Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Rhodium-catalyzed aminohydroxylation of unactivated alkenes in aqueous media for the benign synthesis of 1, 2-amino alcohols

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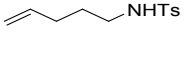
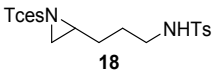
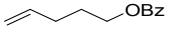
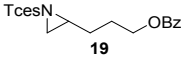
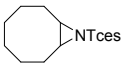
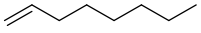
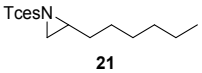
A. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts of ^{1}H were reported in part per million relative to the $CDCl_3$ residual peak (δ 7.26). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16). And for CD_3OD the chemical shifts of ^{1}H NMR residual peak (δ 3.31), chemical shifts of ^{13}C NMR were reported relative to CD_3OD (δ 49.00). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), q. (Quartet), quint. (Quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (*virt.*) High resolution mass spectra (HRMS) data were measured on a ESI-microTOF Ⅱ. Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Further visualization was achieved by staining with iodine, or $KMnO_4$ followed by heating on a hot plate. Flash column chromatography was performed on silica gel 60 Å, 10–40 μm.

The catalyst $Rh_2(esp)_2$ was prepared following the literature procedure;[1] sulfamates **2** were synthesized by reported procedures.[2]

B. Results for Some Other Alkenes

entry	substrate	product	Yield (%)
1		 **18**	74
2		 **19**	74
4		 **20**	95
5		 **21**	99

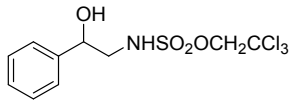
Reaction conditions refer to the representative procedure below. For entries 2 and 5, no amino alcohols were observed when 1 eq. of BF_3•Et_2O was added.

C. Representative Procedure

To a 5 mL vial containing $Rh_2(esp)_2$ (1.1 mg, 1.5 mol %), $TcesNH_2$ (22.8 mg, 0.1 mmol, 1.0 eq), alkene substrate (15.6 mg, 0.15 mmol, 1.5 eq) in 2.0 mL PBS buffer was added $PhI(OAc)_2$ (64.4 mg, 0.2 mmol, 2.0 eq). The reaction mixture was heated to 40 °C for 48 h, and then extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were dried over Na_2SO_4, filtered, concentrated in vacuum and the residue was purified by chromatography on silica gel.

D. Analytical Data of Aminohydroxylation Products

2, 2, 2-Trichloroethyl (2-hydroxy-2-phenylethyl) sulfamate (4a)



4a

A pale yellow oil. 38.0 mg, 91% yield.

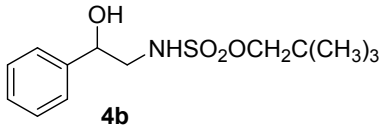
TLC: R_f = 0.35 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 5H), 5.44 (br, 1H), 5.02 (dd, *J* = 8.8, 3.6Hz, 1H), 4.65 (d, *J* = 11.0 Hz,1H), 4.61 (d, *J* = 11.0 Hz,1H), 3.54 (ddd, *J* = 13.2, 8.0, 3.6 Hz, 1H), 3.37 (ddd, *J* = 13.2, 8.8, 3.4 Hz, 1H), 2.49 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 128.9, 128.7, 125.6, 93.4, 78.3, 72.5, 50.6.

HRMS (ESI): $C_{10}H_{10}{}^{35}Cl_3NO_3S$ [$(M+Na)^+$]: calcd.: 328.9447; found: 328.9449.

Neopentyl (2-hydroxy-2-phenylethyl) sulfamate (4b)



4b

A pale yellow oil. 22.4 mg, 82% yield.

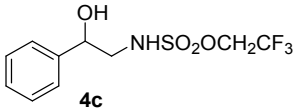
TLC: R_f = 0.35 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 5H), 5.05 (dd, *J* = 8.2, 4.3 Hz, 1H), 4.98 (*virt.* dt, *J* ≈ 8.7, 3.5 Hz, 1H), 3.82 (d, *J* = 8.9 Hz, 1H), 3.76 (d, *J* = 8.9 Hz, 1H), 3.47 – 3.40 (m, 1H), 3.27 (ddd, *J* = 13.3, 8.7, 4.3 Hz, 1H), 2.47 (d, *J* = 3.5 Hz, 1H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 128.8, 128.4, 125.9, 79.8, 72.7, 50.5, 31.6, 26.1.

HRMS (ESI): $C_{13}H_{21}NO_4S$ [$(M+Na)^+$]: calcd.: 310.1083; found: 310.1085.

2, 2, 2-Trifluoroethyl (2-hydroxy-2-phenylethyl) sulfamate (4c)



4c

A pale yellow oil. 22.8 mg, 77% yield.

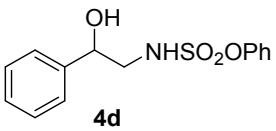
TLC: R_f = 0.43 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 5H), 5.48 (dd, *J* = 8.1, 4.0 Hz, 1H), 4.98 (*virt*. dt, *J* ≈ 8.8, 3.3 Hz, 1H), 4.50 – 4.33 (m, 2H), 3.48 (ddd, *J* = 13.5, 8.0, 3.6 Hz, 1H), 3.34 (ddd, *J* = 13.2, 8.8, 3.8 Hz, 1H), 2.56 (d, *J* = 3.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 128.9, 128.7, 125.8, 122.1 (q, *J* = 278.5 Hz), 72.5, 65.1 (q, *J* = 38.6 Hz), 50.5.

HRMS (ESI): $C_{10}H_{12}F_3NO_4S$ [$(M+Na)^+$]: calcd.: 322.0331; found: 322.0336.

Phenyl (2-hydroxy-2-phenylethyl) sulfamate (4d)



4d

A pale yellow oil. 27.4 mg, 70% yield.

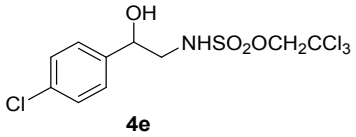
TLC: R_f = 0.40 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.24 (m, 10H), 5.31 (s, 1H), 4.90 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.50 (ddd, *J* = 13.3, 8.0, 4.1 Hz, 1H), 3.33 (ddd, *J* = 13.3, 8.9, 4.1 Hz, 1H), 2.41 – 1.98 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 ,140.4, 129.9, 128.8, 128.6, 127.1, 125.9, 121.9, 72.7, 50.9.

HRMS (ESI): $C_{14}H_{15}NO_4S$ [$(M+Na)^+$]: calcd.: 316.0614; found: 316.0618.

2, 2, 2-Trichloroethyl (2-(4-chlorophenyl)-2-hydroxyethyl) sulfamate (4e)



4e

A pale yellow oil. 30.5 mg, 84% yield.

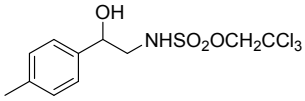
TLC: R_f = 0.35 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.37 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 5.28 (br, 1H), 5.04 – 5.00 (m, 1H), 4.66 (d, *J* = 10.9 Hz, 1H), 4.63 (d, *J* = 10.9 Hz, 1H), 3.52 (ddd, *J* = 13.6, 8.5, 3.8Hz, 1H), 3.33 (ddd, *J* = 13.3, 8.5, 3.8 Hz, 1H), 2.37 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 134.5, 129.1, 127.3, 93.4, 71.9, 50.6.

HRMS (ESI): $C_{10}H_{11}{}^{35}Cl_4NO_4S$ [$(M+Na)^+$]: calcd.: 403.9055; found: 403.9060.

2, 2, 2-Trichloroethyl (2-hydroxy-2-(p-tolyl) ethyl) sulfamate (4f)



4f

A pale yellow oil. 33.9 mg, 93% yield.

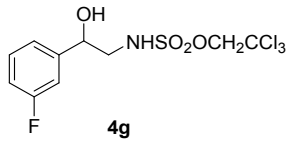
TLC: R_f = 0.34 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.54 (s, 1H), 4.96 (dd, *J* = 8.7, 3.6 Hz, 1H), 4.62 (d, *J* = 10.9 Hz, 1H), 4.57 (d, *J* = 10.9 Hz, 1H), 3.50 (dd, *J* = 13.5, 3.7 Hz, 1H), 3.35 (dd, *J* = 13.7, 8.9 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 137.3, 129.6, 125.8, 93.5, 78.3, 72.3, 50.6, 21.2.

HRMS (ESI): $C_{11}H_{14}{}^{35}Cl_3NO_4S$ [$(M+Na)^+$]: calcd.: 383.9601; found: 383.9607.

2, 2, 2-Trichloroethyl (2-(4-fluorophenyl)-2-hydroxyethyl) sulfamate (4g)



4g

A pale yellow oil. 22.5 mg, 73% yield.

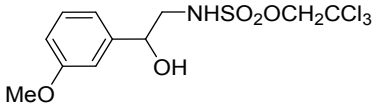
TLC: R_f = 0.37 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (*virt.* td, *J* ≈ 8.1, 5.9 Hz, 1H), 7.19 – 7.11 (m, 2H), 7.08 – 7.03 (m, 1H), 5.46 (brs, 1H), 5.04 (dd, *J* = 8.8, 3.5 Hz, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.63 (d, *J* = 11.0 Hz, 1H), 3.54 (dd, *J* = 14.8, 3.3 Hz, 1H), 3.33 (dd, *J* = 13.8, 8.9 Hz, 1H), 2.62 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 246.6 Hz), 142.9 (d, *J* = 6.6 Hz), 130.5 (d. *J* = 8.0 Hz), 121.4 (d, *J* = 2.3 Hz), 115.5 (d, *J* = 22.0 Hz), 112.9 (d, *J* = 23.3 Hz), 93.4, 78.3, 71.9 (d, *J* = 1.7 Hz), 50.5.

HRMS (ESI): $C_{10}H_{11}{}^{35}Cl_3FNO_4S$ [(M+Na)$^+$]: calcd.: 364.9458; found: 364.9458.

2, 2, 2-Trichloroethyl (2-hydroxy-2-(3-methoxyphenyl) ethyl) sulfamate (4h)



4h

A colorless oil. 22.8 mg, 60% yield.

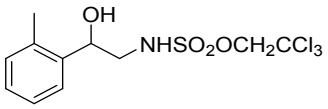
TLC: R_f = 0.47 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (*virt.* t, *J* ≈ 7.9 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.89 (m, *J* = 8.3, 2.6, 0.9 Hz, 1H), 4.98 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.61 (d, *J* = 11.0 Hz, 1H), 4.57 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H), 3.52 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.35 (dd, *J* = 13.6, 8.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 142.0, 130.0, 118.0, 114.1, 111.5, 93.4, 78.2, 72.4, 55.3, 50.6.

HRMS (ESI): $C_{11}H_{14}{}^{35}Cl_3NO_5S$ [(M+Na)$^+$]: calcd.: 399.9550; found: 399.9557.

2, 2, 2-Trichloroethyl (2-hydroxy-2-(o-tolyl) ethyl) sulfamate (4i)



4i

A pale yellow oil. 30.2 mg, 83% yield.

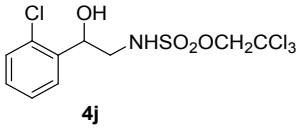
TLC: R_f = 0.36 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.19 (dd, *J* = 7.0, 2.0 Hz, 1H), 5.39 (br, 1H), 5.26 (dd, *J* = 9.1, 3.2 Hz, 1H), 4.67 (d, *J* = 10.9 Hz, 1H), 4.61 (d, *J* = 10.9 Hz, 1H), 3.52 (dd, *J* = 13.8, 3.2 Hz, 1H), 3.28 (dd, *J* = 13.7, 9.1 Hz, 1H), 2.39 (s, 3H), 2.22 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 130.8, 128.4, 126.6, 125.2, 93.4, 78.3, 69.3, 49.6, 18.9.

HRMS (ESI): $C_{11}H_{14}{}^{35}Cl_3NO_4S$ [(M+Na)$^+$]: calcd.: 383.9601; found: 383.9606.

2, 2, 2-Trichloroethyl (2-(2-chlorophenyl)-2-hydroxyethyl) sulfamate (4j)



4j

A pale yellow oil. 30.1 mg, 96% yield.

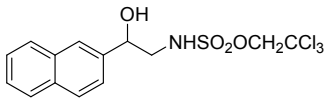
TLC: R_f = 0.35 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.41 – 7.29 (m, 3H), 5.47 – 5.40 (m, 2H), 4.66 (d, *J* = 10.9 Hz, 1H), 4.59 (d, *J* = 10.9 Hz, 1H), 3.69 (ddd, *J* = 13.5, 7.9, 3.1 Hz, 1H), 3.31 (ddd, *J* = 13.5, 8.4, 4.2 Hz, 1H), 2.65 (d, *J* = 3.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 131.8, 129.8, 129.6, 127.4, 127.2, 93.4, 78.4, 69.3, 48.8.

HRMS (ESI): $C_{10}H_{11}{}^{35}Cl_4NO_4S$ [(M+Na)$^+$]: calcd.: 403.9055; found: 403.9060.

2, 2, 2-Trichloroethyl (2-hydroxy-2-(naphthalen-2-yl) ethyl) sulfamate (4k)



4k

A pale yellow oil. 30.8 mg, 77% yield.

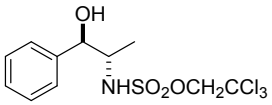
TLC: R_f = 0.33 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 4H), 7.58 – 7.53 (m, 2H), 7.47 (dd, J = 8.5, 1.7 Hz, 1H), 5.41 (br, 1H), 5.18 (dd, *J* = 8.7, 3.6 Hz, 1H), 4.64 (d, *J* = 10.9 Hz, 1H), 4.60 (d, *J* = 10.9 Hz, 1H), 3.62 (ddd, *J* = 13.3, 7.9, 3.7 Hz, 1H), 3.46 (ddd, *J* = 13.3, 8.6, 3.5 Hz, 1H), 2.56 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 133.3, 133.2, 128.9, 128.0, 127.8, 126.7, 126.5, 125.0, 123.4, 93.4, 78.3, 72.6, 50.6.

HRMS (ESI): $C_{14}H_{14}{}^{35}Cl_3NO_4S$ [$(M+Na)^+$]: calcd.: 419.9601; found: 419.9610.

2, 2, 2-Trichloroethyl ((1R, 2S)-1-hydroxy-1-phenylpropan-2-yl) sulfamate (4l)



4l

A colorless oil. 28.7 mg, 82% yield.

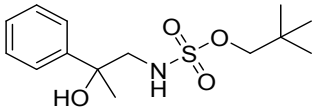
TLC: R_f = 0.40 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 5H), 5.24 (d, *J* = 9.1 Hz, 1H), 5.12 (d, *J* = 3.2 Hz, 1H), 4.66 (s, 2H), 3.93 – 3.85 (m, 1H), 2.42 (s, 1H), 1.15 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 128.7, 128.2, 125.9, 93.5, 78.1, 75.3, 56.12, 14.3.

HRMS (ESI): $C_{11}H_{14}{}^{35}Cl_3NO_4S$ [$(M+Na)^+$]: calcd.: 383.9601; found: 383.9605.

Neopentyl (2-hydroxy-2-phenylpropyl) sulfamate (4m)



4m

A colorless oil. 21.0 mg, 70% yield.

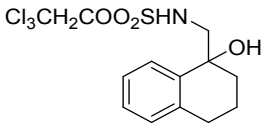
TLC: R_f = 0.45 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 4H), 7.33 – 7.27 (m, 1H), 4.76 (s, 1H), 3.70 (d, *J* = 8.8 Hz, 1H), 3.57 (d, *J* = 8.9 Hz, 1H), 3.43 – 3.33 (m, 2H), 2.38 (d, *J* = 6.6 Hz, 1H), 1.63 (s, 3H), 0.93 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 128.7, 127.6, 124.8, 79.7, 73.8, 54.2, 31.6, 27.6, 26.1.

HRMS (ESI): $C_{14}H_{23}NO_4S$ [$(M+Na)^+$]: calcd.: 324.1240; found: 324.1243.

2, 2, 2-Trichloroethyl ((1-hydroxy-1, 2, 3, 4-tetrahydronaphthalen-1-yl) methyl) sulfamate (4n)



4n

A pale yellow oil. 13.3 mg, 35% yield.

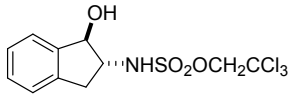
TLC: R_f = 0.45 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.28 – 7.22 (m, 2H), 7.18 – 7.10 (m, 1H), 5.35 – 5.32 (m, 1H), 4.64 (s, 2H), 3.64 – 3.28 (m, 2H), 3.00 – 2.73 (m, 2H), 2.49 – 2.24 (m, 1H), 2.05 – 1.93 (m, 2H), 1.92 – 1.85 (m, 1H), 1.84 – 1.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.4, 129.2, 128.3, 126.6, 126.2, 93.5, 78.3, 72.2, 52.2, 34.2, 29.4, 20.0.

HRMS (ESI): $C_{13}H_{16}{}^{35}Cl_3NO_4S$ [(M+Na) $^+$]: calcd.: 409.9758; found: 409.9762.

2, 2, 2-Trichloroethyl ((1*RS*, 2*RS*)-1-hydroxy-2, 3-dihydro-1H-inden-2-yl) sulfamate (4o)



4o

A pale yellow oil. 32.2mg, 90% yield. The product contains a mixture of two inseparable diastereoisomers (d.r. ≈ 4:1).

TLC: R_f = 0.39 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

The major diastereoisomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 1H), 7.32 – 7.27 (m, 3H), 5.11 (*virt*. q, *J* ≈ 7.6 Hz, 1H), 5.07 – 4.98 (m, 1H), 4.70 (s, 2H), 3.05 (ddd, *J* = 16.0, 8.6, 4.2 Hz, 1H), 2.90 (*virt*. dt, *J* ≈ 15.9, 7.9 Hz, 1H), 2.72 – 2.67 (m, 1H), 2.12 – 2.08 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.8, 128.9, 127.2, 125.1, 124.4, 93.5, 78.2, 60.1, 34.4, 30.0.

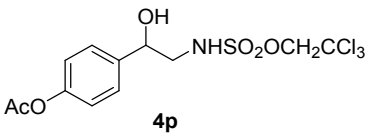
The minor diastereoisomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 0.5H), 7.47 – 7.36 (m, 0.5H), 5.69 (d, *J* = 9.3 Hz, 0.25H), 5.27 – 5.20 (m, 0.28H), 4.70 (s, 0.5H), 3.71 (q, *J* = 7.0 Hz, 0.21H), 3.32 – 3.27 (m, 0.21H), 3.18 – 3.13 (m, 0.25H), 2.72 – 2.67 (m, 0.25H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 134.8, 129.8, 126.7, 124.9, 123.8, 93.4, 78.2, 56.7, 42.7, 36.2, 25.9.

HRMS (ESI): $C_{11}H_{12}{}^{35}Cl_3NO_4S$ [(M+Na) $^+$]: calcd.: 381.9445; found: 381.9439.

4-1-Hydroxy-2-((2, 2, 2-trichloroethoxy) sulfonyl) amino-ethyl phenyl acetate (4p)



4p

A pale yellow oil. 36.5 mg, 90% yield.

TLC: R_f = 0.35 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

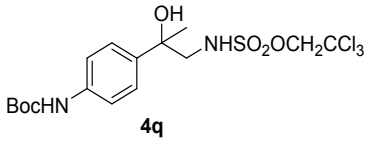
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.13 – 7.09 (m, 2H), 5.60 (dd, *J* = 8.2, 4.2 Hz, 1H),

5.01 – 4.89 (m, 1H), 4.65 (d, *J* = 11.0 Hz, 1H), 4.62 (d, *J* = 11.0 Hz, 1H), 3.47 (ddd, *J* = 13.4, 8.0, 3.7 Hz, 1H), 3.30 (ddd, *J* = 13.4, 8.8, 4.0 Hz, 1H), 2.80 (br, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 150.6, 138.1, 127.1, 122.0, 93.4, 78.2, 71.9, 50.5, 21.1.

HRMS (ESI): $C_{12}H_{14}{}^{35}Cl_3NO_6S$ [$(M+Na)^+$]: calcd.: 427.9500; found: 427.9507.

2, 2, 2-Trichloroethyl (2-(4-((tert-butoxycarbonyl) amino) phenyl)-2-hydroxypropyl) sulfamate (4q)



4q

A pale yellow oil. 19.5 mg, 40% yield.

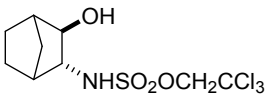
TLC: R_f = 0.45 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 5H), 6.57 (br, 1H), 5.12 (br, 1H), 4.54 (d, *J* = 11.0 Hz, 1H), 4.39 (d, *J* = 11.0 Hz, 1H), 3.46 (dd, *J* = 5.9, 3.2 Hz, 2H), 2.31 (br, 1H), 1.65 (s, 3H), 1.54 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 138.8, 137.9, 125.6, 118.8, 93.4, 80.9, 78.2, 73.5, 54.5, 28.3, 27.5.

HRMS (ESI): $C_{15}H_{21}{}^{35}Cl_3N_2O_6S$ [$(M+Na)^+$]: calcd.: 485.0078; found: 485.0083.

2, 2, 2-Trichloroethyl ((2*RS*, 3*RS*)-3-hydroxybicyclo [2.2.1] heptan-2-yl) sulfamate (4r)



4r

A pale yellow oil. 24.6mg, 73% yield.

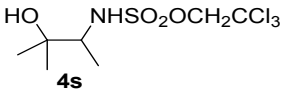
TLC: R_f = 0.38 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (d, *J* = 8.6 Hz, 1H), 4.72 – 4.58 (m, 2H), 4.11 – 4.01 (m, 1H), 3.66 (*virt.*dt, *J* ≈ 8.6, 1.5 Hz, 1H), 2.58 – 2.56 (m, 1H), 2.29 (d, *J* = 4.5 Hz, 1H), 1.93 (dd, *J* = 14.1, 6.9 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.71 – 1.59 (m, 4H), 1.20 – 1.12 (m, 1H), 1.10 – 1.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 93.7, 78.0, 75.9, 62.9, 45.7, 39.7, 38.7, 25.9, 22.0.

HRMS (ESI): $C_9H_{14}{}^{35}Cl_3NO_4S$ [$(M+Na)^+$]: calcd.: 336.9709; found: 336.9705.

2, 2, 2-Trichloroethyl (3-hydroxy-3-methylbutan-2-yl) sulfamate (4s)



4s

A pale yellow oil. 27.4 mg, 87% yield.

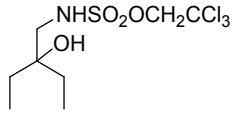
TLC: R_f = 0.42 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.17 (d, *J* = 8.2 Hz, 1H), 4.68 (d, *J* = 11.0 Hz, 1HJ), 4.66 (d, *J* = 11.0 Hz, 1H), 3.53 – 3.46 (m, 1H), 1.67 (d, *J* = 3.4 Hz, 2H), 1.37 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H), 1.27 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 93.6, 78.0, 72.5, 59.3, 27.7, 25.8, 16.2.

HRMS (ESI): $C_7H_{14}{}^{35}Cl_3NO_4S$ [$(M+Na)^+$]: calcd.: 335.9601; found: 335.9605.

2, 2, 2-Trichloroethyl (2-ethyl-2-hydroxybutyl) sulfamate (4t)



4t

A pale yellow oil. 22.4 mg, 69% yield.

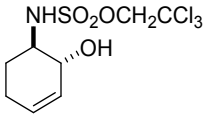
TLC: R_f = 0.40 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 – 5.33 (m, 1H), 4.64 (s, 2H), 3.20 (d, *J* = 5.9 Hz, 2H), 1.68 (br, 1H), 1.63 – 1.50 (m, 4H), 0.90 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 93.5, 78.2, 74.5, 50.3, 28.7, 7.6.

HRMS (ESI): $C_8H_{16}{}^{35}Cl_3NO_4S$ $(M+Na)^+$]: calcd.: 349.9758; found: 349.9760.

2, 2, 2-Trichloroethyl ((1*RS*, 2*RS*)-2-hydroxycyclohex-3-en-1-yl) sulfamate (4u)



4u

A pale yellow oil. 20.2 mg, 62% yield.

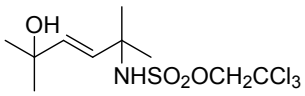
TLC: R_f = 0.43 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.78 (m, 1H), 5.73 – 5.60 (m, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.14 (br, 1H), 3.52 (dtd, *J* = 10.7, 7.4, 2.6 Hz, 1H), 2.34 – 2.13 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.90, 127.7, 93.4, 78.3, 70.1, 57.9, 26.4, 24.0.

HRMS (ESI): $C_8H_{12}{}^{35}Cl_3NO_4S$ [$(M+Na)^+$]: calcd.: 322.9553; found: 322.9555.

2, 2, 2-Trichloroethyl (*E*)-(5-hydroxy-2, 5-dimethylhex-3-en-2-yl) sulfamate (4v)



4v

A white solid. 23.9 mg, 68% yield.

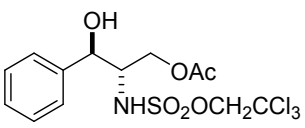
TLC: R_f = 0.41 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (d, *J* = 15.7 Hz, 1H), 5.79 (d, *J* = 15.7 Hz, 1H), 4.67 (s, 1H), 4.62 (s, 2H), 1.59 (s, 6H), 1.34 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 131.3, 93.5, 78.2, 70.6, 57.7, 29.8, 27.8.

HRMS (ESI): $C_{10}H_{18}{}^{35}Cl_3NO_4S$ $(M+Na)^+$]: calcd.: 375.9914; found: 375.9921.

(2*SR*, 3*RS*)-3-Hydroxy-3-phenyl-2-((2, 2, 2-trichloroethoxy) sulfonyl) Amino-propyl acetate(5)



5

A pale yellow oil. 40mg. 90% yield.

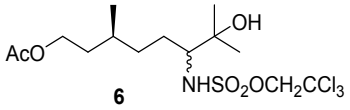
TLC: R_f = 0.45 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 5H), 5.37 (br, 1H), 5.02 (d, *J* = 4.1 Hz, 1H), 4.49 (d, *J* = 10.8 Hz, 1H), 4.35 (d, *J* = 10.8 Hz, 1H), 4.29 (dd, *J* = 11.9, 6.8 Hz, 1H), 4.03 (dd, *J* = 11.9, 4.0 Hz, 1H), 3.90 (d, *J* = 6.8 Hz, 1H), 2.56 (s, 1H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 139.2, 129.0, 128.6, 125.9, 100.0, 78.2, 73.7, 61.6, 59.1, 20.8.

HRMS (ESI): [$C_{13}H_{16}{}^{35}Cl_3NO_6S$ $(M+Na)^+$]: calcd.: 441.9656; found: 441.9659.

(3*S*)-7-Hydroxy-3, 7-dimethyl-6-(((2, 2, 2-trichloroethoxy) sulfonyl) amino) octyl acetate (6)



6

A yellow oil. 19.9 mg, 41% yield. The product contains a mixture of two inseparable diastereoisomers (d.r. = 1:1)

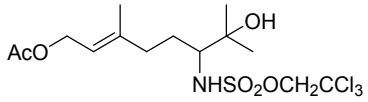
TLC: $R_{f=}$ 0.30 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 – 5.11 (m, 1H), 4.74 – 4.62 (m, 2H), 4.24 – 4.00 (m, 2H), 3.40 – 3.30 (m, 1H), 2.05 (s, 3H), 1.87 – 1.85 (m, 1H), 1.82 – 1.60 (m, 4H), 1.50 – 1.27 (m, 5H), 1.27 (s, 3H), 0.98 – 0.92 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 93.6, 78.0, 72.9, 64.7, 64.6, 62.8, 62.7, 35.5, 35.0, 33.4, 33.2, 30.0, 29.8, 28.4, 28.1, 28.0, 27.9, 26.3, 26.2, 21.1, 19.7, 19.2.

HRMS (ESI): $C_{14}H_{26}{}^{35}Cl_3NO_6S$ $(M+Na)^+$]: calcd.: 464.0439; found: 464.0442.

(*E*)-7-Hydroxy-3, 7-dimethyl-6-((2, 2, 2-trichloroethoxy) sulfonyl) Amino oct-2-en-1-yl acetate (7)



7

A pale yellow oil. 25.5 mg, 55% yield.

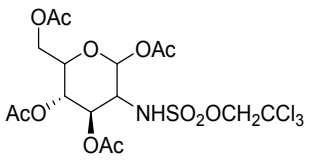
TLC: R_f = 0.39 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (t, *J* = 7.3 Hz, 1H), 5.29 (d, *J* = 8.8 Hz, 1H), 4.69 (s, 2H), 4.59 (d, *J* = 7.3 Hz, 2H), 3.36 (td, *J* = 9.6, 3.0 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.25 – 2.08 (m, 2H), 2.06 (s, 3H), 1.92 – 1.83 (m, 1H), 1.72 (s, 3H), 1.62 – 1.49 (m, 1H), 1.35 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 141.2, 118.9, 93.6, 78.1, 72.9, 64.1, 61.4, 35.9, 28.9, 27.9, 26.3, 21.1, 16.8.

HRMS (ESI): $C_{14}H_{24}{}^{35}Cl_3NO_6S$ $(M+Na)^+$]: calcd.: 462.0282; found: 462.0286.

(4*R*, 5*S*)-6-Acetoxymethyl-3-((2, 2, 2-trichloroethoxy) sulfonyl) Amino-Tetrahydro-2H-pyran-2, 4, 5-triyl triacetate (8)



8

A pale yellow oil. 32.2 mg. 58% yield.

TLC: R_f = 0.42 (Hexane/EtOAc = 1:1) [$KMnO_4$].

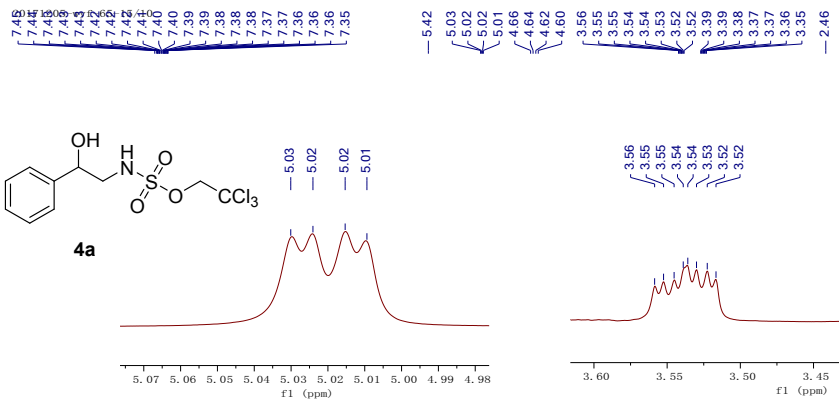
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (s, 1H), 5.65 (d, *J* = 8.5 Hz, 1H), 5.15 (t, *J* = 9.8Hz, 1H), 5.04 (t, *J* = 9.7 Hz, 1H), 4.56 (m, 2H), 4.22 (dd, *J* = 12.6, 4.5 Hz, 1H), 4.05 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.81 (ddd, *J* = 10.1, 4.5, 2.2 Hz, 1H), 3.70 (q, *J* = 10.1 Hz, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H).

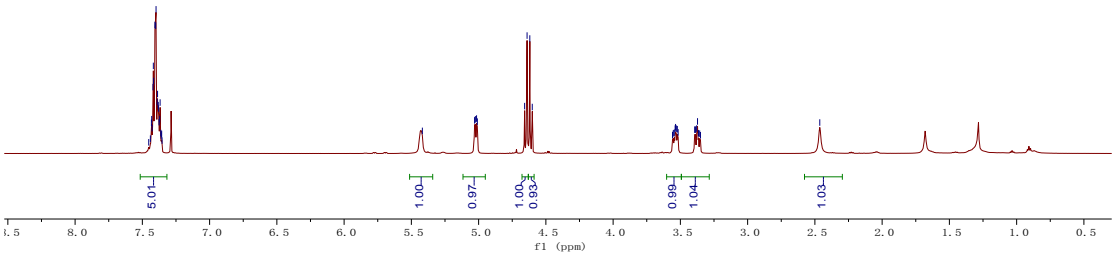
The spectra data are matched with those reported.[3]

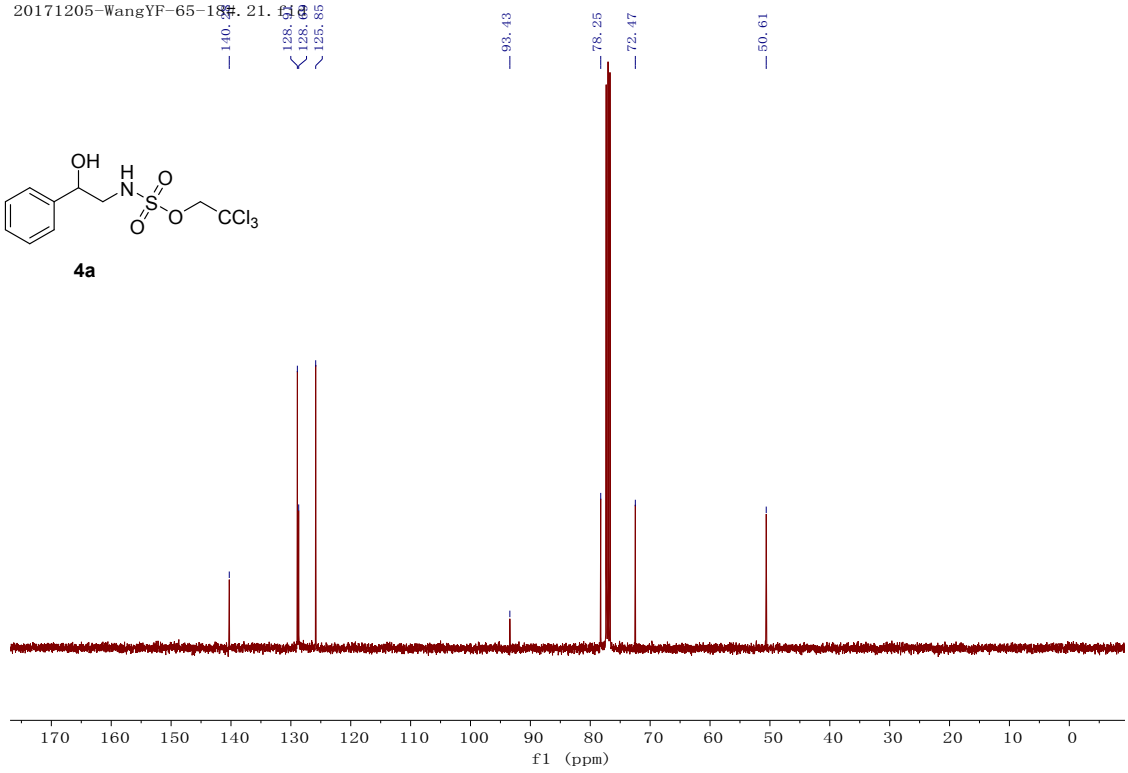
Reference:

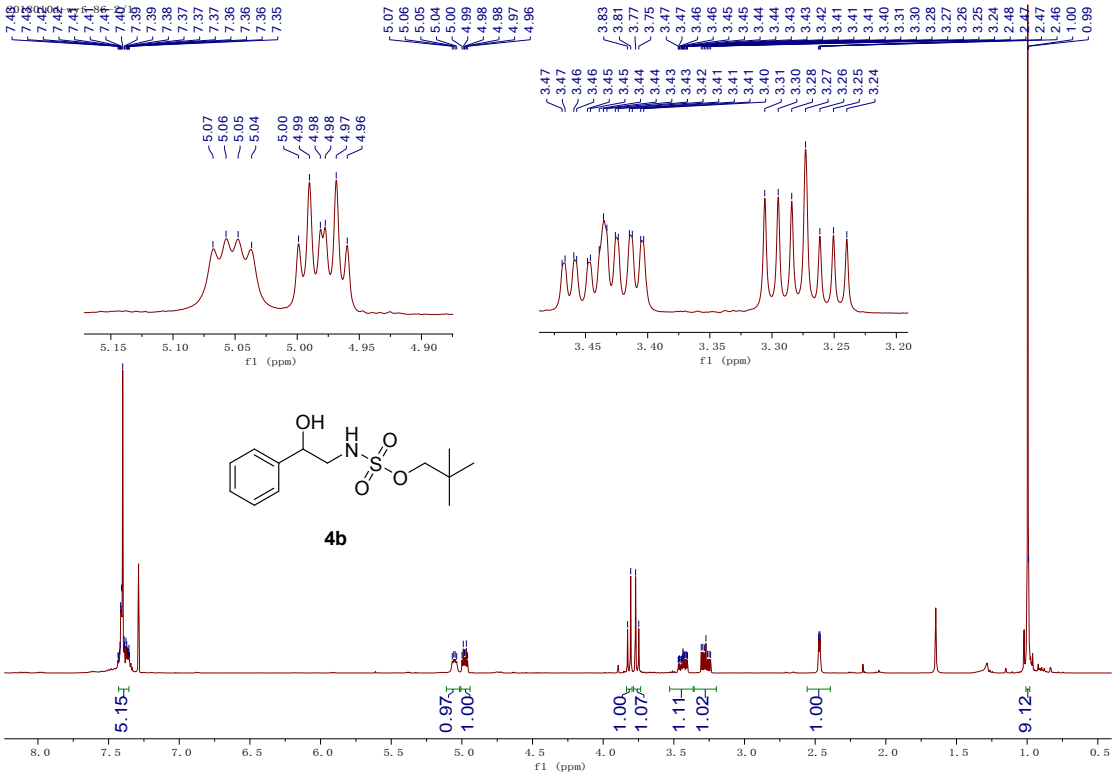
1. C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.*, 2004 , **126**, 15378.
2. K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc.*, 2007, **129**, 562.
3. K. Guthikonda, P. M. When, B. J. Caliando, J. Du Bois, *Tetrahedron,* 2006, **62**, 11331.

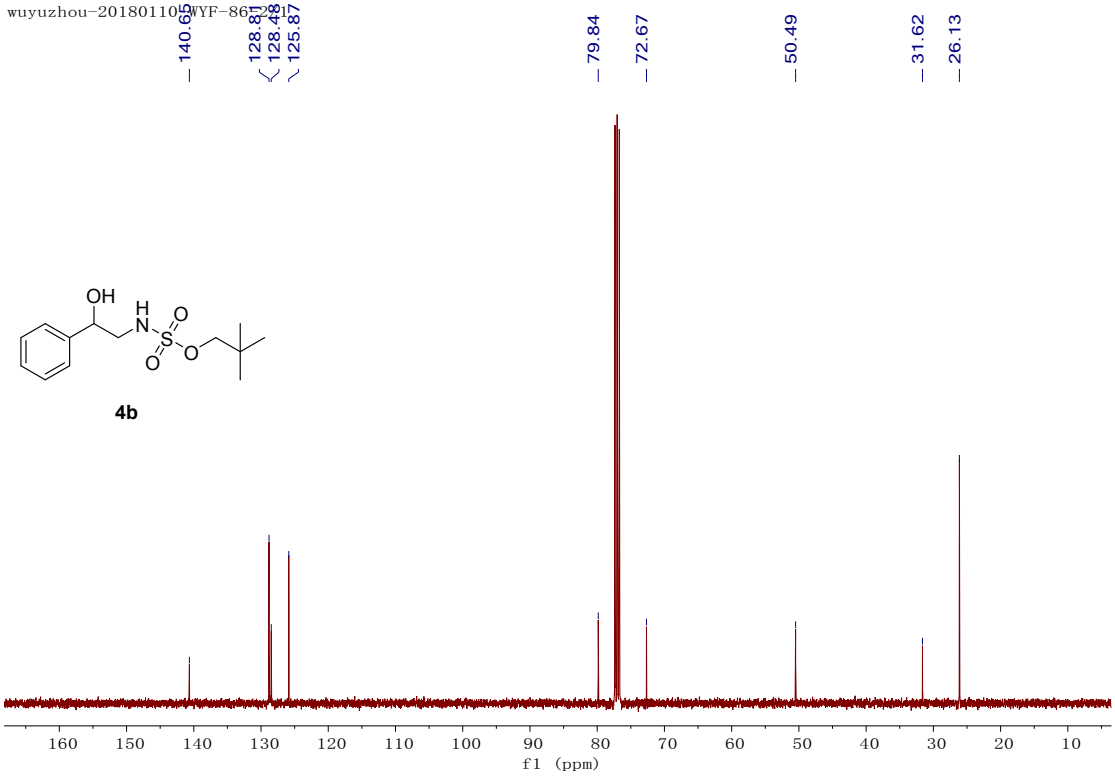
E.^{1}H and ^{13}C NMR Spectra Data of All Products








4b
f1 (ppm)


wuyuzhou-20180110-WYF-867
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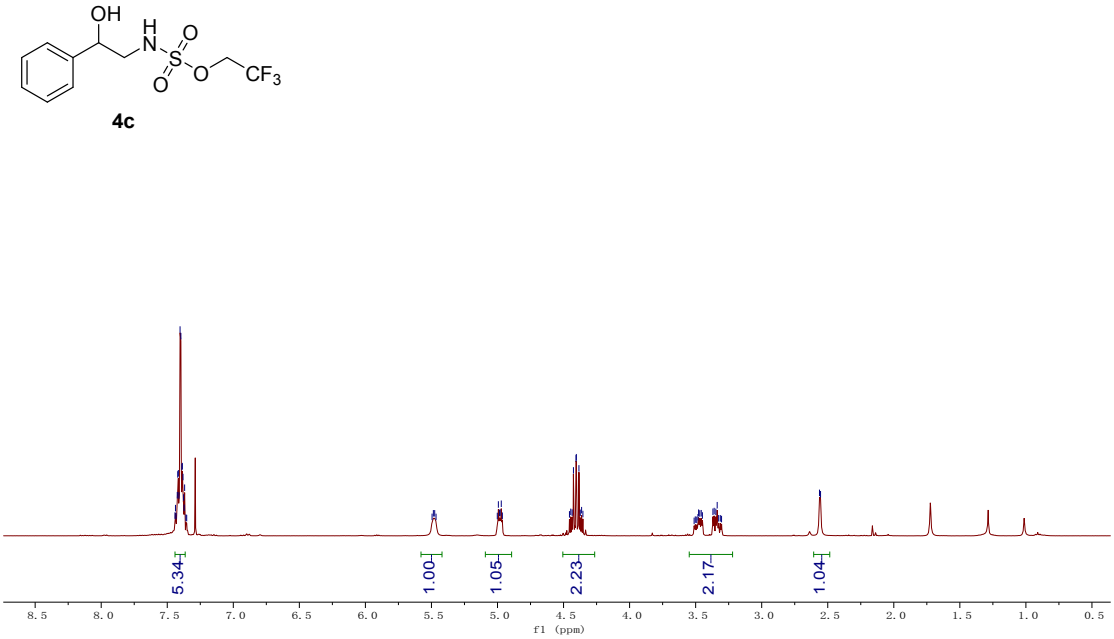
4b
f1 (ppm)


OH
H
N
S
O
O
O
O
CF3
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1.00
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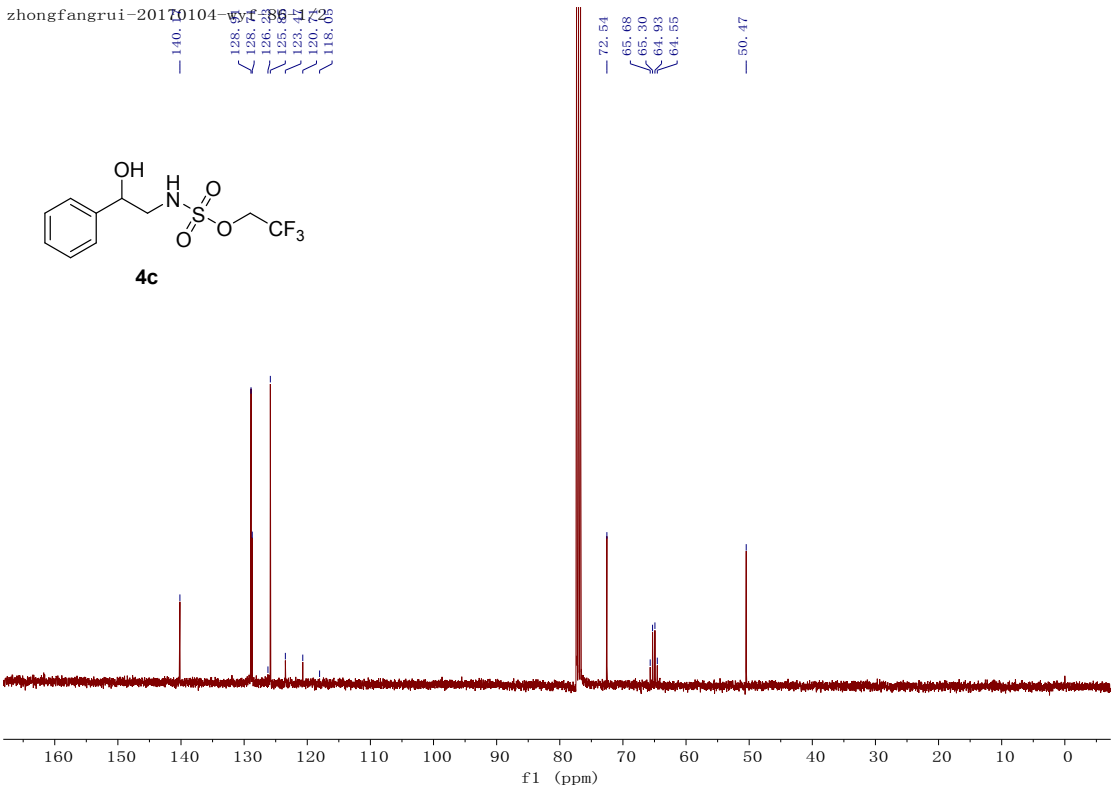
f1 (ppm)


OH
H
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S
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O
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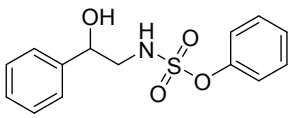
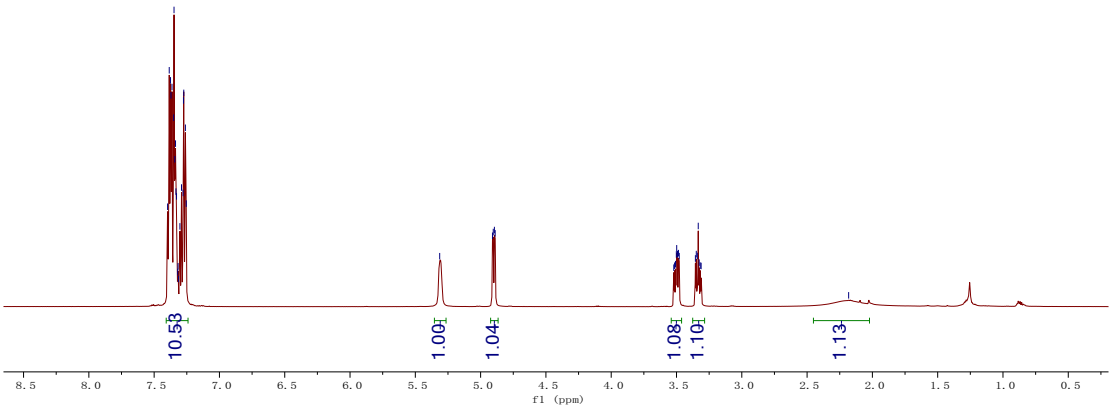
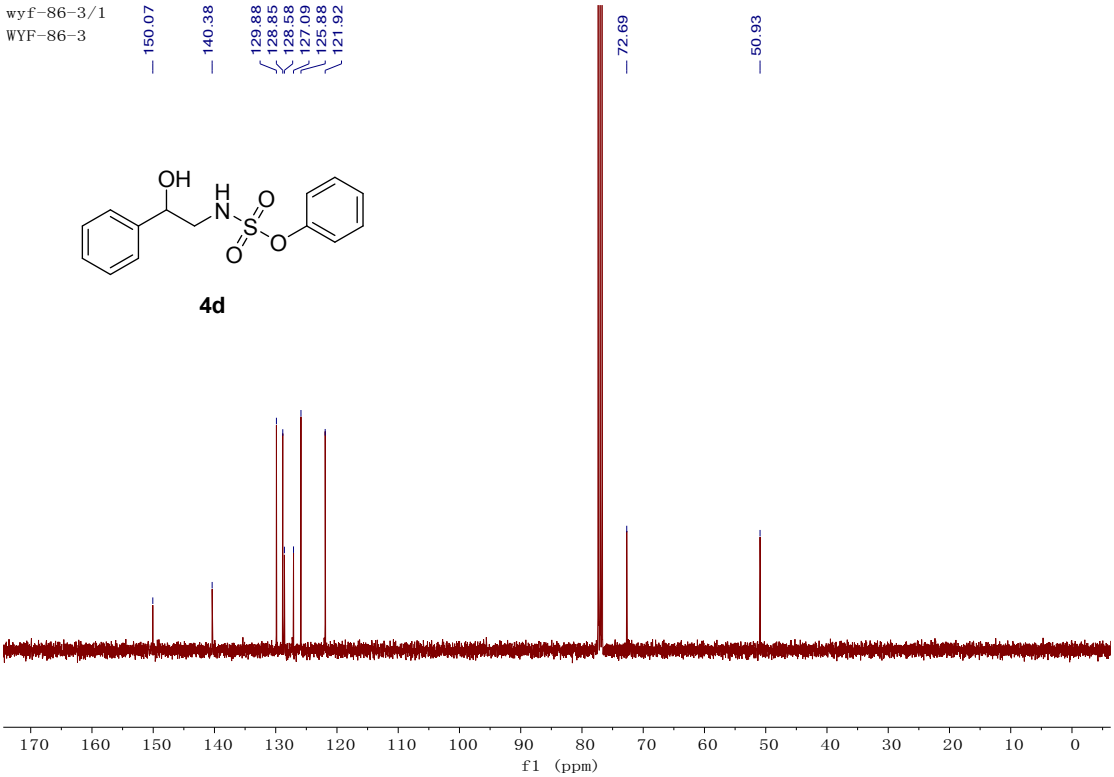
64.55
50.47
f1 (ppm)

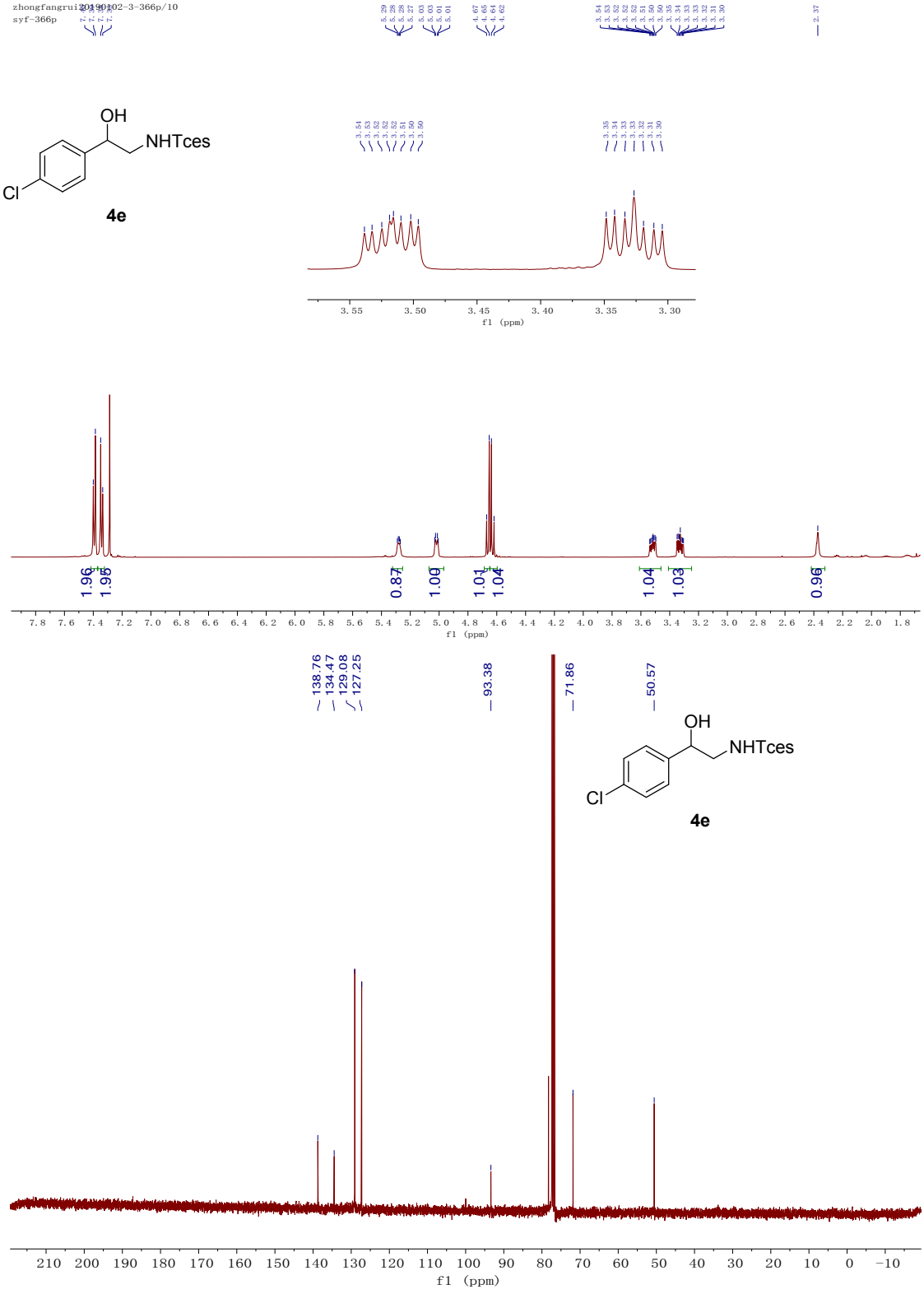


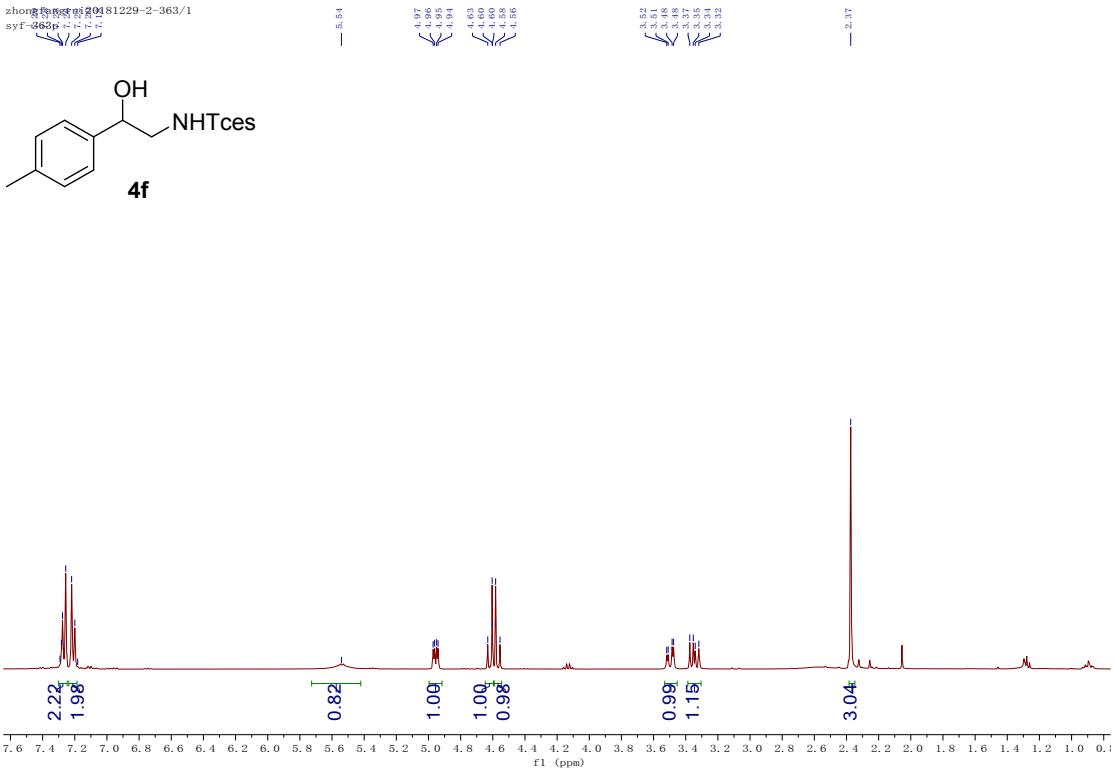
4d

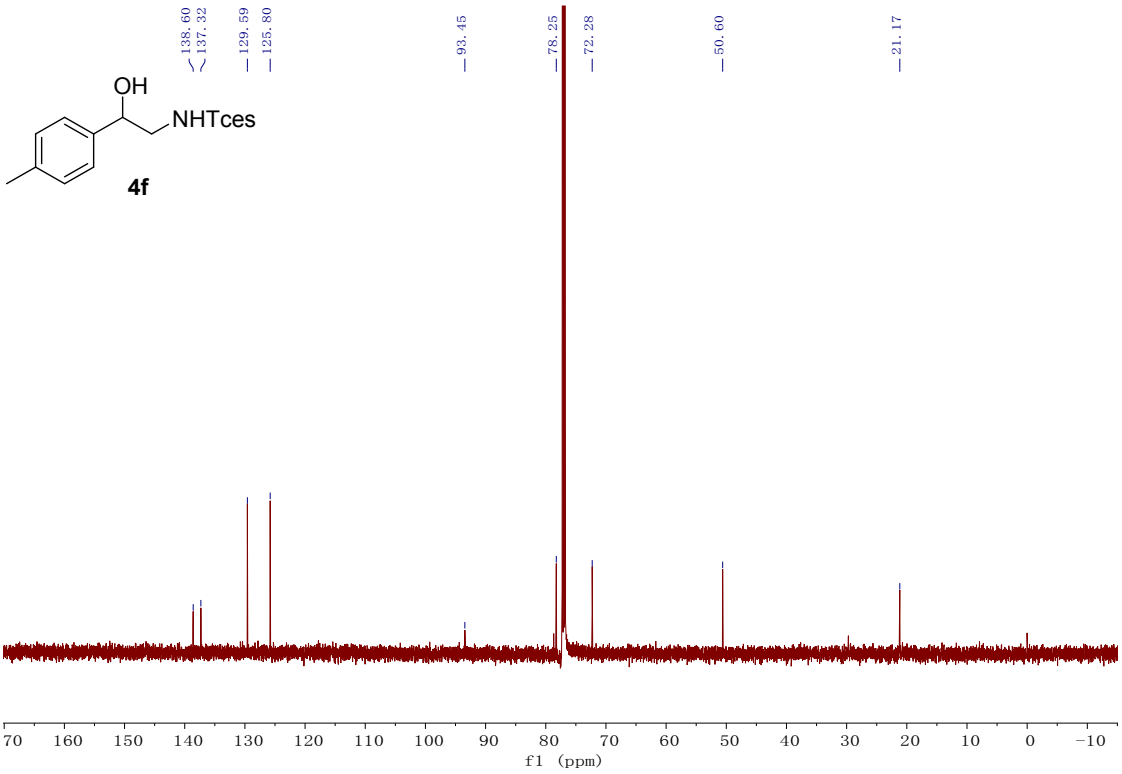

10.53
1.00
1.04
1.08
1.10
1.13
f1 (ppm)

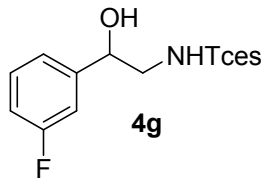

wyf-86-3/1
WYF-86-3
150.07
140.38
129.88
128.85
128.58
127.09
125.88
121.92
72.69
50.93
f1 (ppm)

4d

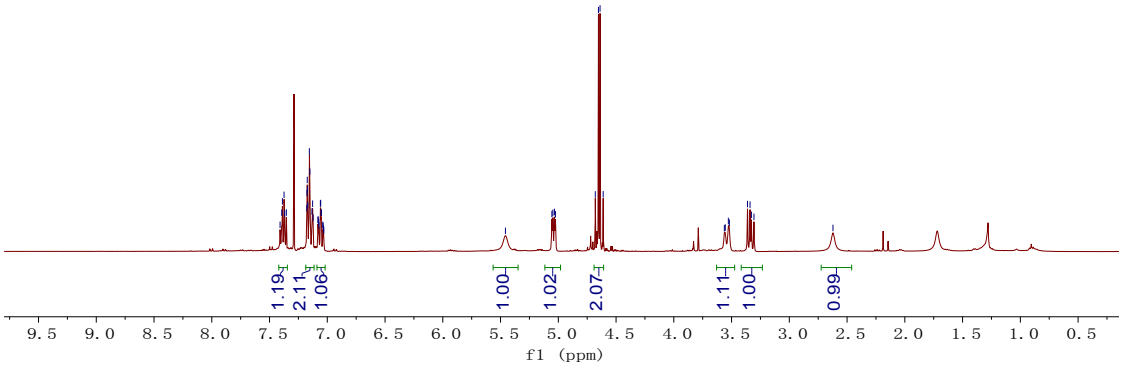

zhongfangrui20190102-3-366p/10
syf-366p
OH
NHTces
Cl
4e
1.96
1.95
0.87
1.00
1.01
1.04
1.04
1.03
0.96
f1 (ppm)
138.76
134.47
129.08
127.25
93.38
71.86
50.57
OH
NHTces
Cl
4e
f1 (ppm)

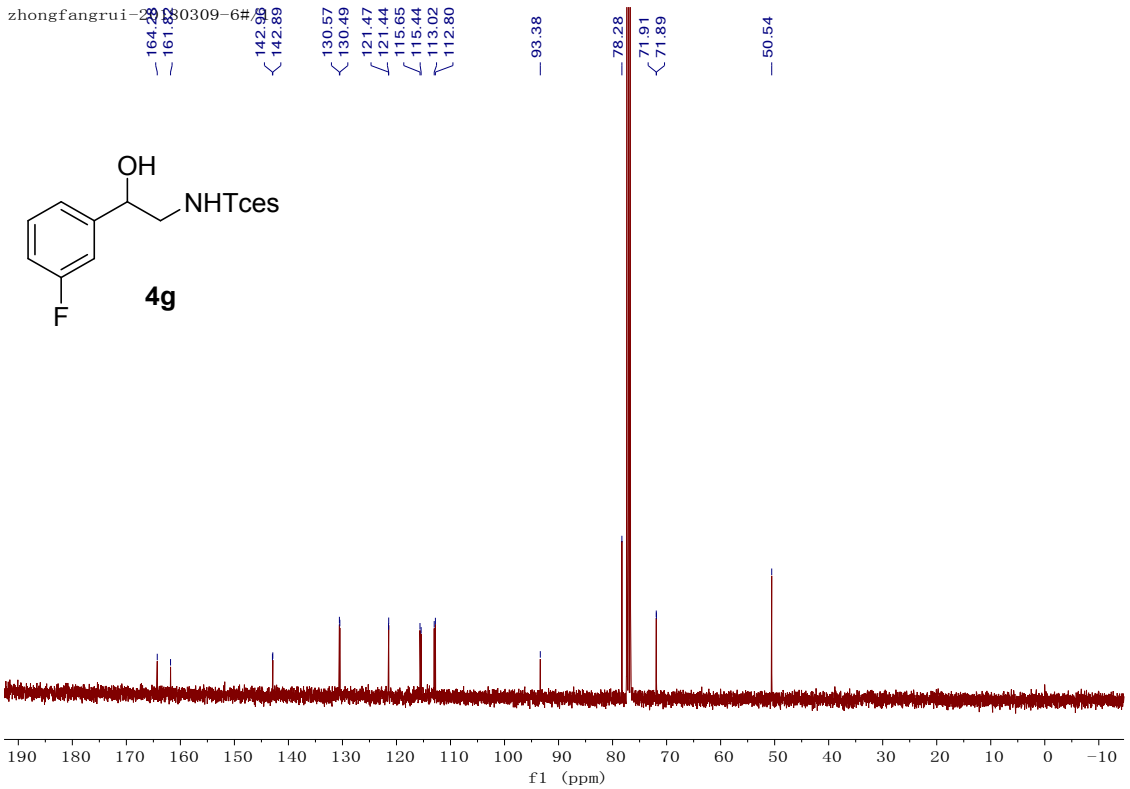

OH
NHTces
4f
2.22
1.98
0.82
1.00
1.00
0.98
0.99
1.15
3.04
f1 (ppm)


OH
NHTces
4f
138.60
137.32
129.59
125.80
93.45
78.25
72.28
50.60
21.17
f1 (ppm)


OH
NHTces
F

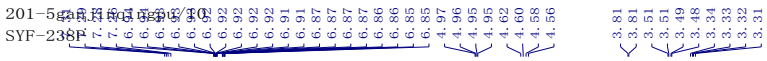
4g

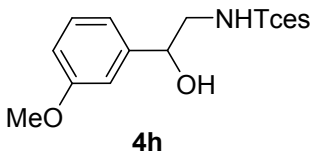

1.19
2.11
1.06
1.00
1.02
2.07
1.11
1.00
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


164.21
161.83
142.89
130.57
130.49
121.47
121.44
115.65
115.44
113.02
112.80
93.38
78.28
71.91
71.89
50.54
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

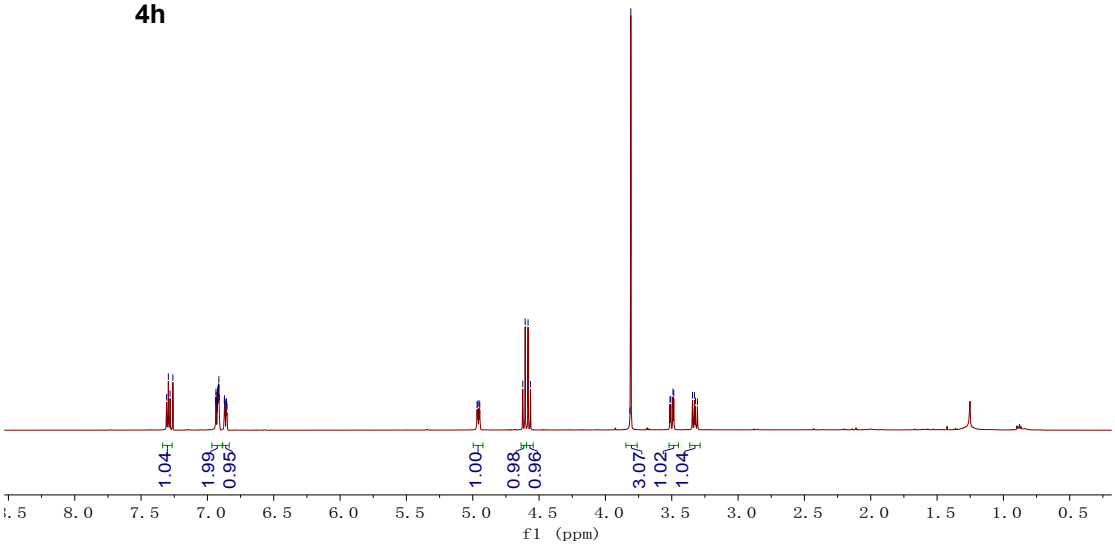
OH
NHTces
F

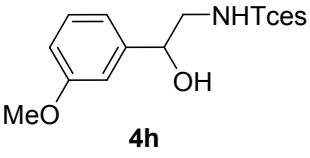
4g



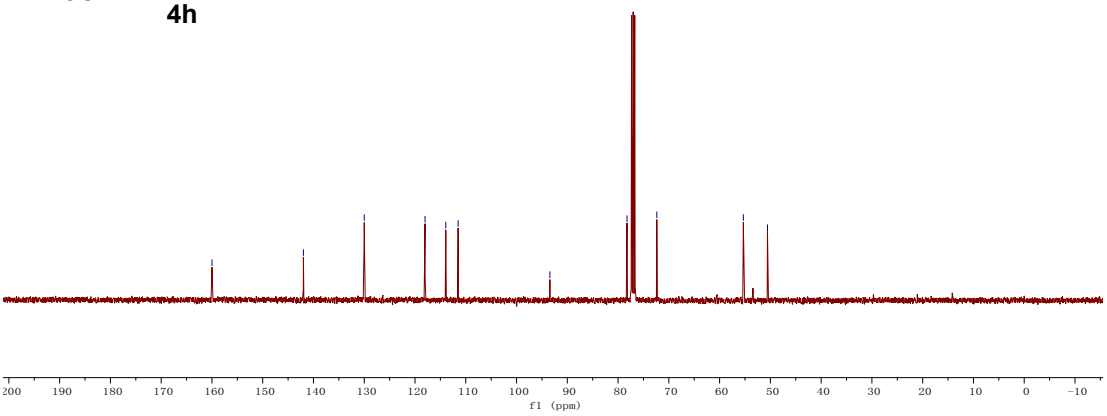

NHTces
OH
MeO

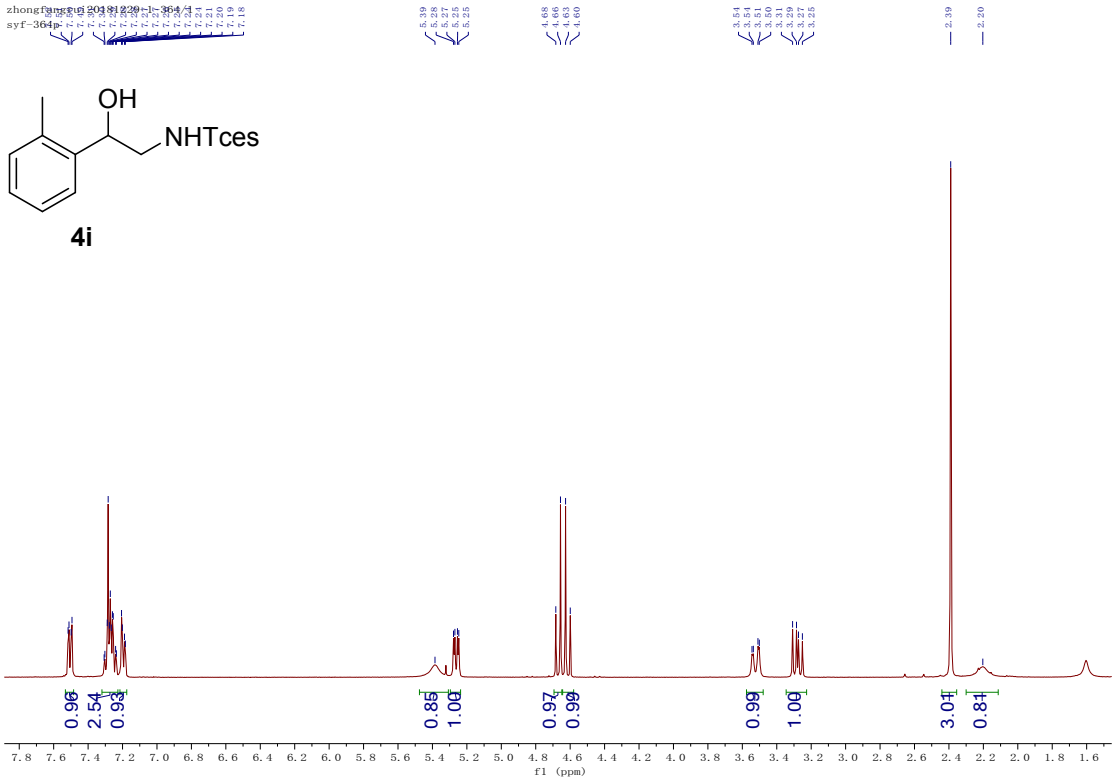
4h

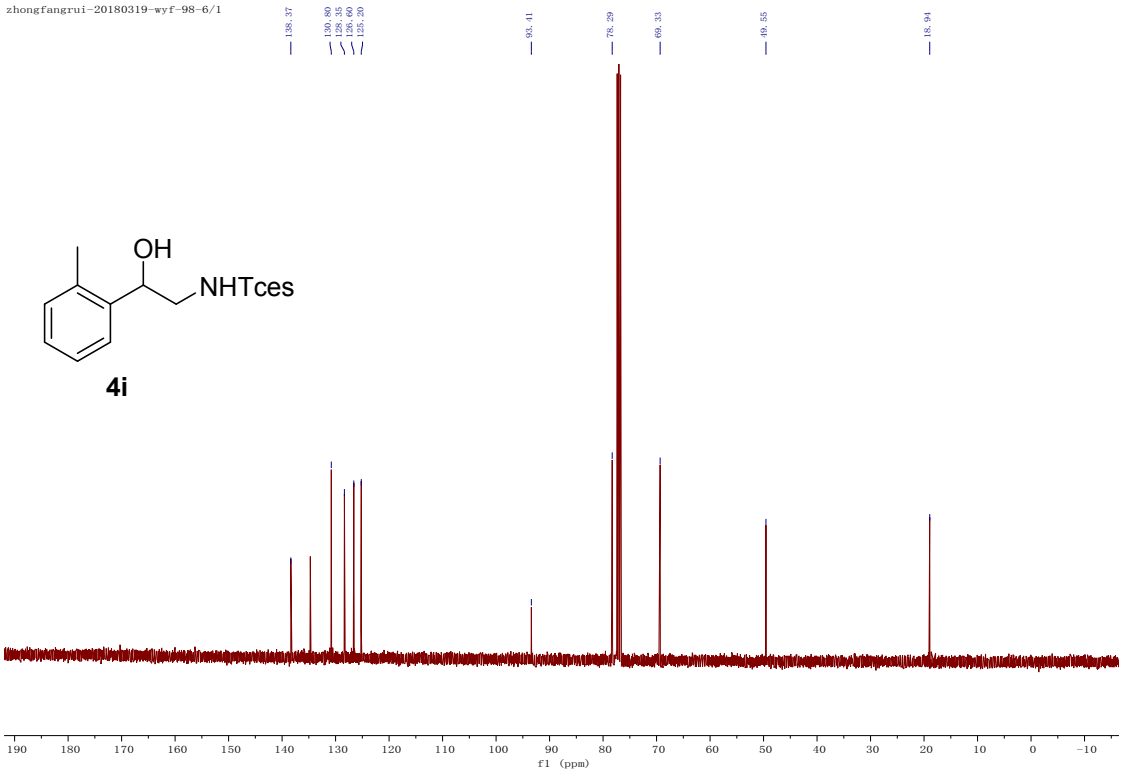

1.04
1.99
0.95
1.00
0.98
0.96
3.07
1.02
1.04
f1 (ppm)

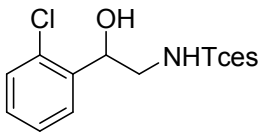

NHTces
OH
MeO

4h

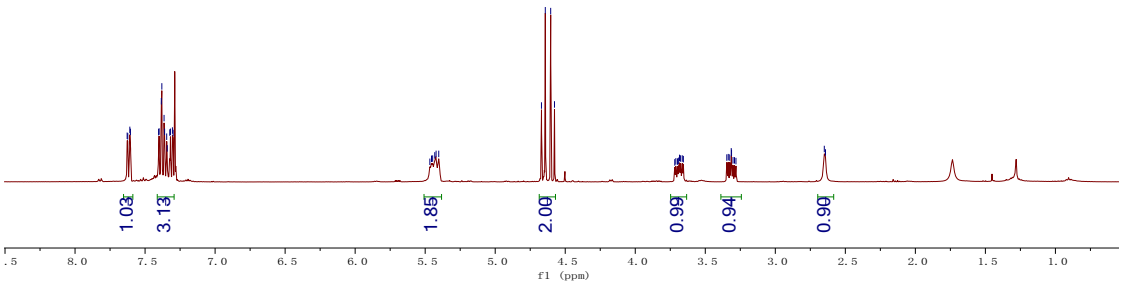

f1 (ppm)

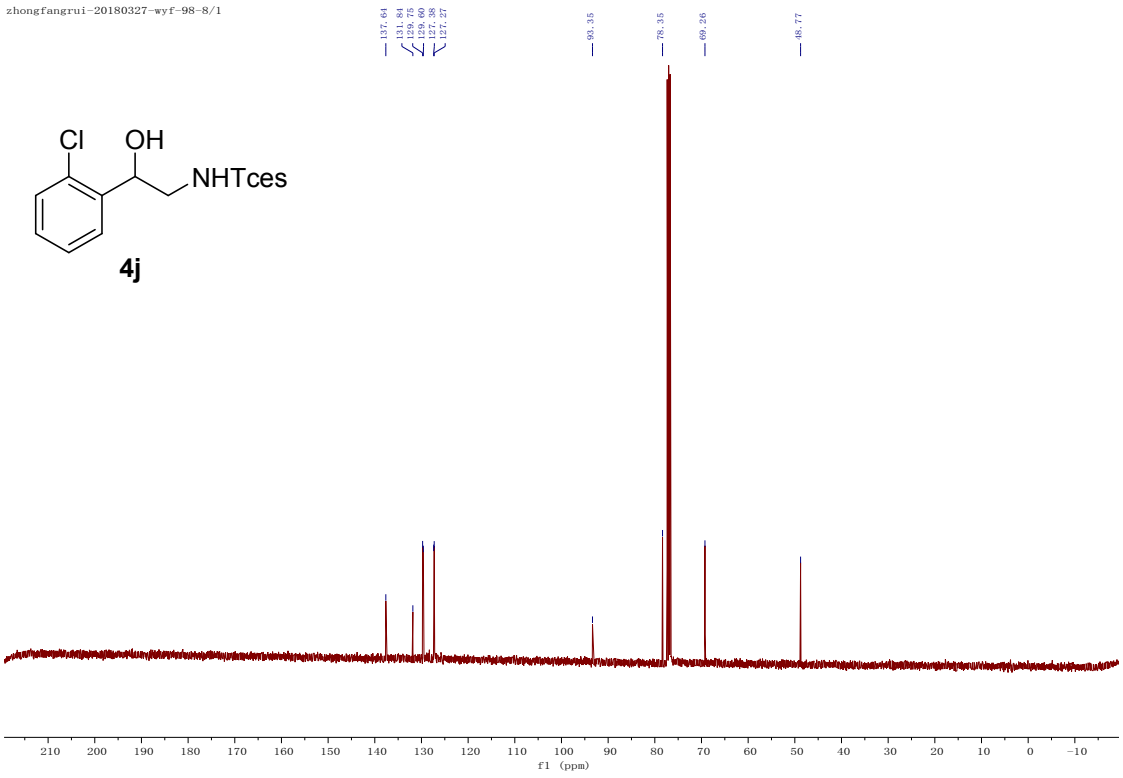

OH
NHTces
4i
0.96
2.54
0.93
0.85
1.00
0.97
0.99
0.99
1.00
3.04
0.81
f1 (ppm)


OH
NHTces
4i
f1 (ppm)


Cl
OH
NHTces

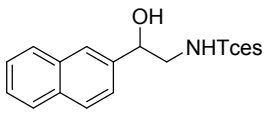
4j


1.03
3.13
1.85
2.00
0.99
0.94
0.90
f1 (ppm)

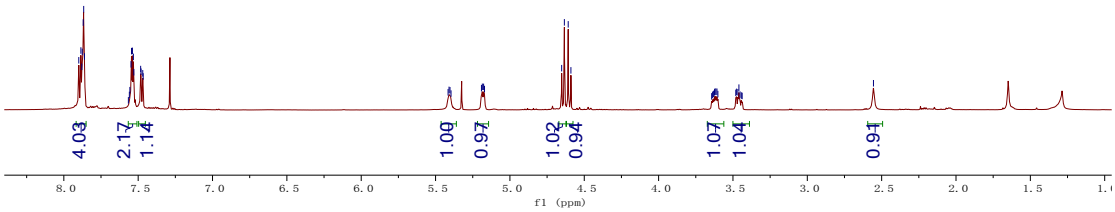

zhongfangrui-20180327-wyf-98-8/1
137.64
131.84
129.75
129.66
127.38
127.27
93.35
78.35
69.26
48.77
f1 (ppm)

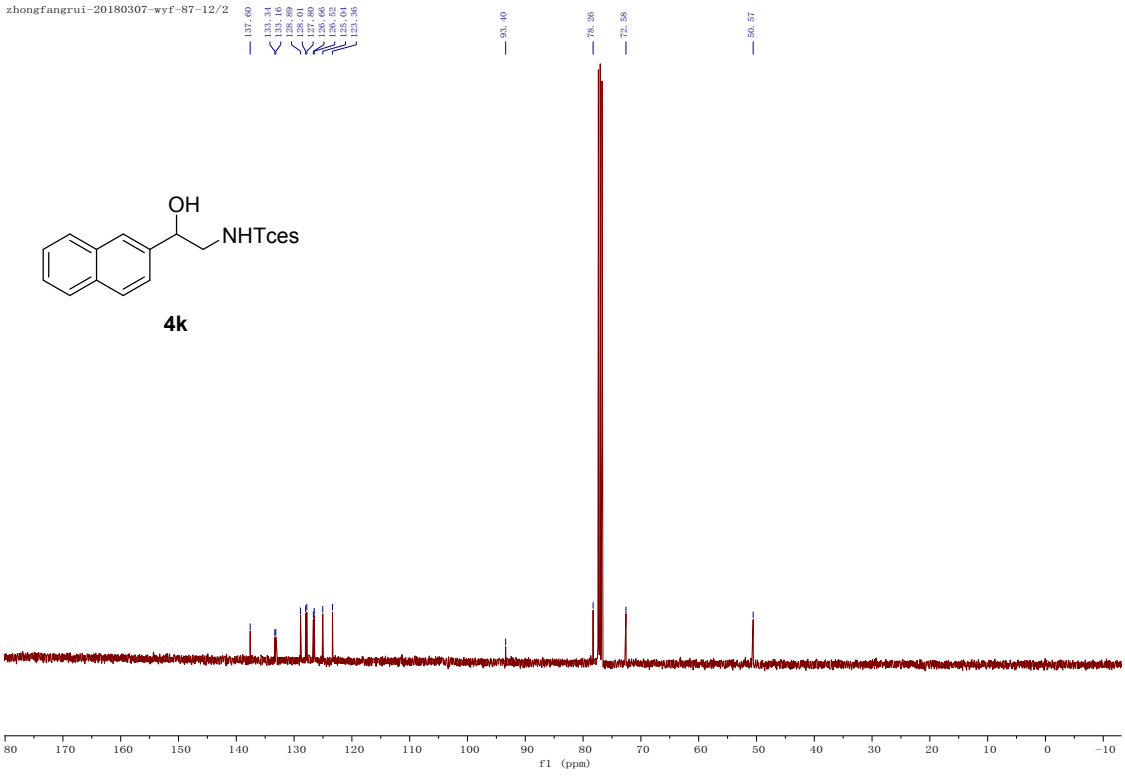
Cl
OH
NHTces

4j


OH
NHTces

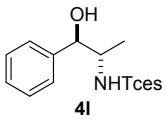
4k


4.03
2.17
1.14
1.00
0.97
1.02
0.94
1.07
1.04
0.91
f1 (ppm)

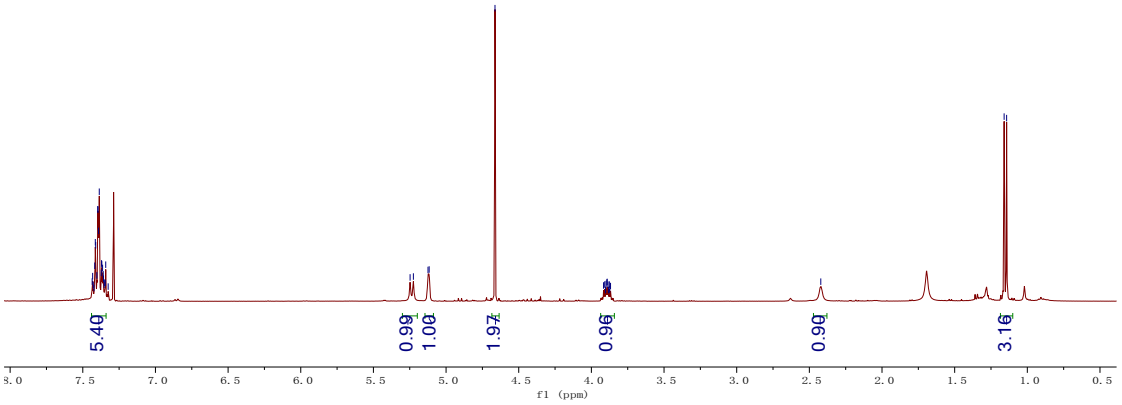

zhongfangrui-20180307-wyf-87-12/2
137.69
133.34
133.16
128.89
128.01
127.69
126.66
126.52
125.04
123.36
93.40
78.26
72.88
50.57
f1 (ppm)

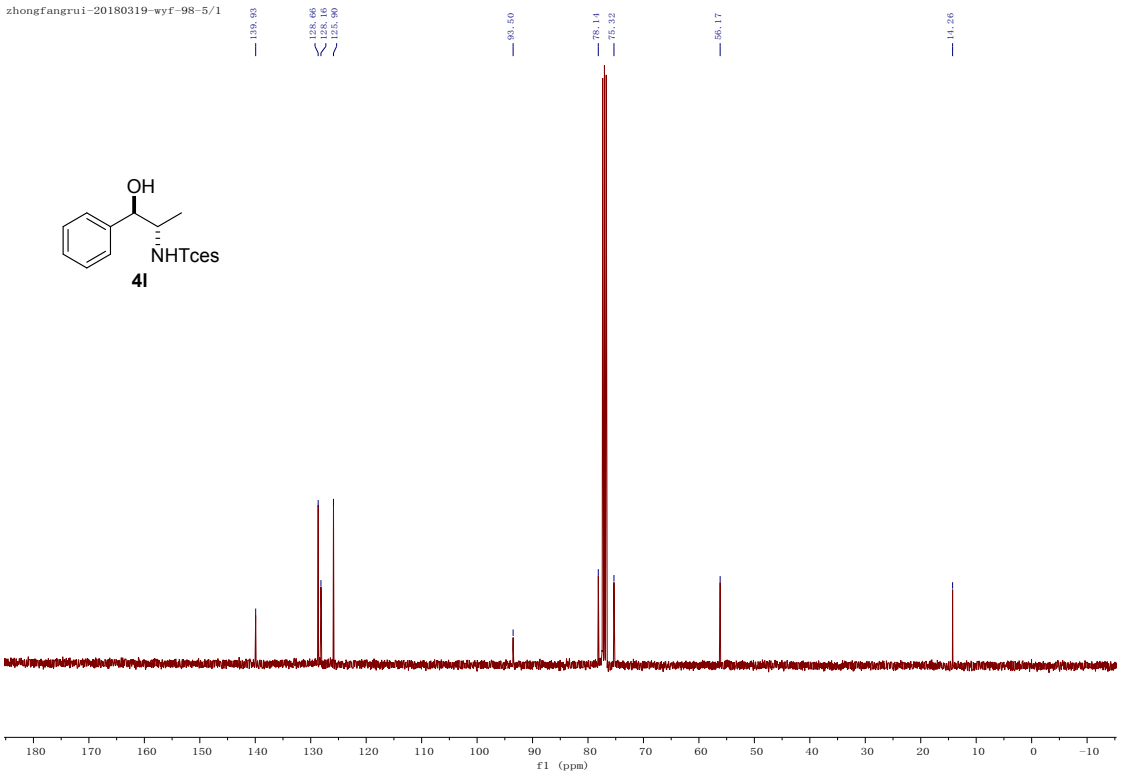
OH
NHTces

4k


OH
NHTces

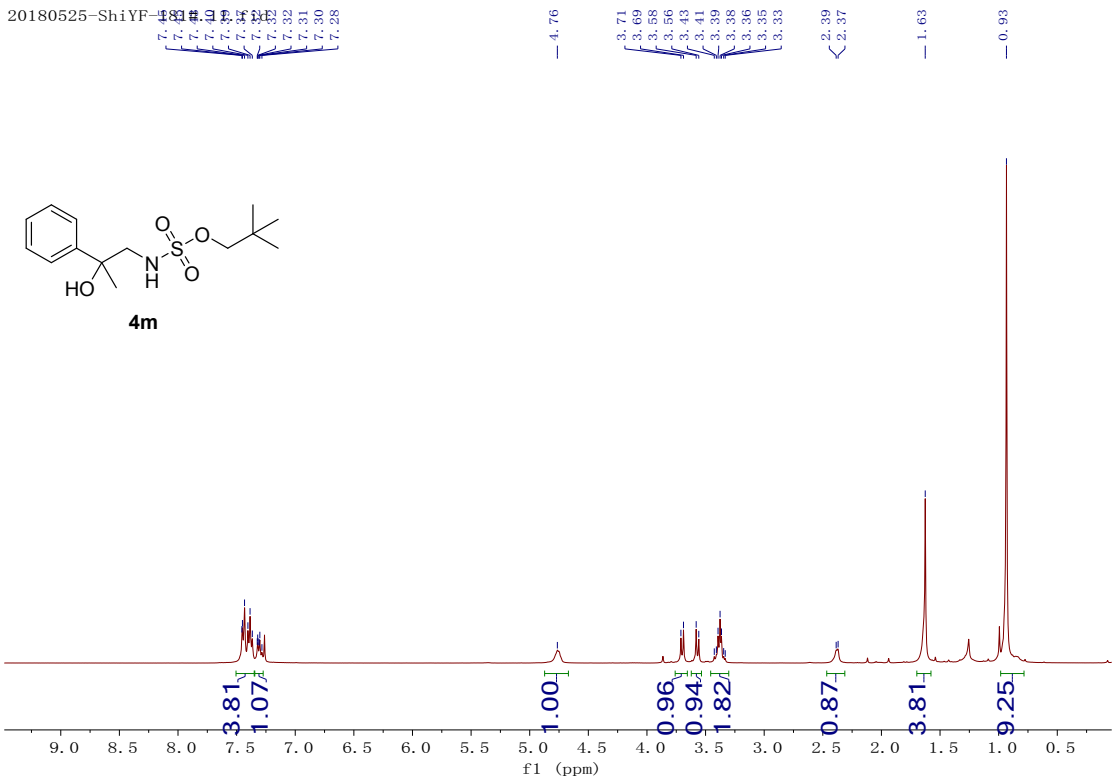
4l

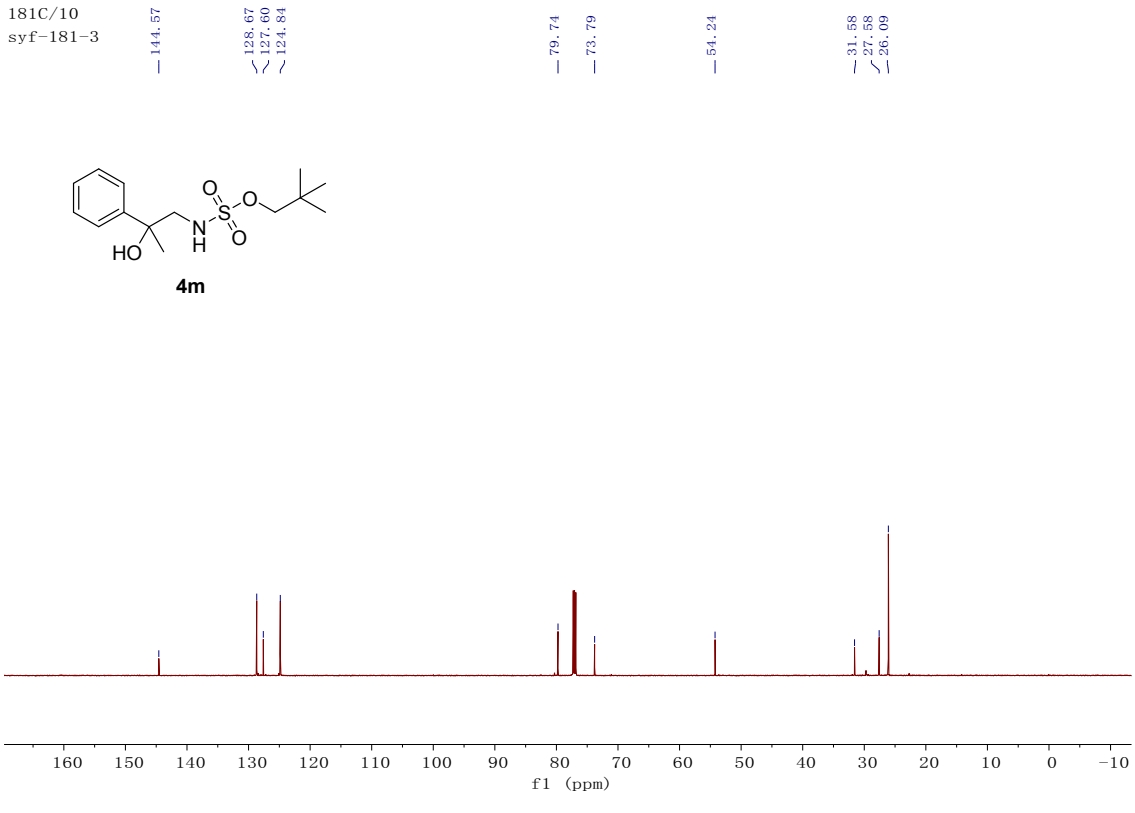

5.40
0.99
1.00
1.97
0.96
0.90
3.16
f1 (ppm)

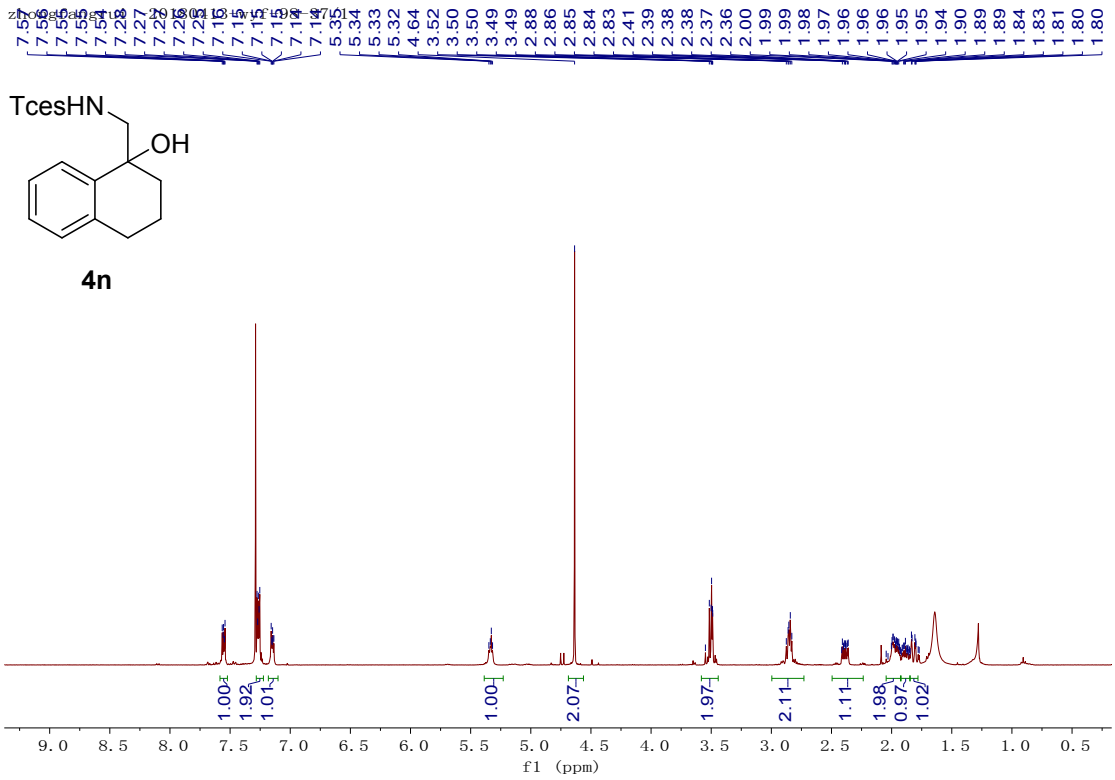

zhongfangrui-20180319-wyf-98-5/1
139.93
128.66
128.16
125.90
93.50
78.14
75.32
56.17
14.26
f1 (ppm)

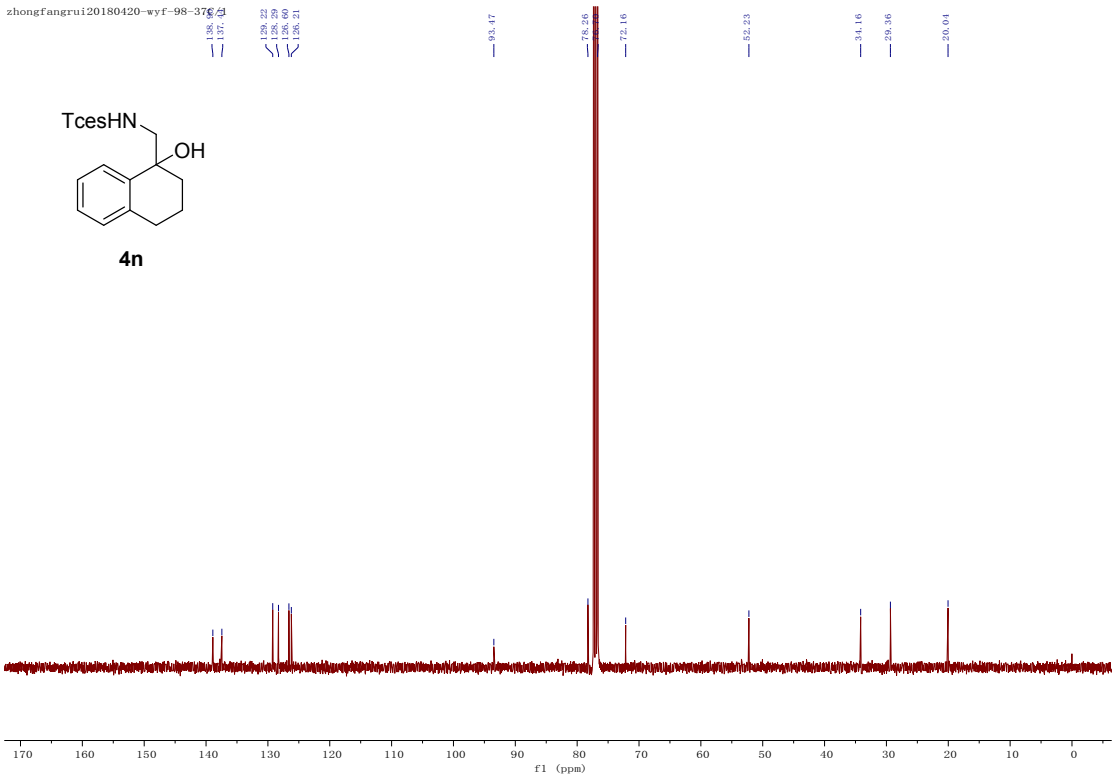
OH
NHTces

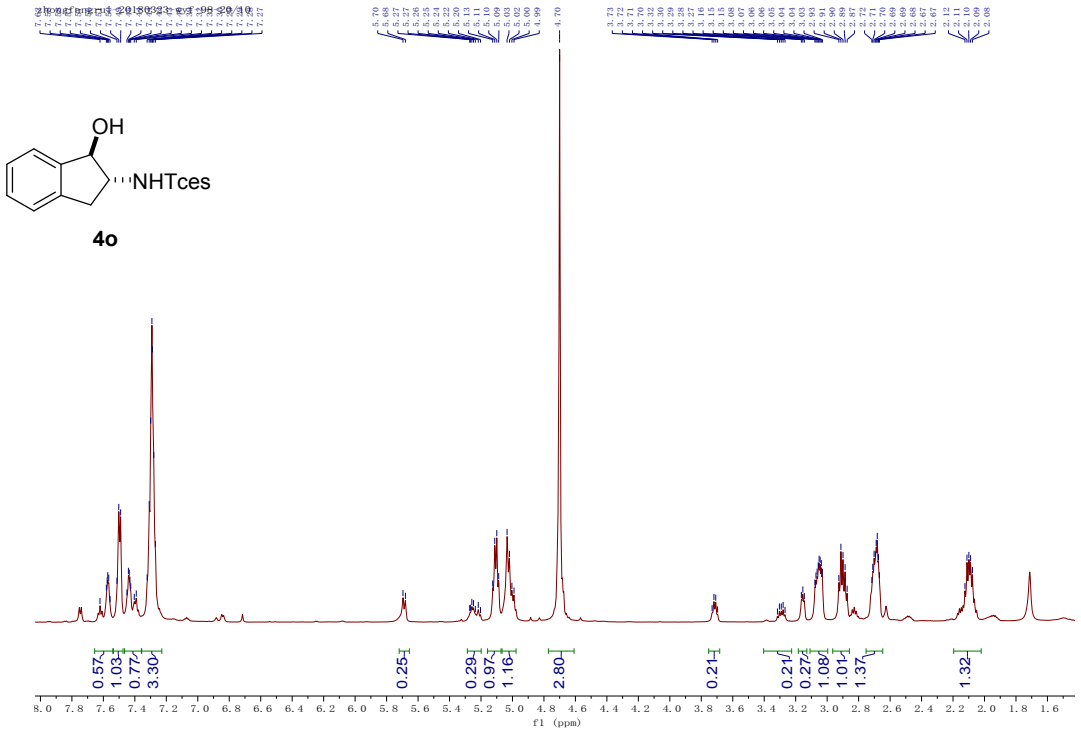
4l

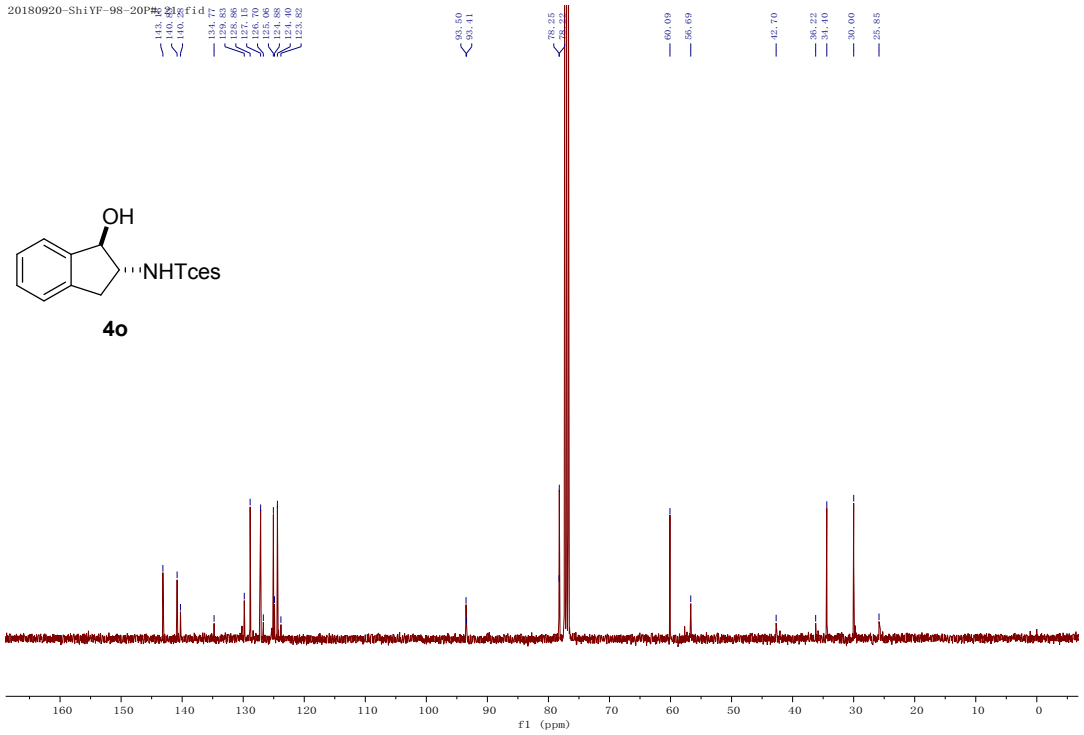

20180525-ShiYF-181#
7.44
7.43
7.41
7.40
7.33
7.32
7.32
7.31
7.30
7.28
4.76
3.71
3.69
3.58
3.56
3.43
3.41
3.39
3.38
3.36
3.35
3.33
2.39
2.37
1.63
0.93
O
S
O
O
N
H
HO
4m
3.81
1.07
1.00
0.96
0.94
1.82
0.87
3.81
9.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

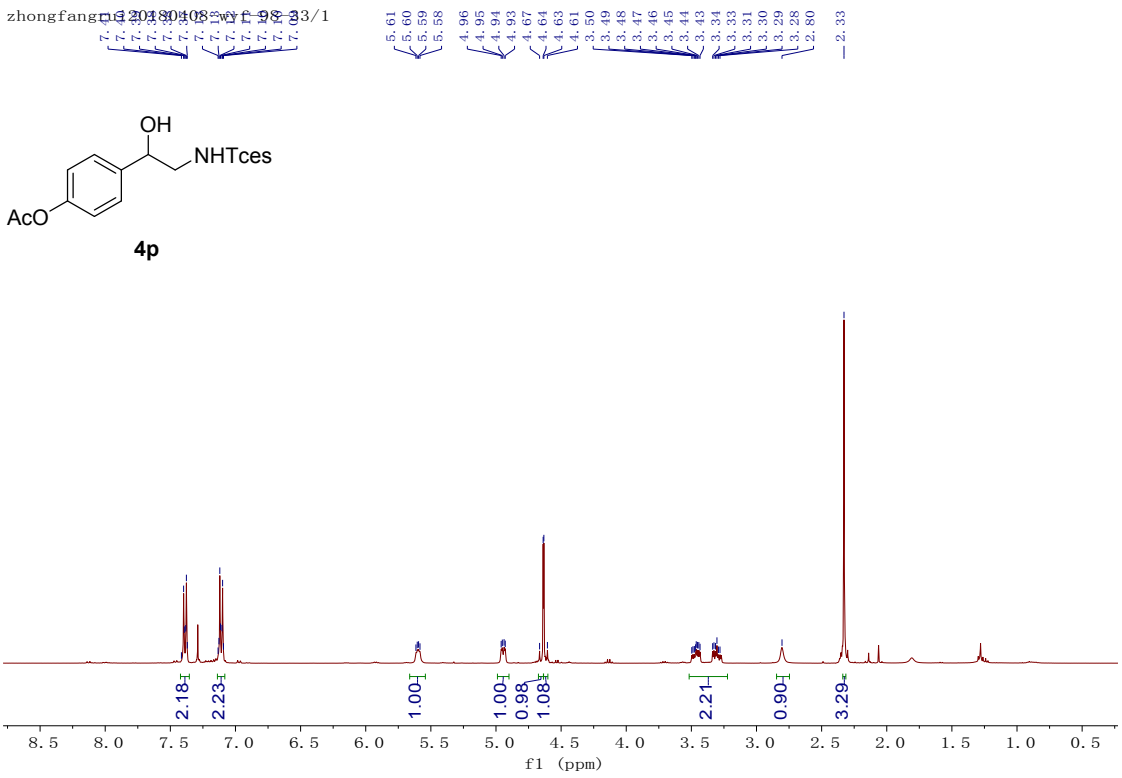

181C/10
syf-181-3
144.57
128.67
127.60
124.84
79.74
73.79
54.24
31.58
27.58
26.09
O
S
O
O
N
H
HO
4m
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

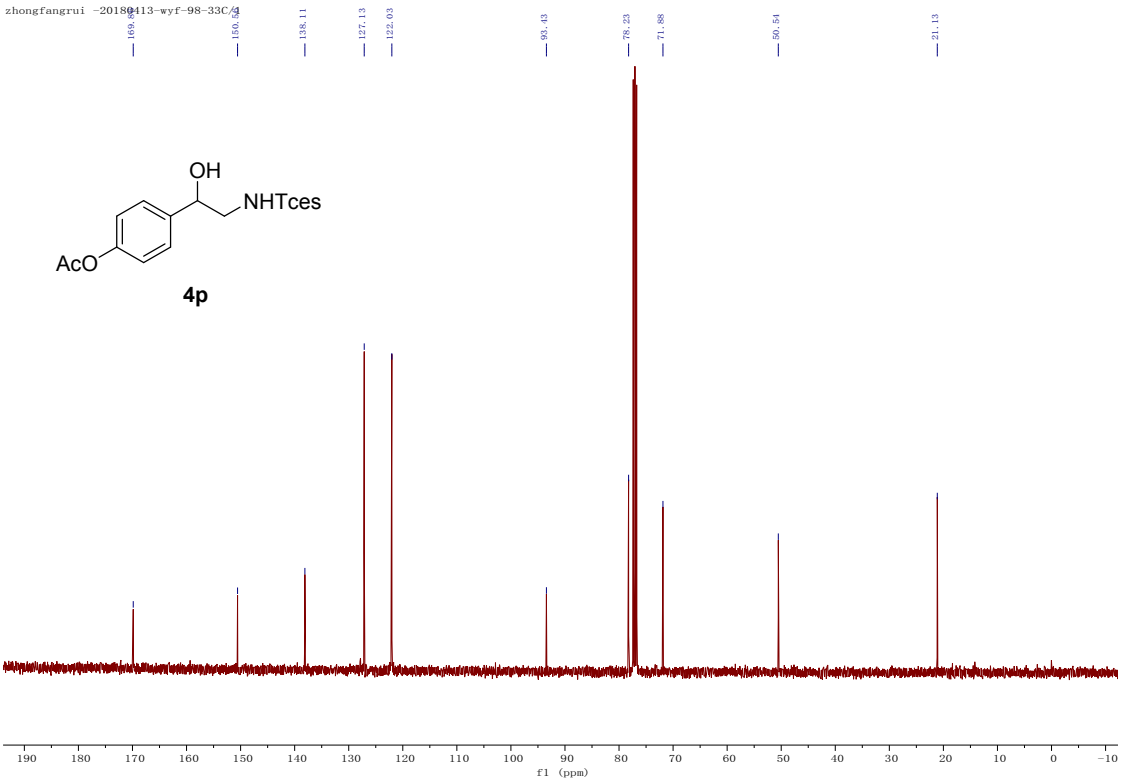

TcesHN
OH
4n
1.00
1.92
1.01
1.00
2.07
1.97
2.11
1.11
1.98
0.97
1.02
f1 (ppm)

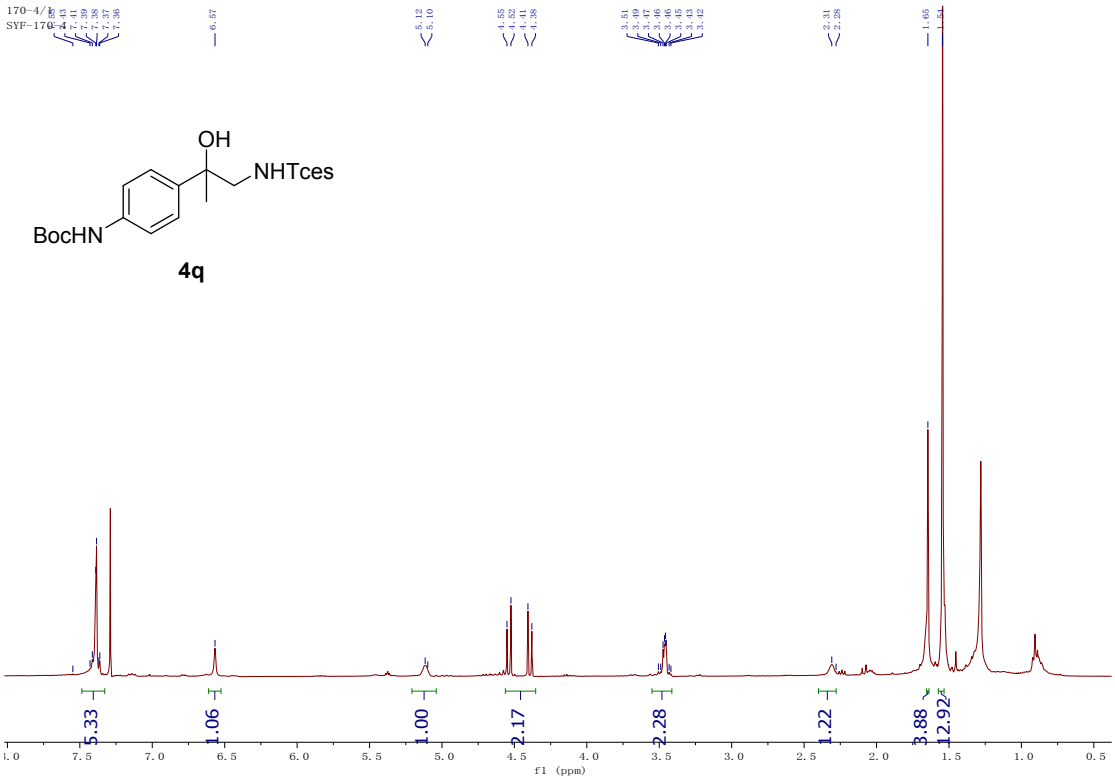

TcesHN
OH
4n
f1 (ppm)

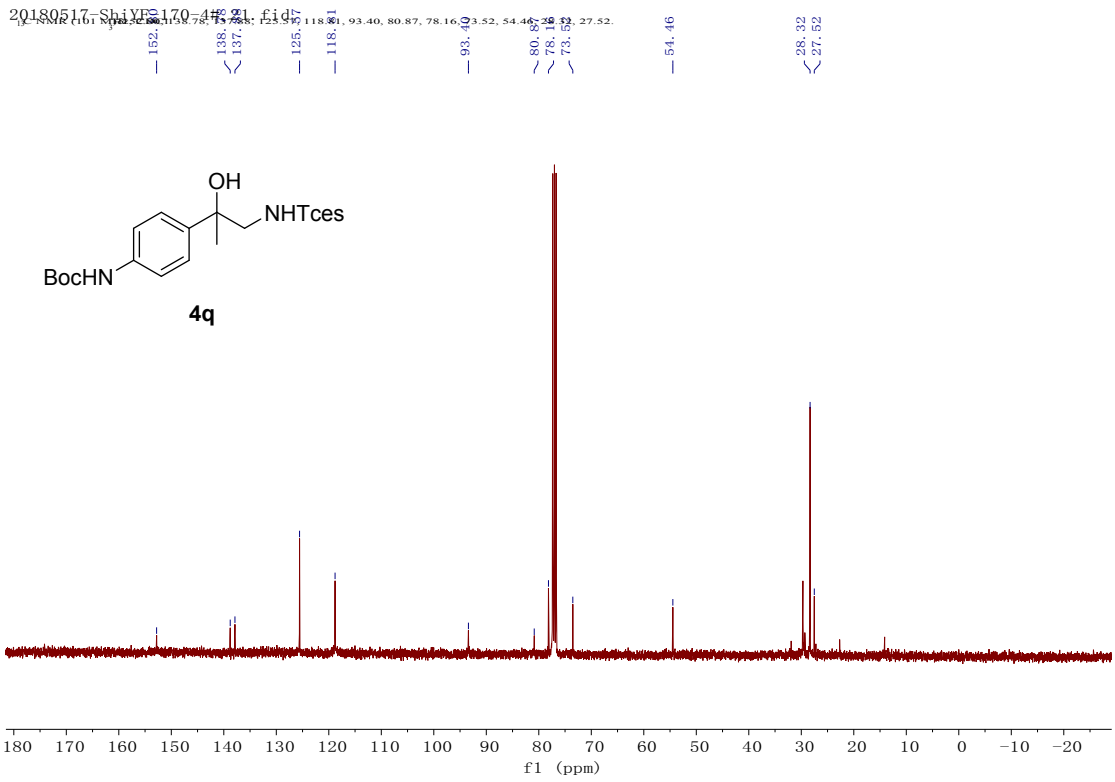

OH
NHTces
4o
0.57
1.03
0.77
3.30
0.25
0.29
0.97
1.16
2.80
0.21
0.21
0.27
1.08
1.01
1.37
1.32
f1 (ppm)

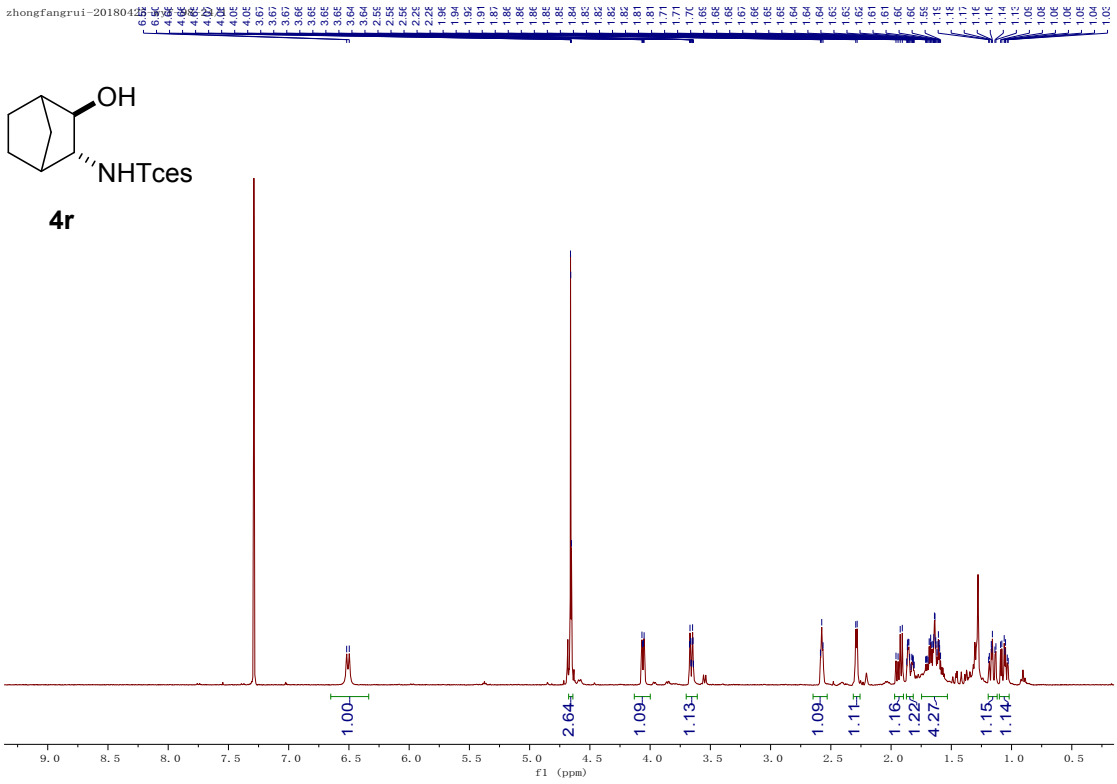

OH
NHTces
4o
93.50
93.41
78.25
78.22
60.09
56.69
42.70
36.22
34.10
30.00
25.85
f1 (ppm)

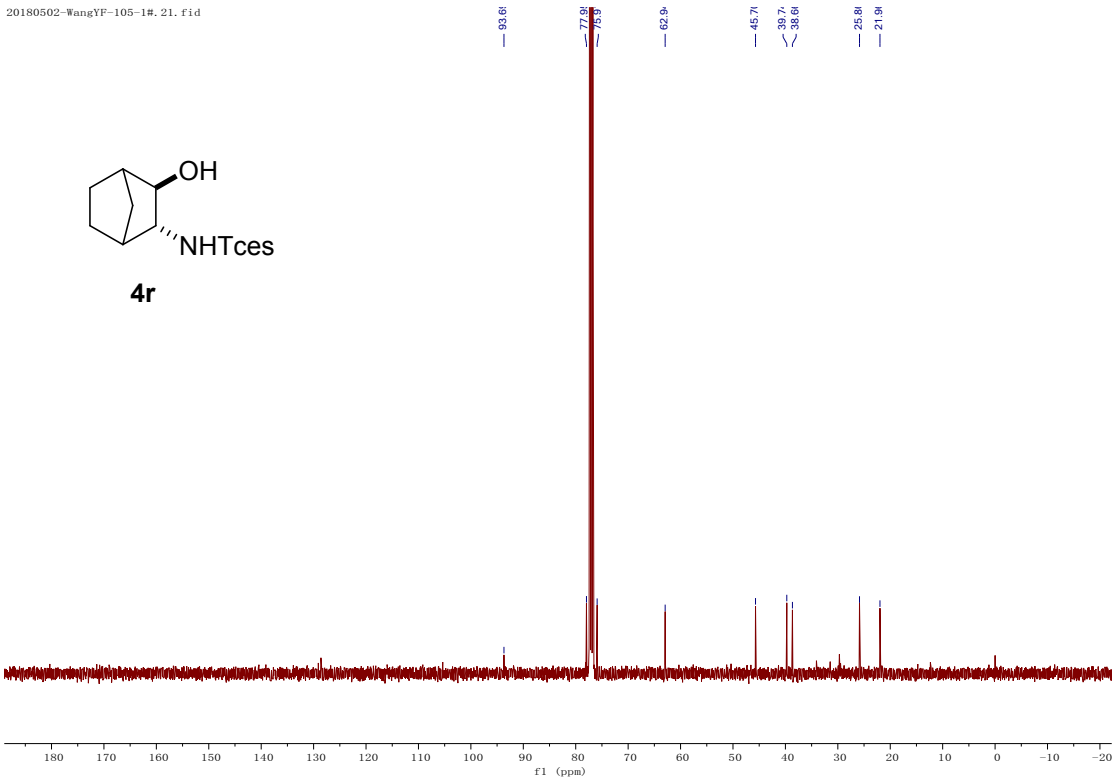

zhongfangrui -20180408-wyf-98-33/1
OH
NHTces
AcO
4p
2.18
2.23
1.00
1.00
0.98
1.08
2.21
0.90
3.29
f1 (ppm)

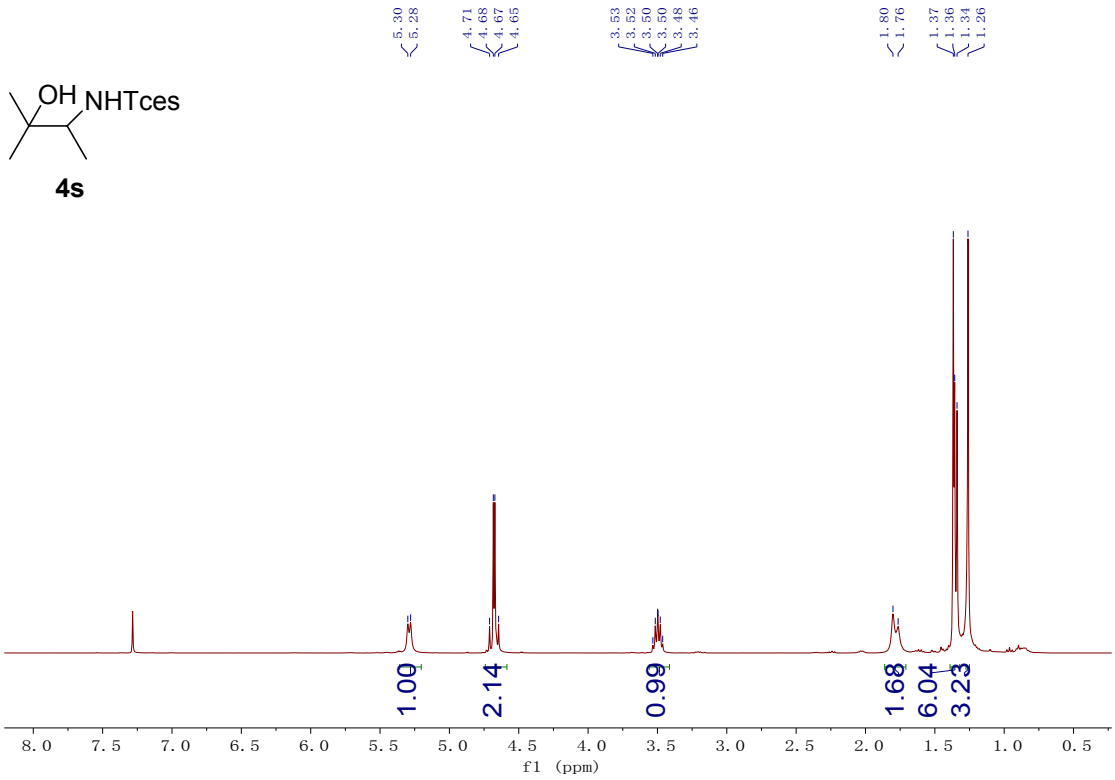

zhongfangrui -20180413-wyf-98-33C/4
OH
NHTces
AcO
4p
f1 (ppm)

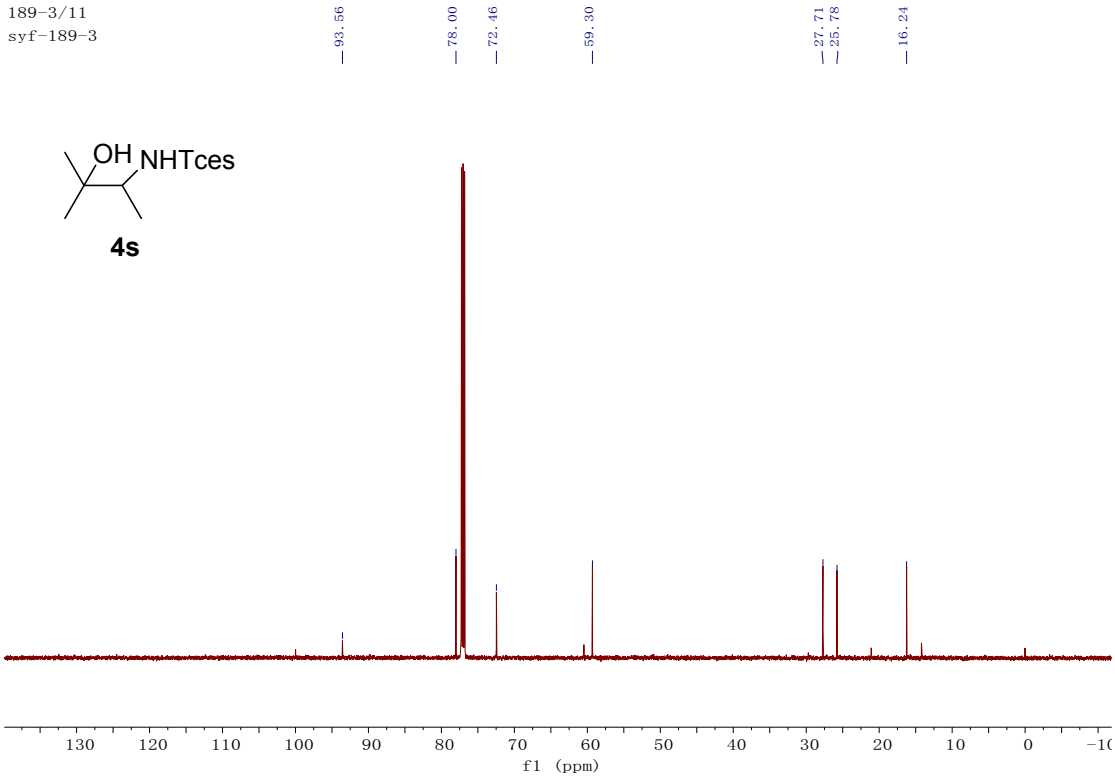

OH
NHTces
BocHN
4q
5.33
1.06
1.00
2.17
2.28
1.22
3.88
12.92
f1 (ppm)

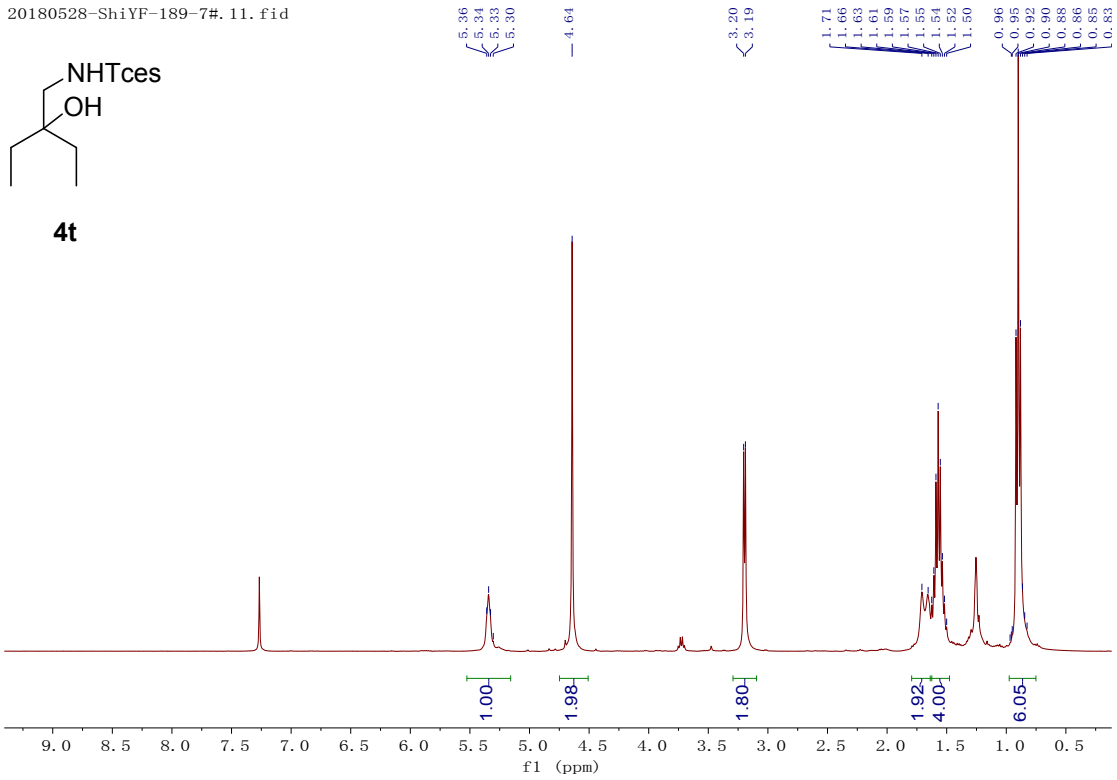

OH
NHTces
BocHN
4q
f1 (ppm)

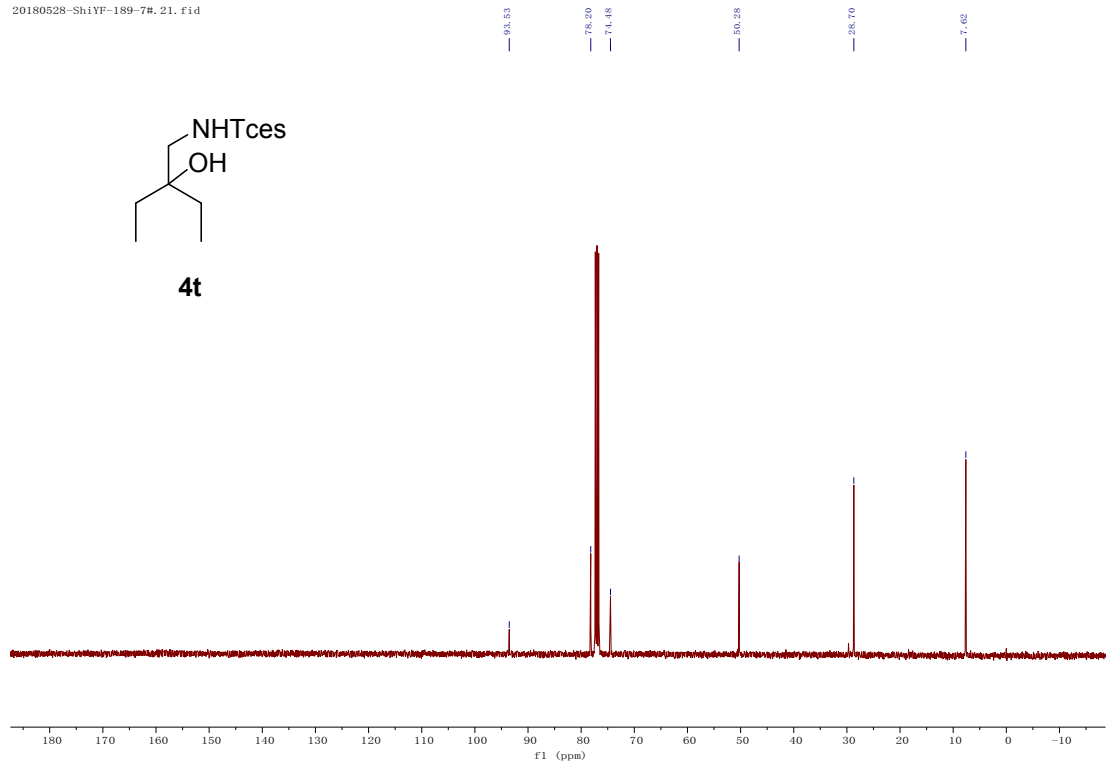

OH
NHTces
4r
1.00
2.64
1.09
1.13
1.09
1.11
1.16
1.22
4.27
1.15
1.14
f1 (ppm)

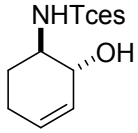

20180502-WangYF-105-1#.21.fid
OH
NHTces
4r
f1 (ppm)


5.30
5.28
4.71
4.68
4.67
4.65
3.53
3.52
3.50
3.50
3.48
3.46
1.80
1.76
1.37
1.36
1.34
1.26
OH NHTces
4s
1.00
2.14
0.99
1.68
6.04
3.23
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

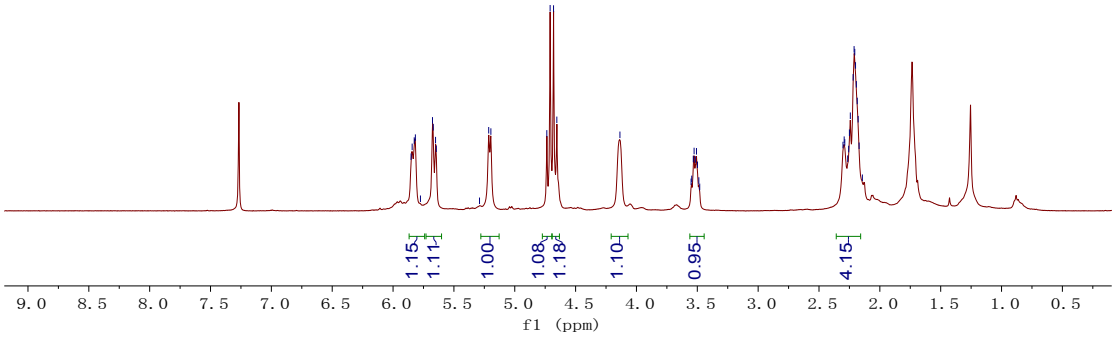

189-3/11
syf-189-3
93.56
78.00
72.46
59.30
27.71
25.78
16.24
OH NHTces
4s
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20180528-ShiYF-189-7#.11.fid
NHTces
OH
4t
5.36
5.34
5.33
5.30
4.64
3.20
3.19
1.71
1.66
1.63
1.61
1.59
1.57
1.55
1.54
1.52
1.50
0.96
0.95
0.92
0.90
0.88
0.86
0.85
0.83
1.00
1.98
1.80
1.92
4.00
6.05
f1 (ppm)

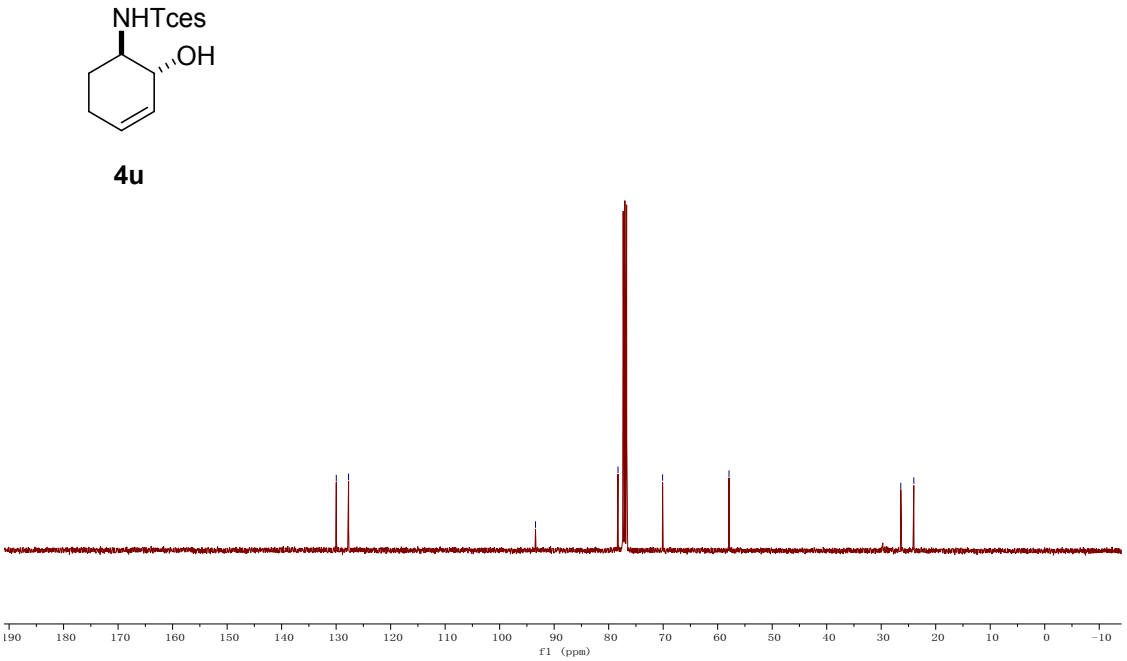

20180528-ShiYF-189-7#.21.fid
NHTces
OH
4t
93.53
78.20
74.48
50.28
28.70
7.62
f1 (ppm)



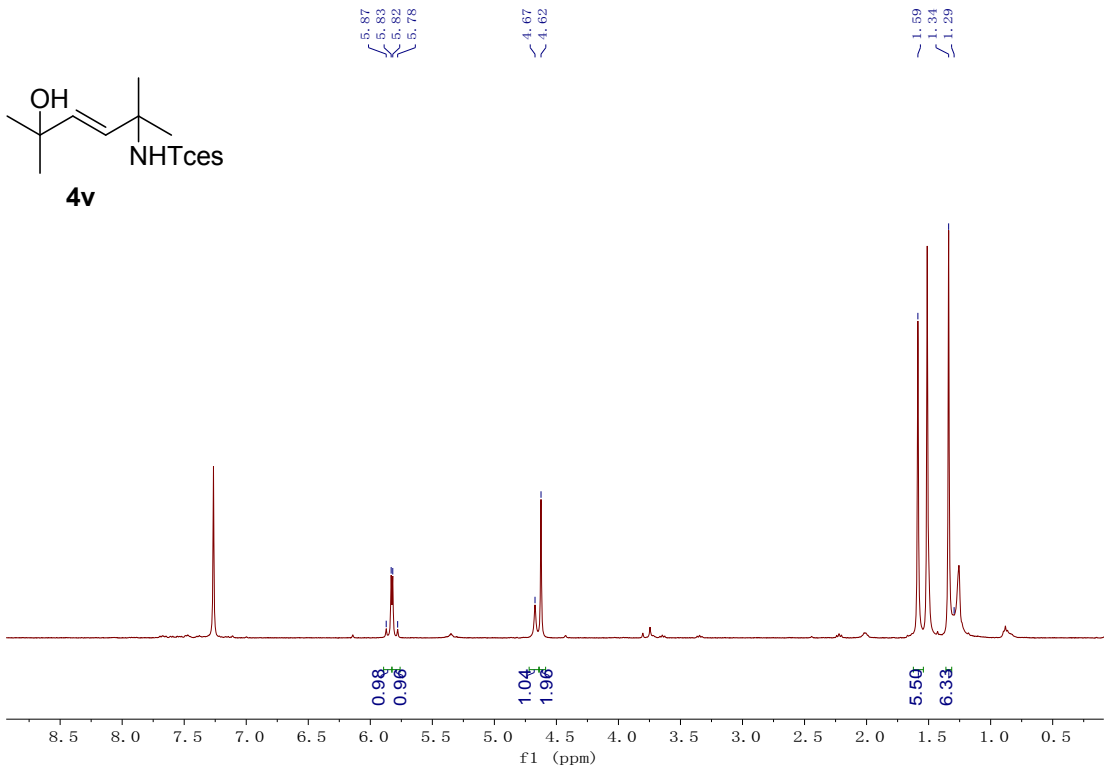
4u

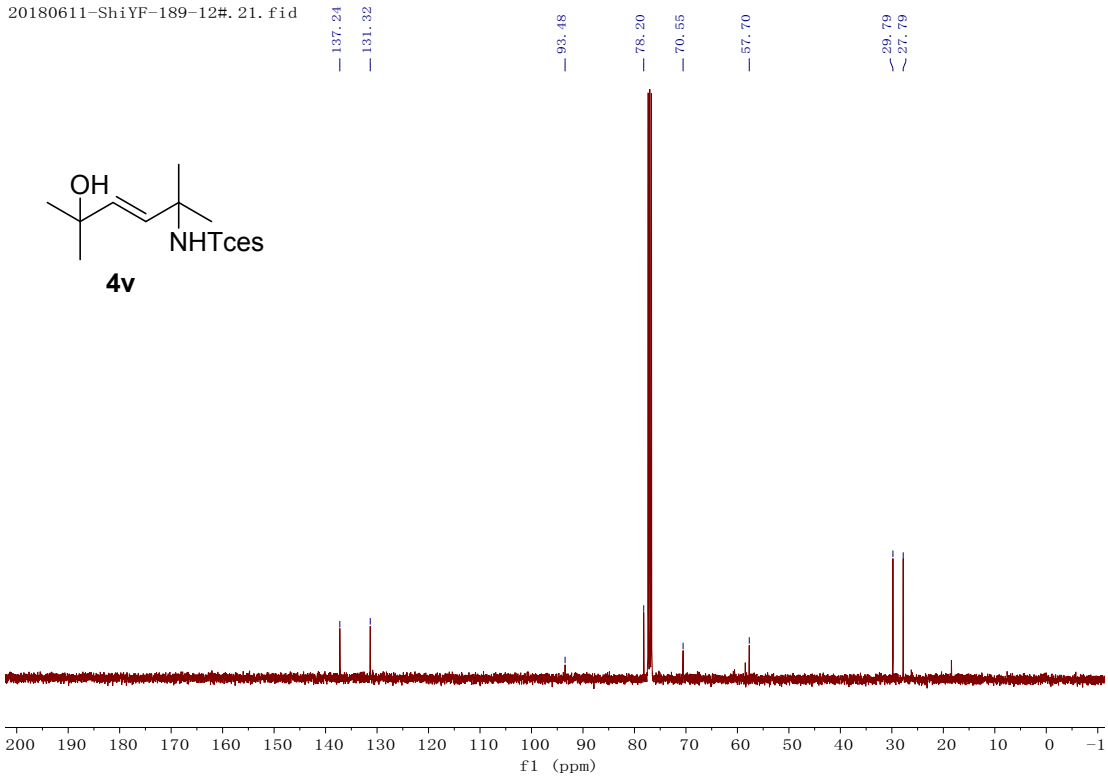


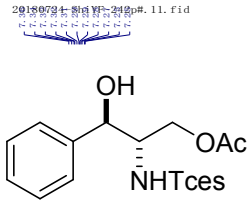
20180525-ShiYF-189-6#.21.fid



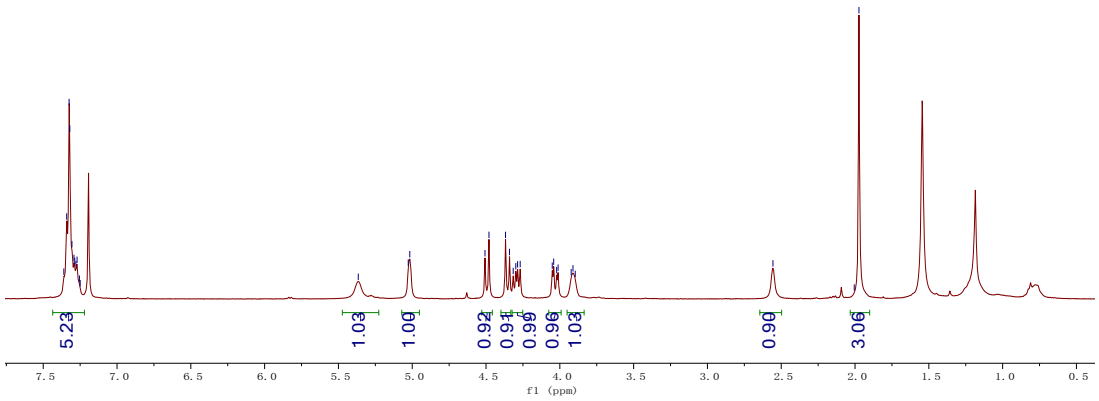
4u

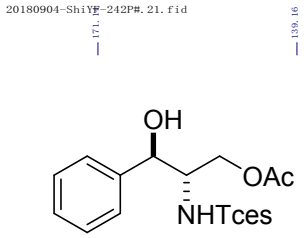

5.87
5.83
5.82
5.78
4.67
4.62
1.59
1.34
1.29
OH
NHTces
4v
0.98
0.96
1.04
1.96
5.50
6.33
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


20180611-ShiYF-189-12#.21.fid
137.24
131.32
93.48
78.20
70.55
57.70
29.79
27.79
OH
NHTces
4v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


OH
OAc
NHTces

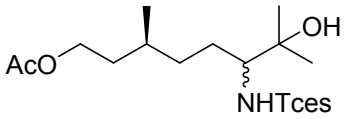
5


5.23
1.03
1.00
0.92
0.91
0.99
0.96
1.03
0.90
3.06
f1 (ppm)

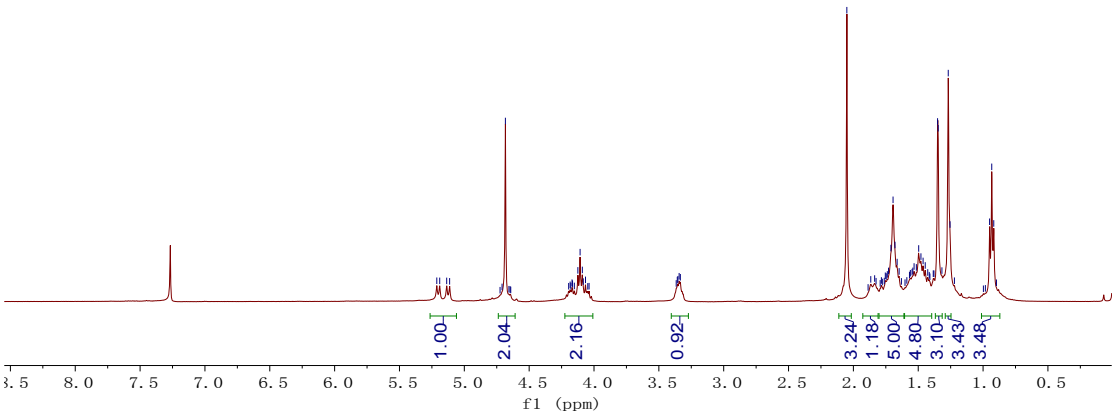

OH
OAc
NHTces

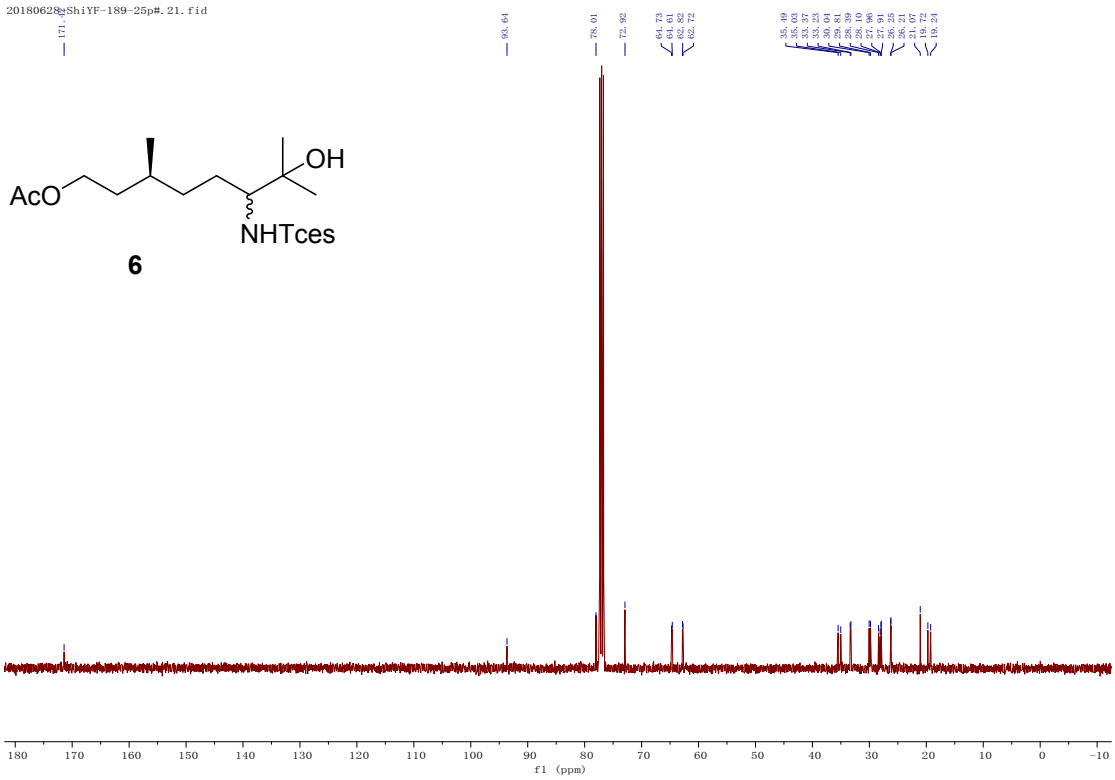
5

171.12
139.16
128.95
128.58
125.86
99.98
78.18
73.66
61.64
59.15
20.81
f1 (ppm)


AcO
OH
NHTces

6

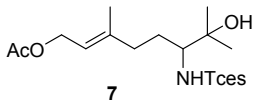

1.00
2.04
2.16
0.92
3.24
1.18
5.00
4.80
3.10
3.43
3.48
f1 (ppm)


f1 (ppm)

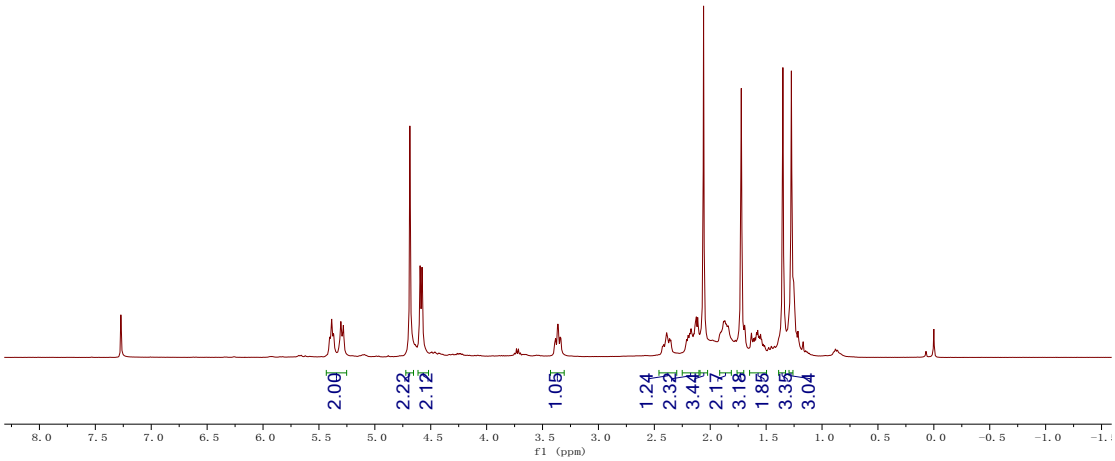
AcO
OH
NHTces

6

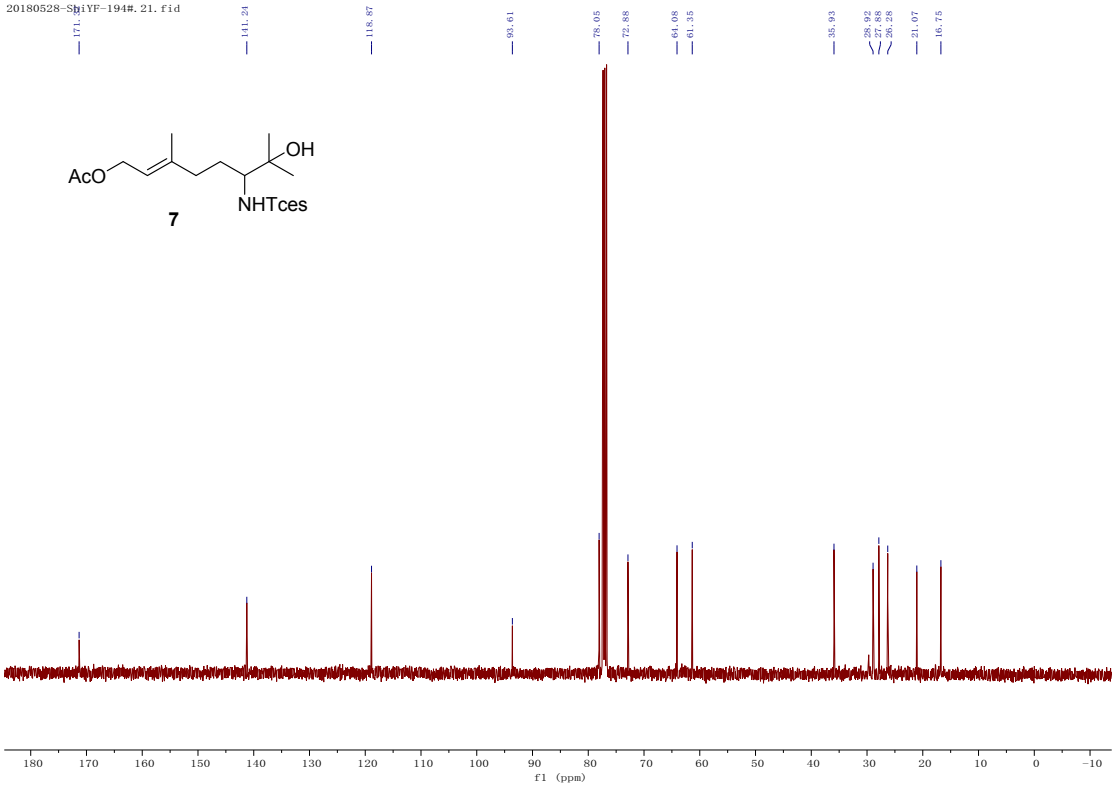
20180528-ShiYF-194#.11.fid



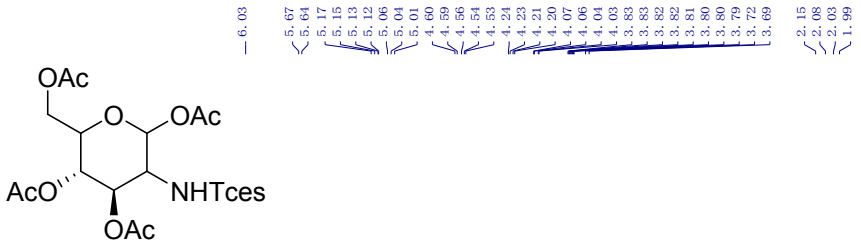
7



20180528-ShiYF-194#.21.fid



7


OAc
O
OAc
AcO
NHTces
OAc

8

6.03
5.67
5.64
5.17
5.15
5.13
5.12
5.06
5.04
5.01
4.60
4.59
4.56
4.54
4.53
4.24
4.23
4.21
4.20
4.07
4.06
4.04
4.03
3.83
3.83
3.82
3.82
3.81
3.80
3.80
3.79
3.72
3.69
2.15
2.08
2.03
1.99
1.00
1.17
1.12
1.03
2.12
1.17
1.06
1.09
1.00
3.48
3.16
3.07
3.84
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)