Electronic Supporting Information

Rhodium(III)-Catalyzed Oxidative Olefination of *N*-Allyl Sulfonamides

Shui Hu,[a] Dongqi Wang,[b] Jiexiang Liu [a] and Xingwei Li [*b]

[a]*School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, China*

[b]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

xwli@dicp.ac.cn

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1. General Considerations

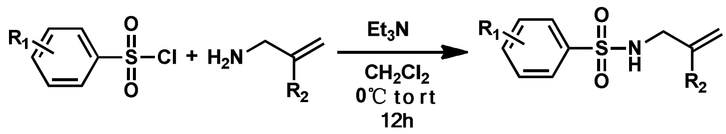
All reactions were carried out under an atmosphere of argon unless otherwise noted. Reactions temperatures are reported as those of the oil bath. The solvents used were purified by distillation and were transferred under argon.

Commercially available chemicals were obtained from Sigma-Aldrich, Alfa Aesar, TCI and Aladdin and were used as received unless otherwise stated. $[RhCp^*Cl_2]_2$ were purchased from Strem.

Reactions were monitored with analytical thin-layer chromatography (TLC) on silica. GC analyses were performed on Shimadzu GC-2010 (Column: GL Science, TCWAX, 0.25 mm ID, 0.25 mm, 60.0 m; Gas pressure: 85 kPa; Total flow: 8.6 mL/min; Column flow: 1.14 mL/min; Velocity: 39.8 cm/sec; Column program: starting from 100℃， 10 min hold, 100℃/min to 270℃, 25 min hold. NMR spectra were recorded on Bruker-DRX (400 MHz or 500 MHz) spectrometers. Chemical shifts (δ) are given in ppm relative to $SiMe_4$. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_c = 77.00 ppm; MeOD: δ_H = 3.31 ppm, δ_C = 49.15 ppm).

2. Preparation of starting materials

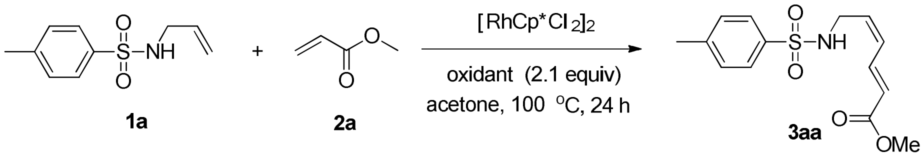
Synthesis of *N*-allyl Sulfonamides



In a round-bottom flask, allylamine and triethylamine were combined in CH_2Cl_2. The flask was cooled in an ice bath, to which was slowly added the sulfonyl chloride. The ice bath was allowed to warm to room temperature and the mixture was stirred for 12 h. The reaction mixture was then diluted with CH_2Cl_2 and washed with HCl (1M) and water. The organic layer was dried over Na_2SO_4 and taken to dryness under reduced pressure. The product obtained was pure enough for further reaction.

3. Optimization of the Reaction Conditions

Table 1. Optimization Studies



Entry	Catalyst	Loading (%)	Oxidant	Yield(%)[b]
1	$[RhCp^{*}Cl_2]_2$	5	$Cu(OAc)_2$	42
2	$[RhCp^{*}Cl_2]_2$	5	Ag_2CO_3	53
3	$[RhCp^{*}Cl_2]_2$	5	Ag_2O	nd
4	$[RhCp^{*}Cl_2]_2$	5	AgOAc	76
5	**$[RhCp^{*}Cl_2]_2$**	**4**	**AgOAc**	**75**
6	$[RhCp^{*}Cl_2]_2$	3	AgOAc	60
7[c]	$[RhCp^{*}Cl_2]_2$	4	AgOAc	72
8[d]	$[RhCp^{*}Cl_2]_2$	4	AgOAc	78

[a] Conditions: *N*-Ts allylamine (0.3 mmol), methyl acrylate (0.45 mmol), $[RhCp^{*}Cl_2]_2$ (3-5 mol %), oxidant (2.1 equiv), acetone (3 mL), 100 °C, 24 h, sealed tube under argon. [b] isolated yield. [c] 4.5 equiv of AgOAc was used. [d] 36 h.

4. Preparation and Characterization of the Products

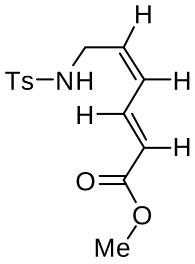
General procedure for the synthesis of 3 and 4

Sulfonamide **(1a)** (0.3 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), acrylate (**2**) (0.45 mmol), and AgOAc (0.63 mmol for **3;** 1.35 mmol for **4)** were weighed into a 25 mL pressure tube, to which was added acetone (4 mL) in a glove box. The reaction vessel was heated in a preheated oil bath at 100 ^oC for 24 h (1 h for KIE studies) with efficient stirring. After cooled to room temperature, the mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to afford the product. Products **3** decompose in $CDCl_3$ so acetone-d_6 was used as an NMR solvent in most cases.

General procedure for the synthesis of 5a, 5b and 6

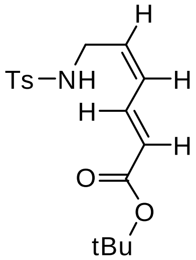
To a mixture of a butadiene product (0.3 mmol) and $Pd(OAc)_2$ (0.015 mmol) in toluene (3.0 mL) was added pyridine (0.03 mmol). The solution was stirred under an oxygen atmosphere at 80 ^oC for 12 h. After cooled to room temperature, the mixture was filtered and was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to give the product.

5. Characterization Data



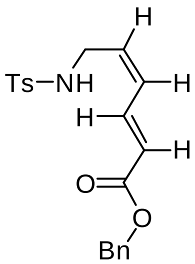
3aa yield:75%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.30 (m, 3H), 6.15 (t, *J* = 11.3 Hz, 1H), 5.91 (d, *J* = 15.2 Hz, 1H), 5.72 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.72 (t, *J* = 5.9 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 2H), 3.75 (s, 3H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.1, 143.8, 137.6, 136.6, 134.0, 129.9, 129.0, 127.2, 123.5, 51.7, 40.4, 21.5. **HRMS (ESI):** Calcd for $[C_{14}H_{17}NO_4S+Na]^+$ 318.0776; Found: 318.0774.



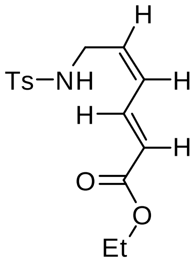
3ab yield:71%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.14 (t, *J* = 11.2 Hz, 1H), 5.84 (d, *J* = 15.2 Hz, 1H), 5.67 (dt, *J* = 10.8, 7.0 Hz, 1H), 4.41 (t, *J* = 6.1 Hz, 1H), 3.82 (t, *J* = 5.9 Hz, 1H), 2.44 (s, 3H), 1.48 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.0, 143.5, 136.5, 133.3, 129.7, 128.3, 127.1, 125.6, 80.6, 40.3, 29.6, 27.9, 21.4. **HRMS (ESI):** Calcd for $[C_{17}H_{23}NO_4S+Na]^+$ 360.1245; Found: 360.1249.



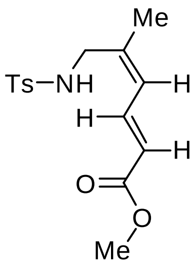
3ac yield:55%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.37 (m, 5H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.16 (t, *J* = 11.4 Hz, 1H), 5.96 (d, *J* = 15.2 Hz, 1H), 5.79 – 5.62 (m, 1H), 5.19 (s, 2H), 4.47 (t, *J* = 6.0 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 2H), 3.72 (t, *J* = 6.0 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 143.7, 137.9, 135.8, 134.3, 129.8, 128.8, 128.5, 128.2, 128.2, 127.1, 123.4, 66.3, 40.4, 29.6, 21.5. **HRMS (ESI):** Calcd for $[C_{20}H_{21}NO_4S+Na]^+$ 394.1089; Found: 394.1092.



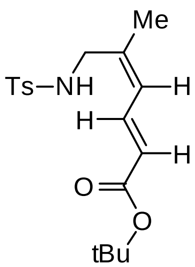
3ad yield:79%

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.35 (m, 3H), 6.15 (t, *J* = 11.3 Hz, 1H), 5.90 (d, *J* = 15.2 Hz, 1H), 5.71 (dt, *J* = 10.7, 7.2 Hz, 1H), 4.74 (t, *J* = 6.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.83 (t, *J* = 6.7 Hz, 2H), 2.44 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 166.7, 143.8, 137.3, 136.5, 133.8, 129.9, 129.0, 127.1, 123.9, 60.6, 40.4, 21.5, 14.2. **HRMS (ESI):** Calcd for $[C_{15}H_{19}NO_4S+Na]^+$ 332.0932; Found: 332.0939.



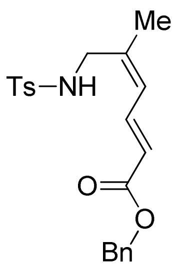
3ba yield:68%

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.29 (m, 3H), 6.03 (d, *J* = 11.8 Hz, 1H), 5.80 (d, *J* = 15.1 Hz, 1H), 4.71 (t, *J* = 6.2 Hz, 1H), 3.75 (d, *J* = 6.3 Hz, 2H), 3.73 (s, 3H), 2.44 (s, 3H), 1.86 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 167.4, 143.7, 142.6, 138.5, 136.7, 129.8, 127.1, 127.0, 121.2, 51.6, 43.5, 22.3, 21.5. **HRMS (ESI):** Calcd for $[C_{15}H_{19}NO_4S+Na]^+$ 332.0932; Found: 332.0940.



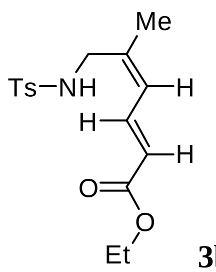
3bb yield: 65%

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.02 (d, *J* = 11.8 Hz, 1H), 5.74 (d, *J* = 15.0 Hz, 1H), 4.40 (t, *J* = 6.3 Hz, 1H), 3.74 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 1.87 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 166.4, 143.7, 141.6, 137.2, 136.7, 129.9, 127.2, 127.1, 123.7, 80.5, 43.6, 28.1, 22.3, 21.5. **HRMS (ESI):** Calcd for $[C_{18}H_{25}NO_4S+Na]^+$ 374.1402; Found: 374.1406.



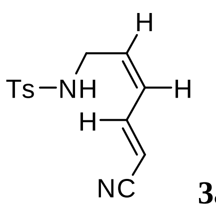
3bc yield: 70%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.21 (m, 8H), 6.00 (d, *J* = 11.7 Hz, 1H), 5.82 (d, *J* = 15.1 Hz, 1H), 5.31 (s, 1H), 5.15 (s, 2H), 3.71 (d, *J* = 3.9 Hz, 2H), 2.39 (s, 3H), 1.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 143.4, 143.2, 139.1, 136.6, 135.9, 129.7, 128.4, 128.1, 128.0, 127.0, 126.7, 120.8, 66.1, 43.3, 22.2, 21.4. **HRMS (ESI):** Calcd for $[C_{21}H_{23}NO_4S+Na]^+$ 408.1245; Found: 408.1241.



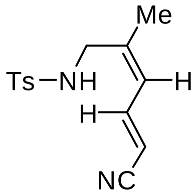
3bd yield:76%

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.29 (m, 3H), 6.03 (d, *J* = 11.7 Hz, 1H), 5.80 (d, *J* = 15.1 Hz, 1H), 4.71 (t, *J* = 6.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.75 (d, *J* = 6.3 Hz, 2H), 2.44 (s, 3H), 1.87 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.0, 143.7, 142.4, 138.3, 136.7, 129.8, 127.13, 127.05, 121.7, 60.4, 43.5, 22.3, 21.5, 14.2. **HRMS (ESI):** Calcd for $[C_{16}H_{21}NO_4S+Na]^+$ 346.1089; Found: 346.1084.



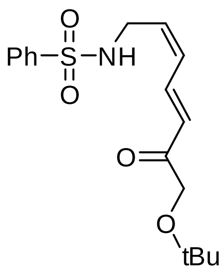
3ae yield:70%

^{1}H NMR (500 MHz, $CDCl_3$) major: δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.03 (ddd, *J* = 11.9, 10.9, 1.1 Hz, 1H), 6.52 – 6.42 (m, 1H), 5.80 – 5.71 (m, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 5.17 (t, *J* = 6.0 Hz, 1H), 3.85 – 3.77 (m, 2H), 2.44 (s, 3H). **minor:** δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.04 (m, 1H), 6.14 – 6.05 (m, 1H), 5.84 – 5.76 (m, 1H), 5.36 (d, *J* = 15.9 Hz, 1H), 5.14 (t, *J* = 6.0 Hz, 1H), 3.77 – 3.72 (m, 2H), 2.43 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) major:** δ 143.87, 142.39, 136.69, 134.92, 129.80, 127.08, 126.97, 115.66, 99.80, 40.23, 21.47; **minor:** δ 143.66, 134.98, 129.87, 129.64, 128.33, 127.11, 126.32, 109.92, 101.28, 40.23, 21.47. **HRMS (ESI):** Calcd for $[C_{13}H_{14}N_2O_2S+Na]^+$ 285.0674; Found: 285.0683.



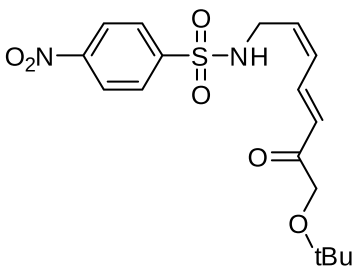
3be **yield:67%**

^{1}H NMR (500 MHz, $CDCl_3$) major: δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.96 (m, 1H), 6.34 (d, *J* = 11.6 Hz, 1H), 5.31 (t, *J* = 6.2 Hz, 1H), 5.15 (d, *J* = 10.9 Hz, 1H), 3.72 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H), 1.82 (s, 3H); **minor:** δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.97 (m, 1H), 5.97 (d, *J* = 11.7 Hz, 1H), δ 5.24 (t, *J* = 6.2 Hz, 1H), 5.23 (d, *J* = 15.7 Hz, 1H), 3.67 (d, *J* = 6.1 Hz, 2H), 2.45 (s, 3H), 1.86 (s, 3H).**^{13}C NMR (126 MHz, $CDCl_3$) major:** δ 144.0, 143.8, 143.3, 136.7, 129.7, 127.0, 125.2, 116.2, 96.9, 43.4, 22.4, 21.5; **minor:** δ 144.5, 143.97, 143.92, 136.4, 129.8, 127.1, 126.4, 118.1, 98.6, 43.3, 22.4, 21.5. **HRMS (ESI):** Calcd for $[C_{14}H_{16}N_2O_2S+Na]^+$ 299.0830; Found: 299.0838.



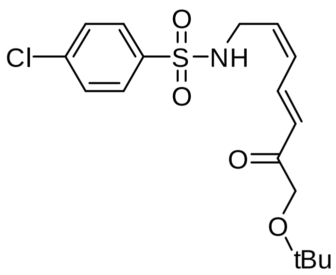
3cb **yield:49%**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.59 (ddd, *J* = 6.4, 3.7, 1.2 Hz, 1H), 7.53 (ddd, *J* = 8.3, 2.2, 0.9 Hz, 2H), 7.32 – 7.23 (m, 1H), 6.12 (t, *J* = 11.3 Hz, 1H), 5.83 (d, *J* = 15.2 Hz, 1H), 5.67 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.89 (s, 1H), 3.84 (t, *J* = 6.6 Hz, 2H), 1.47 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.9, 139.8, 136.3, 133.0, 132.8, 129.22, 129.17, 127.1, 126.0, 80.7, 40. 5, 28.1. **HRMS (ESI):** Calcd for $[C_{16}H_{21}NO_4S+Na]^+$ 360.1245; Found: 360.1240.



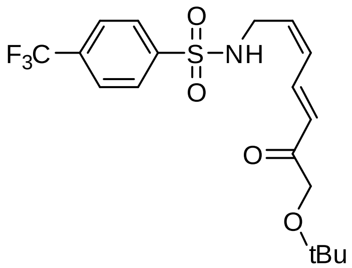
3db **yield:52%**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.9 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.21 (m, 1H), 6.17 (t, *J* = 11.3 Hz, 1H), 5.86 (d, *J* = 15.2 Hz, 1H), 5.65 (dd, *J* = 16.2, 7.7 Hz, 1H), 4.90 (s, 1H), 3.91 (s, 2H), 1.47 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.9, 150.3, 145.8, 135.8, 131.8, 129.9, 128.4, 126.6, 124.5, 81.0, 40.4, 28.1. **HRMS (ESI):** Calcd for $[C_{16}H_{20}N_2O_6S+Na]^+$ 405.1096; Found: 405.1102.



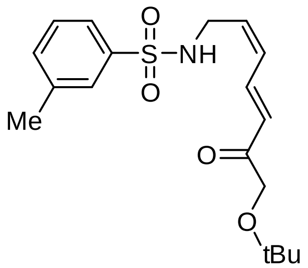
3eb **yield:66%**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.32 – 7.23 (m, 1H), 6.15 (t, J = 11.4 Hz, 1H), 5.85 (d, J = 15.2 Hz, 1H), 5.65 (dt, J = 10.9, 7.1 Hz, 1H), 4.73 (t, J = 5.4 Hz, 1H), 3.85 (t, J = 6.6 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 136.1, 132.5, 129.54, 129.47, 128.6, 126.2, 124.4, 122.8, 80.8, 40.4, 28.1, 27.4. **HRMS (ESI):** Calcd for $[C_{16}H_{20}ClNO_4S+Na]^+$ 394.0856; Found: 394.0861.



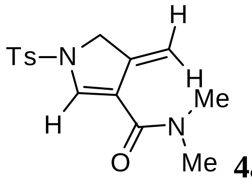
yield:61%

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, J = 7.9 Hz, 2H), 7.80 (d, J = 7.9 Hz, 2H), 7.28 (m, 1H), 6.16 (t, J = 11.3 Hz, 1H), 5.86 (d, J = 15.3 Hz, 1H), 5.66 (dd, J = 17.1, 7.6 Hz, 1H), 4.94 (s, 1H), 3.88 (t, J = 6.5 Hz, 2H), 1.47 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 165.9, 143.6, 136.0, 134.6 (q, J_{C-F} = 33.1 Hz), 132.3, 129.6, 127.7, 126.4 (q, J_{C-F} = 3.6 Hz), 126.3, 123.2 (q, J_{C-F} = 272.8 Hz, CF_3), 80.9, 40.4, 28.1. **HRMS (ESI):** Calcd for $[C_{17}H_{20}F_3NO_4S+Na]^+$ 428.1119; Found: 428.1121.



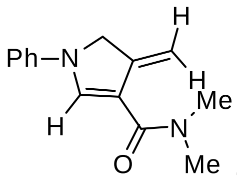
yield:73%

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (m, 2H), 7.45 – 7.35 (m, 2H), 7.27 (m, 1H), 6.13 (t, J = 11.3 Hz, 1H), 5.84 (d, J = 15.2 Hz, 1H), 5.68 (dt, J = 11.1, 7.2 Hz, 1H), 4.71 (s, 1H), 3.83 (t, J = 6.7 Hz, 2H), 2.43 (s, 3H), 1.48 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 165.9, 139.5, 136.3, 133. 7, 133.1, 129.12, 129.09, 127.5, 125.9, 124.2, 80.7, 40.5, 29.3, 28.1, 21.3. **HRMS (ESI):** Calcd for $[C_{17}H_{23}NO_4S+Na]^+$ 374.1402; Found: 374.1405.



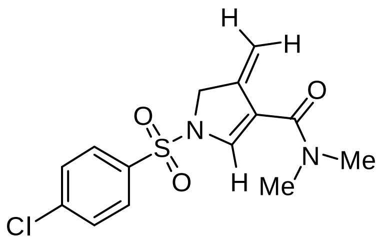
4a **yield:51%**

[1]H NMR (400 MHz, MeOD) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 3.1, 1.5 Hz, 1H), 6.25 (t, *J* = 3.3 Hz, 1H), 6.06 (s, 1H), 3.84 (s, 2H), 2.96 (s, 3H), 2.91 (s, 3H), 2.40 (s, 3H). **[13]C NMR (101 MHz, MeOD)** δ 171.9, 146.9, 137.6, 131.3, 129.7, 128.2, 124.1, 116.0, 112.9, 38.1, 36.1, 34.0, 21.7. **HRMS (ESI):** Calcd for $[C_{15}H_{18}N_2O_3S+Na]^+$ 329.0936; Found: 329.0942.



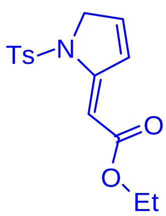
4c **yield:55%**

[1]H NMR (400 MHz, MeOD) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.34 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.27 (t, *J* = 3.4 Hz, 1H), 6.08 (s, 1H), 3.85 (s, 2H), 2.97 (s, 3H), 2.91 (s, 3H). **[13]C NMR (101 MHz, MeOD)** δ 171.9, 140.6, 135.4, 130.8, 129.9, 128.1, 124.2, 116.2, 113.1, 49.2, 38.1, 36.1, 33.9. **HRMS (ESI):** Calcd for $[C_{14}H_{16}N_2O+Na]^+$ 251.1160; Found: 251.1167.



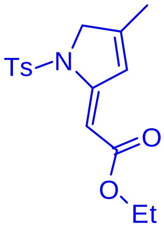
4e **yield:58%**

[1]H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.50 – 7.43 (m, 2H), 7.22 (dd, *J* = 3.3, 1.7 Hz, 1H), 6.25 (t, *J* = 3.4 Hz, 1H), 6.10 (s, 1H), 3.82 (s, 2H), 2.97 (s, 3H), 2.93 (s, 3H). **[13]C NMR (101 MHz, $CDCl_3$)** δ 168.9, 140.4, 137.3, 129.6, 128.6, 128.3, 122.5, 114.7, 112.2, 37.5, 35.5, 32.9. **HRMS (ESI):** Calcd for $[C_{14}H_{15}ClN_2O_3S+H]^+$ 349.0390; Found: 349.0384.



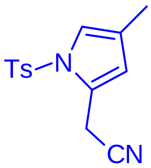
5a **yield:69%**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, *J* = 6.0 Hz, 2H), 7.46 (s, 1H), 7.33 (d, *J* = 7.0 Hz, 2H), 6.45 (s, 1H), 5.99 (s, 1H), 4.53 (s, 2H), 4.14 (q, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 1.28 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.4, 155.4, 144.9, 134.9, 134.4, 130.0, 127.6, 127.3, 93.3, 59.7, 57.5, 21.6, 14.4. **HRMS (ESI):** Calcd for $[C_{15}H_{17}NO_4S+Na]^+$ 330.0776; Found: 330.0779.



5b **yield:81%**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.15 (s, 1H), 5.91 (s, 1H), 4.38 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.95 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.6, 156.5, 147.5, 144.7, 134.4, 129.9, 127.2, 122.9, 91.4, 59.8, 59.4, 21.5, 14.5, 14.3. **HRMS (ESI):** Calcd for $[C_{16}H_{19}NO_4S+Na]^+$ 344.0932; Found: 344.0930.

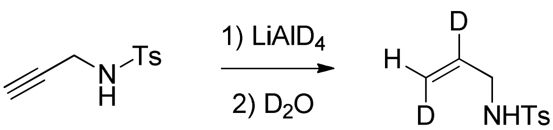


6 **yield:58%**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.02 (s, 1H), 6.22 (s, 1H), 3.88 (s, 2H), 2.42 (s, 3H), 2.02 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.4, 135.7, 130.2, 126.7, 122.7, 122.4, 120.7, 117.6, 116.2, 21.6, 17.3, 11.6. **HRMS (ESI):** Calcd for $[C_{14}H_{14}N_2O_2S+Na]^+$ 297.0674; Found: 297.0665.

6. Deuterium-Labeling Experiment

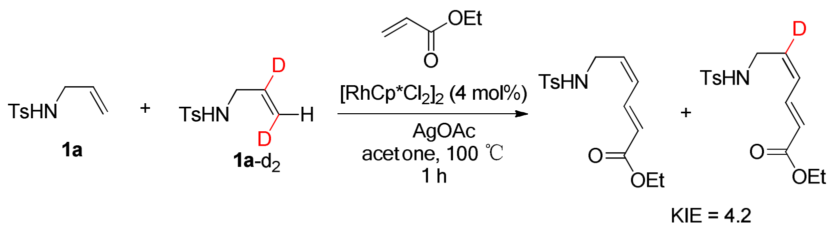
6.1 Synthesis of 1a-*d*$_2$



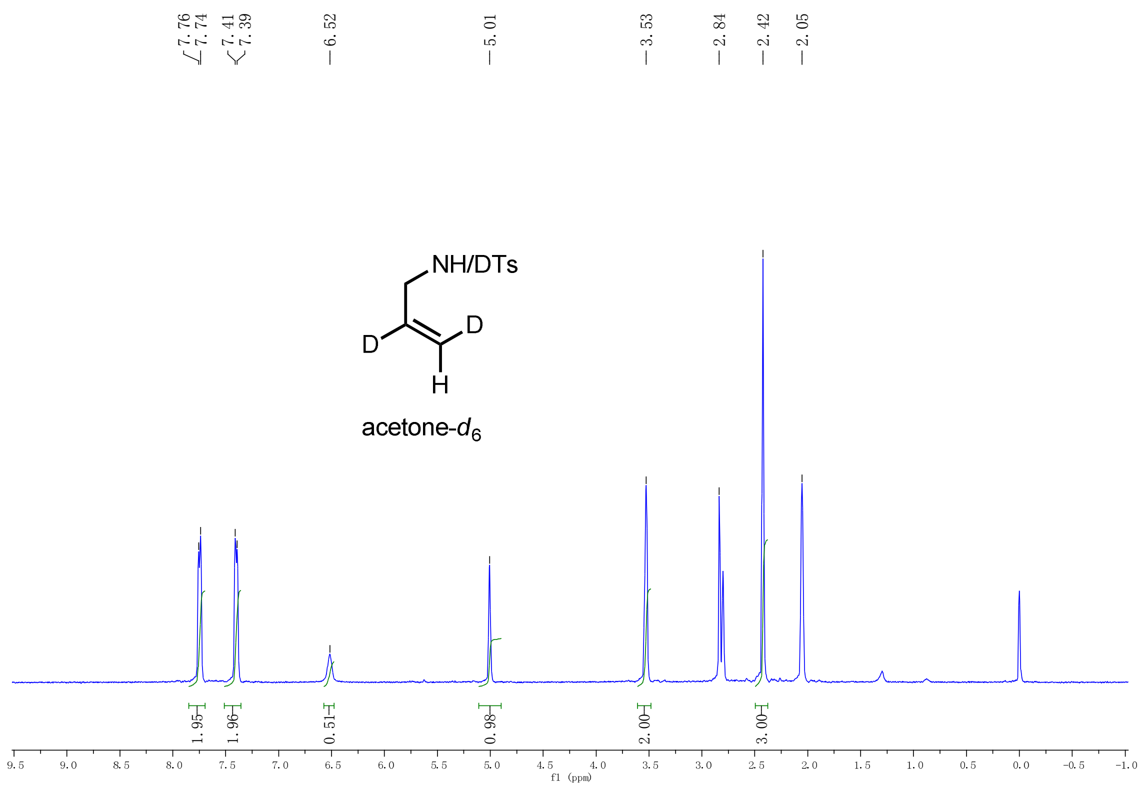
1a-*d*$_2$

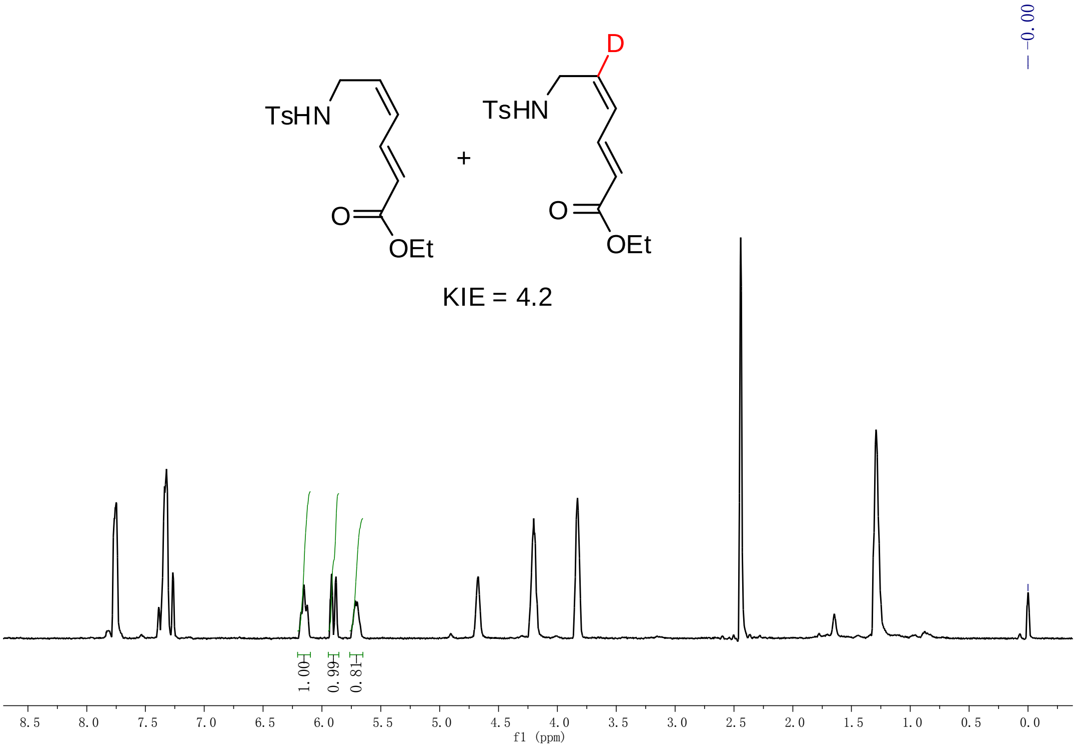
N-Propargyl-*p*-tolylsulfonamide (105 mg, 0.5 mmol) was added in one portion to a stirred suspension of $LiAlD_4$ (25 mg, 0.65 mmol) in THF (2 mL) at -15 °C. The reaction mixture was stirred at -15 °C and was allowed to warm to room temperature (14 h). The reaction mixture was cooled to -10 °C, and was carefully quenched by slow addition of D_2O (50 μL). The mixture was stirred for another hour, filtered, and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the resulting residue was purified by column chromatography on silica gel to provide the desired product **1a**-d_2 (yield: 45%). The degree of deuteration is > 98% at both two positions.

6.2 Kinetic Isotope Effect

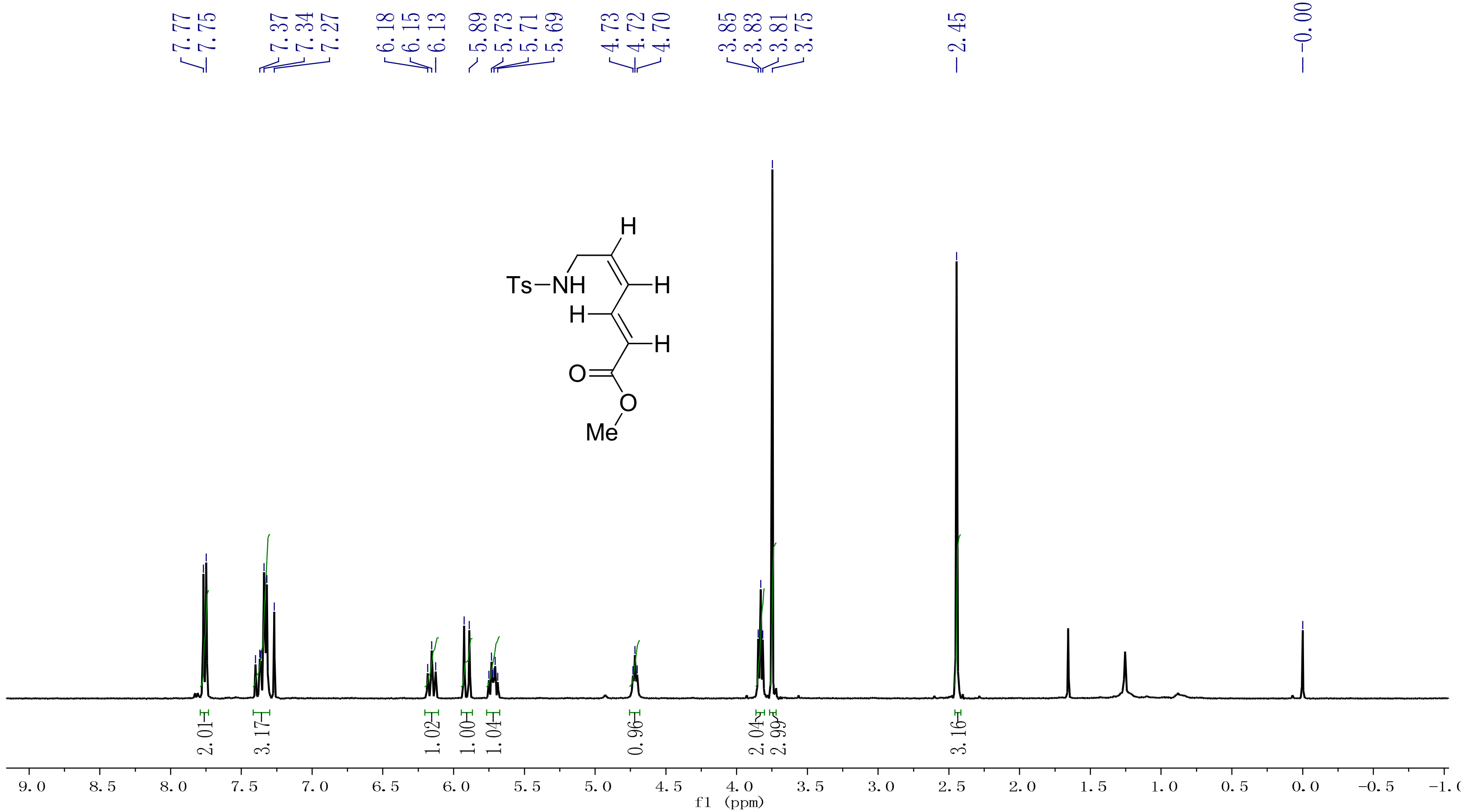


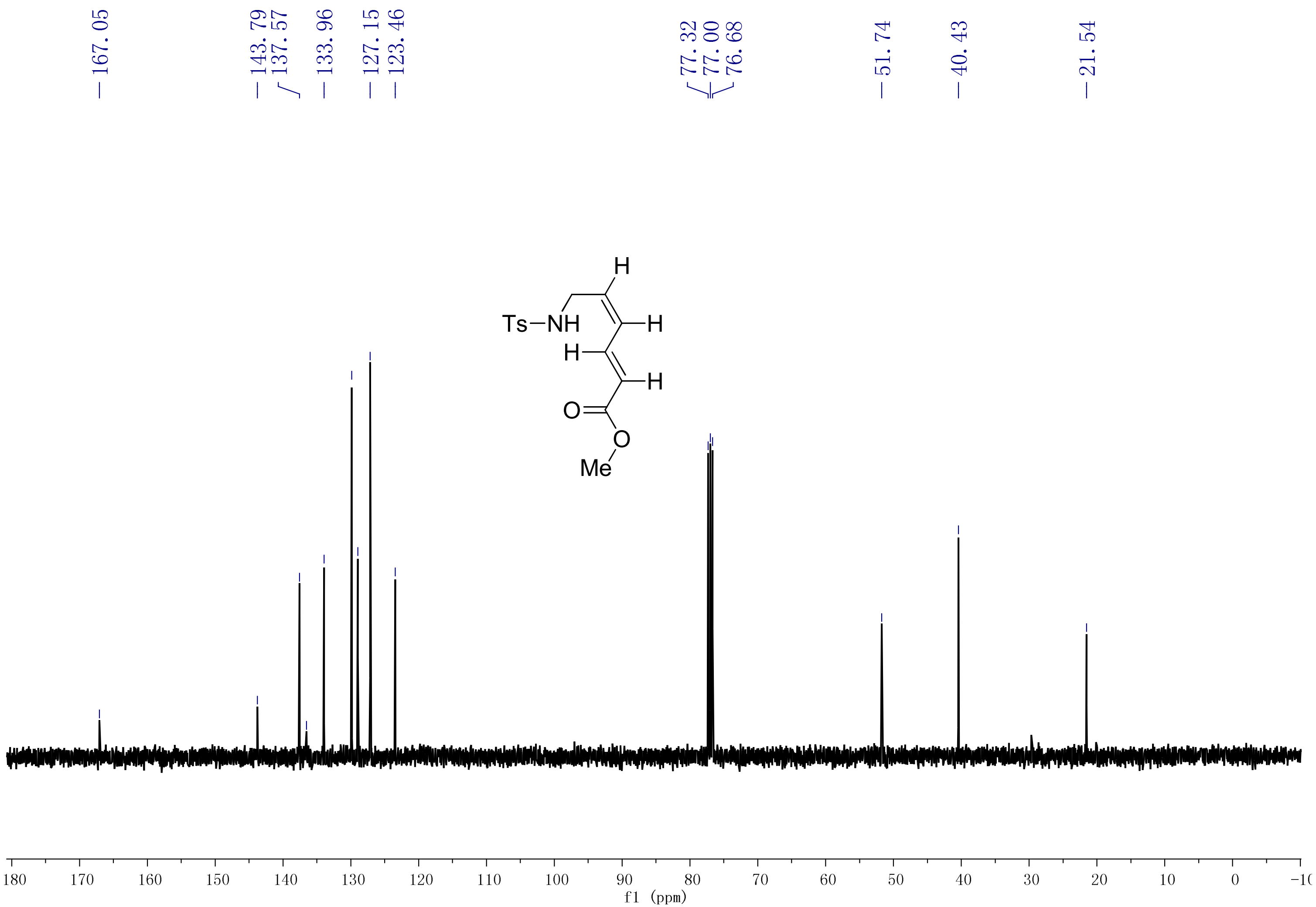
A mixture of **1a**-d_2 (> 98% deuteration, 0.3 mmol), 1a(0.3mmol), ethyl acrylate (0.24 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), and AgOAc (0.63 mmol) were weighed into a pressure tube. Acetone (4 mL) was added. The mixture was then stirred at 100℃ for 1 h. After cooled to room temperature, the mixture was filtered and the crude product was purified by silica gel column chromatography. ^{1}H NMR analysis (400 MHz, $CDCl_3$) showed that a value of k_H/k_D = 4.2 was obtained.



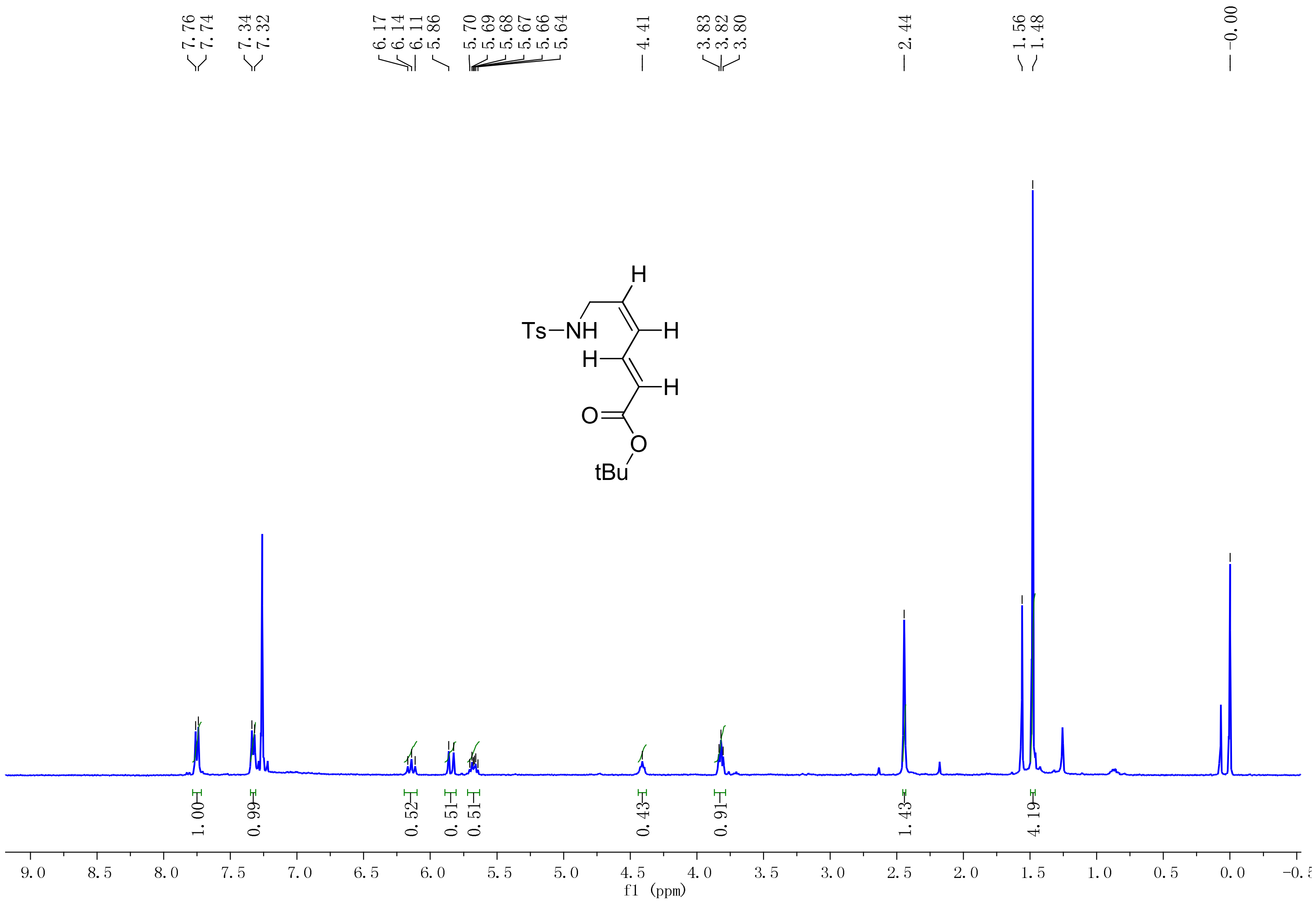

TsHN
OEt
O
+
D
TsHN
OEt
O
KIE = 4.2
-0.00
1.00
0.99
0.81
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

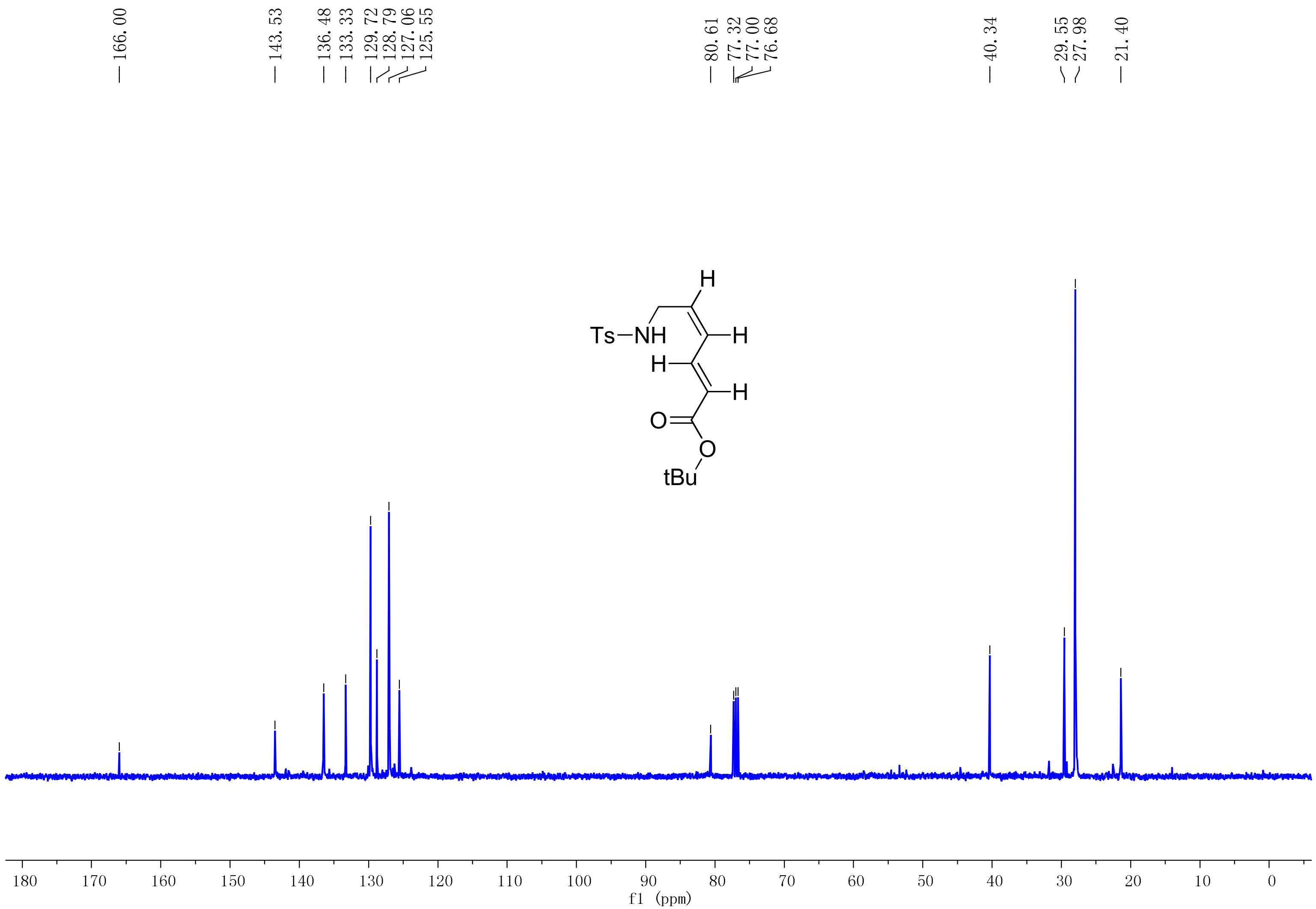
7. NMR Spectra of Products




167.05
143.79
137.57
133.96
127.15
123.46
77.32
77.00
76.68
51.74
40.43
21.54
Ts
NH
H
H
H
H
O
O
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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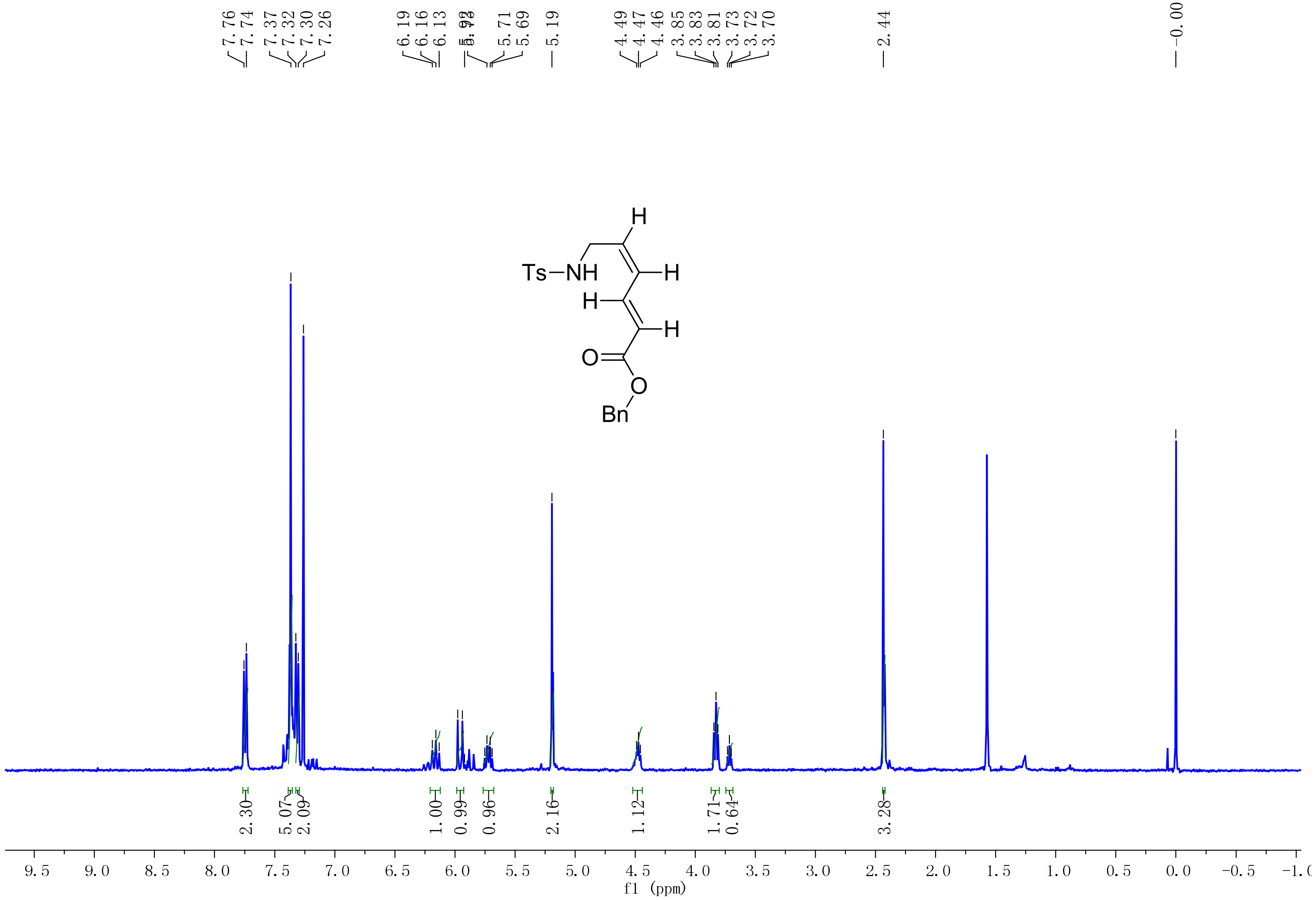
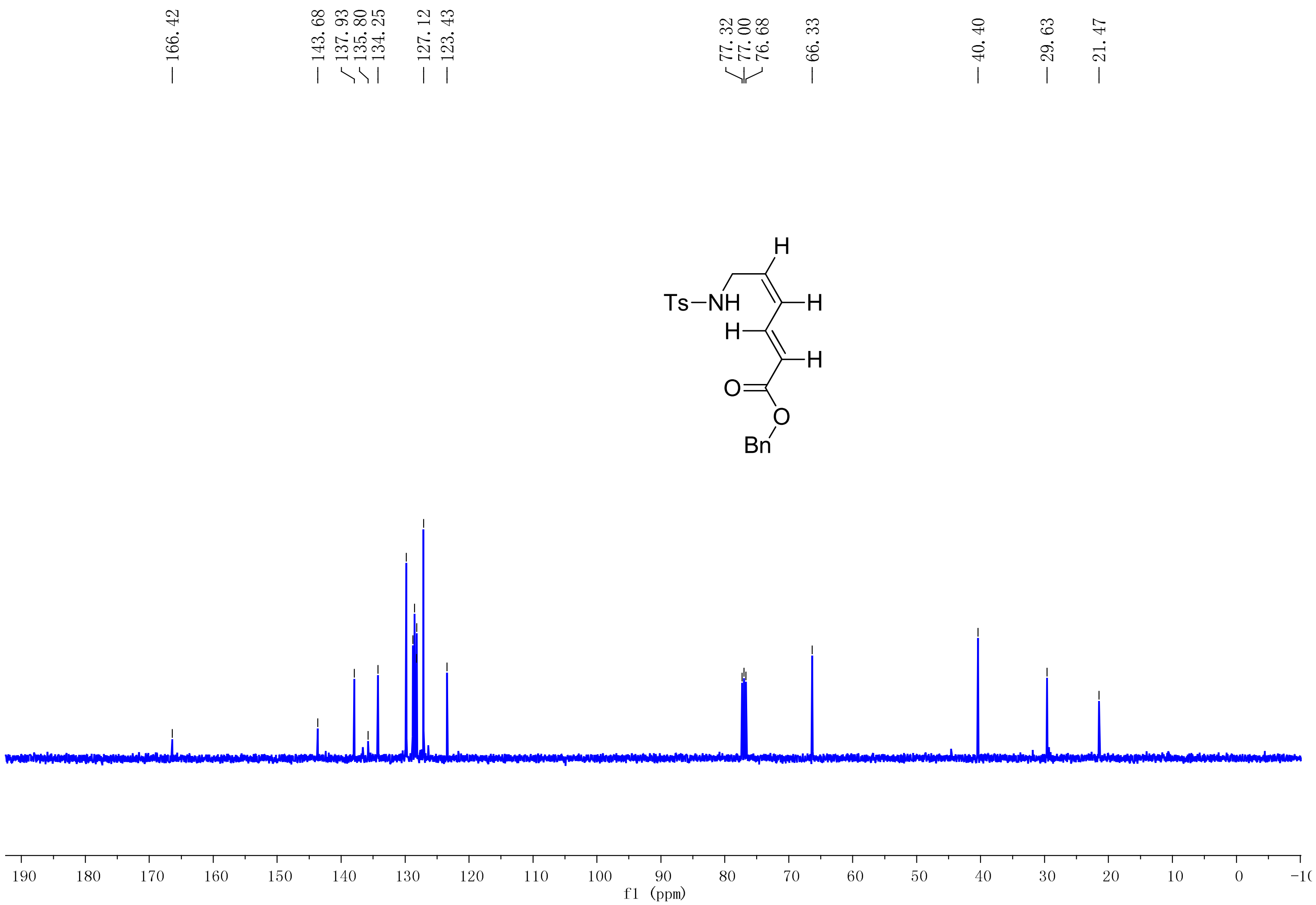
143.53
136.48
133.33
129.72
128.79
127.06
125.55
80.61
77.32
77.00
76.68
40.34
29.55
27.98
21.40
Ts
NH
H
O
tBu
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.76
7.74
7.37
7.32
7.30
7.26
6.19
6.16
6.13
5.98
5.96
5.71
5.69
5.19
4.49
4.47
4.46
3.85
3.83
3.81
3.73
3.72
3.70
2.44
-0.00
Ts—NH
H
H
H
H
O
O
Bn
2.30
5.07
2.09
1.00
0.99
0.96
2.16
1.12
1.71
0.64
3.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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143.68
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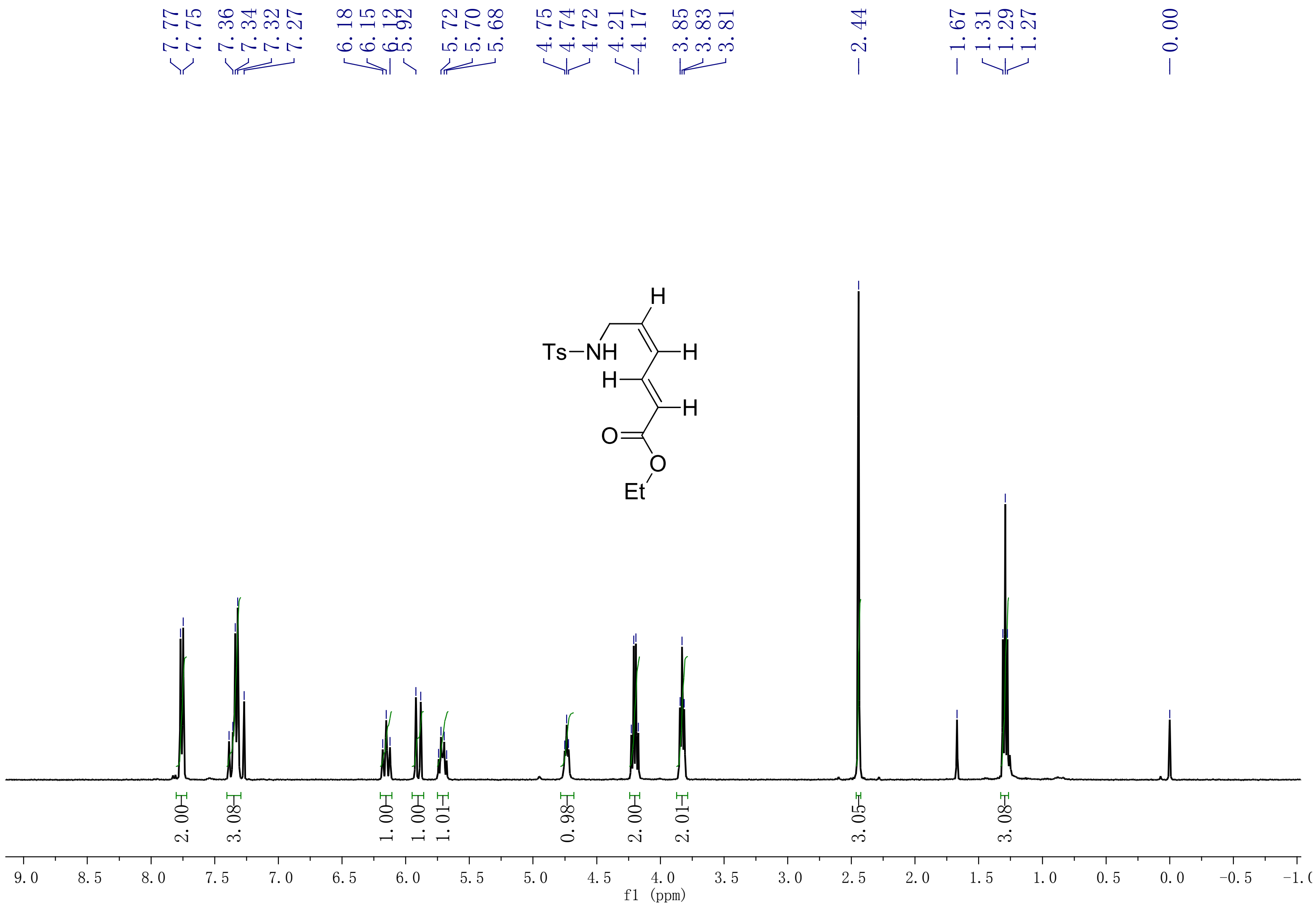
135.80
134.25
127.12
123.43
77.32
77.00
76.68
66.33
40.40
29.63
21.47
Ts
NH
H
O
Bn
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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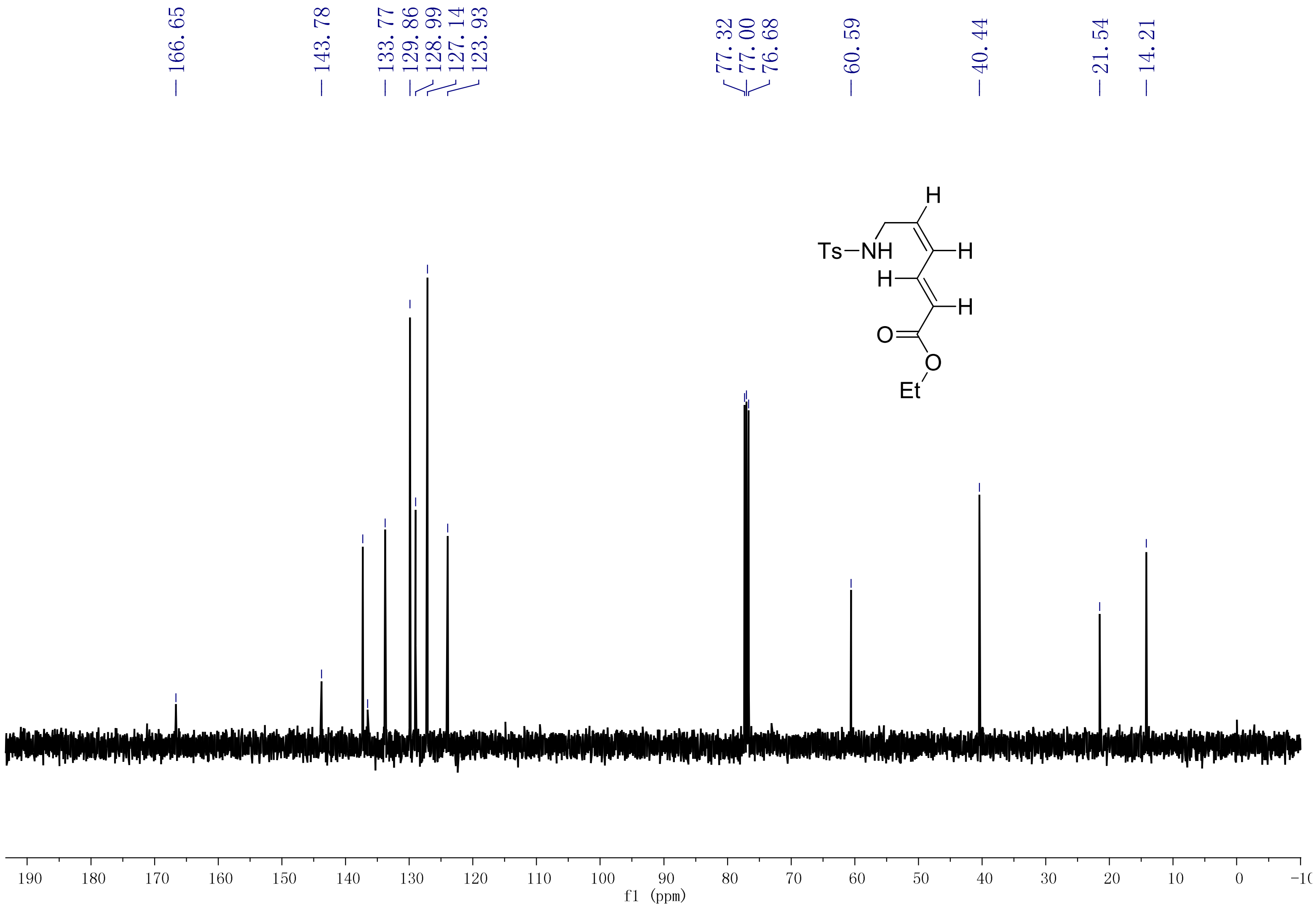
7.75
7.36
7.34
7.32
7.27
6.18
6.15
6.12
5.92
5.72
5.70
5.68
4.75
4.74
4.72
4.21
4.17
3.85
3.83
3.81
2.44
1.67
1.31
1.29
1.27
0.00
Ts—NH
H
H
H
H
O
O
Et
2.00
3.08
1.00
1.00
1.01
0.98
2.00
2.01
3.05
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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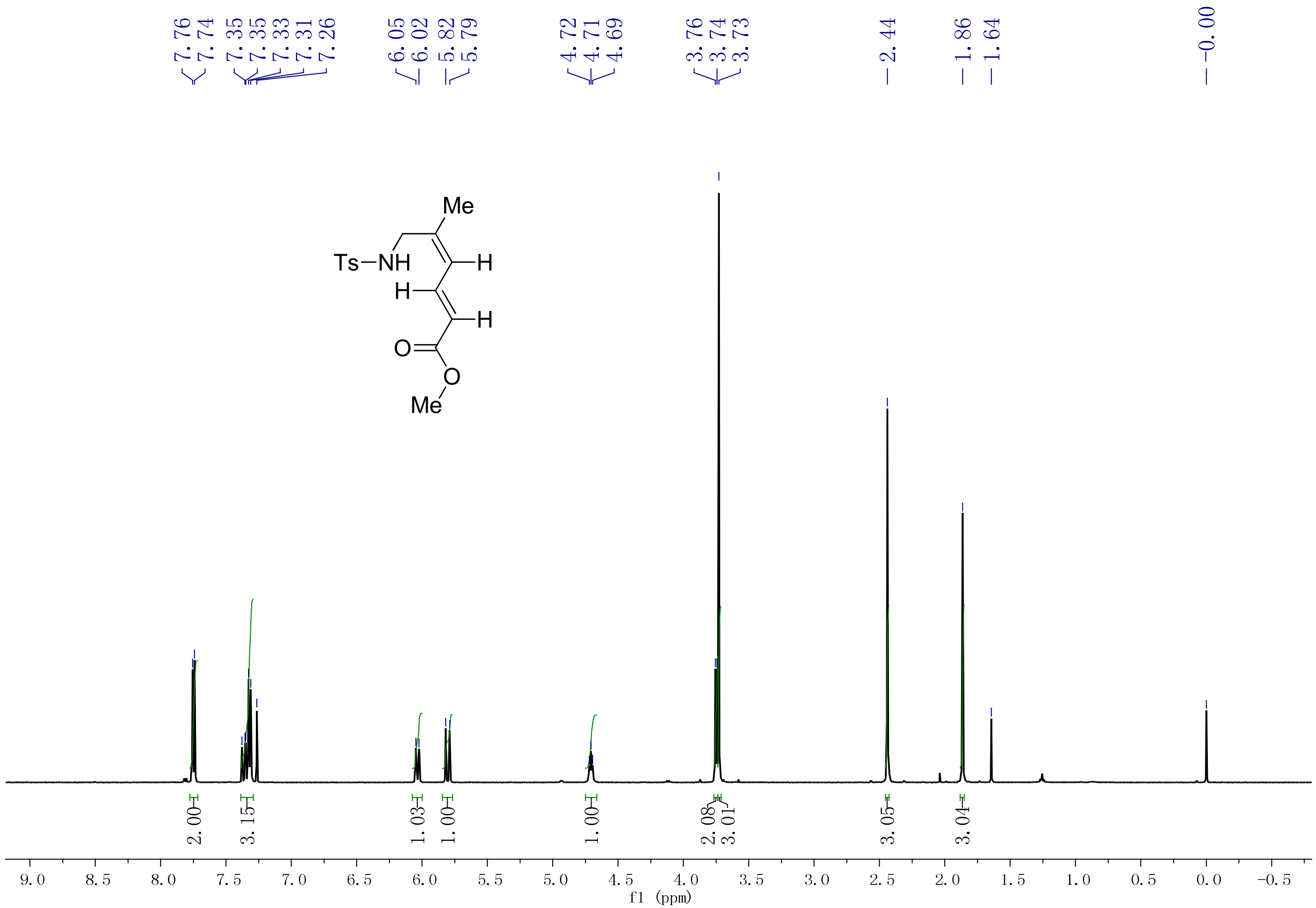
133.77
129.86
128.99
127.14
123.93
77.32
77.00
76.68
60.59
40.44
21.54
14.21
Ts–NH
H
H
H
H
O
O
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.74
7.35
7.35
7.33
7.31
7.26
6.05
6.02
5.82
5.79
4.72
4.71
4.69
3.76
3.74
3.73
2.44
1.86
1.64
-0.00
Me
Ts
NH
H
H
H
O
O
Me
2.00
3.15
1.03
1.00
1.00
2.08
3.01
3.05
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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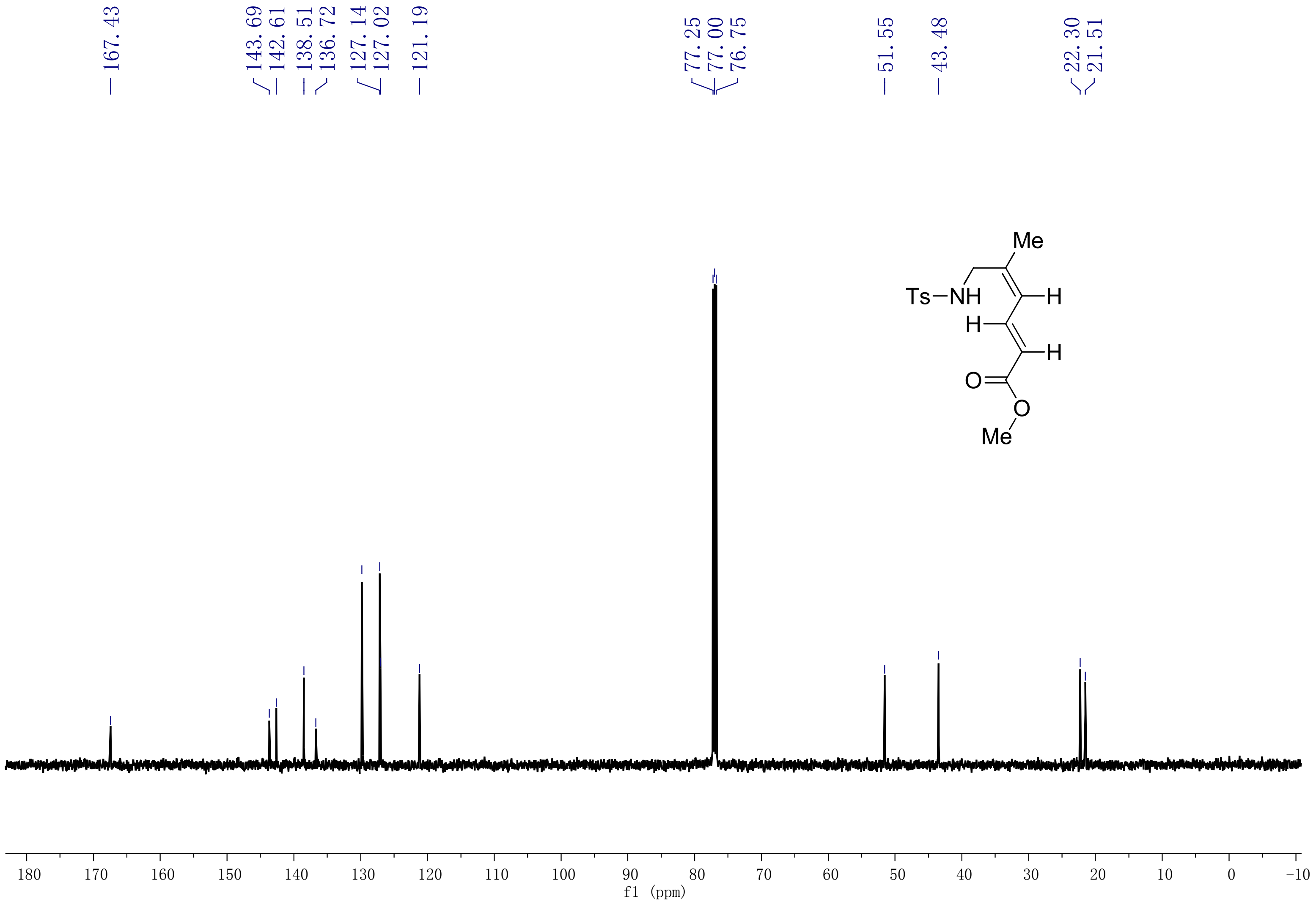
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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127.02
121.19
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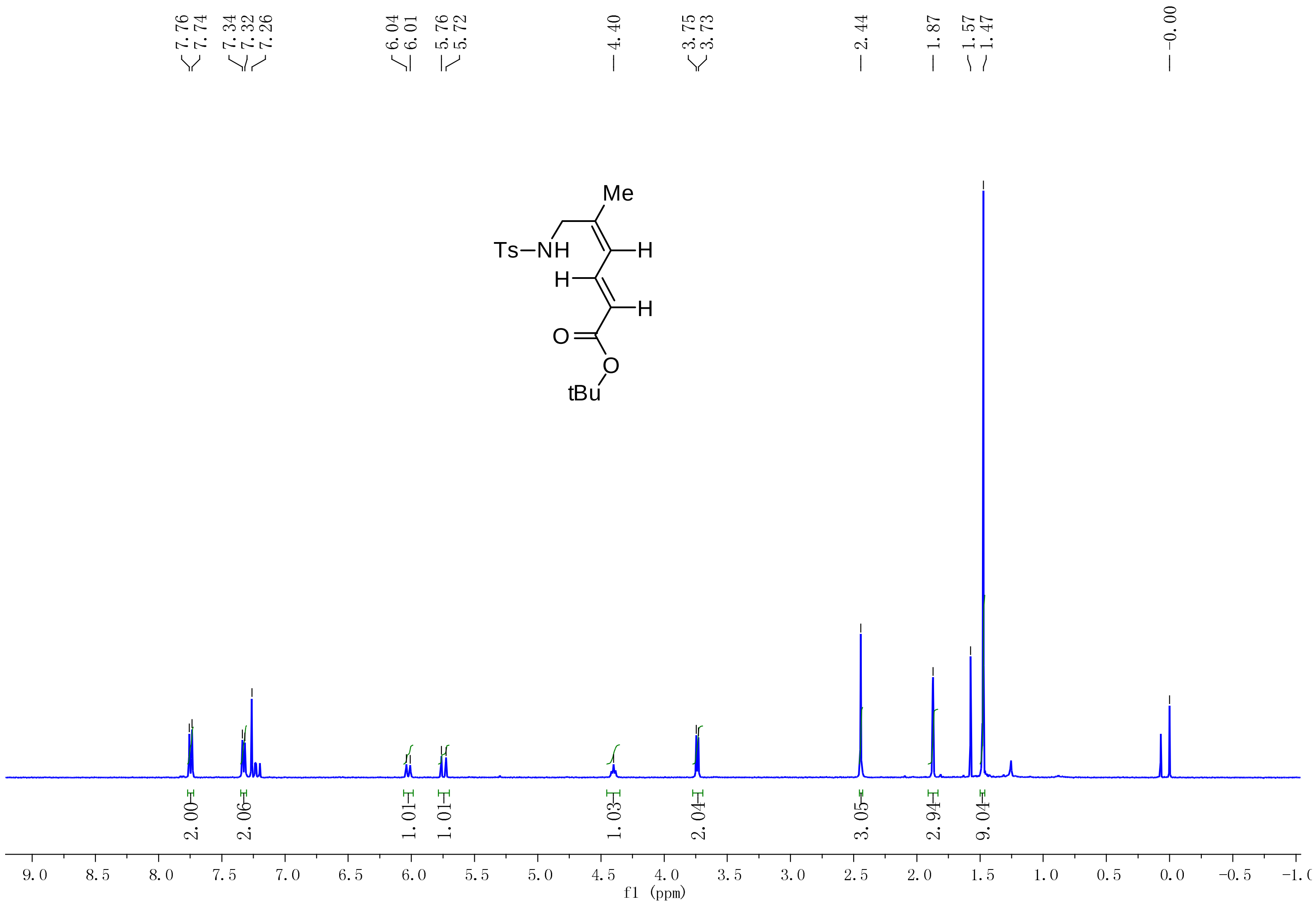
77.00
76.75
51.55
43.48
22.30
21.51
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
Me
Ts
NH
H
H
H
O
O
Me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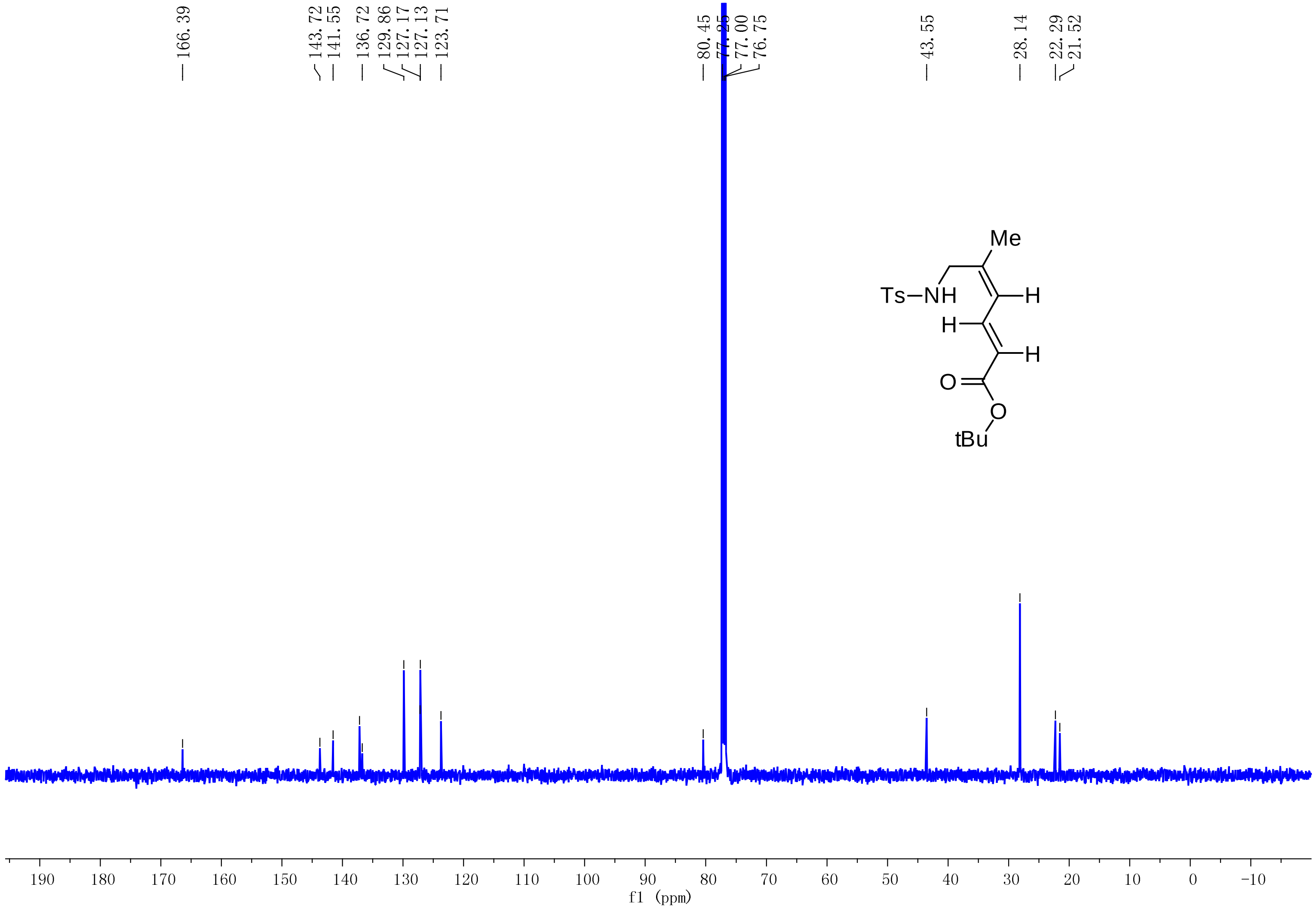
7.32
7.26
6.04
6.01
5.76
5.72
4.40
3.75
3.73
2.44
1.87
1.57
1.47
-0.00
Me
Ts–NH
H
H
H
O
O
tBu
2.00
2.06
1.01
1.01
1.03
2.04
3.05
2.94
9.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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127.17
127.13
123.71
80.45
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76.75
43.55
28.14
22.29
21.52
Me
Ts–NH
H
H
H
O
O
tBu
190
180
170
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100
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80
70
60
50
40
30
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0
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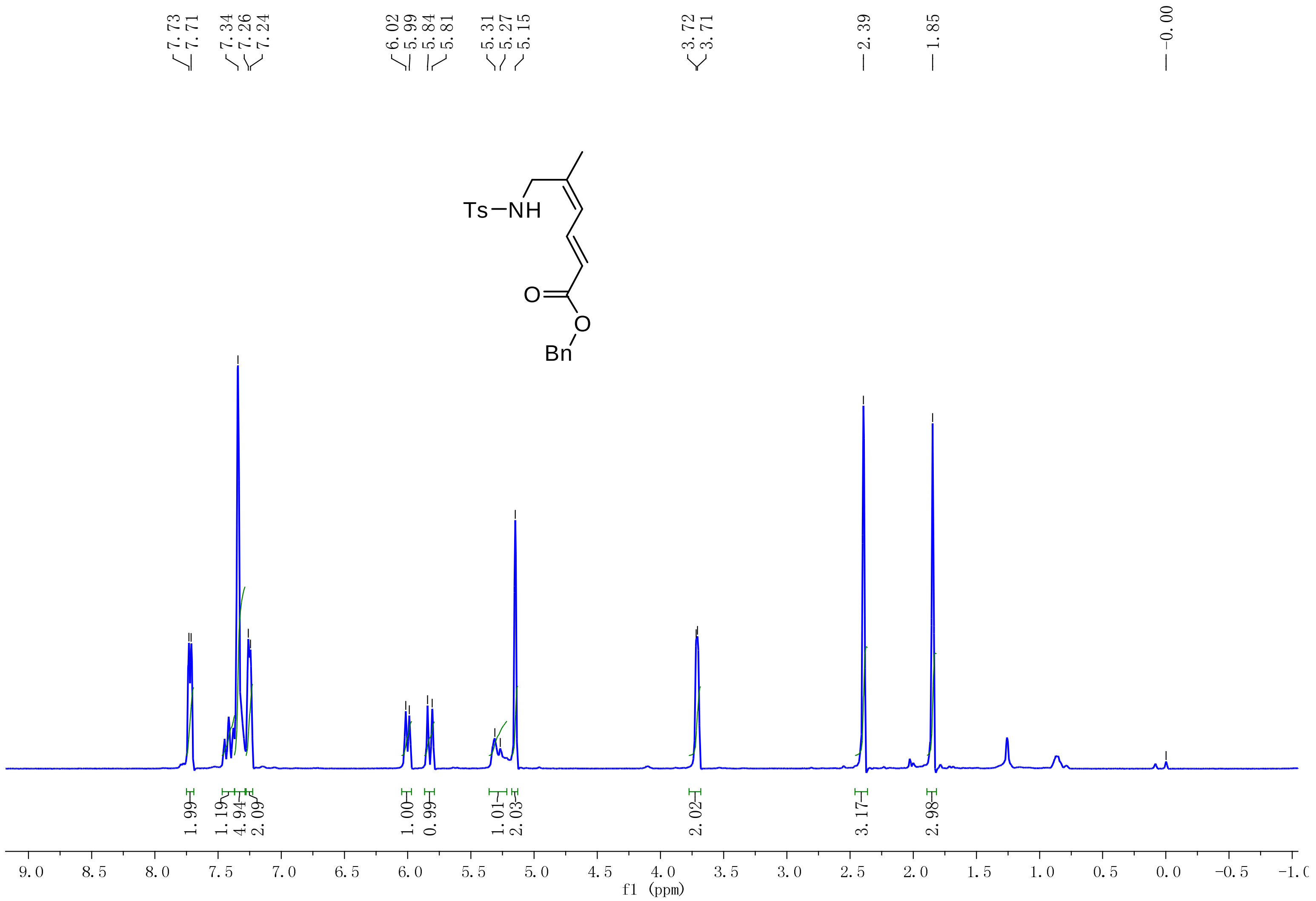
f1 (ppm)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3.71
2.39
1.85
-0.00
Ts–NH
O
O
Bn
1.99
1.19
4.94
2.09
1.00
0.99
1.01
2.03
2.02
3.17
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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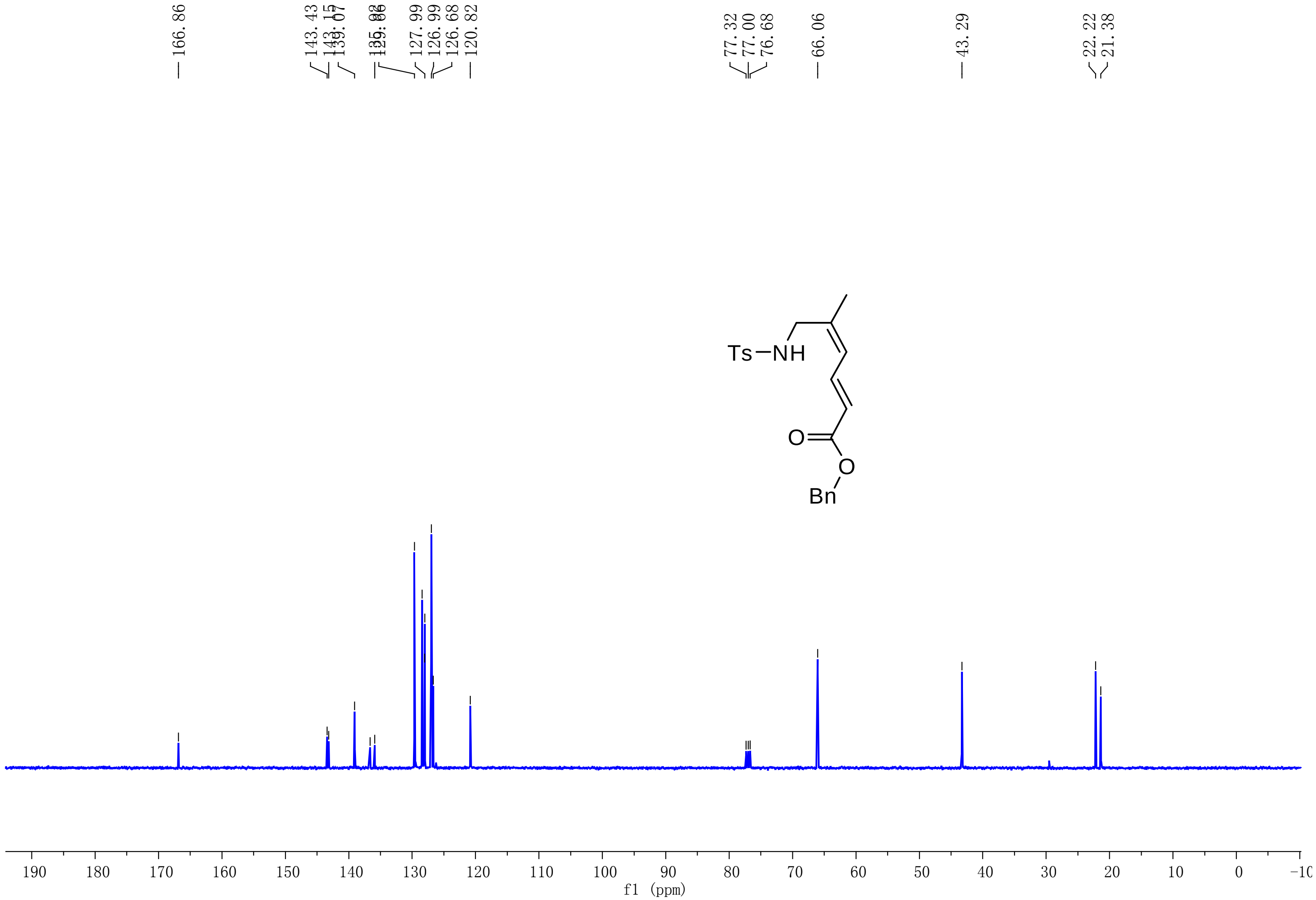
f1 (ppm)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126.99
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120.82
77.32
77.00
76.68
66.06
43.29
22.22
21.38
Ts
NH
O
O
Bn
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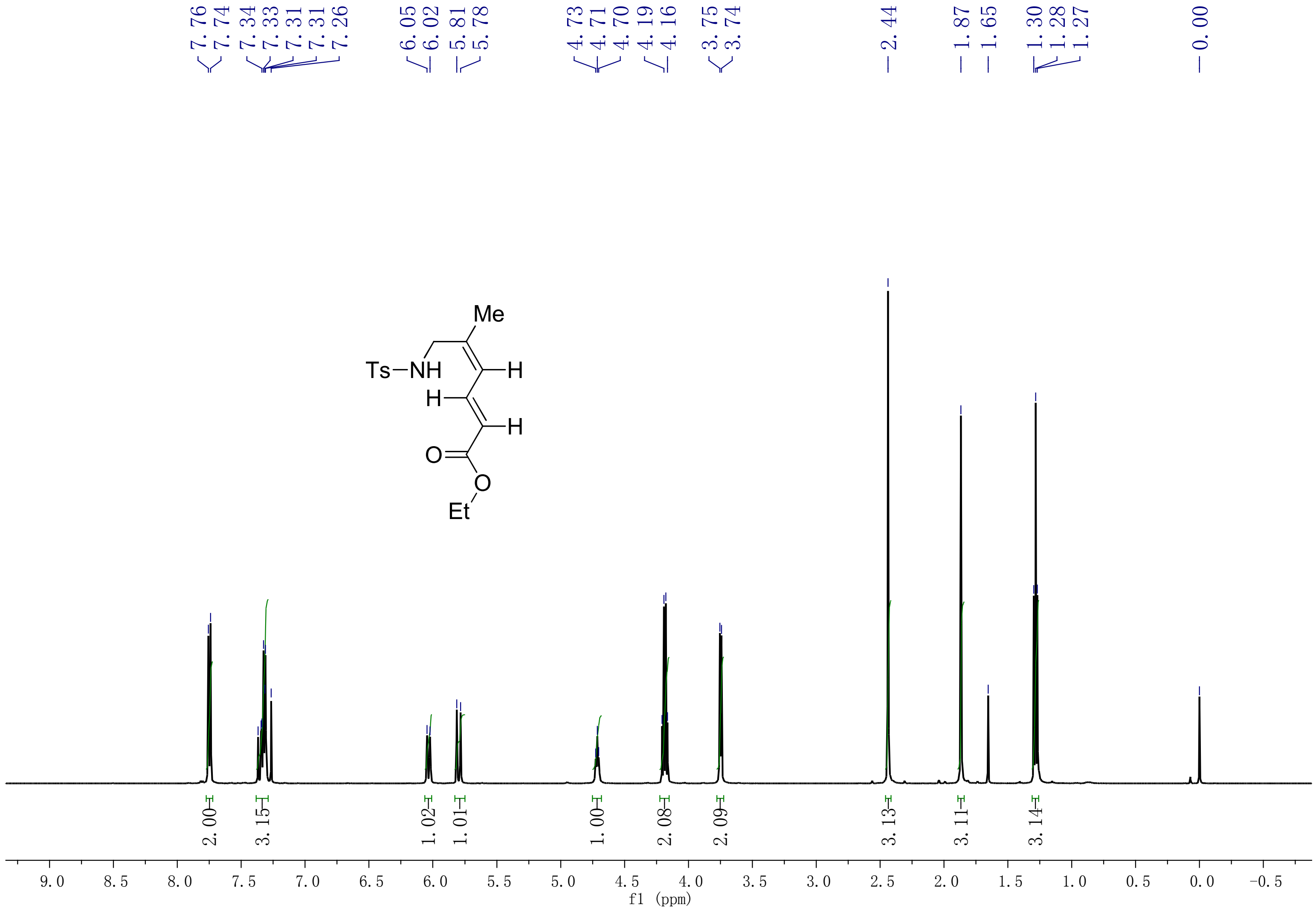
f1 (ppm)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7.74
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7.33
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7.31
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6.05
6.02
5.81
5.78
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4.71
4.70
4.19
4.16
3.75
3.74
2.44
1.87
1.65
1.30
1.28
1.27
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Ts—NH
H
H
H
O
O
Et
2.00
3.15
1.02
1.01
1.00
2.08
2.09
3.13
3.11
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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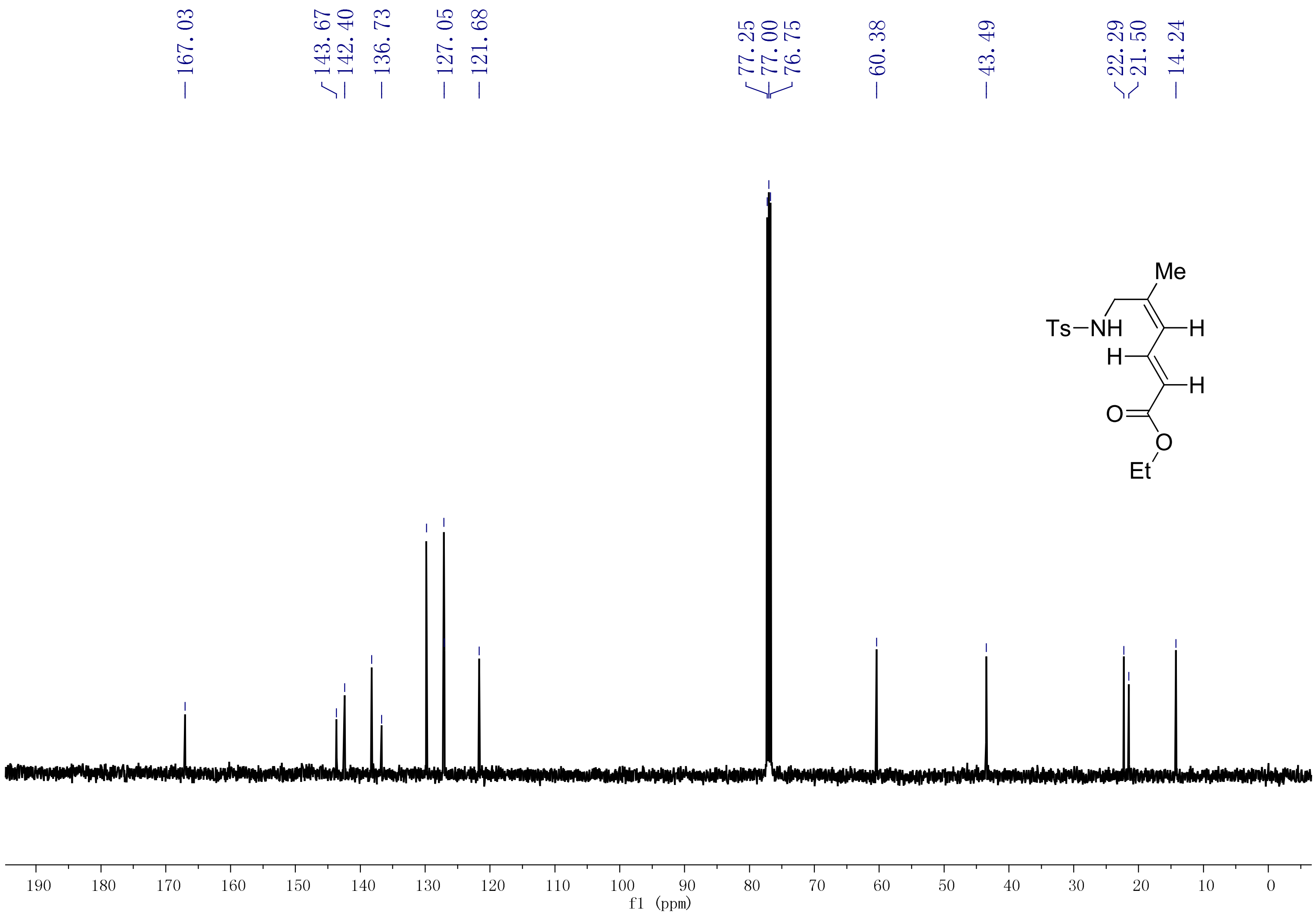
f1 (ppm)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121.68
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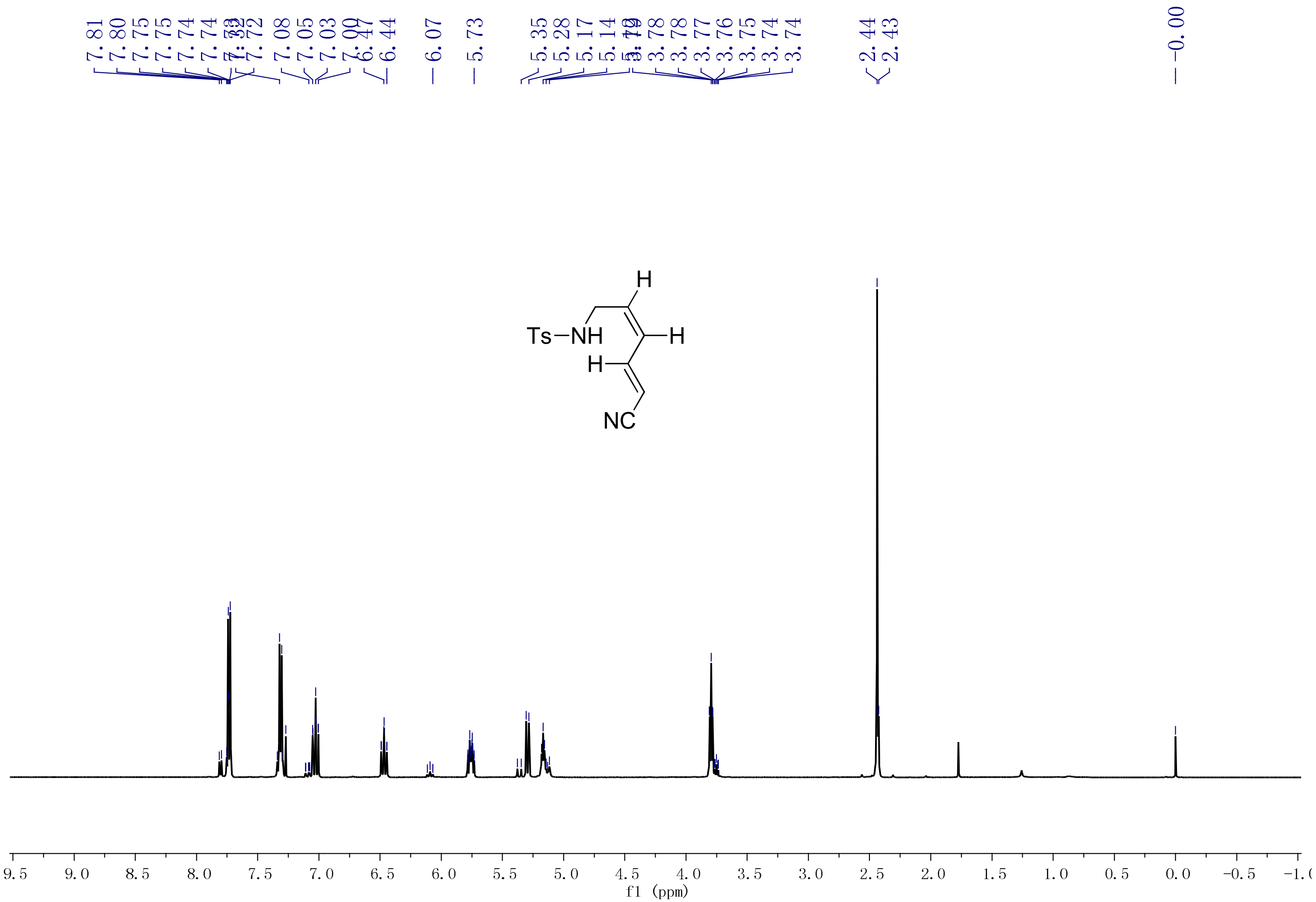
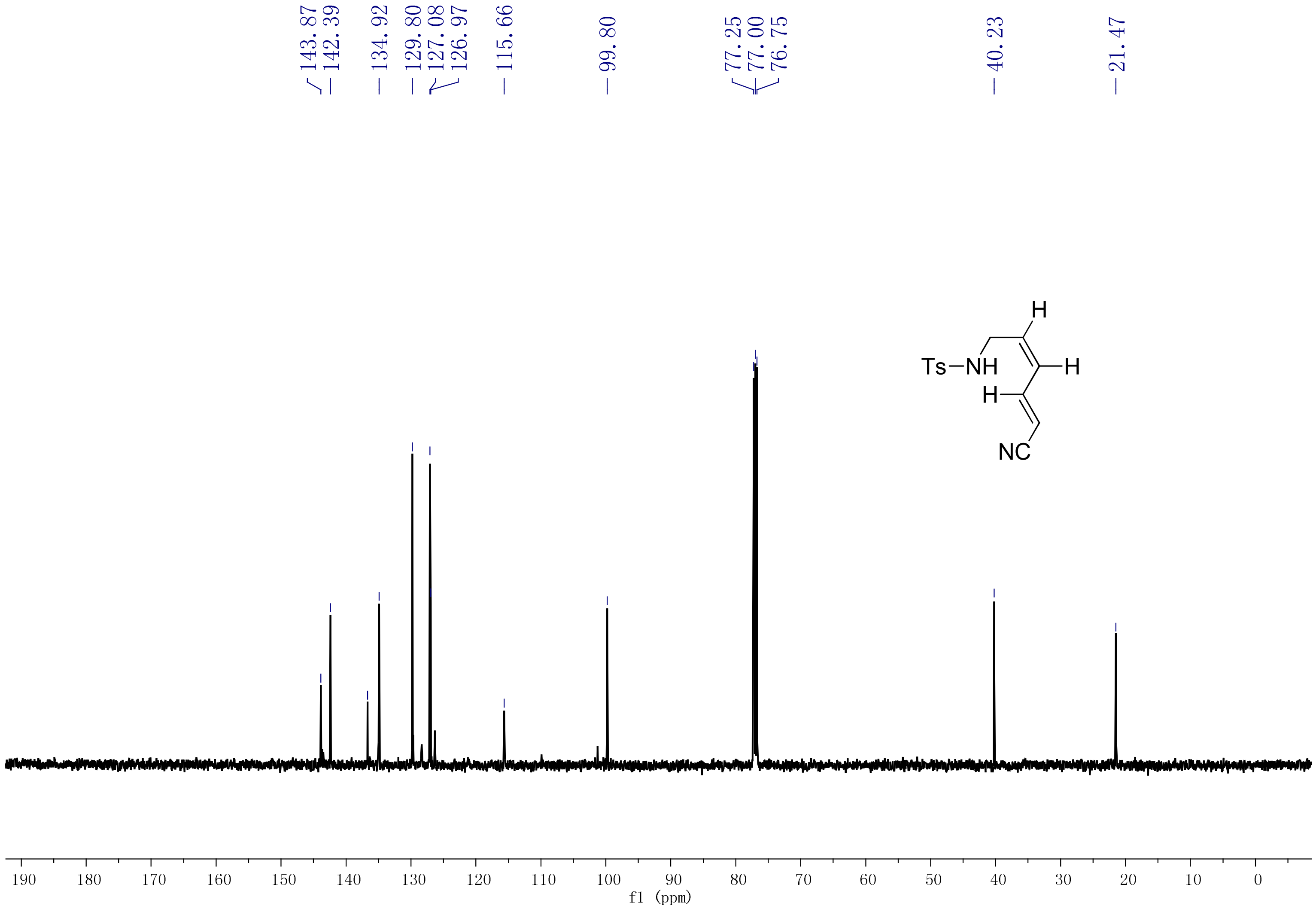
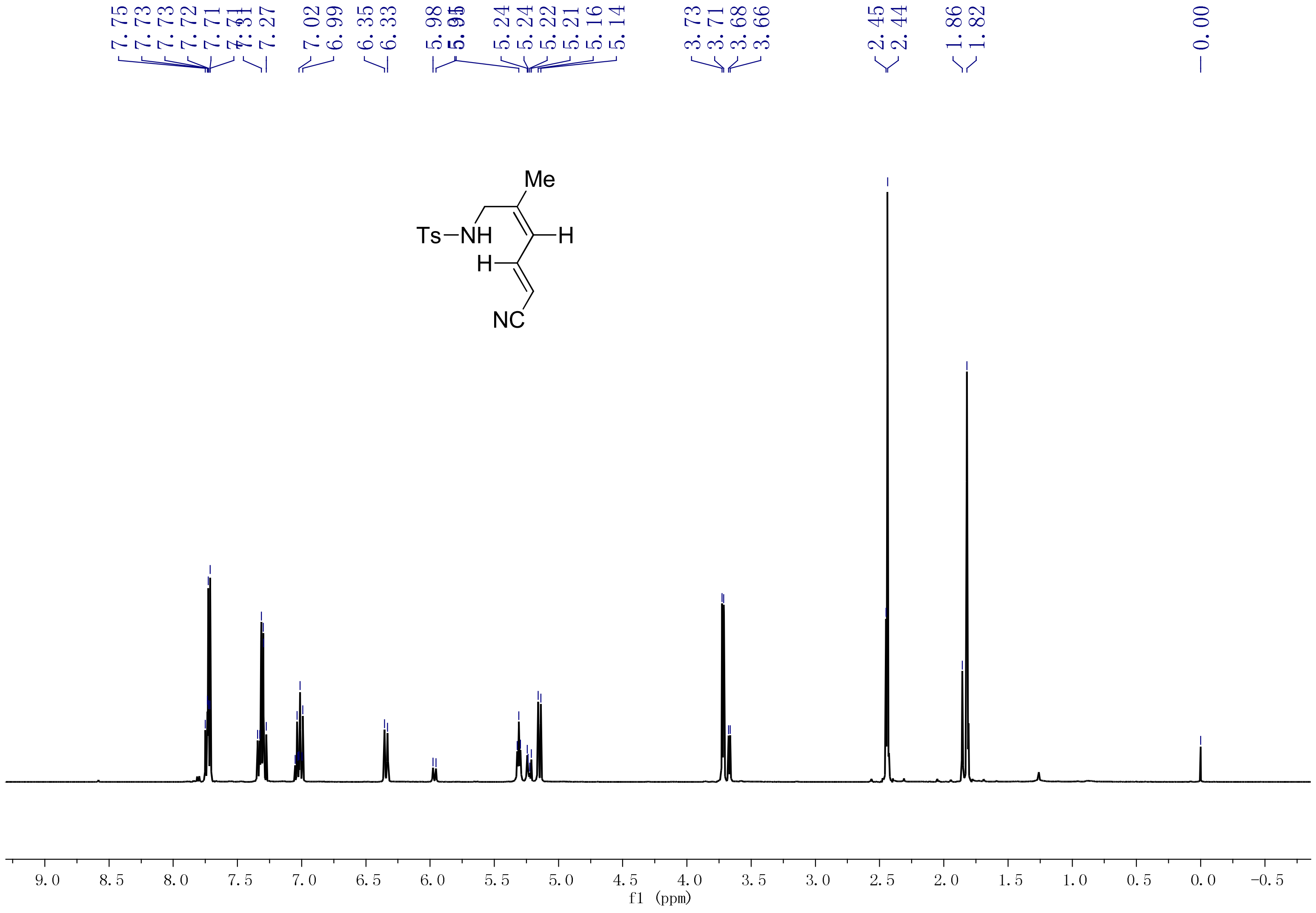
76.75
60.38
43.49
22.29
21.50
14.24
Me
Ts
NH
H
H
H
O
O
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts—NH
H
H
H
NC
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry




7.75
7.73
7.73
7.72
7.71
7.71
7.31
7.27
7.02
6.99
6.35
6.33
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5.95
5.95
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5.22
5.21
5.16
5.14
3.73
3.71
3.68
3.66
2.45
2.44
1.86
1.82
0.00
Me
Ts—NH
H
H
NC
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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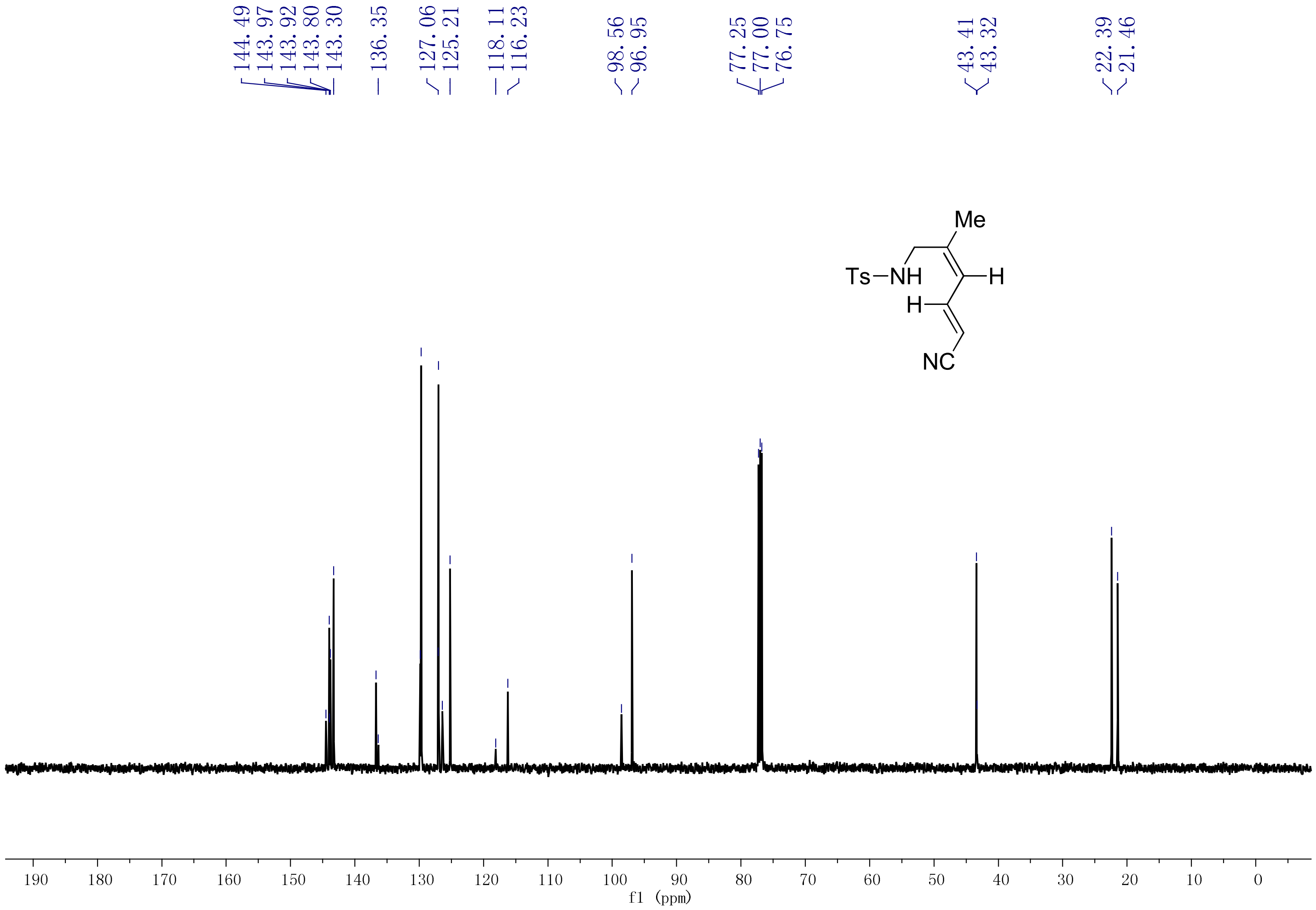
1.0
0.5
0.0
-0.5
f1 (ppm)



144.49
143.97
143.92
143.80
143.30
136.35
127.06
125.21
118.11
116.23
98.56
96.95
77.25
77.00
76.75
43.41
43.32
22.39
21.46
Me
Ts
NH
H
H
NC
190
180
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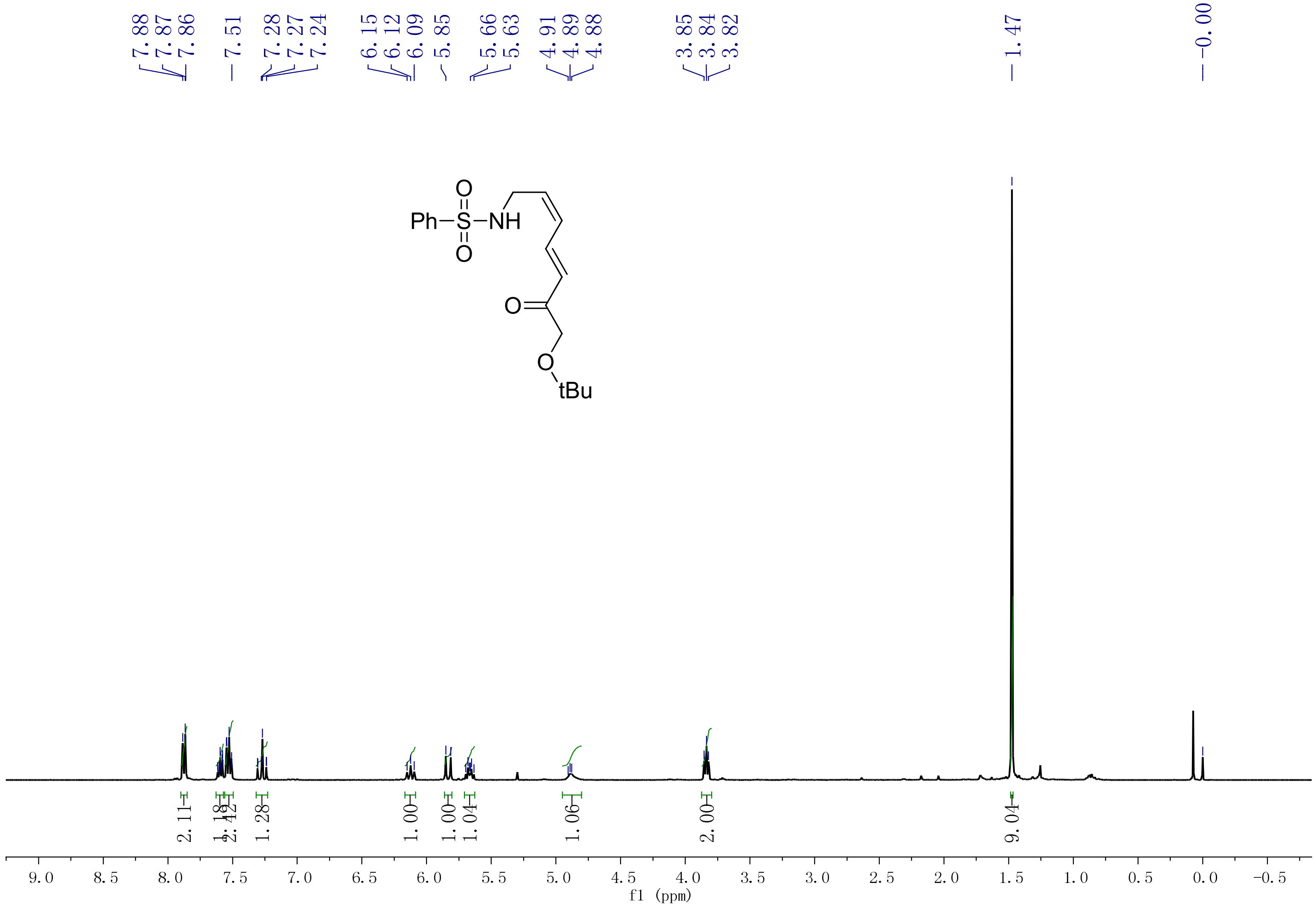
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6.09
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5.66
5.63
4.91
4.89
4.88
3.85
3.84
3.82
1.47
-0.00
Ph
S
NH
O
O
O
O
tBu
2.11
1.18
2.42
1.28
1.00
1.00
1.04
1.06
2.00
9.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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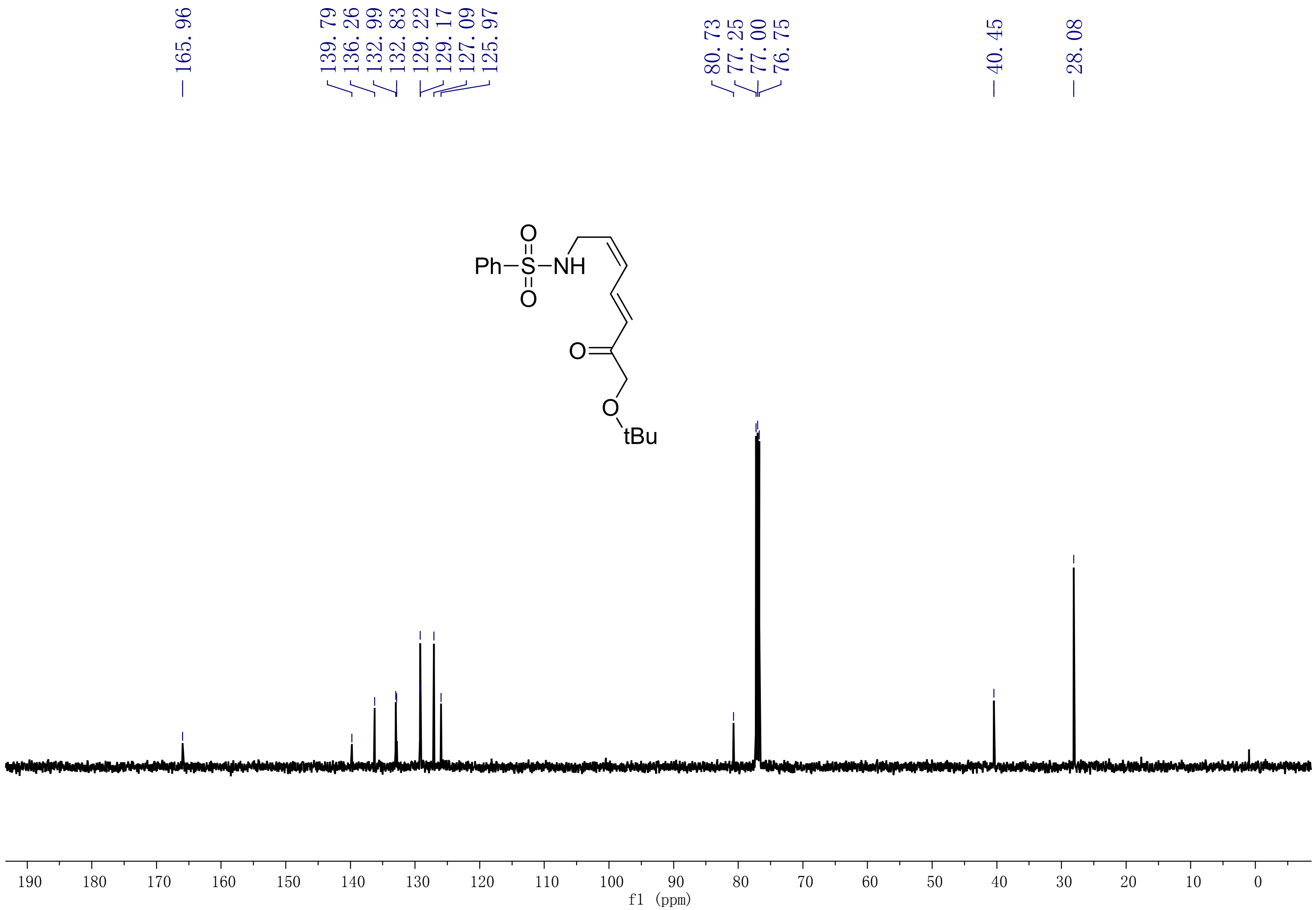
0.5
0.0
-0.5
f1 (ppm)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139.79
136.26
132.99
132.83
129.22
129.17
127.09
125.97
80.73
77.25
77.00
76.75
40.45
28.08
Ph
S
NH
O
O
O
O
tBu
190
180
170
160
150
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90
80
70
60
50
40
30
20
10
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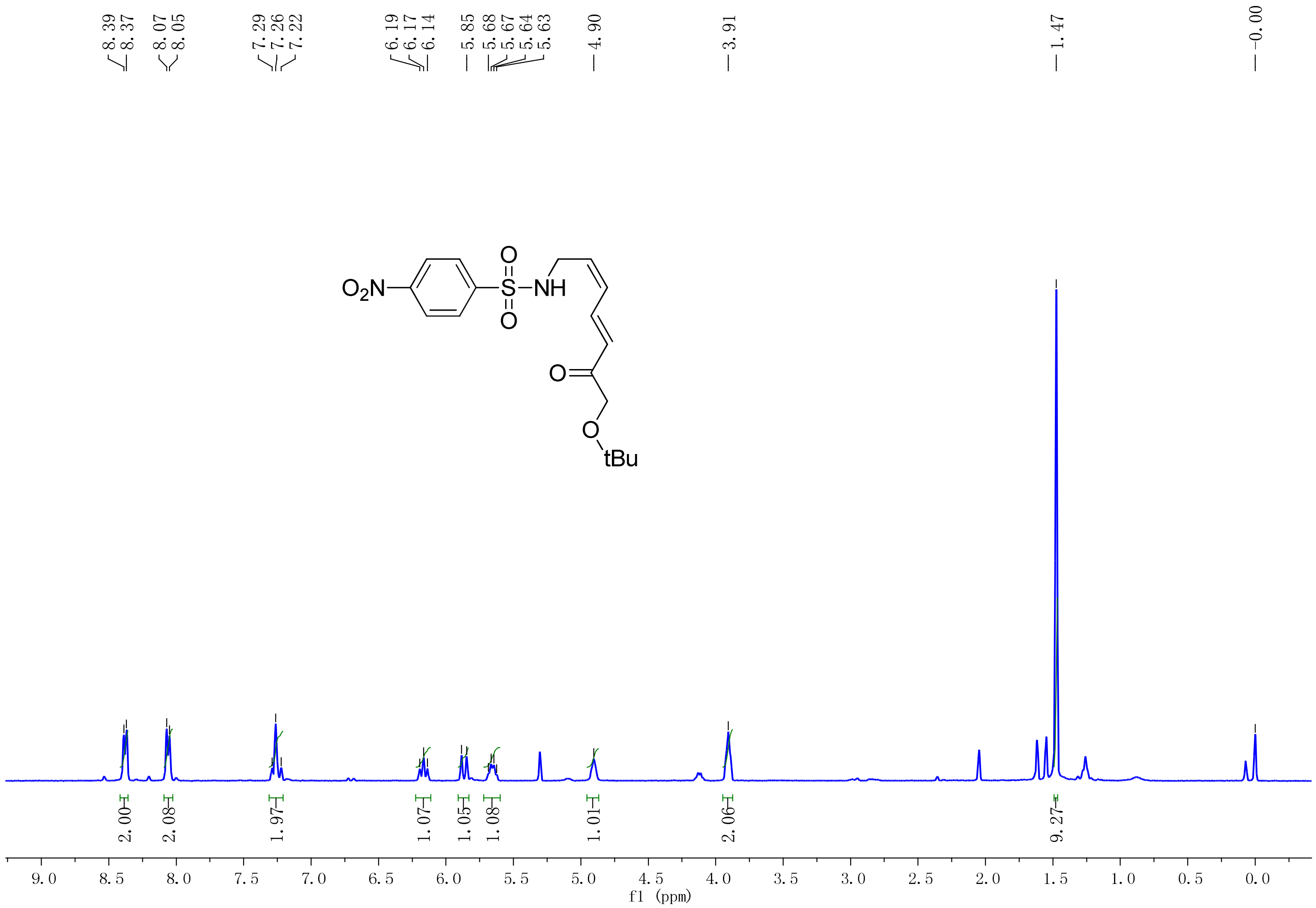
f1 (ppm)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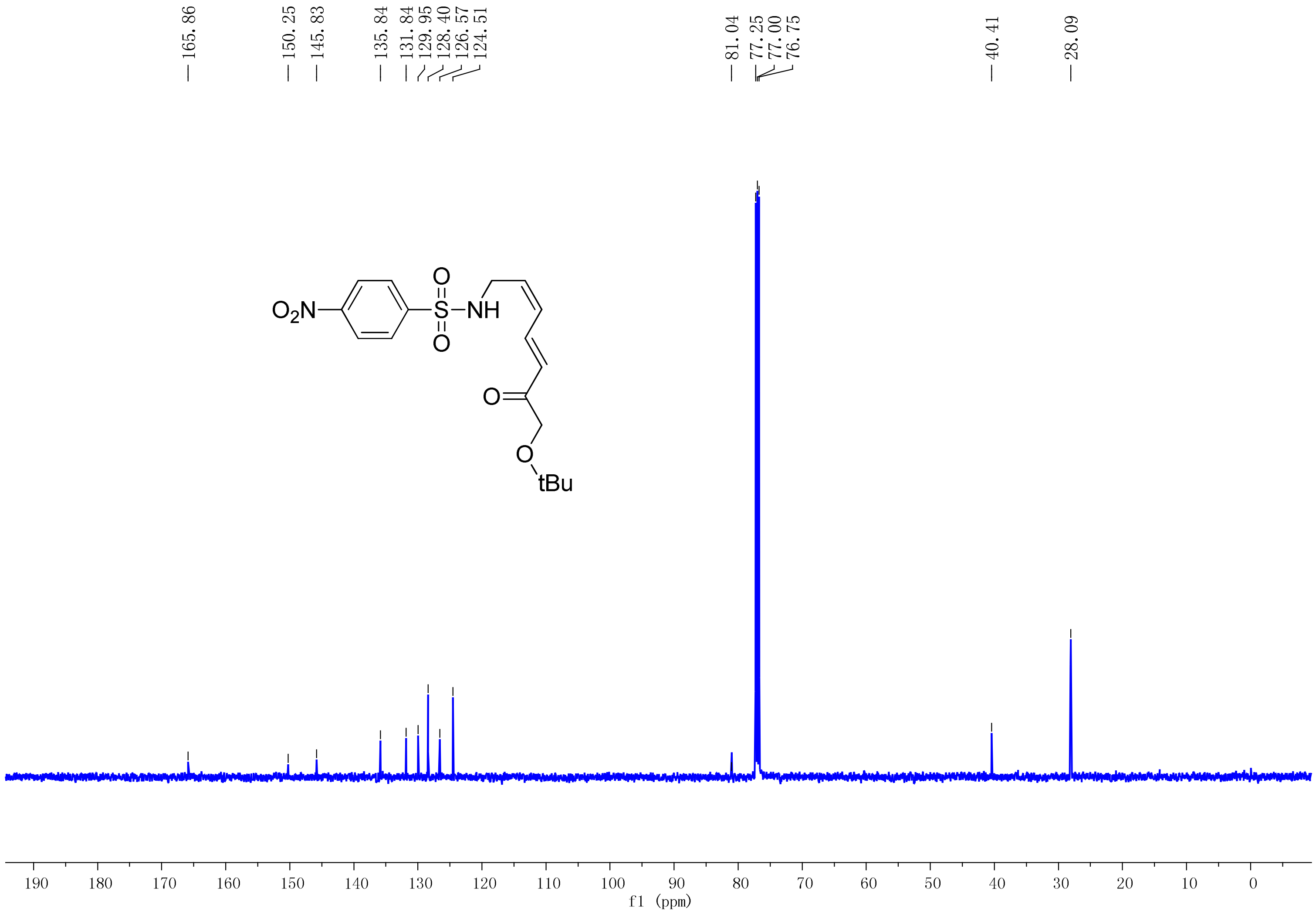
8.37
8.07
8.05
7.29
7.26
7.22
6.19
6.17
6.14
5.85
5.68
5.67
5.64
5.63
4.90
3.91
1.47
-0.00
O_2N
S
O
O
NH
O
O
tBu
2.00
2.08
1.97
1.07
1.05
1.08
1.01
2.06
9.27
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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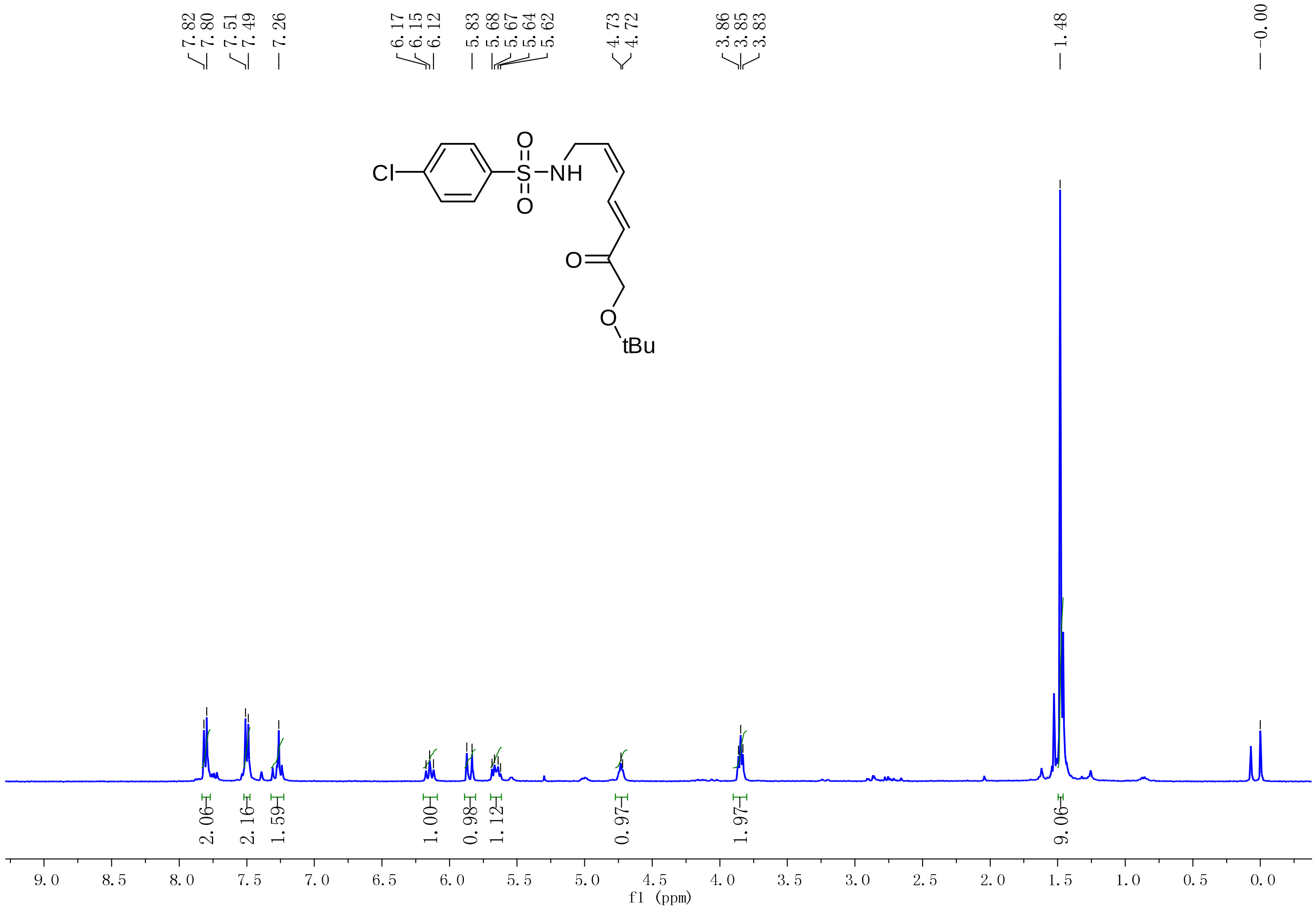
150.25
145.83
135.84
131.84
129.95
128.40
126.57
124.51
81.04
77.25
77.00
76.75
40.41
28.09
O2N
S
O
O
NH
O
O
tBu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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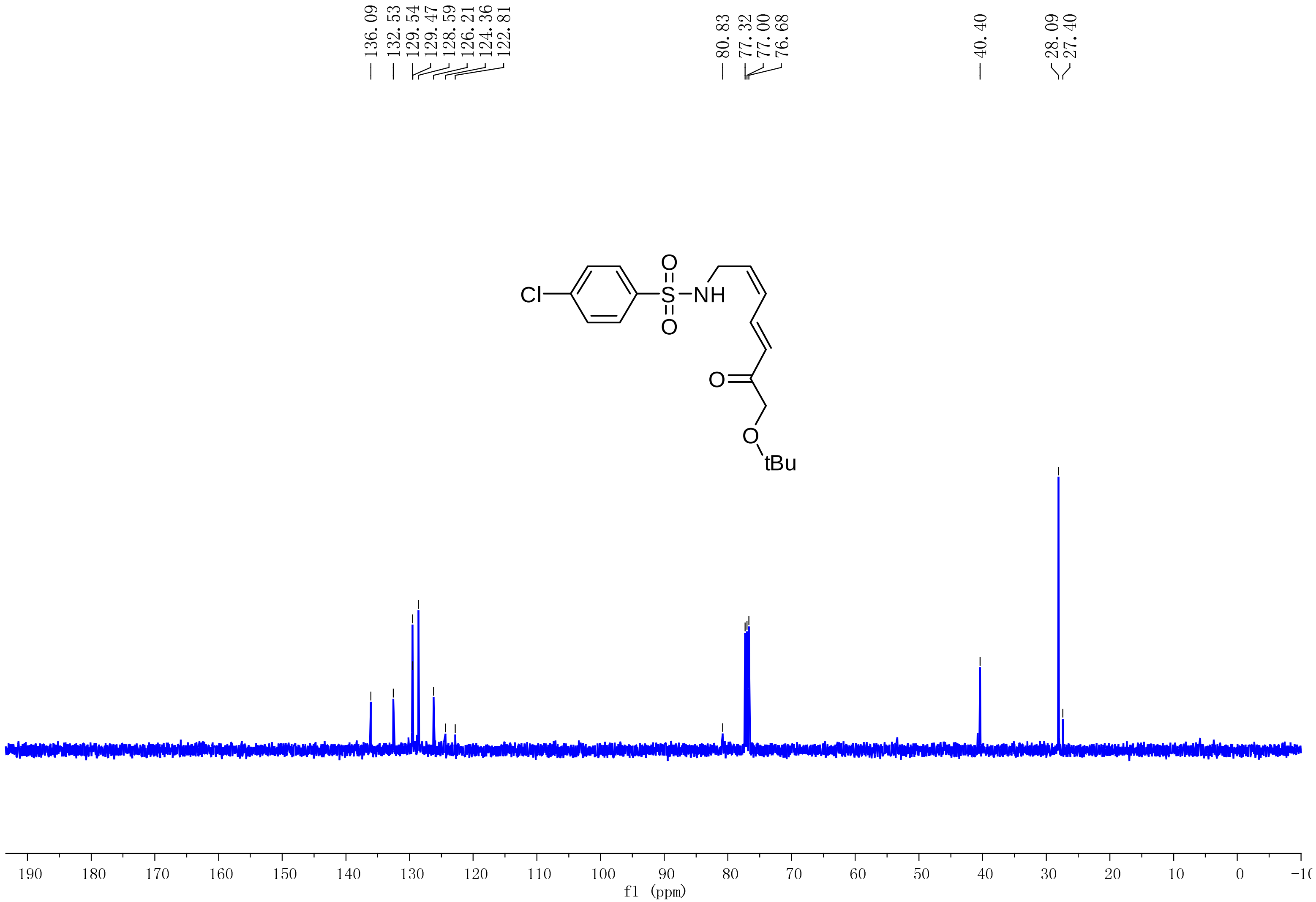
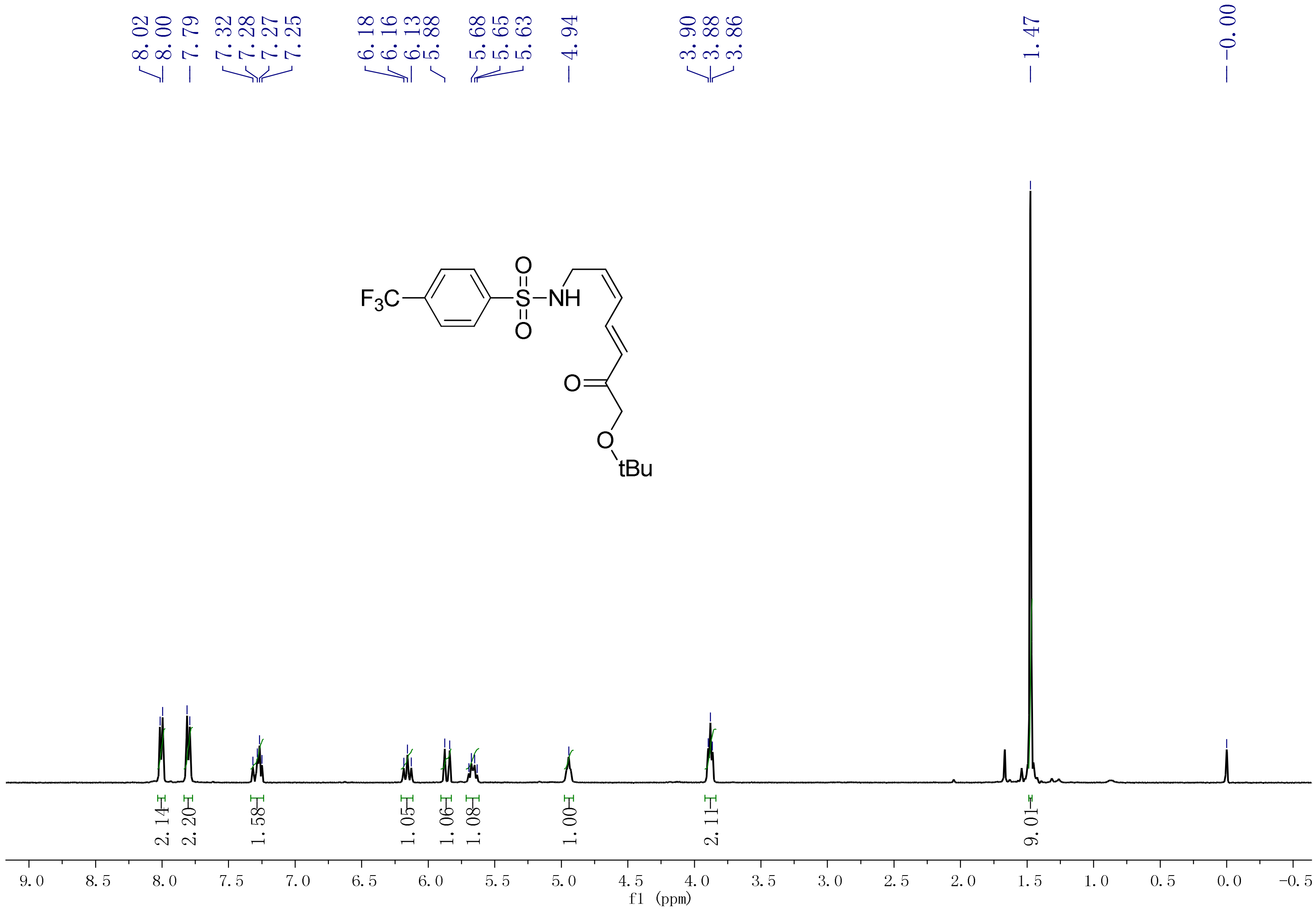
7.80
7.51
7.49
7.26
6.17
6.15
6.12
5.83
5.68
5.67
5.64
5.62
4.73
4.72
3.86
3.85
3.83
1.48
-0.00
Cl
S
O
O
NH
O
O
tBu
2.06
2.16
1.59
1.00
0.98
1.12
0.97
1.97
9.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


136.09
132.53
129.54
129.47
128.59
126.21
124.36
122.81
80.83
77.32
77.00
76.68
40.40
28.09
27.40
Cl
S
O
O
NH
O
O
tBu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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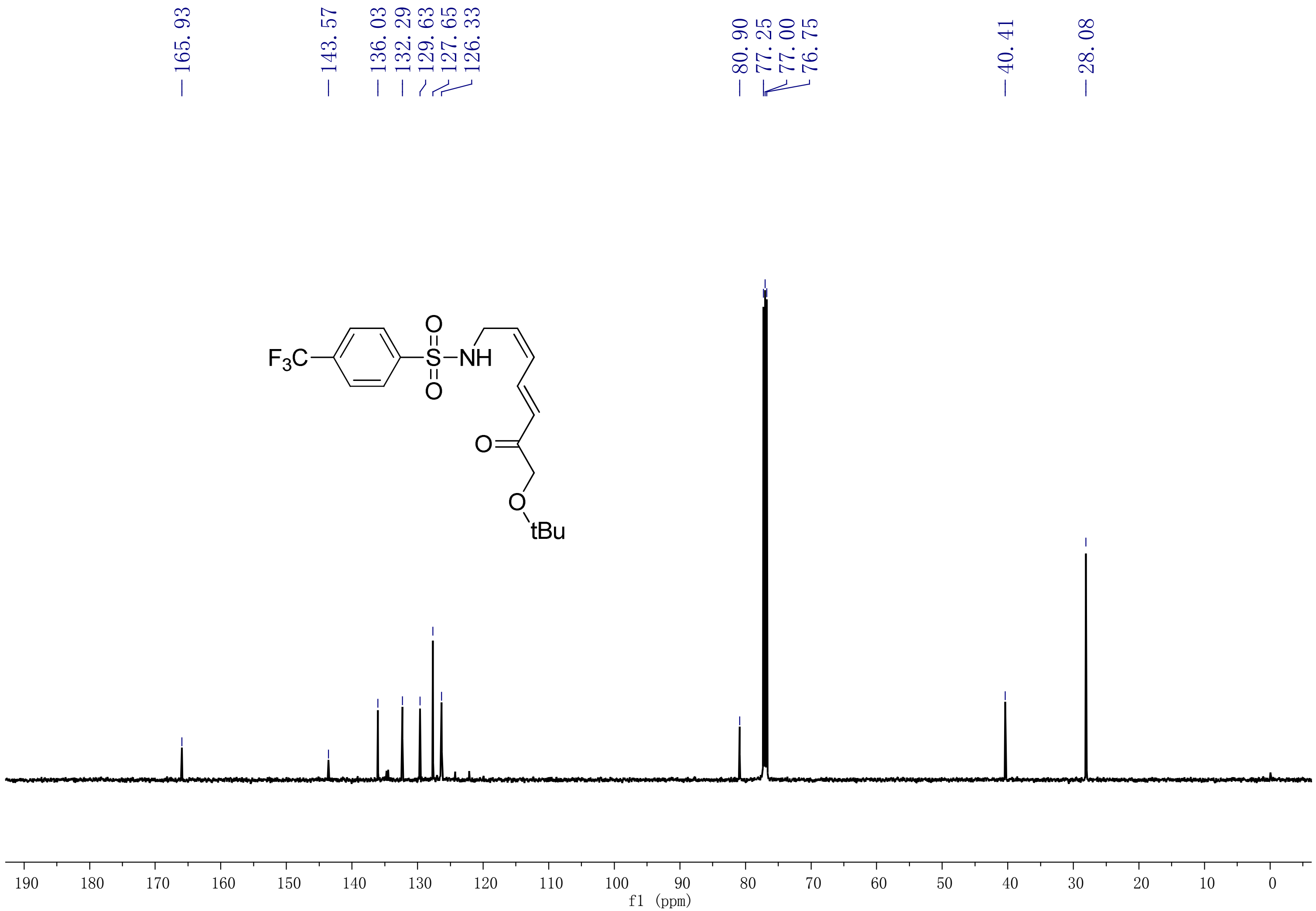
6.18
6.16
6.13
5.88
5.68
5.65
5.63
4.94
3.90
3.88
3.86
1.47
-0.00
F3C
S
O
O
NH
O
O
tBu
2.14
2.20
1.58
1.05
1.06
1.08
1.00
2.11
9.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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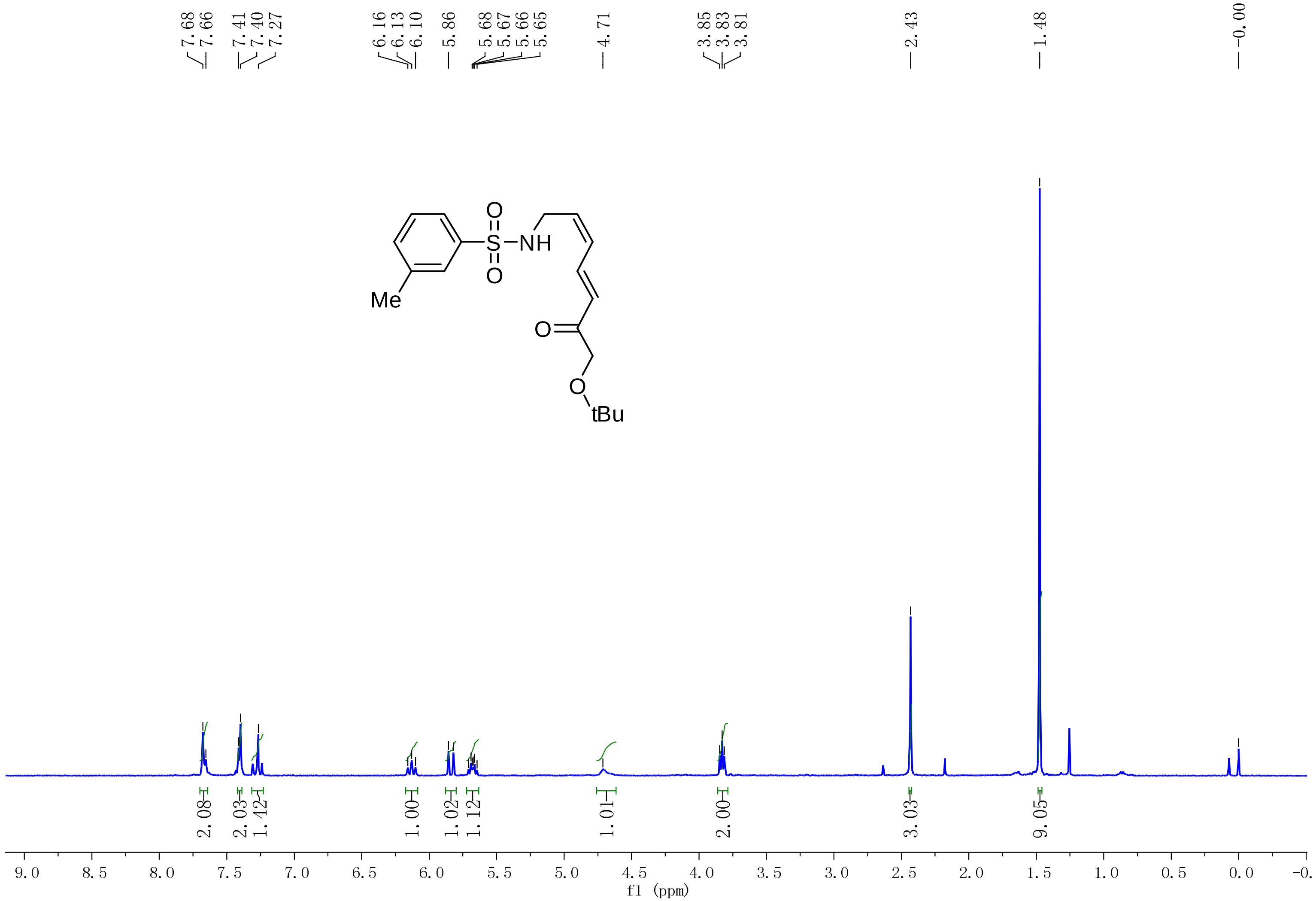
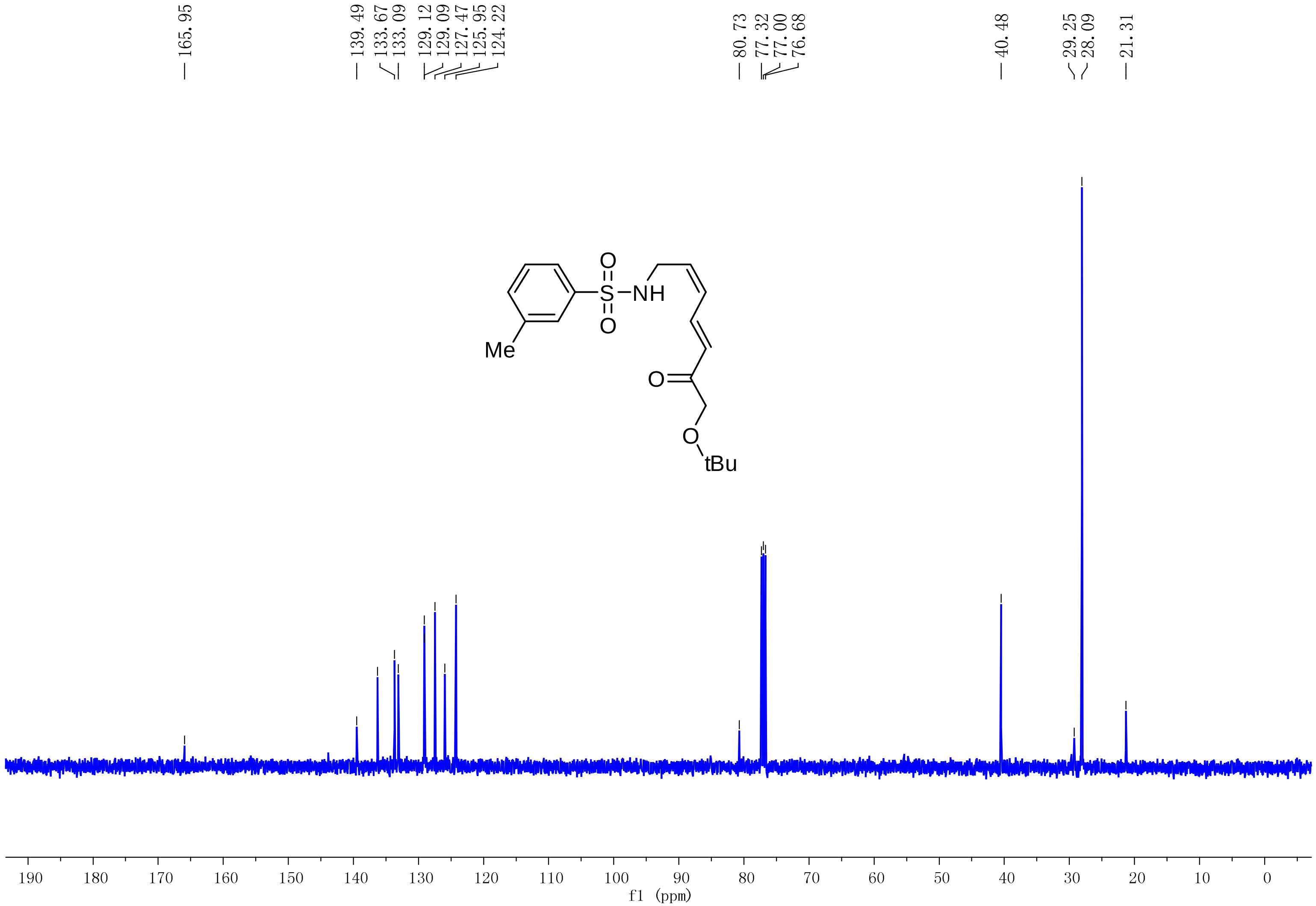
143.57
136.03
132.29
129.63
127.65
126.33
80.90
77.25
77.00
76.75
40.41
28.08
F3C
S
NH
O
O
O
O
tBu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



7.68
7.66
7.41
7.40
7.27
6.16
6.13
6.10
5.86
5.68
5.67
5.66
5.65
4.71
3.85
3.83
3.81
2.43
1.48
-0.00
O
S
NH
O
Me
O
O
tBu
2.08
2.03
1.42
1.00
1.02
1.12
1.01
2.00
3.03
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
0.0
f1 (ppm)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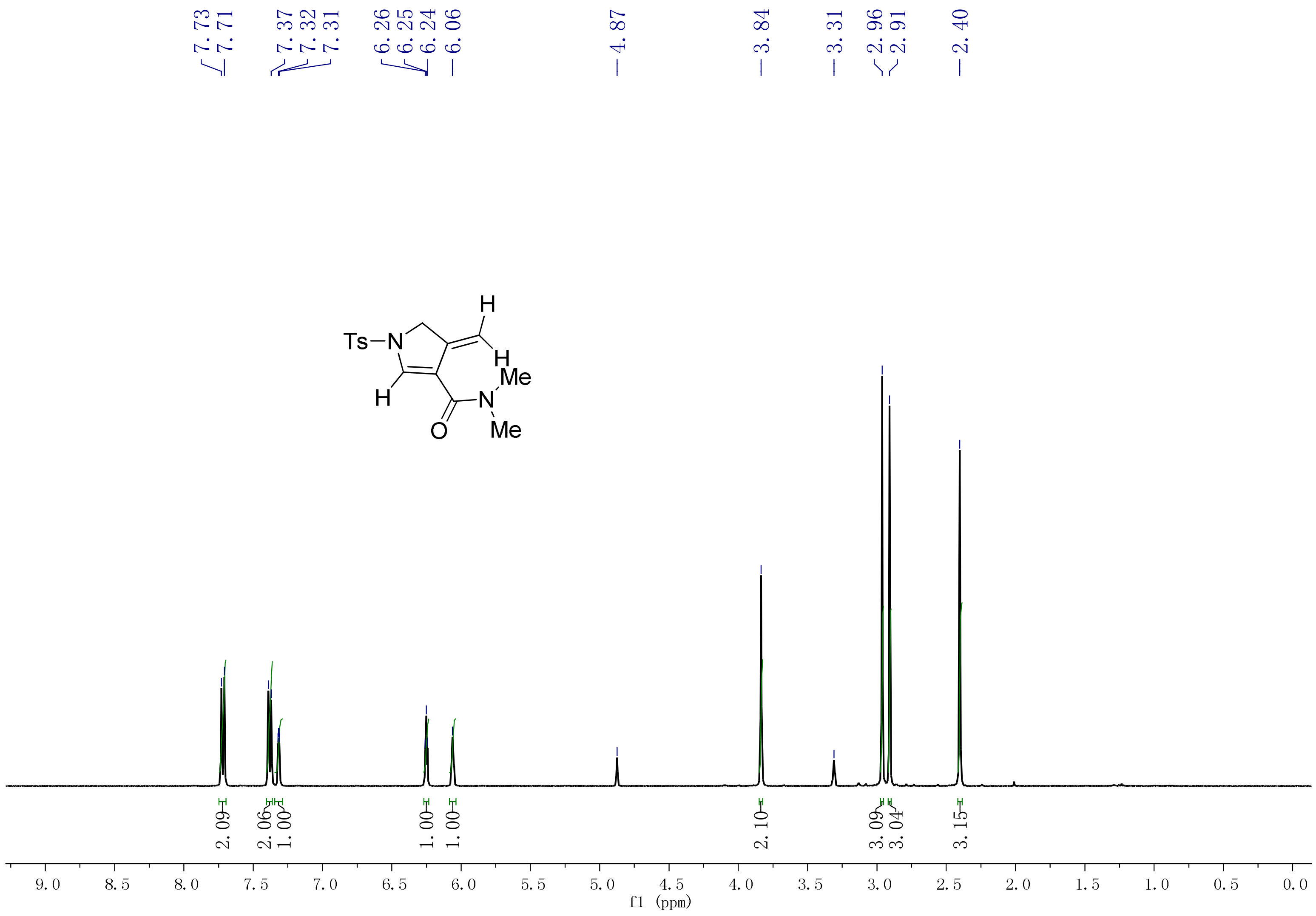
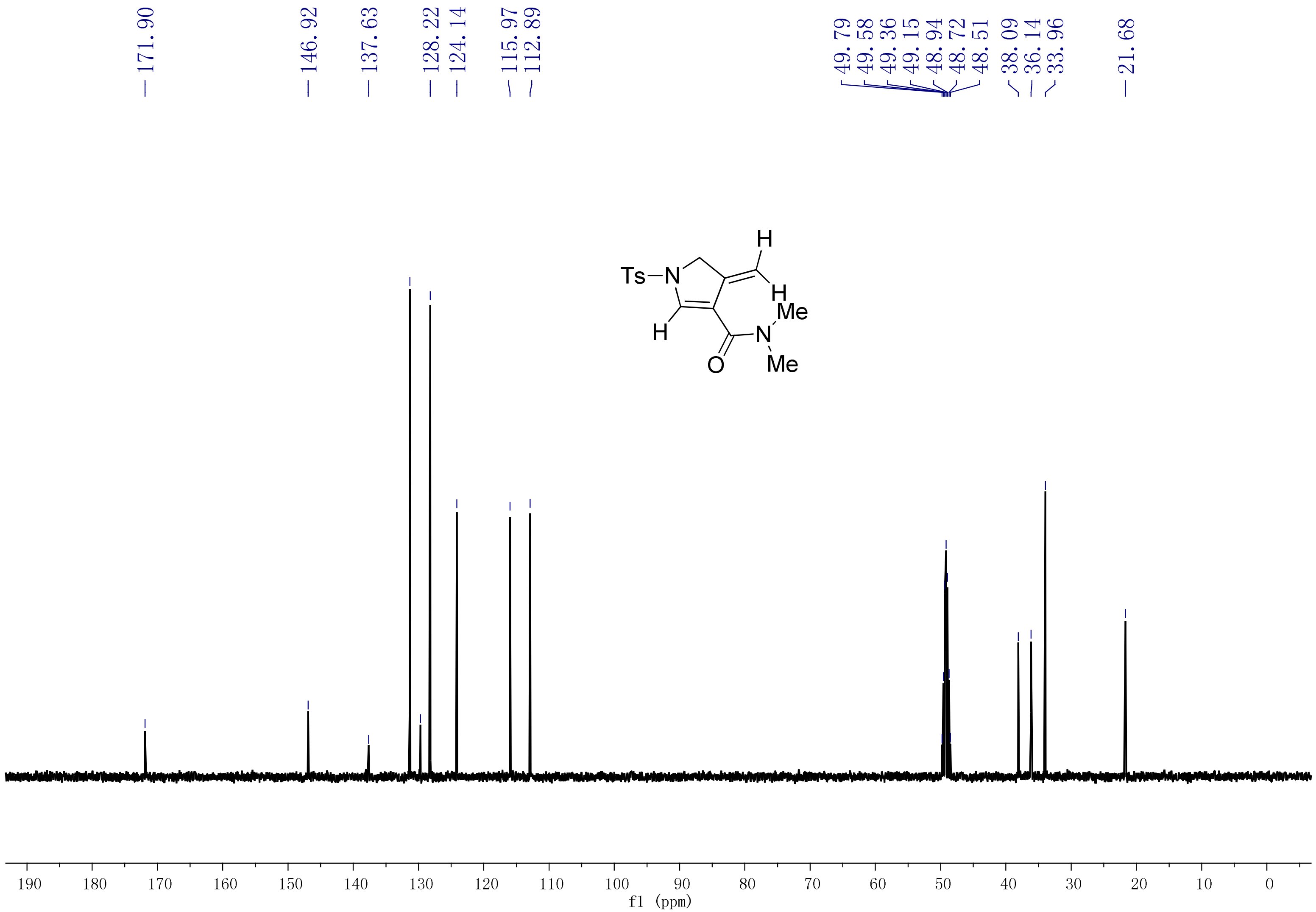
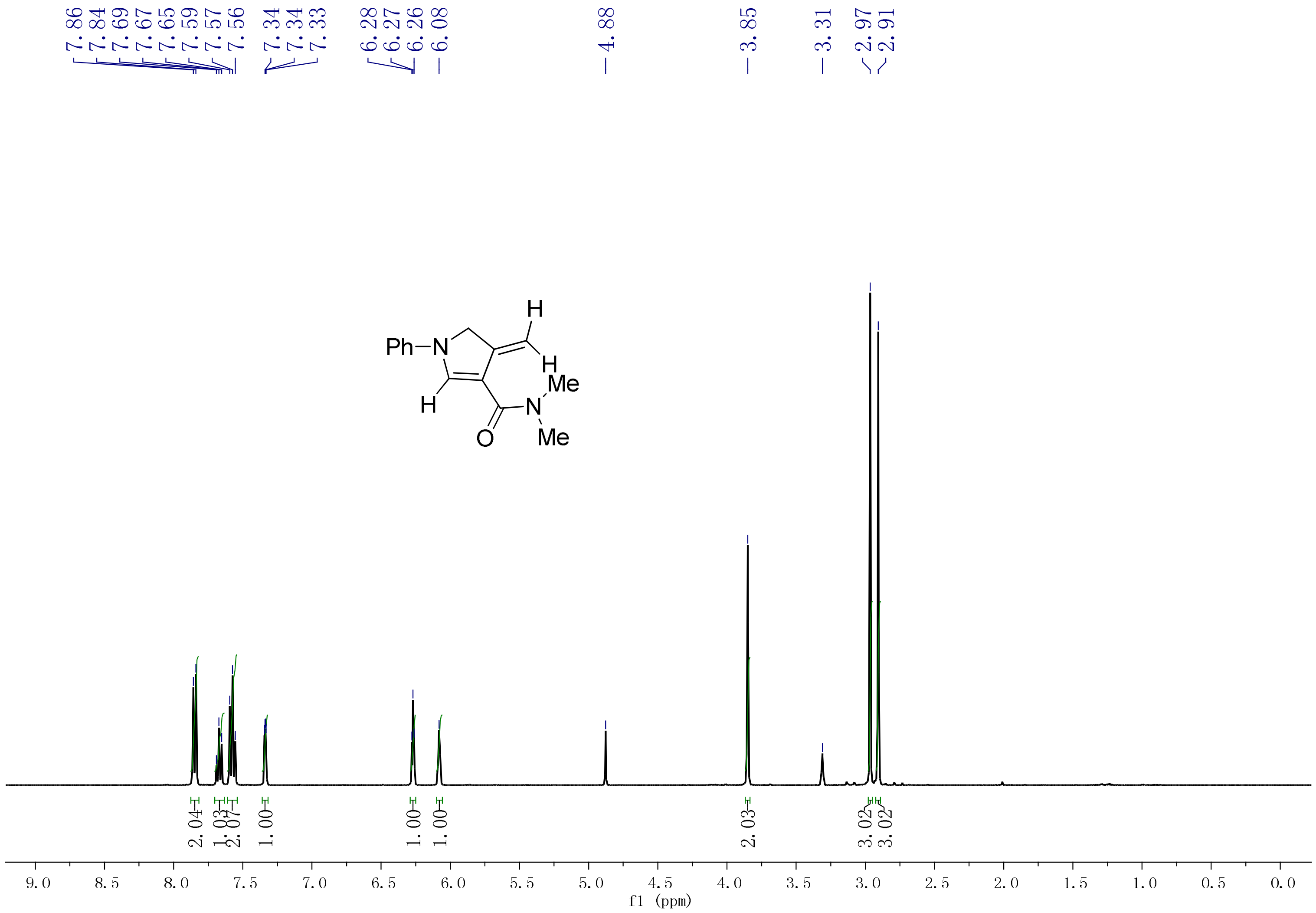
139.49
133.67
133.09
129.12
129.09
127.47
125.95
124.22
80.73
77.32
77.00
76.68
40.48
29.25
28.09
21.31
O
S
NH
O
Me
O
O
tBu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.73
7.71
7.37
7.32
7.31
6.26
6.25
6.24
6.06
4.87
3.84
3.31
2.96
2.91
2.40
Ts
N
H
H
H
Me
N
Me
O
2.09
2.06
1.00
1.00
1.00
2.10
3.09
3.04
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.90
146.92
137.63
128.22
124.14
115.97
112.89
49.79
49.58
49.36
49.15
48.94
48.72
48.51
38.09
36.14
33.96
21.68
Ts
N
H
H
H
Me
N
Me
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.84
7.69
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7.65
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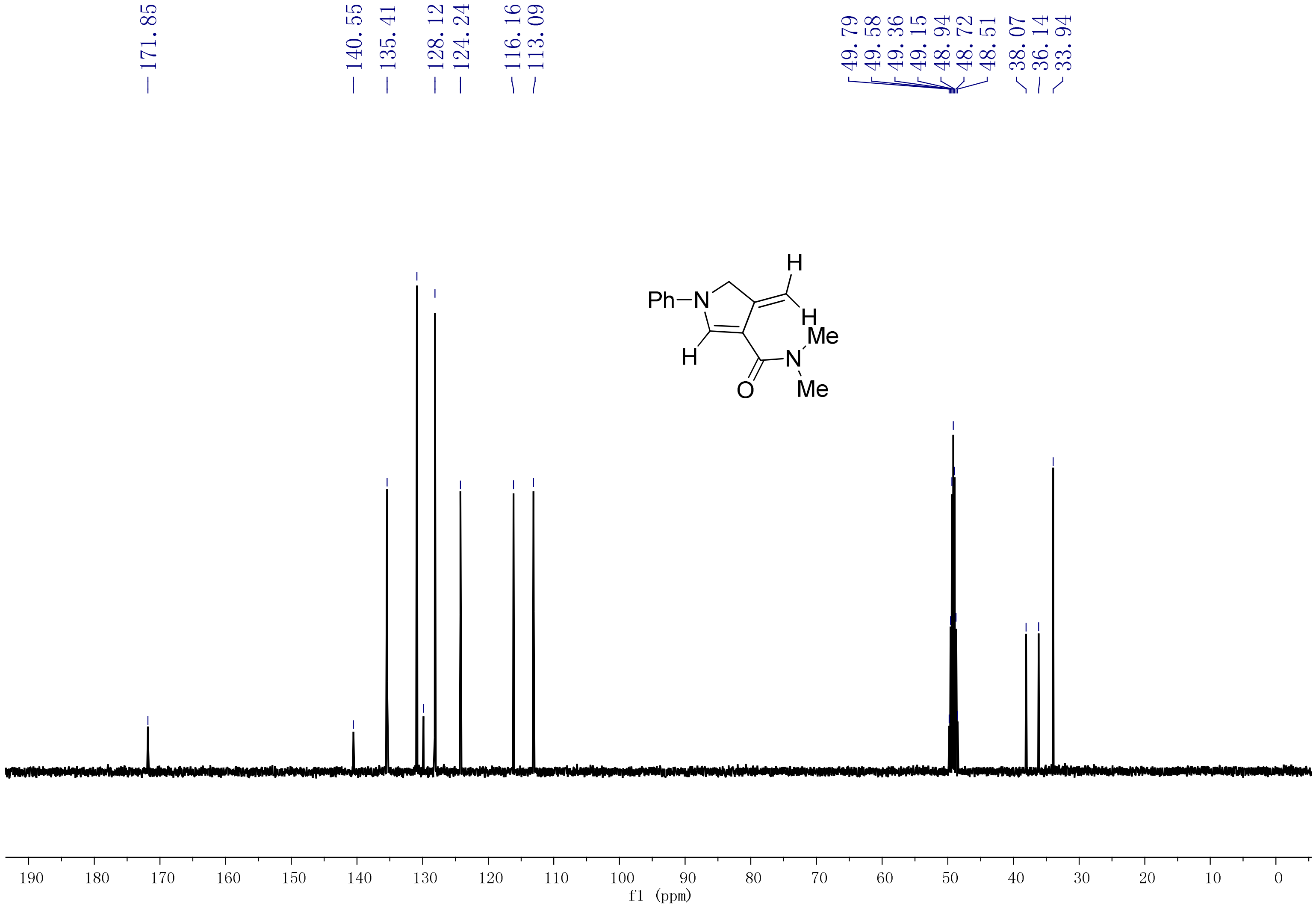
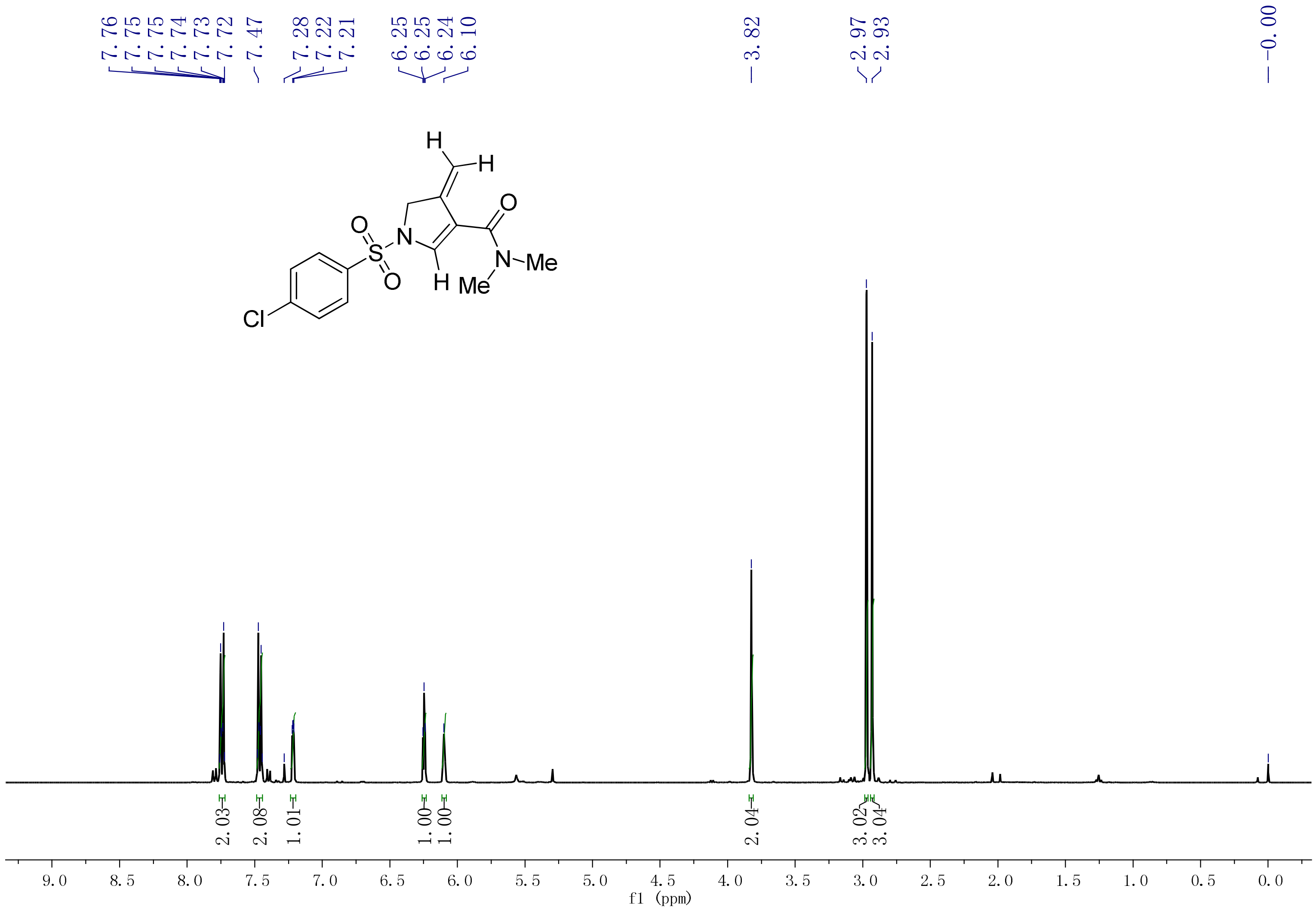
7.57
7.56
7.34
7.34
7.33
6.28
6.27
6.26
6.08
4.88
3.85
3.31
2.97
2.91
H
Ph
N
H
H
Me
N
O
Me
2.04
1.03
2.07
1.00
1.00
1.00
2.03
3.02
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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7.22
7.21
6.25
6.25
6.24
6.10
3.82
2.97
2.93
-0.00
O
N
S
O
Cl
H
H
O
N
Me
H
Me
2.03
2.08
1.01
1.00
1.00
2.04
3.02
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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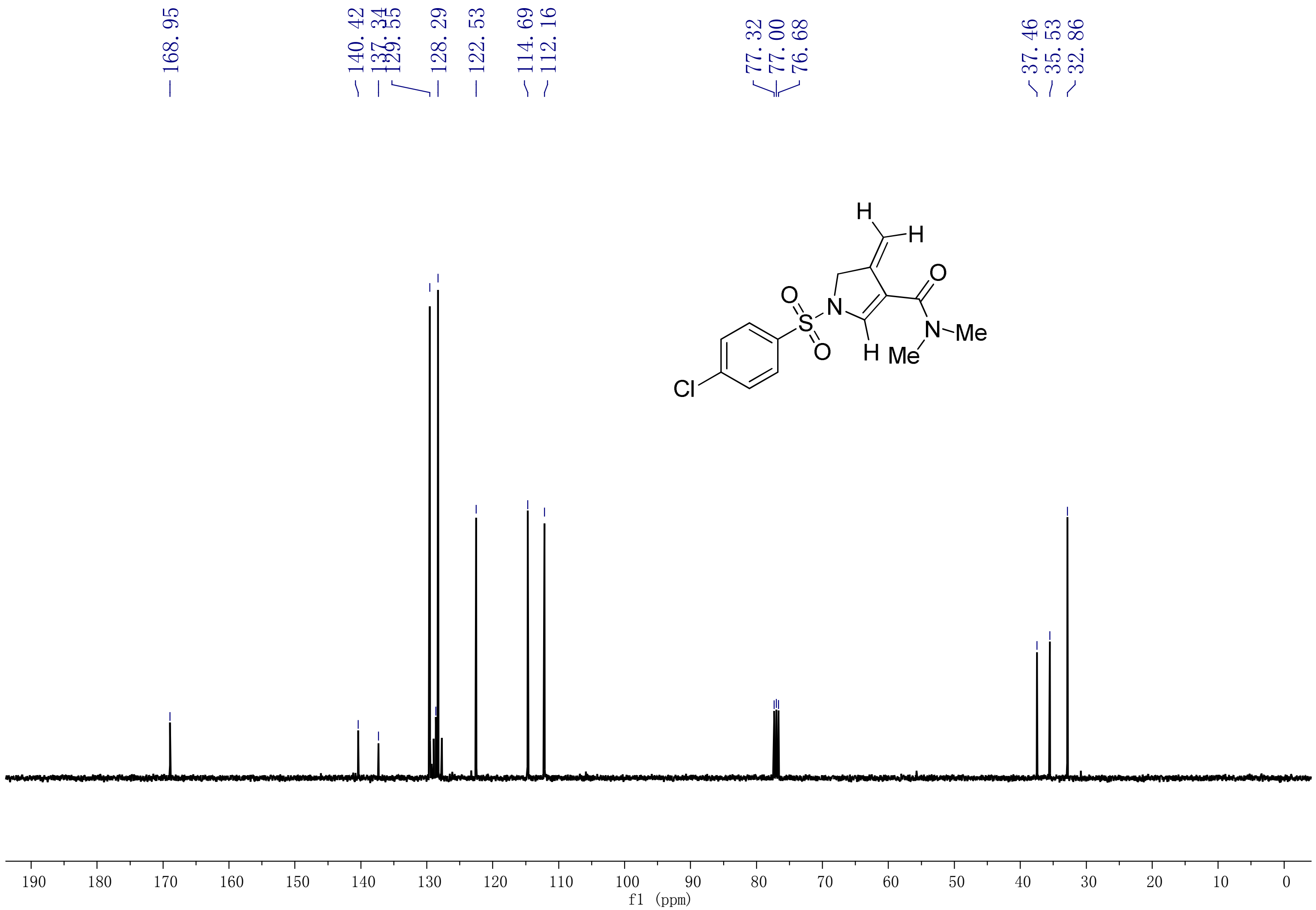
0.0
f1 (ppm)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140.42
137.34
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122.53
114.69
112.16
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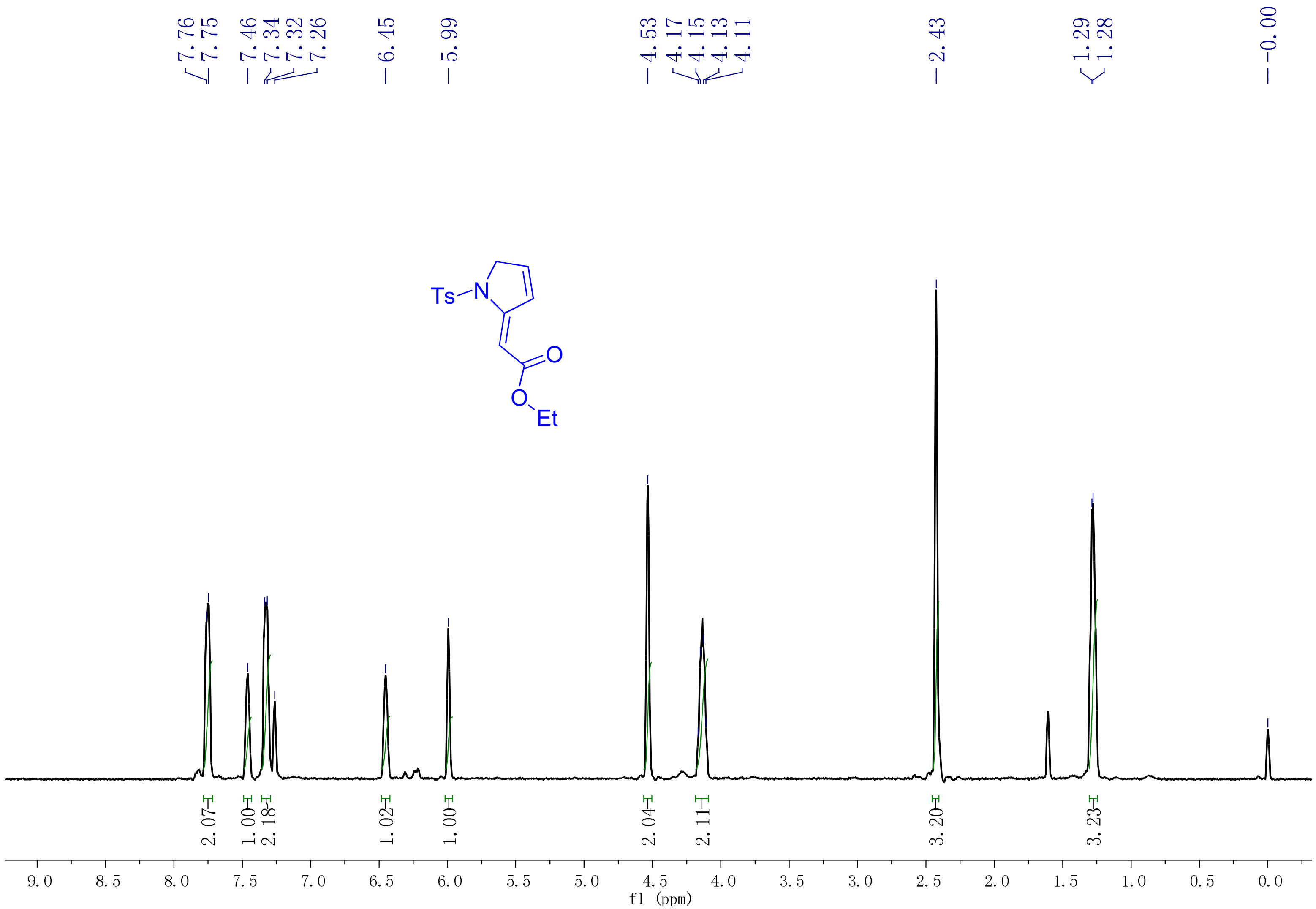
77.00
76.68
37.46
35.53
32.86
H
H
O
O
S
N
O
N
Me
H
Me
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26
6.45
5.99
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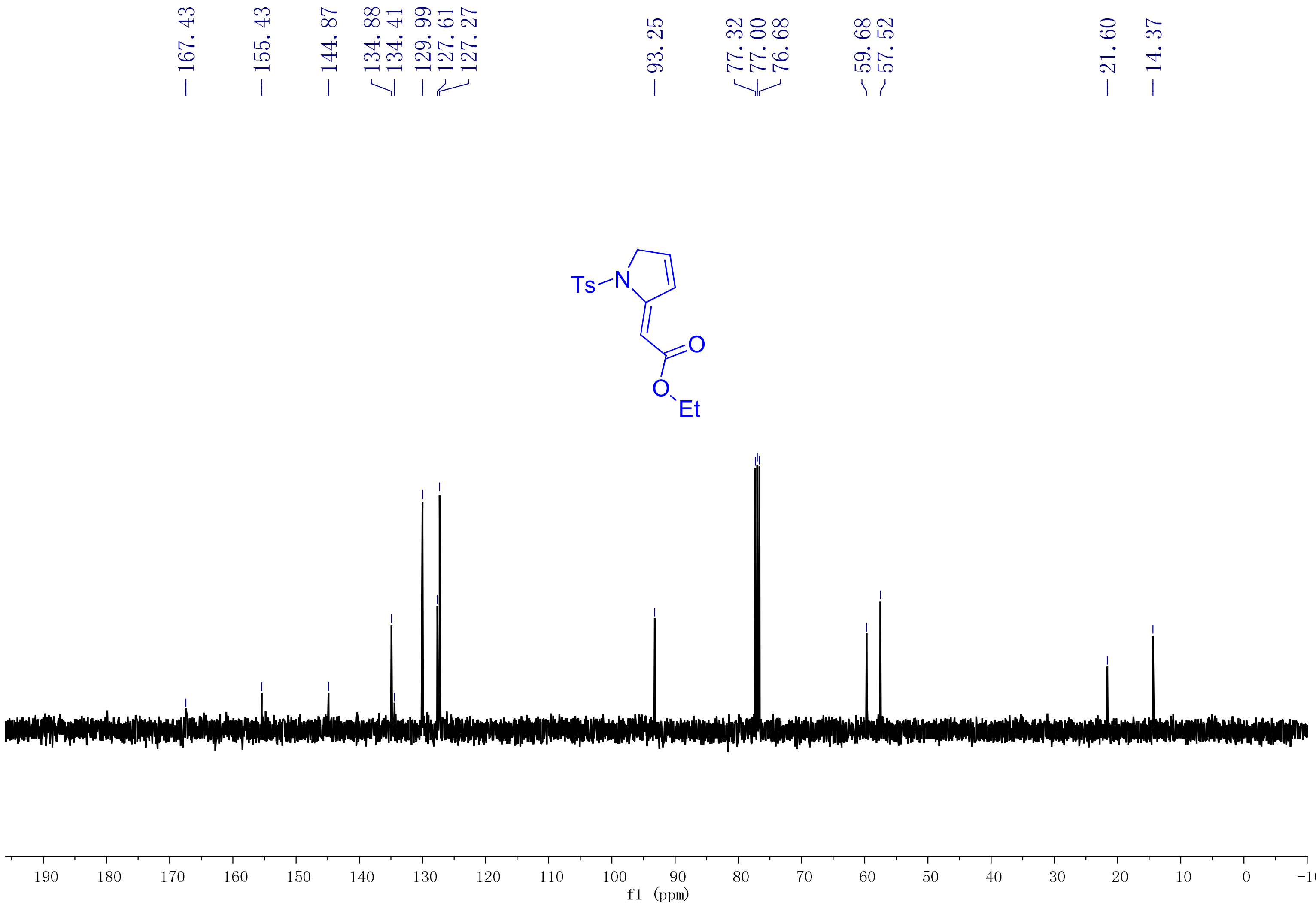
4.17
4.15
4.13
4.11
2.43
1.29
1.28
-0.00
Ts
N
O
O
Et
2.07
1.00
2.18
1.02
1.00
2.04
2.11
3.20
3.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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155.43
144.87
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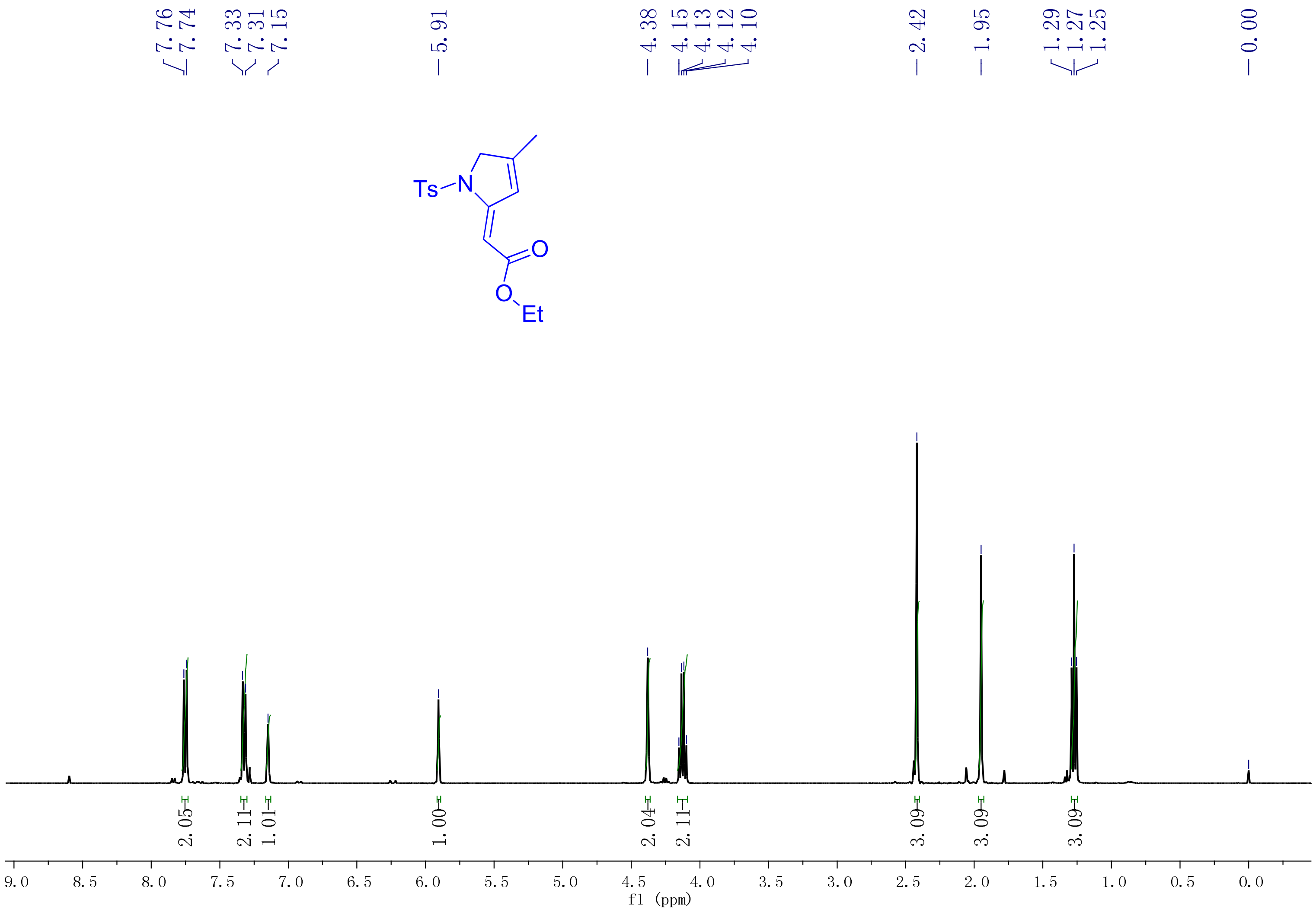
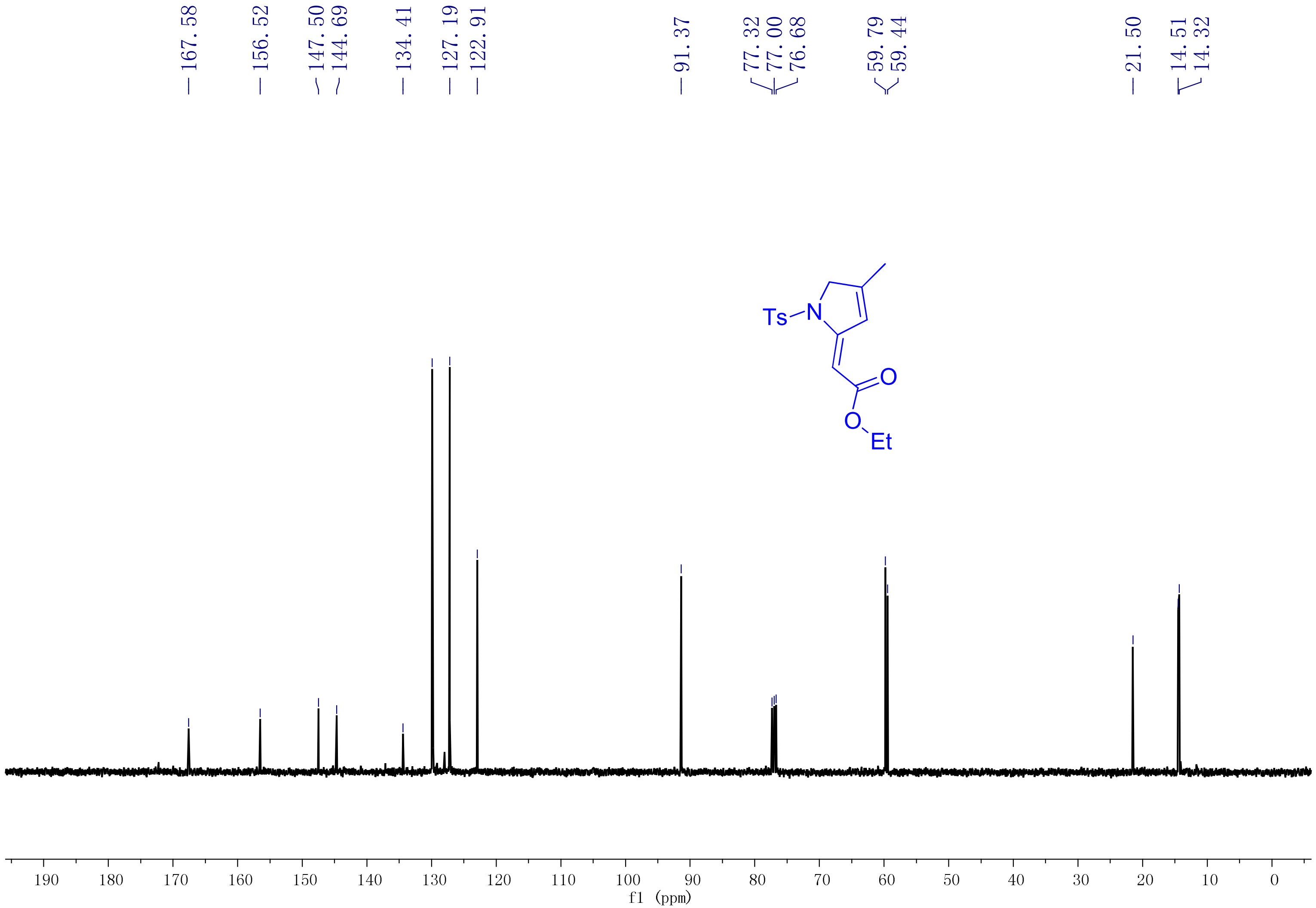
134.41
129.99
127.61
127.27
93.25
77.32
77.00
76.68
59.68
57.52
21.60
14.37
Ts
N
O
O
Et
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.76
7.74
7.33
7.31
7.15
5.91
4.38
4.15
4.13
4.12
4.10
2.42
1.95
1.29
1.27
1.25
0.00
Ts
N
O
O
Et
2.05
2.11
1.01
1.00
2.04
2.11
3.09
3.09
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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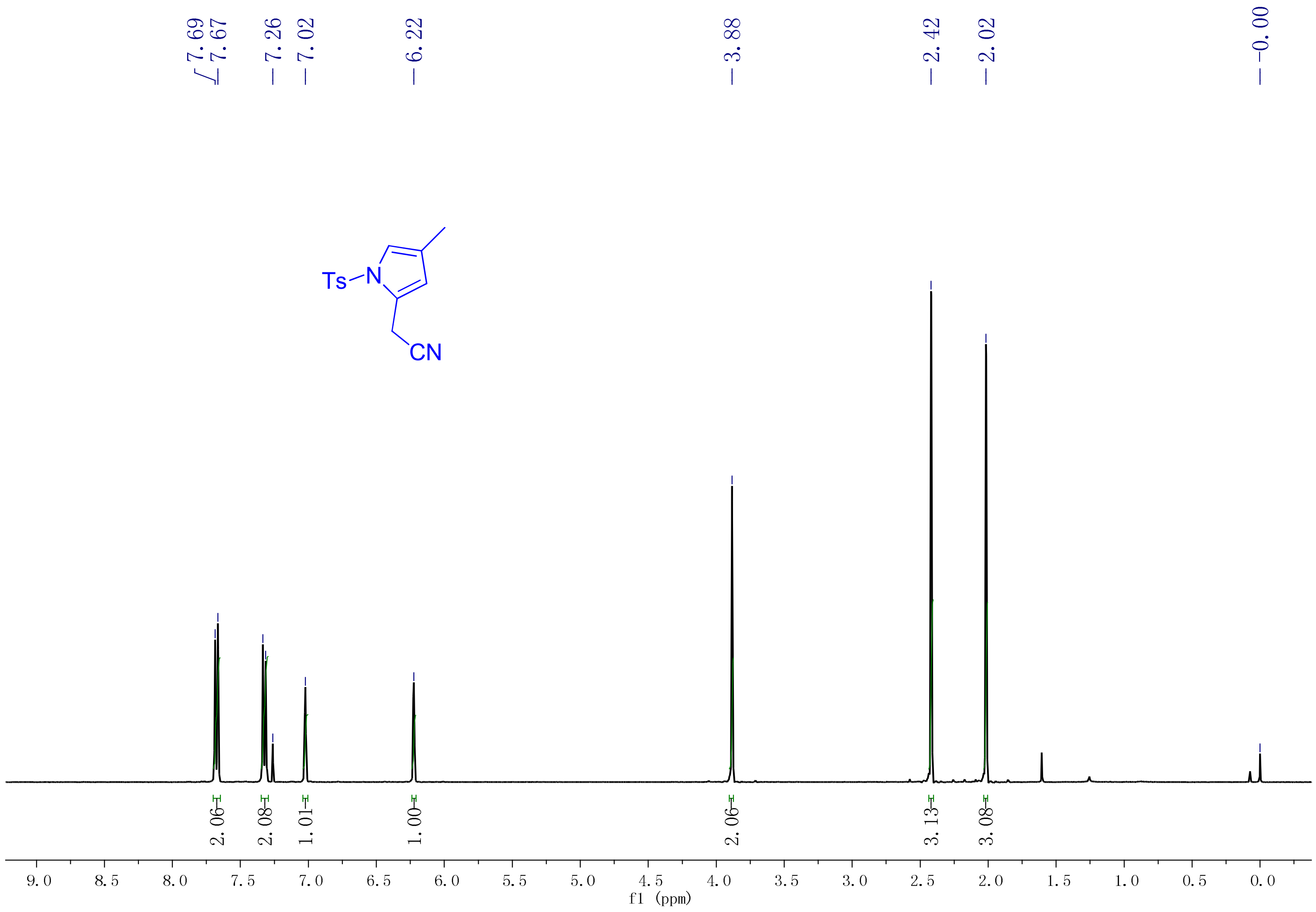
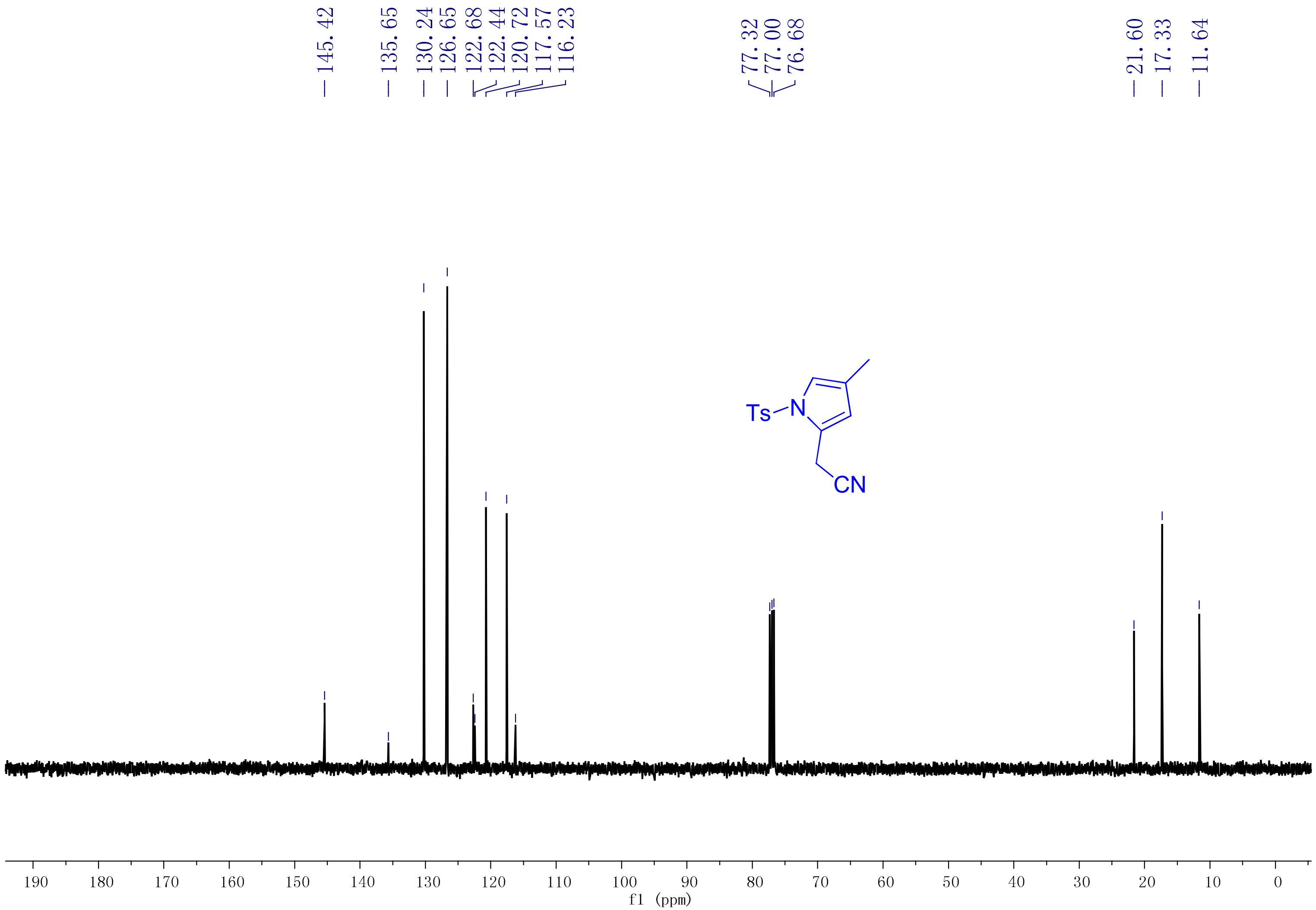
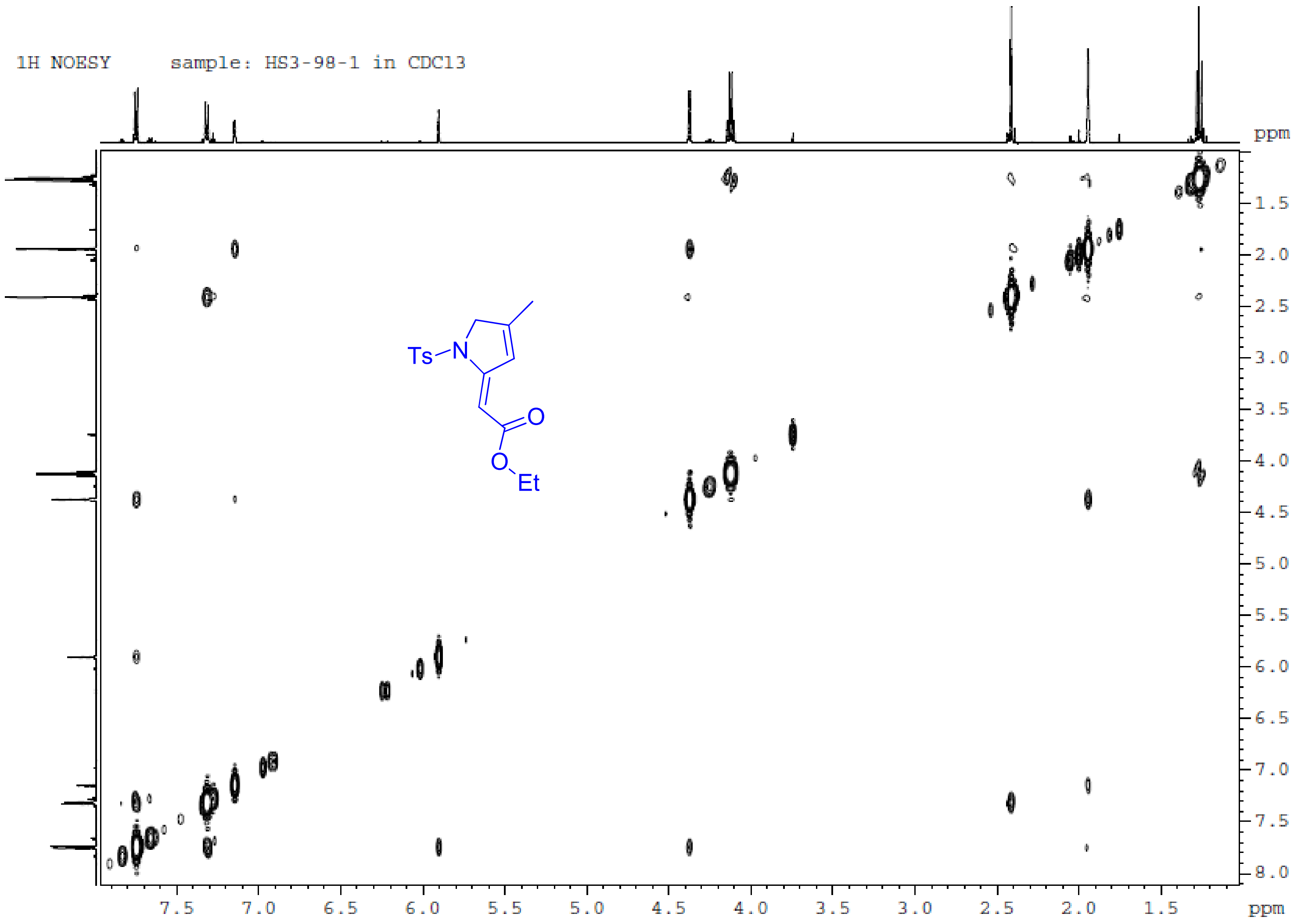
156.52
147.50
144.69
134.41
127.19
122.91
91.37
77.32
77.00
76.68
59.79
59.44
21.50
14.51
14.32
Ts
N
O
O
Et
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.69
7.67
7.26
7.02
6.22
3.88
2.42
2.02
-0.00
Ts
N
CN
2.06
2.08
1.01
1.00
2.06
3.13
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.42
135.65
130.24
126.65
122.68
122.44
120.72
117.57
116.23
77.32
77.00
76.68
21.60
17.33
11.64
Ts
N
CN
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H NOESY sample: HS3-98-1 in CDCl3
Ts
N
O
O
Et
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
ppm