Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2018

Supporting Information

Transition Metal-Free Aminofluorination of β,γ-Unsaturated Hydrazones: Base-Controlled Regioselective Synthesis of Fluorinated Dihydropyrazole and Tetrahydropyridazine Derivatives

Juan Zhao, Min Jiang* and Jin-Tao Liu*

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

jtliu@sioc.ac.cn, *jiangmin@sioc.ac.cn*

General information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Melting points were measured on a melt-Temp apparatus and uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM 400 spectrometer (400 MHz) with TMS as internal standard. ^{19}F NMR spectra were taken on a Bruker AM 400 (376 MHz) spectrometer with $CFCl_3$ as external standard. ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian AM-400 spectrometer (100 MHz) or Agilent AM-400 (100 MHz) spectrometer with TMS as internal standard. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz). Mass spectra were taken on a HP5989A spectrometer. High-resolution mass data were obtained on a high-resolution mass spectrometer in the EI mode. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was performed using 300-400 mesh silica gels.

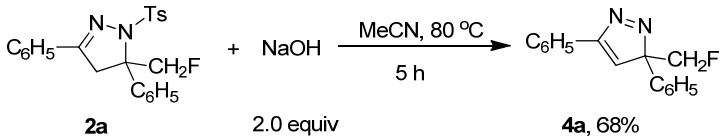
Typical procedure for K_2HPO_4-promoted reaction of 1

To a reactor charged with hydrazones **1** (0.2 mmol), Selectfluor (0.24 mmol) and K_2HPO_4 (0.4 mmol), was added CH_3CN (4 mL) under Ar atmosphere. The mixture was stirred at 100 ^{o}C for 1h. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give **2** (petroleum ether /ethyl acetate = 10:1).

Typical procedure for $NaHCO_3$-promoted reaction of 1

To a reactor charged with hydrazones **1** (0.2 mmol), Selectfluor (0.24 mmol) and $NaHCO_3$ (0.4 mmol), was added CH_3CN (4 mL) under Ar atmosphere. The mixture was stirred at 100 ^{o}C for 1h. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give **3** (petroleum ether /ethyl acetate = 10:1).

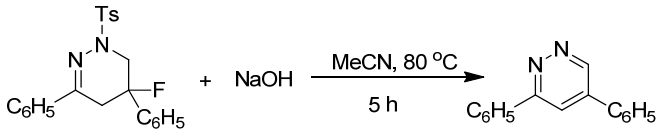
Deprotection of **2a** in the presence of NaOH



2a 2.0 equiv **4a**, 68%

A mixture of **2a** (0.2 mmol), NaOH (0.4 mmol) and CH_3CN (4.0 mL) was stirred at 80 ^oC for 5h under Ar atmosphere. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give **4a** (petroleum ether /ethyl acetate = 10:1).

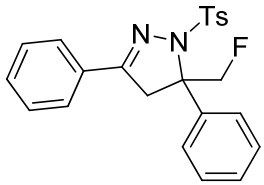
Deprotection of **3a** in the presence of NaOH



3a 2.0 equiv **M**, 80%

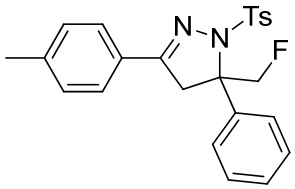
A mixture of **3a** (0.2 mmol), NaOH (0.4 mmol) and CH_3CN (4.0 mL) was stirred at 80 ^oC for 5h under Ar atmosphere. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give compound **M** (petroleum ether /ethyl acetate = 10:1).

Compound characterization



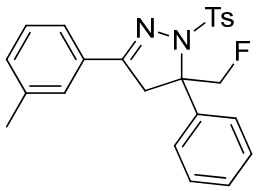
5-(Fluoromethyl)-3,5-diphenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2a):

White solid, mp 141-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73-7.71 (m, 2H), 7.41-7.38 (m, 5H), 7.26-7.21 (m, 1H), 7.16-7.14 (m, 4H), 7.06-7.04 (m, 2H), 5.42 (dd, *J* = 46.8, 9.6 Hz, 1H), 5.14 (dd, *J* = 46.8, 9.6 Hz, 1H), 3.89 (d, *J* = 18.0 Hz, 1H), 3.49 (d, *J* = 17.6 Hz, 1H), 2.33 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.0, 143.2, 138.9, 136.4, 130.7, 130.4, 129.0, 128.7, 128.5, 128.3, 127.4, 126.7, 126.1, 84.3 (d, *J* = 176.3 Hz), 73.1 (d, *J* = 19.8 Hz), 47.8 (d, *J* = 3.0 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -221.14 (t, *J* = 46.8 Hz, 1F); MS (EI) *m/z* (%): 408 (M^+, 15), 253 (100), 191 (20), 103 (42), 91 (47), 77 (24); HRMS (EI) calcd for $C_{23}H_{21}FN_2O_2S$ (M^+) 408.1308, found 408.1302.



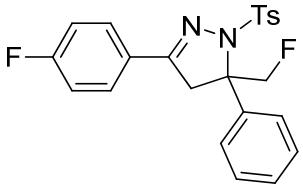
5-(Fluoromethyl)-5-phenyl-3-(p-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2b):

White solid, mp 155-157 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67-7.65 (m, 2H), 7.43-7.40 (m, 2H), 7.28-7.24 (m, 3H), 7.20-7.17 (m, 4H), 7.09-7.07 (m, 2H), 5.47 (dd, *J* = 46.8, 9.2 Hz, 1H), 5.16 (dd, *J* = 46.8, 9.4 Hz, 1H), 3.91 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.51 (dd, *J* = 17.6, 1.2 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 143.1, 140.9, 138.7, 136.3, 129.4, 128.9, 128.5, 128.3, 127.9, 127.4, 126.7, 126.2, 84.4 (d, *J* = 175.9 Hz), 72.9 (d, *J* = 20.1 Hz), 47.9 (d, *J* = 2.8 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -220.85 (t, *J* = 46.8 Hz, 1F); MS (EI) *m/z* (%): 422 (M^+, 17), 267 (65), 149 (46), 119 (100), 91 (68), 57 (43); HRMS (EI) calcd for $C_{24}H_{23}FN_2O_2S$ (M+) 422.1464, found 422.1454.



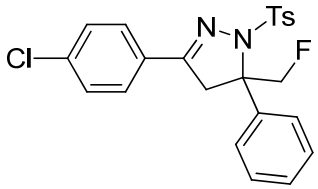
5-(Fluoromethyl)-5-phenyl-3-(m-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2c):

White solid, mp 120-121 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.51-7.49 (m, 1H), 7.39-7.37 (m, 2H), 7.31-7.27 (m, 1H), 7.24-7.20 (m, 2H), 7.16-7.13 (m, 4H), 7.06-7.04 (m, 2H), 5.42 (dd, *J* = 46.8, 9.6 Hz, 1H), 5.14 (dd, *J* = 46.8, 9.2 Hz, 1H), 3.88 (d, *J* = 17.2 Hz, 1H), 3.49 (d, *J* = 17.6 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 143.2, 138.7, 138.5, 136.3, 131.3, 130.6, 129.0, 128.6, 128.5, 128.3, 127.4, 127.3, 126.2, 123.9, 84.4 (d, *J* = 176.3 Hz), 72.9 (d, *J* = 19.9 Hz), 47.9 (d, *J* = 2.7 Hz), 21.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -221.09 (t, *J* = 46.8 Hz, 1F); MS (ESI, *m/z*): 423.1 (M + H^+), 445.1 (M + Na^+); HRMS (ESI): calcd for $C_{24}H_{24}FN_2O_2S$ (M + H^+) 423.1537, found 423.1532.



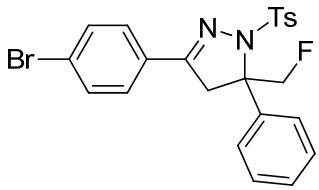
5-(Fluoromethyl)-3-(4-fluorophenyl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2d):

White solid, mp 150-151 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.71 (m, 2H), 7.44-7.42 (m, 2H), 7.30-7.26 (m, 1H), 7.23-7.18 (m, 4H), 7.15-7.10 (m, 4H), 5.43 (dd, *J* = 46.8, 9.6 Hz, 1H), 5.20 (dd, *J* = 46.8, 9.4 Hz, 1H), 3.90 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.49 (dd, *J* = 17.6, 1.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.0 (d, *J* = 249.8 Hz), 152.0, 143.3, 138.8, 136.3, 129.0, 128.7, 128.6 (d, *J* = 5.0 Hz), 128.4, 127.4, 127.0 (d, *J* = 3.2 Hz), 126.1, 115.9 (d, *J* = 21.9 Hz), 84.3 (d, *J* = 176.2 Hz), 73.2 (d, *J* = 19.7 Hz), 47.8 (d, *J* = 3.0 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -109.17~-109.25 (m, 1F), -221.24 (t, *J* = 46.8 Hz, 1F); MS (EI) *m/z* (%): 426 (M^+, 24), 271 (100), 121 (27), 91 (42), 57 (20); HRMS (EI) calcd for $C_{23}H_{20}F_2N_2O_2S$ (M+) 426.1214, found 426.1219.



3-(4-Chlorophenyl)-5-(fluoromethyl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2e):

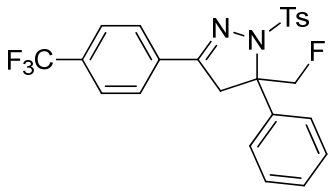
White solid, mp 159-162 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69-7.66 (m, 2H), 7.44-7.39 (m, 4H), 7.31-7.27 (m, 1H), 7.23-7.16 (m, 4H), 7.12-7.10 (m, 2H), 5.42 (dd, *J* = 46.8, 9.4 Hz, 1H), 5.20 (dd, *J* = 46.8, 9.6 Hz, 1H), 3.89 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.49 (dd, *J* = 17.6, 1.6 Hz, 1H), 2.38 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.9, 143.4, 138.7, 136.4, 136.2, 129.2, 129.1, 129.0, 128.6, 128.4, 127.9, 127.4, 126.0, 84.3 (d, *J* = 176.3 Hz), 73.4 (d, *J* = 19.7 Hz), 47.7 (d, *J* = 3.1 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -221.36 (t, *J* = 46.8 Hz, 1F); MS (EI) *m/z* (%): 442 (M^+, 25), 289 (31), 288 (20), 287 (100), 137 (22), 91 (45); HRMS (EI) calcd for $C_{23}H_{20}ClFN_2O_2S$ (M^+) 442.0918, found 442.0915.



3-(4-Bromophenyl)-5-(fluoromethyl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2f):

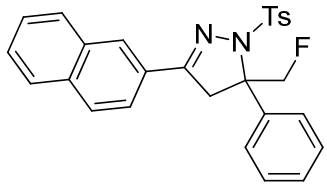
White solid, mp 144-147 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.50 (m, 4H), 7.40-7.37 (m, 2H), 7.27-7.22 (m, 1H), 7.19-7.12 (m, 4H), 7.07-7.05 (m, 2H), 5.38 (dd, *J* = 46.4, 9.6 Hz, 1H), 5.16 (dd, *J* = 46.4, 9.4 Hz, 1H), 3.85 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.44 (dd, *J* = 17.6, 1.6 Hz, 1H), 2.39 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.9, 143.4, 138.7, 136.2, 132.0, 129.7, 129.0, 128.6, 128.4, 128.1, 127.4, 126.0, 124.8, 84.2 (d, *J* = 176.2 Hz), 73.4 (d, *J* = 19.8 Hz), 47.6 (d, *J* = 3.0 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -221.45 (t, *J* = 46.4 Hz, 1F); MS (EI) *m/z* (%): 486 (M^+, 31), 333 (92), 331 (100), 191 (36), 102 (34), 91 (81); HRMS (EI) calcd for $C_{23}H_{20}BrFN_2O_2S$ (M^+)

486.0413, found 486.0418.



5-(Fluoromethyl)-5-phenyl-1-tosyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (2g):

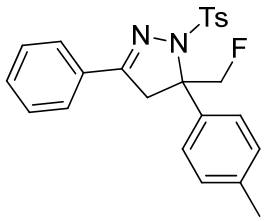
White solid, mp 119-121 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.80 (m, 2H), 7.65-7.63 (m, 2H), 7.42-7.39 (m, 2H), 7.28-7.24 (m, 1H), 7.20-7.13 (m, 4H), 7.09-7.07 (m, 2H), 5.37 (dd, *J* = 46.8, 9.6 Hz, 1H), 5.21 (dd, *J* = 46.8, 9.6 Hz, 1H), 3.90 (d, *J* = 17.6 Hz, 1H), 3.49 (dd, *J* = 17.6, 1.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.4, 143.6, 138.7, 136.2, 134.1, 131.9 (q, *J* = 32.6 Hz), 129.1, 128.7, 128.5, 127.5, 126.9, 126.0, 125.7 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 270.8 Hz), 84.2 (d, *J* = 176.3 Hz), 73.7 (d, *J* = 19.5 Hz), 47.5 (d, *J* = 3.4 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.88 (s, 3F), -221.89 (t, *J* = 46.8 Hz, 1F); MS (EI) *m/z* (%): 476 (M^+, 53), 443 (59), 322 (21), 321 (100), 155 (36), 91 (37); HRMS (EI) calcd for $C_{24}H_{20}F_4N_2O_2S$ (M^+) 476.1182, found 476.1179.



5-(Fluoromethyl)-3-(naphthalen-2-yl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2h):

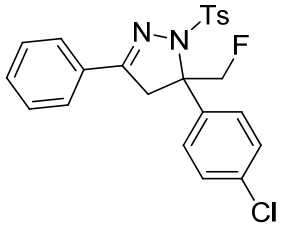
White solid, mp 186-187 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08-8.06 (m, 1H), 7.90-7.80 (m, 4H), 7.54-7.48 (m, 2H), 7.43-7.41 (m, 2H), 7.24-7.22 (m, 1H), 7.17-7.13 (m, 4H), 7.07-7.05 (m, 2H), 5.46 (dd, *J* = 46.8, 9.2 Hz, 1H), 5.18 (dd, *J* = 46.8, 9.6 Hz, 1H), 4.01 (d, *J* = 17.6 Hz, 1H), 3.63 (d, *J* = 17.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 143.3, 138.8, 136.3, 134.2, 132.9, 129.0, 128.6, 128.5, 128.4, 128.3, 127.9, 127.4, 127.3, 127.0, 126.8, 126.2, 123.5, 84.4 (d, *J* = 176.3

Hz), 73.2 (d, J = 19.8 Hz), 47.8 (d, J = 3.0 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -221.02 (t, J = 46.8 Hz, 1F); MS (EI) *m/z* (%): 458 (M^+, 21), 304 (25), 303 (100), 153 (43), 152 (30), 91 (51); HRMS (ESI): calcd for $C_{27}H_{24}FN_2O_2S$ (M + H^+) 459.1537, found 459.1535.



5-(Fluoromethyl)-3-phenyl-5-(p-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2i):

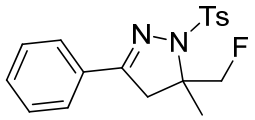
White solid, mp 112-114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74-7.72 (m, 2H), 7.42-7.39 (m, 5H), 7.05-7.01 (m, 4H), 6.94-6.92 (m, 2H), 5.40 (dd, J = 46.8, 9.2 Hz, 1H), 5.15 (dd, J = 46.8, 9.6 Hz, 1H), 3.87 (d, J = 17.6 Hz, 1H), 3.48 (d , J = 17.6 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 143.2, 138.3, 136.4, 135.7, 130.8, 130.4, 129.1, 128.9, 128.7, 127.4, 126.7, 126.0, 84.4 (d, J = 175.9 Hz), 72.9 (d, J = 19.8 Hz), 47.7 (d, J = 3.0 Hz), 21.6, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -221.37 (t, J = 46.8 Hz, 1F); MS (EI) *m/z* (%): 422 (M^+, 34), 267 (100), 163 (49), 103 (47), 91 (91), 84 (42); HRMS (EI) calcd for $C_{24}H_{23}FN_2O_2S$ (M^+) 422.1464, found 422.1457.



5-(4-Chlorophenyl)-5-(fluoromethyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2j):

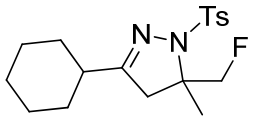
White solid, mp 101-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73-7.71 (m, 2H), 7.44-7.39 (m, 5H), 7.10-7.05 (m, 6H), 5.40 (dd, J = 46.6, 9.6 Hz, 1H), 5.05 (dd, J = 46.6, 9.6 Hz, 1H), 3.88 (dd, J = 17.6, 1.2 Hz, 1H), 3.44 (dd, J = 17.6, 1.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 143.6, 137.2, 136.2, 134.5, 130.6,

130.5, 129.1, 128.8, 128.5, 127.6, 127.2, 126.7, 84.2 (d, J = 176.3 Hz), 72.4 (d, J = 20.5 Hz), 47.8 (d, J = 2.7 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -220.64 (t, J = 46.6 Hz, 1F); MS (EI) *m/z* (%): 442 (M^+, 27), 289 (34), 287 (100), 103 (63), 91 (75), 77 (25); HRMS (EI) calcd for $C_{23}H_{20}ClFN_2O_2S$ (M+) 442.0918, found 442.0919.



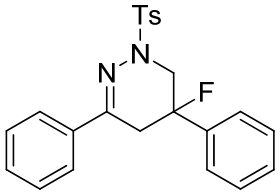
5-(Fluoromethyl)-5-methyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2k):

White solid, mp 129-131 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90-7.89 (m, 2H), 7.64-7.63 (m, 2H), 7.37-7.36 (m, 3H), 7.29-7.24 (m, 3H), 4.78 (dd, J = 47.0, 9.4 Hz, 1H), 4.68 (dd, J = 47.0, 9.2 Hz, 1H), 3.47 (d, J = 18.0 Hz, 1H), 2.97 (d, J = 18.0 Hz, 1H), 2.39 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.5, 143.9, 136.9, 131.0, 130.3, 129.4, 128.6, 128.0, 126.6, 85.9 (d, J = 175.4 Hz), 70.1 (d, J = 19.5 Hz), 44.6 (d, J = 3.1 Hz), 21.6, 21.4 (d, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -222.17 (t, J = 47.0 Hz, 1F); MS (EI) *m/z* (%): 346 (M^+, 71), 313 (57), 191 (100), 103 (38), 91 (37); HRMS (EI) calcd for $C_{18}H_{19}FN_2O_2S$ (M^+) 346.1151, found 346.1158.



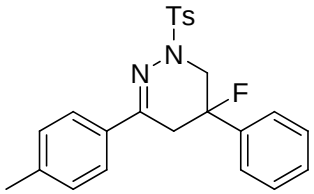
3-Cyclohexyl-5-(fluoromethyl)-5-methyl-1-tosyl-4,5-dihydro-1H-pyrazole (2l):

White solid, mp 84-86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84-7.82 (m, 2H), 7.27-7.24 (m, 2H), 4.74-4.44 (m, 2H), 3.02 (d, J = 17.2 Hz, 1H), 2.48 (d, J = 17.2 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 1H), 1.82-1.74 (m, 4H), 1.67-1.64 (m, 1H), 1.35 (d, J = 1.2 Hz, 3H), 1.31-1.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.2, 143.5, 137.1, 129.2, 128.0, 86.1 (d, J = 174.9 Hz), 69.0 (d, J = 19.9 Hz), 45.1 (d, J = 2.9 Hz), 38.2, 30.2, 30.0, 25.8, 25.7, 25.6, 21.6, 20.8 (d, J = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -222.18 (t, J = 47.0 Hz, 1F); MS (EI) *m/z* (%): 352 (M^+, 32), 320 (23), 319 (100), 237 (60), 155 (53), 91 (41); HRMS (EI) calcd for $C_{18}H_{25}FN_2O_2S$ (M^+) 352.1621, found 352.1620.



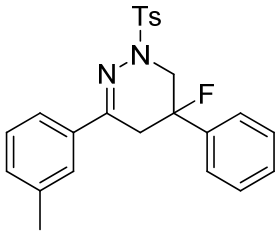
5-Fluoro-3,5-diphenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3a):

White solid, mp 188-190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84-7.82 (m, 2H), 7.71-7.69 (m, 2H), 7.44-7.33 (m, 8H), 7.30-7.28 (m, 2H), 4.20-4.14 (m, 1H), 3.36-3.26 (m, 1H), 3.11-2.88 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 144.2, 139.9 (d, *J* = 21.5 Hz), 136.0, 133.6, 129.8, 129.6, 128.9 (d, *J* = 3.0 Hz), 128.5, 128.4, 125.5, 124.2, 124.1, 89.4 (d, *J* = 179.8 Hz), 50.7 (d, *J* = 25.4 Hz), 35.0 (d, *J* = 26.0 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -149.14~-149.38 (m, 1F); MS (EI) *m/z* (%): 408 (M^+, 68), 253 (100), 205 (61), 204 (53), 104 (64), 103(74); HRMS (EI) calcd for $C_{23}H_{21}FN_2O_2S$ (M^+) 408.1308, found 408.1313.



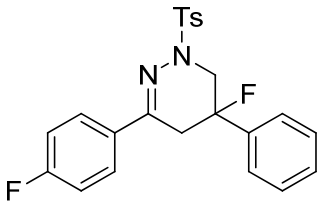
5-Fluoro-5-phenyl-3-(p-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridazine (3b):

White solid, mp 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.81 (m, 2H), 7.61-7.59 (m, 2H), 7.41-7.27 (m, 7H), 7.17-7.15 (m, 2H), 4.16-4.11 (m, 1H), 3.34-3.23 (m, 1H), 3.08-2.86 (m, 2H), 2.39 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 144.1, 140.0 (d, *J* = 21.6 Hz), 139.9, 133.6, 133.3, 129.5, 129.2, 128.9 (d, *J* = 4.3 Hz), 128.4, 125.4, 124.2, 124.1, 89.5 (d, *J* = 179.6 Hz), 50.7 (d, *J* = 25.3 Hz), 35.0 (d, *J* = 25.7 Hz), 21.6, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -149.04~-149.28 (m, 1F); MS (ESI, *m/z*): 423.1 (M + H^+); HRMS (ESI): calcd for $C_{24}H_{24}FN_2O_2S$ (M + H^+) 423.1537, found 423.1536.



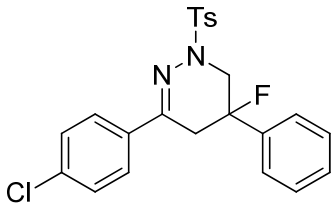
5-Fluoro-5-phenyl-3-(m-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridazine (3c):

White solid, mp 161-163 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.83 (m, 2H), 7.51-7.50 (m, 2H), 7.44-7.38 (m, 3H), 7.35-7.33 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.19-7.17 (m, 1H), 4.19-4.13 (m, 1H), 3.35-3.24 (m, 1H), 3.10-2.86 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.5, 144.2, 140.0 (d, J = 21.7 Hz), 138.1, 136.0, 133.6, 130.6, 129.6, 128.9 (d, J = 4.4 Hz), 128.4, 126.2, 124.2, 124.1, 122.7, 89.5 (d, J = 180.0 Hz), 50.7 (d, J = 25.0 Hz), 35.1 (d, J = 26.0 Hz), 21.6, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -149.15~-149.39 (m, 1F); MS (ESI, *m/z*): 423.2 (M + H^+); HRMS (ESI): calcd for $C_{24}H_{24}FN_2O_2S$ (M + H^+) 423.1537, found 423.1536.



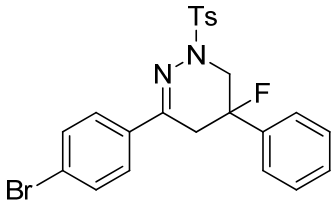
5-Fluoro-3-(4-fluorophenyl)-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3d):

White solid, mp 167-168 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.81 (m, 2H), 7.70-7.66 (m, 2H), 7.44-7.29 (m, 7H), 7.07-7.02 (m, 2H), 4.21-4.15 (m, 1H), 3.35-3.24 (m, 1H), 3.07-2.84 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7 (d, J = 248.4 Hz), 146.2, 144.3, 139.8 (d, J = 21.6 Hz), 133.6, 132.2 (d, J = 2.9 Hz), 129.6, 128.9, 128.4, 127.4 (d, J = 8.3 Hz), 124.2, 124.1, 115.5 (d, J = 21.6 Hz), 89.3 (d, J = 180.2 Hz), 50.5 (d, J = 25.1 Hz), 34.9 (d, J = 26.0 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.97~-111.05 (m, 1F), -149.32~-149.56 (m, 1F); MS (ESI, *m/z*): 427.1 (M + H^+); HRMS (ESI): calcd for $C_{23}H_{21}F_2N_2O_2S$ (M + H^+) 427.1286, found 427.1286.



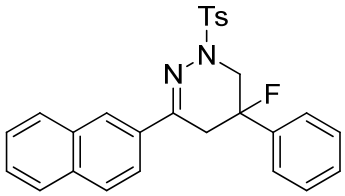
3-(4-Chlorophenyl)-5-fluoro-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3e):

White solid, mp 160-162 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.81 (m, 2H), 7.64-7.62 (m, 2H), 7.42-7.24 (m, 9H), 4.23-4.18 (m, 1H), 3.33-3.23 (m, 1H), 3.05-2.83 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.0, 144.4, 139.7 (d, J = 21.3 Hz), 135.8, 134.5, 133.6, 129.7, 129.0, 128.7, 128.3, 126.7, 124.2, 124.1, 89.2 (d, J = 180.1 Hz), 50.5 (d, J = 25.0 Hz), 34.8 (d, J = 25.9 Hz), 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -149.56~-149.80 (m, 1F); MS (EI) *m/z* (%): 442 (M^+, 39), 287 (69), 204 (100), 203 (52), 102 (65), 91(85); HRMS (ESI): calcd for $C_{23}H_{21}ClFN_2O_2S$ ($M + H^+$) 443.0991, found 443.0987.



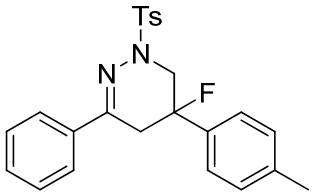
3-(4-Bromophenyl)-5-fluoro-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3f):

White solid, mp 177-179 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.80 (m, 2H), 7.57-7.55 (m, 2H), 7.49-7.47 (m, 2H), 7.42-7.38 (m, 3H), 7.34-7.28 (m, 4H), 4.23-4.17 (m, 1H), 3.35-3.24 (m, 1H), 3.05-2.83 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.0, 144.3, 139.7 (d, J = 21.6 Hz), 134.9, 133.6, 131.7, 129.6, 129.0, 128.3, 127.0, 124.2, 124.1, 124.0, 89.2 (d, J = 179.9 Hz), 50.5 (d, J = 25.1 Hz), 34.8 (d, J = 26.1 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -149.53~-149.77 (m, 1F); MS (ESI, *m/z*): 487.0 ($M + H^+$); HRMS (ESI): calcd for $C_{23}H_{21}BrFN_2O_2S$ ($M + H^+$) 487.0486, found 487.0482.



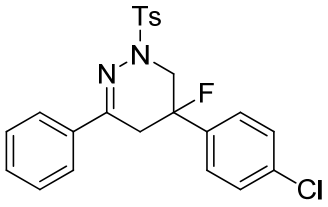
5-Fluoro-3-(naphthalen-2-yl)-5-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3g):

White solid, mp 178-179 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09-8.07 (m, 1H), 7.92-7.77 (m, 6H), 7.50-7.37 (m, 7H), 7.31-7.29 (m, 2H), 4.26-4.21 (m, 1H), 3.40-3.29 (m, 1H), 3.26-3.00 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 144.3, 140.0 (d, *J* = 21.4 Hz), 133.9, 133.7, 133.5, 132.9, 129.6, 128.9 (d, *J* = 3.4 Hz), 128.5, 128.4, 128.3, 127.7, 127.0, 126.5, 125.1, 124.3, 124.2, 123.0, 89.4 (d, *J* = 179.9 Hz), 50.7 (d, *J* = 25.1 Hz), 34.9 (d, *J* = 26.1 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -149.44~-149.68 (m, 1F); MS (ESI, *m/z*): 459.2 (M + H^+); HRMS (ESI): calcd for $C_{27}H_{24}FN_2O_2S$ (M + H^+) 459.1537, found 459.1526.



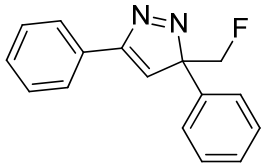
5-Fluoro-3-phenyl-5-(p-tolyl)-1-tosyl-1,4,5,6-tetrahydropyridazine (3h):

White solid, mp 136-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84-7.82 (m, 2H), 7.71-7.69 (m, 2H), 7.37-7.36 (m, 3H), 7.30-7.28 (m, 2H), 7.23 (s, 4H), 4.20-4.14 (m, 1H), 3.32-3.22 (m, 1H), 3.09-2.86 (m, 2H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 144.2, 138.8, 137.0 (d, *J* = 21.7 Hz), 136.0, 133.7, 129.8, 129.6 (d, *J* = 3.3 Hz), 128.5, 128.4, 125.5, 124.2, 124.1, 89.4 (d, *J* = 179.5 Hz), 50.7 (d, *J* = 25.3 Hz), 34.9 (d, *J* = 26.1 Hz), 21.6, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -148.32~-148.56 (m, 1F); MS (ESI, *m/z*): 423.1 (M + H^+); HRMS (ESI): calcd for $C_{24}H_{24}FN_2O_2S$ (M + H^+) 423.1537, found 423.1529.



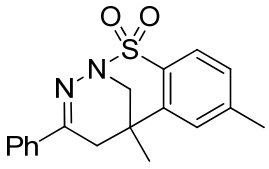
5-(4-Chlorophenyl)-5-fluoro-3-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (3i):

White solid, mp 140-143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87-7.85 (m, 2H), 7.76-7.71 (m, 2H), 7.43-7.37 (m, 5H), 7.34-7.28 (m, 4H), 4.14-4.08 (m, 1H), 3.43-3.33 (m, 1H), 3.13-2.90 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.1, 144.4, 138.5 (d, *J* = 22.3 Hz), 135.8, 135.0, 133.5, 129.9, 129.6, 129.1, 128.6, 128.4, 125.8 (d, *J* = 8.9 Hz), 125.5, 89.3 (d, *J* = 180.5 Hz), 50.5 (d, *J* = 25.8 Hz), 35.0 (d, *J* = 25.8 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -148.23~-148.46 (m, 1F); MS (ESI, *m/z*): 443.0 (M + H^+); HRMS (ESI): calcd for $C_{23}H_{21}ClFN_2O_2S$ (M + H^+) 443.0991, found 443.0986.



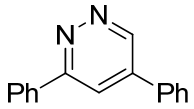
3-(Fluoromethyl)-3,5-diphenyl-3H-pyrazole (4a):

White solid, mp 94-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11-8.10 (m, 2H), 7.60-7.58 (m, 2H), 7.50-7.35 (m, 7H), 5.06-4.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 132.6 (d, *J* = 4.1 Hz), 130.4 (d, *J* = 1.7 Hz), 130.1, 129.7, 129.0, 128.9, 128.8, 127.7, 127.4, 103.9 (d, *J* = 19.0 Hz), 84.2 (d, *J* = 185.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -218.46 (t, *J* = 46.6 Hz, 1F); MS (EI) *m/z* (%): 252 (M^+, 10), 224 (17), 192 (18), 191 (100), 189 (25); HRMS (EI) calcd for $C_{16}H_{13}FN_2$ (M+) 252.1063, found 252.1068.



6,8-dimethyl-4-phenyl-5,6-dihydro-2,6-methanobenzo[g][1,2,3]thiadiazocine 1,1-dioxide (5):

White solid, mp 66-68 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75-7.73 (m, 1H), 7.53-7.51 (m, 2H), 7.35-7.25 (m, 3H), 7.17-7.15 (m, 1H), 7.04 (s, 1H), 3.38 (d, *J* = 15.2Hz, 1H), 3.10 (dd, *J* = 22.0, 17.6 Hz, 2H), 2.82 (d, *J* = 15.2Hz, 1H), 2.32 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 143.8, 135.3, 132.6, 130.6, 130.5, 129.6, 128.5, 128.4, 127.0, 126.2, 69.5, 48.9, 41.2, 31.4, 21.6; MS (ESI, *m/z*): 327.1133 (M + H^+); HRMS (ESI): calcd for $C_{18}H_{18}N_2O_2S$ (M^+) 326.1089, found 326.1061.



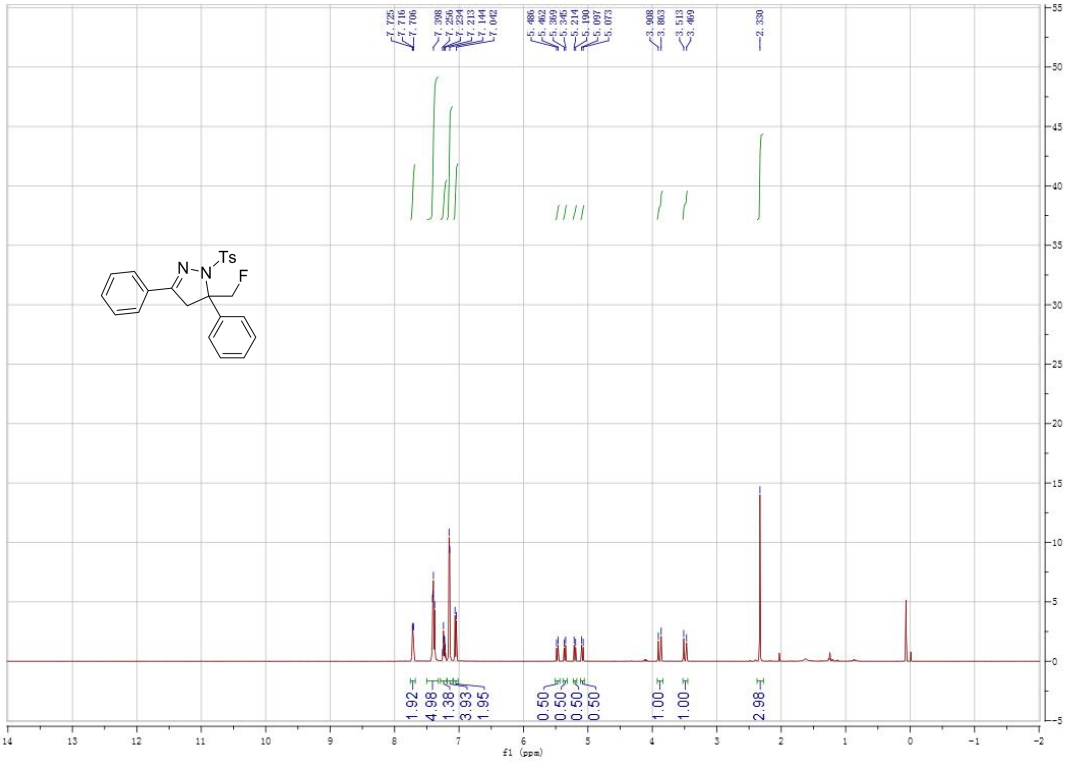
3,5-diphenylpyridazine (M)

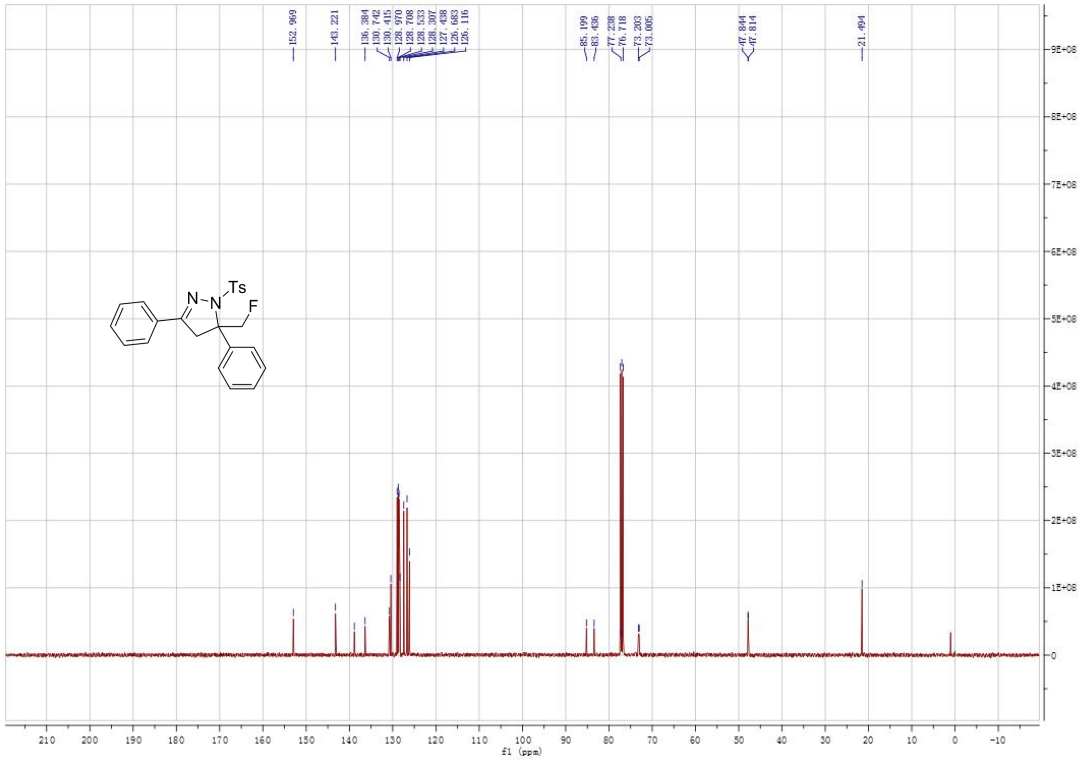
This is a known compound.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.38 (d, *J* = 2.4 Hz, 1H), 8.13-8.11 (m, 2H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.72-7.69 (m, 2H), 7.56-7.57 (m, 6H).

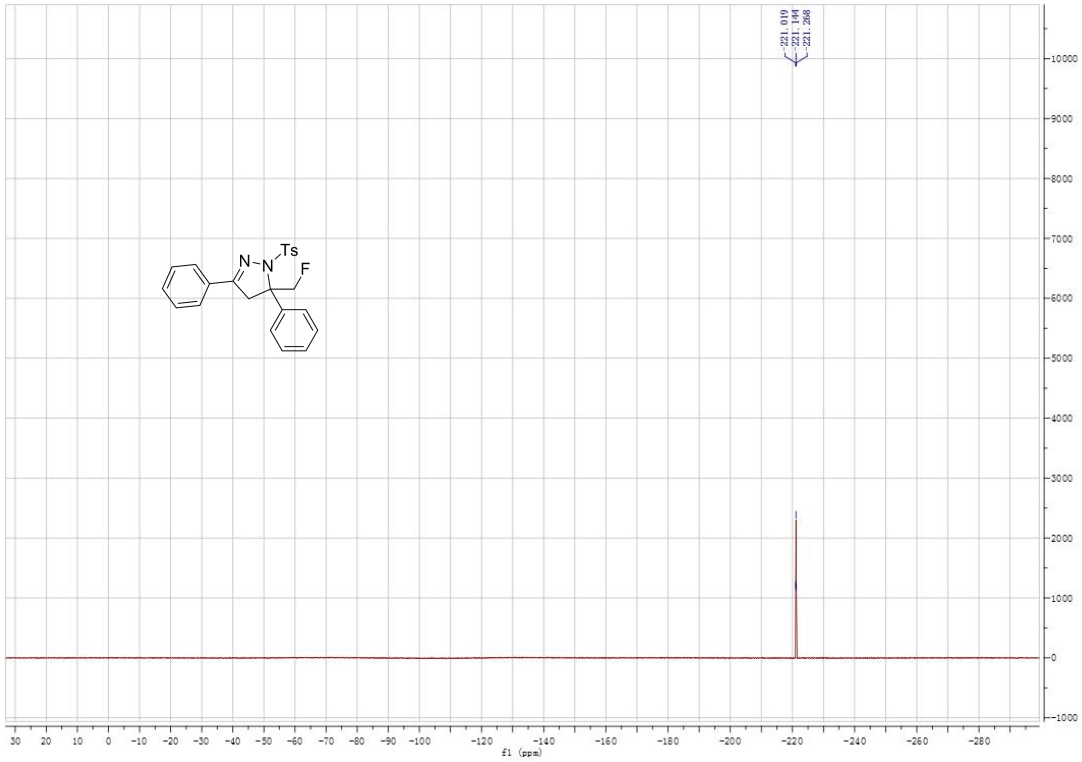
Reference:

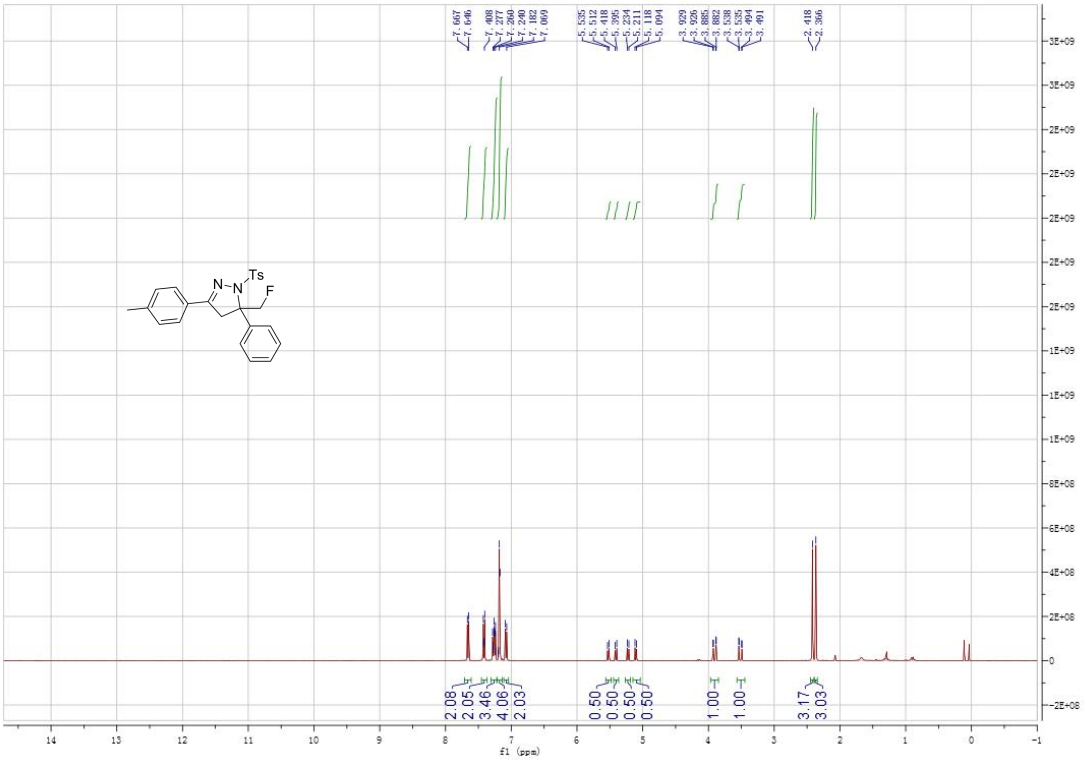
1. X. Q. Hu, X. T. Qi, J. R. Chen, Q. Q. Zhao, Q. Wei, Y. Lan, W. J. Xiao, *Nat. Commun*. **2016**, ***7***, 11188.

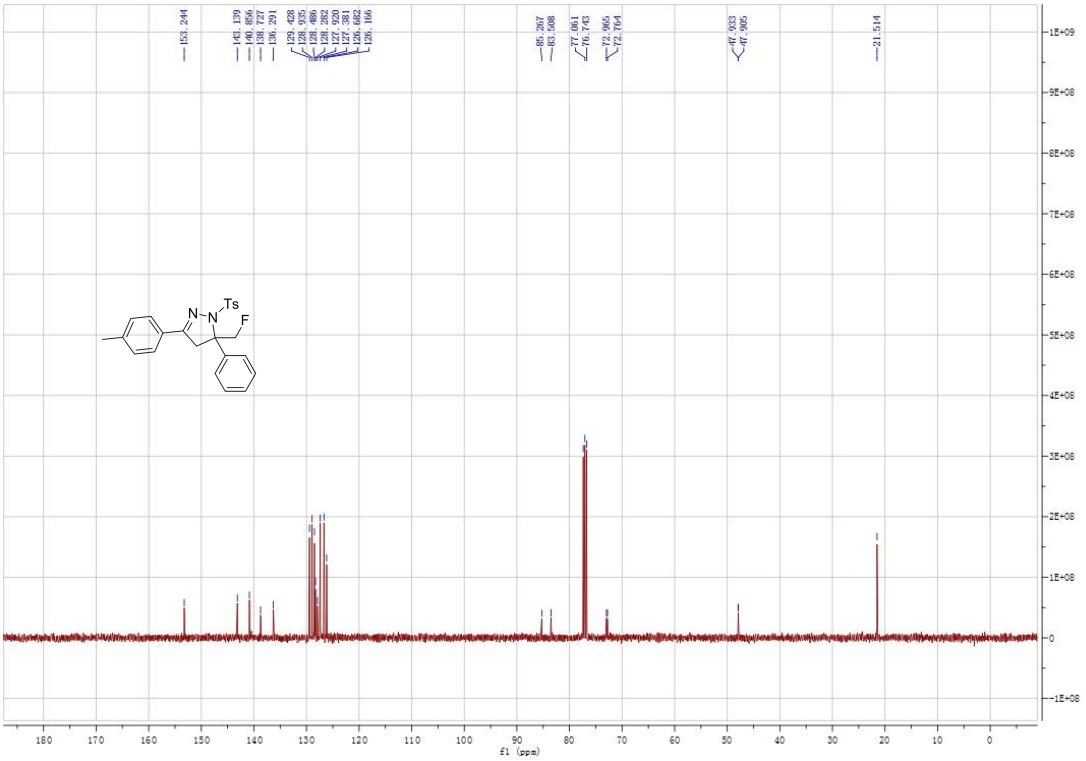
Copies of spectra

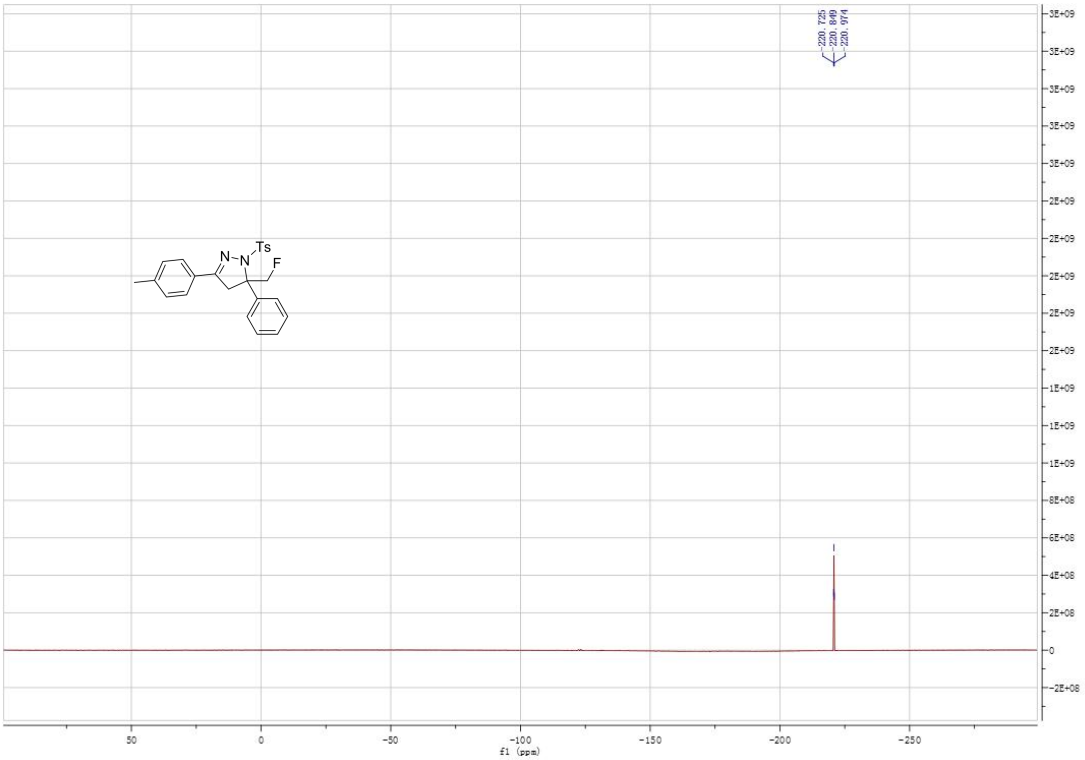


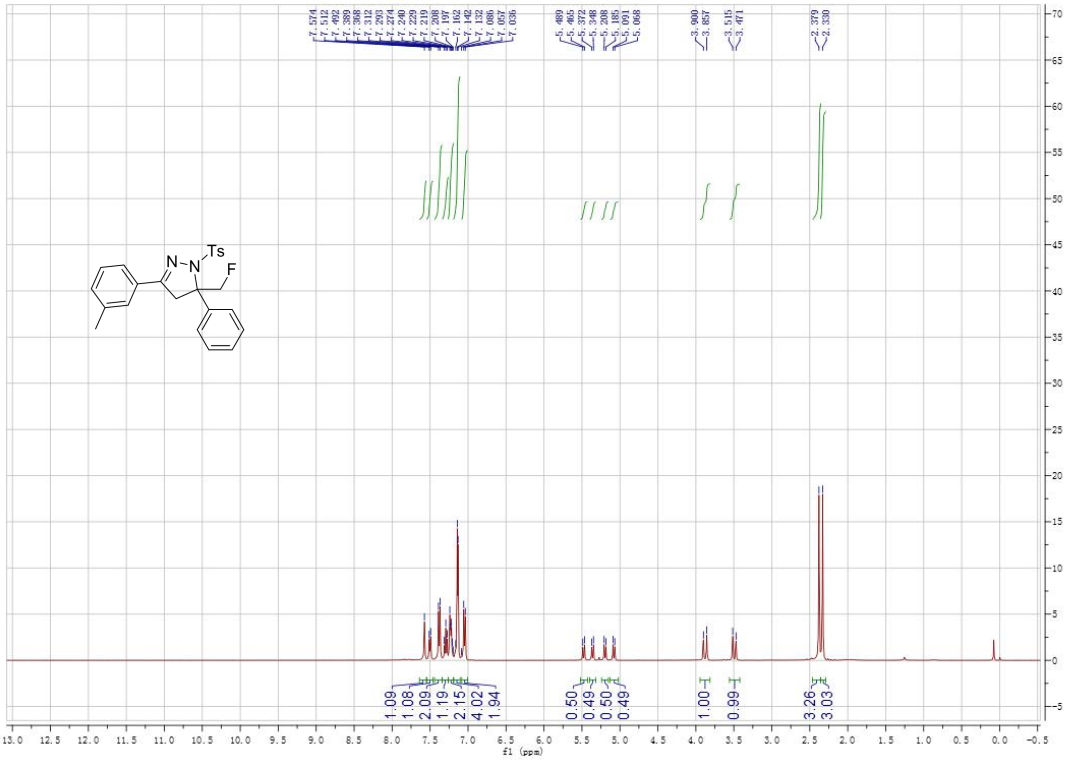


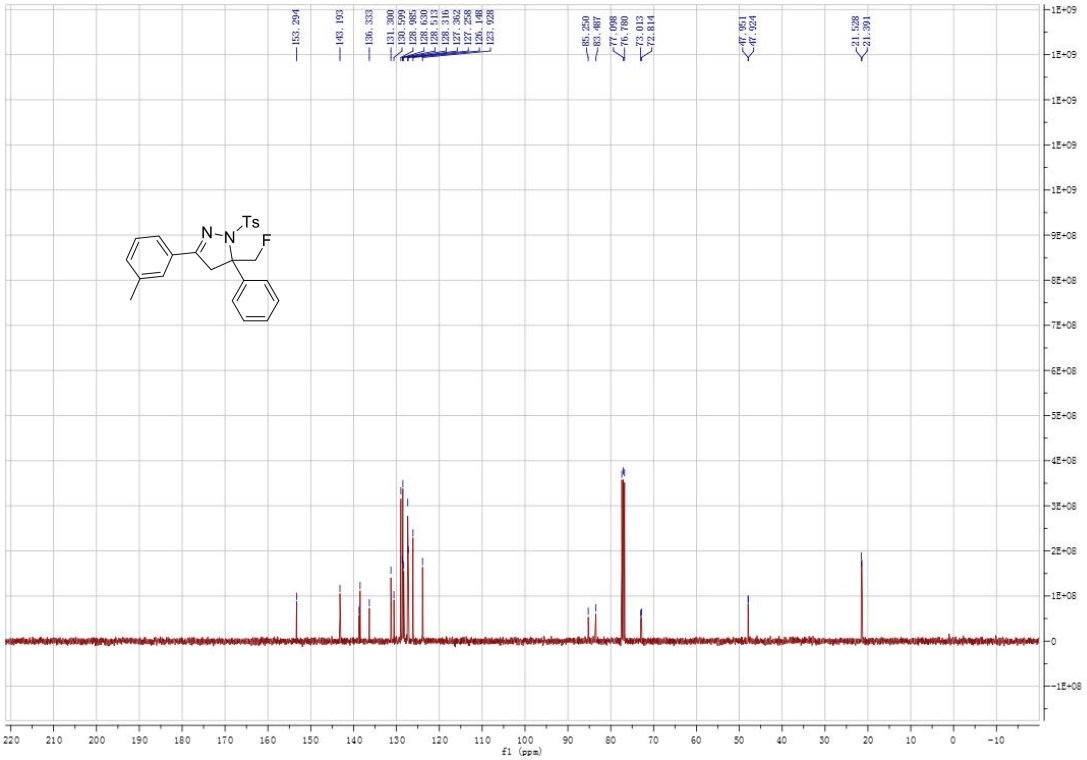

221.019
221.144
221.268
N
N
Ts
F
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

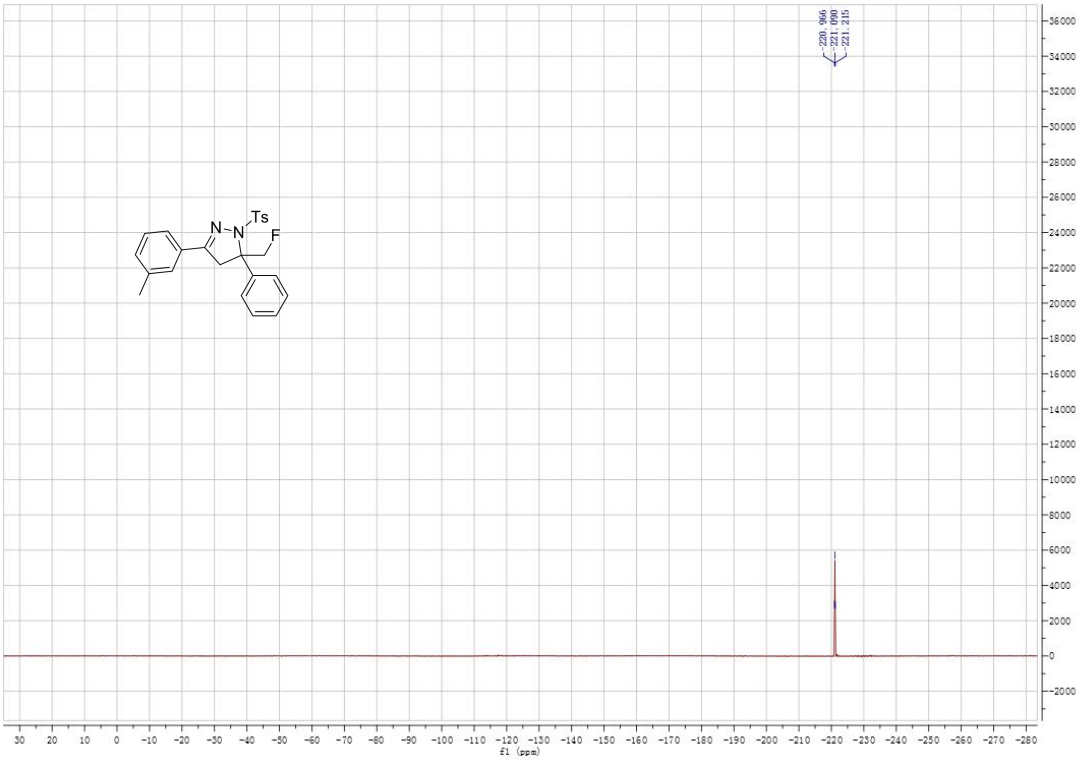

7.667
7.646
7.408
7.277
7.260
7.240
7.182
7.069
5.535
5.512
5.418
5.395
5.234
5.211
5.118
5.094
3.929
3.926
3.895
3.882
3.538
3.525
3.494
3.491
2.418
2.366
Ts
N
N
F
2.08
2.05
3.46
4.06
2.03
0.50
0.50
0.50
0.50
1.00
1.00
3.17
3.03
f1 (ppm)

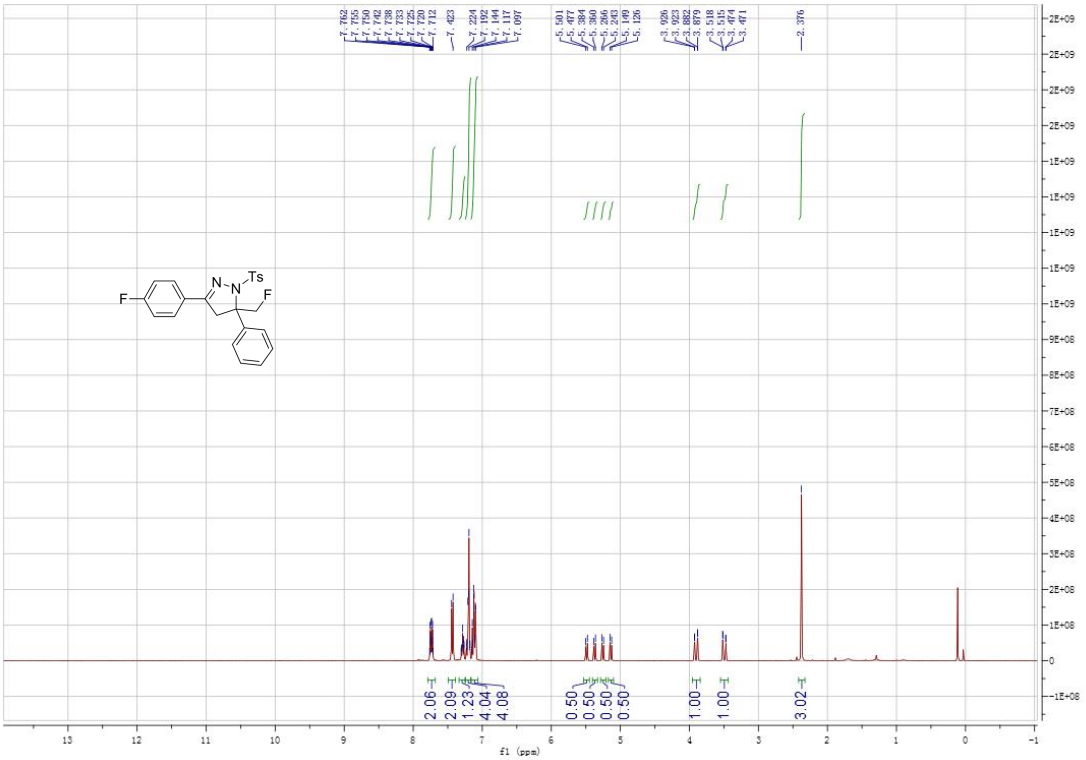

153.244
143.139
140.856
138.727
136.291
129.428
128.935
128.486
128.282
127.920
127.381
126.662
126.106
85.267
83.588
77.061
76.743
72.985
72.764
47.933
47.905
21.514
Ts
N
N
F
f1 (ppm)

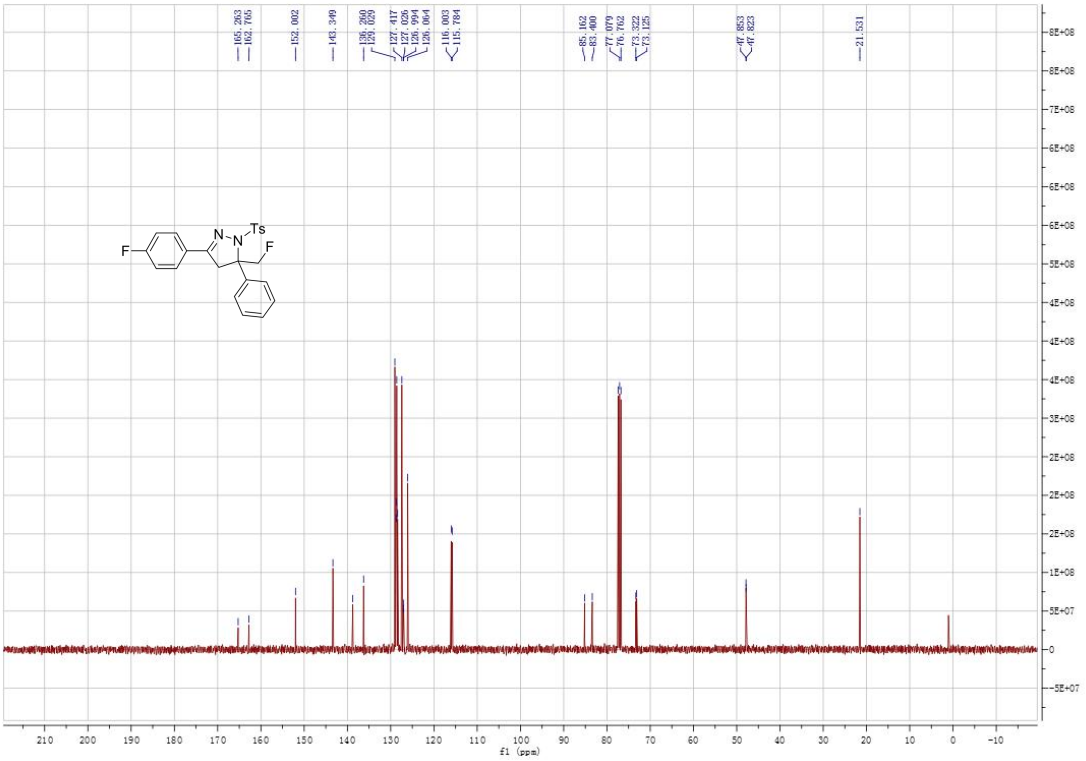

220.725
220.699
220.674
Ts
N
N
F
3E+09
3E+09
3E+09
3E+09
3E+09
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
1E+09
1E+09
1E+09
8E+08
6E+08
4E+08
2E+08
0
-2E+08
50
0
-50
-100
-150
-200
-250
f1 (ppm)

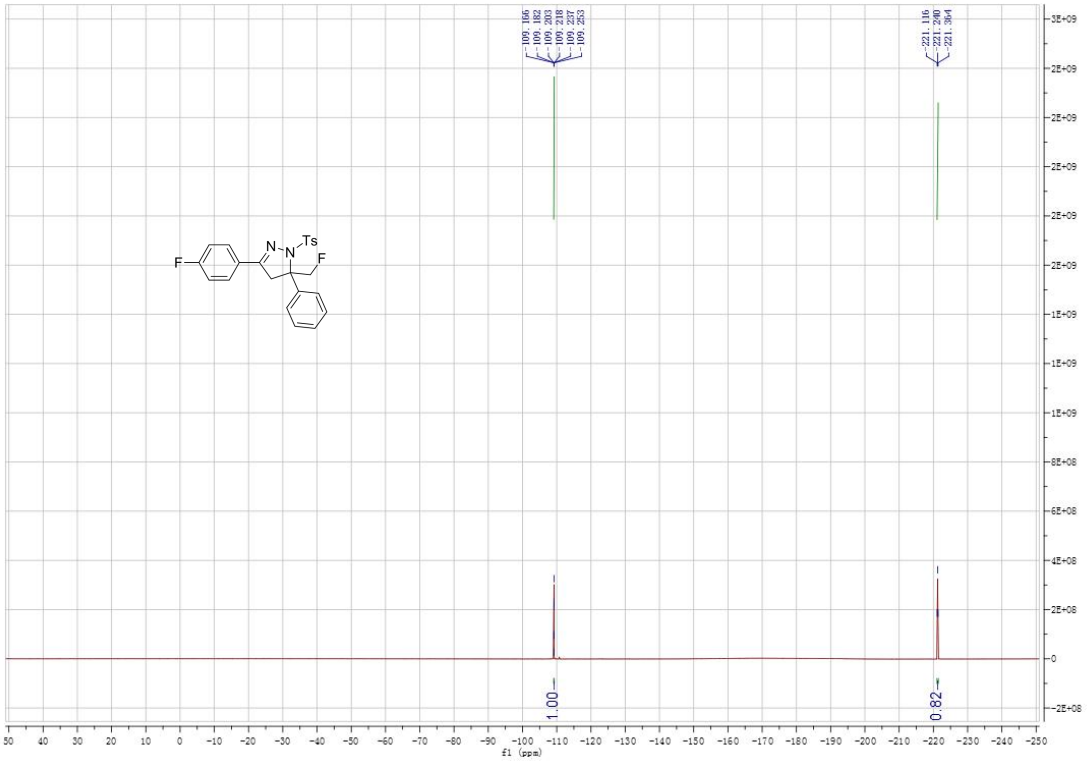

Ts
N
N
F
f1 (ppm)

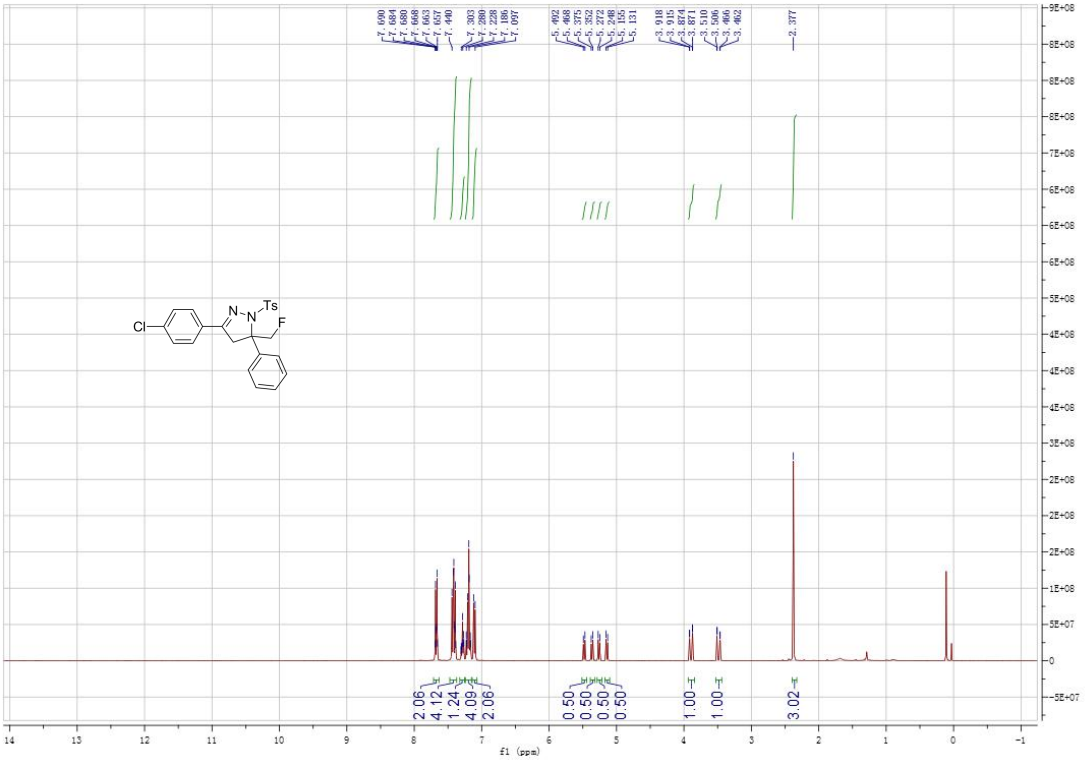

Ts
N
N
F
f1 (ppm)

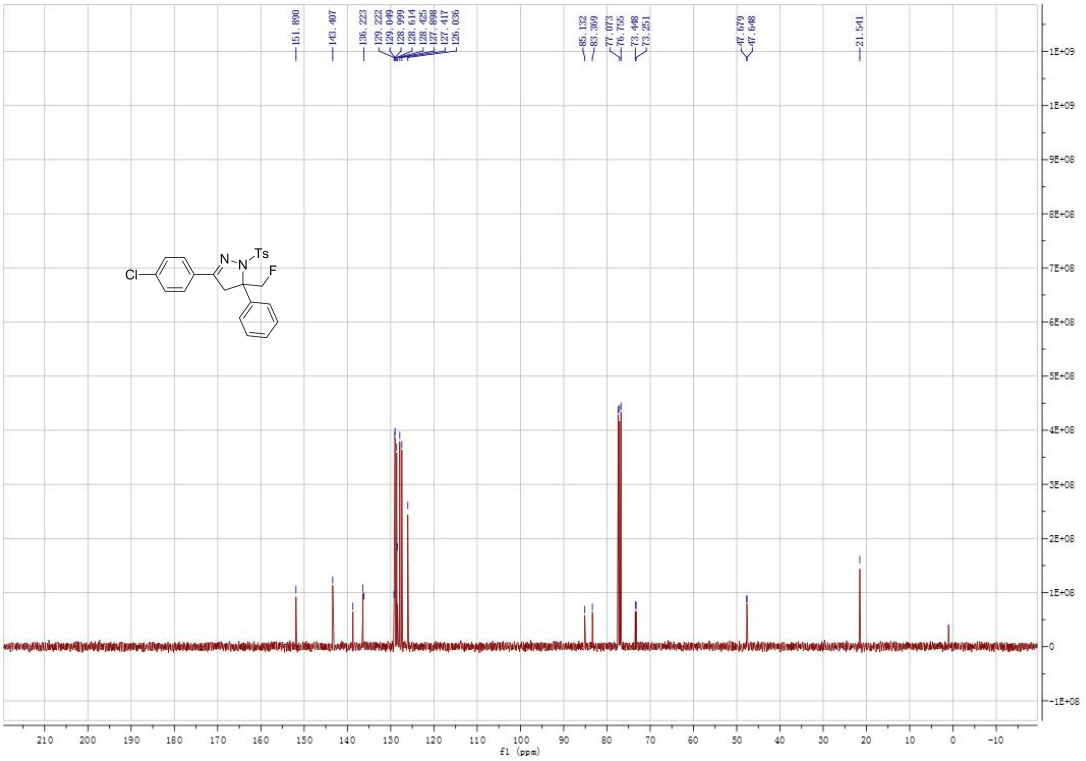

220.966
221.090
221.215
N
N
Ts
F
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280
f1 (ppm)

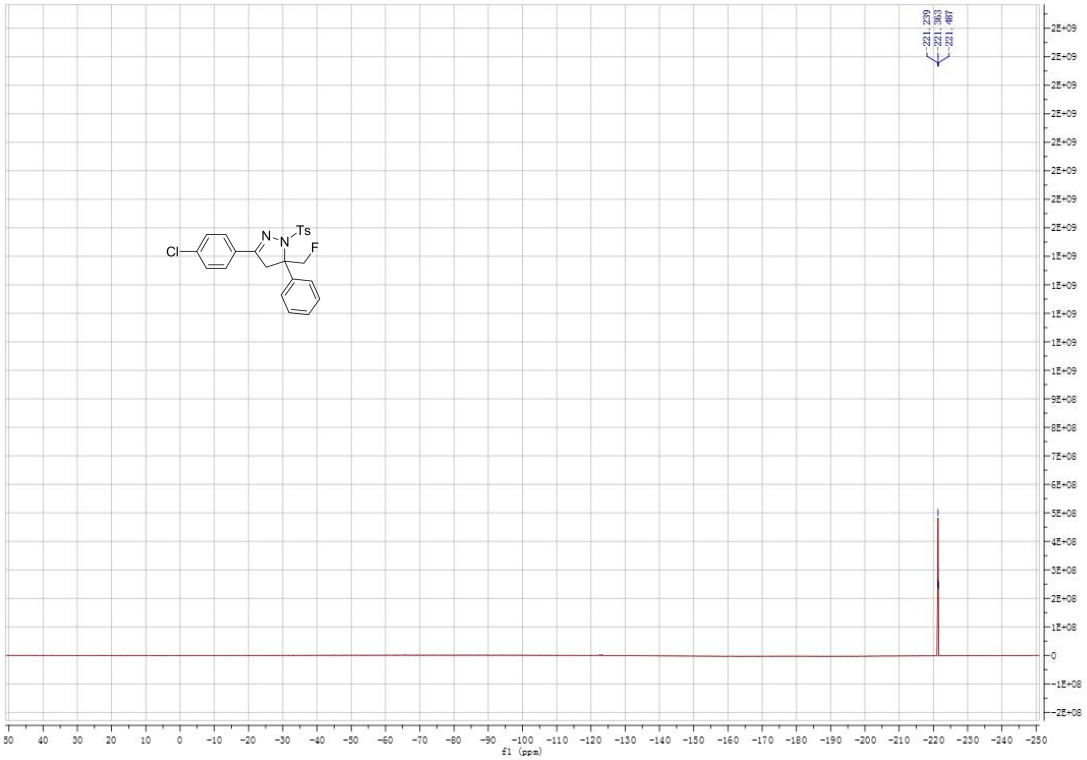

7.762
7.755
7.750
7.742
7.738
7.733
7.725
7.720
7.712
7.423
7.224
7.192
7.144
7.117
7.097
5.501
5.477
5.384
5.360
5.266
5.243
5.149
5.126
3.926
3.923
3.882
3.879
3.518
3.515
3.474
3.471
2.376
2.06
2.09
1.23
4.04
4.08
0.50
0.50
0.50
0.50
1.00
1.00
3.02
f1 (ppm)

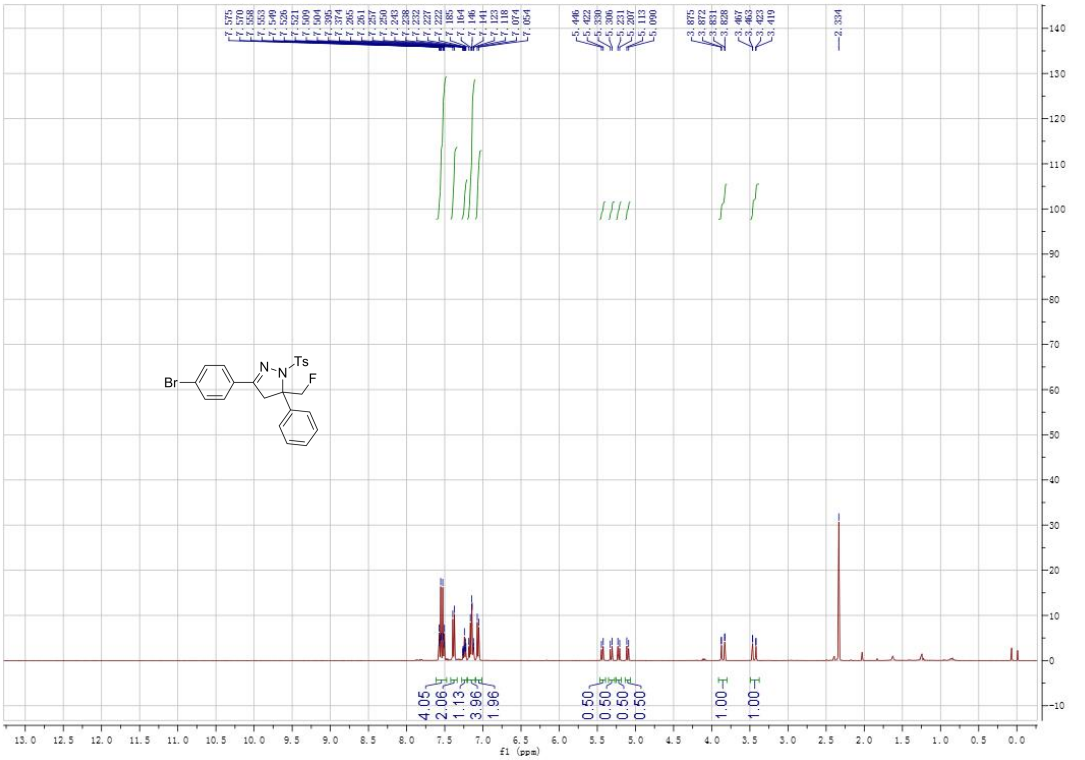

165.263
162.765
152.002
143.349
136.260
129.029
127.417
127.026
126.994
126.064
116.003
115.784
85.162
83.469
77.079
76.762
73.322
73.125
47.853
47.823
21.531
f1 (ppm)

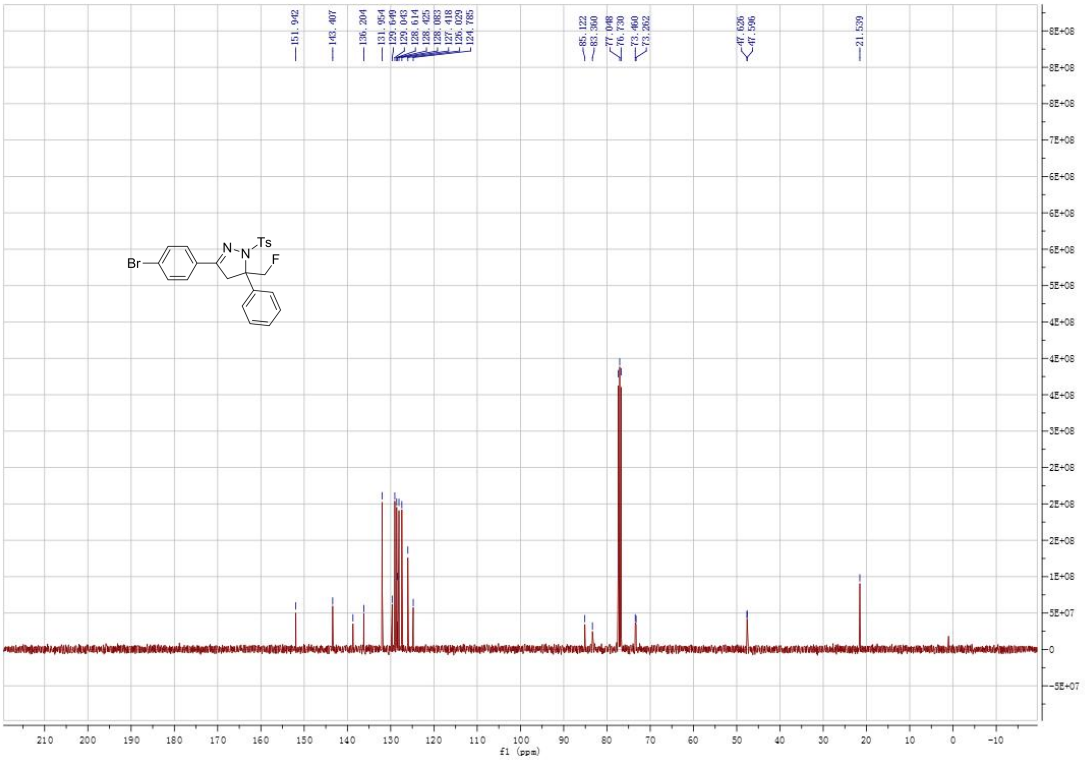

-109.166
-109.182
-109.203
-109.218
-109.237
-109.253
-221.116
-221.290
-221.364
F
N
N
Ts
F
1.00
0.82
f1 (ppm)

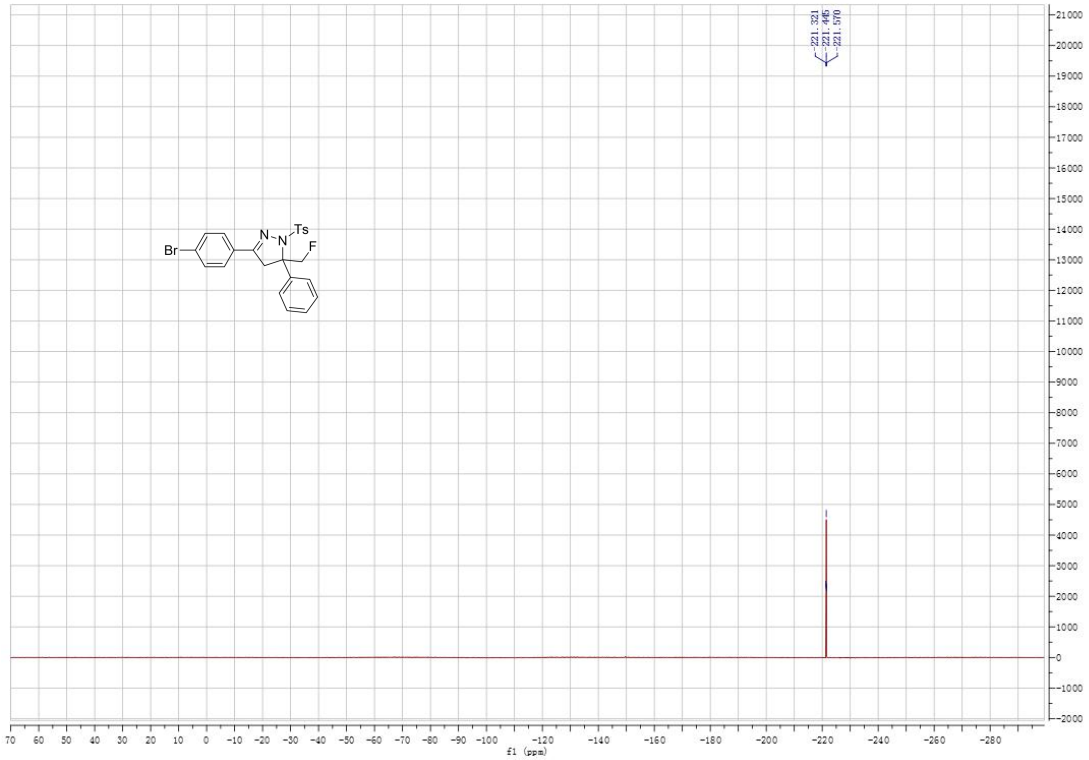

7.690
7.684
7.680
7.668
7.657
7.657
7.440
7.303
7.299
7.228
7.186
7.097
6.492
6.468
5.375
5.352
5.272
5.248
5.155
5.131
3.918
3.915
3.874
3.871
3.510
3.506
3.466
3.462
2.377
Ts
N
N
F
Cl
2.06
4.12
1.24
4.09
2.06
0.50
0.50
0.50
0.50
1.00
1.00
3.02
f1 (ppm)

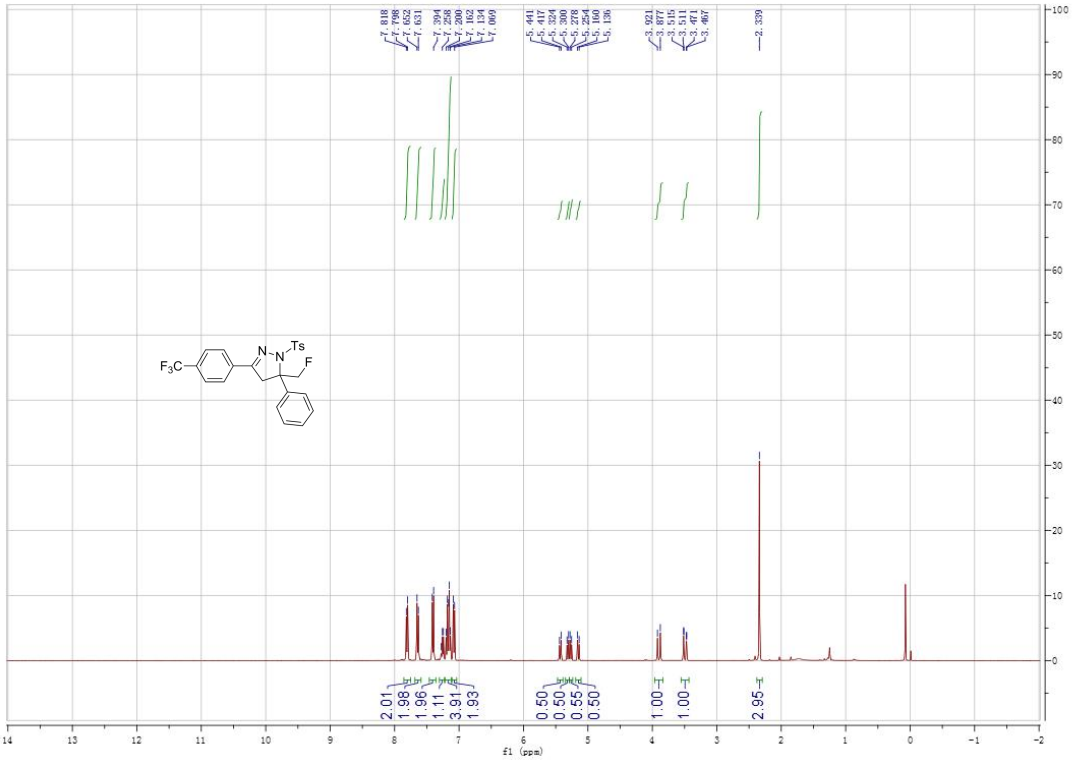

151.890
143.407
136.223
129.222
129.049
128.999
128.514
128.425
127.898
127.417
126.036
85.132
83.999
77.073
76.755
73.498
73.251
47.679
47.648
21.541
Ts
N
N
F
Cl
f1 (ppm)

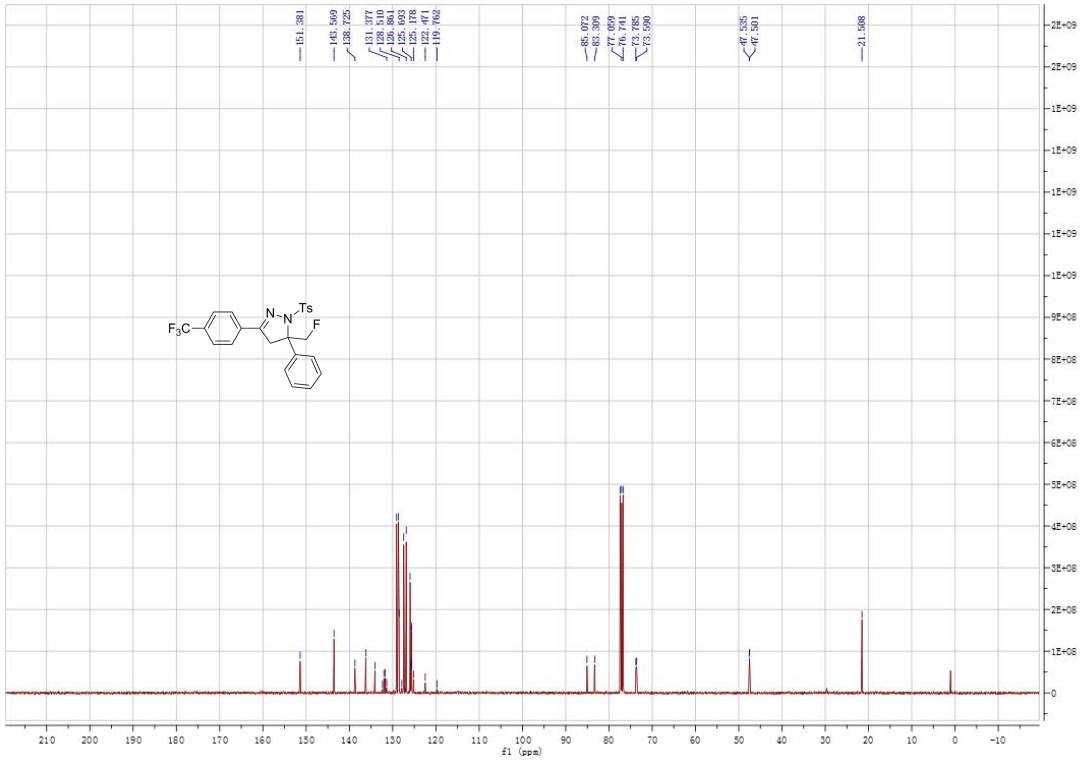

-221.239
-221.363
-221.487
Cl
N
N
Ts
F
f1 (ppm)

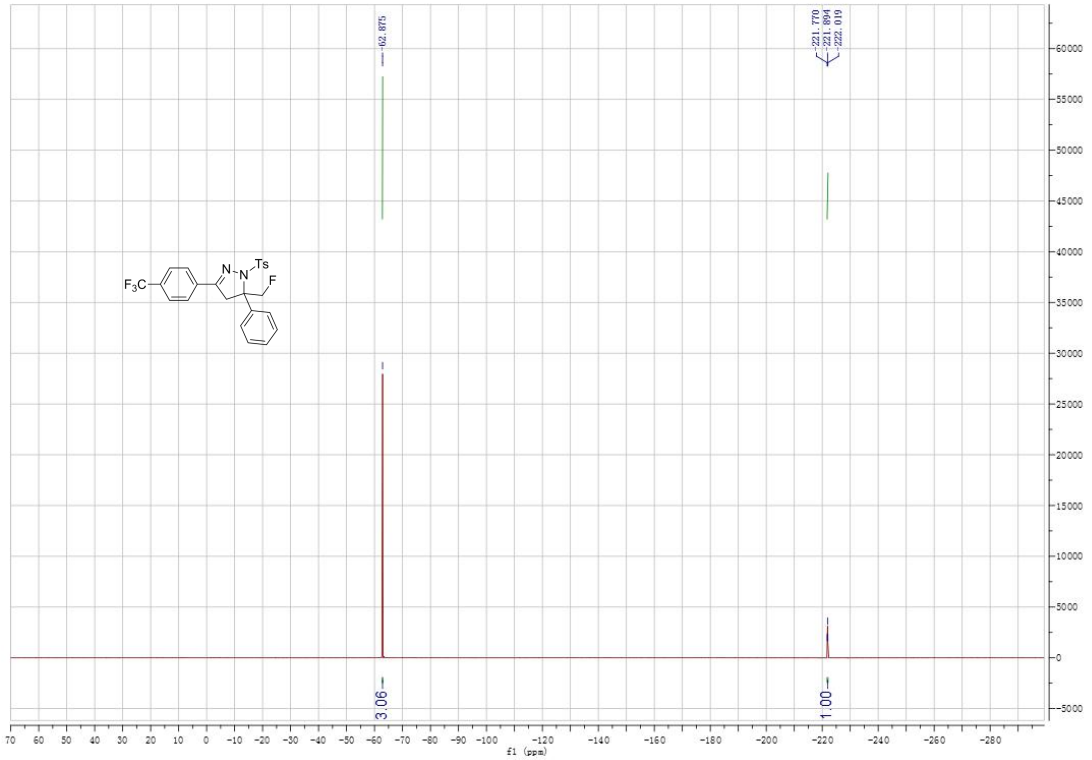

7.575
7.570
7.558
7.553
7.526
7.509
7.504
7.395
7.374
7.265
7.261
7.257
7.250
7.243
7.238
7.232
7.227
7.222
7.185
7.164
7.146
7.141
7.133
7.118
7.074
7.054
5.446
5.422
5.330
5.306
5.271
5.237
5.113
5.090
3.875
3.872
3.831
3.828
3.467
3.463
3.455
3.419
2.334
Br
N
N
Ts
F
4.05
2.06
1.13
3.96
1.96
0.50
0.50
0.50
0.50
1.00
1.00
f1 (ppm)

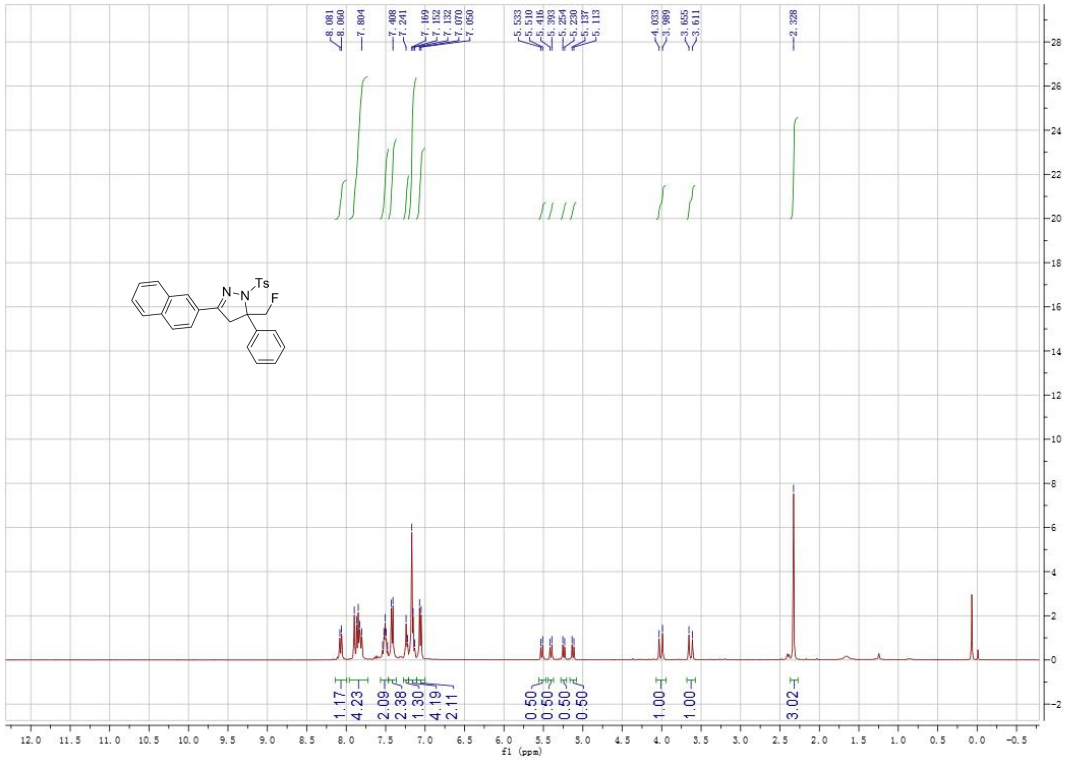

151.942
143.407
136.204
131.954
129.649
129.043
128.614
128.465
128.085
127.418
126.029
124.785
85.122
83.360
77.408
77.079
73.460
73.262
47.626
47.596
21.539
Br
N
N
Ts
F
f1 (ppm)

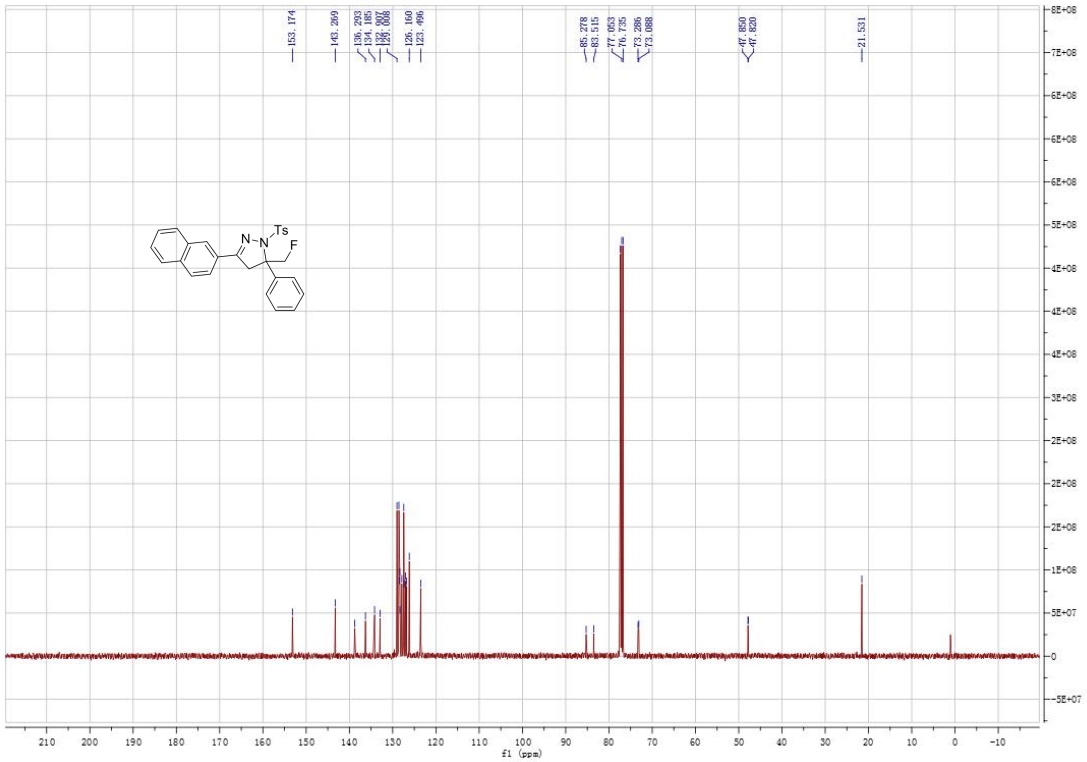

-221.321
-221.446
-221.570
Br
N
N
Ts
F
f1 (ppm)

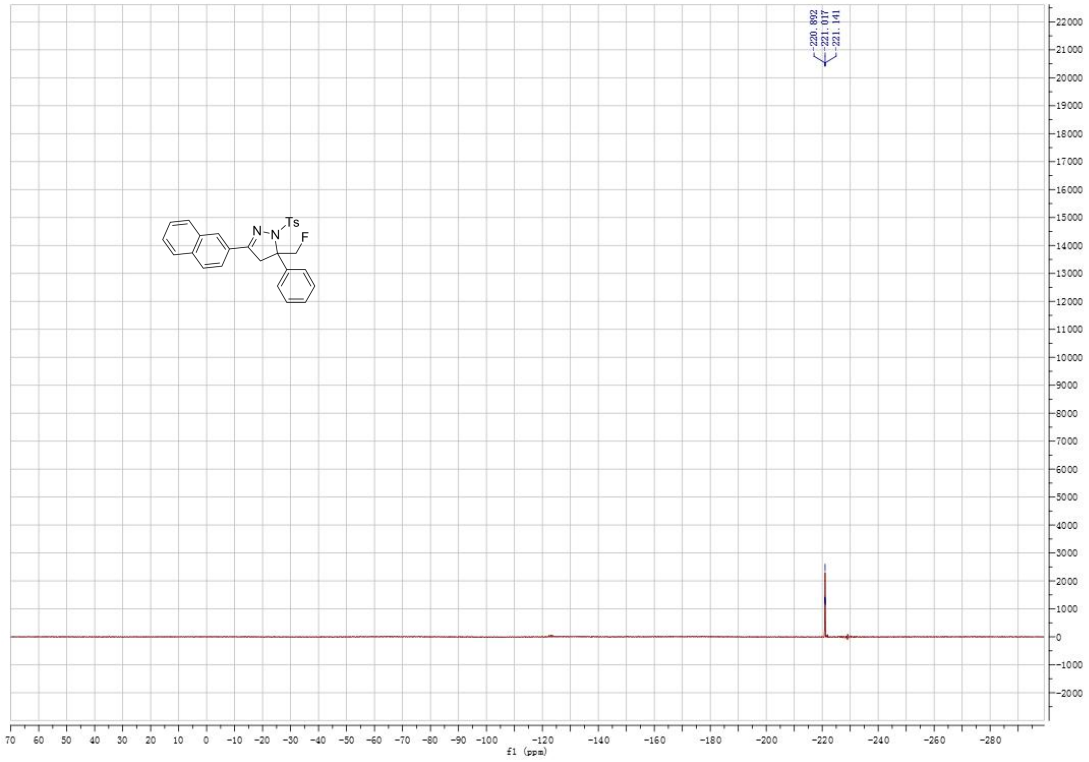

7.818
7.798
7.652
7.631
7.394
7.258
7.200
7.192
7.134
7.069
5.441
5.417
5.324
5.300
5.278
5.254
5.160
5.136
3.921
3.877
3.515
3.511
3.471
3.467
2.339
Ts
N
N
F
F3C
2.01
1.98
1.96
1.11
3.91
1.93
0.50
0.50
0.55
0.50
1.00
1.00
2.95
f1 (ppm)

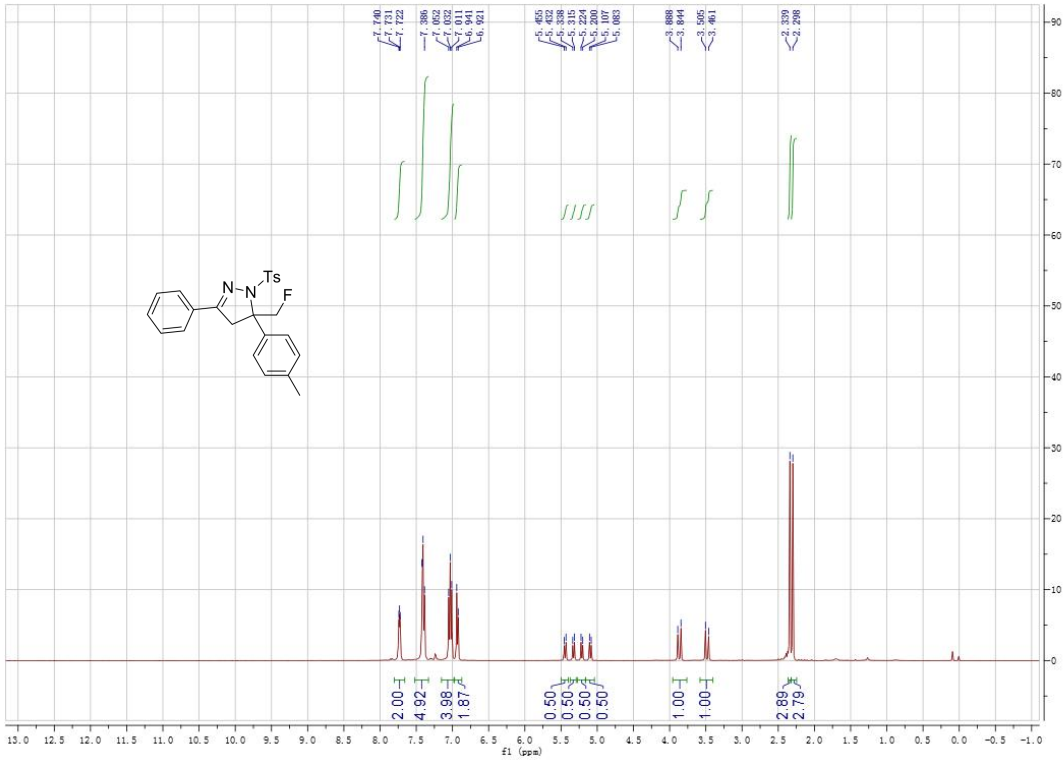

151.381
143.569
138.725
131.377
128.510
126.861
125.693
125.178
122.471
119.762
85.072
83.399
77.409
77.041
73.785
73.590
47.535
47.501
21.598
Ts
N
N
F
F3C
f1 (ppm)

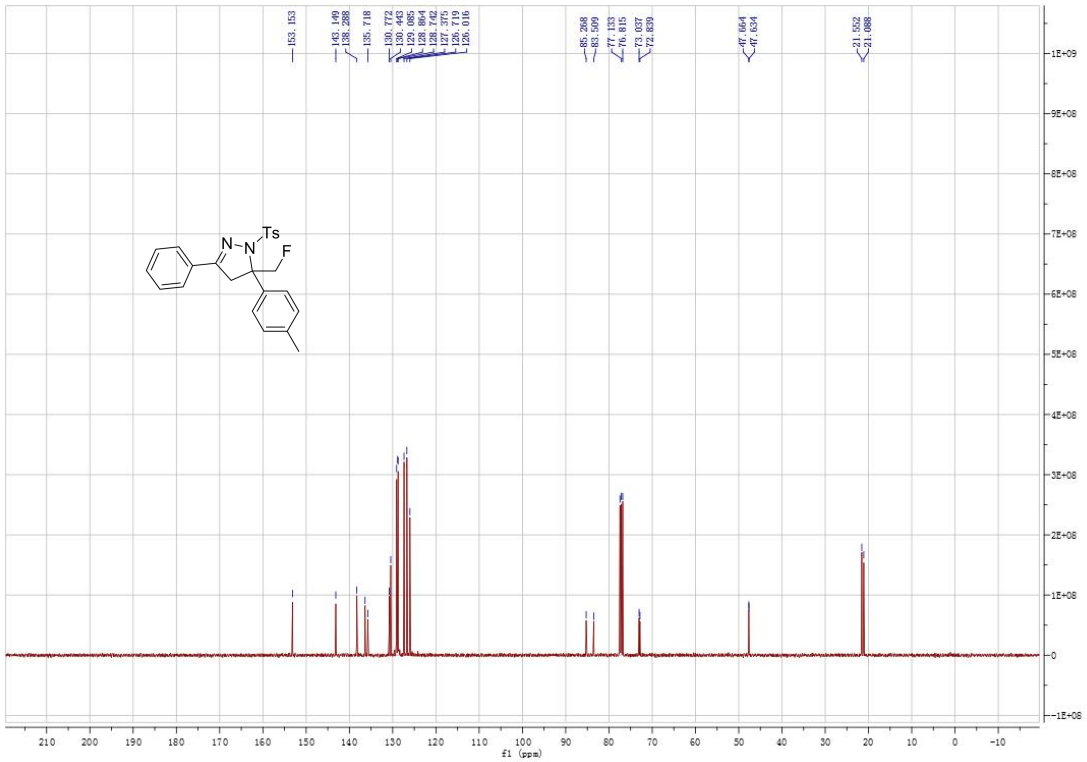

-62.875
-221.770
-221.894
-222.019
Ts
F
F3C
3.06
1.00
f1 (ppm)

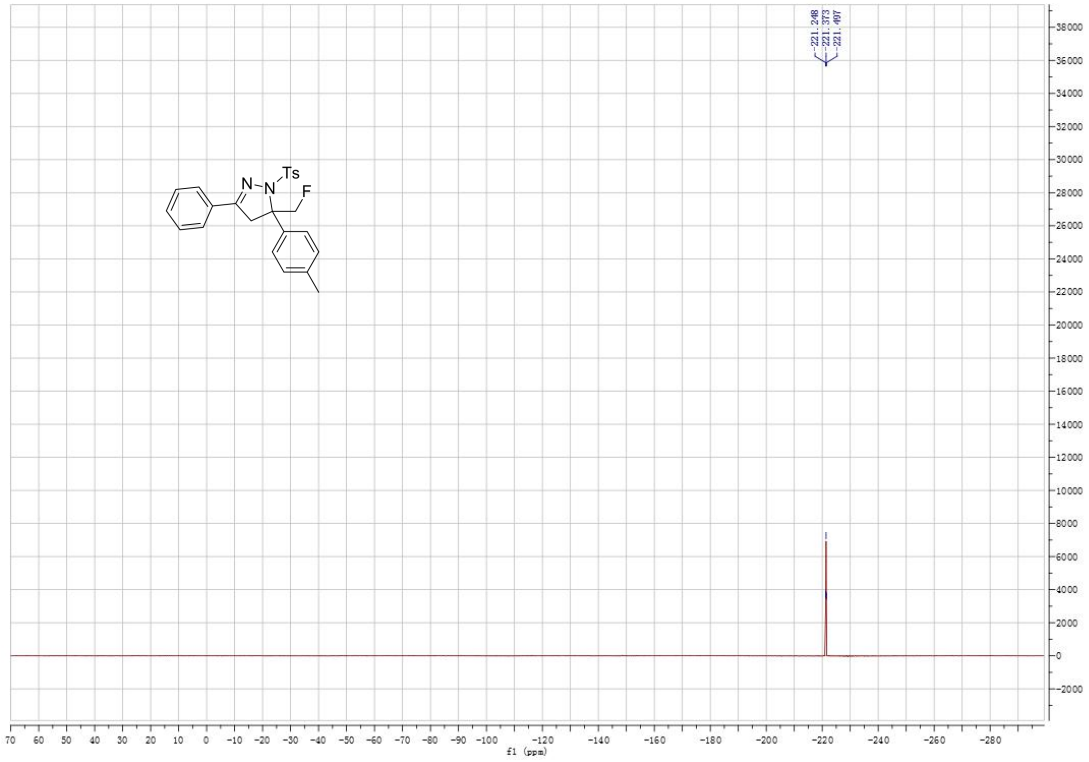

8.081
8.060
7.804
7.408
7.241
7.169
7.152
7.132
7.070
7.050
5.533
5.510
5.416
5.393
5.254
5.230
5.137
5.113
4.033
3.989
3.655
3.611
2.328
Ts
N
N
F
1.17
4.23
2.09
2.38
1.30
4.19
2.11
0.50
0.50
0.50
0.50
1.00
1.00
3.02
f1 (ppm)

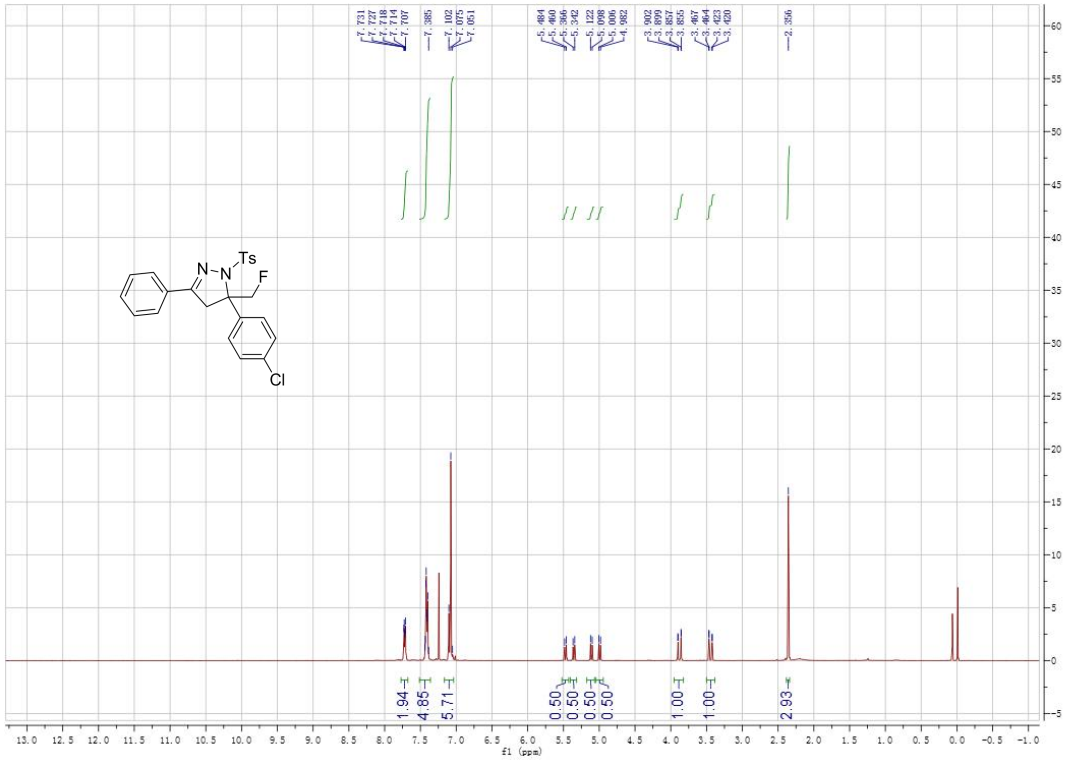

153.174
143.269
136.293
134.185
132.907
129.008
126.160
123.496
85.278
83.515
77.053
76.735
73.296
73.088
47.859
47.820
21.531
Ts
N
N
F
f1 (ppm)

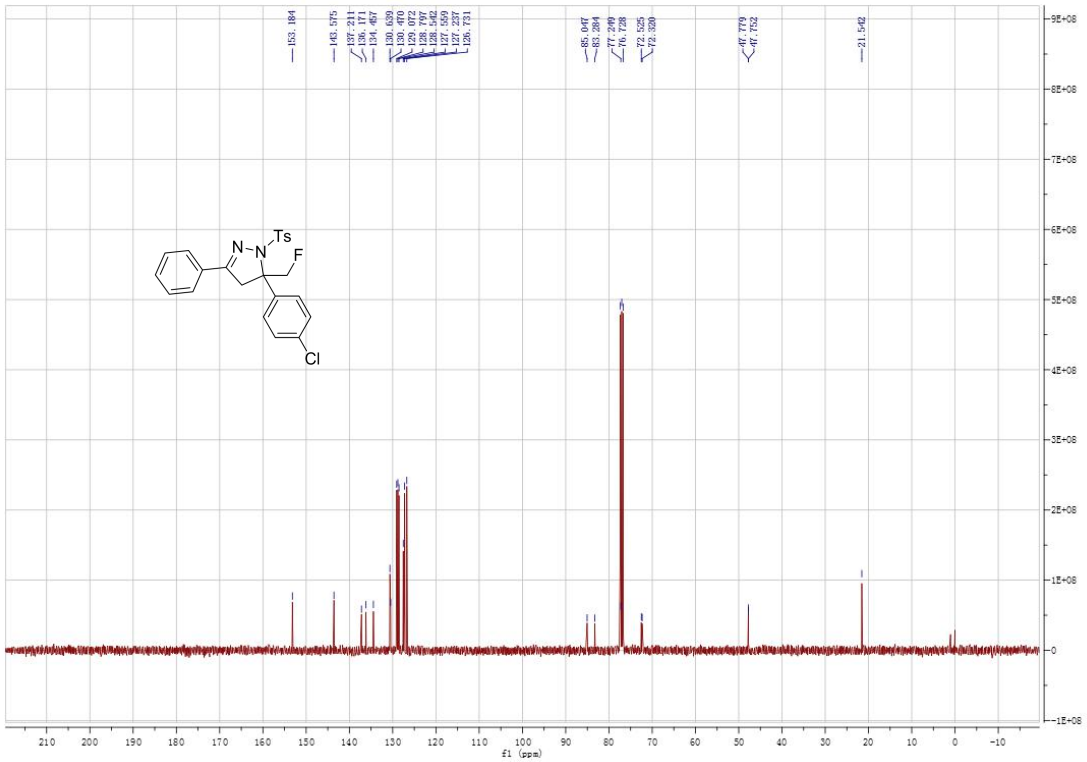

220.892
221.017
221.141
Ts
N
N
F
f1 (ppm)

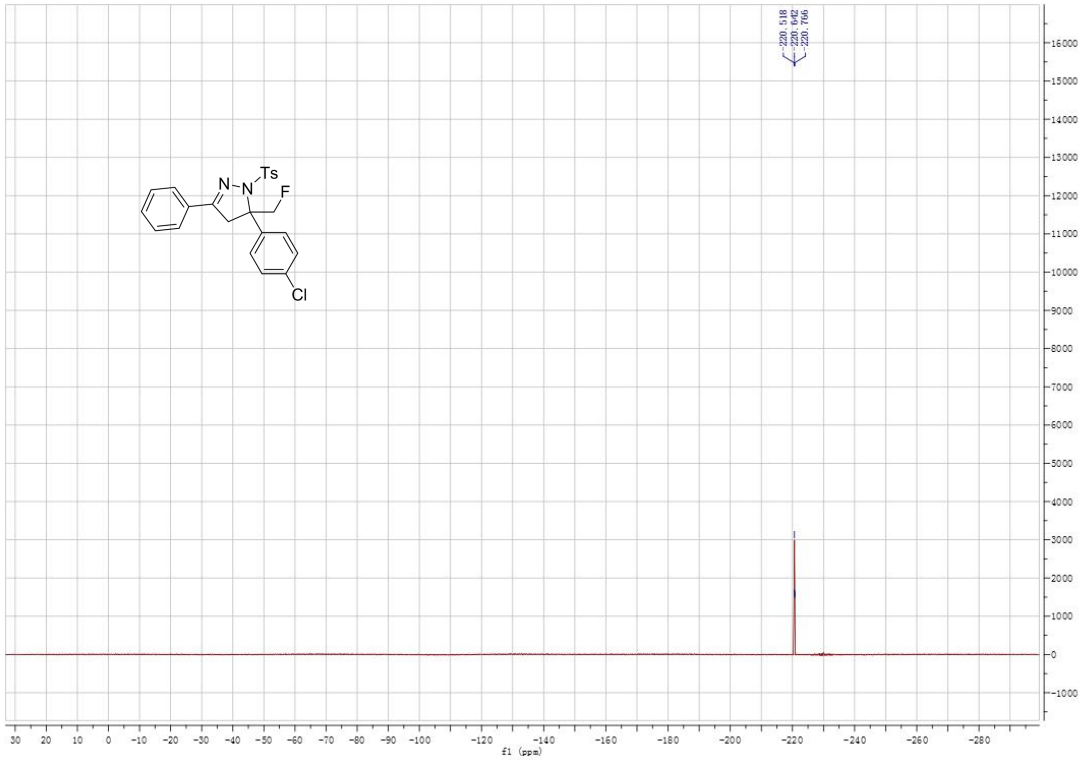

7.740
7.731
7.722
7.386
7.052
7.032
6.944
6.921
5.455
5.432
5.338
5.315
5.224
5.200
5.107
5.083
3.888
3.844
3.595
3.461
2.339
2.298
Ts
N
N
F
2.00
4.92
3.98
1.87
0.50
0.50
0.50
0.50
1.00
1.00
2.89
2.79
f1 (ppm)

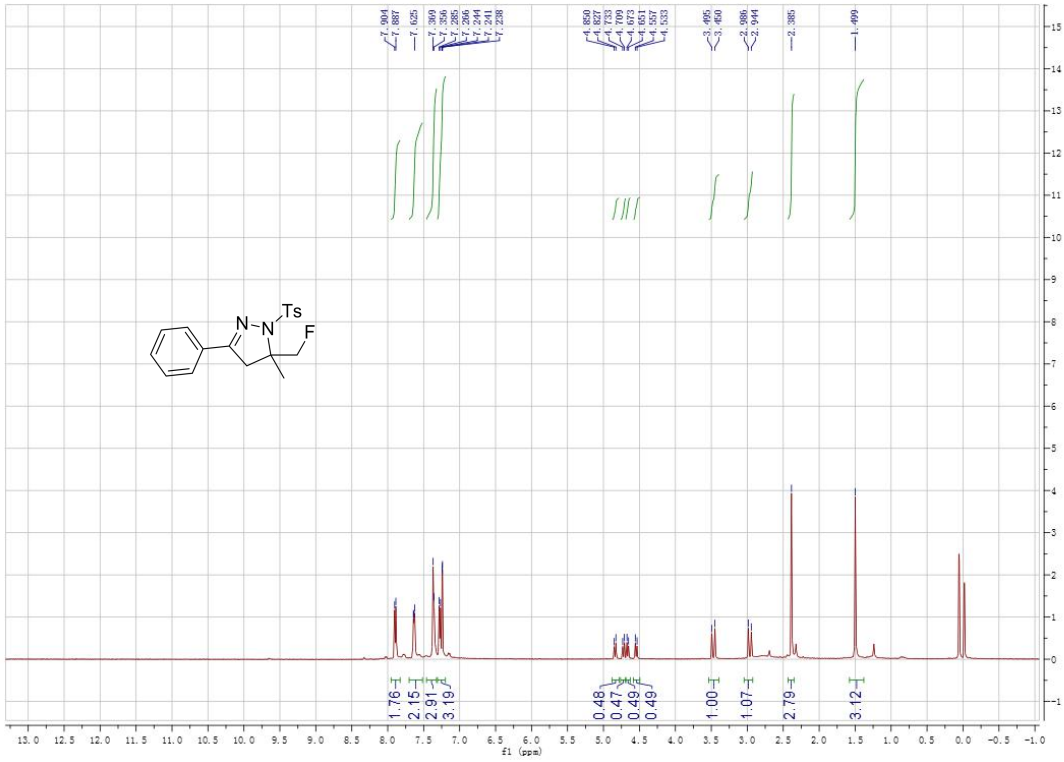

153.153
143.149
138.288
135.718
130.772
130.445
129.085
128.864
128.742
127.375
126.719
126.016
85.268
82.599
77.315
76.815
73.037
72.859
47.664
47.634
21.552
21.088
Ts
N
N
F
f1 (ppm)

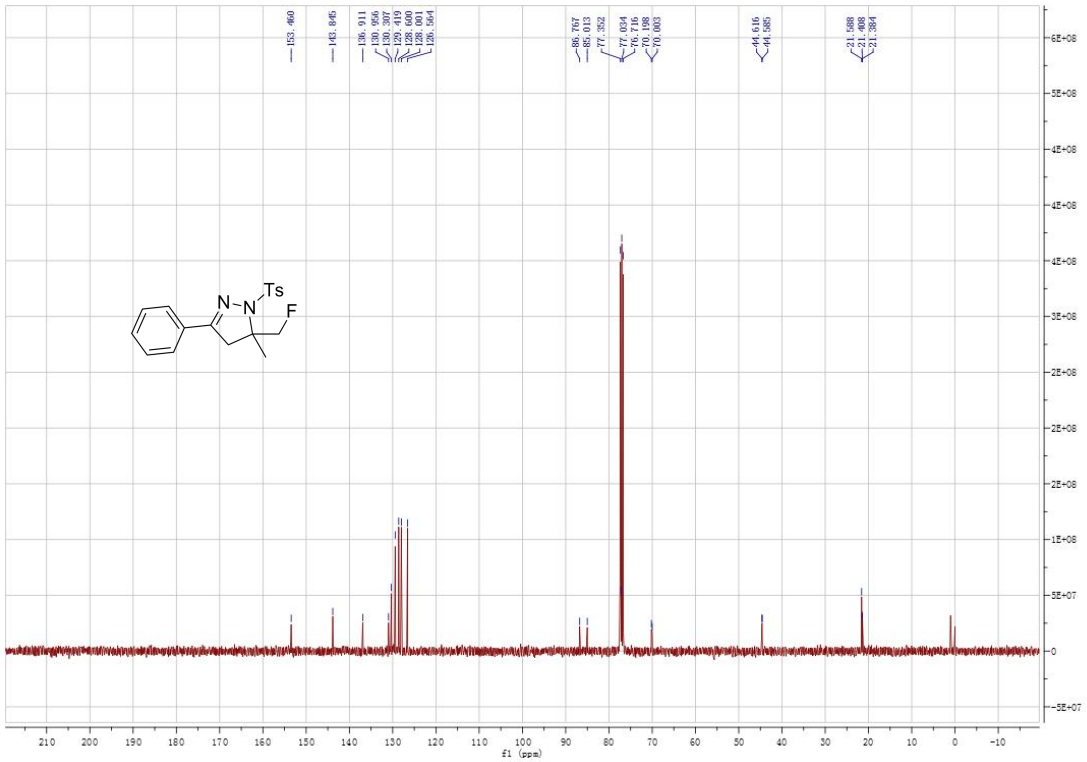

-221.248
-221.373
-221.497
Ts
N
N
F
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

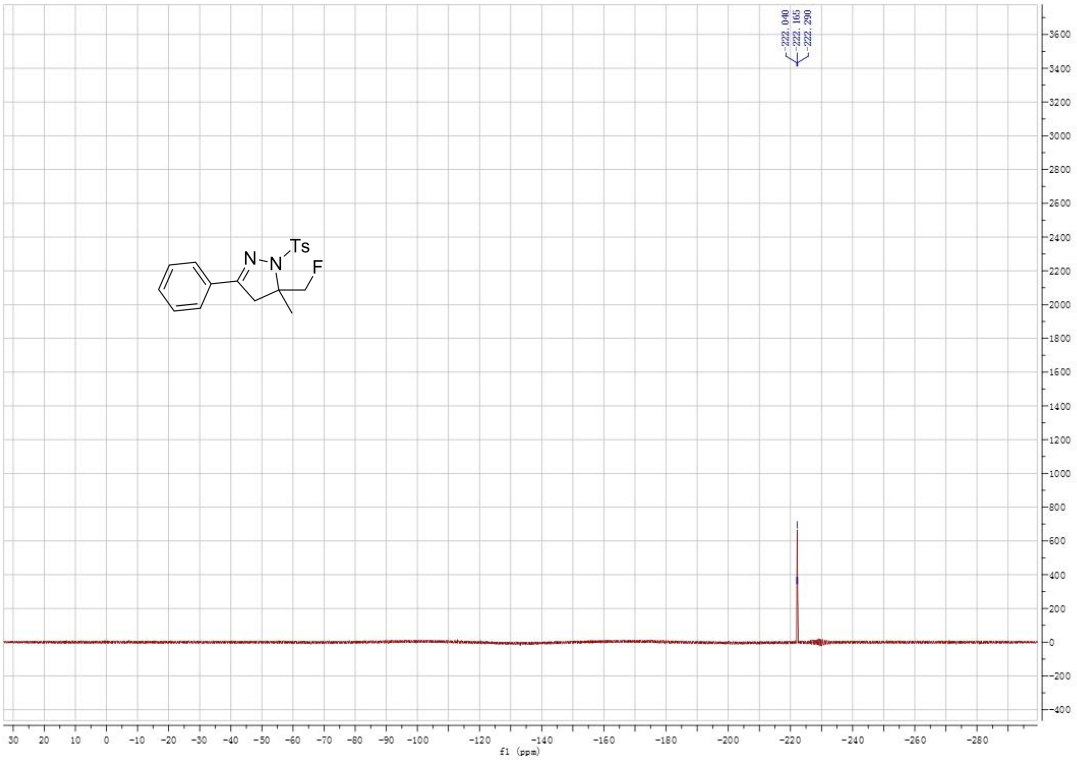

7.731
7.727
7.718
7.714
7.707
7.385
7.102
7.075
7.051
5.404
5.400
5.366
5.342
5.122
5.098
5.006
4.982
3.902
3.899
3.857
3.855
3.447
3.444
3.423
3.420
2.356
1.94
4.85
5.71
0.50
0.50
0.50
0.50
1.00
1.00
2.93
Ts
N
N
F
Cl
f1 (ppm)

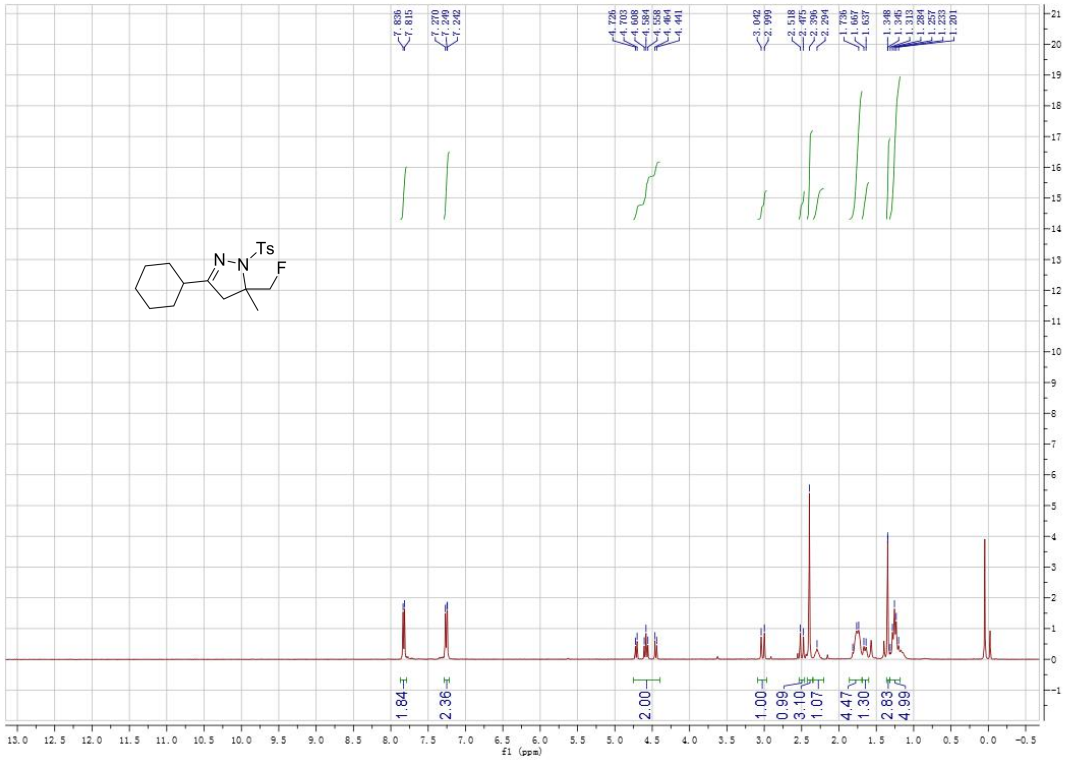

153.184
143.575
137.211
136.171
134.467
130.639
130.470
130.072
128.797
128.562
127.559
127.237
126.731
85.647
83.384
77.299
76.729
72.525
72.330
47.779
47.752
21.542
Ts
N
N
F
Cl
f1 (ppm)

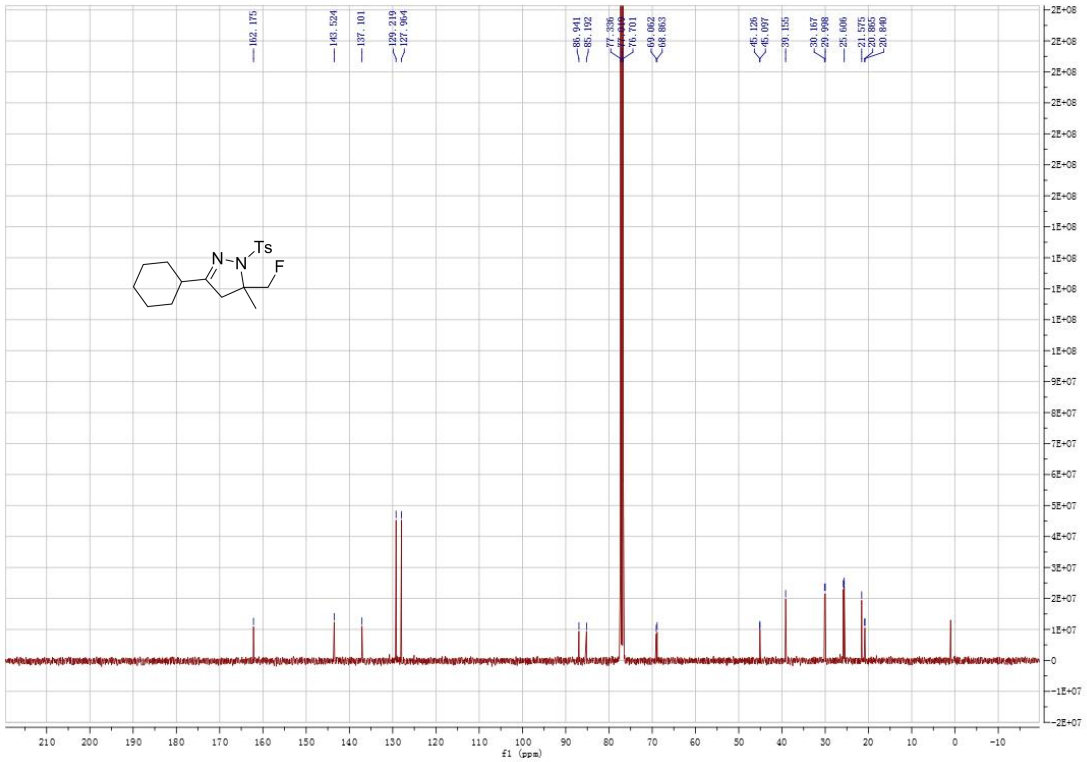

220.518
220.642
220.766
Ts
N
N
F
Cl
f1 (ppm)

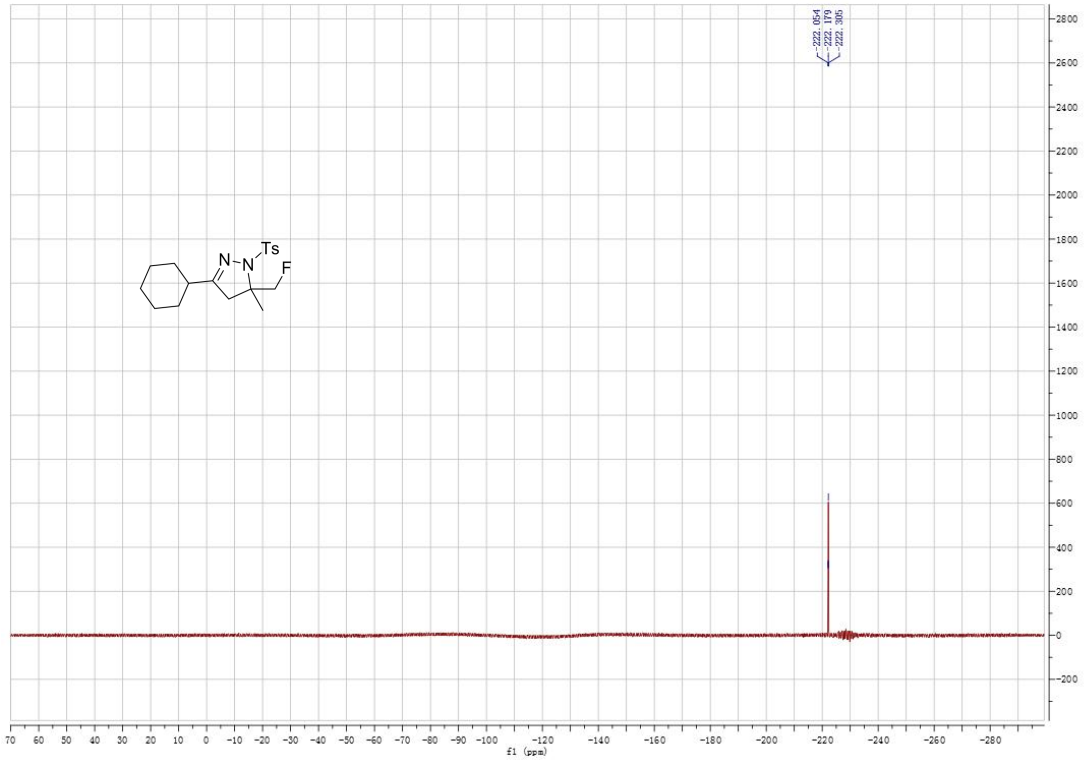

7.904
7.887
7.625
7.359
7.356
7.295
7.266
7.244
7.241
7.238
4.850
4.827
4.755
4.709
4.673
4.651
4.537
4.535
3.495
3.460
2.986
2.944
2.385
1.499
Ts
N
N
F
1.76
2.15
2.91
3.19
0.48
0.47
0.49
0.49
1.00
1.07
2.79
3.12
f1 (ppm)

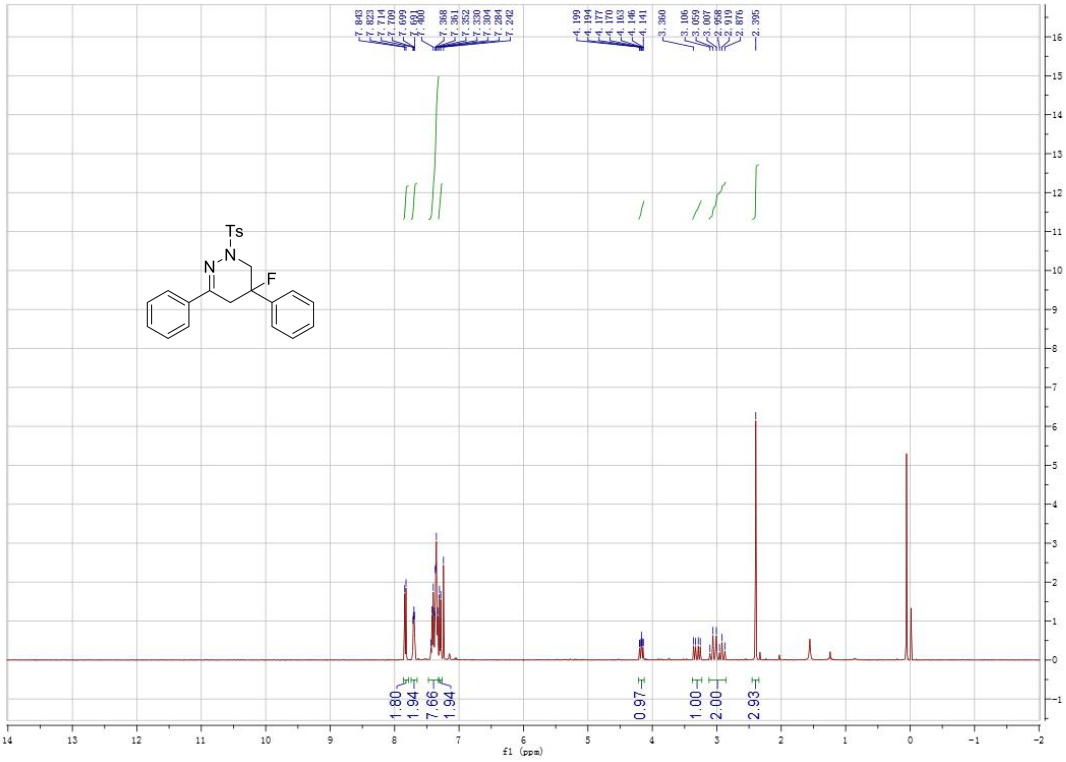

153.460
143.845
136.911
130.956
130.307
129.419
128.600
128.001
126.564
86.767
85.013
77.352
77.024
76.716
70.198
70.003
64.616
64.585
21.588
21.486
21.384
Ts
N
N
F
f1 (ppm)

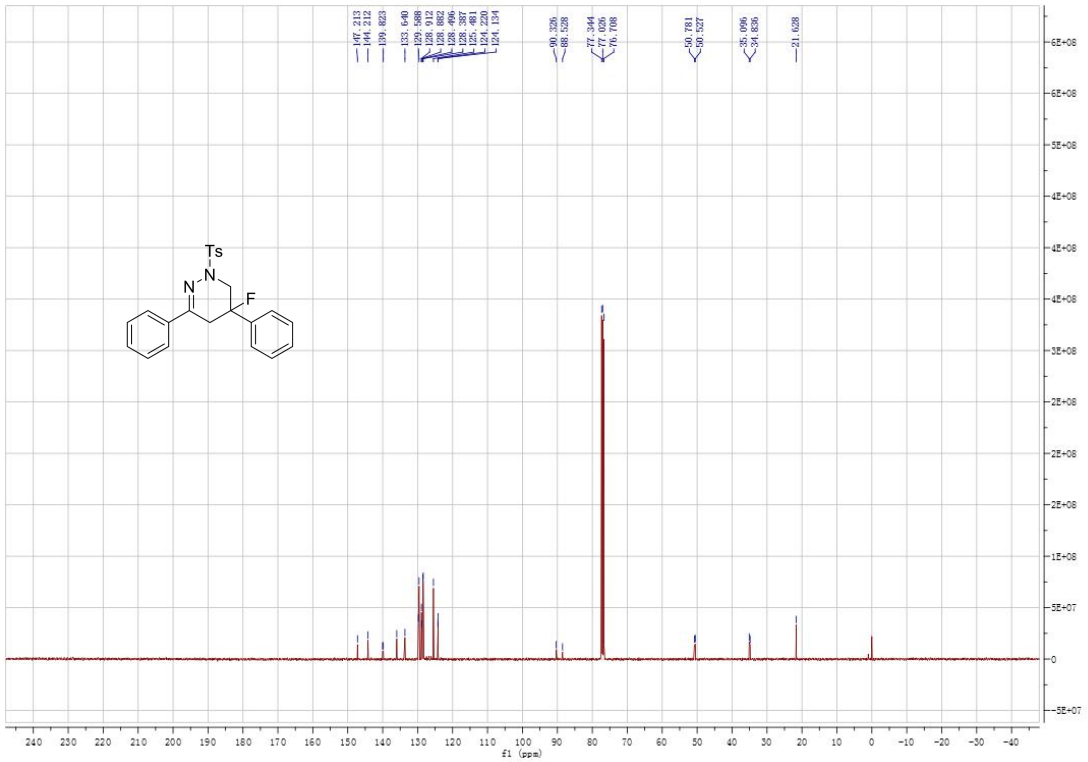

222.040
222.165
222.290
Ts
N
N
F
f1 (ppm)

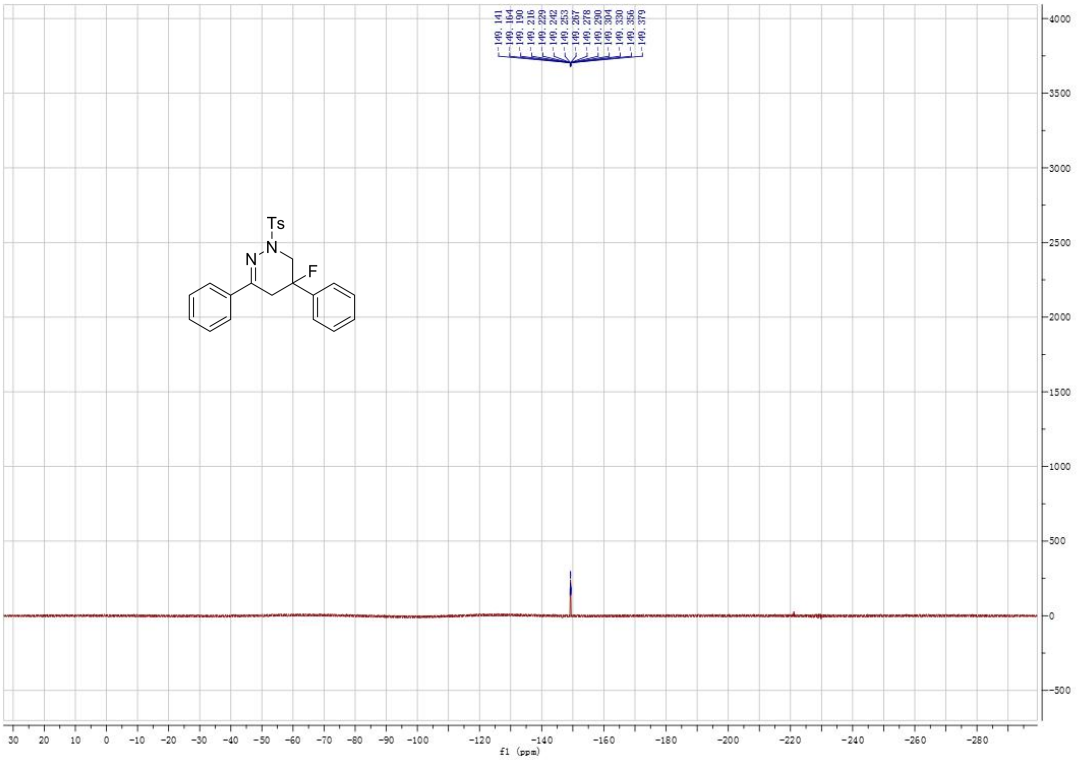

7.836
7.815
7.270
7.249
7.242
4.726
4.703
4.608
4.584
4.558
4.464
4.441
3.042
2.999
2.518
2.475
2.396
2.294
1.736
1.667
1.637
1.348
1.345
1.313
1.284
1.257
1.233
1.201
Ts
N
N
F
1.84
2.36
2.00
1.00
0.99
3.10
1.07
4.47
1.30
2.83
4.99
f1 (ppm)

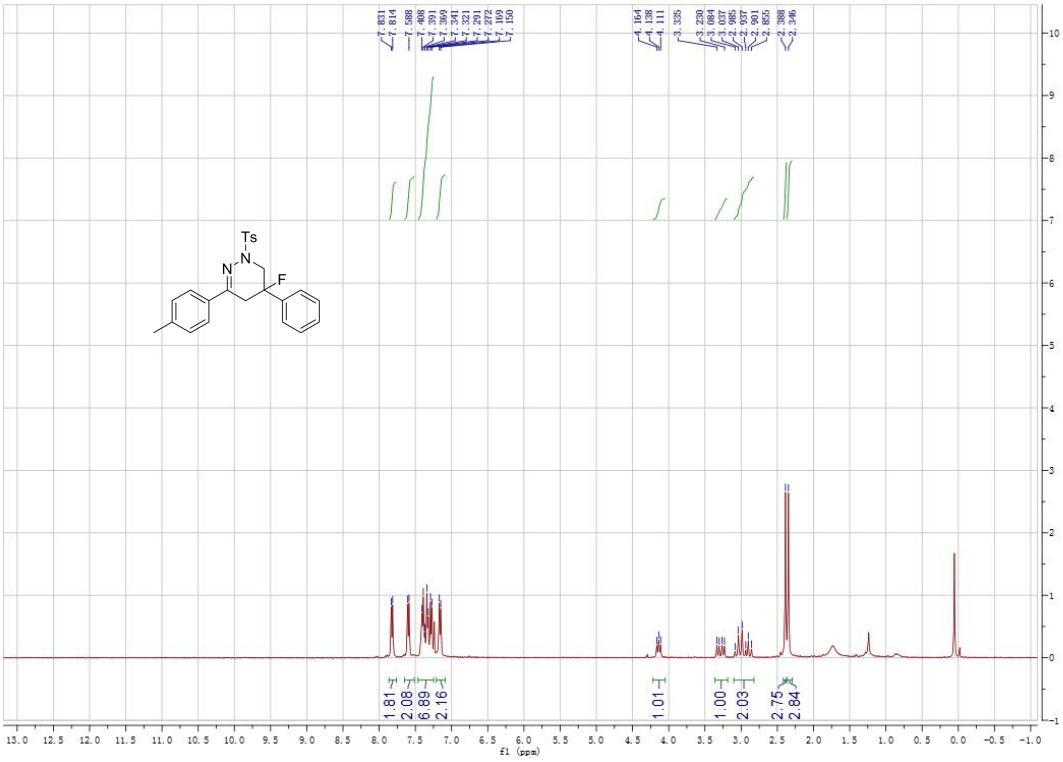

162.175
143.524
137.101
129.219
127.964
86.941
85.192
77.336
76.701
69.062
68.863
45.126
45.697
39.155
30.167
29.998
25.606
21.575
20.865
20.840
Ts
N
N
F
f1 (ppm)

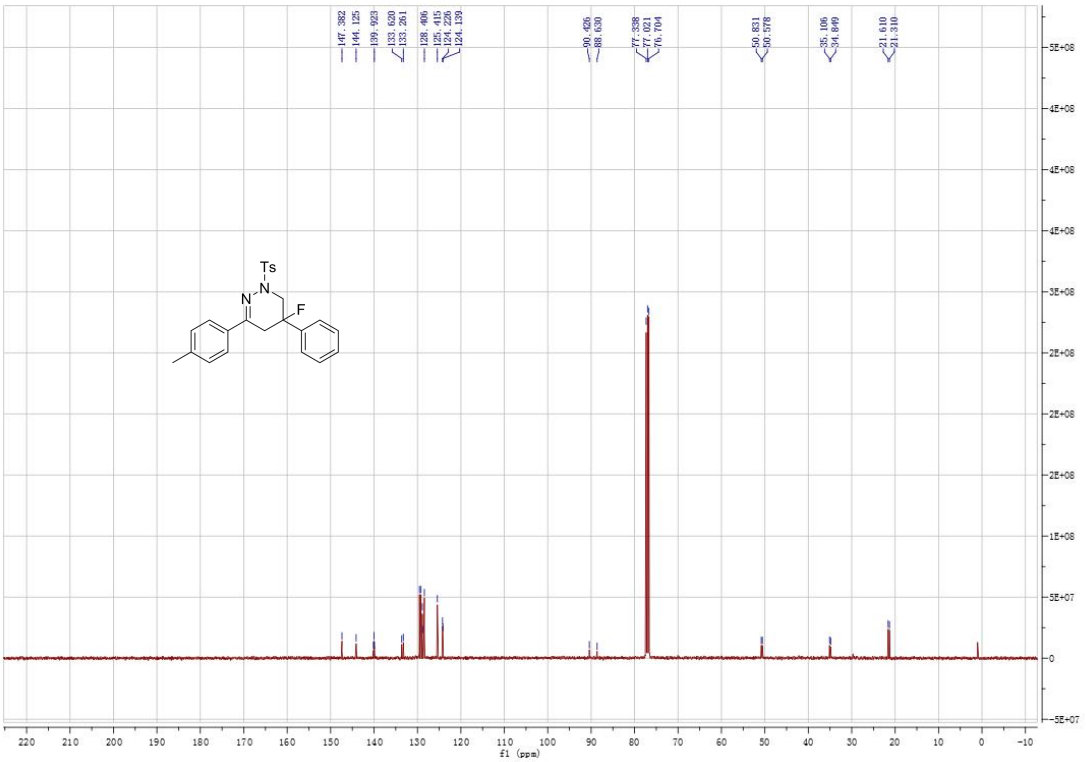

222.054
222.179
222.305
N
N
Ts
F
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

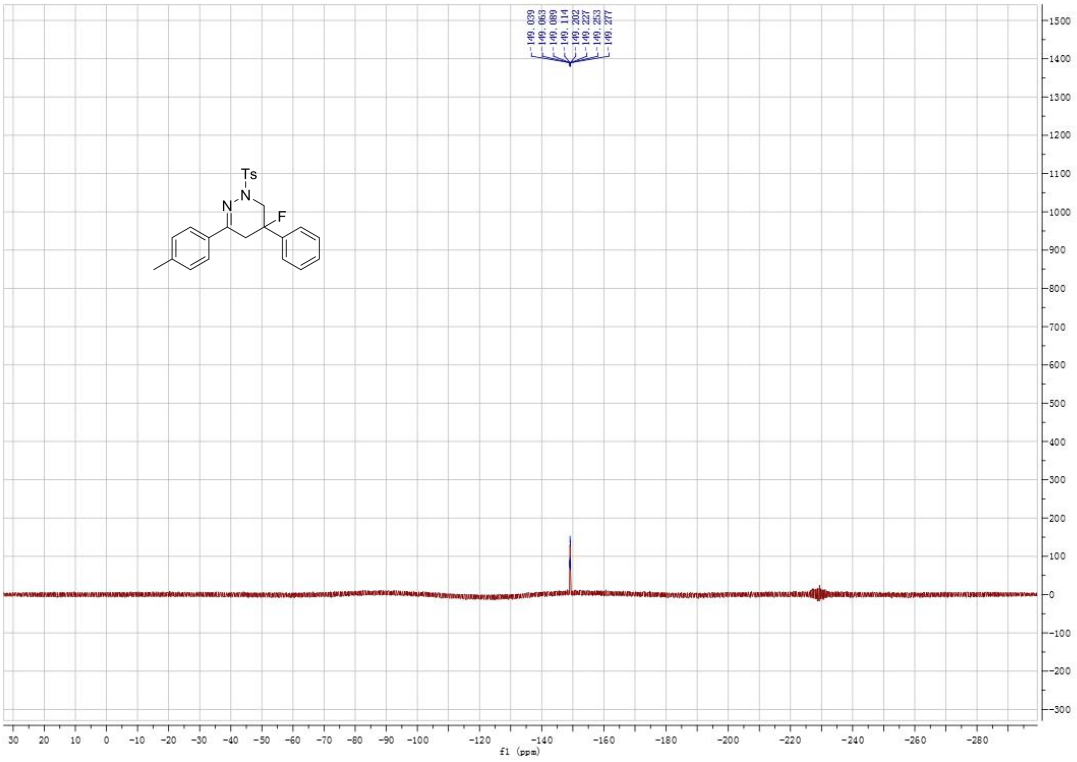

Ts
N
N
F
7.843
7.823
7.714
7.709
7.699
7.693
7.680
7.368
7.361
7.352
7.330
7.304
7.294
7.242
4.199
4.194
4.177
4.170
4.163
4.146
4.141
3.360
3.106
3.059
3.037
2.958
2.919
2.876
2.395
1.80
1.94
7.66
1.94
0.97
1.00
2.00
2.93
f1 (ppm)

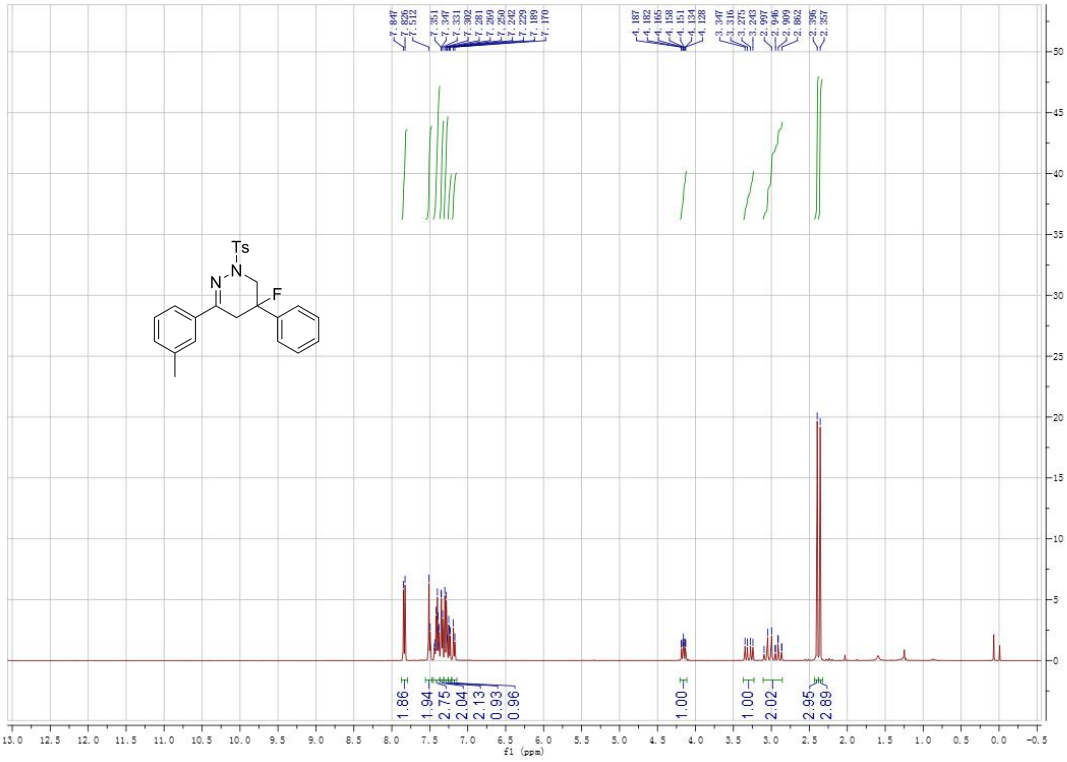

Ts
N
N
F
147.213
144.212
139.823
133.640
129.588
128.912
128.852
128.496
128.387
125.461
124.230
124.134
90.326
88.528
77.344
77.026
76.708
50.781
50.527
35.096
34.836
21.628
f1 (ppm)

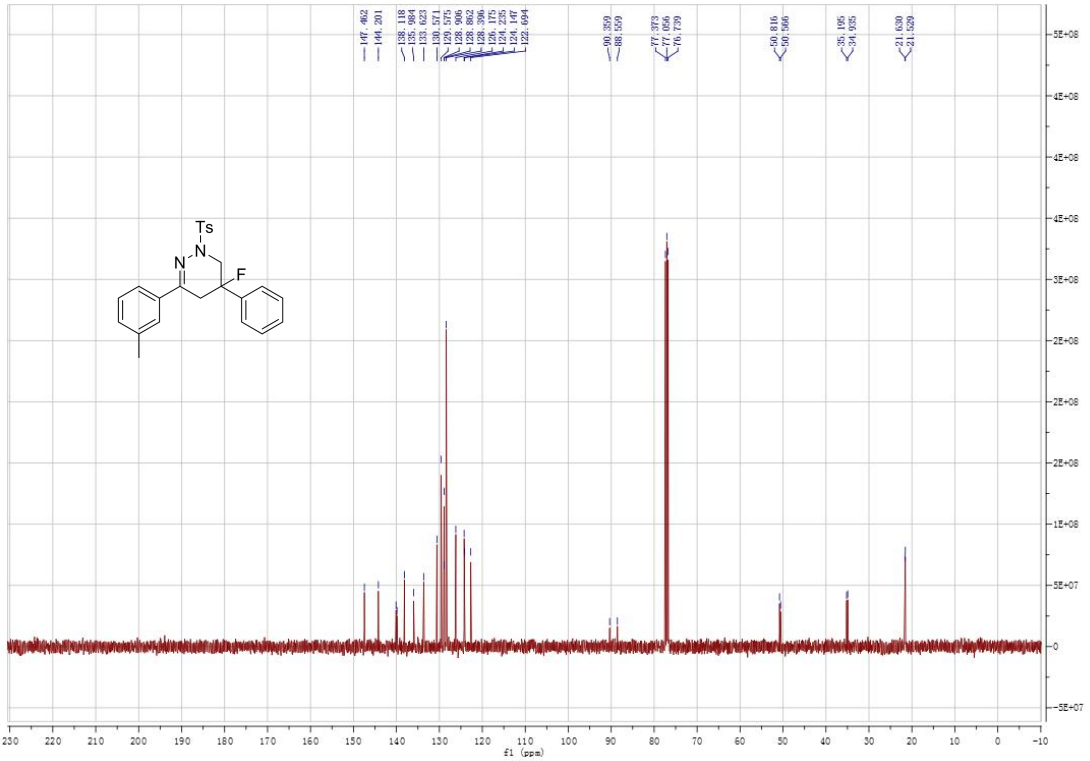

-149.141
-149.164
-149.190
-149.216
-149.229
-149.242
-149.253
-149.267
-149.278
-149.290
-149.304
-149.330
-149.356
-149.379
Ts
N
N
F
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

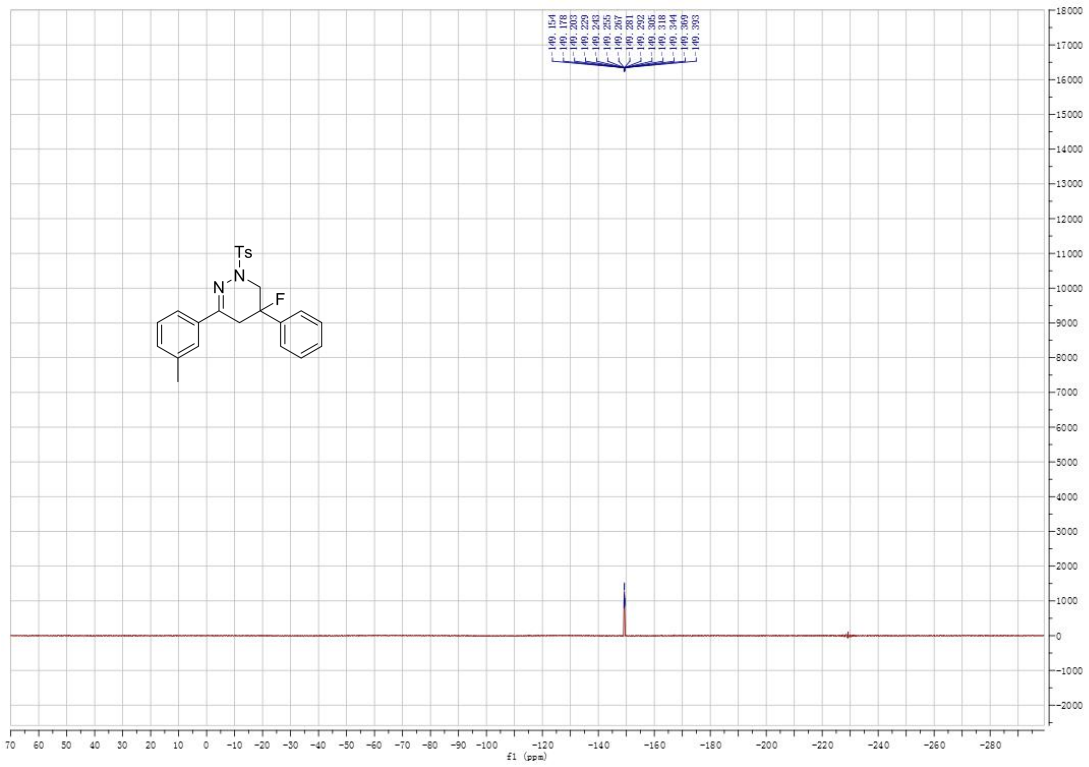

7.831
7.814
7.588
7.408
7.391
7.369
7.351
7.331
7.291
7.272
7.169
7.150
4.164
4.138
4.111
3.335
3.230
3.084
3.037
2.985
2.937
2.901
2.855
2.388
2.346
Ts
N
N
F
1.81
2.08
6.89
2.16
1.01
1.00
2.03
2.75
2.84
f1 (ppm)

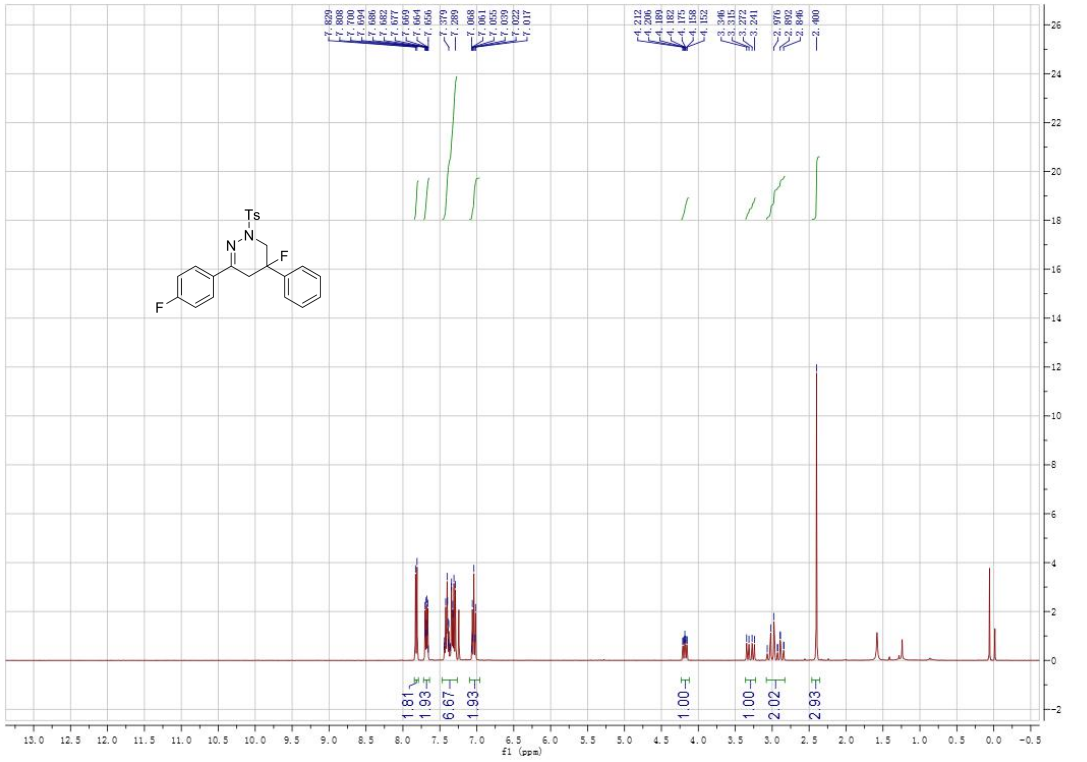

147.382
144.125
139.923
133.620
133.261
128.406
125.415
124.226
124.139
90.625
88.030
77.338
77.021
76.704
50.831
50.578
35.106
34.849
21.610
21.310
Ts
N
N
F
f1 (ppm)

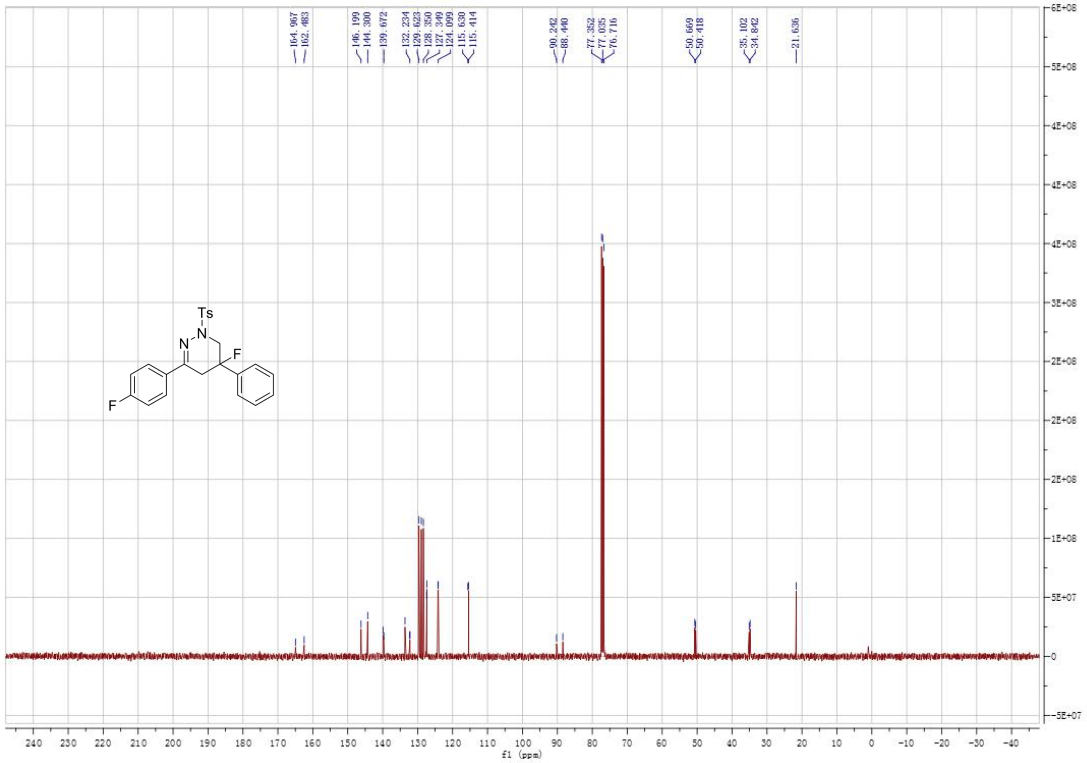

-149.039
-149.063
-149.089
-149.114
-149.202
-149.227
-149.253
-149.277
Ts
N
N
F
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

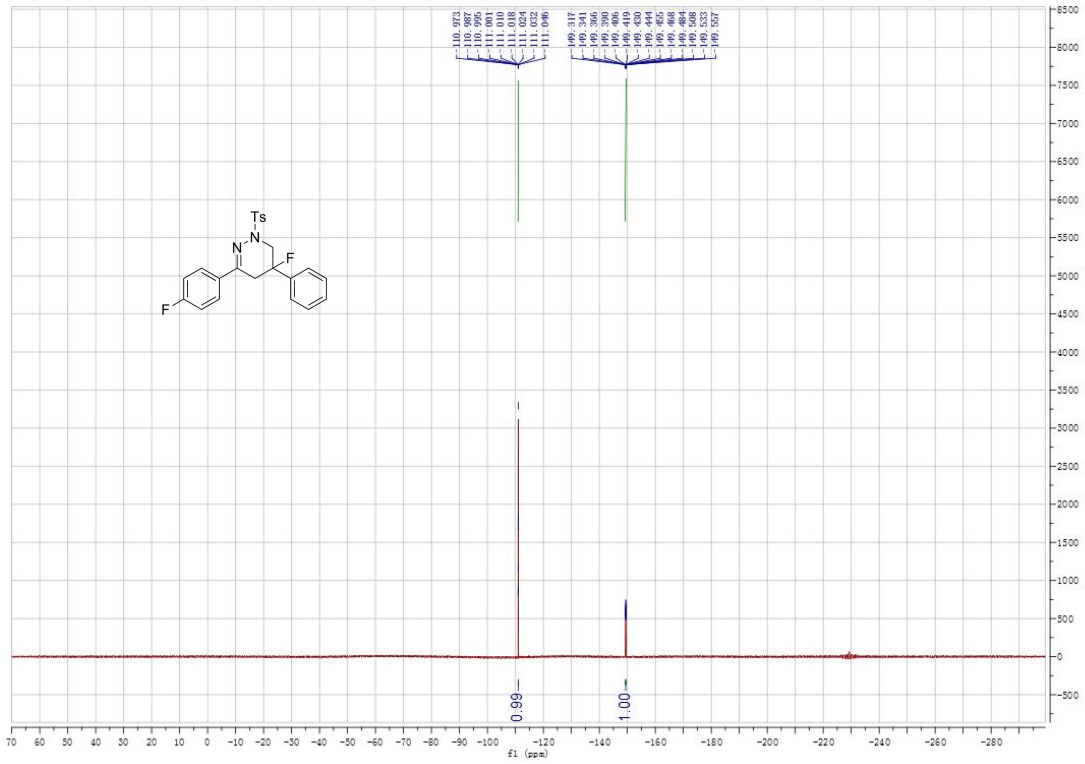

Ts
N
N
F
f1 (ppm)

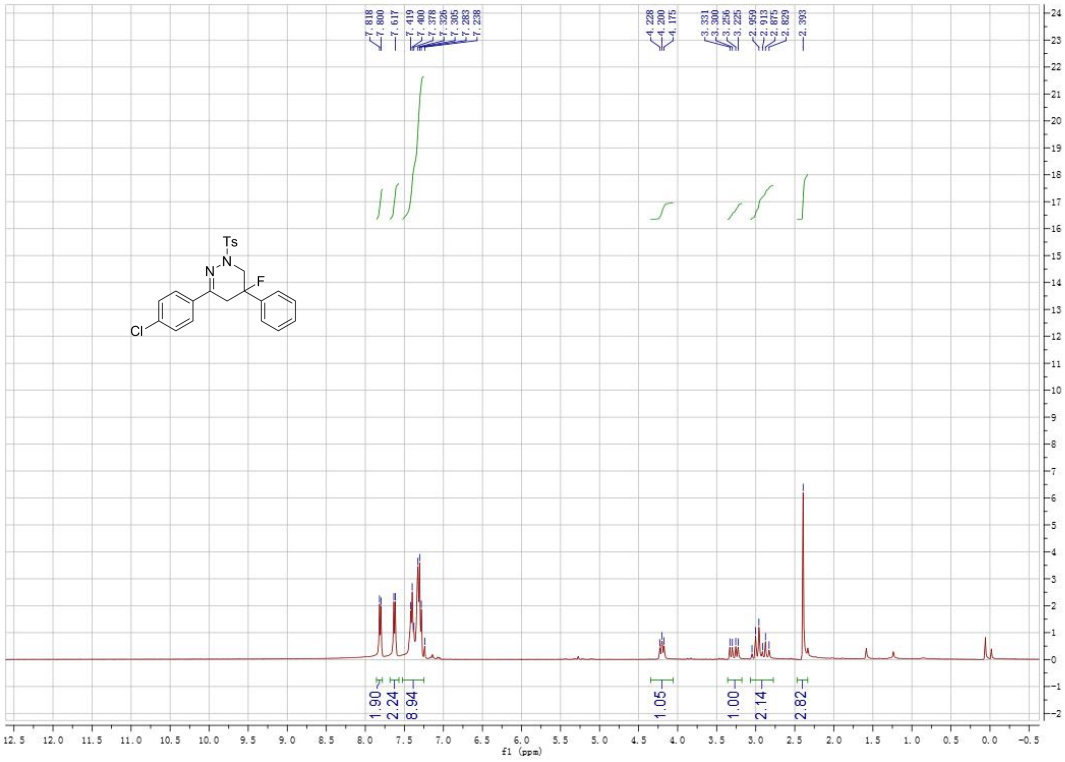

Ts
N
N
F
f1 (ppm)

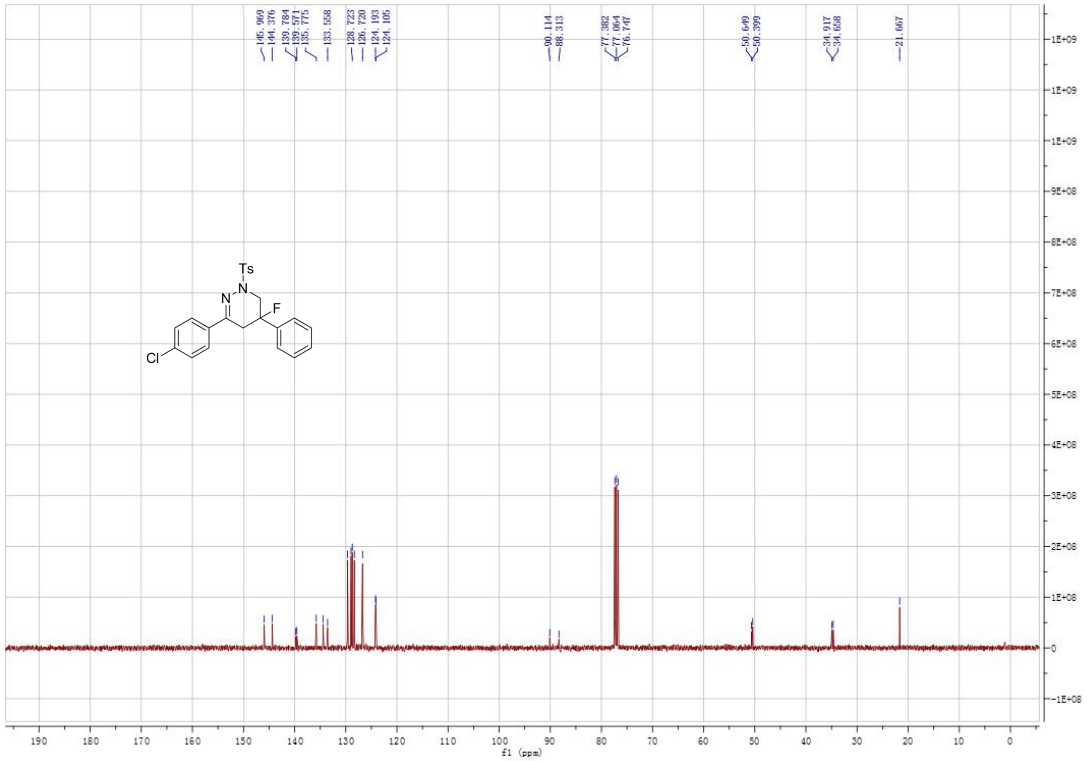

-149.154
-149.178
-149.229
-149.233
-149.243
-149.255
-149.267
-149.291
-149.292
-149.305
-149.318
-149.344
-149.369
-149.393
Ts
N
N
F
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

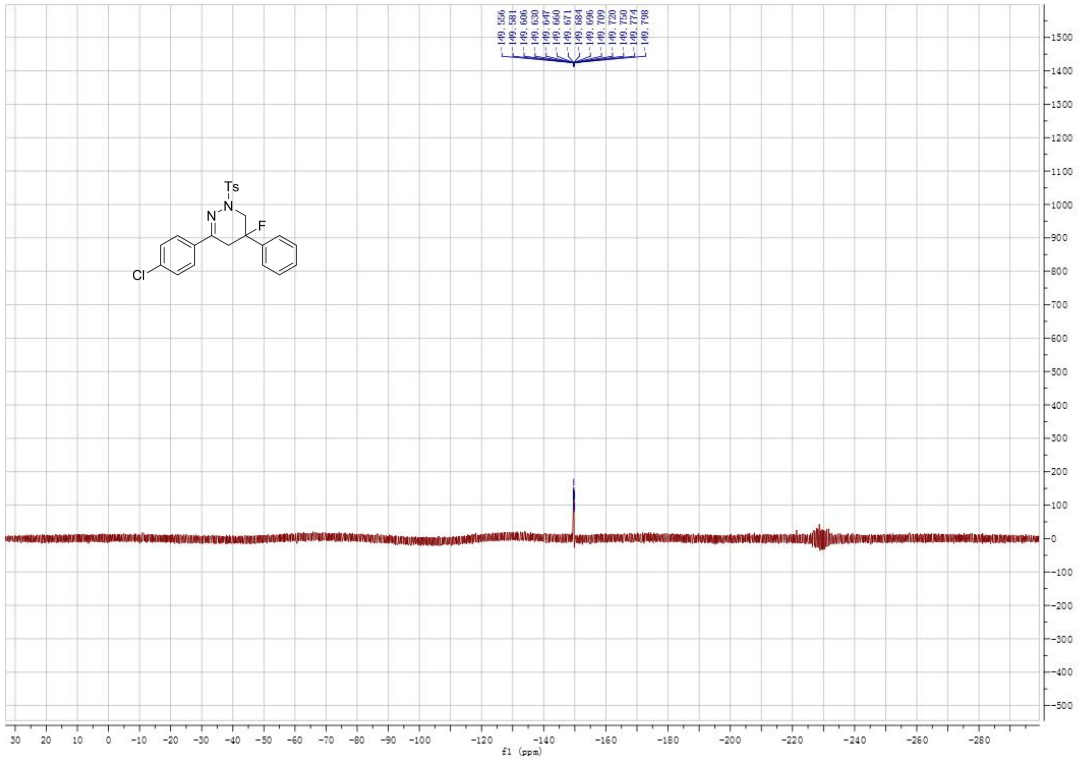

7.829
7.808
7.700
7.694
7.685
7.682
7.677
7.669
7.664
7.656
7.379
7.369
7.063
7.061
7.055
7.039
7.022
7.017
4.212
4.206
4.189
4.182
4.175
4.158
4.152
3.346
3.315
3.272
3.241
2.976
2.892
2.846
2.490
Ts
N
N
F
F
1.81
1.93
6.67
1.93
1.00
1.00
2.02
2.93
f1 (ppm)

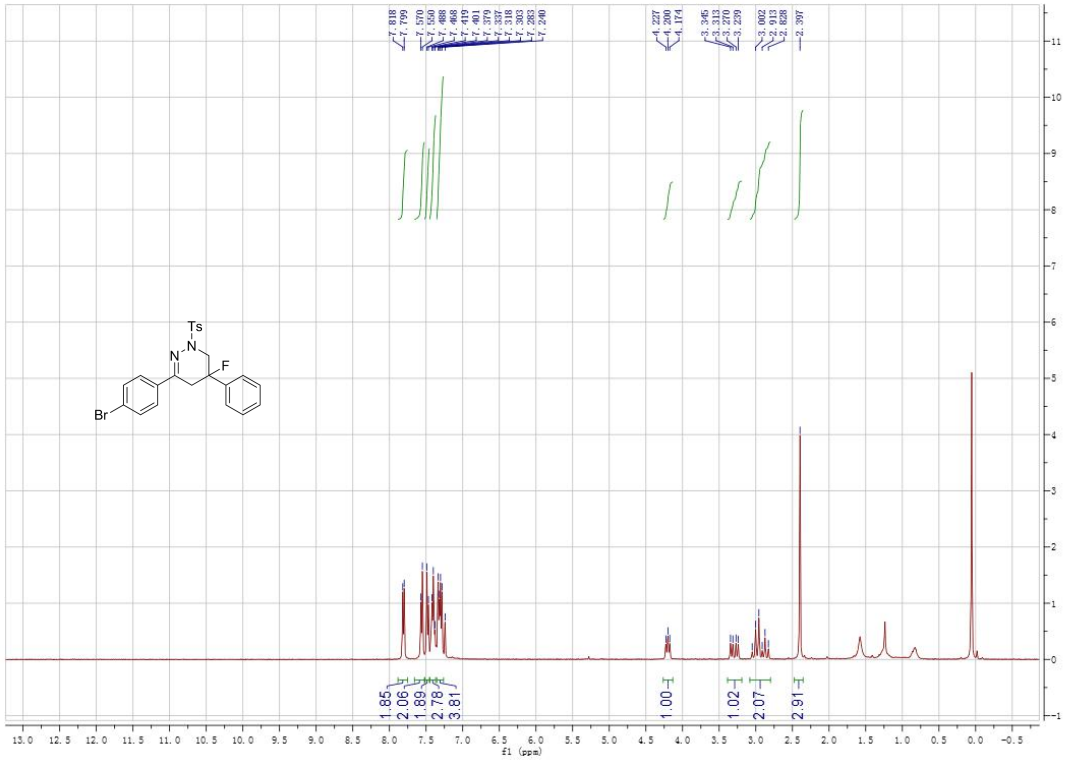

164.967
162.483
146.199
144.300
139.672
132.234
129.623
129.530
127.349
124.099
115.630
115.414
90.262
88.490
77.352
77.035
76.716
60.669
60.418
35.102
34.842
21.636
Ts
N
N
F
F
f1 (ppm)

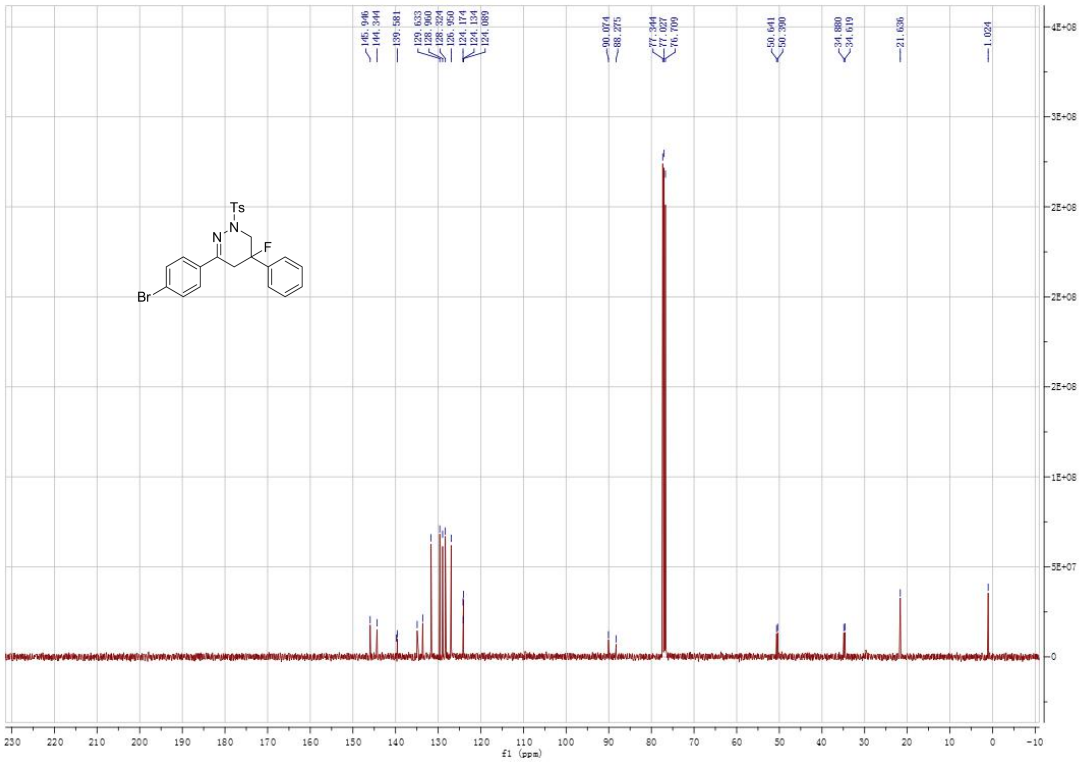

Ts
N
N
F
F
-110.973
-110.987
-110.995
-111.001
-111.010
-111.018
-111.024
-111.032
-111.046
-149.317
-149.341
-149.366
-149.390
-149.406
-149.419
-149.430
-149.444
-149.455
-149.468
-149.484
-149.508
-149.533
-149.557
0.99
1.00
f1 (ppm)

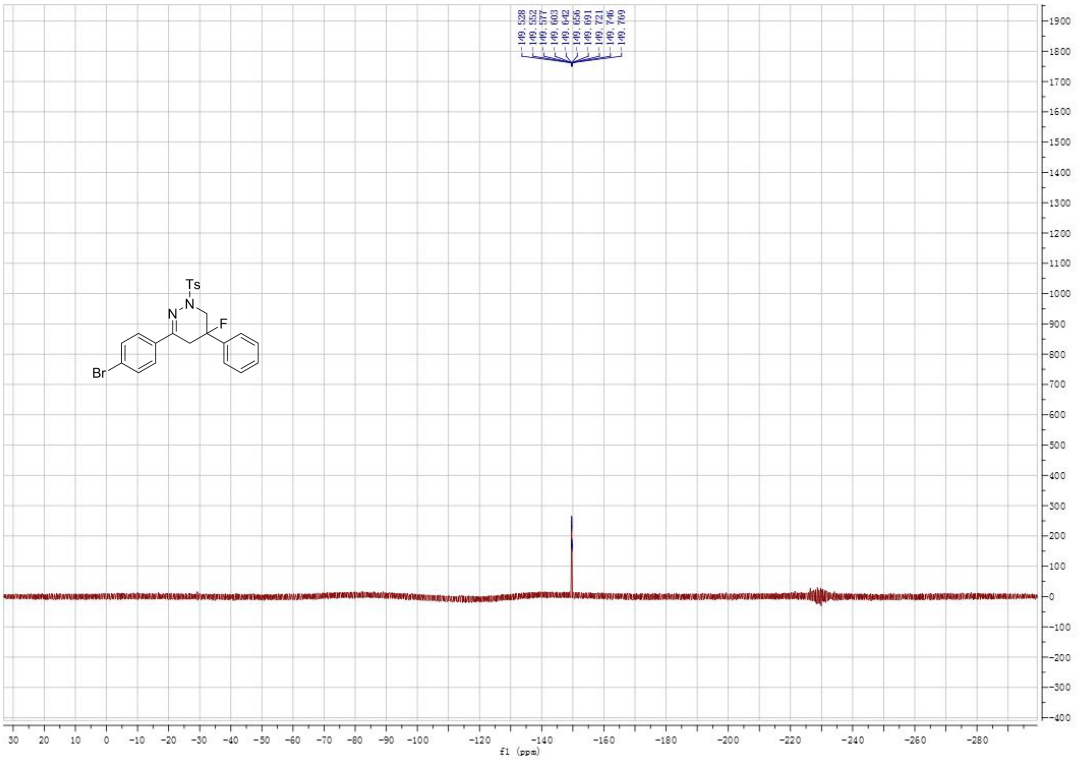

7.818
7.800
7.617
7.419
7.400
7.378
7.336
7.305
7.283
7.238
4.228
4.200
4.175
3.331
3.300
3.256
3.225
2.959
2.913
2.875
2.829
2.393
Ts
N
N
F
Cl
1.90
2.24
8.94
1.05
1.00
2.14
2.82
f1 (ppm)

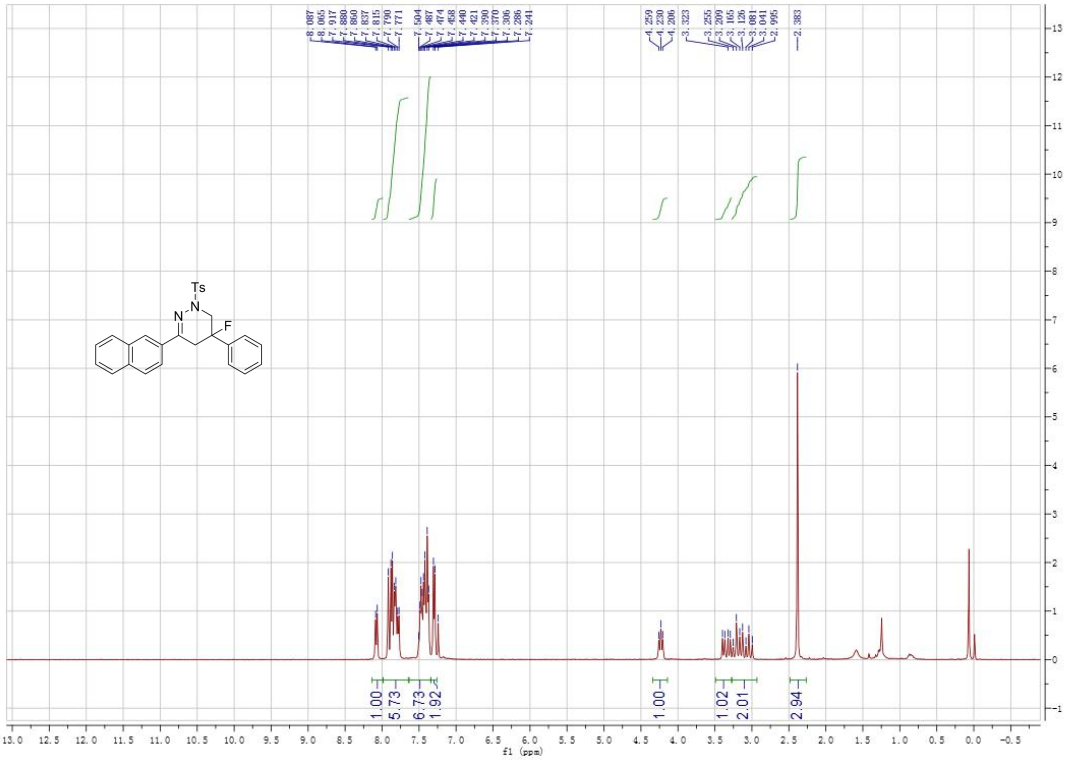

145.960
144.376
139.784
139.571
135.775
133.558
128.723
126.720
124.193
124.105
90.114
88.313
77.382
77.064
76.747
50.649
50.399
34.917
34.658
21.667
Ts
N
N
F
Cl
f1 (ppm)

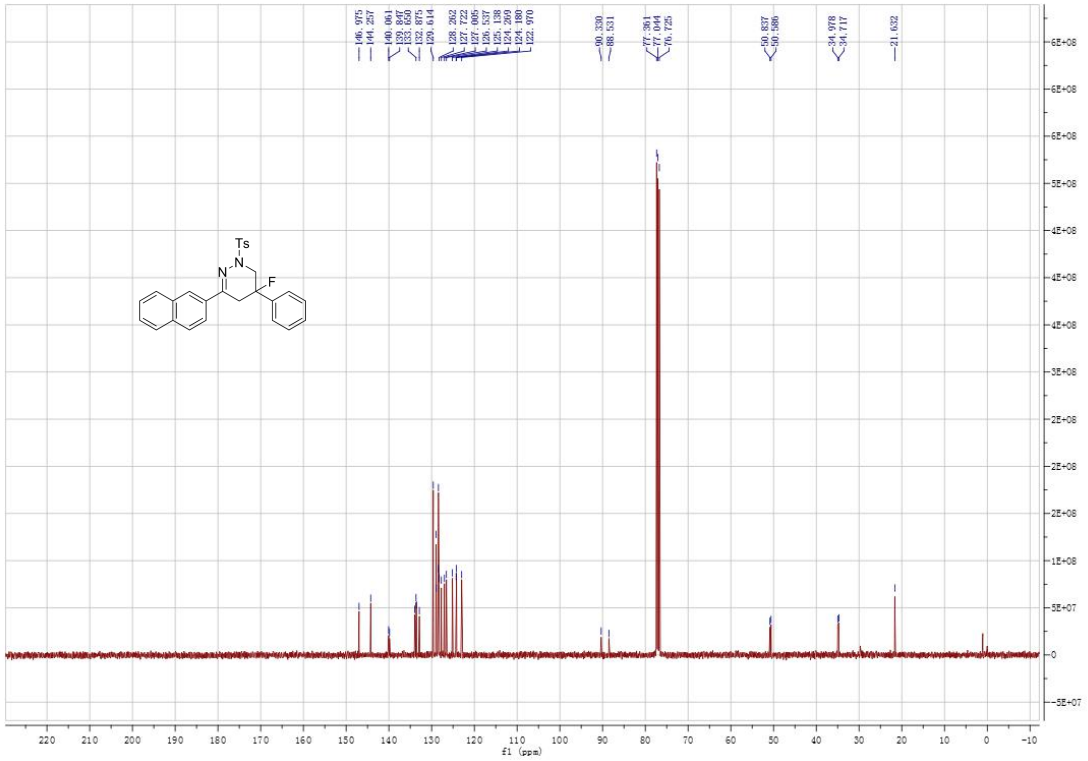

-149.556
-149.581
-149.606
-149.630
-149.647
-149.660
-149.671
-149.684
-149.696
-149.709
-149.720
-149.759
-149.774
-149.798
Ts
N
N
F
Cl
f1 (ppm)

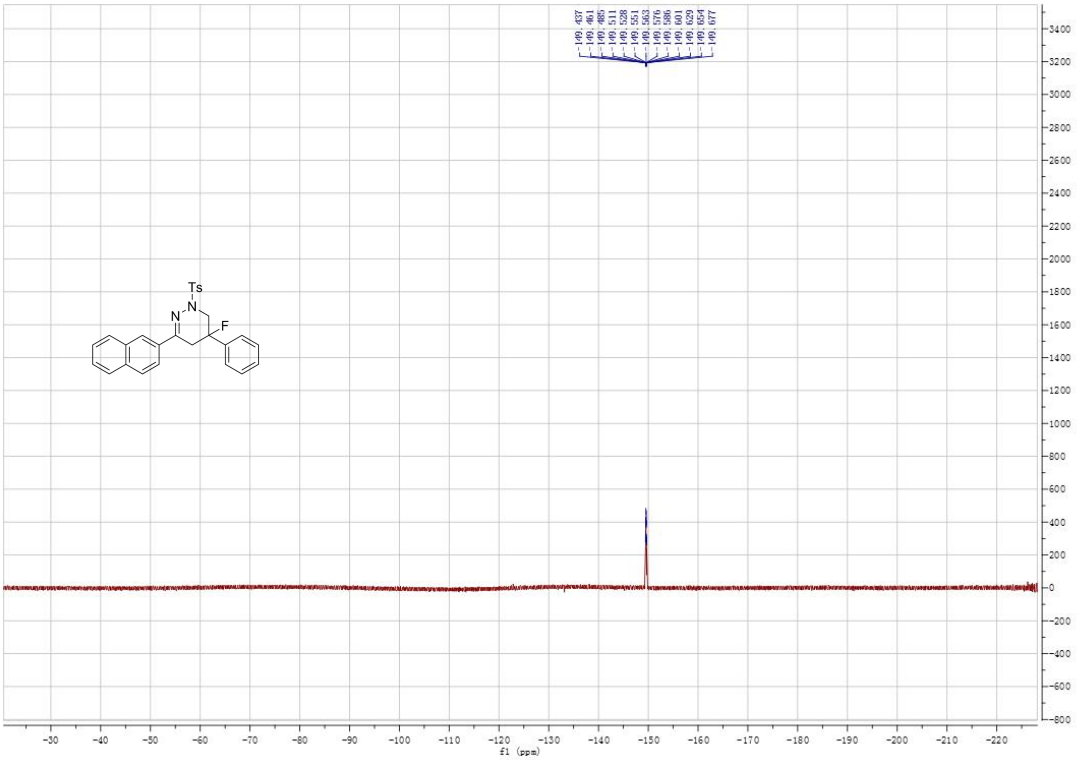

Ts
N
N
F
Br
7.818
7.799
7.570
7.550
7.488
7.468
7.419
7.401
7.379
7.377
7.318
7.303
7.283
7.240
4.227
4.200
4.174
3.345
3.313
3.270
3.239
3.002
2.913
2.828
2.397
1.85
2.06
1.89
2.78
3.81
1.00
1.02
2.07
2.91
f1 (ppm)

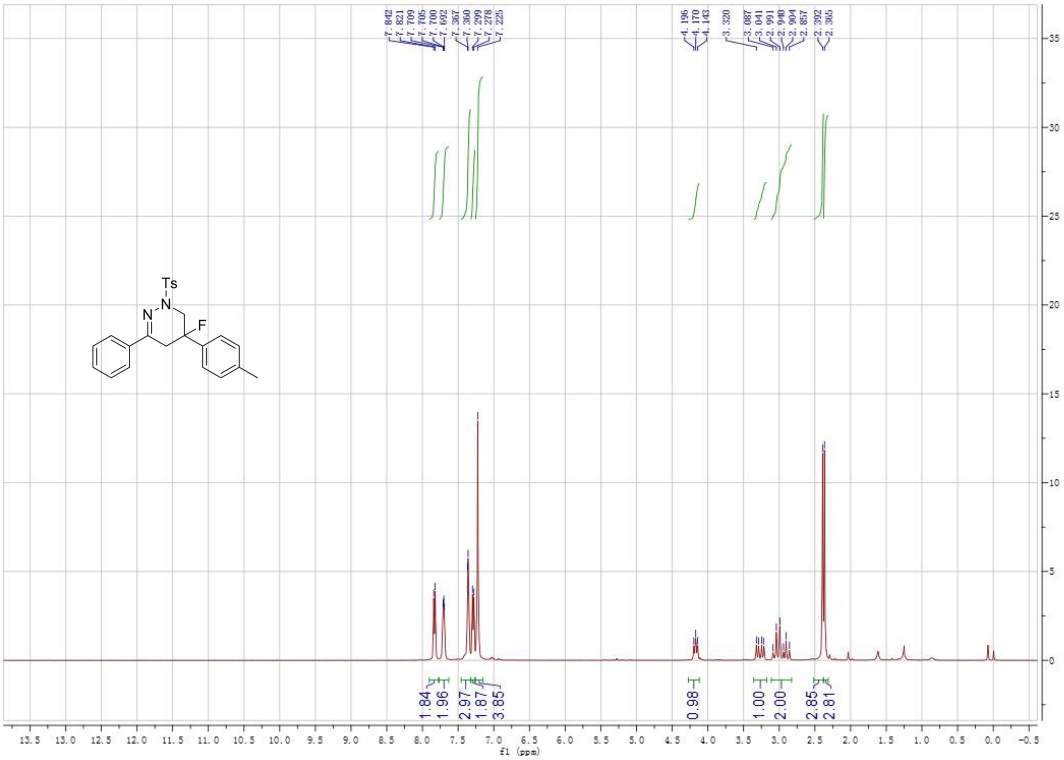

Ts
N
N
F
Br
145.946
144.344
139.581
129.633
129.369
128.324
126.950
124.174
124.134
124.089
90.074
88.275
77.344
77.027
76.709
60.641
60.390
34.880
34.619
21.636
1.024
f1 (ppm)

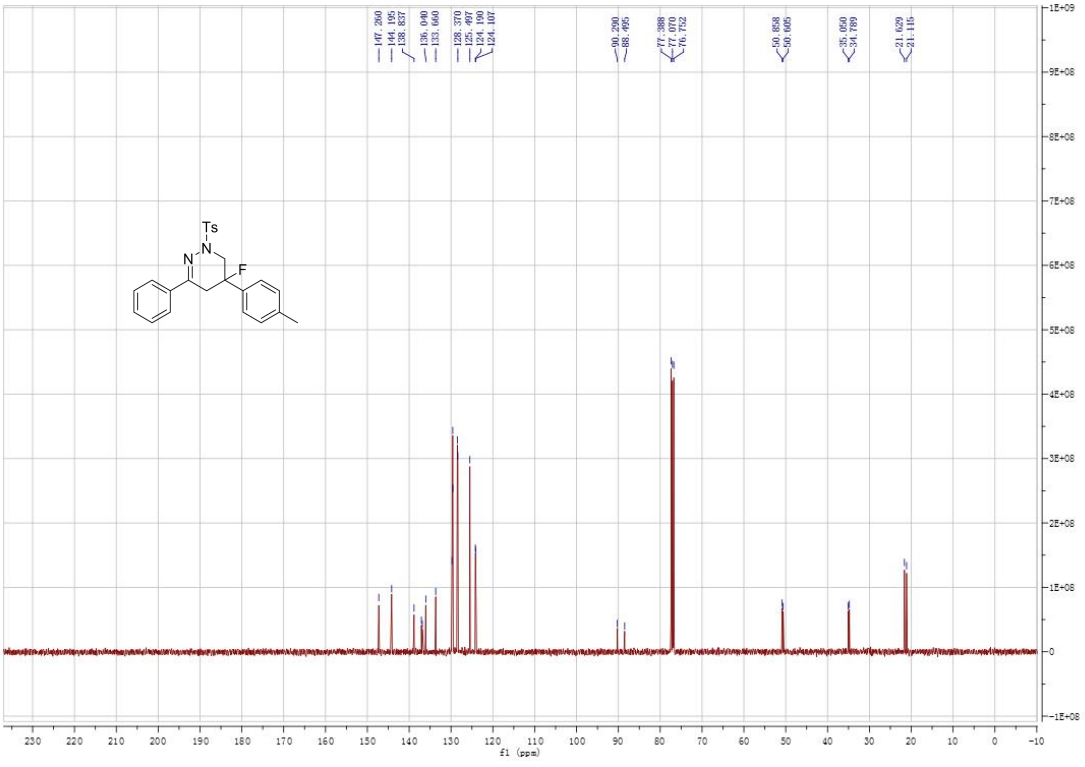

-149.528
-149.552
-149.577
-149.603
-149.627
-149.656
-149.691
-149.721
-149.746
-149.769
Ts
N
N
F
Br
f1 (ppm)

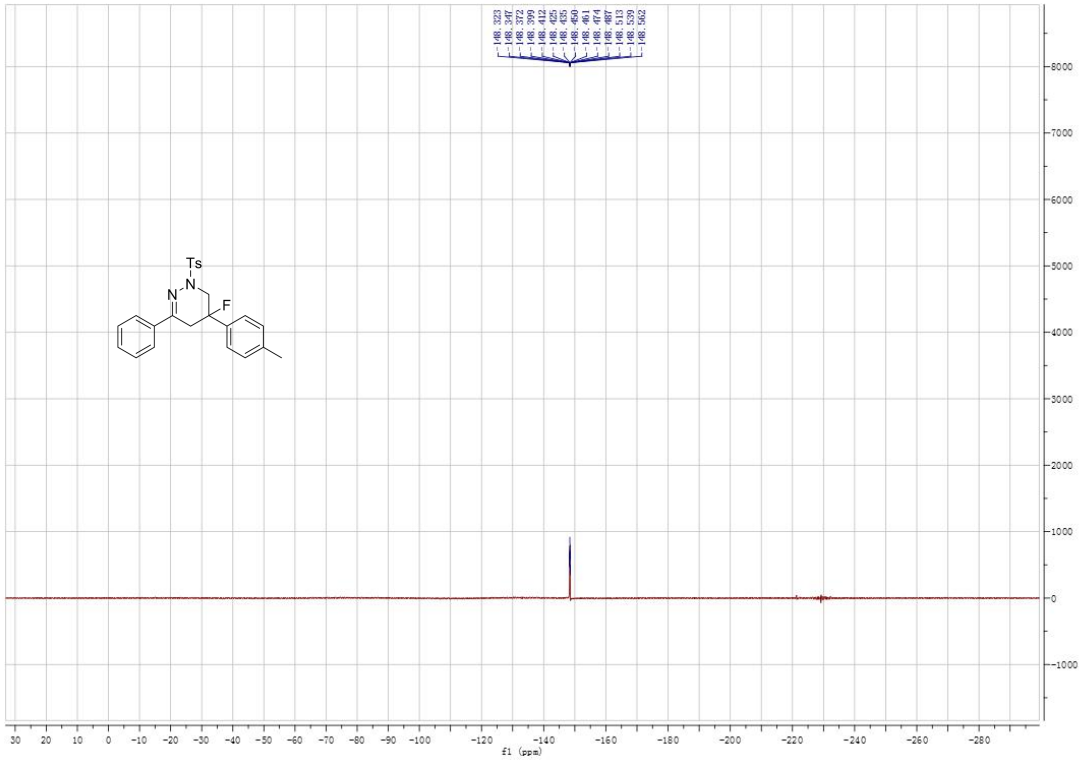

8.087
8.065
7.917
7.898
7.860
7.837
7.815
7.790
7.771
7.504
7.497
7.474
7.458
7.440
7.421
7.399
7.370
7.306
7.286
7.241
4.259
4.230
4.206
3.323
3.255
3.209
3.165
3.126
3.081
3.044
2.995
2.383
Ts
N
N
F
1.00
5.73
6.73
1.92
1.00
1.02
2.01
2.94
f1 (ppm)

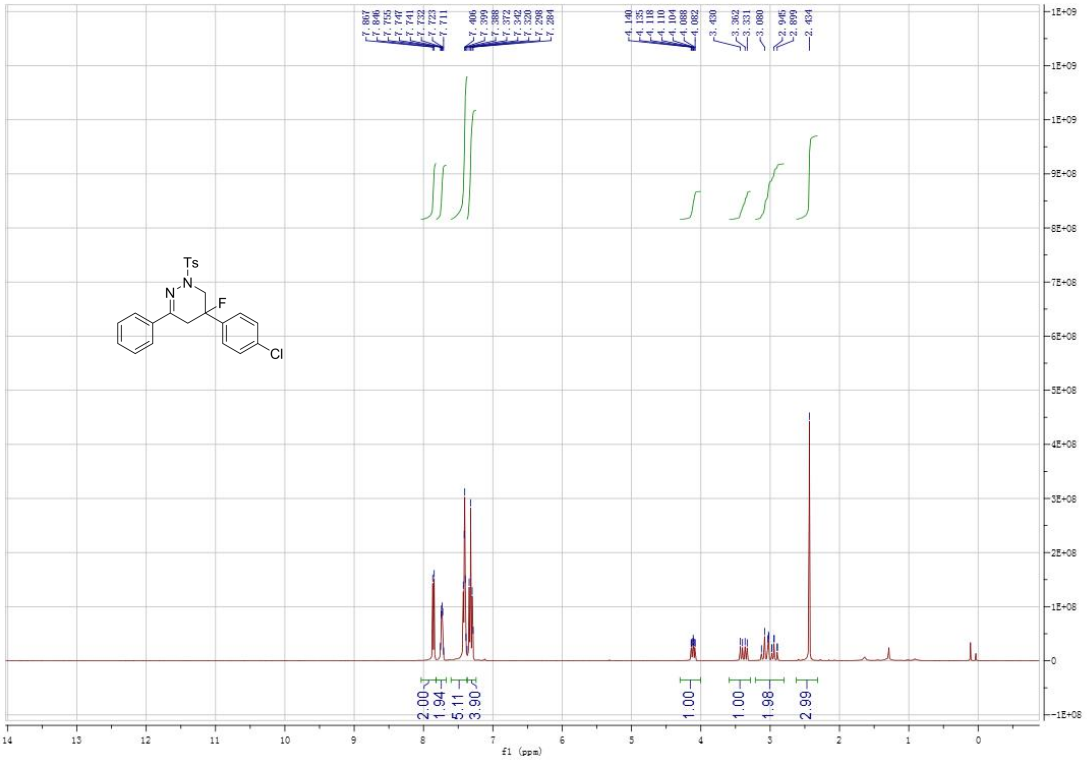

146.975
144.257
140.061
139.847
133.650
132.875
129.614
128.262
127.722
127.005
126.537
125.198
124.269
124.180
122.970
90.330
86.531
77.361
77.044
76.725
50.837
50.586
34.978
34.717
21.632
Ts
N
N
F
f1 (ppm)

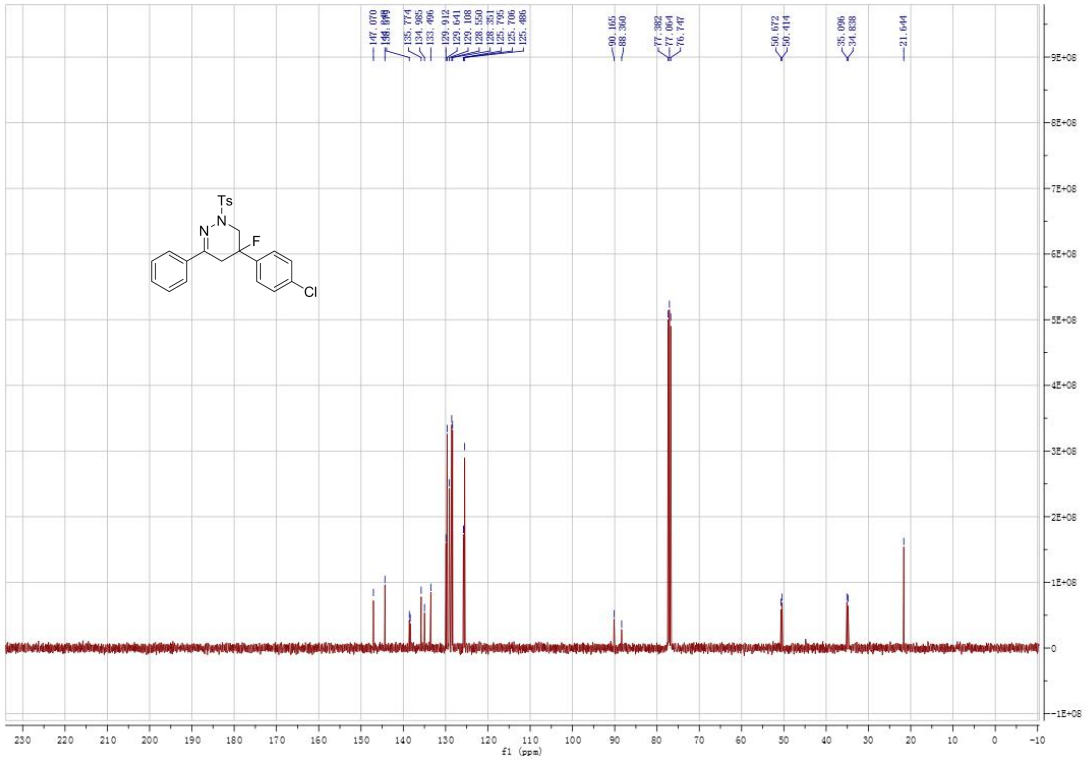

-149.437
-149.461
-149.485
-149.511
-149.528
-149.551
-149.563
-149.576
-149.586
-149.601
-149.629
-149.654
-149.677
Ts
N
N
F
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

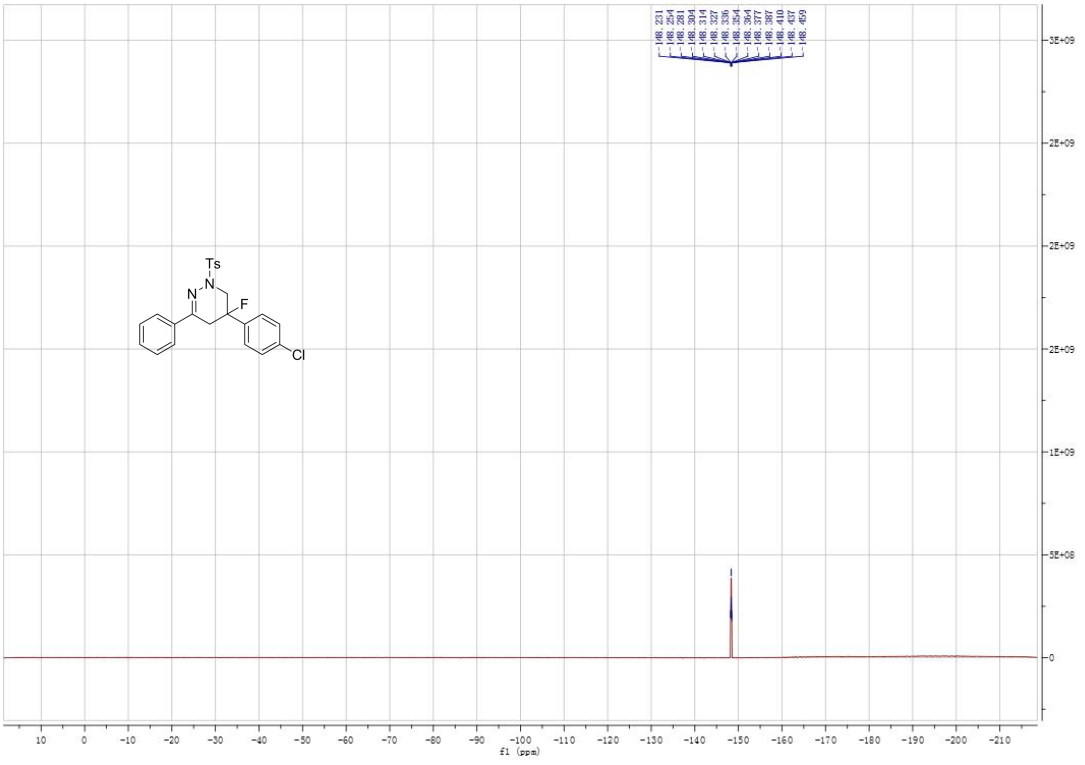

Ts
N
N
F
7.842
7.821
7.709
7.705
7.700
7.692
7.387
7.360
7.299
7.278
7.225
4.196
4.170
4.143
3.320
3.087
3.041
2.991
2.940
2.904
2.857
2.372
2.365
1.84
1.96
2.97
1.87
3.85
0.98
1.00
2.00
2.85
2.81
f1 (ppm)

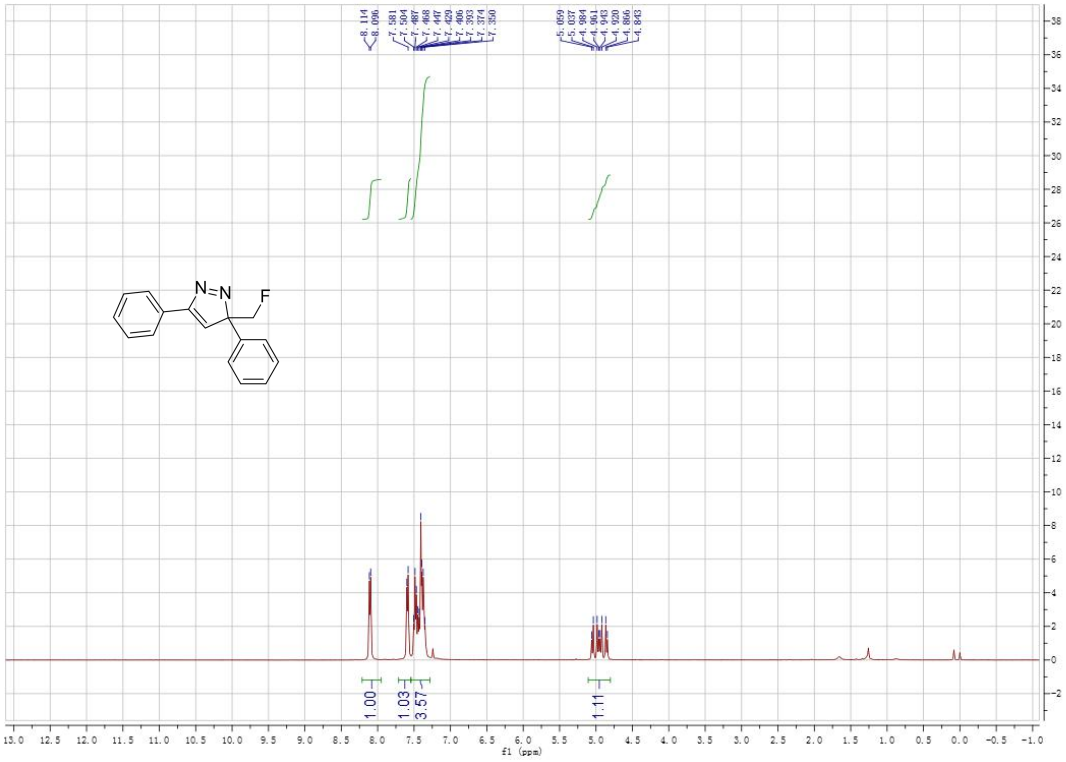

Ts
N
N
F
147.260
144.195
138.837
135.040
133.660
128.370
125.497
125.196
124.107
90.290
88.495
77.388
77.070
76.752
50.858
50.605
35.050
34.789
21.629
21.115
f1 (ppm)

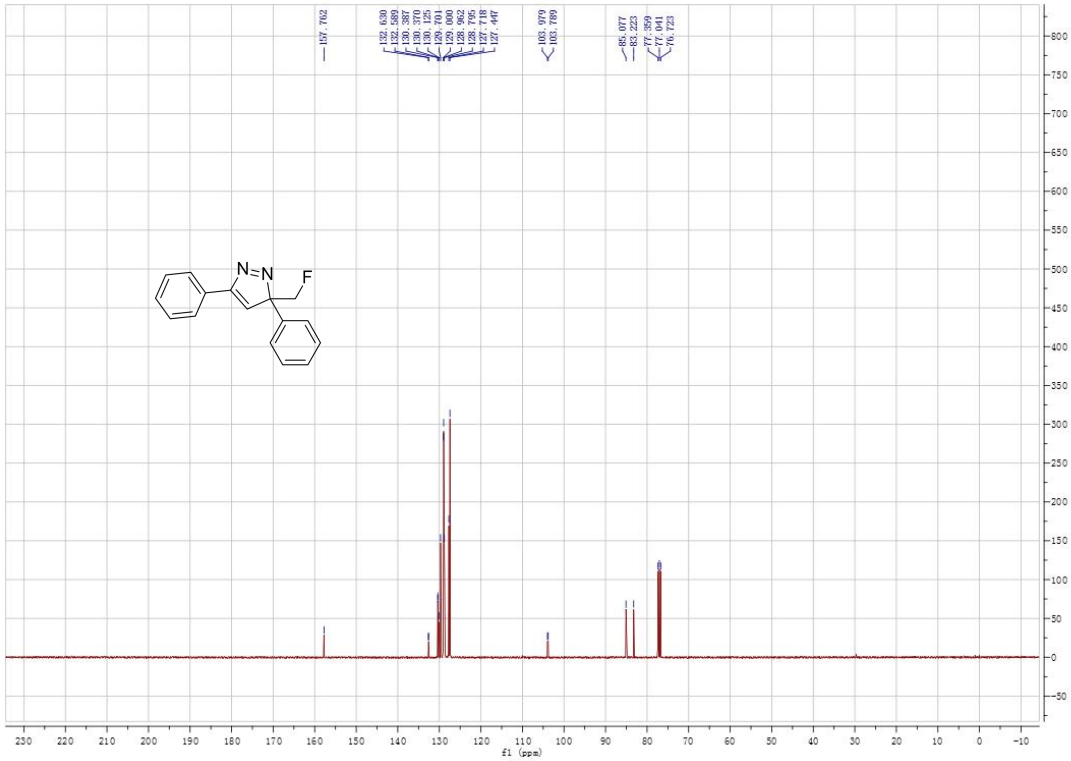

-148.323
-148.347
-148.372
-148.399
-148.412
-148.425
-148.435
-148.450
-148.461
-148.474
-148.487
-148.513
-148.539
-148.562
Ts
N
N
F
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

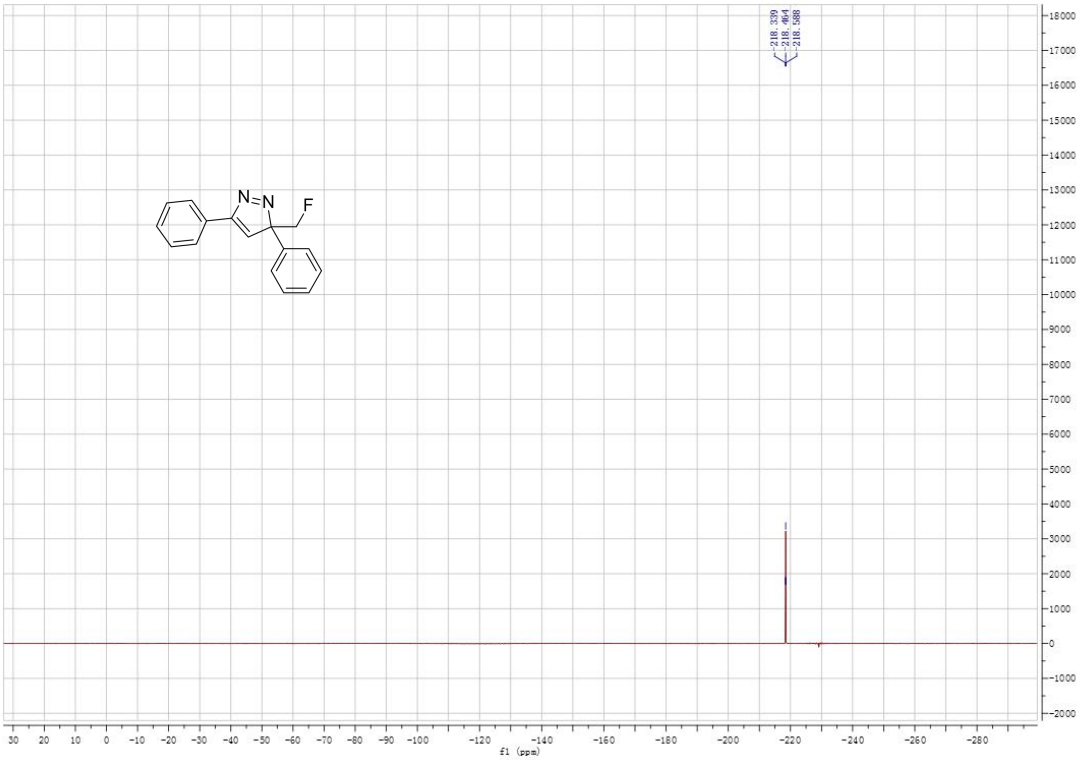

Ts
N
N
F
Cl
7.867
7.846
7.735
7.727
7.741
7.732
7.723
7.711
7.406
7.399
7.388
7.372
7.342
7.320
7.298
7.284
4.140
4.125
4.118
4.110
4.104
4.088
4.082
3.430
3.362
3.331
3.089
2.945
2.899
2.434
2.00
1.94
5.11
3.90
1.00
1.00
1.98
2.99
f1 (ppm)

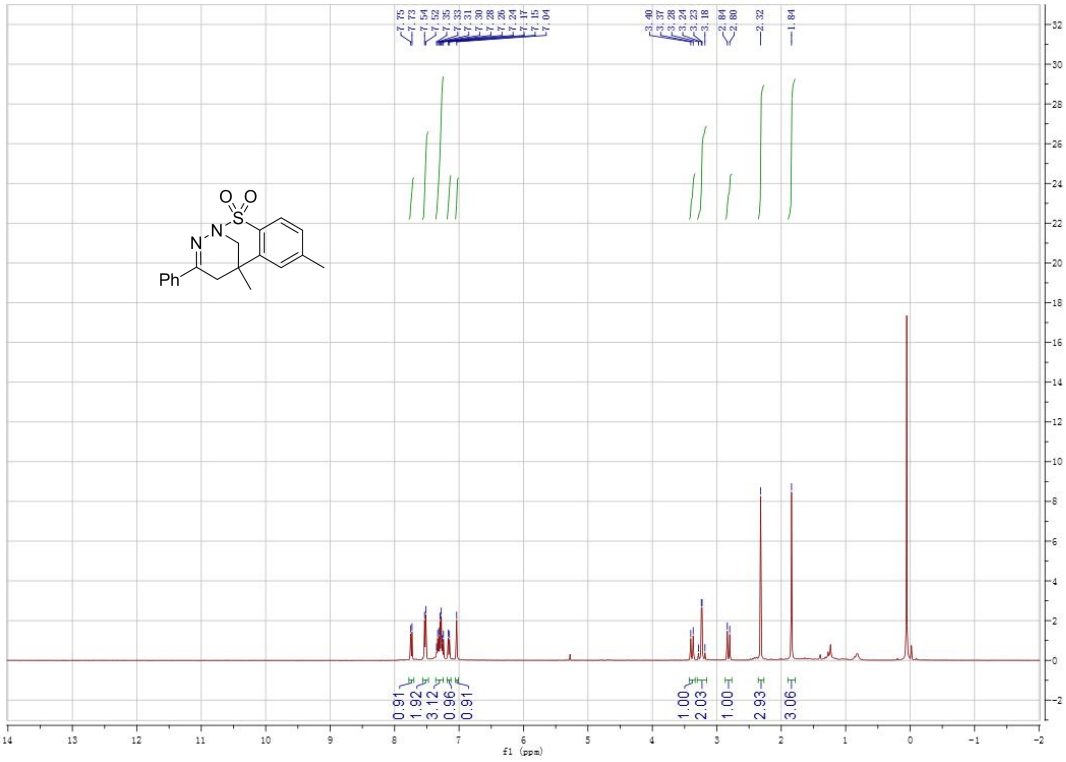

Ts
N
N
F
Cl
147.070
144.099
135.774
134.985
133.496
129.912
129.141
129.108
128.550
128.351
125.795
125.709
125.486
90.165
88.360
77.382
77.064
76.747
50.672
50.414
35.096
34.838
21.644
f1 (ppm)

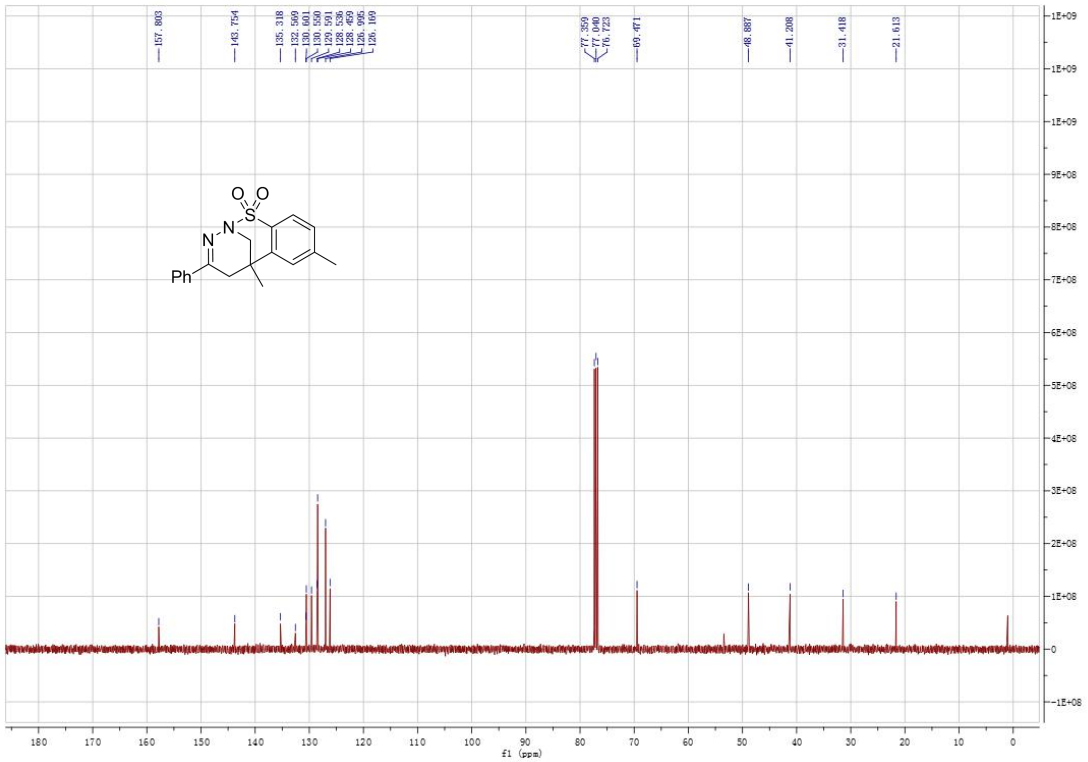

-148.231
-148.254
-148.281
-148.304
-148.314
-148.327
-148.336
-148.354
-148.364
-148.377
-148.387
-148.410
-148.437
-148.459
Ts
N
N
F
Cl
3E+09
2E+09
2E+09
2E+09
1E+09
5E+08
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

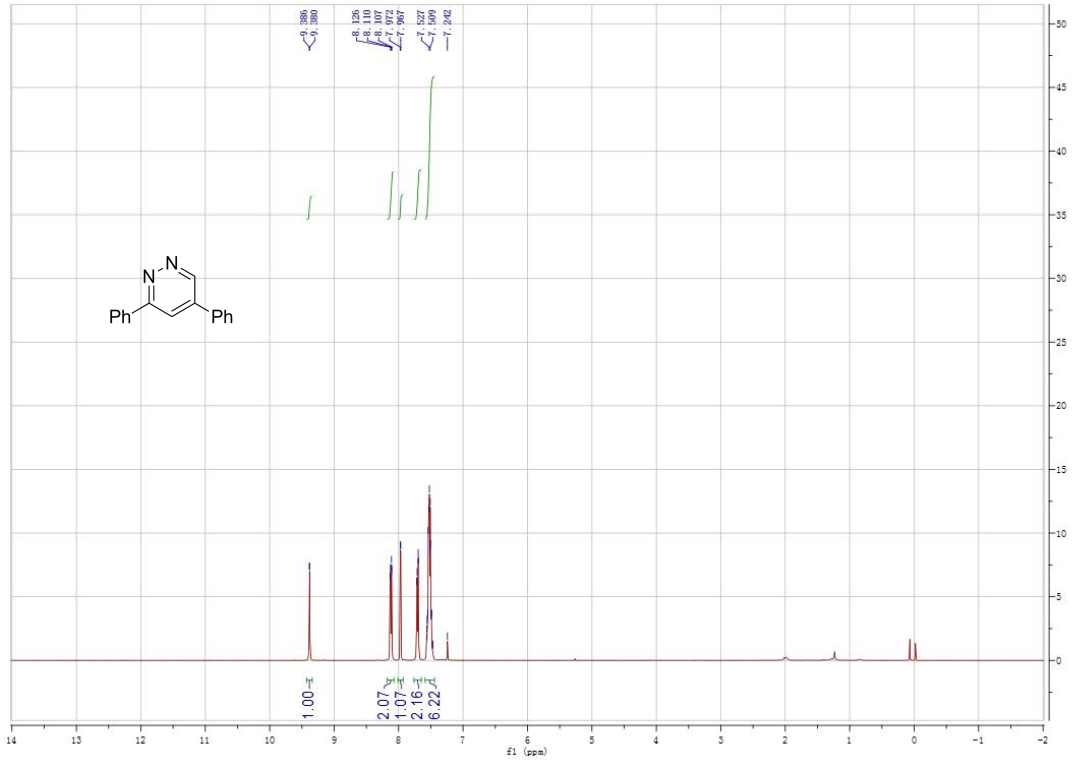

8.114
8.096
7.581
7.564
7.467
7.466
7.447
7.429
7.406
7.393
7.374
7.350
5.059
5.037
4.964
4.941
4.920
1.866
1.845
1.00
1.03
3.57
1.11
f1 (ppm)


157.762
132.630
132.589
130.387
130.370
130.151
129.701
129.000
128.962
128.795
127.717
127.447
103.979
103.789
85.077
83.223
77.359
77.041
76.723
f1 (ppm)


218.339
218.464
218.588
F
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


7.75
7.73
7.54
7.52
7.35
7.33
7.31
7.30
7.28
7.26
7.24
7.17
7.15
7.04
3.40
3.37
3.28
3.24
3.23
3.18
2.84
2.80
2.32
1.84
O
O
S
N
N
Ph
0.91
1.92
3.12
0.96
0.91
1.00
2.03
1.00
2.93
3.06
f1 (ppm)


157.803
143.754
135.318
132.569
130.601
130.560
130.011
128.536
128.459
126.995
126.169
77.359
77.040
76.723
69.471
48.887
41.208
31.418
21.613
O
O
S
N
N
Ph
f1 (ppm)


9.386
9.380
8.126
8.110
8.107
7.972
7.967
7.527
7.509
7.242
Ph
Ph
1.00
2.07
1.07
2.16
6.22
f1 (ppm)