Supporting Information

A Site-Selective Amination Catalyst Discriminates Between Nearly Identical C-H Bonds of Unsymmetrical Disubstituted Alkenes

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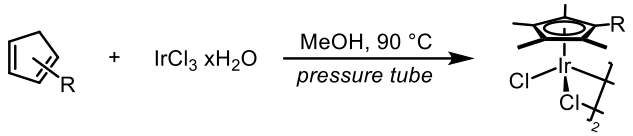
1. General Information

All commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Strem or TCI America, and used without further purification. All reaction solvents were purchased from Sigma Aldrich (Sure/Seal bottles). All reactions were conducted using oven-dried glassware unless otherwise noted. Thin-layer chromatography was performed on Silicycle 250 µm silica gel 60 Å plates. Visualization was accomplished with UV light (254 nm), Iodine, or phosphomolybdic acid. Product purification was done by either flash column chromatography with SiliCycle®SilicaFlash® P60 silica gel (230-400 mesh), preparative thin-layer chromatography with plates (Silica, 1000 µm, 20 x 20 cm, F254) from SiliCycle, or a Teledyne ISCO Lumen CombiFlash with RediSep Rf Disposable Flash columns. ^{1}H, ^{13}C, and ^{19}F NMR spectra were collected on a Bruker 400MHz or 500 MHz spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm), coupling constants (J) are reported in Hz, and multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, or combinations thereof. Regioisomeric ratios were measured by integration of ^{1}H NMR spectra of product mixtures prior to purification. Low resolution mass spectra (LRMS) were recorded on a Waters Acquity H uPLC-MS. High resolution mass spectra (HRMS) were obtained from the Columbia University Chemistry Department Mass Spectrometry Facility on a Waters XEVO G2XS QToF mass spectrometer equipped with a UPC2 SFC inlet and a LockSpray source with one of the following three probes: electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, or atmospheric pressure solids analysis probe (ASAP). Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR Spectrometer.

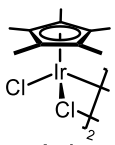
2. Preparation of Catalysts and Substrates

1n[1], **1o**[2], **1p**[3], **3i**[4], and **3j**[5] was prepared according to the known procedure. Spectroscopic data are consistent with those presented in the literature.

General procedure A (Ir-1, Ir-2, Ir-3, Ir-4)



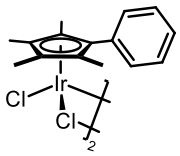
A solution of Cp^X ligand (1.2 equiv) and $IrCl_3 \cdot xH_2O$ (1.0 equiv) in MeOH (0.5 M) was sealed in a heavy-wall pressure tube. The brown reaction mixture was stirred at 85 °C for 3 days. The resulting orange precipitate was collected by vacuum filtration and rinsed with methanol and pentane. The solid was then redissolved in methylene chloride, and the solution was filtered through a plug of celite. The solvent was removed under vacuum to obtain the desired $[Cp^XIrCl_2]_2$. The iridium complex was used without further purification.



Ir-1

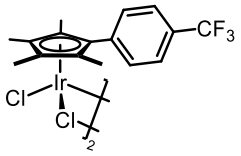
$[Cp^*IrCl_2]_2$ (**Ir-1**) was synthesized using the general procedure A. Spectroscopic data are

consistent with those presented in the literature[6].



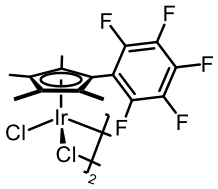
Ir-2

(**Ir-2**) was synthesized using the general procedure A with phenyltetramethylcyclopentadiene. Spectroscopic data are consistent with those presented in the literature[7].



Ir-3

(**Ir-3**) was synthesized using the general procedure A with (*p*-trifluoromethylphenyl) tetramethylcyclopentadiene. Spectroscopic data are consistent with those presented in the literature[7].



Ir-4

(**Ir-4**) was synthesized using the general procedure A with (pentafluorophenyl) tetramethylcyclopentadiene, which was prepared according to the published literature[8].

Orange solid; 37 mg, 15% yield.

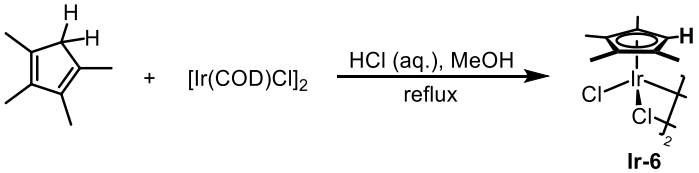
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (s, 6H), 1.64 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 144.6, 143.6, 142.5, 140.6, 139.4, 138.6, 137.4, 136.6, 106.0, 106.0, 105.9, 105.8, 105.7, 105.7, 93.0, 88.0, 66.9, 10.1, 9.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -126.6, -137.9, -150.4, -157.9, -160.7.

IR (neat, cm^{-1}) ν 2921, 1653, 1526, 1496, 1469, 1099, 1043, 983, 836.

Ir-6:



Ir-6

To a round-bottom flask was added $[Ir(COD)Cl]_2$ (400 mg, 0.6 mmol), tetramethylcyclopentadiene (272 µl, 1.8 mmol) and concentrated HCl (1.0 ml, 32% aqueous solution). The reaction mixture was refluxed overnight. After cooled down to room temperature, the mixture was filtered and rinsed with methanol and pentane to give orange precipitate **Ir-6** (307 mg, 66%). It was used

without further purification.

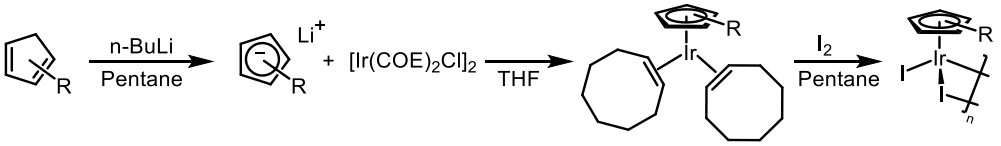
Orange solid; 66% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1H), 1.70 (s, 6H), 1.65 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 91.9, 86.3, 68.0, 11.0, 9.3.

IR (neat, cm^{-1}) ν 3070, 2964, 2918, 1482, 1449, 1380, 1034, 910, 731.

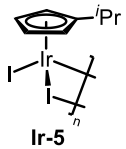
General procedure B (Ir-5, Ir-7, Ir-8, Ir-9)



To a solution of Cp^X ligand (1.0 equiv) in pentane (0.1 M) was added *n*-BuLi (2.0 equiv, 2.5 M in hexane) at 0 °C. The reaction mixture was stirred at room temperature overnight. The resulting white precipitate was collected by vacuum filtration in the glove-box. The solid was rinsed with pentane and dried under vacuum. The Cp^x lithium salt was used directly without further purification.

To a suspension of $[Ir(COE)_2Cl]_2$ (1.0 equiv) in THF (0.2 M) was added Cp^x lithium salt (2.2~2.5 equiv). The reaction mixture was stirred at room temperature for 3 hours. The solvent was removed under vacuum, and the residue was then diluted with pentane. The resultant suspension was filtered through a plug of celite. The filtrate was concentrated to yield desired $[Cp^xIr(COE)_2]$, which was used directly for the next step.

$[Cp^xIr(COE)_2]$ (1.0 equiv) was dissolved in pentane (0.1 M) and cooled to 0 °C. A solution of iodine (1.0 equiv) in pentane was added slowly. The reaction mixture was stirred at 0 °C for 1 hour. The forming brown precipitate was obtained via vacuum filtration, followed by rinsing with pentane. The solid was dissolved in methylene chloride, and the solution was filtered through a plug of celite. The solvent was removed under vacuum to give the desired $[Cp^XIrI_2]_n$. The iridium complex was used without further purification.



Ir-5

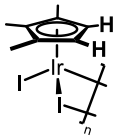
(**Ir-5**) was synthesized using the general procedure B with commercially available sodium isopropylcyclopentadienide.

Brown solid; 47 mg, 85% yield (based on Ir).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 – 5.67 (m, 2H), 5.66 – 5.62 (m, 2H), 2.77 (hept, J = 6.9 Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 105.6, 76.8, 76.2, 26.5, 22.5.

IR (neat, cm^{-1}) ν 3083, 2962, 2925, 2867, 1471, 1390, 1070, 1017, 911, 861, 730.



Ir-7

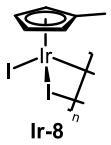
(**Ir-7**) was synthesized using the general procedure B with 1,2,3-trimethylcyclopentadiene, which was prepared according to the published literature[9].

Brown solid; 28 mg, 51% yield (based on Ir).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (s, 2H), 2.00 (s, 6H), 1.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 93.3, 92.2, 73.7, 12.5, 10.6.

IR (neat, cm^{-1}) ν 3071, 2956, 2913, 2851, 1451, 1378, 1027, 910, 729.



Ir-8

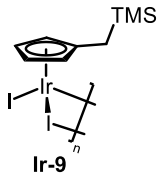
(**Ir-8**) was synthesized using the general procedure B with methylcyclopentadiene, which was prepared according to the published literature[10].

Brown solid; 97 mg, 92% yield (based on Ir).

^{1}H NMR (500 MHz, DMSO-d_6) δ 5.96 – 5.93 (m, 2H), 5.93 – 5.91 (m, 2H), 2.18 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 102.9, 83.3, 82.5, 14.0.

IR (neat, cm^{-1}) ν 3085, 2921, 2851, 1462, 1440, 1362, 1015, 910, 858.



Ir-9

(**Ir-9**) was synthesized using the general procedure B with [(trimethylsilyl) methyl]cyclopentadiene, which was prepared according to the published literature[11].

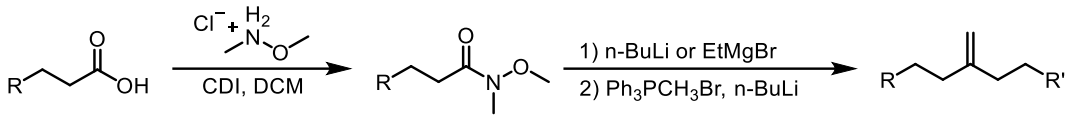
Brown solid; 198 mg, 83% yield (based on Ir).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 (s, 2H), 5.43 (s, 2H), 1.84 (s, 2H), 0.08 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 106.9, 76.0, 73.3, 19.7, -1.7.

IR (neat, cm^{-1}) ν 3080, 2952, 1459, 1248, 1151, 846, 731.

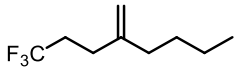
General procedure C



To a solution of carboxylic acid (1.0 equiv) in methylene chloride (0.1 M) was added 1,1'-carbonyldiimidazole (1.2 equiv) at 0 °C. The reaction mixture was stirred at 0 °C until gas evolution ceased (~1 hour). N,O-dimethylhydroxylamine hydrochloride (2.5 equiv) was then added, and the mixture was stirred at room temperature overnight. The resultant suspension was diluted with methylene chloride and washed with water and 1 M hydrogen chloride aqueous solution. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was filtered through a plug of silica, washed with 1:1 hexanes/ethyl acetate, and the filtrate was concentrated to yield the desired weinreb amide, which was used directly for the next step.

To a solution of the weinreb amide (1.0 equiv) in THF (0.1 M) at –78 °C was slowly added *n*-BuLi (1.2 equiv). The mixture was stirred at –78 °C for 1 hour before quenched by the addition of a saturated aqueous solution of ammonium chloride. [In the case of using ethyl magnesium bromide (1.2 equiv), the reaction was conducted at 0 °C instead of –78 °C.] After gradual warming up to room temperature, the mixture was extracted with ethyl acetate 3 times. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under vacuum. The resultant residue was filtered through a plug of silica, washed with 5:1 hexanes/ethyl acetate, and the filtrate was concentrated to yield the desired ketone, which was used directly for the next step.

To a suspension of methyltriphenylphosphonium bromide (2.0 equiv) in THF at 0 °C was slowly added *n*-BuLi (1.8 equiv). The reaction mixture was stirred for 15 min before the slow addition of a solution of the ketone (1.0 equiv) in THF. The reaction was further stirred for 4 hours at room temperature. The resulting suspension was quenched by filtering through a plug of silica and washed with excess amount of pentane. The filtrate was concentrated under vacuum, followed by column chromatography to give the desire 1,1-disubstituted alkene.



1a

(**1a**)

Colorless oil; 747 mg, 42% yield (2 steps).

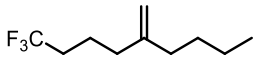
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.76 (s, 1H), 2.32 – 2.19 (m, 4H), 2.06 (t, *J* = 7.0 Hz, 2H), 1.48 – 1.41 (m, 2H), 1.39 – 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 127.1 (q, *J* = 276.3 Hz), 109.8, 35.8, 32.4 (q, *J* = 28.4 Hz), 29.8, 28.0 (q, *J* = 3.1 Hz), 22.4, 13.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -65.72 (t, *J* = 10.0 Hz).

IR (neat, cm^{-1}) *v* 2958, 2928, 2857, 1648, 1451, 1364, 1254, 1177, 1139, 981, 909, 663, 554.

GCMS (EI) calculated for $C_9H_{15}F_3$ [M]: 180.1, found: 180.1.



1j

(**1j**)

Colorless oil; 287 mg, 59% yield (2 steps).

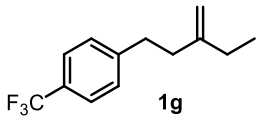
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.80 (s, 1H), 4.75 (s, 1H), 2.14 – 2.00 (m, 6H), 1.77 – 1.69 (m, 2H), 1.47 – 1.39 (m, 2H), 1.34 (h, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 127.3 (q, *J* = 276.2 Hz), 109.8, 35.4, 34.8, 33.2 (q, *J* = 28.4 Hz), 29.9, 22.4, 19.8 (q, *J* = 2.9 Hz), 13.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -65.5 (t, *J* = 11.0 Hz).

IR (neat, cm^{-1}) *v* 2957, 2930, 2874, 1645, 1386, 1252, 1134, 906, 731.

GCMS (EI) calculated for $C_{10}H_{17}F_3$ [M]: 194.1, found: 194.2.



1g

(**1g**)

Colorless oil; 362 mg, 53% yield (2 steps).

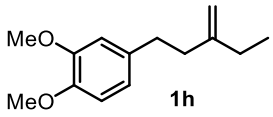
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.35 – 7.30 (m, 2H), 4.80 (s, 1H), 4.76 (s, 1H), 2.87 – 2.80 (m, 2H), 2.40 – 2.33 (m, 2H), 2.10 (q, *J* = 7.5 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 146.4, 128.6, 128.1 (q, *J* = 31.9 Hz), 125.2 (q, *J* = 3.8 Hz), 124.38 (q, *J* = 271.8 Hz), 108.4, 37.6, 34.2, 28.9, 12.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3 (s).

IR (neat, cm^{-1}) *v* 2967, 2937, 1618, 1323, 1162, 1121, 1067, 1019, 890, 825.

GCMS (EI) calculated for $C_{13}H_{15}F_3$ [M]: 228.1, found: 228.2.



1h

(**1h**)

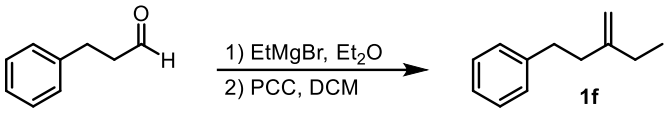
Colorless oil; 430mg, 65% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (d, *J* = 7.8 Hz, 1H), 6.78 – 6.74 (m, 2H), 4.80 – 4.76 (m, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 2.76 – 2.69 (m, 2H), 2.37 – 2.31 (m, 2H), 2.10 (q, *J* = 7.6 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 148.7, 147.1, 135.0, 120.0, 111.7, 111.1, 107.9, 55.9, 55.8, 38.3, 34.0, 29.0, 12.4.

IR (neat, cm^{-1}) *v* 2963, 2934, 2832, 1590, 1514, 1463, 1260, 1235, 1154, 1137, 1030, 886, 803.

HRMS (ESI) *m/z* calculated for $C_{14}H_{20}O_2Na$ [M+Na$^+$]: 243.1361, found: 243.1370.



To a stirred solution of 3-phenylpropionaldehyde (1.3 ml, 10 mmol) in diethyl ether (40 ml) at 0 °C was slowly added ethyl magnesium bromide (7.0 ml, 3 M solution in diethyl ether). The reaction mixture was stirred at 0 °C for 1 hour. The reaction was quenched by adding a saturated aqueous solution of ammonium chloride. The solution was extracted by ethyl acetate 3 times, and the organic layers were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified via flash column chromatography to yield the alcohol as a colorless oil.

To a solution of the obtained alcohol (500 mg, 3.0 mmol) in methylene chloride (30 ml) at room temperature was added pyridinium chlorochromate (985 mg, 4.5 mmol). The reaction mixture was stirred for 3 hours before filtered through a plug of celite. The filtrate was concentrated under vacuum, and the residue was purified via flash column chromatography to give the product (486 mg) as a colorless oil.

To a suspension of methyltriphenylphosphonium bromide (2.2 g, 6.0 mmol) in THF at 0 °C was slowly added *n*-BuLi (2.4 ml, 2.5 M in hexane). The reaction mixture was stirred for 15 min before the slow addition of a solution of the ketone (486 mg, 3.0 mmol) in THF. The reaction was further

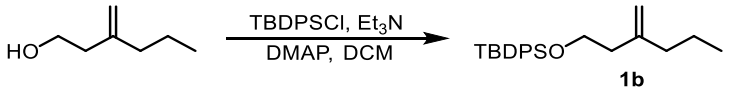
stirred for 4 hours at room temperature. The resulting suspension was quenched by filtering through a plug of silica and washed with excess amount of pentane. The filtrate was concentrated under vacuum, followed by column chromatography (with pure pentane) to give the desired product **1f** (253 mg, 52% for the last 2 steps) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.27 – 7.20 (m, 3H), 4.82 – 4.78 (m, 2H), 2.83 – 2.77 (m, 2H), 2.42 – 2.35 (m, 2H), 2.12 (q, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 142.4, 128.3, 128.3, 125.8, 107.9, 38.1, 34.5, 29.0, 12.4.

IR (neat, cm^{-1}) *v* 3026, 2965, 2933, 1645, 1495, 1453, 887, 743, 696.

GCMS (EI) calculated for $C_{12}H_{16}$ [M]: 160.1, found: 160.2.



1b

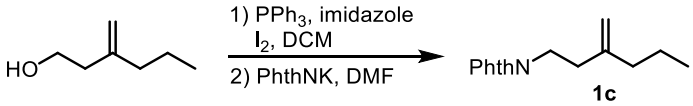
To a solution of the known alcohol[12] (342 mg, 3.0 mmol) in methylene chloride (10 ml) at 0 °C was sequentially added triethyl amine (800 µl, 5.8 mmol), TBDPSCl (1.2 ml, 4.5 mmol) and 4-dimethylaminopyridine (37 mg, 0.3 mmol). The reaction mixture was stirred at room temperature for 4 hours. The resulting solution was concentrated with silica under vacuum. The product **1b** was obtained as a colorless oil (930 mg, 88%) after purified by column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 4H), 7.47 – 7.38 (m, 6H), 4.76 – 4.74 (m, 1H), 4.73 – 4.71 (m, 1H), 3.77 (t, *J* = 7.1 Hz, 2H), 2.29 (t, *J* = 6.5 Hz, 2H), 1.95 (t, *J* = 7.6 Hz, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 1.07 (s, 9H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 135.6, 134.0, 129.5, 127.6, 110.6, 63.1, 39.1, 38.5, 26.9, 20.8, 19.2, 13.8.

IR (neat, cm^{-1}) *v* 2956, 2930, 2858, 1471, 1427, 1108, 1087, 737, 701, 505.

HRMS (ESI) *m/z* calculated for $C_{23}H_{32}OSiNa$ [$M+Na^+$]: 375.2120, found: 375.2145.



1c

To a solution of the known alcohol[12] (342 mg, 3.0 mmol) in methylene chloride (10 ml) at 0 °C was sequentially added triphenylphosphine (944 mg, 3.6 mmol), imidazole (306 mg, 4.5 mmol) and iodine (914 mg, 3.6 mmol). The reaction mixture was gradually warmed up to room temperature and stirred for 1 hour. The solution was diluted with pentane and filtered through a plug of silica. The filtrate was concentrated under vacuum to give crude iodide as an orange oil, which was used directly for the next step.

To a solution of the crude iodide (400 mg, 1.8 mmol) in dimethylformamide (20 ml) was added potassium phthalimide (661 mg, 3.6 mmol). The reaction mixture was stirred at 80 °C overnight. After cooling down to ambient temperature, the mixture was diluted with ethyl acetate and washed with water 5 times. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified via column chromatography to give the desired product **1c** as a colorless oil (208 mg, 48% for the second step).

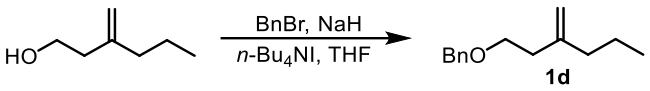
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.75 – 7.70 (m, 2H), 4.77 (d, *J* = 1.6 Hz, 1H), 4.75

(s, 1H), 3.86 – 3.79 (m, 2H), 2.41 (t, *J* = 7.3 Hz, 2H), 2.10 (t, *J* = 7.7 Hz, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 168.3, 146.0, 133.8, 132.1, 123.2, 111.6, 37.7, 36.7, 34.6, 20.8, 13.8.

IR (neat, cm^{-1}) *v* 2957, 2931, 2871, 1772, 1706, 1393, 1359, 1115, 1001, 895, 716, 530.

HRMS (ASAP) *m/z* calculated for $C_{15}H_{18}NO_2$ [M+H$^+$]: 244.1338, found: 244.1339.



1d

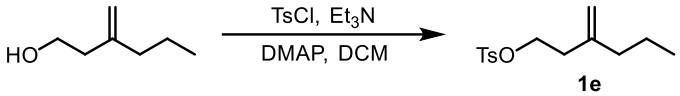
To a solution of the known alcohol[12] (193 mg, 1.7 mmol) in tetrahydrofuran (8.0 ml) at 0 °C was added sodium hydride (135 mg, 3.4 mmol, 60 % dispersion in mineral oil). The reaction mixture was stirred at 0 °C until gas evolution ceased (~1 hour). Benzyl bromide (221 µl, 1.9 mmol) and tetrabutylammonium iodide (62 mg, 0.17 mmol) were added to the reaction mixture, which was further stirred at room temperature overnight. The reaction was quenched by adding a saturated aqueous solution of ammonium chloride. The resulting solution was extracted with ethyl acetate 3 times. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by column chromatography to give the desired product **1d** as a colorless oil (245 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 4.82 – 4.78 (m, 2H), 4.55 (s, 2H), 3.61 (t, *J* = 7.0 Hz, 2H), 2.37 (t, *J* = 6.8 Hz, 2H), 2.03 (t, *J* = 7.7 Hz, 2H), 1.55 – 1.41 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 146.6, 138.5, 128.3, 127.6, 127.5, 110.4, 72.9, 69.1, 38.5, 36.1, 20.8, 13.8.

IR (neat, cm-1) *v* 2957, 2929, 2869, 1645, 1453, 1361, 1098, 1027, 893, 738, 697.

LRMS (ESI+APCI) *m/z* calculated for $C_{14}H_{21}O$ [M+H]$^+$: 205.2, found: 205.2.



1e

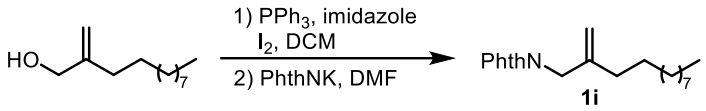
To a solution of the known alcohol[12] (228 mg, 2.0 mmol) in methylene chloride (10 ml) at 0 °C was sequentially added triethyl amine (556 µl, 4.0 mmol), *p*-toluenesulfonyl chloride (381 mg, 2.0 mmol) and 4-dimethylaminopyridine (24 mg, 0.2 mmol). The reaction mixture was stirred at room temperature overnight. The resulting solution was concentrated with silica under vacuum. The product **1e** was obtained as a colorless oil (424 mg, 79%) after purified by column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.84 – 7.78 (m, 2H), 7.40 – 7.34 (m, 2H), 4.80 (s, 1H), 4.72 (s, 1H), 4.14 (t, *J* = 7.0 Hz, 2H), 2.47 (s, 3H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.91 (t, *J* = 7.6 Hz, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 144.7, 144.0, 133.1, 129.8, 127.9, 111.9, 68.8, 38.1, 35.0, 21.7, 20.6, 13.7.

IR (neat, cm^{-1}) *v* 2958, 2930, 2872, 1598, 1357, 1173, 1096, 964, 907, 814, 773, 662, 553.

HRMS (ESI) *m/z* calculated for $C_{14}H_{20}O_3SNa$ [M+Na$^+$]: 291.1031, found: 291.1040.



1i

(**1i**) was synthesized according to the same procedure as **1c**.

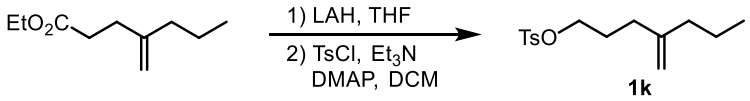
White solid; 412 mg, 60%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.78 – 7.72 (m, 2H), 4.90 (d, J = 1.3 Hz, 1H), 4.85 (s, 1H), 4.25 (s, 2H), 2.08 (t, J = 7.7 Hz, 2H), 1.57 – 1.49 (m, 2H), 1.38 – 1.22 (m, 14H), 0.90 (t, J = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 143.5, 134.0, 132.1, 123.3, 110.7, 42.3, 34.0, 31.9, 29.6, 29.6, 29.5, 29.3, 29.3, 27.5, 22.7, 14.1.

IR (neat, cm-1) *v* 2915, 2847, 1701, 1424, 1394, 1127, 947, 724, 710, 531.

HRMS (ASAP) *m/z* calculated for $C_{21}H_{30}NO_2$ [M+H$^+$]: 328.2277, found: 328.2272.



1k

To a suspension of lithium aluminium hydride (104 mg, 2.7 mmol) in THF at 0 °C was added the known ester[13] (234 mg, 1.4 mmol) in THF (5.0 ml). The reaction mixture was stirred at room temperature for 1 hour before it was quenched by the sequential addition of 100 µl of water, 100 µl of 15% sodium hydroxide aqueous solution, 300 µl of water, and anhydrous sodium sulfate. The resultant mixture was stirred for 30 min, followed by filtering through a plug of celite. The filtrate was concentrated under vacuum to give the crude alcohol, which was used directly for the next step.

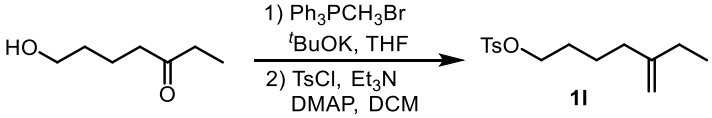
To a solution of the resultant alcohol in methylene chloride (5.0 ml) at 0 °C was sequentially added triethyl amine (290 µl, 2.1 mmol), *p*-toluenesulfonyl chloride (263 mg, 1.4 mmol) and 4-dimethylaminopyridine (17 mg, 0.14 mmol). The reaction mixture was stirred at room temperature overnight. The resulting solution was concentrated with silica under vacuum. The product **1k** was obtained as a colorless oil (252 mg, 65%) after purified by column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.40 – 7.34 (m, 2H), 4.72 (s, 1H), 4.65 (s, 1H), 4.06 (t, J = 6.4 Hz, 2H), 2.48 (s, 3H), 2.03 (t, J = 7.6 Hz, 2H), 1.93 (t, J = 7.6 Hz, 2H), 1.84 – 1.76 (m, 2H), 1.42 (h, J = 7.4 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 144.7, 133.2, 129.8, 127.9, 109.8, 70.2, 38.0, 31.5, 26.9, 21.6, 20.8, 13.8.

IR (neat, cm^{-1}) *v* 2957, 2930, 2862, 1646, 1386, 1252, 1134, 1016, 892.

HRMS (ESI) *m/z* calculated for $C_{15}H_{22}O_3SNa$ [M+Na$^+$]: 305.1187, found: 305.1192.



1l

To a suspension of methyltriphenylphosphonium bromide (2.9 g, 8.0 mmol) in THF (40 ml) at 0 °C was slowly added potassium *tert*-butoxide (900 mg, 8.0 mmol). The reaction mixture was stirred

for 30 min before the slow addition of a solution of the known ketone[14] (530 mg, 4.0 mmol) in THF. The reaction was further stirred for 4 hours at room temperature. The resulting suspension was quenched by filtering through a plug of silica, and washed with 1:2 hexanes/ethyl acetate. The filtrate was concentrated under vacuum to give the crude alkene, which was used without further purification.

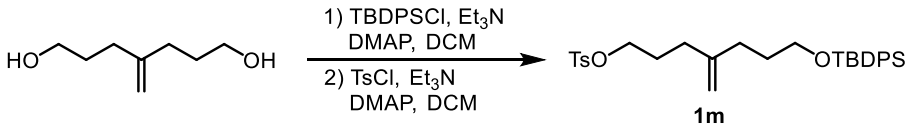
To a solution of the resultant alkene (128 mg, 1.0 mmol) in methylene chloride (10 ml) at 0 °C was sequentially added triethyl amine (200 µl, 1.5 mmol), *p*-toluenesulfonyl chloride (191 mg, 1.0 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol). The reaction mixture was stirred at room temperature overnight. The resulting solution was concentrated with silica under vacuum. The product was obtained as a colorless oil (161 mg, 57% for the second step) after purified by column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.38 – 7.34 (m, 2H), 4.71 (d, J = 1.7 Hz, 1H), 4.66 – 4.62 (m, 1H), 4.06 (t, J = 6.4 Hz, 2H), 2.47 (s, 3H), 2.02 – 1.95 (m, 4H), 1.71 – 1.61 (m, 2H), 1.50 – 1.43 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 144.6, 133.2, 129.8, 127.9, 108.1, 70.5, 35.4, 28.5, 28.4, 23.4, 21.6, 12.3.

IR (neat, cm^{-1}) ν 2963, 2935, 2876, 1598, 1357, 1188, 1174, 1097, 934, 814, 662, 554.

HRMS (ESI) *m/z* calculated for $C_{15}H_{22}O_3SNa$ [M+Na$^+$]: 305.1187, found: 305.1188.



1m

To a solution of the known diol[15] (364 mg, 2.5 mmol) in methylene chloride (50 ml) at 0 °C was sequentially added triethyl amine (700 µl, 5.0 mmol), TBDPSCl (525 µl, 2.0 mmol) and 4-dimethylaminopyridine (31 mg, 0.3 mmol). The reaction mixture was stirred at room temperature 5 hours. The resulting solution was concentrated with silica under vacuum. The mono-protected product was obtained as a colorless oil (296 mg, 31%) after purified by column chromatography (156 mg, 43% of starting material was recovered).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 4H), 7.47 – 7.38 (m, 6H), 4.79 – 4.73 (m, 2H), 3.73 – 3.65 (m, 4H), 2.18 – 2.06 (m, 4H), 1.77 – 1.68 (m, 4H), 1.41 (s, 1H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 135.6, 134.1, 129.5, 127.6, 109.3, 63.6, 62.8, 32.3, 32.2, 30.8, 30.7, 26.9, 19.2.

IR (neat, cm^{-1}) ν 3332, 2931, 2857, 1427, 1105, 700, 611, 503.

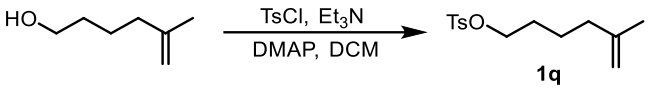
To a solution of the obtained alcohol (296 mg, 0.77 mmol) in methylene chloride (7.0 ml) at 0 °C was sequentially added triethyl amine (160 µl, 1.2 mmol), *p*-toluenesulfonyl chloride (163 mg, 0.85 mmol) and 4-dimethylaminopyridine (10 mg, 0.08 mmol). The reaction mixture was stirred at room temperature overnight. The resulting solution was concentrated with silica under vacuum. The desired product **1m** was obtained as a colorless oil (378 mg, 91%) after purified by column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.73 – 7.67 (m, 4H), 7.48 – 7.39 (m, 6H), 7.39 – 7.34 (m, 2H), 4.73 (s, 1H), 4.66 (s, 1H), 4.06 (t, J = 6.4 Hz, 2H), 3.68 (t, J = 6.4 Hz, 2H), 2.47 (s, 3H), 2.09 – 2.01 (m, 4H), 1.85 – 1.75 (m, 2H), 1.72 – 1.63 (m, 2H), 1.09 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.36, 144.70, 135.58, 133.99, 133.21, 129.84, 129.60, 127.91, 127.64, 109.95, 70.13, 63.45, 32.07, 31.64, 30.67, 26.90, 26.87, 21.66, 19.24.

IR (neat, cm^{-1}) *v* 2930, 2856, 1427, 1360, 1175, 1098, 926, 815, 702, 503.

HRMS (ESI) *m/z* calculated for $C_{31}H_{40}O_4SSiNa$ [M+Na$^+$]: 559.2314, found: 559.2327.



1q

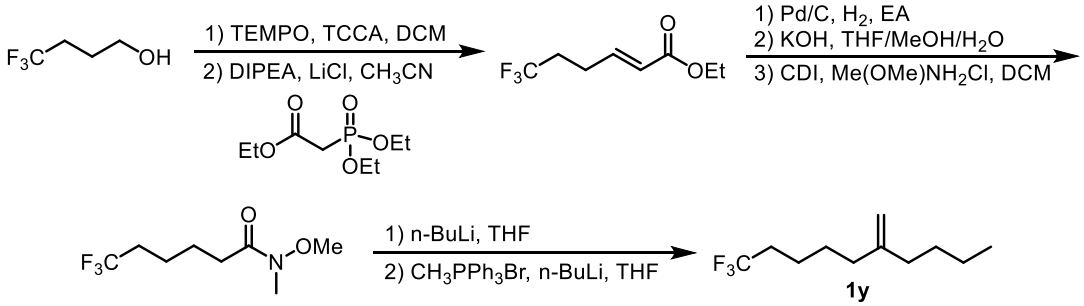
(**1q**) was synthesized from the known alcohol[16] according to the same procedure as **1e**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 2H), 7.39 – 7.34 (m, 2H), 4.72 – 4.69 (m, 1H), 4.64 – 4.60 (m, 1H), 4.06 (t, *J* = 6.4 Hz, 2H), 2.47 (s, 3H), 1.97 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.61 (m, 5H), 1.51 – 1.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.6, 133.2, 129.8, 127.9, 110.4, 70.5, 36.9, 28.3, 23.2, 22.2, 21.6.

IR (neat, cm^{-1}) *v* 2940, 1598, 1451, 1356, 1174, 930, 814, 662, 553.

HRMS (ESI) *m/z* calculated for $C_{14}H_{20}O_3SNa$ [M+Na$^+$]: 291.1031, found: 291.1041.



1y

To a solution of 4,4,4-trifluoro-1-butanol (3.0 ml, 30 mmol) in methylene chloride (60 ml) at 0 °C was added trichloroisocyanuric acid (7.5 g, 33 mmol) and TEMPO (234 mg, 1.5 mmol). The yellow suspension was stirred at 0 °C for 1 hour, followed by filtering through a plug of celite. The filtrate was diluted with methylene chloride and washed with a saturated solution of sodium sulfite. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum to give the corresponding aldehyde, which was used directly for the next step.

To a solution of the aldehyde in acetonitrile (100 ml) was sequentially added triethyl phosphonoacetate (12 ml, 60 mmol), N,N-diisopropylethylamine (7.8 ml, 45 mmol), and lithium chloride (2.5 g, 60 mmol). The reaction mixture was stirred at room temperature overnight. After completion, the solvent was removed under vacuum, and the residue was purified by column chromatography to give the α,β-unsaturated ester (2.4 g, 41% for 2 steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 14.9, 7.2 Hz, 1H), 5.90 (d, *J* = 15.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.50 (q, *J* = 7.9 Hz, 2H), 2.27 (h, *J* = 8.8 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 144.6, 126.5 (q, *J* = 276.6 Hz) 123.0, 60.4, 32.4 (q, *J* = 29.2 Hz), 24.6 (q, *J* = 3.4 Hz), 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, *J* = 10.4 Hz).

IR (neat, cm^{-1}) *v* 2985, 1718, 1659, 1275, 1251, 1230, 1182, 1136, 1033, 971.

To a solution of the α,β-unsaturated ester (3.0 g, 15 mmol) in ethyl acetate (150 ml) was added Pd/C (300 mg, 10% wt). A balloon of hydrogen gas was then introduced, and the reaction mixture was stirred at room temperature overnight. The reaction was quenched by filtering the suspension through a plug of celite. The filtrate was concentrated under vacuum to give crude ester, which was used directly for the next step.

To a solution of the resultant ester in tetrahydrofuran/methanol (120 ml, 5:1) at room temperature was added 20 ml of an aqueous solution of potassium hydroxide (2.5 g, 45 mmol). The mixture was stirred at room temperature overnight. Solvents were removed under vacuum, and the residue was diluted with water, followed by a reverse extraction with ethyl ether. The aqueous layer was acidified to pH 1~2 with 2 M hydrogen chloride aqueous solution. The resultant solution was extracted 3 times with ethyl acetate. Organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude acid was obtained as a colorless oil and used without further purification.

To a solution of acid in methylene chloride (150 ml) was added 1,1'-carbonyldiimidazole (2.4 g, 15 mmol) at 0 °C. The reaction mixture was stirred at 0 °C until gas evolution ceased (~1 hour). N,O-dimethylhydroxylamine hydrochloride (2.9 g, 30 mmol) was then added, and the mixture was stirred at room temperature overnight. The resultant suspension was diluted with methylene chloride and washed with water and 1 M hydrogen chloride aqueous solution. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified via column chromatography to give the desired weinreb amide (2.2 g, 67% for 3 steps) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.19 (s, 3H), 2.47 (t, J = 7.3 Hz, 2H), 2.18 – 2.05 (m, 2H), 1.73 (dt, J = 14.5, 7.3 Hz, 2H), 1.66 – 1.59 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 127.1 (q, J = 276.3 Hz), 61.2, 33.6 (q, J = 28.5 Hz), 32.1, 31.3, 23.6, 21.7 (q, J = 2.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -65.5 (t, J = 10.9 Hz).

IR (neat, cm^{-1}) ν 2945, 2880, 1660, 1388, 1255, 1131, 1028, 995.

The synthesis of **1y** from the weinreb amide was followed the general procedure C.

(**1y**) colorless oil; 335 mg, 59% for 2 steps.

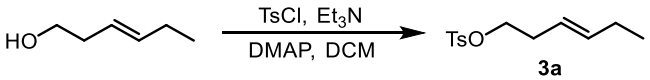
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 – 4.76 (m, 1H), 4.76 – 4.73 (m, 1H), 2.17 – 2.01 (m, 6H), 1.64 – 1.51 (m, 4H), 1.48 – 1.41 (m, 2H), 1.41 – 1.30 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 127.2 (q, J = 276.2 Hz), 109.1, 35.6, 35.5, 33.6 (q, J = 28.4 Hz), 30.0, 26.8, 22.5, 21.6 (q, J = 2.9 Hz), 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, J = 11.0 Hz).

IR (neat, cm^{-1}) ν 2931, 2873, 1645, 1463, 1387, 1254, 1134, 1027, 888.

GCMS (EI) calculated for $C_{11}H_{19}F_3$ [M]: 208.1, found: 208.2.

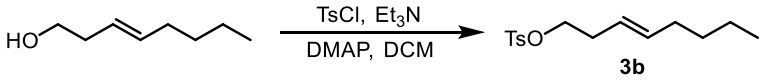


3a

3a was synthesized from *trans*-3-hexen-1-ol according to the same procedure as **1e**.

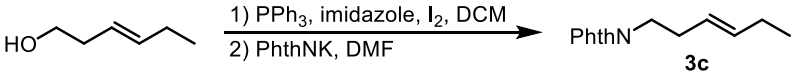
Colorless oil, 3.1 g, 82%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.38 – 7.33 (m, 2H), 5.53 (dtt, *J* = 15.4, 6.3, 1.4 Hz, 1H), 5.25 (dtt, *J* = 15.3, 6.8, 1.7 Hz, 1H), 4.03 (t, *J* = 6.9 Hz, 2H), 2.47 (s, 3H), 2.34 (q, *J* = 6.9, 6.2 Hz, 2H), 1.98 (p, *J* = 6.0 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 136.1, 133.2, 129.8, 127.9, 122.5, 70.2, 32.1, 25.5, 21.6, 13.5.
IR (neat, cm^{-1}) *v* 2962, 2931, 1598, 1358, 1175, 1097, 964, 918, 814, 663, 554.
HRMS (ESI) *m/z* calculated for $C_{13}H_{18}O_3SNa$ [M+Na^+]: 277.0874, found: 277.0886.



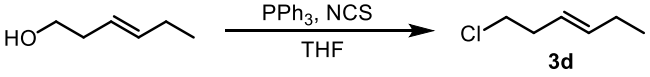
3b

3b was synthesized from the known alcohol[17] according to the same procedure as **1e**.
Colorless oil, 468 mg, 83%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.53 – 5.44 (m, 1H), 5.31 – 5.21 (m, 1H), 4.03 (t, *J* = 6.9 Hz, 2H), 2.47 (s, 3H), 2.35 (q, *J* = 6.9, 6.3 Hz, 2H), 1.96 (q, *J* = 6.7 Hz, 2H), 1.34 – 1.26 (m, 4H), 0.92 – 0.87 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 134.6, 133.3, 129.8, 127.9, 123.4, 70.1, 32.2, 32.1, 31.4, 22.1, 21.6, 13.9.
IR (neat, cm^{-1}) *v* 2956, 2926, 2857, 1598, 1463, 1359, 1175, 1097, 962, 912, 814, 770, 663, 554.
HRMS (ESI) *m/z* calculated for $C_{15}H_{22}O_3SNa$ [M+Na^+]: 305.1187, found: 305.1206.



3c

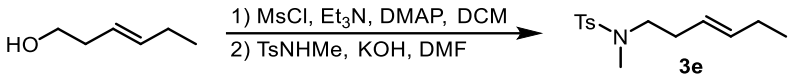
3c was synthesized from *trans*-3-hexen-1-ol according to the same procedure as **1c**.
White solid; 1.5 g, 63%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.74 – 7.69 (m, 2H), 5.55 – 5.46 (m, 1H), 5.43 – 5.34 (m, 1H), 3.73 (t, *J* = 7.2 Hz, 2H), 2.38 (q, *J* = 7.1 Hz, 2H), 1.95 (p, *J* = 6.2 Hz, 2H), 0.87 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 135.3, 133.8, 132.1, 124.7, 123.1, 37.9, 31.6, 25.5, 13.6.
IR (neat, cm^{-1}) *v* 2965, 2937, 1770, 1699, 1433, 1397, 1362, 1069, 967, 720.
HRMS (ASAP) *m/z* calculated for $C_{14}H_{16}NO_2$ [M+H^+]: 230.1181, found: 230.1194.



3d

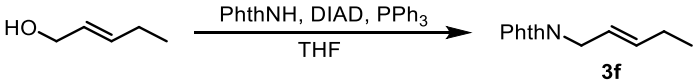
To a stirred solution of *trans*-3-hexen-1-ol (6.1 ml, 50 mmol) in tetrahydrofuran (100 ml) at 0 °C was added triphenylphosphine (15.7 g, 60 mmol) and N-chlorosuccinimide (8.0 g, 60 mmol). The reaction mixture was gradually warmed up to room temperature and stirred for 2 hours. The reaction was filtered through a plug of silica and washed with pentane. The filtrate was carefully concentrated under vacuum at ~10 °C. The residue was distilled to yield the desired product **3d** (3.3 g, 56%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61 (dtt, *J* = 13.9, 6.3, 1.3 Hz, 1H), 5.42 (dtt, *J* = 15.2, 6.8, 1.6 Hz, 1H), 3.53 (t, *J* = 7.1 Hz, 2H), 2.51 – 2.43 (m, 2H), 2.05 (p, *J* = 6.7, 6.2 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 124.5, 44.5, 35.9, 25.6, 13.6.
IR (neat, cm-1) v 2964, 2933, 2875, 1716, 1455, 1291, 966, 814, 720, 657.
GCMS (EI) calculated for $C_6H_{11}Cl$ [M]: 118.1, found: 118.1.



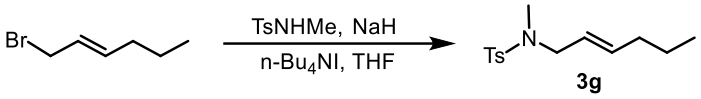
3e

To a stirred solution of *trans*-3-hexen-1-ol (620 µl, 5.0 mmol) in methylene chloride (20 ml) at 0 ^oC was sequentially added triethyl amine (1.0 ml, 7.5 mmol), methanesulfonyl chloride (470 µl, 6.0 mmol) and 4-dimethylaminopyridine (61 mg, 0.5 mmol). The reaction mixture was stirred at room temperature overnight. The solution was diluted with methylene chloride and washed with water and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum to give crude mesylate as a colorless oil, which was used directly for the next step.
To a solution of the resultant mesylate in dimethylformamide (10 ml) was added N-methylbenzenesulfonamide (926 mg, 5.0 mmol) and potassium hydroxide (340 mg, 6.0 mmol). The reaction mixture was stirred at 120 ^oC for 5 hours. After cooling down to ambient temperature, the mixture was diluted with ethyl acetate and washed with water 5 times. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified via column chromatography to give the desired product **3e** as a light yellow oil (840 mg, 63%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.35 – 7.30 (m, 2H), 5.58 – 5.49 (m, 1H), 5.38 – 5.29 (m, 1H), 3.07 – 3.01 (m, 2H), 2.74 (s, 3H), 2.44 (s, 3H), 2.24 (q, *J* = 7.8 Hz, 2H), 2.01 (p, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 134.9, 134.8, 129.6, 127.4, 124.7, 50.2, 34.8, 31.2, 25.6, 21.5, 13.7.
IR (neat, cm^{-1}) *v* 2962, 2926, 2872, 1598, 1457, 1339, 1159, 1089, 966, 815, 718, 652, 549.
HRMS (ESI) *m/z* calculated for $C_{14}H_{21}NO_2SNa$ [M+Na^+]: 290.1191, found: 290.1201.



3f

To a stirred solution of *trans*-2-penten-1-ol (2.0 ml, 20 mmol) in THF (100 ml) at 0 ^oC was sequentially added phthalimide (3.5 g, 24 mmol), triphenylphosphine (6.3 g, 24 mmol), and diisopropyl azodicarboxylate (4.7 ml, 24 mmol). The reaction mixture was stirred at room temperature overnight. The solution was then concentrated with silica, and the resultant silica powder was purified by column chromatography to give desired product **3f** (2.8 g, 65%) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.74 – 7.71 (m, 2H), 5.85 – 5.76 (m, 1H), 5.56 – 5.48 (m, 1H), 4.25 (dd, *J* = 6.2, 1.2 Hz, 2H), 2.09 – 1.99 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 136.6, 133.8, 132.2, 123.2, 122.1, 39.6, 25.1, 13.1.
IR (neat, cm^{-1}) *v* 2963, 2931, 2874, 1771, 1705, 1429, 1390, 1354, 1070, 962, 944, 714, 528.
HRMS (ASAP) *m/z* calculated for $C_{13}H_{14}NO_2$ [M+H^+]: 216.1024, found: 216.1024.



3g

To a stirred solution of N-methylbenzenesulfonamide (555 mg, 3.0 mmol) in THF (20 ml) at 0 °C was added sodium hydride (160 mg, 4.0 mmol). The mixture was stirred at 0 °C until gas evolution ceased (~1 hour). The known ally bromide[18] (324 mg, 2.0 mmol) in THF (2.0 ml) was added to the reaction mixture, followed by the addition of tetrabutylammonium iodide (74 mg, 0.2 mmol). The reaction was stirred at room temperature overnight. The reaction was quenched by adding an aqueous solution of ammonium chloride at 0 °C. The resultant solution was extracted by ethyl acetate 3 times. The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum. The residue was purified via column chromatography to give the desired product **3g** (411 mg, 77%) as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.35 – 7.31 (m, 2H), 5.63 – 5.54 (m, 1H), 5.39 – 5.29 (m, 1H), 3.58 (d, *J* = 6.8 Hz, 2H), 2.66 (s, 3H), 2.45 (s, 3H), 2.00 (q, *J* = 6.5 Hz, 2H), 1.37 (h, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 136.0, 134.6, 129.6, 127.5, 124.1, 52.4, 34.2, 33.9, 22.1, 21.5, 13.6.

IR (neat, cm^{-1}) *v* 2958, 2927, 2870, 1597, 1454, 1338, 1159, 1089, 962, 915, 814, 725, 650, 547.

HRMS (ESI) *m/z* calculated for $C_{14}H_{21}NO_2SNa$ [M+Na^+]: 290.1191, found: 290.1200.

3. General Procedures for Allylic C-H Amination Reactions

General Procedure D (for 1,1-disubstituted alkenes with TsN_3)

To an oven-dried screw-capped vial with a magnetic stir bar was sequentially added alkene (0.1 mmol, 1.0 equiv), tosyl azide (23 µl, 1.5 equiv), $[Cp^{TM}IrCl_2]_2$ (**Ir-6**) (3.9 mg, 5.0 mol%), cesium carbonate (16.3 mg, 50 mol%), silver trifluoroacetate (5.5 mg, 25 mol%), silver tetrafluoroborate (11.7 mg, 60 mol%), and 1,2-dichloroethane (200 µl, 0.5 M). The cap was screwed on, and the reaction was stirred at 35 °C for 20 hours. The reaction mixture was filtered through a plug of Celite, and the filtrate was concentrated under vacuum. The crude mixture was analyzed *via* ^{1}H NMR spectroscopy with mesitylene (12.0 mg, 0.1 mmol) as an internal standard. The sample was further purified by column chromatography to give the desired amination product.

General Procedure E (for 1,1-disubstituted alkenes with dioxazolones)

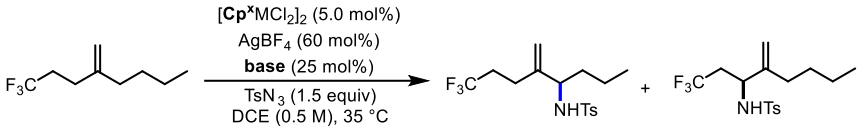
To an oven-dried screw-capped vial with a magnetic stir bar was sequentially added alkene (0.1 mmol, 1.0 equiv), $[Cp^{TM}IrCl_2]_2$ (**Ir-6**) (3.9 mg, 5.0 mol%), cesium carbonate (16.3 mg, 50 mol%), silver trifluoroacetate (5.5 mg, 25 mol%), and silver hexafluoroantimonate (20.6 mg, 60 mol%). In a separated vial, dioxazolone (1.5 equiv) was dissolved in 1,2-dichloroethane (200 µl, 0.5 M), which was then transferred to the first vail. The cap was screwed on, and the reaction was stirred at 35 °C for 20 hours. The reaction mixture was filtered through a plug of Celite, and the filtrate was concentrated under vacuum. The crude mixture was analyzed *via* ^{1}H NMR spectroscopy with mesitylene (12.0 mg, 0.1 mmol) as an internal standard. The sample was further purified by column chromatography to give the desired amination product.

General Procedure F (for 1,2-disubstituted alkenes)

To an oven-dried screw-capped vial with a magnetic stir bar was sequentially added **Ir-9** (9.0 mg, 15 mol% of monomer), lithium acetate (6.6 mg, 1.0 equiv), and silver tetrafluoroborate (11.7 mg, 60 mol%). In a separated vial alkene (0.1 mmol, 1.0 equiv) and tosyl azide (23 µl, 1.5 equiv) were dissolved in 1,2-dichloroethane (200 µl, 0.5 M), and the resultant solution was transferred to the first vial. The cap was screwed on, and the reaction was stirred at 35 °C for 40 hours. The reaction mixture was filtered through a plug of Celite, and the filtrate was concentrated under vacuum. The crude mixture was analyzed *via* ^{1}H NMR spectroscopy with mesitylene (12.0 mg, 0.1 mmol) as an internal standard. The sample was further purified by column chromatography to give the desired amination product.

4. Reaction Optimization

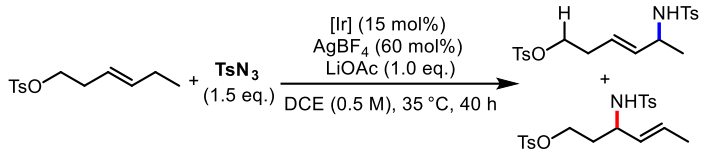
Table 1[a]:

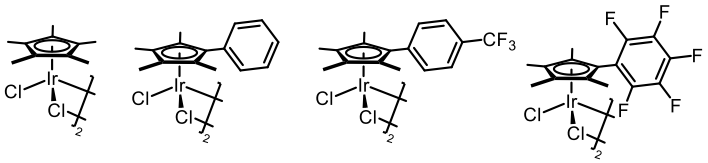


entry	catalyst	base	yield[b]	r.r.[b]
1	$[Cp^*CoCl_2]_2$	LiOAc	N.D.	-
2	$[Cp^*RhCl_2]_2$	LiOAc	trace	-
3	$[Cp^*IrCl_2]_2$	LiOAc	40%	20:1
4	$[Cp^{TM}IrCl_2]_2$	LiOAc	63%	>20:1
5	$[Cp^{TM}IrCl_2]_2$	AgOAc	61%	>20:1
6	$[Cp^{TM}IrCl_2]_2$	AgOTFA	76%	>20:1
7	**$[Cp^{TM}IrCl_2]_2$**	**AgOTFA\Cs$_2$CO$_3$[c]**	**85% (80%)[d]**	**>20:1**
8	-	AgOTFA\Cs$_2$CO$_3$[c]	N.R.	-
9[e]	$[Cp^{TM}IrCl_2]_2$	AgOTFA\Cs$_2$CO$_3$[c]	N.R.	-
10	$[Cp^{TM}IrCl_2]_2$	Cs_2CO_3[c]	33%	>20:1
11[e]	$[Cp^{TM}Ir(OFTA)_2]$	-	N.R.	-
12	$[Cp^{TM}Ir(OFTA)_2]$	-	75%	>20:1

[a]Reactions were conducted on 0.1 mmol scale according to the general procedure D. [b]Yields and regioselectivities were determined by ^{1}H NMR spectroscopy of the crude reaction mixture using mesitylene as an internal standard. [c]50 mol% of Cs_2CO_3. [d]Isolated yield. [e]without $AgBF_4$. Cp^{TM} = tetramethylcyclopentadiene

Table 2 [a]:



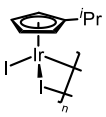


Ir-1
62%, 6.2:1

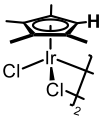
Ir-2
51%, 2.8:1

Ir-3
51%, 2.7:1

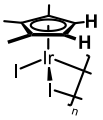
Ir-4
55%, 2.3:1



Ir-5
66%, 14:1

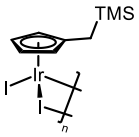


Ir-6
67%, 16:1



Ir-7
70%, 20:1

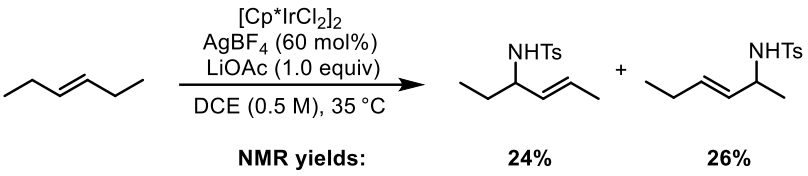
Ir-8
72%, 24:1



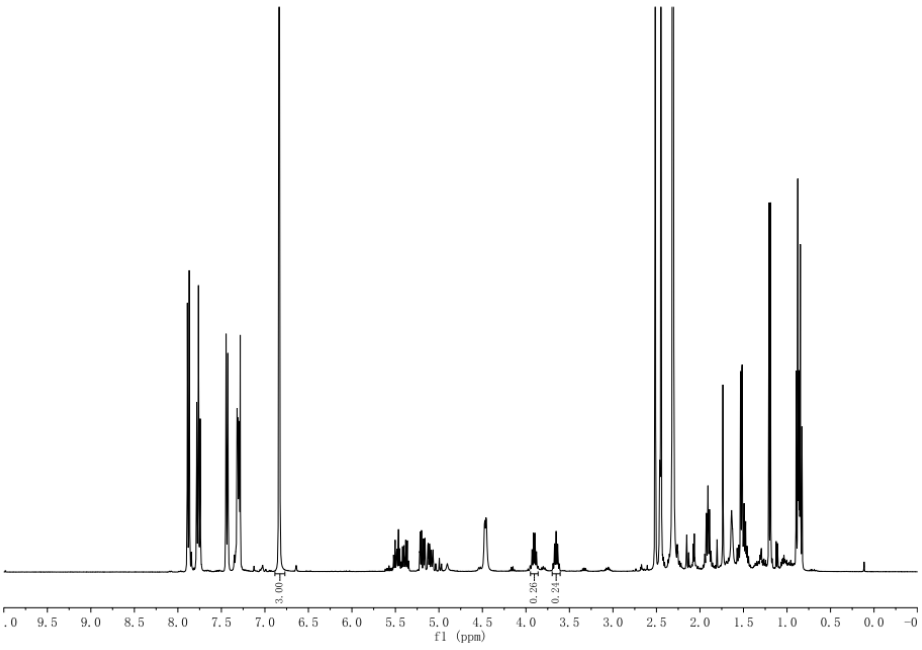
Ir-9
79%, 25:1

[a]Reactions were conducted on 0.1 mmol scale according to the general procedure F. Yields and regioselectivities were determined by ^{1}H NMR spectroscopy of the crude reaction mixture using mesitylene as an internal standard.

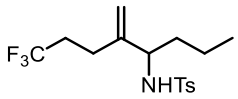
Non-selective C-H amination of *trans*-3-hexene:



NMR yields: **24%** **26%**



5. Product Characterization



2a

4-methyl-N-(8,8,8-trifluoro-5-methyleneoctan-4-yl)benzenesulfonamide (**2a**)

Yield: 80%, >20:1 r.r. (35:1 r.r.); White solid.

R_f = 0.25 (10% ethyl acetate/hexane)

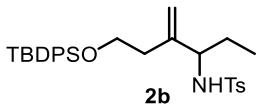
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.32 – 7.28 (m, 2H), 4.98 (s, 1H), 4.85 (d, *J* = 6.8 Hz, 1H), 4.72 (s, 1H), 3.76 (q, *J* = 7.1 Hz, 1H), 2.44 (s, 3H), 2.11 – 1.98 (m, 3H), 1.92 – 1.79 (m, 1H), 1.47 (q, *J* = 7.5 Hz, 2H), 1.32 – 1.14 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 143.5, 137.6, 129.5, 127.3, 126.8 (q, *J* = 276.4 Hz), 112.5, 59.0, 36.2, 31.8 (q, *J* = 28.9 Hz), 22.8 (q, *J* = 2.7 Hz), 21.5, 18.9, 13.5.

^{19}F NMR (^{1}H_decoupled) (471 MHz, $CDCl_3$) δ -66.6.

IR (neat, cm^{-1}) *v* 3276, 2960, 2933, 2873, 1448, 1325, 1257, 1157, 1137, 1112, 1094, 987, 814, 572, 548.

HRMS (ESI) *m/z* calculated for $C_{16}H_{22}F_3NO_2SNa$ [M+Na$^+$]: 372.1221, found: 372.1232.



2b

N-(6-((tert-butyldiphenylsilyl)oxy)-4-methylenehexan-3-yl)-4-methylbenzenesulfonamide (**2b**)

Yield: 73%, >20:1 r.r. (38:1 r.r., detected by GC); Colorless oil.

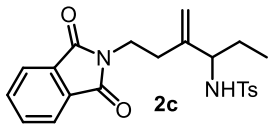
R_f = 0.70 (30% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 6H), 7.51 – 7.39 (m, 6H), 7.21 – 7.15 (m, 2H), 4.99 (d, *J* = 7.9 Hz, 1H), 4.81 (s, 1H), 4.72 (s, 1H), 3.70 – 3.60 (m, 2H), 3.55 (dt, *J* = 10.3, 6.7 Hz, 1H), 2.38 (s, 3H), 2.06 (t, *J* = 6.7 Hz, 2H), 1.57 – 1.44 (m, 2H), 1.07 (s, 9H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 142.9, 138.1, 135.6, 133.5, 133.5, 129.8, 129.3, 127.8, 127.7, 127.2, 114.2, 63.2, 60.7, 34.6, 27.2, 26.9, 21.5, 19.1, 10.3.

IR (neat, cm^{-1}) *v* 3276, 2959, 2930, 2857, 1427, 1325, 1159, 1107, 1090, 905, 815, 703, 666, 549, 504.

HRMS (ESI) *m/z* calculated for $C_{30}H_{39}NO_3SSiNa$ [M+Na$^+$]: 544.2318, found: 544.2319.



2c

N-(6-(1,3-dioxoisoindolin-2-yl)-4-methylenehexan-3-yl)-4-methylbenzenesulfonamide (**2c**)

Yield: 83%, 15:1 r.r.; White solid.

R_f = 0.20 (30% ethyl acetate/hexane)

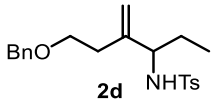
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.78 – 7.72 (m, 4H), 7.30 – 7.26 (m, 2H), 4.96 (d, *J* = 7.4 Hz, 1H), 4.91 (s, 1H), 4.85 (s, 1H), 3.74 – 3.68 (m, 2H), 3.67 – 3.60 (m, 1H), 2.41 (s, 3H), 2.24 (t, *J* = 7.6 Hz, 2H), 1.57 (p, *J* = 7.3 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 143.9, 143.2, 137.9, 134.0, 132.0, 129.5, 127.2, 123.3, 114.3,

60.2, 36.6, 30.4, 27.0, 21.5, 10.2.

IR (neat, cm^{-1}) *v* 3285, 2966, 2934, 2875, 1705, 1397, 1328, 1158, 1091, 908, 720, 665.

HRMS (ESI) *m/z* calculated for $C_{22}H_{24}N_2O_4SNa$ [M+Na^+]: 435.1354, found: 435.1364.



2d

N-(6-(benzyloxy)-4-methylenehexan-3-yl)-4-methylbenzenesulfonamide (**2d**)

Yield: 50%, >20:1 r.r. (33:1 r.r., detected by GC); (70% conversion); Colorless oil.

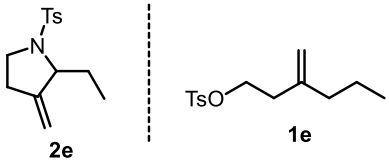
R_f = 0.50 (30% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.69 – 7.65 (m, 2H), 7.41 – 7.31 (m, 5H), 7.25 – 7.21 (m, 2H), 5.45 (d, *J* = 7.4 Hz, 1H), 4.81 (s, 1H), 4.79 (s, 1H), 4.56 – 4.47 (m, 2H), 3.66 (q, *J* = 7.3 Hz, 1H), 3.52 (dt, *J* = 9.1, 6.0 Hz, 1H), 3.40 (ddd, *J* = 9.2, 7.4, 5.8 Hz, 1H), 2.41 (s, 3H), 2.24 – 2.11 (m, 2H), 1.64 – 1.49 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 145.0, 142.9, 138.2, 137.7, 129.3, 128.5, 127.9, 127.8, 127.2, 114.6, 73.2, 69.7, 60.8, 31.7, 27.4, 21.5, 10.3.

IR (neat, cm^{-1}) *v* 3279, 2964, 2929, 2874, 1452, 1321, 1156, 1091, 908, 814, 747, 699, 665, 573, 548.

HRMS (ESI) *m/z* calculated for $C_{21}H_{27}NO_3SNa$ [M+Na^+]: 396.1609, found: 396.1615.



2e **1e**

2-ethyl-3-methylene-1-tosylpyrrolidine (**2e**)

1.0 equivalent of cesium carbonate was applied.

Yield: 86%, >20:1 r.r.; White solid.

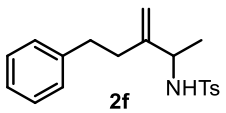
R_f = 0.35 (10% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.74 – 7.70 (m, 2H), 7.34 – 7.30 (m, 2H), 4.90 (q, *J* = 2.0 Hz, 1H), 4.80 (q, *J* = 2.0 Hz, 1H), 4.00 (ddd, *J* = 6.4, 4.5, 1.9 Hz, 1H), 3.49 (ddd, *J* = 10.3, 8.0, 5.2 Hz, 1H), 3.24 (dt, *J* = 10.3, 7.8 Hz, 1H), 2.51 – 2.41 (m, 4H), 2.23 – 2.15 (m, 1H), 1.88 (ddd, *J* = 13.8, 7.4, 6.4 Hz, 1H), 1.82 – 1.73 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 148.0, 143.4, 134.5, 129.6, 127.6, 107.2, 64.4, 47.9, 31.5, 28.9, 21.5, 8.9.

IR (neat, cm^{-1}) *v* 2968, 2925, 2875, 1341, 1158, 1092, 896, 814, 662, 590, 549.

HRMS (ESI) *m/z* calculated for $C_{14}H_{19}NO_2SNa$ [M+Na^+]: 288.1034, found: 288.1043.



2f

4-methyl-N-(3-methylene-5-phenylpentan-2-yl)benzenesulfonamide (**2f**)

Room temperature was applied.

Yield: 78%, 11:1 r.r.; Light yellow oil.

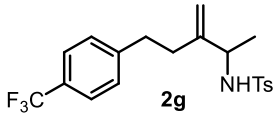
$\mathbf{R_f}$ = 0.45 (20% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.31 – 7.26 (m, 4H), 7.23 – 7.19 (m, 1H), 7.12 – 7.08 (m, 2H), 4.98 (s, 1H), 4.85 (s, 1H), 4.61 (d, *J* = 7.6 Hz, 1H), 3.91 (p, *J* = 6.9 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.44 (s, 3H), 2.24 – 2.12 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 143.3, 141.6, 137.9, 129.6, 128.3, 128.3, 127.2, 125.9, 111.1, 53.9, 34.0, 33.8, 21.5, 20.9.

IR (neat, cm^{-1}) *v* 3276, 3027, 2977, 2930, 1453, 1326, 1159, 1091, 814, 699, 666, 574, 549.

HRMS (ESI) *m/z* calculated for $C_{19}H_{23}NO_2SNa$ [M+Na^+]: 352.1347, found: 352.1349.



2g

4-methyl-N-(3-methylene-5-(4-(trifluoromethyl)phenyl)pentan-2-yl)benzenesulfonamide (**2g**)

Room temperature was applied.

Yield: 89%, 14:1 r.r.; light yellow solid.

$\mathbf{R_f}$ = 0.40 (20% ethyl acetate/hexane)

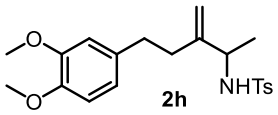
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.54 – 7.50 (m, 2H), 7.31 – 7.27 (m, 2H), 7.23 – 7.20 (m, 2H), 4.99 (s, 1H), 4.83 (s, 1H), 4.79 (d, *J* = 7.7 Hz, 1H), 3.89 (p, *J* = 7.0 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.42 (s, 3H), 2.22 (t, *J* = 8.1 Hz, 2H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 145.8, 143.4, 137.8, 129.6, 128.6, 127.2, 125.20 (q, *J* = 3.7 Hz) 111.4, 53.8, 33.8, 33.4, 21.5, 20.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.3 (s).

IR (neat, cm^{-1}) *v* 3275, 2978, 2932, 1418, 1323, 1157, 1119, 1092, 1067, 815, 666, 582, 549.

HRMS (ESI) *m/z* calculated for $C_{20}H_{22}F_3NO_2SNa$ [M+Na^+]: 420.1221, found: 420.1227.



2h

N-(5-(3,4-dimethoxyphenyl)-3-methylenepentan-2-yl)-4-methylbenzenesulfonamide (**2h**)

Room temperature was applied.

Yield: 85%, 9.0:1 r.r.; White solid.

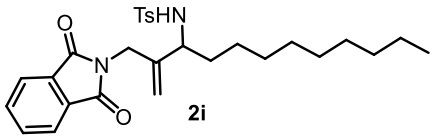
$\mathbf{R_f}$ = 0.10 (20% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.31 – 7.25 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 6.65 (dd, *J* = 8.1, 2.0 Hz, 1H), 4.96 (s, 1H), 4.83 (s, 1H), 4.68 (d, *J* = 7.7 Hz, 1H), 3.92 – 3.85 (m, 7H), 2.64 – 2.51 (m, 2H), 2.42 (s, 3H), 2.20 (t, *J* = 8.1 Hz, 2H), 1.18 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 148.8, 147.2, 143.2, 137.9, 134.3, 129.5, 127.2, 120.1, 111.7, 111.2, 111.0, 55.9, 55.9, 53.9, 34.0, 33.6, 21.5, 20.8.

IR (neat, cm^{-1}) *v* 3277, 2934, 2835, 1514, 1453, 1325, 1260, 1235, 1156, 1091, 1028, 813, 665, 549.

HRMS (ESI) *m/z* calculated for $C_{21}H_{27}NO_4SNa$ [M+Na^+]: 412.1559, found: 412.1559.



2i

N-(2-((1,3-dioxoisoindolin-2-yl)methyl)dodec-1-en-3-yl)-4-methylbenzenesulfonamide (**2i**)

Yield: 70%, >20:1 r.r.; White solid.

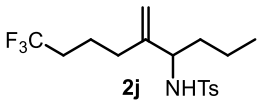
R_f = 0.65 (40% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.78 – 7.74 (m, 2H), 7.68 – 7.64 (m, 2H), 7.14 – 7.11 (m, 2H), 5.18 (d, *J* = 8.1 Hz, 1H), 5.07 (s, 1H), 5.03 (s, 1H), 4.12 (d, *J* = 15.3 Hz, 1H), 4.04 (d, *J* = 15.3 Hz, 1H), 3.89 (q, *J* = 7.5 Hz, 1H), 2.35 (s, 3H), 1.62 – 1.54 (m, 2H), 1.33 – 1.14 (m, 14H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 143.0, 142.2, 137.8, 134.1, 131.9, 129.3, 127.1, 123.4, 116.9, 57.7, 38.5, 34.8, 31.9, 29.5, 29.4, 29.3, 29.1, 25.9, 22.7, 21.5, 14.1.

IR (neat, cm^{-1}) *v* 3282, 2924, 2854, 1712, 1424, 1391, 1329, 1158, 1092, 951, 716, 665.

HRMS (ESI) *m/z* calculated for $C_{28}H_{36}N_2O_4SNa$ [M+Na^+]: 519.2294, found: 519.2303.



2j

4-methyl-N-(9,9,9-trifluoro-5-methylenenonan-4-yl)benzenesulfonamide (**2j**)

Yield: 76%, 6.6:1 r.r.; White solid.

R_f = 0.35 (15% ethyl acetate/hexane)

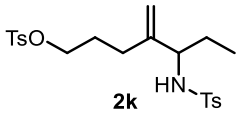
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.31 – 7.26 (m, 2H), 4.95 – 4.90 (m, 2H), 4.74 (s, 1H), 3.74 (q, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 1.98 – 1.81 (m, 4H), 1.62 – 1.52 (m, 1H), 1.51 – 1.37 (m, 3H), 1.35 – 1.16 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 143.4, 137.8, 129.4, 127.3, 127.0 (q, *J* = 276.2 Hz), 112.1, 58.8, 36.4, 33.2 (q, *J* = 28.5 Hz), 29.7, 21.4, 19.4 (q, *J* = 2.9 Hz), 18.9, 13.6.

^{19}F NMR (^{1}H_decoupled) (471 MHz, $CDCl_3$) δ -66.4.

IR (neat, cm^{-1}) *v* 3278, 2959, 2935, 2874, 1438, 1323, 1254, 1157, 1135, 1017, 814, 666, 571, 547.

HRMS (ESI) *m/z* calculated for $C_{17}H_{24}F_3NO_2SNa$ [M+Na^+]: 386.1378, found: 386.1385.



2k

4-methylene-5-((4-methylphenyl)sulfonamido)heptyl 4-methylbenzenesulfonate (**2k**)

1.0 equivalent of cesium carbonate and 1.2 equivalents of silver tetrafluoroborate were applied.

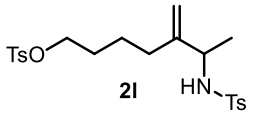
Yield: 71%, 12:1 r.r.; Colorless oil.

R_f = 0.30 (30% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.74 – 7.68 (m, 2H), 7.41 – 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 4.87 (s, 1H), 4.78 (d, *J* = 7.4 Hz, 1H), 4.68 (s, 1H), 3.99 – 3.90 (m, 2H), 3.59 (q, *J* = 7.1 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H), 1.83 (t, *J* = 7.8 Hz, 2H), 1.73 – 1.64 (m, 1H), 1.60 – 1.52 (m, 1H), 1.51 – 1.42 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H).

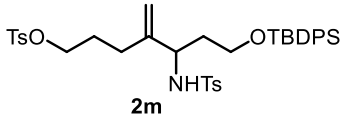
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 144.8, 143.3, 137.8, 133.1, 129.9, 129.5, 127.9, 127.2, 112.3, 69.9, 60.4, 27.1, 26.9, 26.7, 21.7, 21.5, 10.2.

IR (neat, cm^{-1}) *v* 3289, 2965, 2931, 2876, 1451, 1354, 1174, 1159, 1094, 922, 814, 664, 574, 553.
HRMS (ESI) *m/z* calculated for $C_{22}H_{29}NO_5S_2Na$ [M+Na^+]: 474.1385, found: 474.1390.



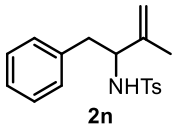
2l

5-methylene-6-((4-methylphenyl)sulfonamido)heptyl 4-methylbenzenesulfonate (**2l**)
Yield: 78%, 6.0:1 r.r.; Colorless oil.
$\mathbf{R_f}$ = 0.30 (30% ethyl acetate/hexane)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.75 – 7.73 (m, 2H), 7.39 – 7.35 (m, 2H), 7.31 – 7.28 (m, 2H), 4.90 (s, 1H), 4.70 (s, 1H), 4.66 (d, *J* = 7.8 Hz, 1H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.80 (p, *J* = 7.0 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H), 1.90 – 1.80 (m, 2H), 1.58 – 1.52 (m, 2H), 1.39 – 1.26 (m, 2H), 1.15 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 144.8, 143.3, 137.8, 133.1, 129.9, 129.6, 127.9, 127.2, 110.9, 70.3, 53.6, 31.3, 28.4, 23.4, 21.7, 21.5, 20.9.
IR (neat, cm^{-1}) *v* 3289, 2934, 1353, 1331, 1173, 1159, 1093, 933, 815, 664, 553.
HRMS (ESI) *m/z* calculated for $C_{22}H_{29}NO_5S_2Na$ [M+Na^+]: 474.1385, found: 474.1389.



2m

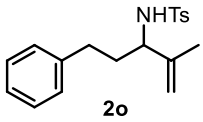
7-((tert-butyldiphenylsilyl)oxy)-4-methylene-5-((4-methylphenyl)sulfonamido)heptyl 4-methylbenzenesulfonate (**2m**)
1.0 equivalent of cesium carbonate was applied.
Yield: 79%, 3.4:1 r.r.; Colorless oil.
$\mathbf{R_f}$ = 0.55 (40% ethyl acetate/hexane)
Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.72 – 7.69 (m, 2H), 7.67 – 7.64 (m, 1H), 7.63 – 7.59 (m, 3H), 7.50 – 7.44 (m, 2H), 7.44 – 7.38 (m, 4H), 7.38 – 7.34 (m, 2H), 7.27 – 7.23 (m, 2H), 5.71 (d, *J* = 5.9 Hz, 1H), 5.03 (s, 1H), 4.79 (s, 1H), 4.04 – 3.95 (m, 2H), 3.90 (q, *J* = 6.0 Hz, 1H), 3.67 – 3.62 (m, 1H), 3.53 – 3.48 (m, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 2.02 – 1.94 (m, 1H), 1.92 – 1.85 (m, 1H), 1.81 – 1.74 (m, 1H), 1.72 – 1.62 (m, 3H), 1.08 (s, 9H).
Major isomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 144.8, 143.2, 137.6, 135.5, 135.5, 129.9, 129.9, 129.5, 127.9, 127.8, 127.8, 127.2, 112.4, 70.0, 61.4, 57.6, 35.5, 27.5, 26.9, 26.8, 21.7, 21.5, 19.0.
IR (neat, cm^{-1}) *v* 3285, 2954, 2930, 2857, 1427, 1359, 1175, 1160, 1109, 1094, 926, 816, 704, 665, 553.
HRMS (ESI) *m/z* calculated for $C_{38}H_{47}NO_6S_2SiNa$ [M+Na^+]: 728.2512, found: 728.2509.



2n

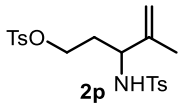
4-methyl-N-(3-methyl-1-phenylbut-3-en-2-yl)benzenesulfonamide (**2n**)
Yield: 74%, 17:1 r.r.; Light yellow solid.
$\mathbf{R_f}$ = 0.45 (20% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.24 – 7.18 (m, 5H), 7.05 – 7.00 (m, 2H), 4.80 – 4.78 (m, 1H), 4.77 (s, 1H), 4.70 (d, *J* = 6.4 Hz, 1H), 3.93 (q, *J* = 6.9 Hz, 1H), 2.85 – 2.74 (m, 2H), 2.43 (s, 3H), 1.67 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 143.1, 137.1, 136.6, 129.4, 129.1, 128.6, 127.2, 126.8, 113.8, 60.5, 40.4, 21.5, 18.2.
IR (neat, cm^{-1}) *v* 3278, 3028, 2923, 2859, 1452, 1325, 1157, 1092, 813, 700, 666, 572, 546.
HRMS (ESI) *m/z* calculated for $C_{18}H_{21}NO_2SNa$ [M+Na$^+$]: 338.1191, found: 338.1199.



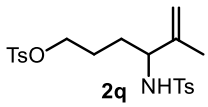
2o

4-methyl-N-(2-methyl-5-phenylpent-1-en-3-yl)benzenesulfonamide (**2o**)
Yield: 65%, >20:1 r.r.; Light yellow solid.
R_f = 0.45 (20% ethyl acetate/hexane)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.29 – 7.25 (m, 4H), 7.22 – 7.18 (m, 1H), 7.11 – 7.07 (m, 2H), 4.81 (d, *J* = 7.8 Hz, 1H), 4.79 – 4.75 (m, 2H), 3.78 (q, *J* = 7.3 Hz, 1H), 2.62 – 2.47 (m, 2H), 2.44 (s, 3H), 1.84 – 1.77 (m, 2H), 1.55 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 142.9, 141.0, 137.8, 129.4, 128.4, 128.3, 127.2, 126.0, 113.8, 59.3, 35.5, 31.9, 21.5, 17.5.
IR (neat, cm^{-1}) *v* 3271, 3026, 2944, 2861, 1449, 1323, 1159, 1092, 902, 701, 668, 577.
HRMS (ESI) *m/z* calculated for $C_{19}H_{23}NO_2SNa$ [M+Na$^+$]: 352.1347, found: 352.1351.



2p

4-methyl-3-((4-methylphenyl)sulfonamido)pent-4-en-1-yl 4-methylbenzenesulfonate (**2p**)
Yield: 77%, 7.7:1 r.r.; Colorless oil.
R_f = 0.20 (30% ethyl acetate/hexane)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.72 – 7.69 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 2H), 4.95 (d, *J* = 8.2 Hz, 1H), 4.72 – 4.67 (m, 1H), 4.67 (s, 1H), 4.03 – 3.96 (m, 2H), 3.83 (q, *J* = 7.4 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 1.91 – 1.82 (m, 2H), 1.45 (t, *J* = 1.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 143.5, 141.8, 137.4, 132.8, 129.9, 129.6, 127.9, 127.2, 114.4, 66.9, 56.2, 33.1, 21.7, 21.6, 17.6.
IR (neat, cm^{-1}) *v* 3286, 2923, 1446, 1353, 1333, 1173, 1158, 1092, 921, 814, 664, 575, 552.
HRMS (ESI) *m/z* calculated for $C_{20}H_{25}NO_5S_2Na$ [M+Na$^+$]: 446.1072, found: 446.1080.



2q

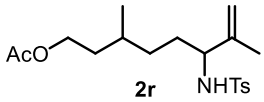
5-methyl-4-((4-methylphenyl)sulfonamido)hex-5-en-1-yl 4-methylbenzenesulfonate (**2q**)
Yield: 87%, >20:1 r.r.; Colorless oil.
R_f = 0.45 (40% ethyl acetate/hexane)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.73 – 7.68 (m, 2H), 7.38 – 7.33 (m, 2H), 7.30 –

7.24 (m, 2H), 4.90 (d, *J* = 8.1 Hz, 1H), 4.68 – 4.64 (m, 2H), 4.03 – 3.94 (m, 2H), 3.67 (q, *J* = 7.1 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 1.67 – 1.48 (m, 4H), 1.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.8, 143.3, 142.7, 137.7, 133.0, 129.9, 129.5, 127.9, 127.1, 113.6, 69.8, 58.9, 29.8, 25.3, 21.6, 21.5, 17.5.

IR (neat, cm^{-1}) *v* 3287, 2953, 2924, 1439, 1353, 1333, 1173, 1157, 1093, 925, 814, 664, 575, 552.

HRMS (ESI) *m/z* calculated for $C_{21}H_{27}NO_5S_2Na$ [M+Na$^+$]: 460.1228, found: 460.1240.



2r

3,7-dimethyl-6-((4-methylphenyl)sulfonamido)oct-7-en-1-yl acetate (**2r**)

Yield: 77%, >20:1 r.r., 1:1 d.r.; Colorless oil.

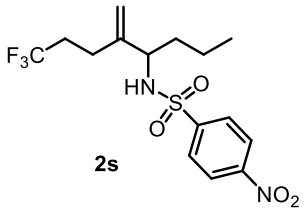
R_f = 0.50 (30% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.77 – 7.71 (m, 2H), 7.31 – 7.24 (m, 2H), 4.87 – 4.81 (m, 1H), 4.73 (s, 1H), 4.72 – 4.69 (m, 1H), 4.10 – 3.99 (m, 2H), 3.72 – 3.65 (m, 1H), 2.43 (s, 3H), 2.05 (s, 3H), 1.61 – 1.34 (m, 8H), 1.28 – 0.94 (m, 2H), 0.87 – 0.81 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 171.2, 171.2, 143.2, 143.1, 143.0, 138.0, 137.9, 129.4, 127.2, 113.6, 113.4, 76.8, 62.7, 62.7, 59.9, 59.8, 35.3, 35.2, 32.7, 32.6, 31.2, 31.1, 29.5, 29.4, 21.5, 21.0, 19.3, 19.2, 17.5, 17.3.

IR (neat, cm^{-1}) *v* 3277, 2954, 2925, 2870, 1735, 1445, 1325, 1238, 1156, 1035, 898, 814, 664, 577, 546.

HRMS (ESI) *m/z* calculated for $C_{19}H_{29}NO_4SNa$ [M+Na$^+$]: 390.1715, found: 390.1728.



2s

4-nitro-N-(8,8,8-trifluoro-5-methyleneoctan-4-yl)benzenesulfonamide (**2s**)

Yield: 51%, >20:1 r.r.; White solid.

R_f = 0.45 (20% ethyl acetate/hexane)

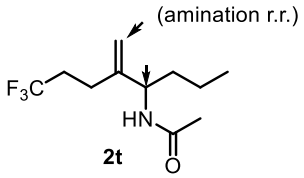
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.40 – 8.34 (m, 2H), 8.07 – 8.02 (m, 2H), 4.98 (s, 1H), 4.91 (d, *J* = 7.5 Hz, 1H), 4.78 (s, 1H), 3.87 (q, *J* = 7.3 Hz, 1H), 2.23 – 1.92 (m, 4H), 1.59 – 1.44 (m, 2H), 1.36 – 1.16 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 150.0, 146.6, 144.8, 128.3, 126.6 (q, *J* = 276.5 Hz), 124.2, 112.8, 59.4, 36.2, 31.9 (q, *J* = 29.1 Hz), 23.1 (q, *J* = 3.1 Hz), 19.0, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$) *δ* -66.6 (t, *J* = 10.1 Hz).

IR (neat, cm^{-1}) *v* 3287, 2961, 2935, 2874, 1531, 1349, 1309, 1257, 1164, 1138, 1093, 855, 737, 619.

HRMS (ESI) *m/z* calculated for $C_{15}H_{19}F_3N_2O_4SNa$ [M+Na$^+$]: 403.0915, found: 403.0929.



2t

N-(8,8,8-trifluoro-5-methyleneoctan-4-yl)acetamide (**2t**)

Yield: 69%, >20:1 r.r. (C-H activation), 10:1 r.r. (amination); White solid.

R_f = 0.40 (50% ethyl acetate/hexane)

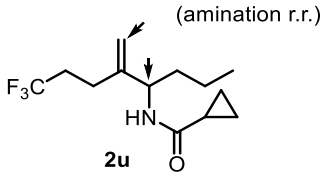
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (d, *J* = 8.6 Hz, 1H), 5.04 (s, 1H), 4.89 (s, 1H), 4.39 (td, *J* = 8.5, 5.7 Hz, 1H), 2.36 – 2.23 (m, 4H), 2.01 (s, 3H), 1.66 – 1.57 (m, 1H), 1.53 – 1.45 (m, 1H), 1.42 – 1.30 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 147.0, 126.9 (q, *J* = 276.5 Hz), 110.7, 52.9, 35.8, 32.3 (q, *J* = 28.6 Hz), 25.5 (q, *J* = 3.2 Hz), 23.4, 19.3, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, *J* = 9.3 Hz).

IR (neat, cm^{-1}) *v* 3276, 2960, 2935, 2874, 1642, 1547, 1375, 1304, 1257, 1137, 985.

HRMS (ASAP) *m/z* calculated for $C_{11}H_{19}F_3NO$ [M+H$^+$]: 238.1419, found: 238.1406.



2u

N-(8,8,8-trifluoro-5-methyleneoctan-4-yl)cyclopropanecarboxamide (**2u**)

7.5 mol% of **Ir-6** was applied.

Yield: 64%, >20:1 r.r. (C-H activation), 15:1 r.r. (amination); White solid.

R_f = 0.25 (20% ethyl acetate/hexane)

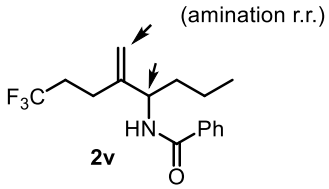
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 (d, *J* = 8.4 Hz, 1H), 5.06 (s, 1H), 4.90 (s, 1H), 4.40 (td, *J* = 8.3, 5.9 Hz, 1H), 2.36 – 2.25 (m, 4H), 1.66 – 1.59 (m, 1H), 1.56 – 1.48 (m, 1H), 1.44 – 1.31 (m, 3H), 1.01 – 0.93 (m, 5H), 0.79 – 0.72 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 147.1, 127.0 (q, *J* = 276.4 Hz), 110.6, 53.1, 35.9, 32.4 (q, *J* = 28.6 Hz), 25.4 (q, *J* = 3.2 Hz), 19.4, 14.7, 13.9, 7.1, 7.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -65.6 (t, *J* = 9.8 Hz).

IR (neat, cm^{-1}) *v* 3290, 2960, 2936, 2874, 1639, 1545, 1255, 1137, 1105.

HRMS (ASAP) *m/z* calculated for $C_{13}H_{21}F_3NO$ [M+H$^+$]: 264.1575, found: 264.1580.



2v

N-(8,8,8-trifluoro-5-methyleneoctan-4-yl)benzamide (**2v**)

Yield: 51%, >20:1 r.r. (C-H activation), 13:1 r.r. (amination); White solid.

R_f = 0.50 (20% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.45 (m, 2H), 6.07 (d,

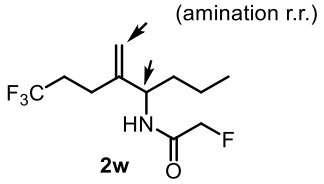
J = 8.3 Hz, 1H), 5.13 (s, 1H), 4.95 (s, 1H), 4.61 (td, *J* = 8.4, 6.1 Hz, 1H), 2.41 – 2.29 (m, 4H), 1.79 – 1.70 (m, 1H), 1.67 – 1.59 (m, 1H), 1.52 – 1.37 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 166.9, 147.0, 134.5, 131.6, 128.7, 126.9 (q, *J* = 276.4 Hz), 126.8, 110.9, 53.3, 35.9, 32.4 (q, *J* = 28.6 Hz), 25.7 (q, *J* = 3.2 Hz), 19.5, 13.9.

^{19}F NMR (471 MHz, $CDCl_3$) *δ* -65.6 (t, *J* = 9.8 Hz).

IR (neat, cm^{-1}) *v* 3287, 2959, 2934, 2873, 1632, 1532, 1304, 1256, 1135, 1114, 985, 694.

HRMS (ASAP) *m/z* calculated for $C_{16}H_{21}F_3NO$ [M+H$^+$]: 300.1575, found: 300.1569.



2w

2-fluoro-N-(8,8,8-trifluoro-5-methyleneoctan-4-yl)acetamide (**2w**)

Yield: 76%, >20:1 r.r. (C-H activation), 18:1 r.r. (amination); Colorless oil.

R_f = 0.20 (20% ethyl acetate/hexane)

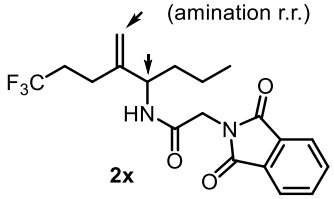
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 6.25 (s, 1H), 5.08 (s, 1H), 4.94 (s, 1H), 4.88 (s, 1H), 4.78 (s, 1H), 4.47 (td, *J* = 8.9, 5.6 Hz, 1H), 2.35 – 2.27 (m, 4H), 1.72 – 1.65 (m, 1H), 1.60 – 1.52 (m, 1H), 1.45 – 1.31 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 167.1, 146.2, 126.9 (q, *J* = 276.5 Hz), 111.2, 80.2 (d, *J* = 185.8 Hz), 52.4, 35.6, 32.3 (q, *J* = 28.7 Hz), 25.4 (q, *J* = 3.2 Hz), 19.3, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, *J* = 9.5 Hz), -224.5 (t, *J* = 47.4 Hz).

IR (neat, cm^{-1}) *v* 3296, 2960, 2874, 1664, 1534, 1445, 1306, 1256, 1136, 1044, 985, 907.

HRMS (ASAP) *m/z* calculated for $C_{11}H_{18}F_4NO$ [M+H$^+$]: 256.1324, found: 256.1333.



2x

2-(1,3-dioxoisoindolin-2-yl)-N-(8,8,8-trifluoro-5-methyleneoctan-4-yl)acetamide (**2x**)

Yield: 79%, >20:1 r.r. (C-H activation), 14:1 r.r. (amination); White solid.

R_f = 0.45 (40% ethyl acetate/hexane)

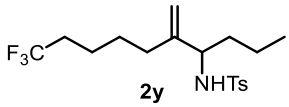
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.91 – 7.87 (m, 2H), 7.78 – 7.74 (m, 2H), 5.91 (d, *J* = 8.5 Hz, 1H), 5.05 (s, 1H), 4.89 (s, 1H), 4.41 – 4.34 (m, 3H), 2.33 – 2.23 (m, 4H), 1.66 – 1.59 (m, 1H), 1.56 – 1.47 (m, 1H), 1.42 – 1.27 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 167.8, 165.6, 146.3, 134.3, 131.9, 126.9 (q, *J* = 276.5 Hz), 123.6, 111.2, 53.5, 40.9, 35.6, 32.3 (q, *J* = 28.6 Hz), 25.3 (q, *J* = 3.1 Hz), 19.3, 13.8.

^{19}F NMR (471 MHz, $CDCl_3$) *δ* -65.56 (t, *J* = 9.7 Hz).

IR (neat, cm^{-1}) *v* 3278, 2957, 2872, 1722, 1656, 1555, 1419, 1255, 1133, 1116, 953, 713.

HRMS (ESI) *m/z* calculated for $C_{19}H_{21}F_3N_2O_3Na$ [M+Na$^+$]: 405.1402, found: 405.1405.



2y

4-methyl-N-(10,10,10-trifluoro-5-methylenedecan-4-yl)benzenesulfonamide (**2y**)

Yield: 80%, 2.0:1 r.r.; White solid.

R_f = 0.55 (20% ethyl acetate/hexane)

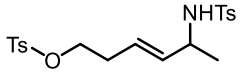
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.31 – 7.27 (m, 2H), 4.93 & 4.84 (d, *J* = 8.1 Hz, 1H), 4.87 & 4.82 (s, 1H), 4.75 & 4.73 (s, 1H), 3.77 – 3.69 (m, 1H), 2.43 (s, 3H), 2.07 – 1.96 (m, 2H), 1.80 & 1.74 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.35 (m, 5H), 1.31 – 1.10 (m, 3H), 0.84 (t, *J* = 7.3 Hz, 3H).

Major isomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 143.2, 138.0, 129.4, 127.2, 127.1 (q, *J* = 276.3 Hz), 111.6, 58.8, 36.5, 33.6 (d, *J* = 28.5 Hz), 30.8, 26.3, 21.6 (q, *J* = 2.9 Hz), 21.4, 19.0, 13.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -65.4 & -65.5 (t, *J* = 10.8 Hz).

IR (neat, cm^{-1}) *v* 3278, 2957, 2934, 2873, 1437, 1322, 1255, 1157, 1137, 1029, 814, 666, 549.

HRMS (ESI) *m/z* calculated for $C_{18}H_{26}F_3NO_2SNa$ [M+Na$^+$]: 400.1534, found: 400.1546.



4a

(E)-5-((4-methylphenyl)sulfonamido)hex-3-en-1-yl 4-methylbenzenesulfonate (**4a**)

Yield: 76%, >20:1 r.r.; Colorless oil.

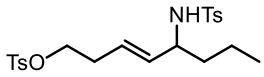
R_f = 0.55 (40% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.75 – 7.71 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 5.36 – 5.25 (m, 2H), 4.60 (d, *J* = 7.5 Hz, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 3.83 (h, *J* = 6.8 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H), 2.23 (q, *J* = 6.3 Hz, 2H), 1.12 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 143.4, 138.0, 134.6, 133.1, 129.9, 129.6, 127.9, 127.1, 125.2, 69.2, 51.1, 31.5, 21.7, 21.7, 21.5.

IR (neat, cm^{-1}) *v* 3284, 2974, 2926, 1353, 1330, 1173, 1156, 1094, 964, 919, 814, 664, 552.

HRMS (ESI) *m/z* calculated for $C_{20}H_{25}NO_5S_2Na$ [M+Na$^+$]: 446.1072, found: 446.1086.



4b

(E)-5-((4-methylphenyl)sulfonamido)oct-3-en-1-yl 4-methylbenzenesulfonate (**4b**)

Yield: 73%, >20:1 r.r.; Light yellow oil.

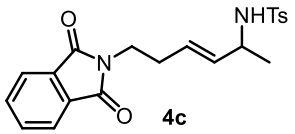
R_f = 0.30 (30% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.73 – 7.68 (m, 2H), 7.40 – 7.34 (m, 2H), 7.30 – 7.25 (m, 2H), 5.24 (dt, *J* = 15.5, 6.4 Hz, 1H), 5.16 (dd, *J* = 15.6, 6.8 Hz, 1H), 4.60 (d, *J* = 7.7 Hz, 1H), 3.88 (t, *J* = 6.7 Hz, 2H), 3.68 (p, *J* = 7.1 Hz, 1H), 2.47 (s, 3H), 2.42 (s, 3H), 2.19 (q, *J* = 6.7 Hz, 2H), 1.44 – 1.33 (m, 2H), 1.29 – 1.17 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 143.3, 138.1, 133.4, 133.1, 129.9, 129.5, 127.8, 127.2, 125.9, 69.1, 55.5, 37.8, 31.5, 21.7, 21.5, 18.6, 13.6.

IR (neat, cm^{-1}) *v* 3286, 2958, 2930, 2871, 1425, 1355, 1330, 1174, 1159, 1174, 1159, 1094, 964, 814, 665, 553.

HRMS (ESI) *m/z* calculated for $C_{22}H_{29}NO_5S_2Na$ [M+Na$^+$]: 474.1385, found: 474.1387.



4c

(E)-N-(6-(1,3-dioxoisoindolin-2-yl)hex-3-en-2-yl)-4-methylbenzenesulfonamide (**4c**)

Yield: 70%, 15:1 r.r.; White solid.

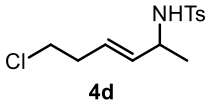
R_f = 0.60 (50% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.75 – 7.69 (m, 4H), 7.30 – 7.26 (m, 2H), 5.43 (dtd, *J* = 15.3, 7.0, 1.2 Hz, 1H), 5.24 (ddt, *J* = 15.4, 6.3, 1.3 Hz, 1H), 4.48 (d, *J* = 7.5 Hz, 1H), 3.87 – 3.76 (m, 1H), 3.63 (t, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 2.25 (q, *J* = 7.2 Hz, 2H), 1.08 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 143.3, 138.0, 134.0, 133.6, 132.0, 129.6, 127.4, 127.2, 123.2, 51.0, 37.2, 31.2, 21.7, 21.5.

IR (neat, cm^{-1}) *v* 3277, 2973, 2929, 2870, 1704, 1396, 1327, 1156, 721, 666, 551.

HRMS (ESI) *m/z* calculated for $C_{21}H_{22}N_2O_4SNa$ [M+Na$^+$]: 421.1198, found: 421.1199.



4d

(E)-N-(6-chlorohex-3-en-2-yl)-4-methylbenzenesulfonamide (**4d**)

Yield: 44%, 8.0:1 r.r.; Colorless oil.

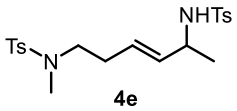
R_f = 0.30 (20% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.34 – 7.30 (m, 2H), 5.45 (dtd, *J* = 15.5, 6.6, 1.1 Hz, 1H), 5.35 (ddt, *J* = 15.5, 6.3, 1.3 Hz, 1H), 4.52 (d, *J* = 7.6 Hz, 1H), 3.91 (h, *J* = 7.0 Hz, 1H), 3.44 – 3.35 (m, 2H), 2.45 (s, 3H), 2.35 (q, *J* = 6.8 Hz, 2H), 1.20 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 138.1, 133.9, 129.6, 127.2, 127.0, 51.2, 43.6, 35.1, 22.0, 21.5.

IR (neat, cm^{-1}) *v* 3273, 2973, 2926, 2869, 1425, 1323, 1156, 1092, 1069, 967, 814, 665, 552.

HRMS (ESI) *m/z* calculated for $C_{13}H_{18}ClNO_2SNa$ [M+Na$^+$]: 310.0645, found: 310.0657.



4e

(E)-N,4-dimethyl-N-(5-((4-methylphenyl)sulfonamido)hex-3-en-1-yl)benzenesulfonamide (**4e**)

Yield: 50%, 6.5:1 r.r.; Colorless oil.

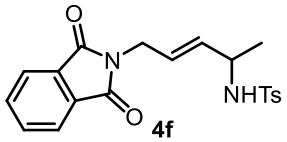
R_f = 0.25 (33% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.69 – 7.64 (m, 2H), 7.36 – 7.29 (m, 4H), 5.43 (dtd, *J* = 15.5, 6.7, 1.1 Hz, 1H), 5.33 (ddt, *J* = 15.4, 6.2, 1.2 Hz, 1H), 4.58 (d, *J* = 7.3 Hz, 1H), 3.85 (h, *J* = 7.1 Hz, 1H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.69 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H), 2.19 – 2.11 (m, 2H), 1.17 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 143.3, 138.0, 134.7, 133.5, 129.7, 129.6, 127.3, 127.3, 127.2, 51.2, 49.5, 34.8, 30.57, 21.8, 21.5.

IR (neat, cm^{-1}) *v* 3277, 2975, 2925, 2869, 1454, 1328, 1154, 1090, 967, 815, 665, 548.

HRMS (ESI) *m/z* calculated for $C_{21}H_{28}N_2O_4S_2Na$ [M+Na$^+$]: 459.1388, found: 459.1398.



4f

(E)-N-(5-(1,3-dioxoisoindolin-2-yl)pent-3-en-2-yl)-4-methylbenzenesulfonamide (**4f**)

5 mol% of **Ir-6** was applied.

Yield: 83%, >20:1 r.r.; Light orange oil.

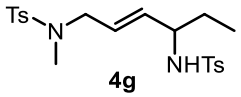
$\mathbf{R_f}$ = 0.15 (30% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.77 – 7.73 (m, 2H), 7.73 – 7.70 (m, 2H), 7.26 – 7.22 (m, 2H), 5.57 – 5.45 (m, 2H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.13 (d, *J* = 5.3 Hz, 2H), 3.96 – 3.88 (m, 1H), 2.36 (s, 3H), 1.17 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 143.3, 137.9, 134.6, 134.1, 132.0, 129.6, 127.1, 124.4, 123.3, 50.6, 38.8, 21.6, 21.5.

IR (neat, cm^{-1}) *v* 3278, 2976, 2928, 1709, 1394, 1328, 1156, 722, 666, 550.

HRMS (ESI) *m/z* calculated for $C_{20}H_{20}N_2O_4SNa$ [M+Na$^+$]: 407.1042, found: 407.1049.



4g

(E)-N,4-dimethyl-N-(4-((4-methylphenyl)sulfonamido)hex-2-en-1-yl)benzenesulfonamide (**4g**)

5 mol% of **Ir-6** was applied.

Yield: 75%, >20:1 r.r.; Light yellow oil.

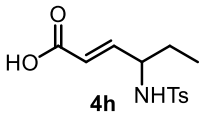
$\mathbf{R_f}$ = 0.40 (40% ethyl acetate/hexane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.66 – 7.62 (m, 2H), 7.35 – 7.29 (m, 4H), 5.38 – 5.25 (m, 2H), 4.78 (d, *J* = 7.6 Hz, 1H), 3.62 (p, *J* = 6.8 Hz, 1H), 3.47 – 3.38 (m, 2H), 2.51 (s, 3H), 2.46 – 2.43 (m, 6H), 1.52 – 1.41 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 143.4, 137.8, 134.3, 134.2, 129.7, 129.6, 127.4, 127.1, 126.3, 56.7, 51.6, 34.2, 28.7, 21.5, 9.8.

IR (neat, cm^{-1}) *v* 3280, 2968, 2928, 2875, 1452, 1329, 1157, 1090, 815, 734, 665, 548.

HRMS (ESI) *m/z* calculated for $C_{21}H_{28}N_2O_4S_2Na$ [M+Na$^+$]: 459.1388, found: 459.1389.



4h

(E)-4-((4-methylphenyl)sulfonamido)hex-2-enoic acid (**4h**)

5 mol% of **Ir-6** was applied at 50 ^{o}C.

Yield: 86%, >20:1 r.r.; Light yellow solid.

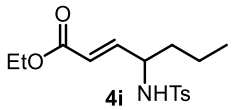
$\mathbf{R_f}$ = 0.25 (10% methanol/methylene chloride)

^{1}H NMR (500 MHz, CD_3CN) δ 7.74 – 7.68 (m, 2H), 7.39 – 7.33 (m, 2H), 6.52 (dd, *J* = 15.7, 6.9 Hz, 1H), 5.79 (d, *J* = 8.5 Hz, 1H), 5.64 (d, *J* = 15.7 Hz, 1H), 3.80 (p, *J* = 7.3 Hz, 1H), 2.41 (s, 3H), 1.58 – 1.42 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 166.1, 147.6, 143.6, 138.3, 129.6, 126.9, 121.1, 56.2, 27.6, 20.5, 9.3.

IR (neat, cm^{-1}) *v* 3267, 2965, 2926, 2855, 1699, 1415, 1321, 1159, 1092, 666, 550.

HRMS (ESI) *m/z* calculated for $C_{13}H_{17}NO_4SNa$ [M+Na$^+$]: 306.0776, found: 306.0782.



4i

ethyl (E)-4-((4-methylphenyl)sulfonamido)hept-2-enoate (**4i**)

5 mol% of **Ir-6** was applied at 50 °C.

Yield: 93%, >20:1 r.r.; White solid.

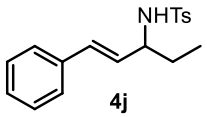
R_f = 0.30 (20% ethyl acetate/hexane)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.33 – 7.26 (m, 2H), 6.59 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 4.99 (d, *J* = 8.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.92 (p, *J* = 7.0 Hz, 1H), 2.42 (s, 3H), 1.49 (q, *J* = 7.5 Hz, 2H), 1.34 – 1.20 (m, 5H), 0.83 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 146.6, 143.5, 137.7, 129.6, 127.2, 121.9, 60.5, 54.5, 37.1, 21.5, 18.5, 14.2, 13.5.

IR (neat, cm^{-1}) *v* 3272, 2960, 2933, 2873, 1717, 1324, 1305, 1158, 1092, 666, 549.

HRMS (ESI) *m/z* calculated for $C_{16}H_{23}NO_4SNa$ [M+Na$^+$]: 348.1245, found: 348.1261.



4j

(E)-4-methyl-N-(1-phenylpent-1-en-3-yl)benzenesulfonamide (**4j**)

Yield: 71%, >20:1 r.r.; White solid.

R_f = 0.25 (20% ethyl acetate/hexane)

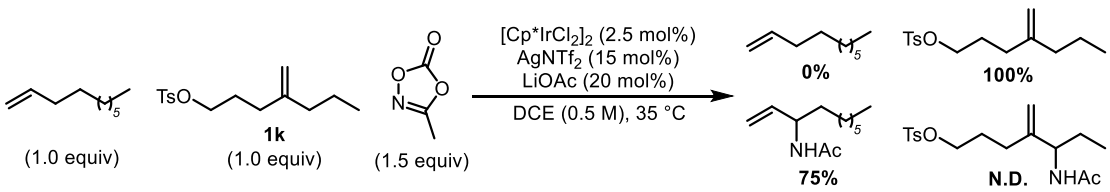
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.19 (m, 3H), 7.15 – 7.12 (m, 2H), 6.23 (d, *J* = 15.9 Hz, 1H), 5.74 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.75 (d, *J* = 7.8 Hz, 1H), 3.88 (p, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 1.68 – 1.57 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 138.2, 136.3, 131.6, 129.5, 128.6, 128.4, 127.7, 127.3, 126.3, 57.8, 29.0, 21.4, 10.0.

IR (neat, cm^{-1}) *v* 3271, 2967, 2931, 2874, 1448, 1321, 1157, 1092, 966, 748, 666, 574.

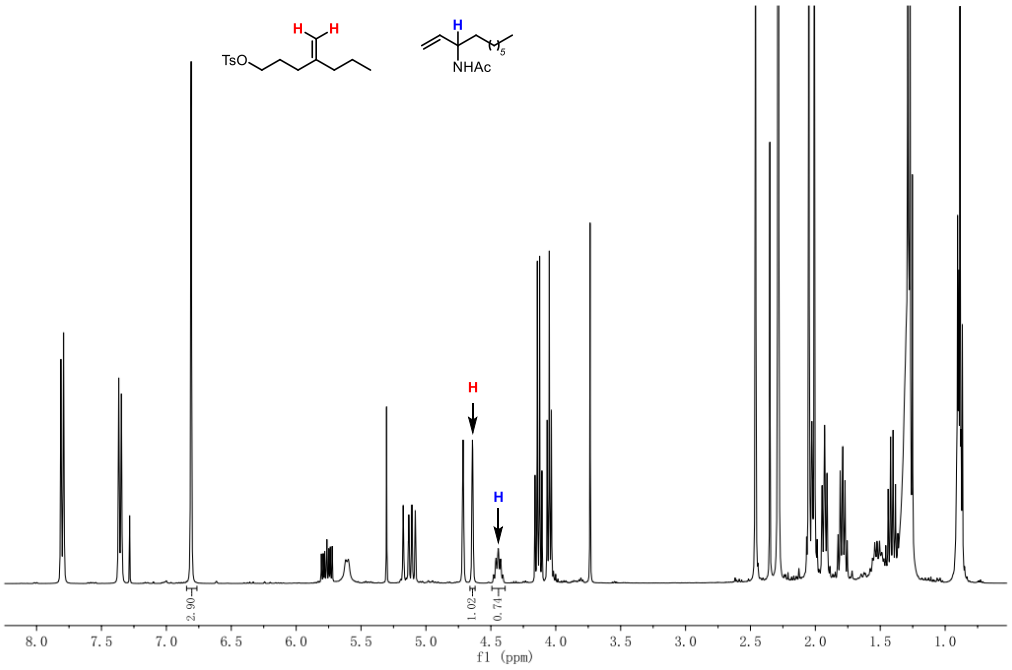
HRMS (ESI) *m/z* calculated for $C_{18}H_{21}NO_2SNa$ [M+Na$^+$]: 338.1191, found: 338.1198.

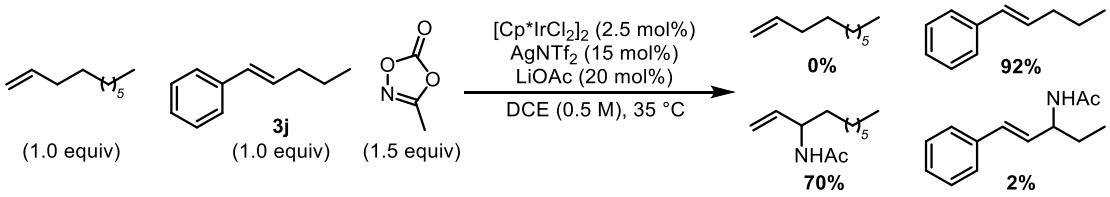
6. Competition Reactions



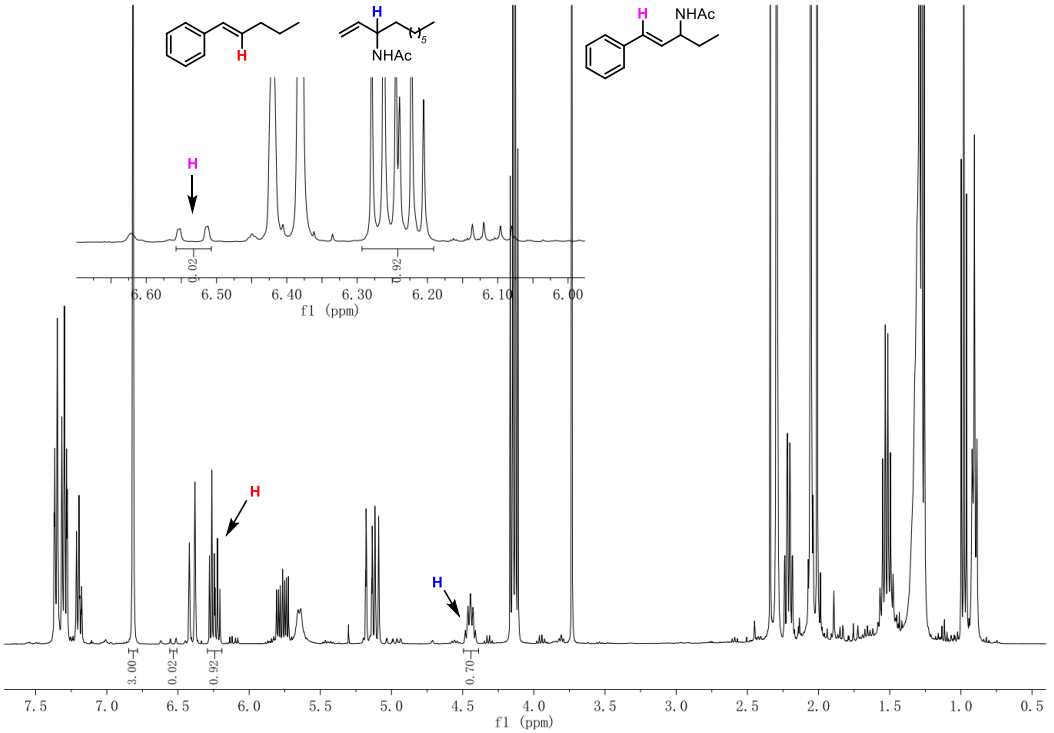
General Procedure G: To an oven-dried screw capped vial with a magnetic stir bar was added 1-decene (0.10 mmol, 1.0 equiv), alkene **1k** (0.1 mmol, 1.0 equiv), $[Cp^*IrCl_2]_2$ (2.0 mg, 2.5 mol%), LiOAc (1.4 mg, 20 mol%) and $AgNTf_2$ (5.8 mg, 15 mol%) in the glove box. In a separate vial, 3-methyl-1,4,2-dioxazol-5-one (0.15 mmol, 1.5 equiv) was dissolved in 1,2-Dichloroethane (200 µl), and then the solution was transferred to the first vial. The cap was screwed on and the reaction was stirred at 35 °C for 20 hours. The reaction mixture was then filtered through a plug

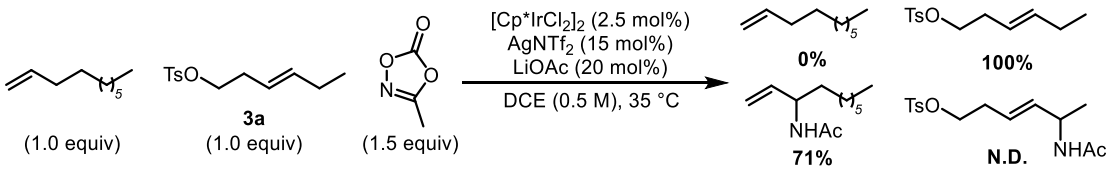
of Celite, and the filtrate was concentrated under vacuum. A crude ^{1}H NMR spectrum was collected with mesitylene as the internal standard (100% of alkene **1k** was remained). The crude mixture was further purified by column chromatography (75% isolated yield).



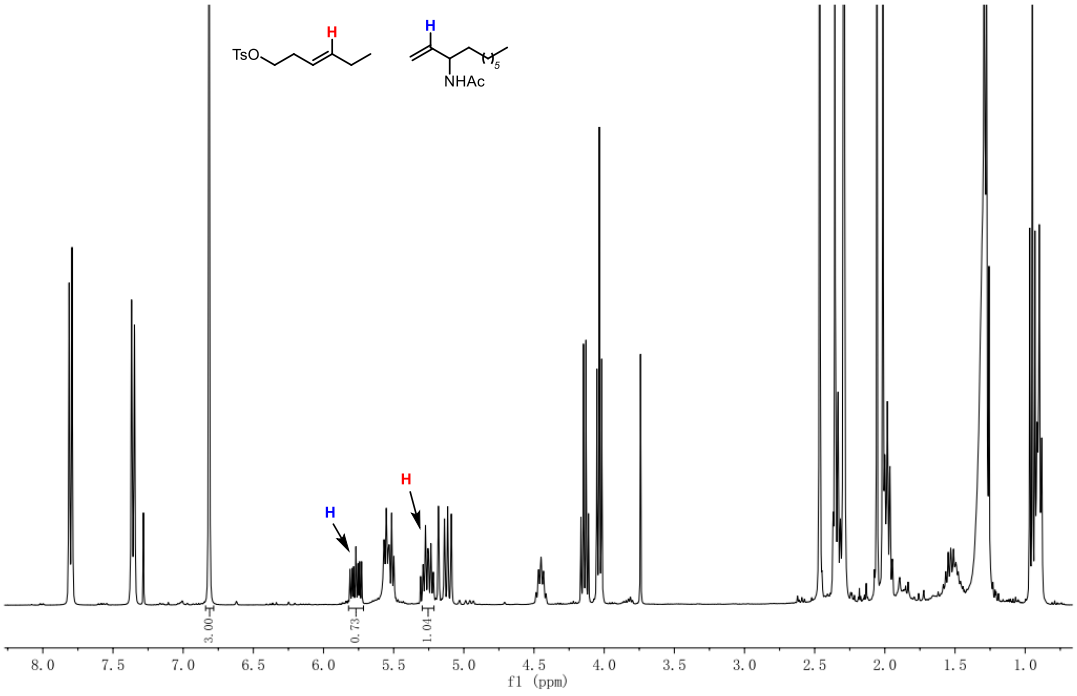


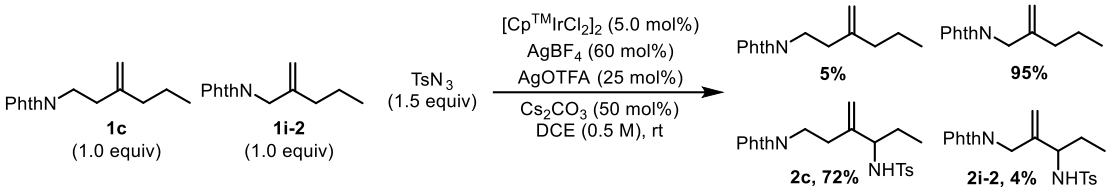
The reaction was conducted according to the general procedure G. 2% of **4j** was detected based on the crude ^{1}H NMR spectrum (8% conversion). 70% isolated yield of N-(dec-1-en-3-yl)acetamide was obtained after column chromatography.



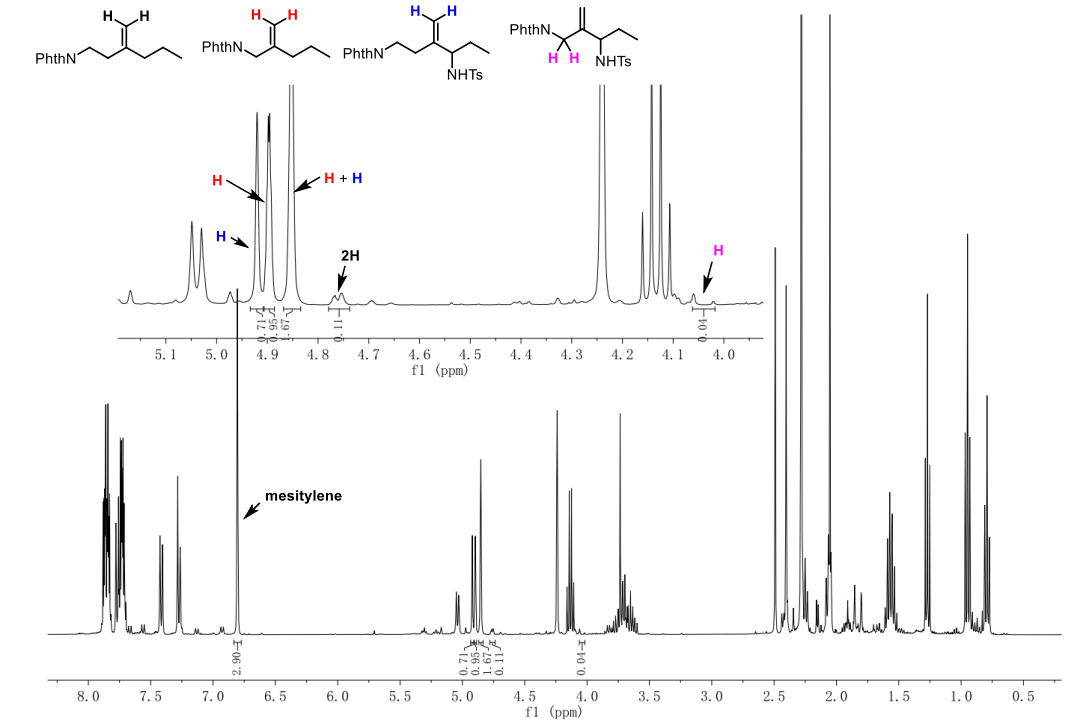


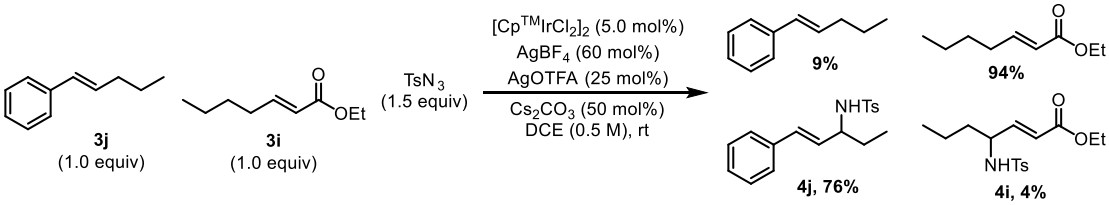
The reaction was conducted according to the general procedure G. 100% of alkene **3a** was remained based on the crude ^{1}H NMR spectrum. 71% isolated yield of N-(dec-1-en-3-yl)acetamide was obtained after column chromatography.



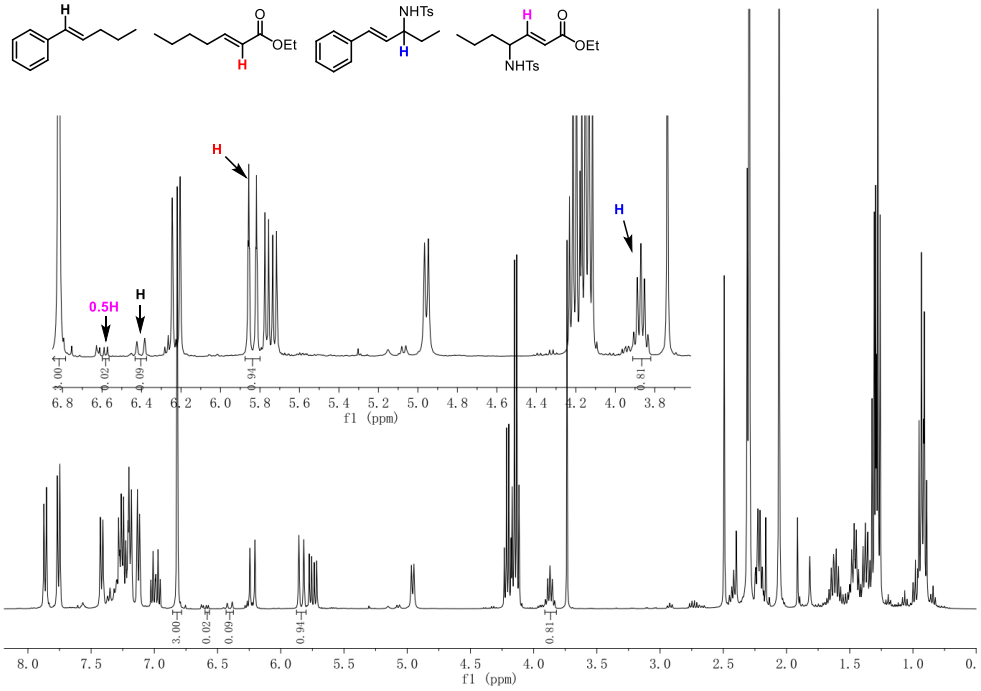


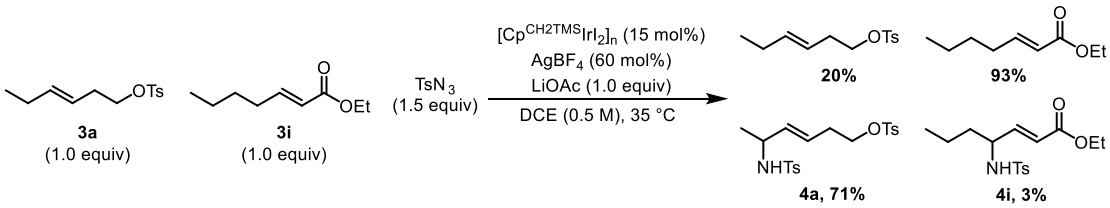
The reaction was conducted according to the general procedure D at room temperature instead of 35 °C. 4% of **2i-2** was detected based on the crude ^{1}H NMR spectrum (5% conversion). 72% isolated yield of **2c** was obtained after column chromatography.



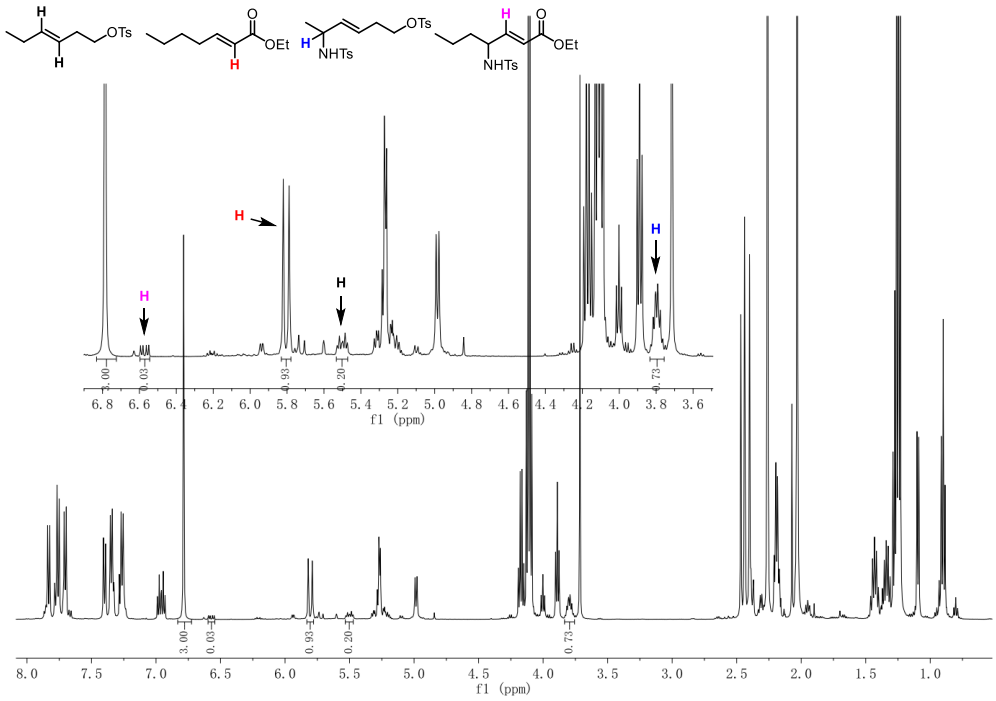


The reaction was conducted according to the general procedure D at room temperature instead of 35 °C. 4% of **4i** was detected based on the crude ^{1}H NMR spectrum (6% conversion). 76% isolated yield of **4j** was obtained after column chromatography.

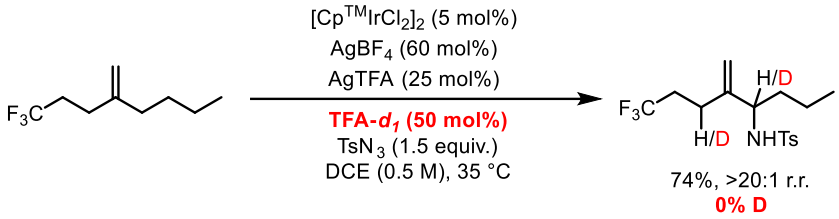




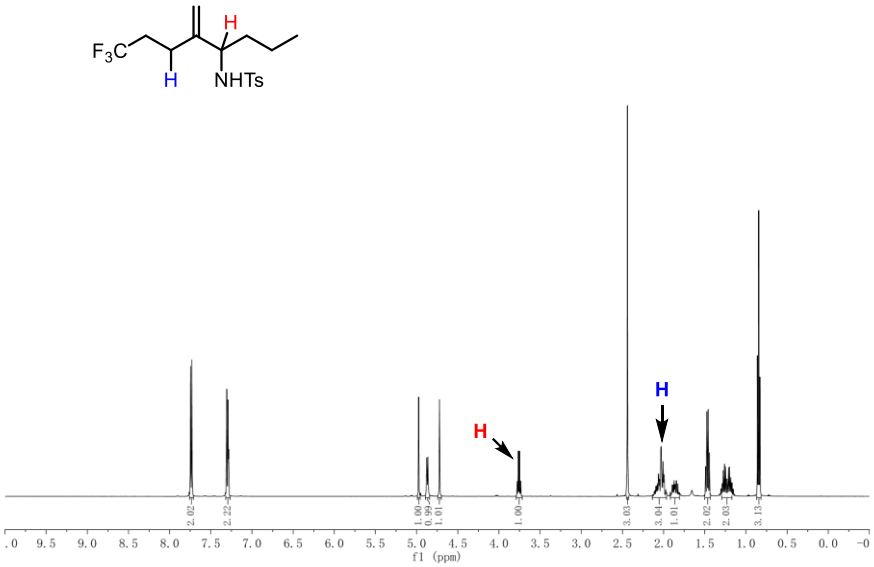
The reaction was conducted according to the general procedure F. 3% of **4i** was detected based on the crude ^{1}H NMR spectrum (7% conversion). 71% isolated yield of **4a** was obtained after column chromatography.

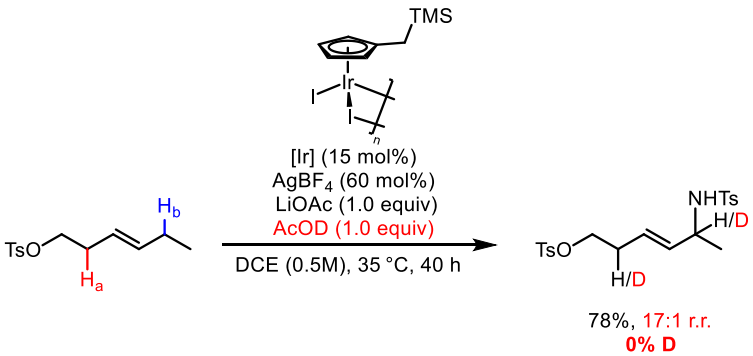


7. Irreversible C-H Activations

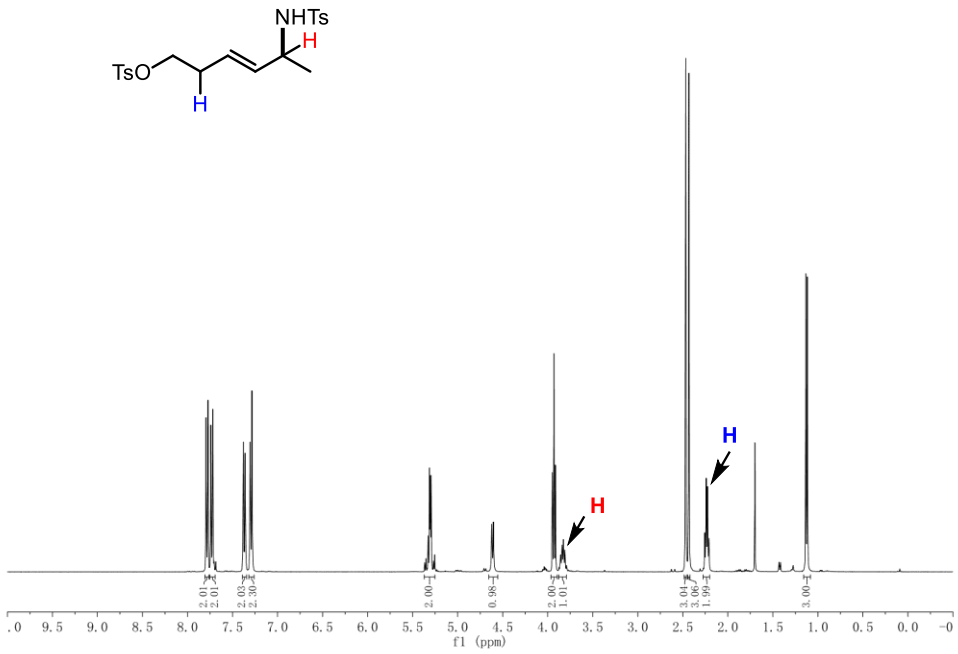


The reaction was performed according to the general procedure D with an additional 50 mol% of deuterated trifluoroacetic acid. The product was isolated (74% yield), and the ^{1}H NNR was shown below.



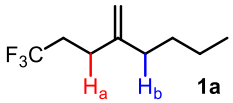


The reaction was performed according to the general procedure F with an additional 1.0 equivalent of deuterated acetic acid (AcOD). The product was isolated (78% yield), and the ^{1}H NNR was shown below.



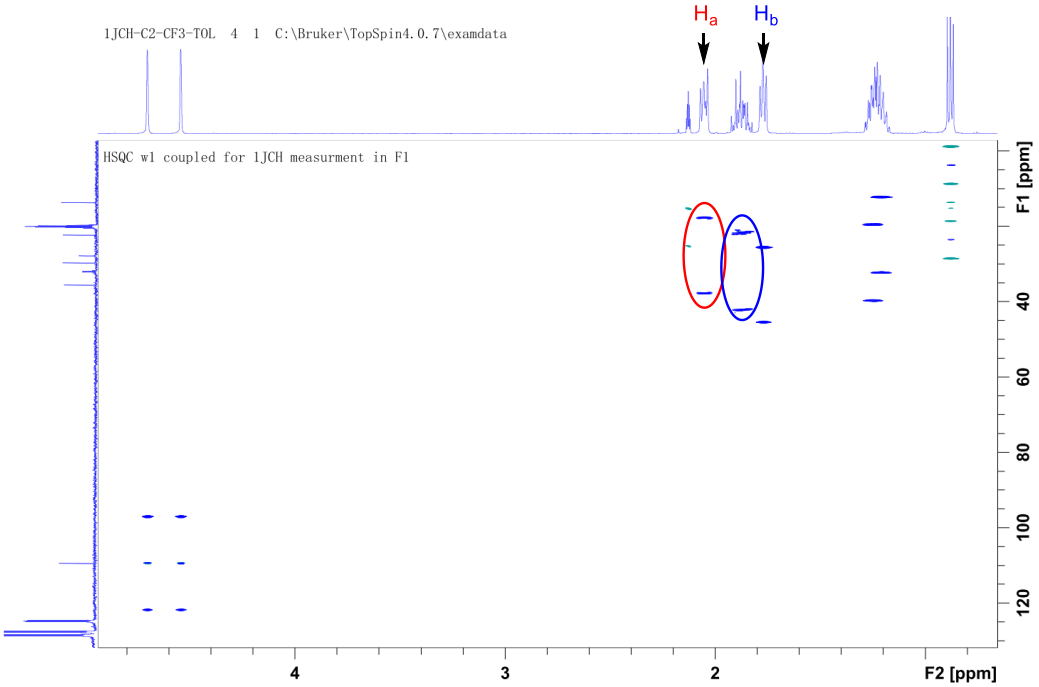
8. Study of $^{1}J_{CH}$ and $^{1}J_{CC}$ Coupling Constants

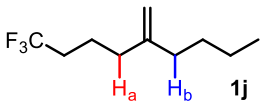
$^{1}J_{CH}$ coupling constants were measured according to the literature[20,21].



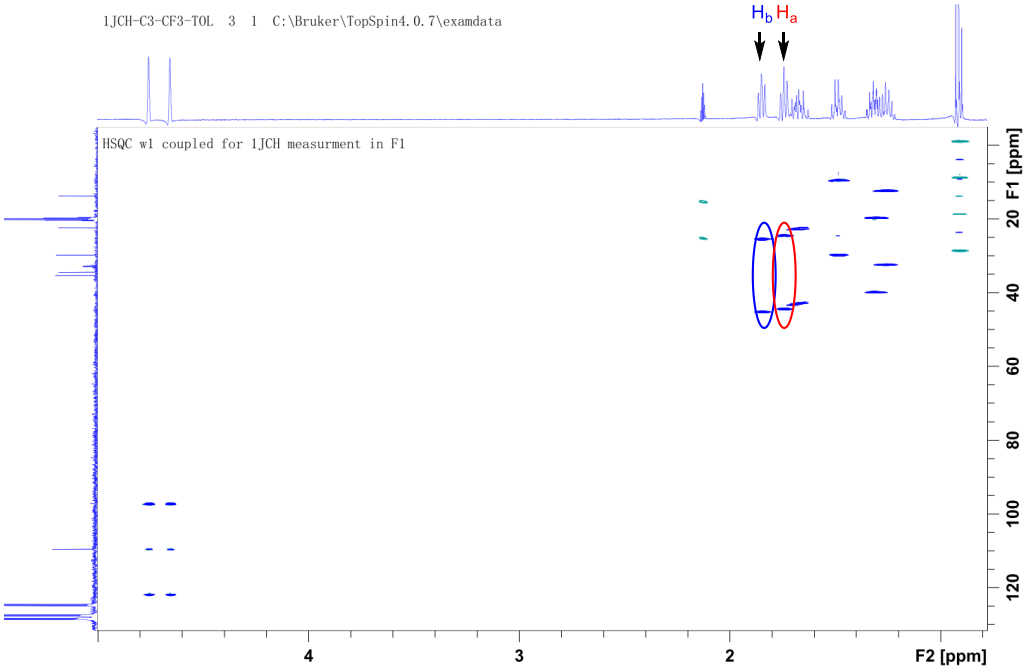
1a

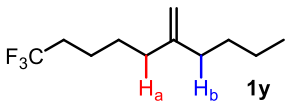
$^{1}J_{CHa}$ = 127.0 Hz
$^{1}J_{CHb}$ = 124.4 Hz (toluene-d_8, 500 MHz)



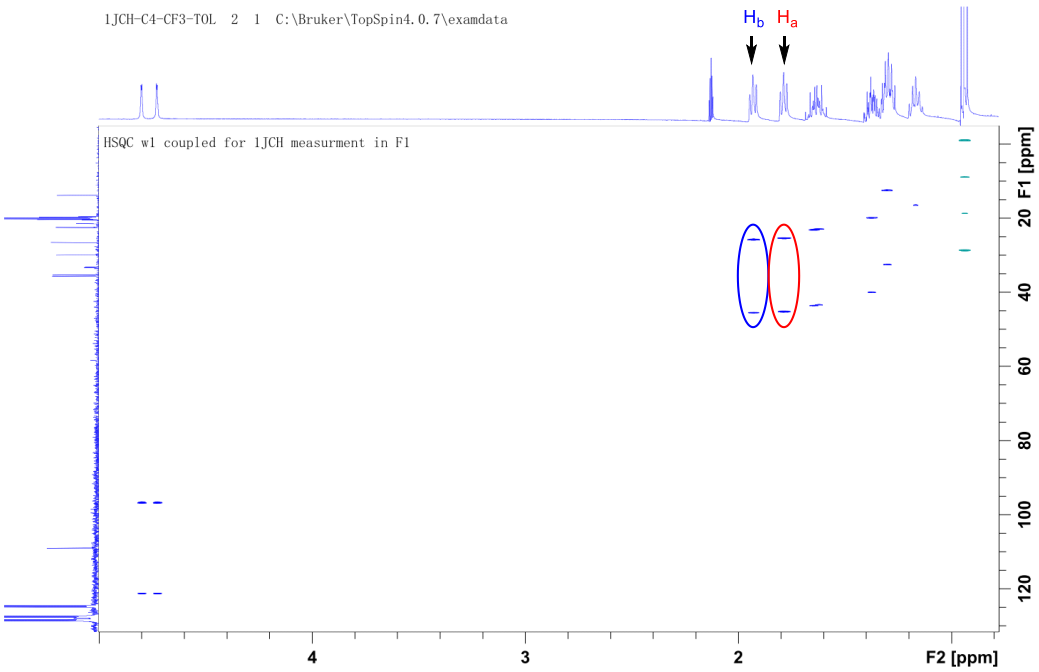


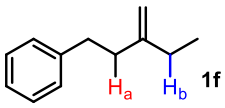
$^1J_{CHa}$ = 125.4 Hz
$^1J_{CHb}$ = 124.5 Hz (toluene-d_8, 500 MHz)





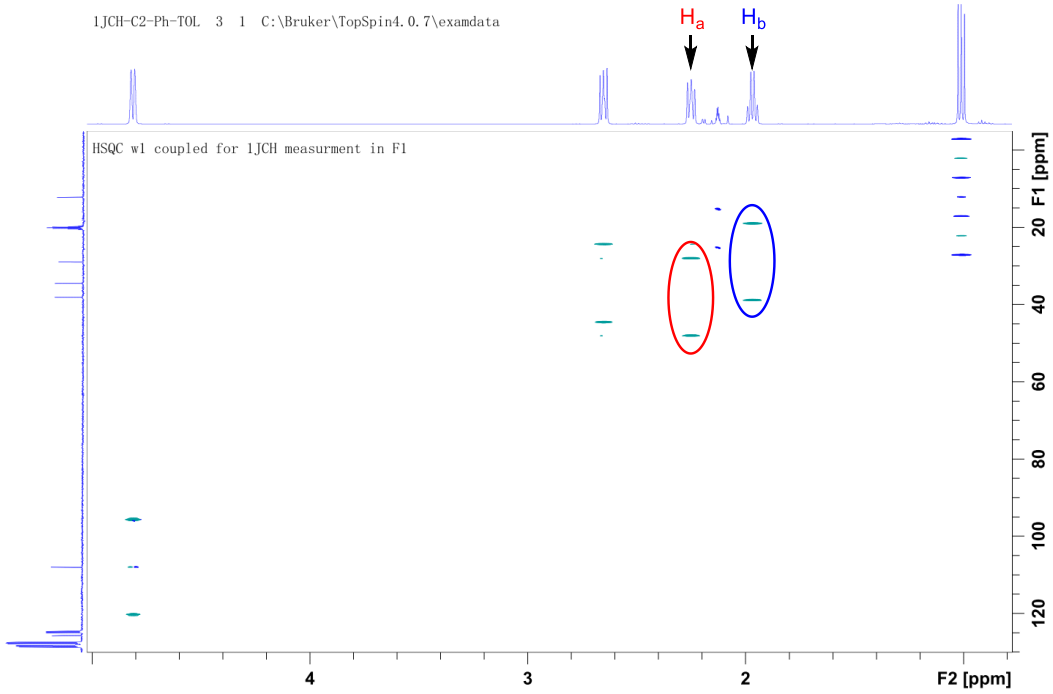
$^1J_{CHa}$ = 124.6 Hz
$^1J_{CHb}$ = 124.4 Hz (toluene-d_8, 500 MHz)

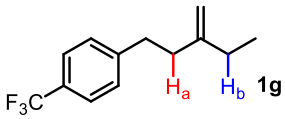




1f

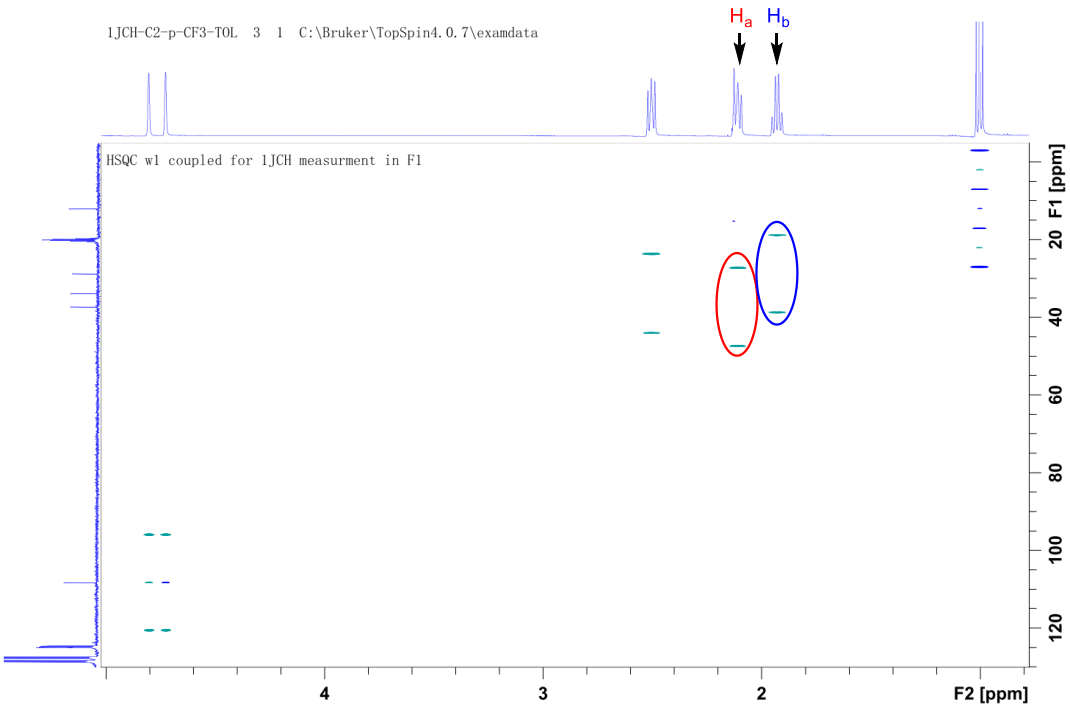
$^1J_{CHa}$ = 126.2 Hz
$^1J_{CHb}$ = 126.8 Hz

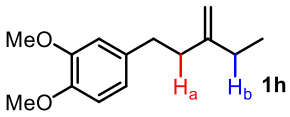




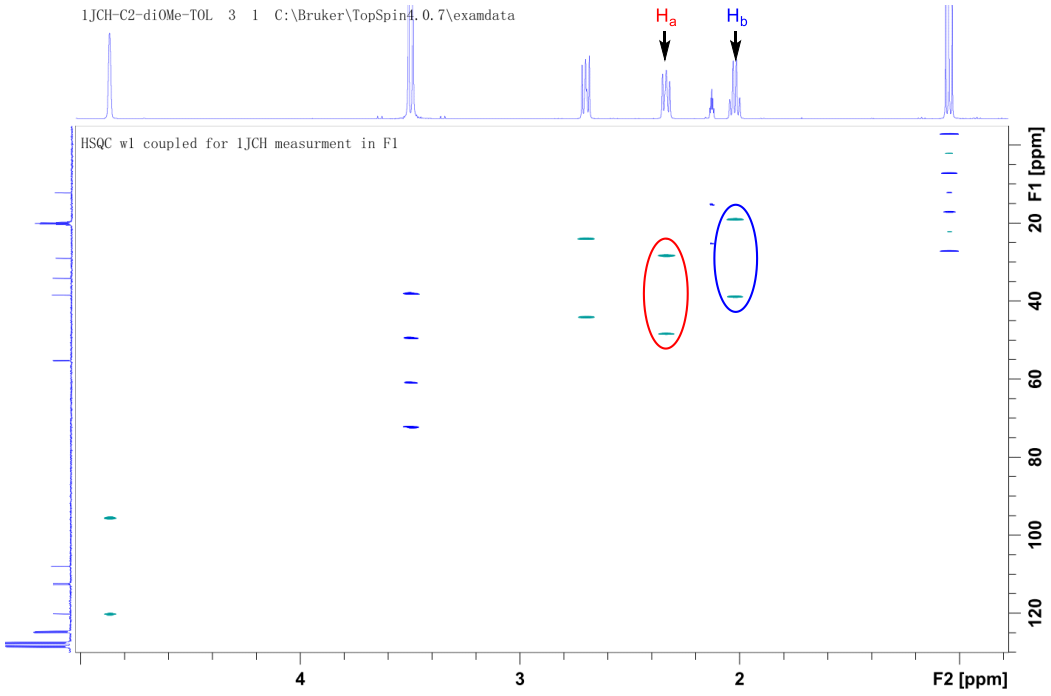
1g

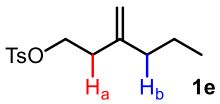
$^1J_{CHa}$ = 126.5 Hz
$^1J_{CHb}$ = 124.9 Hz



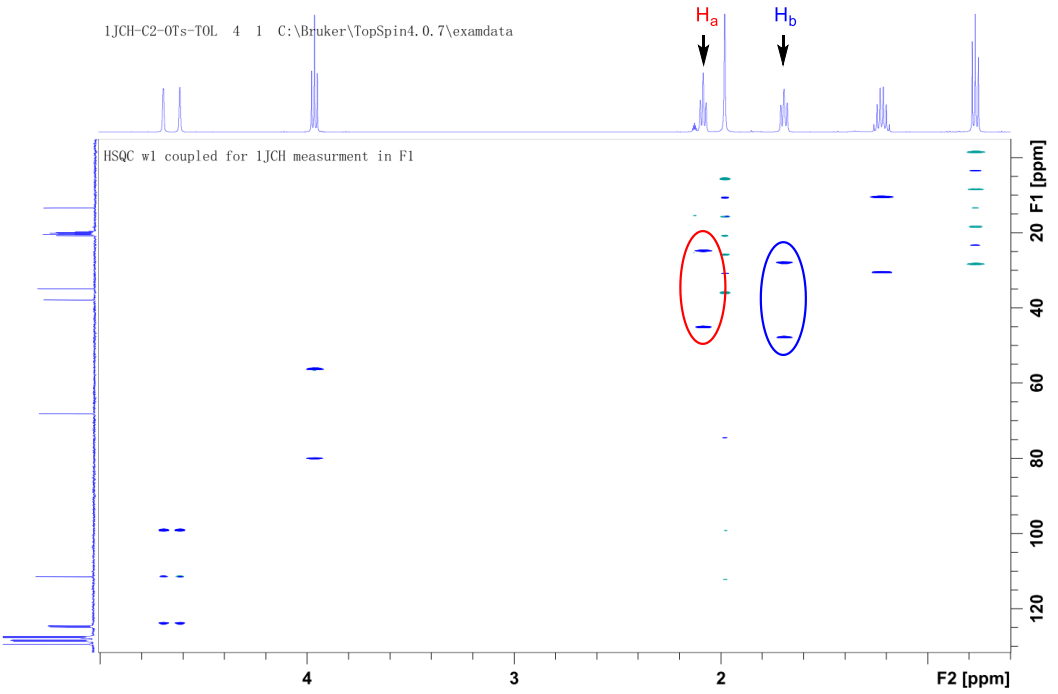


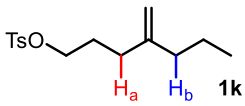
$^1J_{CHa}$ = 126.0 Hz
$^1J_{CHb}$ = 124.8 Hz





$^1J_{CHa}$ = 127.9 Hz
$^1J_{CHb}$ = 124.9 Hz (toluene-d_8, 500 MHz)

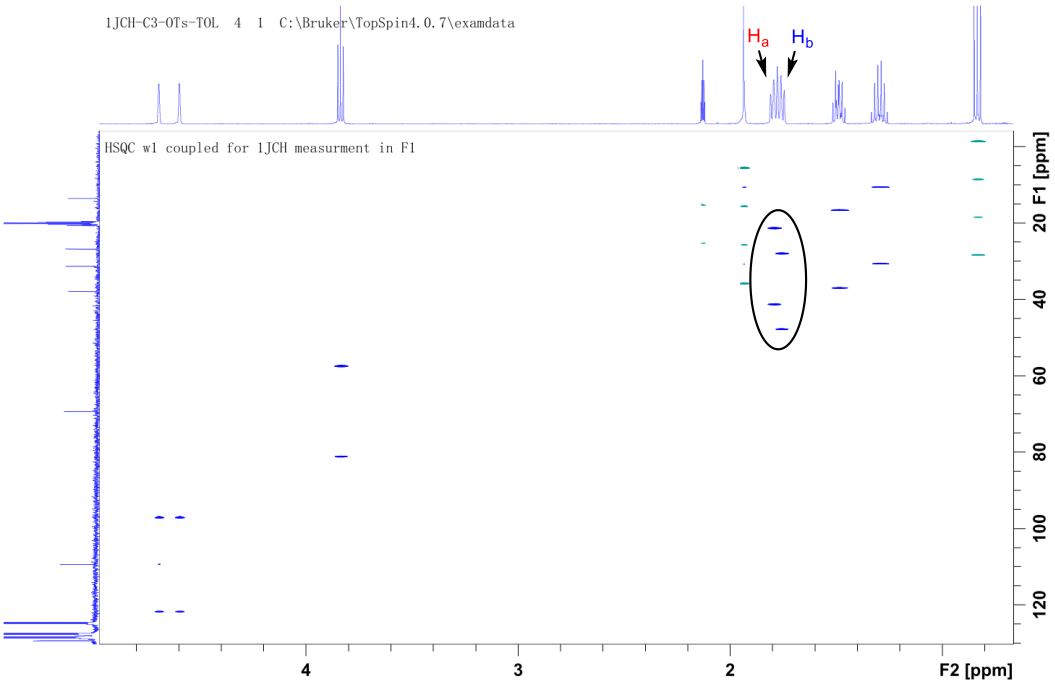


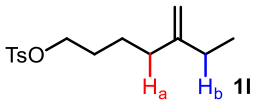


1k

$^1J_{CHa}$ = 126.0 Hz
$^1J_{CHb}$ = 124.5 Hz

(toluene-d_8, 500 MHz)

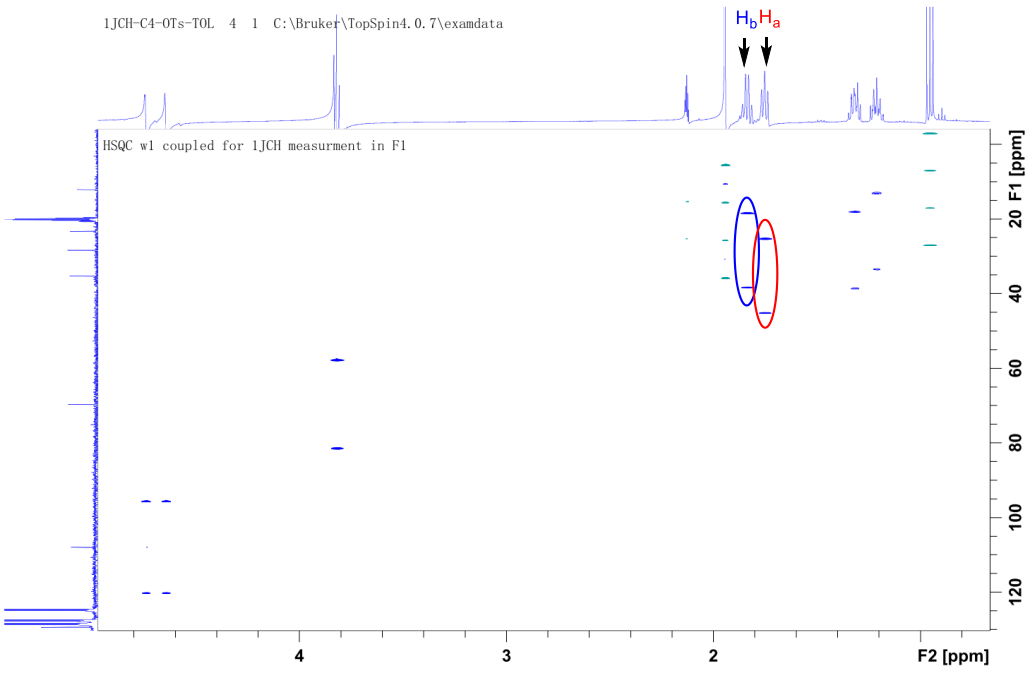


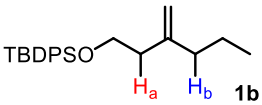


1l

$^1J_{CHa}$ = 125.2 Hz
$^1J_{CHb}$ = 124.6 Hz

(toluene-d_8, 500 MHz)

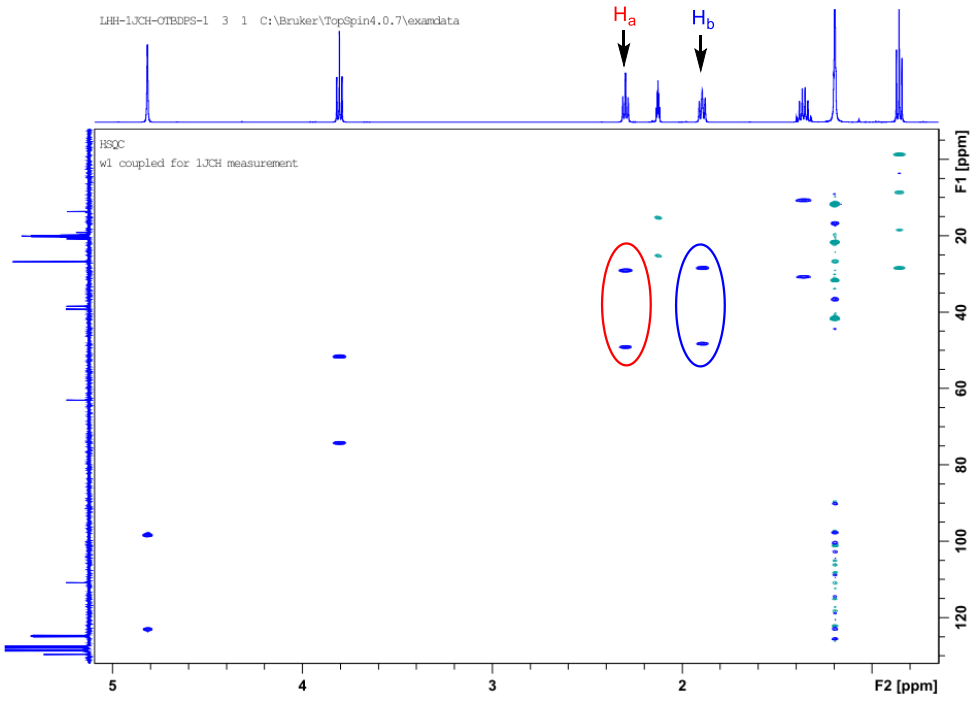


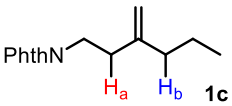


1b

$^{1}J_{CHa}$ = 126.4 Hz

$^{1}J_{CHb}$ = 124.4 Hz

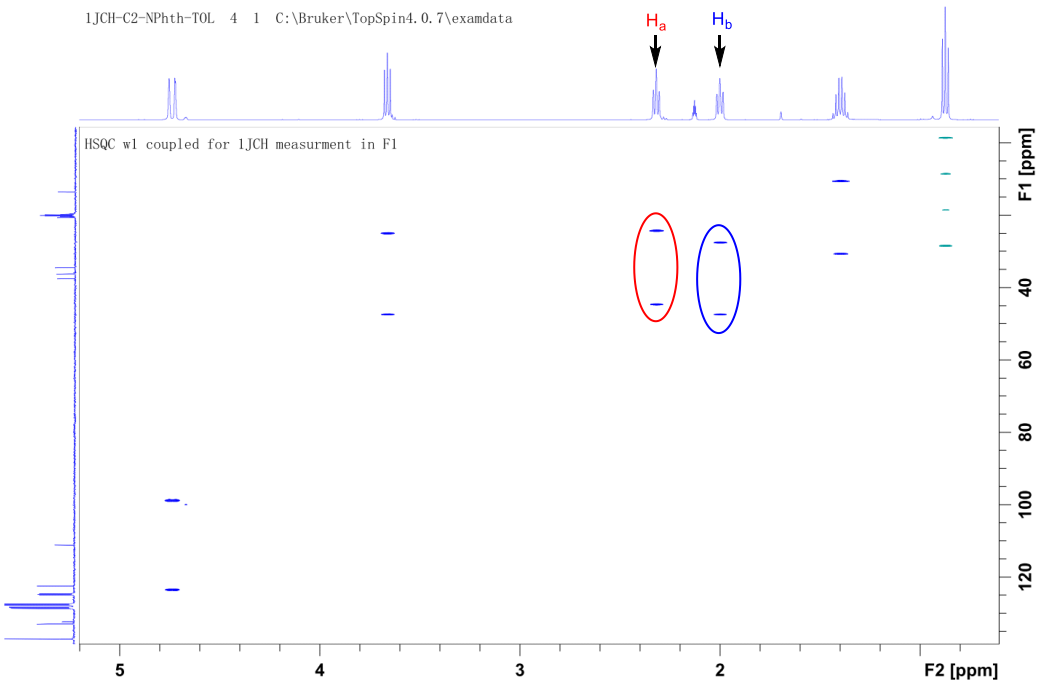


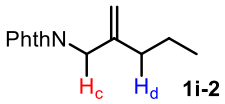


1c

$^{1}J_{CHa}$ = 128.2 Hz

$^{1}J_{CHb}$ = 124.9 Hz

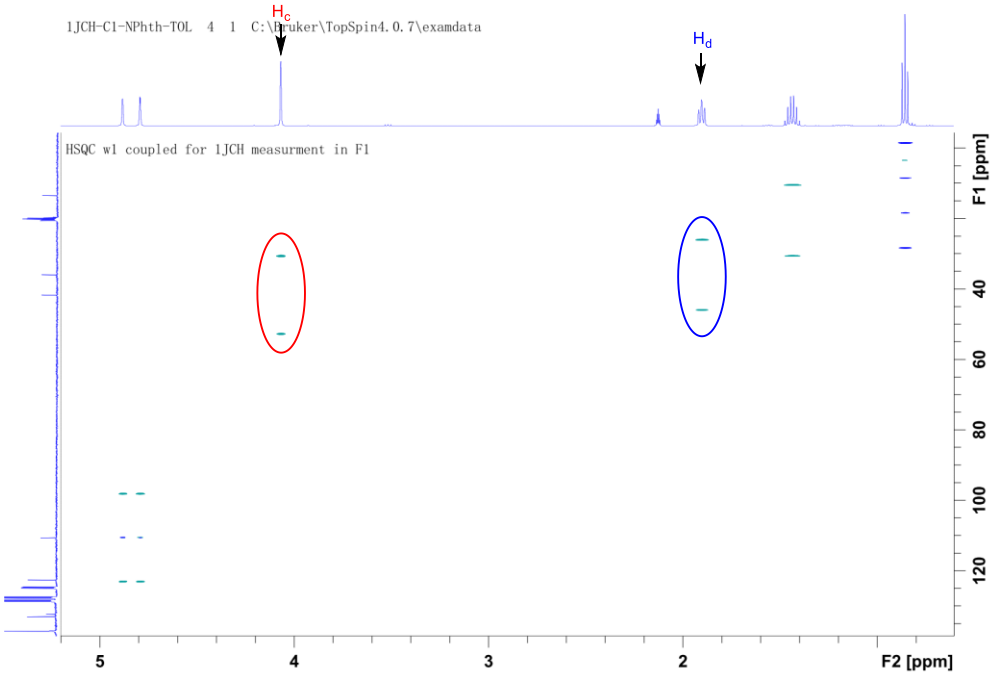


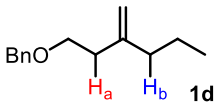


1i-2

$^{1}J_{CHc}$ = 139.3 Hz

$^{1}J_{CHd}$ = 125.4 Hz

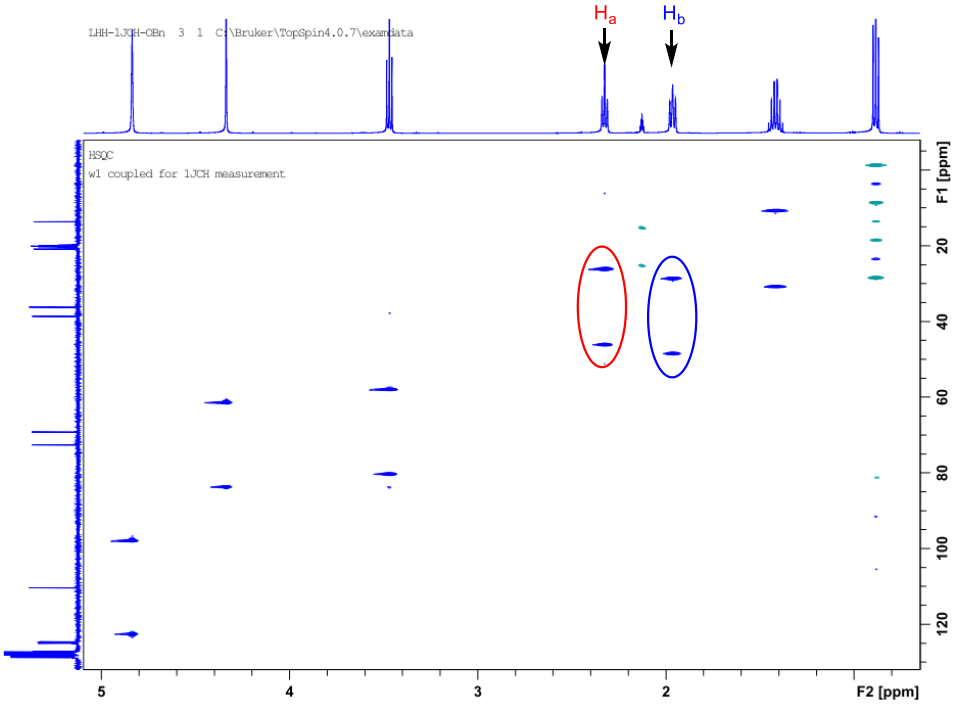


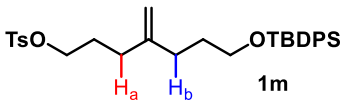


1d

$^{1}J_{CHa}$ = 126.3 Hz

$^{1}J_{CHb}$ = 124.4 Hz

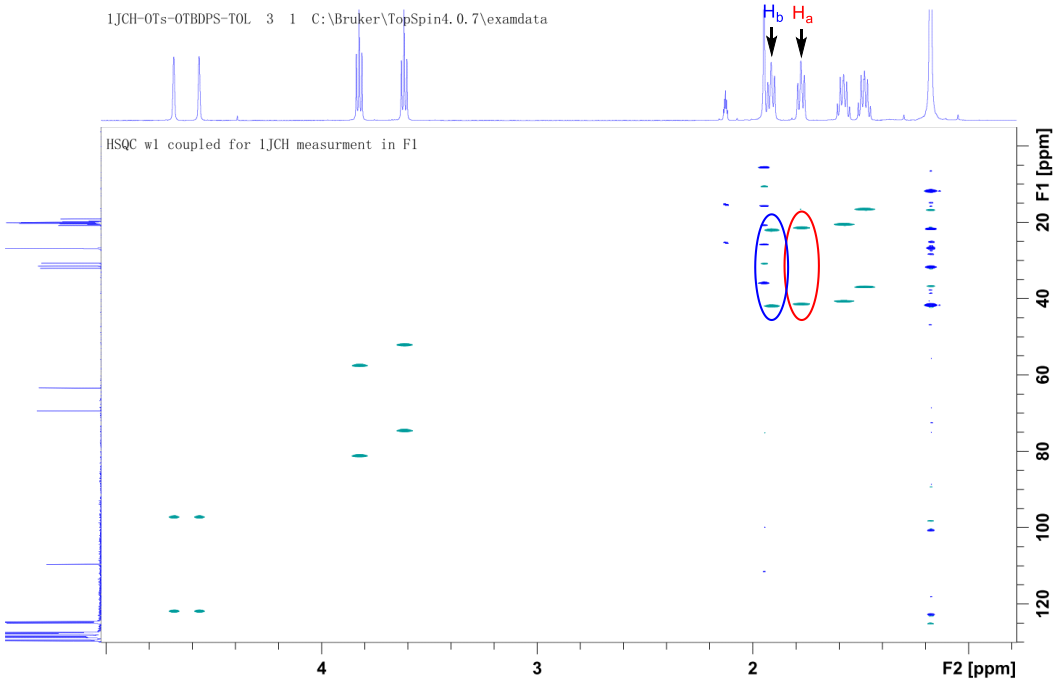


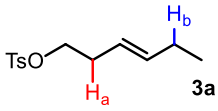


1m

$^{1}J_{CHa}$ = 125.9 Hz

$^{1}J_{CHb}$ = 125.3 Hz

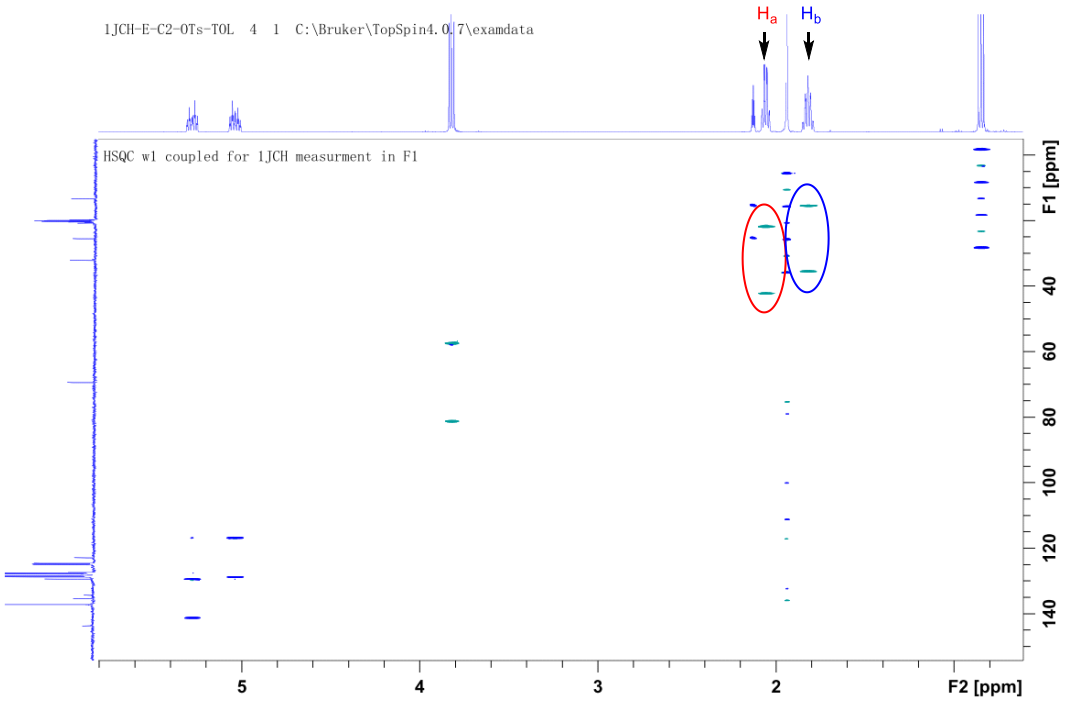


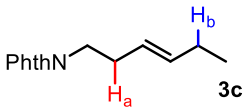


3a

$^{1}J_{CHa}$ = 128.2 Hz

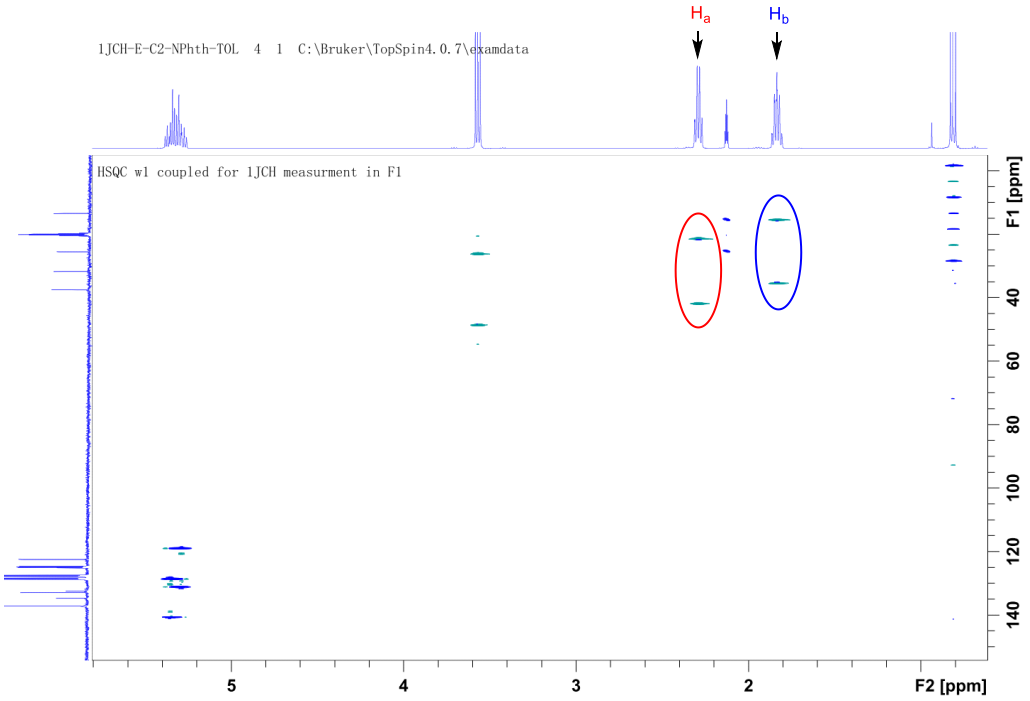
$^{1}J_{CHb}$ = 125.7 Hz (toluene-d_8, 500 MHz)

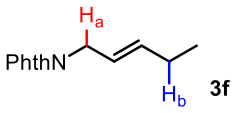




3c

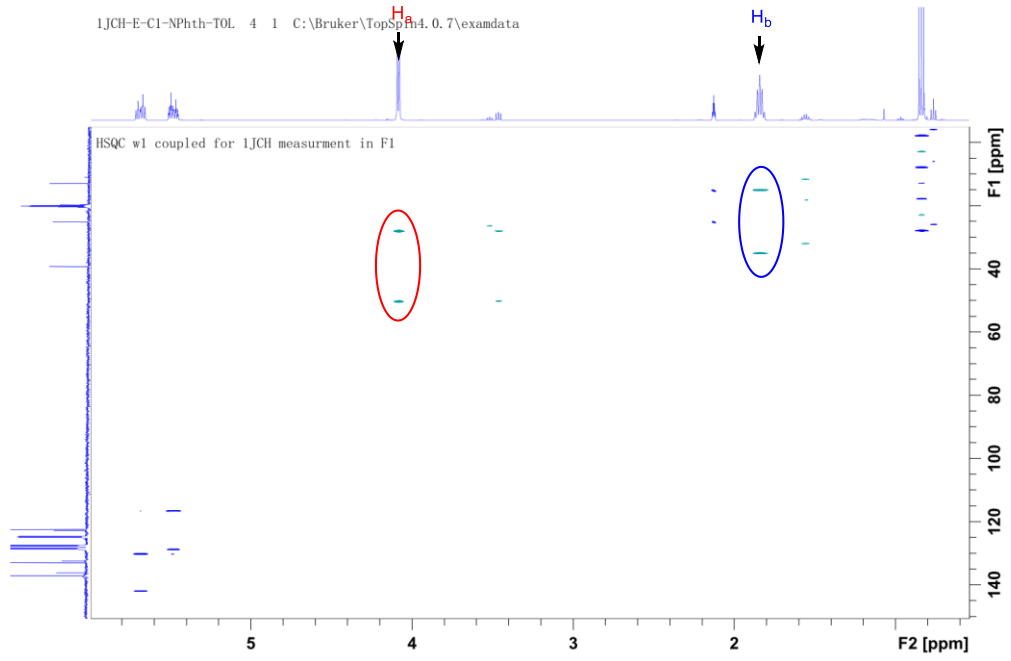
$^1J_{CHa}$ = 128.4 Hz
$^1J_{CHb}$ = 125.7 Hz (toluene-d_8, 500 MHz)

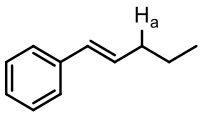




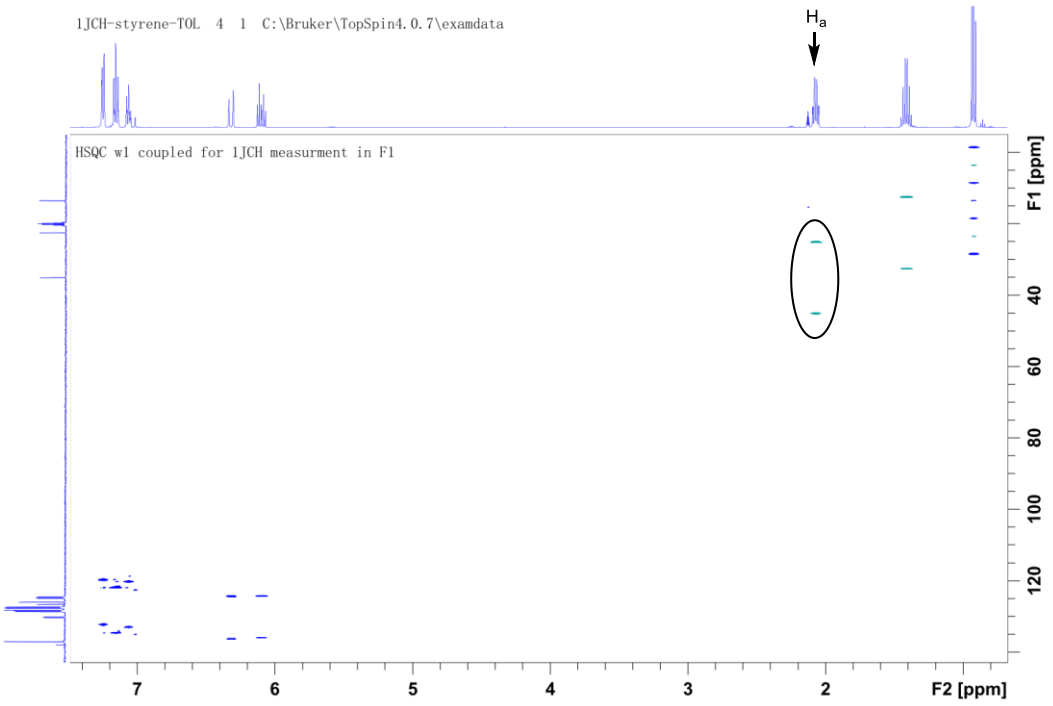
3f

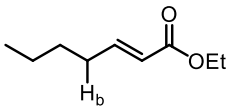
$^1J_{CHa}$ = 139.9 Hz
$^1J_{CHb}$ = 126.2 Hz (toluene-d_8, 500 MHz)



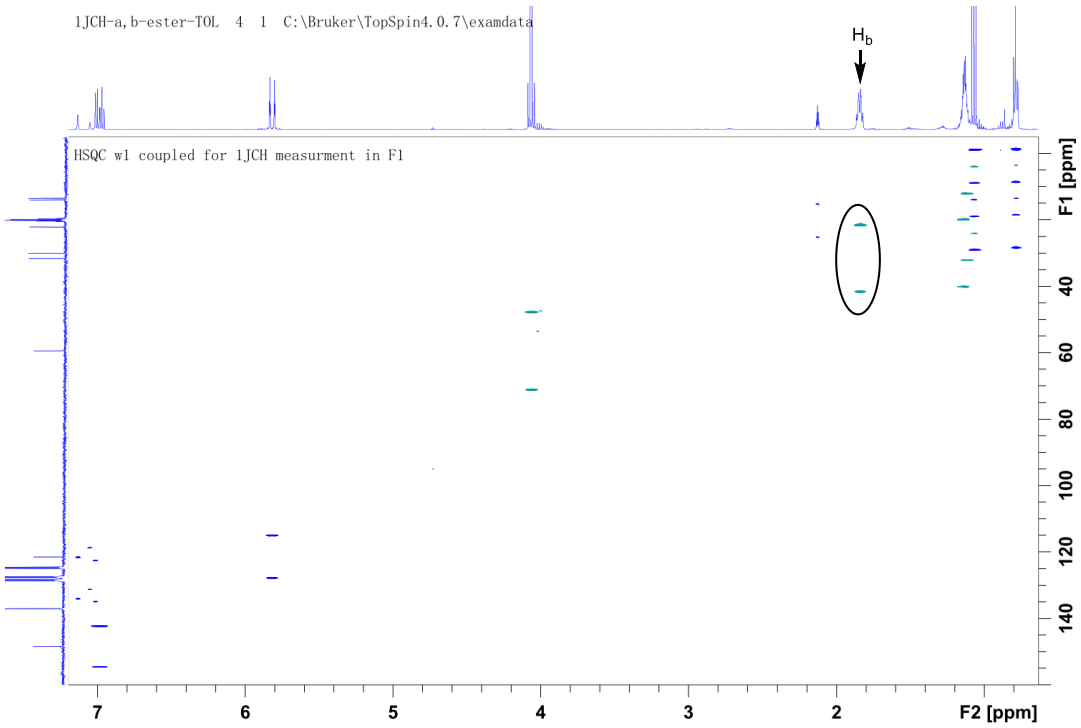


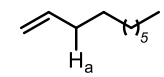
$^1J_{CHa}$ = 125.6 Hz





$^1J_{CHb}$ = 126.3 Hz





$^1J_{CHa}$ = 125.2 Hz

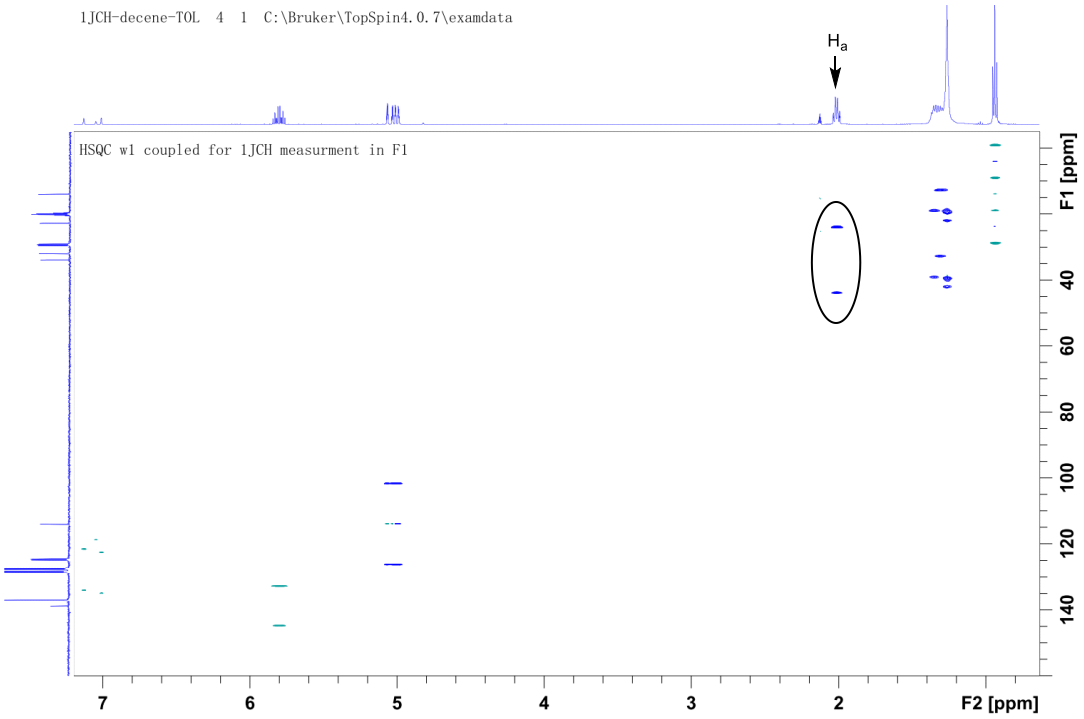
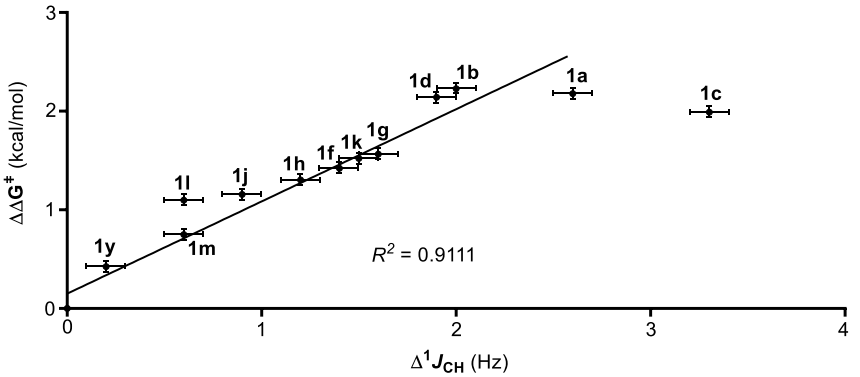


Figure 1. Linear Correlation between ΔΔG‡ (ΔΔG‡ = -RTln(r.r.)) and Δ^1J_{CH}



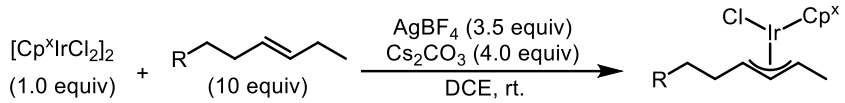
Substrate	Δ^1J_{CH} ±0.1 (Hz)	r.r. ± 10%	ΔΔG‡ ± 0.058 (kcal/mol)
1a	2.6	35:1	2.177142246
1b	2.0	38:1	2.22750132
1c	3.3	15:1	1.658293476
1d	1.9	33:1	2.141110854
1f	1.4	11:1	1.42071686
1g	1.6	14:1	1.563601749
1h	1.2	9:1	1.301822493

1j	0.9	6.6:1	1.155560295
1k	1.5	12:1	1.521649962
1l	0.6	6.0:1	1.09719644
1m	0.6	3.4:1	0.749387443
1y	0.2	2.0:1	0.424453523

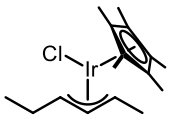
^{13}C Chemical Shifts Analysis:

	Proximal ^{13}C δ (ppm)	Distal ^{13}C δ (ppm)	Δδ (ppm)	r.r.	ΔΔG‡ (kcal/mol)
1a	29.983	35.945	-5.962	35:1	2.177142
1j	34.927	35.588	-0.661	6.6:1	1.15556
1y	35.67	35.776	-0.106	2:1	0.424454
1f	38.221	29.139	9.082	11:1	1.420717
1g	37.767	29.073	8.694	14:1	1.563602
1h	38.386	29.127	9.259	9:1	1.301822
1k	38.153	31.644	6.509	12:1	1.52165
1l	35.5	28.642	6.858	6:1	1.097196
1m	32.147	31.71	0.437	3.4:1	0.749387

General procedure H:



To a stirred solution of the alkene (10 equiv), silver tetrafluoroborate (3.5 equiv), and cesium carbonate (4.0 equiv) in DCE (0.1 M) was added a solution of $[Cp^xIrCl_2]_2$ (1.0 equiv) in DCE (fully dissolved). The resulting mixture was stirred at room temperature for 3 hours. The reaction was filtered through a plug of celite and concentrated under vacuum. The residue was purified through preparative TLC on a basic aluminum oxide plate.

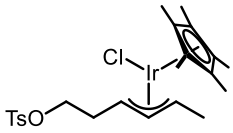


allyl-Ir-1

Allyl-Ir-1 was synthesized from 3-*trans*-hexene and $[Cp^*IrCl_2]_2$ using general procedure H.

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 3.93 (t, *J* = 9.1 Hz, 1H), 3.08 – 2.99 (m, 2H), 1.90 – 1.82 (m, 1H), 1.72 (s, 15H), 1.55 (d, *J* = 6.1 Hz, 3H), 1.52 – 1.43 (m, 1H), 1.17 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 91.7, 85.0, 62.6, 54.5, 26.3, 18.0, 16.7, 8.9.

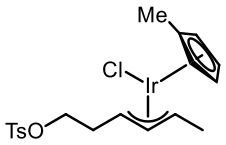


allyl-Ir-2

Allyl-Ir-2 was synthesized from **3a** and $[Cp^*IrCl_2]_2$ (**Ir-1**) using general procedure H.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.33 – 7.26 (m, 2H), 4.11 – 4.05 (m, 1H), 4.04 – 3.97 (m, 1H), 3.89 (t, J = 9.0 Hz, 1H), 2.91 (dq, J = 12.1, 6.2 Hz, 1H), 2.53 (td, J = 9.3, 4.4 Hz, 1H), 2.39 (s, 3H), 2.11 – 2.03 (m, 1H), 1.77 – 1.68 (m, 1H), 1.61 (s, 15H), 1.43 (d, J = 6.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 132.8, 129.9, 127.9, 92.1, 85.5, 70.9, 55.8, 51.8, 32.6, 21.6, 17.8, 8.8.



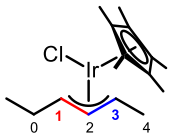
allyl-Ir-3

Allyl-Ir-3 was synthesized from **3a** and $[Cp^{Me}IrCl_2]_2$ (**Ir-8**) using general procedure H.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.39 – 7.30 (m, 2H), 5.13 (s, 1H), 5.08 (s, 1H), 4.98 – 4.86 (m, 3H), 4.15 (ddd, J = 10.4, 7.7, 5.3 Hz, 1H), 4.05 (dt, J = 10.3, 7.5 Hz, 1H), 2.95 (dq, J = 12.6, 6.2 Hz, 1H), 2.56 (q, J = 7.6 Hz, 1H), 2.43 (s, 3H), 2.32 – 2.20 (m, 2H), 1.99 (s, 3H), 1.78 (d, J = 6.1 Hz, 3H).

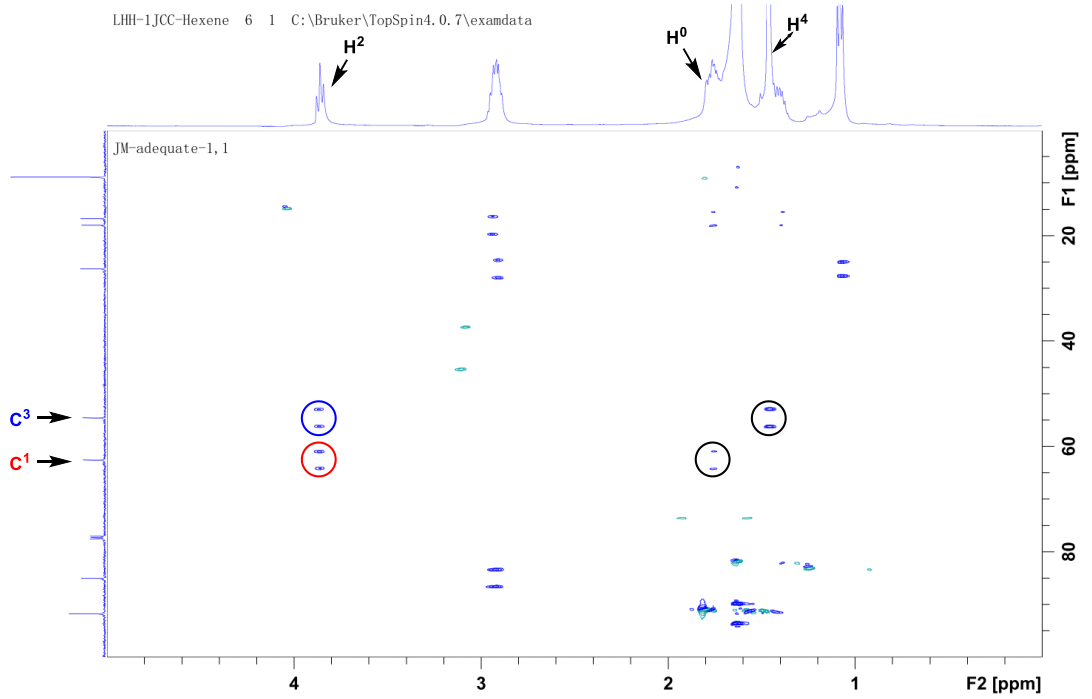
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 132.8, 130.0, 127.9, 104.6, 81.3, 81.2, 80.1, 77.4, 71.5, 60.3, 56.8, 35.6, 21.7, 21.5, 12.2.

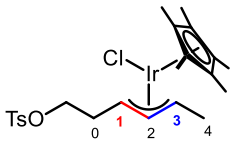
$^1J_{CC}$ coupling constants were measured according to the literature[22]. $^1J_{CC}$ coupling constants of the three allyl-Ir complexes were investigated. The $^1J_{CC}$ coupling constants imply that the Ir-allyl complexes are likely electronically non-biased allyl species.



allyl-Ir-1

$^1J_{C0C1}$ = 41.5 Hz
$^1J_{C3C4}$ = 41.8 Hz
$^1J_{C1C2}$ = 40.1 Hz
$^1J_{C2C3}$ = 40.6 Hz ($CDCl_3$, 500 MHz)

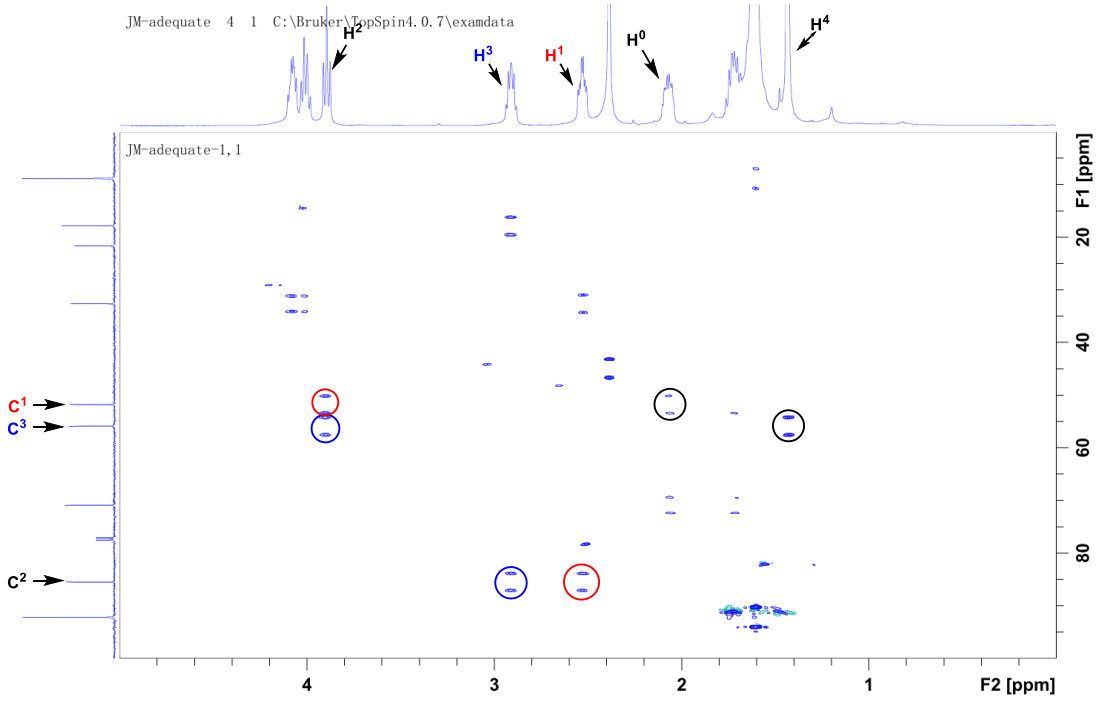


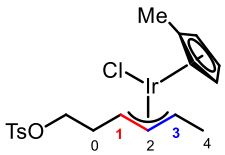


allyl-Ir-2

$^{1}J_{C0C1}$ = 41.7 Hz
$^{1}J_{C3C4}$ = 42.1 Hz
$^{1}J_{C1C2}$ = 40.2 Hz
$^{1}J_{C2C3}$ = 40.9 Hz

($CDCl_3$, 500 MHz)

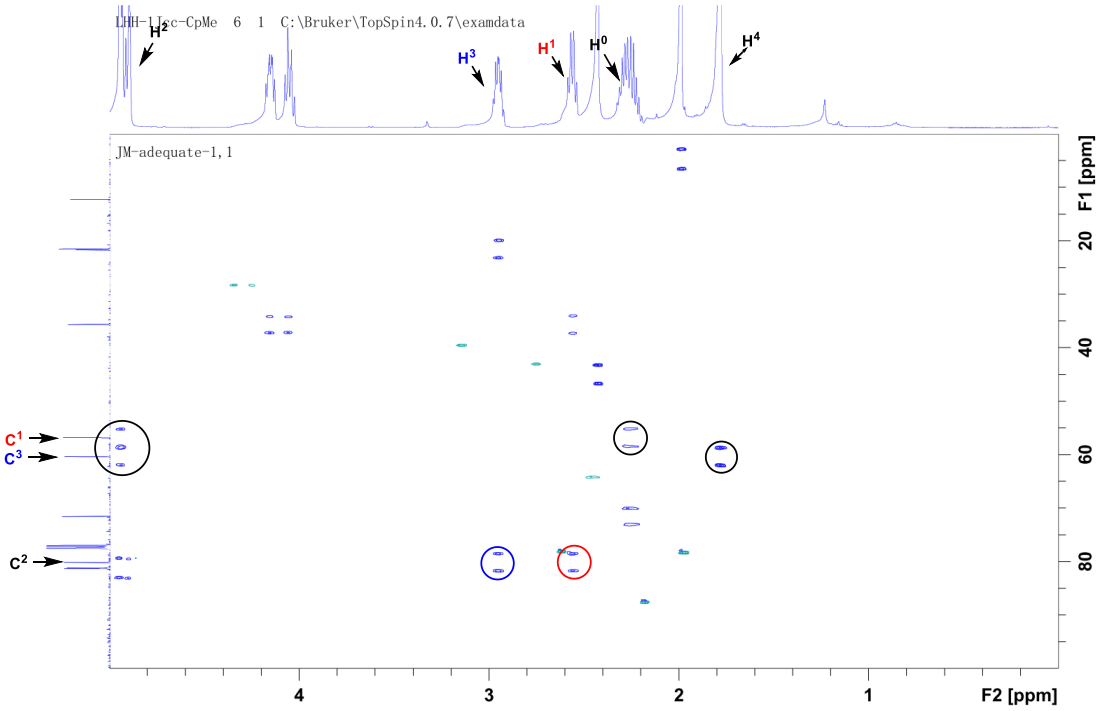




allyl-Ir-3

$^{1}J_{C0C1}$ = 40.8 Hz
$^{1}J_{C3C4}$ = 41.3 Hz
$^{1}J_{C1C2}$ = 40.2 Hz
$^{1}J_{C2C3}$ = 40.5 Hz

($CDCl_3$, 500 MHz)



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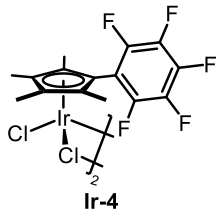
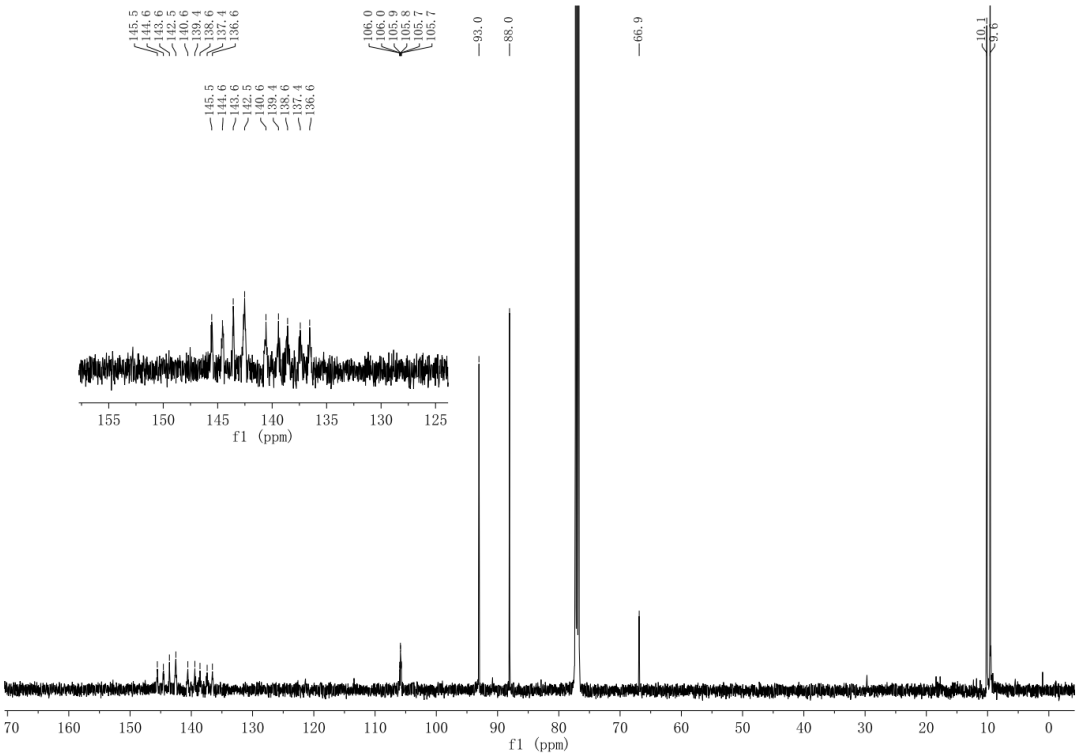
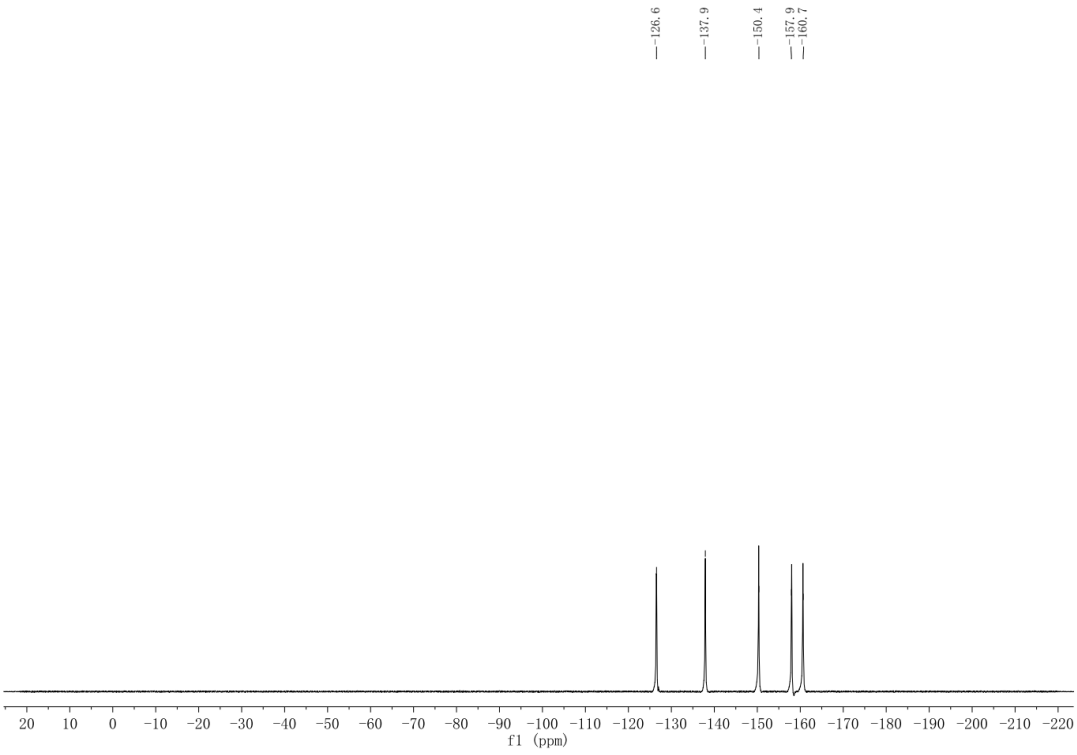
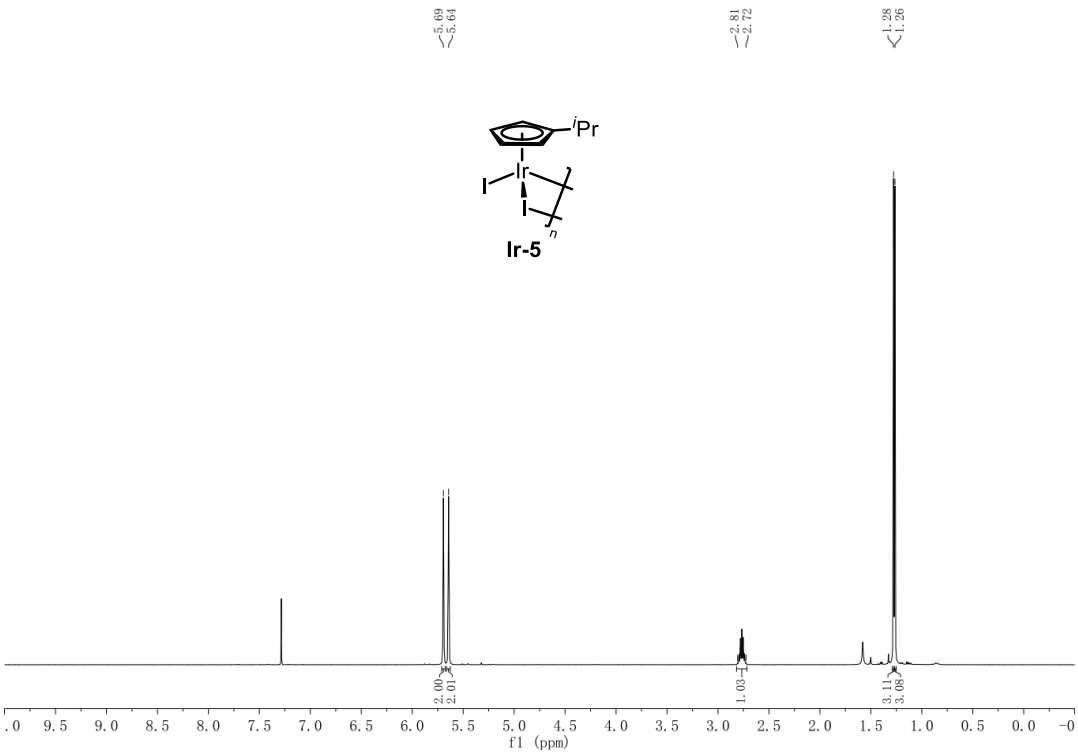
10. NMR Spectra

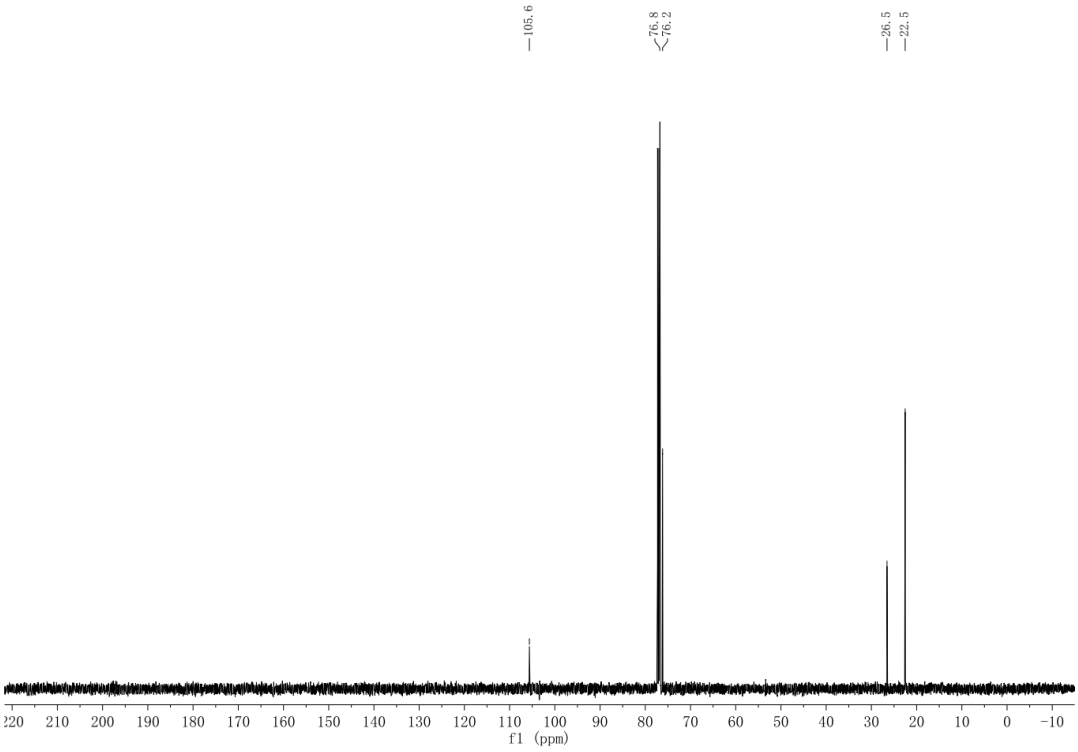


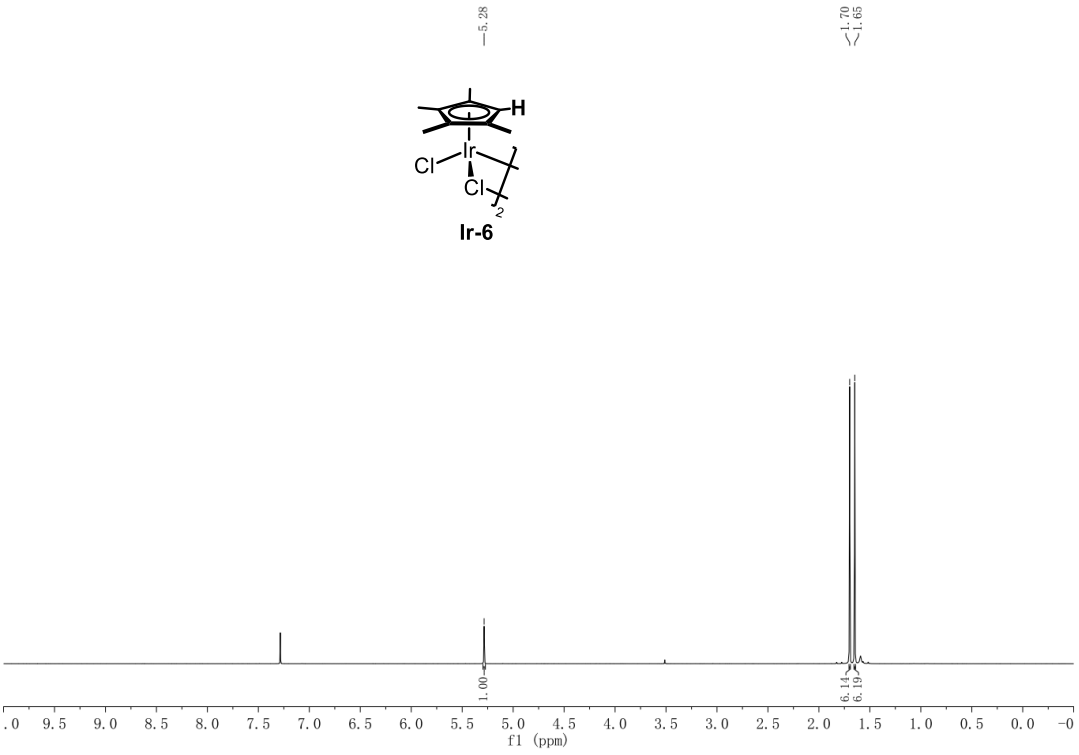
Ir-4



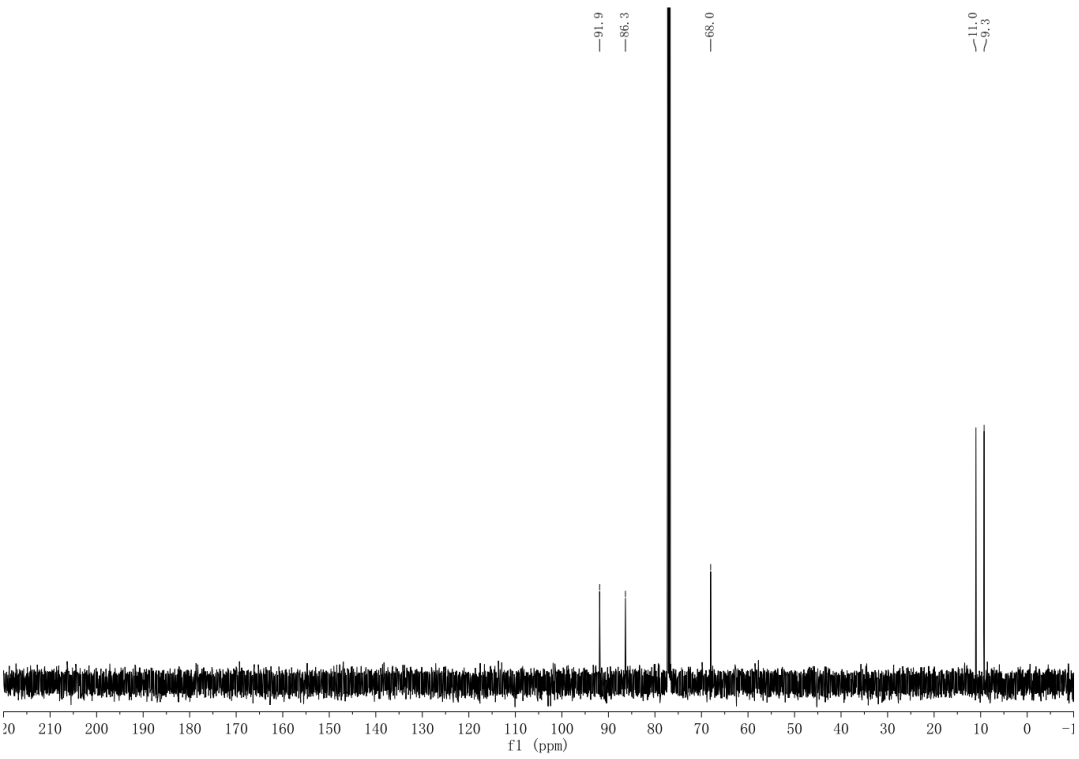

−126.6
−137.9
−150.4
−157.9
−160.7
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

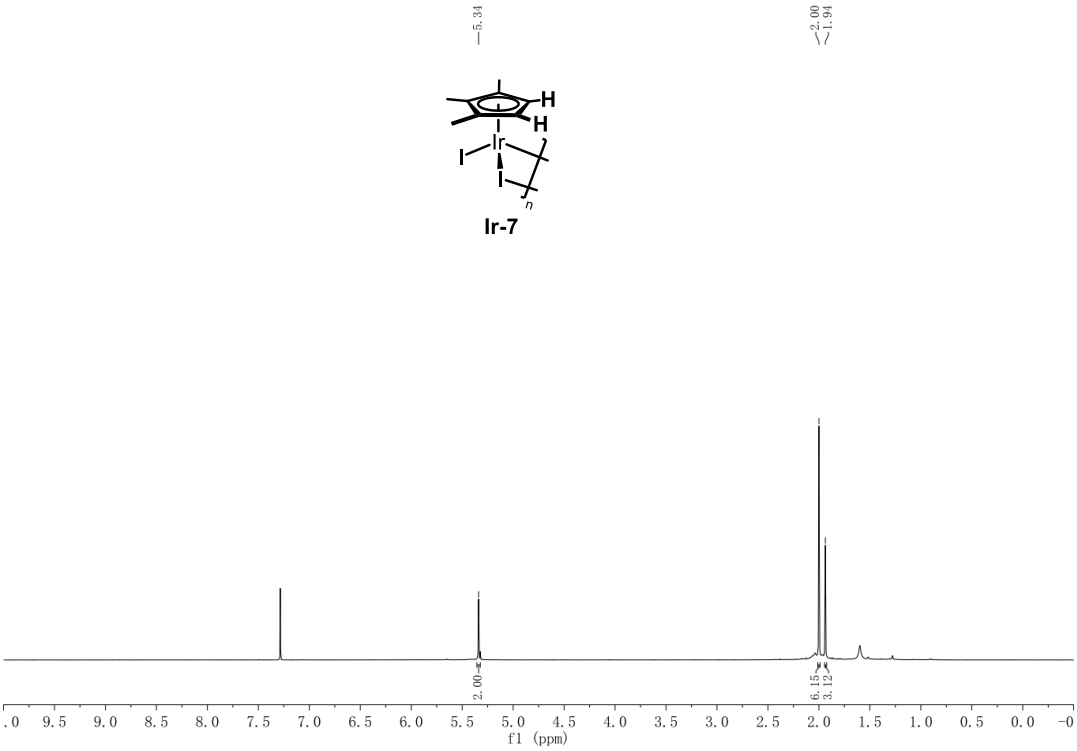

5.69
5.64
2.81
2.72
1.28
1.26
iPr
Ir
I
I
n
Ir-5
2.00
2.01
1.03
3.11
3.08
f1 (ppm)


105.6
76.8
76.2
26.5
22.5
f1 (ppm)

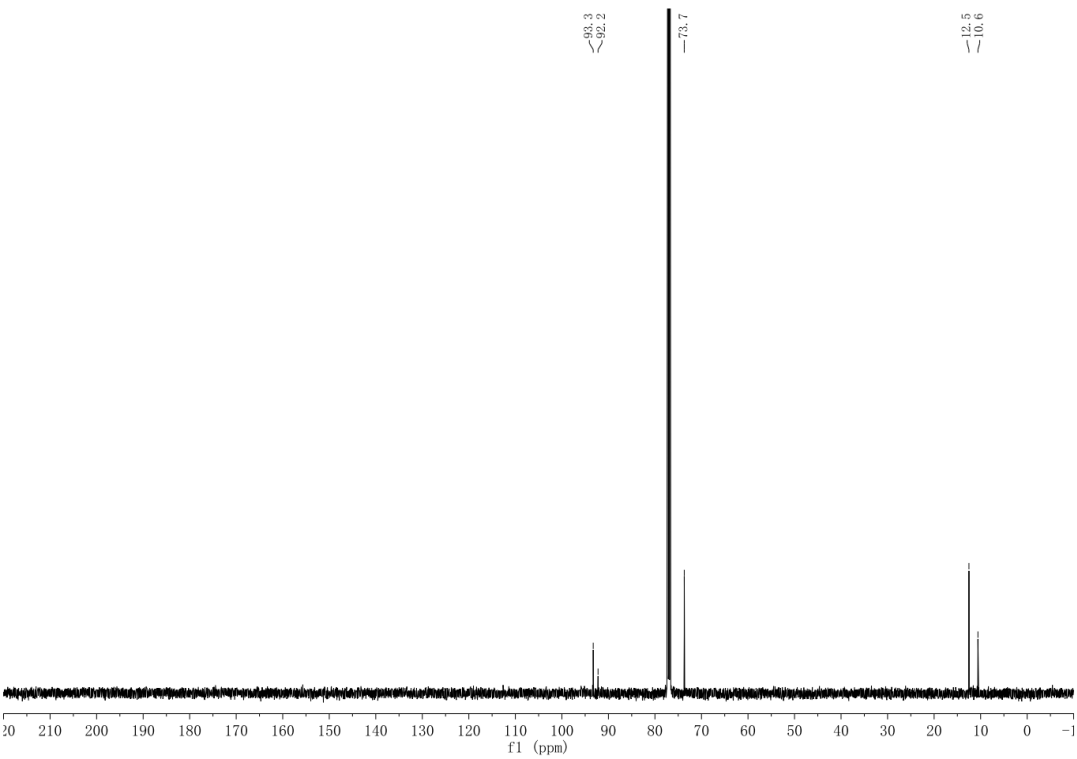


Ir-6

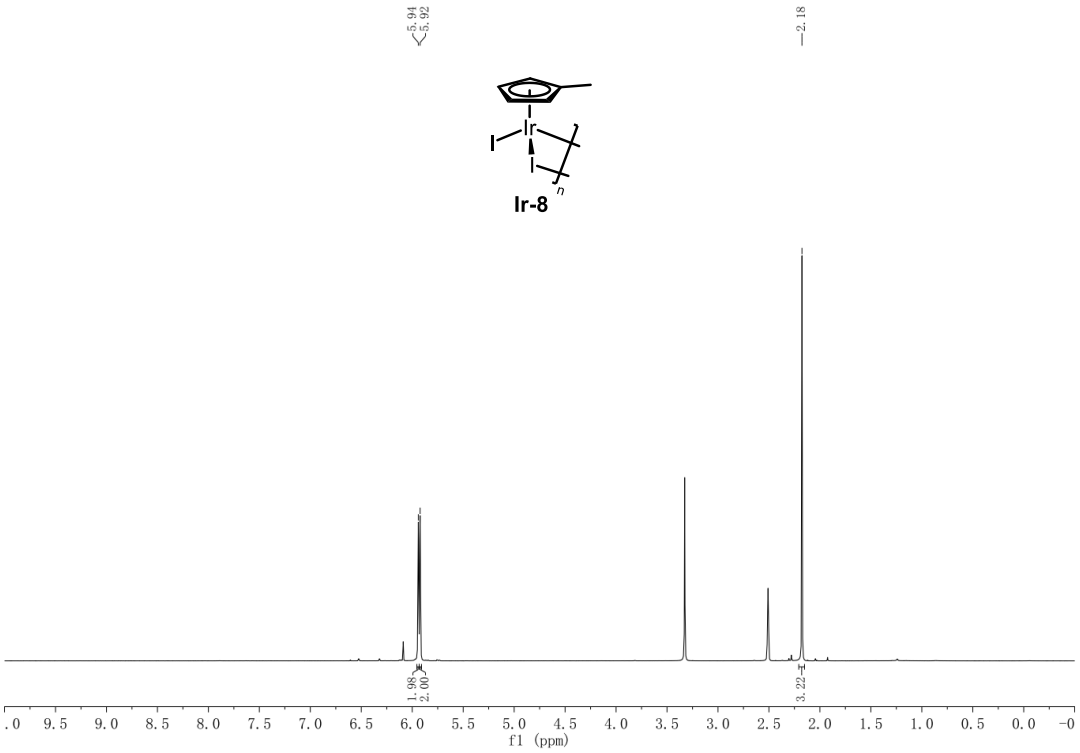


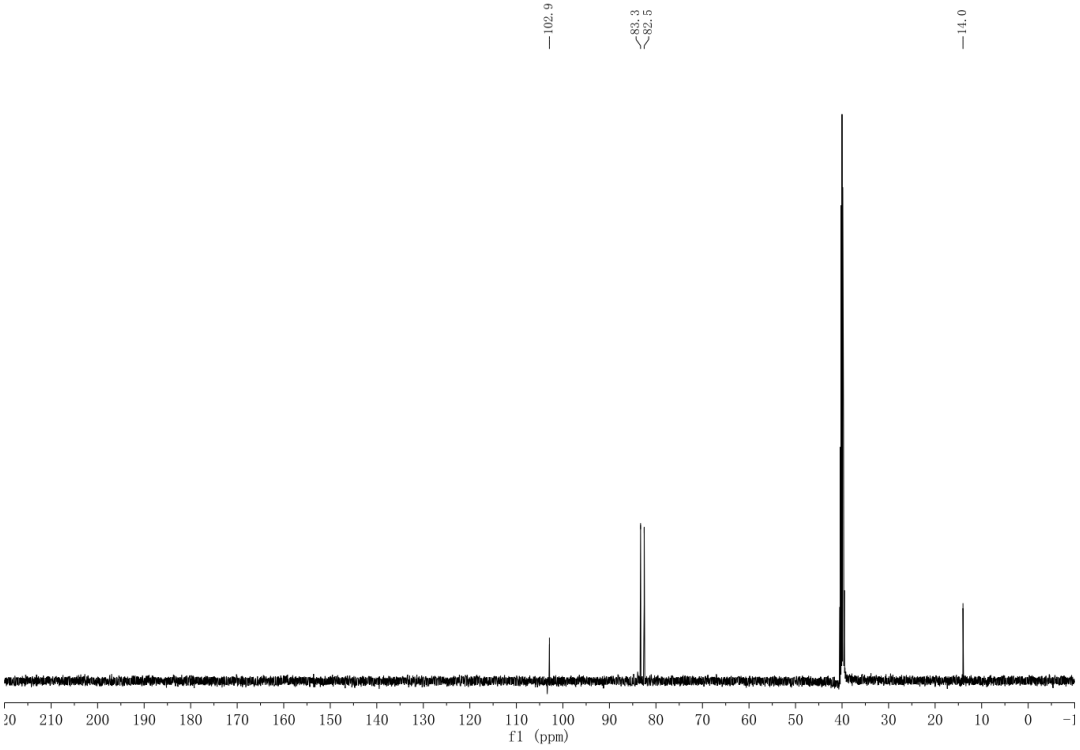

5.34
2.00
1.94
H
H
Ir
I
I
n
2.00
6.15
3.12
f1 (ppm)

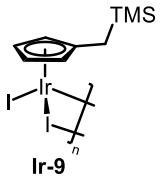
Ir-7


93.3
92.2
73.7
12.5
10.6
f1 (ppm)

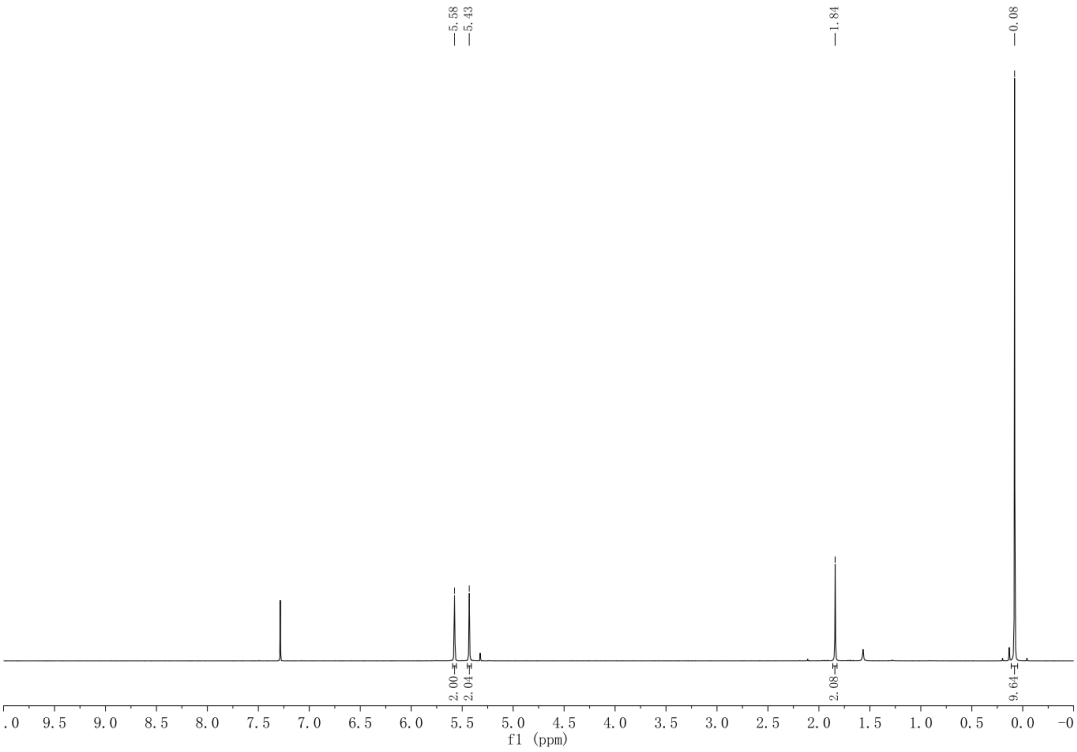
(DMSO-d_6)

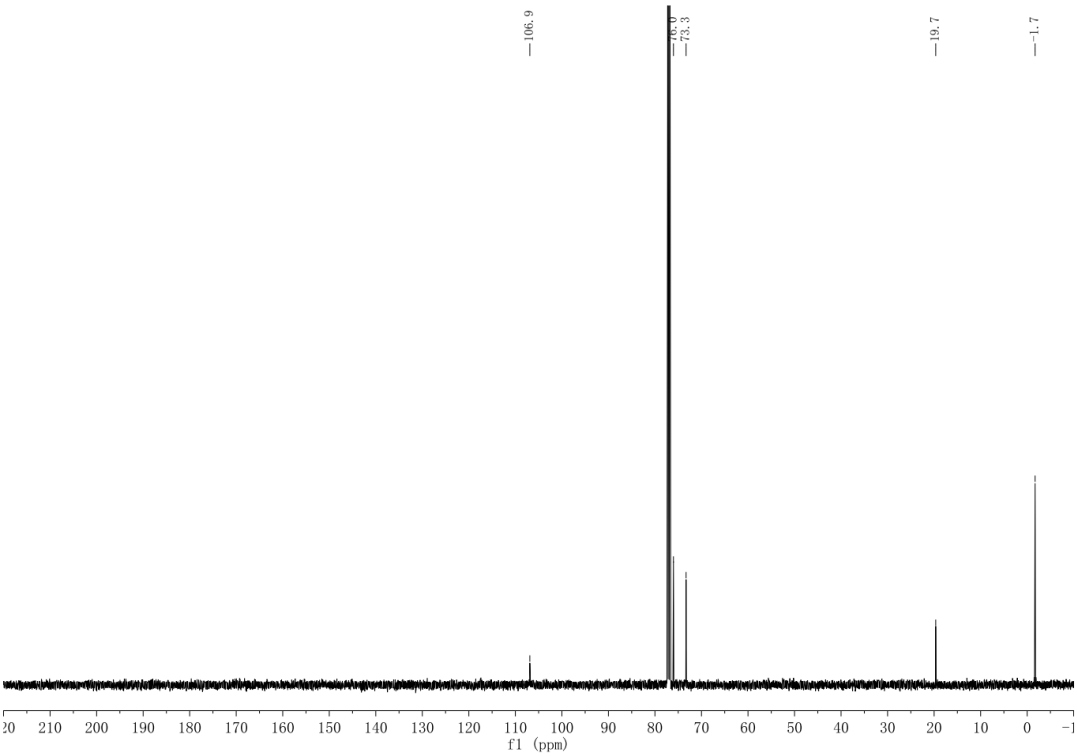


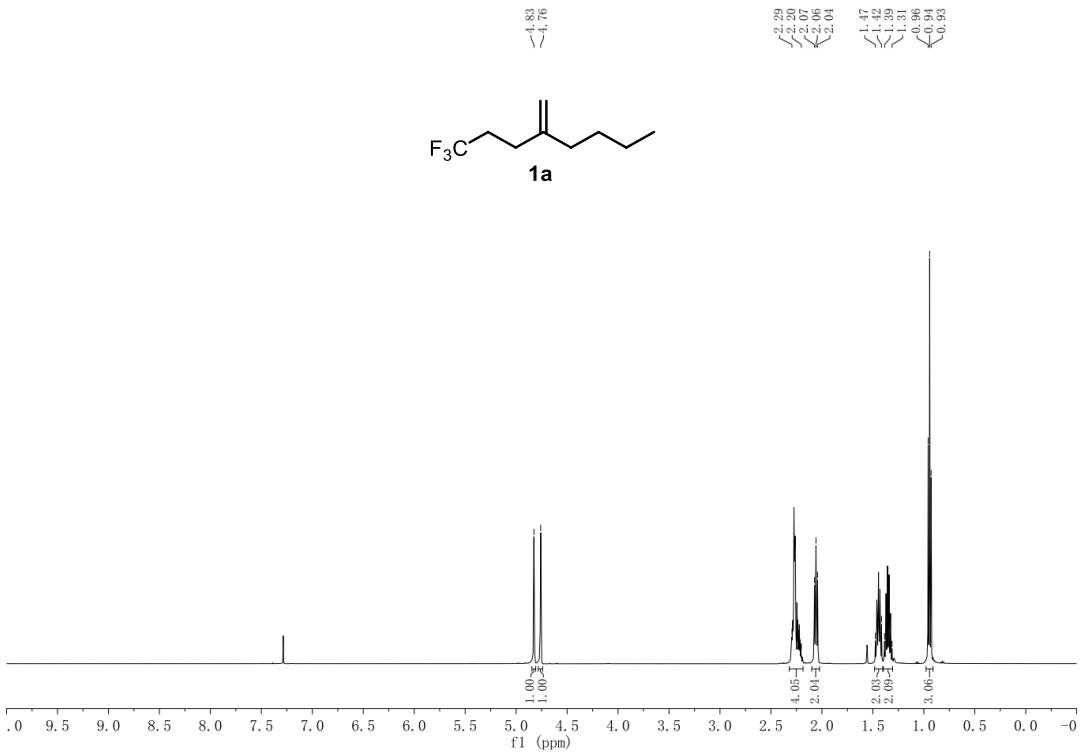


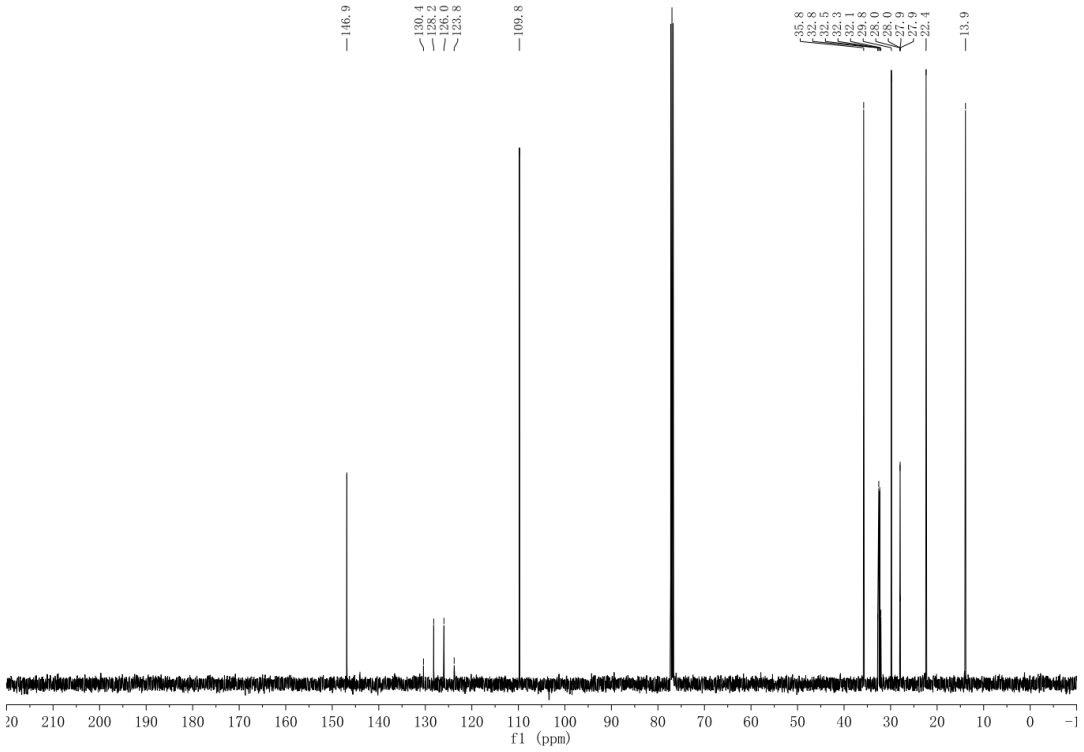

TMS
Ir
I
I
n

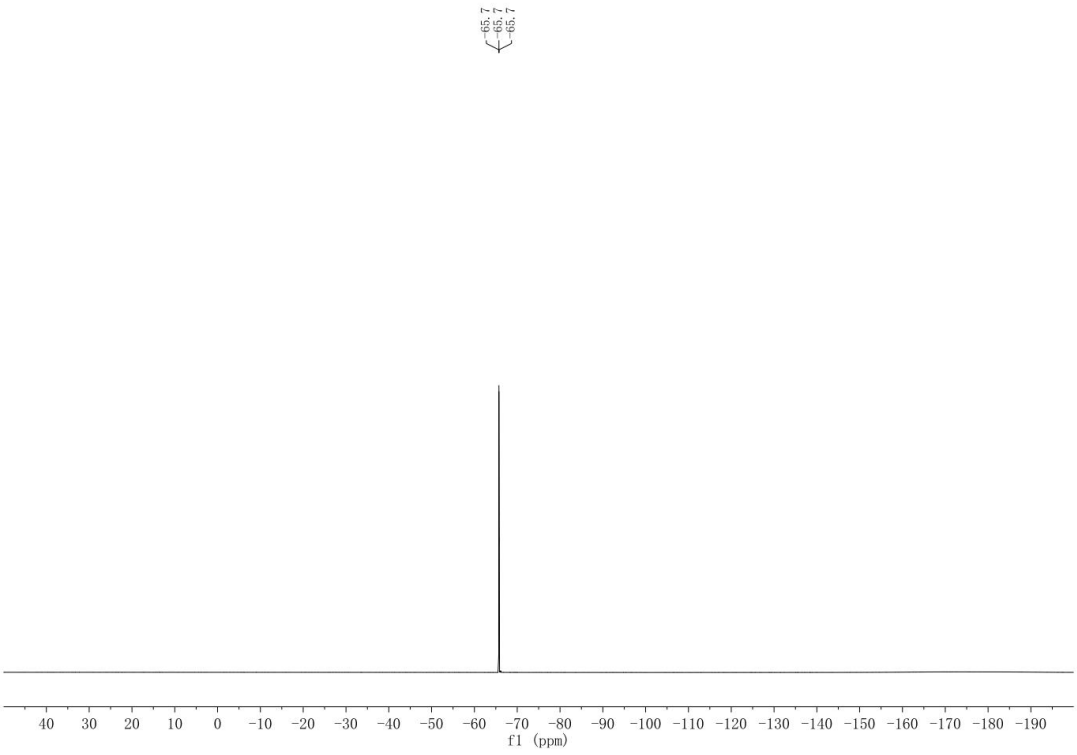
Ir-9

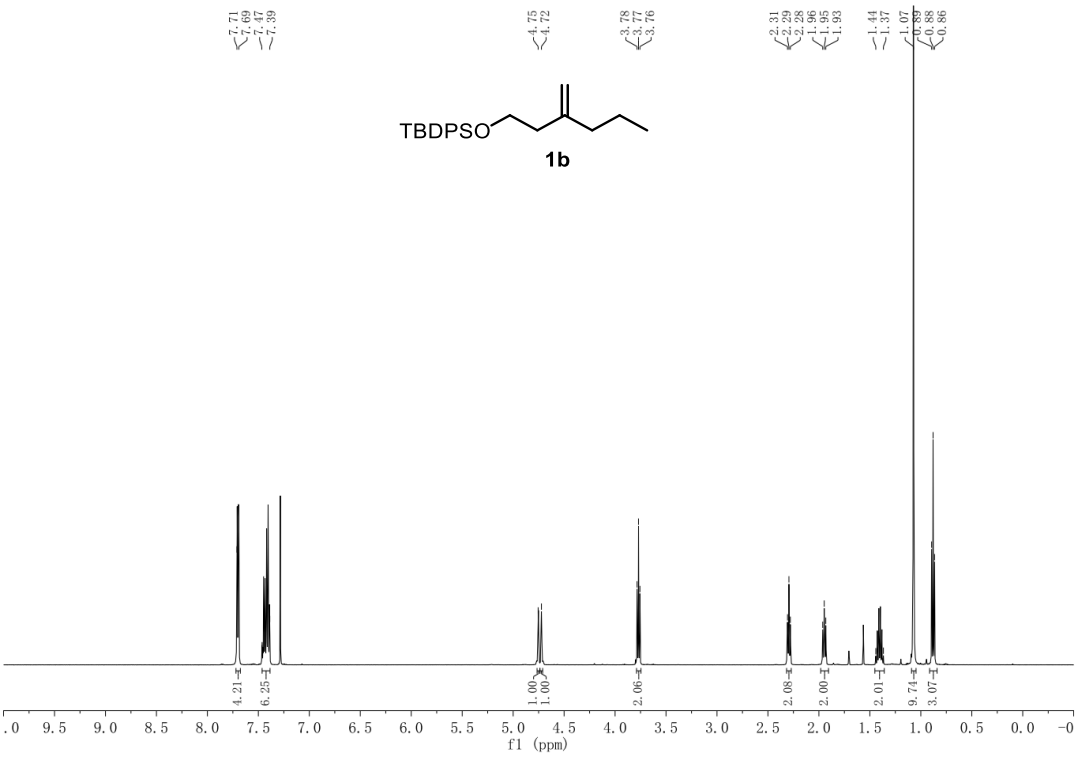

5.58
5.43
1.84
0.08
2.00
2.04
2.08
9.64
f1 (ppm)

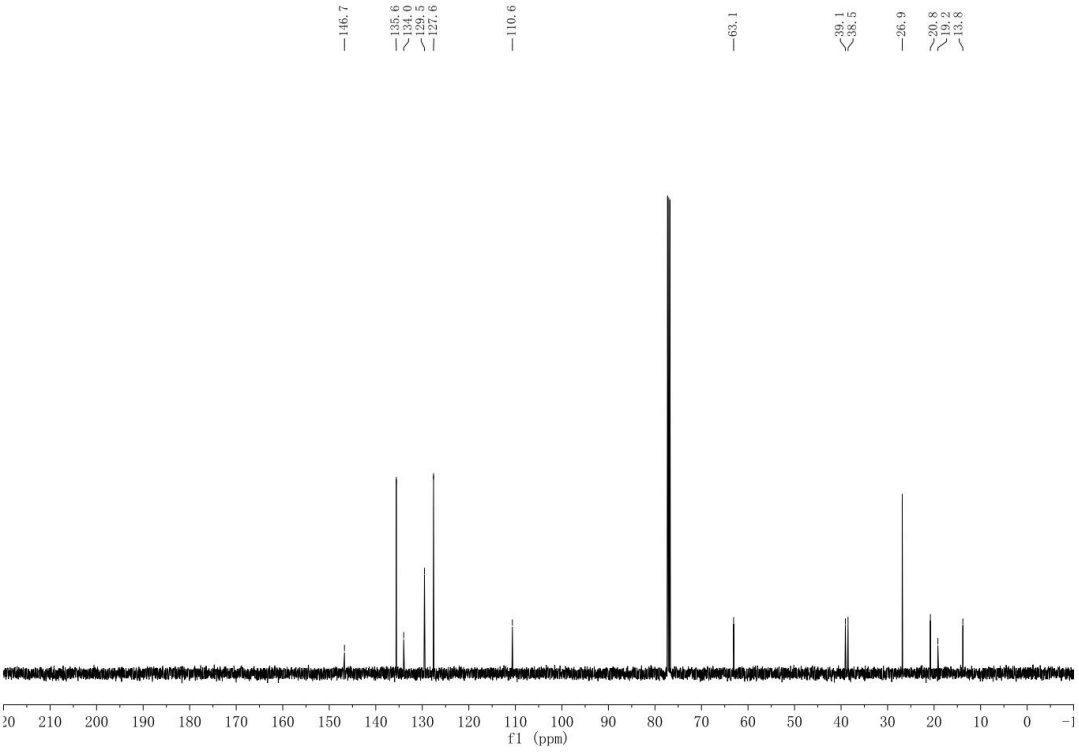

106.9
76.0
73.3
19.7
-1.7
f1 (ppm)

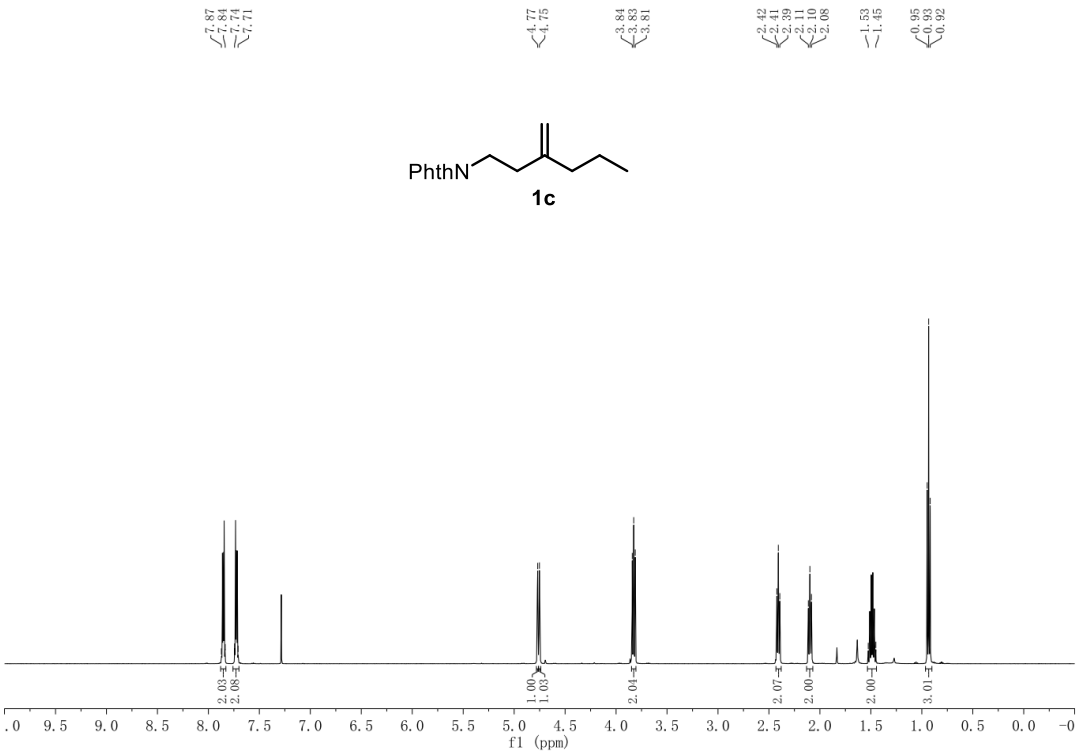

4.83
4.76
2.29
2.20
2.07
2.06
2.04
1.47
1.42
1.39
1.31
0.96
0.94
0.93
F3C
1a
1.00
1.00
4.05
2.04
2.03
2.09
3.06
f1 (ppm)

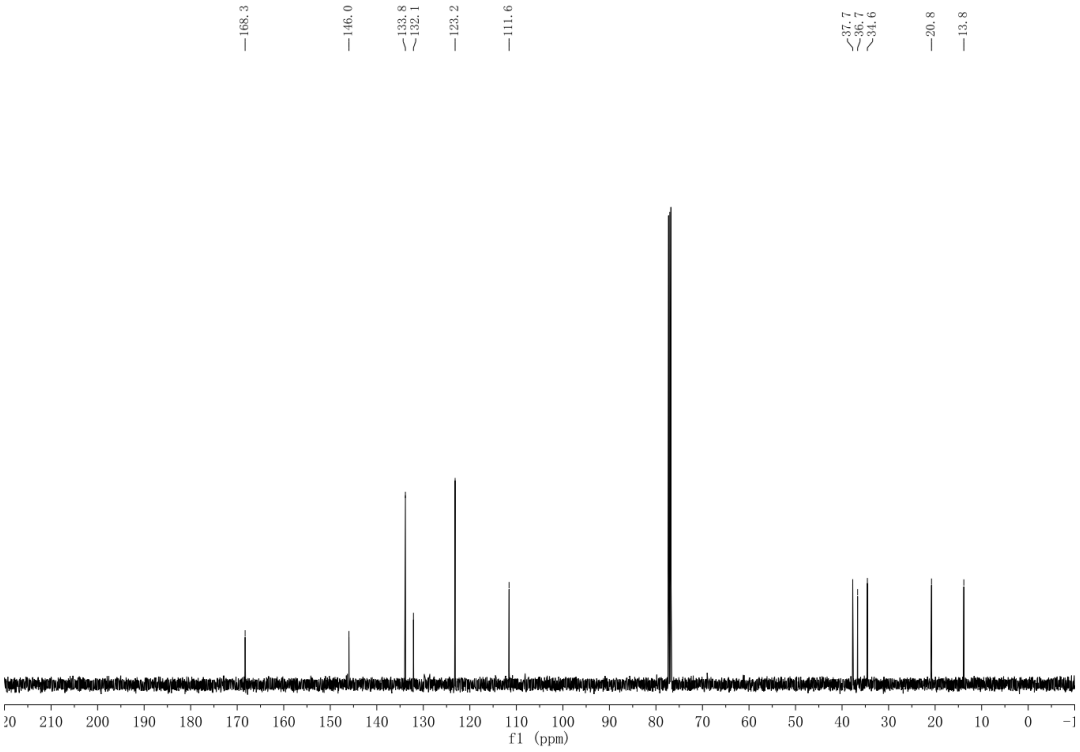

146.9
130.4
128.2
126.0
123.8
109.8
35.8
32.8
32.5
32.3
32.1
29.8
28.0
28.0
27.9
27.9
22.4
13.9
f1 (ppm)

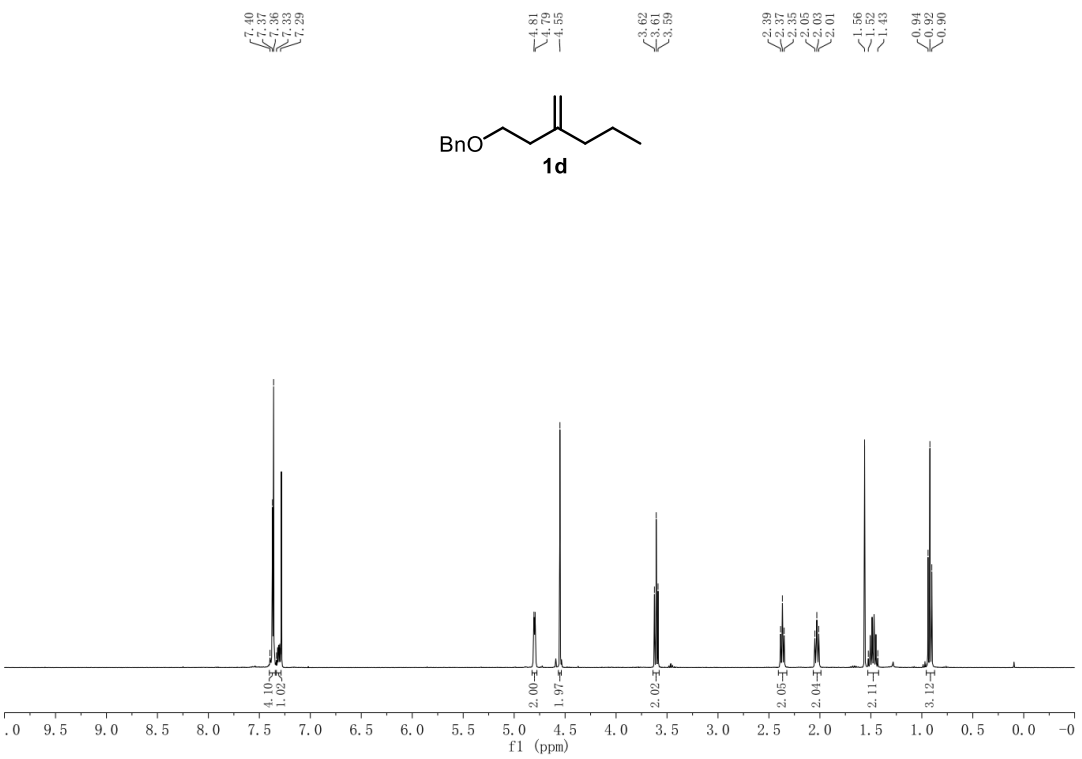

-65.7
-65.7
-65.7
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

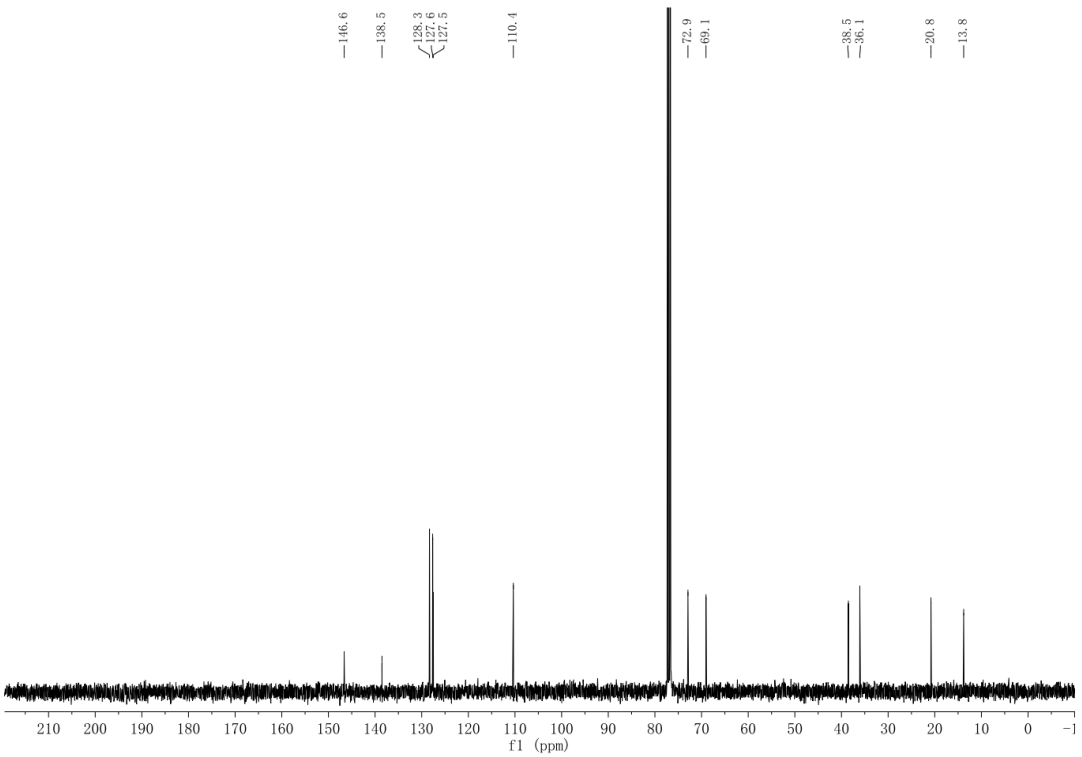

7.71
7.69
7.47
7.39
4.75
4.72
3.78
3.77
3.76
2.31
2.29
2.28
1.96
1.95
1.93
1.44
1.37
1.07
0.89
0.88
0.86
TBDPSO
1b
4.21
6.25
1.00
1.00
2.06
2.08
2.00
2.01
9.74
3.07
f1 (ppm)

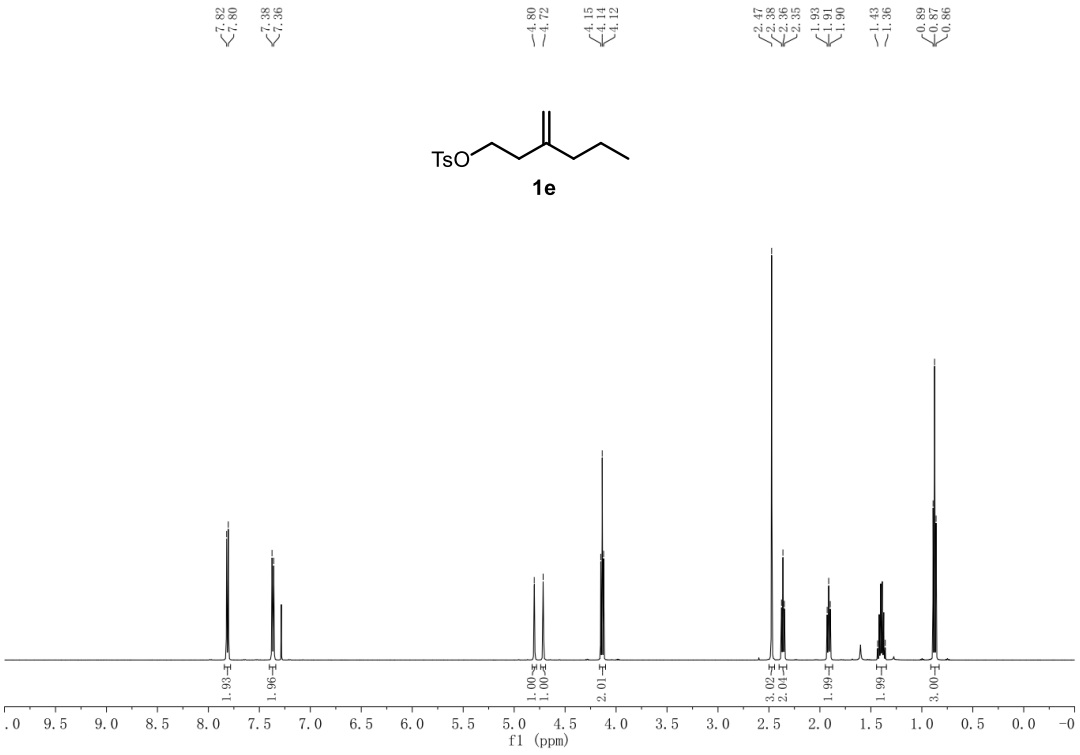

146.7
135.6
134.0
129.5
127.6
110.6
63.1
39.1
38.5
26.9
20.8
19.2
13.8
f1 (ppm)

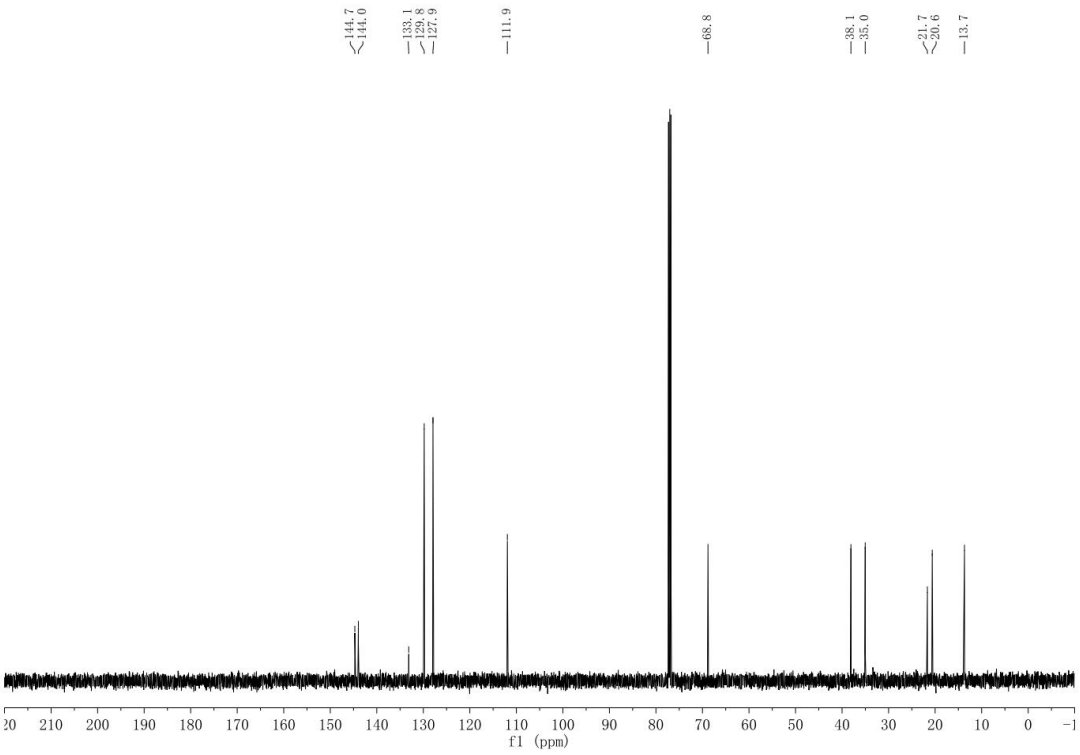

7.87
7.84
7.74
7.71
4.77
4.75
3.84
3.83
3.81
2.42
2.41
2.39
2.11
2.10
2.08
1.53
1.45
0.95
0.93
0.92
PhthN
1c
2.03
2.08
1.00
1.03
2.04
2.07
2.00
2.00
3.01
f1 (ppm)

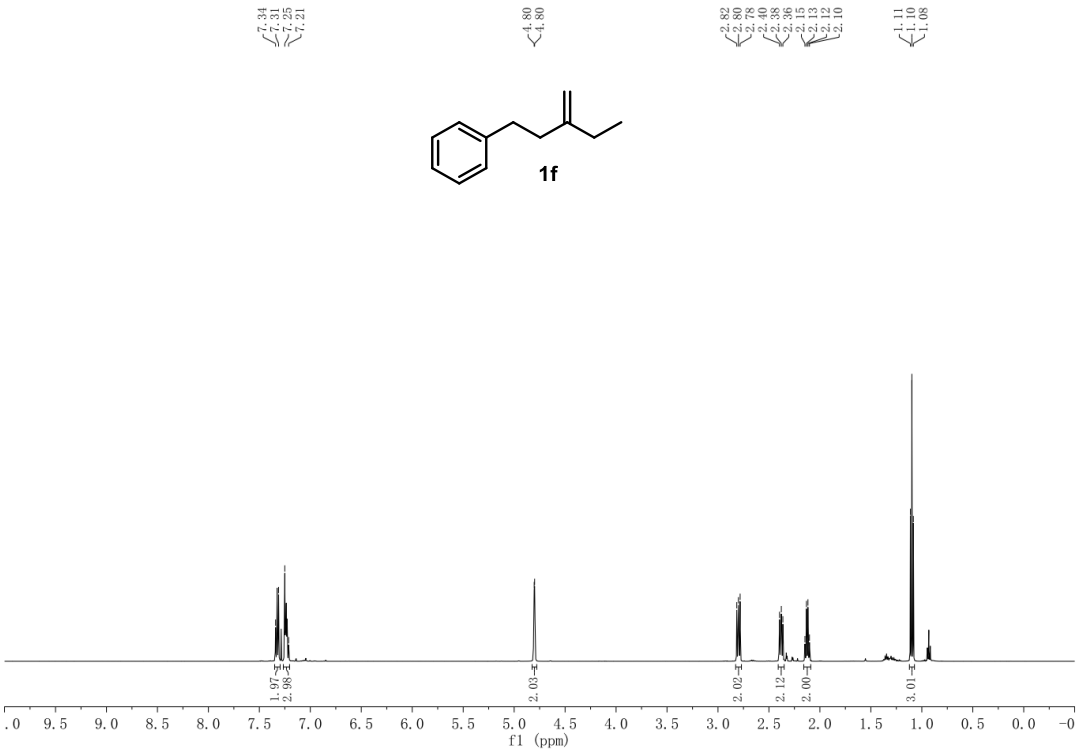

168.3
146.0
133.8
132.1
123.2
111.6
37.7
36.7
34.6
20.8
13.8
f1 (ppm)

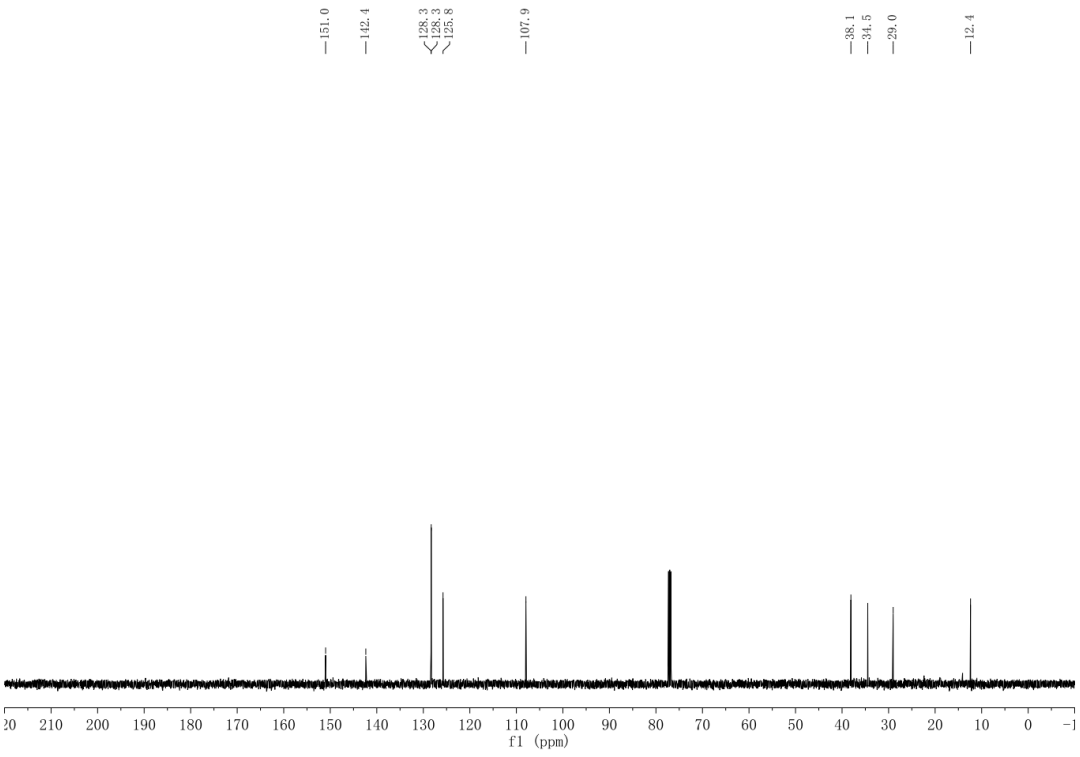

7.40
7.37
7.36
7.33
7.29
4.81
4.79
4.55
3.62
3.61
3.59
2.39
2.37
2.35
2.05
2.03
2.01
1.56
1.52
1.43
0.94
0.92
0.90
BnO
1d
4.10
1.02
2.00
1.97
2.02
2.05
2.04
2.11
3.12
f1 (ppm)

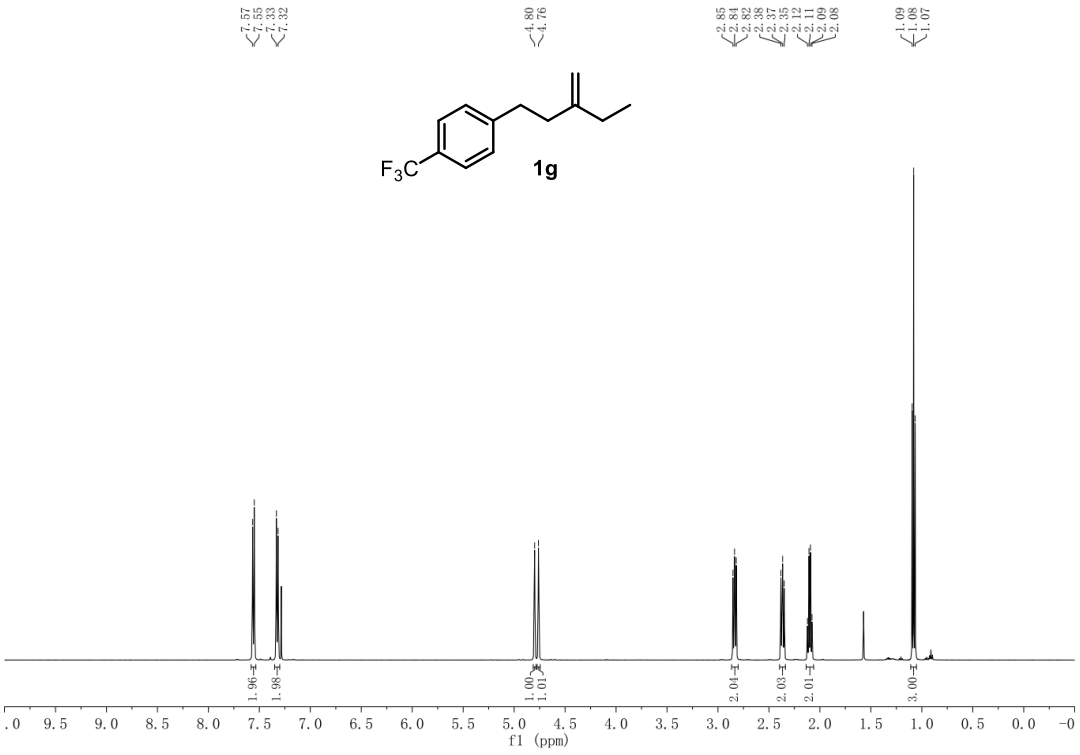

146.6
138.5
128.3
127.6
127.5
110.4
72.9
69.1
38.5
36.1
20.8
13.8
f1 (ppm)

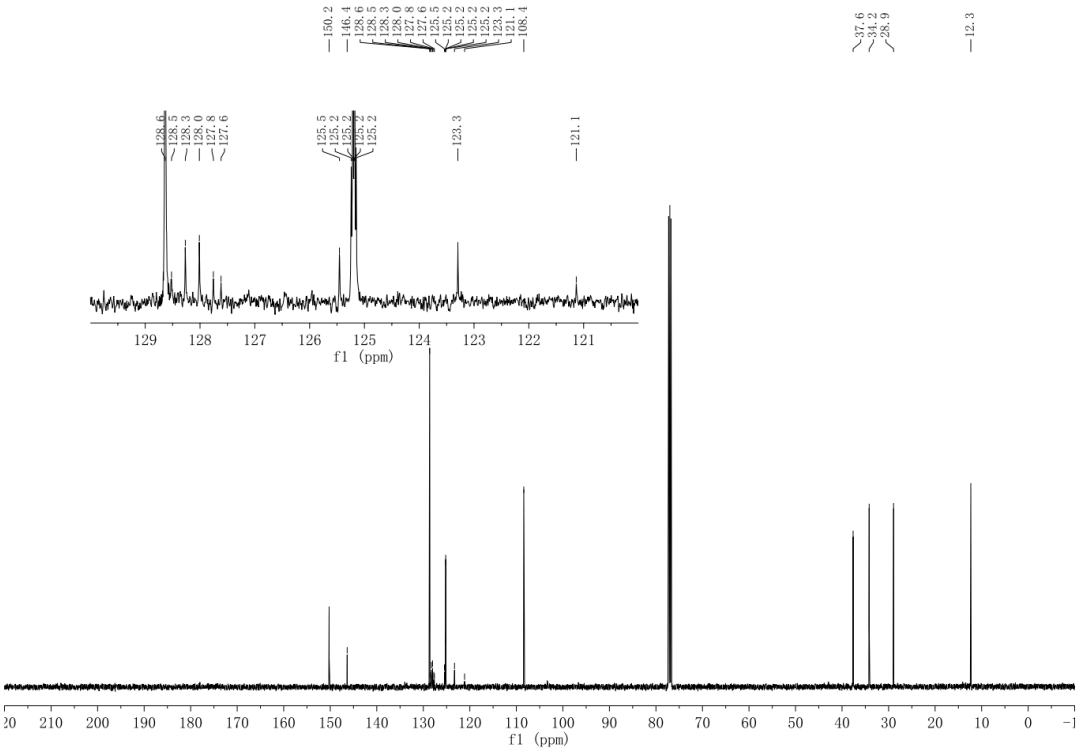

7.82
7.80
7.38
7.36
4.80
4.72
4.15
4.14
4.12
2.47
2.38
2.36
2.35
1.93
1.91
1.90
1.43
1.36
0.89
0.87
0.86
TsO
1e
1.93
1.96
1.00
1.00
2.01
3.02
2.04
1.99
1.99
3.00
f1 (ppm)

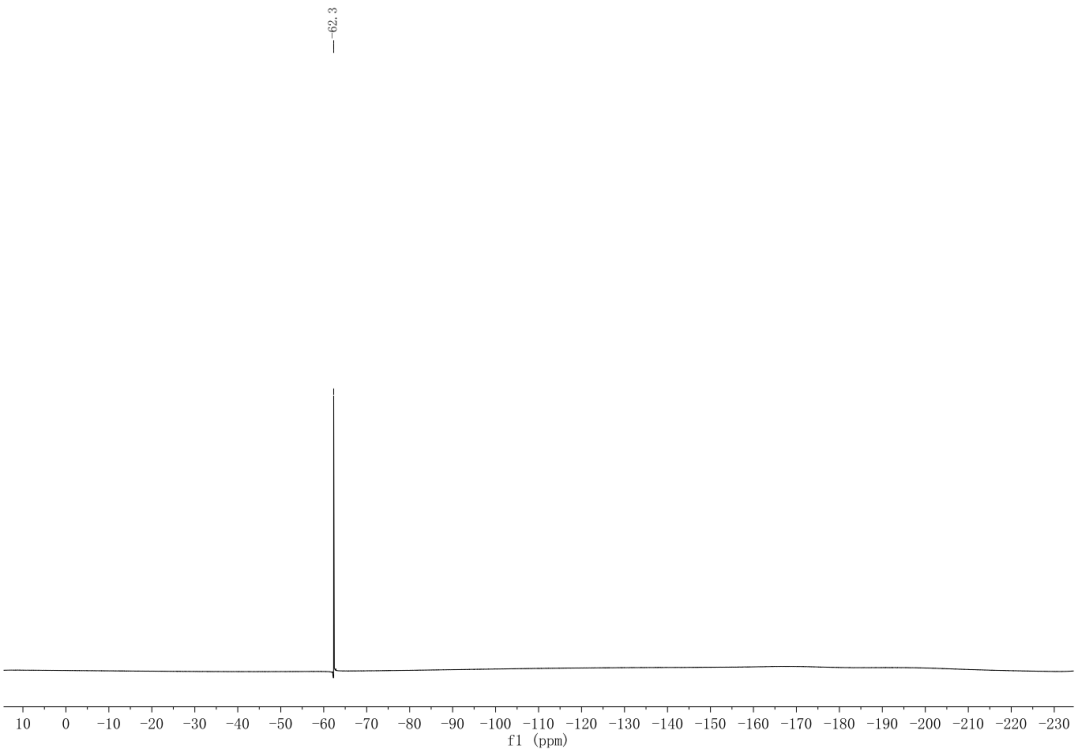

144.7
144.0
133.1
129.8
127.9
111.9
68.8
38.1
35.0
21.7
20.6
13.7
f1 (ppm)

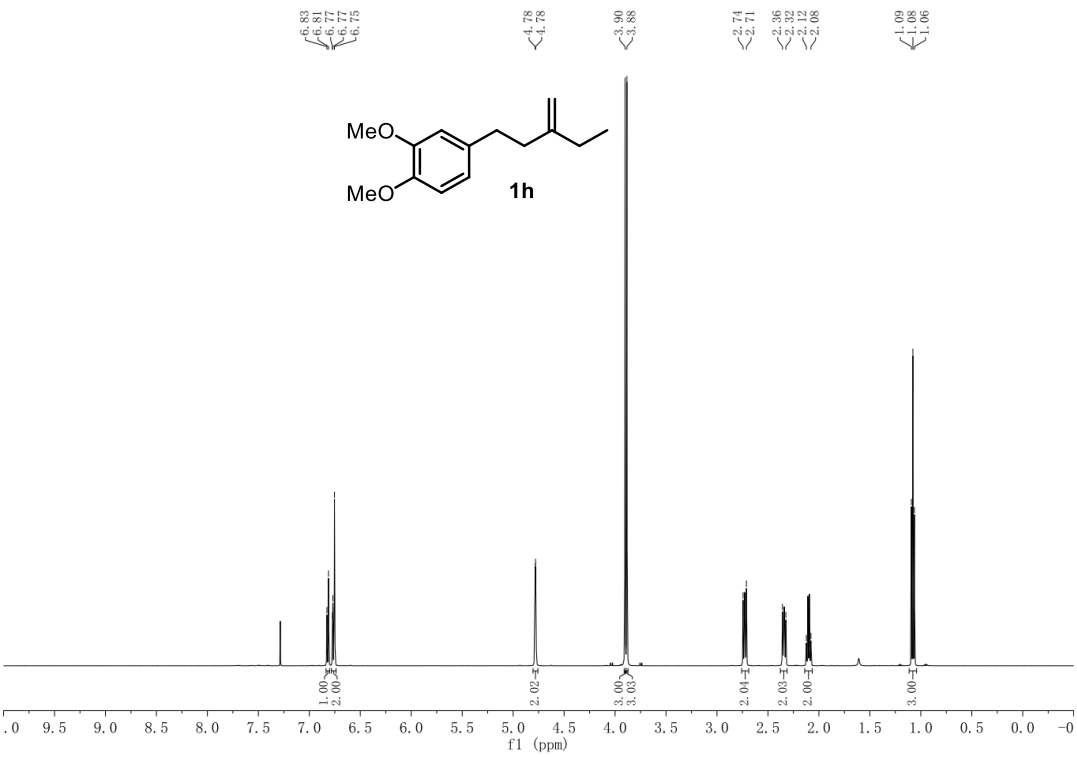

7.34
7.31
7.25
7.21
4.80
4.80
2.82
2.80
2.78
2.40
2.38
2.36
2.15
2.13
2.12
2.10
1.11
1.10
1.08
1f
1.97
2.98
2.03
2.02
2.12
2.00
3.01
f1 (ppm)

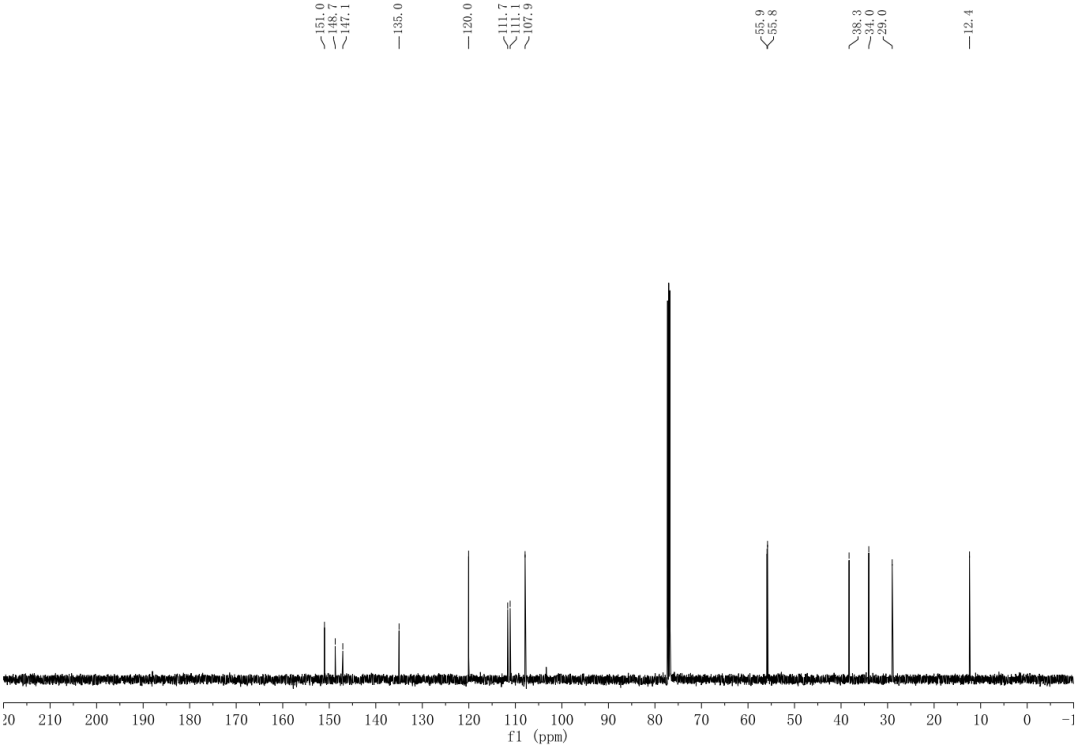

151.0
142.4
128.3
128.3
125.8
107.9
38.1
34.5
29.0
12.4
f1 (ppm)

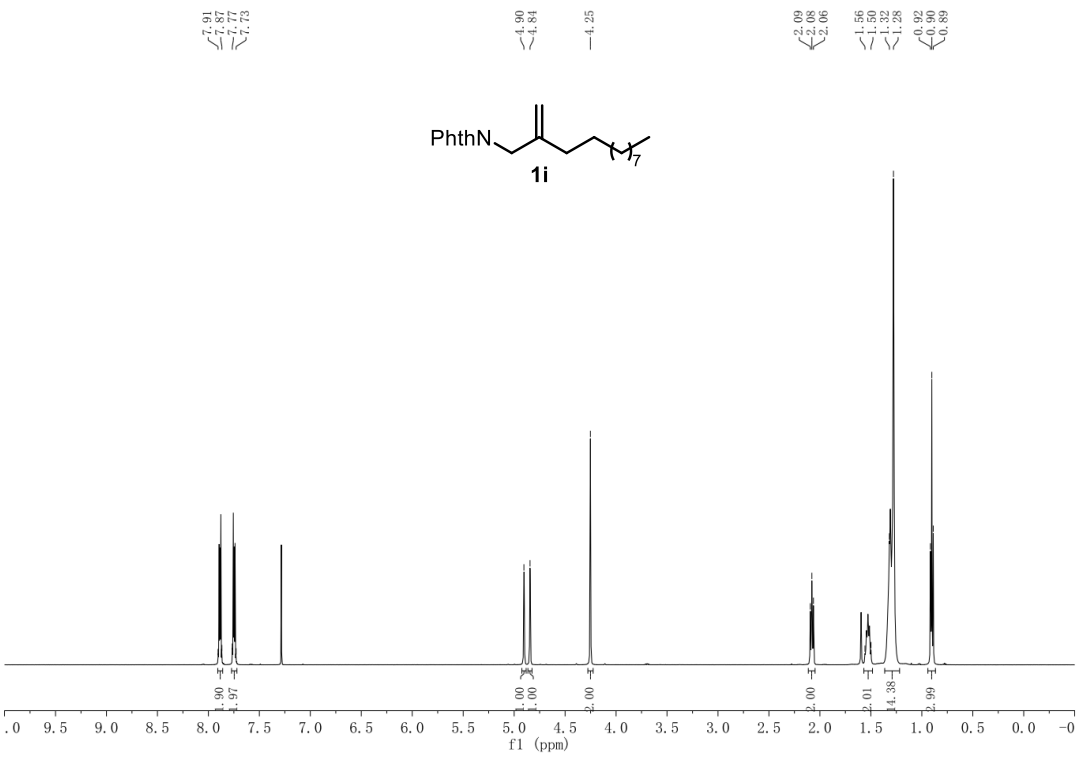

7.57
7.55
7.33
7.32
4.80
4.76
2.85
2.84
2.82
2.38
2.37
2.35
2.12
2.11
2.09
2.08
1.09
1.08
1.07
F3C
1g
1.96
1.98
1.00
1.01
2.04
2.03
2.01
3.00
f1 (ppm)

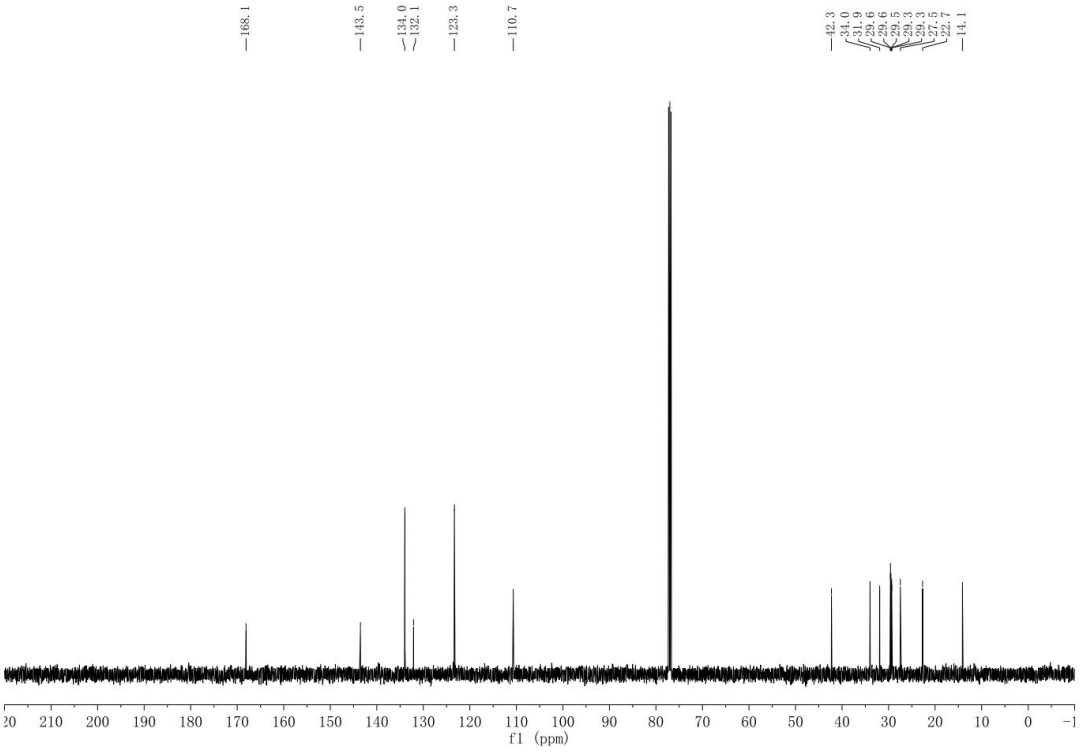

150.2
146.4
128.6
128.5
128.3
128.0
127.8
127.6
125.5
125.2
125.2
125.2
123.3
121.1
108.4
37.6
34.2
28.9
12.3
123.3
121.1
f1 (ppm)

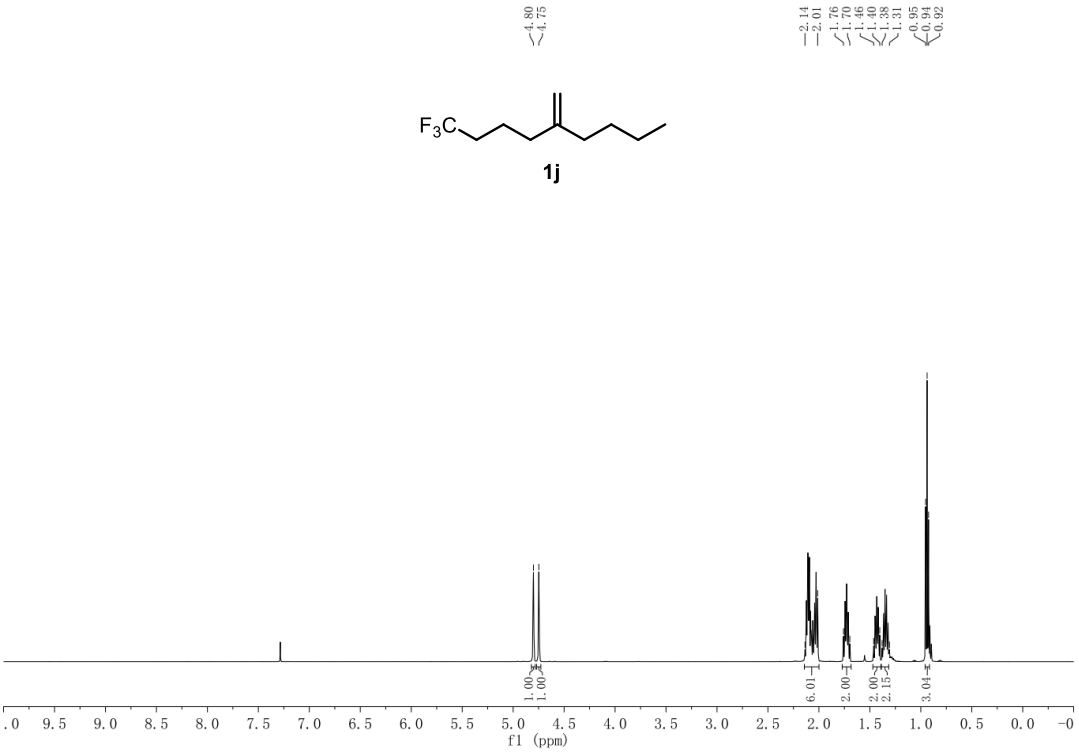

−62.3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230
f1 (ppm)

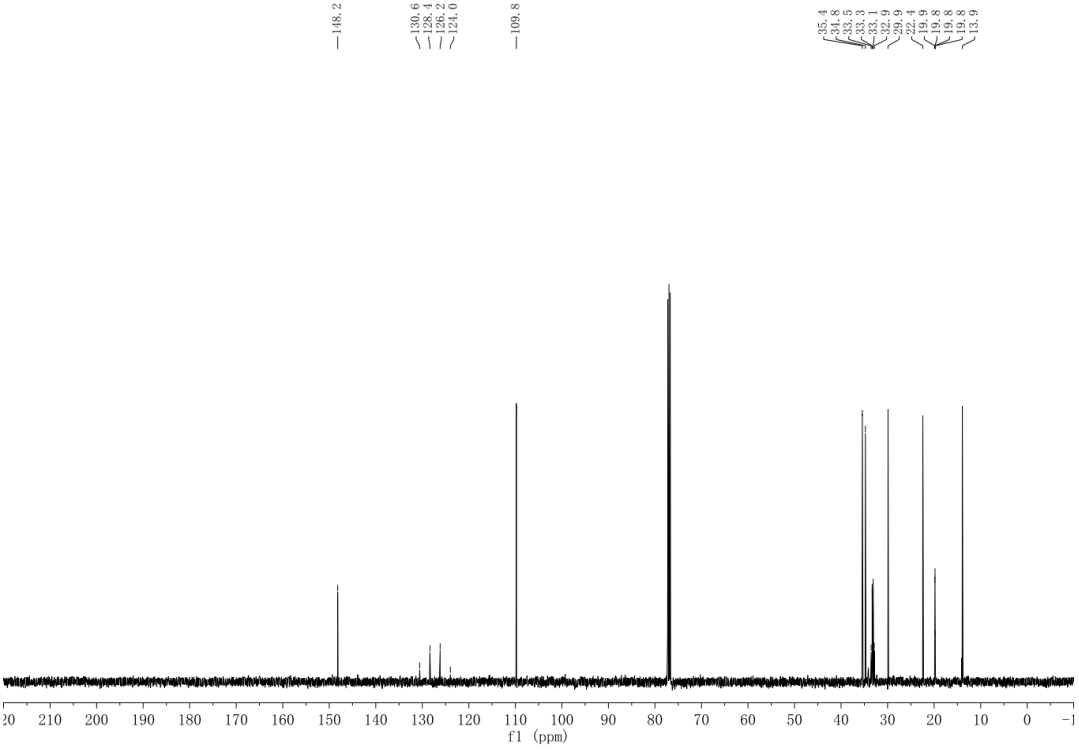

6.83
6.81
6.77
6.77
6.75
4.78
4.78
3.90
3.88
2.74
2.71
2.36
2.32
2.12
2.08
1.09
1.08
1.06
MeO
MeO
1h
1.00
2.00
2.02
3.00
3.03
2.04
2.03
2.00
3.00
f1 (ppm)

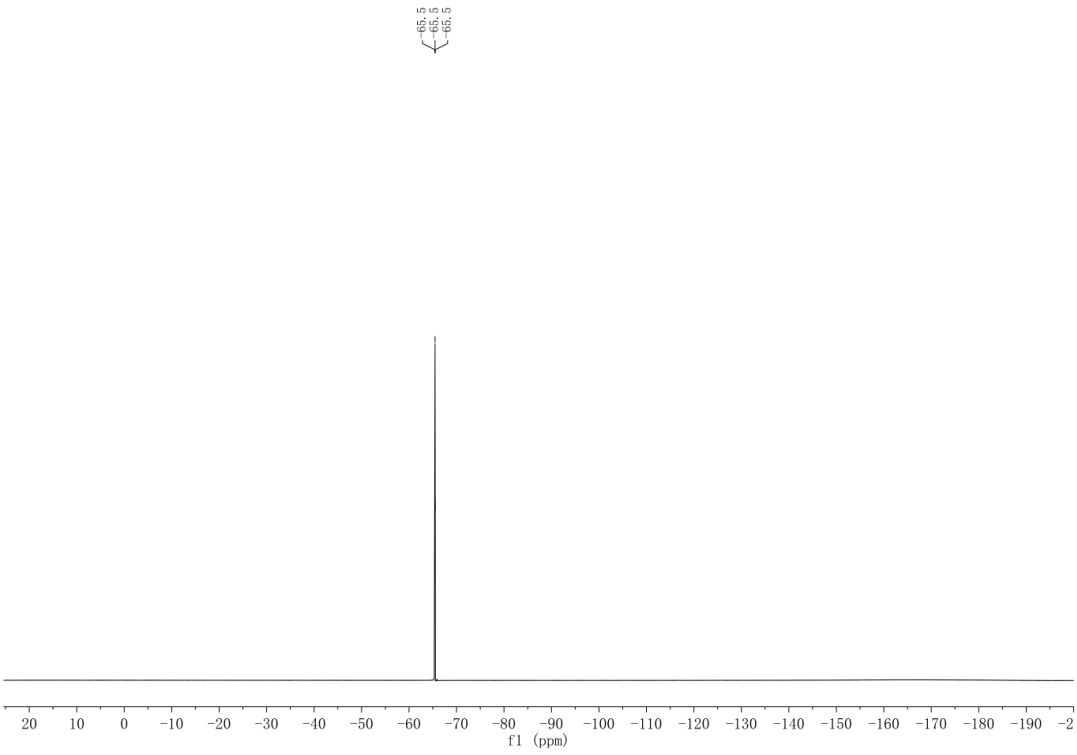

151.0
148.7
147.1
135.0
120.0
111.7
111.1
107.9
55.9
55.8
38.3
34.0
29.0
12.4
f1 (ppm)

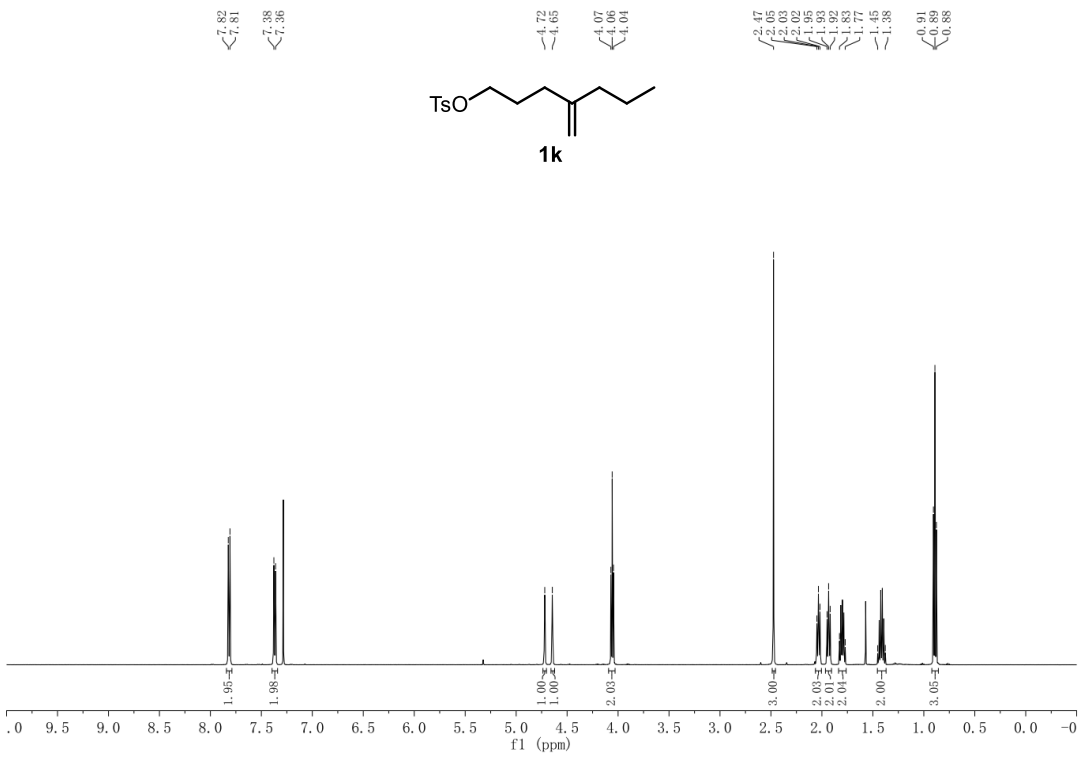

7.91
7.87
7.77
7.73
4.90
4.84
4.25
2.09
2.08
2.06
1.56
1.50
1.32
1.28
0.92
0.90
0.89
PhthN
7
1i
1.90
1.97
1.00
1.00
2.00
2.00
2.01
14.38
2.99
f1 (ppm)

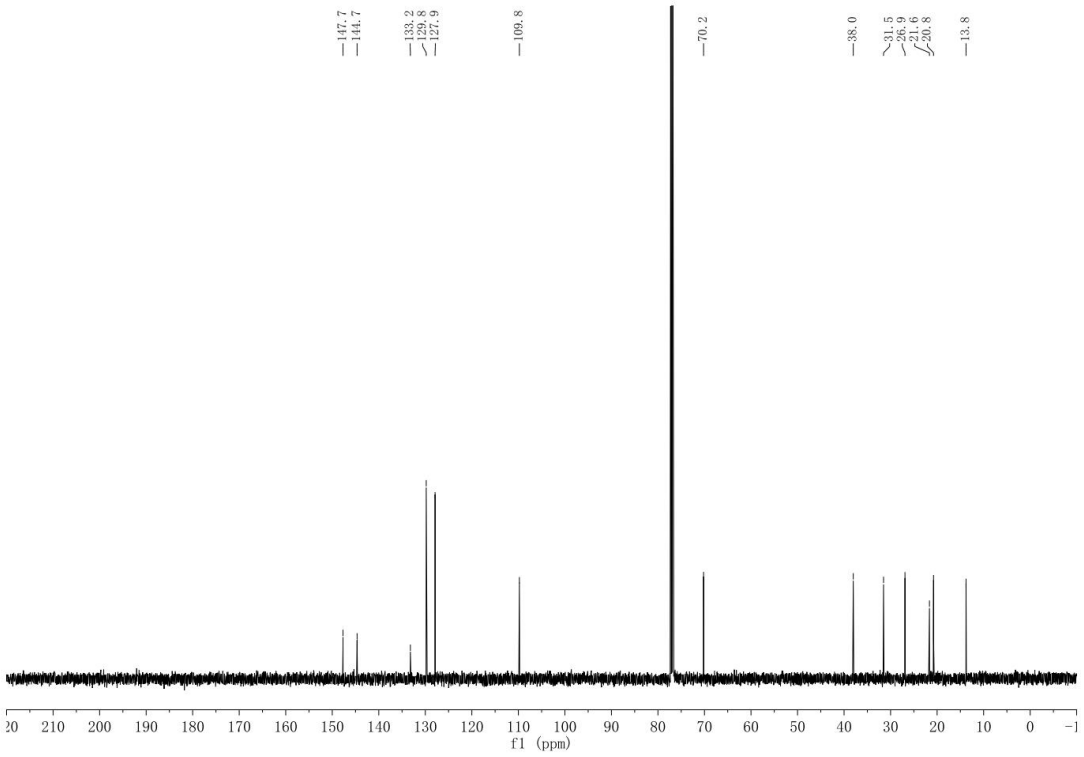

168.1
143.5
134.0
132.1
123.3
110.7
42.3
34.0
31.9
29.6
29.6
29.5
29.3
28.3
27.5
22.7
14.1
f1 (ppm)

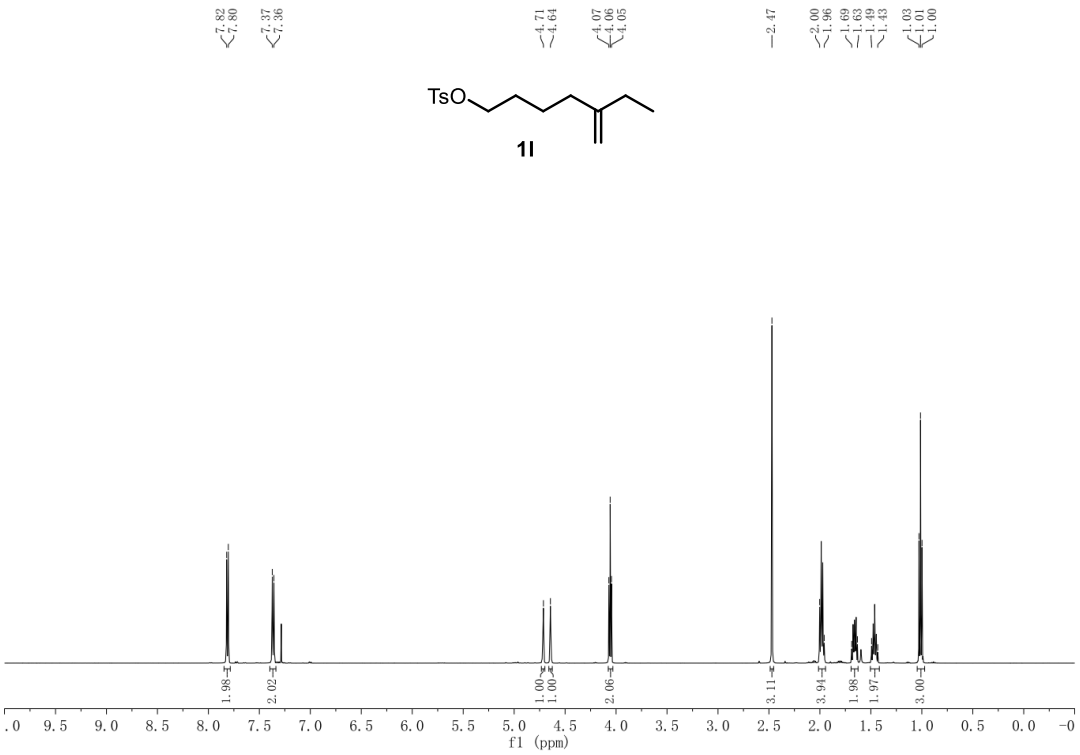

4.80
4.75
2.14
2.01
1.76
1.70
1.46
1.40
1.38
1.31
0.95
0.94
0.92
F3C
1j
1.00
1.00
6.01
2.00
2.00
2.15
3.04
f1 (ppm)


148.2
130.6
128.4
126.2
124.0
109.8
35.4
34.8
33.5
33.3
33.1
32.9
29.9
22.4
19.9
19.8
19.8
19.8
13.9
f1 (ppm)

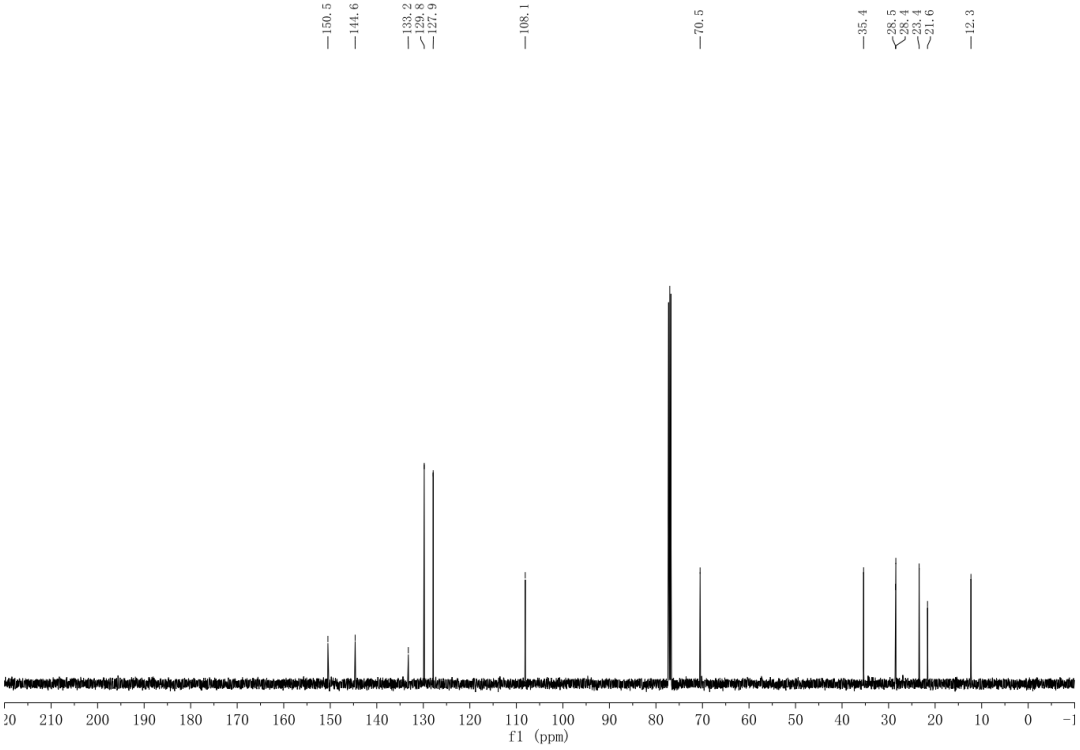

-65.5
-65.5
-65.5
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


7.82
7.81
7.38
7.36
4.72
4.65
4.07
4.06
4.04
2.47
2.05
2.03
2.02
1.95
1.93
1.92
1.83
1.77
1.45
1.38
0.91
0.89
0.88
TsO
1k
1.95
1.98
1.00
1.00
2.03
3.00
2.03
2.01
2.04
2.00
3.05
f1 (ppm)


147.7
144.7
133.2
129.8
127.9
109.8
70.2
38.0
31.5
26.9
21.6
20.8
13.8
f1 (ppm)


7.82
7.80
7.37
7.36
4.71
4.64
4.07
4.06
4.05
2.47
2.00
1.96
1.69
1.63
1.49
1.43
1.03
1.01
1.00
TsO
1.98
2.02
1.00
1.00
2.06
3.11
3.94
1.98
1.97
3.00
f1 (ppm)

1l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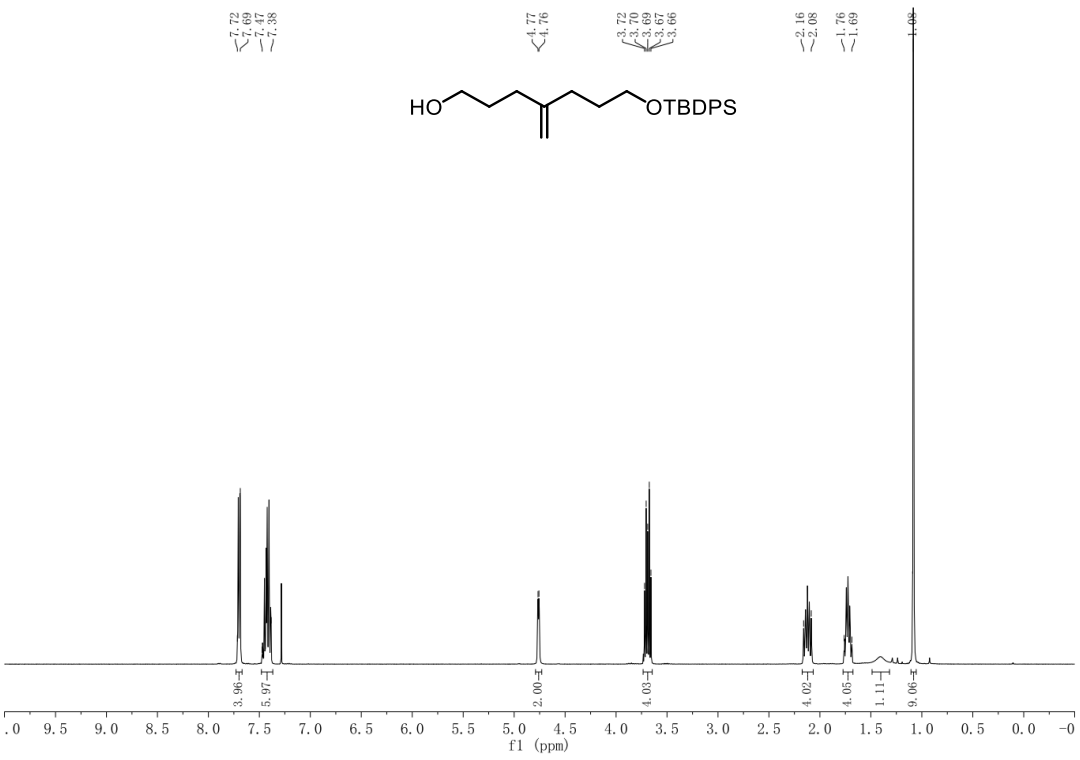
144.6
133.2
129.8
127.9
108.1
70.5
35.4
28.5
28.4
23.4
21.6
12.3
f1 (ppm)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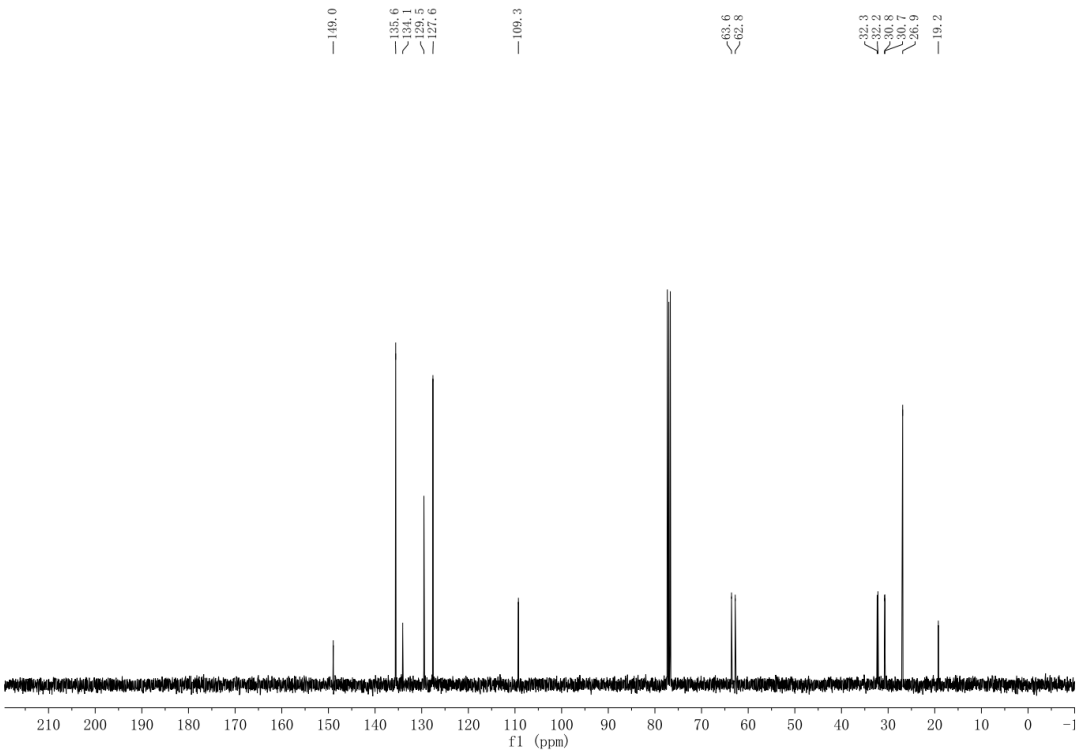
7.69
7.47
7.38
4.77
4.76
3.72
3.70
3.69
3.67
3.66
2.16
2.08
1.76
1.69
1.00
HO
OTBDPS
3.96
5.97
2.00
4.03
4.02
4.05
1.11
9.06
f1 (ppm)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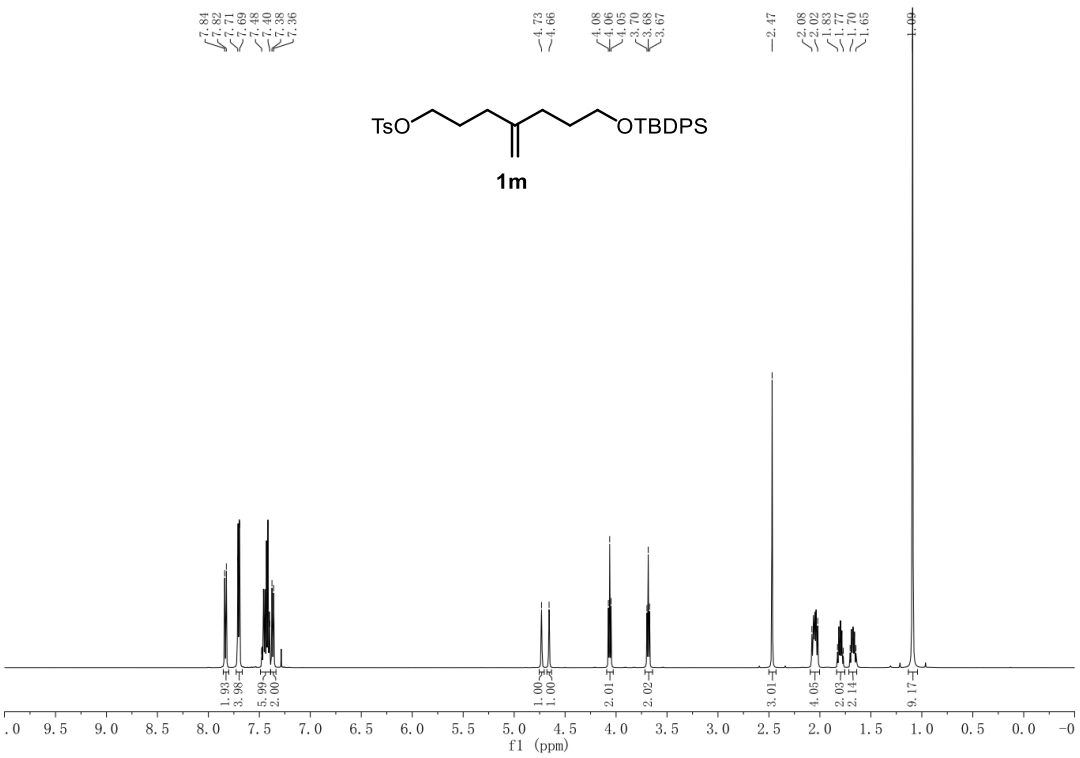
135.6
134.1
129.5
127.6
109.3
63.6
62.8
32.3
32.2
30.8
30.7
26.9
19.2
f1 (ppm)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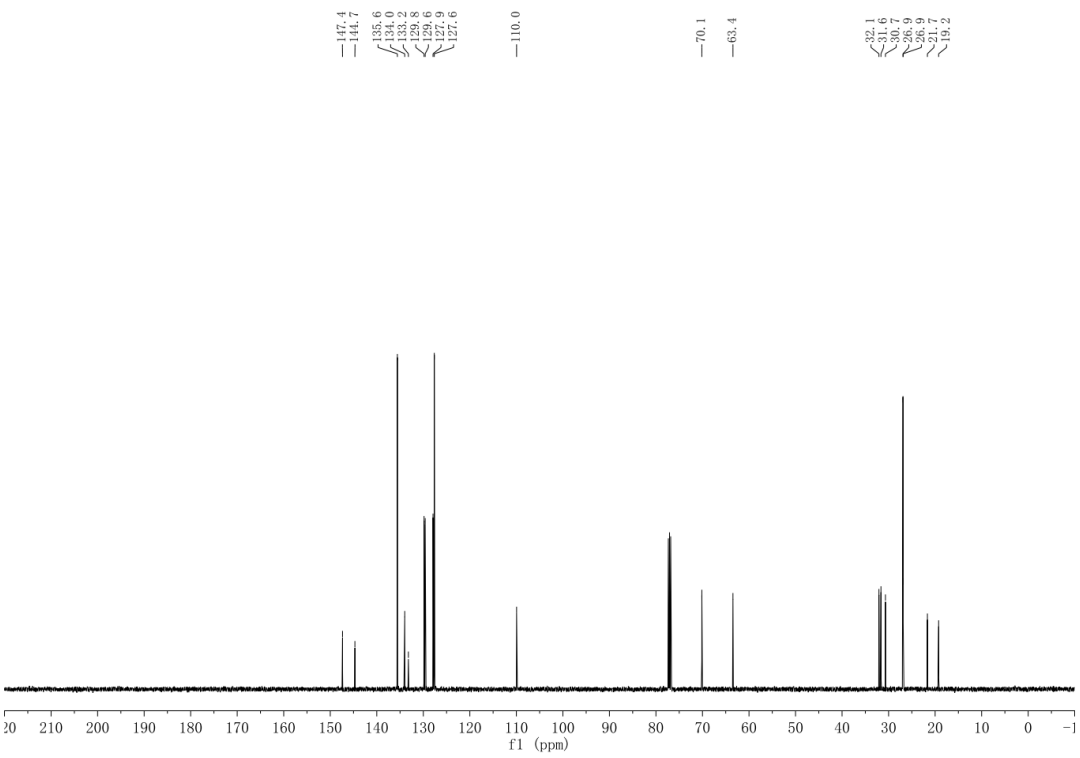
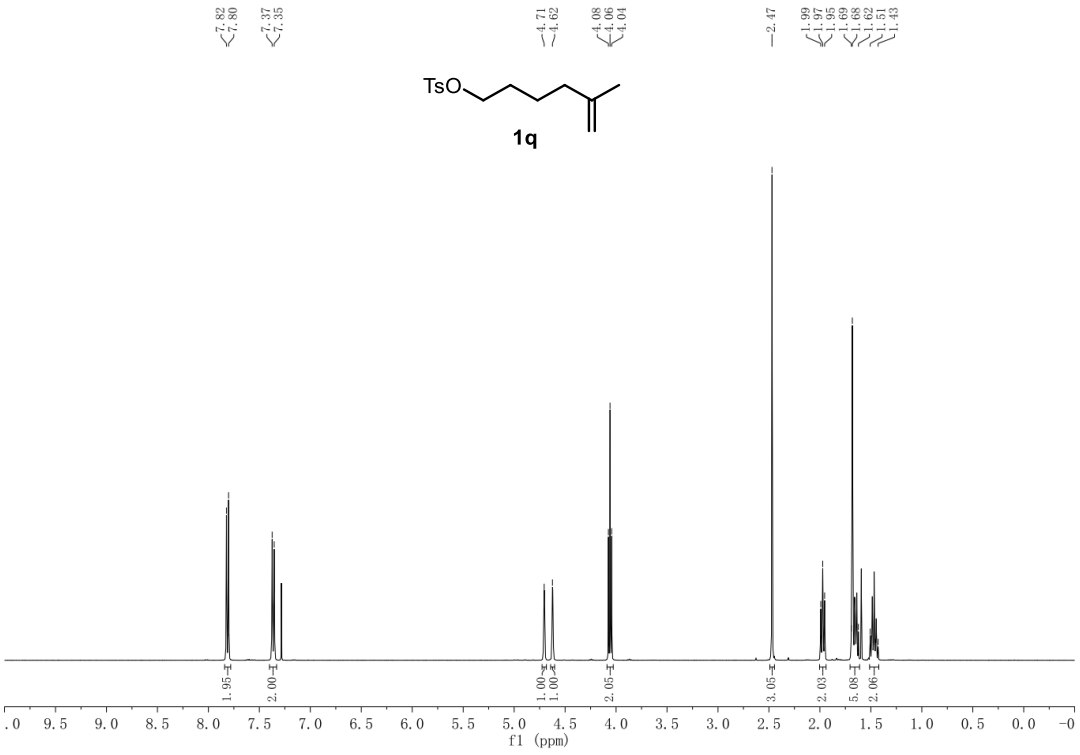
7.40
7.38
7.35
4.73
4.66
4.08
4.06
4.05
3.70
3.68
3.67
2.47
2.08
2.02
1.83
1.77
1.70
1.65
1.00
TsO
OTBDPS
1m
1.93
3.98
5.99
2.00
1.00
1.00
2.01
2.02
3.01
4.05
2.03
2.14
9.17
f1 (ppm)


147.4
144.7
135.6
134.0
133.2
129.8
129.6
127.9
127.6
110.0
70.1
63.4
32.1
31.6
30.7
26.9
26.9
21.7
19.2
f1 (ppm)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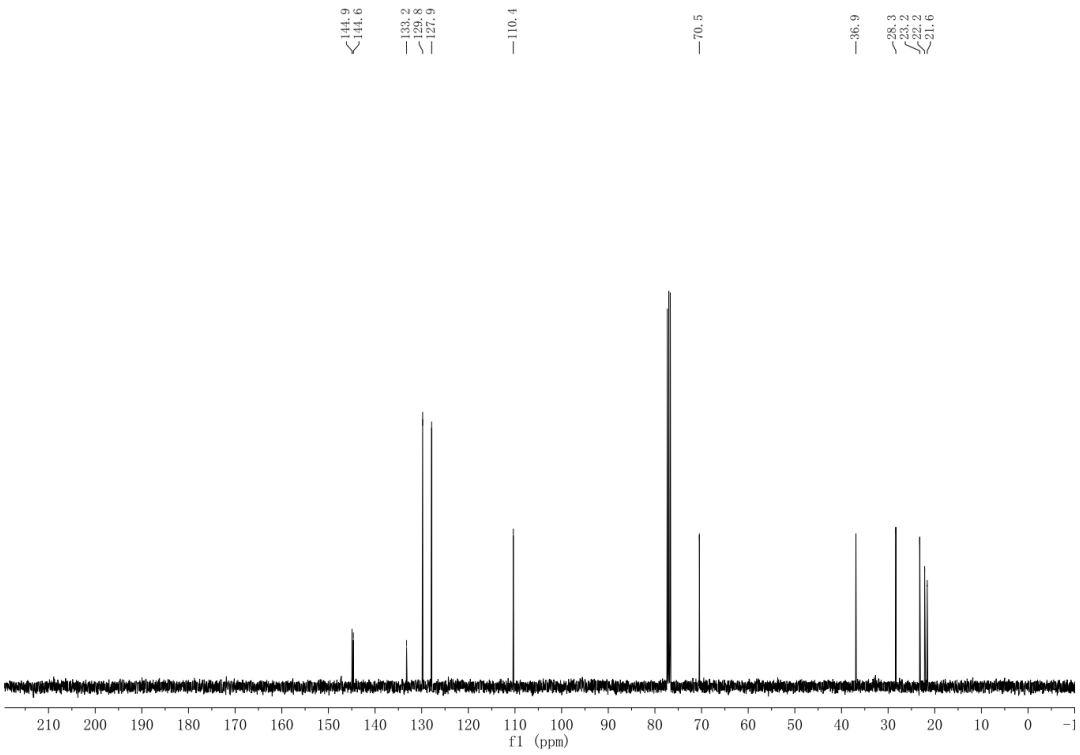
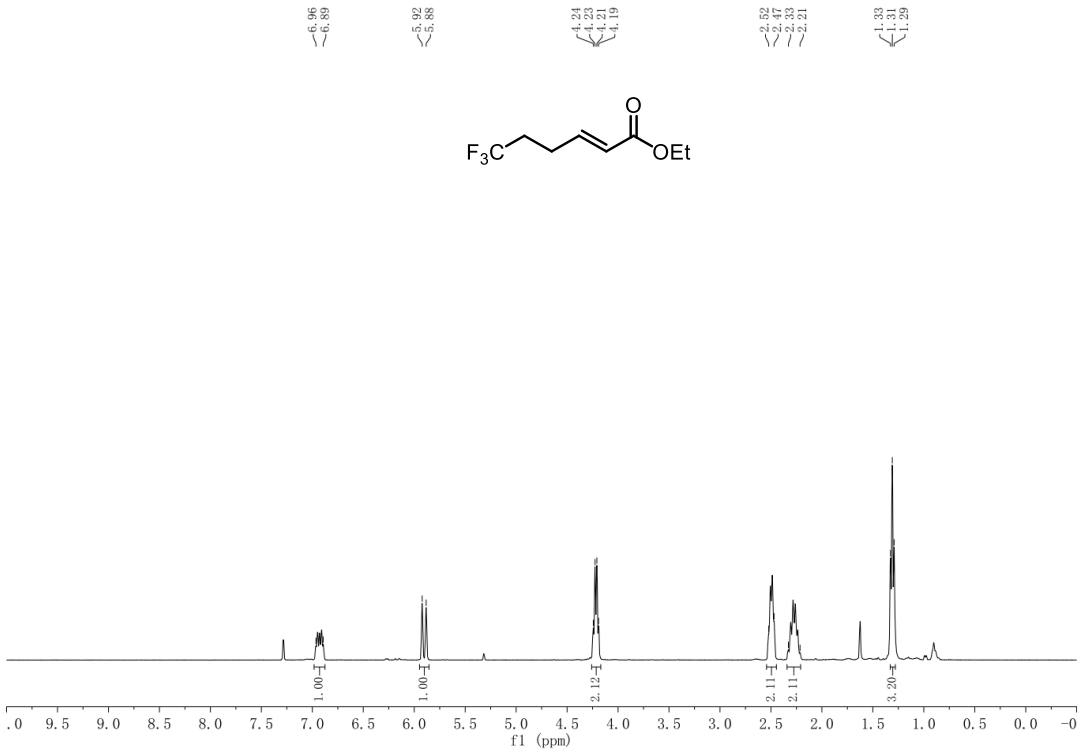
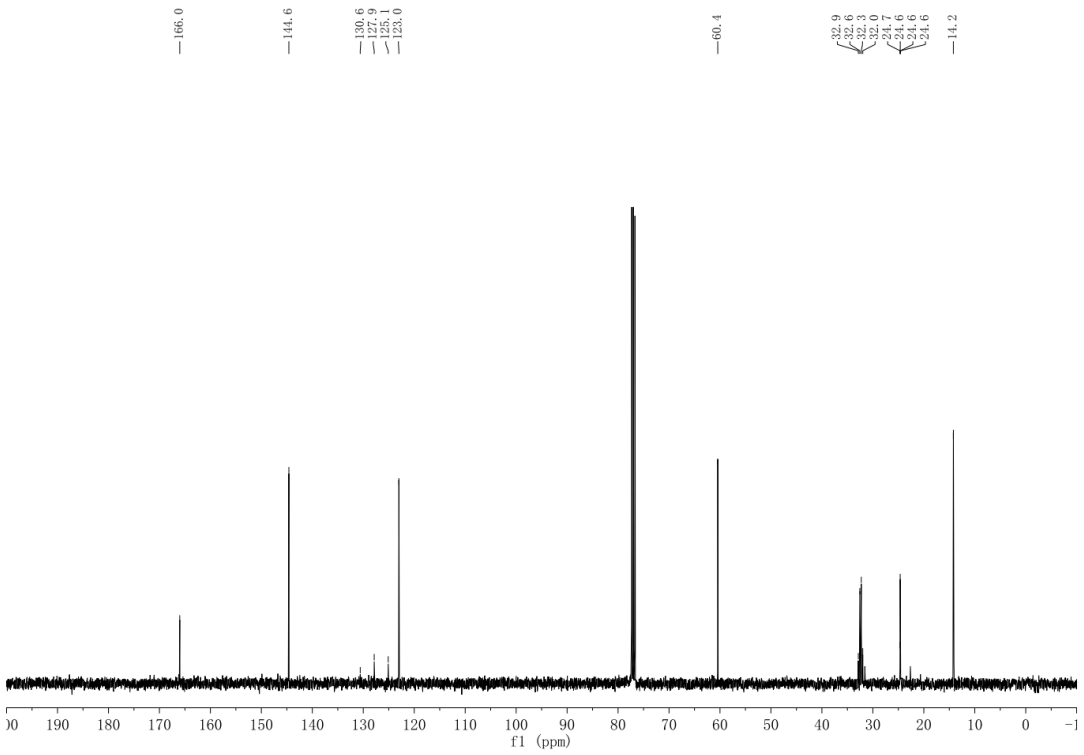
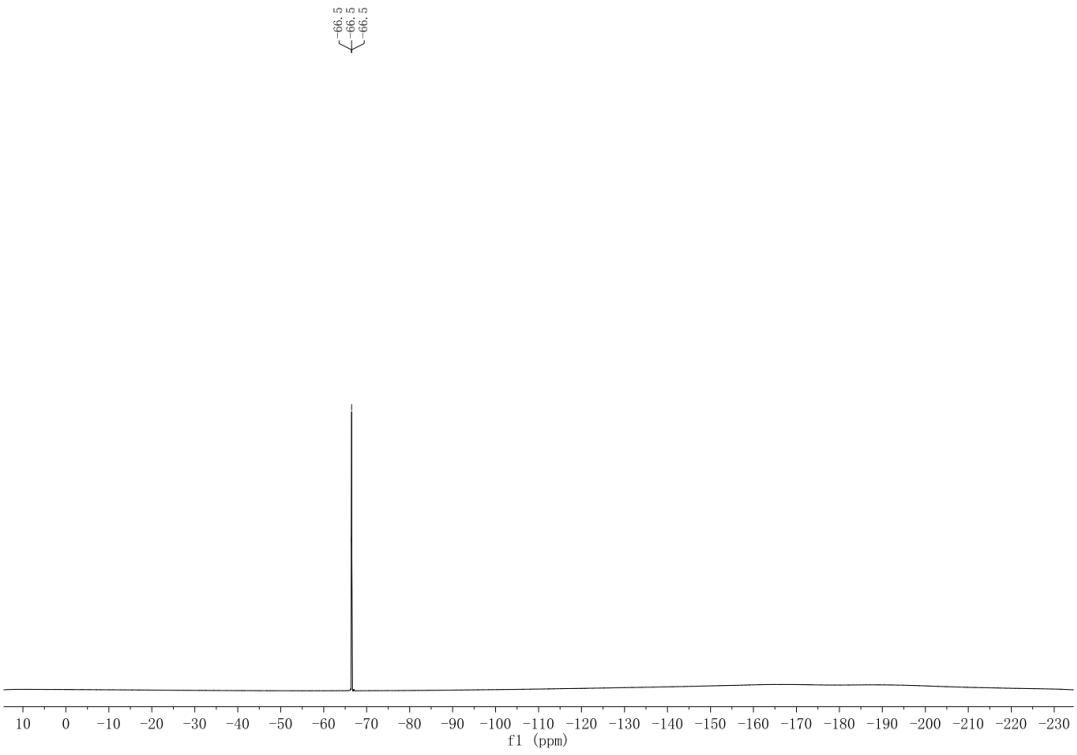
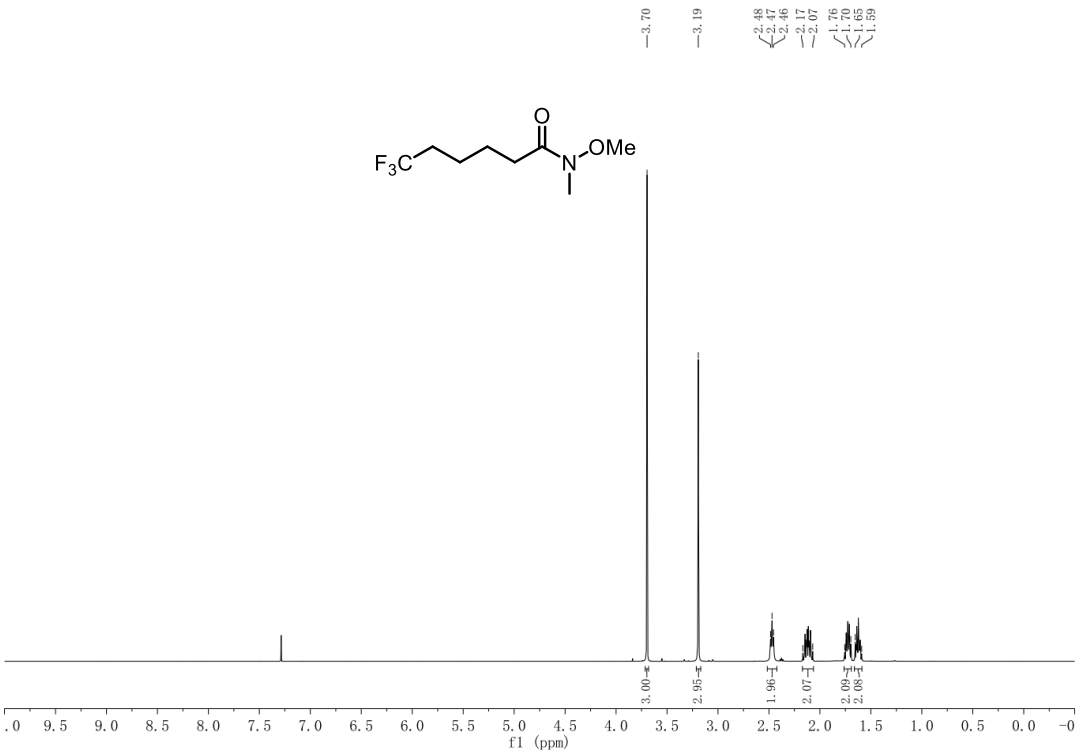
7.80
7.37
7.35
4.71
4.62
4.08
4.06
4.04
2.47
1.99
1.97
1.95
1.69
1.68
1.62
1.51
1.43
TsO
1q
1.95
2.00
1.00
1.00
2.05
3.05
2.03
5.08
2.06
f1 (ppm)


144.9
141.6
133.2
129.8
127.9
110.4
70.5
36.9
28.3
23.2
22.2
21.6
f1 (ppm)


6.96
6.89
5.92
5.88
4.24
4.23
4.21
4.19
2.52
2.47
2.33
2.21
1.33
1.31
1.29
O
F3C
OEt
1.00
1.00
2.12
2.11
2.11
3.20
f1 (ppm)


166.0
144.6
130.6
127.9
125.1
123.0
60.4
32.9
32.6
32.3
32.0
24.7
24.6
24.6
24.6
14.2
f1 (ppm)


-66.5
-66.5
-66.5
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


3.70
3.19
2.48
2.47
2.46
2.17
2.07
1.76
1.70
1.65
1.59
O
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N
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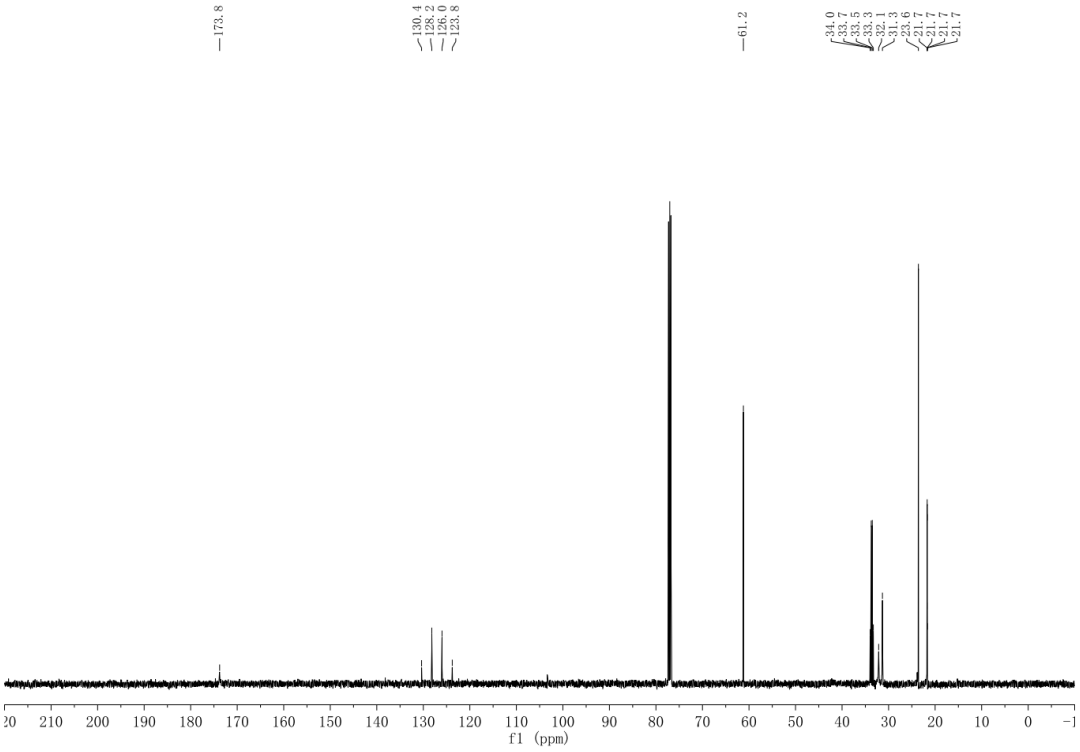
1.96
2.07
2.09
2.08
f1 (ppm)


173.8
130.4
128.2
126.0
123.8
61.2
34.0
33.7
33.5
33.3
32.1
31.3
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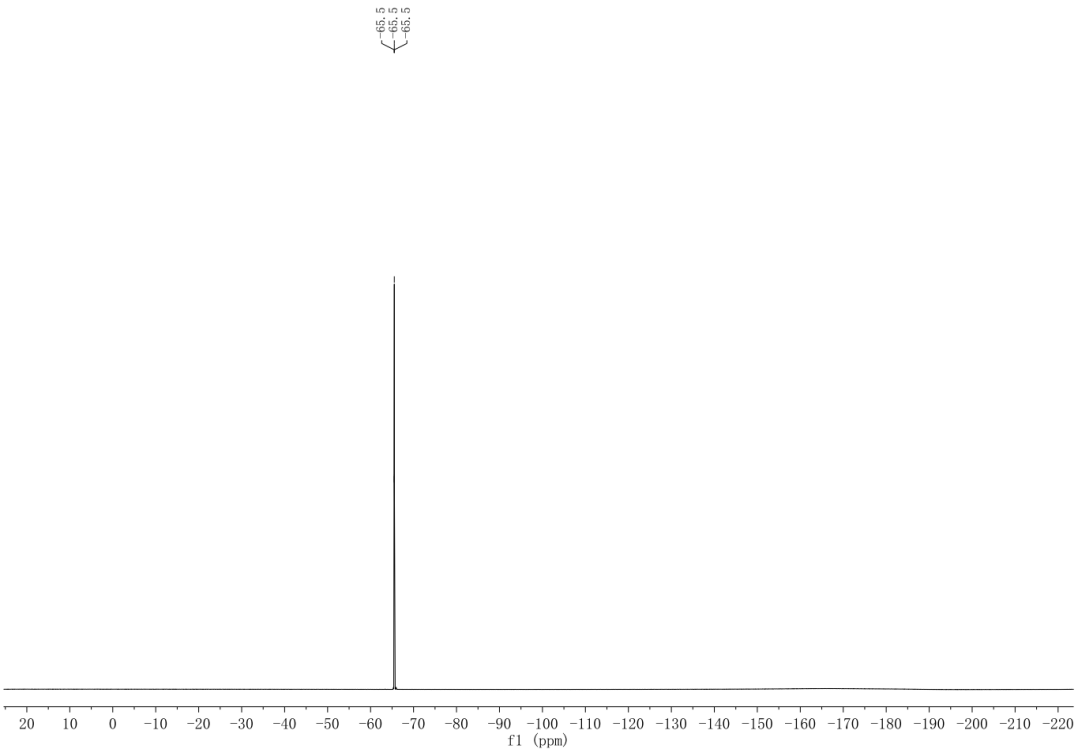
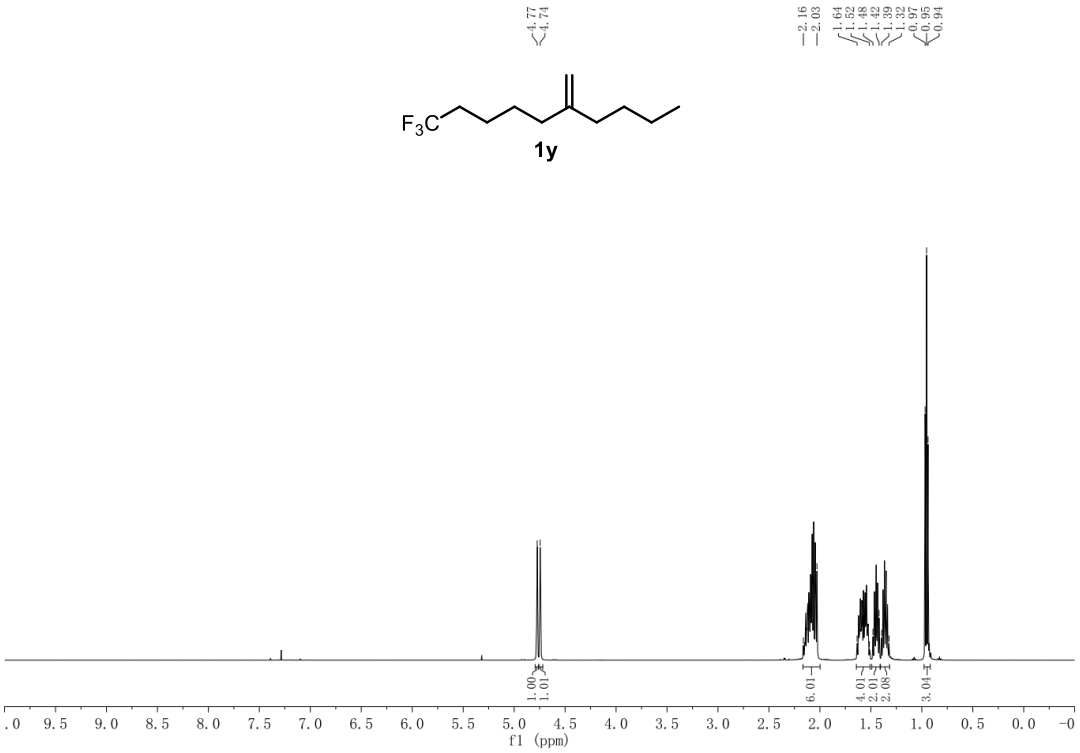
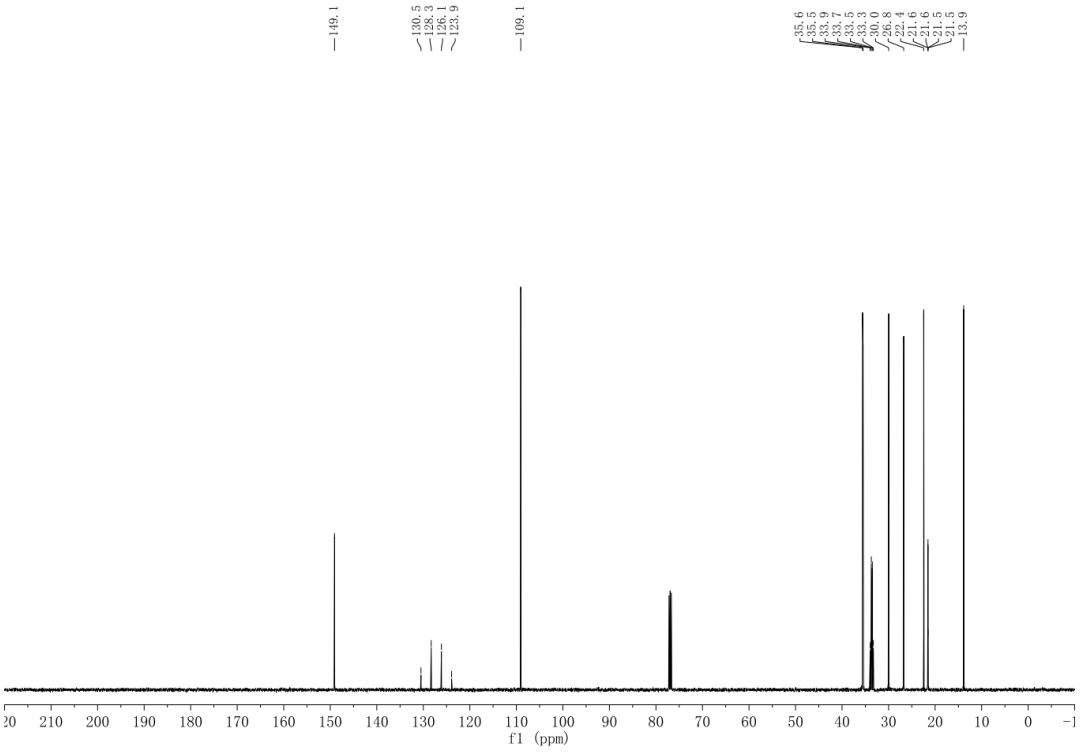
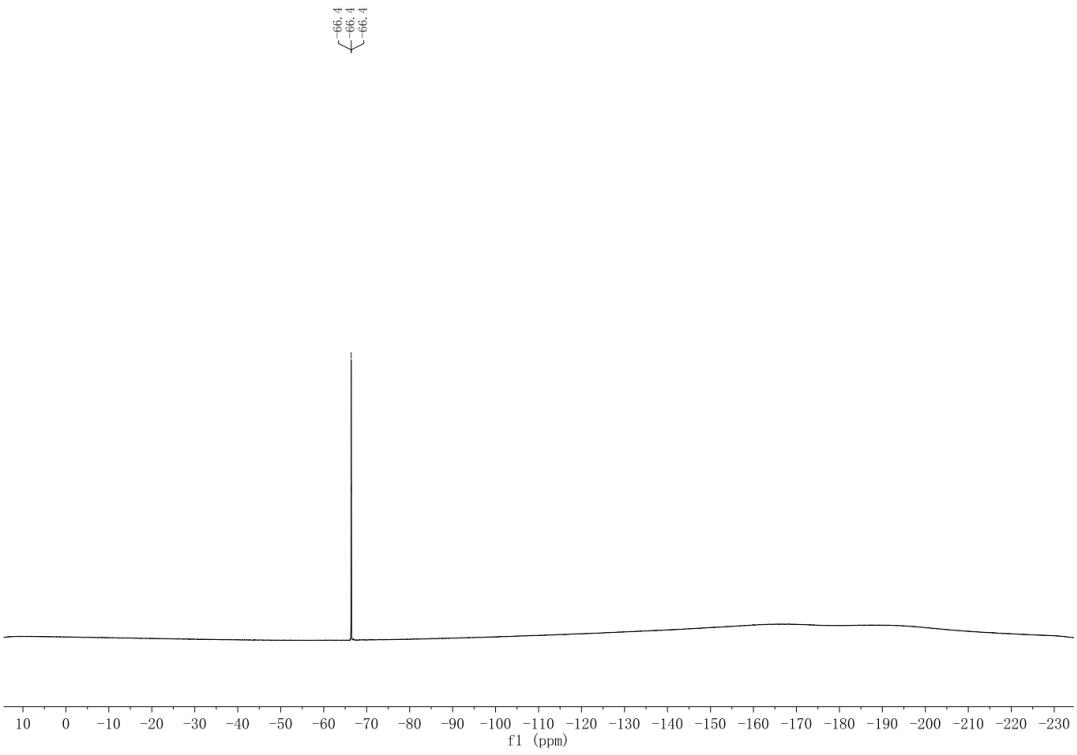
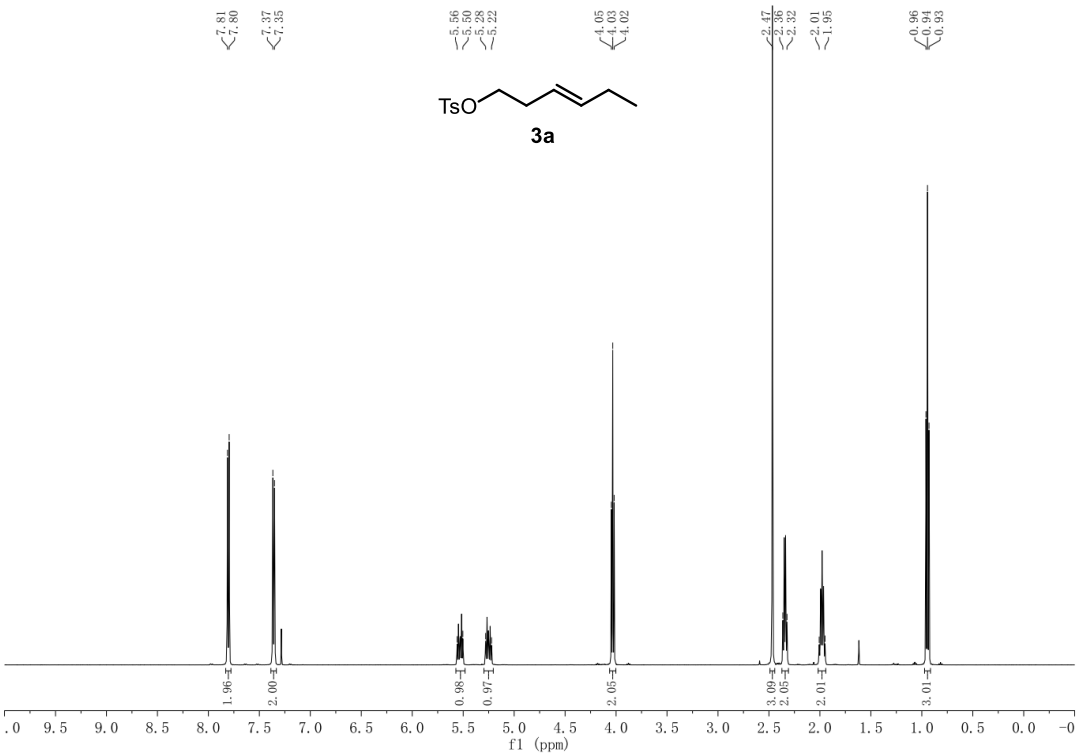
21.7
21.7
21.7
21.7
f1 (ppm)


-65.5
-65.5
-65.5
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


4.77
4.74
2.16
2.03
1.64
1.52
1.48
1.42
1.39
1.32
0.97
0.95
0.94
F3C
1y
1.00
1.01
6.01
4.01
2.01
2.08
3.04
f1 (ppm)


149.1
130.5
128.3
126.1
123.9
109.1
35.6
35.5
33.9
33.7
33.5
33.3
30.0
26.8
22.4
21.6
21.6
21.5
21.5
13.9
f1 (ppm)


-66.4
-66.4
-66.4
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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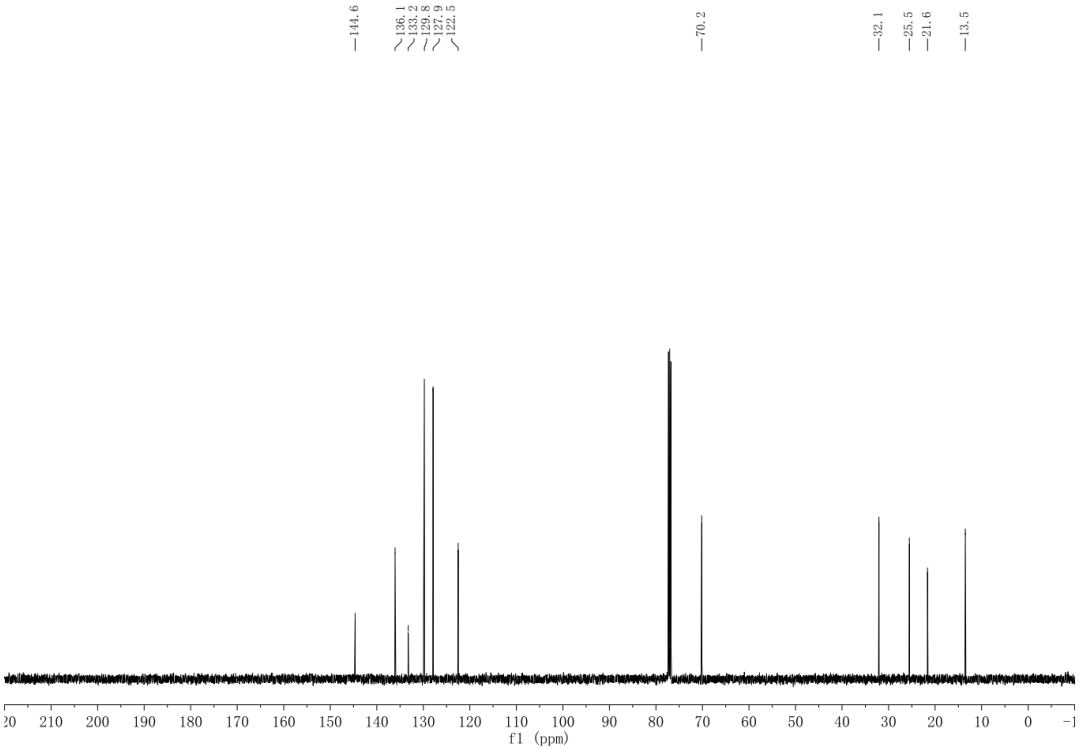
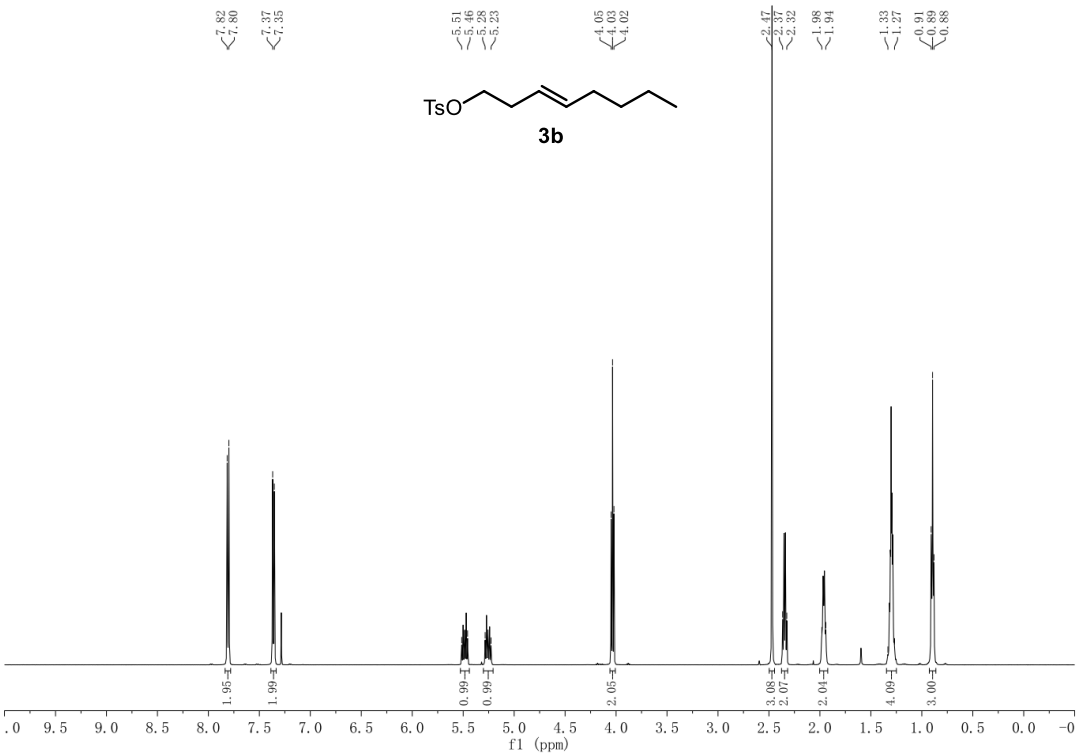
7.80
7.37
7.35
5.56
5.50
5.28
5.22
4.05
4.03
4.02
2.47
2.36
2.32
2.01
1.95
0.96
0.94
0.93
TsO
3a
1.96
2.00
0.98
0.97
2.05
3.09
2.05
2.01
3.01
f1 (ppm)


144.6
136.1
133.2
129.8
127.9
122.5
70.2
32.1
25.5
21.6
13.5
f1 (ppm)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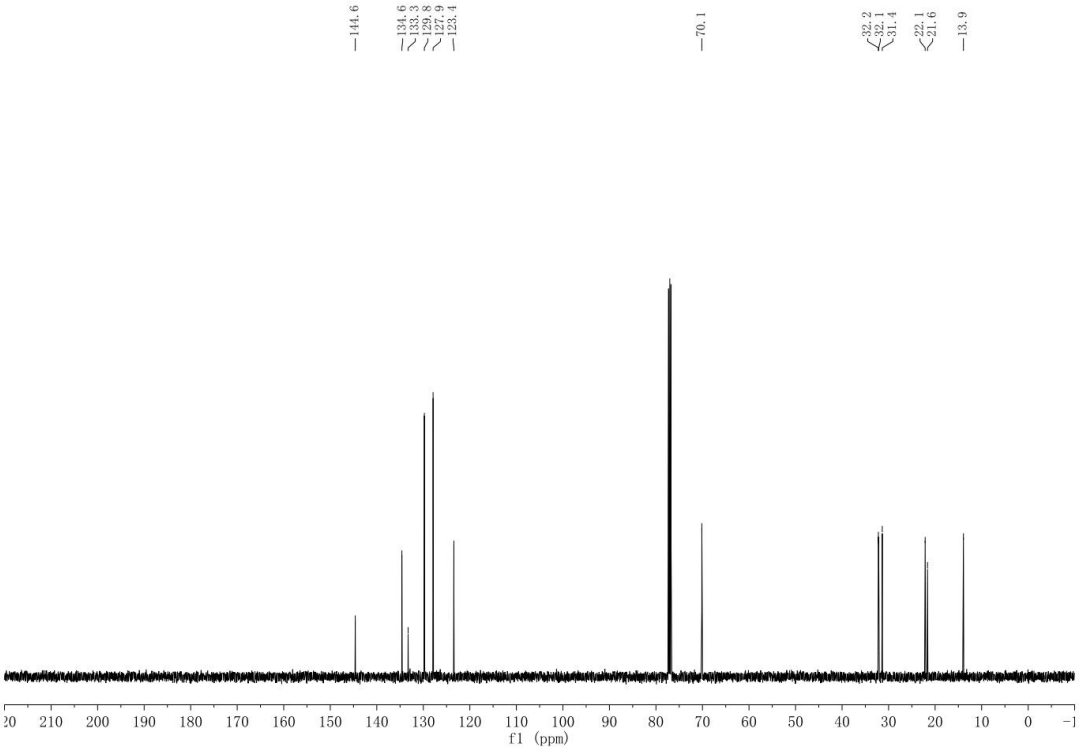
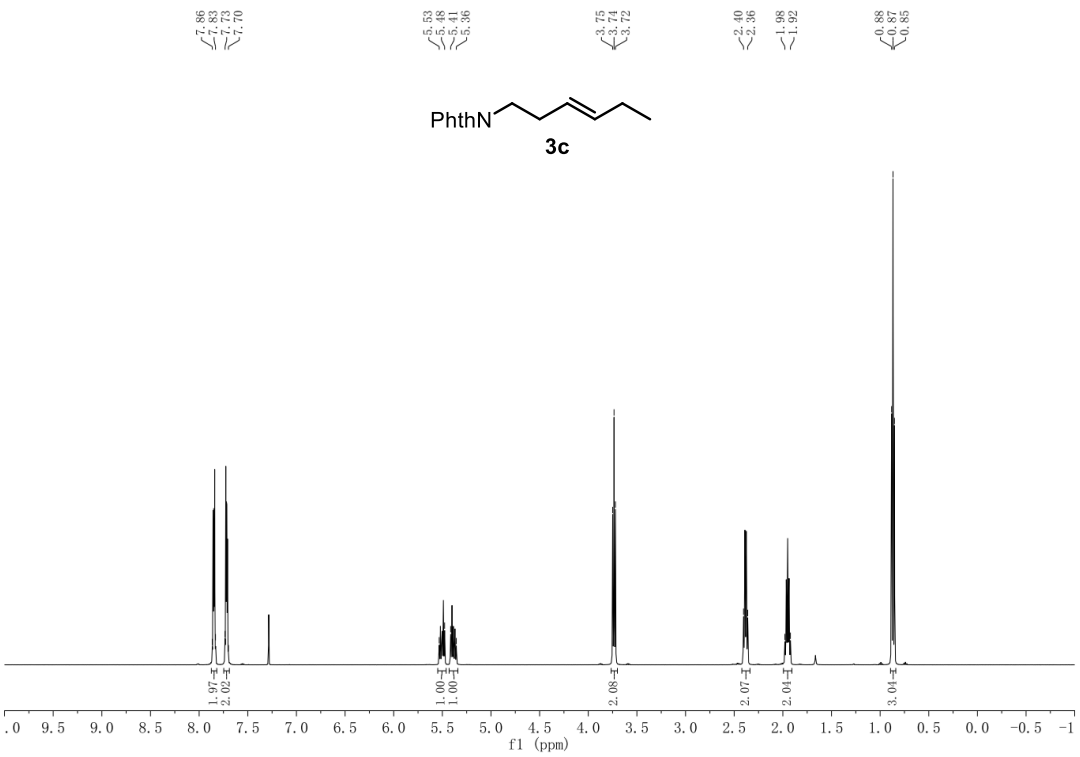
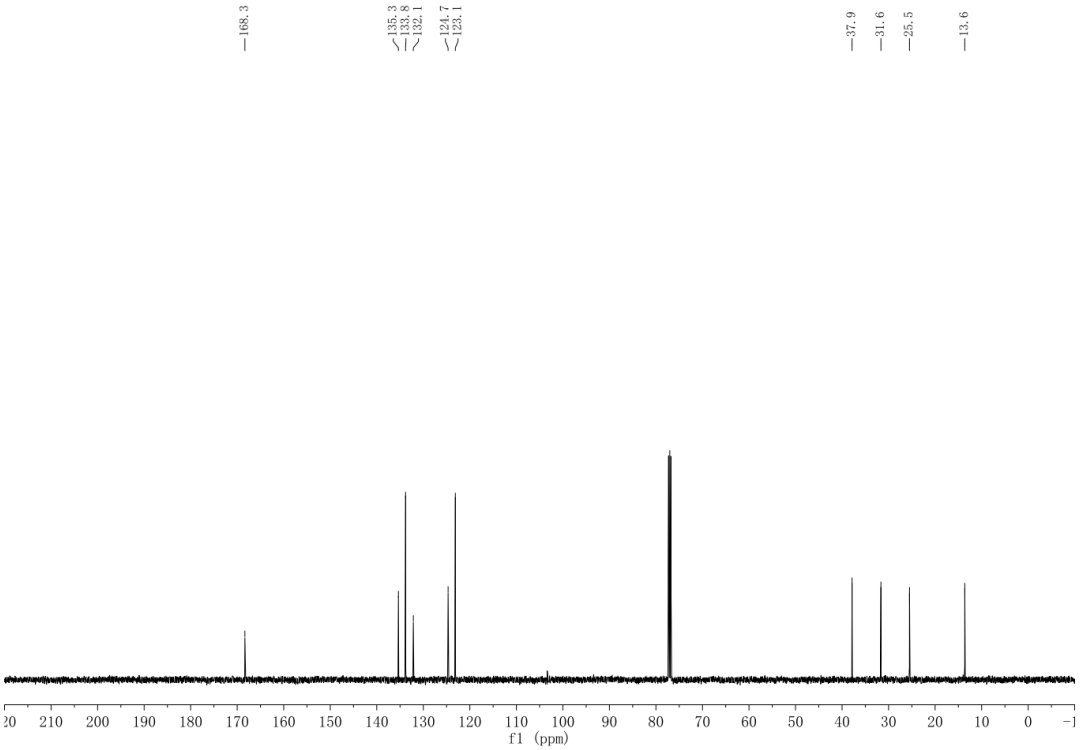
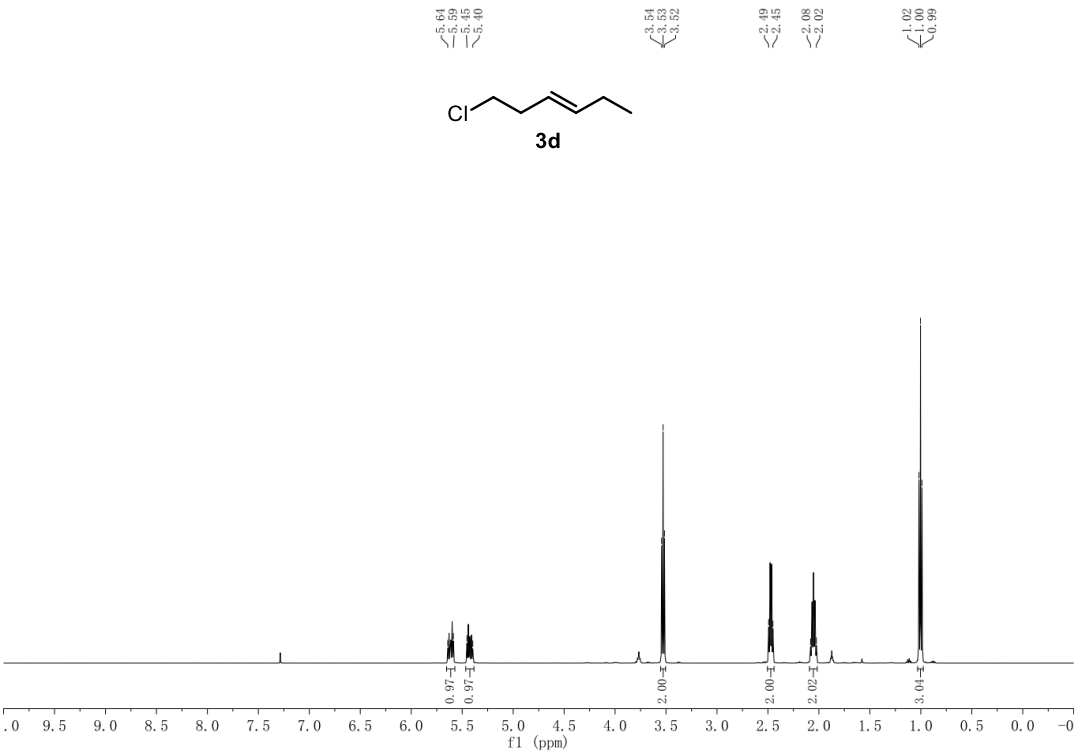
7.80
7.37
7.35
5.51
5.46
5.28
5.23
4.05
4.03
4.02
2.47
2.37
2.32
1.98
1.94
1.33
1.27
0.91
0.89
0.88
TsO
3b
1.95
1.99
0.99
0.99
2.05
3.08
2.07
2.04
4.09
3.00
f1 (ppm)


144.6
134.6
133.3
129.8
127.9
123.4
70.1
32.2
32.1
31.4
22.1
21.6
13.9
f1 (ppm)


7.86
7.83
7.73
7.70
5.53
5.48
5.41
5.36
3.75
3.74
3.72
2.40
2.36
1.98
1.92
0.88
0.87
0.85
PhthN
3c
1.97
2.02
1.00
1.00
2.08
2.07
2.04
3.04
f1 (ppm)


168.3
135.3
133.8
132.1
124.7
123.1
37.9
31.6
25.5
13.6
f1 (ppm)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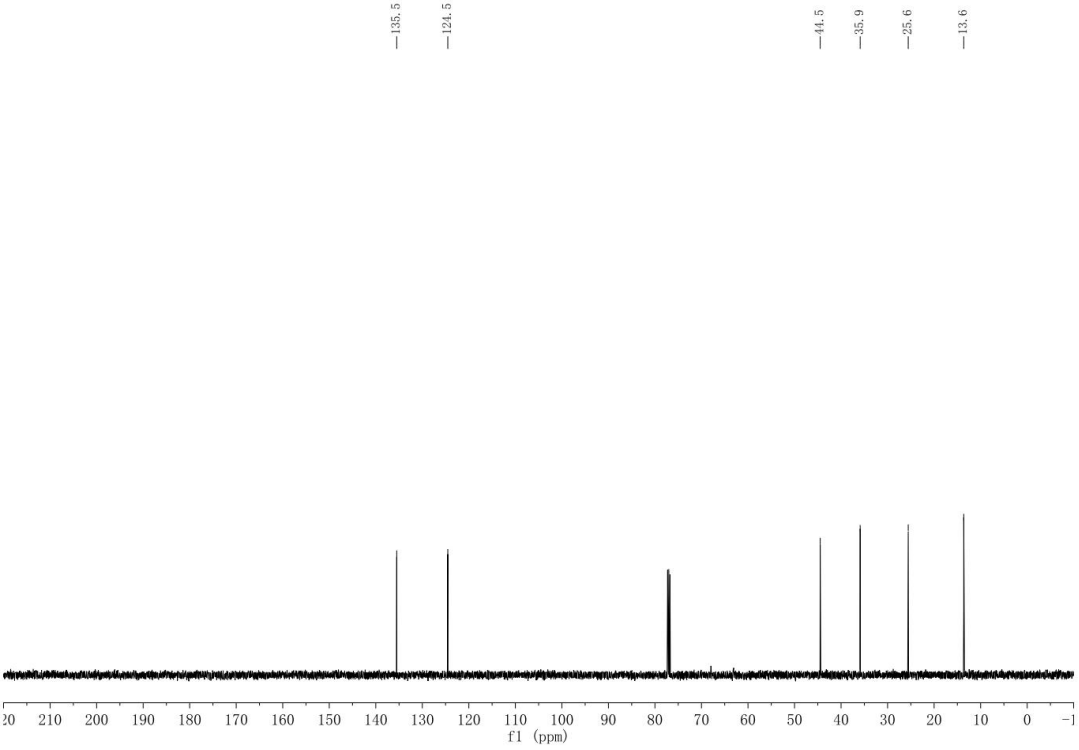
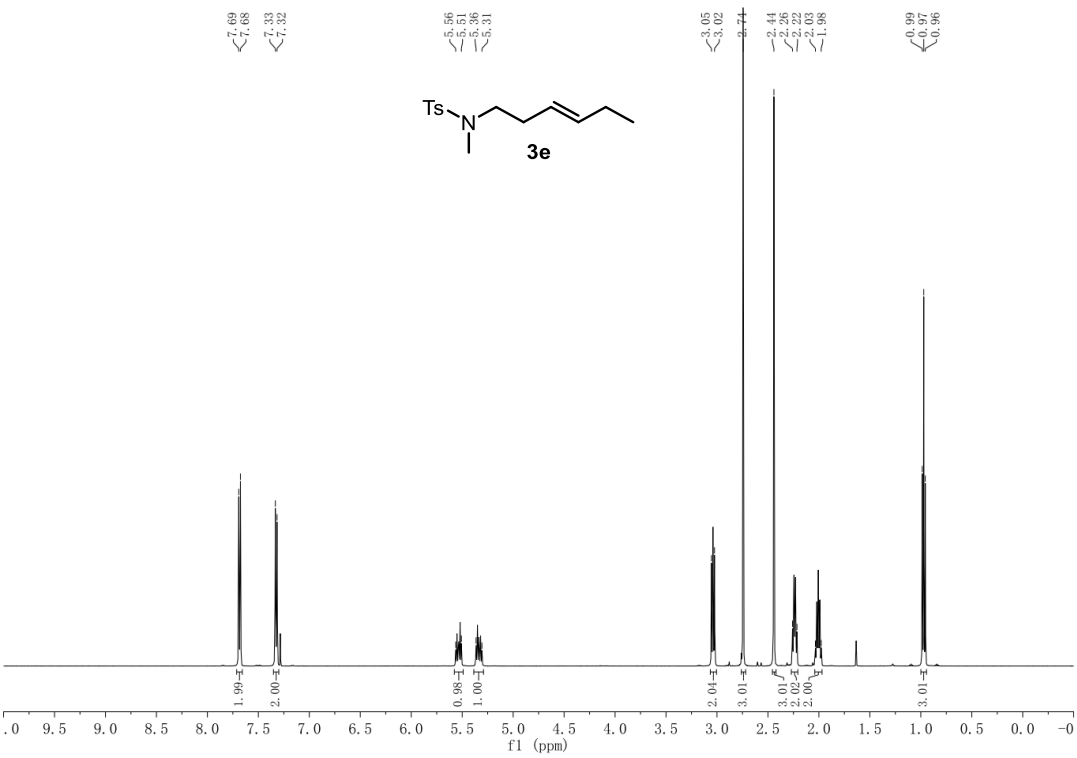
5.59
5.45
5.40
3.54
3.53
3.52
2.49
2.45
2.08
2.02
1.02
1.00
0.99
Cl
3d
0.97
0.97
2.00
2.00
2.02
3.01
f1 (ppm)


135.5
124.5
44.5
35.9
25.6
13.6
f1 (ppm)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7.32
5.56
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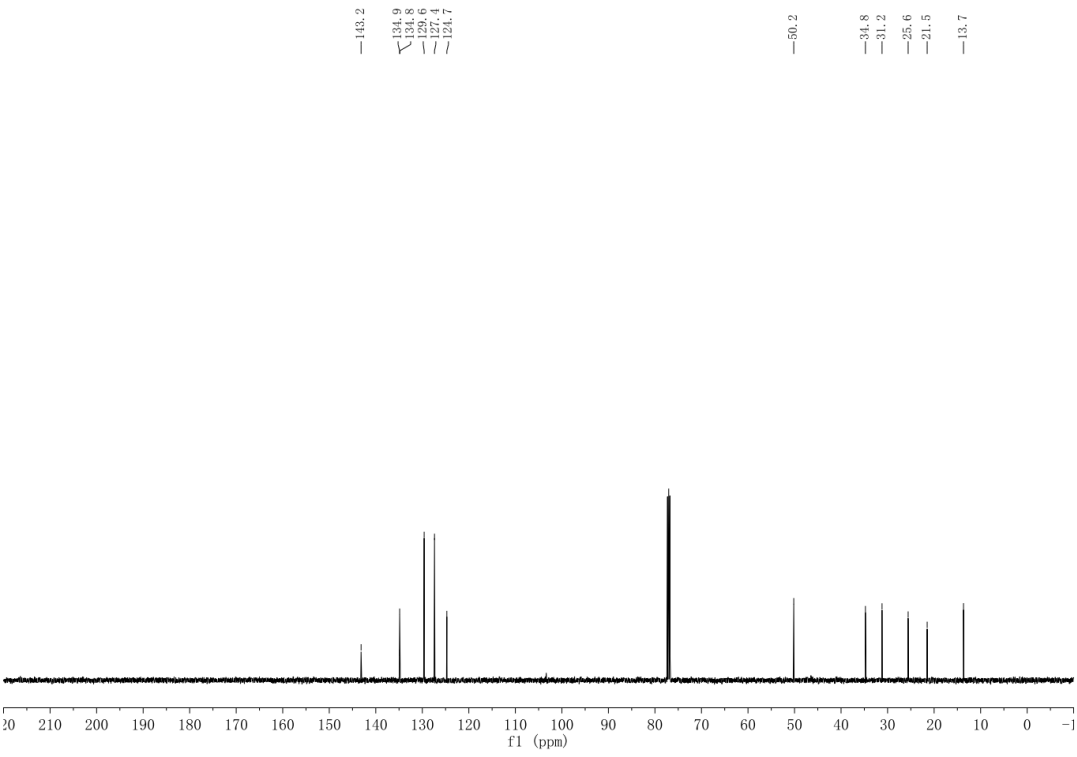
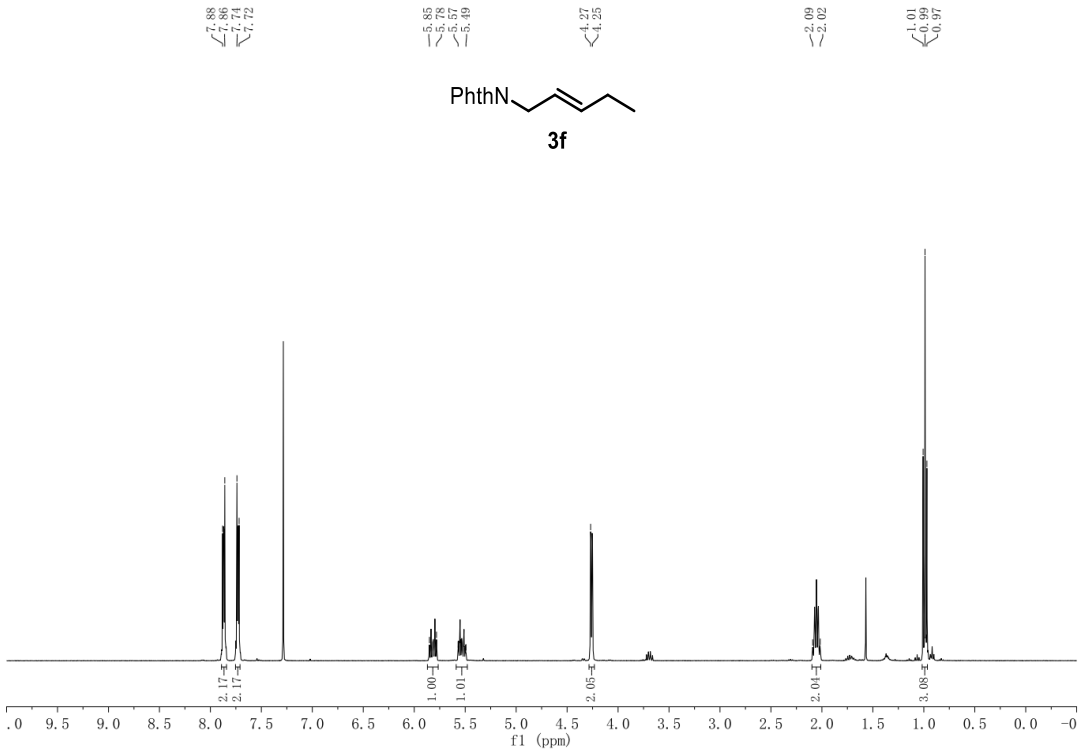
5.36
5.31
3.05
3.02
2.71
2.44
2.26
2.22
2.03
1.98
0.99
0.97
0.96
Ts
N
3e
1.99
2.00
0.98
1.00
2.04
3.01
3.01
2.02
2.00
3.01
f1 (ppm)


143.2
134.9
134.8
129.6
127.4
124.7
50.2
34.8
31.2
25.6
21.5
13.7
f1 (ppm)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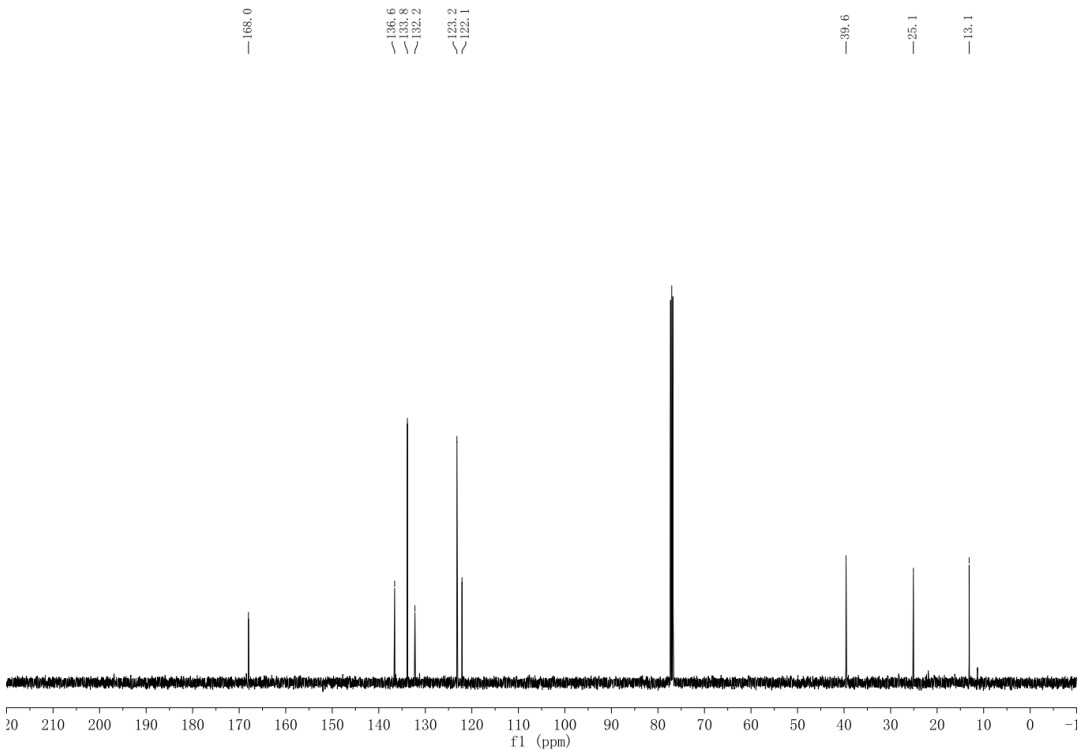
7.74
7.72
5.85
5.78
5.57
5.49
4.27
4.25
2.09
2.02
1.01
0.99
0.97
PhthN
3f
2.17
2.17
1.00
1.01
2.05
2.04
3.08
f1 (ppm)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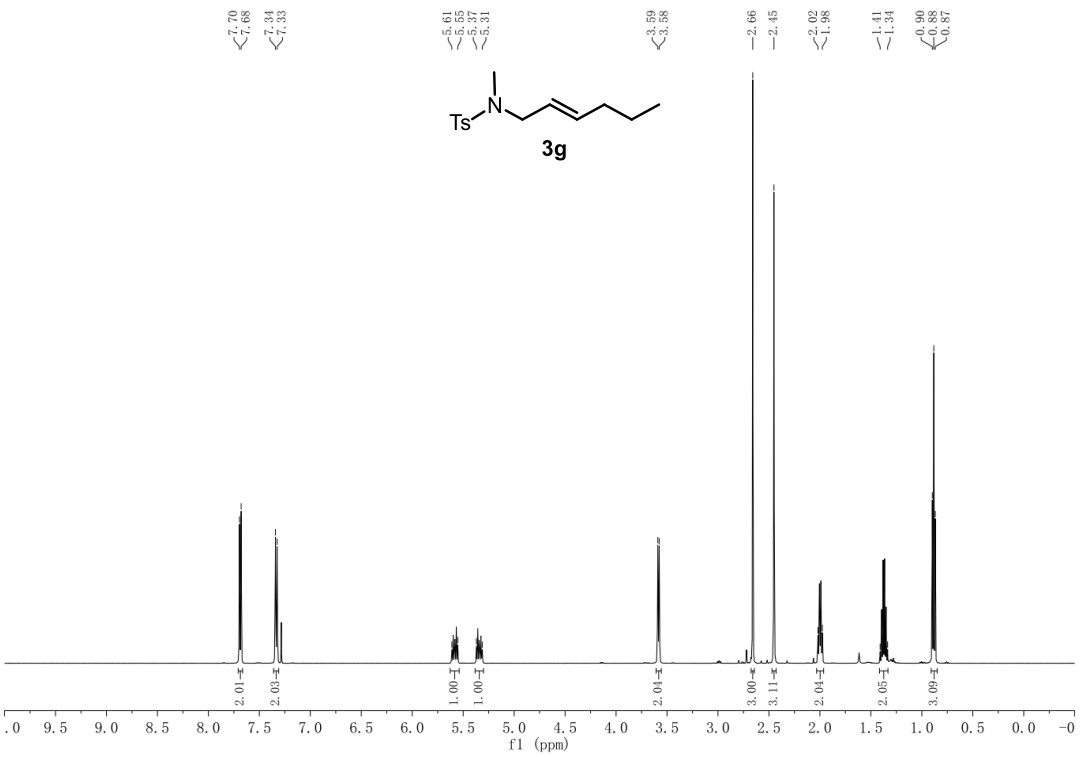
136.6
133.8
132.2
123.2
122.1
39.6
25.1
13.1
f1 (ppm)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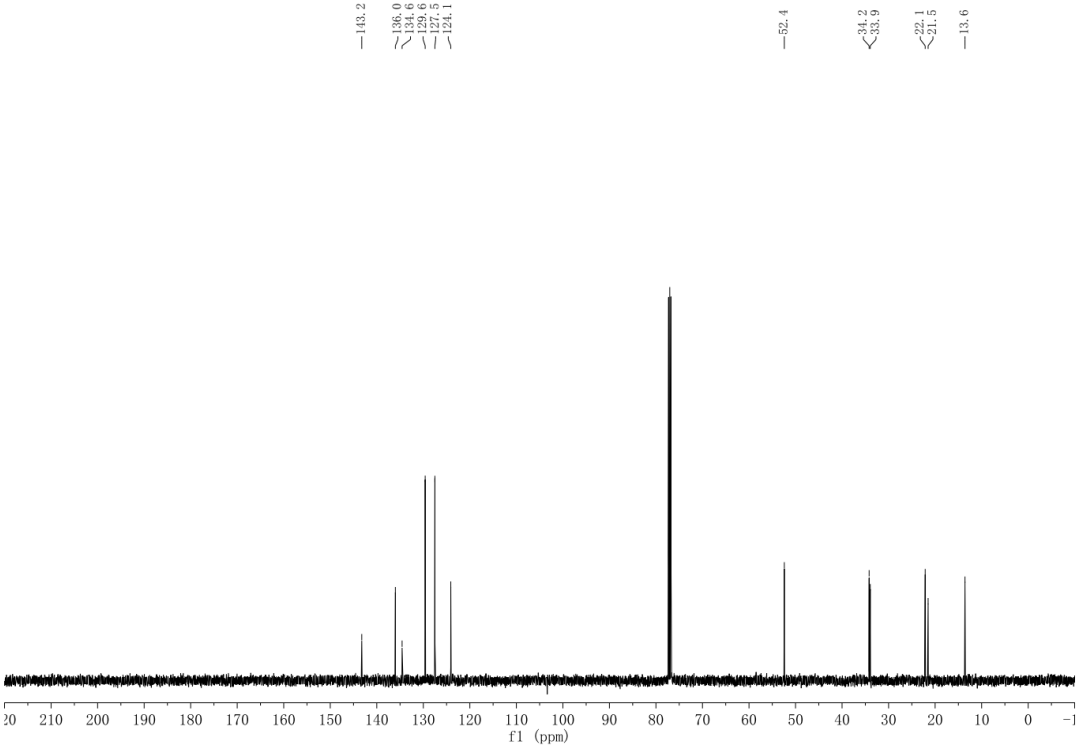
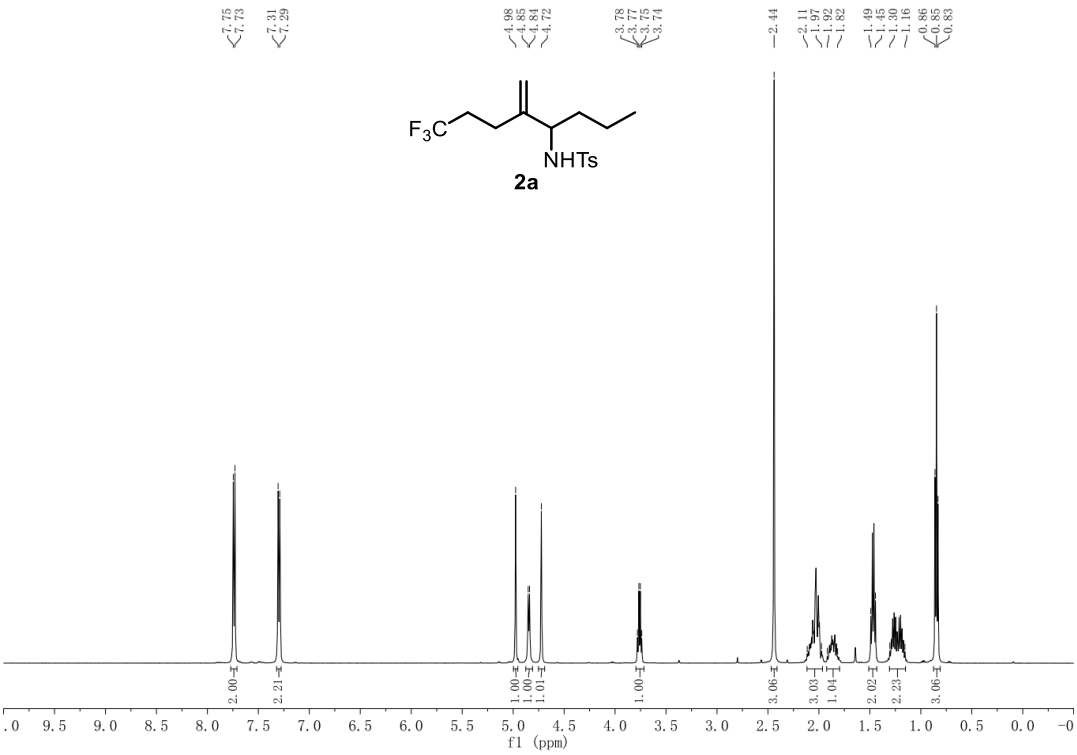
5.55
5.37
5.31
3.59
3.58
2.66
2.45
2.02
1.98
1.41
1.34
0.90
0.88
0.87
Ts
N
3g
2.01
2.03
1.00
1.00
2.04
3.00
3.11
2.04
2.05
3.09
f1 (ppm)


143.2
136.0
134.6
129.6
127.5
124.1
52.4
34.2
33.9
22.1
21.5
13.6
f1 (ppm)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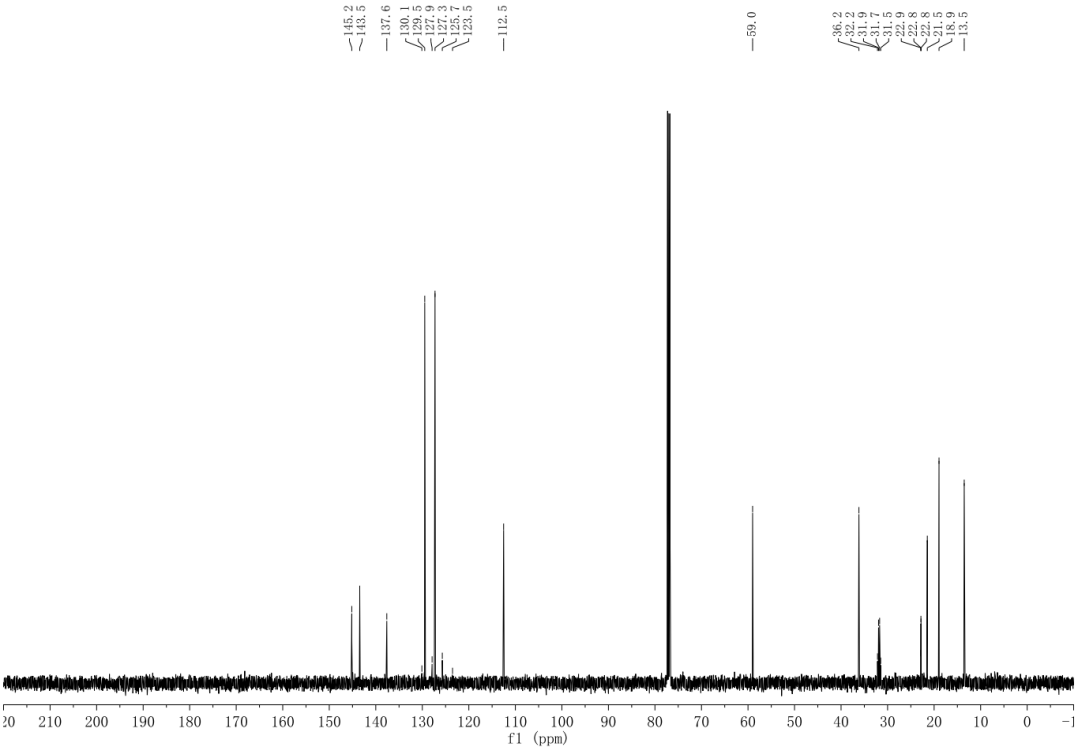
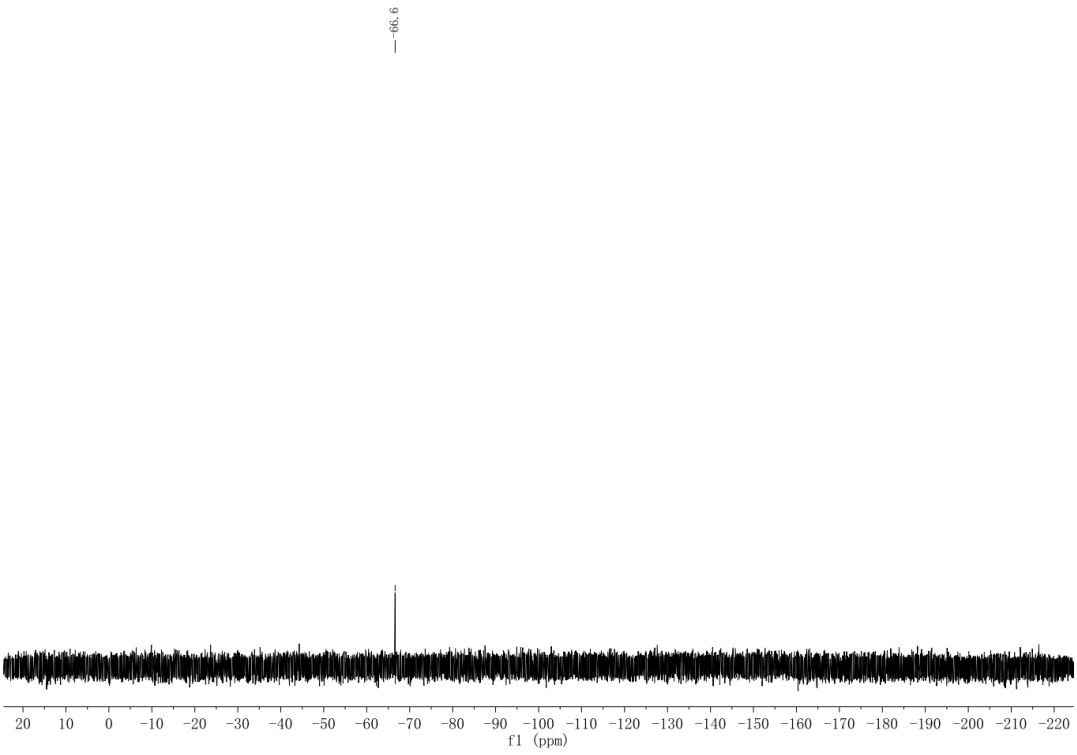
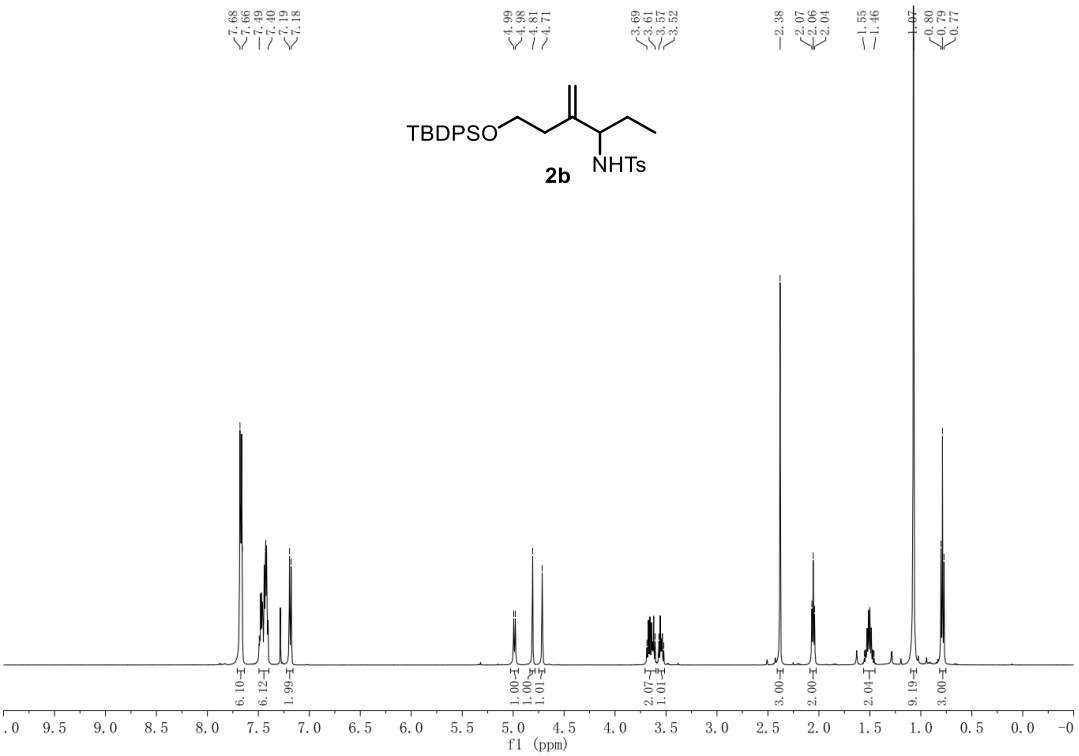
7.73
7.31
7.29
4.98
4.85
4.84
4.72
3.78
3.77
3.75
3.74
2.44
2.11
1.97
1.92
1.82
1.49
1.45
1.30
1.16
0.86
0.85
0.83
F3C
NHTs
2a
2.00
2.21
1.00
1.00
1.01
1.00
3.06
3.03
1.04
2.02
2.23
3.06
f1 (ppm)


145.2
143.5
137.6
130.1
129.5
127.9
127.3
125.7
123.5
112.5
59.0
36.2
32.2
31.9
31.7
31.5
22.9
22.8
22.8
21.5
18.9
13.5
f1 (ppm)


-69.9
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)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4.98
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4.71
3.69
3.61
3.57
3.52
2.38
2.07
2.06
2.04
1.55
1.46
1.07
0.80
0.79
0.77
TBDPSO
NHTs
2b
6.10
6.12
1.99
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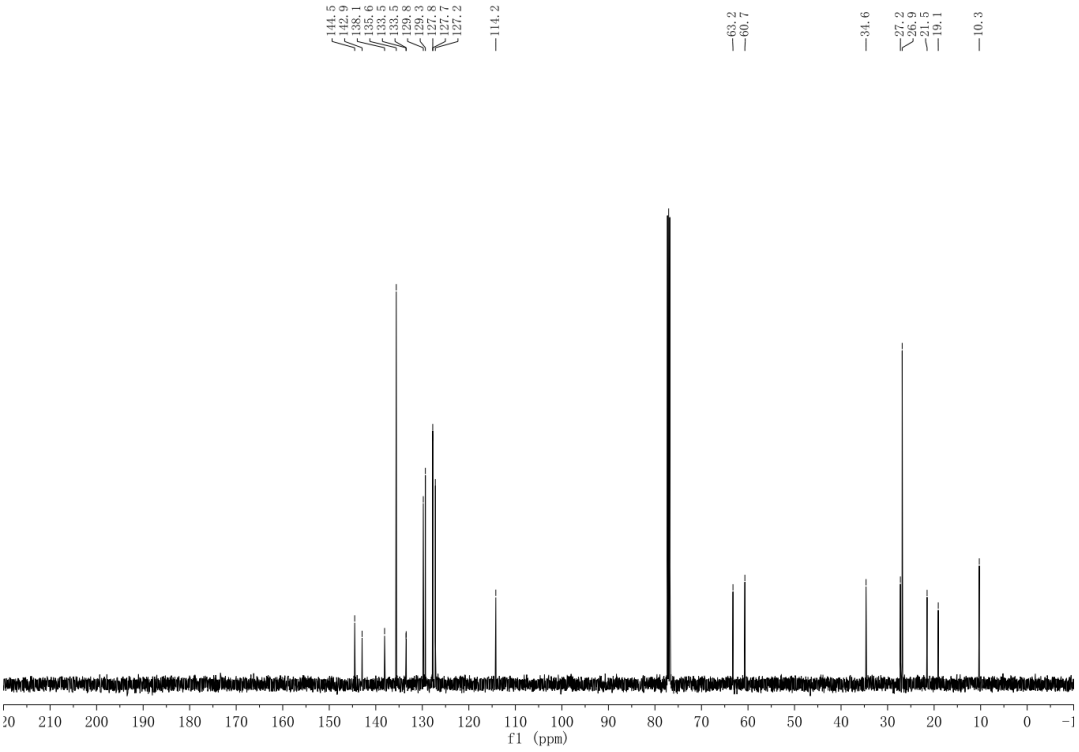
1.01
2.07
1.01
3.00
2.00
2.04
9.19
3.00
f1 (ppm)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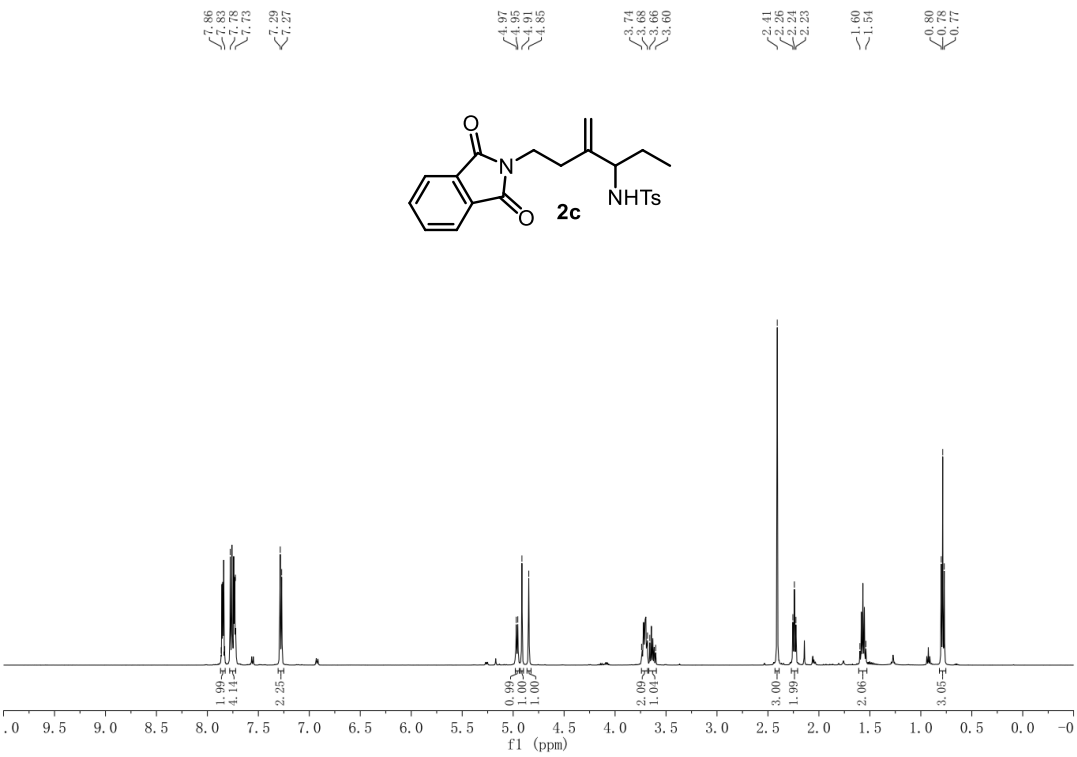
138.1
135.6
133.5
133.5
129.8
129.3
127.8
127.7
127.2
114.2
63.2
60.7
34.6
27.2
26.9
21.5
19.1
10.3
f1 (ppm)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7.73
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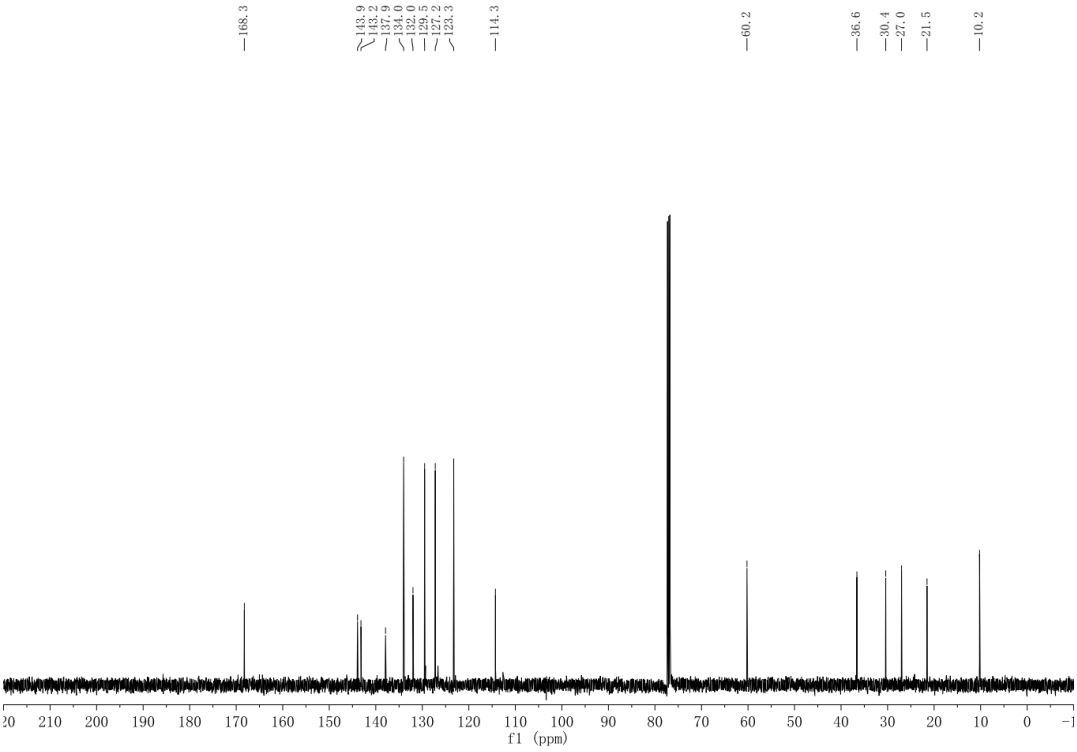
7.27
4.97
4.95
4.91
4.85
3.74
3.68
3.66
3.60
2.41
2.26
2.24
2.23
1.60
1.54
0.80
0.78
0.77
O
N
O
NHTs
2c
1.99
4.14
2.25
0.99
1.00
1.00
2.09
1.04
3.00
1.99
2.06
3.05
f1 (ppm)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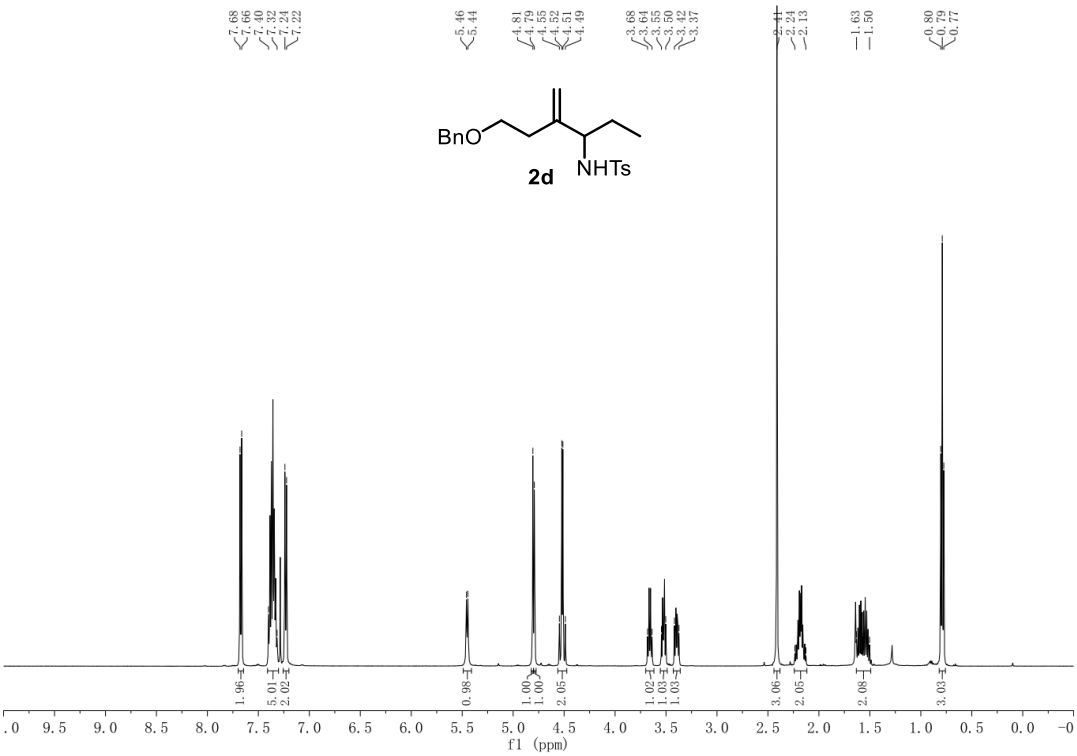
132.0
129.5
127.2
123.3
114.3
60.2
36.6
30.4
27.0
21.5
10.2
f1 (ppm)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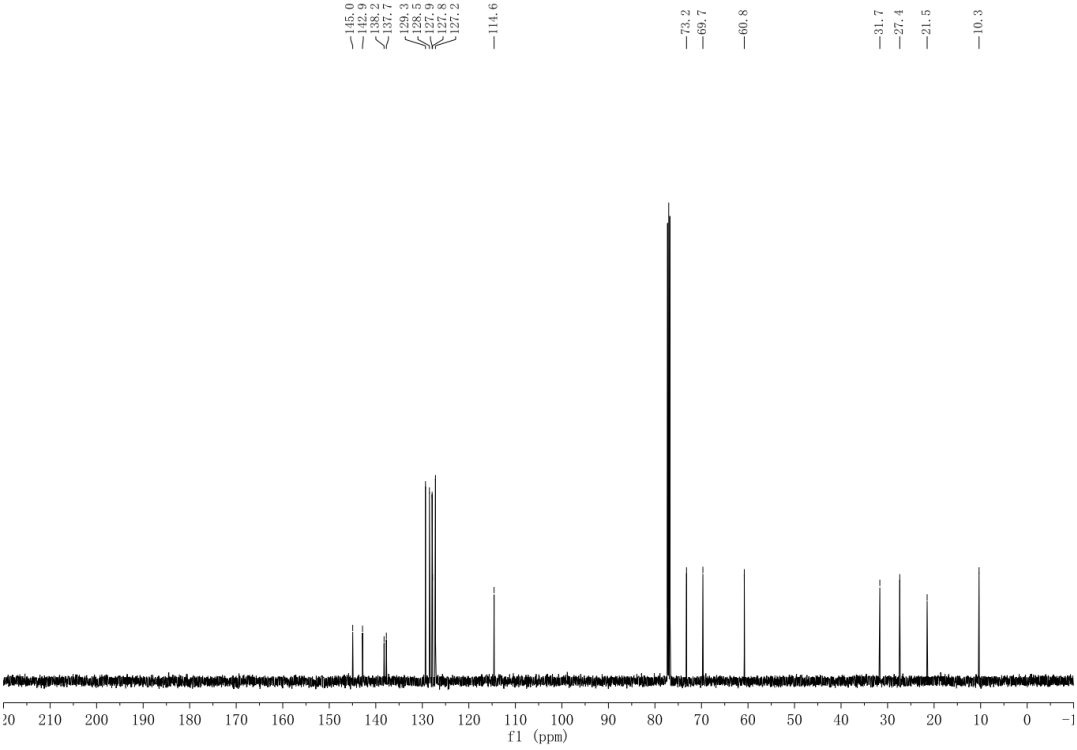
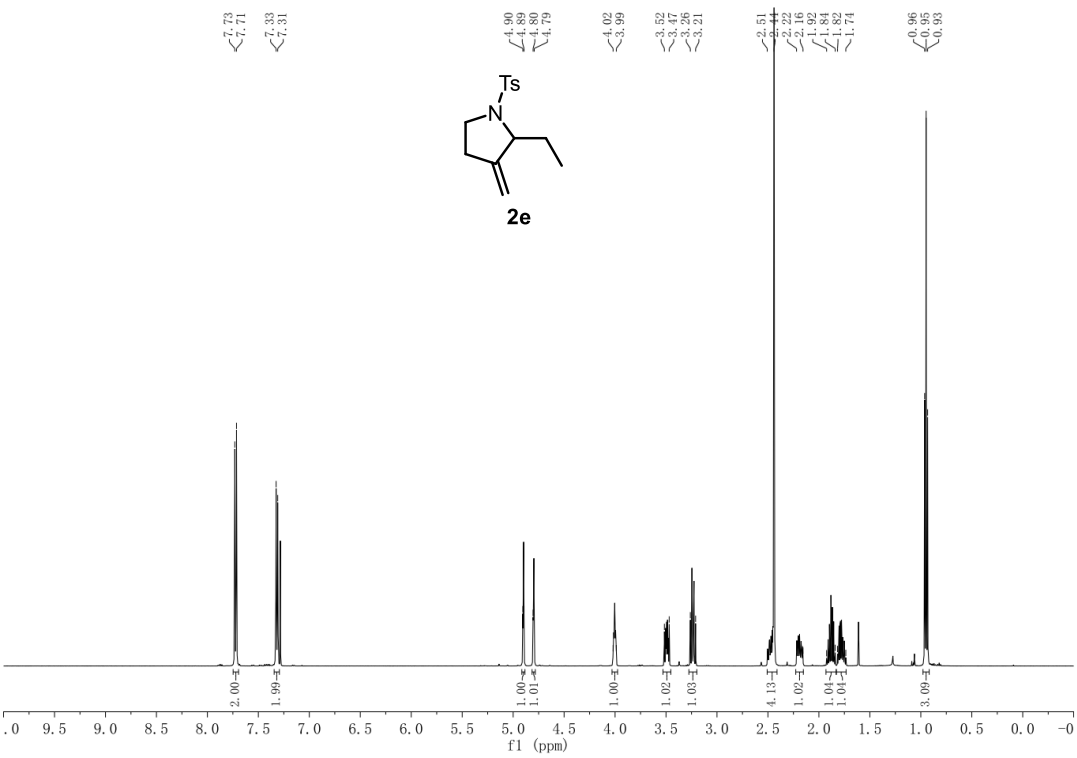
7.66
7.40
7.32
7.24
7.22
5.46
5.44
4.81
4.79
4.55
4.52
4.51
4.49
3.68
3.64
3.55
3.50
3.42
3.37
2.41
2.24
2.13
1.63
1.50
0.80
0.79
0.77
BnO
NHTs
2d
1.96
5.01
2.02
0.98
1.00
1.00
2.05
1.02
1.03
1.03
3.06
2.05
2.08
3.03
f1 (ppm)


145.0
142.9
138.2
137.7
129.3
128.5
127.9
127.8
127.2
114.6
73.2
69.7
60.8
31.7
27.4
21.5
10.3
f1 (ppm)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7.31
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4.79
4.02
3.99
3.52
3.47
3.26
3.21
2.51
2.41
2.22
2.16
1.92
1.84
1.82
1.74
0.96
0.95
0.93
Ts
N
2e
2.00
1.99
1.00
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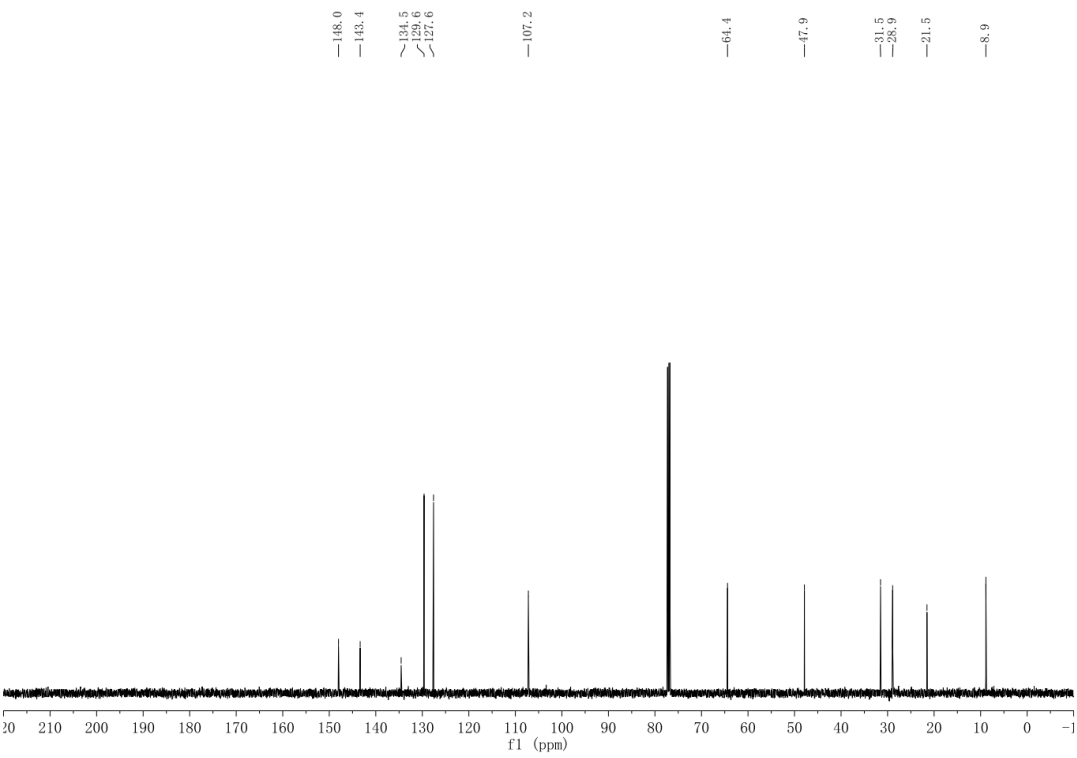
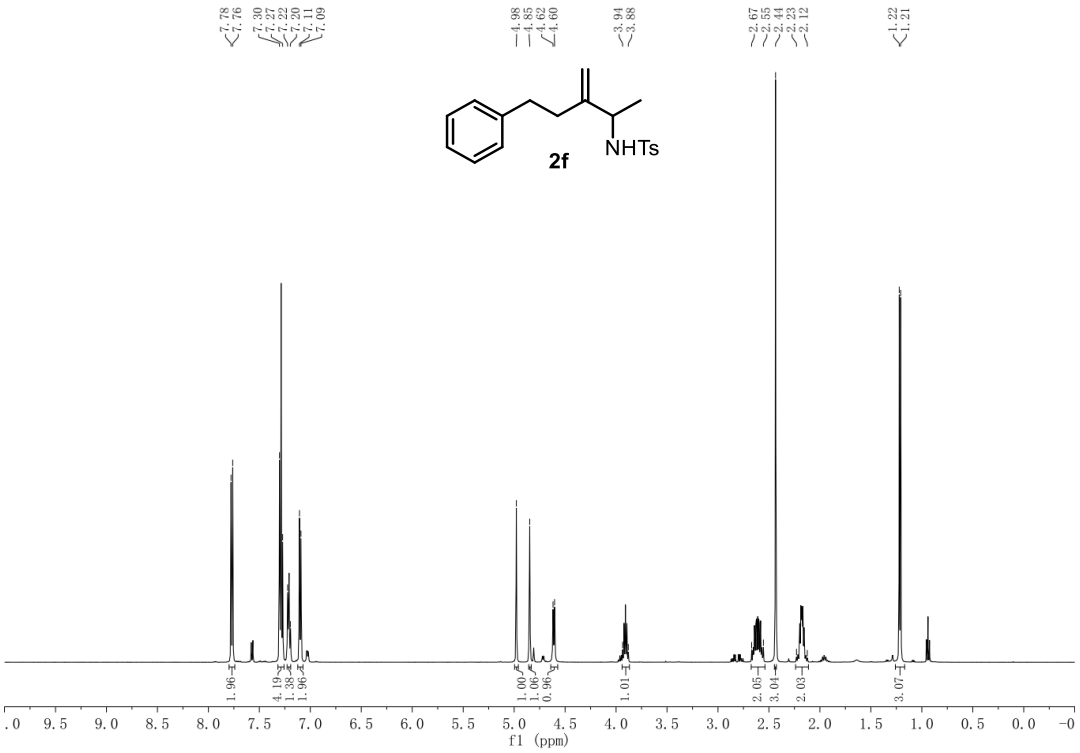
1.00
1.02
1.03
4.13
1.02
1.04
1.04
3.09
f1 (ppm)


148.0
143.4
134.5
129.6
127.6
107.2
64.4
47.9
31.5
28.9
21.5
8.9
f1 (ppm)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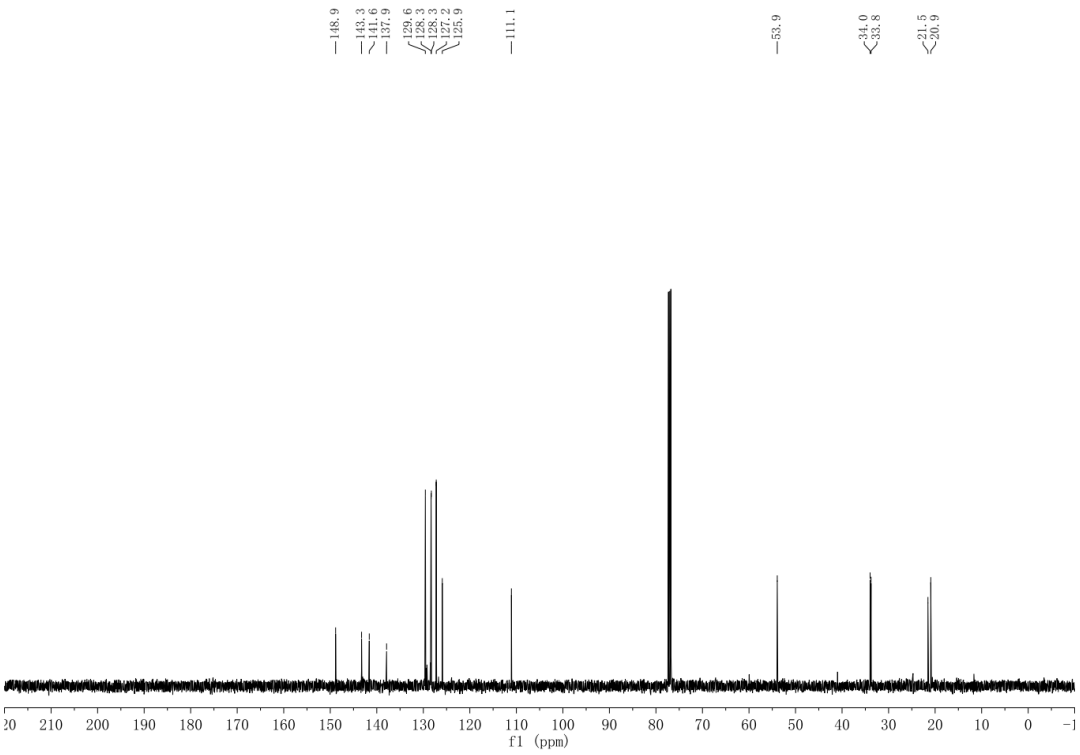
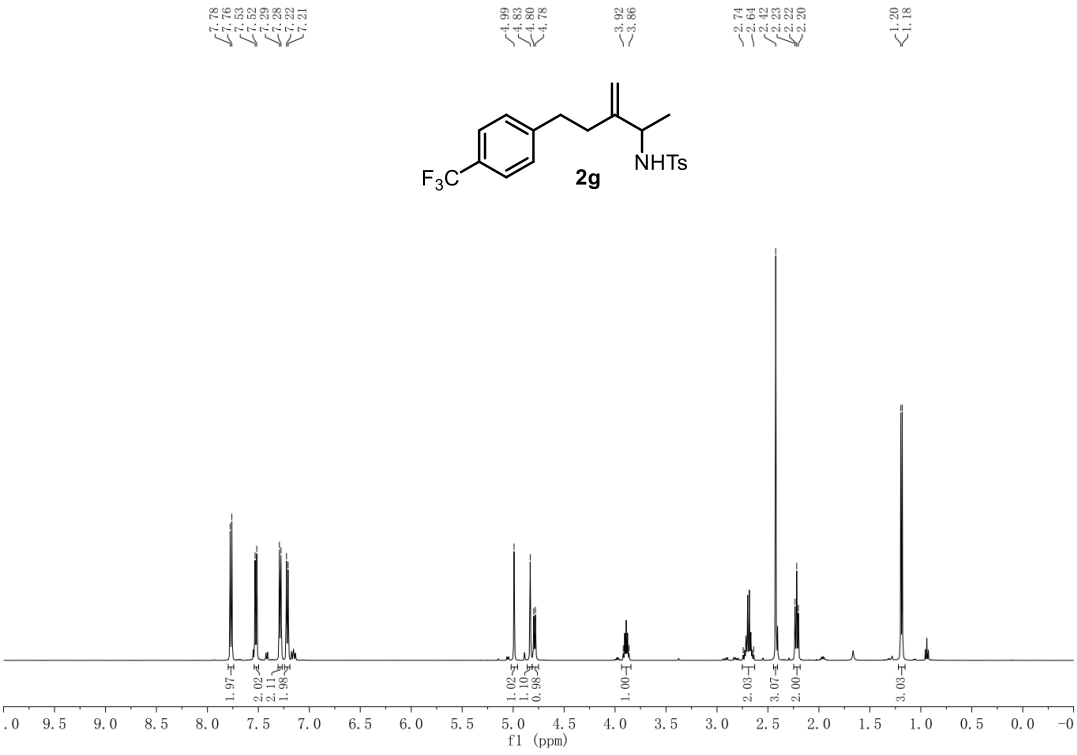
7.76
7.30
7.27
7.22
7.20
7.11
7.09
4.98
4.85
4.62
4.60
3.94
3.88
2.67
2.55
2.44
2.23
2.12
1.22
1.21
NHTs
2f
1.96
4.19
1.38
1.96
1.00
1.06
0.96
1.01
2.05
3.04
2.03
3.07
f1 (ppm)


148.9
143.3
141.6
137.9
129.6
128.3
128.3
127.2
125.9
111.1
53.9
34.0
33.8
21.5
20.9
f1 (ppm)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7.76
7.53
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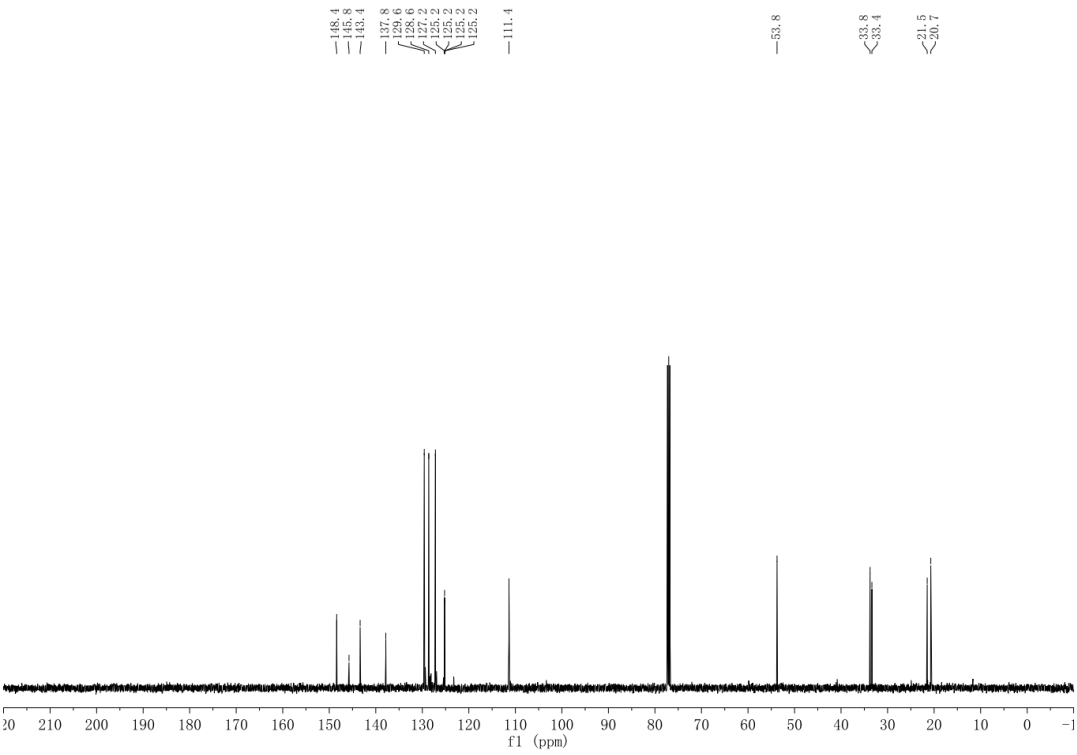
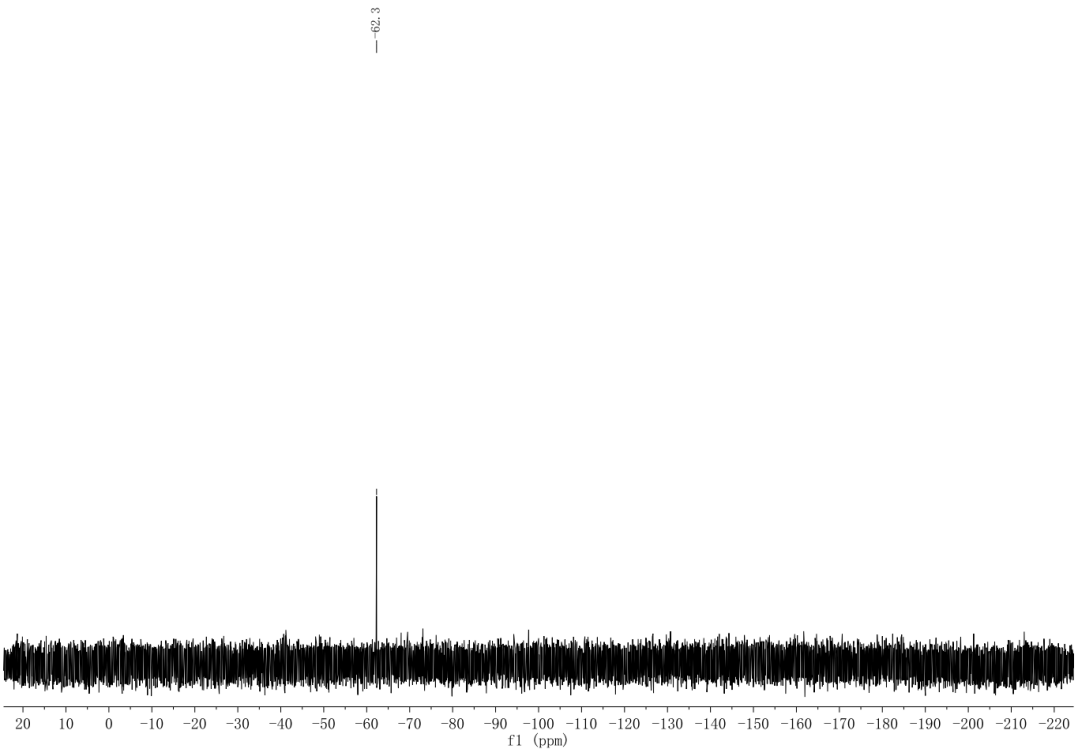
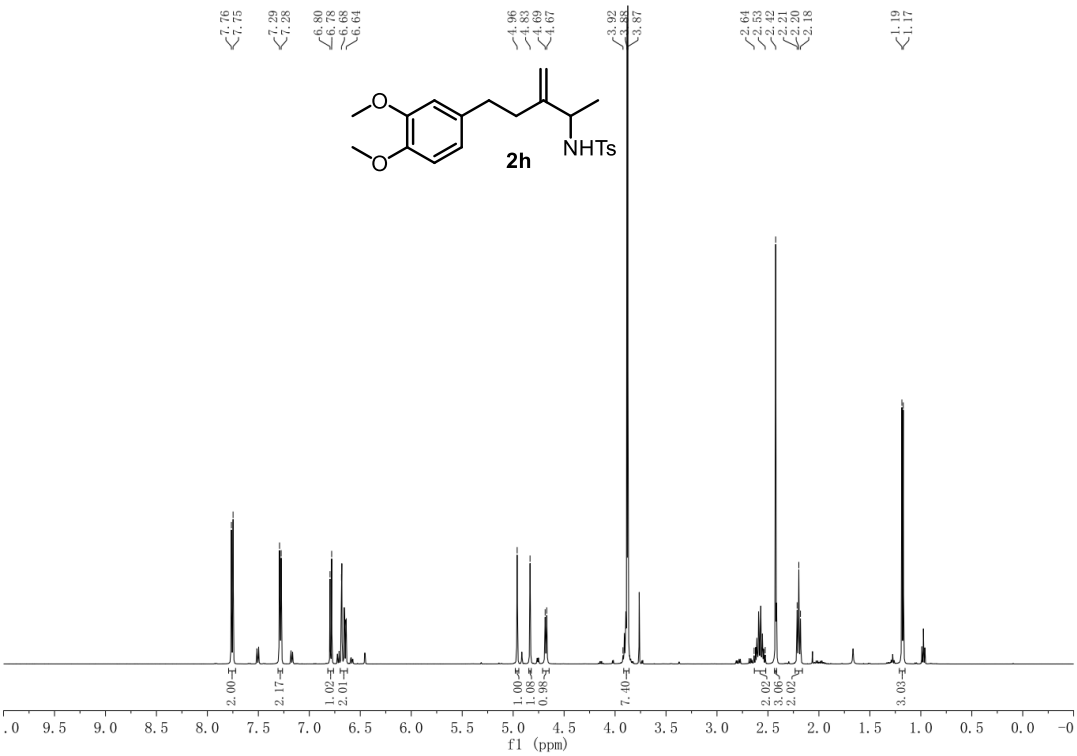
7.28
7.22
7.21
4.99
4.83
4.80
4.78
3.92
3.86
2.74
2.64
2.42
2.23
2.22
2.20
1.20
1.18
F3C
NHTs
2g
1.97
2.02
2.11
1.98
1.02
1.10
0.98
1.00
2.03
3.07
2.00
3.03
f1 (ppm)


148.4
145.8
143.4
137.8
129.6
128.6
127.2
125.2
125.2
125.2
125.2
111.4
53.8
33.8
33.4
21.5
20.7
f1 (ppm)


—62.3
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)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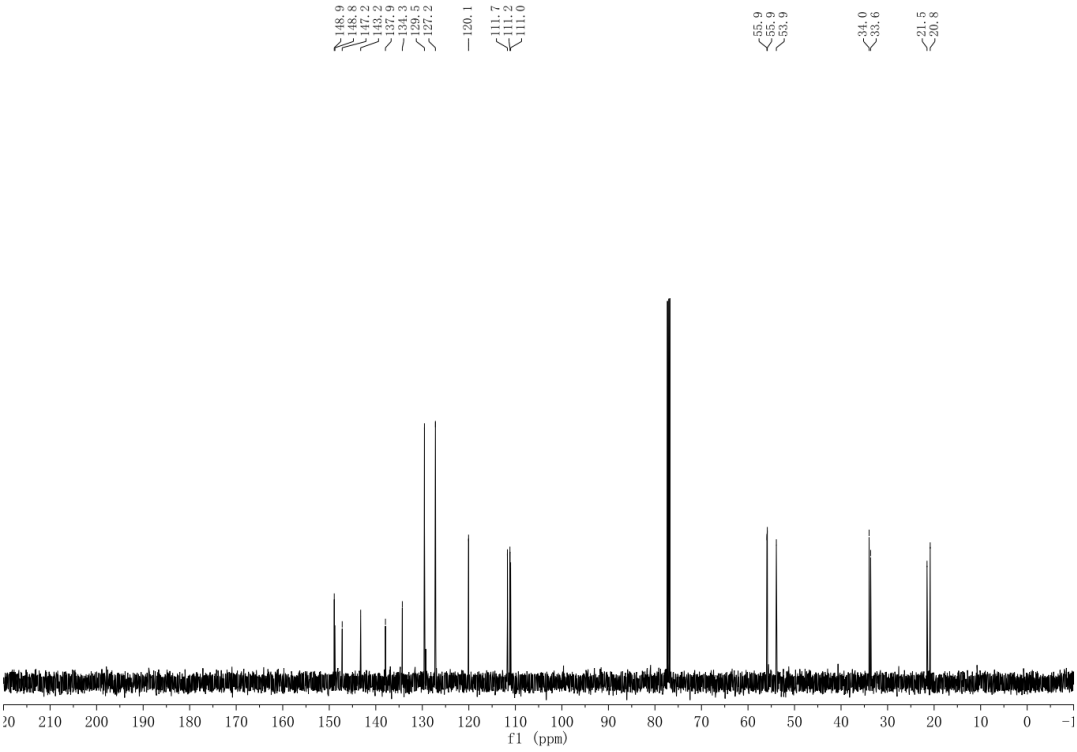
6.64
4.96
4.83
4.69
4.67
3.92
3.88
3.87
2.64
2.53
2.42
2.21
2.20
2.18
1.19
1.17
O
O
NHTs
2h
2.00
2.17
1.02
2.01
1.00
1.08
0.98
7.40
2.02
3.06
2.02
3.03
f1 (ppm)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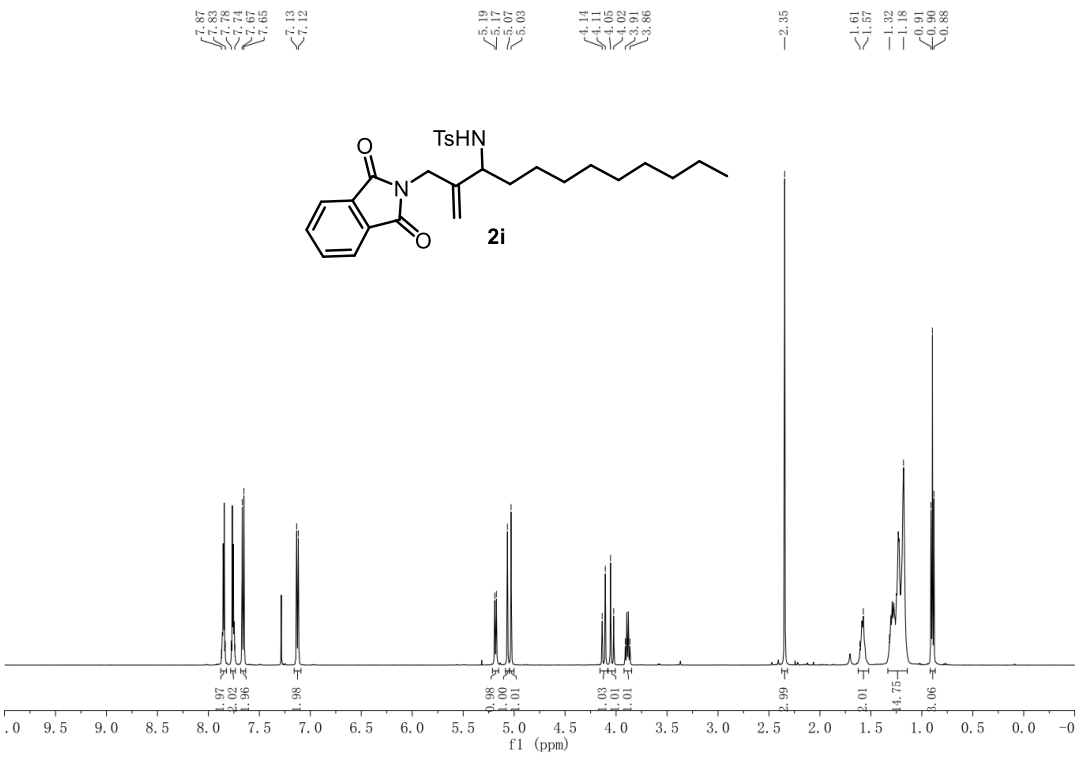
137.9
134.3
129.5
127.2
120.1
111.7
111.2
111.0
55.9
55.9
53.9
34.0
33.6
21.5
20.8
f1 (ppm)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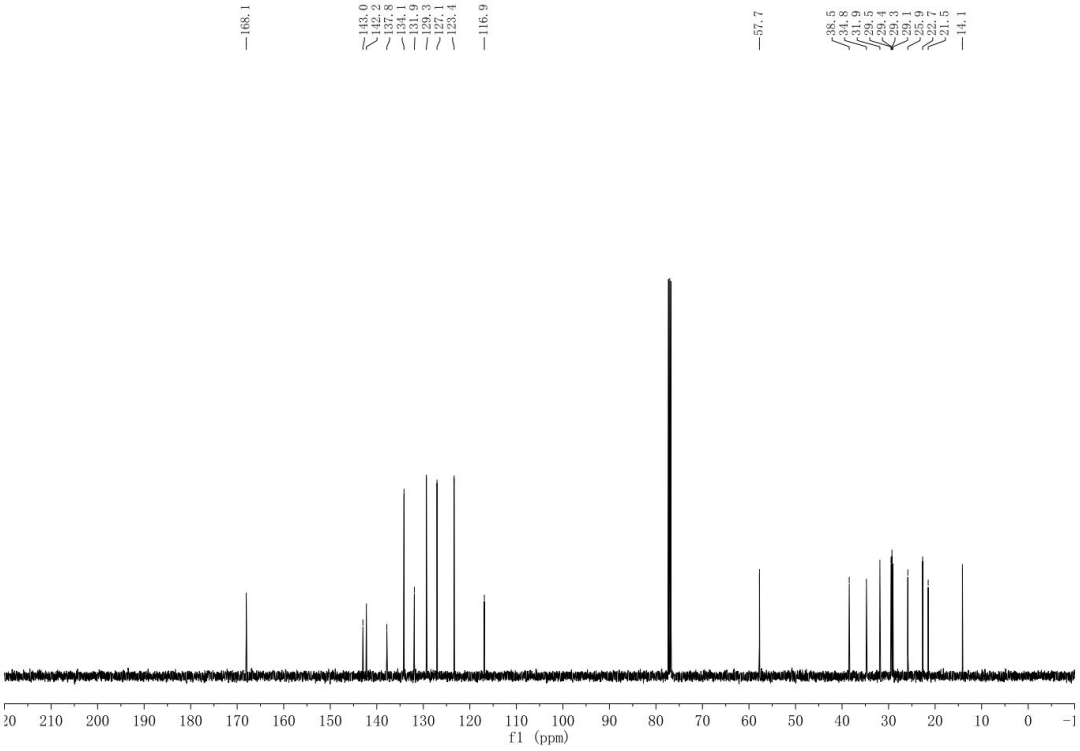
7.13
7.12
5.19
5.17
5.07
5.03
4.14
4.11
4.05
4.02
3.91
3.86
2.35
1.61
1.57
1.32
1.18
0.91
0.90
0.88
TsHN
O
N
O
2i
1.97
2.02
1.96
1.98
0.98
1.00
1.01
1.03
1.01
1.01
2.99
2.01
4.75
3.06
f1 (ppm)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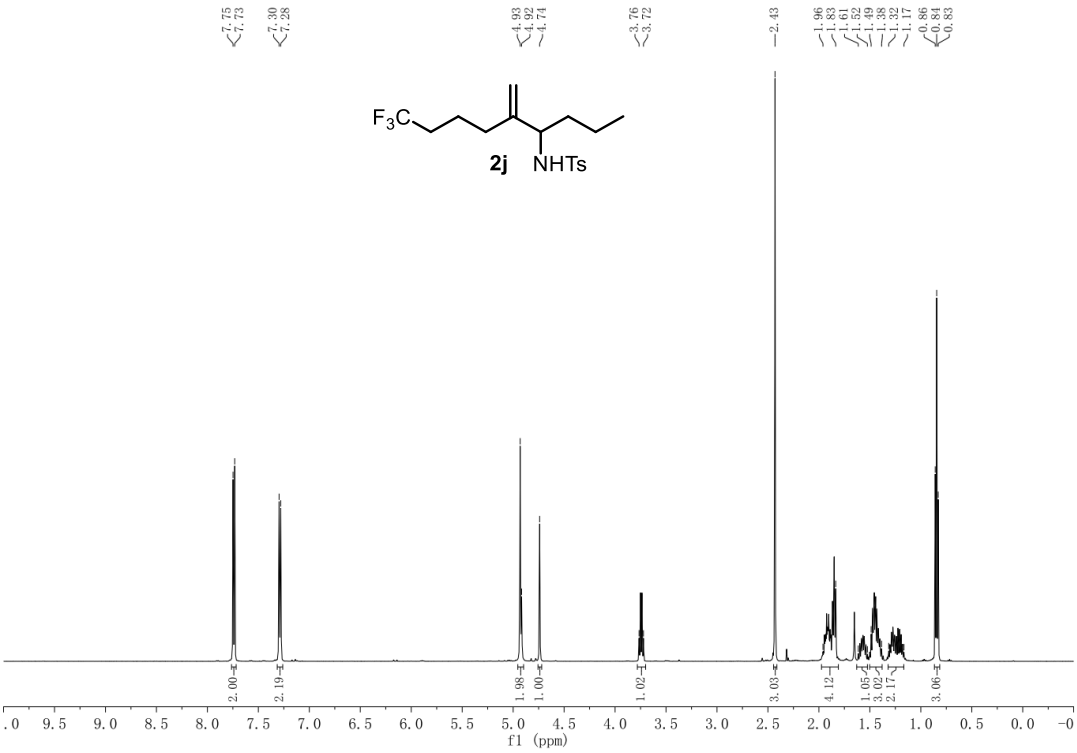
142.2
137.8
134.1
131.9
129.3
127.1
123.4
116.9
57.7
38.5
34.8
31.9
29.5
29.4
29.3
29.1
25.9
22.7
21.5
14.1
f1 (ppm)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4.92
4.74
3.76
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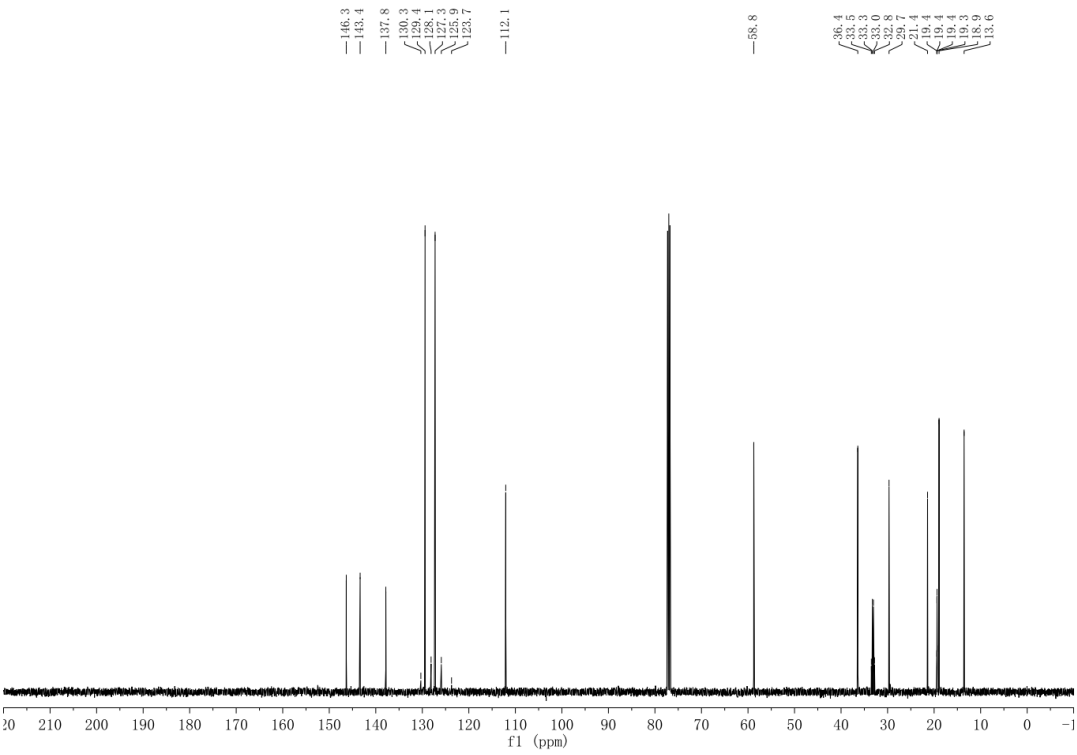
1.96
1.83
1.61
1.52
1.49
1.38
1.32
1.17
0.86
0.84
0.83
F3C
2j NHTs
2.00
2.19
1.98
1.00
1.02
3.03
4.12
1.05
3.02
2.17
3.06
f1 (ppm)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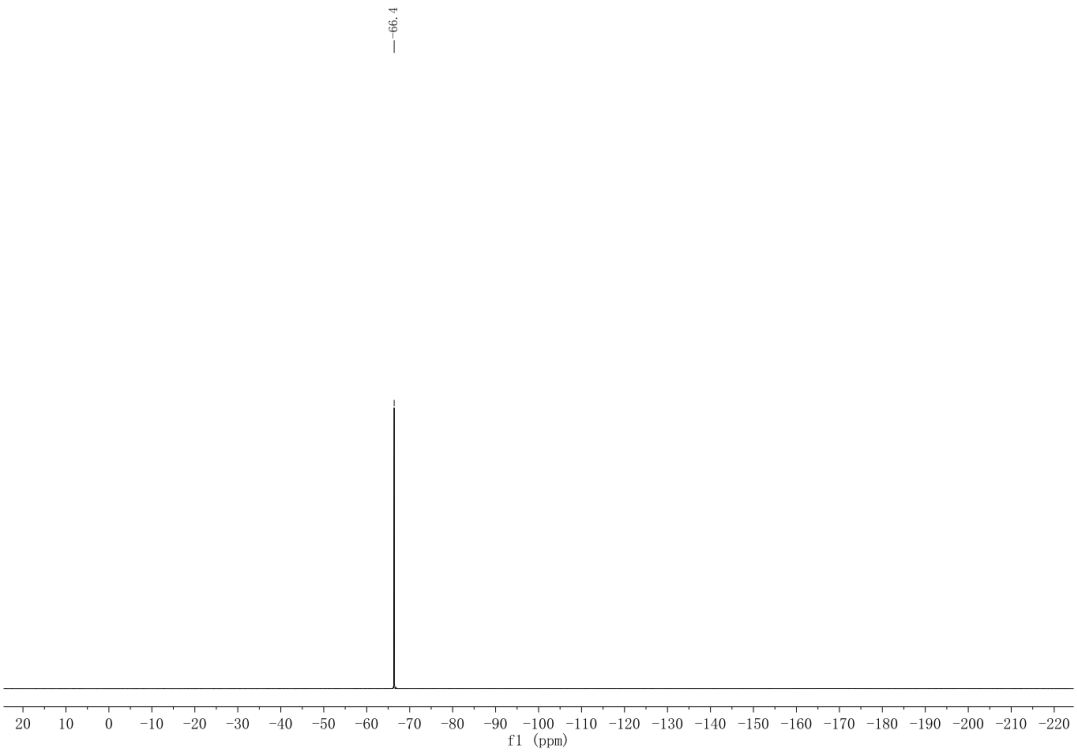
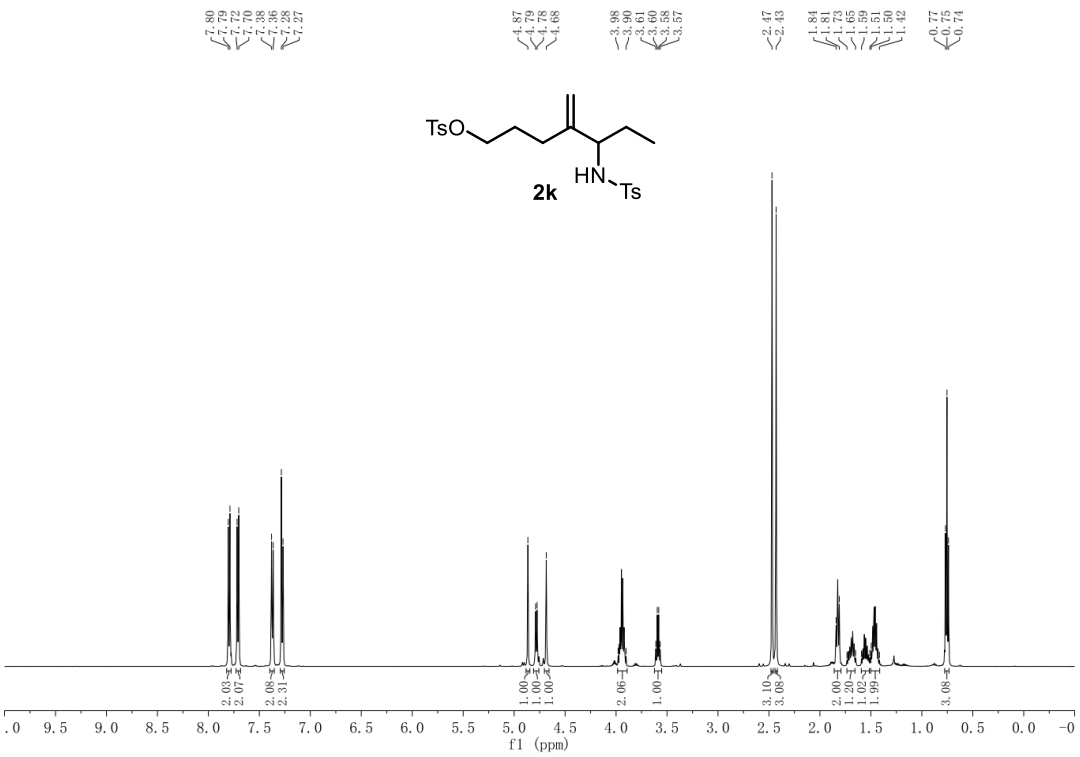
143.4
137.8
130.3
129.4
128.1
127.3
125.9
123.7
112.1
58.8
36.4
33.5
33.3
33.0
32.8
29.7
21.4
19.4
19.4
19.3
18.9
13.6
f1 (ppm)


−66.4
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)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4.78
4.68
3.98
3.90
3.61
3.60
3.58
3.57
2.47
2.43
1.84
1.81
1.73
1.65
1.59
1.51
1.50
1.42
0.77
0.75
0.74
TsO
HN
Ts
2k
2.03
2.07
2.08
2.31
1.00
1.00
1.00
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1.00
3.10
3.08
2.00
1.20
1.02
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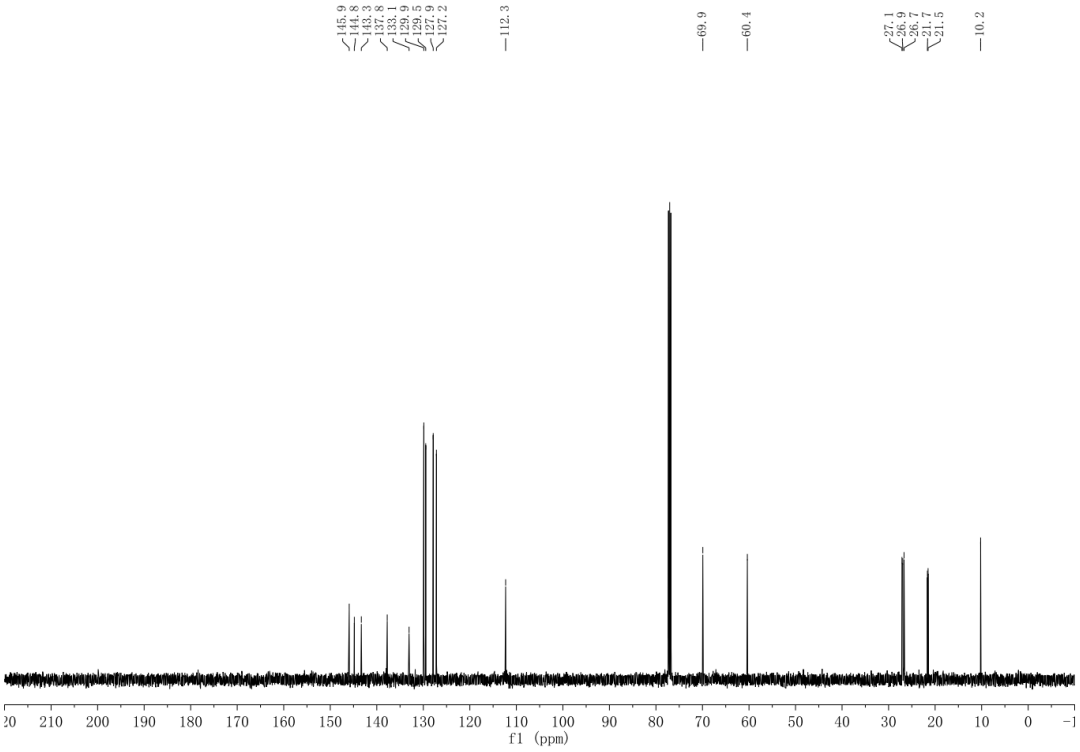
3.08
f1 (ppm)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129.9
129.5
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127.2
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60.4
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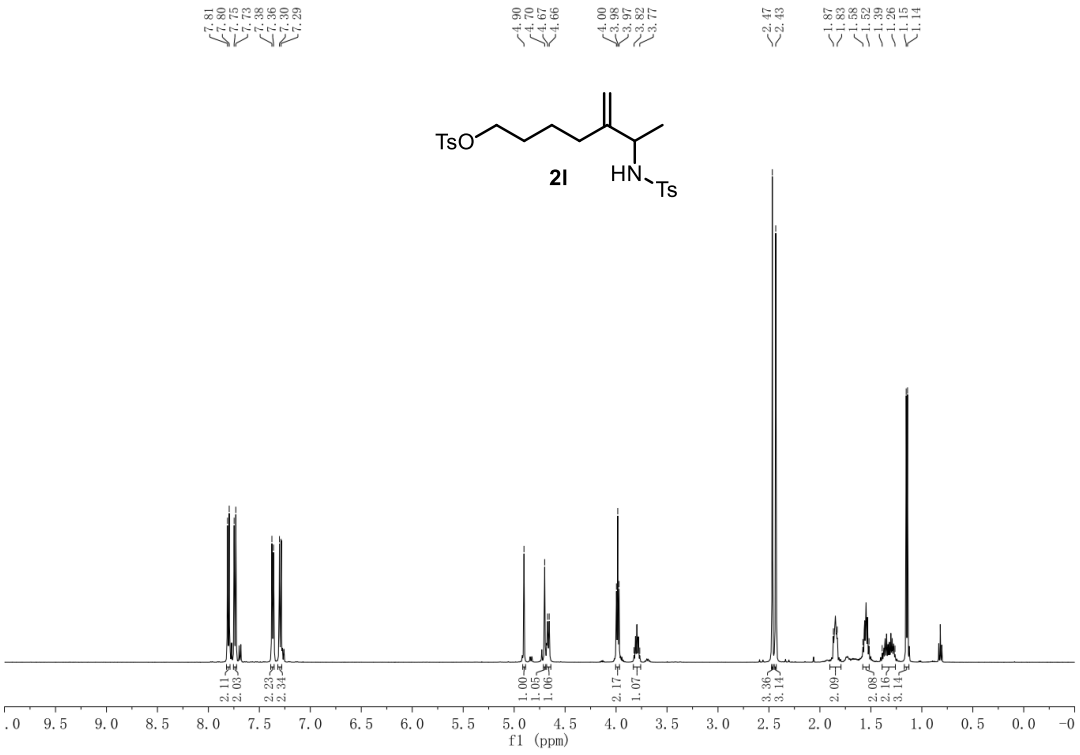
26.7
21.7
21.5
10.2
f1 (ppm)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7.29
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4.70
4.67
4.66
4.00
3.98
3.97
3.82
3.77
2.47
2.43
1.87
1.83
1.58
1.52
1.39
1.26
1.15
1.14
TsO
HN
Ts
2l
2.11
2.03
2.23
2.34
1.00
1.05
1.06
2.17
1.07
3.36
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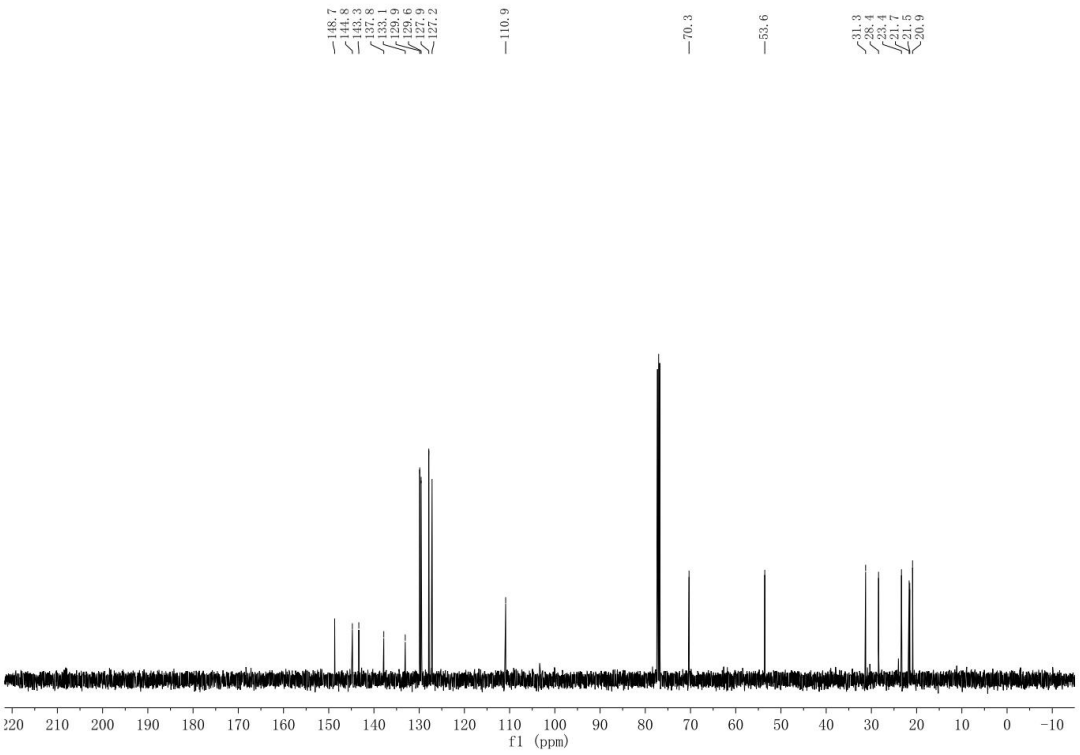
2.09
2.08
2.16
3.14
f1 (ppm)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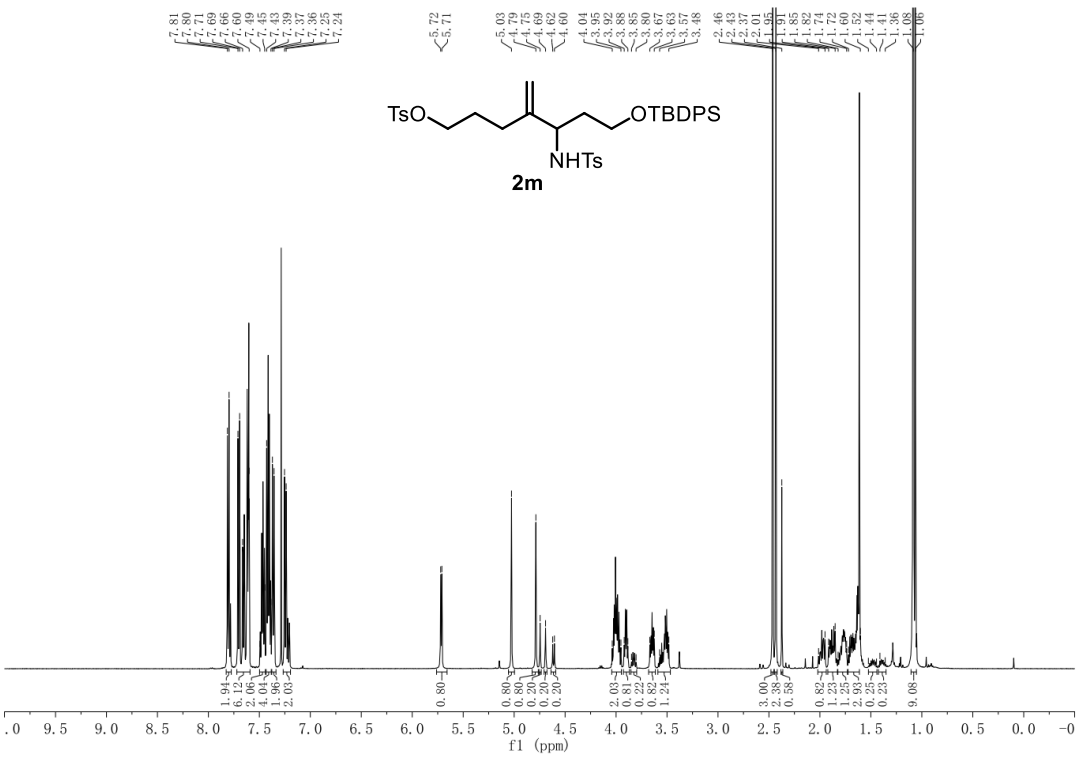
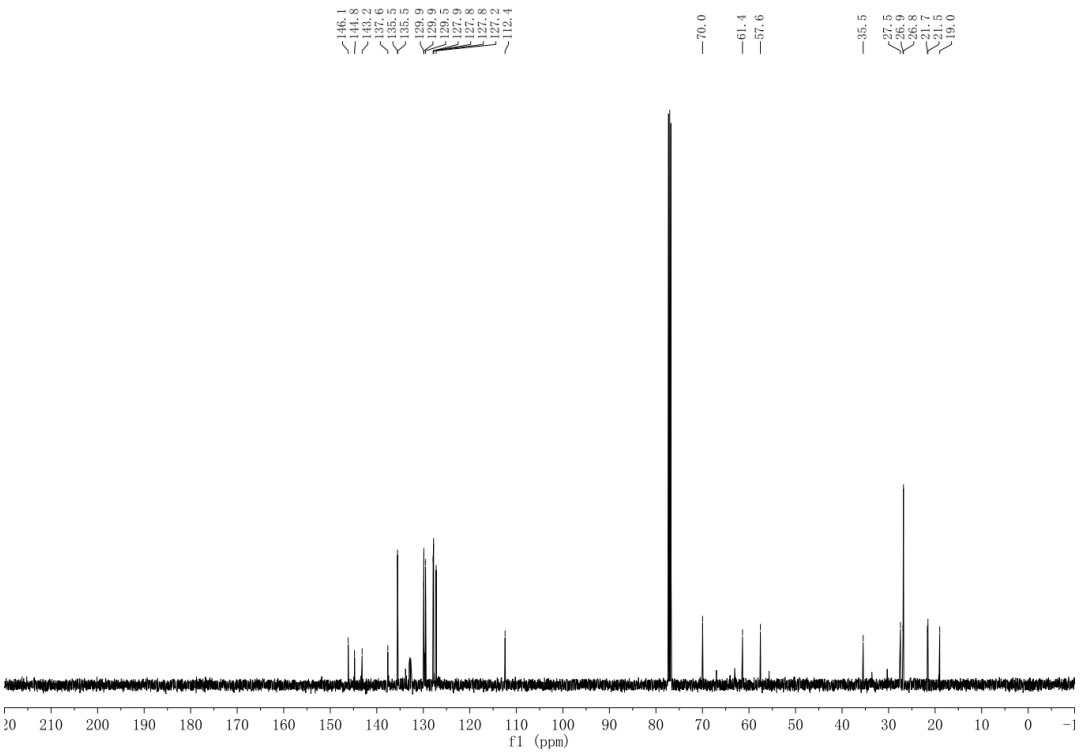
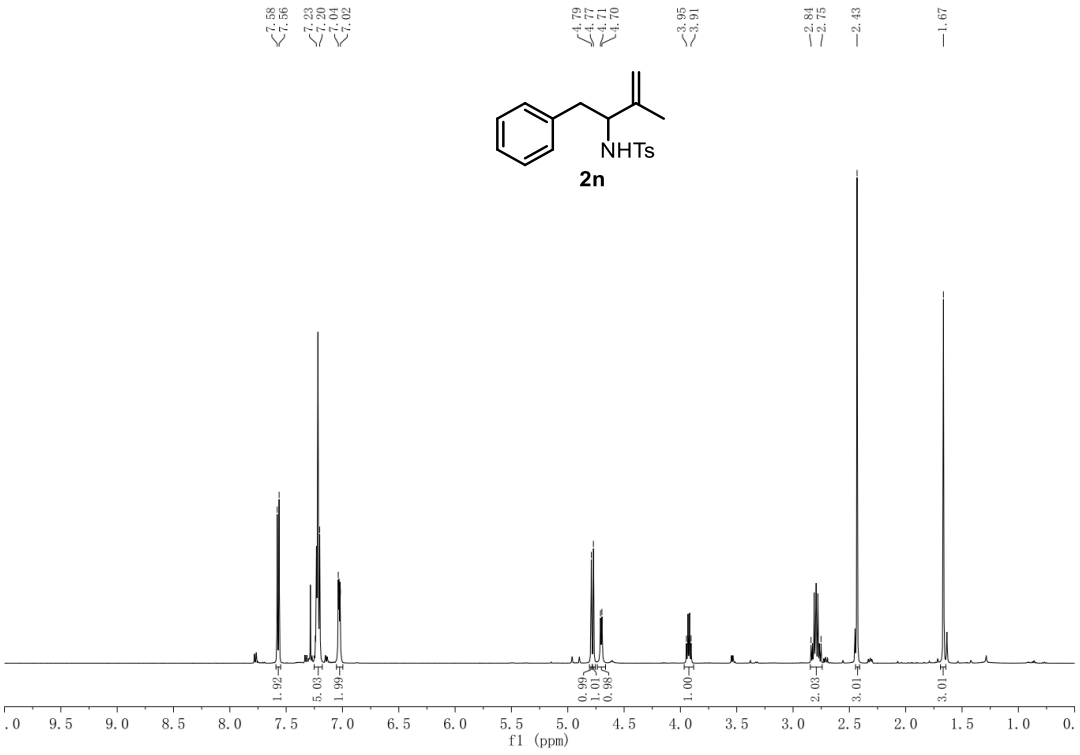
143.3
137.8
133.1
129.9
129.6
127.9
127.2
110.9
70.3
53.6
31.3
28.4
23.4
21.7
21.5
20.9
f1 (ppm)


TsO
OTBDPS
NHTs
2m
f1 (ppm)


f1 (ppm)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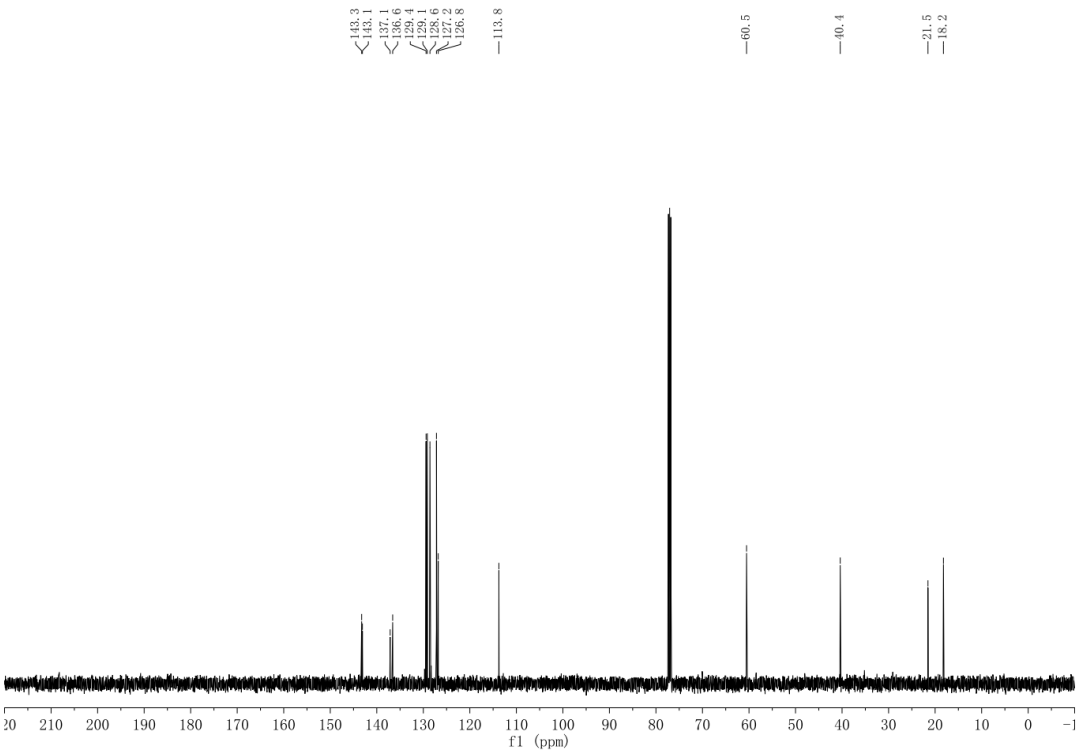
3.91
2.84
2.75
2.43
1.67
NHTs
2n
1.92
5.03
1.99
0.99
1.01
0.98
1.00
2.03
3.01
3.01
f1 (ppm)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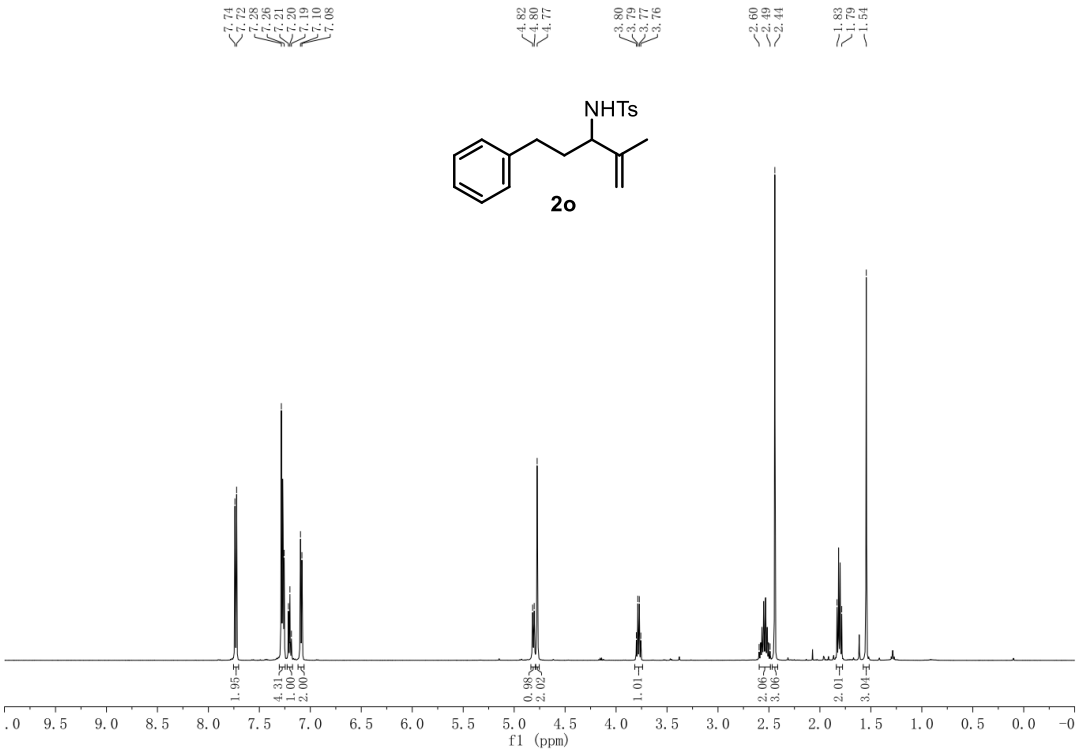
143.1
137.1
136.6
129.4
129.1
128.6
127.2
126.8
113.8
60.5
40.4
21.5
18.2
f1 (ppm)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3.79
3.77
3.76
2.60
2.49
2.44
1.83
1.79
1.54
NHTs
2o
1.95
4.31
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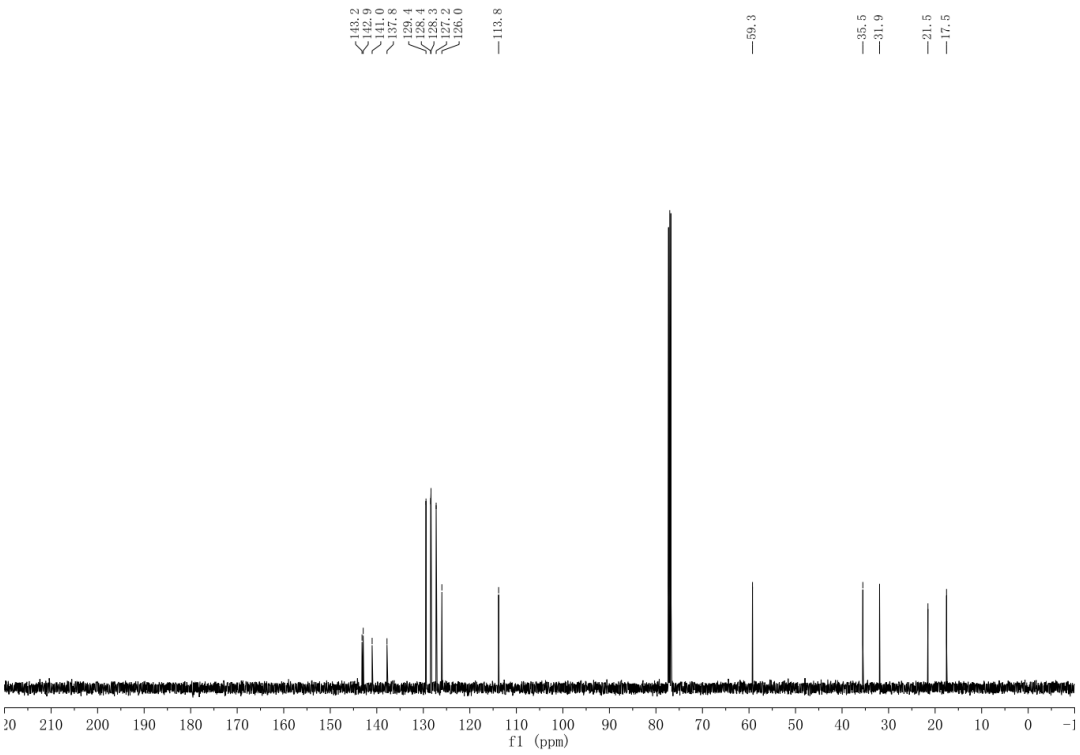
2.00
0.98
2.02
1.01
2.06
3.06
2.01
3.04
f1 (ppm)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142.9
141.0
137.8
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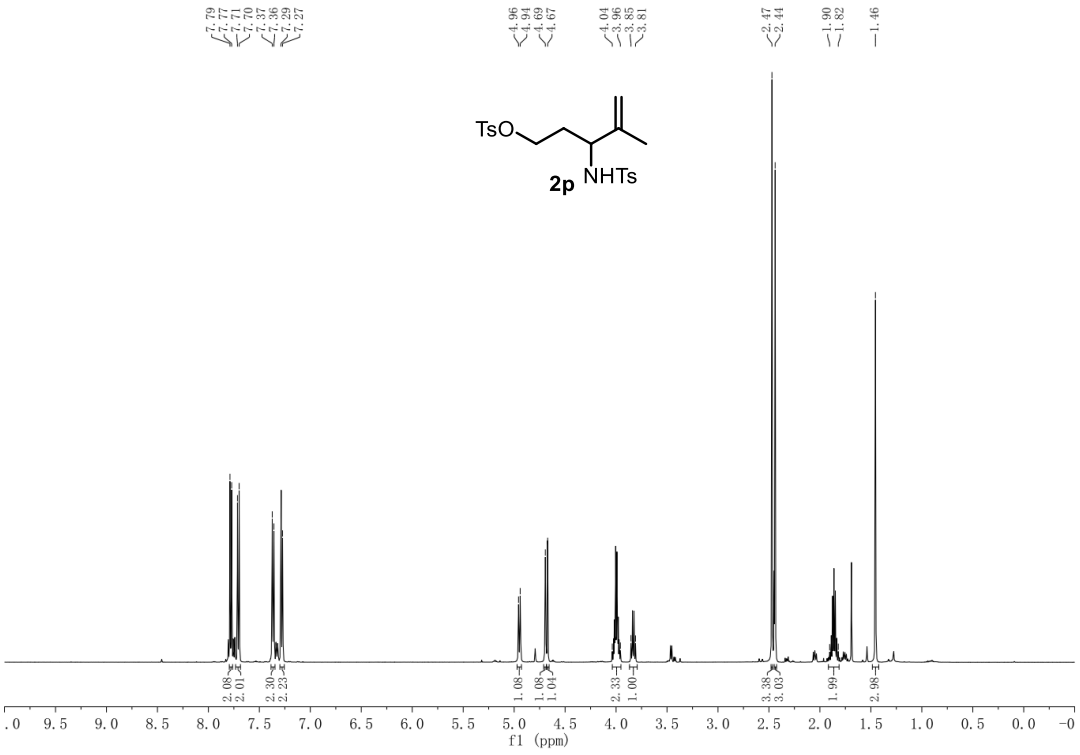
127.2
126.0
113.8
59.3
35.5
31.9
21.5
17.5
f1 (ppm)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7.77
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7.36
7.29
7.27
4.96
4.94
4.69
4.67
4.04
3.96
3.85
3.81
2.47
2.44
1.90
1.82
1.46
TsO
NHTs
2p
2.08
2.01
2.30
2.23
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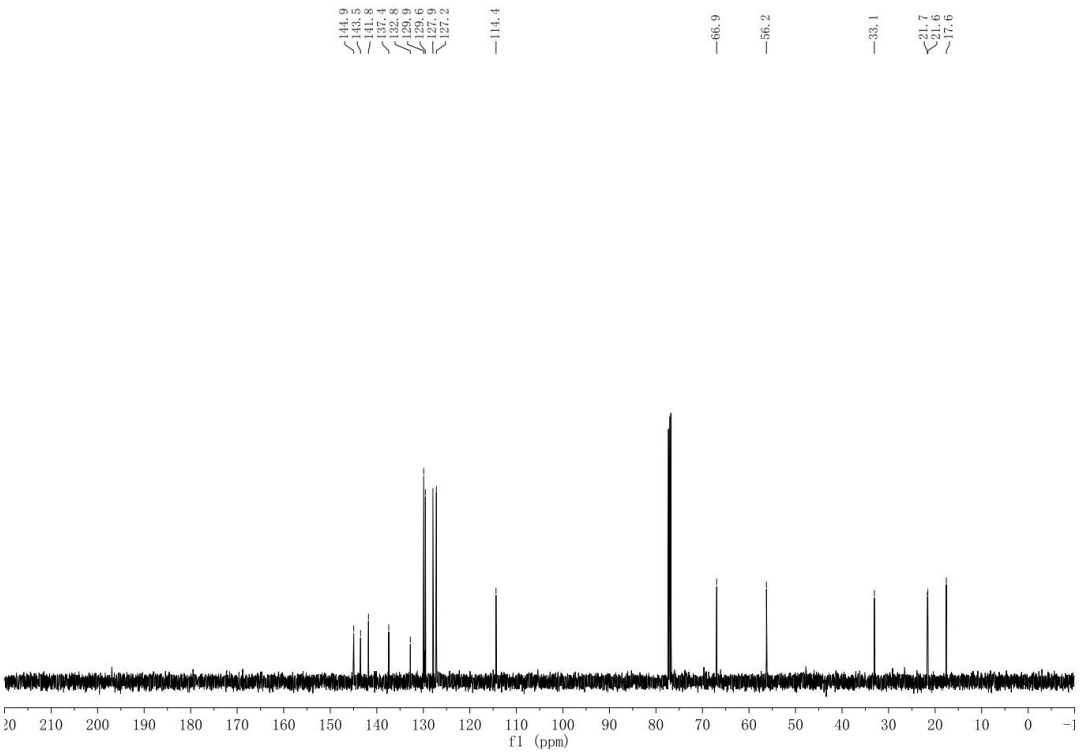
1.08
1.04
2.33
1.00
3.38
3.03
1.99
2.98
f1 (ppm)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137.4
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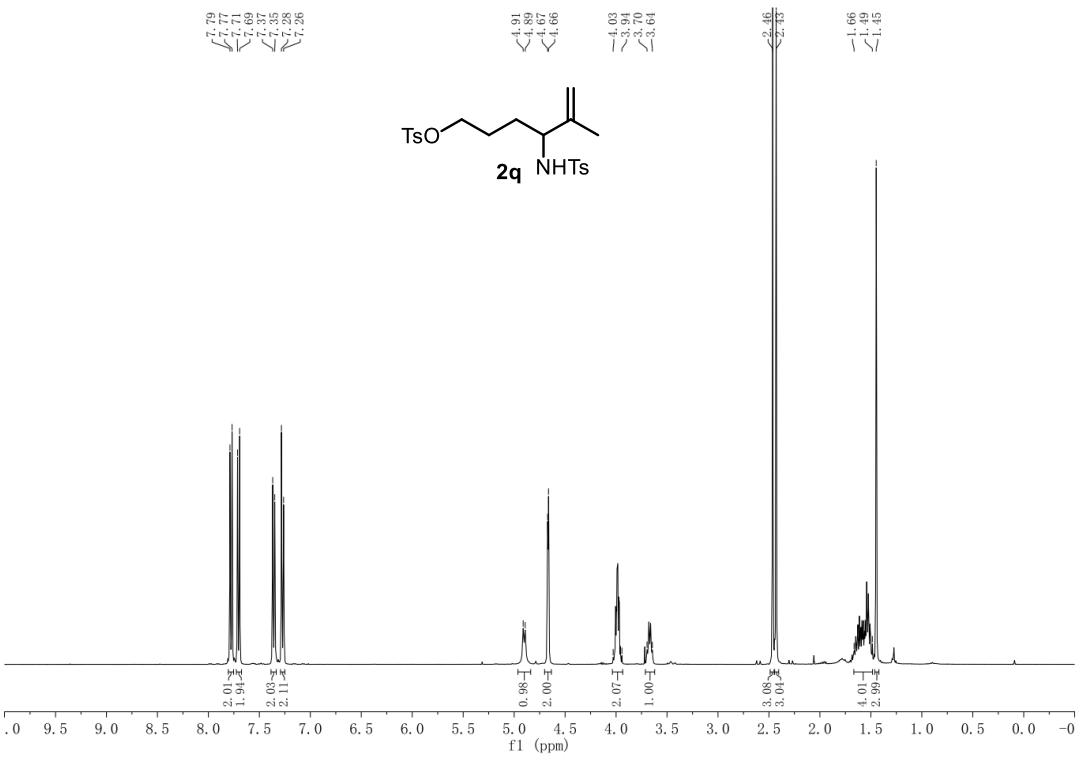
114.4
66.9
56.2
33.1
21.7
21.6
17.6
f1 (ppm)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7.26
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4.89
4.67
4.66
4.03
3.94
3.70
3.64
2.46
2.43
1.66
1.49
1.45
TsO
NHTs
2q
2.01
1.94
2.03
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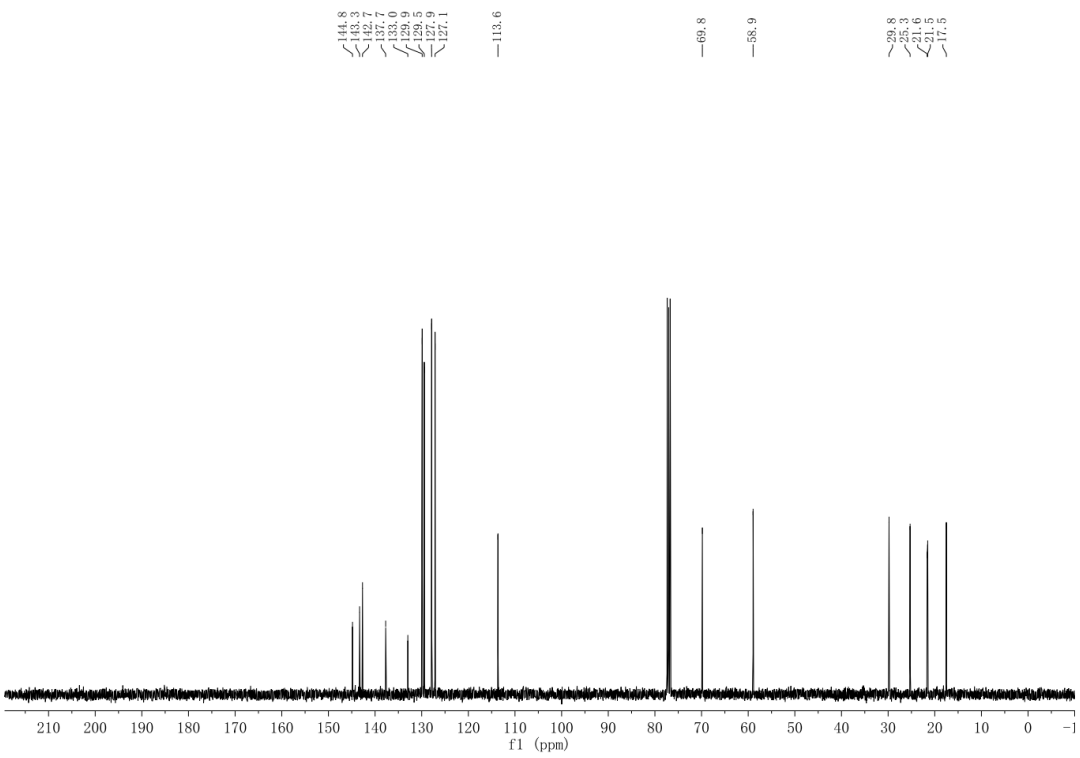
0.98
2.00
2.07
1.00
3.08
3.04
4.01
2.99
f1 (ppm)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142.7
137.7
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129.9
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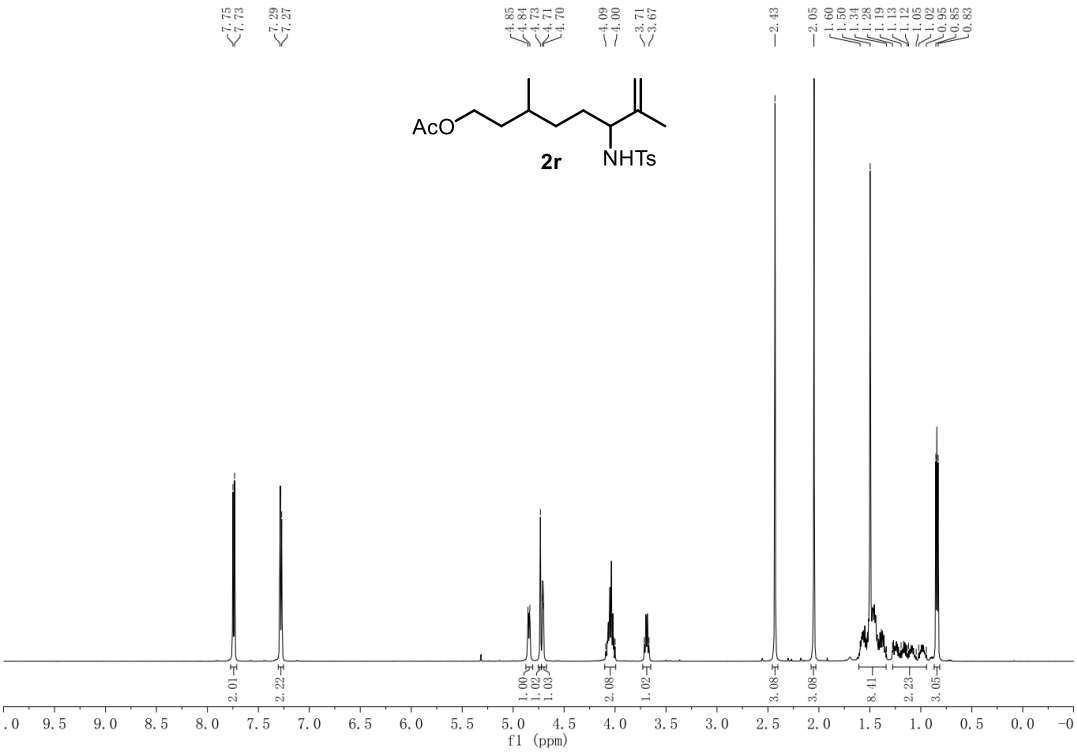
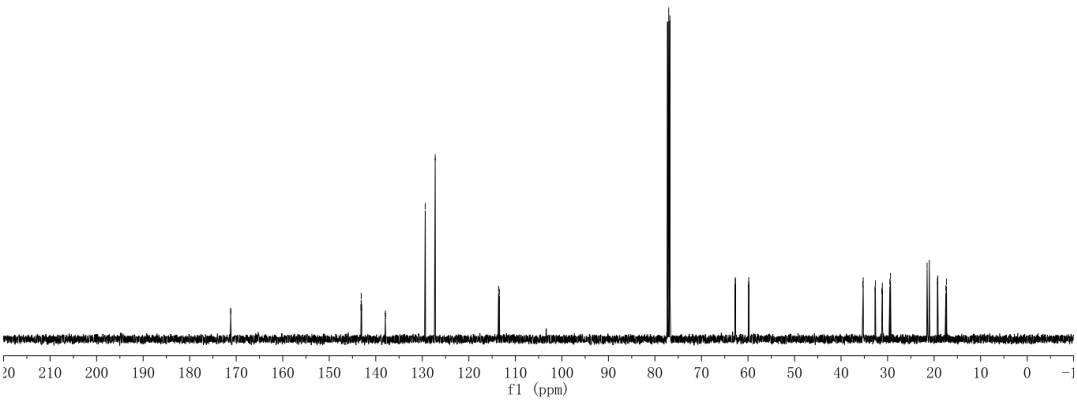
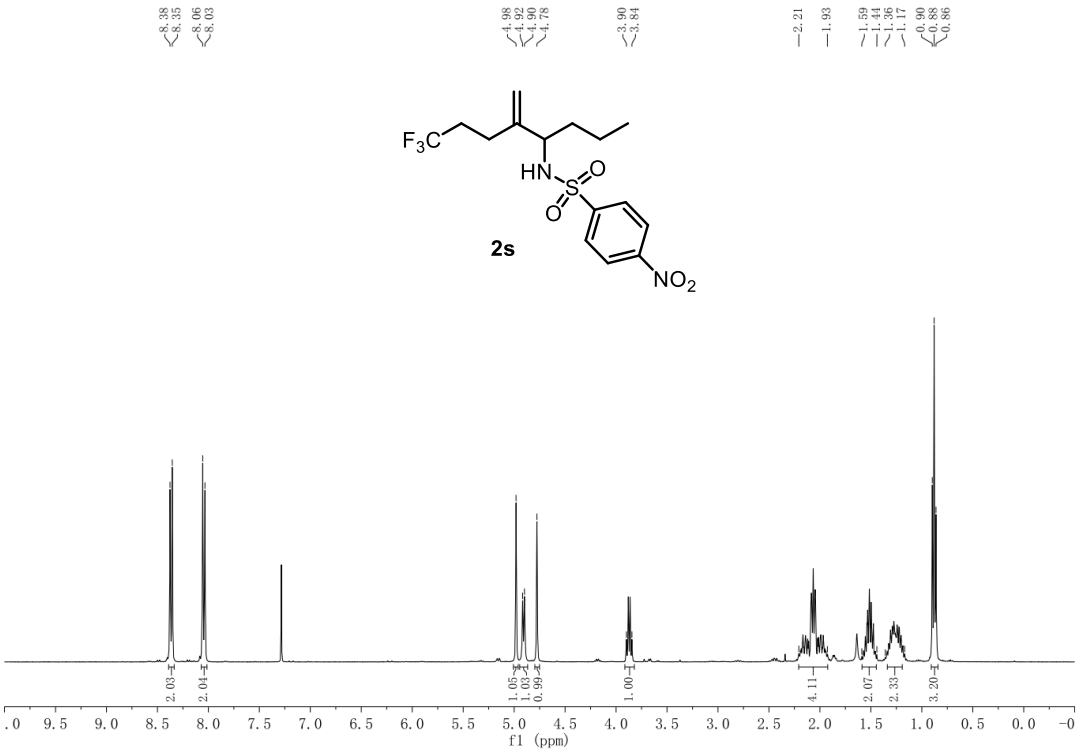
127.9
127.1
113.6
69.8
58.9
29.8
25.3
21.6
21.5
17.5
f1 (ppm)


AcO
NHTs
2r
f1 (ppm)


f1 (ppm)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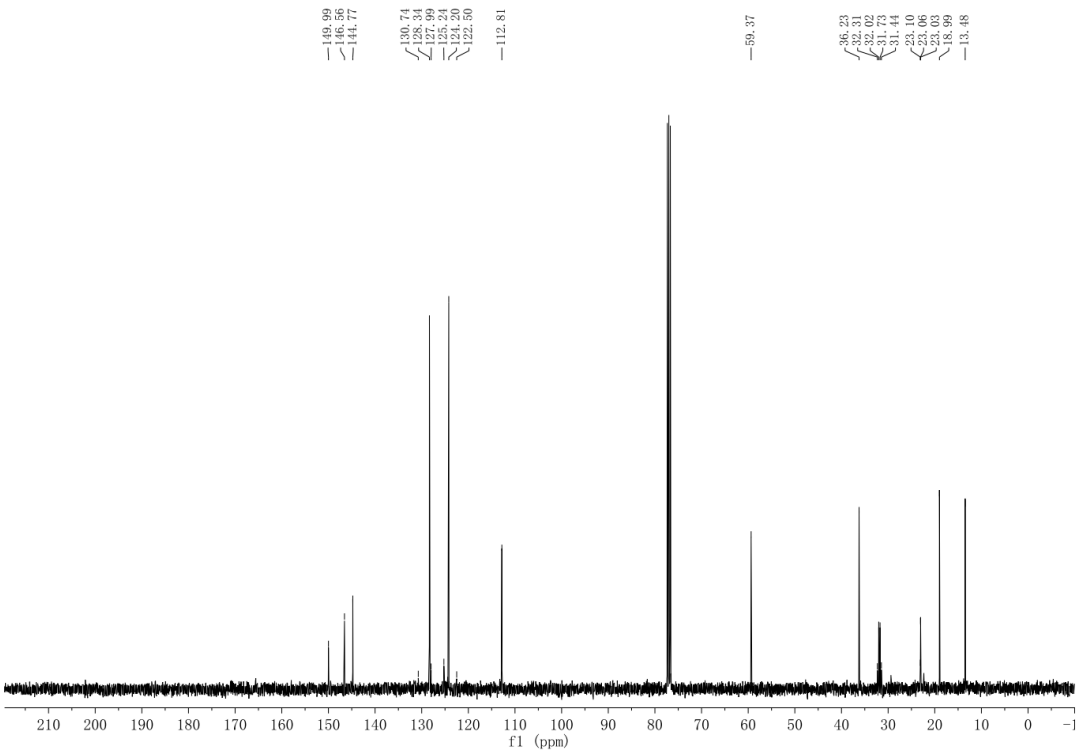
4.92
4.90
4.78
3.90
3.84
2.21
1.93
1.59
1.44
1.36
1.17
0.90
0.88
0.86
F3C
HN
S
O
O
2s
NO2
2.03
2.04
1.05
1.03
0.99
1.00
4.11
2.07
2.33
3.20
f1 (ppm)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124.20
122.50
112.81
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36.23
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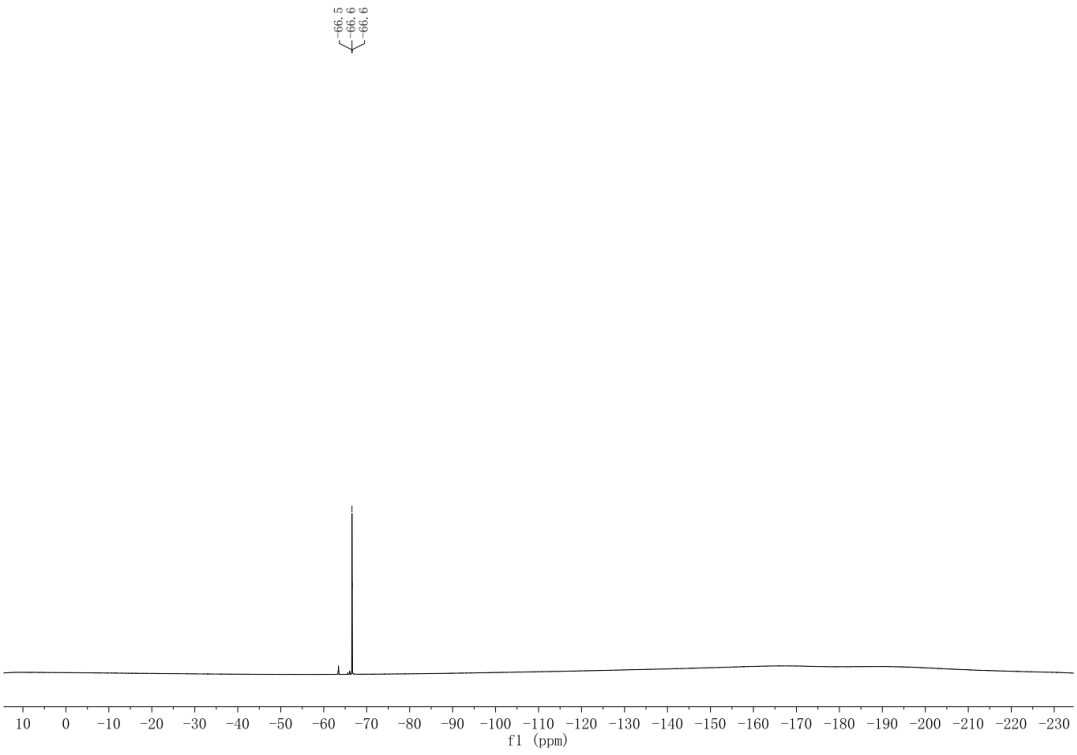
32.02
31.73
31.44
23.10
23.06
23.03
18.99
13.48
f1 (ppm)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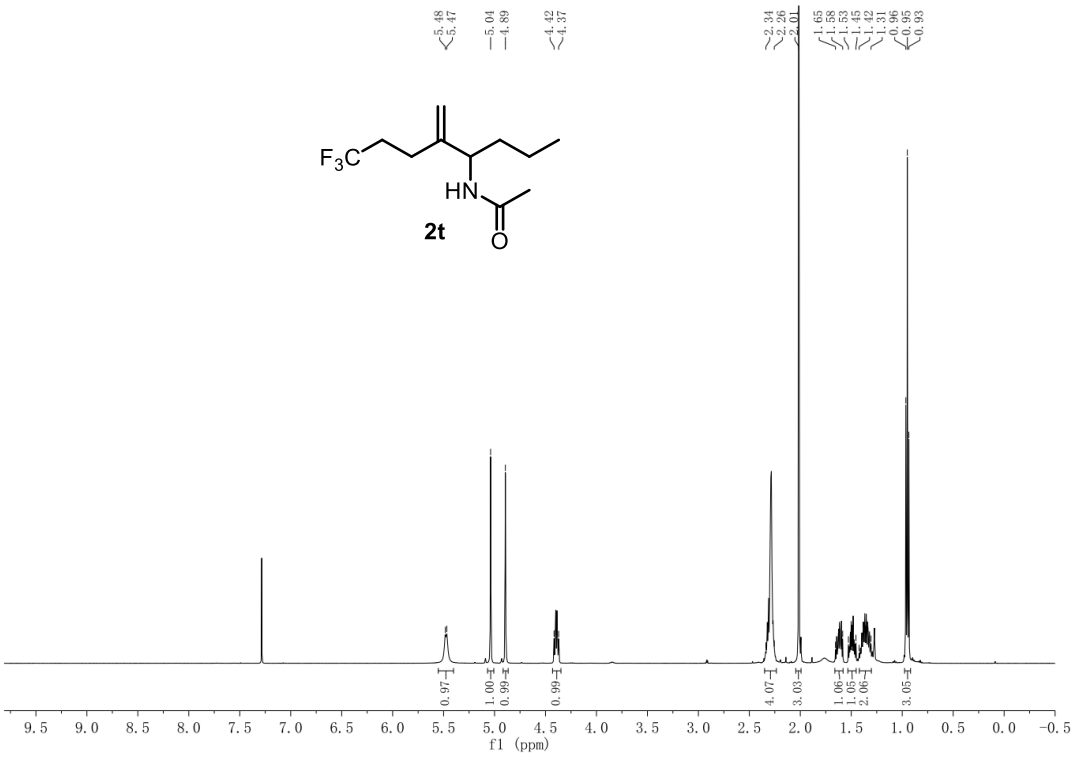
-66.6
-66.6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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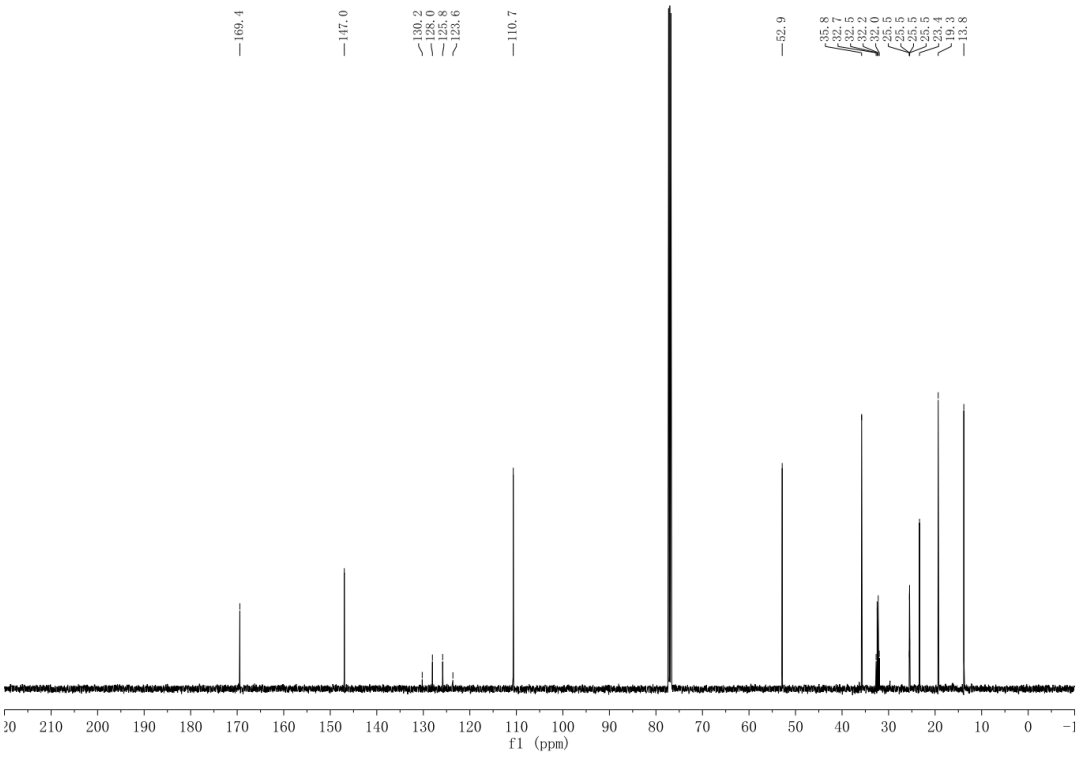
4.42
4.37
2.34
2.26
2.01
1.65
1.58
1.53
1.45
1.42
1.31
0.96
0.95
0.93
F3C
HN
O
2t
0.97
1.00
0.99
0.99
4.07
3.03
1.06
1.05
2.06
3.05
f1 (ppm)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128.0
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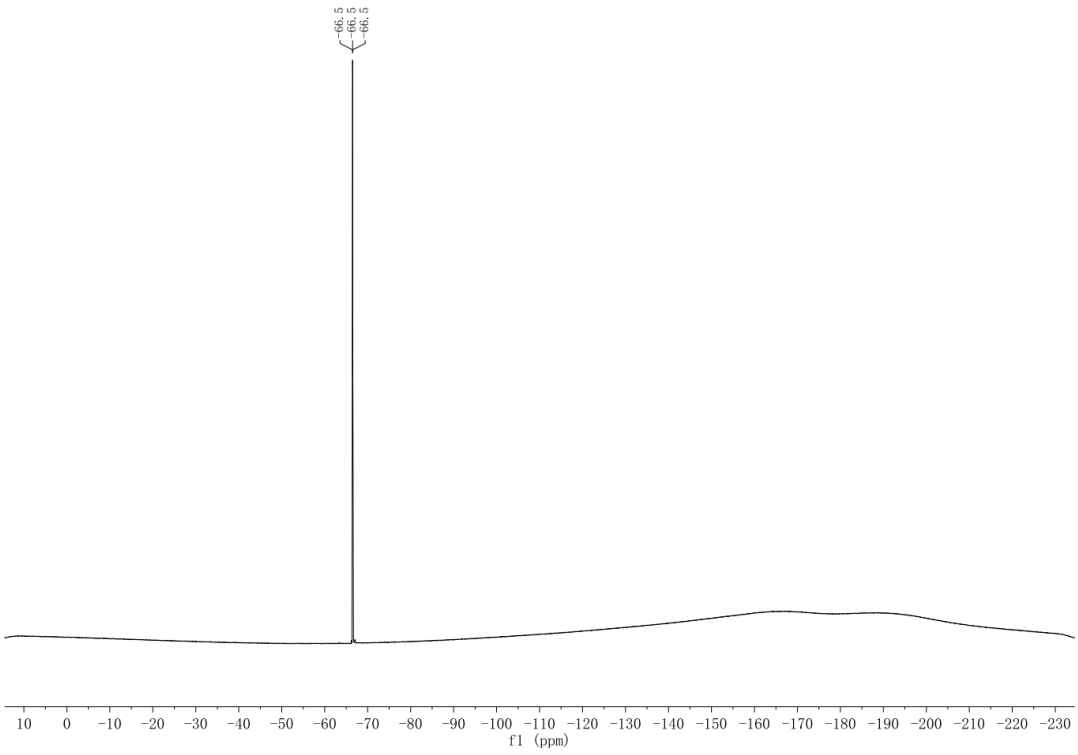
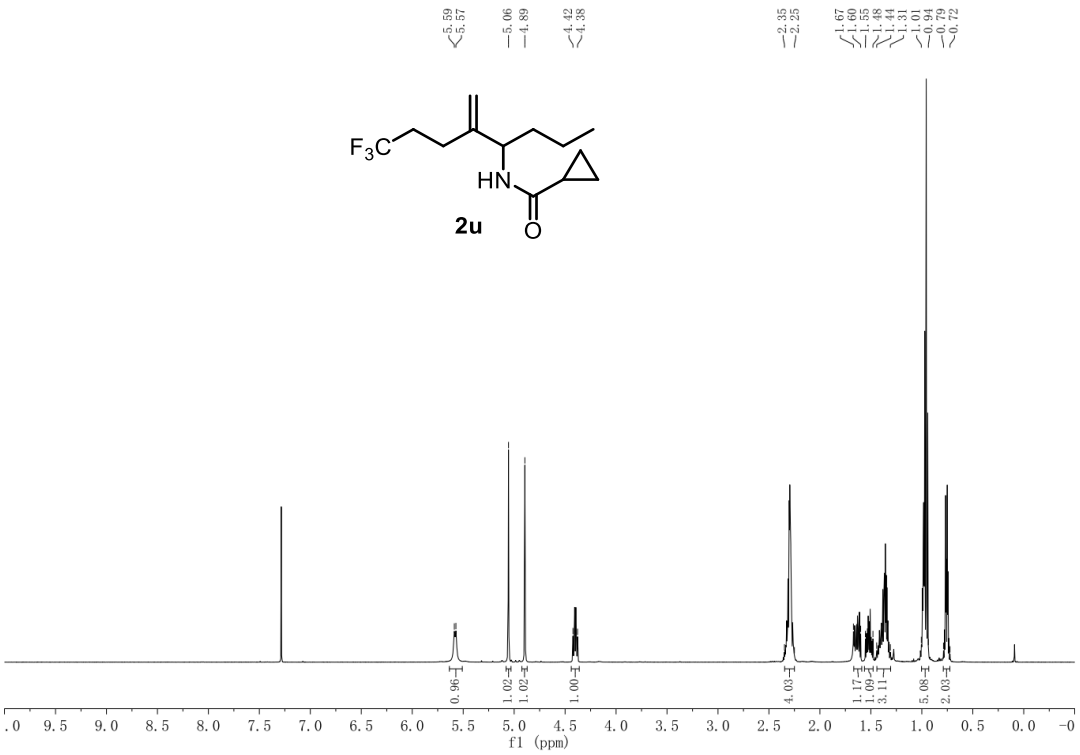
123.6
110.7
52.9
35.8
32.7
32.5
32.2
32.0
25.5
25.5
25.5
25.5
23.4
19.3
13.8
f1 (ppm)


-66.5
-66.5
-66.5
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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5.57
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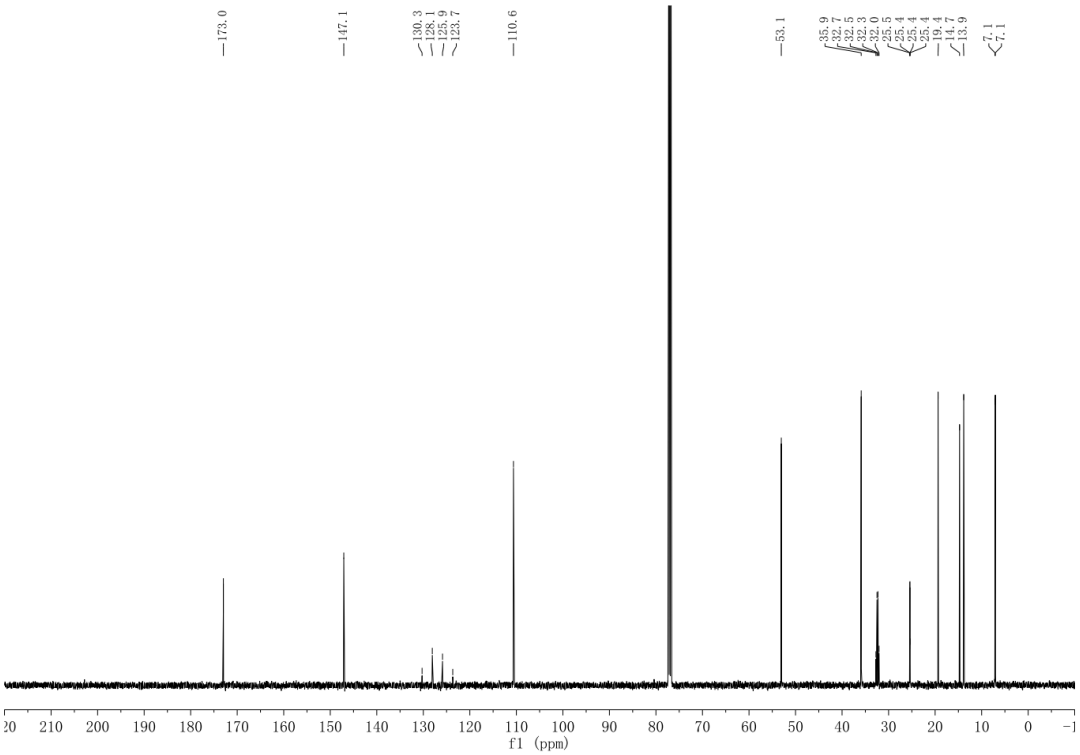
4.89
4.42
4.38
2.35
2.25
1.67
1.60
1.55
1.48
1.44
1.31
1.01
0.94
0.79
0.72
F3C
HN
O
2u
0.96
1.02
1.02
1.00
4.03
1.17
1.09
3.11
5.08
2.03
f1 (ppm)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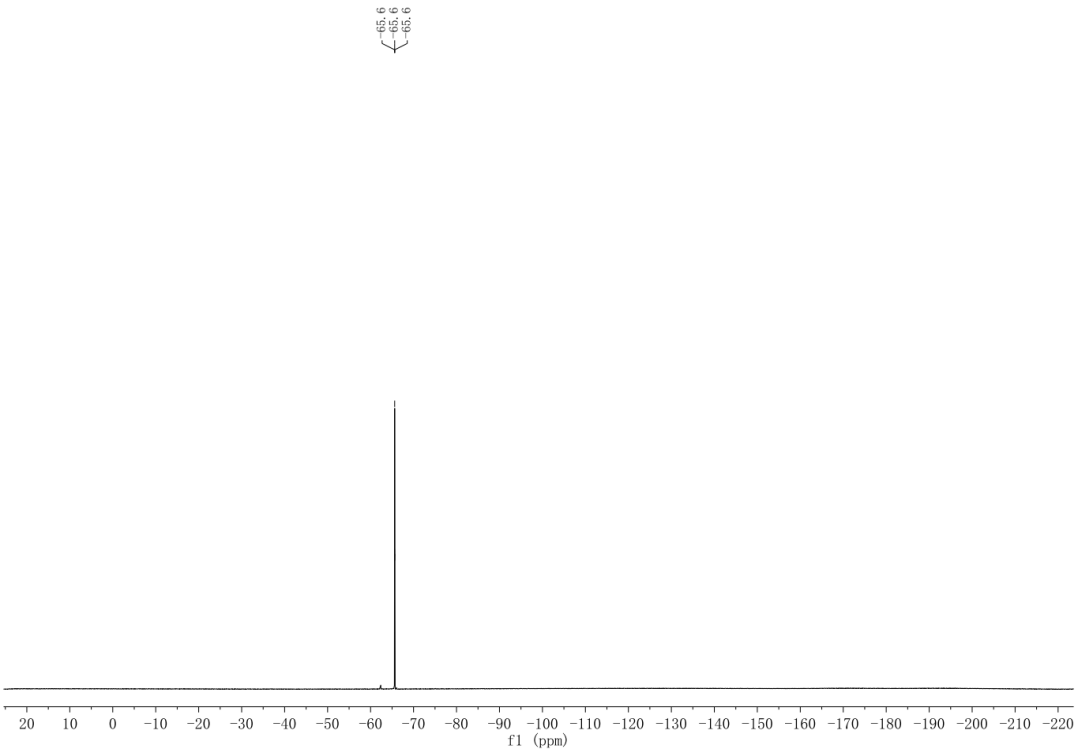
128.1
125.9
123.7
110.6
53.1
35.9
32.7
32.5
32.3
32.0
25.5
25.4
25.4
19.4
14.7
13.9
7.1
7.1
f1 (ppm)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-65.6
-65.6
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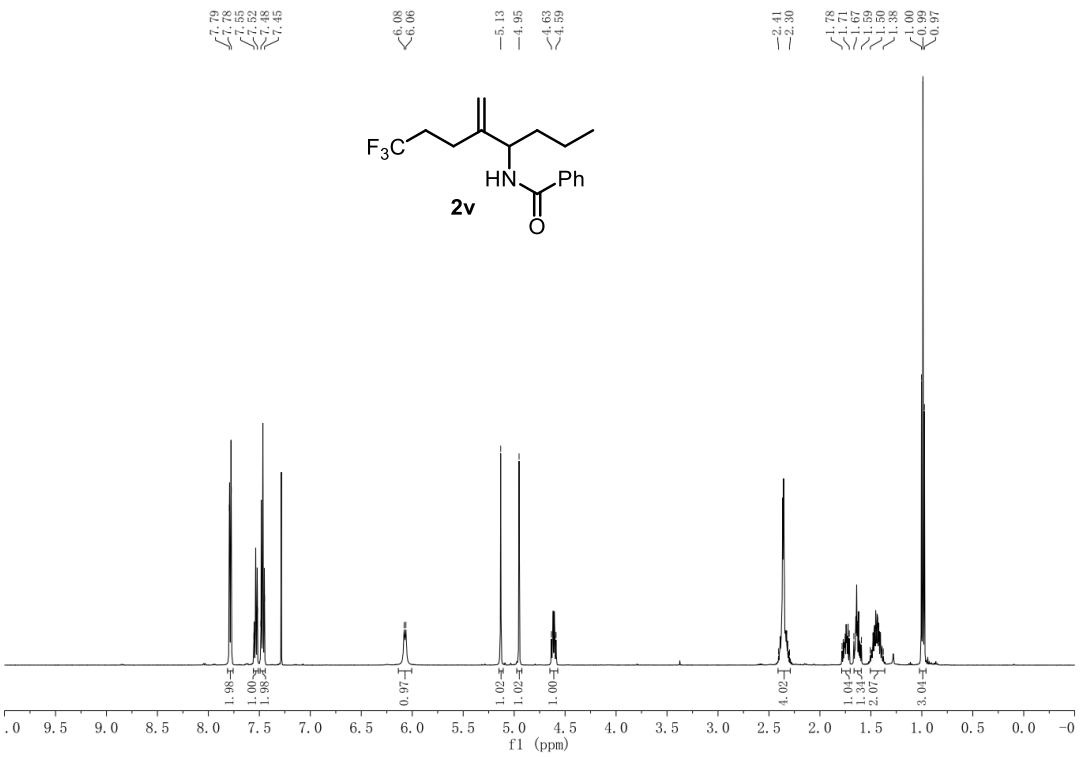
f1 (ppm)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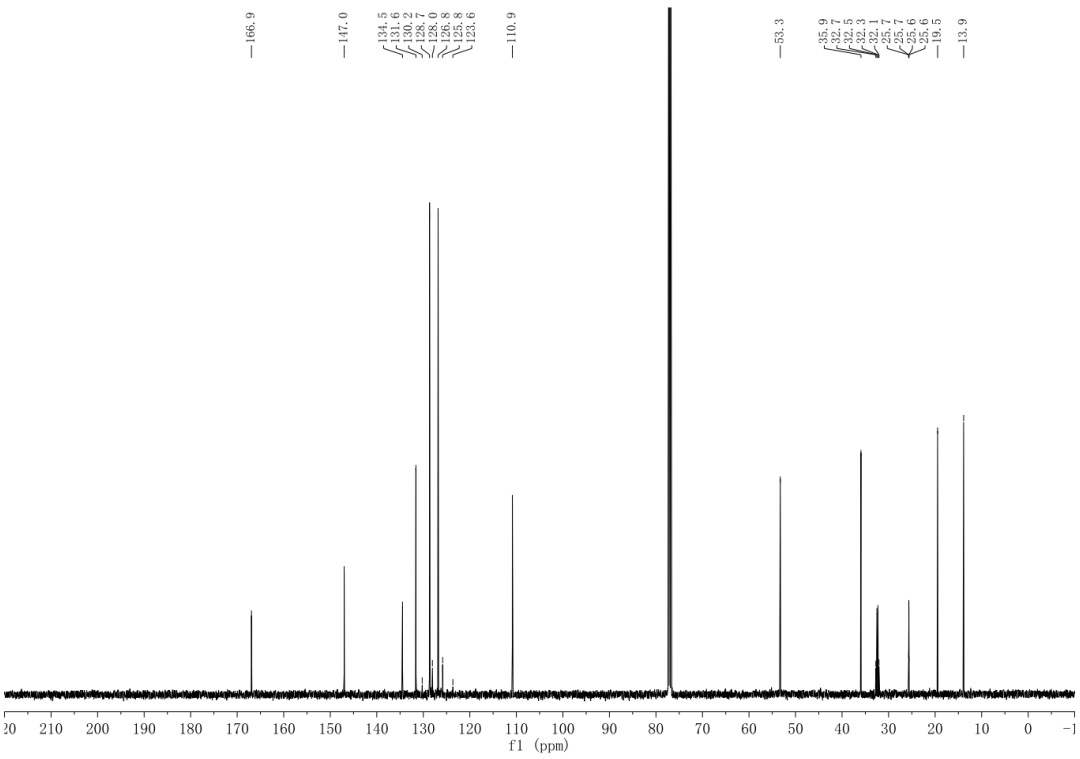
7.48
7.45
6.08
6.06
5.13
4.95
4.63
4.59
2.41
2.30
1.78
1.71
1.67
1.59
1.50
1.38
1.00
0.99
0.97
F3C
HN
Ph
O
2v
1.98
1.00
1.98
0.97
1.02
1.02
1.00
4.02
1.04
1.34
2.07
3.04
f1 (ppm)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126.8
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123.6
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53.3
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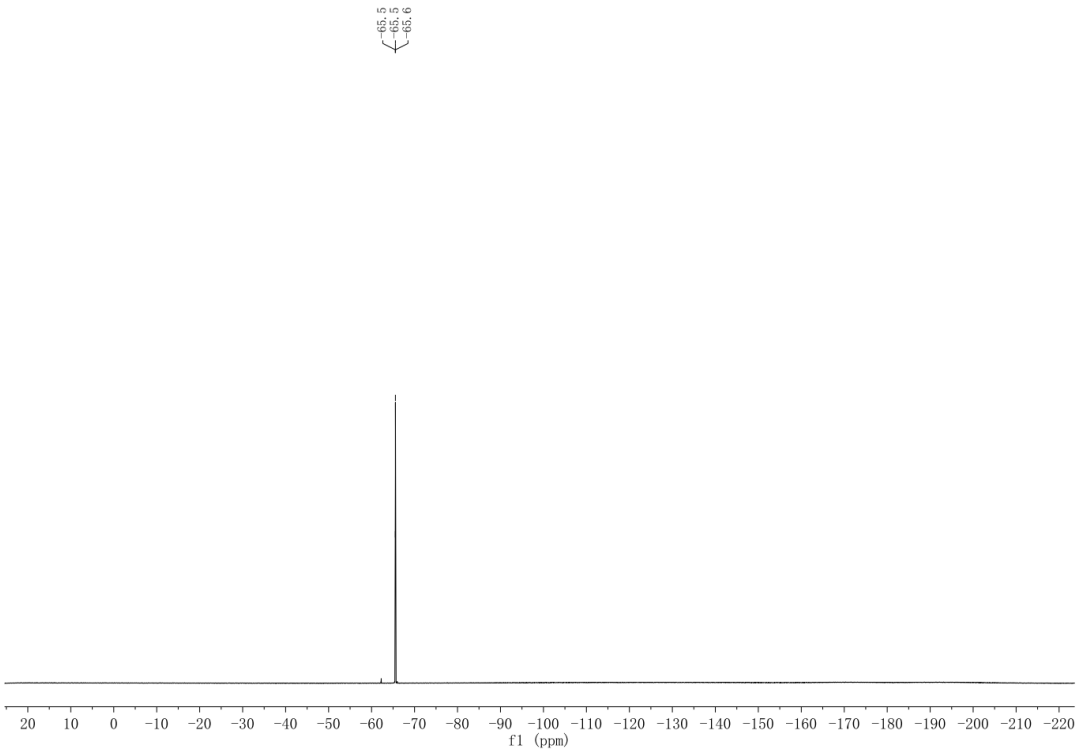
25.6
25.6
19.5
13.9
f1 (ppm)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-65.5
-65.6
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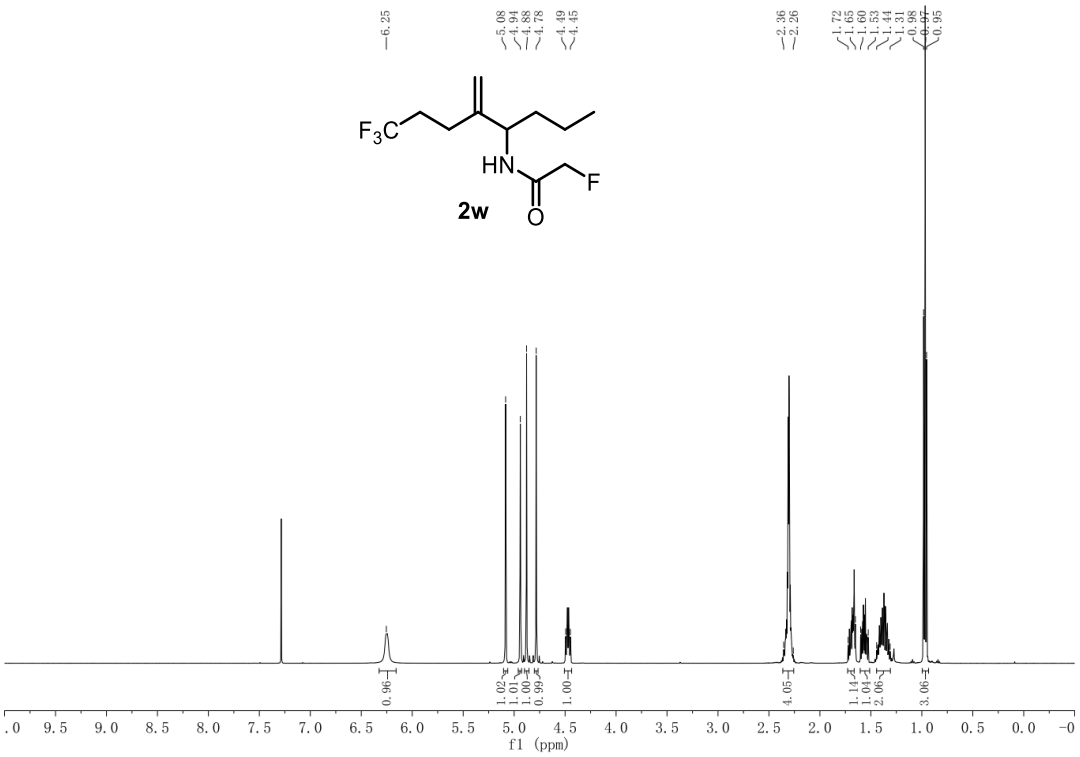
f1 (ppm)


6.25
5.08
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4.78
4.49
4.45
2.36
2.26
1.72
1.65
1.60
1.53
1.44
1.31
0.98
0.97
0.95
F3C
HN
F
O
2w
0.96
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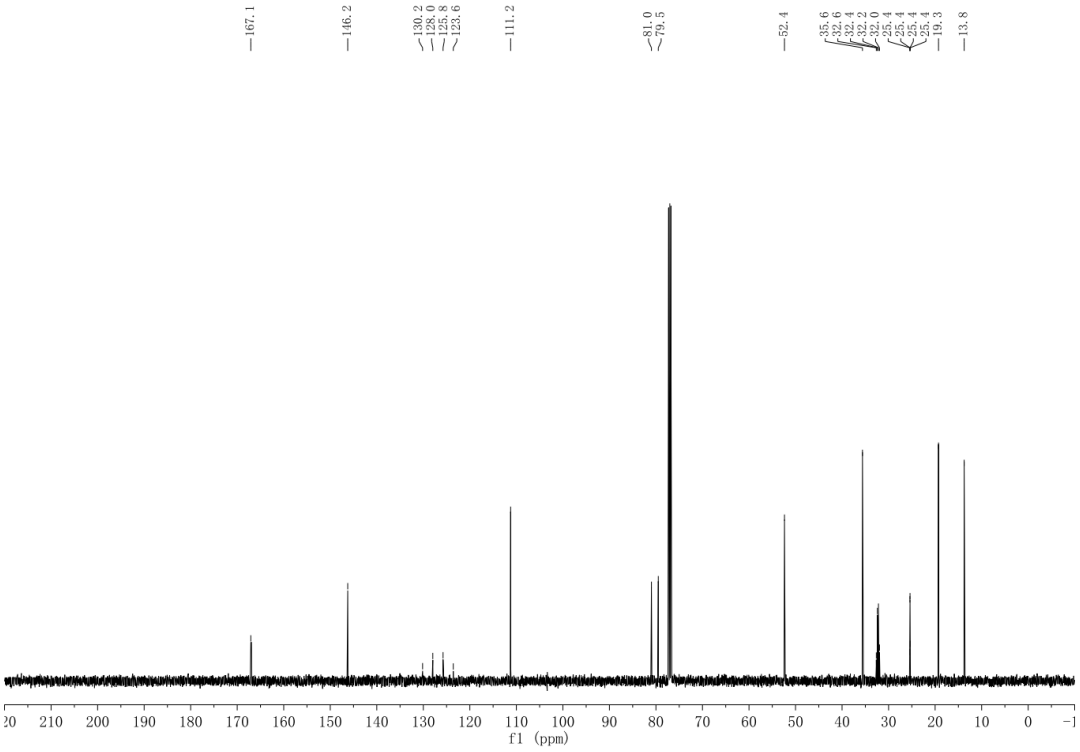
1.00
0.99
1.00
4.05
1.14
1.04
2.06
3.06
f1 (ppm)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130.2
128.0
125.8
123.6
111.2
81.0
79.5
52.4
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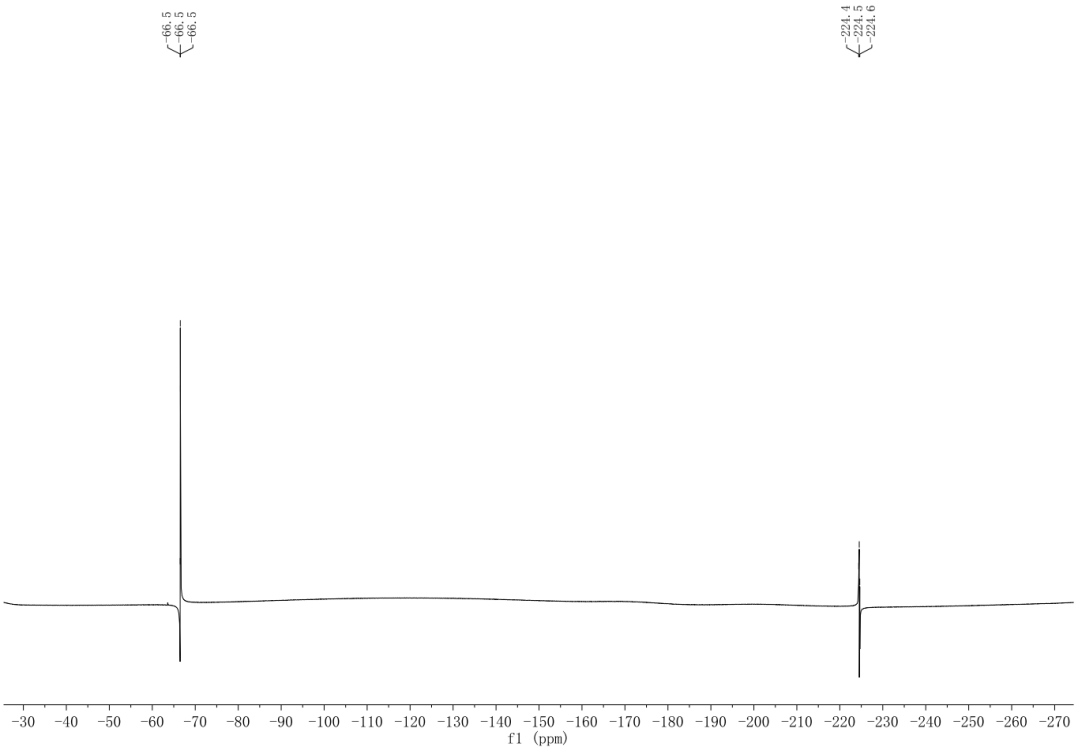
32.2
32.0
25.4
25.4
25.4
25.4
19.3
13.8
f1 (ppm)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-66.5
-66.5
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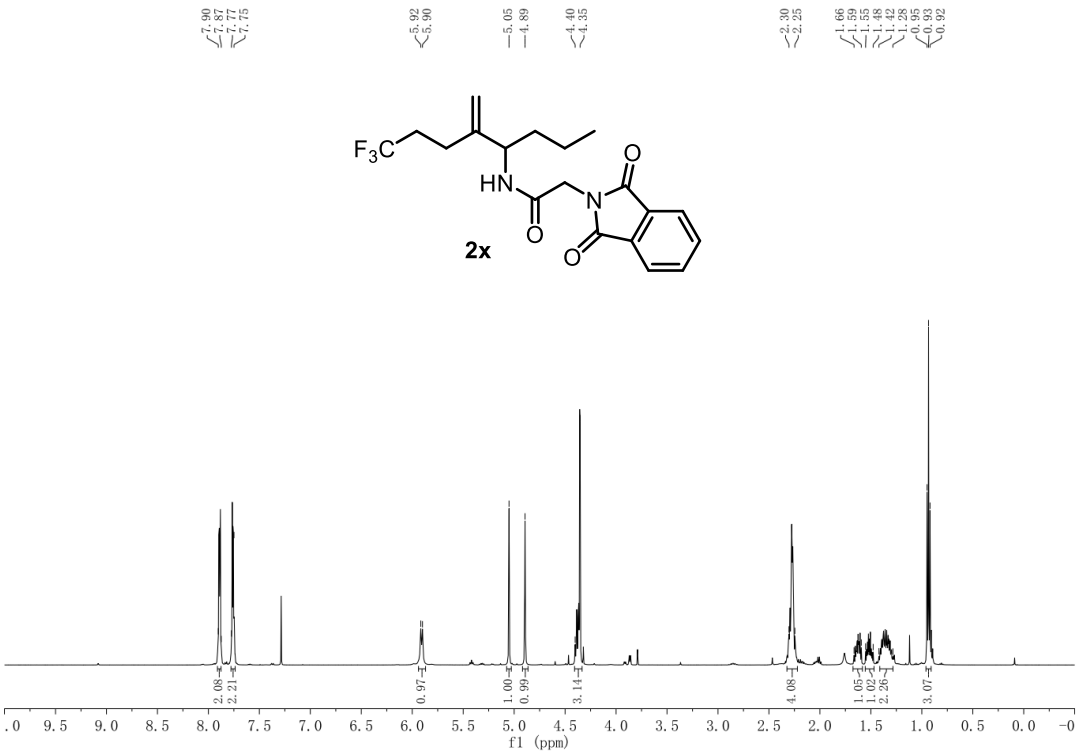
-224.5
-224.6
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)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5.90
5.05
4.89
4.40
4.35
2.30
2.25
1.66
1.59
1.55
1.48
1.42
1.28
0.95
0.93
0.92
F3C
HN
O
N
O
O
2x
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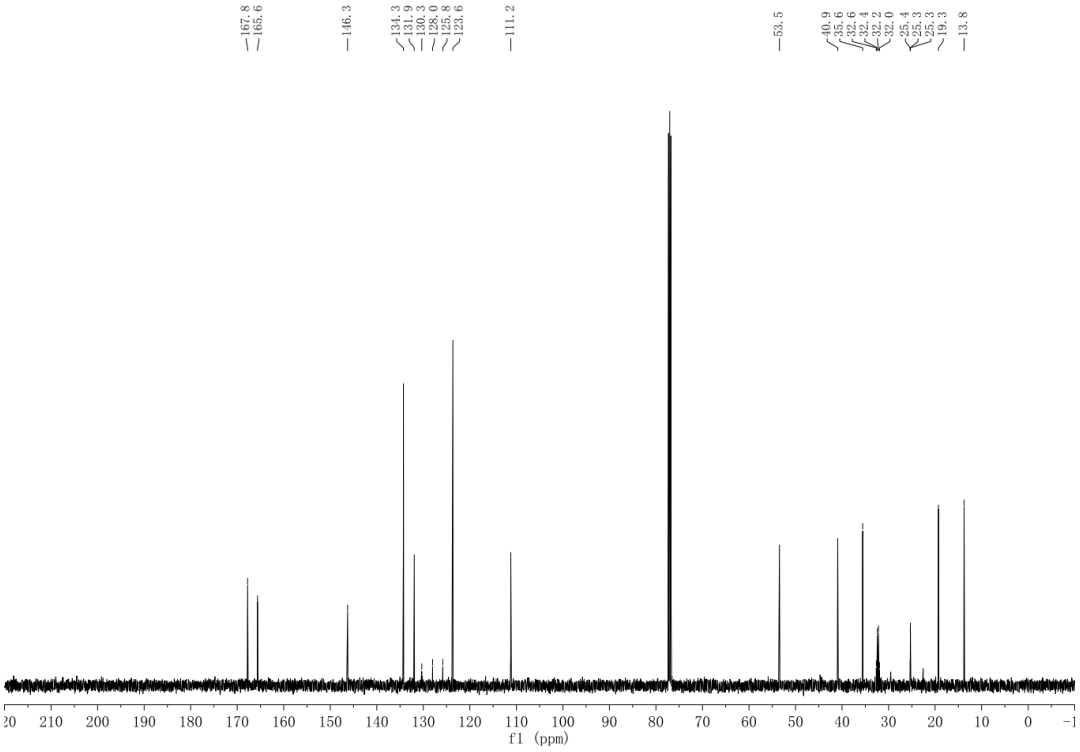
1.00
0.99
3.14
4.08
1.05
1.02
2.26
3.07
f1 (ppm)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130.3
128.0
125.8
123.6
111.2
53.5
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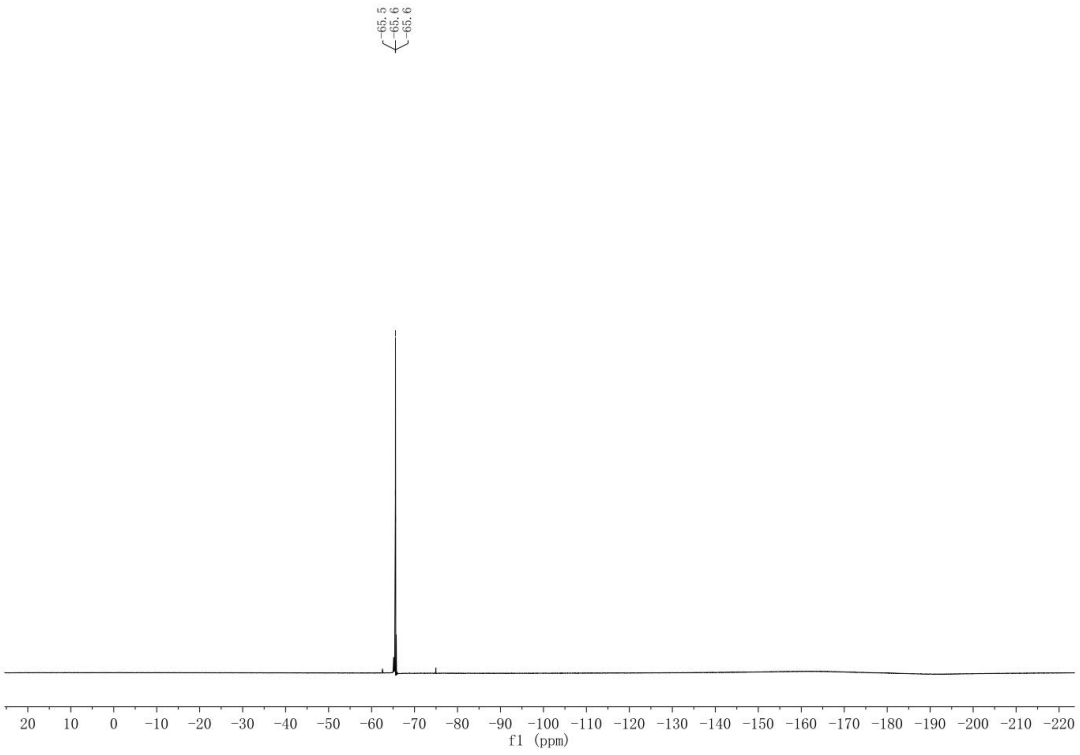
35.6
32.6
32.4
32.2
32.0
25.4
25.3
25.3
19.3
13.8
f1 (ppm)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-65.6
-65.6
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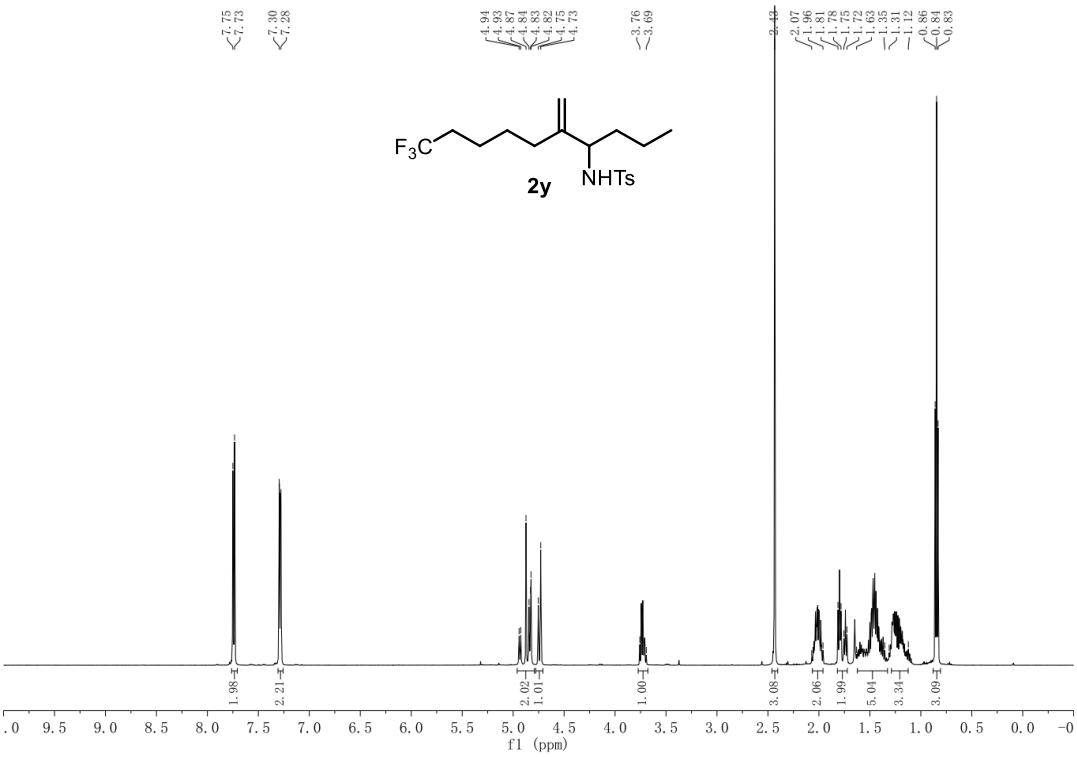
f1 (ppm)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4.82
4.75
4.73
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3.69
2.49
2.07
1.96
1.81
1.78
1.75
1.72
1.63
1.35
1.31
1.12
0.86
0.84
0.83
F3C
NHTs
2y
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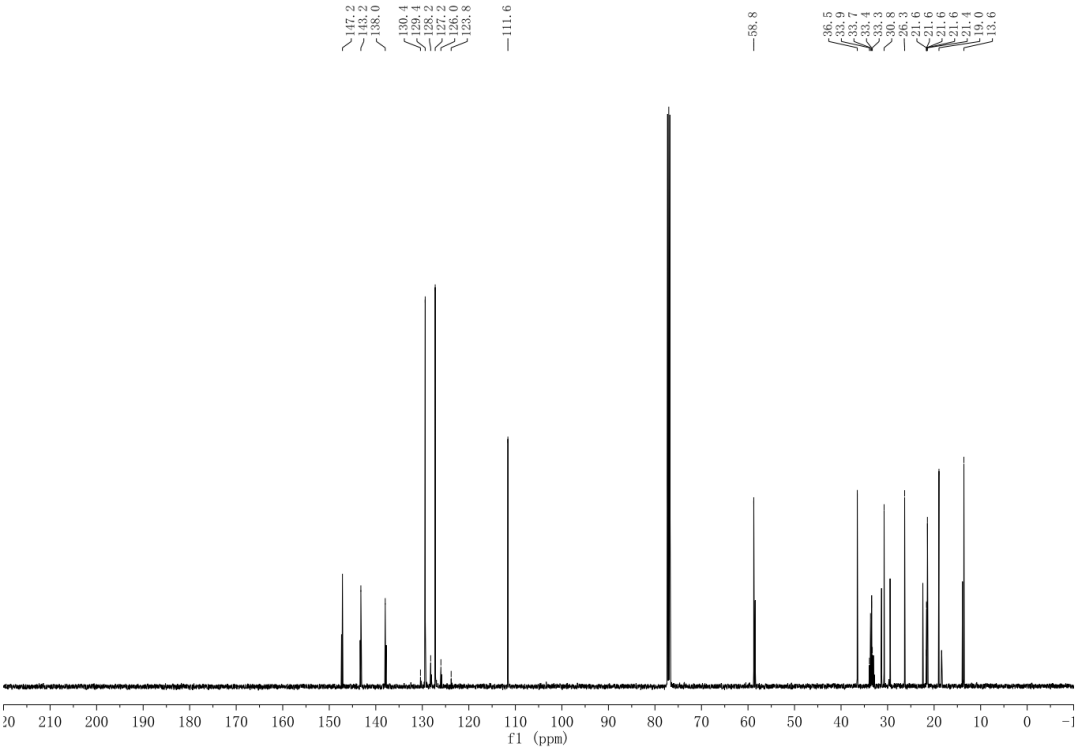
1.00
3.08
2.06
1.99
5.04
3.34
3.09
f1 (ppm)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127.2
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123.8
111.6
58.8
36.5
33.9
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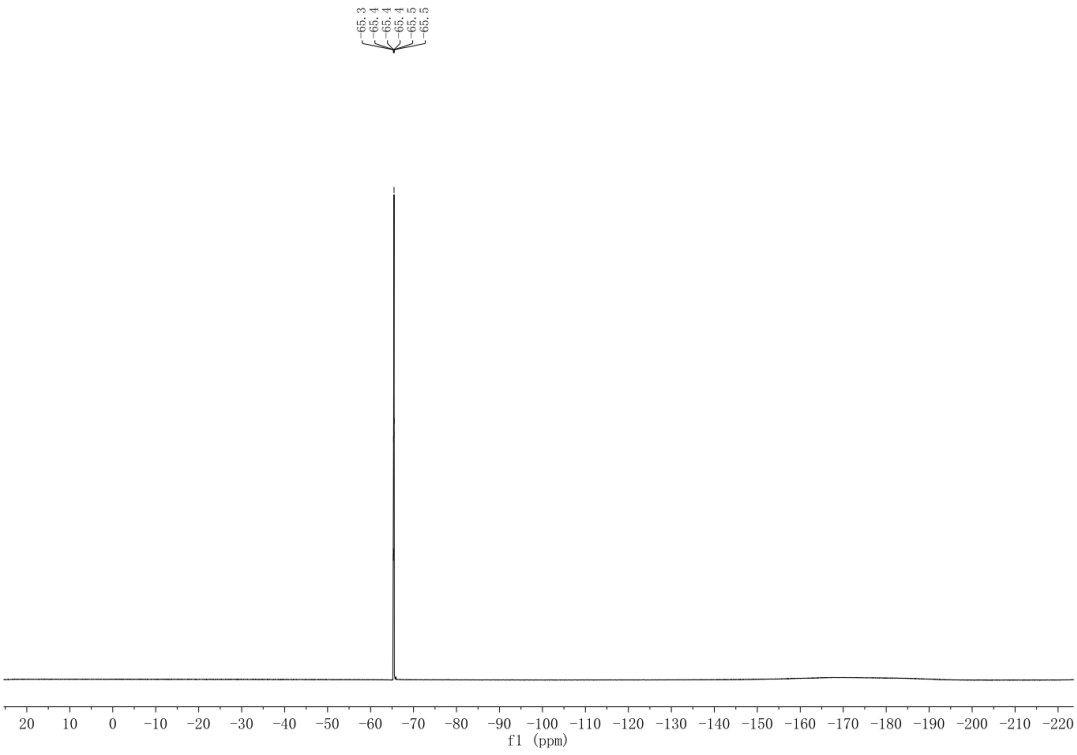
30.8
26.3
21.6
21.6
21.6
21.4
19.0
13.6
f1 (ppm)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-65.5
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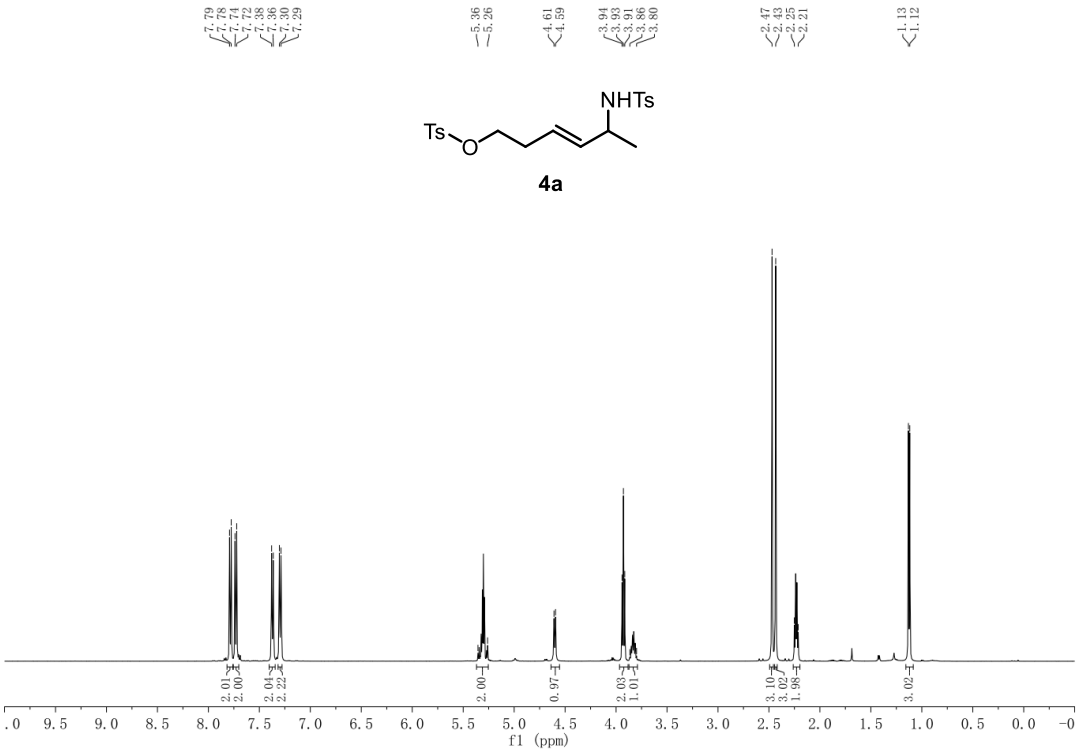
f1 (ppm)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5.25
4.61
4.59
3.94
3.93
3.91
3.86
3.80
2.47
2.43
2.25
2.21
1.13
1.12
NHTs
Ts
O
4a
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2.03
1.01
3.10
3.02
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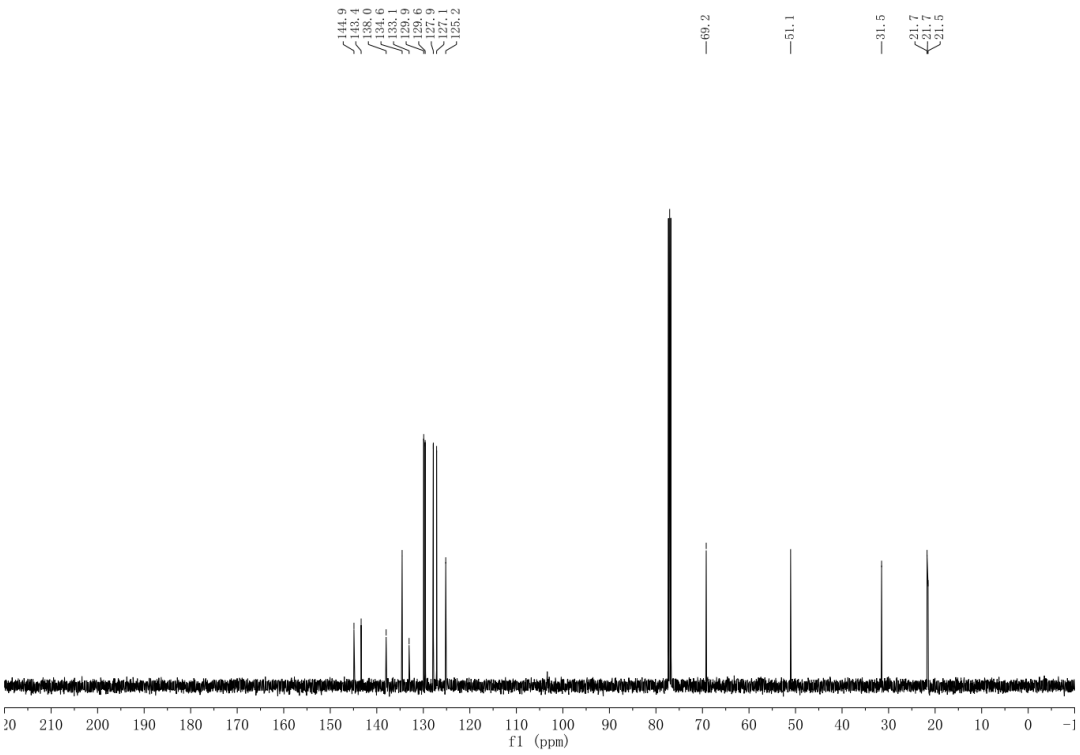
3.02
f1 (ppm)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133.1
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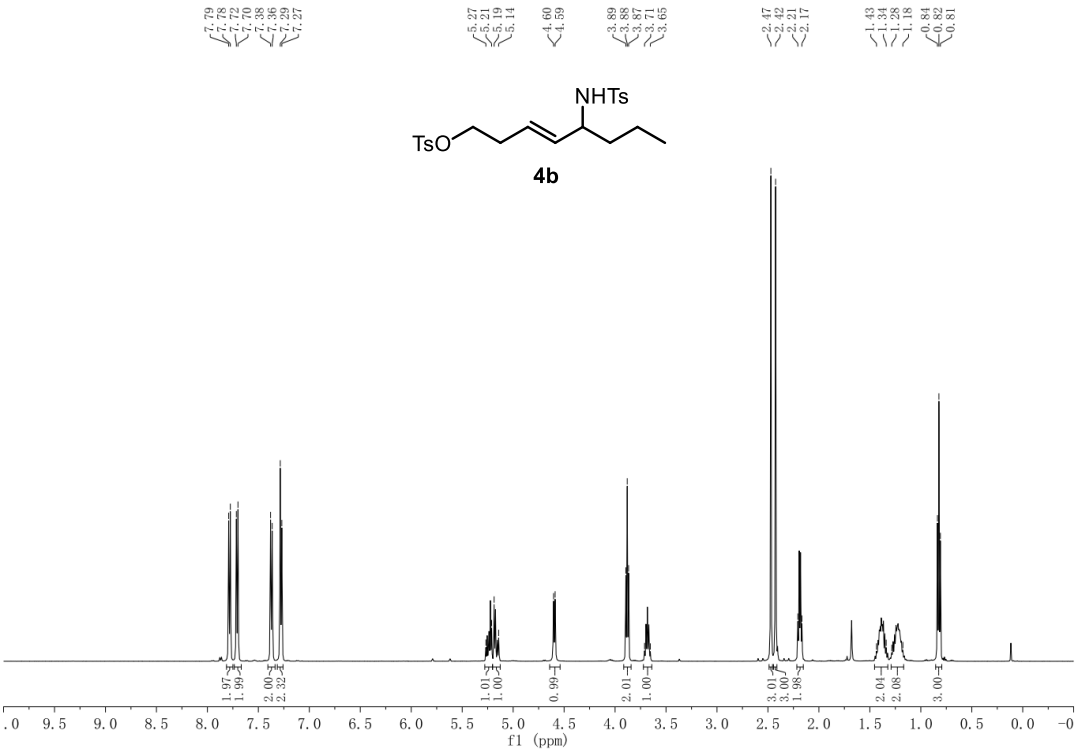
129.6
127.9
127.1
125.2
69.2
51.1
31.5
21.7
21.7
21.5
f1 (ppm)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5.27
5.21
5.19
5.14
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4.59
3.89
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3.87
3.71
3.65
2.47
2.42
2.21
2.17
1.43
1.34
1.28
1.18
0.84
0.82
0.81
NHTs
TsO
4b
1.97
1.99
2.00
2.32
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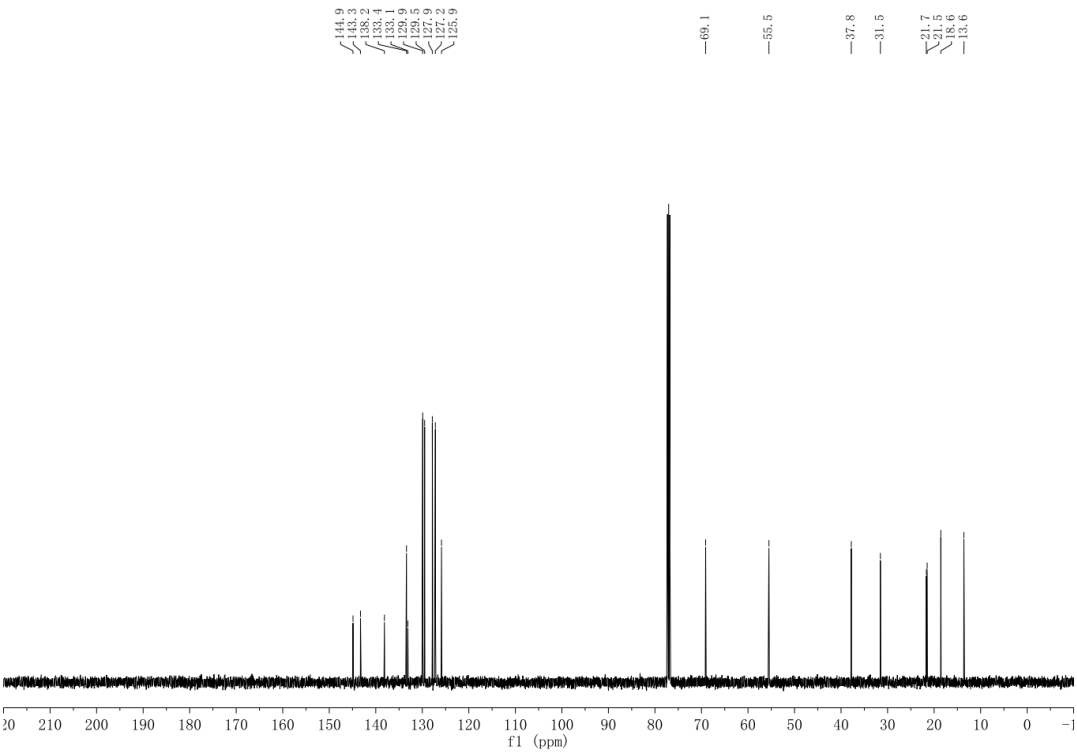
2.01
1.00
3.01
3.00
1.98
2.04
2.08
3.00
f1 (ppm)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127.2
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69.1
55.5
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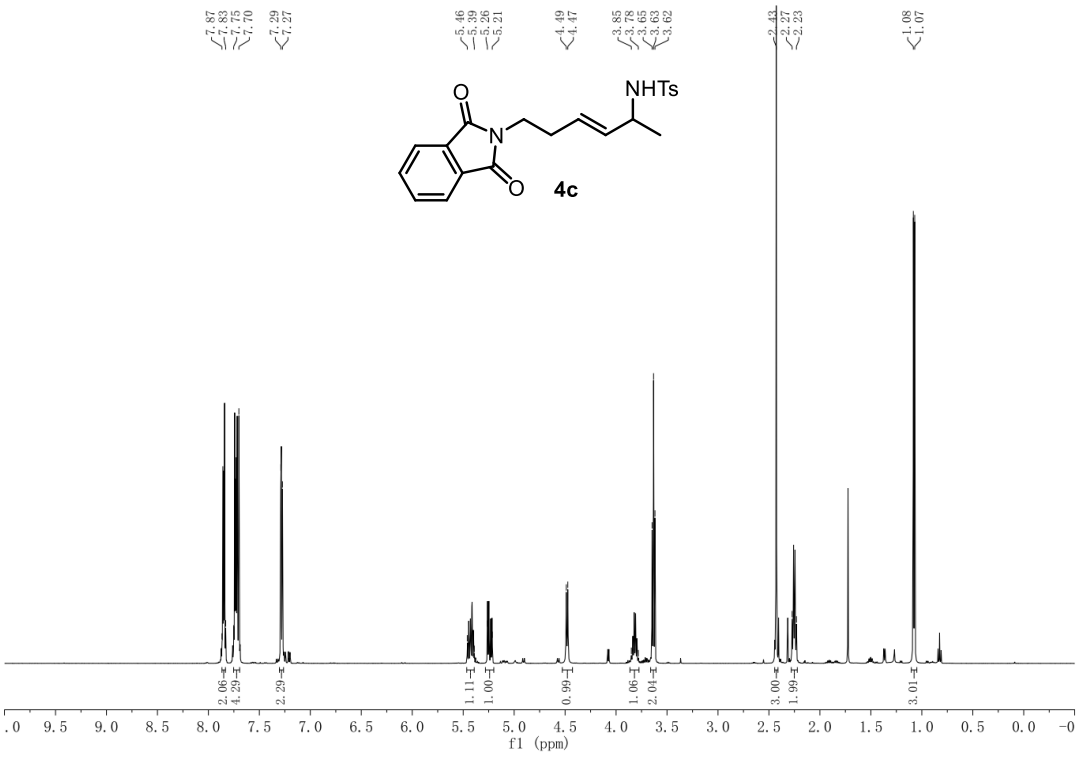
21.7
21.5
18.6
13.6
f1 (ppm)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5.21
4.49
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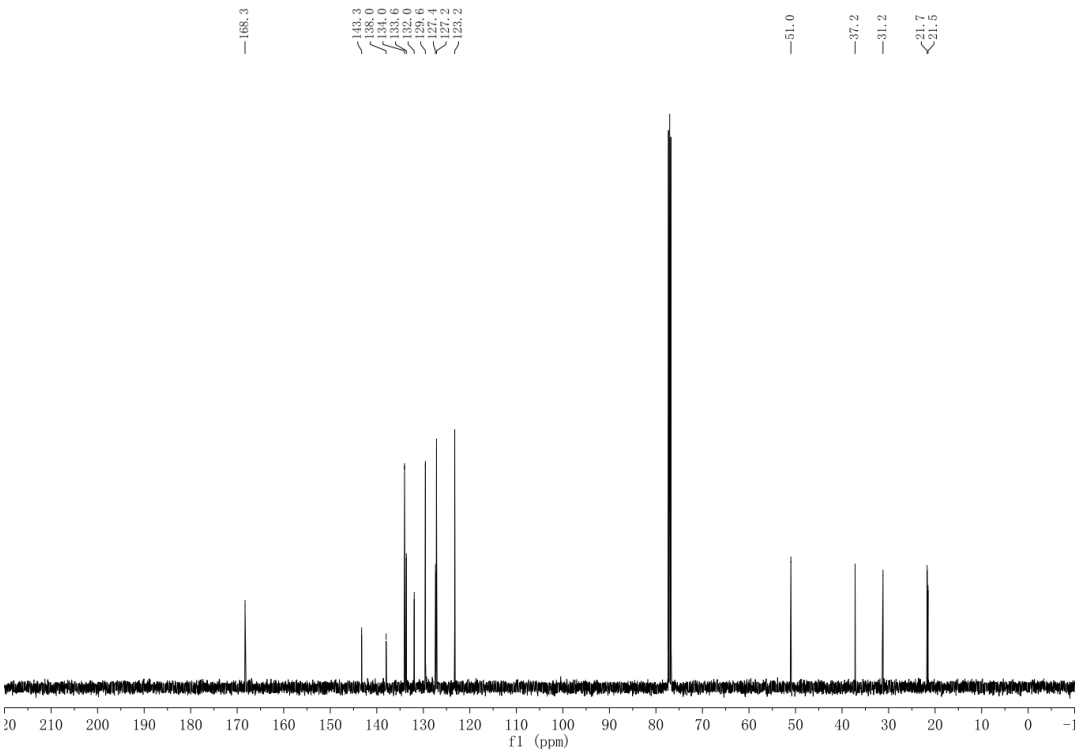
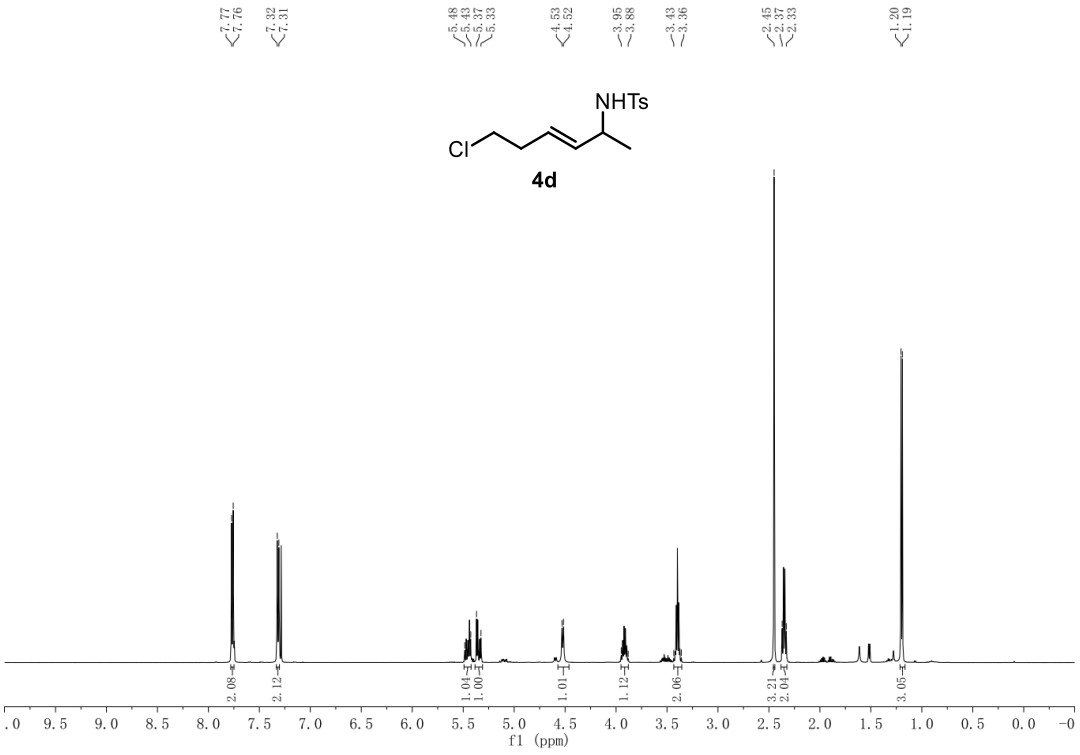
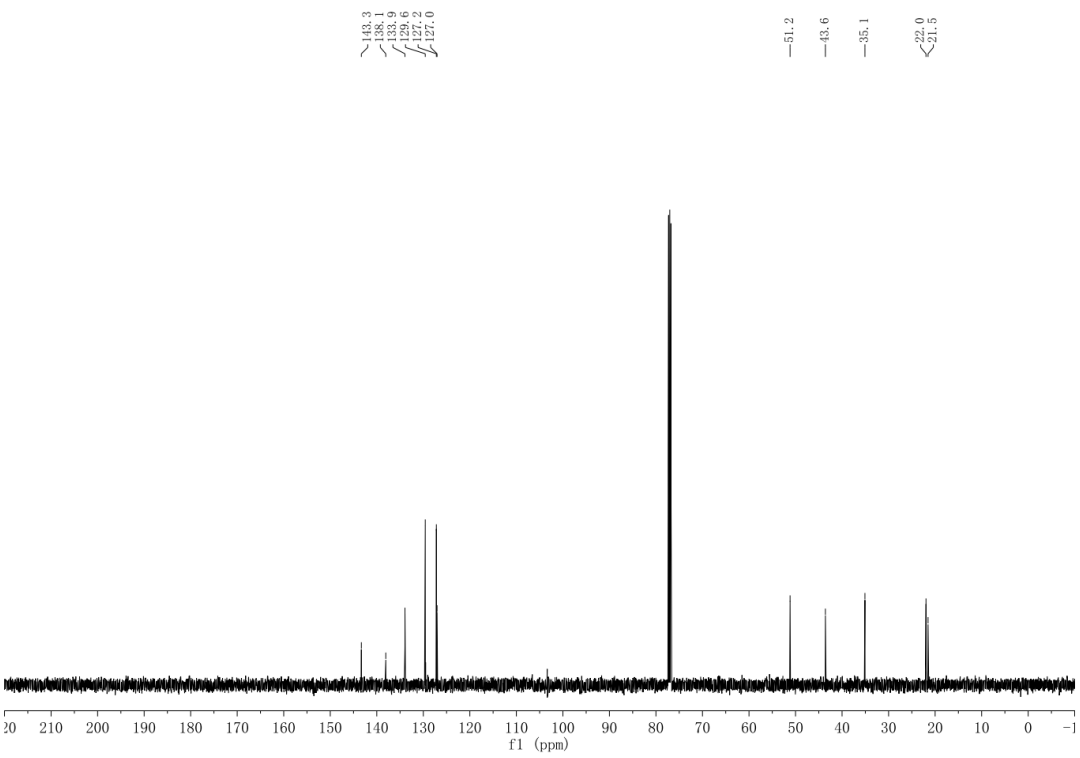
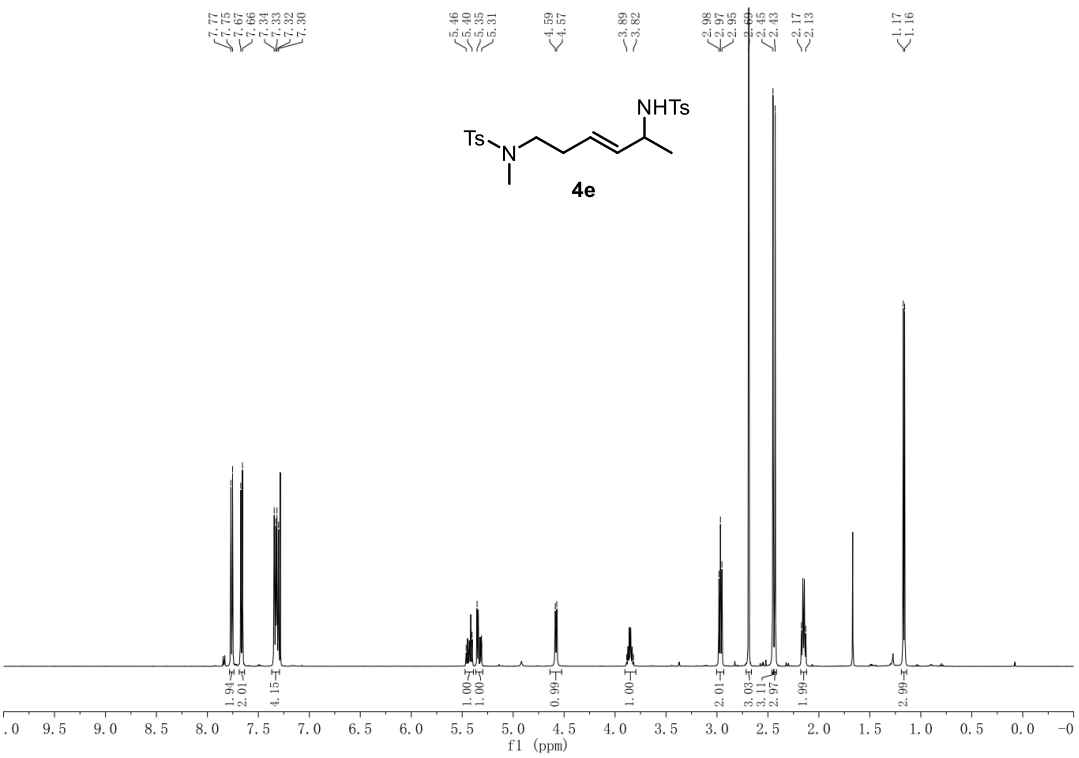
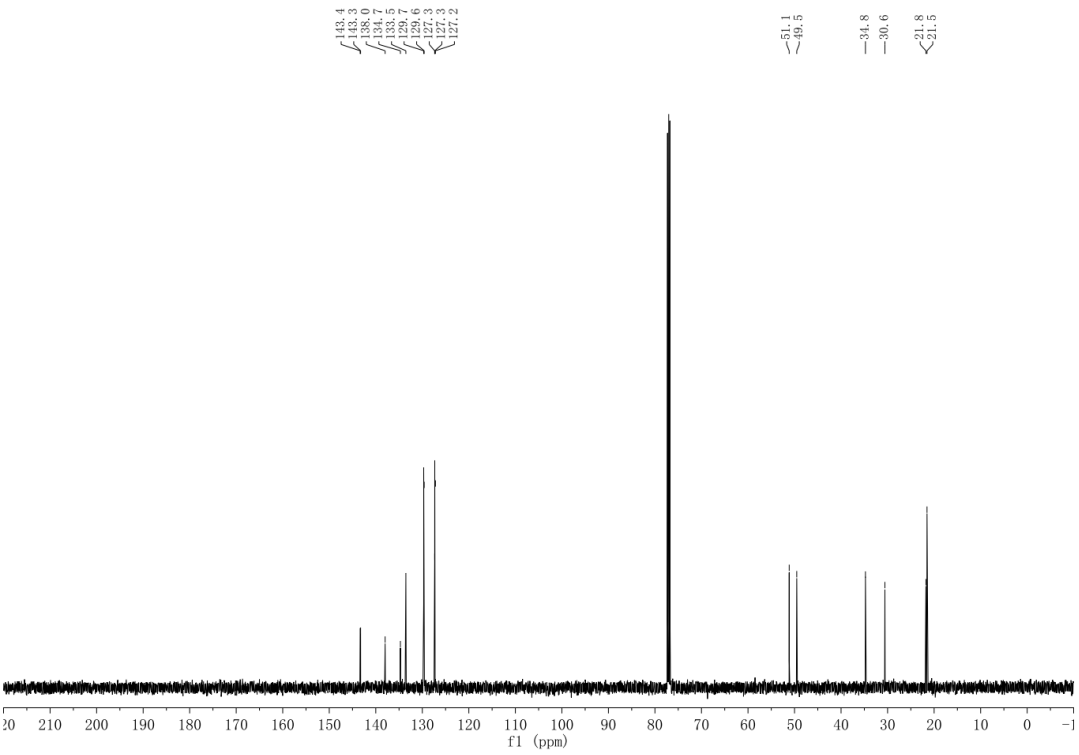
2.23
1.08
1.07
NHTs
O
N
O
O
4c
2.06
4.29
2.29
1.11
1.00
0.99
1.06
2.04
3.00
1.99
3.01
f1 (ppm)

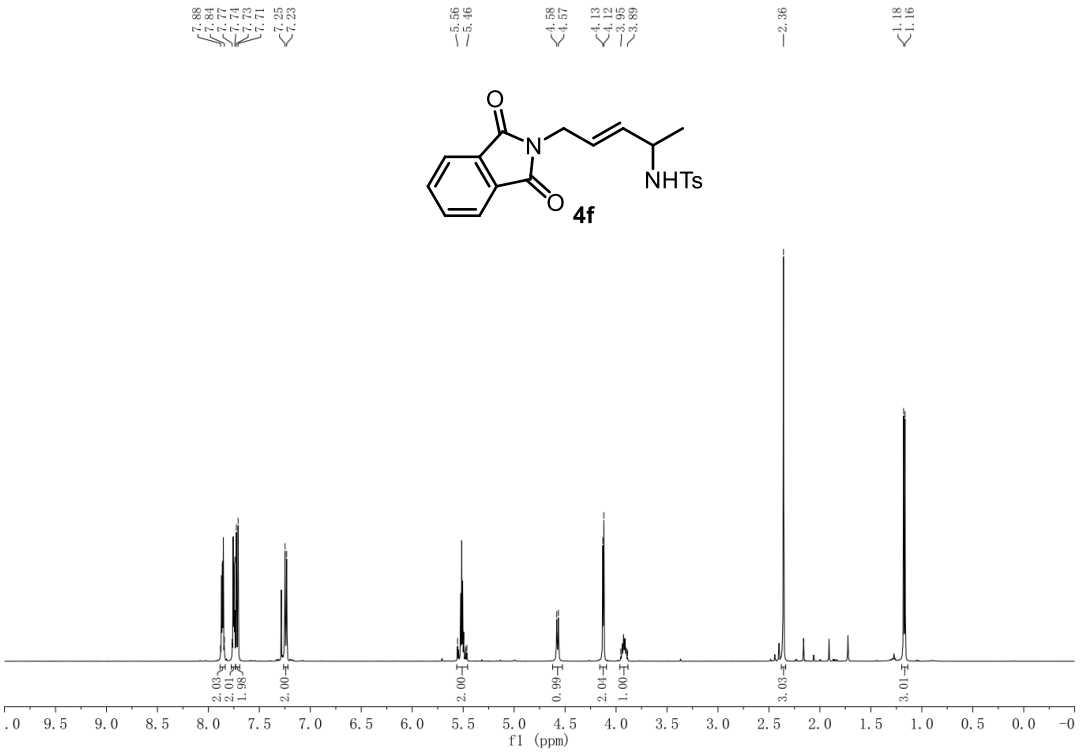

168.3
143.3
138.0
134.0
133.6
132.0
129.6
127.4
127.2
123.2
51.0
37.2
31.2
21.7
21.5
f1 (ppm)

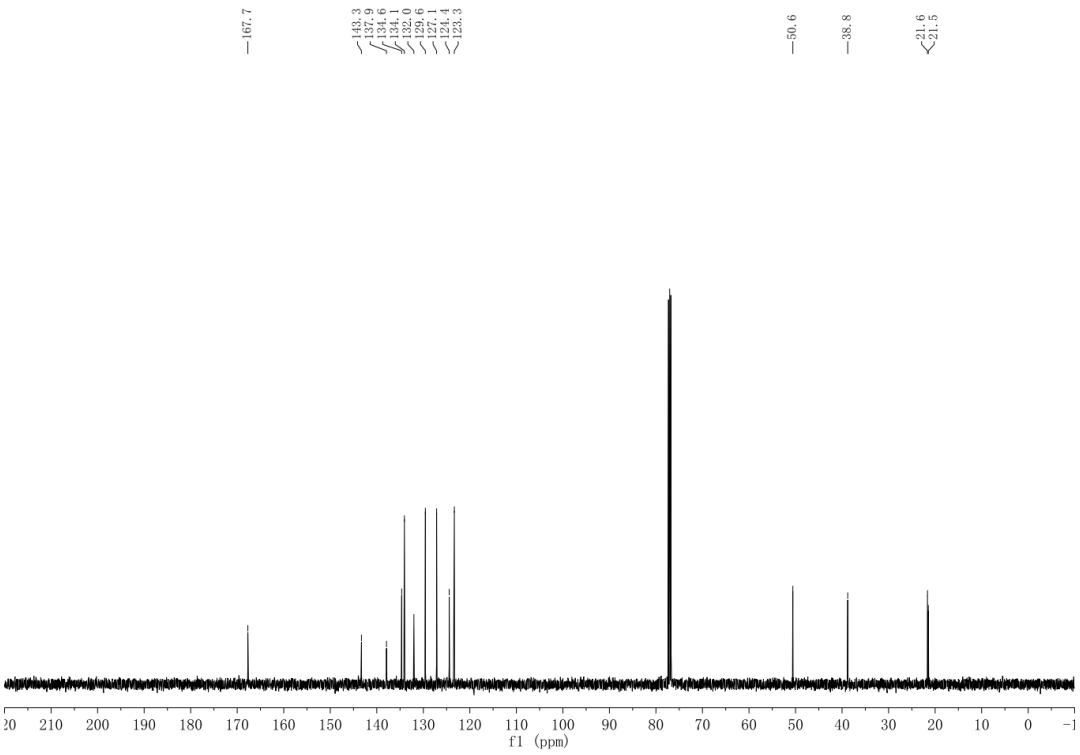

7.77
7.76
7.32
7.31
5.48
5.43
5.37
5.33
4.53
4.52
3.95
3.88
3.43
3.36
2.45
2.37
2.33
1.20
1.19
NHTs
Cl
4d
2.08
2.12
1.04
1.00
1.01
1.12
2.06
3.21
2.04
3.05
f1 (ppm)

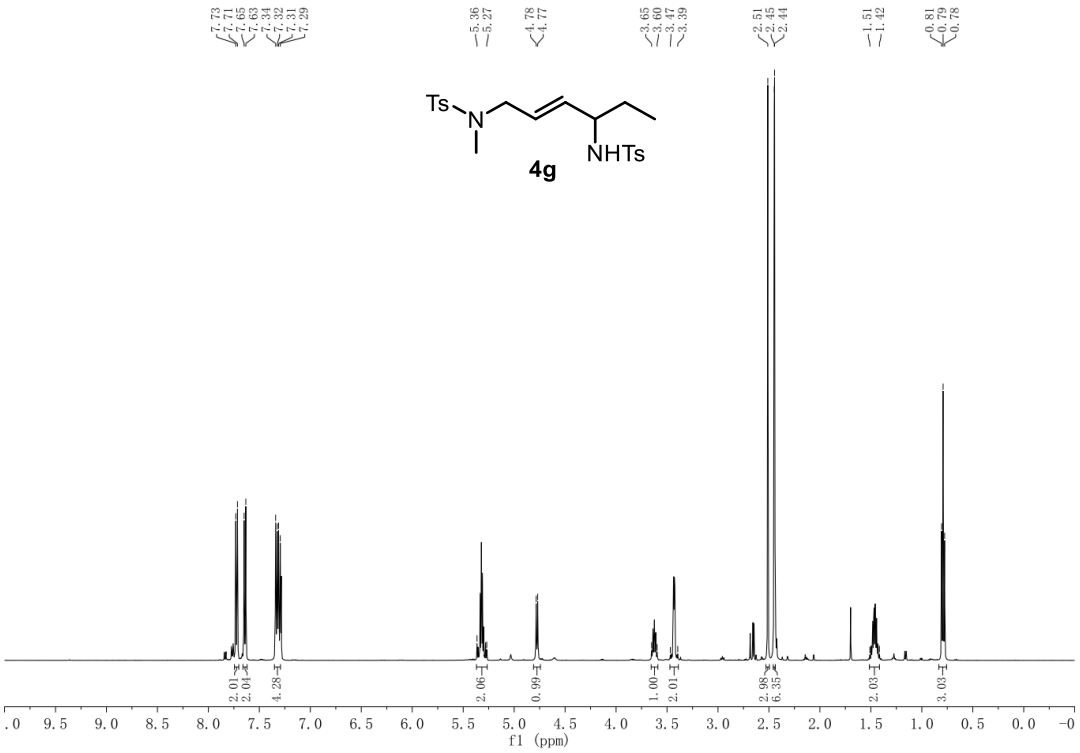

143.3
138.1
133.9
129.6
127.2
127.0
51.2
43.6
35.1
22.0
21.5
f1 (ppm)

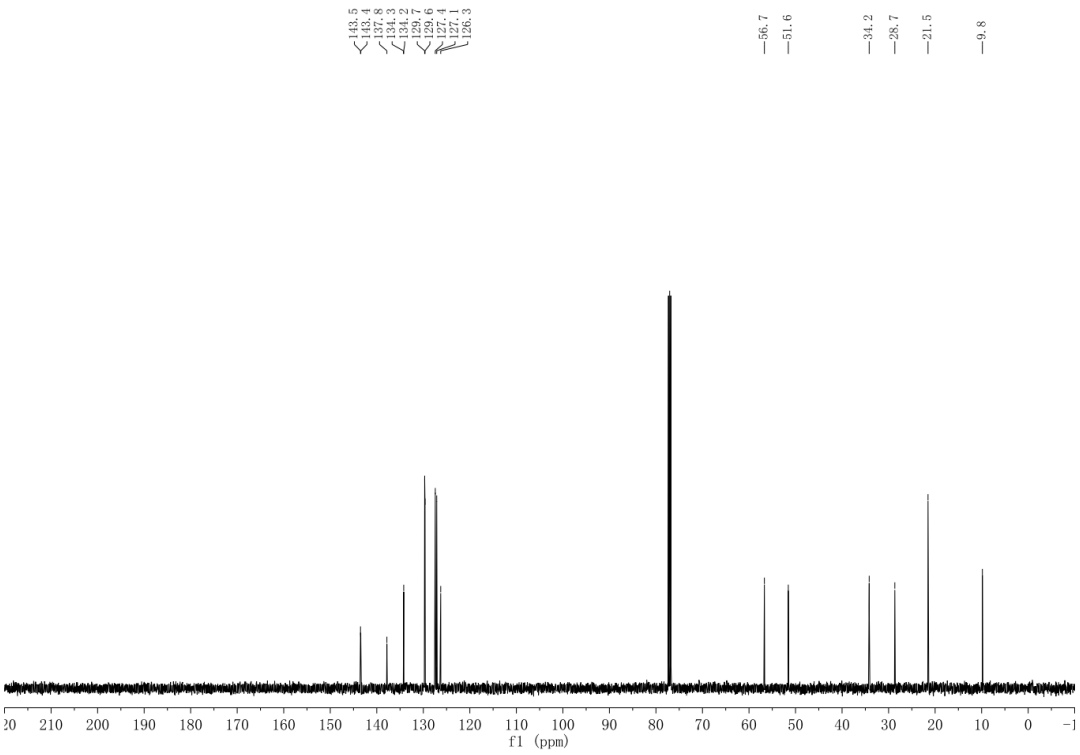

7.77
7.75
7.67
7.66
7.34
7.33
7.32
7.30
5.46
5.40
5.35
5.31
4.59
4.57
3.89
3.82
2.98
2.97
2.95
2.69
2.45
2.43
2.17
2.13
1.17
1.16
NHTs
Ts
N
4e
1.94
2.01
4.15
1.00
1.00
0.99
1.00
2.01
3.03
3.11
2.97
1.99
2.99
f1 (ppm)

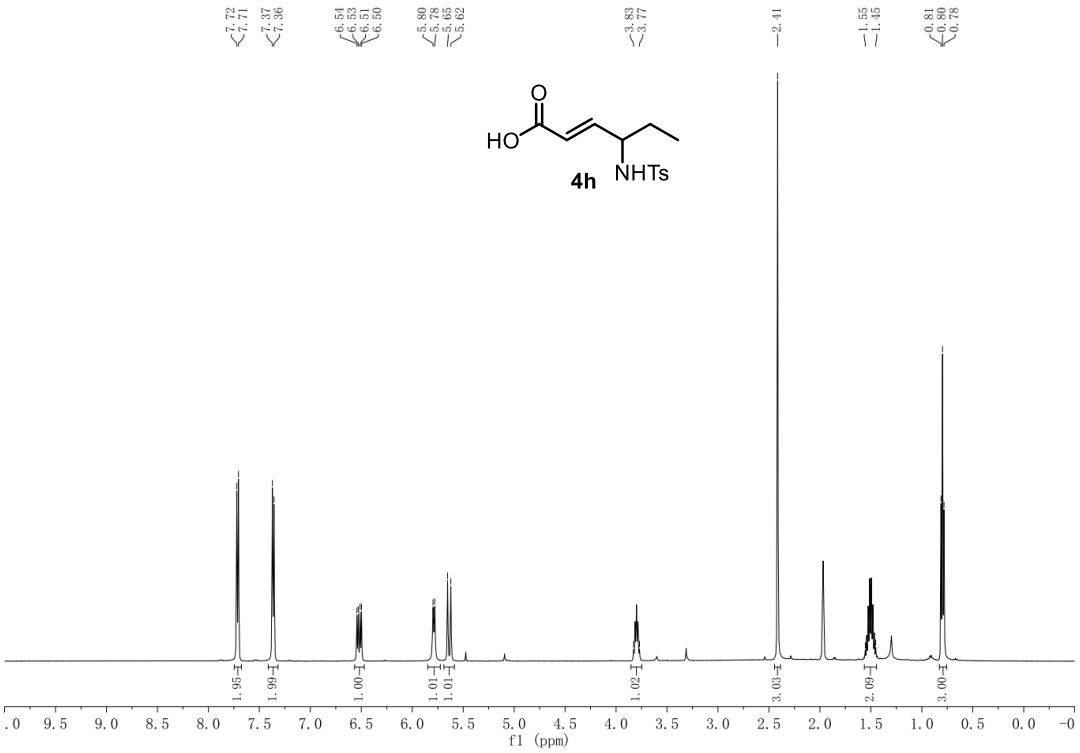

143.4
143.3
138.0
134.7
133.5
129.7
129.6
127.3
127.3
127.2
51.1
49.5
34.8
30.6
21.8
21.5
f1 (ppm)

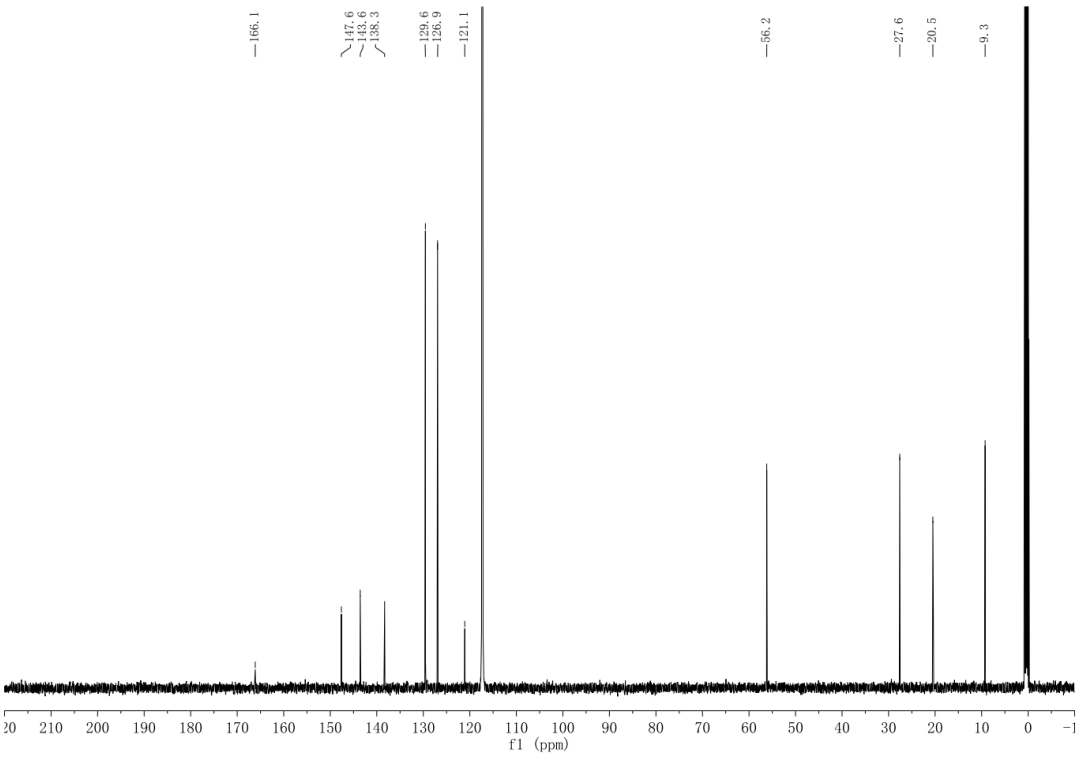

7.88
7.84
7.77
7.74
7.73
7.71
7.25
7.23
5.56
5.46
4.58
4.57
4.13
4.12
3.95
3.89
2.36
1.18
1.16
O
N
O
NHTs
4f
2.03
2.01
1.98
2.00
2.00
0.99
2.04
1.00
3.03
3.01
f1 (ppm)

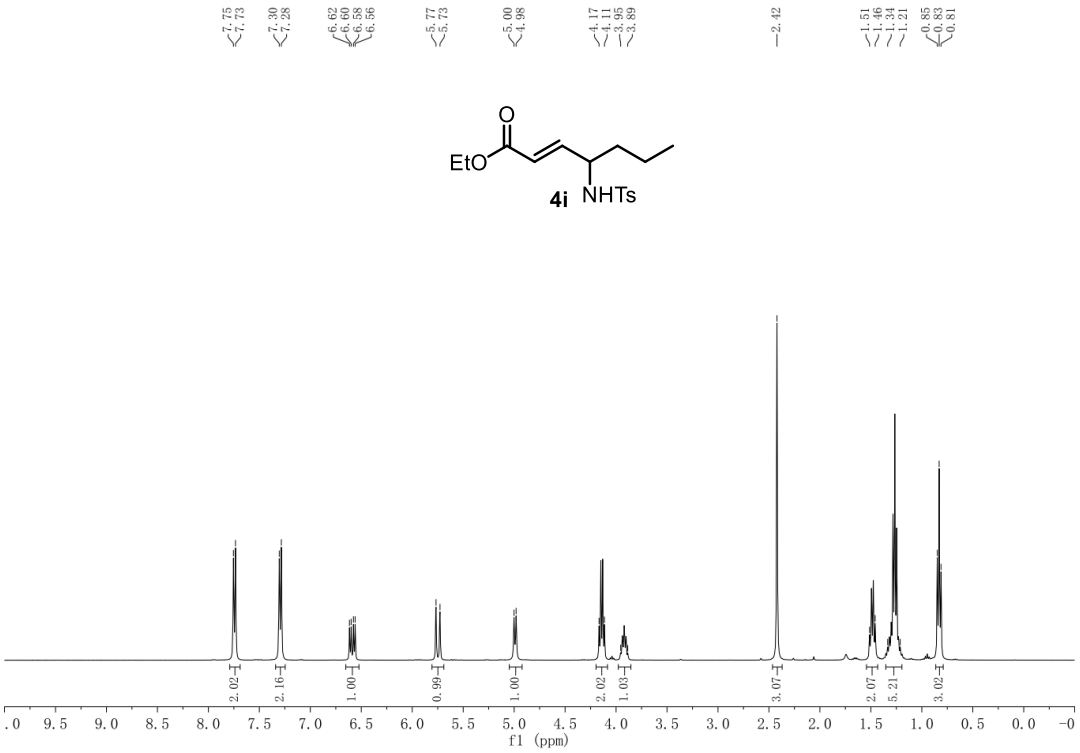

167.7
143.3
137.9
134.6
134.1
132.0
129.6
127.1
124.4
123.3
50.6
38.8
21.6
21.5
f1 (ppm)

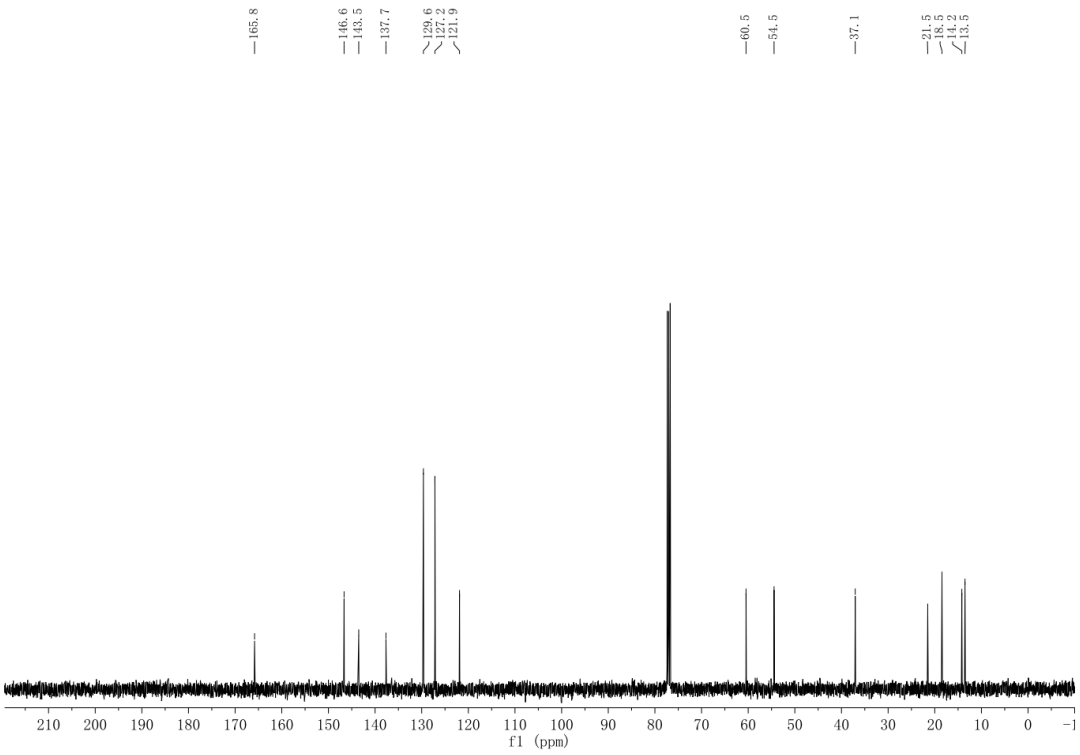

7.73
7.71
7.65
7.63
7.34
7.32
7.31
7.29
5.36
5.27
4.78
4.77
3.65
3.60
3.47
3.39
2.51
2.45
2.44
1.51
1.42
0.81
0.79
0.78
Ts
N
NHTs
4g
2.01
2.04
4.28
2.06
0.99
1.00
2.01
2.98
6.35
2.03
3.03
f1 (ppm)

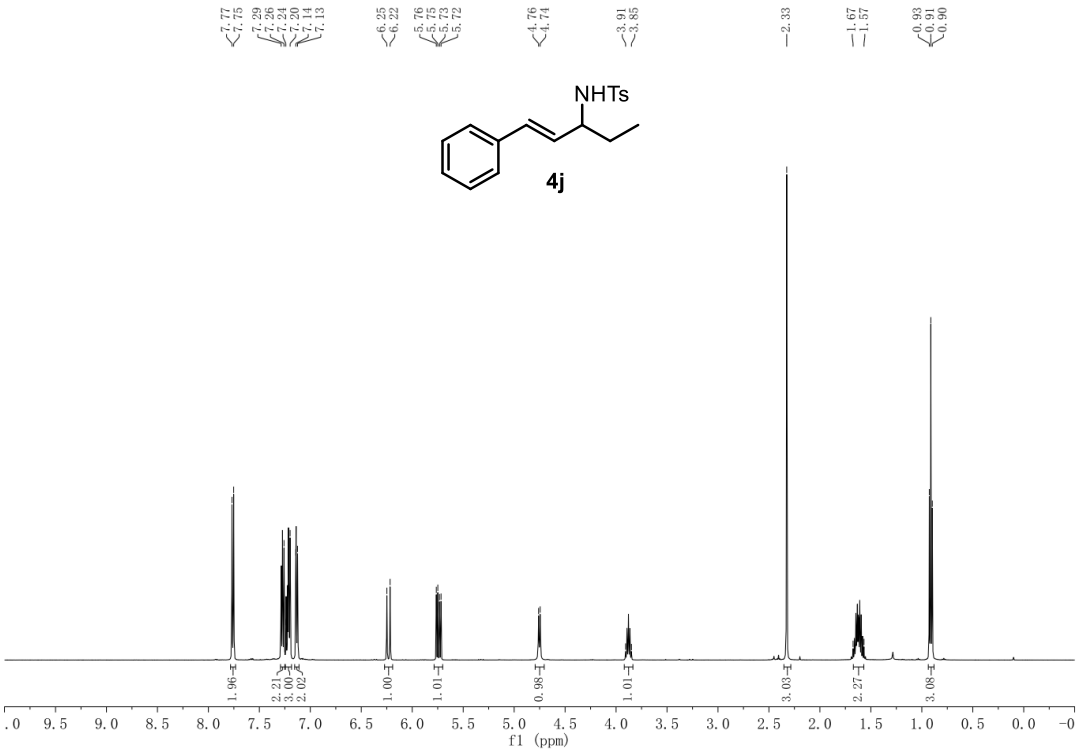

143.5
143.4
137.8
134.3
134.2
129.7
129.6
127.4
127.1
126.3
56.7
51.6
34.2
28.7
21.5
9.8
f1 (ppm)

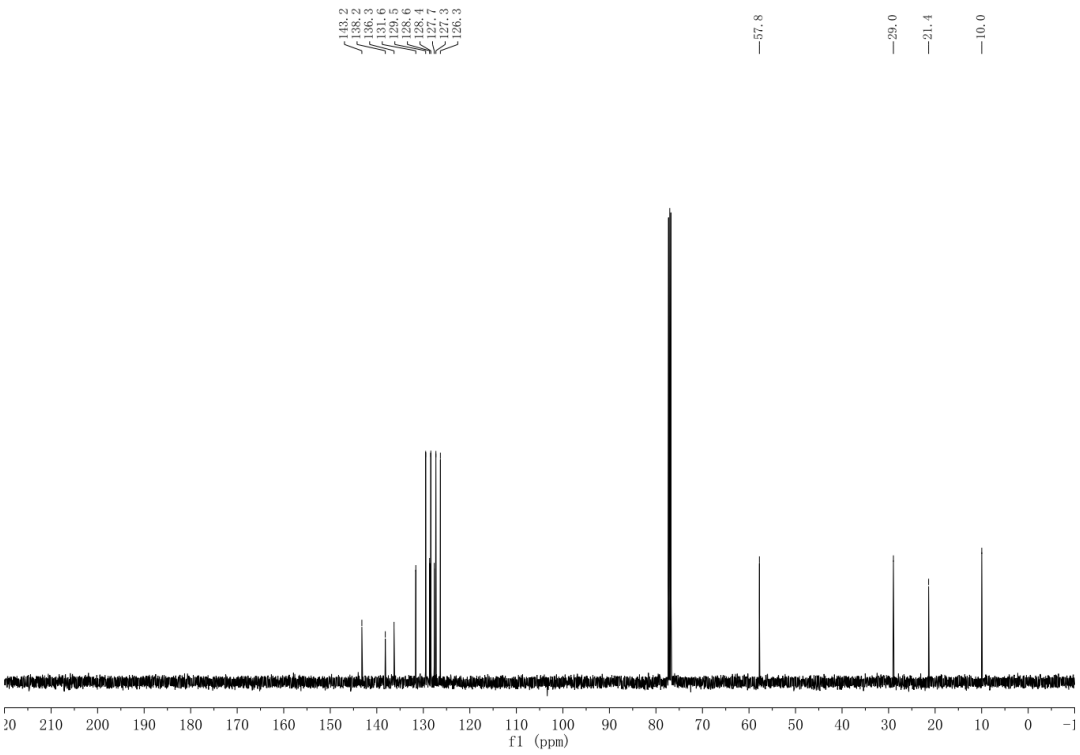

7.72
7.71
7.37
7.36
6.54
6.53
6.51
6.50
5.80
5.78
5.65
5.62
3.83
3.77
2.41
1.55
1.45
0.81
0.80
0.78
HO
O
NHTs
4h
1.95
1.99
1.00
1.01
1.01
1.02
3.03
2.09
3.00
f1 (ppm)

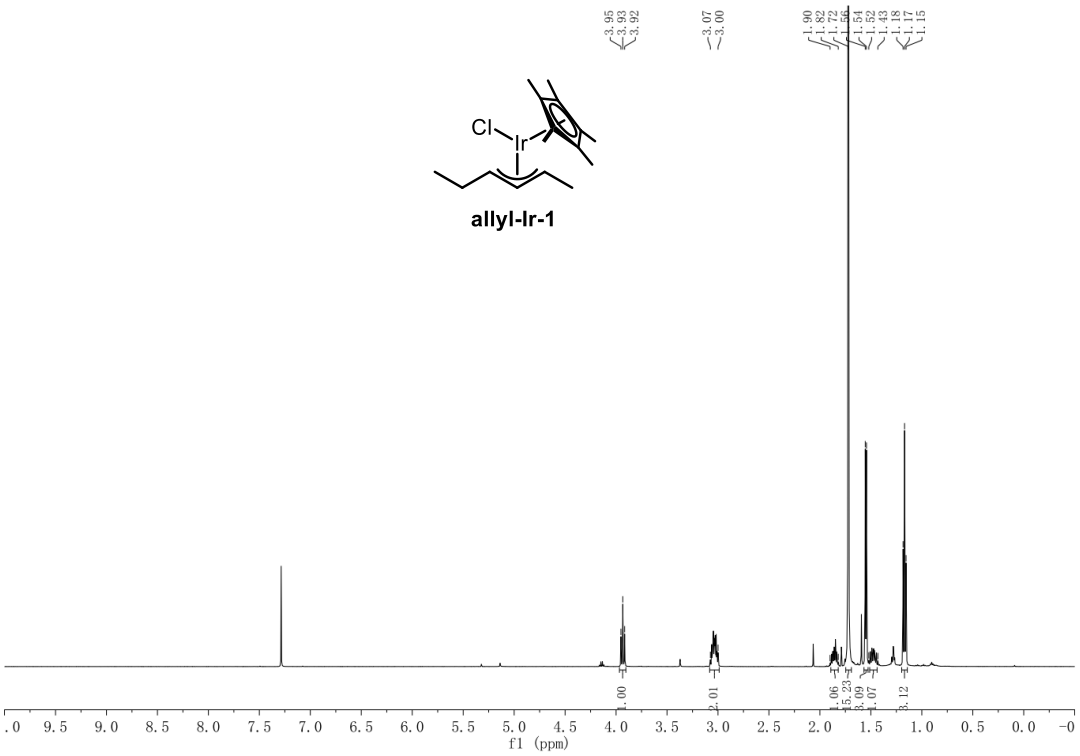

166.1
147.6
143.6
138.3
129.6
126.9
121.1
56.2
27.6
20.5
9.3
f1 (ppm)

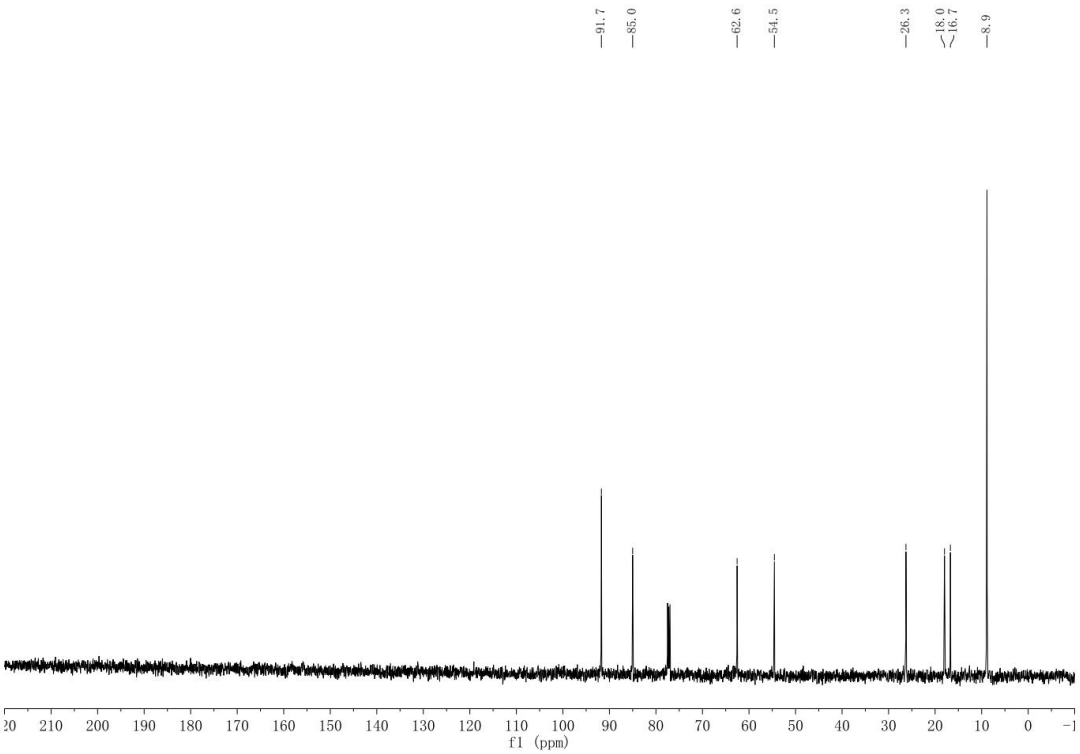

7.75
7.73
7.30
7.28
6.62
6.60
6.58
6.56
5.77
5.73
5.00
4.98
4.17
4.11
3.95
3.89
2.42
1.51
1.46
1.34
1.21
0.85
0.83
0.81
O
EtO
NHTs
4i
2.02
2.16
1.00
0.99
1.00
2.02
1.03
3.07
2.07
5.21
3.02
f1 (ppm)

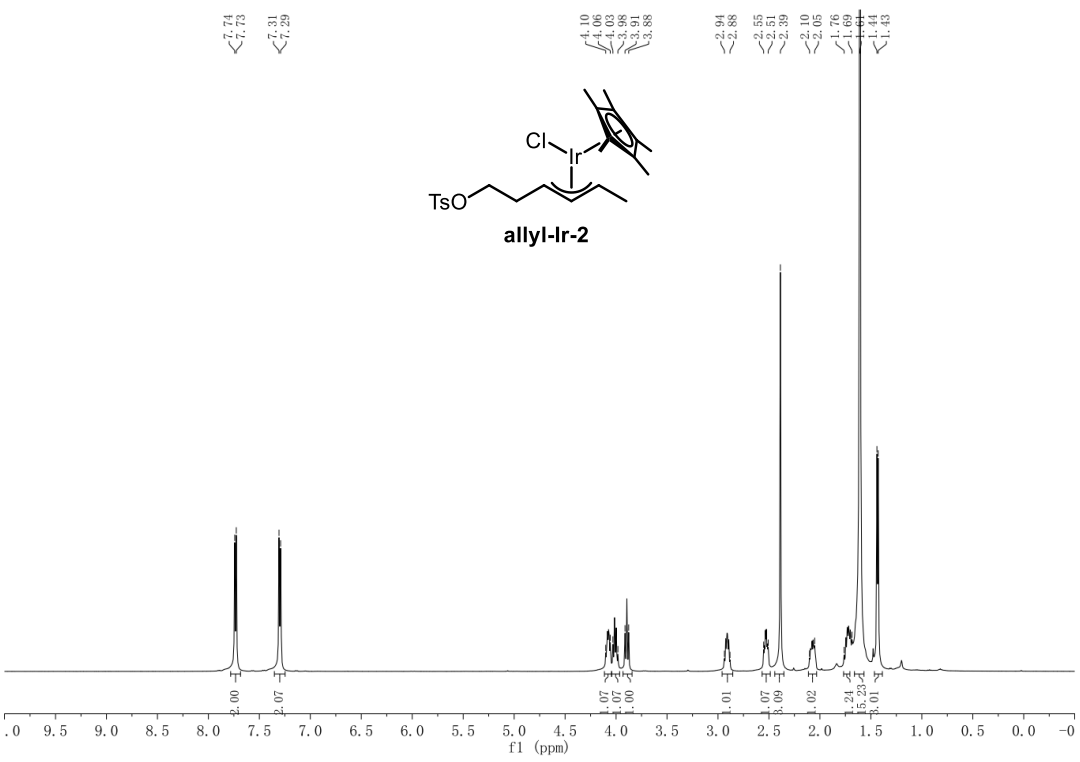

165.8
146.6
143.5
137.7
129.6
127.2
121.9
60.5
54.5
37.1
21.5
18.5
14.2
13.5
f1 (ppm)

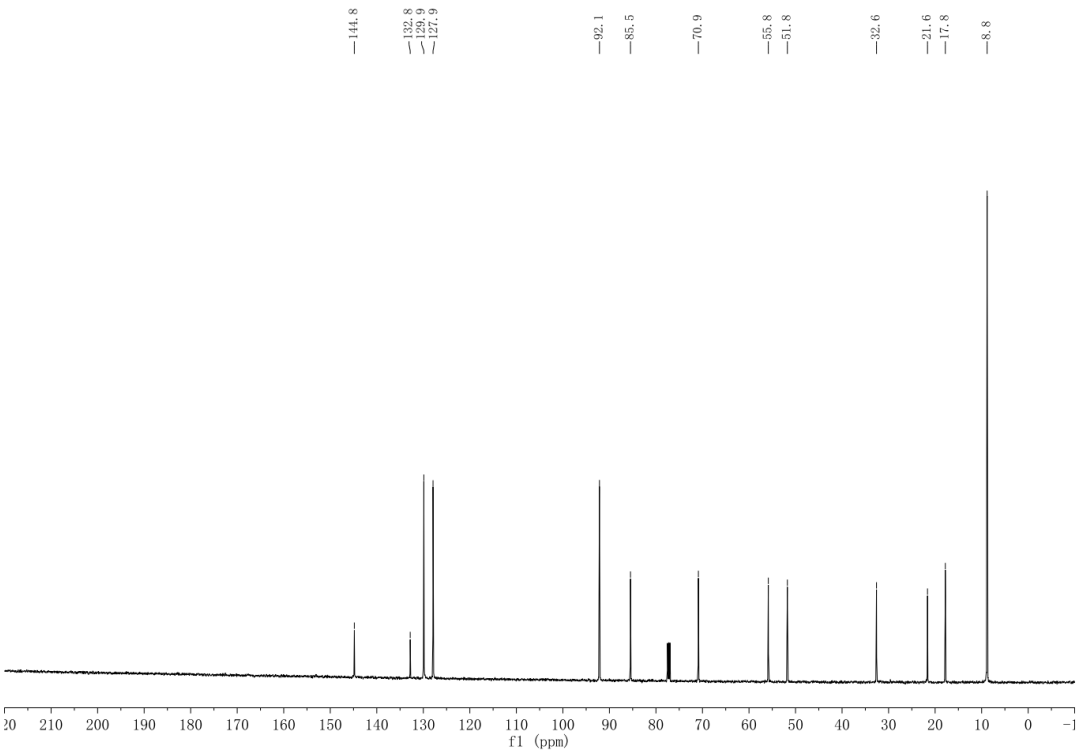

7.77
7.75
7.29
7.26
7.24
7.20
7.14
7.13
6.25
6.22
5.76
5.75
5.73
5.72
4.76
4.74
3.91
3.85
2.33
1.67
1.57
0.93
0.91
0.90
NHTs
4j
1.96
2.21
3.00
2.02
1.00
1.01
0.98
1.01
3.03
2.27
3.08
f1 (ppm)

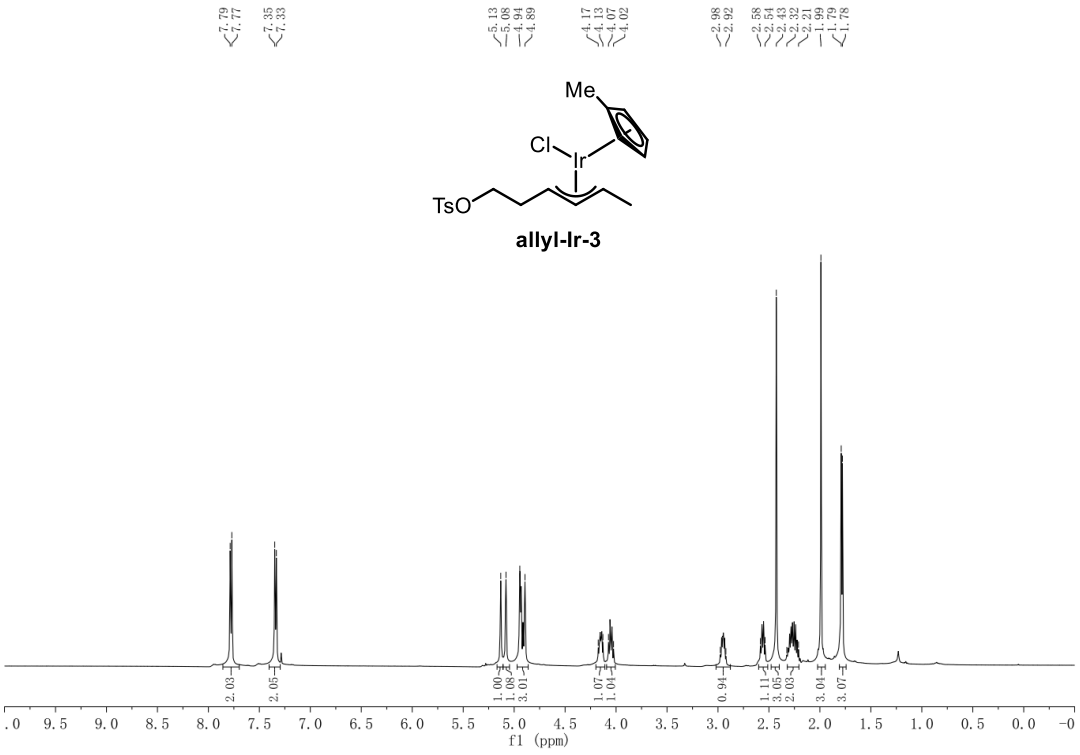

143.2
138.2
136.3
131.6
129.5
128.6
128.4
127.7
127.3
126.3
57.8
29.0
21.4
10.0
f1 (ppm)

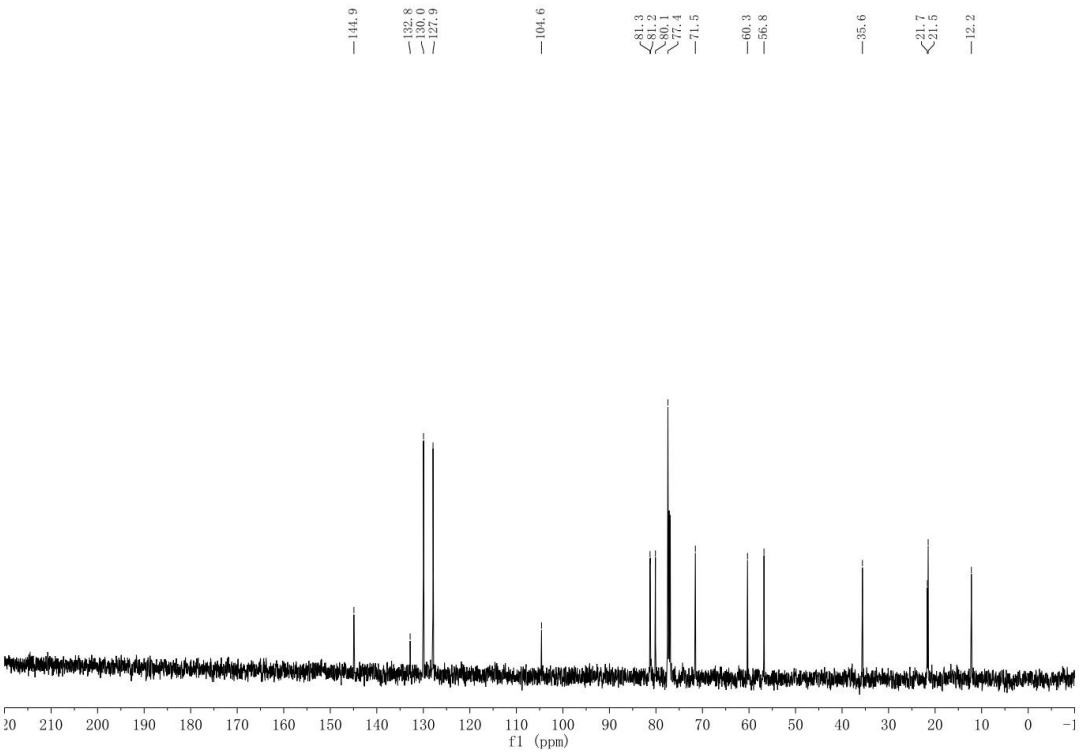

Cl
Ir
allyl-Ir-1
3.95
3.93
3.92
3.07
3.00
1.90
1.82
1.72
1.56
1.54
1.52
1.43
1.18
1.17
1.15
1.00
2.01
1.06
15.23
3.09
1.07
3.12
f1 (ppm)


91.7
85.0
62.6
54.5
26.3
18.0
16.7
8.9
f1 (ppm)


7.74
7.73
7.31
7.29
4.10
4.06
4.03
3.98
3.91
3.88
2.94
2.88
2.55
2.51
2.39
2.10
2.05
1.76
1.69
1.61
1.44
1.43
Cl
Ir
TsO
allyl-Ir-2
2.00
2.07
1.07
1.07
1.00
1.01
1.07
3.09
1.02
1.24
5.23
3.01
f1 (ppm)


144.8
132.8
129.9
127.9
92.1
85.5
70.9
55.8
51.8
32.6
21.6
17.8
8.8
f1 (ppm)


7.79
7.77
7.35
7.33
5.13
5.08
4.94
4.89
4.17
4.13
4.07
4.02
2.98
2.92
2.58
2.54
2.43
2.32
2.21
1.99
1.79
1.78
Me
Cl
Ir
TsO
allyl-Ir-3
2.03
2.05
1.00
1.08
3.01
1.07
1.04
0.94
1.11
3.05
2.03
3.04
3.07
f1 (ppm)


144.9
132.8
130.0
127.9
104.6
81.3
81.2
80.1
77.4
71.5
60.3
56.8
35.6
21.7
21.5
12.2
f1 (ppm)