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Electronic Supplementary Information

Phosphine-Catalyzed [5+1] Annulation of δ-Sulfonamido-Substituted Enones with *N*-Sulfonylimines: A Facile Synthesis of Tetrahydropyridines

Leijie Zhou, Chunhao Yuan, Yuan Zeng, Honglei Liu, Chang Wang, Xing Gao, Qijun Wang, Cheng Zhang, and Hongchao Guo*

Department of Applied Chemistry, China Agricultural University, Beijing 100193, P. R. China

Fax: (+86) 10-6273-0784; E-mail: hchguo@cau.edu.cn

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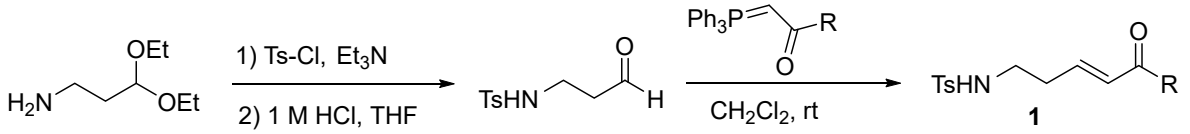
General Information

All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 using a 300 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on an Autopol VI automatic polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Melting points were determined on a Stuard SMP3 melting point apparatus. X-ray crystallographic data were collected using a MM007HF Saturn724+. HPLC analysis was performed on Agilent 1100 or 1200 series, UV detection monitored at 254 nm, using Chiralpak RC-OD column with hexane and *i*-PrOH as the eluent.

General procedure for preparation of δ-Sulfonamido-substituted enones 1[1]

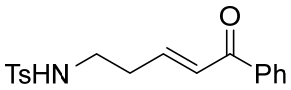


δ-Sulfonamido-substituted enones were prepared according to a reported procedure. To a solution of 1-amino-3,3-diethoxyaminopropane (7.36 g, 50.0 mmol) in CH_2Cl_2 (200 mL) was added Et_3N (8.30 mL, 60.0 mmol). The solution was cooled to 0 °C and p-toluenesulfonyl chloride (10.5 g, 55.0 mmol, 1.0 equiv) in CH_2Cl_2 (100 mL) was added over 30 min. The resulting mixture was allowed to warm to room temperature and treated with saturated aqueous NH_4Cl solution. The layers were separated, the organic layer was extracted with CH_2Cl_2, dried over sodium sulfate, and concentrated to a yellow

[1] B.-L. Zhao, Y. Lin, H.-H. Yan, D.-M. Du. *Org. Biomol. Chem.* **2015**, *13*, 11351–11361.

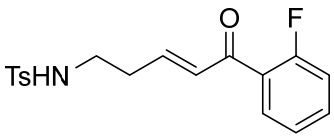
oil. The crude sulfonamide was dissolved in THF (100 mL), treated with 1 M HCl (50 mL), and stirred at room temperature about 3 h. Upon complete consumption of the acetal as judged by TLC analysis (petroleumether/EtOAc 1:1), EtOAc (100 mL) was added and the layers were separated. The organic layer was washed (H_2O, brine), dried over Na_2SO_4 and concentrated. Wittig reagent (5 mmol, 1 equiv) was added to a solution of the crude tosylamino propaldehyde (5 mmol, 1 equiv) in CH_2Cl_2 (30 mL) in round bottom flask. The solution was stirred at room temperature for 30 h. After concentration under reduced pressure, the residue was purified by flash chromatography on silica gel (petroleumether/EtOAc 3:1) to afford δ-Sulfonamido-substituted enones **1**.

(*E*)-4-Methyl-*N*-(5-oxo-5-phenylpent-3-en-1-yl)benzenesulfonamide (1a)



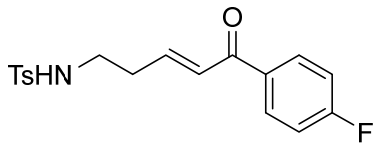
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 – 7.83 (m, 2H), 7.85 – 7.67 (m, 2H), 7.66 – 7.54 (m, 1H), 7.51 – 7.46 (m, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.94 – 6.77 (m, 2H), 5.06 (t, J = 6.3 Hz, 1H), 3.18 (q, J = 6.6 Hz, 2H), 2.52 (q, J = 6.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 190.1, 144.3, 143.6, 137.4, 136.8, 132.9, 129.8, 128.6, 128.0, 127.1, 41.6, 32.9, 21.5; HRMS (ESI) calcd for $C_{18}H_{19}NO_3SH^+$ $[M+H]^+$ 330.1158, found 330.1156.

(*E*)-*N*-(5-(2-Fluorophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1b)



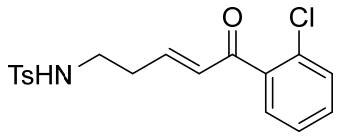
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 – 7.73 (m, 2H), 7.72 – 7.70 (m, 1H), 7.54 – 7.48 (m, 1H), 7.37 – 7.26 (m, 2H), 7.24 – 7.22 (m, J = 7.6, 1H), 7.16 – 7.10 (m, 1H), 6.83 – 6.79 (m, 1H), 6.74 – 6.69 (m, 1H), 5.06 (t, J = 6.3 Hz, 1H), 3.15 (q, J = 6.7 Hz, 2H), 2.50 – 2.46 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8 (d, J = 2.3 Hz), 161.1 (d, J = 253.5 Hz), 144.7, 143.5, 136.8, 134.1, 134.0, 131.6, 131.5, 130.9, 130.8, 129.8, 127.0, 126.5, 126.4, 124.5, 124.4, 116.5 (d, J = 23.1 Hz), 41.5, 32.7, 21.5; HRMS (ESI) calcd for $C_{18}H_{18}FNO_3SH^+$ $[M+H]^+$ 348.1064, found 348.1059.

(*E*)-*N*-(5-(4-Fluorophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1c)



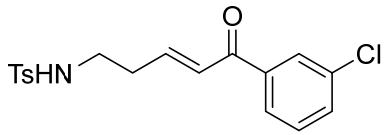
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 – 7.86 (m, 2H), 7.83 – 7.66 (m, 2H), 7.34 – 7.25 (m, 2H), 7.20 – 7.06 (m, 2H), 6.94 – 6.82 (m, 2H), 5.22 (t, J = 6.3 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.53 – 2.50 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 165.6 (d, J = 254.6 Hz), 144.6, 143.6, 136.7, 133.7, 133.7, 131.3, 131.2, 129.8, 127.6, 127.1, 127.0, 115.7 (d, J = 21.8 Hz), 41.6, 32.8, 21.5; HRMS (ESI) calcd for $C_{18}H_{18}FNO_3SH^+$ $[M+H]^+$ 348.1064, found 348.1060.

(*E*)-*N*-(5-(2-Chlorophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1d)



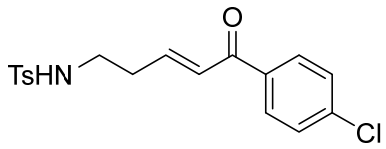
Prepared according to the general procedure as a white solid. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.77 – 7.70 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.26 (m, 4H), 6.69 – 6.35 (m, 2H), 5.17 (t, J = 6.3 Hz, 1H), 3.10 (q, J = 6.7 Hz, 2H), 2.48 – 2.44 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 146.3, 143.2, 138.1, 136.4, 131.8, 131.1, 130.8, 129.9, 129.4, 129.3, 129.0, 126.8, 126.7, 126.4, 41.0, 32.4, 21.1; HRMS (ESI) calcd for $C_{18}H_{18}ClNO_3SH^+$ $[M+H]^+$ 364.0769, found 364.0763.

(*E*)-*N*-(5-(3-Chlorophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1e)



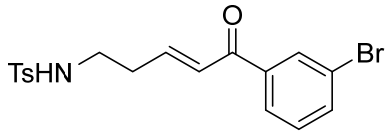
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 (t, J = 1.9 Hz, 1H), 7.81 – 7.70 (m, 3H), 7.53 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.34 – 7.21 (m, 2H), 7.01 – 6.74 (m, 2H), 5.24 (t, J = 6.3 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.57 – 2.45 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 145.4, 143.6, 139.0, 136.7, 134.8, 132.8, 129.9, 129.8, 128.5, 127.5, 127.1, 127.0, 126.7, 41.5, 32.9, 21.5; HRMS (ESI) calcd for $C_{18}H_{18}ClNO_3SH^+$ $[M+H]^+$ 364.0769, found 364.0765.

(*E*)-*N*-(5-(4-Chlorophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1f)



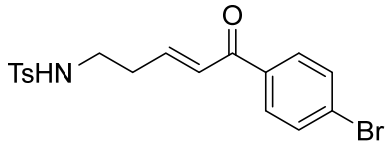
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 – 7.79 (m, 2H), 7.81 – 7.70 (m, 2H), 7.50 – 7.37 (m, 2H), 7.39 – 7.20 (m, 2H), 6.94 – 6.86 (m, 2H), 5.08 (t, J = 6.3 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.58 – 2.47 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 144.9, 143.6, 139.3, 136.7, 135.7, 130.0, 129.9, 129.8, 129.0, 128.9, 127.6, 127.1, 127.0, 41.5, 32.9, 21.5; HRMS (ESI) calcd for $C_{18}H_{18}ClNO_3SH^+$ $[M+H]^+$ 364.0769, found 364.0765.

(*E*)-*N*-(5-(3-Bromophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1g)



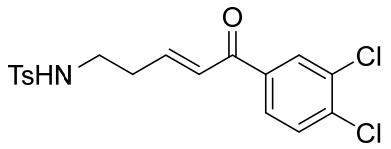
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (t, J = 1.8 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.79 – 7.73 (m, 2H), 7.69 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.39 – 7.24 (m, 3H), 6.97 – 6.79 (m, 2H), 5.09 (t, J = 6.3 Hz, 1H), 3.18 (q, J = 6.6 Hz, 2H), 2.58 – 2.48 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 145.4, 143.6, 139.2, 136.7, 135.7, 131.5, 130.2, 129.8, 127.5, 127.1, 127.0, 122.9, 41.5, 32.9, 21.5; HRMS (ESI) calcd for $C_{18}H_{18}BrNO_3SH^+$ $[M+H]^+$ 408.0264, found 408.0262.

(*E*)-*N*-(5-(4-Bromophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1h)



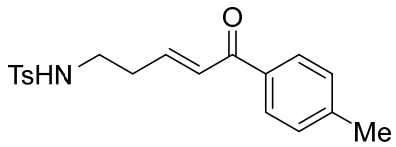
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.69 (m, 4H), 7.69 – 7.54 (m, 2H), 7.40 – 7.20 (m, 2H), 6.92 – 6.81 (m, 2H), 5.18 (t, J = 6.3 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.51 (dtd, J = 6.7, 5.3, 1.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 145.0, 143.6, 136.7, 136.1, 131.9, 131.8, 130.1, 130.0, 129.8, 129.6, 128.0, 127.5, 127.1, 127.0, 41.5, 32.8, 21.5; HRMS (ESI) calcd for $C_{18}H_{18}BrNO_3SH^+$ $[M+H]^+$ 408.0264, found 408.0263.

(*E*)-*N*-(5-(3,4-Dichlorophenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1i)



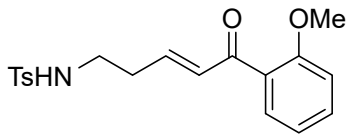
Prepared according to the general procedure as a pale yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 (d, J = 2.0 Hz, 1H), 7.81 – 7.67 (m, 3H), 7.53 (d, J = 8.3 Hz, 1H), 7.37 – 7.23 (m, 2H), 7.00 – 6.76 (m, 2H), 5.19 (t, J = 6.3 Hz, 1H), 3.17 (q, J = 6.5 Hz, 2H), 2.55 – 2.51 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 145.8, 143.6, 137.4, 136.9, 136.7, 133.2, 130.8, 130.7, 130.4, 129.8, 129.6, 127.6, 127.1, 127.0, 126.9, 41.5, 32.9, 21.5. HRMS (ESI) calcd for $C_{18}H_{18}Cl_2NO_3SH^+$ $[M+H]^+$ 398.0379, found 398.0377.

(*E*)-4-Methyl-*N*-(5-oxo-5-(p-tolyl)pent-3-en-1-yl)benzenesulfonamide (1j)



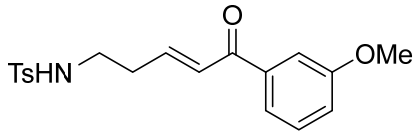
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.72 (m, 2H), 7.52 – 7.43 (m, 2H), 7.37 (t, J = 7.9 Hz, 1H), 7.33 – 7.23 (m, 2H), 7.12 (ddd, J = 8.2, 2.7, 1.0 Hz, 1H), 6.92 – 6.82 (m, 2H), 5.12 (t, J = 6.3 Hz, 1H), 3.87 (s, 3H), 3.17 (q, J = 6.6 Hz, 2H), 2.57 – 2.46 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 159.8, 144.4, 143.5, 138.8, 136.8, 129.8, 129.5, 128.0, 127.0, 121.2, 119.5, 112.8, 55.4, 41.6, 32.8, 21.5; HRMS (ESI) calcd for $C_{19}H_{21}NO_3SH^+$ $[M+H]^+$ 344.1315, found 344.1312.

(*E*)-*N*-(5-(2-Methoxyphenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1k)



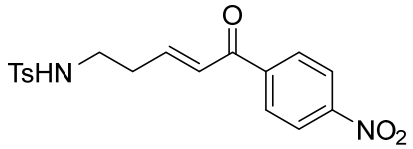
Prepared according to the general procedure as a white solid. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.75 – 7.68 (m, 2H), 7.53 – 7.38 (m, 2H), 7.27 – 7.20 (m, 2H), 7.02 – 6.89 (m, 2H), 6.77 – 6.55 (m, 2H), 5.33 (t, J = 6.2 Hz, 1H), 3.83 (s, 3H), 3.07 (q, J = 6.6 Hz, 2H), 2.43 – 2.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 157.7, 143.1, 142.6, 136.5, 132.7, 132.3, 129.9, 129.3, 128.2, 126.7, 120.3, 111.5, 55.3, 41.2, 32.1, 21.1; HRMS (ESI) calcd for $C_{19}H_{21}NO_4SH^+$ $[M+H]^+$ 360.1264, found 360.1259.

(*E*)-*N*-(5-(3-Methoxyphenyl)-5-oxopent-3-en-1-yl)-4-methylbenzenesulfonamide (1l)



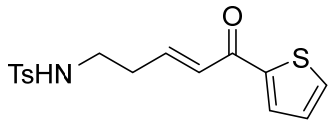
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.80 (m, 2H), 7.78 – 7.73 (m, 2H), 7.30 – 7.25 (m, 4H), 6.96 – 6.77 (m, 2H), 5.15 (t, J = 6.3 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.51 (td, J = 6.8, 5.8 Hz, 2H), 2.42 (d, J = 5.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 143.9, 143.8, 143.5, 136.8, 134.8, 129.8, 129.3, 128.7, 128.0, 127.0, 41.7, 32.8, 21.6, 21.5; HRMS (ESI) calcd for $C_{19}H_{21}NO_4SH^+$ $[M+H]^+$ 360.1264, found 360.1259.

(*E*)-4-Methyl-*N*-(5-(4-nitrophenyl)-5-oxopent-3-en-1-yl)benzenesulfonamide (1m)



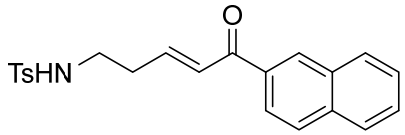
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.38 – 8.25 (m, 2H), 8.09 – 8.03 (m, 2H), 7.81 – 7.70 (m, 2H), 7.34 – 7.29 (m, 2H), 7.04 – 6.80 (m, 2H), 5.18 (t, J = 6.3 Hz, 1H), 3.19 (q, J = 6.5 Hz, 2H), 2.56 (q, J = 6.3 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 150.0, 146.6, 143.7, 142.2, 136.6, 129.8, 129.7, 129.5, 127.7, 127.0, 123.7, 41.4, 32.9, 21.5; HRMS (ESI) calcd for $C_{18}H_{18}N_2O_5SH^+$ $[M+H]^+$ 375.1009, found 375.1006.

(*E*)-4-Methyl-*N*-(5-oxo-5-(thiophen-2-yl)pent-3-en-1-yl)benzenesulfonamide (1n)



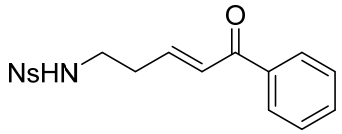
Prepared according to the general procedure as a pale yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 1.8 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.66 (dd, J = 4.9, 1.1 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.14 (dd, J = 4.9, 3.8 Hz, 1H), 6.98 – 6.77 (m, 2H), 5.25 (t, J = 6.2 Hz, 1H), 3.16 (q, J = 6.6 Hz, 2H), 2.53 – 2.48 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.8, 144.7, 143.8, 143.5, 136.8, 134.2, 132.4, 129.7, 128.3, 127.5, 127.0, 41.6, 32.7, 21.5; HRMS (ESI) calcd for $C_{16}H_{17}NO_3S_2H^+$ $[M+H]^+$ 336.0723, found 336.0720.

(*E*)-4-Methyl-*N*-(5-(naphthalen-2-yl)-5-oxopent-3-en-1-yl)benzenesulfonamide (1o)



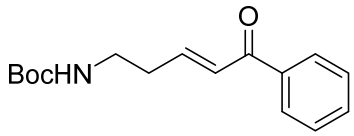
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.43 (d, J = 1.6 Hz, 1H), 7.99 – 7.93(m, 2H), 7.91 – 7.84 (m, 2H), 7.79 – 7.74 (m, 2H), 7.68 – 7.56 (m, 2H), 7.28 – 7.23 (m, 2H), 7.12 – 7.06 (m, 1H), 6.96 – 6.92 (m, 1H), 5.30 (t, J = 6.2 Hz, 1H), 3.20 (q, J = 6.6 Hz, 2H), 2.58 – 2.54 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 144.3, 143.5, 136.8, 135.5, 134.7, 132.4, 130.3, 129.8, 129.6, 128.5, 128.4, 128.0, 127.7, 127.0, 126.7, 124.3, 41.7, 32.9, 21.4; HRMS (ESI) calcd for $C_{22}H_{21}NO_3SH^+$ $[M+H]^+$ 380.1315, found 380.1314.

(*E*)-4-Nitro-*N*-(5-oxo-5-phenylpent-3-en-1-yl)benzenesulfonamide (1p)



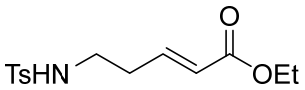
Prepared according to the general procedure as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.67 (t, J = 2.0 Hz, 1H), 8.36 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 8.19 (dt, J = 7.8, 1.3 Hz, 1H), 7.92 – 7.80 (m, 2H), 7.71 (t, J = 8.0 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.44 (dd, J = 8.4, 7.0 Hz, 2H), 7.03 – 6.78 (m, 2H), 5.92 (t, J = 6.2 Hz, 1H), 3.26 (q, J = 6.5 Hz, 2H), 2.57 (q, J = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 148.2, 144.4, 142.1, 137.1, 133.1, 132.5, 130.6, 128.6, 128.5, 128.1, 127.1, 122.1, 41.8, 32.9; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_5SH^+$ $[M+H]^+$ 361.0853, found 361.0851.

***tert*-Butyl (*E*)-(5-oxo-5-phenylpent-3-en-1-yl)carbamate (1q)**



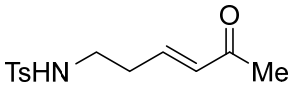
Prepared according to the general procedure as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 (d, J = 9.0 Hz, 2H), 7.54 (s, 1H), 7.46 (s, 2H), 6.96 (d, J = 10.7 Hz, 2H), 4.71 (s, 1H), 3.32 (d, J = 5.6 Hz, 2H), 2.51 (d, J = 8.3 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-d) δ 190.5, 155.9, 145.8, 137.7, 132.9, 128.6, 127.7, 79.5, 39.1, 33.4, 28.4; HRMS (ESI) calcd for $C_{16}H_{21}NO_3SH^+$ $[M+H]^+$ 298.1414, found 298.1412.

Ethyl (*E*)-5-((4-methylphenyl)sulfonamido)pent-2-enoate (1r)



Prepared according to a literature procedure.

(*E*)-4-Methyl-N-(5-oxohex-3-en-1-yl)benzenesulfonamide (1s)



Prepared according to the general procedure as a pale yellow solid. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.88 – 7.61 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.65 (dt, J = 16.0, 6.9 Hz, 1H), 6.02 (dt, J = 16.0, 1.5 Hz, 1H), 5.35 (t, J = 6.3 Hz, 1H), 3.09 (q, J = 6.6 Hz, 2H), 2.45 – 2.35 (m, 5H), 2.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 143.2, 143.0, 136.4, 132.8, 129.4, 126.7, 41.2, 32.1, 26.6, 21.1; HRMS (ESI) calcd for $C_{13}H_{17}NO_3SH^+$ $[M+H]^+$ 268.1002, found 268.0998.

General procedure for preparation of *N*-Sulfonylimine 2[2]

N-Sulfonylimines were prepared according to the literature.

General Procedure for Achiral Phosphine-Catalyzed [5+1] Annulation

Under a nitrogen atmosphere, to a stirred solution of δ-sulfonamido-substituted enones **1** (0.2 mmol, 1.0 equiv) and *N*-sulfonylimine **2** (0.3 mmol, 1.5 equiv) in DCM (2 mL) was added catalyst PBu_3 (0.04 mmol, 20 mol%) via a syringe. Then the reaction solution was vigorously stirred at room temperature and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to furnish the corresponding product.

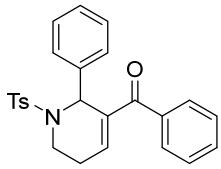
General Procedure for Chiral Phosphine-Catalyzed Asymmetric [5+1] Annulation

Under a nitrogen atmosphere, to a mixture of δ-sulfonamido-substituted enone **1** (0.1 mmol, 1.0 equiv), *N*-sulfonylimine 2 (0.15 mmol, 1.5 equiv) and catalyst P^* (0.02 mmol, 20 mol%) was added CF_3Ph (1 mL) via a syringe. Then the reaction solution was vigorously stirred at -10°C and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (Petroleum Ether/EtOAc as the eluent) to furnish the corresponding product.

[2] M. K. Ghorai, S. Das, K. Das, A. Kumar. *Org. Biomol. Chem*. **2015**, *13*, 9042–9049.

Characterization Data for the [5+1] Annulation Products 3

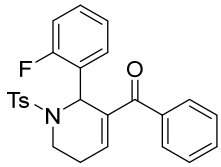
Phenyl (2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3aa)



3aa

Prepared according to the general procedure as described above in 95% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 161 – 163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.64 – 7.57 (m, 2H), 7.55 – 7.48 (m, 1H), 7.47 – 7.34 (m, 4H), 7.33 – 7.25 (m, 3H), 7.24 – 7.18 (m, 2H), 6.64 – 6.52 (m, 1H), 6.29 (s, 1H), 3.94 – 3.86 (m, 1H), 3.31 – 3.04 (m, 1H), 2.38 (s, 3H), 2.25 – 2.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 143.0, 141.3, 138.2, 137.5, 137.3, 135.1, 130.3, 129.2, 128.3, 128.2, 127.8, 127.6, 126.8, 54.2, 36.9, 24.0, 21.1; IR (film) ν_{max} 3061, 2927, 1645, 1597, 1493, 1447, 1342, 1275, 1212, 1161, 1091, 962, 891, 815, 718, 699, 671, 653, 574, 548 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{23}NO_3SH^+$ $[M+H]^+$ 418.1471, found 418.1470.

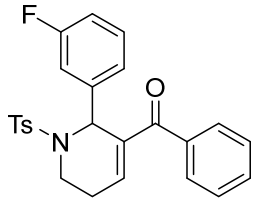
(2-(2-Fluorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ab)



3ab

Prepared according to the general procedure as described above in 96% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 66 – 68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.73 – 7.64 (m, 2H), 7.62 – 7.55 (m, 2H), 7.54 – 7.46 (m, 1H), 7.44 – 7.34 (m, 3H), 7.25 – 7.15 (m, 3H), 7.09 – 7.04 (m, 1H),7.00 – 6.93 (m, 1H), 6.68 – 6.68 (m, 1H), 6.41 (s, 1H), 3.89 (dd, *J* = 14.7, 6.5 Hz, 1H), 3.35 – 3.25 (m, 1H), 2.49 – 2.23 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7 , 160.6 (d, *J* = 249.2 Hz), 143.0, 141.0, 137.1 (d, *J* = 3.6 Hz), 137.0, 131.7, 130.6 (d, *J* = 3.6 Hz), 129.7, 129.5, 129.1, 128.9, 127.9, 126.9, 125.4 (d, *J* = 13.4 Hz), 123.6 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 22.5 Hz), 50.3, 37.5 (d, *J* = 2.6 Hz), 24.2, 21.1; IR (film) ν_{max} 2924, 1645, 1597, 1511, 1447, 1342, 1275, 1212, 1160, 1091, 963, 893, 815, 713, 668, 652, 581, 550 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}FNO_3SH^+$ $[M+H]^+$ 436.1377, found 436.1378.

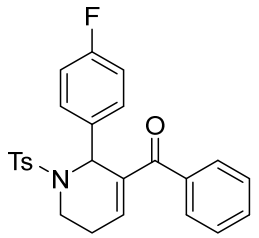
(2-(3-Fluorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ac)



3ac

Prepared according to the general procedure as described above in 85% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 180 – 182 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 2H), 7.61 – 7.48 (m, 3H), 7.44 – 7.40 (m, 2H), 7.33 – 7.20 (m, 3H), 7.19 – 7.12 (m, 1H), 7.09 – 7.05 (m, 1H), 6.97 – 6.93 (m, 1H), 6.65 – 6.62 (m, 1H), 6.25 (s, 1H), 4.02 – 3.80 (m, 1H), 3.16 – 3.10 (m, 1H), 2.38 (s, 3H), 2.32 – 2.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 162.4 (d, *J* = 246.4 Hz) , 143.2, 142.0, 137.4, 136.8 (d, *J* = 10.6 Hz) , 131.9, 129.6 (d, *J* = 8.2 Hz), 129.3, 128.8, 128.0, 126.8, 123.6 (d, *J* = 2.8 Hz),114.9 (d, *J* = 22.2 Hz) , 114.5 (d, *J* = 20.9 Hz), 53.8 (d, *J* = 2.0 Hz) , 37.0, 23.8, 21.1; IR (film) ν_{max} 1644, 1591, 1486, 1446, 1343, 1274, 1161, 1091, 980, 885, 816, 765, 713, 670, 655, 555 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}FNO_3SH^+$ $[M+H]^+$ 436.1377, found 436.1378.

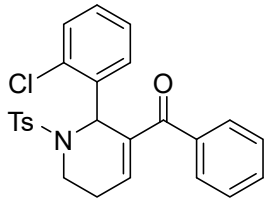
(2-(4-Fluorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ad)



3ad

Prepared according to the general procedure as described above in 93% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 176 – 178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.67 (m, 2H), 7.62 – 7.47 (m, 3H), 7.41 – 7.35 (m, 4H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.87 (m, 2H), 6.67 – 6.48 (m, 1H), 6.25 (s, 1H), 4.06 – 3.71 (m, 1H), 3.15 – 3.09 (m, 1H), 2.38 (s, 3H), 2.24 – 2.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 162.0 (d, *J* = 247.0 Hz), 143.1, 141.8, 137.5, 137.1, 136.7, 134.4 (d, *J* = 3.3 Hz), 131.9, 129.6 (d, *J* = 8.3 Hz), 129.3, 128.8, 128.0, 126.7, 115.0 (d, *J* = 21.7 Hz) , 53.6, 36.8, 23.8, 21.1; IR (film) ν_{max} 2927, 1644, 1598, 1507, 1447, 1342, 1275, 1224, 1160, 1091, 963, 893, 815, 773, 751, 713, 669, 652, 580, 550 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}FNO_3SH^+$ $[M+H]^+$ 436.1377, found 436.1378.

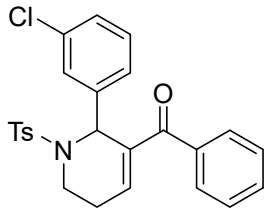
(2-(2-Chlorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ae)



3ae

Prepared according to the general procedure as described above in 75% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 172 – 174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.70 (m, 2H), 7.64 – 7.46 (m, 4H), 7.44 – 7.34 (m, 2H), 7.29 (dd, J = 7.7, 1.9 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.12 – 7.10 (m, J = 7.6, 1.9 Hz, 1H), 6.76 (t, J = 4.0 Hz, 1H), 6.59 (s, 1H), 3.76 (dd, J = 14.9, 7.1 Hz, 1H), 3.38 – 3.33 (m, 1H), 2.73 – 2.49 (m, 1H), 2.39 (s, 3H), 2.37 – 2.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 143.1, 141.5, 137.4, 137.0, 136.9, 135.6, 134.6, 131.6, 130.5, 129.4, 129.1, 129.0, 128.8, 127.9, 127.3, 125.9, 52.0, 37.3, 24.0, 21.2; IR (film) ν_{max} 2924, 1645, 1597, 1446, 1346, 1273, 1162, 1090, 1039, 959, 886, 816, 733, 713, 698, 670, 652, 550 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}ClNO_3SH^+$ $[M+H]^+$ 452.1082, found 452.1082.

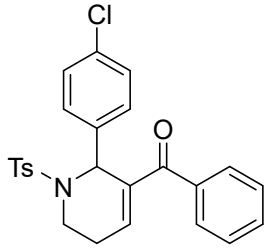
(2-(3-Chlorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3af)



3af

Prepared according to the general procedure as described above in 82% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 172 – 174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.55 – 7.42 (m, 3H), 7.41 – 7.29 (m, 5H), 7.29 – 7.21 (m, 3H), 6.72 – 6.55 (m, 1H), 6.23 (s, 1H), 3.97 – 3.80 (m, 1H), 3.17 – 3.11 (m, 1H), 2.40 (s, 3H), 2.26 – 2.22 (m, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 193.7, 143.2, 142.2, 140.6, 137.4, 136.7, 134.0, 131.9, 129.4, 129.3, 128.8, 128.0, 127.8, 126.8, 126.1, 53.8, 37.0, 23.9, 21.1; IR (film) ν_{max} 2926, 1644, 1596, 1447, 1343, 1274, 1161, 1091, 967, 794, 746, 697, 670, 654, 553 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}ClNO_3SH^+$ $[M+H]^+$ 452.1082, found 452.1082.

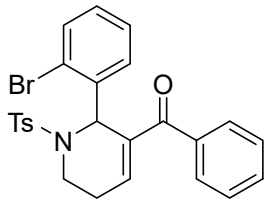
(2-(4-Chlorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ag)



3ag

Prepared according to the general procedure as described above in 85% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 136 – 138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.62 (m, 2H), 7.62 – 7.51 (m, 2H), 7.43 – 7.36 (m, 2H), 7.36 – 7.25 (m, 5H), 7.25 – 7.17 (m, 2H), 6.61 – 6.57 (m, 1H), 6.25 (s, 1H), 3.92– 3.90 (m, 1H), 3.17 – 3.14 (m, 1H), 2.38 (s, 3H), 2.34 – 2.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 143.2, 141.9, 137.4, 137.1, 136.9, 136.7, 133.5, 131.9, 129.3, 129.3, 128.8, 128.3, 128.0, 126.7, 53.7, 36.9, 23.8, 21.1; IR (film) ν_{max} 2927, 1644, 1597, 1489, 1447, 1343, 1274, 1212, 1161, 1090, 1016, 963, 892, 815, 751, 711, 651, 576, 548 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}ClNO_3SH^+$ $[M+H]^+$ 452.1082, found 452.1082.

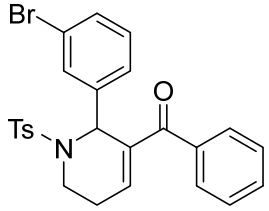
(2-(2-Bromophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ah)



3ah

Prepared according to the general procedure as described above in 68% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 184 – 186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.70 (m, 2H), 7.64 – 7.46 (m, 4H), 7.44 – 7.34 (m, 2H), 7.32 – 7.26 (m, 1H), 7.26 – 7.18 (m, 3H), 7.13 – 7.09 (m, 1H), 6.76 (t, *J* = 4.0 Hz, 1H), 6.59 (s, 1H), 3.78 – 3.74 (m, 1H), 3.40 – 3.31 (m, 1H), 2.73 – 2.49 (m, 1H), 2.39 (s, 4H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 193.7, 143.1, 141.1, 137.7, 137.3, 137.0, 136.8, 134.0, 131.6, 129.4, 129.2, 129.1, 128.8, 127.9, 127.4, 126.5, 125.0, 54.3, 37.4, 24.0, 21.2; IR (film) ν_{max} 3060, 2960, 1644, 1597, 1467, 1446, 1346, 1273, 1160, 1090, 1026, 958, 712, 699, 652, 550 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}BrNO_3SH^+$ $[M+H]^+$ 496.0577, found 496.0576.

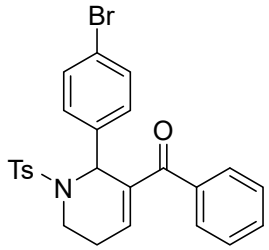
(2-(3-Bromophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ai)



3ai

Prepared according to the general procedure as described above in 81% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 157 – 160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.61 – 7.49 (m, 3H), 7.47 – 7.34 (m, 4H), 7.29 – 7.17 (m, 4H), 6.65 (t, *J* = 3.9 Hz, 1H), 6.20 (s, 1H), 4.08 – 3.81 (m, 1H), 3.14 – 3.10 (m, 1H), 2.39 (s, 3H), 2.33 – 2.19 (m, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 193.6, 143.2, 142.1, 140.8, 137.3, 136.7, 131.9, 130.9, 130.7, 129.7, 129.3, 128.8, 128.0, 126.8, 126.6, 122.3, 53.7, 37.0, 23.9, 21.2; IR (film) ν_{max} 2925, 1645, 1597, 1447, 1343, 1274, 1161, 1091, 966, 795, 728, 696, 666, 653, 552 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}BrNO_3SH^+$ $[M+H]^+$ 496.0577, found 496.0576.

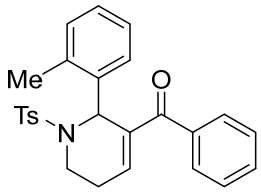
(2-(4-Bromophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3aj)



3aj

Prepared according to the general procedure as described above in 84% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 142 – 144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.60 – 7.48 (m, 3H), 7.46 – 7.37 (m, 4H), 7.27 –7.21 (m, 4H), 6.63 (t, *J* = 3.9 Hz, 1H), 6.20 (s, 1H), 4.11 – 3.82 (m, 1H), 3.17 – 3.12 (m, 1H), 2.39 (s, 3H), 2.28 – 2.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 143.2, 141.9, 137.6, 137.4, 136.8, 136.7, 131.9, 131.3, 129.6, 129.3, 128.8, 128.0, 126.7, 121.7, 53.8, 37.0, 23.8, 21.2; IR (film) ν_{max} 2926, 1644, 1597, 1486, 1447, 1342, 1274, 1161, 1091, 1071, 1011, 963, 892, 815, 710, 674, 651, 575, 547 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}BrNO_3SH^+$ $[M+H]^+$ 496.0577, found 496.0577.

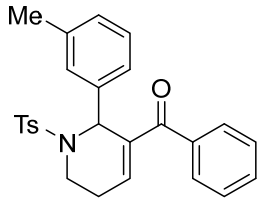
Phenyl(2-(*o*-tolyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ak)



3ak

Prepared according to the general procedure as described above in 41% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 143 – 145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 2H), 7.56 – 7.48 (m, 3H), 7.46 – 7.38 (m, 2H), 7.29 – 7.08 (m, 6H), 6.57 (t, *J* = 3.9 Hz, 1H), 6.52 (s, 1H), 3.88 (dd, *J* = 15.2, 6.5 Hz, 1H), 3.50 – 3.28 (m, 1H), 2.75 (s, 3H), 2.40 (s, 3H), 2.36 – 2.17 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 143.1, 140.6, 138.3, 137.9, 137.1, 137.1, 135.7, 131.6, 131.3, 129.1, 128.7, 127.9, 127.8, 127.3, 127.1, 124.9, 51.3, 36.9, 23.3, 21.1, 19.6; IR (film) ν_{max} 2924, 1643, 1597, 1447, 1342, 1274, 1212, 1160, 1090, 958, 886, 815, 742, 712, 670, 653, 579, 551 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_3SH^+$ $[M+H]^+$ 432.1628, found 432.1624.

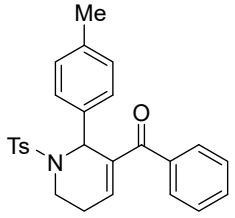
Phenyl(2-(*m*-tolyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3al)



3al

Prepared according to the general procedure as described above in 79% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 146 – 149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.63 – 7.56 (m, 2H), 7.56 – 7.48 (m, 1H), 7.46 – 7.37 (m, 2H), 7.25 – 7.01 (m, 6H), 6.59 (t, *J* = 4.0 Hz, 1H), 6.24 (s, 1H), 3.92 (dd, *J* = 14.9, 6.0 Hz, 1H), 3.28 – 3.09 (m, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 2.28 – 2.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 148.8, 144.9, 141.9, 138.9, 135.6, 134.8, 134.0, 133.3, 130.0, 129.5, 129.2, 128.7, 127.7, 125.9, 125.6, 125.3, 124.6, 61.5, 61.1, 57.3, 38.4, 21.5, 13.9; IR (film) ν_{max} 2922, 1645, 1597, 1447, 1368, 1342, 1275, 1161, 1091, 1019, 801, 761, 744, 713, 671, 654, 552 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_3SH^+$ $[M+H]^+$ 432.1628, found 432.1626.

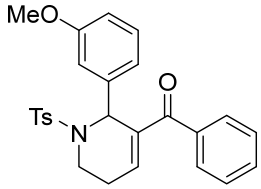
Phenyl(2-(*p*-tolyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3am)



3am

Prepared according to the general procedure as described above in 95% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 170 – 173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.66 (m, 2H), 7.64 – 7.56 (m, 2H), 7.56 – 7.47 (m, 1H), 7.46 – 7.35 (m, 2H), 7.27 (s, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.58 (t, *J* = 3.9 Hz, 1H), 6.25 (s, 1H), 4.06 – 3.72 (m, 1H), 3.27 – 3.10 (m, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 2.26 – 2.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 142.9, 141.3, 137.7, 137.4, 137.3, 136.9, 135.4, 131.7, 129.2, 128.9, 128.8, 127.9, 127.8, 126.8, 54.0, 36.9, 23.9, 21.1, 20.7; IR (film) ν_{max} 2926, 1644, 1597, 1489, 1447, 1345, 1274, 1162, 1091, 961, 891, 815, 763, 713, 670, 652, 578, 552 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_3SH^+$ $[M+H]^+$ 432.1628, found 432.1626.

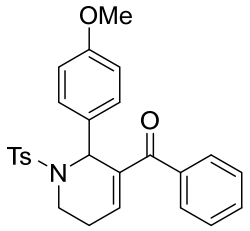
(2-(3-Methoxyphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3an)



3an

Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 106 – 108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 2H), 7.65 – 7.57 (m, 2H), 7.56 – 7.46 (m, 1H), 7.46 – 7.35 (m, 2H), 7.25 – 7.13 (m, 3H), 7.01 – 6.89 (m, 2H), 6.87 – 6.71 (m, 1H), 6.59 (t, *J* = 3.9 Hz, 1H), 6.26 (s, 1H), 3.98 – 3.82 (m, 1H), 3.75 (s, 3H), 3.29 – 3.08 (m, 1H), 2.37 (s, 3H), 2.29 – 2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ193.7, 159.4, 143.0, 141.5, 140.0, 137.6, 137.2, 136.8, 131.8, 129.2, 129.0, 128.9, 128.0, 126.8, 120.2, 113.7, 113.2, 54.8, 54.1, 37.0, 23.9, 21.1; IR (film) ν_{max} 2933, 1644, 1598, 1488, 1447, 1342, 1275, 1161, 1091, 1048, 970, 884, 815, 762, 713, 670, 658, 557 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_4SH^+$ $[M+H]^+$ 448.1577, found 448.1576.

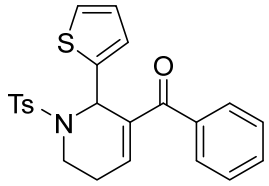
(2-(4-Methoxyphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3ao)



3ao

Prepared according to the general procedure as described above in 98% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 112 – 115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.55 (m, 2H), 7.55 – 7.47 (m, 1H), 7.46 – 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 6.85 – 6.77 (m, 2H), 6.65 – 6.43 (m, 1H), 6.22 (s, 1H), 3.97 – 3.81 (m, 1H), 3.75 (s, 3H), 3.26 – 3.03 (m, 1H), 2.37 (s, 3H), 2.28 – 2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 158.9, 143.0, 141.2, 137.6, 137.5, 136.9, 131.8, 130.5, 129.3, 129.2, 129.1, 128.9, 127.9, 126.8, 126.0, 113.5, 54.9, 53.8, 36.8, 23.9, 21.1; IR (film) ν_{max} 2932, 2360, 1643, 1597, 1511, 1446, 1340, 1305, 1276, 1250, 1160, 1090, 1031, 984, 962, 892, 815, 752, 713, 668, 652, 552 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_4SH^+$ $[M+H]^+$ 448.1577, found 448.1576.

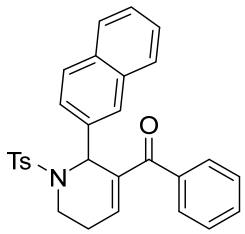
Phenyl(2-(thiophen-2-yl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ap)



3ap

Prepared according to the general procedure as described above in 95% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 116 – 118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.60 (m, 4H), 7.58 – 7.48 (m, 1H), 7.48 – 4.39 (m, 2H), 7.25 – 7.11 (m, 3H), 7.01 – 6.95 (m, 1H), 6.91 – 6.87 (m, 1H), 6.54 (d, *J* = 3.1 Hz, 2H), 4.03 – 3.86 (m, 1H), 3.45 – 3.26 (m, 1H), 2.37 (s, 3H), 2.32 – 2.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 143.0, 141.7, 140.3, 138.0, 137.3, 136.8, 131.9, 129.2, 129.0, 128.0, 126.9, 126.8, 126.5, 125.2, 50.2, 37.1, 24.2, 21.2; IR (film) ν_{max} 2926, 1645, 1597, 1447, 1342, 1271, 1212, 1161, 1091, 991, 957, 884, 815, 708, 655, 562 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{21}NO_3S_2H^+$ $[M+H]^+$ 424.1036, found 424.1034.

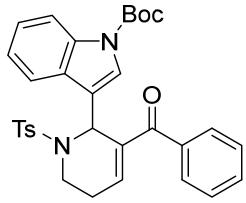
(2-(Naphthalen-2-yl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3aq)



3aq

Prepared according to the general procedure as described above in 98% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 165 – 167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.72 (m, 5H), 7.69 – 7.59 (m, 4H), 7.58 – 7.50 (m, 1H), 7.50 – 7.39 (m, 4H), 7.24 – 7.14 (m, 2H), 6.68 (t, *J* = 3.9 Hz, 1H), 6.44 (s, 1H), 4.02 – 3.83 (m, 1H), 3.25 – 3.13 (m, 1H), 2.37 (s, 3H), 2.32 – 2.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 143.0, 141.7, 137.6, 137.3, 136.9, 135.9, 132.6, 132.6, 131.8, 129.2, 128.9, 128.2, 128.0, 127.7, 127.3, 126.9, 126.7, 126.2, 125.9, 125.8, 54.4, 37.0, 23.9, 21.3; IR (film) ν_{max} 3061, 1643, 1597, 1493, 1447, 1342, 1276, 1212, 1161, 1091, 962, 891, 816, 718, 699, 671, 653, 574, 548 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}NO_3SH^+$ $[M+H]^+$ 468.1628, found 468.1628.

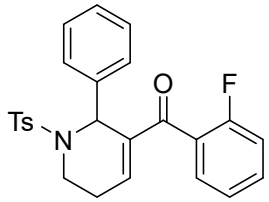
***tert*-Butyl 3-(3-benzoyl-1-tosyl-1,2,5,6-tetrahydropyridin-2-yl)-1*H*-indole-1-carboxylate (3ar)**



3ar

Prepared according to the general procedure as described above in 72% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 170 – 172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.14 (m, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.66 – 7.60 (m, 2H), 7.60 – 7.51 (m, 1H), 7.51 – 7.42 (m, 2H), 7.41 – 7.29 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.61 (s, 1H), 6.54 (t, *J* = 3.9 Hz, 1H), 3.94 (m, 1H), 3.40 – 3.25 (m, 1H), 2.40 (s, 3H), 2.23 (d, *J* = 5.4 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.6, 149.3, 143.1, 141.2, 137.4, 137.1, 136.9, 135.3, 131.8, 129.2, 128.8, 128.0, 127.0, 124.8, 124.6, 122.7, 120.7, 118.9, 114.5, 83.7, 47.6, 37.1, 27.8, 23.3, 21.1; IR (film) ν_{max} 2978, 1735, 1646, 1453, 1368, 1268, 1224, 1161, 1083, 979, 739, 712, 671, 564 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{32}N_2O_5SH^+$ $[M+H]^+$ 557.2105, found 557.2104.

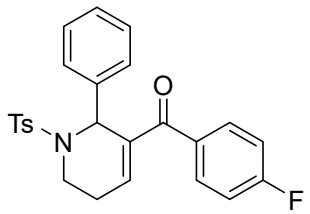
(2-Fluorophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ba)



3ba

Prepared according to the general procedure as described above in 97% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 146 – 148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.62 (m, 2H), 7.50 – 7.36 (m, 3H), 7.36 – 7.27 (m, 3H), 7.27 – 7.15 (m, 4H), 7.13 – 7.07 (m, 1H), 6.70 – 6.56 (m, 1H), 6.26 (s, 1H), 3.89 – 3.85 (m, 1H), 3.14 – 3.05 (m, 1H), 2.39 (s, 3H), 2.33 – 2.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 158.9 (d, *J* = 250.5 Hz), 144.1 (d, *J* = 2.0 Hz), 138.3, 138.1, 137.5, 132.2(d, *J* = 8.3 Hz), 129.7 (d, *J* = 3.3 Hz), 129.2, 128.1, 127.9, 127.6, 126.8, 126.1 (d, *J* = 15.9 Hz), 123.9 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 21.8 Hz), 53.9, 36.7, 24.2, 21.1; IR (film) ν_{max} 2926, 1653, 1611, 1484, 1451, 1343, 1290, 1215, 1162, 1090, 963, 751, 724, 705, 661, 569, 549 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}FNO_3SH^+$ $[M+H]^+$ 436.1377, found 436.1375.

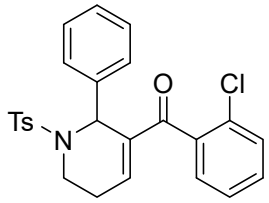
(4-Fluorophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ca)



3ca

Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 165 – 167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.70 – 7.60 (m, 2H), 7.38 – 7.18 (m, 7H), 7.17 – 7.02 (m, 2H), 6.58 (t, *J* = 4.0 Hz, 1H), 6.27 (s, 1H), 4.01 – 3.78 (m, 1H), 3.22 – 3.14 (m, 1H), 2.38 (s, 3H), 2.29 – 2.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 164.8 (d, *J* = 254.0 Hz), 143.0, 140.8, 138.3, 137.4 (d, *J* = 13.2 Hz), 132.9 (d, *J* = 3.1 Hz), 131.5, 131.4, 129.2, 128.1, 127.8, 127.6, 126.8, 115.1(d, *J* = 21.6 Hz), 54.3, 36.9, 23.9, 21.1; IR (film) ν_{max} 2927, 1646, 1598, 1504, 1453, 1342, 1275, 1161, 1091, 963, 891, 820, 751, 724, 705, 658, 568, 548 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}FNO_3SH^+$ $[M+H]^+$ 436.1377, found 436.1376.

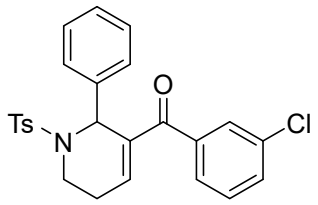
(2-Chlorophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3da)



3da

Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 155 – 157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 2H), 7.50 – 7.18 (m, 10H), 7.11 – 6.95 (m, 1H), 6.55 (t, *J* = 3.9 Hz, 1H), 6.20 (s, 1H), 4.00 – 3.70 (m, 1H), 3.14 – 3.03 (m, 1H), 2.41 (s, 3H), 2.36 – 2.02 (m, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 192.7, 145.7, 143.0, 138.1, 137.8, 137.6, 137.5, 130.5, 130.4, 129.6, 129.3, 128.2, 128.0, 127.9, 127.6, 126.8, 126.1, 53.7, 36.6, 24.2, 21.1; IR (film) ν_{max} 2927, 1659, 1493, 1452, 1376, 1343, 1287, 1161, 1092, 963, 893, 765, 724, 700, 659, 645, 566, 547 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}ClNO_3SH^+$ $[M+H]^+$ 452.1082, found 452.1082.

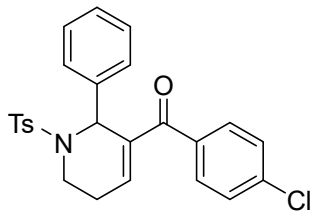
(3-Chlorophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ea)



3ea

Prepared according to the general procedure as described above in 91% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 157 – 159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.55 – 7.42 (m, 3H), 7.41 – 7.29 (m, 5H), 7.29 – 7.21 (m, 3H), 6.72 – 6.55 (m, 1H), 6.23 (s, 1H), 3.97 – 3.80 (m, 1H), 3.24 – 3.11 (m, 1H), 2.40 (s, 3H), 2.37 – 2.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 143.1, 142.4, 138.6, 138.2, 137.5, 137.2, 134.1, 131.6, 129.4, 129.3, 128.6, 128.2, 127.8, 127.6, 126.8, 126.8, 54.2, 36.8, 23.9, 21.2; IR (film) ν_{max} 2927, 1653, 1493, 1452, 1417, 1343, 1275, 1211, 1161, 1090, 966, 893, 814, 731, 704, 661, 547 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}ClNO_3SH^+$ $[M+H]^+$ 452.1082, found 452.1081.

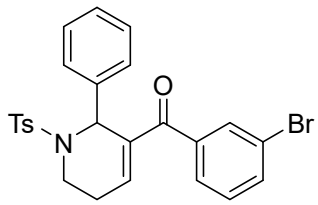
(4-Chlorophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3fa)



3fa

Prepared according to the general procedure as described above in 84% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 169 – 172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.62 (m, 2H), 7.62 – 7.51 (m, 2H), 7.43 – 7.36 (m, 2H), 7.36 – 7.25 (m, 5H), 7.25 – 7.17 (m, 2H), 6.59 (t, *J* = 3.9 Hz, 1H), 6.25 (s, 1H), 3.90 (dd, *J* = 14.8, 6.0 Hz, 1H), 3.24 – 3.13 (m, 1H), 2.38 (s, 3H), 2.34 – 2.14 (m, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 192.5, 143.0, 141.3, 138.2, 137.5, 137.3, 135.1, 130.3, 129.2, 128.3, 128.2, 127.8, 127.6, 126.8, 54.2, 36.8, 23.9, 21.1; IR (film) ν_{max} 2923, 1646, 1587, 1494, 1452, 1338, 1274, 1211, 1161, 1091, 1014, 962, 891, 816, 747, 700, 656, 548 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}ClNO_3SH^+$ $[M+H]^+$ 452.1082, found 452.1082.

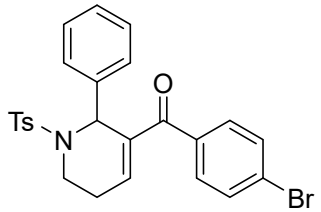
(3-Bromophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ga)



3ga

Prepared according to the general procedure as described above in 98% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 155 – 156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.68 – 7.60 (m, 2H), 7.52 – 7.46 (m, 1H), 7.37 – 7.19 (m, 8H), 6.62 (t, *J* = 4.0 Hz, 1H), 6.23 (s, 1H), 4.02 – 3.77 (m, 1H), 3.24 – 3.06 (m, 1H), 2.40 (s, 3H), 2.36 – 2,10 (m, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 192.2, 143.1, 142.4, 138.8, 138.2, 137.5, 137.2, 134.5, 131.5, 129.6, 129.3, 128.2, 127.8, 127.6, 127.3, 126.8, 122.1, 54.2, 36.8, 23.9, 21.2; IR (film) ν_{max} 2926, 1649, 1493, 1452, 1415, 1343, 1274, 1210, 1161, 1091, 965, 893, 802, 727, 702, 658, 547 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}BrNO_3SH^+$ $[M+H]^+$ 496.0577, found 496.0579.

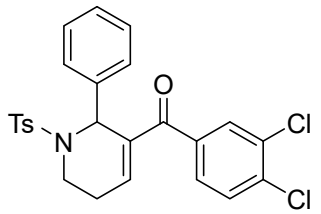
(4-Bromophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ha)



3ha

Prepared according to the general procedure as described above in 87% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 156 – 158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.65 (m, 2H), 7.61 – 7.50 (m, 2H), 7.51 – 7.41 (m, 2H), 7.39 – 7.16 (m, 7H), 6.59 (t, *J* = 3.9 Hz, 1H), 6.25 (s, 1H), 4.00 – 3.75 (m, 1H), 3.23 – 3.10 (m, 1H), 2.38 (s, 3H), 2.31 – 2.12 (m, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 192.7, 143.0, 141.5, 138.2, 137.5, 137.3, 135.6, 131.3, 130.4, 129.2, 128.2, 127.8, 127.6, 126.8, 126.7, 54.2, 36.9, 23.9, 21.2; IR (film) ν_{max} 2926, 1649, 1585, 1493, 1452, 1342, 1275, 1161, 1091, 1070, 1011, 962, 890, 815, 746, 727, 704, 655, 575, 548 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}BrNO_3SH^+$ $[M+H]^+$ 496.0577, found 496.0576.

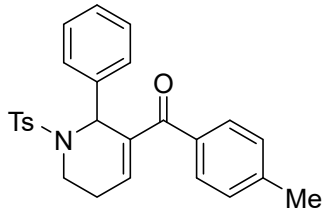
(3,4-Dichlorophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ia)



3ia

Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 173 – 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.34 – 7.26 (m, 5H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.62 (t, *J* = 3.9 Hz, 1H), 6.21 (s, 1H), 3.90 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.20 – 3.08 (m, 1H), 2.40 (s, 3H), 2.35 – 2.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 143.2, 142.2, 138.1, 137.4, 137.1, 136.5, 136.3, 132.6, 130.6, 130.2, 129.3, 128.2, 127.9, 127.8, 127.7, 126.8, 54.2, 36.8, 24.0, 21.2; IR (film) ν_{max} 2926, 1652, 1583, 1494, 1453, 1384, 1343, 1281, 1244, 1211, 1162, 1091, 1031, 967, 894, 816, 741, 720, 704, 656, 572, 550 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{21}Cl_2NO_3SH^+$ $[M+H]^+$ 484.0546, found 484.0554.

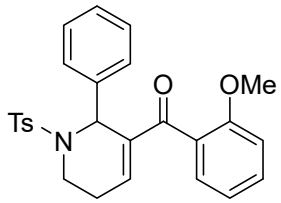
(2-Phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(p-tolyl)methanone (3ja)



3ja

Prepared according to the general procedure as described above in 91% yield. It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. mp = 168 – 169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 2H), 7.60 – 7.50 (m, 2H), 7.42 – 7.33 (m, 2H), 7.33 – 7.15 (m, 7H), 6.57 (t, *J* = 3.9 Hz, 1H), 6.30 (s, 1H), 4.05 – 3.80 (m, 1H), 3.21 – 3.10 (m, 1H), 2.39 (d, *J* = 6.4 Hz, 6H), 2.29 – 2.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 142.9, 142.6, 140.5, 138.5, 137.6, 137.4, 134.1, 129.2, 129.1, 128.6, 128.1, 127.91 127.5, 126.8, 54.3, 37.0, 23.8, 21.2, 21.1; IR (film) ν_{max} 2925, 1642, 1606, 1493, 1452, 1342, 1276, 1211, 1161, 1091, 962, 890, 815, 744, 724, 705, 657, 569, 548 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_3SH^+$ $[M+H]^+$ 432.1628, found 432.1626.

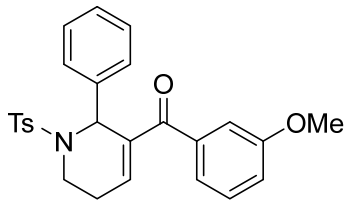
(2-Methoxyphenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ka)



3ka

Prepared according to the general procedure as described above in 98% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 164 – 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.61 (m, 2H), 7.48 – 7.41 (m, 2H), 7.41 – 7.27 (m, 4H), 7.25 – 7.18 (m, 2H), 7.07 – 6.88 (m, 3H), 6.53 (t, *J* = 4.0 Hz, 1H), 6.25 (s, 1H), 3.79 (s, 4H), 3.12 – 3.01 (m, 1H), 2.41 (s, 3H), 2.35 – 1.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 156.3, 143.1, 142.8, 138.6, 138.5, 137.7, 130.9, 129.1, 128.4, 128.2, 128.1, 127.8, 127.4, 126.8, 120.1, 111.0, 55.3, 53.8, 36.8, 24.0, 21.1; IR (film) ν_{max} 2926, 1653, 1598, 1488, 1454, 1373, 1342, 1293, 1245, 1161, 1090, 1068, 1020, 963, 755, 724, 698, 664, 570, 548 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_4SH^+$ $[M+H]^+$ 448.1577, found 448.1577.

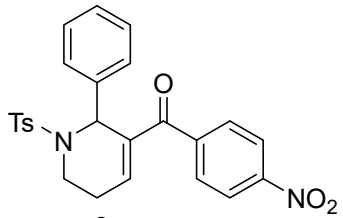
(3-Methoxyphenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3la)



3la

Prepared according to the general procedure as described above in 98% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 62 – 64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.25 (m, 4H), 7.25 – 7.18 (m, 2H), 7.18 – 7.10 (m, 2H), 7.09 – 7.03 (m, 1H), 6.63 (t, *J* = 3.9 Hz, 1H), 6.27 (s, 1H), 3.96 – 3.85 (m, 1H), 3.83 (s, 3H), 3.17 – 3.10 (m, 1H), 2.38 (s, 3H), 2.33 – 2.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 159.2, 143.0, 141.5, 138.4, 138.2, 137.6, 137.3, 129.2, 128.9, 128.1, 127.9, 127.5, 126.8, 121.4, 117.6, 114.0, 55.1, 54.3, 36.9, 23.9, 21.1; IR (film) ν_{max} 2929, 1644, 1596, 1579, 1485, 1451, 1431, 1342, 1277, 1160, 1091, 1043, 977, 895, 801, 743, 723, 705, 656, 548 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_4SH^+$ $[M+H]^+$ 448.1577, found 448.1578.

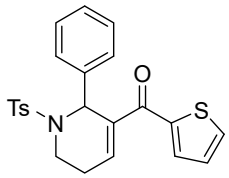
(4-Nitrophenyl)(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3ma)



3ma

Prepared according to the general procedure as described above in 75% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 134 – 136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 – 8.22 (m, 2H), 7.76 – 7.64 (m, 4H), 7.31 (d, *J* = 3.5 Hz, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.65 (t, *J* = 4.0 Hz, 1H), 6.22 (s, 1H), 3.90 (dd, *J* = 14.9, 6.6 Hz, 1H), 3.21 –3.09 (m, 1H), 2.40 (s, 3H), 2.38 – 2.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 149.3, 143.5, 143.2, 142.3, 137.9, 137.5, 137.3, 129.5, 129.3, 129.2, 128.3, 127.8, 127.7, 126.9, 126.1, 123.2, 54.0, 36.7, 24.3, 21.2; IR (film) ν_{max} 2928, 1653, 1602, 1524, 1494, 1453, 1348, 1275, 1161, 1091, 963, 853, 722, 704, 656, 549 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}N_2O_5SH^+$ $[M+H]^+$ 461.1177, found 461.1183.

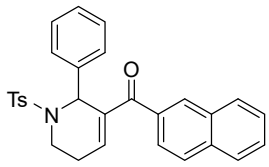
(2-Phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)(thiophen-2-yl)methanone (3na)



3na

Prepared according to the general procedure as described above in 93% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 130 – 132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.68 – 7.54 (m, 2H), 7.41 – 7.34 (m, 2H), 7.29 – 7.18 (m, 5H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.77 (t, *J* = 4.0 Hz, 1H), 6.30 (s, 1H), 3.96 – 3.82 (m, 1H), 3.25 – 3.03 (m, 1H), 2.37 (s, 3H), 2.27 – 2.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.1, 142.9, 142.1, 138.2, 138.1, 137.7, 137.6, 133.5, 132.9, 129.3, 128.1, 127.9, 127.6, 127.5, 126.8, 54.6, 36.9, 23.6, 21.1; IR (film) νmax 2926, 1621, 1513, 1493, 1452, 1413, 1341, 1281, 1211, 1160, 1090, 982, 959, 856, 815, 718, 704, 655, 578, 550 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{21}NO_3S_2H^+$ $[M+H]^+$ 424.1036, found 424.1032.

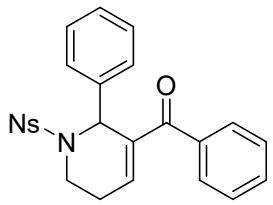
Naphthalen-2-yl(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3oa)



3oa

Prepared according to the general procedure as described above in 88% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 160 – 162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 1H), 7.97 – 7.84 (m, 3H), 7.79 – 7.68 (m, 3H), 7.61 – 7.55 (m, 2H), 7.47 – 7.39 (m, 2H), 7.34 – 7.30 (m, 2H), 7.29 – 7.18 (m, 3H), 6.68 (t, *J* = 3.9 Hz, 1H), 6.36 (s, 1H), 3.94 (dd, *J* = 14.9, 5.9 Hz, 1H), 3.26 – 3.19 (m, 1H), 2.39 (s, 3H), 2.33 – 2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 142.9, 141.4, 138.5, 137.6, 137.5, 134.7, 134.1, 131.8, 130.0, 129.2, 128.8, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 126.9, 126.5, 125.0, 54.4, 37.0, 23.9, 21.2; IR (film) ν_{max} 3059, 2926, 1653, 1641, 1597, 1453, 1371, 1342, 1284, 1161, 1090, 757, 722, 657 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}NO_3SH^+$ $[M+H]^+$ 468.1628, found 468.1628.

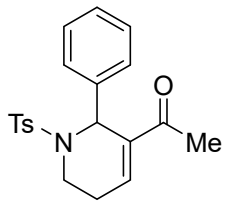
(1-((4-Nitrophenyl)sulfonyl)-2-phenyl-1,2,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (3pa)



3pa

Prepared according to the general procedure as described above in 94% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 159 – 161°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 – 8.10 (m, 2H), 8.12 – 7.89 (m, 2H), 7.69 – 7.59 (m, 2H), 7.59 – 7.49 (m, 1H), 7.48 – 7.34 (m, 4H), 7.31 – 7.25 (m, 3H), 6.60 (t, *J* = 4.0 Hz, 1H), 6.36 (s, 1H), 4.08 – 3.86 (m, 1H), 3.31 –3.23 (m, 1H), 2.38 – 2.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 149.5, 146.2, 140.0, 137.5, 137.4, 136.4, 132.2, 128.9, 128.3, 128.1, 128.0, 127.9, 123.7, 54.7, 37.4, 24.2; IR (film) ν_{max} 3103, 3063, 2931, 1645, 1530, 1371, 1349, 1309, 1276, 1165, 1090, 991, 961, 856, 749, 740, 726, 714, 699, 606 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_5SH^+$ $[M+H]^+$ 447.1026, found 447.1026.

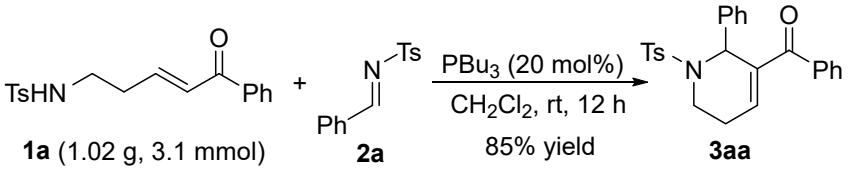
1-(2-Phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)ethan-1-one (3sa)



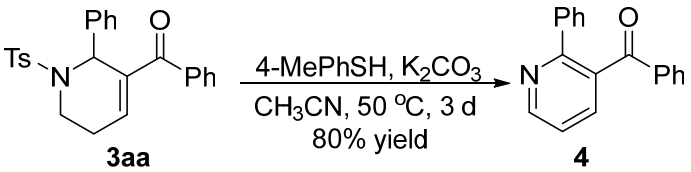
3sa

Prepared according to the general procedure as described above in about 73% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid (contains some $TsNH_2$ which can't be separated completely, the ratio between **3sa** and $TsNH_2$ is 1:1.4, determined by ^{1}H NMR, isolated yield was calculated based on the ratio); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.64 (m, 2H), 7.30 – 7.28 (m, 2H), 7.28 – 7.25 (m, 2H), 7.24 (d, J = 0.8 Hz, 1H), 7.22 (d, J = 2.5 Hz, 2H), 6.94 (dd, J = 4.6, 3.3 Hz, 1H), 6.04 (s, 1H), 3.85 – 3.79 (m, 1H), 3.05 – 2.97 (m, 1H), 2.44 – 2.41 (m, 2H) 2.41 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 143.5, 143.3, 139.5, 139.1, 138.7, 138.5, 137.7, 129.6, 129.5, 128.3, 128.1, 127.8, 127.1, 126.4, 54.1, 36.8, 25.2, 24.2, 21.5; HRMS (ESI) calcd for $C_{20}H_{21}NO_3SH^+$ $[M+H]^+$ 356.1315, found 356.1312.

The reaction on the gram-scale and further transformation of the product

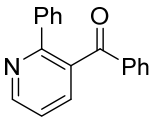


Under a nitrogen atmosphere, to a stirred solution of δ-sulfonamido-substituted enones **1** (3.1 mmol, 1.0 equiv) and *N*-sulfonylimine **2** (4.65 mmol, 1.5 equiv) in DCM (30 mL) was added catalyst PBu_3 (0.62 mmol, 20 mol%) via a syringe. Then the reaction solution was vigorously stirred at room temperature and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to furnish the corresponding product.



The cycloaddition **3aa** (83.5 mg, 0.2 mmol) was dissolved in 5 mL CH_3CN, then 4-MePhSH (29.8 mg, 0.24 mmol) and K_2CO_3 (82.8mg, 0.6 mmol) was added, the mixture was stirred at 50 °C for 72 hours. Once starting material was consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE) to afford the corresponding product **4** as a white solid (41.6 mg), 80% yield.

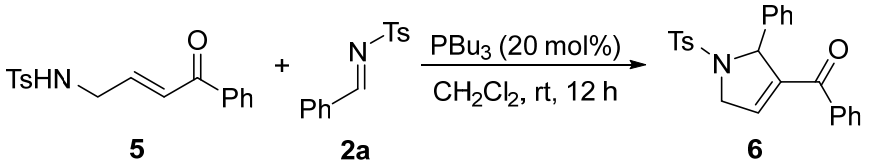
Phenyl(2-phenylpyridin-3-yl)methanone (4)



4

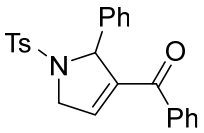
Prepared according to the general procedure as described above in 80% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid. mp = 106 – 108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.6 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.49 – 7.39 (m, 1H), 7.39 – 7.29 (m, 3H), 7.29 – 7.24 (m, 2H), 7.18 – 7.04 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 152.4, 148.1, 138.5, 137.7, 135.9, 134.9, 133.2, 129.6, 128.6, 128.1, 128.0, 127.9, 123.8; IR (film) ν_{max} 3727, 2925, 1653, 1449, 1321, 749, 696 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{13}NOH^+$ $[M+H]^+$ 260.1070, found 260.1068.

General Procedure for the Phosphine-Catalyzed [4+1] Annulation



Under a nitrogen atmosphere, to a stirred solution of γ-sulfonamido-substituted enone **5** (0.2 mmol, 1.0 equiv) and *N*-sulfonylimine **2a** (3.0 mmol, 1.5 equiv) in DCM (2 mL) was added the catalyst PBu_3 (0.04 mmol, 20 mol%) via a syringe. Then the reaction solution was vigorously stirred at room temperature and monitored by TLC. After the reaction was stirred for 12 h, the mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to furnish the corresponding product **6** in 23% yield.

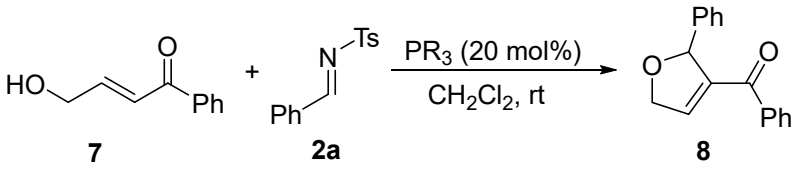
Phenyl(2-phenyl-1-tosyl-2,5-dihydro-1H-pyrrol-3-yl)methanone (6)



6

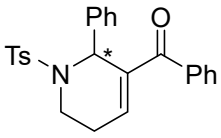
Prepared according to the general procedure as described above in 23% yield. It was purified by flash chromatography (15% EtOAc/PE) to afford a white solid (contains tracement of unknown impurities). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.67 – 7.60 (m, 2H), 7.60 – 7.46 (m, 4H), 7.46 – 7.34 (m, 4H), 7.27 – 7.20 (m, 4H), 6.42 (t, *J* = 2.0 Hz, 1H), 6.03 – 6.00 (m, 1H), 4.61 – 4.58 (m , 2H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 143.4, 142.7, 139.4, 137.2, 135.1, 132.8, 129.9, 129.8, 129.6, 128.8, 128.4, 128.3, 127.5, 127.3, 69.7, 55.7, 21.5; HRMS (ESI) calcd for $C_{24}H_{21}NO_3SH^+$ $[M+H]^+$ 404.1315, found 404.1313.

Phosphine-Catalyzed Annulation of (*E*)-4-hydroxy-1-phenylbut-2-en-1-one



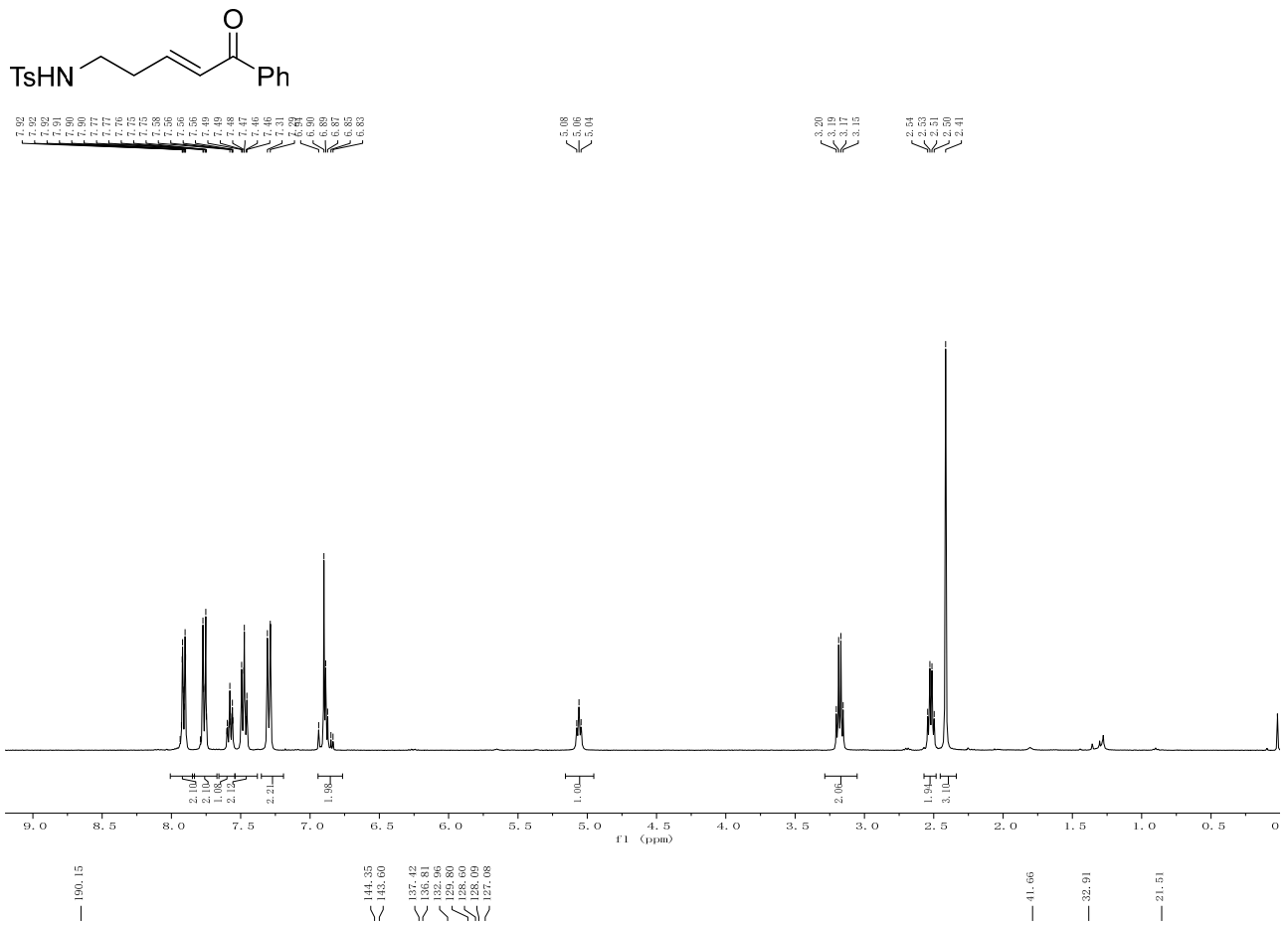
A hydroxyl-substituted enone, (*E*)-4-hydroxy-1-phenylbut-2-en-1-one (**7**), has also been examined under the standard reaction conditions. Unfortunately, no desired [4+1] annulation product **8** was observed. Further exploration through screening different phosphines such as PPh_3, Ph_2PMe, $PhPMe_2$ and Me_3P had been carried out, but no product was observed on the TLC.

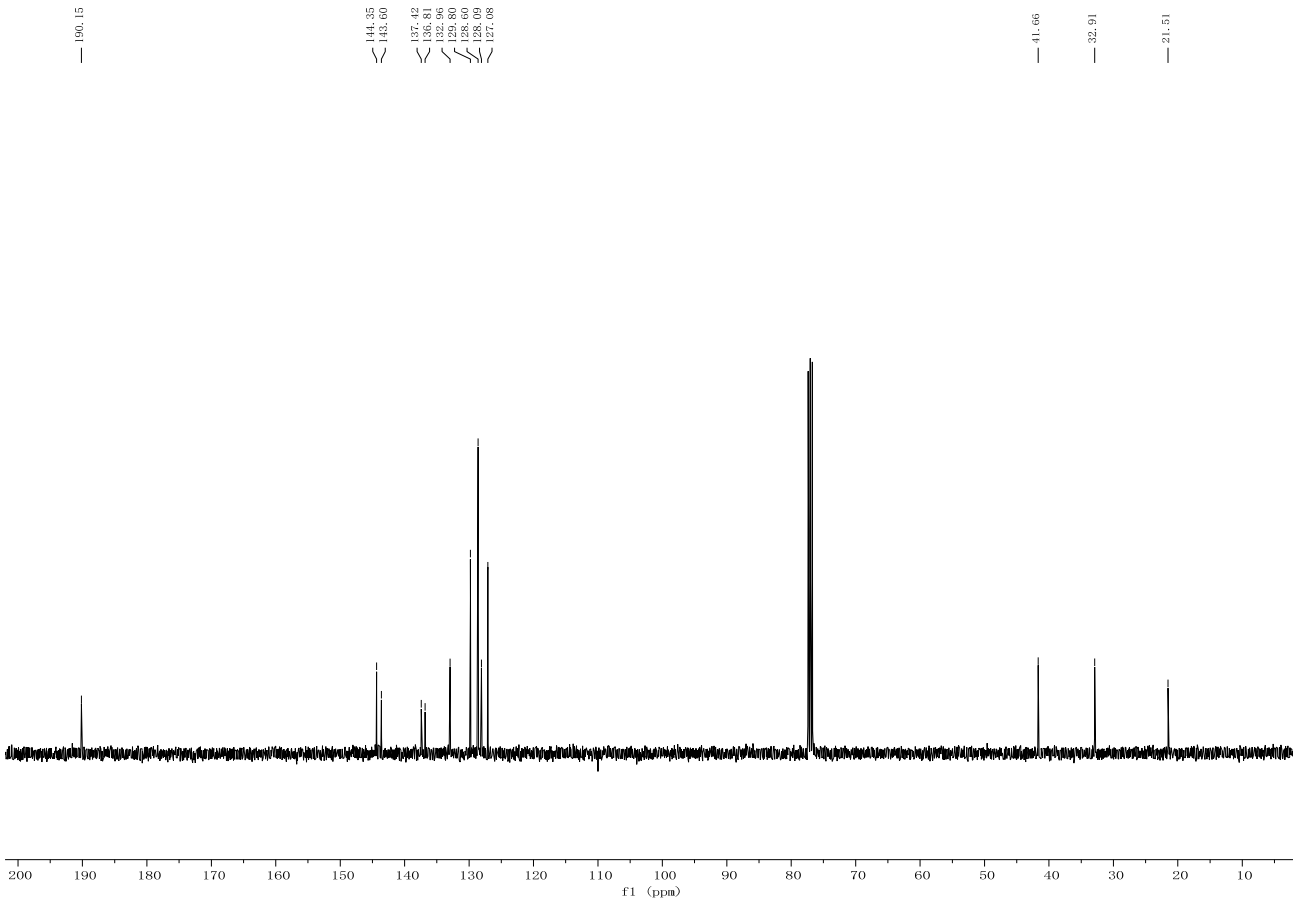
(-)-Phenyl(2-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanone (3aa)



3aa

Prepared according to the general procedure as described above in 28% yield. It was purified by flash chromatography (20% EtOAc/PE) to afford a white solid. mp = 161 – 163 °C; $[\alpha]^{20}_{D}$= – 139.4 (*c* 0.34, CH_2Cl_2); mp = 161 – 163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.64 – 7.57 (m, 2H), 7.55 – 7.48 (m, 1H), 7.47 – 7.34 (m, 4H), 7.33 – 7.25 (m, 3H), 7.24 – 7.18 (m, 2H), 6.64 – 6.52 (m, 1H), 6.29 (s, 1H), 3.94 – 3.86 (m, 1H), 3.31 – 3.04 (m, 1H), 2.38 (s, 3H), 2.25 – 2.18 (m, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 192.5, 143.0, 141.3, 138.2, 137.5, 137.3, 135.1, 130.3, 129.2, 128.3, 128.2, 127.8, 127.6, 126.8, 54.2, 36.9, 24.0, 21.1; IR (film) ν_{max} 3061, 2927, 1645, 1597, 1493, 1447, 1342, 1275, 1212, 1161, 1091, 962, 891, 815, 718, 699, 671, 653, 574, 548 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{23}NO_3SH^+$ $[M+H]^+$ 418.1471, found 418.1470; HPLC analysis: 73% ee (RC-OD, isopropanol/hexane = 8:92, 1.0 mL/min, UV: 254 nm), t_R = 20.364 min (minor), 22.279 min (major).


TsHN
O
Ph
f1 (ppm)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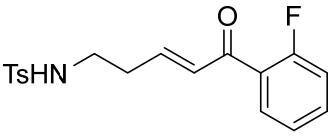
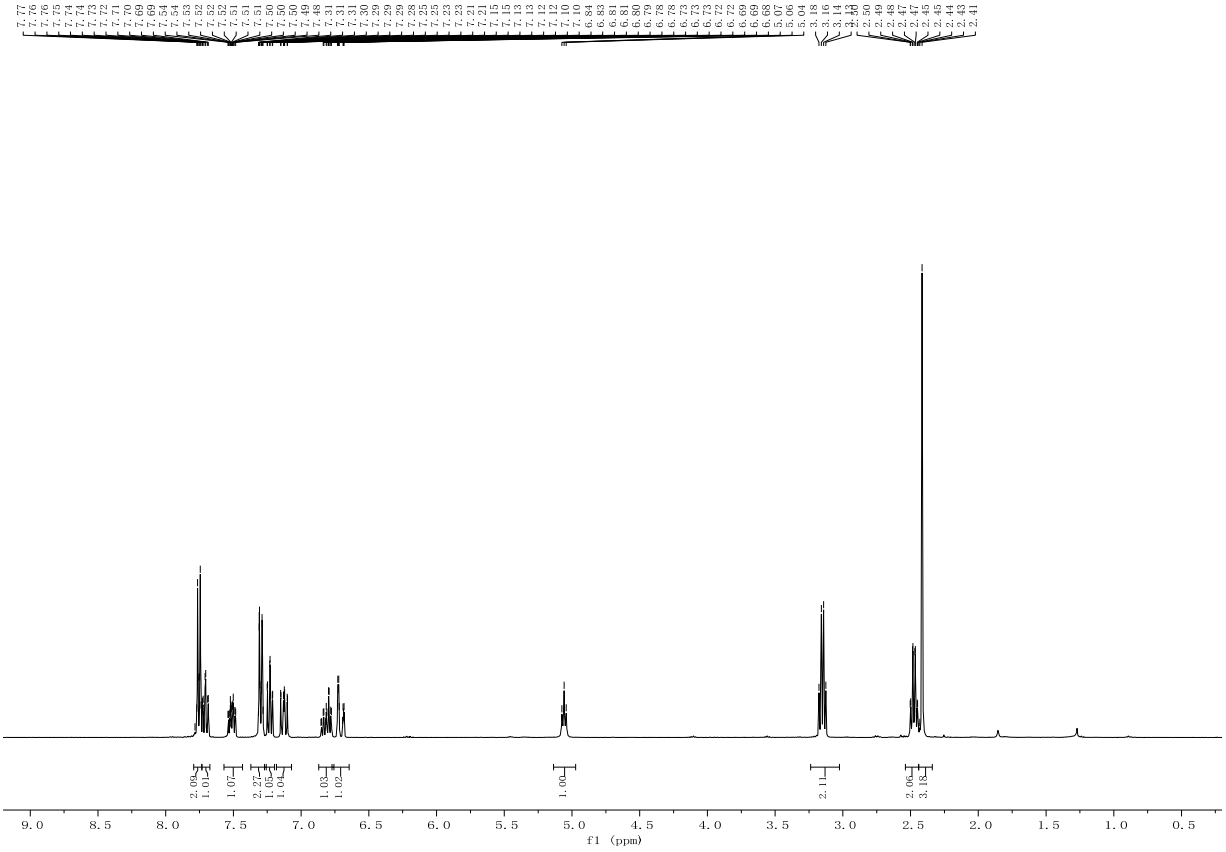
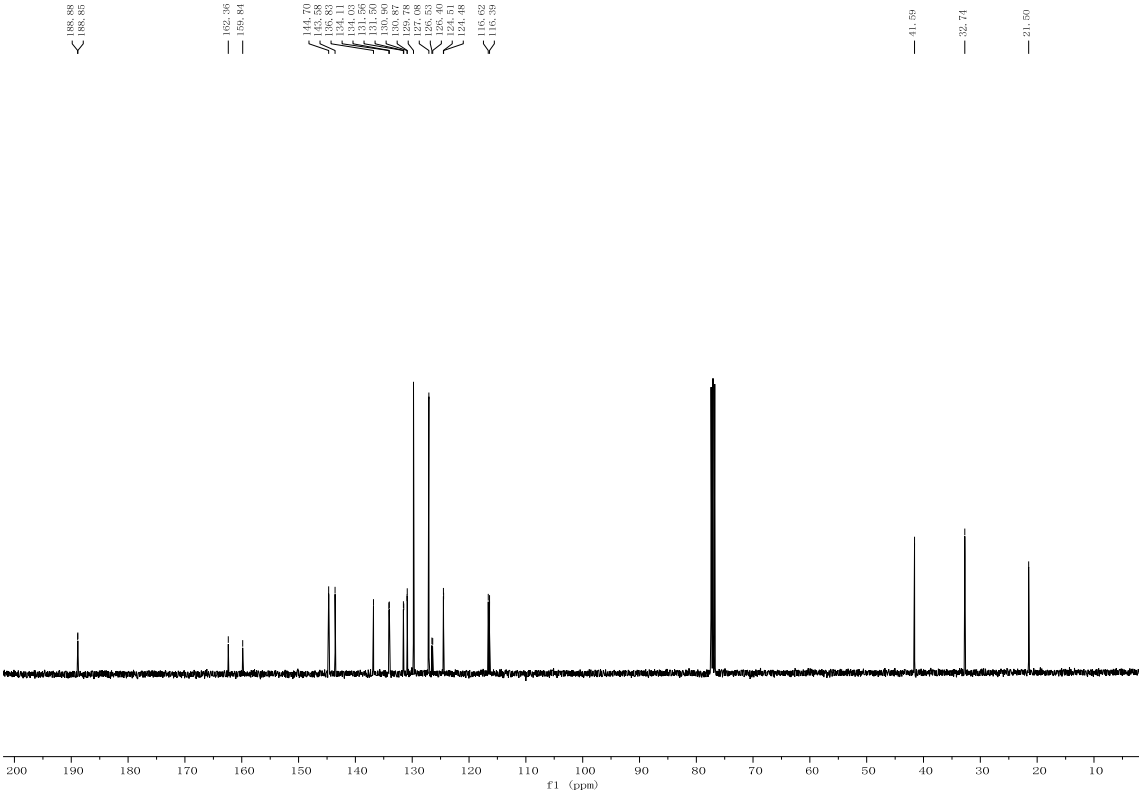
132.96
129.80
128.60
128.09
127.08
41.66
32.91
21.51
f1 (ppm)


O
F
TsHN


f1 (ppm)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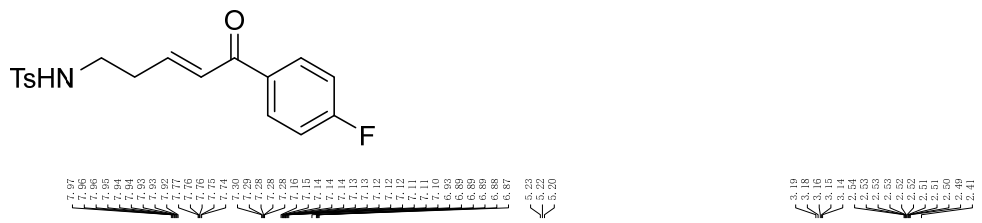
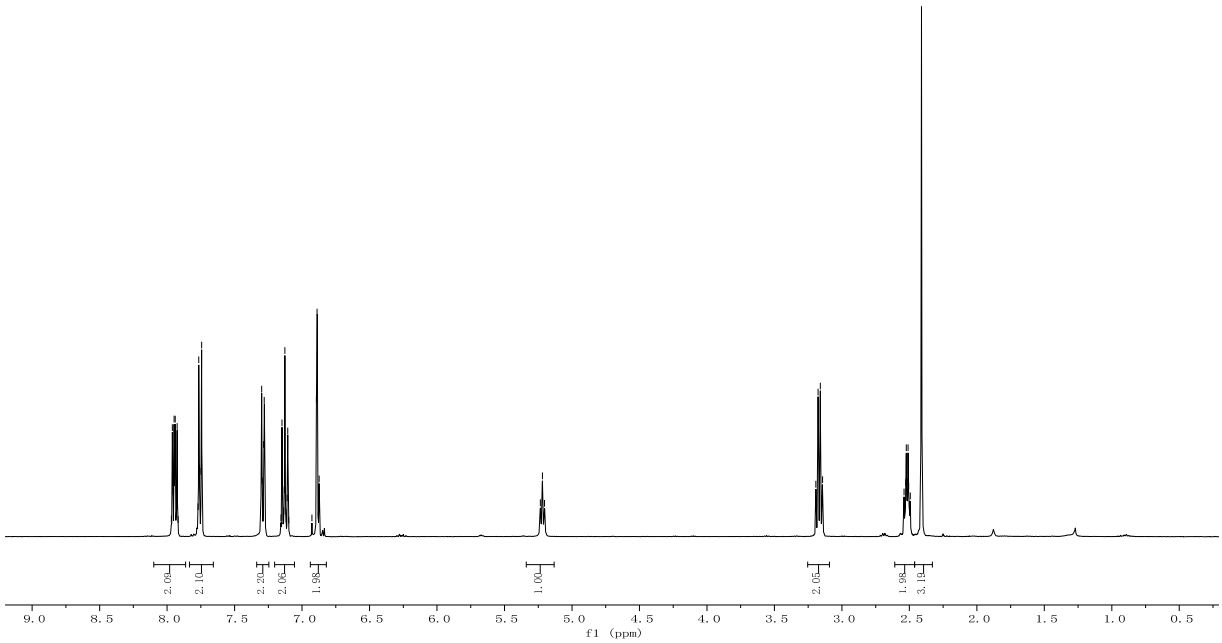

TsHN
O
F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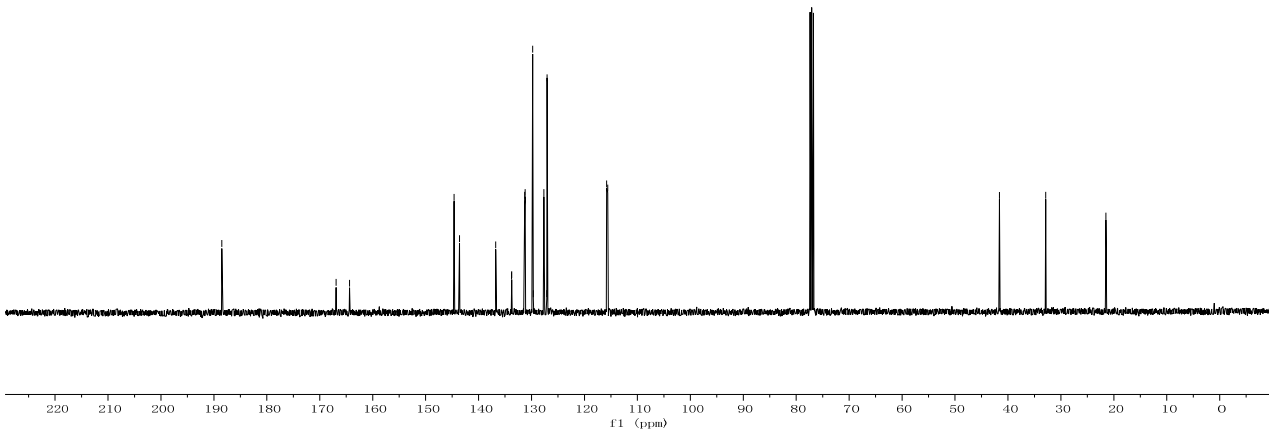
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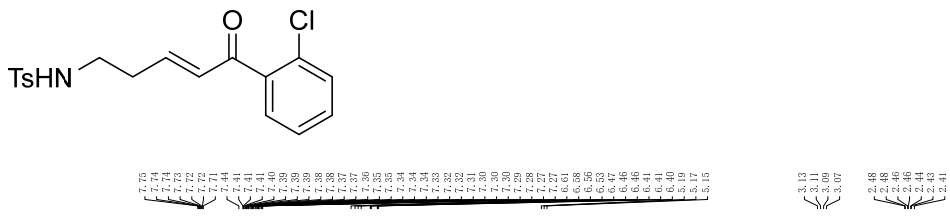
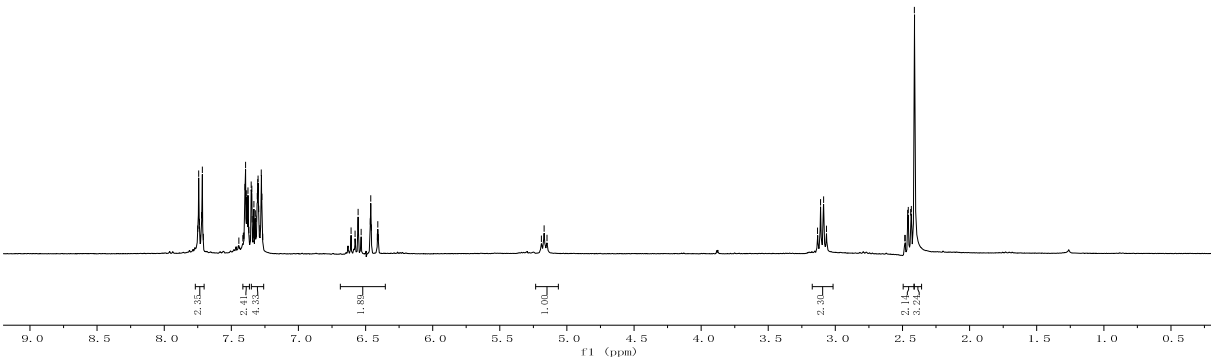

O
Cl
TsHN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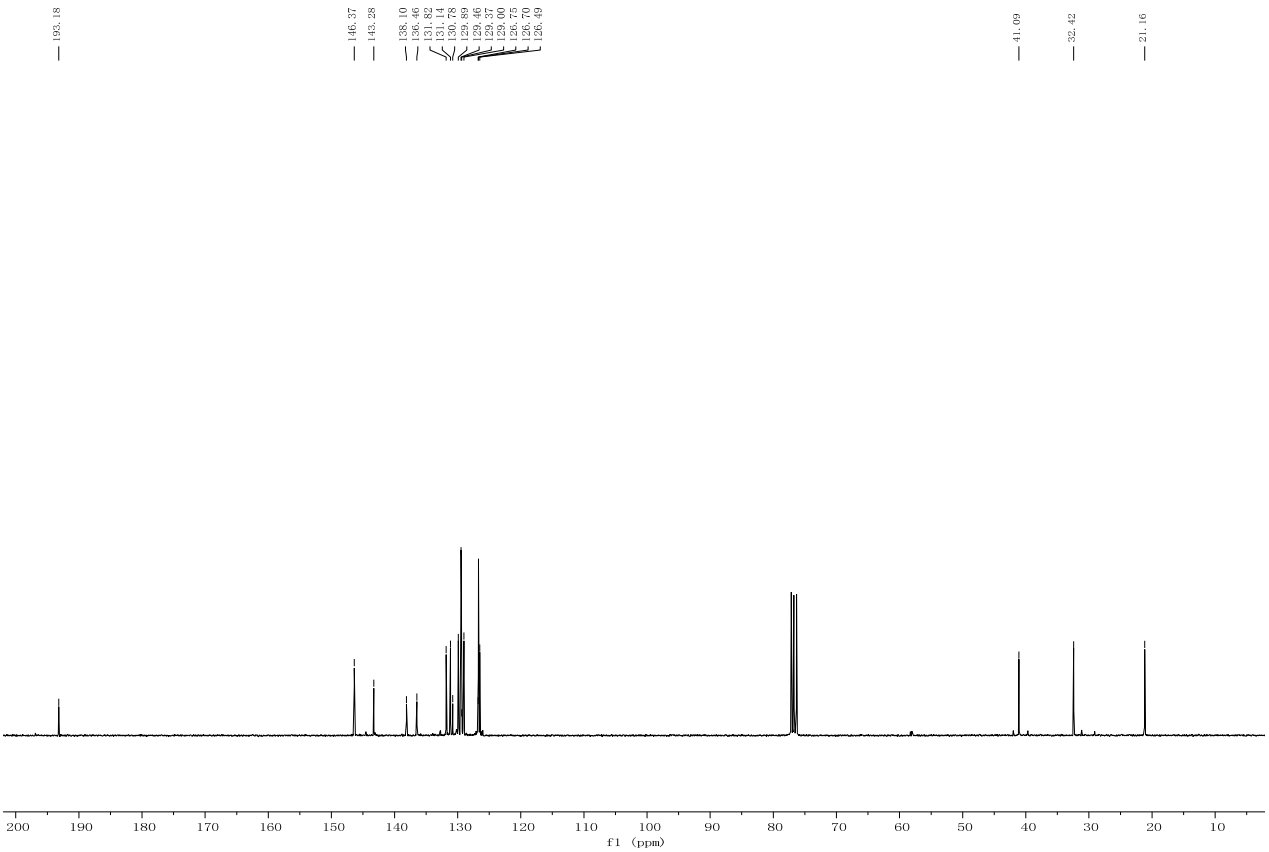
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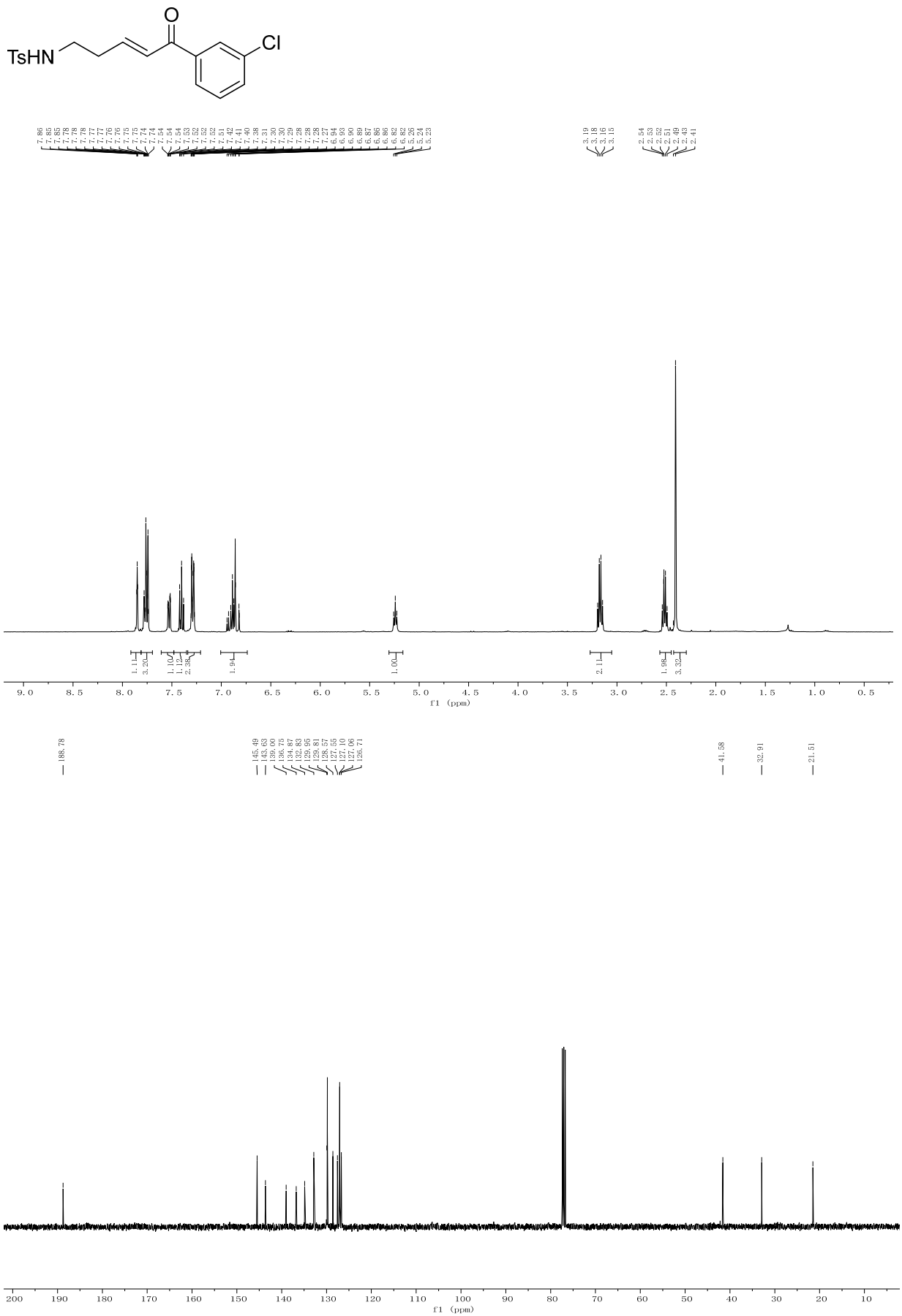
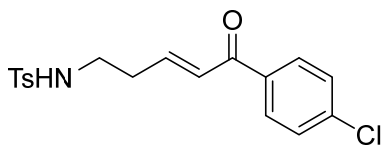

TsHN
O
Cl
f1 (ppm)
f1 (ppm)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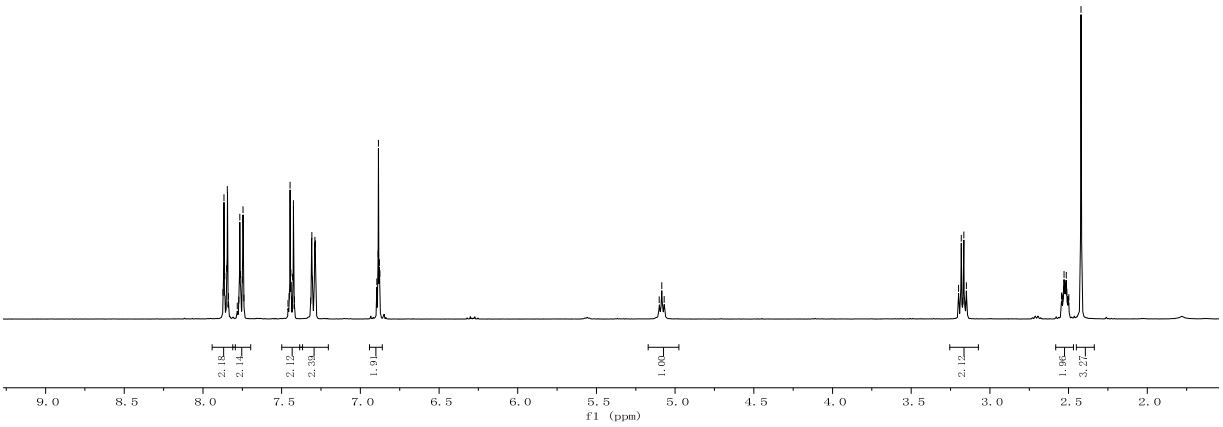
TsHN
Cl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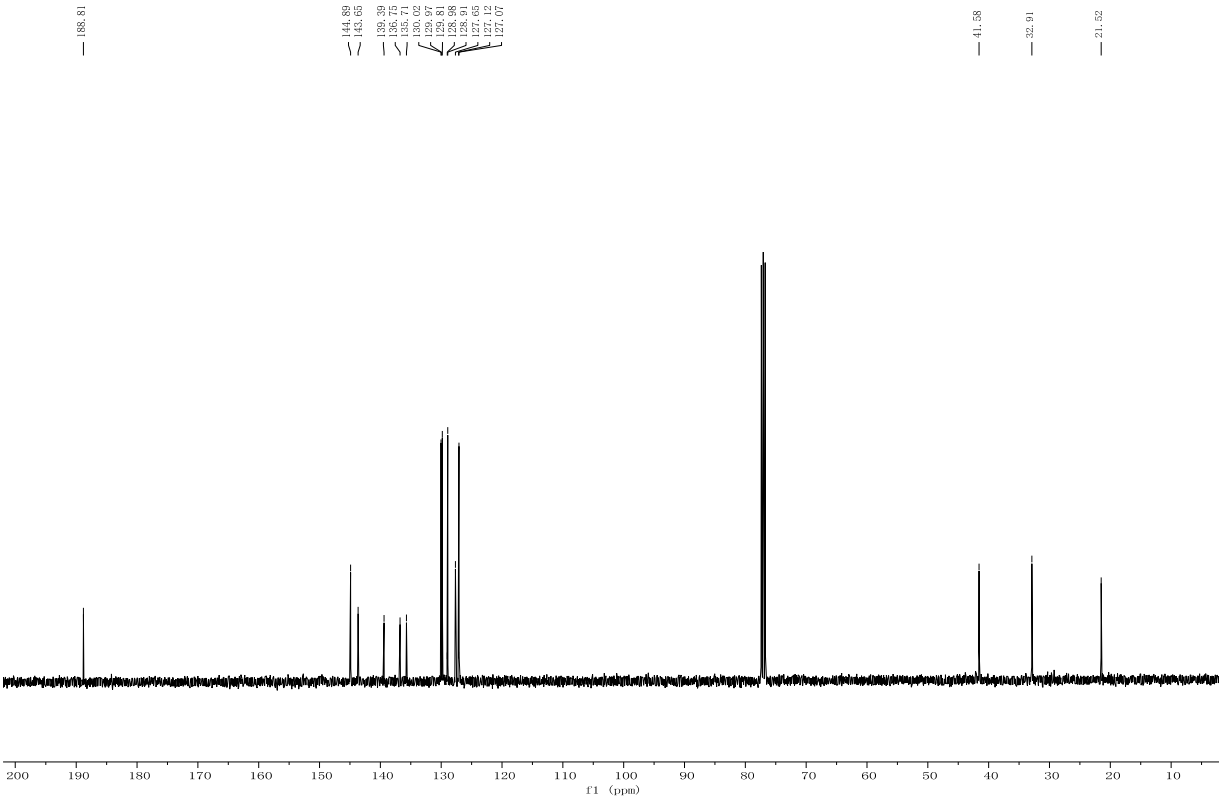
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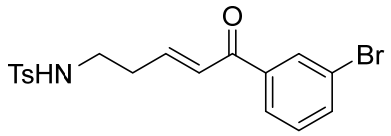
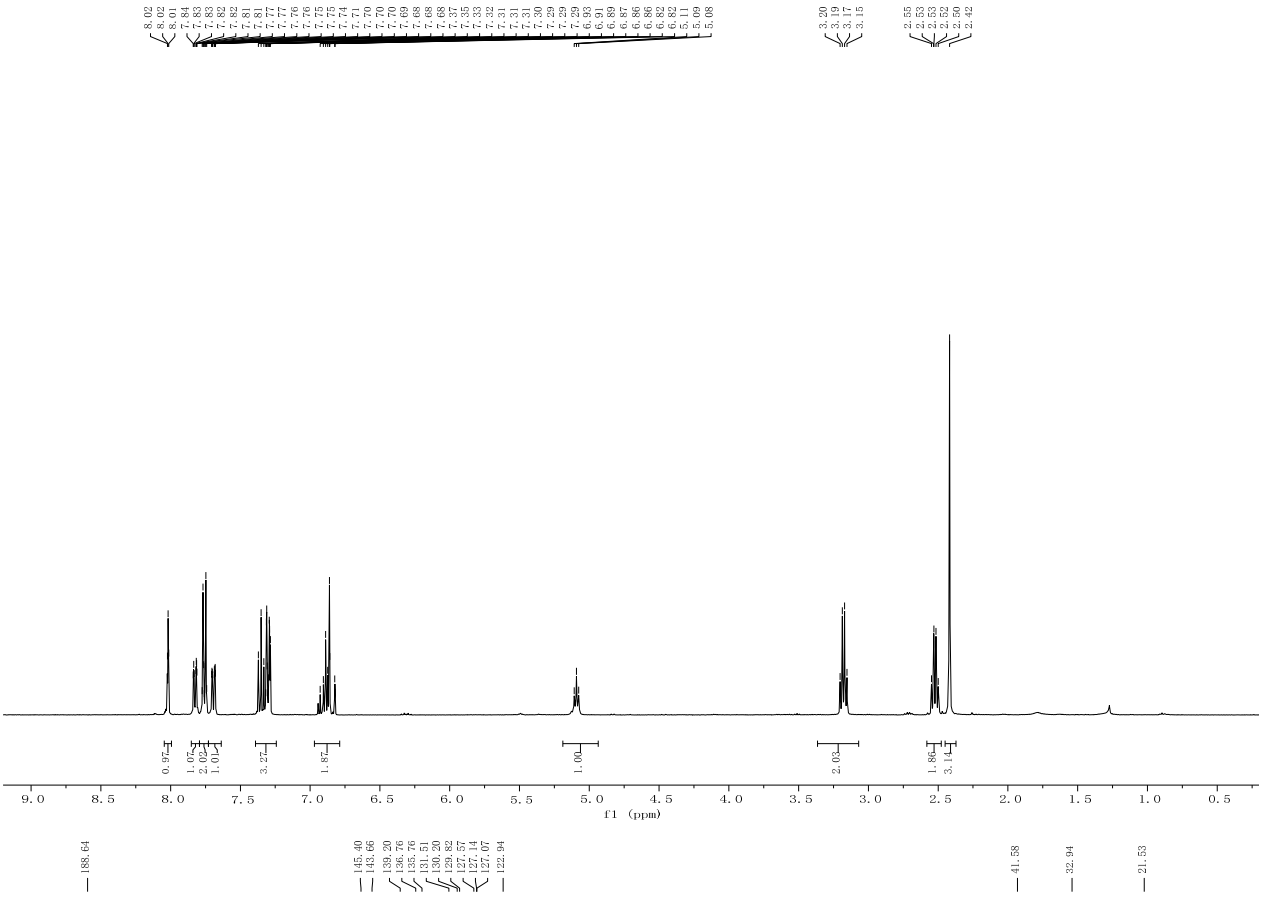

O
TsHN
Br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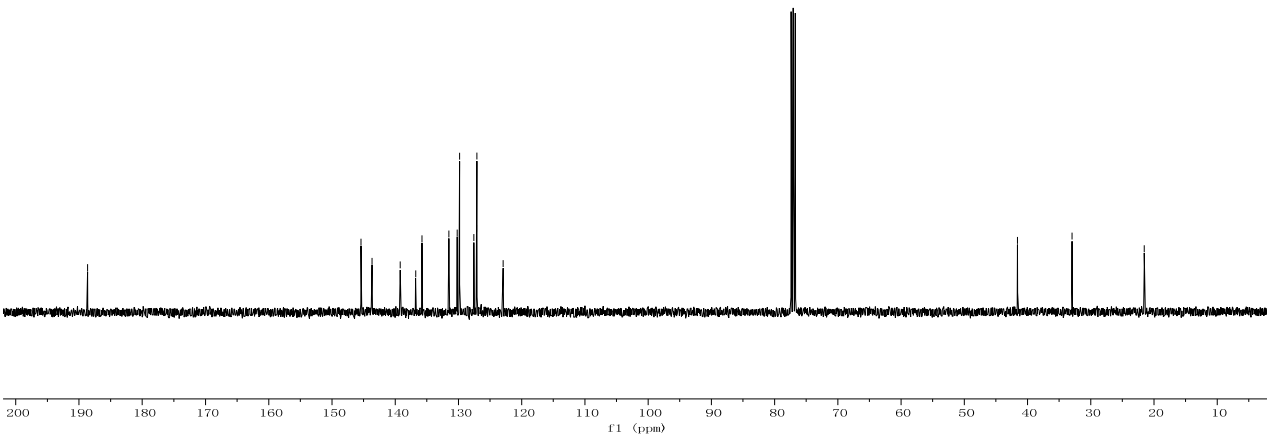
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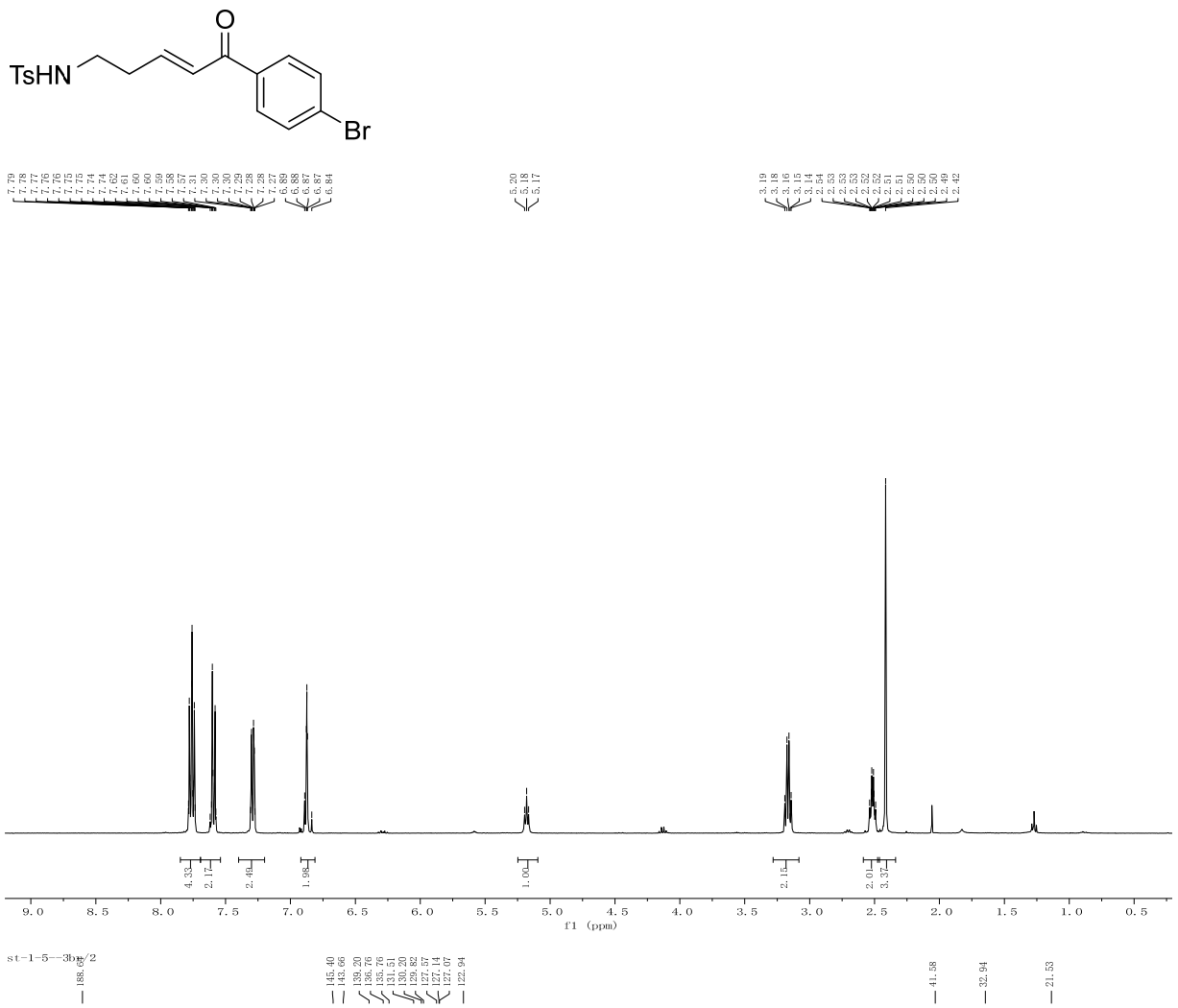
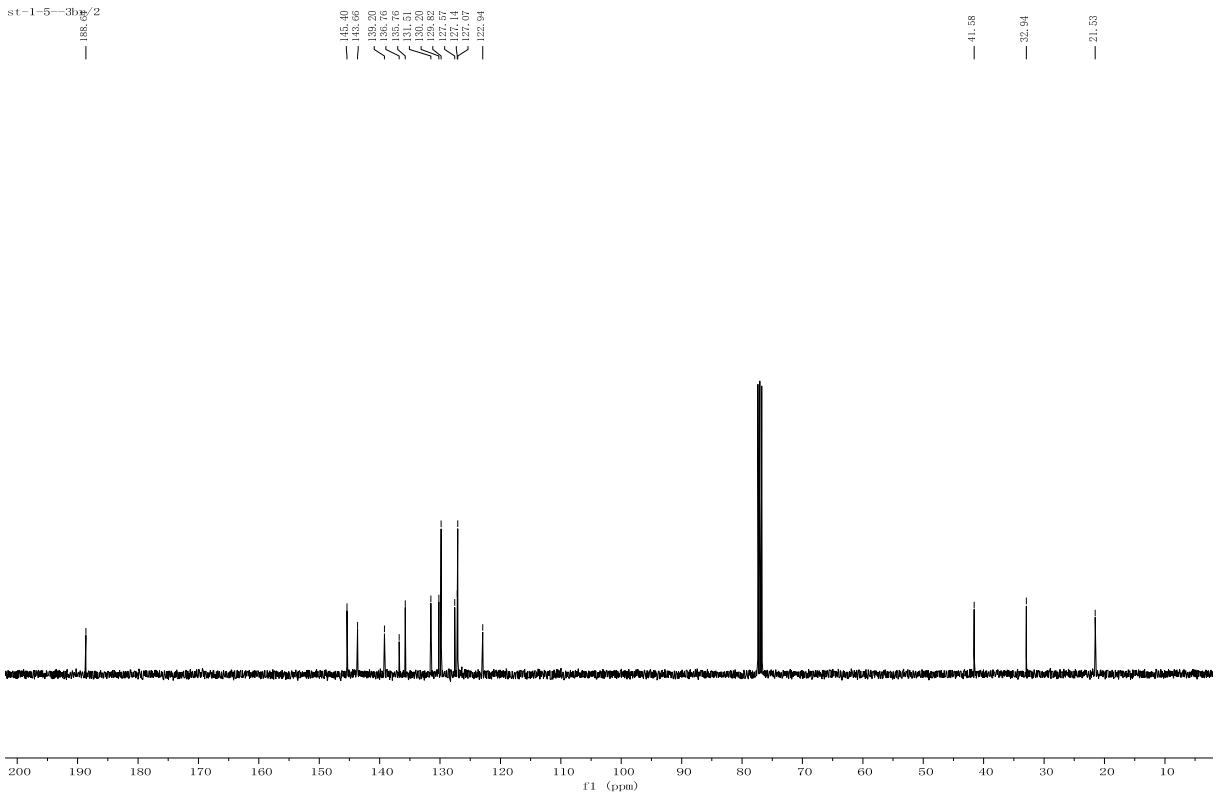

TsHN
O
Br
f1 (ppm)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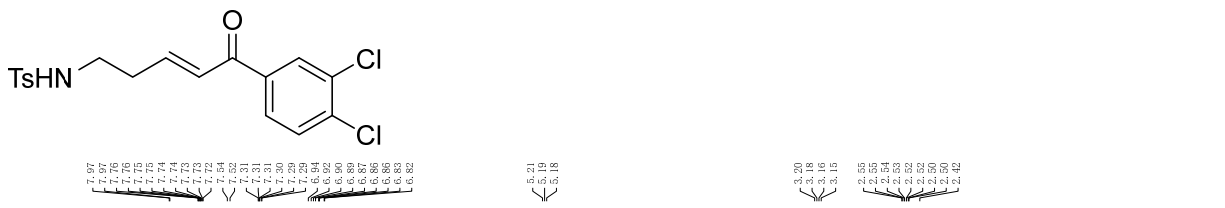
TsHN
O
Cl
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2.55
2.54
2.53
2.52
2.52
2.50
2.50
2.42
1.04
3.02
1.02
2.26
1.88
0.93
1.97
1.81
3.04
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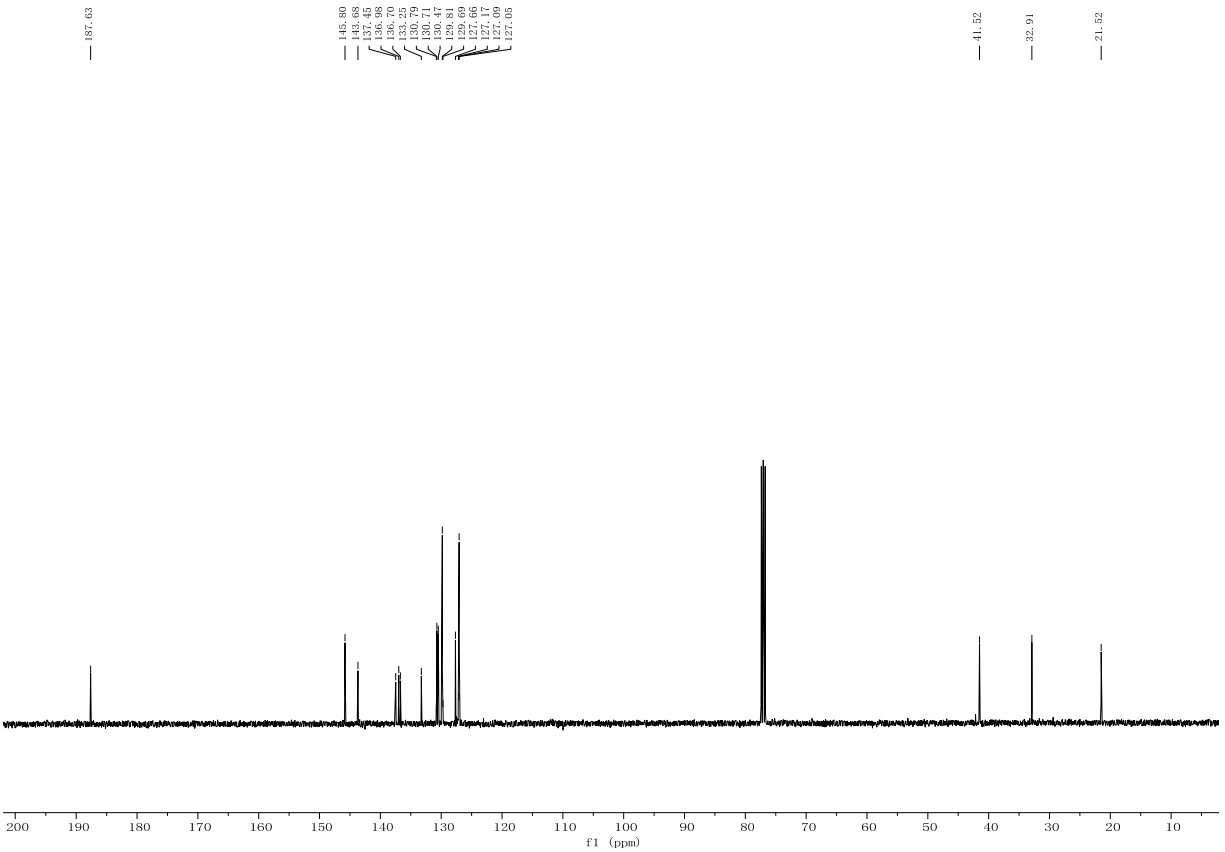
f1 (ppm)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130.79
130.71
130.47
129.81
129.69
127.66
127.17
127.09
127.05
41.52
32.91
21.52
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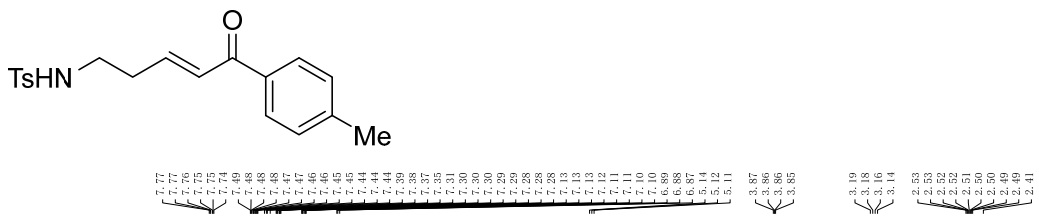
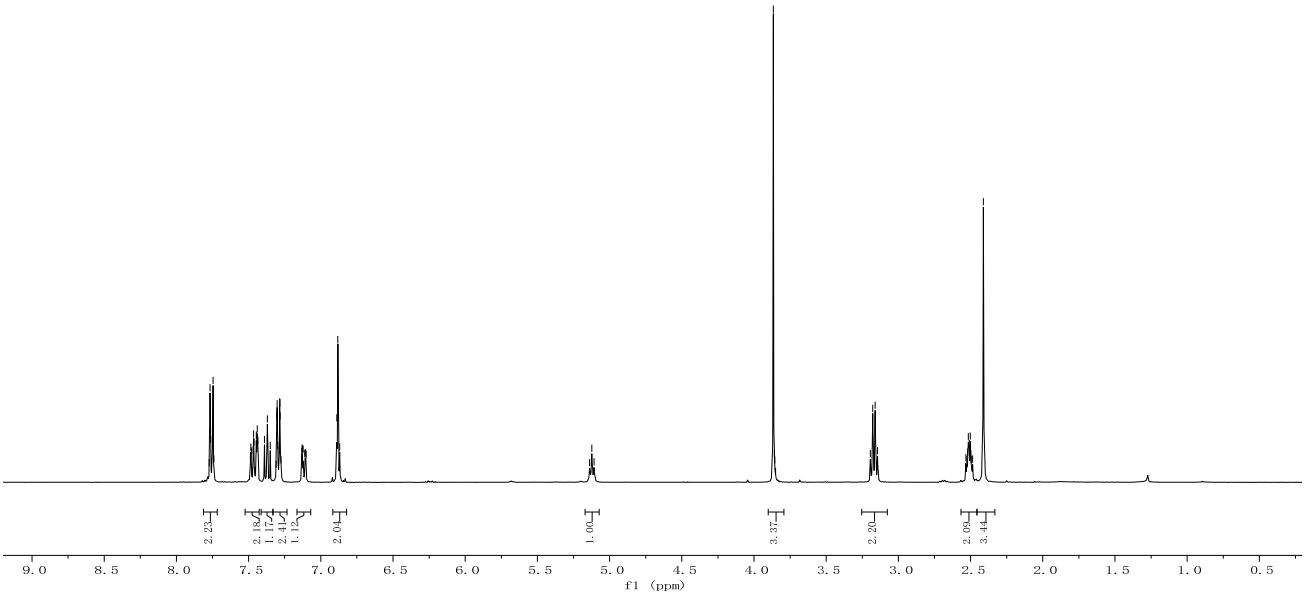
f1 (ppm)


TsHN
O
Me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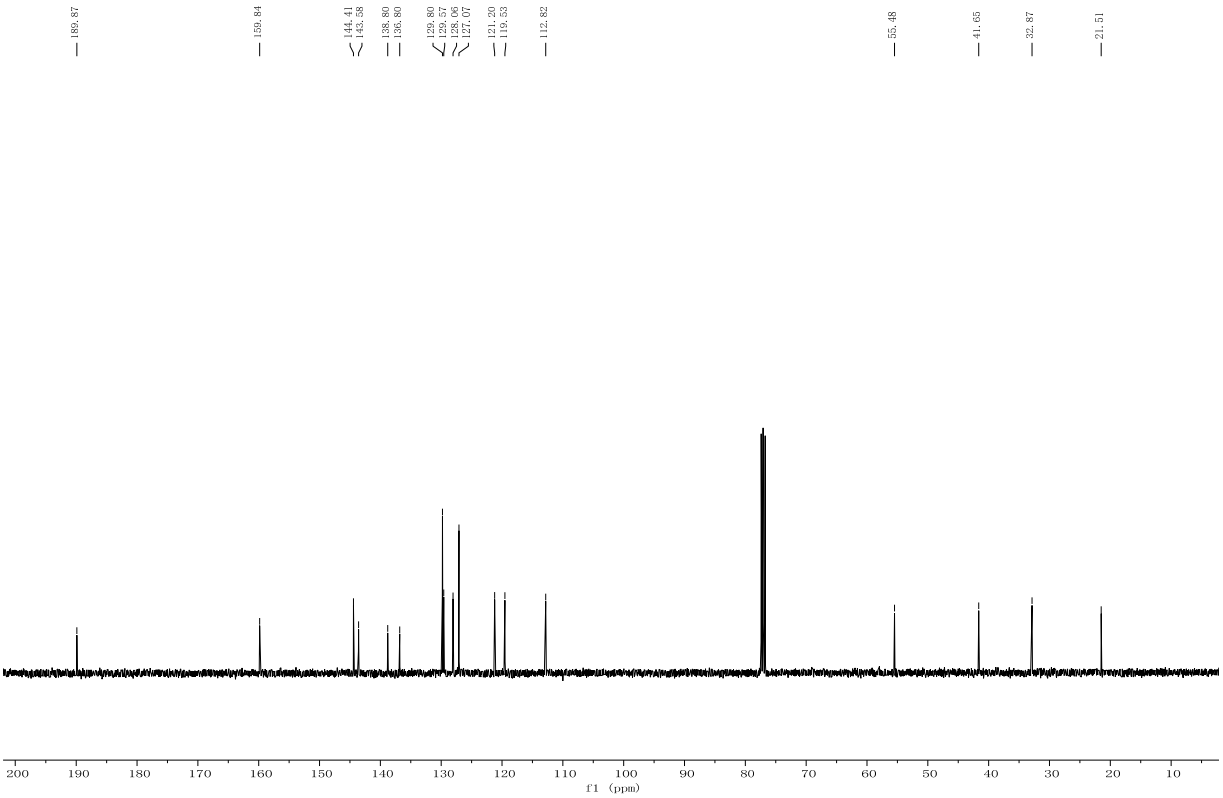
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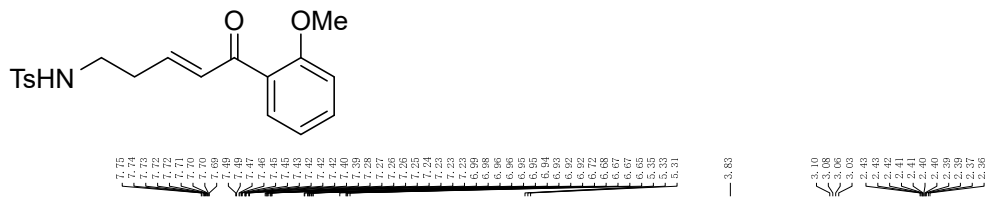
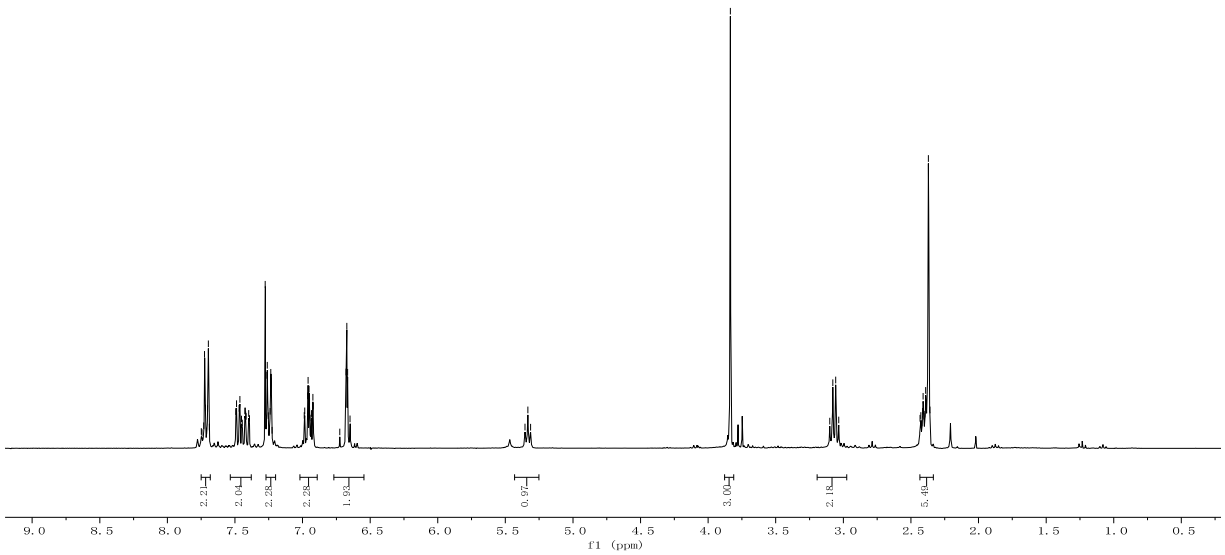

O
OMe
TsHN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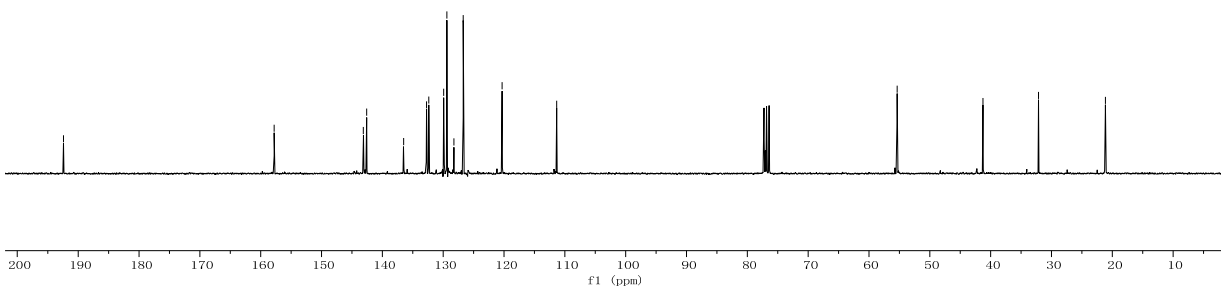
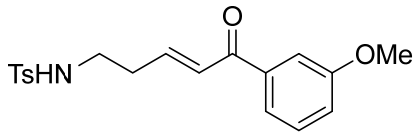

f1 (ppm)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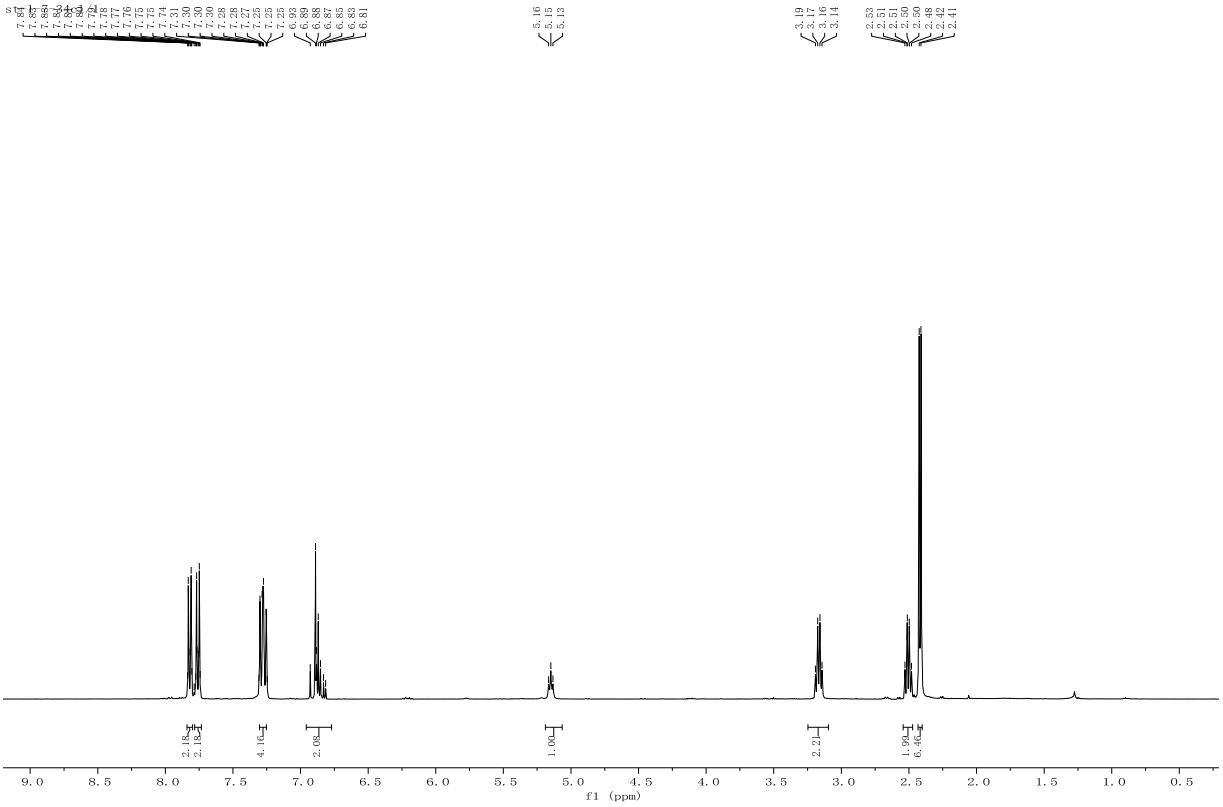
TsHN
OMe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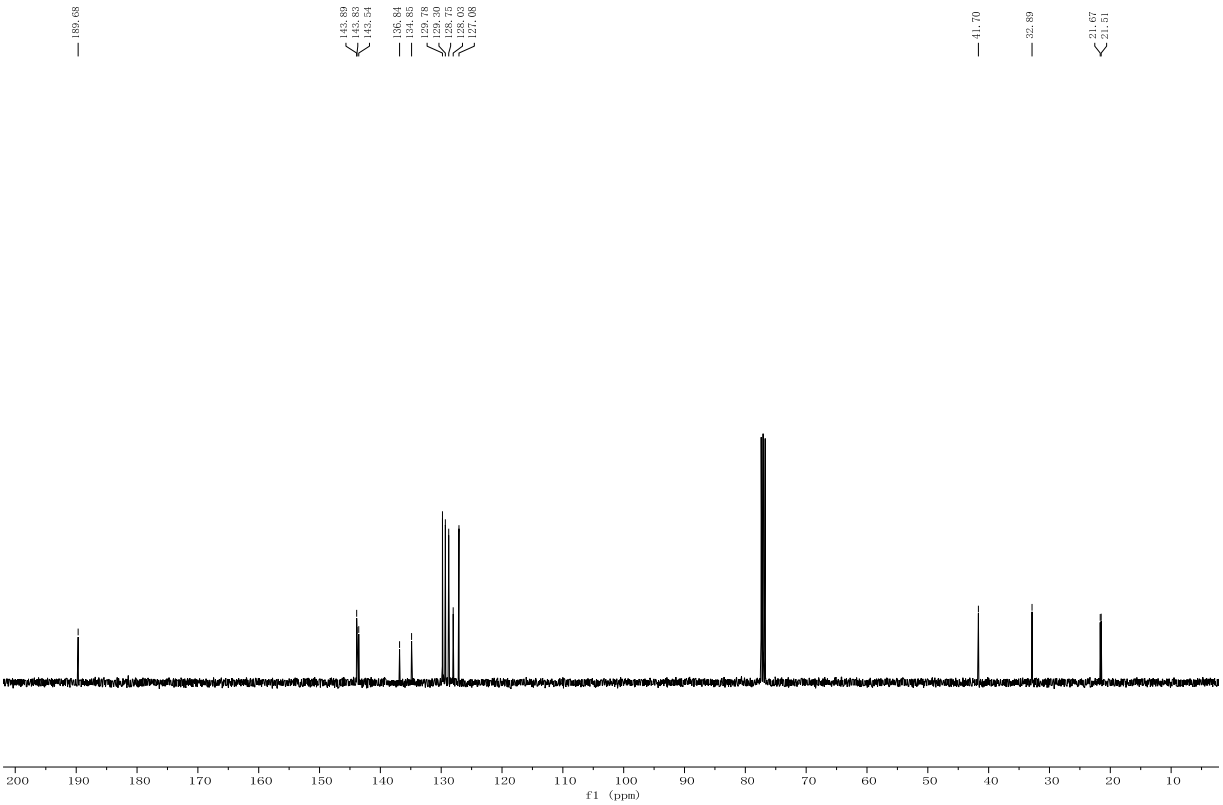
2.08
1.00
2.21
1.99
6.46
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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134.85
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129.30
128.75
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41.70
32.89
21.67
21.51
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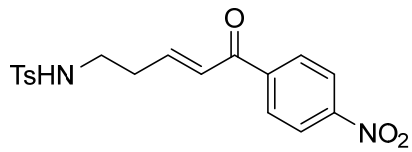
f1 (ppm)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O
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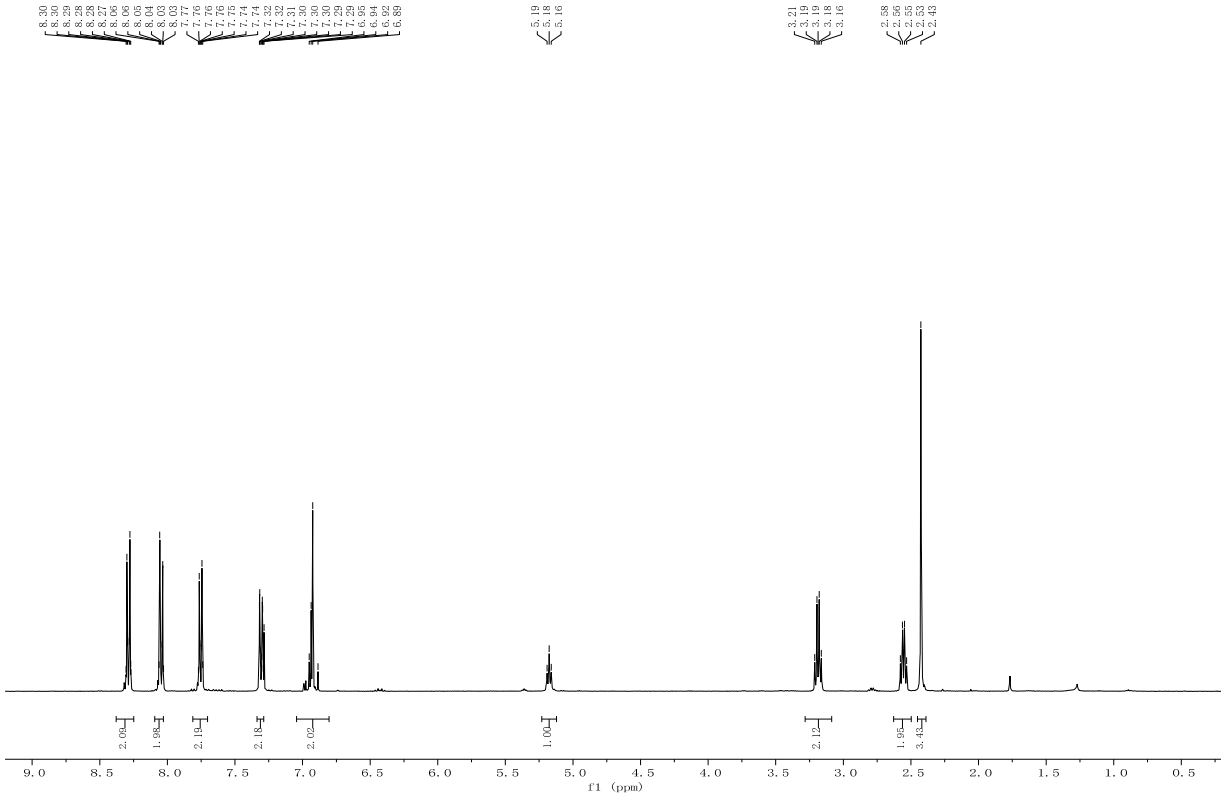
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8.06
8.05
8.04
8.03
8.03
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7.76
7.76
7.76
7.75
7.74
7.74
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.29
6.95
6.94
6.92
6.89
5.19
5.18
5.16
3.21
3.19
3.19
3.18
3.16
2.58
2.56
2.55
2.53
2.43
2.09
1.98
2.19
2.18
2.02
1.00
2.12
1.95
3.43
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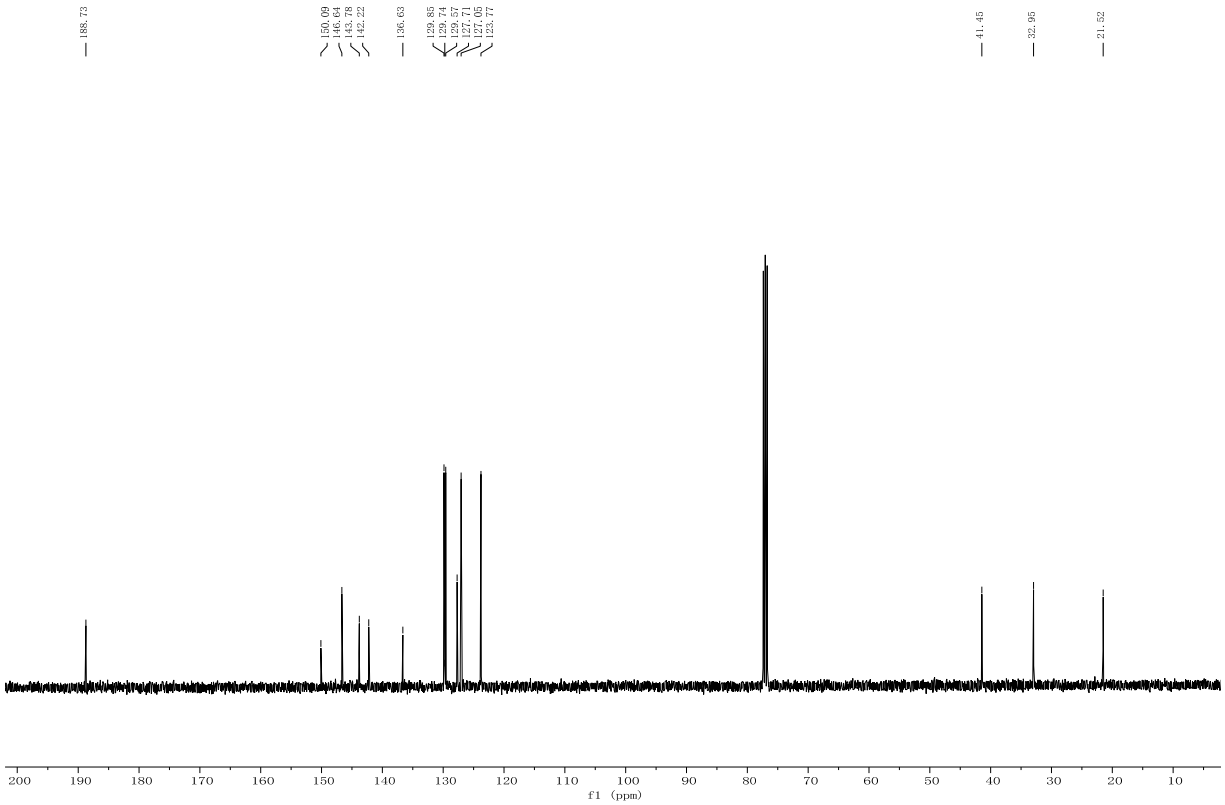
f1 (ppm)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129.74
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123.77
41.45
32.95
21.52
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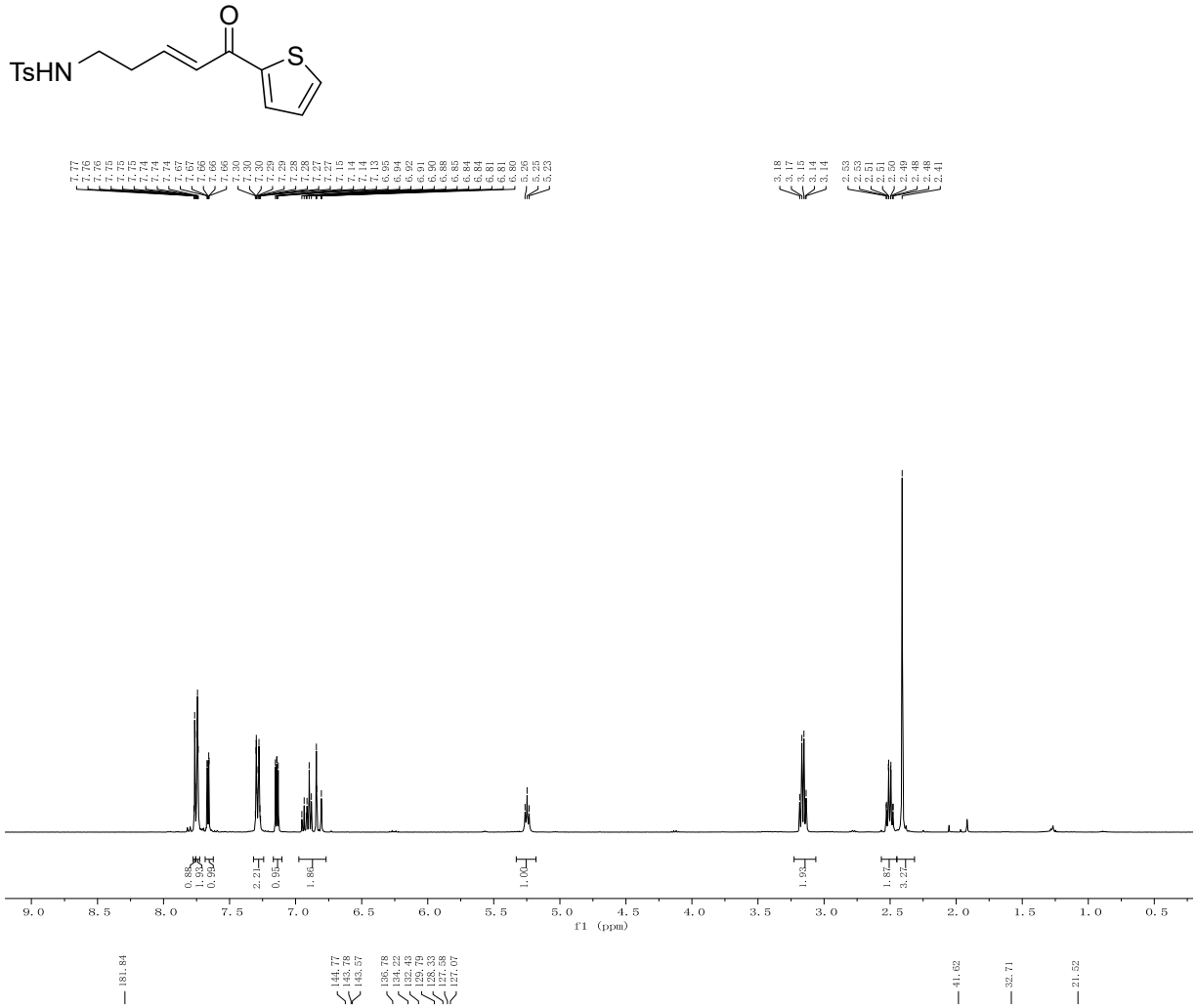
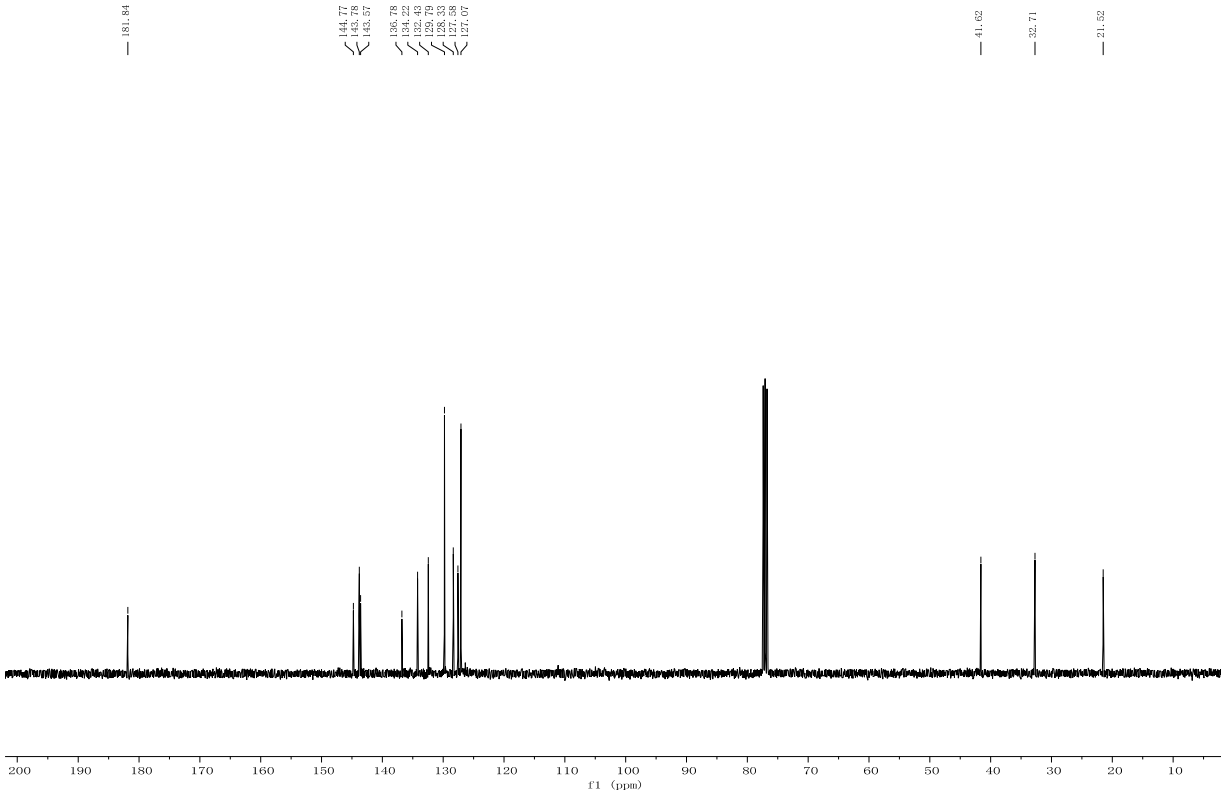
f1 (ppm)


TsHN
O
S
f1 (ppm)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41.62
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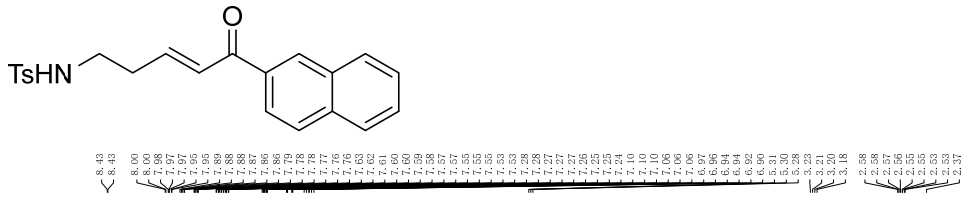
21.52
f1 (ppm)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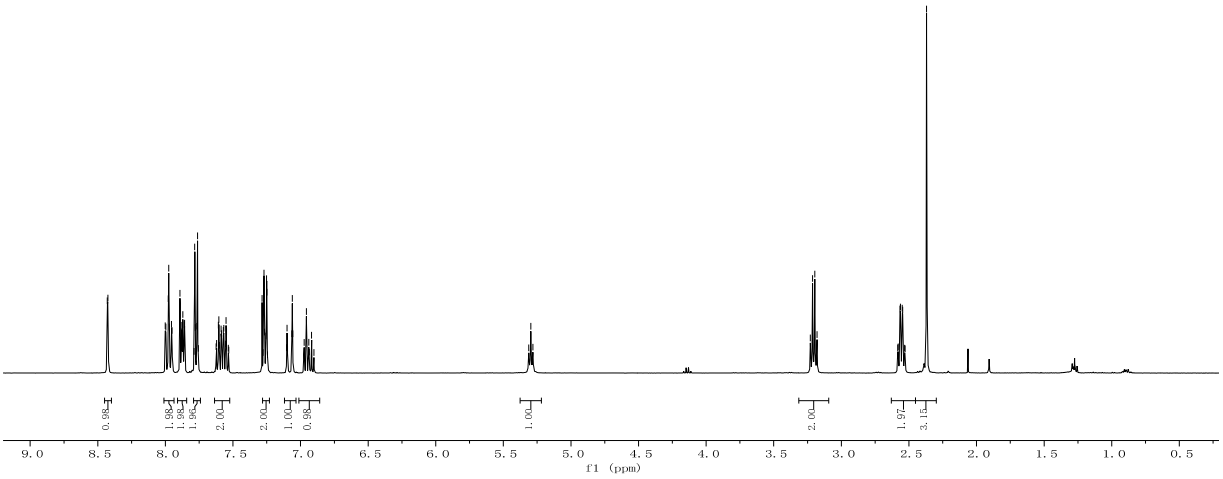
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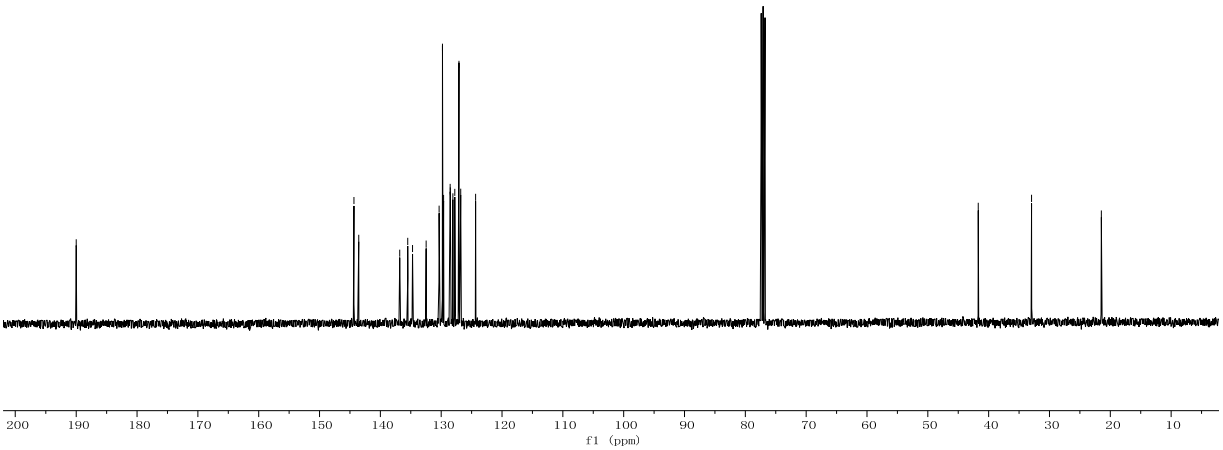
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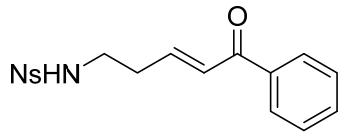
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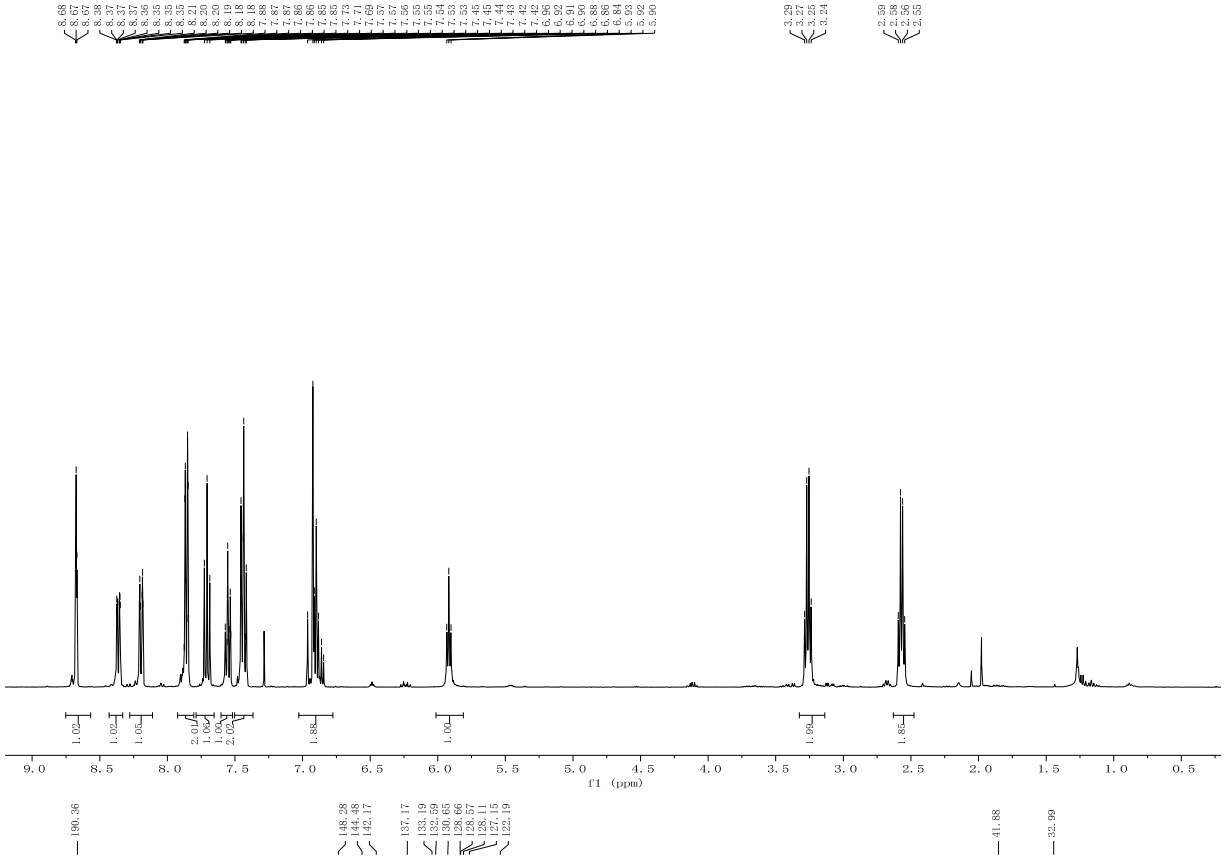
NsHN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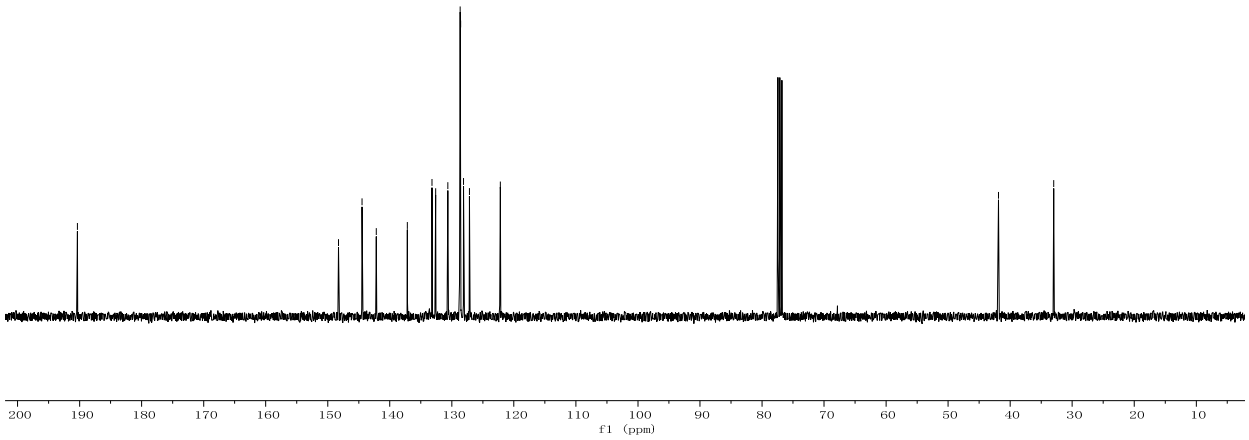
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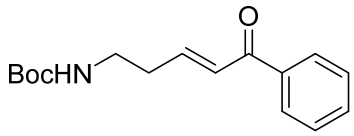
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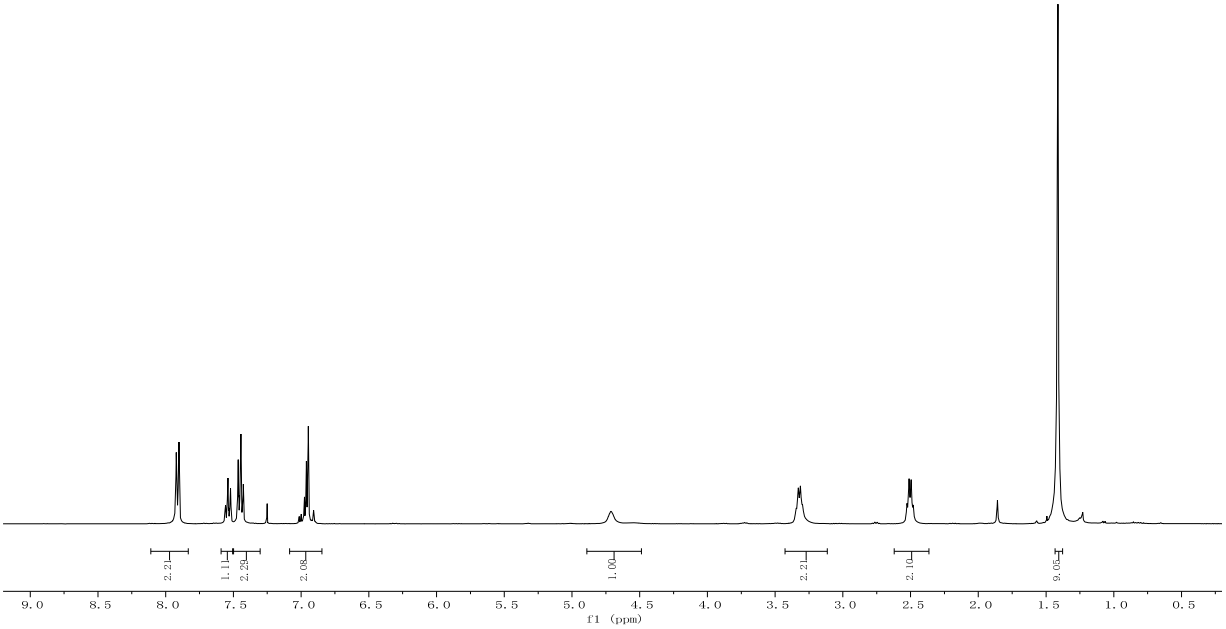
BocHN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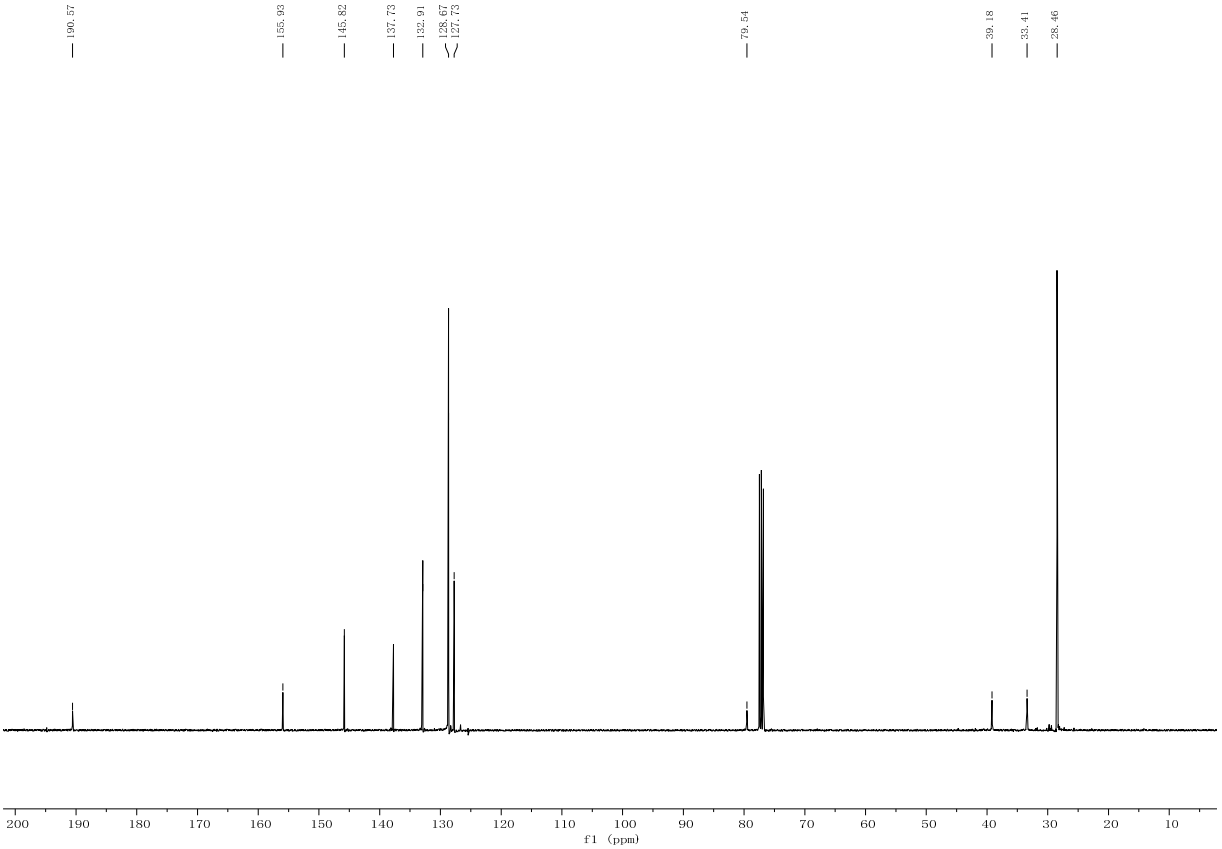
1.11
2.29
2.08
1.00
2.21
2.10
9.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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132.91
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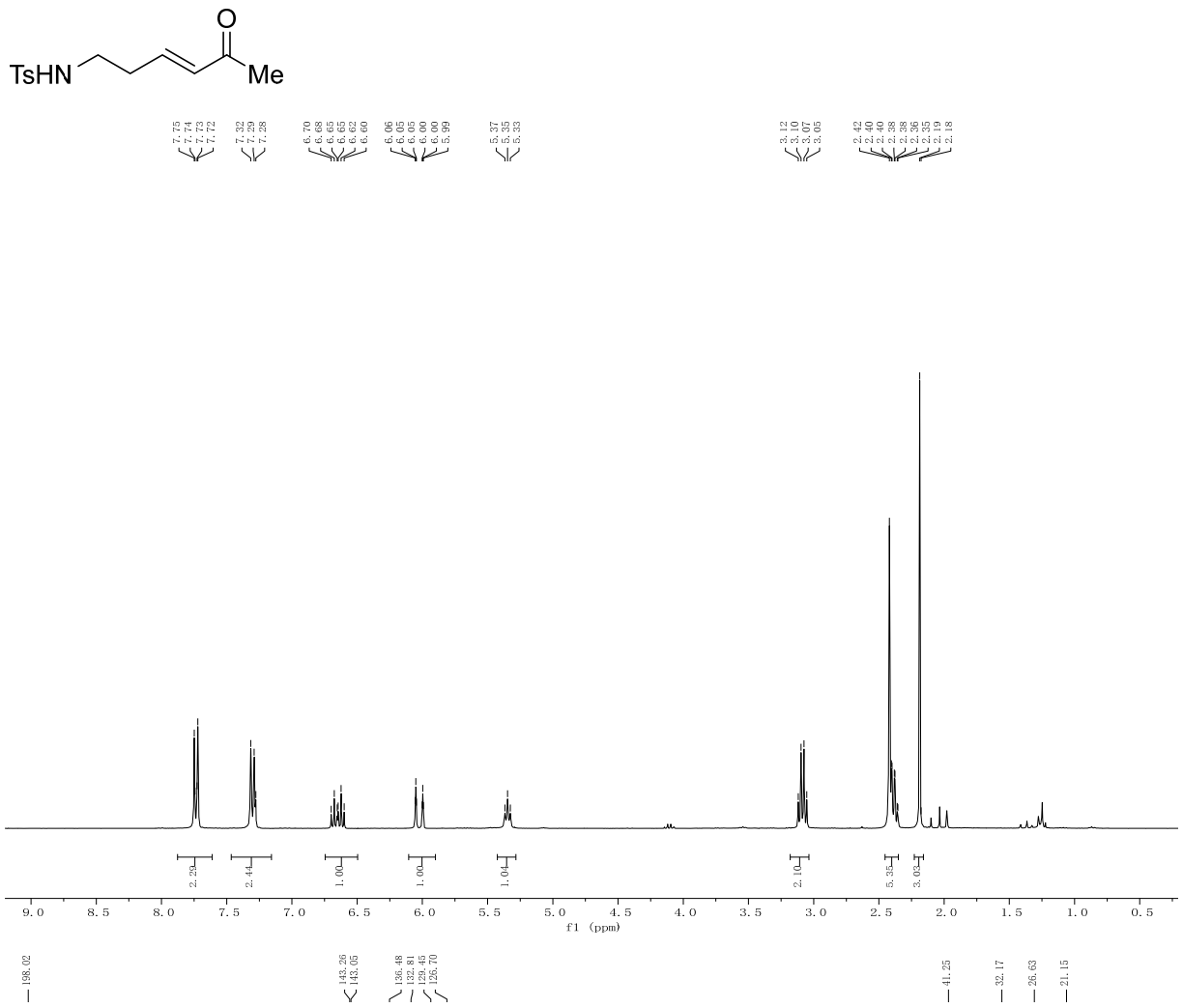
79.54
39.18
33.41
28.46
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


TsHN
O
Me
7.75 7.74 7.73 7.72
7.32 7.29 7.28
6.70 6.68 6.65 6.63 6.62 6.60
6.06 6.05 6.05 6.00 6.00 5.99
5.37 5.35 5.33
3.12 3.10 3.07 3.05
2.42 2.40 2.40 2.40 2.38 2.38 2.36 2.35 2.19 2.18
2.29
2.44
1.00
1.00
1.04
2.10
5.35
3.03
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
f1 (ppm)
198.02
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143.05
136.48
132.81
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41.25
32.17
26.63
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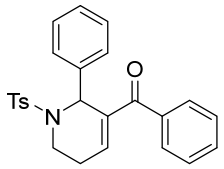
f1 (ppm)



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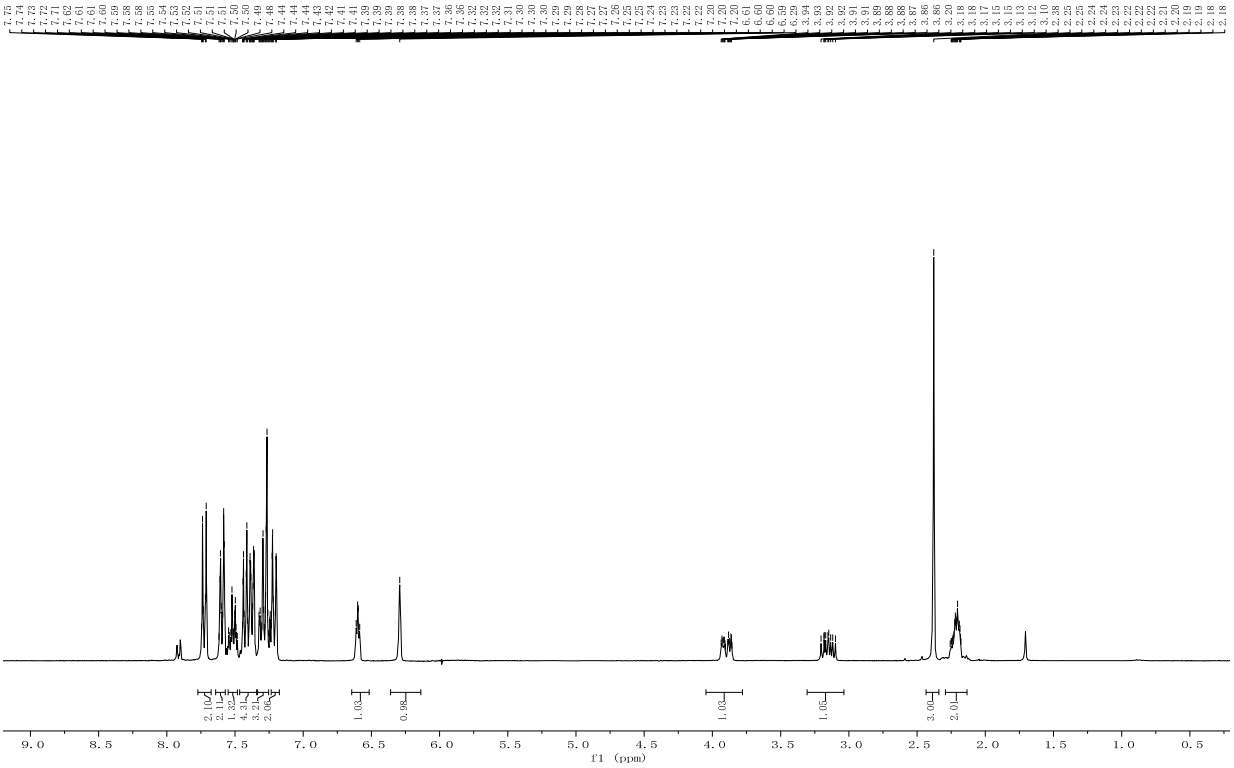

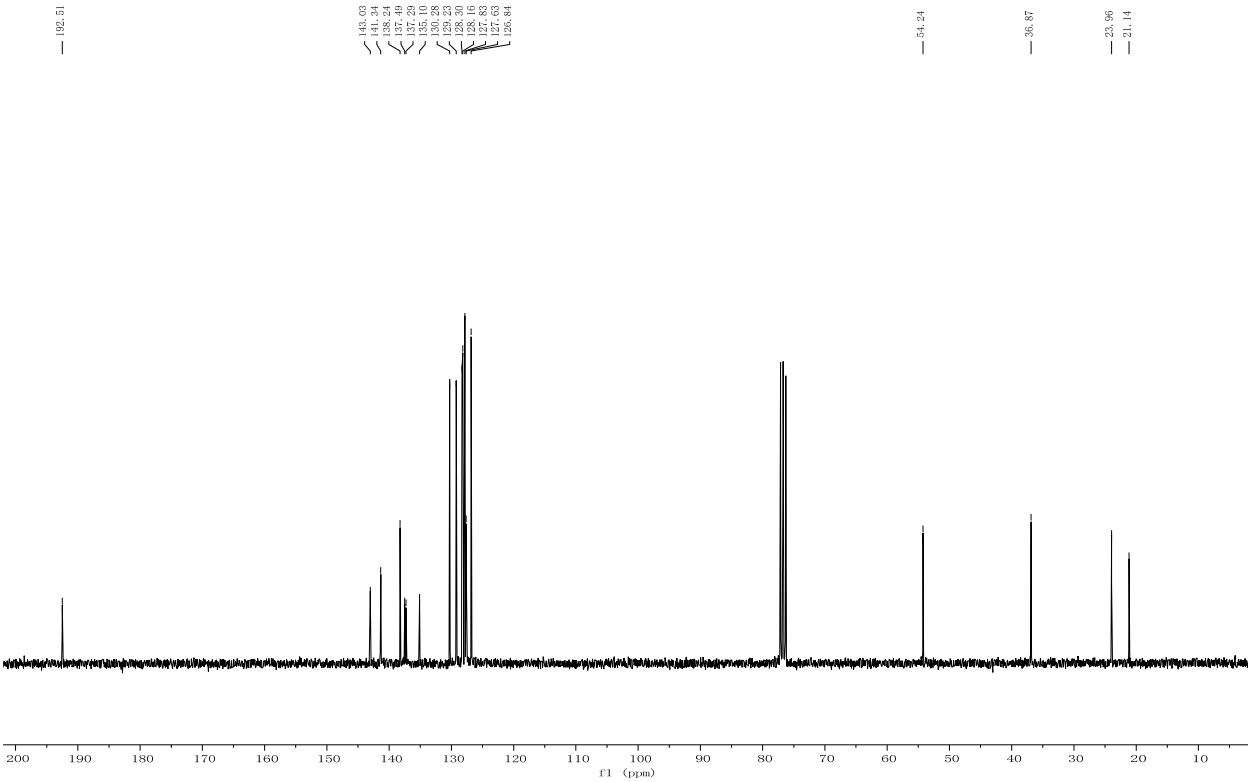

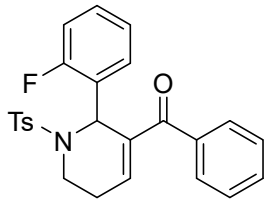

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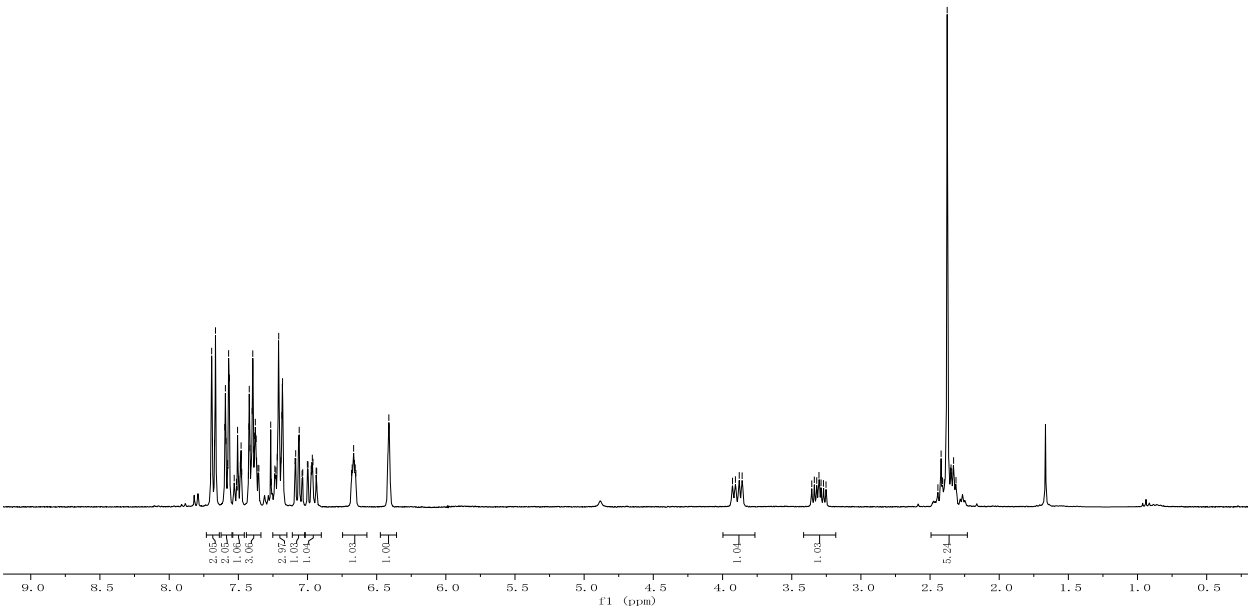

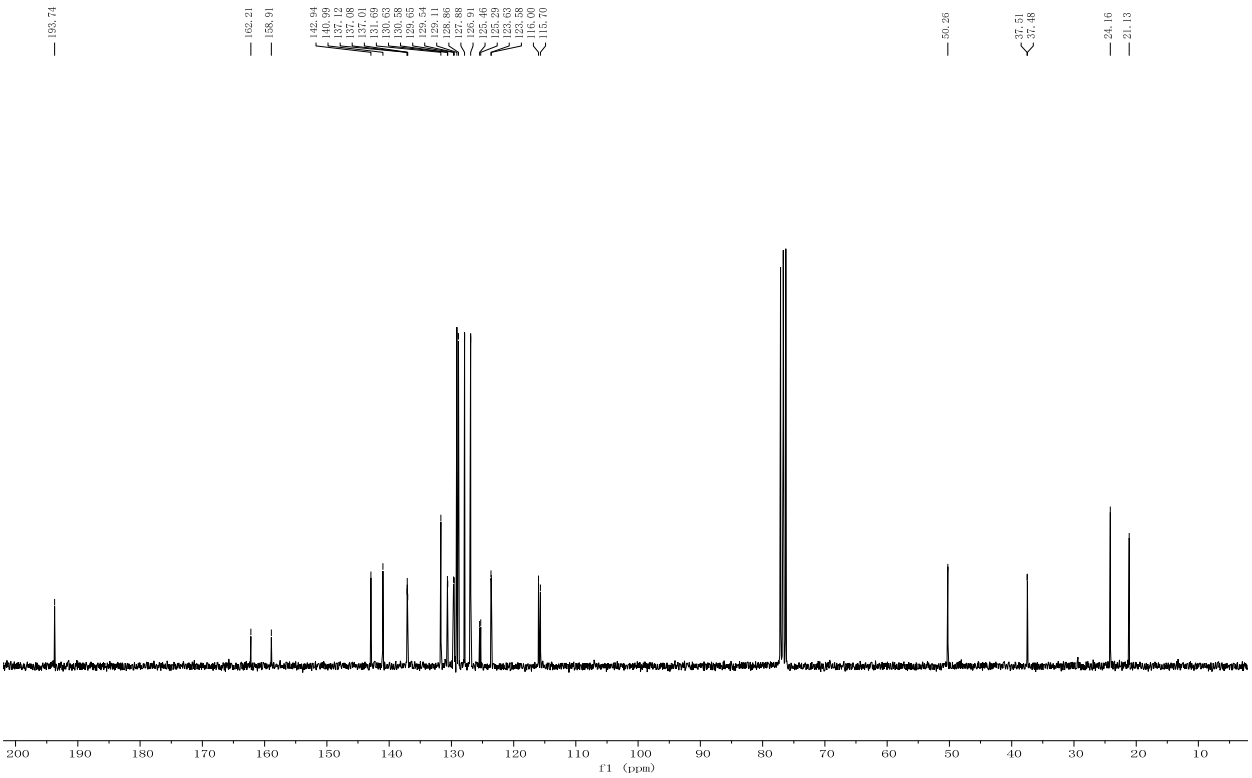

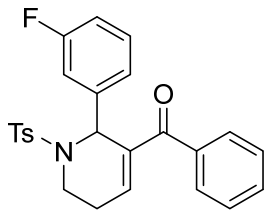

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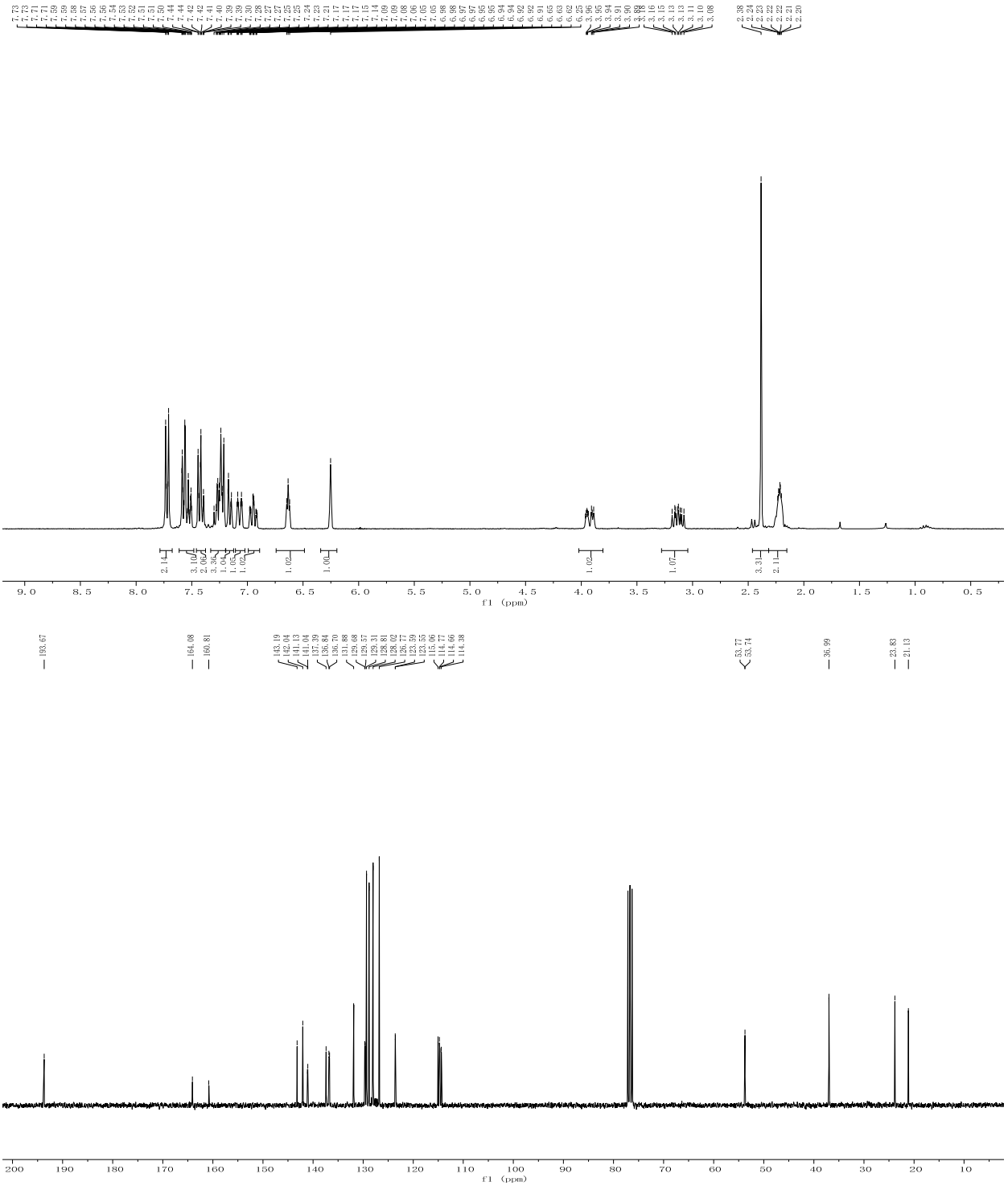

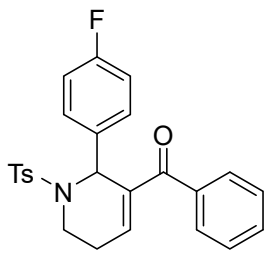

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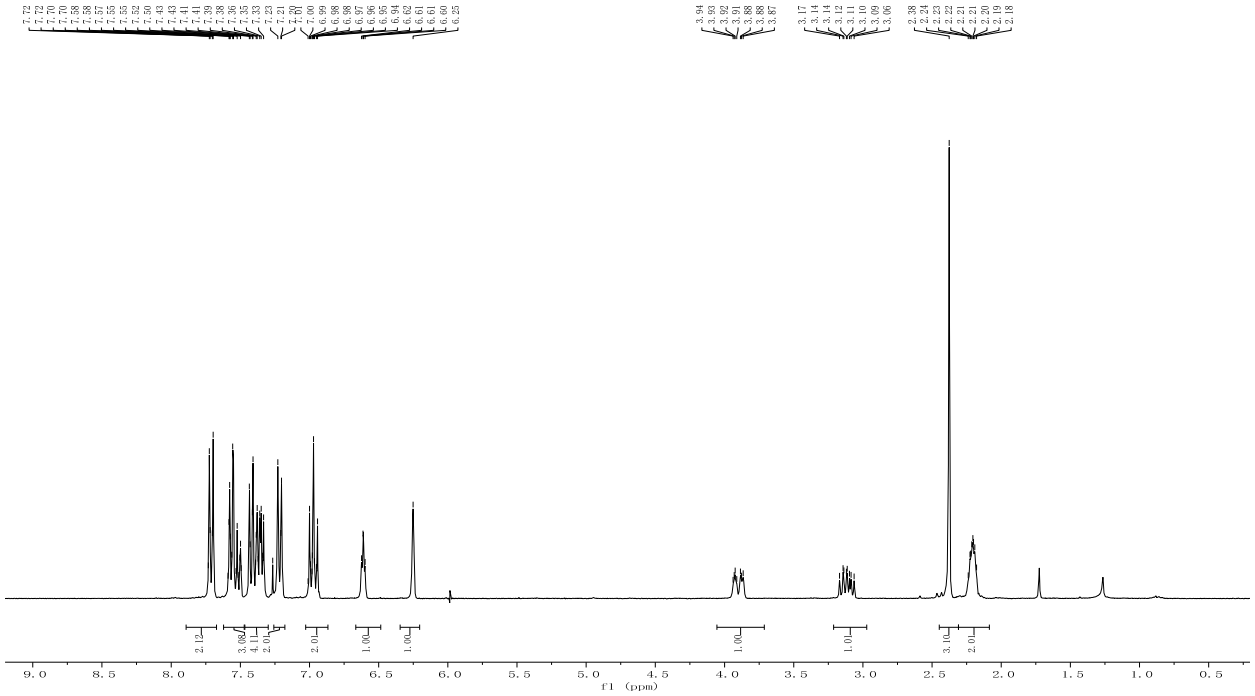

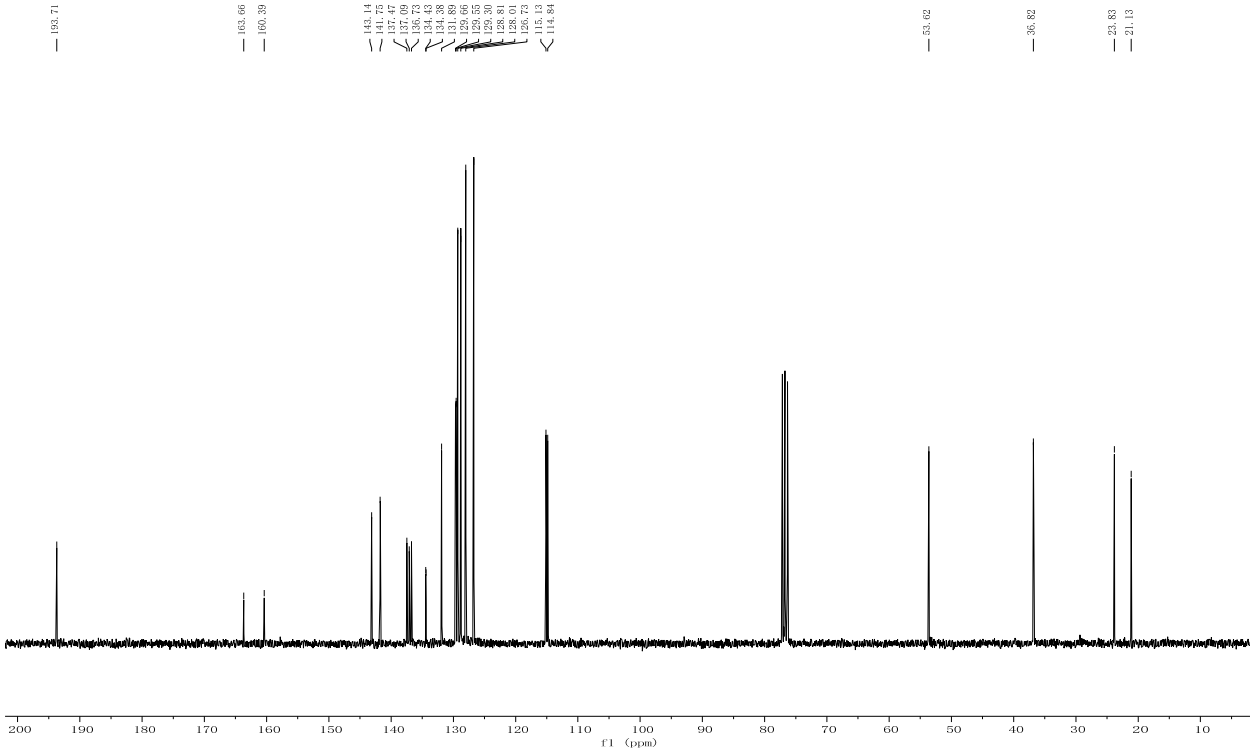

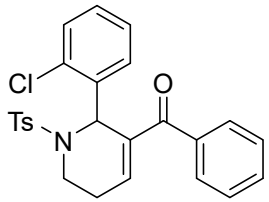

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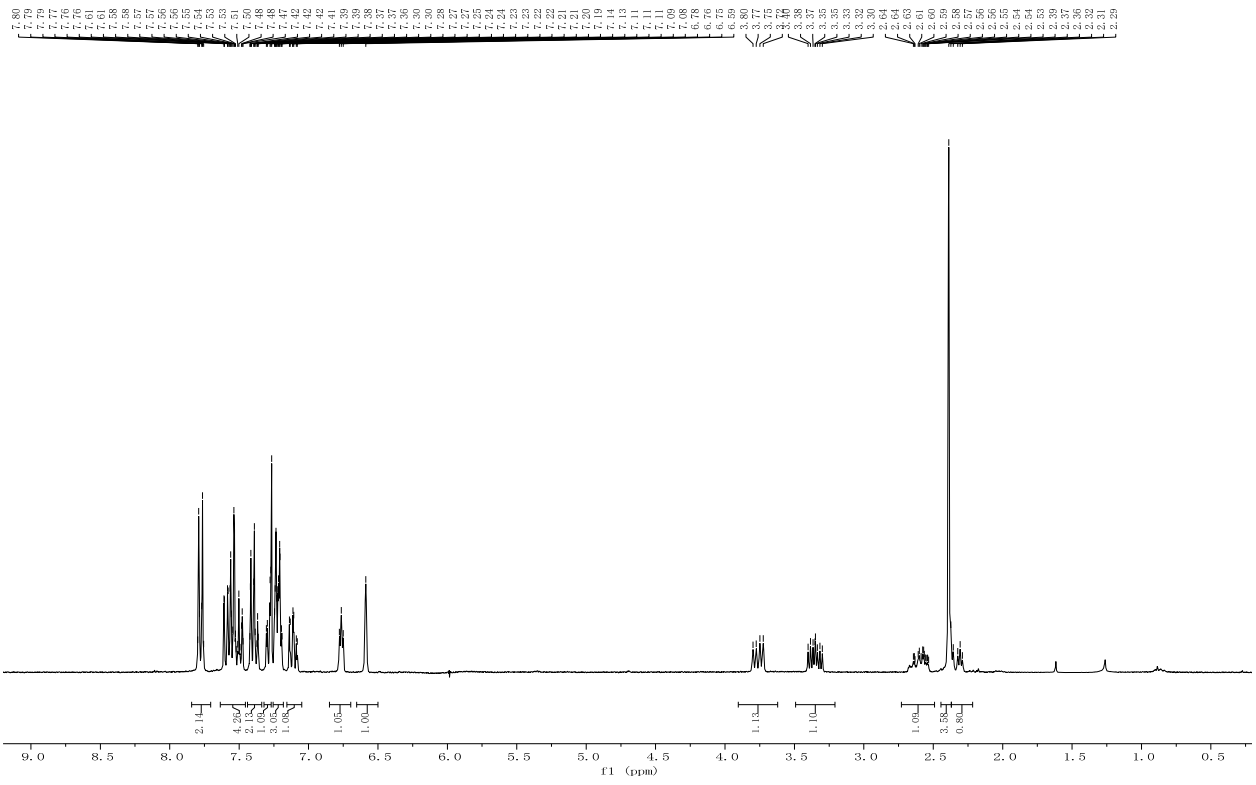

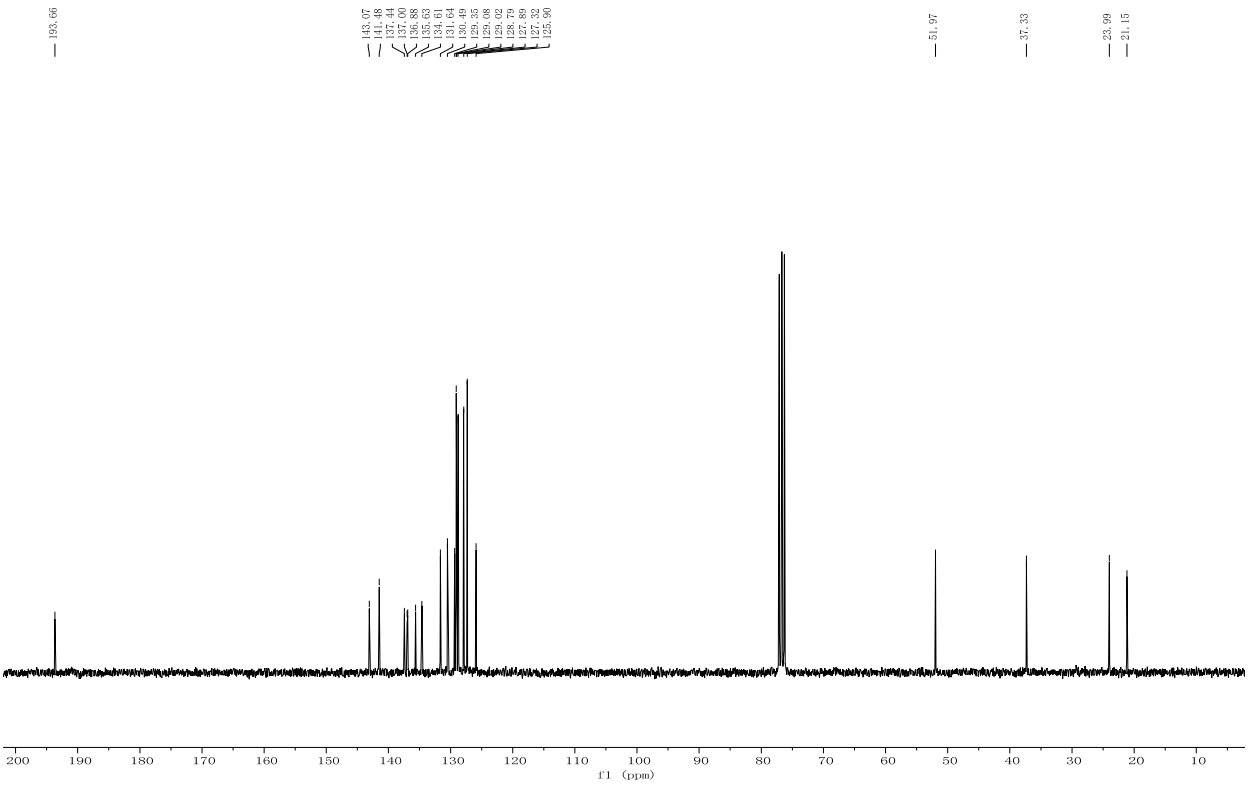

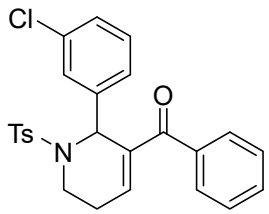

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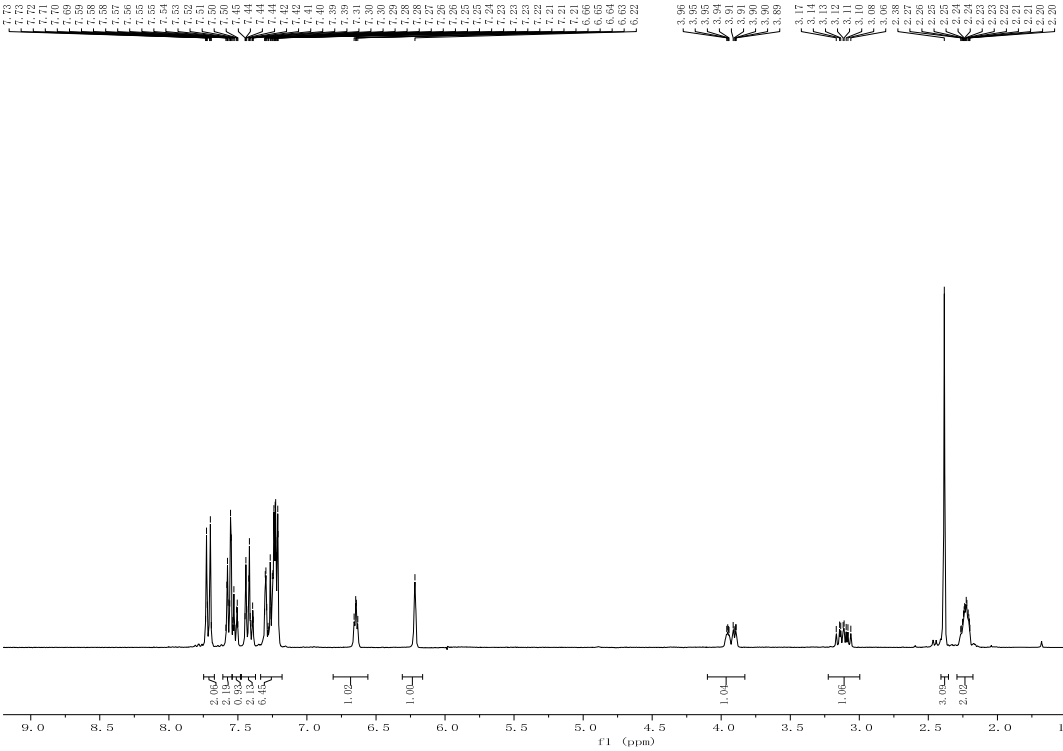

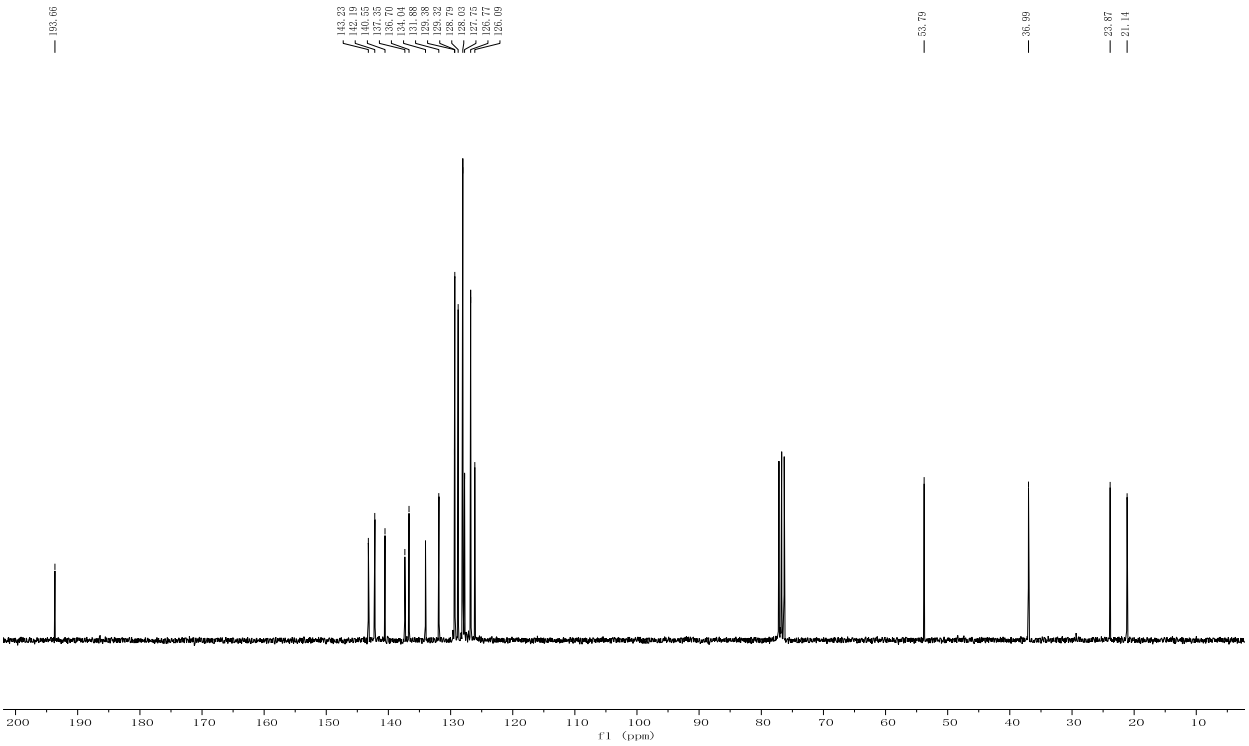

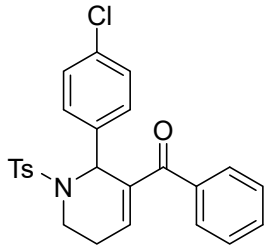

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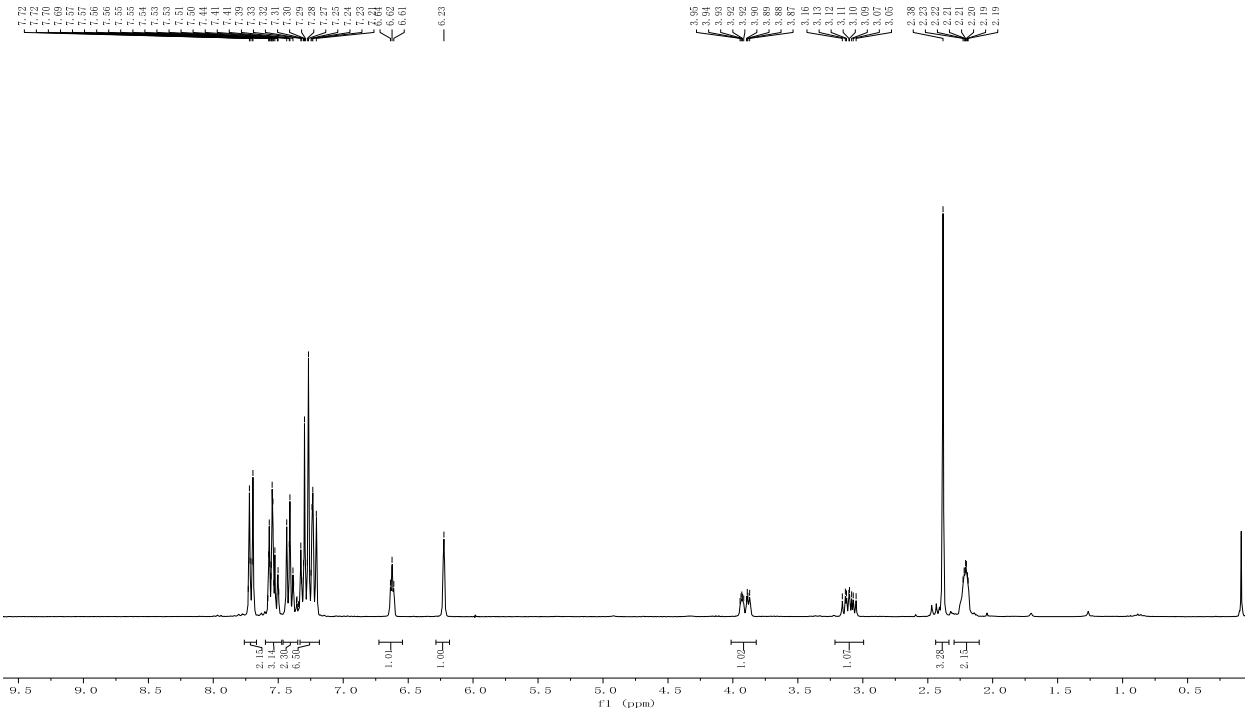
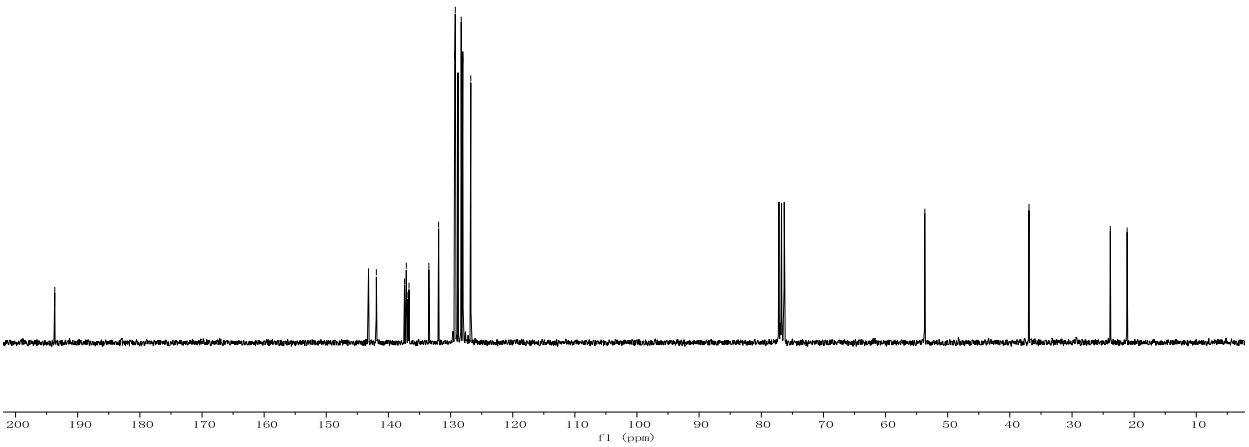
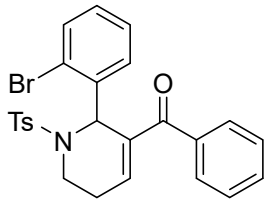
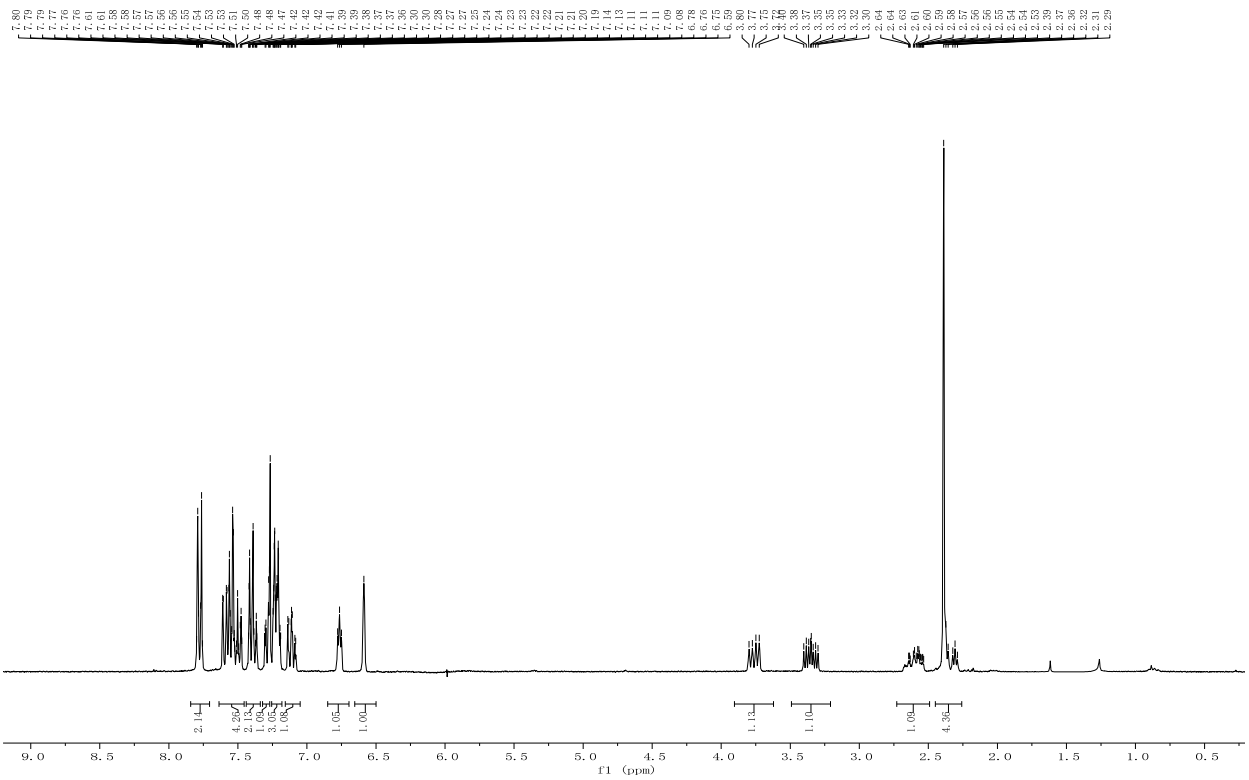
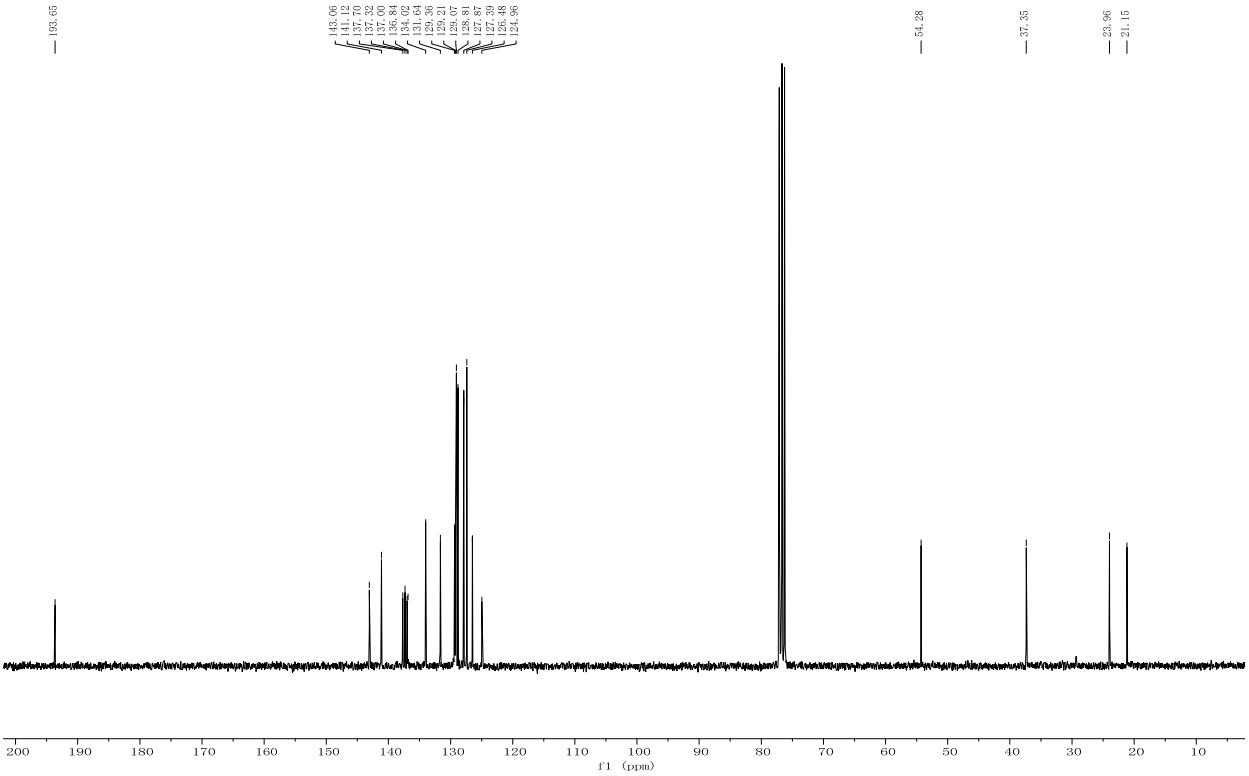





Br
O
Ts
N

3ah


f1 (ppm)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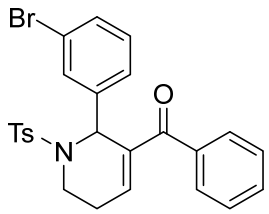
f1 (ppm)



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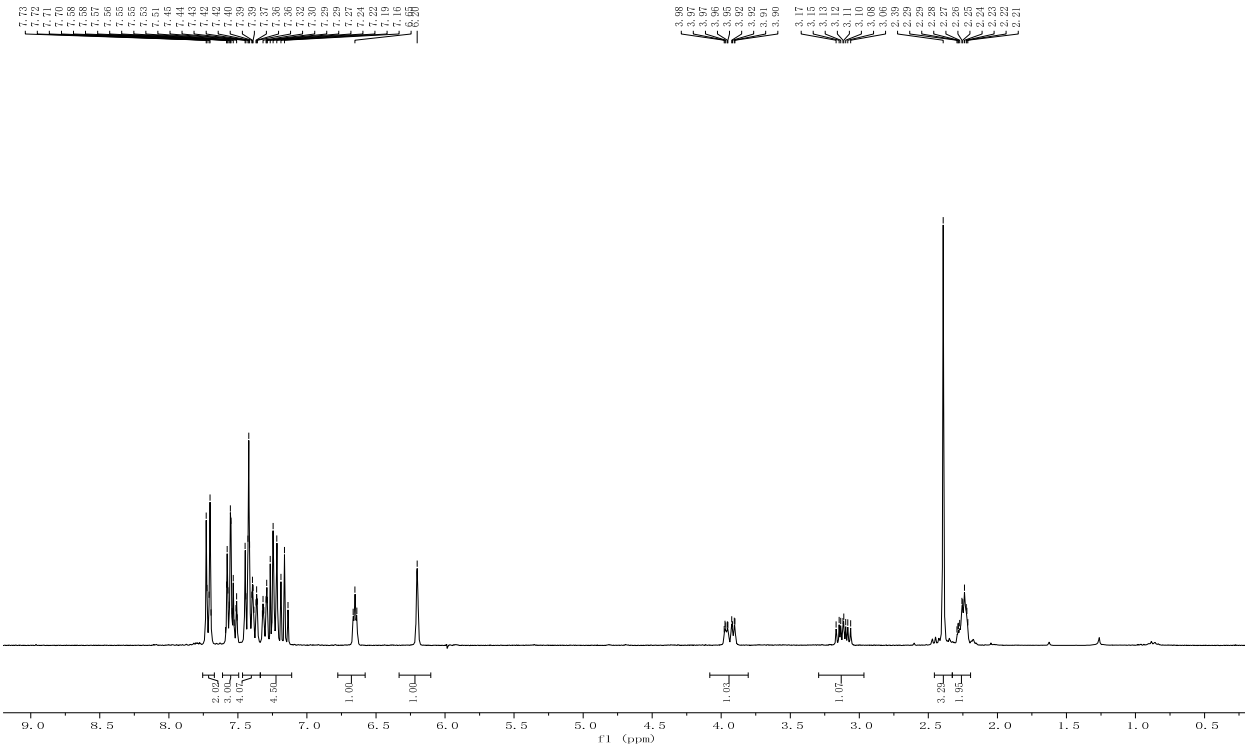
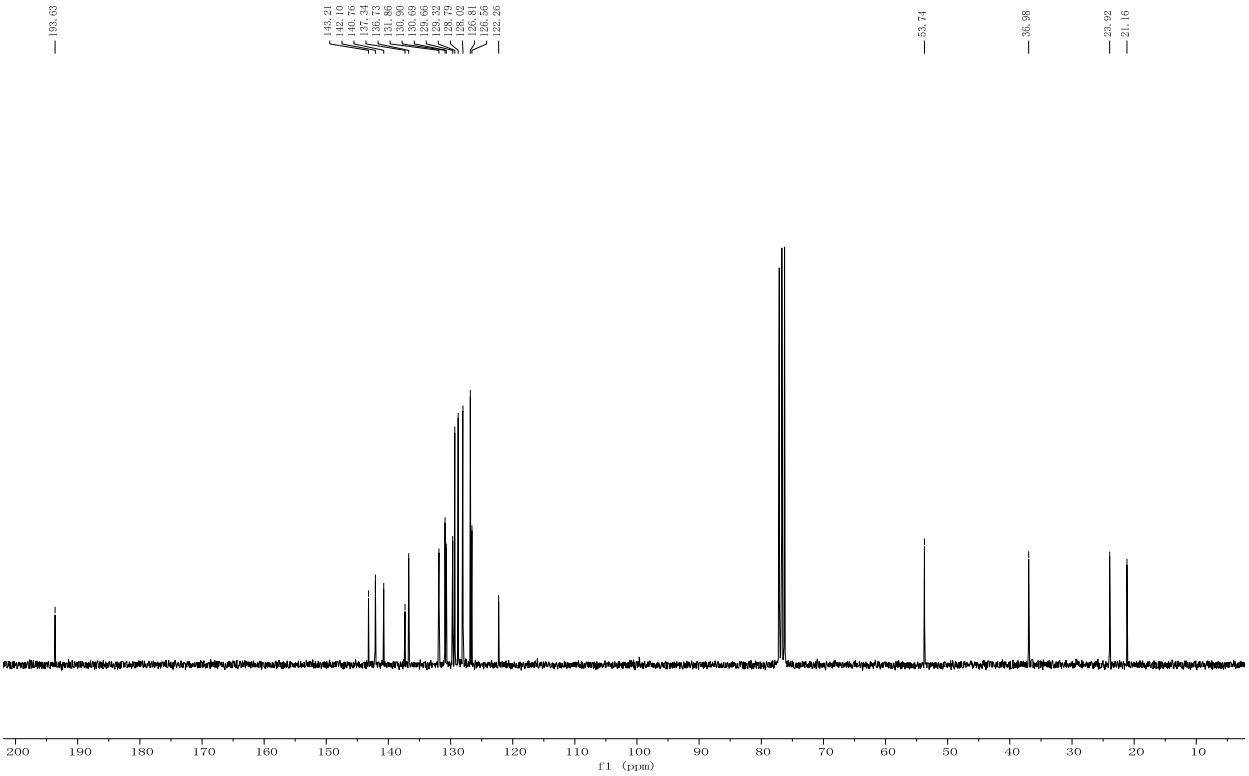
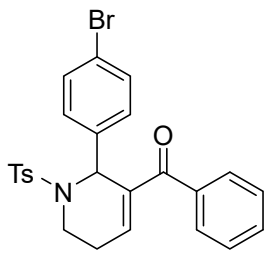
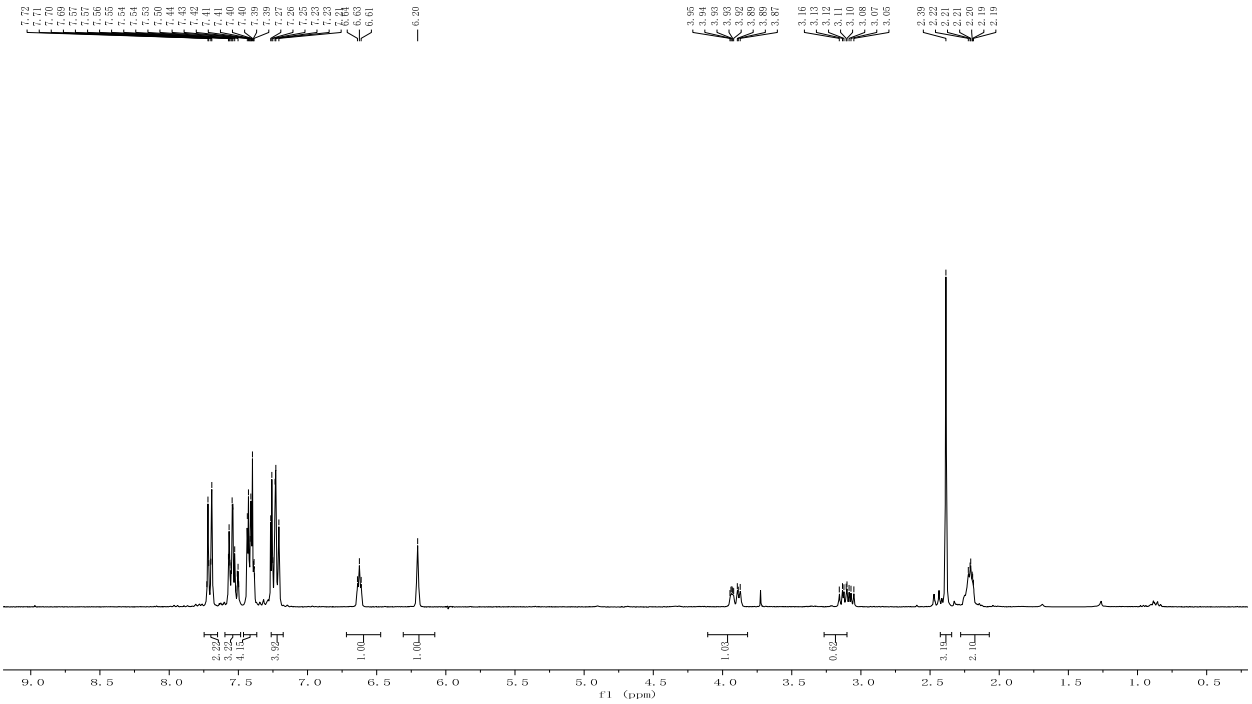
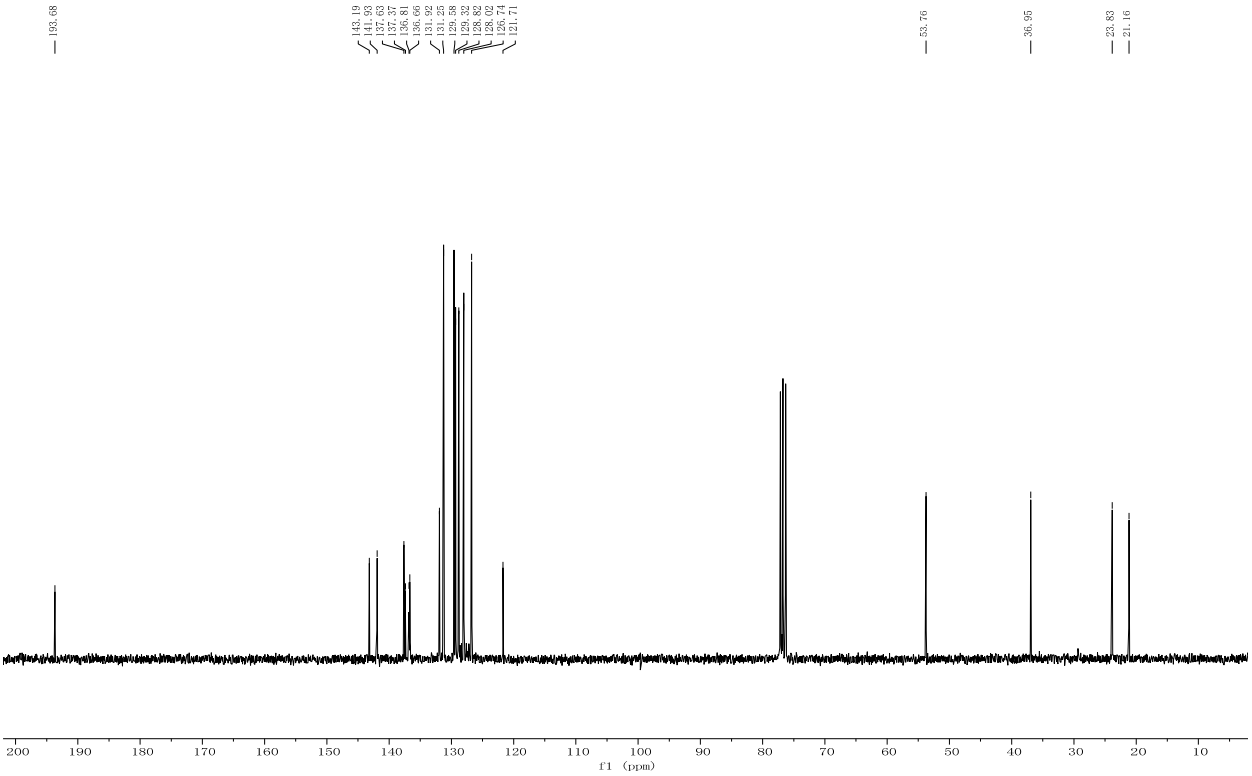


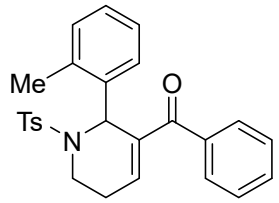




3aj







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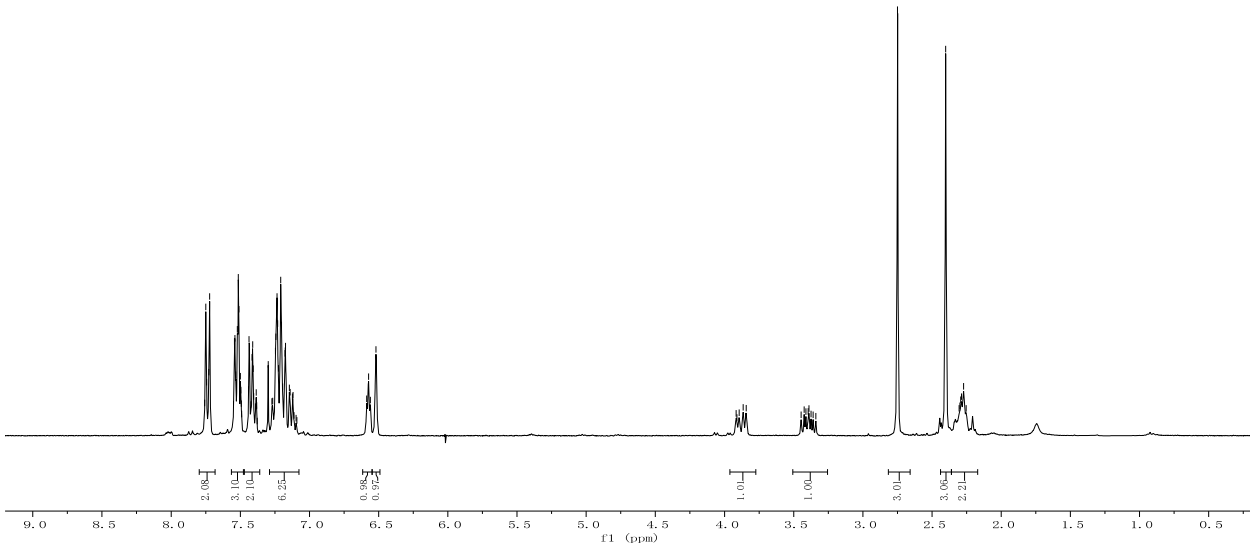

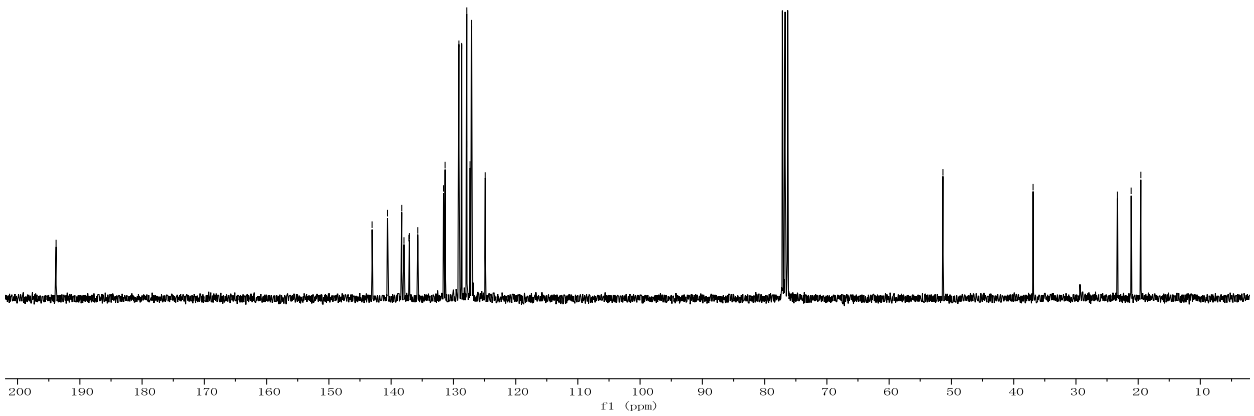

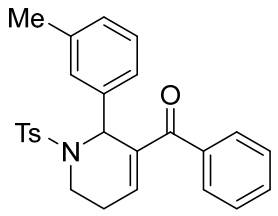
Me
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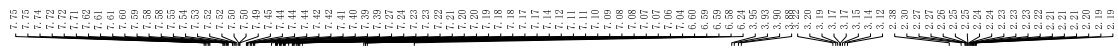
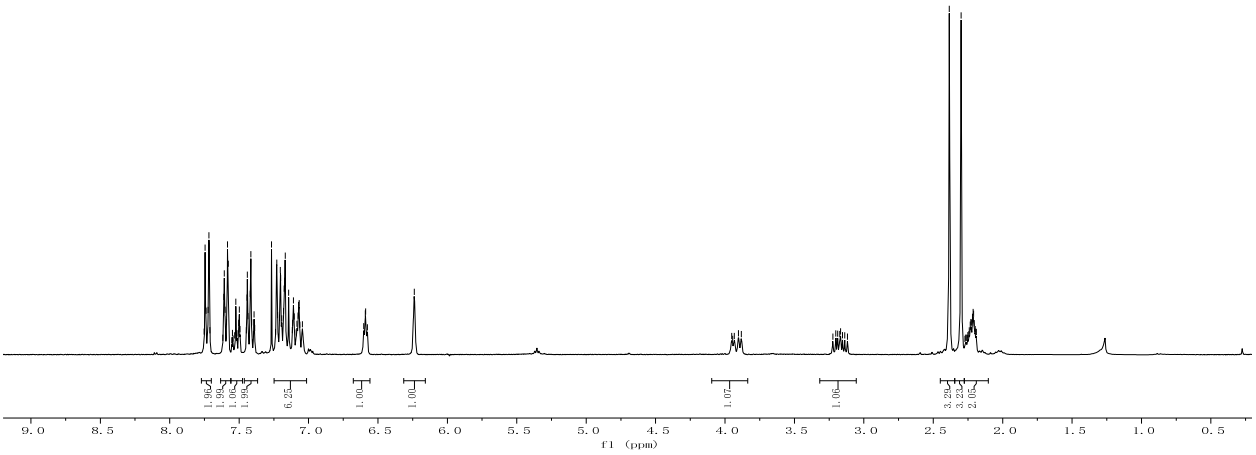
Ts
N

3al

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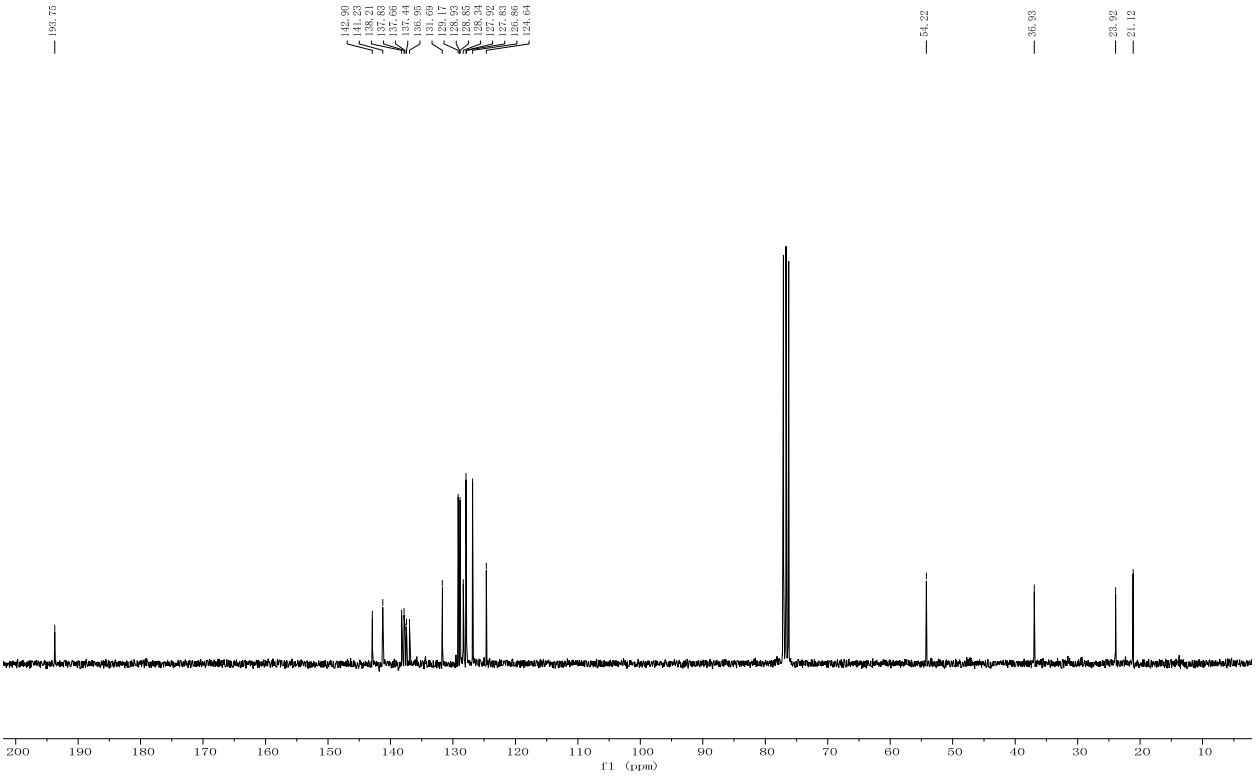
1.06
1.94
6.25
1.00
1.00
1.07
1.06
3.29
3.23
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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136.95
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128.85
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127.92
127.83
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54.22
36.93
23.92
21.12
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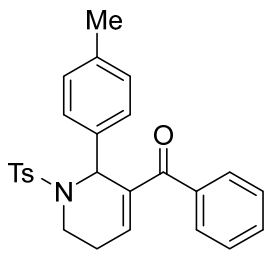
f1 (ppm)



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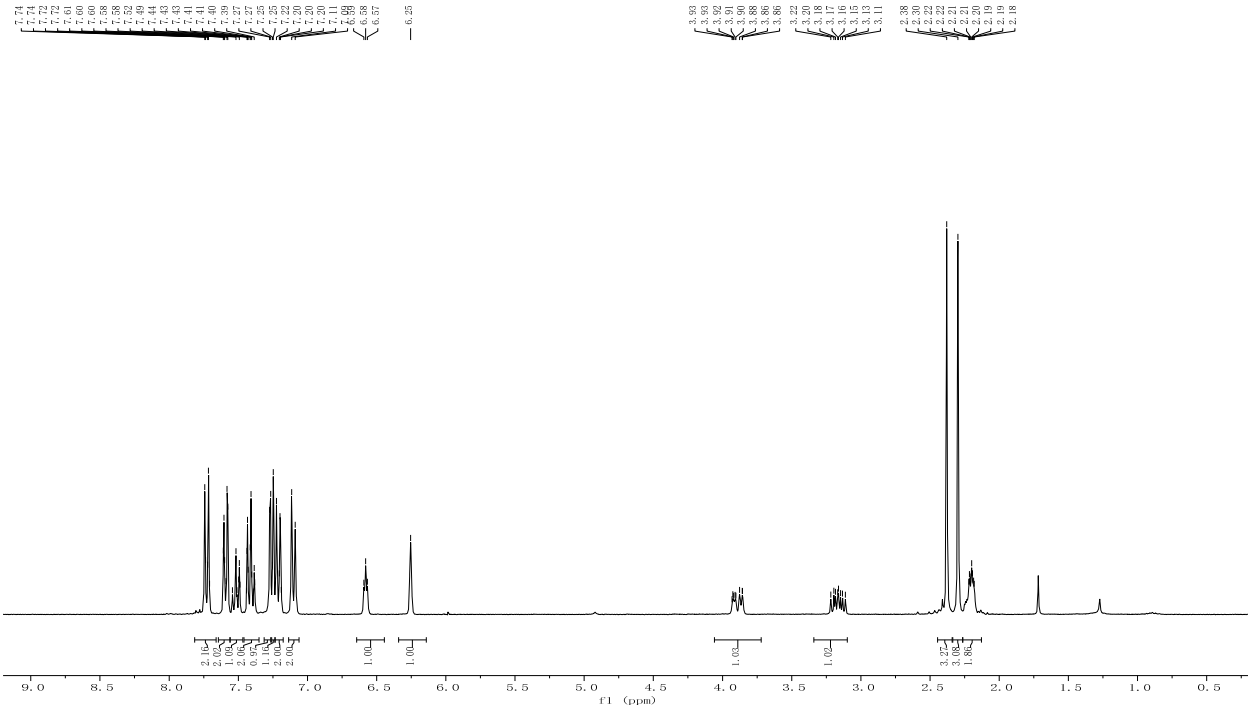

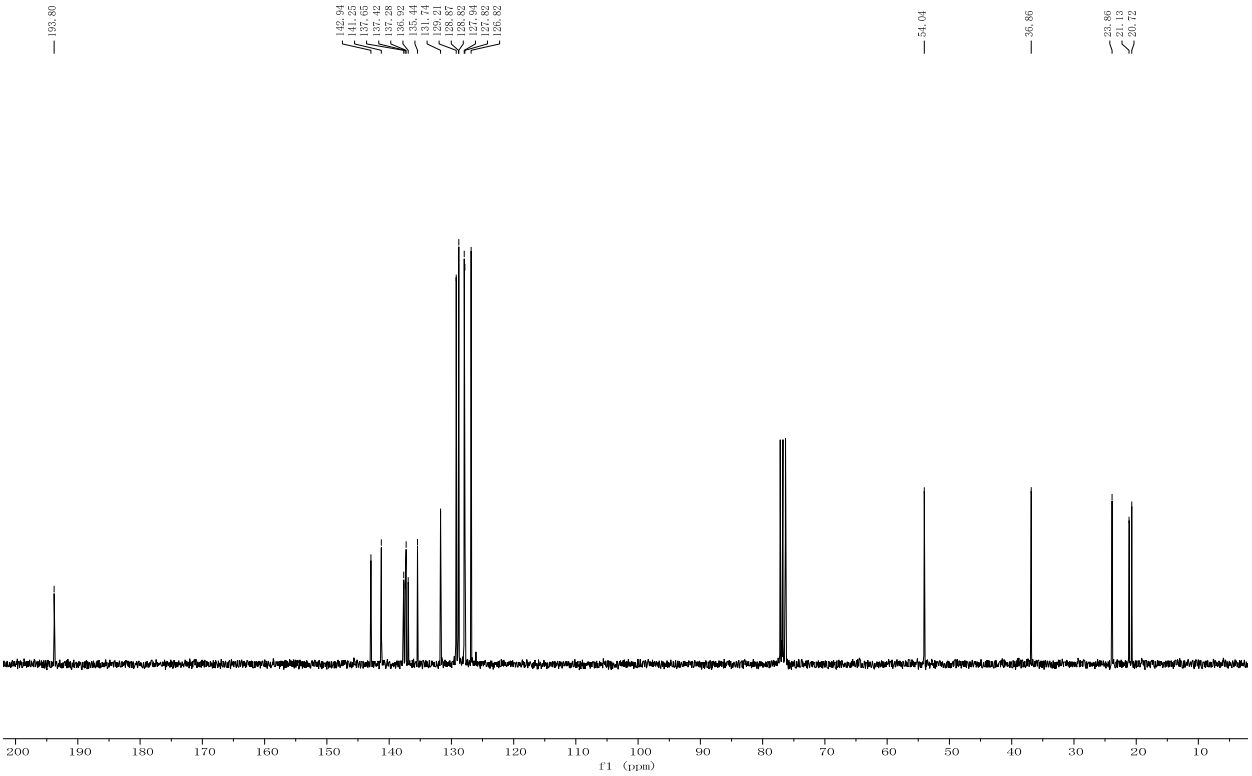

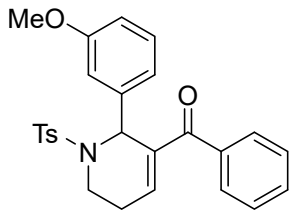

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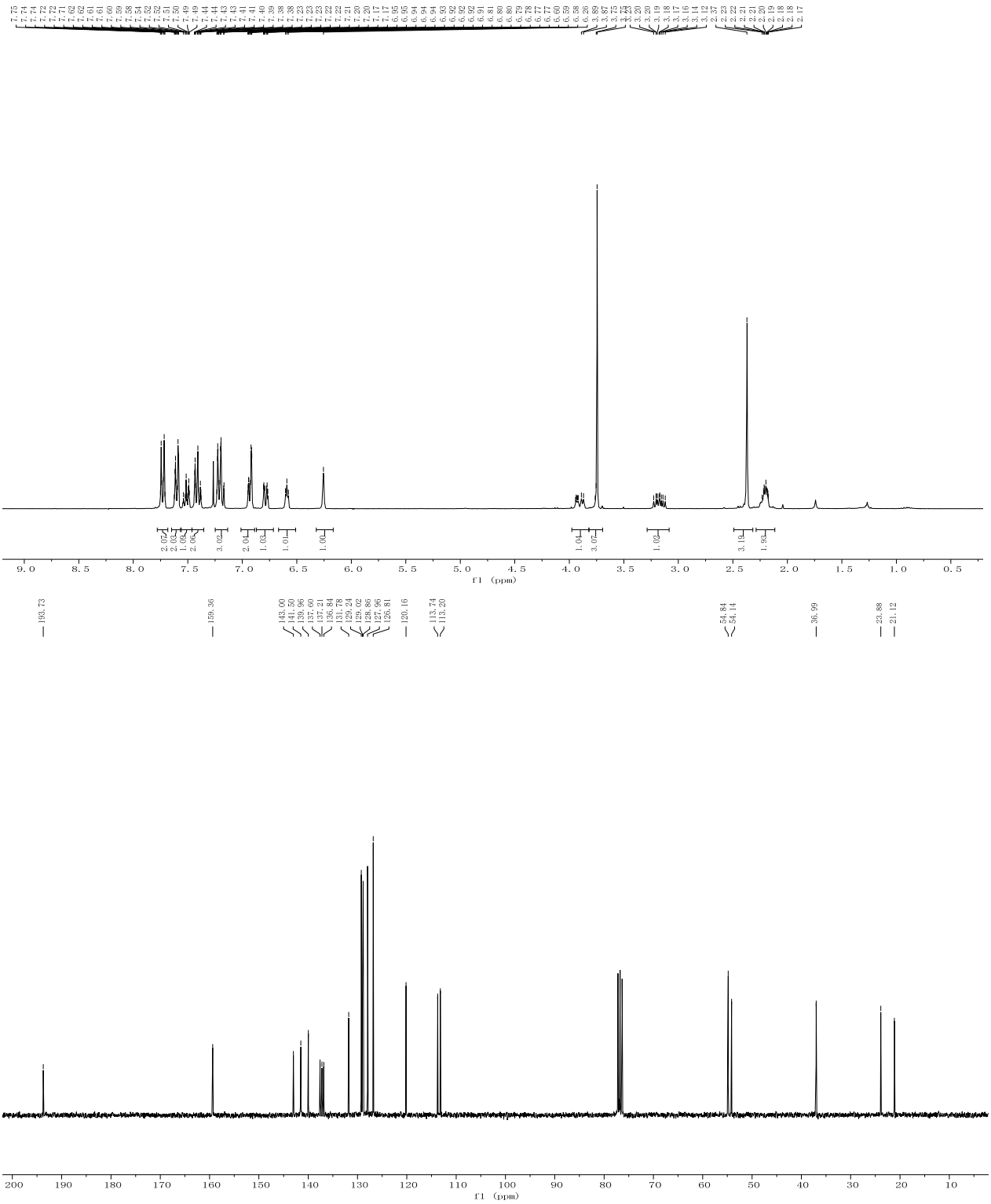

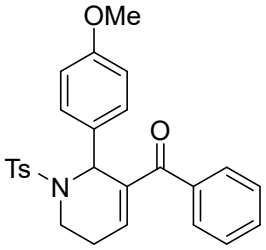

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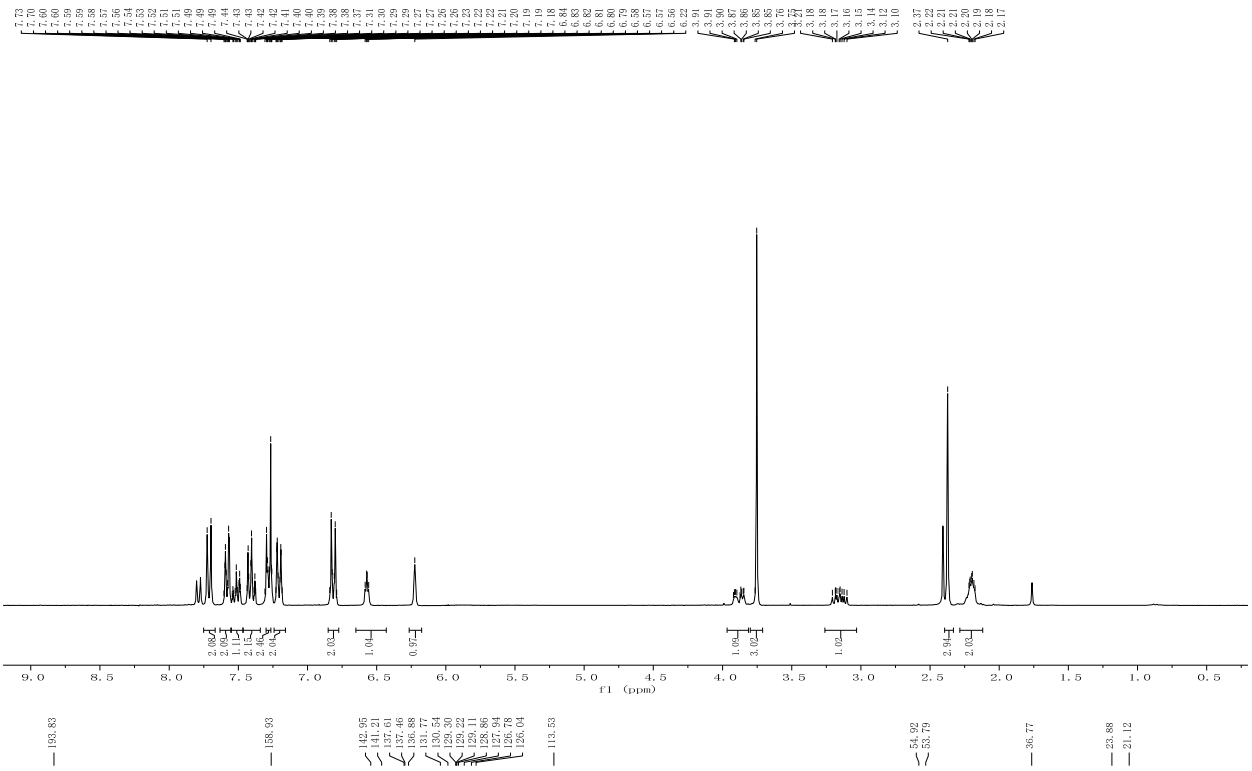

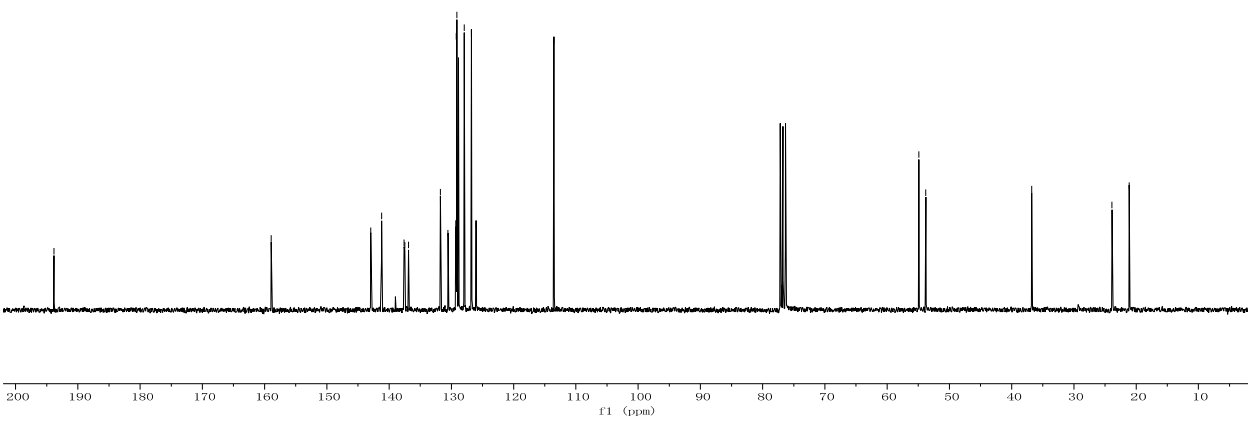

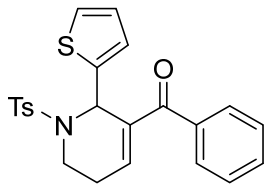

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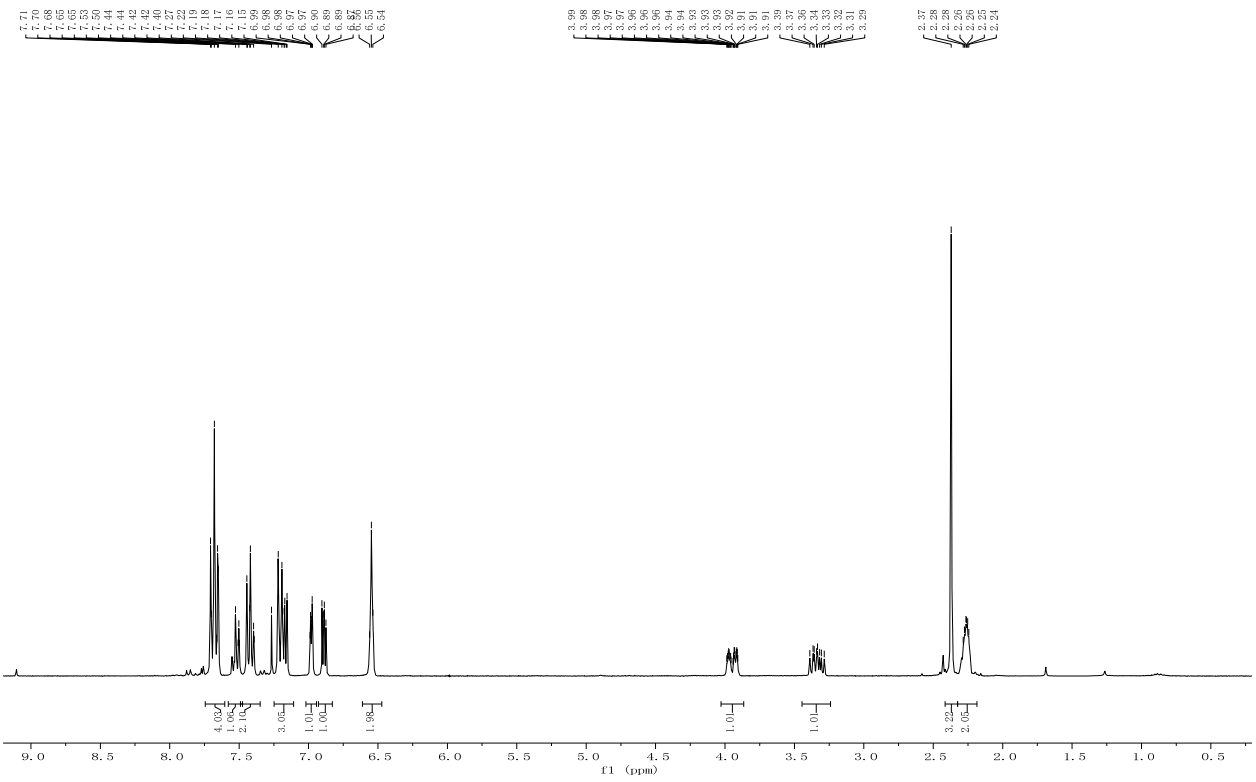

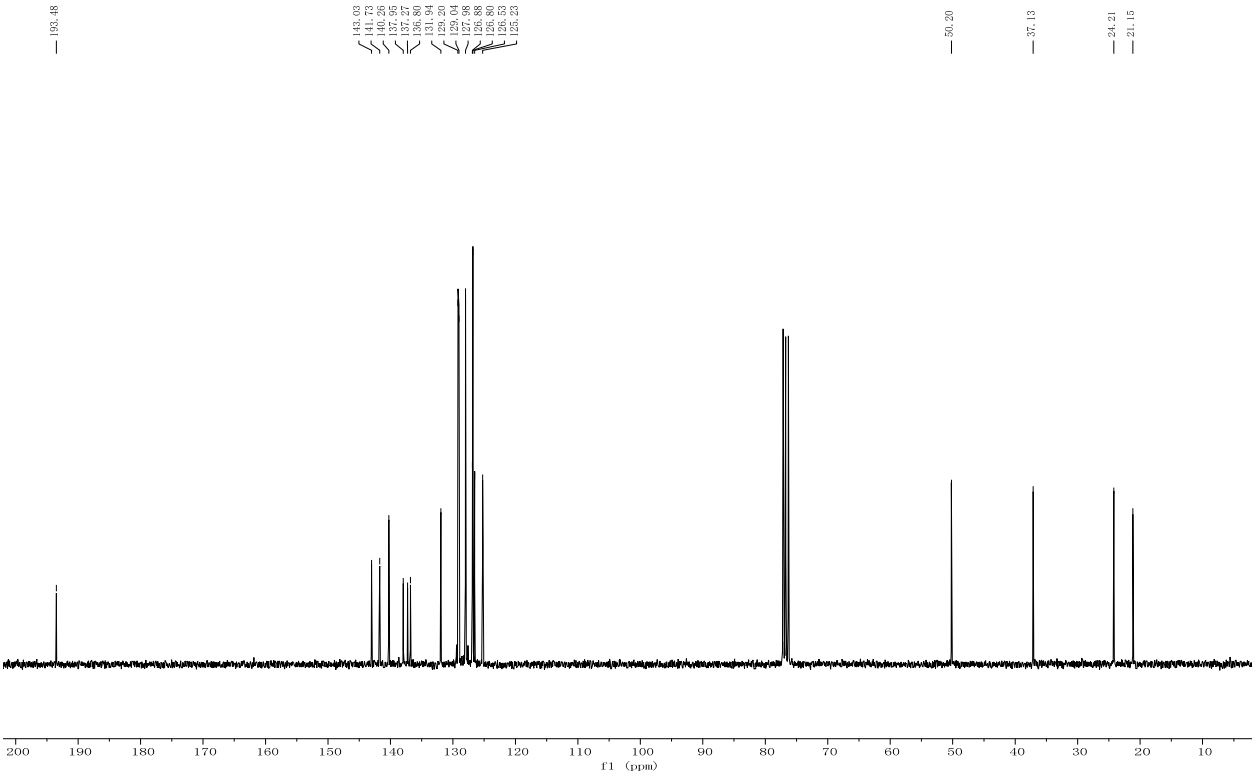

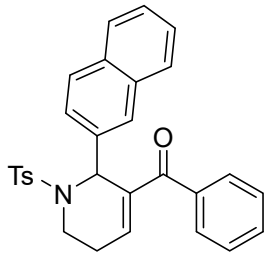

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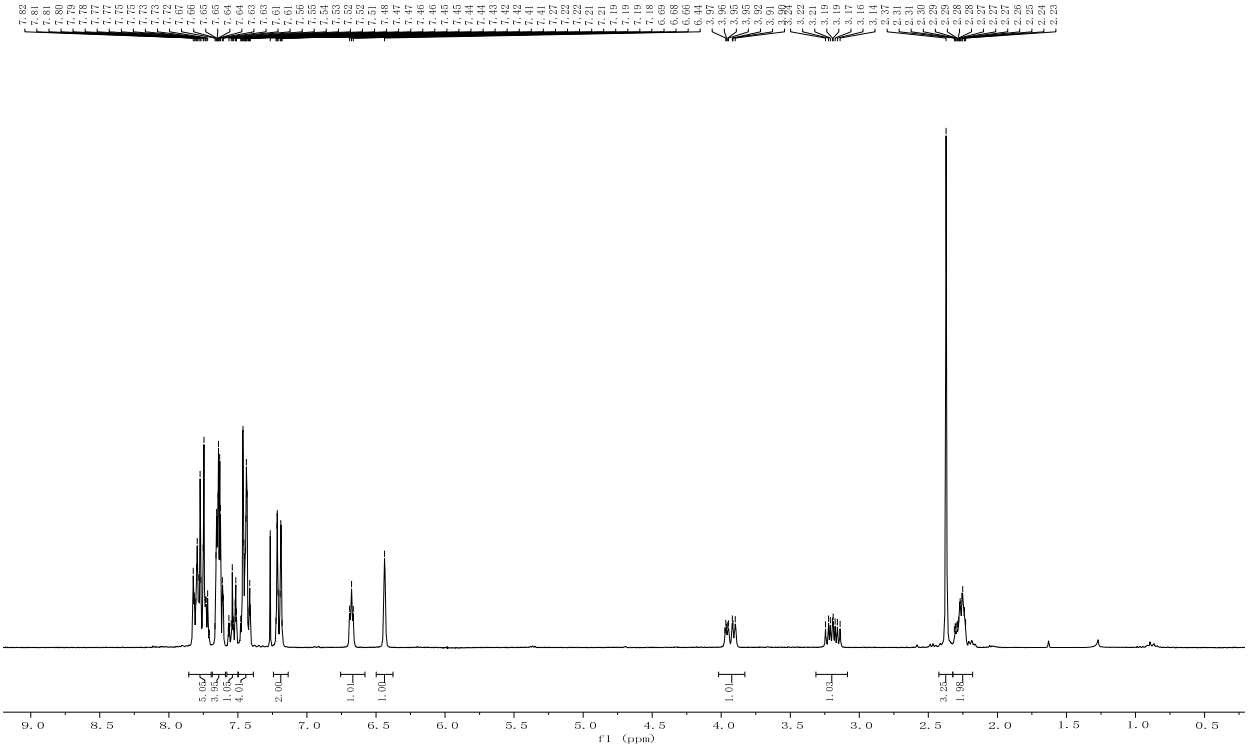

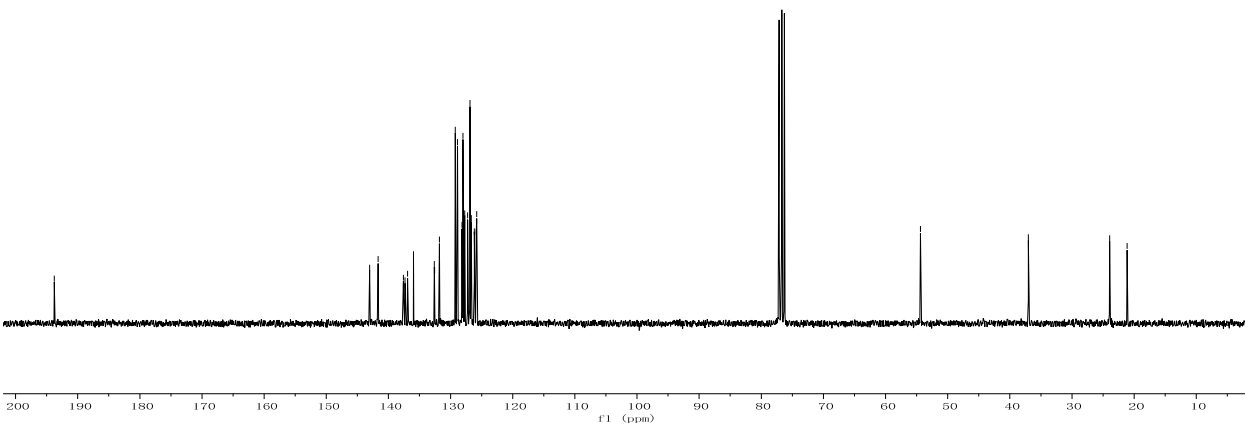

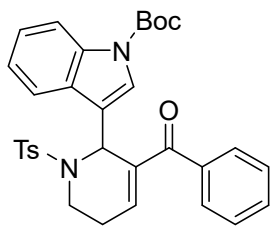

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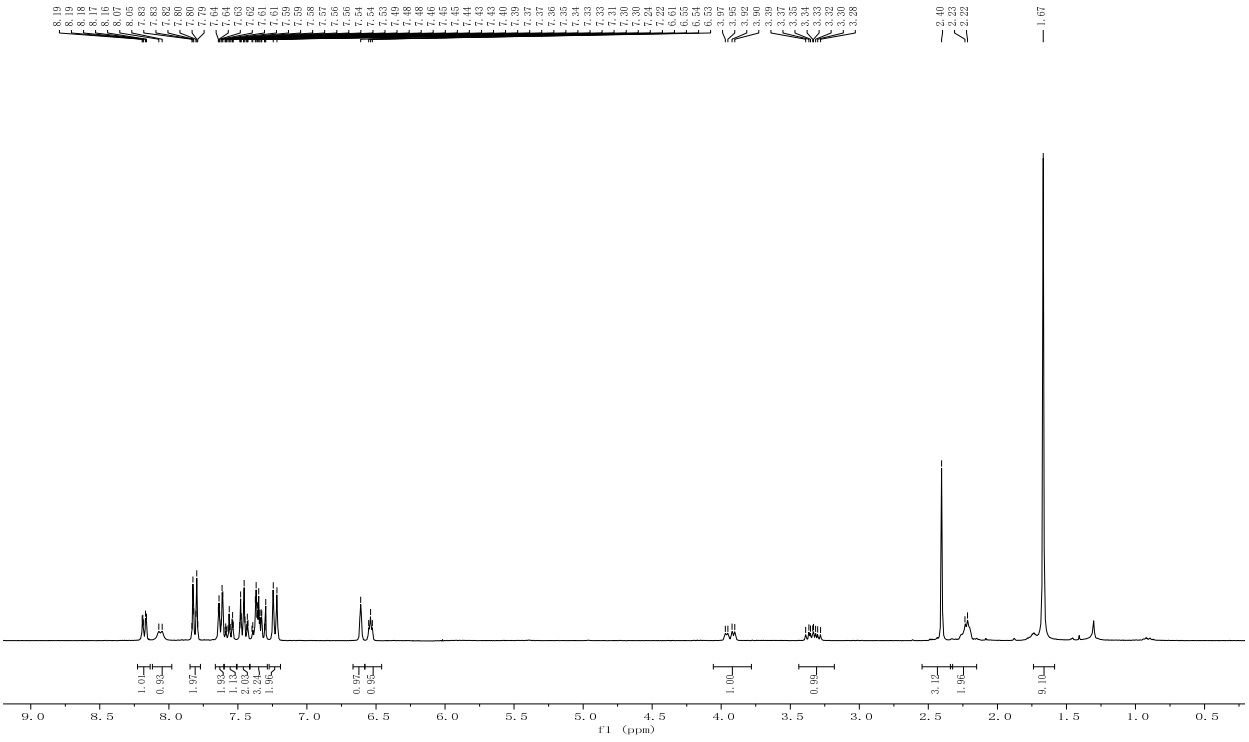
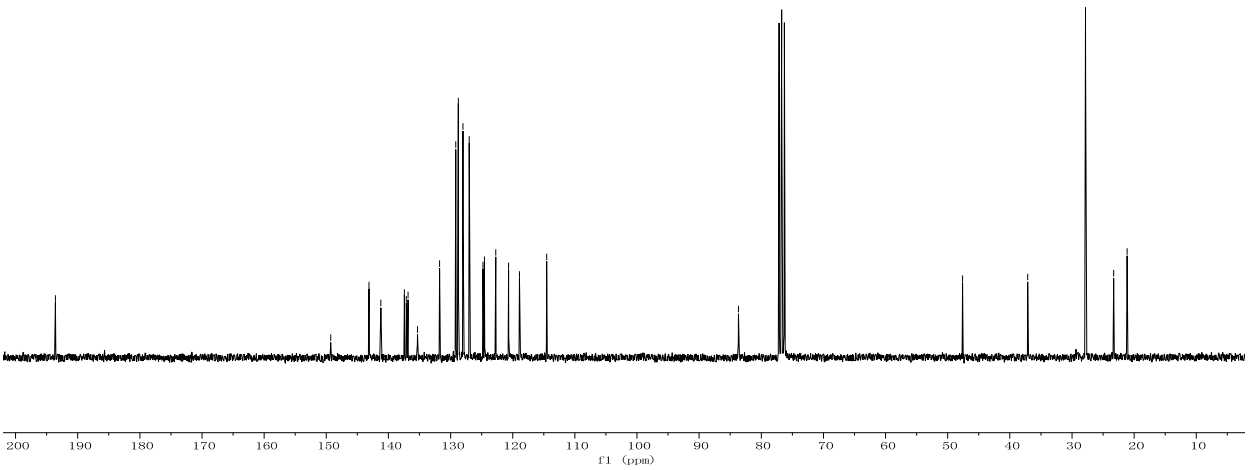
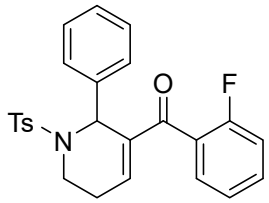
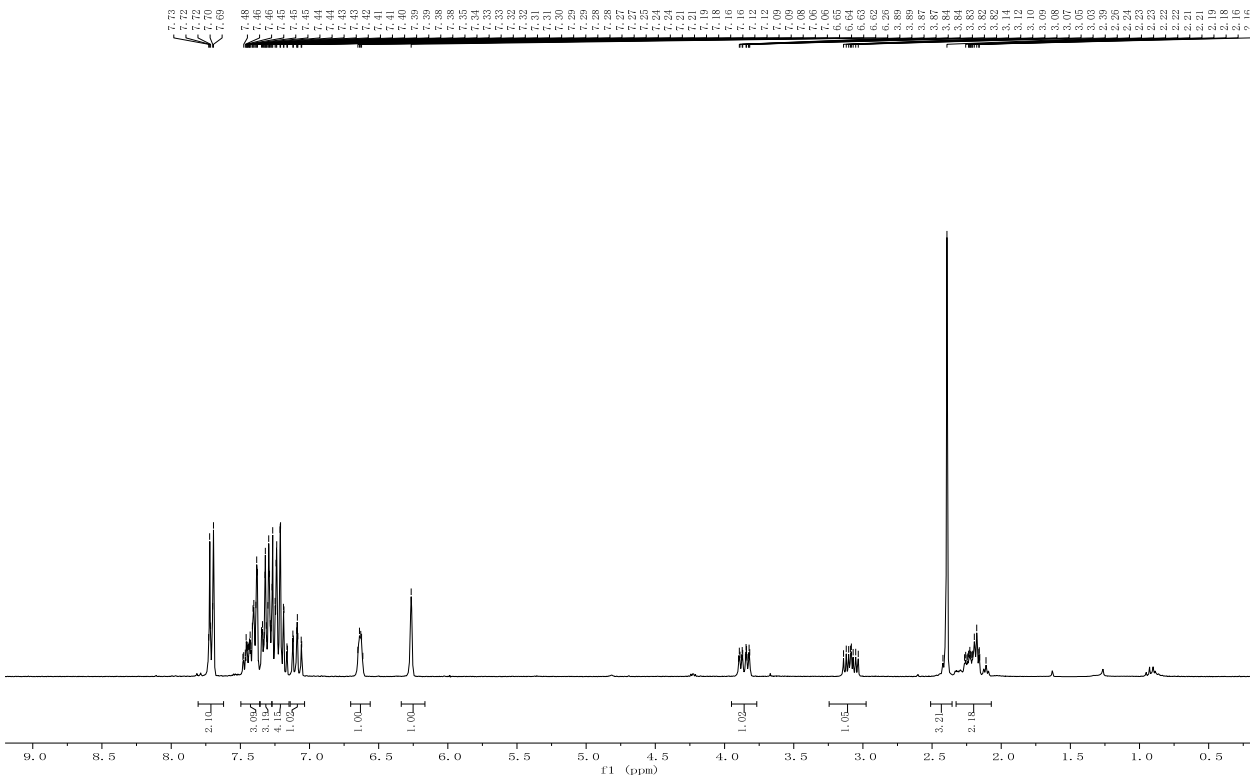





Ts
N
O
F

3ba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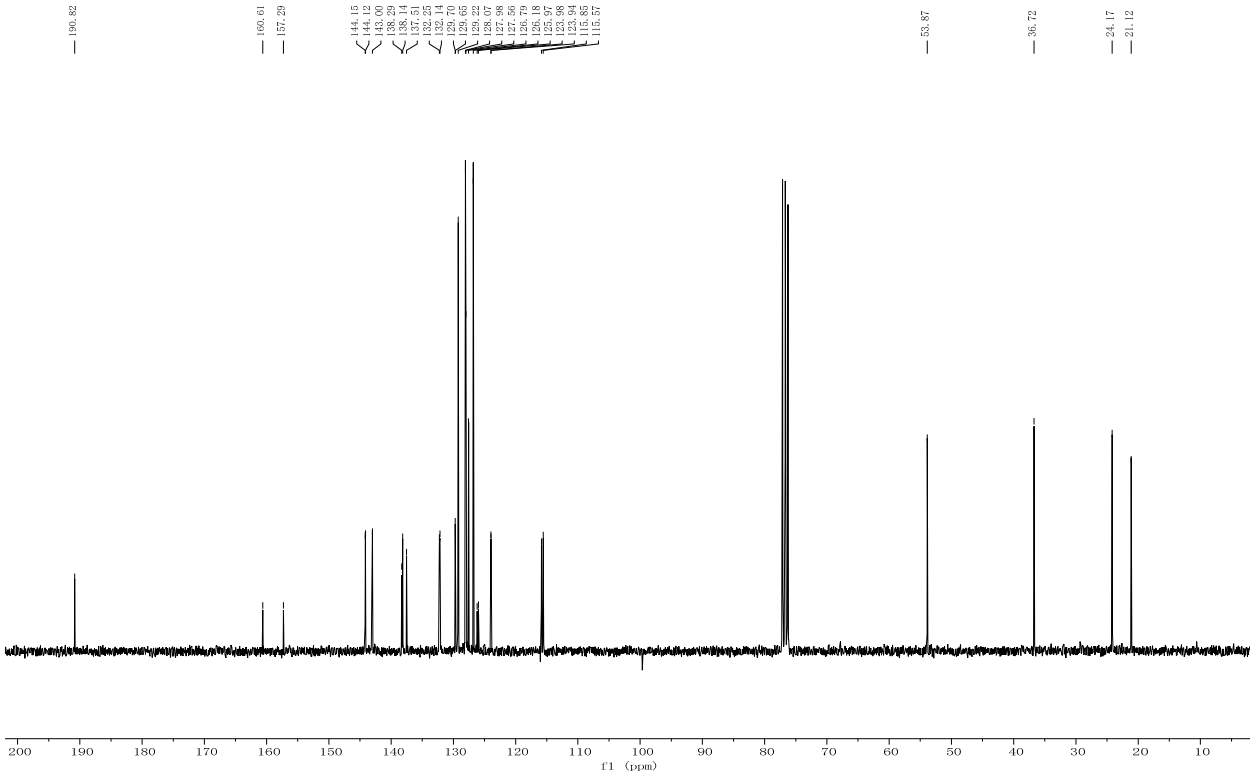
1.00
1.02
1.05
3.21
2.18
f1 (ppm)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129.65
129.22
128.07
127.98
127.56
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123.94
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115.57
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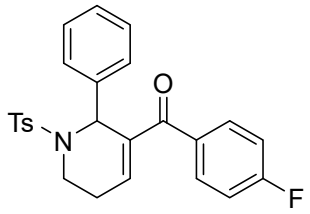
24.17
21.12
f1 (ppm)



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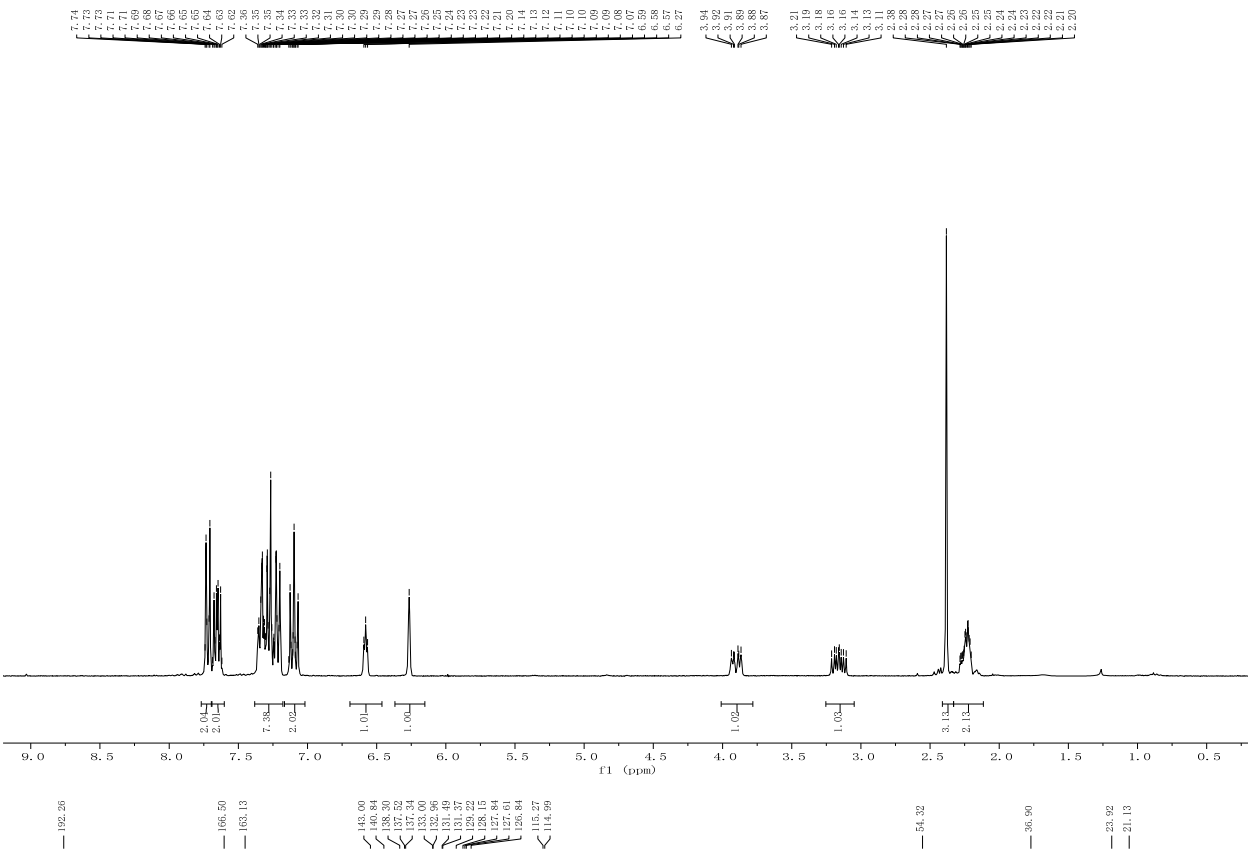
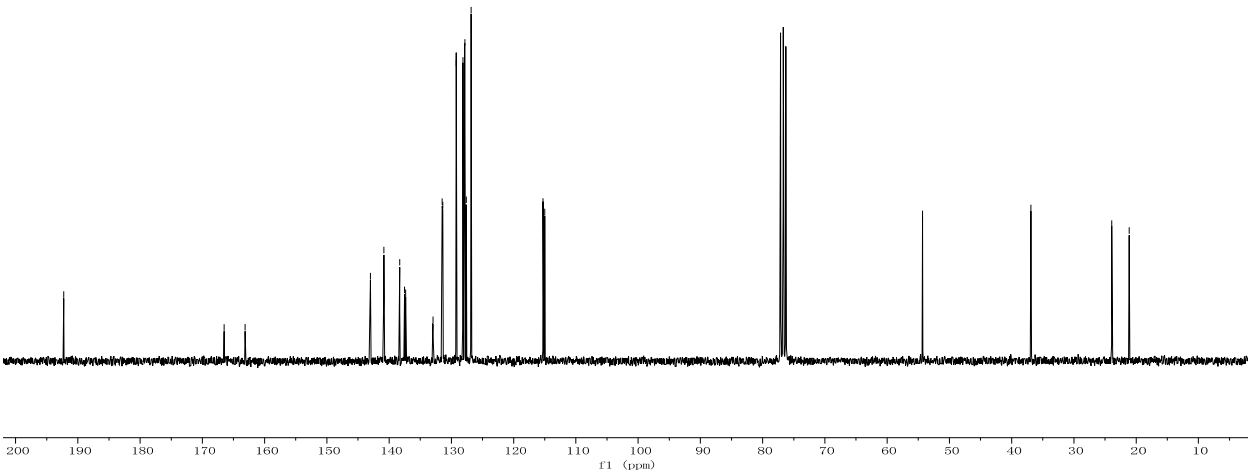
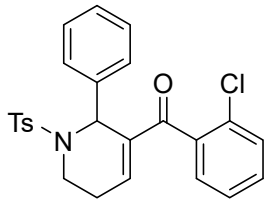
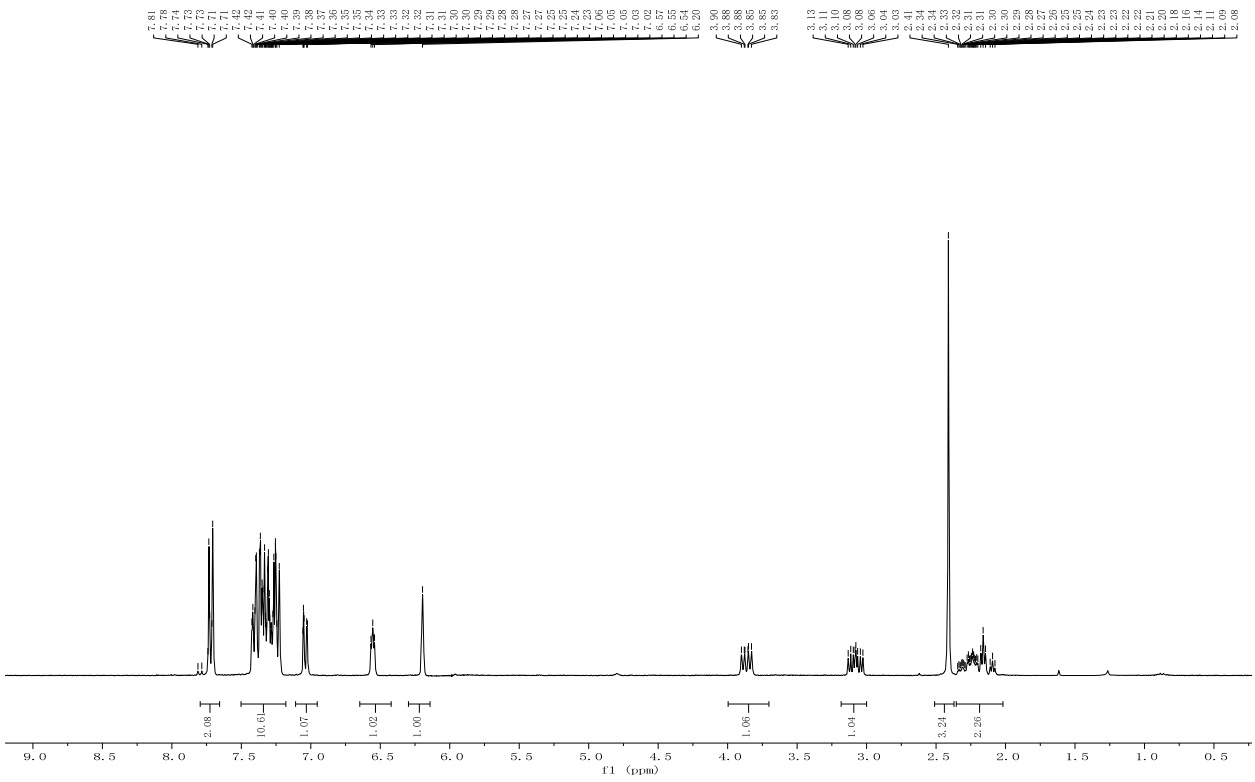





Ts
N
O
Cl

3da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1.04
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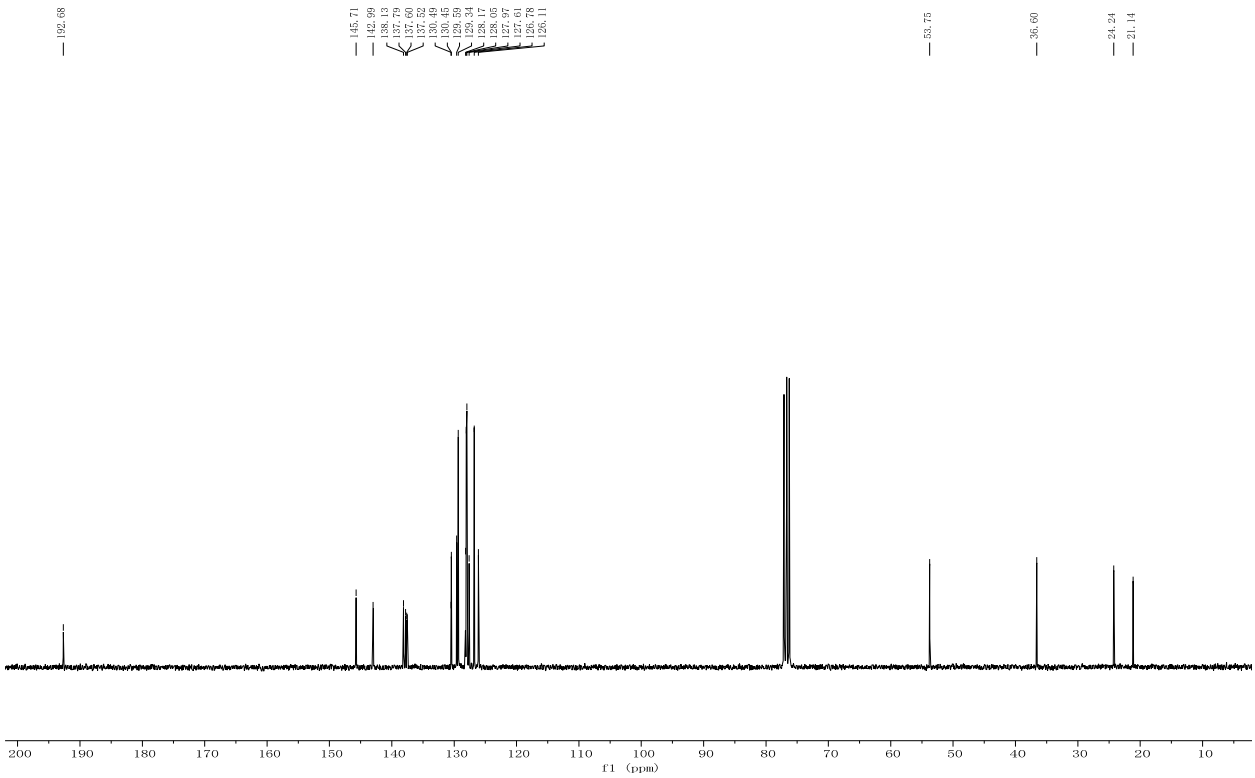
2.36
f1 (ppm)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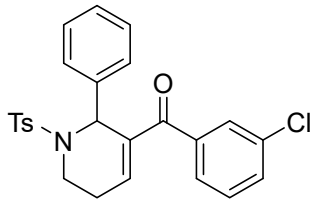
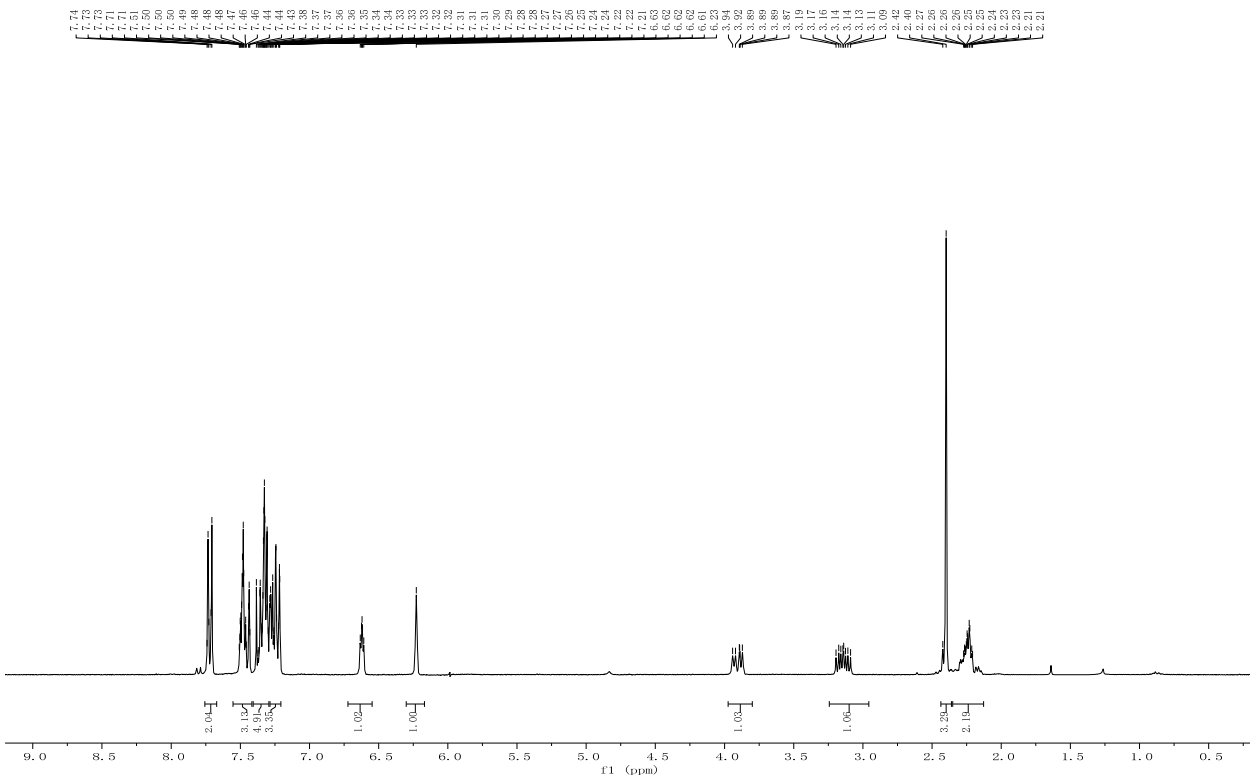
21.14
f1 (ppm)


Ts
N
O
Cl

3ea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1.06
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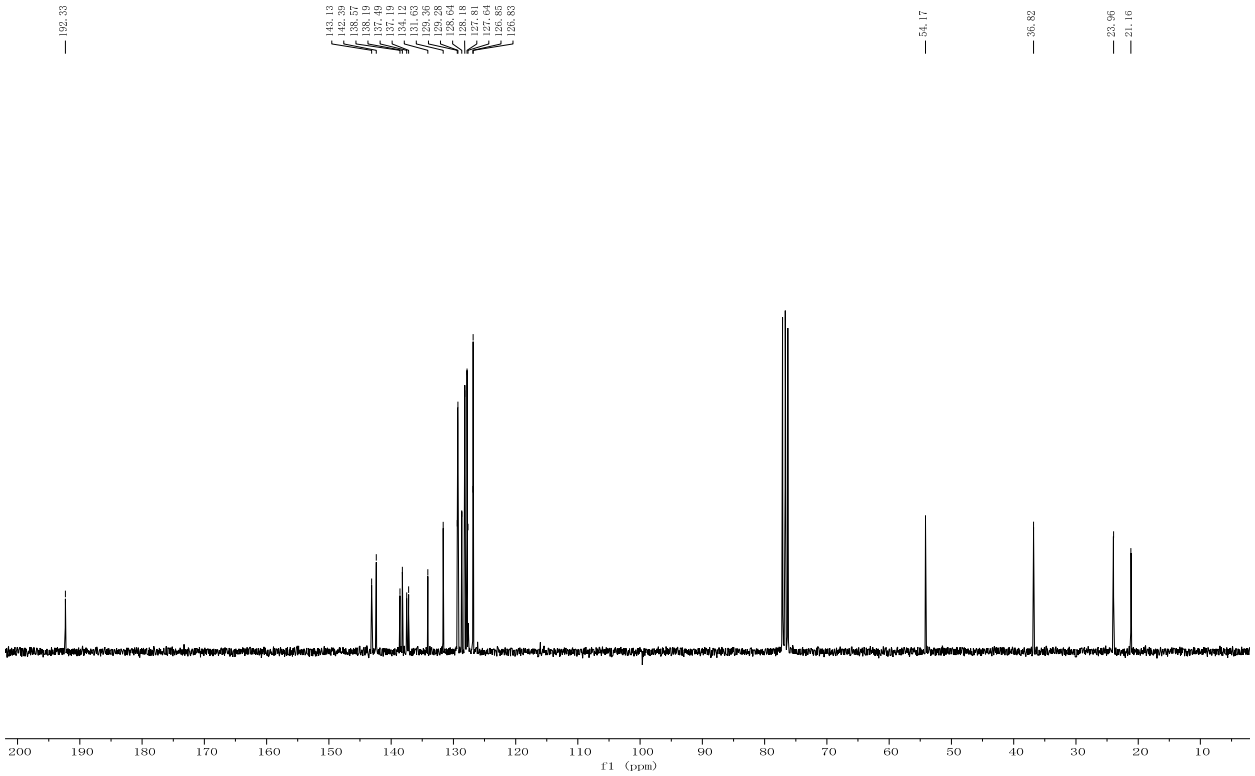
2.19
f1 (ppm)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134.12
131.63
129.36
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127.81
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126.85
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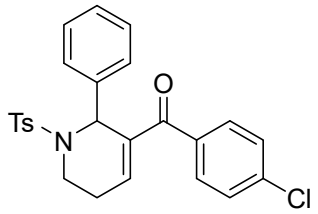
54.17
36.82
23.96
21.16
f1 (ppm)



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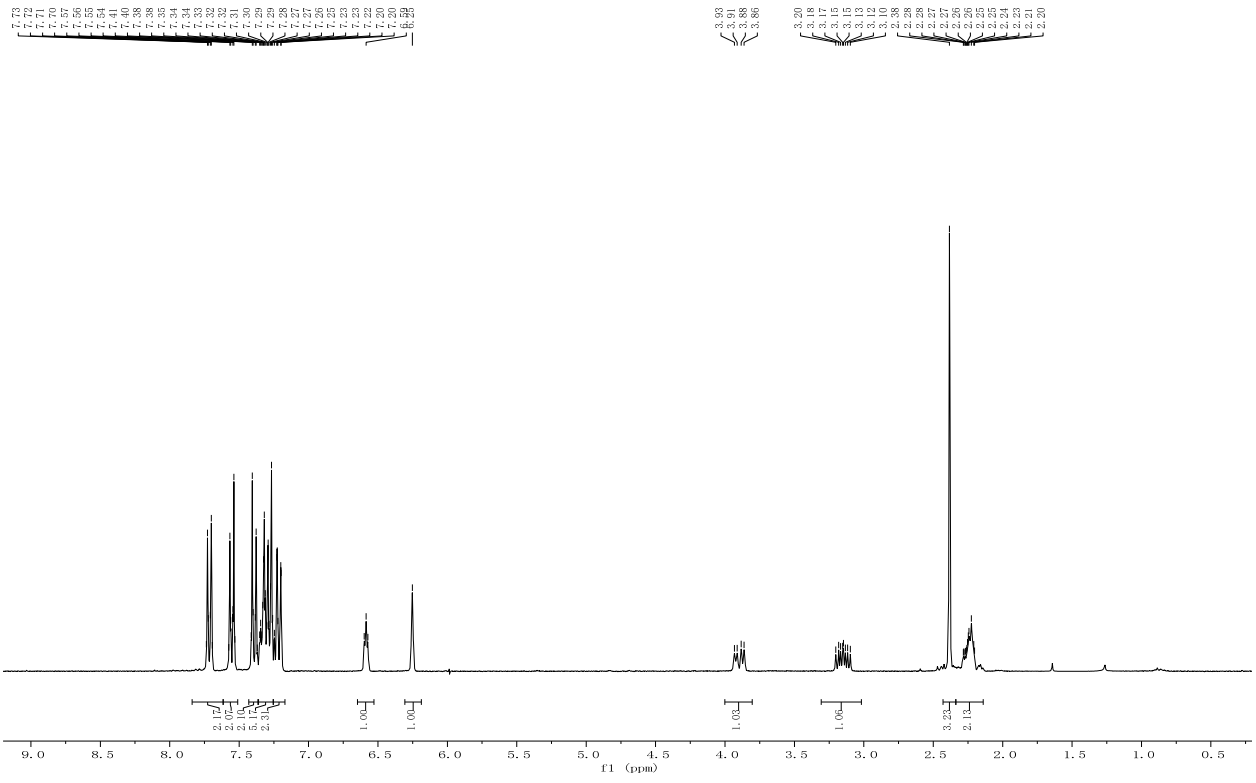

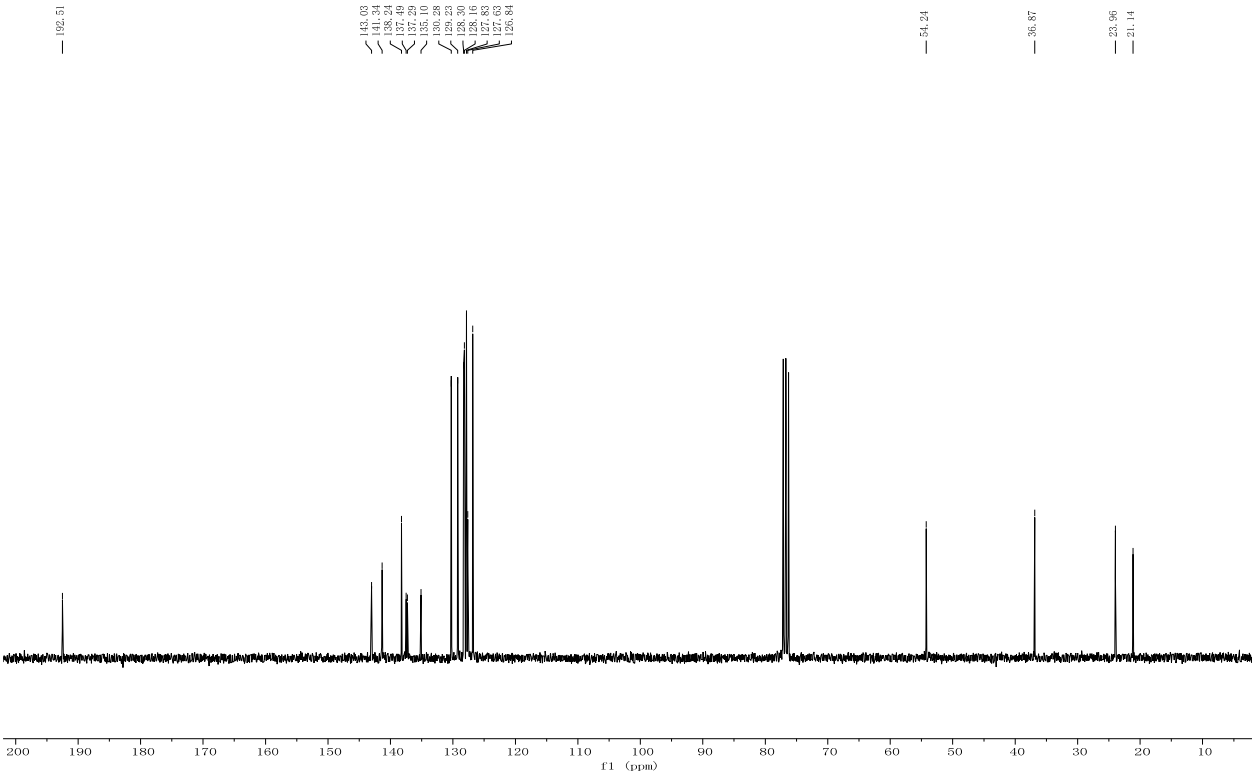

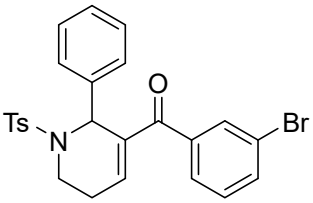

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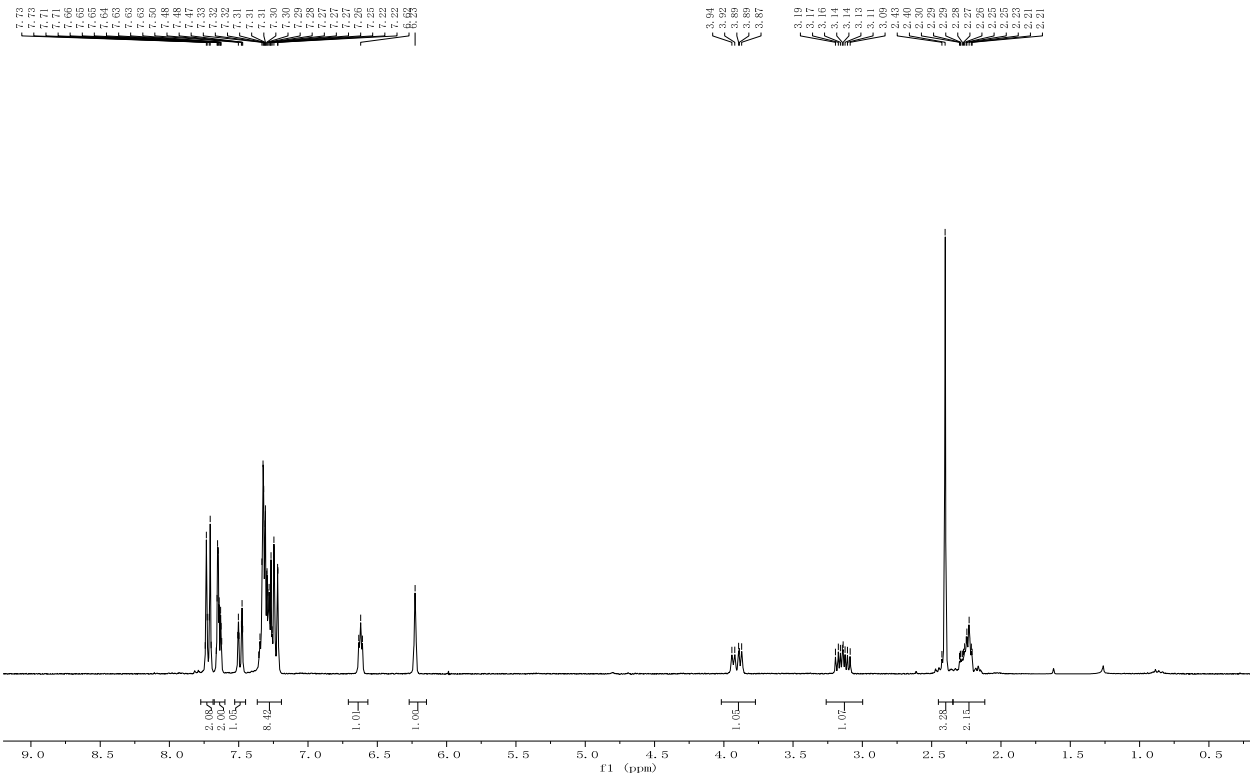

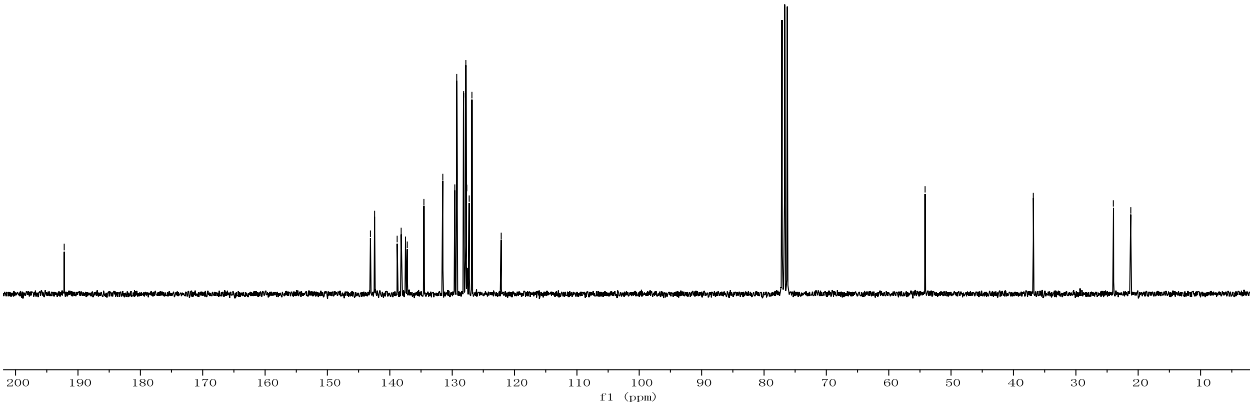

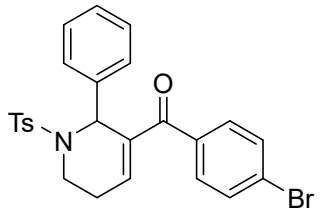

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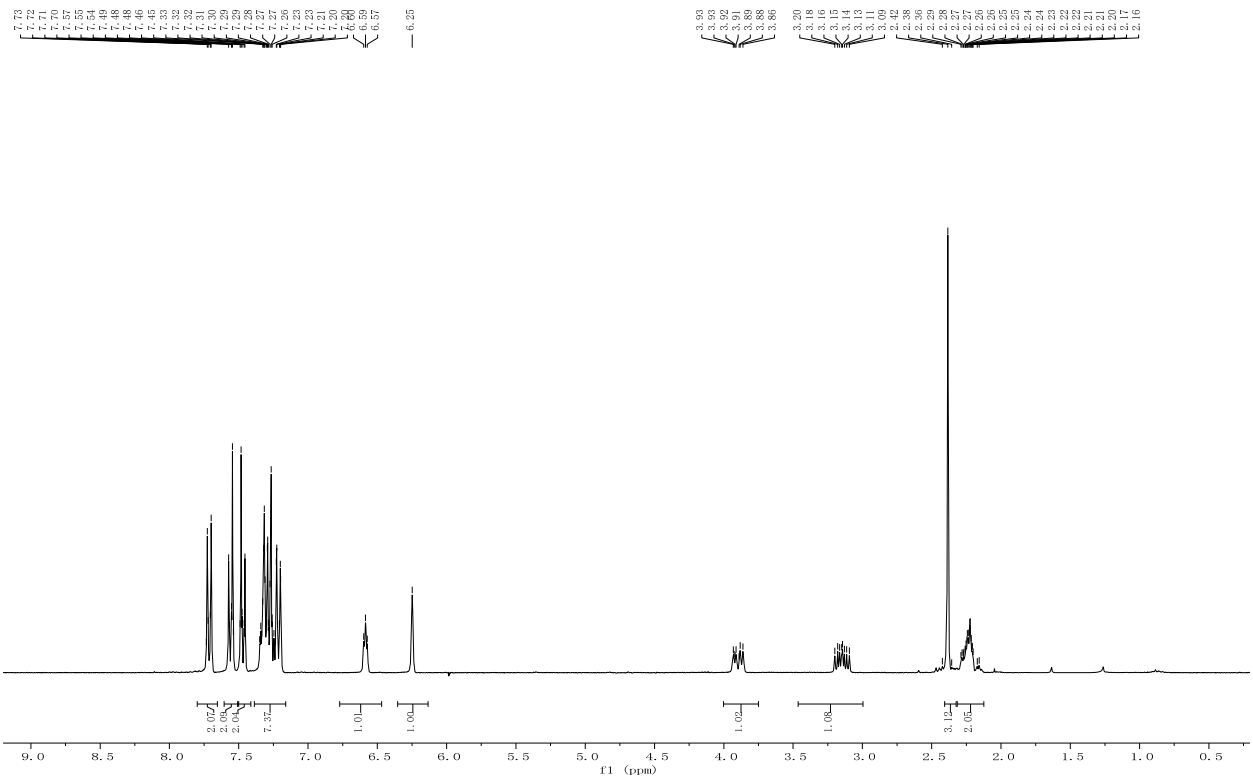
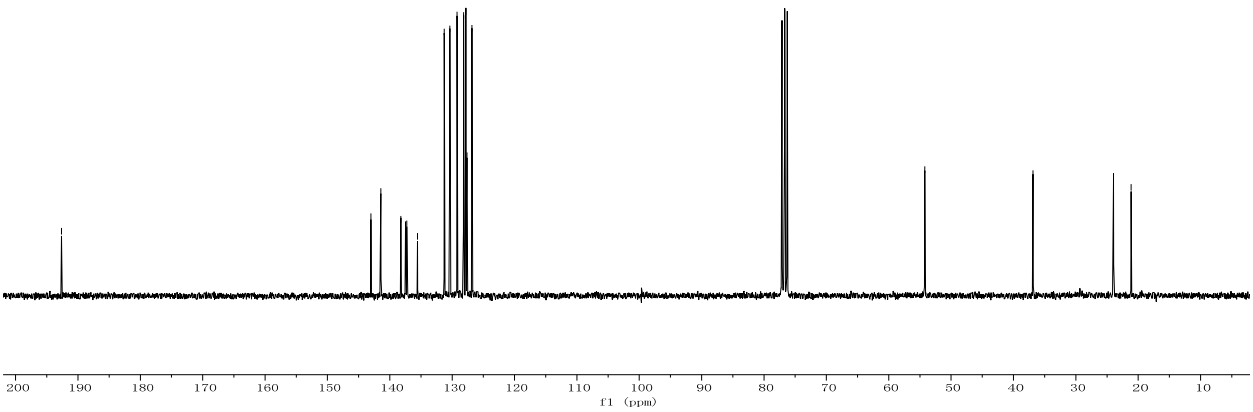
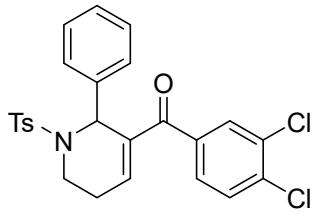
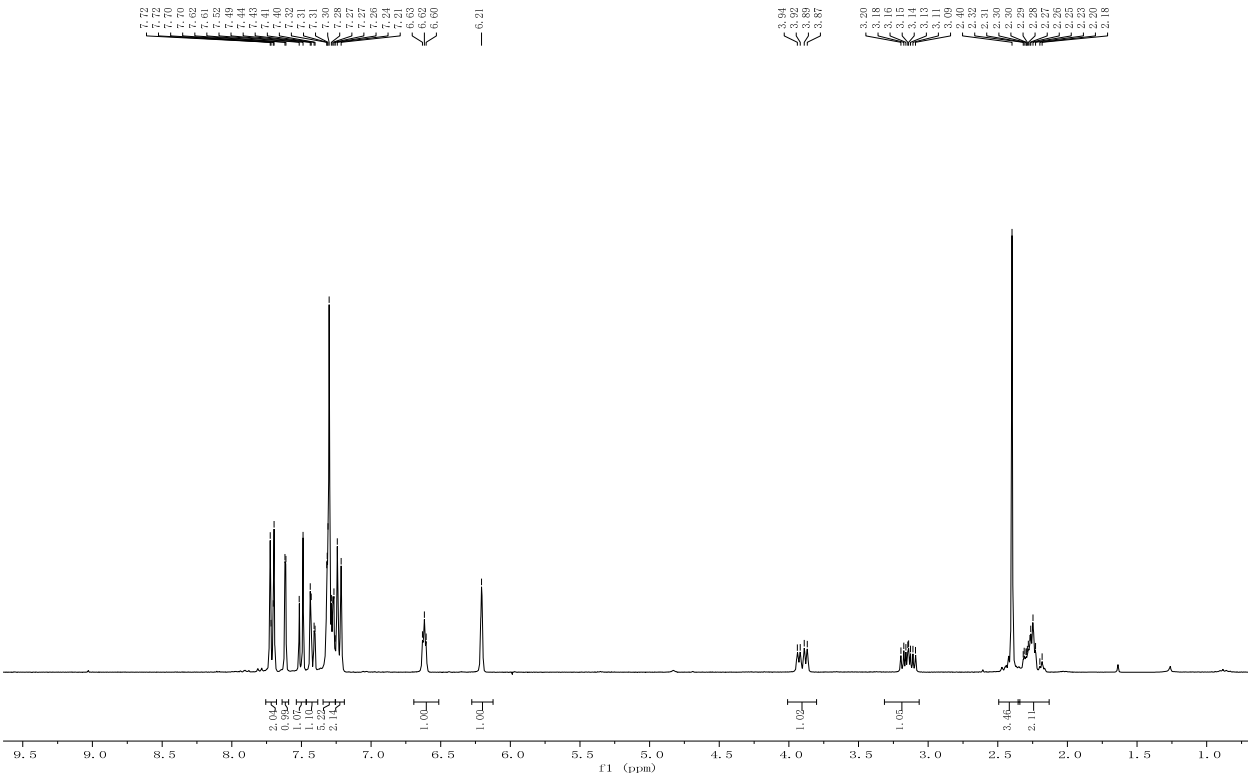





Ts
N
O
Cl
Cl

3ia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7.72
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7.52
7.49
7.44
7.43
7.41
7.40
7.32
7.31
7.31
7.30
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7.27
7.26
7.24
7.21
6.63
6.62
6.60
6.21
3.94
3.92
3.89
3.87
3.20
3.18
3.16
3.15
3.14
3.13
3.11
3.09
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2.28
2.27
2.26
2.25
2.23
2.20
2.18
2.04
0.96
1.07
1.10
1.10
2.14
1.00
1.00
1.02
1.05
3.46
2.11
9.5
9.0
8.5
8.0
7.5
7.0
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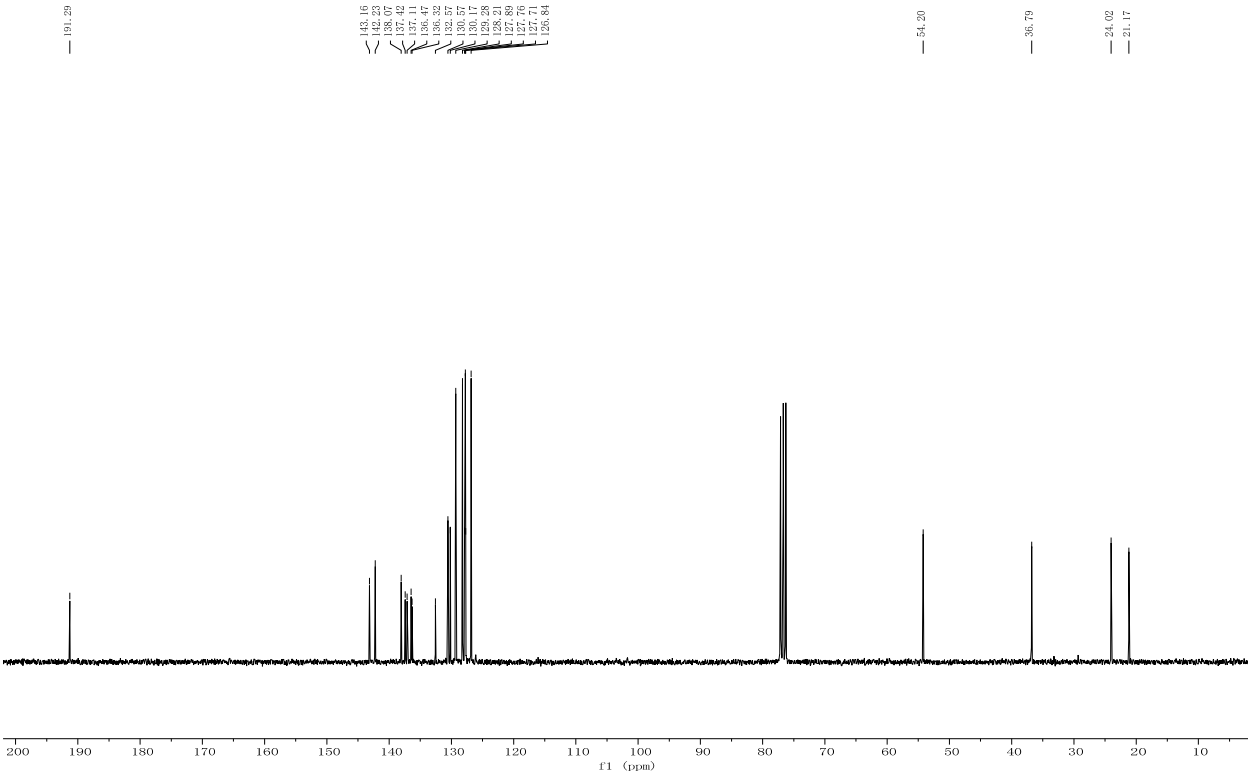
f1 (ppm)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127.76
127.71
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36.79
24.02
21.17
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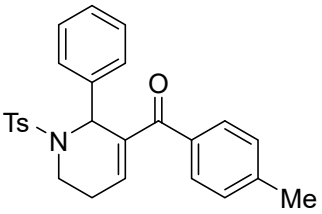
f1 (ppm)



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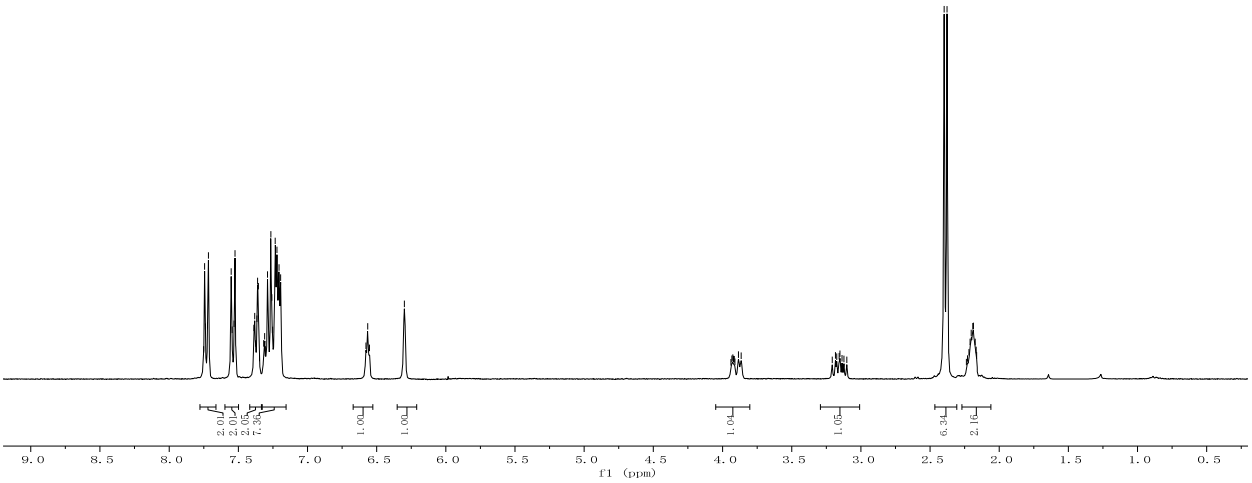

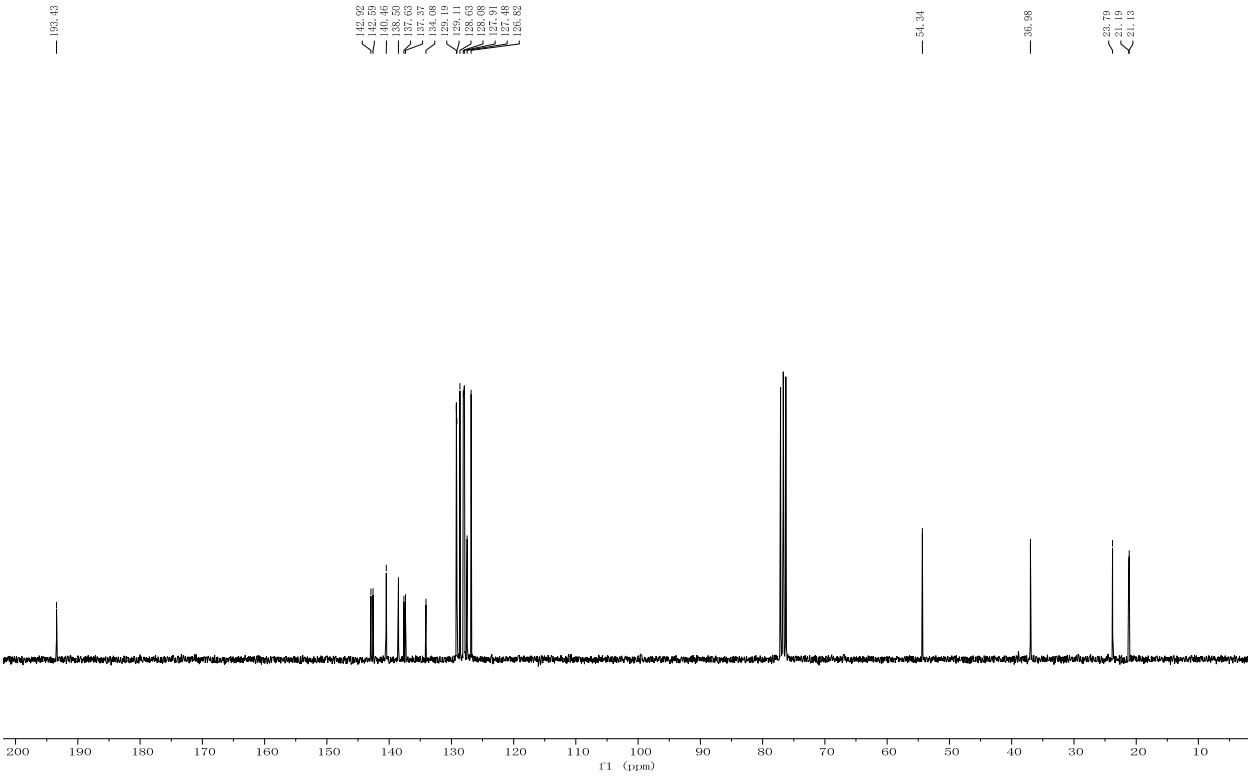

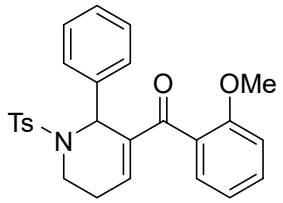
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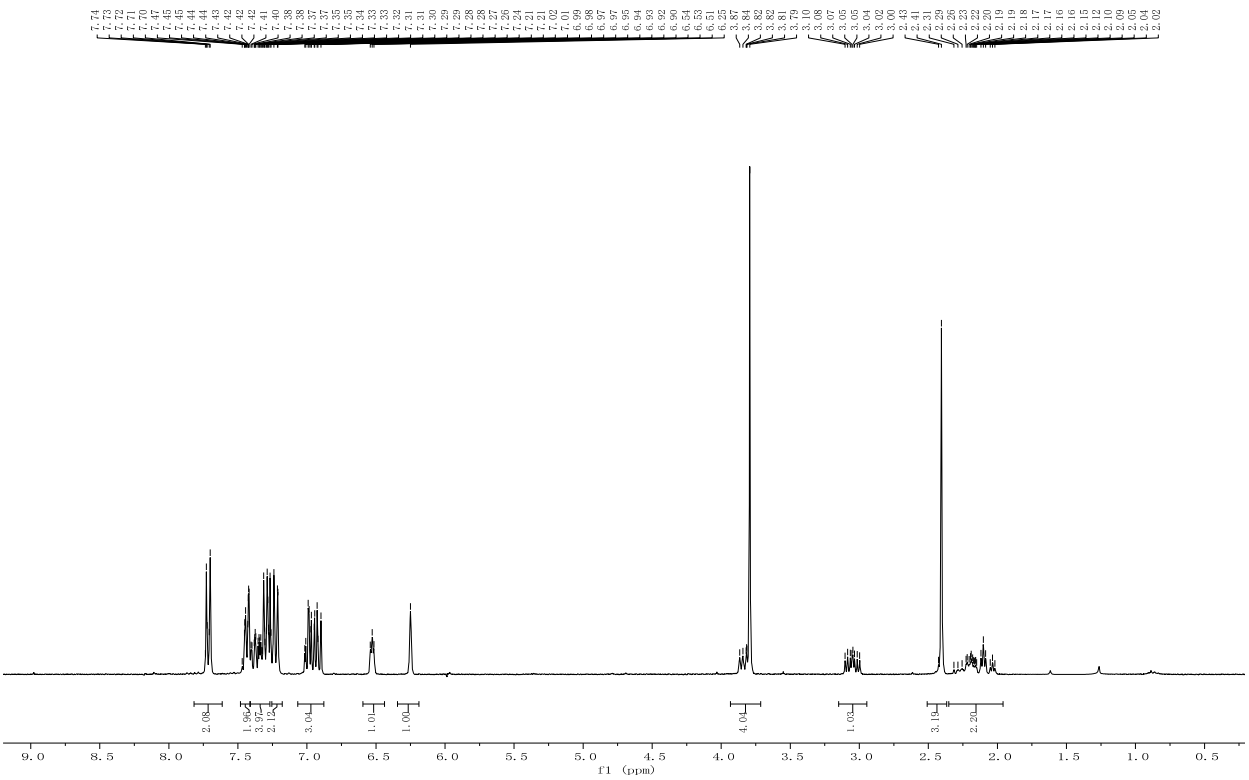
N
O
OMe

3ka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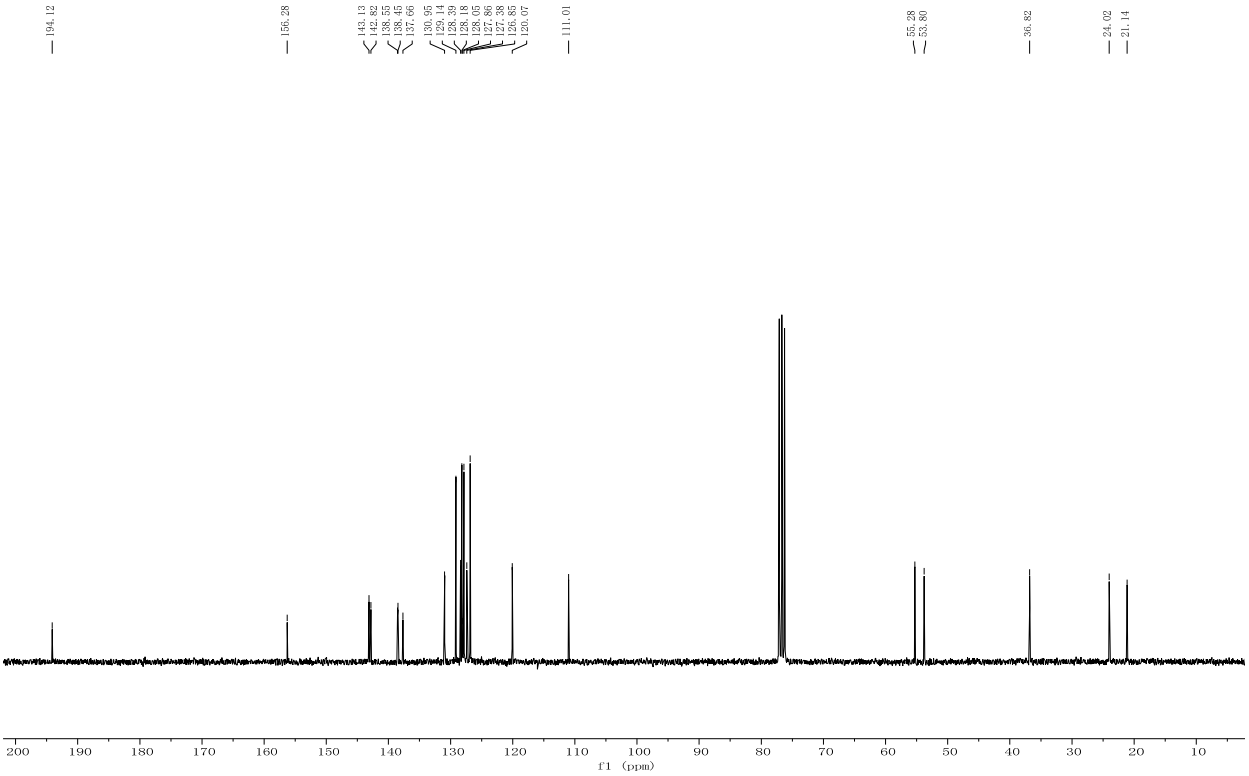
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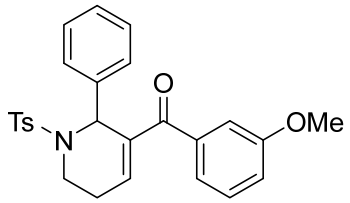
21.14
f1 (ppm)



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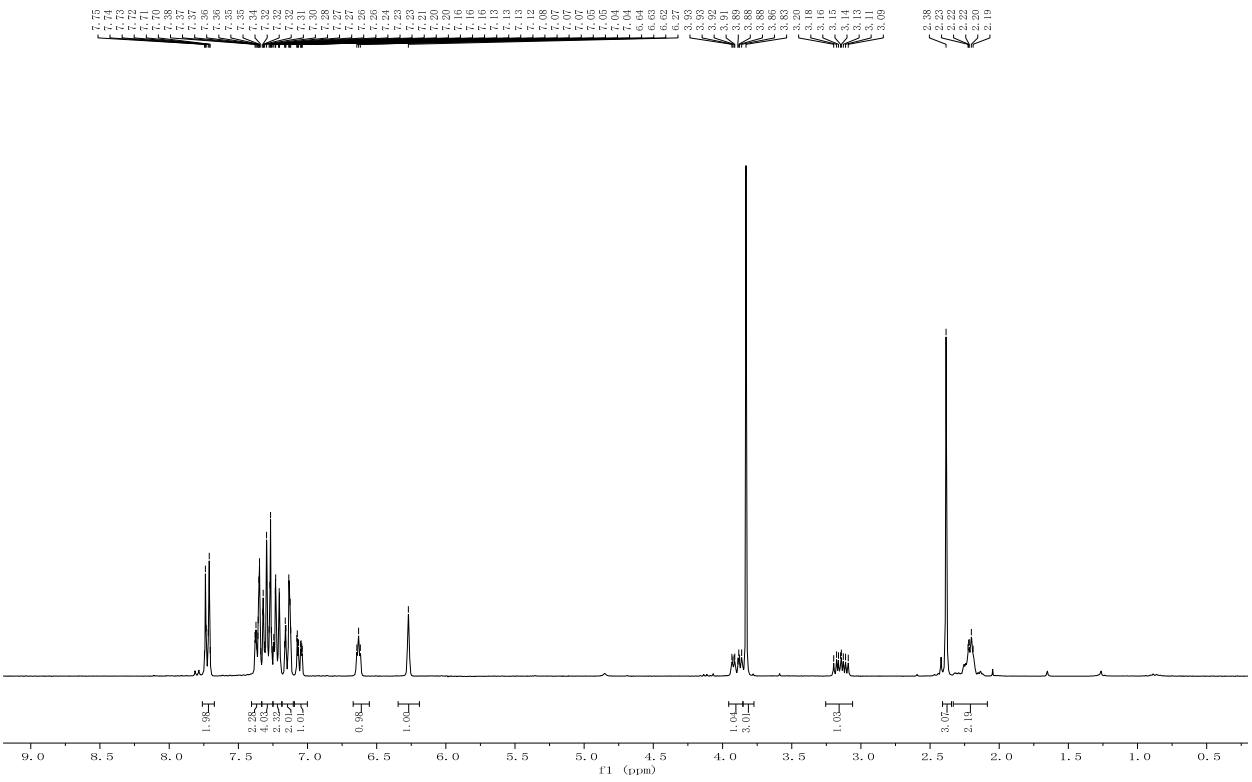

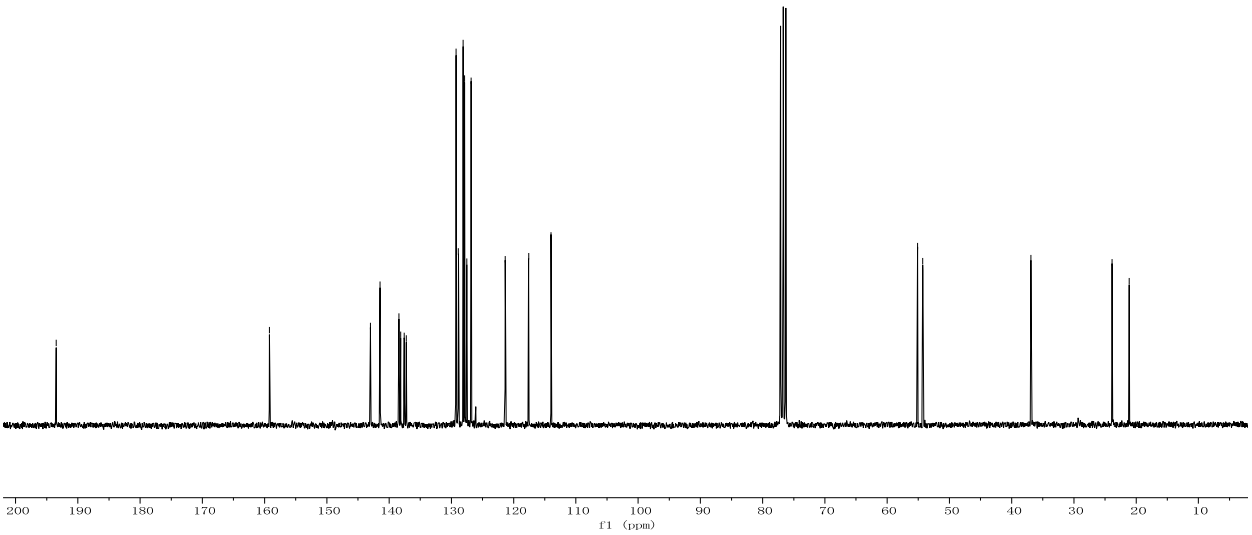

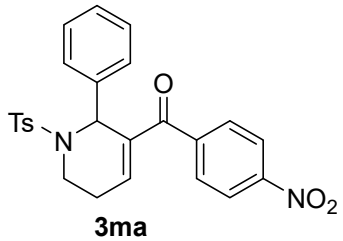

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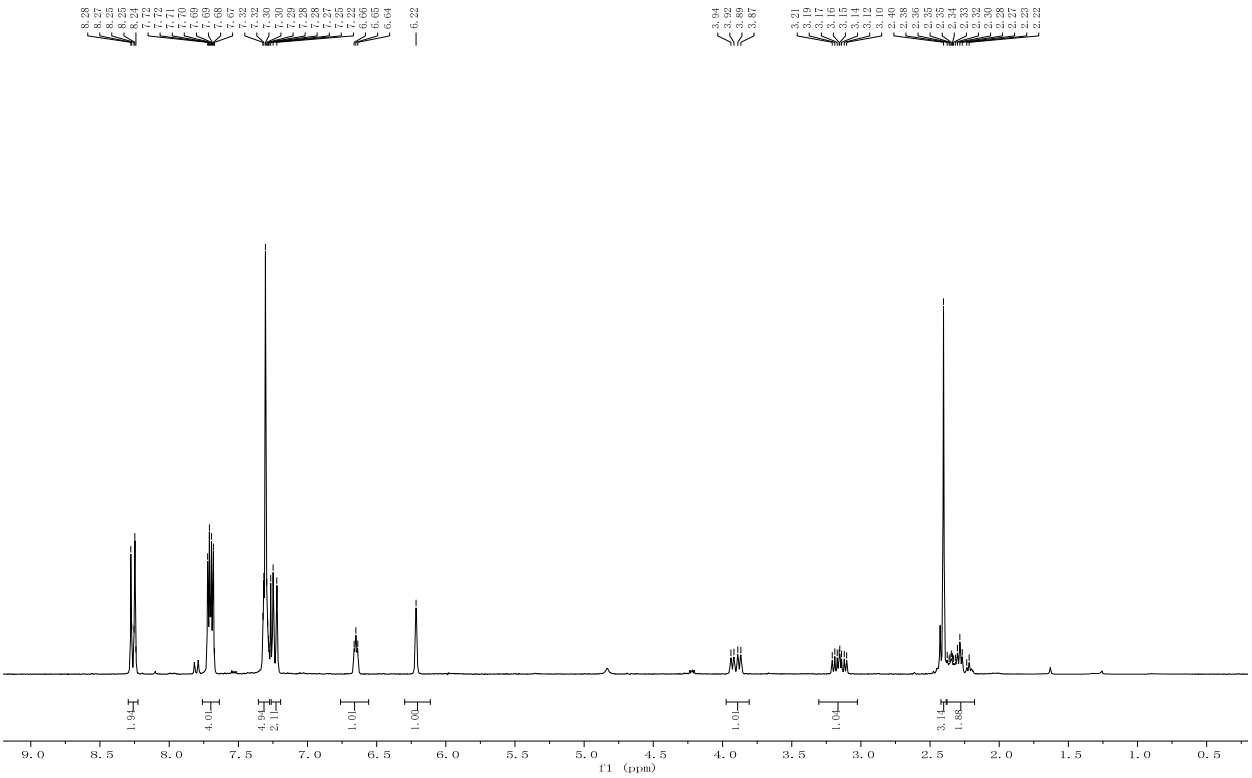

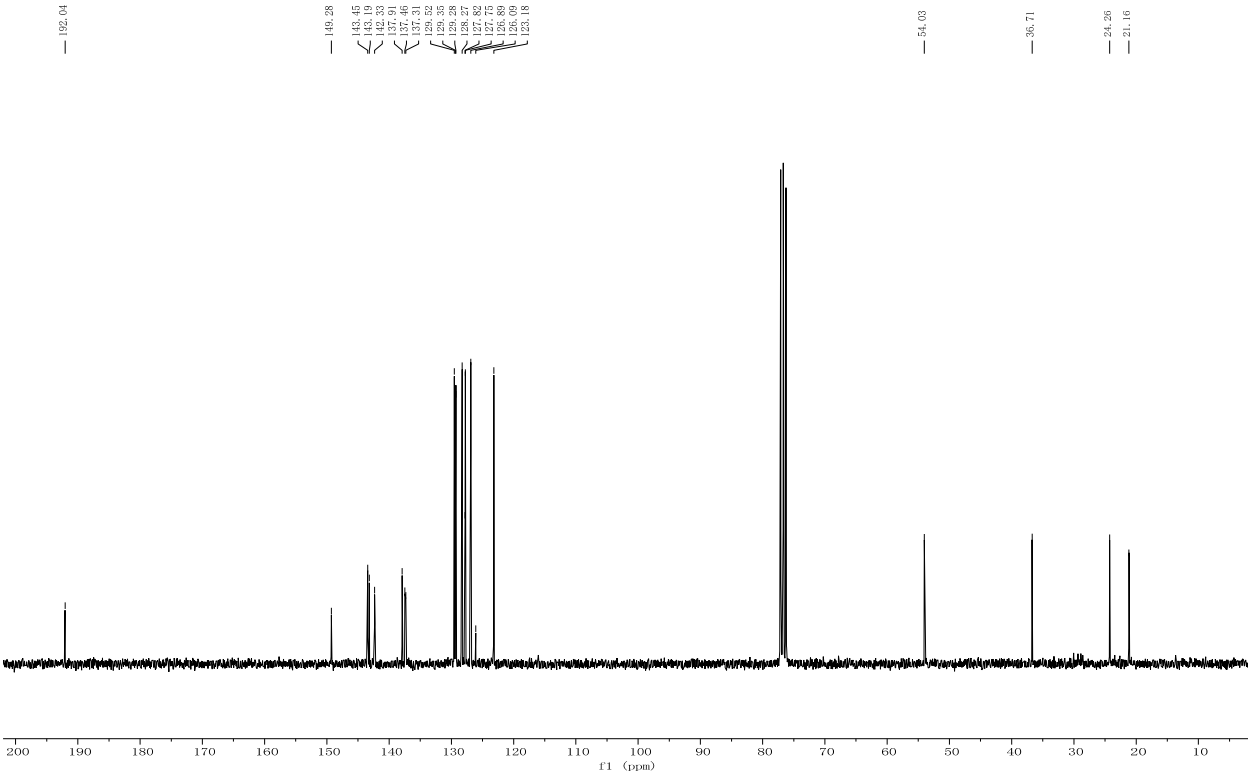

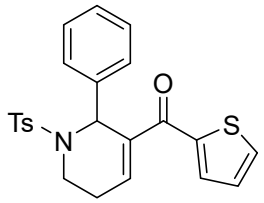

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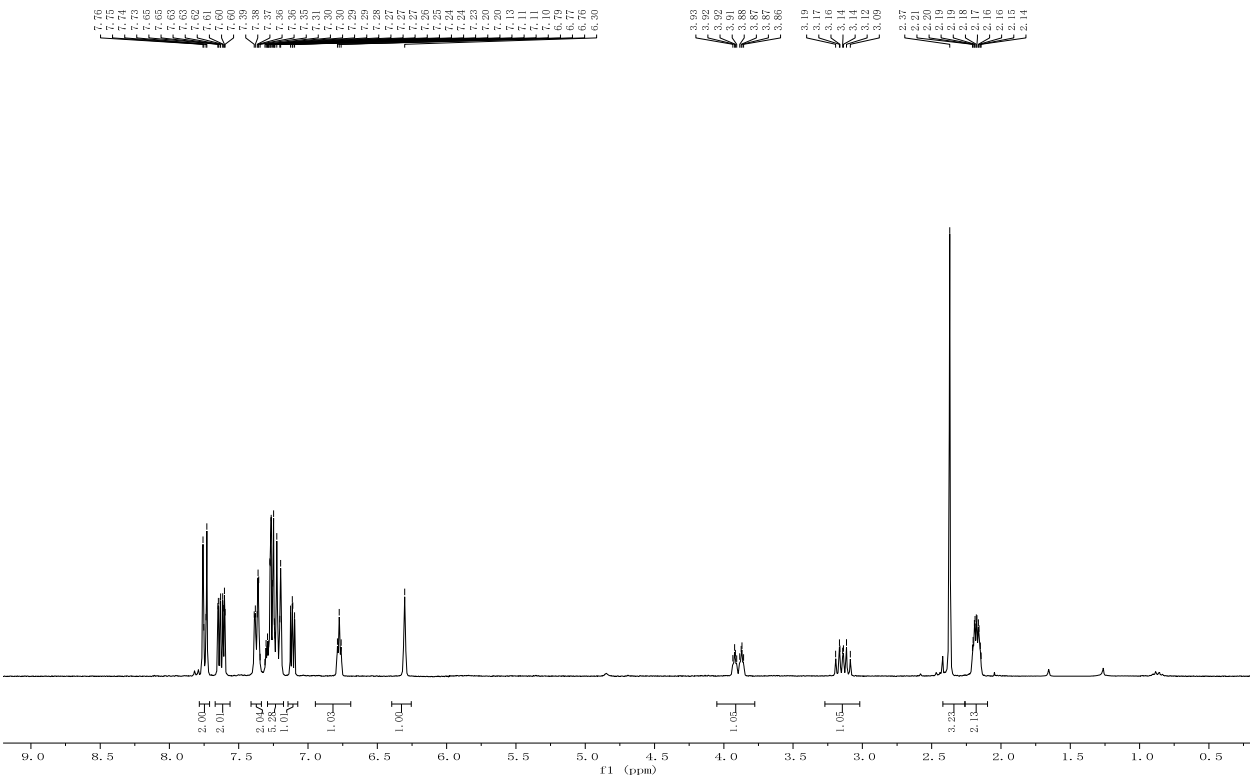

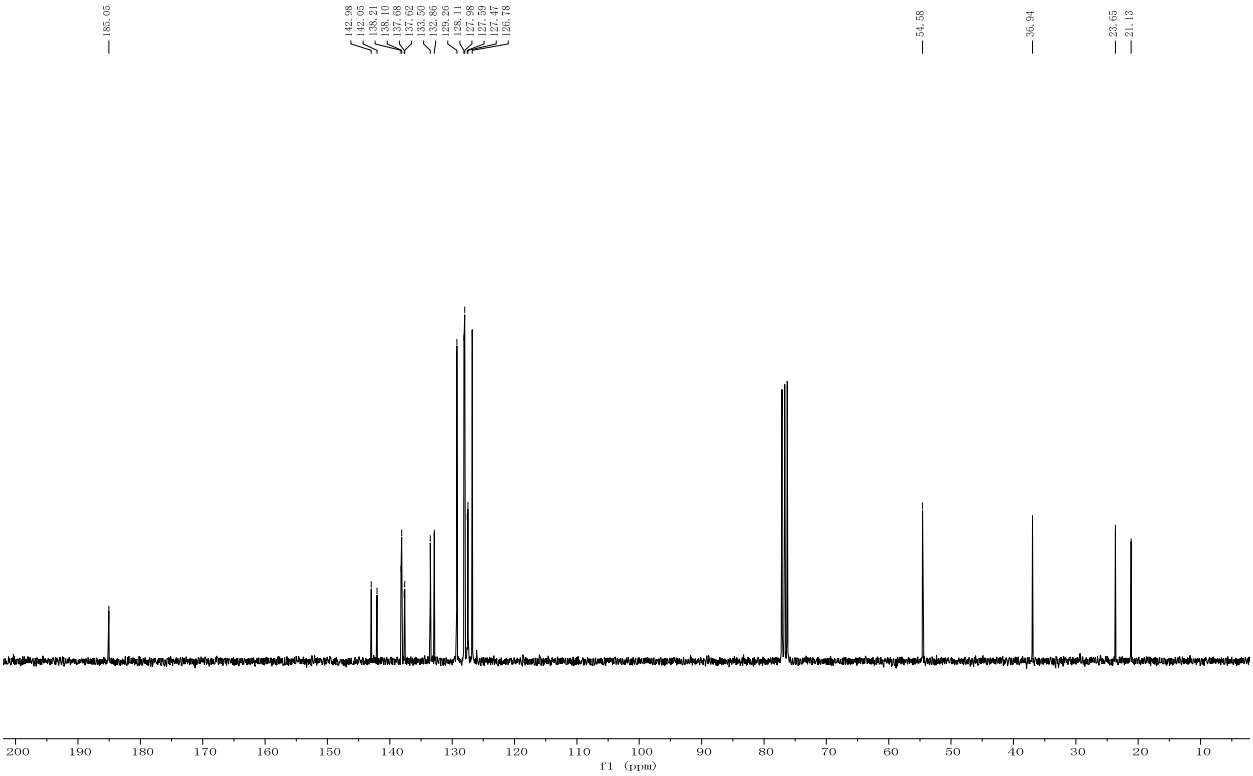

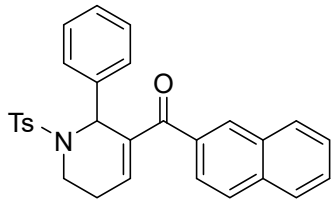

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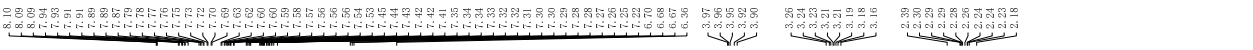
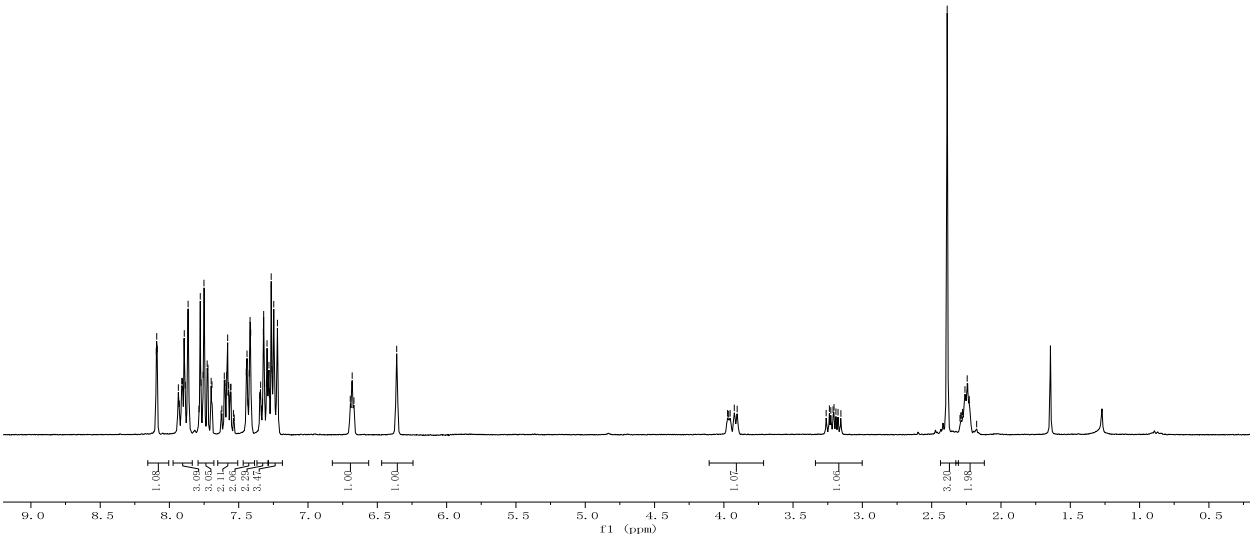
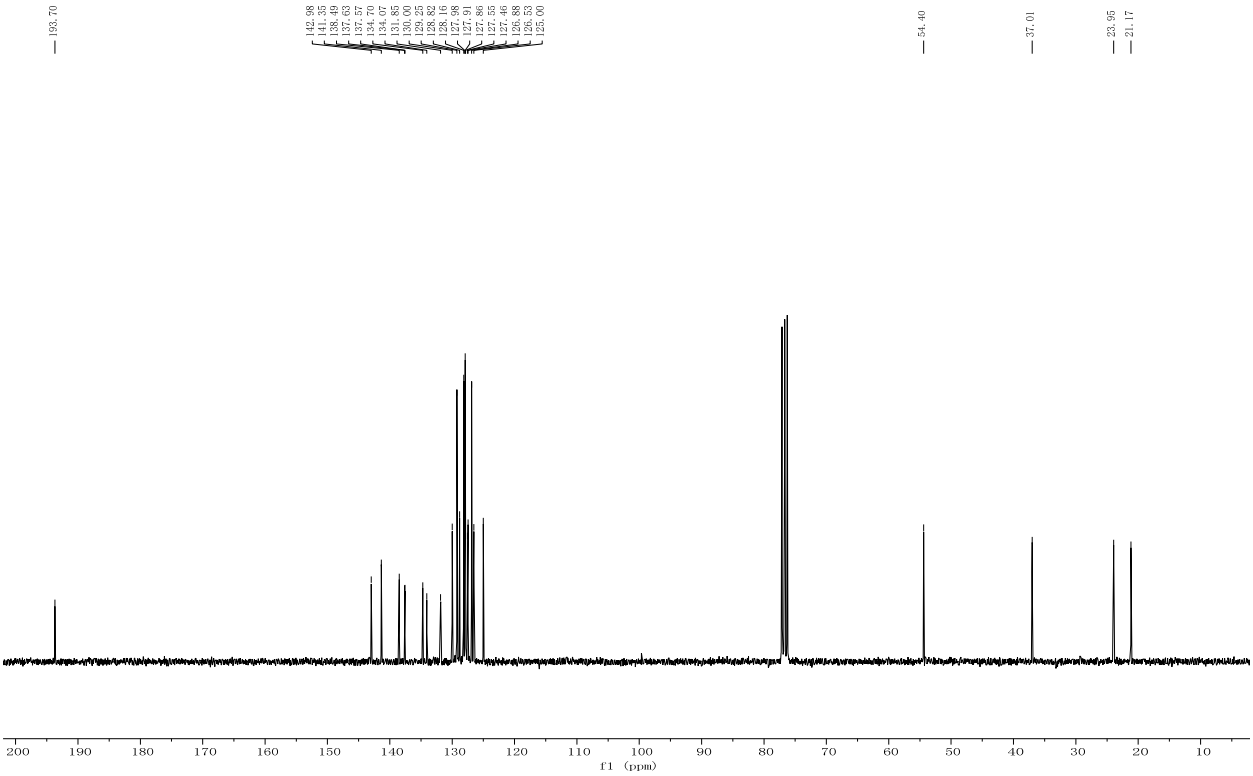
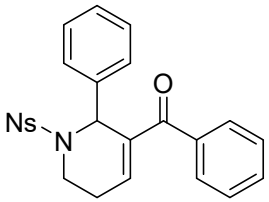
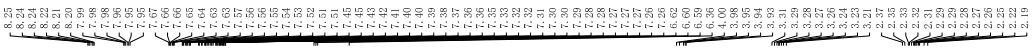


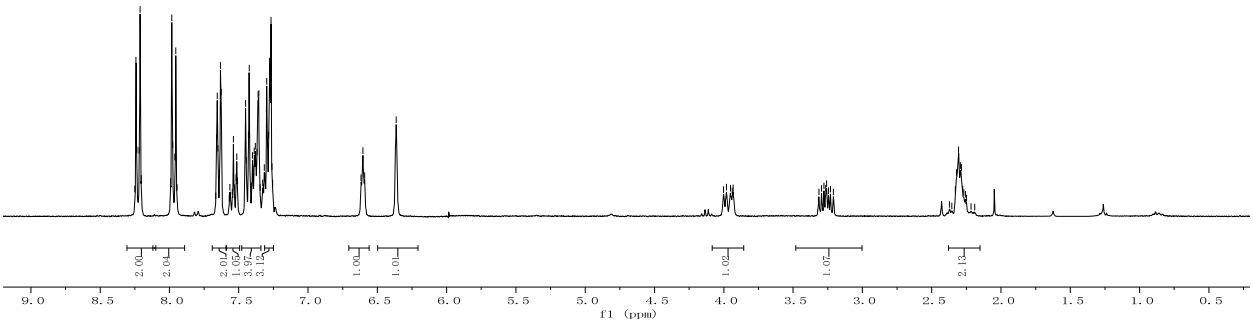





Ns
N
O

3pa

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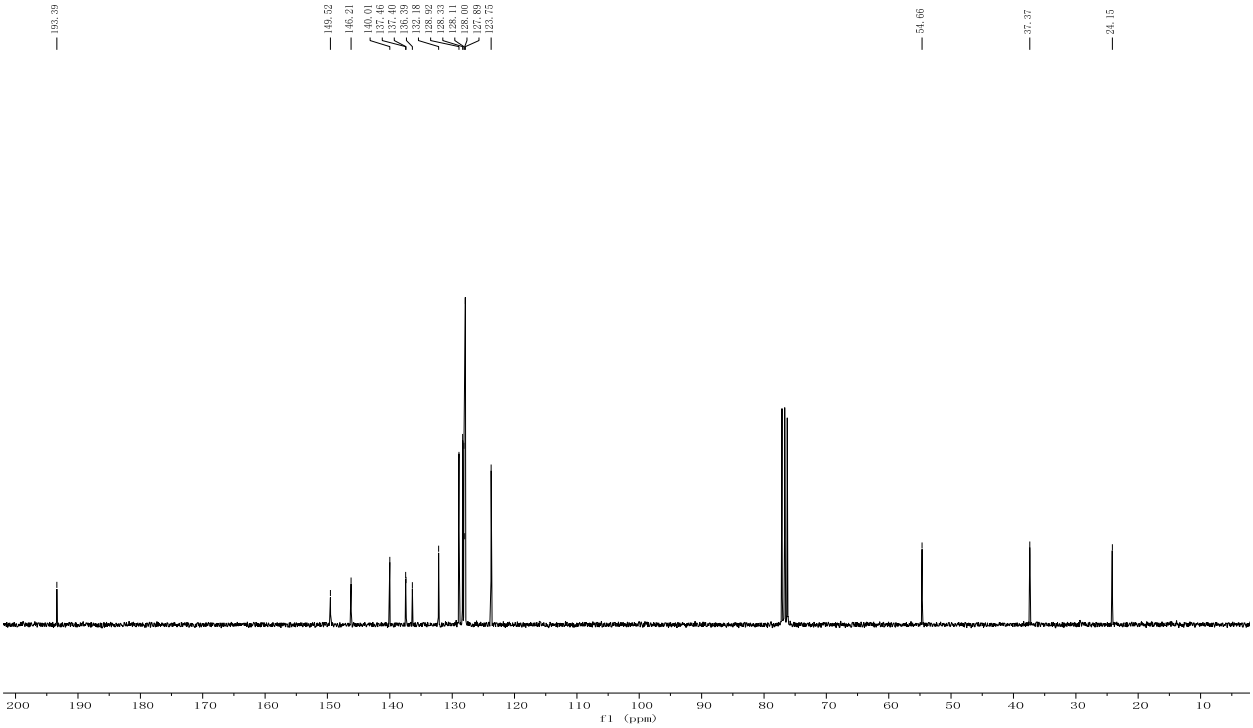
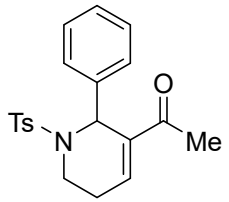
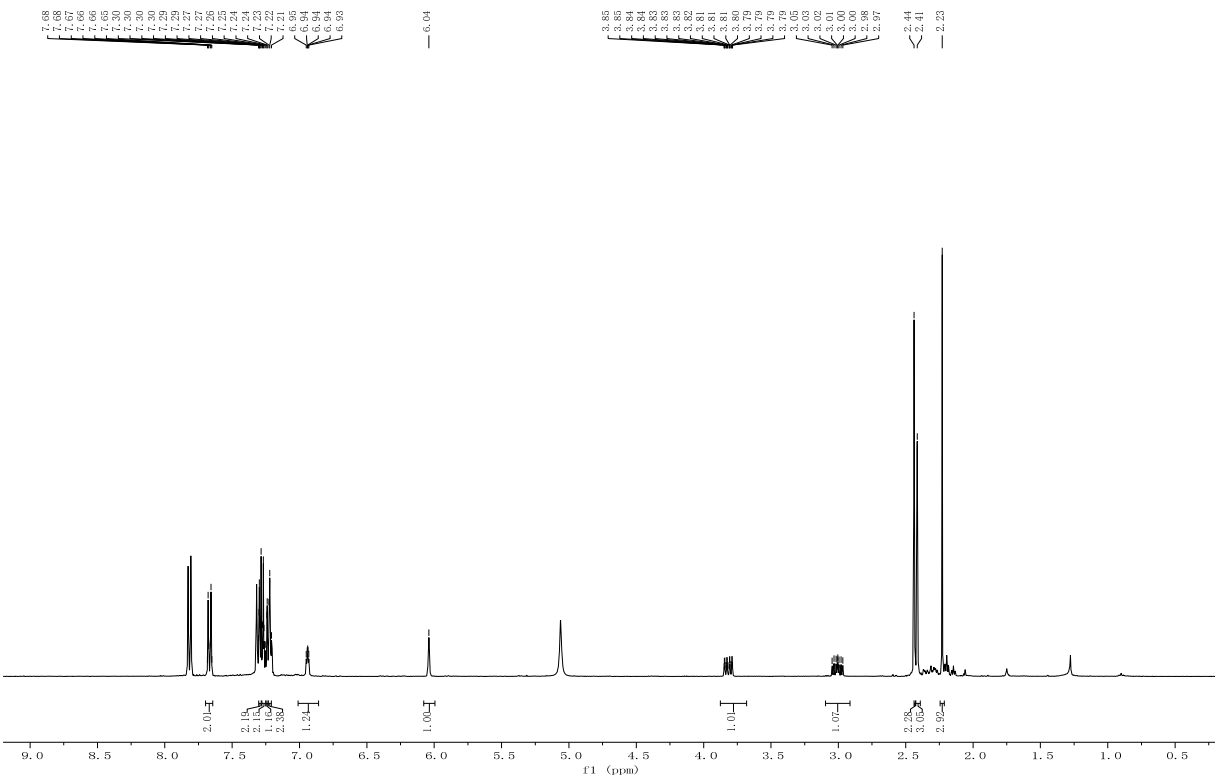
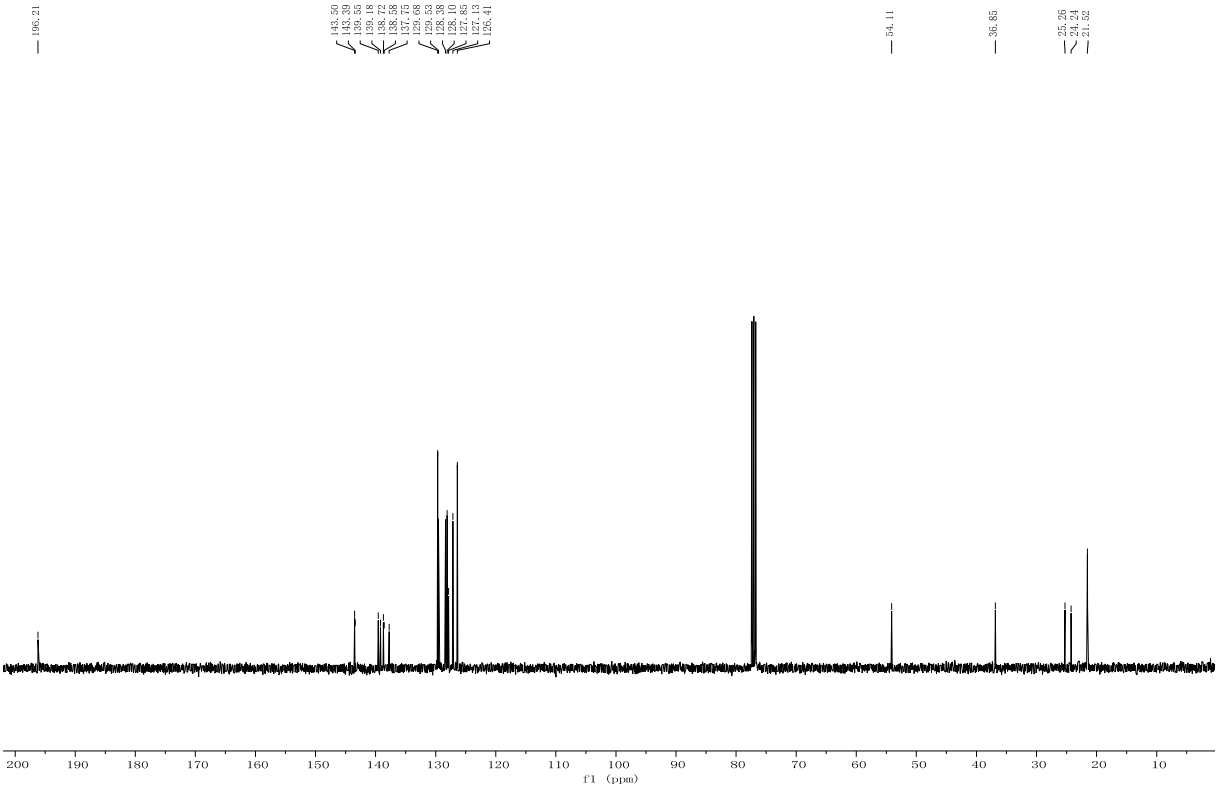
2.07
1.05
3.97
3.12
1.00
1.01
1.02
1.07
2.13
f1 (ppm)

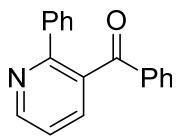

193.39
149.52
146.21
140.01
137.46
137.40
135.39
132.18
128.92
128.33
128.11
128.00
127.89
123.75
54.66
37.37
24.15
f1 (ppm)



3sa







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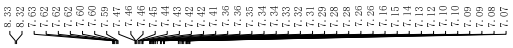

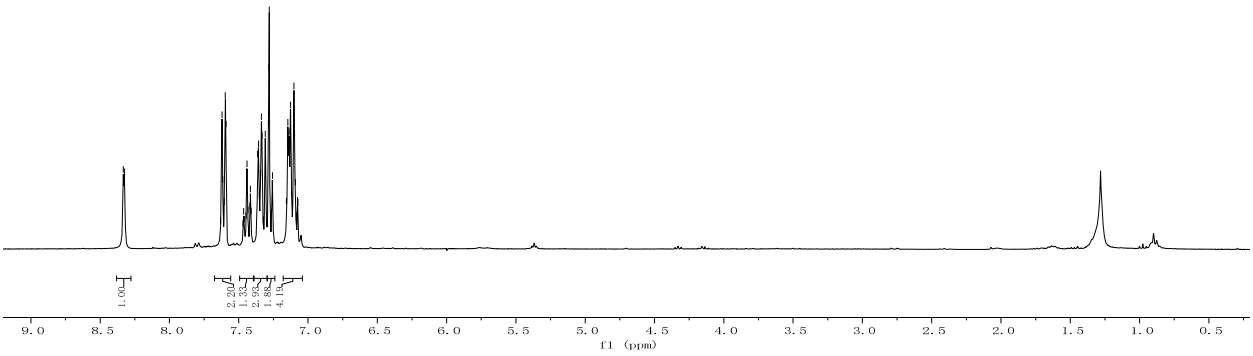
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1.33
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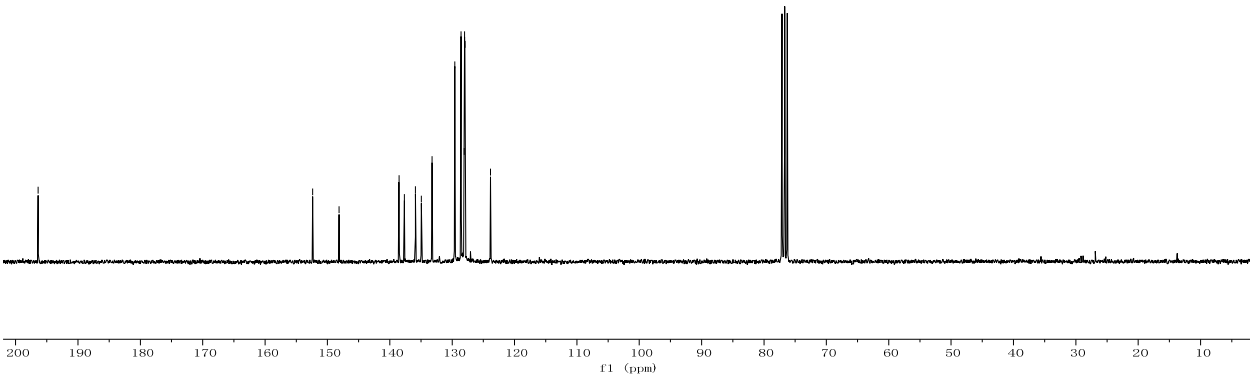
1.88
4.10
f1 (ppm)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152.37
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129.59
128.57
128.06
128.02
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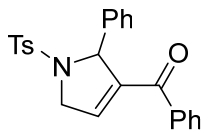
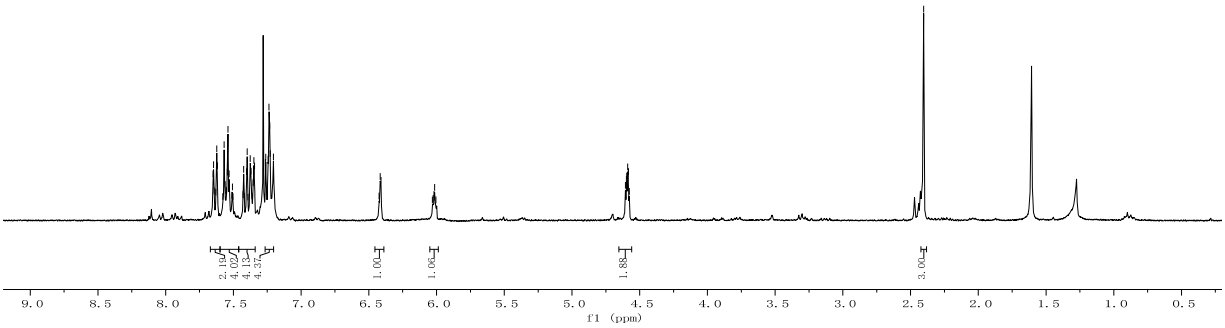
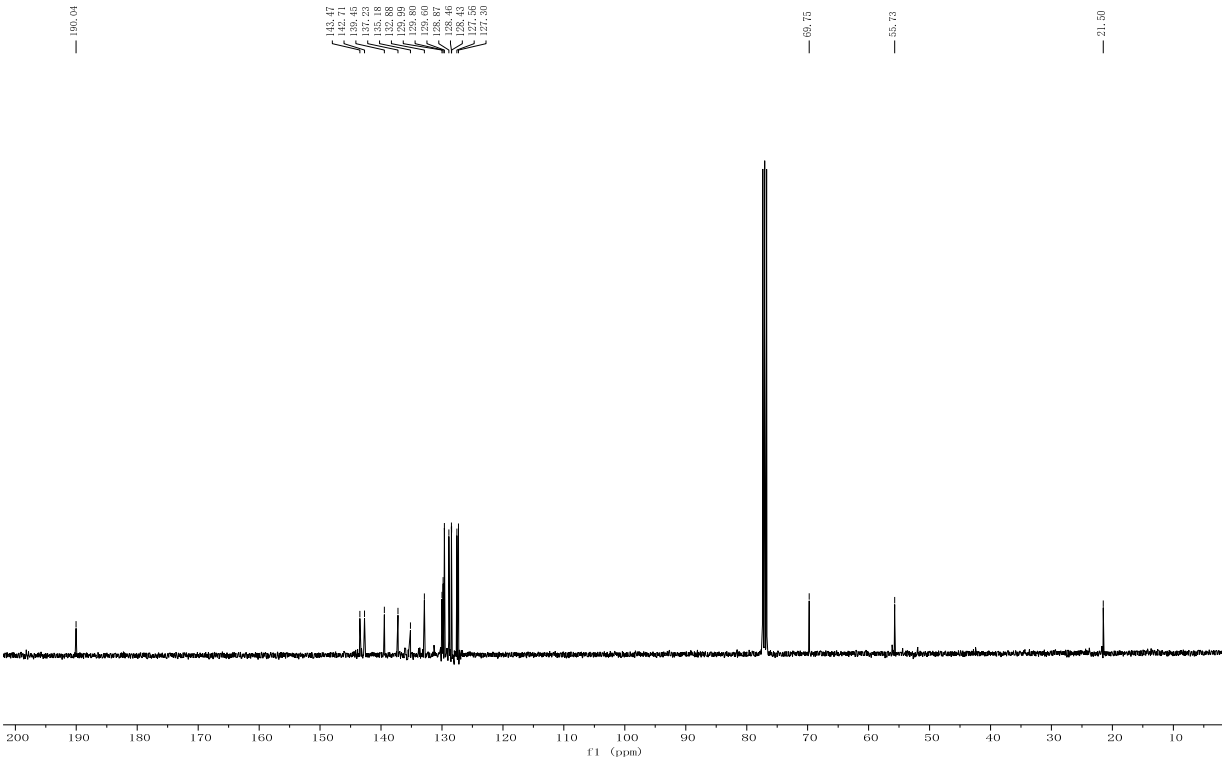
123.85
f1 (ppm)

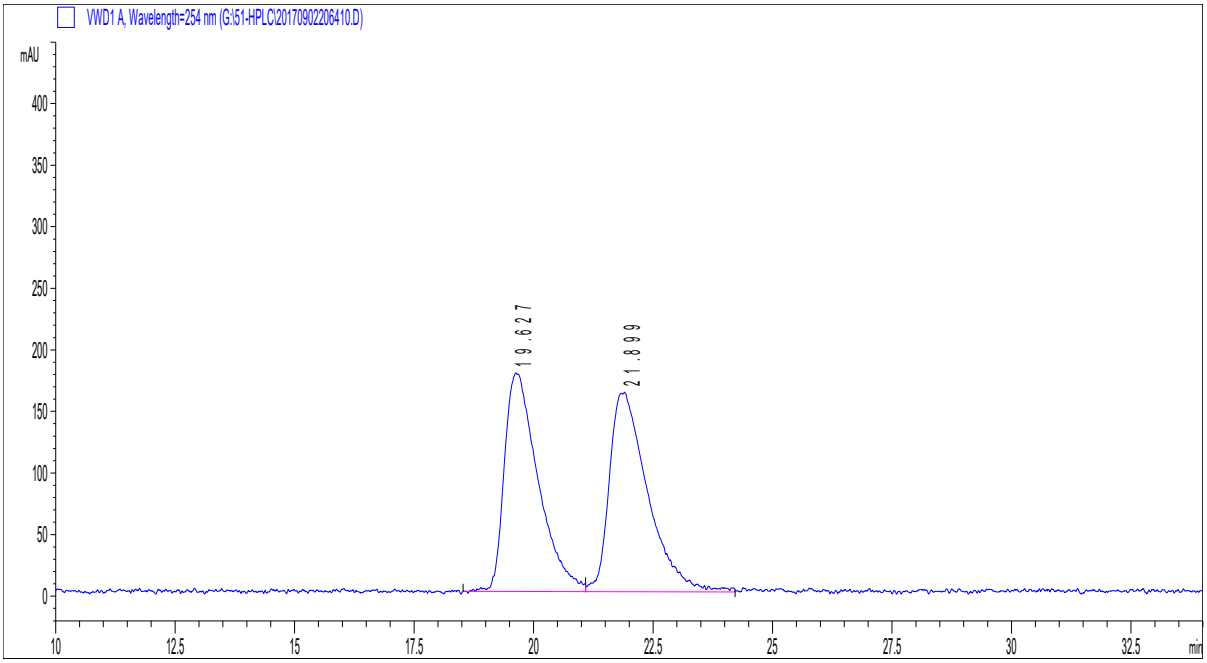

Ph
Ts
N
O
Ph

6


2.19
4.02
4.13
4.37
1.00
1.06
1.88
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
f1 (ppm)

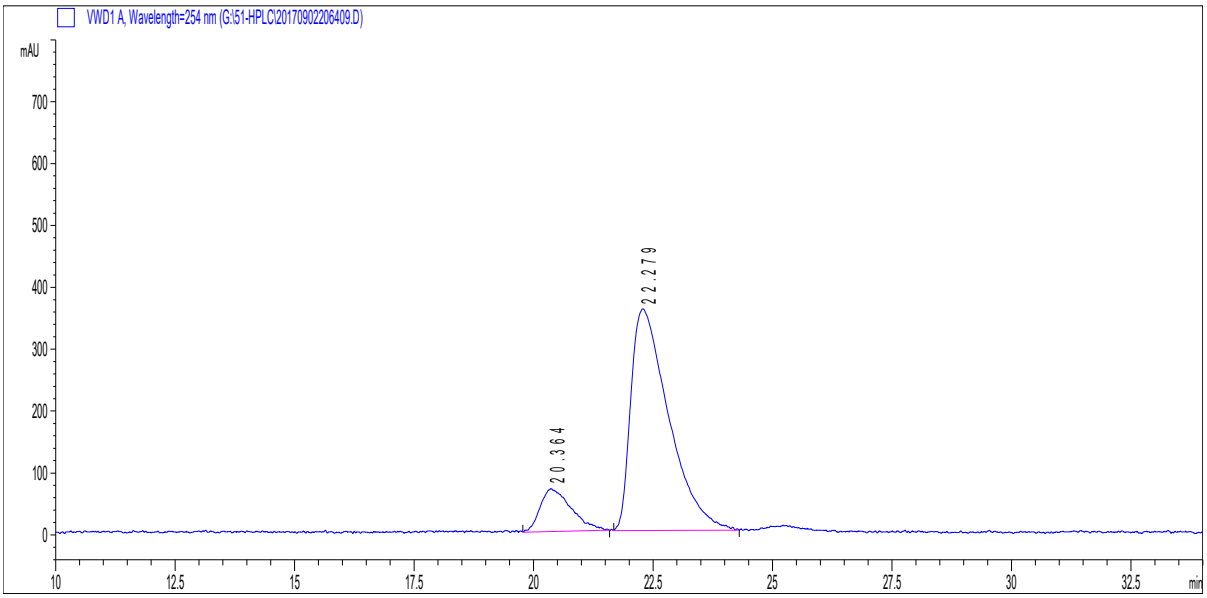

190.04
143.47
142.71
139.45
137.23
135.18
132.88
129.99
129.80
129.60
128.87
128.46
128.43
127.56
127.30
69.75
55.73
21.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

HPLC chromatogram of racemic 3aa



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.627	MF	0.8182	8717.53906	177.56789	49.0440
2	21.899	FM	0.9324	9057.38965	161.89520	50.9560

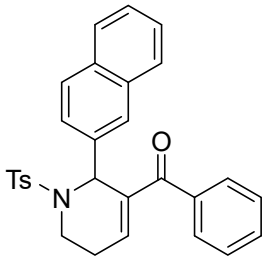
HPLC chromatogram of chiral 3aa



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.364	MM	0.7506	3121.38257	69.31057	13.6582
2	22.279	MM	0.9181	1.97321e4	358.21002	86.3418

X-Ray Crystallography Data

Crystallographic data for **3aq** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1575011. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



3aq

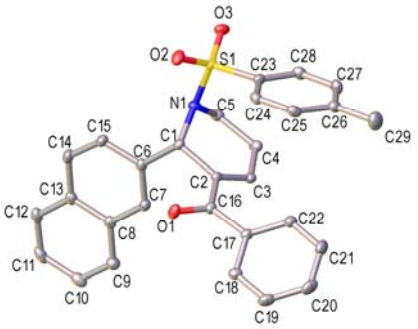


Table S1. Crystal data and structure refinement for **3aq**.

Identification code: **3aq**		
Empirical formula, $C_{29}H_{25}NO_3S$		
Formula weight, 467.56		
Temperature, 173.1500 K		
Wavelength, 0.71073 Å		
Crystal system, Monoclinic		
Space group, P 1 21 1		
Unit cell dimensions	a = 9.769(3) Å	a= 90°.
	b = 13.123(3) Å	b= 114.345(3)°.
	c = 10.039(3) Å	g = 90°.
Volume	1172.6(5) Å3	
Z	2	
Density (calculated)	1.324 Mg/m3	
Absorption coefficient	0.170 mm-1	
F(000)	492	
Crystal size	0.406 x 0.315 x 0.166 mm3	
Theta range for data collection	2.899 to 27.482°.	
Index ranges	-12<=h<=12, -17<=k<=16, -10<=l<=13	
Reflections collected	7830	
Independent reflections	4984 [R(int) = 0.0263]	
Completeness to theta = 26.000°	99.3 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.88525
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4984 / 1 / 308
Goodness-of-fit on F2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0895
R indices (all data)	R1 = 0.0433, wR2 = 0.0909
Absolute structure parameter	-0.05(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.190 and -0.220 e.Å-3

Table S2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters ($Å^2$ x 103) for **3aq**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S1	6054(1)	2631(1)	6739(1)	26(1)
O1	8272(2)	4804(2)	4139(2)	35(1)
O2	7061(3)	1983(2)	6426(2)	35(1)
O3	4939(3)	2204(2)	7158(2)	35(1)
N1	5133(3)	3283(2)	5230(2)	23(1)
C1	6019(3)	3768(2)	4515(3)	22(1)
C2	6447(3)	4850(2)	5076(3)	21(1)
C3	5577(3)	5392(2)	5548(3)	24(1)
C4	4213(3)	4975(2)	5681(3)	28(1)
C5	3811(3)	3889(2)	5095(3)	28(1)
C6	5118(3)	3722(2)	2863(3)	24(1)
C7	4580(3)	4580(2)	2037(3)	25(1)
C8	3714(3)	4525(2)	503(3)	26(1)
C9	3193(3)	5412(3)	-356(3)	31(1)
C10	2334(3)	5337(3)	-1837(3)	35(1)
C11	1965(3)	4381(3)	-2509(3)	37(1)
C12	2473(4)	3507(3)	-1709(3)	35(1)
C13	3372(3)	3552(2)	-177(3)	28(1)
C14	3964(3)	2670(3)	704(3)	33(1)
C15	4814(3)	2757(2)	2163(3)	30(1)
C16	7786(3)	5264(2)	4921(3)	24(1)
C17	8570(3)	6213(2)	5672(3)	24(1)

C18	9327(3)	6761(2)	4995(3)	28(1)
C19	10144(3)	7619(3)	5650(4)	38(1)
C20	10224(4)	7937(2)	6987(4)	42(1)
C21	9501(4)	7402(2)	7676(4)	40(1)
C22	8667(3)	6536(2)	7032(3)	31(1)
C23	7172(3)	3477(2)	8138(3)	25(1)
C24	8635(3)	3684(2)	8317(3)	28(1)
C25	9476(3)	4383(2)	9368(3)	30(1)
C26	8890(3)	4877(2)	10237(3)	31(1)
C27	7436(4)	4641(2)	10052(3)	33(1)
C28	6575(3)	3945(2)	9014(3)	30(1)
C29	9826(5)	5639(3)	11377(4)	52(1)

Table S3. Bond lengths [Å] and angles [°] for **3aq**.

S1-O2	1.430(2)
S1-O3	1.434(2)
S1-N1	1.647(2)
S1-C23	1.770(3)
O1-C16	1.230(3)
N1-C1	1.477(3)
N1-C5	1.475(4)
C1-H1	0.9800
C1-C2	1.521(4)
C1-C6	1.525(4)
C2-C3	1.336(4)
C2-C16	1.483(4)
C3-H3	0.9300
C3-C4	1.496(4)
C4-H4A	0.9700
C4-H4B	0.9700
C4-C5	1.530(4)
C5-H5A	0.9700
C5-H5B	0.9700
C6-C7	1.367(4)
C6-C15	1.419(4)
C7-H7	0.9300

C7-C8	1.421(4)
C8-C9	1.413(4)
C8-C13	1.420(4)
C9-H9	0.9300
C9-C10	1.377(4)
C10-H10	0.9300
C10-C11	1.400(5)
C11-H11	0.9300
C11-C12	1.370(5)
C12-H12	0.9300
C12-C13	1.424(4)
C13-C14	1.426(5)
C14-H14	0.9300
C14-C15	1.358(4)
C15-H15	0.9300
C16-C17	1.493(4)
C17-C18	1.393(4)
C17-C22	1.395(4)
C18-H18	0.9300
C18-C19	1.380(4)
C19-H19	0.9300
C19-C20	1.376(5)
C20-H20	0.9300
C20-C21	1.369(5)
C21-H21	0.9300
C21-C22	1.392(4)
C22-H22	0.9300
C23-C24	1.391(4)
C23-C28	1.384(4)
C24-H24	0.9300
C24-C25	1.384(4)
C25-H25	0.9300
C25-C26	1.386(4)
C26-C27	1.390(4)
C26-C29	1.511(4)
C27-H27	0.9300
C27-C28	1.380(4)
C28-H28	0.9300

C29-H29A	0.9600
C29-H29B	0.9600
C29-H29C	0.9600

O2-S1-O3	120.49(14)
O2-S1-N1	105.75(13)
O2-S1-C23	106.97(14)
O3-S1-N1	106.25(13)
O3-S1-C23	107.86(14)
N1-S1-C23	109.18(13)
C1-N1-S1	117.64(18)
C5-N1-S1	119.4(2)
C5-N1-C1	112.9(2)
N1-C1-H1	108.3
N1-C1-C2	110.4(2)
N1-C1-C6	108.7(2)
C2-C1-H1	108.3
C2-C1-C6	112.8(2)
C6-C1-H1	108.3
C3-C2-C1	120.6(2)
C3-C2-C16	124.1(2)
C16-C2-C1	115.1(2)
C2-C3-H3	118.1
C2-C3-C4	123.9(2)
C4-C3-H3	118.1
C3-C4-H4A	108.8
C3-C4-H4B	108.8
C3-C4-C5	113.7(2)
H4A-C4-H4B	107.7
C5-C4-H4A	108.8
C5-C4-H4B	108.8
N1-C5-C4	113.0(2)
N1-C5-H5A	109.0
N1-C5-H5B	109.0
C4-C5-H5A	109.0
C4-C5-H5B	109.0
H5A-C5-H5B	107.8
C7-C6-C1	122.1(2)

C7-C6-C15	119.0(2)
C15-C6-C1	118.8(2)
C6-C7-H7	119.2
C6-C7-C8	121.6(3)
C8-C7-H7	119.2
C9-C8-C7	121.5(3)
C9-C8-C13	119.6(3)
C13-C8-C7	118.9(3)
C8-C9-H9	119.8
C10-C9-C8	120.3(3)
C10-C9-H9	119.8
C9-C10-H10	119.8
C9-C10-C11	120.4(3)
C11-C10-H10	119.8
C10-C11-H11	119.7
C12-C11-C10	120.6(3)
C12-C11-H11	119.7
C11-C12-H12	119.6
C11-C12-C13	120.8(3)
C13-C12-H12	119.6
C8-C13-C12	118.3(3)
C8-C13-C14	118.4(2)
C12-C13-C14	123.3(3)
C13-C14-H14	119.6
C15-C14-C13	120.8(3)
C15-C14-H14	119.6
C6-C15-H15	119.4
C14-C15-C6	121.2(3)
C14-C15-H15	119.4
O1-C16-C2	118.4(2)
O1-C16-C17	118.7(3)
C2-C16-C17	122.9(2)
C18-C17-C16	116.7(3)
C18-C17-C22	119.0(3)
C22-C17-C16	124.2(3)
C17-C18-H18	119.7
C19-C18-C17	120.5(3)
C19-C18-H18	119.7

C18-C19-H19	120.0
C20-C19-C18	120.1(3)
C20-C19-H19	120.0
C19-C20-H20	119.9
C21-C20-C19	120.2(3)
C21-C20-H20	119.9
C20-C21-H21	119.7
C20-C21-C22	120.6(3)
C22-C21-H21	119.7
C17-C22-H22	120.2
C21-C22-C17	119.6(3)
C21-C22-H22	120.2
C24-C23-S1	119.4(2)
C28-C23-S1	119.9(2)
C28-C23-C24	120.7(3)
C23-C24-H24	120.5
C25-C24-C23	118.9(3)
C25-C24-H24	120.5
C24-C25-H25	119.3
C24-C25-C26	121.4(3)
C26-C25-H25	119.3
C25-C26-C27	118.4(3)
C25-C26-C29	120.6(3)
C27-C26-C29	121.0(3)
C26-C27-H27	119.3
C28-C27-C26	121.3(3)
C28-C27-H27	119.3
C23-C28-H28	120.4
C27-C28-C23	119.3(3)
C27-C28-H28	120.4
C26-C29-H29A	109.5
C26-C29-H29B	109.5
C26-C29-H29C	109.5
H29A-C29-H29B	109.5
H29A-C29-H29C	109.5
H29B-C29-H29C	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3aq**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
S1		30(1)	19(1)	25(1)	2(1)	
O1		36(1)	30(1)	48(1)	-12(1)	
O2		40(1)	25(1)	34(1)	-1(1)	
O3		39(1)	29(1)	32(1)	4(1)	
N1		22(1)	22(1)	22(1)	3(1)	
C1		21(1)	18(1)	25(1)	0(1)	
C2		22(1)	19(1)	21(1)	1(1)	
C3		27(1)	20(1)	22(1)	2(1)	
C4		30(1)	25(1)	36(2)	3(1)	
C5		23(1)	30(2)	30(1)	4(1)	
C6		24(1)	24(1)	25(1)	-4(1)	
C7		26(1)	24(1)	27(1)	-4(1)	
C8		21(1)	32(2)	26(1)	-3(1)	
C9		30(2)	33(2)	30(2)	1(1)	
C10		27(2)	50(2)	29(2)	9(1)	
C11		26(2)	64(2)	23(1)	-3(2)	
C12		31(2)	45(2)	30(2)	-13(1)	
C13		23(1)	34(2)	28(1)	-4(1)	
C14		41(2)	27(1)	33(2)	-10(1)	
C15		37(2)	21(2)	33(2)	-2(1)	
C16		22(1)	23(1)	25(1)	-2(1)	
C17		21(1)	22(1)	26(1)	1(1)	
C18		28(1)	26(2)	31(2)	4(1)	
C19		32(2)	29(1)	50(2)	5(2)	
C20		38(2)	28(2)	48(2)	-6(1)	
C21		47(2)	34(2)	32(2)	-10(1)	
C22		35(2)	27(1)	28(2)	2(1)	
C23		27(1)	22(1)	22(1)	2(1)	
C24		29(2)	32(1)	24(1)	2(1)	
C25		25(1)	37(2)	28(2)	4(1)	
C26		34(2)	32(2)	26(1)	0(1)	
C27		34(2)	38(2)	30(2)	-4(1)	
C28		24(1)	37(2)	30(2)	3(1)	
C29		51(2)	57(2)	45(2)	-18(2)	

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3aq**.

	x	y	z	U(eq)
H1	6944	3374	4762	26
H3	5834	6068	5810	29
H4A	3367	5418	5154	34
H4B	4380	4984	6703	34
H5A	3306	3549	5624	33
H5B	3116	3920	4073	33
H7	4785	5214	2491	30
H9	3432	6051	82	38
H10	1998	5925	-2394	42
H11	1370	4338	-3507	44
H12	2228	2878	-2172	42
H14	3766	2028	275	40
H15	5203	2172	2714	36
H18	9281	6548	4094	34
H19	10640	7983	5187	45
H20	10772	8517	7423	51
H21	9567	7619	8582	48
H22	8178	6176	7505	37
H24	9040	3359	7740	33
H25	10455	4524	9495	37
H27	7035	4958	10640	39
H28	5605	3793	8905	36
H29A	10801	5693	11366	78
H29B	9930	5416	12325	78
H29C	9341	6292	11164	78

Table S6. Torsion angles [°] for **3aq**.

S1-N1-C1-C2	-91.4(2)
S1-N1-C1-C6	144.45(19)
S1-N1-C5-C4	88.7(3)
S1-C23-C24-C25	177.0(2)
S1-C23-C28-C27	-176.8(2)
O1-C16-C17-C18	27.7(4)
O1-C16-C17-C22	-148.0(3)
O2-S1-N1-C1	-48.0(2)
O2-S1-N1-C5	169.0(2)
O2-S1-C23-C24	24.1(3)
O2-S1-C23-C28	-157.7(2)
O3-S1-N1-C1	-177.19(19)
O3-S1-N1-C5	39.8(2)
O3-S1-C23-C24	155.1(2)
O3-S1-C23-C28	-26.7(3)
N1-S1-C23-C24	-89.9(2)
N1-S1-C23-C28	88.4(2)
N1-C1-C2-C3	-28.7(3)
N1-C1-C2-C16	156.8(2)
N1-C1-C6-C7	113.7(3)
N1-C1-C6-C15	-65.5(3)
C1-N1-C5-C4	-55.9(3)
C1-C2-C3-C4	5.0(4)
C1-C2-C16-O1	13.0(4)
C1-C2-C16-C17	-166.9(2)
C1-C6-C7-C8	-178.6(2)
C1-C6-C15-C14	177.3(3)

C2-C1-C6-C7	-9.1(4)
C2-C1-C6-C15	171.7(2)
C2-C3-C4-C5	-5.2(4)
C2-C16-C17-C18	-152.4(3)
C2-C16-C17-C22	31.8(4)
C3-C2-C16-O1	-161.4(3)
C3-C2-C16-C17	18.7(4)
C3-C4-C5-N1	29.9(3)
C5-N1-C1-C2	53.9(3)
C5-N1-C1-C6	-70.3(3)
C6-C1-C2-C3	93.1(3)
C6-C1-C2-C16	-81.4(3)
C6-C7-C8-C9	-178.2(3)
C6-C7-C8-C13	1.6(4)
C7-C6-C15-C14	-2.0(4)
C7-C8-C9-C10	-178.9(3)
C7-C8-C13-C12	178.5(3)
C7-C8-C13-C14	-2.4(4)
C8-C9-C10-C11	0.1(5)
C8-C13-C14-C15	1.1(4)
C9-C8-C13-C12	-1.7(4)
C9-C8-C13-C14	177.4(3)
C9-C10-C11-C12	-1.1(5)
C10-C11-C12-C13	0.7(5)
C11-C12-C13-C8	0.7(5)
C11-C12-C13-C14	-178.3(3)
C12-C13-C14-C15	-179.9(3)
C13-C8-C9-C10	1.3(4)
C13-C14-C15-C6	1.1(5)

C15-C6-C7-C8	0.6(4)
C16-C2-C3-C4	179.0(3)
C16-C17-C18-C19	-176.8(3)
C16-C17-C22-C21	176.2(3)
C17-C18-C19-C20	0.4(5)
C18-C17-C22-C21	0.6(4)
C18-C19-C20-C21	0.3(5)
C19-C20-C21-C22	-0.5(5)
C20-C21-C22-C17	0.0(5)
C22-C17-C18-C19	-0.8(4)
C23-S1-N1-C1	66.7(2)
C23-S1-N1-C5	-76.2(2)
C23-C24-C25-C26	-0.2(4)
C24-C23-C28-C27	1.4(4)
C24-C25-C26-C27	1.3(5)
C24-C25-C26-C29	-179.9(3)
C25-C26-C27-C28	-1.1(5)
C26-C27-C28-C23	-0.2(5)
C28-C23-C24-C25	-1.2(4)
C29-C26-C27-C28	-179.9(3)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for **3aq** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)