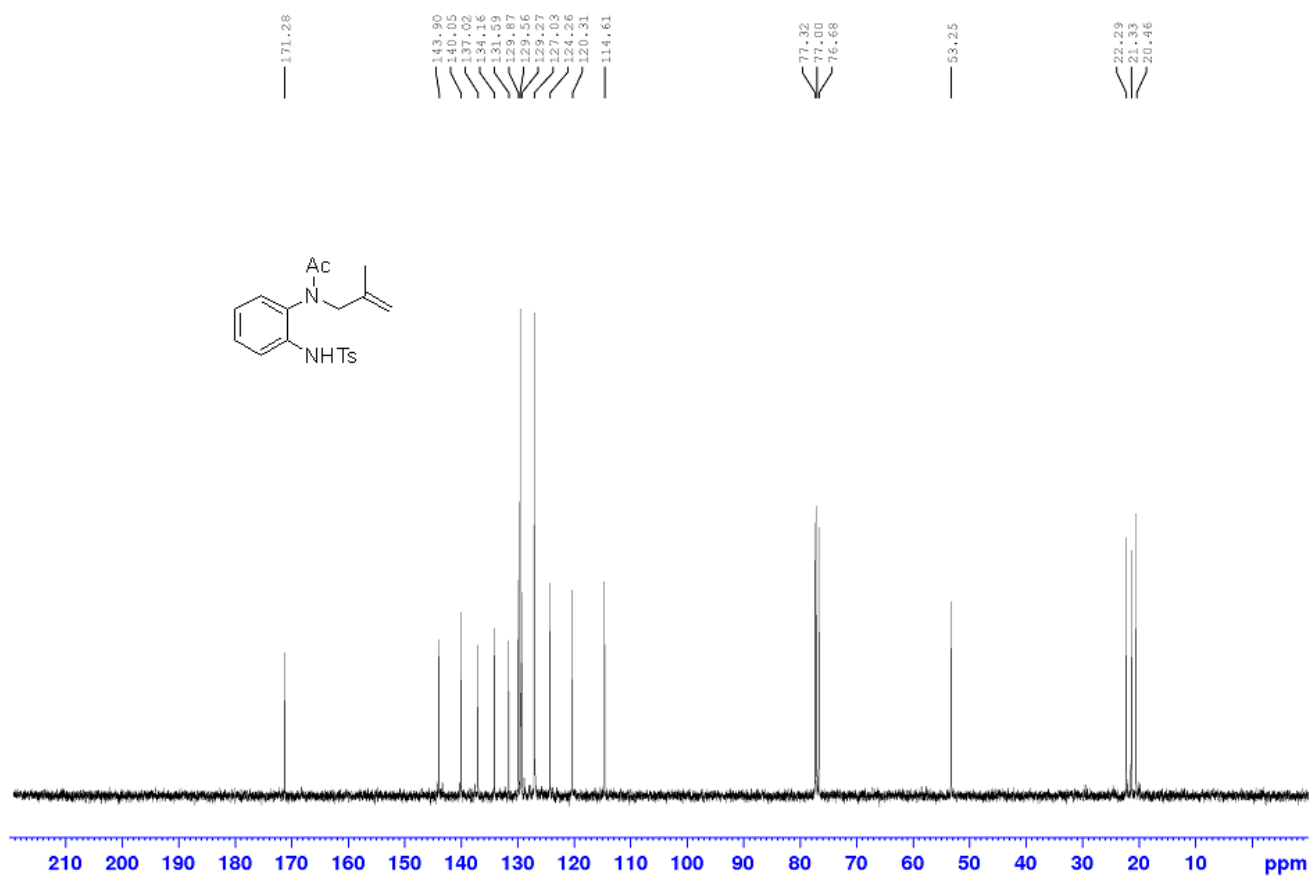
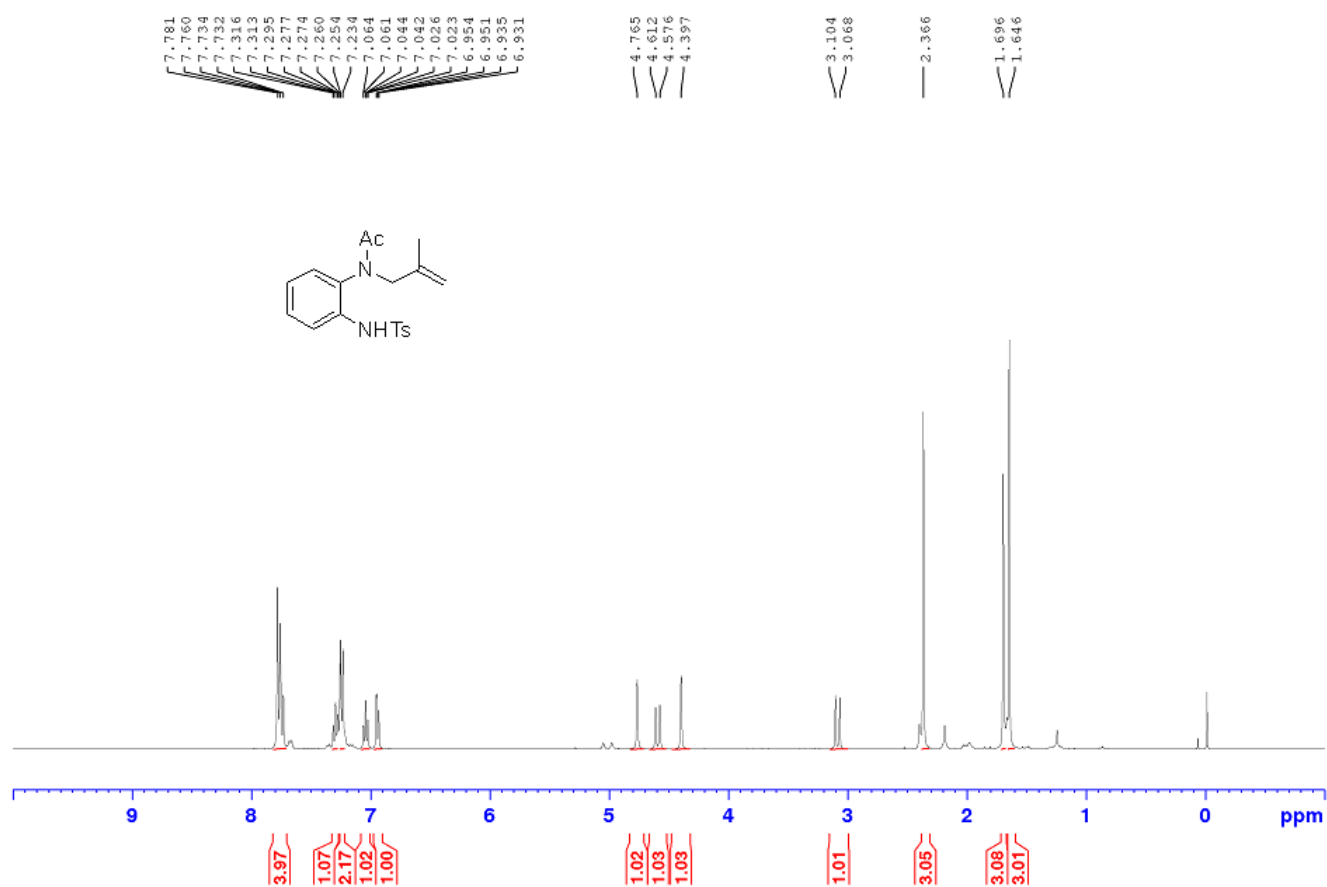
***N*¹,*N*²-BisTs-*N*¹-Methallylbenzene-1,2-diamine (in CDCl₃)**



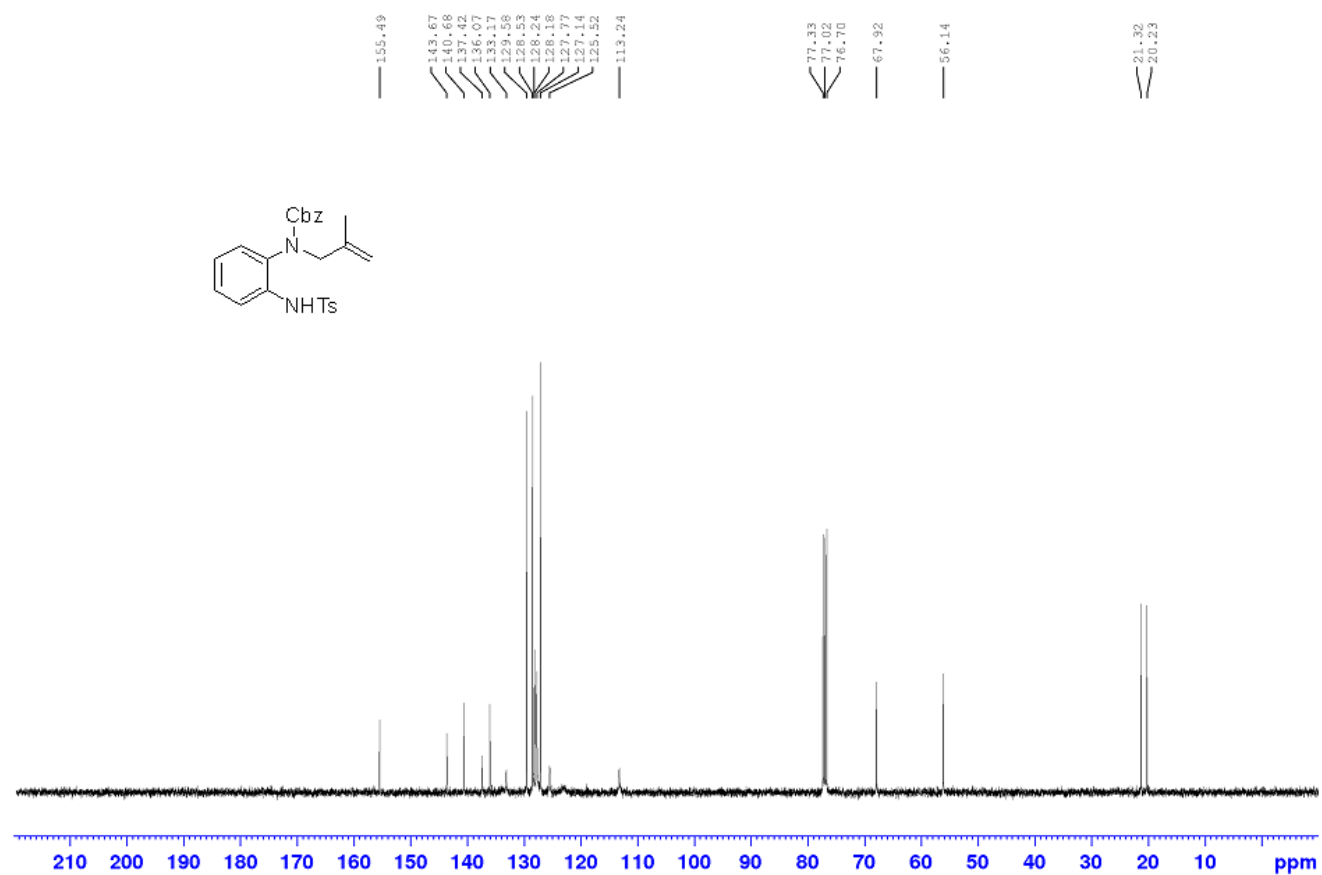
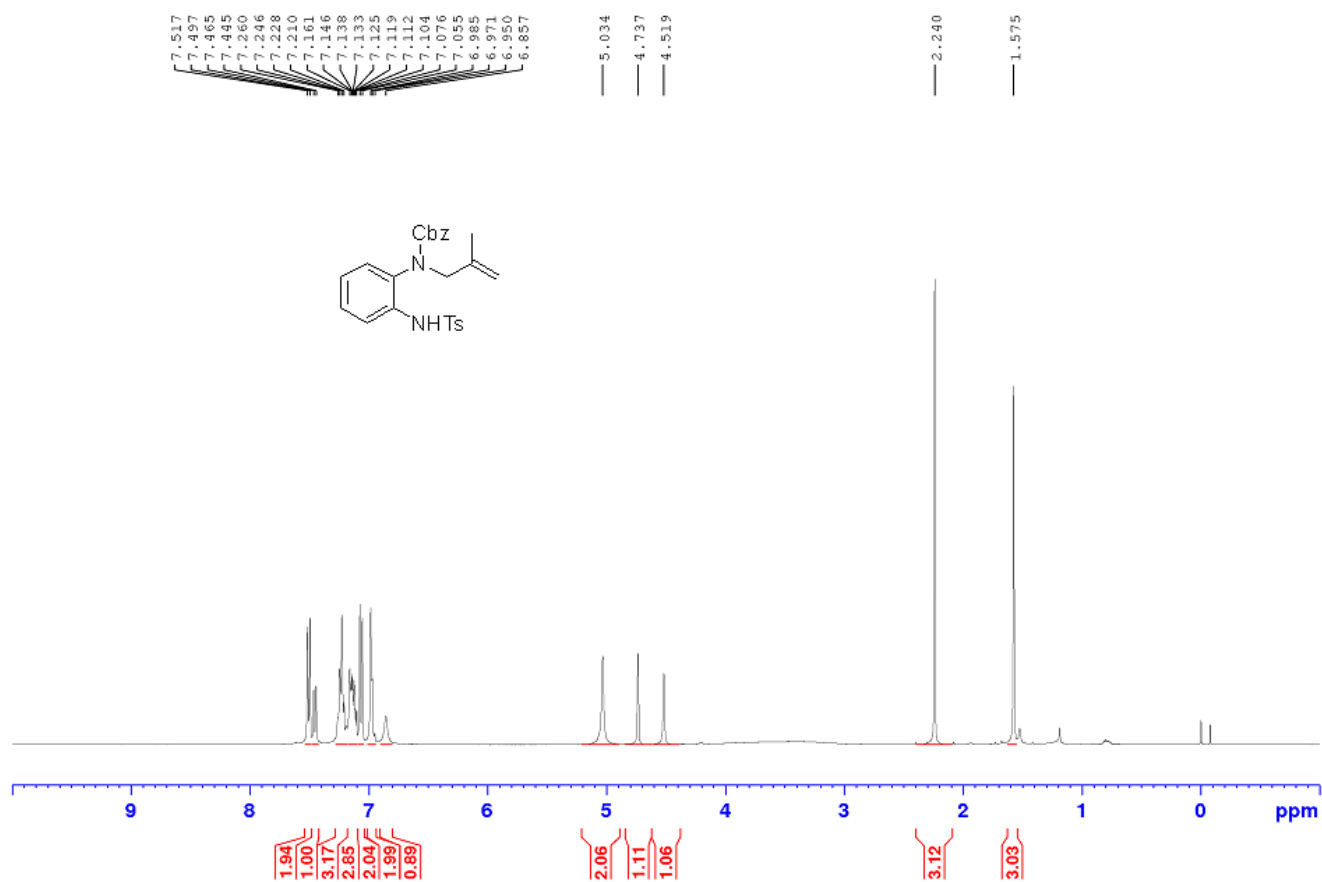
***N*²-Ts-*N*^I-Methallyl-*N*^I-methylbenzene-1,2-diamine (in CDCl₃)**



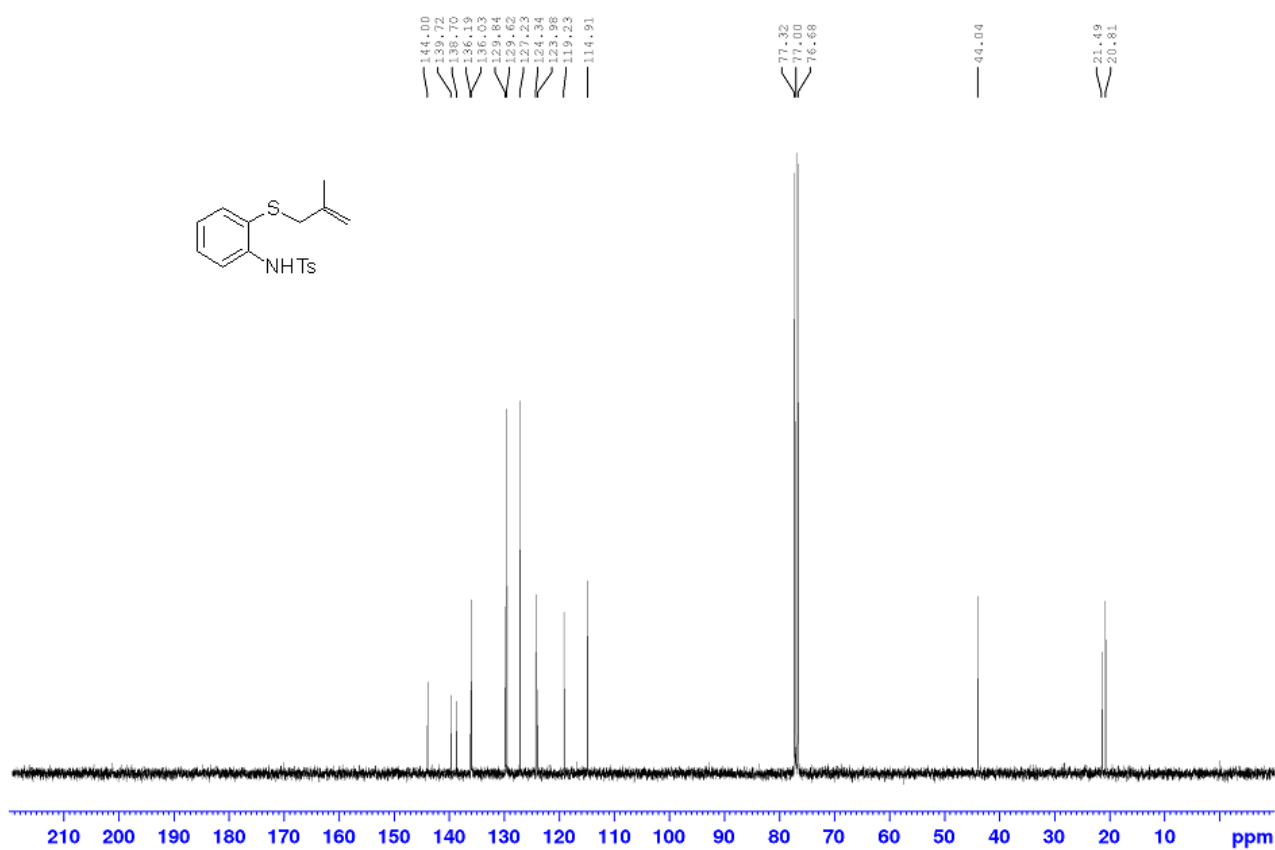
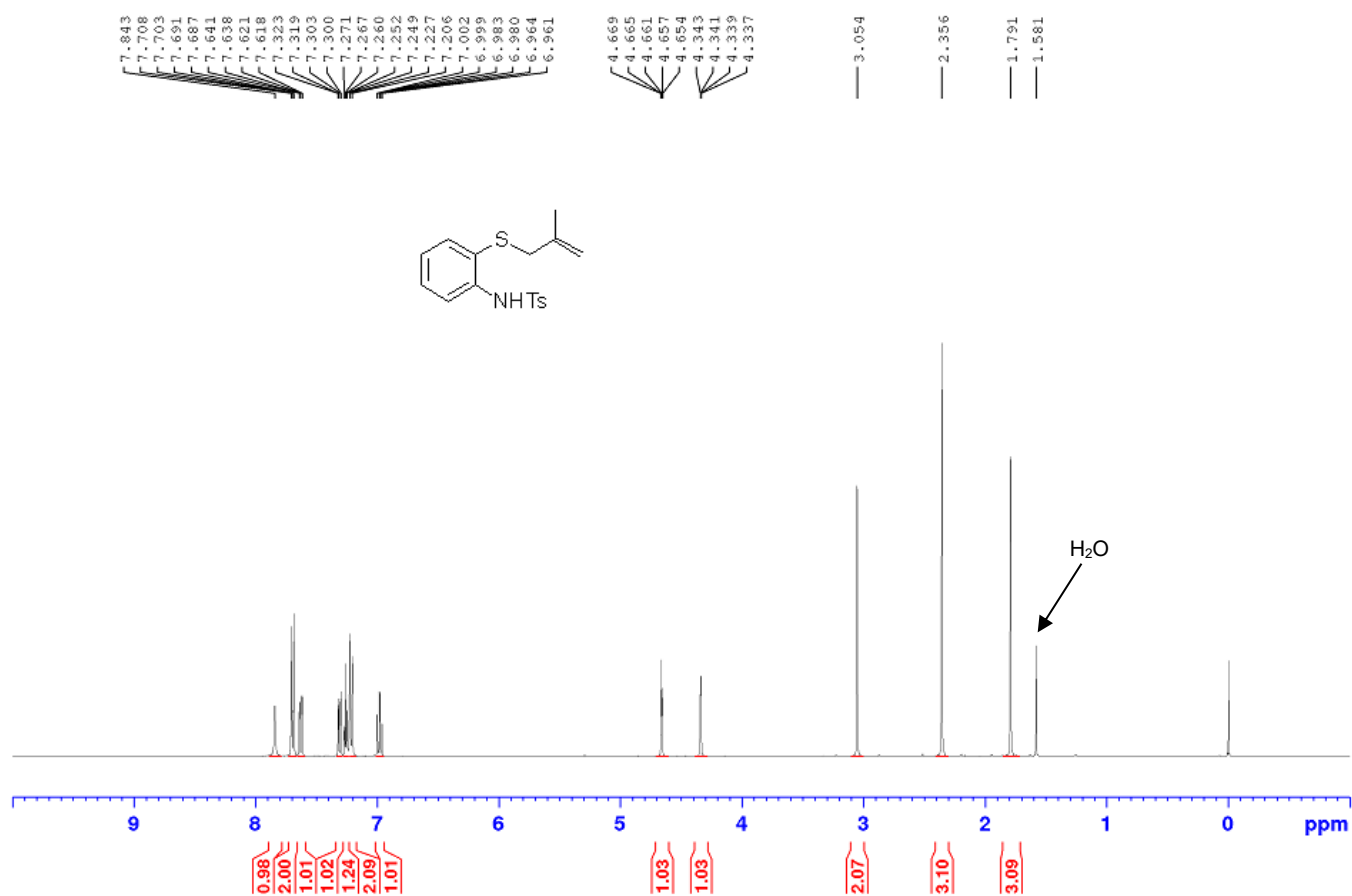
***N*¹-Ac-*N*²-Ts-*N*¹-Methallylbenzene-1,2-diamine (in CDCl₃)**



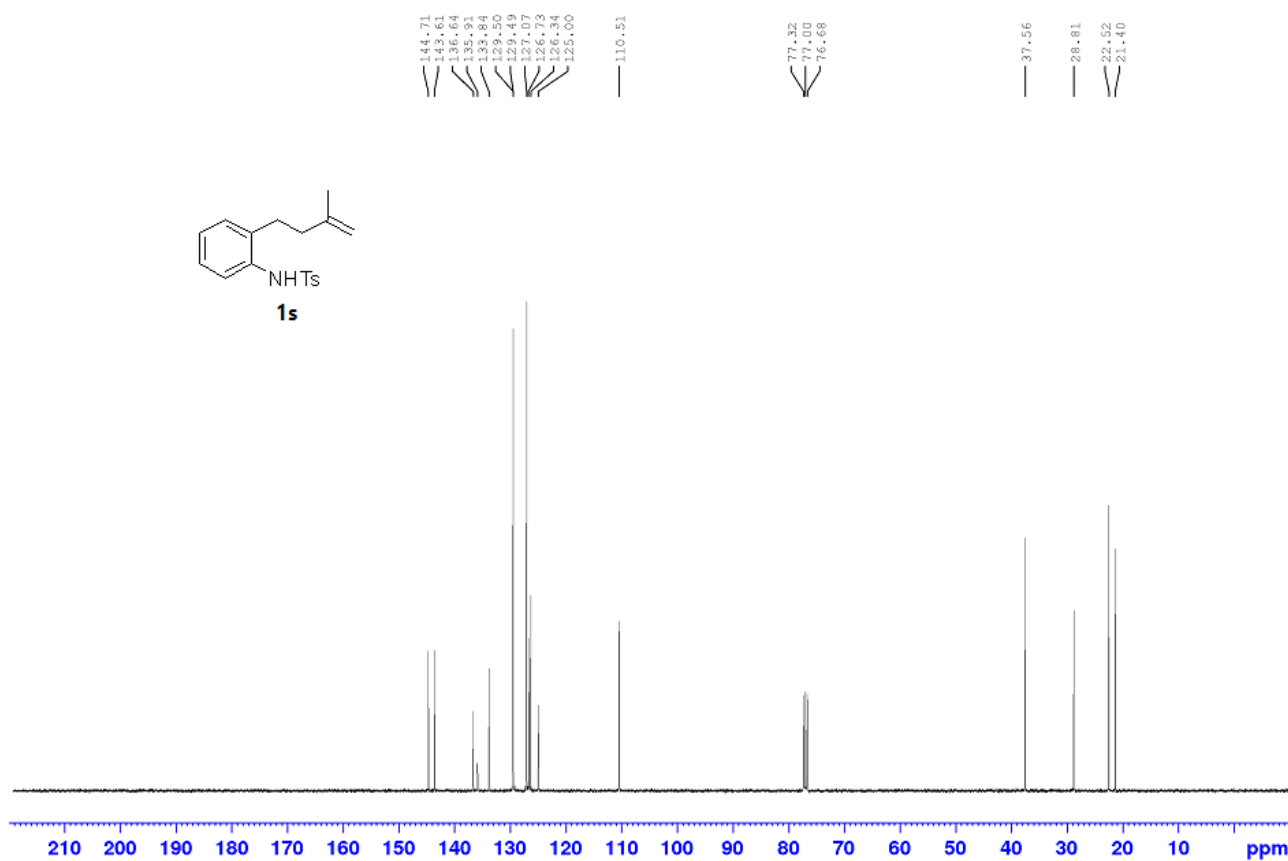
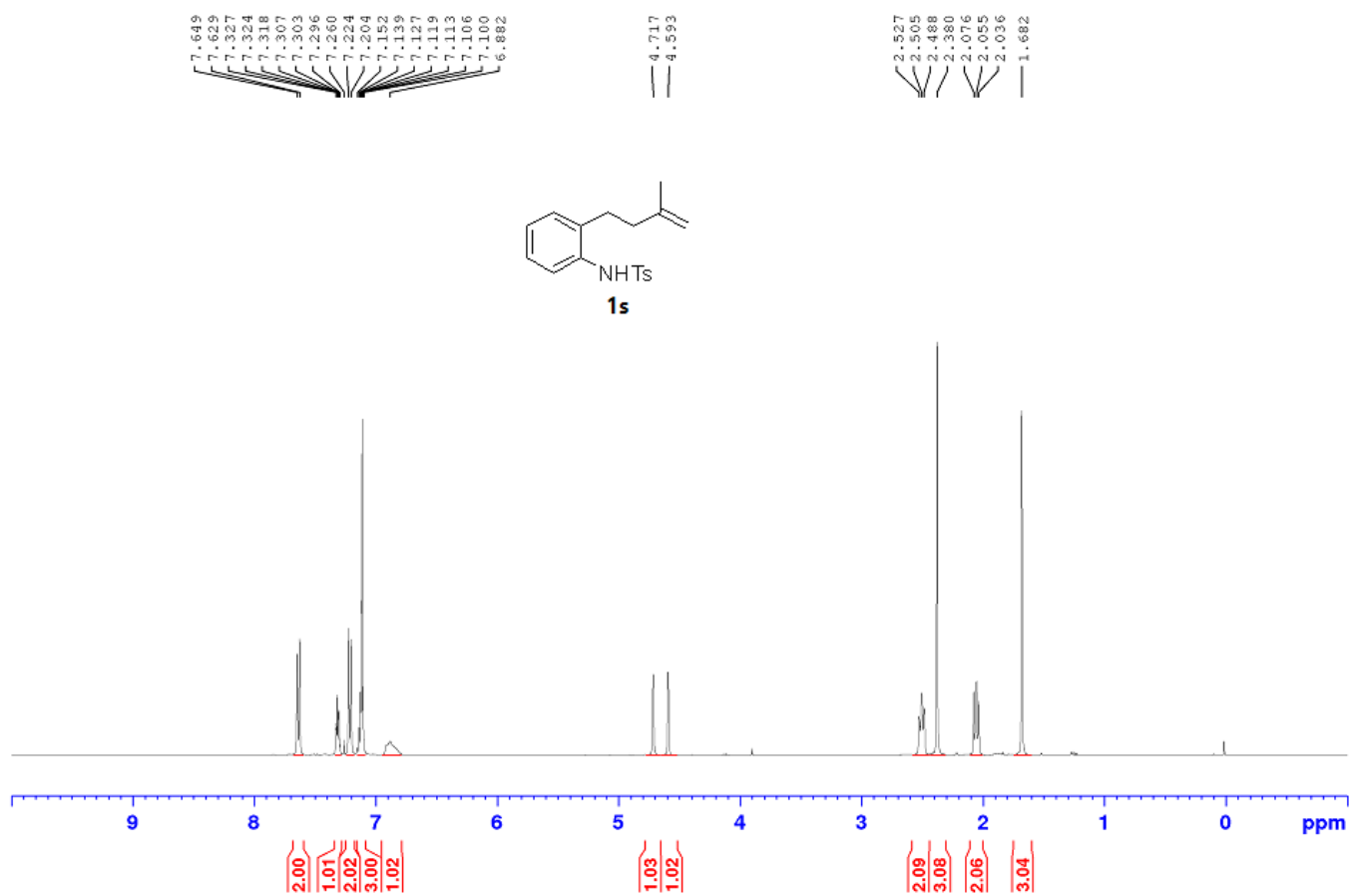
***N*¹-Cbz-*N*²-Ts-*N*¹-Methallylbenzene-1,2-diamine (in CDCl₃)**



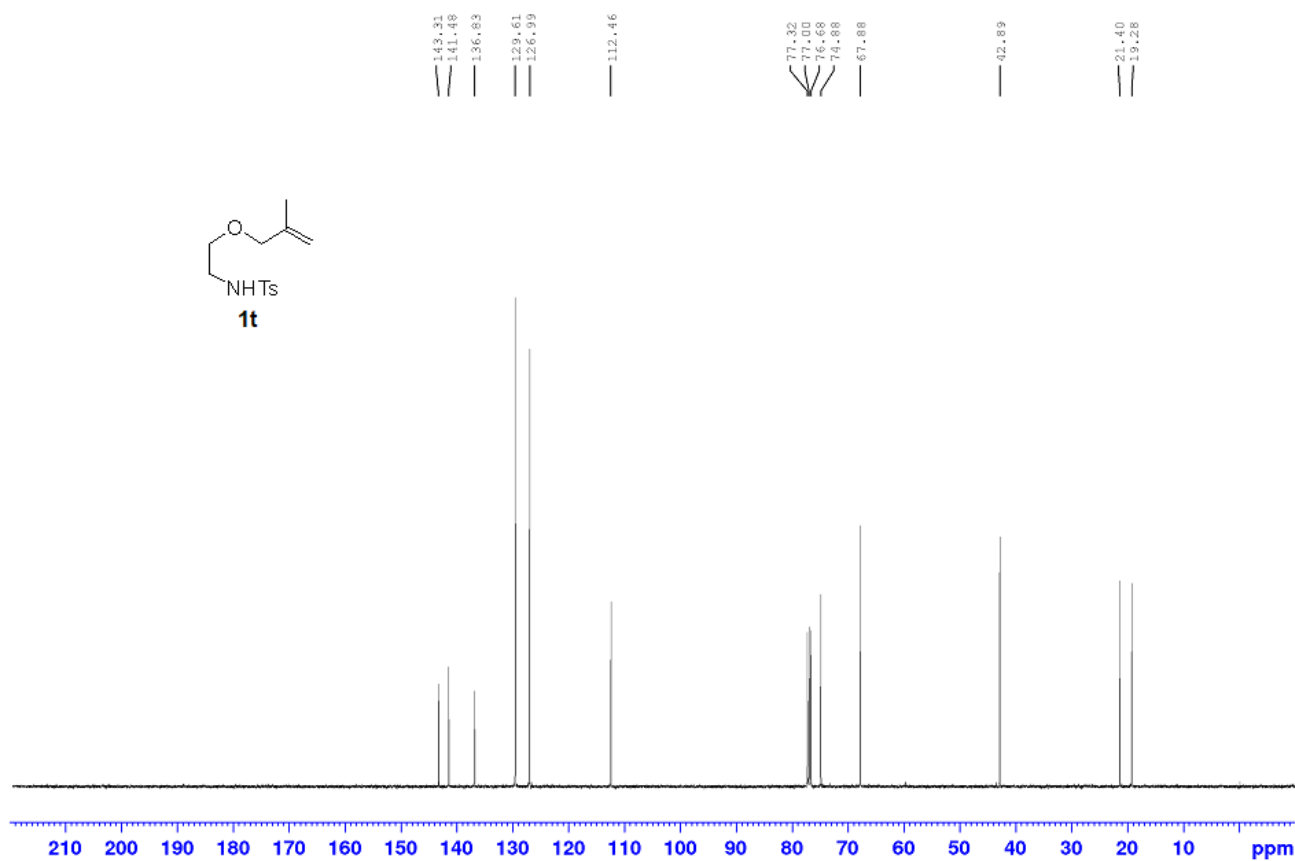
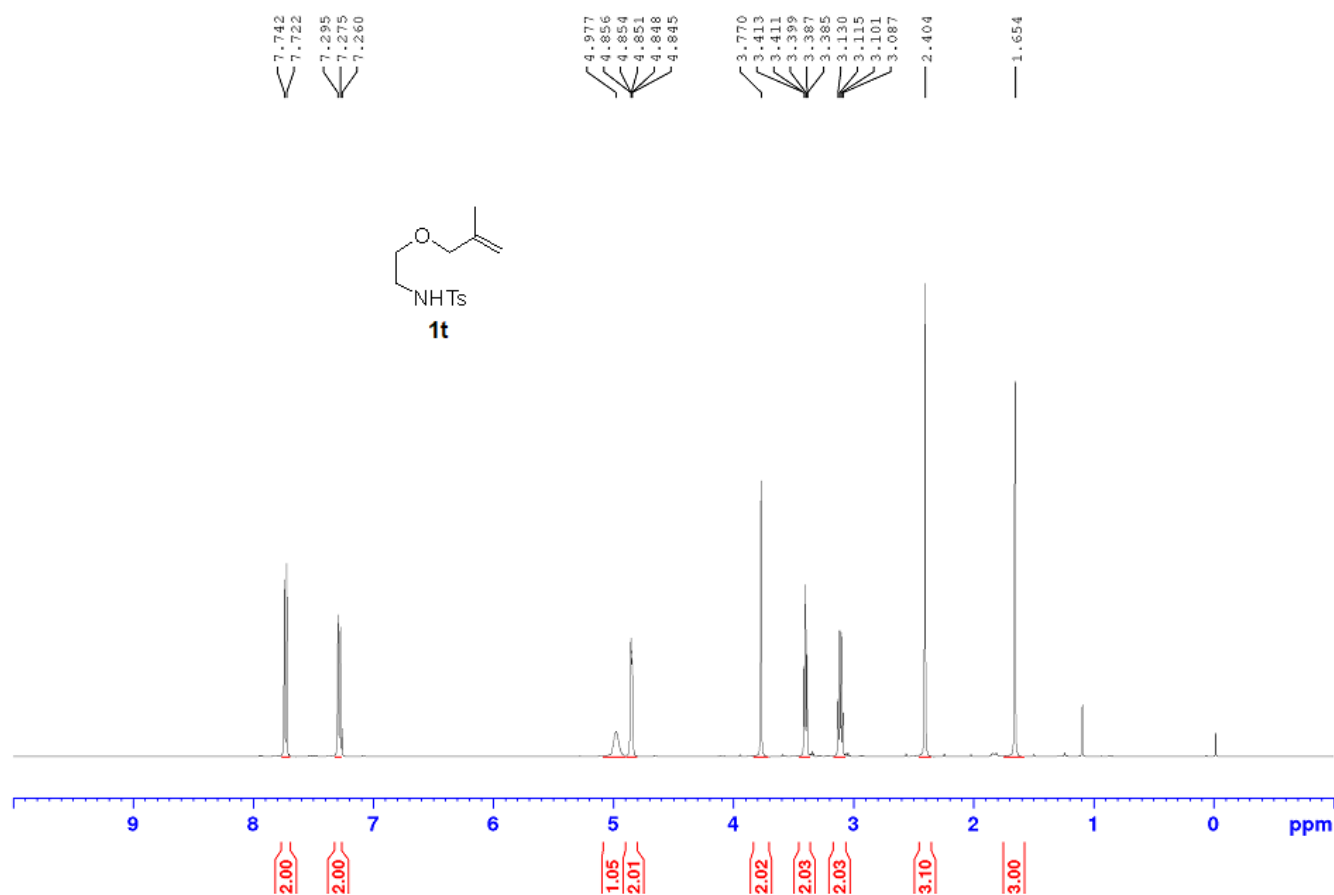
***N*-Ts-2-(Methallylthio)aniline (in CDCl₃)**



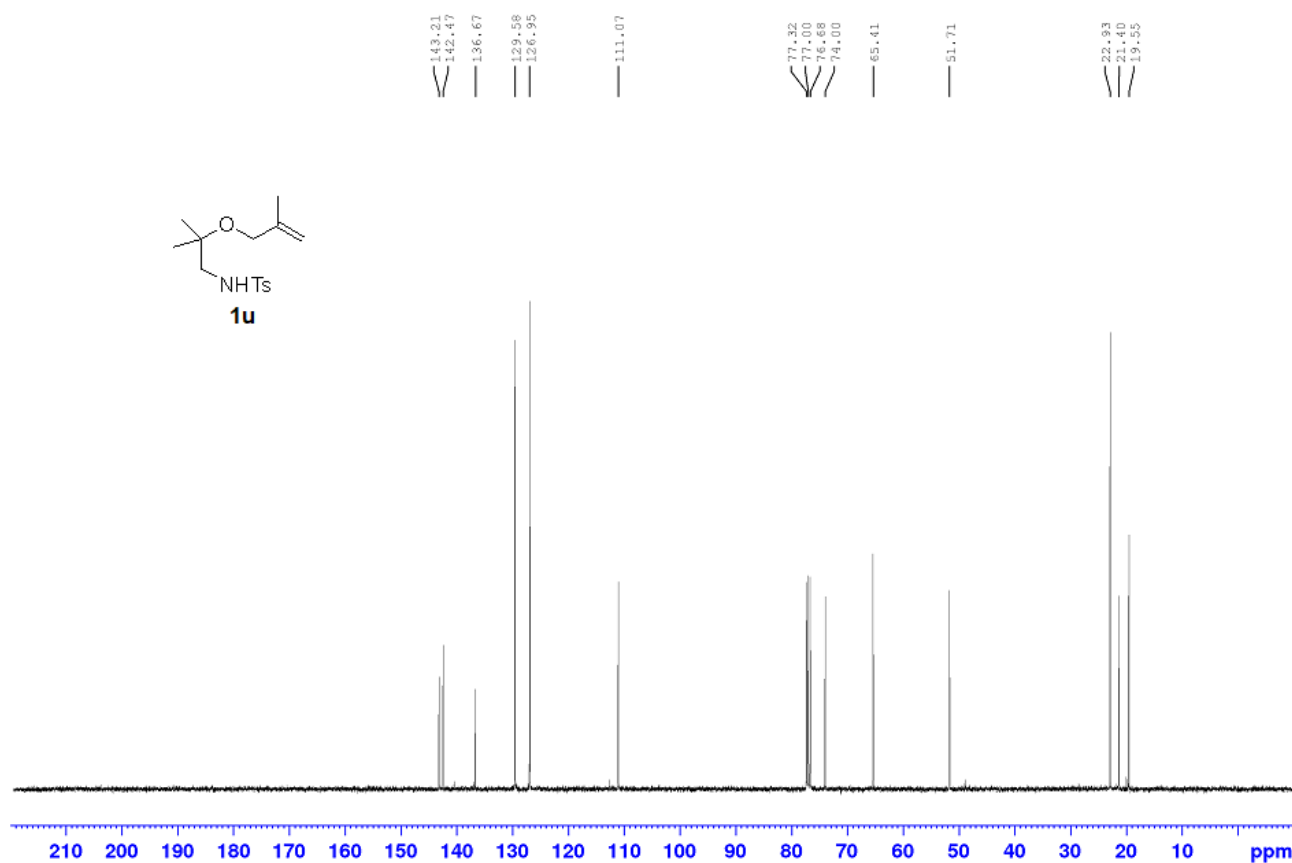
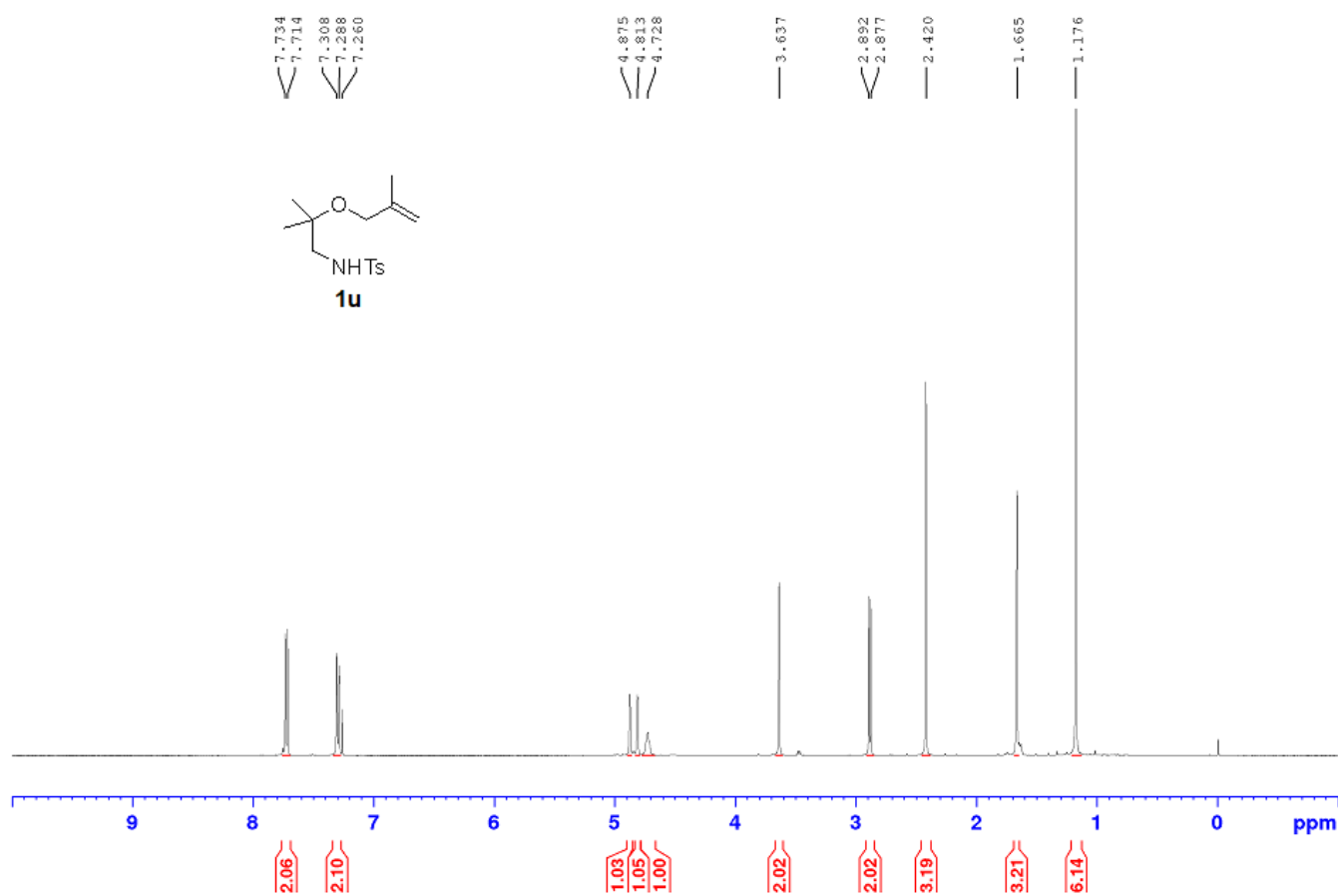
***N*-Ts-2-(3-Methylbut-3-en-1-yl)aniline (**1s**) (in CDCl₃)**



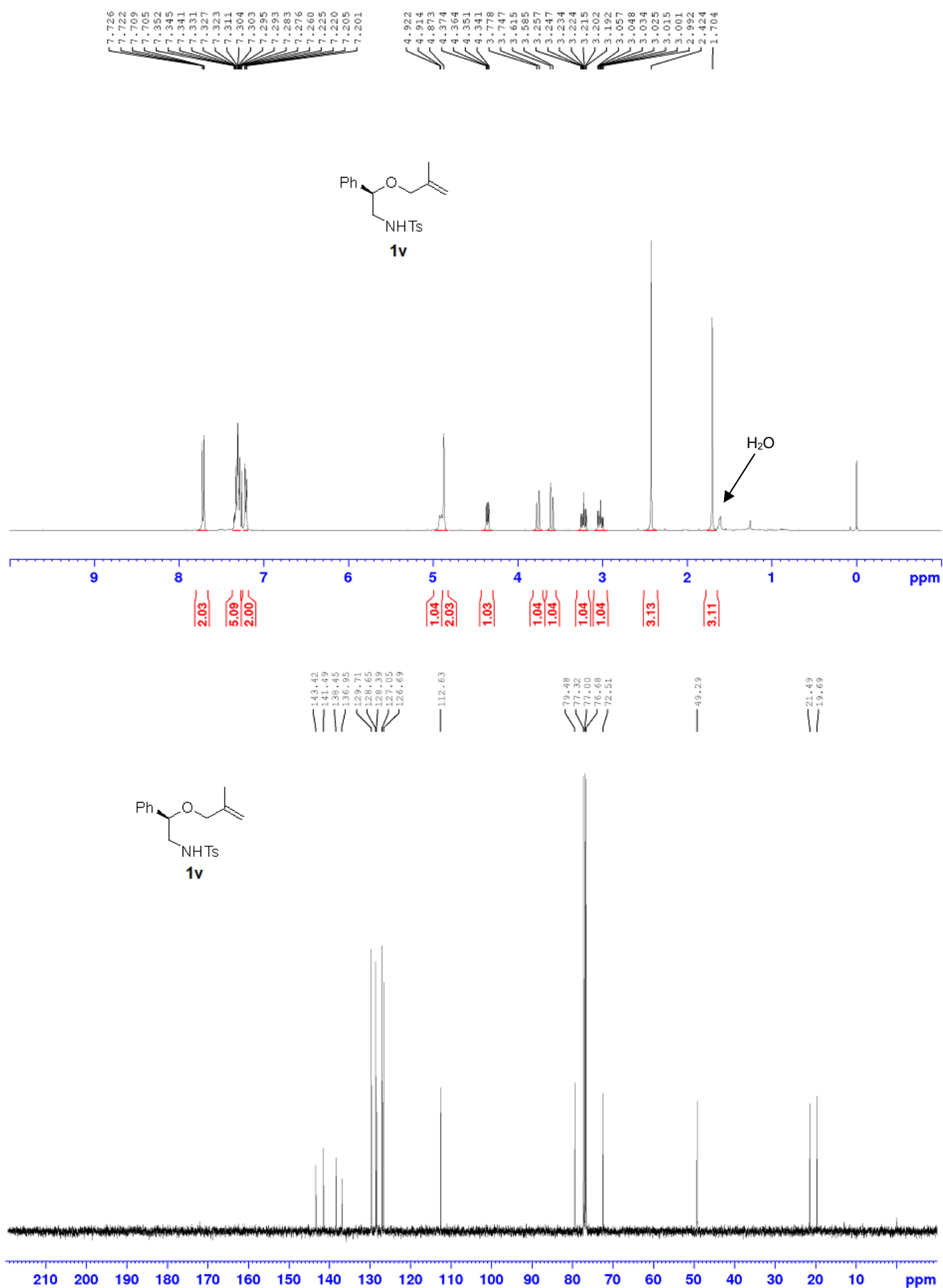
***N*-Ts-2-(Methallyloxy)ethanamine (**1t**) (in CDCl₃)**



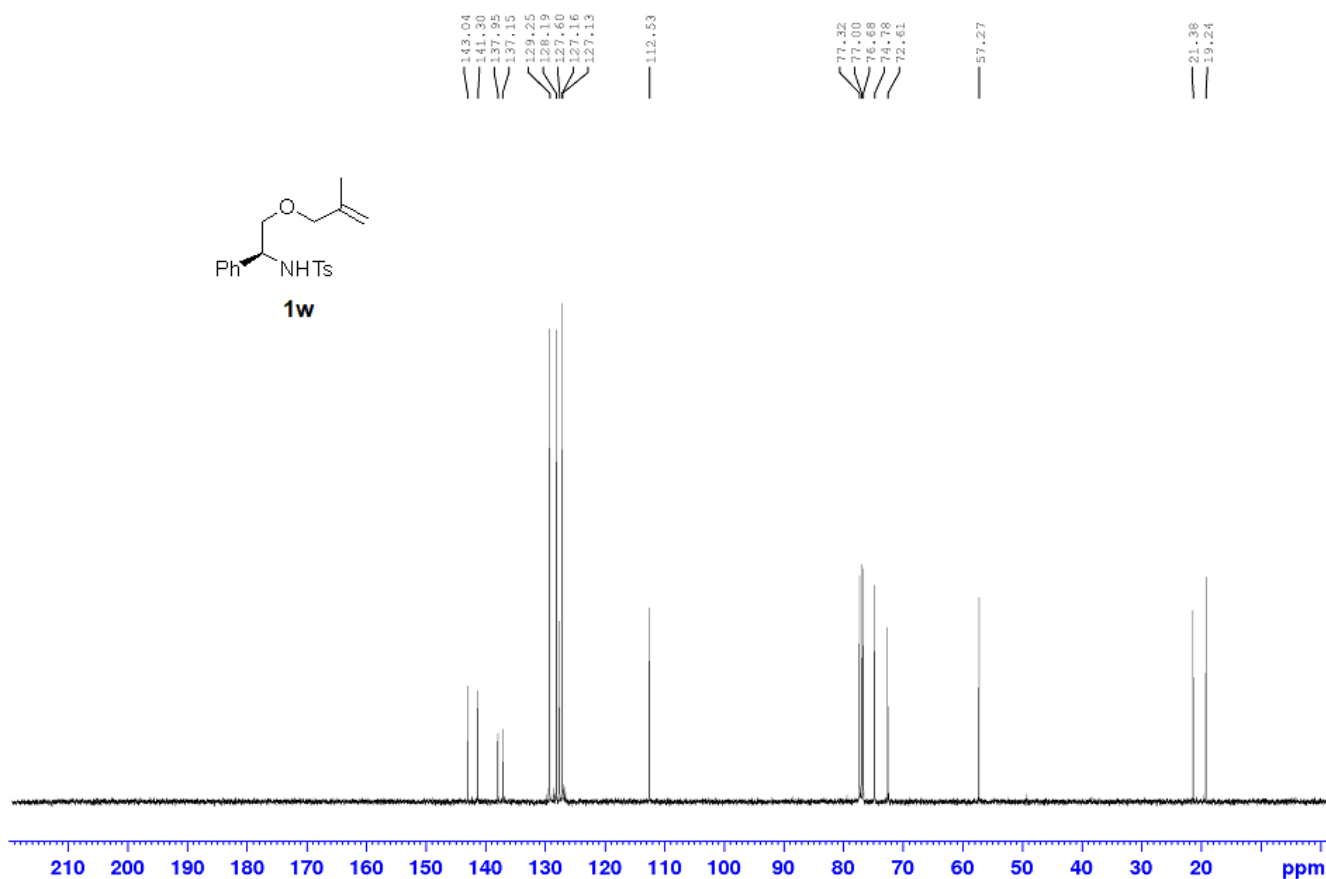
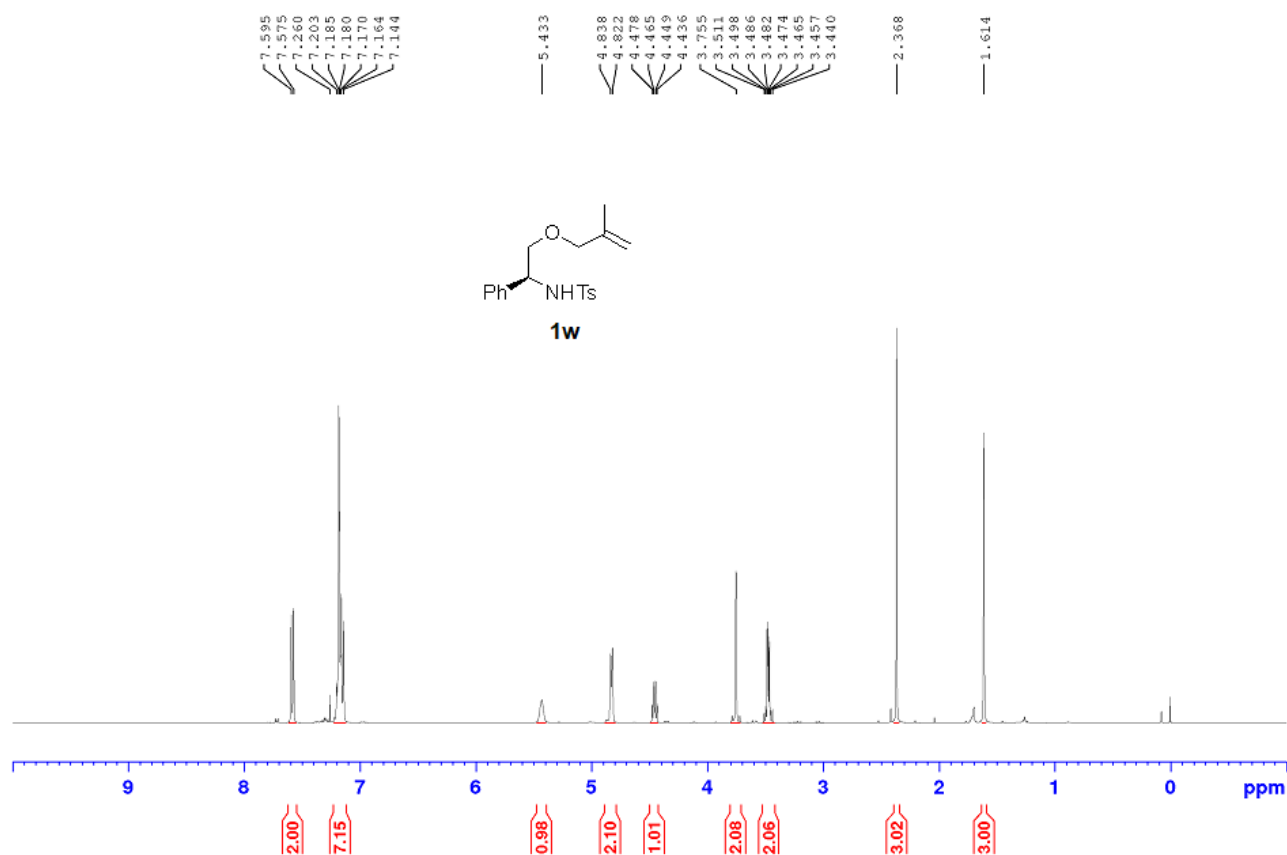
***N*-Ts-2-(Methallyloxy)-2-methylpropanamine (1u) (in CDCl₃)**



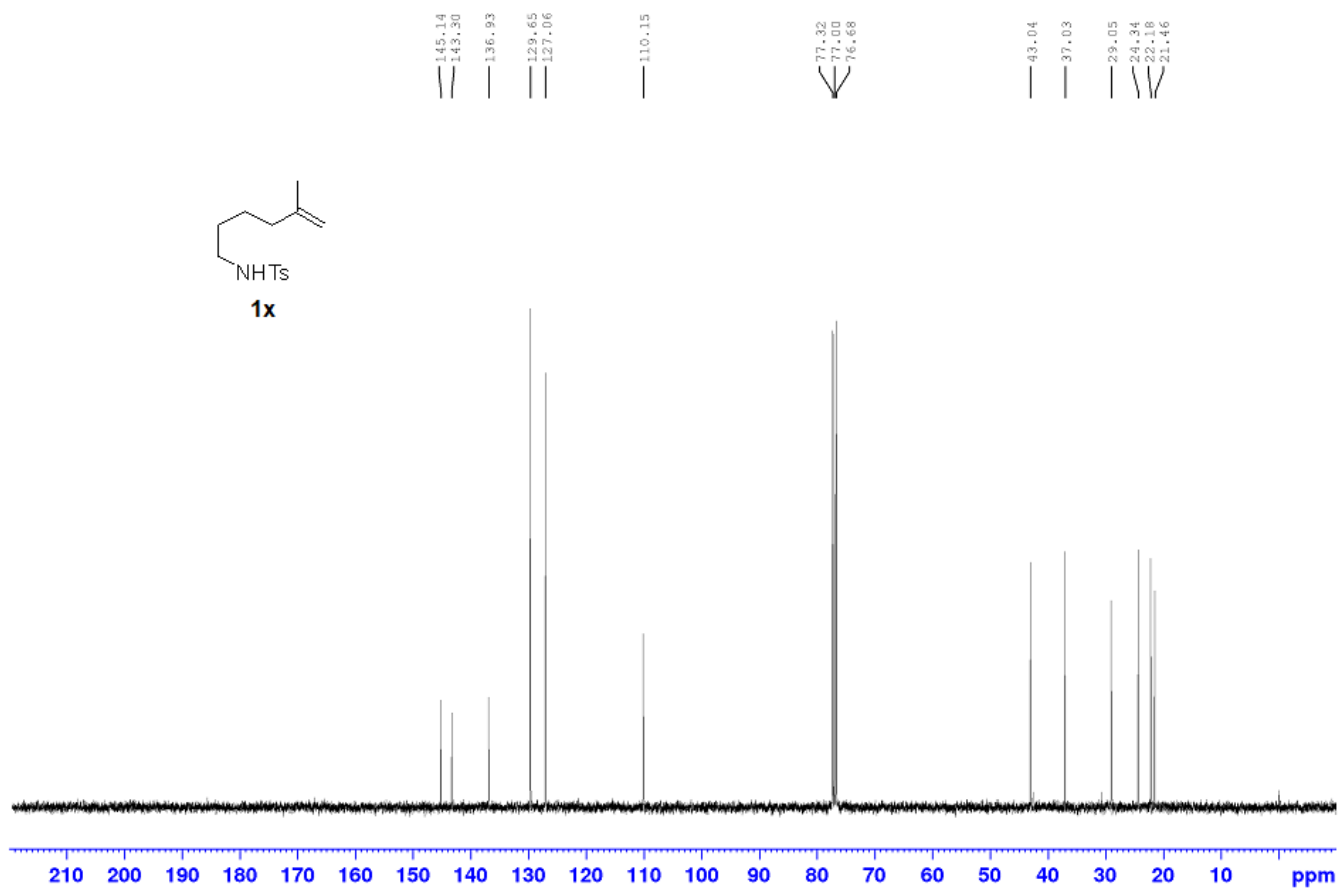
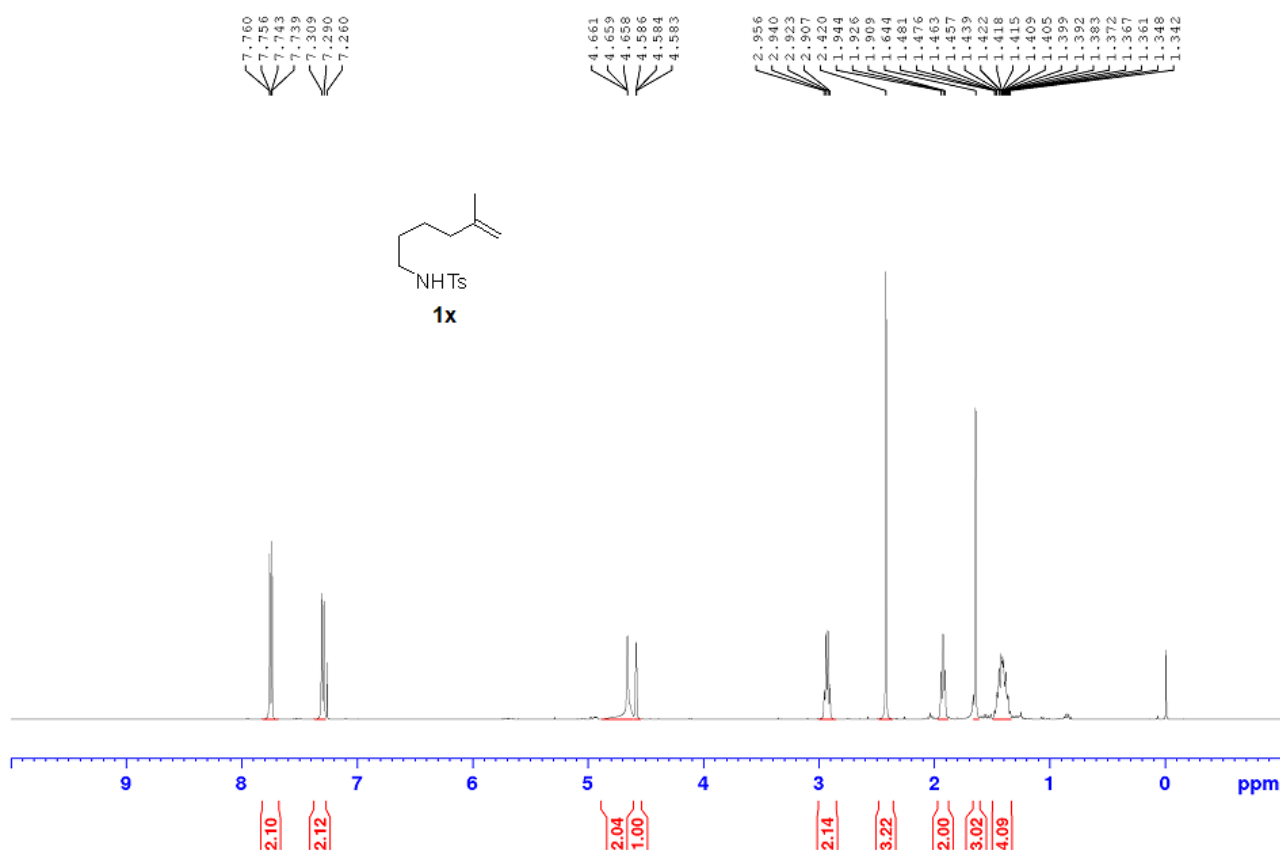
(*R*)-*N*-Ts-2-(Methallyloxy)-2-phenylethylamine (1v) (in CDCl₃)



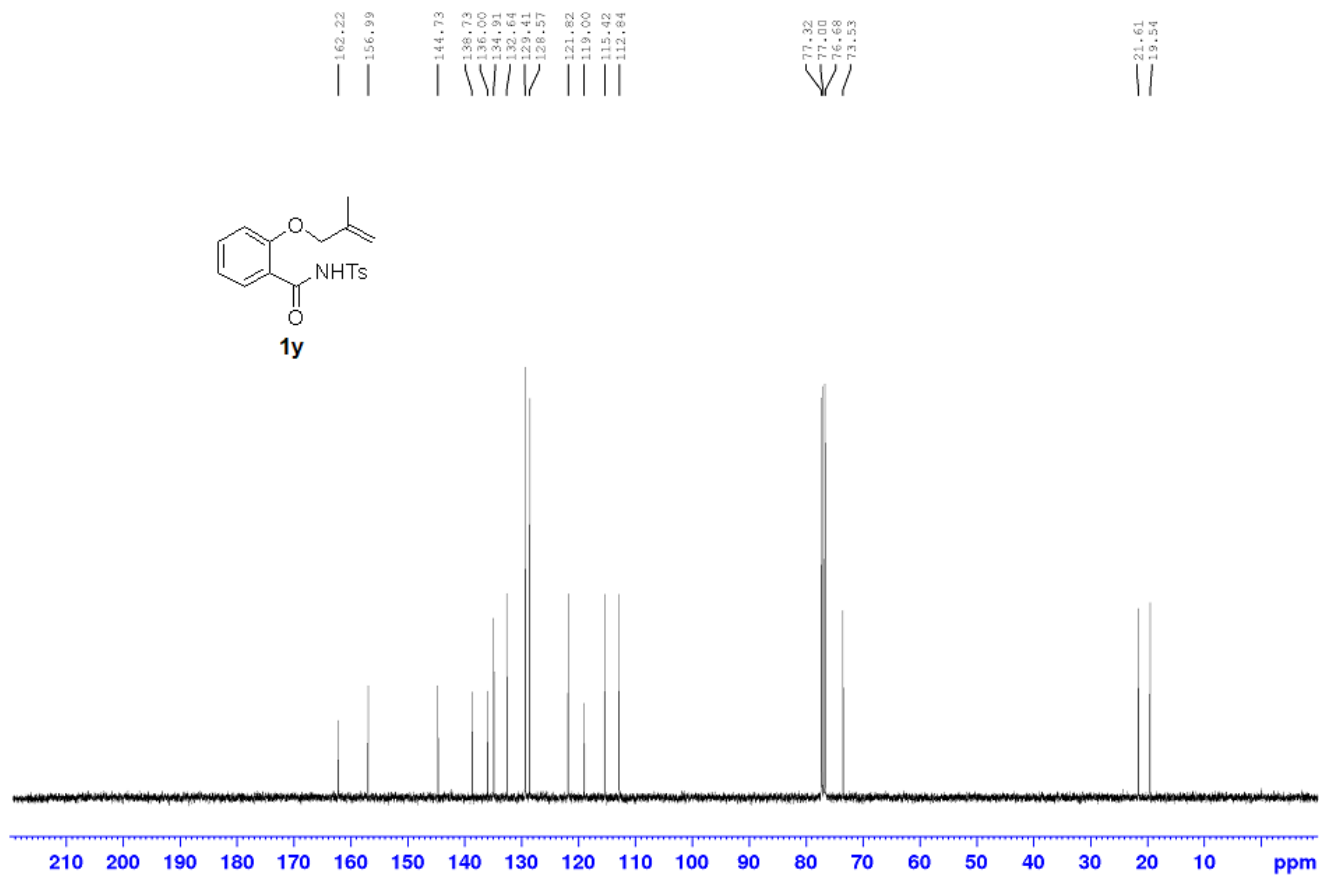
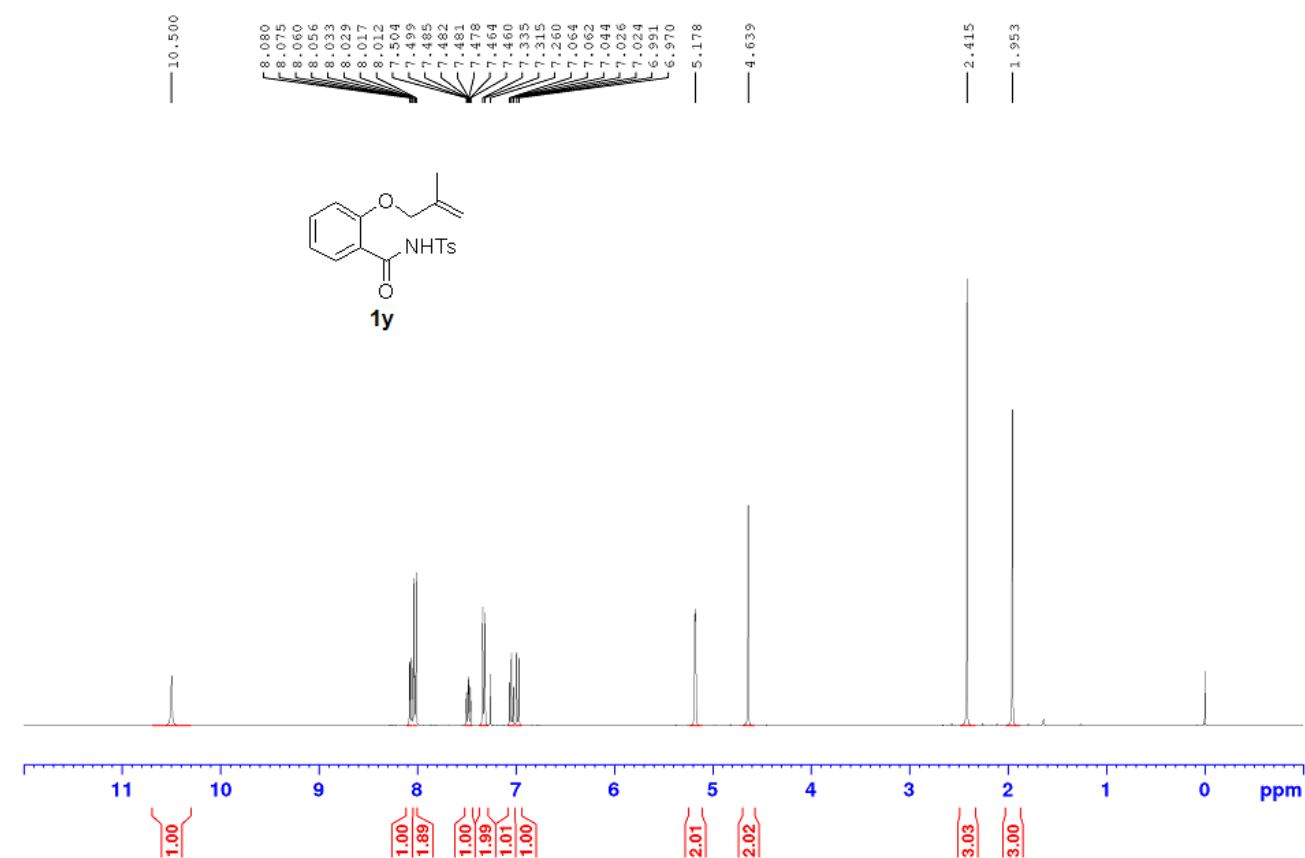
(S)-N-Ts-2-(Methallyloxy)-1-phenylethylamine (1w) (in CDCl₃)



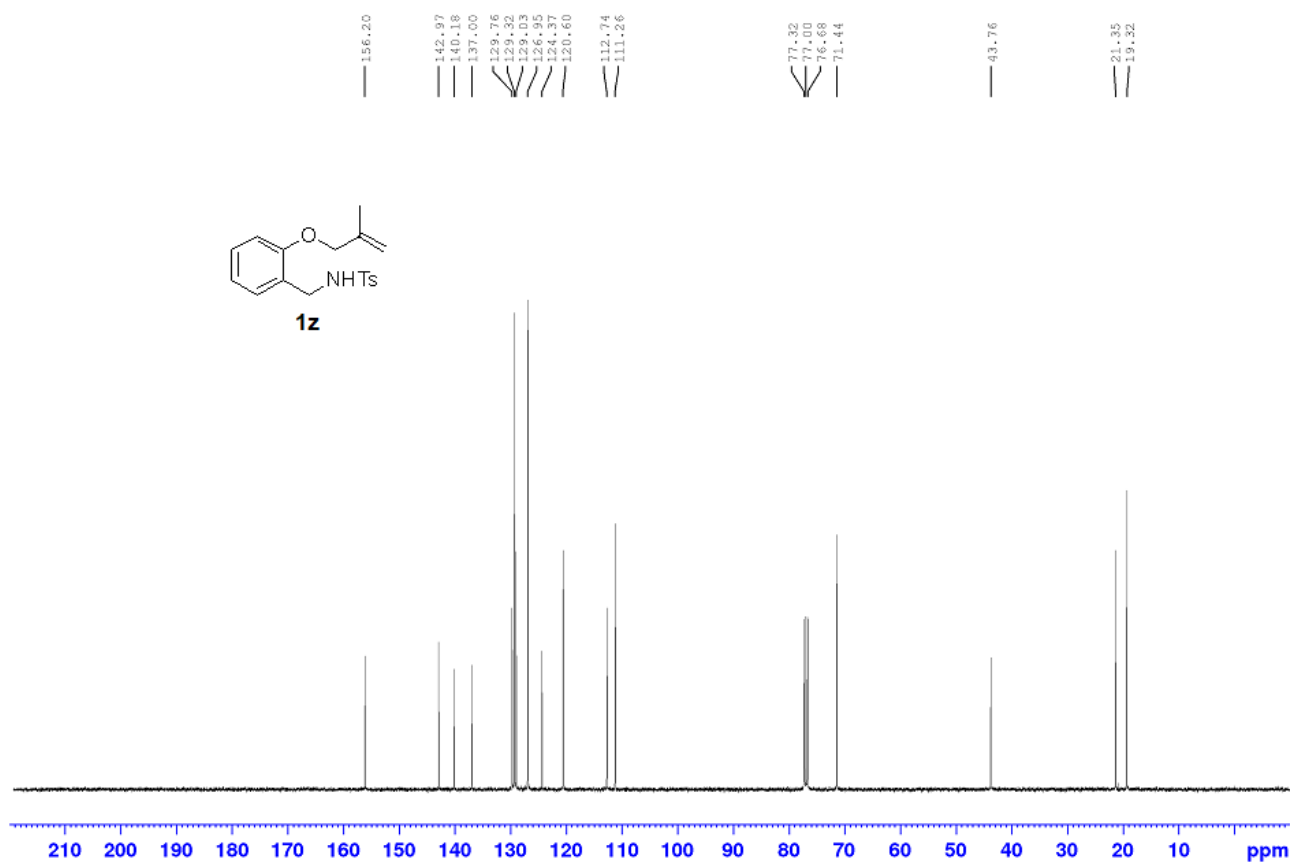
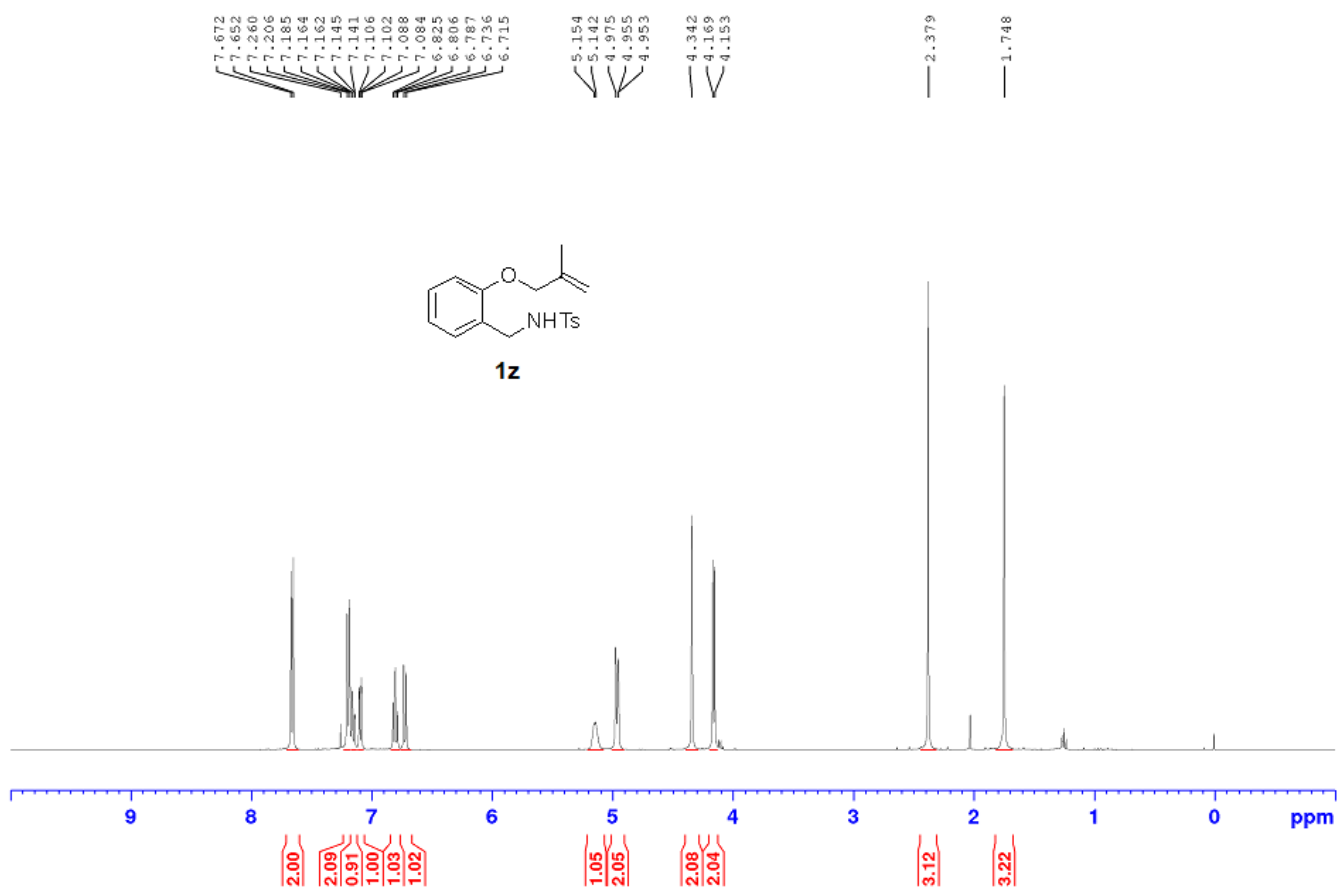
***N*-Ts-5-Methylhex-5-en-1-amine (1x) (in CDCl₃)**



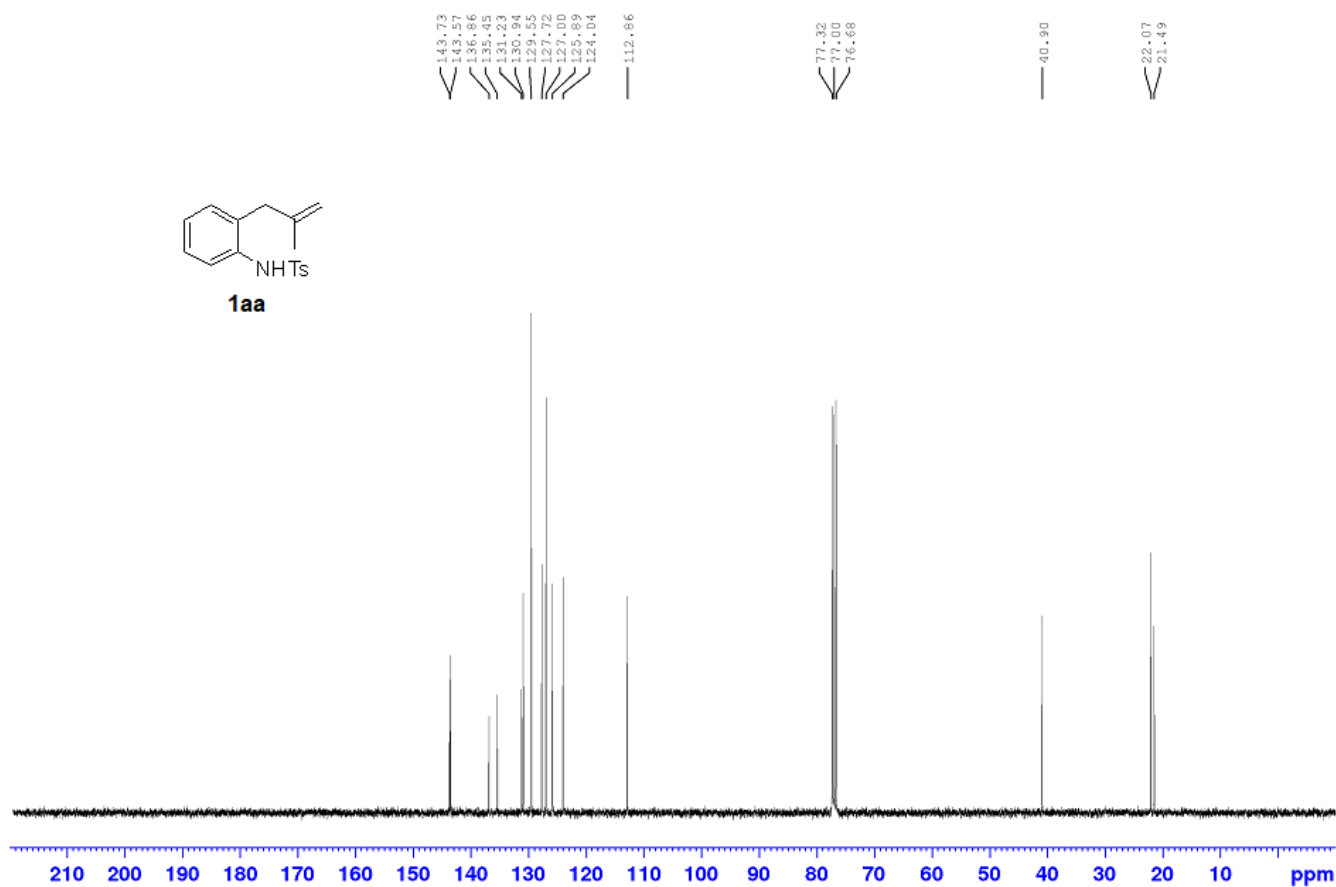
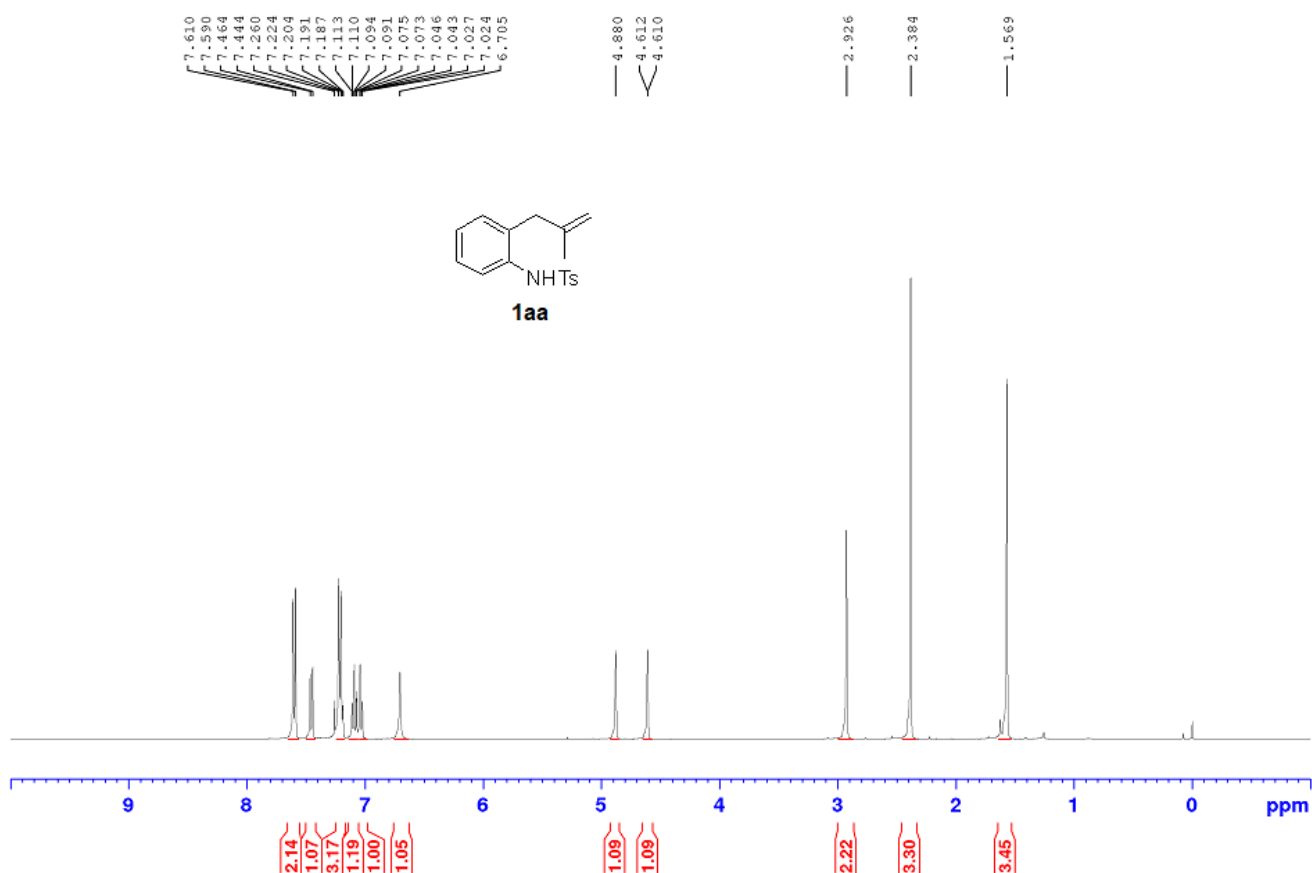
***N*-Ts-2-(Methallyloxy)benzamide (1y) (in CDCl₃)**



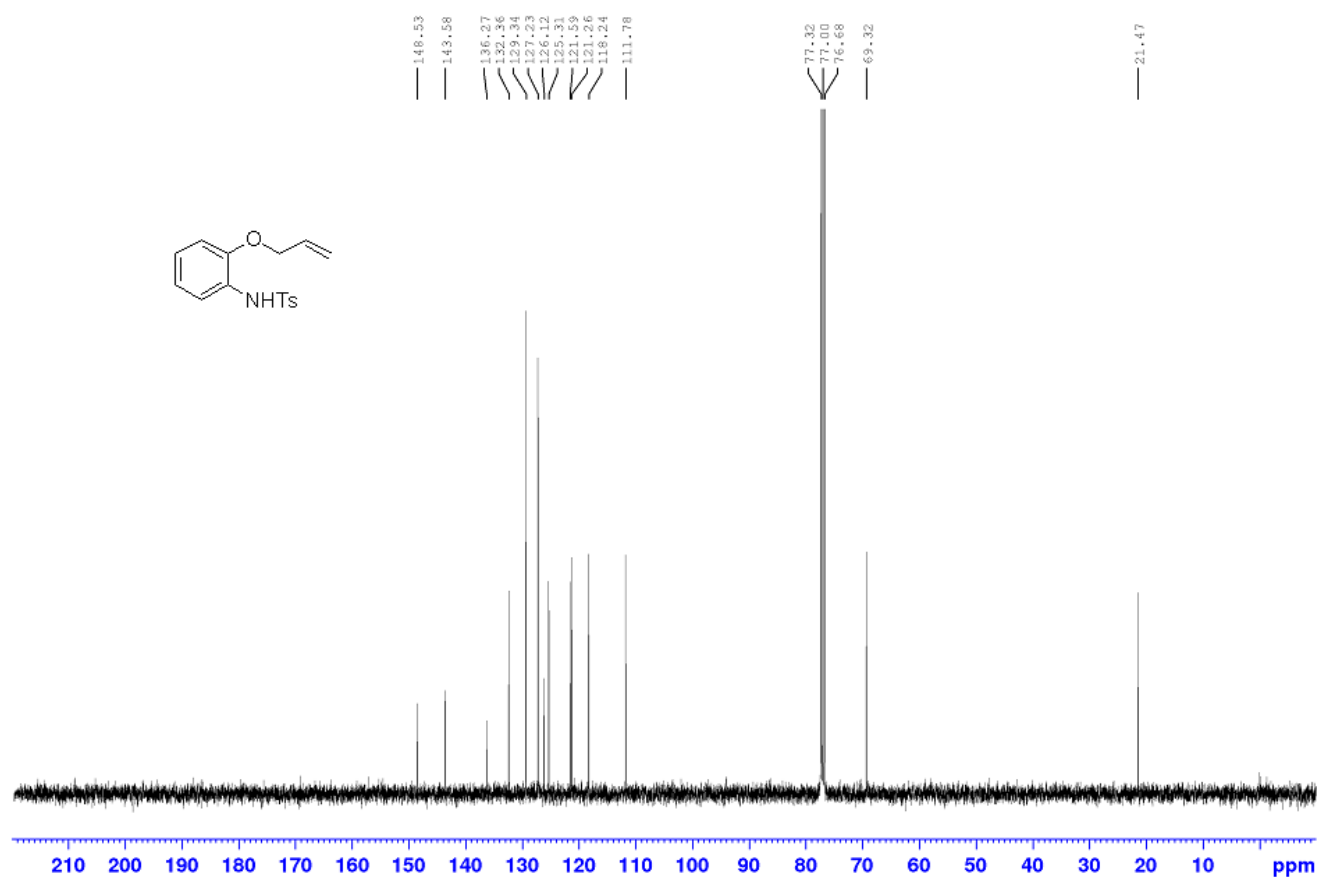
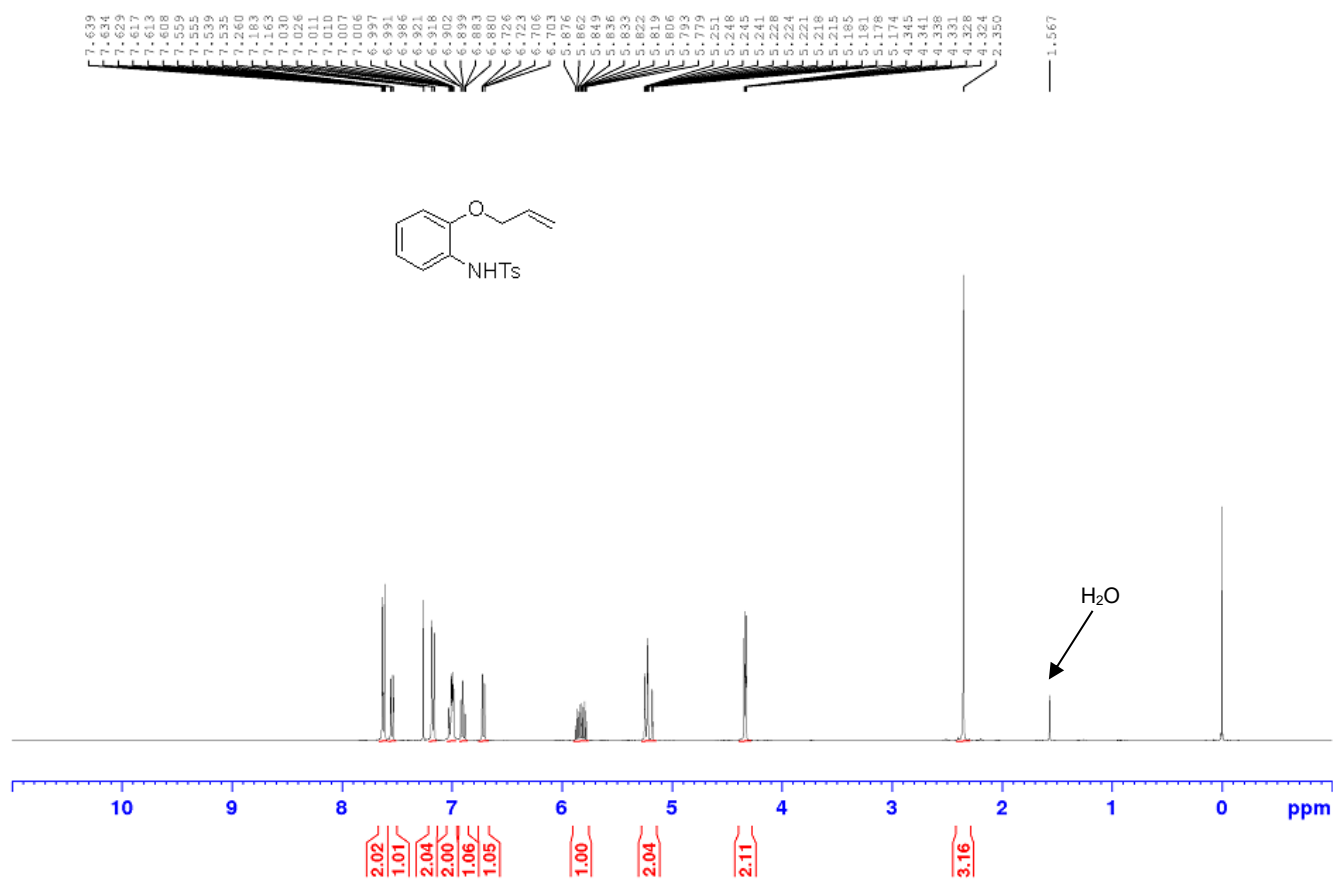
***N*-Ts-(2-Methallyloxy)benzylamine (**1z**) (in CDCl₃)**



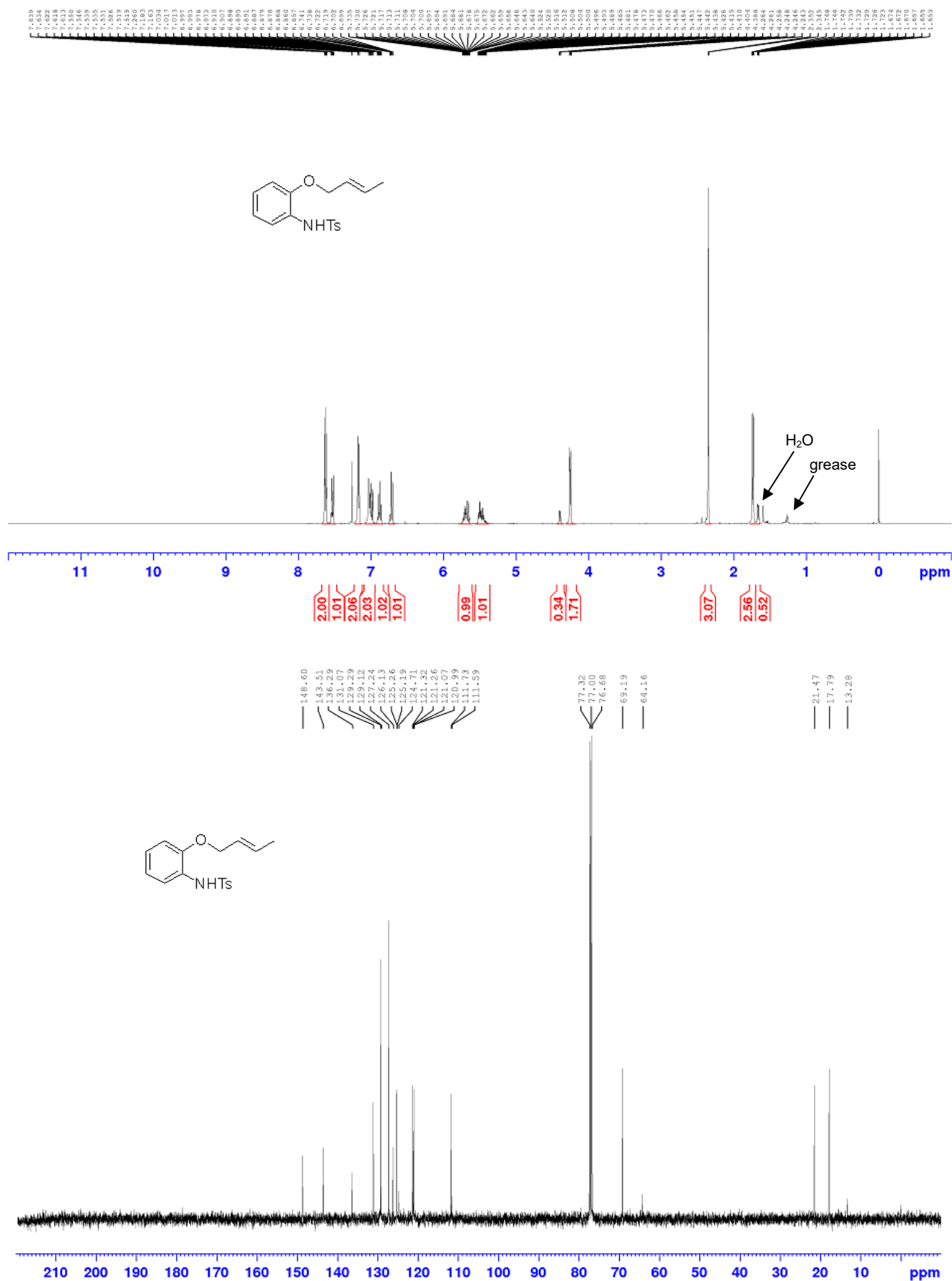
***N*-Ts-2-Methallylaniline (1aa) (in CDCl₃)**



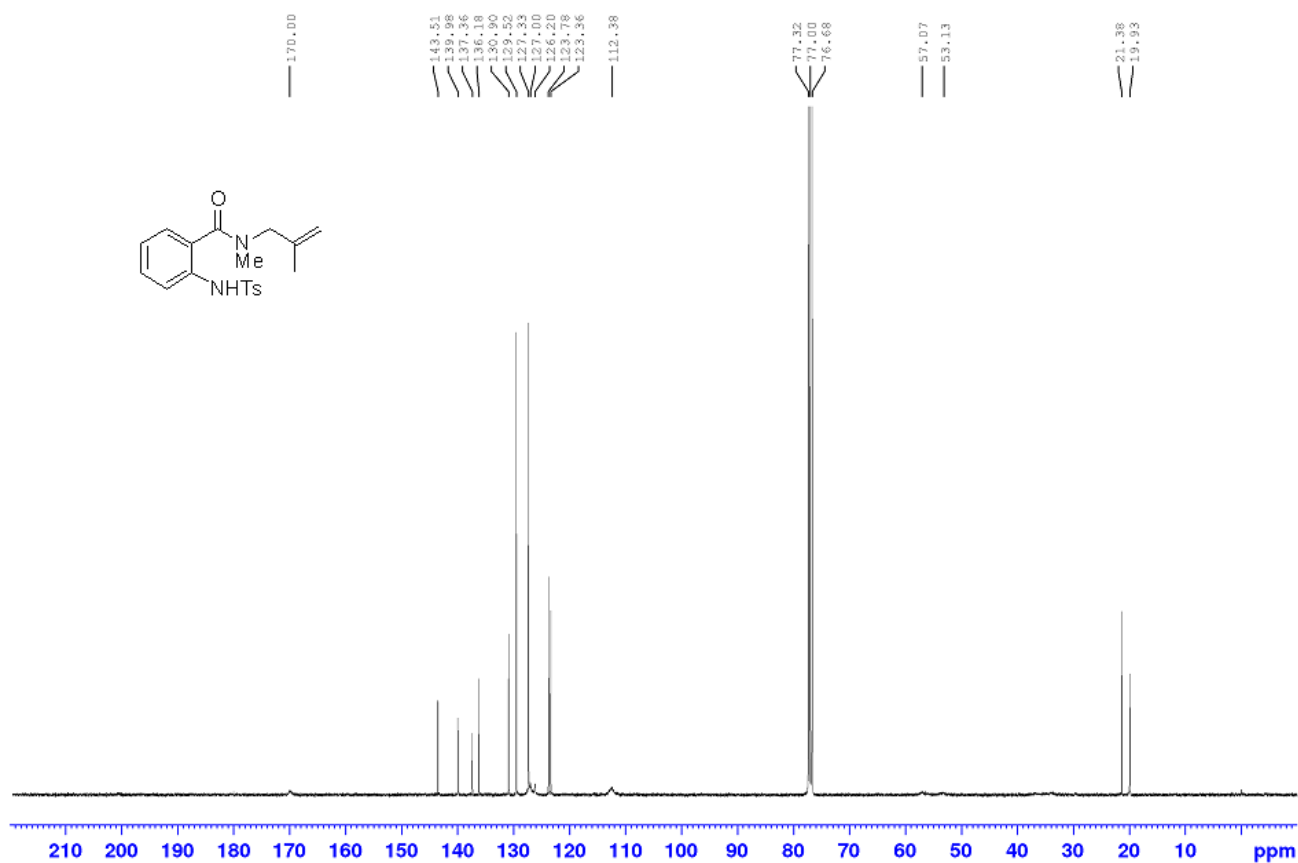
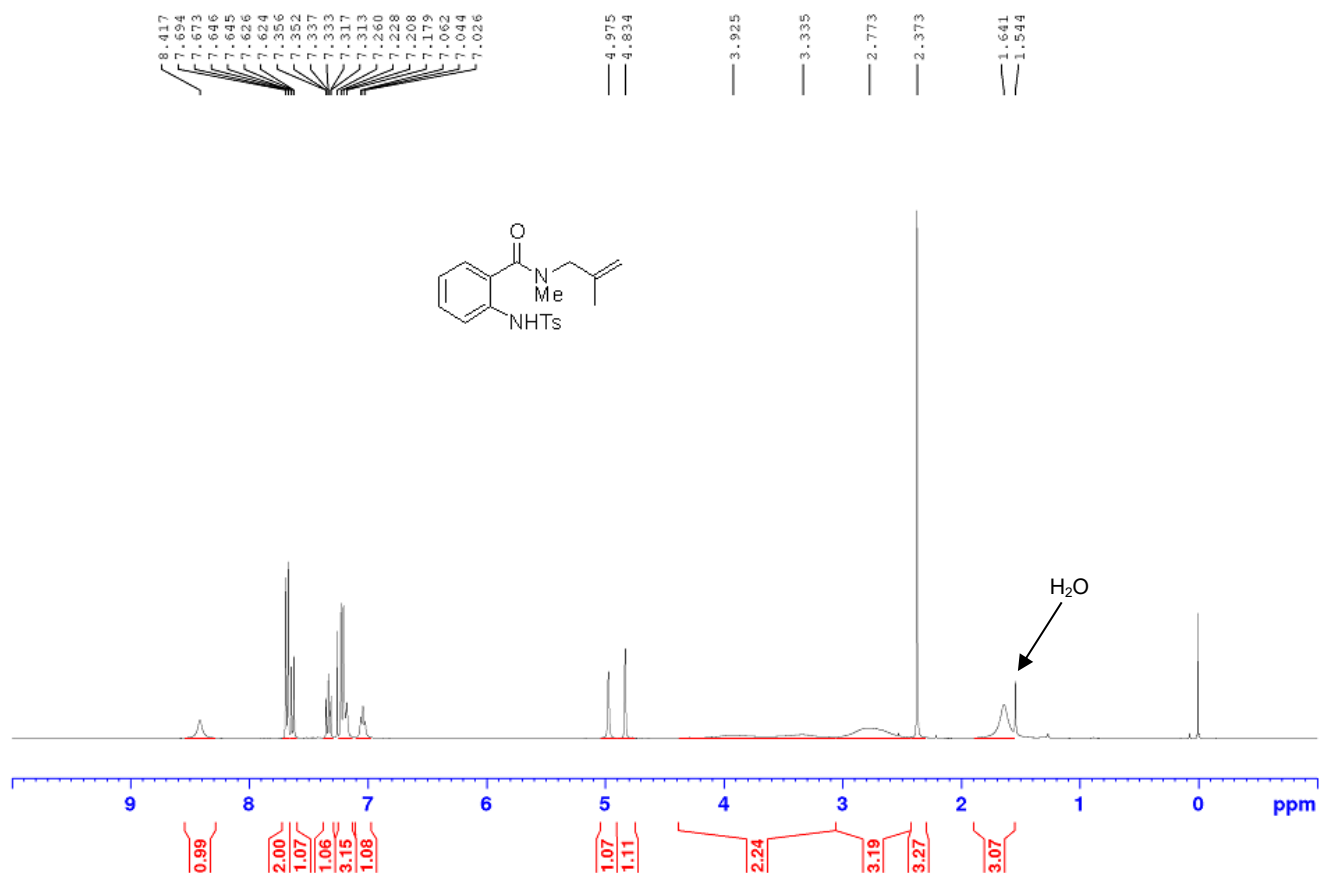
***N*-Ts-2-Allyloxyaniline (in CDCl₃)**



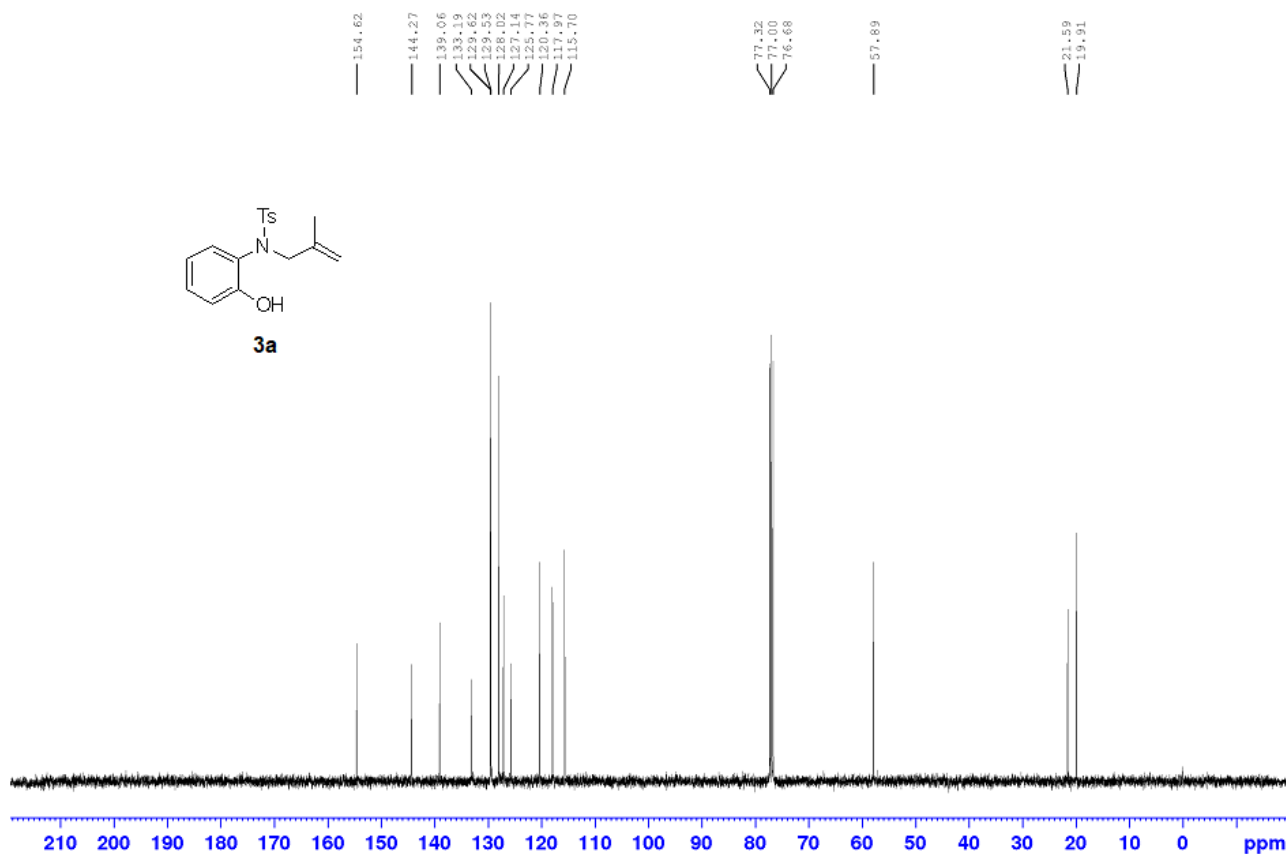
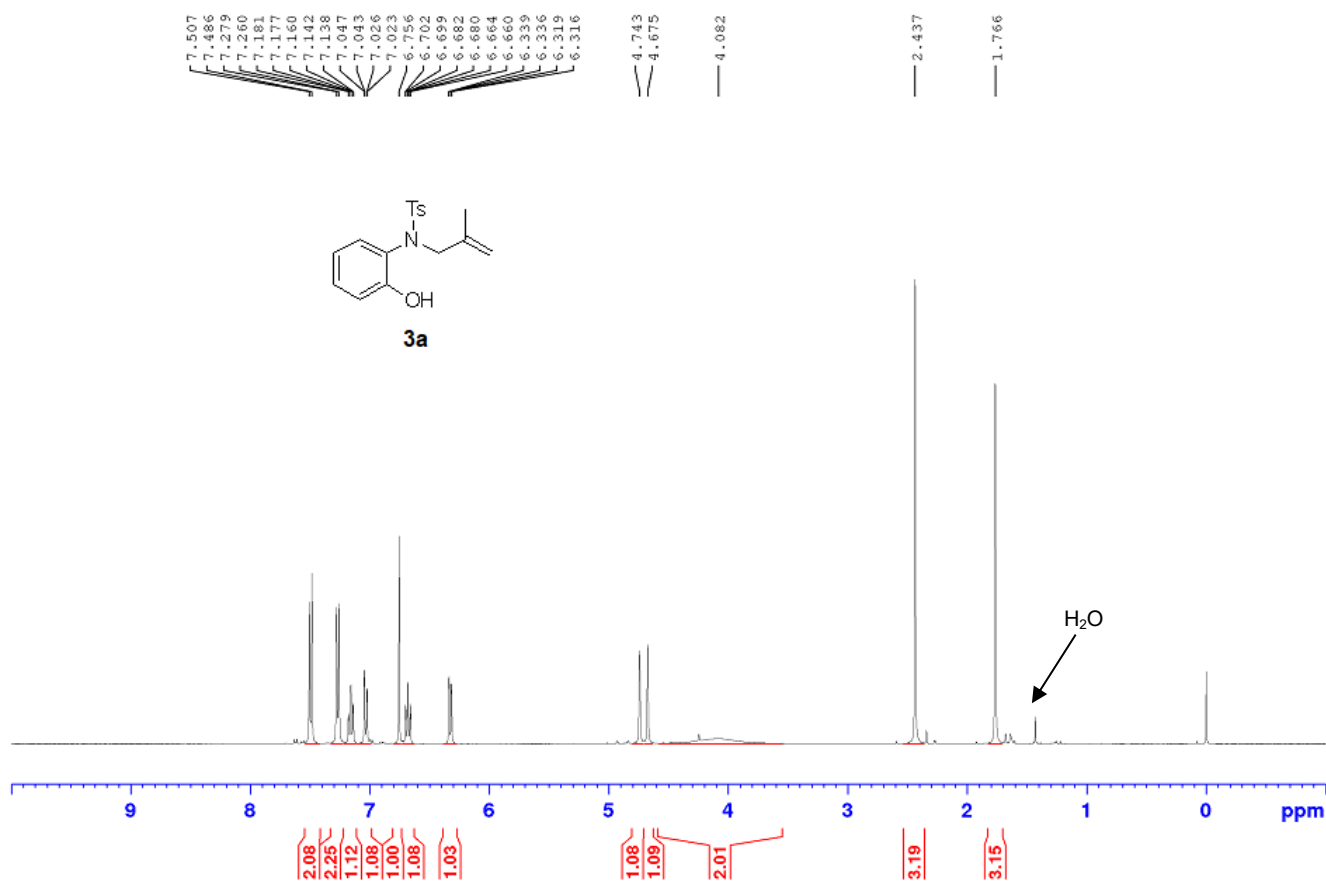
***N*-Ts-2-(But-2-en-1-yloxy)aniline (in CDCl₃)**



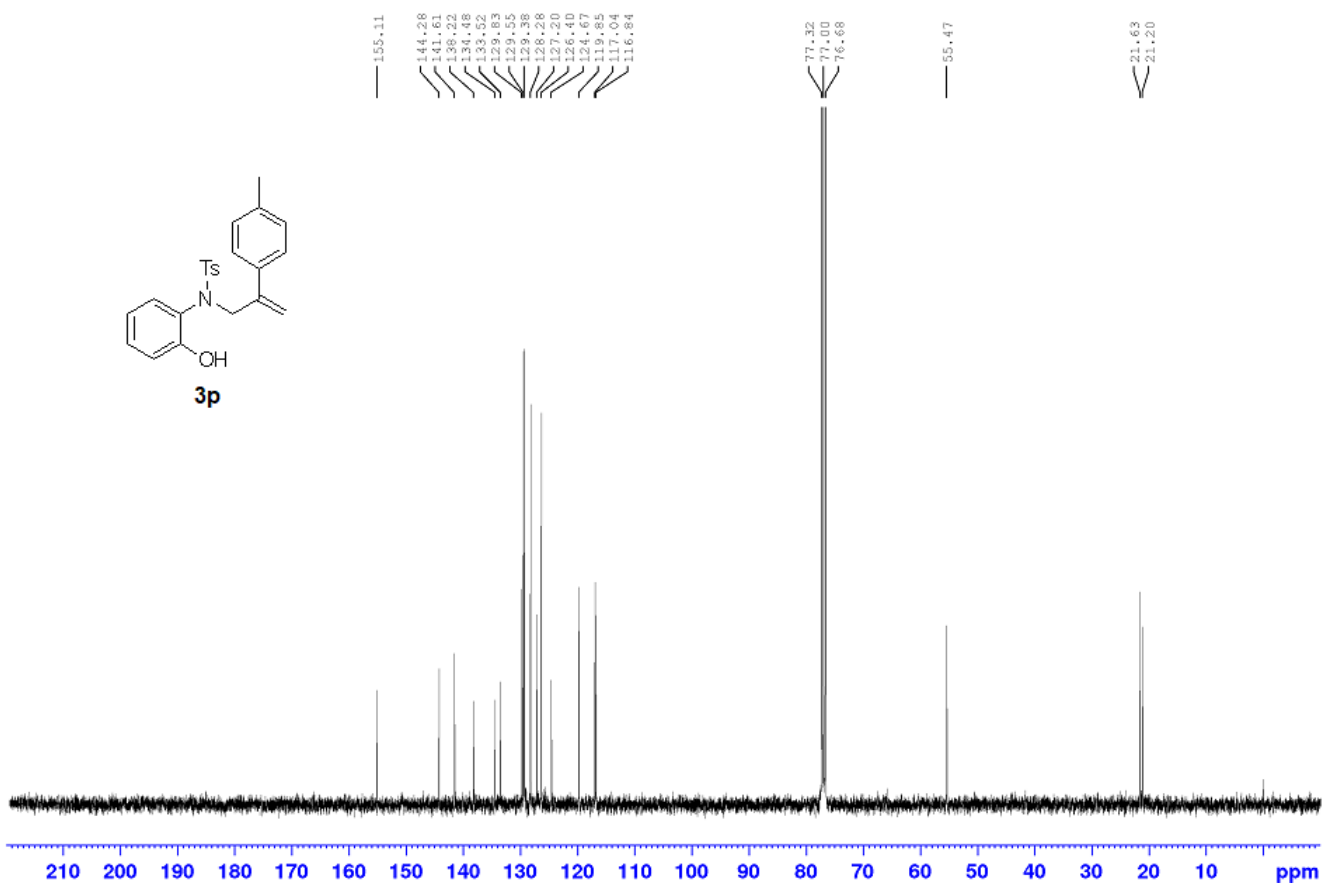
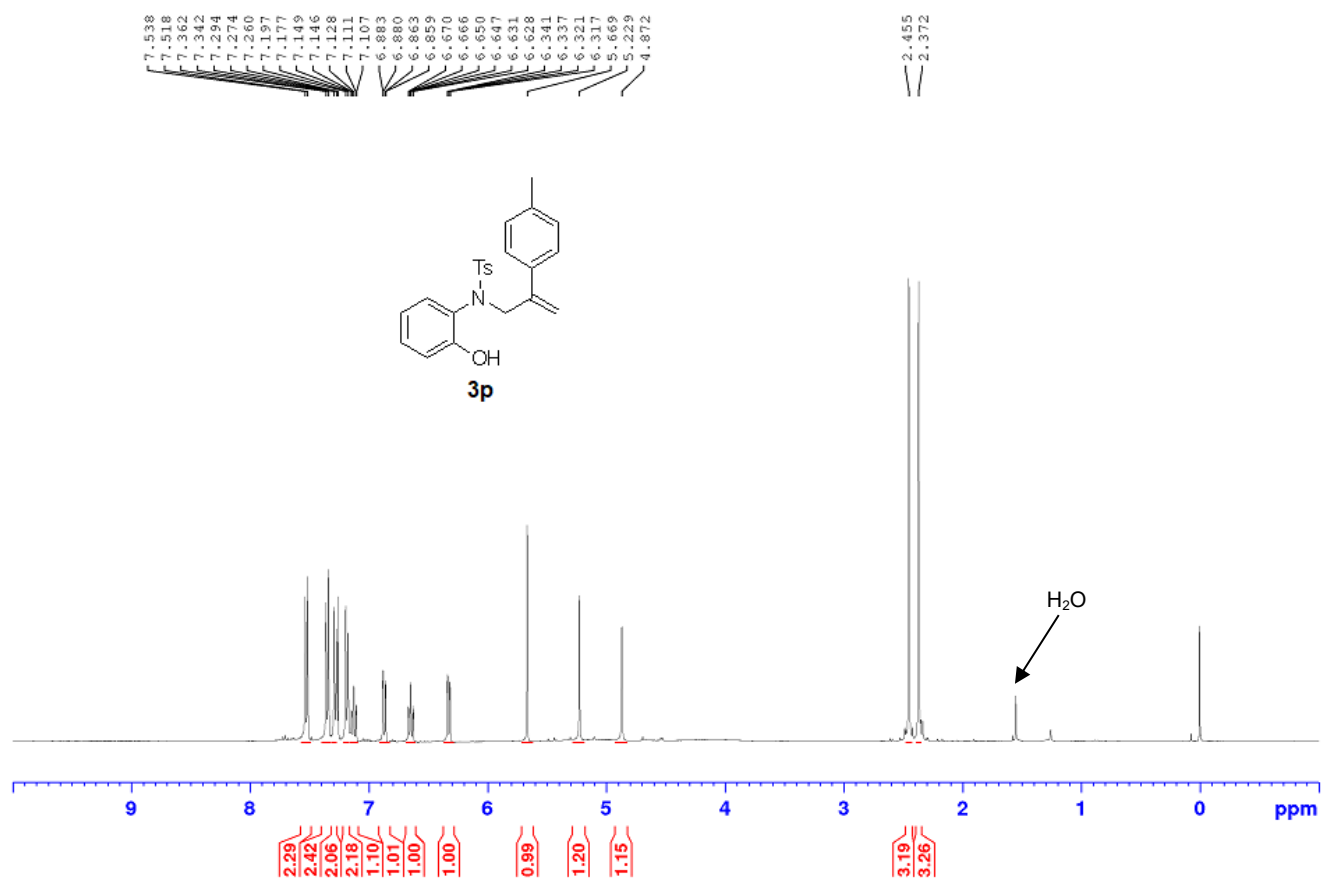
***N*-Methyl-*N*-methallyl-2-tosylaminobenzamide (in CDCl₃)**



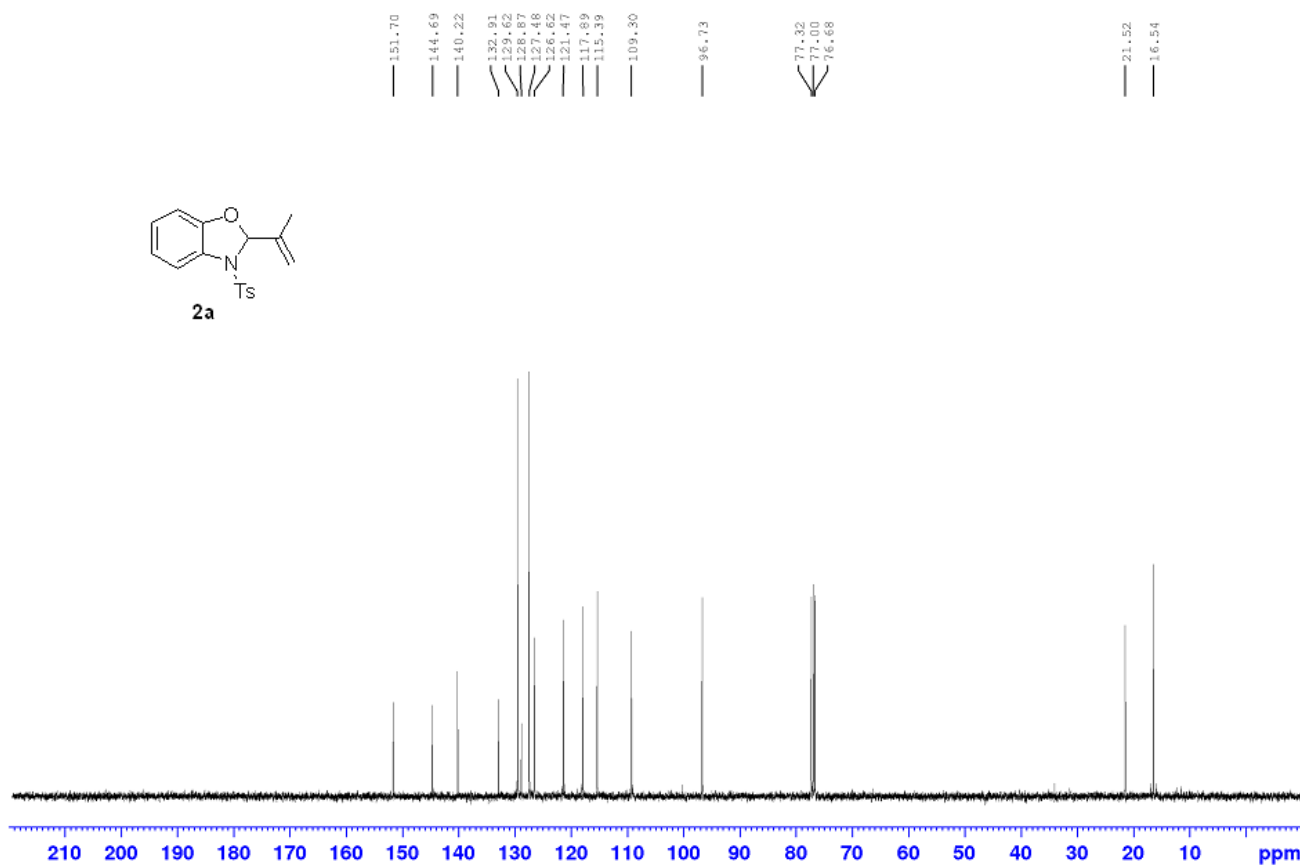
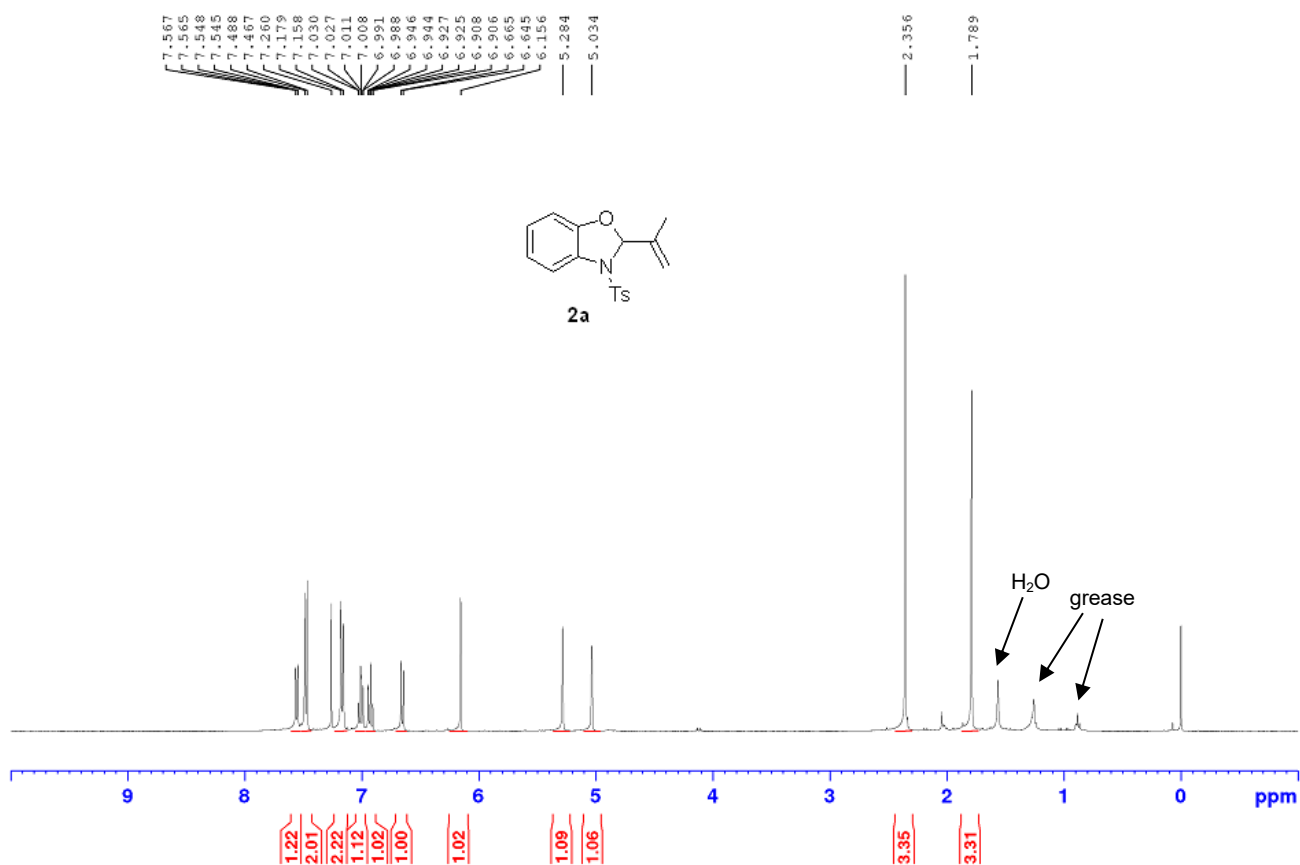
***N*-Ts-*N*-Methallyl-2-aminophenol (**3a**) (in CDCl₃)**



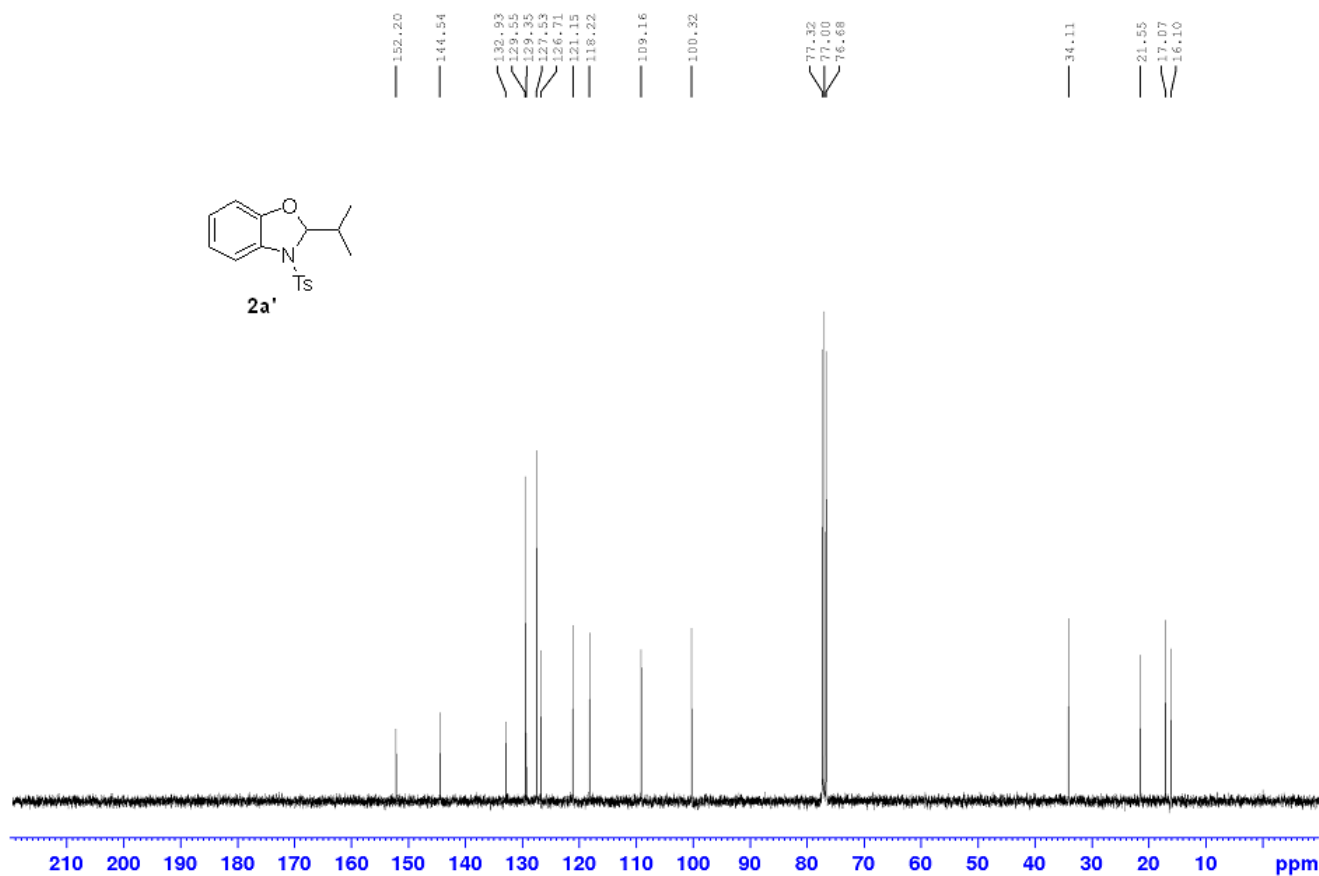
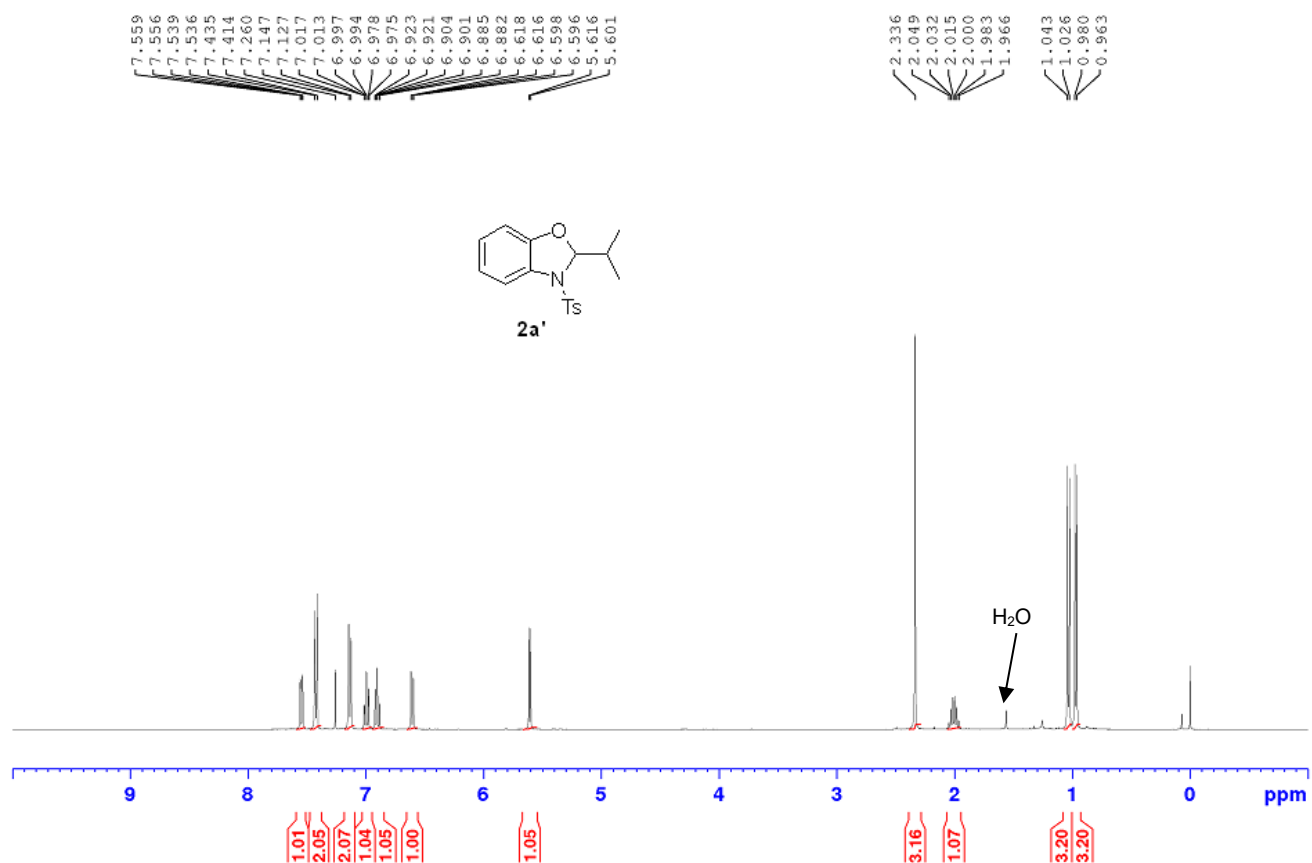
***N*-Ts-*N*-(2-(*p*-Tolyl)allyl)-2-aminophenol (**3p**) (in CDCl₃)**



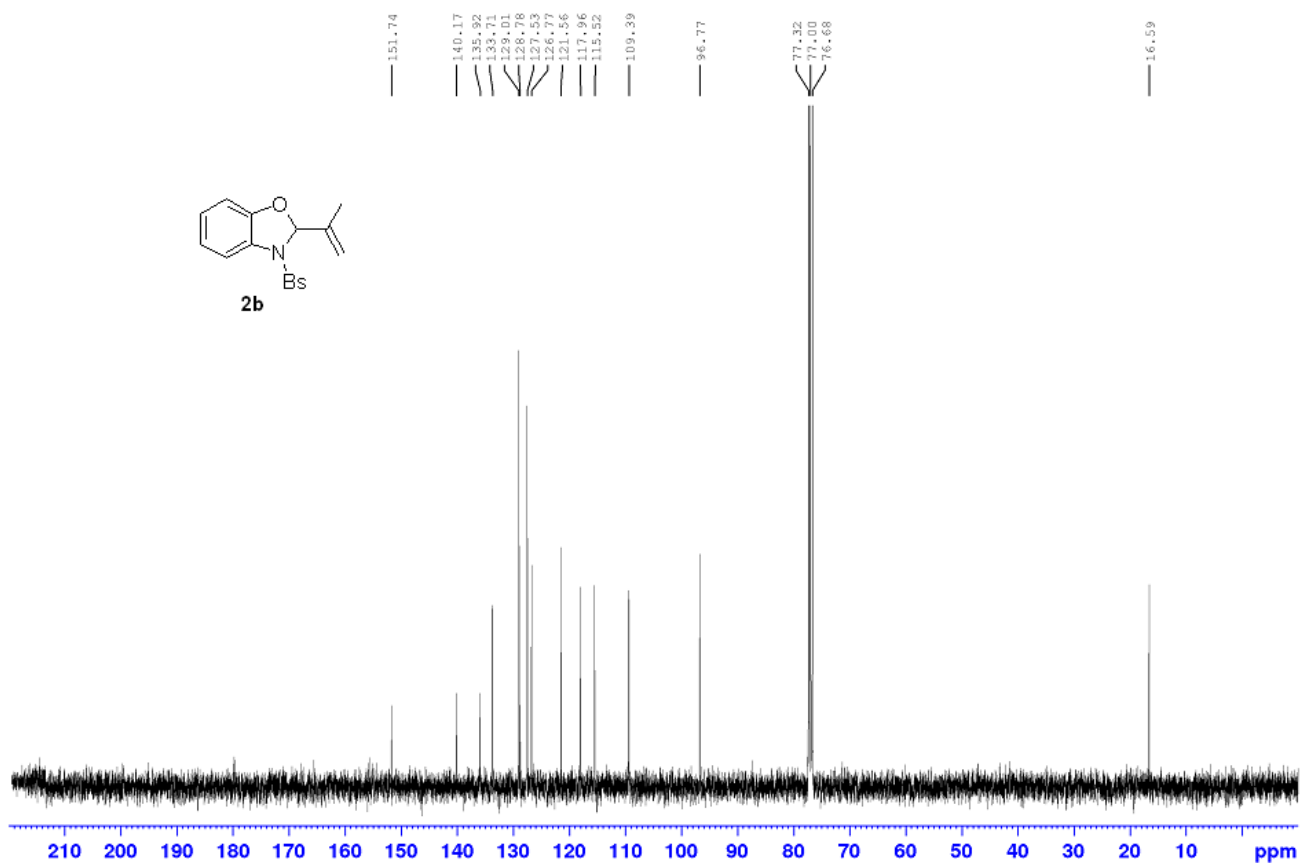
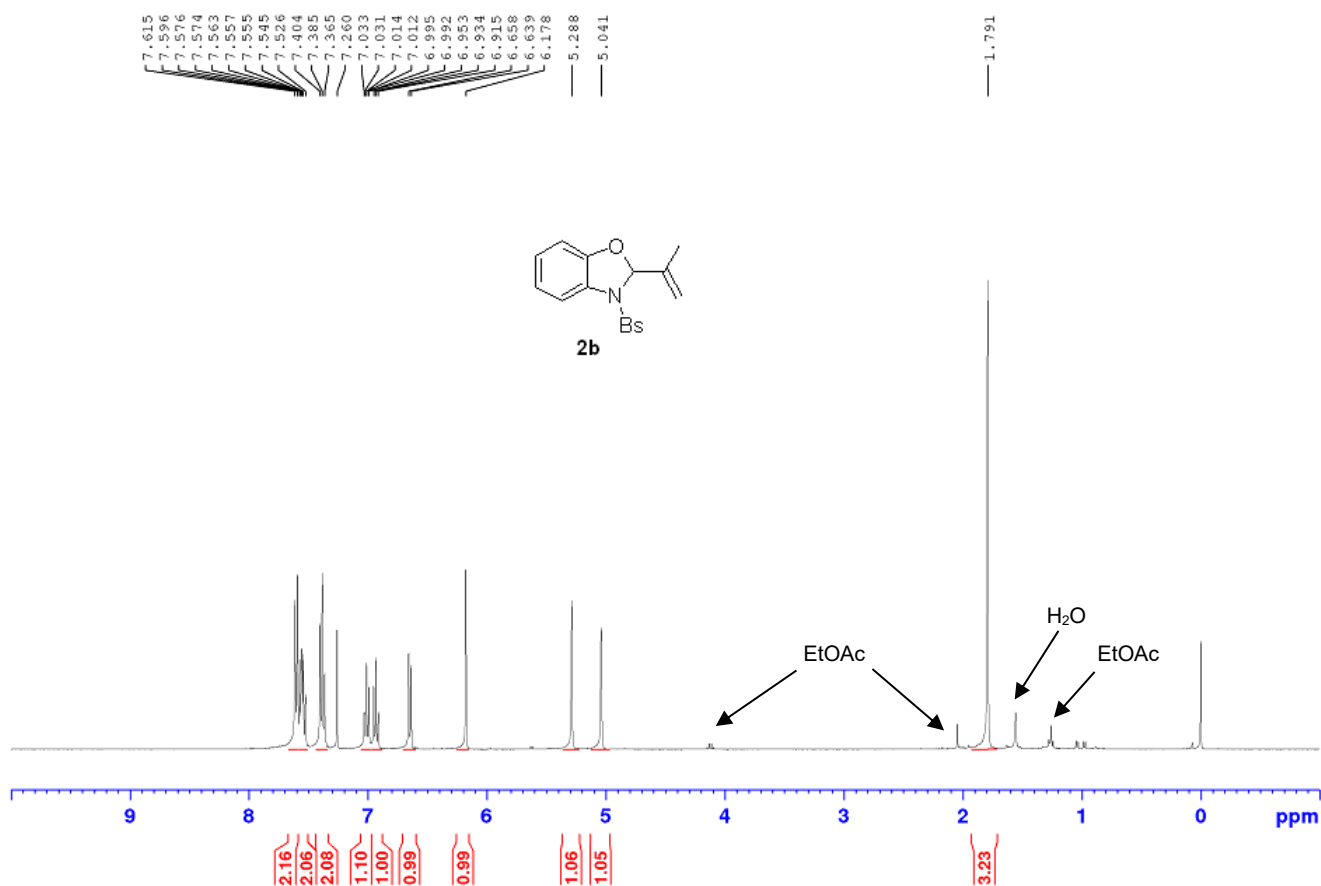
***N*-Ts-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2a) (in CDCl₃)**



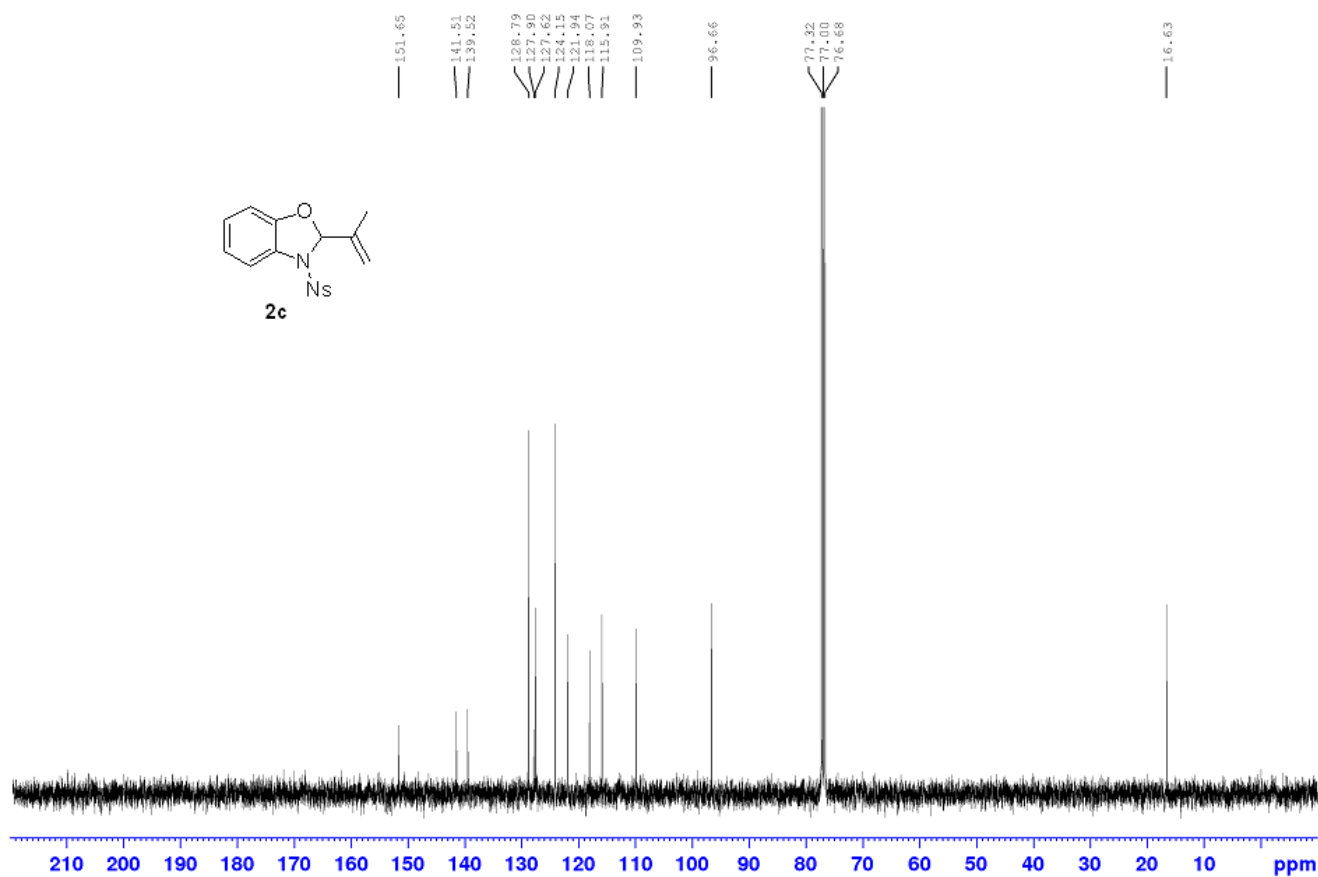
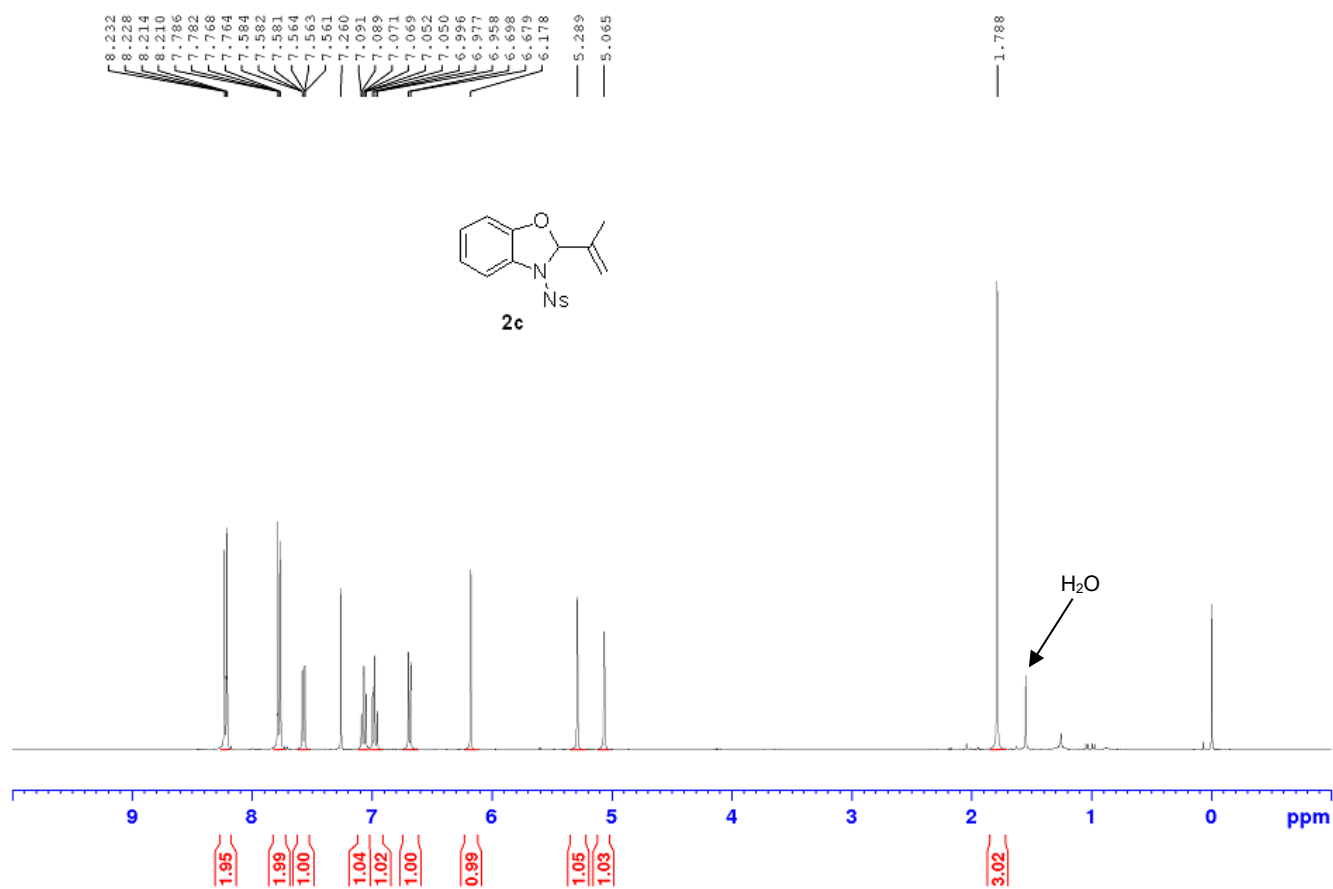
***N*-Ts-2-Isopropyl-2,3-dihydrobenzo[*d*]oxazole (**2a'**) (in CDCl₃)**



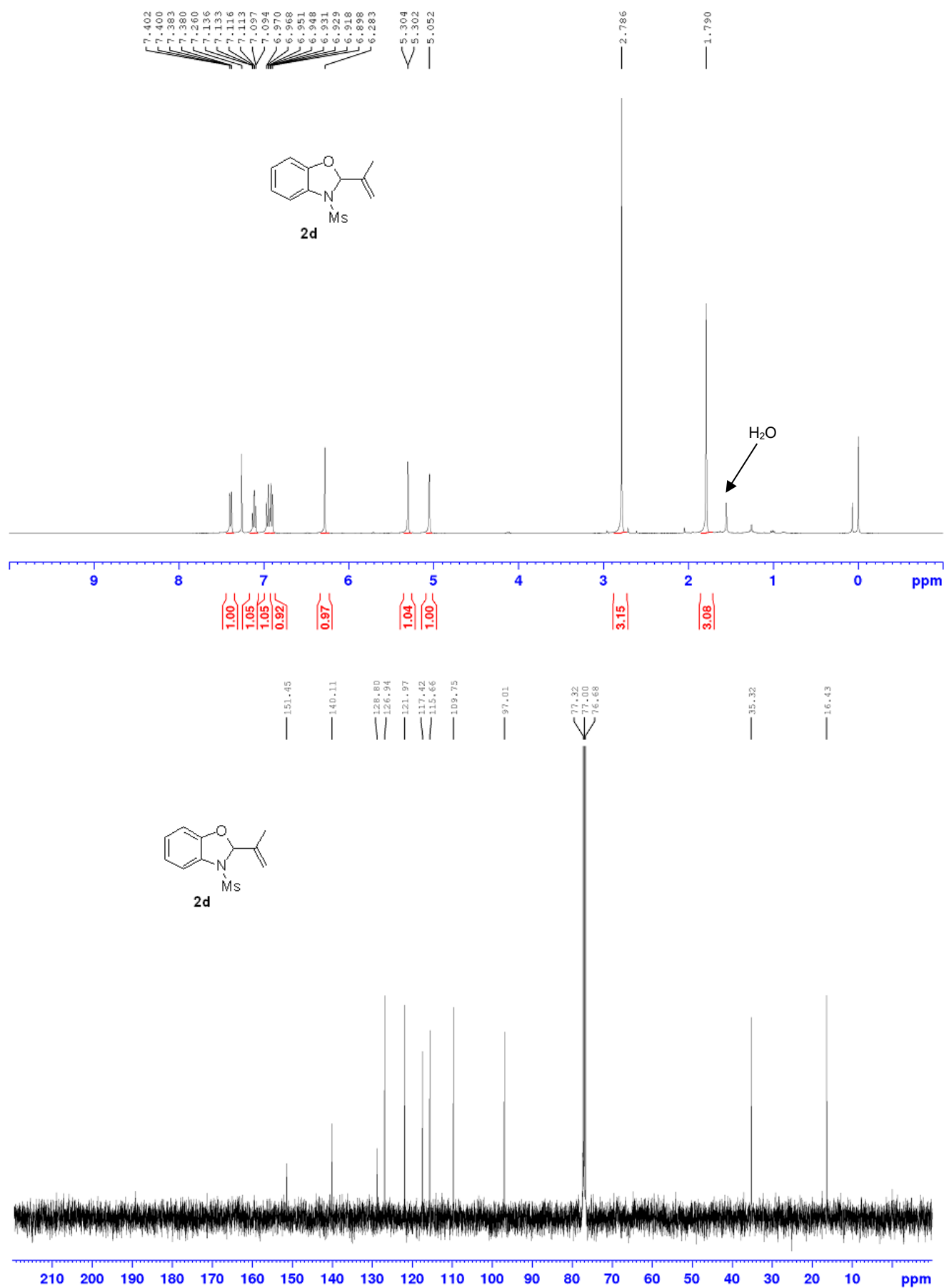
***N*-Bs-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2b) (in CDCl₃)**



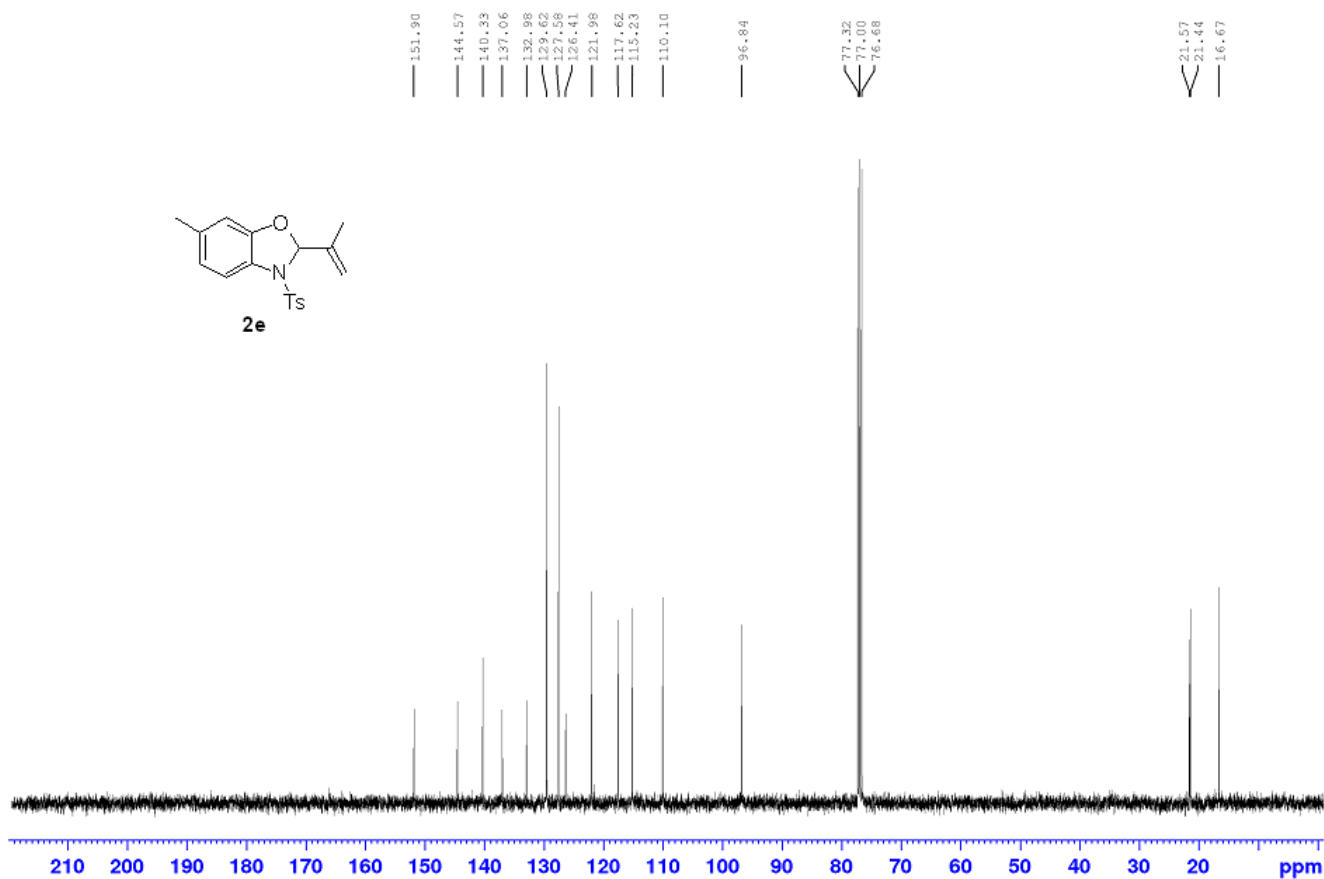
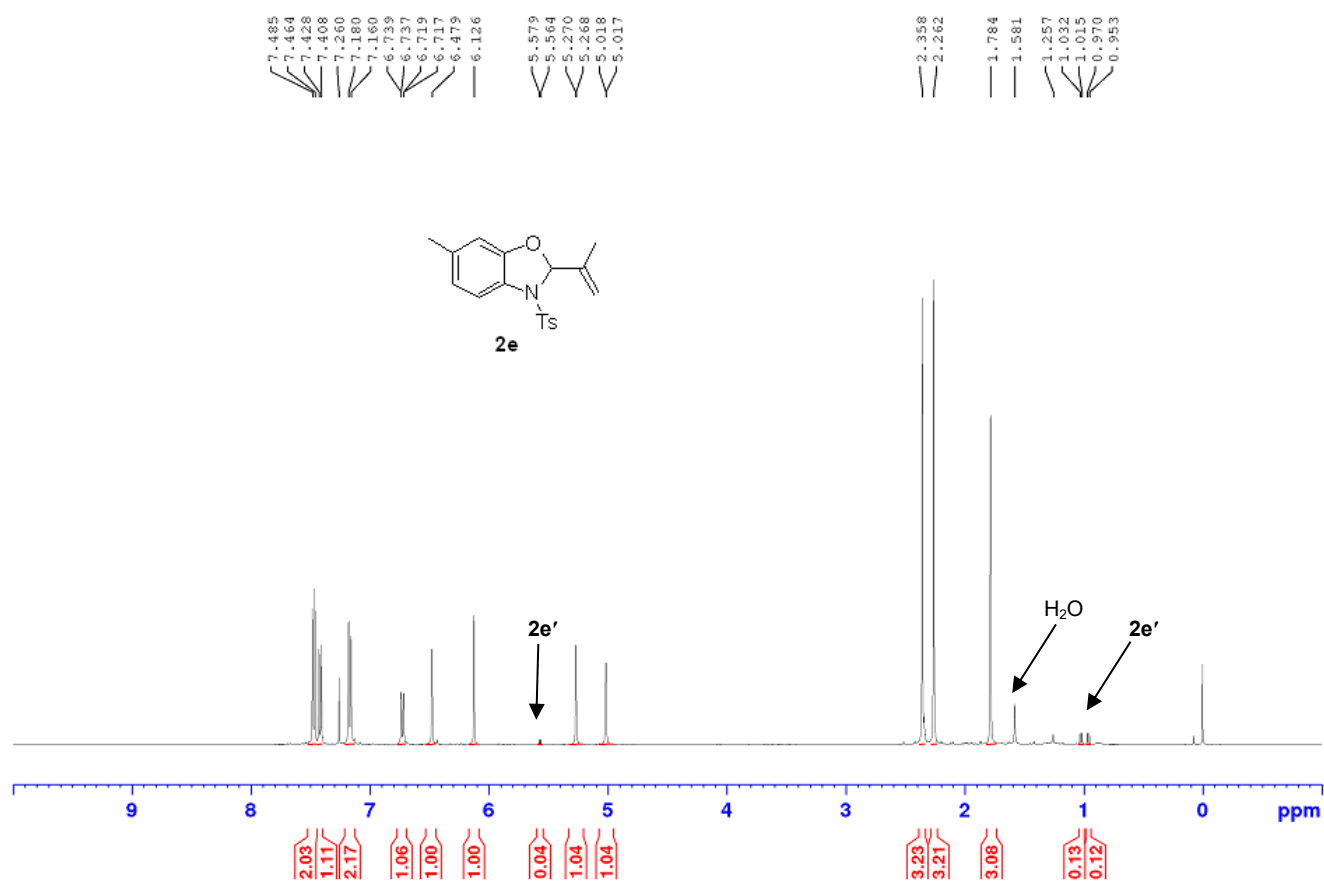
***N*-Ns-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2c) (in CDCl₃)**



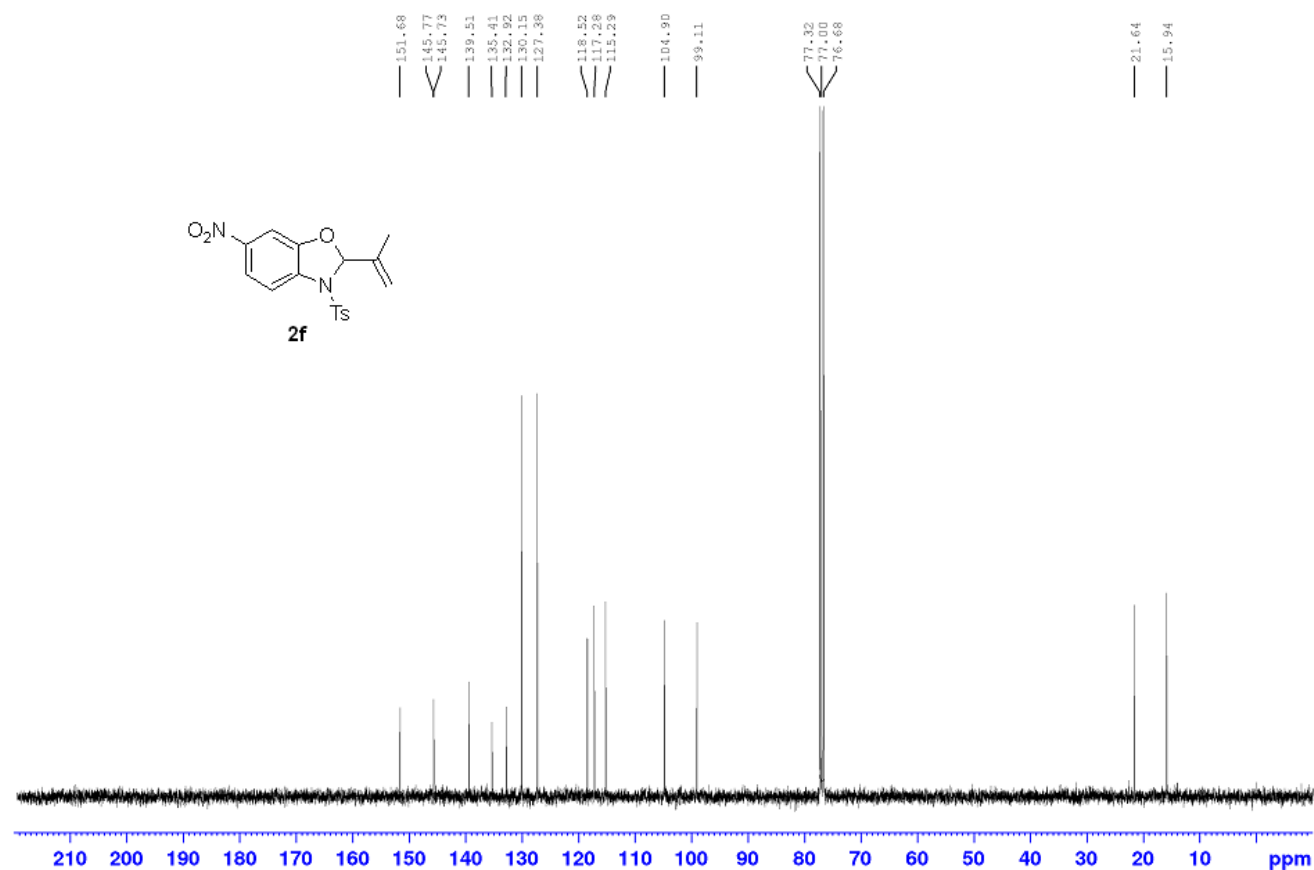
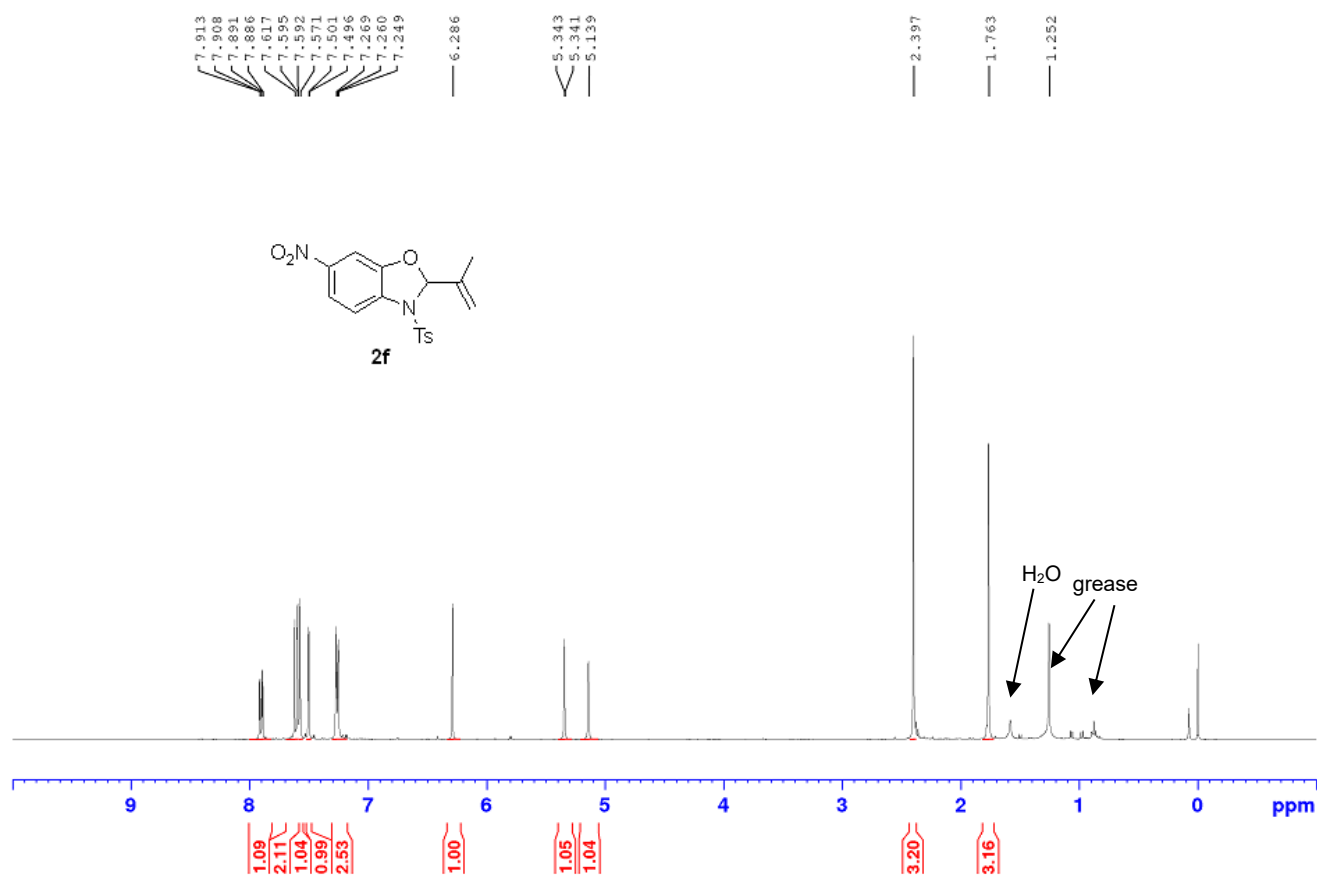
***N*-Ms-2-(Prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2d) (in CDCl₃)**



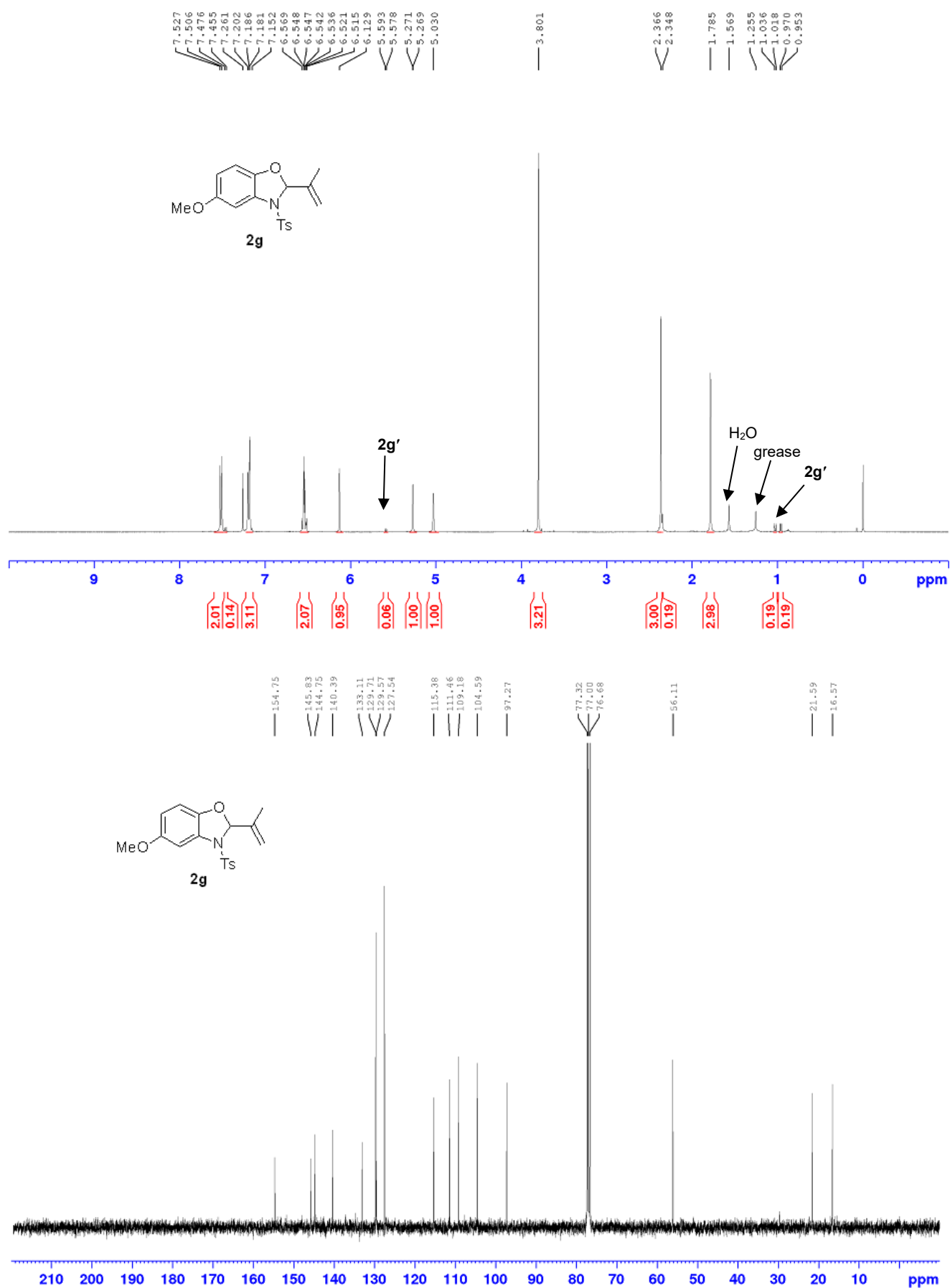
***N*-Ts-6-Methyl-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2e) (in CDCl₃)**



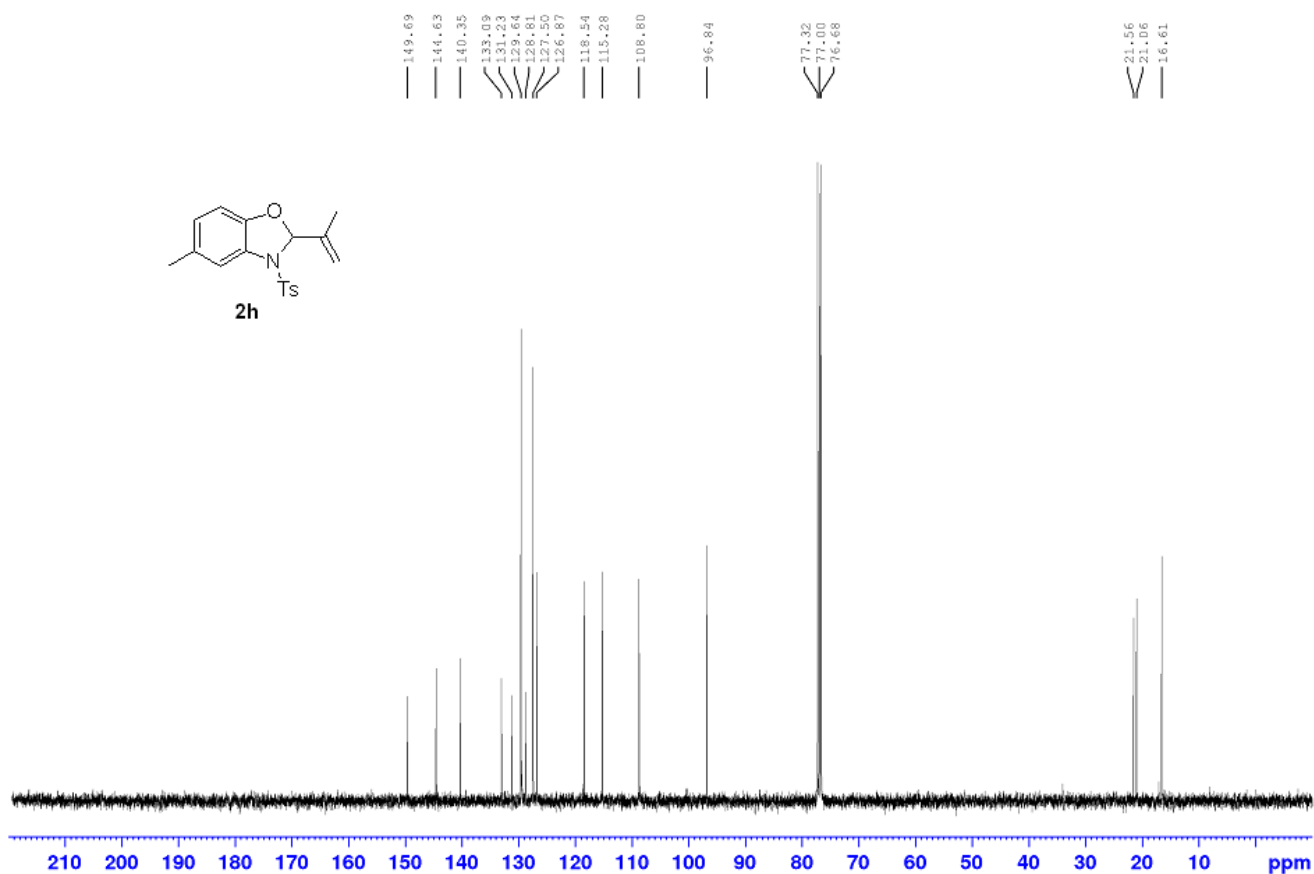
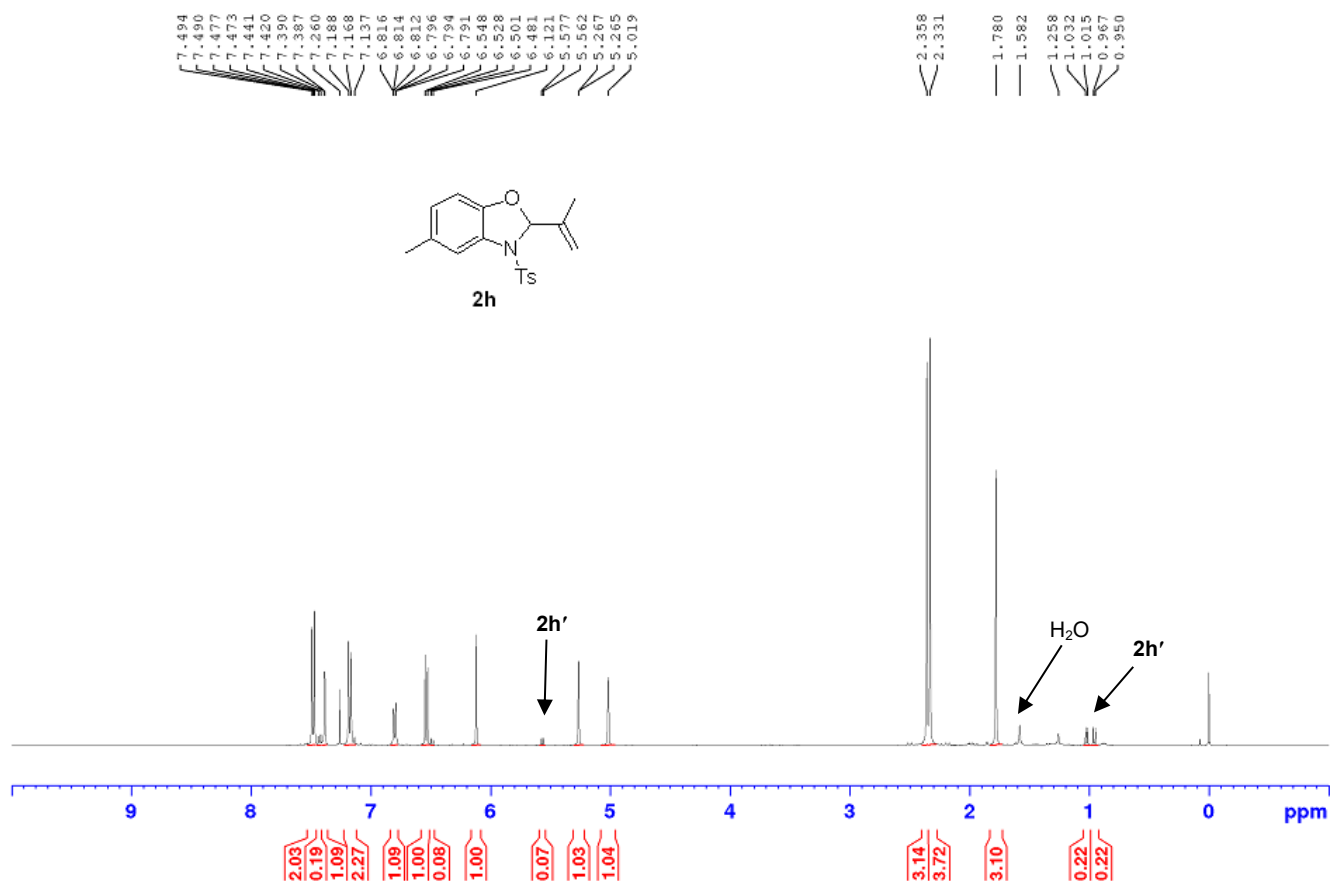
***N*-Ts-6-Nitro-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2f) (in CDCl₃)**



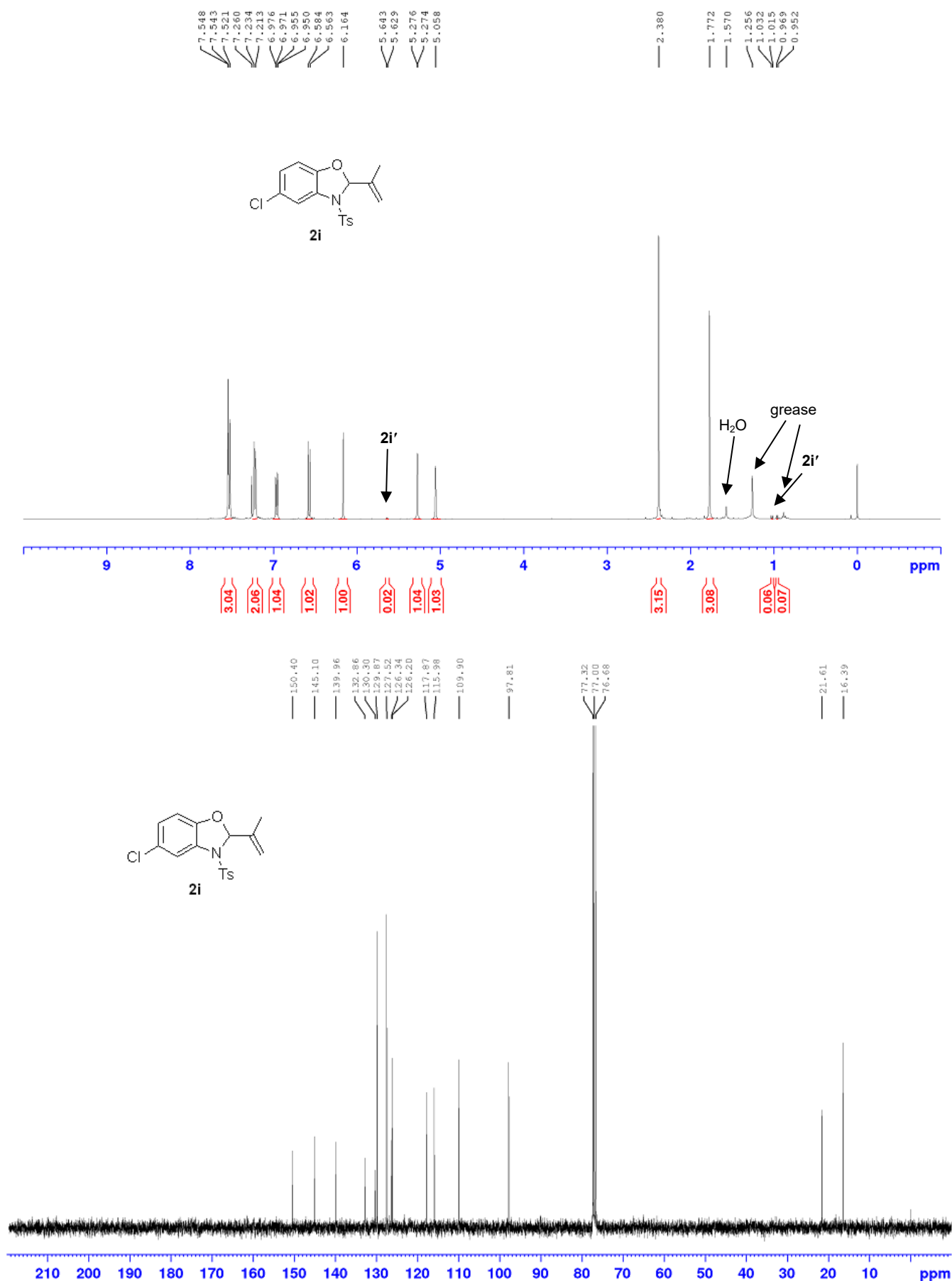
***N*-Ts-5-Methoxy-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2g) (in CDCl₃)**



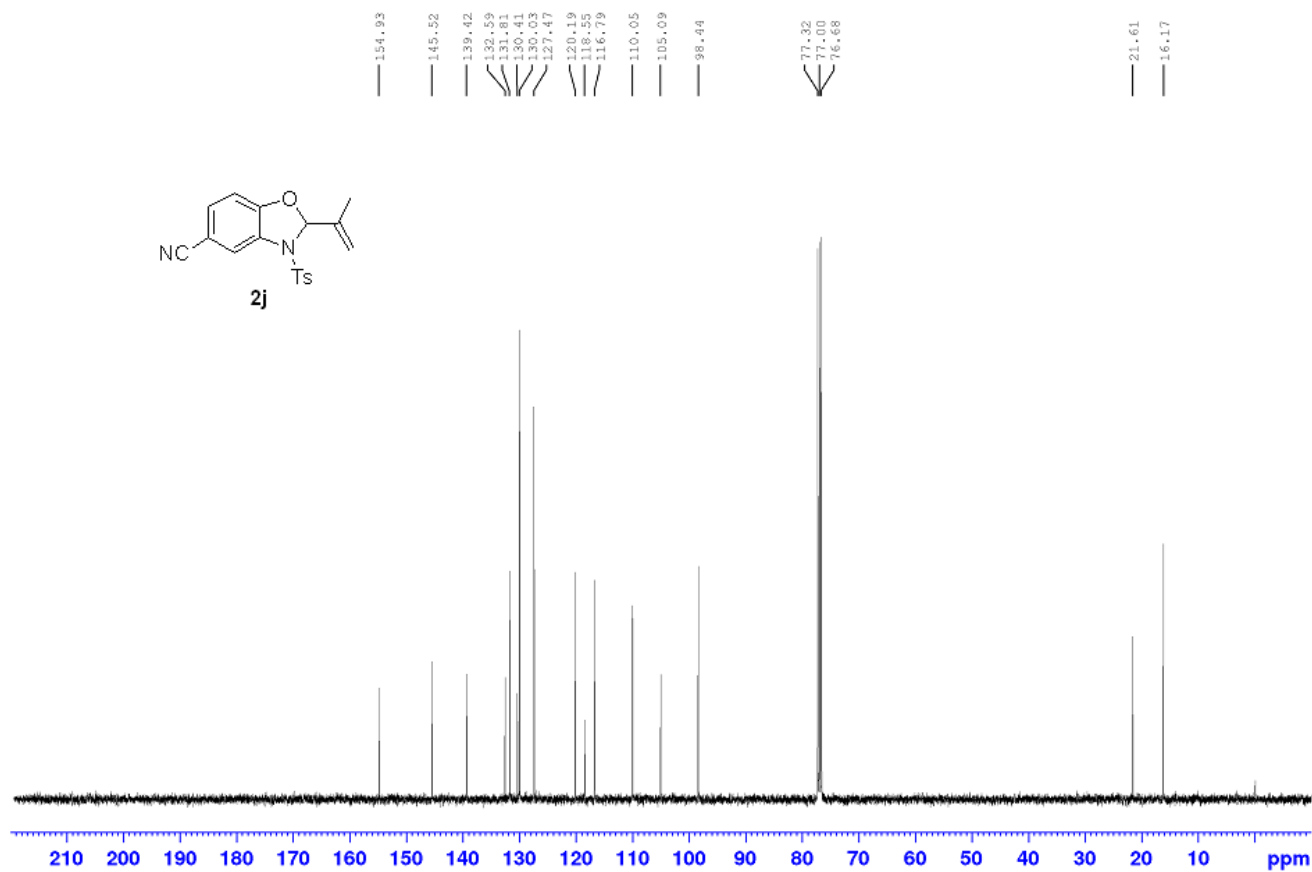
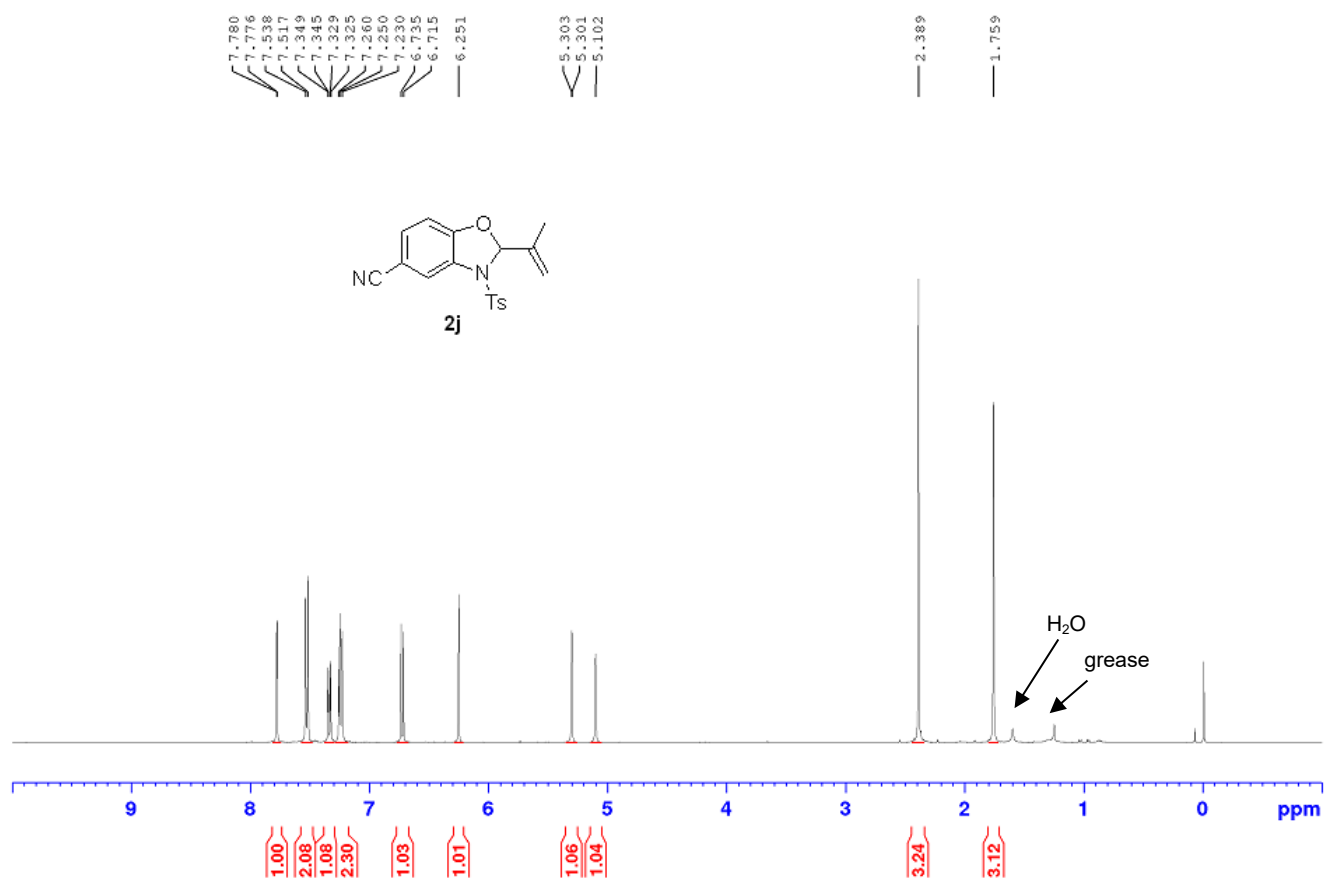
***N*-Ts-5-Methyl-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2h) (in CDCl₃)**



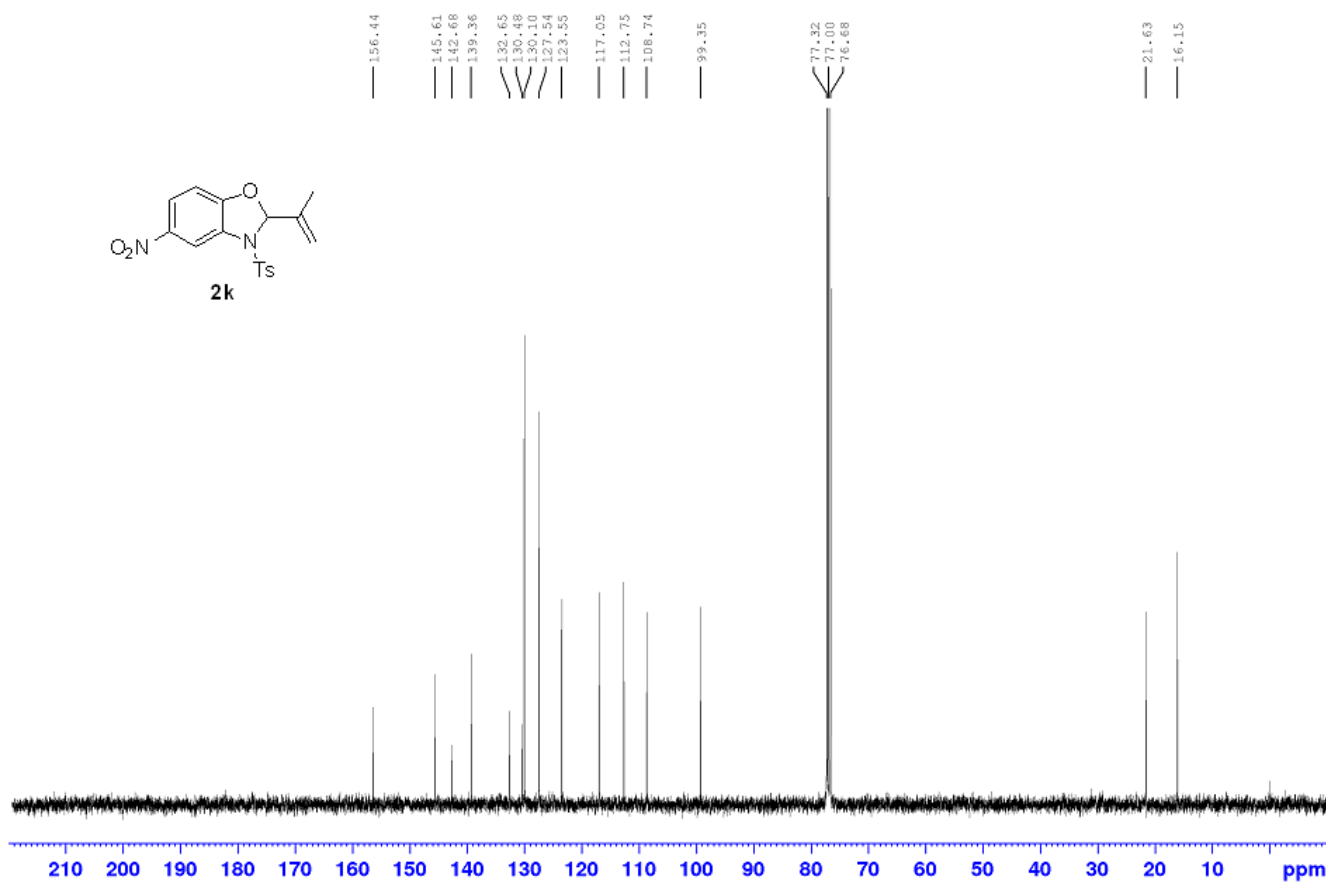
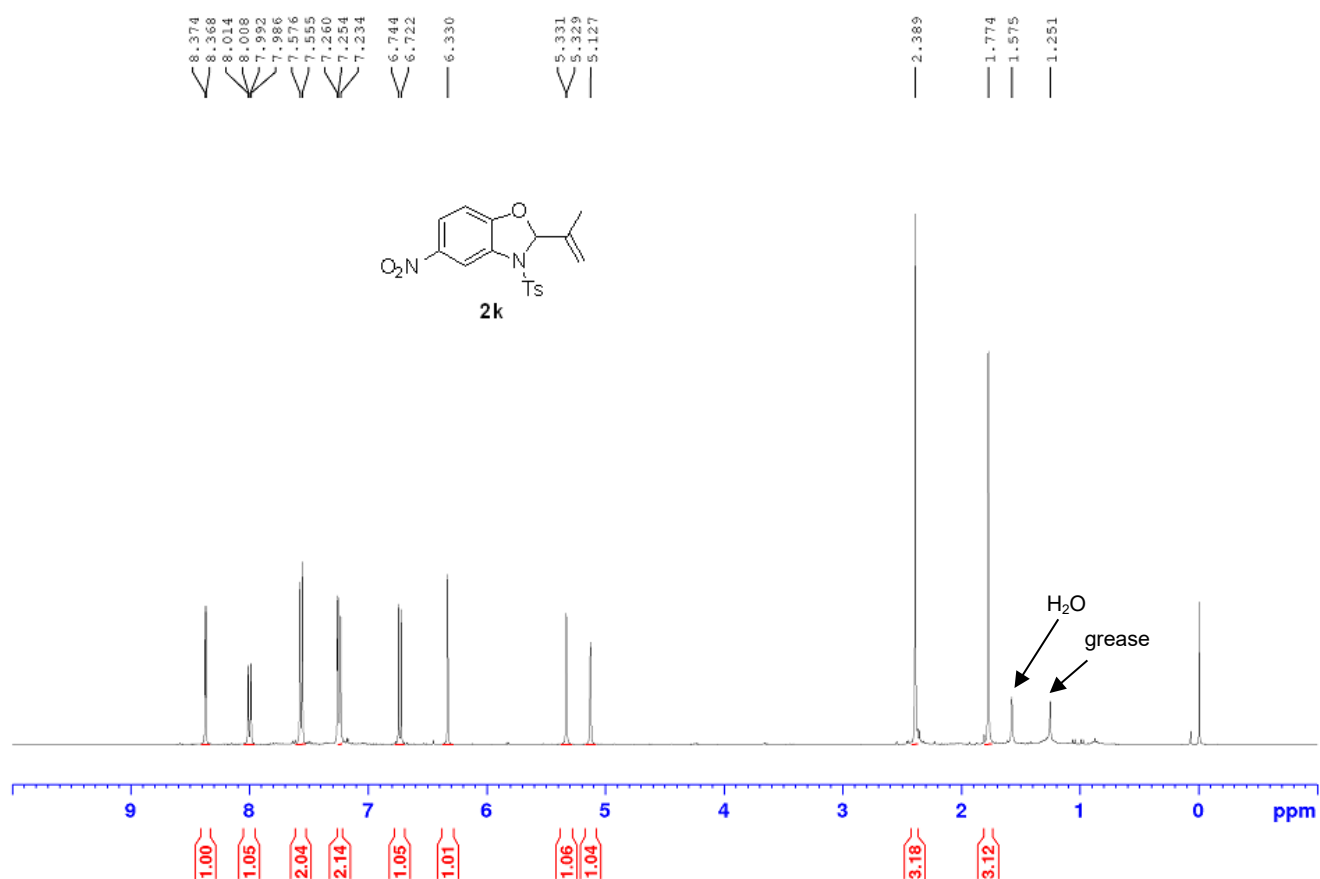
***N*-Ts-5-Chloro-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2i) (in CDCl₃)**



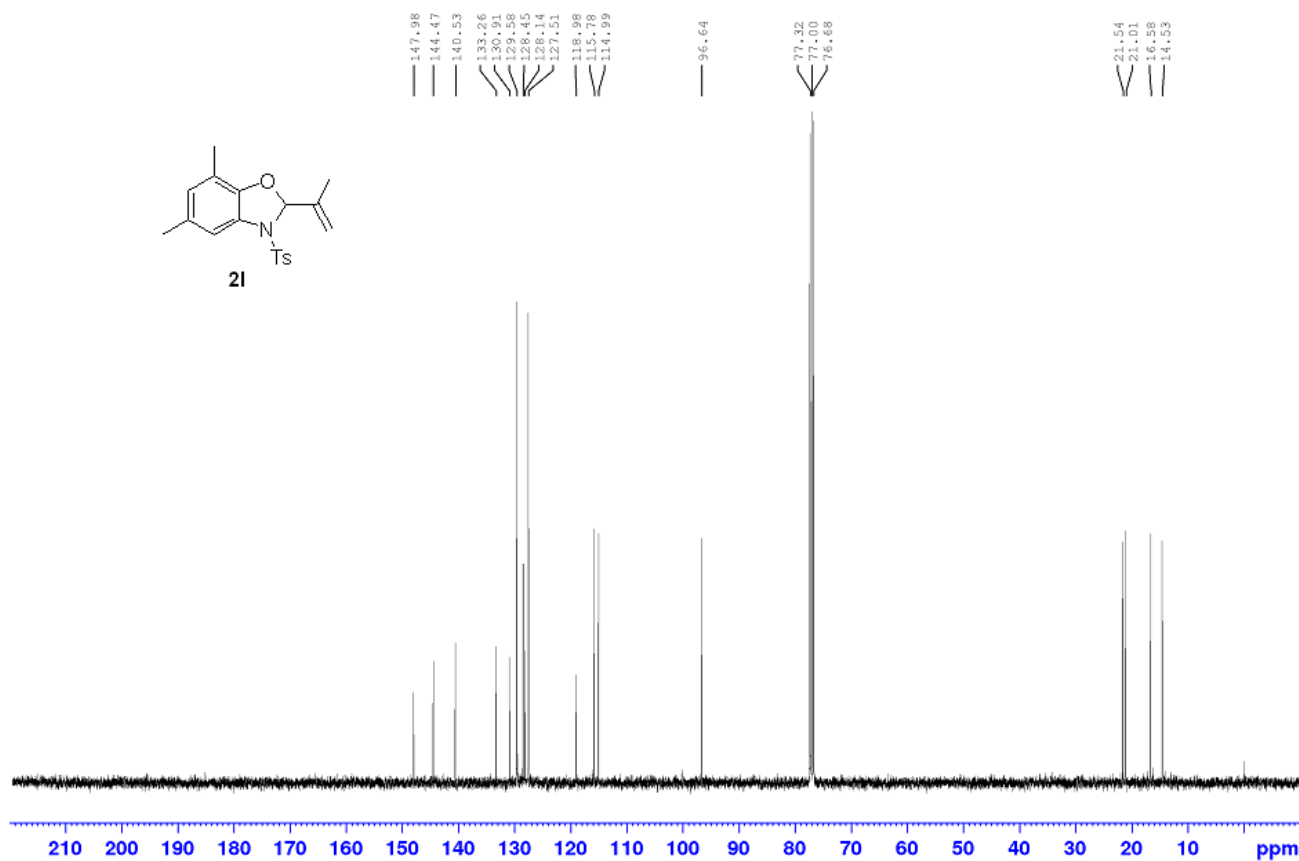
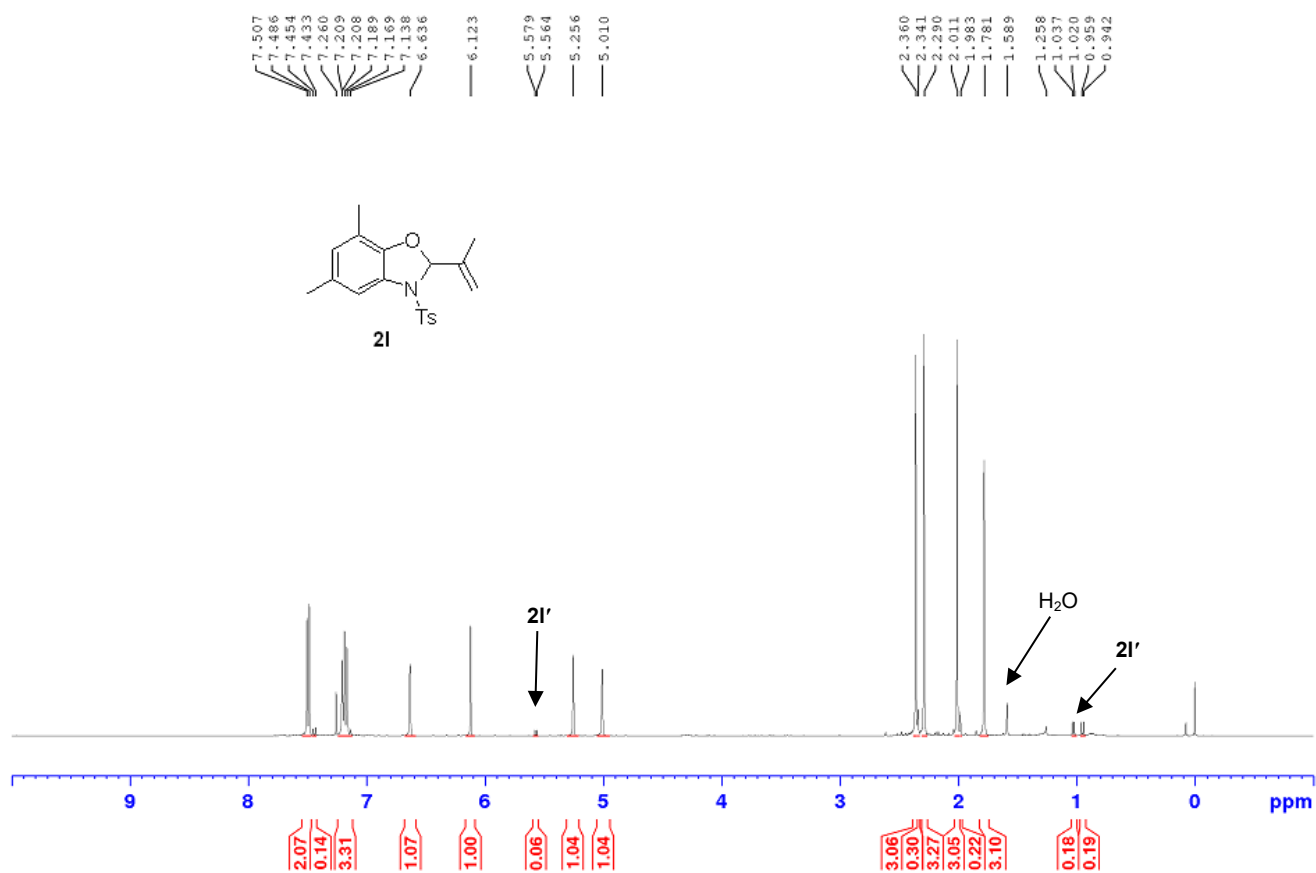
***N*-Ts-5-Cyano-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2j)** (in CDCl₃)



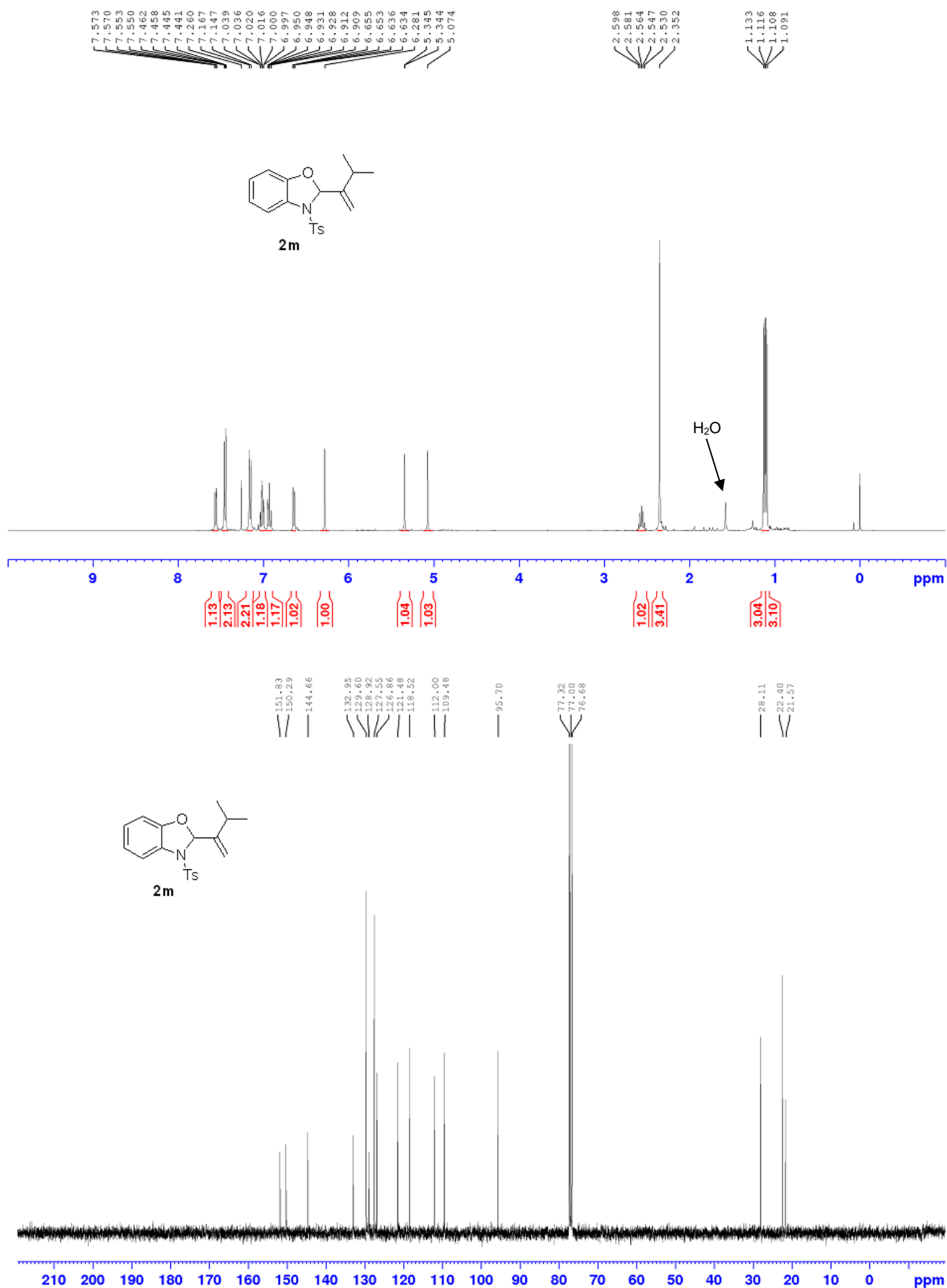
***N*-Ts-5-Nitro-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2k) (in CDCl₃)**



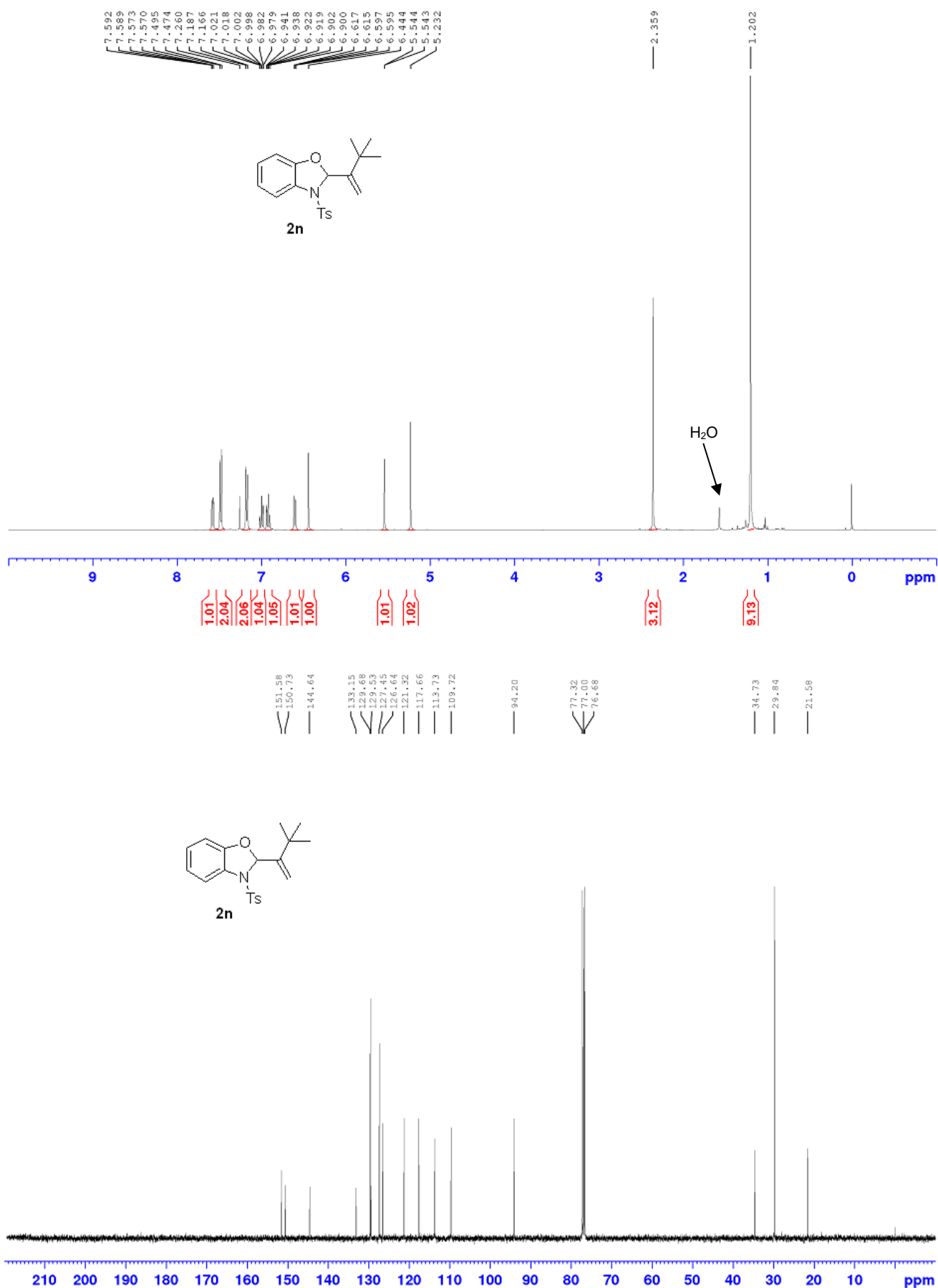
***N*-Ts-5,7-Dimethyl-2-(prop-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2I) (in CDCl₃)**



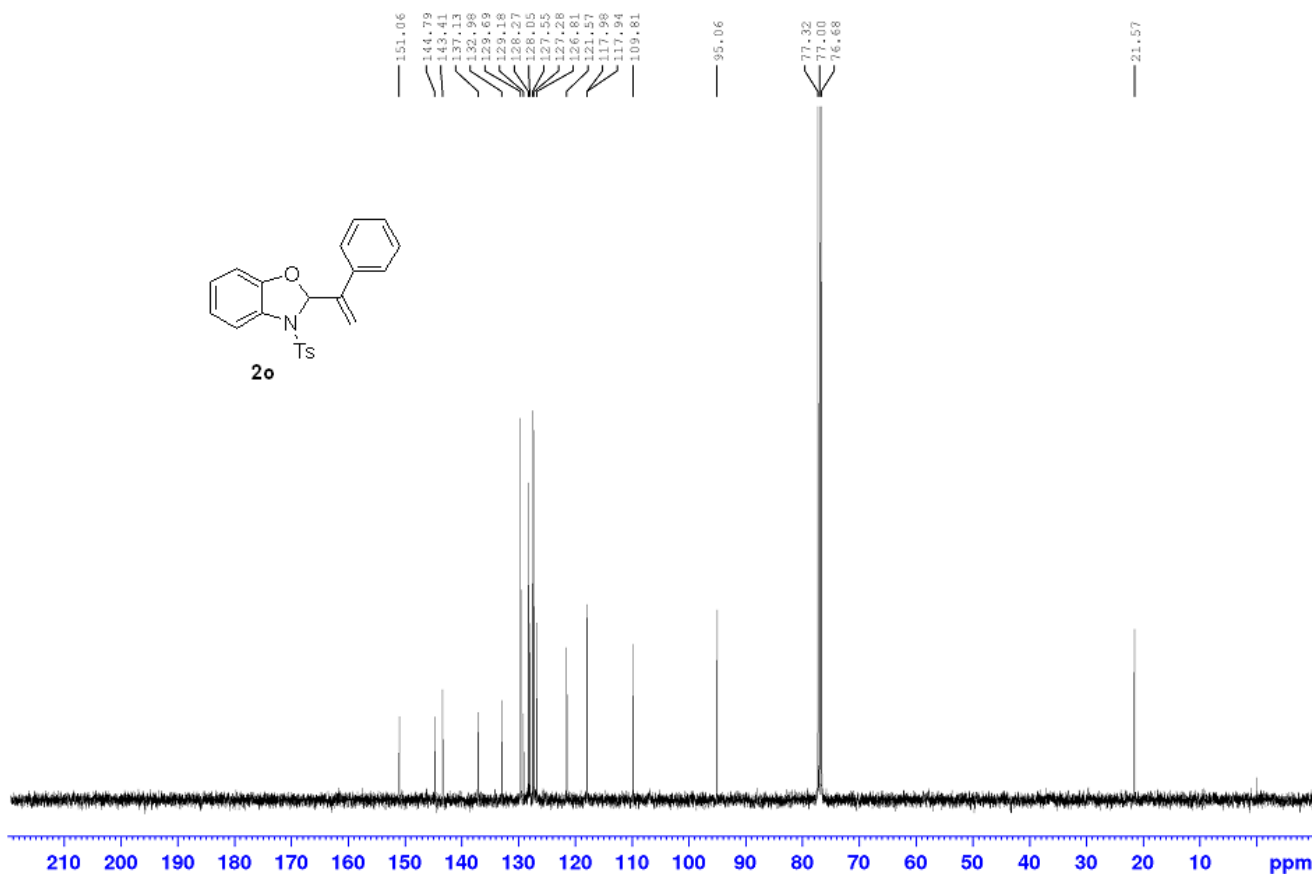
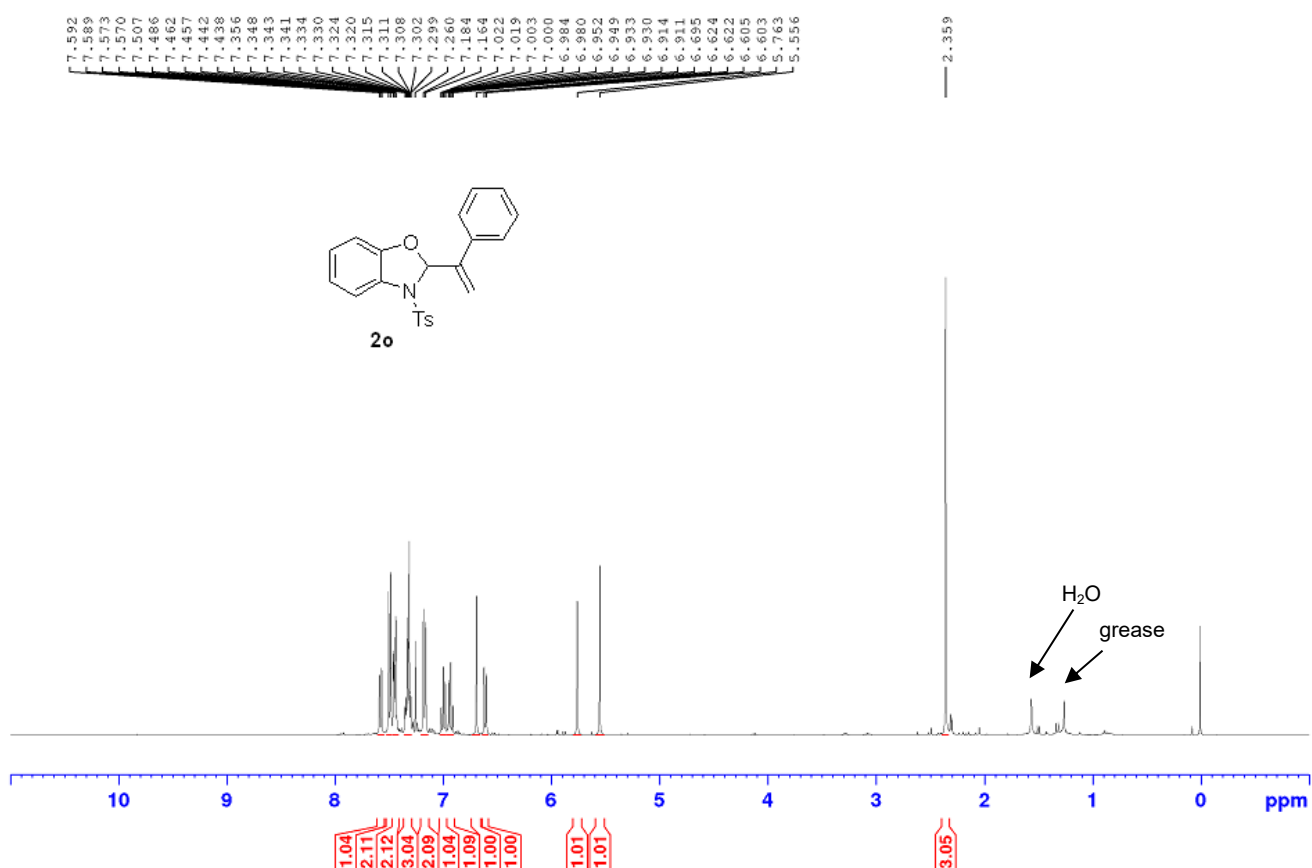
***N*-Ts-2-(3-Methylbut-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2m) (in CDCl₃)**



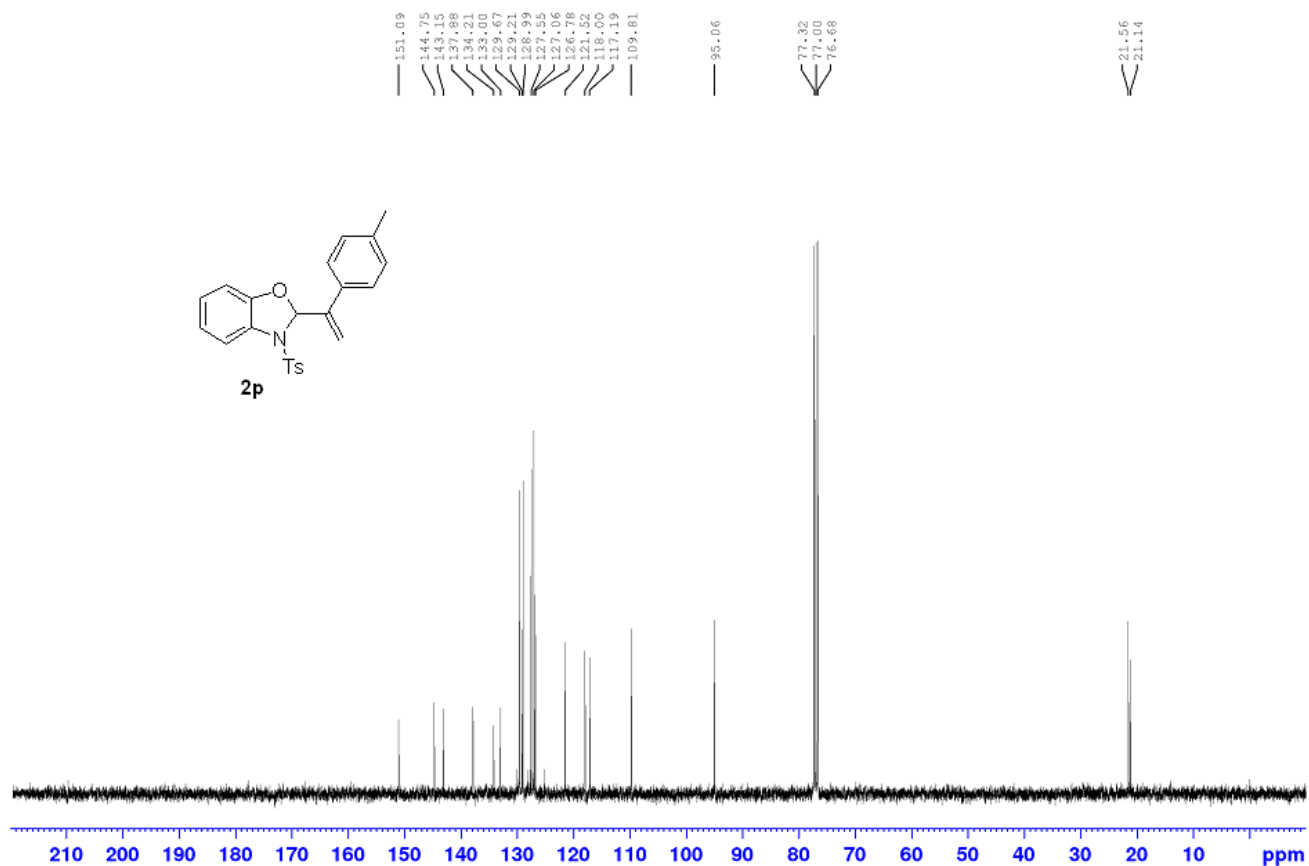
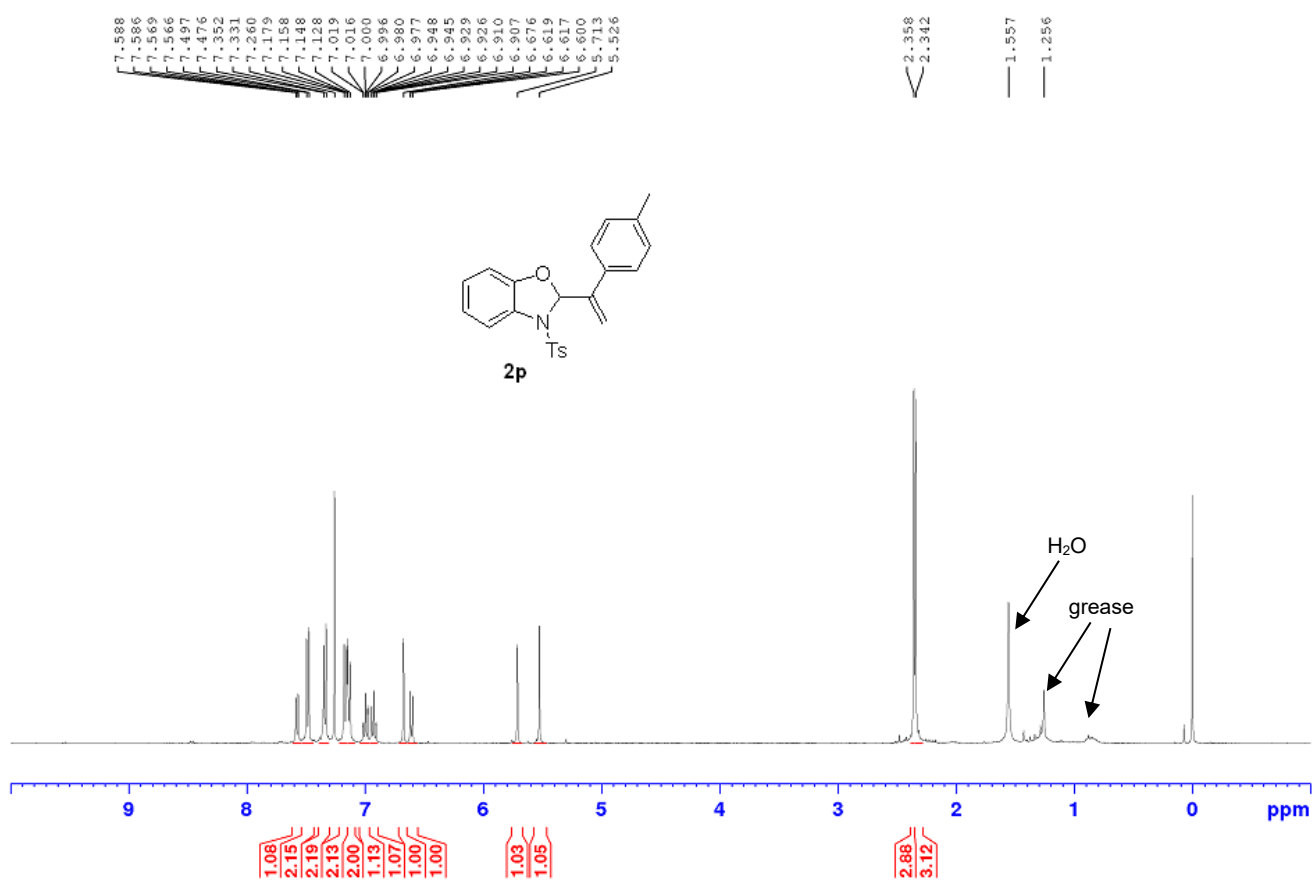
***N*-Ts-2-(3,3-Dimethylbut-1-en-2-yl)-2,3-dihydrobenzo[*d*]oxazole (2n) (in CDCl₃)**



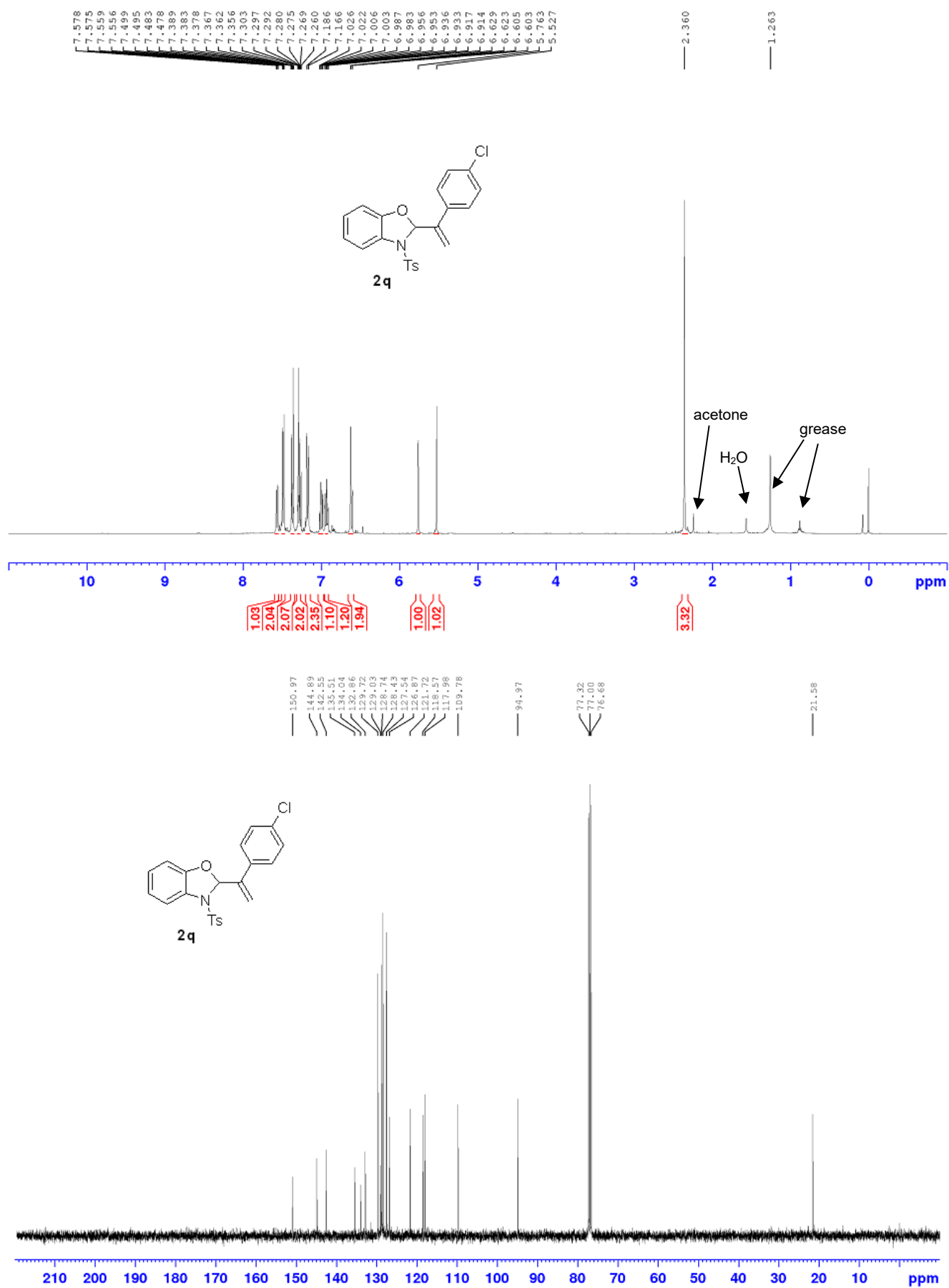
***N*-Ts-2-(1-Phenylvinyl)-2,3-dihydrobenzo[d]oxazole (**2o**) (in CDCl₃)**



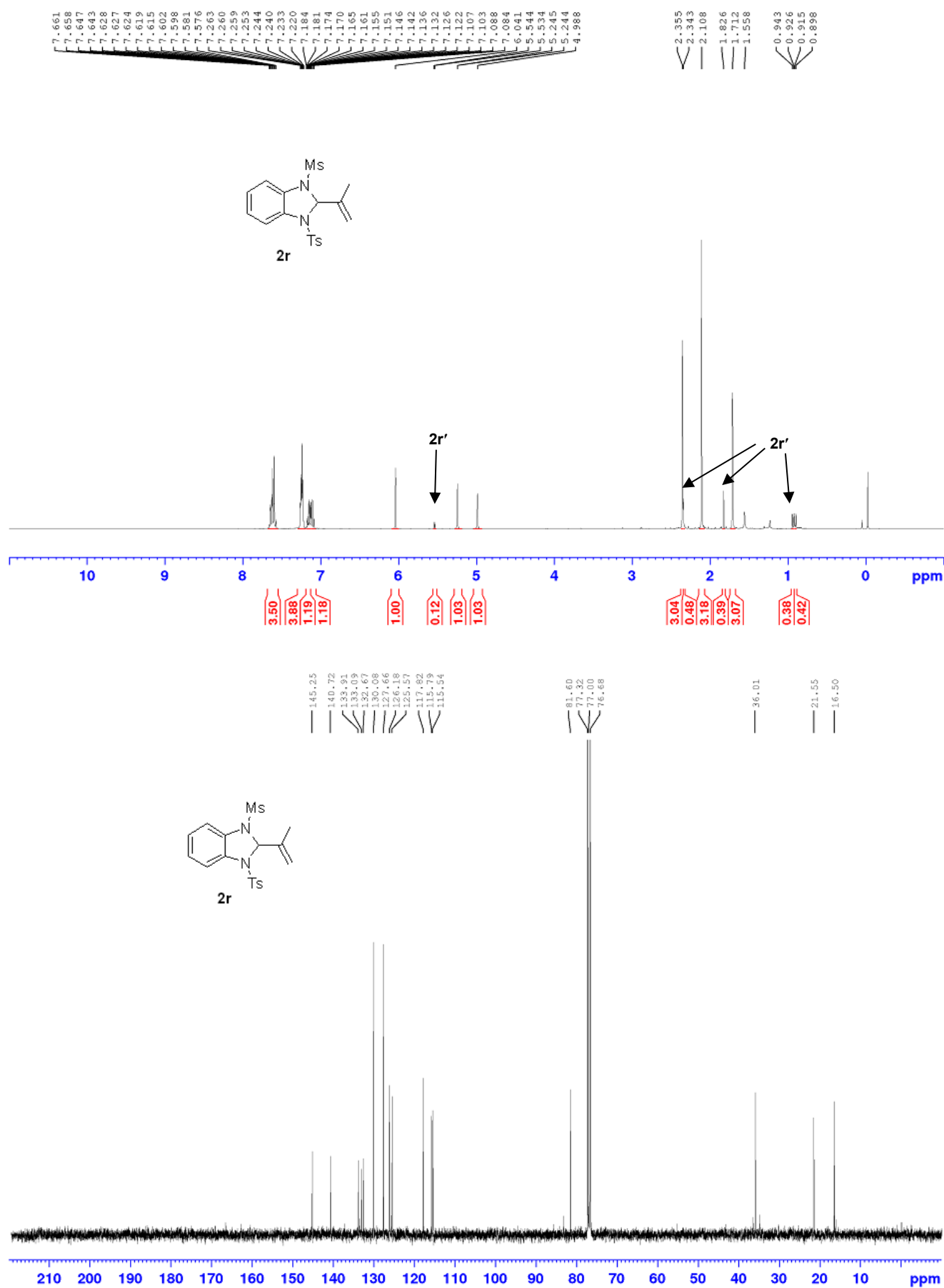
***N*-Ts-2-(1-(*p*-Tolyl)vinyl)-2,3-dihydrobenzo[*d*]oxazole (2p) (in CDCl₃)**



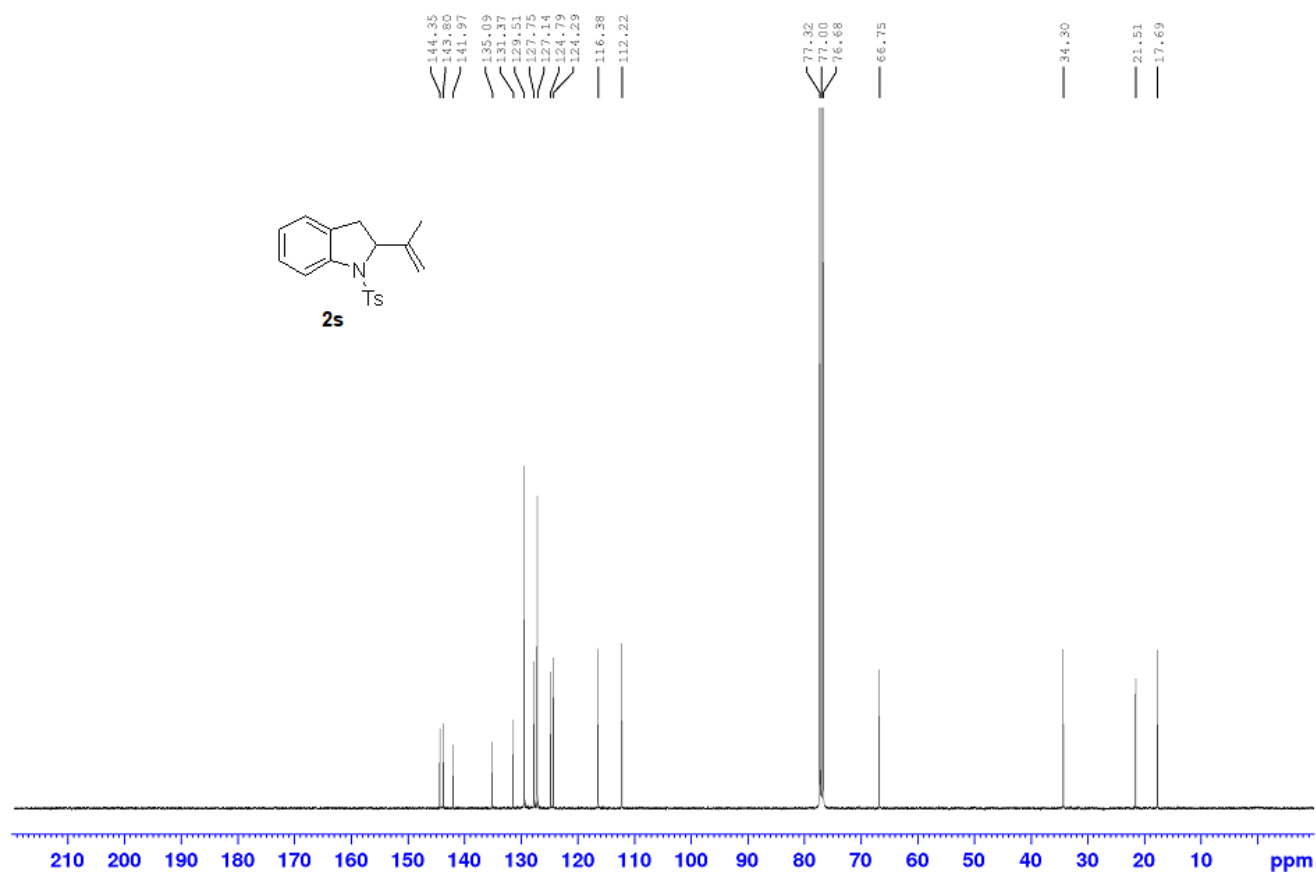
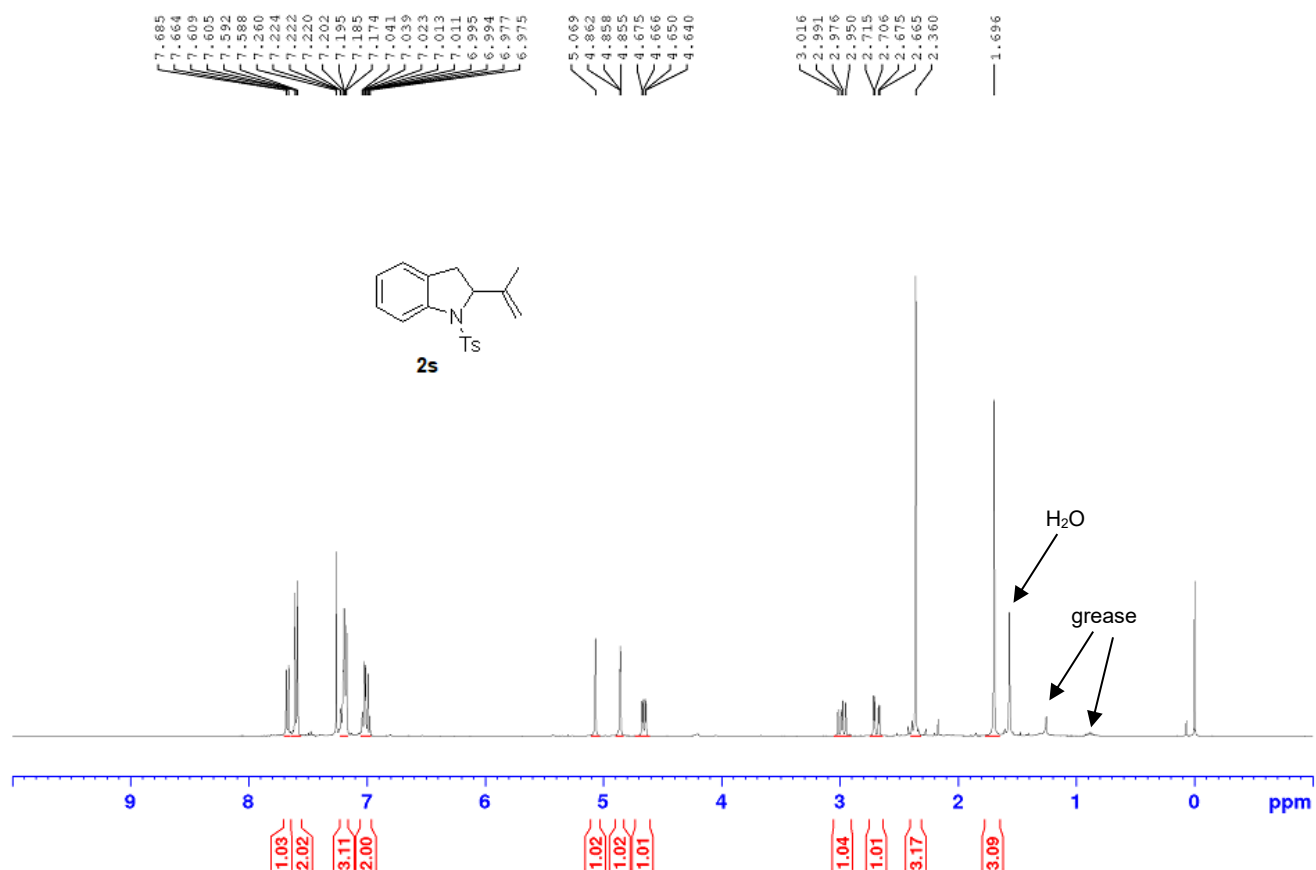
***N*-Ts-2-(1-(4-Chlorophenyl)vinyl)-2,3-dihydrobenzo[*d*]oxazole (2q) (in CDCl₃)**



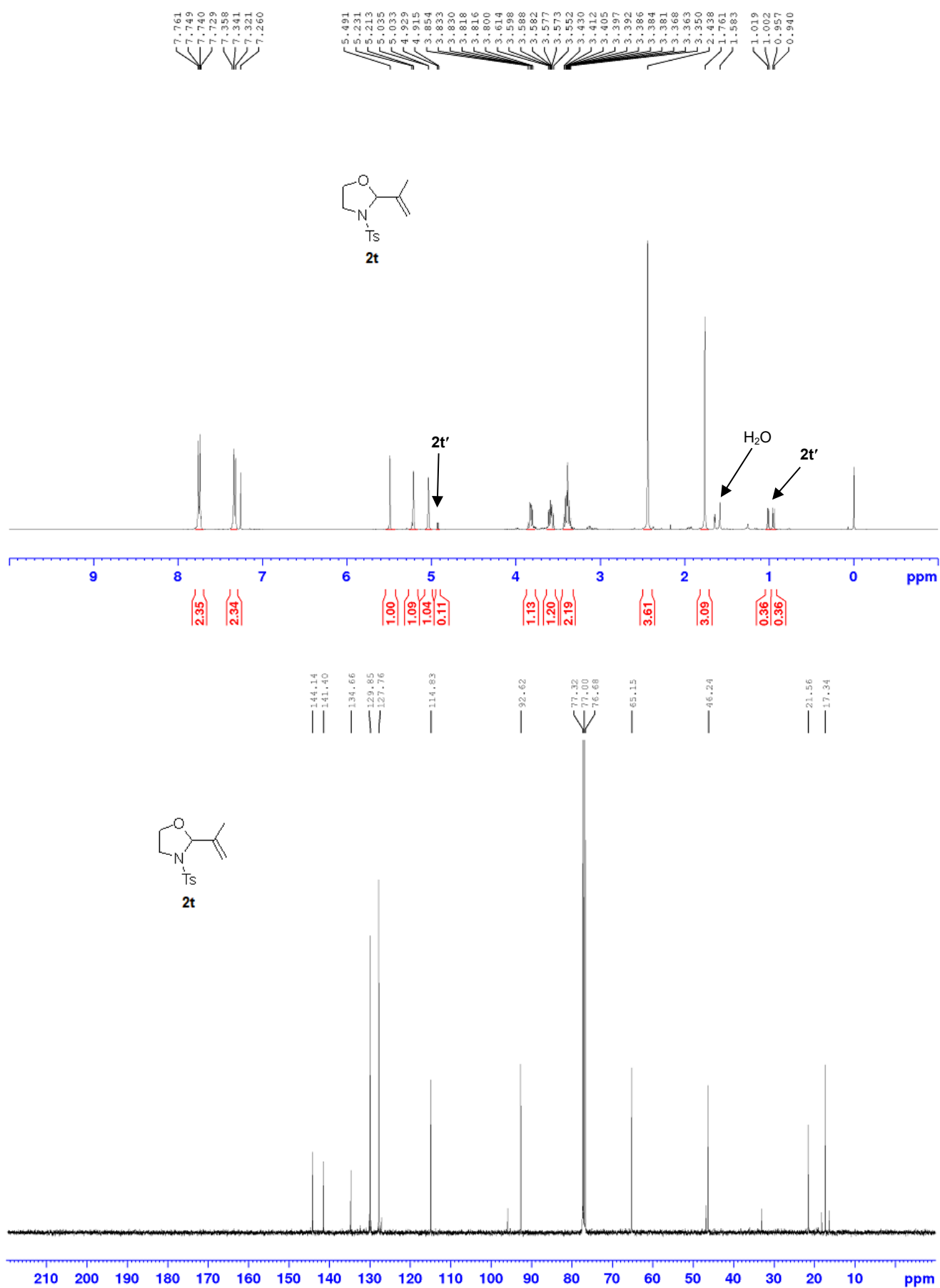
***N*-Ts-*N'*-Ms-2-(Prop-1-en-2-yl)-2,3-dihydro-1*H*-benzo[*d*]imidazole (2r) (in CDCl₃)**



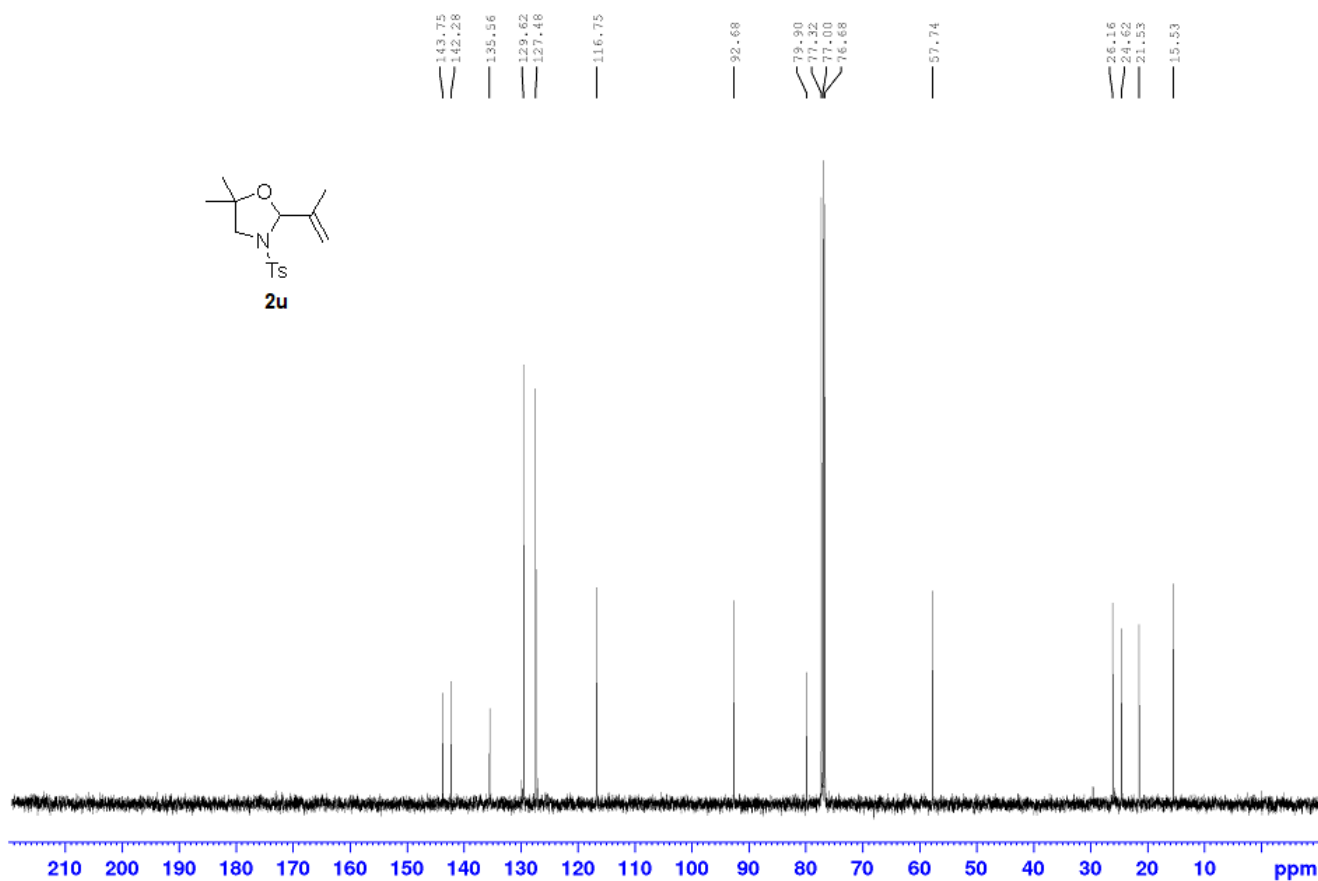
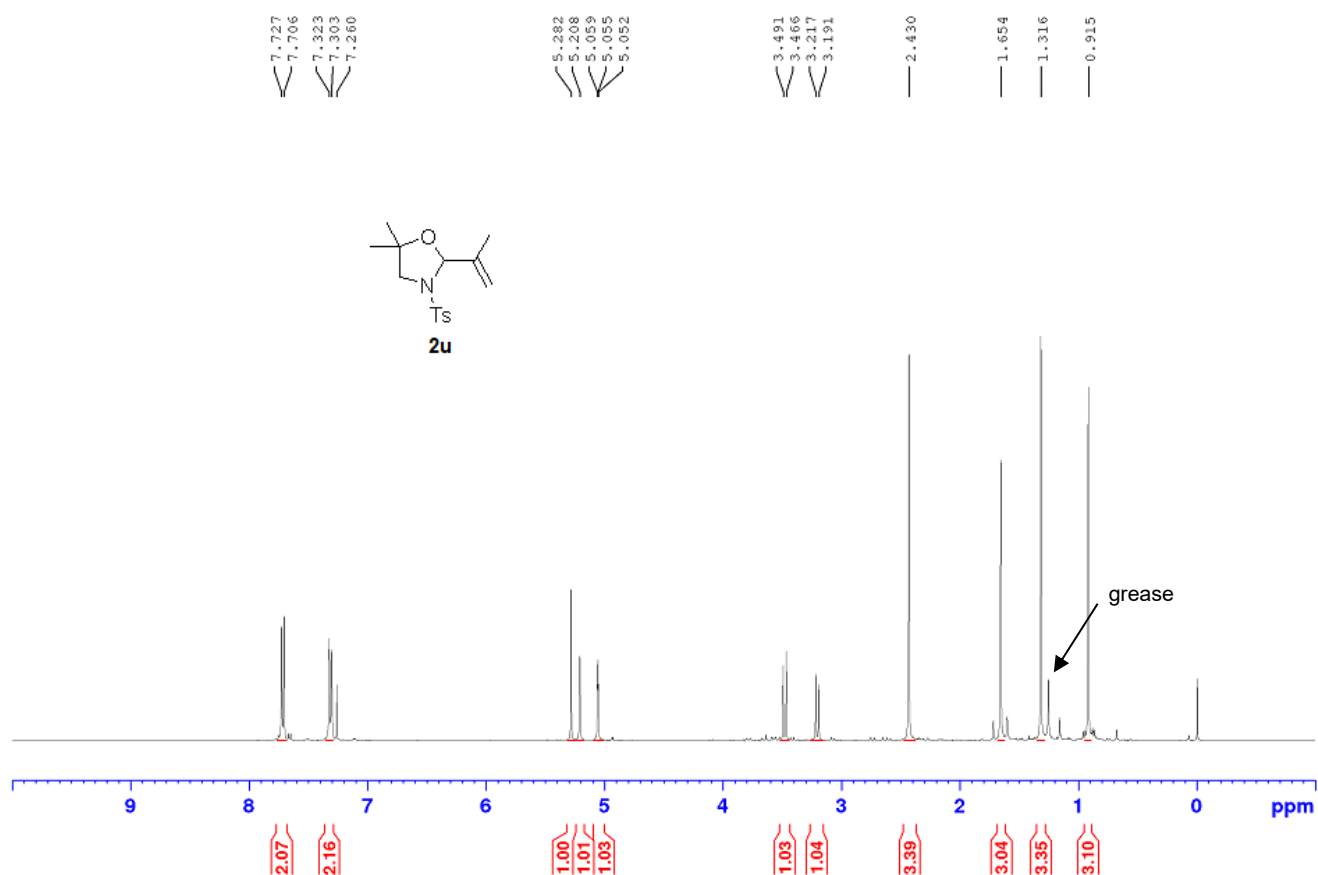
***N*-Ts-2-(Prop-1-en-2-yl)indoline (**2s**) (in CDCl₃)**



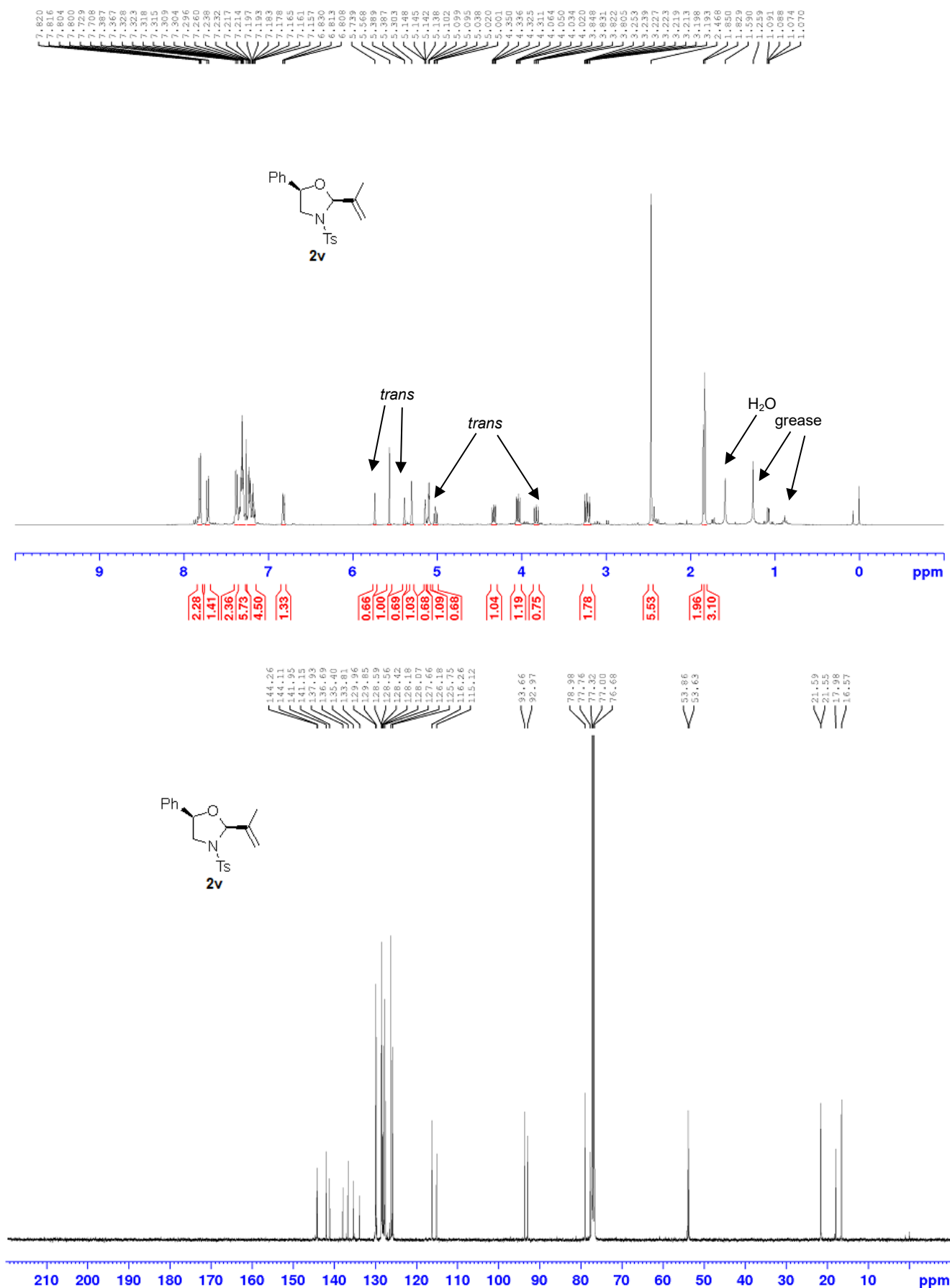
***N*-Ts-2-(prop-1-en-2-yl)oxazolidine (**2t**) (in CDCl₃)**



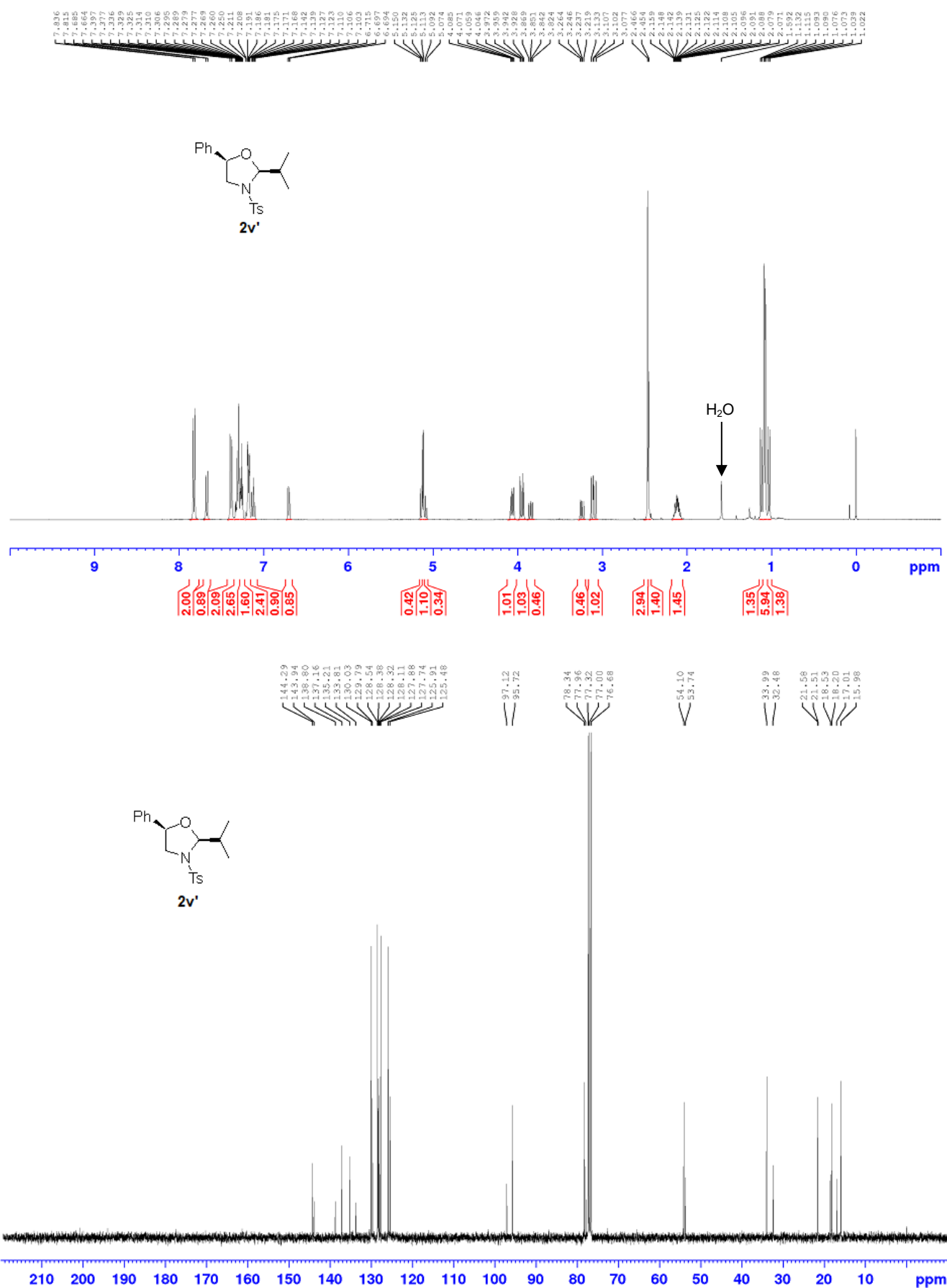
***N*-Ts-5,5-Dimethyl-2-(prop-1-en-2-yl)oxazolidine (**2u**) (in CDCl₃)**



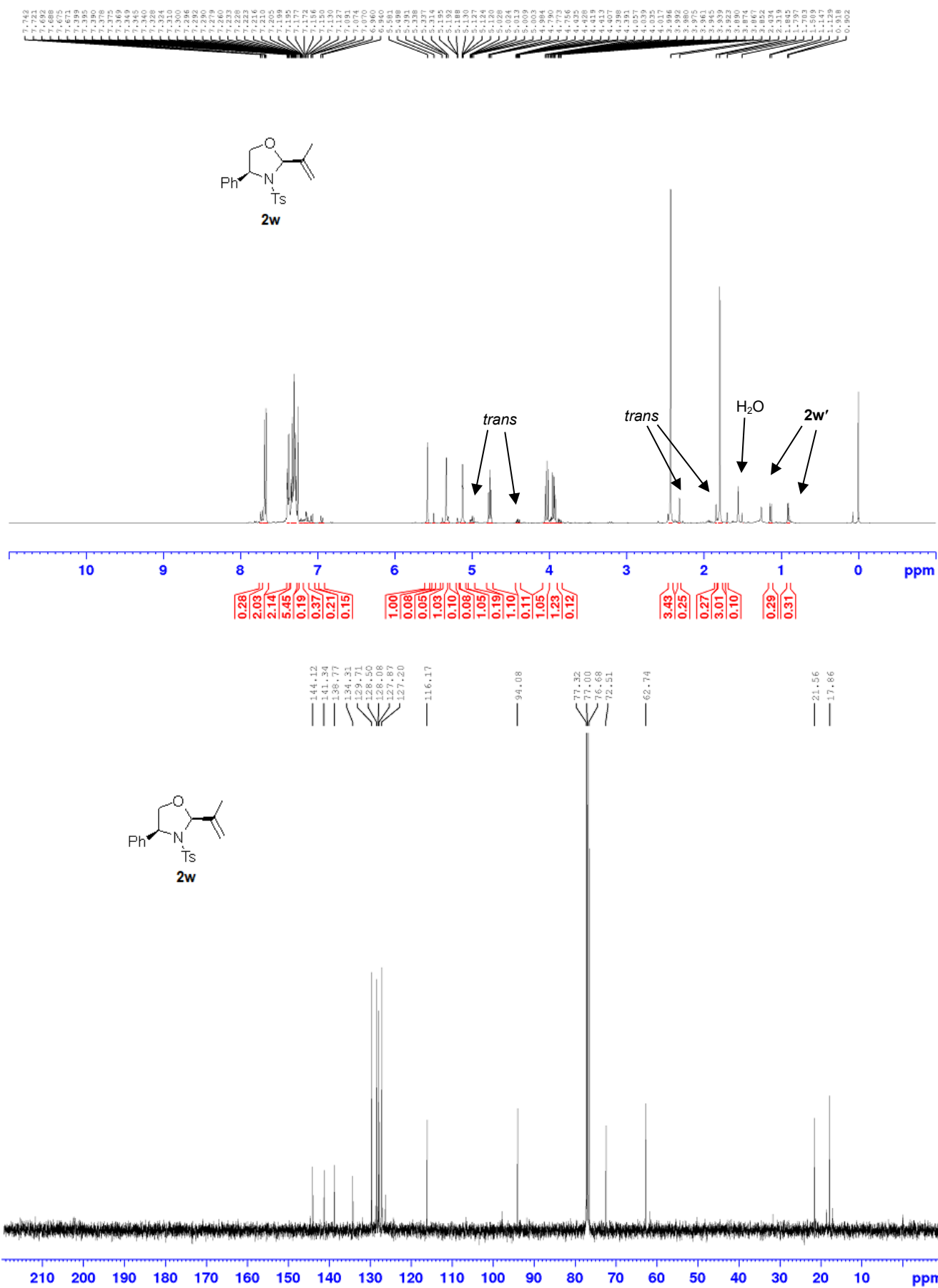
(2*S*,5*R*)-*N*-Ts-5-Phenyl-2-(prop-1-en-2-yl)oxazolidine (**2v**) (in CDCl₃)



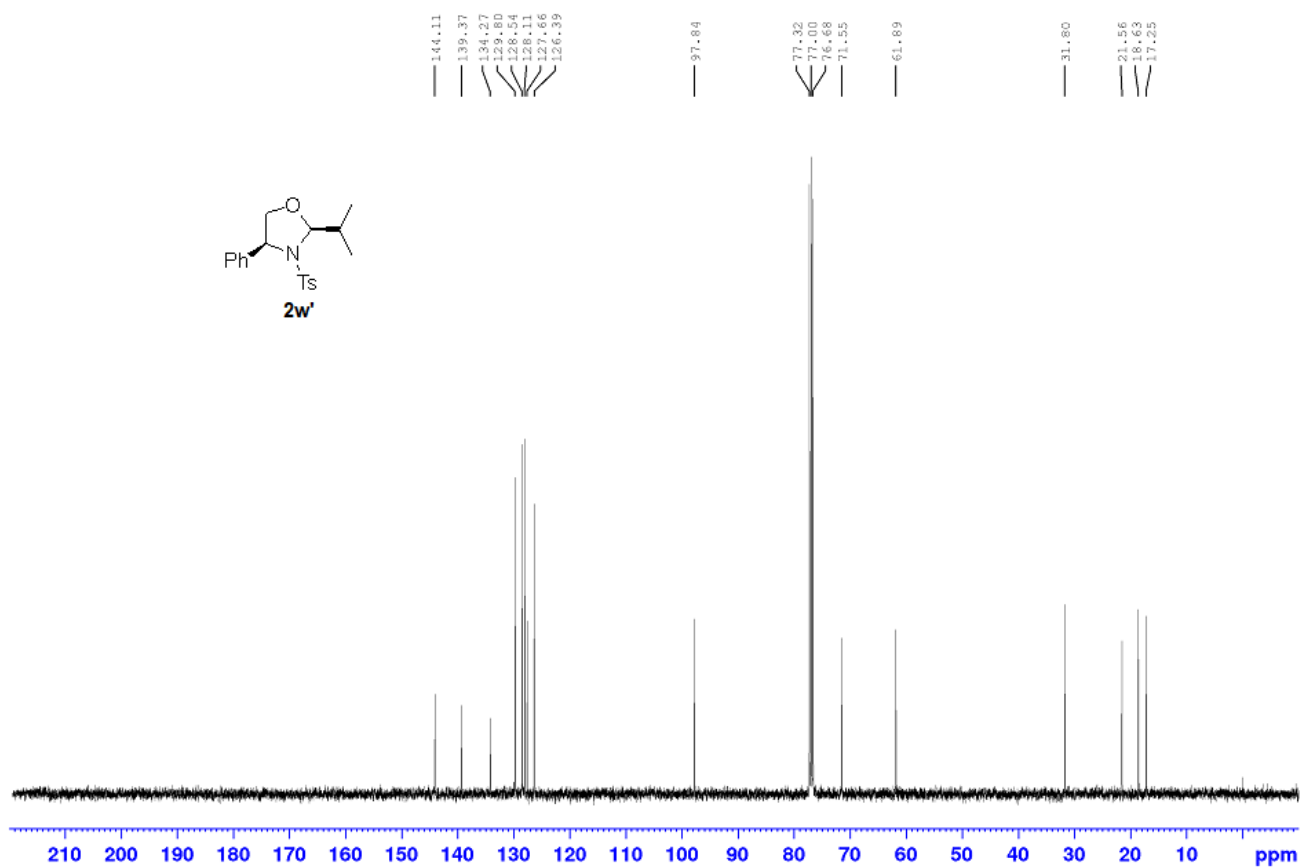
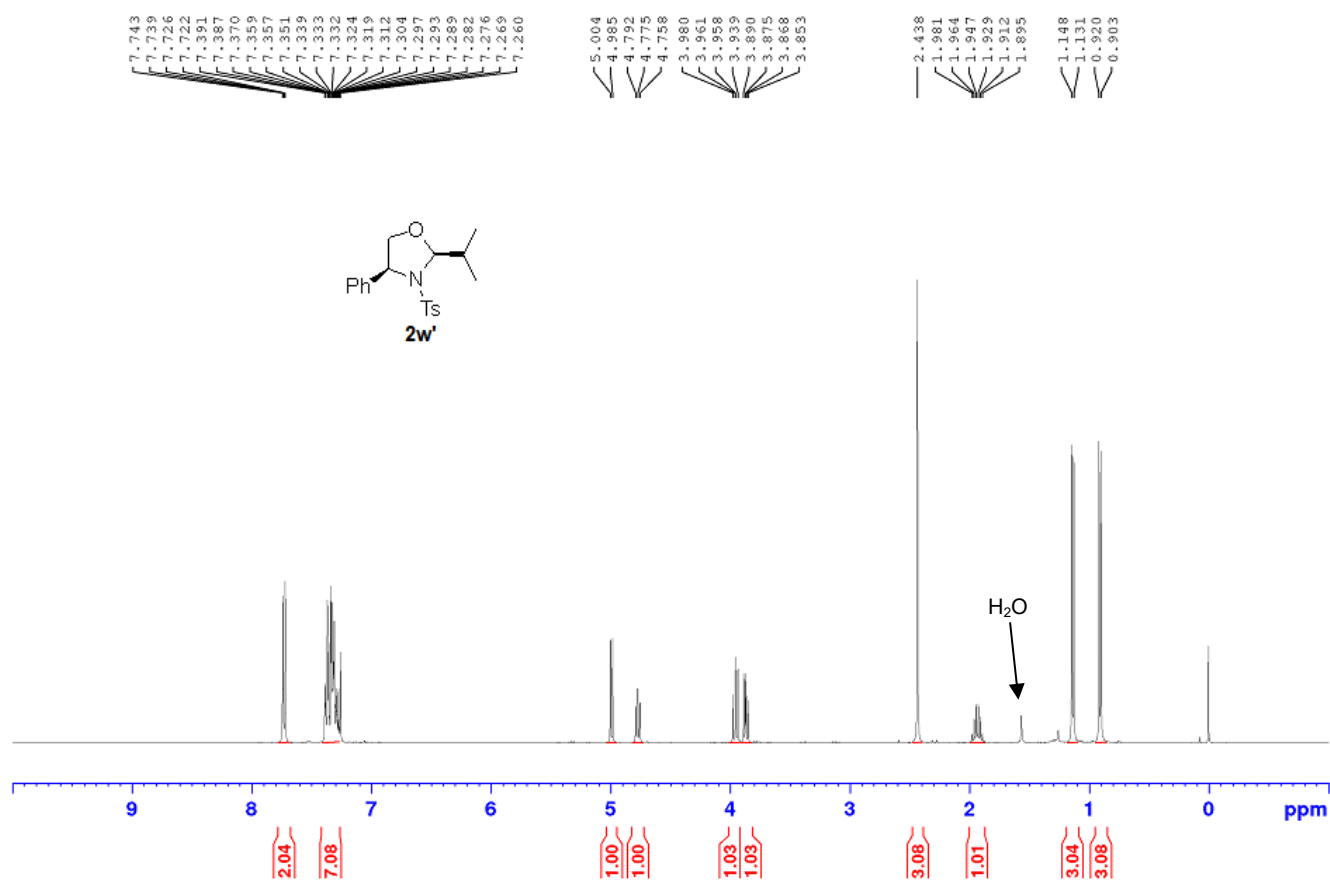
(2*S*,5*R*)-*N*-Ts-2-Isopropyl-5-phenyloxazolidine (**2v'**) (in CDCl₃)



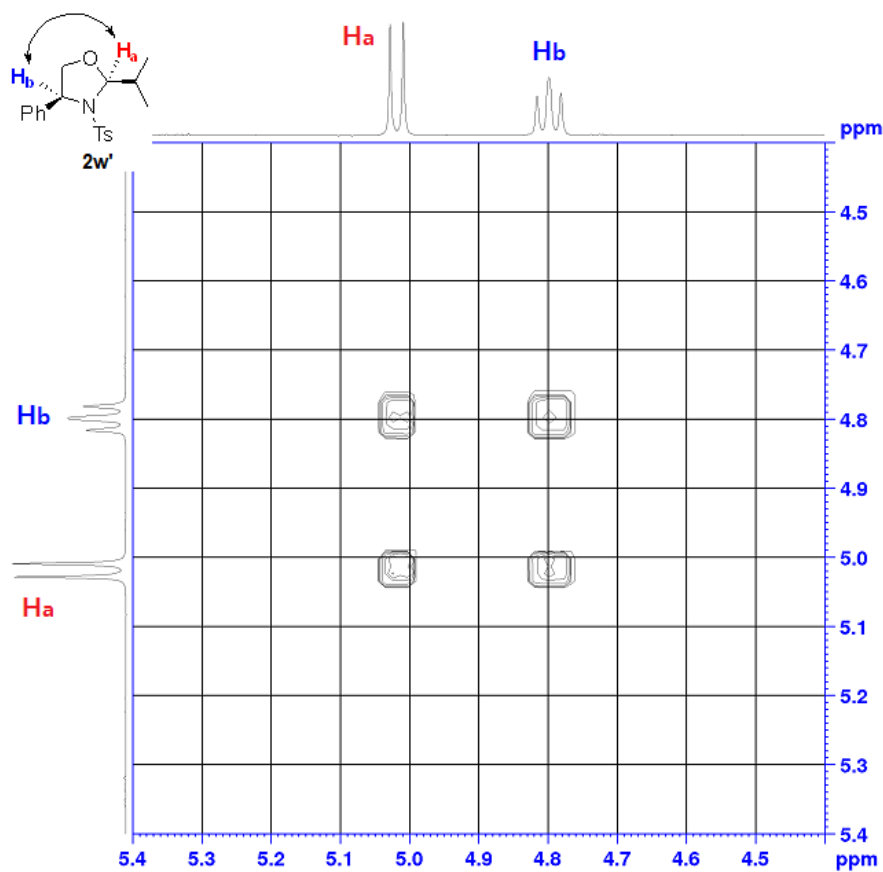
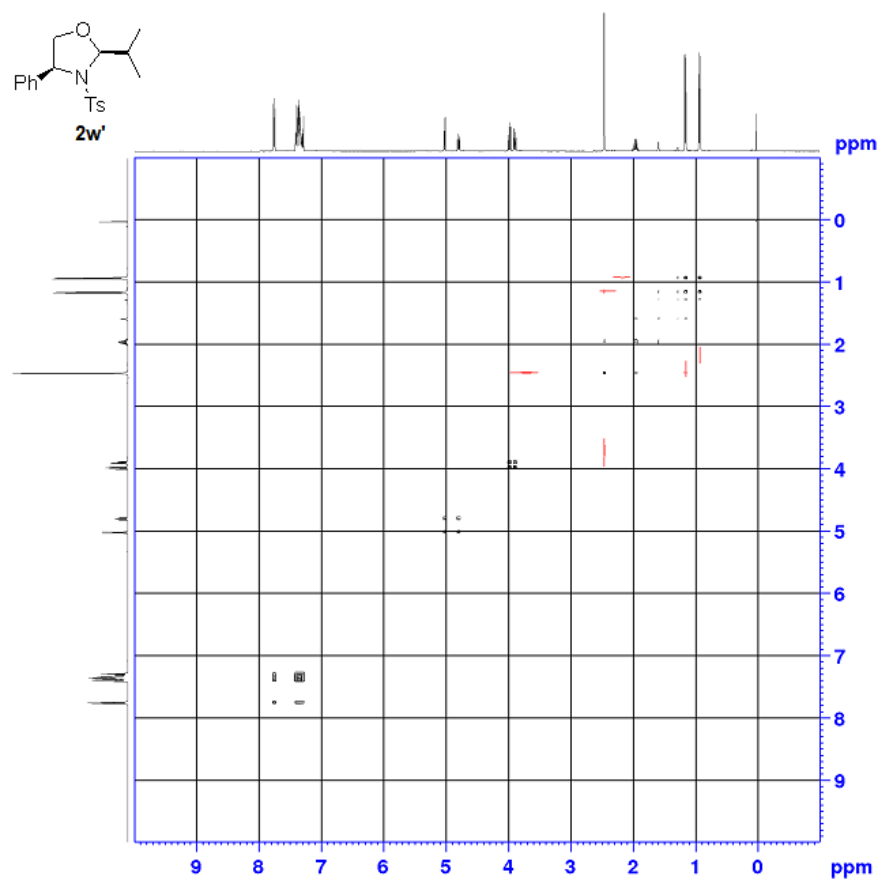
(2*S*,4*S*)-*N*-Ts-4-Phenyl-2-(prop-1-en-2-yl)oxazolidine (2w) (in CDCl₃)



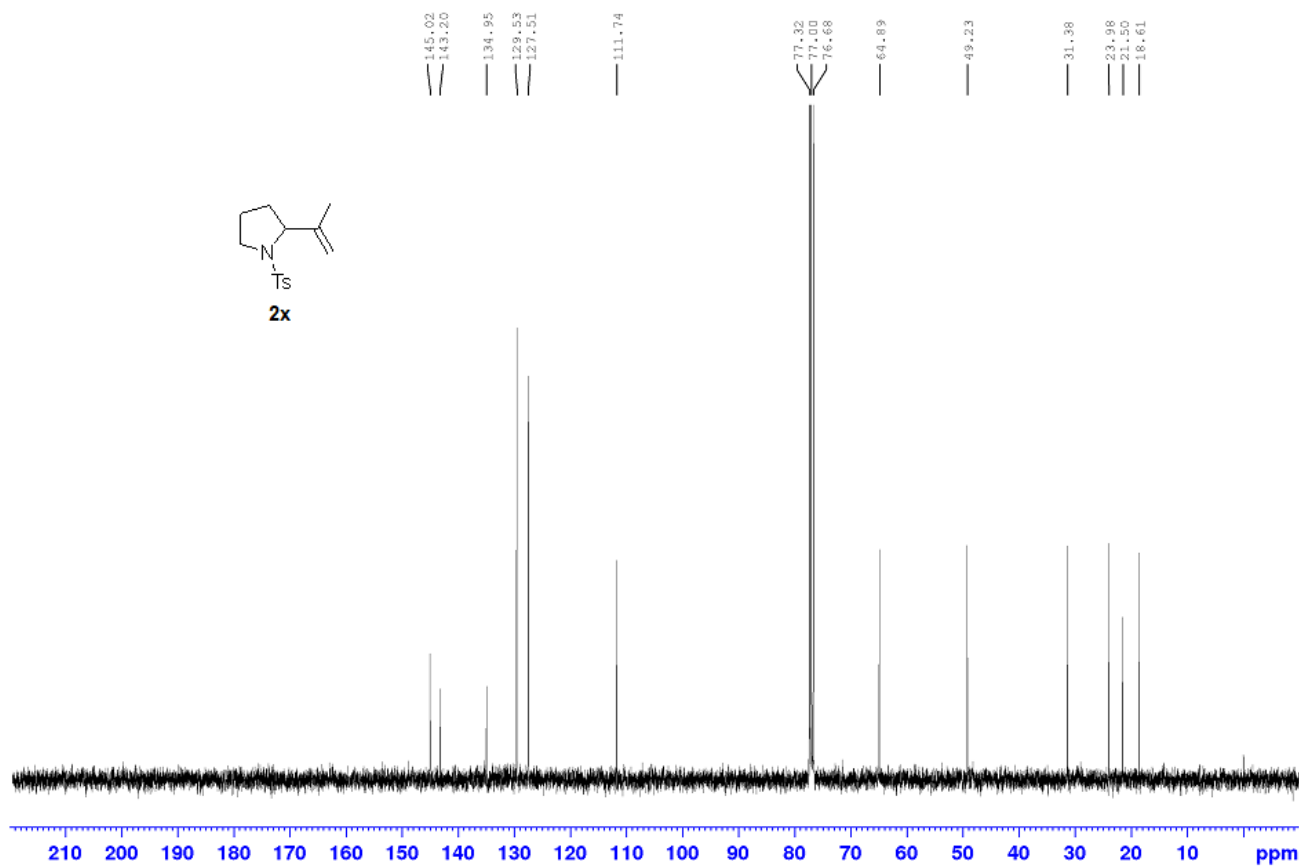
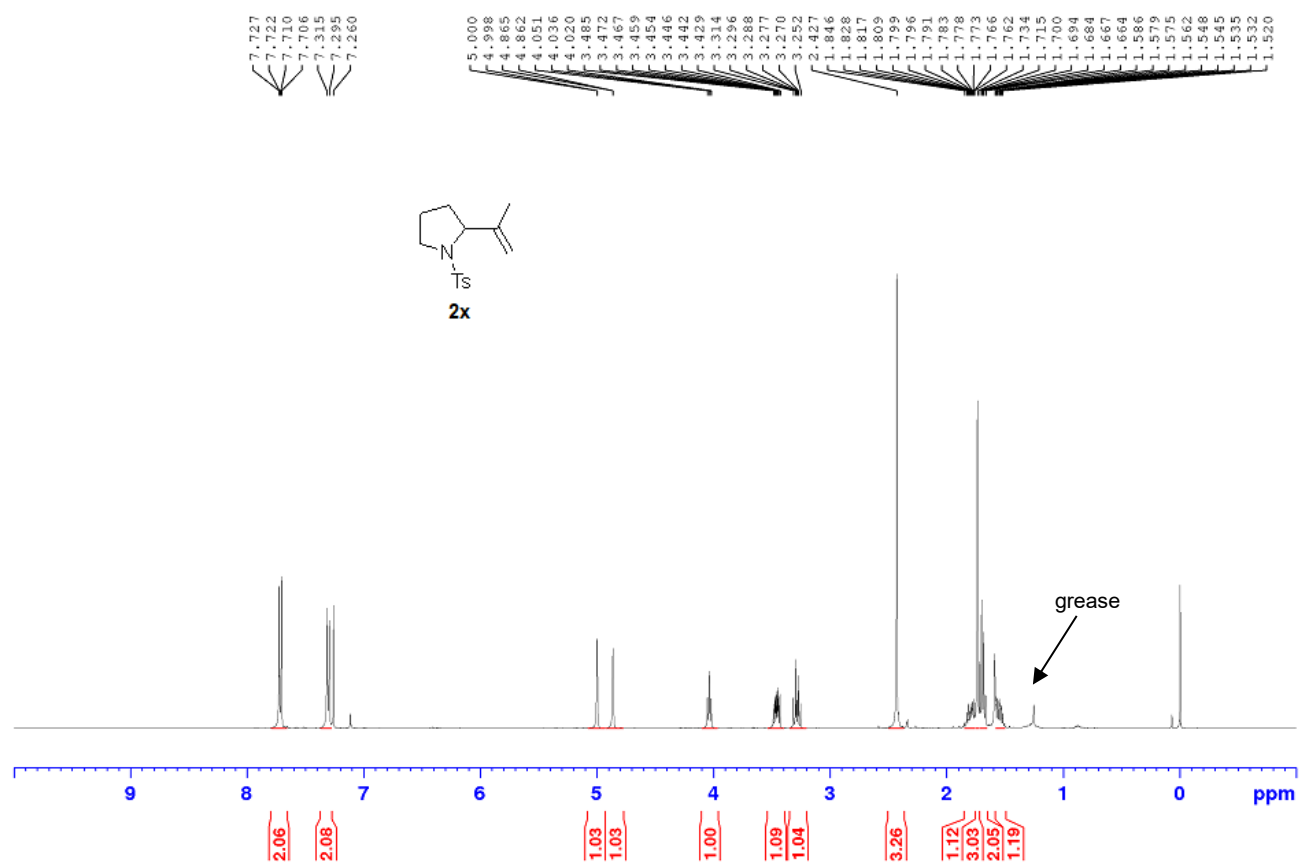
(2*S*,4*S*)-*N*-Ts-2-Isopropyl-4-phenyloxazolidine (2w'**) (in CDCl₃)**



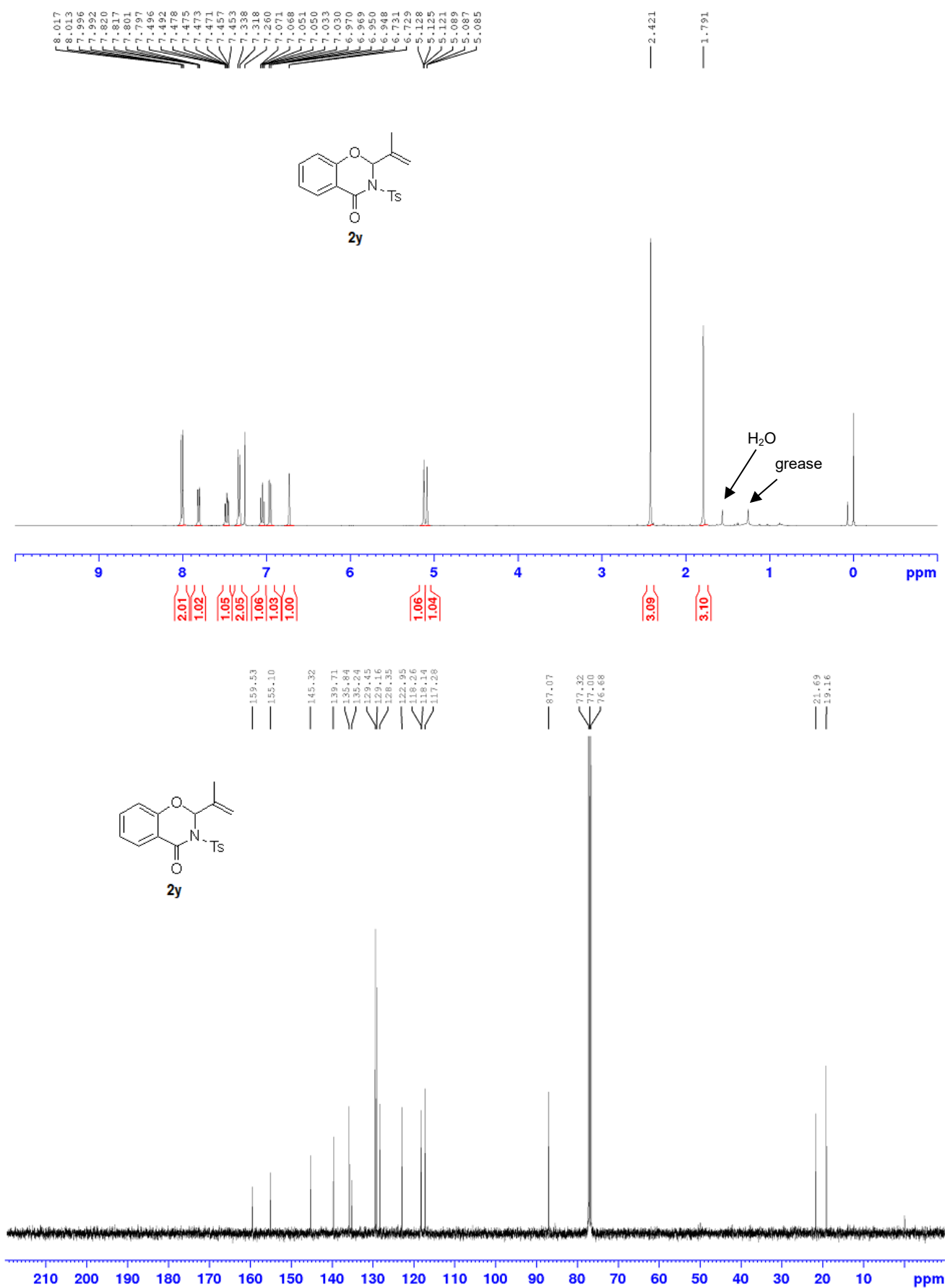
NOESY of 2w'



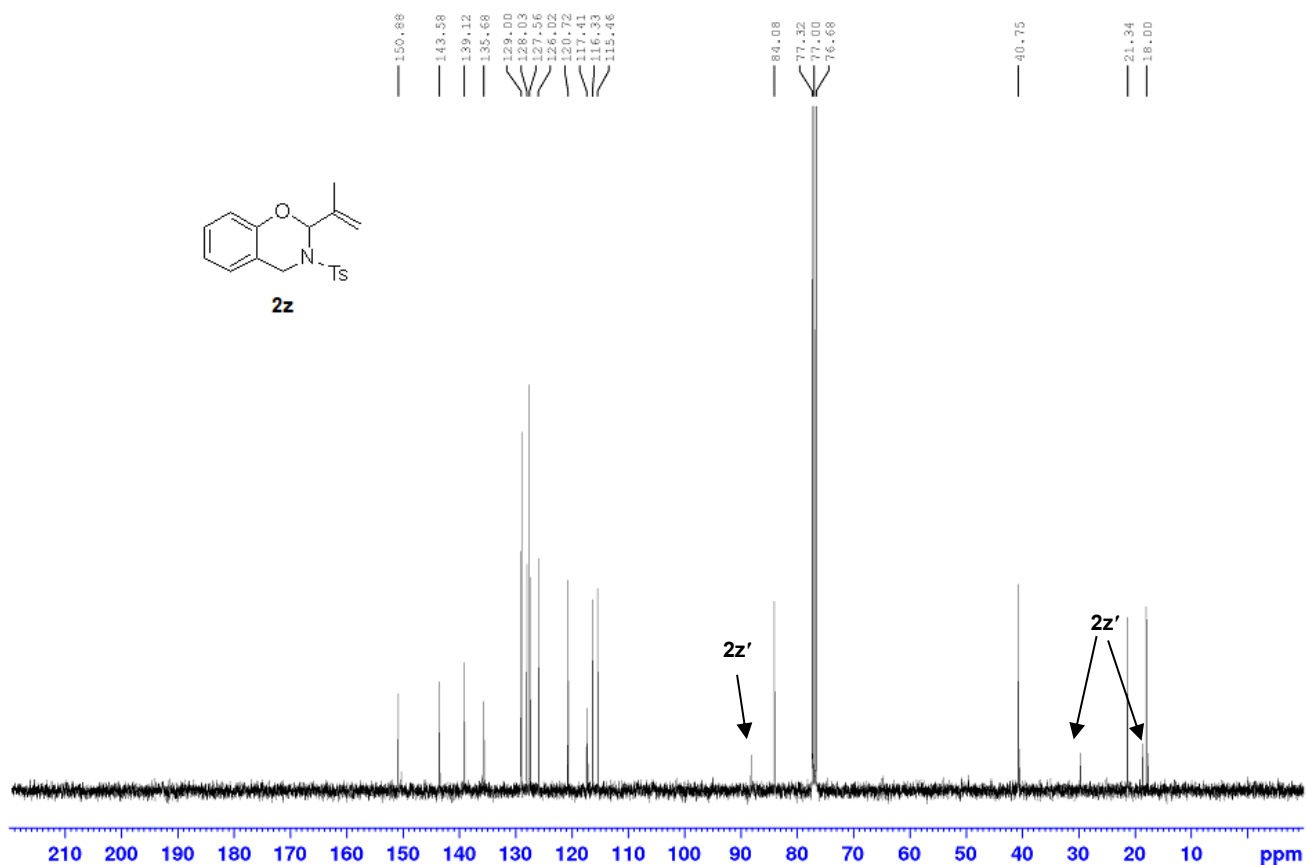
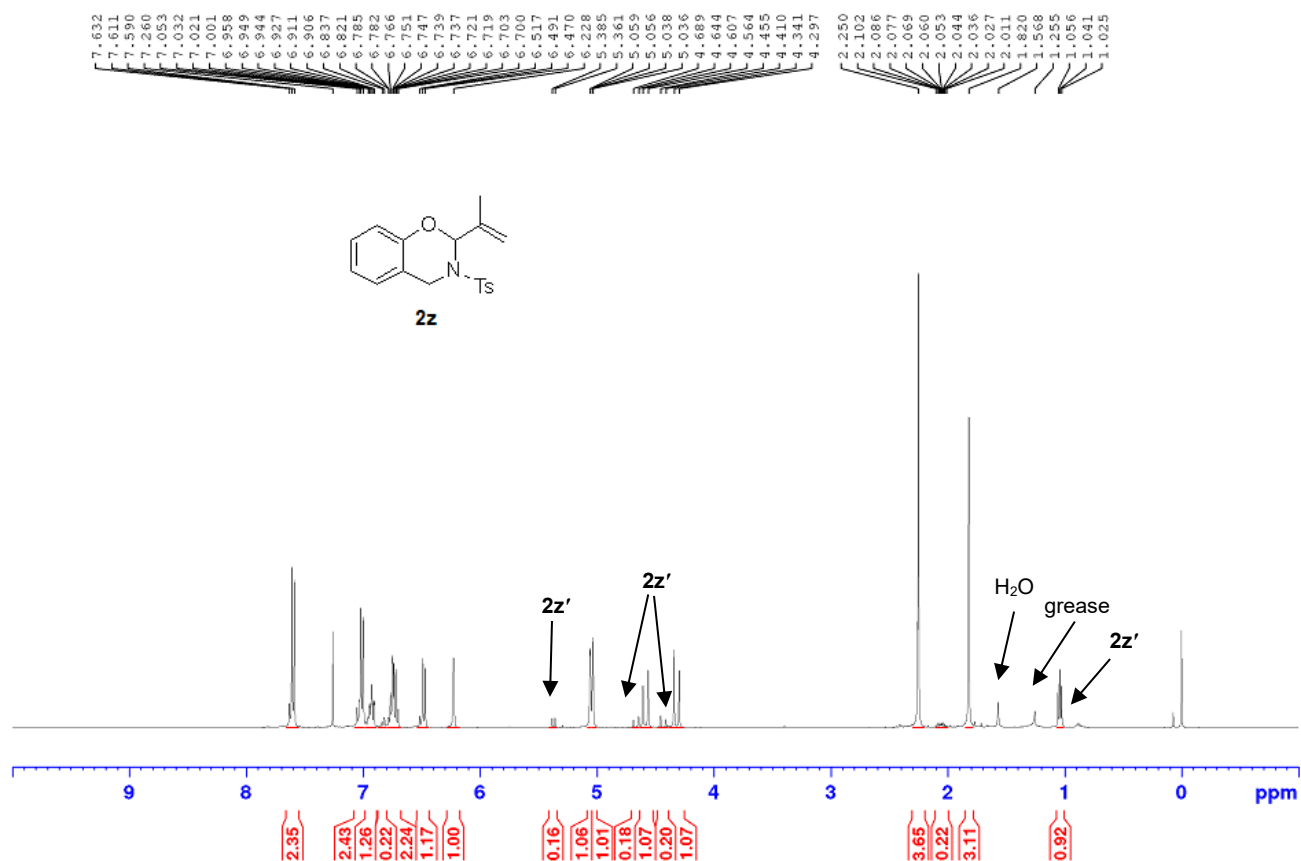
***N*-Ts-2-(Prop-1-en-2-yl)pyrrolidine (**2x**) (in CDCl₃)**



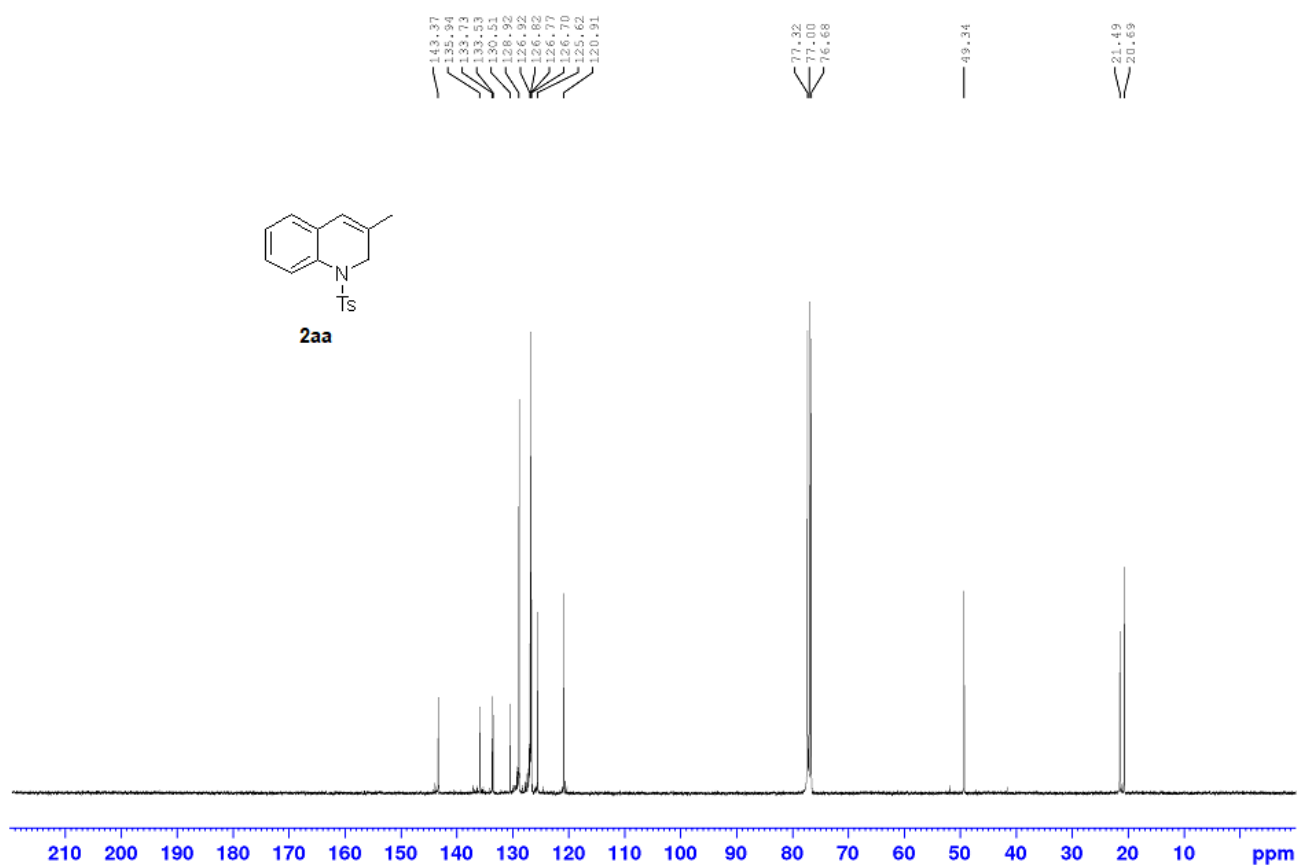
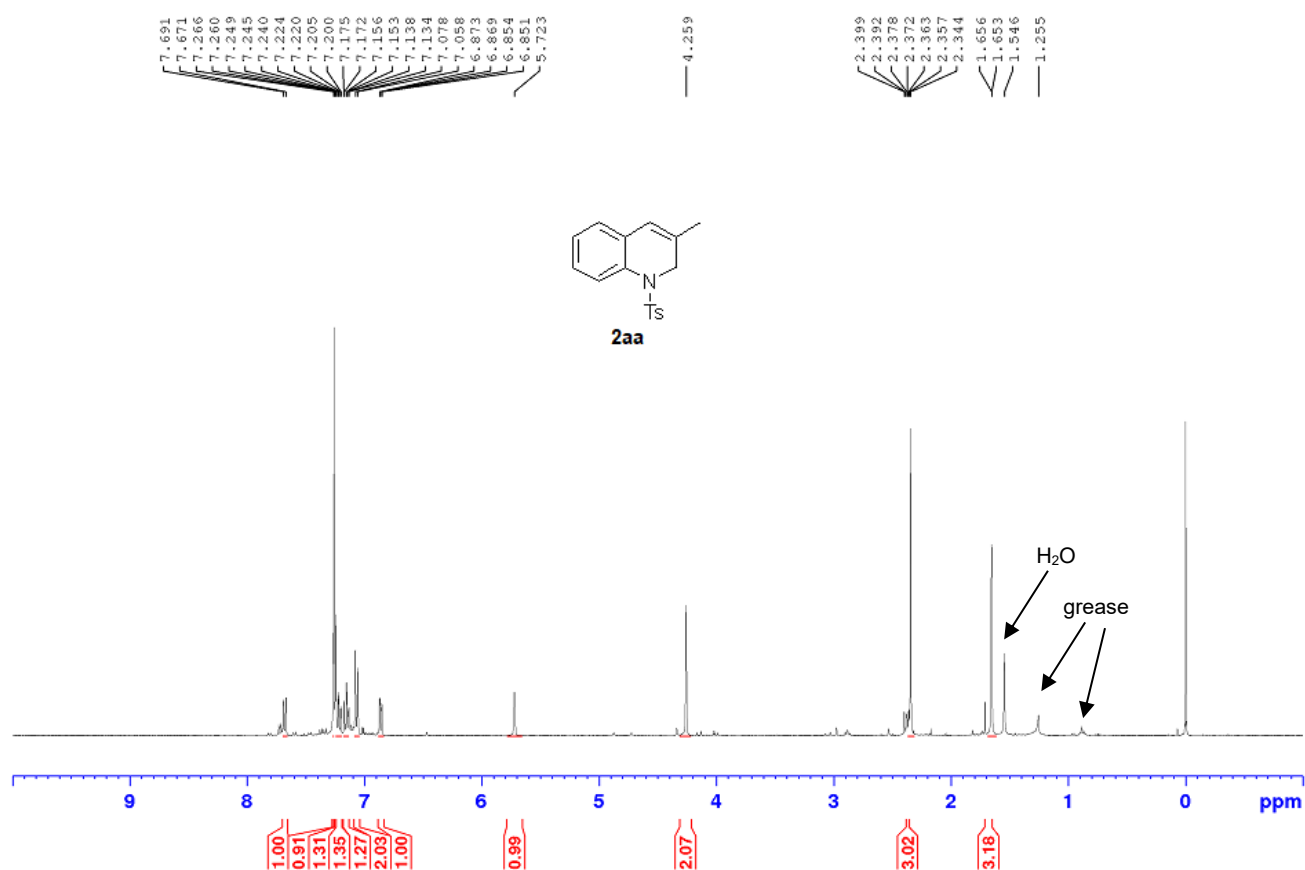
***N*-Ts-2-(Prop-1-en-2-yl)-2,3-dihydro-4*H*-benzo[*e*][1,3]oxazin-4-one (2y) (in CDCl₃)**



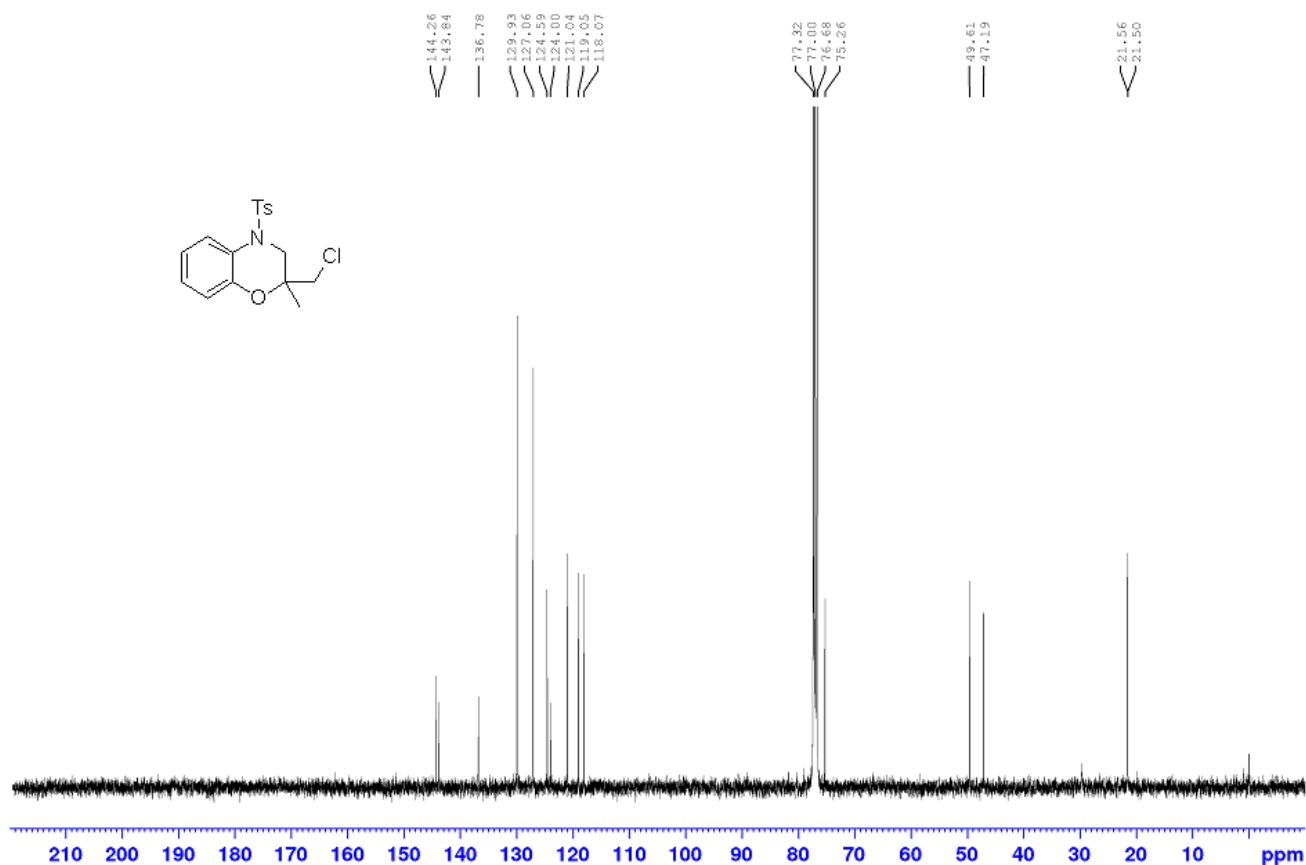
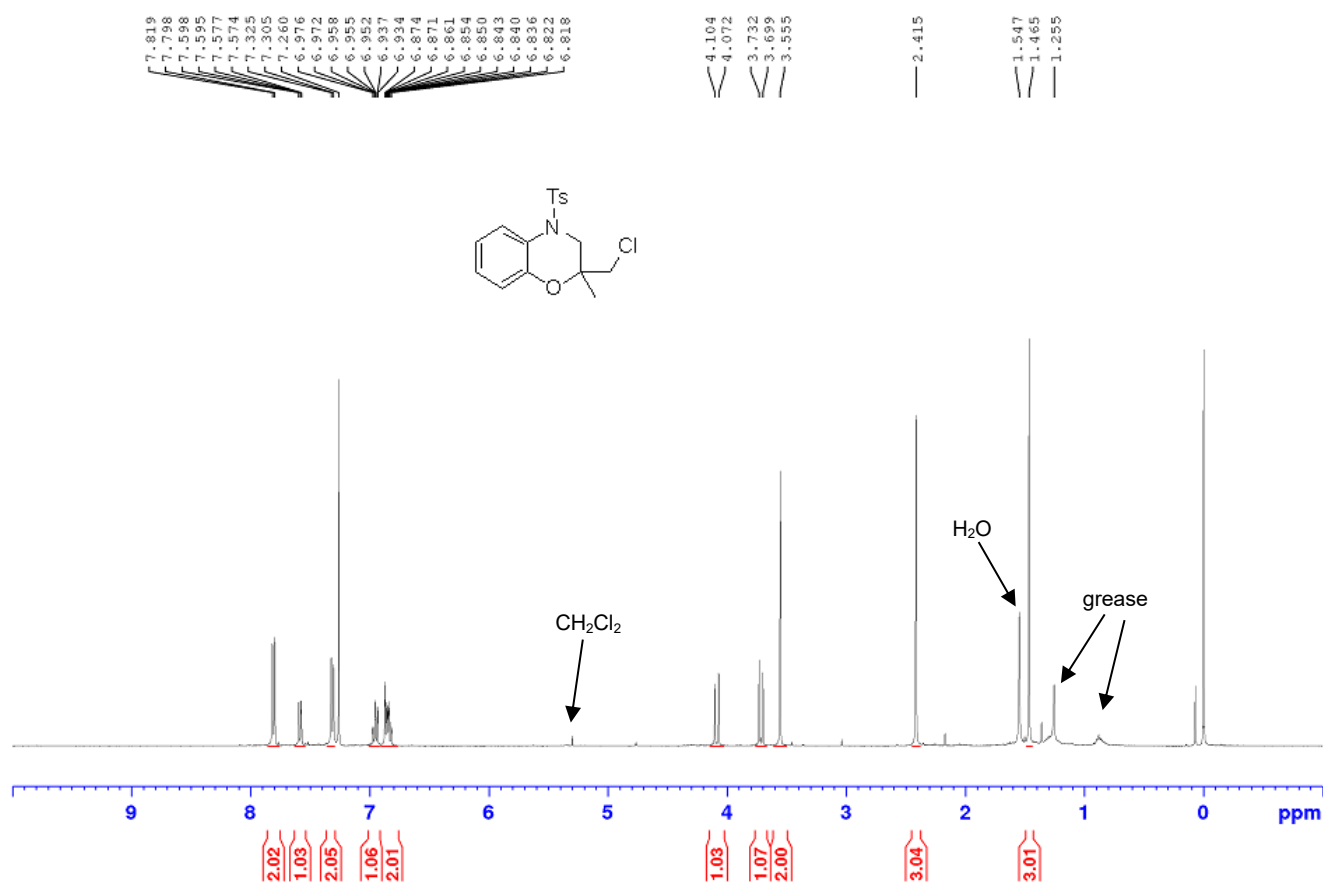
***N*-Ts-2-(Prop-1-en-2-yl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine (**2z**) (in CDCl₃)**



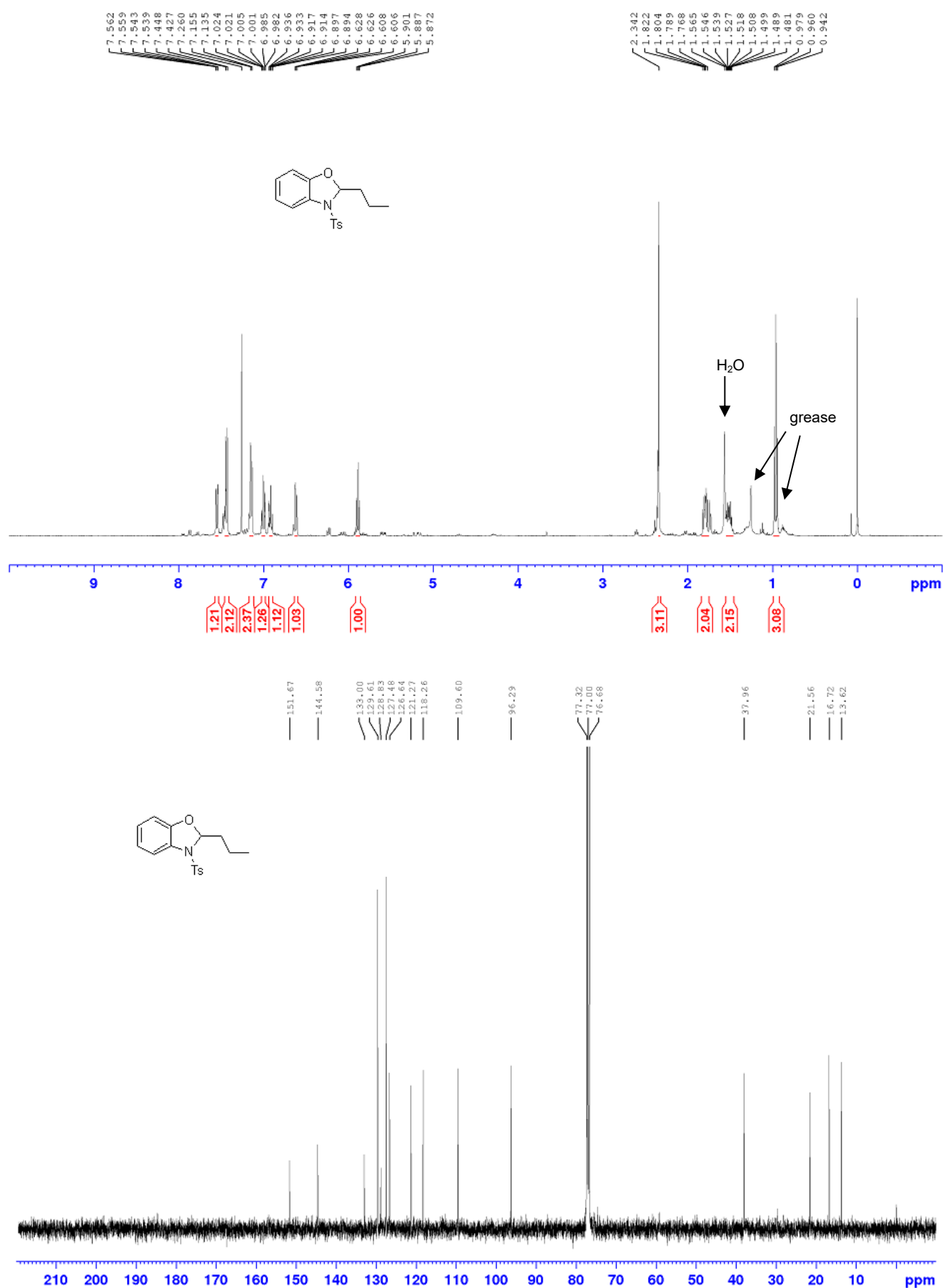
***N*-Ts-3-Methyl-1,2-dihydroquinoline (2aa) (in CDCl₃)**



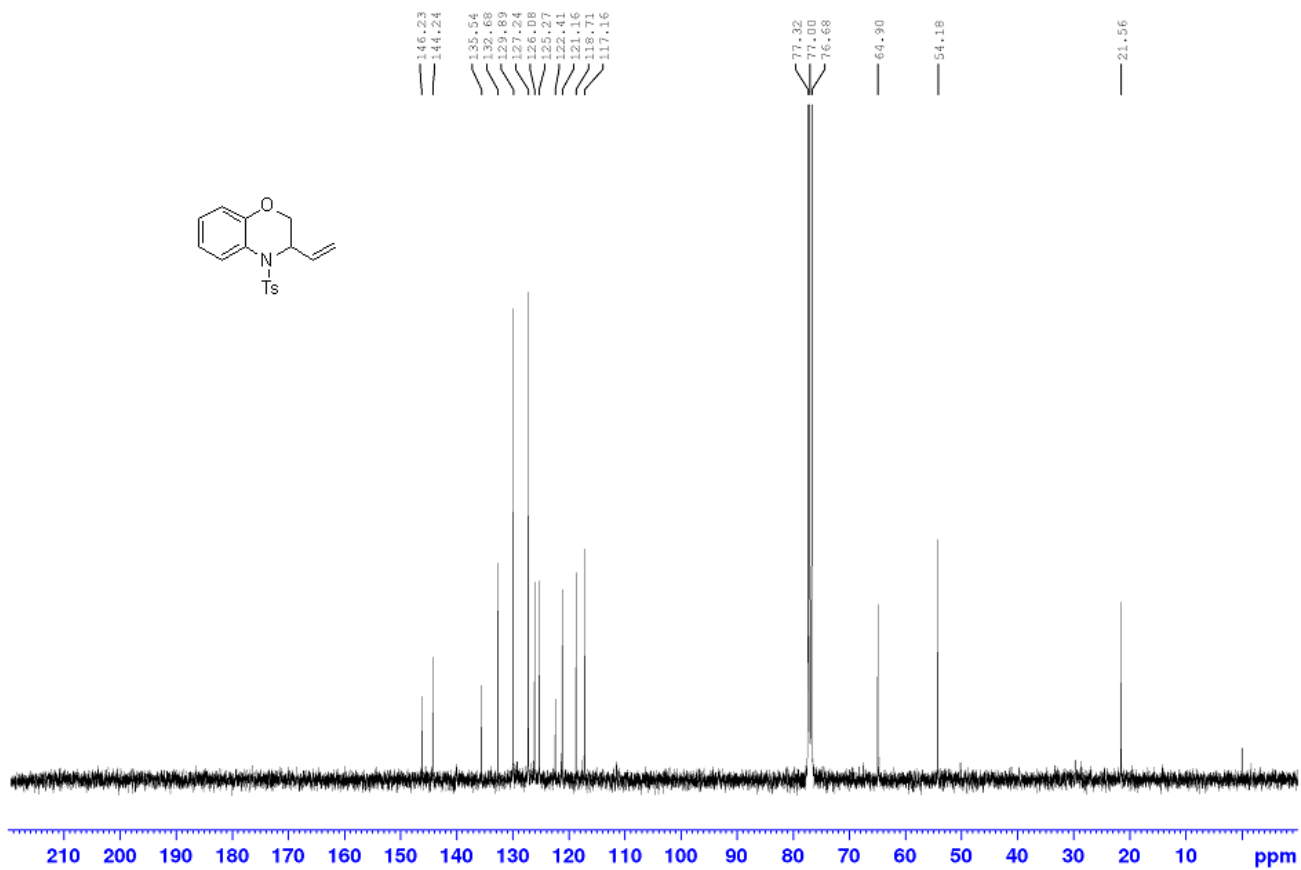
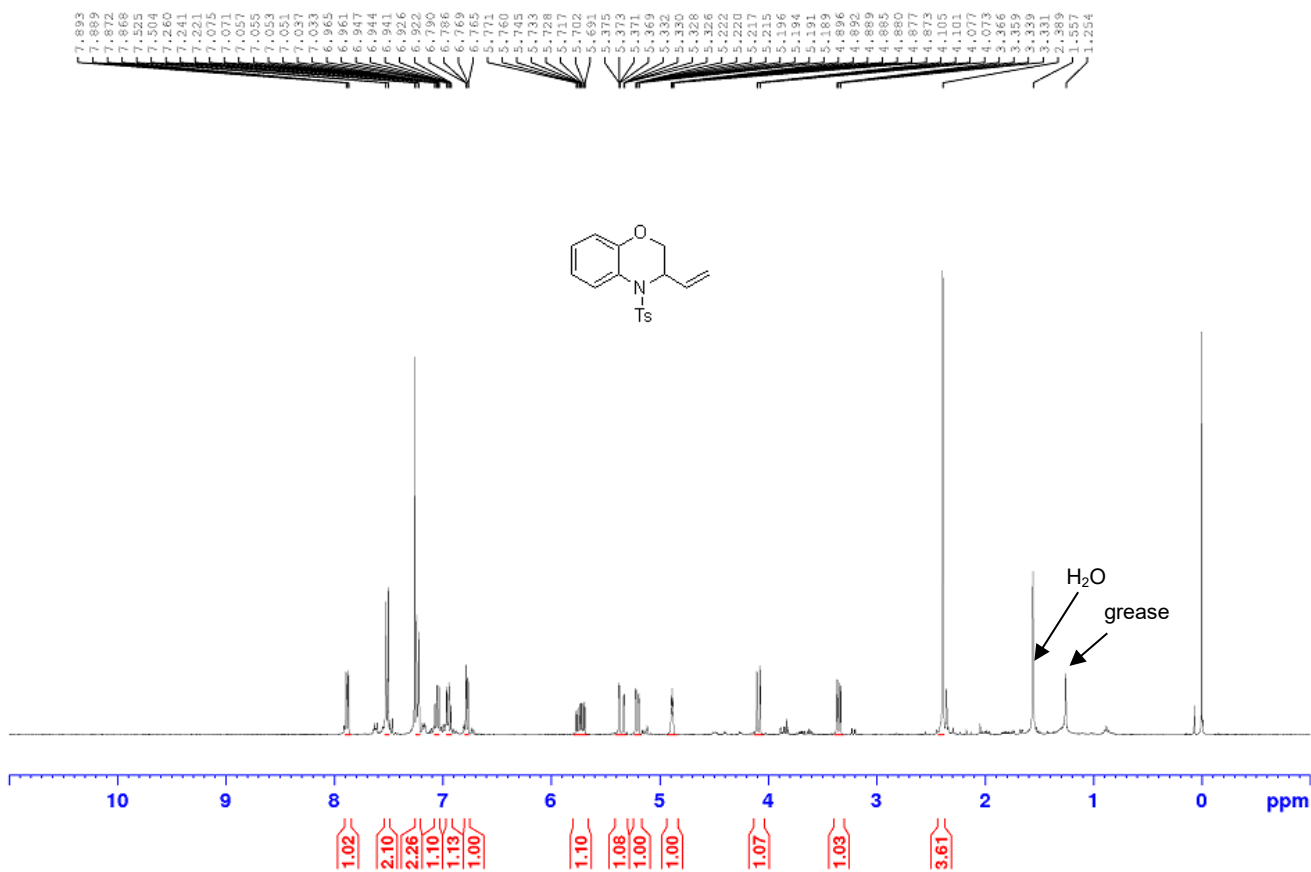
***N*-Ts-2-(Chloromethyl)-2-methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (4a-Cl) (in CDCl₃)**



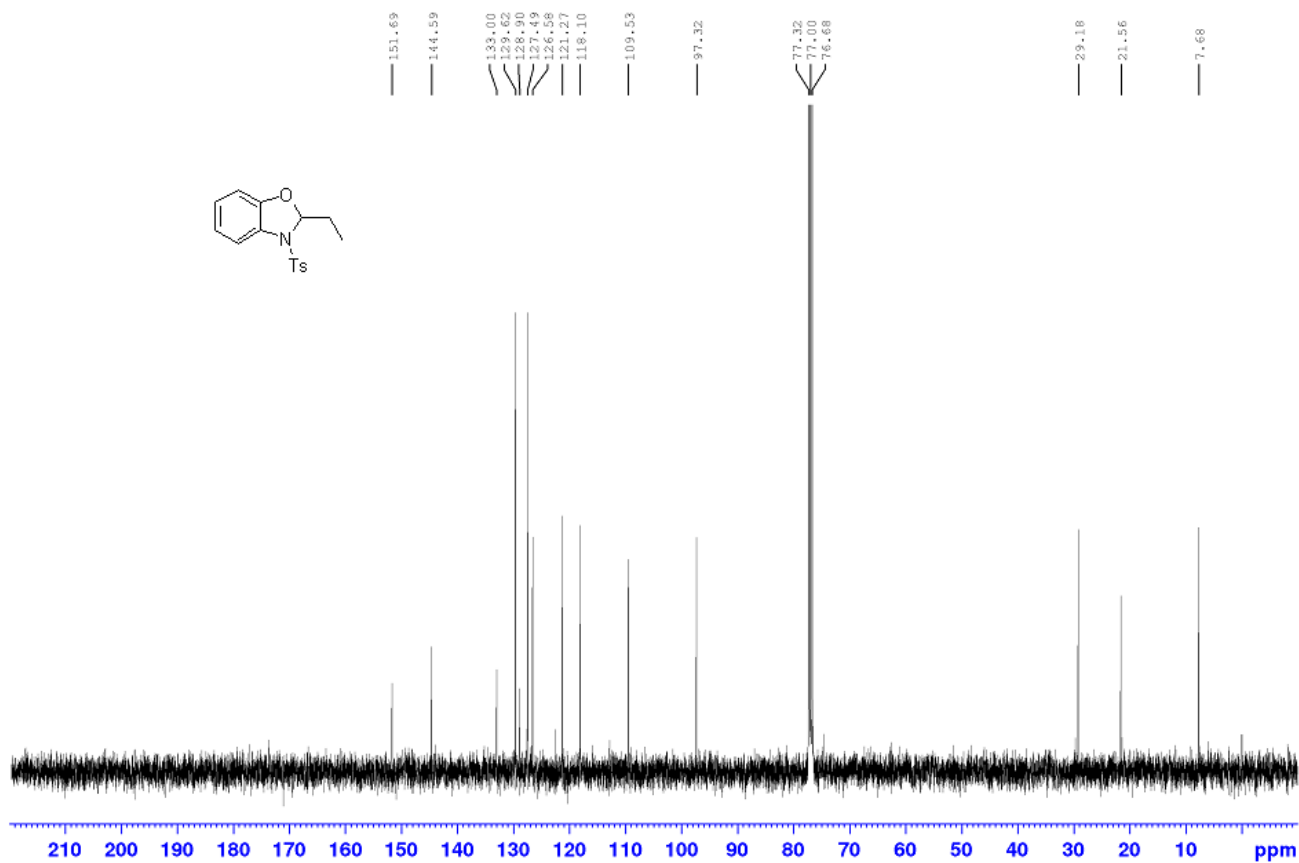
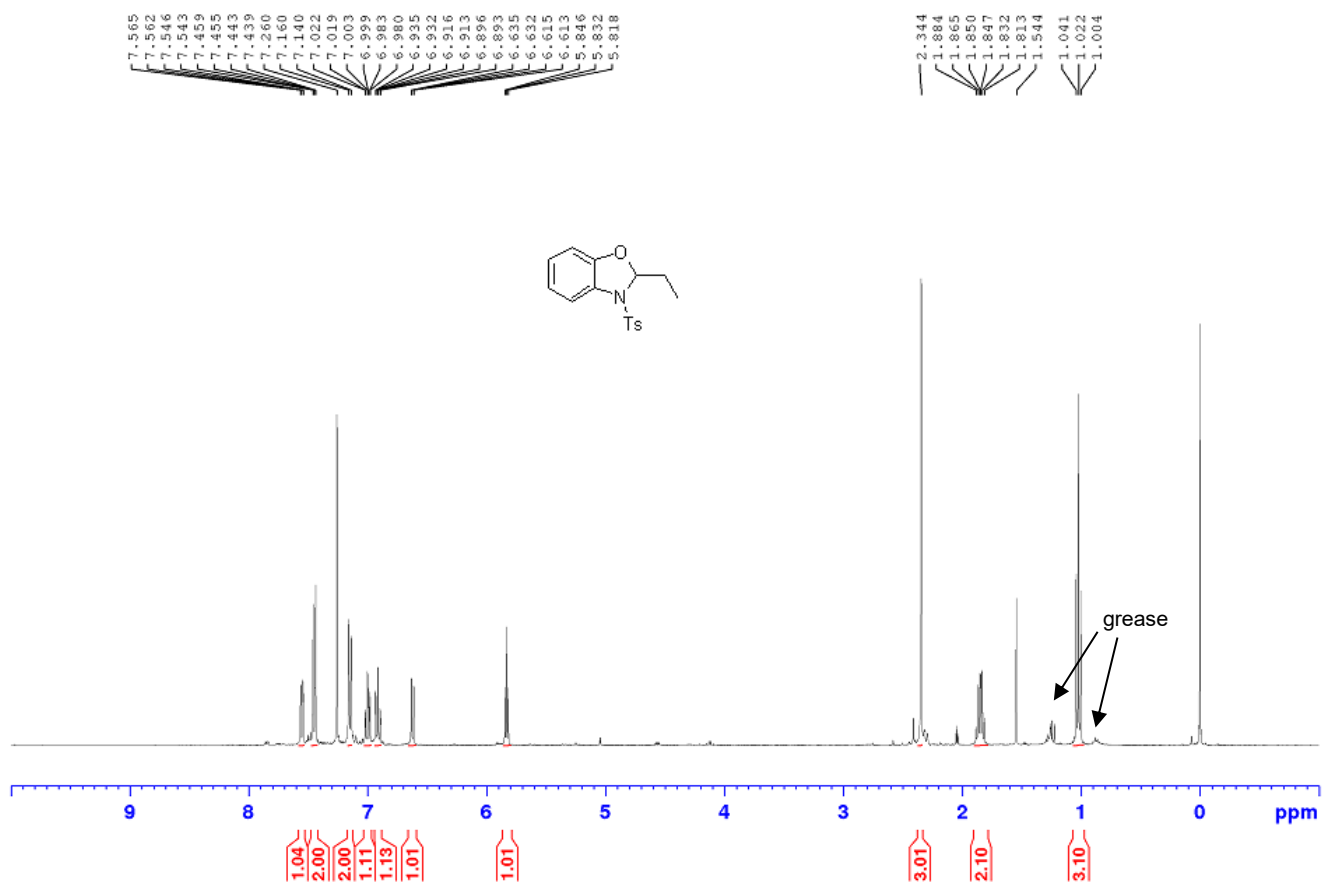
***N*-Ts-2-Propyl-2,3-dihydrobenzo[*d*]oxazole (in CDCl₃)**



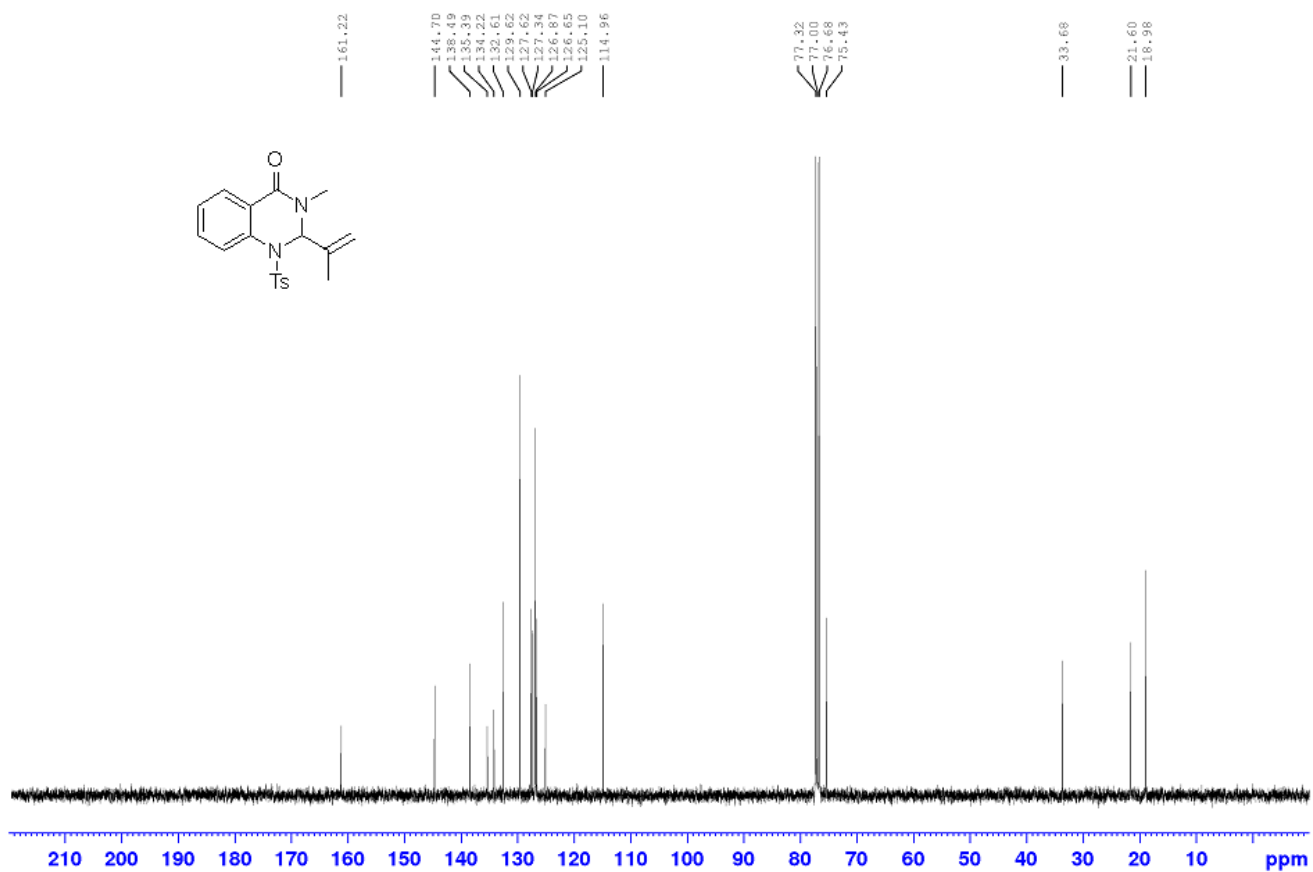
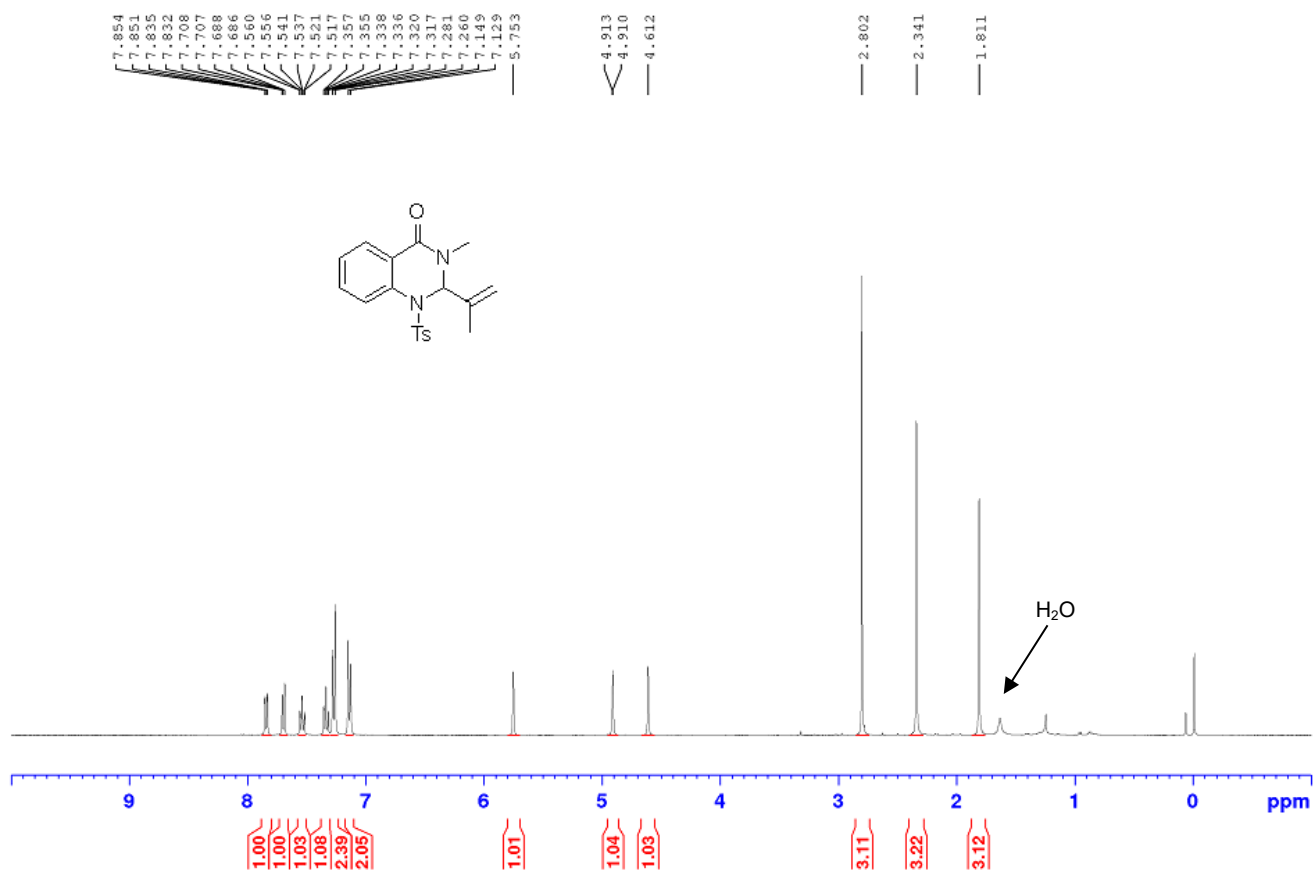
***N*-Ts-3-Vinyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine** (in CDCl₃)



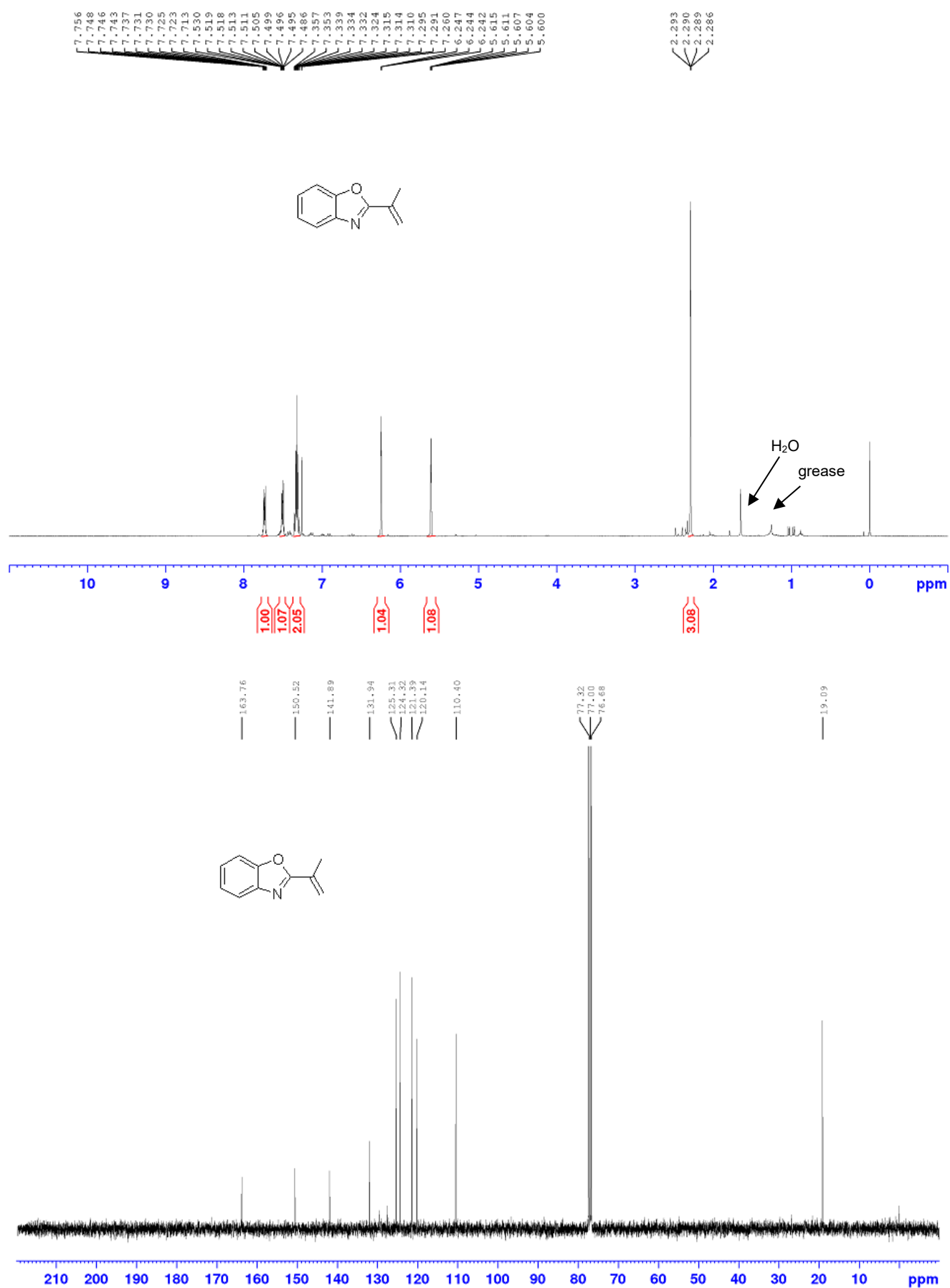
***N*-Ts-2-Ethyl-2,3-dihydrobenzo[*d*]oxazole (in CDCl₃)**



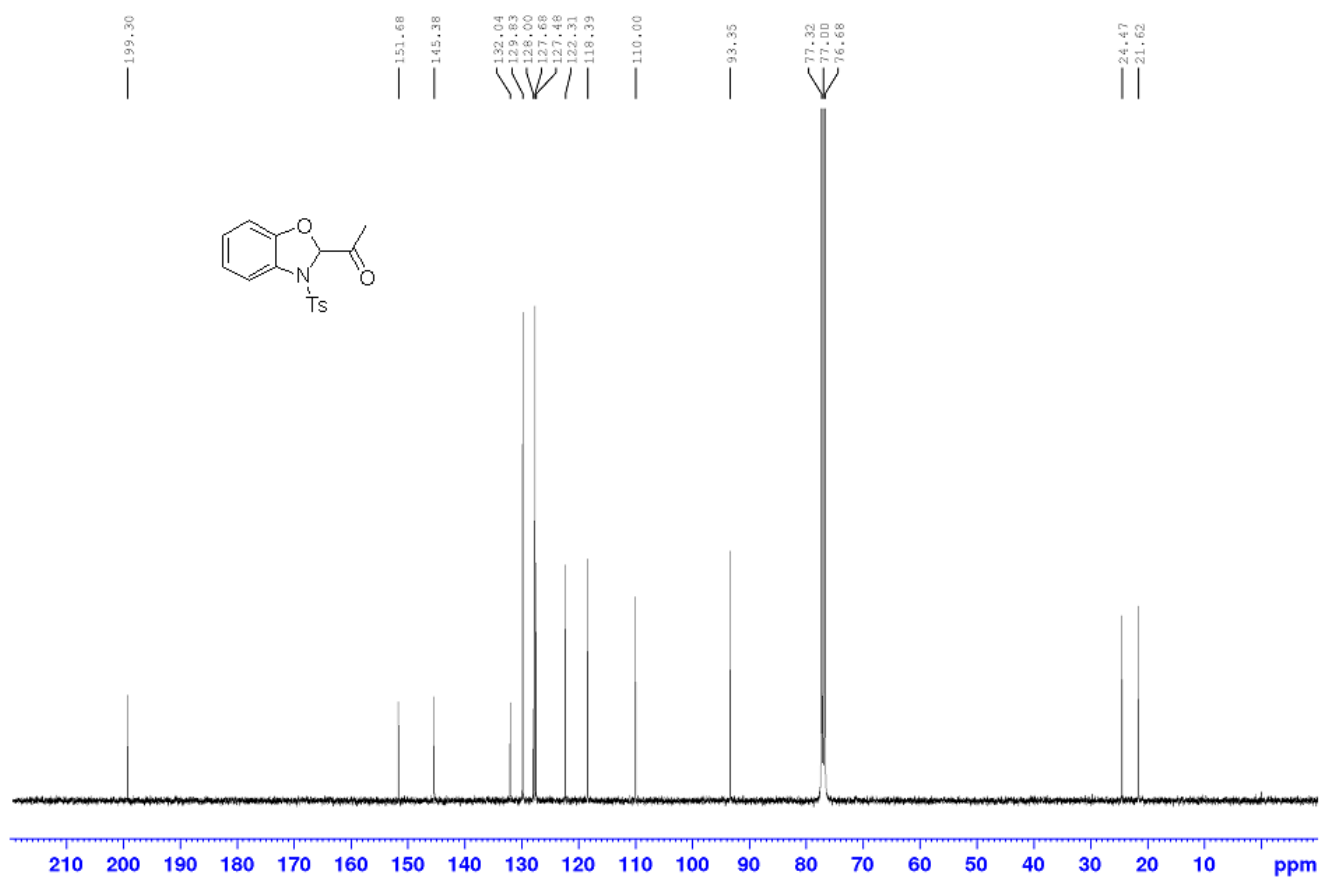
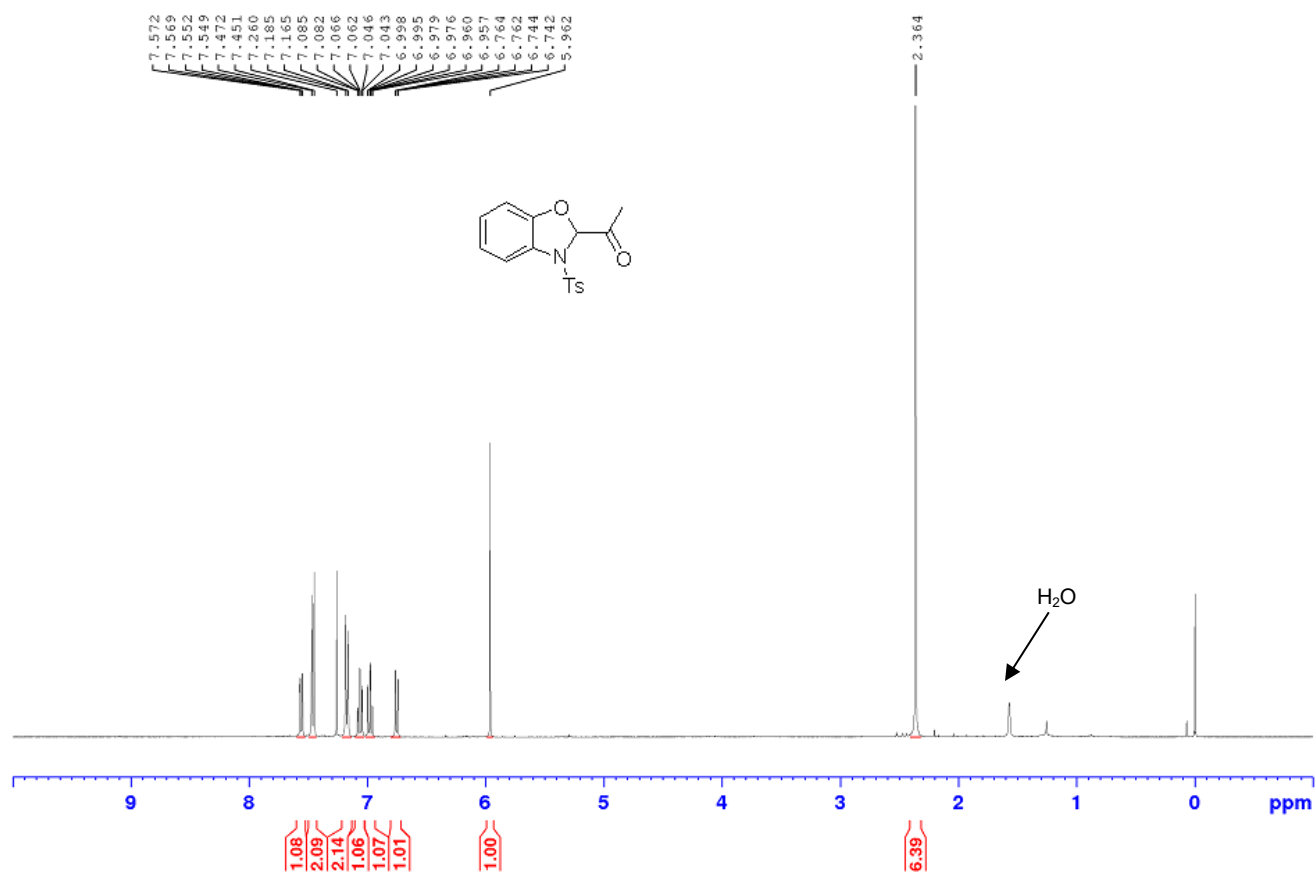
***N*-Ts-3-Methyl-2-(prop-1-en-2-yl)-2,3-dihydroquinazolin-4(1*H*)-one** (in CDCl₃)



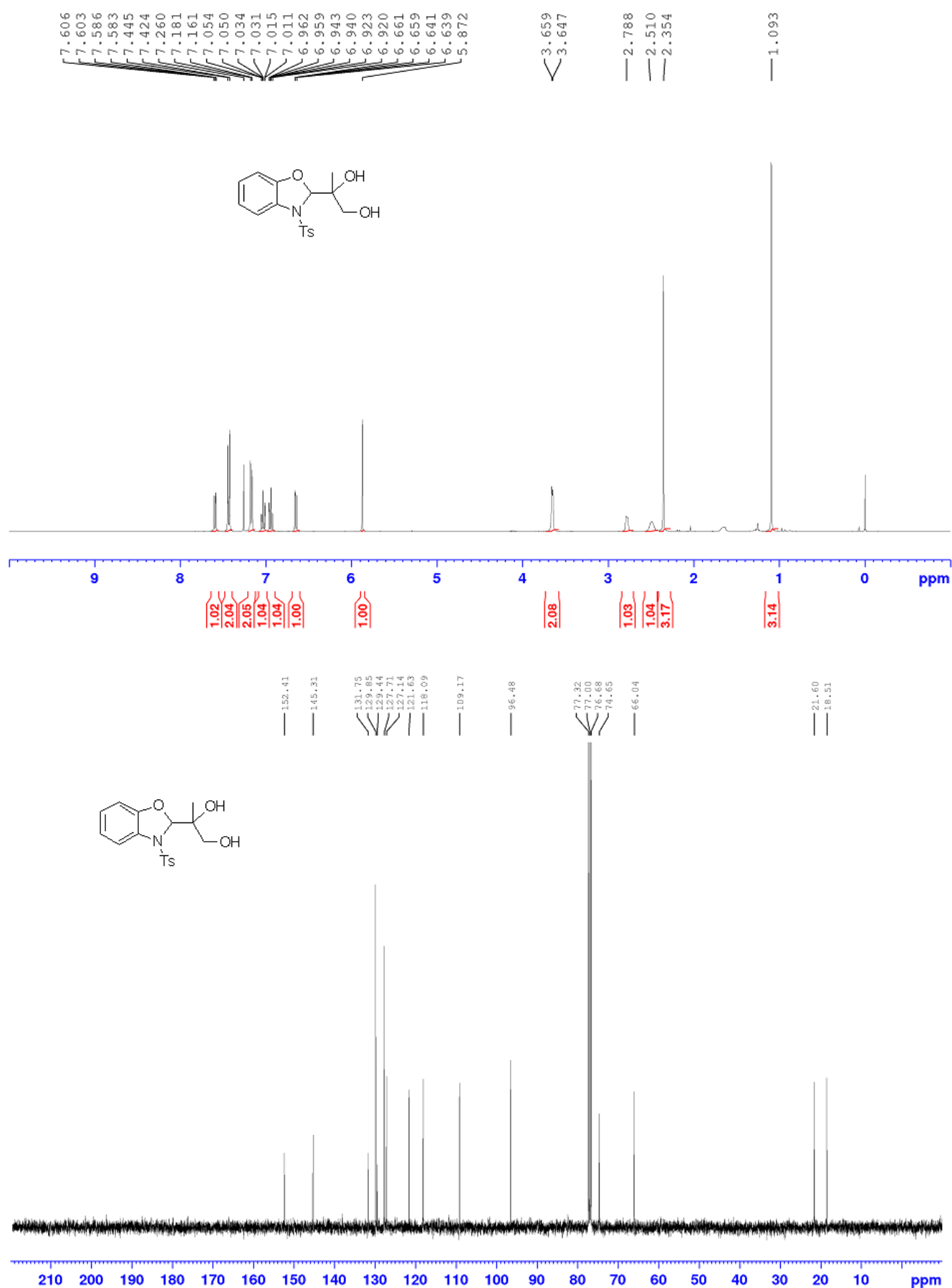
2-(Prop-1-en-2-yl)benzo[d]oxazole (in CDCl₃)



***N*-Ts-2-Acetyl-2,3-dihydrobenzo[*d*]oxazole (in CDCl₃)**



***N*-Ts-2-(1,2-Dihydroxypropan-2-yl)-2,3-dihydrobenzo[*d*]oxazole (A isomer) (in CDCl₃)**



***N*-Ts-2-(1,2-Dihydroxypropan-2-yl)-2,3-dihydrobenzo[*d*]oxazole (B isomer) (in CDCl₃)**

