Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Iron-catalyzed *N*-alkylation using π- activated ethers as electrophiles

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Supporting Information

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A. General Information

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a rotary evaporator with a desktop vacuum pump. Tetrahydrofuran and diethyl ether were distilled from sodium prior to use. Dichloromethane, dichloroethane, CH_3NO_2, dimethylbenzene, ethyl acetate and 1, 4-dioxane were distilled from calcium hydride. Synthetic reagents were used as received without further purification, unless otherwise indicated. Analytical TLC was performed with silica gel plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

Melting points were measured on a micro melting apparatus and uncorrected. NMR spectra were measured on Bruker Avance-III 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) and Varian Mercury 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). HRMS (ESI) analysis was measured on a Bruker APEX II (ESI) mass spectrometer.

B. General Procedures for the Synthesis of starting materials[1]

To a stirred solution of alcohol (0.0123 mol) in anhydrous THF (30 mL) was added sodium hydride (60 percent in oil, 2 equiv, 0.0246 mol) partially at 0 °C . The mixture was further stirred at 0 °C for 1h before slowly addition of MeI (1.5 equiv). After stirred at room temperature for 8h, the reaction was quenched by addition of ice-water and extracted with EtOAc twice. The combined organic phase was washed with brine and dried over $MgSO_4$. Evaporation of solvent provided the crude product as a color residue. The crude product was purified by column chromatography on silica gel (petroleum ether /ethyl acetate = 20 : 1) to afford ethers **1b-x**.

C. Typical Procedure for Iron-catalyzed N-Alkylation

To a stirred solution of (1-methoxyethyl)benzene **1b** (47.7mg, 0.35 mmol, 1equiv) in 4 mL anhydrous CH_2Cl_2 under argon was added *p*-toluenesulfonamide **2a** (77.9mg, 0.455mmol) and $FeCl_3$ (11.4mg, 0.07 mmol, 20mol%) successively at room temperature. After stirred at room temperature for 1h (monitored by TLC), the reaction was

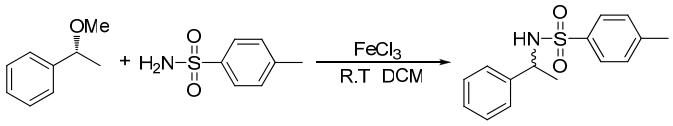
quenched by addition of H_2O (3 mL) and then extracted with ethyl acetate (3×3mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford the corresponding amidation product **3b**.

D. Data of Mechanistic Study

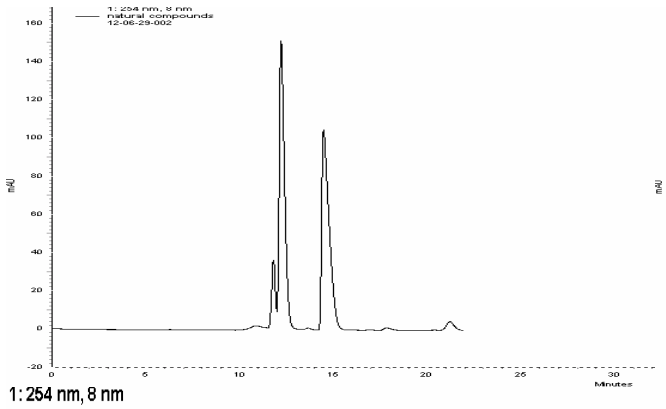
The enantiomeric excess values (*ee*) were measured by chiral HPLC analysis using a chiralcel OD-H column.

HPLC conditions for **R-1b** and **rac-1b**: chinalcel OD-H column, hexane, flow rate = 0.5 mL/min, wavelength = 254 nm;

HPLC conditions for **rac-3b**: chinalcel OD-H column, i-prOH/ hexane = 30:70, flow rate = 0.5 mL/min, wavelength = 254 nm.



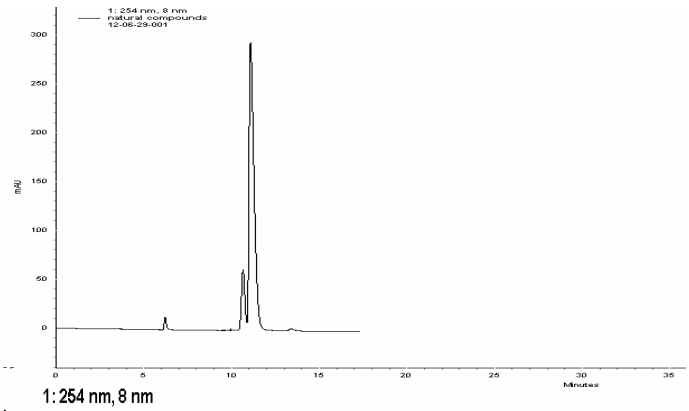
R-1b **2a** **rac-3b**



1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Capacity factor	Response Factor	Resolution
80	?	12.196	2999824	0.00	0.00	0.88
84	?	14.471	2903238	0.00	0.00	1.00

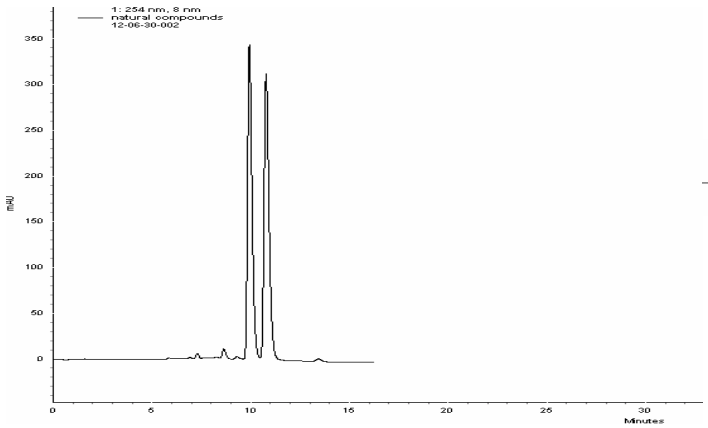
rac-1b: 1.6% *ee*.



1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Capacity factor	Response Factor	Resolution
46	?	11.083	5880079	0.00	0.00	0.96
49	?	13.413	44506	0.00	0.00	3.01

R-1b: 98.5% *ee*.

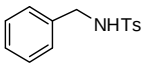


1: 254 nm, 8 nm

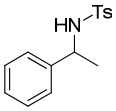
Pk #	Name	Retention Time	Area	Capacity factor	Response Factor	Resolution
26	?	9.930	5420236	0.00	0.00	1.57
27	?	10.776	5484994	0.00	0.00	1.95

rac-3b: 1.0% *ee*.

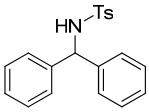
E. Characterization Data



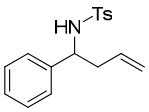
N-benzyl-4-methylbenzenesulfonamide (3a). White solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.29-7.25 (m, 3H), 7.20 (dd, J = 5.3, 2.4 Hz, 2H), 4.74 (s, 1H), 4.11 (d, J = 5.7 Hz, 2H), 2.44 (s, 3H). m.p. 107-109 °C. This compound was known.[2]



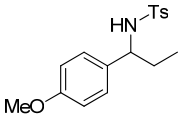
4-Methyl-N-(1-phenyl-ethyl)-benzenesulfonamide (3b). White solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.60 (m, 2H), 7.18 (dtd, J = 6.9, 5.2, 1.7 Hz, 5H), 7.12-7.08 (m, 2H), 5.14 (d, J = 6.5 Hz, 1H), 4.50-4.41 (m, 1H), 2.37 (s, 3H), 1.41 (d, J = 6.9 Hz, 3H). m.p. 80-81 °C. This compound was known.[5]



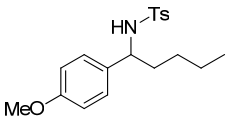
N-*p*-methylphenylsulfonyl diphenylmethylamine (3c). White solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.1 Hz, 2H), 7.09-7.21 (m, 12H), 5.56 (d, J = 7.0 Hz, 1H), 5.05 (d, J = 6.9 Hz, 1H), 2.38 (s, 3H). m.p. 153-154 °C. This compound was known.[3]



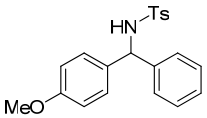
N-(1-phenylbut-3-enyl)-4-methylbenzenesulfonamide (3d). White solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.1 Hz, 2H), 7.18-7.04 (m, 7H), 5.57-5.45 (m, 1H), 5.03 (dd, J = 13.6, 9.8 Hz, 3H), 4.37 (t, J = 6.6 Hz, 1H), 2.45 (dd, J = 12.6, 6.4 Hz, 2H), 2.36 (s, 3H). m.p. 70-71 °C. This compound was known.[4]



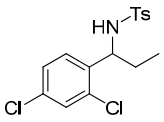
N-[1-(4-methoxyphenyl)propan-1-yl]-4-methylbenzenesulfonamide (3e). White solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.3 Hz, 2H), 7.14-7.09 (m, 2H), 6.95-6.90 (m, 2H), 6.68-6.64 (m, 2H), 5.34 (d, J = 7.3 Hz, 1H), 4.12 (q, J = 7.3 Hz, 1H), 3.74 (d, J = 5.1 Hz, 3H), 2.36 (s, 3H), 1.80 (dt, J = 14.2, 7.1 Hz, 1H), 1.68 (dt, J = 13.8, 7.8 Hz, 1H). m.p. 96-97 °C. This compound was known.[7]



N-[1-(4-methoxyphenyl)pentyl]-4-toluenesulfonamide (3f). White solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.92 (dd, J = 6.8, 4.8 Hz, 2H), 6.68 (dd, J = 6.8, 4.7 Hz, 2H), 4.88 (d, J = 7.0 Hz, 1H), 4.19 (q, J = 7.2 Hz, 1H), 3.75 (d, J = 0.9 Hz, 3H), 2.36 (s, 3H), 1.81-1.58 (m, 3H), 1.21 (tdd, J = 22.2, 14.7, 7.2 Hz, 4H), 1.05 (ddd, J = 15.6, 10.2, 5.6 Hz, 1H), 0.79 (t, J = 7.1 Hz, 3H). m.p. 120-122 °C. This compound was known.[8]

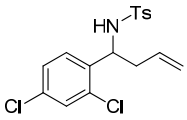


N-[(4-methoxyphenyl)(phenyl)methyl]-4-methylbenzenesulfonamide (3g). White solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.3 Hz, 2H), 7.20-7.16 (m, 3H), 7.13-7.09 (m, 4H), 6.99 (dd, J = 10.1, 1.6 Hz, 2H), 6.71 (dt, J = 4.8, 2.3 Hz, 2H), 5.51 (d, J = 7.2 Hz, 1H), 5.32-5.25 (m, 1H), 3.73 (s, 3H), 2.36 (s, 3H). m.p. 127-128 °C. This compound was known.[9]



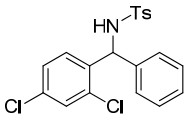
N-(1-(2,4-dichlorophenyl)propyl)-4-methylbenzenesulfonamide (3h). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, J = 8.2, 1.5 Hz, 2H), 7.16-6.99 (m, 5H), 5.82-5.66 (m, 1H), 4.67-4.60 (m, 1H), 2.37 (s, 3H), 1.74-1.68 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 143.32, 136.99, 133.27, 132.94, 129.24, 129.07, 127.11, 126.96, 56.03, 29.42, 21.37, 10.19. HRMS (ESI): $(M+NH_4)^+$ $C_{16}H_{21}Cl_2N_2O_2S$, Calcd 375.0701, found 375.0695. m.p. 153-154 °C.



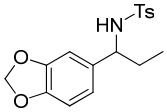
N-(1-(2,4-dichlorophenyl)but-3-enyl)-4-methylbenzenesulfonamide (3i). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.56 (m, 2H), 7.24-7.12 (m, 4H), 7.06 (dd, J = 8.4, 2.1 Hz, 1H), 5.52-5.39 (m, 1H), 5.17-5.04 (m, 3H), 4.74 (dd, J = 13.8, 6.1 Hz, 1H), 2.45-2.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.51, 136.53, 133.46, 132.66, 132.27, 129.33, 129.12, 127.07, 119.77, 53.51, 40.09, 21.41. HRMS (ESI): $(M+Na)^+$ $C_{17}H_{17}Cl_2NNaO_2S$, Calcd 392.0255, found 392.0249. m.p. 132-133 °C.



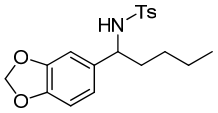
N-((2,4-dichlorophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (3j). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.25-7.11 (m, 7H), 7.02 (dd, J = 6.6, 2.9 Hz, 2H), 5.85 (d, J = 6.9 Hz, 1H), 5.34 (d, J = 6.9 Hz, 1H), 2.41 (s, 3H). m.p. 159-160 °C. This compound was known.[9]



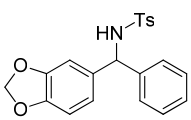
N-(1-(benzo[*d*][1,3]dioxol-5-yl)propyl)-4-methylbenzenesulfonamide (3k). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.62-6.41 (m, 3H), 5.85 (d, J = 7.3 Hz, 2H), 5.43 (d, J = 6.5 Hz, 1H), 4.08 (q, J = 7.1 Hz, 1H), 2.36 (s, 3H), 1.77 (dt, J = 14.1, 7.1 Hz, 1H), 1.68-1.59 (m, 1H), 0.76 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.45, 146.58, 142.75, 137.71, 134.64, 129.11, 127.01, 120.28, 107.79, 106.80, 100.85, 59.68, 30.42, 21.37, 10.44. m.p. 91-92 °C.



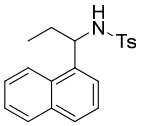
N-(1-(benzo[*d*][1,3]dioxol-5-yl)pentyl)-4-methylbenzenesulfonamide (3l). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.54 (dd, J = 37.6, 7.9 Hz, 2H), 6.44 (s, 1H), 5.87 (d, J = 7.5 Hz, 2H), 4.93 (s, 1H), 4.16 (t, J = 7.2 Hz, 1H), 2.37 (s, 3H), 1.77-1.68 (m, 1H), 1.61 (dd, J = 7.5, 5.5 Hz, 1H), 1.22 (dt, J = 33.3, 14.5 Hz, 4H), 1.06 (dd, J = 12.1, 7.0 Hz, 1H), 0.80 (dd, J = 13.7, 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.52, 146.63, 142.81, 137.69, 134.89, 129.12, 127.04, 120.18, 107.85, 106.70, 100.89, 58.13, 37.17, 27.92, 22.12, 21.37, 13.77. HRMS (ESI): $(M+Na)^+$ $C_{19}H_{23}NNaO_4S$, Calcd 384.1245, found 384.1240. m.p. 97-98 °C.



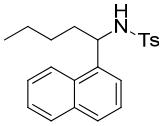
N-(benzo[*d*][1,3]dioxol-5-yl(phenyl)methyl)-4-methylbenzenesulfonamide (3m). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1 Hz, 2H), 7.24-7.08 (m, 7H), 6.68-6.51 (m, 3H), 5.89 (d, J = 3.2 Hz, 2H), 5.47 (s, 1H), 4.96 (s, 1H), 2.39 (s, 3H). m.p. 154-155 °C. This compound was known.[10]



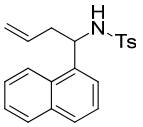
4-Methyl-N-(1-(naphthalen-1-yl)propyl)benzenesulfonamide (3n). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, 1H), 7.81-7.75 (m, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.43 (t, J = 7.5 Hz, 3H), 7.27 (dd, J = 9.1, 5.4 Hz, 3H), 6.91 (d, J = 7.9 Hz, 2H), 5.04 (s, 2H), 2.24 (s, 3H), 1.95 (d, J = 6.9 Hz, 2H), 0.86 (t, J = 7.3 Hz, 3H). m.p. 94-95 °C. This compound was known.[7]



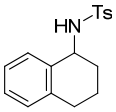
4-Methyl-N-(1-(naphthalen-1-yl)pentyl)benzenesulfonamide (3o). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 5.3 Hz, 1H), 7.78-7.71 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 7.1 Hz, 4H), 7.31-7.20 (m, 2H), 6.84 (d, J = 8.0 Hz, 2H), 5.75 (d, J = 7.1 Hz, 1H), 5.12 (d, J = 6.9 Hz, 1H), 2.20 (s, 3H), 1.88 (dd, J = 14.2, 7.0 Hz, 2H), 1.38-1.29 (m, 1H), 1.23 (dd, J = 13.4, 6.6 Hz, 3H), 0.77 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.60, 137.28, 137.13, 133.63, 130.47, 128.85, 128.71, 127.60, 126.88, 126.05, 125.41, 125.21, 123.91, 122.57, 54.11, 37.24, 28.28, 22.27, 21.27, 13.86. HRMS (ESI): $(M+Na)^+$ $C_{22}H_{25}NNaO_2S$, Calcd 390.1504, found 390.1499. m.p. 131-132 °C.



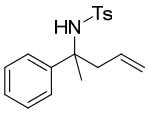
4-Methyl-N-(1-(naphthalen-1-yl)but-3-en-1-yl)benzenesulfonamide (3p). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.6 Hz, 1H), 7.82-7.72 (m, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.51-7.40 (m, 4H), 7.34-7.21 (m, 2H), 6.94 (d, J = 7.9 Hz, 2H), 5.63-5.50 (m, 2H), 5.23 (dd, J = 13.3, 6.6 Hz, 1H), 5.06 (t, J = 14.6 Hz, 2H), 2.62 (t, J = 6.5 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.82, 137.10, 135.90, 133.62, 133.17, 130.17, 128.95, 128.75, 127.75, 126.94, 126.11, 125.40, 125.03, 124.17, 122.36, 119.05, 53.23, 41.17, 21.28. HRMS (ESI): $(M+NH_4)^+$ $C_{21}H_{25}N_2O_2S$, Calcd 369.1637, found: 369.1631. m.p. 96-97 °C.



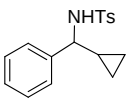
4-Methyl-N-(1,2,3,4-tetrahydronaphthalen-1-yl)benzenesulfonamide (3q). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.17-7.02 (m, 3H), 6.93 (d, J = 7.5 Hz, 1H), 4.62 (d, J = 7.6 Hz, 1H), 4.45 (d, J = 4.5 Hz, 1H), 2.80-2.61 (m, 2H), 2.46 (s, 3H), 2.46 (s, 3H), 1.85 (dd, J = 16.4, 5.7 Hz, 3H), 1.77-1.66 (m, 1H). m.p. 140-141 °C.This compound was known.[6]



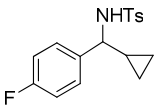
4-Methyl-N-(2-phenylpent-4-en-2-yl)benzenesulfonamide (3r). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.2 Hz, 2H), 7.28 (dd, J = 7.7, 1.5 Hz, 2H), 7.21-7.12 (m, 5H), 5.54-5.43 (m, 1H), 5.26 (d, J = 4.0 Hz, 1H), 5.10 (dd, J = 13.3, 6.9 Hz, 2H), 2.69 (dd, J = 13.7, 7.1 Hz, 1H), 2.53 (dd, J = 13.6, 7.4 Hz, 1H), 2.38 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.56, 142.55, 139.86, 132.60, 129.18, 128.00, 126.85, 125.94, 120.00, 60.60, 47.98, 25.59, 21.38. HRMS (ESI): $(M+Na)^+$ $C_{18}H_{21}NNaO_2S$, Calcd 338.1191, found, 338.1185. m.p. 83-84 °C.



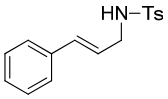
N-(cyclopropyl(phenyl)methyl)-4-methylbenzenesulfonamide (3s). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.2 Hz, 2H), 7.21-7.08 (m, 7H), 5.31 (d, J = 5.8 Hz, 1H), 3.70 (dd, J = 8.4, 6.2 Hz, 1H), 2.36 (s, 3H), 1.15-1.04 (m, 1H), 0.53-0.42 (m, 2H), 0.30-0.20 (m, 2H). m.p. 129-130 °C. This compound was known.[13]



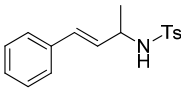
N-(cyclopropyl(4-fluorophenyl)methyl)-4-methylbenzenesulfonamide (3t). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 2H), 7.18-7.05 (m, 4H), 6.84 (t, J = 8.6 Hz, 2H), 5.57 (d, J = 5.6 Hz, 1H), 3.67 (dd, J = 8.3, 6.2 Hz, 1H), 2.37 (s, 3H), 1.11-1.02 (m, 1H), 0.47 (ddd, J = 12.8, 8.5, 4.2 Hz, 2H), 0.26-0.17 (m, 2H). m.p. 126-128 °C. This compound was known.[13]



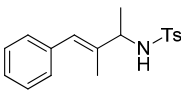
N-cinnamyl-4-methylbenzenesulfonamide (3v). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 2H), 7.32-7.21 (m, 7H), 6.44 (d, J = 16 Hz, 1H), 6.05-5.97 (m, 1H), 4.51 (s, 1H), 3.75 (d, J = 6.0 Hz, 2H), 2.41 (s, 3H). m.p. 105-106 °C. This compound was known.[11]



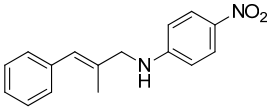
4-Methyl-N-(4-phenylbut-3-en-2-yl)benzenesulfonamide (3w). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.27-7.19 (m, 5H), 7.17-7.12 (m, 2H), 6.29 (d, J = 15.9 Hz, 1H), 5.83 (dd, J = 15.9, 6.7 Hz, 1H), 4.72 (d, J = 7.6 Hz, 1H), 4.13-4.04 (m, 1H), 2.34 (s, 3H), 1.27 (d, J = 6.8 Hz, 3H). m.p. 87-88 °C. This compound was known.[12]



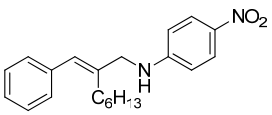
4-Methyl-N-(3-methyl-4-phenylbut-3-en-2-yl)benzenesulfonamide (3x). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.2 Hz, 2H), 7.30-7.15 (m, 5H), 7.01 (d, J = 7.4 Hz, 2H), 6.25 (s, 1H), 5.03 (d, J = 7.2 Hz, 1H), 4.10-4.00 (m, 1H), 2.36 (s, 3H), 1.56 (s, 3H), 1.28 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.09, 137.87, 137.23, 137.00, 129.40, 128.81, 127.91, 127.29, 126.79, 126.46, 57.26, 21.40, 20.71, 13.12. HRMS (ESI): $(M+Na)^+$ $C_{18}H_{21}NNaO_2S$, Calcd 338.1191, found 338.1185. m.p. 101-102 °C.



N-(2-methyl-3-phenylallyl)-4-nitroaniline (3y). Yellow solid.

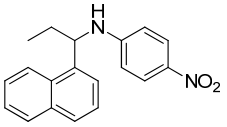
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 9.2 Hz, 2H), 7.35-7.32 (m, 2H), 7.25-7.21 (m, 3H), 6.60 (d, J = 9.2 Hz, 2H), 6.49 (s, 1H), 4.86 (s, 1H), 3.94 (d, J = 5.8 Hz, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.39, 138.22, 137.09, 133.61, 128.80, 128.22, 126.71, 126.55, 126.39, 111.35, 51.44, 16.20. HRMS (ESI): $(M+H)^+$ $C_{16}H_{17}N_2O_2$, Calcd 269.1290, found 269.1285. m.p. 114-115 °C.



N-(2-benzylideneoctyl)-4-nitroaniline (3z). Yellow solid.

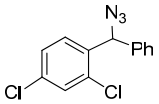
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 9.1 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 7.5 Hz, 2H), 6.59 (d, J = 9.1 Hz, 2H), 6.48 (s, 1H), 4.77 (s, 1H), 3.95 (d, J = 5.7 Hz, 2H), 2.31-2.26 (m, 2H), 1.29 (dd, J = 17.0, 7.8 Hz, 8H), 0.87 (t, J =

6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.25, 138.10, 137.04 128.46, 128.16, 126.57, 126.29, 111.25, 49.14, 31.46, 29.52, 29.34, 28.30, 22.50, 13.96. HRMS (ESI): $(M+H)^+$ $C_{21}H_{27}N_2O_2$, Calcd 339.2073, found 339.2067. m.p. 74-75 °C.



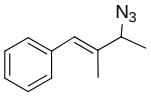
N-(1-(naphthalen-1-yl)propyl)-4-nitroaniline (3nb).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 1H), 7.91 (t, J = 9.4 Hz, 3H), 7.74 (d, J = 8.1 Hz, 1H), 7.60-7.50 (m, 2H), 7.45 (d, J = 7.1 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 6.40 (d, J = 9.0 Hz, 2H), 5.20-5.13 (m, 2H), 2.17-2.05 (m, 1H), 1.95-1.87 (m, 1H), 1.06 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.74, 137.98, 137.16, 134.15, 130.78, 129.41, 128.08, 126.50, 126.29, 125.78, 125.61, 122.80, 122.10, 111.86, 55.36, 30.37, 11.11. HRMS (ESI): $(M+H)^+$ $C_{19}H_{19}N_2O_2$, Calcd 307.1447, found 307.1441.



1-(1-azido-1-phenylmethyl)-2,4-dichlorobenzene (3je).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 1.8 Hz, 1H), 7.33 (d, J = 5.2 Hz, 2H), 7.29 (dd, J = 7.0, 5.9 Hz, 4H), 6.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.68, 135.95, 134.43, 133.65, 129.62, 129.56, 128.79, 128.42, 127.51, 64.43.



4-phenyl-3-methyl-3-buten-2-yl azide (3xe).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, J = 7.5 Hz, 2H), 7.30-7.22 (m, 3H), 6.51 (s, 1H), 4.16 (q, J = 6.8 Hz, 1H), 1.89 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.91, 136.73, 129.08, 128.37, 128.19, 127.79, 126.83, 65.47, 18.66, 13.64.

F. References

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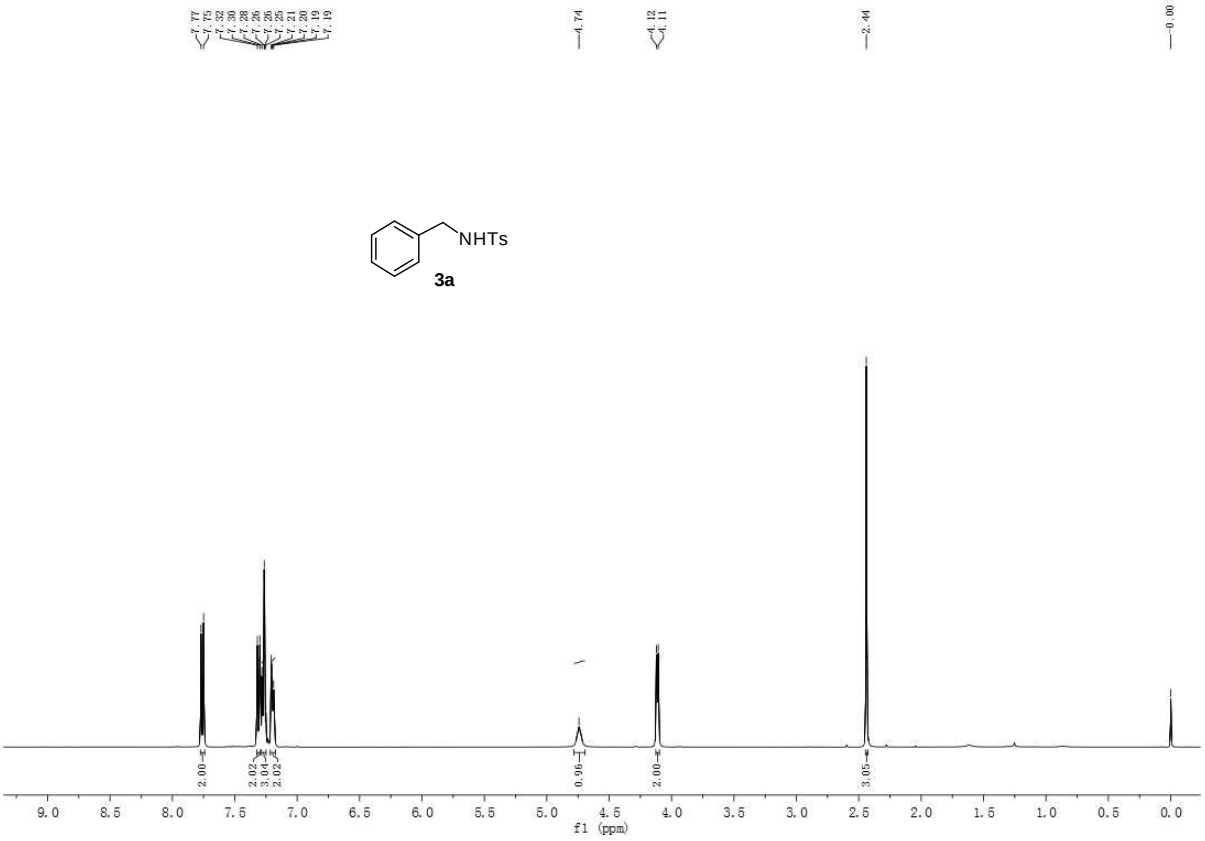
G. ^{1}H and ^{13}C NMR Spectra

^{1}H NMR



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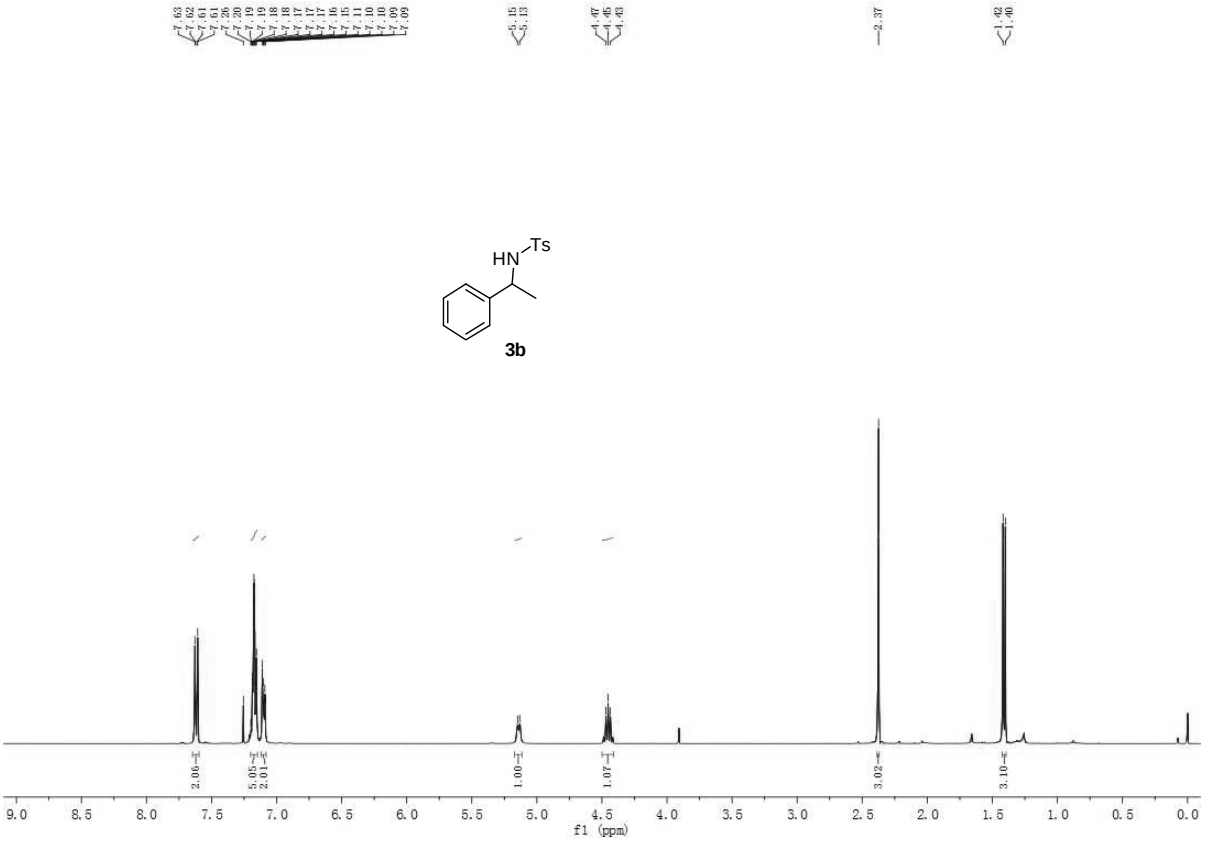

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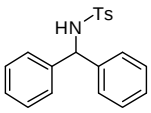
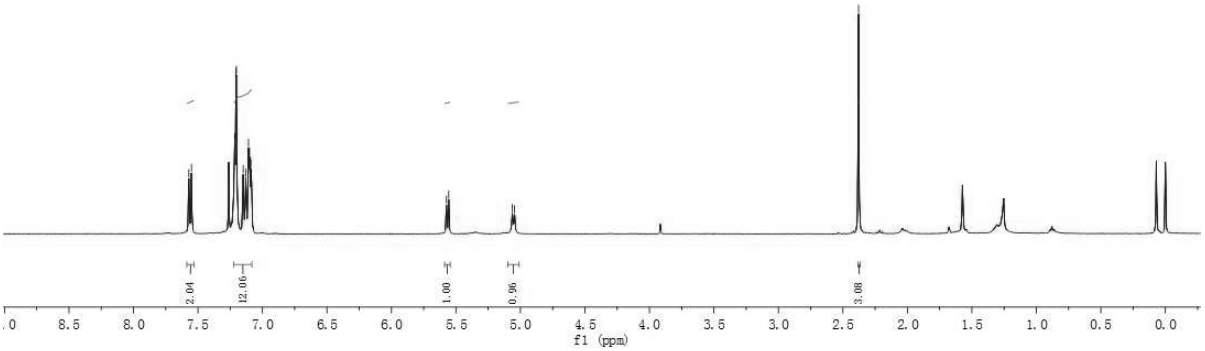
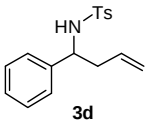


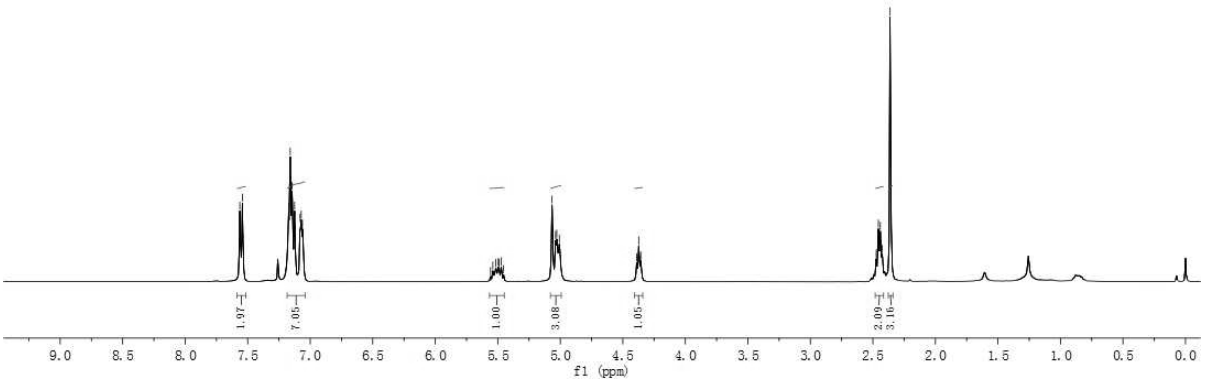
3c



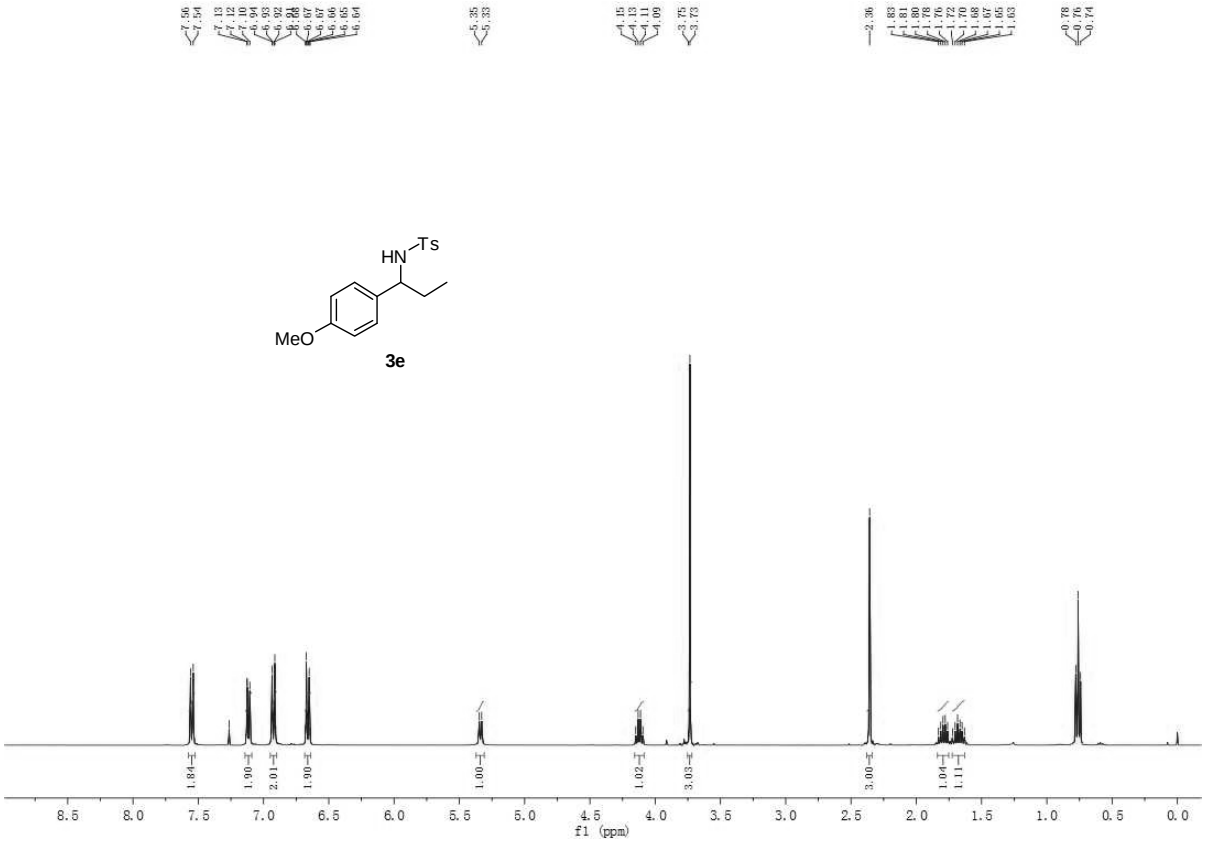
^{1}H NMR



3d



^{1}H NMR



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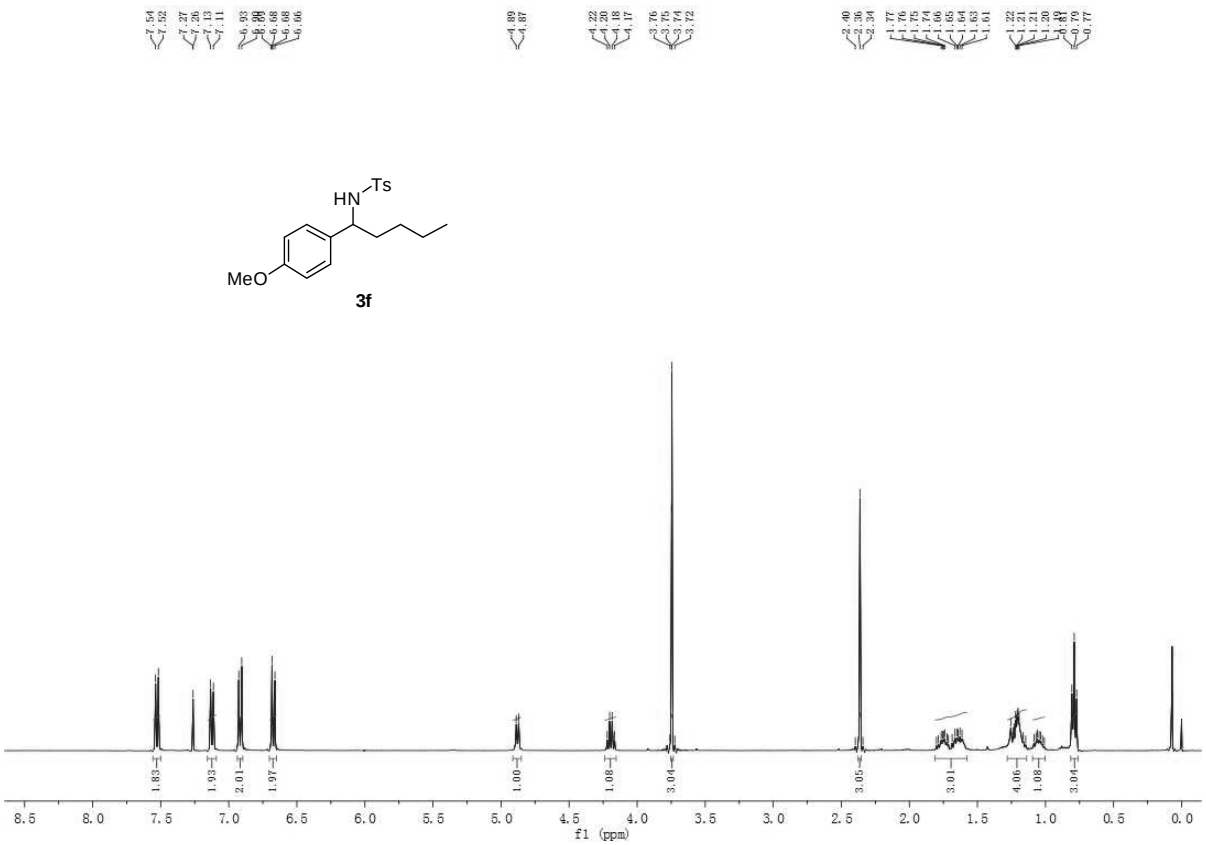
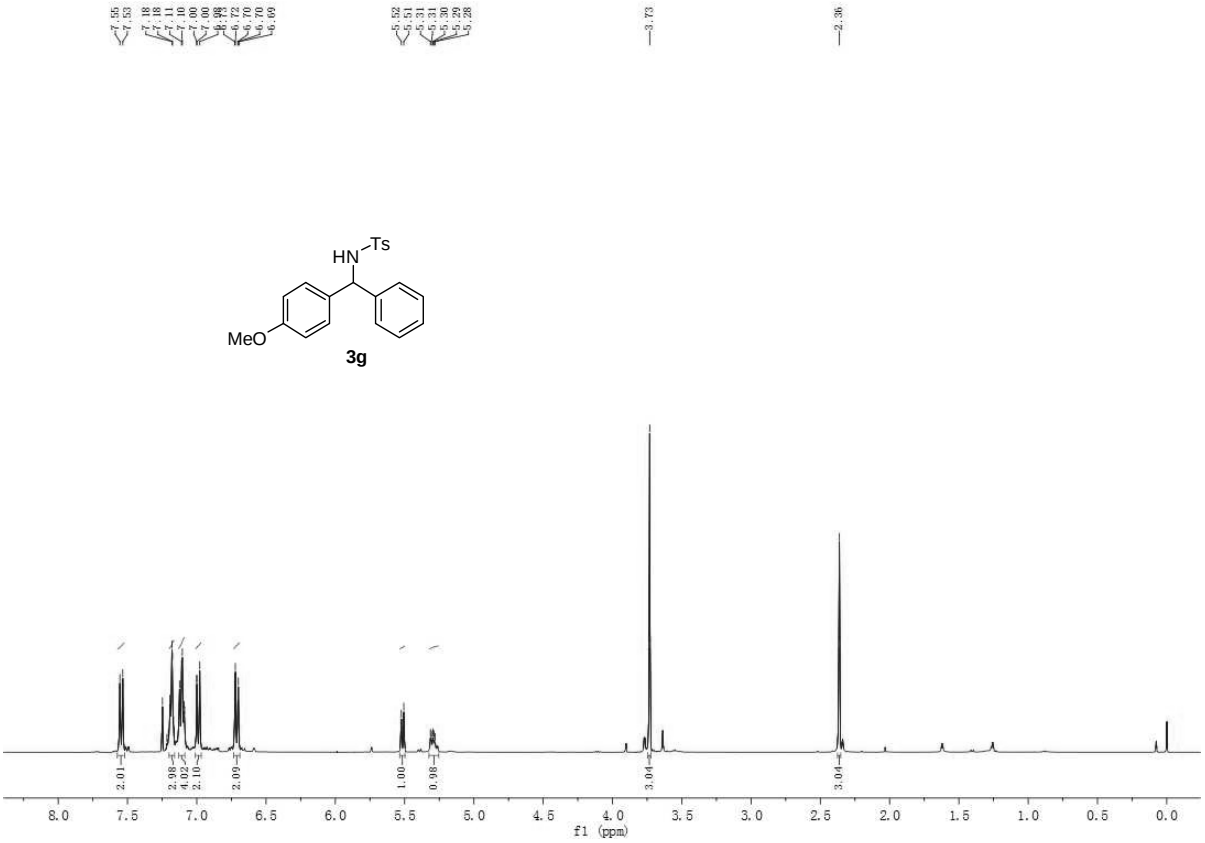
^{1}H NMR

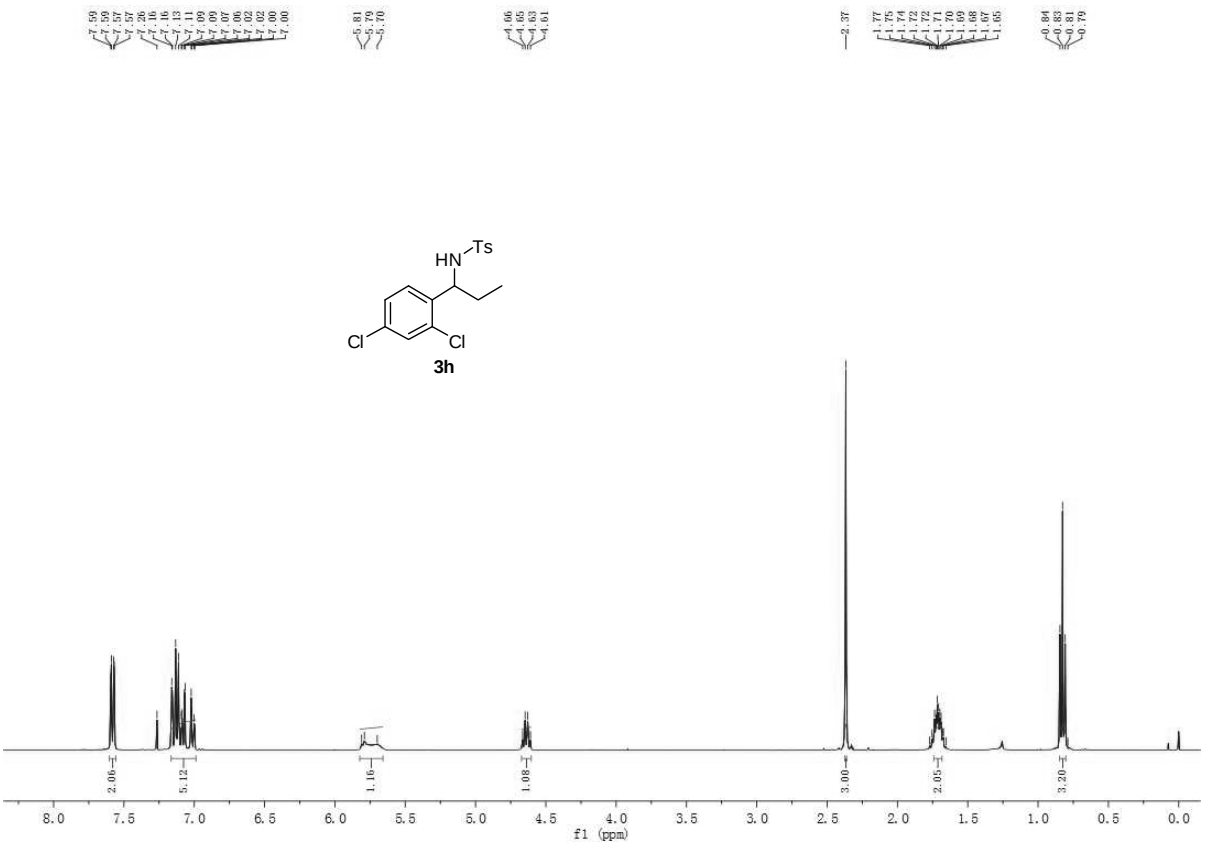


3f

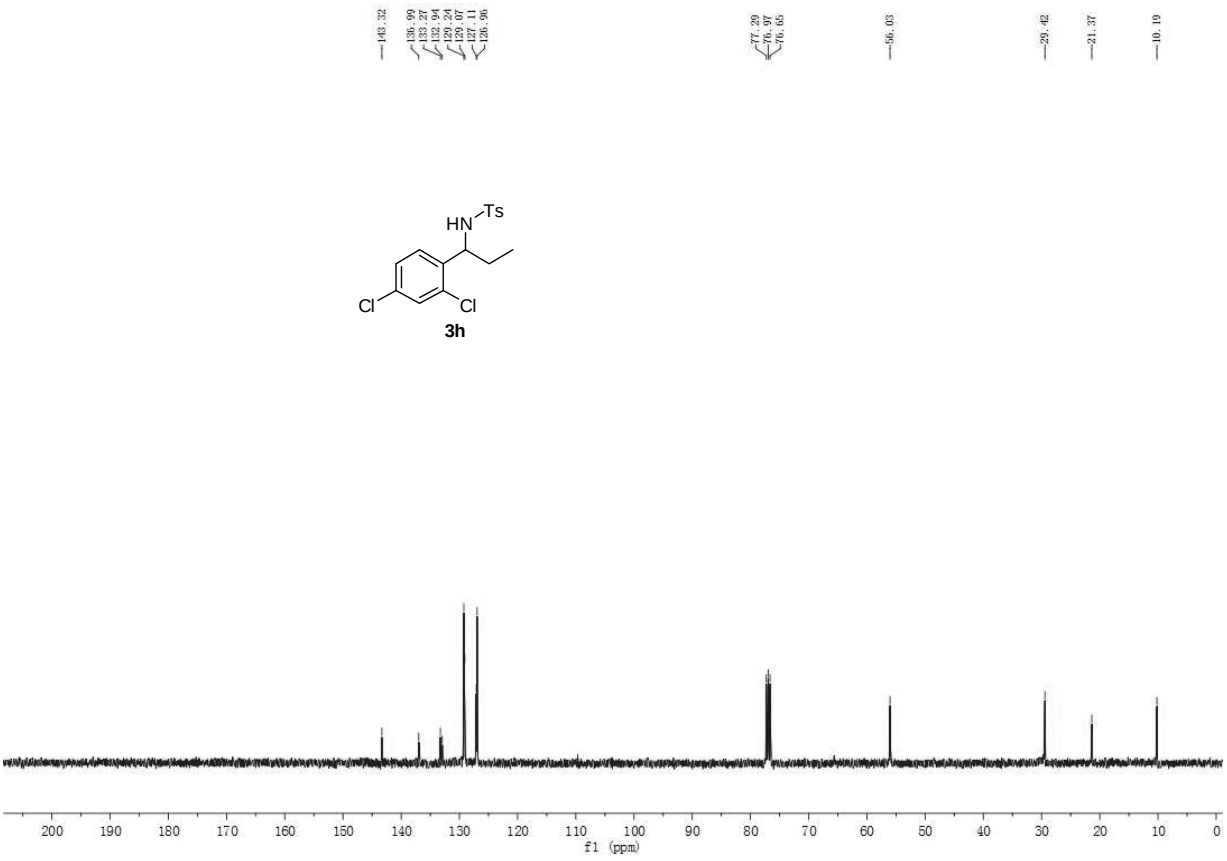
^{1}H NMR



^{1}H NMR



^{13}C NMR



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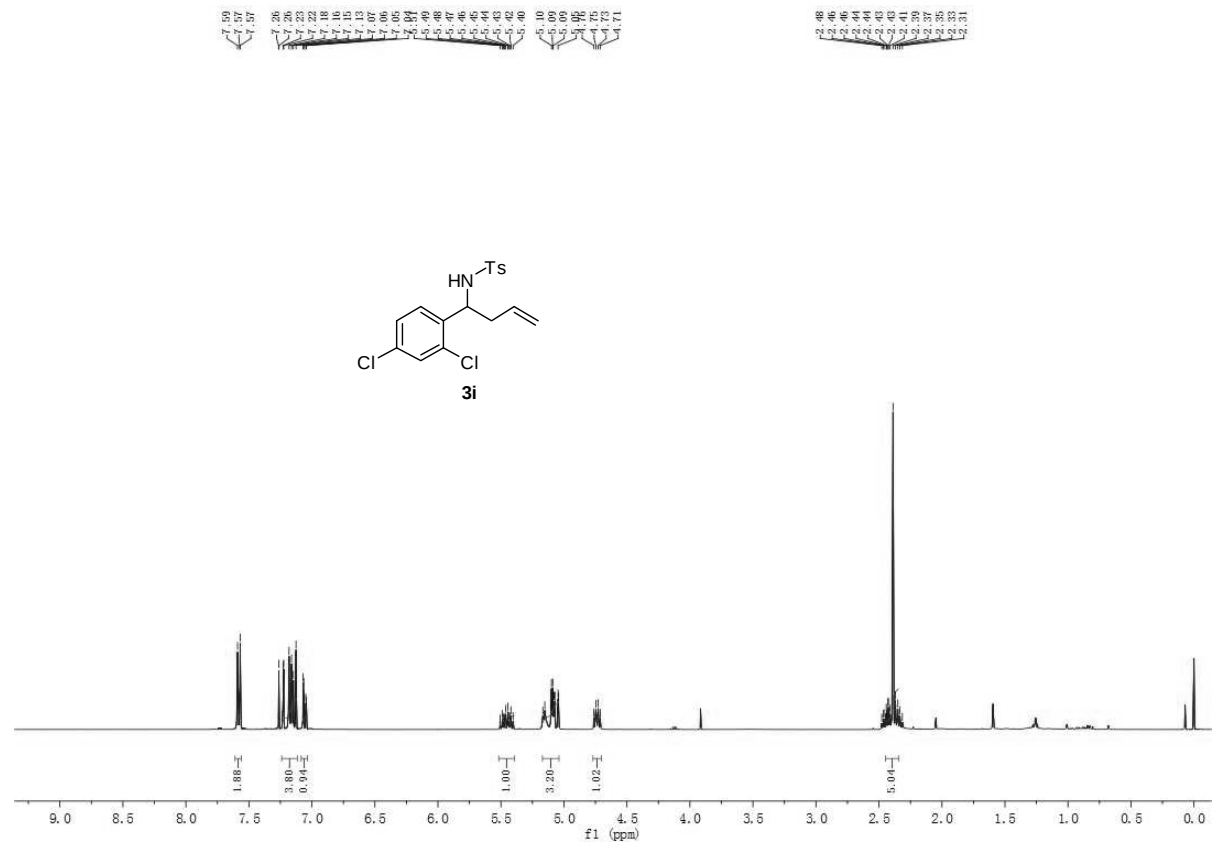

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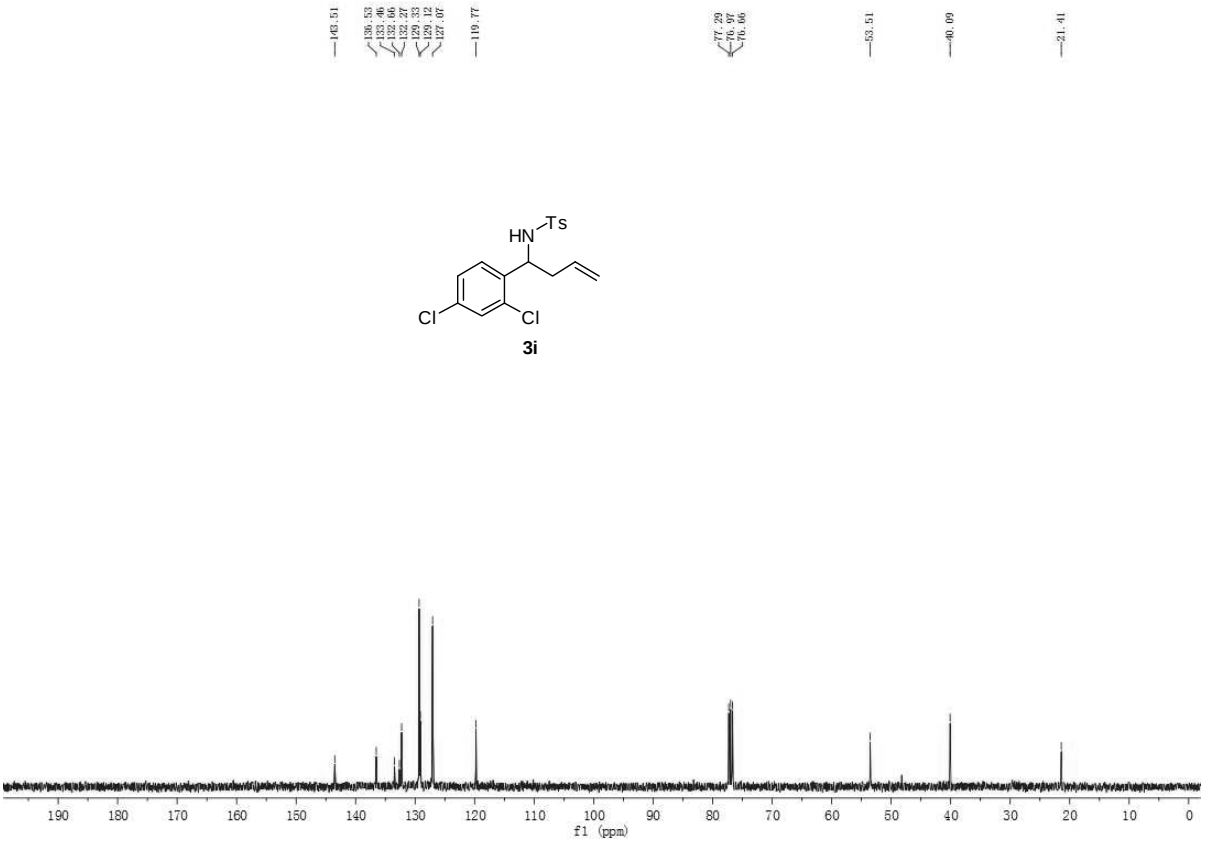

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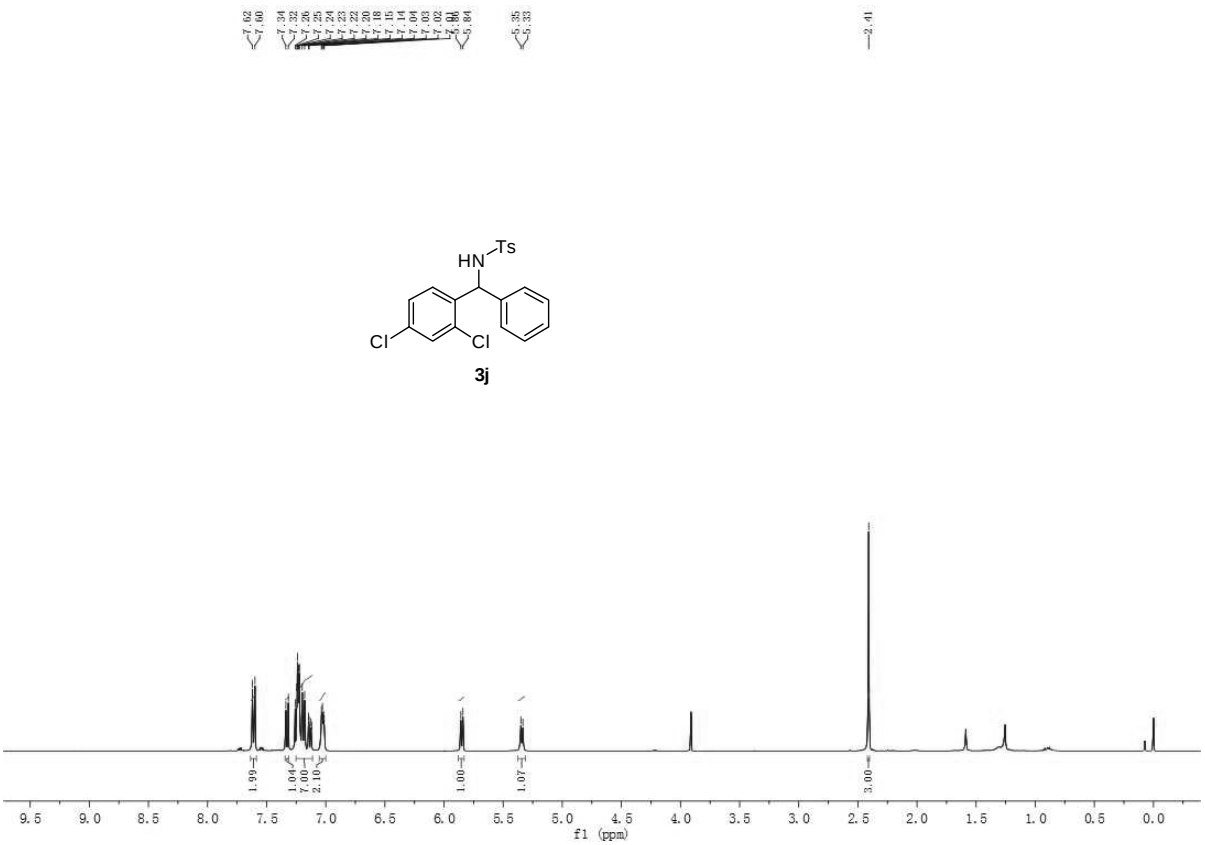
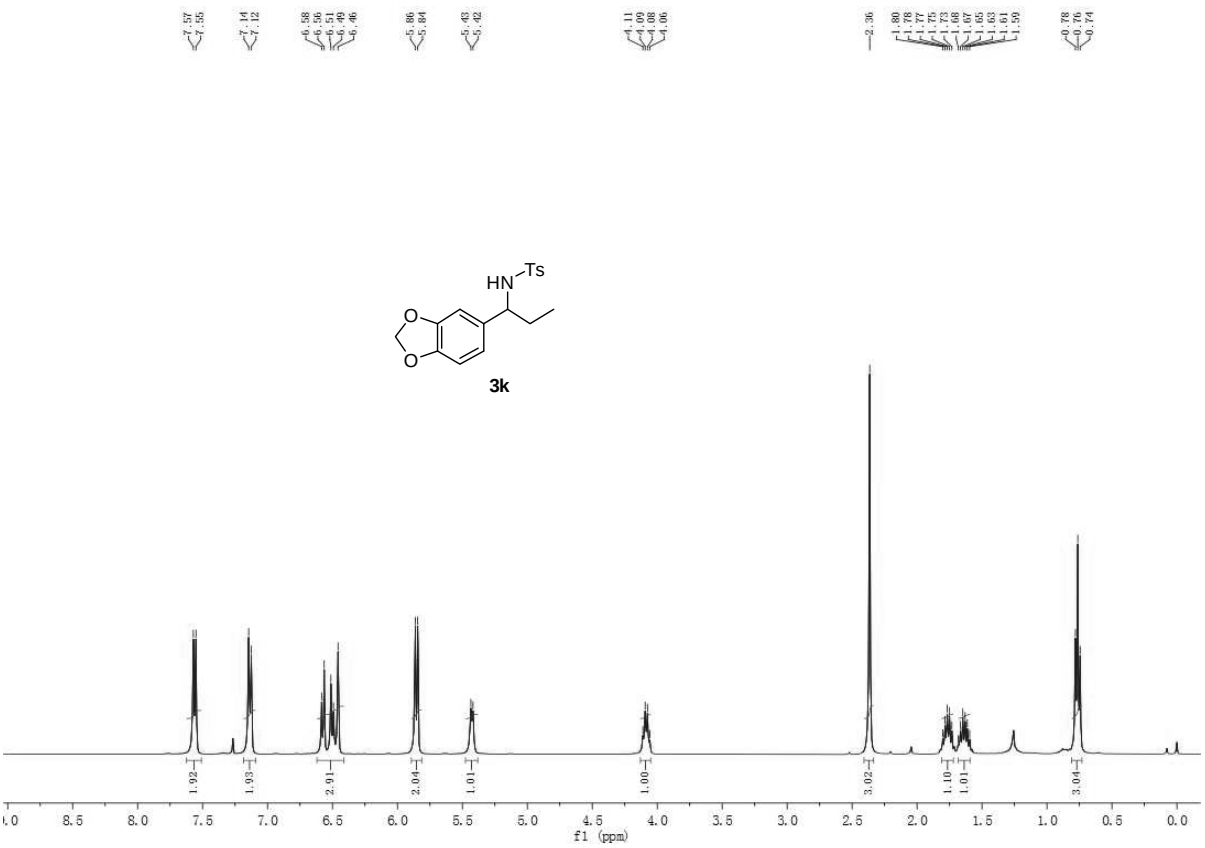


^{1}H NMR



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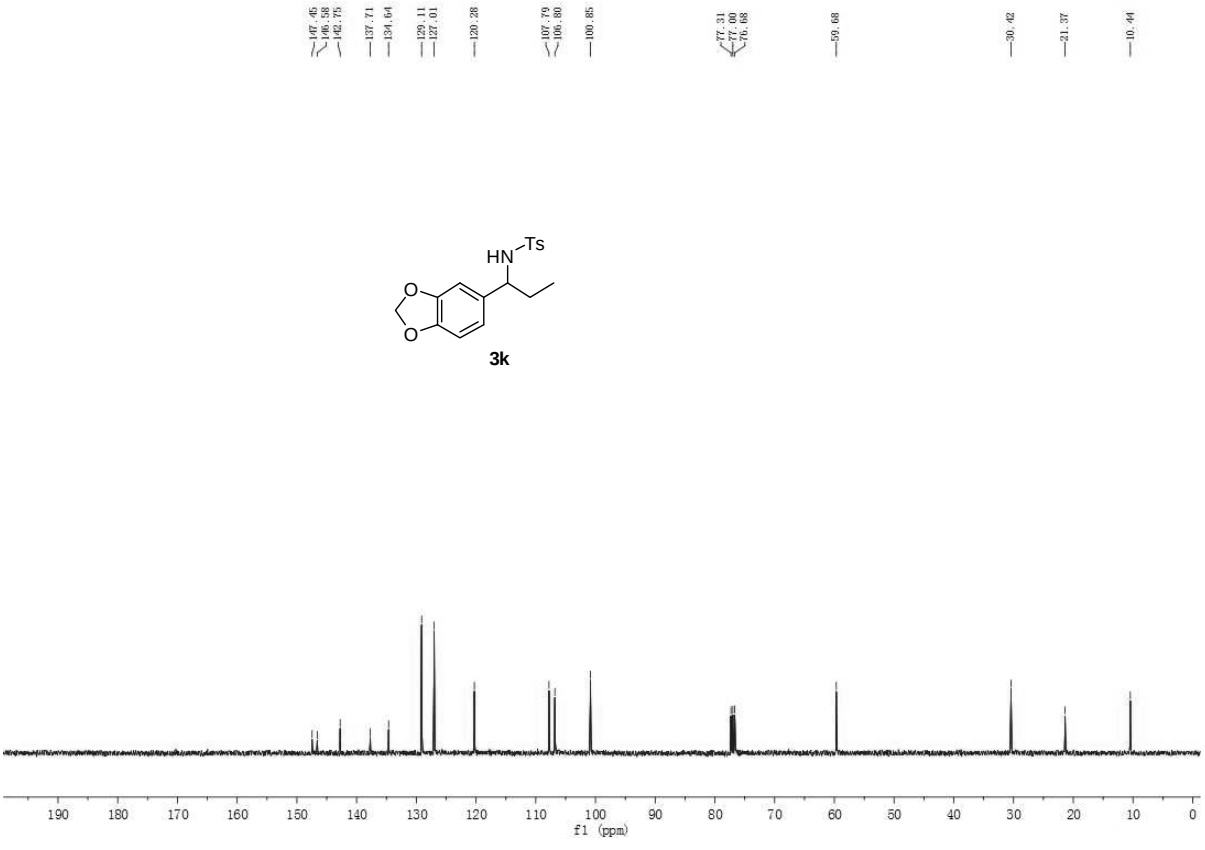

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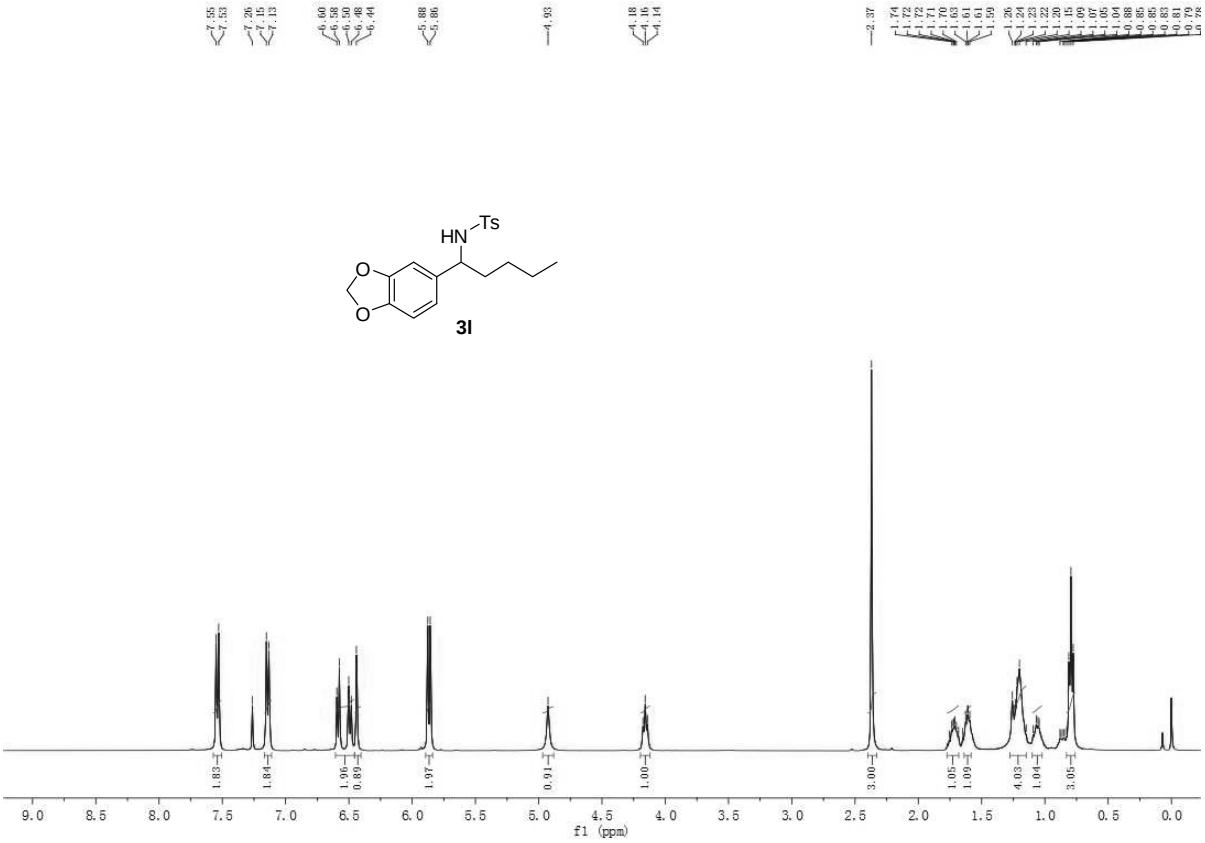

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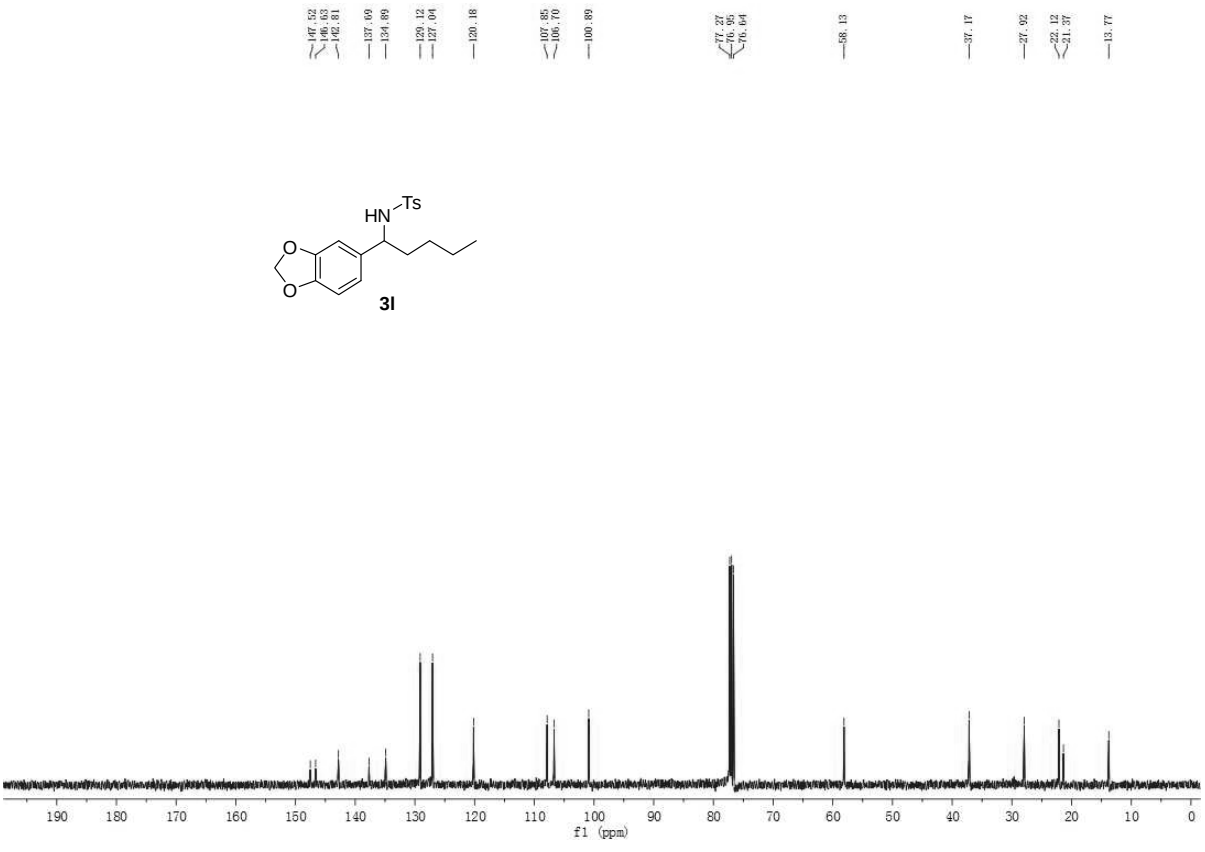

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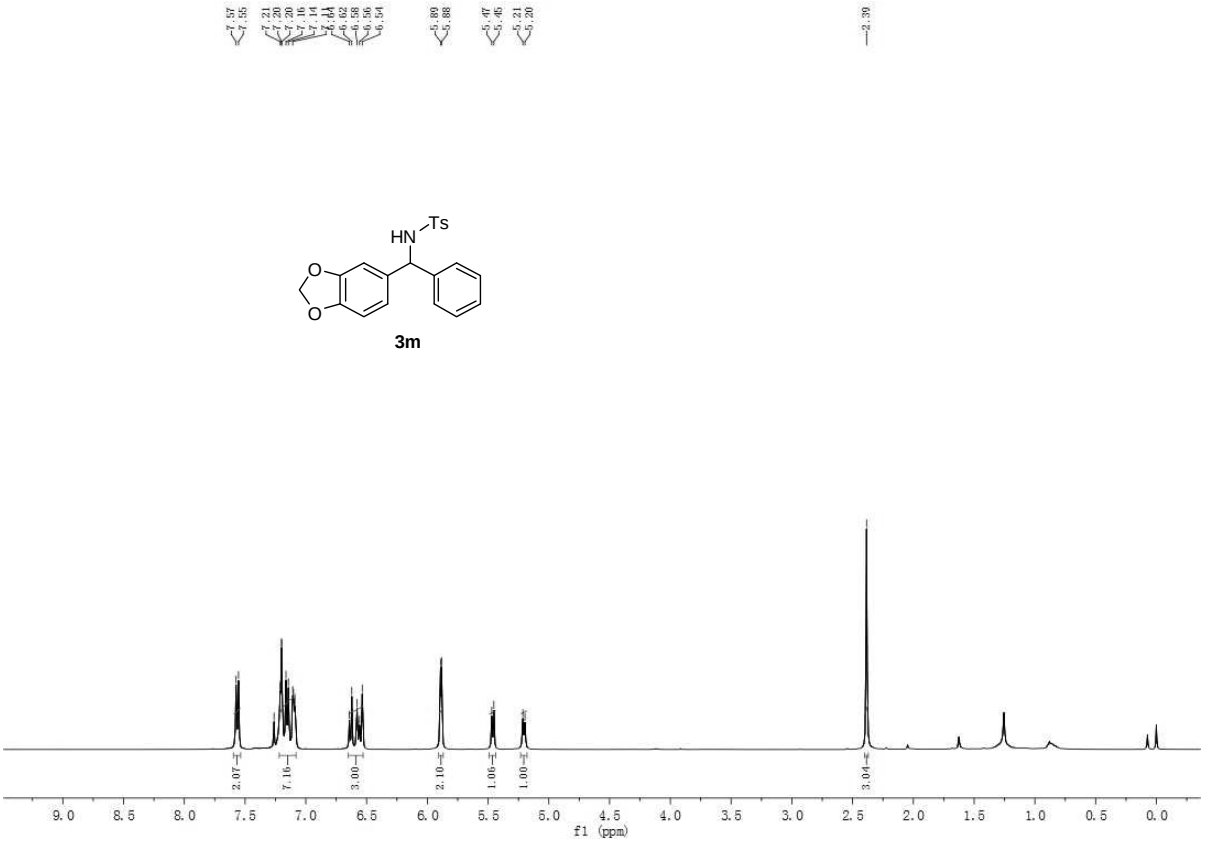

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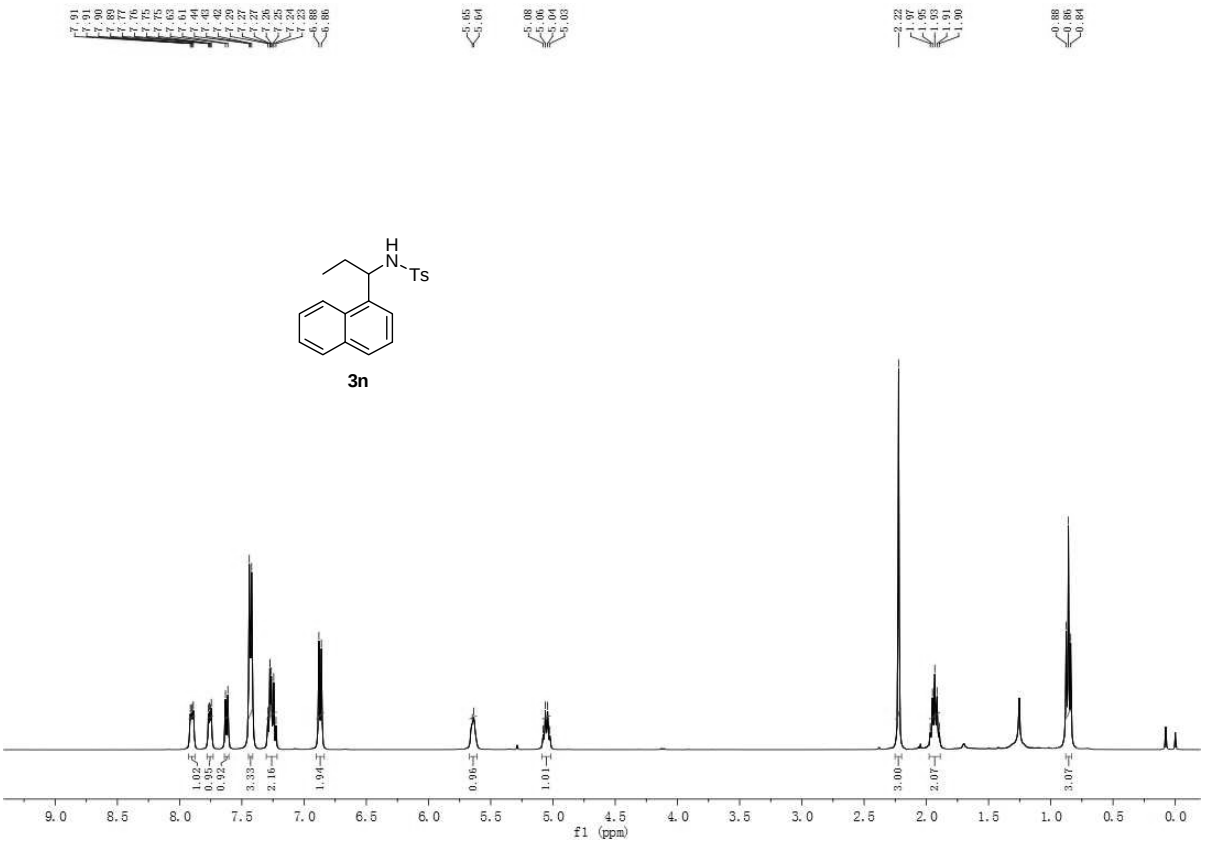

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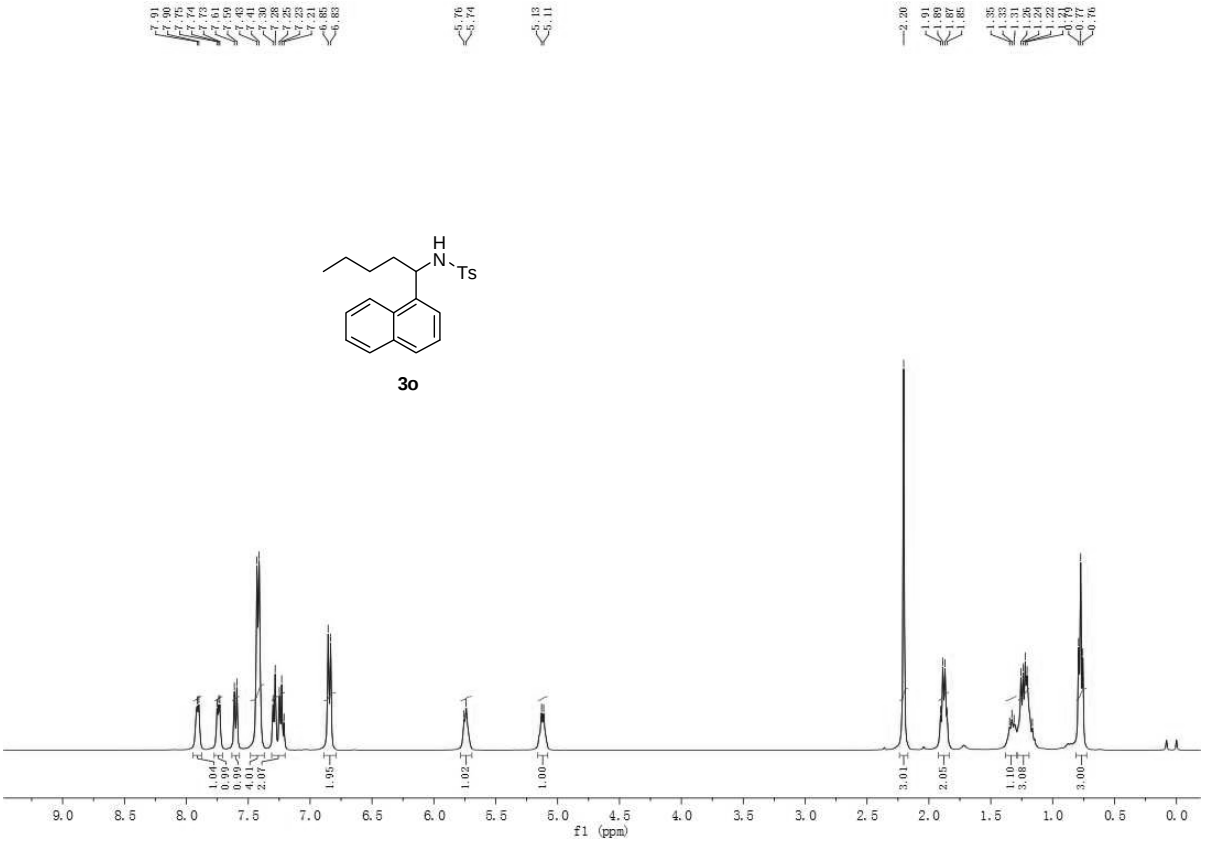
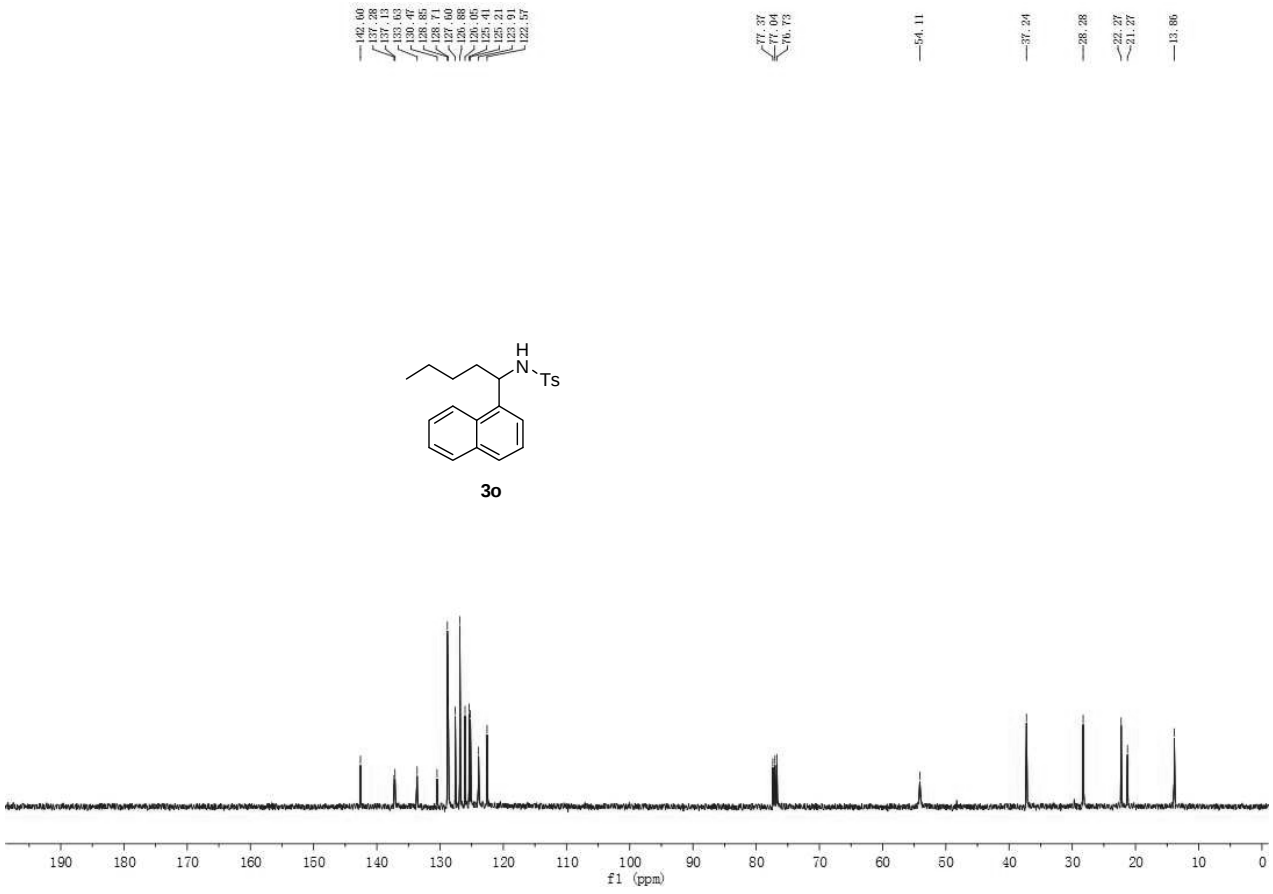


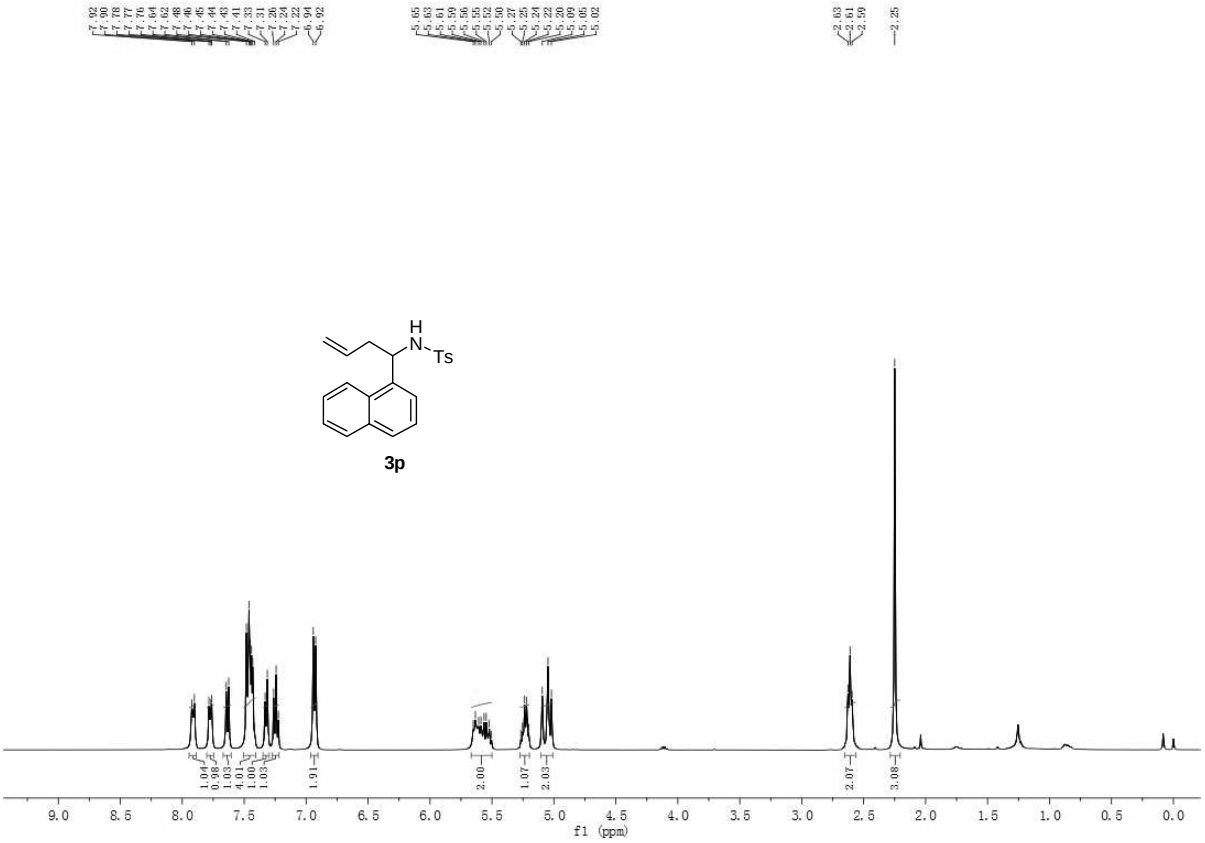
3o

^{13}C NMR



3o

^{1}H NMR



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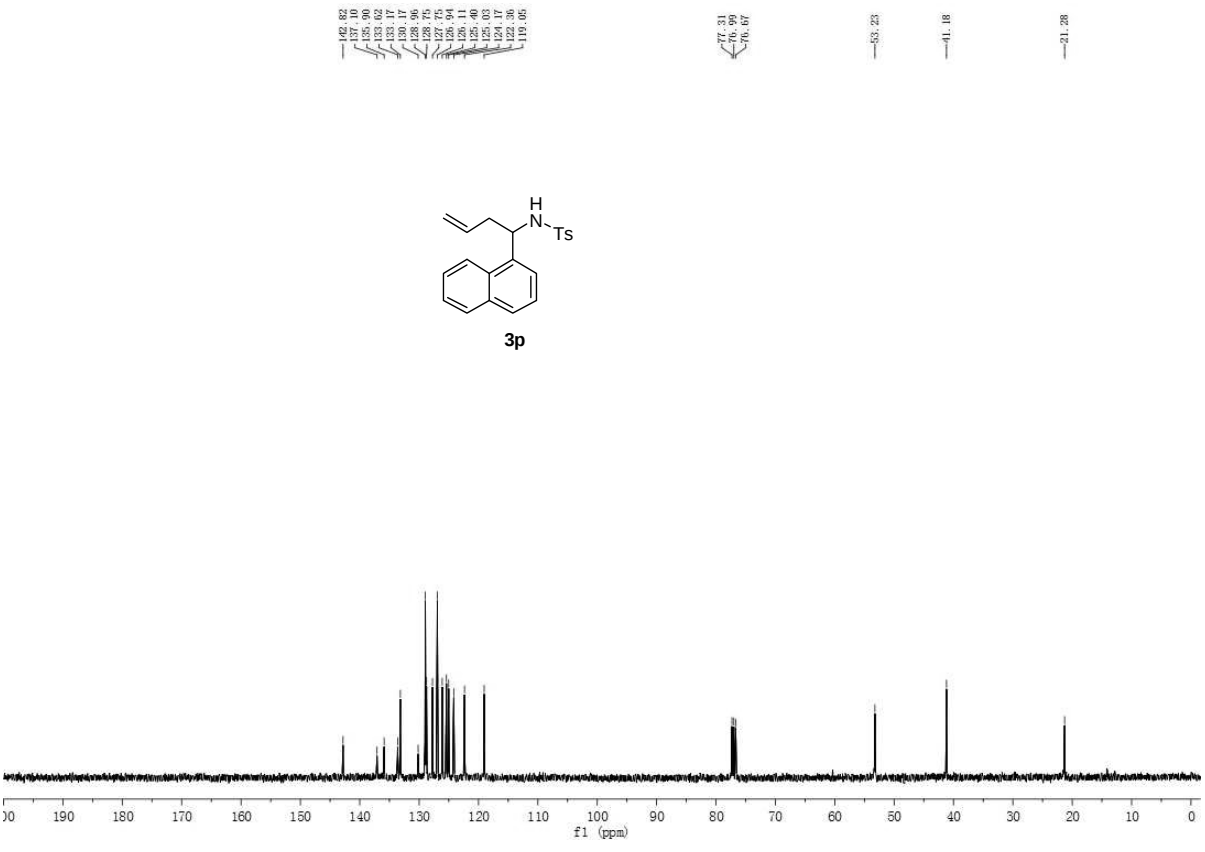

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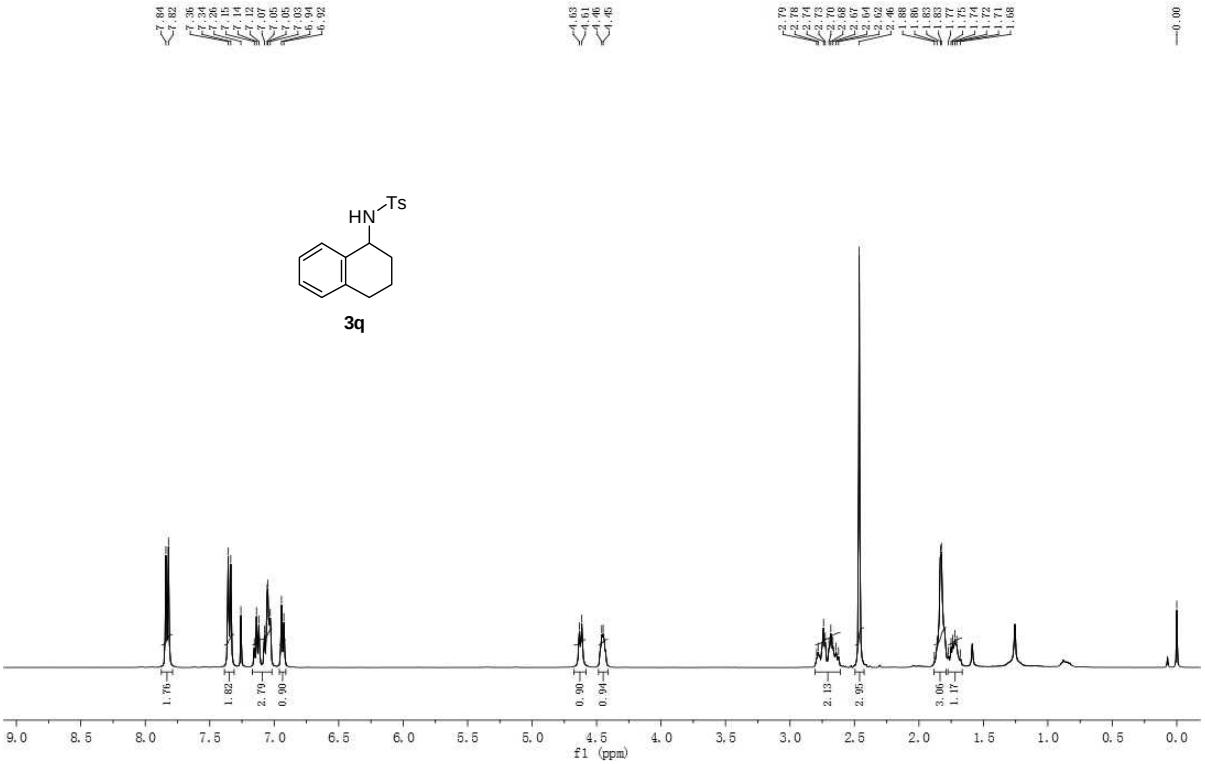

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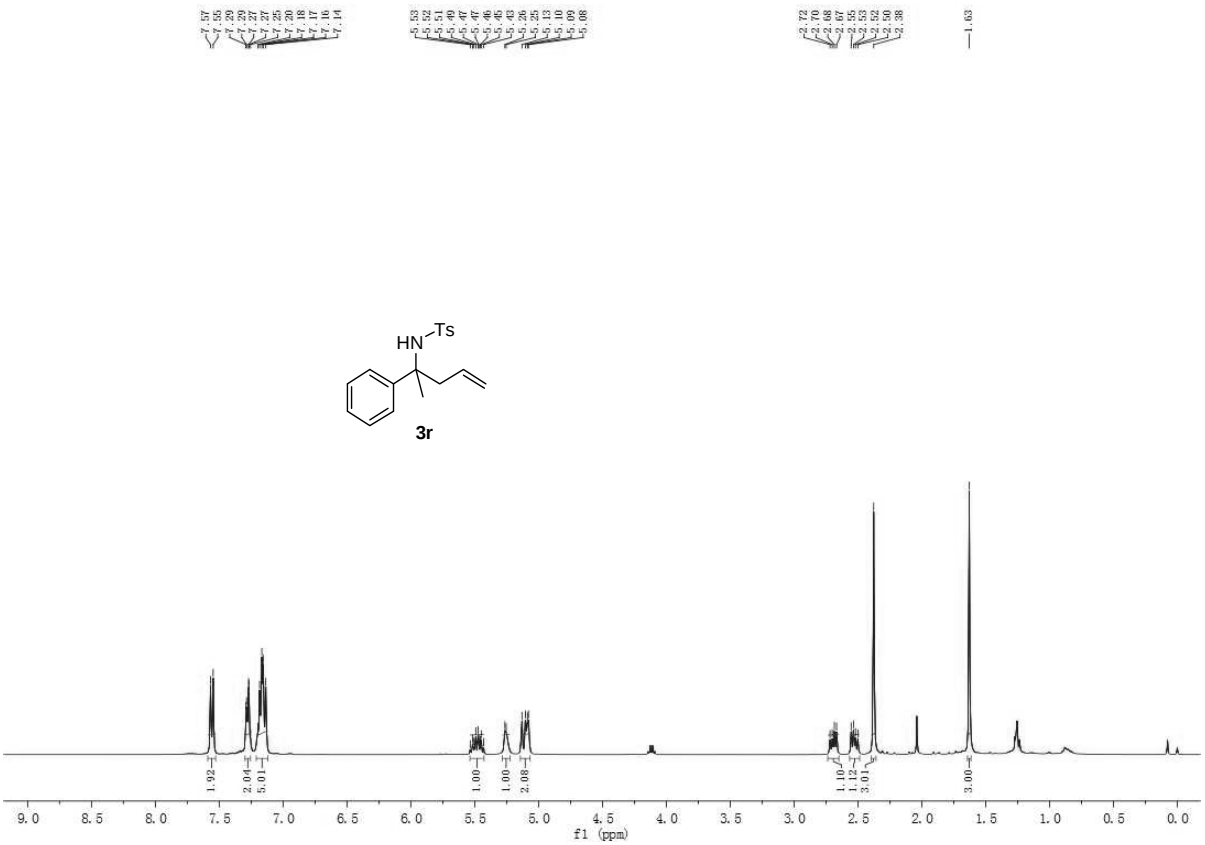

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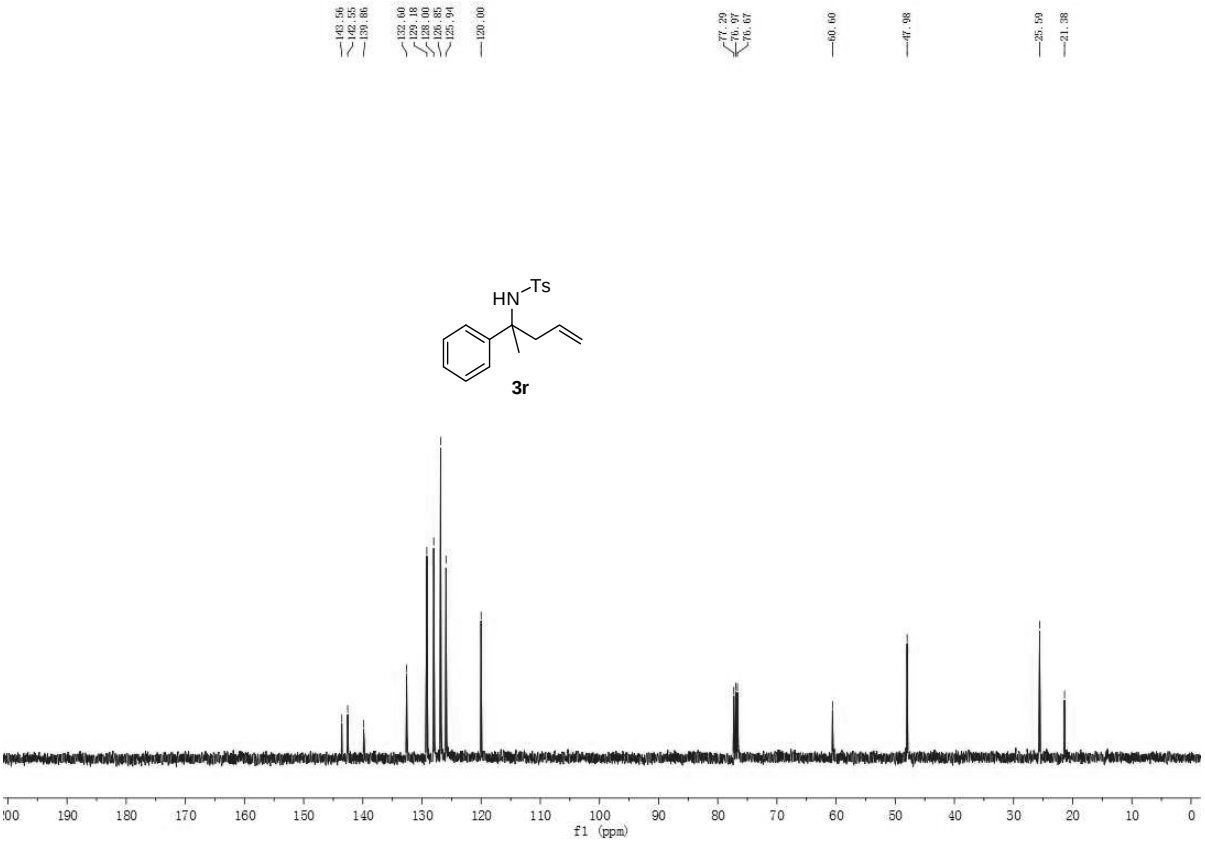

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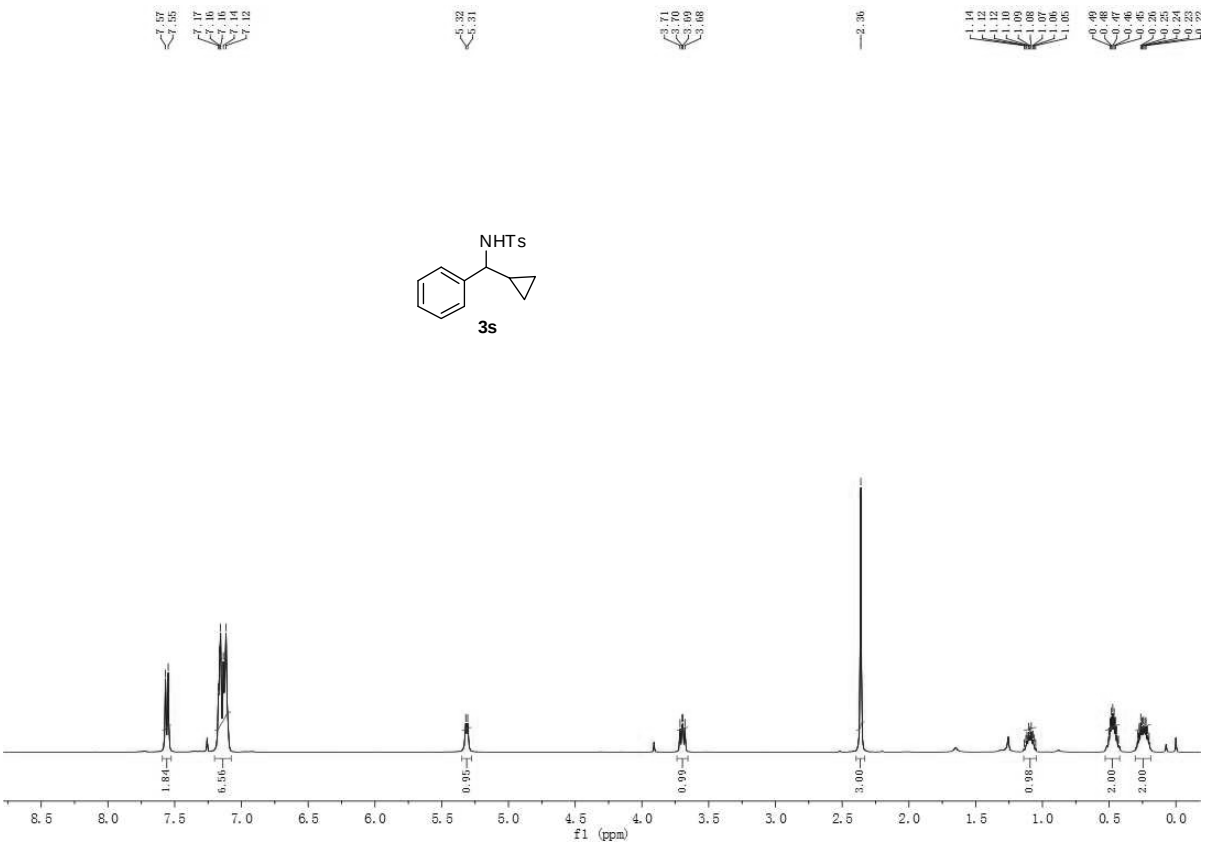

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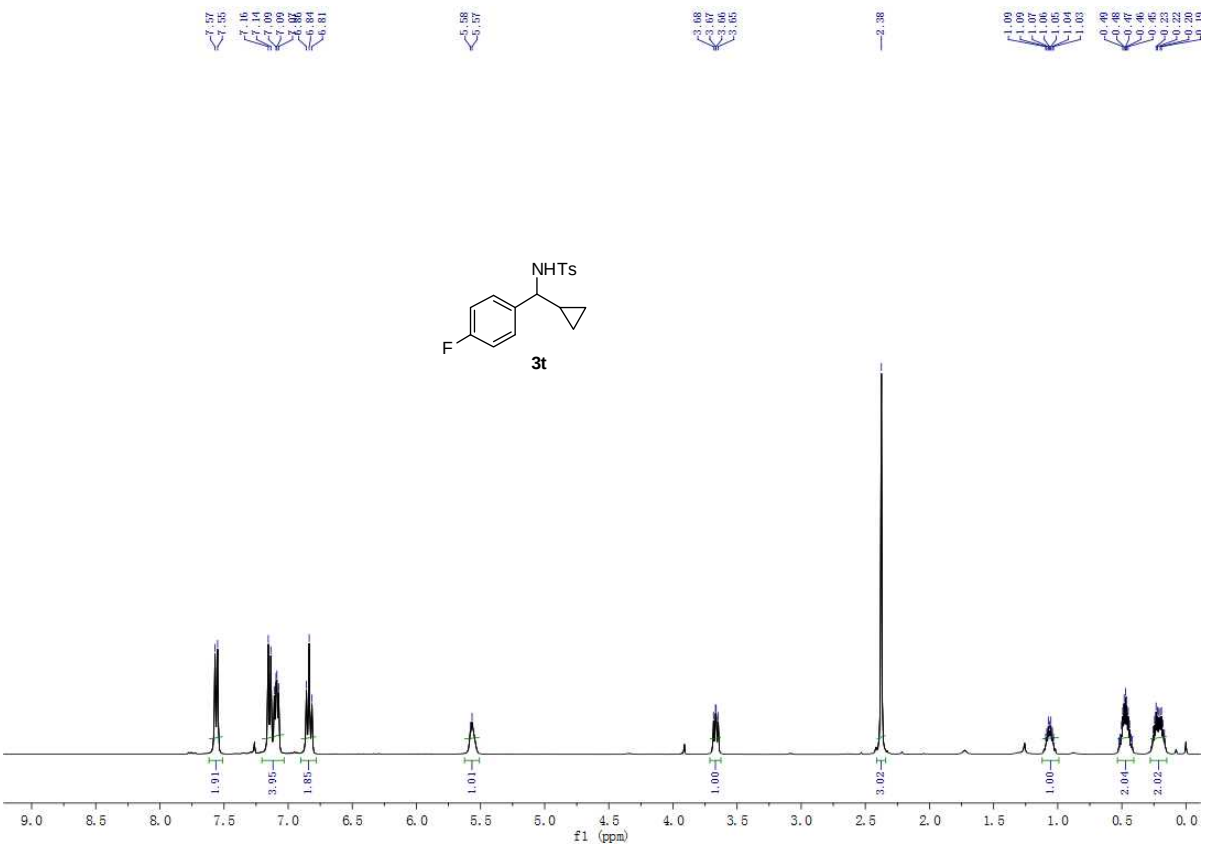

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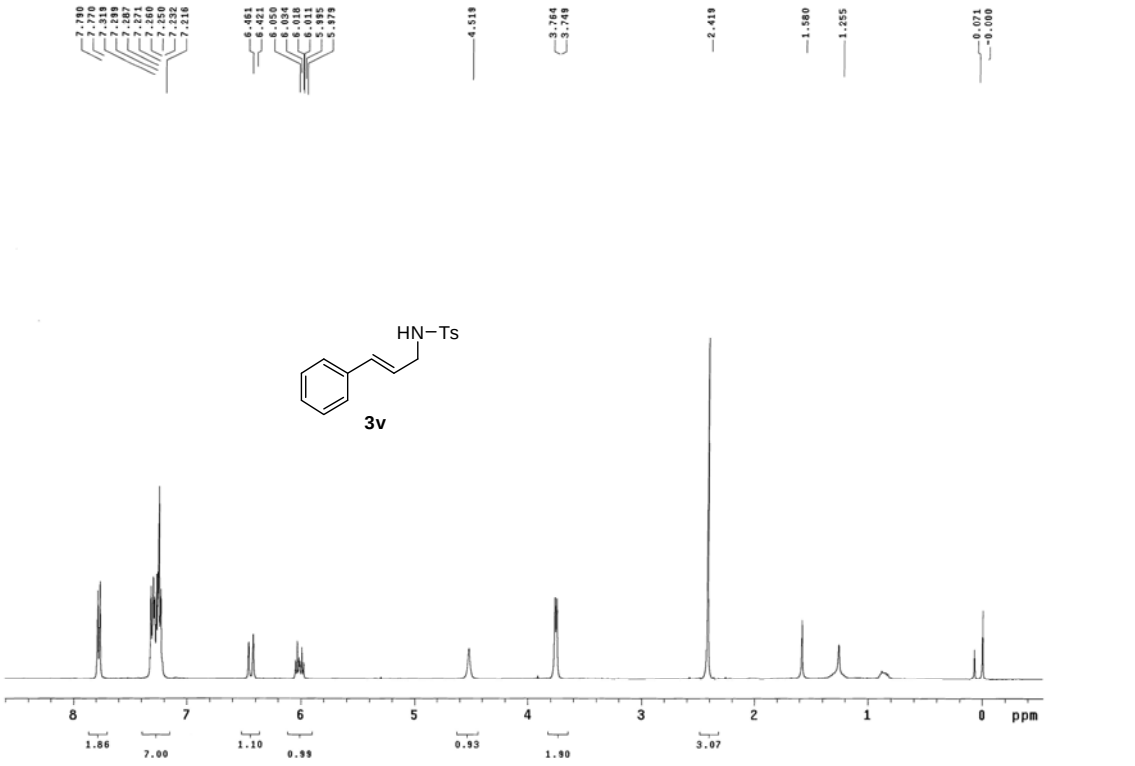

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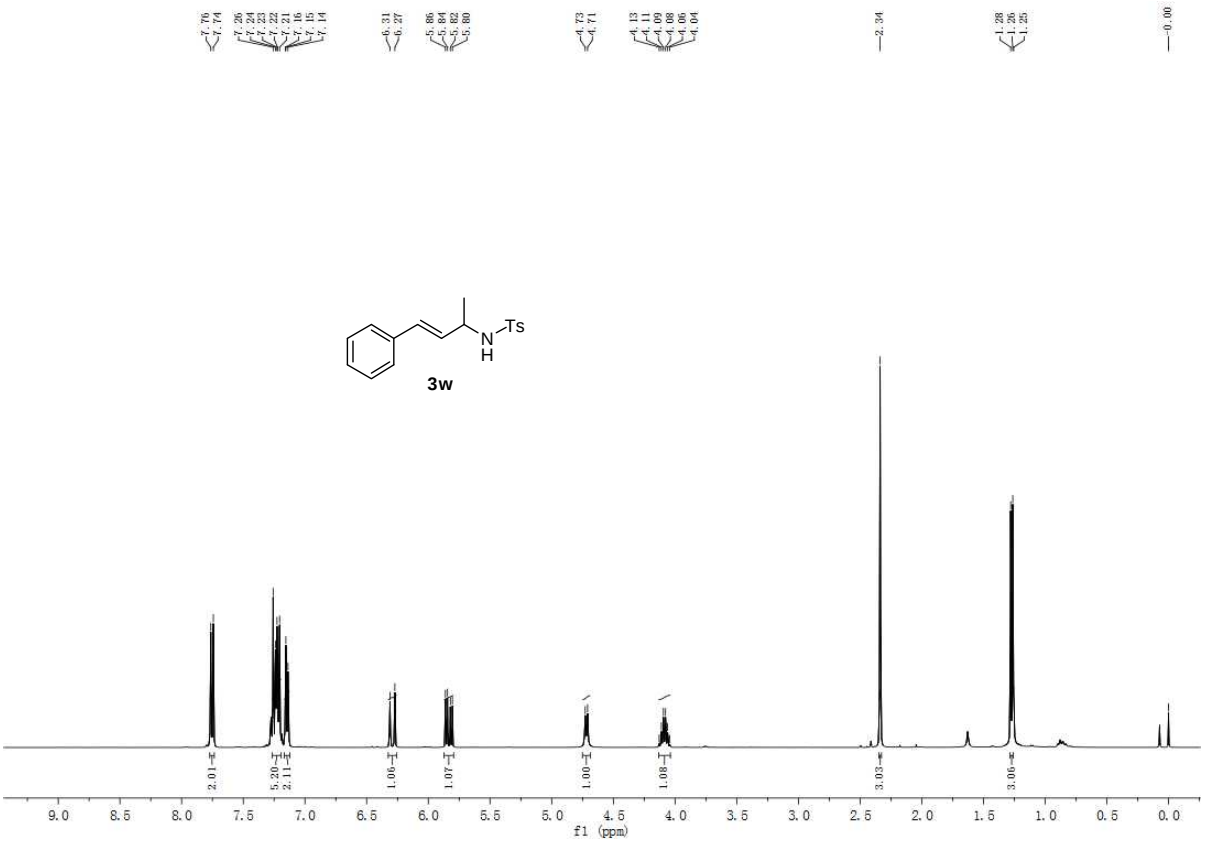

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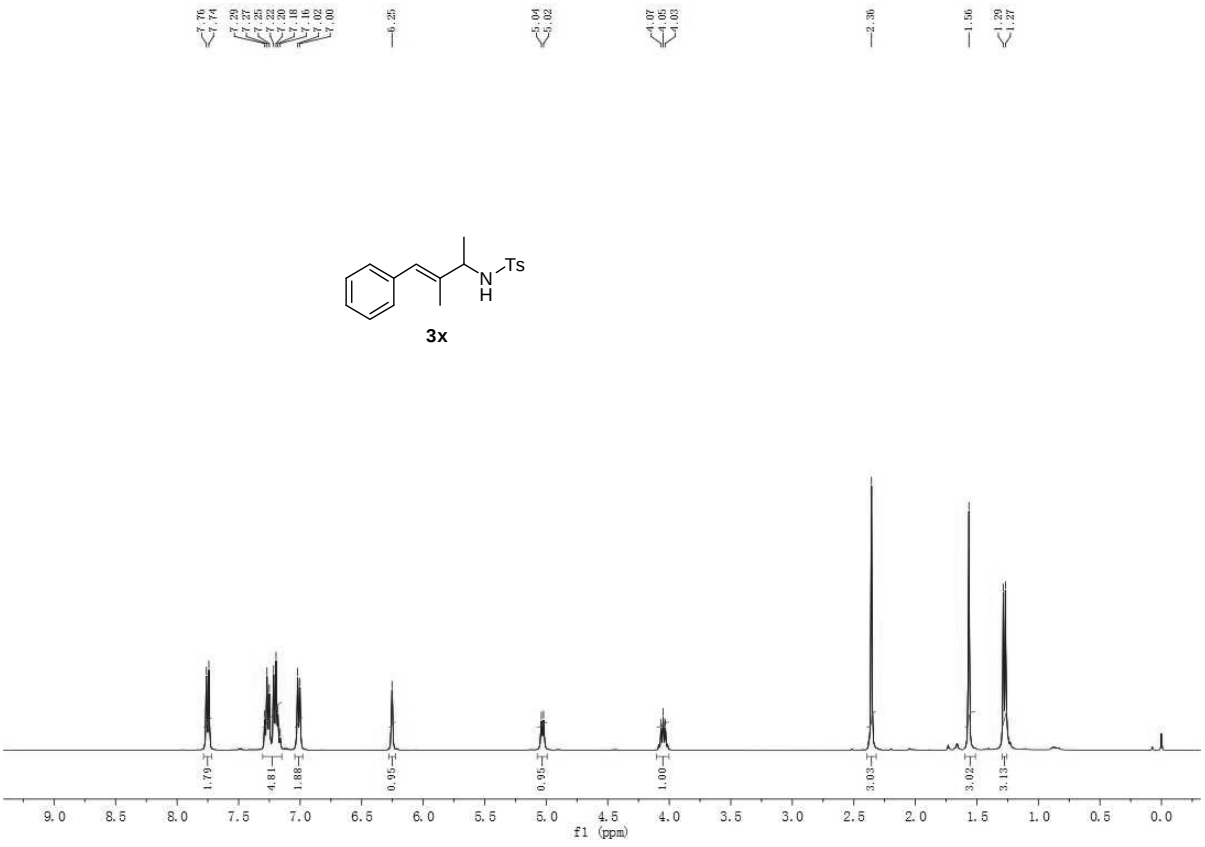

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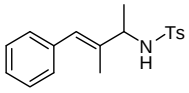

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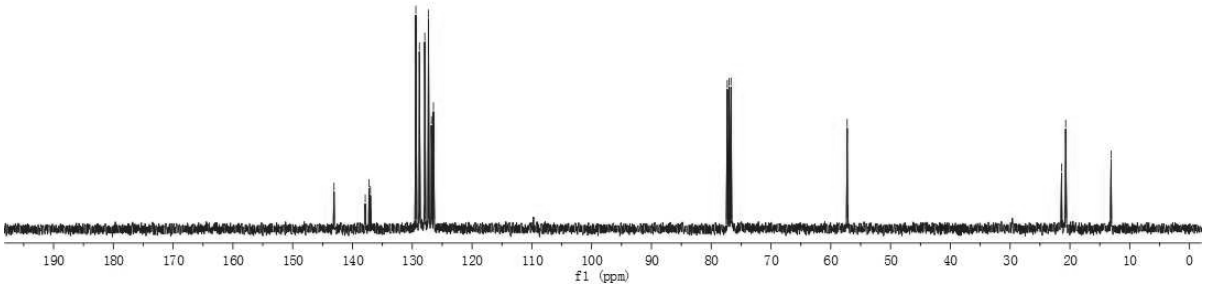

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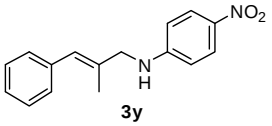

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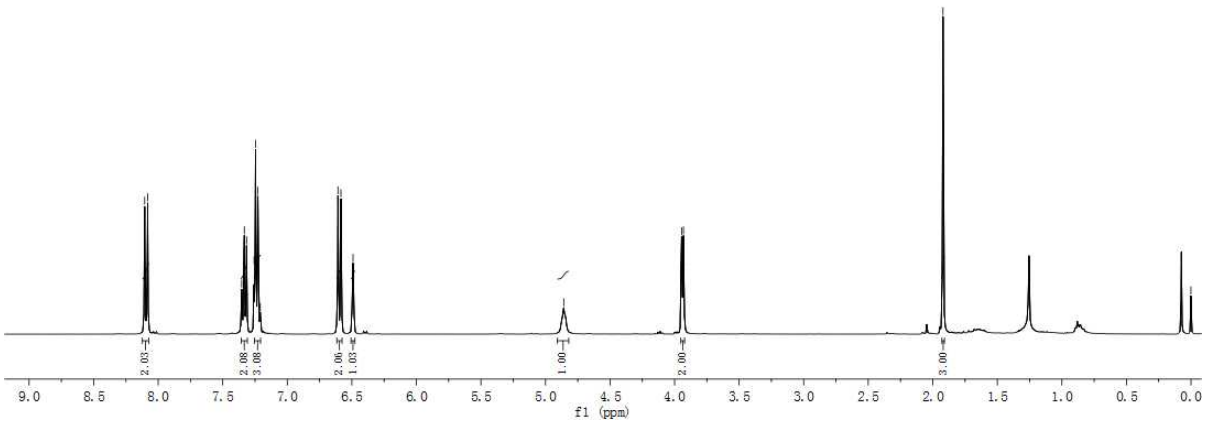

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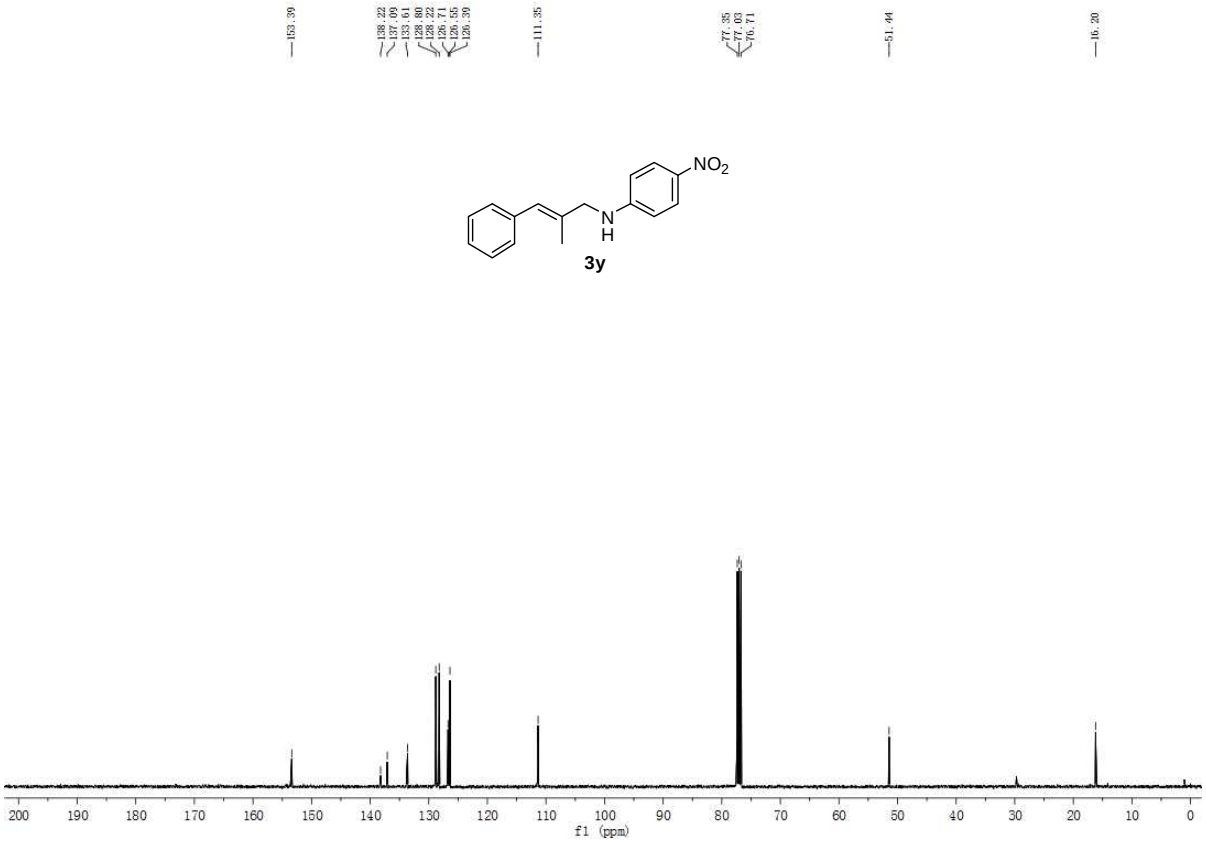

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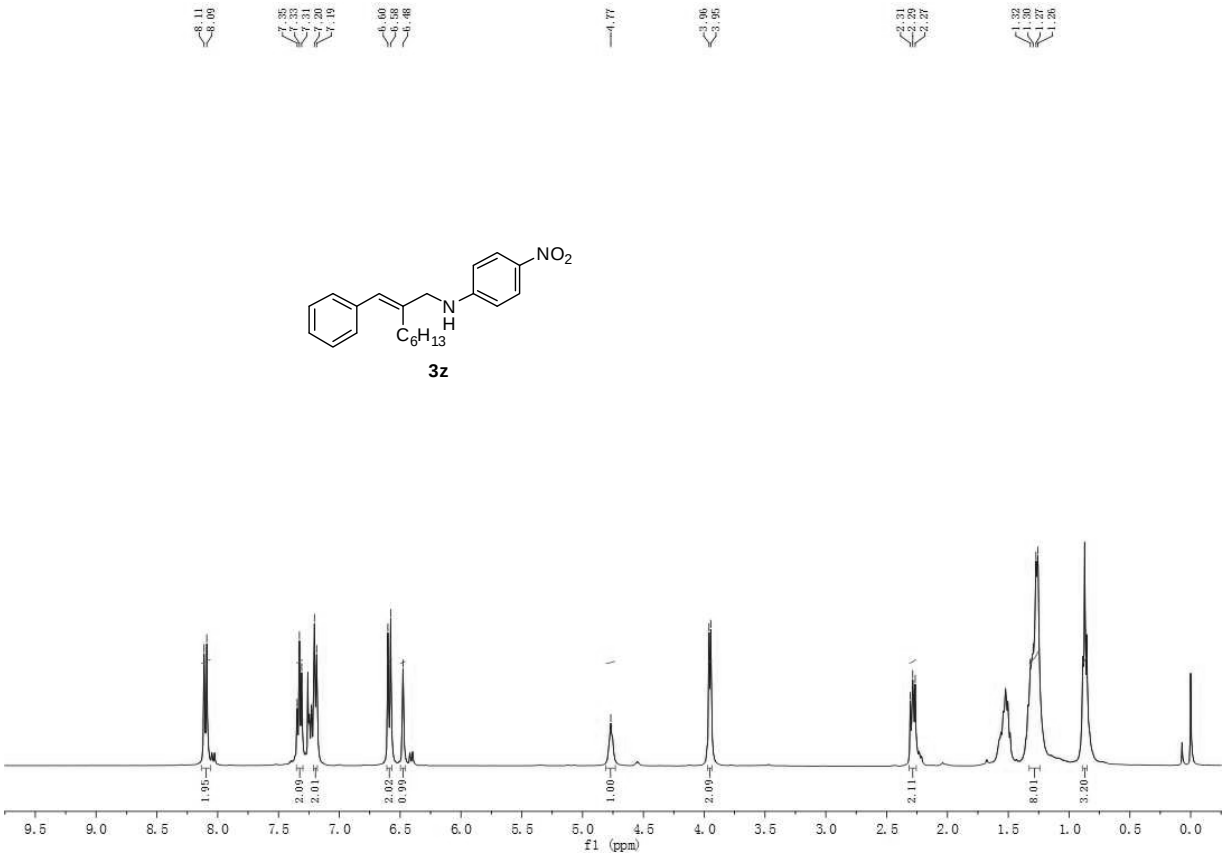

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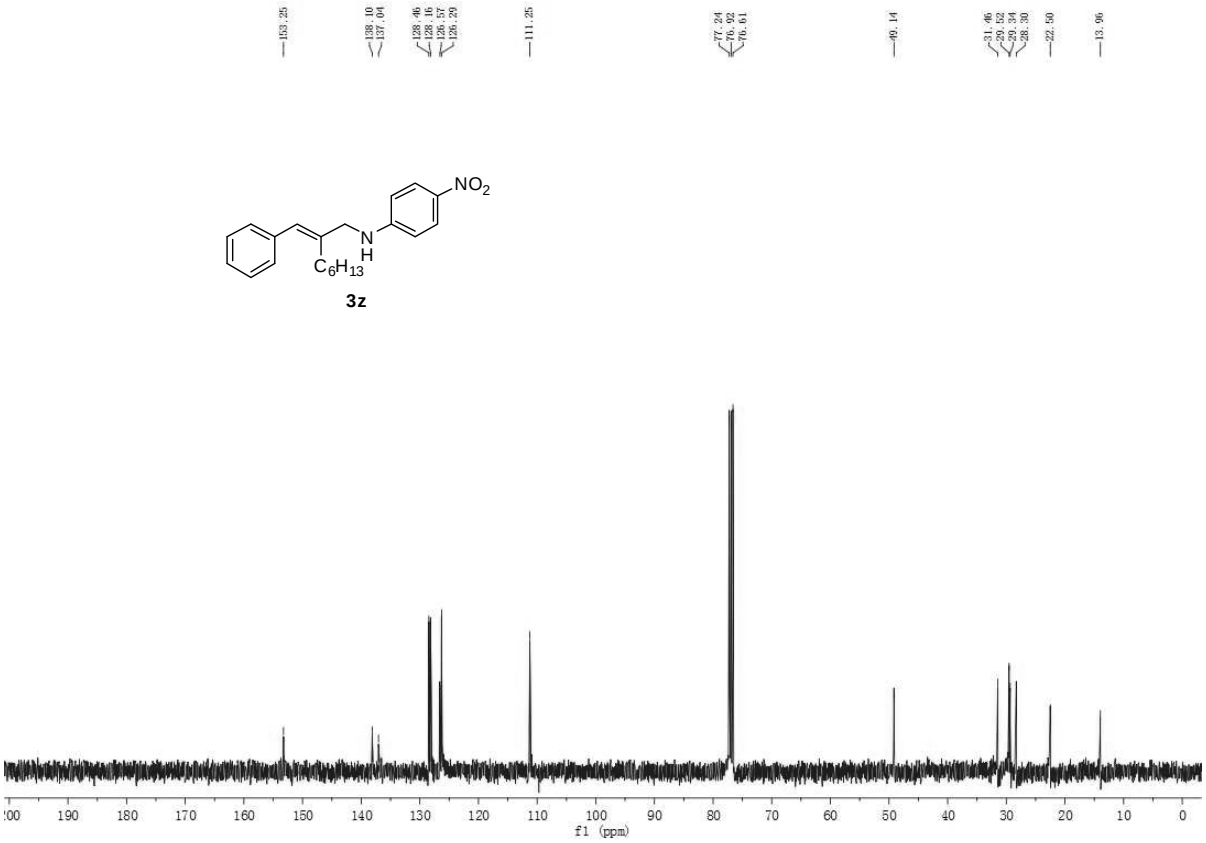

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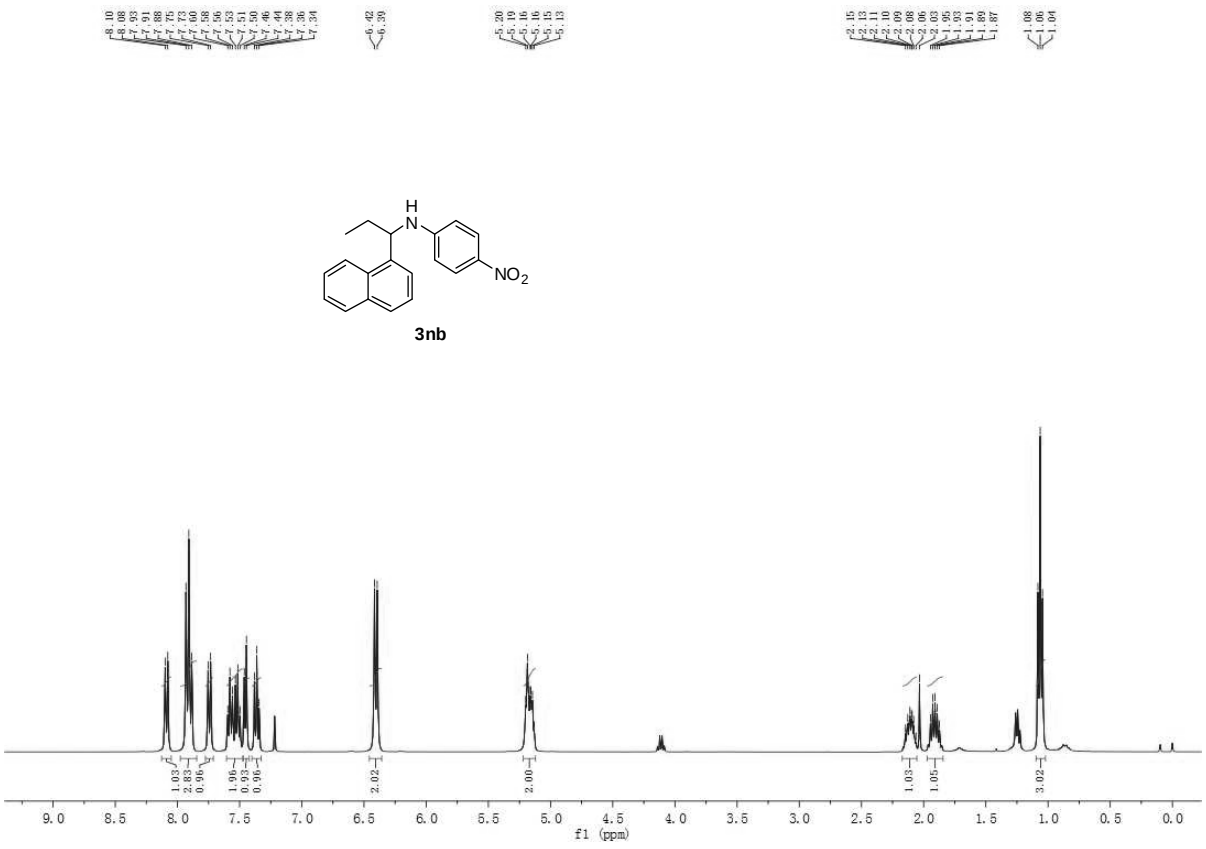

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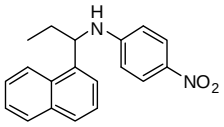

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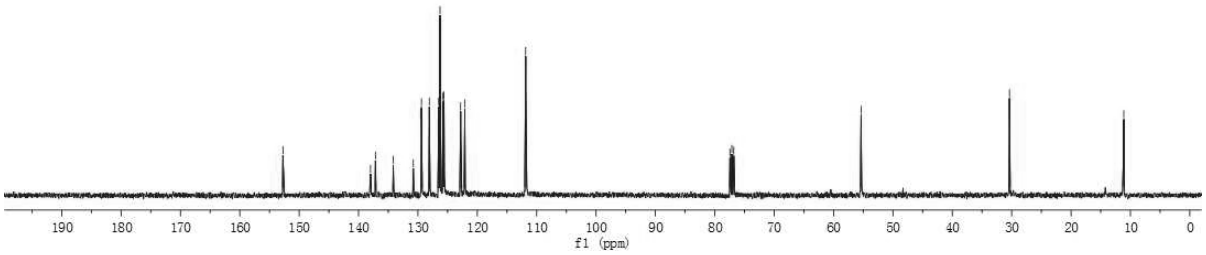

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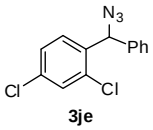

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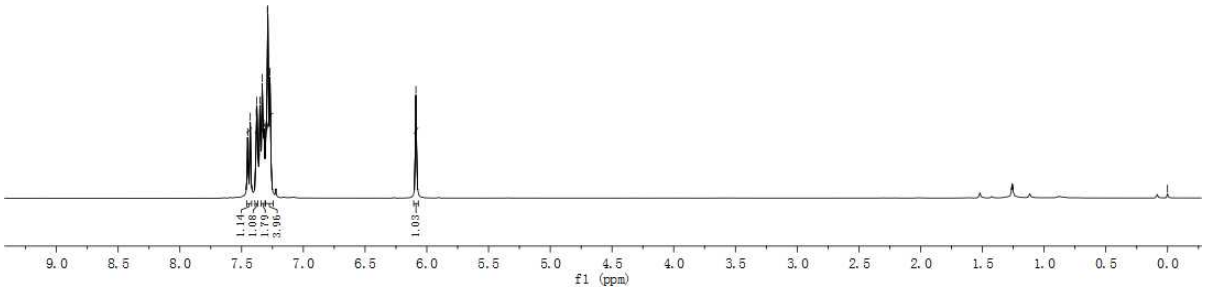

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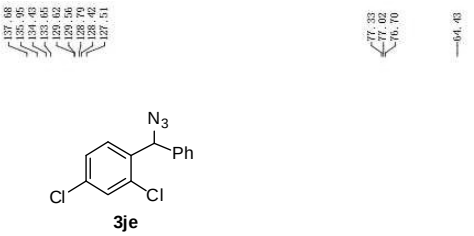

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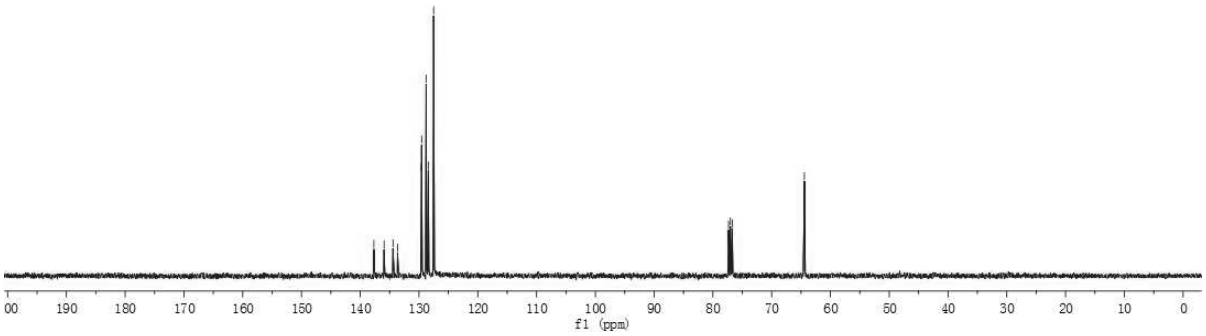

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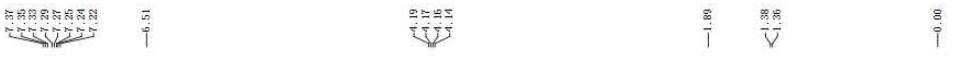

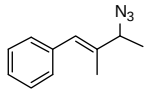

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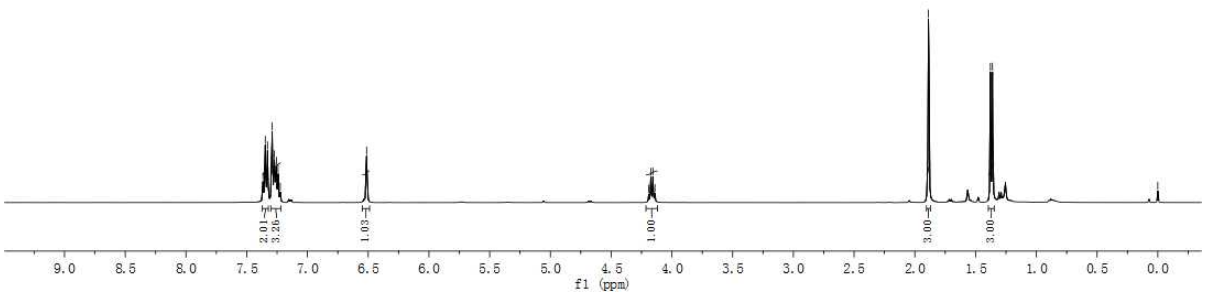

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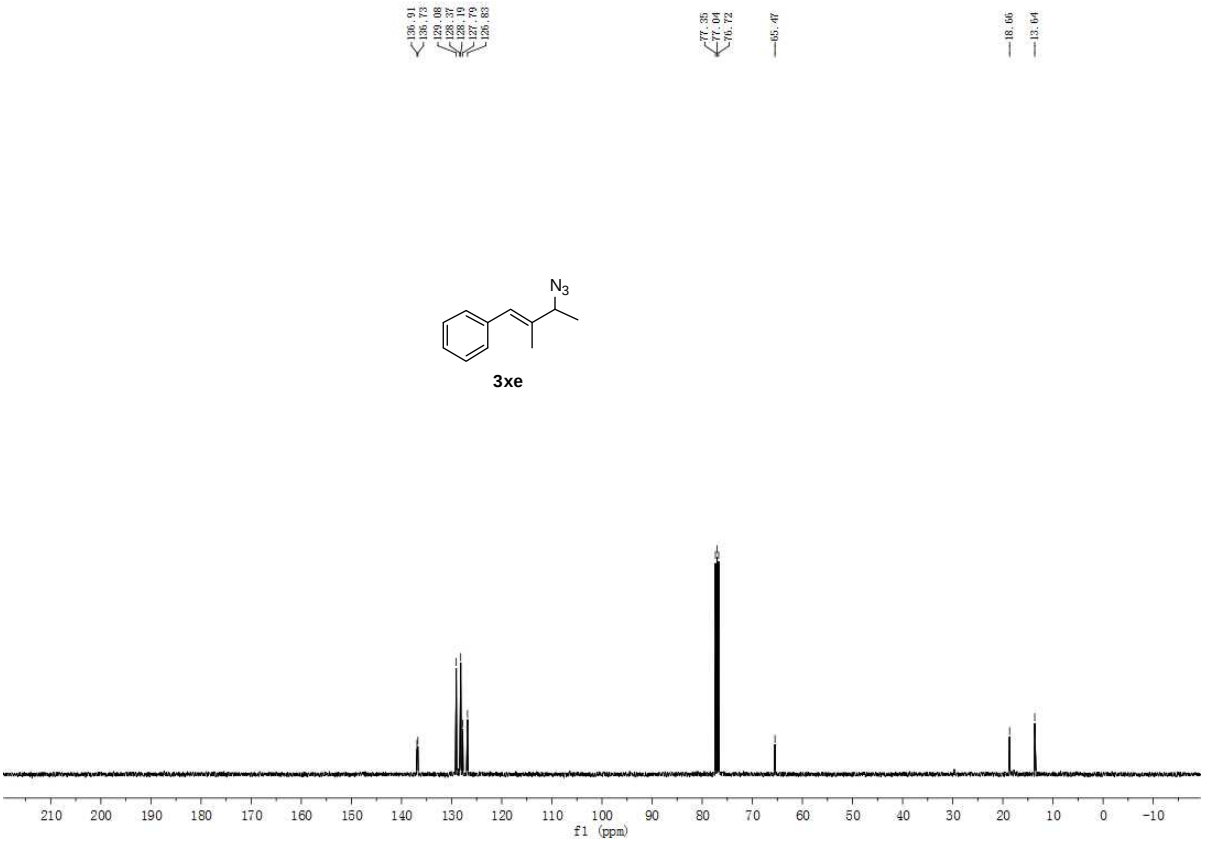
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f1 (ppm)