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Supporting Information

A General Method for Site-Selective Csp^3-S Bond Formation *via* Cooperative Catalysis

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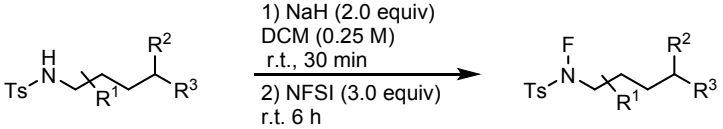
Instrumentation and Chemicals

NMR spectra were recorded on Bruker 400 and 600 M spectrometers, operating at 400 and 600 MHz for ^{1}H NMR and 100 and 150 MHz for ^{13}C NMR spectrophotometer using $CDCl_3$ and TMS as the internal standard. Chemical shift values for ^{1}H and ^{13}C are referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C; Chemical shifts are reported in δ ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz) and integration. Column chromatography was performed on silica gel 200-300 mesh. High-resolution mass spectra (HRMS) were recorded on electron-spray ionization (ESI) technique.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard note procedures unless otherwise noted. $Cu(acac)_2$ was purchased from Shanghai Macklin Bio-Chemical Reagent Co., Ltd., 1,10-phenanthroline was purchased from Alfa Aesar Chemical Co., Ltd., Indium powder was purchased from Meryer Chemical Technology Co., Ltd., Anhydrous DCE was purchased from Energy Chemical Reagent Co., Ltd.

General Procedure: Preparation of *N*-fluoroamides and disulfides

Procedure for *N*-fluoroamides



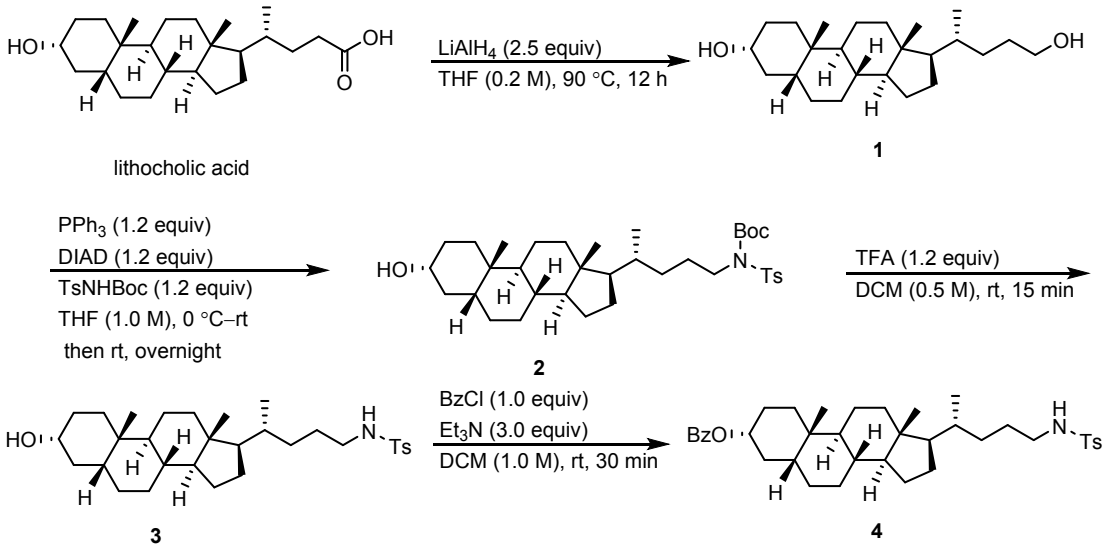
The corresponding N-fluorotosylamides are prepared according to a reported procedure[1]: To a solution of tosylamine (5 mmol, 1.0 equiv) in dichloromethane (20

mL) was added NaH (0.24 g, 10 mmol, 2.0 equiv) at 0 ºC. The mixture was allowed to stir for 30 min at room temperature under nitrogen atmosphere. After that, NFSI (15 mmol, 3.0 equiv) was added portion wise to the resulted mixture. Then the mixture was stirring for another 6 hours and after completion the reaction was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried with anhydrous Na_2SO_4. Evaporation the solvent to give the residue, the residue was washed with DCM and PE (DCM:PE = 1:50) several times. Combining the filtrate and evaporation under reduce pressure to give the crude product. Column chromatography on silica gel (ethyl acetate/PE/DCM = 1:35:0.5 as eluent) afforded corresponding N-fluoroamides as white solid or liquid.

N-fluorocarboxyamides **1d** and **1e** were prepared according to Ref. 2.

The corresponding tosyl amides precursors of **1a**, **1b**, **1c**, **1f**, **1g**, **1h**, **1n**, **1o**, **1p**, **1t**, **1u**, **1x**, **1y**, **1z**, **1ab**, **1ac**, **1ad**, **1ae**, **1af**, **1ag**, **8a**, **8b**, **11a** were prepared according to Ref. 3.

The corresponding tosyl amides precursors of **1q**, **1r**, **1v**, **1s** and **1ai** were prepared from the alcohols. A representative example was shown below.



Lithocholic acid (1.0 equiv) was dissolved in THF (0.2 M), $LiAlH_4$ (2.5 equiv) was added portion wise under 0 ºC, then the mixture was refluxing for 12 h. After that, the

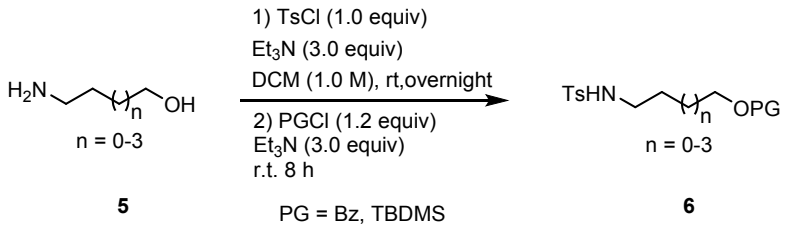
reaction was cooled down, the $Na_2SO_4 \cdot 10H_2O$ was added slowly until the mixture was clear to quench the reaction, filtered, solid was washed with Et_2O, the combined ether solution was concentrated in vacuo to give the **1**.

In an oven dried round bottom flask, PPh_3 (1.2 equiv) and TsNHBoc (1.2 equiv) were dissolved in anhydrous THF. Then, a solution of alcohol **1** in THF (1.0 M) was added. The mixture was cooled to 0 ºC and DIAD (1.2 equiv) was slowly added and the reaction was slowly warmed to room temperature and stirred overnight. Upon completion, the reaction was quenched by water (20 mL). The aq. Layer was extracted with EtOAc (25 mL × 3), the combined organic layer dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:10:0.5 as eluent) afforded **2**.

TFA (1.2 equiv) was added to a solution of **2** in DCM (0.5 M), the reaction stirred for 15 min. Then the reaction was quenched by Sat. $NaHCO_3$ solution. The aq. Layer was extracted with DCM (25 mL × 3), the combined organic layer dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:5:0.5 as eluent) afforded **3**

To a solution of **3** (1.0 equiv) in dichloromethane (1.0 M) was added triethylamine (3.0 equiv) at room temperature. Benzoyl chloride (0.95 equiv) was added dropwise under the same temperature. Then the mixture was stirring for 30 min at room temperature (detected by TLC). After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:5:0.5 as eluent) afforded compound **4** as white solid.

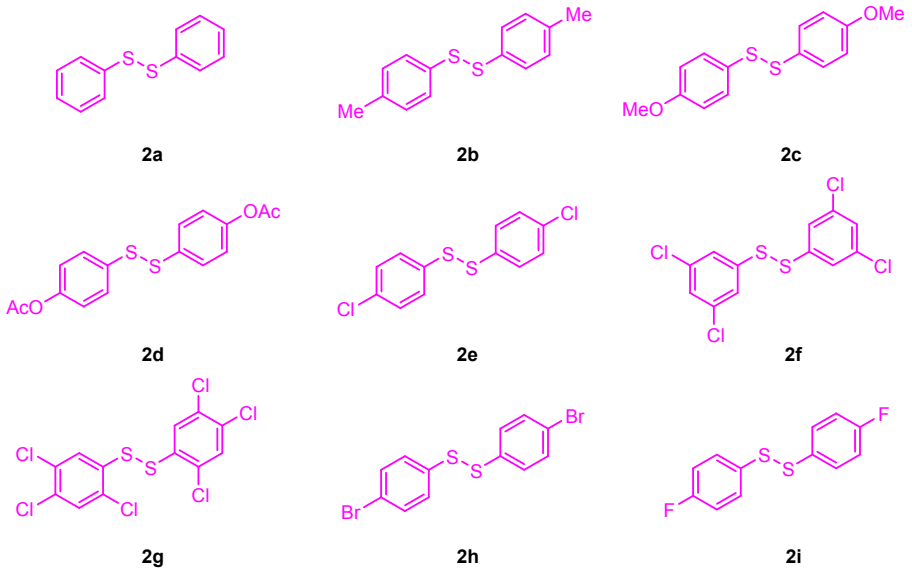
The corresponding tosyl amides precursors of **1k**, **1l**, **1m**, **6a**, **6c** were prepared from the amino alcohols. A representative example was shown below.

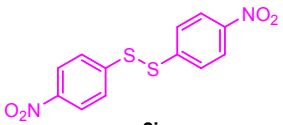


In an oven dried round bottom flask was added amino alcohol **5** and dried DCM (0.5 M), the mixture was cooled to 0 ºC, Et_3N (3.0 equiv) and TsCl (1.0 equiv) were added slowly, the reaction was warmed to room temperature and stirred overnight. After completion, the solvent was evaporated and the desired residue was dissolved in dried DCM (0.5 M) again, Et_3N (3.0 equiv) and PGCl (1.2 equiv) were added slowly, the reaction was warmed to room temperature and stirred for 8 hours. After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 3). The combined organic phase was washed with brine (30 mL), and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:5:0.5 as eluent) afforded compound **6**.

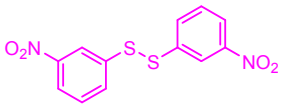
Disulfides **2a**–**2k**, **2m**–**2o** are commerical available. **2l** was prepared according to Ref. 4. **10a**, **10b**, **10c** were prepared according to Ref. 5.

List of disulfides:

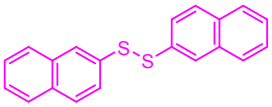




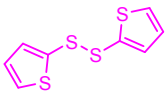
2j



2k



2l



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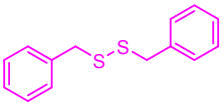
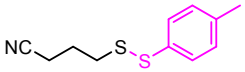
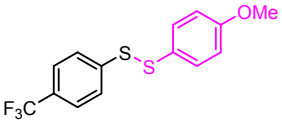


2n



10a



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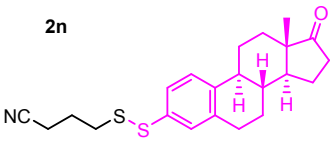
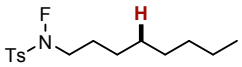
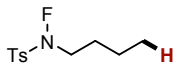


10c

List of N-fluoroamides:



1a



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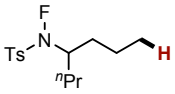

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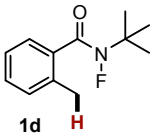

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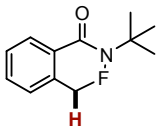

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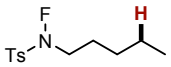

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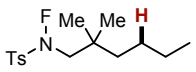

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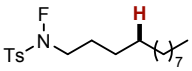

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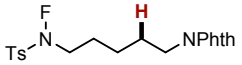

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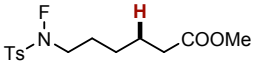

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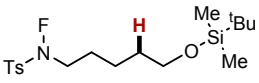

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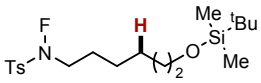

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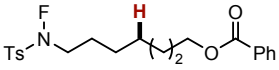

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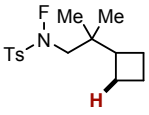

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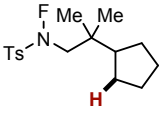

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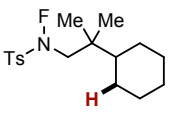

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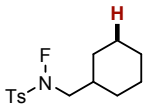

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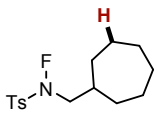

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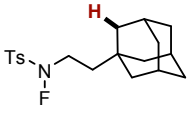

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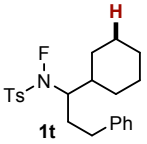

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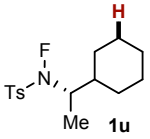

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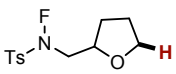

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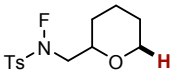

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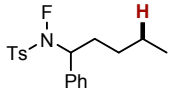
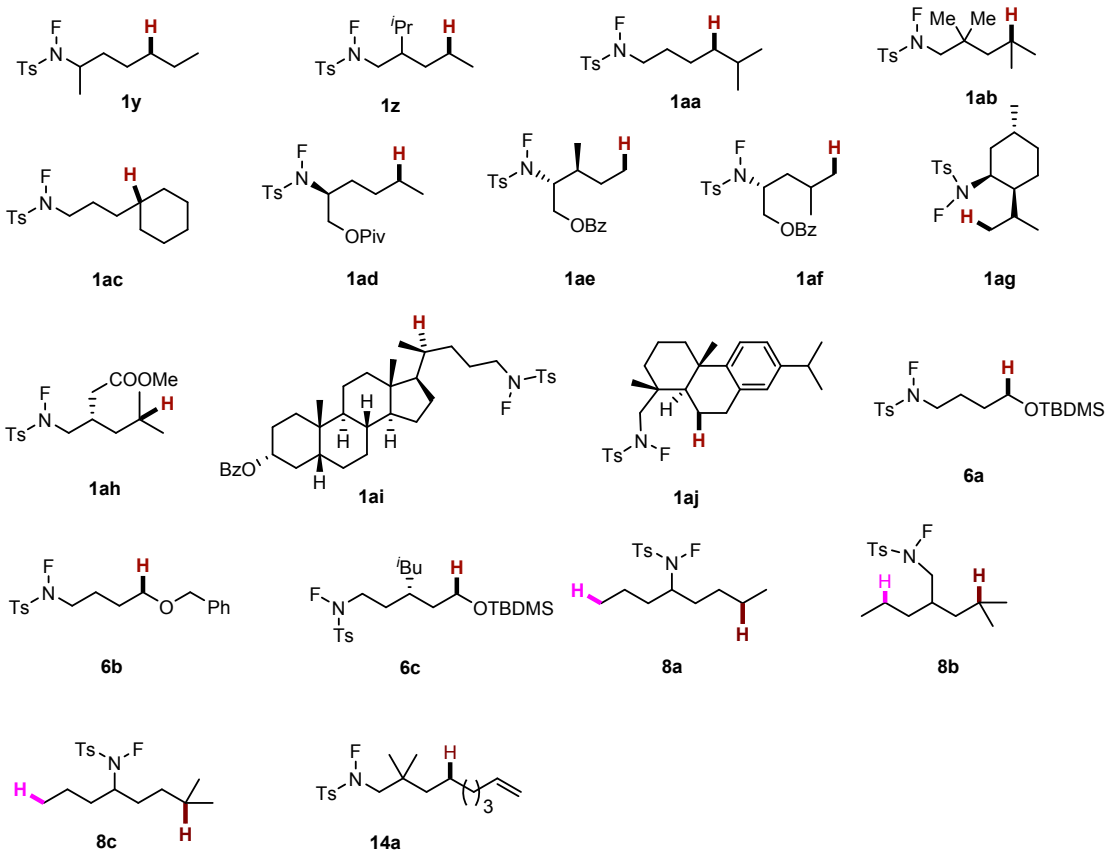
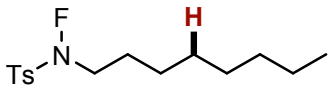


1x



Characterization Data for *N*-fluorotosylamides and disulfides

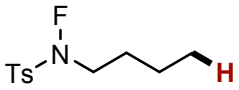
N-fluoro-4-methyl-*N*-octylbenzenesulfonamide (1a)



1a

Yellow solid. mp: 32.3–33.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.20 (dt, J = 40.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.70 (quint, J = 7.2 Hz, 2H), 1.35–1.40 (m, 2H), 1.26 (s, 8H), 0.87 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.12, 129.95, 129.89, 129.04, 53.70 (d, J = 12.0 Hz), 31.69, 29.05, 26.57, 26.29, 22.59, 21.75, 14.04.

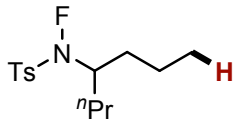
N-butyl-*N*-fluoro-4-methylbenzenesulfonamide (1b)



1b

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.21 (dt, J = 40.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.69 (quint, J = 7.0 Hz, 2H), 1.38–1.47 (m,2H), 0.92 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.14, 129.92, 129.88, 128.96, 53.38 (d, J = 13.0 Hz), 28.25, 21.72, 19.75, 13.52.

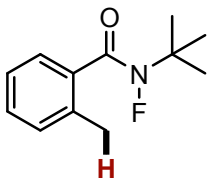
***N*-fluoro-*N*-(heptan-4-yl)-4-methylbenzenesulfonamide (1c)**



1c

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.90 (dp, J = 38.8, 6.5 Hz, 1H), 2.46 (s, 3H), 1.51–1.70 (m, 4H), 1.35–1.46 (m, 4H), 0.89 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.53, 133.12, 129.77, 129.11, 62.95 (d, J = 13.0 Hz), 32.89 (d, J = 6.0 Hz), 21.70, 19.50, 13.81. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{22}FNNaO_2S$, 310.1247; found, 310.1253. **IR** (KBr, cm^{-1}): ν 3517, 3450, 2962, 2873, 1632, 1171.

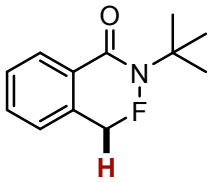
***N*-(*tert*-butyl)-*N*-fluoro-2-methylbenzamide (1d)**



1d

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.33 (m, 2H), 7.18–7.23 (m, 2H), 2.40 (s, 3H), 1.55 (d, J = 1.9 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.99 (d, J = 10.8 Hz), 135.34 (d, J = 2.4 Hz), 135.08, 130.42, 129.90 (d, J = 1.2 Hz), 127.14 (d, J = 4.4 Hz), 125.31, 64.37 (d, J = 11.0 Hz), 27.18 (d, J = 5.0 Hz), 19.31.

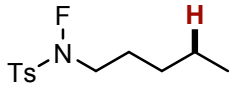
***N*-(*tert*-butyl)-2-ethyl-*N*-fluorobenzamide (1e)**



1e

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 6.9 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 2.74 (q, J = 7.5 Hz, 2H), 1.56 (d, J = 1.8 Hz, 9H), 1.24 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.98 (d, J = 11.0 Hz), 141.59, 134.65, 129.99, 128.89, 127.10 (d, J = 4.3 Hz), 125.33, 64.30 (d, J = 10.3 Hz), 27.16 (d, J = 5.6 Hz), 26.08, 15.61.

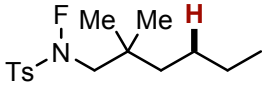
***N*-fluoro-4-methyl-*N*-pentylbenzenesulfonamide (1f)**



1f

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 3.10 (dt, J = 40.8, 7.0 Hz, 2H), 2.39 (s, 3H), 1.62 (quint, J = 7.1 Hz, 2H), 1.20–1.30 (m, 4H), 0.80 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.14, 129.84, 129.82, 128.76, 53.72 (d, J = 12.0 Hz), 28.58, 25.87, 22.06, 21.61, 13.73.

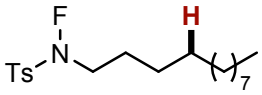
***N*-(2,2-dimethylhexyl)-*N*-fluoro-4-methylbenzenesulfonamide (1g)**



1g

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.01 (d, J = 44.6 Hz, 2H), 2.48 (s, 3H), 1.24–1.32 (m, 4H), 1.17–1.23 (m, 2H), 0.95 (s, 6H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.00, 129.89, 129.79, 129.65, 63.07 (d, J = 10.5 Hz), 39.93, 34.25, 25.82, 25.54, 23.37, 21.72, 14.00.

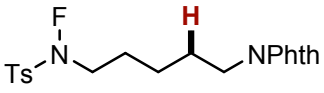
***N*-fluoro-*N*-hexyl-4-methylbenzenesulfonamide (1h)**



1h

Yellow solid. mp: 46.3–47.1 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 3.20 (dt, J = 40.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.70 (quint, J = 4.8 Hz, 2H), 1.38 (quint, J = 4.8 Hz, 2H), 1.24–1.31 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.12, 129.95, 129.89, 129.06, 53.70 (d, J = 12.4 Hz), 31.89, 29.59, 29.49, 29.40, 29.32, 29.10, 26.58, 26.30, 22.67, 21.75, 14.09.

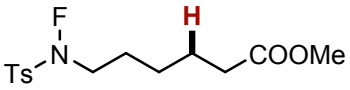
***N*-(5-(1,3-dioxoisoindolin-2-yl)pentyl)-*N*-fluoro-4-methylbenzenesulfonamide (1i)**



1i

Yellow solid. mp: 93.3–94.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.5, 3.0 Hz 2H), 7.81 (d, J = 8.2 Hz 2H), 7.71 (dd, J = 5.5, 3.0 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.68 (t, J = 7.2 Hz, 2H), 3.20 (dt, J = 40.5, 6.9 Hz, 2H), 2.48 (s, 3H), 1.68–1.79 (m, 4H), 1.43–1.49 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.38, 146.18, 133.90, 132.09, 129.95, 129.92, 128.89, 123.20, 53.43 (d, J = 12.5 Hz), 37.62, 28.11, 25.90, 23.86, 21.75.

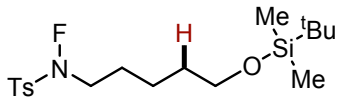
Methyl 6-((*N*-fluoro-4-methylphenyl)sulfonamido)hexanoate (1j)



1j

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 3.66 (s, 3H), 3.21 (dt, J = 40.6, 6.9 Hz, 2H), 2.48 (s, 3H), 2.31 (t, J = 7.4 Hz, 2H), 1.69–1.76 (m, 2H), 1.60–1.67 (m, 2H), 1.40–1.47 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.78, 146.20, 129.89 (C×2), 128.82, 53.44 (d, J = 12.4 Hz), 51.44, 33.71, 26.04, 25.96, 24.33, 21.69.

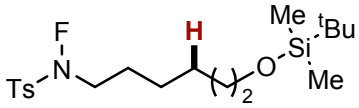
***N*-(5-((tert-butyldimethylsilyl)oxy)pentyl)-*N*-fluoro-4-methylbenzenesulfonamide(1k)**



1K

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.60 (t, J = 6.0 Hz, 2H), 3.21 (dt, J = 40.7, 6.9 Hz, 2H), 2.48 (s,3H) 1.73 (quint, J = 7.2 Hz, 2H), 1.42–1.54 (m, 4H), 0.88 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.14, 129.95, 129.90, 129.03, 62.81, 53.61 (d, J = 12.4 Hz), 32.21, 26.11, 25.94, 22.98, 21.75, 18.32, -5.33. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{32}FNNaO_3SSi$, 412,1748; found, 412,1750. **IR** (KBr, cm^{-1}): ν 3573, 3520, 3455, 3391, 2932, 1636.

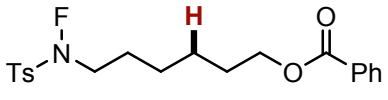
_N_-(5-((tert-butyldimethylsilyl)oxy)pentyl)-_N_-fluoro-4-methylbenzenesulfonamide(1l)



1l

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.58 (t, J = 6.6 Hz, 2H), 3.20 (dt, J = 40.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.68–1.74 (m, 2H), 1.47–1.53 (m, 2H), 1.38–1.43 (m, 2H), 1.32–1.36 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.13, 129.95, 129.90, 129.02, 62.99, 53.64 (d, J = 12.5 Hz), 32.59, 26.41, 26.30, 25.95, 25.37, 21.76, 18.34, -5.30. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{34}FNNaO_3SSi$, 426.1905; found, 426.1915. **IR** (KBr, cm^{-1}): ν 3684, 3556, 3474, 3411, 1728.

6-((_N_-fluoro-4-methylphenyl)sulfonamido)hexyl benzoate (1m)

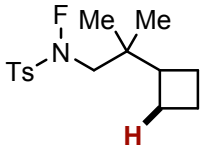


1m

White solid. mp: 44.6–45.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.55 (t, J = 6.8 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 4.31 (t, J = 6.6 Hz, 2H), 3.22 (dt, J = 40.6, 6.9 Hz, 2H), 2.48 (s,

3H), 1.63–1.83 (m, 4H), 1.43–1.58 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.62, 146.18, 132.83, 130.40, 129.93, 129.91, 129.52, 128.94, 128.33, 64.76, 53.52 (d, J = 12.5 Hz), 28.53, 26.26, 26.19, 25.61, 21.75. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{24}FNNaO_4S$, 416.1302; found, 416.1299. **IR** (KBr, cm^{-1}): ν 3714, 3471, 1716, 1280.

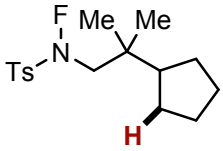
***N*-(2-cyclobutyl-2-methylpropyl)-*N*-fluoro-4-methylbenzenesulfonamide (1n)**



1n

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 2.94 (d, J = 44.8 Hz, 2H), 2.48 (s, 3H), 2.32–2.41 (m, 1H), 1.75–1.81 (m, 5H), 1.61–1.68 (m, 1H), 0.89 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.99, 129.89, 129.78, 129.62,61.82 (d, J = 10.8 Hz), 43.67, 35.47, 22.83, 22.00, 21.75, 17.12. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}FNNaO_2S$, 322.1247; found, 322.1245. **IR** (KBr, cm^{-1}): ν 3553, 3411, 2967, 1373.

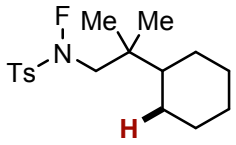
***N*-(2-cyclopentyl-2-methylpropyl)-4-methylbenzenesulfonamide (1o)**



1o

Yellow solid. mp: 53.3–54.7 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 3.05 (d, J = 44.8 Hz, 2H), 2.48 (s, 3H), 1.84–1.91 (m, 1H), 1.58–1.65 (m, 2H), 1.52–1.58 (m, 2H), 1.45–1.52 (m, 2H), 1.17–1.25 (m, 2H), 0.93 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.99, 129.89, 129.78, 129.63, 63.12 (d, J = 10.5 Hz), 47.52, 36.26, 26.73, 25.59, 23.07, 21.75. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{24}FNNaO_2S$, 336.1404; found, 336.1400. **IR** (KBr, cm^{-1}): ν 3713, 3558, 3474, 3408, 1742.

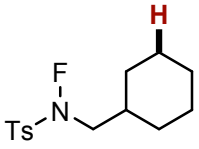
***N*-(2-cyclohexyl-2-methylpropyl)-4-methylbenzenesulfonamide (1p)**



1p

White solid. mp: 82.1–83.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.08 (d, J = 44.8 Hz, 2H), 2.49 (s, 3H), 1.26–1.36 (m, 5H), 1.15–1.24 (m, 2H), 1.6–1.15 (m, 2H), 0.87–1.00 (m, 2H), 0.91 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.99, 129.91, 129.79, 129.70, 61.80 (d, J = 10.5 Hz), 44.74, 36.66, 27.06, 26.94, 26.58, 23.35, 21.77. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{26}FNNaO_2S$, 350.1560; found, 350.1558. **IR** (KBr, cm^{-1}): ν 3687, 3060, 1727, 1560.

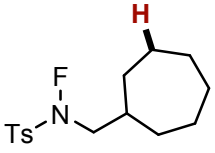
***N*-(cyclohexylmethyl)-4-methylbenzenesulfonamide (1q)**



1q

Yellow solid. mp: 71.5–72.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.02 (dd, J = 42.4, 6.8 Hz, 2H), 2.48 (s, 3H), 1.79–1.83 (m, 2H), 1.63–1.77 (m, 4H), 1.18–1.31 (m, 3H), 0.92–1.03 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.07, 129.89, 129.88, 129.09, 59.54 (d, J = 12.0 Hz), 35.23, 30.80, 26.22, 25.61, 21.73. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{20}FNNaO_2S$, 308.1091; found, 308.1087. **IR** (KBr, cm^{-1}): ν 3711, 3058, 1732, 1371.

***N*-(cycloheptylmethyl)-4-methylbenzenesulfonamide (1r)**

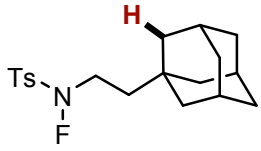


1r

Yellow solid. mp: 57.3–58.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz,

2H), 7.40 (d, J = 8.2 Hz, 2H), 3.01 (dd, J = 41.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.86–1.94 (m,1H), 1.78–1.84 (m, 2H), 1.62–1.69 (m, 2H), 1.55–1.61 (m, 2H), 1.36–1.53 (m, 4H), 1.18–1.29 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.07, 129.90, 129.88, 129.14, 59.73 (d, J = 12.2 Hz), 36.52, 31.96, 28.28, 26.08, 21.75. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}FNNaO_2S$, 322.1247; found, 322.1244. **IR** (KBr, cm^{-1}): ν 3713, 3551, 3479, 3409, 1737, 1170.

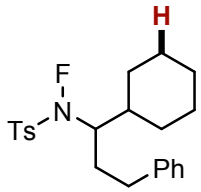
***N*-(2-((3r,5r,7r)-adamantan-1-yl)ethyl)-4-methylbenzenesulfonamide (1s)**



1s

White solid. mp:103.3–104.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.27 (ddd, J = 40.2, 9.2, 6.4 Hz,2H), 2.49 (s, 3H), 1.95 (brs, 3H), 1.70 (d, J = 12.0 Hz, 3H), 1.61 (d, J = 12.0 Hz, 3H), 1.54 (m, 1H), 1.52 (t, J = 2.6, 1H), 1.48 (d, J = 2.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.12, 129.92, 129.91, 129.26, 48.91 (d, J = 12.7 Hz), 42.24, 39.90, 36.92, 31.74, 28.49, 21.78.

***N*-(1-cyclohexyl-3-phenylpropyl)-4-methylbenzenesulfonamide (1t)**

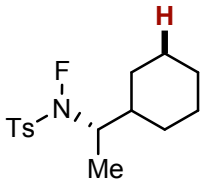


1t

Yellow solid. mp: 83.3–84.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.26 (dd, J = 7.8, 6.8 Hz, 2H), 7.18 (t, J = 6.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 3.79 (ddd, J = 39.2, 9.6, 5.1 Hz, 1H), 2.63 (t, J = 8.2 Hz, 2H), 2.46 (s, 3H), 1.82–1.91 (m, 1H), 1.60–1.80 (m, 7H), 1.21–1.30 (m, 2H), 1.05–1.19 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.61, 141.33, 132.91, 129.89, 129.17, 128.38, 128.36, 126.03, 67.10 (d, J = 12.0 Hz), 40.12, 33.28, 30.30, 28.68 (d, J = 11.5 Hz), 28.57, 26.35 (d, J = 4.5 Hz), 26.25, 21.71. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for

$C_{22}H_{28}FNNaO_2S$, 412,1717; found, 412,1716. **IR** (KBr, cm^{-1}): ν 3687, 3472, 3059, 1727, 1560.

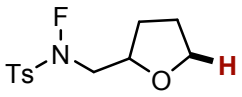
(*S*)-*N*-(1-cyclohexylethyl)-*N*-fluoro-4-methylbenzenesulfonamide (1u)



1u

Yellow solid. mp: 68.1–69.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.84 (dp, J = 37.1, 6.7 Hz, 1H), 2.46 (s, 3H), 1.89 (d, J = 12.8 Hz, 1H), 1.71–1.80 (m, 3H), 1.65 (d, J = 10.3 Hz, 1H), 1.51–1.61 (m, 1H), 1.14–1.25 (m, 3H), 1.12 (dd, J = 6.7, 2.3 Hz, 3H), 0.98–1.10 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.58, 132.77, 129.82, 129.20, 63.03 (d, J = 12.7 Hz), 42.17, 29.45 (d, J = 12.0 Hz), 26.25, 26.06 (d, J = 6.1 Hz), 21.72, 12.18 (d, J = 15.7 Hz). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}FNNaO_2S$, 322.1247; found, 322.1246. **IR** (KBr, cm^{-1}): ν 3713, 3556, 3474, 3410, 1740.

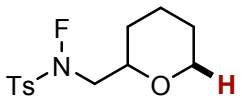
***N*-fluoro-4-methyl-*N*-((tetrahydrofuran-2-yl)methyl)benzenesulfonamide (1v)**



1v

Yellow solid. mp: 83.3–84.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 4.19 (quint, J = 6.4 Hz, 1H), 3.87 (ddd, J = 14.8, 7.8, 7.0 Hz, 1H), 3.77 (ddd, J = 14.8, 7.8, 7.0 Hz, 1H), 3.34 (ddd, J = 21.1, 14.1, 5.6 Hz, 1H), 3.22 (ddd, J = 21.1, 14.1, 5.6 Hz, 1H), 2.48 (s, 3H), 2.05–2.13 (m, 1H), 1.88–1.96 (m, 2H), 1.68–1.77 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.35, 130.00, 129.96, 128.78,75.26, 68.38, 57.39 (d, J = 11.1 Hz), 29.76, 25.41, 21.76. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{12}H_{16}FNNaO_3S$, 296.0727; found, 296.0726. **IR** (KBr, cm^{-1}): ν 3713, 3409, 1732, 1173.

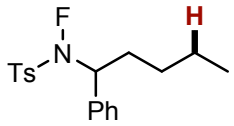
***N*-fluoro-4-methyl-*N*-((tetrahydro-2H-pyran-2-yl)methyl)benzenesulfonamide (1w)**



1w

Yellow solid. mp: 79.9–80.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.96–3.99 (m, 1H), 3.63 (ddd, J = 15.6, 10.2, 5.6 Hz, 1H), 3.43 (ddd, J = 15.6, 10.2, 5.6 Hz, 1H), 3.29 (ddd, J = 21.2, 14.2, 6.2 Hz, 1H), 3.16 (ddd, J = 21.2, 14.2, 6.2 Hz, 1H), 2.47 (s, 3H), 1.85–1.88 (m, 1H), 1.72–1.75 (m, 1H), 1.44–1.62 (m, 3H), 1.24–1.37 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.30, 130.00, 129.93, 128.73, 77.32, 68.58, 58.45 (d, J = 11.6 Hz),29.73, 25.67, 22.88, 21.73. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{13}H_{18}FNNaO_3S$, 310.0884; found, 310.0883. **IR** (KBr, cm^{-1}): ν 3711, 3410, 1735, 1172.

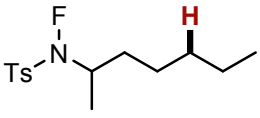
***N*-fluoro-4-methyl-*N*-(1-phenylpentyl)benzenesulfonamide (1x)**



1x

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, J = 8.1 Hz, 2H), 7.22–7.26 (m, 5H), 7.21 (d, J = 8.1 Hz, 2H), 4.75 (ddd, J = 37.8, 8.7, 6.3 Hz, 1H), 2.40 (s, 3H), 2.12–2.18 (m, 1H), 1.92–1.98 (m, 1H), 1.24–1.33 (m, 3H), 1.11–1.19 (m, 1H), 0.84 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.35, 136.64 (d, J = 3.7 Hz), 131.86, 129.46, 129.31, 128.66, 128.26, 128.19, 67.76 (d, J = 12.4 Hz), 32.65 (d, J = 4.6 Hz), 28.11, 22.22, 21.63, 13.80.

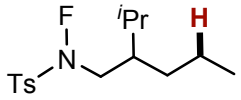
***N*-fluoro-*N*-(heptan-2-yl)-4-methylbenzenesulfonamide (1y)**



1y

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 4.01 (dtq, J = 37.3, 16.6, 6.6 Hz, 1H), 2.46 (s, 3H), 1.71–1.77 (m, 1H), 1.50–1.56 (m, 1H), 1.36–1.43 (m, 2H), 1.25–1.33 (m, 4H), 1.23 (d, J = 6.5 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.61, 132.78, 129.78, 129.18, 59.10 (d, J = 13.1 Hz), 34.17 (d, J = 1.9 Hz), 31.39, 25.61, 22.45, 21.67, 15.78 (d,J = 11.3 Hz), 13.95. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{22}FNNaO_2S$, 310.1247; found, 310.1249. **IR** (KBr, cm^{-1}): ν 3684, 3555, 3410, 1736, 1170.

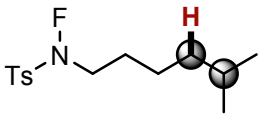
***N*-fluoro-*N*-(2-isopropylpentyl)-4-methylbenzenesulfonamide (1z)**



1z

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.13 (dddd, J = 42.8, 32.8, 14.2, 6.8 Hz, 2H), 2.49 (s, 3H), 1.85–1.93 (m, 1H), 1.62–1.70 (m, 1H), 1.33–1.41 (m, 1H), 1.22–1.33 (m, 3H), 0.88 (t, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.07, 129.89, 129.87, 129.30, 55.09 (d, J = 12.4 Hz), 40.75, 30.92, 28.21, 21.77, 20.48, 19.01, 18.63, 14.26. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{24}FNNaO_2S$, 324.1404; found, 324.1408. **IR** (KBr, cm^{-1}): ν 3688, 3412, 1739, 1375, 1176.

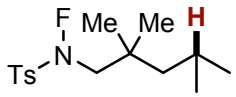
***N*-fluoro-4-methyl-*N*-(5-methylhexyl)benzenesulfonamide (1aa)**



1aa

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.20 (dt, J = 40.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.65–1.72 (m, 2H), 1.47–1.57 (m, 1H), 1.34–1.43 (m, 2H), 1.15–1.20 (m, 2H), 0.87 (s, 3H), 0.85 (s, 3H). **^{13}CNMR** (100 MHz, $CDCl_3$) δ 146.14, 129.91, 129.88, 128.95, 53.73 (d, J = 12.4 Hz), 38.36, 27.78, 26.53, 24.36, 22.46, 21.72.

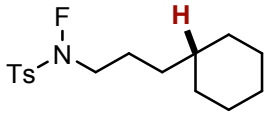
***N*-fluoro-4-methyl-*N*-(2,2,4-trimethylpentyl)benzenesulfonamide (1ab)**



1ab

White solid. mp: 67.4–68.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.01 (d, J = 44.6 Hz, 2H), 2.49 (s, 3H), 1.66 (sept, J = 6.4 Hz,1H), 1.25 (d, J = 5.4 Hz, 2H), 0.98 (s, 6H), 0.91 (s,3H), 0.90 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.02, 129.90, 129.81, 129.61, 63.84 (d, J = 10.5 Hz), 49.03, 35.06, 25.92, 25.91, 25.34, 23.94, 21.76.

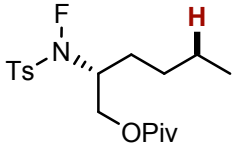
***N*-(3-cyclohexylpropyl)-*N*-fluoro-4-methylbenzenesulfonamide (1ac)**



1ac

White solid. mp: 73.1–74.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.18 (dt, J = 40.7, 7.2 Hz, 2H), 2.48 (s, 3H), 1.62–1.76 (m, 7H), 1.20–1.30 (m, 4H), 1.15–1.21 (m, 2H), 0.82–0.90 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.12, 129.96, 129.89, 129.05, 54.07 (d, J = 12.4 Hz), 37.25, 34.24, 33.18, 26.57, 26.25, 23.74, 21.76.

(*S*)-2-((*N*-fluoro-4-methylphenyl)sulfonamido)hexyl pivalate (1ad)

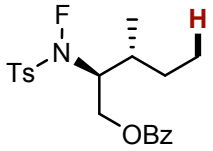


1ad

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.37 (d, J= 8.2 Hz, 2H), 4.10–4.31 (m, 3H), 2.47 (s, 3H), 1.69–1.78 (m, 1H), 1.60–1.69 (m, 1H), 1.35–1.43 (m, 2H), 1.25–1.34 (m, 2H), 1.21 (s, 9H), 0.88 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.13, 145.91, 132.55, 129.86, 129.22, 62.42 (d, J = 6.5 Hz), 61.77 (d, J = 12.2 Hz), 38.76, 28.18, 27.70 (d, J = 7.0 Hz), 27.09, 22.35, 21.72,

13.75. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{28}FNNaO_4S$, 396.1615; found, 396.1619. **IR** (KBr, cm^{-1}): ν 3555, 3416, 3235, 1732, 1169.

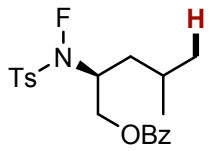
(2*R*,3*S*)-2-((*N*-fluoro-4-methylphenyl)sulfonamido)-3-methylpentylbenzoate (1ae)



1ae

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.49–4.59 (m, 2H), 4.27 (dtd, J = 36.4, 6.0, 4.0 Hz, 1H), 2.43 (s, 3H), 1.96–2.06 (m, 1H), 1.60–1.68 (m, 1H), 1.29–1.39 (m, 1H), 1.08 (d, J = 6.8 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.17, 145.84, 133.08, 132.53, 129.85, 129.83, 129.78, 129.22, 128.36, 65.11 (d, J = 10.9 Hz), 60.72 (d, J = 13.4 Hz), 36.06, 25.88, 21.73, 15.85, 11.27. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{24}FNNaO_4S$, 416.1302; found, 416.1304. **IR** (KBr, cm^{-1}): ν 3554, 3408, 3233, 1723, 1171.

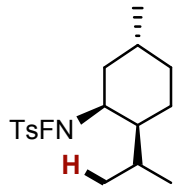
(*R*)-2-((*N*-fluoro-4-methylphenyl)sulfonamido)-4-methylpentyl benzoate (1af)



1af

White solid. mp: 69.3–70.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 4.42–4.59 (m, 3H), 2.45 (s, 3H), 1.74–1.85 (m 2H), 1.52–1.61 (m, 1H), 0.98 (s, 3H), 0.96 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.20, 145.86, 133.11, 132.74, 129.85, 129.81, 129.77, 129.21, 128.38, 63.05 (d, J = 7.7 Hz), 59.98 (d, J = 12.3 Hz), 37.07 (d, J = 5.1 Hz), 24.94, 22.34 (d, J = 7.1 Hz), 21.72. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{24}FNNaO_4S$, 416.1302; found, 416.1307. **IR** (KBr, cm^{-1}): ν 3711, 3473, 3063, 1719, 1172.

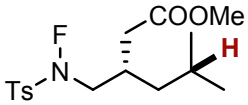
***N*-((1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-4-methylbenzenesulfonamide (1ag)**



1ag

White solid. mp: 78.9–79.7 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 4.43 (d, J = 50.4 Hz, 1H), 2.47 (s, 3H), 2.22 (d, J = 13.8 Hz, 1H), 1.65–1.82 (m, 4H), 1.25–1.34 (m, 1H), 1.13–1.18 (m, 1H), 1.06–1.12(m, 1H), 0.97 (d, J = 6.6 Hz, 3H), 0.92 (d, J= 6.6 Hz, 3H), 0.87 (dd, J = 21.0, 8.7 Hz, 1H), 0.79 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.48, 133.11, 129.77, 129.13, 58.57 (d, J = 10.9 Hz), 48.10, 37.69 (d, J = 6.9 Hz), 34.76, 29.18, 28.67 (d, J = 6.4 Hz), 25.94 (d, J = 3.3 Hz), 22.95, 21.71, 20.97, 20.89. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{26}FNNaO_2S$, 350.1560; found, 350.1556. **IR** (KBr, cm^{-1}): ν 3555, 3468, 3234, 1764, 1616, 1167.

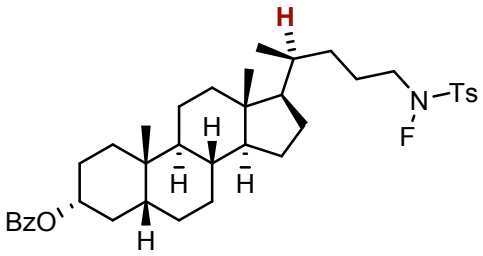
Methyl(*S*)-3-(((*N*-fluoro-4-methylphenyl)sulfonamido)methyl)-5-methylhexanoate (1ah)



1ah

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 3.64 (s, 3H), 3.28 (ddd, J = 44.4, 14.4, 7.5 Hz,1H), 3.18 (ddd, J = 44.4, 14.4, 7.5 Hz,1H), 2.48 (s, 3H), 2.46–2.50 (m, 1H), 2.30–2.41 (m, 2H), 1.53–1.64 (m, 1H), 1.26–1.32 (m, 1H), 1.20–1.26 (m, 1H), 0.88 (d, J = 7.8 Hz,3H), 0.86 (d, J = 7.8 Hz,3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.63, 146.23, 129.92, 129.84, 129.06, 56.65 (d, J = 11.7 Hz), 51.45, 41.25, 36.57, 30.97, 24.99, 22.49, 22.44, 21.71.

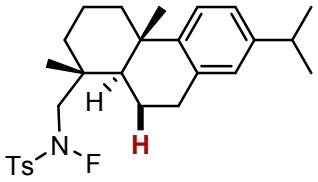
(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*S*)-5-((*N*-fluoro-4-methylphenyl)sulfonamido)pentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (1ai)



1ai

White solid. mp: 83.3–84.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 4.95–4.99 (m, 1H), 3.18 (dt, J = 40.6, 7.0 Hz, 2H), 2.49 (s, 3H), 1.97 (q, J = 12.5 Hz, 2H), 1.84–1.90 (m, 2H), 1.75–1.84 (m, 3H), 1.66–1.68 (m, 1H), 1.56–1.62 (m, 3H), 1.37–1.49 (m, 6H), 1.23–1.30 (m, 3H), 1.15–1.21(m, 2H), 1.04–1.14 (m, 5H), 0.96 (s, 3H), 0.91 (d, J = 6.6 Hz, 3H), 0.82–0.86 (m, 1H), 0.65 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.05, 146.07, 132.59, 130.94, 129.90, 129.85, 129.47, 129.06, 128.18, 74.94, 56.46, 56.04, 54.15 (d, J = 12.3 Hz), 42.70, 41.95, 40.48, 40.12, 35.79, 35.34, 35.07, 34.61, 32.76, 32.35, 28.20, 27.03, 26.74, 26.32, 24.13, 23.32, 23.00, 21.70, 20.84, 18.52, 12.00. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{38}H_{52}FNNaO_4S$, 660.3493; found, 660.3501. **IR** (KBr, cm^{-1}): ν 3552, 3410, 3234, 1714, 1174.

_N_-fluoro-_N_-(((1_R_,4a_S_,10a_R_)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-methylbenzenesulfonamide (1aj)

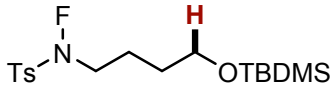


1aj

White solid. mp: 139.3–140.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.2 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.86 (s, 1H), 3.13 (ddd, J = 70.2, 44.0, 15.6 Hz, 2H), 2.77–2.87 (m, 3H), 2.47 (s, 3H), 2.27 (d, J = 12.8 Hz, 1H), 1.63–1.80 (m, 5H), 1.65–1.62 (m, 1H), 1.41–1.45 (m, 2H), 1.21 (s, 3H), 1.20 (d, J = 6.5 Hz, 6H), 0.97 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.02,

146.03, 145.58, 134.69, 129.93, 129.90, 129.73, 126.81, 124.14, 123.77, 63.17 (d, J = 9.9 Hz), 44.62, 38.15, 37.60, 37.52, 36.43, 33.42, 29.94, 25.38, 23.97, 23.94, 21.74, 18.98, 18.92, 18.58.

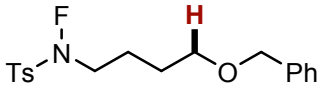
_N_-(4-((_tert_-butyldimethylsilyl)oxy)butyl)-_N_-fluoro-4-methylbenzenesulfonamide (6a)



6a

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 3.62 (t, J = 6.0 Hz, 2H), 3.24 (dt, J = 40.8, 6.8 Hz, 2H), 2.47 (s, 3H), 1.75–1.82 (m 2H), 1.58–1.65 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.13, 129.94, 129.89, 128.96, 62.35, 53.61 (d, J = 12.4 Hz), 29.60, 25.89, 23.09, 21.74, 18.25, -5.40. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{30}FNNaO_3SSi$, 398.1592; found, 398.1594. **IR** (KBr, cm^{-1}): ν 3683, 3560, 3473, 3411, 1597, 1177.

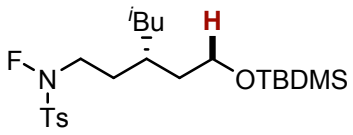
_N_-(4-(benzyloxy)butyl)-_N_-fluoro-4-methylbenzenesulfonamide (6b)



6b

Yellow solid. mp: 30.4–31.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.36–7.26 (m, 5H), 4.48 (s, 2H), 3.49 (t, J = 6.0 Hz, 2H), 3.24 (dt, J = 40.8, 6.8 Hz, 2H), 2.47 (s, 3H), 1.79–1.87 (m, 2H), 1.69–1.76 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.15, 138.41, 129.94, 129.89, 128.91, 128.36, 127.58, 127.54, 72.89, 69.48, 53.52 (d, J = 12.4 Hz), 26.69, 23.36, 21.75. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{22}FNNaO_3S$, 374.1197; found, 374.1199. **IR** (KBr, cm^{-1}): ν 3712, 3457, 3474, 3509, 1736, 1171.

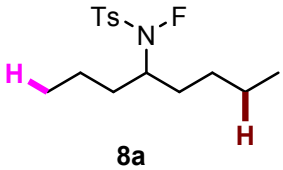
(_R_)-_N_-(3-(2-((_tert_-butyldimethylsilyl)oxy)ethyl)-5-methylhexyl)-_N_-fluoro-4-methylbenzenesulfonamide (6c)



6c

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.60 (t, J = 6.6 Hz, 2H), 3.25 (dt, J = 40.4, 6.8 Hz, 2H), 2.48 (s, 3H), 1.66–1.70 (m, 3H), 1.58–1.65 (m, 1H), 1.46–1.52 (m, 1H), 1.39–1.45 (m, 1H), 1.09–1.13 (m, 1H), 0.99–1.08 (m, 1H), 0.87 (s, 9H), 0.85 (d, J = 6.6Hz, 6H), 0.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.11, 129.93, 129.89, 129.15, 60.74, 51.61 (d, J = 12.4 Hz), 43.58, 36.64, 30.45, 29.84, 25.92, 25.20, 22.78, 22.73,21.76, 18.23, -5.38, -5.39. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{40}FNNaO_3SSi$, 468.2374; found, 468.2370. **IR** (KBr, cm^{-1}): ν 3683, 3556, 3473, 3411, 1725, 1597, 1176.

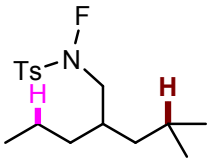
***N*-fluoro-4-methyl-*N*-(octan-4-yl)benzenesulfonamide (8a)**



8a

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.87 (dp,J = 38.8, 6.4 Hz, 1H), 2.46 (s, 3H), 1.51–1.70 (m, 4H), 1.24–1.46 (m, 6H), 0.89 (t, J = 5.6 Hz, 3H), 0.87 (t, J = 5.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.54, 133.12, 129.78, 129.12, 63.25 (d, J = 12.9 Hz), 32.94 (d, J = 5.8 Hz), 30.49 (d, J = 6.2 Hz), 28.44, 22.45, 21.70, 19.51, 13.88, 13.82. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{24}FNNaO_2S$, 324.1404; found, 324.1407. **IR** (KBr, cm^{-1}): ν 3711, 3554, 3477, 3409, 1730, 1596, 1171.

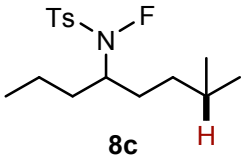
***N*-fluoro-4-methyl-*N*-(4-methyl-2-propylpentyl)benzenesulfonamide (8b)**



8b

White solid. mp: 45.3–46.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.09 (ddd, J = 24.4, 14.2, 6.6 Hz, 1H), 3.03 (ddd, J = 24.4, 14.2, 6.6 Hz, 1H)，2.48 (s, 3H), 1.78–1.88 (m, 1H), 1.61 (quint, J = 6.6 Hz, 1H), 1.35–1.44 (m, 1H), 1.24–1.34 (m, 3H), 1.14–1.24 (m, 2H), 0.87 (t, J = 7.0 Hz,3H), 0.86 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ146.06, 129.85, 129.78, 129.08, 57.53 (d, J = 11.9 Hz), 41.52, 34.30, 33.07, 25.05, 22.74, 22.54, 21.66, 19.16, 14.21. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{26}FNNaO_2S$, 338.1560; found, 338.1565. **IR** (KBr, cm^{-1}): ν 3750, 3558, 3481, 3408, 3234, 1740, 1616, 1172.

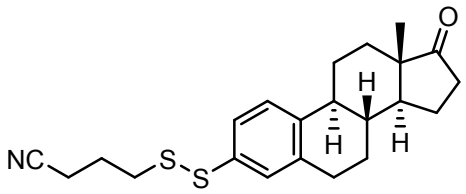
***N*-(7-methyloctan-4-yl)-4-methylbenzenesulfonamide (8c)**



8c

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 3.83 (dp, J = 38.4, 6.3 Hz, 1H), 2.46 (s, 3H), 1.61–1.67 (m, 2H), 1.56 (dd, J = 14.2, 7.8 Hz, 2H), 1.45–1.51 (m, 1H), 1.38–1.43 (m, 2H), 1.24 (dt, J = 12.0, 5.7 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, CDCl3) δ 145.55, 133.12, 129.80, 129.12, 63.58 (d, J = 12.8 Hz), 35.40, 33.00 (d, J = 5.5 Hz), 28.64 (d, J = 6.4 Hz), 27.90, 22.47, 22.38, 21.68, 19.51, 13.81. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{26}FNNaO_2S$, 338.1560; found, 338.1567. **IR** (KBr, cm^{-1}): ν 3540, 3474, 3405, 3235, 1728, 1616, 1171.

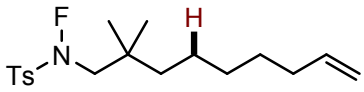
4-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)disulfaneyl)butanenitrile (10c)



10c

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.3, 1.9 Hz, 1H), 7.25 (dd, J = 9.6, 4.6 Hz, 2H), 2.92 (dd, J = 8.6, 4.0 Hz, 2H), 2.82 (t, J = 6.8 Hz, 2H), 2.49–2.57 (m, 1H), 2.46 (t, J = 7.1 Hz, 2H), 2.37–2.45 (m, 1H), 2.29 (td, J = 10.6, 4.3 Hz, 1H), 2.12 (dd, J = 12.8, 5.5 Hz, 1H), 2.04–2.10 (m, 3H), 2.00–2.05 (m, 1H), 1.94–1.99 (m, 1H), 1.58–1.64 (m, 2H), 1.50–1.57 (m, 3H), 1.44–1.49 (m, 1H), 0.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.54, 139.56, 137.73, 133.52, 129.07, 126.27, 126.10, 118.88, 50.43, 47.88, 44.22, 37.95, 36.53, 35.77, 31.51, 29.28, 26.28, 25.63, 24.21, 21.53, 15.66, 13.79. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{27}NNaOS_2$, 408.1426; found, 408.1434. **IR** (KBr, cm^{-1}): ν 3440, 2931, 1648, 1630, 552.

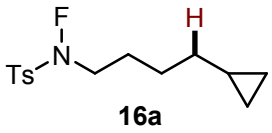
_N_-(2,2-dimethylnon-8-en-1-yl)-_N_-fluoro-4-methylbenzenesulfonamide (14a)



14a

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.98 (dd, J = 16.9, 1.6 Hz, 1H), 4.93 (dd, J = 10.2, 1.6 Hz, 1H), 3.01 (d, J = 44.6 Hz, 2H), 2.49 (s, 3H), 2.03 (q, J = 7.5 Hz, 2H), 1.34–1.42 (m, 2H), 1.18–1.33 (m, 6H), 0.94 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.02, 139.07, 129.90, 129.81, 129.62, 114.20, 63.01 (d, J = 10.5 Hz), 40.13, 34.29, 33.73, 29.80, 28.80, 25.56, 23.45, 21.76. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{28}FNNaO_2S$, 364.1717; found, 364.1723. **IR** (KBr, cm^{-1}): ν 3711, 3473, 3407, 1731, 1560, 1175.

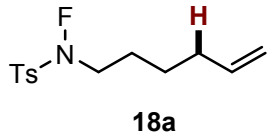
_N_-(4-cyclopropylbutyl)-_N_-fluoro-4-methylbenzenesulfonamide (16a)



16a

White solid. mp: 31.3–32.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 3.14 (dt, J = 40.8, 7.0 Hz, 2H), 2.41 (s, 3H), 1.64–1.69 (m, 2H), 1.40–1.45 (m, 2H), 1.12–1.15 (m, 2H), 0.53–0.60 (m, 1H), 0.28–0.37 (m, 2H),(-0.09)–(-0.07) (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.14, 129.94, 129.89, 128.98, 53.74 (d, J = 12.4 Hz), 34.12, 26.64, 26.11, 21.75, 10.60, 4.37, 1.00. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{20}FNNaO_2S$, 308.1091; found, 308.1089. **IR** (KBr, cm^{-1}): ν 3576, 3516, 3352, 1636, 1117, 548.

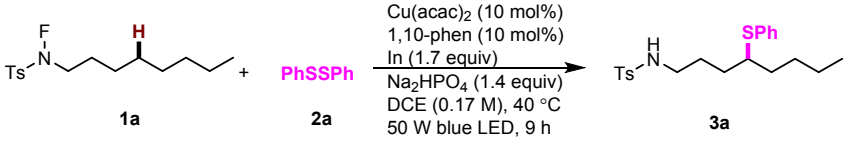
***N*-fluoro-*N*-(hex-5-en-1-yl)-4-methylbenzenesulfonamide(18a)**



18a

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 5.77 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.00 (dd, J = 16.9, 1.5 Hz, 1H), 4.95 (d, J = 10.2 Hz, 1H), 3.22 (dt, J = 40.6, 6.9 Hz, 2H), 2.48 (s, 3H), 2.05–2.09 (m, 2H), 1.67–1.76 (m, 2H), 1.45–1.55 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.18, 138.01, 129.95, 129.91, 128.96, 115.01, 53.47 (d, J = 12.3 Hz), 33.09, 25.74, 25.68, 21.76. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{13}H_{18}FNNaO_2S$, 294.0934; found, 294.0930. **IR** (KBr, cm^{-1}): ν 3565, 3419, 3337, 2929, 2361, 1638, 1176.

General Procedures for Site-Selective C*sp*^{3}-S Bond Formation



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

In an oven-dried 8 mL screwed-capped vial $Cu(acac)_2$ (2.6 mg, 0.01 mmol, 10 mol%),

1,10-phen (1.8 mg, 0.01 mmol, 10 mol%), Na_2HPO_4 (19.9 mg, 0.14 mmol, 1.4 equiv), **1a** (30.1 mg, 0.1 mmol, 1.0 equiv), **2a** (26.2 mg, 0.12 mmol, 1.2 equiv) were weighted. Then the vial was transferred into the glove-box, indium powder (19.6 mg, 0.17 mmol, 1.7 equiv) and anhydrous DCE (0.6 mL) were added to the vial. The vial was sealed and moved outside of the glove-box. The vial was kept in a 40 ℃ water bath and irradiated with two 50 W blue LED lamps which were cooled by a fan (2−3 cm away from the vial). After the reaction completion monitored by TLC (R_f = 0.4, PE/EA/DCM = 10:1:0.5, about 9 hours), the reaction was quenched by brine (2 mL), and extracted with EtOAc (5 mL × 2), the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification (EtOAc/petroleum ether/DCM = 1:15:0.5 as eluent) of the crude product provided **3a** (29.3 mg) in 75% isolated yield.

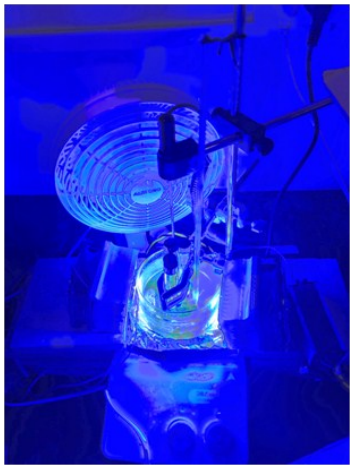


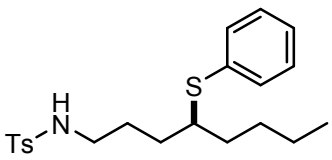
Figure S1. two 50 W LED lamps with a fan

Figure S2. Before reaction

Figure S3. After reaction

Characterization Data for Products

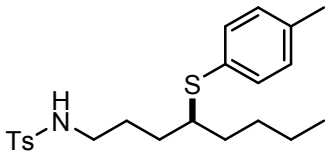
N-(4-(phenylthio)octyl)-4-methylbenzenesulfonamide (3a)



3a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 4.29 (t, J = 6.0 Hz, 1H), 2.98 (quint, J = 6.6 Hz, 1H), 2.88–2.96 (m, 2H), 2.42 (s, 3H), 1.58–1.68 (m, 2H), 1.47–1.54 (m, 3H), 1.33–1.45 (m, 3H), 1.24–1.30 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.38, 137.01, 135.23, 132.01, 129.70, 128.86, 127.10, 126.82, 48.71, 43.10, 34.32, 31.39, 28.94, 26.72, 22.54, 21.49, 13.95. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{29}NNaO_2S_2$, 414.1532; found, 414.1530. **IR** (KBr, cm^{-1}): ν 3554, 3474, 3414, 2928, 1616, 1159.

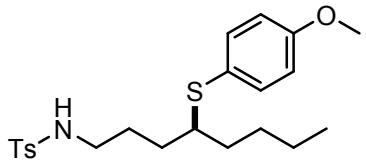
***N*-(4-(*p*-tolylthio)octyl)-4-methylbenzenesulfonamide (3b)**



3b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 4.33 (t, J = 6.0 Hz, 1H), 2.86–2.95 (m, 3H), 2.42 (s, 3H), 2.33 (s, 3H), 1.59–1.67 (m, 2H), 1.48–1.55 (m, 1H), 1.41–1.48 (m, 3H), 1.32–1.41 (m, 2H), 1.23–1.30 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.37, 137.11, 136.98, 132.84, 131.12, 129.69, 129.63, 127.09, 49.11, 43.09, 34.23, 31.29, 28.94, 22.54, 21.49, 21.06, 13.97. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{31}NNaO_2S_2$, 428.1688; found, 428.1685. **IR** (KBr, cm^{-1}): ν 3698, 3059, 1729, 1561, 900.

***N*-(4-((4-methoxyphenyl)thio)octyl)-4-methylbenzenesulfonamide (3c)**

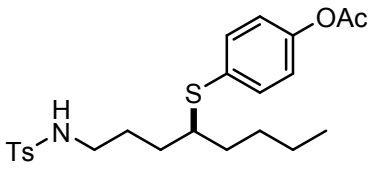


3c

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 4.45 (t, J = 6.0 Hz,

1H), 3.80 (s, 3H), 2.87–2.95 (m, 2H), 2.76 (quint,*J*=5.4 Hz, 1H), 2.42 (s, 3H), 1.59–1.68 (m, 2H), 1.47–1.51 (m, 1H), 1.38–1.44 (m, 4H), 1.33–1.38 (m, 1H), 1.22–1.29 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.40, 143.35, 136.97, 135.60, 129.68, 127.08, 124.72, 114.41, 55.29, 49.87, 43.08, 34.10, 31.17, 28.92, 26.68, 22.52, 21.48, 13.97. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{31}NNaO_3S_2$, 444.1638; found, 444.1635. **IR** (KBr, cm^{-1}): ν 3746, 3423, 2930, 1591, 1493, 1159.

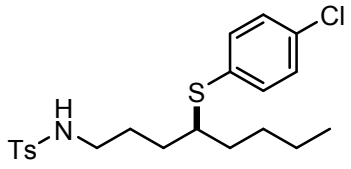
4-((1-((4-methylphenyl)sulfonamido)octan-4-yl)thio)phenyl acetate (3d)



3d

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 4.32 (t, *J* = 6.3 Hz, 1H), 2.96–2.90 (m, 3H), 2.42 (s, 3H), 2.30 (s, 3H), 1.60–1.66 (m, 2H), 1.45–1.51 (m, 3H), 1.33–1.44 (m, 3H), 1.24–1.30 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.26, 149.81, 143.39, 136.98, 133.52, 132.28, 129.71, 127.10, 122.04, 49.27, 43.08, 34.25, 31.36, 28.91, 26.76, 22.53, 21.50, 21.12, 13.96. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{31}NNaO_4S_2$, 472.1587; found, 472.1583. **IR** (KBr, cm^{-1}): ν 3472, 1620, 1400, 1119, 619.

***N*-(4-((4-chlorophenyl)thio)octyl)-4-methylbenzenesulfonamide (3e)**

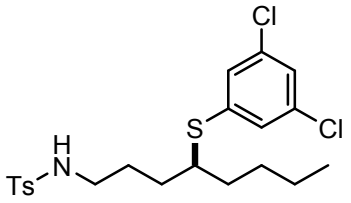


3e

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1l Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 4.34 (t, *J* = 6.1 Hz, 1H), 2.89–2.98 (m, 3H), 2.43 (s, 3H), 1.60–1.64 (m, 2H), 1.56–1.59 (m, 1H), 1.45–

1.50 (m, 3H), 1.33–1.41 (m, 2H), 1.23–1.30 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.43, 137.02, 133.76, 133.36, 132.97, 129.72, 129.02, 127.10, 49.11, 43.07, 34.25, 31.34, 28.90, 26.78, 22.52, 21.49, 13.93. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{28}ClNNaO_2S_2$, 448.1142; found, 448.1139. **IR** (KBr, cm^{-1}): ν 3557, 3417, 2928, 1615, 1158, 1013.

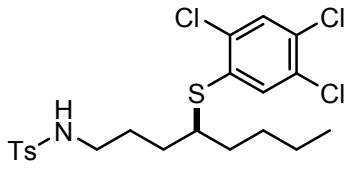
***N*-(4-((3,5-dichlorophenyl)thio)octyl)-4-methylbenzenesulfonamide (3f)**



3f

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.17 (t, J = 1.8 Hz, 1H), 7.15 (d, J = 1.8 Hz, 2H), 4.41 (t, J = 6.3 Hz, 1H), 3.04–3.09 (m, 1H), 2.91–2.97 (m, 2H), 2.42 (s, 3H), 1.59–1.64 (m, 3H), 1.49–1.55 (m, 3H), 1.33–1.41 (m, 2H), 1.25–1.31 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.47, 139.70, 136.92, 135.07, 129.73, 128.34, 127.09, 126.44, 48.50, 43.02, 34.15, 31.27, 28.77, 26.73, 22.48, 21.50, 13.90. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{27}Cl_2NNaO_2S_2$, 482.0752; found, 482.0752. **IR** (KBr, cm^{-1}): ν 3555, 3416, 2929, 1616, 1159.

***N*-(4-((2,4,5-trichlorophenyl)thio)octyl)-4-methyl benzenesulfonamide (3g)**

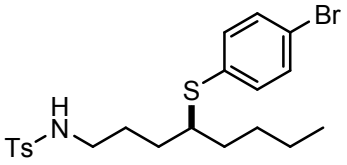


3g

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.47 (s, 1H), 7.36 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 4.35 (t, J = 6.3 Hz, 1H), 3.13–3.17 (m, 1H), 2.91–2.98 (m, 2H), 2.43 (s, 3H), 1.61–1.65 (m, 3H), 1.53–1.56 (m, 3H), 1.35–1.41 (m, 2H), 1.25–1.32 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ

143.48, 137.00, 135.57, 134.01, 131.90, 131.26, 130.94, 130.74, 129.74, 127.10, 47.90, 43.07, 33.97, 31.01, 28.71, 26.68, 22.53, 21.49, 13.89. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{26}Cl_3NNaO_2S_2$, 516.0363; found, 516.0353. **IR** (KBr, cm^{-1}): ν 3715, 3415, 2929, 1740, 1435, 1158.

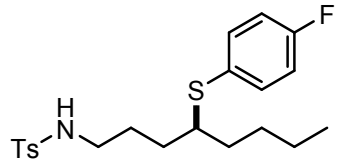
***N*-(4-((4-bromophenyl)thio)octyl)-4-methylbenzenesulfonamide (3h)**



3h

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 4.30 (t, J = 6.0 Hz, 1H), 2.94–2.91 (m, 1H), 2.88–2.95 (m, 2H), 2.43 (s, 3H), 1.58–1.65 (m, 2H), 1.45–1.52 (m, 3H), 1.33–1.42 (m, 2H), 1.22–1.31 (m, 3H), 0.88 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.45, 136.94, 134.47, 133.44, 131.94, 129.72, 127.09, 120.84, 48.92, 43.05, 34.22, 31.30, 28.89, 26.75, 22.52, 21.51, 13.95. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{28}BrNNaO_2S_2$, 492.0637; found, 492.0633. **IR** (KBr, cm^{-1}): ν 3558, 3417, 3234, 2927, 1615.

***N*-(4-((4-fluorophenyl)thio)octyl)-4-methylbenzenesulfonamide (3i)**

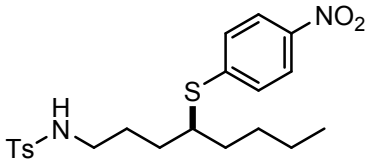


3i

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.28–7.36(m, 4H), 6.95–6.99(m, 2H), 4.41 (t, J = 6.3 Hz, 1H), 2.92 (q, J = 6.9 Hz, 2H), 2.86 (quint, J = 6.6 Hz, 1H), 2.43 (s, 3H), 1.60–1.67 (m, 2H), 1.49–1.56 (m, 1H), 1.40–1.49 (m, 3H), 1.33–1.41 (m, 1H), 1.21–1.31 (m, 3H), 0.87 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.29 (d, J = 247.5 Hz), 143.42, 136.99, 135.05 (d, J = 8.0 Hz), 129.79 (d, J = 3.2 Hz), 129.70, 127.09, 115.94 (d, J = 21.8 Hz), 49.73, 43.07, 34.16,

31.27, 28.87, 26.75, 22.50, 21.49, 13.94. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{28}FNNaO_2S_2$, 432.1438; found, 432.1432. **IR** (KBr, cm^{-1}): ν 3555, 3416, 2929, 1616, 1159.

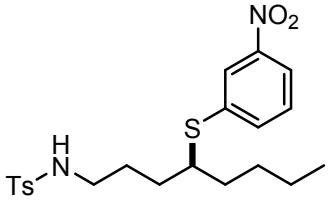
***N*-(4-((4-nitrophenyl)thio)octyl)-4-methylbenzenesulfonamide (3j)**



3j

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 4.37 (t, J = 6.2 Hz, 1H), 3.25–3.32 (m, 1H), 2.95 (q, J = 6.2 Hz, 2H), 2.42 (s, 3H), 1.67–1.74 (m, 1H), 1.59–1.67 (m, 4H), 1.35–1.44 (m, 2H), 1.26–1.34 (m, 3H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.99, 145.33, 143.54, 136.87, 129.75, 127.99, 127.06, 123.97, 47.08, 42.94, 34.18, 31.22, 28.87, 26.79, 22.53, 21.50, 13.91. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{28}N_2NaO_4S_2$, 459.1383; found, 459.1380. **IR** (KBr, cm^{-1}): ν 3717, 3560, 2929, 1742, 1512, 1336.

***N*-(4-((3-nitrophenyl)thio)octyl)-4-methylbenzenesulfonamide (3k)**

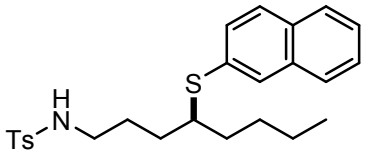


3k

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 4.41 (t, J= 6.2 Hz, 1H), 3.12–3.20 (m, 1H), 2.94 (q, J = 6.2 Hz, 2H), 2.42 (s, 3H), 1.60–1.70 (m, 2H), 1.54–1.59 (m, 3H), 1.36–1.44 (m, 2H), 1.23–1.34 (m, 3H), 0.88 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.49, 143.50, 138.87, 136.91, 136.32, 129.73, 129.58, 127.06, 124.74, 121.13, 48.51, 43.00, 34.16, 31.27,

28.83, 26.78, 22.50, 21.49, 13.90. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{28}N_2NaO_4S_2$, 459.1383; found, 459.1386. **IR** (KBr, cm^{-1}): ν 3715, 2930, 1734, 1527, 1348, 1158.

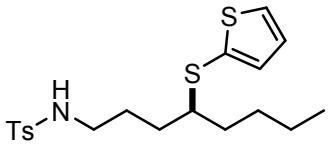
***N*-(4-(naphthalen-2-ylthio)octyl)-4-methylbenzenesulfonamide (3l)**



3l

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (brs, 2H), 7.74 (t, J = 7.5 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.43–7.50 (m, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 6.3 Hz, 2H), 4.39 (t, J = 6.0 Hz, 1H), 3.12 (quint, J =6.7Hz, 1H), 2.69–2.95 (m, 2H), 2.39 (s, 3H), 1.64–1.71 (m, 2H), 1.59–1.64 (m, 1H), 1.51–1.56 (m, 3H), 1.39–1.46 (m, 2H), 1.23–1.31 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.35, 136.95, 133.67, 132.79, 132.11, 130.22, 129.67, 129.45, 128.34, 127.67, 127.25, 127.07, 126.50, 125.96, 48.61, 43.10, 34.31, 31.41, 28.96, 26.74, 22.55, 21.46, 13.96. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{31}NNaO_2S_2$, 464.1688; found, 464.1687. **IR** (KBr, cm^{-1}): ν 3727, 3557, 3414, 2929, 1742, 1576.

***N*-(4-(thiophen-2-ylthio)octyl)-4-methylbenzenesulfonamide (3m)**

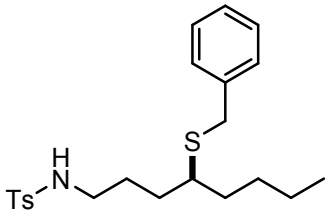


3m

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.35 (dd, J = 5.4, 1.0 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.05 (dd, J = 3.6, 1.0 Hz, 1H), 6.98 (dd, J = 5.4, 3.6 Hz, 1H), 4.36 (t, J = 6.0 Hz, 1H), 2.95 (q, J = 6.3 Hz, 2H), 2.63–2.68 (m, 1H), 2.43 (s, 3H), 1.67–1.75 (m, 1H), 1.61–1.66 (m, 1H), 1.41–1.52 (m, 5H), 1.33–1.40 (m, 1H), 1.24–1.32 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

143.40, 136.99, 135.32, 131.82, 129.95, 129.71, 127.53, 127.11, 51.54, 43.02, 34.03, 31.07, 28.98, 26.83, 22.45, 21.50, 13.97. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{27}NNaO_2S_3$, 420.1096; found, 420.1090. **IR** (KBr, cm^{-1}): ν 3717, 2928, 1739, 1613, 1158.

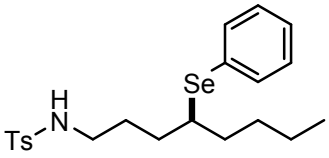
***N*-(4-(benzylthio)octyl)-4-methylbenzenesulfonamide (3n)**



3n

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.39 (s, 5H), 7.30 (d, J = 8.2 Hz, 2H), 4.65 (t, J = 6.2 Hz, 1H), 4.21 (s, 2H), 2.96–2.84 (m, 2H), 2.68–2.74 (m, 1H), 2.42 (s, 3H), 1.91–1.78 (m, 2H), 1.74–1.64 (m, 2H), 1.61–1.50 (m, 2H), 1.43–1.34 (m, 1H), 1.34–1.26 (m, 3H), 0.89 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.33, 138.76, 137.03, 129.67, 128.84, 128.41, 127.08, 126.88, 44.80, 43.07, 35.10, 34.53, 31.38, 28.84, 26.59, 22.55, 21.48, 13.97. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{31}NNaO_2S_2$, 428.1688; found, 428.1687. **IR** (KBr, cm^{-1}): ν 3700, 3416, 2929, 1738, 1556.

***N*-(4-(phenylselanyl)octyl)-4-methylbenzenesulfonamide (3o)**

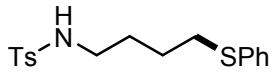


3o

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 4.29 (t, J = 6.0 Hz, 1H), 2.98 (quint, J = 6.6 Hz, 1H), 2.88–2.96 (m, 2H), 2.42 (s, 3H), 1.57–1.66 (m, 2H), 1.46–1.50 (m, 3H), 1.37–1.42 (m, 3H), 1.24–1.30 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.53, 137.13, 135.04, 129.81, 129.26, 129.07, 127.59, 127.21, 45.98, 42.91, 35.08, 32.23, 30.22, 28.05,

22.86, 21.91, 14.34. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{29}NNaO_2SSe$, 462.0976; found, 462.0972. **IR** (KBr, cm^{-1}): ν 3695, 3476, 3419, 2926, 1912, 1158.

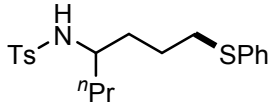
***N*-(4-(phenylthio)butyl)-4-methylbenzenesulfonamide (4a)**



4a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.27–7.31 (m, 6H), 7.16–7.20 (m, 1H), 4.26 (t, J = 6.0 Hz, 1H), 2.95 (q, J = 6.6 Hz, 2H), 2.86 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 1.60–1.63 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.46, 136.94, 136.19, 129.73, 129.31, 128.93, 127.09, 126.07, 42.69, 33.13, 28.59, 26.02, 21.50. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{21}NNaO_2S_2$, 358.0906; found, 358.0912. **IR** (KBr, cm^{-1}): ν 3483, 3387, 3104, 1758, 1614, 1158.

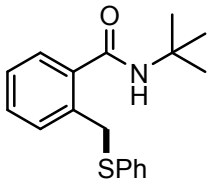
***N*-(1-(phenylthio)heptan-4-yl)-4-methylbenzenesulfonamide (4b)**



4b

White solid. mp: 58.3–59.5 ºC;**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.26–7.28 (m, 6H), 7.15–7.20 (m, 1H), 4.25 (d, J = 8.4 Hz, 1H), 3.19–3.24 (m, 1H), 2.77 (t, J = 6.9 Hz, 2H), 2.41 (s, 3H), 1.52–1.57 (m, 2H), 1.46–1.51 (m, 1H), 1.39–1.45 (m, 1H), 1.29–1.35 (m, 1H), 1.17–1.28 (m, 2H), 1.10–1.17 (m, 1H), 0.76 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.23, 138.26, 136.44, 129.59, 129.10, 128.87, 126.99, 125.91, 53.43, 37.34, 33.97, 33.35, 24.76, 21.49, 18.43, 13.75. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{27}NNaO_2S_2$, 400.1375; found, 400.1373. **IR** (KBr, cm^{-1}): ν 3718, 3555, 3412, 2925, 1745, 1614.

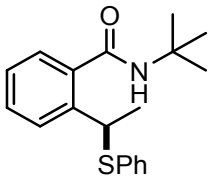
***N*-(*tert*-butyl)-2-((phenylthio)methyl)benzamide (4c)**



4c

White solid. mp: 66.3–67.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40–7.44 (m, 1H), 7.30–7.31 (m, 2H), 7.26–7.29 (m, 4H), 7.19–7.22 (m, 2H), 6.06 (s, 1H), 4.30 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.79, 137.95, 135.96, 134.24, 130.65, 129.91, 129.60, 128.93, 127.75, 127.53, 126.63, 51.96, 36.71, 28.74. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{21}NNaOS$, 322.1236; found, 322.1238. **IR** (KBr, cm^{-1}): ν 3742, 3553, 3410, 2968, 1746, 1617.

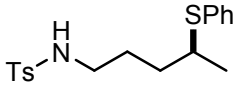
***N*-(*tert*-butyl)-2-(1-(phenylthio)ethyl)benzamide (4d)**



4d

White solid. mp: 67.3–68.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.26–7.29 (m, 3H), 7.19–7.24 (m, 4H), 5.64 (brs, 1H), 4.91 (q, J = 6.9 Hz, 1H), 1.64 (d, J = 6.9 Hz, 3H), 1.40 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.19, 140.46, 137.57, 134.99, 132.14, 129.79, 128.75, 127.71, 127.15, 127.00, 126.71, 51.81, 43.43, 28.69, 22.15. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{23}NNaOS$, 336.1393; found, 336.1393. **IR** (KBr, cm^{-1}): ν 3738, 3554, 3412, 2969, 1762, 1614.

***N*-(4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4e)**

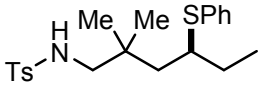


4e

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.27–7.31 (m, 3H), 7.26–7.27 (m, 1H), 7.23 (t, J = 7.2 Hz, 1H), 4.47 (t, J

= 6.0 Hz, 1H), 3.09–3.15 (m, 1H), 2.89–2.97 (m, 2H), 2.42 (s, 3H), 1.60–1.65 (m, 2H), 1.47–1.56 (m, 2H), 1.22 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.41, 136.93, 134.79, 132.15, 129.70, 128.84, 127.08, 126.93, 42.98, 42.87, 33.39, 26.97, 21.49, 21.17. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{23}NNaO_2S_2$, 372.1062; found, 372.1061. **IR** (KBr, cm^{-1}): ν 3731, 3550, 2925, 1747, 1158, 1092.

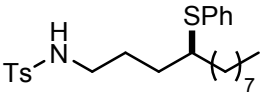
***N*-(2,2-dimethyl-4-(phenylthio)hexyl)-4-methylbenzenesulfonamide (4f)**



4f

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.25–7.16 (m, 4H), 7.21–7.24 (m, 3H), 5.04 (t, *J* = 8.1 Hz, 1H), 2.87–2.91 (m, 1H), 2.71–2.78 (m, 2H), 2.39 (s, 3H), 1.57–1.63 (m, 1H), 1.51 (dd, *J* = 15.9, 7.5 Hz, 2H), 1.42 (dd, *J* = 15.4, 2.7 Hz, 1H), 0.98 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.11, 137.13, 135.11, 131.70, 129.63, 128.95, 127.05, 127.01, 52.03, 45.96, 42.95, 34.36, 30.23, 26.81, 25.10, 21.48, 10.71. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{29}NNaO_2S_2$, 414.1532; found, 414.1528. **IR** (KBr, cm^{-1}): ν 3720, 3553, 2967, 1740, 1614, 1560.

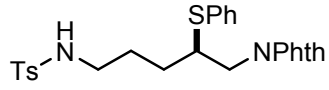
***N*-(4-(phenylthio)hexyl)-4-methyl benzenesulfonamide (4g)**



4g

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.31–7.34 (m, 2H), 7.28–7.30 (m, 2H), 7.25–7.27 (m, 2H), 7.19–7.24 (m, 1H), 4.32 (t, *J* = 6.3 Hz, 1H), 2.96–3.01 (m, 1H), 2.89–2.95 (m, 2H), 2.42 (s, 3H), 1.59–1.69 (m, 2H), 1.52–1.56 (m, 1H), 1.44–1.52 (m, 3H), 1.35–1.43 (m, 2H), 1.21–1.31 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.37, 136.99, 135.23, 132.01, 129.69, 128.84, 127.09, 126.80, 48.75, 43.09, 34.63, 31.84, 31.40, 29.46, 29.44, 29.23, 26.77, 26.71, 22.64, 21.49, 14.08. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{37}NNaO_2S_2$, 470.2158; found, 470.2152. **IR** (KBr, cm^{-1}): ν 3714, 2926, 1735, 1573, 1573, 1159.

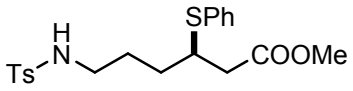
***N*-(5-(1,3-dioxoisoindolin-2-yl)-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4h)**



4h

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 2H), 7.79 (d, J = 3.0 Hz, 2H), 7.71 (d, J = 7.5 Hz, 4H), 7.54–7.58 (m, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 4.65 (t, J = 6.0 Hz, 1H), 4.02 (dd, J = 14.1, 6.6 Hz, 1H), 3.74 (dd, J = 14.1, 6.6 Hz, 1H), 3.70 (t, J = 6.0 Hz, 1H), 2.91–3.01 (m, 2H), 2.42 (s, 3H), 1.93–2.00 (m, 1H), 1.78–1.84 (m, 2H), 1.62–1.68 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.79, 143.44, 137.37, 136.82, 134.26, 133.89, 131.60, 129.73, 129.29, 128.75, 127.06, 123.50, 60.43, 42.50, 36.65, 26.18, 23.63, 21.48. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{26}NNaO_2S_2$, 517.1226; found, 517.1226. **IR** (KBr, cm^{-1}): ν 3714, 3552, 2928, 1714, 1589, 1402.

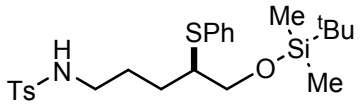
Methyl-6-((4-methylphenyl)sulfonamido)-3-(phenylthio)hexanoate (4i)



4i

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 4.64 (t, J = 6.0 Hz, 1H), 3.63 (s, 3H), 3.51–3.55 (m, 1H), 2.92 (quint, J = 4.8 Hz,2H), 2.84 (dd, J = 16.8, 4.8 Hz, 1H), 2.43 (s, 3H), 2.42 (t, J = 12.4 Hz, 1H), 1.92–1.96 (m, 1H), 1.65–1.68 (m, 1H), 1.59–1.63 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.65, 143.50, 137.01, 136.89, 134.11, 129.75, 129.37, 128.98, 127.06, 60.01, 52.34, 42.47, 33.45, 26.63, 25.56, 21.50. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{25}NNaO_4S_2$, 430.1117; found, 430.1119. **IR** (KBr, cm^{-1}): ν 3719, 3553, 3063, 1738, 1560, 1154.

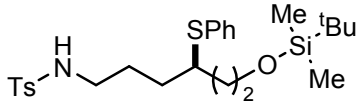
***N*-(5-((tert-butyldimethylsilyl)oxy)-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4j)**



4j

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 4.51 (t, J = 6.3 Hz, 1H), 3.86 (dd, J = 11.0, 6.4 Hz, 1H), 3.81 (dd, J = 11.0, 6.4 Hz,1H), 3.02–3.08 (m, 1H), 2.95 (q, J = 6.6 Hz, 2H), 2.43 (s, 3H), 1.90–1.99 (m, 1H), 1.73–1.79 (m, 2H), 1.39–1.52 (m, 1H), 0.76 (s, 9H), -0.06 (s, 3H), -0.08 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.46, 138.60, 136.88, 133.67, 129.75, 129.08, 128.78, 127.08, 66.07, 60.43, 42.80, 29.68 (grease), 27.03, 25.70, 22.70, 21.50, 18.09, -5.67, -5.71. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{37}NNaO_3S_2Si$, 502.1876; found, 502.1881. **IR** (KBr, cm^{-1}): ν 3718, 3554, 3063, 1736, 1560.

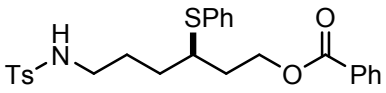
_N_-(5-((tert-butyldimethylsilyl)oxy)-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4k)



4k

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 7.5 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 4.32 (t, J = 6.0 Hz, 1H), 3.75–3.79 (m, 1H), 3.69–3.73 (m, 1H), 3.21 (dt, J = 13.6, 6.9 Hz, 1H), 2.92 (dt, J = 9.9, 6.6 Hz, 2H), 2.42 (s, 3H), 1.71 (dd, J = 12.6, 6.3 Hz, 2H), 1.66 (dd, J = 12.6, 6.6 Hz, 1H), 1.59–1.64 (m, 2H), 1.47–1.53 (m, 1H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.36, 137.00, 135.20, 131.68, 129.69, 128.86, 127.09, 126.72, 60.25, 45.00, 43.06, 37.78, 31.83, 26.81, 25.91, 21.49, 18.23, -5.37. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{39}NNaO_3S_2Si$, 516.2033; found, 516.2026. **IR** (KBr, cm^{-1}): ν 3725, 3554, 3408, 2933, 1742, 1562.

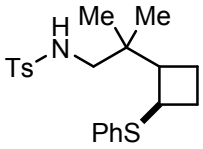
6-((4-methylphenyl)sulfonamido)-3-(phenylthio)hexyl benzoate (4l)



4l

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 10.8 Hz, 2H), 7.88(d, J = 10.8 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.54–7.60 (m, 3H), 7.44 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 4.56 (t, J = 6.2 Hz, 1H), 4.35 (t, J = 6.4 Hz, 2H), 3.15 (quint, J = 6.2 Hz, 1H), 2.93 (q, J = 6.2 Hz, 2H), 2.42 (s, 3H), 2.24–2.31 (m, 1H), 1.87–1.99 (m, 2H), 1.61–1.80 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.21, 143.51, 137.31, 136.84, 133.97, 133.26, 129.76, 129.66, 129.56, 129.38, 128.82, 128.48, 127.05, 61.67, 60.92, 42.70, 27.84, 26.69, 25.21, 21.49. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{29}NNaO_4S_2$, 506.1430; found, 506.1427. **IR** (KBr, cm^{-1}): ν 3717, 3553, 3063, 1719, 1560, 1276.

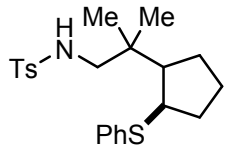
***N*-(2-methyl-2-2-(phenylthio)cyclobutyl)propyl)-4-methylbenzenesulfonamide (4m)**



4m

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.25–7.27 (m, 4H), 7.20–7.24 (m, 1H), 5.14 (t, J = 7.2 Hz, 1H), 3.47 (q, J = 8.7 Hz, 1H), 2.68 (dd, J = 7.2, 3.9 Hz, 2H), 2.42 (s, 3H), 2.23–2.28 (m, 1H), 2.19 (q, J = 9.3 Hz, 1H), 1.83–1.90 (m, 1H), 1.76–1.82 (m, 1H), 1.61–1.65 (m, 1H), 0.89 (s, 3H), 0.81 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.14, 137.22, 134.98, 131.01, 129.65, 128.94, 127.03, 126.86, 52.49, 50.38, 42.11, 35.29, 28.06, 22.82, 21.49, 21.06, 19.54. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{27}NNaO_2S_2$, 412.1375; found, 412.1374. **IR** (KBr, cm^{-1}): ν 3713, 3284, 3062, 2965, 1730, 1577.

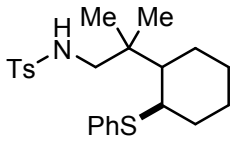
***N*-(2-methyl-2-2-(phenylthio)cyclopentylpropyl)-4-methylbenzenesulfonamide (4n)**



4n

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.26–7.28 (m, 2H), 7.24–7.25 (m, 2H), 7.22 (d, J = 7.8 Hz, 3H), 5.15 (dd, J = 5.7, 5.7 Hz, 1H), 3.22–3.25 (m, 1H), 2.80 (dd, J = 12.9, 5,7 Hz, 1H), 2.74 (dd, J = 12.9, 5,7 Hz, 1H), 2.39 (s, 3H), 1.75–1.82 (m, 3H), 1.70–1.74 (m, 1H), 1.65–1.70 (m, 1H), 1.62–1.63 (m, 1H), 1.28–1.35 (m, 1H), 0.94 (s, 3H), 0.84 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.09, 137.14, 136.39, 130.51, 129.64, 128.93, 127.01, 126.65, 53.19, 51.85, 47.36, 36.51, 35.96, 28.37, 24.99, 24.18, 21.47, 20.89. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{29}NNaO_2S_2$, 426.1532; found, 426.1527. **IR** (KBr, cm^{-1}): ν 3721, 3397, 3066, 1731, 1563, 1160.

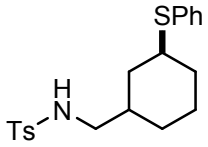
***N*-(2-methyl-2--2-(phenylthio)cyclohexylpropyl)-4-methylbenzenesulfonamide (4o)**



4o

White solid. mp: 168.3–169.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.25–7.26 (m, 7H), 4.75 (dd, J = 5.8, 5.8 Hz, 1H), 3.10–3.14 (m, 1H), 2.94 (dd, J = 12.6, 5.6 Hz, 1H), 2.87 (dd, J = 12.6, 5.6 Hz, 1H), 2.40 (s, 3H), 1.63–1.81 (m, 4H), 1.39–1.51 (m, 2H), 1.16–1.33 (m, 3H), 1.00 (s, 3H), 0.91 (s, 3H). **^{13}CNMR** (100 MHz, $CDCl_3$) δ 143.17,137.04, 135.36, 131.95, 129.65, 128.94, 127.10, 127.07, 52.82, 47.44, 45.58, 37.64, 29.91, 25.11, 24.11, 23.00, 22.45, 21.49, 21.11. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{31}NNaO_2S_2$, 440.1668; found, 440.1691. **IR** (KBr, cm^{-1}): ν 3710, 3062, 1734, 1559, 1159.

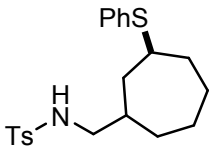
***N*-(-3-(phenylthio)cyclohexylmethyl)-4-methyl benzenesulfonamide (4p)**



4p

White solid. mp: 108.0–109.0 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.26–7.30 (m, 4H),7.22 (t, J = 7.2 Hz, 1H), 4.29 (t, J = 6.3 Hz, 1H), 3.54–3.55 (m, 1H), 2.81 (td, J = 6.6, 2.7 Hz, 2H), 2.42 (s, 3H), 1.89–1.96 (m, 1H), 1.71–1.81 (m, 2H), 1.61–1.69 (m, 3H), 1.48–1.54 (m, 1H), 1.41–1.46 (m,1H), 0.98–1.09 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.37, 137.04, 135.51, 131.48, 129.71, 128.93, 127.06, 126.71, 48.30, 44.37, 34.69, 32.71, 30.97, 29.64, 21.50, 20.63. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{25}NNaO_2S_2$, 398.1219; found, 398.1219. **IR** (KBr, cm^{-1}): ν 3721, 3554, 2928, 1733, 1572, 1158.

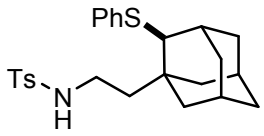
***N*-(-3-(phenylthio)cycloheptylmethyl)-4-methylbenzenesulfonamide (4q)**



4q

White solid. mp: 93.1–94.0 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.36–7.38 (m, 2H), 7.32–7.34 (m, 2H), 7.27–7.32 (m, 1/2×8H, 1/2×8H), 7.20–7.26 (m, 1/2×2H, 1/2×2H), 4.47 (t, J = 6.3 Hz, 1H), 4.27 (t, J = 6.3 Hz, 1H), 3.38–3.42 (m, 1H), 3.15–3.20 (m, 1H), 2.74–2.77 (m, 2H), 2.68–2.73 (m, 1H), 2.62–2.67 (m, 1H), 2.42 (s, 1/2×6H, 1/2×6H), 2.01–2.07 (m, 1H), 1.97–1.99 (m, 1H), 1.79–1.84 (m, 1H), 1.70–1.79 (m, 5H), 1.59–1.68 (m, 5H), 1.51–1.57 (m, 1H), 1.43–1.51 (m, 3H), 1.31–1.34 (m, 2H), 1.24–1.27 (m, 1H), 1.14–1.21 (m, 1H), 1.05–1.11 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.38, 143.27, 137.10, 137.04, 135.60 (C×2), 131.89, 131.32, 129.70, 129.65, 129.01, 128.91, 127.09, 127.06, 126.91, 126.64, 49.40, 49.18, 46.81, 45.99, 38.69, 38.59, 36.74, 35.17, 34.76, 34.59, 32.22, 31.88, 27.93, 26.73, 25.55, 25.29, 21.49 (C×2). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{27}NNaO_2S_2$, 412.1375; found, 412.1375. **IR** (KBr, cm^{-1}): ν 3724, 3553, 2925, 2856, 1734, 1158.

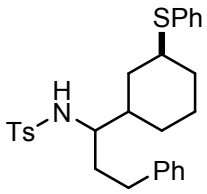
***N*-(2-((1r,3s,5*R*,7*S*)-2-(phenylthio)adamantan-1-yl)ethyl)-4-methylbenzenesulfonamide (4r)**



4r

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.23–7.27 (m, 4H), 7.23 (t, J = 6.9 Hz, 1H), 4.25 (t, J = 5.4 Hz, 1H), 3.21 (s, 1H), 2.92–3.03 (m, 2H), 2.40 (s, 3H), 2.24 (d, J = 12.6 Hz, 1H), 1.92–1.95 (m, 3H), 1.76–1.83 (m, 2H), 1.65–1.71 (m, 3H), 1.60 (d, J = 12.3 Hz, 2H), 1.46–1.52 (m, 2H), 1.31–1.37 (m, 1H), 1.27 (d, J = 12.9 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.22, 136.93, 136.00, 131.76, 129.63, 128.96, 127.15, 126.74, 59.64, 42.73, 40.55, 38.92, 38.08, 38.04, 37.04, 36.29, 33.21, 31.26, 28.06, 28.00, 21.49. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{31}NNaO_2S_2$, 464.1688; found, 464.1682. **IR** (KBr, cm^{-1}): ν 3715, 3554, 2925, 1738, 1558, 1372.

***N*-(3-phenyl-1-(-3-(phenylthio)cyclohexylpropyl)-4-methylbenzenesulfonamide (4s)**

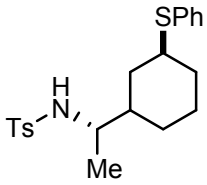


4s

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 1/3×2H), 7.70 (d, J = 8.1 Hz, 2/3×2H), 7.33–7.35 (m, 1/3×2H,2/3×2H), 7.25–7.30(m, 1/3×4H,2/3×4H), 7.19–7.24 (m, 1/3×3H,2/3×3H), 7.14–7.17 (m, 1/3×1H,2/3×1H), 6.95 (d, J = 7.2 Hz, 1/3×2H), 6.90 (d, J = 7.2 Hz, 2/3×2H), 4.50 (d, J = 9.0 Hz, 1/3×1H), 4.37 (d, J = 9.0 Hz, 2/3×1H), 3.64 (t, J = 3.0 Hz, 2/3×1H), 3.11–3.18 (m, 1/3×1H,2/3×1H), 2.85–2.89 (m, 1/3×1H), 2.31–2.49 (m, 1/3×1H,2/3×1H), 2.41 (s, 1/3×3H,2/3×3H), 2.40 (t, J = 7.2 Hz, 1/3×2H, 2/3×2H), 1.94–2.00 (m, 1/3×1H, 2/3×1H), 1.76–1.84 (m, 1/3×1H,2/3×1H), 1.62–1.71 (m, 1/3×2H, 2/3×2H), 1.50–1.63 (m, 1/3×2H, 2/3×2H),

1.40–1.49 (m, 1/3×1H, 2/3×1H), 1.08–1.22 (m, 1/3×1H,2/3×1H), 0.98 (quint, J = 12.3 Hz,1/3×1H,2/3×1H), 0.82-0.89 (m, 1/3×1H,2/3×1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.33, 143.17, 141.19 (C×2), 138.44, 138.40, 135.77, 134.64, 132.03, 131.31, 129.63 (C×2), 128.94, 128.81, 128.38, 128.34, 128.25, 128.21, 127.04, 127.02, 126.85, 126.59, 125.97, 125.91, 58.12, 57.69, 46.19, 45.22, 41.72, 35.46, 35.13, 34.13, 33.75, 33.72, 33.26, 31.94, 31.52, 30.60, 27.37, 27.26, 25.92, 21.51, 21.49, 20.90. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{28}H_{33}NNaO_2S_2$, 502.1845; found, 502.1839. **IR** (KBr, cm^{-1}): ν 3716, 3554, 3061, 1740, 1558, 1371.

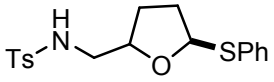
***N*-((1*S*)-1-(3-(phenylthio)cyclohexyl)ethyl)-4-methylbenzenesulfonamide (4t)**



4t

White solid. mp: 107.0–108.0 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.34–7.38 (m, 2H), 7.26–7.32 (m, 4H), 7.19–7.24 (m, 1H), 4.12 (d, J = 9.2 Hz, 1H), 3.60–3.61 (m, 1H), 3.14–3.21 (m, 1H), 2.42 (s, 3H), 1.75–1.83 (m, 2H), 1.66–1.75 (m, 3H), 1.5 –1.66 (m, 2H), 1.51–1.58 (m, 2H), 0.90 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.20, 138.28, 135.70, 131.56, 129.64, 128.92, 127.04, 126.70, 53.65, 45.18, 38.14, 33.73, 30.68, 27.44, 21.51, 20.80, 19.07. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{27}NNaO_2S_2$, 412.1375; found, 412.1372. **IR** (KBr, cm^{-1}): ν 3736, 3553, 3034, 1738, 1613, 1557.

***N*-((5-(phenylthio)tetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide (4u)**

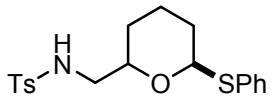


4u

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.42–7.46 (m, 2H), 7.27–7.31 (m, 4H), 7.23–7.26 (m, 1H), 5.59 (dd, J = 7.2, 4.2 Hz, 1H), 4.69 (t, J =

6.3 Hz, 1H), 4.26–4.31 (m, 1H), 3.19 (ddd, *J* = 12.9, 6.3, 3.6 Hz, 1H), 2.99–3.04 (m, 1H), 2.42 (s, 3H), 2.35–2.40 (m, 1H), 1.95–2.07 (m, 2H), 1.68–1.75 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.50, 136.94, 135.01, 131.49, 129.76, 128.89, 127.18, 127.04, 87.63, 76.47, 46.05, 32.72, 27.37, 21.52. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{21}NNaO_3S_2$, 386.0855; found, 386.0854. **IR** (KBr, cm^{-1}): ν 3719, 3553, 3059, 1740, 1612, 1557.

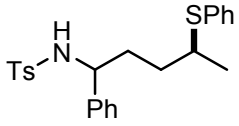
***N*-((6-(phenylthio)tetrahydro-2H-pyran-2-yl)methyl)-4-methylbenzenesulfonamide (4v)**



4v

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 7.5 Hz,2H), 5.53 (d, *J* = 4.5 Hz, 1H), 4.42 (dd, *J* = 7.5, 3.9 Hz, 1H), 4.25–4.29 (m, 1H), 3.05–3.10 (m, 1H), 2.80–2.85 (m, 1H), 2.41 (s, 3H), 1.90–1.98 (m, 2H), 1.79–1.84 (m, 1H), 1.68–1.73 (m, 1H), 1.30–1.40 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.23, 136.98, 134.62, 131.91, 129.62, 129.08, 127.35, 127.01, 84.86, 67.76, 47.42, 30.28, 28.23, 21.49, 18.82. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{23}NNaO_3S_2$, 400.1012; found, 400.1013. **IR** (KBr, cm^{-1}): ν 3703, 3063, 1732, 1557, 1368, 918.

***N*-(1-phenyl-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4w)**

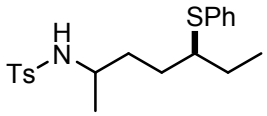


4w

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 1/2×4H, 1/2×4H), 7.29 (d, *J* = 7.2 Hz, 1/2×4H, 1/2×4H), 7.20–7.26 (m,1/2×6H, 1/2×6H),7.12–7.18 (m, 1/2×6H, 1/2×6H), 7.10 (d,*J* = 8.1 Hz, 2H), 7.09 (d,*J* = 8.1 Hz, 2H), 6.96–6.99 (m, 1/2×4H, 1/2×4H), 4.80 (d, *J* = 7.4 Hz, 1/2×2H, 1/2×2H), 4.24 (q, *J* = 7.4 Hz, 1/2×2H, 1/2×2H), 3.09 (quint, *J* = 13.2, 6.6 Hz, 1/2×2H, 1/2×2H), 2.34 (s, 1/2×6H,

1/2×6H), 1.84–1.99 (m, 1/2×4H, 1/2×4H), 1.46–1.54 (m, 1/2×2H, 1/2×2H), 1.32–1.39 (m, 1/2×2H, 1/2×2H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 143.04, 143.01, 140.63, 140.58, 137.68, 137.66, 134.78, 134.67, 132.31, 132.26, 129.32, 129.30, 128.81 (C×2), 128.53, 128.52, 127.50, 127.46, 127.07 (C×2), 126.94, 126.91, 126.46, 126.40, 58.32, 58.02, 43.12, 42.95, 34.72, 34.68, 32.67, 32.56, 21.40 (C×2), 21.30, 21.26. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{27}NNaO_2S_2$, 448.1375; found, 448.1371. **IR** (KBr, cm^{-1}): ν 3715, 3554, 3062, 1735, 1557, 1327.

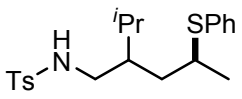
***N*-(5-(phenylthio)heptan-2-yl)-4-methylbenzenesulfonamide (4x)**



4x

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.74 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 1/2×4, 1/2×4H), 7.25–7.30 (m, 1/2×8H, 1/2×8H), 7.21 (t, *J* = 7.2 Hz, 1/2×2H,1/2×2H), 4.37 (d, *J* = 8.1 Hz, 1/2×2, 1/2×2H), 3.24–3.30 (m, 1/2×2H, 1/2×2H), 2.85–2.92 (m, 1/2×2H, 1/2×2H), 2.41 (s,1/2×6H, 1/2×6H), 1.40–1.59 (m, 1/2×12H, 1/2×12H), 1.01 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H),0.94 (t, *J* = 7.2 Hz, 1/2×6H, 1/2×6H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 143.20, 143.18, 138.20, 138.19, 135.30, 135.28, 132.00, 131.99, 129.62 (C×2), 128.81, 128.80, 127.02 (C×2), 126.74, 126.72, 50.53, 50.32, 50.19, 49.77, 34.46, 34.43, 29.74 (C×2), 27.58, 27.31, 21.89, 21.86, 21.46 (C×2), 11.09, 11.06. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{27}NNaO_2S_2$, 400.1375; found, 400.1375. **IR** (KBr, cm^{-1}): ν 3718, 3278, 2966, 1734, 1576, 1158.

***N*-(2-isopropyl-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4y)**

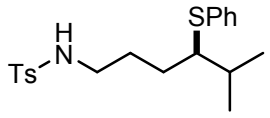


4y

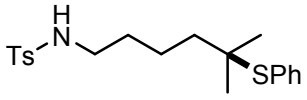
White solid. mp: 100.3–101.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.73 (d, *J* = 8.4 Hz,

2H), 7.72 (d, J = 8.4 Hz, 2H), 7.34–7.38 (m, 1/2×4H, 1/2×4H), 7.28–7.31 (m, 1/2×8H, 1/2×8H), 7.22–7.25 (m, 1/2×2H, 1/2×2H), 4.42 (t, J = 6.3 Hz, 1H), 4.37 (t, J = 6.3 Hz, 1H), 3.15–3.20 (m, 1H), 3.09–3.18 (m, 1H), 2.93–2.97 (m, 1H), 2.85–2.88 (m, 1H), 2.80–2.89 (m, 1/2×2H, 1/2×2H), 2.43 (s, 3H), 2.42 (s, 3H), 1.70–1.75 (m, 1H), 1.65–1.69 (m, 1H), 1.50–1.54 (m, 1/2×2H, 1/2×2H), 1.36–1.46 (m, 1/2×4H, 1/2×4H), 1.22 (d, J = 6.6 Hz, 3H), 1.21 (d, J = 6.6 Hz, 3H),0.79 (t, J = 6.9 Hz, 6H), 0.78 (t, J = 6.9 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.38 (C×2), 136.91, 136.86, 134.92, 134.72, 132.31, 132.08, 129.70 (C×2), 128.91, 128.86, 127.14 (C×2), 126.98 (C×2), 44.32, 44.16, 41.87, 41.73, 41.70, 41.12, 36.08, 36.04, 29.69, 28.62, 28.43, 22.44, 21.55, 21.50, 19.31, 19.12, 18.87, 18.68. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{29}NNaO_2S_2$, 414.1532; found, 414.1529. **IR** (KBr, cm^{-1}): ν 3741, 3551, 2960, 1748, 1159.

Mixture of *N*-(5-methyl-4-(phenylthio)hexyl)-4-methylbenzenesulfonamide(4z) and *N*-(5-methyl-5-(phenylthio)hexyl)-4-methylbenzenesulfonamide (4z')



4z

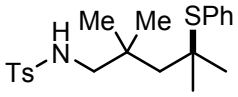


4z'

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2/5×2H), 7.72 (d, J = 8.1 Hz, 3/5×2H), 7.45 (d, J = 6.9 Hz, 2/5×2H), 7.34 (d, J = 7.2 Hz, 3/5×2H), 7.28–7.31 (m, 2/5×3H, 3/5×3H), 7.23–7.26 (m, 2/5×1H, 3/5×1H, 2/5×1H), 7.22 (t, J = 7.2 Hz, 3/5×1H), 4.56 (t, J = 6.0 Hz, 2/5×1H), 4.51 (t, J = 6.0 Hz, 3/5×1H), 2.87–2.95 (m, 3/5×1H, 2/5×1H, 3/5×2H), 2.42 (s, 2/5×3H), 2.41 (s, 3/5×3H), 1.84–1.90 (m, 3/5×1H), 1.69–1.76 (m, 2/5×1H), 1.42–1.45 (m, 2/5×4H), 1.54–1.64 (m, 2/5×2H, 3/5×2H), 1.36–1.38 (m, 3/5×2H), 1.17 (s, 2/5×6H), 0.96 (d, J = 6.6 Hz, 3/5×3H), 0.93 (d, J = 6.6 Hz, 3/5×3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.33 (C×2), 137.40, 137.06, 137.01, 136.73, 132.18, 131.22, 129.69, 129.68, 128.85, 128.66, 128.46, 127.10, 127.09, 126.38, 56.47, 49.07, 43.15, 43.06, 41.75, 31.90, 29.99, 28.80, 28.71, 27.63, 21.84, 21.47, 21.46, 19.22, 19.15. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for

$C_{20}H_{27}NNaO_2S_2$, 400.1375; found, 400.1370. **IR** (KBr, cm^{-1}): ν 3722, 3552, 2959, 1326, 1158.

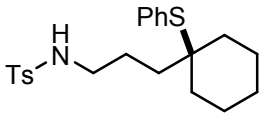
***N*-(2,2,4-trimethyl-4-(phenylthio)pentyl)-4-methyl benzenesulfonamide (4aa)**



4aa

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 4.91 (t, J = 7.2 Hz, 1H), 2.83 (d, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.63 (s, 2H), 1.26 (s, 6H), 1.03 (s, 6H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.22, 137.55, 137.19, 131.79, 129.67, 128.95, 128.57, 127.06, 53.94, 51.06, 49.93, 35.97, 31.02, 27.44, 21.49. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{29}NNaO_2S_2$, 414.1532; found, 414.1531. **IR** (KBr, cm^{-1}): ν 3690, 3523, 3451, 1722, 1572, 619.

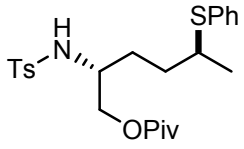
***N*-(3-(1-(phenylthio)cyclohexyl)propyl)-4-methyl benzenesulfonamide (4ab)**



4ab

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.27–7.30 (m, 4H), 4.31 (t, J = 6.0 Hz, 1H), 2.92 (q, J = 6.6 Hz, 2H), 2.42 (s, 3H), 1.69–1.78 (m, 4H), 1.53–1.57 (m, 2H), 1.47–1.52 (m, 1H), 1.38–1.42 (m, 2H), 1.29–1.38 (m, 3H), 1.24–1.28 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.37, 137.27, 137.04, 131.61, 129.68, 128.69, 128.58, 127.13, 53.46, 43.56, 36.23, 25.84, 23.91, 22.10, 21.49. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{29}NNaO_2S_2$, 426.1532; found, 426.1545. **IR** (KBr, cm^{-1}): ν 3687, 3557, 3232, 1616, 619.

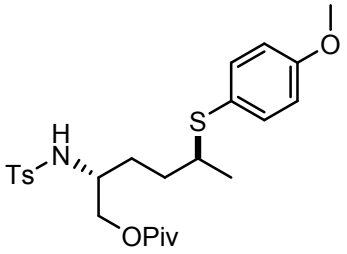
(2*S*)-2-((4-methylphenyl)sulfonamido)-5-(phenylthio)hexyl pivalate (5a)



5a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1/2×4H, 1/2×4H), 7.27–7.30 (m,1/2×8H, 1/2×8H), 7.22–7.24 (m, 1/2×2H, 1/2×2H), 4.71 (d, J = 8.4 Hz,1H), 4.70 (d, J = 8.4 Hz, 1H), 3.98 (dd, J = 11.4, 4.5 Hz,1H), 3.96 (dd, J = 11.4, 4.5 Hz,1H), 3.84 (dd, J = 11.4, 4.5 Hz,1H), 3.81 (dd, J = 11.4, 4.5 Hz,1H), 3.42–3.48 (m, 1/2×2H, 1/2×2H), 3.00–3.10 (m, 1/2×2H, 1/2×2H), 2.41 (s, 1/2×6H, 1/2×6H), 1.63–1.71 (m, 1/2×2H, 1/2×2H), 1.51–1.59 (m, 1/2×2H, 1/2×2H), 1.43–1.50 (m, 1/2×2H, 1/2×2H), 1.36–1.43 (m, 1/2×2H, 1/2×2H), 1.17 (s, 9H), 1.17 (d, J = 7.5 Hz, 3H), 1.16 (s, 9H), 1.15 (d, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.19 (C×2), 143.58 (C×2), 137.95, 137.91, 134.74, 134.72, 132.19, 132.16, 129.78, 129.77, 128.86 (C×3), 126.98, 126.95 (C×2), 65.59, 65.49, 53.04, 52.63, 43.09, 42.85, 38.85 (C×2), 32.24, 32.14, 29.49 (C×2), 27.13 (C×2), 21.49, 21.42, 21.10 (C×2). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{33}NNaO_4S_2$, 486.1743; found, 486.1743. **IR** (KBr, cm^{-1}): ν 3688, 3375, 3319, 1726, 1573, 1160.

(2*S*)-5-((4-methoxyphenyl)thio)-2-((4-methylphenyl)sulfonamido)hexyl pivalate (5b)

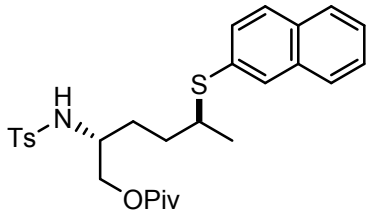


5b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 1/2×4H, 1/2×4H), 7.30 (d, J = 8.4 Hz, 1/2×4H, 1/2×4H), 7.28 (d, J = 8.4 Hz, 1/2×4H, 1/2×4H), 6.84 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 4.72 (d, J = 8.3 Hz, 1/2×2H, 1/2×2H), 3.96–3.99 (m, 1/2×2H, 1/2×2H), 3.80–3.85 (m, 1/2×2H, 1/2×2H), 3.80 (s,

1/2×6H, 1/2×6H), 3.42–3.48 (m, 1/2×2H, 1/2×2H), 2.85–2.90 (m, 1H), 2.79–2.84 (m, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 1.62–1.70 (m, 1/2×2H, 1/2×2H), 1.50–1.60 (m, 1/2×2H, 1/2×2H), 1.30–1.44 (m, 1/2×4H, 1/2×4H), 1.17 (s, 1/2×18H, 1/2×18H), 1.11 (d, J = 9.3 Hz, 3H), 1.10 (d, J = 9.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.18 (C×2), 159.57, 159.56, 143.54, 143.52, 138.04, 137.99, 135.77, 135.72, 129.76, 129.75, 126.96 (C×2), 124.50, 124.41, 114.44 (C×2), 65.60, 65.50, 55.30 (C×2), 53.08, 52.66, 44.26, 44.02, 38.85 (C×2), 32.13, 32.00, 29.54, 29.49, 27.13 (C×2), 21.46, 21.37, 21.04 (C×2). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{35}NNaO_5S_2$, 516.1849; found, 516.1845. **IR** (KBr, cm^{-1}): ν 3553, 3412, 3235, 1617, 1160, 617.

(2*S*)-2-((4-methylphenyl)sulfonamido)-5-(naphthalen-2-ylthio)hexyl pivalate (5c)

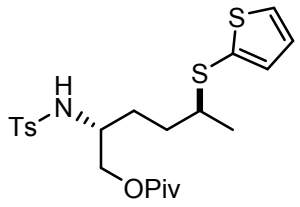


5c

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, J = 6.0 Hz, 1/2×4H, 1/2×4H), 7.75 (t, J = 8.1 Hz, 1/2×4H, 1/2×4H), 7.71 (d, J = 8.1 Hz,2H), 7.70 (d, J = 8.1 Hz, 2H), 7.44–7.50 (m, 1/2×4H, 1/2×4H), 7.41 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.1 Hz, 1/2×4H, 1/2×4H), 4.80 (d, J = 8.4, 1H), 4.79 (d, J = 8.4 Hz,1H), 4.00 (dd, J = 11.4, 4.5 Hz, 1H), 3.97 (dd, J = 11.4, 4.5 Hz, 1H), 3.84 (dd, J = 11.4, 4.5 Hz, 1H), 3.84 (dd, J = 11.4, 4.5 Hz, 1H), 3.44–3.50 (m, 1/2×2H, 1/2×2H), 3.13–3.23 (m, 1/2×2H, 1/2×2H), 2.37 (s, 3H), 2.36 (s, 3H),1.68–1.73 (m, 1/2×2H, 1/2×2H), 1.58–1.63 (m, 1/2×2H, 1/2×2H), 1.43–1.54 (m, 1/2×4H, 1/2×4H), 1.21 (t, J = 6.5 Hz, 1/2×6H, 1/2×6H), 1.15 (s, 9H), 1.14 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.19 (C×2), 143.53, 143.52, 137.92, 137.89, 133.66, 133.66 (C×2), 132.25, 132.18, 130.54, 130.52, 129.74, 129.73, 129.56 (C×2), 128.34 (C×2), 127.66 (C×2), 127.29, 127.28, 126.91 (C×3), 126.53, 126.51, 126.05 (C×2), 65.59, 65.50, 53.03, 52.67, 43.05, 42.85, 38.83 (C×2), 32.29, 32.19, 29.53, 29.51, 27.11 (C×2),

21.44, 21.43, 21.14 (C×2). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{28}H_{35}NNaO_4S_2$, 536.1900; found, 536.1894. **IR** (KBr, cm^{-1}): ν 3449, 3279, 3053, 1729, 1160, 666.

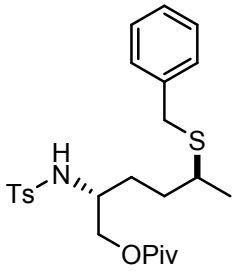
(2*S*)-2-((4-methylphenyl)sulfonamido)-5-(thiophen-2-ylthio)hexyl pivalate (5d)



5d

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 5.4 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 3.4 Hz, 1H), 6.99–7.02 (m, 1H), 4.57 (d, J = 8.4 Hz, 1H), 4.00 (dd, J = 11.4, 4.2 Hz, 1H), 3.85 (dd, J = 11.4, 4.2 Hz, 1H), 3.45–3.50 (m, 1H), 2.71–2.77 (m, 1H), 2.41 (s, 3H), 1.59–1.67 (m, 2H), 1.37–1.44 (m, 1H), 1.29–1.35 (m, 1H), 1.17 (s, 9H), 1.15 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.22, 143.60, 137.92, 135.51, 131.63, 130.15, 129.80, 127.61, 126.99, 65.71, 52.66, 45.70, 38.89, 31.66, 29.64, 27.17, 21.50, 21.41. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{31}NNaO_2S_2$, 492.1307; found, 492.1303. **IR** (KBr, cm^{-1}): ν 3458, 2920, 1729, 1637, 1161, 667.

(2*S*)-5-(benzylthio)-2-((4-methylphenyl)sulfonamido)hexyl pivalate (5e)

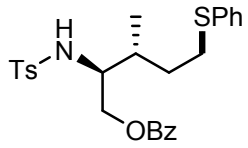


5e

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H),7.28–7.31 (m, 1/2×12H, 1/2×12H), 7.20–7.25 (m, 1/2×2H, 1/2×2H), 4.62 (d, J = 8.4 Hz, 1H), 4.59 (d, J = 8.4 Hz, 1H), 3.93 (dd, J = 12.0, 4.2 Hz, 1H), 3.92 (dd, J = 12.0, 4.2 Hz, 1H), 3.79 (dd, J = 12.0, 4.2 Hz, 1H), 3.78 (dd, J = 12.0, 4.2 Hz, 1H), 3.66 (s, 1/2×4H, 1/2×4H), 3.40–3.45 (m, 1H), 3.32–3.36 (m, 1H), 2.51–

2.55 (m, 1H), 2.44–2.50 (m, 1H), 2.41 (s, 1/2×6H, 1/2×6H), 1.50–1.60 (m, 1/2×4H, 1/2×4H), 1.34–1.41 (m, 1/2×4H, 1/2×4H), 1.16 (s, 1/2×18H, 1/2×18H), 1.15 (d,*J* = 7.8 Hz, 3H), 1.14 (d,*J* = 7.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.19 (C×2), 143.55, 143.53, 138.66, 138.58, 138.09, 138.02, 129.76, 129.75, 128.76 (C×2), 128.48, 128.46, 126.94(C×3), 126.92, 65.71, 65.52, 53.15, 52.61, 39.31, 38.85, 34.93, 34.75, 32.35, 32.06, 29.68 (C×2), 29.36, 29.32, 27.14 (C×2), 21.48, 21.37, 21.15 (C×2). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{35}NNaO_4S_2$, 500.1900; found, 500.1984. **IR** (KBr, cm^{-1}): ν 3506, 3446, 3289, 1730, 1161, 667.

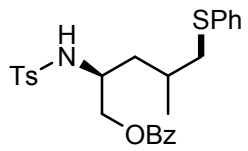
(2*R*,3*S*)-3-methyl-2-((4-methylphenyl)sulfonamido)-5-(phenylthio)pentylbenzoate(5f)



5f

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.27–7.31 (m, 4H), 7.16–7.21 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 4.89 (d, *J* = 8.4 Hz, 1H), 4.27 (dd, *J* = 11.7, 6.3 Hz, 1H), 4.10 (dd, *J* = 11.7, 6.3 Hz, 1H), 3.47–3.51 (m, 1H), 3.00 (ddd, *J* = 12.8, 8.7, 7.2 Hz, 1H), 2.84 (ddd, *J* = 12.8, 8.7, 7.2 Hz, 1H), 2.29 (s, 3H), 1.99–2.05 (m, 1H), 1.77–1.83 (m, 1H), 1.42–1.49 (m, 1H), 0.96 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.36, 143.36, 137.62, 136.11, 133.26, 129.67, 129.66, 129.34, 129.32, 128.94, 128.36, 126.88, 126.09, 63.90, 57.16, 34.85, 32.06, 31.46, 21.47, 15.17. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{29}NNaO_4S_2$, 506.1430; found, 506.1426. **IR** (KBr, cm^{-1}): ν 3420, 1720, 1617, 1161, 614.

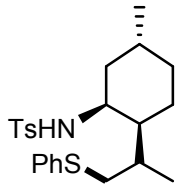
(2*R*)-4-methyl-2-((4-methylphenyl)sulfonamido)-5-(phenylthio)pentyl benzoate (5g)



5g

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.28–7.32 (m, 4H), 7.17–7.24 (m, 1H), 7.14 (d, J = 8.1 Hz, 2H), 4.58 (d, J = 8.7 Hz, 1H), 4.23 (dd, J = 11.4, 4.5 Hz, 1H), 4.12 (dd, J = 11.4, 4.5 Hz, 1H), 3.64–3.70 (m, 1H), 2.83 (dd, J = 12.9, 6.1 Hz, 1H), 2.74 (dd, J = 12.9, 6.1 Hz, 1H), 2.34 (s, 3H), 1.79–1.88 (m, 1H), 1.68–1.72 (m, 1H), 1.31–1.39 (m, 1H), 0.87 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.22, 143.43, 137.70, 137.46, 136.55, 133.25, 129.66, 129.53, 129.39, 129.02, 128.42, 126.97, 126.17, 66.91, 51.10, 41.37, 38.88, 29.49, 21.48, 19.24. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{29}NNaO_4S_2$, 506.1430; found, 506.1430. **IR** (KBr, cm^{-1}): ν 3685, 3411, 3083, 1721, 1159, 749.

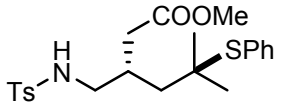
_N_-((1_S_,2_S_,5_R_)-5-methyl-2-((_S_)-1-(phenylthio)propan-2-yl)cyclohexyl)-4-methyl benzenesulfonamide (5h)



5h

White solid. mp: 123.3–124.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 4.50 (d, J = 9.3 Hz, 1H), 3.64 (dd, J = 9.3, 2.8 Hz, 1H), 2.92 (d, J = 5.1 Hz, 2H), 2.39 (s, 3H), 1.80–1.83 (m, 1H), 1.67–1.73 (m, 2H), 1.33–1.41 (m, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.76–0.91 (m, 3H), 0.69 (d, J = 6.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.32, 138.47, 137.42, 129.66, 129.03, 128.80, 126.95, 125.59, 51.26, 43.58, 39.28, 38.66, 34.31, 33.54, 26.09, 24.32, 21.90, 21.49, 17.27. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{31}NNaO_2S_2$, 400.1688; found, 400.1683. **IR** (KBr, cm^{-1}): ν 3506, 3439, 1631, 749.

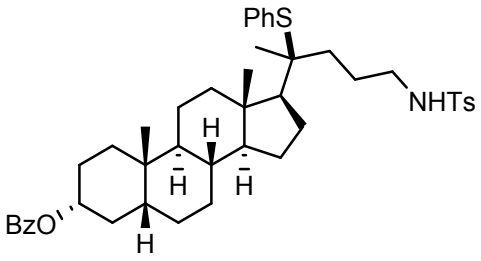
Methyl(_R_)-5-methyl-3-(((4-methylphenyl)sulfonamido)methyl)-5-(phenylthio)hexanoate (5i)



5i

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 8.4 Hz, 4H), 4.95 (t, J = 6.3 Hz, 1H), 3.64 (s, 3H), 3.01–3.07 (m, 1H), 2.89–2.95 (m, 1H), 2.49 (dd, J = 15.9, 4.8 Hz, 1H), 2.38–2.43 (m, 1H), 2.41 (s, 3H), 2.31–2.36 (m, 1H), 1.54 (dd, J = 15.0, 4.8 Hz, 1H), 1.47 (dd, J = 15.0, 4.8 Hz, 1H), 1.19 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.15, 143.34, 137.37, 137.01, 131.65, 129.69, 128.85, 128.56, 127.08, 51.68, 49.06, 47.63, 44.09, 38.20, 32.06, 29.50, 28.96, 21.47. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{29}NNaO_4S_2$, 458.1430; found, 451432.**IR** (KBr, cm^{-1}): ν 3745, 3561, 3420, 3236, 1734, 1160, 616.

(3*R*,5*R*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-10,13-dimethyl-17-(5-((4-methylphenyl)sulfonamido)-2-(phenylthio)pentan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (5j)

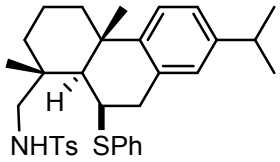


5j

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.39–7.46 (m, 4H), 7.27–7.38 (m, 5H), 4.92–5.01 (m, 1H), 4.31 (t, J = 6.3 Hz, 1H), 2.91 (dd, J = 13.8, 6.9 Hz, 2H), 2.42 (s, 3H), 1.80–1.95 (m, 7H), 1.59–1.72 (m, 5H), 1.50–1.55 (m, 2H), 1.38–1.44 (m, 4H), 1.35–1.38 (m,1H), 1.30–1.33 (m, 1H), 1.21 (s, 3H), 1.15 (d, J = 4.9 Hz, 2H), 1.06–1.12 (m, 3H), 0.95 (s, 3H), 0.88–0.92 (m, 2H), 0.82 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.14, 143.35, 137.50, 137.10, 132.68, 130.94, 129.69, 129.52, 128.57, 128.47, 128.25, 127.13, 127.11, 74.92, 57.37, 56.58, 44.32, 43.59, 41.89, 40.78, 40.38, 38.26, 35.35,

35.06, 34.63, 32.37, 27.03, 26.75, 26.14, 25.37, 24.35, 23.93, 23.85, 23.71, 23.32, 21.52, 20.73, 14.90. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{44}H_{57}NNa_4S_2$, 750.3621; found, 750.3620. **IR** (KBr, cm^{-1}): ν 3692, 3467, 3410, 3064, 1715, 1566, 750.

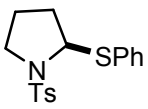
***N*-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-10-(phenylthio)-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-methylbenzenesulfonamide (5k)**



5k

White solid. mp: 157.3–158.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.27–7.31 (m, 3H), 7.20–7.23 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.10 (s, 2H), 6.90 (s, 1H), 5.69 (dd, J = 15.3, 5.1 Hz, 1H), 3.53 (t, J = 6.0 Hz, 1H), 3.34 (dd, J = 15.6, 6.0 Hz, 1H), 2.94 (dd, J = 13.2, 5.1 Hz, 1H), 2.87 (sept, J = 6.9 Hz, 1H), 2.75 (d, J = 15.3 Hz, 1H), 2.67 (dd, J = 13.2, 10.2 Hz, 1H), 2.35 (s, 3H), 2.12 (d, J = 12.9 Hz, 1H), 1.71–1.87 (m, 3H), 1.54–1.63 (m, 1H), 1.29–1.38 (m,2H), 1.25 (d, J = 6.9 Hz, 6H), 1.24 (s, 3H), 1.12 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.59, 146.19, 142.84, 137.38, 134.94, 133.90, 131.52, 129.54, 129.16, 127.45, 127.40, 126.86, 124.76, 121.38, 53.88, 50.59, 45.06, 38.74, 38.61, 38.18, 35.93, 35.59, 33.51, 24.06, 23.99, 22.32, 21.43, 20.02, 18.03. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{33}H_{41}NNaO_2S_2$, 570.2471; found, 570.2470. **IR** (KBr, cm^{-1}): ν 3686, 3409, 1729, 1572, 1161, 617.

2-(phenylthio)-1-tosylpyrrolidine (7a)

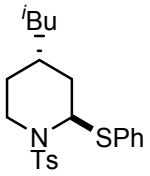


7a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.47 (dd, J = 6.3, 3.0 Hz, 2H), 7.29–7.33 (m, 3H), 7.28 (d, J = 8.1 Hz, 2H), 5.38 (d, J = 6.3 Hz, 1H), 3.32–3.39 (m, 2H), 2.42 (s, 3H), 1.90–2.00 (m, 3H), 1.75–1.81 (m, 1H). **^{13}C NMR**

(150 MHz, $CDCl_3$) δ 143.53, 136.14, 134.14, 133.38, 129.58, 128.99, 128.10, 127.60, 68.98, 47.79, 34.12, 23.55, 21.52. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{19}NNaO_2S_2$, 356.0749; found, 356.0758. **IR** (KBr, cm^{-1}): ν 3710, 3553, 3475, 3412, 1747, 1616, 663.

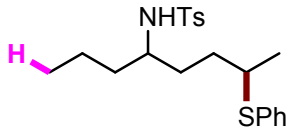
(4*S*)-4-isobutyl-2-(phenylthio)-1-tosylpiperidine (7b)



7b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 2H), 7.44 (dd, J = 6.5, 1.8 Hz, 2H), 7.27–7.31 (m, 3H), 7.18 (d, J = 8.1 Hz, 2H), 5.78 (s, 1H), 3.64–3.66 (m, 1H), 3.21–3.30 (m, 1H), 2.39 (s, 3H), 1.93–1.99 (m, 2H), 1.62–1.65 (m, 1H), 1.54–1.61 (m, 1H), 1.45 (td, J = 12.7, 4.5 Hz, 1H), 1.05–1.12 (m, 1H), 0.97–1.05 (m, 2H), 0.85 (d, J = 6.6 Hz, 6H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.16, 136.99, 133.62, 133.46, 129.40, 129.04, 127.80, 127.58, 65.02, 45.61, 41.32, 38.12, 31.66, 28.09, 24.44, 22.77, 22.55, 21.49. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{29}NNaO_2S_2$, 426.1532; found, 426.1530. **IR** (KBr, cm^{-1}): ν 3552, 3480, 3414, 3234, 1617, 1158, 614.

***N*-(7-(phenylthio)octan-4-yl)-4-methylbenzenesulfonamide (9a)**

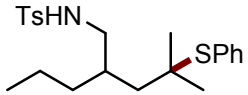


9a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.31–7.35 (m, 1/2×4H, 1/2×4H), 7.25–7.30 (m, 1/2×8H, 1/2×8H), 7.23 (t, J = 7.2 Hz, 1/2×2H, 1/2×2H), 4.35 (d, J = 8.4 Hz, 1H), 4.34 (d, J = 8.4 Hz, 1H), 3.17–3.24 (m, 1/2×2H, 1/2×2H), 2.98–3.10 (m, 1/2×2H, 1/2×2H), 2.40 (s, 1/2×6H, 1/2×6H), 1.56–1.62(m, 1/2×2H, 1/2×2H), 1.35–1.49 (m, 1/2×6H,

1/2×6H), 1.29–1.35 (m, 1/2×2H,1/2×2H),1.18–1.28 (m,1/2×4H, 1/2×4H), 1.11–1,18 (m, 1/2×2H, 1/2×2H), 1.15 (d, J = 6.9 Hz,3H), 1.14 (d, J = 6.9 Hz,3H), 0.77 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.17 (C×2), 138.35, 138.32, 134.99, 134.98, 132.06, 132.01, 129.57 (C×2), 128.81, 128.80, 127.01 (C×2), 126.82 (C×2), 53.91, 53.55, 43.23, 43.08, 37.32, 37.29, 32.22 (C×2), 32.08, 32.01, 21.46, 21.37, 21.07 (C×2), 18.45, 18.44, 13.75 (C×2). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{29}NNaO_2S_2$, 414.1532; found, 414.1522. **IR** (KBr, cm^{-1}): ν 3682, 3437, 3279, 1719, 1159, 666.

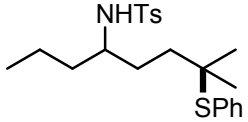
***N*-(4-methyl-4-(phenylthio)-2-propylpentyl)-4-methylbenzenesulfonamide (9b)**



9b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.45(d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.28–7.32 (m, 4H), 4.62 (t, J = 6.3 Hz, 1H), 2.96 (dt, J = 12.0, 6.0 Hz, 1H), 2.88 (dt, J = 12.6, 6.3 Hz, 1H), 2.41 (s, 3H), 1.77 (dt, J = 11.1, 5.4 Hz, 1H), 1.49 (dd, J = 14.7, 5.4 Hz, 1H), 1.42 (dd, J = 14.7, 5.4 Hz, 1H), 1.25–1.34 (m, 2H), 1.18–1.25 (m, 2H), 1.16 (s, 6H), 0.85 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.28, 137.41, 137.06, 131.90, 129.65, 128.75, 128.50, 127.17, 49.41, 47.26, 44.77, 35.98, 34.44, 29.68, 28.90, 21.46, 19.60, 14.21. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{31}NNaO_2S_2$, 428.1688; found, 428.1679. **IR** (KBr, cm^{-1}): ν 3695, 3523, 3438, 3297, 3079, 1717, 1572, 666.

***N*-(7-methyl-7-(phenylthio)octan-4-yl)-4-methylbenzenesulfonamide (9c)**

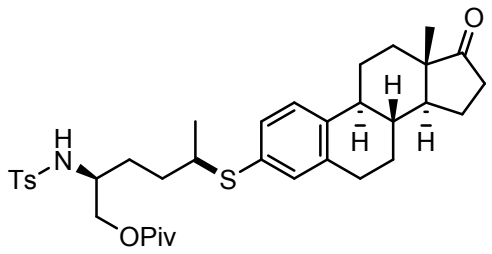


9c

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H),

4.30 (d, *J* = 8.7 Hz, 1H), 3.15 (dt, *J* = 8.7, 6.3 Hz, 1H), 2.38 (s, 3H), 1.60–1.64 (m, 1H), 1.44–1.51 (m, 1H), 1.34–1.41 (m, 1H), 1.24–1.32 (m, 3H), 1.13–1.18 (m, 2H), 1.09 (s, 3H), 1.08 (s, 3H), 0.80 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 143.11, 138.39, 137.34, 132.09, 129.53, 128.74, 128.52, 127.04, 54.29, 48.73, 37.69, 37.61, 30.18, 28.85, 28.71, 21.43, 18.53, 13.80. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{31}NNaO_2S_2$, 428.1688; found, 428.1702. **IR** (KBr, cm^{-1}): ν 3697, 3563, 2958, 1734, 1159.

(2*S*)-5-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)thio)-2-((4-methylphenyl)sulfonamido)hexyl pivalate (11a)

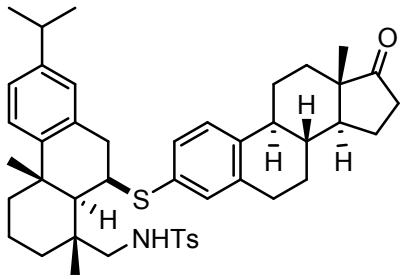


11a

White solid. mp: 73.6–74.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 1/2×4H, 1/2×4H), 7.21 (d, *J* = 8.1 Hz, 1/2×2H, 1/2×2H), 7.09–7.13 (m, 1/2×4H, 1/2×4H), 4.63 (d, *J* = 8.7 Hz, 1H), 4.60 (d, *J* = 8.7 Hz, 1H), 3.97 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.95 (dd, *J* = 11.4, 4.5 Hz, 1H),3.83 (dd, *J* = 9.3, 4.5 Hz, 1H), 3.80 (dd, *J* = 9.3, 4.5 Hz, 1H), 3.42–3.50 (m, 1/2×2H, 1/2×2H), 3.00–3.09 (m, 1H), 2.95–3.00 (m, 1H), 2.87–2.91 (m, 1/2×4H, 1/2×4H), 2.38–2.44 (m, 1/2×2H, 1/2×2H), 2.41 (s, 1/2×6H, 1/2×6H), 2.29 (t, *J* = 11.1 Hz, 1H),2.26 (t, *J* = 11.1 Hz, 1H), 1.95–2.19 (m, 1/2×9H, 1/2×9H), 1.41–1.71 (m, 1/2×21H, 1/2×21H), 1.18 (d, *J* = 7.2 Hz, 3H), 1.17 (s, 9H), 1.16 (s, 9H), 1.15 (d, *J* = 7.2 Hz, 3H), 0.91 (s, 1/2×6H, 1/2×6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.71(C×2), 178.19(C×2), 143.58, 143.56, 139.02(C×2), 137.98, 137.96, 137.31, 137.28, 133.02, 132.98, 131.48, 131.43, 129.87, 129.84, 129.78, 129.76, 126.95(C×2), 125.91(C×2),

65.57, 65.50, 53.05, 52.66, 50.51(C×2), 47.95(C×2), 44.28(C×2), 43.16, 42.94, 38.86(C×2), 38.03(C×2), 35.83(C×2), 32.13(C×2), 31.57(C×2), 29.54, 29.37, 29.25, 29.24, 27.15(C×2), 26.38(C×2), 25.64(C×2), 21.57, 21.55(C×2), 21.51, 21.14(C×2), 13.84(C×2). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{36}H_{49}NNaO_5S_2$, 662.2944; found, 662.2943. **IR** (KBr, cm^{-1}): ν3693, 2928, 1736, 1555, 1482.

***N*-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-10-(((8*R*,9*S*,13*S*,14*S*)-8,9,13,14-tetramethyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)thio)-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-methylbenzenesulfonamide (12a)**

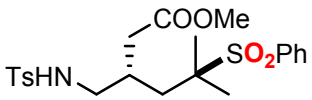


12a

White solid. mp: 115.3–116.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68(d, J = 8.2 Hz, 1/3×2H), 7.65 (d, J = 8.2 Hz, 2/3×2H), 7.29 (d, J = 8.2 Hz, 1/3×2H), 7.23 (d, J = 8.2 Hz, 2/3×2H), 7.13–7.19 (m, 1/3×3H, 2/3×3H), 7.09 (s, 1/3×2H, 2/3×2H), 7.06 (s, 2/3×1H), 7.03 (s, 1/3×1H), 7.01 (s, 1/3×1H), 7.00 (s, 2/3×1H), 6.91 (s, 2/3×1H), 6.59 (s, 1/3×1H), 5.81 (dd, J = 9.8, 5.2 Hz, 2/3×1H), 5.10 (dd, J = 9.8, 5.2 Hz, 1/3×1H), 3.49 (t, J = 6.2 Hz, 2/3×1H), 3.28–3.34 (m, 1/3×2H, 2/3×2H), 2.98–3.04 (m, 1/3×1H), 2.49–2.97 (m, 1/3×8H, 2/3×8H), 2.26–2.44 (m, 1/3×4H, 2/3×4H), 2.41 (s, 1/3×3H), 2.36 (s, 2/3×3H), 1.99–2.21 (m, 1/3×6H, 2/3×6H), 1.41–1.87 (m, 1/3×6H, 2/3×6H), 1.20–1.37 (m, 1/3×8H, 2/3×8H), 1.12 (s, 2/3×3H), 1.02 (s, 1/3×3H), 0.94 (s, 2/3×3H), 0.93 (s, 1/3×3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.55, 220.52, 146.61, 146.57, 146.12, 146.08, 143.03, 142.72, 139.66, 139.59, 137.64, 137.61, 137.58, 137.54, 134.04, 134.00, 133.83, 132.48, 131.74, 129.89, 129.68, 129.54, 129.52, 127.47, 127.42, 126.97, 126.92, 126.84, 126.24, 126.18, 124.74, 124.63, 121.39, 121.31,

54.02, 53.79, 50.80, 50.74, 50.51, 49.98, 47.93, 47.92, 45.22, 44.35, 44.29, 38.91, 38.73, 38.68, 38.62, 38.18, 38.07, 37.99, 36.05, 35.82, 35.39, 34.00, 33.56, 33.50, 31.91, 31.58, 31.42, 30.19, 29.64, 29.35, 29.26, 26.39, 26.33, 25.65, 24.25, 24.05, 24.03, 23.82, 22.67, 22.40, 22.35, 21.59, 21.52, 21.49, 19.98, 19.53, 18.05, 17.94, 14.09, 13.85, 13.82. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{45}H_{57}NNaO_3S_2$, 747.0642; found, 662.2943. **IR** (KBr, cm^{-1}): ν 3693, 3411, 3080, 1735, 1552.

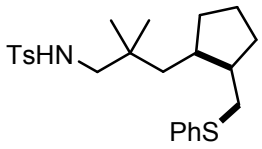
Methyl (R)-5-methyl-3-(((4-methylphenyl)sulfonamido)methyl)-5-(phenylsulfonyl)hexanoate (13a)



13a

White solid. mp: 149.3–150.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$)δ 7.84 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.67 (t, J = 7.5 Hz, 2H), 7.56 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 1H), 5.11 (t, J = 6.6 Hz, 1H), 3.62 (s, 3H), 2.94 (ddd, J =13.2, 6.6, 6.3 Hz, 1H), 2.89 (ddd, J =13.2, 6.6, 6.3 Hz, 1H), 2.41 (s, 3H), 2.39–2.45 (m, 2H), 2.22–2.29 (m, 1H), 1.84 (dd, J = 14.7, 4.8 Hz, 1H), 1.68 (dd, J = 14.7, 4.8 Hz, 1H), 1.27 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.72, 143.45, 136.89, 135.16, 133.74, 130.49, 129.74, 128.82, 126.98, 62.95, 51.71, 47.57, 38.19, 36.39, 31.37, 21.81, 21.46, 21.29. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{29}NNaO_6S_2$, 490.1329; found, 490.1326. **IR** (KBr, cm^{-1}): ν 3704, 3556, 3411, 3064, 1735, 1616, 1553.

***N*-(2,2-dimethyl-3-(2-((phenylthio)methyl)cyclopentyl)propyl)-4-methylbenzenesulfonamide (15a)**

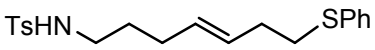


15a

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.58 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H),

5.13 (t, J = 7.0 Hz, 1H), 3.16 (dd, J = 14.0, 5.4 Hz, 1H), 2.91 (dd, J = 14.0, 7.8 Hz, 1H), 2.68 (dd, J = 12.8, 6.5 Hz, 1H), 2.62 (dd, J = 12.8, 6.5 Hz, 1H), 2.41 (s, 3H), 2.37–2.44 (m, 1H), 1.92–1.99 (m, 1H), 1.63–1.75 (m, 2H), 1.49–1.64 (m, 2H), 1.24–1.36 (m, 3H), 0.91–0.95 (m, 1H), 0.89 (s, 3H), 0.83 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.15, 139.88, 137.20, 133.68, 129.65, 129.37, 127.92, 127.02, 56.27, 52.79, 38.33, 37.77, 37.62, 34.38, 31.91, 30.22, 26.36, 25.40, 21.46, 21.41. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{33}NNaO_2S_2$, 454.1845; found, 454.1847. **IR** (KBr, cm^{-1}): ν 3692, 3521, 3438, 3288, 3065, 1719, 1159, 664.

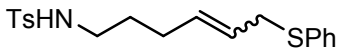
(*E*) *N*-(7-(phenylthio)hept-4-en-1-yl)-4-methylbenzenesulfonamide (17a)



17a

Colorless oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.26–7.32 (m, 6H), 7.15–7.19 (m, 1H), 5.32–5.44 (m, 2H), 4.38 (t, J = 6.0 Hz, 1H), 2.93 (dt, J = 6.0, 13.4 Hz, 2H), 2.89 (t, J = 7.3 Hz, 2H), 2.41 (s, 3H), 2.26–2.32 (m, 2H), 1.97–2.02 (m, 2H), 1.49–1.56 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.35, 136.99, 136.49, 130.67, 129.67, 129.17, 128.86, 127.09, 125.88, 42.56, 33.54, 32.11, 29.41, 29.06, 21.50. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{25}NNaO_2S_2$, 398.1219; found, 398.1216. **IR** (KBr, cm^{-1}): ν 3530, 3421, 2376, 1654, 1166.

(*E*) -*N*-(6-(phenylthio)hex-4-en-1-yl)-4-methylbenzenesulfonamide (19a)

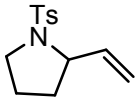


19a

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.29–7.35 (m, 4H), 7.23–7.25 (m, 2H), 7.15–7.17 (m, 1H), 5.37–5.58 (m, 2H), 4.24 (t, J = 5.7 Hz, 1H), 3.46 (d, J = 6.3 Hz, 2H), 2.83 (dt, J = 13.4, 6.6 Hz, 2H), 2.42 (s, 3H), 1.94–1.98 (m, 2H), 1.42–1.47 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.39, 137.06, 135.93,

132.39, 130.06, 129.70, 128.74, 127.08, 126.36, 126.22, 42.42, 36.34, 29.08, 29.04, 21.51. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{23}NNaO_2S_2$, 384.1062; found, 384.1062. **IR** (KBr, cm^{-1}): ν 3831, 3509, 2426, 2338, 1636.

1-tosyl-2-vinylpyrrolidine (20a)

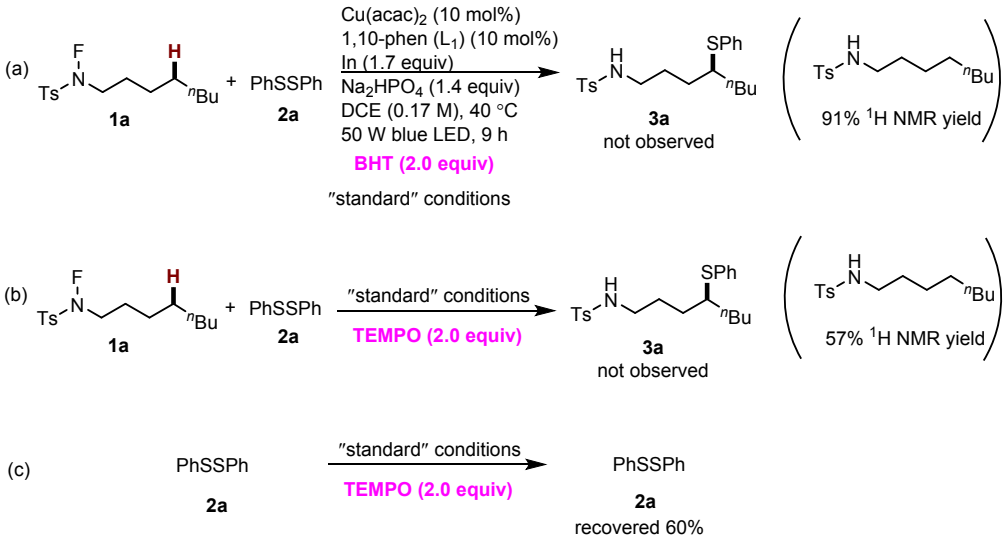


20a

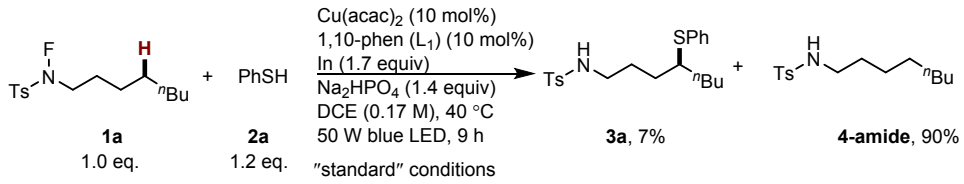
Colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.81 (ddd, J = 16.9, 10.2, 6.0 Hz, 1H), 5.27 (d, J = 16.9 Hz, 1H), 5.12 (d, J = 10.2 Hz, 1H), 4.12–4.15 (m, 1H), 3.45 (ddd, J = 9.9, 7.5, 4.5 Hz, 1H), 3.24 (dt, J = 9.9, 7.5 Hz, 1H), 2.43 (s, 3H), 1.86–1.76 (m, 1H), 1.74–1.65 (m, 2H), 1.65–1.59 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.21, 138.68, 135.21, 129.55, 127.53, 115.28, 61.89, 48.75, 32.28, 23.72, 21.49. **IR** (KBr, cm^{-1}): ν 3704, 3556, 3411, 3064, 1735, 1616, 1553.

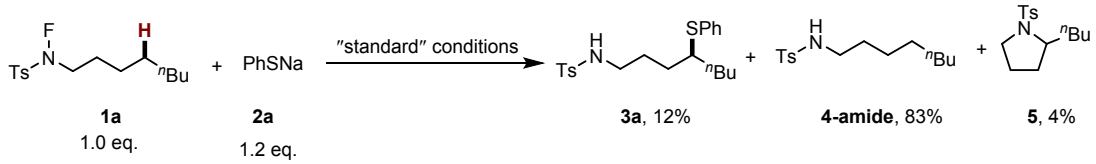
Mechanism Studies:

1. Radical Capture Experiments

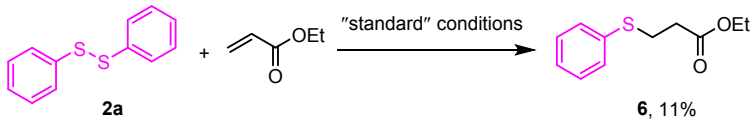


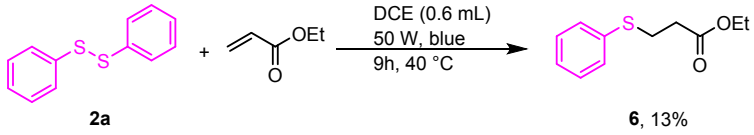
2. Control Experiments



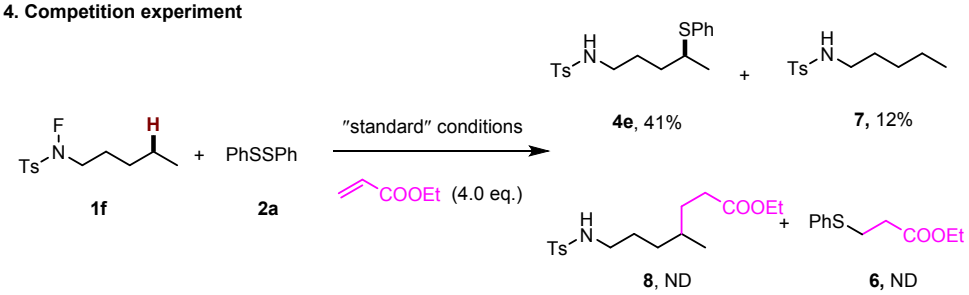


3 Homolytic cleavage of S-S bond under visible light





4. Competition experiment



Results:

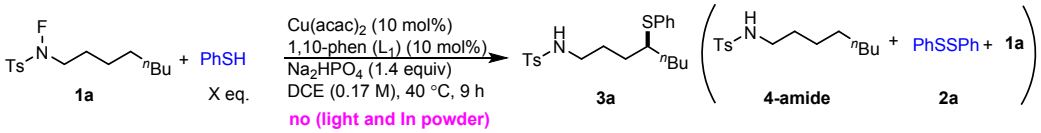
1. By adding TEMPO and 2,6-di-*tert*-butylphenol to the reaction mixture independently, the desired product **3a** can not be observed.
2. The control experiments showed that both of benzenethiol and sodium benzenethiolate could afford thiolation product **3a,** but with low efficiency. The defluoro tosylamide is the major product. Thus, the thiol is a possible intermediate in this reactiton
3. The disulfide **2a** can be traped by a Michael acceptor, giving the Michael addition product **6** under the standard condition, or even only under the

irradiation of the 50 W blue LED (λ = 450 nm). This result indicated that the visible light can promote the homolytic cleavage of S-S bond.

4. The competition experiment between disulfide and ethyl acrylate was carried out. With the additon of 4.0 qeuiv of ethyl acrylate under the standard condition 41% of the thiolated product **4e** was oberved indicated the rate of thiolation is very fast. The copper catalyst maybe locate on the carbon center to promote the C-S bond formation.

Direct use of thiophenol can make the reaction system overall redox neutral. Based on this suggestion, we tested thiophenol as the thiolation reagent in the absence of light and In powder, the results were shown in (Eq.1). Different amounts of thiophenol (0.6-2.0 equiv.) were tested. No any desired product was detected. The disulfide can be obtained under this condition. And also, SM **1a** can be recovered.

(1)

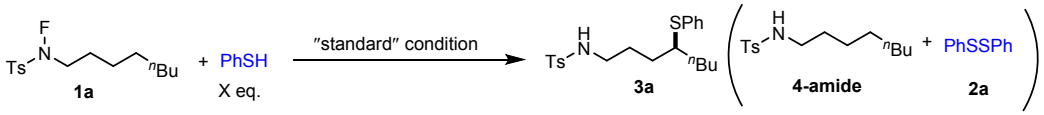


X eq. (PhSH)	**3a** yield	**4-amide** yield	**2a** yield	**1a** yield
2.0	ND	100%	100%	0
1.5	ND	68%	71%	24%
1.2	ND	61%	58%	28%
1.0	ND	45%	49%	51%
0.6	ND	30%	35%	56%

We also test different amounts of thiophenol (0.6-2.0 equiv.) under the standard condition. By using 1.0 equiv. or 0.6 equiv. of thiophenol, 20% or 25% of thiolation product can be obtained (Eq. 2). However, we did not get any disulfide product by using different amounts of thiophenol. Decreasing the amount of thiophenol can increase the product yield, indicated that remained N-F amide may be consumed by the disulfide which generated in situ.

Both of the above results indicated that the disulfide may be the real thiolation reagent.

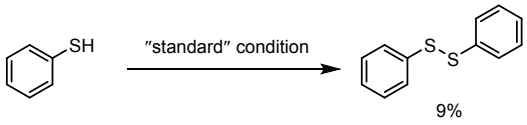
(2)



X eq. (PhSH)	**3a** yield	**4-amide** yield	**2a** yield
2.0	ND	100%	ND
1.5	5%	85%	ND
1.2	7%-13%	90%-80%	ND
1.0	20%	73%	ND
0.6	25%	64%	ND

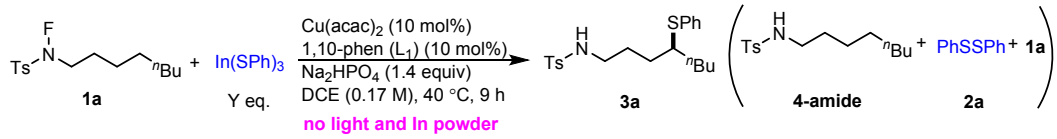
Furthermore, the thiophenol was subject to the "standard condition" in the absence of N-F amide, to confirm whether corresponding disulfide can be generated under this condition. The blank experiment indicated that this hypothesis was possible (Eq. 3).

(3)



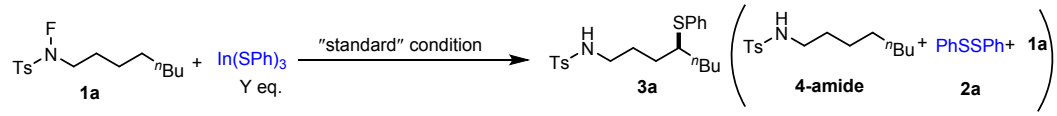
Next, according to the referee's suggestion, the compound $In(SPh)_3$ was prepared and subjected to the reaction system, however there was no any thiolation product could be detected (Eq. 4-5).

(4)



Y eq. $In(SPh)_3$	X eq. SPh	**3a** yield	**4-amide** yield	**2a** yield	**1a** (RSM)
0.67	2.0	ND	100%	100%	0
0.5	1.5	ND	79%	77%	11%
0.4	1.2	ND	57%	62%	32%
0.33	1.0	ND	45%	47%	49%
0.2	0.6	ND	30%	31%	56%

(5)



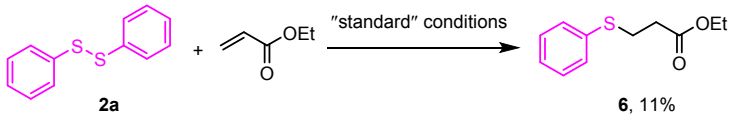
Y eq. $In(SPh)_3$	X eq. SPh	**3a** yield	**4-amide** yield	**2a** yield	**1a** (RSM)
0.67	2.0	ND	100%	ND	ND
0.5	1.5	ND	100%	ND	ND
0.4	1.2	ND	100%	ND	ND
0.33	1.0	ND	100%	ND	ND
0.2	0.6	ND	67%	ND	22%

Above experiments indicated that both of PhSH and $In(SPh)_3$ were not the active thiolation species under this reaction system. Furthermore, we will continue to

explore redox neutral reaction system by using thiophenol based on the refree's construction and insightful suggestion (future plan).

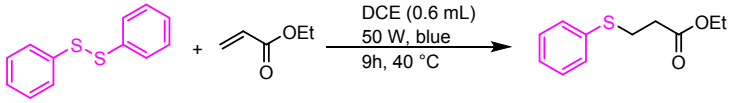
We state that the visible light promotes the homolysis of the S-S bond of sulfide (Eq. 6-7). However, only a small amount of Michael addition product was obtained. This result indicated that may be PhS • radical was not the major active species in this thiolation reaction.

(6)



2a **6**, 11%

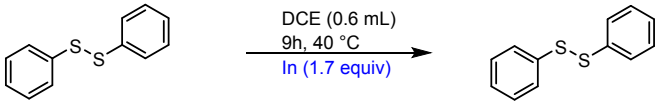
(7)



2a **6**, 13%

We also tested whether In powder could reduce the disulfide to generate PhS • radical (Eq. 8). The blank experiment shown that In powder may not reduce the disulfide.

(8)

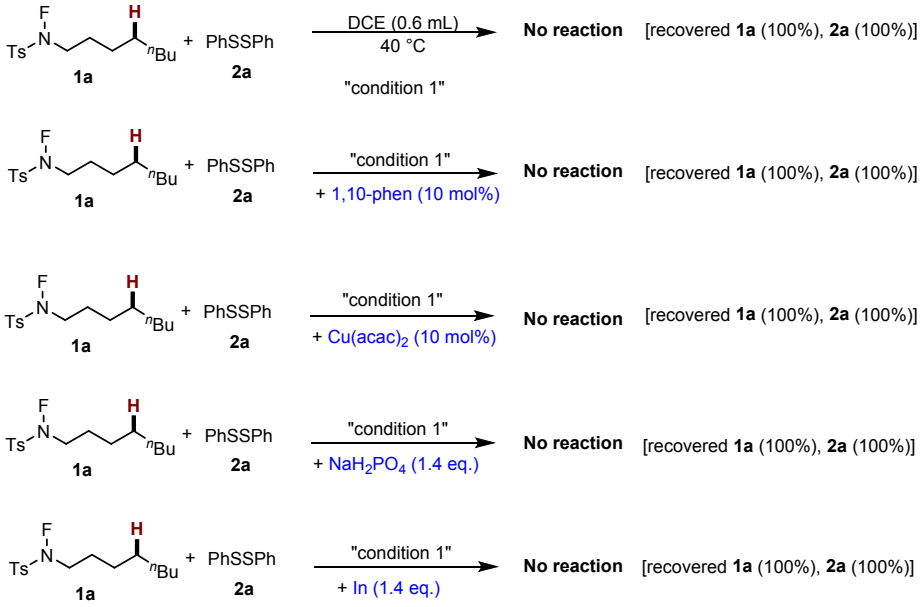


2a **2a**

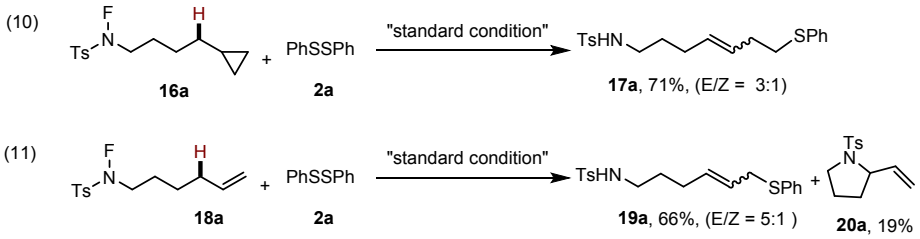
recovered 90%

The blank experiments were carried out to confirm the role of each additives in this reaction condition (Eq. 9). The results indicated that each addition cannot induce this reaction independently.

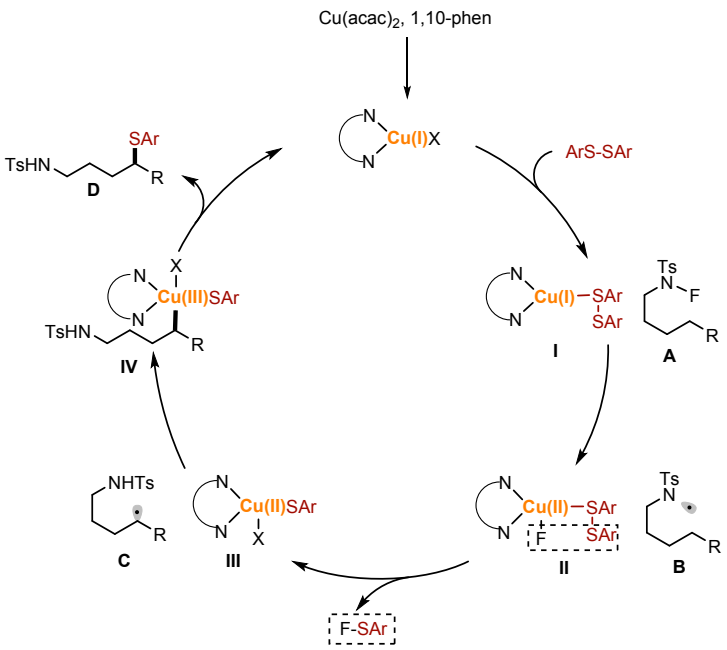
(9). Blank Experiments



Finally, the real radical clock was carried out. We prepared the N-fluoro-tosylamide precursors with a cyclopropyl group (16a) and a double bond (18a) next to the delta-position, and subjected these two substrates to the reaction system. For the cyclopropane 16a, the ring-opened product was obtained, indicating an intramolecular 1,5-HAT process might be involved (Eq. 10). For 18a, 66% of the linear thiolation was obtained (Eq. 11). Based on this result, we considered that the allylic radical (η^1 or η^3), facilitated by the intramolecular 1,5-HAT process, was intercepted by copper catalyst, due to the steric effect, the linear selectivity is major.



Base on the above all experiments, we proposed the possible mechanism. Ligand exchang between an in situ generated Cu(I) catalyst and disulfide was occurred to generate Cu(I)-I species, which may reduce the N–F amide A to afford the N-centered radical B and Cu(II)-II intermediate. The Cu(II)-II release one molecular of PhSF through the metathesis process to afford the Cu(II)-III. Translocation of N-centered radical B to C-centered radical C via 1,5-HAT occurred, and then the δ C-radical was intercepted by the Cu(II)-III to form the Cu(III)-IV intermediate. Finally, the reductive elimination of Cu(III)-IV to give the desired product D and regenerated active Cu(I) catalyst.



References

(1) Z. Zhang, L. M. Stateman and D. A. Nagib, *Chem. Sci*., 2019, **10**, 1207.

(2) Z. Li, Q. Wang and J. Zhu, *Angew. Chem., Int. Ed*., 2018, **57**, 13288.

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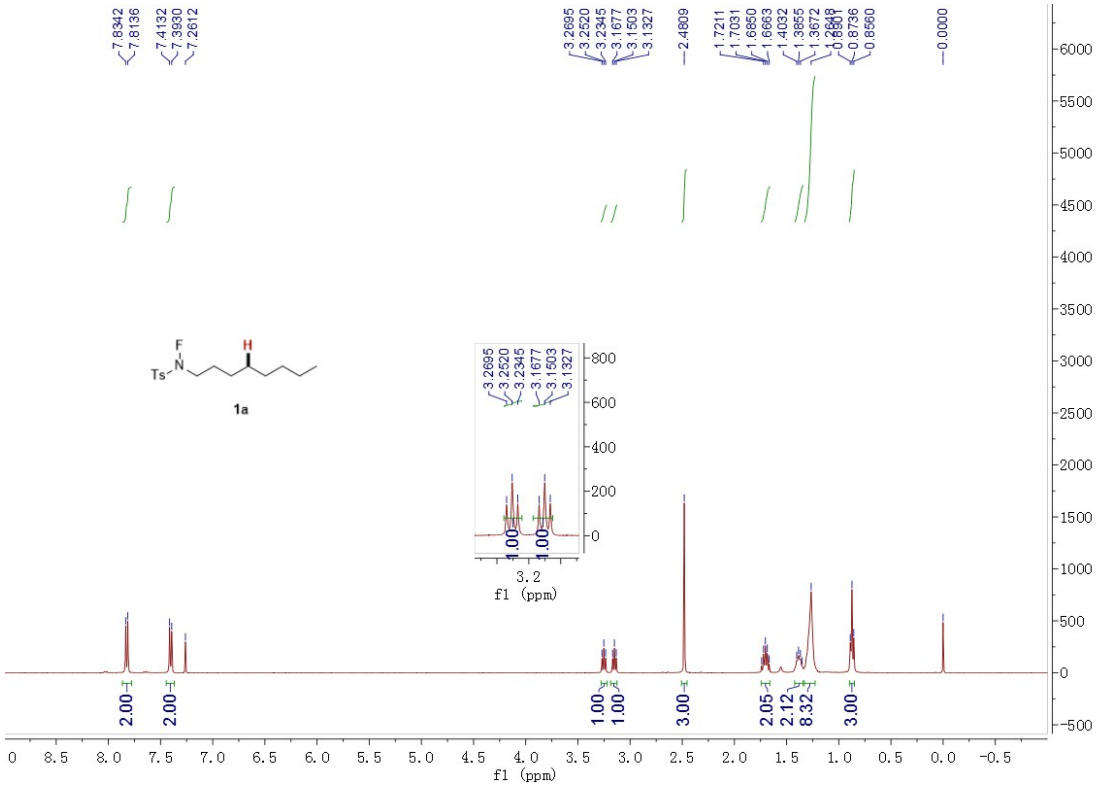
NMR Spectra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1.7031
1.6850
1.6683
1.4032
1.3855
1.3672
0.8736
0.8560
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1.00
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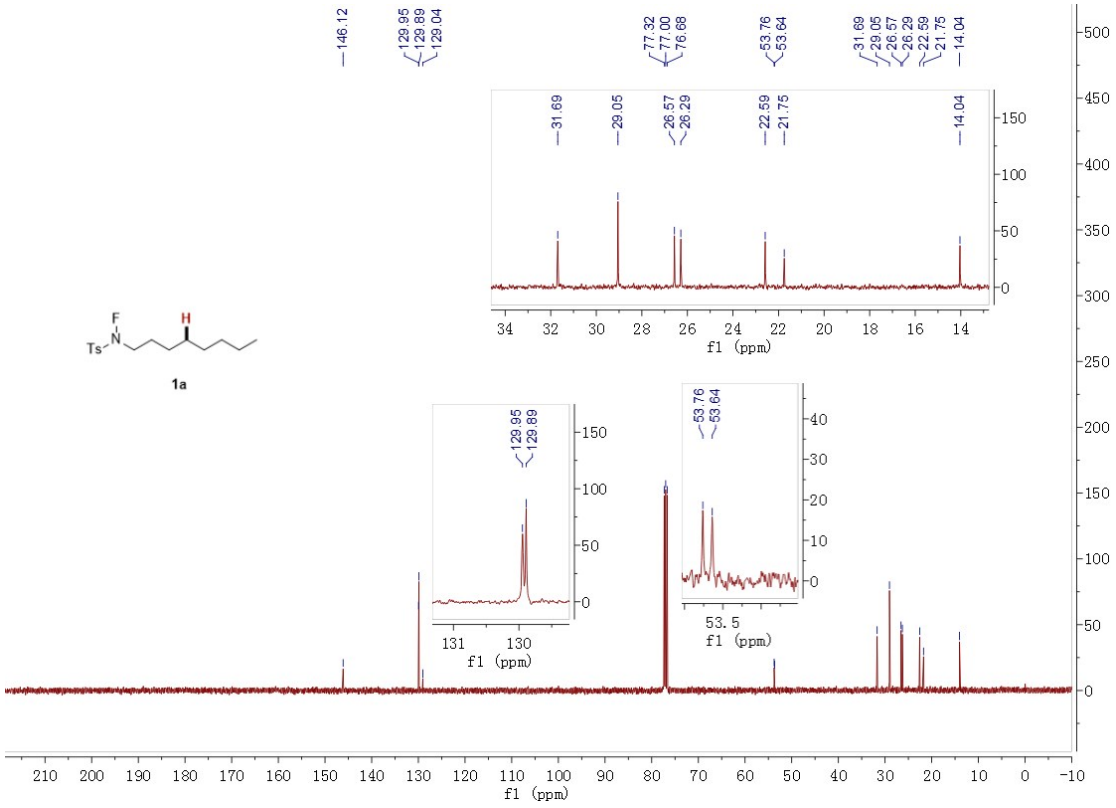
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22.59
21.75
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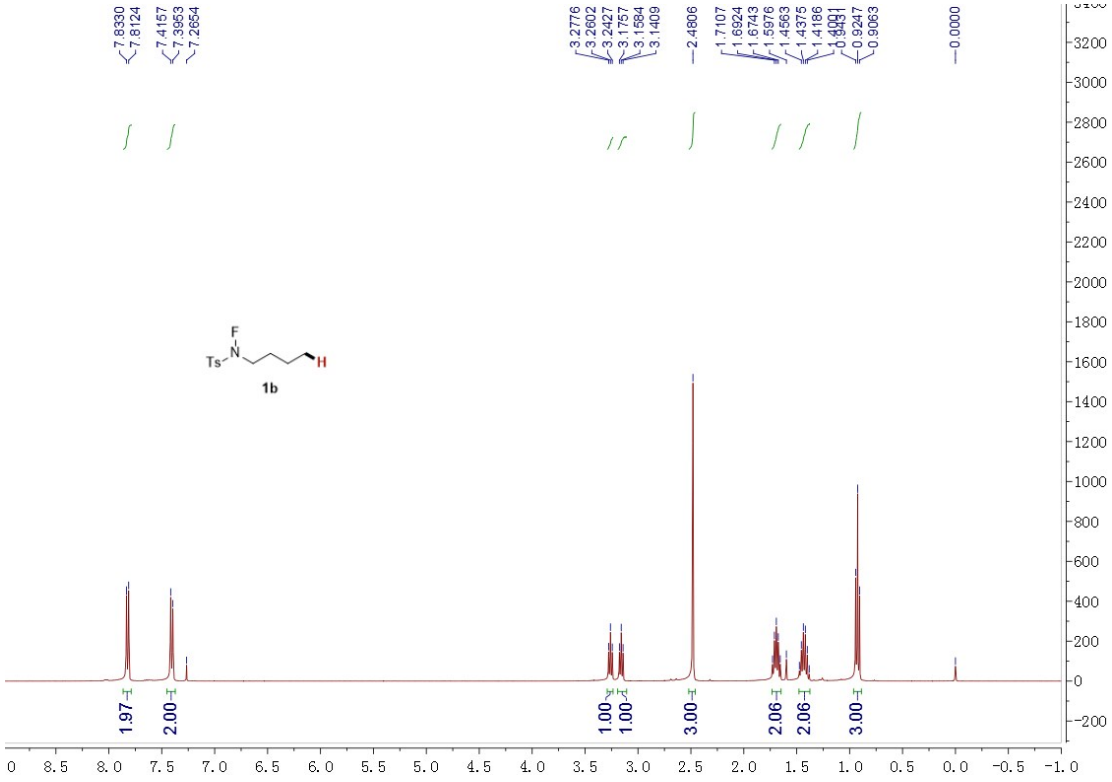
f1 (ppm)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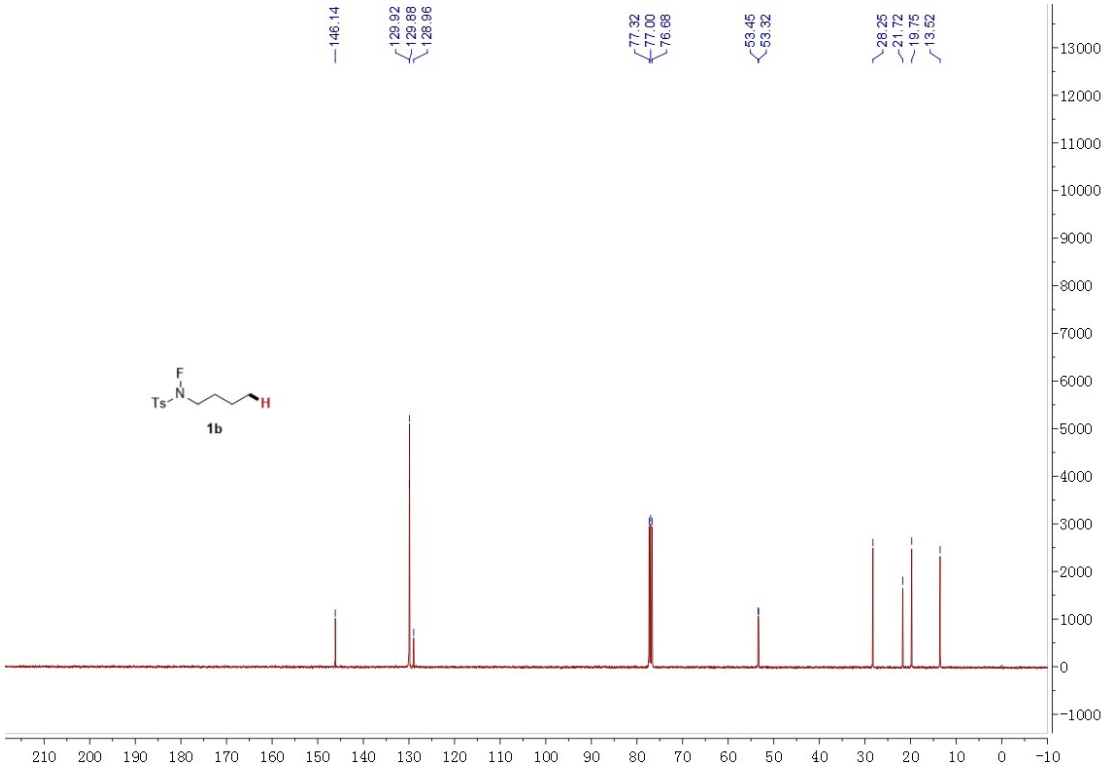
3.00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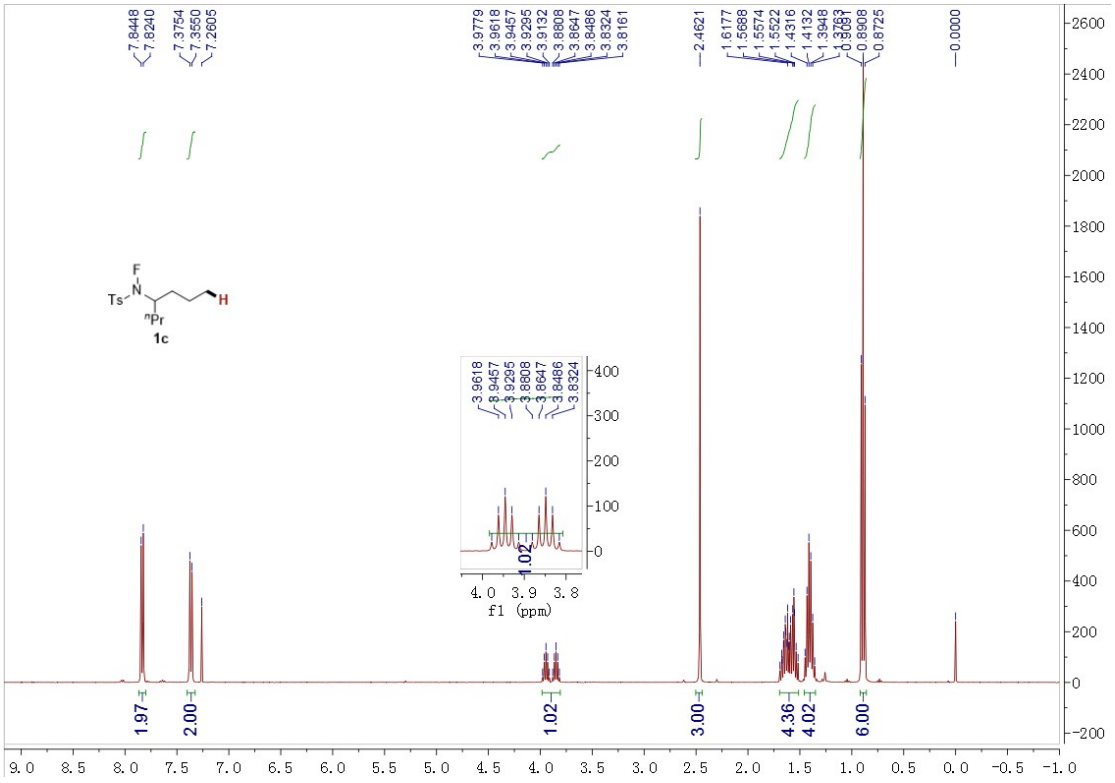
N
Ts
H
1b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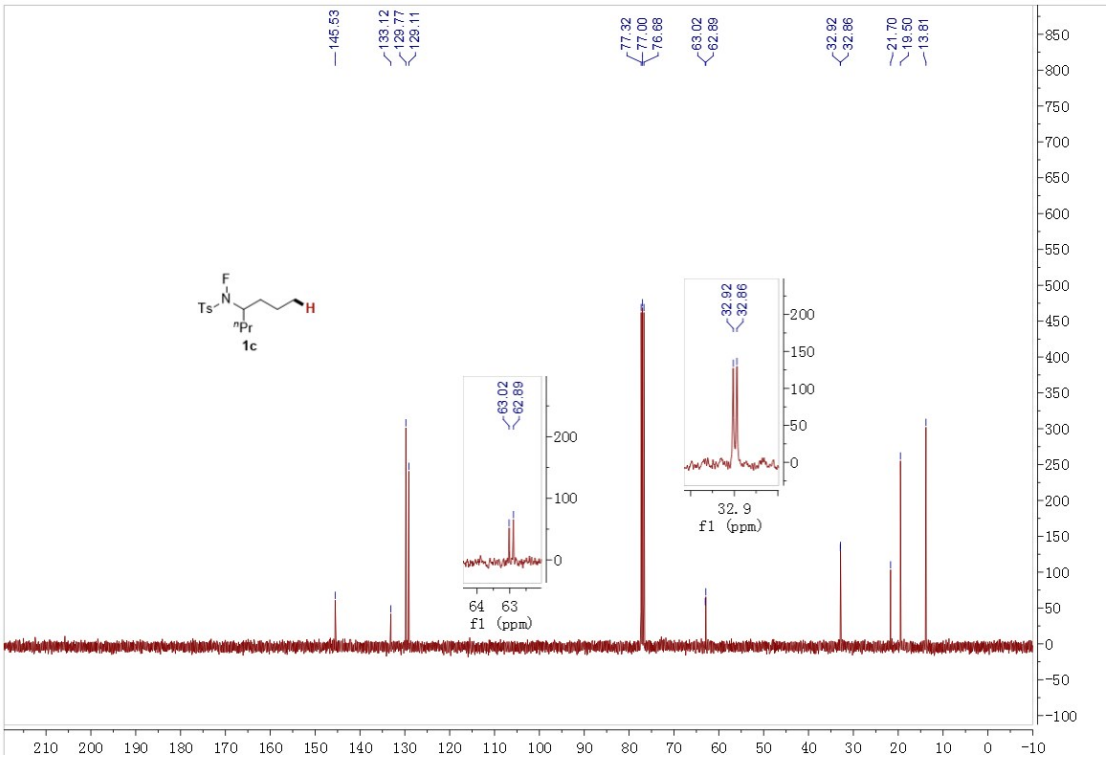
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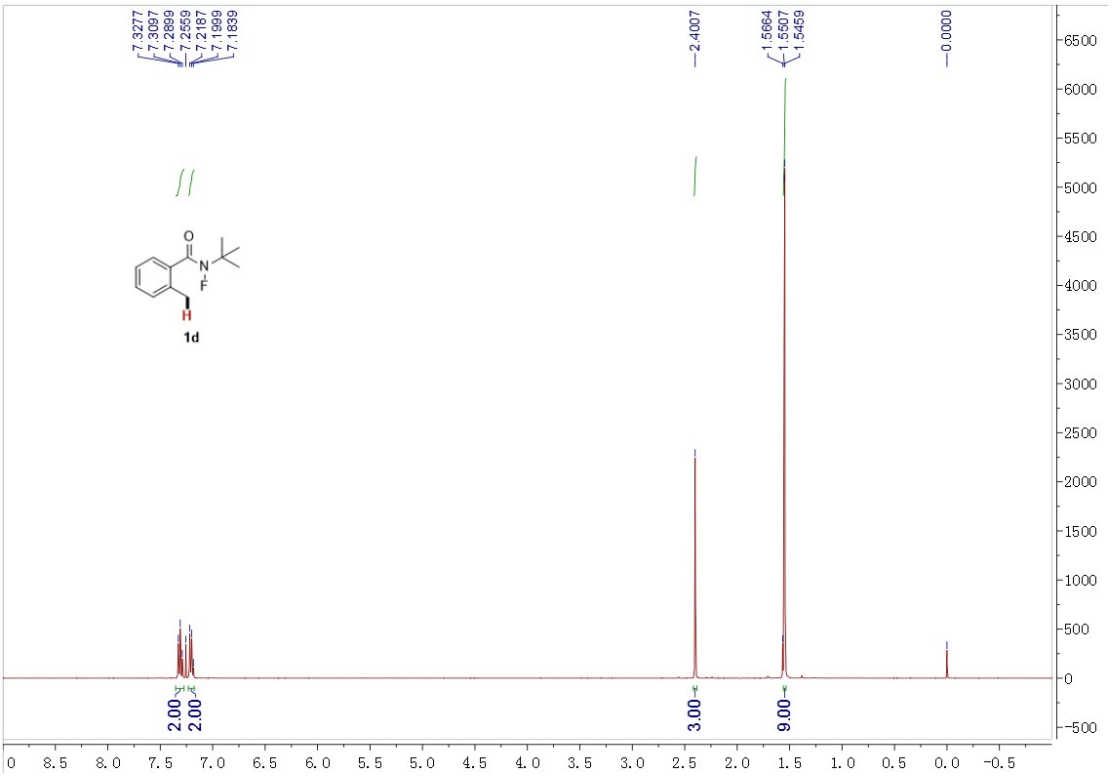
32.9
f1 (ppm)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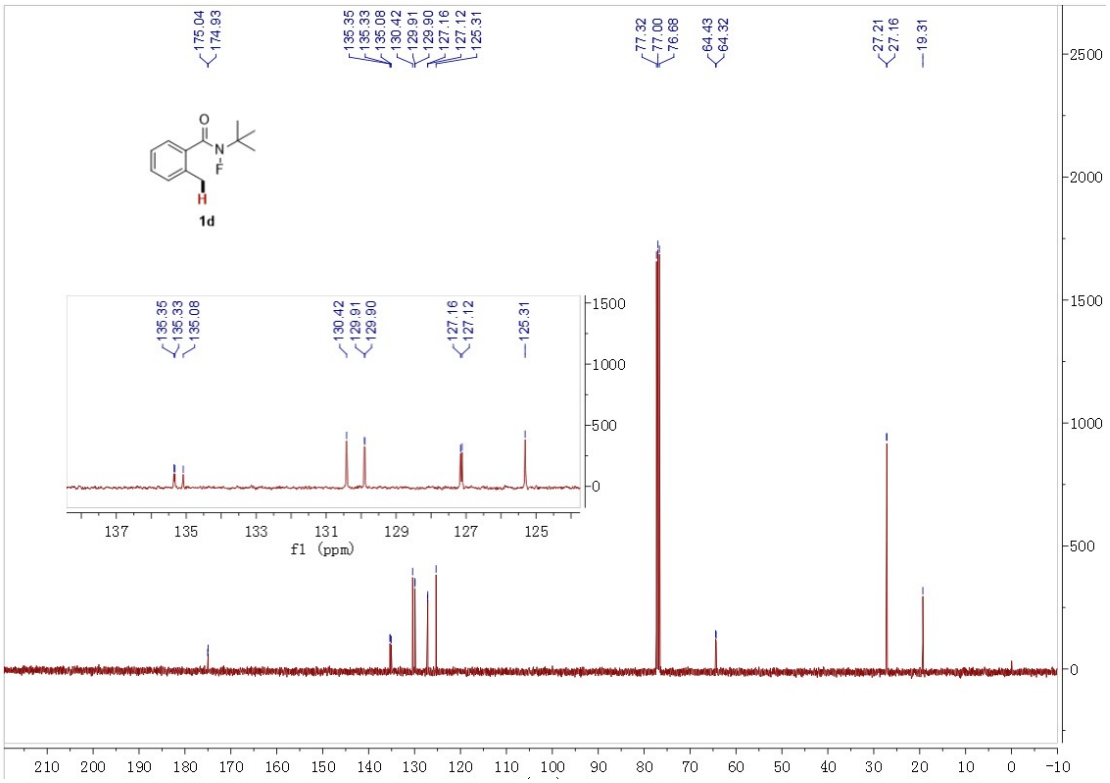
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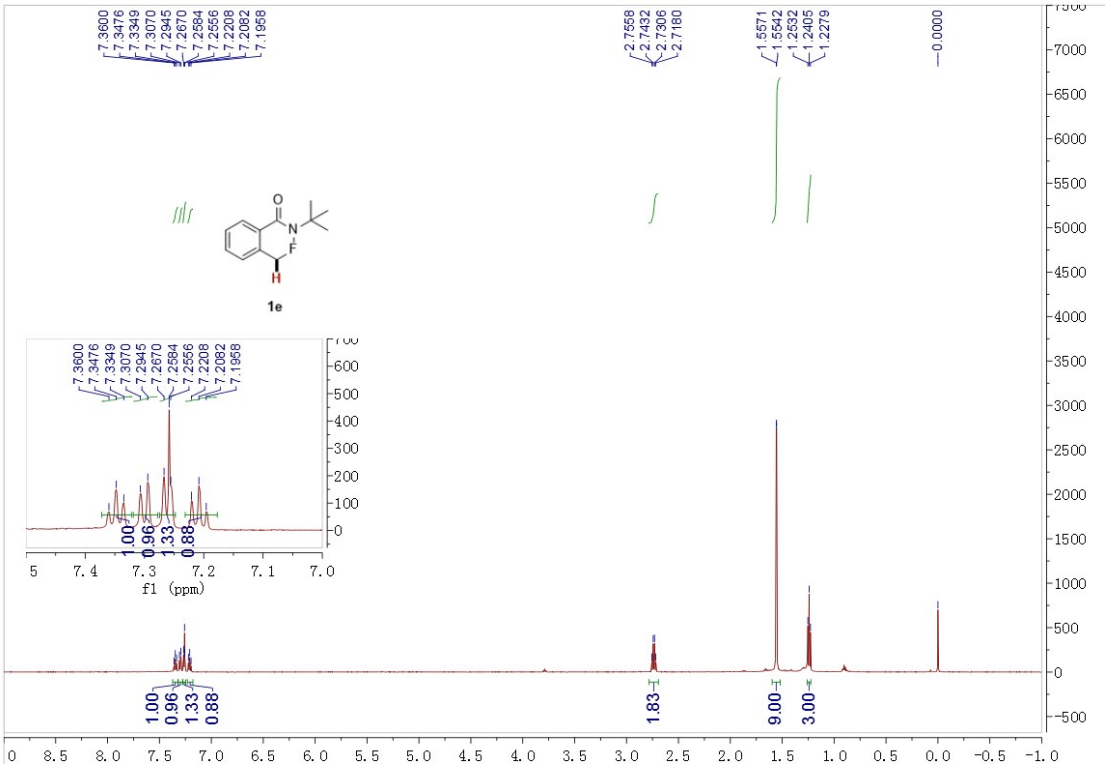
f1 (ppm)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7.1958
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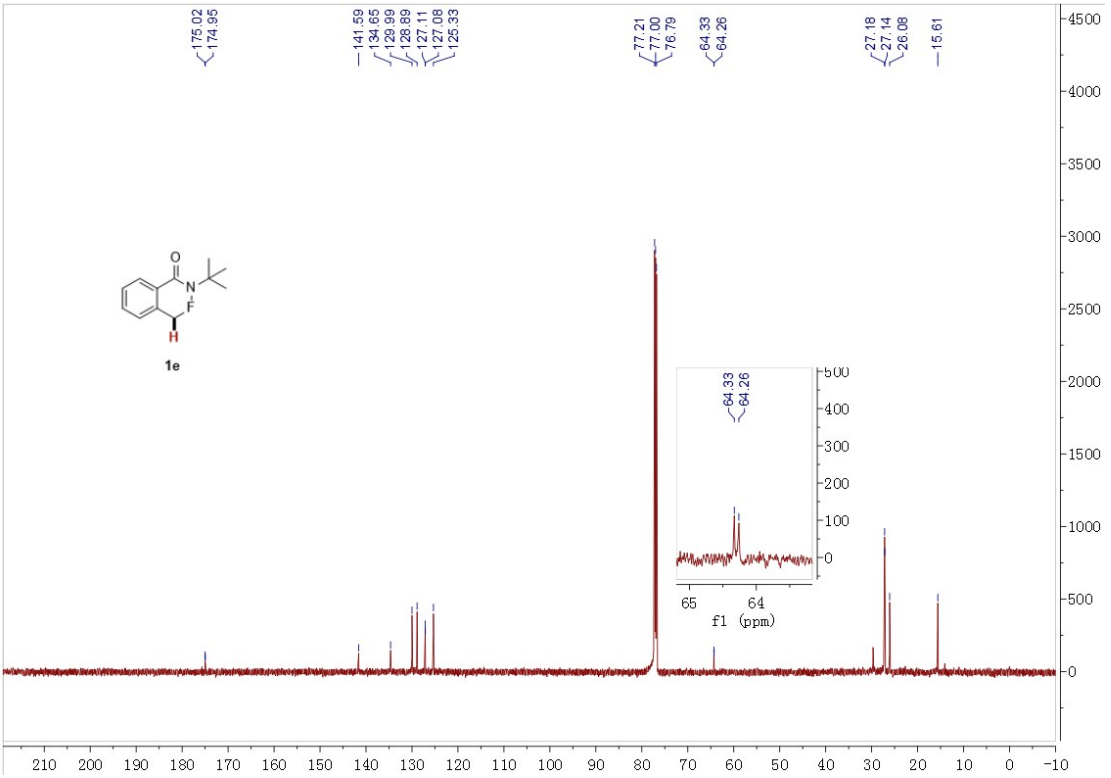
f1 (ppm)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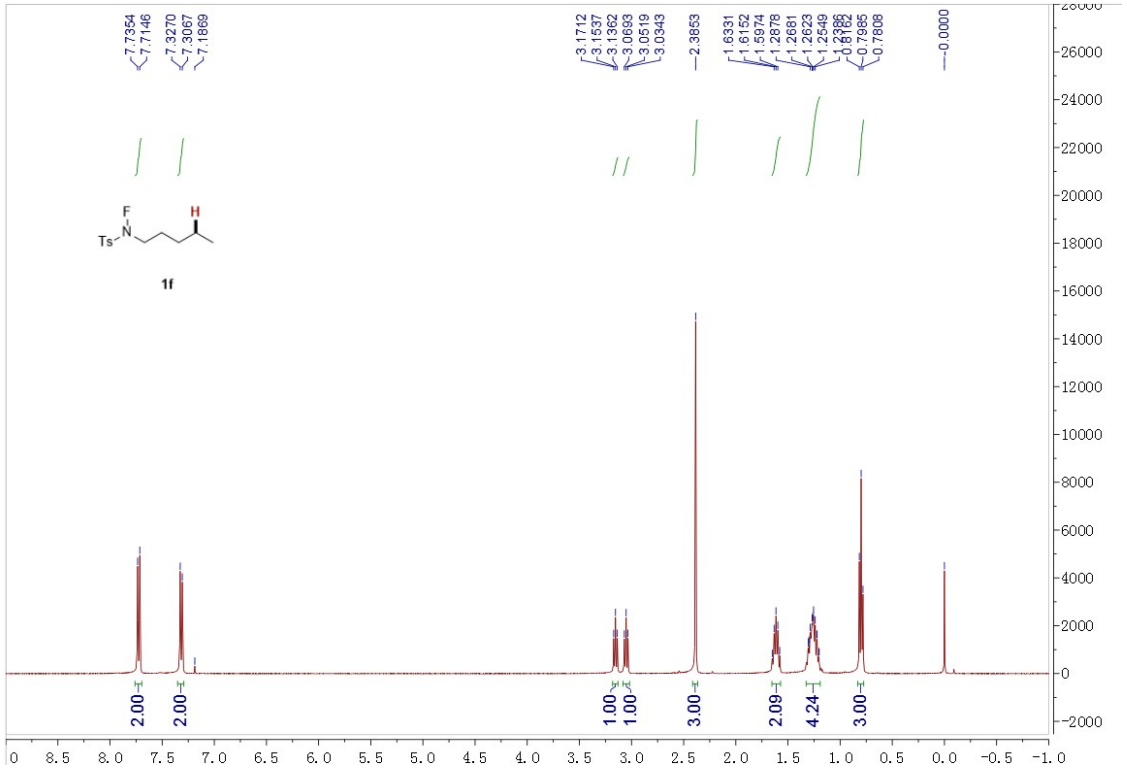
f1 (ppm)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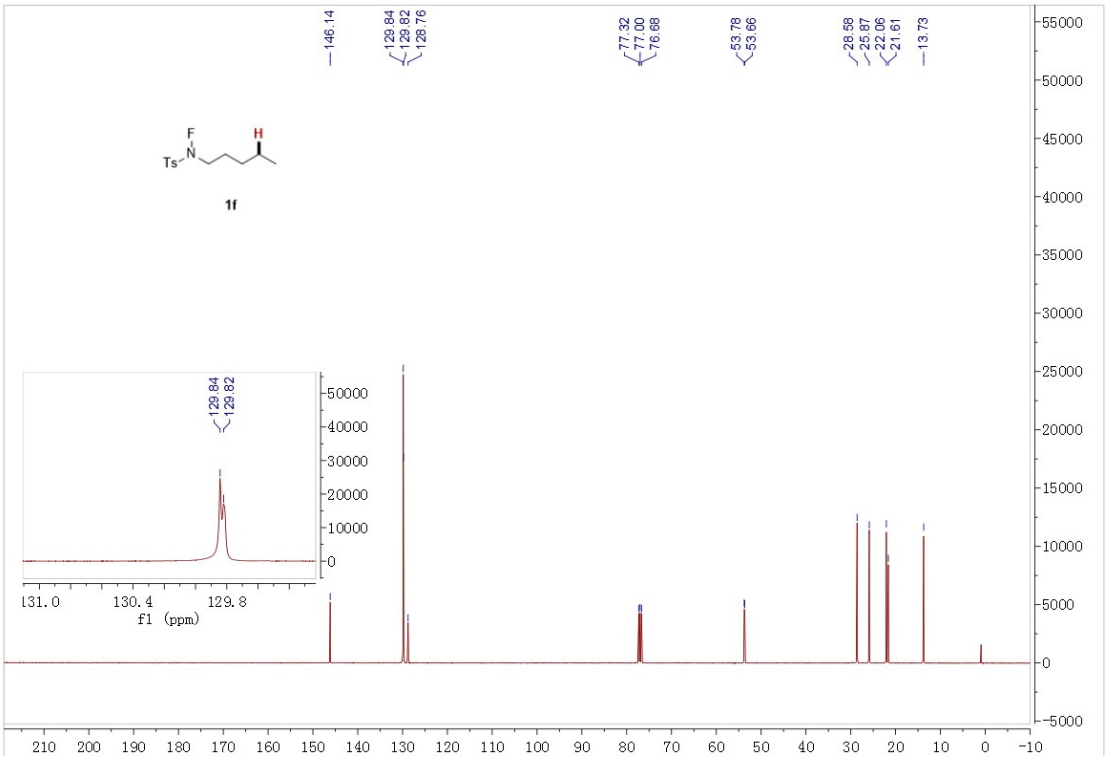
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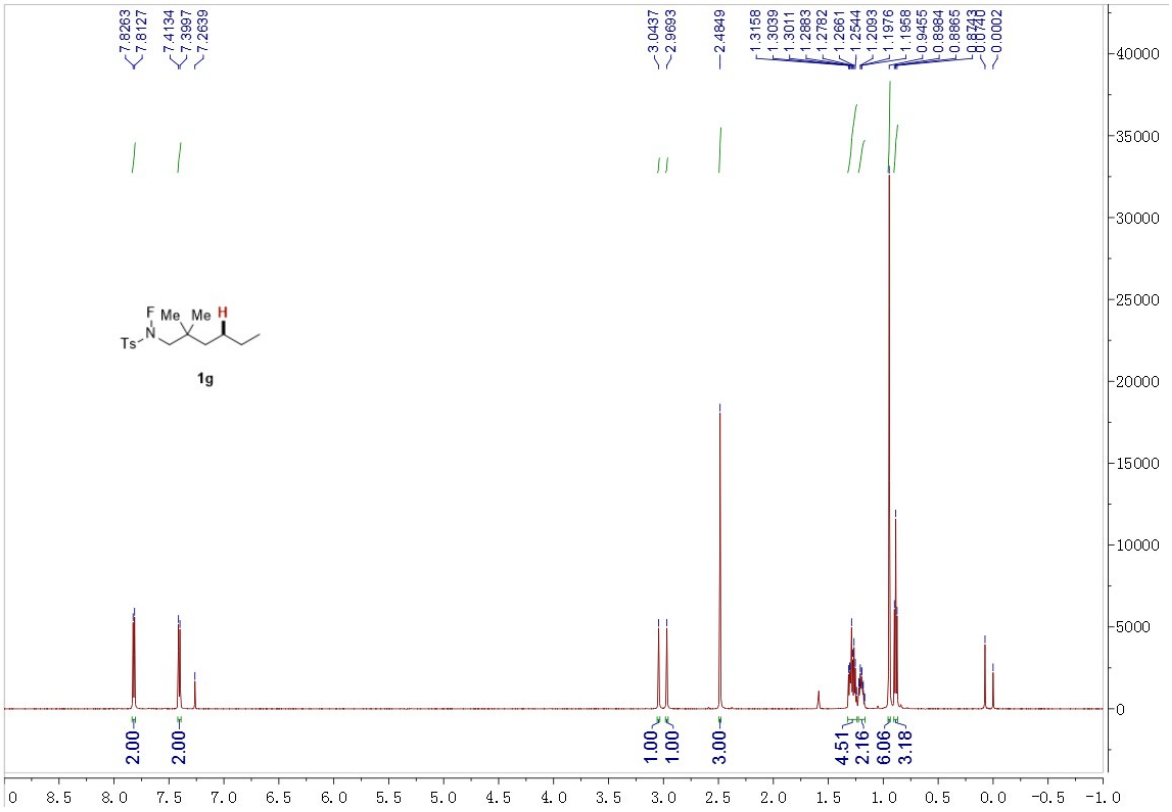
129.82
f1 (ppm)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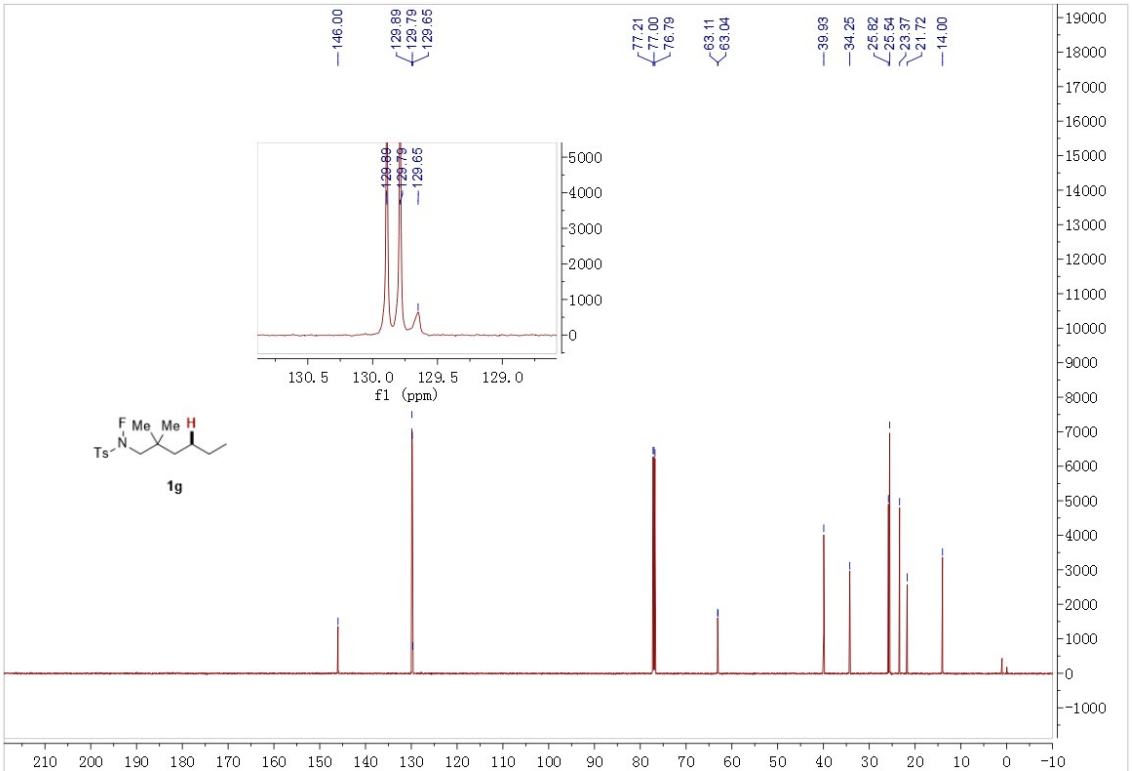
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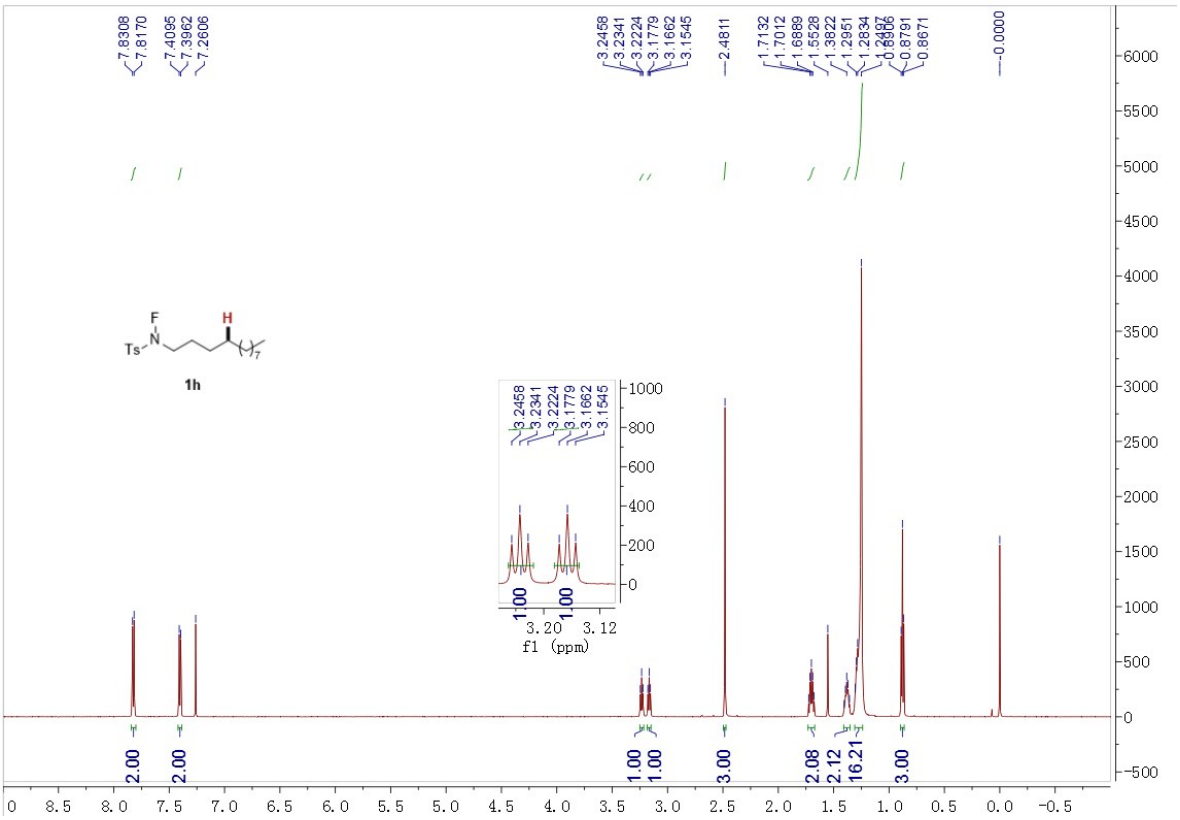
F Me Me H
Ts N
1g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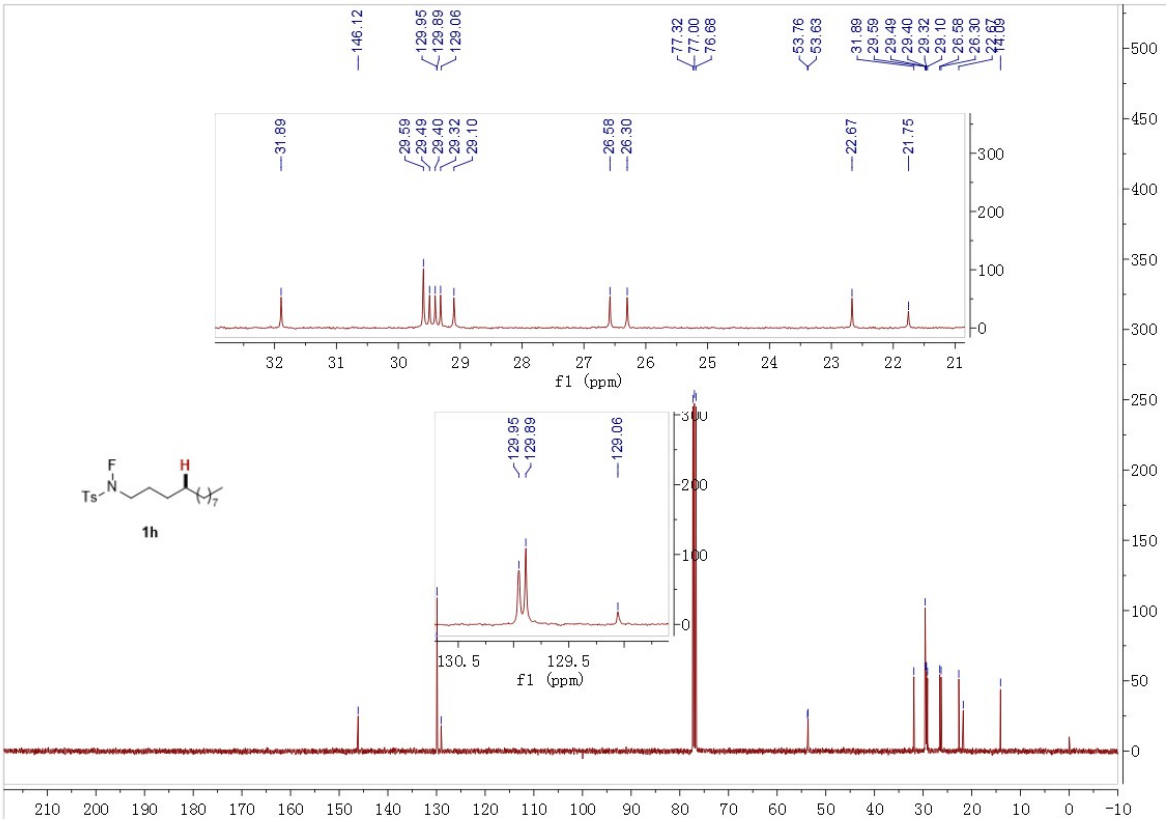
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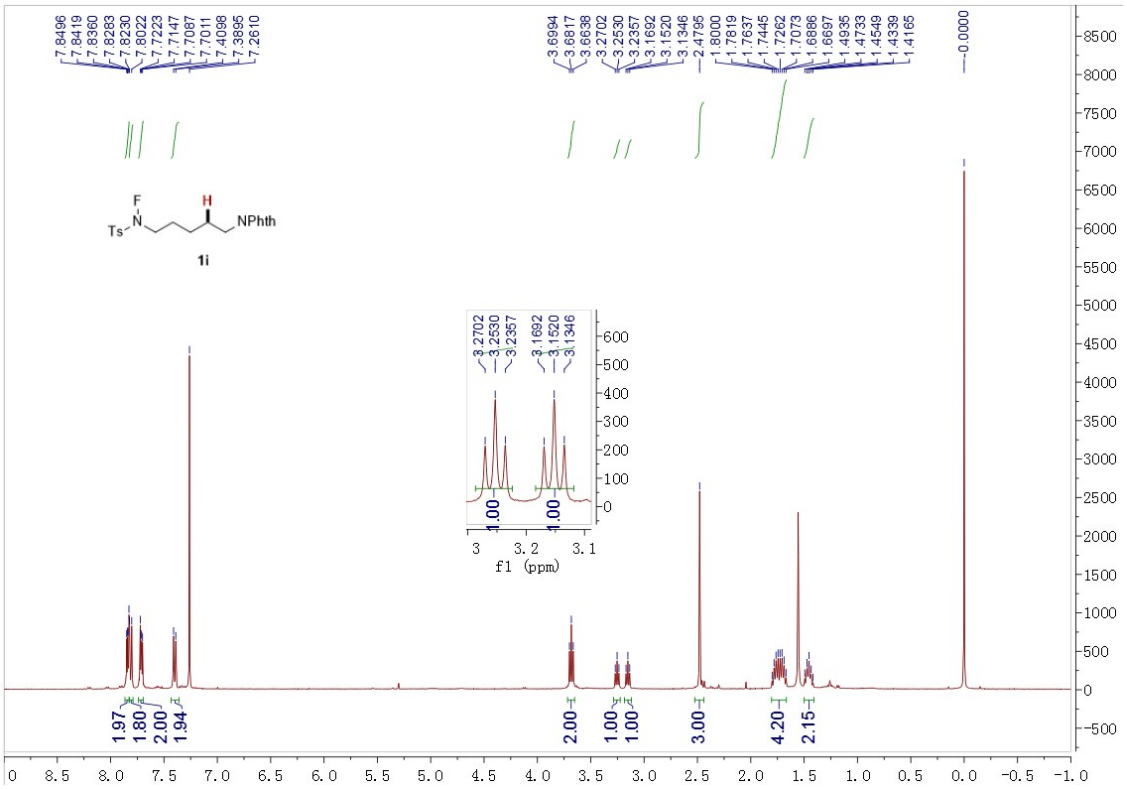
f1 (ppm)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H
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NPhth
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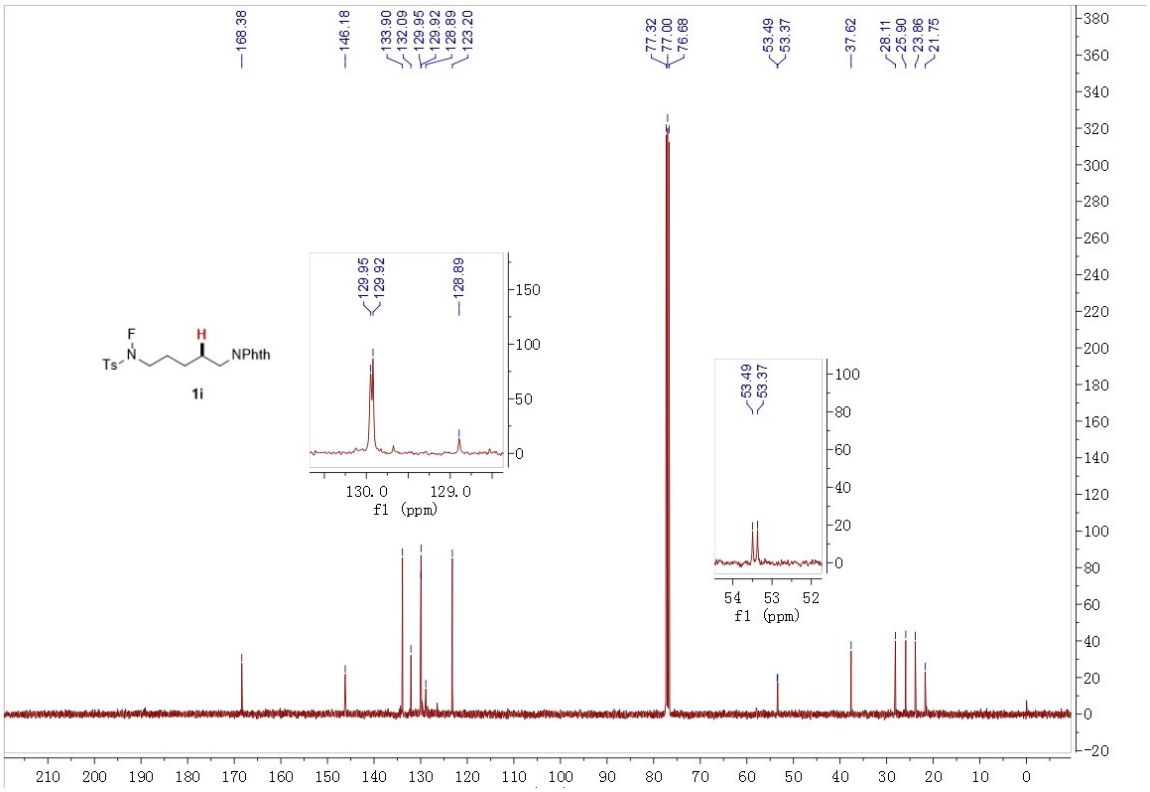
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H
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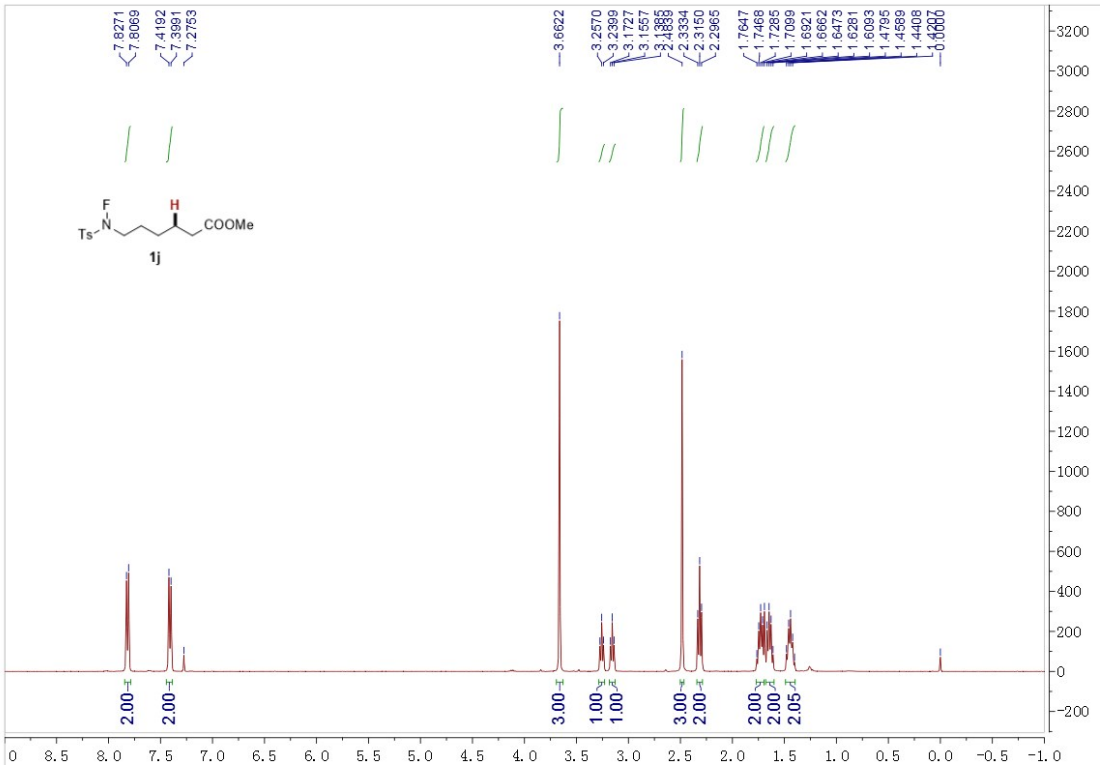
1i
f1 (ppm)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H
Ts
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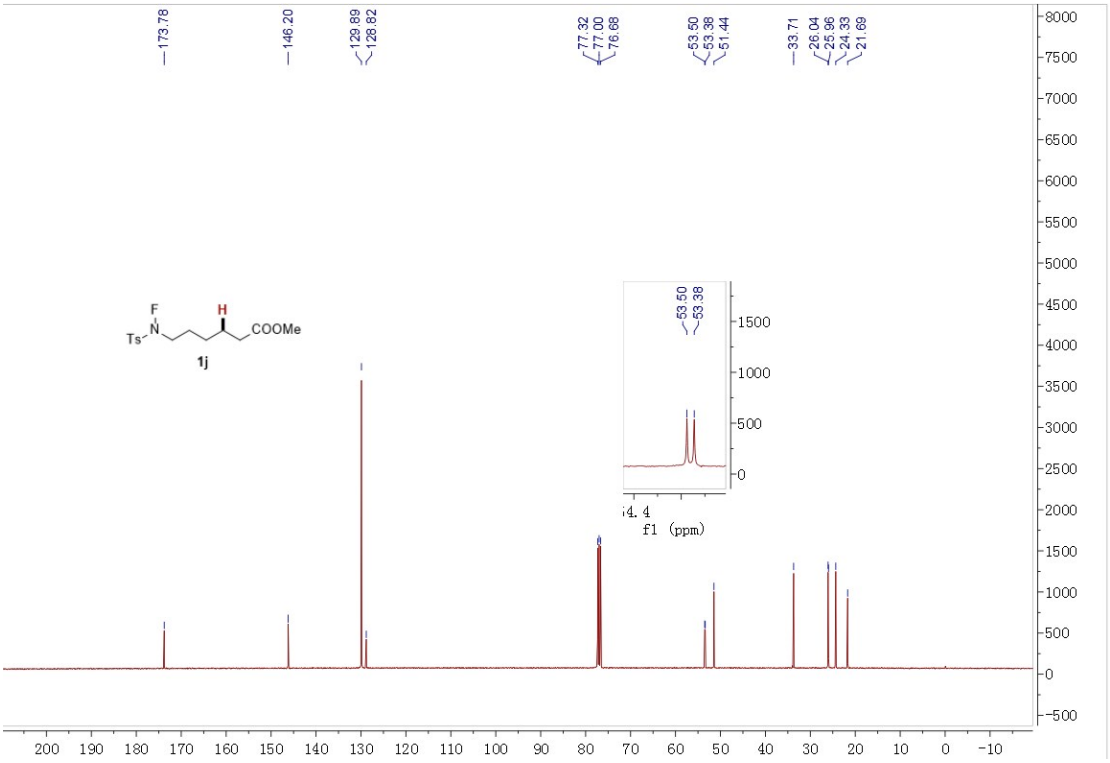
2.00
2.05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51.44
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24.33
21.69
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COOMe
1j
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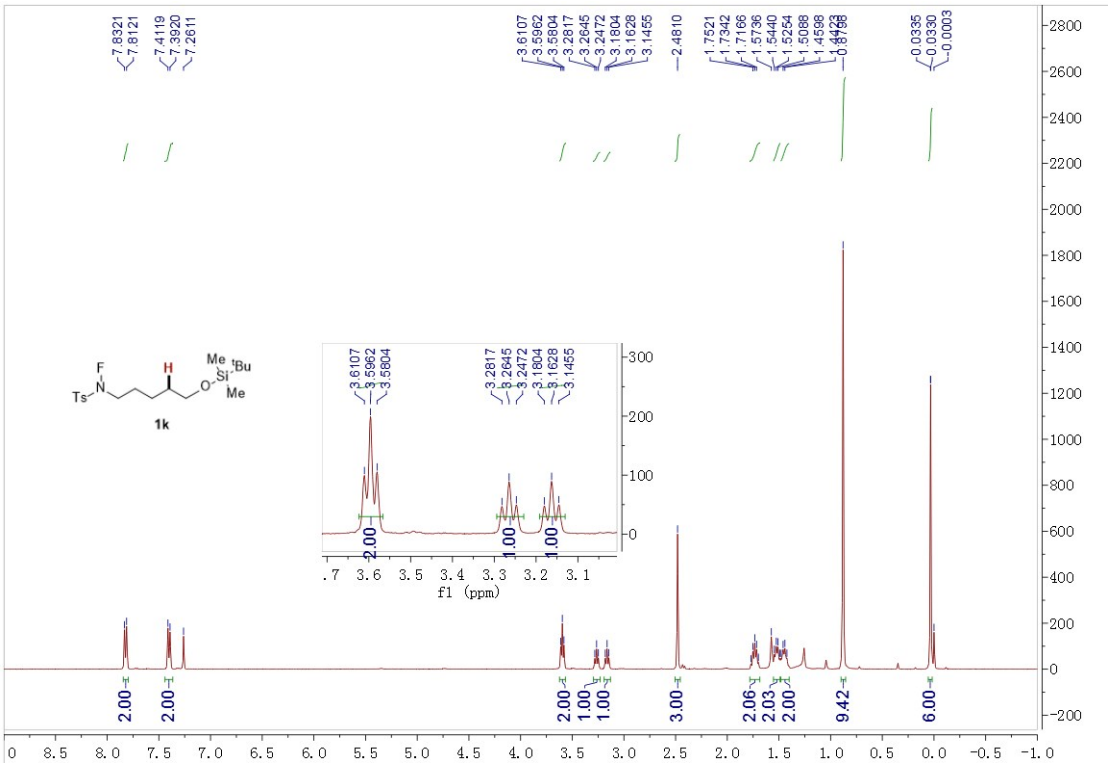
53.38
f1 (ppm)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0.0330
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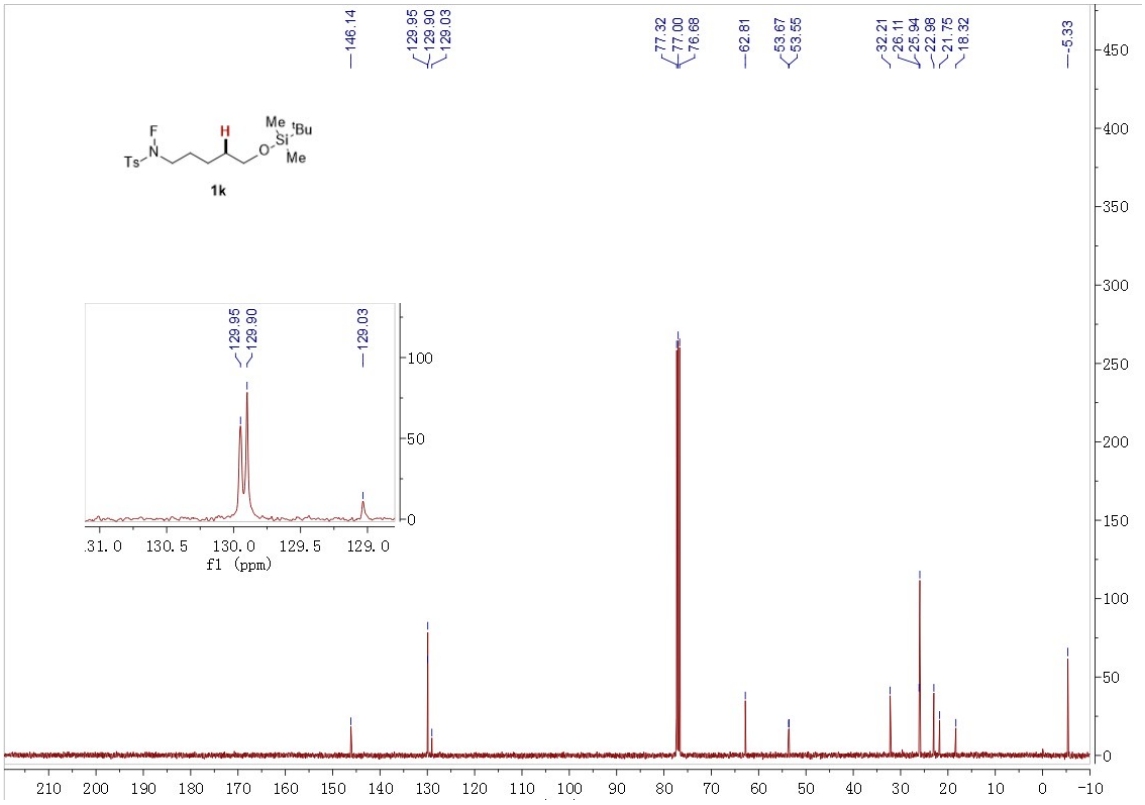
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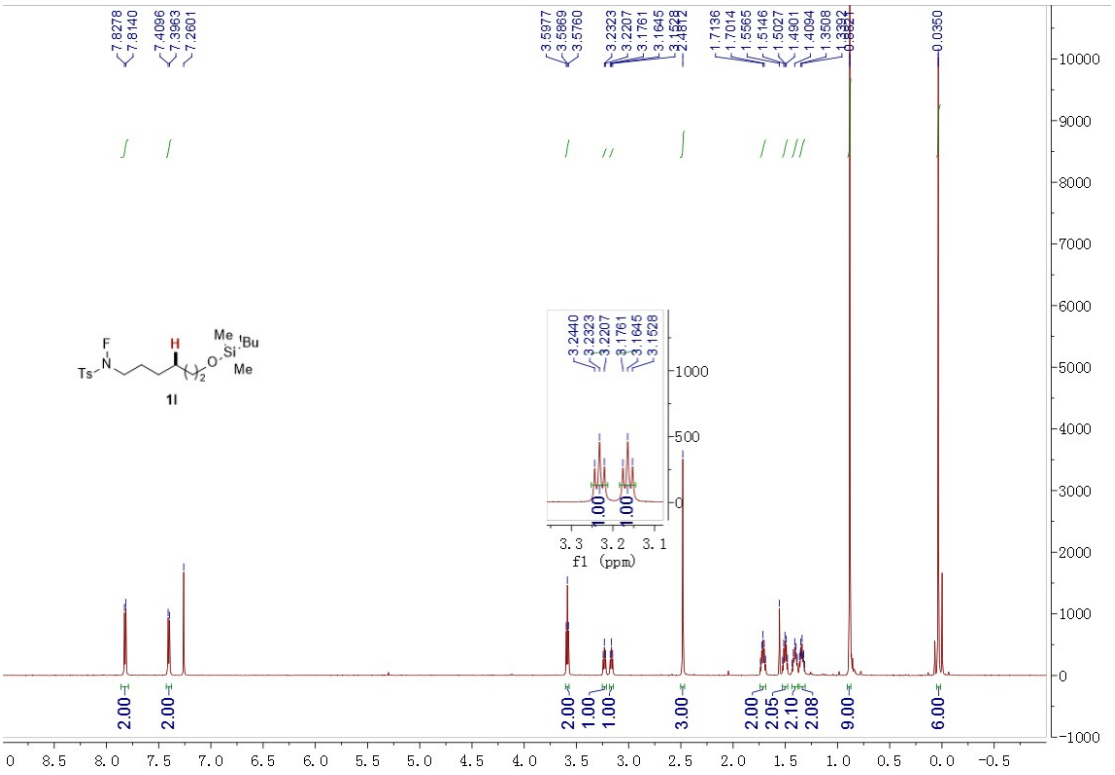
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3.2323
3.2207
3.1761
3.1645
3.1528
3.3 3.2 3.1
f1 (ppm)
2.00
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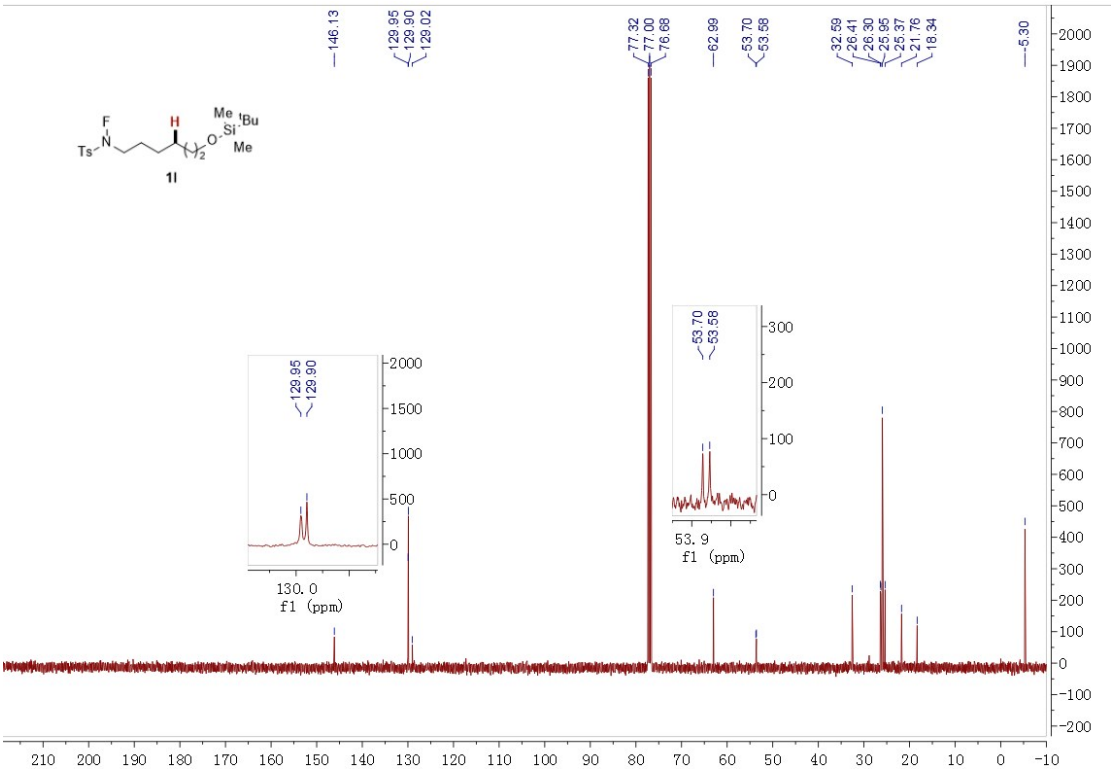
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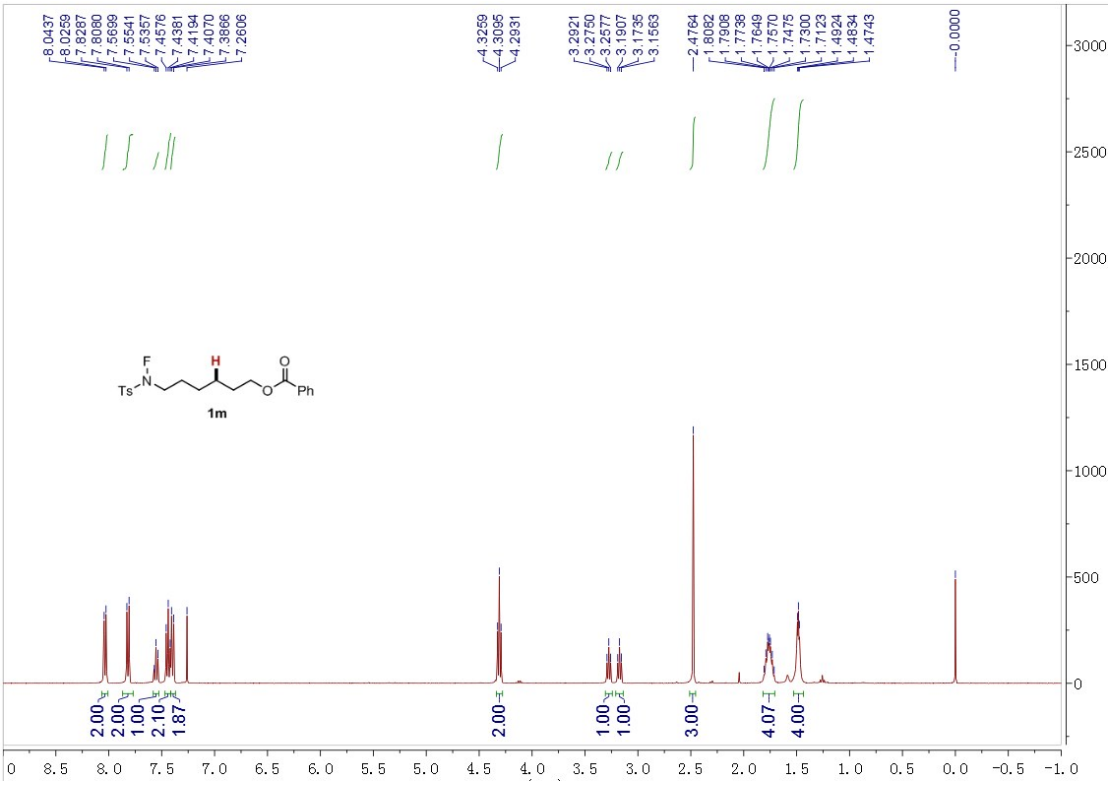
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3.2577
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1.7570
1.7475
1.7300
1.7123
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1.4834
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H
O
Ts
N
O
Ph
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1.00
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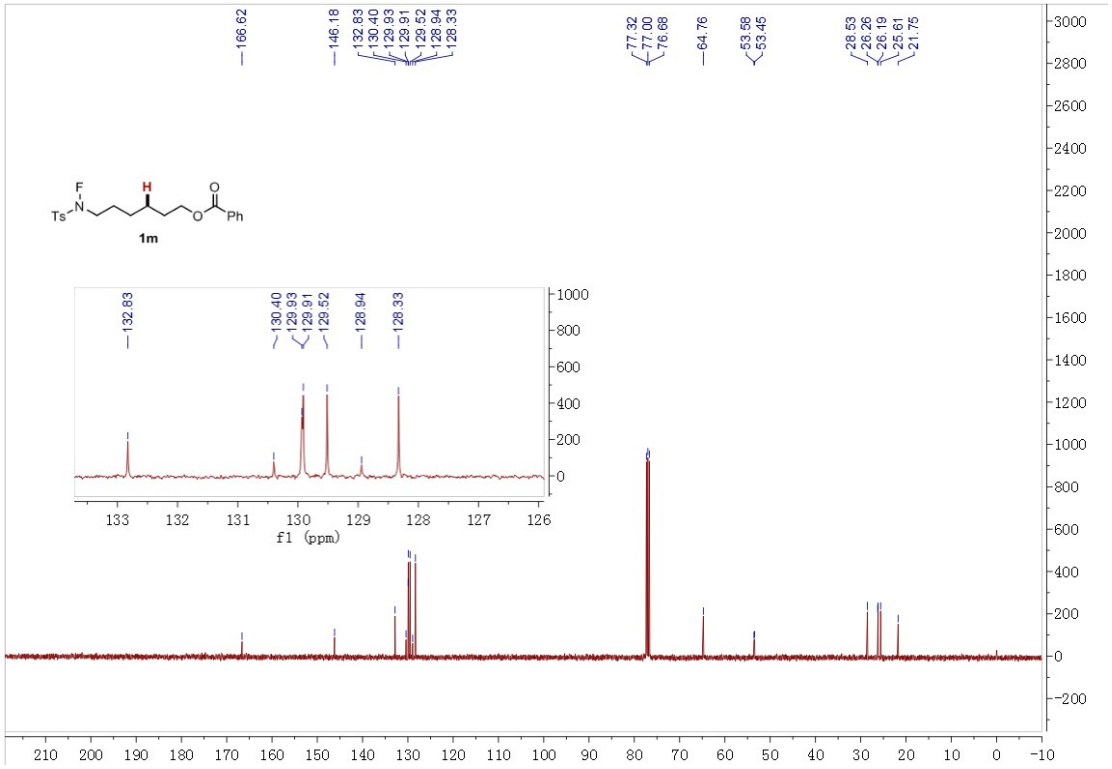
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128.94
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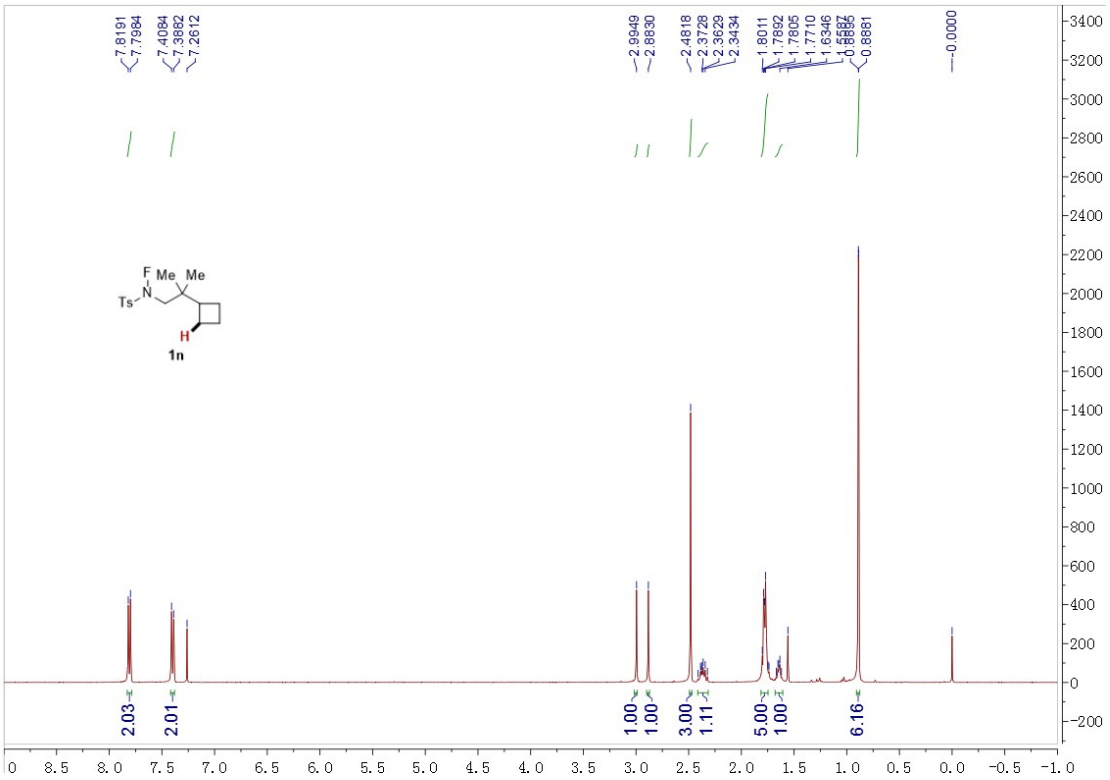
77.32
77.00
76.68
64.76
53.58
53.45
28.53
26.26
26.19
25.61
21.75
F
H
O
Ts
N
O
Ph
1m
f1 (ppm)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2.8830
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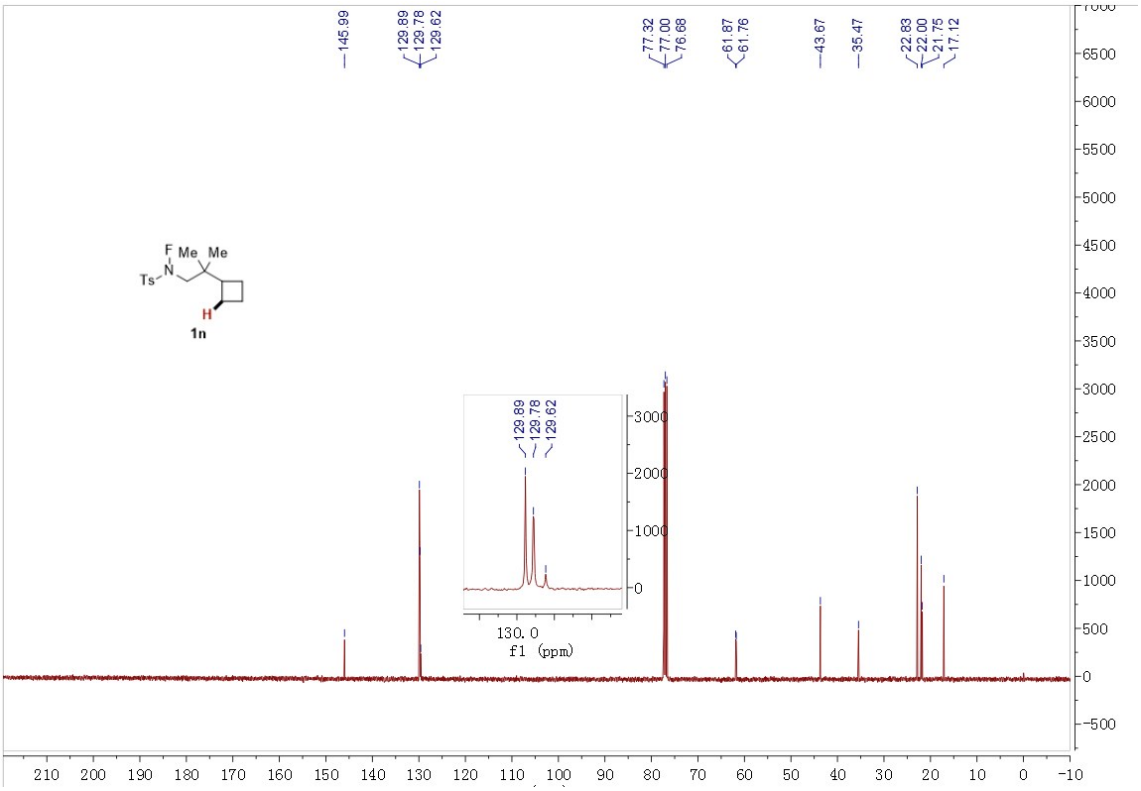
2.3728
2.3629
2.3434
1.8011
1.7892
1.7805
1.7710
1.6346
0.8885
0.8881
0.0000
F Me Me
Ts
N
H
1n
2.03
2.01
1.00
1.00
3.00
1.11
5.00
1.00
6.16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129.78
129.62
77.32
77.00
76.68
61.87
61.76
43.67
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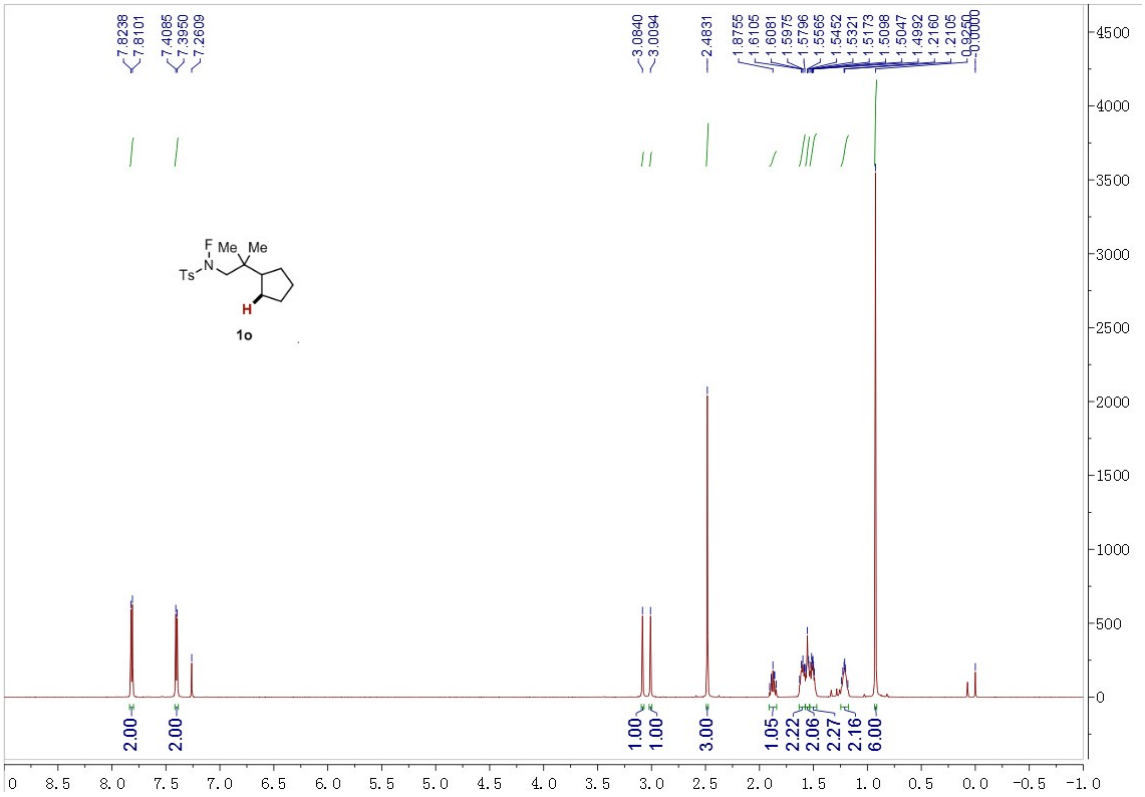
22.83
22.00
21.75
17.12
F Me Me
Ts
N
H
1n
130.0
f1 (ppm)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1.6081
1.5975
1.5796
1.5565
1.5452
1.5321
1.5173
1.5098
1.5047
1.4992
1.2160
1.2105
0.9250
0.0000
F Me Me
Ts N
H
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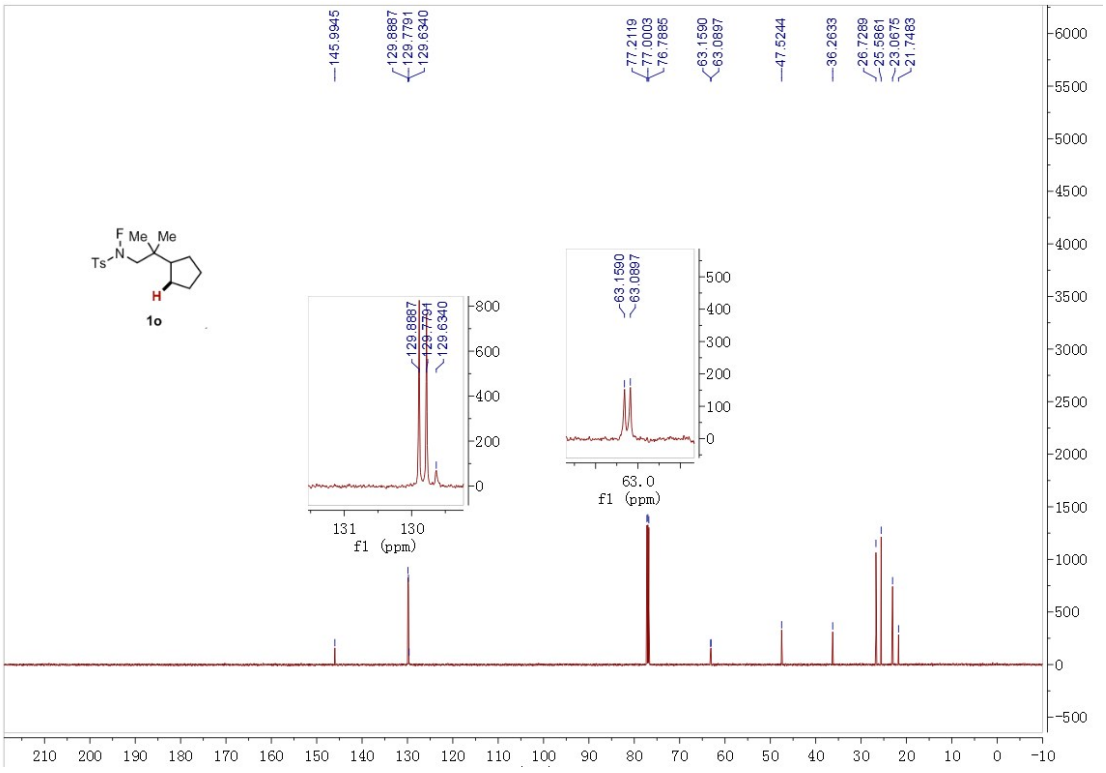
2.00
1.00
1.00
3.00
1.05
2.22
2.06
2.27
2.16
6.00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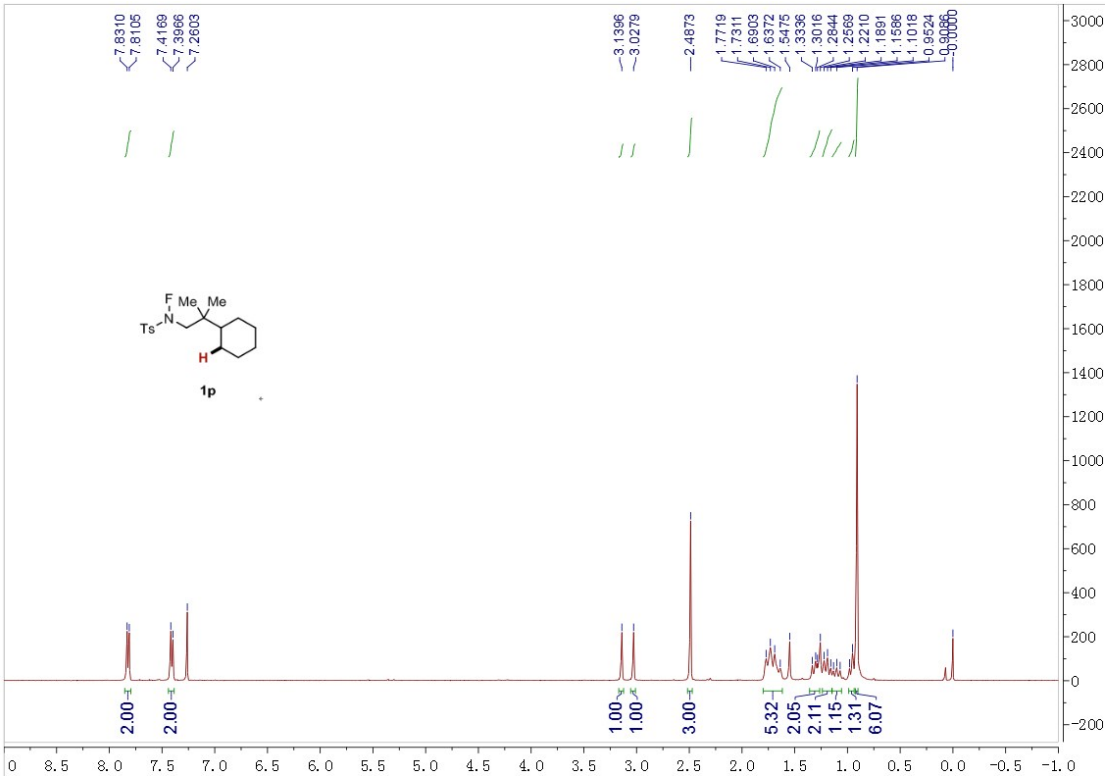
63.0897
47.5244
36.2633
26.7289
25.5861
23.0675
21.7483
F Me Me
Ts N
H
1o
129.8887
129.7791
129.6340
131
130
f1 (ppm)
63.1590
63.0897
63.0
f1 (ppm)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3.0279
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1.6372
1.5475
1.3336
1.3016
1.2844
1.2569
1.2210
1.1891
1.1586
1.1018
0.9524
0.9086
0.8886
2.00
2.00
1.00
1.00
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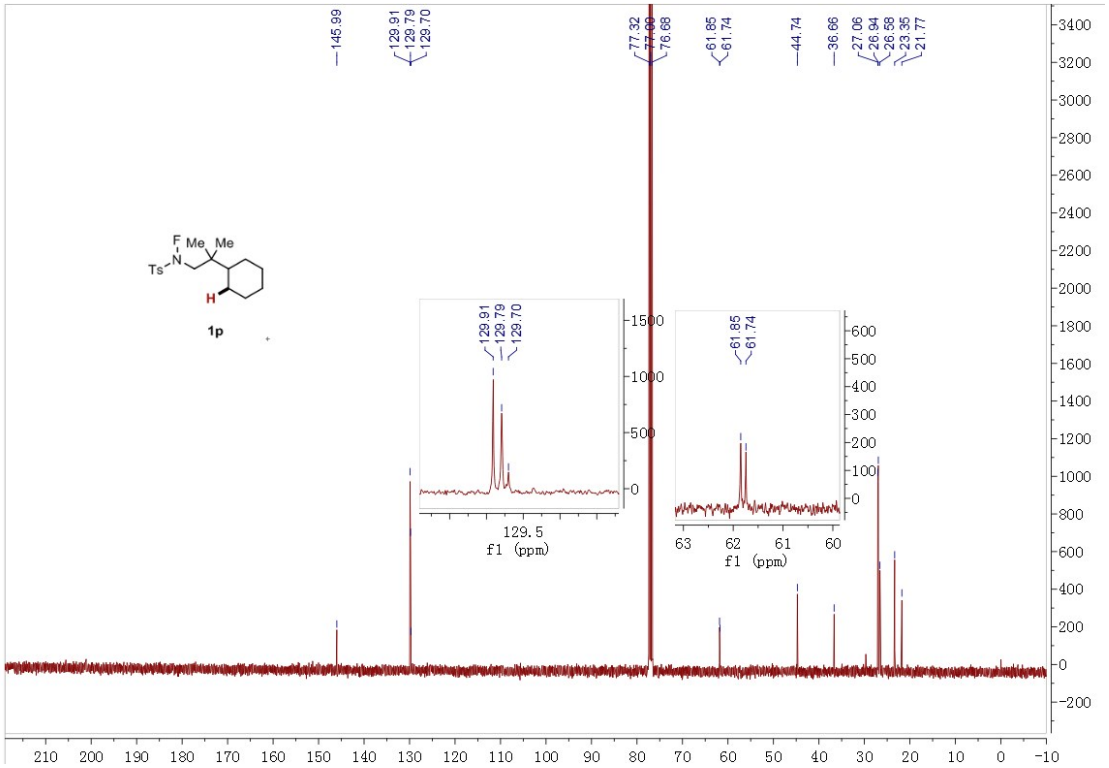
5.32
2.05
2.11
1.15
1.31
6.07
F Me Me
Ts N
H
1p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129.79
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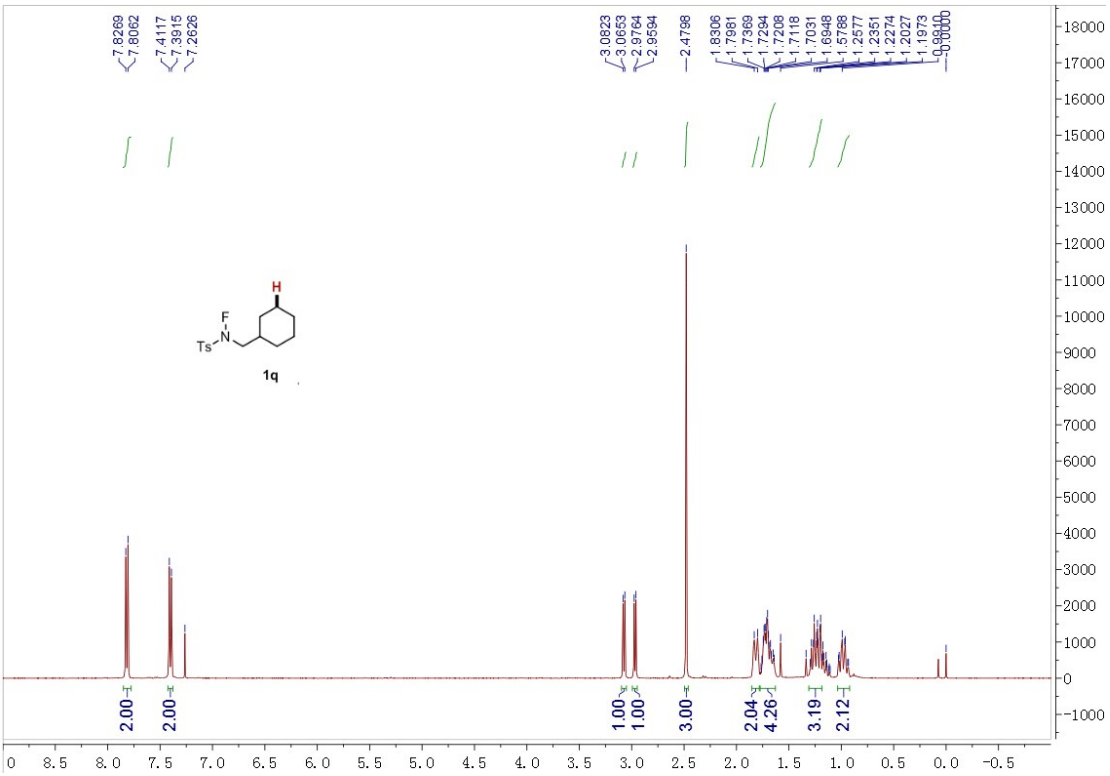
77.32
77.00
76.68
61.85
61.74
44.74
36.66
27.06
26.94
26.58
23.35
21.77
F Me Me
Ts N
H
1p
129.91
129.79
129.70
129.5
f1 (ppm)
61.85
61.74
63
62
61
60
f1 (ppm)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1.7031
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1.5788
1.2577
1.2351
1.2274
1.2027
1.1973
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2.04
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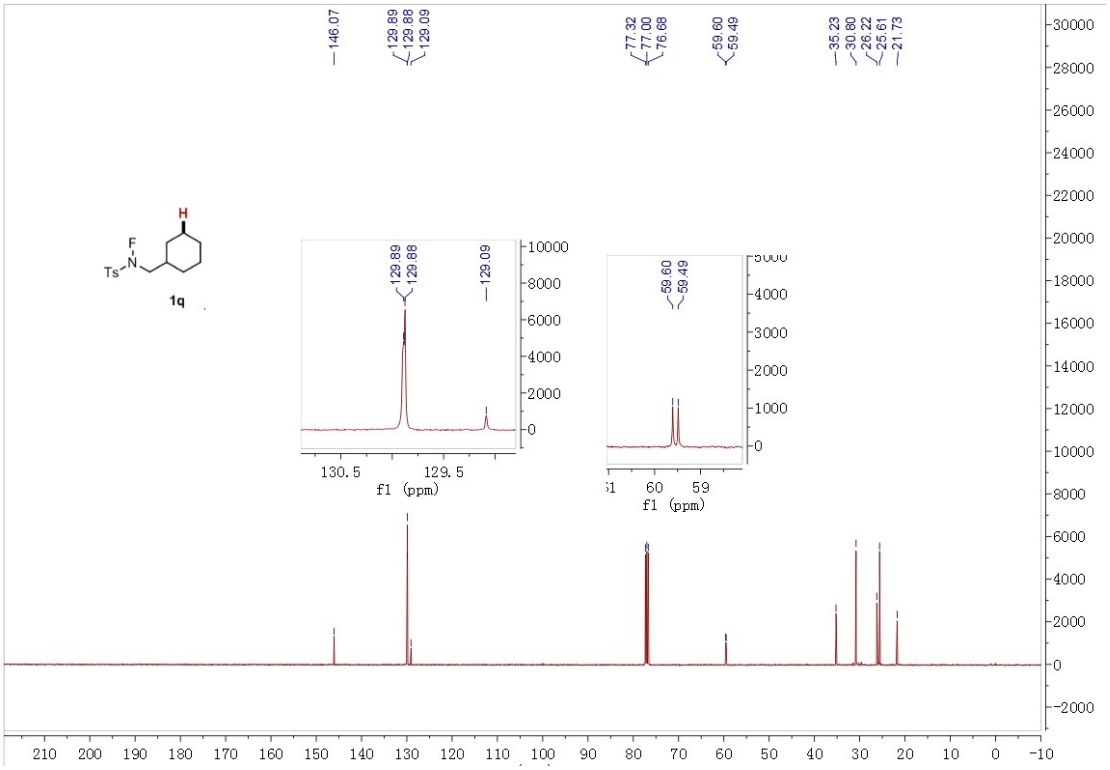
3.19
2.12
1q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129.89
129.88
129.09
77.32
77.00
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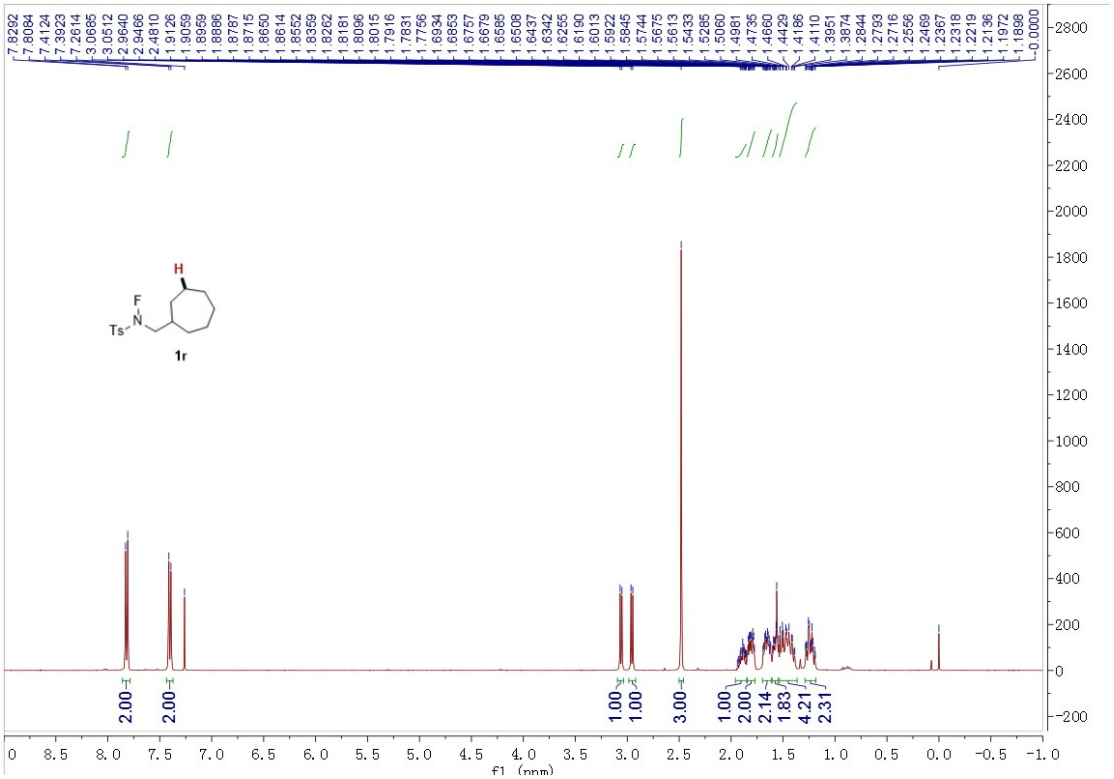
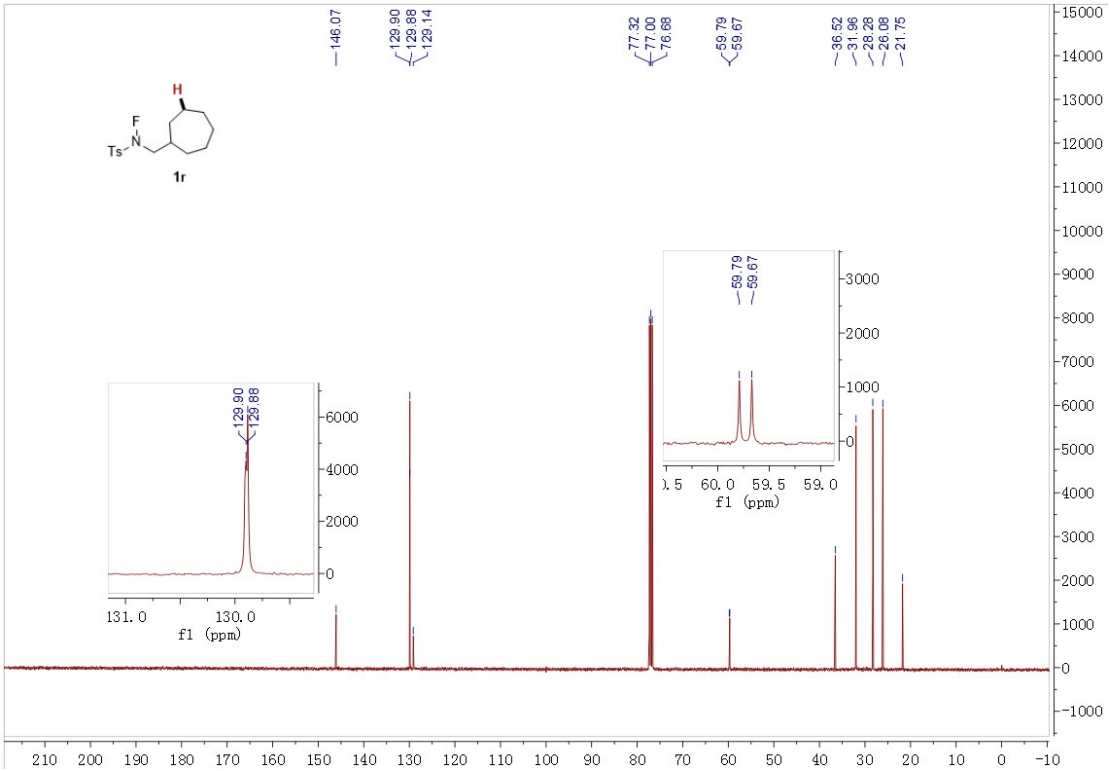
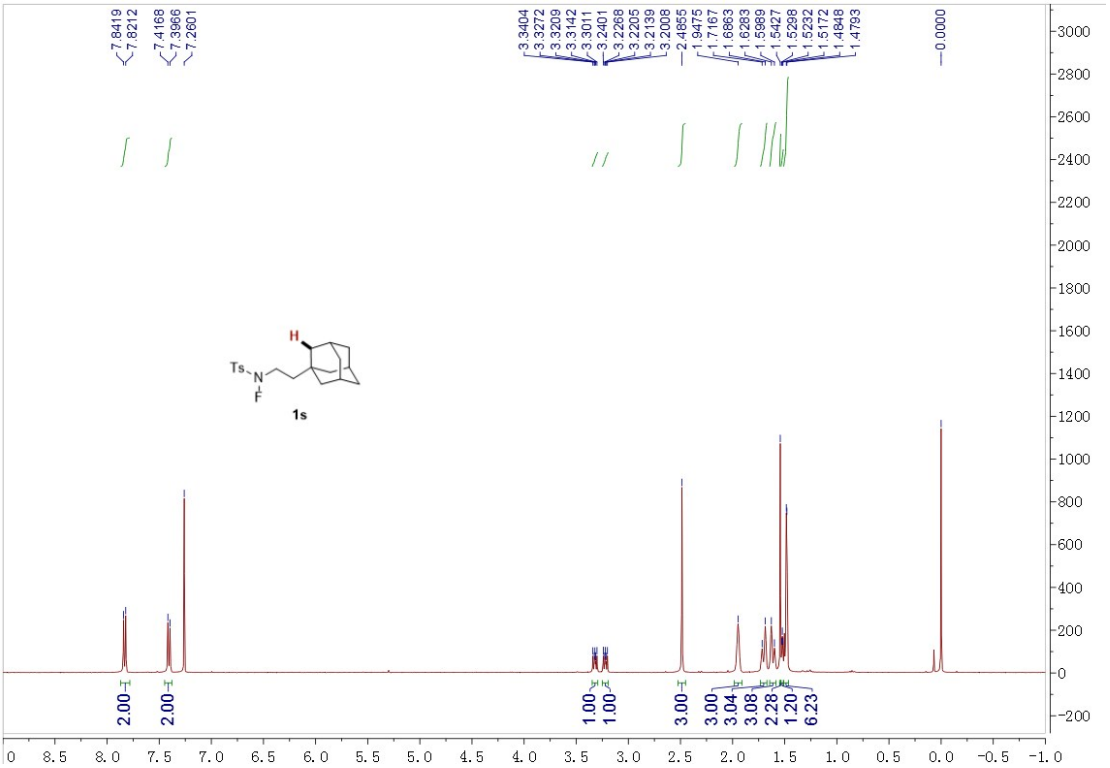
30.80
26.22
25.61
21.73
1q
f1 (ppm)
f1 (ppm)


1r
f1 (ppm)


1r
f1 (ppm)
f1 (ppm)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7.4168
7.3966
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3.3272
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3.3142
3.3011
3.2401
3.2268
3.2205
3.2139
3.2008
2.4885
1.9475
1.7167
1.6863
1.6283
1.5989
1.5427
1.5298
1.5232
1.5172
1.4848
1.4793
0.0000
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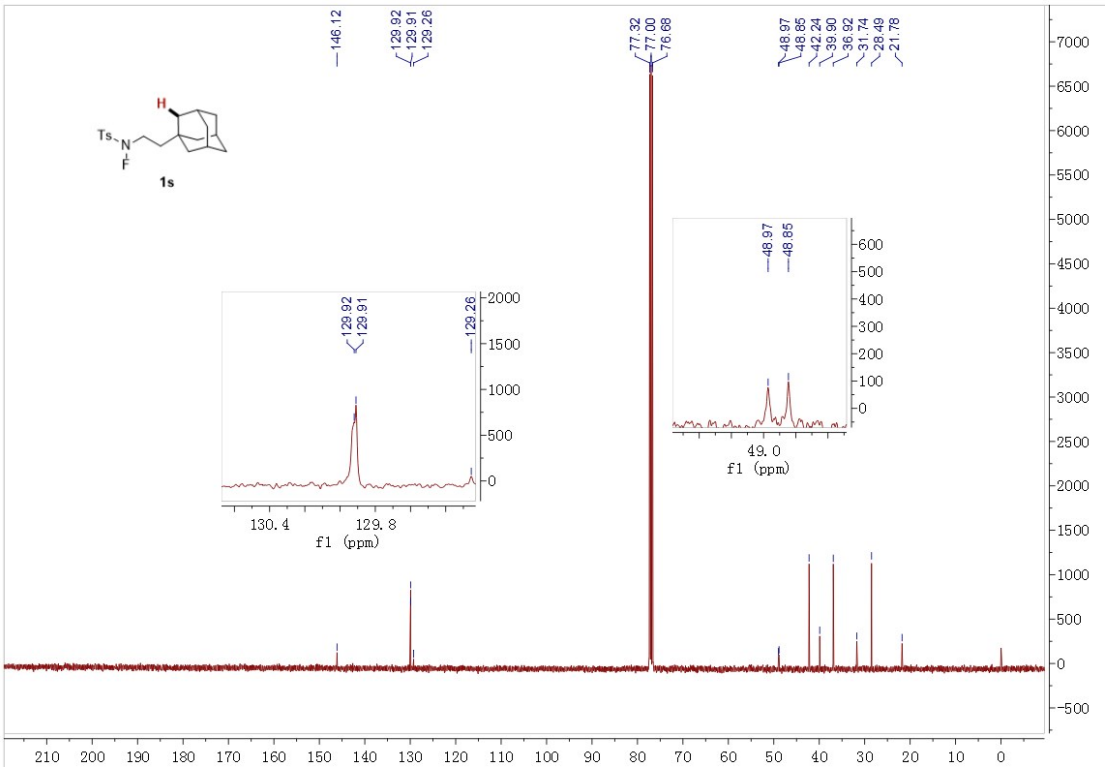
2.00
1.00
1.00
3.00
3.00
3.04
3.08
2.28
1.20
6.23
1s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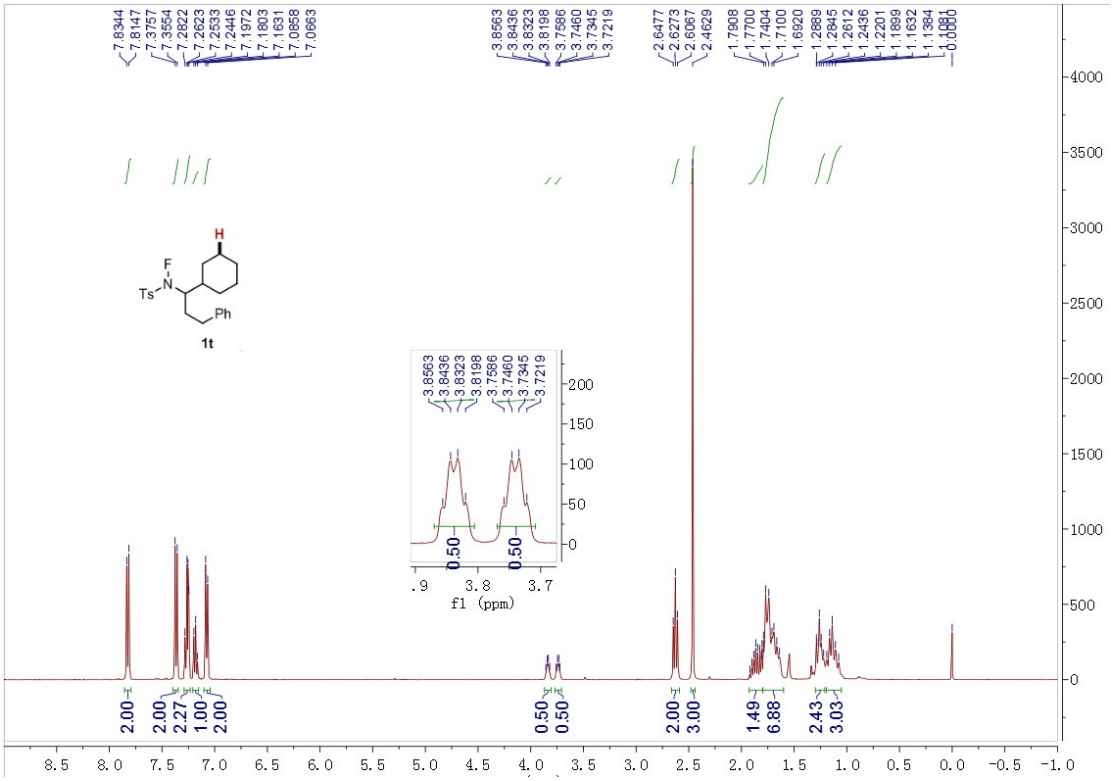
129.92
129.91
129.26
77.32
77.00
76.68
48.97
48.85
42.24
39.90
36.92
31.74
28.49
21.78
1s
f1 (ppm)
f1 (ppm)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7.3554
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7.2533
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7.1631
7.0858
7.0663
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3.8198
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3.7460
3.7345
3.7219
2.6477
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2.6067
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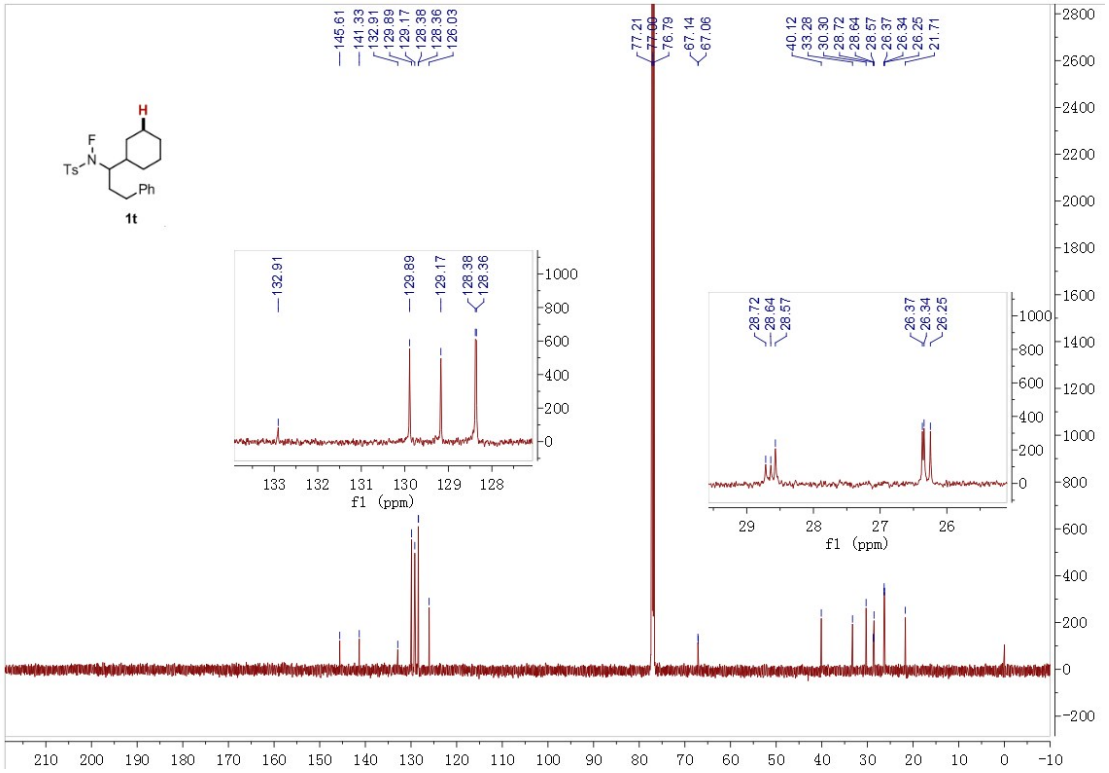
1.7700
1.7404
1.7100
1.6920
1.2889
1.2845
1.2612
1.2436
1.2201
1.1899
1.1632
1.1384
1.1081
0.0000
H
F
N
Ts
Ph
1t
f1 (ppm)
2.00
2.00
2.27
1.00
2.00
0.50
0.50
2.00
3.00
1.49
6.88
2.43
3.03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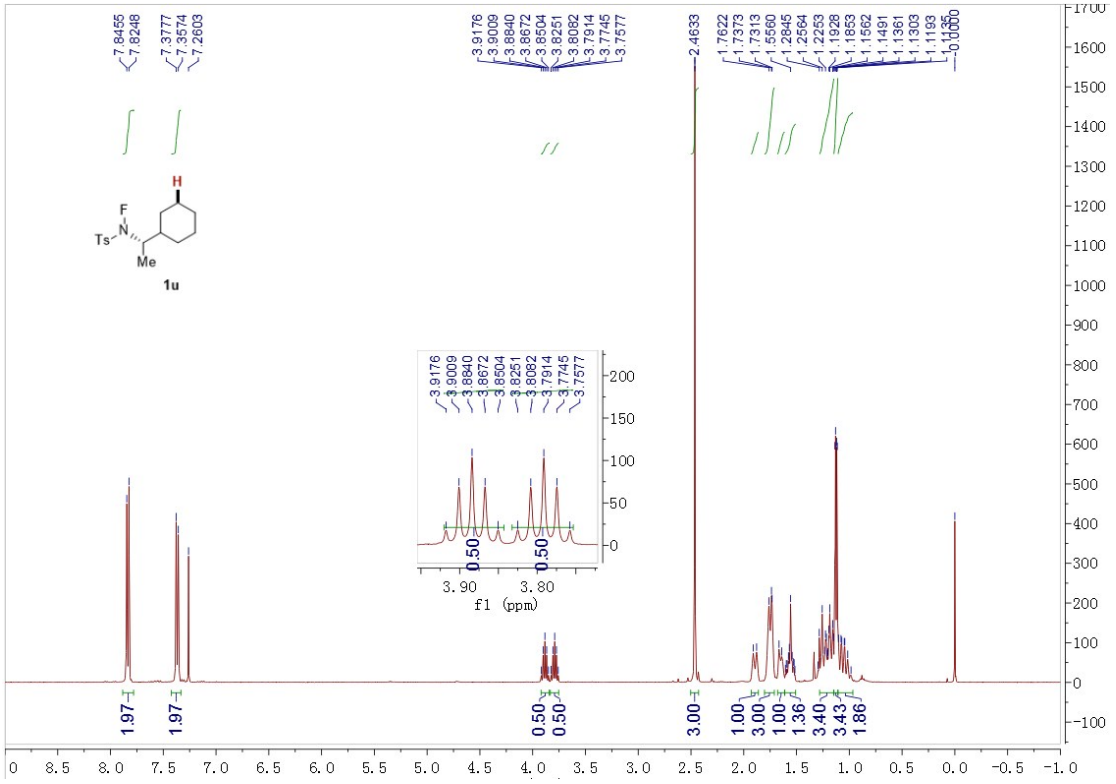
132.91
129.89
129.17
128.38
128.36
126.03
77.21
76.79
67.14
67.06
40.12
33.28
30.30
28.72
28.64
28.57
26.37
26.34
26.25
21.71
H
F
N
Ts
Ph
1t
132.91
129.89
129.17
128.38
128.36
f1 (ppm)
28.72
28.64
28.57
26.37
26.34
26.25
f1 (ppm)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3.7577
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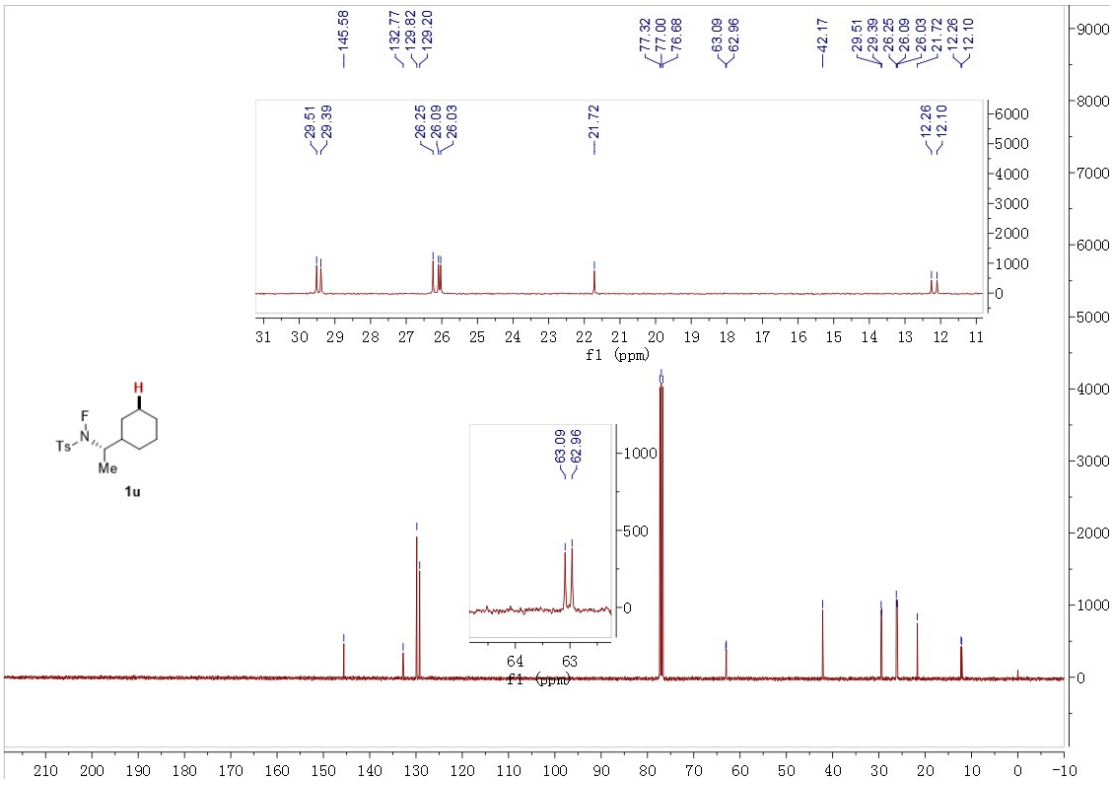
1.7622
1.7373
1.7313
1.5560
1.2845
1.2564
1.2253
1.1928
1.1853
1.1562
1.1491
1.1361
1.1303
1.1193
1.1135
0.0000
1u
1.97
1.97
0.50
0.50
3.00
1.00
3.00
1.00
1.36
3.40
3.43
1.86
f1 (ppm)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132.77
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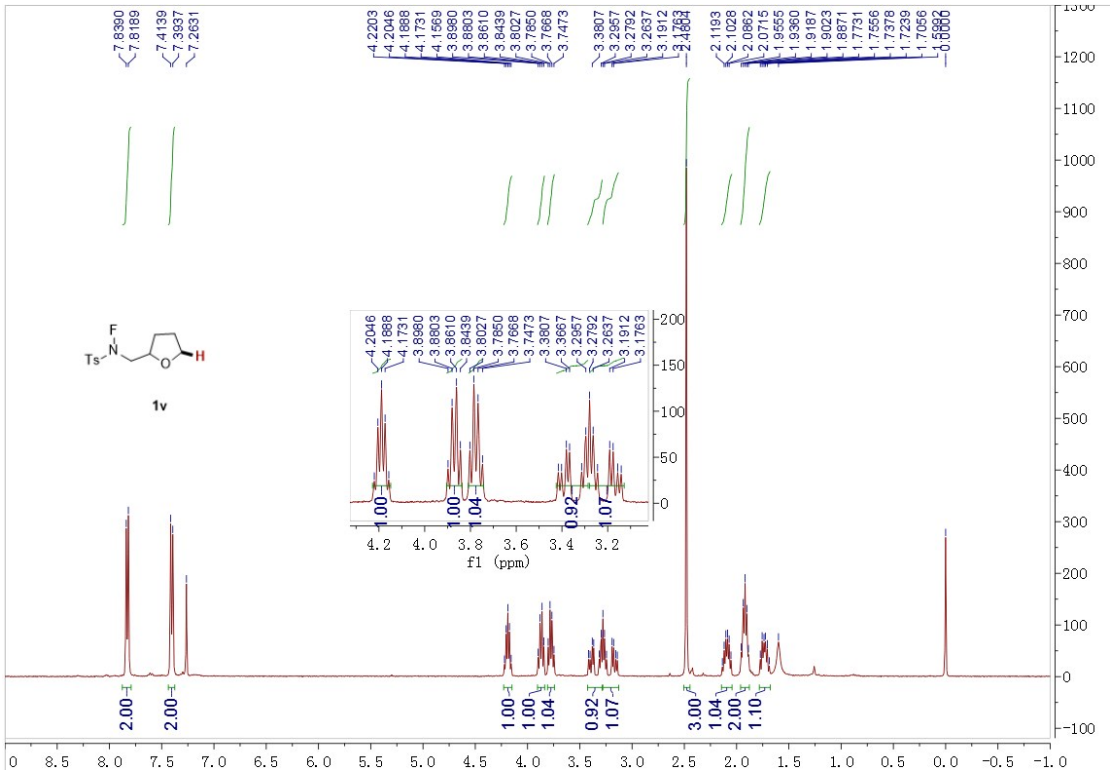
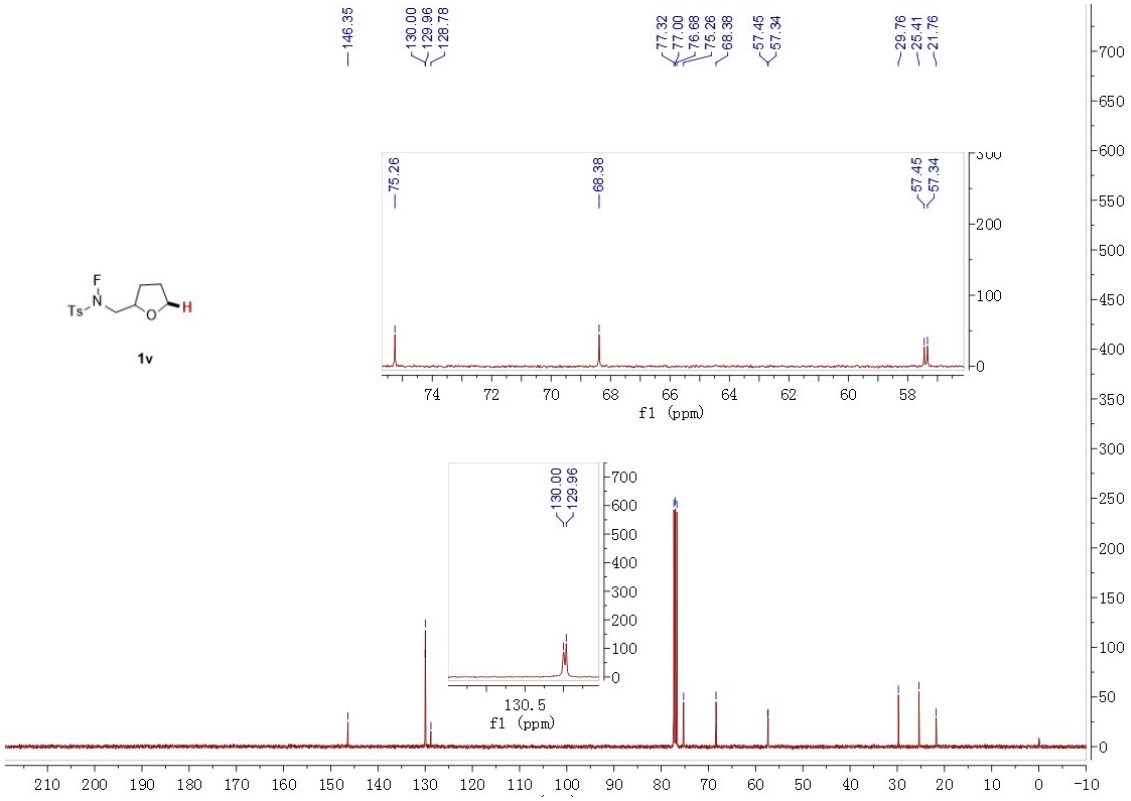
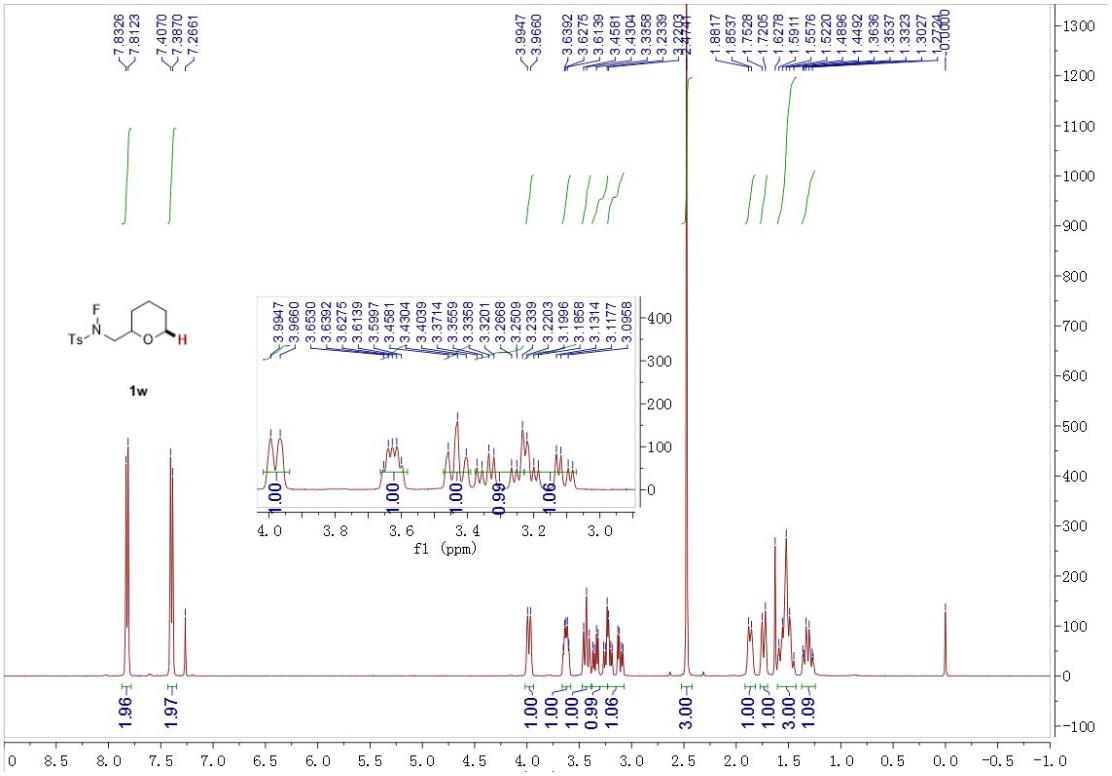
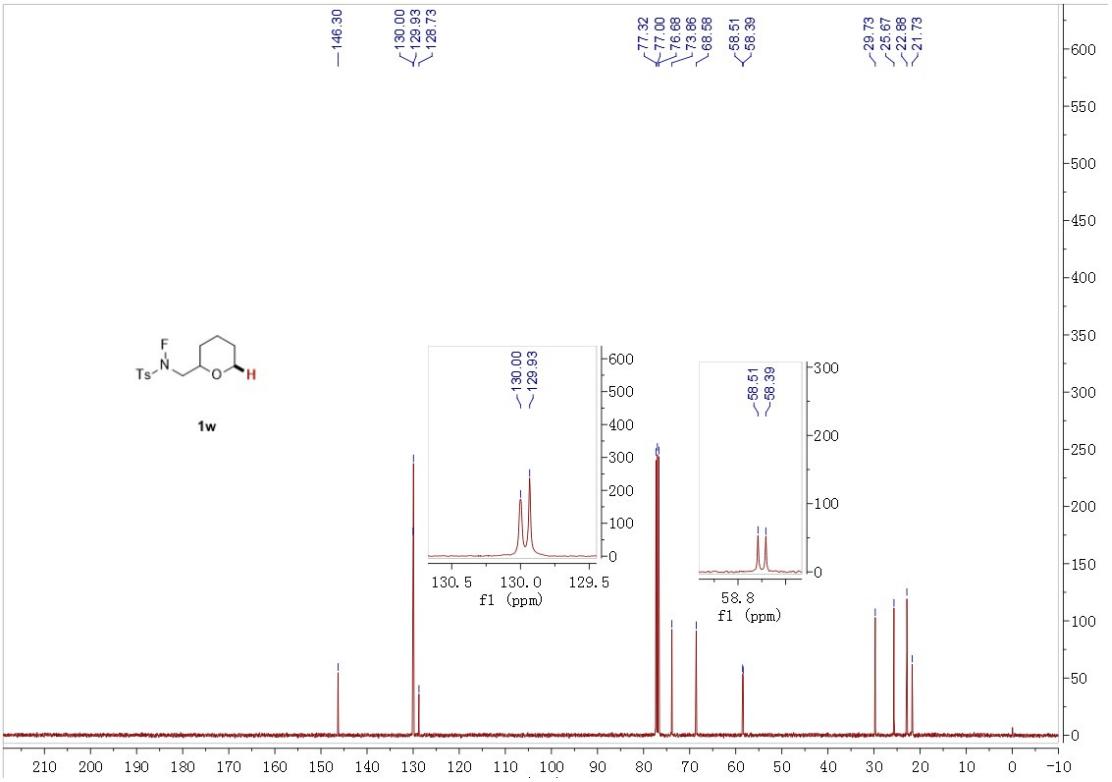
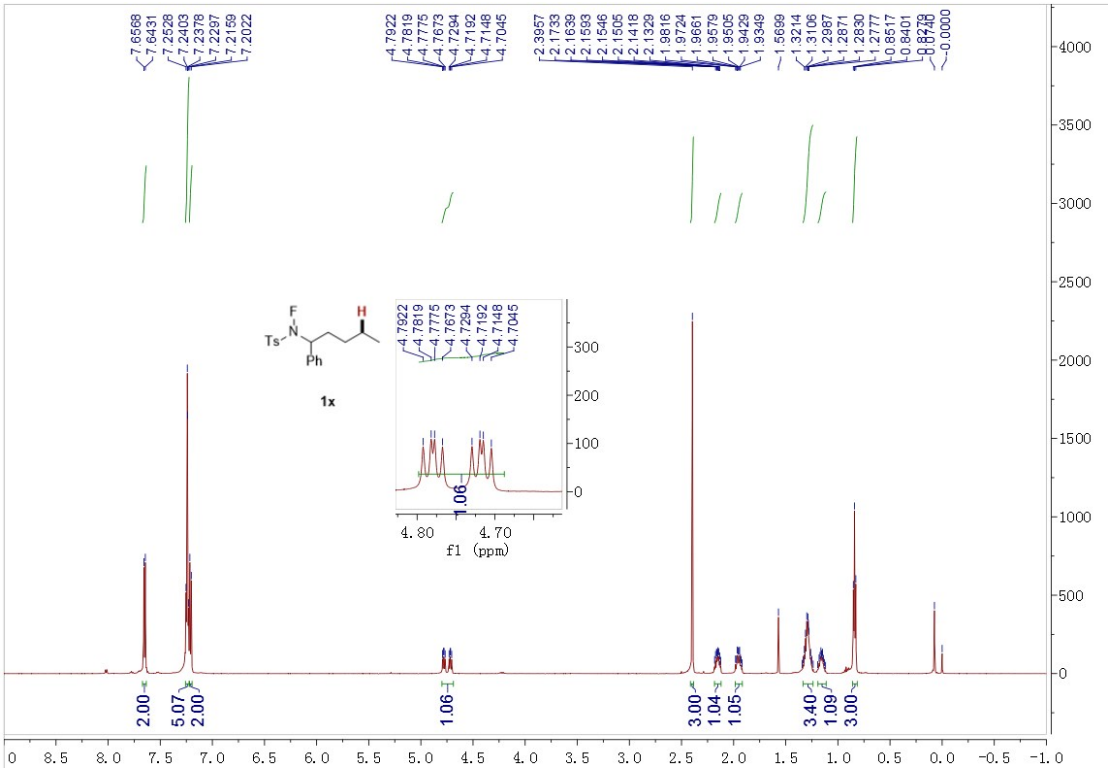
77.32
77.00
76.68
63.09
62.96
42.17
29.51
29.39
26.25
26.09
26.03
21.72
12.26
12.10
1u
f1 (ppm)


1v
f1 (ppm)


1v
f1 (ppm)
f1 (ppm)


1w
f1 (ppm)


1w
f1 (ppm)
f1 (ppm)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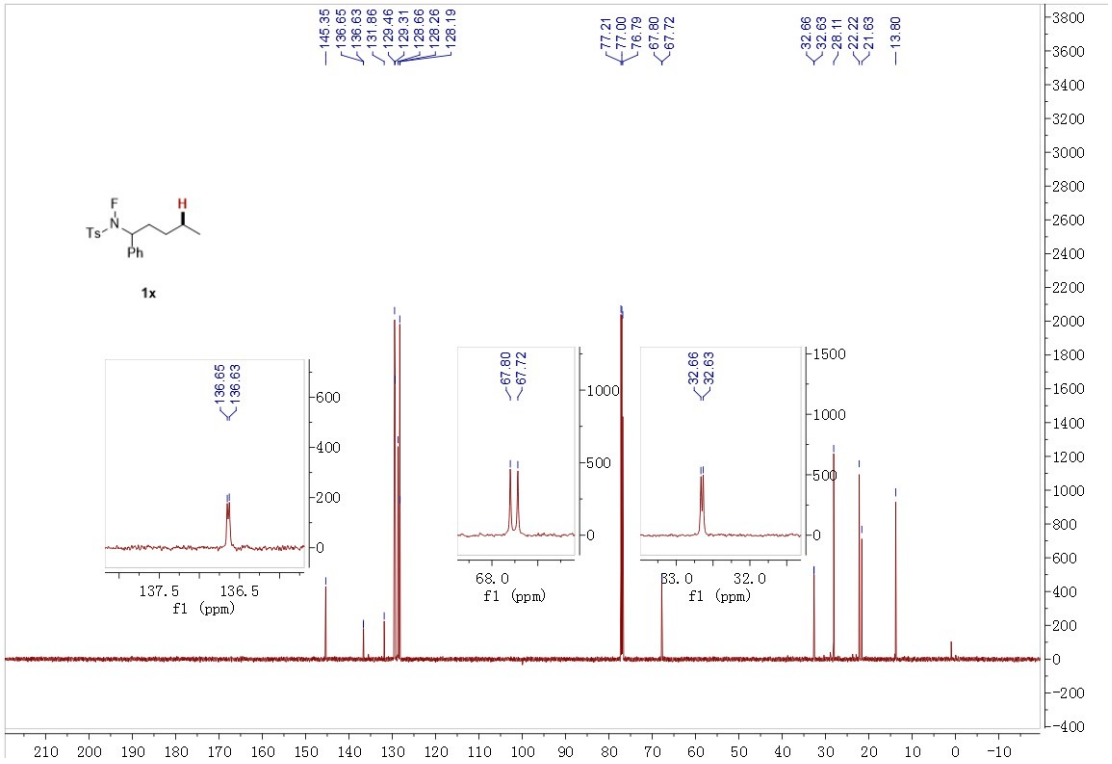
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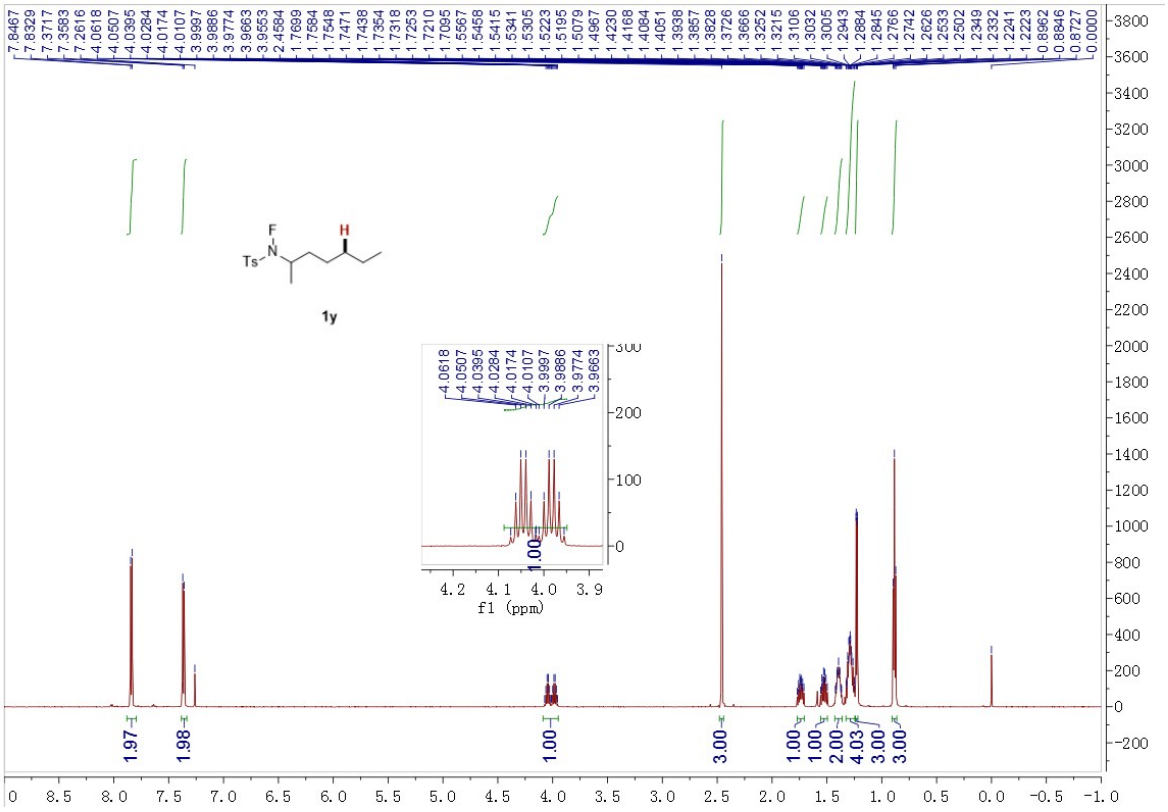
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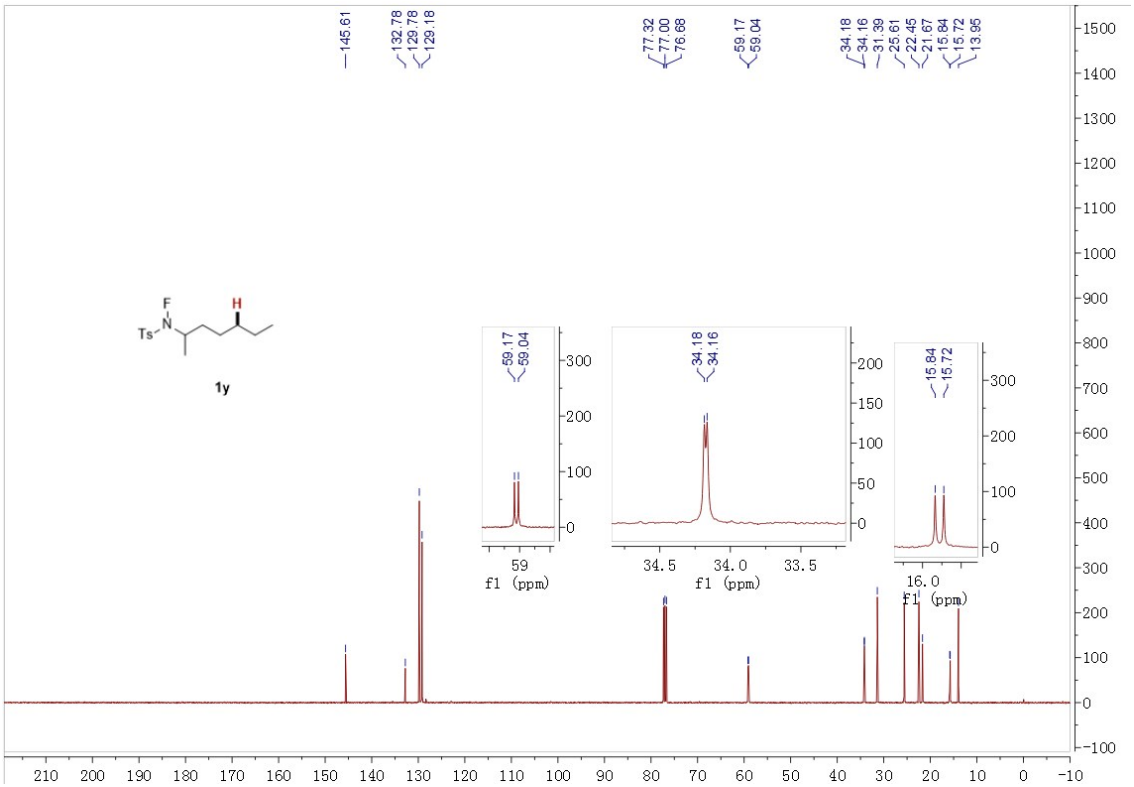
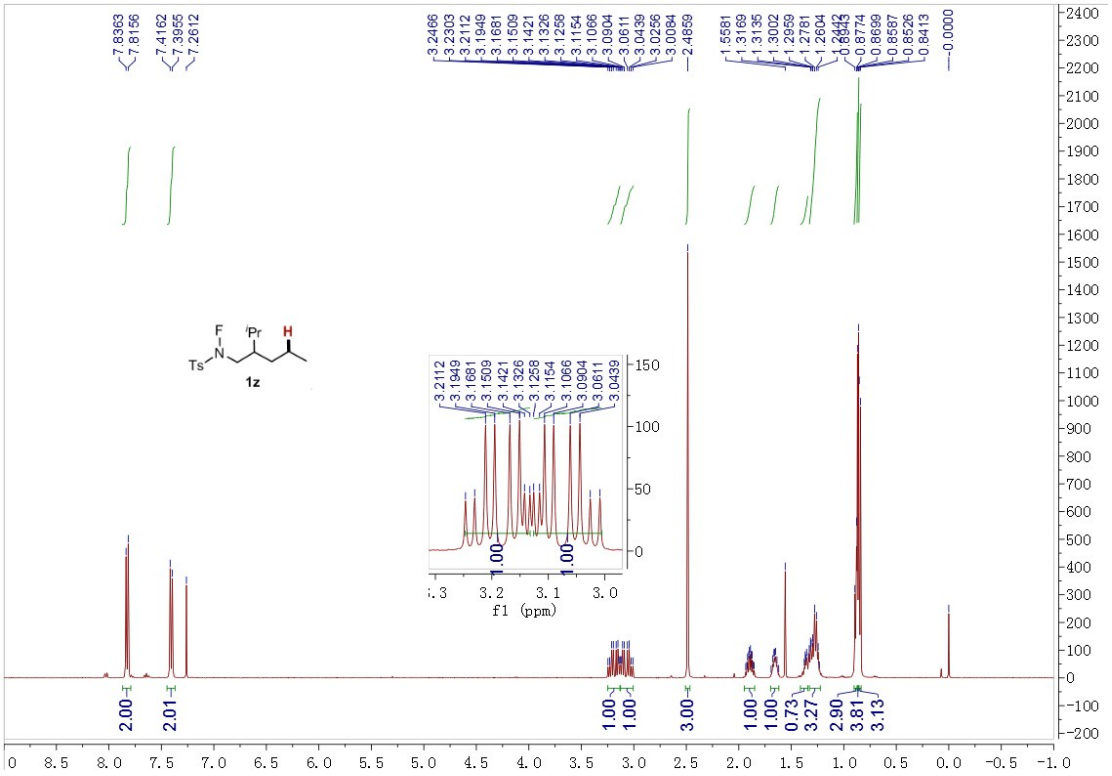
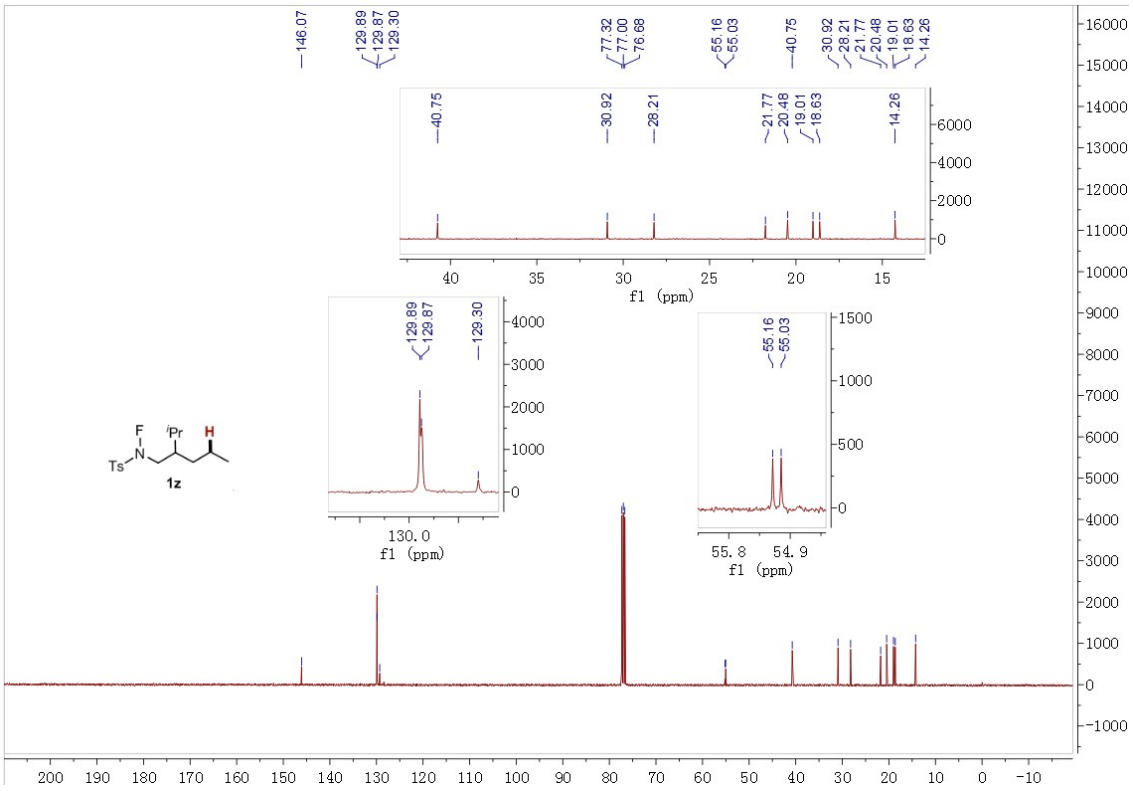
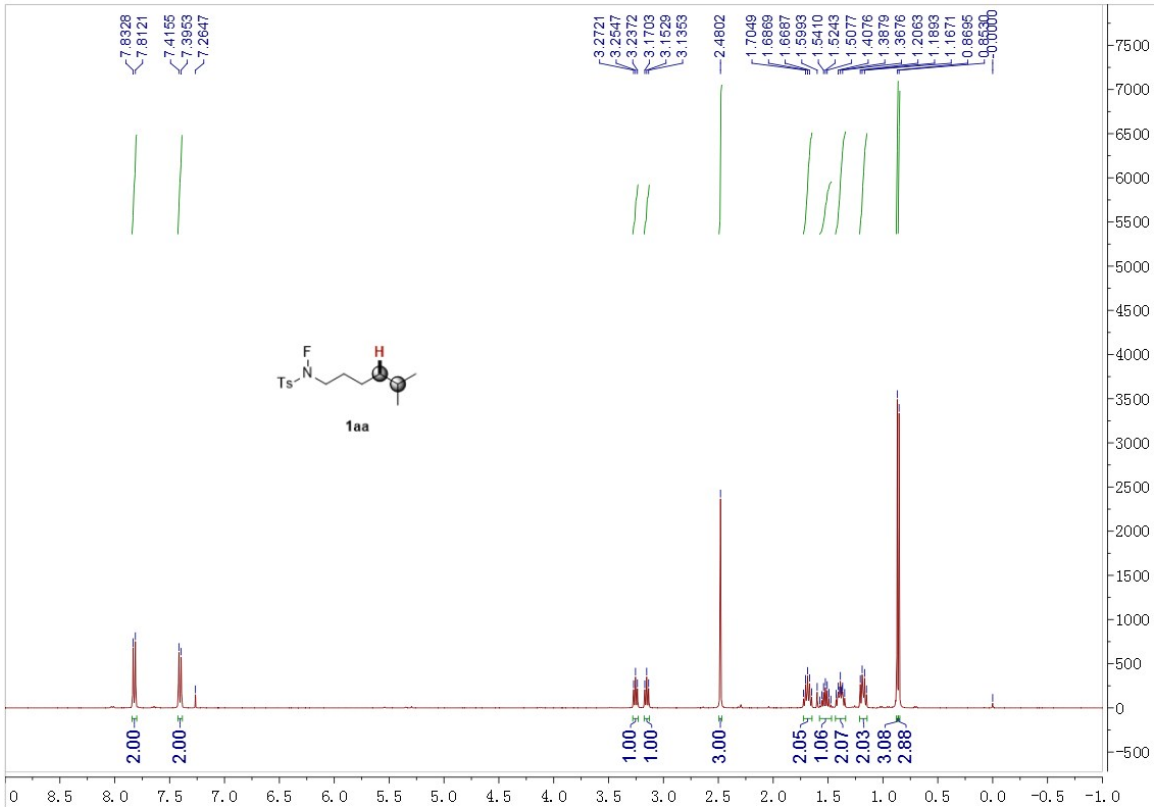

1y
f1 (ppm)


1z
f1 (ppm)


1z
f1 (ppm)
f1 (ppm)
f1 (ppm)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3.2372
3.1703
3.1529
3.1353
2.4802
1.7049
1.6869
1.6687
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1.5410
1.5243
1.5077
1.4076
1.3879
1.3676
1.2063
1.1893
1.1671
0.8695
0.0000
F
H
Ts
N
1aa
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1.00
1.00
3.00
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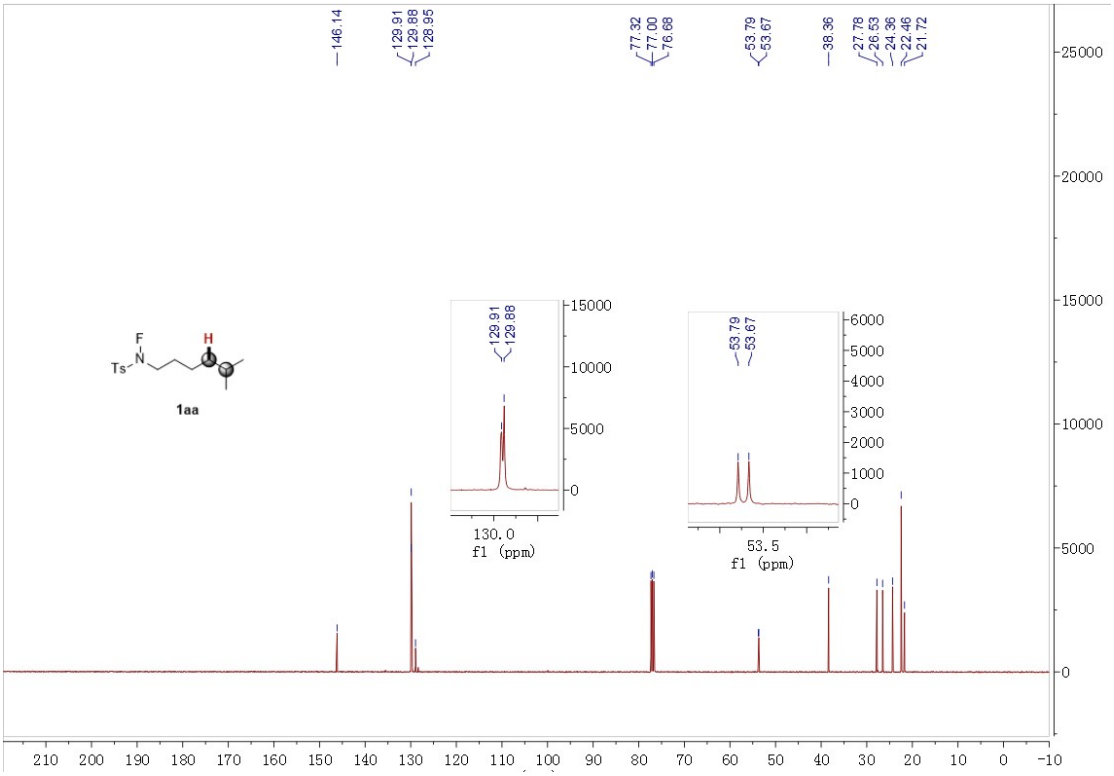
1.06
2.07
2.03
3.08
2.88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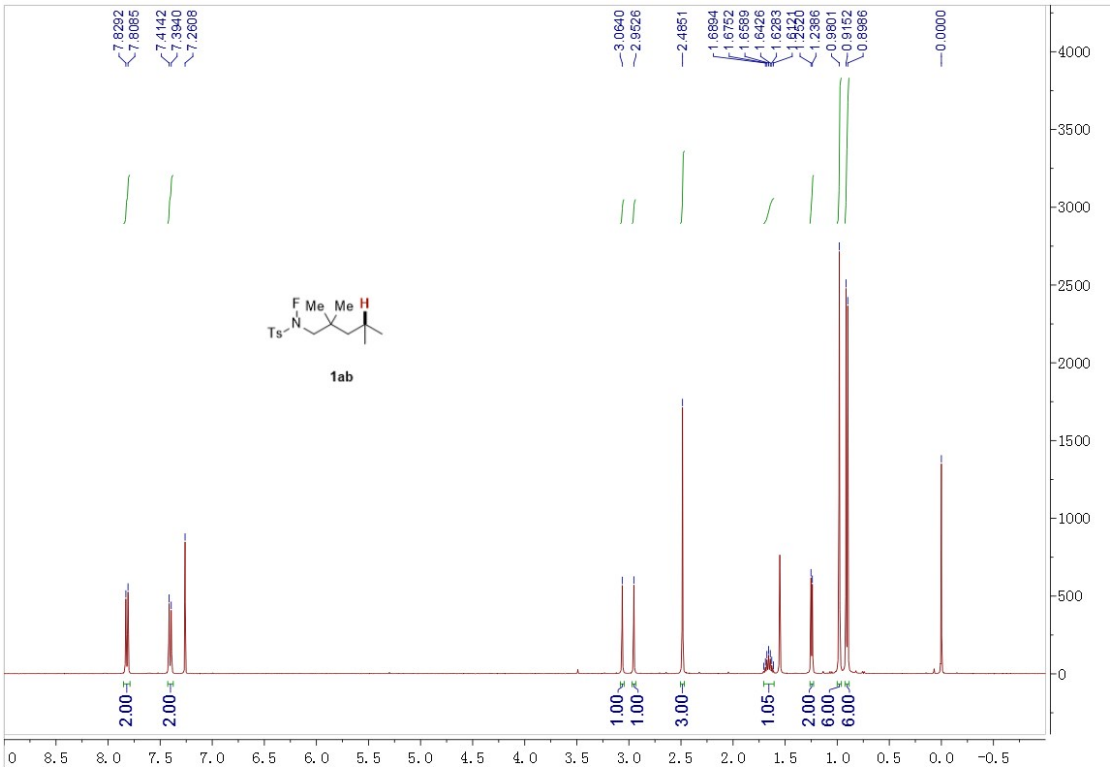
53.67
38.36
27.78
26.53
24.36
22.46
21.72
F
H
Ts
N
1aa
129.91
129.88
130.0
f1 (ppm)
53.79
53.67
53.5
f1 (ppm)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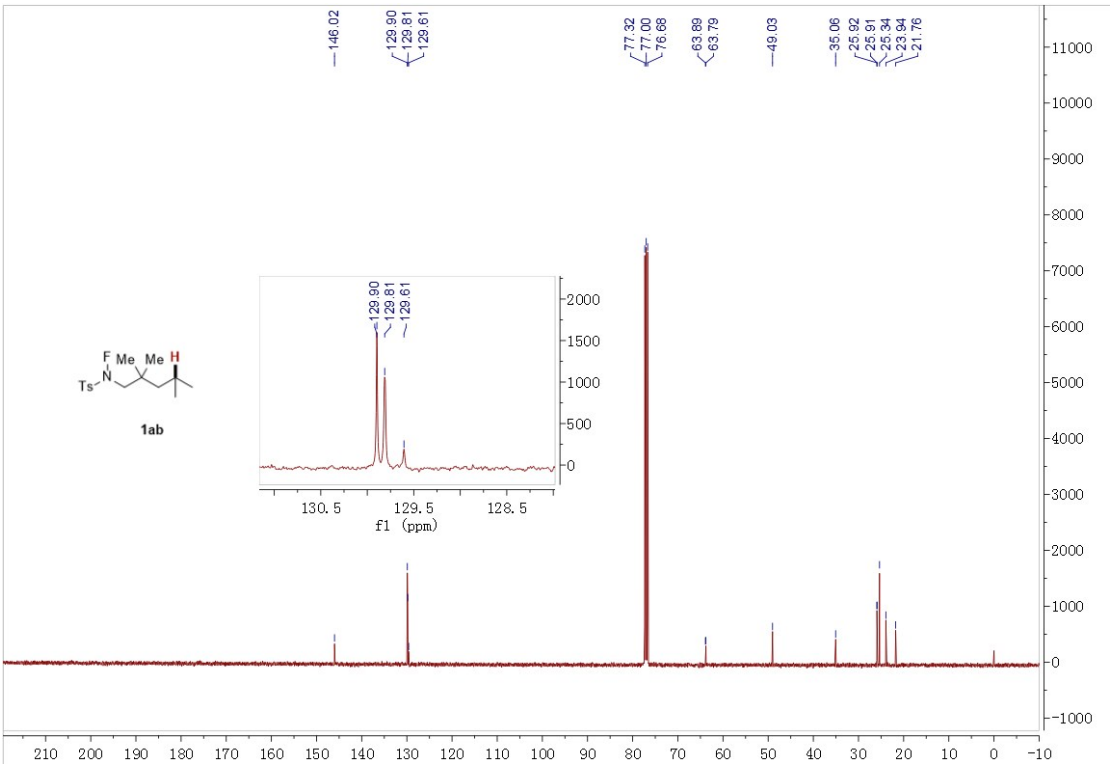
1.6426
1.6283
1.6121
1.2520
1.2386
0.9801
0.9152
0.8986
0.0000
F Me Me H
Ts N
1ab
2.00
2.00
1.00
1.00
3.00
1.05
2.00
6.00
6.00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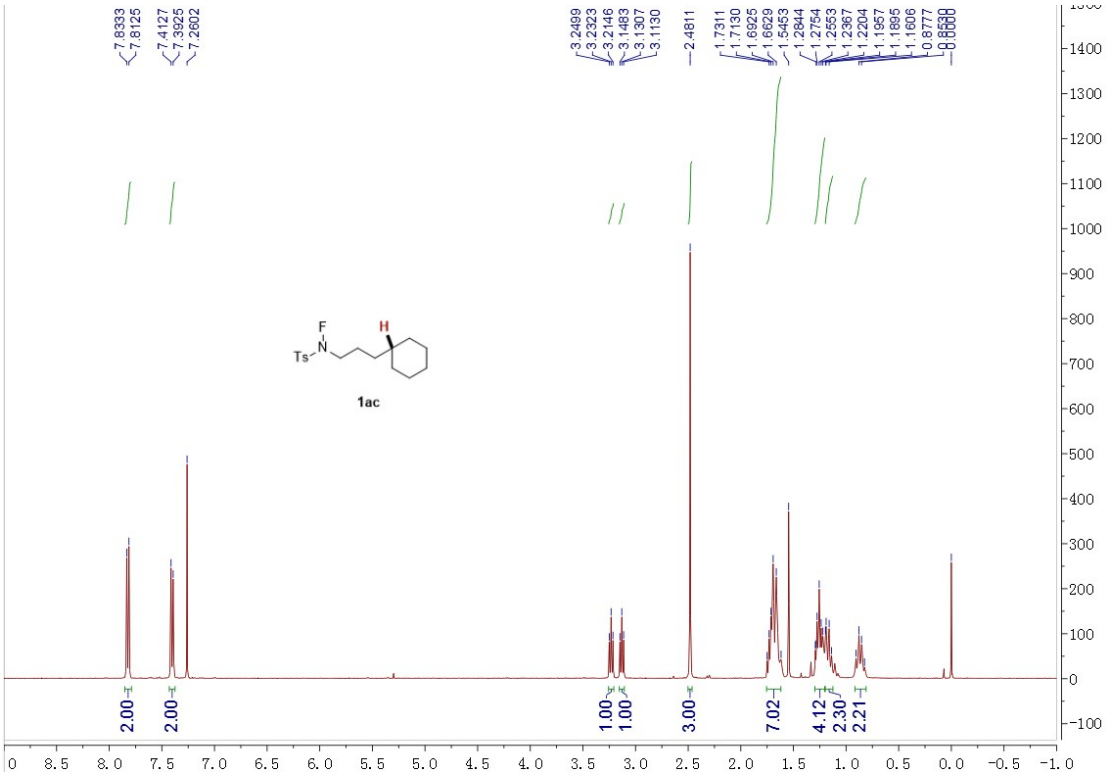
63.79
49.03
35.06
25.92
25.91
25.34
23.94
21.76
F Me Me H
Ts N
1ab
129.90
129.81
129.61
130.5
129.5
128.5
f1 (ppm)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3.1130
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1.7130
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1.2844
1.2754
1.2553
1.2367
1.2204
1.1957
1.1895
1.1606
0.8777
F
H
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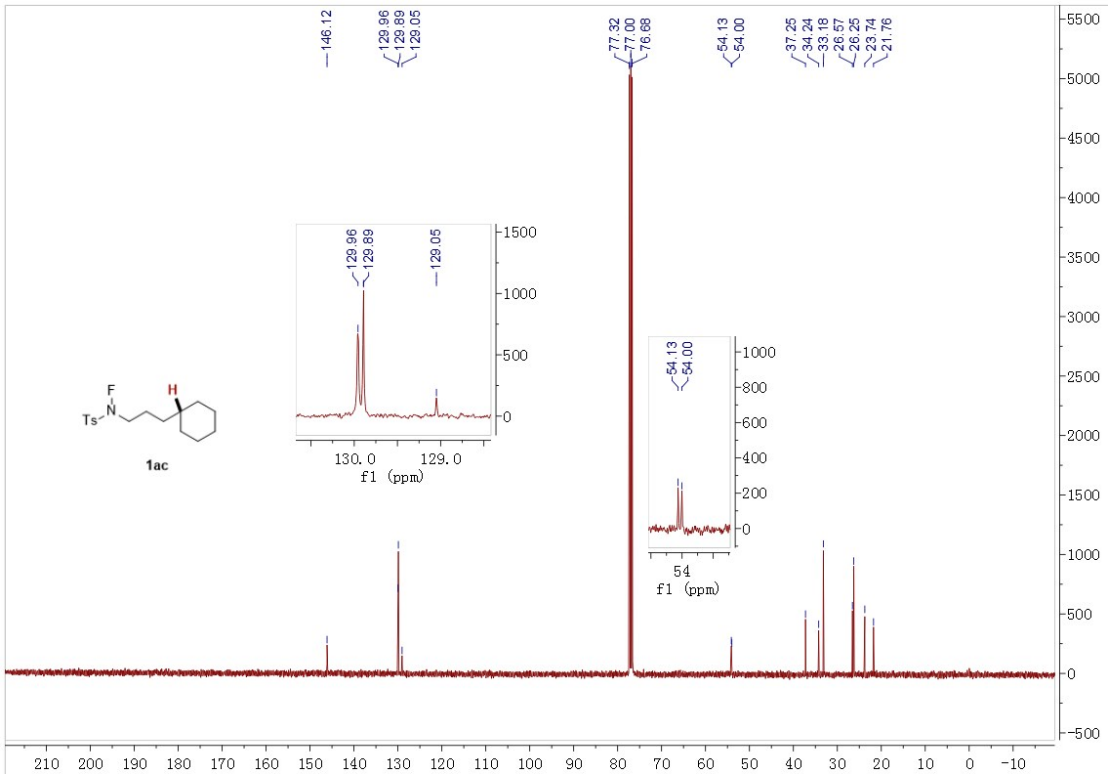
2.30
2.21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54.00
37.25
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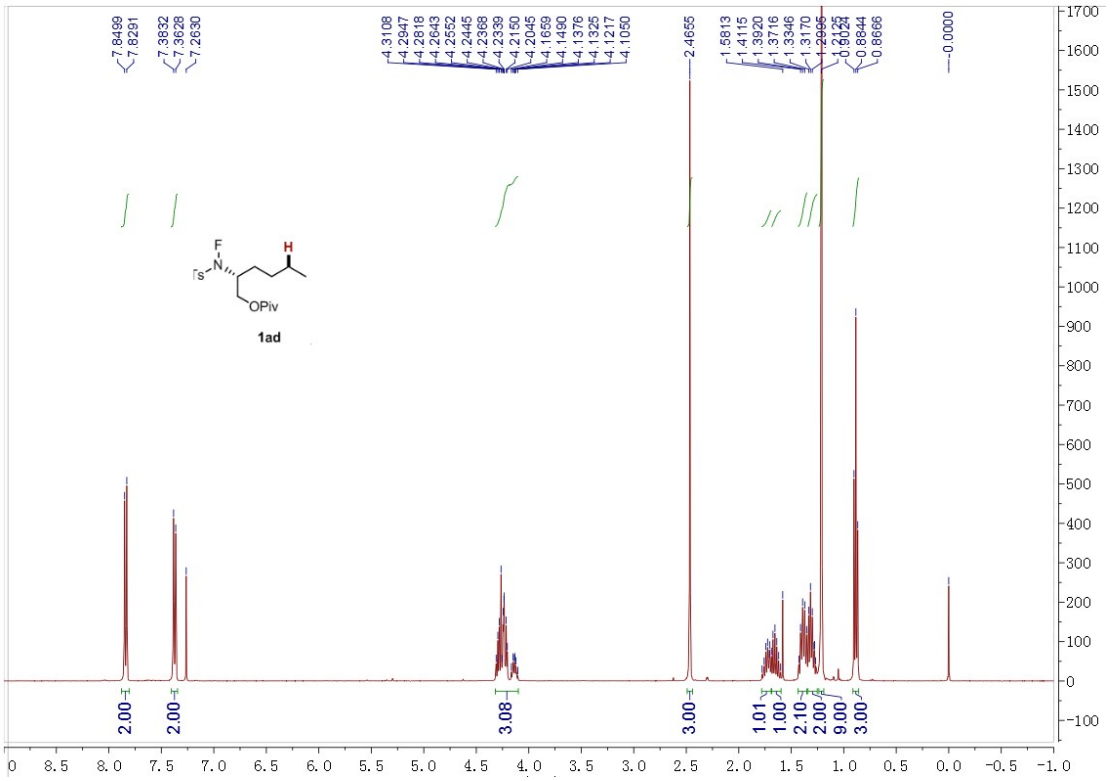
26.57
26.25
23.74
21.76
F
H
Ts
N
1ac
f1 (ppm)
f1 (ppm)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4.2368
4.2339
4.2150
4.2045
4.1659
4.1490
4.1376
4.1325
4.1217
4.1050
2.4655
1.5813
1.4115
1.3920
1.3716
1.3346
1.3170
1.2995
0.8844
0.8666
0.0000
F
H
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1.00
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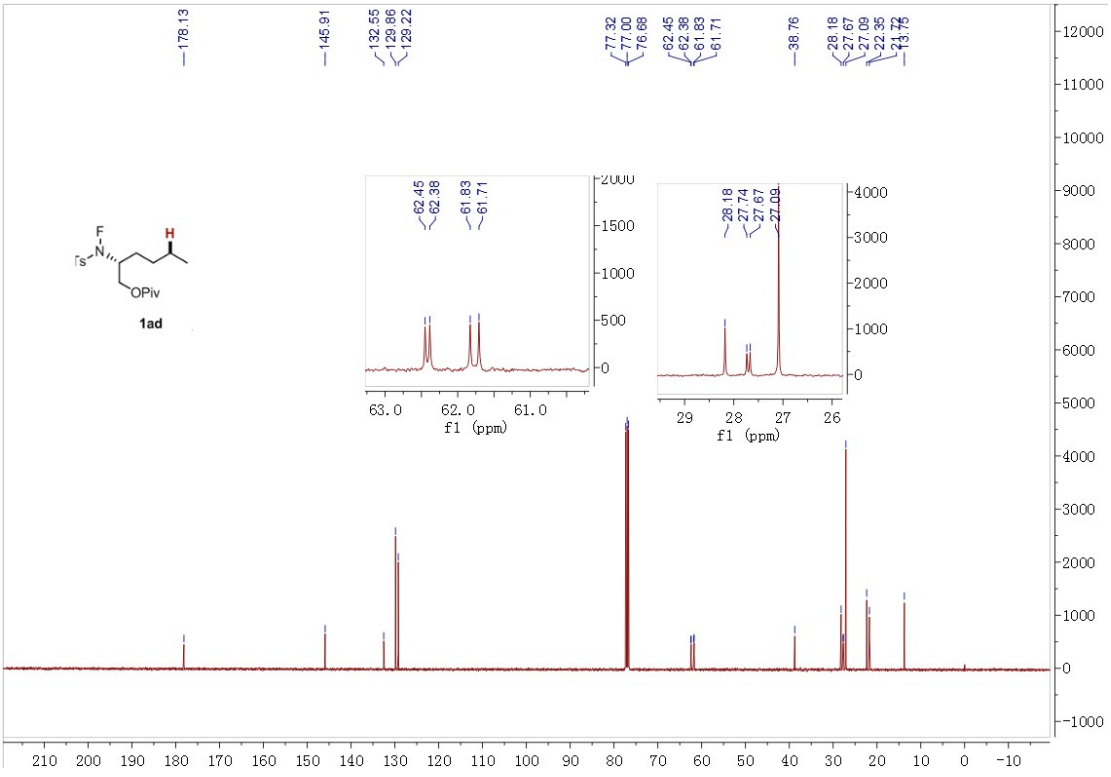
9.00
3.00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76.68
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62.38
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61.71
38.76
28.18
27.67
27.09
22.35
21.72
13.75
F
H
OPiv
1ad
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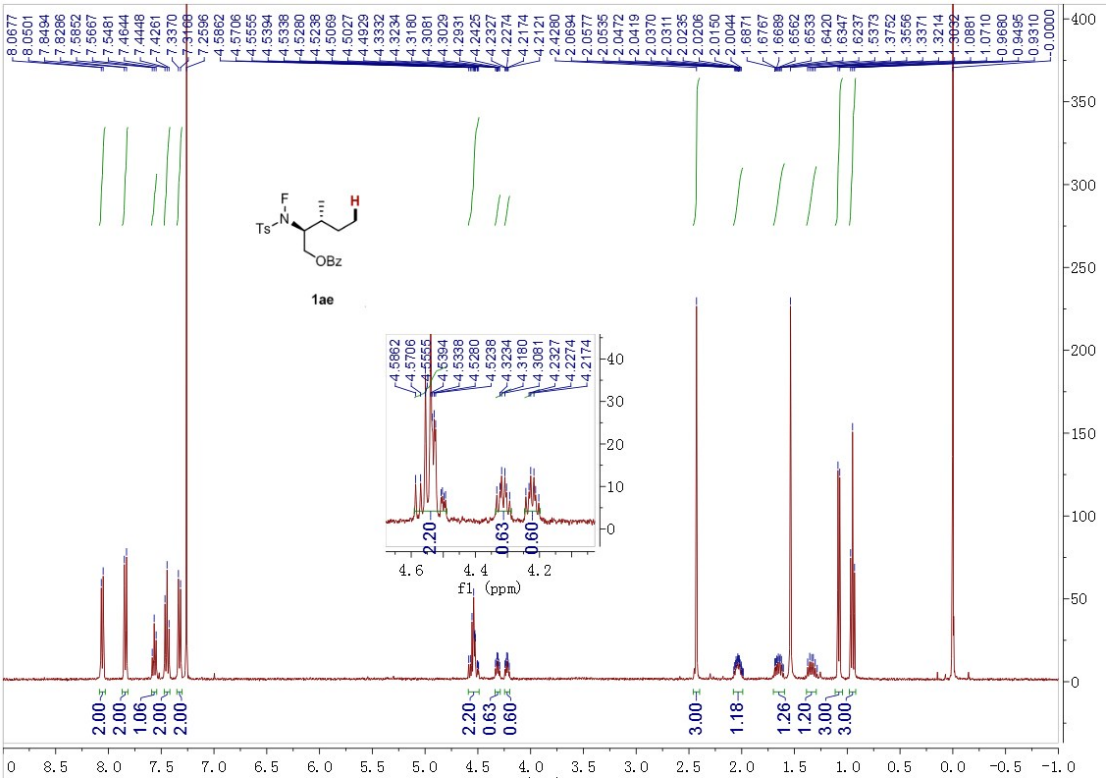
62.38
61.83
61.71
f1 (ppm)
28.18
27.74
27.67
27.09
f1 (ppm)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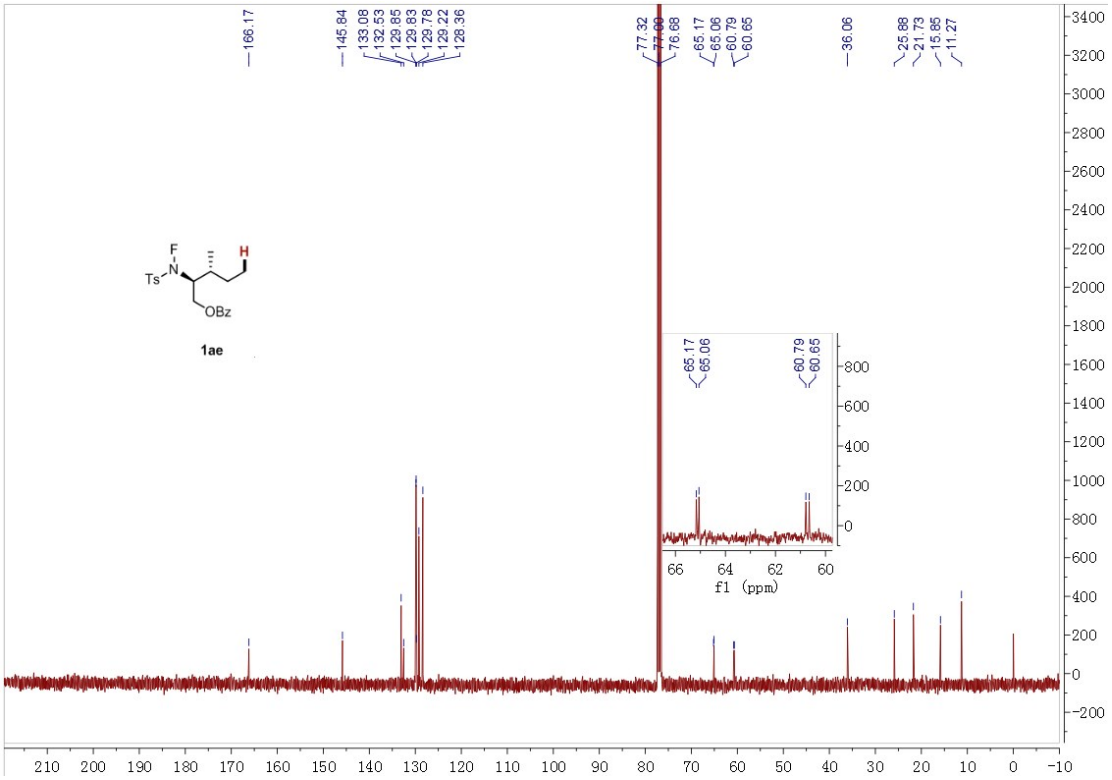
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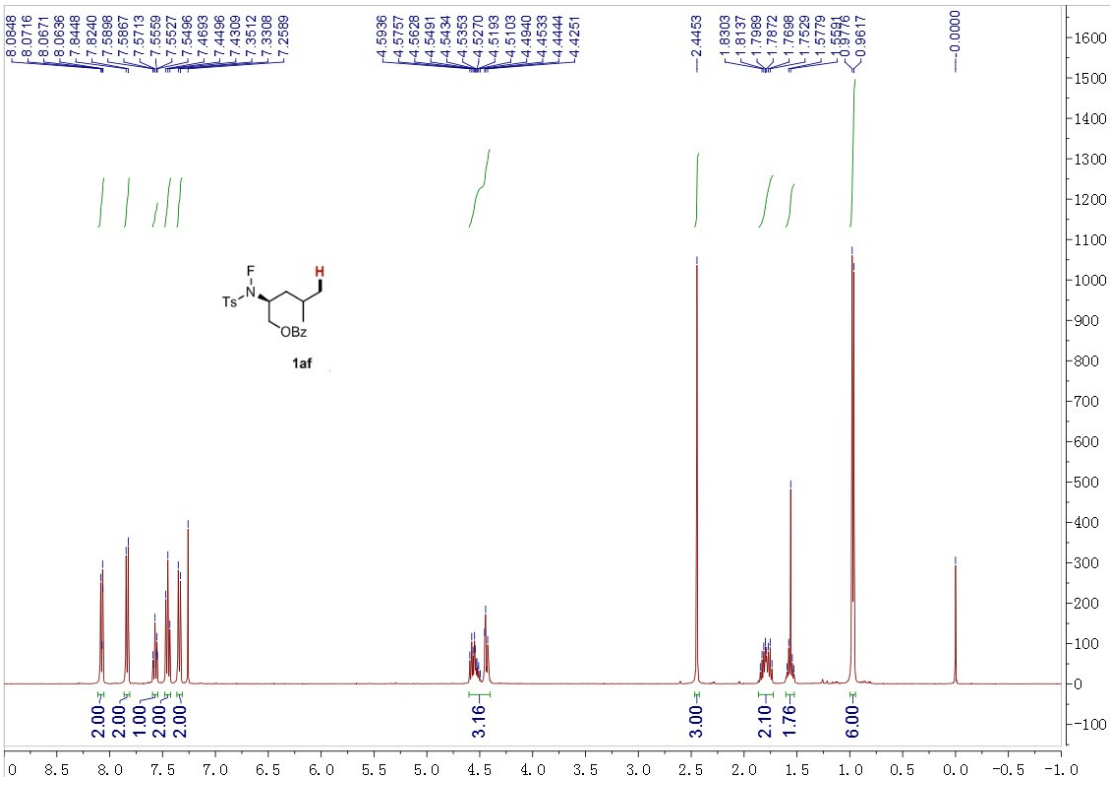
f1 (ppm)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7.5527
7.5496
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7.4496
7.4309
7.3512
7.3308
7.2589
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4.5757
4.5628
4.5491
4.5434
4.5353
4.5270
4.5193
4.5103
4.4940
4.4533
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4.4251
2.4453
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1.8137
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1.7698
1.7529
1.5779
1.5591
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0.9617
-0.0000
F
H
Ts
N
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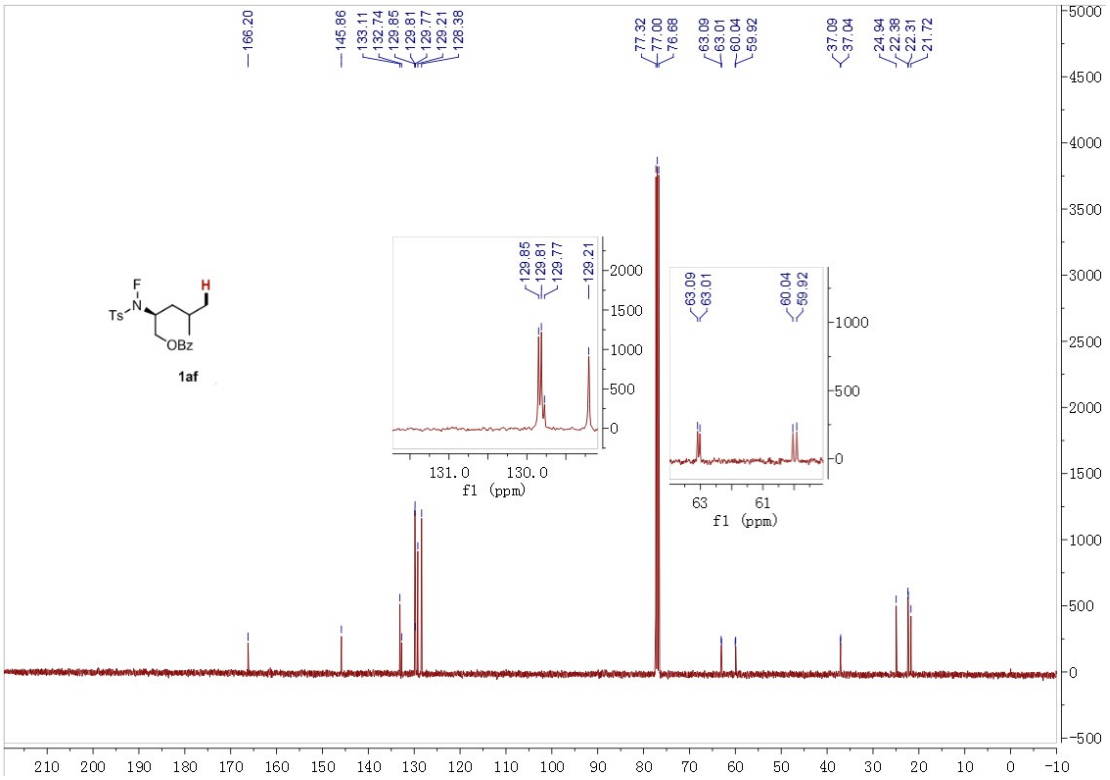
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129.21
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77.32
77.00
76.68
63.09
63.01
60.04
59.92
37.09
37.04
24.94
22.38
22.31
21.72
F
H
Ts
N
OBz
1af
129.85
129.81
129.77
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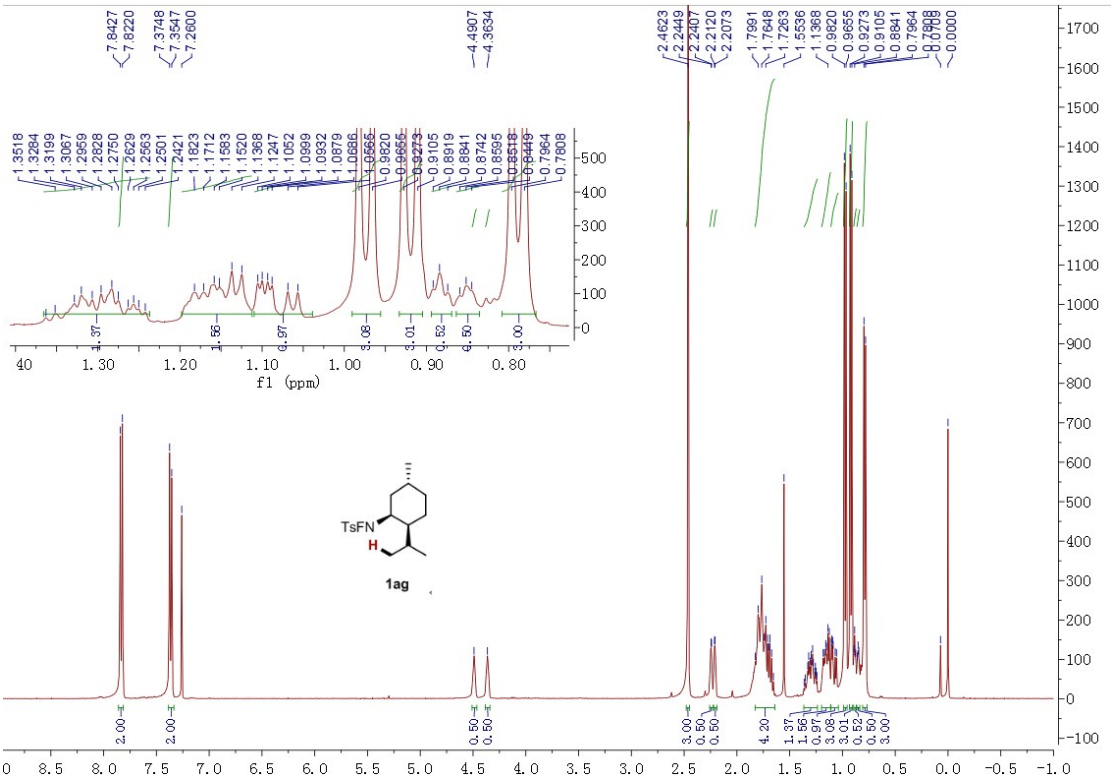
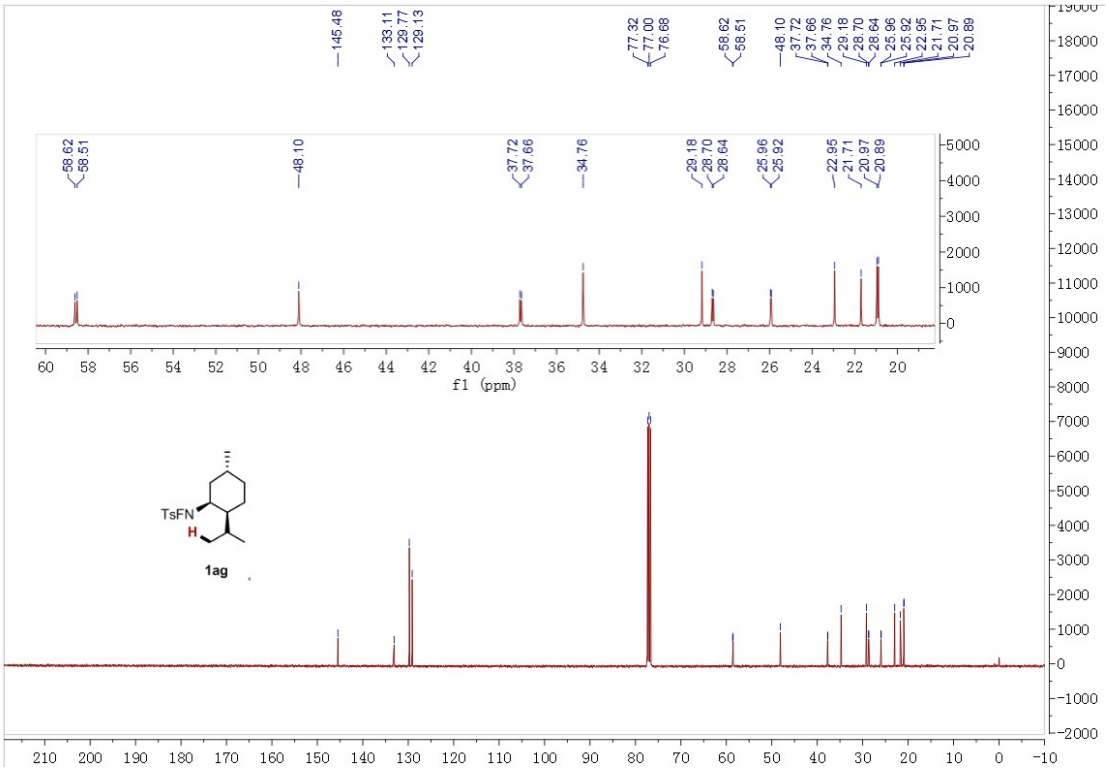
131.0
130.0
f1 (ppm)
63.09
63.01
60.04
59.92
63
61
f1 (ppm)


TsFN
H
1ag
f1 (ppm)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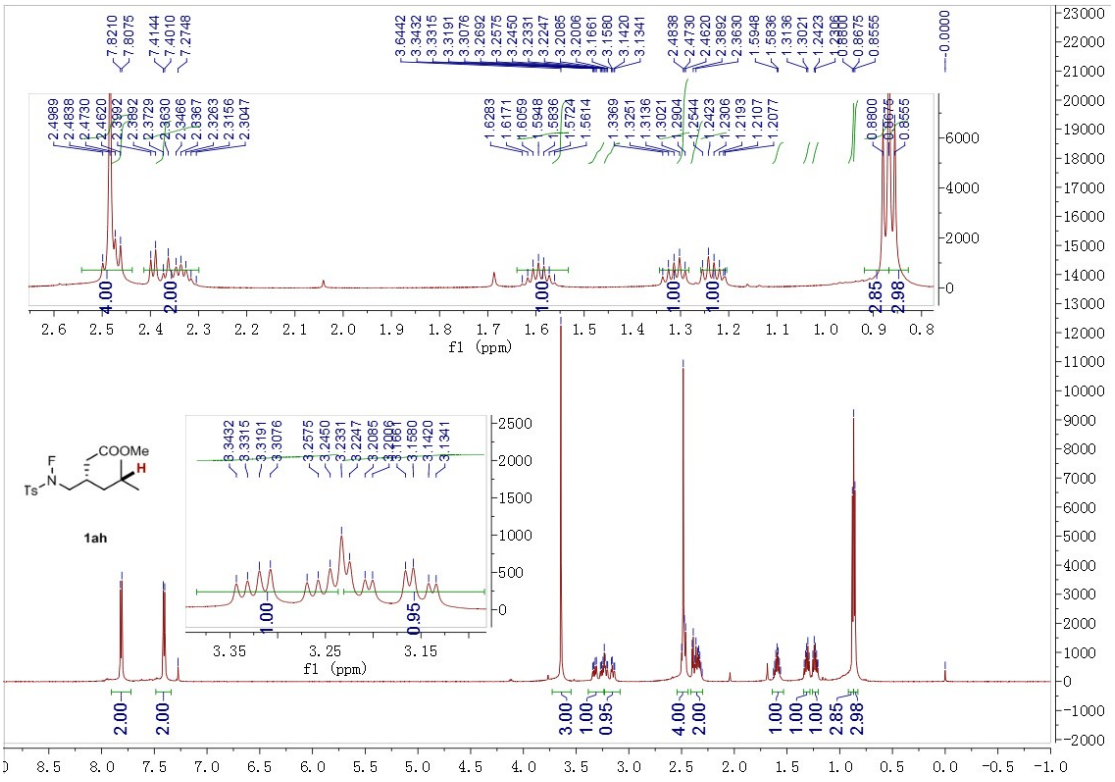
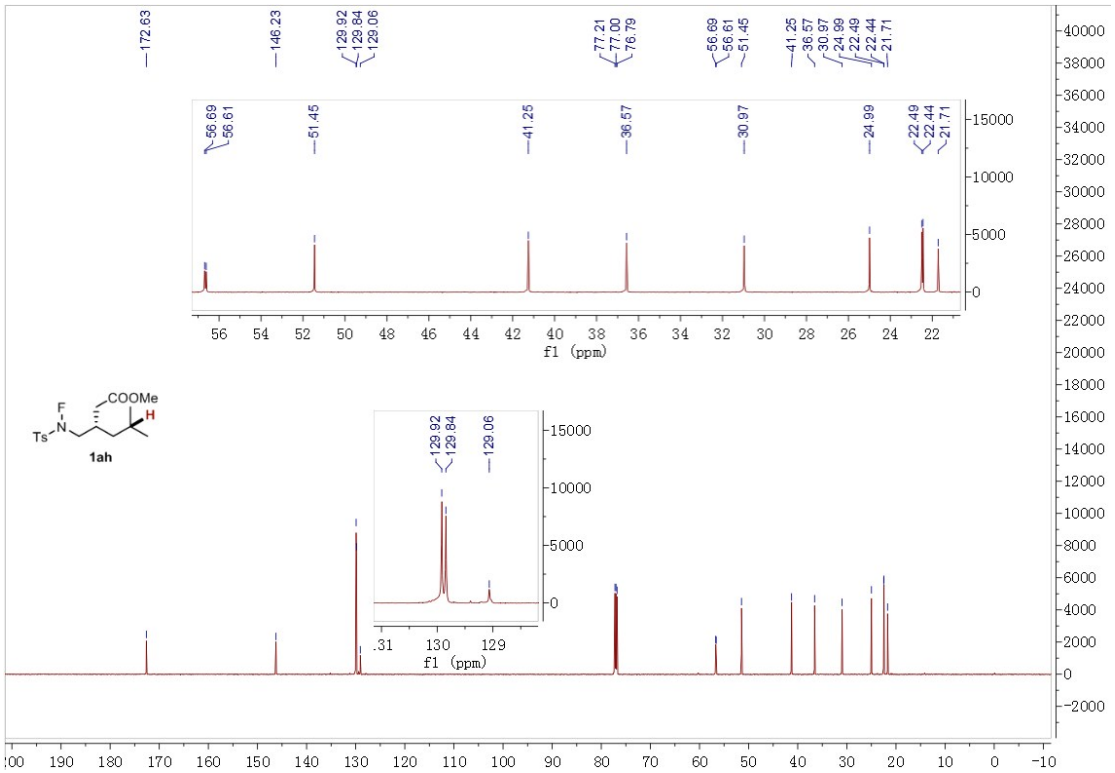
H
1ag
f1 (ppm)


1ah
f1 (ppm)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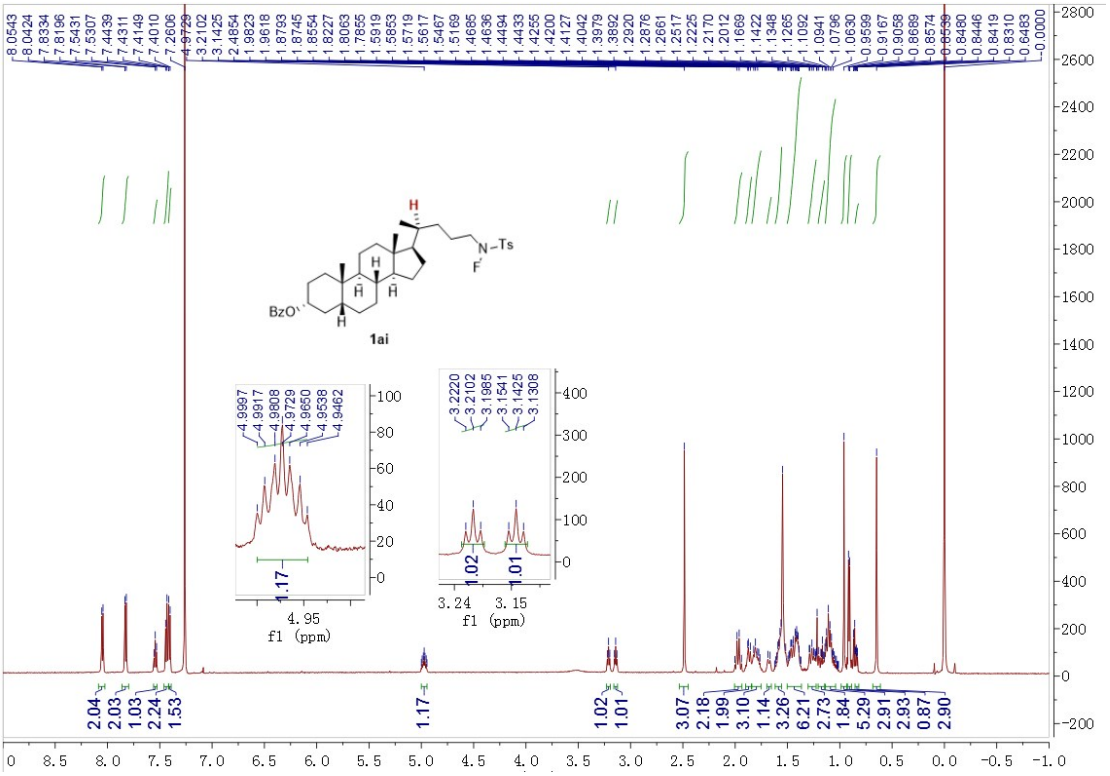
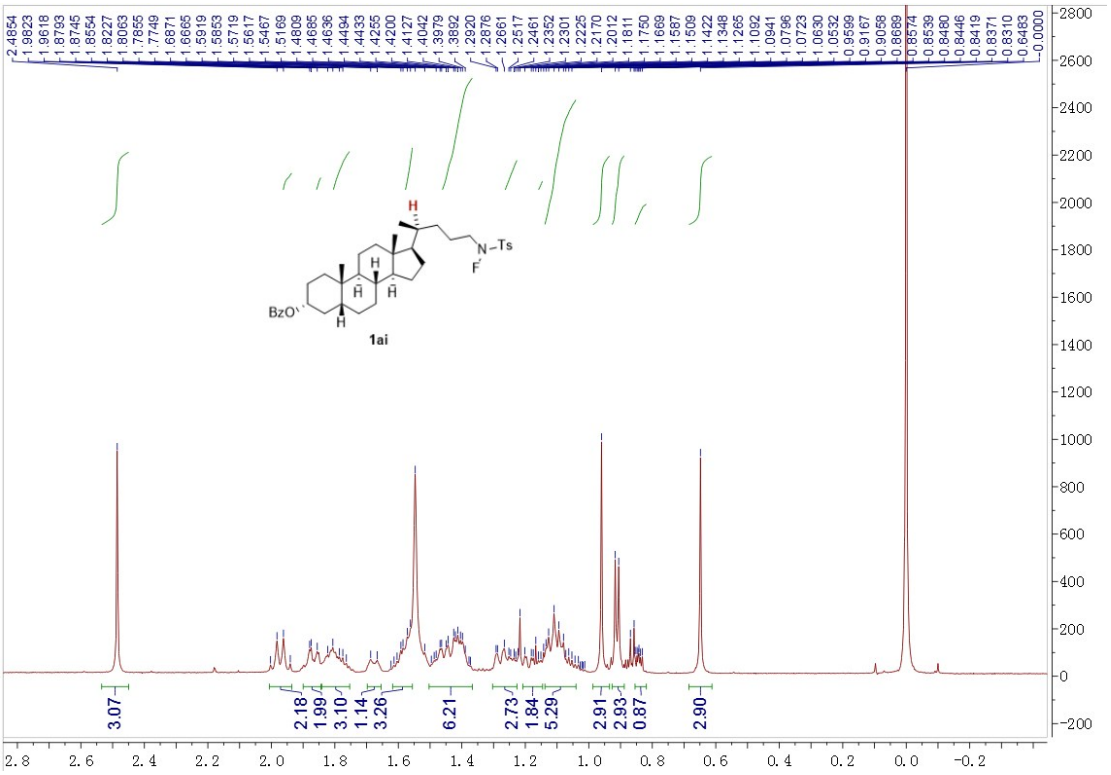
f1 (ppm)


1ai
4.95
f1 (ppm)
3.24
3.15
f1 (ppm)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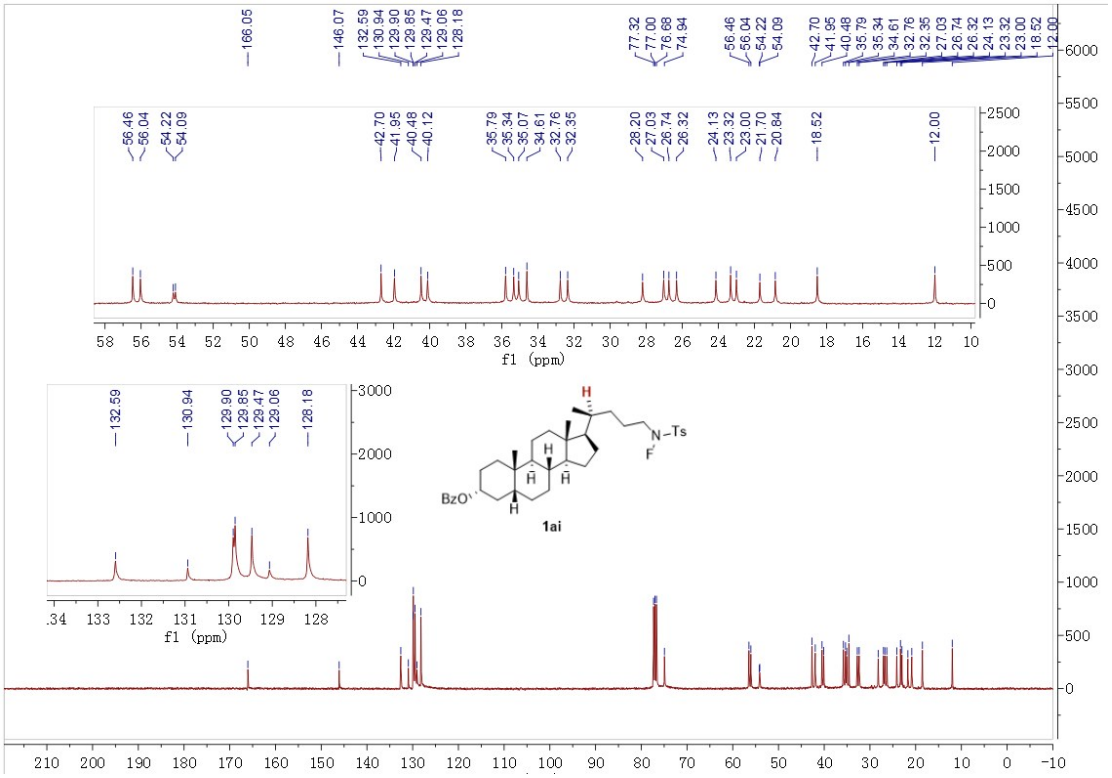
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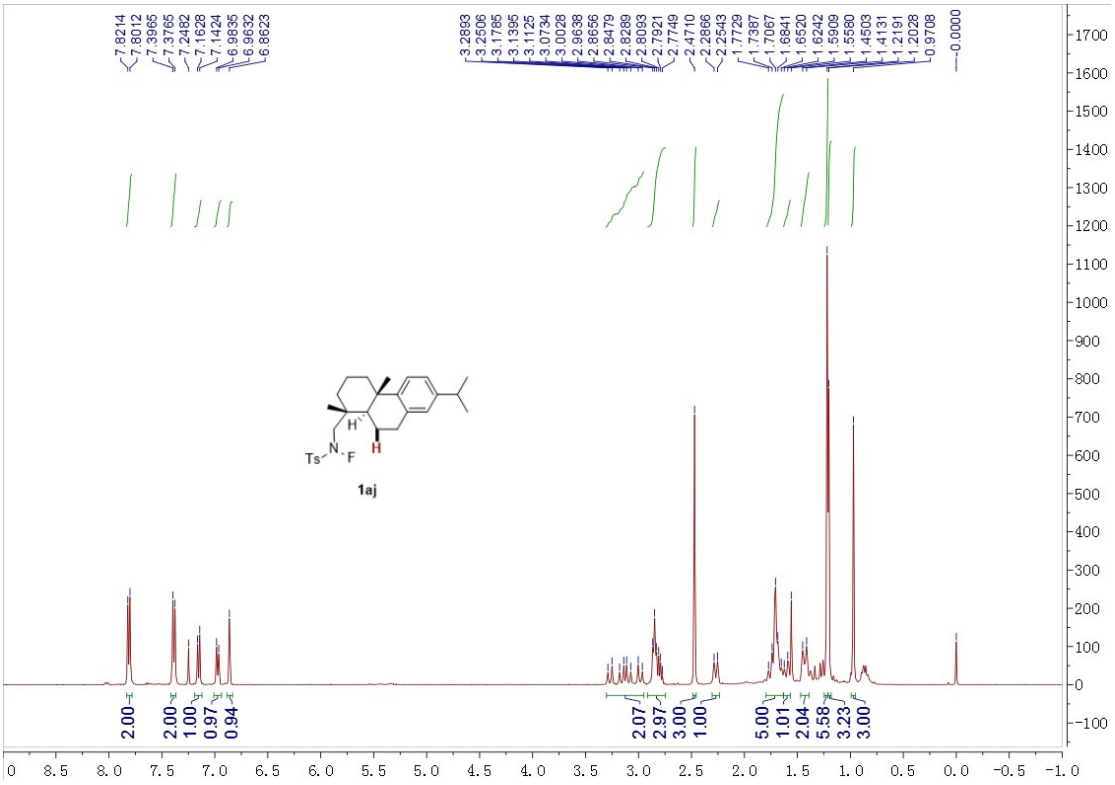
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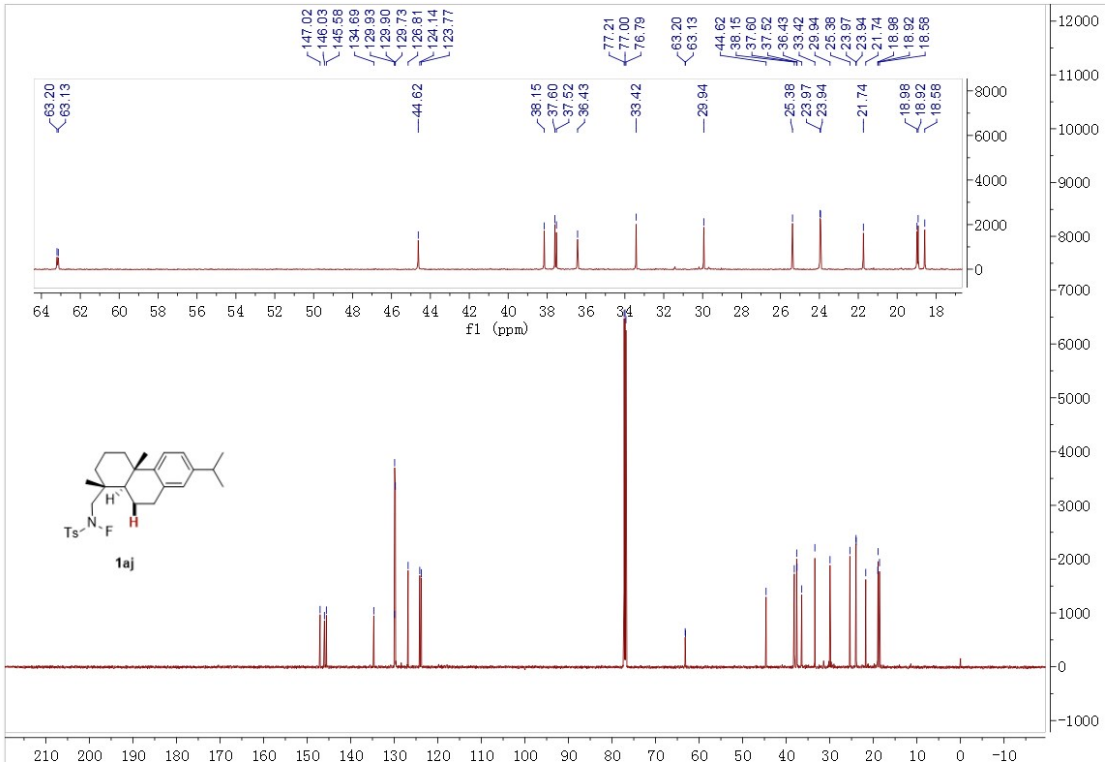
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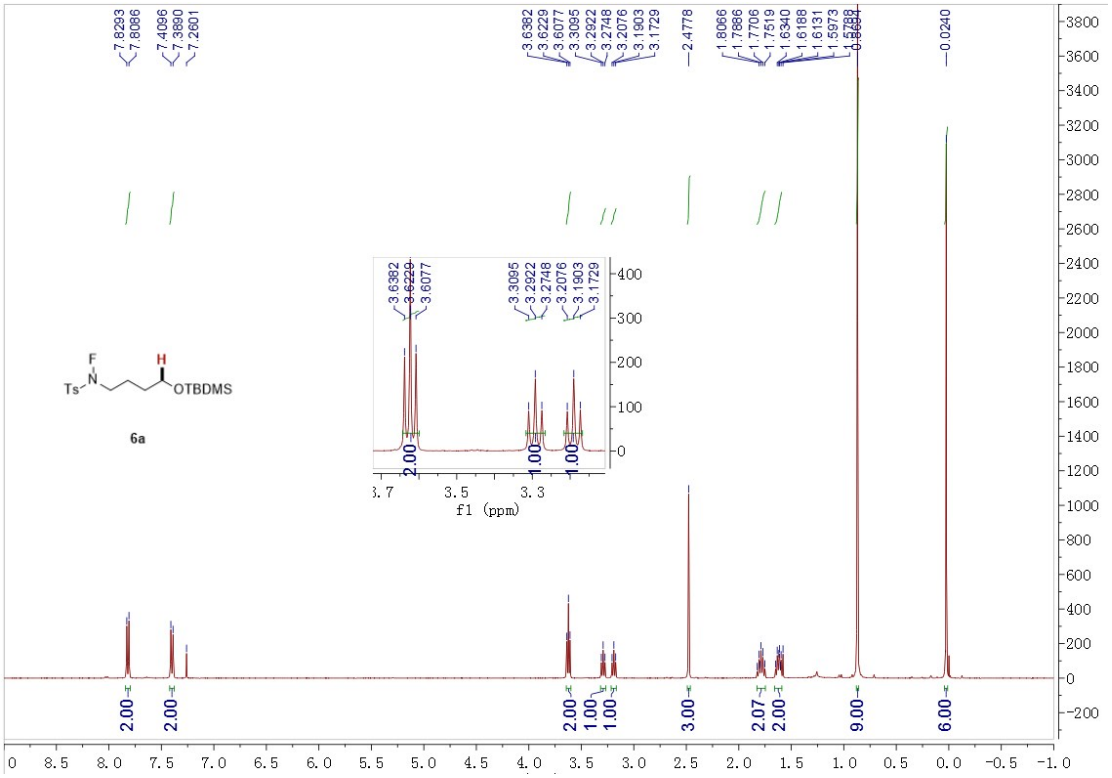
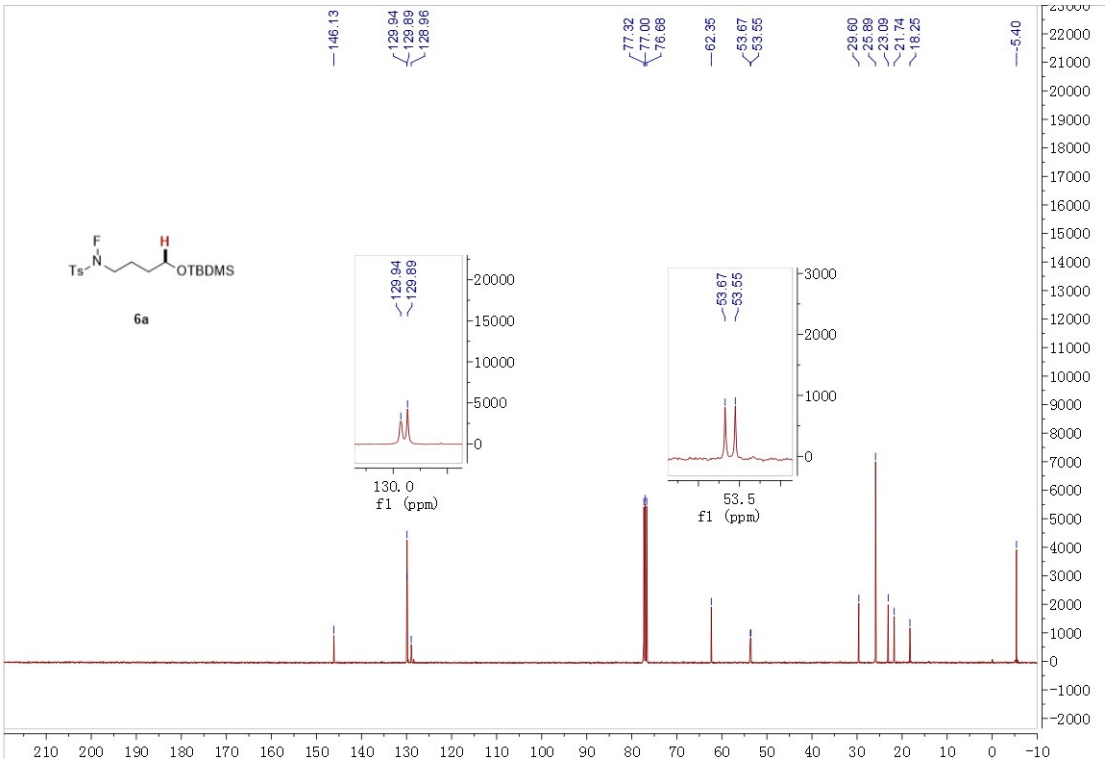

6a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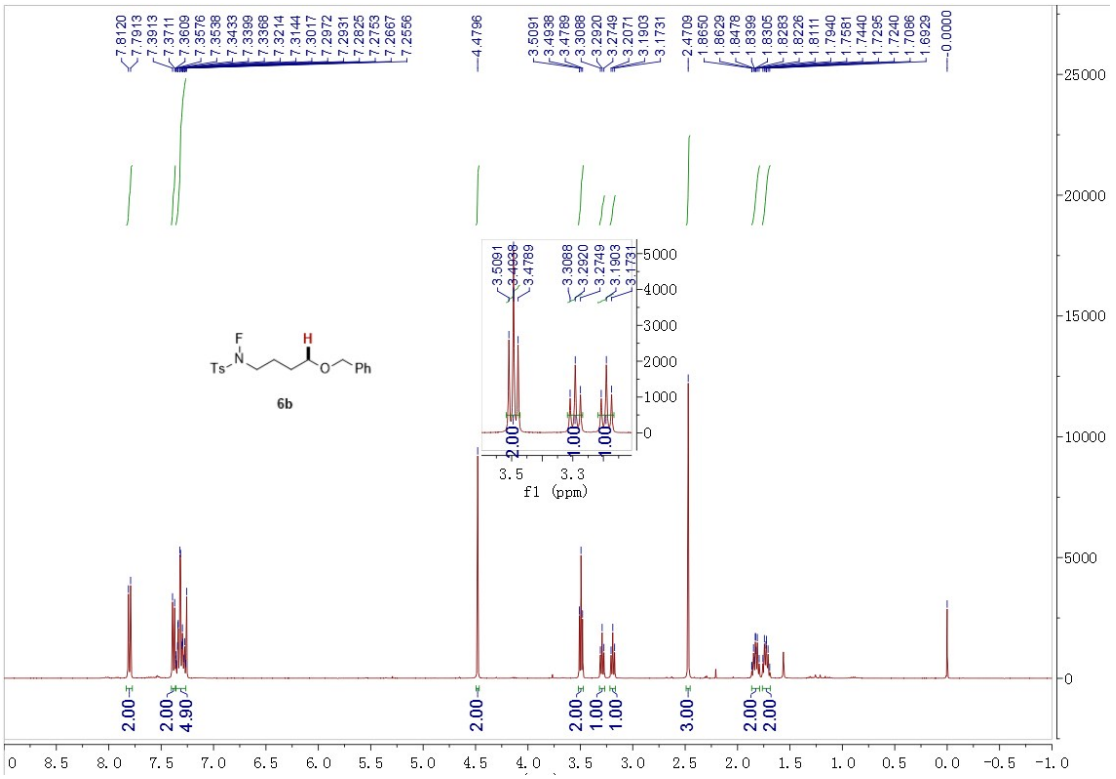
129.94
129.89
128.96
77.32
77.00
76.68
62.35
53.67
53.55
29.60
25.89
23.09
21.74
18.25
-5.40
F
H
Ts
N
OTBDMS
6a
129.94
129.89
130.0
f1 (ppm)
53.67
53.55
53.5
f1 (ppm)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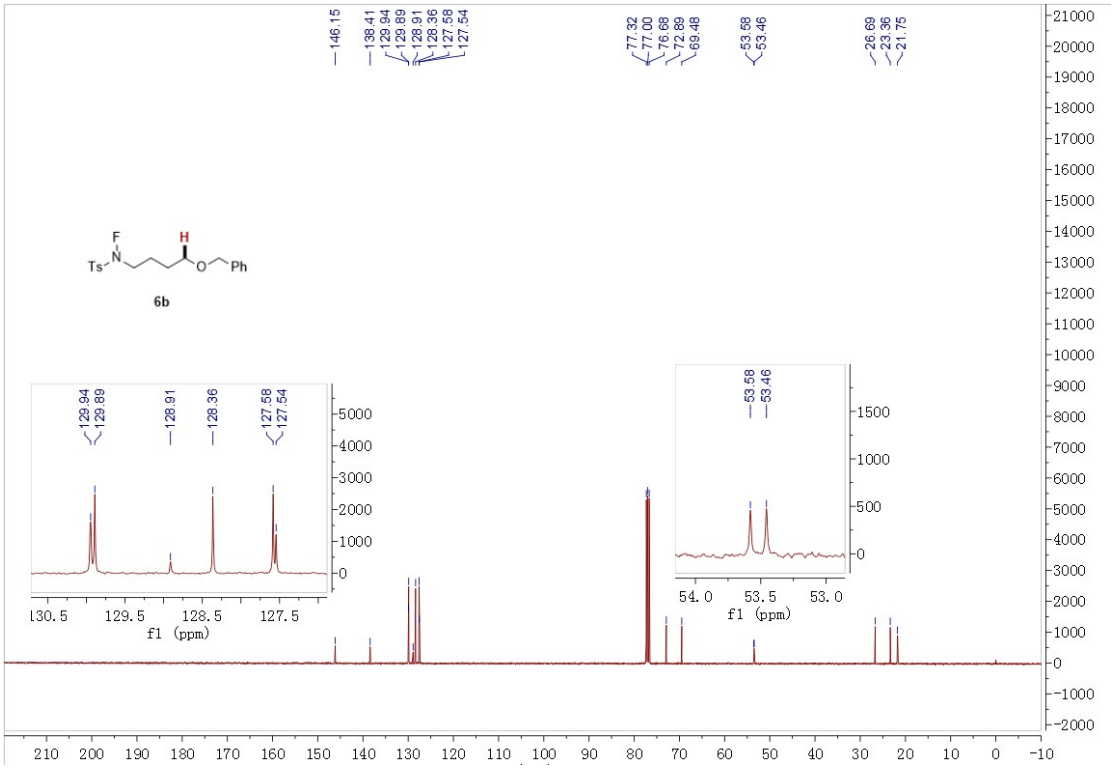
7.3711
7.3609
7.3576
7.3538
7.3433
7.3399
7.3368
7.3214
7.3144
7.3017
7.2972
7.2931
7.2825
7.2753
7.2667
7.2556
4.4796
3.5091
3.4938
3.4789
3.3088
3.2920
3.2749
3.2071
3.1903
3.1731
2.4709
1.8650
1.8629
1.8478
1.8399
1.8305
1.8283
1.8226
1.8111
1.7940
1.7581
1.7440
1.7295
1.7240
1.7086
1.6929
0.0000
F
H
Ts
N
O
Ph
6b
3.5
3.3
f1 (ppm)
2.00
1.00
1.00
2.00
4.90
2.00
2.00
1.00
1.00
3.00
2.00
2.00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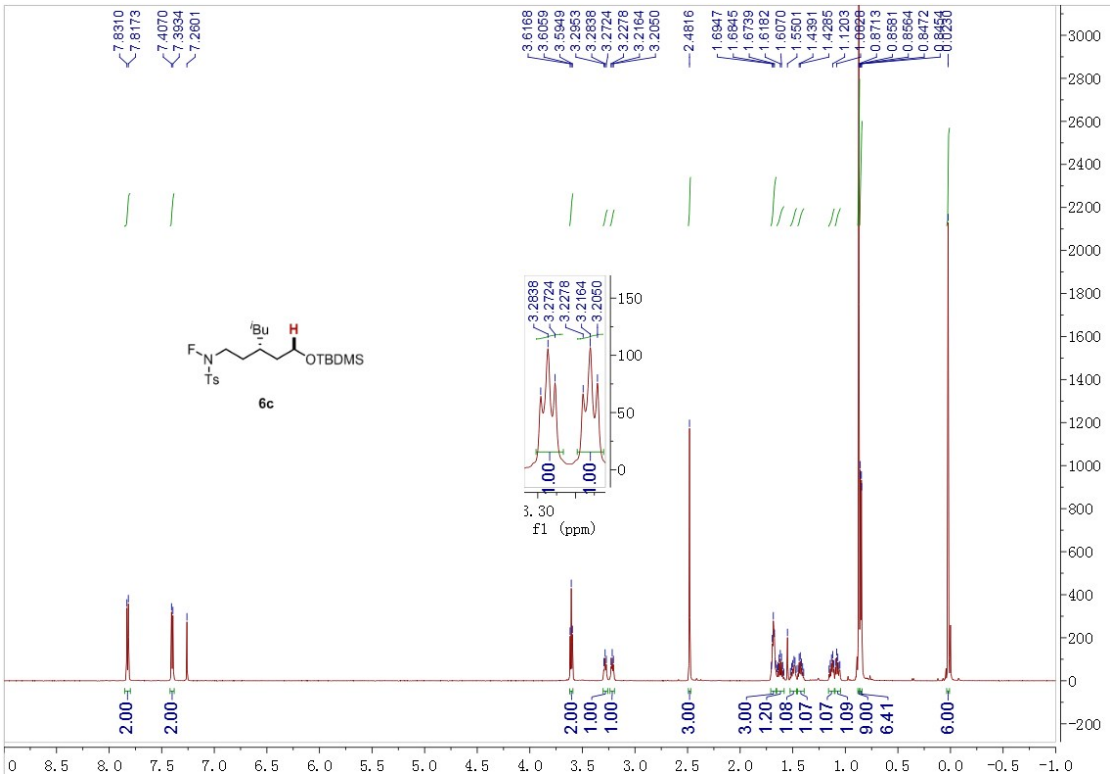
138.41
129.94
129.89
128.91
128.36
127.58
127.54
77.32
77.00
76.68
72.89
69.48
53.58
53.46
26.69
23.36
21.75
6b
f1 (ppm)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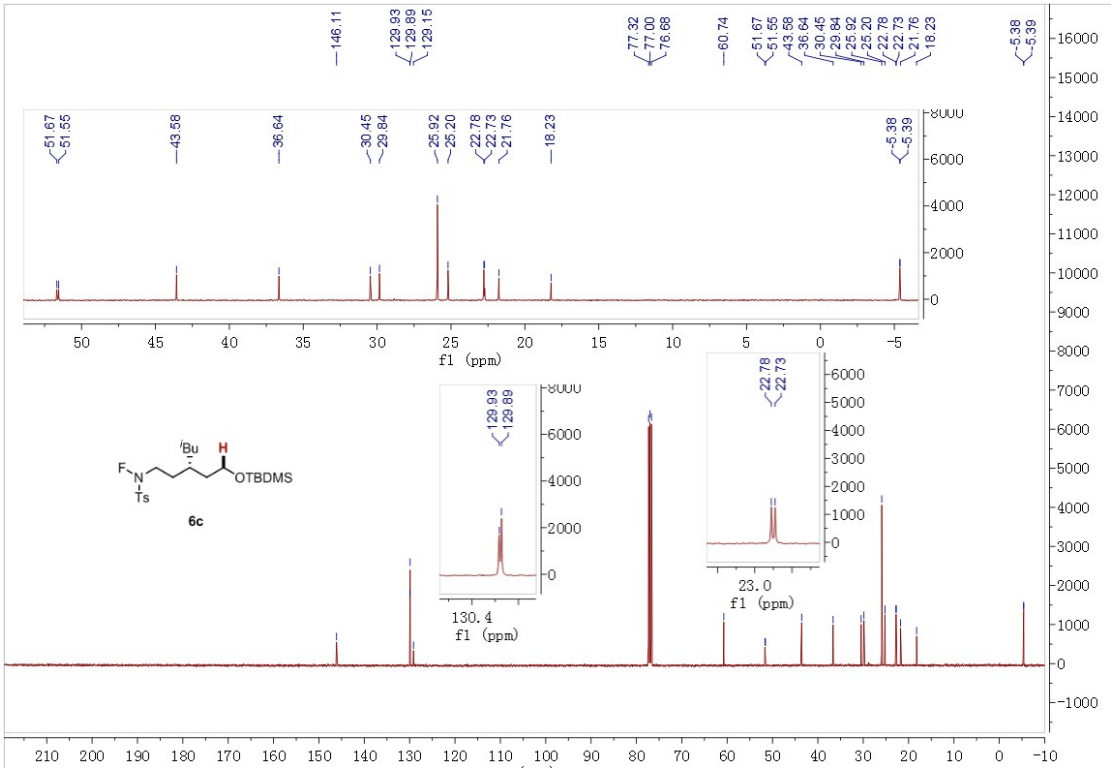
7.3934
7.2601
3.6168
3.6059
3.5949
3.2953
3.2838
3.2724
3.2278
3.2164
3.2050
2.4816
1.6947
1.6845
1.6739
1.6182
1.6070
1.5501
1.4391
1.4285
1.1203
1.0828
0.8713
0.8581
0.8564
0.8472
0.8454
0.0250
6c
f1 (ppm)
2.00
2.00
2.00
1.00
1.00
3.00
3.00
1.20
1.08
1.07
1.07
1.09
9.00
6.41
6.00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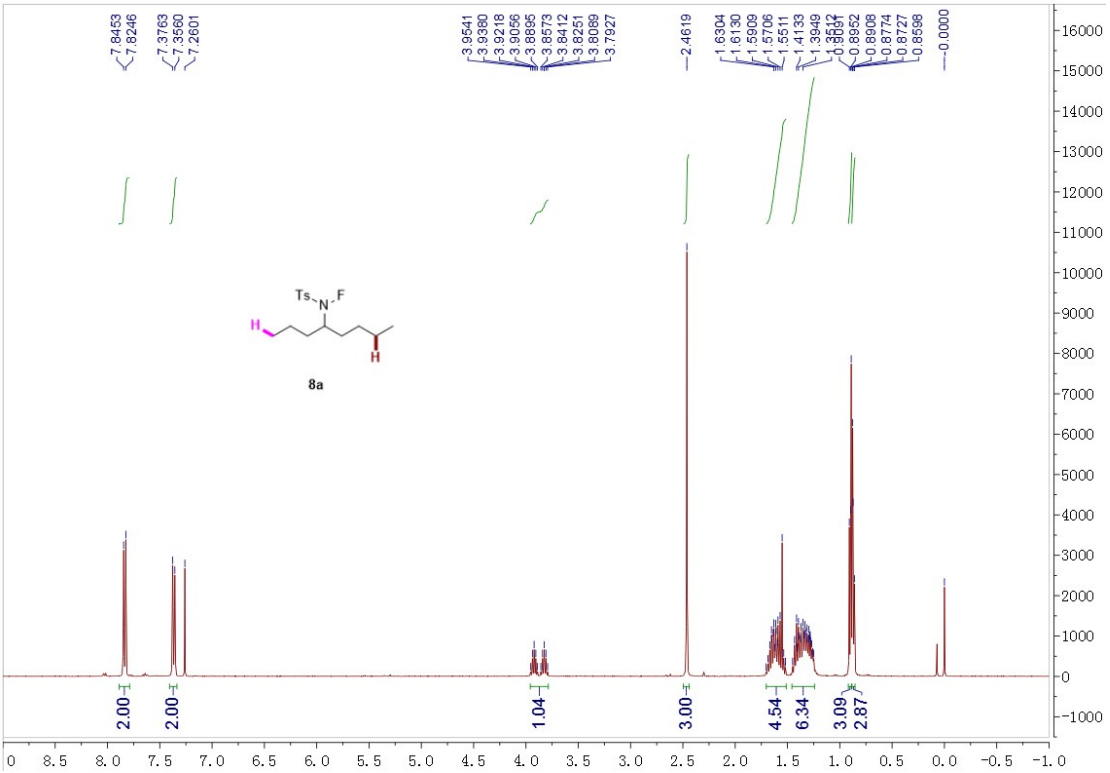
77.32
77.00
76.68
60.74
51.67
51.55
43.58
36.64
30.45
29.84
25.92
25.20
22.78
22.73
21.76
18.23
5.38
5.39
f1 (ppm)
130.4
23.0
6c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7.3560
7.2601
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3.9218
3.9056
3.8895
3.8573
3.8412
3.8251
3.8089
3.7927
2.4619
1.6304
1.6130
1.5909
1.5706
1.5511
1.4133
1.3949
0.8952
0.8906
0.8774
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3.00
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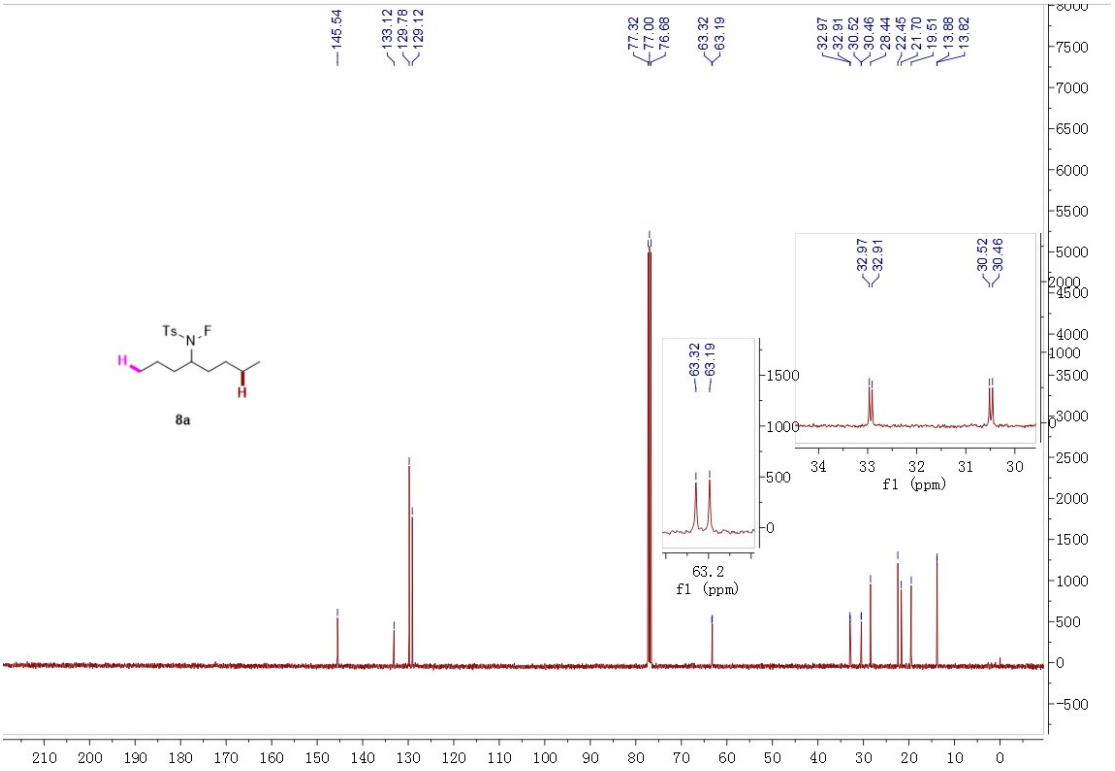
3.09
2.87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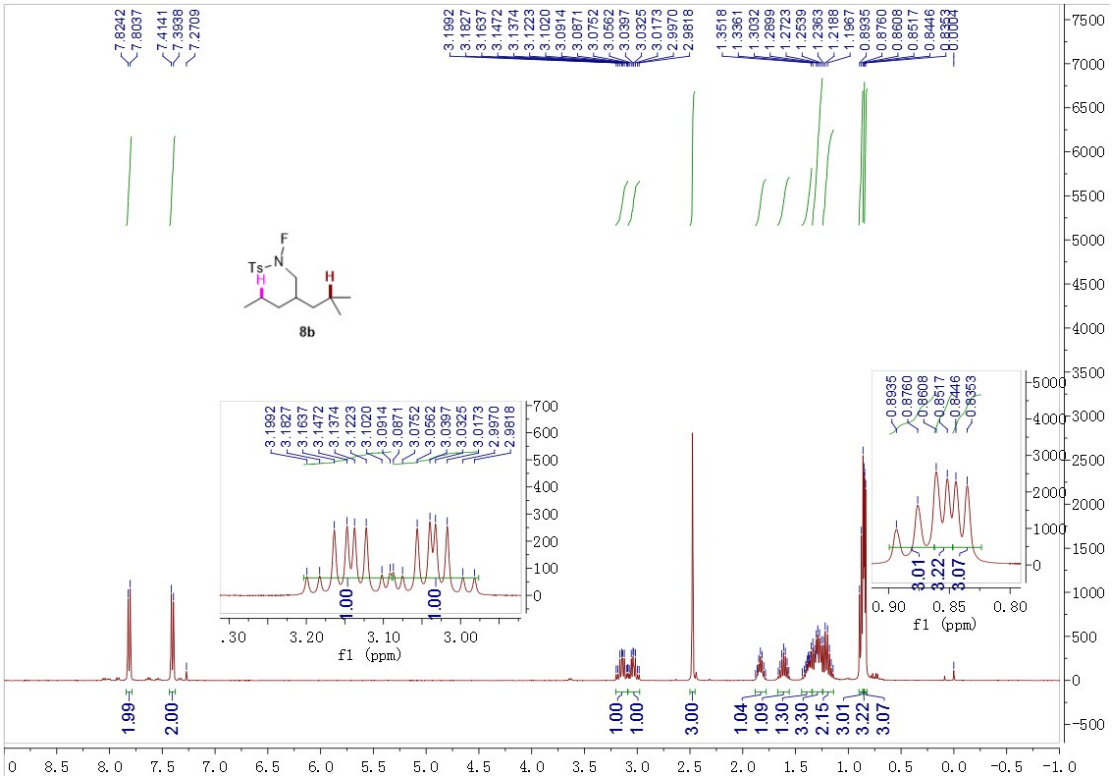
77.00
76.68
63.32
63.19
32.97
32.91
30.52
30.46
28.44
22.45
21.70
19.51
13.88
13.62
Ts
N
F
H
H
8a
f1 (ppm)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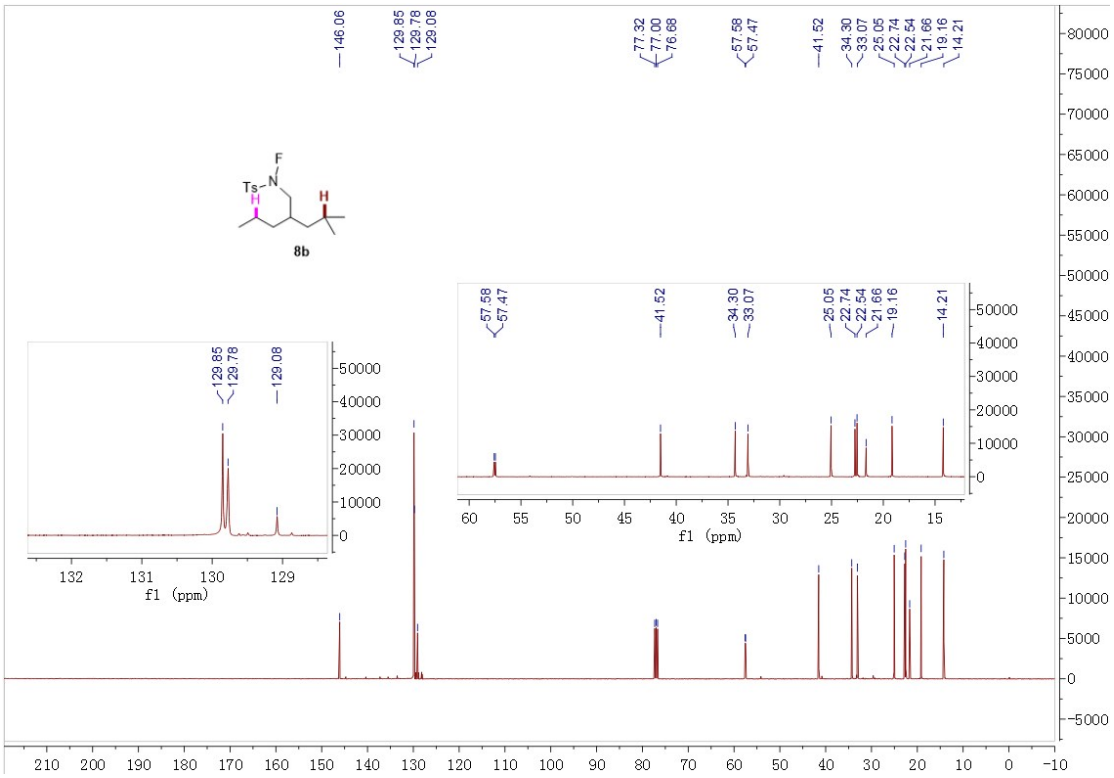
3.1374
3.1223
3.1020
3.0914
3.0871
3.0752
3.0562
3.0397
3.0325
3.0173
2.9970
2.9818
1.3518
1.3361
1.3032
1.2889
1.2723
1.2539
1.2363
1.2188
1.1967
0.8935
0.8760
0.8608
0.8517
0.8446
0.8353
F
Ts
N
H
H
8b
1.99
2.00
1.00
1.00
3.00
1.04
1.09
1.30
3.30
2.15
3.01
3.22
3.07
f1 (ppm)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77.00
76.68
57.58
57.47
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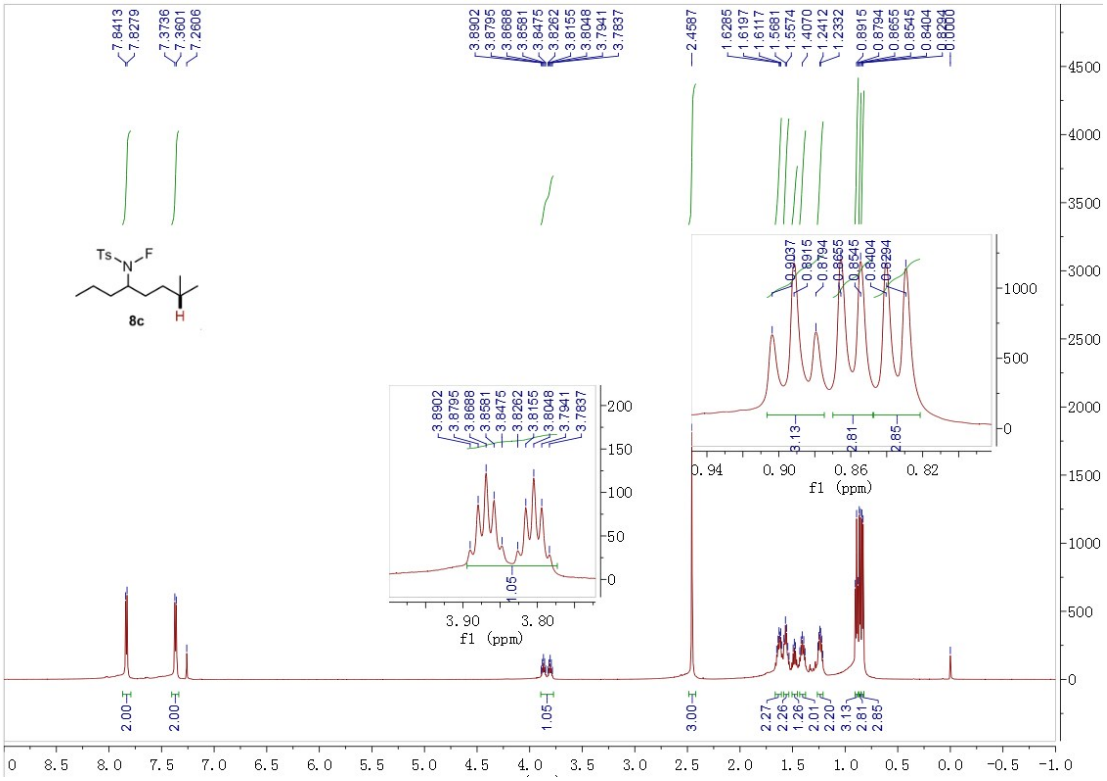
34.30
33.07
25.05
22.74
22.54
21.66
19.16
14.21
8b
f1 (ppm)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3.8155
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3.7837
2.4587
1.6285
1.6197
1.6117
1.5681
1.5574
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0.8545
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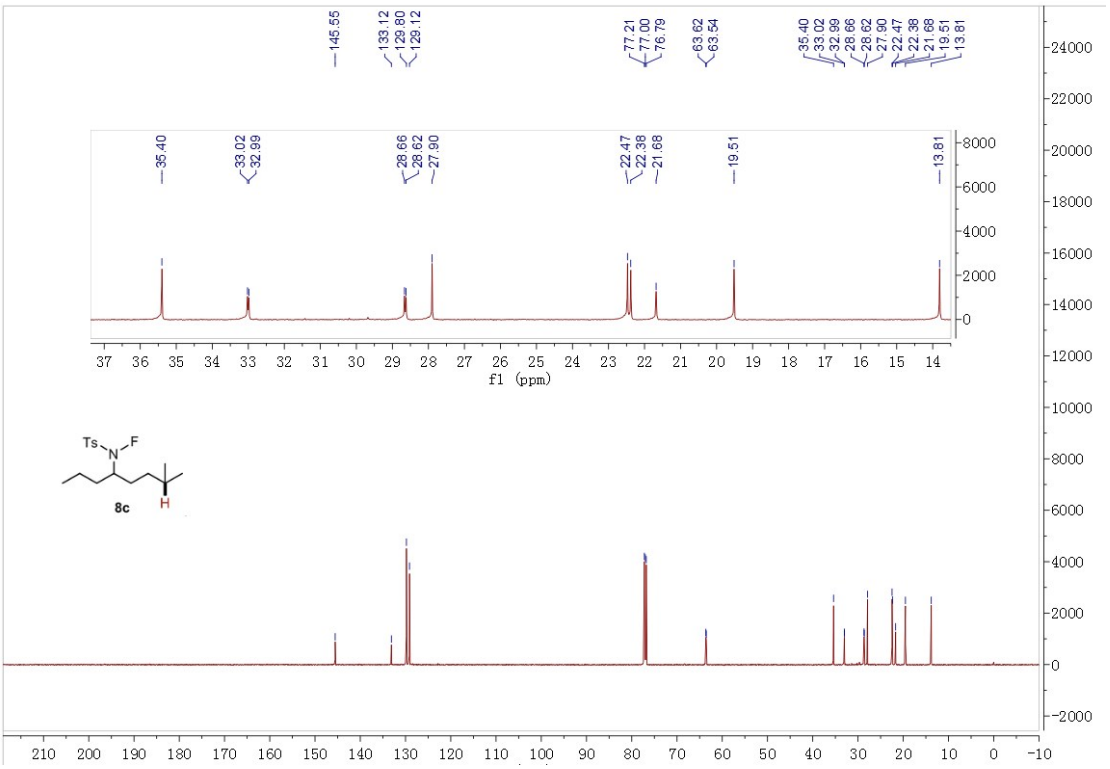
8c
f1 (ppm)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129.12
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77.00
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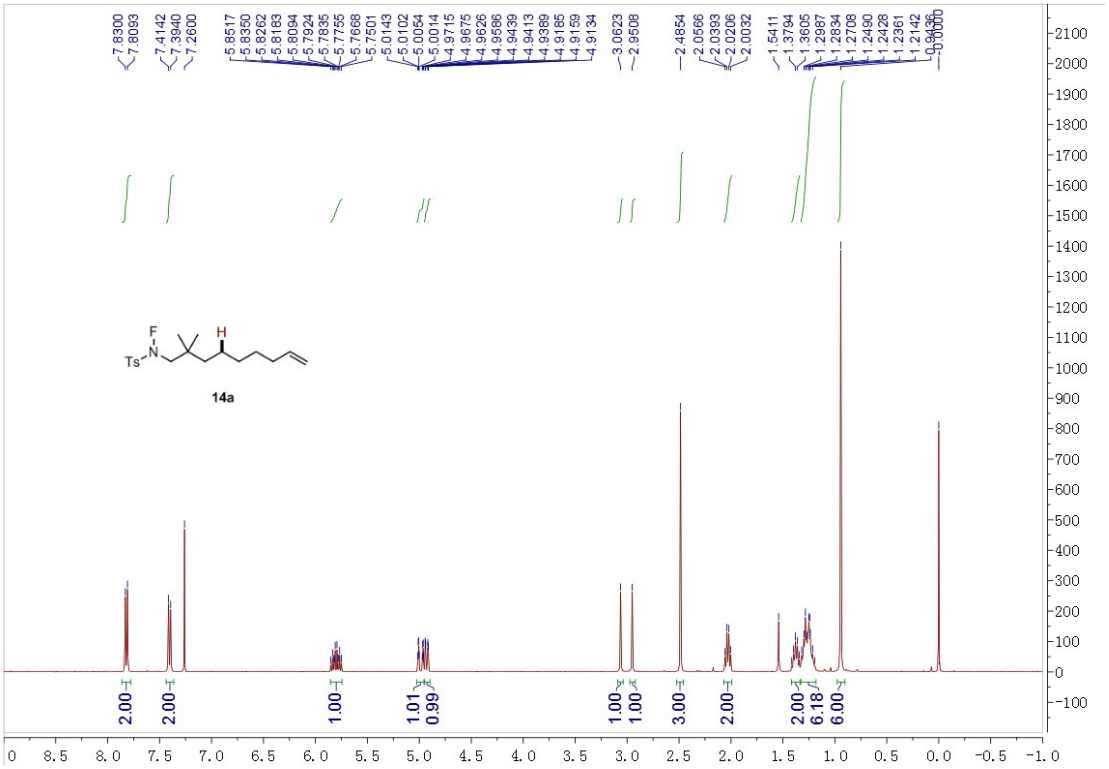
63.62
63.54
35.40
33.02
32.99
28.66
28.62
27.90
22.47
22.38
21.68
19.51
13.81
f1 (ppm)
Ts
N
F
H
8c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5.7835
5.7755
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5.7501
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5.0014
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4.9675
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4.9439
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4.9389
4.9186
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4.9134
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2.4854
2.0566
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2.0206
2.0032
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1.3794
1.3605
1.2987
1.2834
1.2708
1.2490
1.2428
1.2361
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0.9836
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2.00
2.00
1.00
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1.00
3.00
2.00
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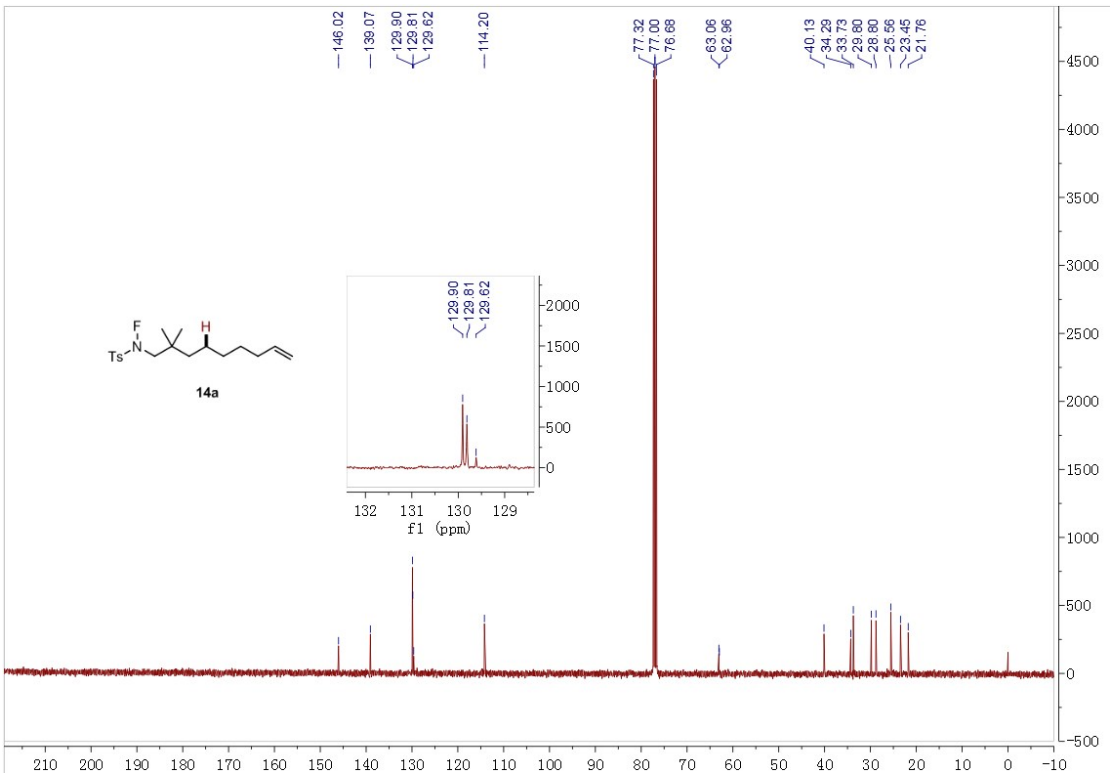
6.00
F
N
Ts
H
14a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114.20
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76.68
63.06
62.96
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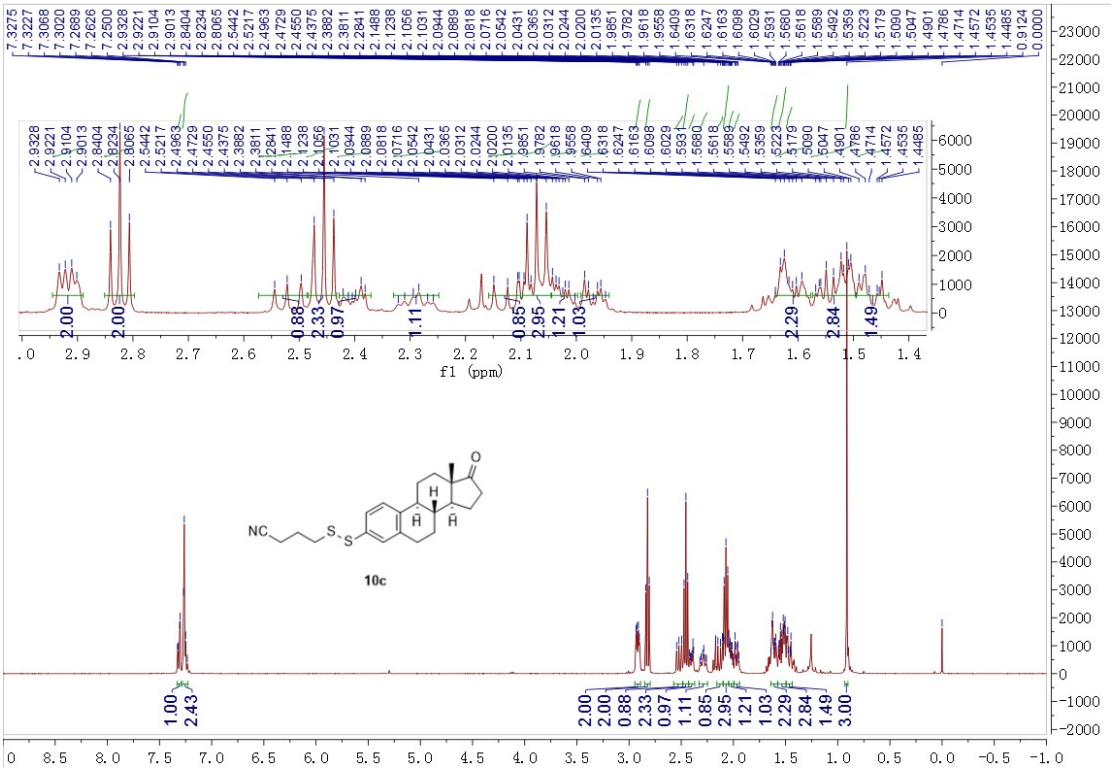
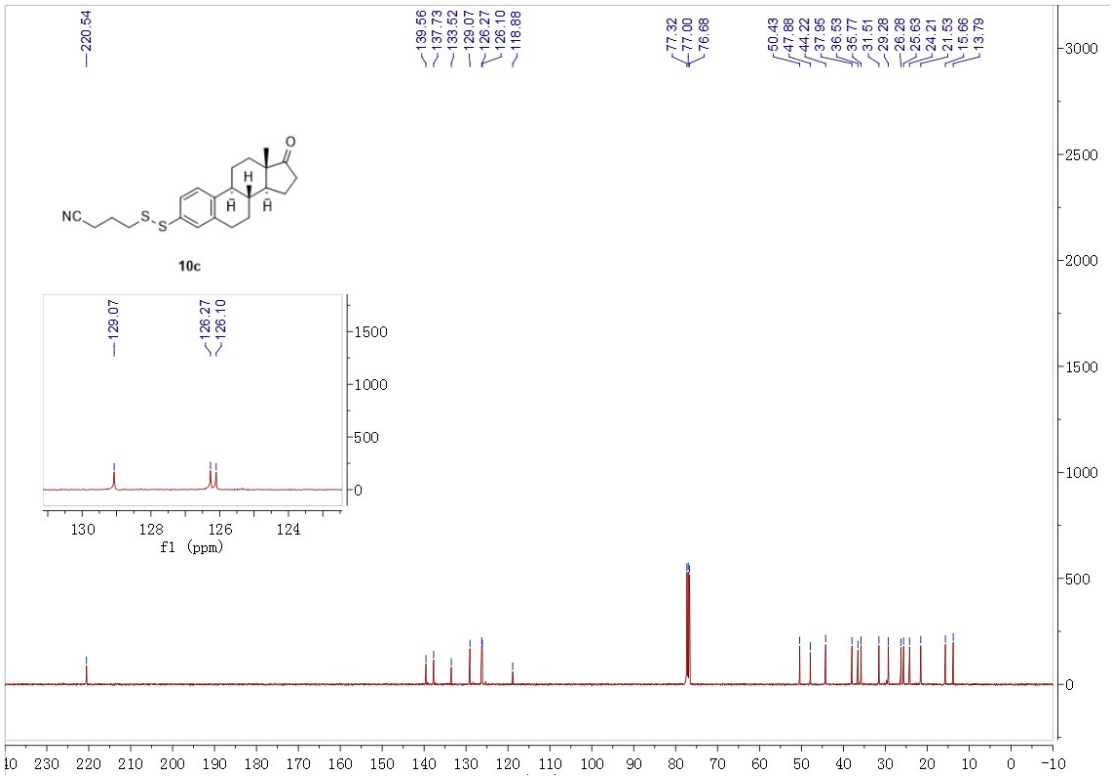
33.73
29.80
28.80
25.56
23.45
21.76
F
N
Ts
H
14a
f1 (ppm)


f1 (ppm)
O
H
NC
S
S
10c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133.52
129.07
126.27
126.10
118.88
77.32
77.00
76.68
50.43
47.88
44.22
37.95
36.53
35.77
31.51
29.28
26.28
25.63
24.21
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15.66
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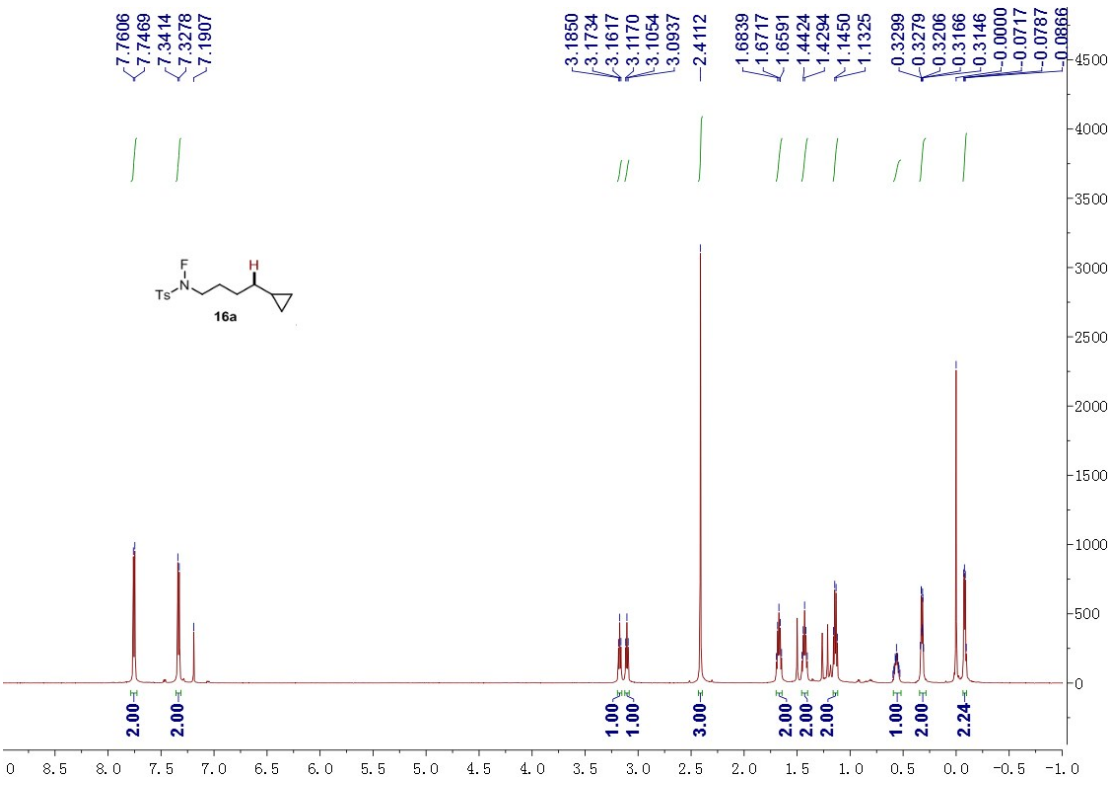
NC
S
S
O
H
H
H
10c
129.07
126.27
126.10
f1 (ppm)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1.6839
1.6717
1.6591
1.4424
1.4294
1.1450
1.1325
0.3299
0.3279
0.3206
0.3166
0.3146
0.0000
-0.0717
-0.0787
-0.0866
F
N
Ts
H
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1.00
1.00
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2.00
2.00
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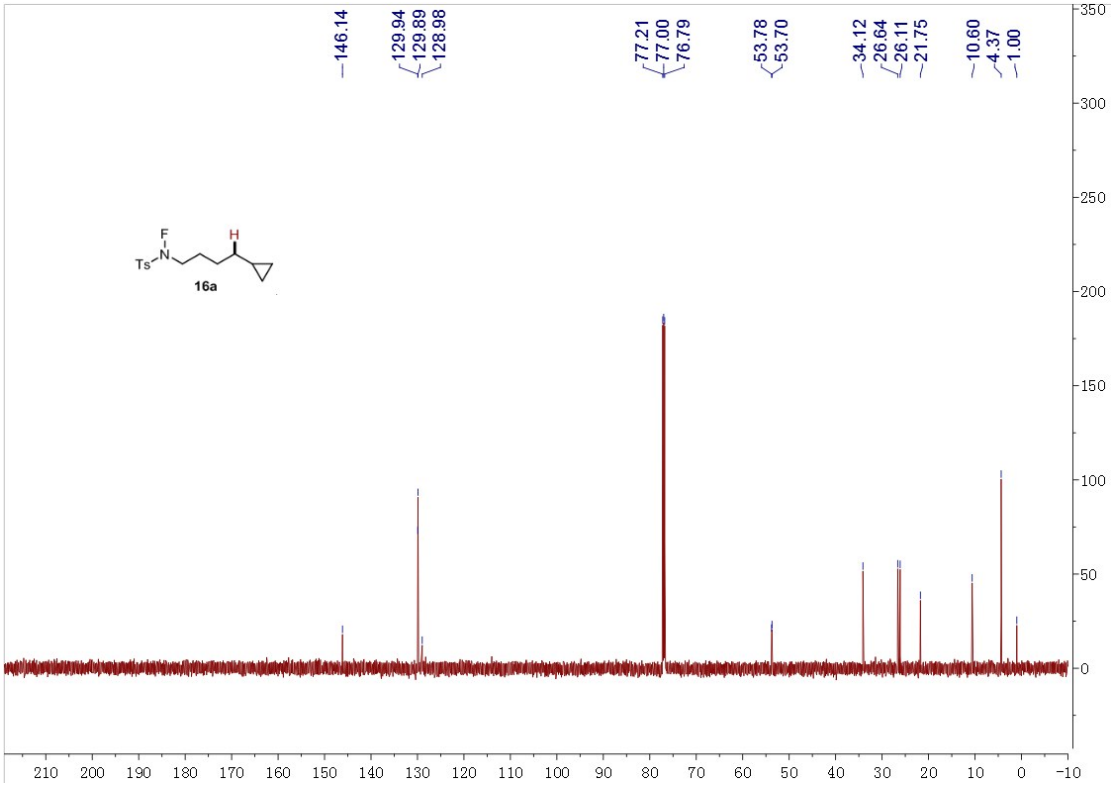
2.00
2.24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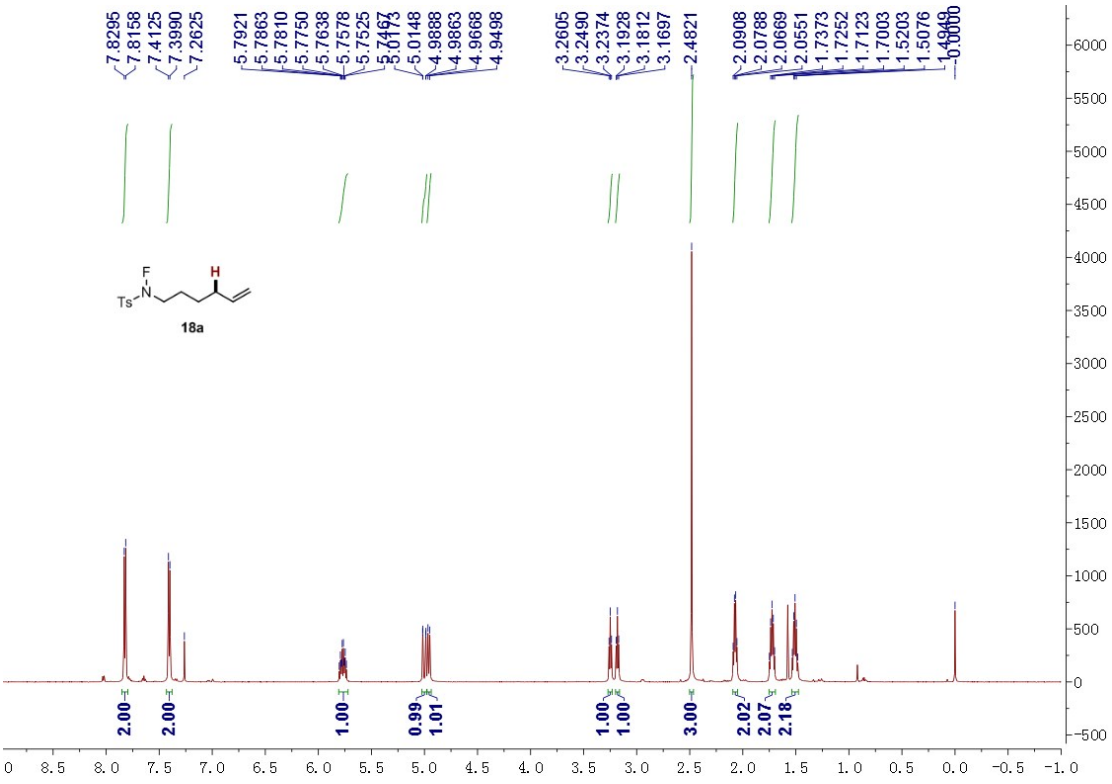
26.11
21.75
10.60
4.37
1.00
16a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5.7578
5.7525
5.0173
5.0148
4.9888
4.9863
4.9668
4.9498
3.2605
3.2490
3.2374
3.1928
3.1812
3.1697
2.4821
2.0908
2.0788
2.0669
2.0551
1.7373
1.7252
1.7123
1.7003
1.5203
1.5076
0.0000
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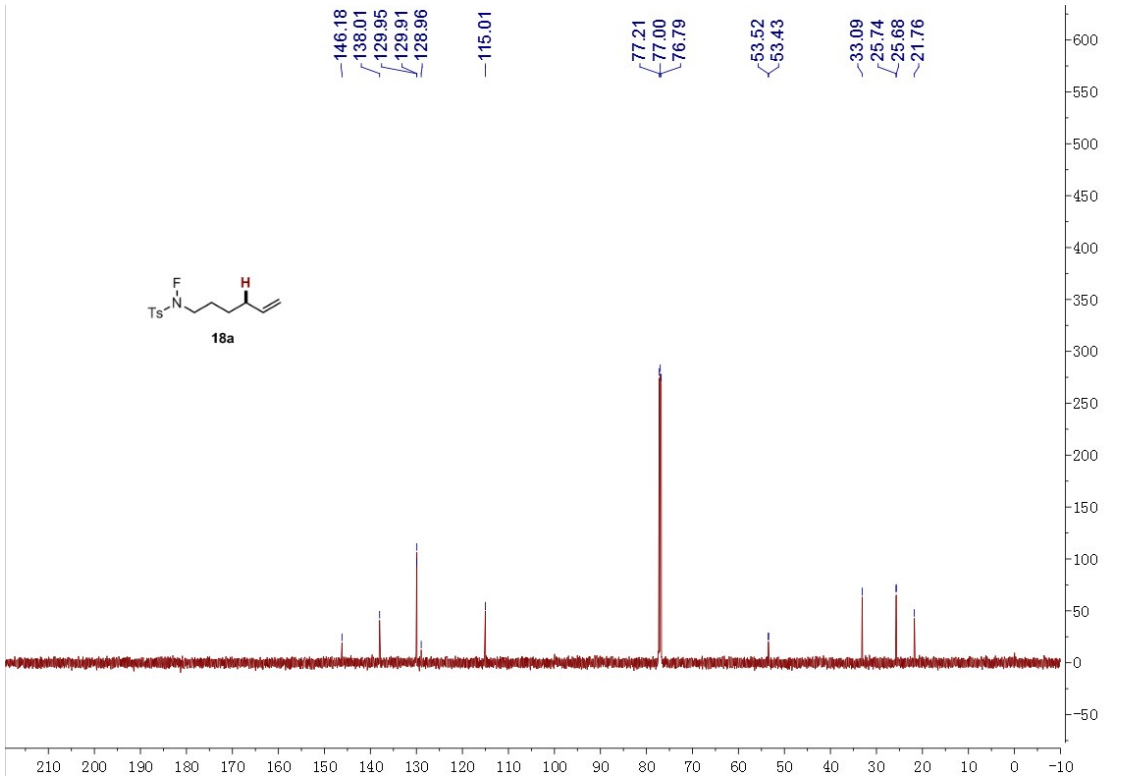
1.01
1.00
1.00
3.00
2.02
2.07
2.18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128.96
115.01
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77.00
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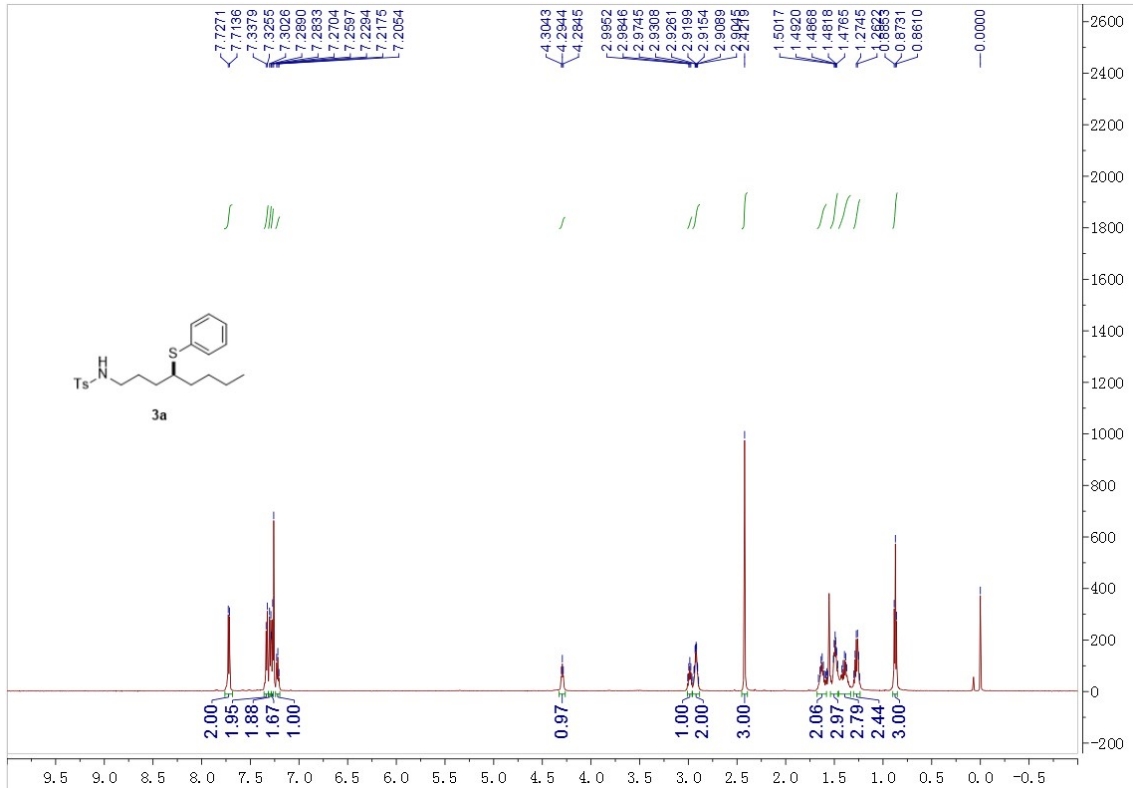
53.52
53.43
33.09
25.74
25.68
21.76
F
N
Ts
H
18a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7.3255
7.3026
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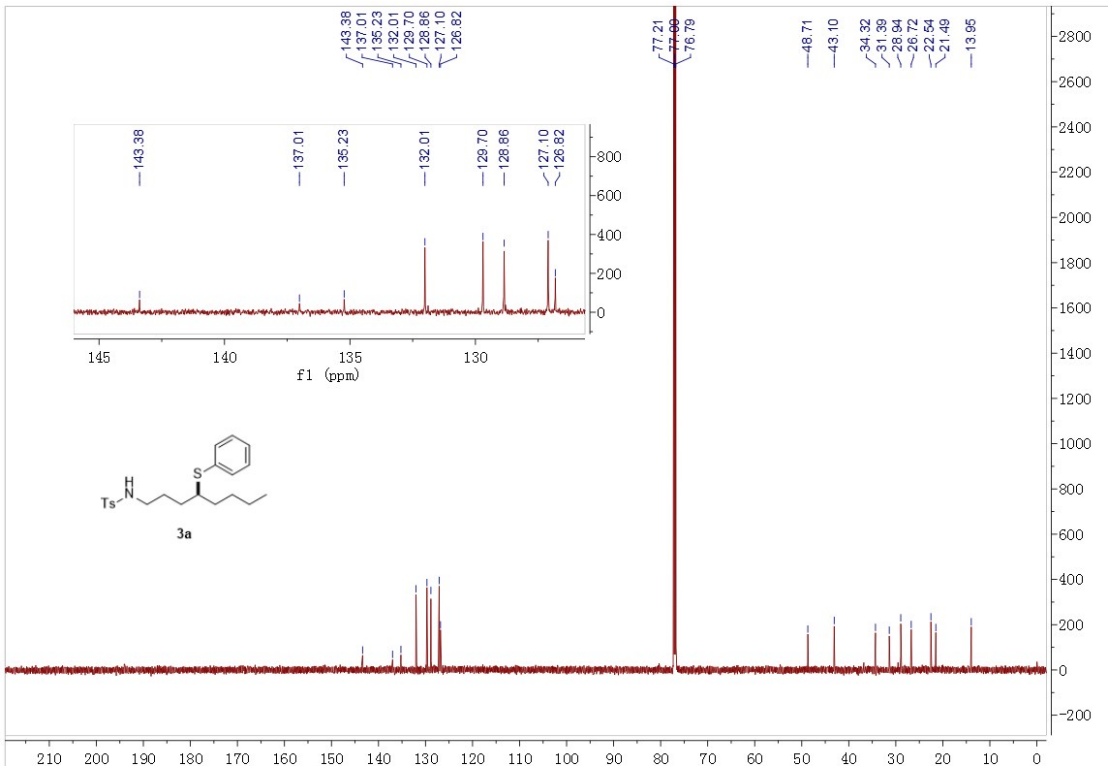
7.2704
7.2597
7.2294
7.2175
7.2054
4.3043
4.2944
4.2845
2.9952
2.9846
2.9745
2.9308
2.9261
2.9199
2.9154
2.9089
2.9045
2.4219
1.5017
1.4920
1.4868
1.4818
1.4765
1.2745
1.2622
0.8853
0.8731
0.8610
0.0000
H
N
Ts
S
3a
2.00
1.95
1.88
1.67
1.00
0.97
1.00
2.00
3.00
2.06
2.97
2.79
2.44
3.00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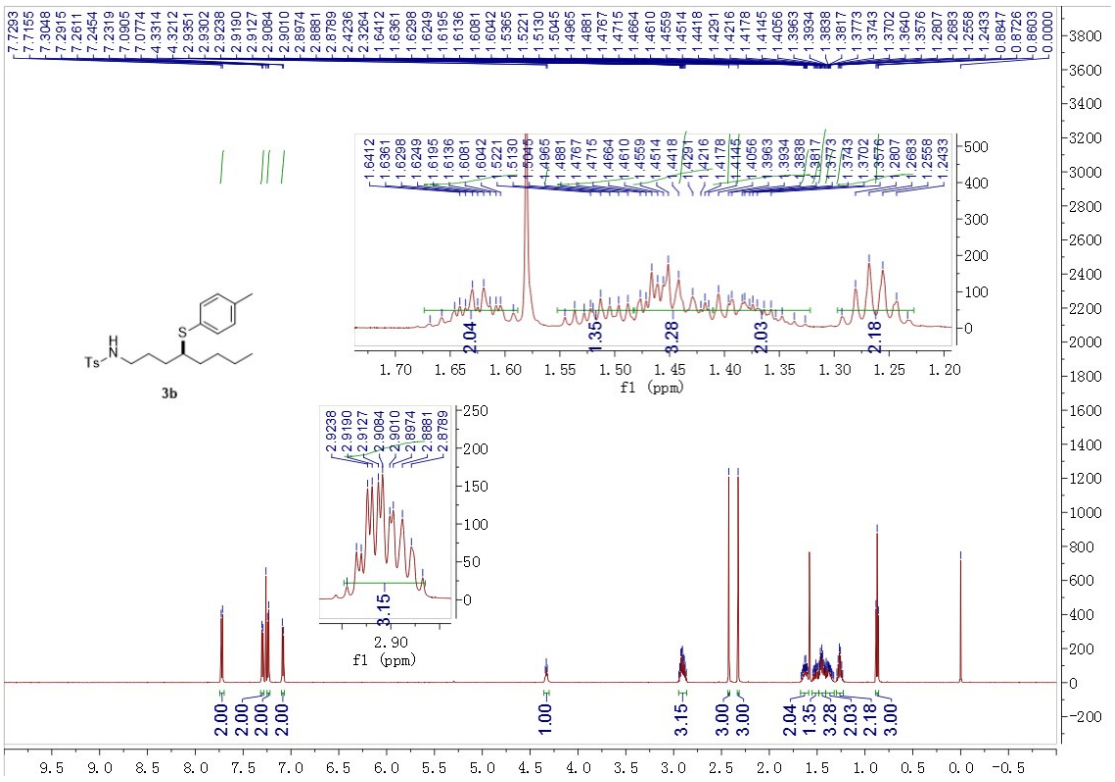
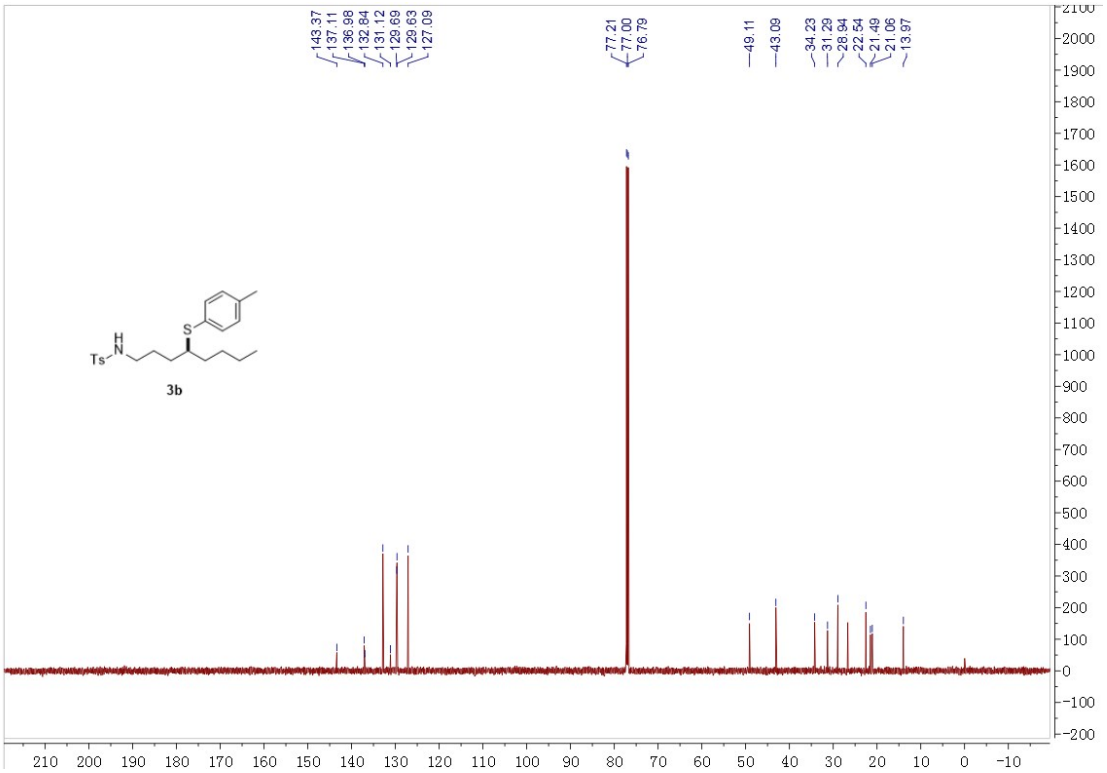
137.01
135.23
132.01
129.70
128.86
127.10
126.82
77.21
77.00
76.79
48.71
43.10
34.32
31.39
28.94
26.72
22.54
21.49
13.95
f1 (ppm)
Ts
H
N
S
3a


2.04
1.35
3.28
2.03
2.18
3.15
f1 (ppm)
Ts
H
N
S
3b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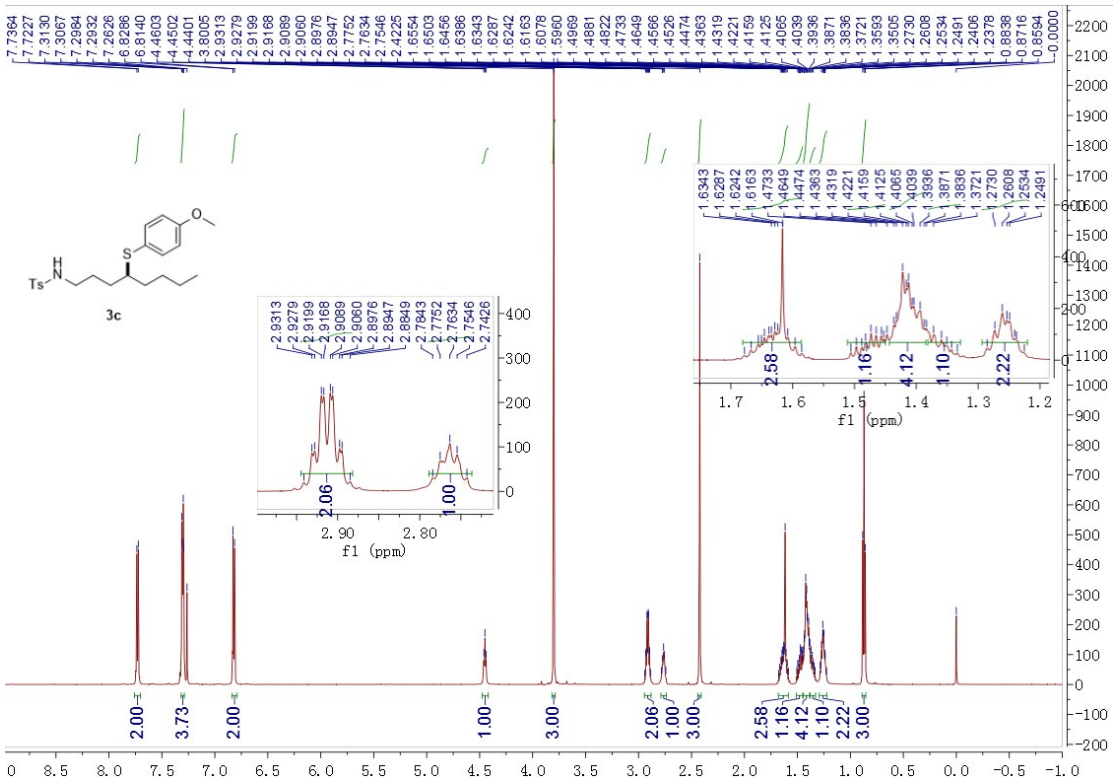
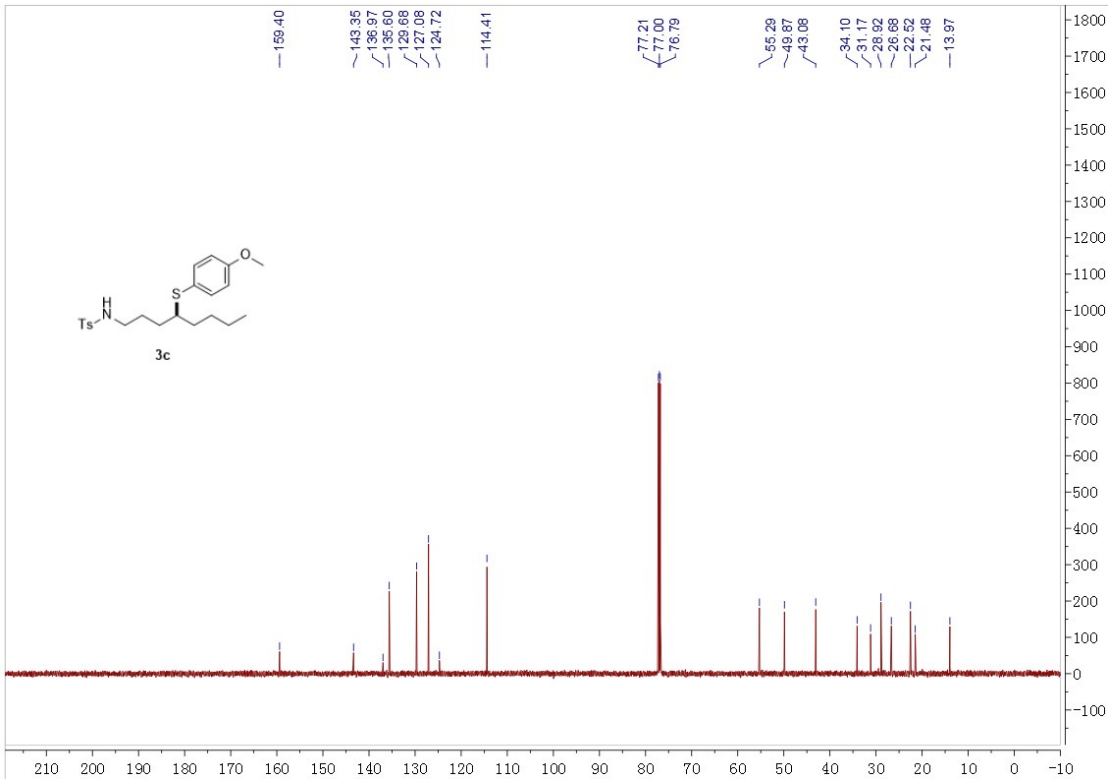
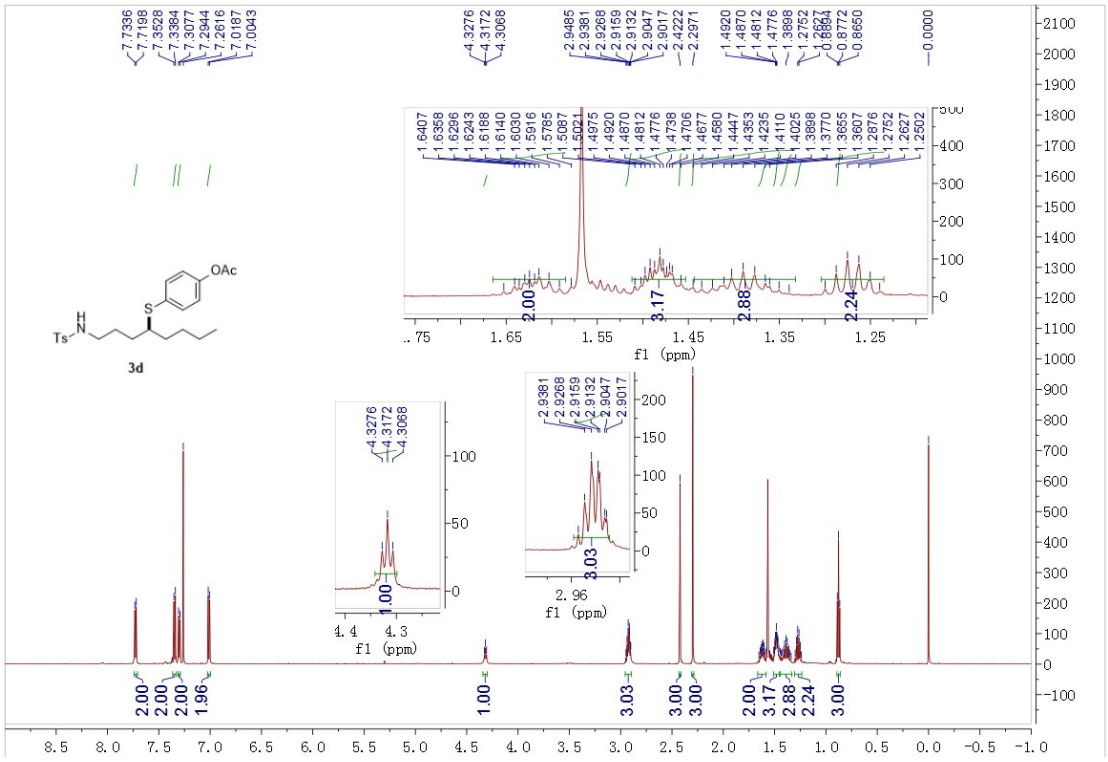
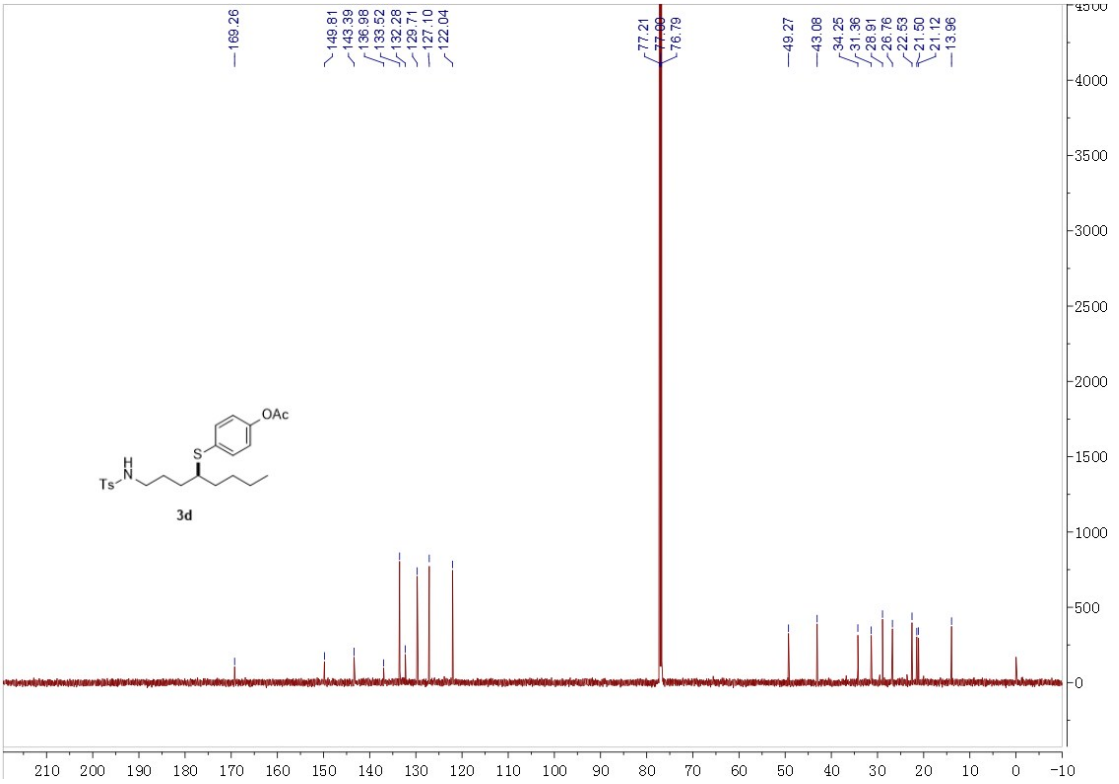
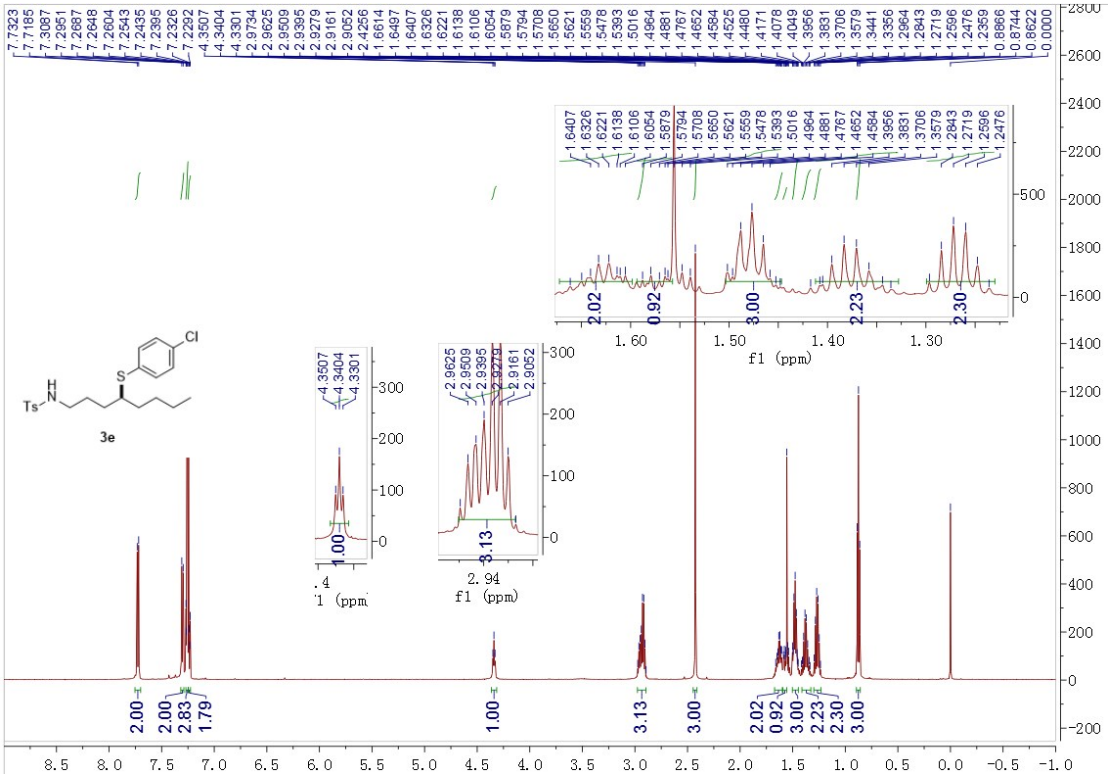
136.98
132.84
131.12
129.69
129.63
127.09
77.21
77.00
76.79
49.11
43.09
34.23
31.29
28.94
22.54
21.49
21.06
13.97
Ts
N
H
S
3b

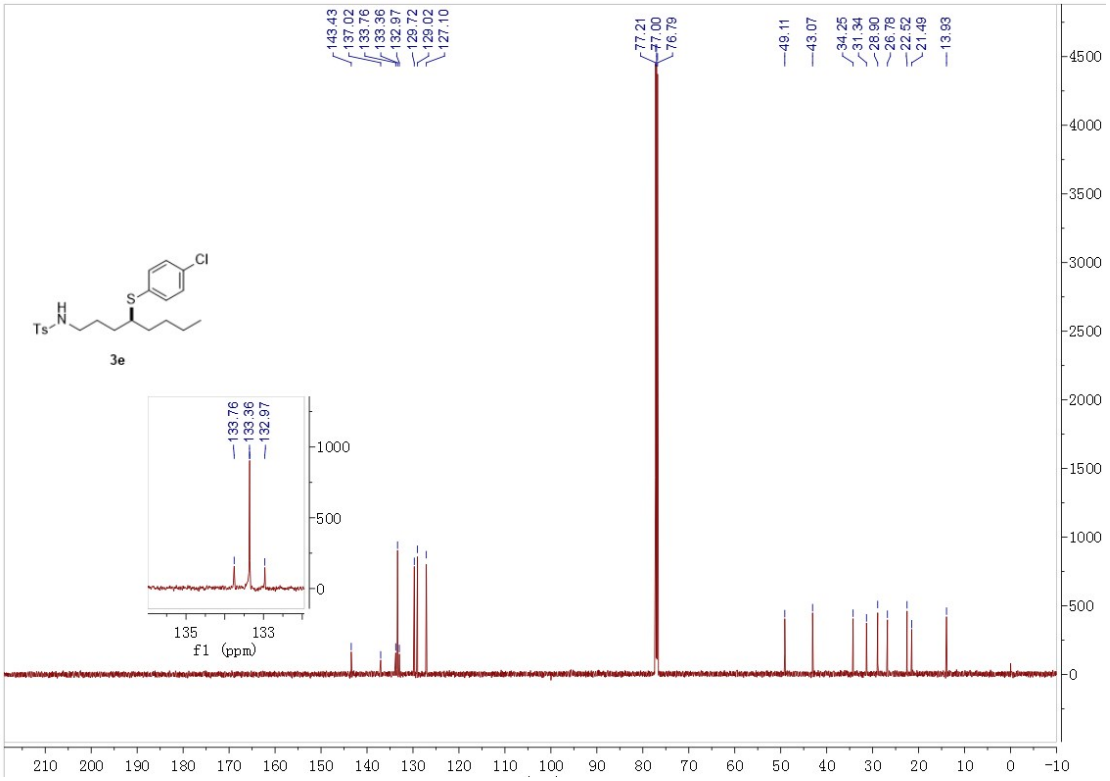

Ts
N
H
S
O
3c
f1 (ppm)
2.06
1.00
2.58
1.16
4.12
1.10
2.22
2.00
3.73
2.00
1.00
3.00
2.06
1.00
3.00
2.58
1.16
4.12
1.10
2.22
3.00

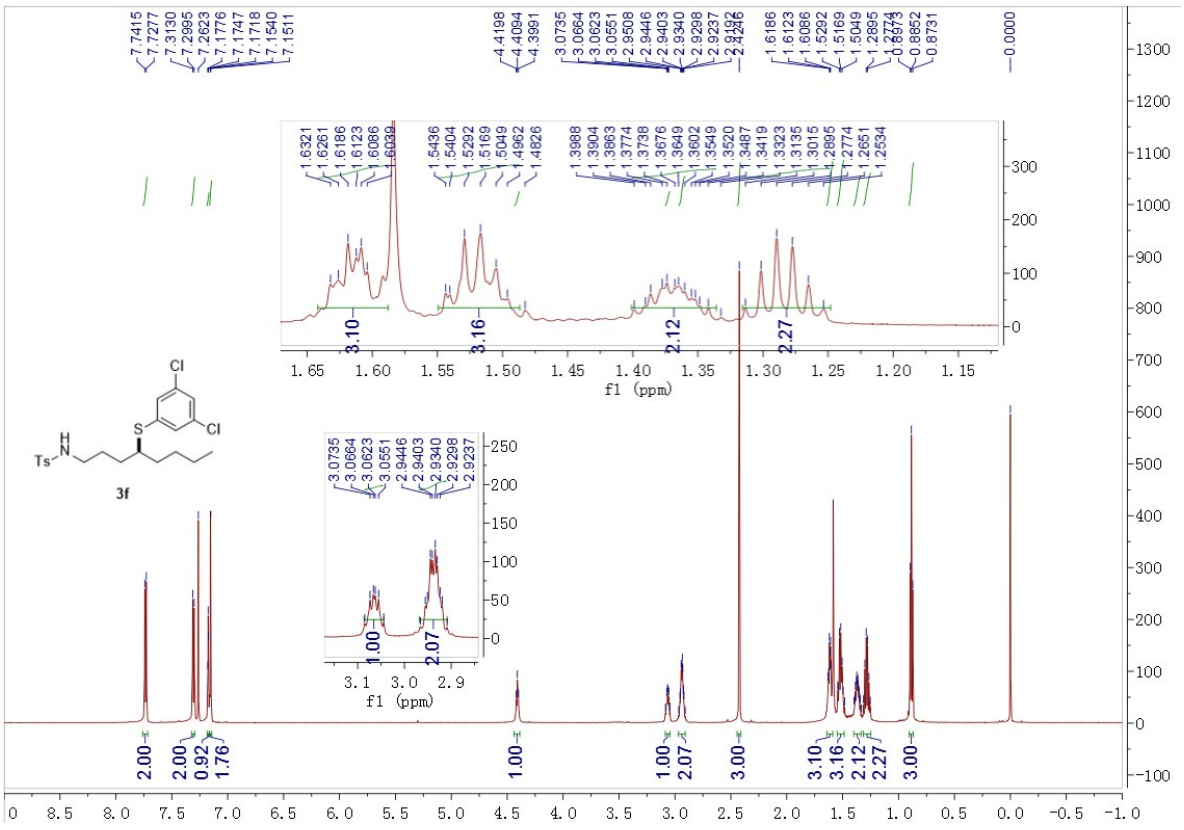

159.40
143.35
136.97
135.60
129.68
127.08
124.72
114.41
77.21
77.00
76.79
55.29
49.87
43.08
34.10
31.17
28.92
26.68
22.52
21.48
13.97
3c

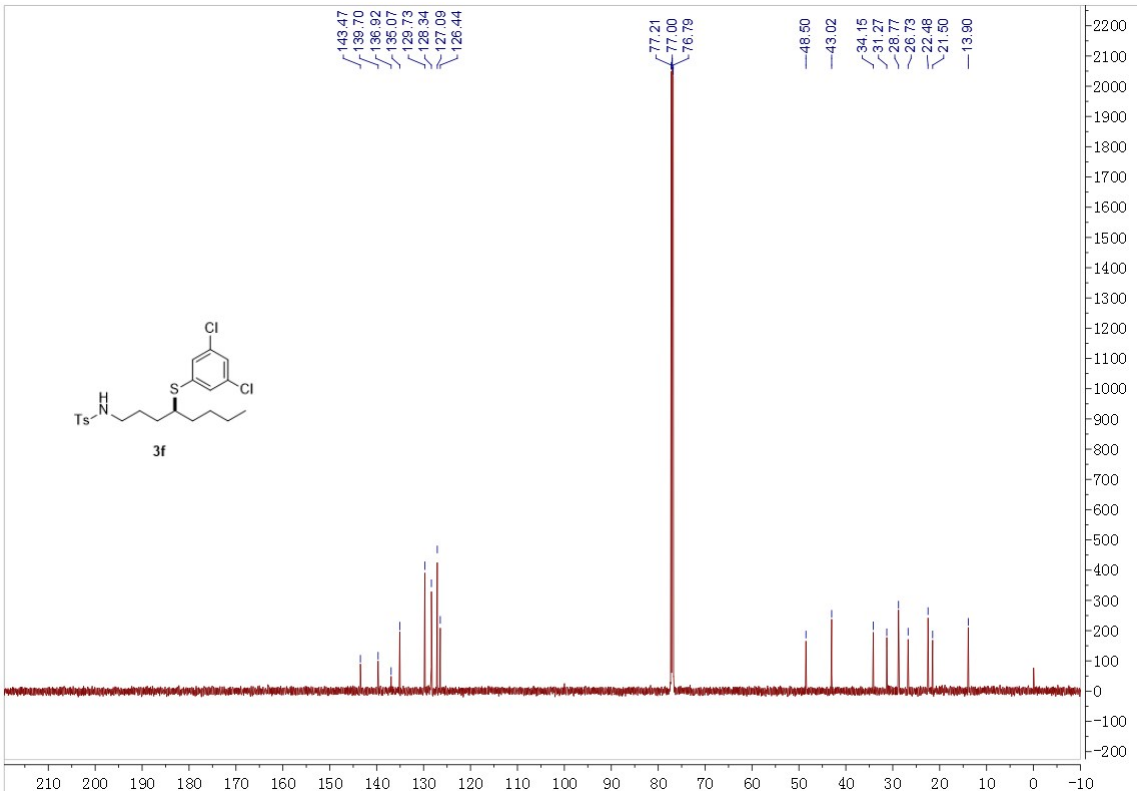

3d
f1 (ppm)


169.26
149.81
143.39
136.98
133.52
132.28
129.71
127.10
122.04
77.21
77.00
76.79
49.27
43.08
34.25
31.36
28.91
26.76
22.53
21.50
21.12
13.96
OAc
S
H
N
Ts
3d


Cl
S
H
N
Ts
3e
2.00
2.00
2.83
1.79
1.00
3.13
3.00
2.02
0.92
3.00
2.23
2.30
3.00
f1 (ppm)


3e
143.43
137.02
133.76
133.36
132.97
129.72
129.02
127.10
77.21
77.00
76.79
49.11
43.07
34.25
31.34
28.90
26.78
22.52
21.49
13.93
f1 (ppm)


3f
7.7415
7.7277
7.3130
7.2995
7.2623
7.1776
7.1747
7.1718
7.1540
7.1511
4.4198
4.4094
4.3991
3.0735
3.0664
3.0623
3.0551
2.9508
2.9446
2.9403
2.9340
2.9298
2.9237
1.6186
1.6123
1.6086
1.5292
1.5169
1.5049
1.2895
0.8973
0.8852
0.8731
0.0000
3.10
3.16
2.12
2.27
1.00
2.07
f1 (ppm)
2.00
2.00
0.92
1.76
1.00
1.00
2.07
3.00
3.10
3.16
2.12
2.27
3.00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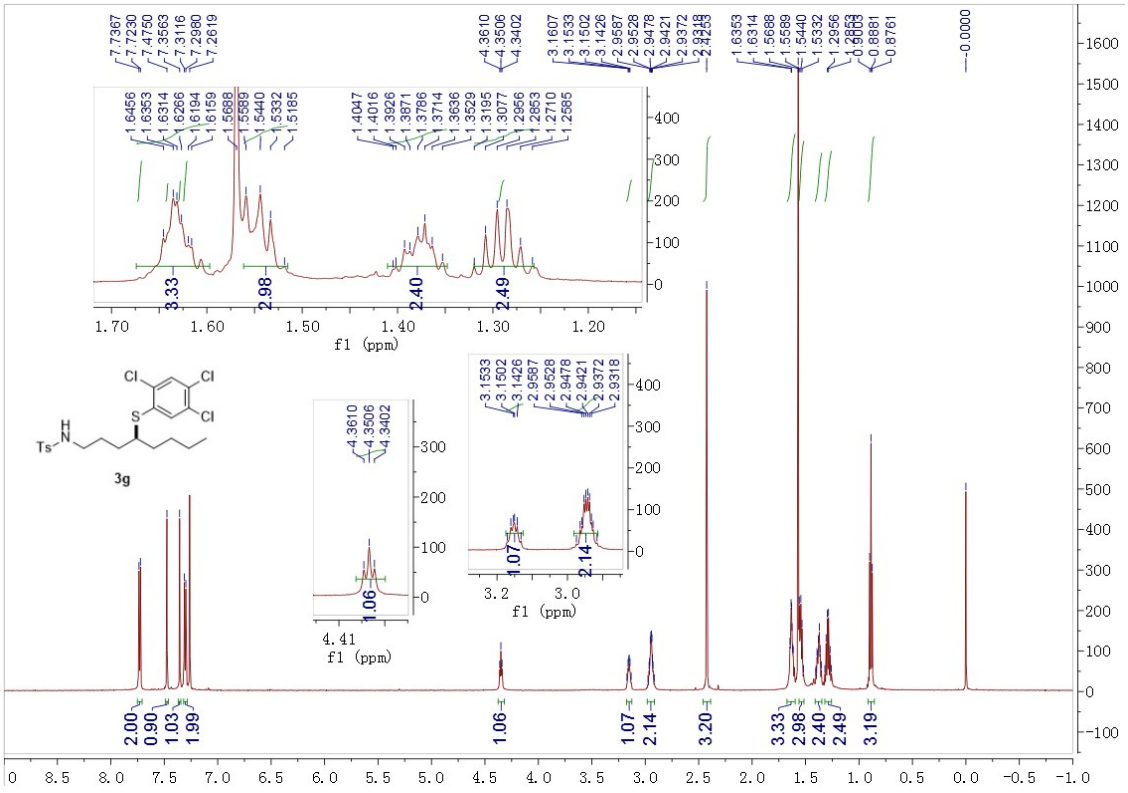
136.92
135.07
129.73
128.34
127.09
126.44
77.21
77.00
76.79
48.50
43.02
34.15
31.27
28.77
26.73
22.48
21.50
13.90
Cl
Cl
S
H
N
Ts
3f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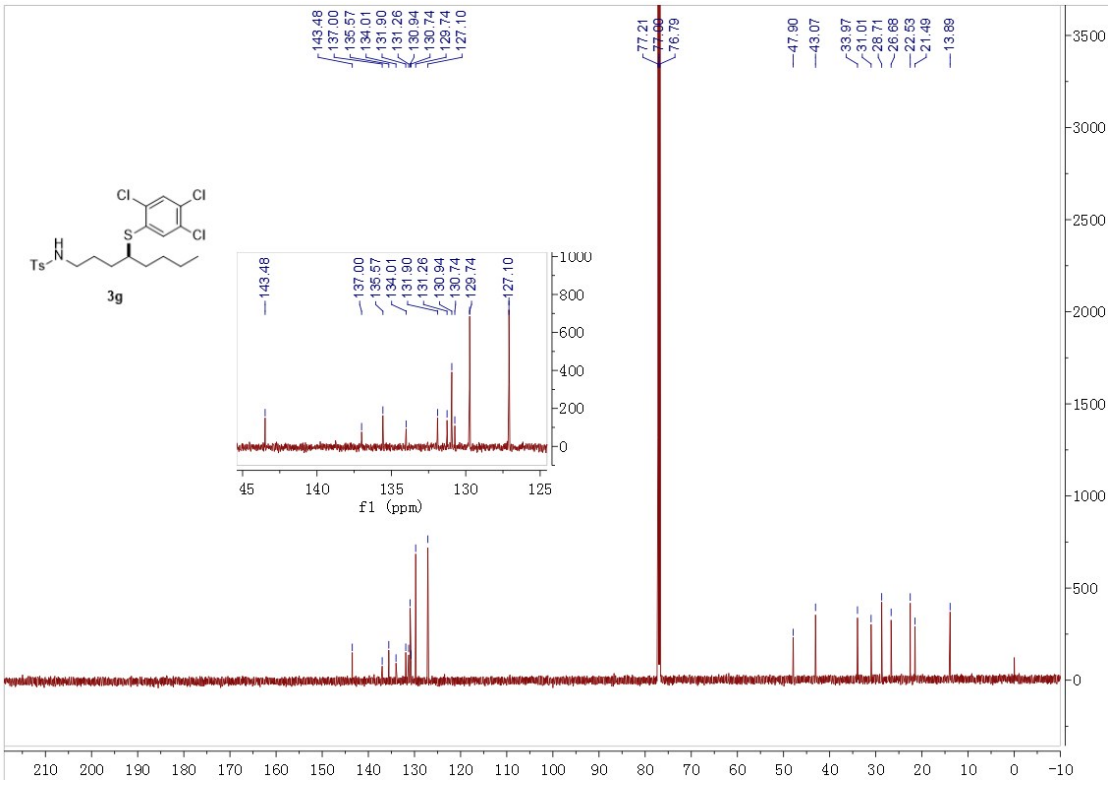
7.4750
7.3563
7.3116
7.2980
7.2619
4.3610
4.3506
4.3402
3.1607
3.1533
3.1502
3.1426
2.9587
2.9528
2.9478
2.9421
2.9372
2.9318
1.6353
1.6314
1.5688
1.5589
1.5440
1.5332
1.2956
0.8881
0.8761
0.0000
3.33
2.98
2.40
2.49
f1 (ppm)
1.06
1.07
2.14
4.41
3.2
3.0
Cl
Cl
Cl
S
H
N
Ts
3g
2.00
0.90
1.03
1.99
1.06
1.07
2.14
3.20
3.33
2.98
2.40
2.49
3.19


3g
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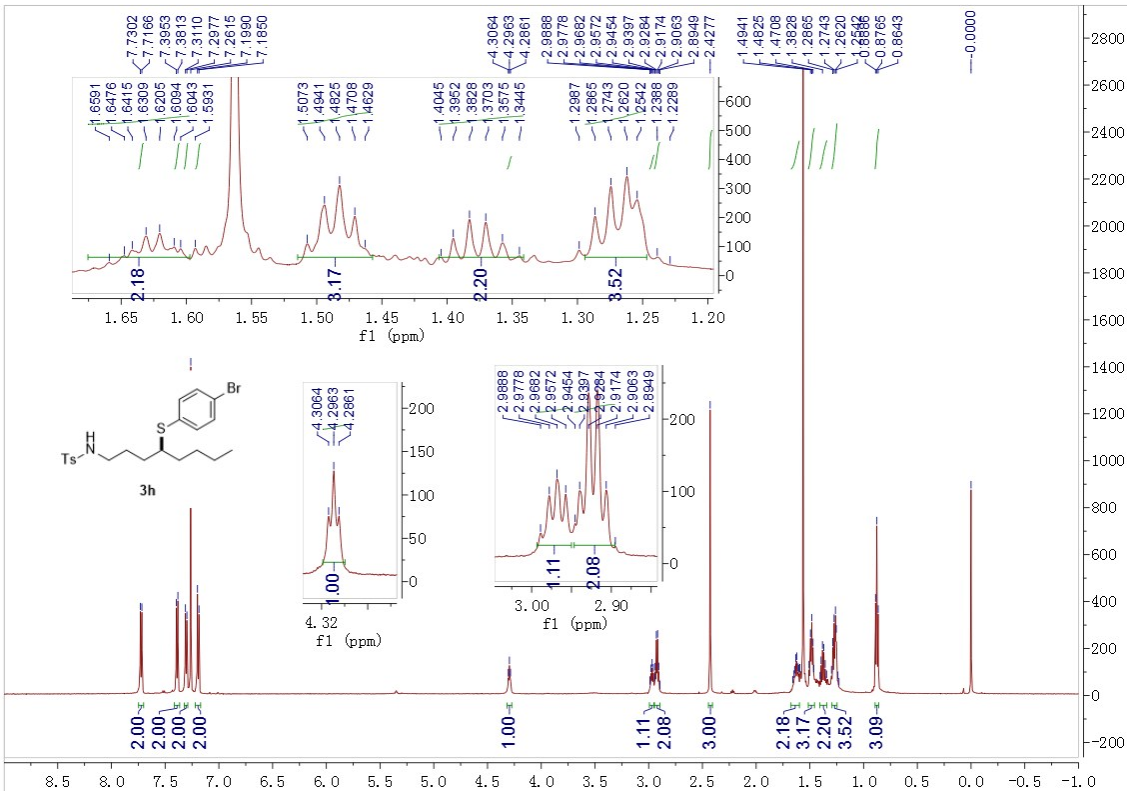
137.00
135.57
134.01
131.90
131.26
130.94
130.74
129.74
127.10
77.21
77.00
76.79
47.90
43.07
33.97
31.01
28.71
26.68
22.53
21.49
13.89
f1 (ppm)


3h
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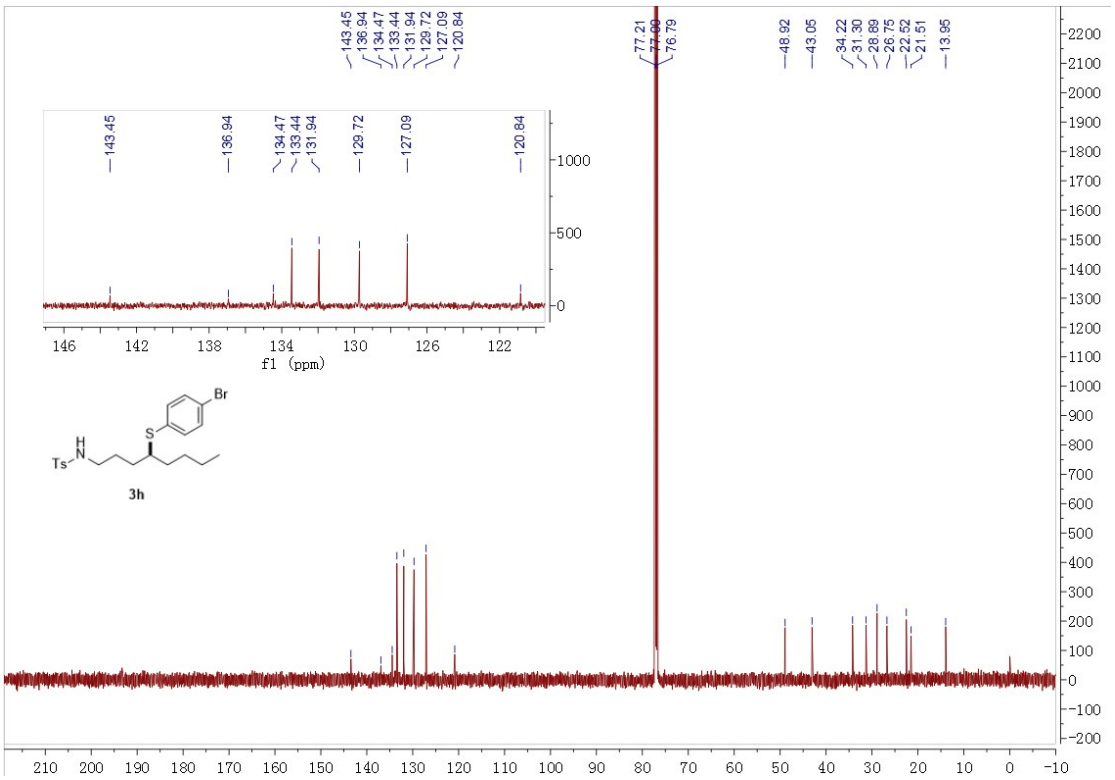
7.7166
7.3953
7.3813
7.3110
7.2977
7.2615
7.1990
7.1850
4.3064
4.2963
4.2861
2.9888
2.9778
2.9682
2.9572
2.9454
2.9397
2.9284
2.9174
2.9063
2.8949
2.4277
1.4941
1.4825
1.4708
1.3828
1.2865
1.2743
1.2620
0.8886
0.8765
0.8643
-0.0000
2.18
3.17
2.20
3.52
1.00
1.11
2.08
3.00
2.18
3.17
2.20
3.52
3.09
f1 (ppm)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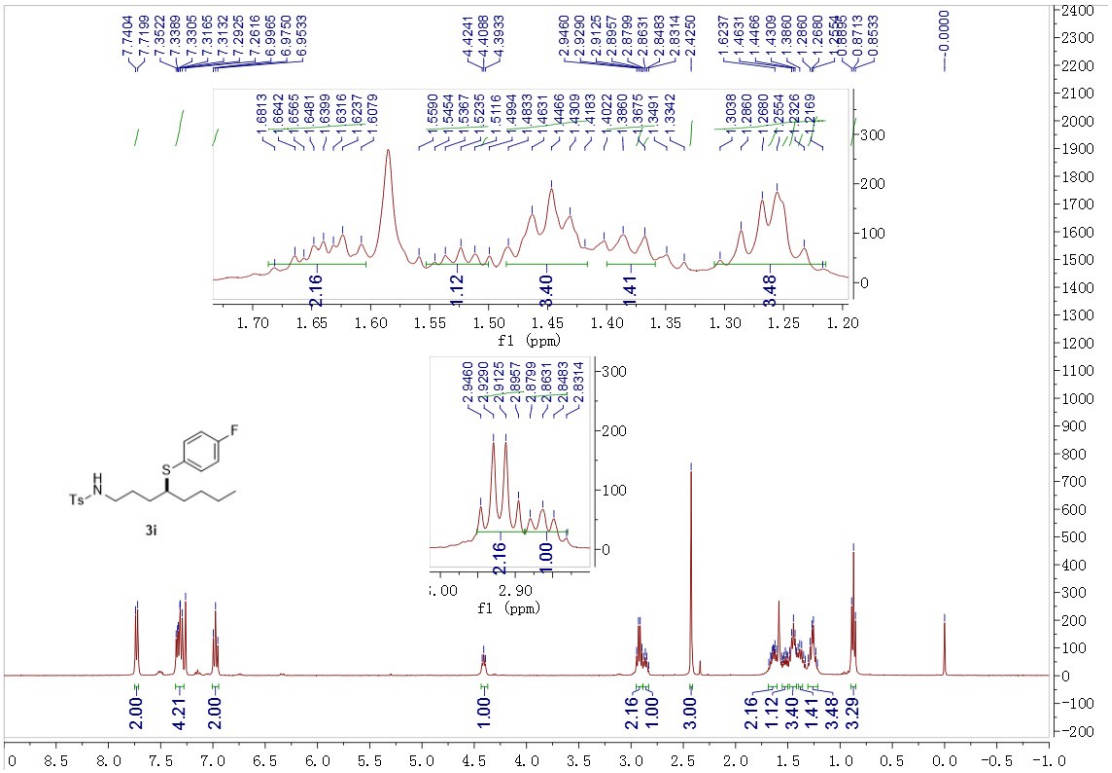
136.94
134.47
133.44
131.94
129.72
127.09
120.84
77.21
77.00
76.79
48.92
43.05
34.22
31.30
28.89
26.75
22.52
21.51
13.95
f1 (ppm)
Br
S
H
N
Ts
3h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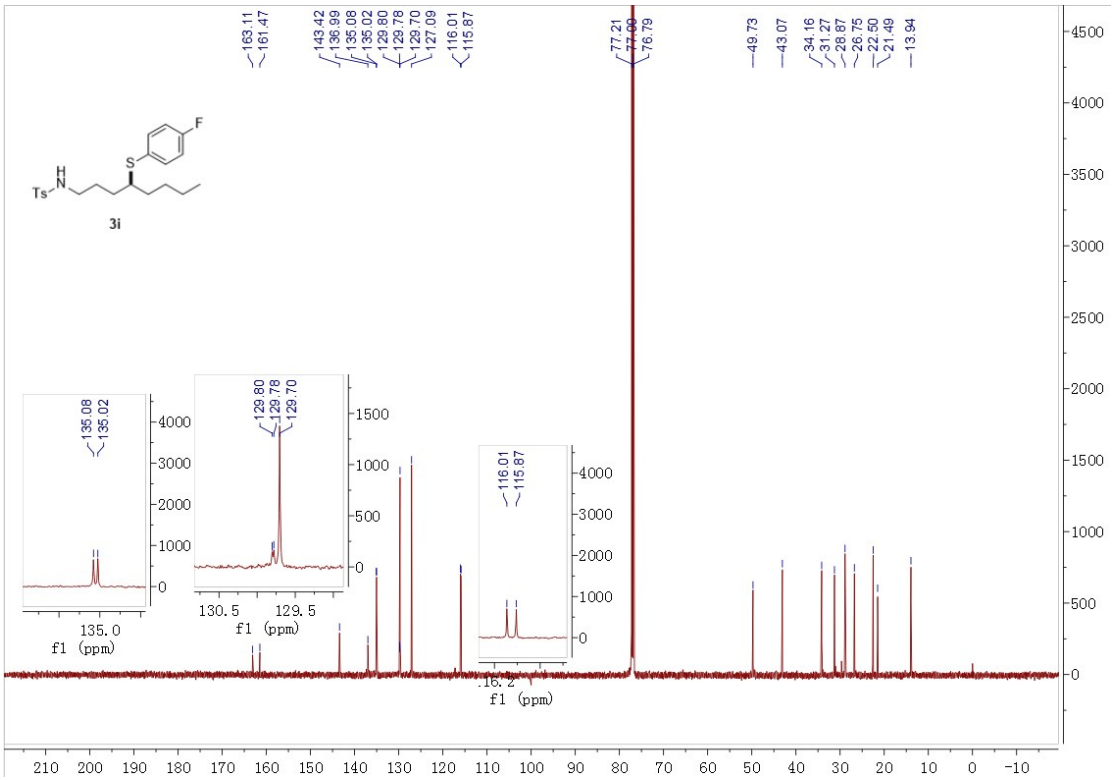
7.7199
7.3522
7.3389
7.3305
7.3165
7.3132
7.2925
7.2616
6.9965
6.9750
6.9533
4.4241
4.4088
4.3933
2.9460
2.9290
2.9125
2.8957
2.8799
2.8631
2.8483
2.8314
2.4250
1.6237
1.4631
1.4466
1.4309
1.3860
1.2860
1.2680
1.2554
0.8713
0.8533
0.0000
2.16
1.12
3.40
1.41
3.48
f1 (ppm)
F
S
H
N
Ts
3i
2.00
4.21
2.00
1.00
2.16
1.00
3.00
2.16
1.12
3.40
1.41
3.48
3.29


163.11
161.47
143.42
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135.02
129.80
129.78
129.70
127.09
116.01
115.87
77.21
77.00
76.79
49.73
43.07
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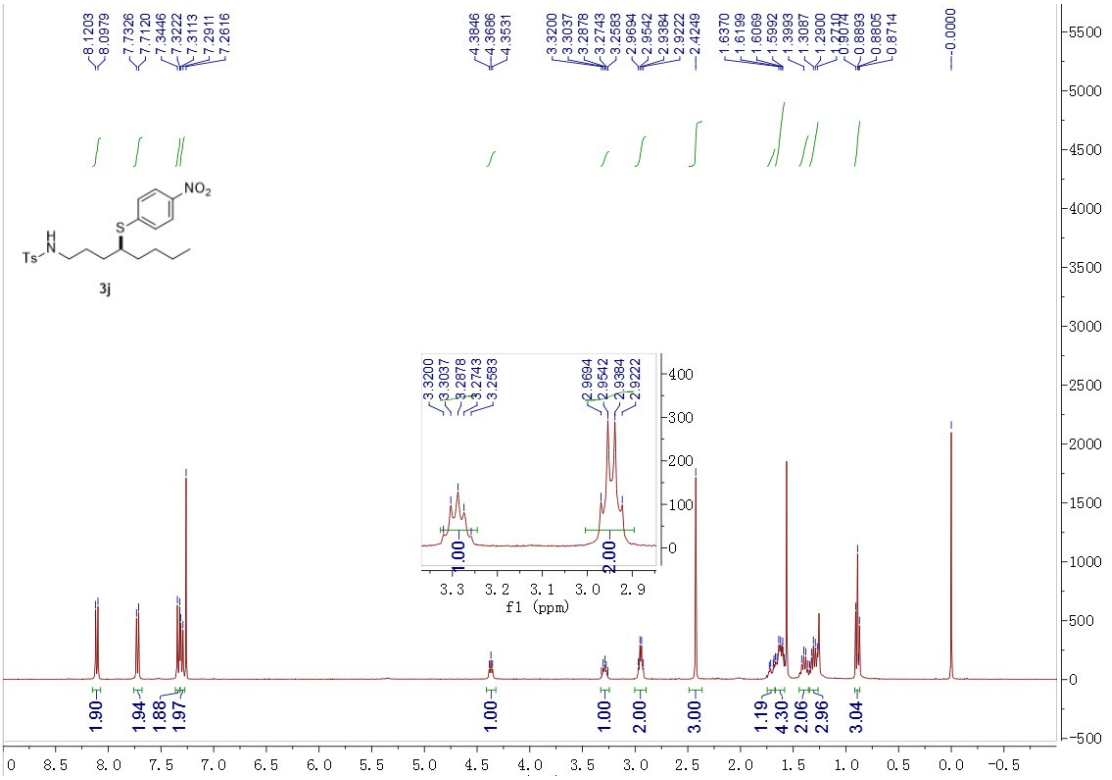
13.94
F
S
Ts
N
H
3i
f1 (ppm)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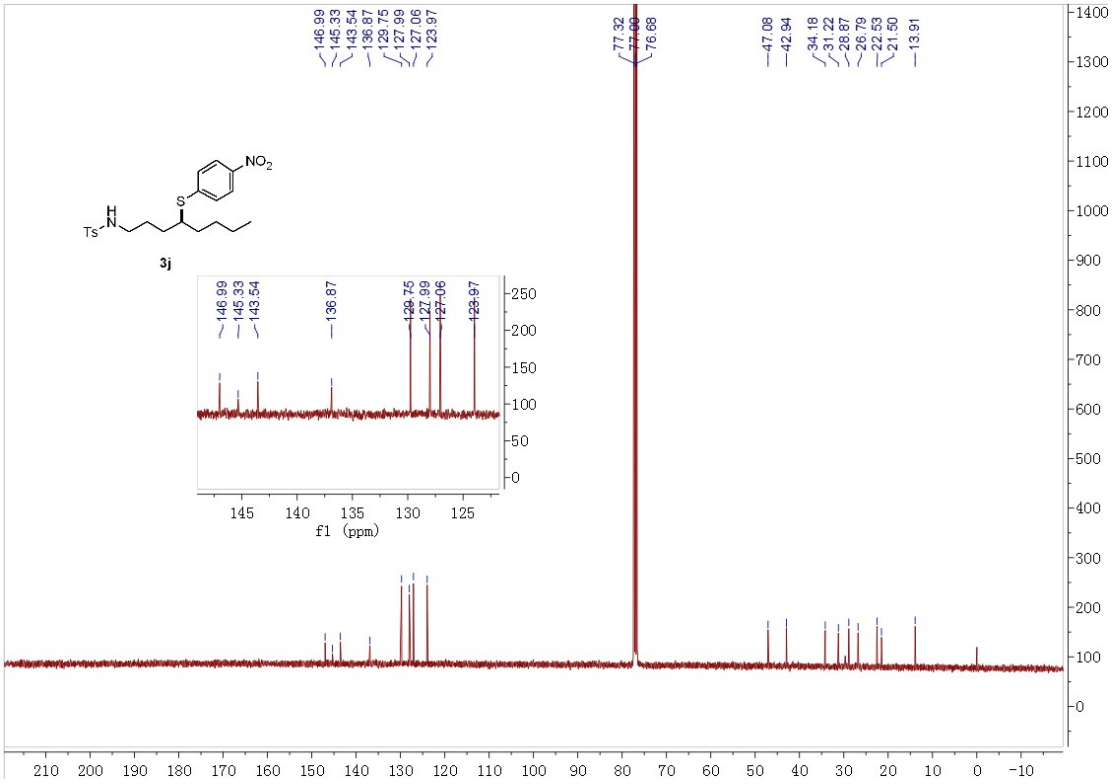
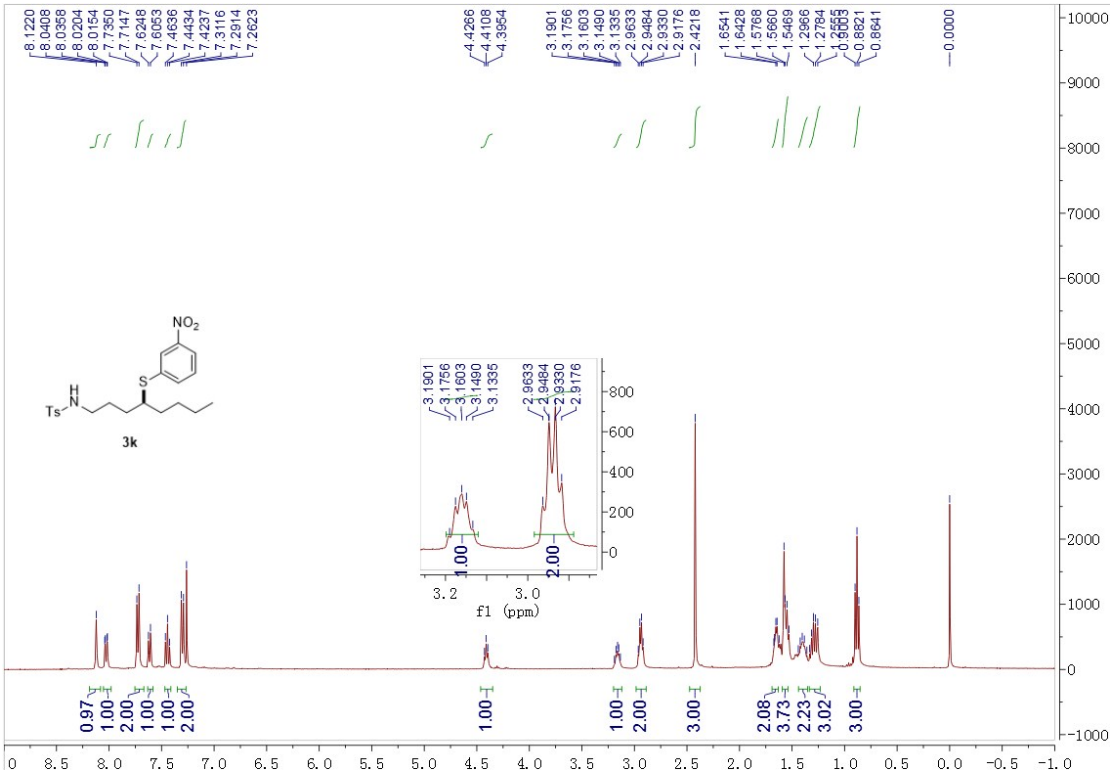
7.7326
7.7120
7.3446
7.3222
7.3113
7.2911
7.2616
4.3846
4.3686
4.3531
3.3200
3.3037
3.2878
3.2743
3.2583
2.9694
2.9542
2.9384
2.9222
2.4249
1.6370
1.6199
1.6069
1.5992
1.3993
1.3087
1.2900
0.8893
0.8805
0.8714
0.0000
NO2
S
Ts
N
H
3j
1.00
2.00
f1 (ppm)


146.99
145.33
143.54
136.87
129.75
127.99
127.06
123.97
77.32
77.00
76.68
47.08
42.94
34.18
31.22
28.87
26.79
22.53
21.50
13.91
NO2
S
H
N
Ts
3j
f1 (ppm)


8.1220
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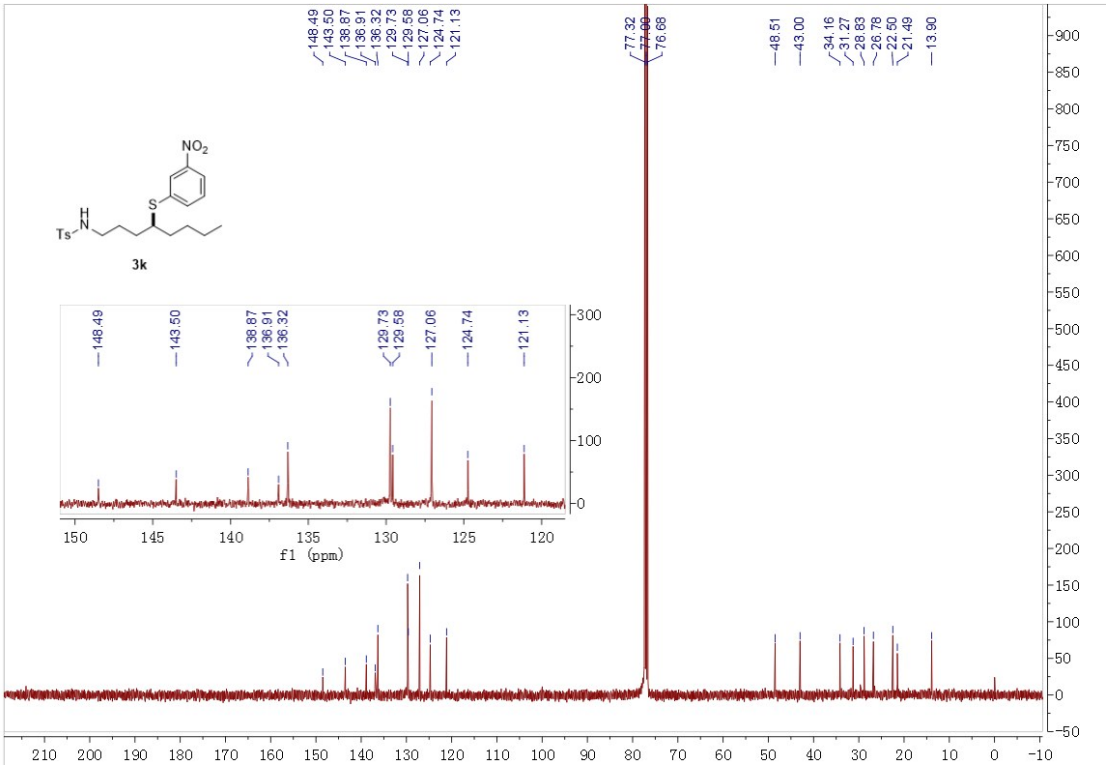
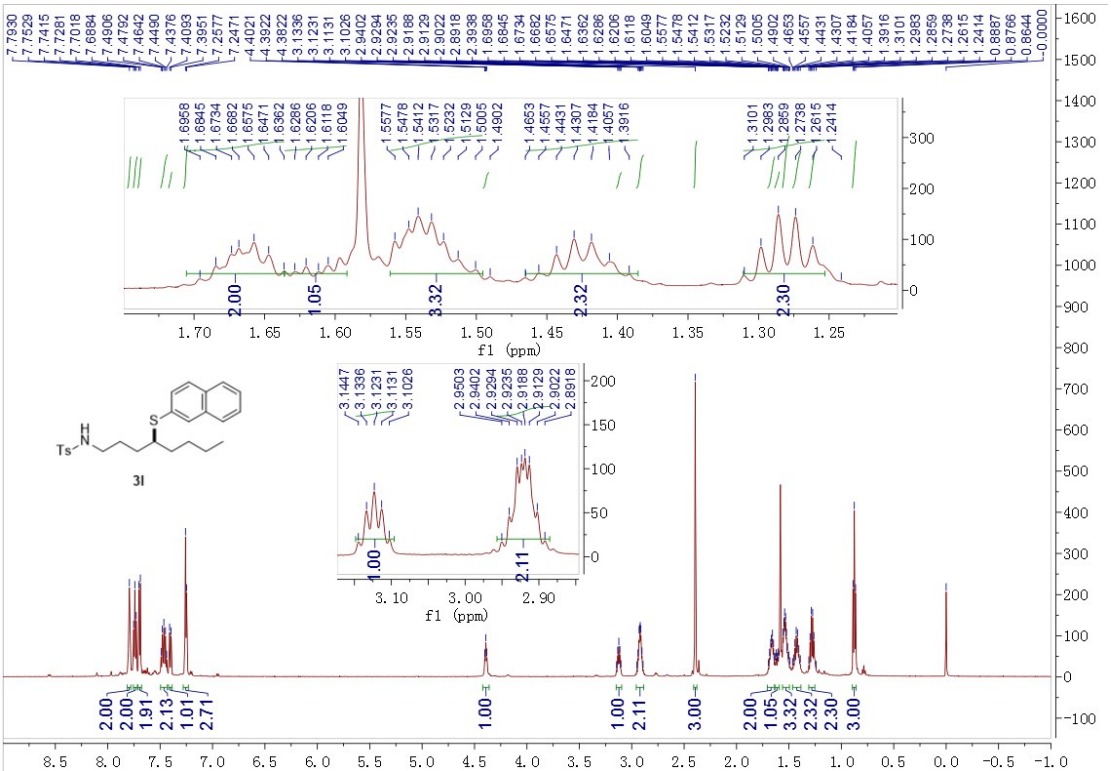
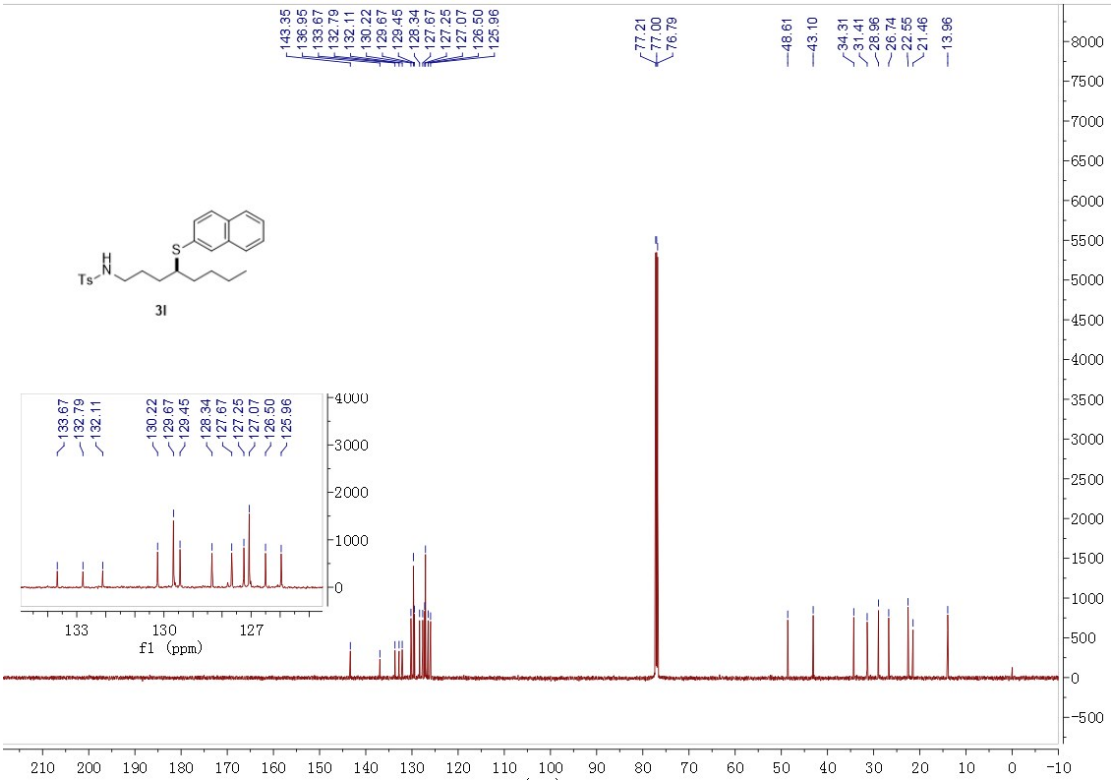
8.0358
8.0204
8.0154
7.7350
7.7147
7.6248
7.6053
7.4636
7.4434
7.4237
7.3116
7.2914
7.2623
4.4266
4.4108
4.3954
3.1901
3.1756
3.1603
3.1490
3.1335
2.9633
2.9484
2.9330
2.9176
2.4218
1.6541
1.6428
1.5768
1.5660
1.5469
1.2966
1.2784
1.2555
0.9003
0.8821
0.8641
0.0000
NO2
S
H
N
Ts
3k
f1 (ppm)
0.97
1.00
2.00
1.00
1.00
2.00
1.00
1.00
2.00
3.00
2.08
3.73
2.23
3.02
3.00


148.49
143.50
138.87
136.91
136.32
129.73
129.58
127.06
124.74
121.13
77.32
77.00
76.68
48.51
43.00
34.16
31.27
28.83
26.78
22.50
21.49
13.90
NO2
S
Ts
N
H
3k
f1 (ppm)


2.00
1.05
3.32
2.32
2.30
1.00
2.11
f1 (ppm)
3l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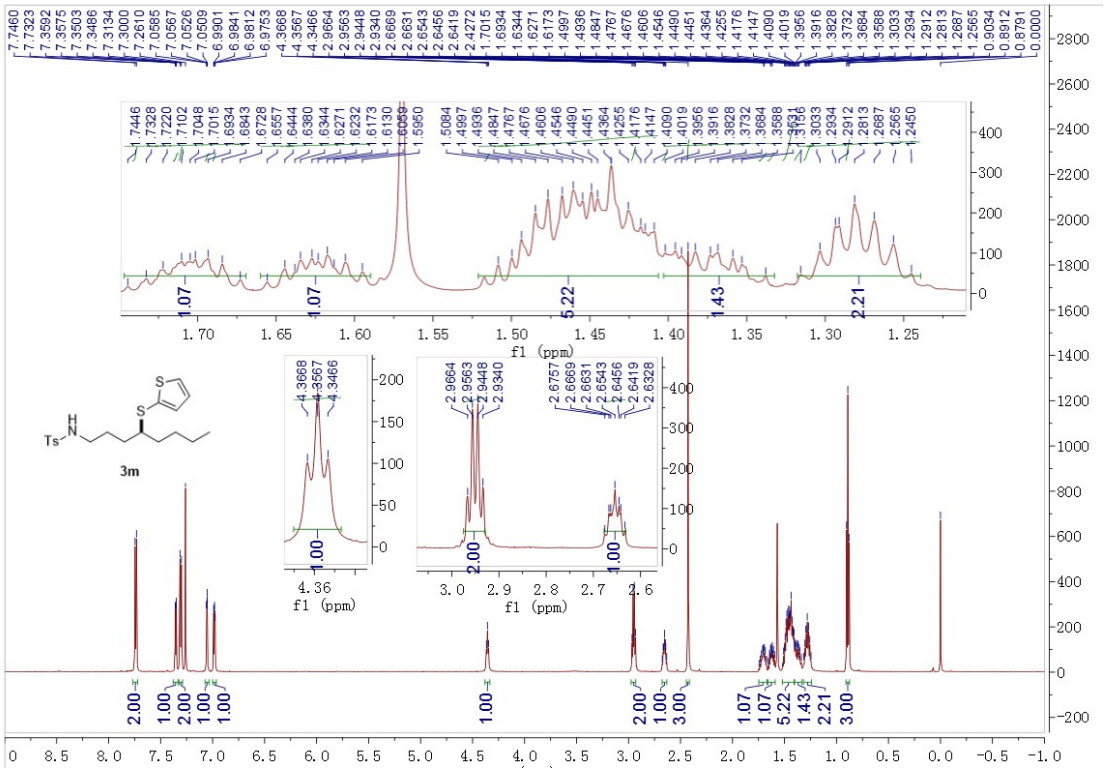
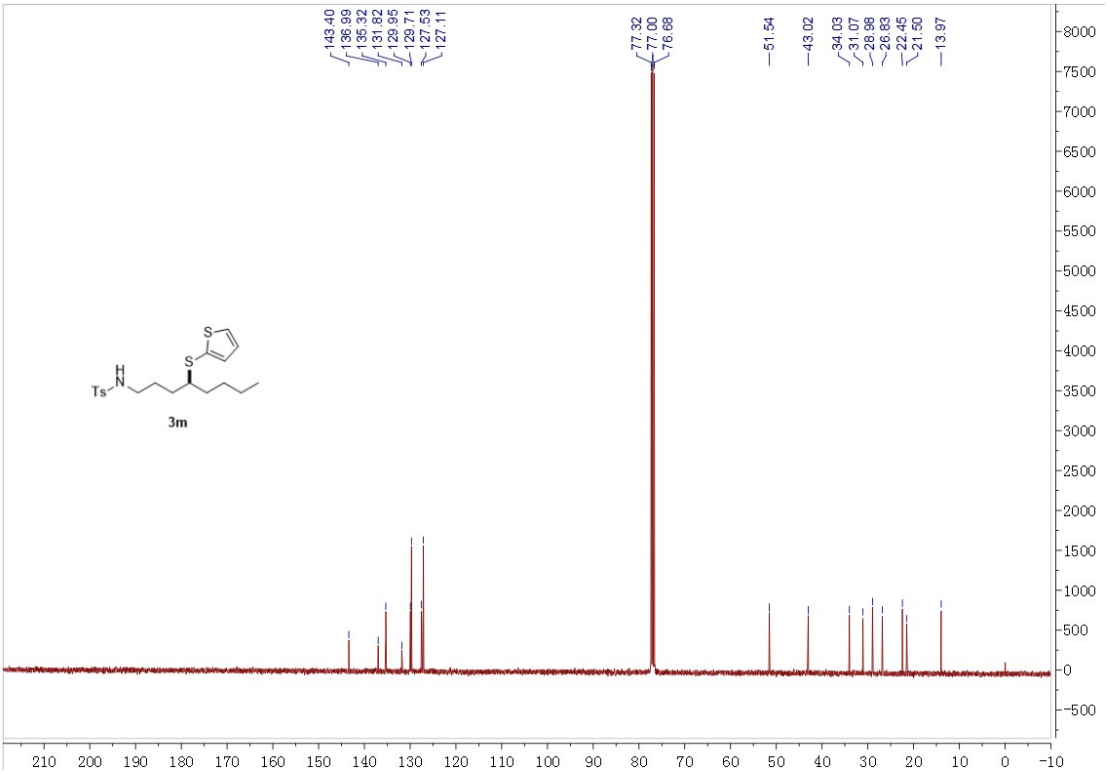
136.95
133.67
132.79
132.11
130.22
129.67
129.45
128.34
127.67
127.25
127.07
126.50
125.96
77.21
77.00
76.79
48.61
43.10
34.31
31.41
28.96
26.74
22.55
21.46
13.96
3l
f1 (ppm)


1.07
1.07
5.22
1.43
2.21
3m
f1 (ppm)
2.00
1.00
2.00
1.00
1.00
2.00
1.00
3.00
1.07
1.07
5.22
1.43
2.21
3.00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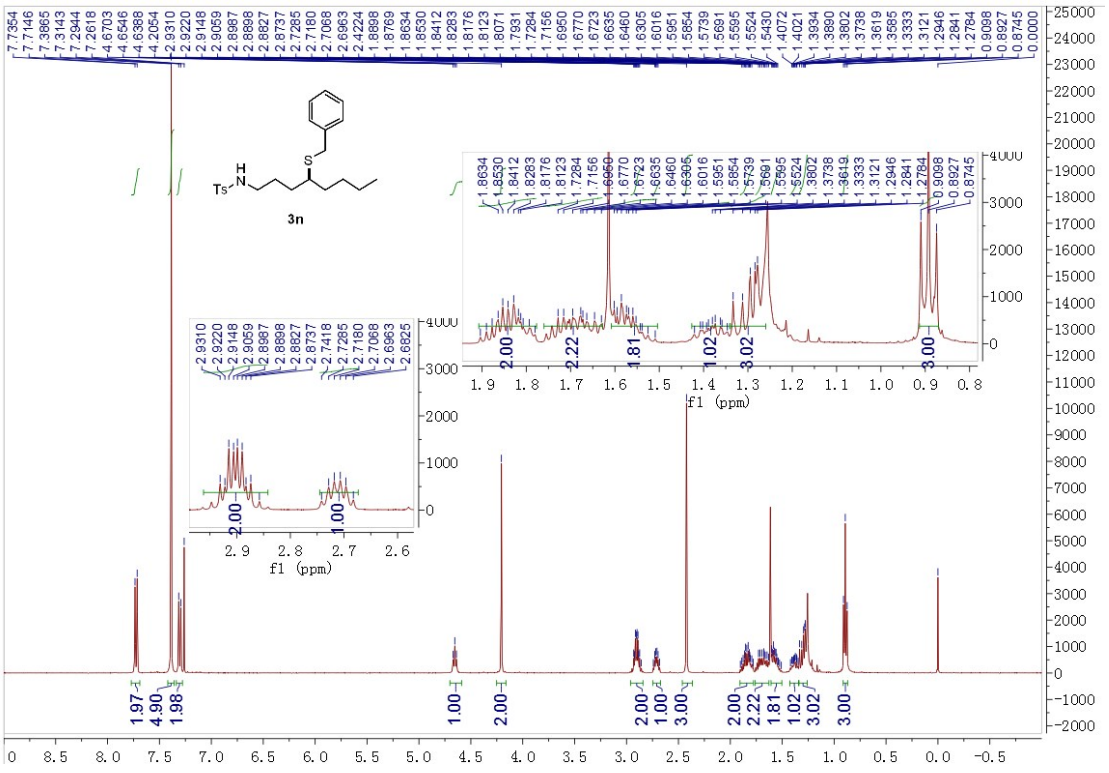
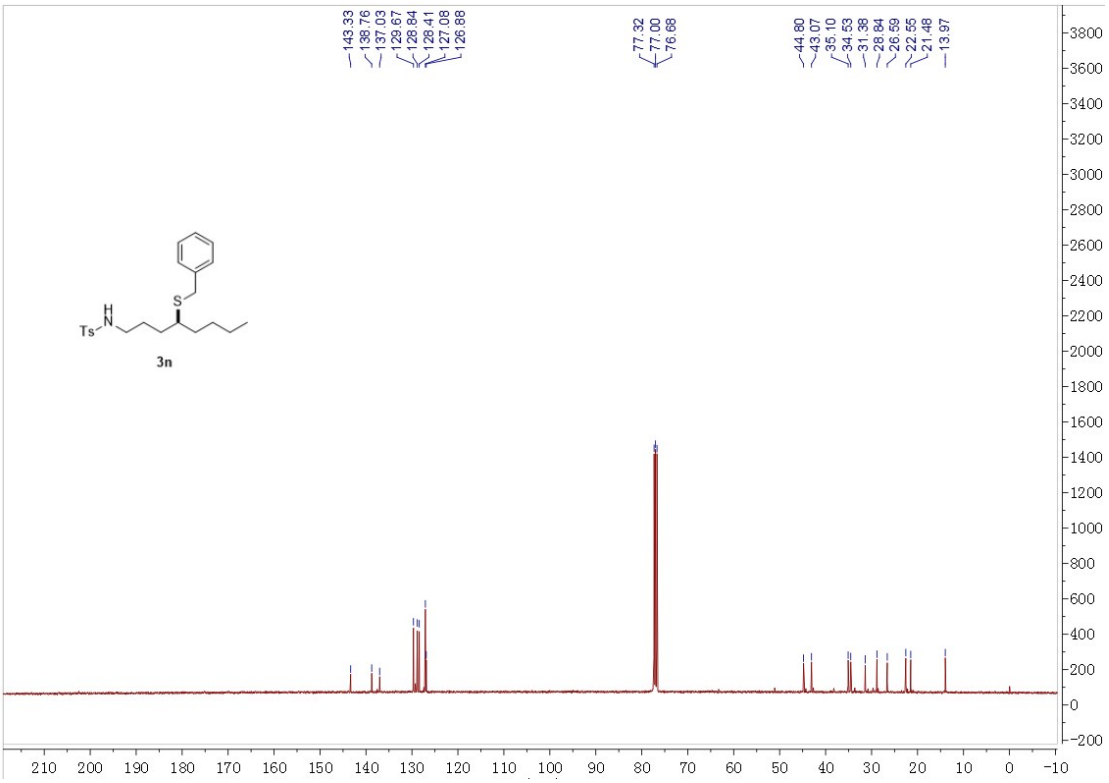
136.99
135.32
131.82
129.95
129.71
127.53
127.11
77.32
77.00
76.68
51.54
43.02
34.03
31.07
28.98
26.83
22.45
21.50
13.97
Ts
H
N
S
S
3m


Ts
H
N
S
3n
2.00
2.22
1.81
1.02
3.02
3.00
2.00
1.00
f1 (ppm)
1.97
4.90
1.98
1.00
2.00
2.00
1.00
3.00
2.00
2.22
1.81
1.02
3.02
3.00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138.76
137.03
129.67
128.84
128.41
127.08
126.88
77.32
77.00
76.68
44.80
43.07
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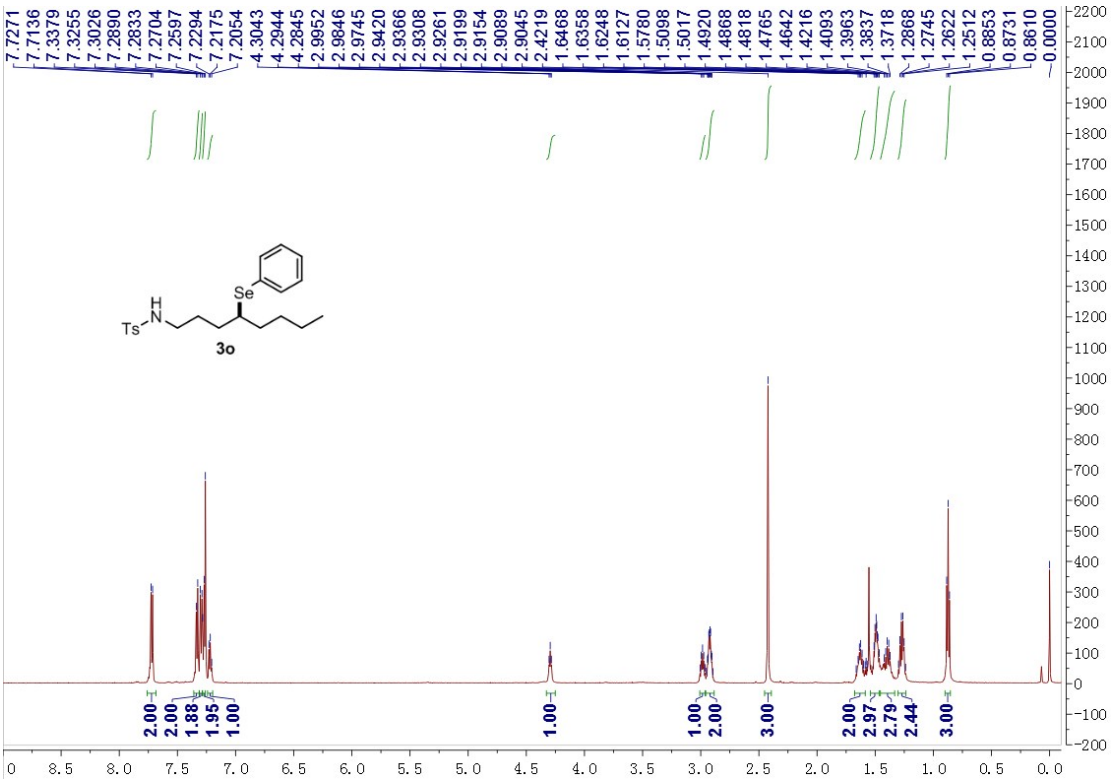
34.53
31.38
28.84
26.59
22.55
21.48
13.97
S
H
N
Ts
3n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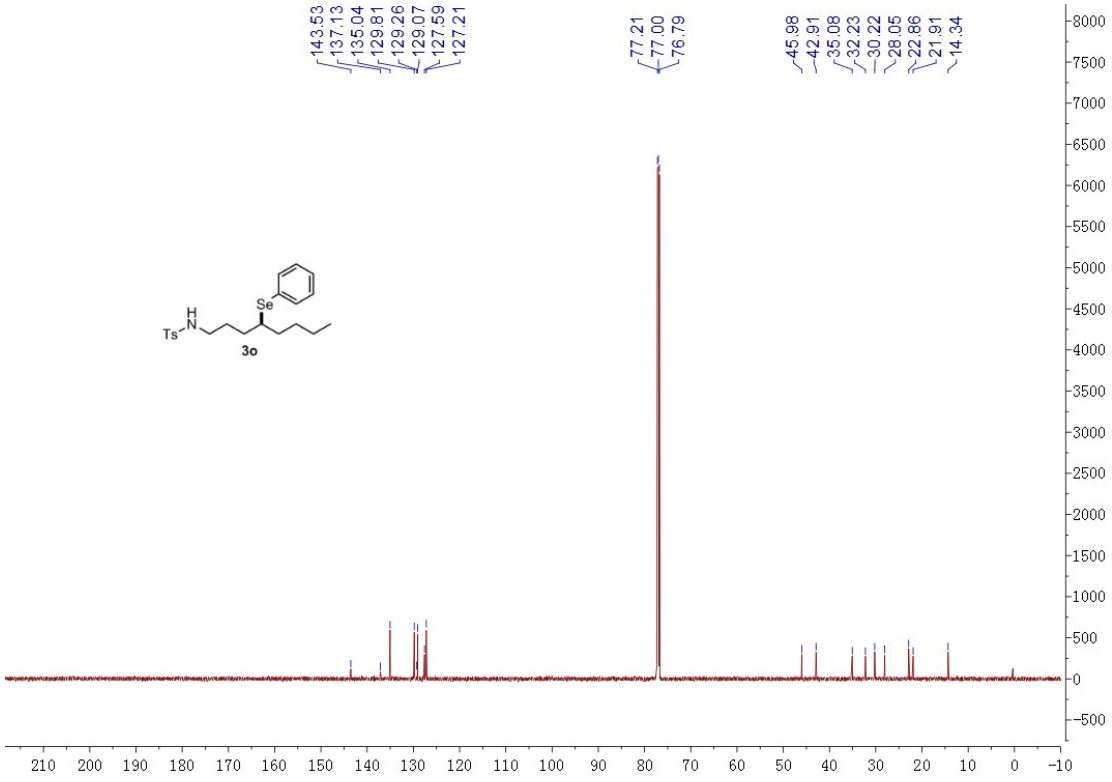
7.7136
7.3379
7.3255
7.3026
7.2890
7.2833
7.2704
7.2597
7.2294
7.2175
7.2054
4.3043
4.2944
4.2845
2.9952
2.9846
2.9745
2.9420
2.9366
2.9308
2.9261
2.9199
2.9154
2.9089
2.9045
2.4219
1.6468
1.6358
1.6248
1.6127
1.5780
1.5098
1.5017
1.4920
1.4868
1.4818
1.4765
1.4642
1.4216
1.4093
1.3963
1.3837
1.3718
1.2868
1.2745
1.2622
1.2512
0.8853
0.8731
0.8610
0.0000
Se
H
N
Ts
3o
2.00
2.00
1.88
1.95
1.00
1.00
1.00
2.00
3.00
2.00
2.97
2.79
2.44
3.00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129.81
129.26
129.07
127.59
127.21
77.21
77.00
76.79
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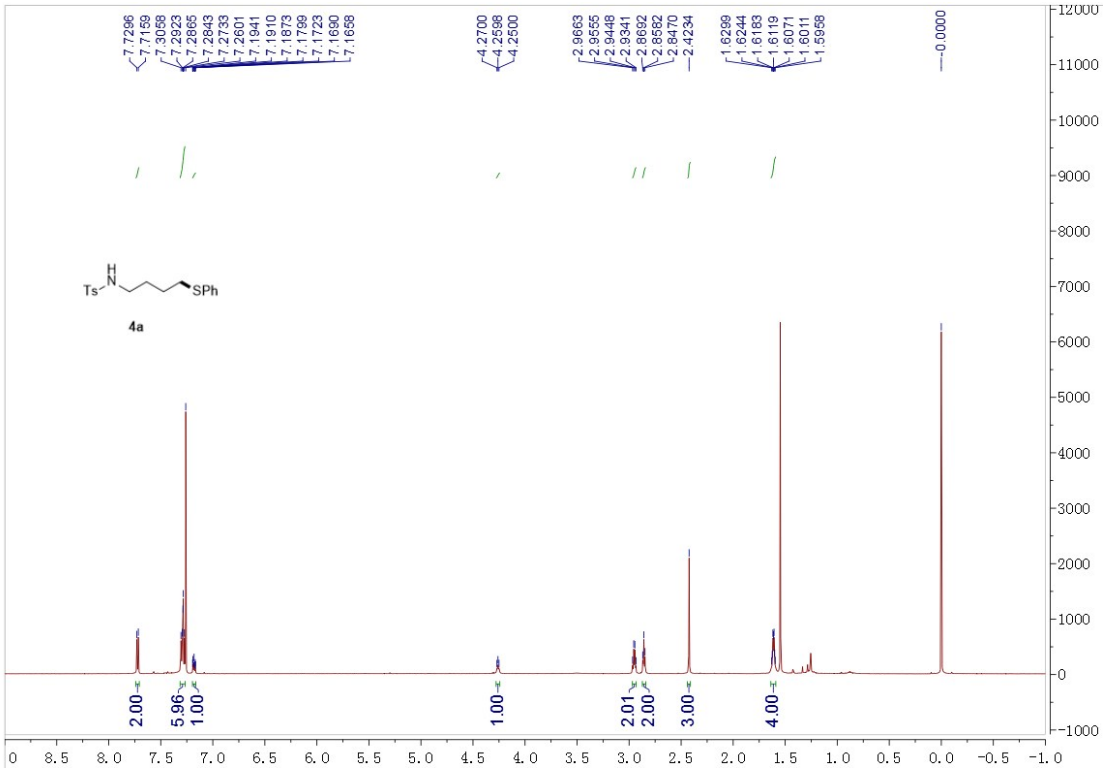
42.91
35.08
32.23
30.22
28.05
22.86
21.91
14.34
Ts
N
H
Se
3o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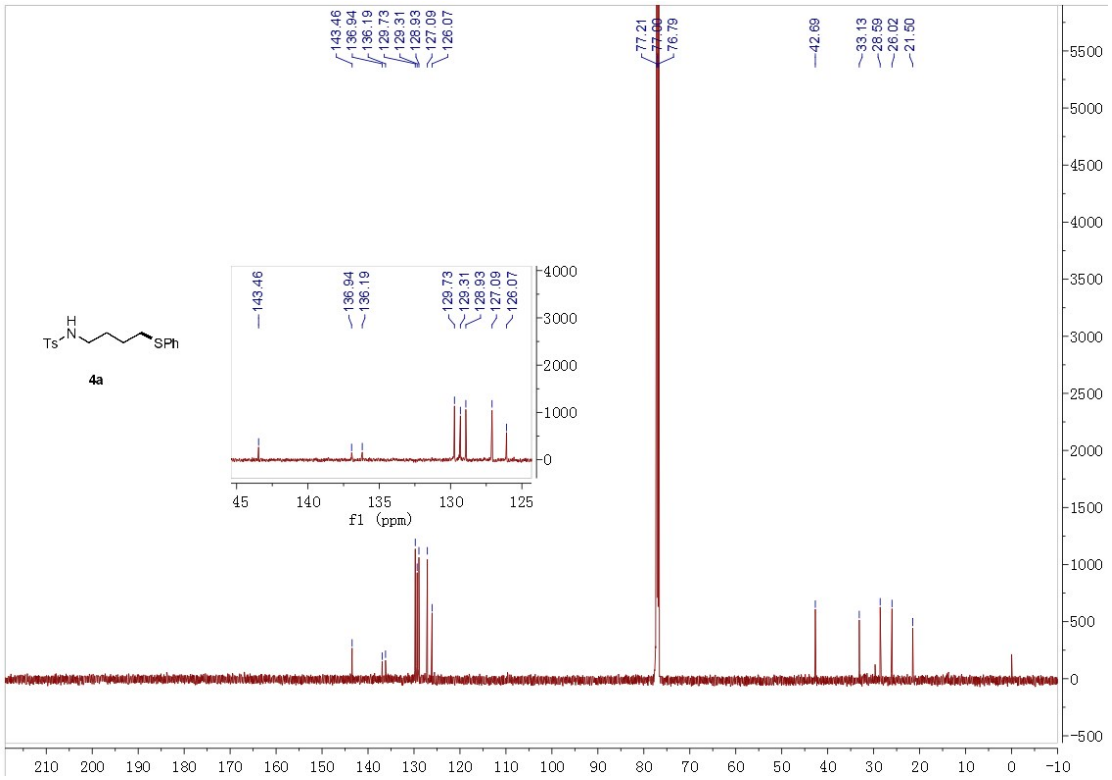
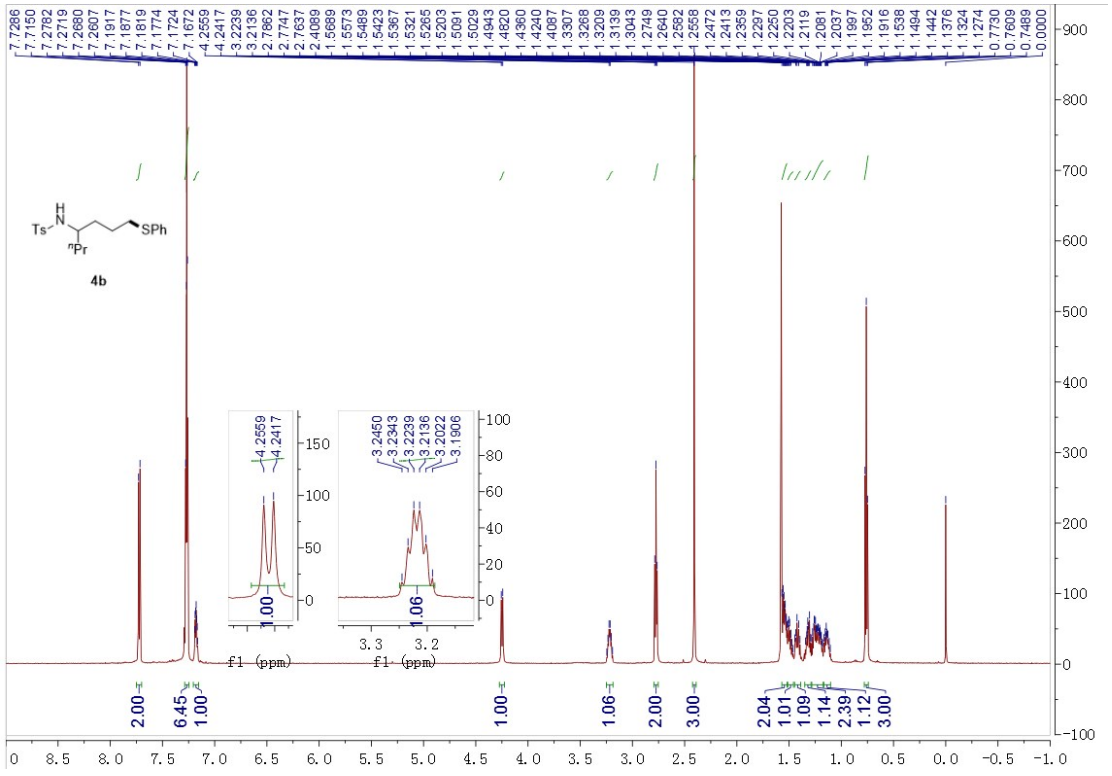
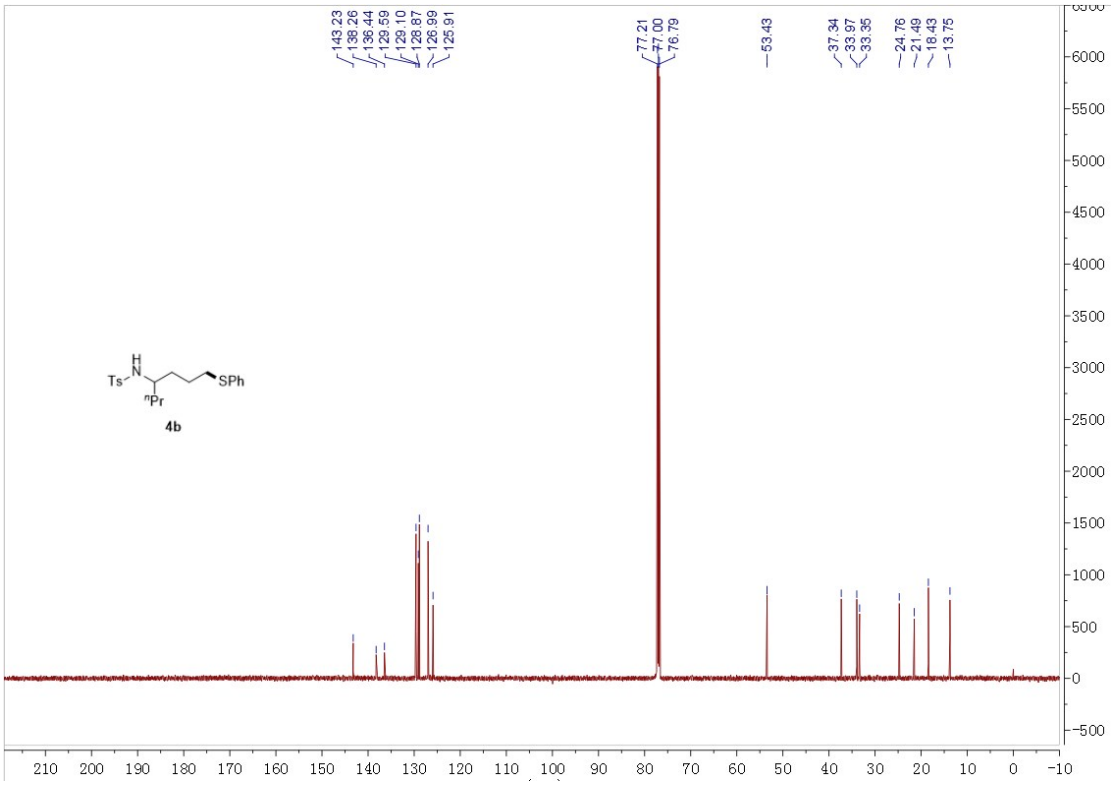
7.7159
7.3068
7.2923
7.2865
7.2843
7.2733
7.2601
7.1941
7.1910
7.1873
7.1799
7.1723
7.1690
7.1658
4.2700
4.2598
4.2500
2.9663
2.9555
2.9448
2.9341
2.8692
2.8582
2.8470
2.4234
1.6299
1.6244
1.6183
1.6119
1.6071
1.6011
1.5958
0.0000
Ts
N
H
SPh
4a
2.00
5.96
1.00
1.00
2.01
2.00
3.00
4.00


143.46
136.94
136.19
129.73
129.31
128.93
127.09
126.07
77.21
77.00
76.79
42.69
33.13
28.59
26.02
21.50
Ts
N
H
SPh
4a
f1 (ppm)


Ts
N
H
SPh
nPr
4b
f1 (ppm)
2.00
6.45
1.00
1.00
1.06
2.00
3.00
2.04
1.01
1.09
1.14
2.39
1.12
3.00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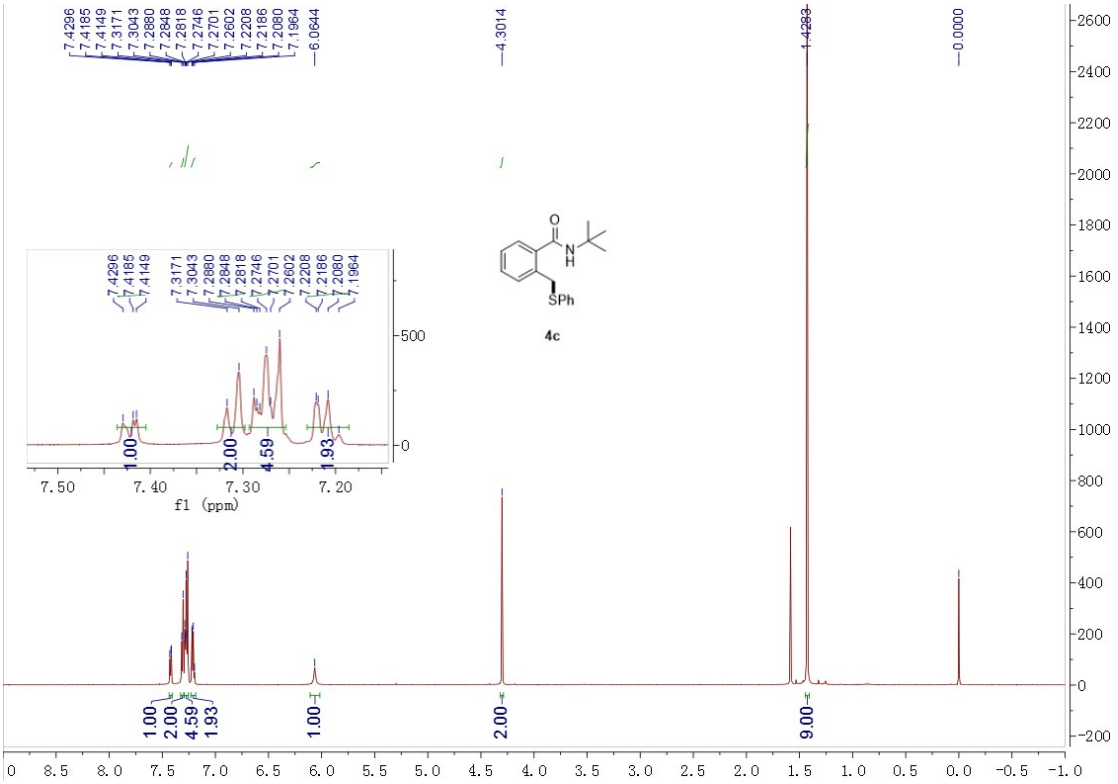
138.26
136.44
129.59
129.10
128.87
126.99
125.91
77.21
77.00
76.79
53.43
37.34
33.97
33.35
24.76
21.49
18.43
13.75
Ts
N
H
nPr
SPh
4b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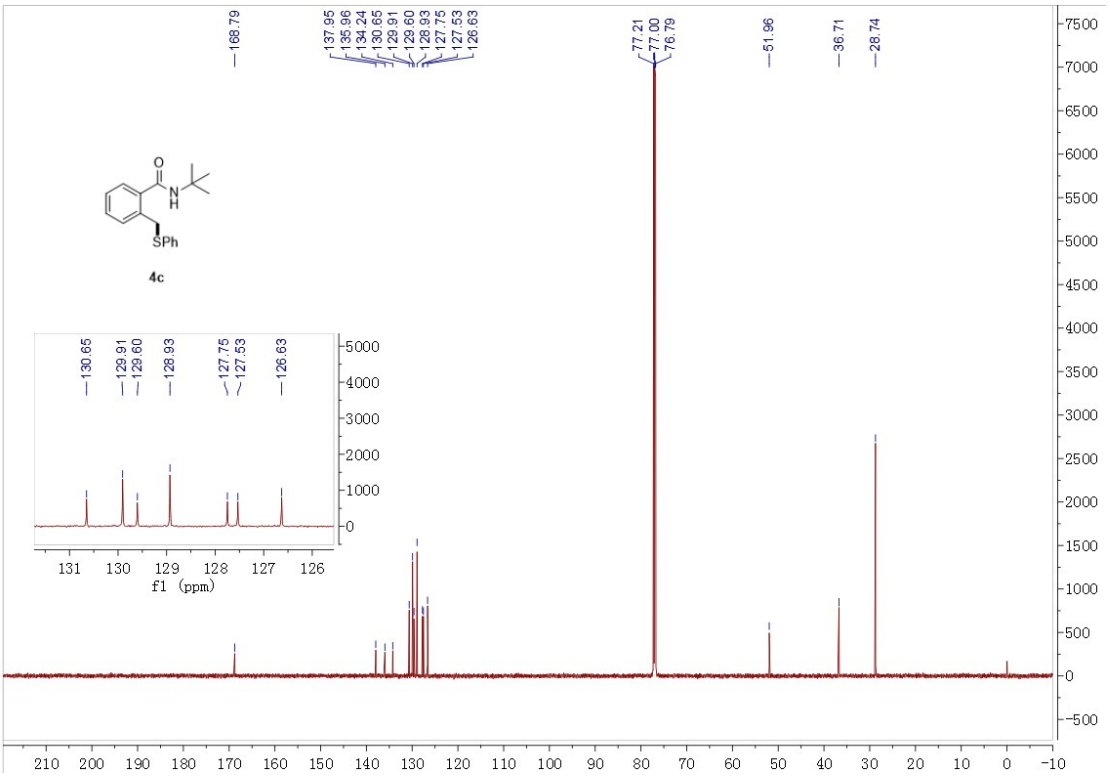
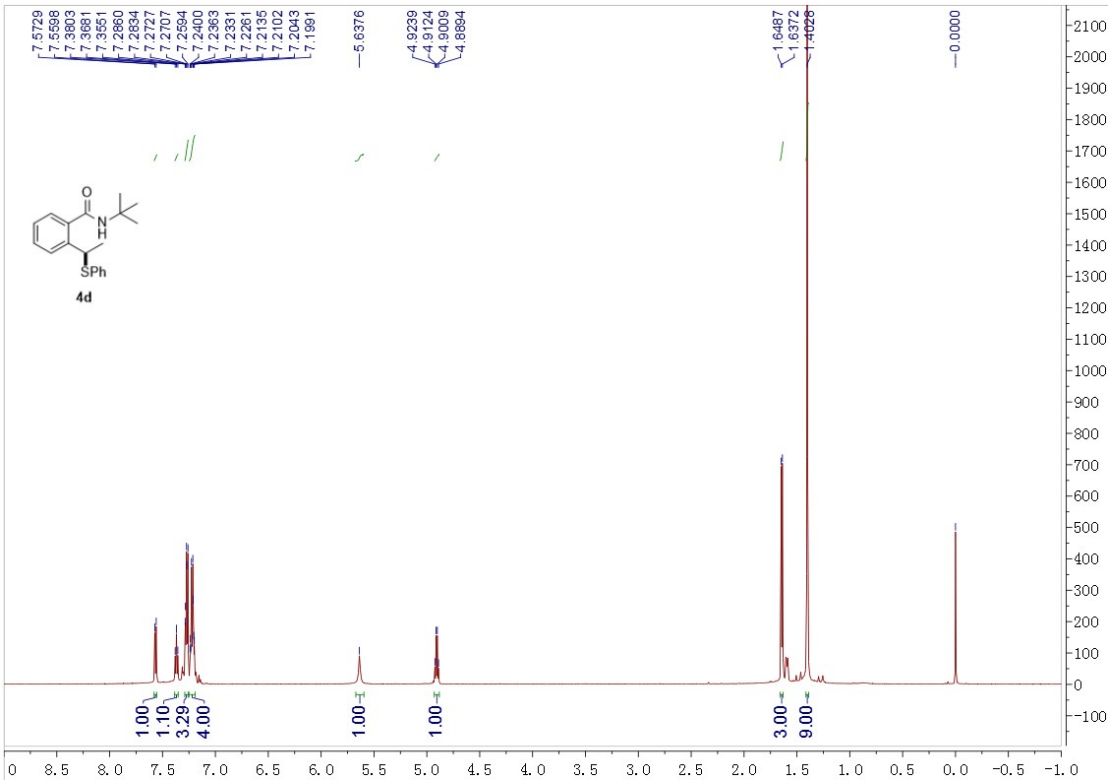
7.4185
7.4149
7.3171
7.3043
7.2880
7.2848
7.2818
7.2746
7.2701
7.2602
7.2208
7.2186
7.2080
7.1964
6.0644
4.3014
1.4283
0.0000
O
N
H
SPh
4c
1.00
2.00
4.59
1.93
1.00
2.00
9.00
f1 (ppm)


168.79
137.95
135.96
134.24
130.65
129.91
129.60
128.93
127.75
127.53
126.63
77.21
77.00
76.79
51.96
36.71
28.74
SPh
4c
f1 (ppm)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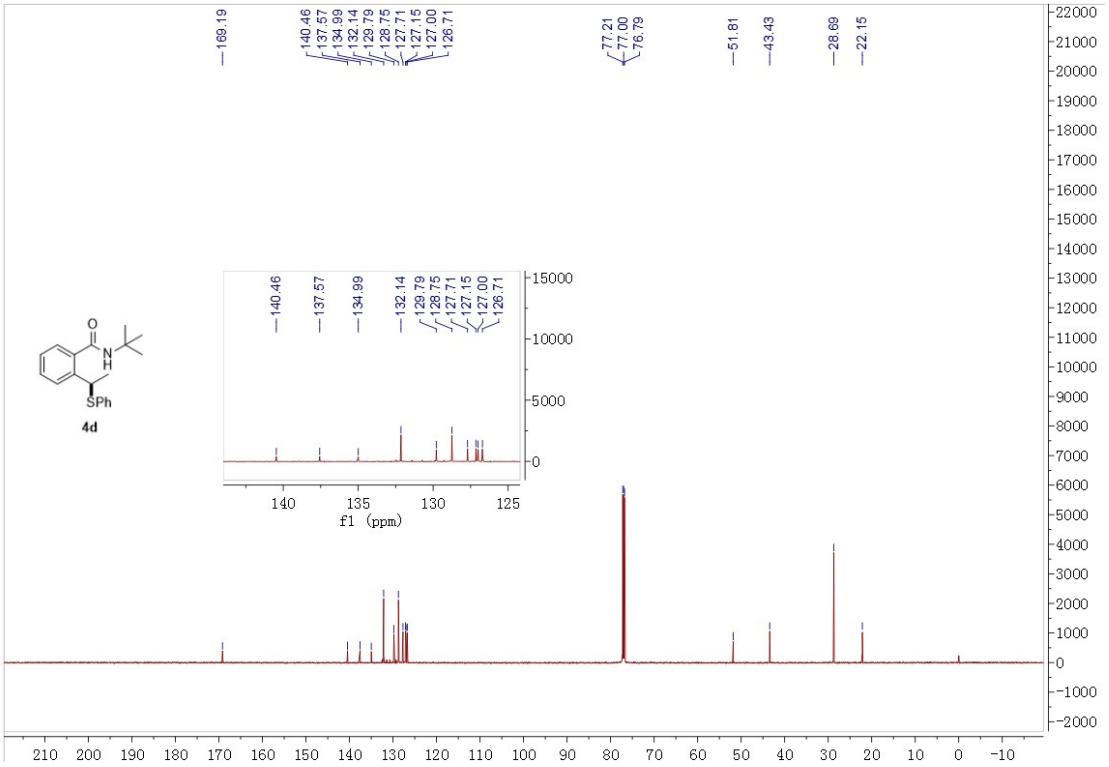
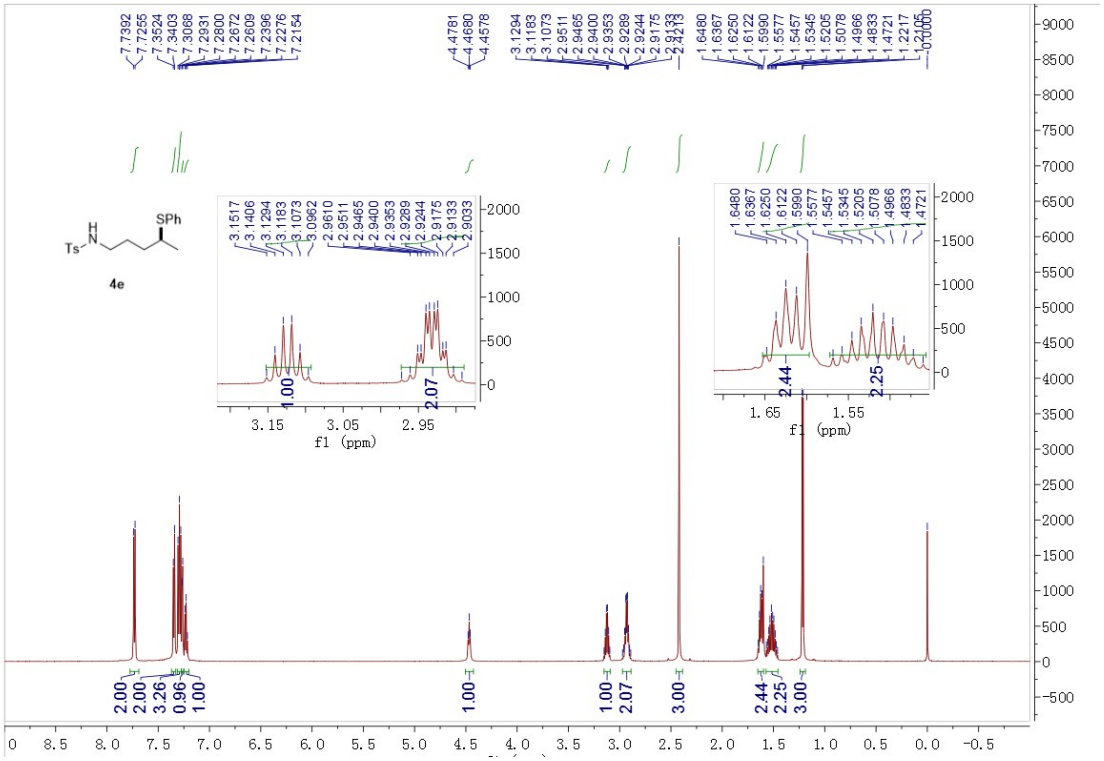
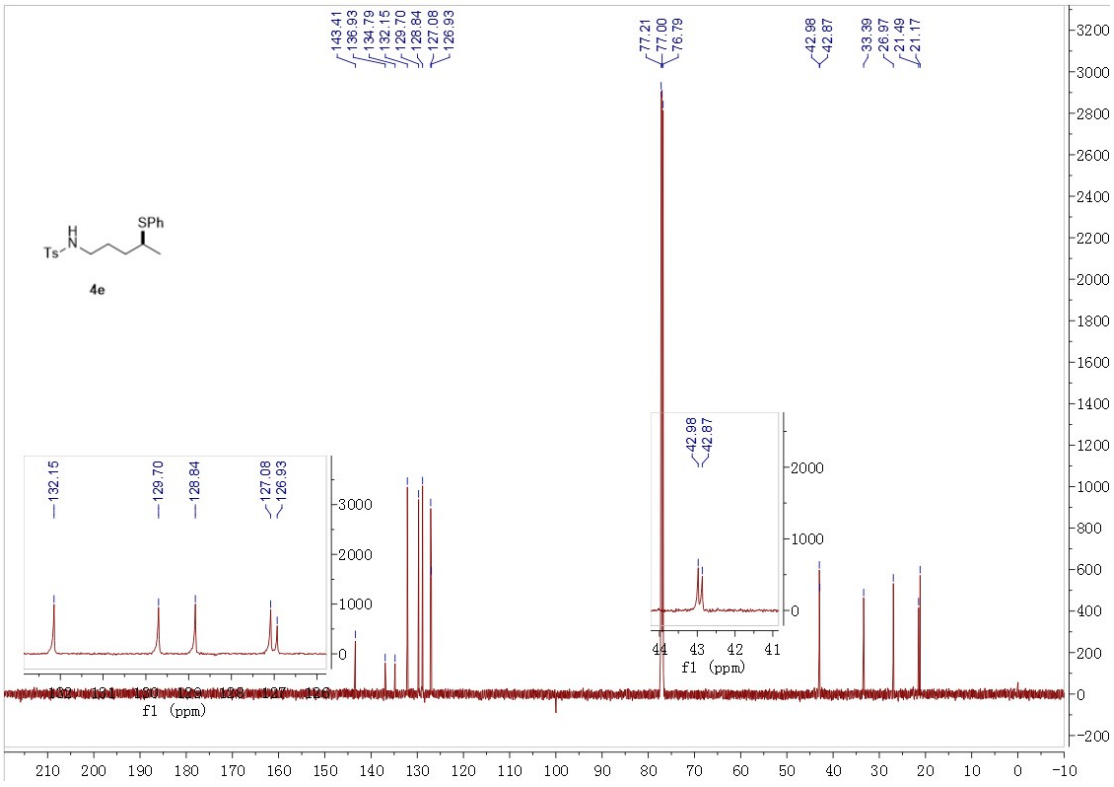
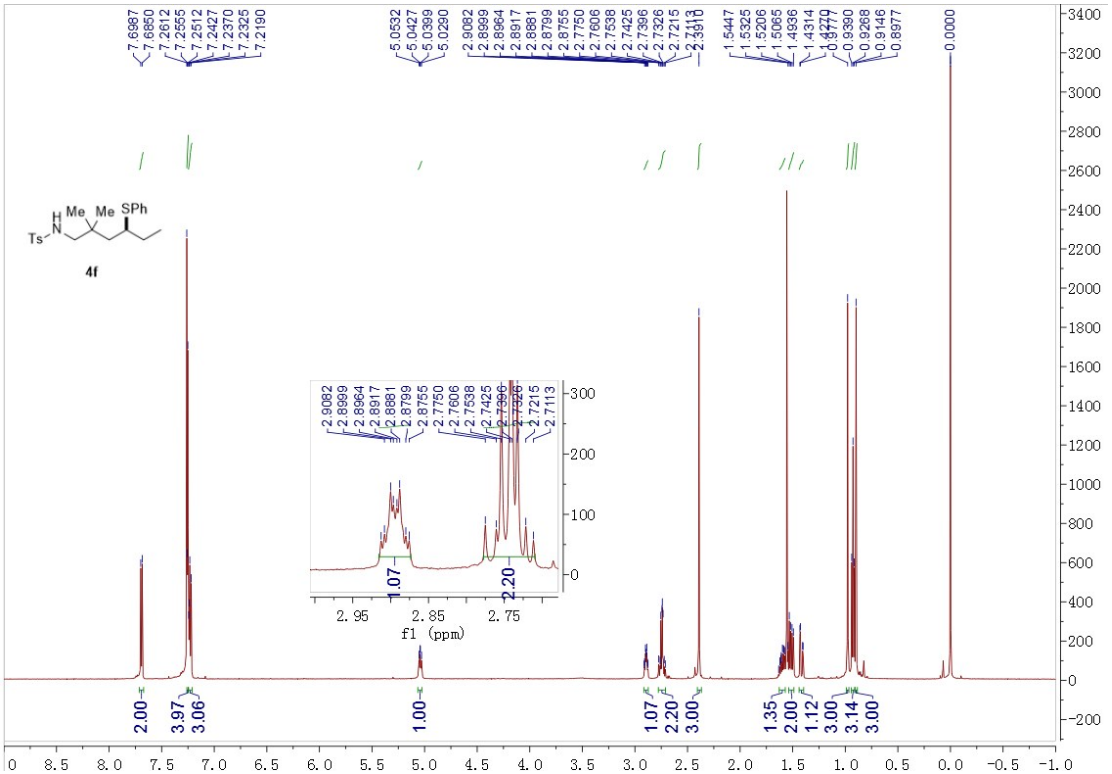
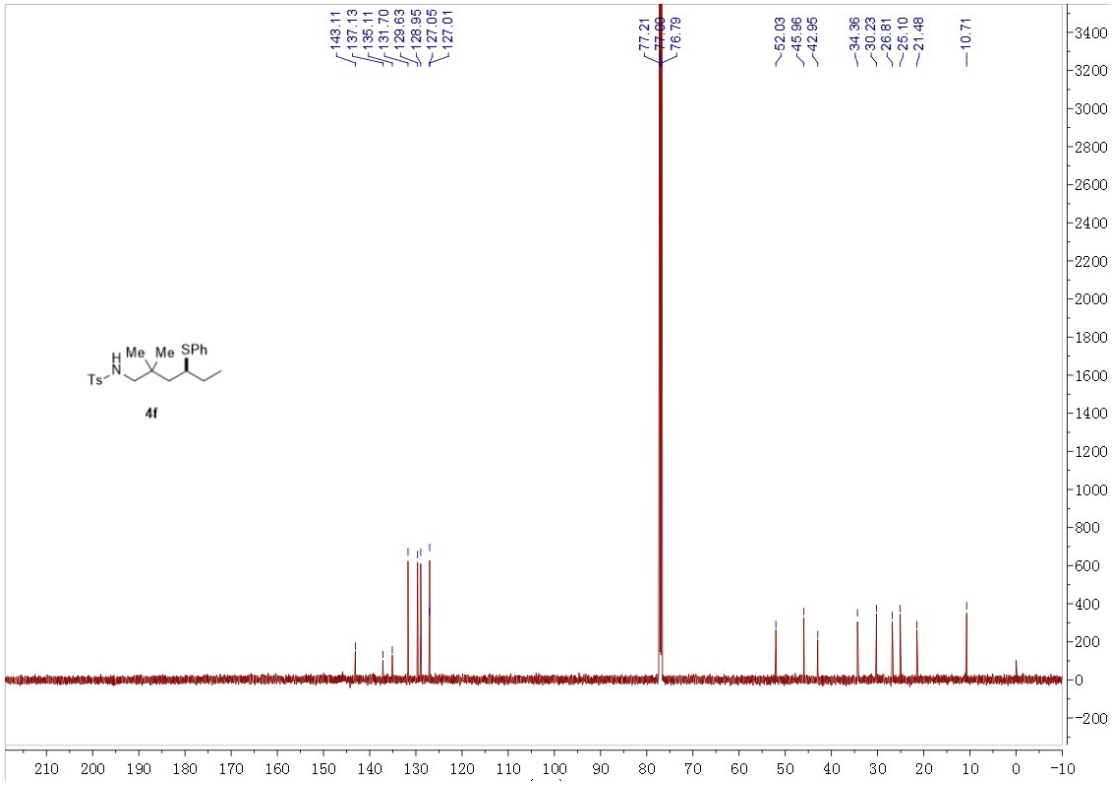
7.3803
7.3681
7.3551
7.2860
7.2834
7.2727
7.2707
7.2694
7.2400
7.2363
7.2331
7.2261
7.2135
7.2102
7.2043
7.1991
5.6376
4.9239
4.9124
4.9009
4.8894
1.6487
1.6372
1.4028
0.0000
SPh
4d
1.00
1.10
3.29
4.00
1.00
1.00
3.00
9.00


169.19
140.46
137.57
134.99
132.14
129.79
128.75
127.71
127.15
127.00
126.71
77.21
77.00
76.79
51.81
43.43
28.69
22.15
4d
f1 (ppm)


4e
f1 (ppm)
2.00
2.00
3.26
0.96
1.00
1.00
1.00
2.07
3.00
2.44
2.25
3.00


4e
143.41
136.93
134.79
132.15
129.70
128.84
127.08
126.93
77.21
77.00
76.79
42.98
42.87
33.39
26.97
21.49
21.17
f1 (ppm)


4f
f1 (ppm)
1.07
2.20
2.00
3.97
3.06
1.00
1.07
2.20
3.00
1.35
2.00
1.12
3.00
3.14
3.00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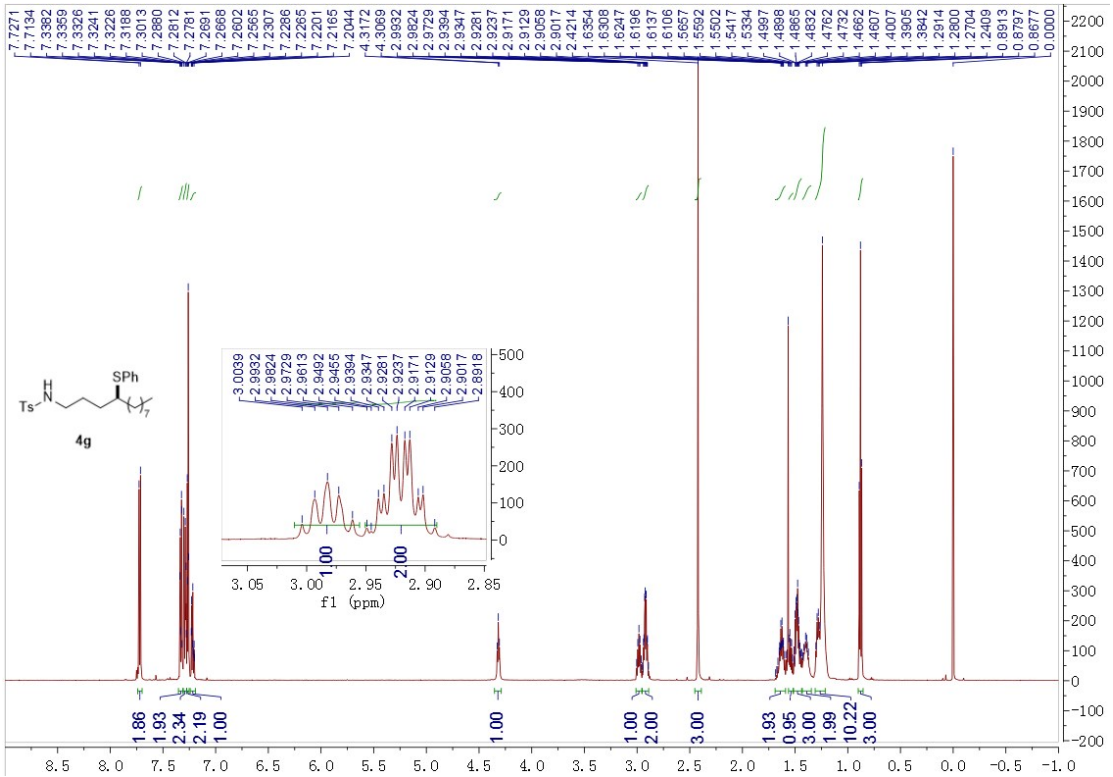
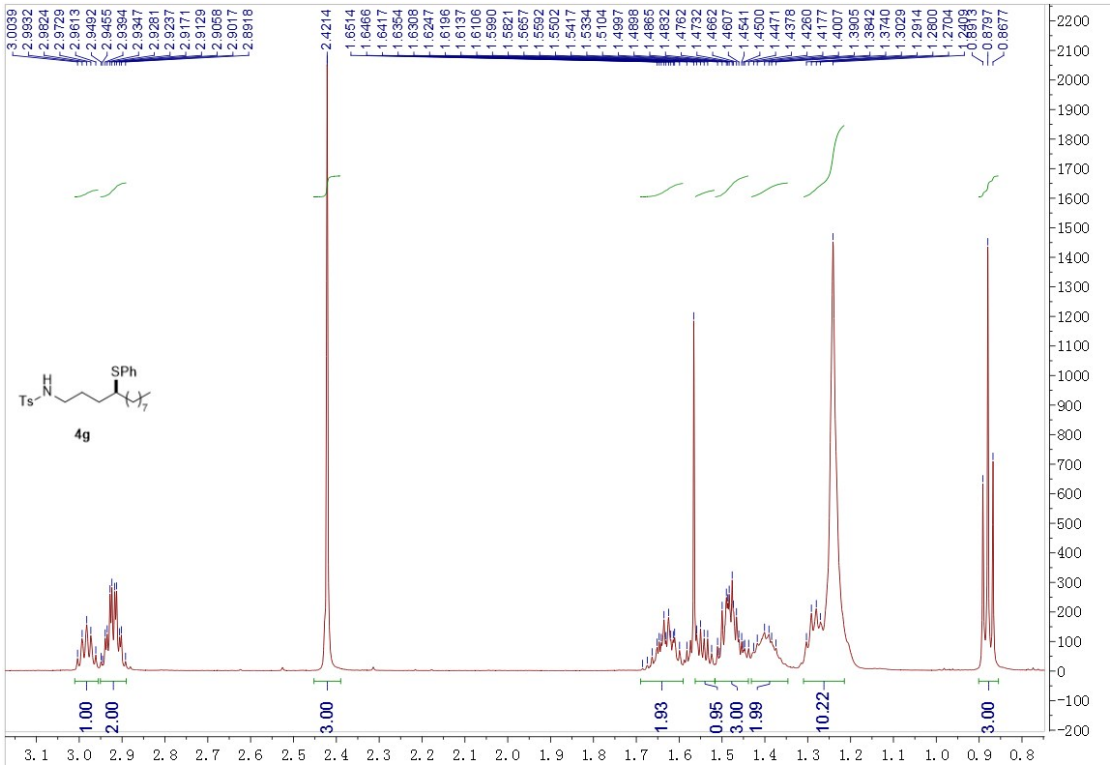
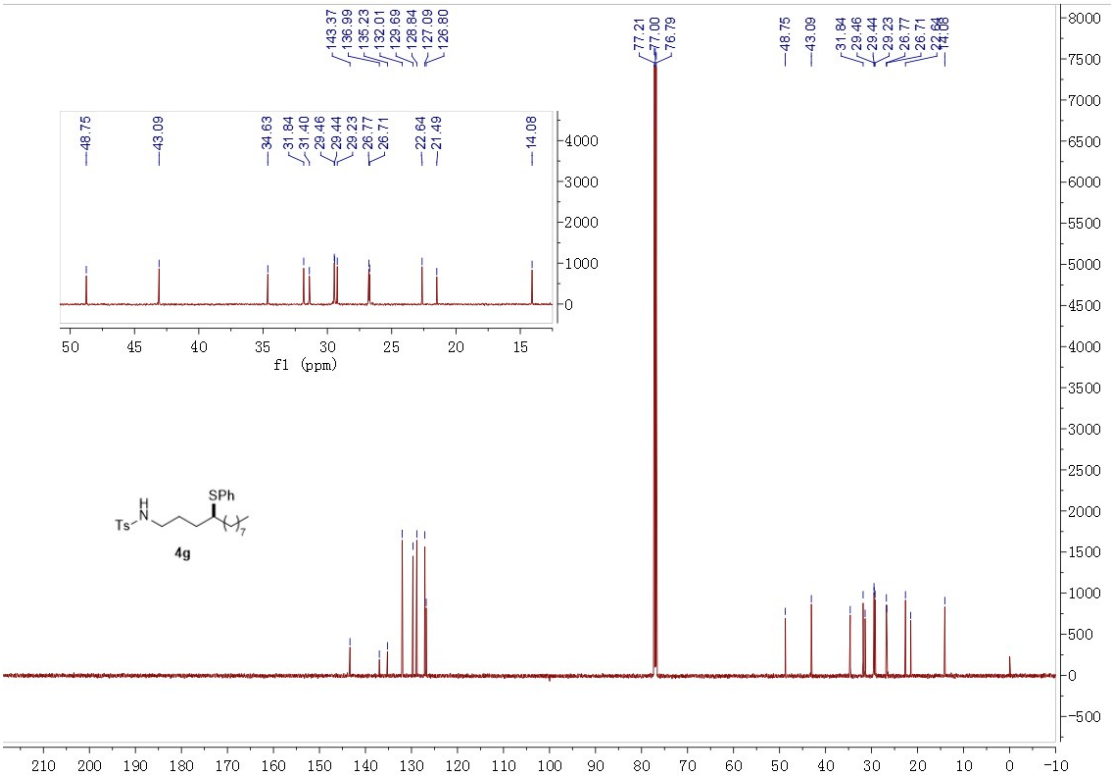
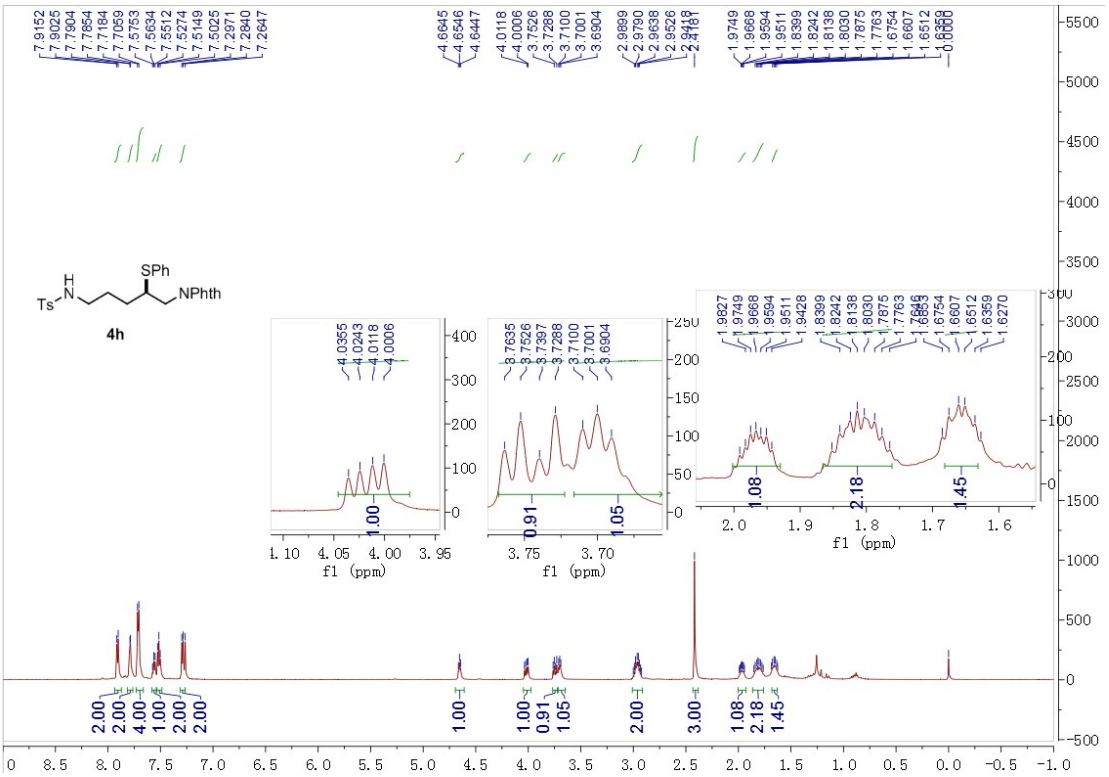
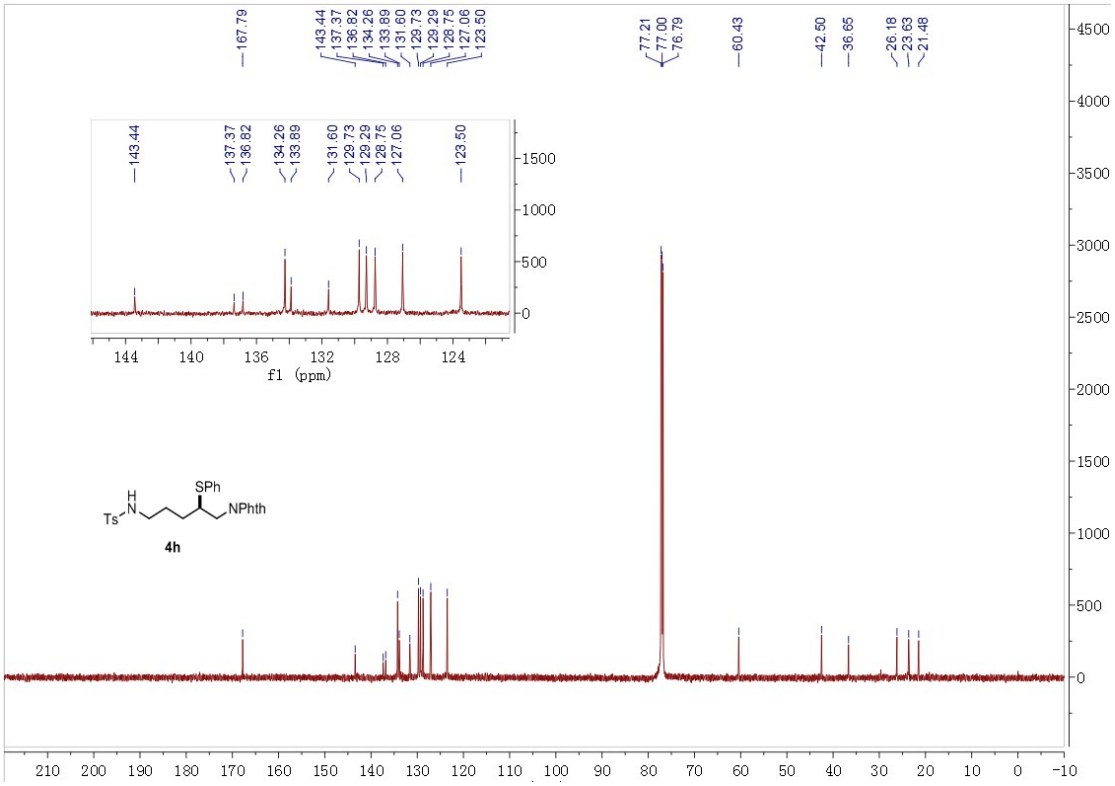
137.13
135.11
131.70
129.63
128.95
127.05
127.01
77.21
77.00
76.79
52.03
45.96
42.95
34.36
30.23
26.81
25.10
21.48
10.71
Me
Me
SPh
H
N
Ts
4f

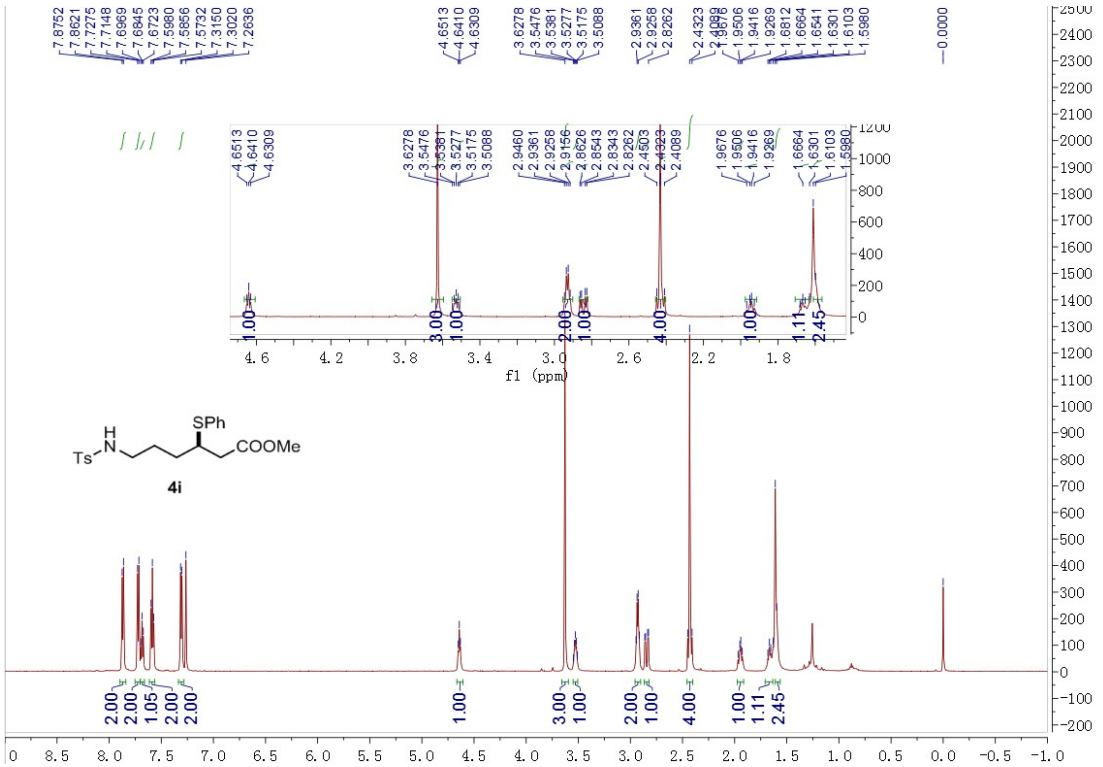

SPh
H
N
Ts
4g
1.86
1.93
2.34
2.19
1.00
1.00
1.00
2.00
3.00
1.93
0.95
3.00
1.99
10.22
3.00
1.00
2.00
f1 (ppm)

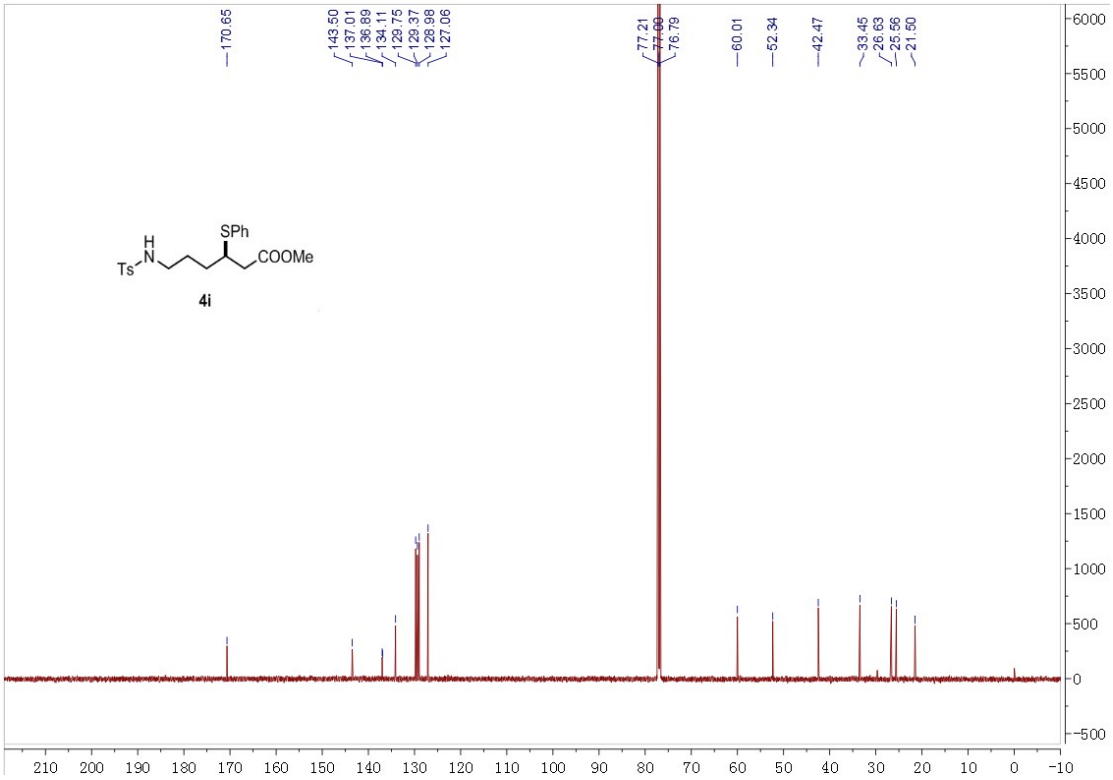

4g
1.00
2.00
3.00
1.93
0.95
3.00
1.99
10.22
3.00

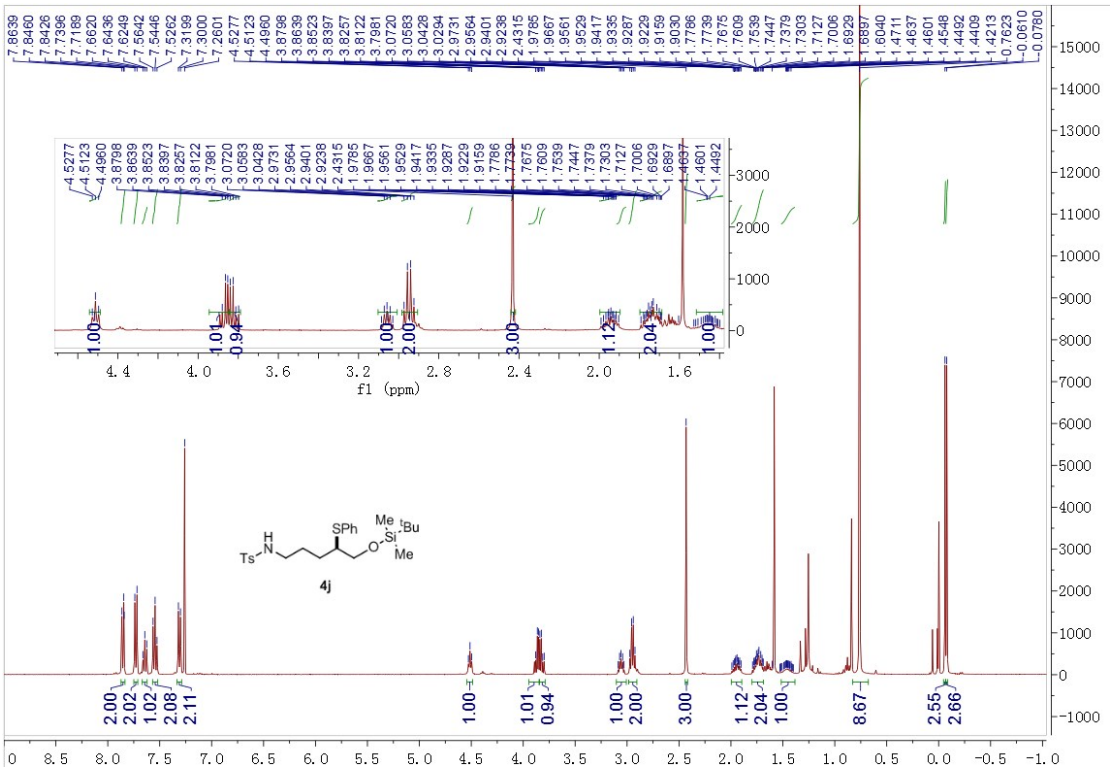

f1 (ppm)
4g


SPh
NPhth
Ts
H
N
4h
f1 (ppm)


SPh
NPhth
Ts
H
N
4h
f1 (ppm)


SPh
H
N
Ts
COOMe
4i
f1 (ppm)


SPh
H
N
Ts
COOMe
4i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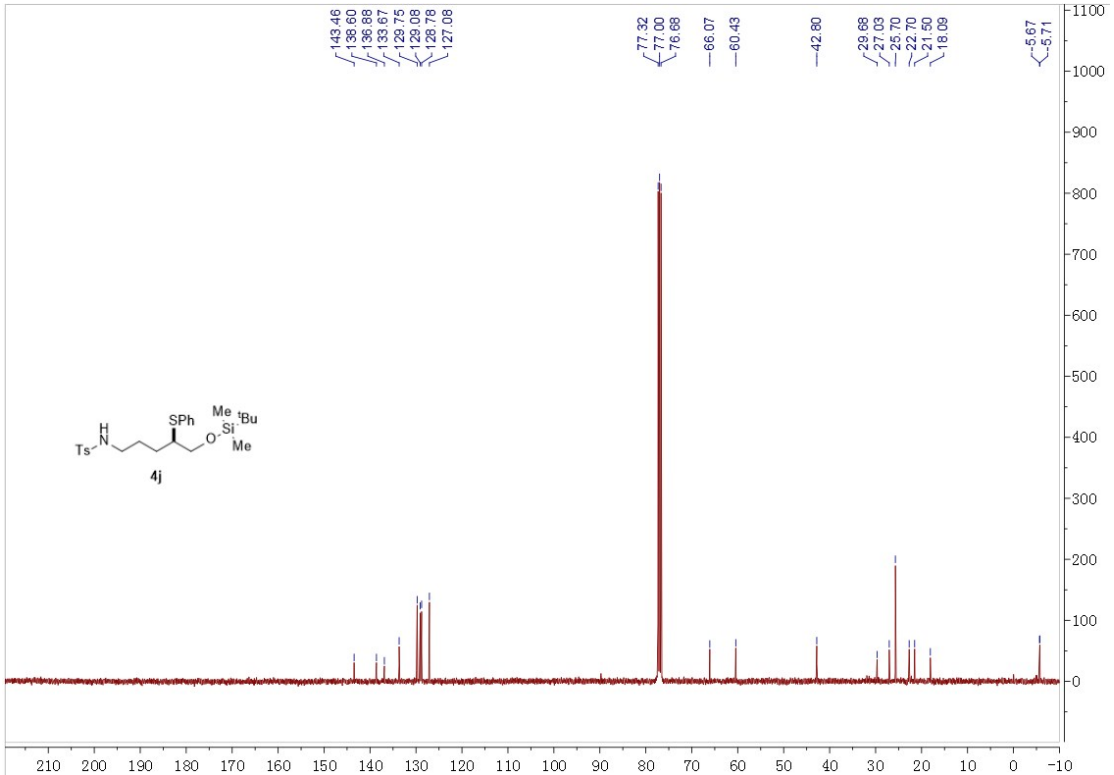
f1 (ppm)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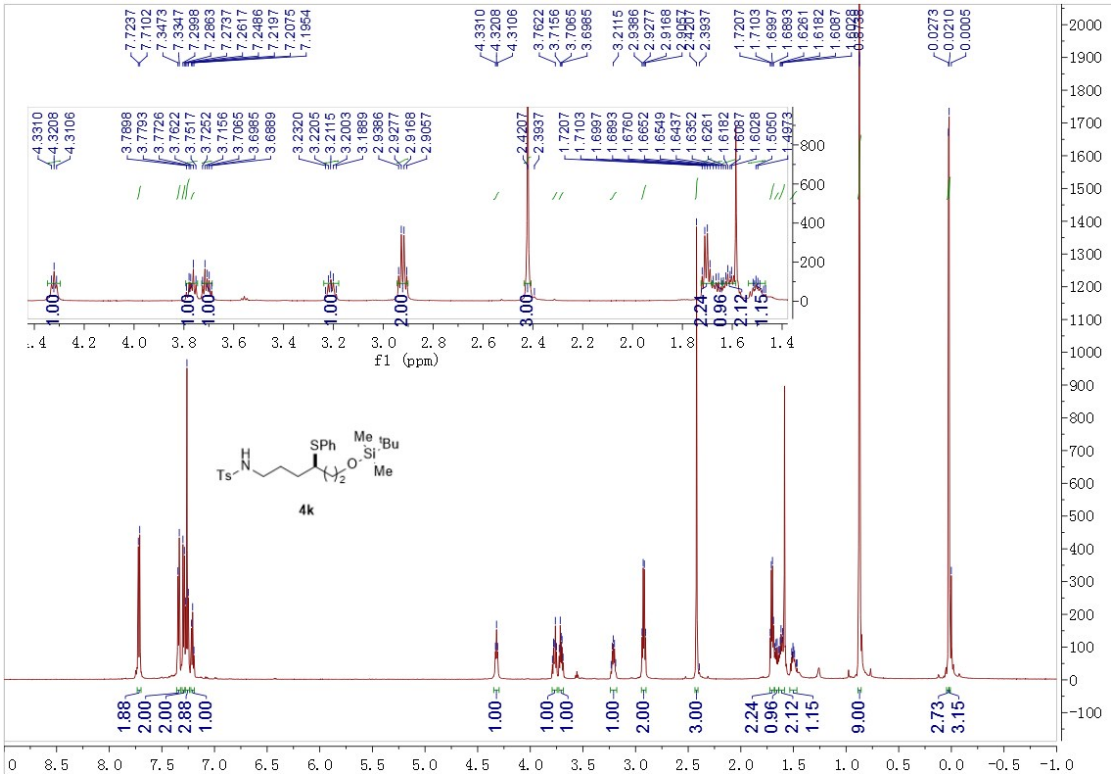
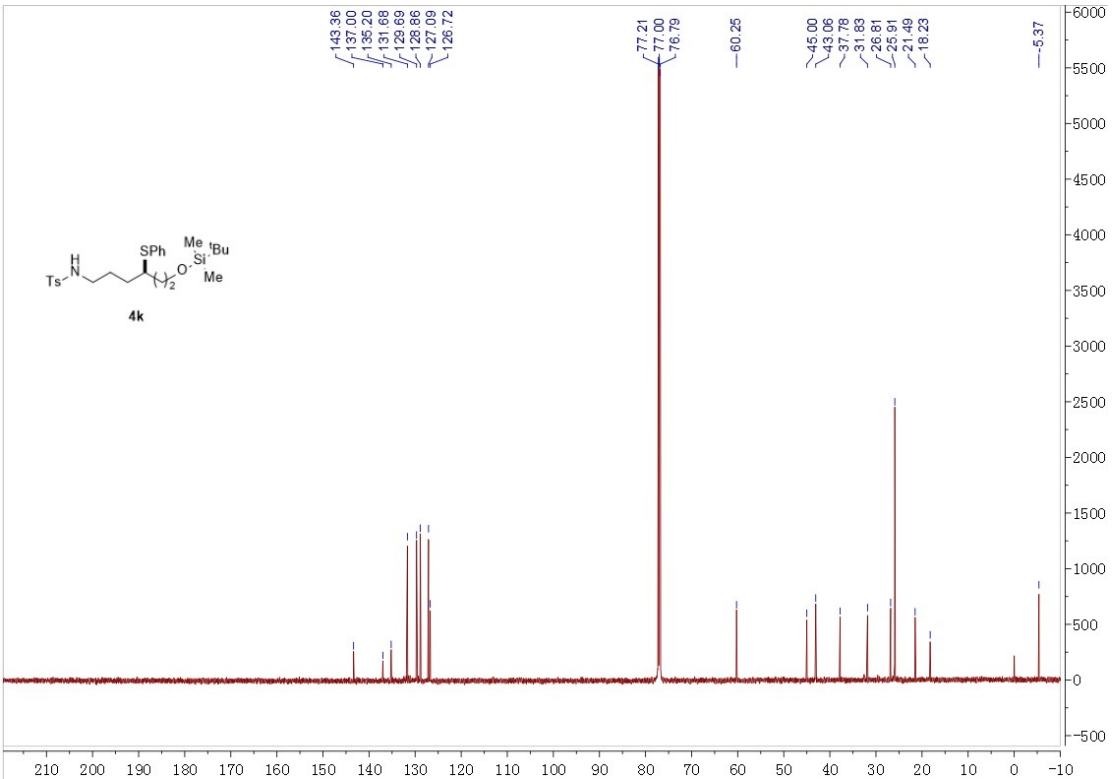

4k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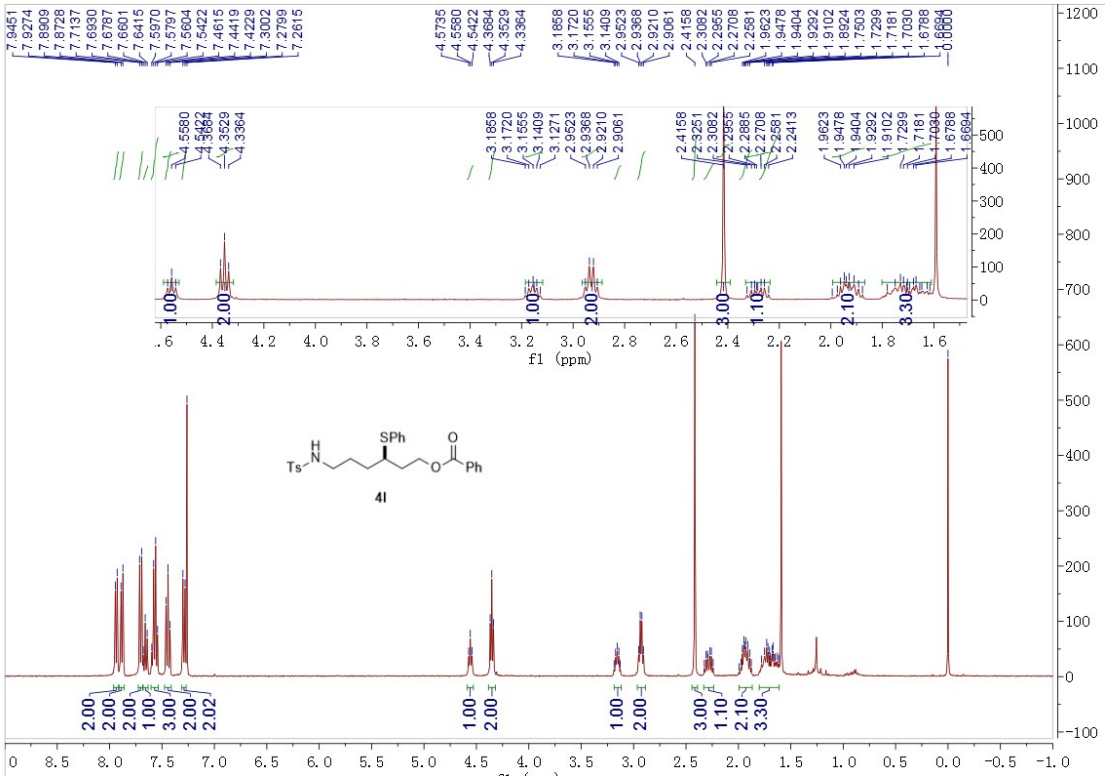
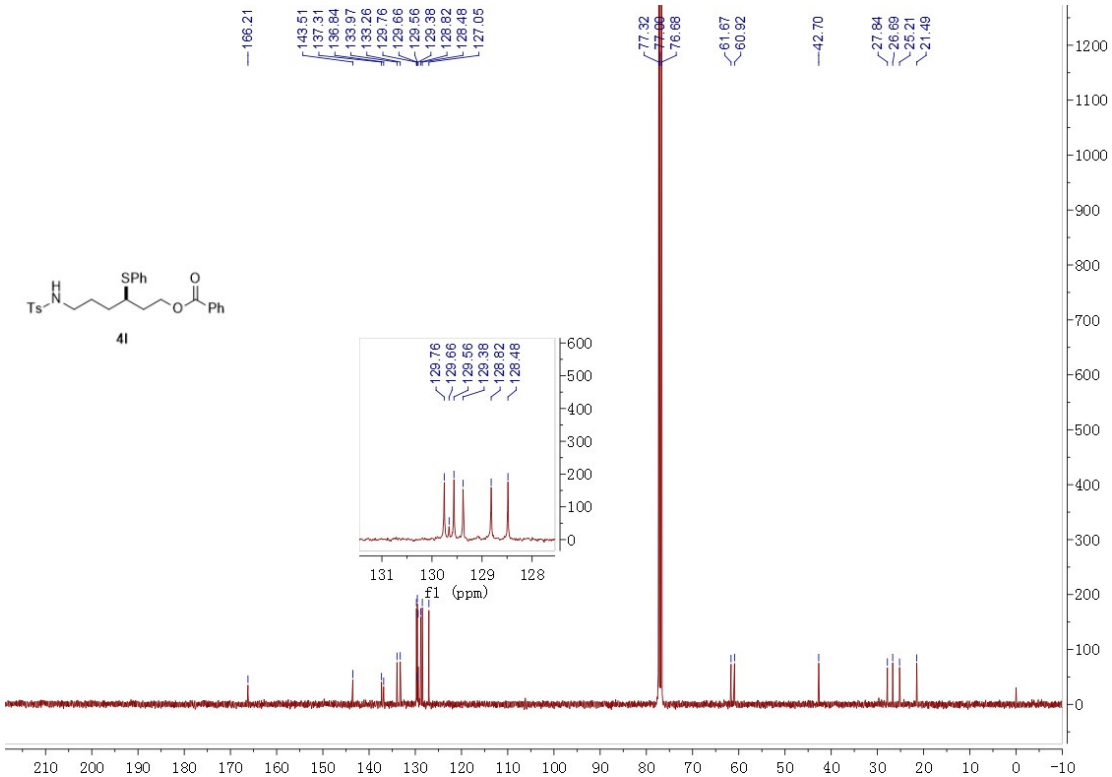
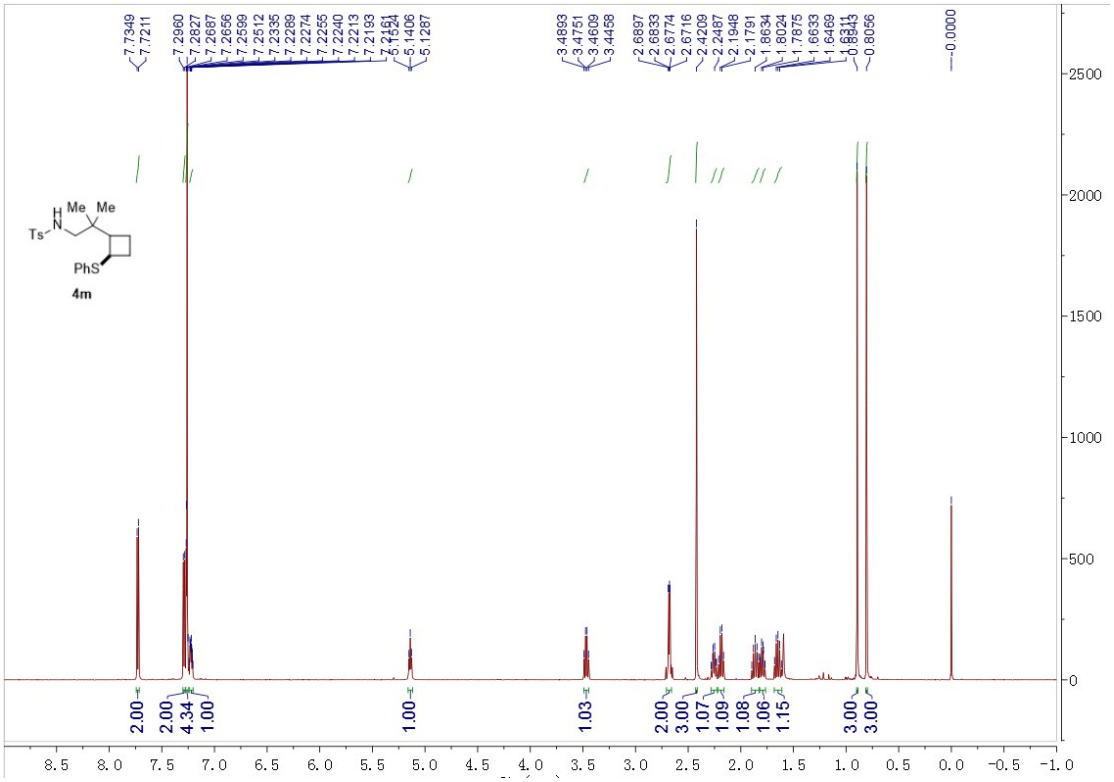

4l


4l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7.2827
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7.2512
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7.2289
7.2274
7.2255
7.2240
7.2213
7.2193
7.2161
5.1524
5.1406
5.1287
3.4893
3.4751
3.4609
3.4458
2.6897
2.6833
2.6774
2.6716
2.4209
2.2487
2.1948
2.1791
1.8634
1.8024
1.7875
1.6633
1.6469
1.6311
0.8943
0.8056
-0.0000
Me
Me
Ts
N
H
PhS
4m
2.00
2.00
4.34
1.00
1.00
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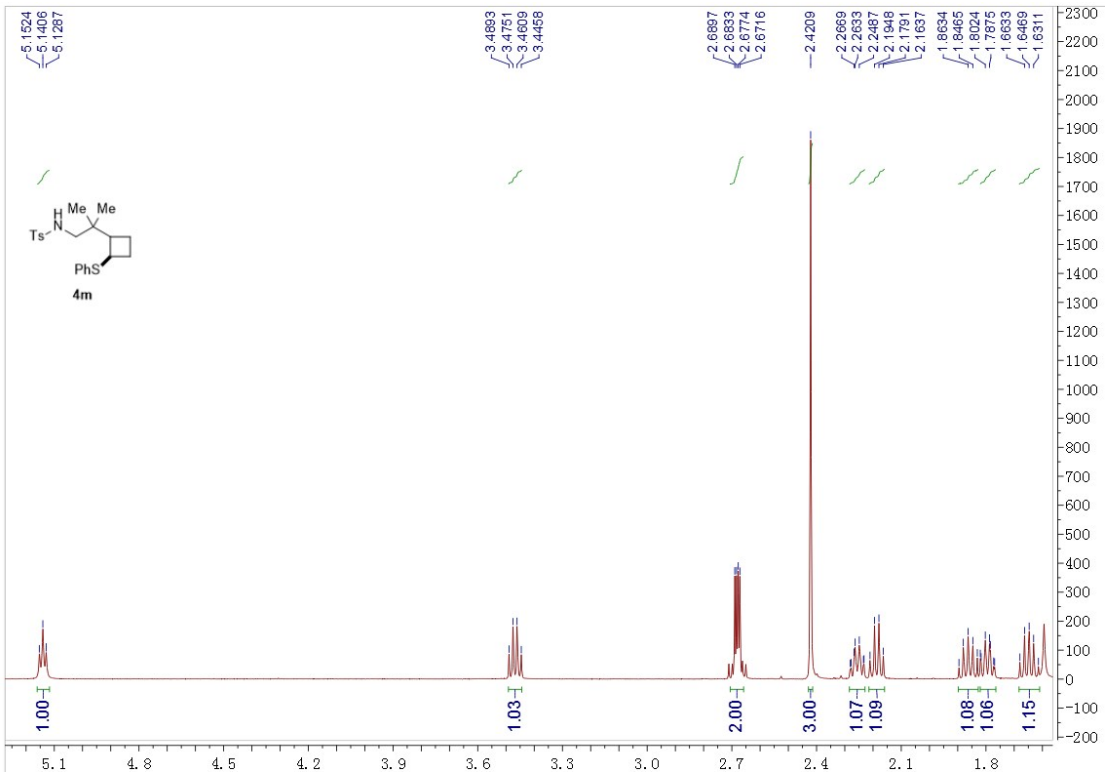
2.00
3.00
1.07
1.09
1.08
1.06
1.15
3.00
3.00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5.1406
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2.6774
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2.2669
2.2633
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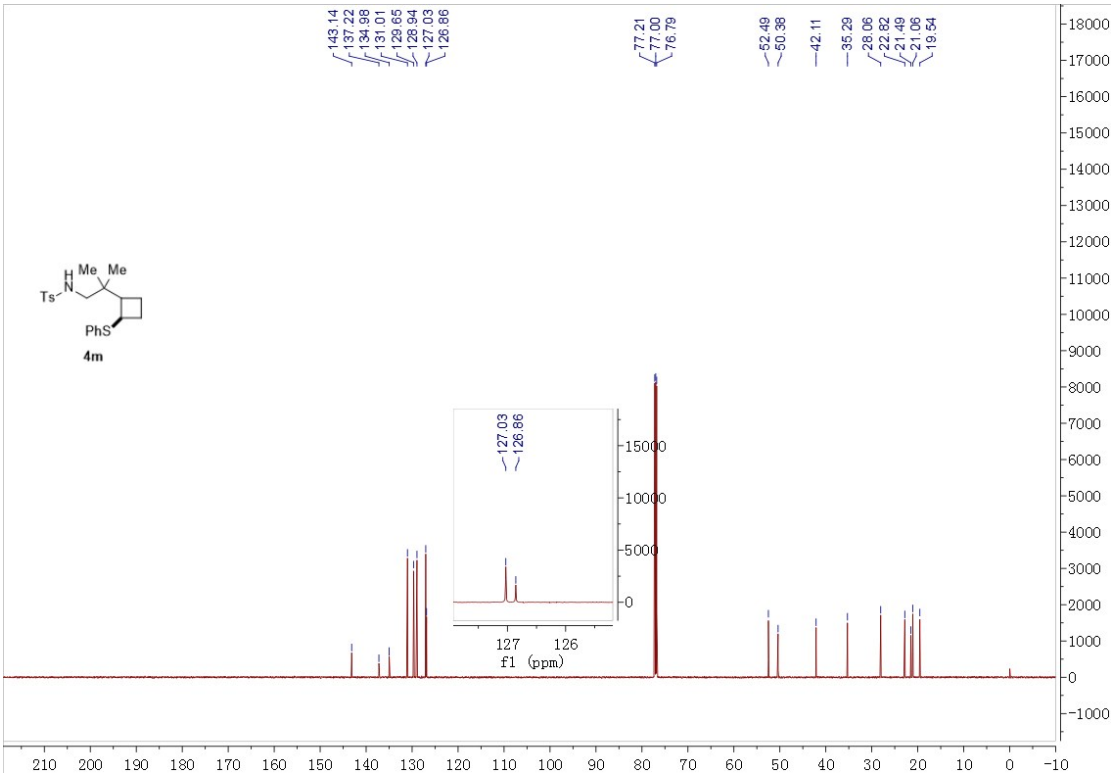
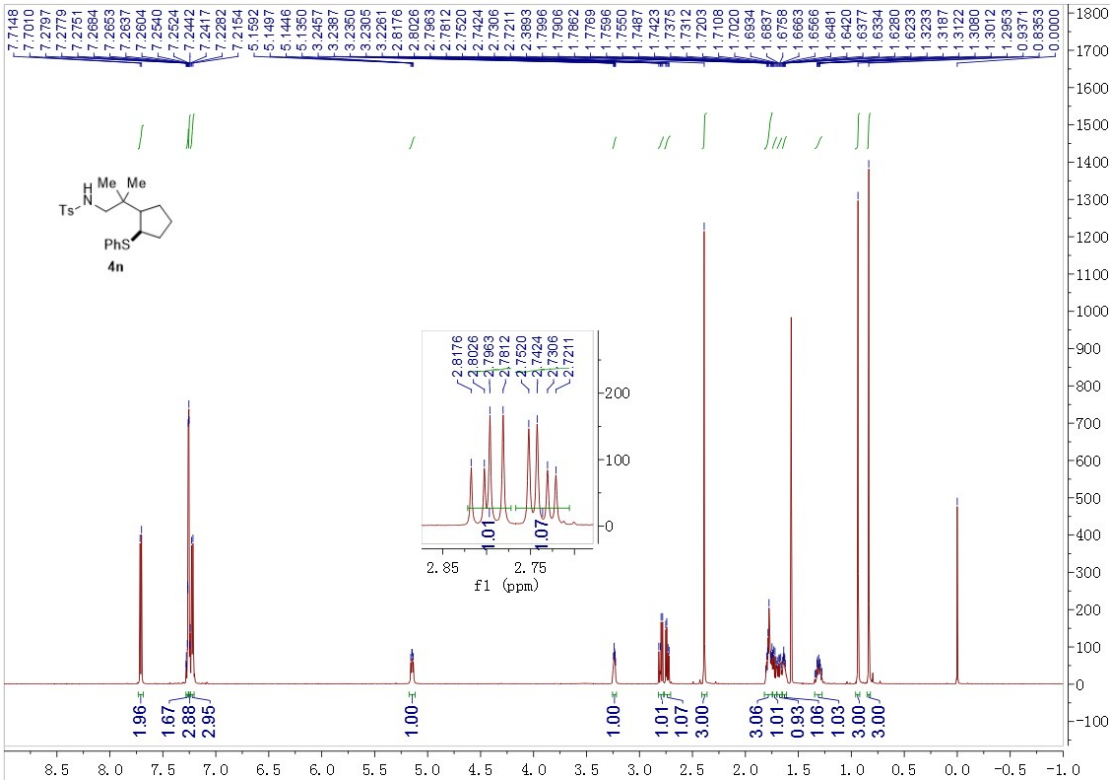
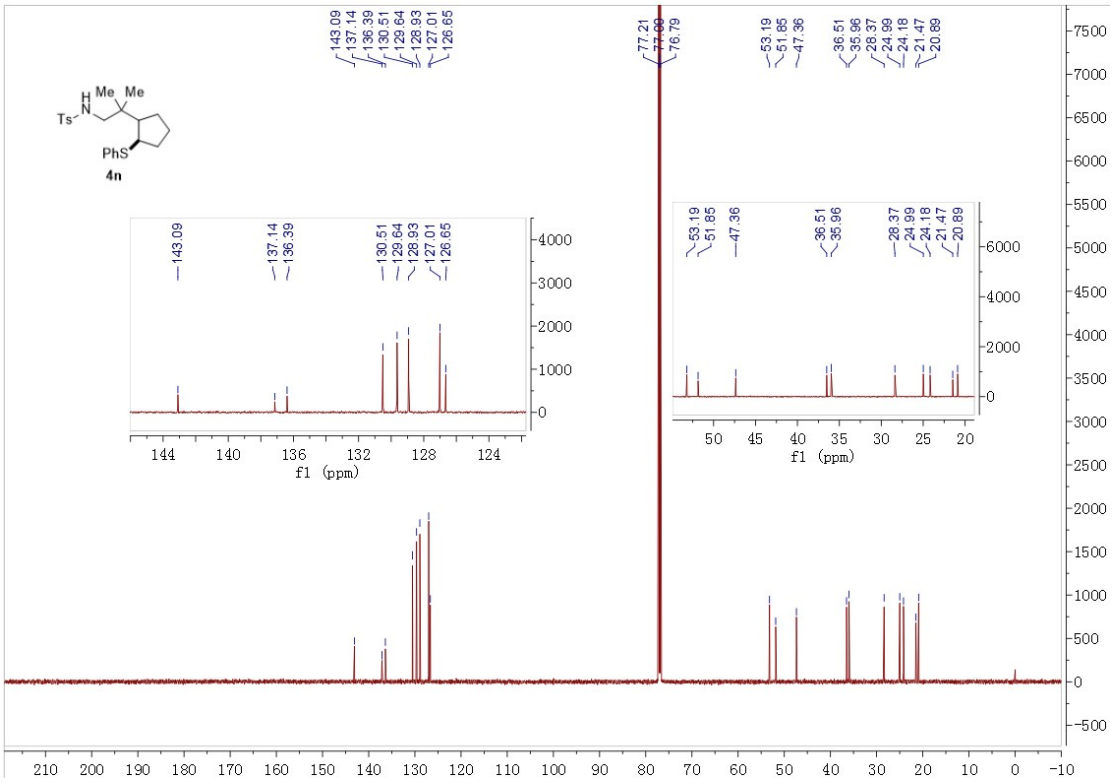
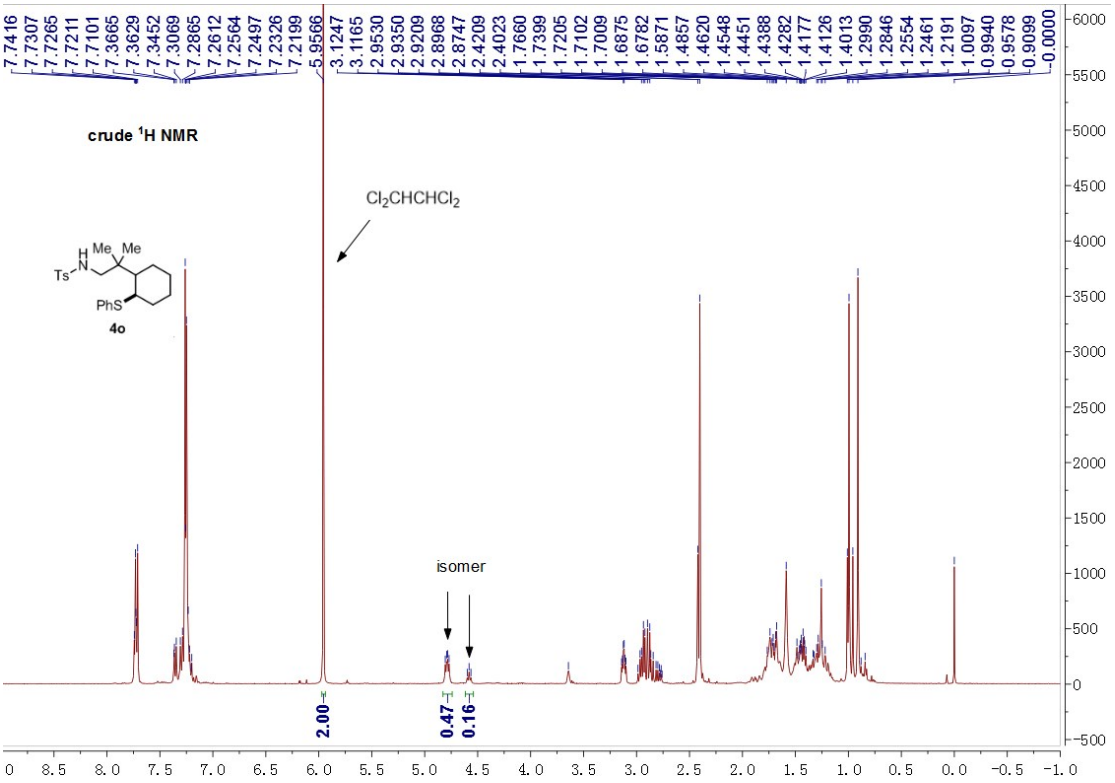
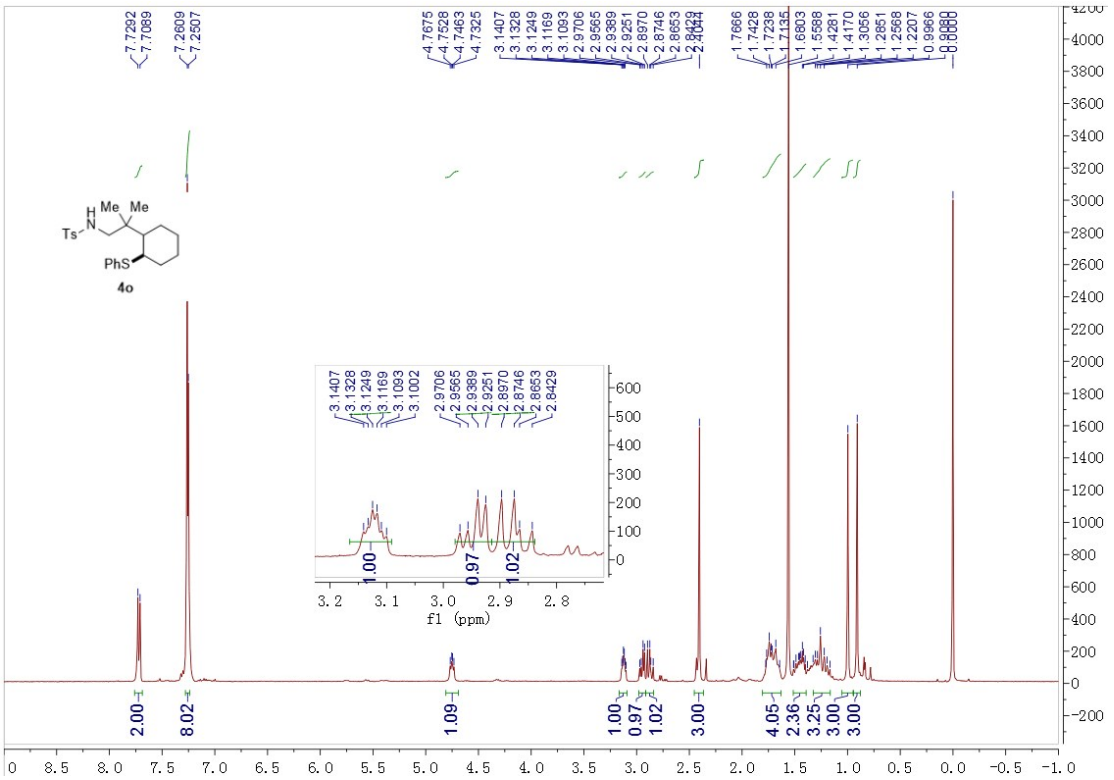
2.1948
2.1791
2.1637
1.8634
1.8465
1.8024
1.7875
1.6633
1.6469
1.6311
Me
Me
Ts
N
H
PhS
4m
1.00
1.03
2.00
3.00
1.07
1.09
1.08
1.06
1.15

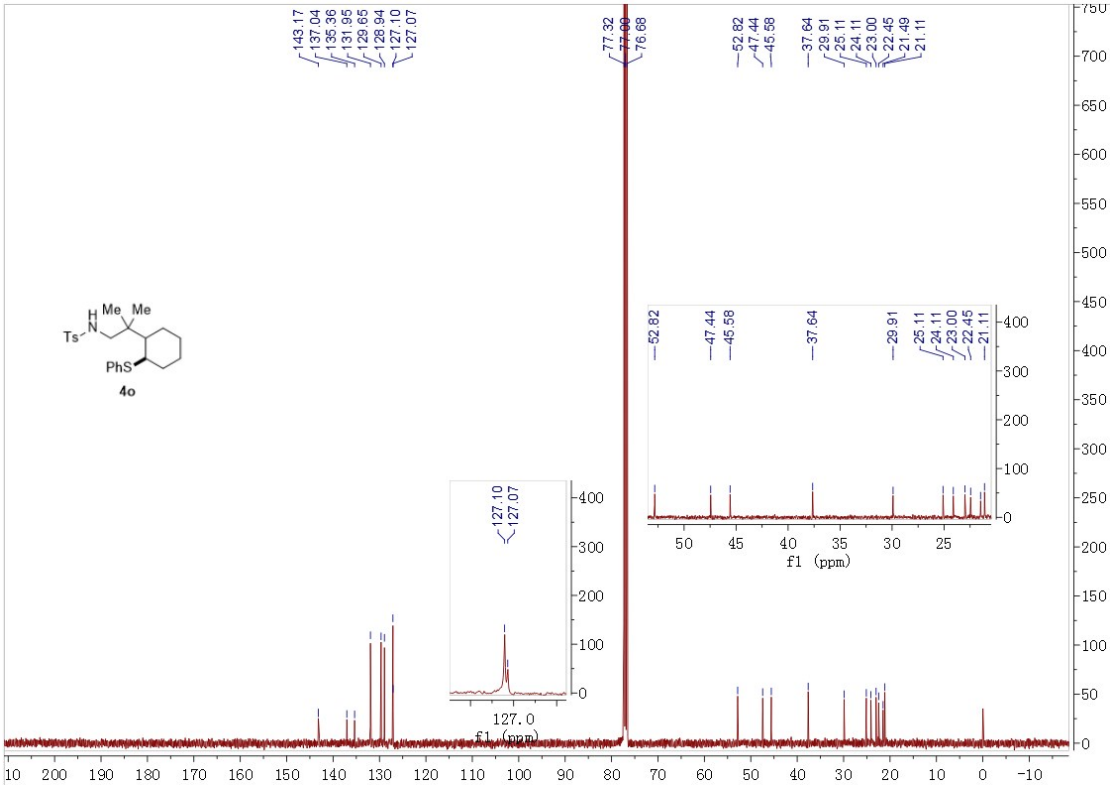

143.14
137.22
134.98
131.01
129.65
128.94
127.03
126.86
77.21
77.00
76.79
52.49
50.38
42.11
35.29
28.06
22.82
21.49
21.06
19.54
Me Me
Ts
N
H
PhS
4m
f1 (ppm)

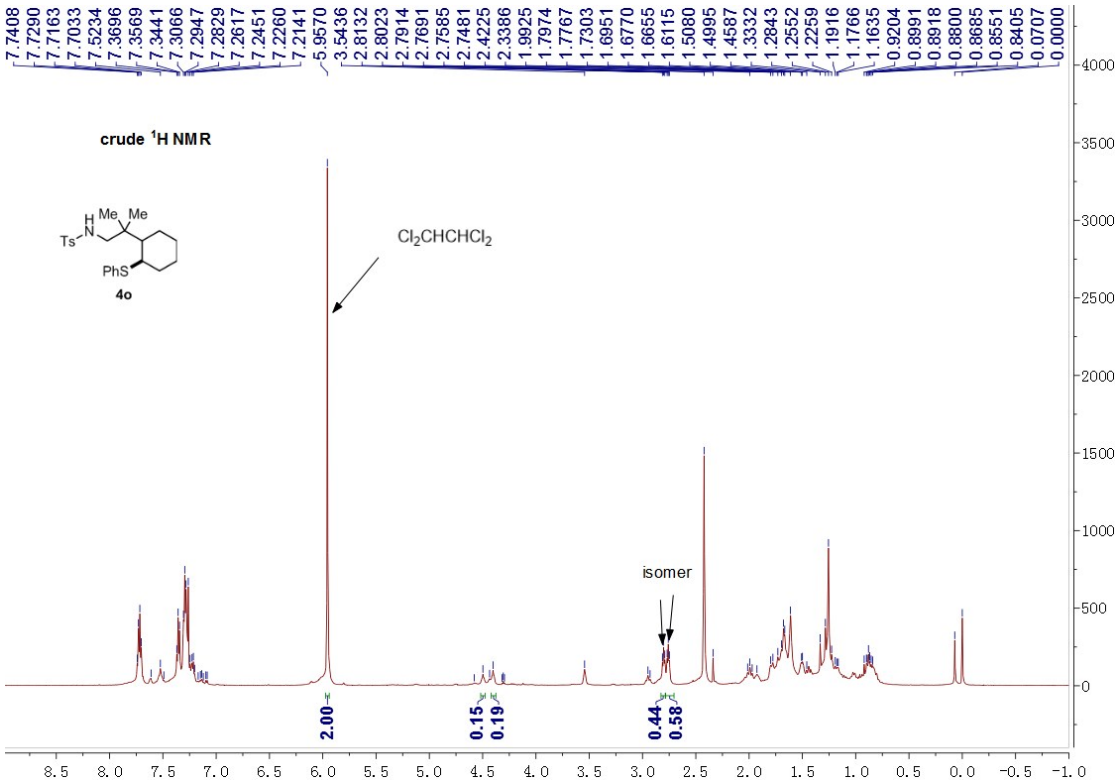

Me Me
Ts
N
H
PhS
4n
f1 (ppm)
1.96
1.67
2.88
2.95
1.00
1.00
1.01
1.07
3.00
3.06
1.01
0.93
1.06
1.03
3.00
3.00

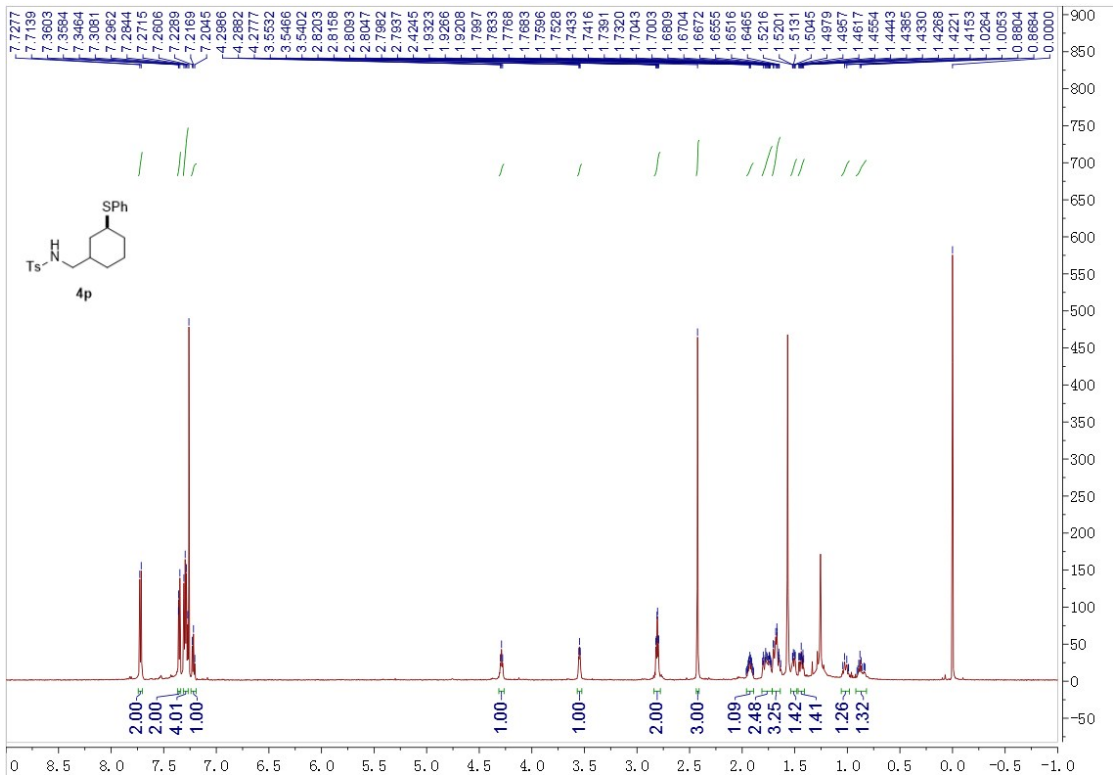

4n
f1 (ppm)
f1 (ppm)

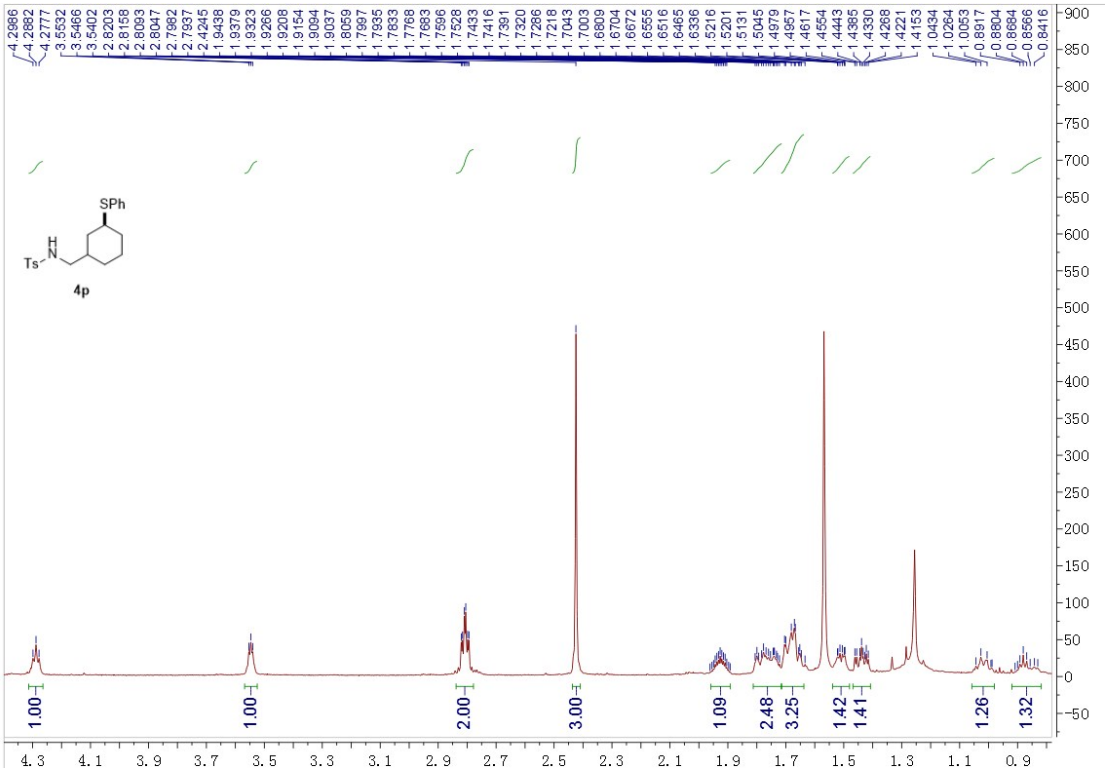

crude ^{1}H NMR
$Cl_2CHCHCl_2$
4o
isomer
2.00
0.47
0.16

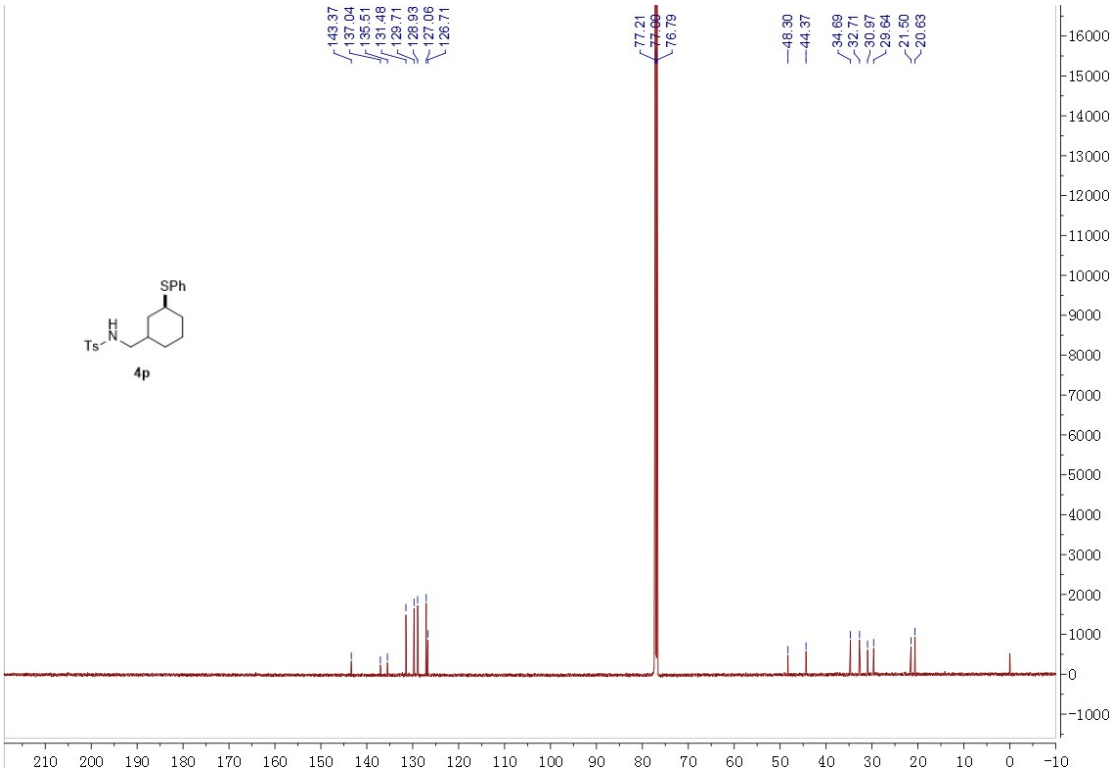

4o
f1 (ppm)


4o
f1 (ppm)
f1 (ppm)


crude ^{1}H NMR
Me
Me
H
N
Ts
PhS
4o
$Cl_2CHCHCl_2$
isomer
2.00
0.15
0.19
0.44
0.58


SPh
H
N
Ts
4p
2.00
2.00
4.01
1.00
1.00
1.00
2.00
3.00
1.09
2.48
3.25
1.42
1.41
1.26
1.32


SPh
Ts
H
N
4p
1.00
1.00
2.00
3.00
1.09
2.48
3.25
1.42
1.41
1.26
1.32


SPh
Ts
H
N
4p
143.37
137.04
135.51
131.48
129.71
128.93
127.06
126.71
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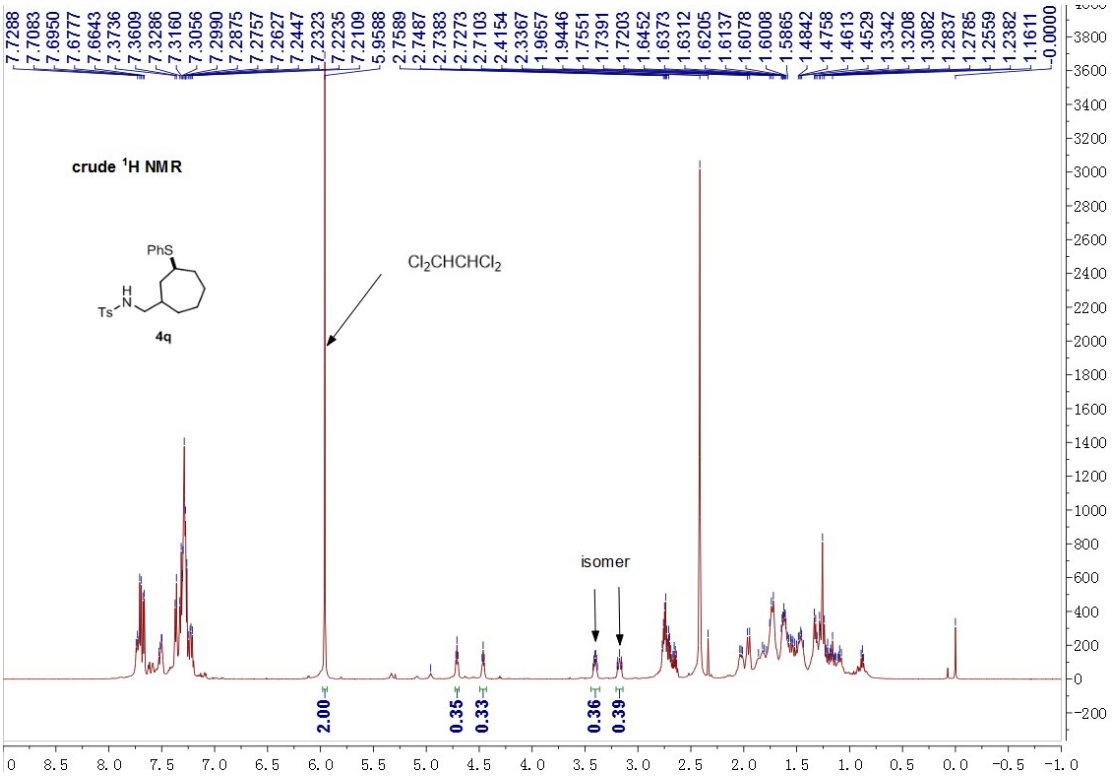
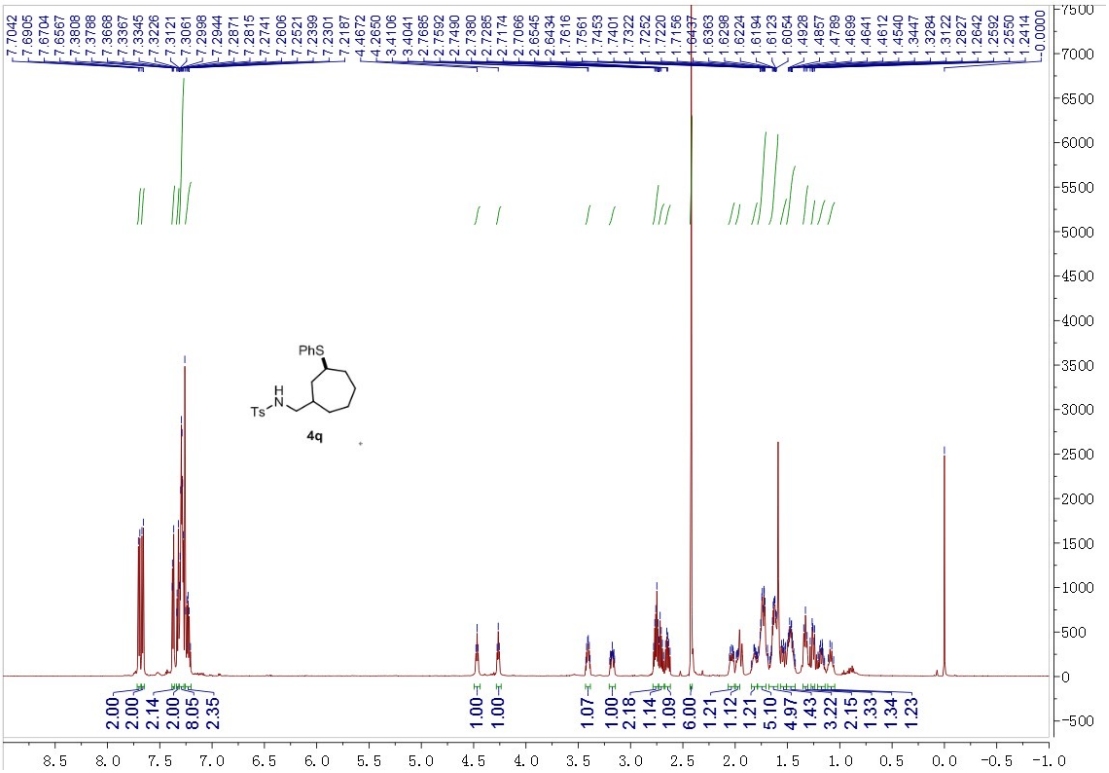
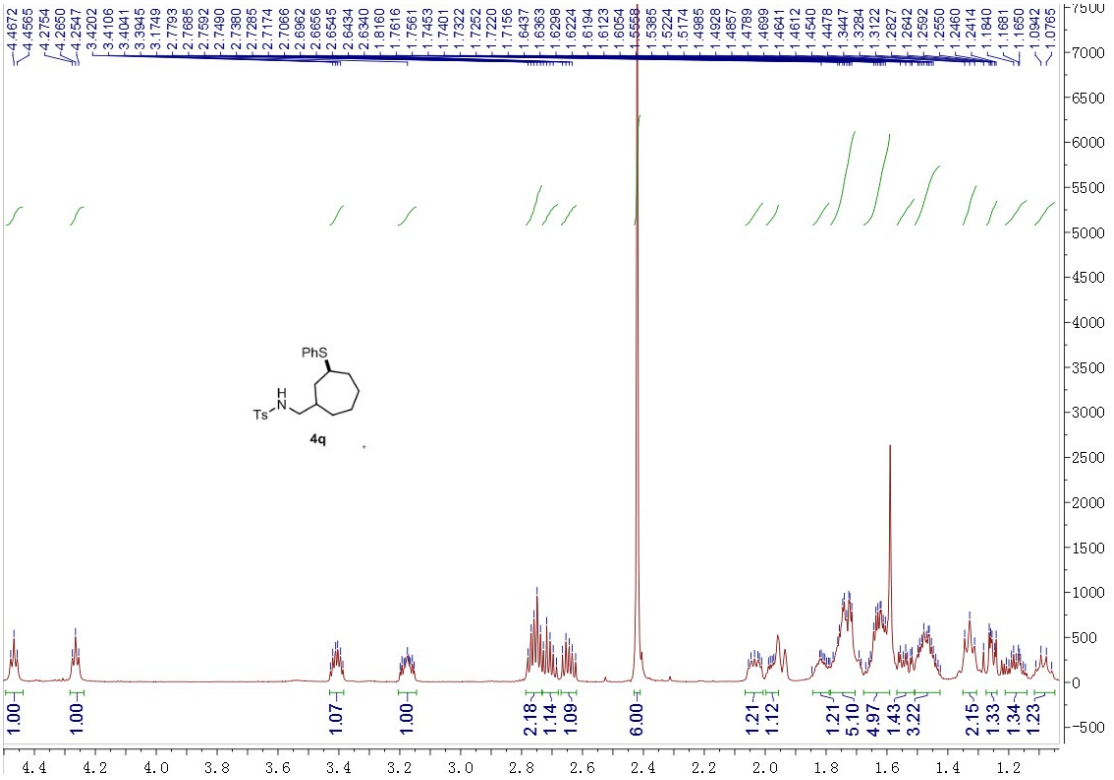
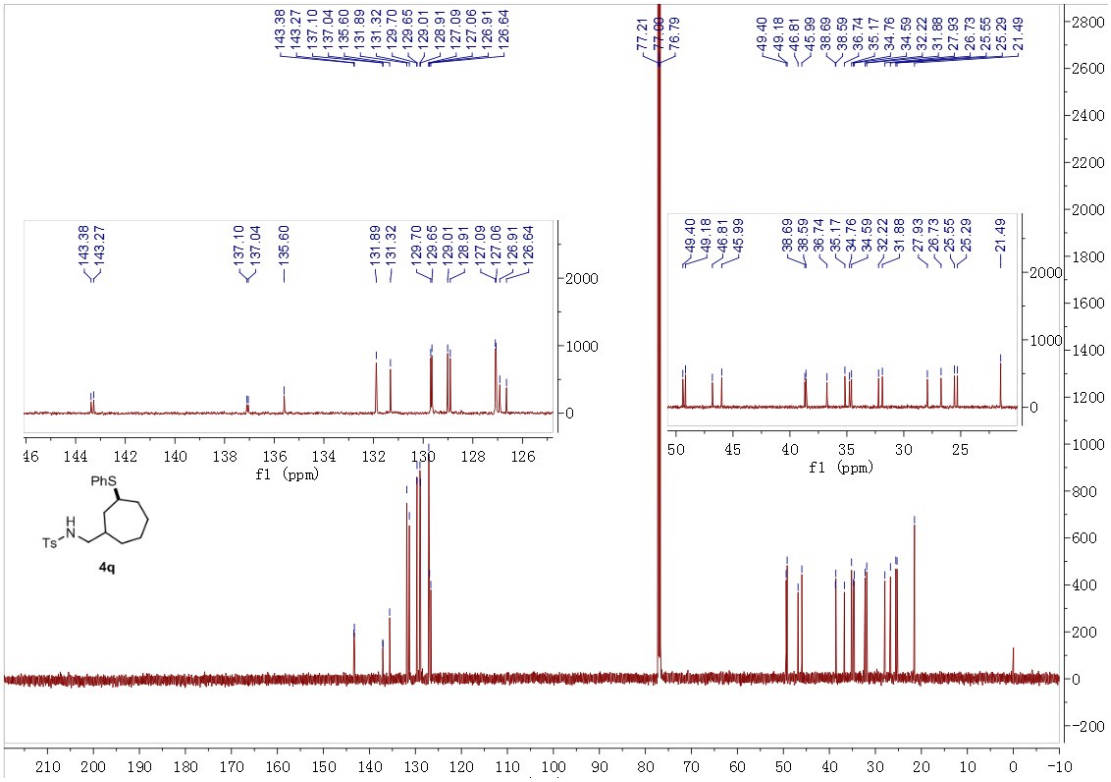
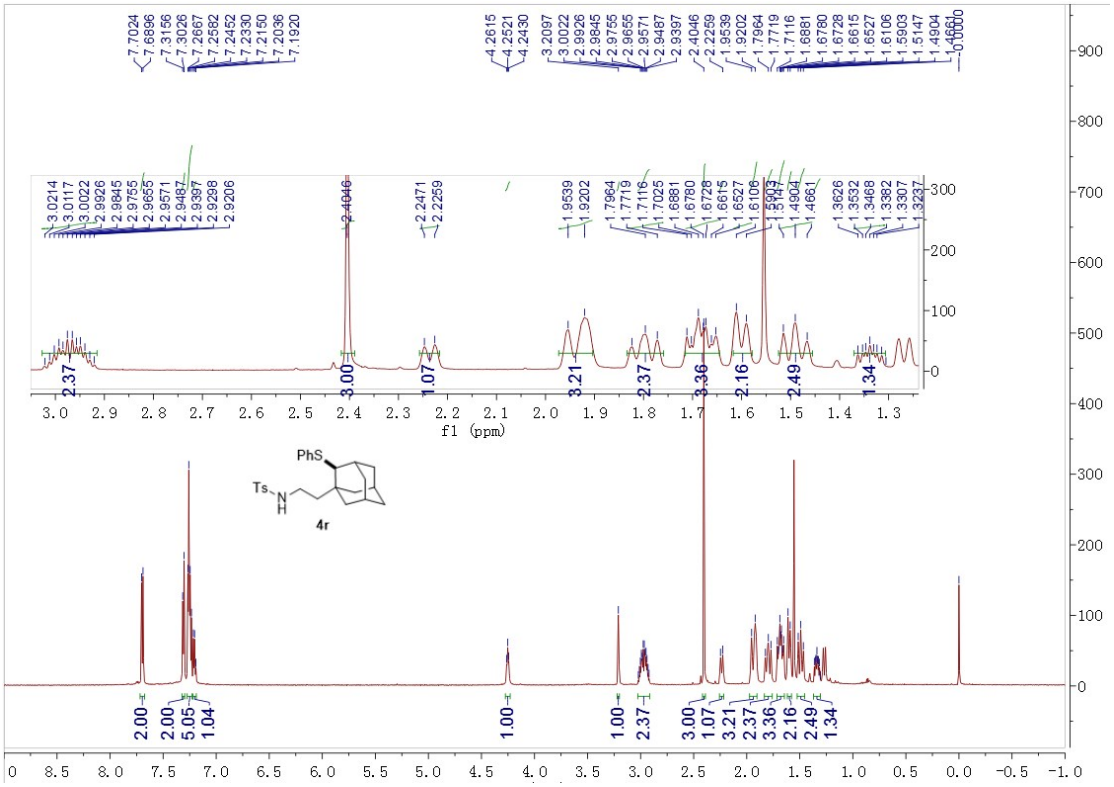
77.00
76.79
48.30
44.37
34.69
32.71
30.97
29.64
21.50
20.63

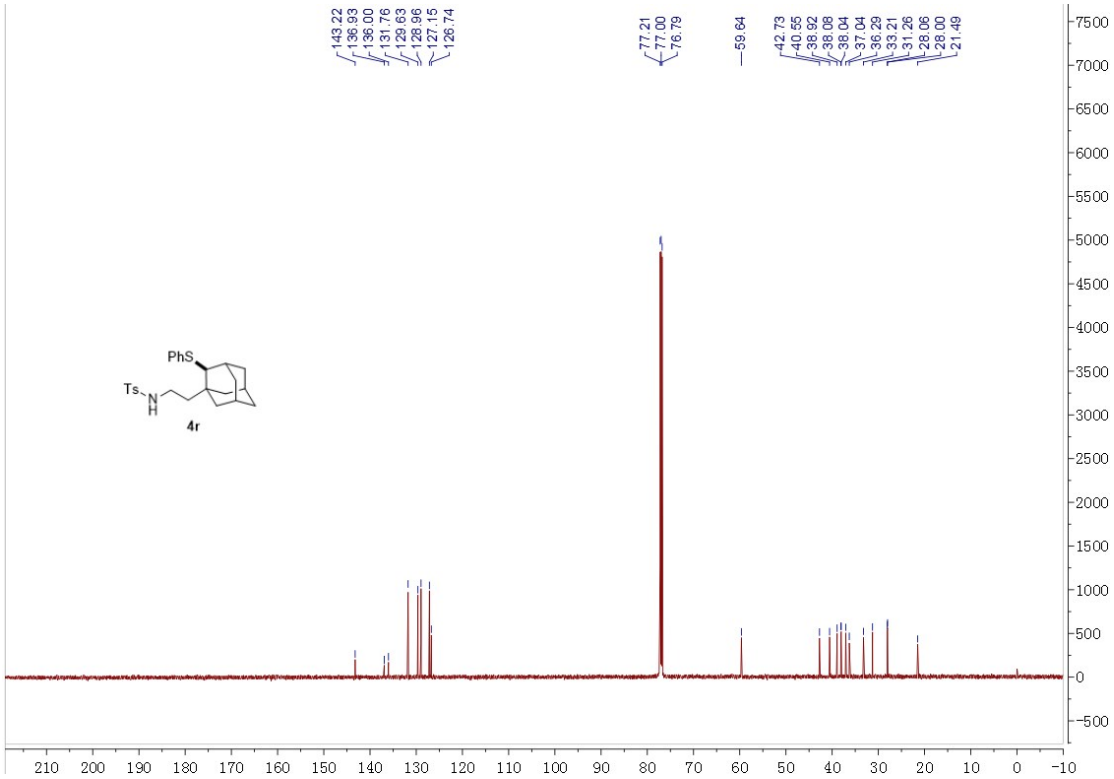

crude ^{1}H NMR
PhS
Ts
H
N
4q
$Cl_2CHCHCl_2$
isomer
2.00
0.35
0.33
0.36
0.39

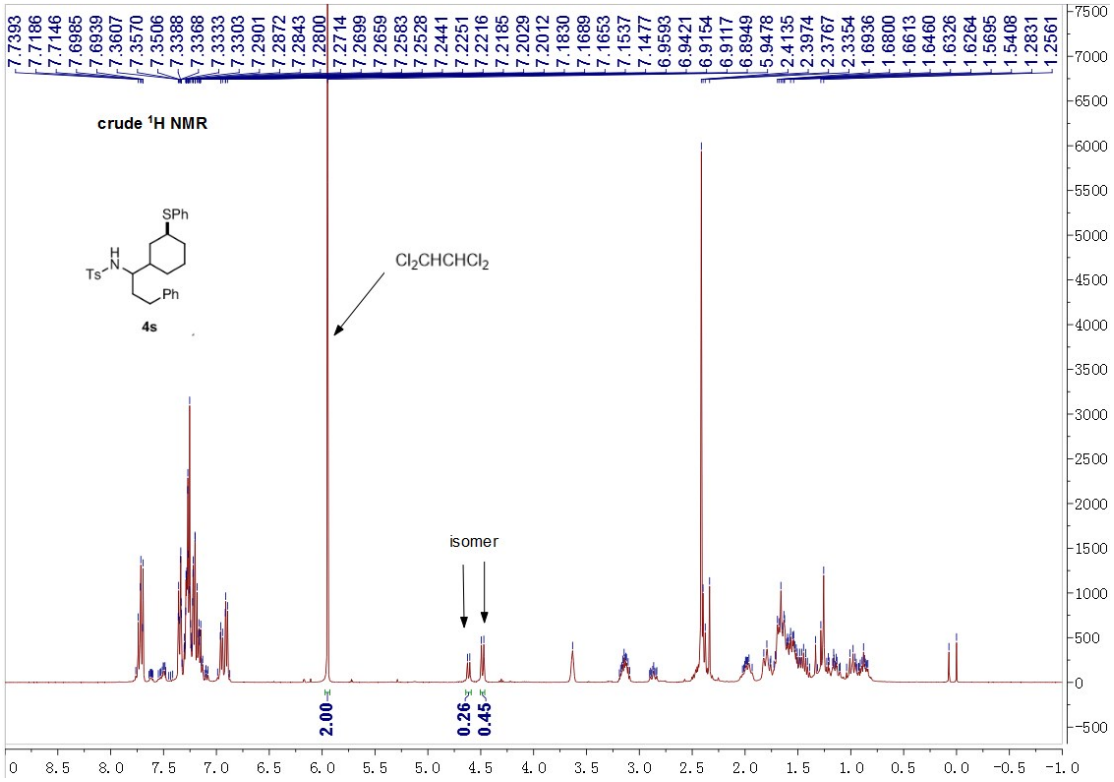

PhS
Ts
H
N
4q
2.00
2.00
2.14
2.00
8.05
2.35
1.00
1.00
1.07
1.00
2.18
1.14
1.09
6.00
1.21
1.12
1.21
5.10
4.97
1.43
3.22
2.15
1.33
1.34
1.23

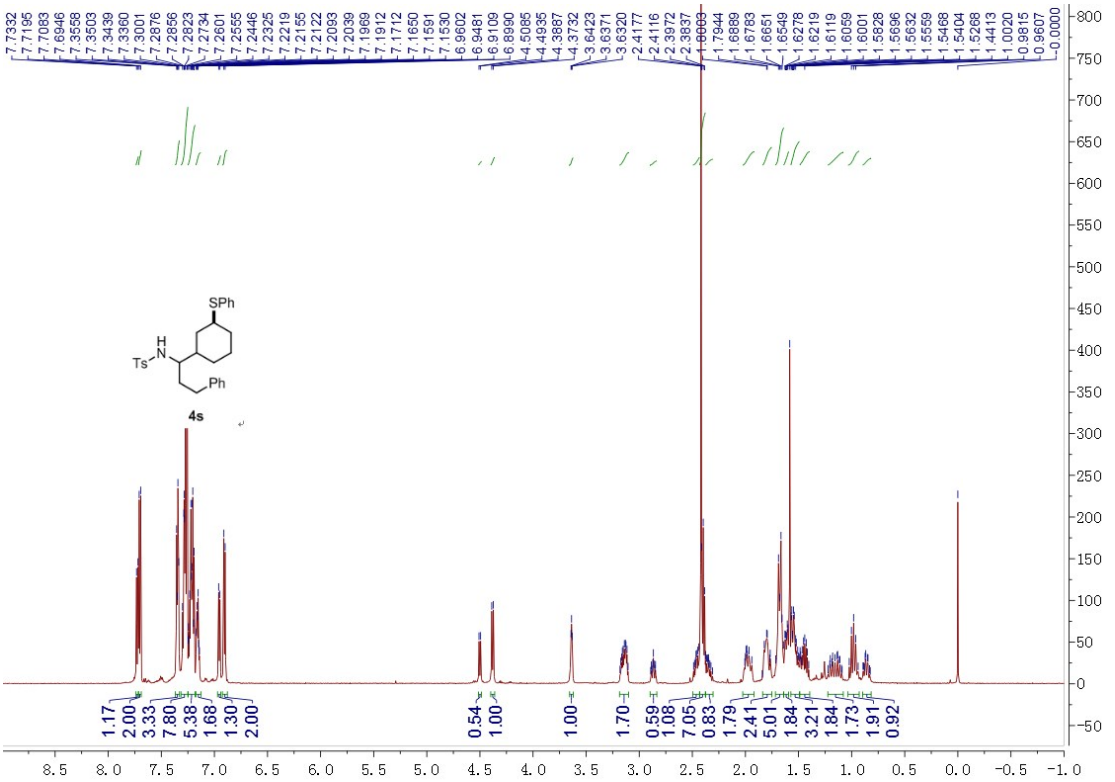

PhS
H
N
Ts
4q

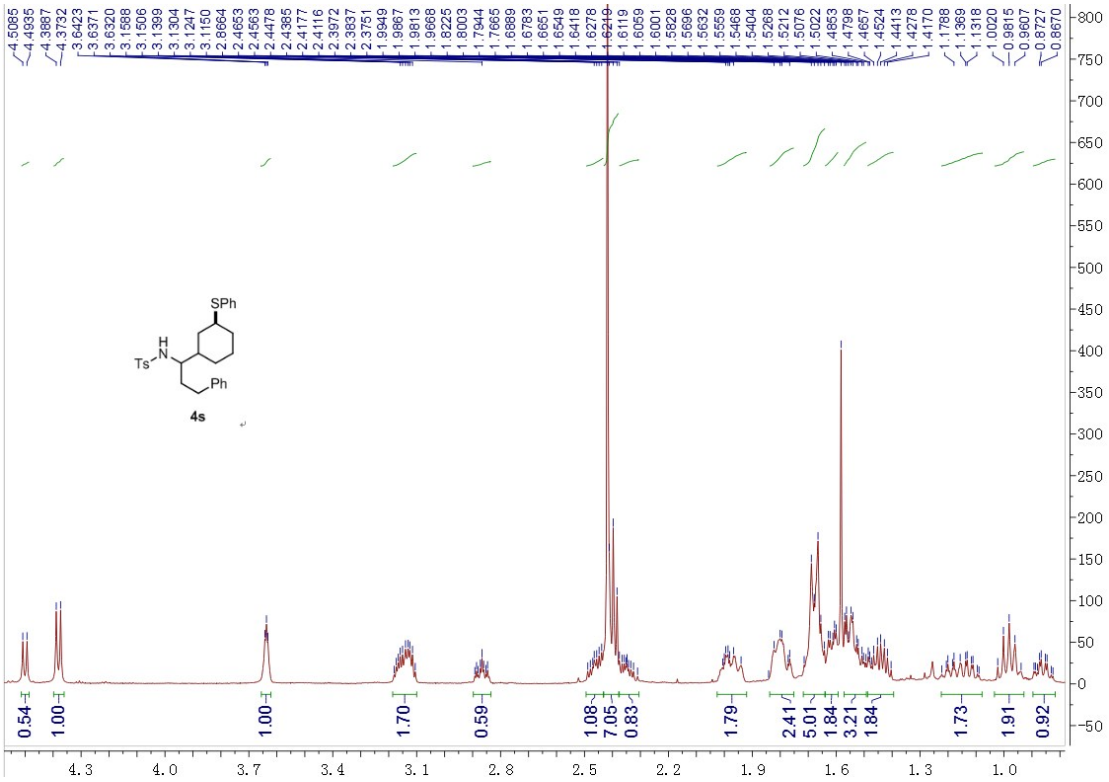

PhS
H
N
Ts
4q
f1 (ppm)
f1 (ppm)

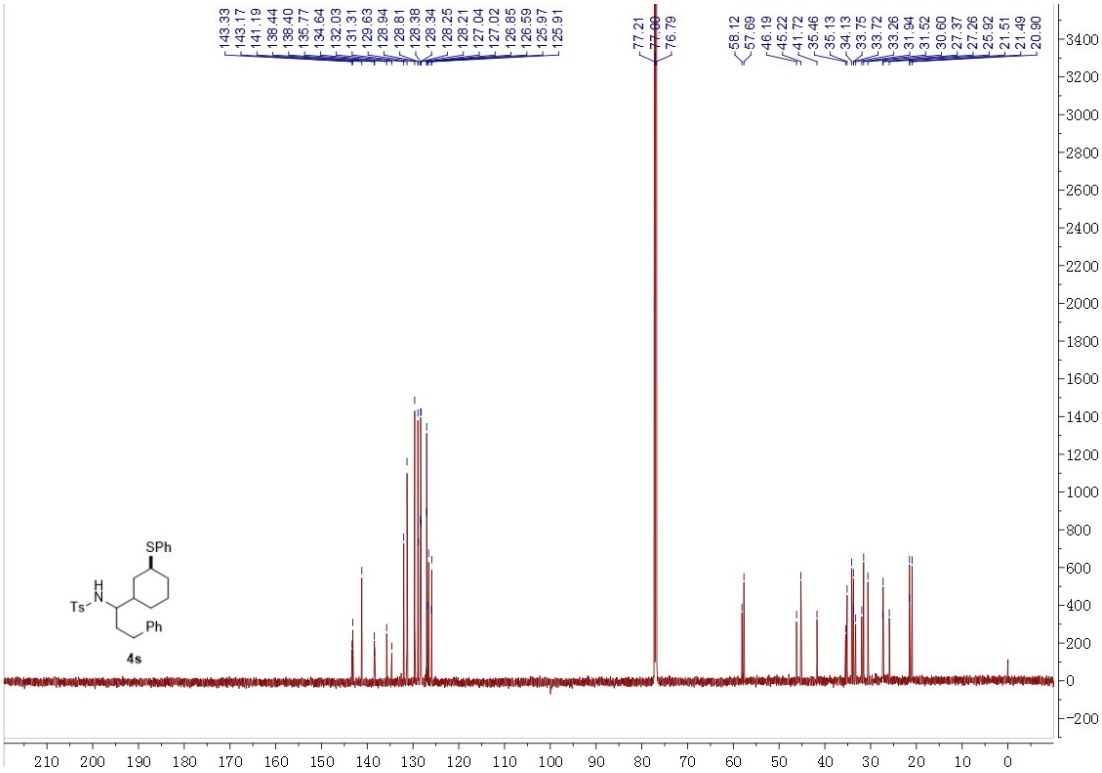

PhS
Ts
N
H
4r
f1 (ppm)

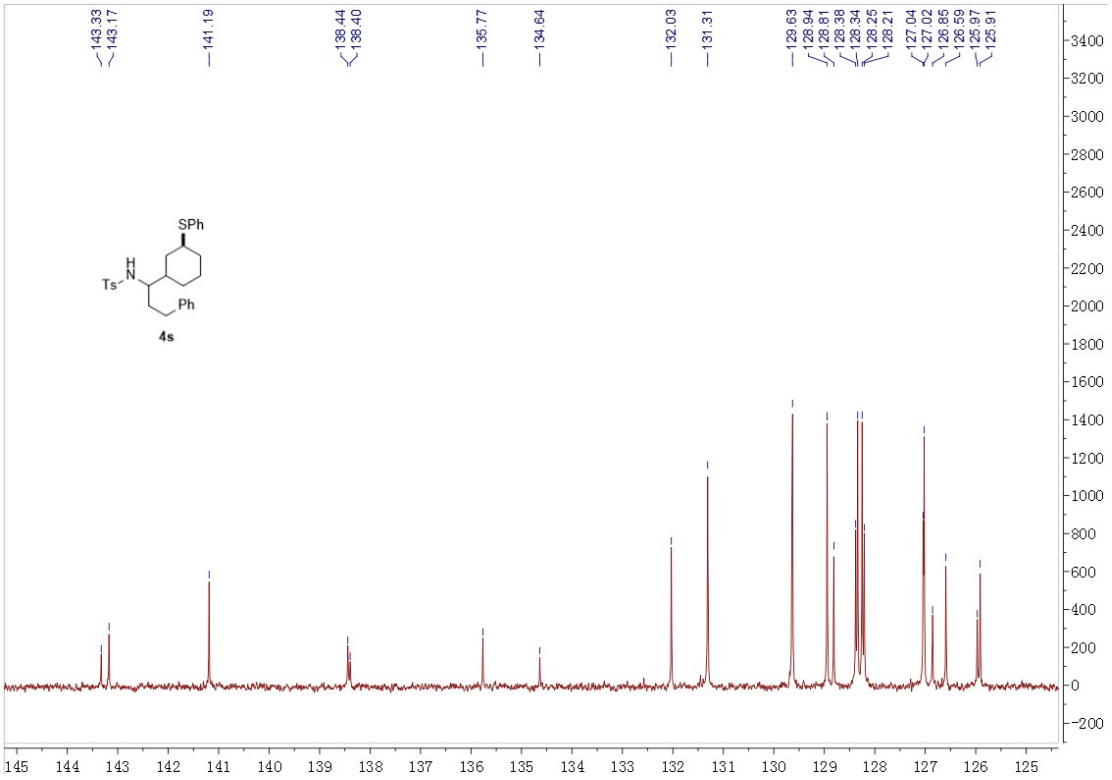

PhS
Ts
N
H
4r

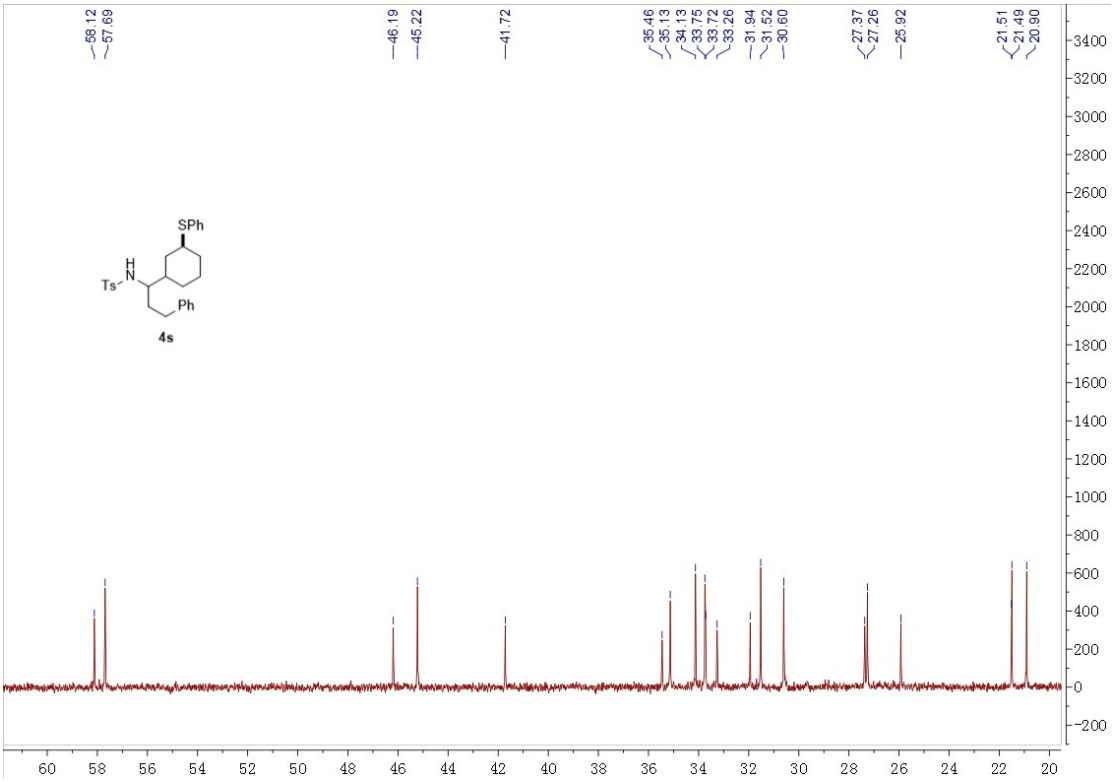

crude ^{1}H NMR
SPh
Ts
N
H
Ph
4s
$Cl_2CHCHCl_2$
isomer
2.00
0.26
0.45

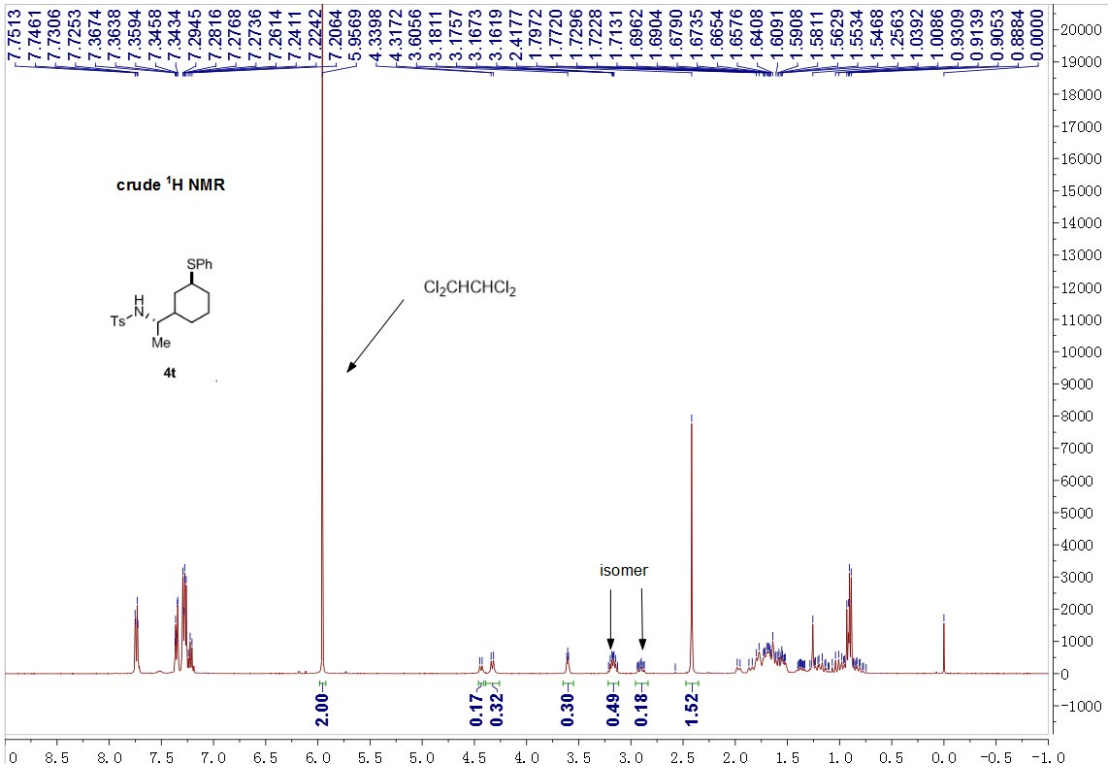

SPh
Ts
N
H
Ph
4s
1.17
2.00
3.33
7.80
5.38
1.68
1.30
2.00
0.54
1.00
1.00
1.70
0.59
1.08
7.05
0.83
1.79
2.41
5.01
1.84
3.21
1.84
1.73
1.91
0.92

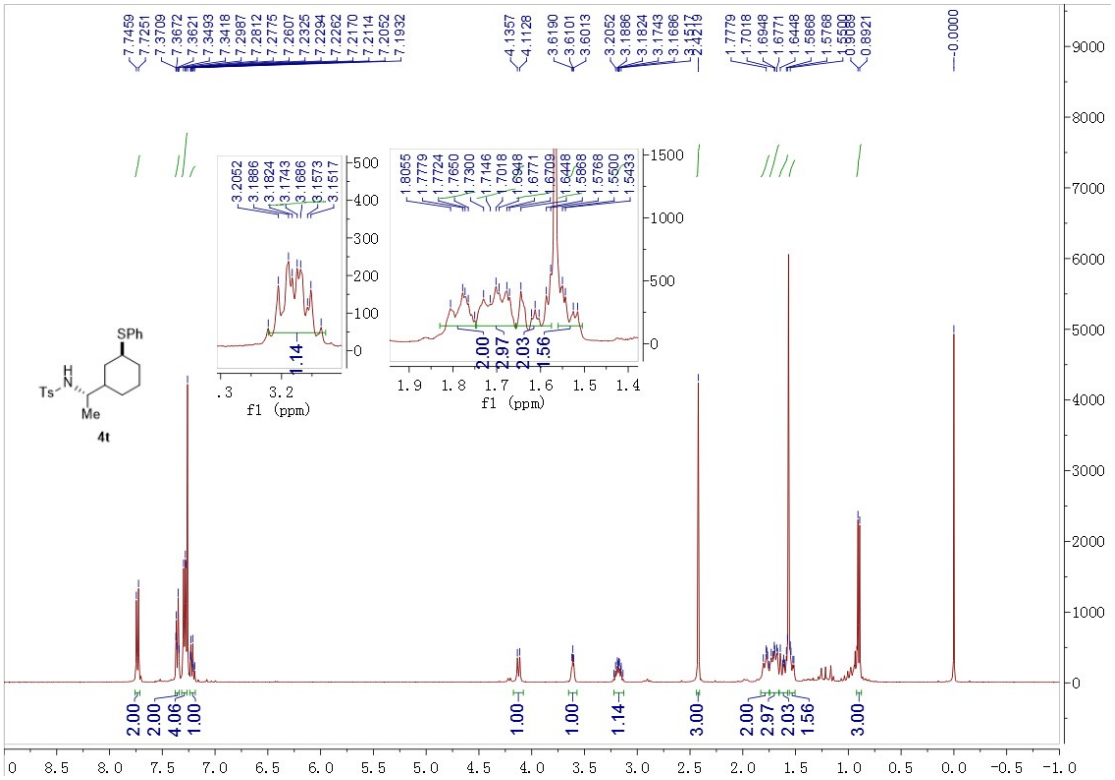

SPh
H
N
Ts
Ph
4s

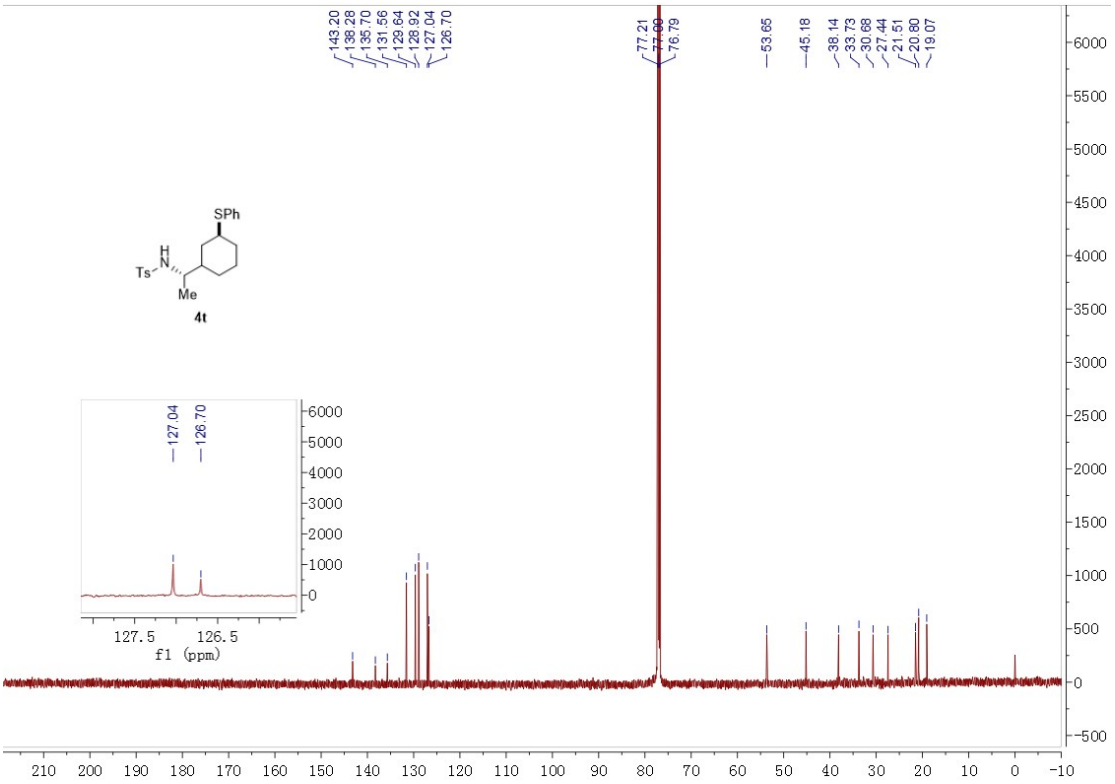

SPh
H
N
Ts
Ph
4s

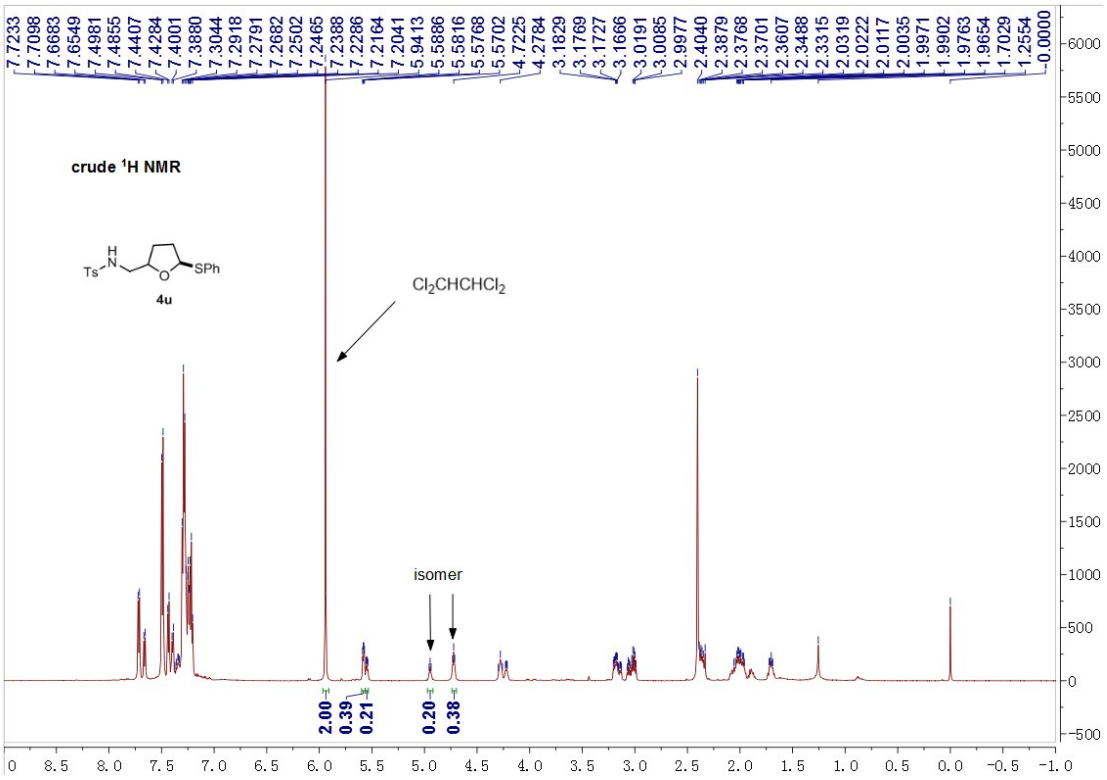

143.33
143.17
141.19
138.44
138.40
135.77
134.64
132.03
131.31
129.63
128.94
128.81
128.38
128.34
128.25
128.21
127.04
127.02
126.85
126.59
125.97
125.91
SPh
Ts
N
H
Ph
4s

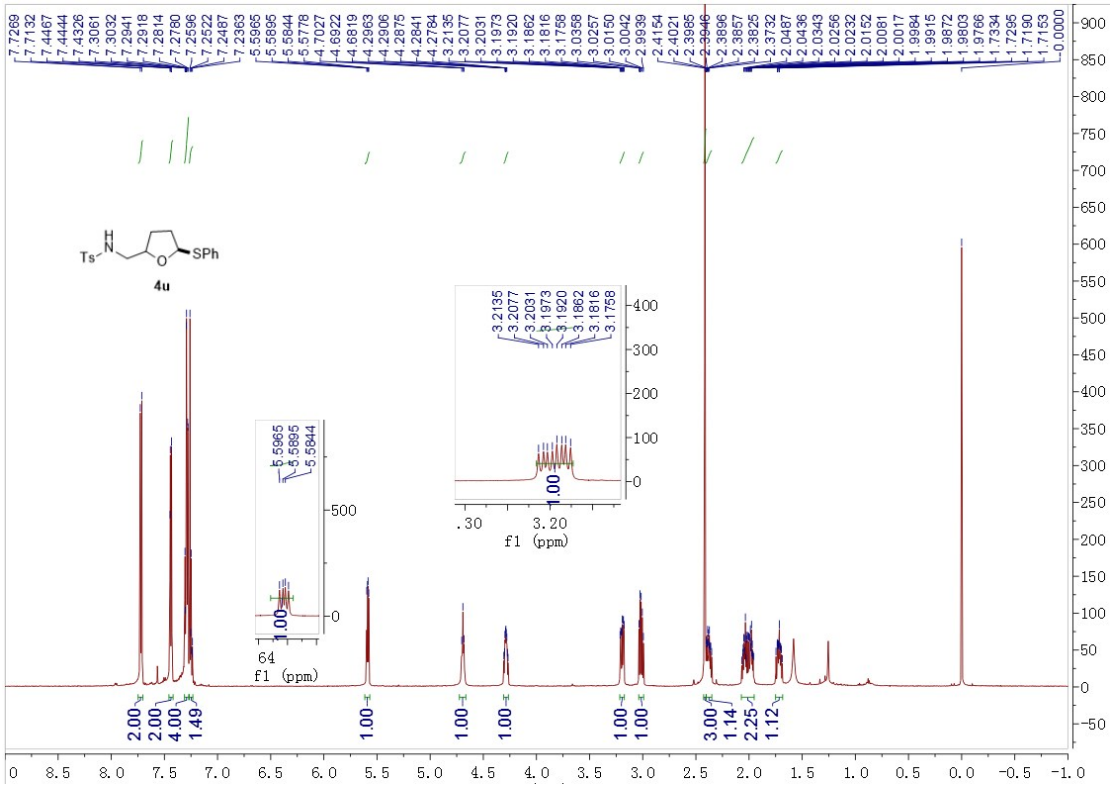

58.12
57.69
46.19
45.22
41.72
35.46
35.13
34.13
33.75
33.72
33.26
31.94
31.52
30.60
27.37
27.26
25.92
21.51
21.49
20.90
SPh
Ts
N
H
Ph
4s

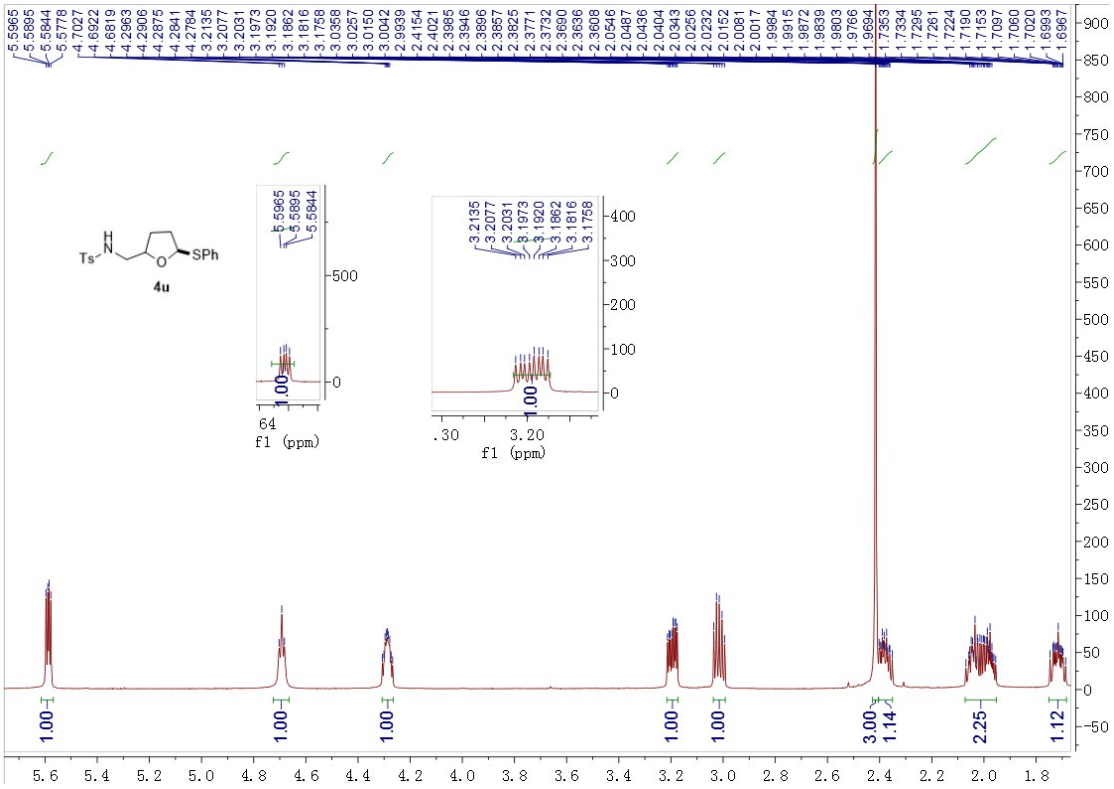

crude ^{1}H NMR
SPh
Ts
N
H
Me
4t
$Cl_2CHCHCl_2$
isomer
2.00
0.17
0.32
0.30
0.49
0.18
1.52

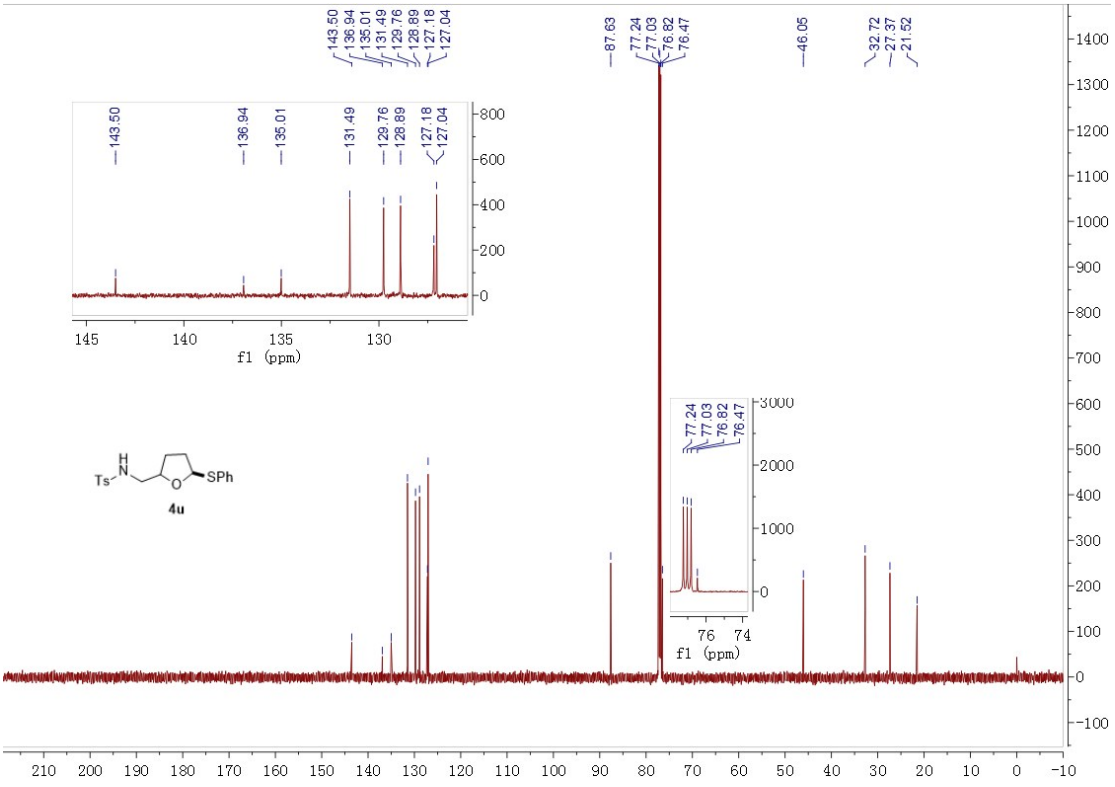

SPh
Ts
N
H
Me
4t
f1 (ppm)
2.00
2.00
4.06
1.00
1.00
1.00
1.14
3.00
2.00
2.97
2.03
1.56
3.00


143.20
138.28
135.70
131.56
129.64
128.92
127.04
126.70
77.21
77.00
76.79
53.65
45.18
38.14
33.73
30.68
27.44
21.51
20.80
19.07
SPh
H
N
Ts
Me
4t
127.04
126.70
127.5
126.5
f1 (ppm)


crude ¹H NMR
SPh
4u
Cl2CHCHCl2
isomer
2.00
0.39
0.21
0.20
0.38


4u
Ts
SPh
f1 (ppm)


4u
Ts
SPh
f1 (ppm)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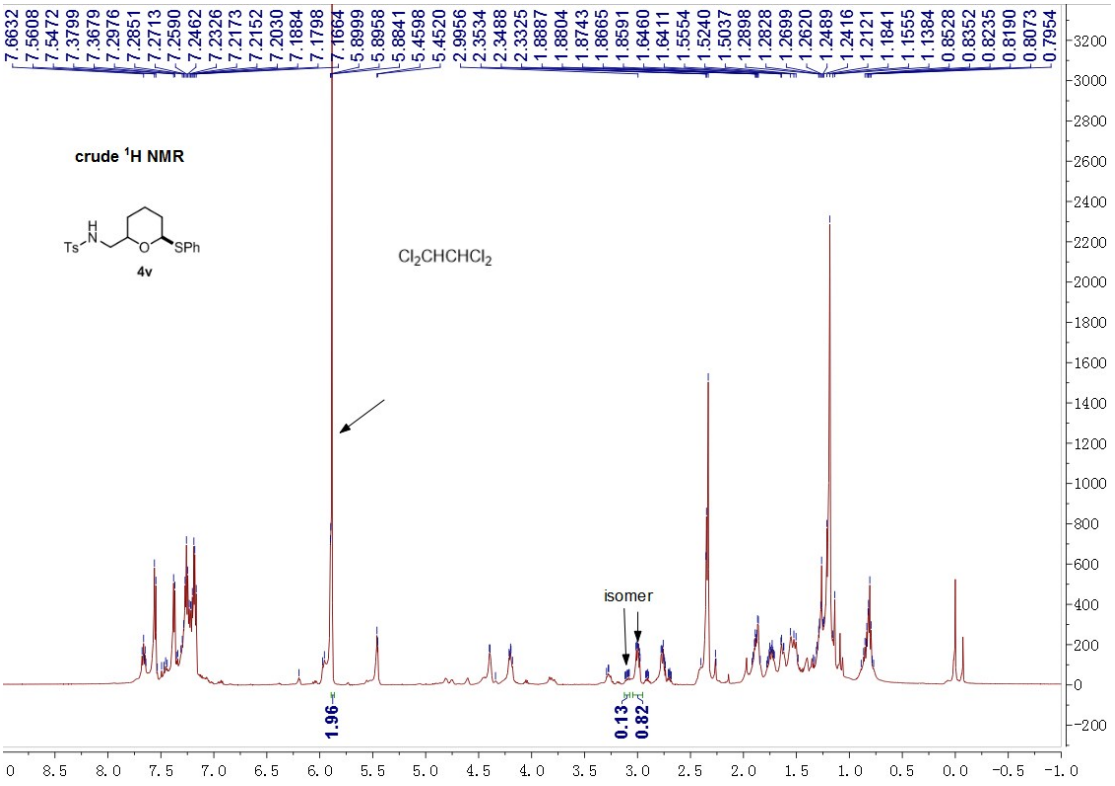
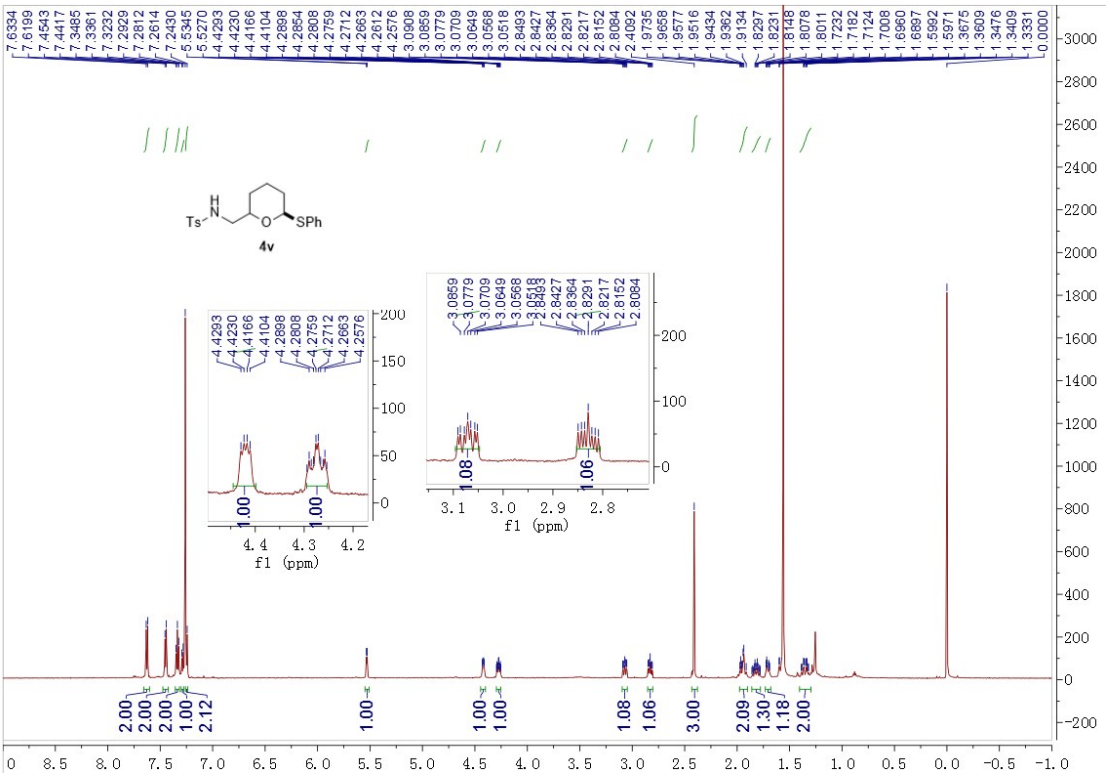
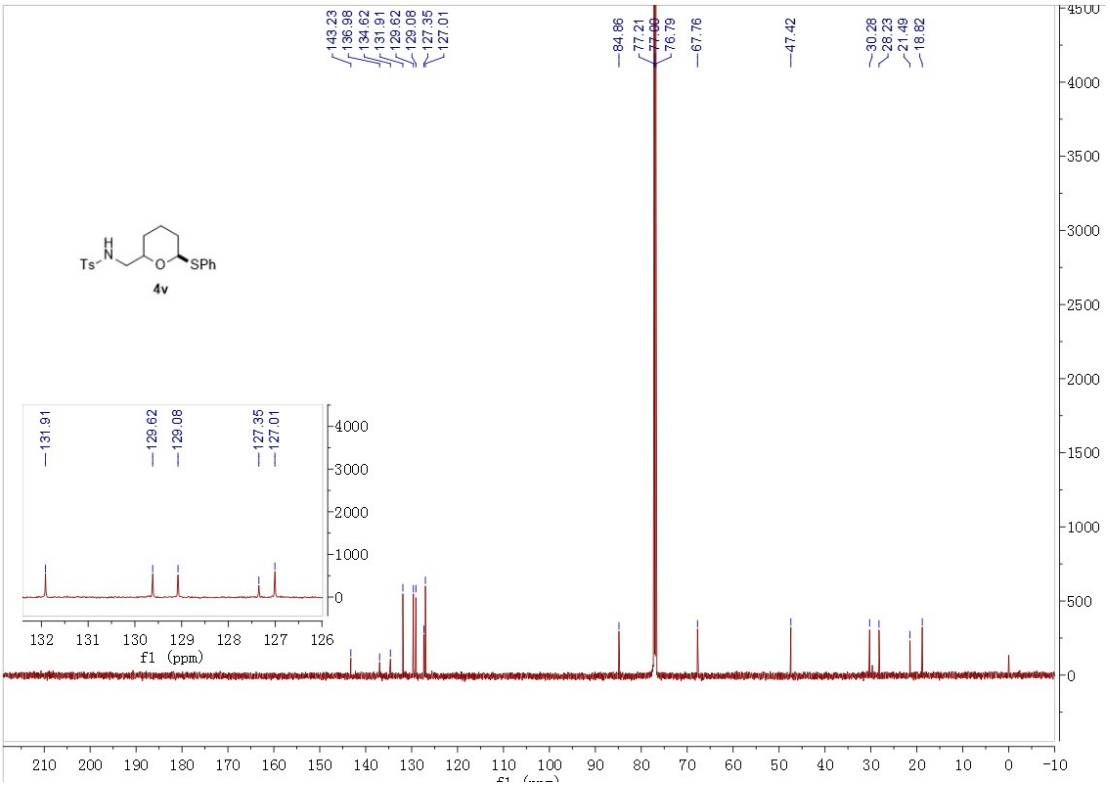
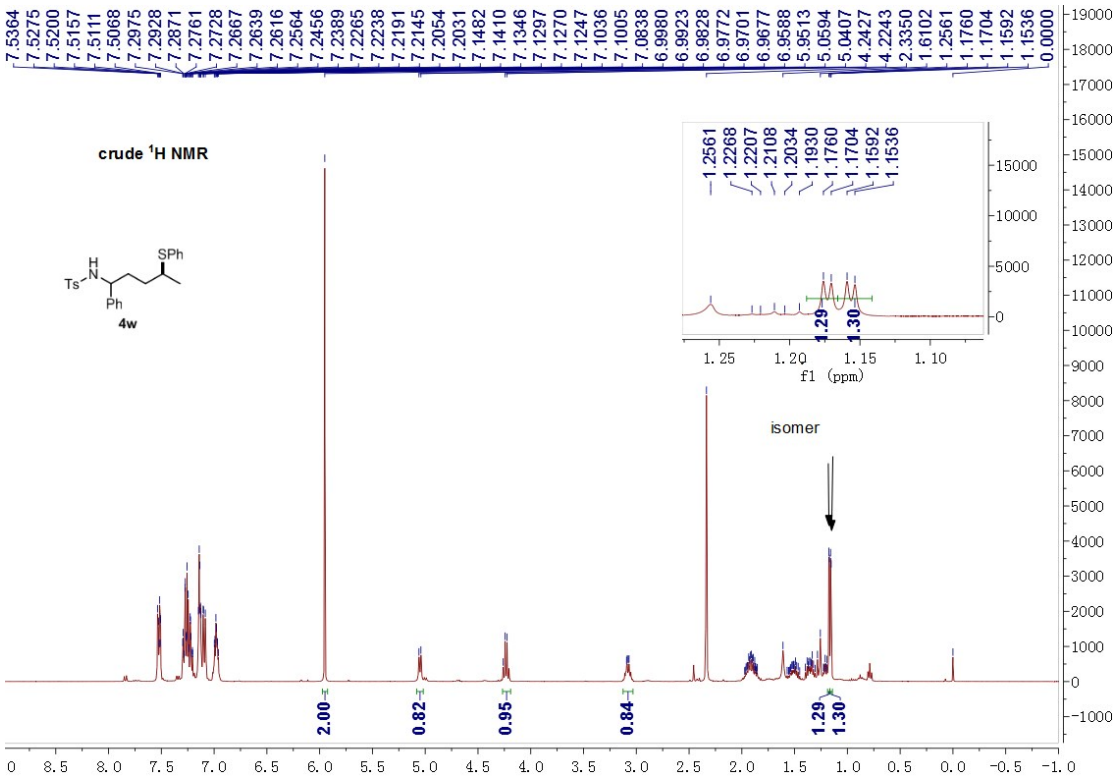
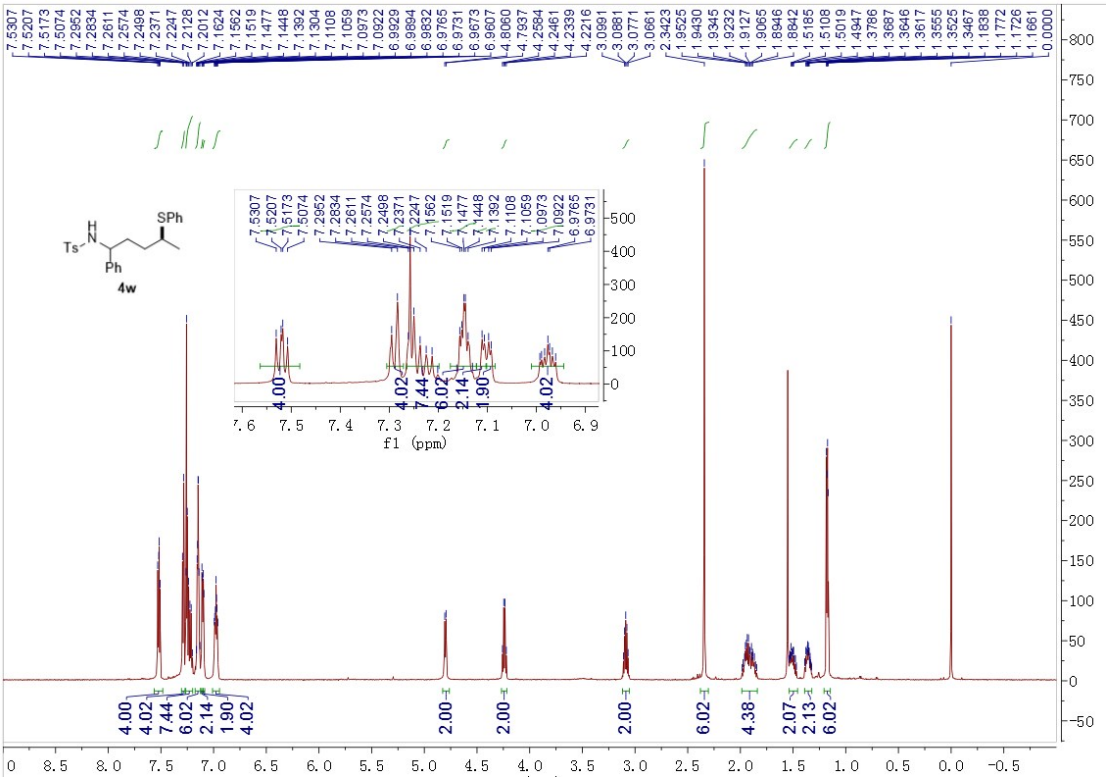
136.94
135.01
131.49
129.76
128.89
127.18
127.04
87.63
77.24
77.03
76.82
76.47
46.05
32.72
27.37
21.52
f1 (ppm)
Ts
SPh
4u

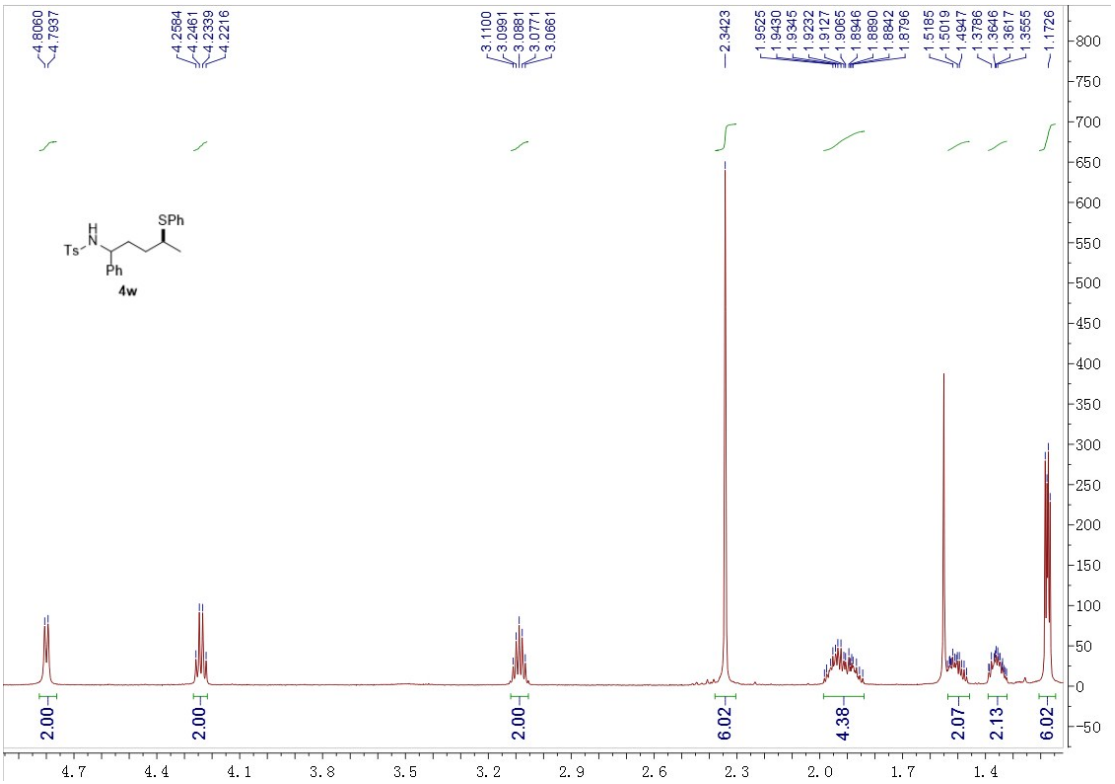

crude ¹H NMR
Ts
SPh
4v
Cl2CHCHCl2
isomer
1.96
0.13
0.82


4v
f1 (ppm)


4v
f1 (ppm)


crude ¹H NMR
4w
isomer
2.00
0.82
0.95
0.84
1.29
1.30
f1 (ppm)


4w
4.00
4.02
7.44
6.02
2.14
1.90
4.02
2.00
2.00
2.00
6.02
4.38
2.07
2.13
6.02
f1 (ppm)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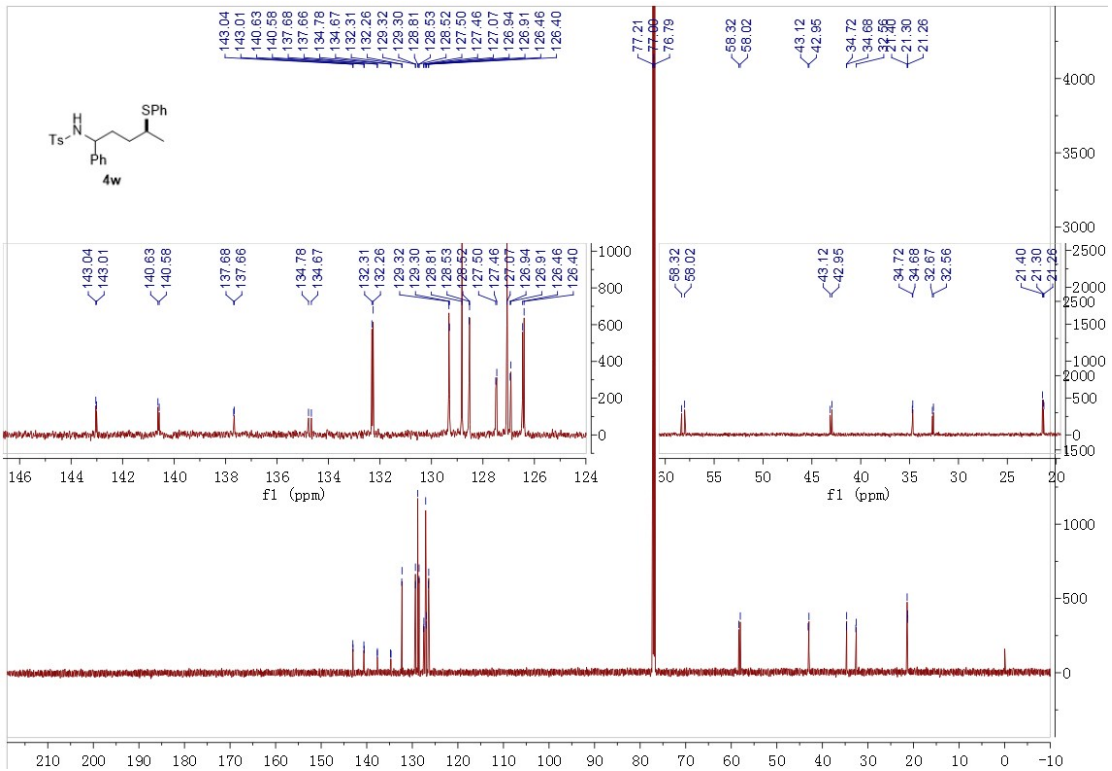
3.0771
3.0661
2.3423
1.9525
1.9430
1.9345
1.9232
1.9127
1.9065
1.8946
1.8890
1.8842
1.8796
1.5185
1.5019
1.4947
1.3786
1.3646
1.3617
1.3555
1.1726
SPh
Ts
N
H
Ph
4w
2.00
2.00
2.00
6.02
4.38
2.07
2.13
6.02


143.04
143.01
140.63
140.58
137.68
137.66
134.78
134.67
132.31
132.26
129.32
129.30
128.81
128.53
128.52
127.50
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127.07
126.94
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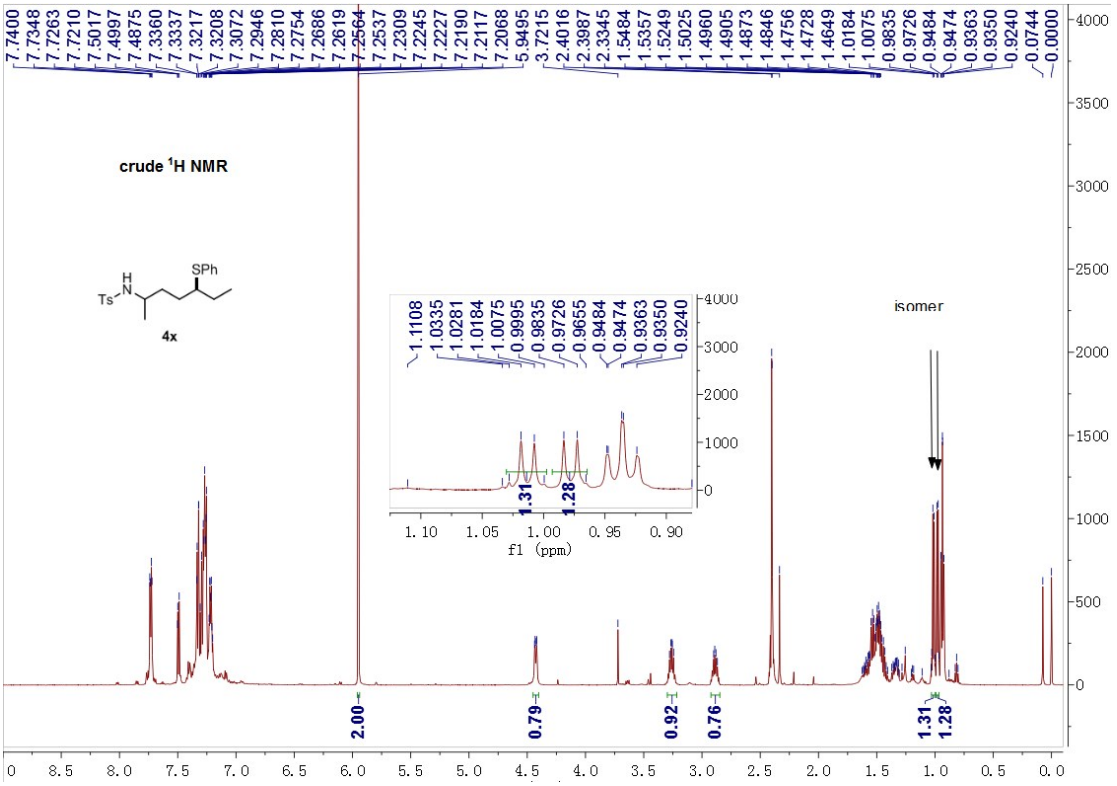
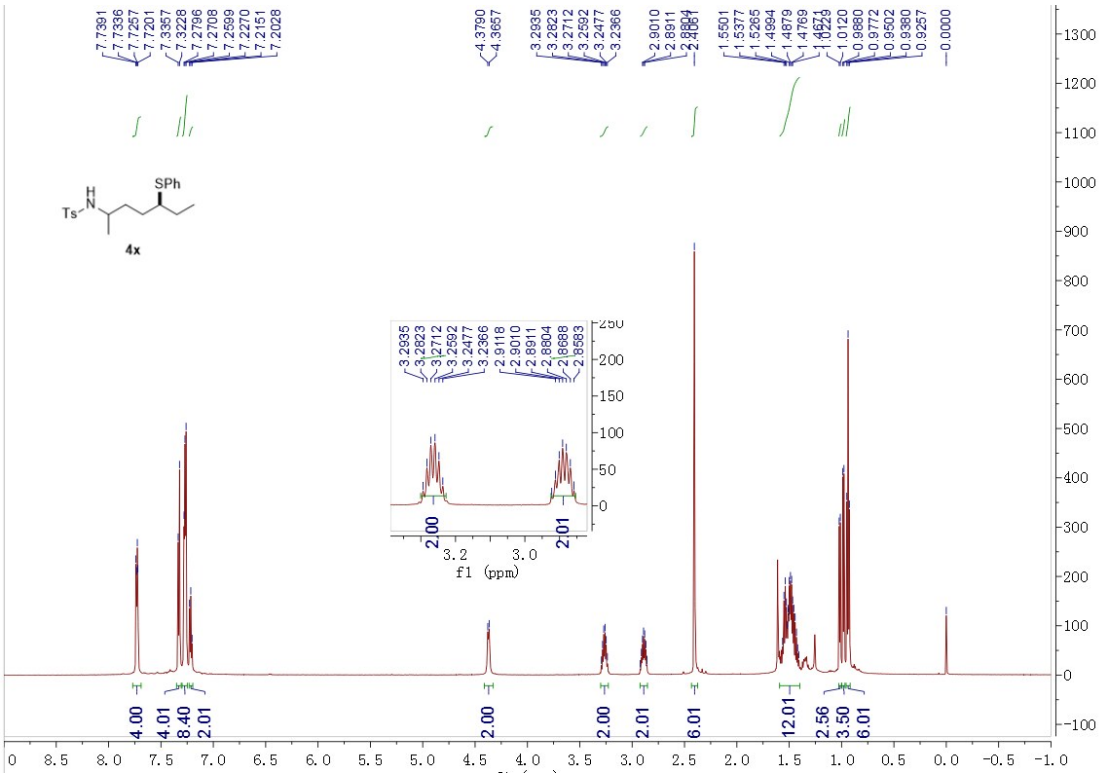
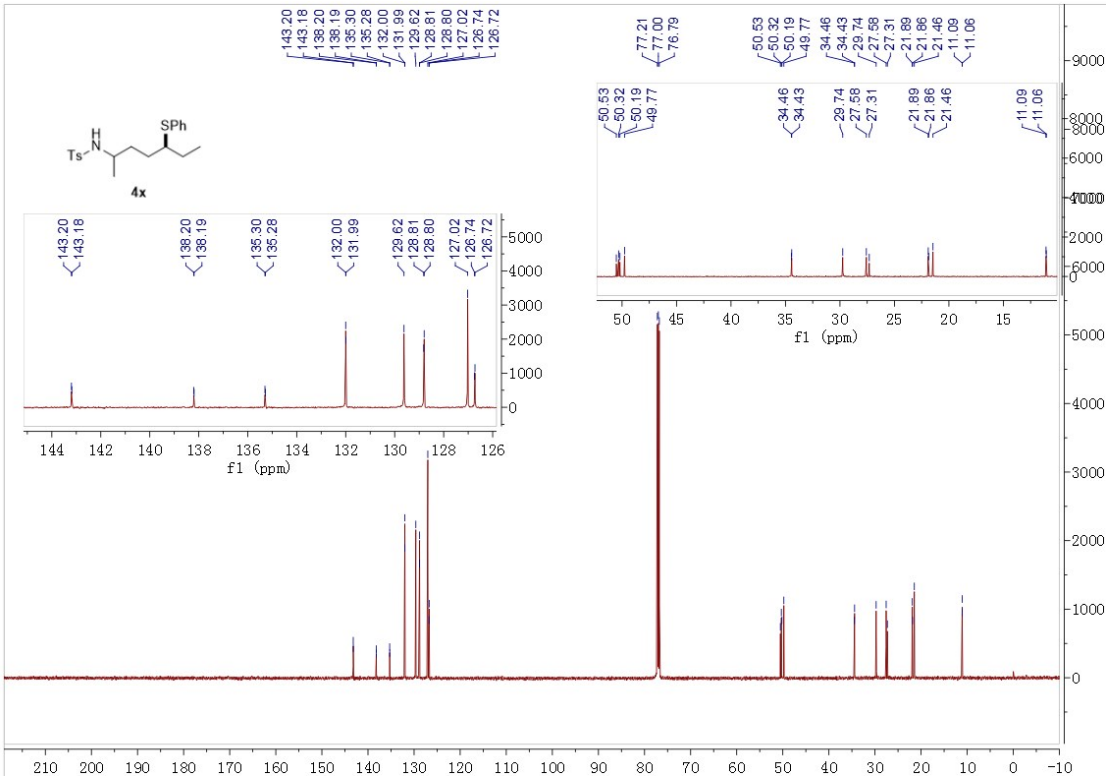
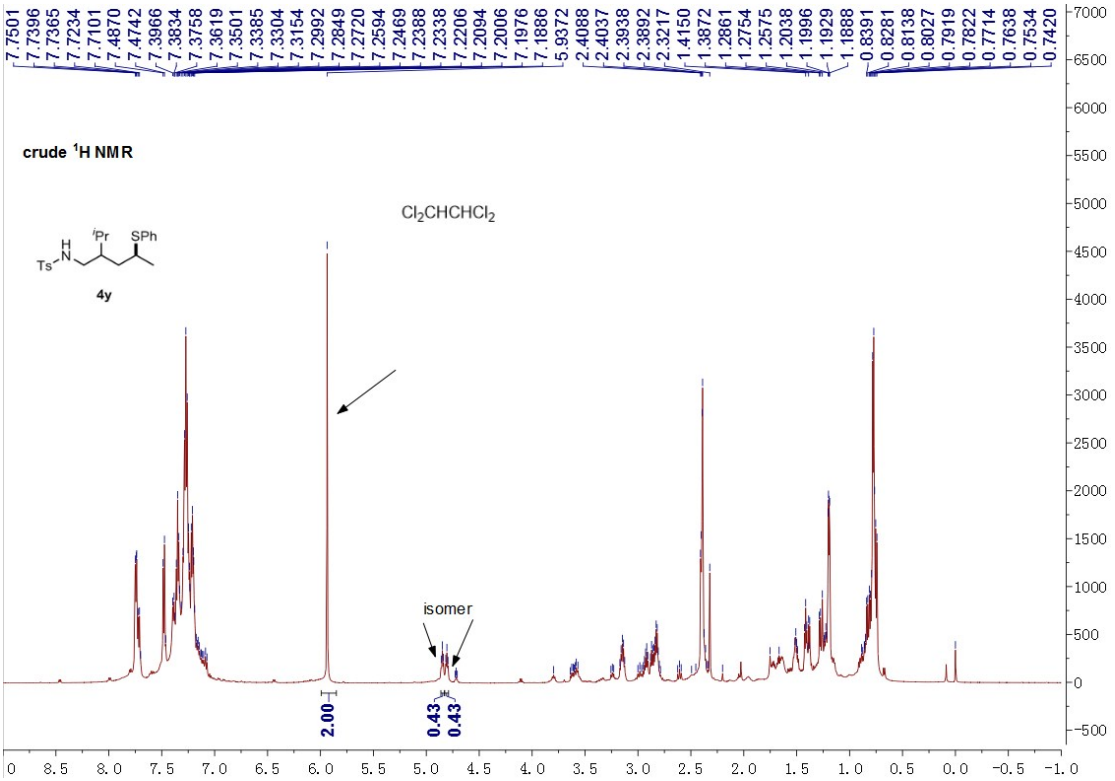
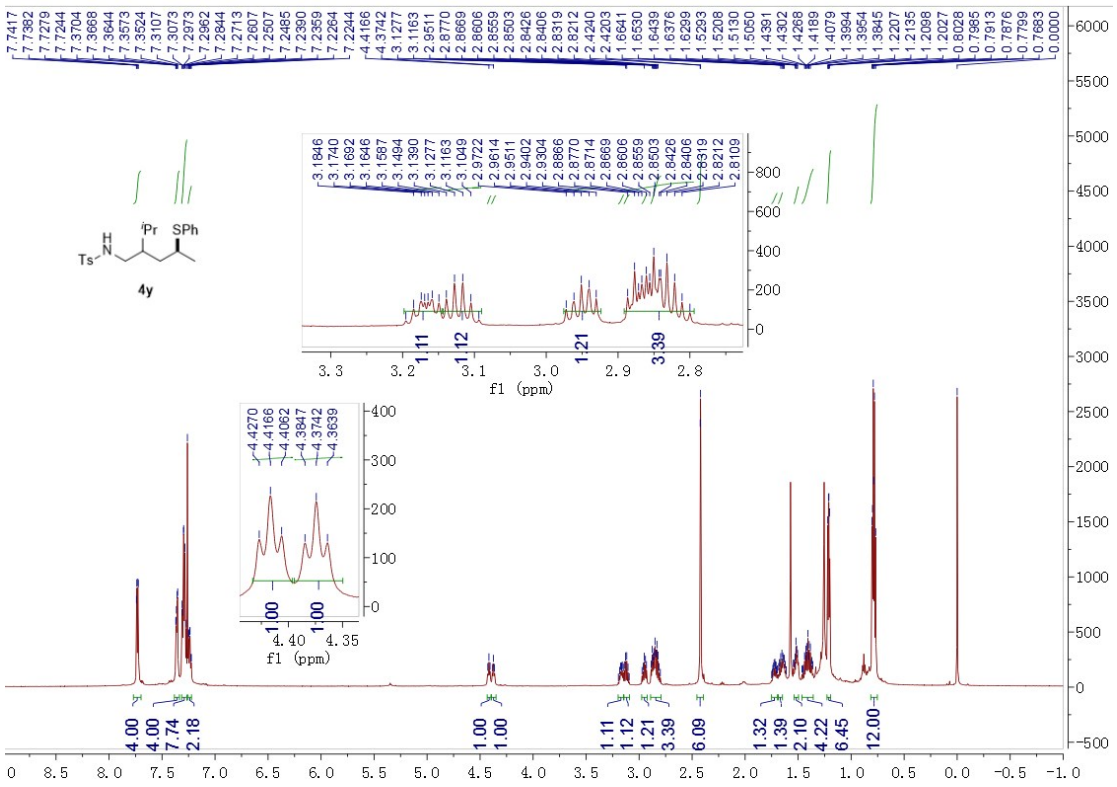
126.46
126.40
77.21
77.00
76.79
58.32
58.02
43.12
42.95
34.72
34.68
32.67
32.56
21.40
21.30
21.26
SPh
Ts
N
H
Ph
4w
f1 (ppm)
f1 (ppm)

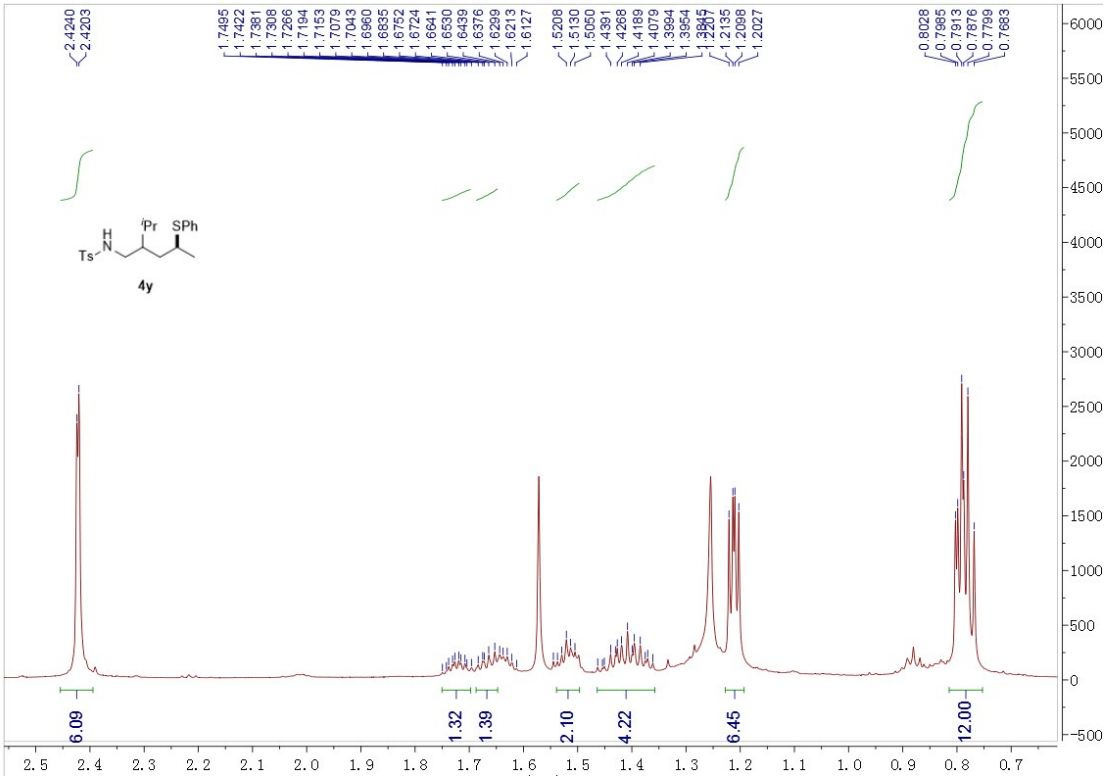

crude ^{1}H NMR
SPh
Ts
H
N
4x
isomer
1.31
1.28
f1 (ppm)
2.00
0.79
0.92
0.76
1.31
1.28

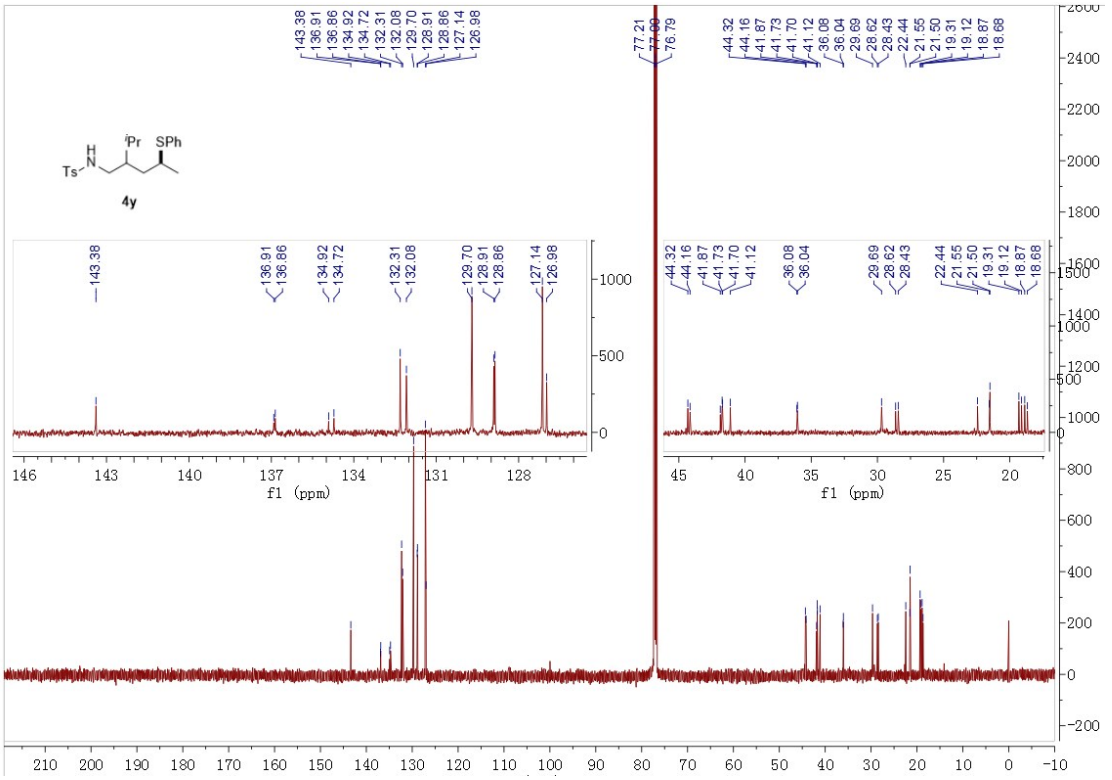

SPh
Ts
H
N
4x
f1 (ppm)
2.00
2.01
4.00
4.01
8.40
2.01
2.00
2.00
2.01
6.01
12.01
2.56
3.50
6.01

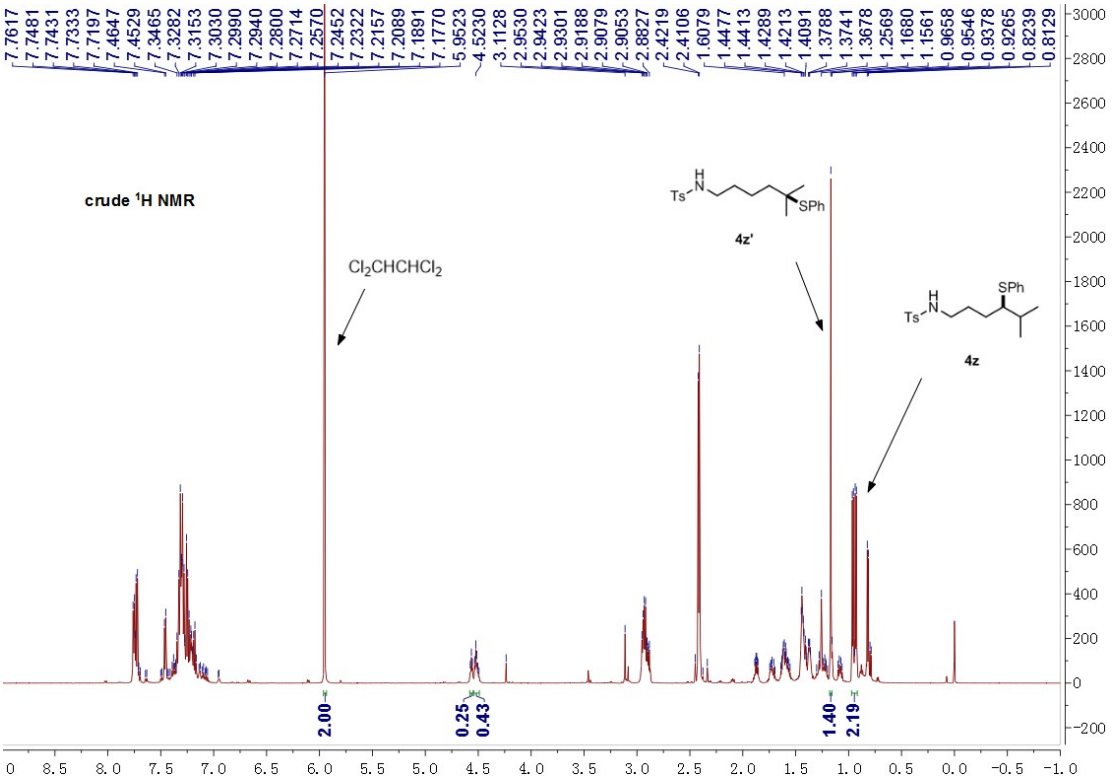

4x
f1 (ppm)
f1 (ppm)

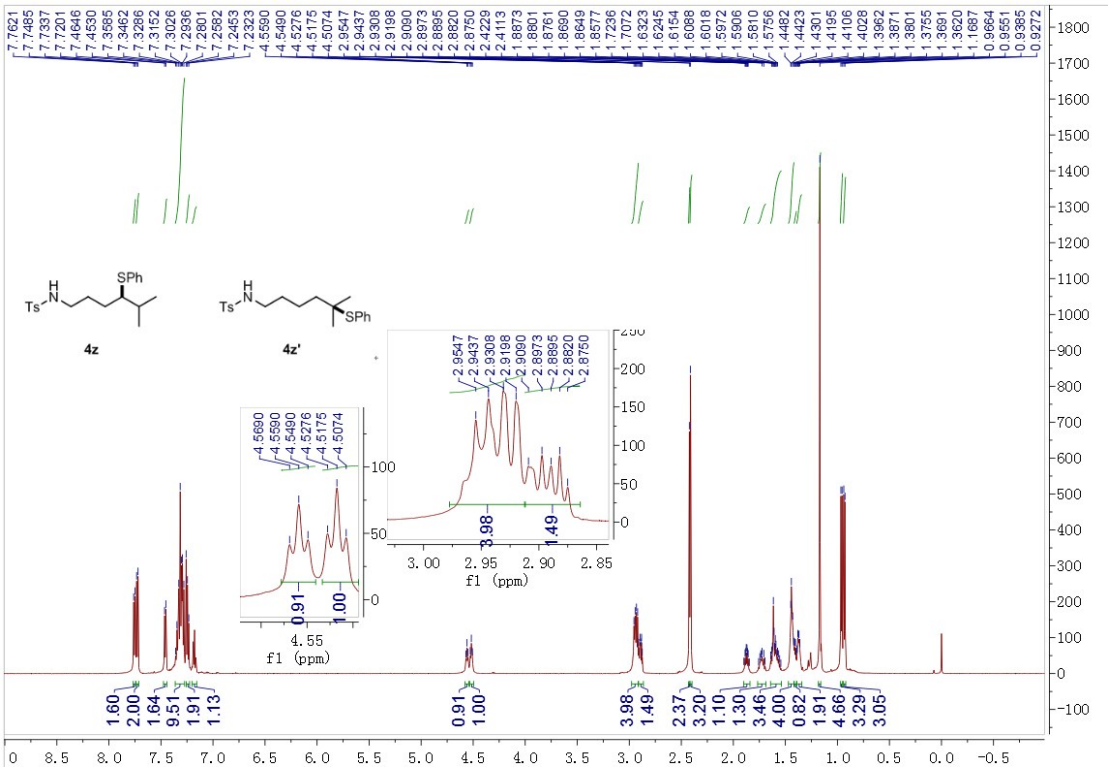

crude ^{1}H NMR
$Cl_2CHCHCl_2$
4y
isomer
2.00
0.43
0.43

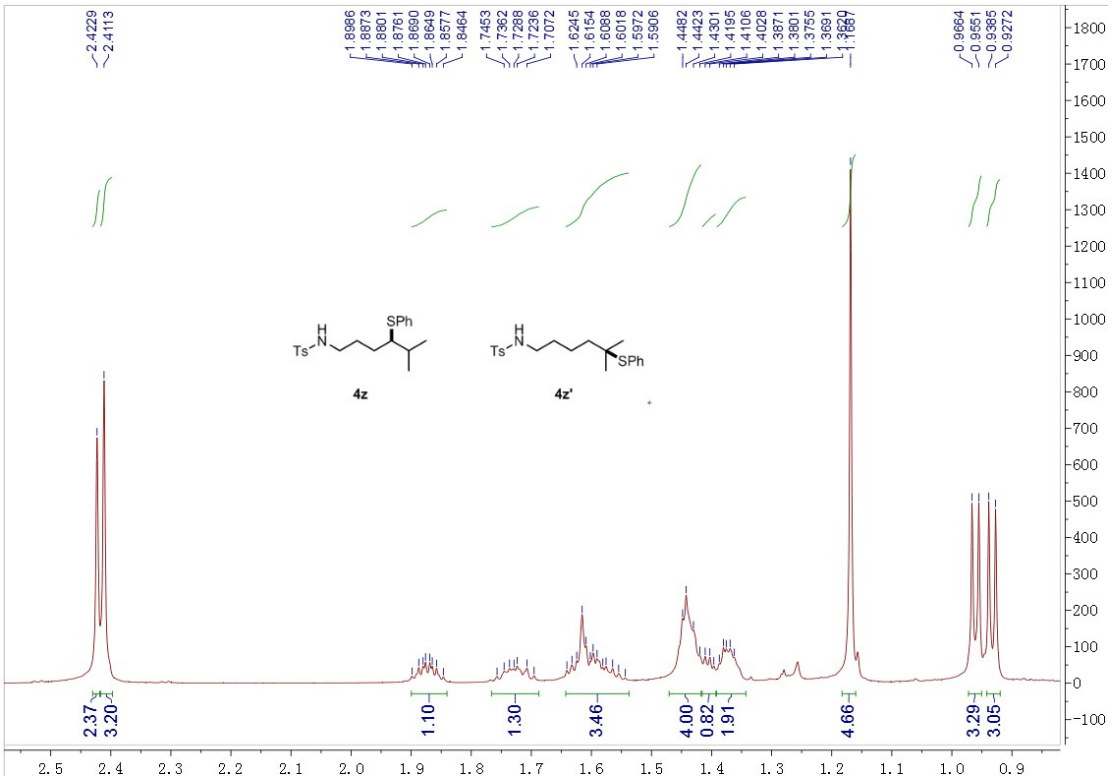

4y
f1 (ppm)
f1 (ppm)

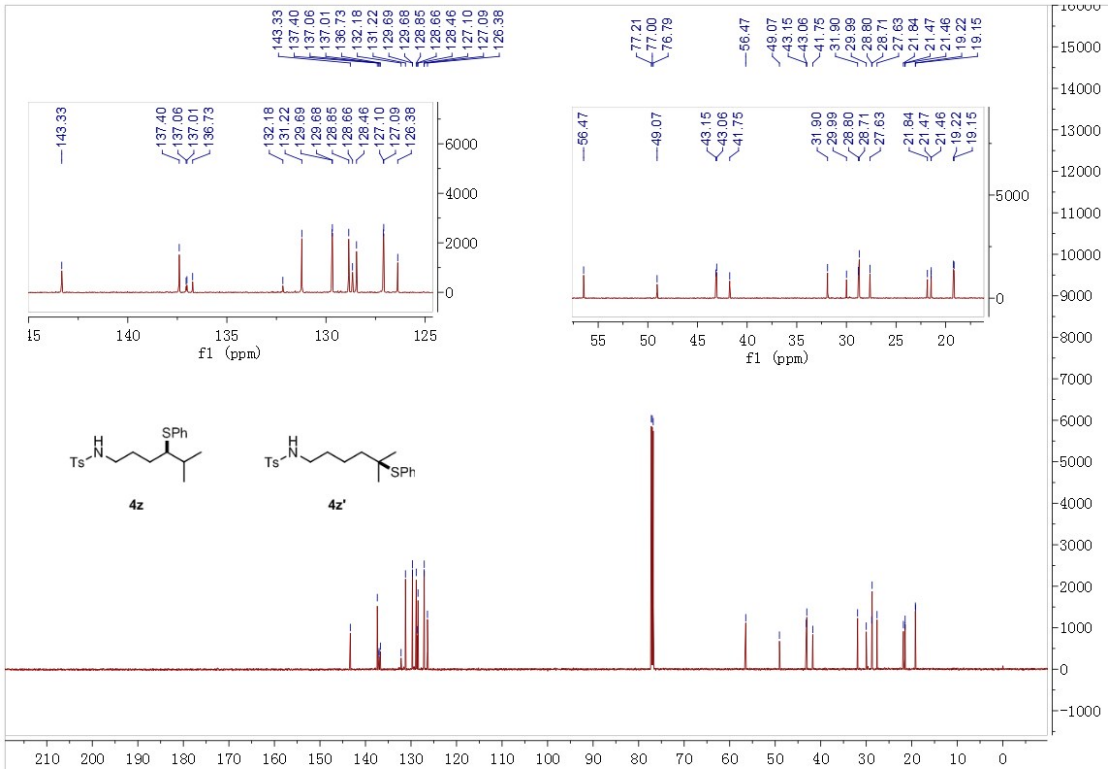

4y

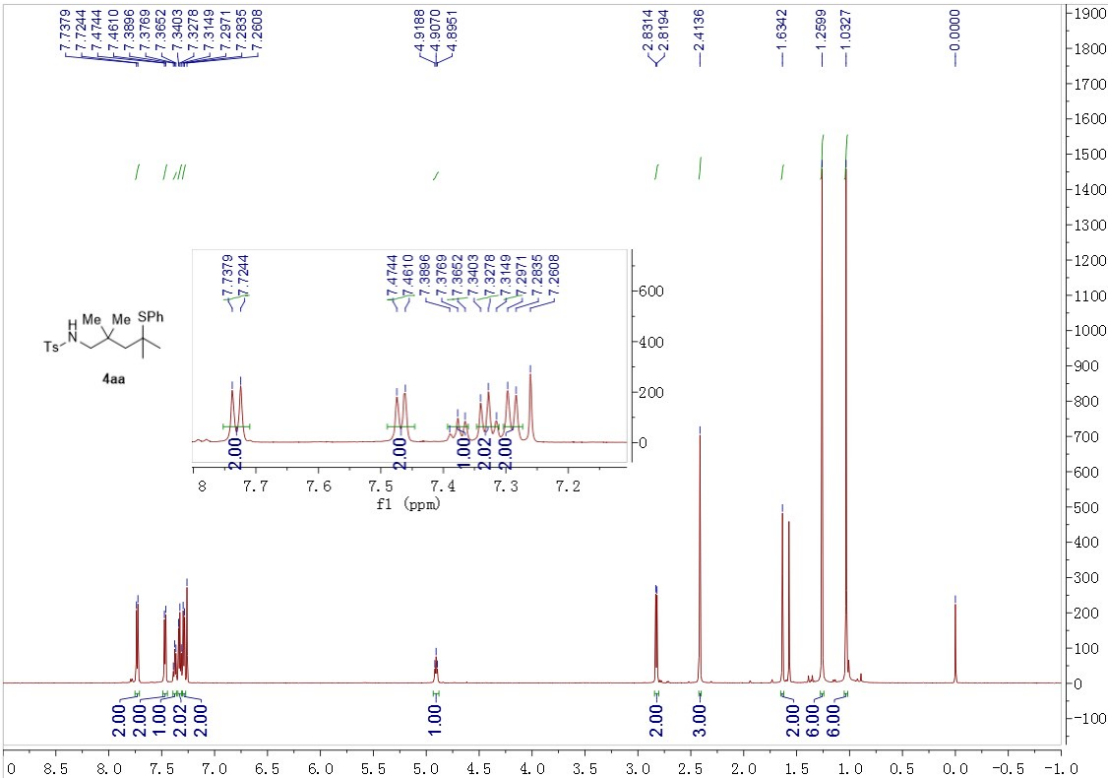

4y
f1 (ppm)
f1 (ppm)

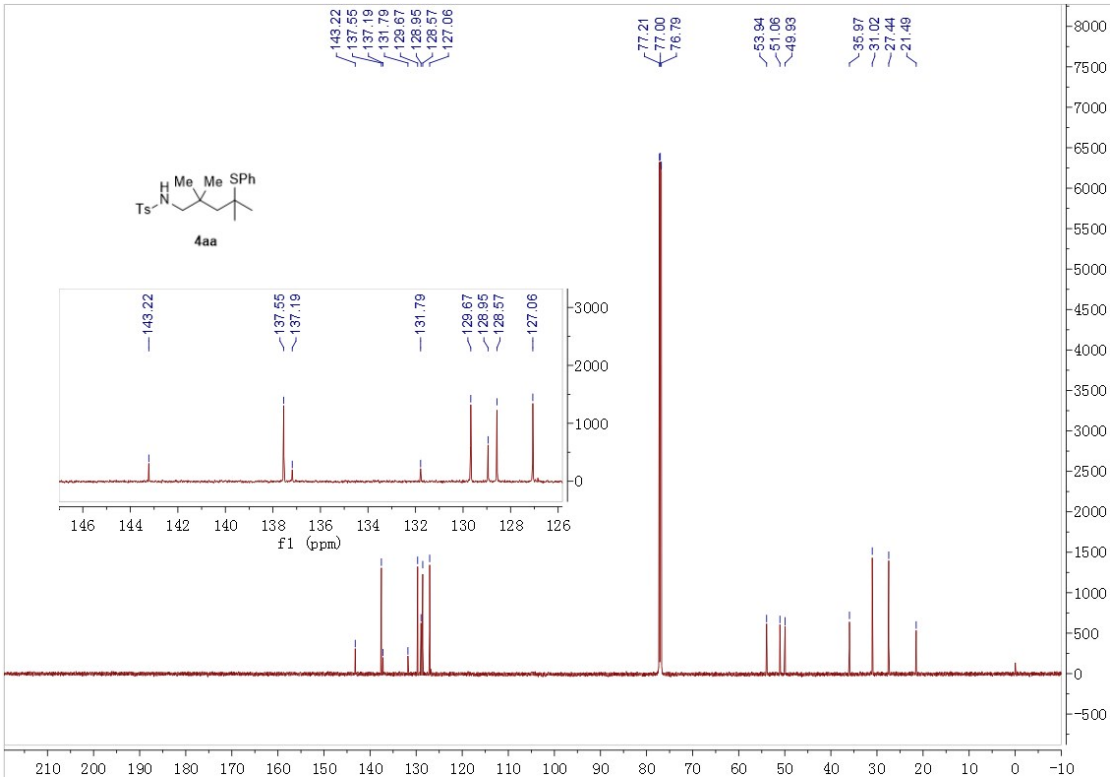

crude ¹H NMR
Cl2CHCHCl2
4z'
4z
2.00
0.25
0.43
1.40
2.19

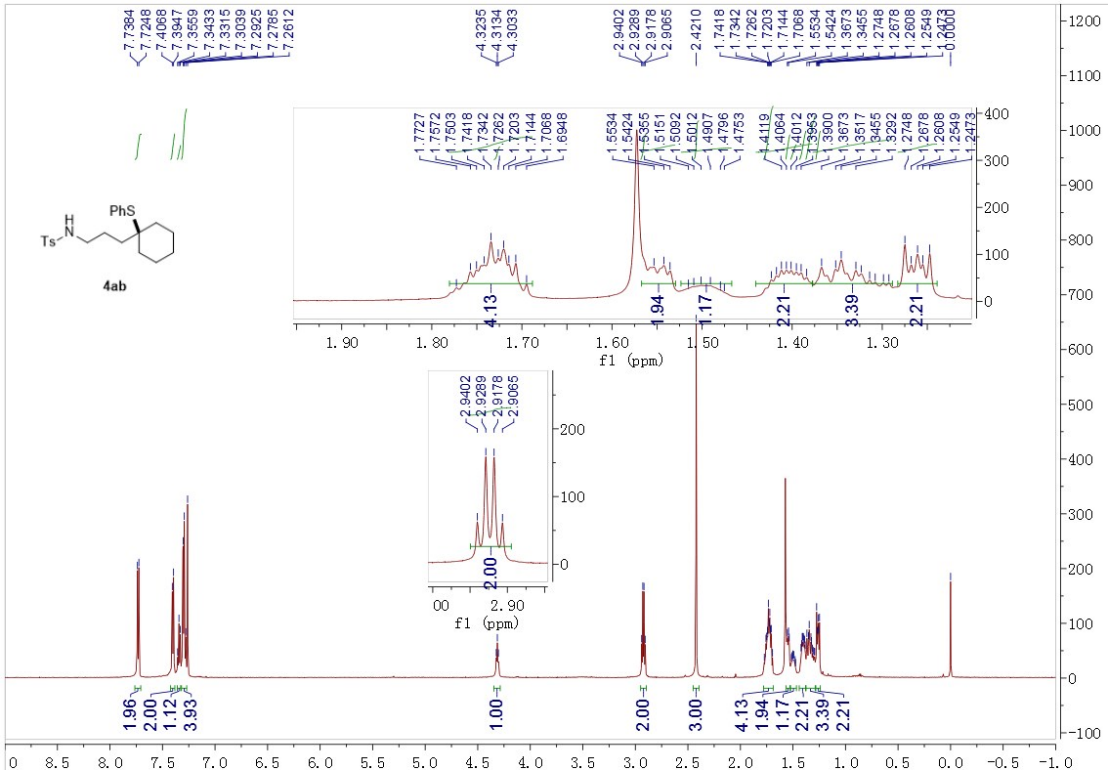

4z
4z'
f1 (ppm)

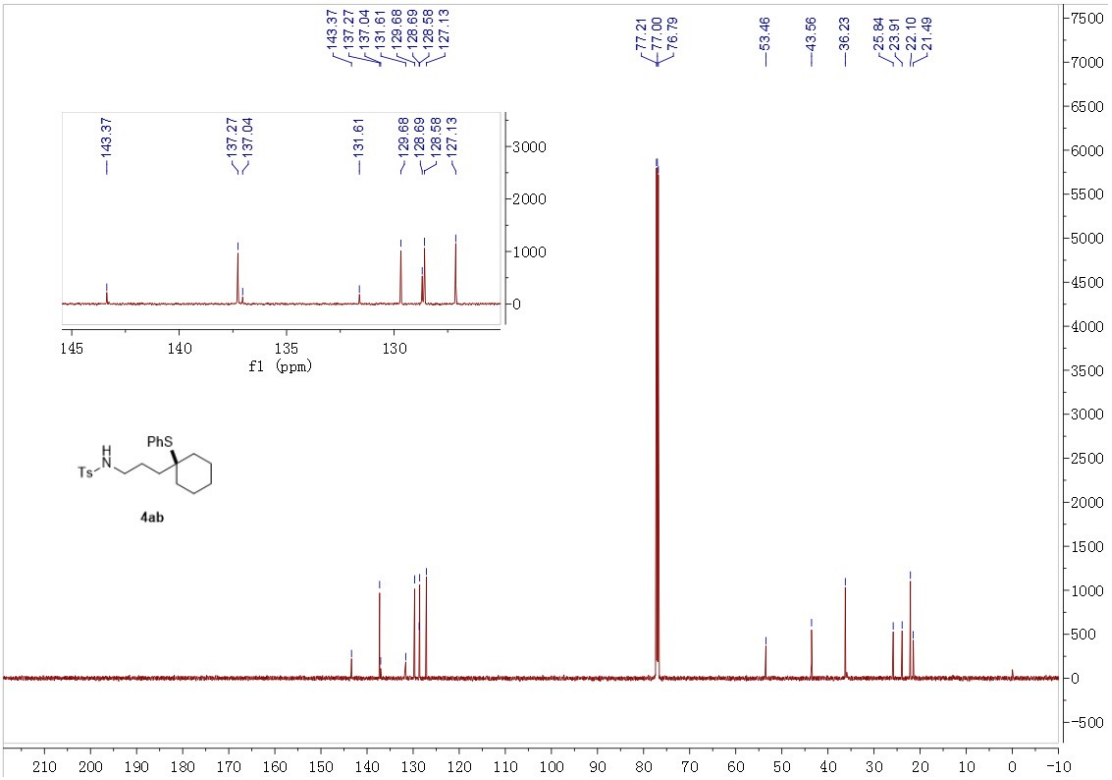

4z
4z'

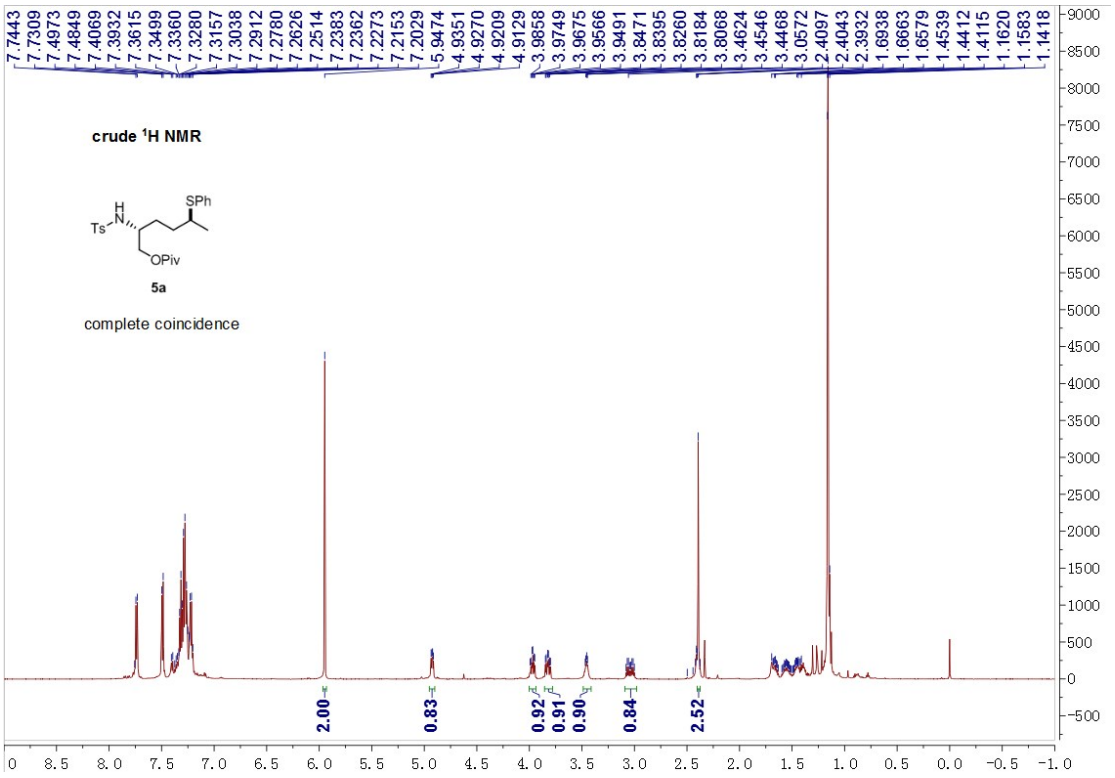

143.33
137.40
137.06
137.01
136.73
132.18
131.22
129.69
129.68
128.85
128.66
128.46
127.10
127.09
126.38
77.21
77.00
76.79
56.47
49.07
43.15
43.06
41.75
31.90
29.99
28.80
28.71
27.63
21.84
21.47
21.46
19.22
19.15
f1 (ppm)
SPh
Ts
4z
4z'

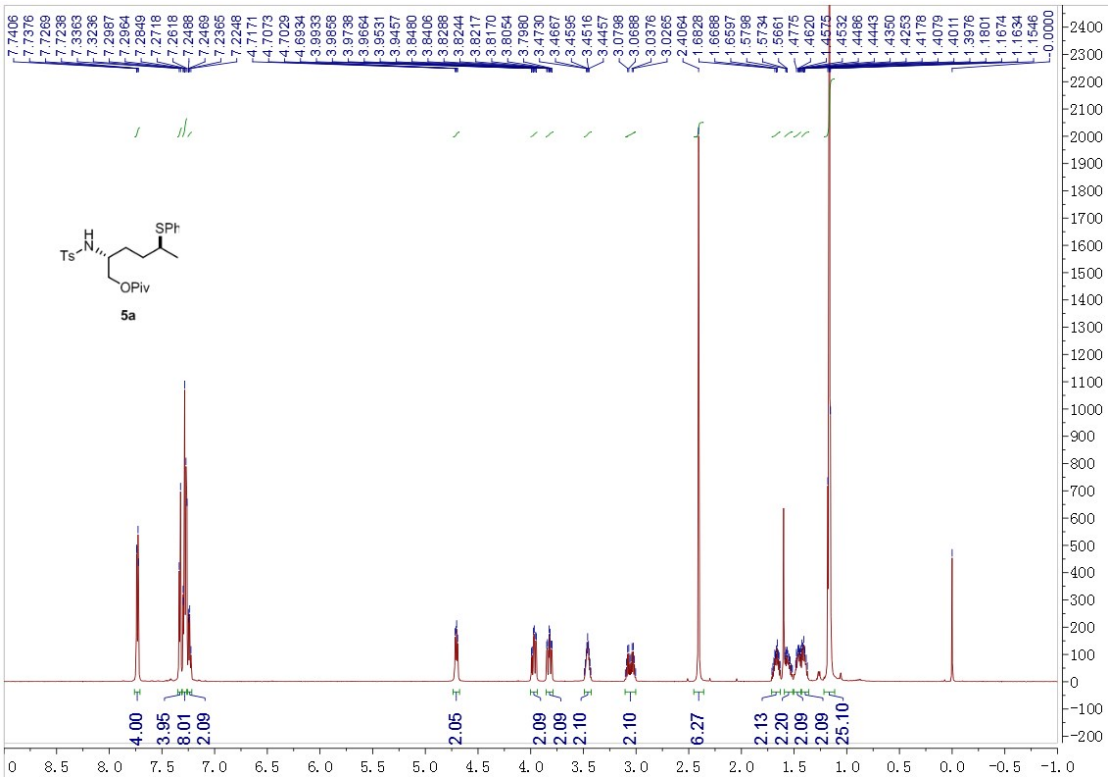

7.7379
7.7244
7.4744
7.4610
7.3896
7.3769
7.3652
7.3403
7.3278
7.3149
7.2971
7.2835
7.2608
4.9188
4.9070
4.8951
2.8314
2.8194
2.4136
1.6342
1.2599
1.0327
0.0000
Me
Me
SPh
Ts
4aa
f1 (ppm)
2.00
2.00
1.00
2.02
2.00
1.00
2.00
3.00
2.00
6.00
6.00

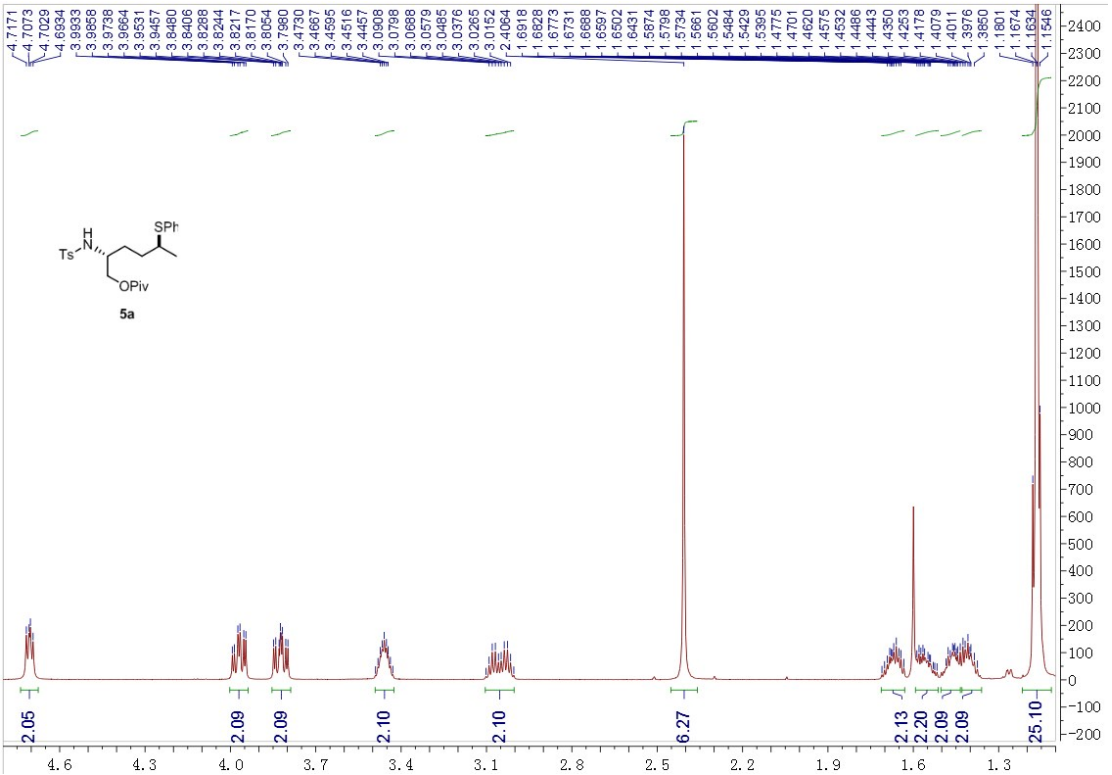

143.22
137.55
137.19
131.79
129.67
128.95
128.57
127.06
77.21
77.00
76.79
53.94
51.06
49.93
35.97
31.02
27.44
21.49
Me Me SPh
Ts
H
N
4aa
f1 (ppm)

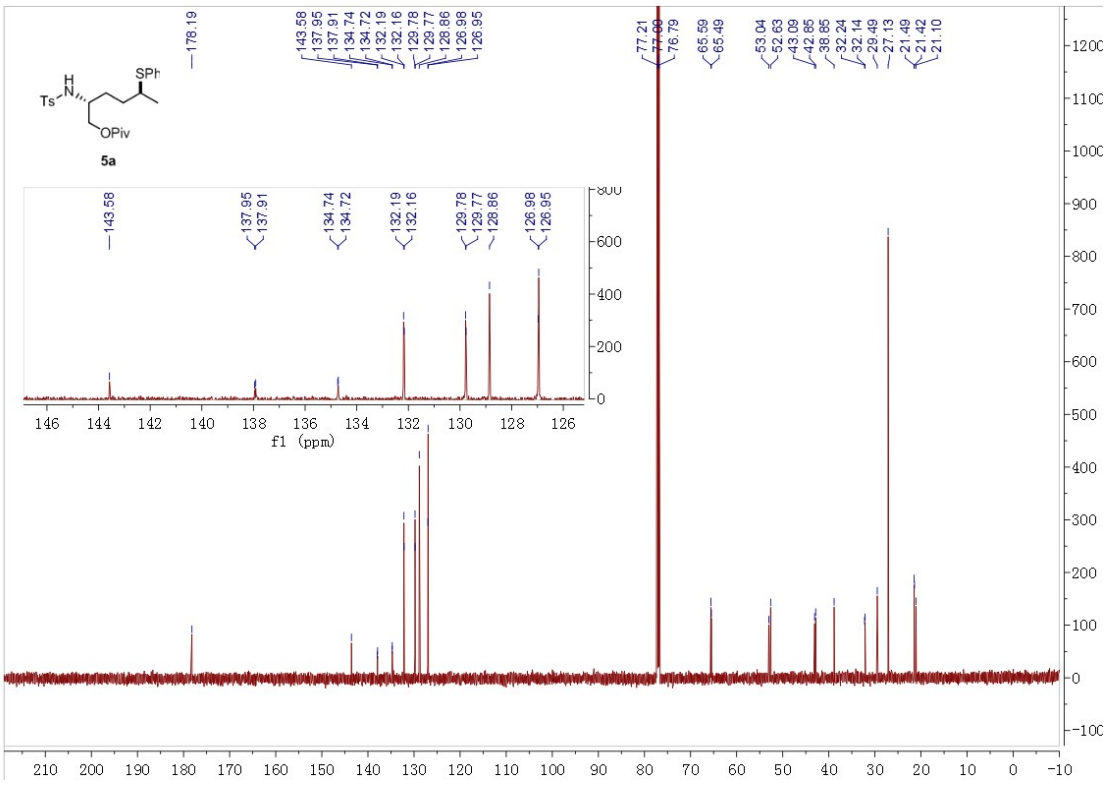

PhS
Ts
H
N
4ab
4.13
1.94
1.17
2.21
3.39
2.21
2.00
f1 (ppm)
1.96
2.00
1.12
3.93
1.00
2.00
3.00
4.13
1.94
1.17
2.21
3.39
2.21

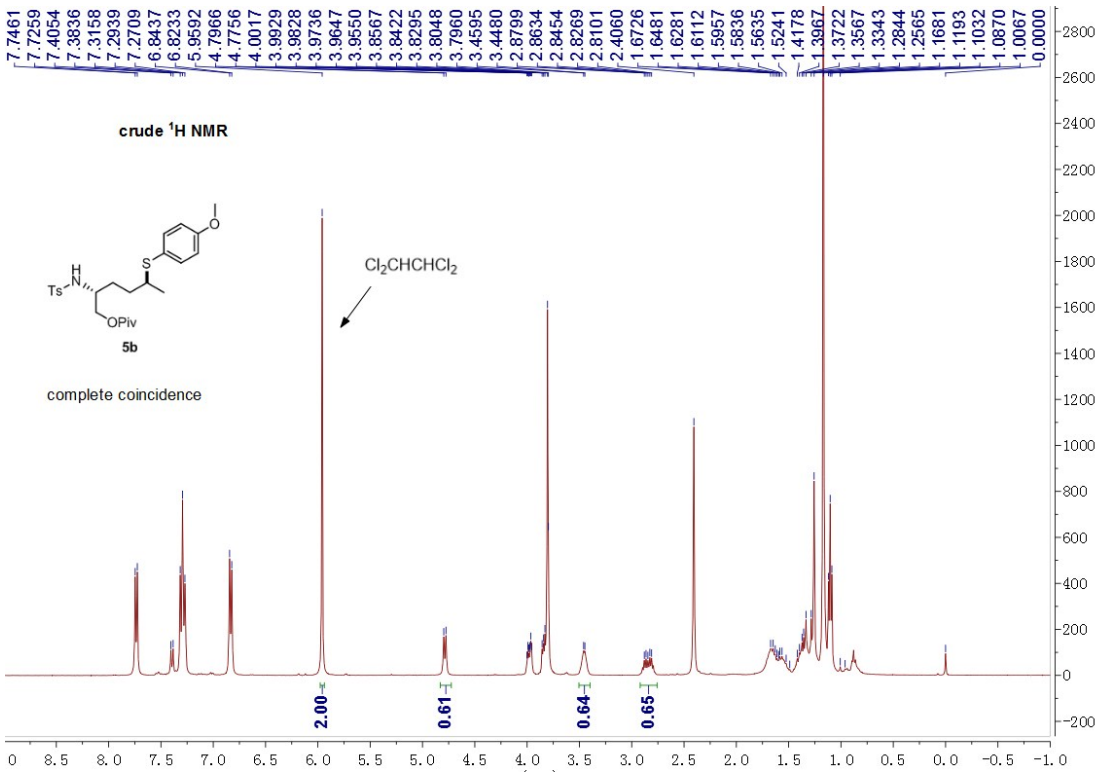

143.37
137.27
137.04
131.61
129.68
128.69
128.58
127.13
77.21
77.00
76.79
53.46
43.56
36.23
25.84
23.91
22.10
21.49
f1 (ppm)
PhS
Ts
H
N
4ab

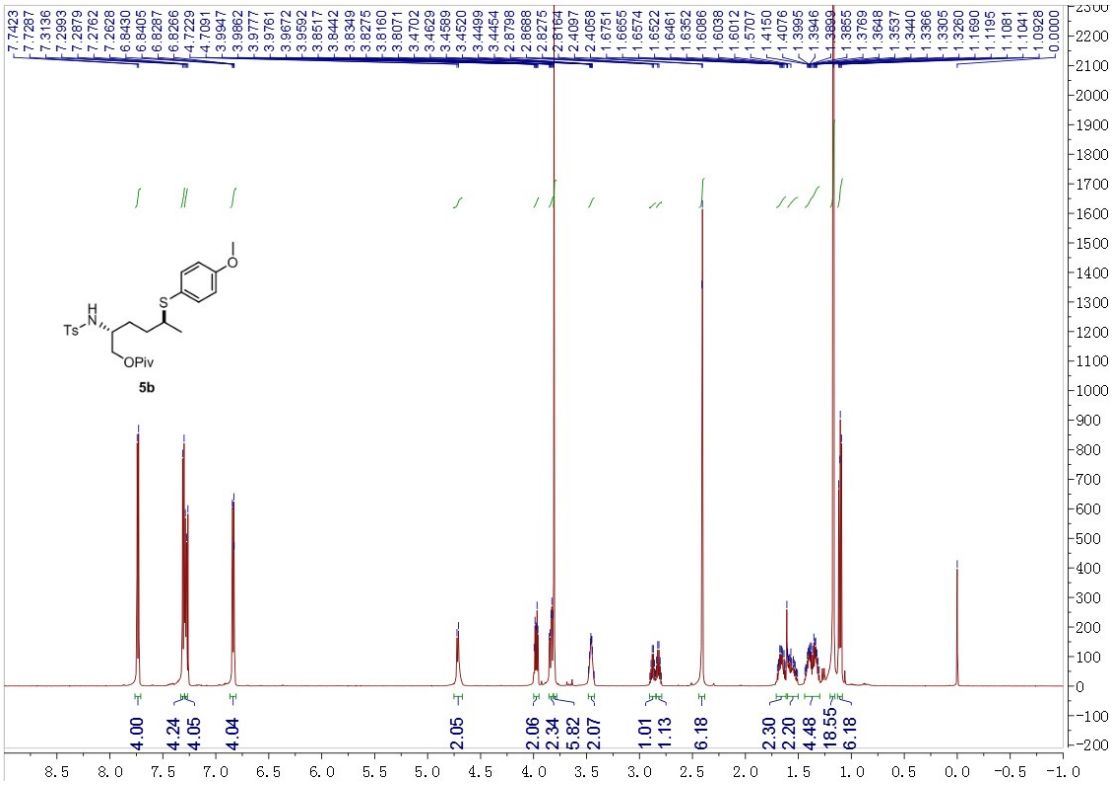

crude ^{1}H NMR
SPh
Ts
H
N
OPiv
5a
complete coincidence
2.00
0.83
0.92
0.91
0.90
0.84
2.52

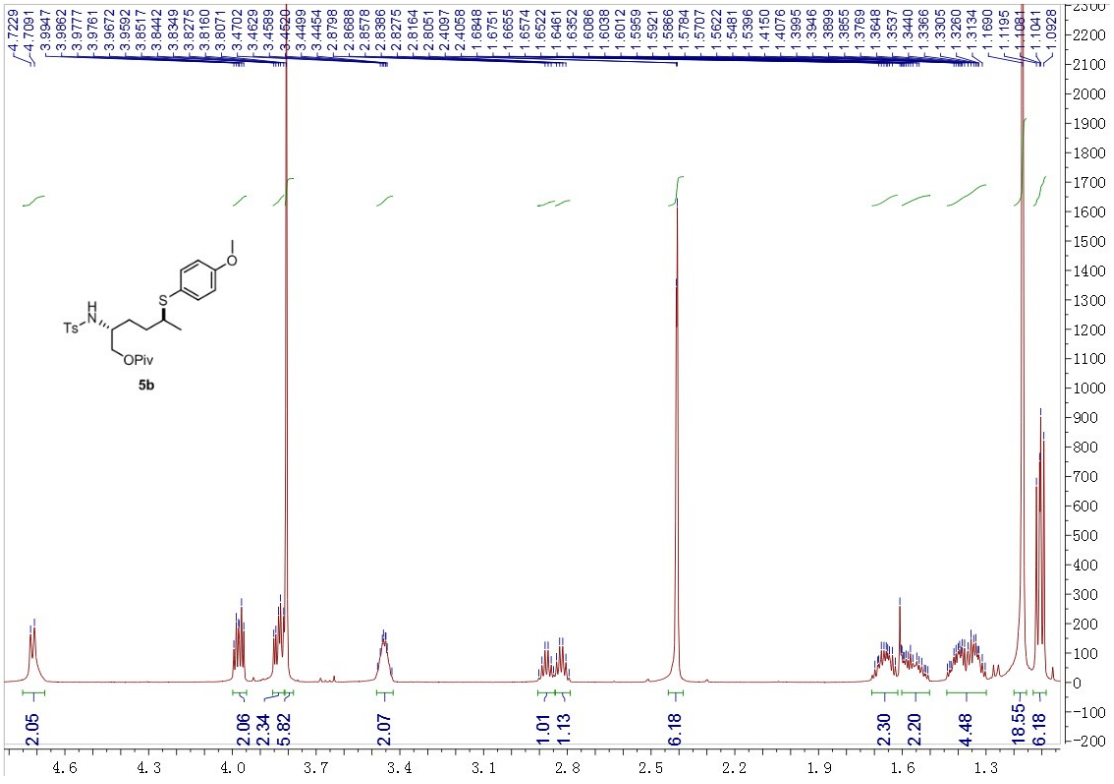

SPh
Ts
N
H
OPiv
5a

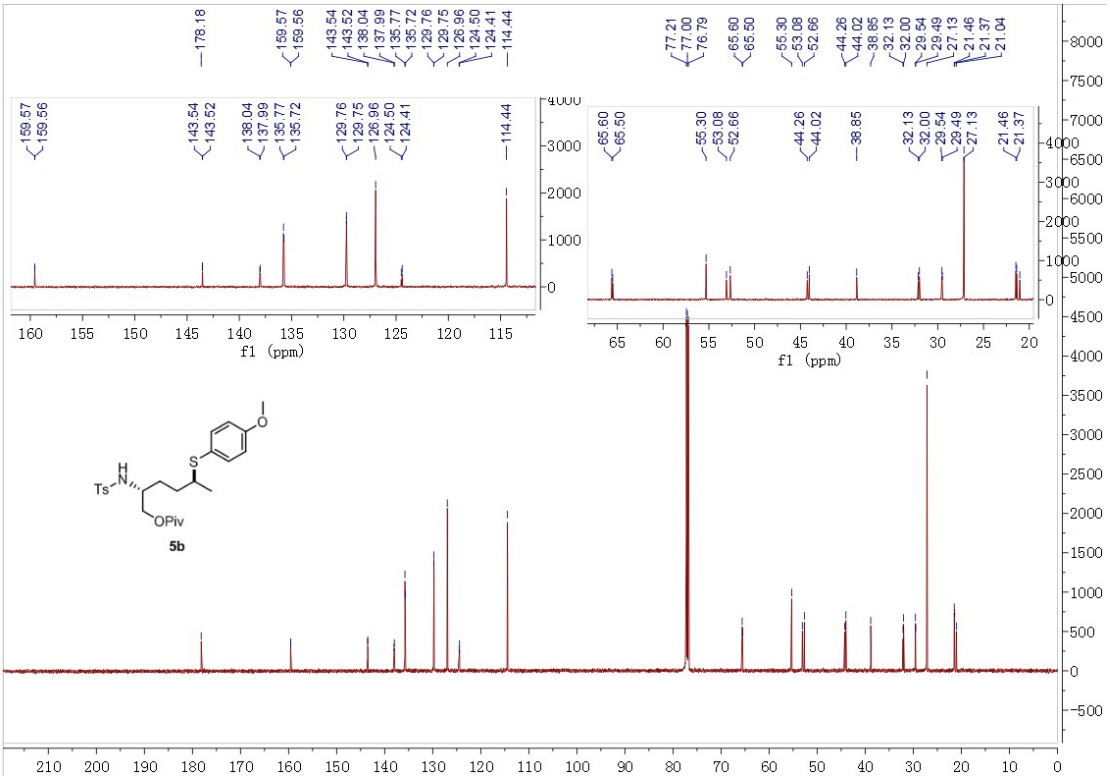

SPh
Ts
N
H
OPiv
5a

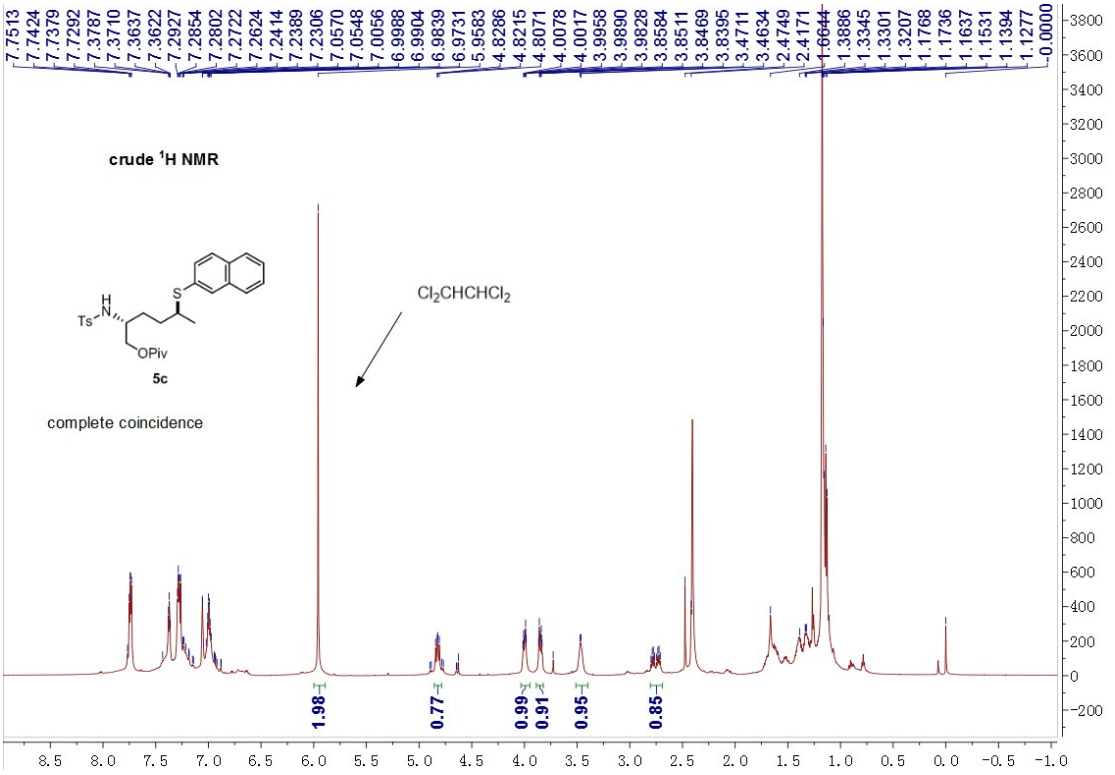

5a
f1 (ppm)

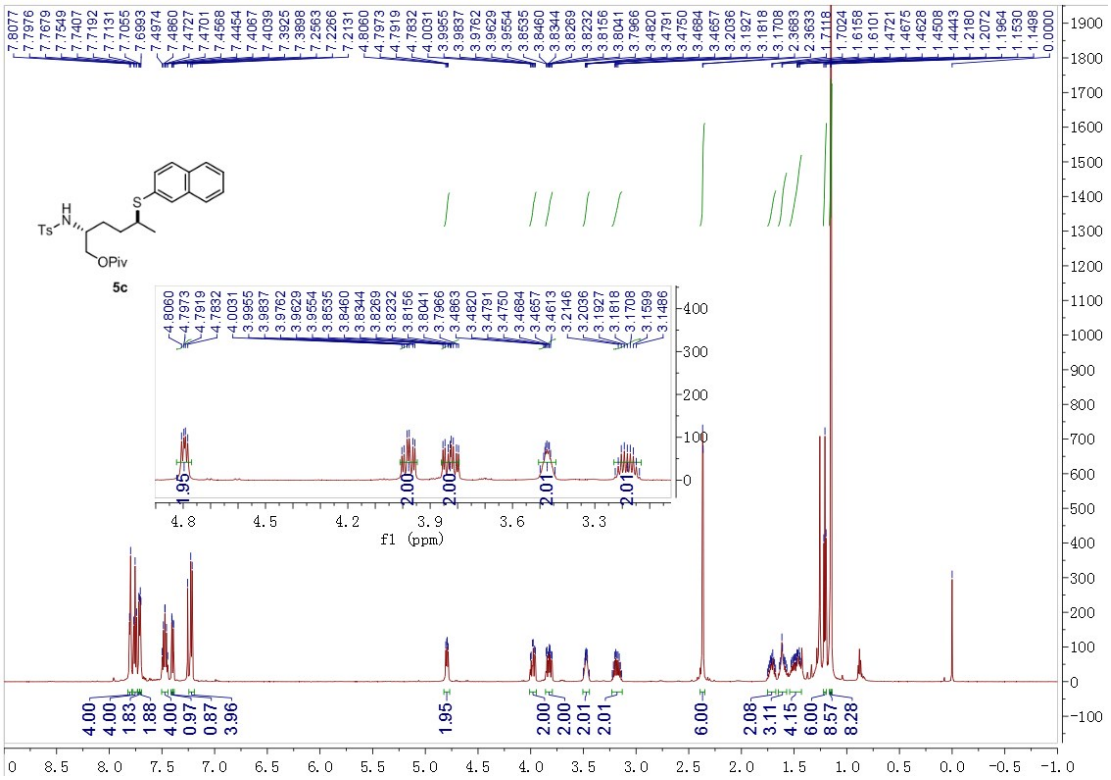

crude ^{1}H NMR
5b
complete coincidence
$Cl_2CHCHCl_2$
2.00
0.61
0.64
0.65

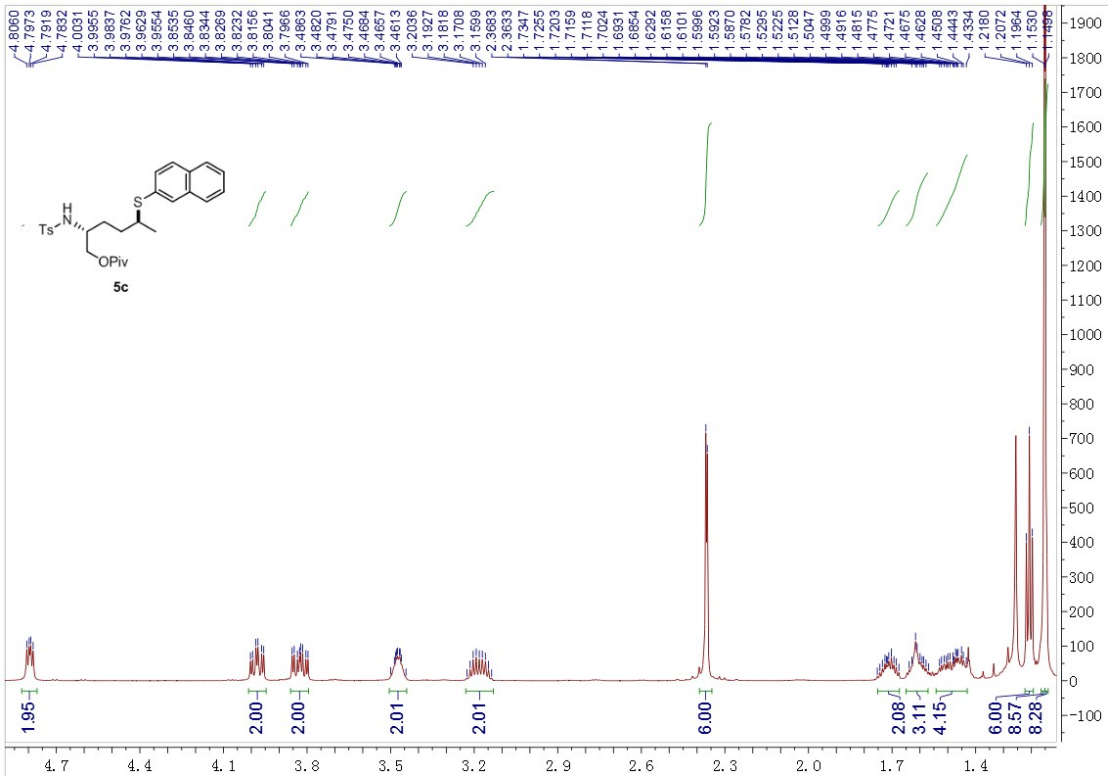

5b

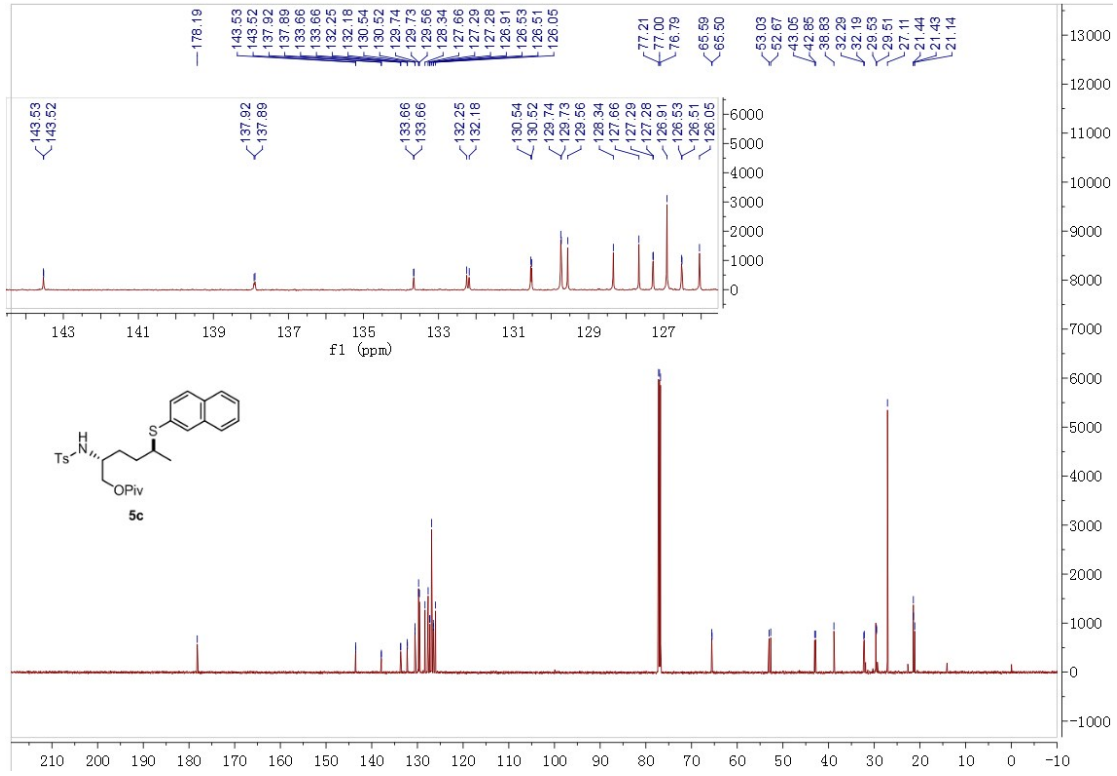

5b

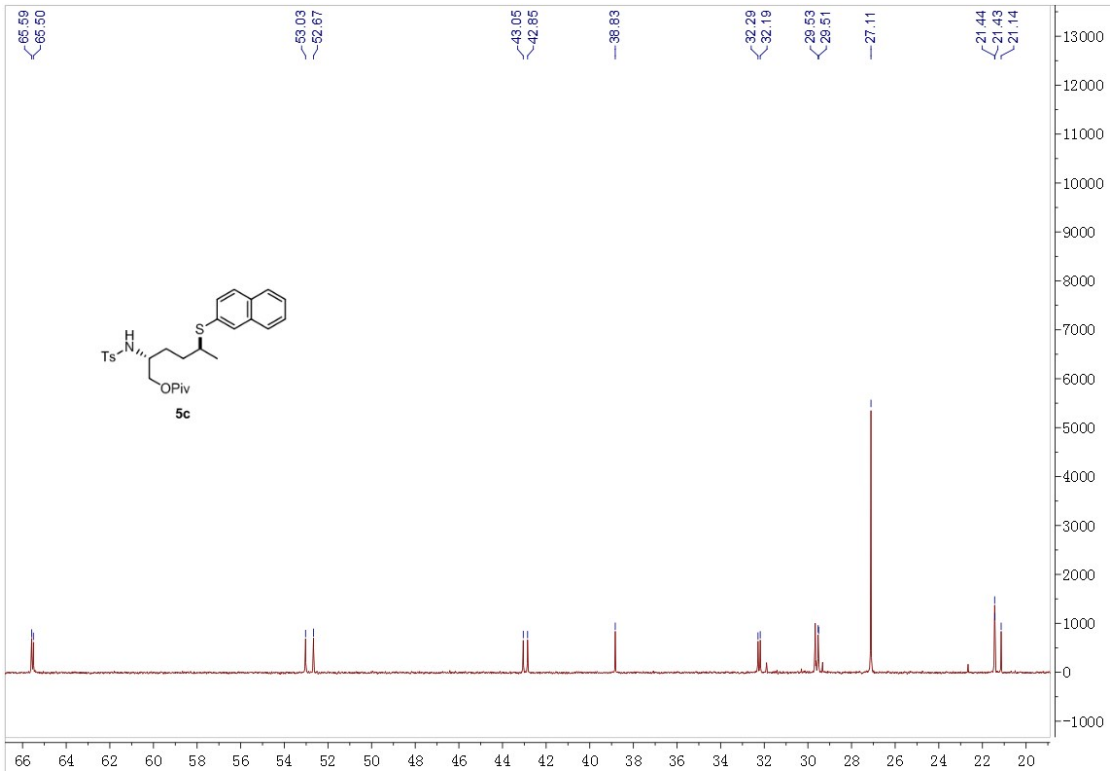

178.18
159.57
159.56
143.54
143.52
138.04
137.99
135.77
135.72
129.76
129.75
126.96
124.50
124.41
114.44
77.21
77.00
76.79
65.60
65.50
55.30
53.08
52.66
44.26
44.02
38.85
32.13
32.00
29.54
29.49
27.13
21.46
21.37
21.04
f1 (ppm)
f1 (ppm)
Ts
N
H
S
O
OPiv
5b

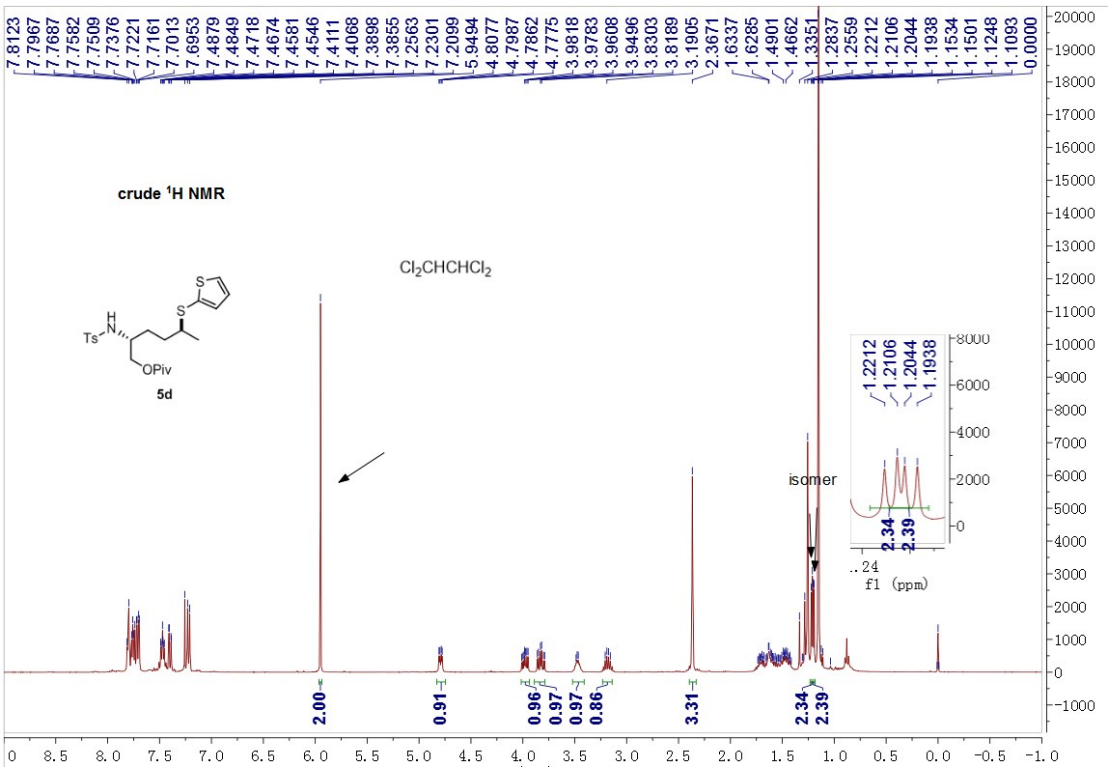

crude ^{1}H NMR
Ts
N
H
S
OPiv
5c
$Cl_2CHCHCl_2$
complete coincidence
1.98
0.77
0.99
0.91
0.95
0.85

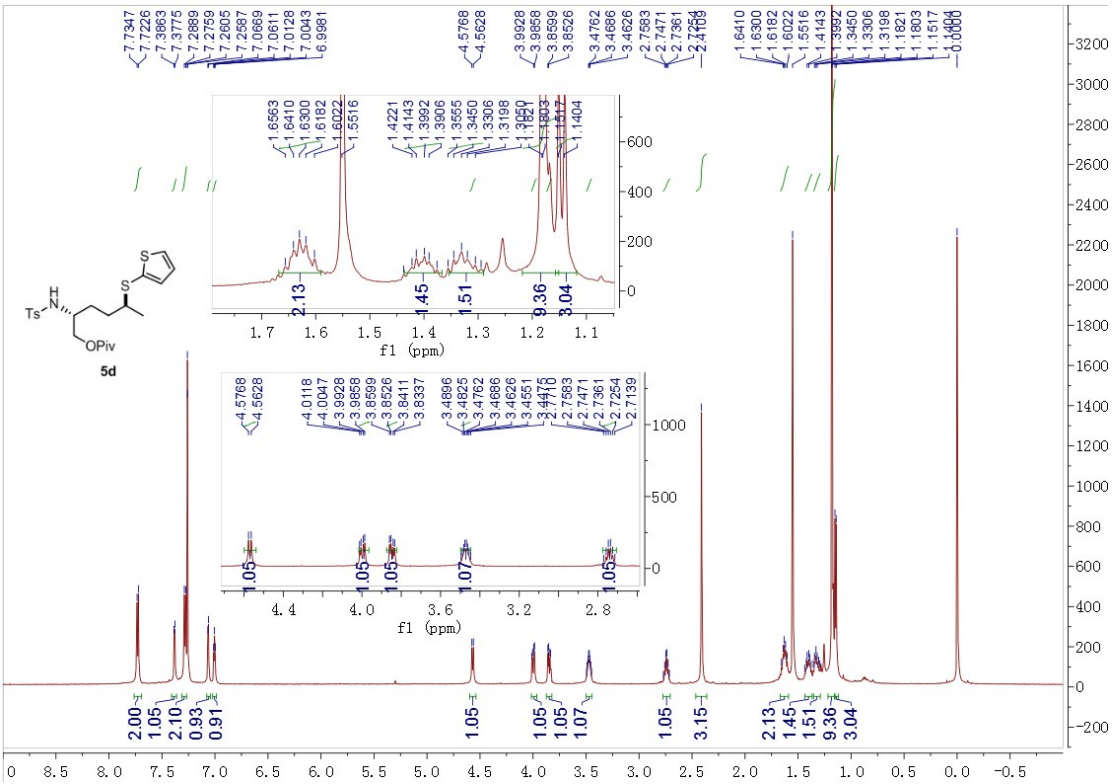

5c
f1 (ppm)

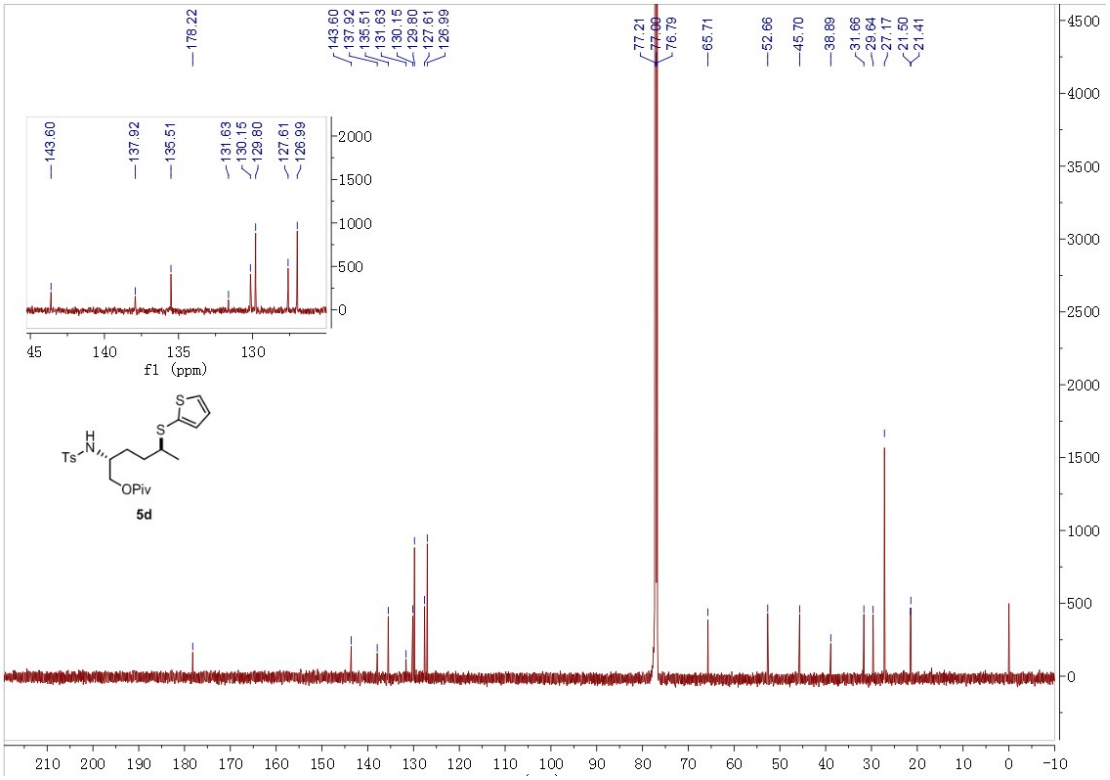

5c

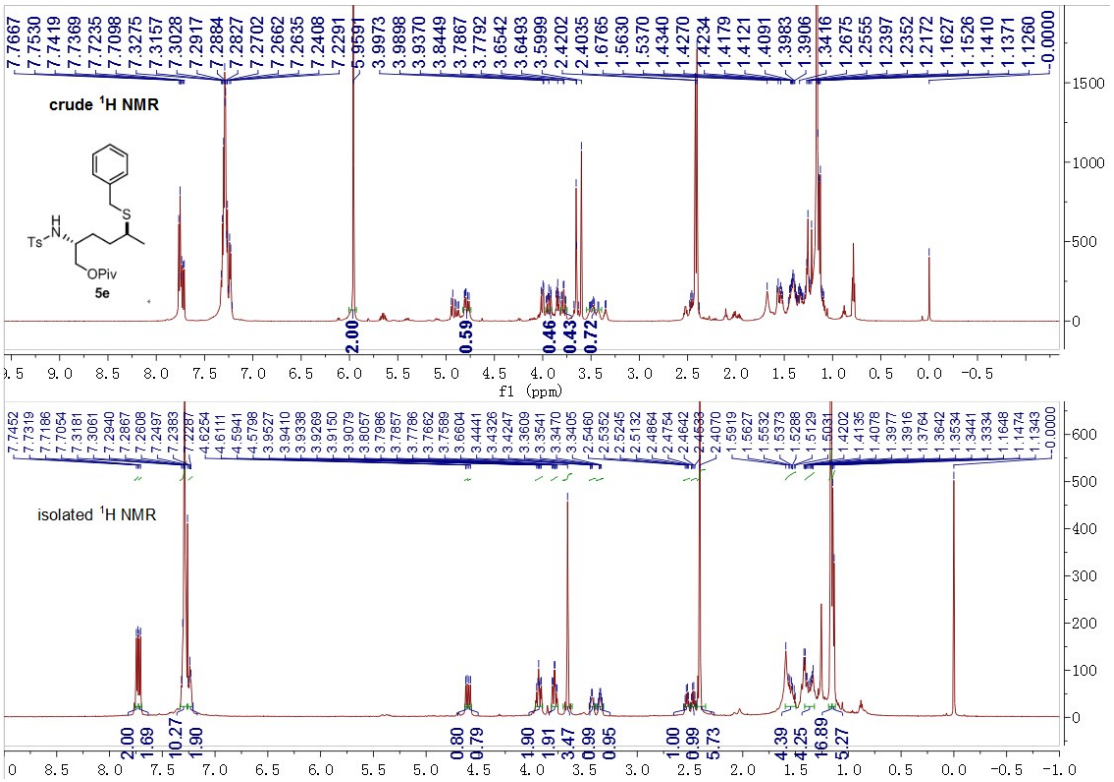

178.19
143.53
143.52
137.92
137.89
133.66
133.66
132.25
132.18
130.54
130.52
129.74
129.73
129.56
128.34
127.66
127.29
127.28
126.91
126.53
126.51
126.05
77.21
77.00
76.79
65.59
65.50
53.03
52.67
43.05
42.85
38.83
32.29
32.19
29.53
29.51
27.11
21.44
21.43
21.14
f1 (ppm)
Ts
OPiv
5c

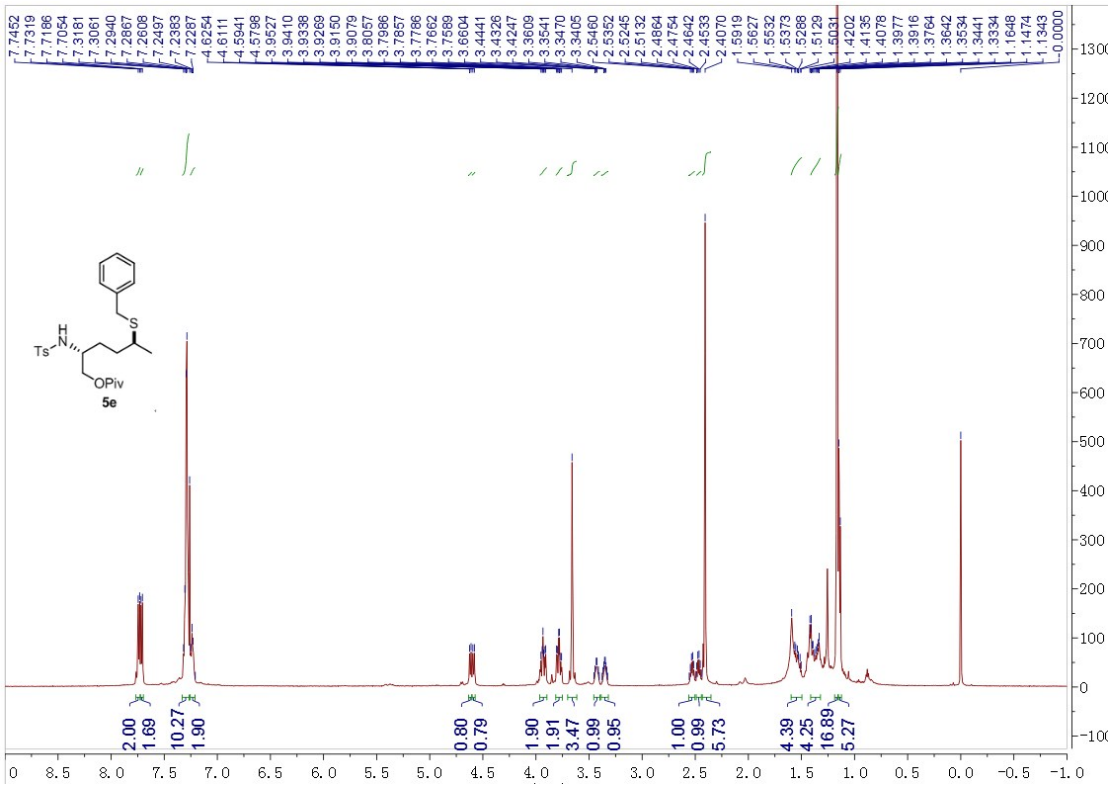

65.59
65.50
53.03
52.67
43.05
42.85
38.83
32.29
32.19
29.53
29.51
27.11
21.44
21.43
21.14
Ts
OPiv
5c

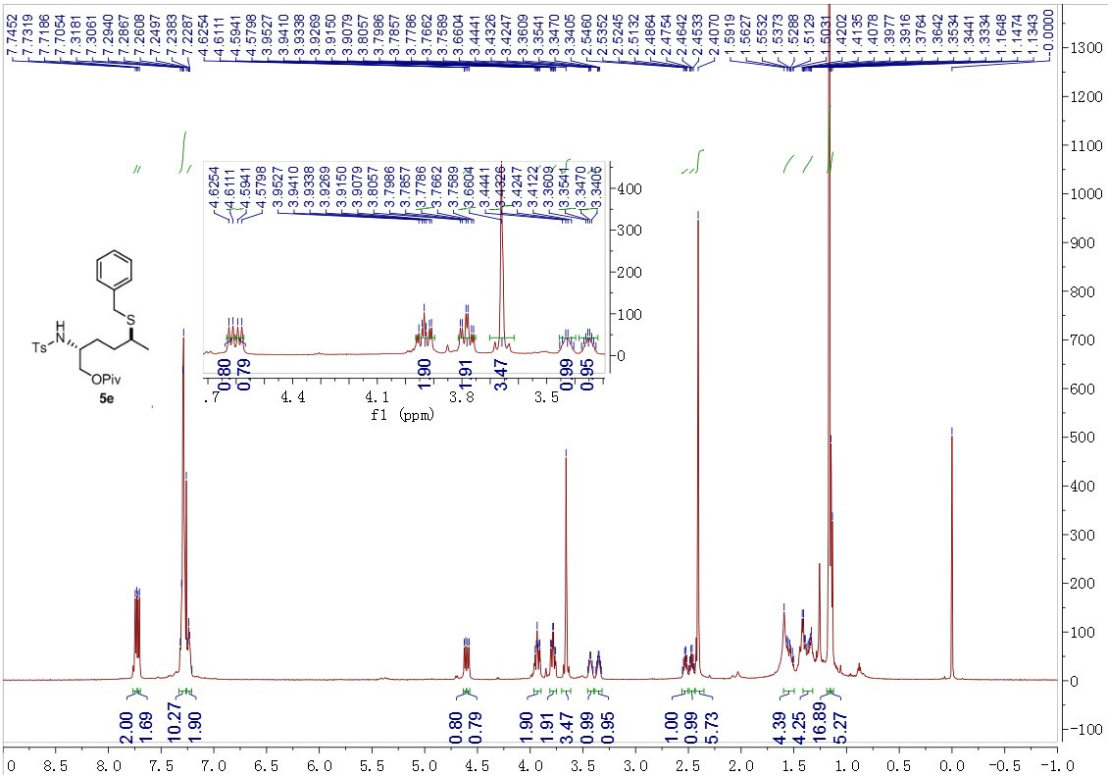

crude ^{1}H NMR
$Cl_2CHCHCl_2$
isomer
5d
f1 (ppm)

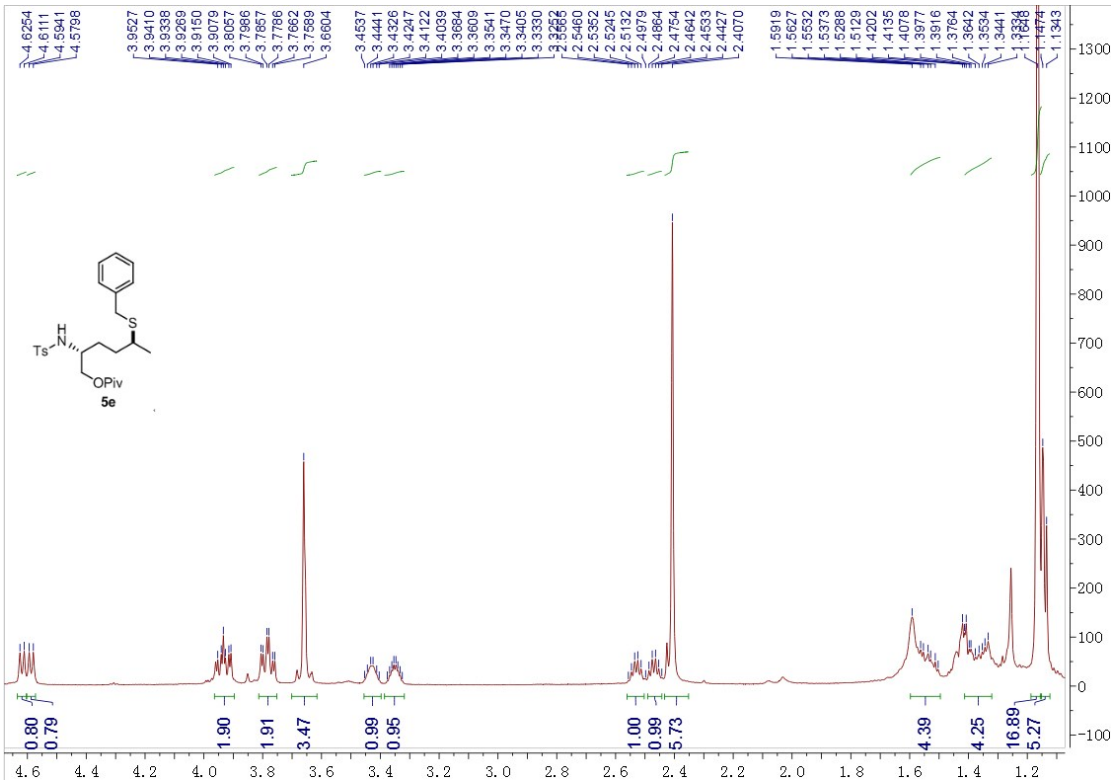

5d
f1 (ppm)

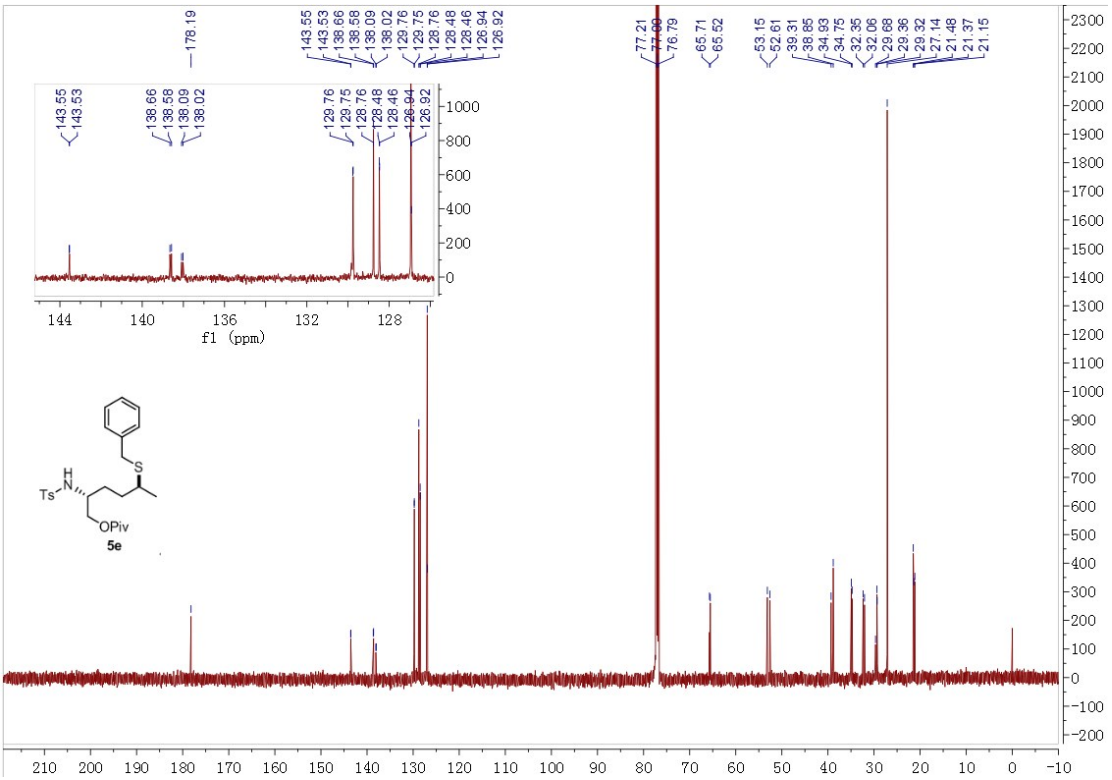

178.22
143.60
137.92
135.51
131.63
130.15
129.80
127.61
126.99
77.21
77.00
76.79
65.71
52.66
45.70
38.89
31.66
29.64
27.17
21.50
21.41
f1 (ppm)
Ts
OPiv
5d

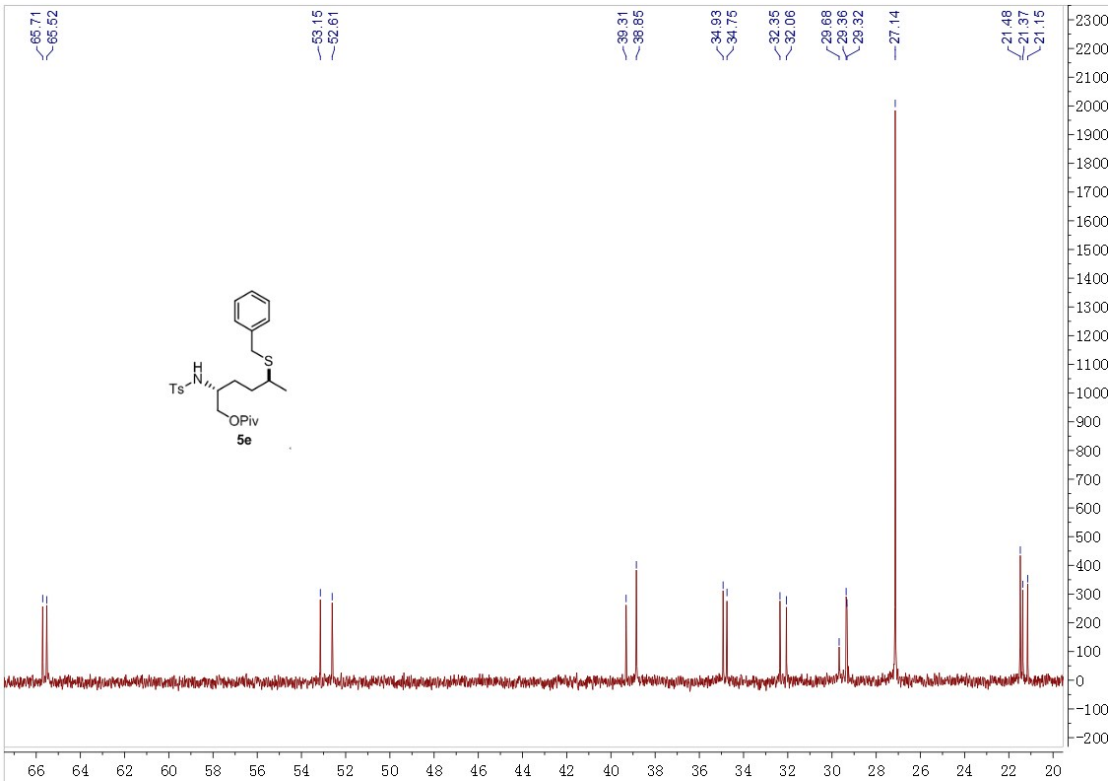

crude ¹H NMR
Ts
OPiv
5e
2.00
0.59
0.46
0.43
0.72
f1 (ppm)
isolated ¹H NMR
2.00
1.69
10.27
1.90
0.80
0.79
1.90
1.91
3.47
0.99
0.95
1.00
0.99
5.73
4.39
4.25
16.89
5.27

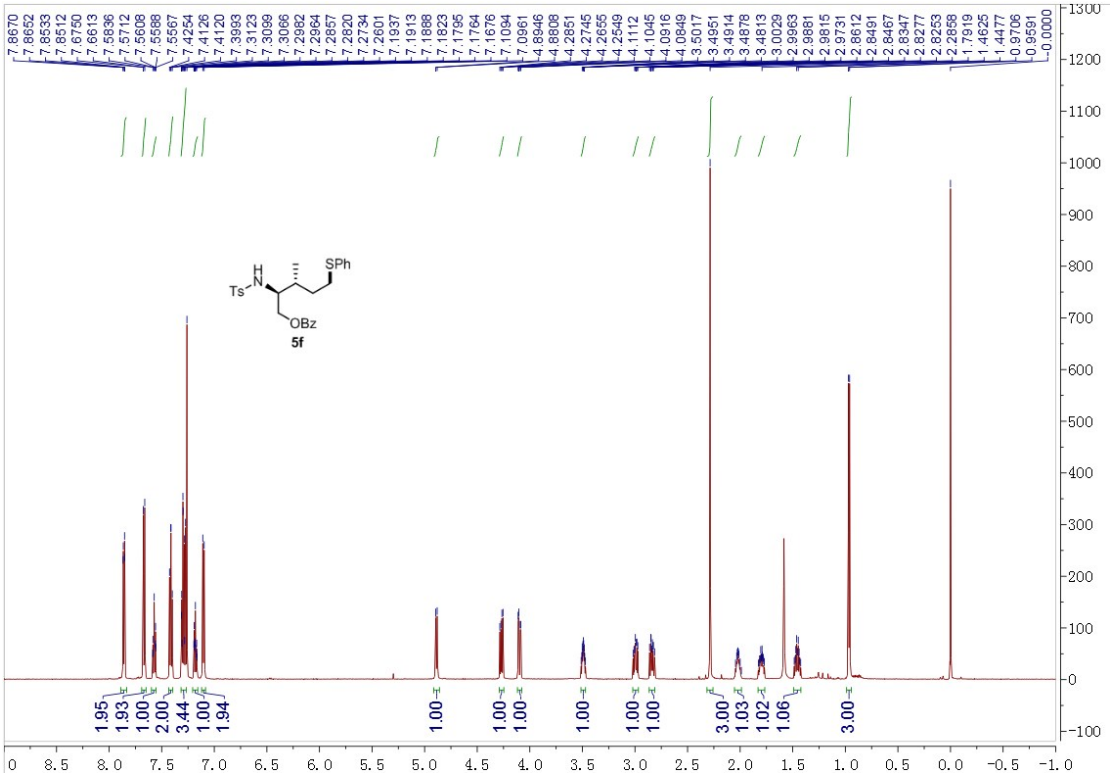

5e
2.00
1.69
10.27
1.90
0.80
0.79
1.90
1.91
3.47
0.99
0.95
1.00
0.99
5.73
4.39
4.25
16.89
5.27


5e
f1 (ppm)
2.00
1.69
10.27
1.90
0.80
0.79
1.90
1.91
3.47
0.99
0.95
1.00
0.99
5.73
4.39
4.25
16.89
5.27


5e


f1 (ppm)
5e


65.71
65.52
53.15
52.61
39.31
38.85
34.93
34.75
32.35
32.06
29.68
29.36
29.32
27.14
21.48
21.37
21.15
Ts
N
H
S
OPiv
5e


Ts
N
H
SPh
OBz
5f
1.95
1.93
1.00
2.00
3.44
1.00
1.94
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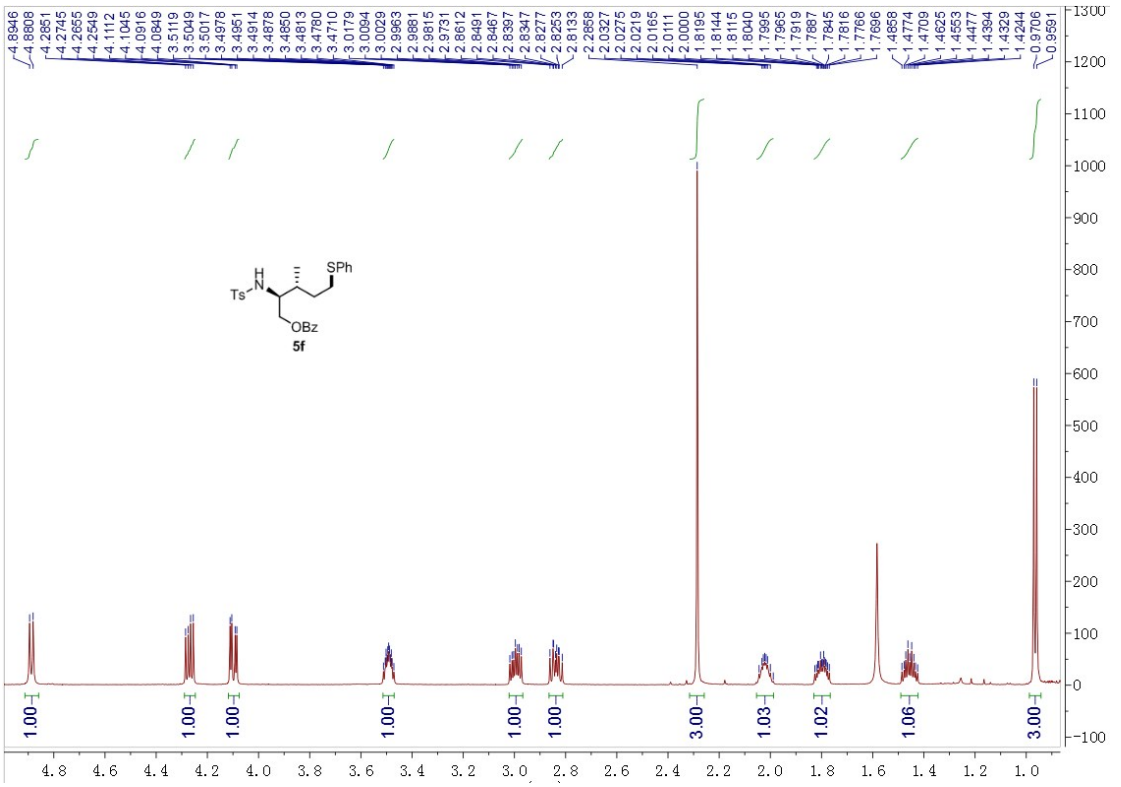
1.06
3.00


SPh
Ts
N
H
OBz
5f
1.00
1.00
1.00
1.00
1.00
1.00
3.00
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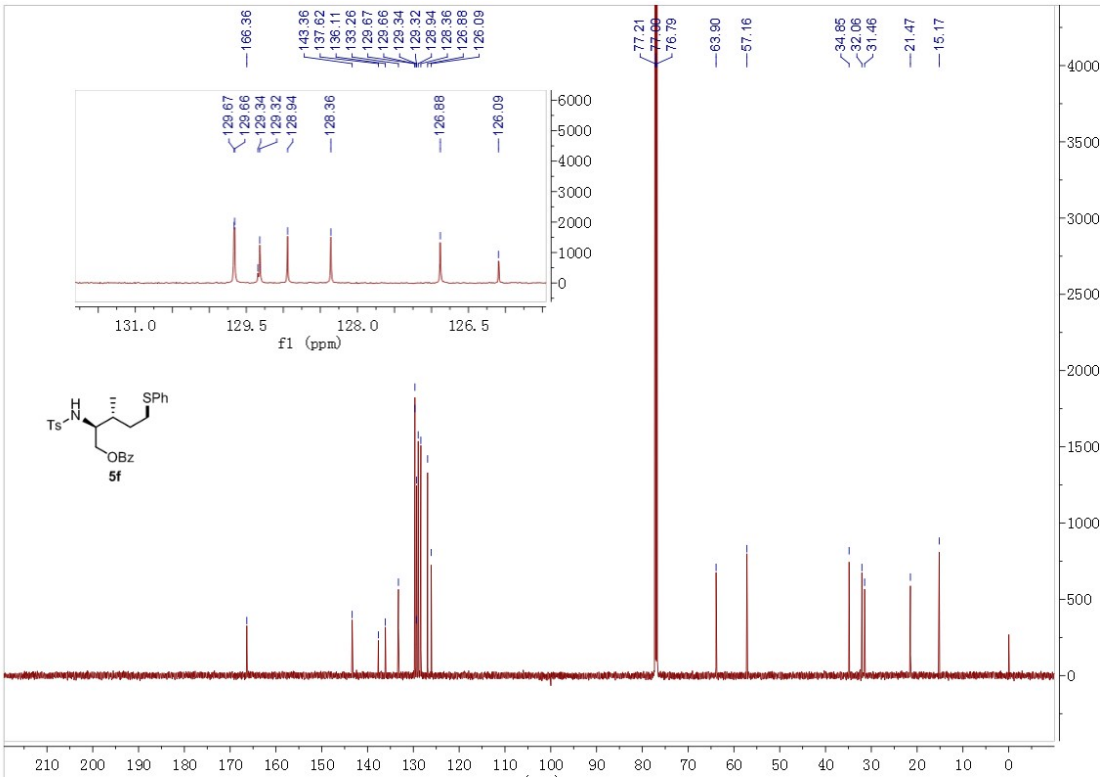
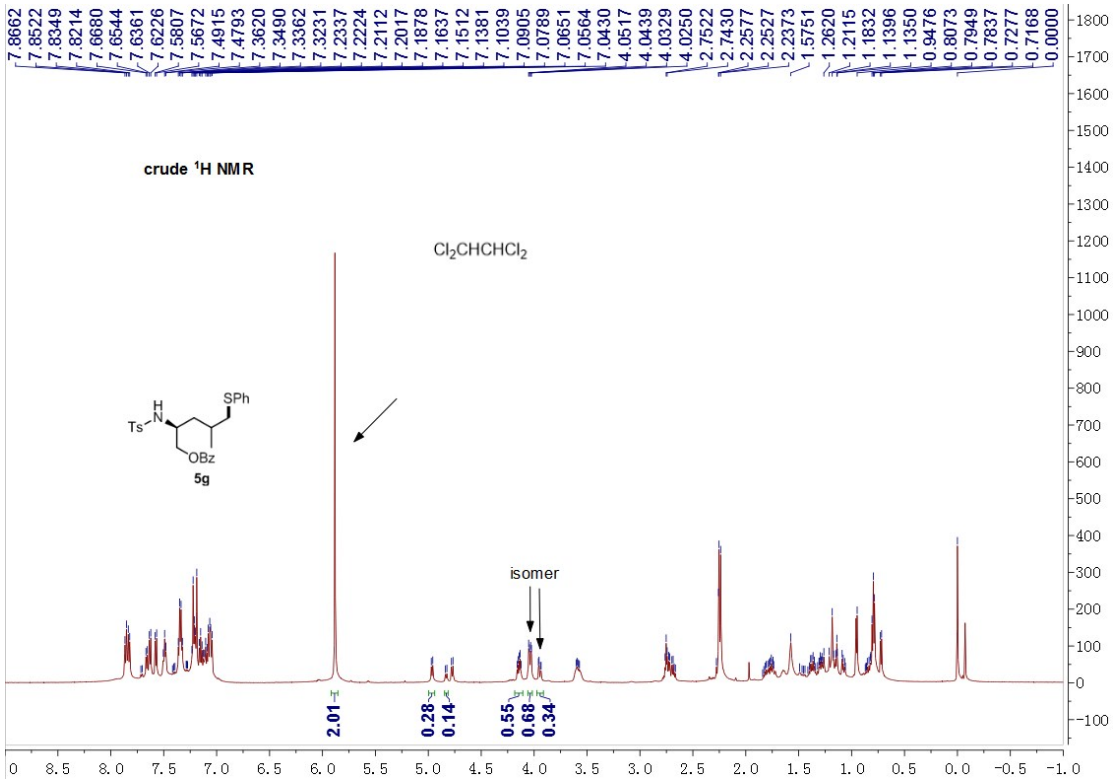
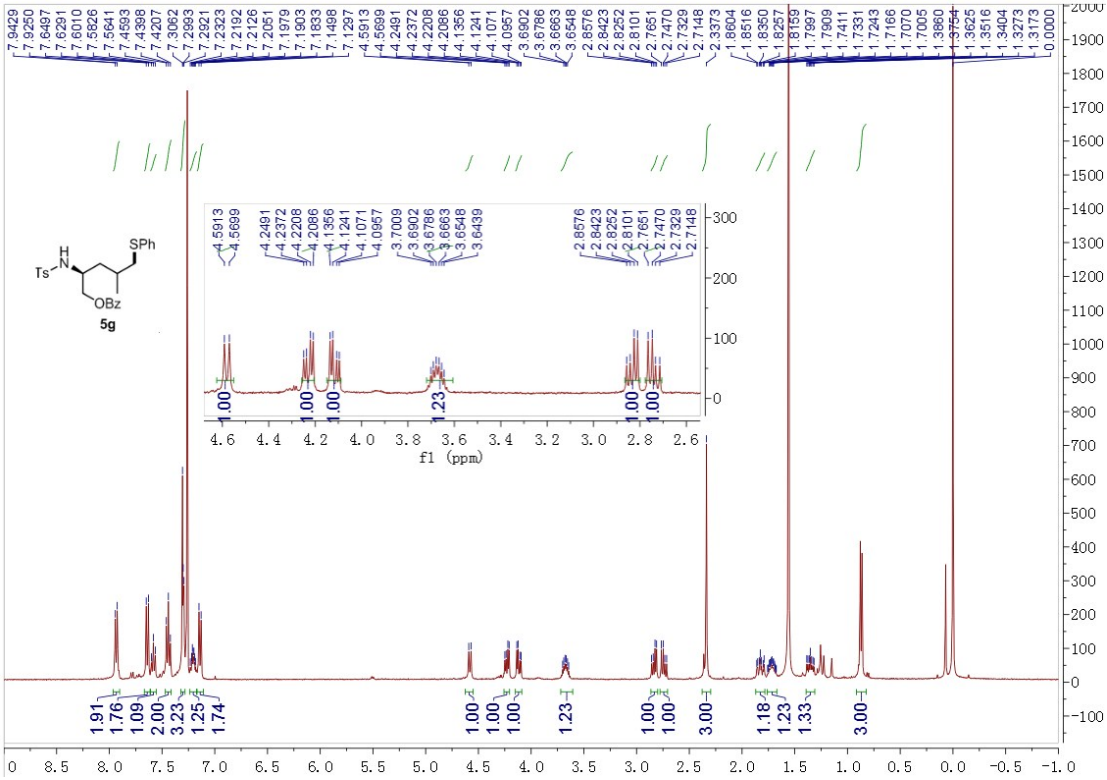
1.02
1.06
3.00


166.36
143.36
137.62
136.11
133.26
129.67
129.66
129.34
129.32
128.94
128.36
128.36
128.88
126.09
77.21
77.00
76.79
63.90
57.16
34.85
32.06
31.46
21.47
15.17
f1 (ppm)
SPh
Ts
N
H
OBz
5f


crude ^{1}H NMR
$Cl_2CHCHCl_2$
isomer
5g
2.01
0.28
0.14
0.55
0.68
0.34


5g
f1 (ppm)
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1.76
1.09
2.00
3.23
1.25
1.74
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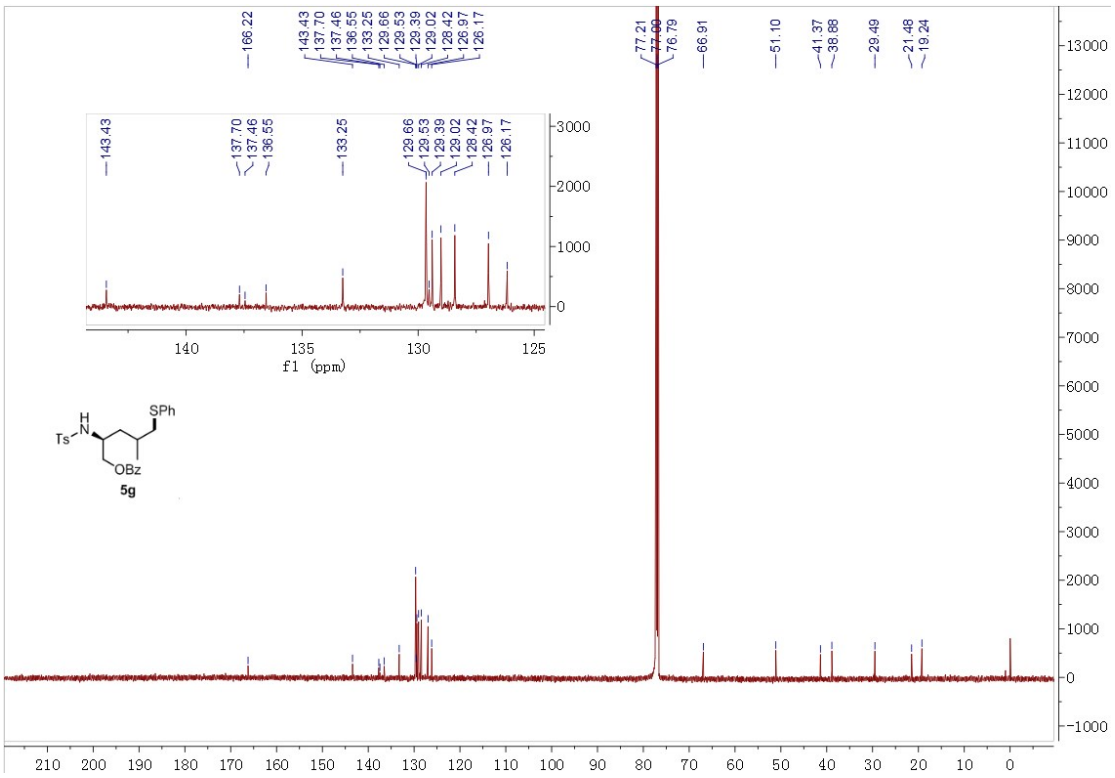
1.00
1.00
1.23
1.00
1.00
3.00
1.18
1.23
1.33
3.00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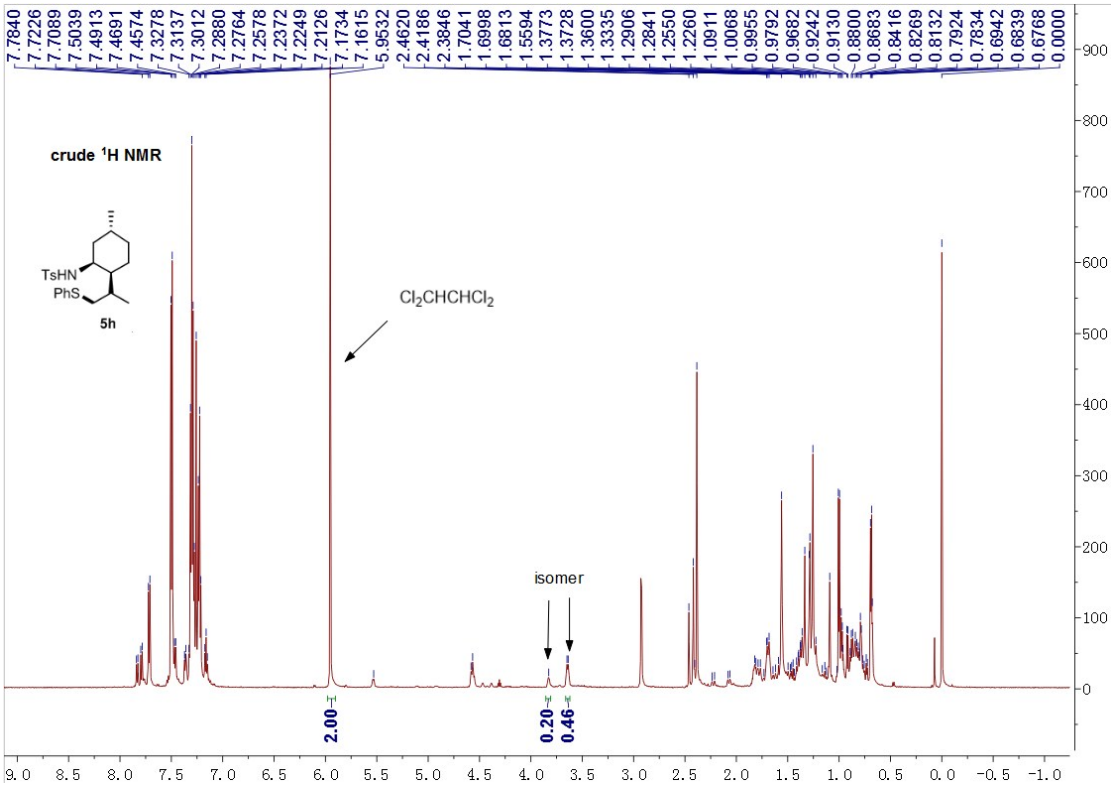
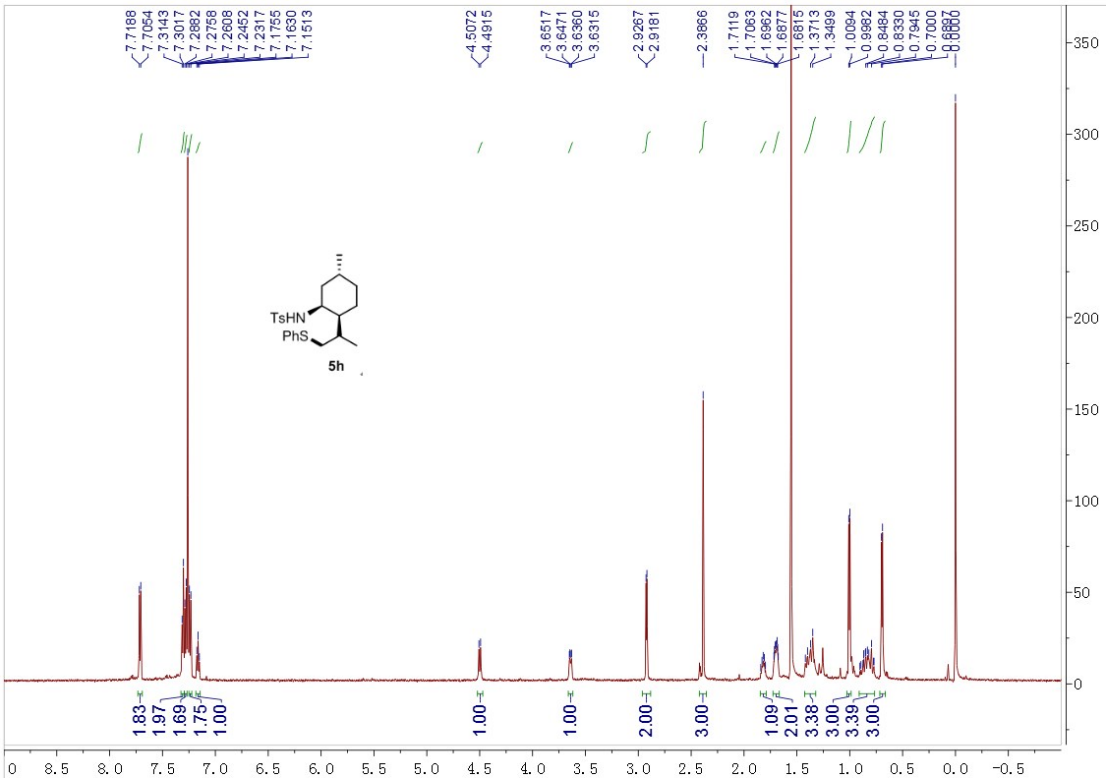
143.43
137.70
137.46
136.55
133.25
129.66
129.53
129.39
129.02
128.42
126.97
126.17
77.21
77.00
76.79
66.91
51.10
41.37
38.88
29.49
21.48
19.24
f1 (ppm)
SPh
Ts
N
H
OBz
5g


crude ¹H NMR
TsHN
PhS
5h
Cl2CHCHCl2
isomer
2.00
0.20
0.46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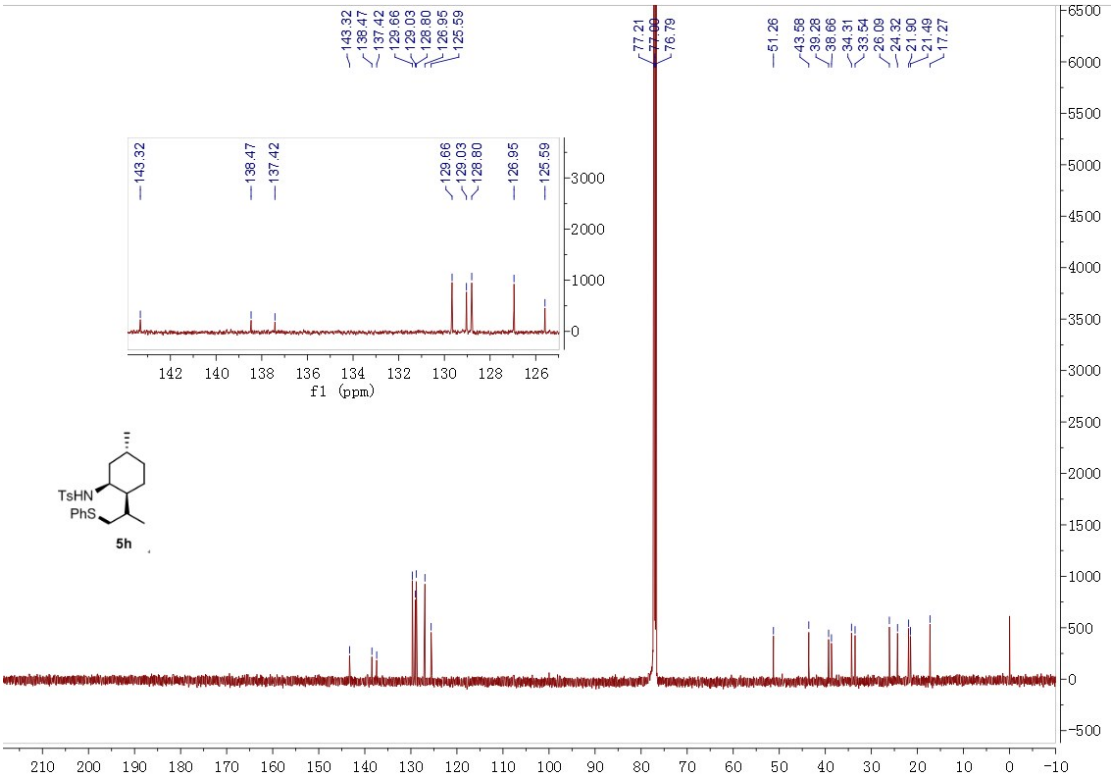
7.7054
7.3143
7.3017
7.2882
7.2758
7.2608
7.2452
7.2317
7.1755
7.1630
7.1513
4.5072
4.4915
3.6517
3.6471
3.6360
3.6315
2.9267
2.9181
2.3866
1.7119
1.7063
1.6962
1.6877
1.6815
1.3713
1.3499
1.0094
0.9982
0.8484
0.8330
0.7945
0.7000
TsHN
PhS
5h
1.83
1.97
1.69
1.75
1.00
1.00
1.00
2.00
3.00
1.09
2.01
3.38
3.00
3.39
3.00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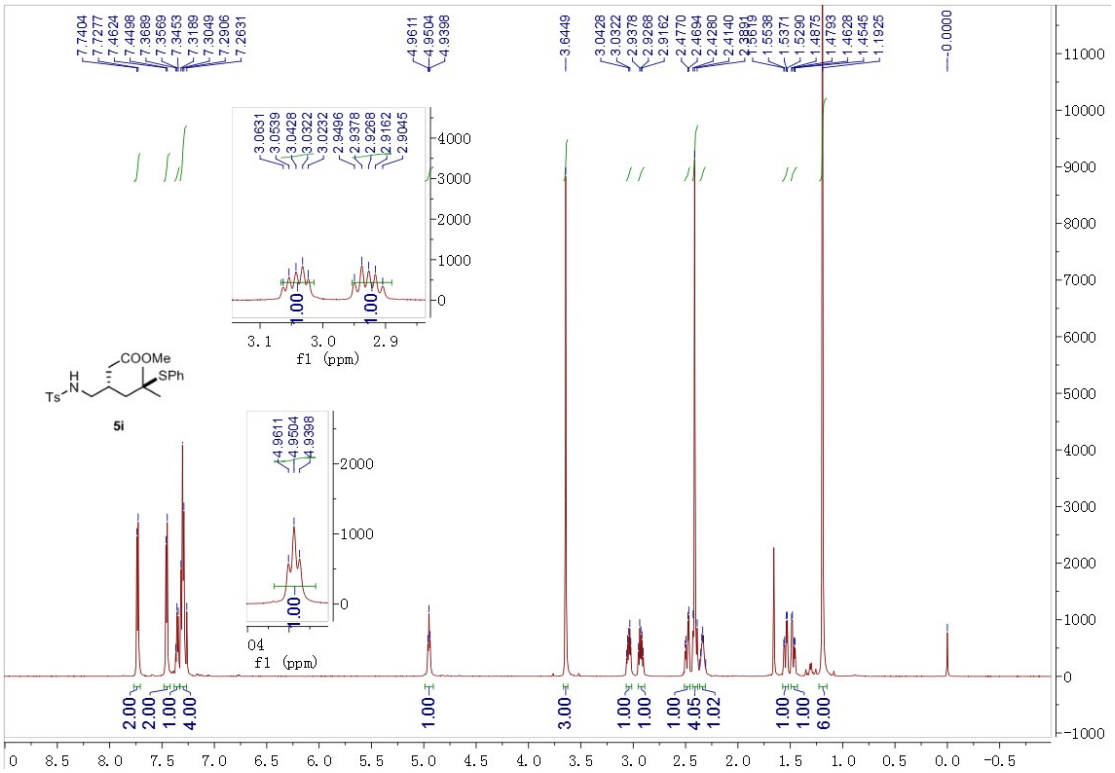
138.47
137.42
129.66
129.03
128.80
126.95
125.59
77.21
77.00
76.79
51.26
43.58
39.28
38.66
34.31
33.54
26.09
24.32
21.90
21.49
17.27
f1 (ppm)
TsHN
PhS
5h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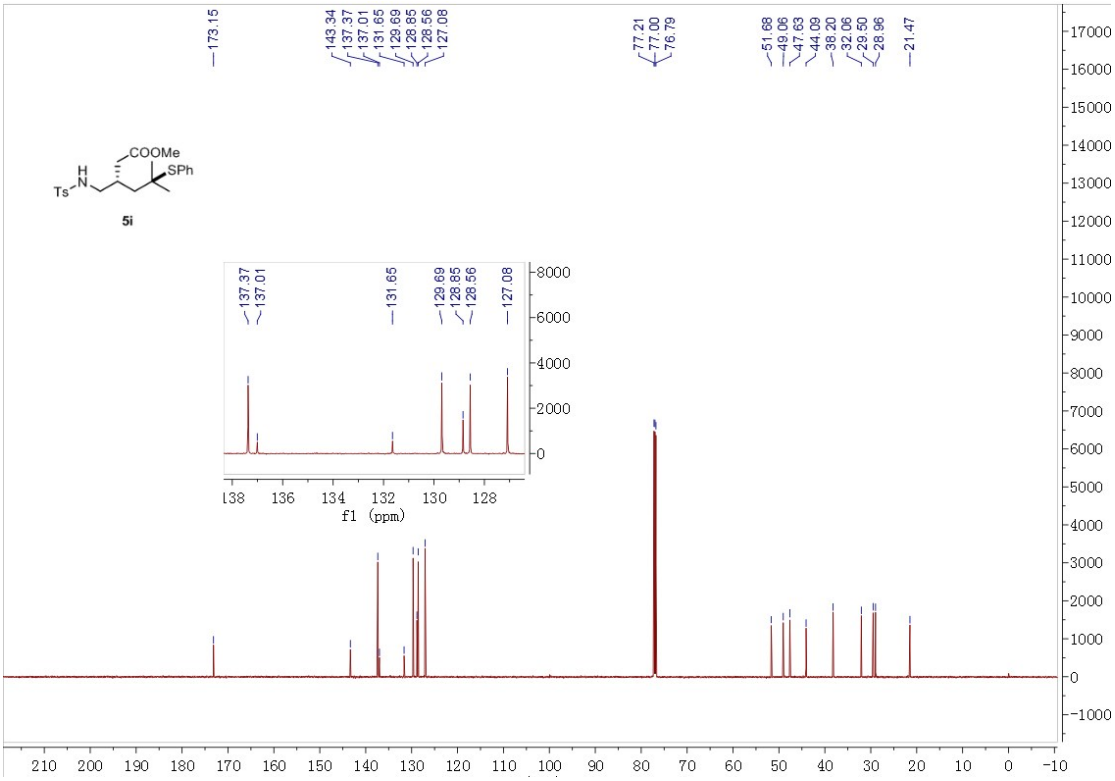
7.7277
7.4624
7.4498
7.3689
7.3569
7.3453
7.3189
7.3049
7.2906
7.2631
4.9611
4.9504
4.9398
3.6449
3.0428
3.0322
2.9378
2.9268
2.9162
2.4770
2.4694
2.4280
2.4140
1.5538
1.5371
1.5290
1.4875
1.4793
1.4628
1.4545
1.1925
0.0000
COOMe
SPh
Ts
H
N
5i
f1 (ppm)
2.00
2.00
1.00
4.00
1.00
3.00
1.00
1.00
1.00
4.05
1.02
1.00
1.00
6.00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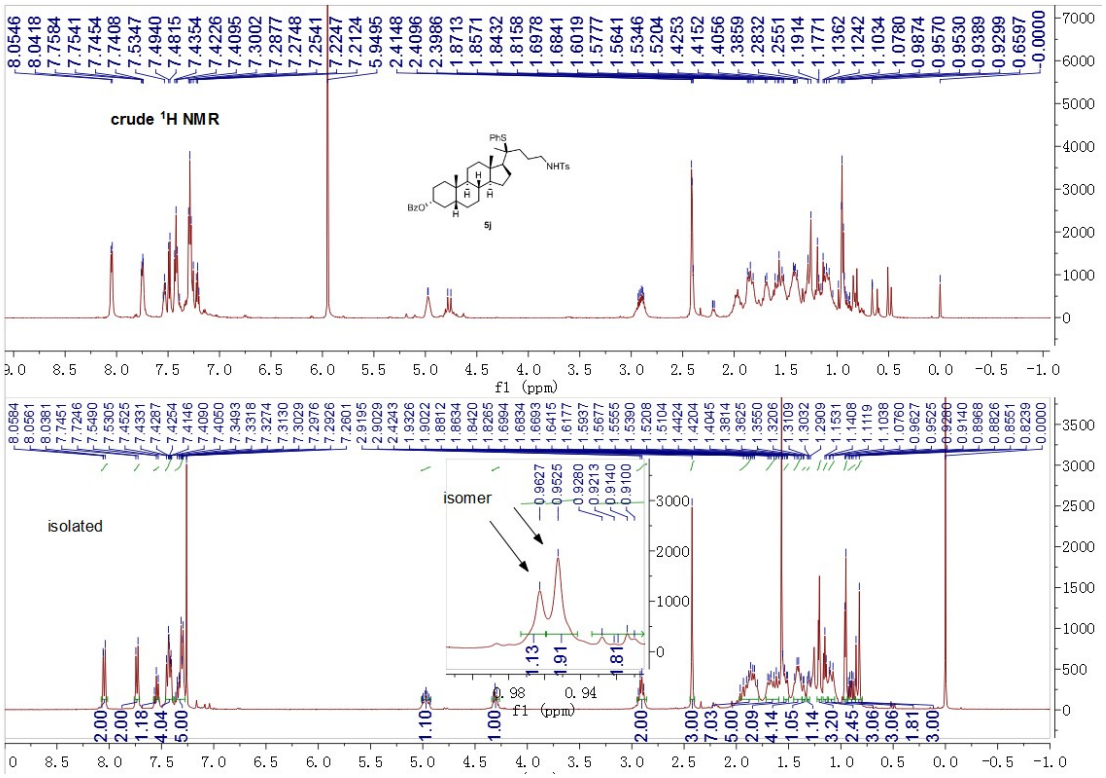
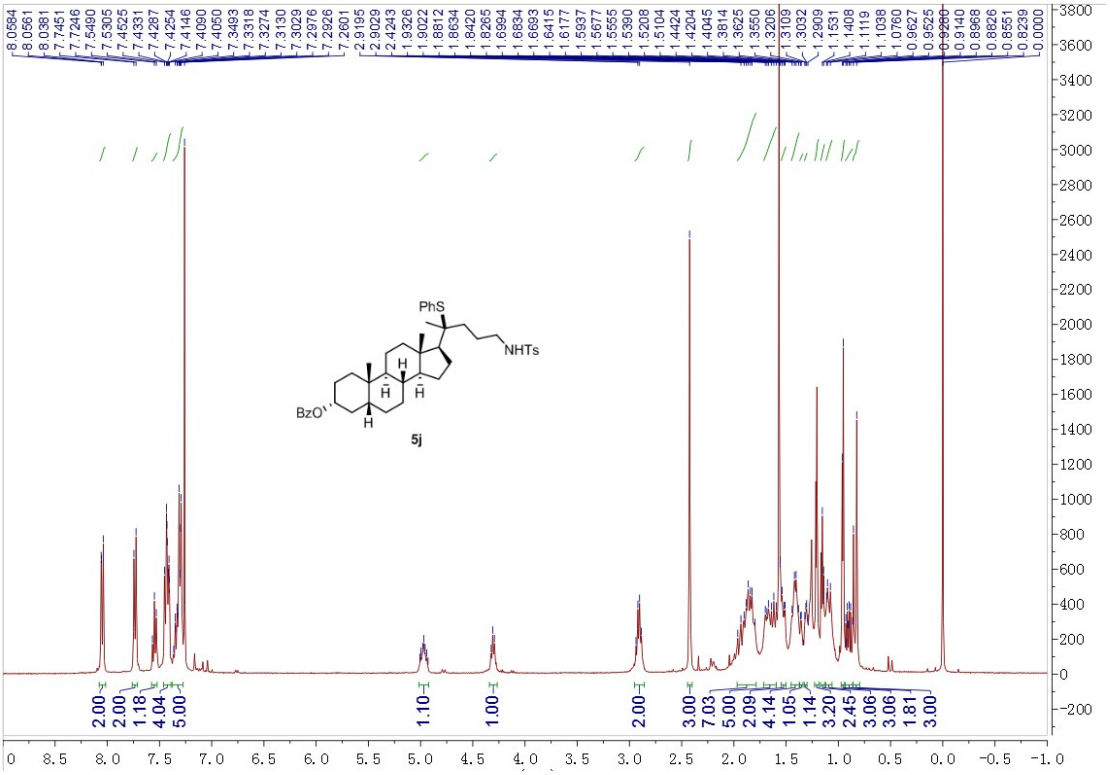
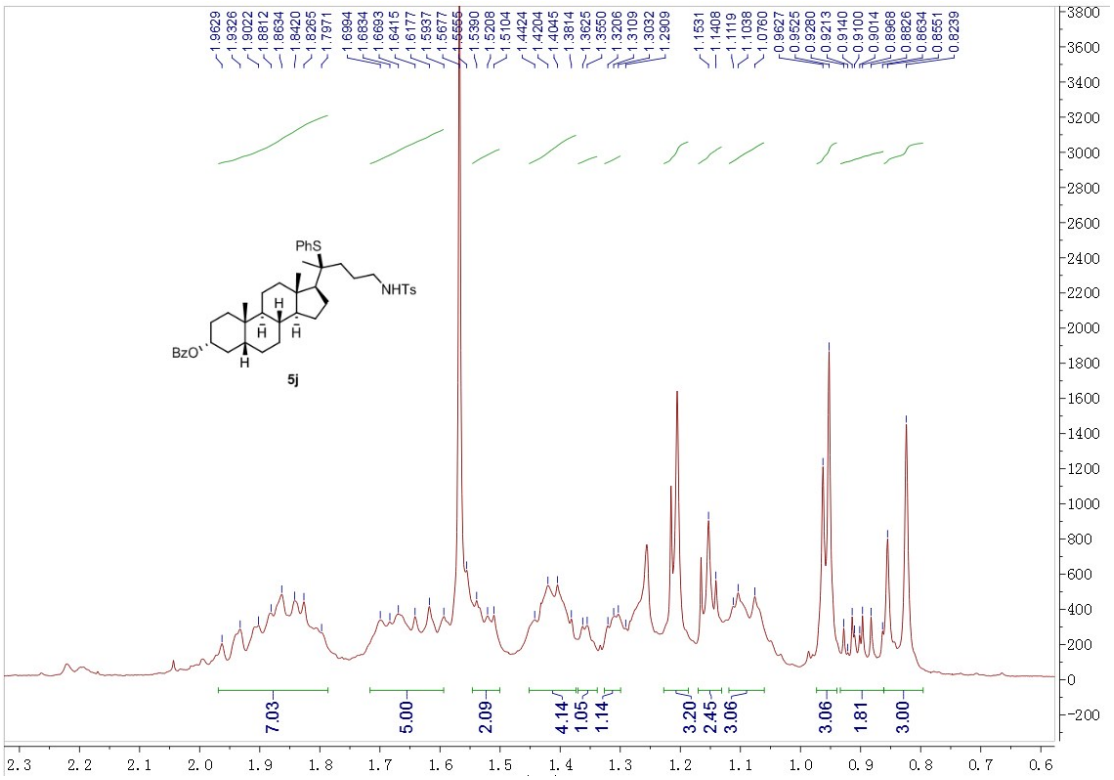
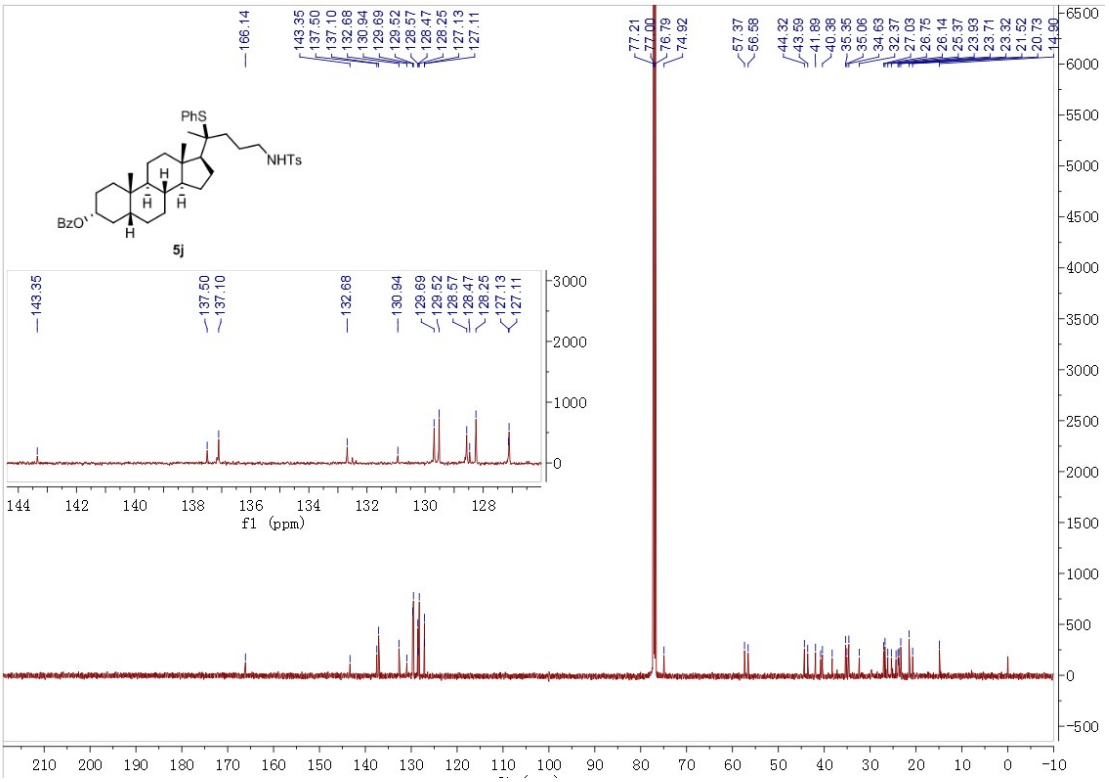
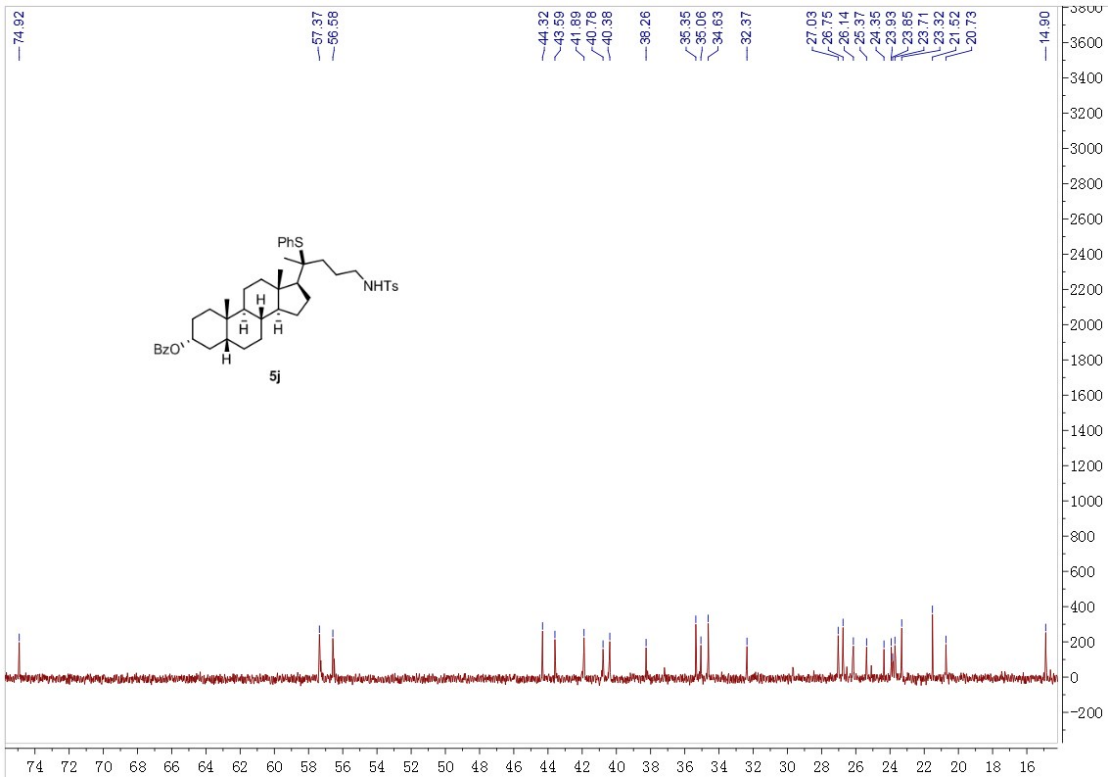
143.34
137.37
137.01
131.65
129.69
128.85
128.56
127.08
77.21
77.00
76.79
51.68
49.06
47.63
44.09
38.20
32.06
29.50
28.96
21.47
COOMe
SPh
Ts
H
N
5i
f1 (ppm)

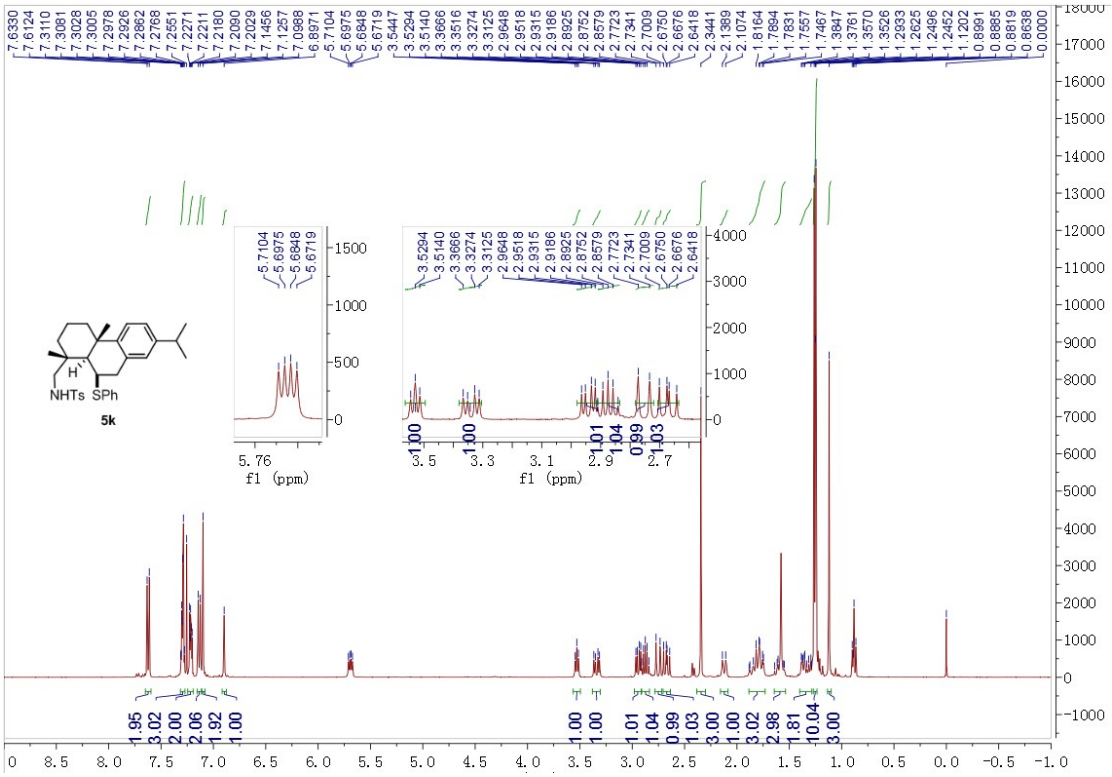

crude ¹H NMR
PhS
NHTs
BzO
5j
f1 (ppm)
isolated
isomer

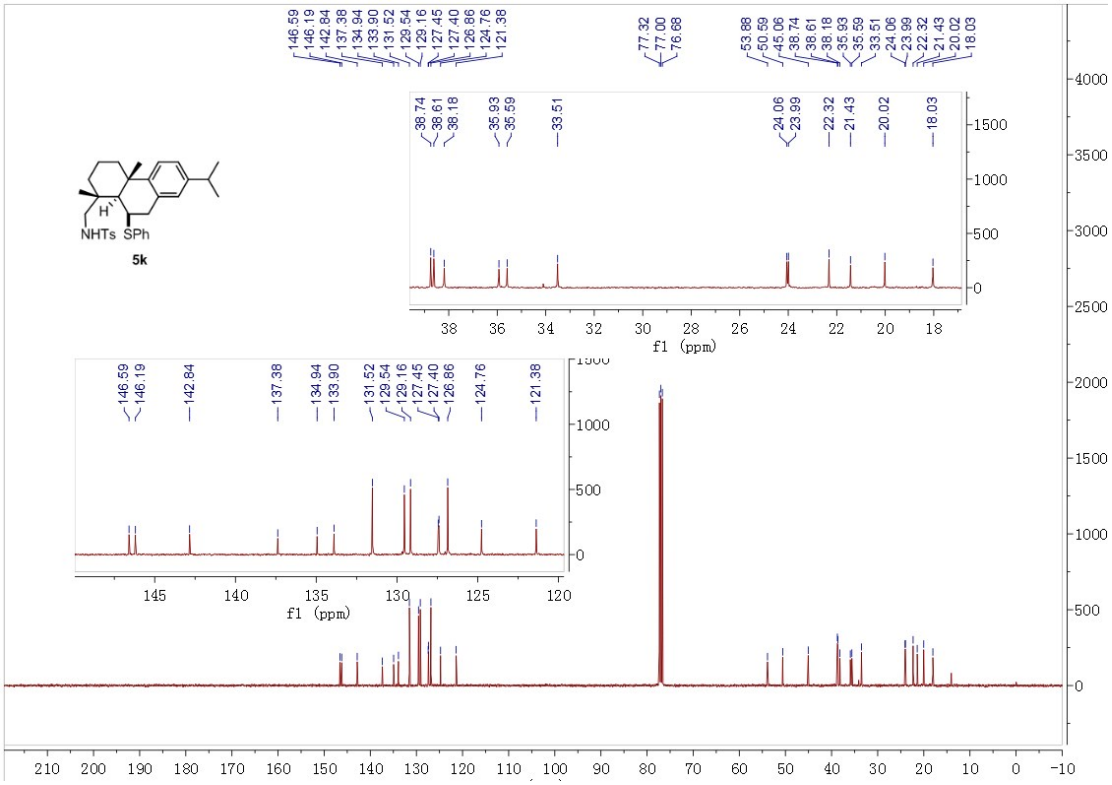

PhS
NHTs
BzO
5j

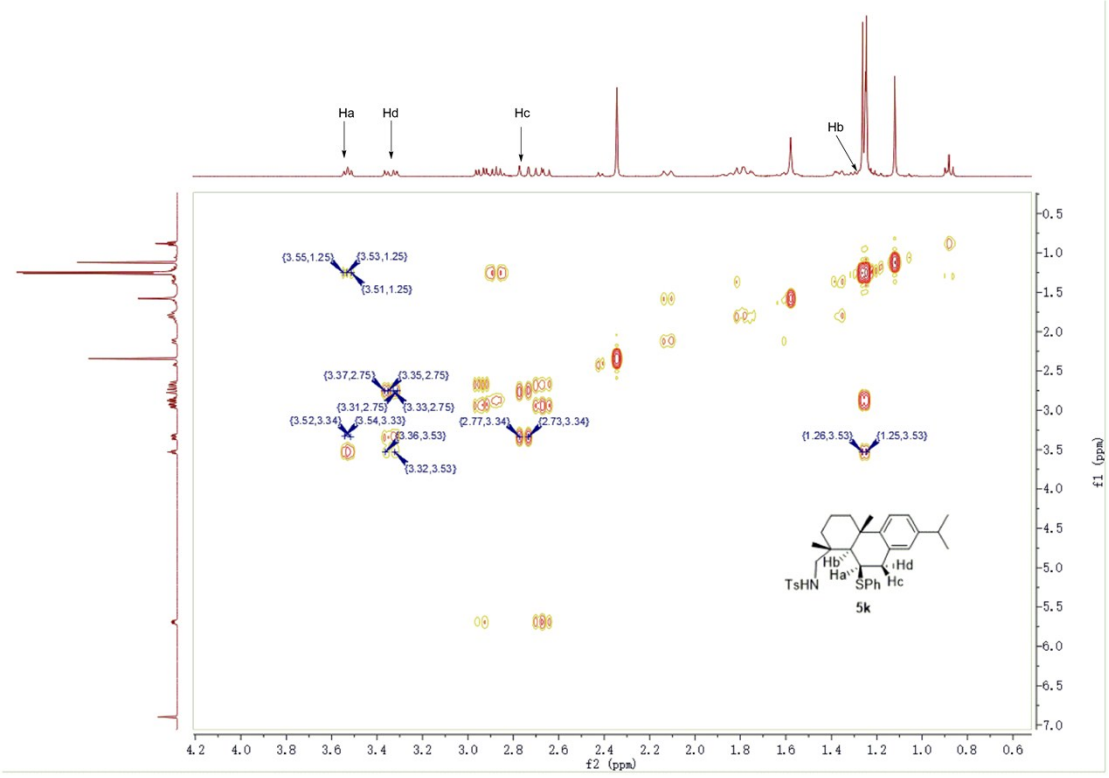

PhS
NHTs
BzO
5j
7.03
5.00
2.09
4.14
1.05
1.14
3.20
2.45
3.06
3.06
1.81
3.00

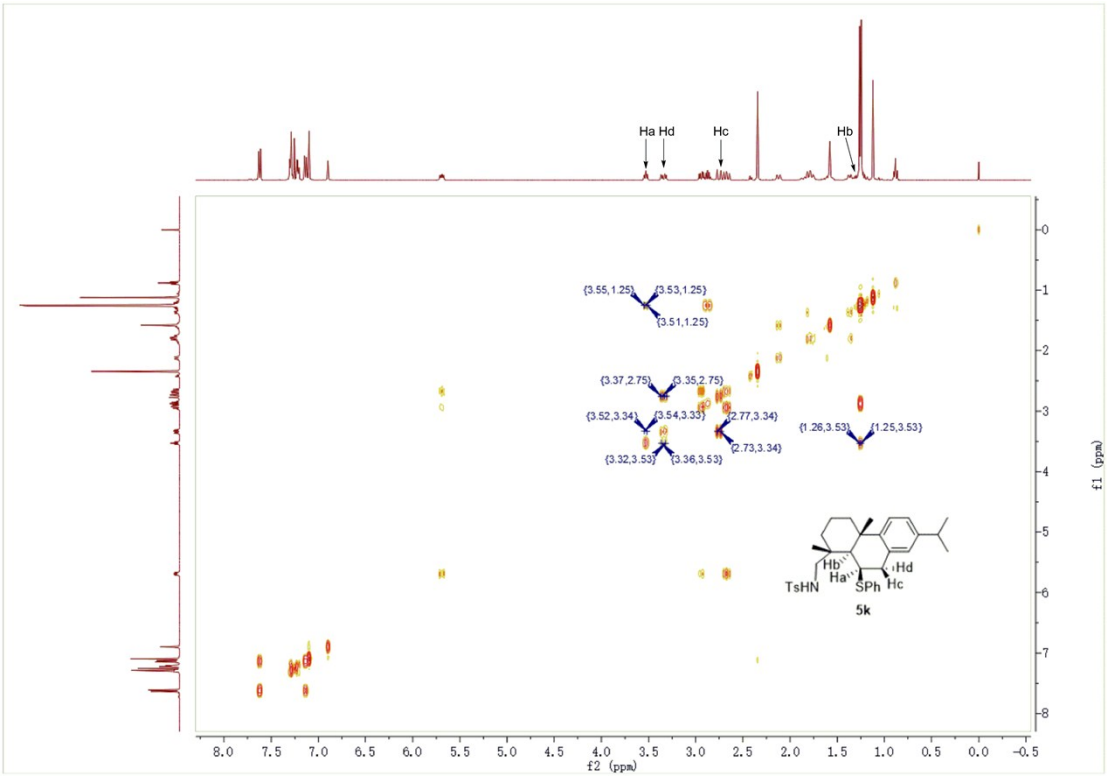

PhS
NHTs
BzO
5j
f1 (ppm)

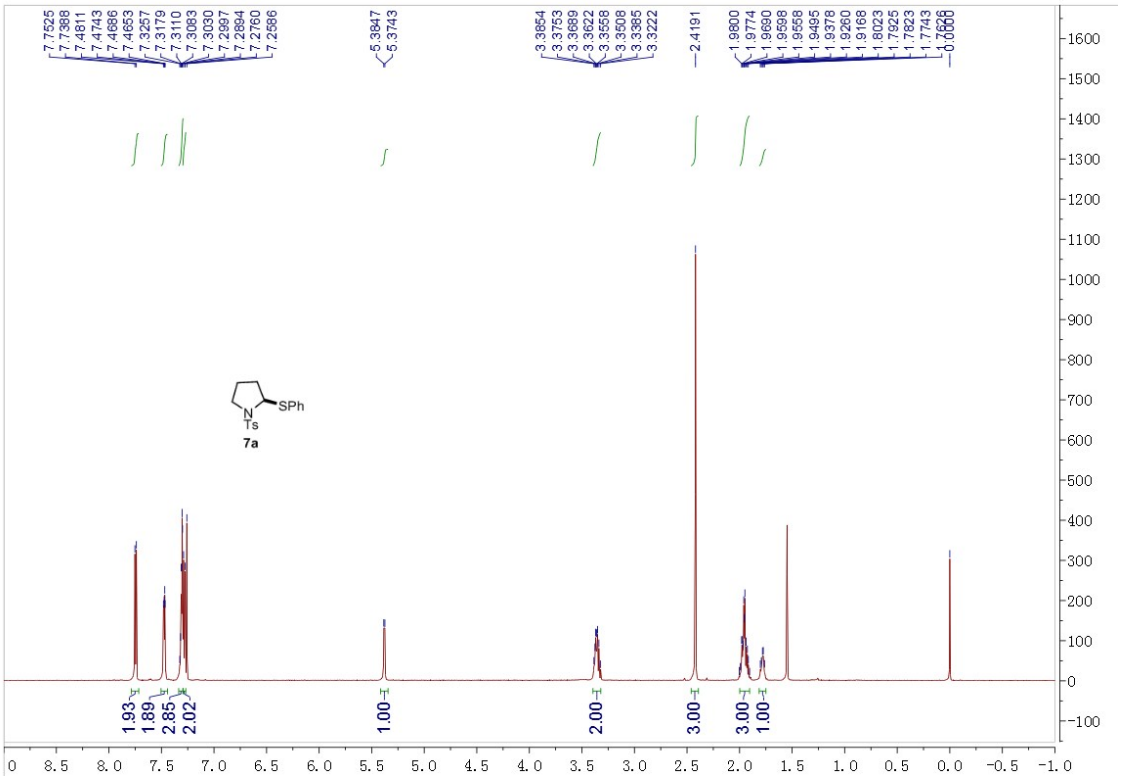

PhS
NHTs
BzO
5j


NHTs SPh
5k
f1 (ppm)
f1 (ppm)


5k
NHTs SPh
f1 (ppm)


Ha
Hd
Hc
Hb
f2 (ppm)
f1 (ppm)
5k


Ha Hd
Hc
Hb
{3.55,1.25}
{3.53,1.25}
{3.51,1.25}
{3.37,2.75}
{3.35,2.75}
{3.52,3.34}
{3.54,3.33}
{2.77,3.34}
{2.73,3.34}
{3.32,3.53}
{3.36,3.53}
{1.26,3.53}
{1.25,3.53}
Hb
Ha
Hd
TsHN
SPh
Hc
5k
f2 (ppm)
f1 (ppm)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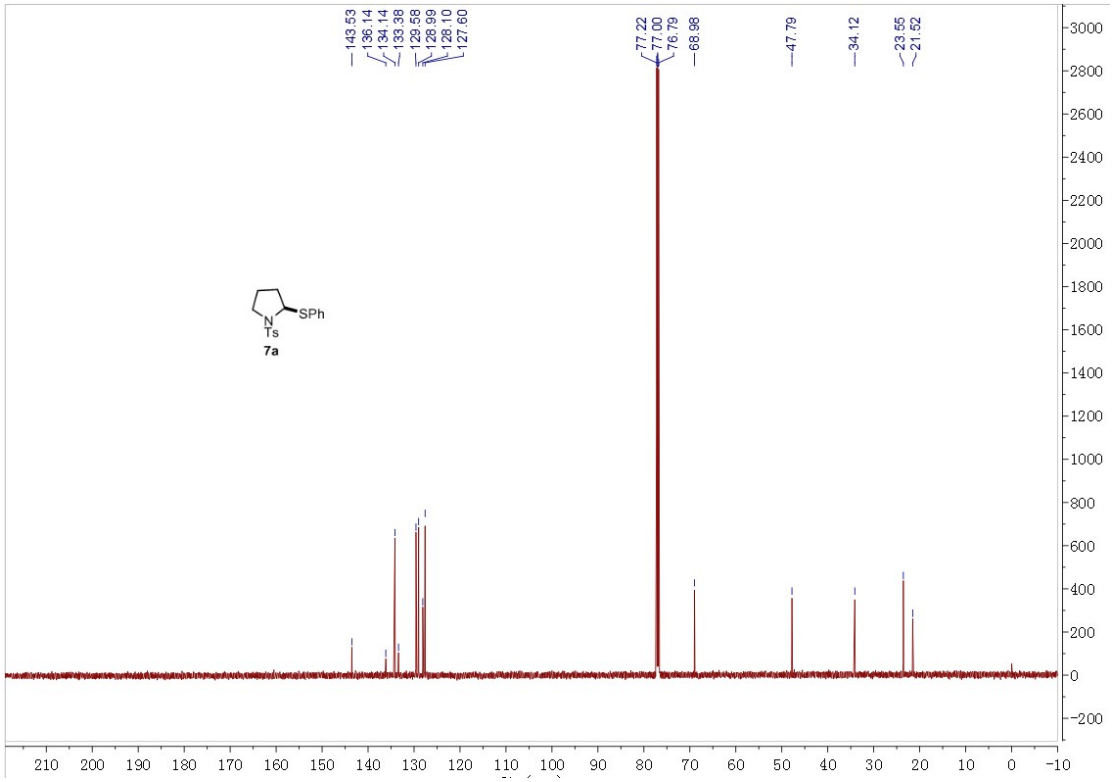
7.4811
7.4743
7.4686
7.4653
7.3257
7.3179
7.3110
7.3083
7.3030
7.2997
7.2894
7.2760
7.2686
5.3847
5.3743
3.3854
3.3753
3.3689
3.3622
3.3558
3.3508
3.3385
3.3222
2.4191
1.9800
1.9774
1.9690
1.9598
1.9558
1.9495
1.9378
1.9260
1.9168
1.8023
1.7925
1.7823
1.7743
1.7638
0.0000
SPh
N
Ts
7a
1.93
1.89
2.85
2.02
1.00
2.00
3.00
3.00
1.00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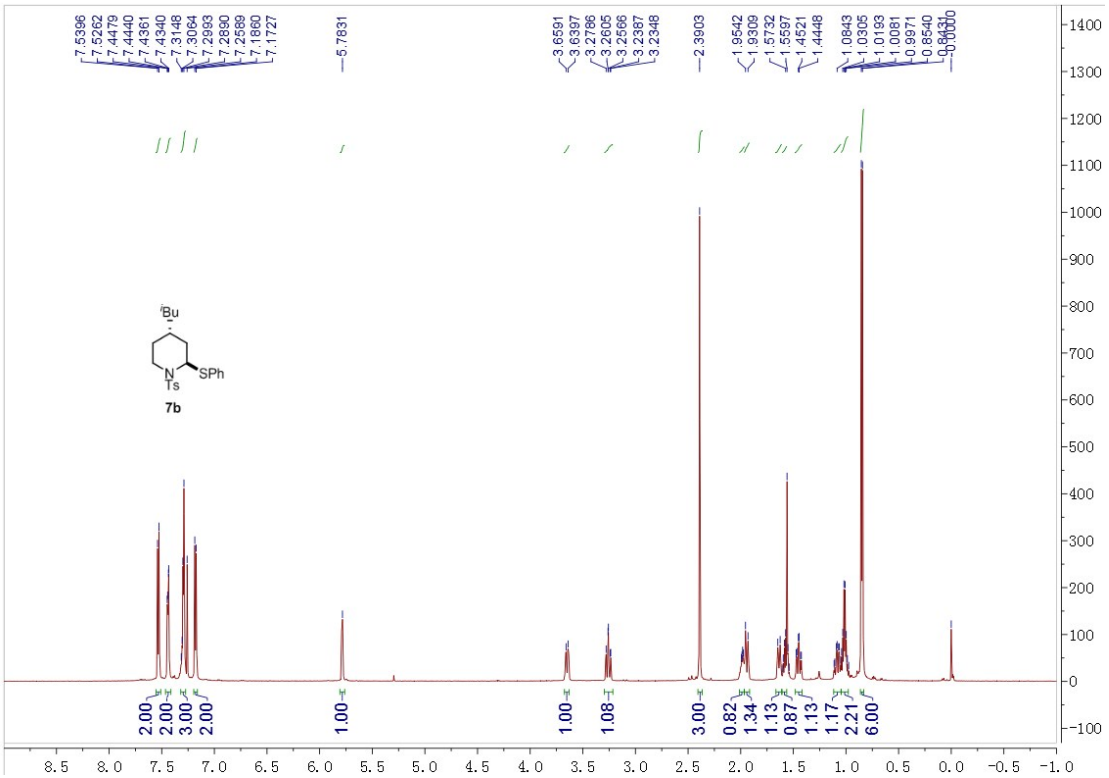
136.14
134.14
133.38
129.58
128.99
128.10
127.60
77.22
77.00
76.79
68.98
47.79
34.12
23.55
21.52
SPh
N
Ts
7a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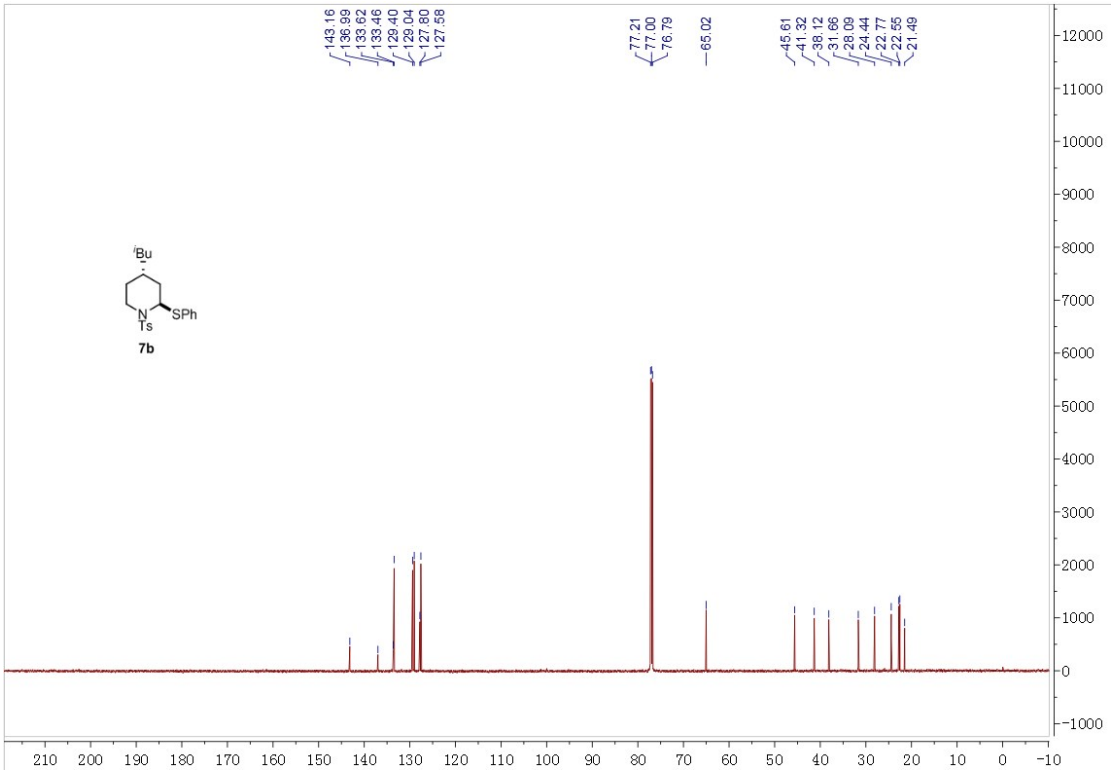
7.4479
7.4440
7.4361
7.4340
7.3148
7.3064
7.2993
7.2890
7.2589
7.1860
7.1727
5.7831
3.6591
3.6397
3.2786
3.2605
3.2566
3.2387
3.2348
2.3903
1.9542
1.9309
1.5732
1.5597
1.4521
1.4448
1.0843
1.0305
1.0193
1.0081
0.9971
0.8540
0.0000
tBu
SPh
N
Ts
7b
2.00
2.00
3.00
2.00
1.00
1.00
1.08
3.00
0.82
1.34
1.13
0.87
1.13
1.17
2.21
6.00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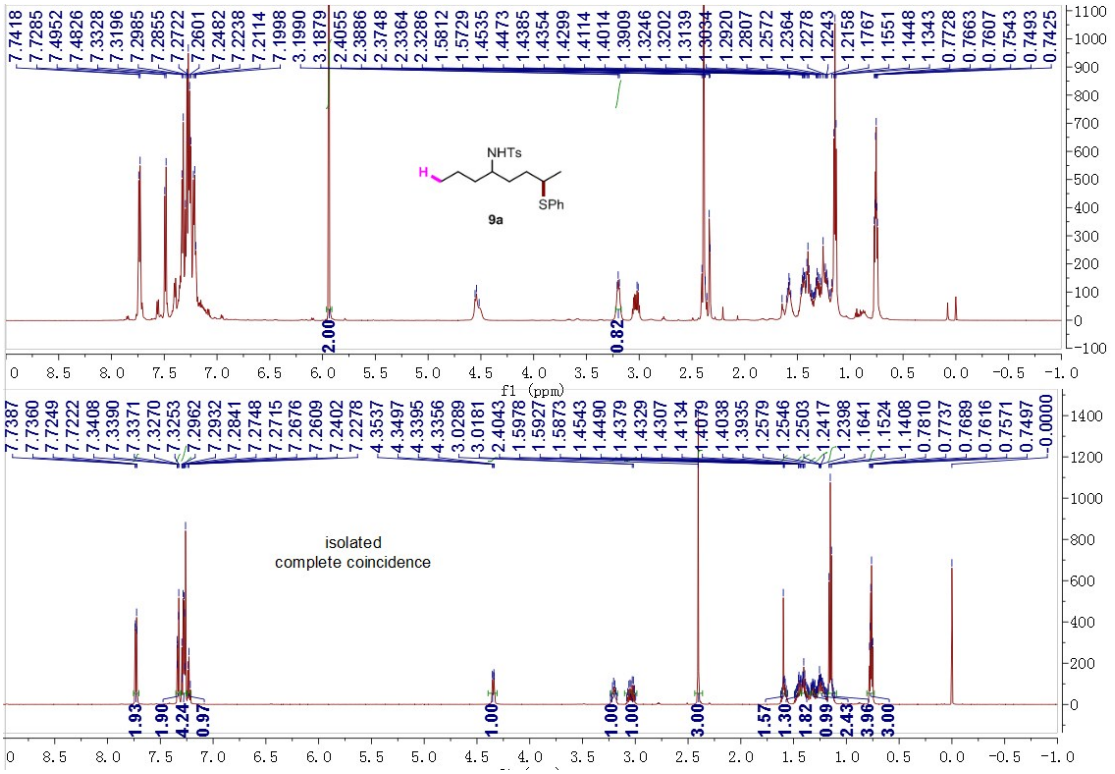
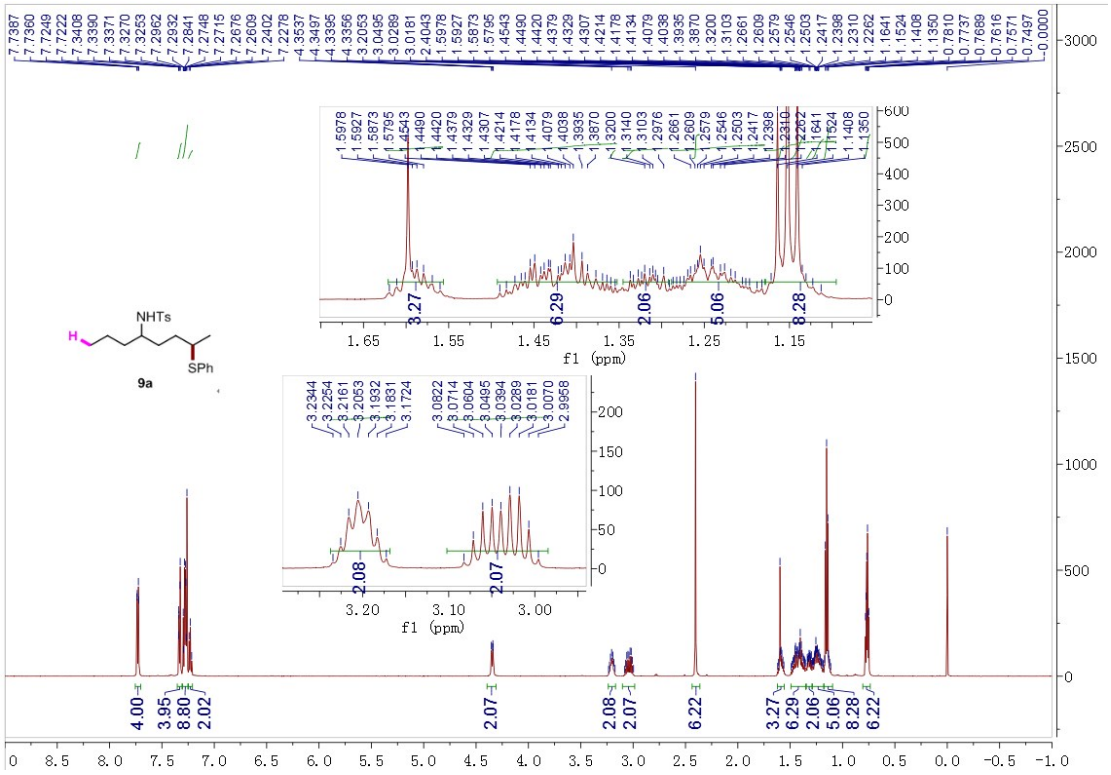
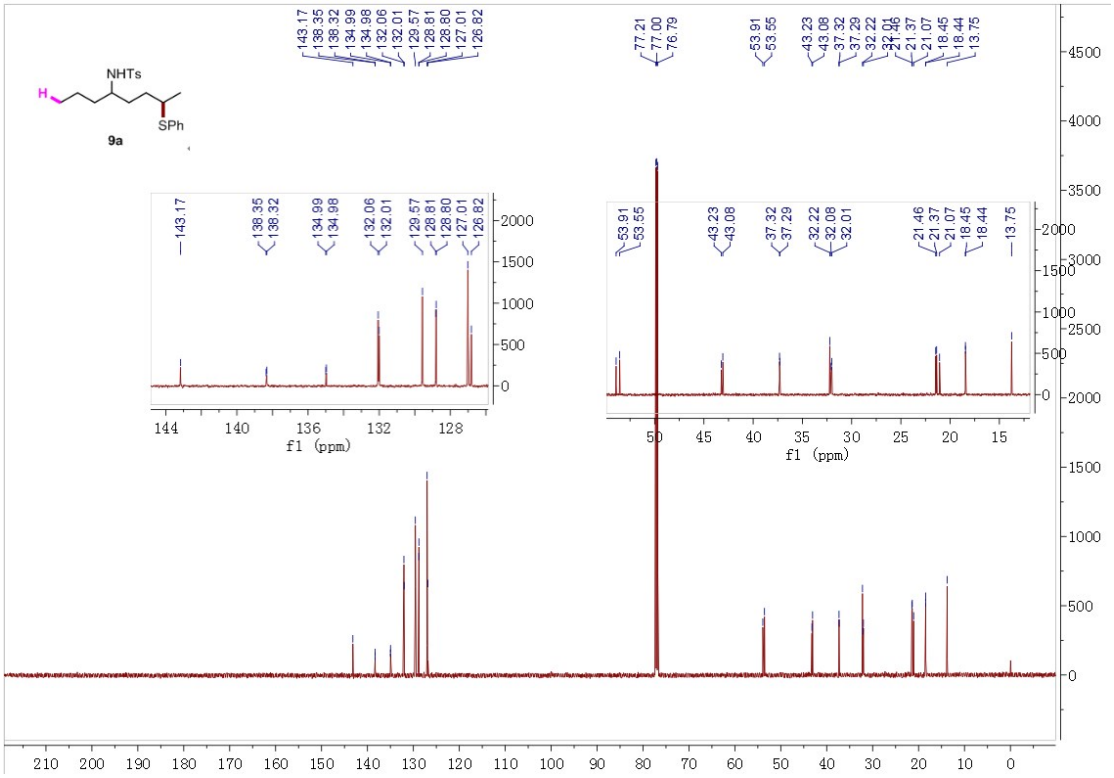
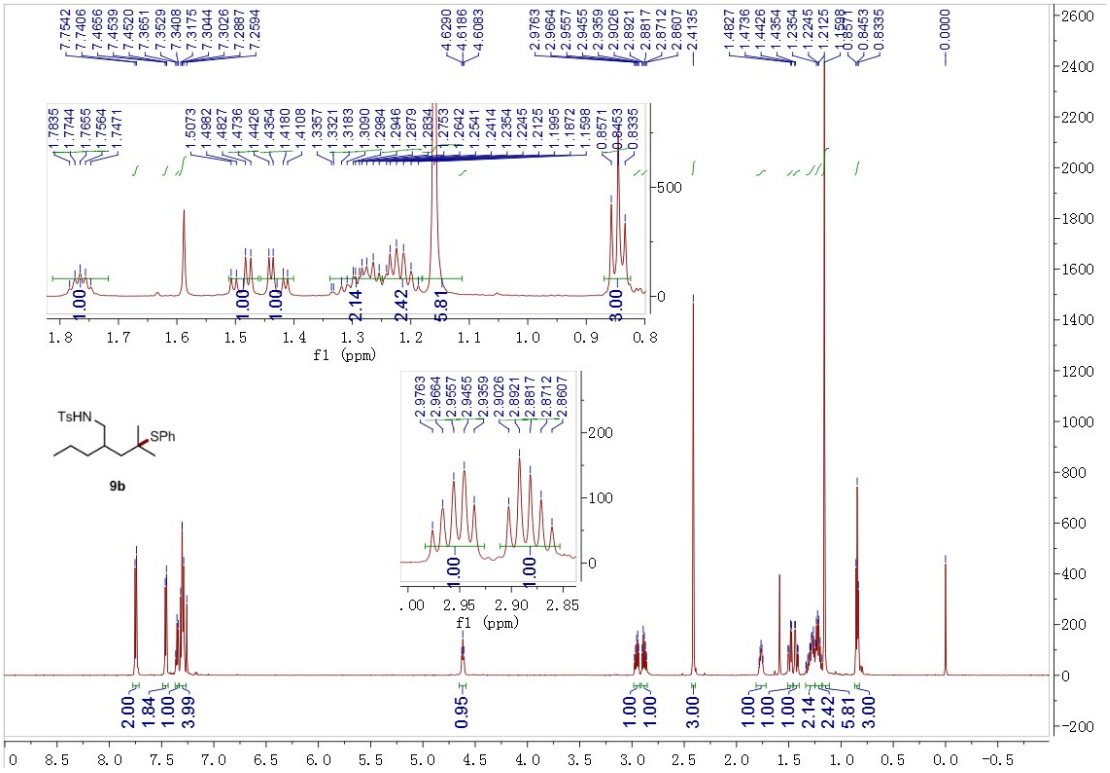
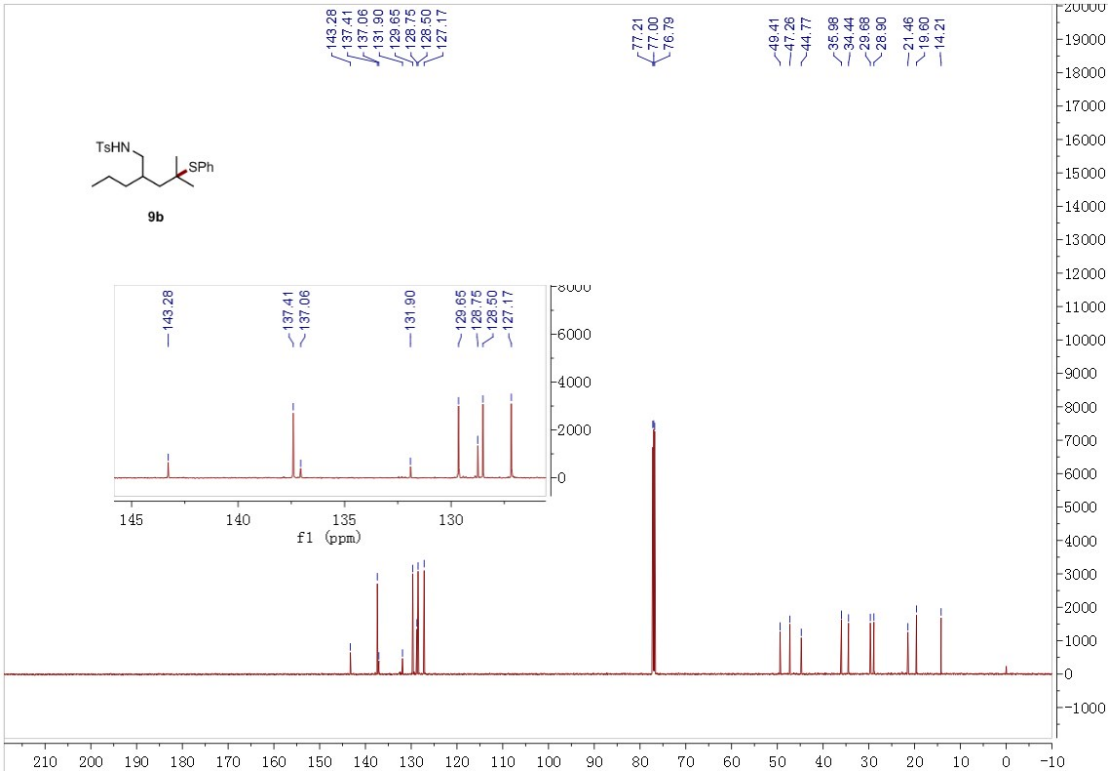
129.04
127.80
127.58
77.21
77.00
76.79
65.02
45.61
41.32
38.12
31.66
28.09
24.44
22.77
22.55
21.49
tBu
N
Ts
SPh
7b

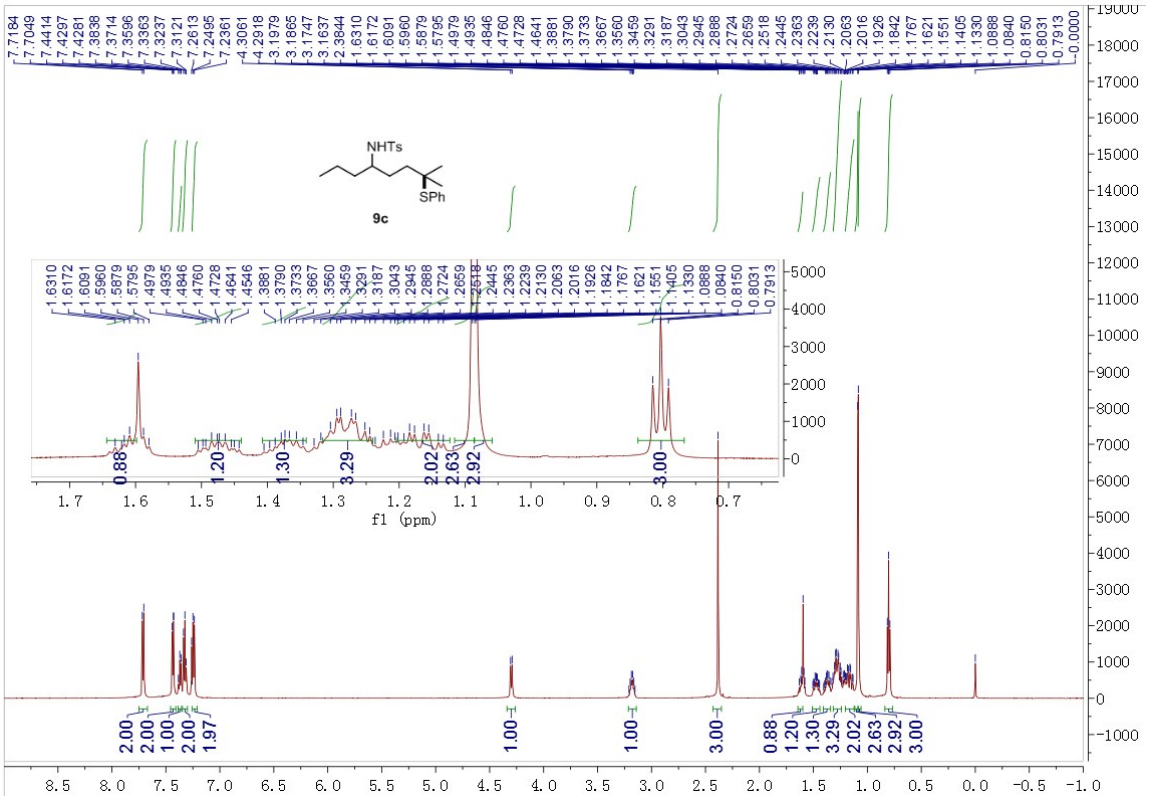

NHTs
H
SPh
9a
2.00
0.82
f1 (ppm)
isolated
complete coincidence
1.93
1.90
4.24
0.97
1.00
1.00
1.00
3.00
1.57
1.30
1.82
0.99
2.43
3.96
3.00

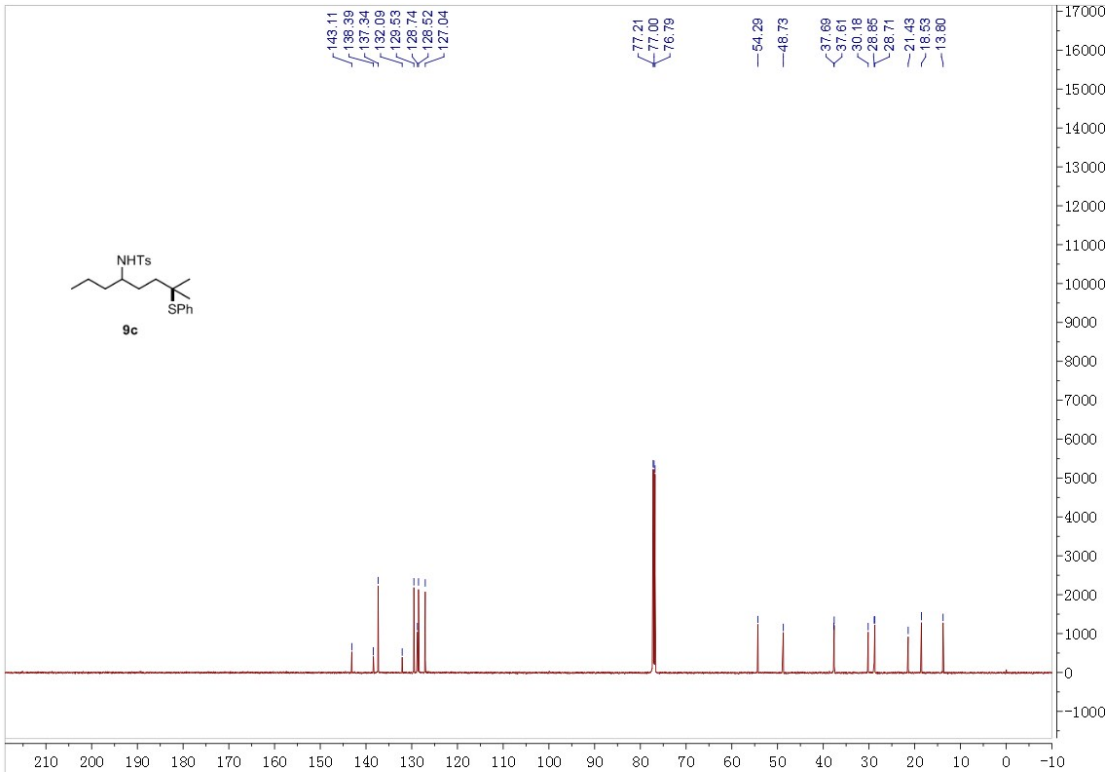

NHTs
H
SPh
9a
f1 (ppm)

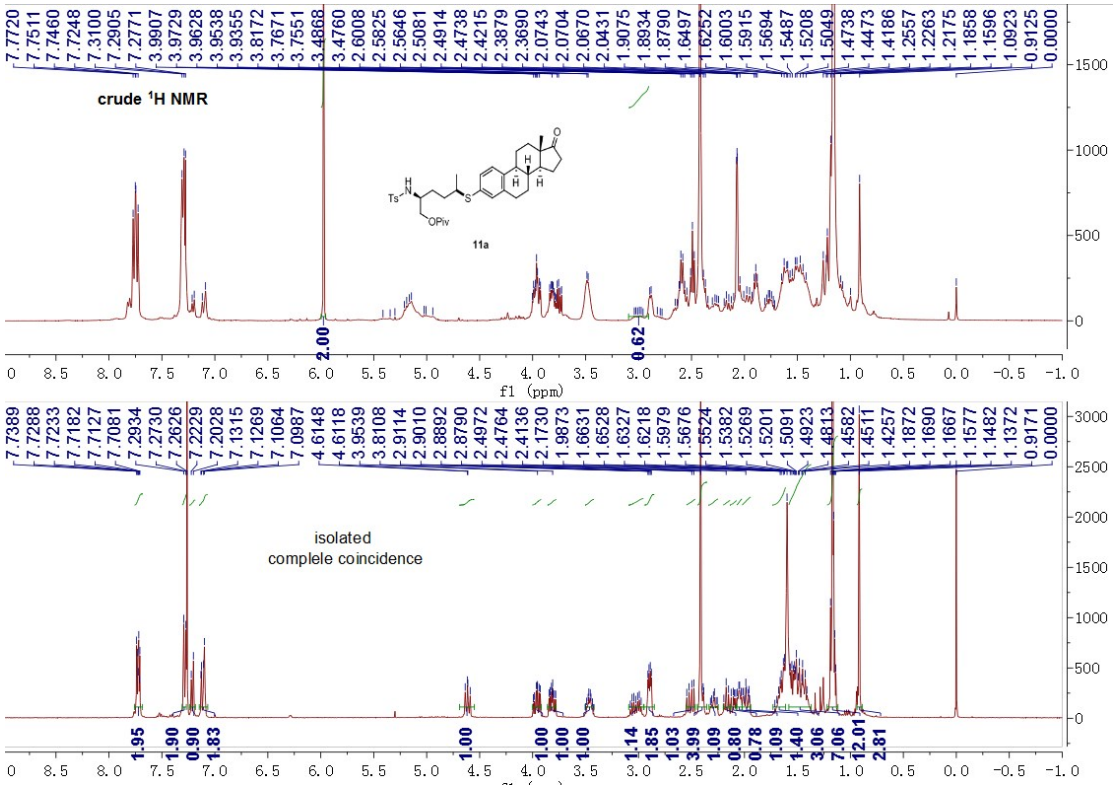

NHTs
H
SPh
9a
f1 (ppm)
f1 (ppm)

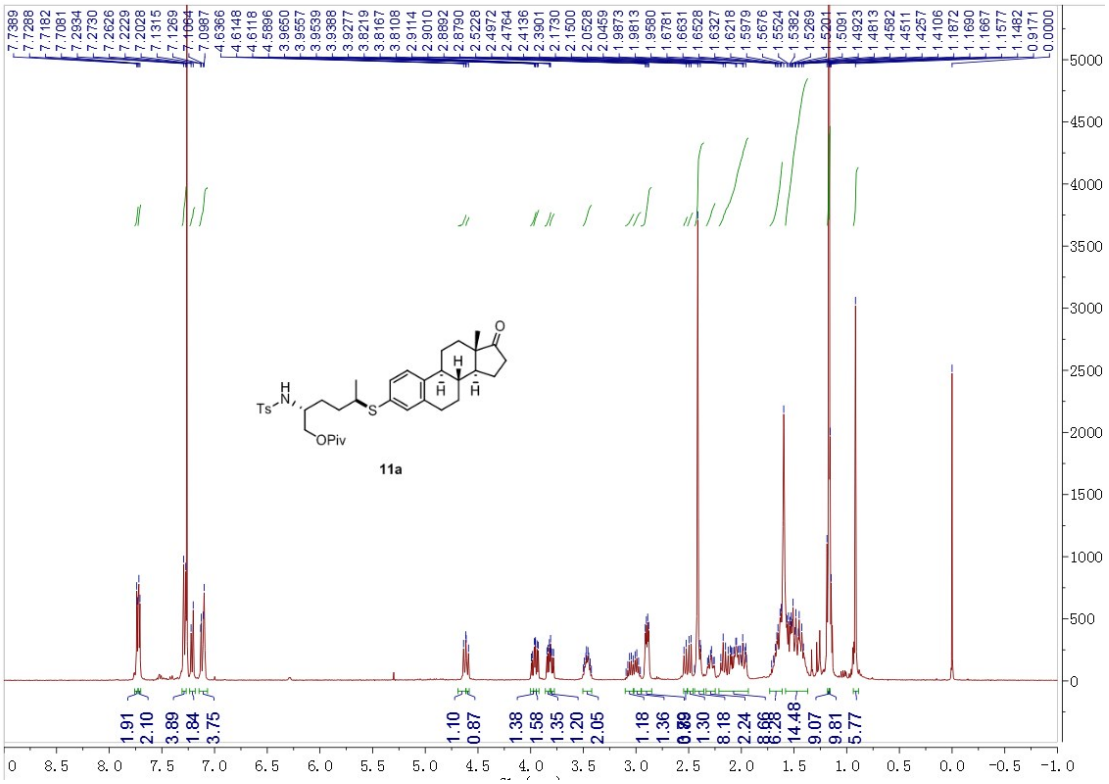

TsHN
SPh
9b
f1 (ppm)


TsHN
SPh
9b
f1 (ppm)


NHTs
SPh
9c
f1 (ppm)


NHTs
SPh
9c


crude ¹H NMR
11a
isolated
complele coincidence
f1 (ppm)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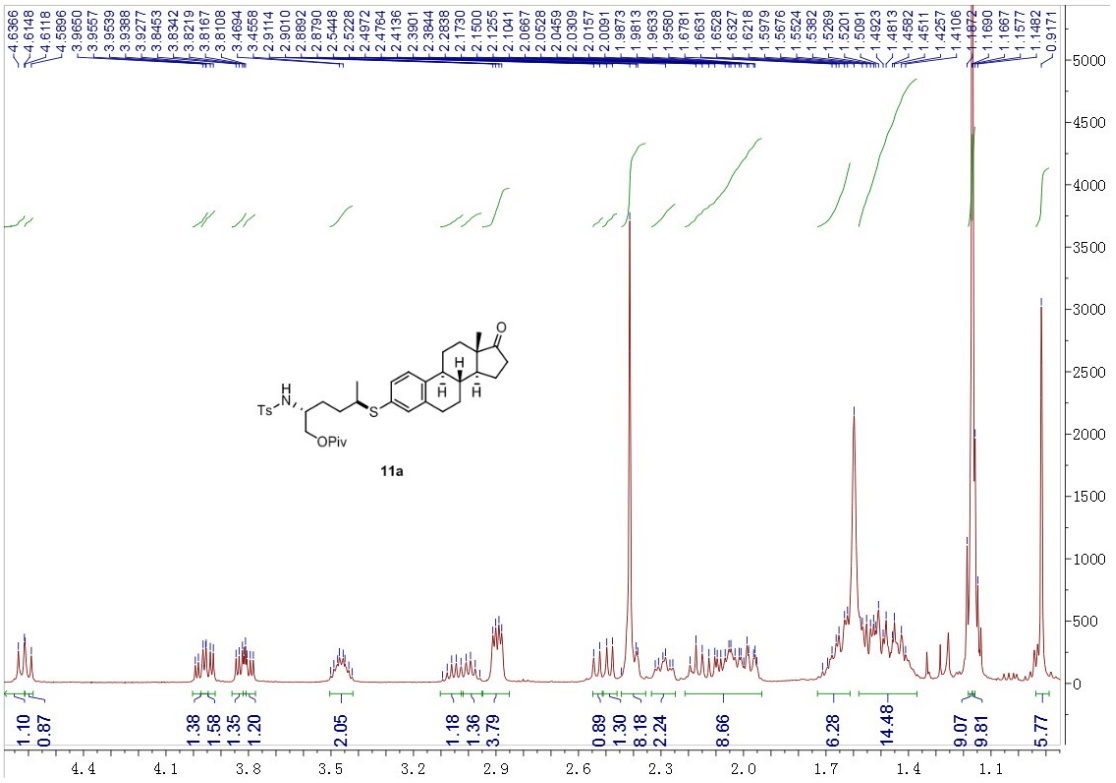
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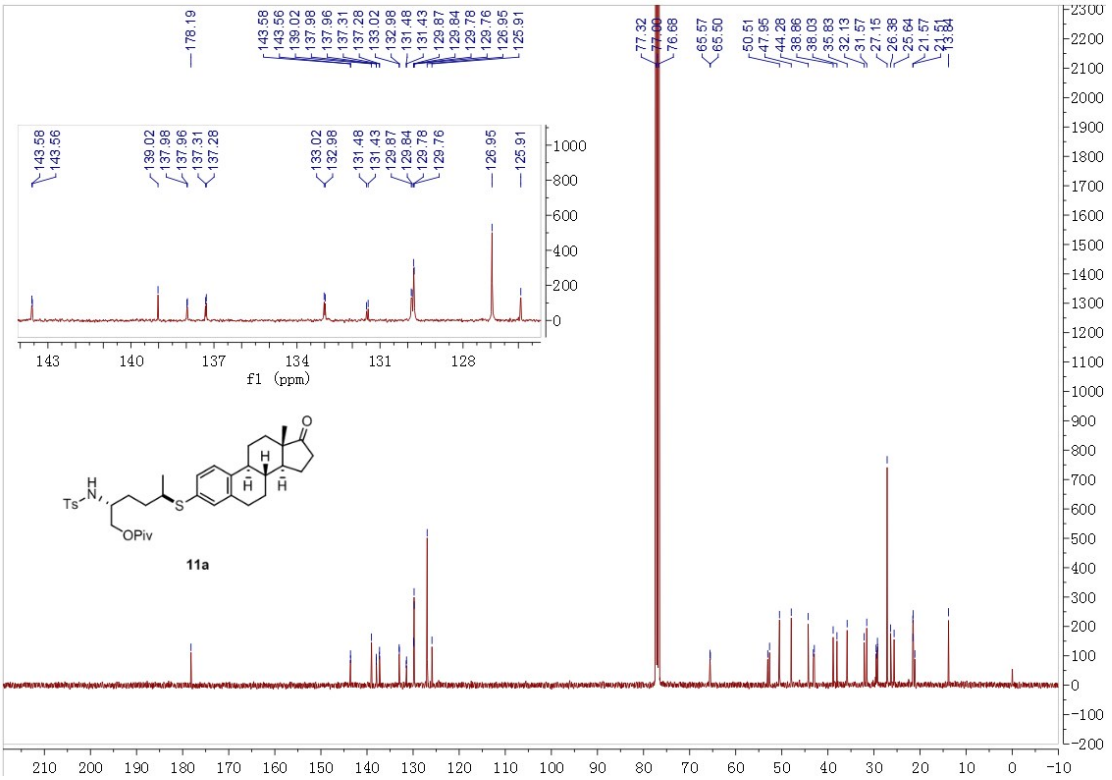
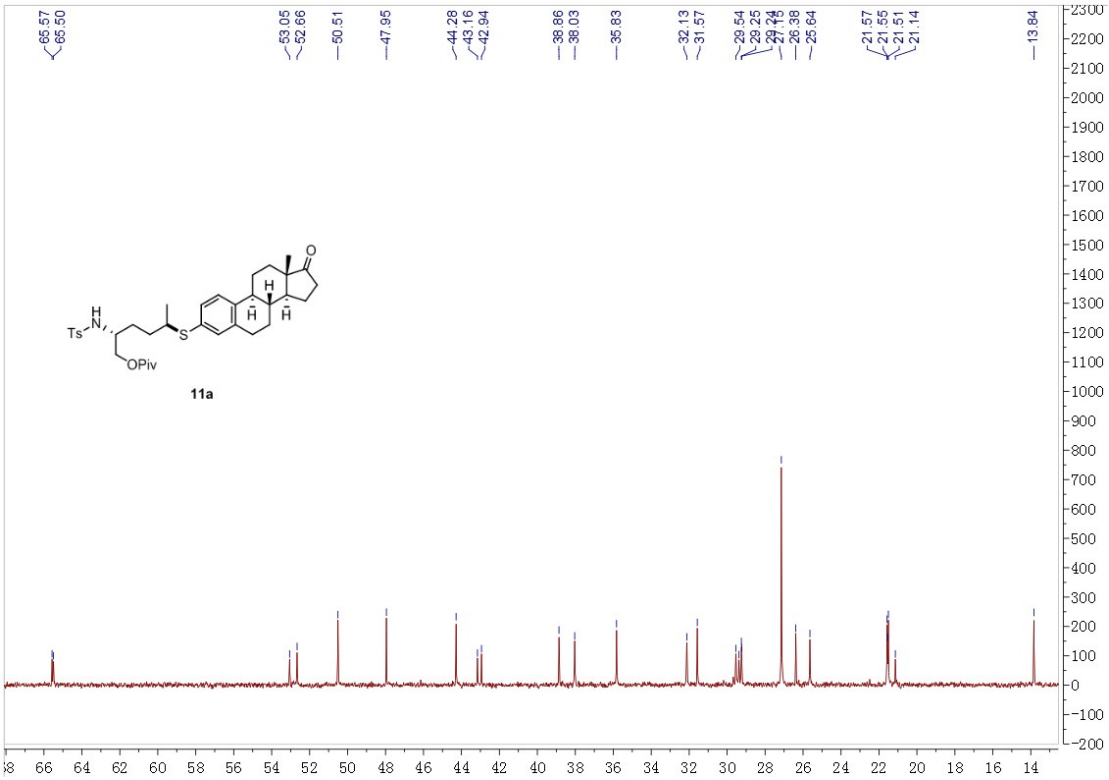

f1 (ppm)
11a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52.66
50.51
47.95
44.28
43.16
42.94
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38.03
35.83
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31.57
29.54
29.25
27.15
26.38
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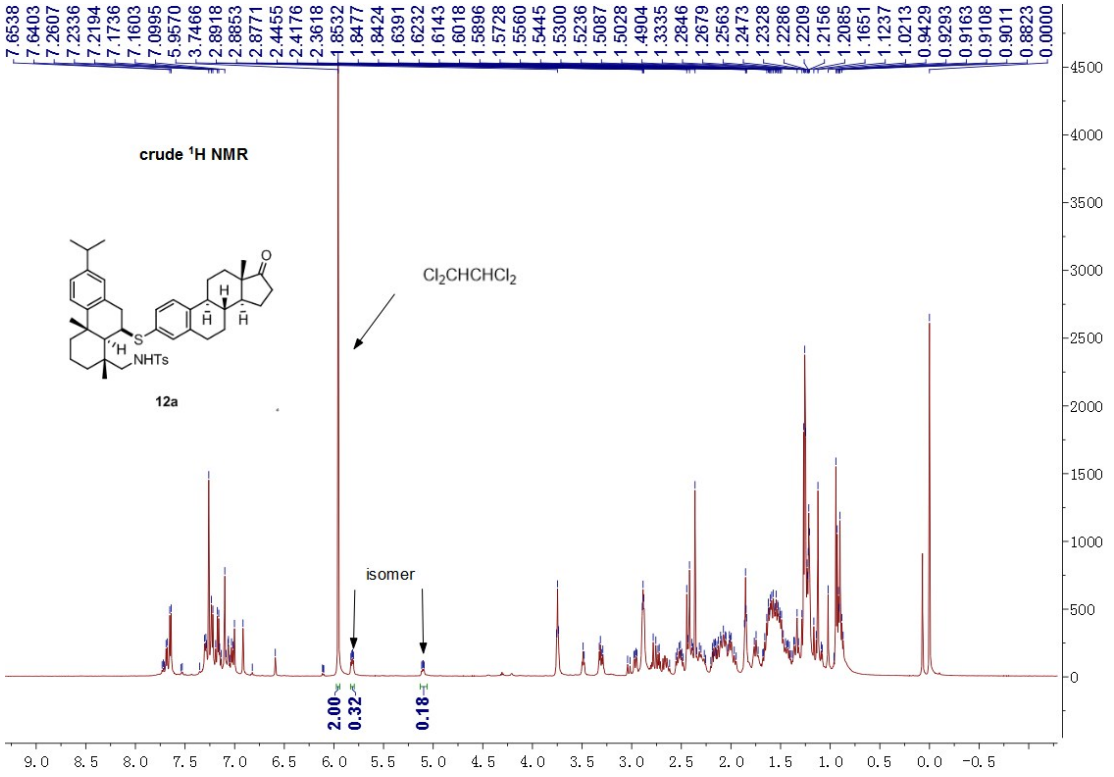
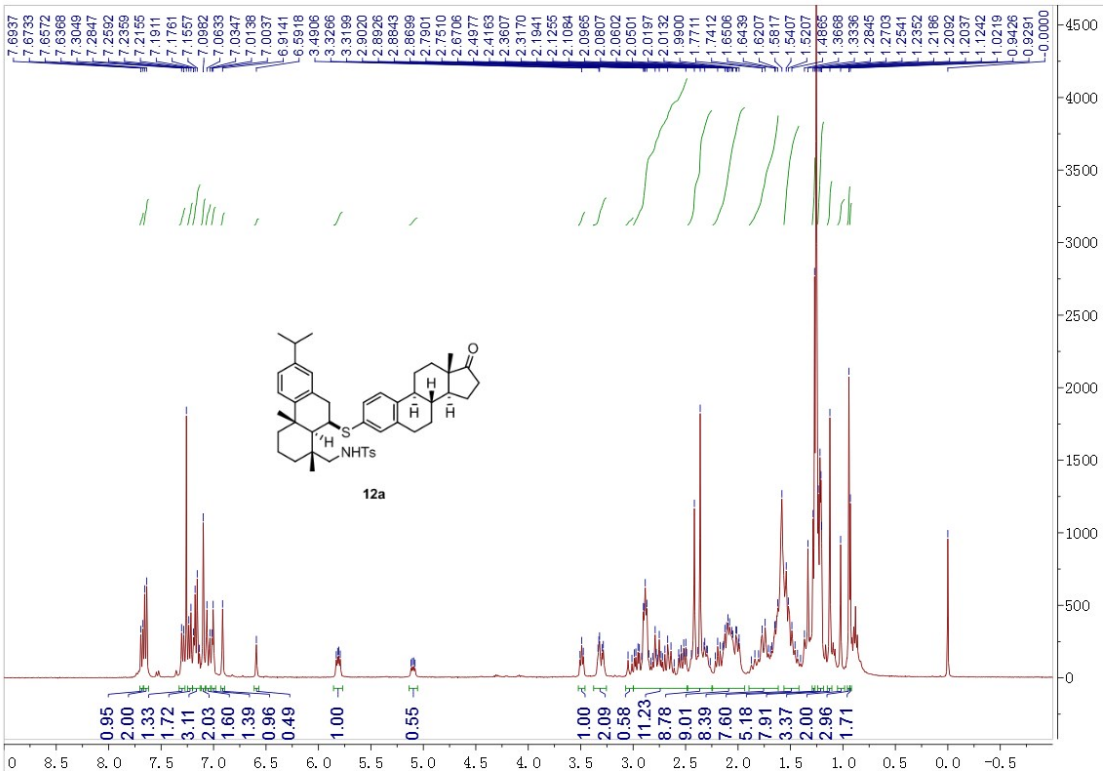
21.57
21.55
21.51
21.14
13.84
Ts
N
H
S
OPiv
O
11a


crude ¹H NMR
Cl2CHCHCl2
isomer
NHTs
12a
2.00
0.32
0.18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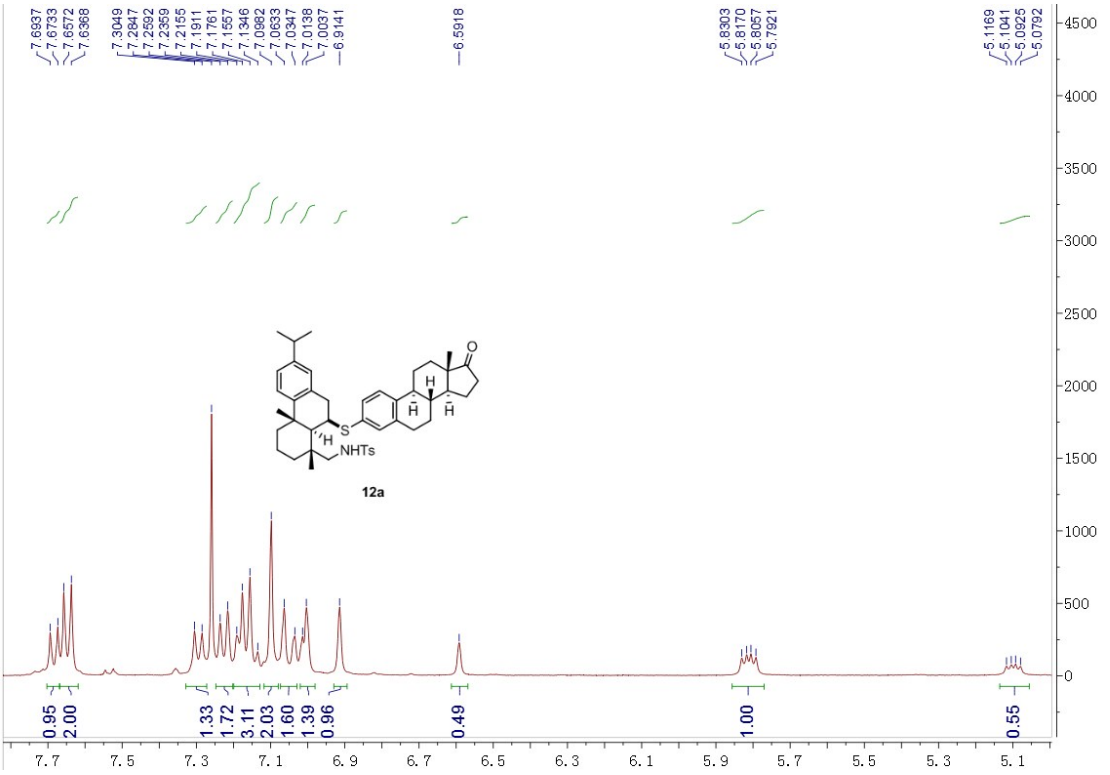
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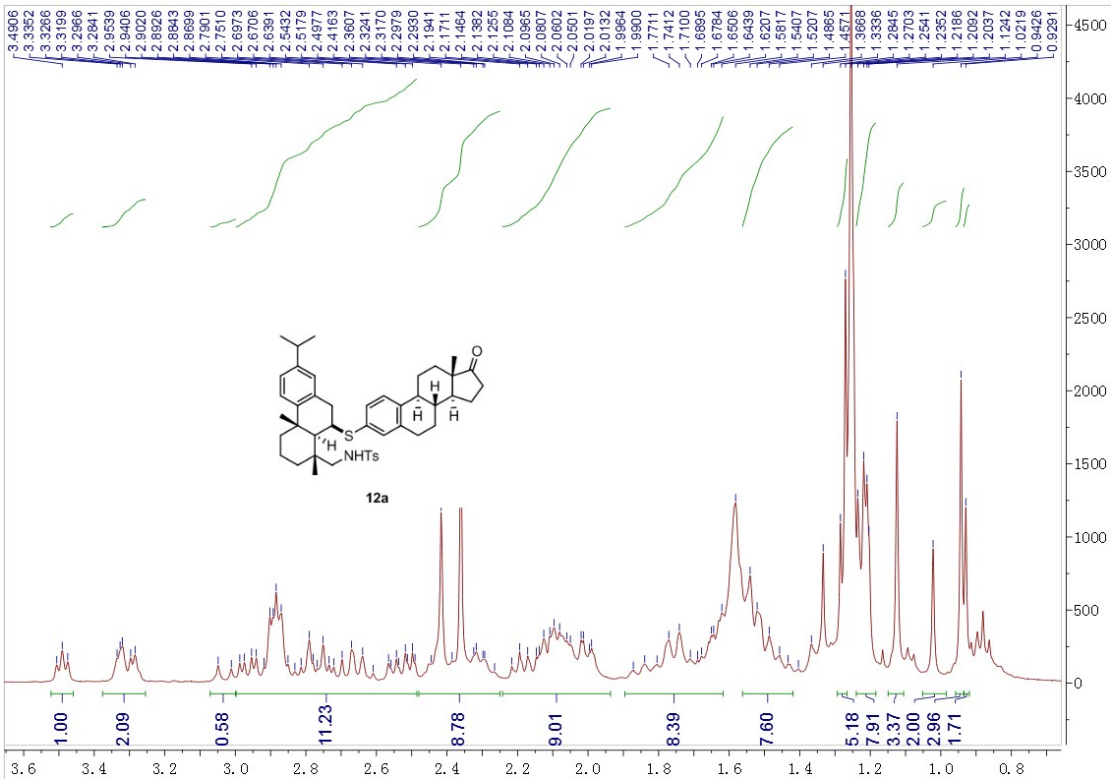
12a
1.00
2.09
0.58
11.23
8.78
9.01
8.39
7.60
5.18
7.91
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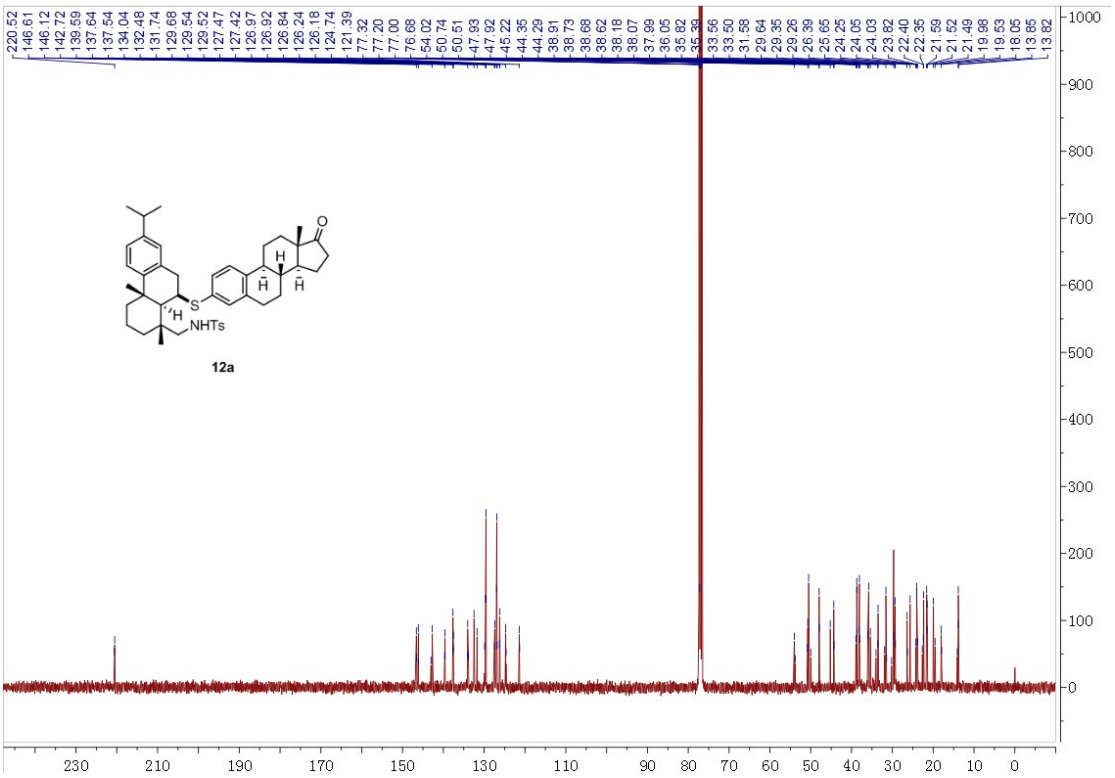
2.96
1.71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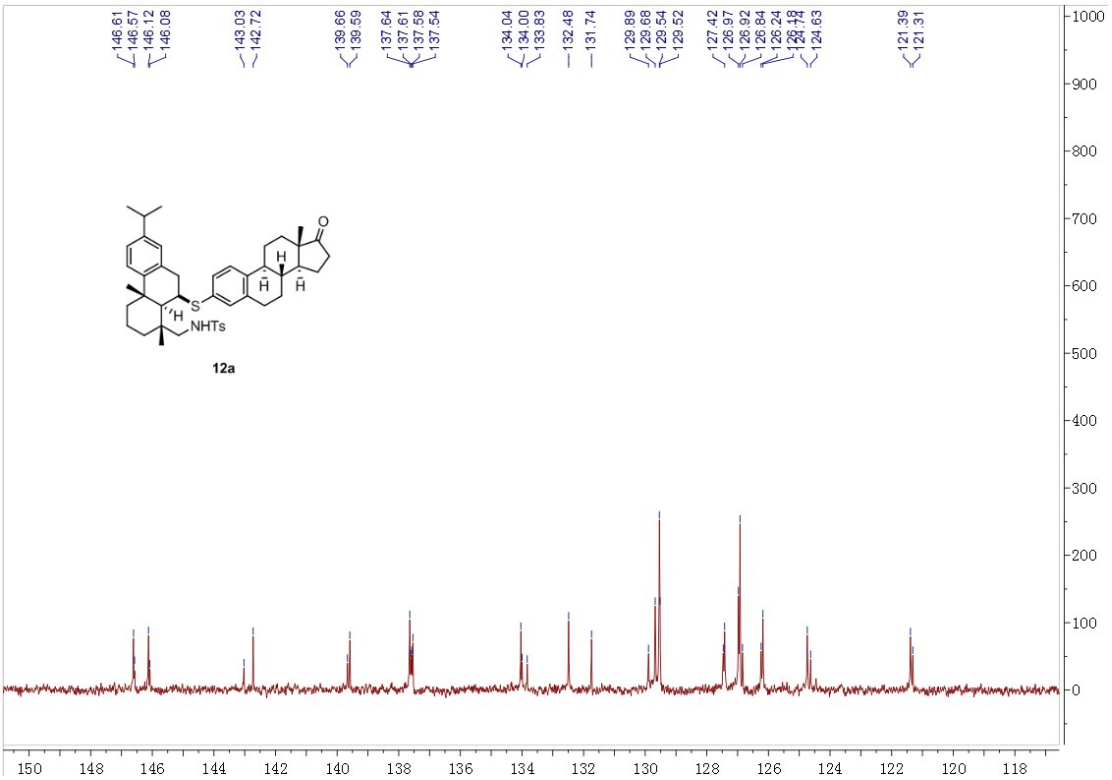
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146.57
146.12
146.08
143.03
142.72
139.66
139.59
137.64
137.61
137.58
137.54
134.04
134.00
133.83
132.48
131.74
129.89
129.68
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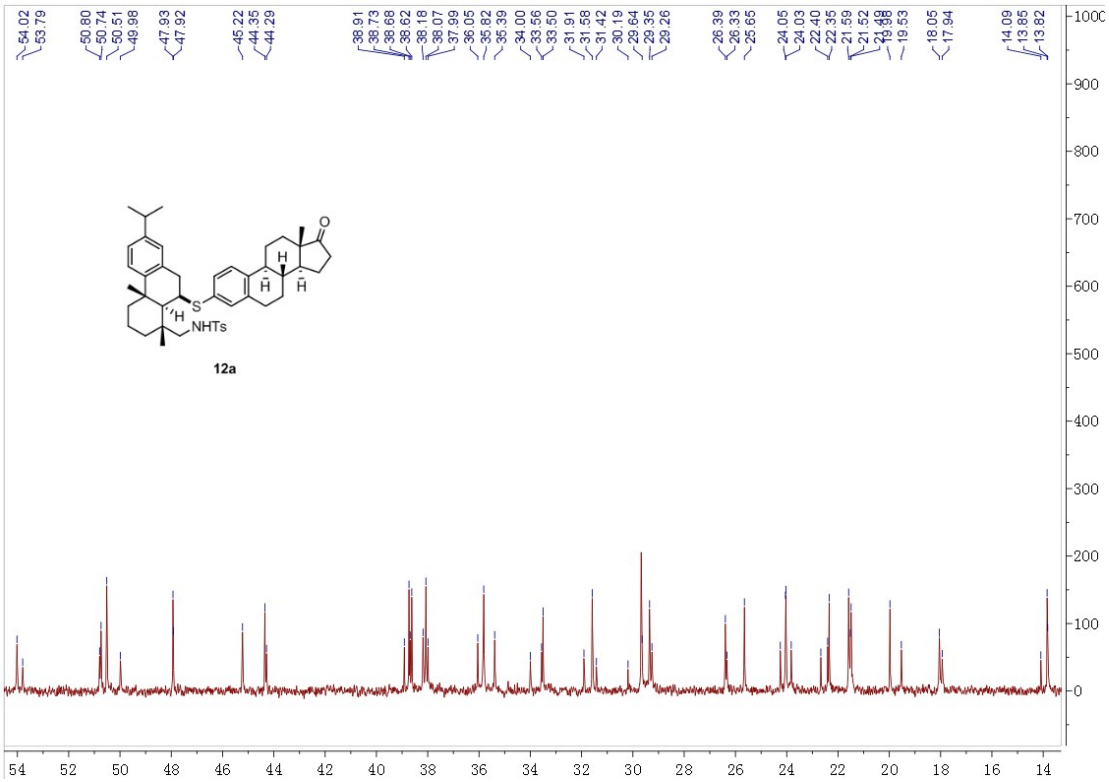
127.42
126.97
126.92
126.84
126.24
124.63
121.39
121.31
NHTs
12a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47.92
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38.73
38.68
38.62
38.18
38.07
37.99
36.05
35.82
35.39
34.00
33.56
33.50
31.91
31.58
31.42
30.19
29.64
29.35
29.26
26.39
26.33
25.65
24.05
24.03
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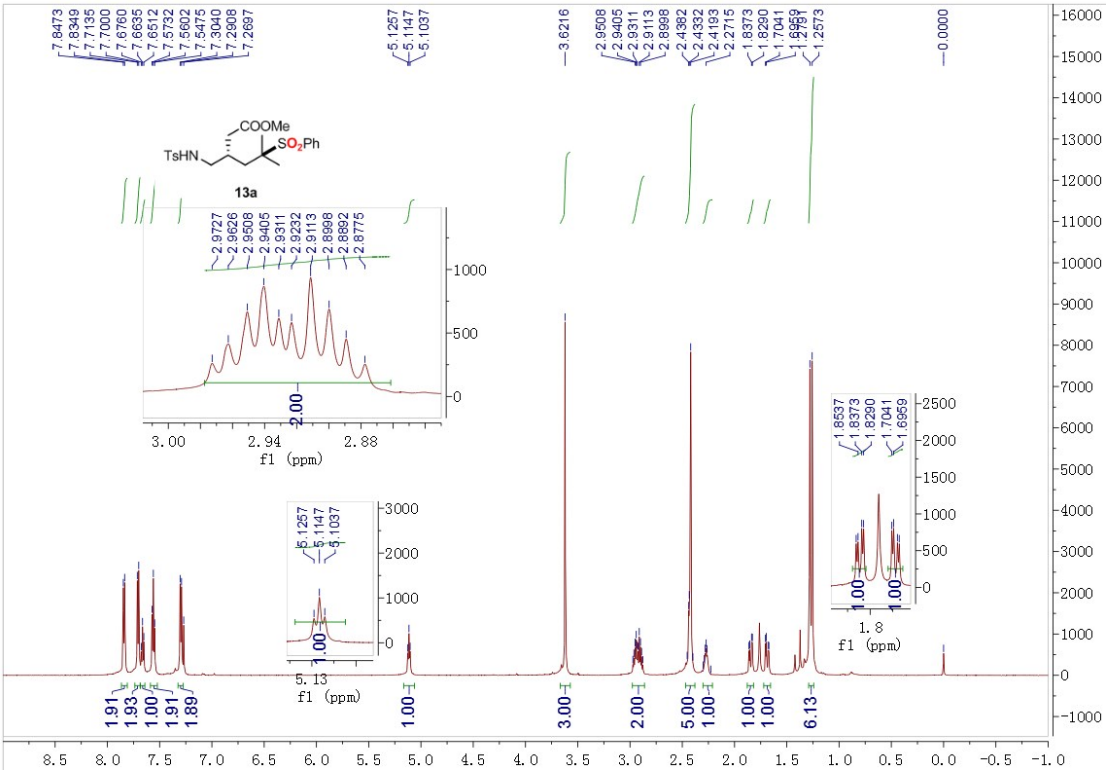
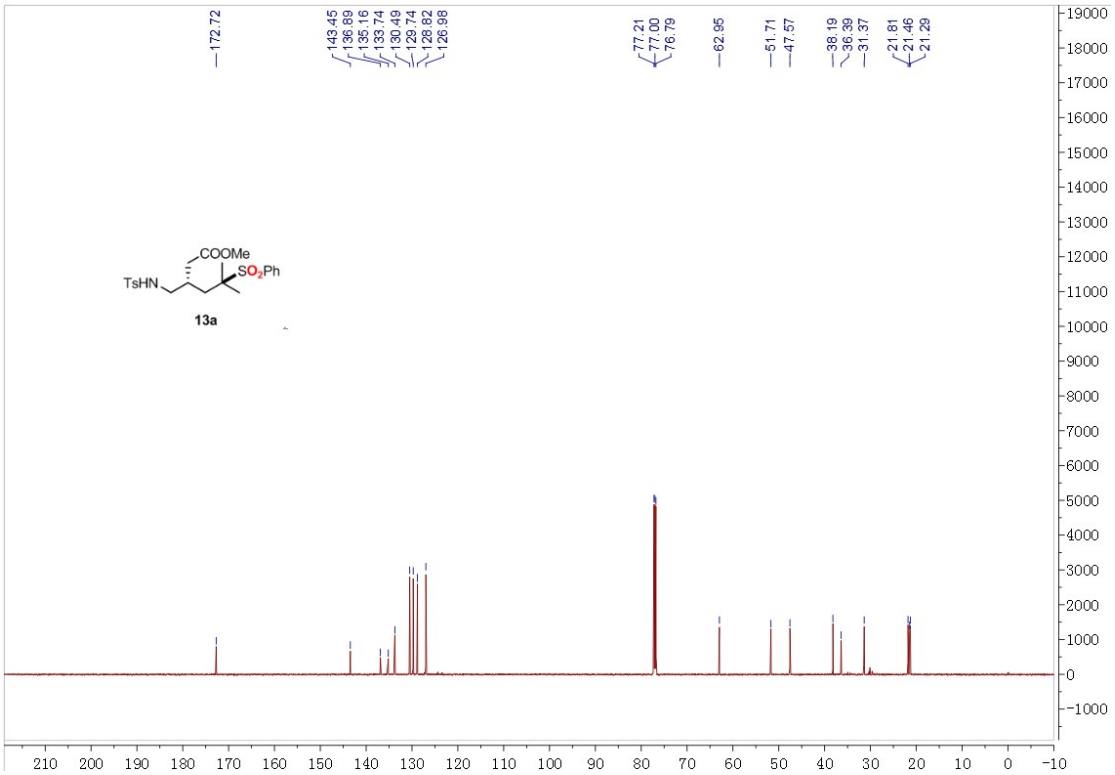
21.59
21.52
19.53
18.05
17.94
14.09
13.85
13.82
NHTs
12a


13a
f1 (ppm)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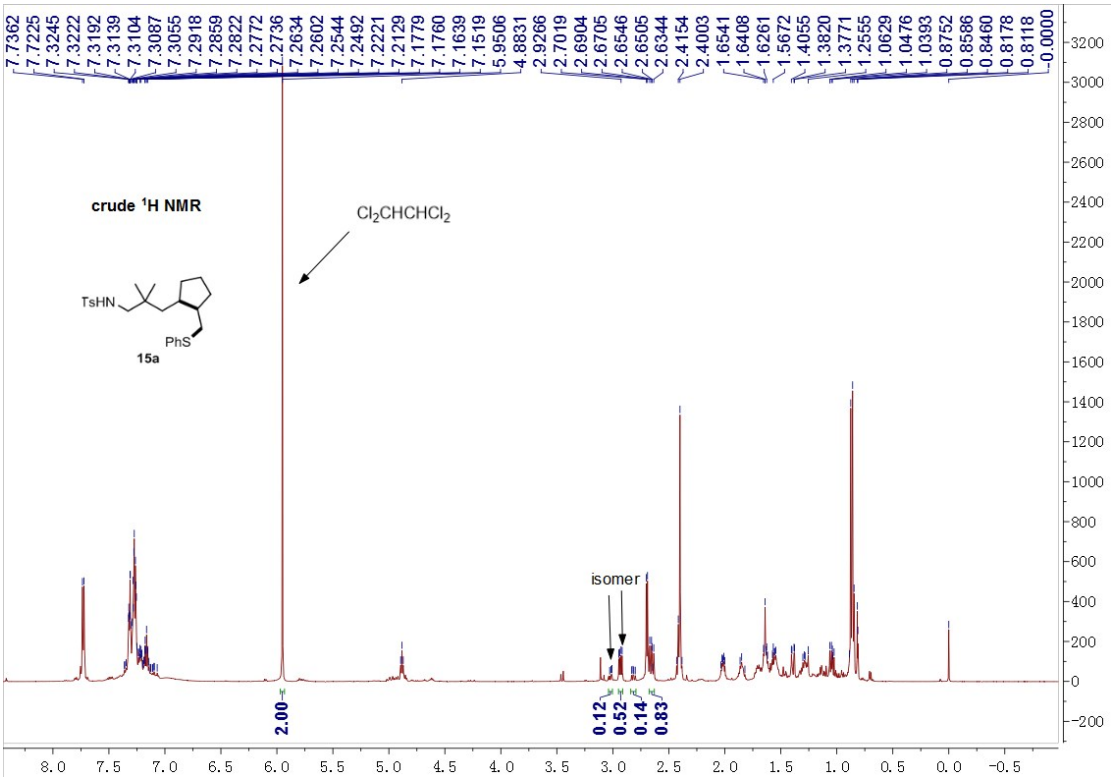
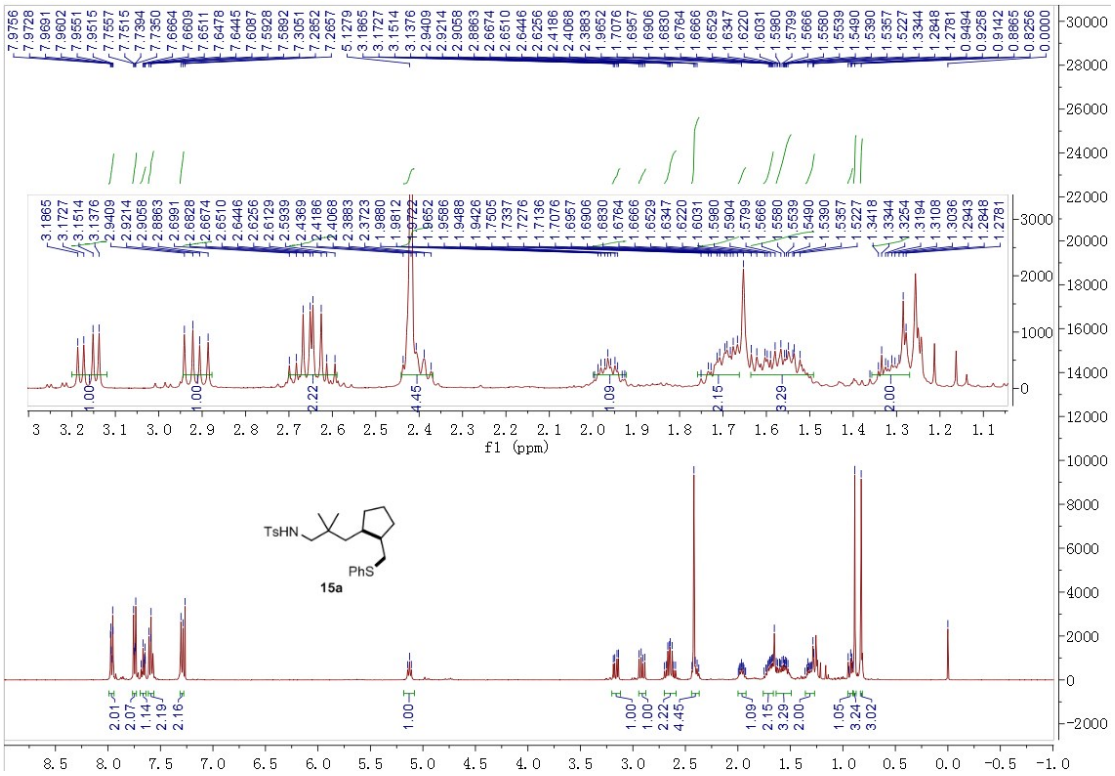
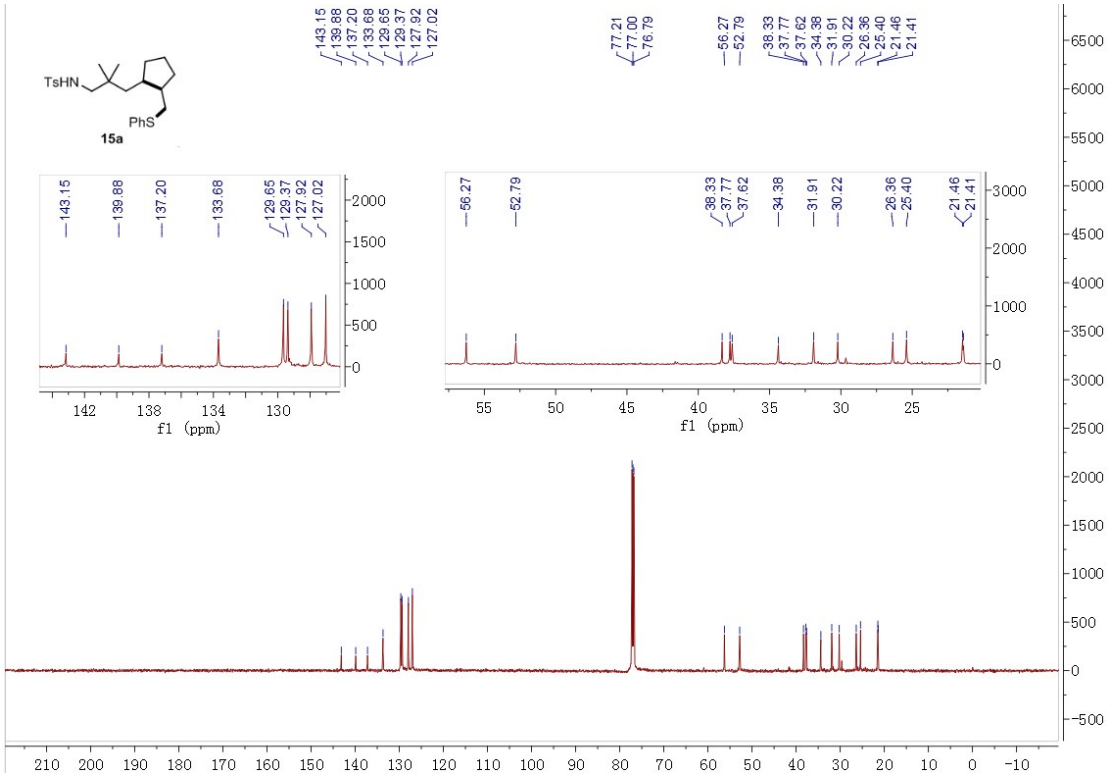

crude ^{1}H NMR
$Cl_2CHCHCl_2$
TsHN
PhS
15a
isomer
2.00
0.12
0.52
0.14
0.83


f1 (ppm)
TsHN
PhS
15a


TsHN
PhS
15a
143.15
139.88
137.20
133.68
129.65
129.37
127.92
127.02
77.21
77.00
76.79
56.27
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30.22
26.36
25.40
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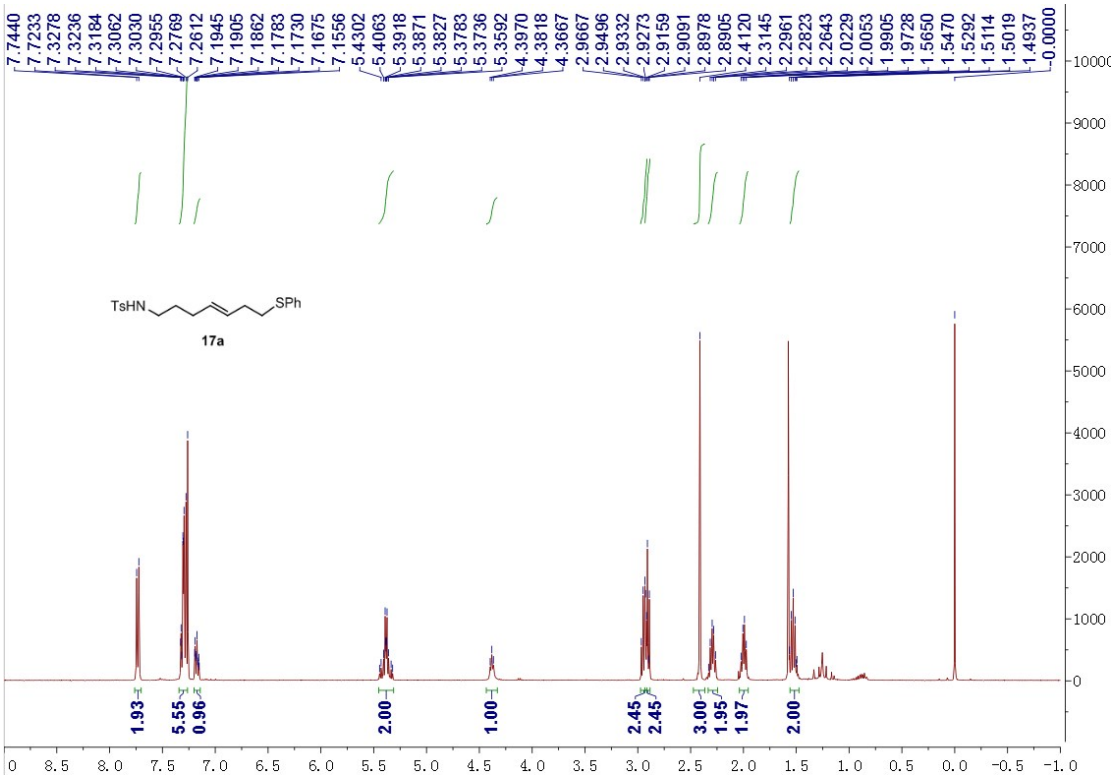
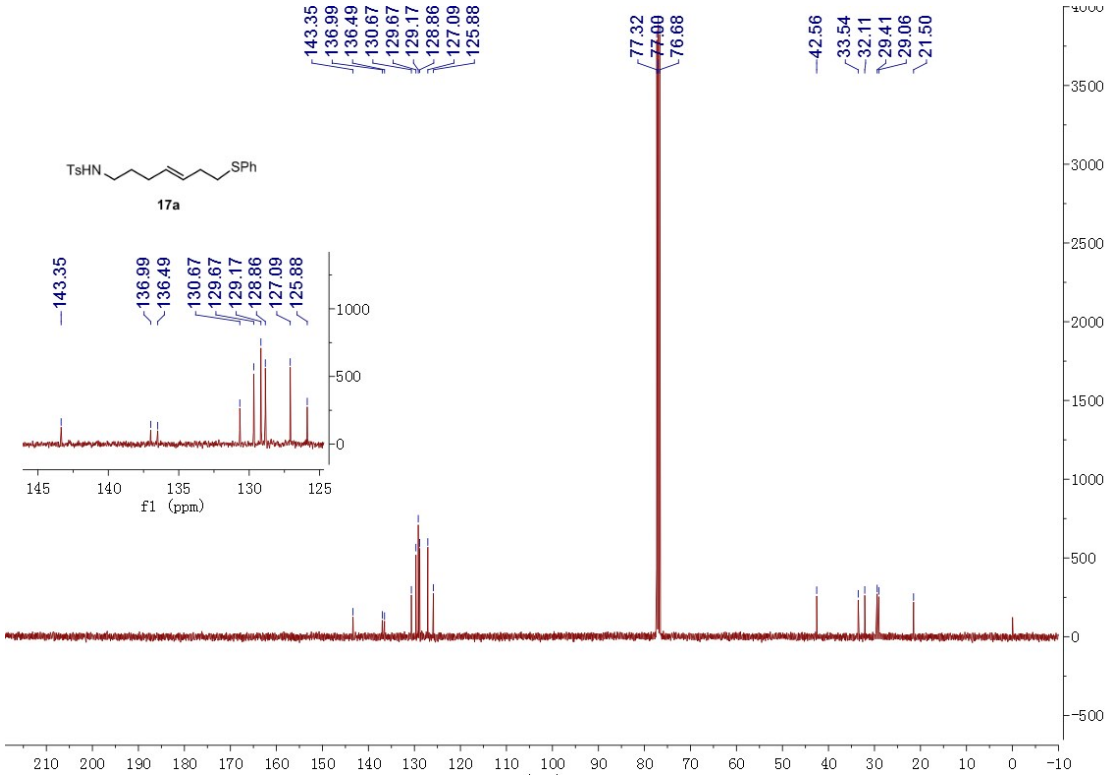
21.41
f1 (ppm)


TsHN
SPh
17a
1.93
5.55
0.96
2.00
1.00
2.45
2.45
3.00
1.95
1.97
2.00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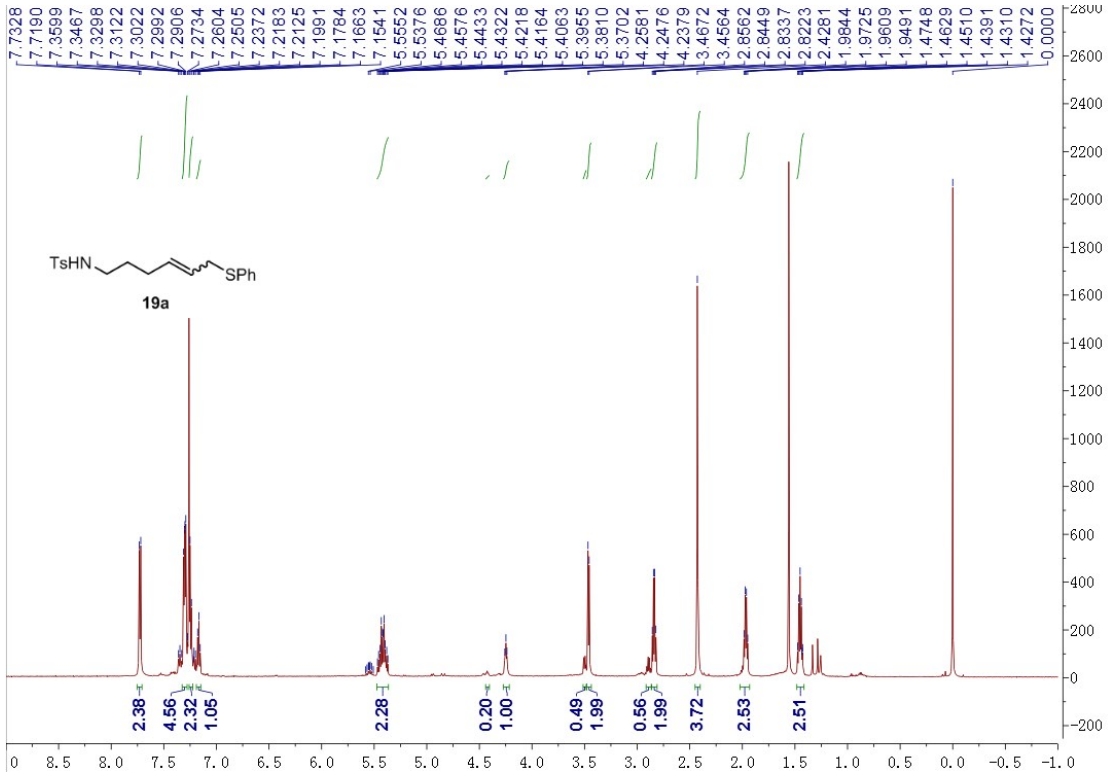
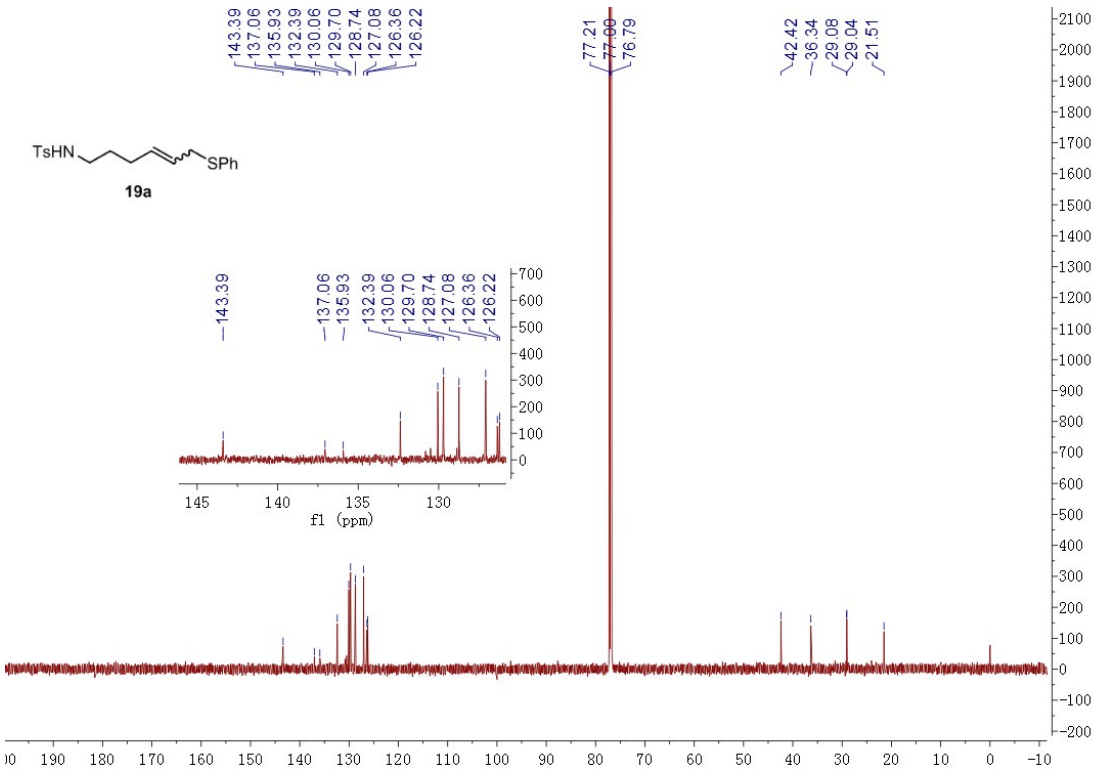
136.49
130.67
129.67
129.17
128.86
127.09
125.88
77.32
77.00
76.68
42.56
33.54
32.11
29.41
29.06
21.50
TsHN
SPh
17a
f1 (ppm)


TsHN
SPh
19a
2.38
4.56
2.32
1.05
2.28
0.20
1.00
0.49
1.99
0.56
1.99
3.72
2.53
2.51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128.74
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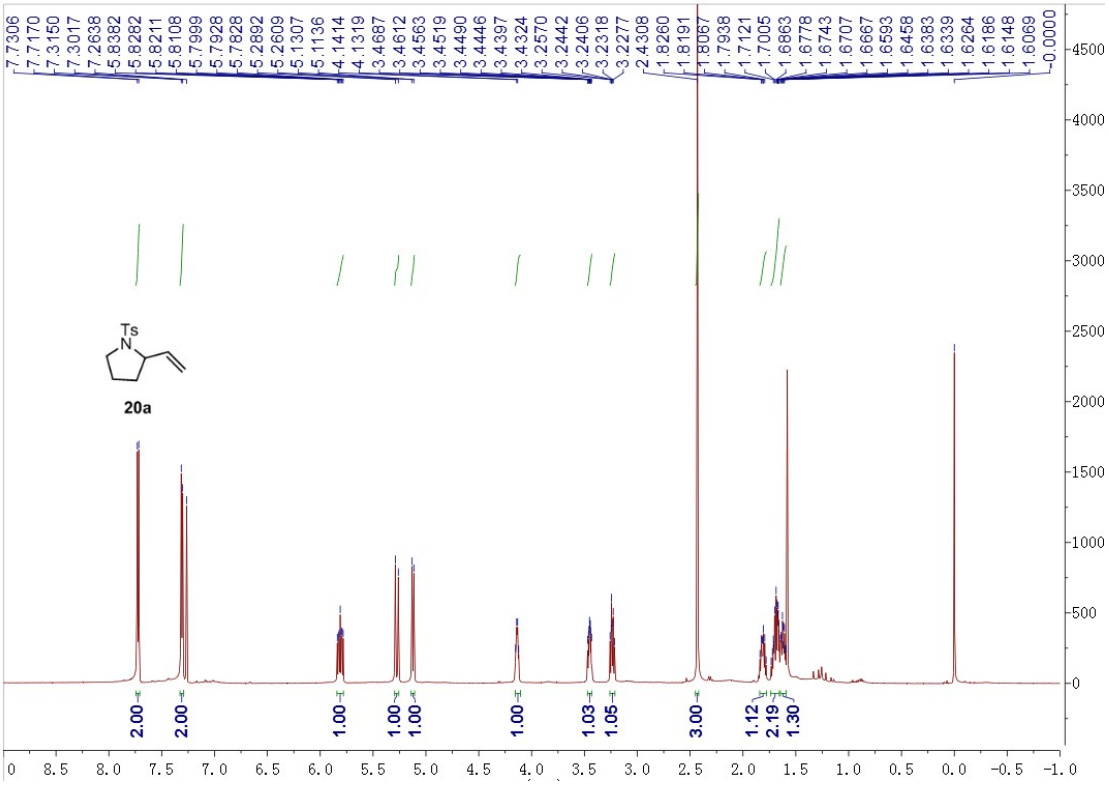
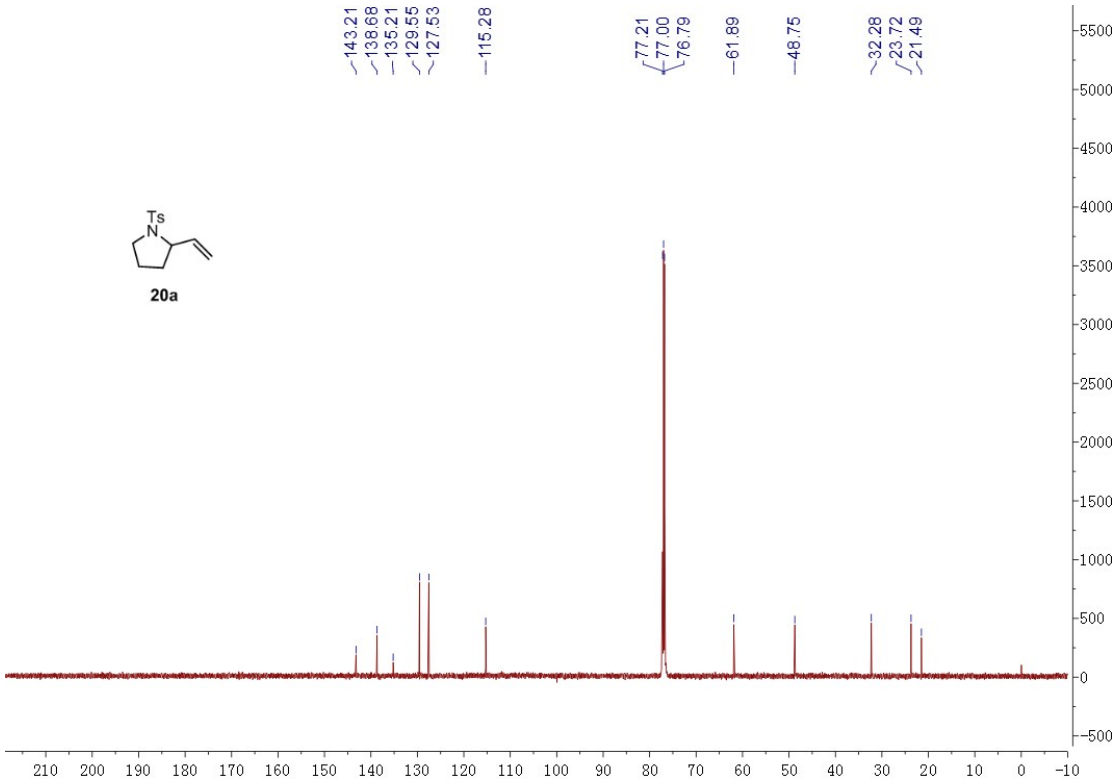
126.22
77.21
77.00
76.79
42.42
36.34
29.08
29.04
21.51
TsHN
SPh
19a
f1 (ppm)


Ts
N
20a
2.00
2.00
1.00
1.00
1.00
1.00
1.03
1.05
3.00
1.12
2.19
1.30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138.68
135.21
129.55
127.53
115.28
77.21
77.00
76.79
61.89
48.75
32.28
23.72
21.49
Ts
N
20a