Supporting Information

Palladium-Catalyzed Regiocontrollable Hydroarylation Reaction of Allenamides with B_2pin_2/H_2O

Jie Cui,[†] Long Meng,[†] Xiaochen Chi,[†] Qing Liu,[†] Pingping Zhao,[‡] Dao-peng Zhang,[†] Lei Chen,[†] Xinjin Li,[†] Yunhui Dong[†] and Hui Liu*[†]

[†]School of Chemistry & Chemical Engineering, Shandong University of Technology, 266 West Xincun Road, Zibo 255049, P. R. China

[‡]College of chemical and environmental engineering, Shandong university of science and technology, 579 Qianwangang Road, Huangdao District, Qingdao, 266590, P.R.China

*E-mail: huiliu1030@sdut.edu.cn

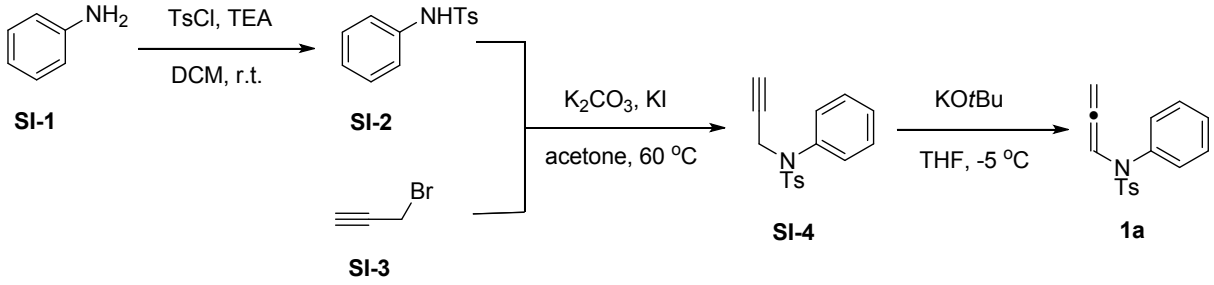
Table of Contents

1. General Information

Organic solvents (Aldrich) were used without further purification. Purifications of reactions products were carried out by flash chromatography using Merck silica gel (40-63 μm). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), …. Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF Mariner Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

2. Preparation of Starting Material.

General Procedure I:

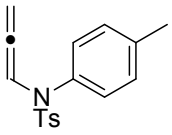


Preparation of SI-2: To a solution of Aniline **SI-1** (9.3 g, 100 mmol, 1.0 equiv) in DCM (70 mL) at room temperature was added TsCl (19.1 g, 100 mmol, 1.0 equiv). Then a solution of triethylamine (11.2 g, 110 mmol, 1.1 equiv) in 30 mL DCM was added dropwise by constant pressure funnel under vigorous stirring. The mixture was stirred at room temperature overnight and then washed three times with water. The organic layer was dried over Na_2SO_4 and concentrated to afford the crude material **SI-2** (22.8 g, 92 mmol, 92 yield) as a white solid, which was used without further purification.

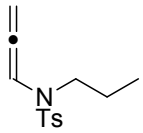
Preparation of SI-4: The **SI-2** (1.98 g, 8 mmol, 1.0 equiv) was dissolved in 35 mL acetone, and **SI-3** (0.9 mL, 10.4 mmol, 1.3 equiv), K_2CO_3 (2.21 g, 16 mmol, 2.0 equiv), KI (0.66 g, 4 mmol, 0.5 equiv) was added successively. The mixture was stirred for 3h and refluxed at 60 °C. Then the reaction system was quenched with water, the organic layer was exacted three times with EtOAc. Drying over Na_2SO_4 and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography to give **SI-4** (2.12 g, 7.43 mmol, 93% yield) as a white solid.

Preparation of 1a: The solution of potassium tert-butylate (1.01 g, 9 mmol, 1.5 equiv) was stirred in dry THF (25 mL) at -5 °C under a nitrogen atmosphere. The 4-methyl-N-phenyl-N-(prop-2-yn-1-yl)benzenesulfonamide (1.71 g, 6 mmol, 1.0 equiv) was dissolved in 5 mL THF and added into the solution. Then the reaction mixture was stirred for 0.5 h. The aqueous layer was extracted three times with EtOAc. The organic phase was combined, dried over Na_2SO_4, evaporated and purified by flash chromatography to give **1a** (1.49 g, 5.22 mmol, 87% yield) as a yellow solid.

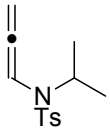
The following compounds were prepared according to **general procedure I**.



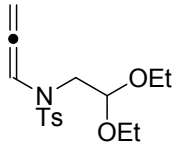
1b



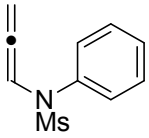
1c

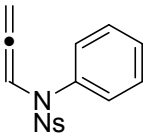


1d

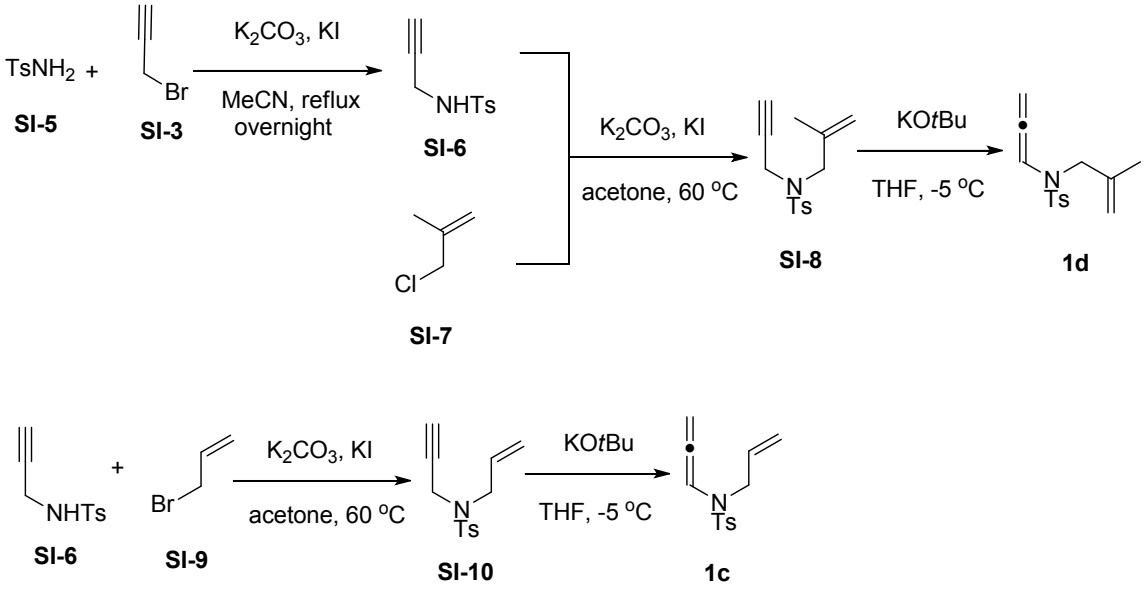


1e





General Procedure II:



Preparation of SI-6: To a solution of **SI-5** (1.23 g, 7.2 mmol, 3.0 equiv) in MeCN (7 mL) was added K_2CO_3 (0.67 g, 4.8 mmol, 2.0 equiv), KI (0.08 g, 2 mmol, 0.2 equiv). The solution was warmed slowly to reflux. Then propargyl bromides (0.2 mL, 2.4 mmol, 1.0 equiv) were added dropwise. The solution was kept reflux overnight. Then the mixture was cooled to room temperature and neutralized with 1N HCl/H_2O solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers was dried with Na_2SO_4, and concentrated *in vacuo*. Purification by column chromatography afforded 4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide **SI-6** (361.6 mg, 1.73 mmol, 72%) as a white solid.

Preparation of SI-8: The **SI-6** (1.5 g, 7.2 mmol, 1.0 equiv) was dissolved in 40 mL acetone, and **SI-7** (1.41 mL, 14.4 mmol, 2.0 equiv), K_2CO_3 (2.0 g, 14.4 mmol, 2.0 equiv), KI (0.12 g, 0.72 mmol, 0.1 equiv) was added successively. The mixture was stirred and refluxed at 60 °C overnight and then washed three times with water. The organic layer was exacted three times with EtOAc. Drying over Na_2SO_4 and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography to give **SI-8** (1.65 g, 2.47 mmol, 87% yield) as a white solid.

Preparation of 1d: The solution of potassium tert-butylate (0.96 g, 8.55 mmol, 1.5 equiv) was stirred in dry THF (25 mL) at -5 °C under a nitrogen atmosphere. The 4-methyl-N-(2-methylallyl)-N-(prop-2-yn-1-yl)benzenesulfonamide (1.50 g, 5.7 mol, 1.0 equiv) was dissolved in 5 mL THF and added into the solution. Then the reaction mixture was stirred for 0.5 h. The aqueous layer was extracted three times with EtOAc. The organic phase was combined, dried

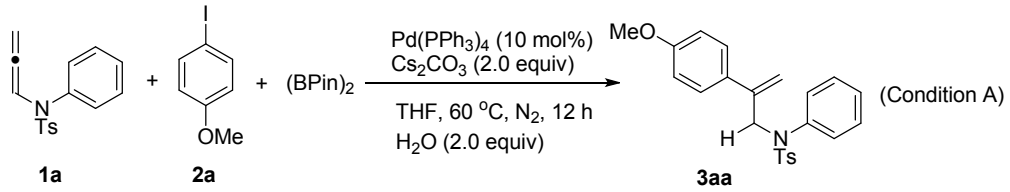
over Na_2SO_4, evaporated and purified by flash chromatography to give **1d** (1.26 g, 4.79 mmol, 84% yield) as a white solid.

Preparation of SI-10: The **SI-6** (1.67 g, 8 mmol, 1.0 equiv) was dissolved in 40 mL acetone, and 3-bromoprop-1-ene **SI-9** (0.83 mL, 9.6 mmol, 1.2 equiv), K_2CO_3 (2.21 g, 16 mmol, 2.0 equiv), KI (0.13 g, 0.8 mmol, 0.1 equiv) was added successively. The mixture was stirred and refluxed at 60 ^oC overnight and then washed three times with water. The organic layer was exacted three times with EtOAc. Drying over Na_2SO_4 and concentration in vacuo afforded the crude material, which was then purified by silica gel column chromatography to give **SI-10** (1.72 g, 6.90 mmol, 86% yield) as a white solid.

Preparation of 1c: The solution of potassium tert-butylate (1.01 g, 9 mmol, 1.5 equiv) was stirred in dry THF (25 mL) at -5 ^oC under a nitrogen atmosphere. N-allyl-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (1.50 g, 6 mmol, 1.0 equiv) was dissolved in 5 mL THF and added into the solution. The mixture was stirred at -5 ^oC for 0.5 h. The aqueous layer was extracted three times with EtOAc. The organic phase was combined, dried over Na_2SO_4, evaporated and purified by flash chromatography to afford **1c** (1.30 g, 5.21 mmol, 87% yield) as a white solid.

Substrate **1i** was prepared according to **general procedure II**.

3. Typical Procedure and Analytical Data for Reaction.

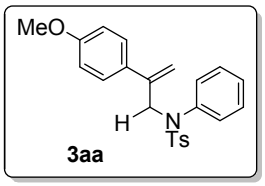


1a **2a** **3aa**

Typical Procedure:

Allenamide **1a** (57.1 mg, 0.20 mmol), $(Bpin)_2$ (101.6 mg, 0.40 mmol), 4-Iodoanisole **2a** (56.2 mg, 0.24 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and Cs_2CO_3 (130.3 mg, 0.40 mmol) were added to a reaction tube. Then the dry THF (2 mL) and H_2O (7.2 mg, 0.40 mmol) were added under nitrogen atmosphere. The resulting mixture was stirred at 60 °C for 12 h. After cooling the reaction mixture at room temperature, it was quenched by H_2O and extracted with EtOAc three times. The combined organic phase was dried over Na_2SO_4 and then concentrated in vacuo. The mixture was purified by silica gel column chromatography (PE:EA, 30:1) to give the product **3aa** (66.1 mg, 0.17 mmol, 84% yield).

Analytical Data:



N-(2-(4-methoxyphenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{23}H_{23}NO_3S$ **MW:** 393.50 g·mol^{-1}

White Solid

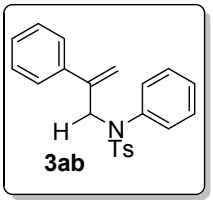
Isolated Amount: 66.1 mg **Yield:** 84%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.40 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 3H), 7.11 (d, *J* = 6.8 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 6.8 Hz, 2H), 6.33 (s, 0.18H), 5.10 (s, 1H), 4.83 (s, 1H), 4.50 (s, 2H), 3.74 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.4, 143.5, 141.7, 138.4, 135.1, 130.6, 129.4, 129.1, 128.5, 127.8, 127.7, 127.3, 115.5, 113.6, 55.3, 54.4, 21.6.

MS (EI) m/z 393 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{23}NO_3S$ +H 394.1477, Found 394.1478.

……...



4-methyl-N-phenyl-N-(2-phenylallyl)benzenesulfonamide

$C_{22}H_{21}NO_2S$ **MW:** 363.47 g·mol^{-1}

Brown Solid

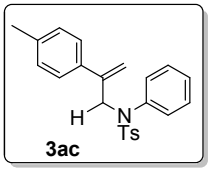
Isolated Amount: 44.3 mg **Yield:** 61%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (d, *J* = 7.6 Hz, 2H), 7.37-7.30 (m, 5H), 7.25-7.19 (m, 5H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.51 (s, 0.04H), 5.27 (s, 1H), 5.04 (s, 1H), 4.61 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.5, 142.5, 138.4, 138.2, 135.1, 129.5, 129.4, 129.2, 129.0, 128.7, 128.5, 128.3, 127.9, 126.6, 54.3, 21.7.

MS (EI) m/z 363 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{21}NO_2S$ +H 364.1371, Found 364.1373.

……....



4-methyl-N-phenyl-N-(2-(p-tolyl)allyl)benzenesulfonamide

$C_{23}H_{23}NO_2S$ **MW:** 377.50 g·mol^{-1}

Yellow Solid

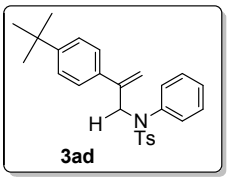
Isolated Amount: 47.6 mg **Yield:** 63%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.20-7.17 (m, 3H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 7.2 Hz, 2H), 6.46 (s, 0.02H), 5.23 (s, 1H), 4.97 (s, 1H), 4.59 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.5, 142.2, 138.5, 137.7, 135.3, 135.1, 129.5, 129.4, 129.2, 129.0, 128.7, 127.9, 126.5, 116.3, 54.4, 21.5, 21.3.

MS (EI) m/z 377 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{23}NO_2S$+H 378.1527, Found 378.1525.

……...



N-(2-(4-(tert-butyl)phenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{26}H_{29}NO_2S$ **MW:** 419.58 g·mol^{-1}

White Solid

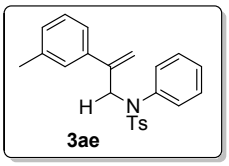
Isolated Amount: 59.6 mg **Yield:** 71%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.40 (d, *J* = 7.6 Hz, 2H), 7.27 -7.23 (m, 4H), 7.17 -7.11 (m, 5H), 6.75 (d, *J* = 6.8 Hz, 2H), 5.17 (s, 1H), 4.91 (s, 1H), 4.52 (s, 2H), 2.35 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.9, 143.5, 142.1, 138.6, 135.3, 135.1, 129.5, 129.3, 129.2, 129.0, 128.7, 127.9, 126.2, 125.2, 116.3, 54.4, 34.6, 31.4, 31.3, 21.5.

MS (EI) m/z 419 (M+); **HRMS (ESI)** Calcd for $C_{26}H_{29}NO_2S$+H 420.1997, Found 420.1994.

……..



4-methyl-N-phenyl-N-(2-(m-tolyl)allyl)benzenesulfonamide

$C_{23}H_{23}NO_2S$ **MW:** 377.50 g·mol^{-1}

Yellow Solid

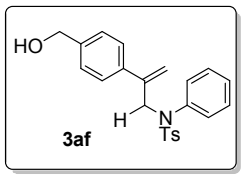
Isolated Amount: 42.2 mg **Yield**: 56%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (d, *J* = 7.6 Hz, 2H), 7.25-7.09 (m, 8H), 7.10 (d, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 6.4 Hz, 2H), 6.49 (s, 0.02H), 5.26 (s, 1H), 5.04 (s, 1H), 4.60 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.5, 142.6, 138.6, 138.3, 137.7, 135.2, 129.5, 129.4, 129.2, 129.0, 128.7, 128.5, 127.8, 127.3, 127.2, 116.7, 54.4, 21.7, 21.5.

MS (EI) m/z 377 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{23}NO_2S$+H 378.1527, Found 378.1526.

……...



N-(2-(4-(hydroxymethyl)phenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{23}H_{23}NO_3S$ **MW:** 393.50 g·mol^{-1}

White Solid

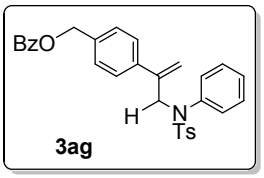
Isolated Amount: 55.9 mg **Yield:** 71%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 -7.23 (m, 4H), 7.19 -7.11 (m, 5H), 6.72 (d, *J* = 7.2 Hz, 2H), 6.43 (s, 0.03H), 5.19 (s, 1H), 4.95 (s, 1H), 4.63 (s, 2H), 4.53 (s, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.5, 142.1, 140.6, 138.4, 137.5, 135.0, 129.4, 129.0, 128.6, 127.8, 127.8, 126.9, 126.8, 117.1, 65.1, 21.6.

MS (EI) m/z 393 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{23}NO_3S$+H 394.1477, Found 394.1478.

……...



4-(3-(4-methyl-N-phenylphenylsulfonamido)prop-1-en-2-yl)benzyl benzoate

$C_{30}H_{27}NO_4S$ **MW:** 497.60 g·mol^{-1}

White Solid

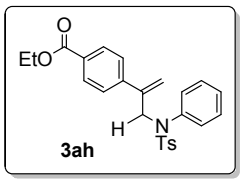
Isolated Amount: 67.6 mg **Yield:** 68%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.02 (d, *J* = 8.0 Hz, 2H), 7.50 -7.47 (m, 1H), 7.38 (d, *J* = 7.6 Hz, 4H), 7.33 (s, 4H), 7.17 -7.11 (m, 5H), 6.72 (d, *J* = 6.8 Hz, 2H), 6.45 (s, 0.01H), 5.29 (s, 2H), 5.19 (s, 1H), 4.95 (s, 1H), 4.63 (s, 2H), 4.53 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 165.4, 142.5, 140.9, 137.3, 137.1, 134.6, 133.9, 132.0, 129.0, 128.7, 128.4, 128.0, 127.6, 127.4, 127.0, 126.8, 125.7, 116.4, 65.3, 53.3, 20.5.

MS (EI) m/z 497 (M+); **HRMS (ESI)** Calcd for $C_{30}H_{27}NO_4S$+H 498.1739, Found 498.1741.

……....



ethyl 4-(3-(4-methyl-N-phenylphenylsulfonamido)prop-1-en-2-yl)benzoate

$C_{25}H_{25}NO_4S$ **MW:** 435.54 g·mol^{-1}

Yellow Solid

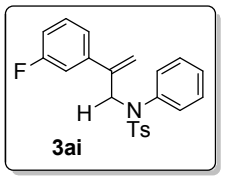
Isolated Amount: 55.8 mg **Yield:** 64%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14-7.09 (m, 3H), 6.69 (d, *J* = 7.2 Hz, 2H), 5.27 (s, 1H), 5.04 (s, 1H), 4.56 (s, 2H), 4.31 (q, *J* = 6.8 Hz, 2H), 2.35 (s, 3H), 1.33 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 166.4, 143.6, 142.5, 141.9, 138.2, 134.9, 129.8, 129,6, 129.5, 129.4, 129.1, 128.9, 128.8, 128.6, 127.9, 127.8, 126.6, 126.5, 118.8, 61.0, 54.2, 21.7, 14.3.

MS (EI) m/z 435 (M+); **HRMS (ESI)** Calcd for $C_{25}H_{25}NO_4S$+H 436.1582, Found 436.1585.

……..



N-(2-(3-fluorophenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{22}H_{20}FNO_2S$ **MW**: 381.46 g·mol^{-1}

White Solid

Isolated Amount: 41.2 mg **Yield**: 54%

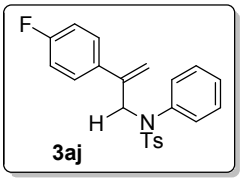
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.40 (d, *J* = 8.0 Hz, 2H), 7.22-7.11 (m, 7H), 6.95-6.88 (m, 2H), 6.73 (d, *J* = 7.2 Hz, 2H), 5.21 (s, 1H), 5.00 (s, 1H), 4.51 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.0, 161.5, 143.6, 141.6, 141.5, 140.5, 140.4, 138.4, 135.0, 129.8, 129.5, 129.4, 129.1, 128.9, 128.8, 128.6, 127.9, 118.1, 115.0, 114.7, 113.7, 113.5, 54.2, 25.1.

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -113.4.

MS (EI) m/z 381 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{20}FNO_2S$+H 382.1277, Found 382.1276.

……..



N-(2-(4-fluorophenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{22}H_{20}FNO_2S$ **MW:** 381.46 g·mol^{-1}

Brown Solid

Isolated Amount: 46.5 mg **Yield:** 61%

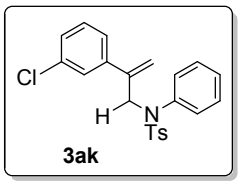
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.39 (d, *J* = 7.6 Hz, 2H), 7.29-7.26 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.14-7.10 (m, 3H), 6.95-6.91 (m, 2H), 6.70 (d, *J* = 6.8 Hz, 2H), 6.30 (s, 0.02H), 5.13 (s, 1H), 4.91 (s, 1H), 4.51 (s, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 162.7, 160.2, 142.5, 140.4, 137.1, 133.8, 133.0, 128.4, 128.3, 128.0, 127.8, 127.6, 127.4, 127.3, 127.2, 127.1, 126.7, 116.0, 114.2, 114.0, 113.8, 53.3, 20.4.

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -114.3.

MS (EI) m/z 381 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{20}FNO_2S$+H 382.1277, Found 382.1275.

……..



3ak

N-(2-(3-chlorophenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{22}H_{20}ClNO_2S$ **MW**: 397.92 g·mol^{-1}

Yellow Oil

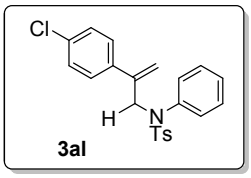
Isolated Amount: 40.6 mg **Yield**: 51%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (d, *J* = 7.6 Hz, 2H), 7.30-7.20 (m, 9H), 6.81 (d, *J* = 7.2 Hz, 2H), 5.28 (s, 1H), 5.09 (s, 1H), 4.58 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 141.4, 140.1, 138.3, 134.9, 134.1, 129.9, 129.6, 129.5, 129.0, 128.7, 127.9, 127.8, 126.7, 124.8, 118.2, 54.2, 21.6.

MS (EI) m/z 397 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{20}ClNO_2S$+H 398.0981, Found 398.0980.

……..



3al

N-(2-(4-chlorophenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{22}H_{20}ClNO_2S$ **MW**: 397.92 g·mol^{-1}

Yellow Solid

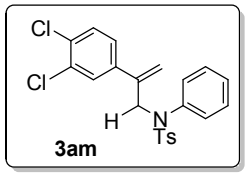
Isolated Amount: 51.0 mg **Yield**: 64%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.39 (d, *J* = 7.6 Hz, 2H), 7.23-7.22 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 3H), 7.13-7.10 (m, 3H), 6.70 (d, *J* = 7.2 Hz, 2H), 5.17 (s, 1H), 4.94 (s, 1H), 4.51 (s, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 141.5, 138.2, 136.5, 134.9, 133.8, 129.5, 129.4, 129.1, 128.9, 128.7, 128.5, 127.9, 117.6, 54.3, 21.5.

MS (EI) m/z 397 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{20}ClNO_2S$+H 398.0981, Found 398.0979.

……



N-(2-(3,4-dichlorophenyl)allyl)-4-methyl-N-phenylbenzenesulfonamide

$C_{22}H_{19}Cl_2NO_2S$ **MW:** 432.36 g·mol^{-1}

Brown Oil.

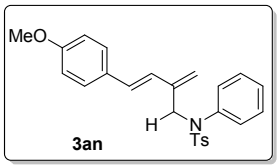
Isolated Amount: 31.1 mg **Yield:** 36%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.39 (d, *J* = 7.6 Hz, 2H), 7.32 (s, 1H), 7.22-7.13 (m, 7H), 6.72 (d, *J* = 6.8 Hz, 2H), 5.20 (s, 1H), 4.99 (s, 1H), 4.48 (s, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 142.6, 139.4, 137.1, 137.0, 133.7, 131.3, 130.8, 129.2, 128.5, 128.3, 127.9, 127.7, 126.8, 124.9, 124.8, 117.5, 53.0, 20.4.

MS (EI) m/z 432 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{19}Cl_2NO_2S$+H 432.0592, Found 432.0594.

……



(E)-N-(4-(4-methoxyphenyl)-2-methylenebut-3-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide

$C_{25}H_{25}NO_3S$ **MW:** 419.54 g·mol^{-1}

Yellow Oil.

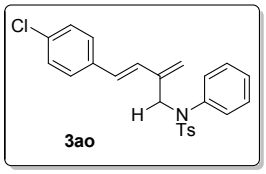
Isolated Amount: 38.6 mg **Yield:** 46%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.46 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.21 -7.17 (m, 6H), 6.93 -6.91 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 8.0 Hz, 2H), 6.34 (s, 0.23H), 4.98 (s, 1H), 4.83 (s, 1H), 4.35 (s, 2H), 3.75 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.4, 143.5, 139.9, 138.7, 135.0, 129.9, 129.8, 129.5, 129.4, 129.1, 128.9, 128.7, 127.9, 125.8, 125.6, 119.5, 114.2, 55.5, 52.8, 21.7.

MS (EI) m/z 419 (M+); **HRMS (ESI)** Calcd for $C_{25}H_{25}NO_3S$+H 420.1633, Found 420.1632..

……



(E)-N-(4-(4-chlorophenyl)-2-methylenebut-3-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide

$C_{24}H_{22}ClNO_2S$ **MW:** 423.95 g·mol^{-1}

White Solid

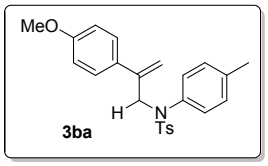
Isolated Amount: 35.6 mg **Yield:** 42%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.45 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 -7.17 (m, 8H), 6.90 (s, 2H), 6.53 (d, *J* = 16.4 Hz, 1H), 6.43 (s, 0.03H), 5.04 (s, 1H), 4.89 (s, 1H), 4.35 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.6, 139.6, 138.5, 135.7, 134.9, 133.3, 129.6, 129.5, 129.2, 129.0, 128.8, 128.7, 128.3, 128.1, 127.9, 121.0, 52.7, 21.7.

MS (EI) m/z 423 (M+); **HRMS (ESI)** Calcd for $C_{24}H_{22}ClNO_2S$+H 424.1138, Found 424.1140.

……



N-(2-(4-methoxyphenyl)allyl)-4-methyl-N-(p-tolyl)benzenesulfonamide

$C_{24}H_{25}NO_3S$ **MW:** 407.53 g·mol^{-1}

Yellow Oil

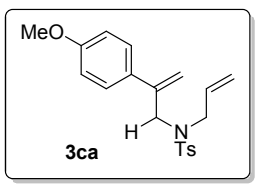
Isolated Amount: 58.7 mg **Yield:** 72%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.41 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 6.31 (q, *J* = 1.6 Hz, 0.14H), 5.10 (s, 1H), 4.83 (s, 1H), 4.47 (s, 2H), 3.75 (s, 3H), 2.35 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.4, 143.4, 141.7, 137.7, 135.7, 130.7, 129.5, 129.4, 129.2, 128.8, 127.9, 127.8, 115.4, 113.6, 115.4, 113.6, 55.3, 54.5, 21.6, 21.1.

MS (EI) m/z 407 (M+); **HRMS (ESI)** Calcd for $C_{24}H_{25}NO_3S$+H 408.1633, Found 420.1632.

……



N-allyl-N-(2-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide

$C_{20}H_{23}NO_3S$ **MW:** 357.47 g·mol^{-1}

Yellow Solid

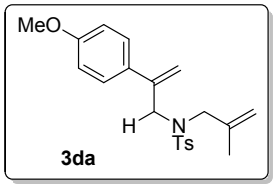
Isolated Amount: 48.0 mg **Yield:** 67%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.58 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 2H), 5.46 -5.40 (m, 1H), 5.30 (s, 1H), 5.04 (s, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.12 (s, 2H), 3.73 (s, 3H), 3.65 (d, *J* = 6.4 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.5, 143.2, 141.8, 137.1, 132.3, 130.9, 129.6, 127.7, 127.4, 119.2, 118.8, 113.7, 55.3, 50.5, 49.3, 21.5.

MS (EI) m/z 357 (M+); **HRMS (ESI)** Calcd for $C_{20}H_{23}NO_3S$+H 358.4743, Found 358.4746.

……..



N-(2-(4-methoxyphenyl)allyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide

$C_{21}H_{25}NO_3S$ **MW:** 371.49 g·mol^{-1}

Yellow Solid

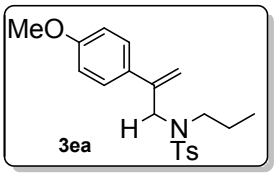
Isolated Amount: 46.8 mg **Yield:** 63%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.64 (d, *J* = 8.4 Hz, 2H), 7.28 -7.24 (m, 4H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.28 (s, 1H), 5.05 (s, 1H), 4.81 (s, 1H), 4.74 (s, 1H), 4.19 (s, 2H), 3.80 (s, 3H), 3.67 (s, 2H), 2.42 (s, 3H), 1.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.5, 143.1, 142.1, 140.3, 137.1, 131.3, 129.5, 127.7, 127.3, 114.8, 114.3, 113.6, 55.3, 53.3, 51.4, 21.5, 20.2.

MS (EI) m/z 371 (M+); **HRMS (ESI)** Calcd for $C_{21}H_{25}NO_3S$+H 372.1633, Found 372.1637.

……..



N-(2-(4-methoxyphenyl)allyl)-4-methyl-N-propylbenzenesulfonamide

$C_{20}H_{25}NO_3S$ **MW:** 359.48 g·mol^{-1}

Yellow Oil

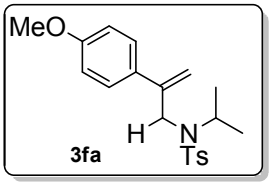
Isolated Amount: 41.0 mg **Yield:** 57%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.60 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 4.8 Hz, 1H), 6.81 -6.77 (m, 2H), 5.32 (s, 1H), 5.06 (s, 1H), 4.09 (s, 2H), 3.74 (s, 3H), 2.99 (t, *J* = 7.2 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 1H), 2.35 (s, 3H), 1.45 (q, *J* = 7.6 Hz, 1H), 1.32 (q, *J* = 7.6 Hz, 1H), 0.86 (t, *J* = 7.6 Hz, 1H), 0.64 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.5, 143.1, 142.4, 136.7, 130.7, 129.6, 127.6, 127.3, 122.0, 113.7, 55.3, 52.3, 49.5, 21.5, 21.3, 11.2.

MS (EI) m/z 359 (M+); **HRMS (ESI)** Calcd for $C_{20}H_{25}NO_3S$+H 360.1633, Found 372.1635.

……..



N-isopropyl-N-(2-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide

$C_{20}H_{25}NO_3S$ **MW:** 359.48 g·mol^{-1}

Yellow Oil

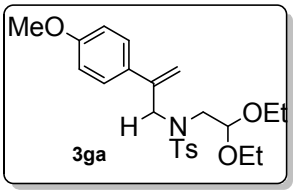
Isolated Amount: 46.7 mg **Yield:** 65%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.61 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 12.0 Hz, 2H), 7.22 (d, *J* = 5.6 Hz, 2H), 6.81 (d, *J* = 12.4 Hz, 2H), 5.30 (s, 1H), 5.24 (s, 1H), 4.13 (s, 2H), 4.02 - 3.95 (m, 1H), 3.75 (s, 3H), 2.35 (s, 3H), 0.91 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.3, 144.6, 143.0, 137.8, 131.6, 129.6, 127.7, 127.2, 116.2, 113.7, 55.3, 50.0, 47.0, 21.5, 20.6.

MS (EI) m/z 359 (M+); **HRMS (ESI)** Calcd for $C_{20}H_{25}NO_3S$+H 360.1633, Found 372.1634.

……..



N-(2,2-diethoxyethyl)-N-(2-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide

$C_{23}H_{31}NO_5S$ **MW:** 433.56 g·mol^{-1}

Yellow Oil

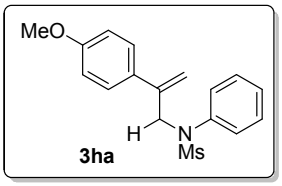
Isolated Amount: 54.6 mg **Yield:** 63%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.57 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.25 (s, 1H), 4.98 (s, 1H), 4.52 (t, *J* = 5.2 Hz, 1H), 4.30 (s, 2H), 3.73 (s, 3H), 3.55 (q, *J* = 6.8 Hz, 2H), 3.32 (q, *J* = 7.2 Hz, 2H), 3.15 (d, *J* = 5.6 Hz, 2H), 2.34 (s, 3H), 1.05 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.4, 143.1, 141.9, 137.3, 131.3, 129.5, 127.6, 127.3, 115.0, 113.7, 102.3.

MS (EI) m/z 433 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{31}NO_5S$+H 434.2001, Found 434.1998.

……..



N-(2-(4-methoxyphenyl)allyl)-N-phenylmethanesulfonamide

$C_{17}H_{19}NO_3S$ **MW:** 317.40 g·mol^{-1}

Yellow Oil

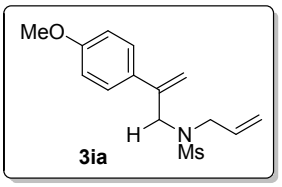
Isolated Amount: 30.0 mg **Yield:** 47%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.34 (d, *J* = 8.8 Hz, 2H), 7.32 -7.28 (m, 3H), 7.12 (d, *J* = 6.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.23 (s, 1H), 5.00 (s, 1H), 4.73 (s, 2H), 3.82 (s, 3H), 2.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.5, 142.2, 138.5, 129.7, 129.2, 129.0, 128.1, 127.9, 120.8, 115.7, 113.7, 55.3, 54.7, 37.9.

MS (EI) m/z 317 (M+); **HRMS (ESI)** Calcd for $C_{17}H_{19}NO_3S$+H 318.1164, Found 318.1162.

……..



N-allyl-N-(2-(4-methoxyphenyl)allyl)methanesulfonamide

$C_{14}H_{19}NO_3S$ **MW:** 281.37 g·mol^{-1}

Yellow Oil

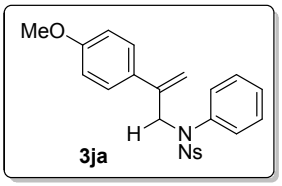
Isolated Amount: 25.2mg **Yield:** 43%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.40 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.85-5.75 (m, 1H), 5.42 (s, 1H), 5.27 (s, 1H), 5.25 (s, 1H), 5.24 (d, *J* = 8.8 Hz, 1H), 5.21 (s, 1H), 4.28 (s, 2H), 3.82 (s, 3H), 3.76 (d, *J* = 6.4 Hz, 2H), 2.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.6, 142.3, 132.3, 131.0, 127.8, 119.7, 115.3, 113.9, 55.3, 50.2, 48.6, 39.9.

MS (EI) m/z 281 (M+); **HRMS (ESI)** Calcd for $C_{14}H_{19}NO_3S$+H 282.1164, Found 282.1163.

……..



N-(2-(4-methoxyphenyl)allyl)-4-nitro-N-phenylbenzenesulfonamide

$C_{22}H_{20}N_2O_5S$ **MW:** 424.47 g·mol^{-1}

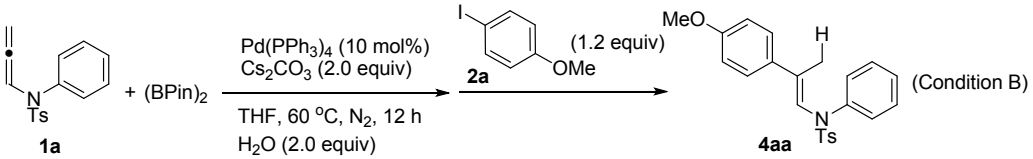
Yellow Powder

Isolated Amount: 13.5 mg **Yield:** 32%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.21 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.17-7.13 (m, 3H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 7.6 Hz, 2H), 5.12 (s, 1H), 4.84 (s, 1H), 4.57 (s, 2H), 3.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 158.5, 149.0, 142.9, 140.3, 136.3, 129.2, 128.0, 127.9, 127.8, 127.4, 126.7, 123.0, 115.2, 112.7, 54.3, 53.9.

MS (EI) m/z 424 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{20}N_2O_5S$+H 425.1171, Found 425.1173.



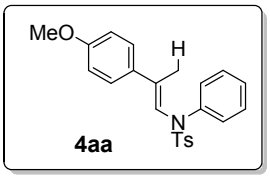
Typical Procedure:

This reaction was carried out in two steps. The specific reaction steps were as follows.

The first step: Allenamide **1a** (57.1 mg, 0.20 mmol), $(Bpin)_2$ (101.6 mg, 0.40 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and Cs_2CO_3 (130.3 mg, 0.40 mmol) were added to a reaction tube. Then the dry THF (2 mL) and H_2O (7.2 mg, 0.40 mmol) were added under nitrogen atmosphere. The resulting mixture was stirred at 60 °C for 12 h.

The second step: After 4-Iodoanisole **2a** (56.2 mg, 0.24 mmol) was added to a reaction tube under nitrogen atmosphere. Upon completion, the reaction mixture was quenched by H_2O and extracted with EtOAc three times. The combined organic phase was dried over Na_2SO_4 and then concentrated in vacuo. The mixture was purified by silica gel column chromatography (PE:EA, 30:1) to give the product **4aa** (45.6 mg, 0.116 mmol, 58% yield).

Analytical Data:



(E)-N-(2-(4-methoxyphenyl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide

$C_{23}H_{23}NO_3S$ **MW:** 393.50 g·mol^{-1}

Yellow Oil

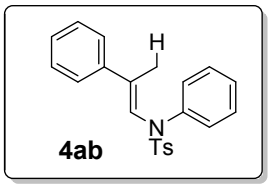
Isolated Amount: 45.6 mg **Yield:** 58%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.35 (d, *J* = 8.4 Hz, 2H), 7.30-7.23 (m, 7H), 7.20-7.17 (m, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 6.40 (q, *J* = 1.2 Hz, 1H), 4.58 (s, 0.13H), 3.81 (s, 3H), 2.42 (s, 3H), 1.90 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.9, 141.4, 140.6, 136.6, 134.5, 129.5, 129.0, 128.4, 127.8, 127.1, 126.2, 124.7, 123.0, 21.6, 16.3.

MS (EI) m/z 393 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{23}NO_3S$+H 394.1477, Found 364.1476.

……..



(E)-4-methyl-N-phenyl-N-(2-phenylprop-1-en-1-yl)benzenesulfonamide

$C_{22}H_{21}NO_2S$ **MW:** 363.47 g·mol^{-1}

Yellow Oil

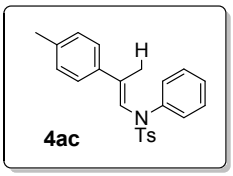
Isolated Amount: 47.2 mg **Yield:** 65%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 (d, *J* = 8.4 Hz, 2H), 7.34-7.32 (m, 4H), 7.30-7.28 (m, 3H), 7.25 (d, *J* = 7.2 Hz, 3H), 7.20-7.18 (m, 2H), 6.51 (q, J = 1.2 Hz, 1H),, 2.41 (s, 3H), 1.89 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.9, 141.4, 140.6, 136.6, 134.5, 129.5, 129.0, 128.4, 127.8, 127.1, 126.2, 124.7, 123.0, 21.6, 16.3.

MS (EI) m/z 363 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{21}NO_2S$+H 364.1371, Found 364.1373.

……..



(E)-4-methyl-N-phenyl-N-(2-(p-tolyl)prop-1-en-1-yl)benzenesulfonamide

$C_{23}H_{23}NO_2S$ **MW:** 377.50 g·mol^{-1}

Yellow Oil

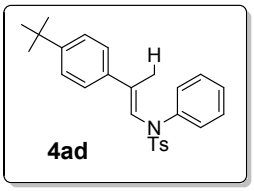
Isolated Amount: 41.5 mg **Yield:** 55%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.25-7.23 (m, 5H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.46 (q, *J* = 1.6 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 1.88 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.8, 141.5, 137.7, 137.6, 137.0, 134.6, 129.5, 129.1, 129.0, 127.8, 127.0, 126.9, 126.0, 123.9, 21.6, 21.1, 16.2.

MS (EI) m/z 377 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{23}NO_2S$+H 378.1527, Found 378.1525.

……..



(E)-N-(2-(4-(tert-butyl)phenyl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide

$C_{26}H_{29}NO_2S$ **MW:** 419.58 g·mol^{-1}

Brown Oil

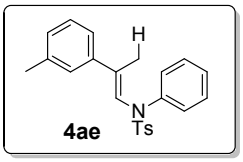
Isolated Amount: 45.3 mg **Yield:** 54%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.30-7.27 (m, 4H), 7.25-7.22 (m, 3H), 7.18 (d, *J* = 6.8 Hz, 2H), 6.50 (q, J = 1.2 Hz, 1H), 2.41 (s, 3H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.9, 143.8, 141.6, 137.6, 136.5, 134.6, 129.5, 128.9, 127.8, 127.0, 126.9, 125.8, 125.3, 124.1, 34.6, 31.3, 21.6, 16.1.

MS (EI) m/z 419 (M+); **HRMS (ESI)** Calcd for $C_{26}H_{29}NO_2S$+H 420.1997, Found 420.1999.

……..



(E)-4-methyl-N-phenyl-N-(2-(m-tolyl)prop-1-en-1-yl)benzenesulfonamide

$C_{23}H_{23}NO_2S$ **MW:** 377.50 g·mol^{-1}

Brown Oil

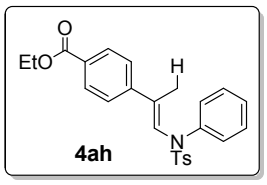
Isolated Amount: 37.0 mg **Yield:** 49%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.26-7.23 (m, 3H), 7.21-7.18 (m, 3H), 7.14-7.10 (m, 3H), 6.49 (q, *J* = 1.6 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 1.87 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.8, 141.5, 140.6, 138.0, 136.9, 134.6, 129.5, 129.0, 128.5, 128.3, 127.8, 127.1, 126.9, 124.5, 123.3, 21.6, 21.5, 16.3.

MS (EI) m/z 377 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{23}NO_2S$+H 378.1527, Found 378.1524.

……..



((E)-ethyl 4-(1-(4-methyl-N-phenylphenylsulfonamido)prop-1-en-2-yl)benzoate

$C_{25}H_{25}NO_4S$ **MW:** 435.54 g·mol^{-1}

Yellow Oil

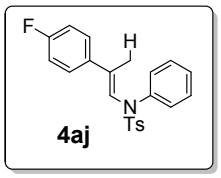
Isolated Amount: 45.3 mg **Yield:** 52%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.99 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.31-7.24 (m, 5H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.65 (q, J = 1.2 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.85 (d, *J* = 1.2 Hz, 3H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 166.3, 145.2, 144.1, 141.0, 134.3, 134.1, 129.7, 129.6, 129.5, 129.1, 127.8, 127.4, 127.2, 126.4, 125.9, 61.0, 21.6, 16.1, 14.4.

MS (EI) m/z 435 (M+); **HRMS (ESI)** Calcd for $C_{25}H_{25}NO_4S$+H 436.1582, Found 436.1583.

……..



(E)-N-(2-(4-fluorophenyl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide

$C_{22}H_{20}FNO_2S$ **MW:** 381.46 g·mol^{-1}

Yellow Solid

Isolated Amount: 36.6 mg **Yield:** 48%

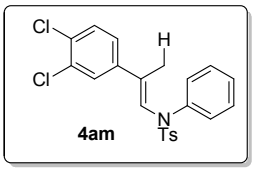
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 (d, *J* = 8.0 Hz, 2H), 7.32-7.24 (m, 7H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.03-6.99 (m, 2H), 6.44 (q, *J* = 1.2 Hz, 1H), 2.42 (s, 3H), 1.88 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 163.7, 161.3, 143.9, 141.3, 136.6, 136.5, 135.8, 134.5, 129.5, 129.0, 127.8, 127.7, 127.1, 124.5, 123.8, 115.4, 115.2, 21.6, 16.4.

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -114.4.

MS (EI) m/z 381 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{20}FNO_2S$+H 382.1277, Found 364.1278.

……..



(E)-N-(2-(3,4-dichlorophenyl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide

$C_{22}H_{19}Cl_2NO_2S$ **MW:** 432.36 g·mol^{-1}

Yellow Solid

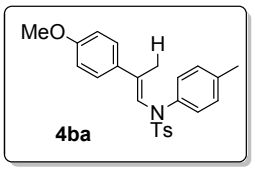
Isolated Amount: 44.1 mg **Yield:** 51%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.48 (d, *J* = 8.4 Hz, 2H), 7.39-7.37 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.27-7.24 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.56 (q, J = 1.2 Hz, 1H), 2.42 (s, 3H), 1.81 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.1, 140.9, 140.8, 134.3, 132.5, 131.6, 130.3, 129.6, 129.1, 128.0, 127.8, 127.3, 126.1, 125.4, 21.6, 16.1.

MS (EI) m/z 432 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{19}Cl_2NO_2S$+H 432.0592, Found 432.0594.

……..



(E)-N-(2-(4-methoxyphenyl)prop-1-en-1-yl)-4-methyl-N-(p-tolyl)benzenesulfonamide

$C_{24}H_{25}NO_3S$ **MW:** 407.53 g·mol^{-1}

Yellow Oil

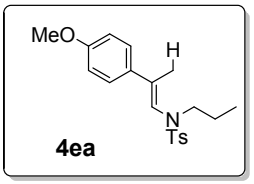
Isolated Amount: 44.8 mg **Yield:** 55%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.43 (d, *J* = 8.0 Hz, 2H), 7.21-7.16 (m, 4H), 7.00 (dd, *J* = 17.2 Hz, *J* = 8.4 Hz, 4H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.30 (q, J = 1.6 Hz, 1H), 4.47 (s, 0.06H), 3.73 (s, 3H), 2.34 (s, 3H), 2.25 (s, 3H), 1.83 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.4, 143.7, 139.0, 136.9, 136.8, 134.7, 133.0, 129.6, 129.4, 127.9, 127.3, 127.0, 123.3, 113.7, 55.3, 21.6, 21.1, 16.2.

MS (EI) m/z 407 (M+); **HRMS (ESI)** Calcd for $C_{24}H_{25}NO_3S$+H 408.1633, Found 408.1632.

……..



(E)-N-(2-(4-methoxyphenyl)prop-1-en-1-yl)-4-methyl-N-propylbenzenesulfonamide

$C_{20}H_{25}NO_3S$ **MW:** 359.48 g·mol^{-1}

Yellow Oil

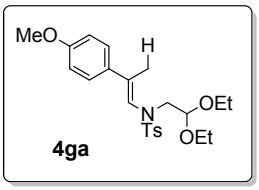
Isolated Amount: 36.0 mg **Yield:** 50%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.67 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 6.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.38 (q, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.19 (d, *J* = 1.2 Hz, 3H), 1.53 (q, *J* = 7.2 Hz, 2H), 0.93 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 160.0, 143.3, 143.0, 134.9, 132.6, 129.6, 127.6, 127.2, 121.9, 113.8, 55.3, 52.7, 21.7, 21.6, 16.9, 11.4.

MS (EI) m/z 359 (M+); **HRMS (ESI)** Calcd for $C_{20}H_{25}NO_3S$+H 360.1633, Found 360.1636.

……..



(E)-N-(2,2-diethoxyethyl)-N-(2-(4-methoxyphenyl)prop-1-en-1-yl)-4-methylbenzenesulfonamide

$C_{23}H_{31}NO_5S$ **MW:** 433.56 g·mol^{-1}

Yellow Oil

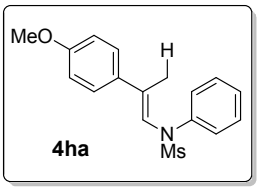
Isolated Amount: 49.4 mg **Yield:** 57%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.67 (d, *J* = 8.4 Hz, 2H), 7.32-7.29 (m, 4H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.52 (q, *J* = 1.2 Hz, 1H), 4.65 (t, *J* = 5.6 Hz, 1H), 3.81 (s, 3H), 3.71 (q, *J* = 6.8 Hz, 2H), 3.52 (q, *J* = 6.8 Hz, 2H), 3.25 (d, *J* = 5.6 Hz, 2H), 2.43 (s, 3H), 2.14 (d, *J* = 1.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.5, 143.6, 142.5, 135.0, 132.5, 129.6, 127.5, 127.3, 122.3, 113.7, 100.7, 61.9, 55.3, 52.8, 21.6, 16.8, 15.3.

MS (EI) m/z 433 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{31}NO_5S$+H 434.2001, Found 434.2003.

……..



(E)-N-(2-(4-methoxyphenyl)prop-1-en-1-yl)-N-phenylmethanesulfonamide

$C_{17}H_{19}NO_3S$ **MW:** 317.40 g·mol^{-1}

Yellow Oil

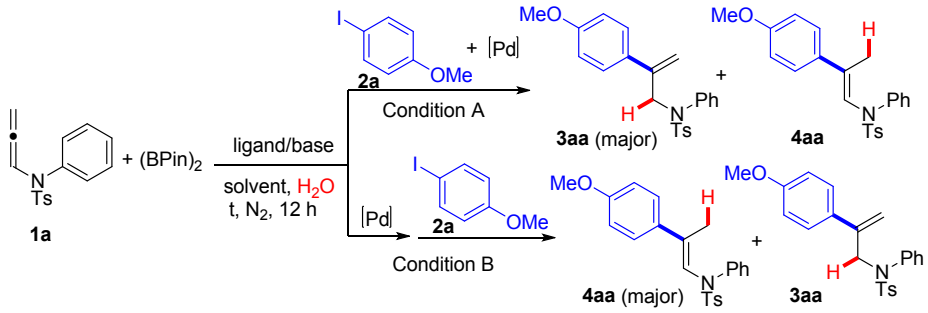
Isolated Amount: 21.6 mg **Yield:** 34%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.35-7.26 (m, 6H), 7.21-7.17 (m, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 1H), 3.74 (s, 3H), 2.90 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 158.5, 140.2, 135.7, 131.5, 128.4, 126.2, 125.8, 125.1, 121.7, 112.8, 54.3, 36.1, 15.0.

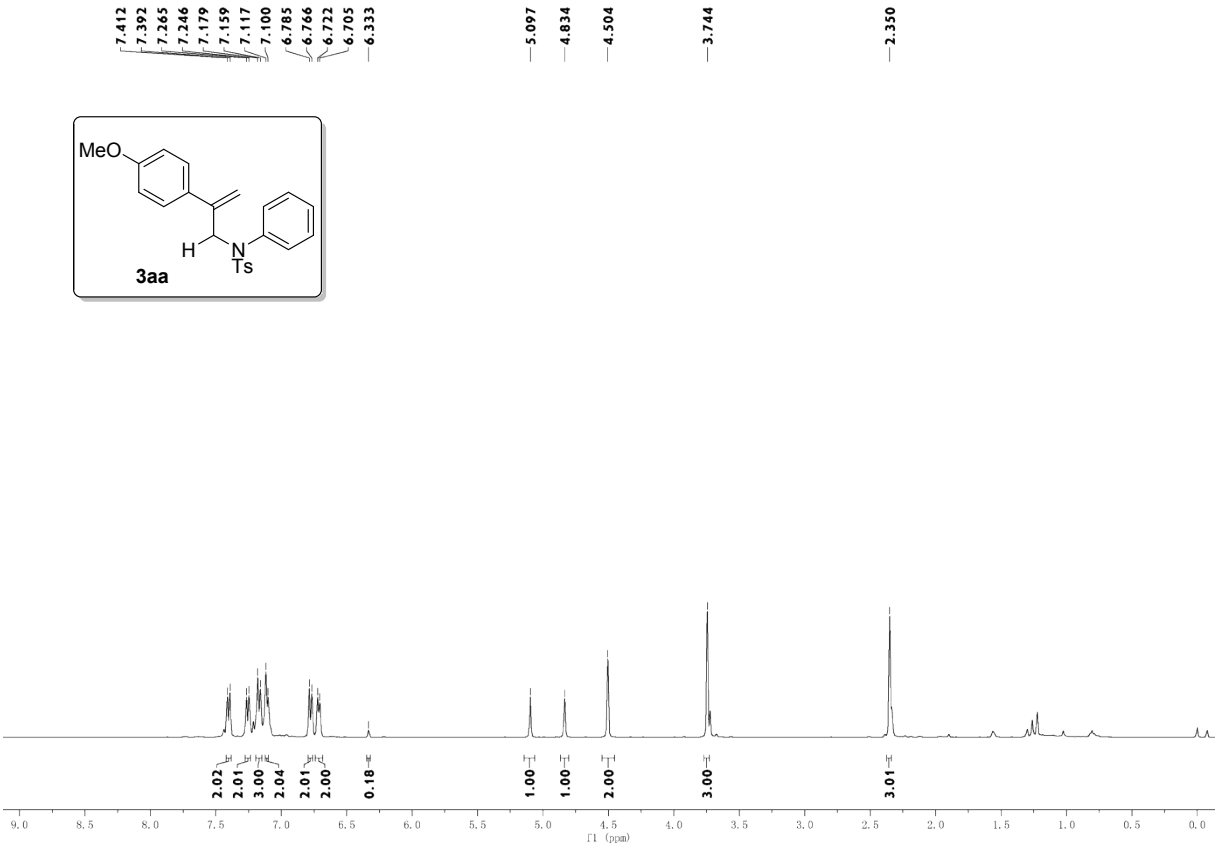
MS (EI) m/z 317 (M+); **HRMS (ESI)** Calcd for $C_{17}H_{19}NO_3S$+H 318.1164, Found 318.1167.

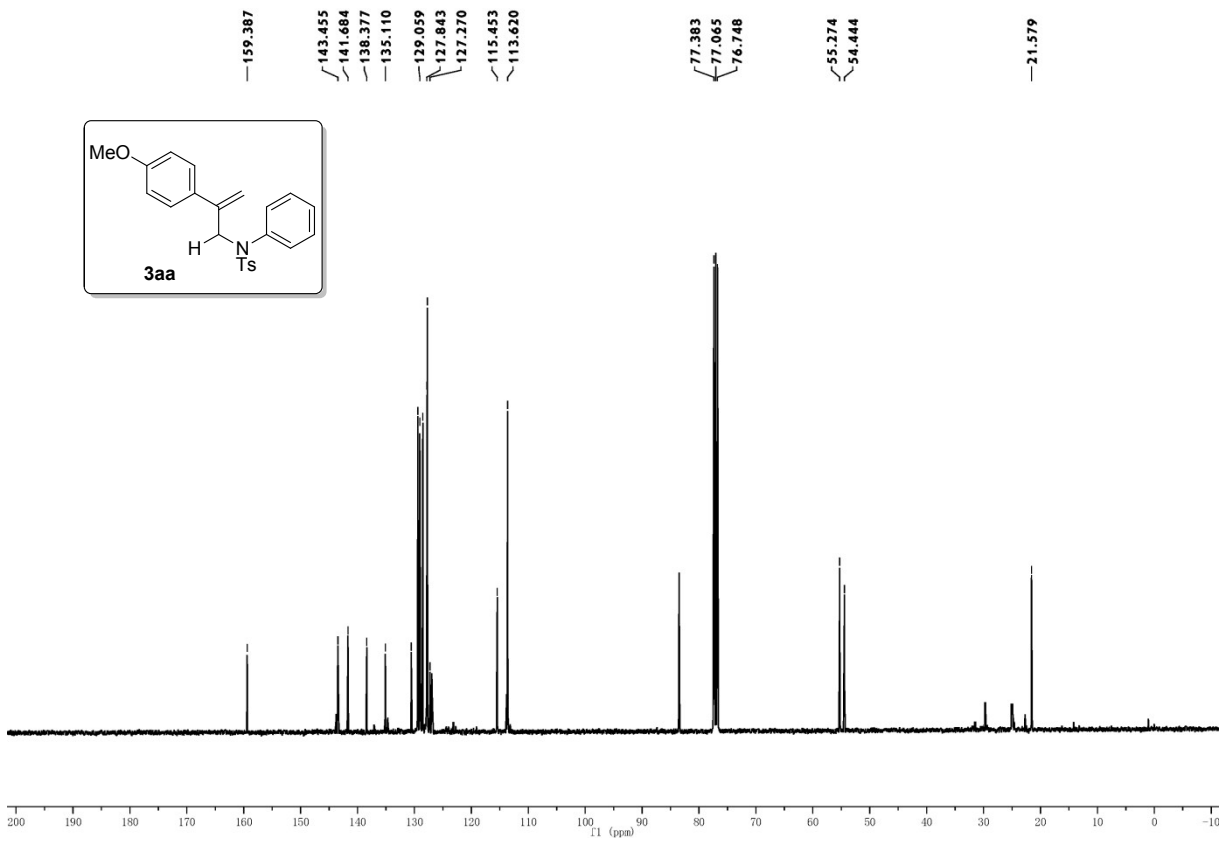
4. Optimization of the Reaction Conditions.



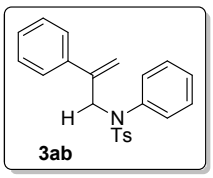
entry	catalyst	ligand	base	solvent	t (°C)	yield[c] of **3aa** (%)	yield[c] of **4aa** (%)
1	$Pd(OAc)_2$	dppf	Cs_2CO_3	toluene	60	57	trace
2	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	toluene	60	39	trace
3	$Pd(OAc)_2$	BINAP	Cs_2CO_3	toluene	60	34	trace
4	$Pd(OAc)_2$	$(2\text{-}OMe)_3P$	Cs_2CO_3	toluene	60	31	trace
5	$Pd(OAc)_2$	Ph_2PCy	Cs_2CO_3	toluene	60	23	trace
6	$Pd(OAc)_2$	dppm	Cs_2CO_3	toluene	60	24	trace
7	$Pd(OAc)_2$	Ruphos	Cs_2CO_3	toluene	60	26	trace
8	$Pd(OAc)_2$	Davephos	Cs_2CO_3	toluene	60	23	trace
9	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	toluene	60	34	trace
10	$Pd(OAc)_2$	dppf	Cs_2CO_3	toluene	80	48	trace
11	$Pd(OAc)_2$	dppf	Cs_2CO_3	toluene	100	43	trace
12	$Pd_2(dba)_3$	dppf	Cs_2CO_3	toluene	60	40	trace
13	$PdCl_2$	dppf	Cs_2CO_3	toluene	60	32	trace
14	$Pd(TFA)_2$	dppf	Cs_2CO_3	toluene	60	42	trace
15	$PdCl_2$(dppf)	-	Cs_2CO_3	toluene	60	59	trace
16	$Pd(PPh_3)_4$	-	Cs_2CO_3	toluene	60	66	trace
17	$PdCl_2(PPh_3)_2$	-	Cs_2CO_3	toluene	60	61	trace
18	$Pd(PPh_3)_4$	-	K_2CO_3	toluene	60	13	trace
19	$Pd(PPh_3)_4$	-	KOtBu	toluene	60	trace	trace
20	$Pd(PPh_3)_4$	-	K_3PO_4	toluene	60	36	trace
21	$Pd(PPh_3)_4$	-	Cy_2NMe	toluene	60	trace	trace
22	$Pd(PPh_3)_4$	$(2\text{-furyl})_3P$	Cs_2CO_3	toluene	60	57	trace
23	$Pd(PPh_3)_4$	dppf	Cs_2CO_3	toluene	60	38	trace
24	$Pd(PPh_3)_4$	PCy_3	Cs_2CO_3	toluene	60	42	trace
25	**$Pd(PPh_3)_4$**	**-**	**Cs_2CO_3**	**THF**	**60**	**84**	trace
26	$Pd(PPh_3)_4$	-	Cs_2CO_3	1,4-dioxane	60	57	trace
27	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	60	59	trace
28	$Pd(PPh_3)_4$	-	Cs_2CO_3	DMF	60	34	trace
29	-	-	Cs_2CO_3	toluene	60	NR	-
30	**$Pd(PPh_3)_4$**	**-**	**Cs_2CO_3**	**THF**	**60**	**-**	**58**
31	$PdCl_2$(dppf)	-	Cs_2CO_3	THF	60	-	42
32	$PdCl_2(PPh_3)_2$	-	Cs_2CO_3	THF	60	-	44
33	$Pd(dba)_2$	dppf	Cs_2CO_3	THF	60	-	27
34	$Pd(PPh_3)_4$	-	K_2CO_3	THF	60	-	trace
35	$Pd(PPh_3)_4$	-	K_3PO_4	THF	60	-	trace
36	$Pd(PPh_3)_4$	-	Cy_2NMe	THF	60	-	trace
37	$Pd(PPh_3)_4$	-	KOtBu	THF	60	-	trace
38	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	60	-	trace
39	$Pd(PPh_3)_4$	-	Cs_2CO_3	1,4-dioxane	60	-	trace

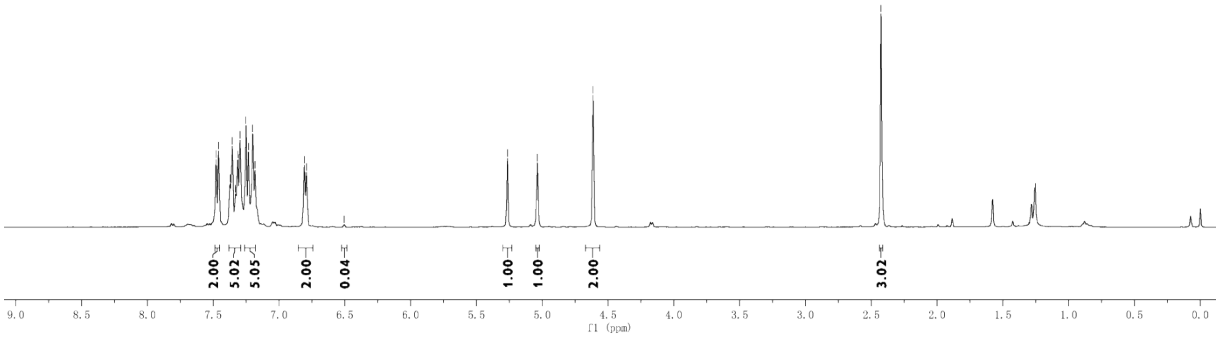
5. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR for allylamines.


7.412
7.392
7.265
7.246
7.179
7.159
7.117
7.100
6.785
6.766
6.722
6.705
6.333
5.097
4.834
4.504
3.744
2.350
MeO
H
N
Ts
3aa
2.02
2.01
3.00
2.04
2.01
2.00
0.18
1.00
1.00
2.00
3.00
3.01
f1 (ppm)

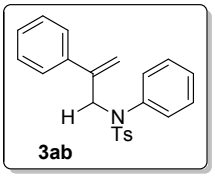

159.387
143.455
141.684
138.377
135.110
129.059
127.843
127.270
115.453
113.620
77.383
77.065
76.748
55.274
54.444
21.579
MeO
H
N
Ts
3aa
f1 (ppm)


7.478
7.459
7.372
7.355
7.330
7.314
7.297
7.251
7.232
7.200
7.183
6.808
6.790
6.505
5.265
5.037
4.614
2.426

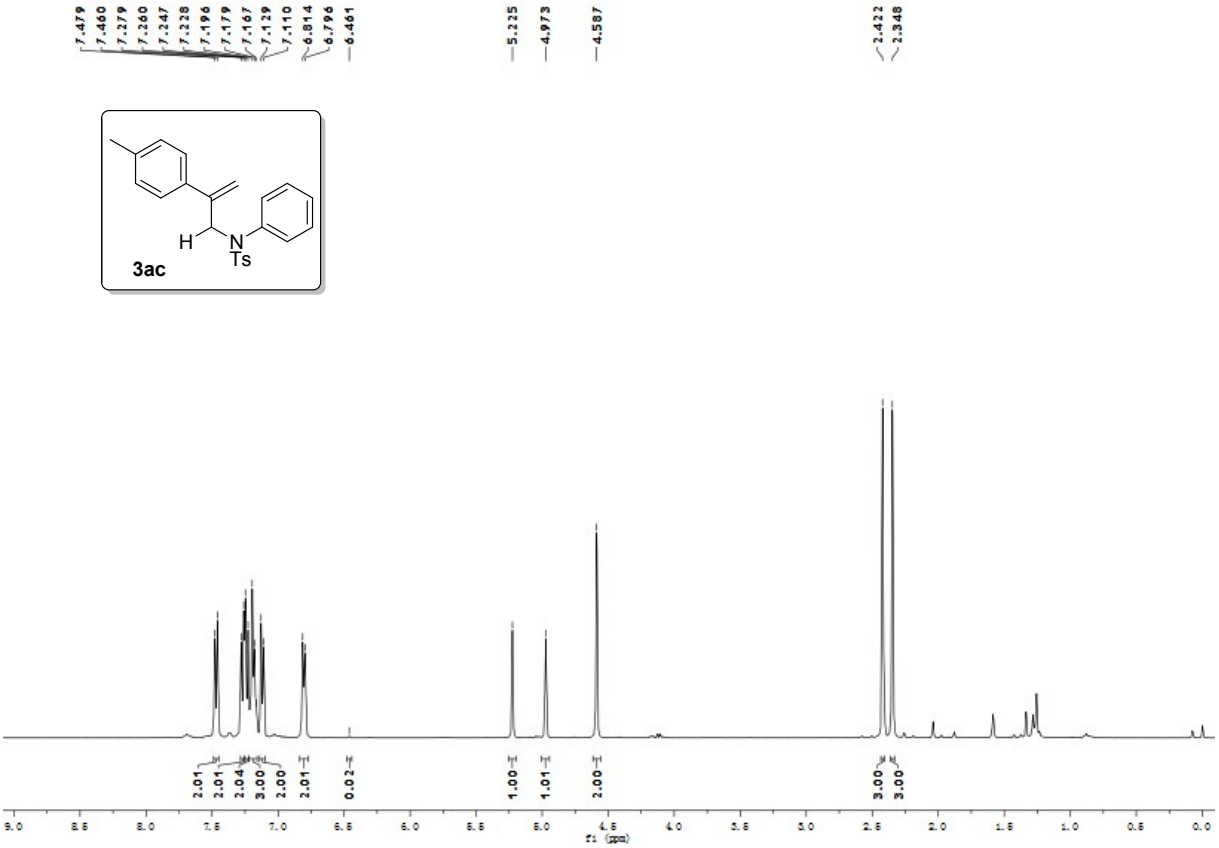

H
N
Ts
3ab

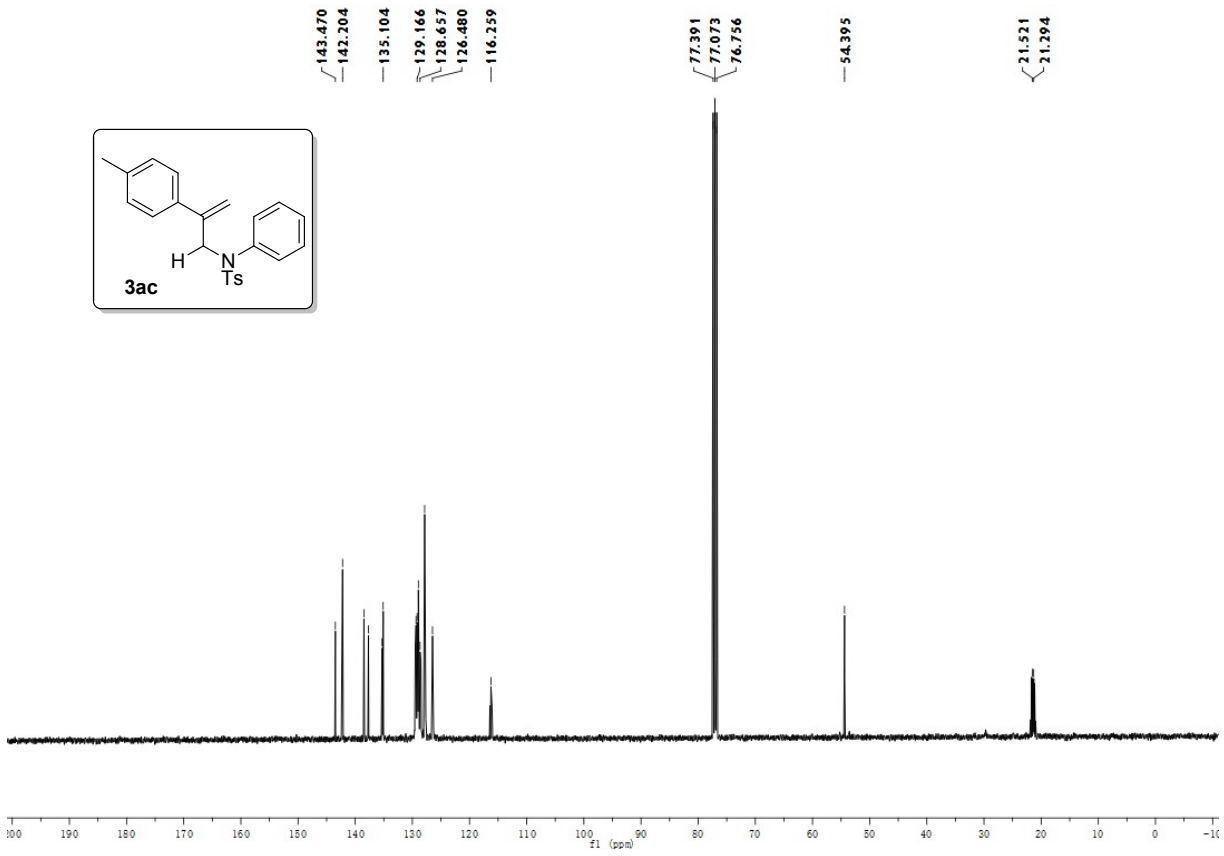

2.00
5.02
5.05
2.00
0.04
1.00
1.00
2.00
3.02
f1 (ppm)

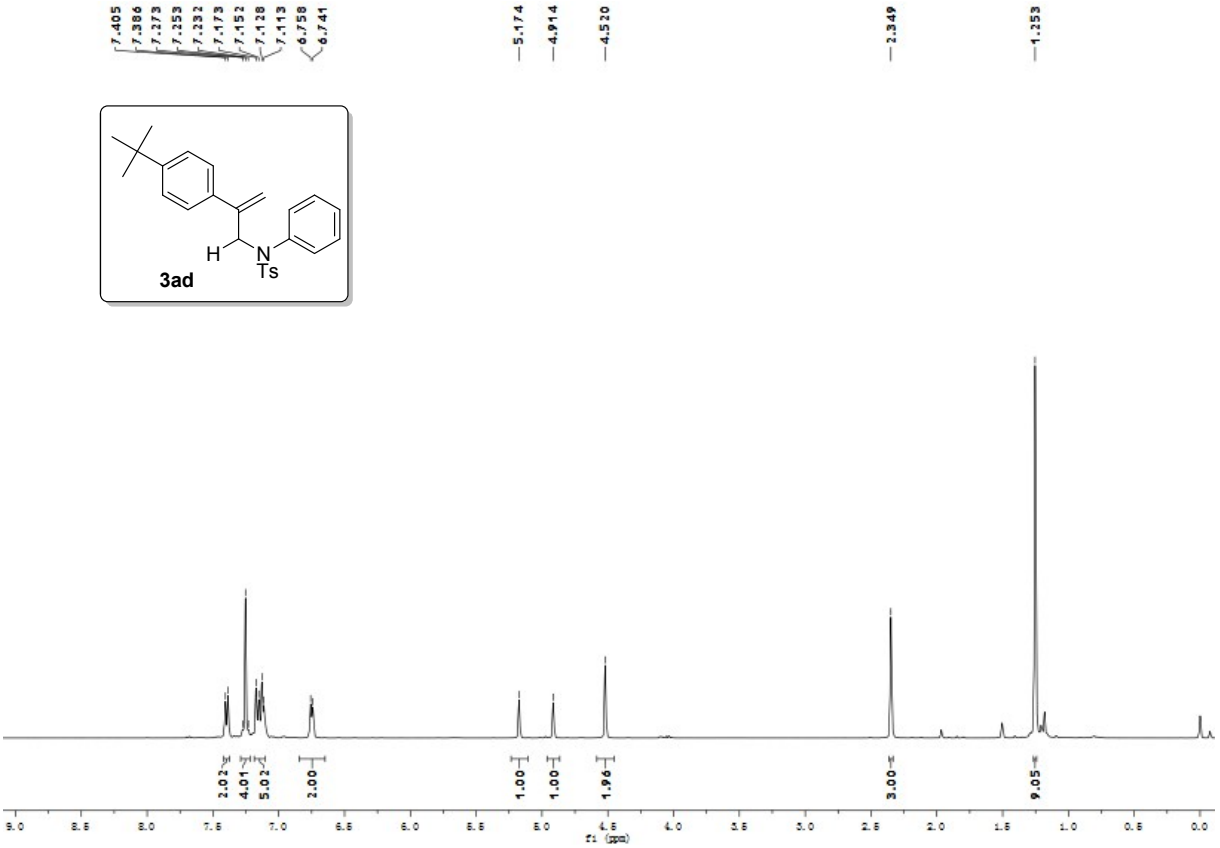

143.504
138.430
135.056
129.152
128.528
126.549
117.023
77.382
77.065
76.746
54.340
21.686

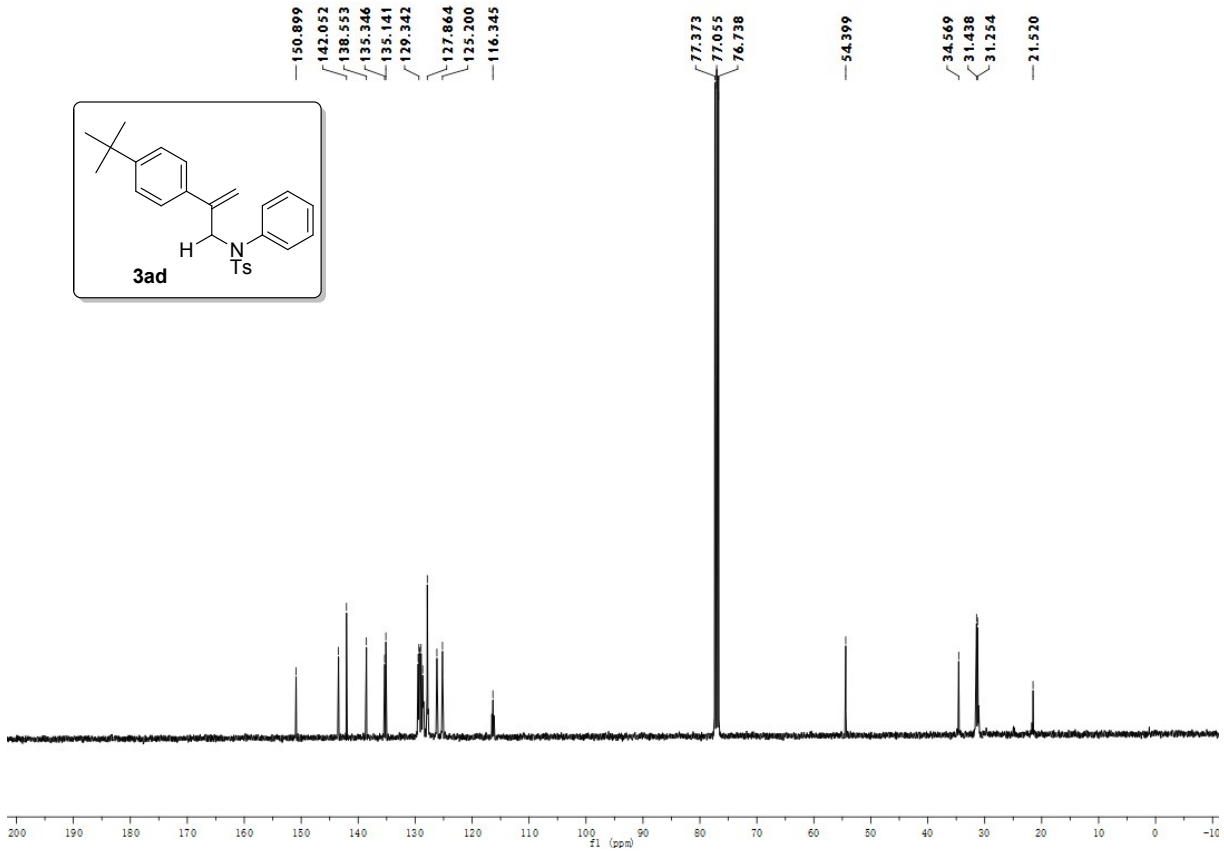

H
N
Ts
3ab

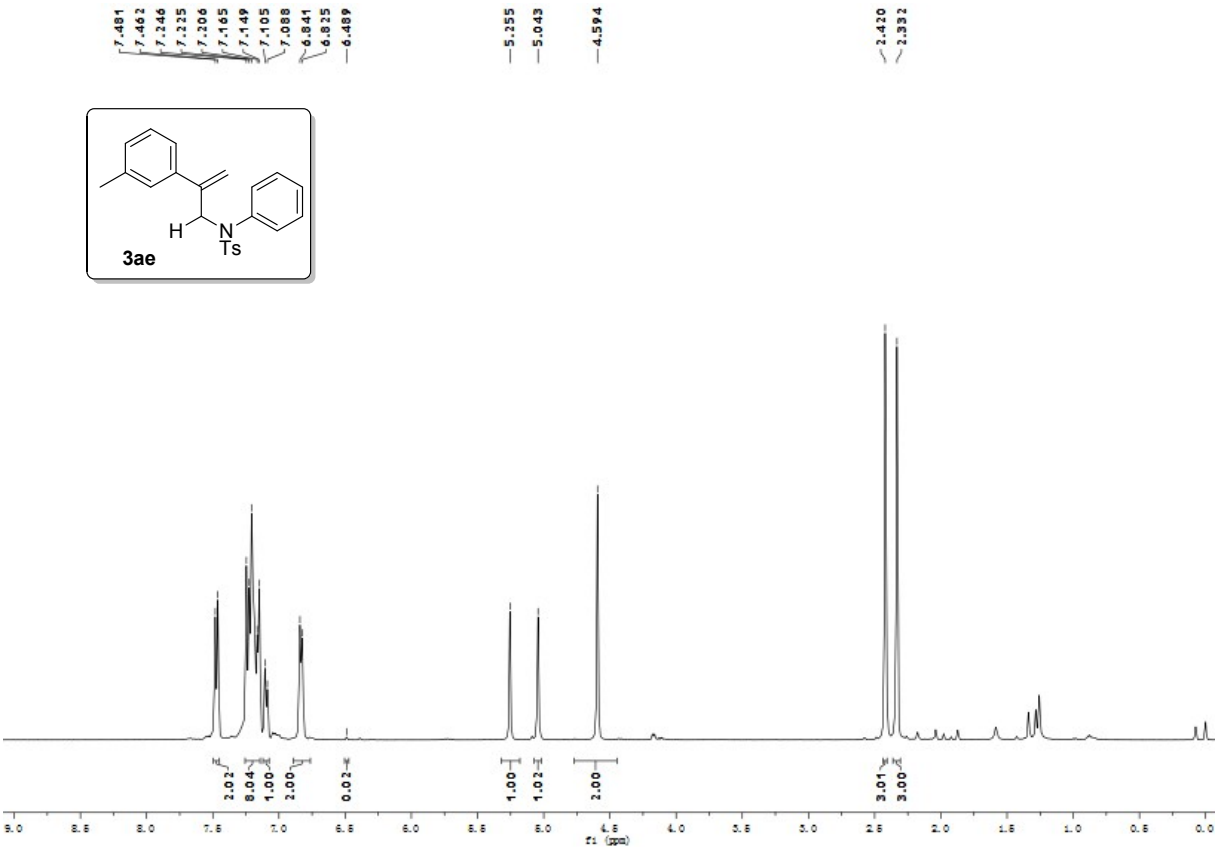
f1 (ppm)

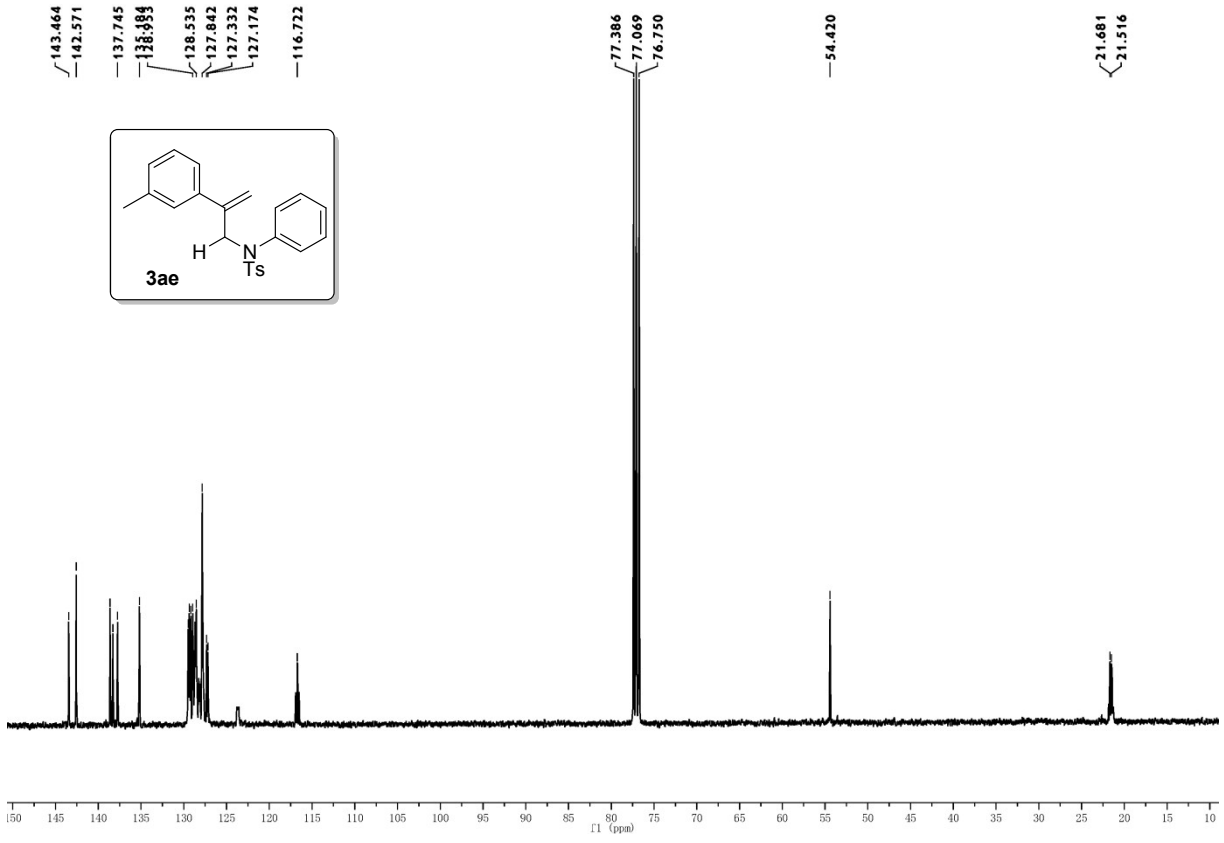

7.479
7.460
7.279
7.260
7.247
7.238
7.196
7.179
7.167
7.139
7.110
6.814
6.796
6.461
5.225
4.973
4.587
2.422
2.348
H
N
Ts
3ac
2.01
2.01
2.04
3.00
2.00
2.01
0.02
1.00
1.01
2.00
3.00
3.00
f1 (ppm)

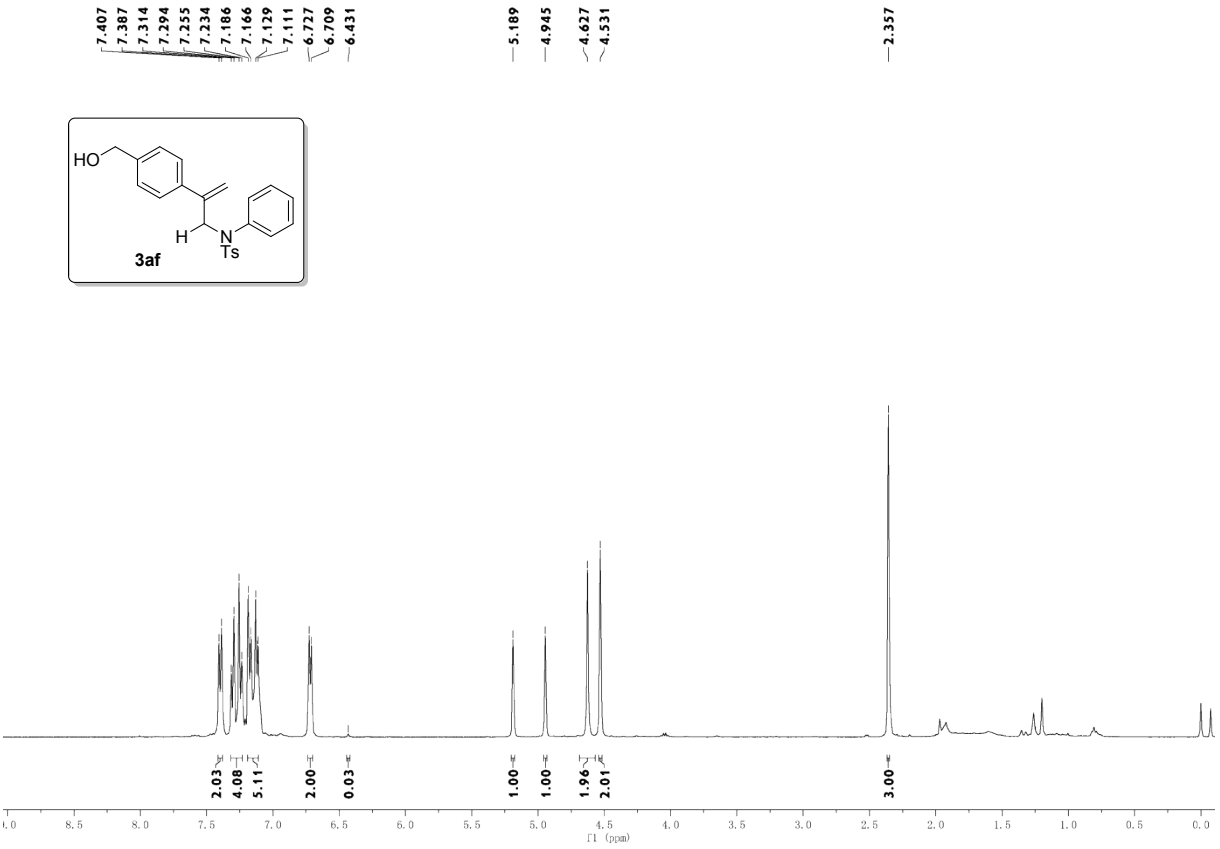

143.470
142.204
135.104
129.166
128.657
126.480
116.259
77.391
77.073
76.756
54.395
21.521
21.294
H
N
Ts
3ac
f1 (ppm)

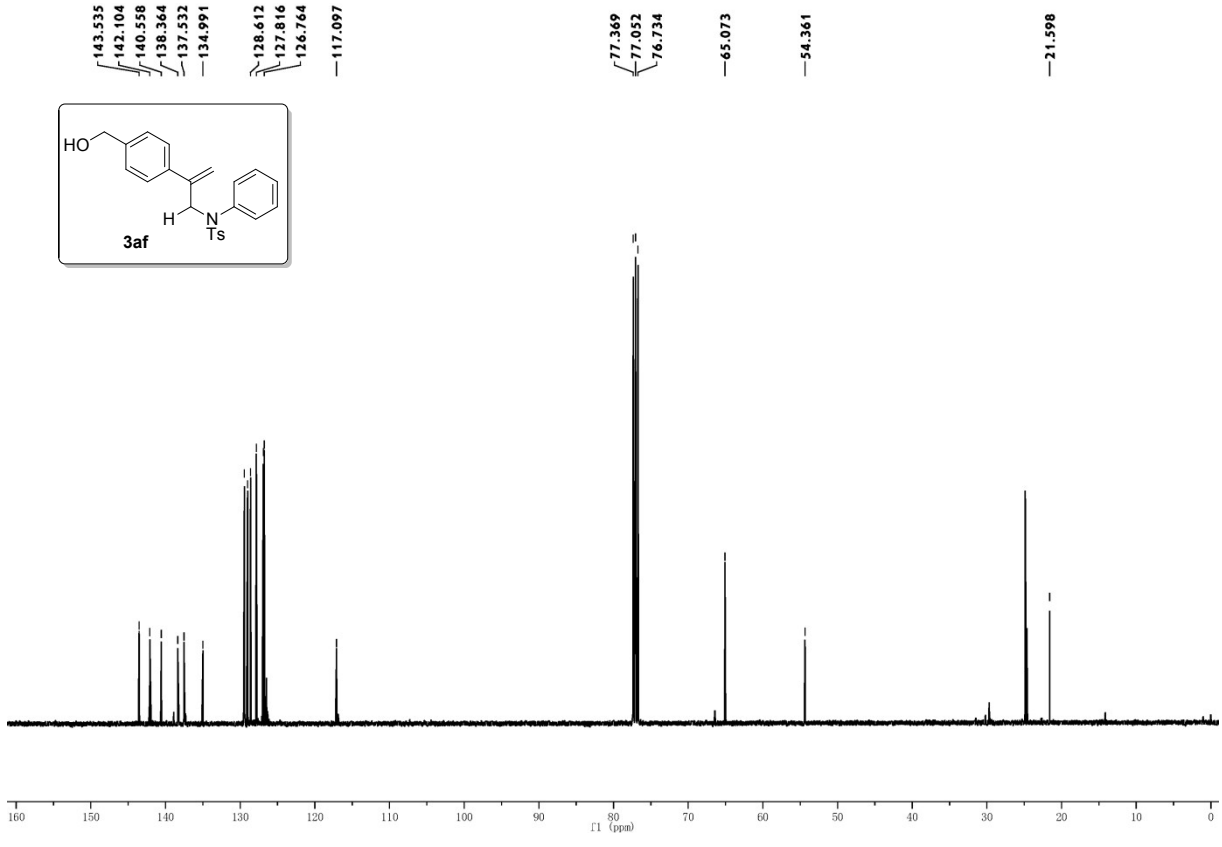

7.405
7.386
7.273
7.253
7.232
7.173
7.152
7.128
7.113
6.758
6.741
5.174
4.914
4.520
2.349
1.253
3ad
H
N
Ts
2.02
4.01
5.02
2.00
1.00
1.00
1.96
3.00
9.05
f1 (ppm)

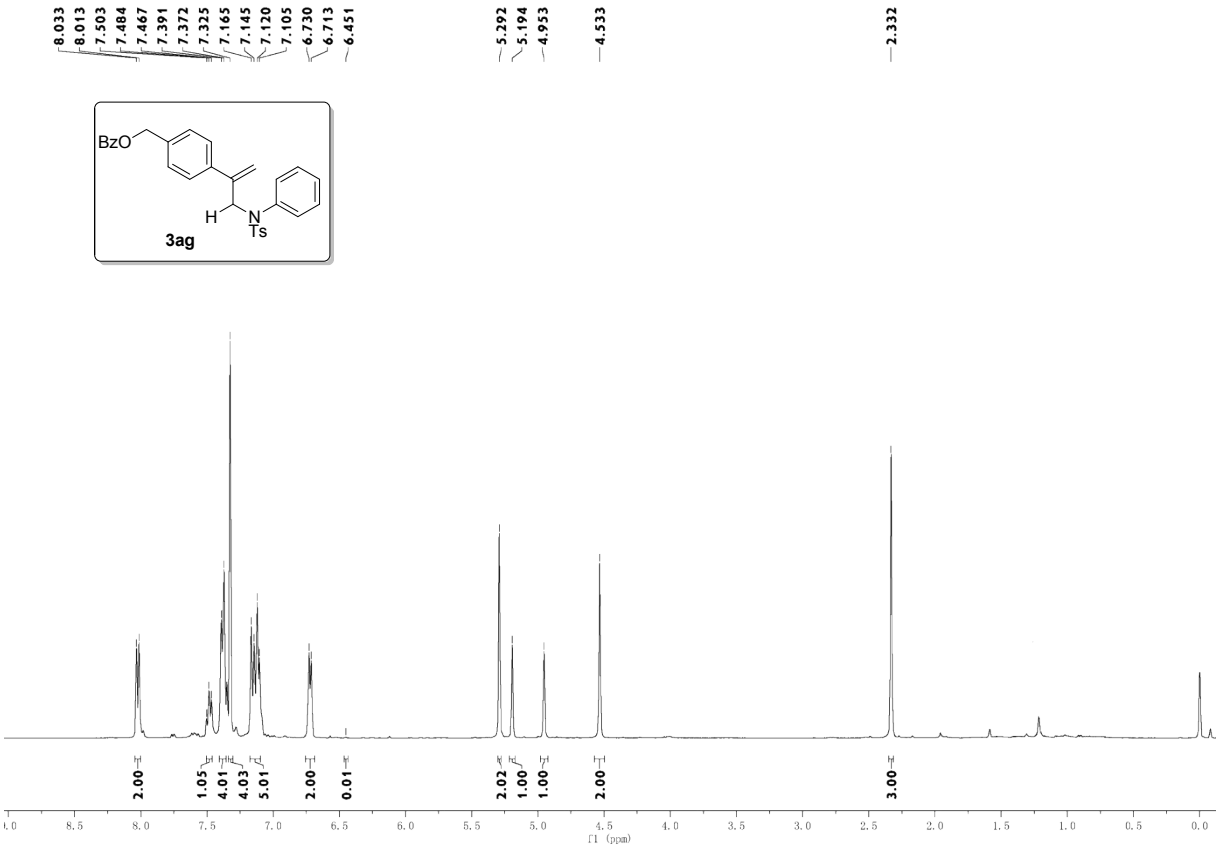

150.899
142.052
138.553
135.346
135.141
129.342
127.864
125.200
116.345
77.373
77.055
76.738
54.399
34.569
31.438
31.254
21.520
3ad
H
N
Ts
f1 (ppm)

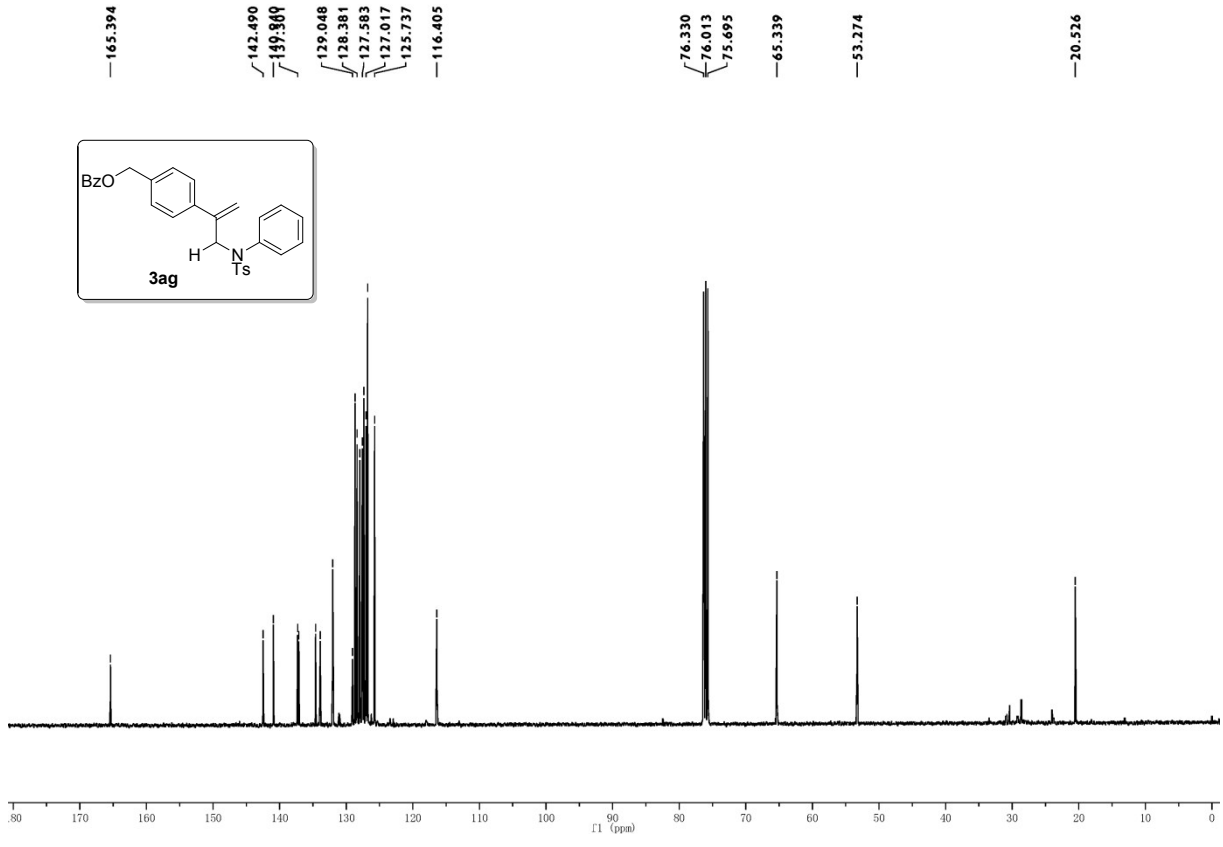

7.481
7.462
7.246
7.225
7.206
7.165
7.149
7.105
7.088
6.841
6.825
6.489
5.255
5.043
4.594
2.420
2.332
H
N
Ts
3ae
2.02
8.04
1.00
2.00
0.02
1.00
1.02
2.00
3.01
3.00
f1 (ppm)

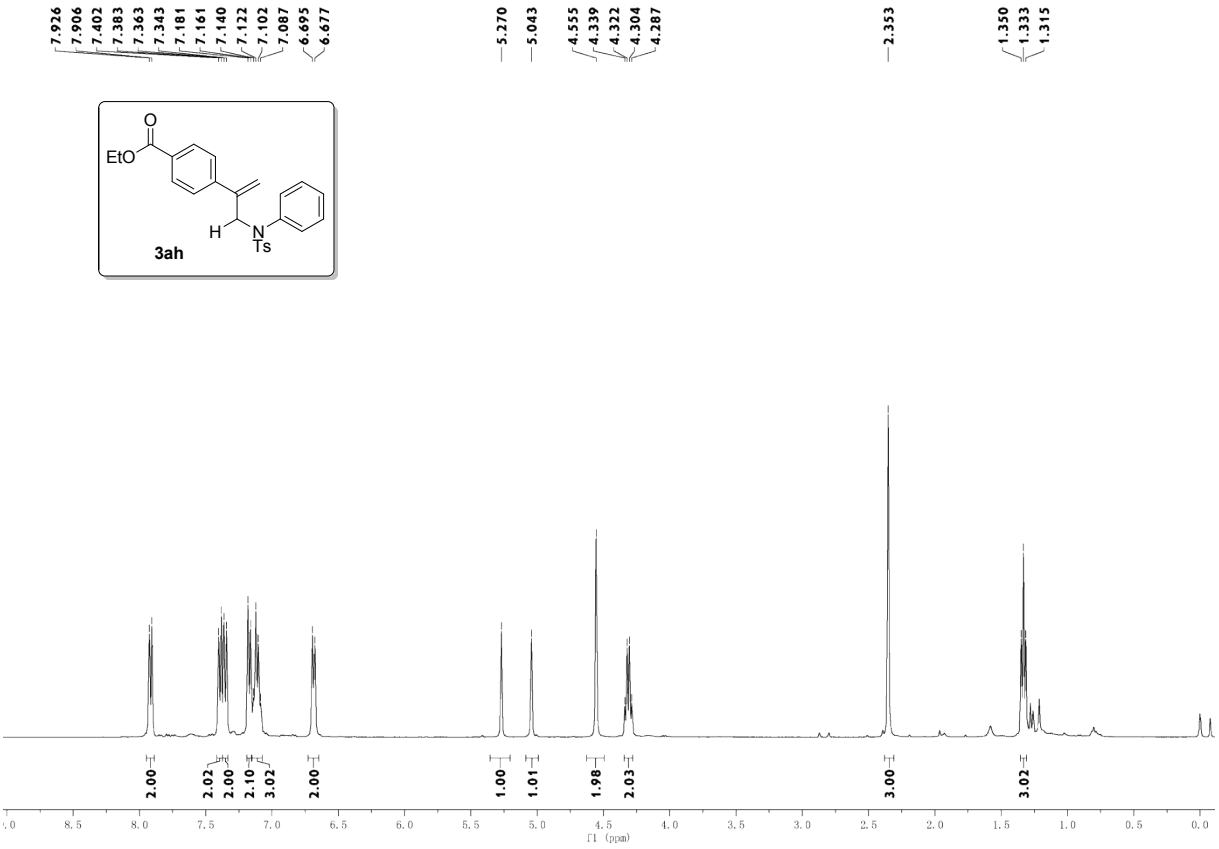

143.464
142.571
137.745
128.535
127.842
127.332
127.174
116.722
77.386
77.069
76.750
54.420
21.681
21.516
H
N
Ts
3ae
f1 (ppm)

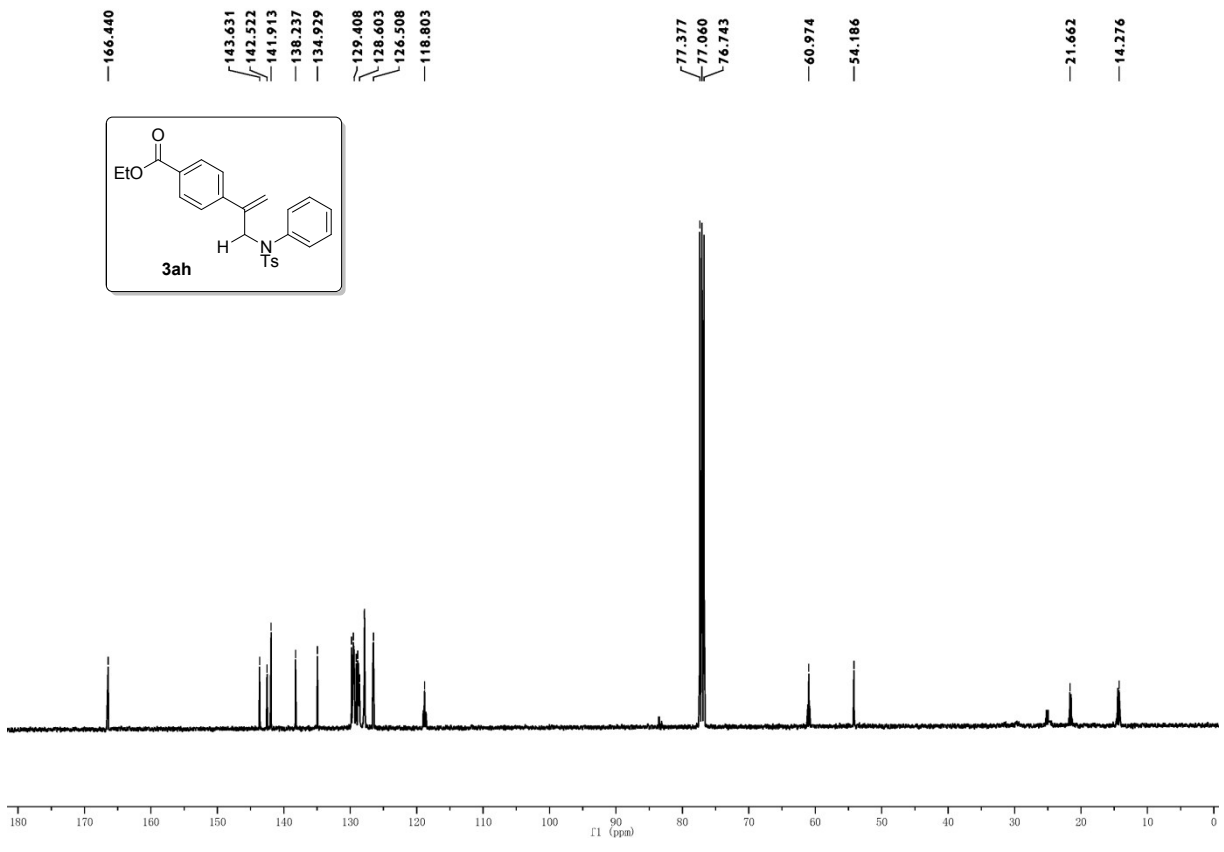

7.407
7.387
7.314
7.294
7.255
7.234
7.186
7.166
7.129
7.111
6.727
6.709
6.431
5.189
4.945
4.627
4.531
2.357
HO
H
N
Ts
3af
2.03
4.08
5.11
2.00
0.03
1.00
1.00
1.96
2.01
3.00
f1 (ppm)

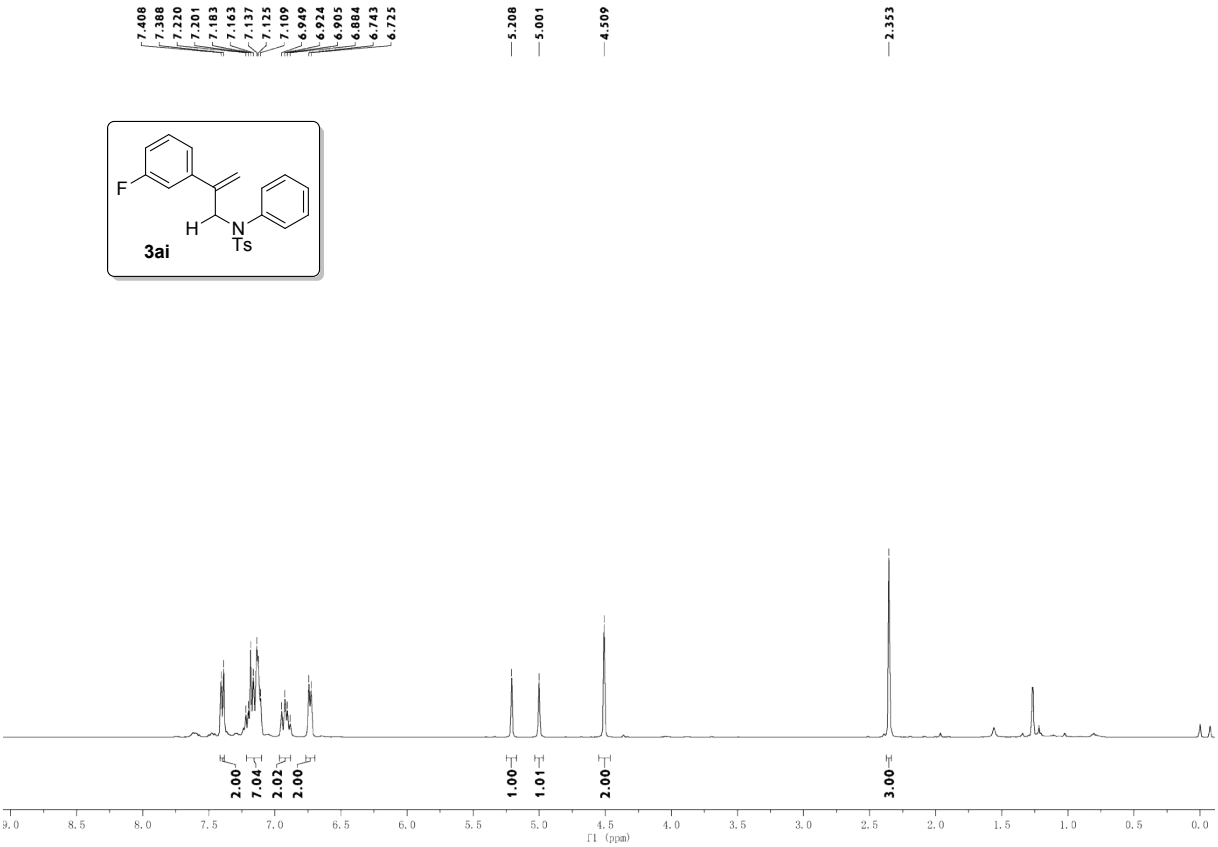

143.535
142.104
140.558
138.364
137.532
134.991
128.612
127.816
126.764
117.097
77.369
77.052
76.734
65.073
54.361
21.598
HO
H
N
Ts
3af
f1 (ppm)

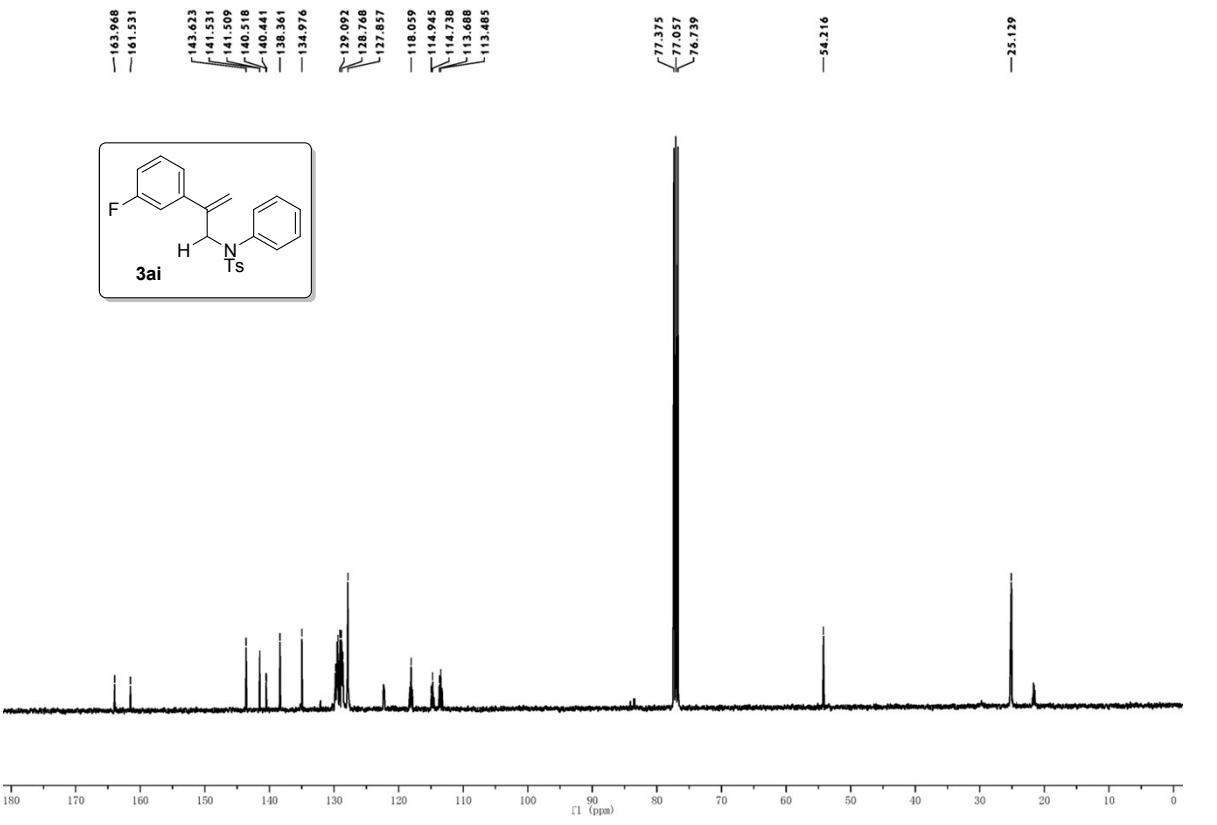

8.033
8.013
7.503
7.484
7.467
7.391
7.372
7.325
7.165
7.145
7.120
7.105
6.730
6.713
6.451
5.292
5.194
4.953
4.533
2.332
BzO
H
N
Ts
3ag
2.00
1.05
4.01
4.03
5.01
2.00
0.01
2.02
1.00
1.00
2.00
3.00
f1 (ppm)

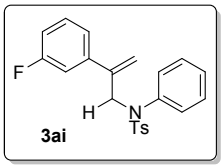

165.394
142.490
139.849
139.301
129.048
128.381
127.583
127.017
125.737
116.405
76.330
76.013
75.695
65.339
53.274
20.526
BzO
H
N
Ts
3ag
f1 (ppm)


7.926
7.906
7.402
7.383
7.363
7.343
7.181
7.161
7.140
7.122
7.102
7.087
6.695
6.677
5.270
5.043
4.555
4.339
4.322
4.304
4.287
2.353
1.350
1.333
1.315
EtO
O
H
N
Ts
3ah
2.00
2.02
2.00
2.10
3.02
2.00
1.00
1.01
1.98
2.03
3.00
3.02
f1 (ppm)


166.440
143.631
142.522
141.913
138.237
134.929
129.408
128.603
126.508
118.803
77.377
77.060
76.743
60.974
54.186
21.662
14.276
EtO
O
H
N
Ts
3ah
f1 (ppm)

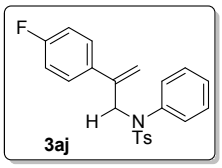

7.408
7.388
7.220
7.201
7.183
7.163
7.137
7.125
7.109
6.949
6.924
6.905
6.884
6.743
6.725
5.208
5.001
4.509
2.353
F
H
N
Ts
3ai
2.00
7.04
2.02
2.00
1.00
1.01
2.00
3.00
f1 (ppm)

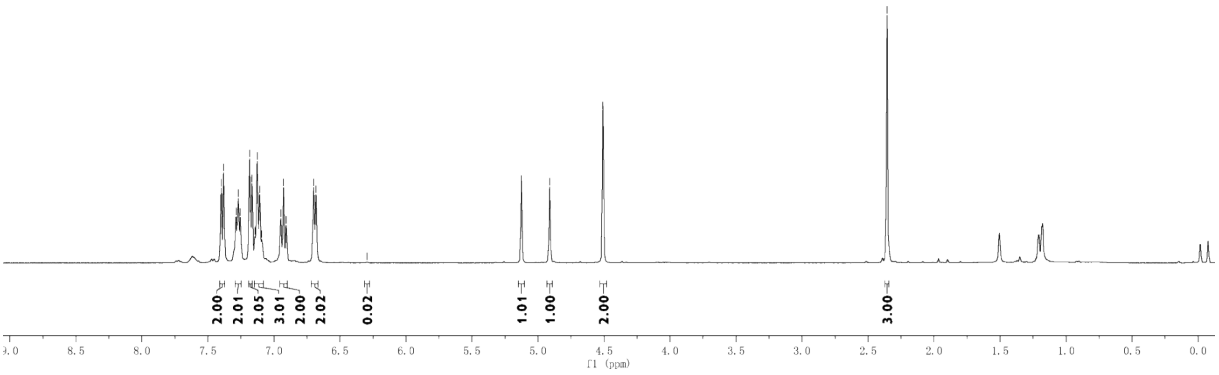

163.968
161.531
143.623
141.531
141.509
140.518
140.441
138.361
134.976
129.092
128.768
127.857
118.059
114.945
114.738
113.688
113.485
77.375
77.057
76.739
54.216
25.129
F
H
N
Ts
3ai
f1 (ppm)

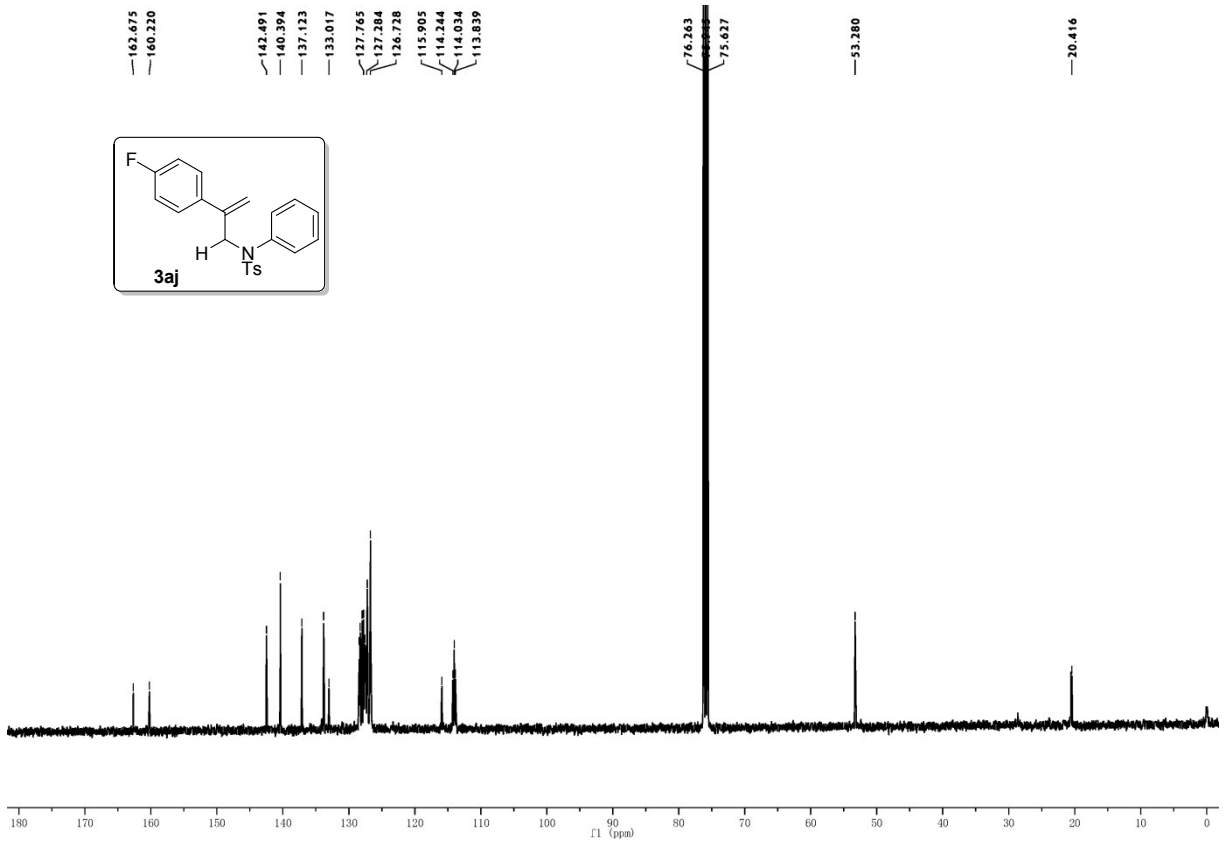

F
H
N
Ts
3ai

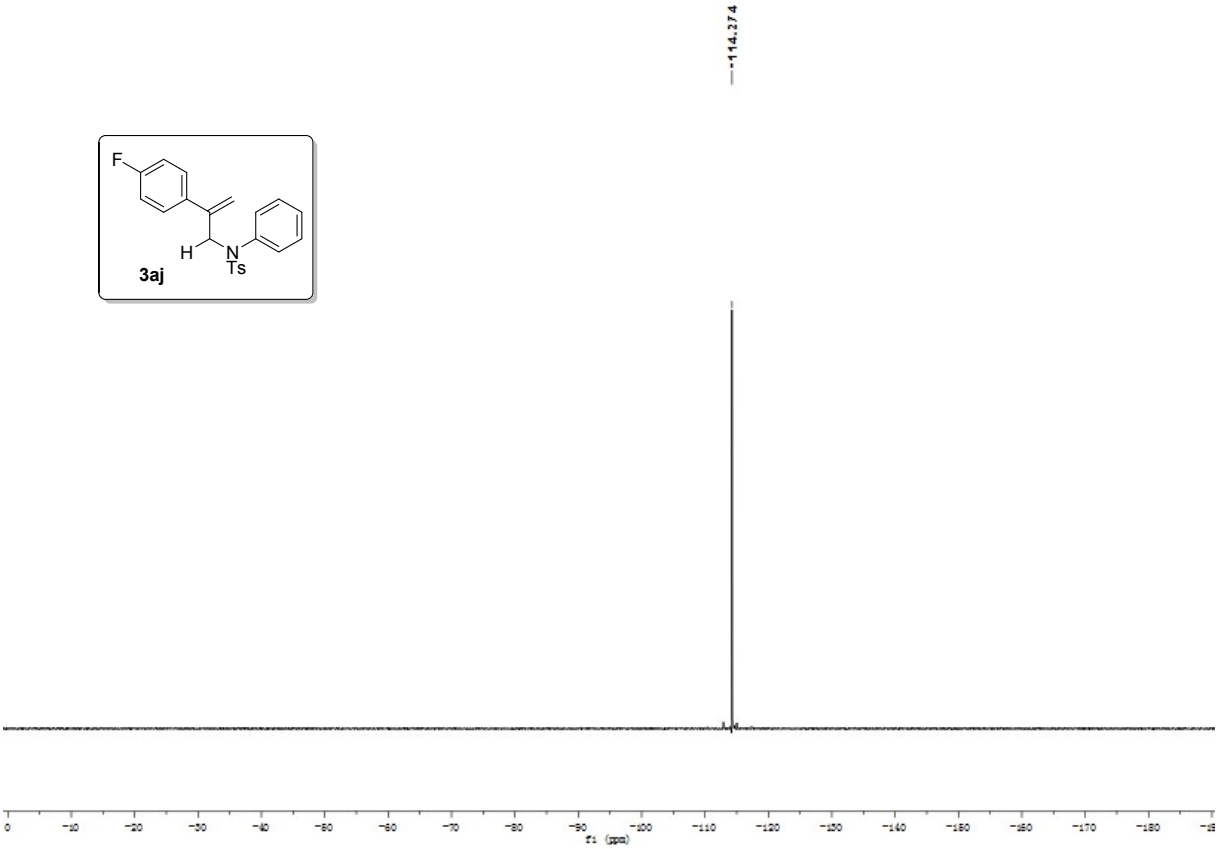
-113.349
f1 (ppm)

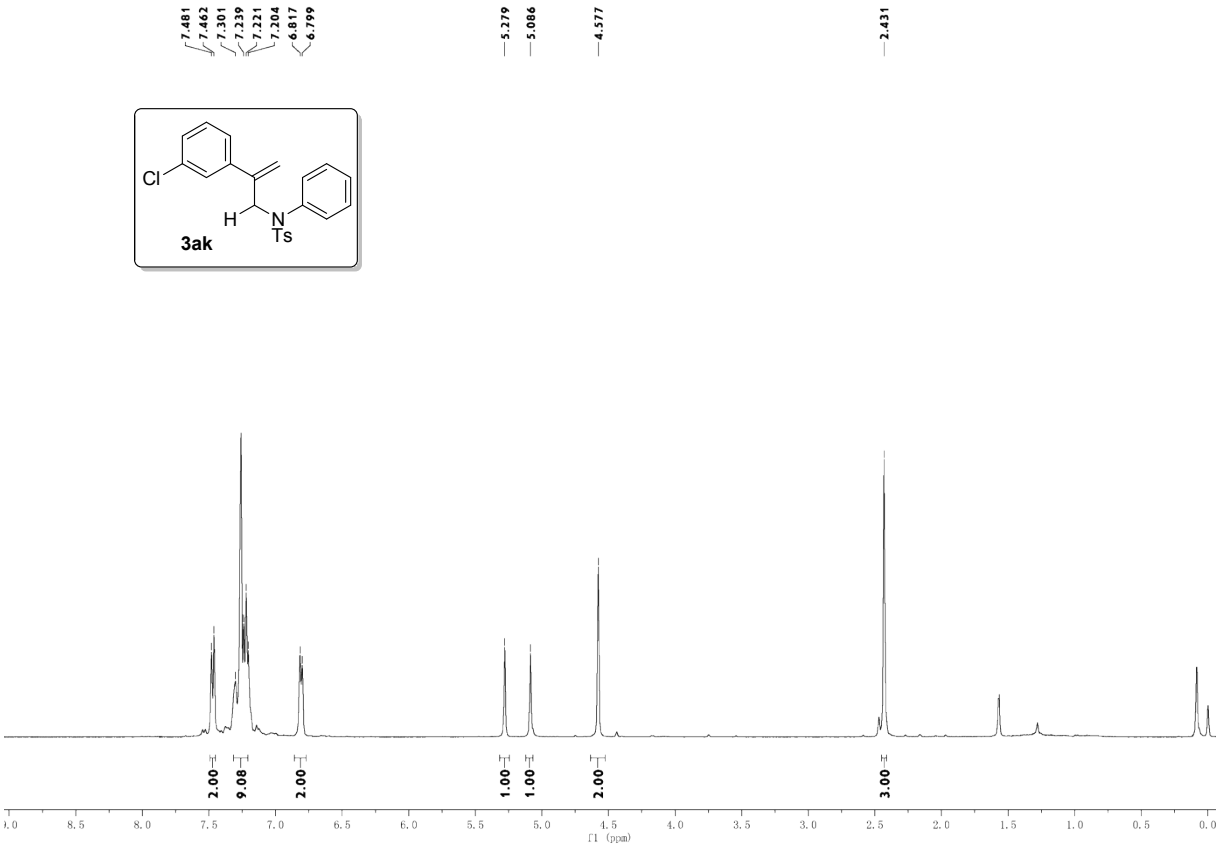

7.400
7.381
7.287
7.270
7.255
7.184
7.166
7.143
7.127
7.108
7.094
6.948
6.927
6.907
6.699
6.682
6.294
5.127
4.911
4.509
2.357

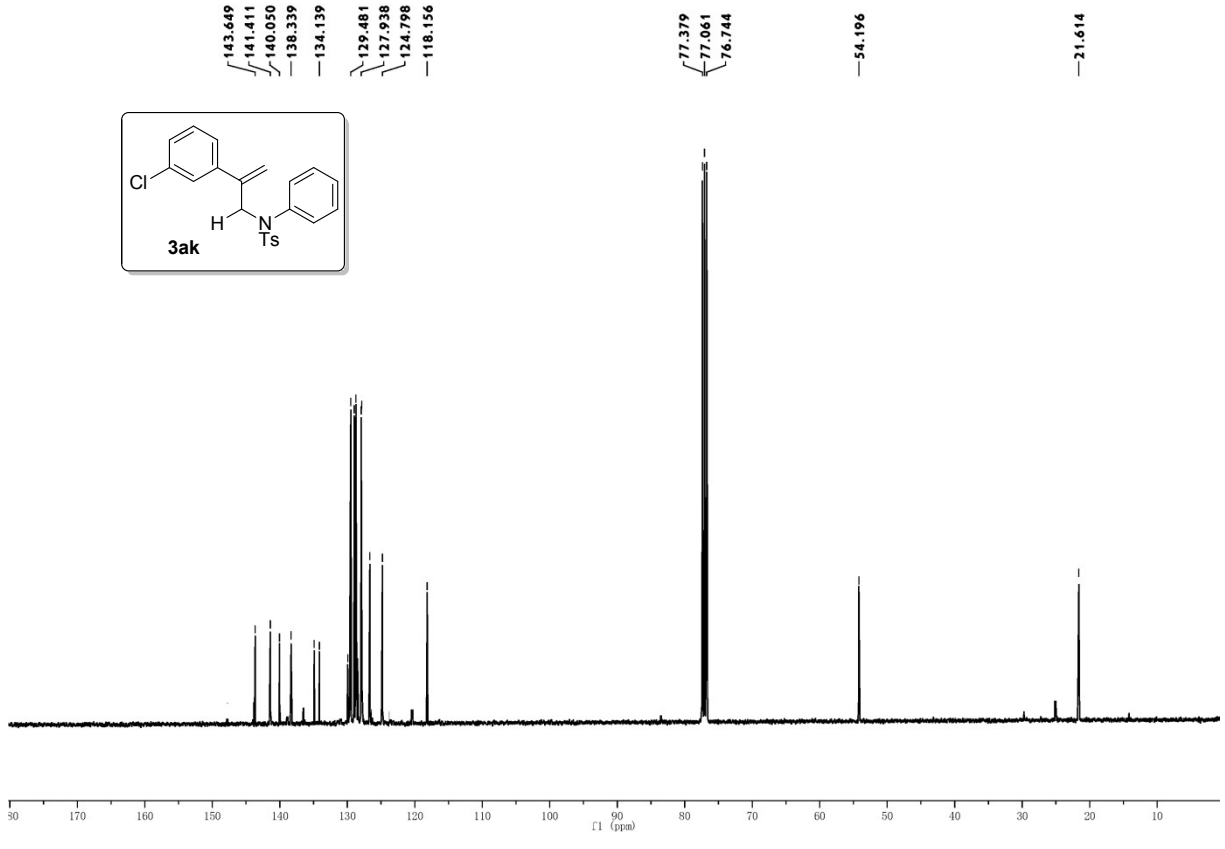

F
H
N
Ts
3aj

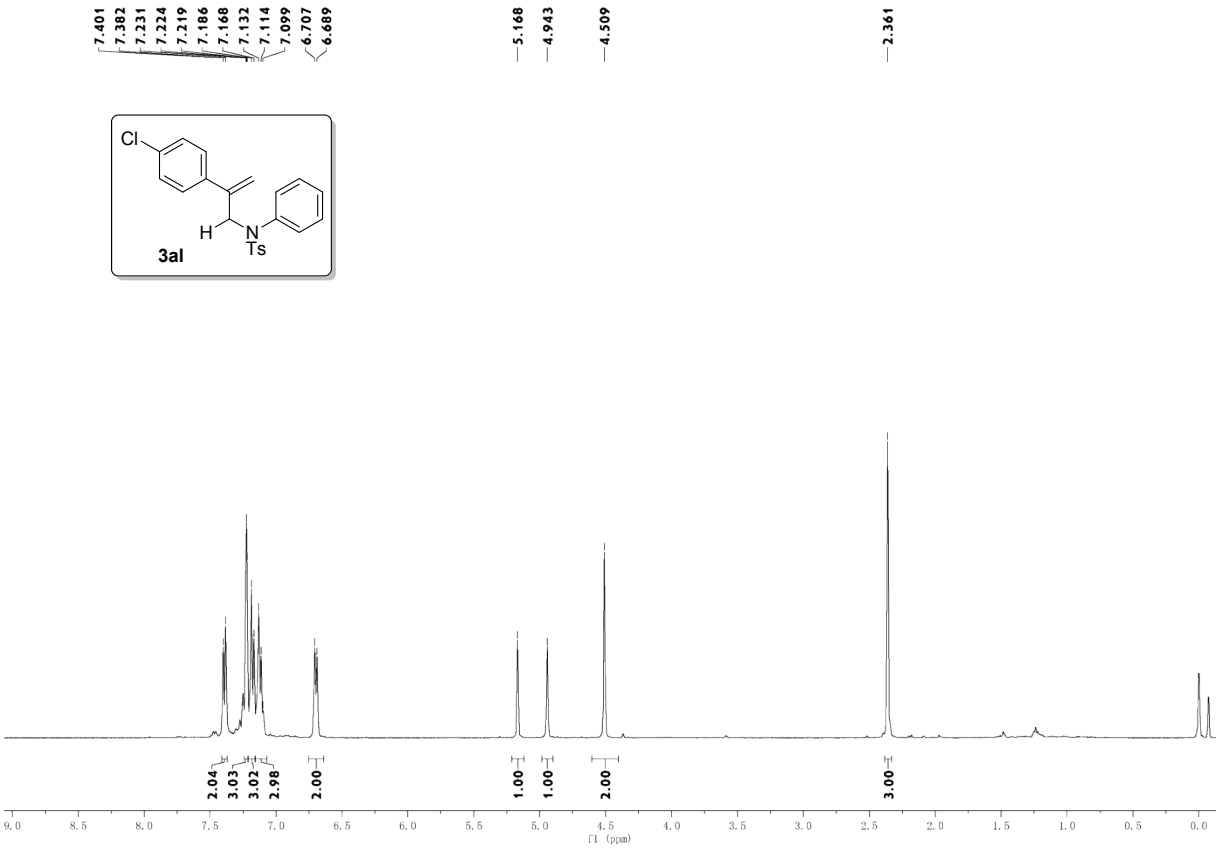

2.00
2.01
2.05
3.01
2.00
2.02
0.02
1.01
1.00
2.00
3.00
f1 (ppm)

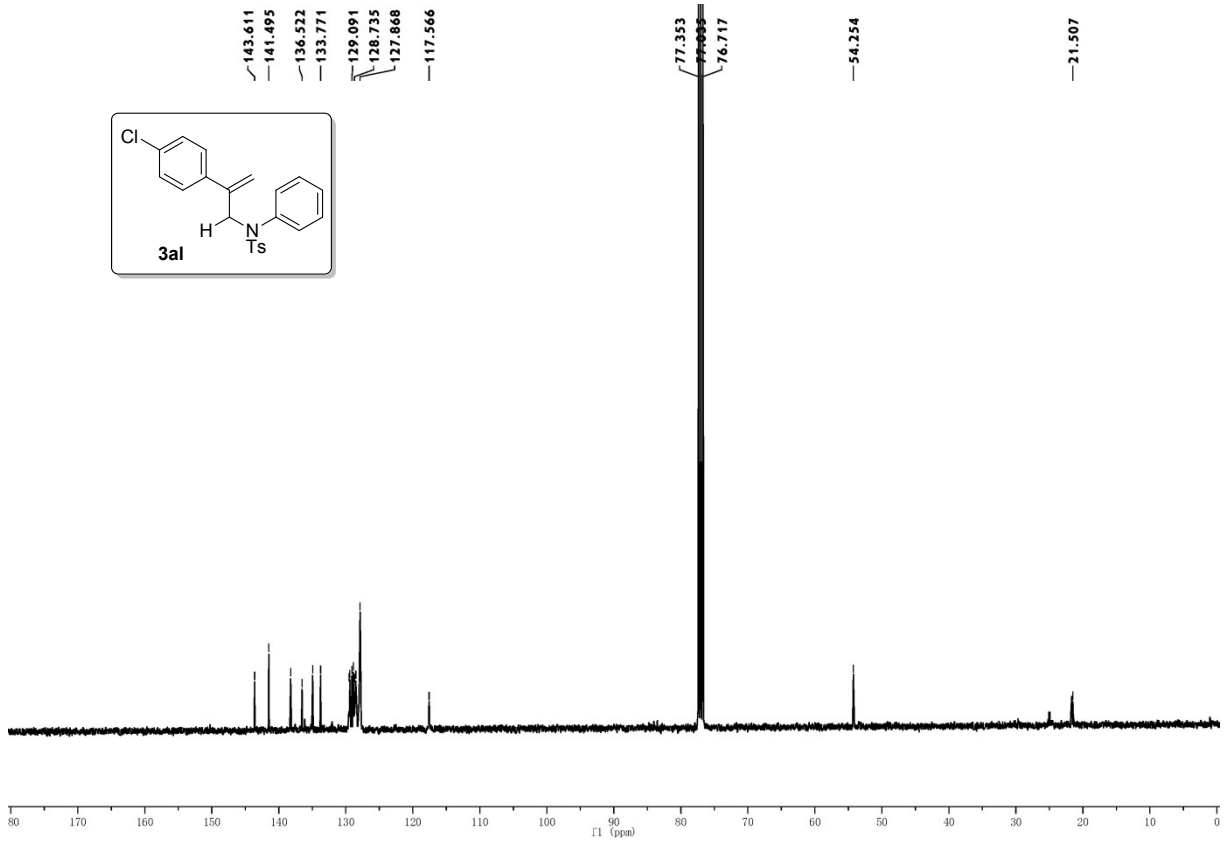

162.675
160.220
142.491
140.394
137.123
133.017
127.765
127.284
126.728
115.905
114.244
114.034
113.839
76.263
75.627
53.280
20.416
F
H
N
Ts
3aj
f1 (ppm)

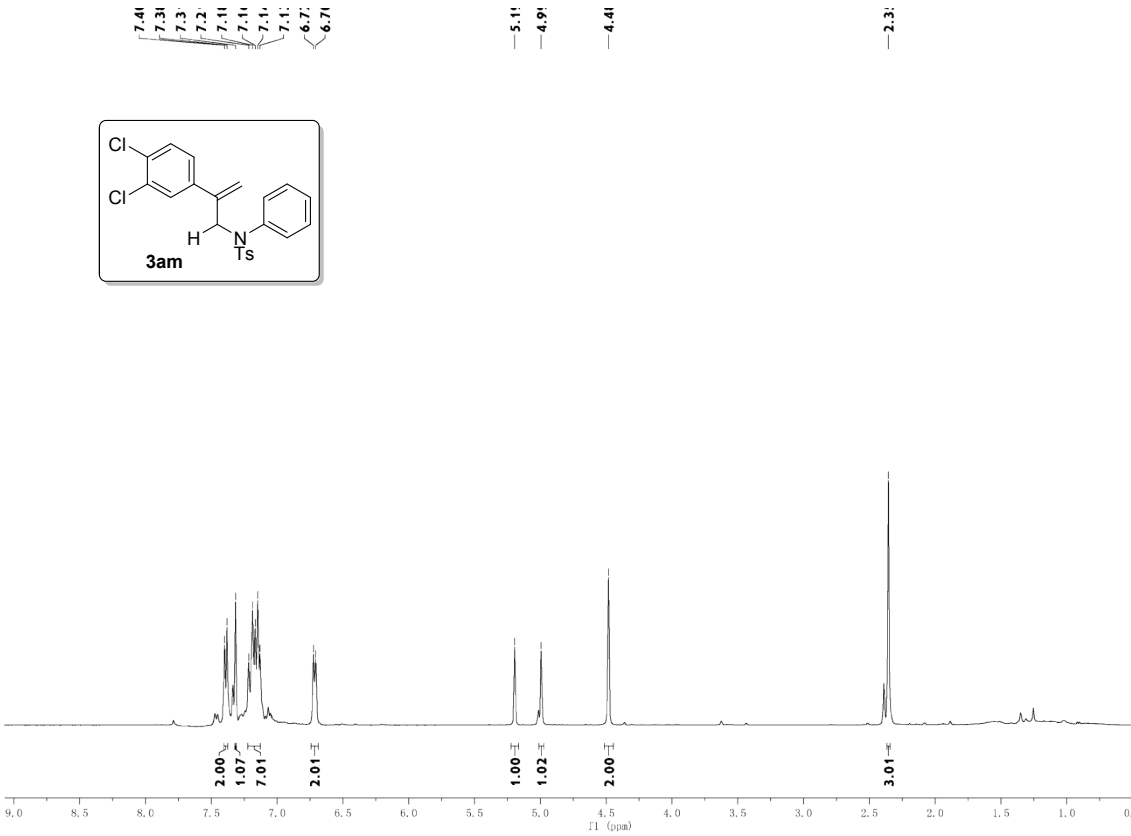

-114.274
F
H
N
Ts
3aj
f1 (ppm)

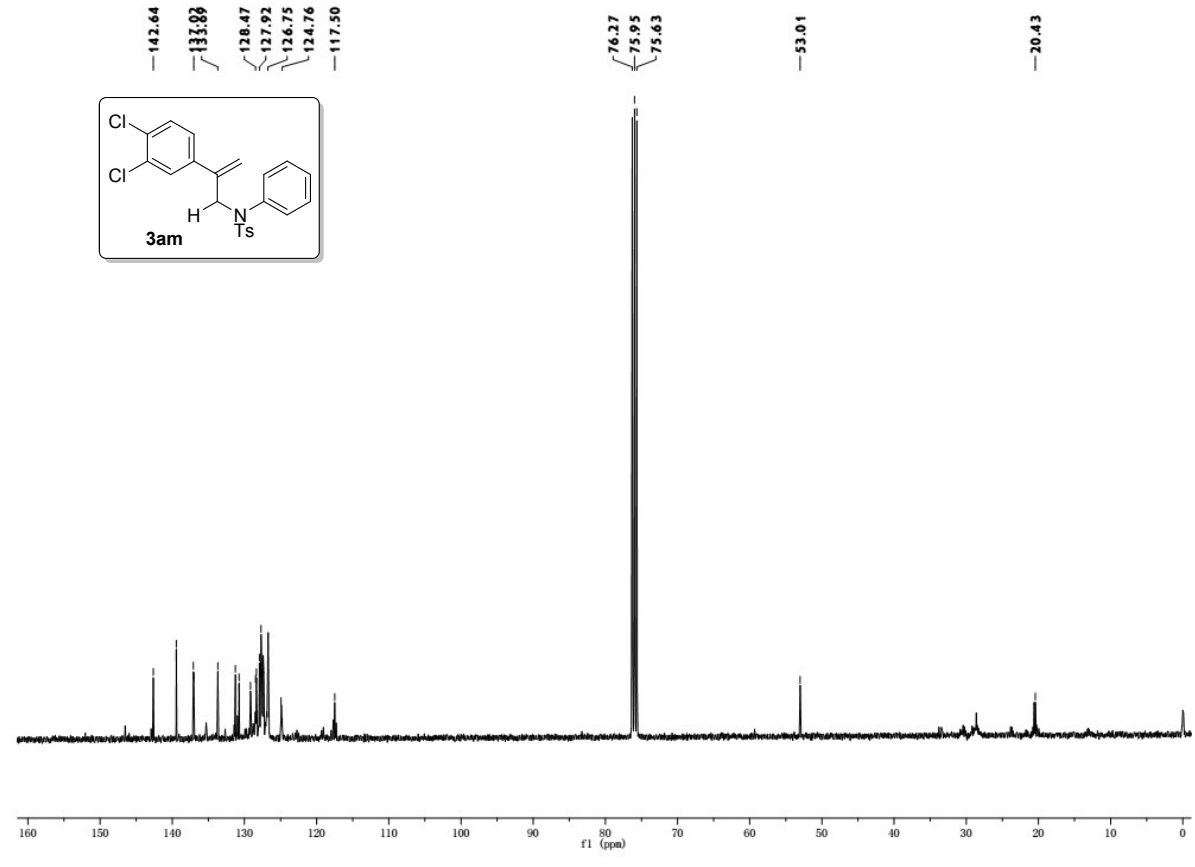

7.481
7.462
7.301
7.239
7.221
7.204
6.817
6.799
5.279
5.086
4.577
2.431
Cl
H
N
Ts
3ak
2.00
9.08
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

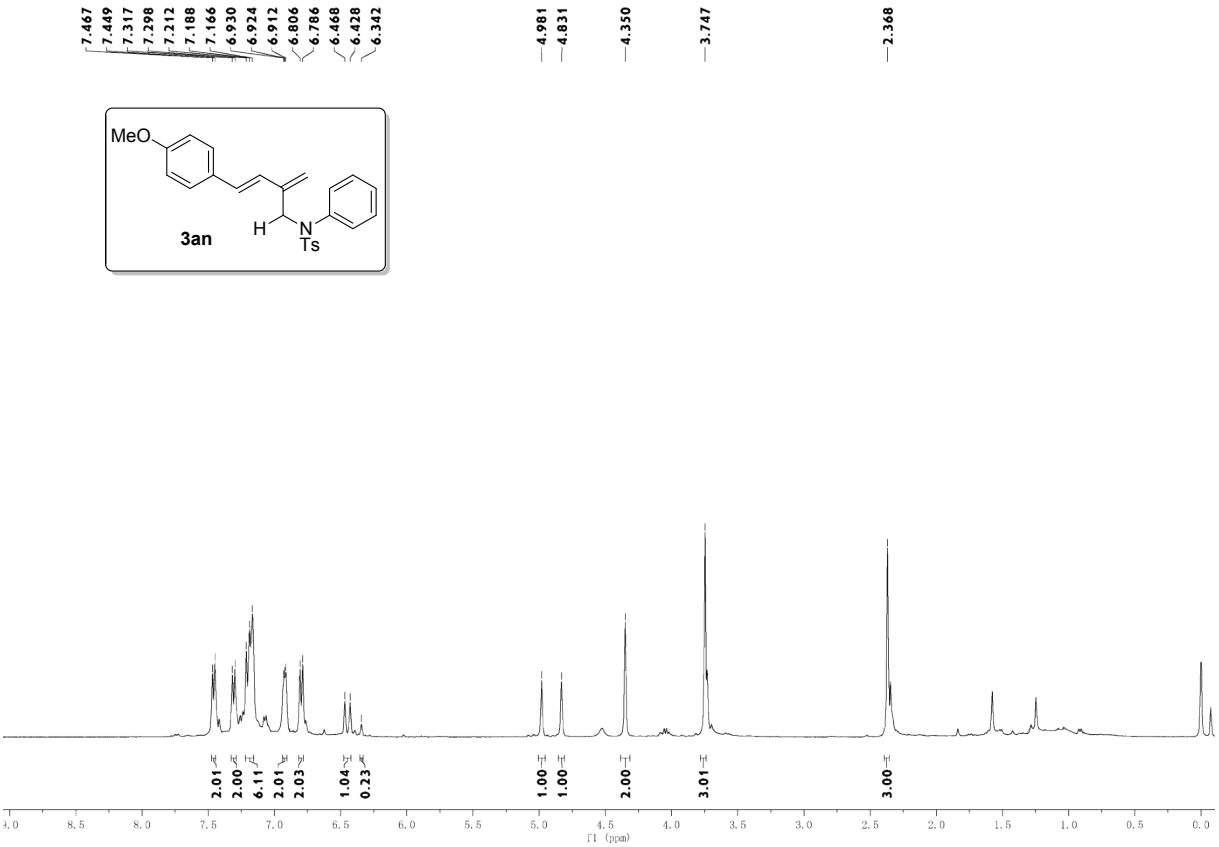

143.649
141.411
140.050
138.339
134.139
129.481
127.938
124.798
118.156
77.379
77.061
76.744
54.196
21.614
Cl
H
N
Ts
3ak
f1 (ppm)

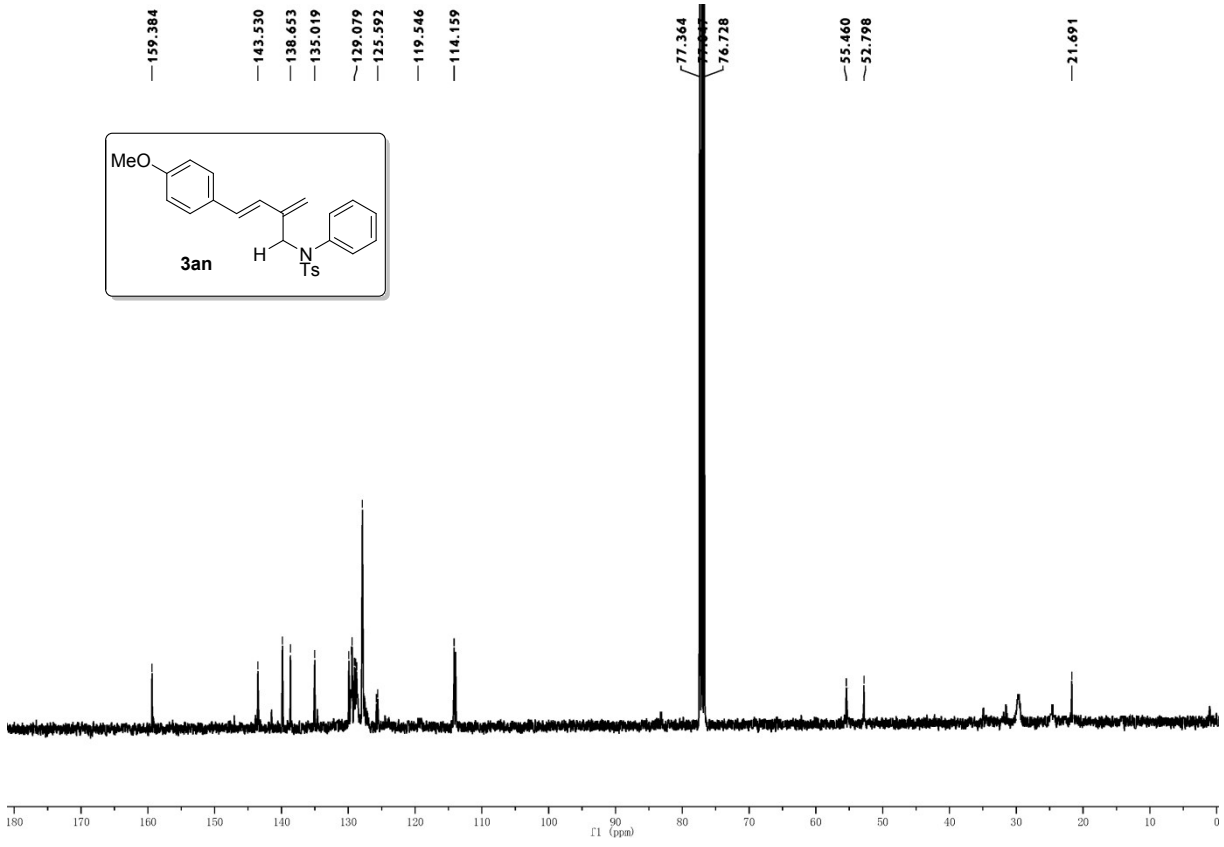

7.401
7.382
7.231
7.224
7.219
7.186
7.168
7.132
7.114
7.099
6.707
6.689
5.168
4.943
4.509
2.361
Cl
H
N
Ts
3al
2.04
3.03
3.02
2.98
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

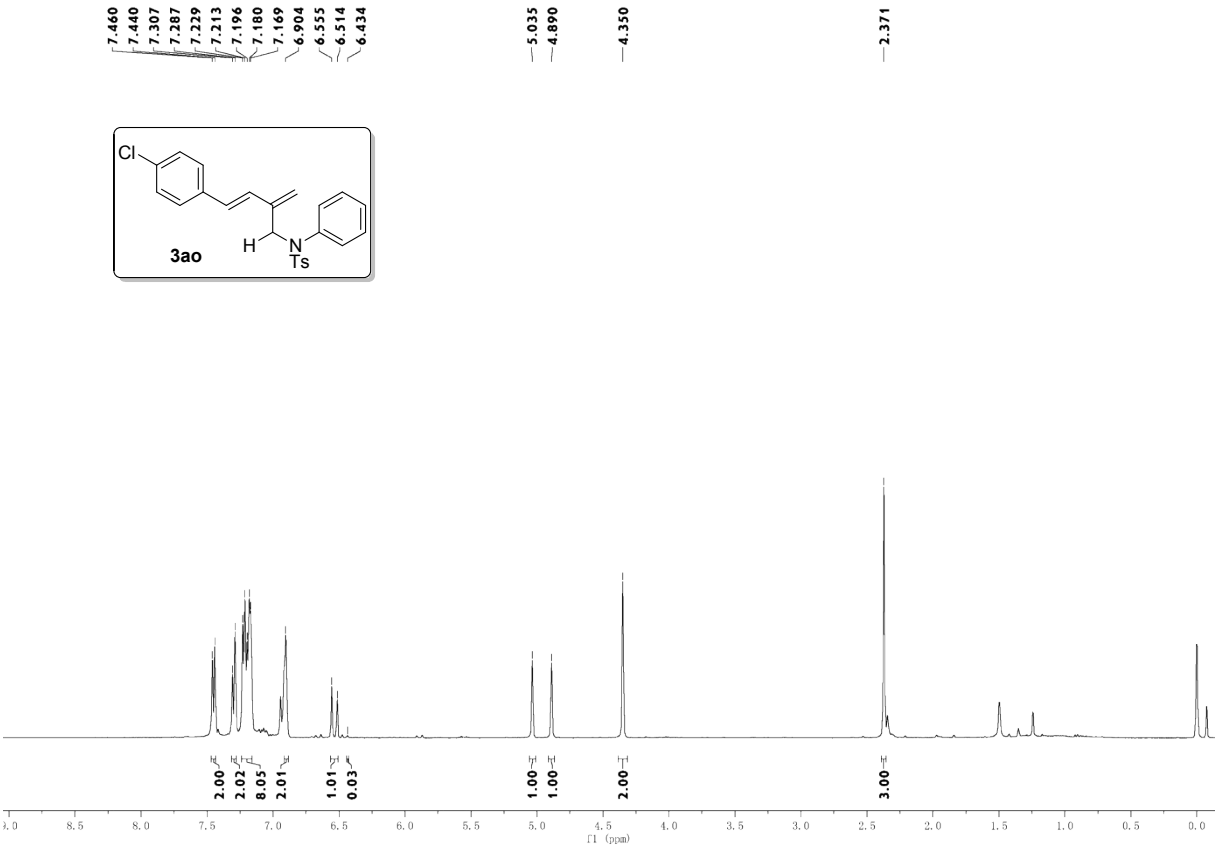

143.611
141.495
136.522
133.771
129.091
128.735
127.868
117.566
77.353
76.717
54.254
21.507
Cl
H
N
Ts
3al
f1 (ppm)

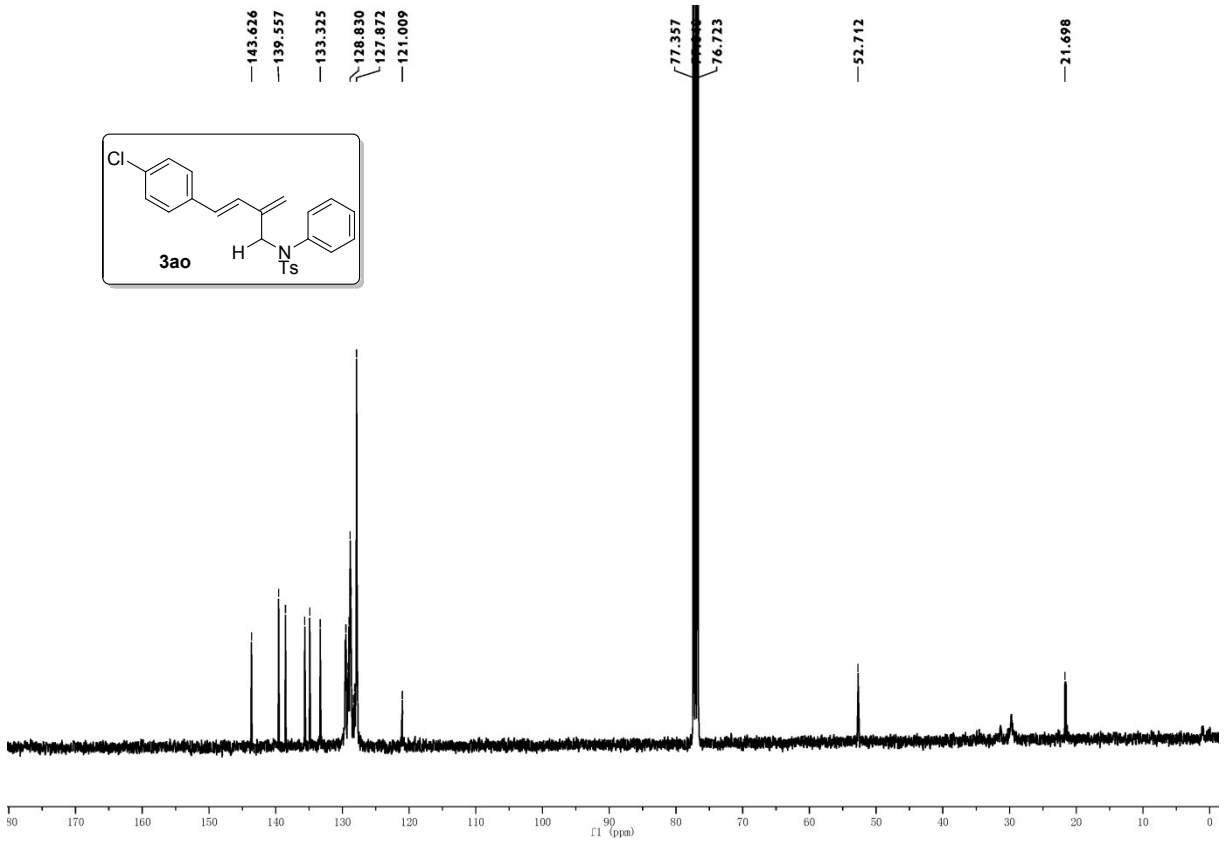

Cl
Cl
H
N
Ts
3am
2.00
1.07
7.01
2.01
1.00
1.02
2.00
3.01
f1 (ppm)

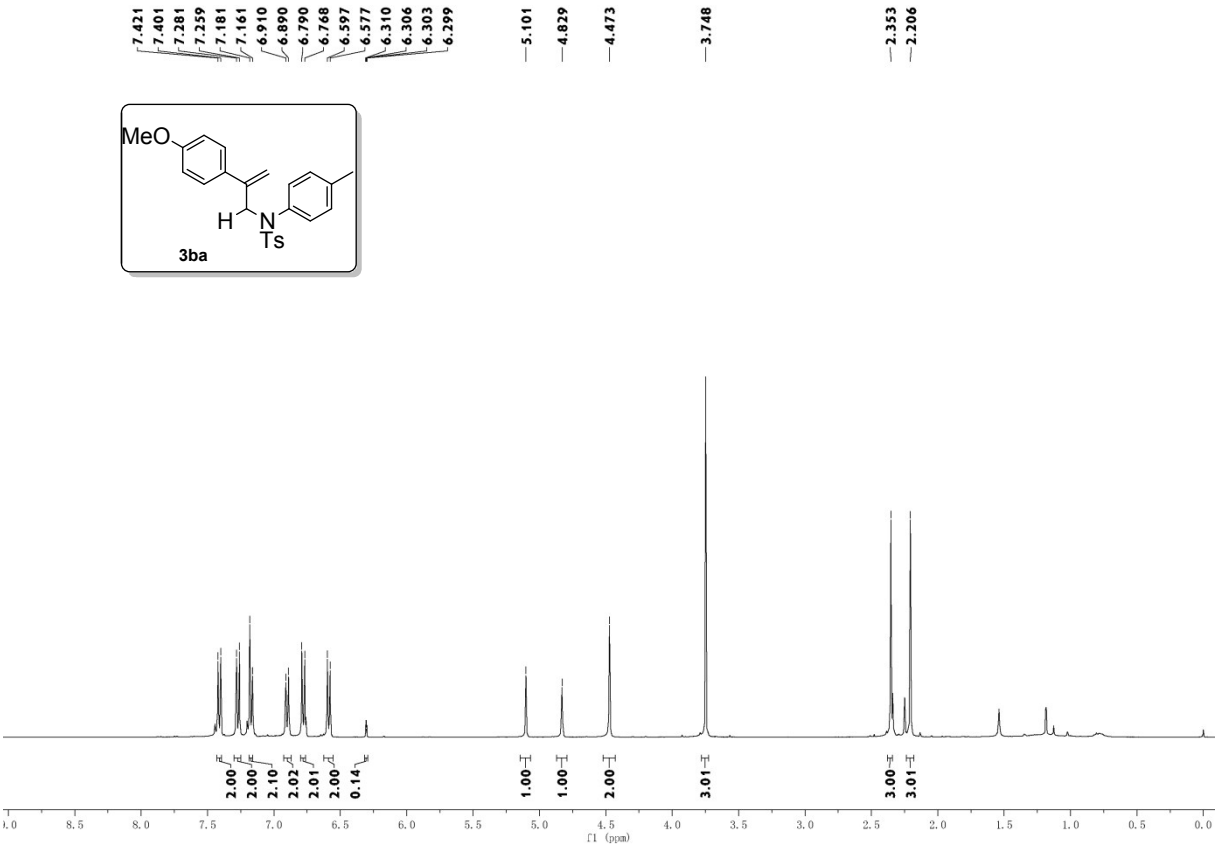

142.64
128.47
127.92
126.75
124.76
117.50
76.27
75.95
75.63
53.01
20.43
Cl
Cl
H
N
Ts
3am
f1 (ppm)

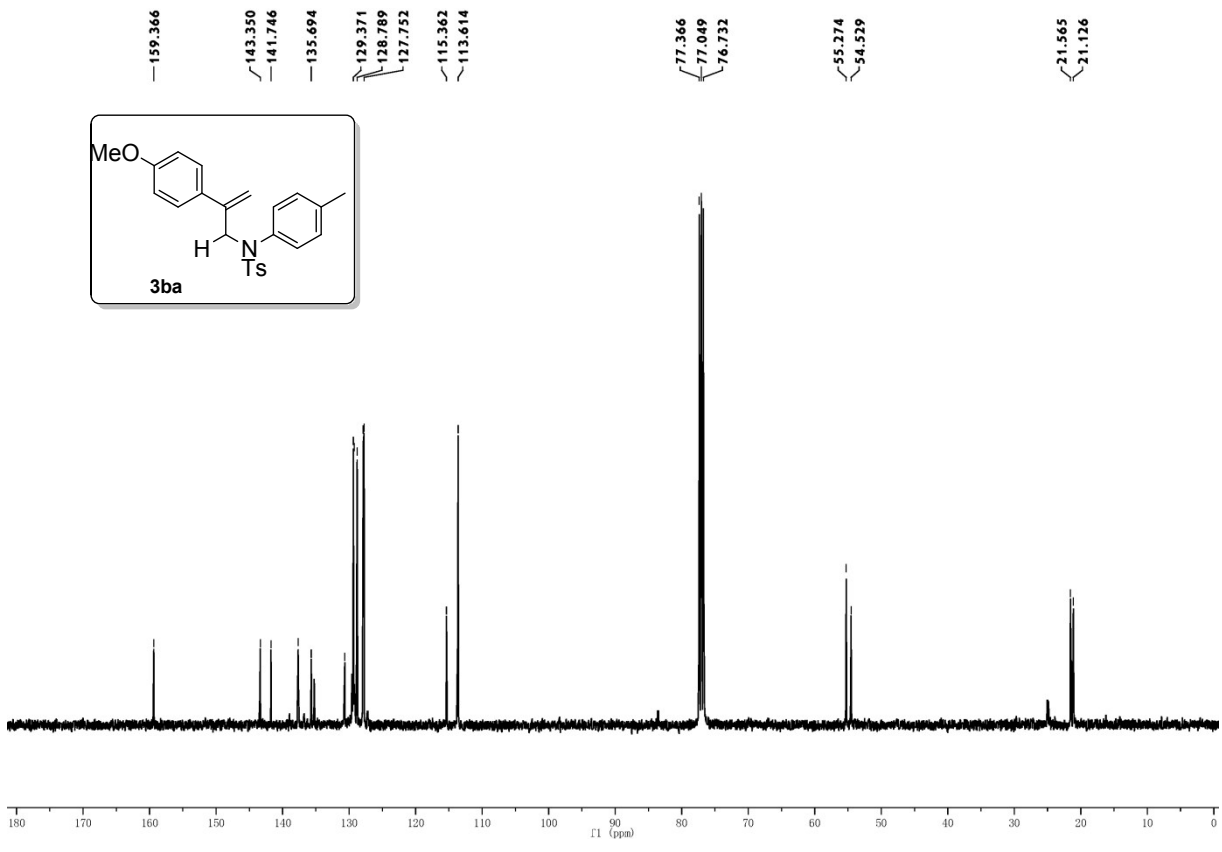

7.467
7.449
7.317
7.298
7.212
7.188
7.166
6.930
6.924
6.912
6.806
6.786
6.468
6.428
6.342
4.981
4.831
4.350
3.747
2.368
MeO
H
N
Ts
3an
2.01
2.00
6.11
2.01
2.03
1.04
0.23
1.00
1.00
2.00
3.01
3.00
f1 (ppm)

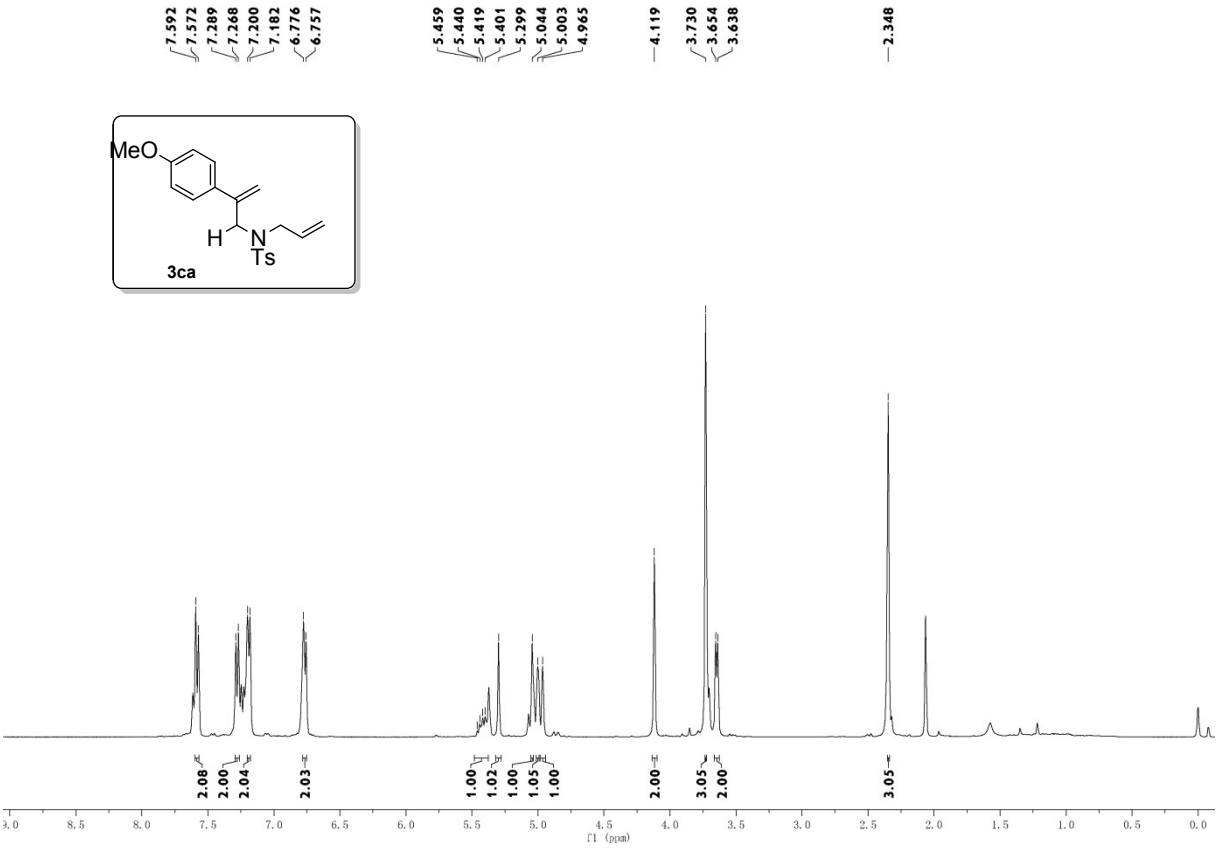

159.384
143.530
138.653
135.019
129.079
125.592
119.546
114.159
77.364
76.728
55.460
52.798
21.691
MeO
H
N
Ts
3an
f1 (ppm)

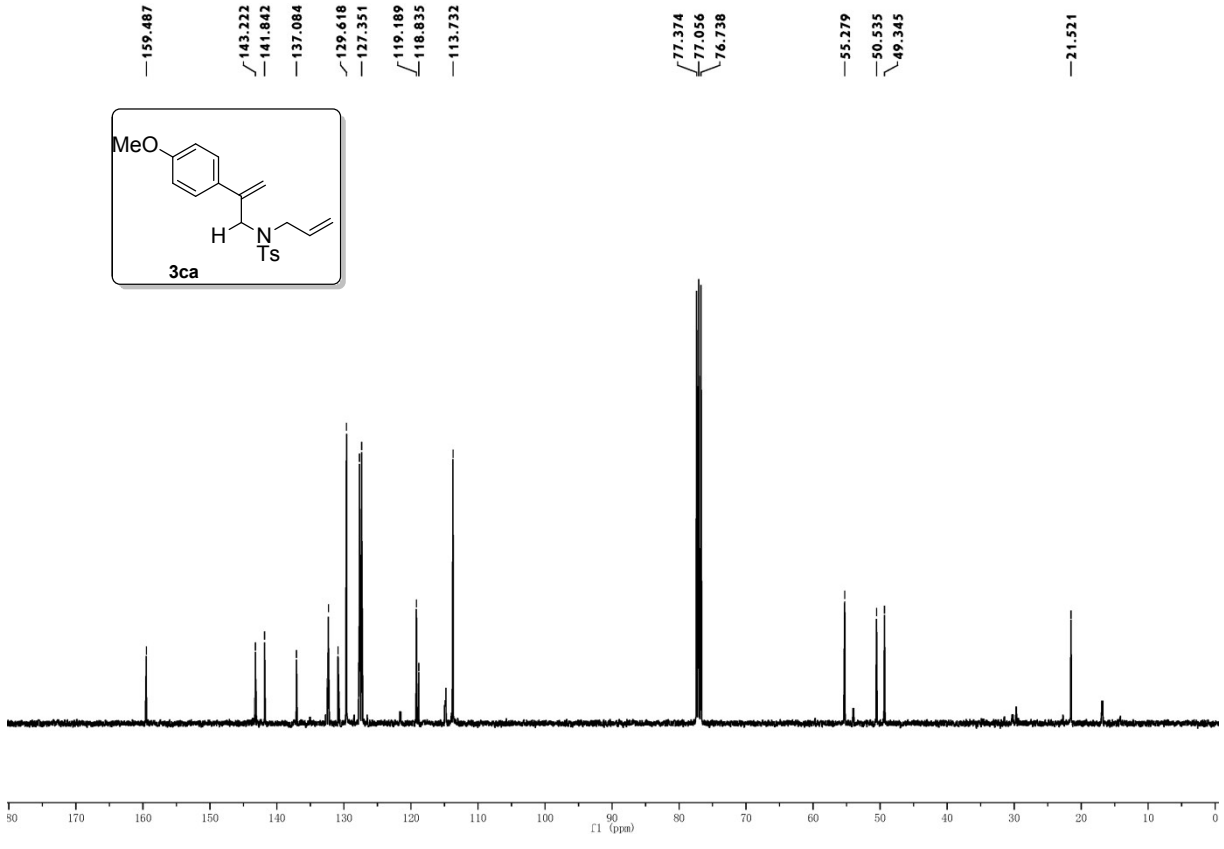

7.460
7.440
7.307
7.287
7.229
7.213
7.196
7.180
7.169
6.904
6.555
6.514
6.434
5.035
4.890
4.350
2.371
Cl
H
N
Ts
3ao
2.00
2.02
8.05
2.01
1.01
0.03
1.00
1.00
2.00
3.00
f1 (ppm)

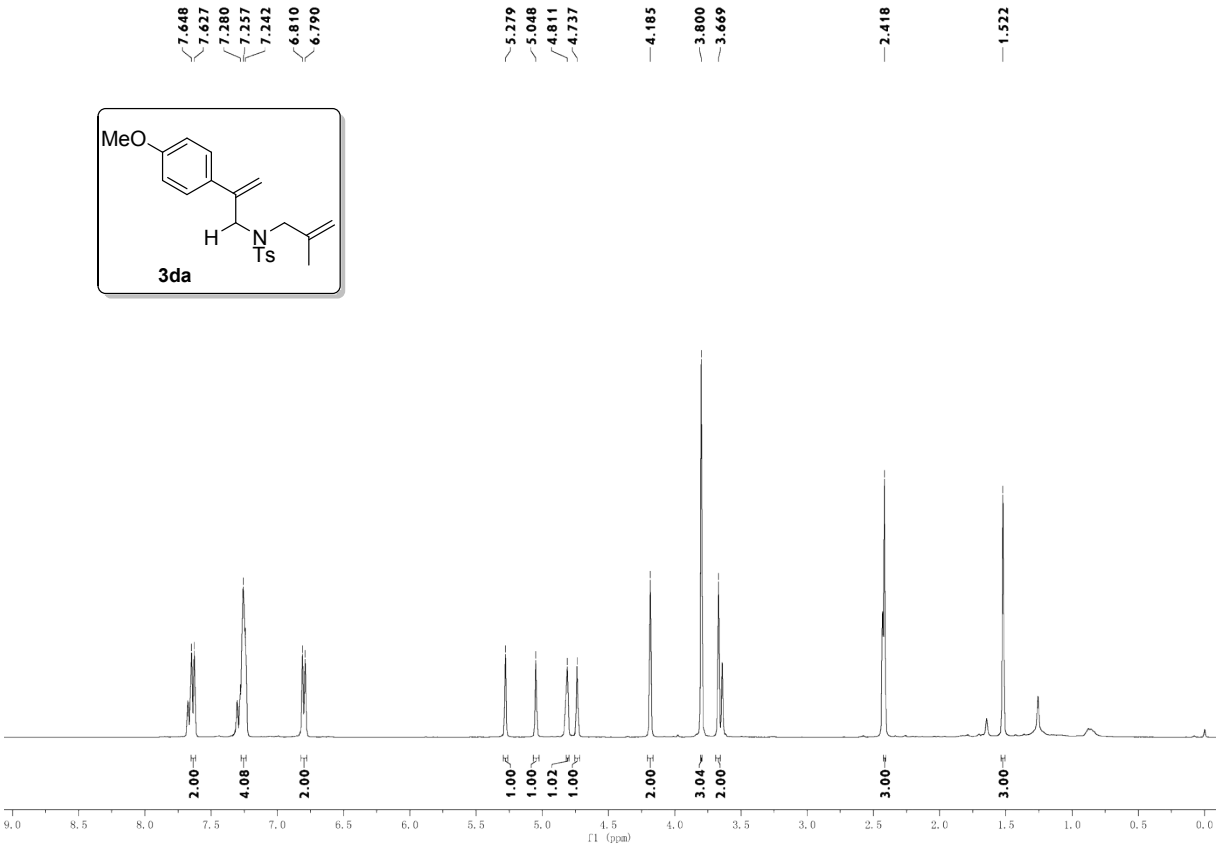

143.626
139.557
133.325
128.830
127.872
121.009
77.357
76.723
52.712
21.698
Cl
H
N
Ts
3ao
f1 (ppm)

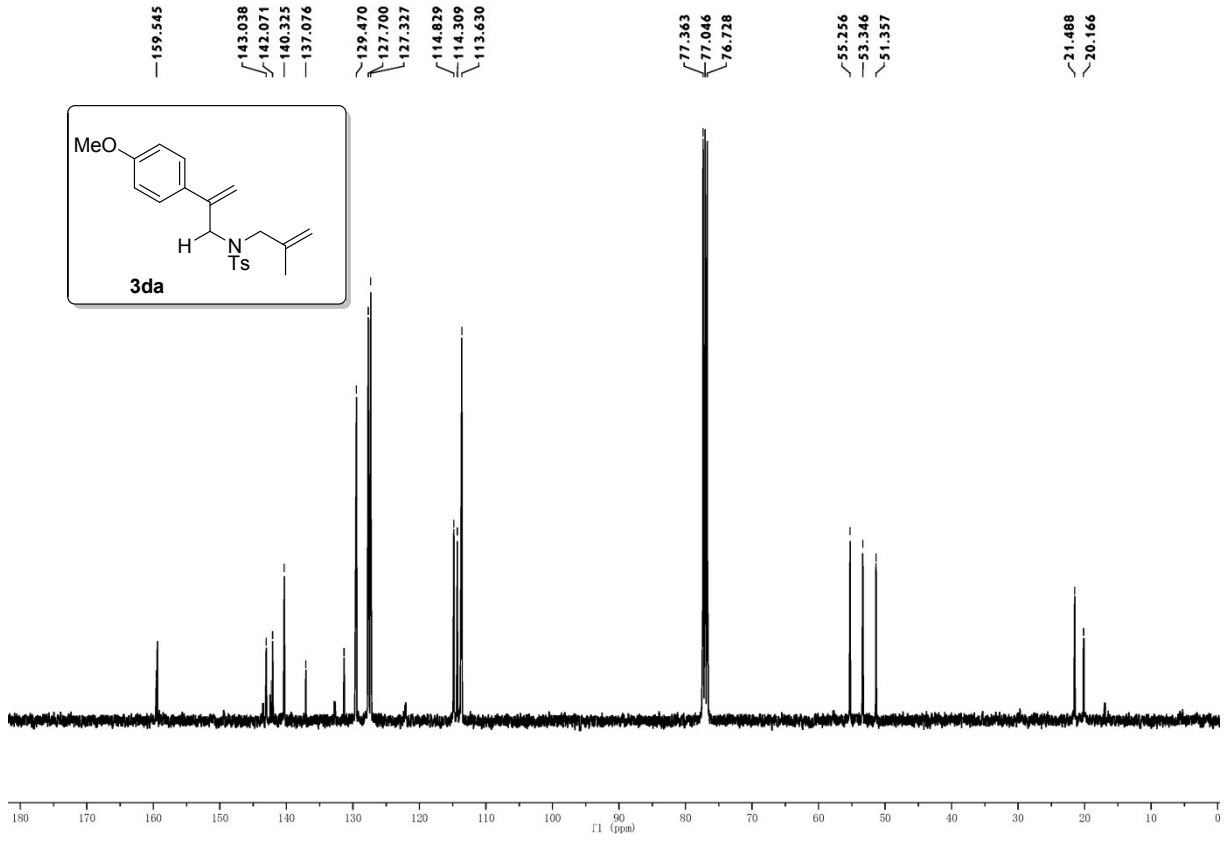

7.421
7.401
7.281
7.259
7.181
7.161
6.910
6.890
6.790
6.768
6.597
6.577
6.310
6.306
6.303
6.299
5.101
4.829
4.473
3.748
2.353
2.206
MeO
H
N
Ts
3ba
2.00
2.00
2.10
2.02
2.01
2.00
0.14
1.00
1.00
2.00
3.01
3.00
3.01
f1 (ppm)

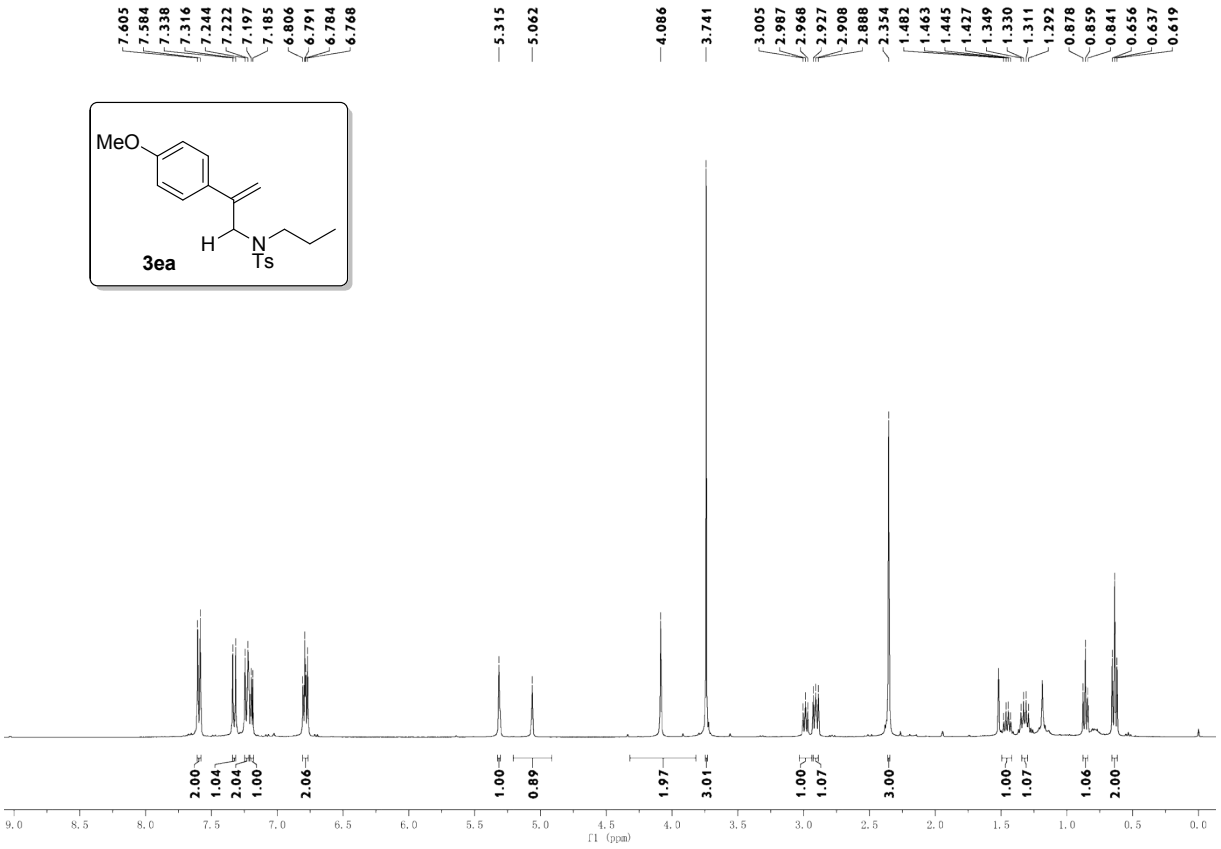

159.366
143.350
141.746
135.694
129.371
128.789
127.752
115.362
113.614
77.366
77.049
76.732
55.274
54.529
21.565
21.126
MeO
H
N
Ts
3ba
f1 (ppm)

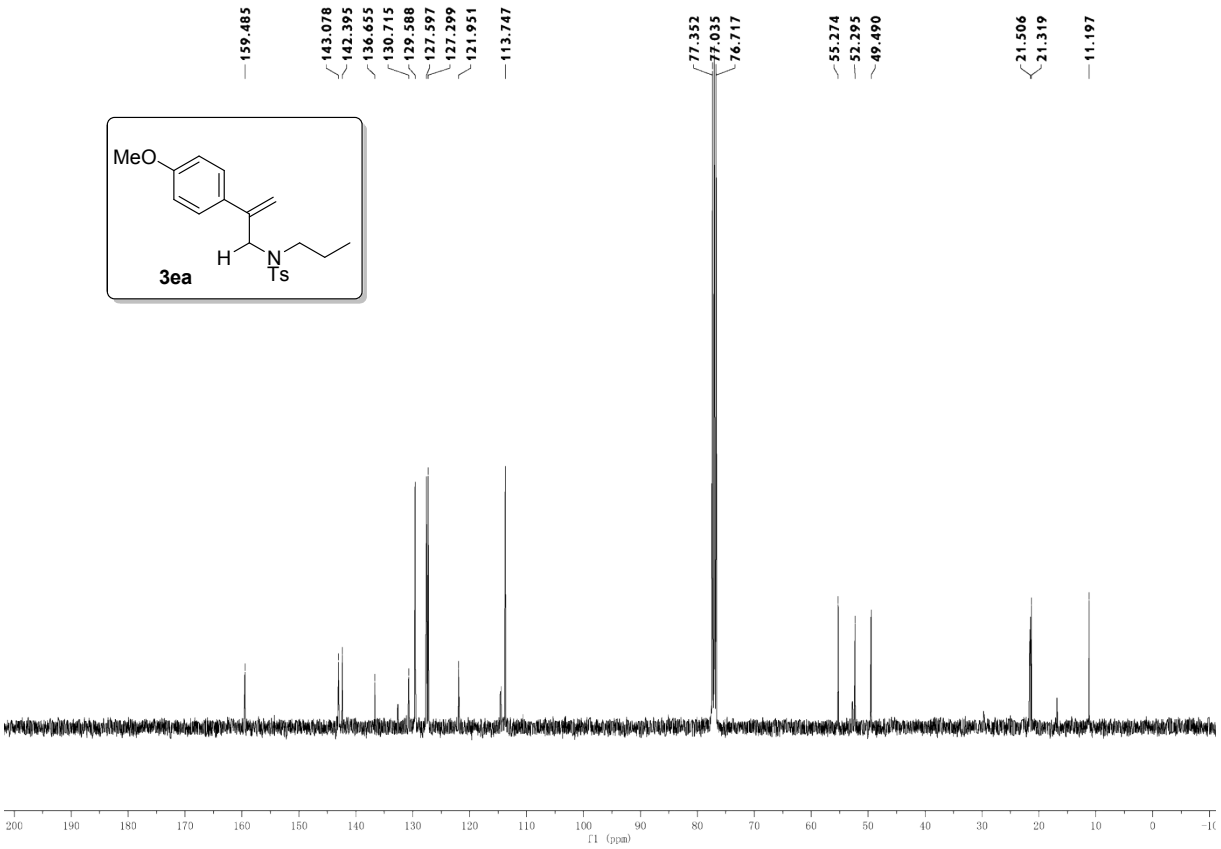

7.592
7.572
7.289
7.268
7.200
7.182
6.776
6.757
5.459
5.440
5.419
5.401
5.299
5.044
5.003
4.965
4.119
3.730
3.654
3.638
2.348
MeO
H
N
Ts
3ca
2.08
2.00
2.04
2.03
1.00
1.02
1.00
1.05
1.00
2.00
3.05
2.00
3.05
f1 (ppm)

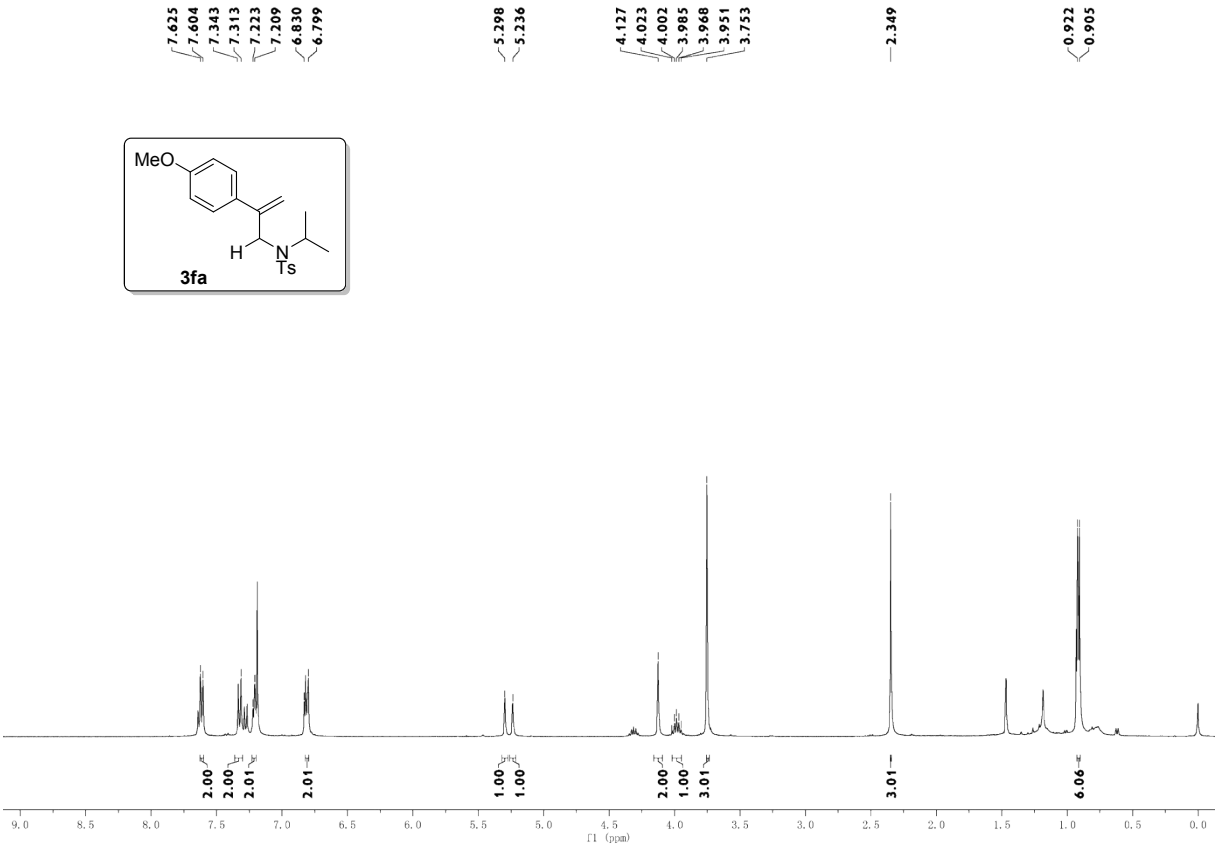

159.487
143.222
141.842
137.084
129.618
127.351
119.189
118.835
113.732
77.374
77.056
76.738
55.279
50.535
49.345
21.521
MeO
H
N
Ts
3ca
f1 (ppm)

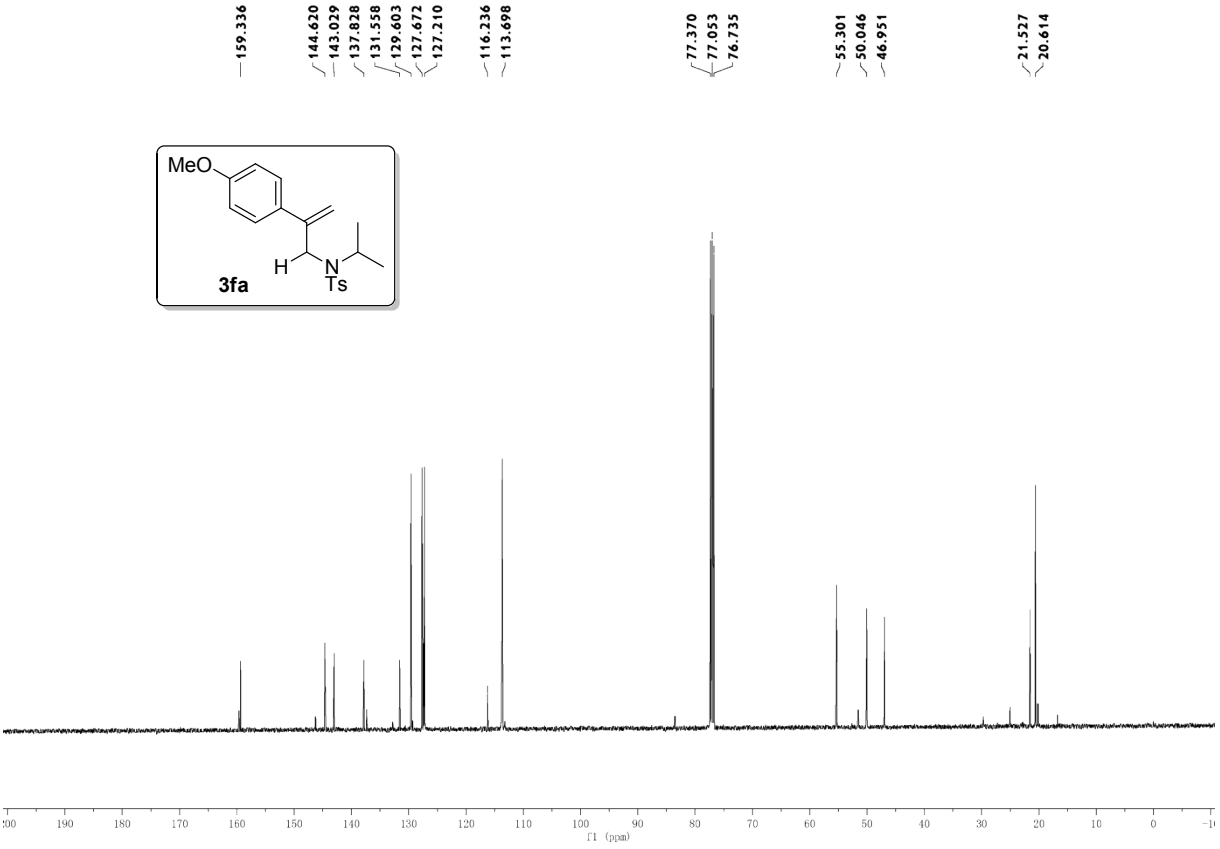

7.648
7.627
7.280
7.257
7.242
6.810
6.790
5.279
5.048
4.811
4.737
4.185
3.800
3.669
2.418
1.522
MeO
H
N
Ts
3da
2.00
4.08
2.00
1.00
1.00
1.02
1.00
2.00
3.04
2.00
3.00
3.00
f1 (ppm)

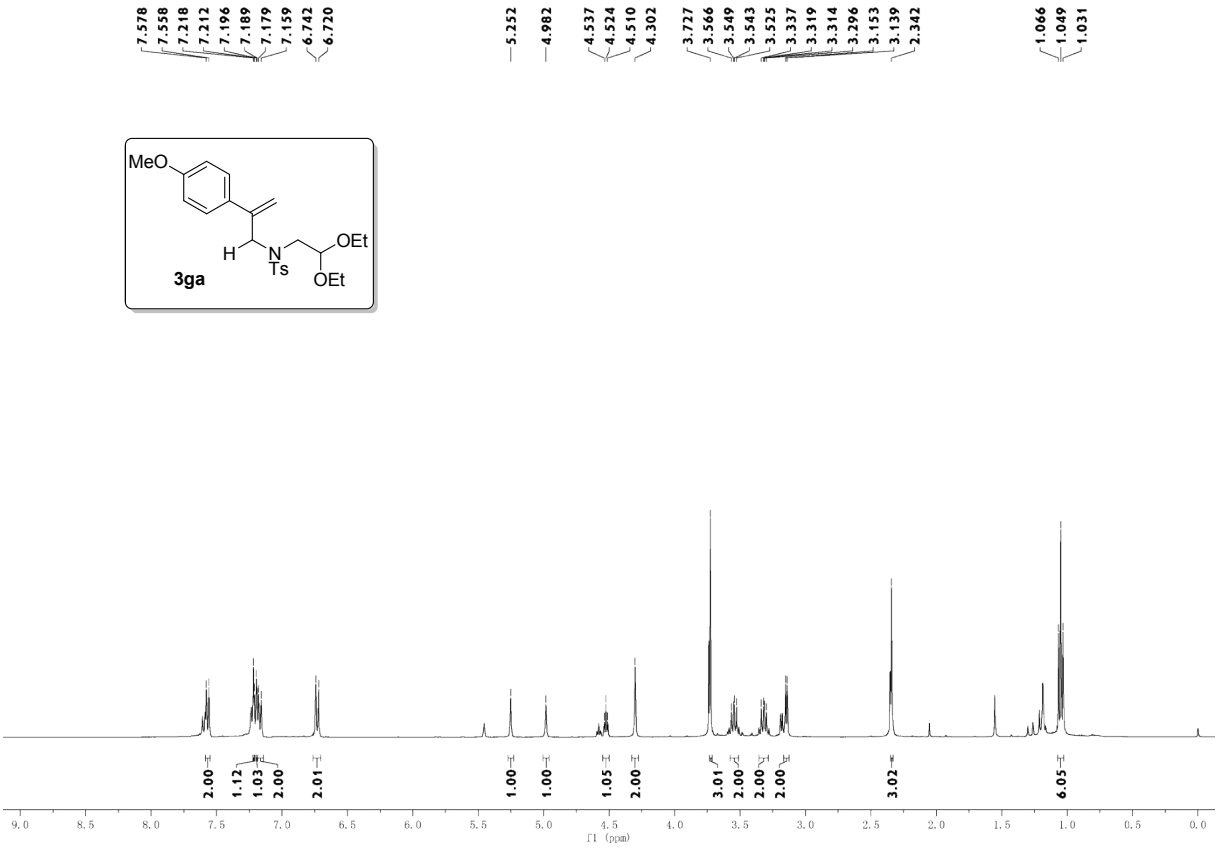

159.545
143.038
142.071
140.325
137.076
129.470
127.700
127.327
114.829
114.309
113.630
77.363
77.046
76.728
55.256
53.346
51.357
21.488
20.166
MeO
H
N
Ts
3da
f1 (ppm)

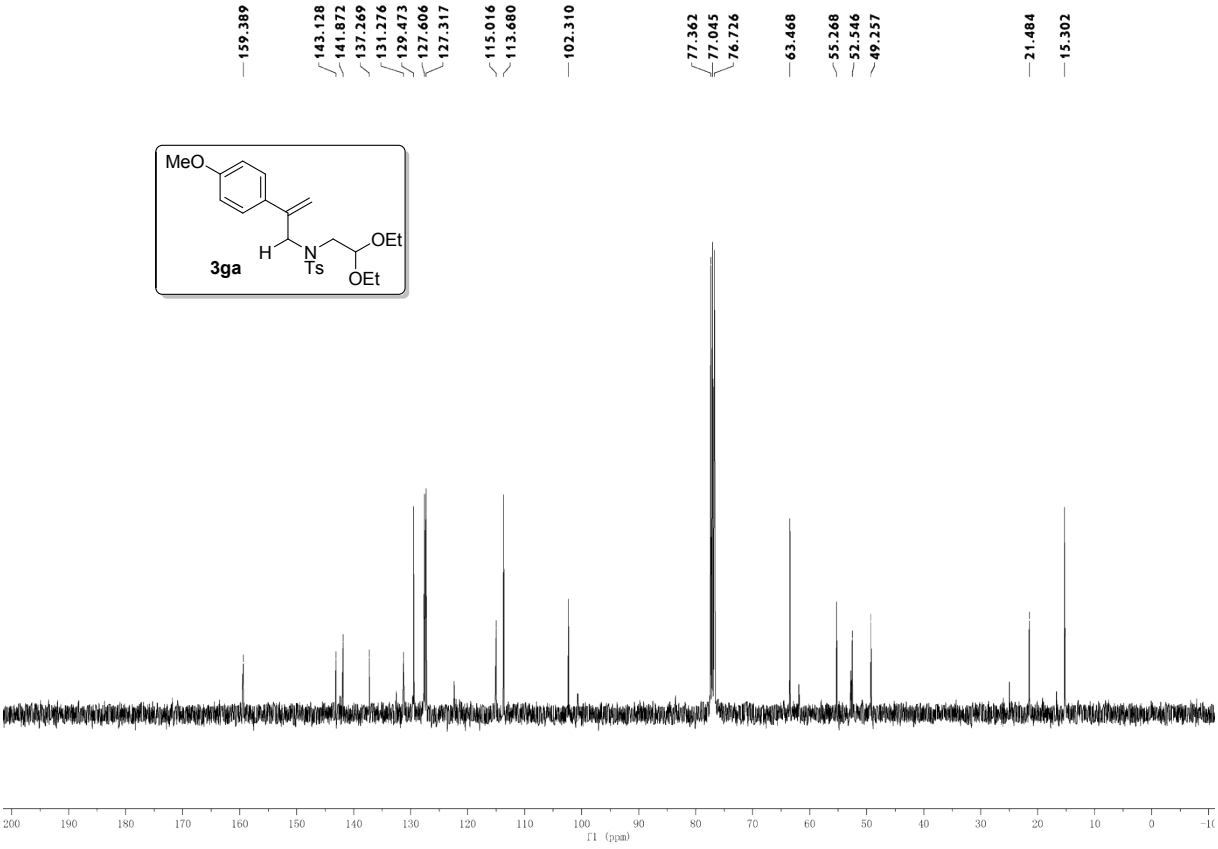

7.605
7.584
7.338
7.316
7.244
7.222
7.197
7.185
6.806
6.791
6.784
6.768
5.315
5.062
4.086
3.741
3.005
2.987
2.968
2.927
2.908
2.888
2.354
1.482
1.463
1.445
1.427
1.349
1.330
1.311
1.292
0.878
0.859
0.841
0.656
0.637
0.619
MeO
H
N
Ts
3ea
2.00
1.04
2.04
1.00
2.06
1.00
0.89
1.97
3.01
1.00
1.07
3.00
1.00
1.07
1.06
2.00
f1 (ppm)

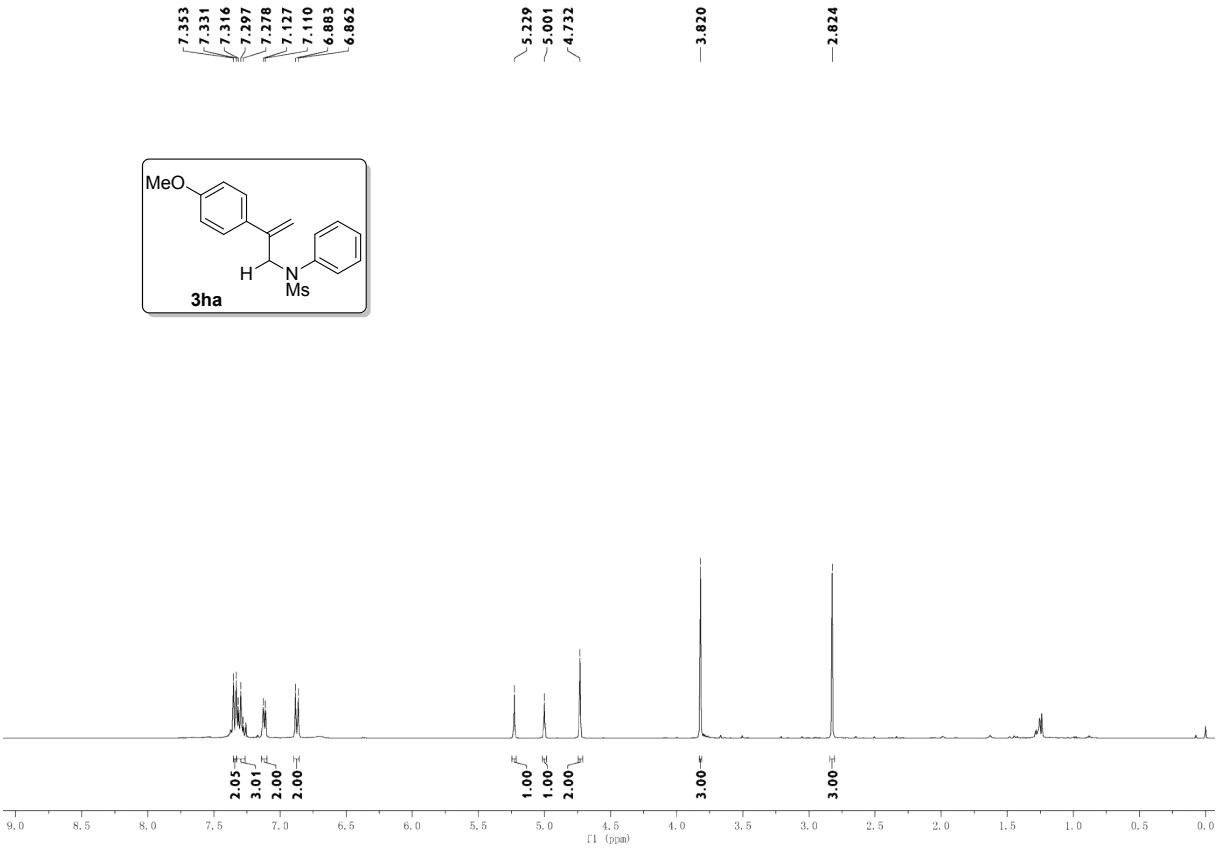

159.485
143.078
142.395
136.655
130.715
129.588
127.597
127.299
121.951
113.747
77.352
77.035
76.717
55.274
52.295
49.490
21.506
21.319
11.197
MeO
H
N
Ts
3ea
f1 (ppm)

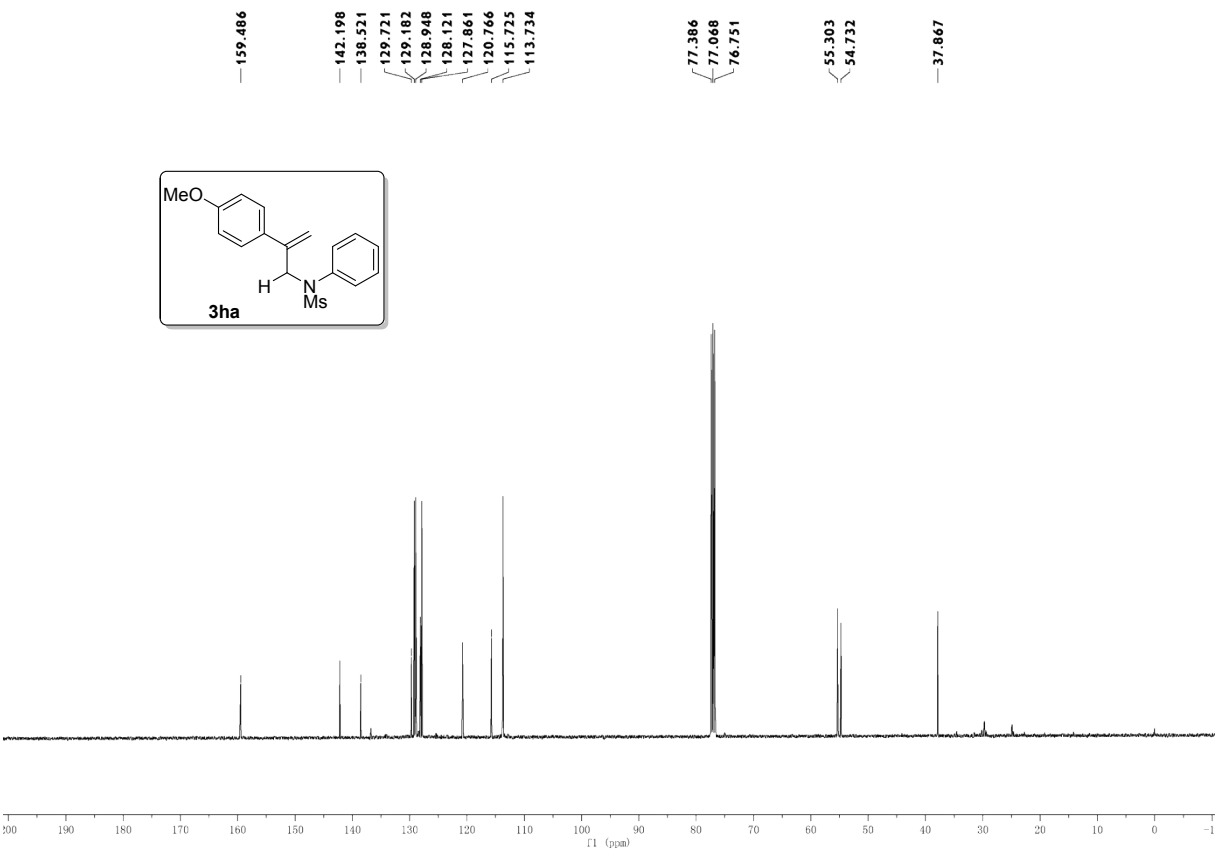

7.625
7.604
7.343
7.313
7.223
7.209
6.830
6.799
5.298
5.236
4.127
4.023
4.002
3.985
3.968
3.951
3.753
2.349
0.922
0.905
MeO
H
N
Ts
3fa
2.00
2.00
2.01
2.01
1.00
1.00
2.00
1.00
3.01
3.01
6.06
f1 (ppm)

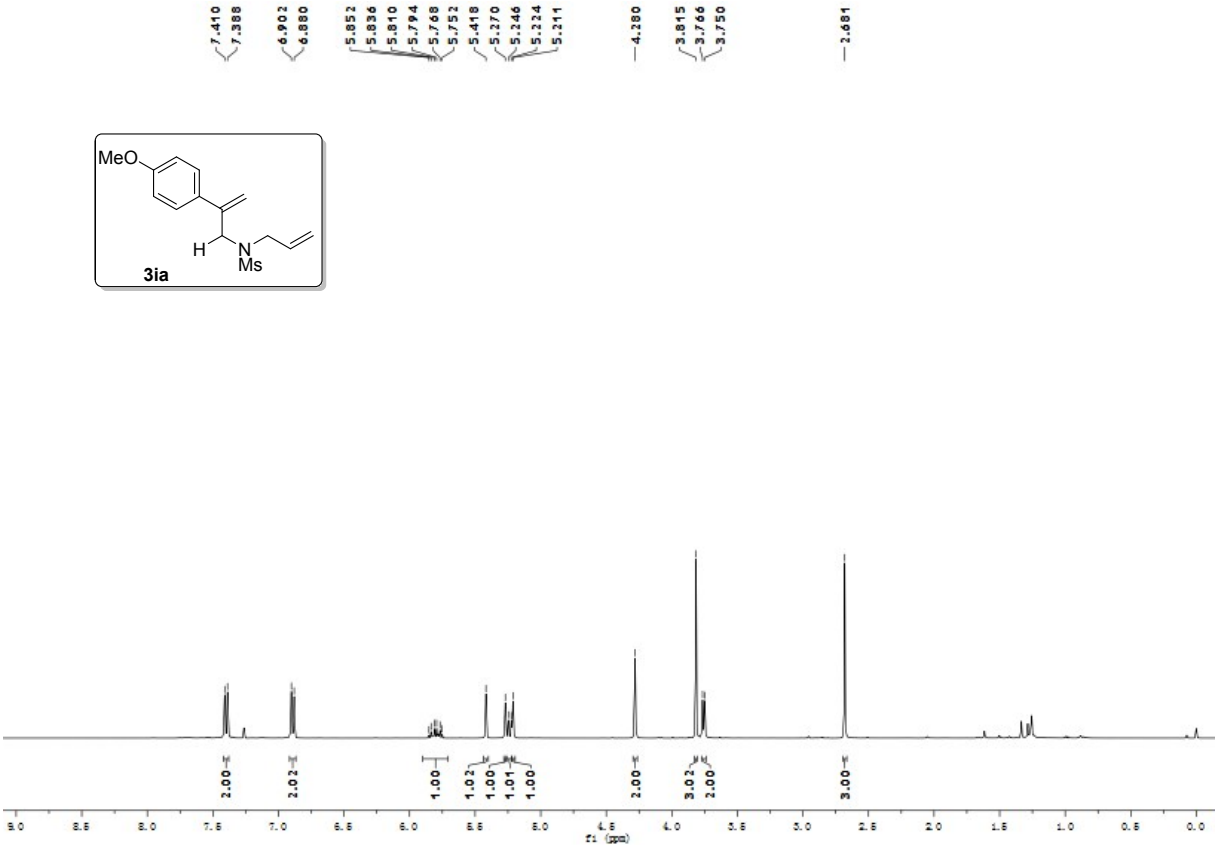

159.336
144.620
143.029
137.828
131.558
129.603
127.672
127.210
116.236
113.698
77.370
77.053
76.735
55.301
50.046
46.951
21.527
20.614
MeO
H
N
Ts
3fa
f1 (ppm)

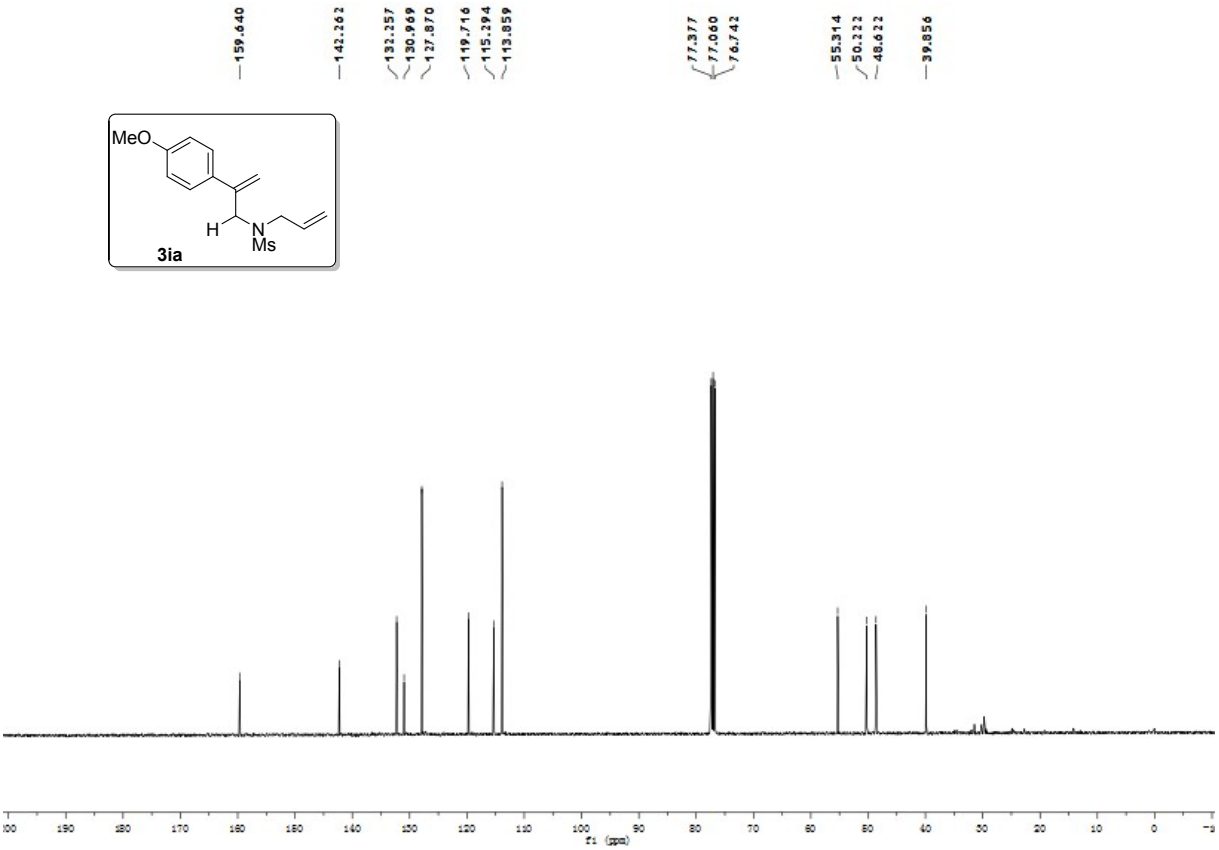

7.578
7.558
7.218
7.212
7.196
7.189
7.179
7.159
6.742
6.720
5.252
4.982
4.537
4.524
4.510
4.302
3.727
3.566
3.549
3.543
3.525
3.337
3.319
3.314
3.296
3.153
3.139
2.342
1.066
1.049
1.031
MeO
H
N
Ts
OEt
OEt
3ga
2.00
1.12
1.03
2.00
2.01
1.00
1.00
1.05
2.00
3.01
2.00
2.00
2.00
3.02
6.05
f1 (ppm)

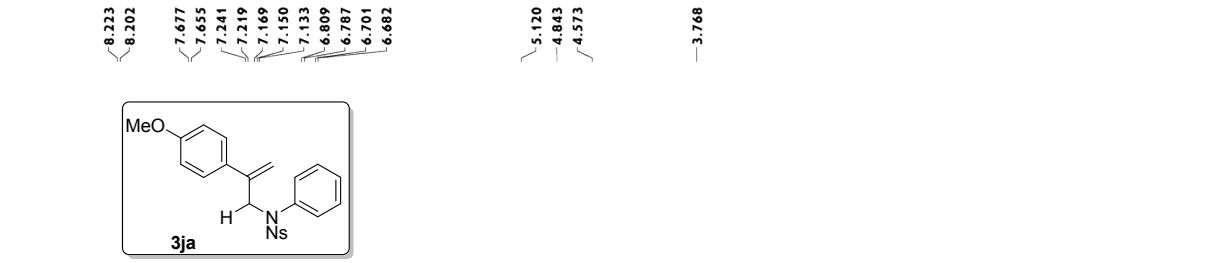

159.389
143.128
141.872
137.269
131.276
129.473
127.606
127.317
115.016
113.680
102.310
77.362
77.045
76.726
63.468
55.268
52.546
49.257
21.484
15.302
MeO
H
N
Ts
OEt
OEt
3ga
f1 (ppm)

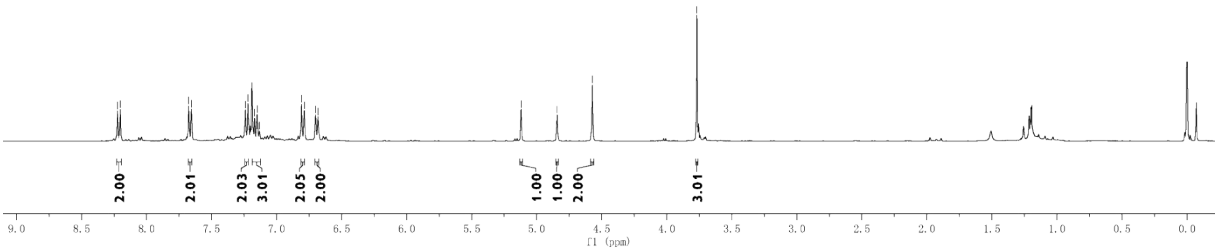

7.353
7.331
7.316
7.297
7.278
7.127
7.110
6.883
6.862
5.229
5.001
4.732
3.820
2.824
MeO
H
N
Ms
3ha
2.05
3.01
2.00
2.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

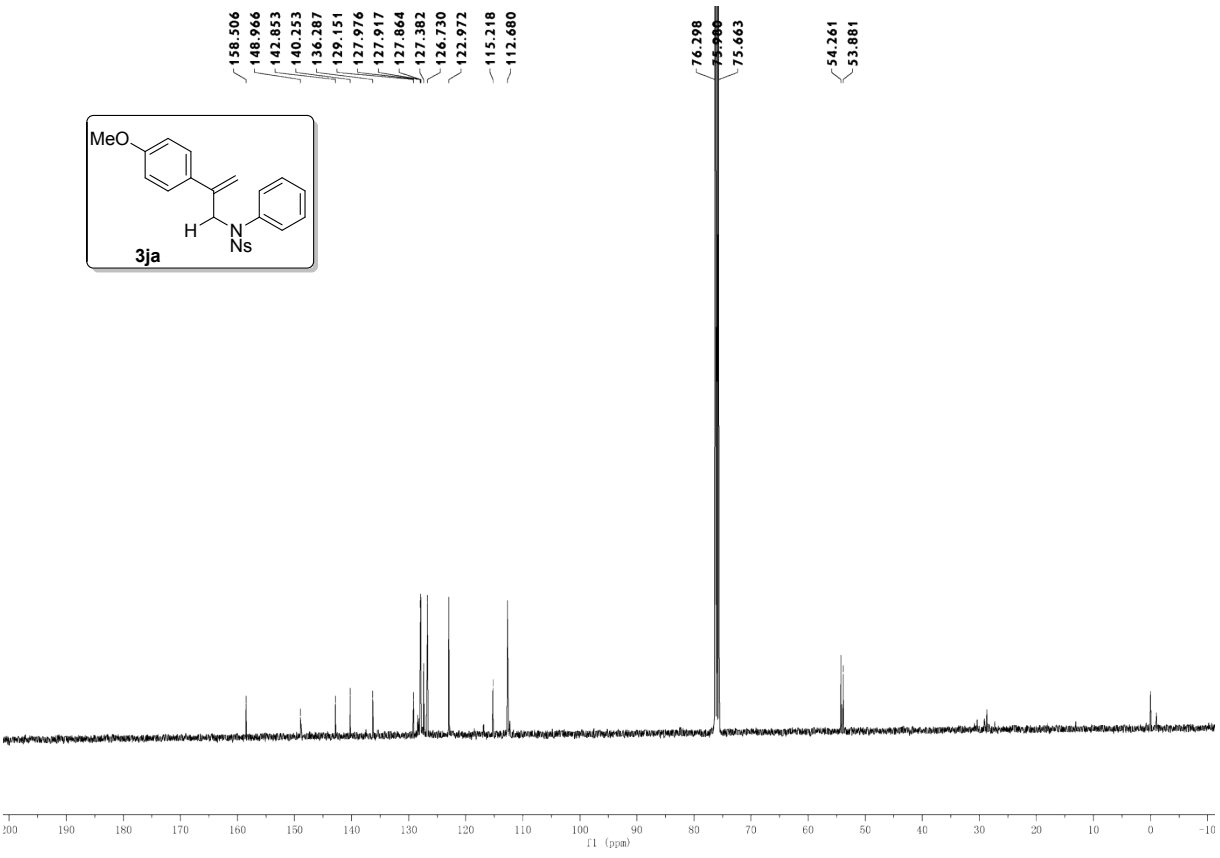

159.486
142.198
138.521
129.721
129.182
128.948
128.121
127.861
120.766
115.725
113.734
77.386
77.068
76.751
55.303
54.732
37.867
MeO
H
N
Ms
3ha
f1 (ppm)


7.410
7.388
6.902
6.880
5.852
5.836
5.810
5.794
5.768
5.752
5.418
5.270
5.246
5.224
5.211
4.280
3.815
3.766
3.750
2.681
MeO
H
N
Ms
3ia
2.00
2.02
1.00
1.02
1.00
1.01
1.00
2.00
3.02
2.00
3.00
f1 (ppm)

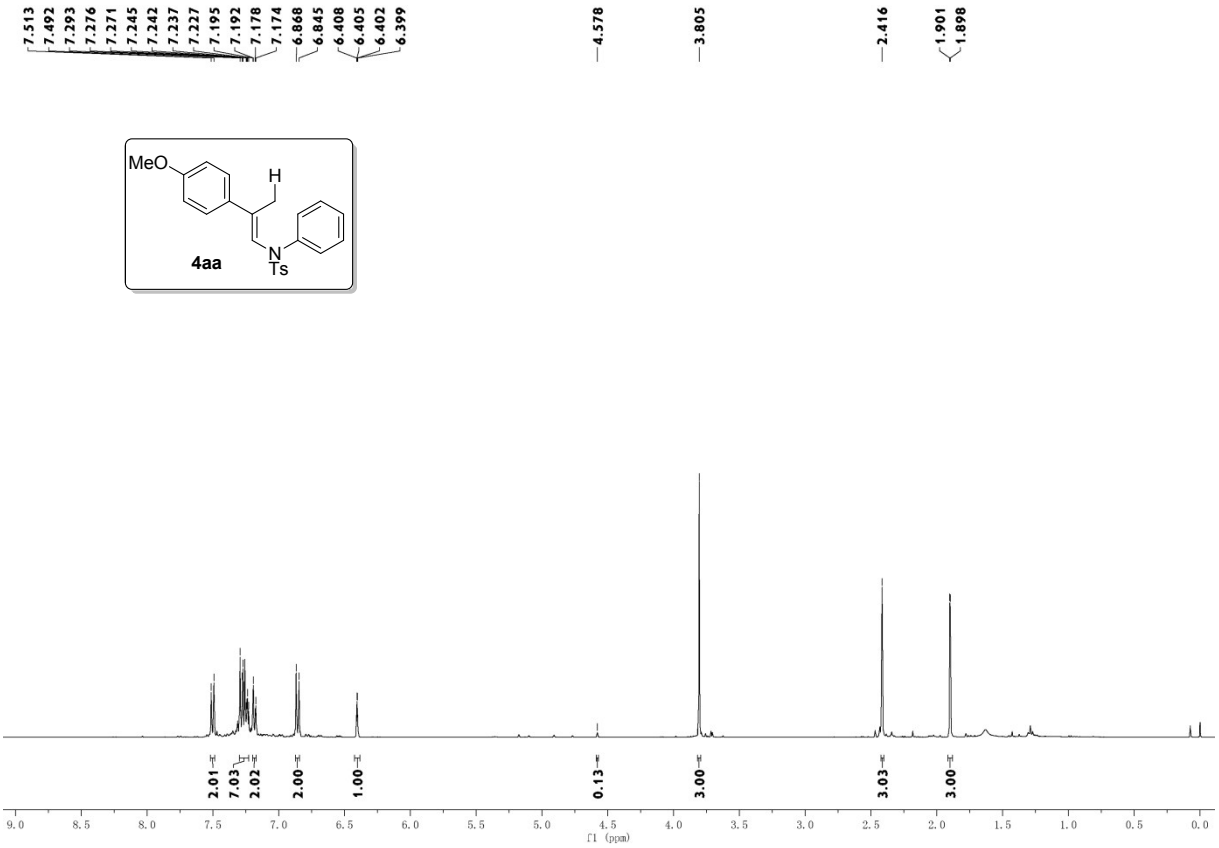

159.640
142.262
132.257
130.969
127.870
119.716
115.294
113.859
77.377
77.060
76.742
55.314
50.222
48.622
39.856
MeO
H
N
Ms
3ia
f1 (ppm)

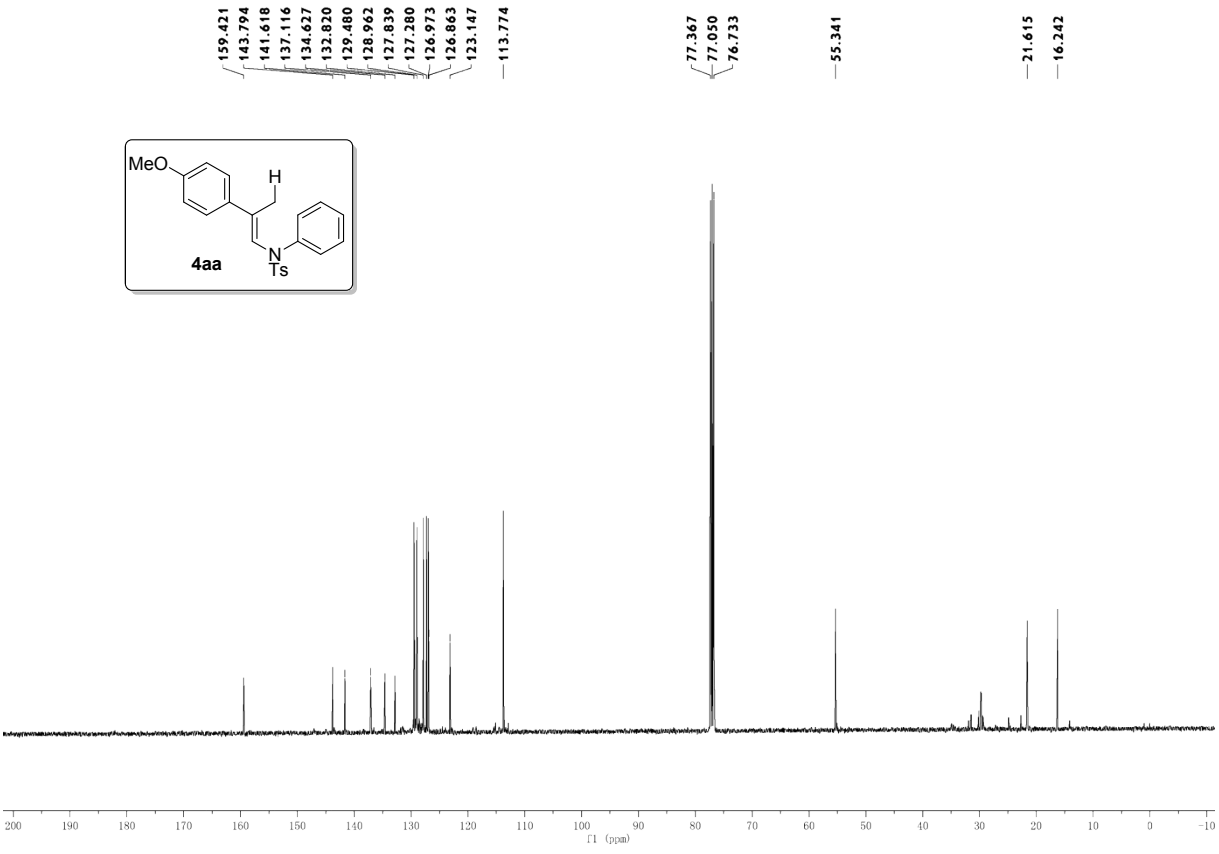

8.223
8.202
7.677
7.655
7.241
7.219
7.169
7.150
7.133
6.809
6.787
6.701
6.682
5.120
4.843
4.573
3.768
MeO
H
N
Ns
3ja

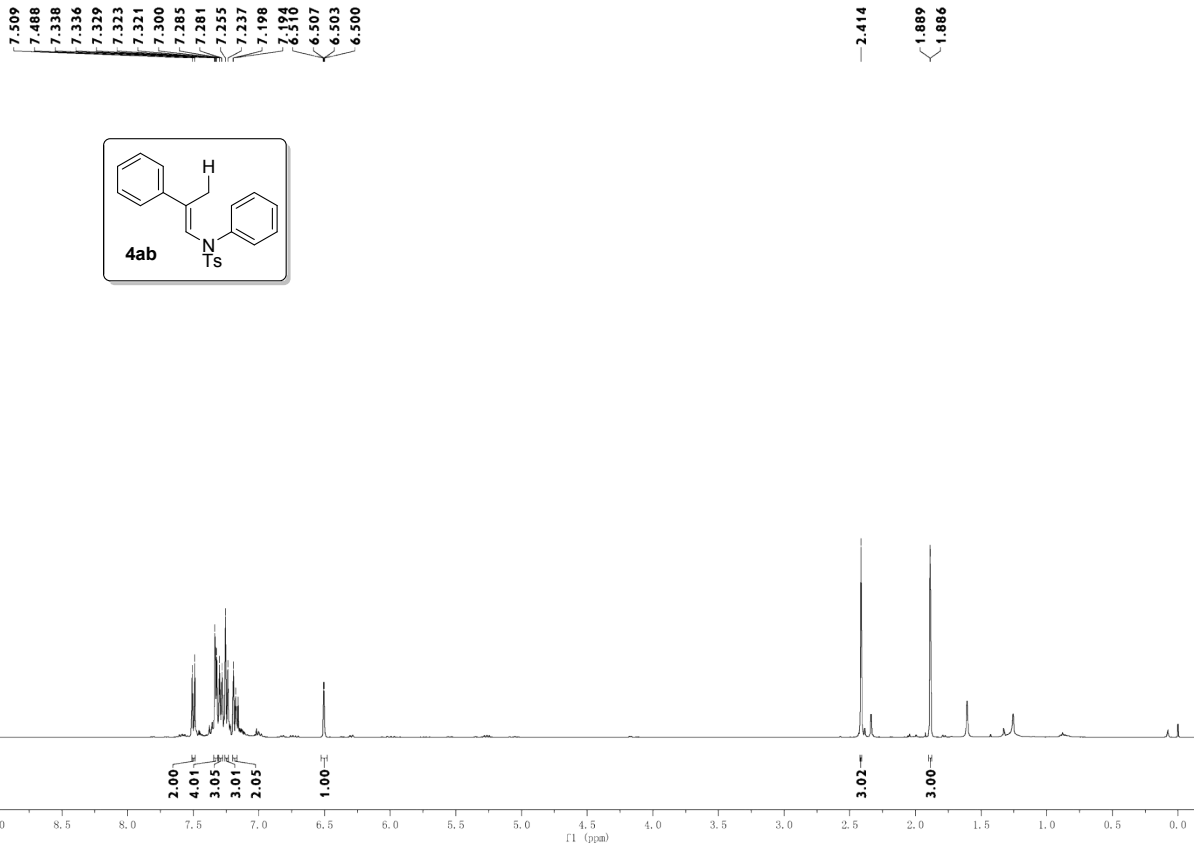

2.00
2.01
2.03
3.01
2.05
2.00
1.00
1.00
2.00
3.01
f1 (ppm)

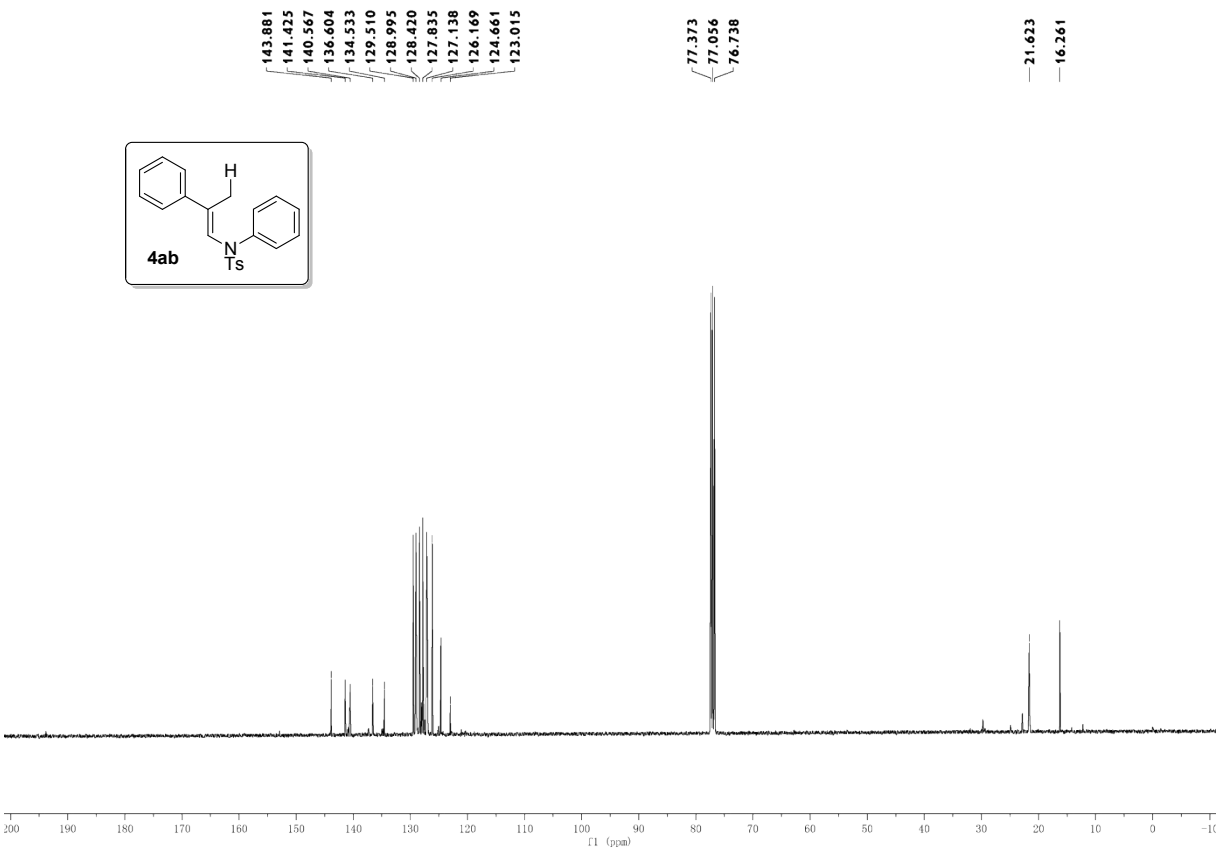

158.506
148.966
142.853
140.253
136.287
129.151
127.976
127.917
127.864
127.382
126.730
122.972
115.218
112.680
76.298
75.663
54.261
53.881
MeO
H
N
Ns
3ja
f1 (ppm)

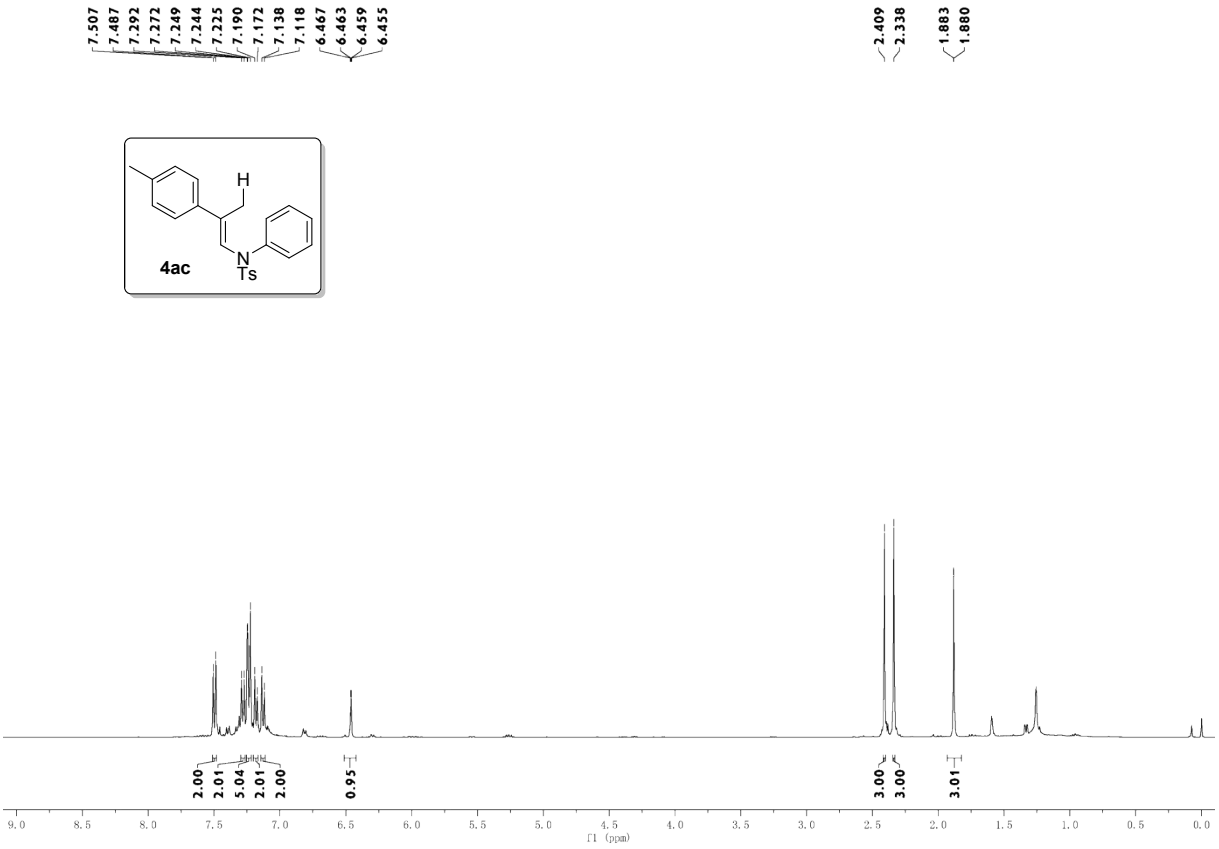
6. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR for enamines.

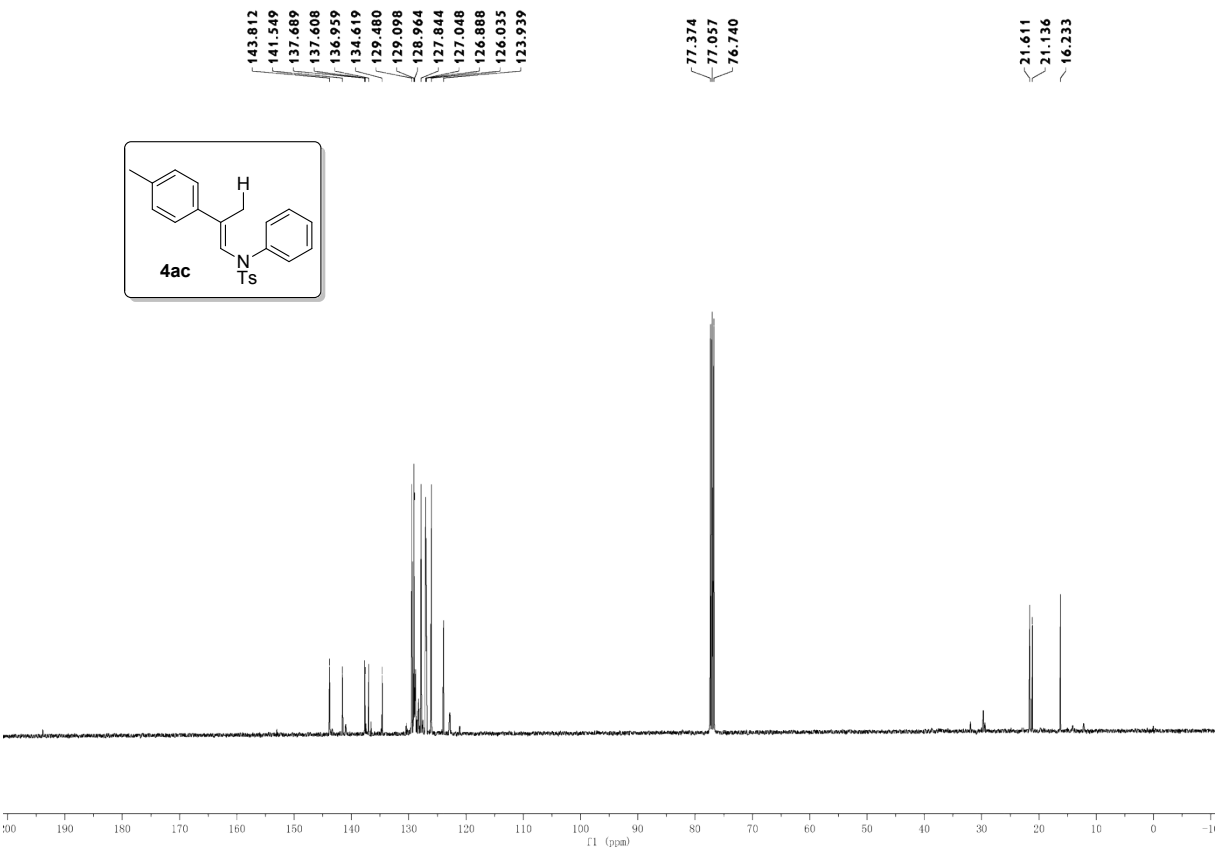


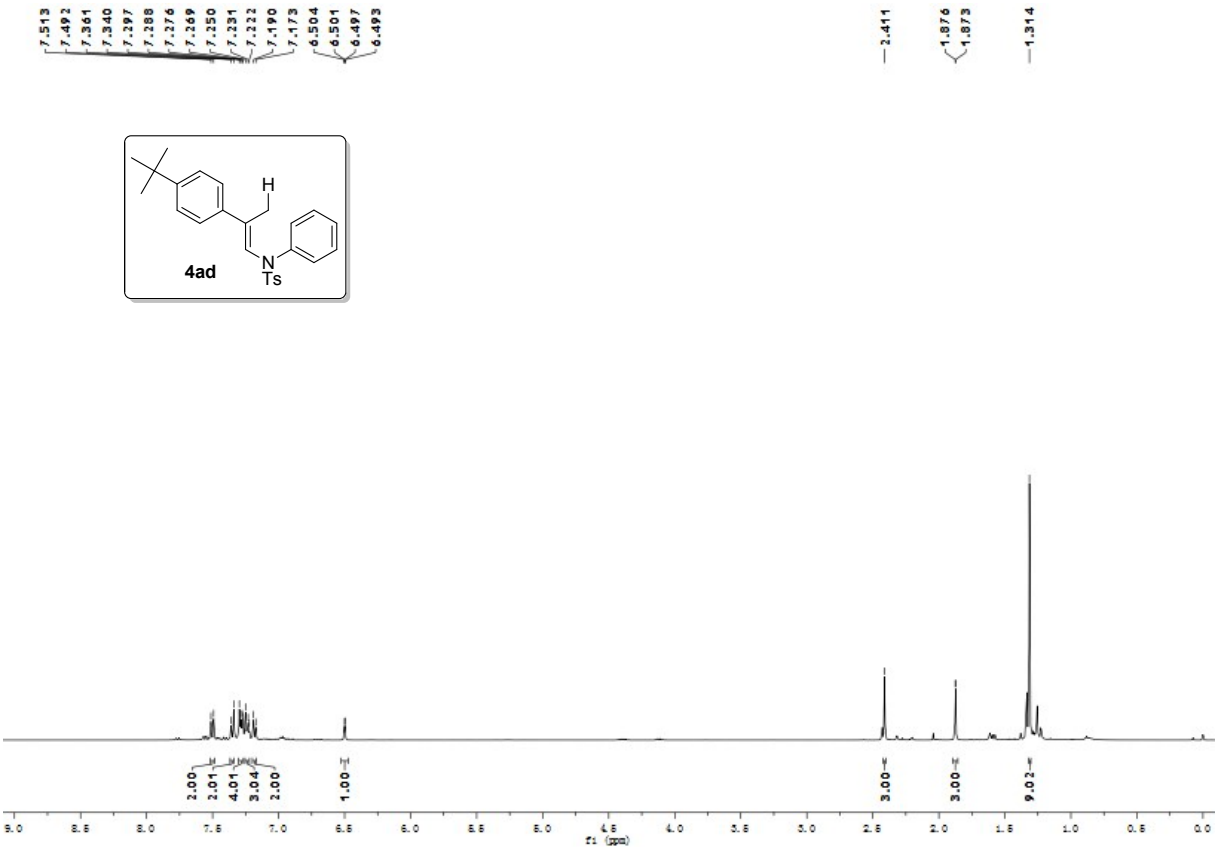


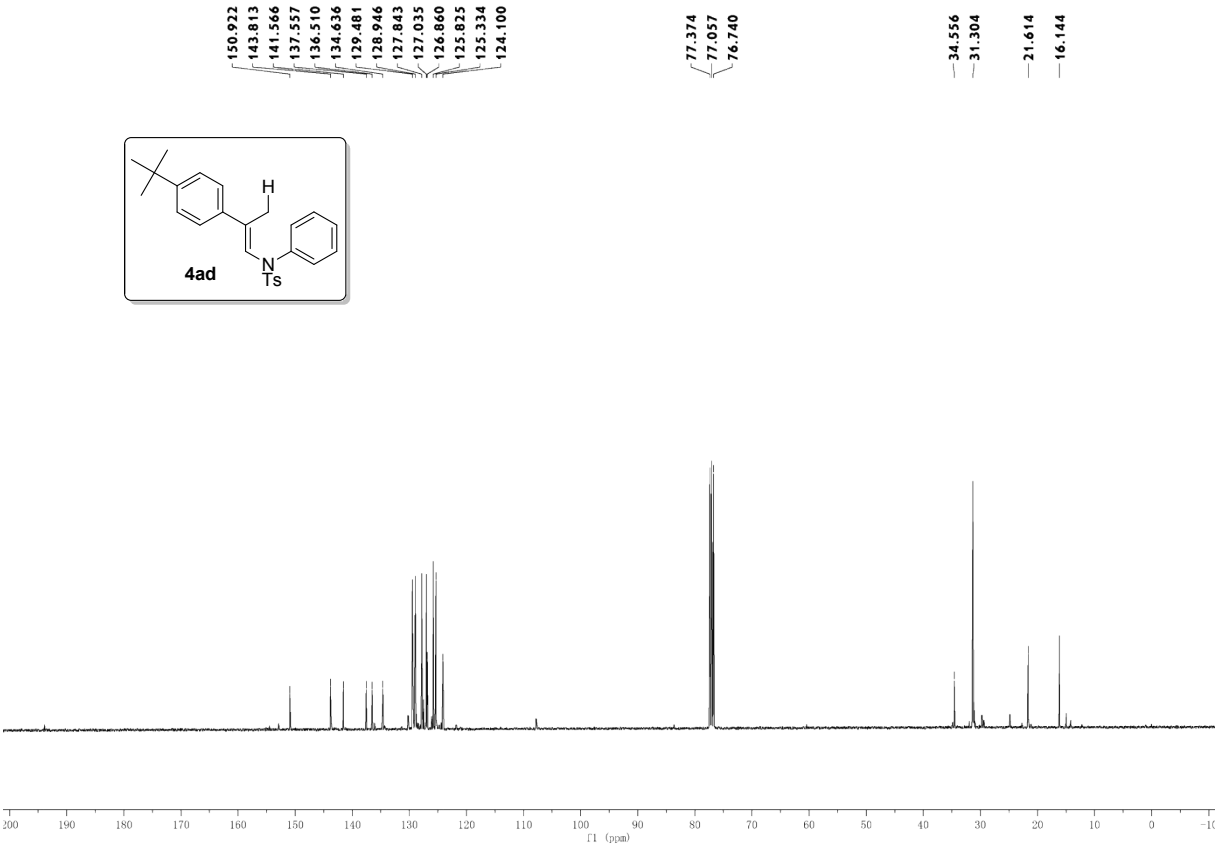

7.509
7.488
7.338
7.336
7.329
7.323
7.321
7.300
7.285
7.281
7.255
7.237
7.198
7.194
6.510
6.507
6.503
6.500
2.414
1.889
1.886
H
N
Ts
4ab
2.00
4.01
3.05
3.01
2.05
1.00
3.02
3.00
f1 (ppm)

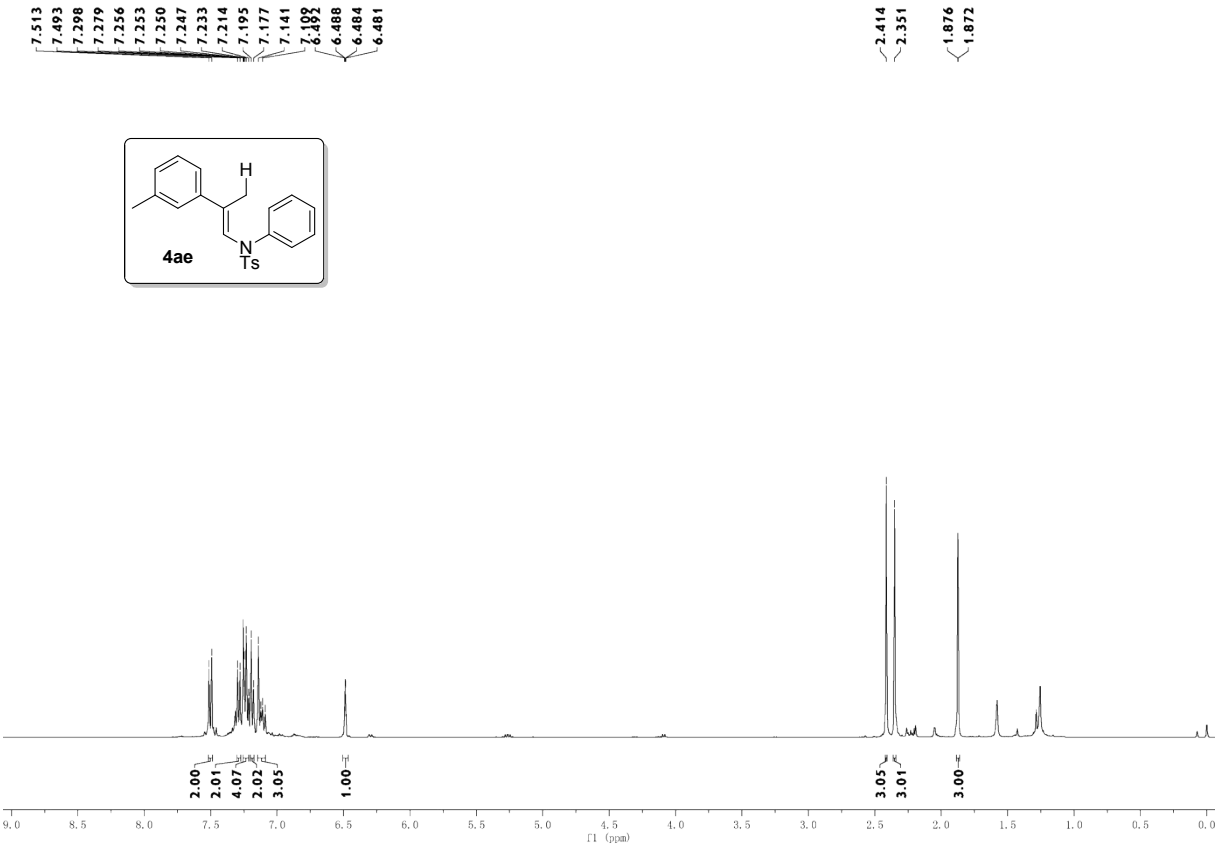

143.881
141.425
140.567
136.604
134.533
129.510
128.995
128.420
127.835
127.138
126.169
124.661
123.015
77.373
77.056
76.738
21.623
16.261
H
N
Ts
4ab
f1 (ppm)

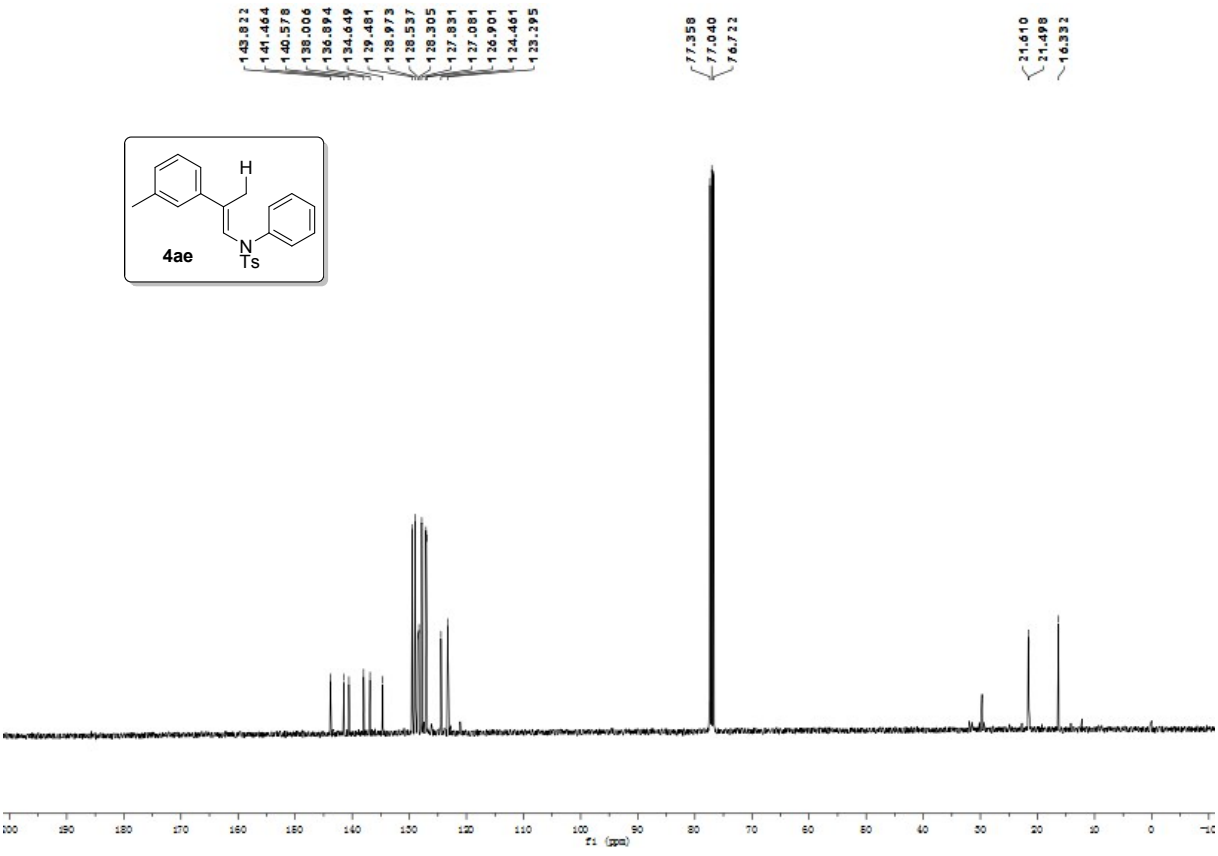

7.507
7.487
7.292
7.272
7.249
7.244
7.225
7.190
7.172
7.138
7.118
6.467
6.463
6.459
6.455
2.409
2.338
1.883
1.880
4ac
2.00
2.01
5.04
2.01
2.00
0.95
3.00
3.00
3.01
f1 (ppm)


143.812
141.549
137.689
137.608
136.959
134.619
129.480
129.098
128.964
127.844
127.048
126.888
126.035
123.939
77.374
77.057
76.740
21.611
21.136
16.233
4ac
f1 (ppm)


7.513
7.492
7.361
7.340
7.297
7.288
7.276
7.269
7.250
7.231
7.222
7.190
7.173
6.504
6.501
6.497
6.493
2.411
1.876
1.873
1.314
H
N
Ts
4ad
2.00
2.01
4.01
3.04
2.00
1.00
3.00
3.00
9.02
f1 (ppm)


150.922
143.813
141.566
137.557
136.510
134.636
129.481
128.946
127.843
127.035
126.860
125.825
125.334
124.100
77.374
77.057
76.740
34.556
31.304
21.614
16.144
H
N
Ts
4ad
f1 (ppm)

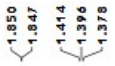

7.513
7.493
7.298
7.279
7.256
7.253
7.250
7.247
7.233
7.214
7.195
7.177
7.141
6.488
6.484
6.481
2.414
2.351
1.876
1.872
H
N
Ts
4ae
2.00
2.01
4.07
2.02
3.05
1.00
3.05
3.01
3.00
f1 (ppm)

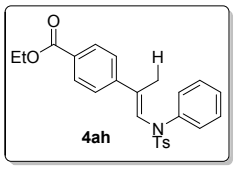

143.822
141.464
140.578
138.006
136.894
134.649
129.481
128.973
128.537
128.305
127.831
127.081
126.901
124.461
123.295
77.358
77.040
76.722
21.610
21.498
16.332
H
N
Ts
4ae
f1 (ppm)

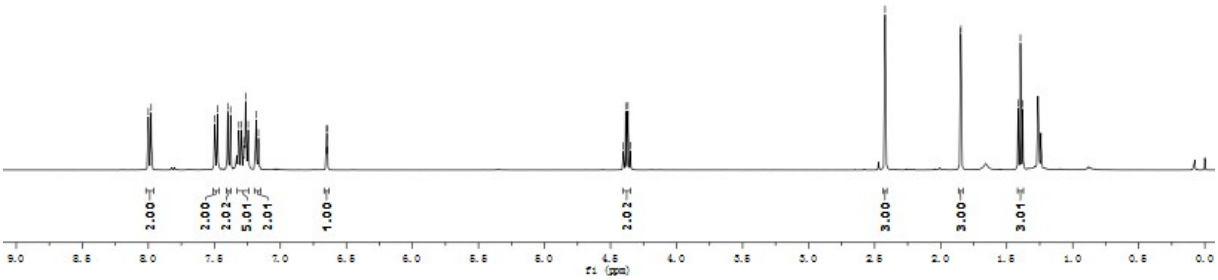

8.000
7.978
7.498
7.477
7.399
7.378
7.314
7.295
7.276
7.264
7.244
7.184
7.166
6.653
6.650
6.646
6.643

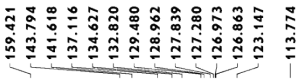

4.403
4.385
4.367
4.350


2.420


1.850
1.847
1.414
1.396
1.378


O
EtO
H
N
Ts
4ah

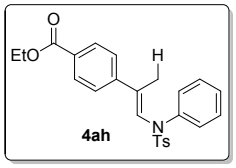

2.00
2.00
2.02
5.01
2.01
1.00
2.02
3.00
3.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.421
143.794
141.618
137.116
134.627
132.820
129.480
128.962
127.839
127.280
126.973
126.863
123.147
113.774

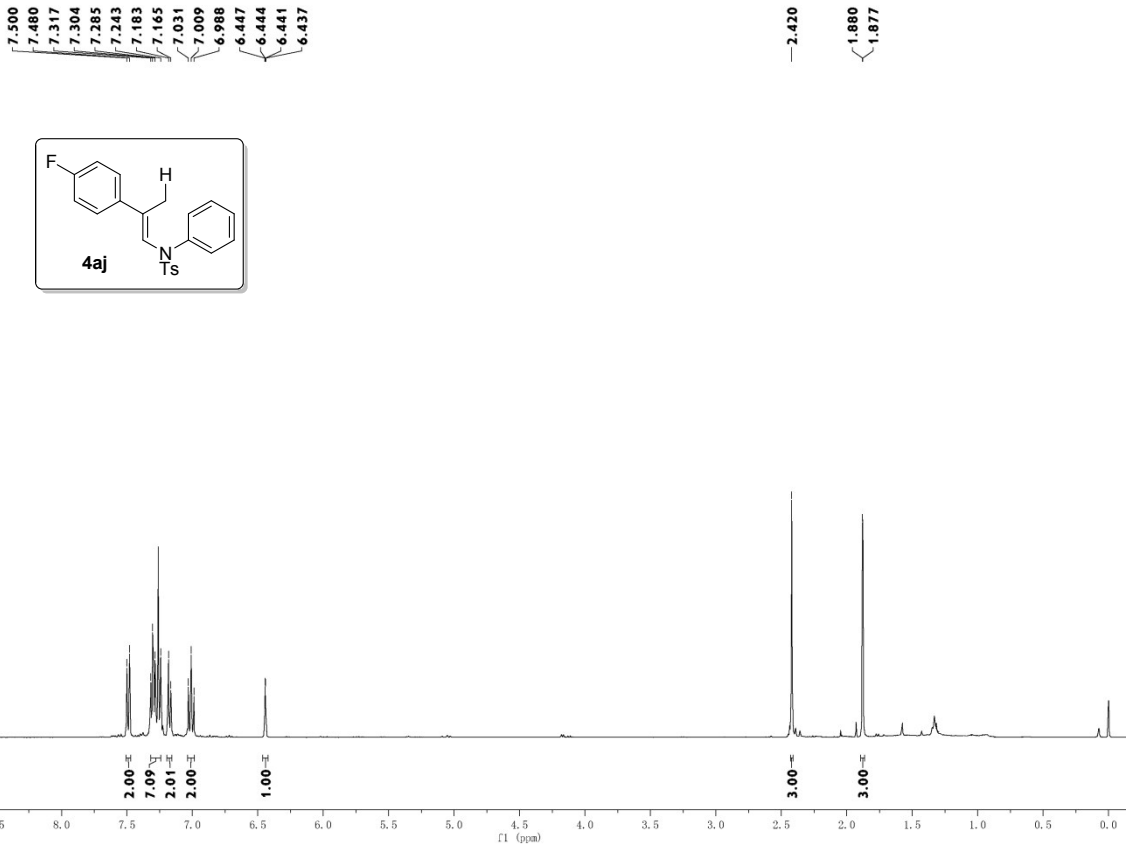

77.367
77.050
76.733

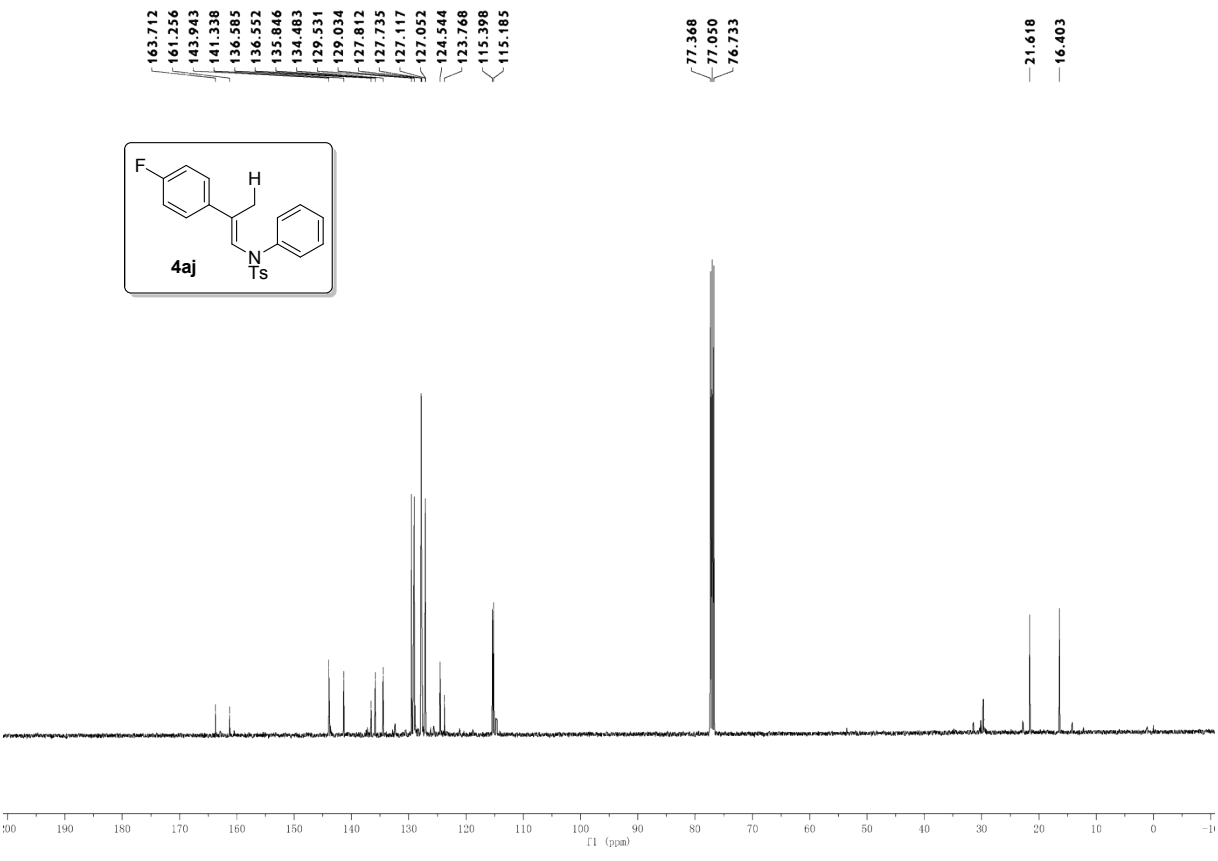

55.341

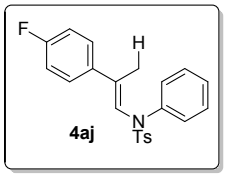

21.615
16.242


O
EtO
H
N
Ts
4ah

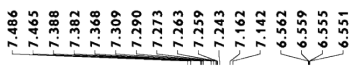
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

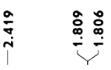

7.500
7.480
7.317
7.304
7.285
7.243
7.183
7.165
7.031
7.009
6.988
6.447
6.444
6.441
6.437
2.420
1.880
1.877
F
H
N
Ts
4aj
2.00
7.09
2.01
2.00
1.00
3.00
3.00
f1 (ppm)

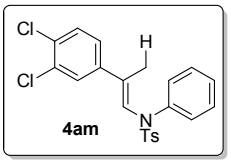

163.712
161.256
143.943
141.338
136.585
136.552
135.846
134.483
129.531
129.034
127.812
127.735
127.117
127.052
124.544
123.768
115.398
115.185
77.368
77.050
76.733
21.618
16.403
F
H
N
Ts
4aj
f1 (ppm)

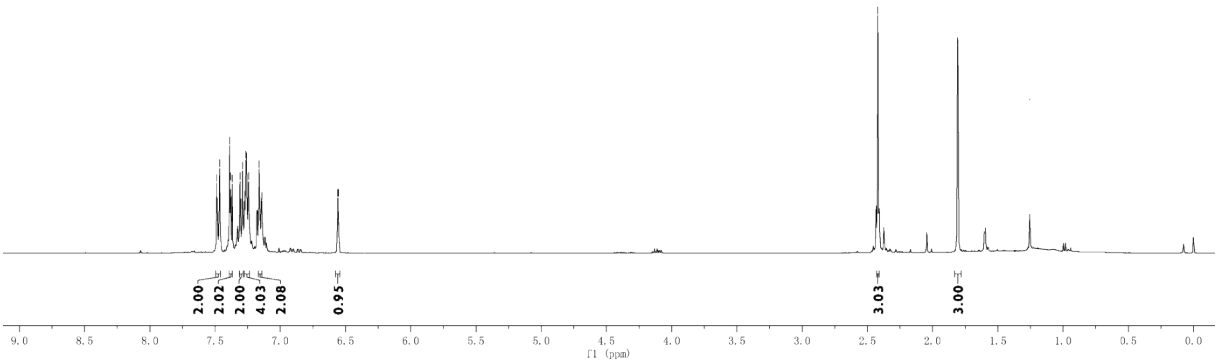

F
H
N
Ts
4aj

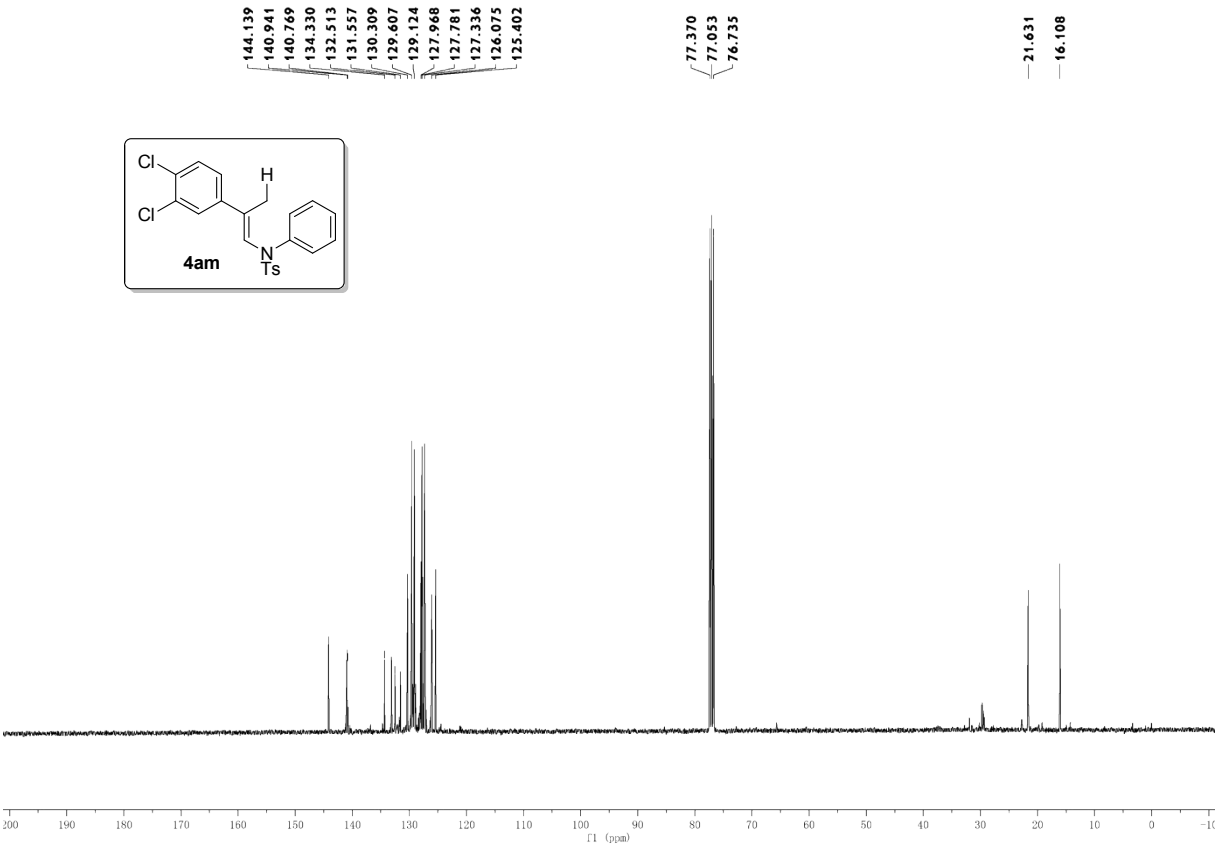
-114.422
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

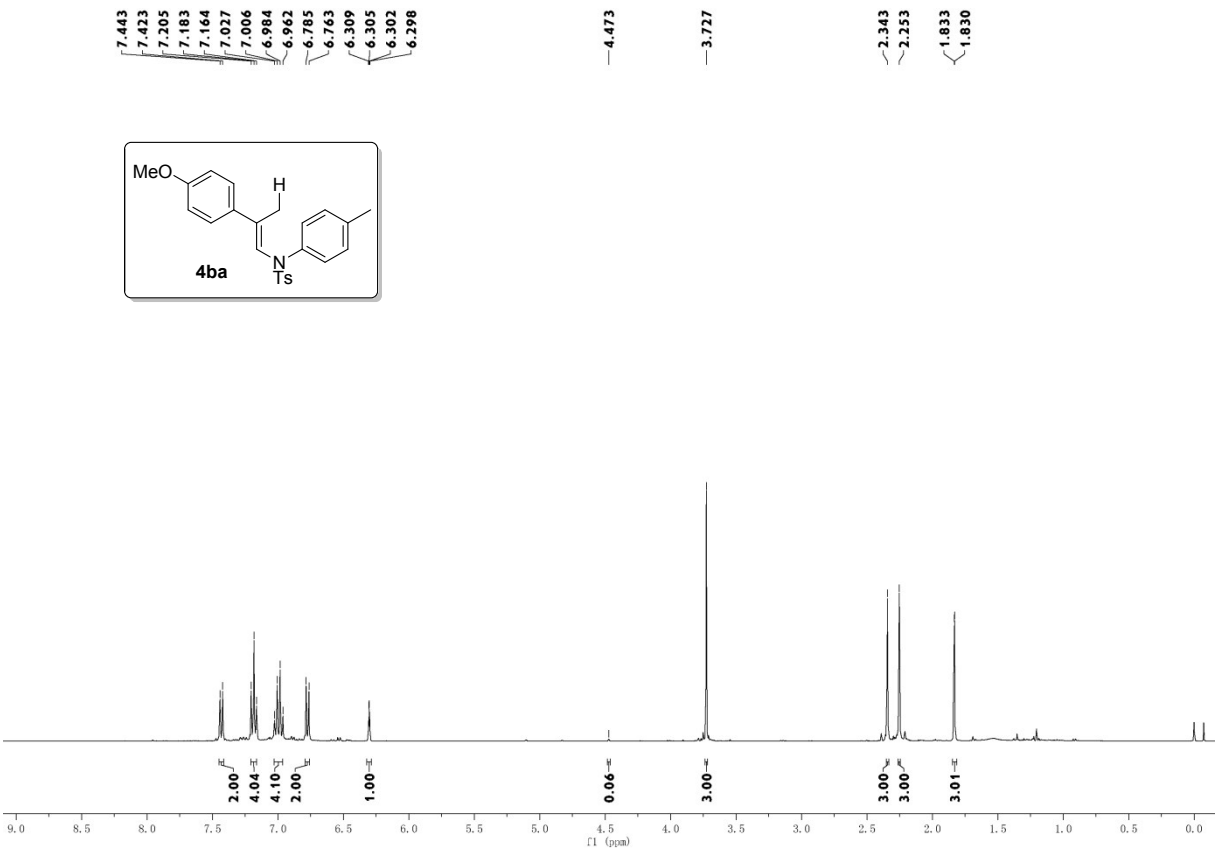

7.486
7.465
7.388
7.382
7.368
7.309
7.290
7.273
7.263
7.259
7.243
7.162
7.142
6.562
6.559
6.555
6.551

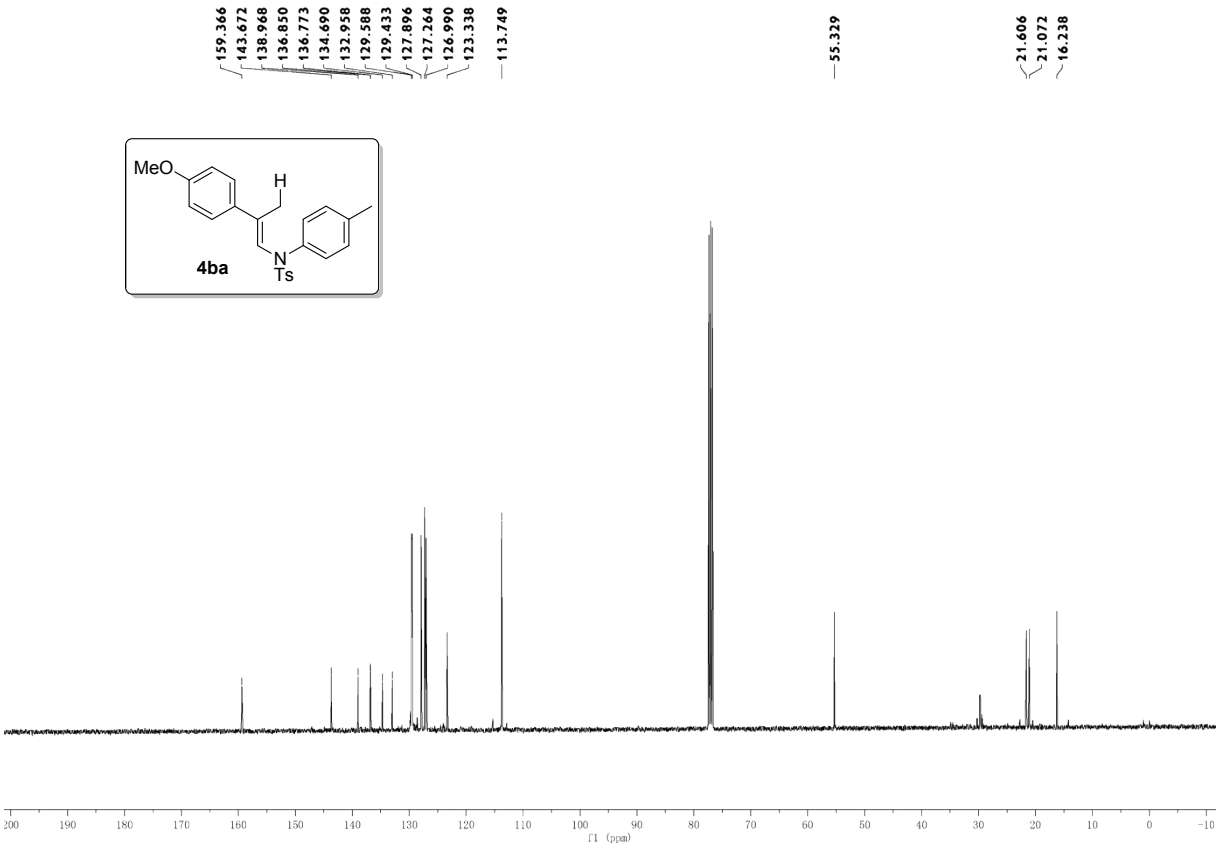

2.419
1.809
1.806

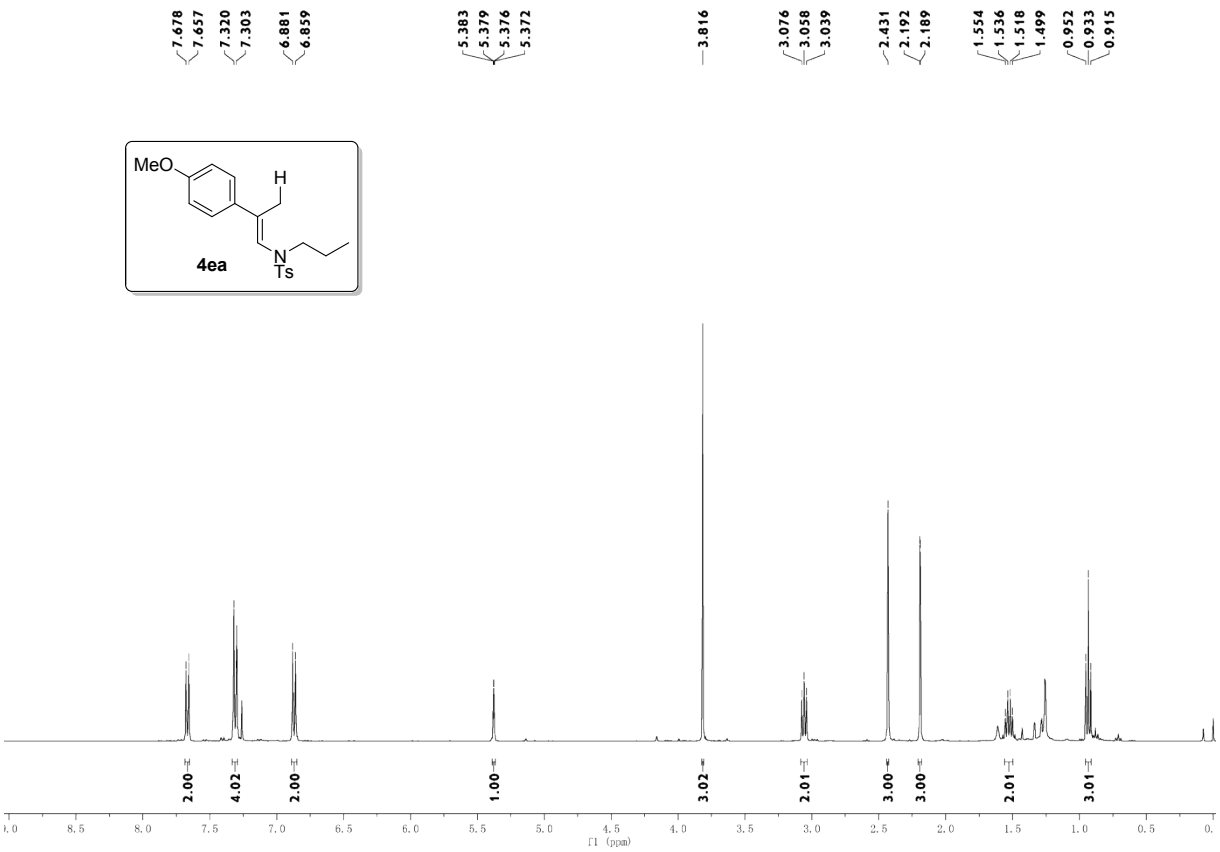

Cl
Cl
H
N
Ts
4am

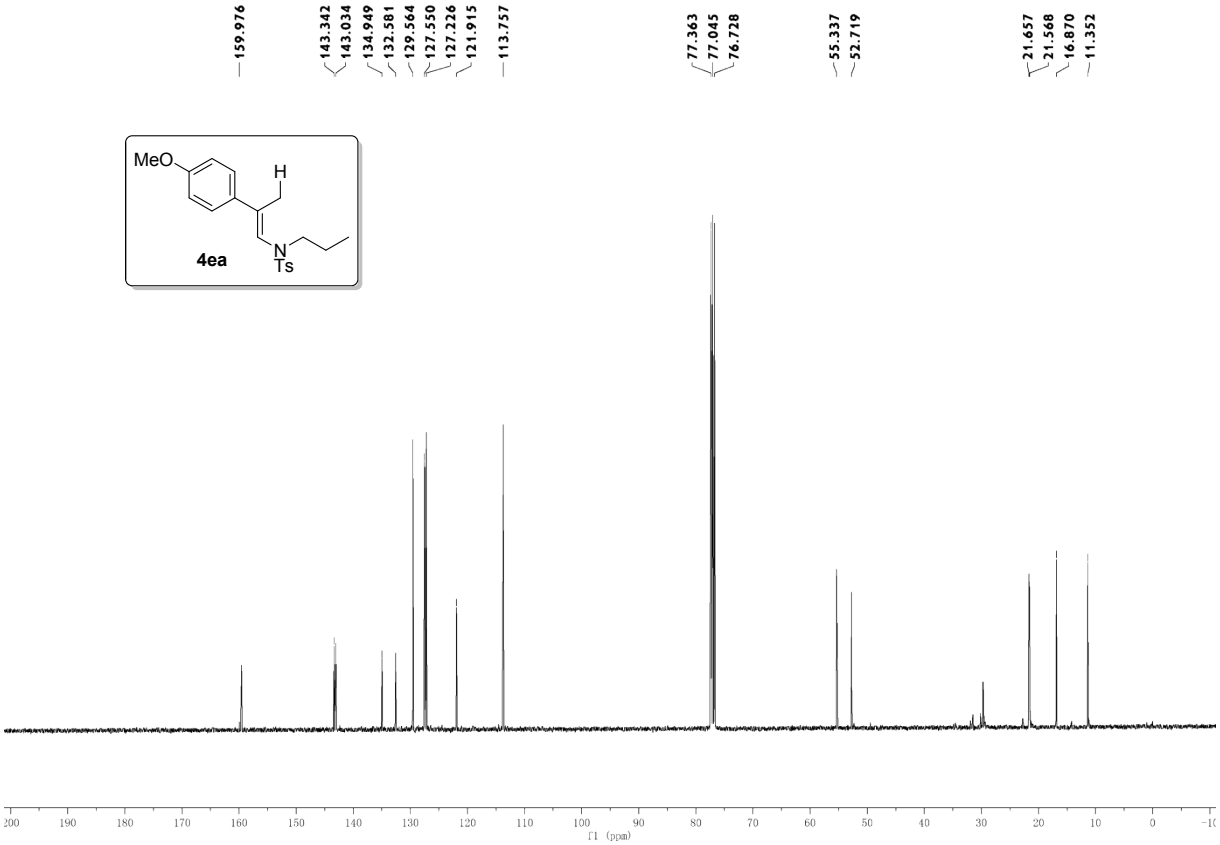

2.00
2.02
2.00
4.03
2.08
0.95
3.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

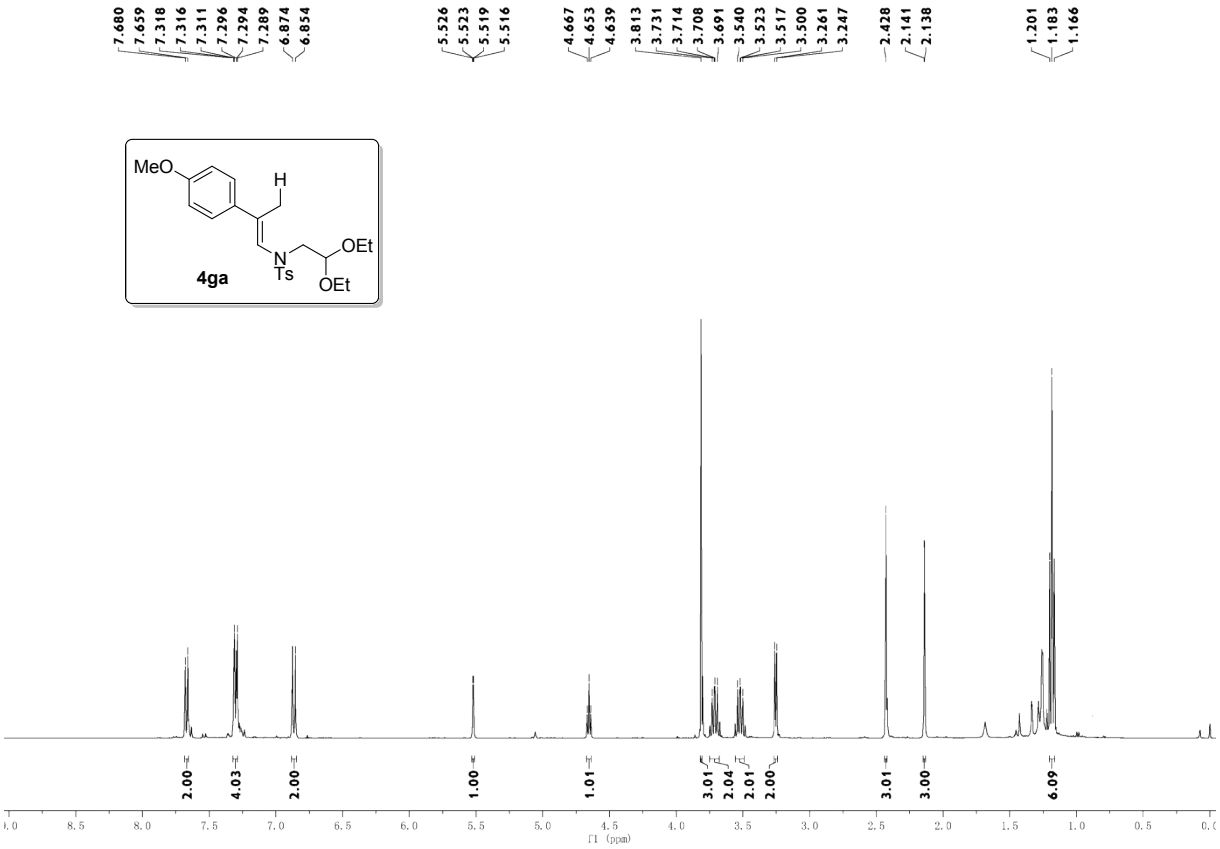

144.139
140.941
140.769
134.330
132.513
131.557
130.309
129.607
129.124
127.968
127.781
127.336
126.075
125.402
77.370
77.053
76.735
21.631
16.108
Cl
Cl
H
N
Ts
4am
f1 (ppm)

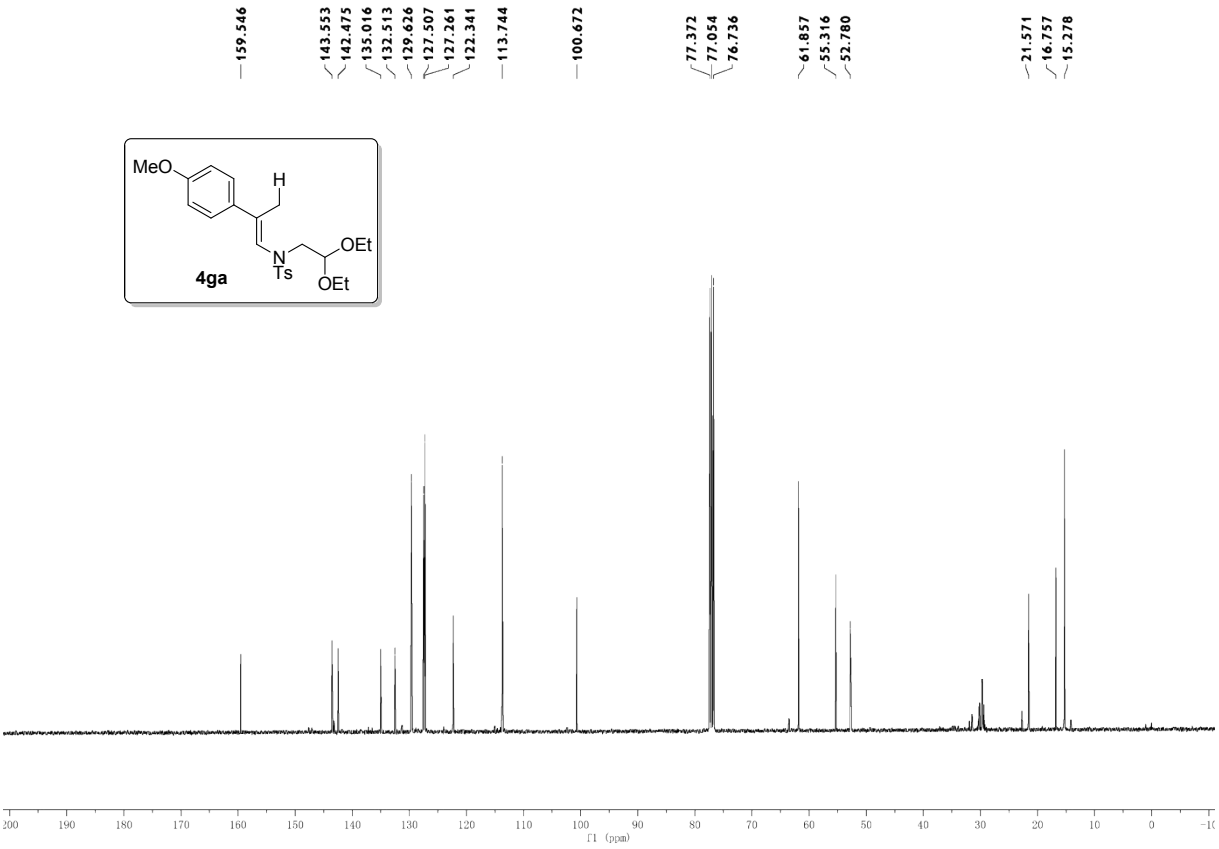

7.443
7.423
7.205
7.183
7.164
7.027
7.006
6.984
6.962
6.785
6.763
6.309
6.305
6.302
6.298
4.473
3.727
2.343
2.253
1.833
1.830
MeO
H
N
Ts
4ba
2.00
4.04
4.10
2.00
1.00
0.06
3.00
3.00
3.00
3.01
f1 (ppm)

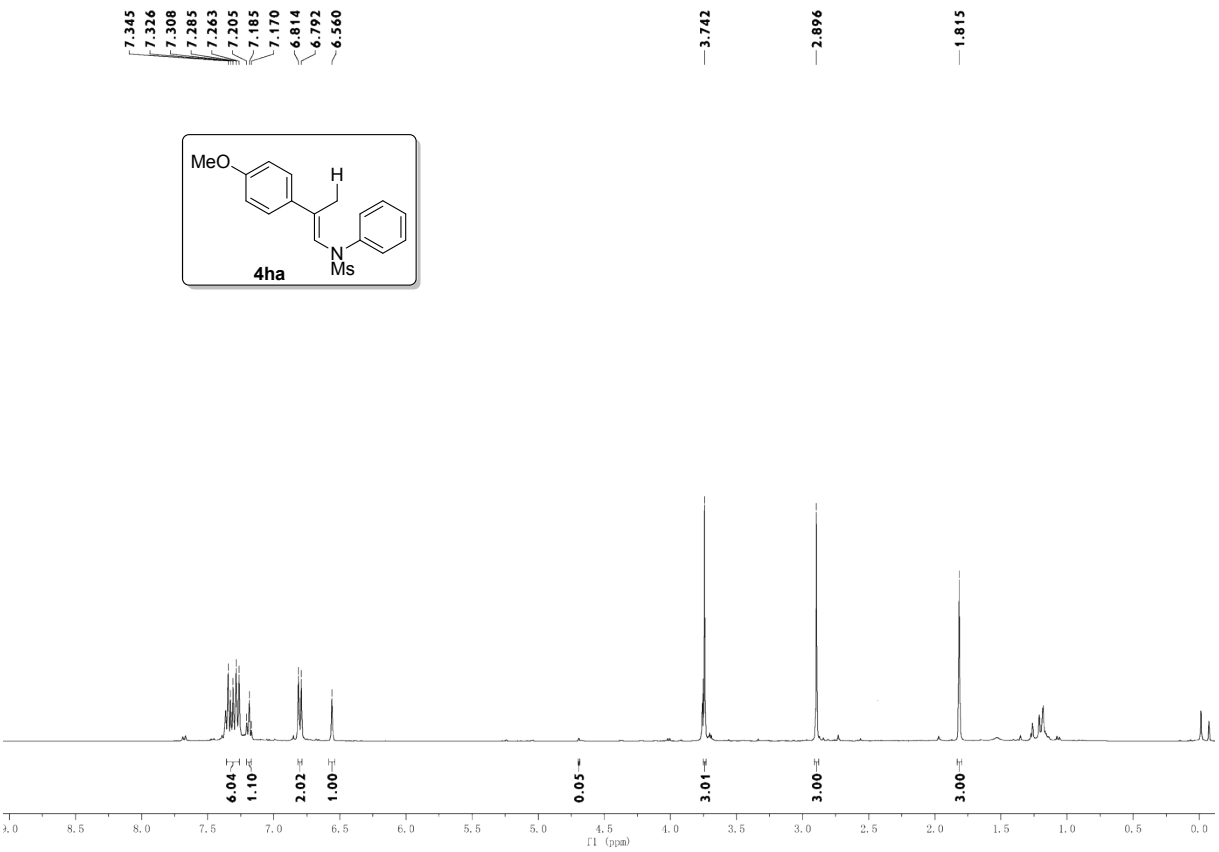

159.366
143.672
138.968
136.850
136.773
134.690
132.958
129.588
129.433
127.896
127.264
126.990
123.338
113.749
55.329
21.606
21.072
16.238
MeO
H
N
Ts
4ba
f1 (ppm)

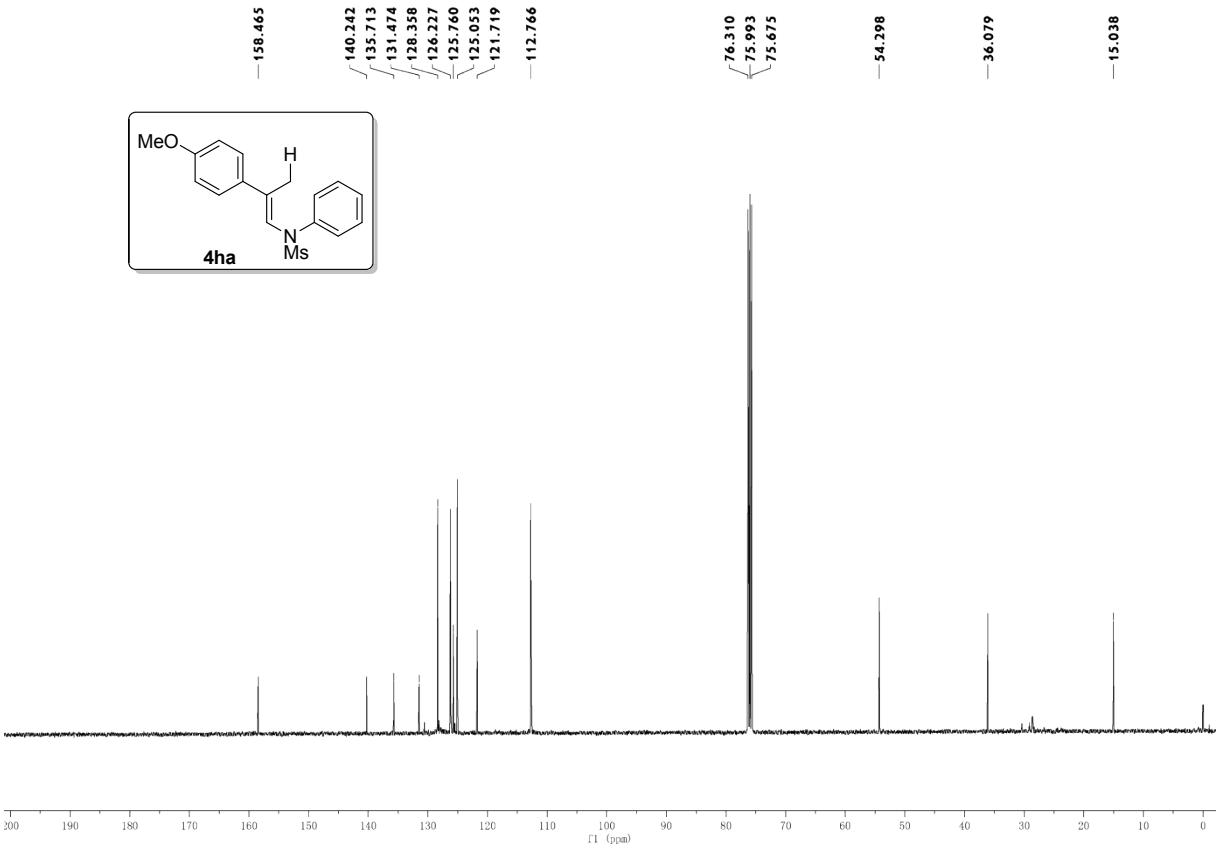

7.678
7.657
7.320
7.303
6.881
6.859
5.383
5.379
5.376
5.372
3.816
3.076
3.058
3.039
2.431
2.192
2.189
1.554
1.536
1.518
1.499
0.952
0.933
0.915
MeO
H
N
Ts
4ea
2.00
4.02
2.00
1.00
3.02
2.01
3.00
3.00
2.01
3.01
f1 (ppm)


159.976
143.342
143.034
134.949
132.581
129.564
127.550
127.226
121.915
113.757
77.363
77.045
76.728
55.337
52.719
21.657
21.568
16.870
11.352
MeO
H
N
Ts
4ea
f1 (ppm)

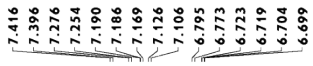

7.680
7.659
7.318
7.316
7.311
7.296
7.294
7.289
6.874
6.854
5.526
5.523
5.519
5.516
4.667
4.653
4.639
3.813
3.731
3.714
3.708
3.691
3.540
3.523
3.517
3.500
3.261
3.247
2.428
2.141
2.138
1.201
1.183
1.166
MeO
H
N
Ts
OEt
OEt
4ga
2.00
4.03
2.00
1.00
1.01
3.01
2.04
2.01
2.00
3.01
3.00
6.09
f1 (ppm)

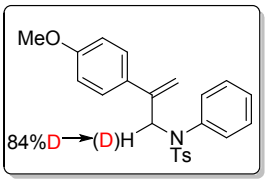

159.546
143.553
142.475
135.016
132.513
129.626
127.507
127.261
122.341
113.744
100.672
77.372
77.054
76.736
61.857
55.316
52.780
21.571
16.757
15.278
MeO
H
N
Ts
OEt
OEt
4ga
f1 (ppm)


7.345
7.326
7.308
7.285
7.263
7.205
7.185
7.170
6.814
6.792
6.560
3.742
2.896
1.815
MeO
H
N
Ms
4ha
6.04
1.10
2.02
1.00
0.05
3.01
3.00
3.00
f1 (ppm)

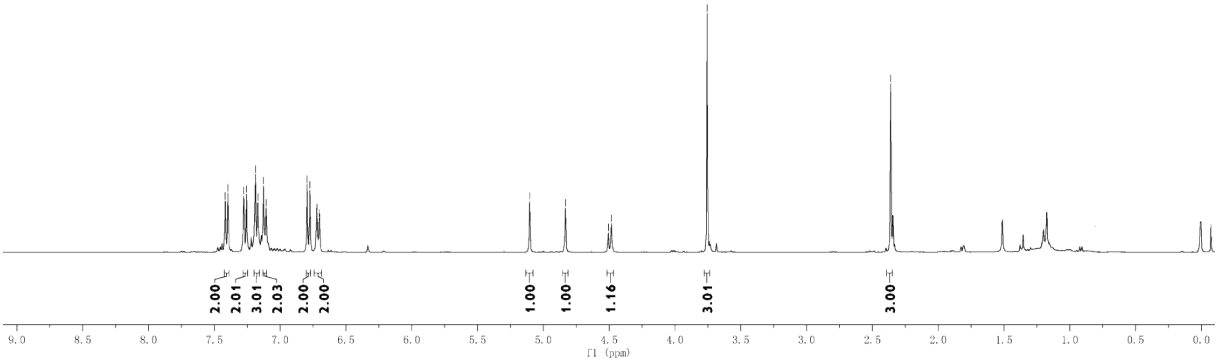

158.465
140.242
135.713
131.474
128.358
126.227
125.760
125.053
121.719
112.766
76.310
75.993
75.675
54.298
36.079
15.038
MeO
H
N
Ms
4ha
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

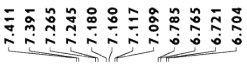
7. Copies of the ^{1}H NMR for Product 3aa and 4aa in deuterium-labeled experiments

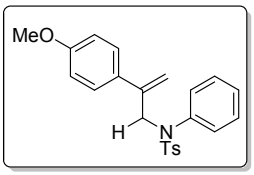




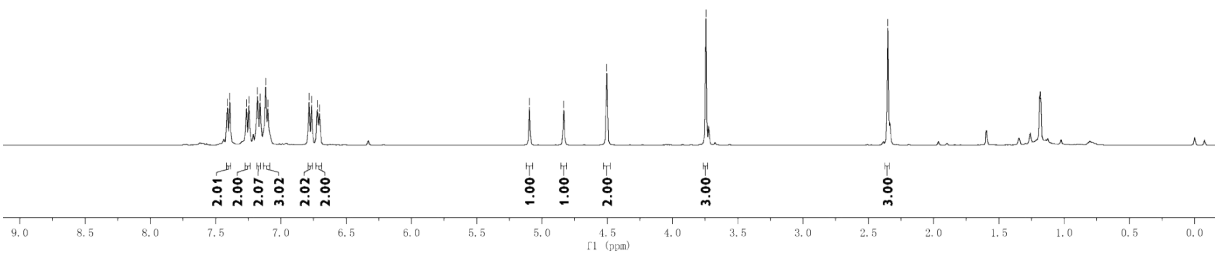
(entry 1, Scheme 2a)

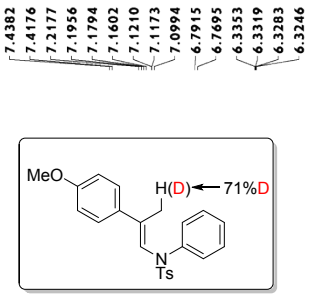




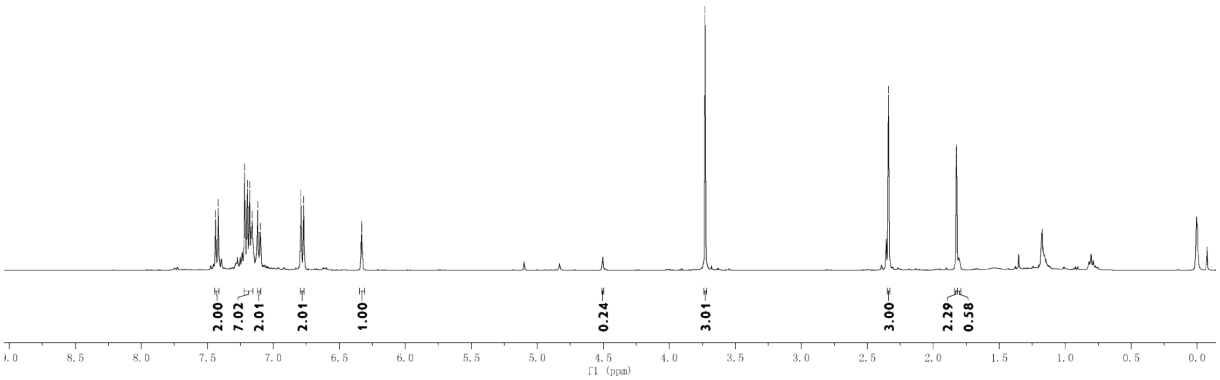


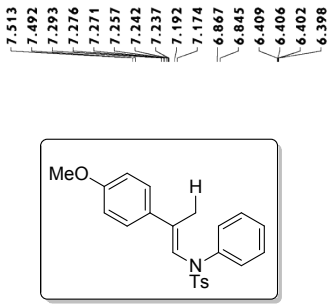
(entry 2, Scheme 2a)



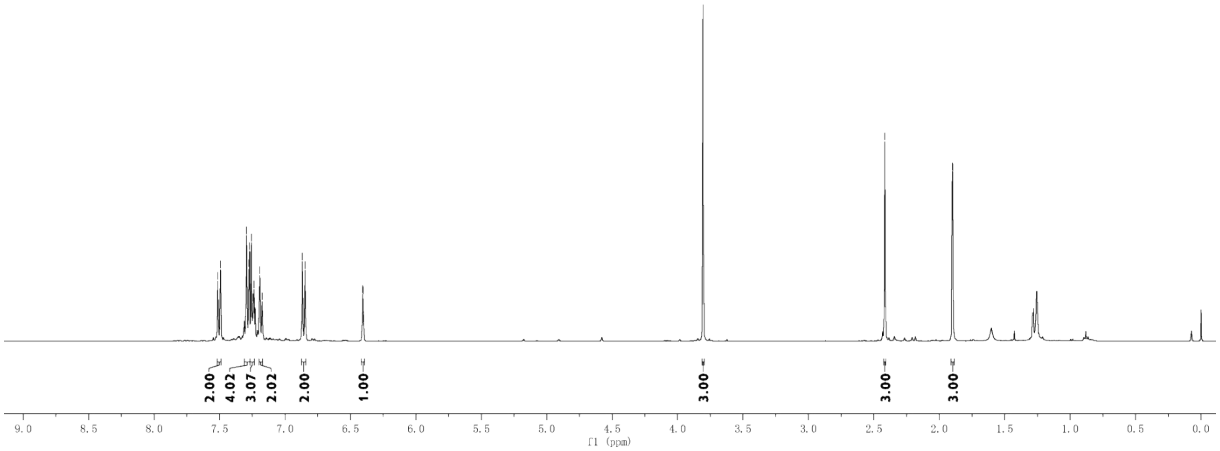


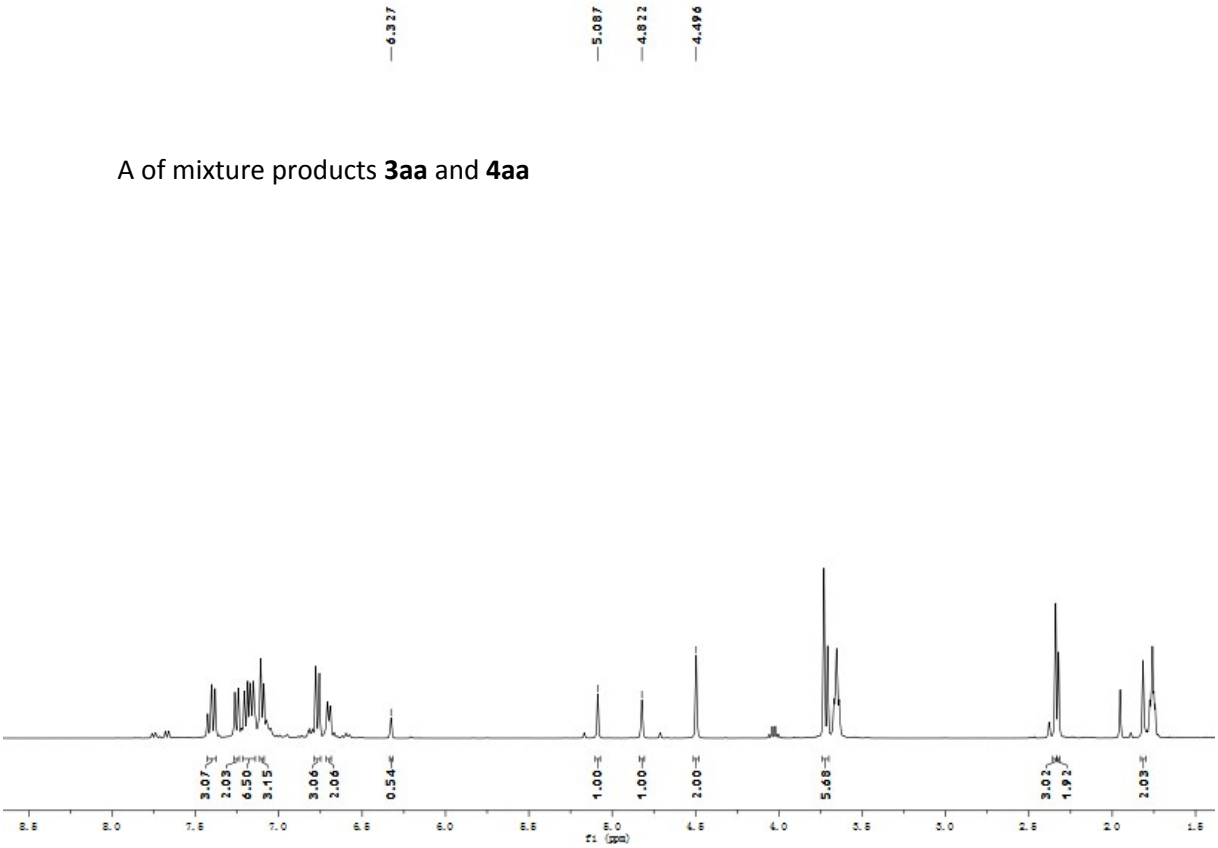
(entry 1, Scheme 2b)





(entry 2, Scheme 2b)





A of mixture products **3aa** and **4aa**