Electronic Supplementary Material (ESI) for Green Chemistry.

Rhodium-catalyzed intermolecular C(sp^3)-H amination in a purely aqueous system

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Supporting Information

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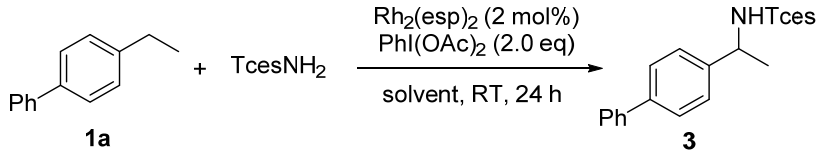
(A). General Information

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). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (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). Reaction Condition Optimizations

Table S1. Solvent screening [a]



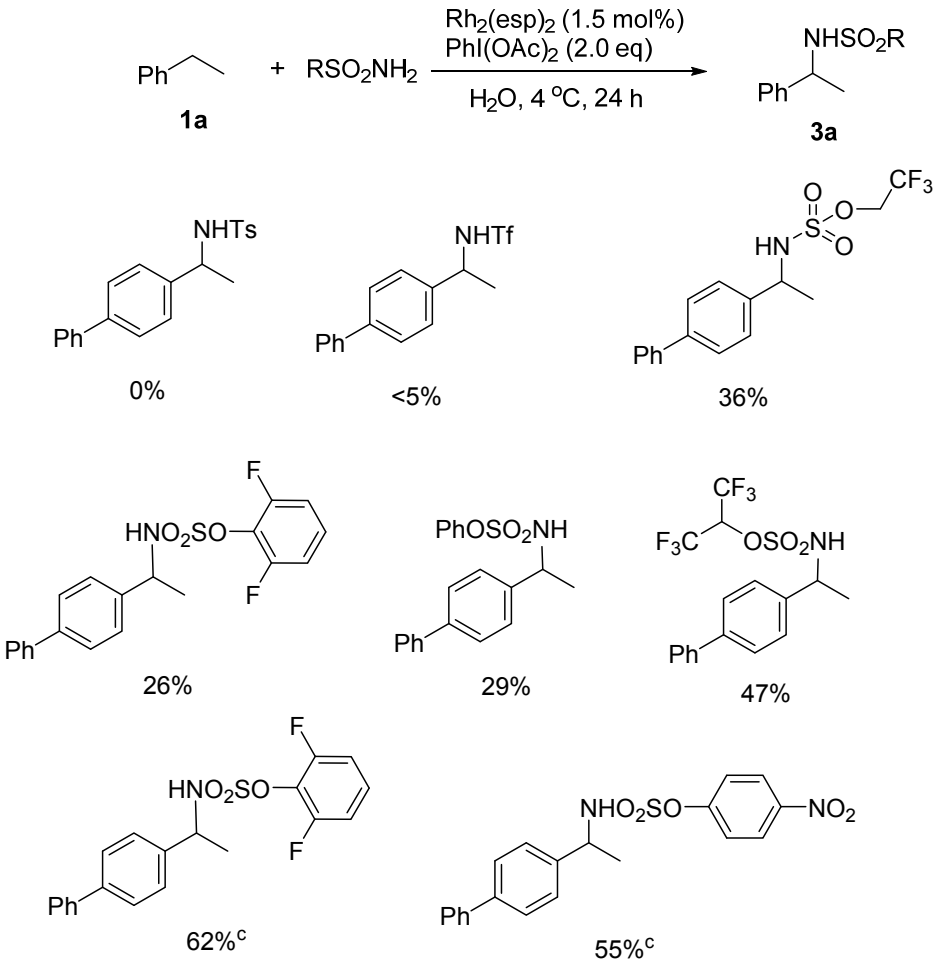
1a **3**

Entry	Solvent(M)	Yield(%)[b]
1	THF	Trace
2	PhH	44
3	DCM	48
4	Toluene	20
5	EtOAc	51
6	MTBE	14
7	DMSO	Trace
8	H_2O	**57**
9[c]	PhH	33
10[d]	H_2O	57

[a] Reactions were performed with substrate **1a** (0.075 mmol), $TcesNH_2$ (0.075 mmol, 1.0 equiv.), $Rh_2(esp)_2$ (2.0 mol%), and $PhI(OAc)_2$ (0.15 mmol, 2.0 equiv.) and solvent (0.25 ml) at room

temperature. [b] Yields are for isolated products. [c] 20 eq. of H_2O was added. [d] 2.0 eq. $PhI(O_2C^tBu)_2$ as oxidant.

B2. The effect of sulfamates [a]



[a] Reactions were performed with **1a** (0.075 mmol), nitrogen source (0.075 mmol, 1.0 equiv.), $Rh_2(esp)_2$ (2.0 mol%), and $PhI(OAc)_2$(0.15 mmol, 2.0 equiv.) and H_2O (0.25 ml) at room temperature. [b] Yields are for isolated products. [c] Reactions were performed with nitrogen source (0.0825 mmol, 1.1 equiv.).

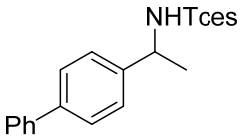
(C). Representative procedures and analytical data of amination products

General procedure 1: A 5 ml sample vial was charged with $Rh_2(esp)_2$ (1.7 mg, 1.5 mol%), $TcesNH_2$ (34.3 mg, 0.15 mmol,1.0 equiv.) and 3.0 mL H_2O, and corresponding substrate (0.225 mmol, 1.5 equiv.) was then added. The reaction mixture was cooled to 4 °C, and $PhI(OAc)_2$ (96.6 mg, 0.3 mmol, 2.0 equiv.) was added in three portions over 3 hours and the reaction was stirred at 4 °C for 24 h. Water (5 ml) was added and the mixture was extracted with $CHCl_3$ (3 x 10 mL).The

organic layers were dried over Na_2SO_4, filtered, concentrated in vacuo and the residue was purified by chromatography on silica gel.

General procedure 2: A 5 ml sample vial was charged with $Rh_2(esp)_2$ (1.7 mg, 1.5 mol%), $TcesNH_2$ (34.3 mg, 0.15 mmol,1.0 equiv.) and 3.0 mL H_2O, and corresponding substrate (0.225 mmol, 1.5 equiv.) was then added. And $PhI(OAc)_2$ (96.6 mg, 0.3 mmol, 2.0 equiv.) was added in three portions over 3 hours and the reaction was stirred at room temperature for 24 h. Water (5 ml) was added and the mixture was extracted with $CHCl_3$ (3 x 10 mL).The organic layers were dried over Na_2SO_4, filtered, concentrated in vacuo and the residue was purified by chromatography on silica gel.

2,2,2-Trichloroethyl (1-([1,1'-biphenyl]-4-yl)ethyl)sulfamate(3a)



3a

Compound **3a** was synthesized following the *general procedure 1*.

A white solid, 93% yield.

m.p.: 108 – 110 °C.

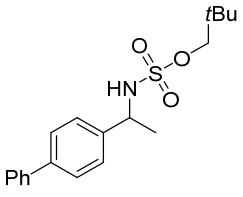
TLC: R_f = 0.30 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.52 (m, 4H), 7.49 – 7.40 (m, 4H), 7.39 – 7.32 (m, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.77 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.43 (d, *J* = 11.0 Hz, 1H), 1.65 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 140.4, 140.4, 128.9, 127.7, 127.6, 127.1, 126.8, 93.3, 78.1, 54.7, 22.9.

HRMS (ESI): $C_{16}H_{16}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 429.9809; found: 429.9809.

Neopentyl (1-([1,1'-biphenyl]-4-yl)ethyl)sulfamate (3b)



3b

Compound **3b** was synthesized following the *general procedure 1*.

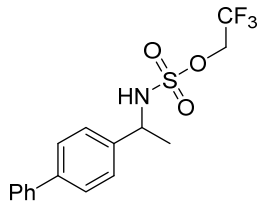
A white solid, 89% yield.

m.p.: 114 – 116 °C.

TLC: R_f = 0.4 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 4H), 7.50 – 7.32 (m, 5H), 4.86 (d, *J* = 6.9 Hz, 1H), 4.68 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 3.69 (d, *J* = 8.8 Hz, 1H), 3.59 (d, *J* = 8.8 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H), 0.85 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 141.1, 140.7, 129.0, 127.7, 127.6, 127.2, 126.8, 79.6, 54.3, 31.6, 26.2, 23.4.
HRMS (ESI): $C_{19}H_{25}NNaO_3S$ [$(M+Na)^+$]: calcd.: 370.1447; found: 370.1449.

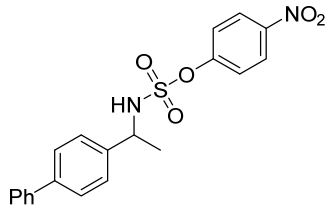
2, 2, 2-Trifluoroethyl (1-([1,1'-biphenyl]-4-yl)ethyl)sulfamate (3c)



3c

Compound **3c** was synthesized following the *general procedure 1*.
A white solid, 93% yield.
m.p.: 86 – 88 °C.
TLC: R_f = 0.25 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 11.8, 7.8 Hz, 4H), 7.50 – 7.32 (m, 5H), 5.05 (d, *J* = 6.9 Hz, 1H), 4.72 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.41 – 4.11 (m, 2H), 1.63 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.5, 140.2, 129.0, 127.8, 127.7, 127.2, 126.8, 122.11 (q, *J* = 281 Hz), 120.7, 118.0, 65.12 (q, *J* = 37.8 Hz), 54.8, 22.7.
HRMS (ESI): $C_{16}H_{16}F_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 382.0695; found: 382.0695.

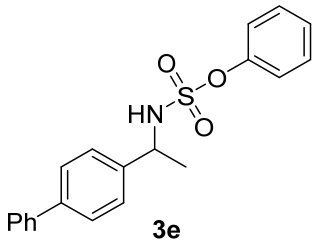
4-Nitrophenyl (1-([1,1'-biphenyl]-4-yl)ethyl)sulfamate (3d)



3d

Compound **3d** was synthesized following the *general procedure 1*.
A pale yellow oil, 78% yield.
TLC: R_f = 0.12 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.12 (m, 2H), 7.65 – 7.53 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.22 – 7.12 (m, 2H), 5.28 (d, *J* = 7.0 Hz, 1H), 4.83 (*virt.* quint., *J* ≅ 7.0 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 145.8, 141.6, 140.3, 140.1, 129.1, 127.8, 127.8, 127.2, 126.9, 125.5, 122.2, 55.2, 23.1.
HRMS (ESI): $C_{20}H_{18}N_2NaO_5S$ [$(M+Na)^+$]: calcd.: 421.0829; found: 421.0830.

Phenyl (1-([1,1'-biphenyl]-4-yl)ethyl)sulfamate(3e)



3e

Compound **3e** was synthesized following the *general procedure 1*.

A white solid, 85% yield.

m.p.: 80 – 82 ^{o}C.

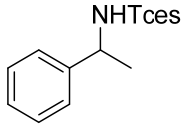
TLC: R_f = 0.3 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 7.50 – 7.41 (m, 2H), 7.41 – 7.21 (m, 6H), 7.15 – 7.05 (m, 2H), 5.02 (d, *J* = 6.9 Hz, 1H), 4.80 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 1.63 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 141.2, 140.7, 140.6, 129.8, 129.0, 127.7, 127.7, 127.2, 126.9, 126.9, 121.8, 54.9, 23.2.

HRMS (ESI): $C_{20}H_{19}NNaO_3S$ [$(M+Na)^+$]: calcd.: 376.0978 ; found: 376.0980.

2, 2, 2-Trichloroethyl (1-phenylethyl)sulfamate (3f)[2]



3f

Compound **3f** was synthesized following the *general procedure 1*.

A pale yellow oil, 86% yield.

TLC: R_f = 0.32 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

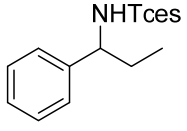
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 5.06 (d, *J* = 6.9 Hz, 1H), 4.74 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.43 (d, *J* = 10.8 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 1.63 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 129.2, 128.4, 126.4, 93.5, 78.3, 55.1, 23.0.

HRMS (ESI): $C_{10}H_{12}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 353.9496; found: 353.9486.

The spectra data are matched with those reported[2].

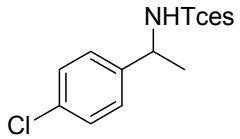
2, 2, 2-Trichloroethyl (1-phenylpropyl)sulfamate (3g)



3g

Compound **3g** was synthesized following the *general procedure 1*.
A pale yellow oil, 74% yield.
TLC: R_f = 0.34 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 5.15 (d, *J* = 7.5 Hz, 1H), 4.42 (quart., *J* = 7.5 Hz, 1H), 4.33 (d, *J* = 10.9 Hz, 1H), 4.28 (d, *J* = 10.9 Hz, 1H), 2.06 – 1.92 (m, 1H), 1.91 – 1.79 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 129.1, 128.4, 126.8, 93.4, 78.2, 61.2, 30.1, 10.7.
HRMS (ESI): $C_{11}H_{14}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 367.9652 ; found: 367.9652.

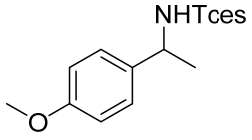
2, 2, 2-Trichloroethyl (1-(4-chlorophenyl)ethyl)sulfamate (3h)



3h

Compound **3h** was synthesized following the *general procedure 1*.
A pale yellow oil, 73% yield.
TLC: R_f = 0.45 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 4H), 5.04 (d, *J* = 6.9 Hz, 1H), 4.72 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.50 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0, 134.2, 129.3, 127.8, 93.4, 78.2, 54.4, 22.9.
HRMS (ESI): $C_{10}H_{11}Cl_4NNaO_3S$ [$(M+Na)^+$]: calcd.: 389.9076 ; found: 389.9061.

2, 2, 2-Trichloroethyl (1-(4-methoxyphenyl)ethyl)sulfamate (3i)[1]

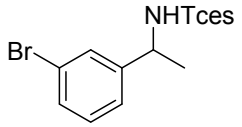


3i

Compound **3i** was synthesized following the *general procedure 1*.
A pale yellow oil, 73% Yield.
TLC: R_f = 0.4 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 6.92 – 6.86 (m, 2H), 5.31 (d, *J* = 6.9 Hz, 1H), 4.70 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.43 (d, *J* = 10.8 Hz, 1H), 3.80 (s, 3H), 1.61 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 133.5, 127.7, 114.4, 93.5, 78.2, 55.5, 54.6, 22.8.
HRMS (ESI): $C_{11}H_{14}Cl_3NNaO_4S$ [$(M+Na)^+$]: calcd.: 383.9601; found: 383.9601.

The spectra data are matched with those reported[1].

2, 2, 2-Trichloroethyl (1-(3-bromophenyl)ethyl)sulfamate (3j)



3j

Compound **3j** was synthesized following the *general procedure 1*.

A yellow oil, 59% yield.

TLC: R_f = 0.27 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

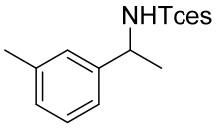
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 1H), 7.47 – 7.42 (m, 1H), 7.33 – 7.22 (m, 2H), 5.14 (d, *J* = 6.9 Hz, 1H), 4.70 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 4.47 (d, *J* = 10.8 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 131.5, 130.7, 129.6, 125.1, 123.1, 93.4, 78.3, 54.5, 23.0.

HRMS (ESI): $C_{10}H_{11}{}^{79}BrCl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 431.8601; found: 431.8604.

$C_{10}H_{11}{}^{81}BrCl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 433.8580; found: 433.8581.

2, 2, 2-Trichloroethyl (1-(m-tolyl)ethyl)sulfamate (3k)



3k

Compound **3k** was synthesized following the *general procedure 1*.

A pale yellow oil, 56% yield.

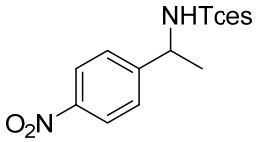
TLC: R_f = 0.47 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 1H), 7.21 – 7.10 (m, 3H), 4.96 (d, *J* = 6.9 Hz, 1H), 4.69 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.42 (d, *J* = 10.8 Hz, 1H), 2.36 (s, 3H), 1.62 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 138.9, 129.2, 129.1, 127.2, 123.3, 93.5, 78.3, 55.1, 23.0, 21.6.

HRMS (ESI): $C_{11}H_{14}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 367.9652; found: 367.9653.

2, 2, 2-Trichloroethyl (1-(4-nitrophenyl)ethyl)sulfamate (3l)



3l

Compound **3l** was synthesized following the *general procedure 1*.

A pale yellow oil, 35% yield.

TLC: R_f = 0.21 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

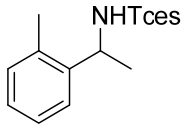
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 – 8.23 (m, 2H), 7.61 – 7.56 (m, 2H), 4.58 (br, 1H), 4.88 (*virt.* quint., *J* ≅ 6.9 Hz, 1H), 4.59 (d, *J* = 11.3 Hz, 1H), 4.58 (d, *J* = 11.3 Hz, 1H), 1.68 (d, *J* = 6.9 Hz,

3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 147.8, 127.3, 124.3, 93.4, 78.3, 54.3, 23.2.

HRMS (ESI): $C_{10}H_{10}Cl_3N_2O_5S$ [$(M-H)^-$]: calcd.: 374.9381; found: 374.9385.

2, 2, 2-Trichloroethyl (1-(o-tolyl)ethyl)sulfamate (3m)



3m

Compound **3m** was synthesized following the *general procedure 1*.

A yellow oil, 56% yield.

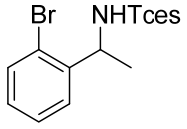
TLC: R_f = 0.37 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.28 – 7.24 (m, 1H), 7.24 – 7.16 (m, 2H), 5.05 – 4.95 (m, 2H), 4.43 (d, *J* = 11.0 Hz, 1H), 4.39 (d, *J* = 11.0 Hz, 1H), 2.42(s, 3H), 1.61 (d, *J* = 3.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 135.3, 131.1, 128.2, 126.9, 125.1, 93.5, 78.2, 51.2, 22.6, 19.3.

HRMS (ESI): $C_{11}H_{14}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 367.9652; found: 367.9652.

2, 2, 2-Trichloroethyl (1-(2-bromophenyl)ethyl)sulfamate (3n)



3n

Compound **3n** was synthesized following the *general procedure 1*.

A pale yellow oil, 43% yield.

TLC: R_f = 0.36 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

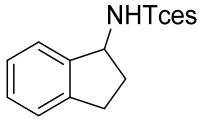
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 1H), 7.42 – 7.31 (m, 2H), 7.24 – 7.17 (m, 1H), 5.28 (d, *J* = 7.5 Hz, 1H), 5.12 (*virt.* quint., *J* = 7.5 Hz, 1H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.63, 133.70, 129.67, 128.29, 127.82, 122.30, 93.37, 78.34, 54.71, 22.46.

HRMS (ESI): $C_{10}H_{11}{}^{79}BrCl_3KNO_3S$ [$(M+K)^+$]: calcd.: 447.8340; found: 447.8343.

$C_{10}H_{11}{}^{81}BrCl_3KNO_3S$ [$(M+K)^+$]: calcd.: 449.8320; found: 449.8320.

2, 2, 2-Trichloroethyl (2,3-dihydro-1H-inden-1-yl)sulfamate (3o)



3o

Compound **3o** was synthesized following the *general procedure 1*.

A white solid, 99% yield.

m.p.: 81 – 83 °C.

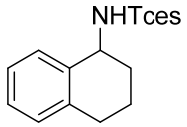
TLC: R_f = 0.24 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 1H), 7.36 – 7.25 (m, 3H), 5.14 – 5.11(m, 1H), 4.91 (d, *J* = 8.6 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 3.06 (ddd, *J* = 16.0, 8.6, 4.2 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.76 – 2.66 (m, 1H), 2.10 (dddd, *J* = 13.2, 8.6, 7.6, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$+CD_3OD) δ 143.2, 141.3, 128.6, 127.0, 125.0, 124.5, 93.7, 78.1, 59.7, 34.3, 30.1.

HRMS (ESI): $C_{11}H_{12}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 365.9496 ; found: 365.9498.

2,2,2-Trichloroethyl (1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate(3p)



3p

Compound **3p** was synthesized following the *general procedure 1*.

A white solid, 72% yield.

m.p.: 114 – 116 °C.

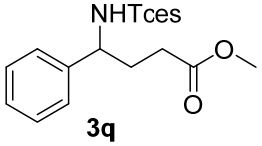
TLC: R_f = 0.62 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 1H), 7.27 – 7.22 (m, 2H), 7.17 – 7.11 (m, 1H), 4.90 (d, *J* = 7.8 Hz, 1H), 4.82 (dt, *J* = 7.8, 5.2 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 2.90 – 2.82 (m, 1H), 2.82 – 2.72 (m, 1H), 2.23 – 2.07 (m, 2H), 1.95 – 1.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 134.4, 129.4, 129.2, 128.2, 126.6, 93.6, 78.1, 53.5, 30.3, 28.8, 19.0.

HRMS (ESI): $C_{12}H_{14}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 379.9652 ; found: 379.9653.

Methyl 4-phenyl-4-(((2,2,2-trichloroethoxy)sulfonyl)amino)butanoate(3q)[2]



3q

Compound **3q** was synthesized following the *general procedure 1*.

A white solid, 98% yield.

TLC: R_f = 0.36 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.29 (m, 3H), 5.87 (d, *J* = 7.7 Hz, 1H),

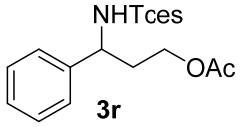
4.58 (dt, *J* = 7.7, 6.3 Hz, 1H,), 4.34 (d, *J* = 10.8 Hz, 1H), 4.29 (d, *J* = 10.8 Hz, 1H), 3.69 (s, 3H), 2.51 – 2.38 (m, 2H), 2.30 – 2.20 (m, 1H), 2.18 – 2.09 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 140.1, 129.2, 128.5, 126.7, 93.4, 78.1, 59.2, 52.2, 31.7, 30.8.

HRMS (ESI): $C_{13}H_{16}Cl_3NNaO_5S$ [$(M+Na)^+$]: calcd.: 425.9707; found: 425.9709.

The spectra data are matched with those reported[2].

3-Phenyl-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)propyl acetate(3r)[2]



3r

Compound **3r** was synthesized following the *general procedure 1*.

A white solid, 83% yield.

TLC: R_f = 0.2 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

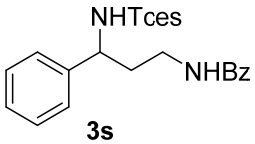
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 5.67 (d, *J* = 7.6 Hz, 1H), 4.69 (q, *J* = 7.6 Hz, 1H), 4.33 (d, *J* = 10.8 Hz, 1H), 4.28 (d, *J* = 10.8 Hz, 1H), 4.15 (ddd, *J* = 11.5, 6.7, 5.4 Hz, 1H), 4.04 (ddd, *J* = 11.5, 7.0, 5.3 Hz, 1H), 2.29 (dddd, *J* = 14.3, 7.0, 7.0, 5.4 Hz, 1H), 2.16 (dddd, *J* = 14.3, 14.3, 6.7, 5.3 Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 139.6, 129.3, 128.7, 126.7, 93.4, 78.2, 61.1, 56.96, 35.7, 21.0.

HRMS (ESI): $C_{13}H_{16}Cl_3NNaO_5S$ [$(M+Na)^+$]: calcd.: 425.9707; found: 425.9709.

The spectra data are matched with those reported[2].

2, 2, 2-Trichloroethyl (3-benzamido-1-phenylpropyl)sulfamate (3s)



3s

Compound **3s** was synthesized following the *general procedure 1*.

A white solid, 78% yield.

m.p.: 141 – 143 ^oC.

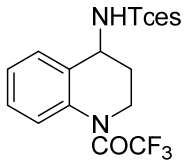
TLC: R_f = 0.24 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.77 (m, 2H), 7.57 – 7.50 (m, 1H), 7.47 – 7.41 (m, 2H), 7.41 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.72 (t, *J* = 6.3 Hz, 1H), 4.67 (quart., *J* = 7.8 Hz, 1H), 4.41 (dd, *J* = 10.7, 0.7 Hz, 1H), 4.25 (dd, *J* = 10.7, 0.7 Hz, 1H), 3.85 – 3.76 (m, 1H), 3.52 – 3.43 (m, 1H), 2.26 – 2.18 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 140.4, 133.9, 131.8, 129.0, 128.7, 128.3, 126.9, 126.5, 93.2, 77.9, 57.1, 36.9, 36.4.

HRMS (ESI): $C_{18}H_{19}Cl_3N_2NaO_4S$ [$(M+Na)^+$]: calcd.: 487.0023 ; found: 487.0023.

2,2,2-Trichloroethyl (1-(2,2,2-trifluoroacetyl)-1,2,3,4-tetrahydroquinolin-4-yl)sulfamate(3t)[2]



3t

Compound **3t** was synthesized following the *general procedure 1*.

A white solid, 98% yield.

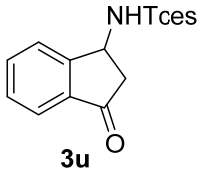
TLC: R_f = 0.75 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.58 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 (td, *J* = 7.8, 1.6 Hz, 1H), 7.33 – 7.29 (m, 1H), 5.60 (d, *J* = 7.7 Hz, 1H), 4.88 (q, *J* = 6.8 Hz, 1H), 4.69 (m, 2H), 3.90 (m, 2H), 2.46 (m, 1H), 2.34 (m, 1H).

HRMS (ESI): $C_{13}H_{12}Cl_3F_3N_2NaO_4S$ [$(M+Na)^+$]: calcd.:476.9428 ; found: 476.9428.

The spectra data are matched with those reported[2].

2,2,2-Trichloroethyl (3-oxo-2,3-dihydro-1H-inden-1-yl)sulfamate (3u)



3u

Compound **3u** was synthesized following the *general procedure 1*.

A colorless oil, 95% yield.

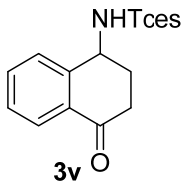
TLC: R_f = 0.67 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 1H), 7.78 – 77.1 (t, *J* = 7.6 Hz, 2H), 7.58 – 7.50 (t, *J* = 7.6 Hz, 1H), 5.50 (d, *J* = 7.8 Hz, 1H), 5.30 (m, 1H), 4.75 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 3.27 (dd, *J* = 19.2, 7.8 Hz, 1H), 2.78 (dd, *J* = 19.2, 3.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$ + CD_3OD) δ 203.2, 152.3, 136.4, 135.7, 129.7, 126.5, 123.3, 93.5, 78.0, 52.0, 44.8.

HRMS (ESI): $C_{11}H_{11}Cl_3NO_4S$ [$(M+H)^+$]: calcd.: 357.9469; found: 357.9470.

2, 2, 2-Trichloroethyl (4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate(3v)



3v

Compound **3v** was synthesized following the *general procedure 1*.

A white solid, 94% yield.

m.p.: 141 – 143 °C.

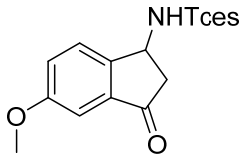
TLC: R_f = 0.69 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 1H), 7.75 – 7.60 (m, 2H), 7.52 – 7.44 (m, 1H), 5.53 (d, *J* = 8.0 Hz, 1H), 4.99 (dt, *J* = 8.0, 4.0 Hz, 1H), 4.75 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 2.90 (ddd, *J* = 17.6, 8.6, 4.6 Hz, 1H), 2.69 (ddd, *J* = 17.6, 8.6, 4.6 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.45 – 2.34 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 141.0, 134.7, 132.0, 129.3, 128.1, 127.8, 93.6, 78.3, 53.3, 35.1, 29.9.

HRMS (ESI): $C_{12}H_{12}Cl_3NNaO_4S$ [$(M+Na)^+$]: calcd.: 393.9445; found: 393.9435.

2, 2, 2-Trichloroethyl (5-methoxy-3-oxo-2,3-dihydro-1H-inden-1-yl)sulfamate (3w)



3w

Compound **3w** was synthesized following the *general procedure 1*.

A white solid, 94% yield.

m.p.: 109 – 111 °C.

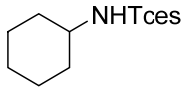
TLC: R_f = 0.42 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 5.42 (d, *J* = 9.1 Hz, 1H), 5.28 – 5.17 (m, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 4.73 (d, *J* = 10.8 Hz, 1H), 3.85 (s, 3H), 3.26 (dd, *J* = 19.3, 7.3 Hz, 1H), 2.78 (dd, *J* = 19.3, 3.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$+CD_3OD) δ 203.0, 161.1, 144.9, 137.9, 127.4, 124.7, 104.7, 93.6, 78.0, 55.7, 51.6, 45.5.

HRMS (ESI): $C_{12}H_{12}Cl_3NNaO_5S$ [$(M+Na)^+$]: calcd.: 409.9394; found: 409.9395.

2, 2, 2-Trichloroethyl cyclohexylsulfamate(3x)[2]



3x

Compound **3x** was synthesized following the *general procedure 1*.

A white solid, 64% yield.

TLC: R_f = 0.96 (Hexane/EtOAc = 3:1) [$KMnO_4$].

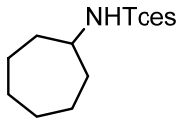
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (s, 2H), 4.50 (d, *J* = 7.8 Hz, 1H), 3.50 – 3.37 (m, 1H), 2.12 – 2.04 (m, 2H), 1.81 – 1.74 (m, 2H), 1.67 - 1.61 (m, 1H), 1.40 – 1.24 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 93.7, 78.3, 54.3, 33.8, 25.2, 24.8.

HRMS (ESI): $C_8H_{14}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 331.9652; found: 331.9663.

The spectra data are matched with those reported[2].

2, 2, 2-Trichloroethyl cycloheptylsulfamate(3y)



3y

Compound **3y** was synthesized following the *general procedure 1*.

A white solid, 70% yield.

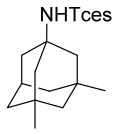
TLC: R_f = 0.58 (Hexane/EtOAc = 10:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (s, 2H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.72 – 3.58 (m, 1H), 2.14 – 2.02 (m, 2H), 1.70 – 1.43 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 93.7, 78.2, 56.6, 35.7, 28.0, 23.6.

HRMS (ESI): $C_9H_{16}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 345.9809 ; found: 345.9810.

2, 2, 2-Trichloroethyl ((1r,3R,5S,7r)-3,5-dimethyladamantan-1-yl)sulfamate (3z)



3z

Compound **3z** was synthesized following the *general procedure 1*.

A pale yellow oil, 76% Yield.

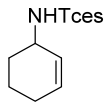
TLC: R_f = 0.41 (Hexane/EtOAc = 10:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (s, 2H), 2.12 (s, 1H), 1.83 (s, 2H), 1.58 – 1.67 (m, 5H), 1.25 – 1.37 (m, 4H), 1.16 (s, 2H), 0.87 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 93.7, 78.3, 57.8, 50.2, 48.7, 42.3, 41.2, 32.9, 30.3, 30.0.

HRMS (ESI): $C_{14}H_{22}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 412.0278 ; found: 412.0259.

2, 2, 2-Trichloroethyl cyclohex-2-en-1-ylsulfamate (3a')[3]



3a'

Compound **3a'** was synthesized following the *general procedure 1*.

A white solid, 60% yield.

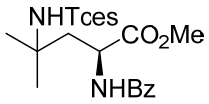
TLC: R_f = 0.3 (Hexane/EtOAc = 3:1) [$KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 6.02 (m, 1H), 5.79 – 5.68 (m, 1H), 4.74 – 4.57 (m, 3H),

4.26 – 3.97 (m, 1H), 2.06 – 1.96 (m, 3H), 1.82 – 1.71 (m, 1H), 1.71 – 1.64(m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.8, 126.2, 93.6, 78.3, 50.6, 29.9, 24.7, 19.3.
HRMS (ESI): $C_8H_{12}Cl_3NNaO_3S$ [$(M+Na)^+$]: calcd.: 329.9496; found: 329.9497.

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

Methyl (S)-2-benzamido-4-methyl-4-(((2,2,2-trichloroethoxy)sulfonyl)amino)pentanoate(4)



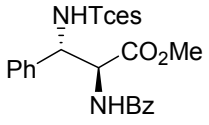
4

Compound **4** was synthesized following the *general procedure 2*.
A colorless oil, 44% yield.
TLC: R_f = 0.27 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.60 – 7.50 (m, 1H), 7.49 – 7.39 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.70 (br, 1H), 4.92 (dt, *J* = 8.0, 3.2 Hz, 1H), 4.59 (d, *J* = 10.8 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 3.83 (s, 3H), 2.29 – 2.18 (m, 1H), 2.15 – 2.08 (m, 1H), 1.51 (d, *J* = 21.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 168.7, 133.3, 132.4, 128.8, 127.5, 93.6, 78.3, 56.1, 53.3, 49.9, 45.0, 28.1, 27.8.
HRMS (ESI): $C_{16}H_{21}Cl_3KN_2O_6S$ [$(M+K)^+$]: calcd.: 512.9817; found: 512.9825.

Compound **5** was synthesized using methyl benzoyl-L-phenylalaninate as substrate following the *general procedure 2*. The diastereoselectivity was 4.2:1, which determined from ^{1}H NMR analysis of crude product. The relative configuration of two stereogenic carbons were assigned by comparing the coupling constants with analogues compounds in literature.[4]

Major diastereoisomer **5a**

Methyl
(2*S*,3*S*)-2-benzamido-3-phenyl-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)propanoate(5b)



5a

A colorless oil, 51% Yield.
TLC: R_f = 0.41 (CH_2Cl_2) [UV, $KMnO_4$].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.29 (m, 8H), 7.27 – 7.25 (m, 1H), 5.25 (t, *J* = 8.1 Hz, 1H), 4.98 (d, *J* = 7.9 Hz, 1H), 4.36 (d, *J* = 10.7 Hz, 1H), 4.28 (d, *J* = 10.7 Hz, 1H), 3.58 (s, 3H).

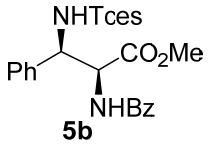
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.6, 136.5, 132.9, 132.5, 129.1, 129.1, 128.9, 127.5, 127.3, 93.2, 78.3, 61.0, 57.7, 53.0.

HRMS (ESI): $C_{19}H_{19}Cl_3N_2NaO_6S$ [$(M+Na)^+$]: calcd.: 530.9922; found: 530.9922.

Minor diastereoisomer **5b**:

Methyl

(2*S*,3*R*)-2-benzamido-3-phenyl-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)propanoate(5b)



5b

A colorless oil, 13% Yield.

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

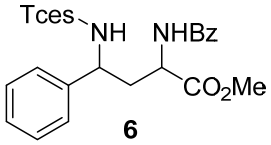
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 2H),7.61 – 7.54 (m, 1H), 7.52 – 7.43 (m, 2H), 7.39 – 7.25 (m, 3H), 7.18 (dd, *J* = 6.6, 2.7 Hz, 2H), 7.28 – 7.24 (m, 1H), 6.89 (d, *J* = 6.3 Hz, 1H), 5.39 (d, *J* = 2.2 Hz, 1H), 5.27 (dd, *J* = 6.3, 2.3 Hz, 1H), 4.50 (d, *J* = 10.9 Hz, 1H), 4.48 (d, *J* = 10.9 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 169.1, 135.4, 132.9, 132.4, 129.0, 129.0, 128.9, 127.4, 127.0, 93.5, 78.3, 61.3, 58.9, 53.7.

HRMS (ESI): $C_{19}H_{19}Cl_3N_2NaO_6S$ [$(M+Na)^+$]: calcd.: 530.9922; found: 530.9921.

Compound **6** was synthesized using racemic methyl 2-benzamido-4-phenylbutanoate following the *general procedure 2*. The diastereoselectivity was 4.2:1, which determined from ^{1}H NMR analysis of crude product. The two diastereoisomers were separated by column chromatography.

Methyl 2-benzamido-4-phenyl-4-(((2,2,2-trichloroethoxy)sulfonyl)amino)butanoate(6)



6

Diastereoisomer **1:**

A colorless oil, 31% yield.

TLC: R_f = 0.71 (CH_2Cl_2/MeOH = 20:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.53 (d, *J* = 1.2 Hz, 1H), 7.46 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.30 – 7.24(m, 2H), 7.15 (d, *J* = 6.7 Hz, 1H), 4.99 – 4.87 (m, 1H), 4.83 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.42 (d, *J* = 10.7 Hz, 1H), 4.28 (d, *J* = 10.7 Hz, 1H), 3.89 (s, 3H), 2.51 – 2.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 167.6, 140.2, 133.1, 132.4, 129.2, 128.8, 128.5, 127.3, 126.5, 93.4, 78.0, 57.0, 53.4, 50.4, 39.9.

HRMS (ESI): $C_{20}H_{21}Cl_3N_2NaO_6S$ [$(M+Na)^+$]: calcd.: 545.0078; found: 545.0078.

Diastereoisomer **2:**

A colorless oil, 32% yield.

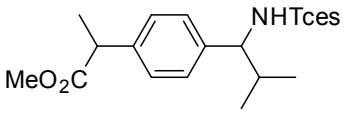
TLC: R_f = 0.48 (CH_2Cl_2/MeOH = 20:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.35 (m, 6H), 7.35 – 7.28 (m, 1H), 7.27 – 7.25 (m, 1H),7.04 (d, *J* = 7.4 Hz, 1H), 4.85 – 4.67 (m, 2H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.28 (d, *J* = 10.8 Hz, 1H), 3.72 (s, 3H), 2.71 (ddd, *J* = 14.6, 7.6, 4.7 Hz, 1H), 2.43 (ddd, *J* = 14.5, 7.6, 5.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 167.6, 140.2, 133.1, 132.4, 129.2, 128.8, 128.5, 127.3, 126.5, 93.4, 78.0, 57.0, 53.4, 50.4, 39.9.

HRMS (ESI): $C_{20}H_{21}Cl_3N_2NaO_6S$ [$(M+Na)^+$]: calcd.: 545.0078; found: 545.0078.

Methyl 2-(4-(2-methyl-1-(((2,2,2-trichloroethoxy)sulfonyl)amino)propyl)phenyl)propanoate (7)



7

Compound **7** was synthesized following the *general procedure 2*.

A colorless oil, 74% Yield.

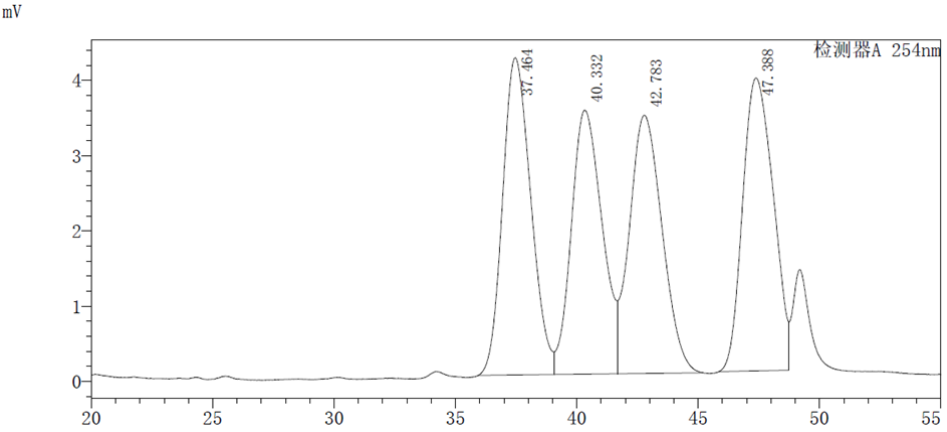
TLC: R_f = 0.25 (Hexane/EtOAc = 10:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.25 – 7.16 (m, 2H), 5.53 – 5.38 (m, 1H), 4.26 – 4.07 (m, 3H), 3.72 (q, *J* = 7.5 Hz, 1H), 3.67 (s, 3H), 2.10 – 1.95 (m, 1H), 1.48 (d, *J* = 7.5 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 140.4, 139.0, 128.0, 127.5, 93.3, 78.0, 65.2, 52.3, 45.2, 34.2, 19.7, 19.2, 18.8.

HRMS (ESI): $C_{16}H_{22}Cl_3NNaO_5S$ [$(M+Na)^+$]: calcd.: 468.0176; found: 468.0175.

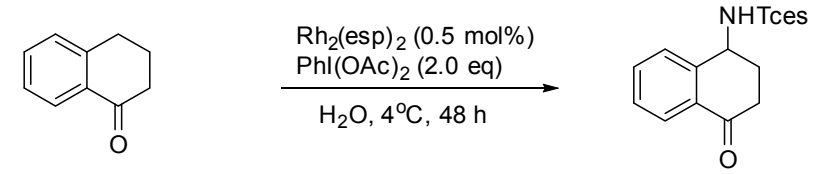
Due to the spatial separation between the two sterogenic centers across the phenyl ring of **7,** its diastereoisomers was found not distinguishable in the NMR spectra. Thus the NMR data given above is for a mixture of diastereoisomers (d.r. was approximately 1:1), which was proved by HPLC analysis (Chiralcel IC-H, λ = 254 nm, 2% i-PrOH/hexanes, flow rate = 1.0 L/min).



〈峰表〉
检测器A 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	37.464	341259	4211	25.965			
2	40.332	309542	3507	23.552		V	
3	42.783	322823	3431	24.563		V	
4	47.388	340665	3891	25.920			
总计		1314289	15040				

(D) Scale-up Experment



6.0 mmol, 0.87 g

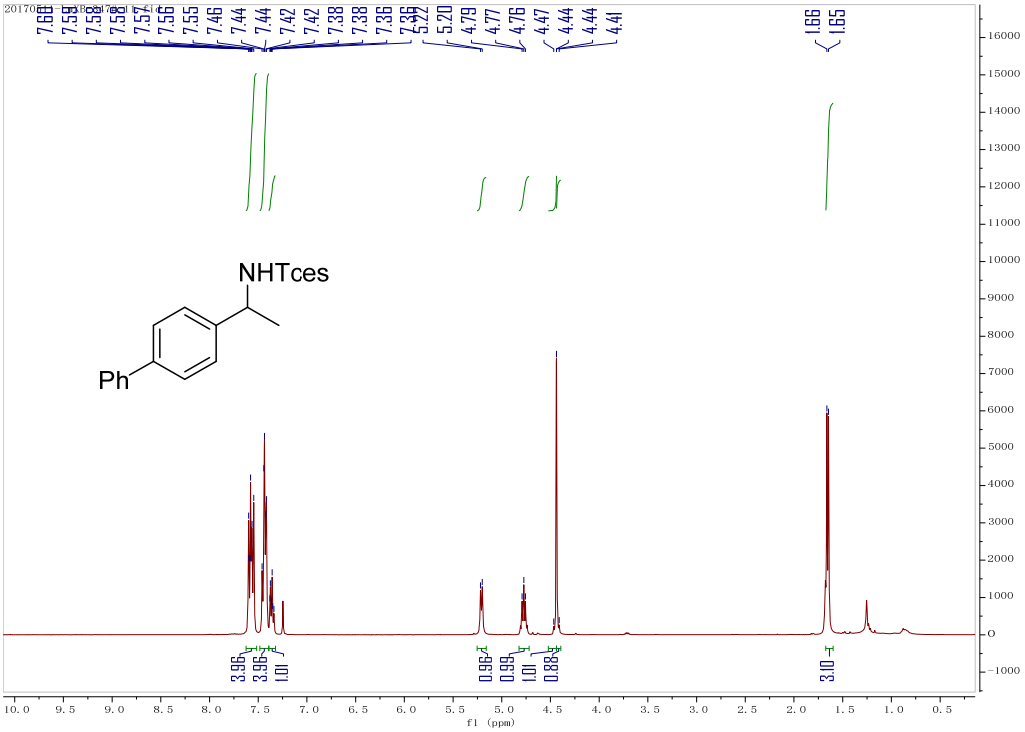
3v (1.27 g, 90%)

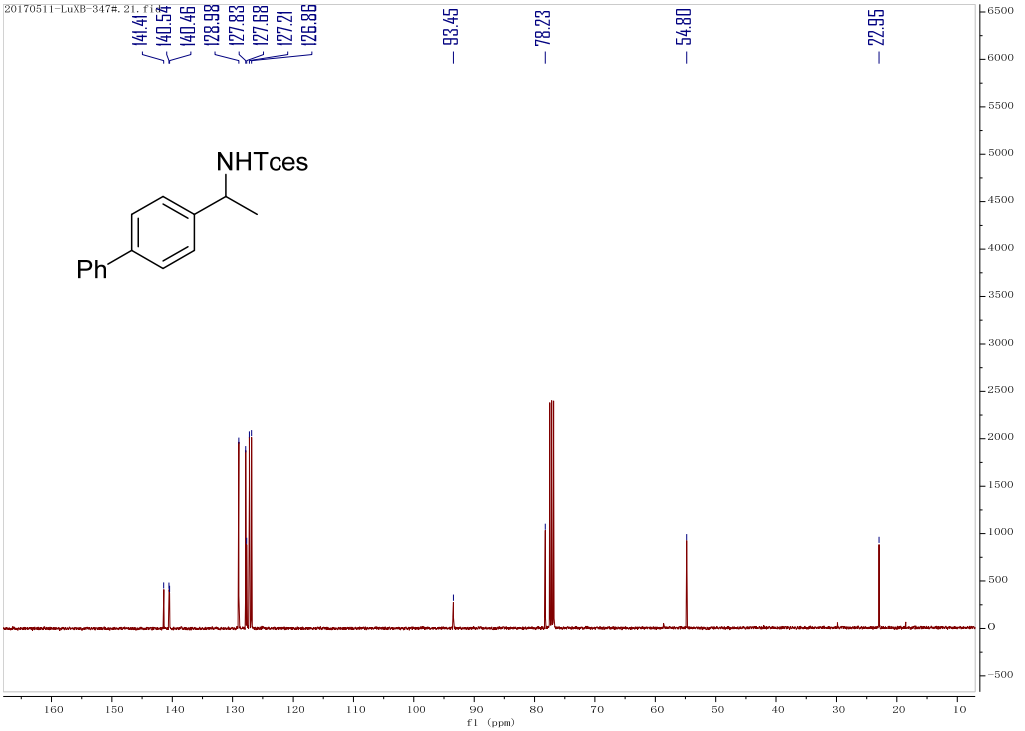
A 50 ml round-bottom flask was charged with $Rh_2(esp)_2$ (15.2 mg, 0.5 mol%), $TcesNH_2$ (914 mg, 4.0 mmol, 1.0 equiv.) and 20 mL H_2O, and 3,4-dihydronaphthalen-1(2H)-one (6.0 mmol, 1.5 equiv.) was then added. The reaction mixture was cooled to 4 °C, and $PhI(OAc)_2$ (2.57g, 8 mmol, 2.0 equiv.) was added in three portions over 3 hours and the reaction was stirred at room temperature for 48 h. Water (10 ml) was added and the mixture was extracted with $CHCl_3$ (3 x 30 mL). The organic layers were dried over Na_2SO_4, filtered, concentrated in vacuo and the residue was purified by chromatography on silica gel.

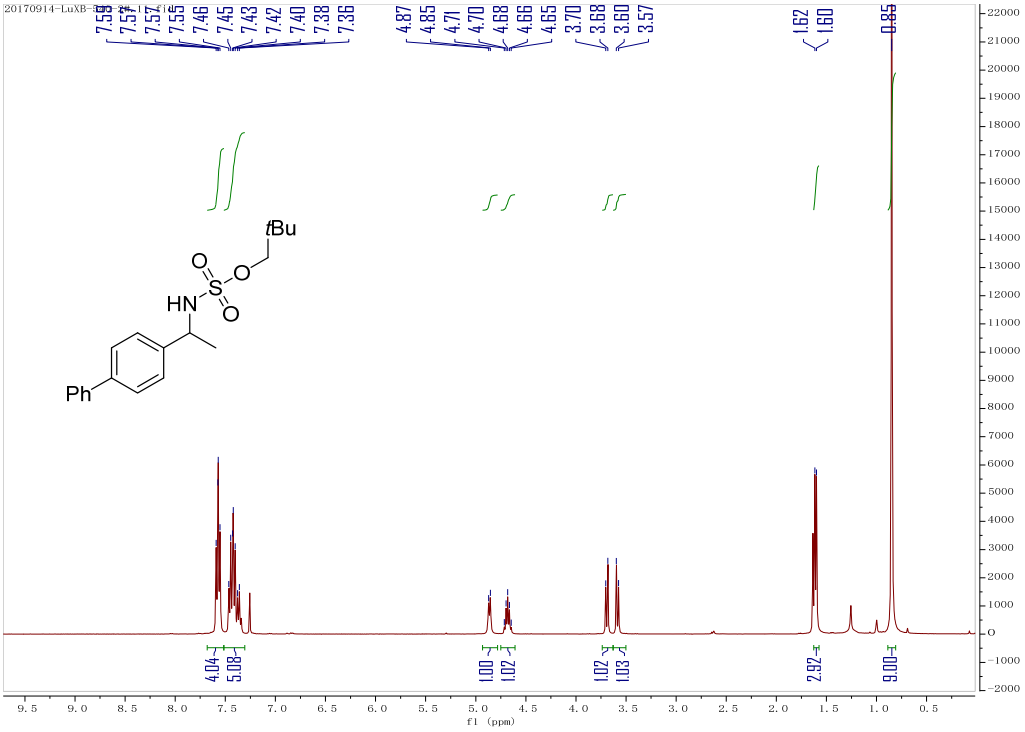
Reference:

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. H.Yamamoto, E. Ho, I. Sasaki, M. Mitsutake,Y. Takagi, H. Imagawa, and M. Nishizawa , *Eur. J. Org. Chem.* 2011, **2011**, 2417.
4. Y. Singjunla, J,Baudoux, and J, Rouden, *Eur. J. Org. Chem.* 2017, 3240.

(E) ^{1}H and ^{13}C NMR spectra data of all products



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7.45
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7.42
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7.38
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4.85
4.71
4.70
4.68
4.66
4.65
3.70
3.68
3.60
3.57
1.62
1.60
0.85
tBu
O
S
O
HN
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Ph
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1.02
1.02
1.03
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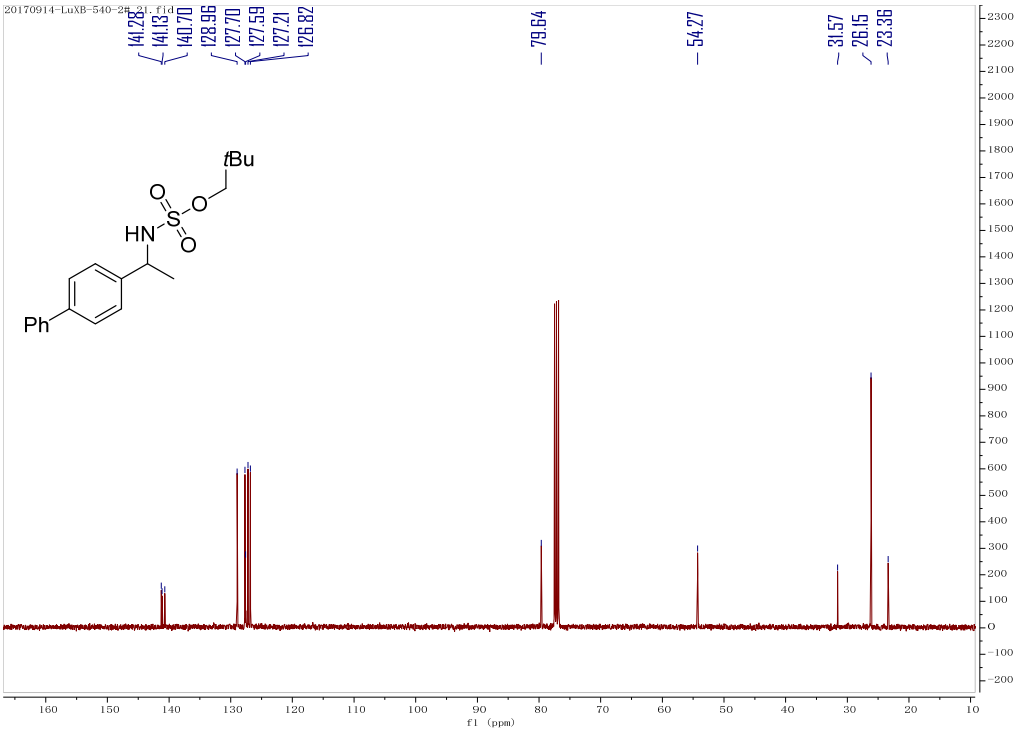
9.00
f1 (ppm)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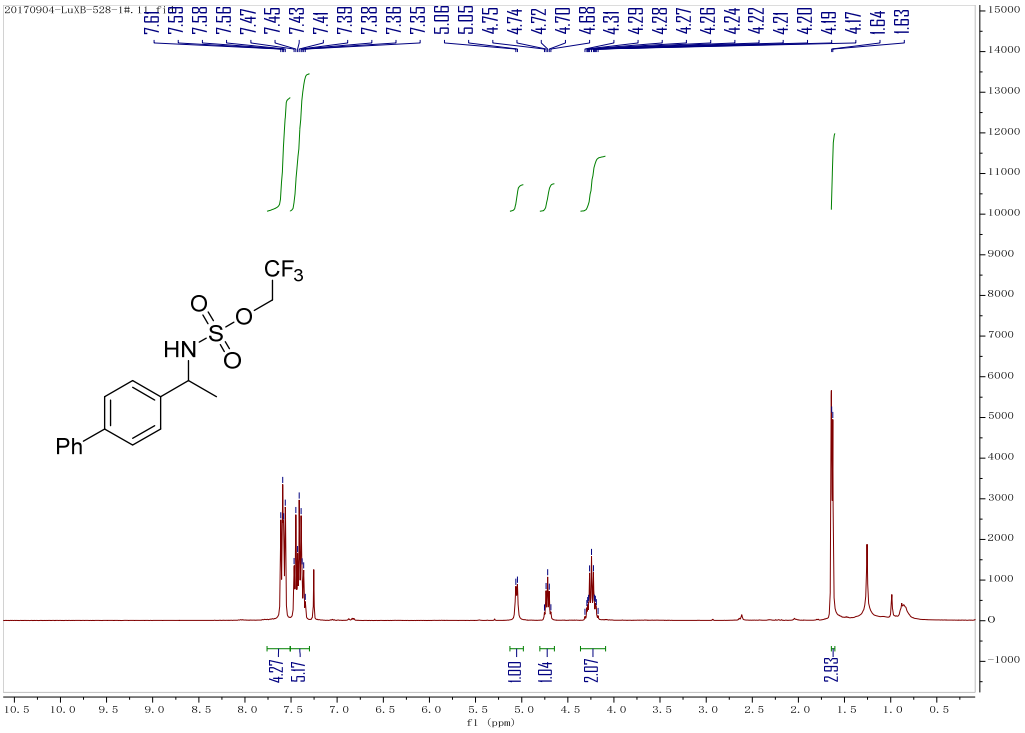
Ph
f1 (ppm)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4.27
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4.21
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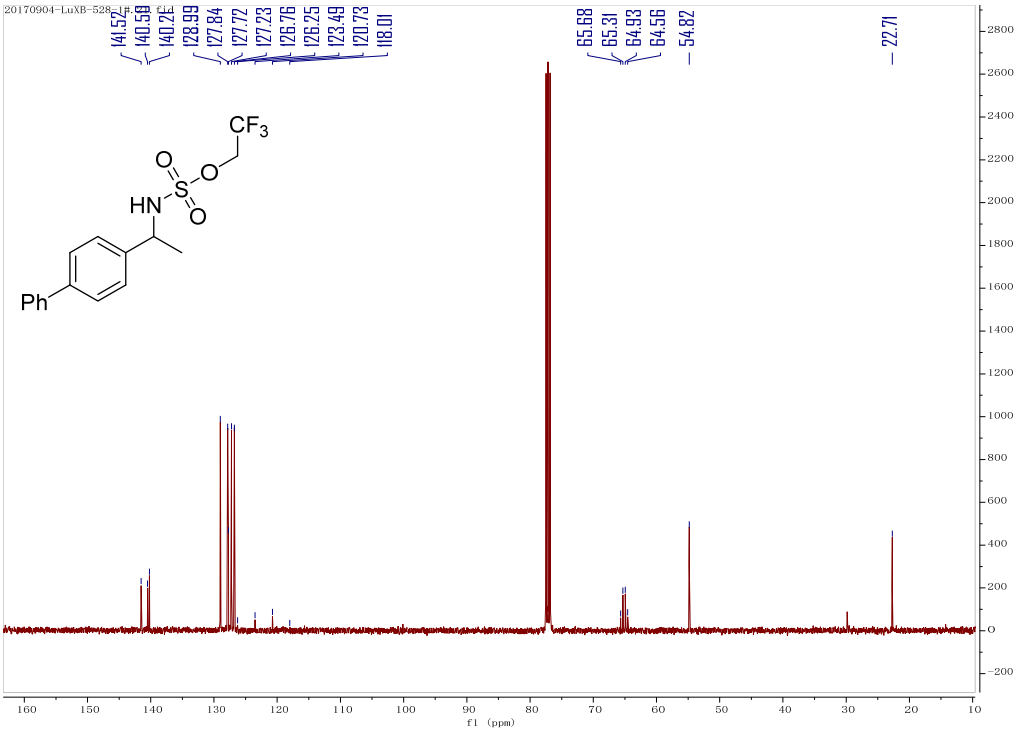
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O
S
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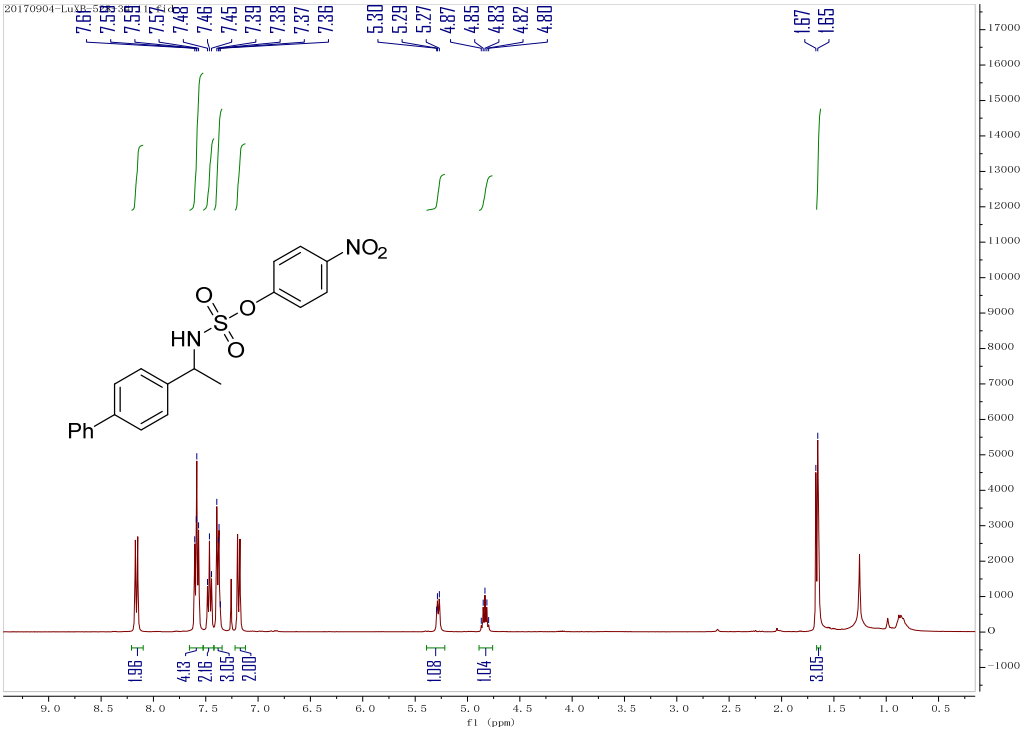
HN
O
Ph
f1 (ppm)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5.27
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4.85
4.83
4.82
4.80
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1.65
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S
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Ph
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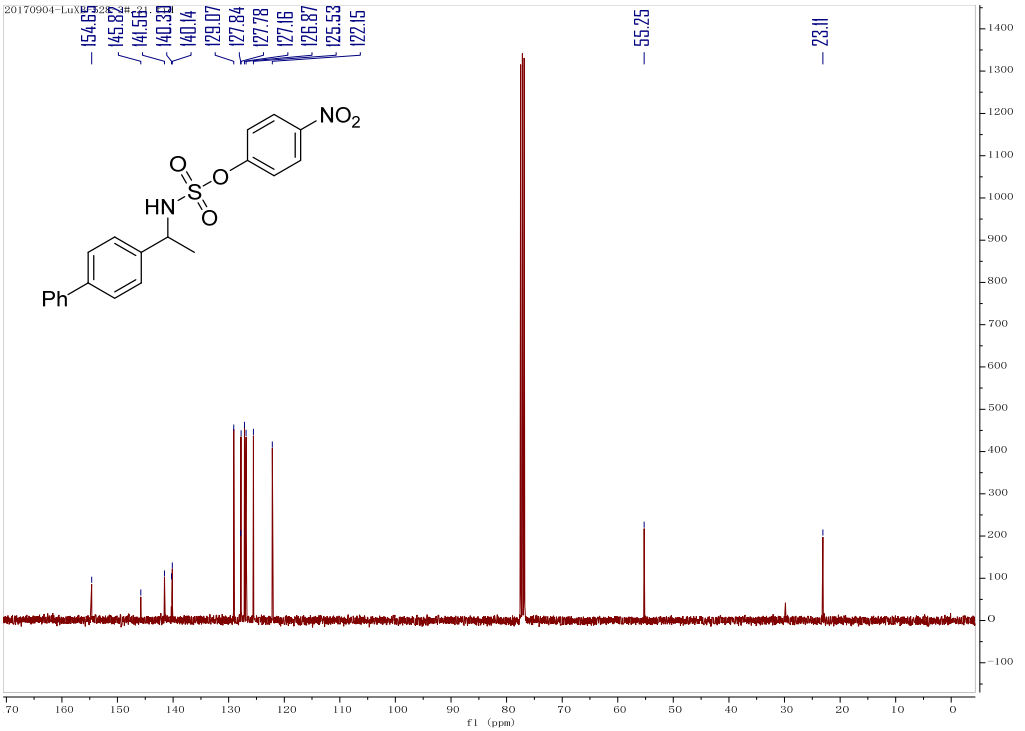
3.05
f1 (ppm)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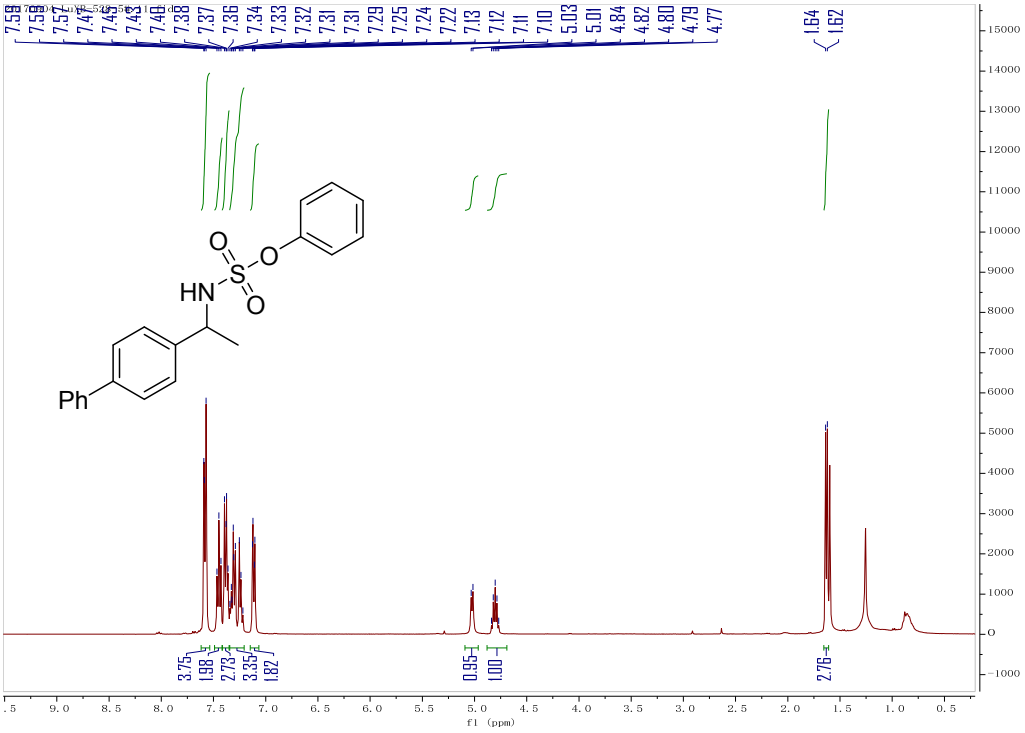
Ph
f1 (ppm)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7.13
7.12
7.11
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5.01
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4.77
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Ph
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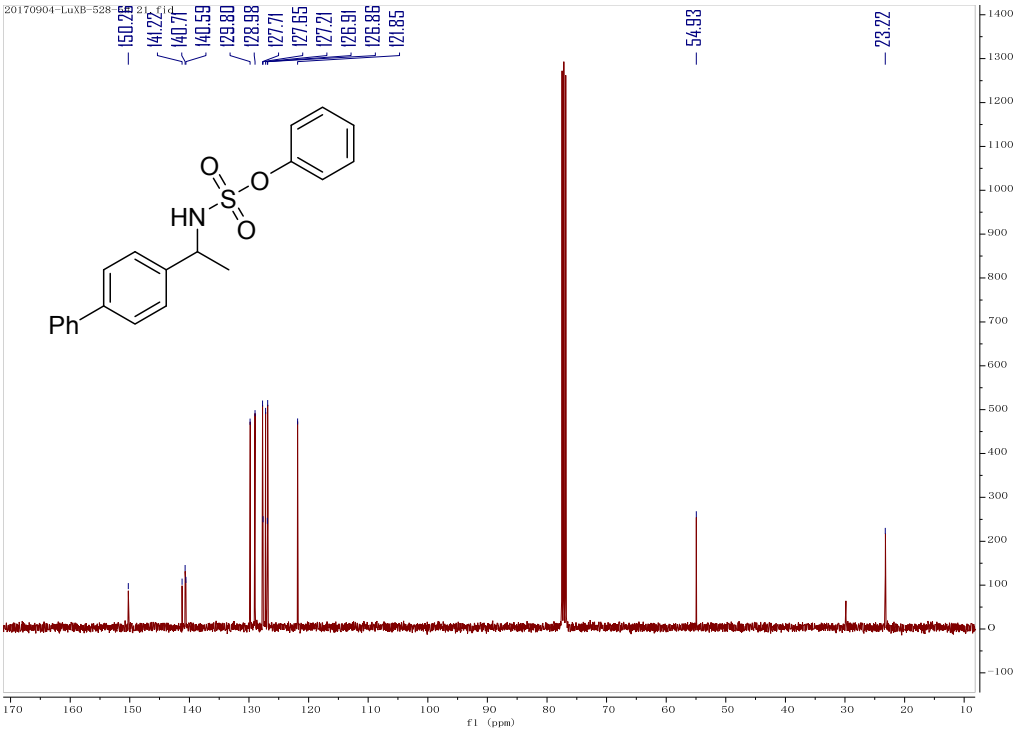
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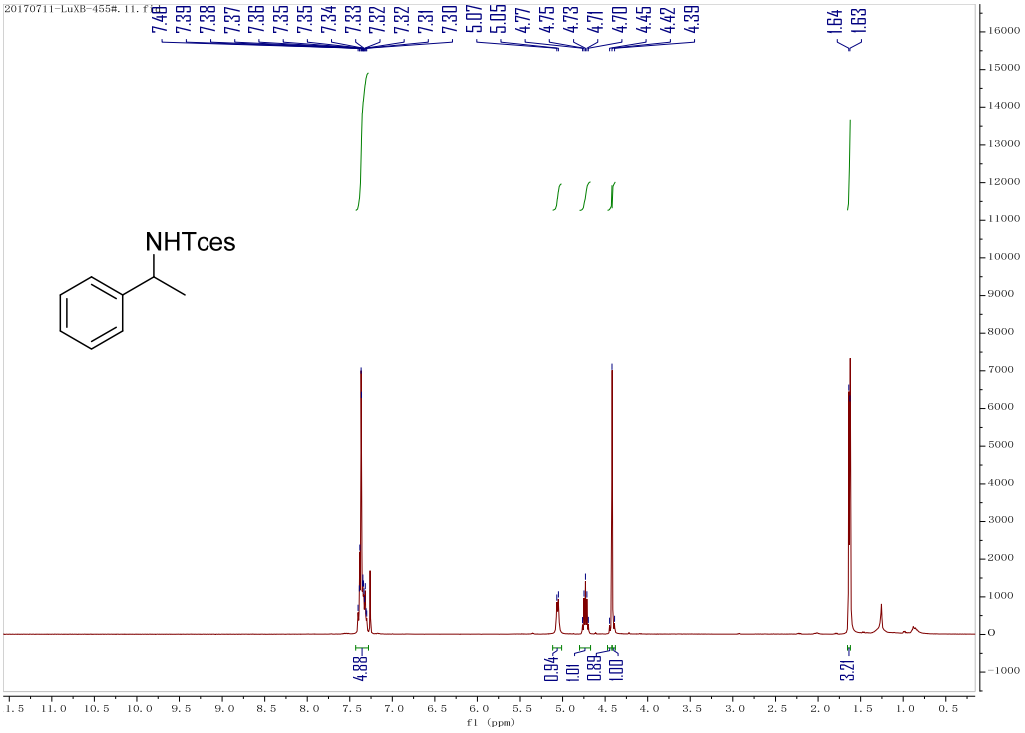
O
S
O
HN
O
Ph
f1 (ppm)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4.71
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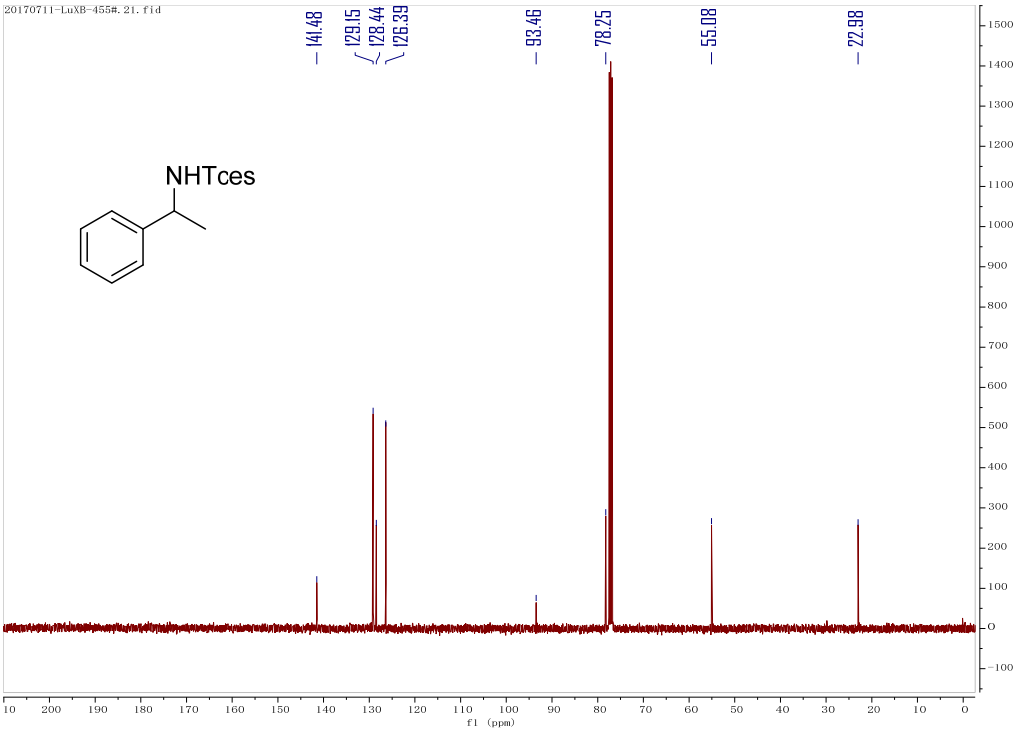
f1 (ppm)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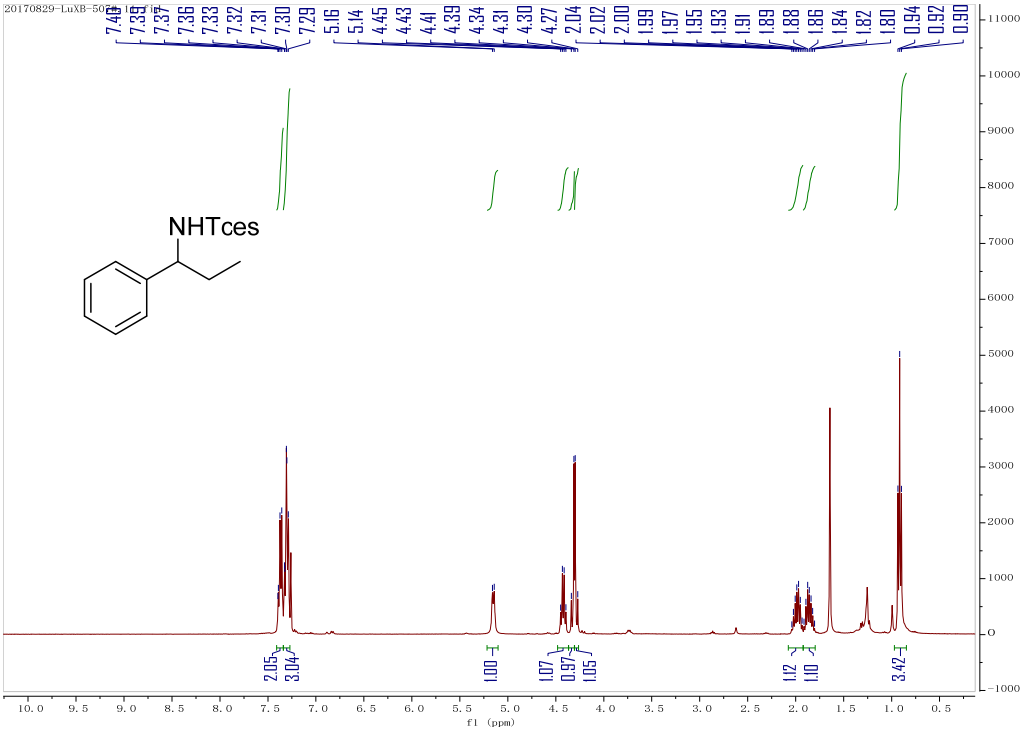
NHTces
f1 (ppm)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1.91
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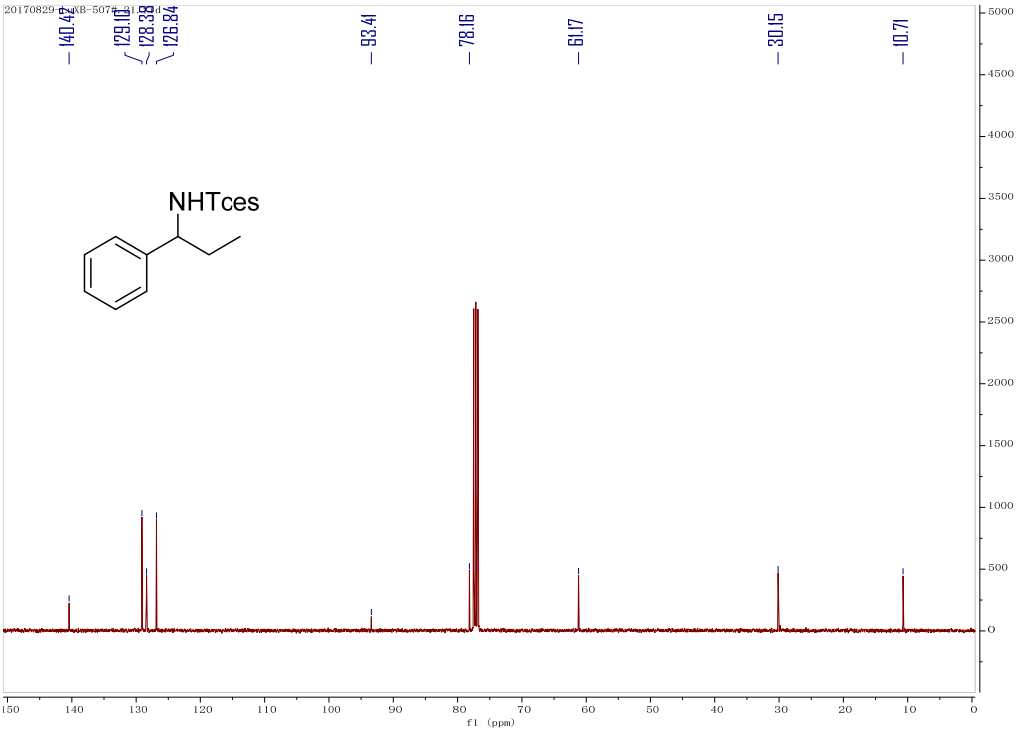
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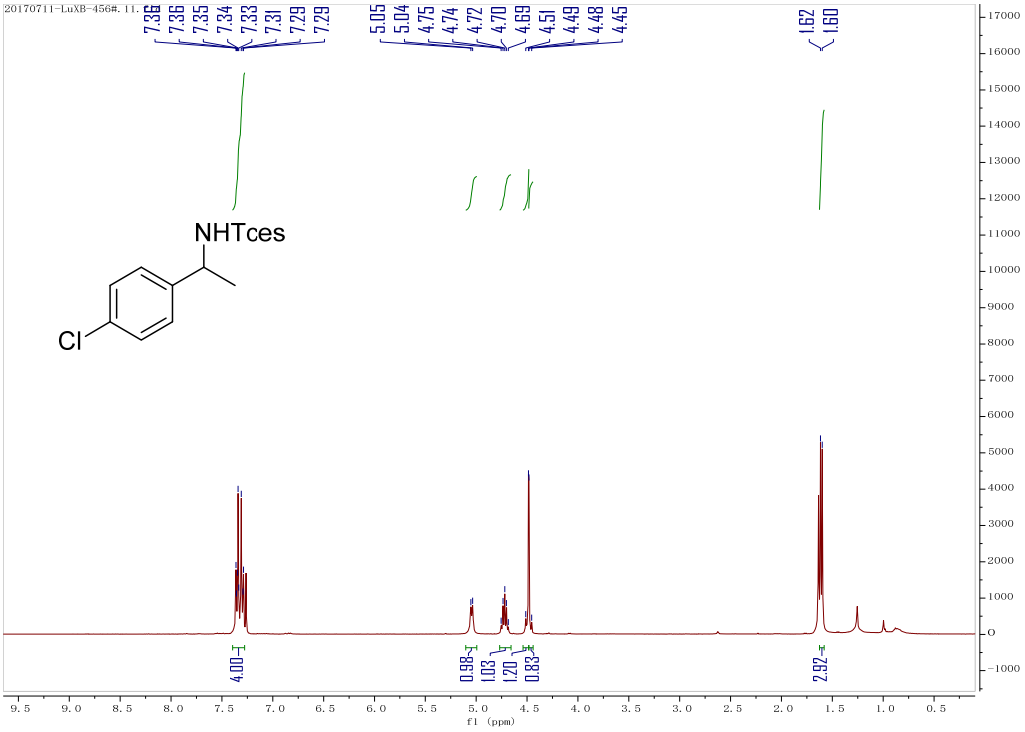
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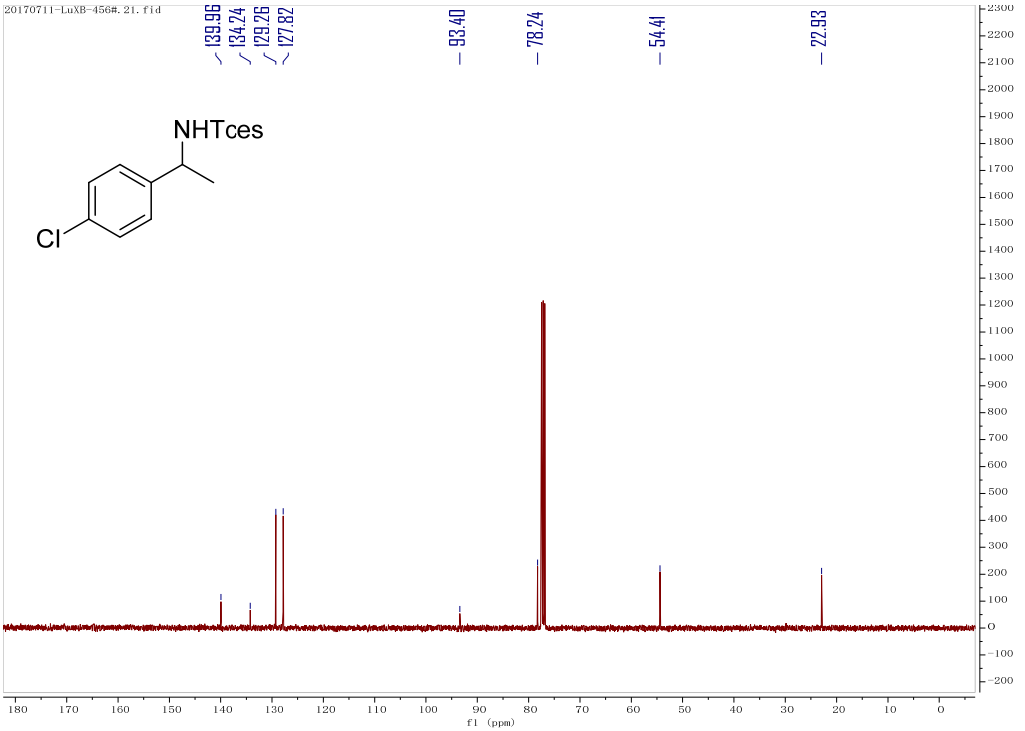
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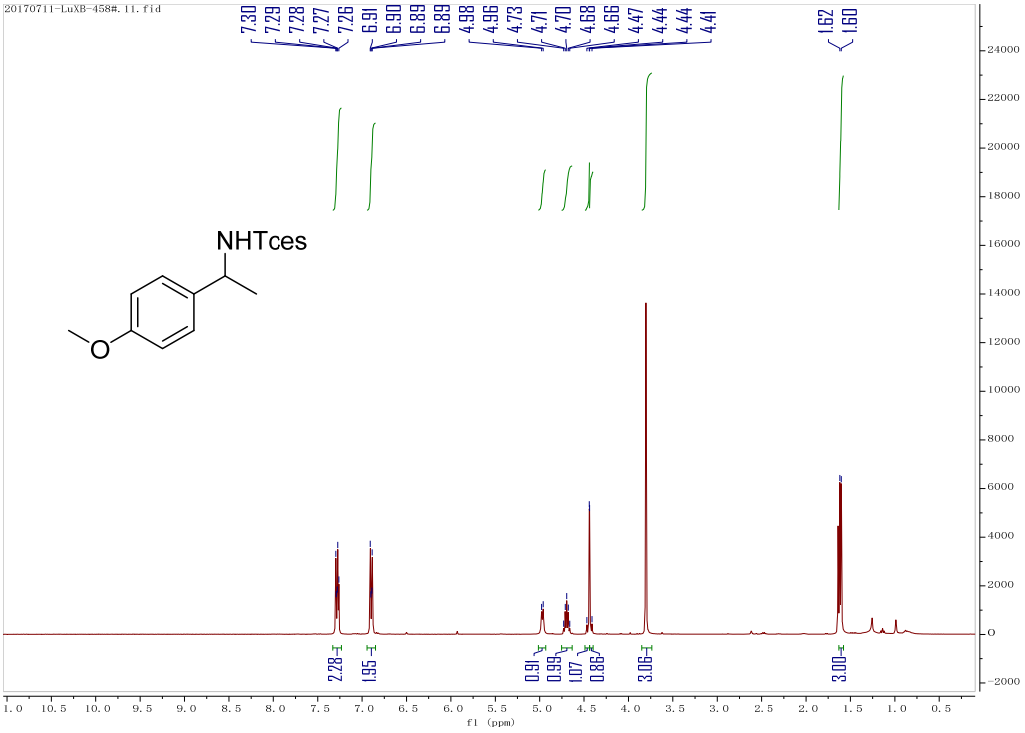
NHTces
Cl
f1 (ppm)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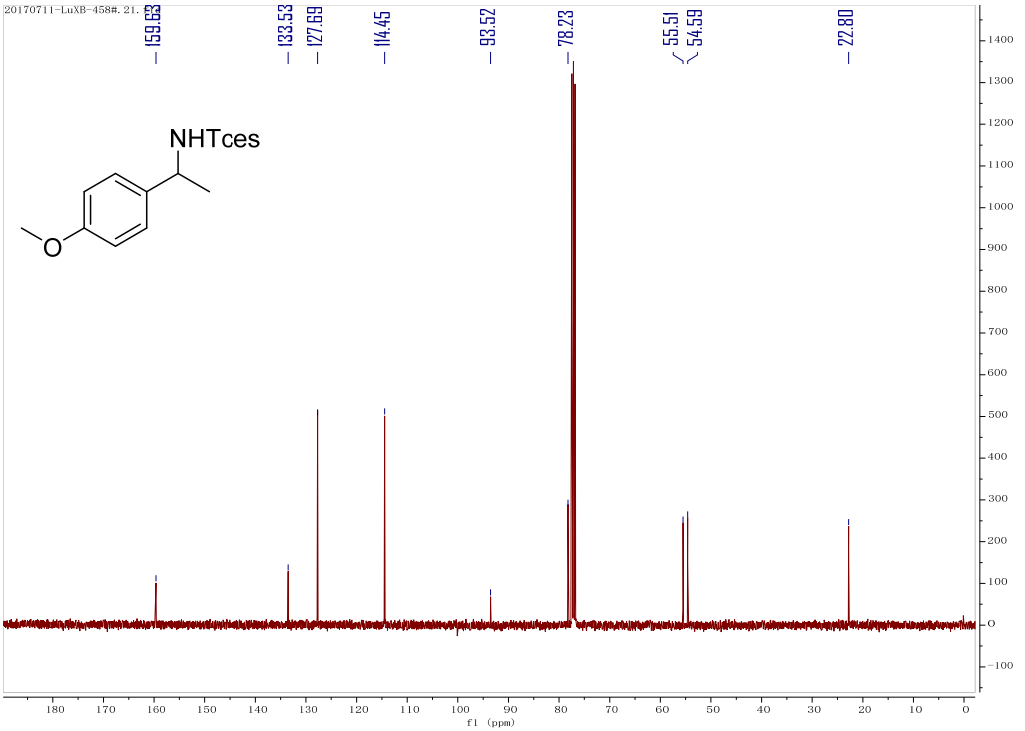
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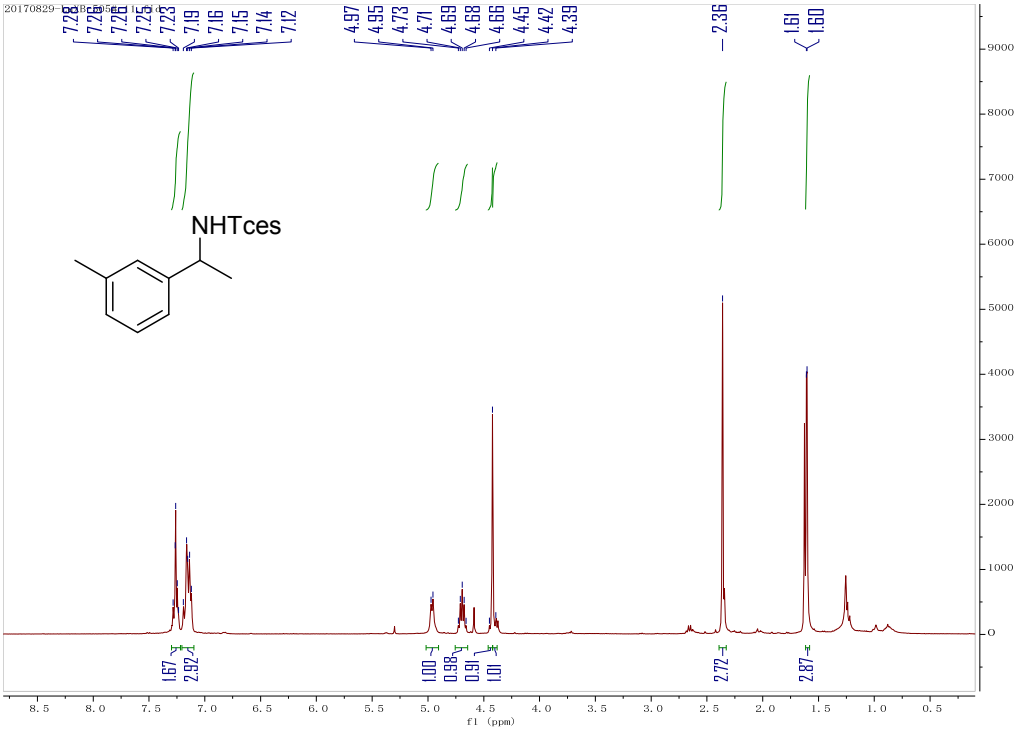
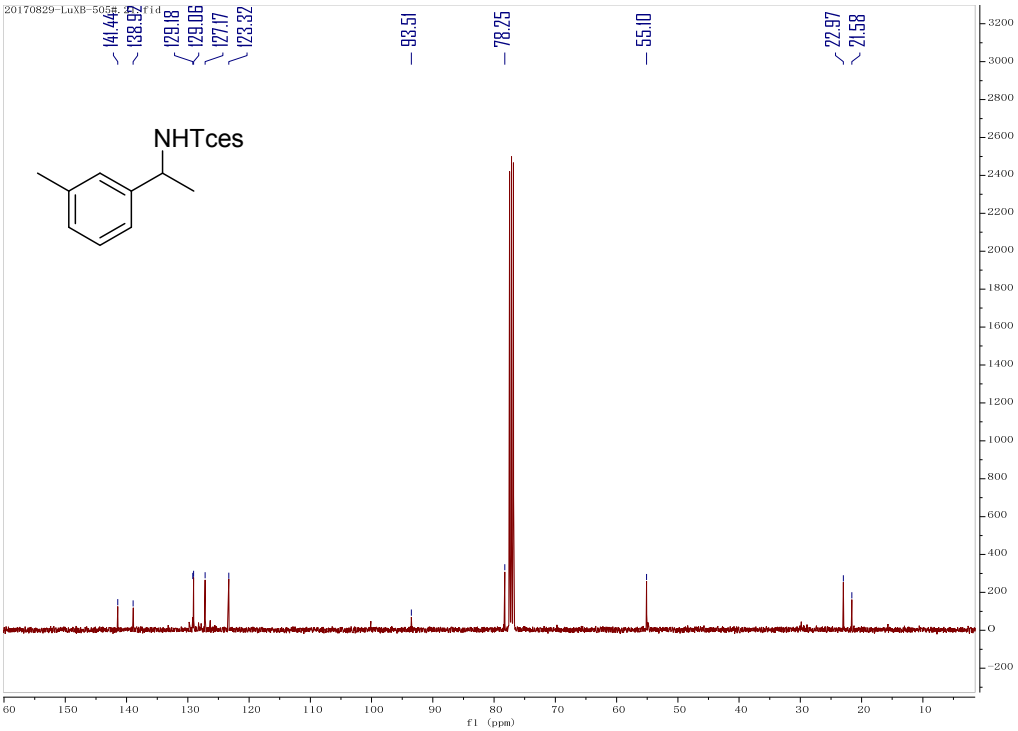
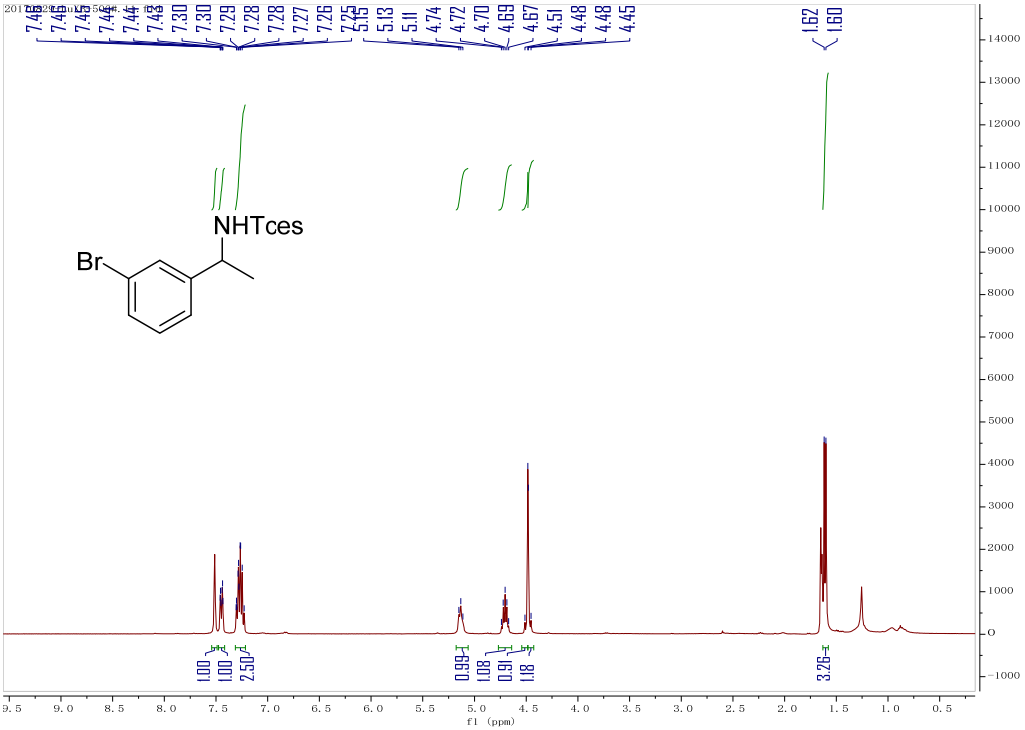
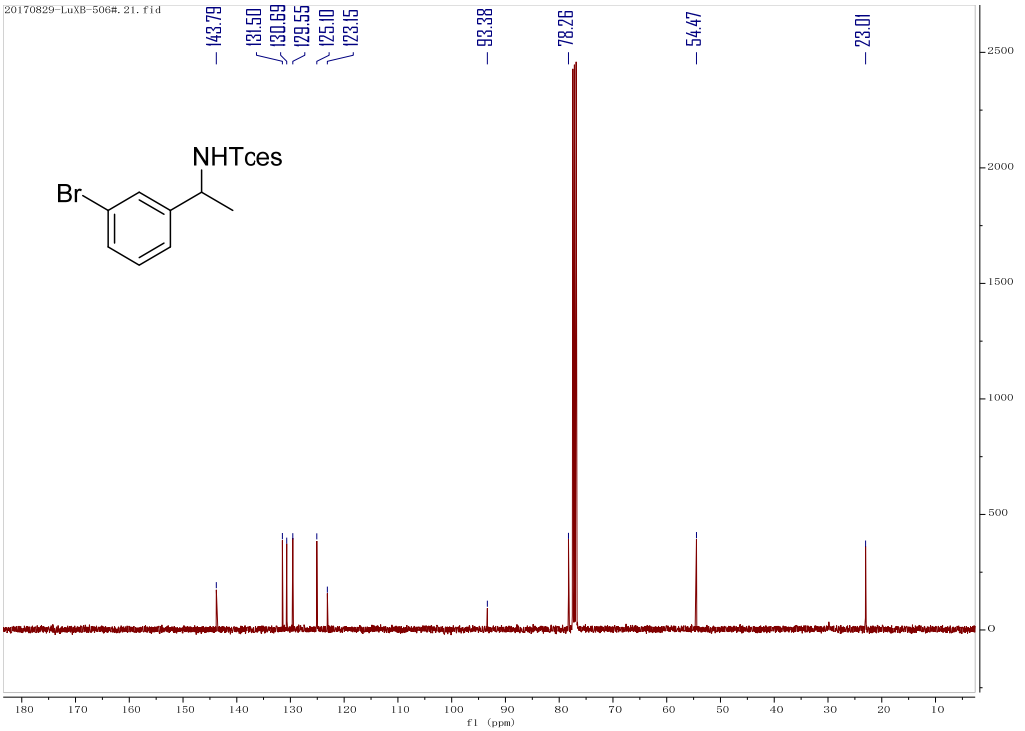
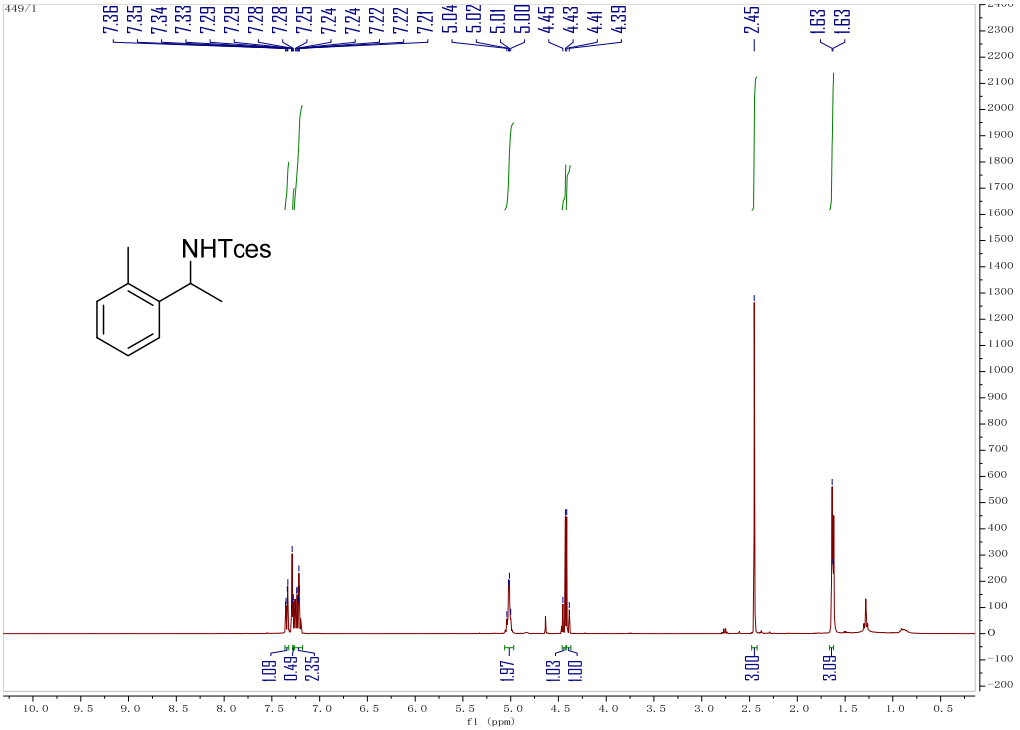
NHTces
O
f1 (ppm)

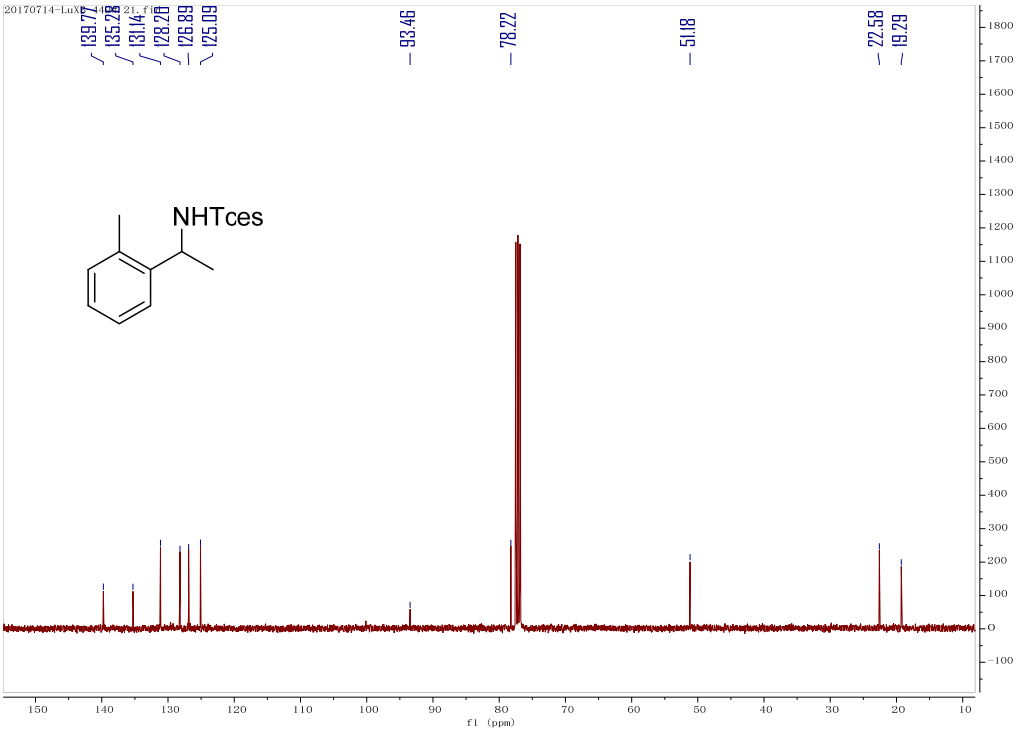

NHTces
7.28
7.26
7.25
7.23
7.19
7.16
7.15
7.14
7.12
4.97
4.95
4.73
4.71
4.69
4.68
4.66
4.45
4.42
4.39
2.36
1.61
1.60
1.67
2.92
1.00
0.98
0.91
1.01
2.72
2.87
f1 (ppm)

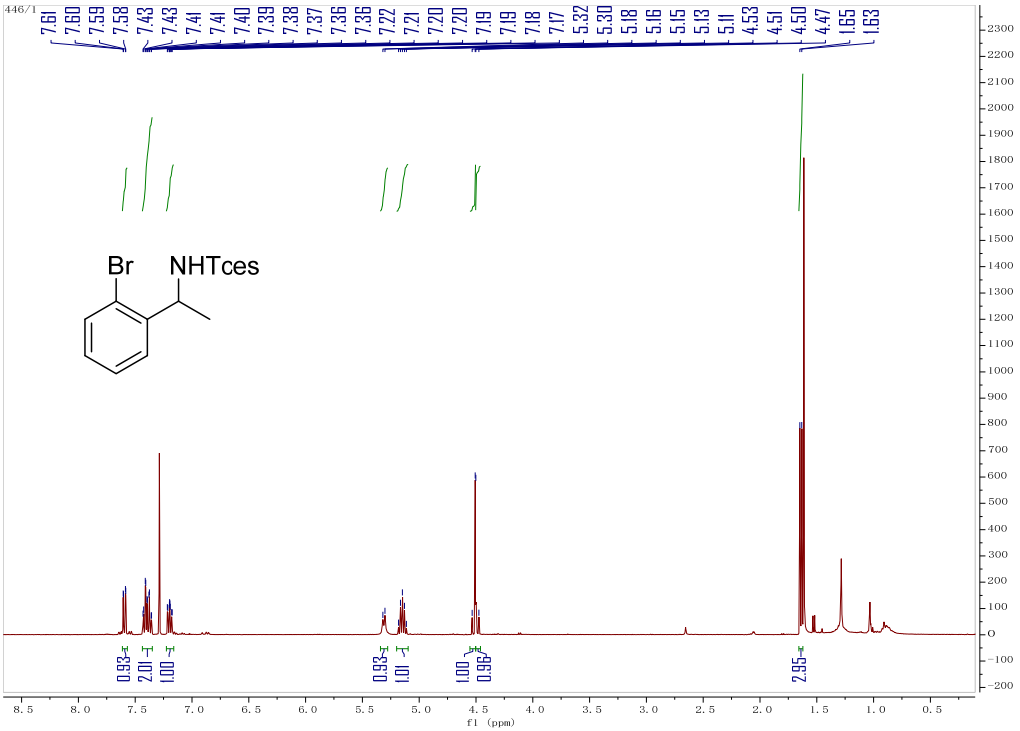

NHTces
141.44
138.92
129.18
129.06
127.17
123.32
93.51
78.25
55.10
22.97
21.58
f1 (ppm)

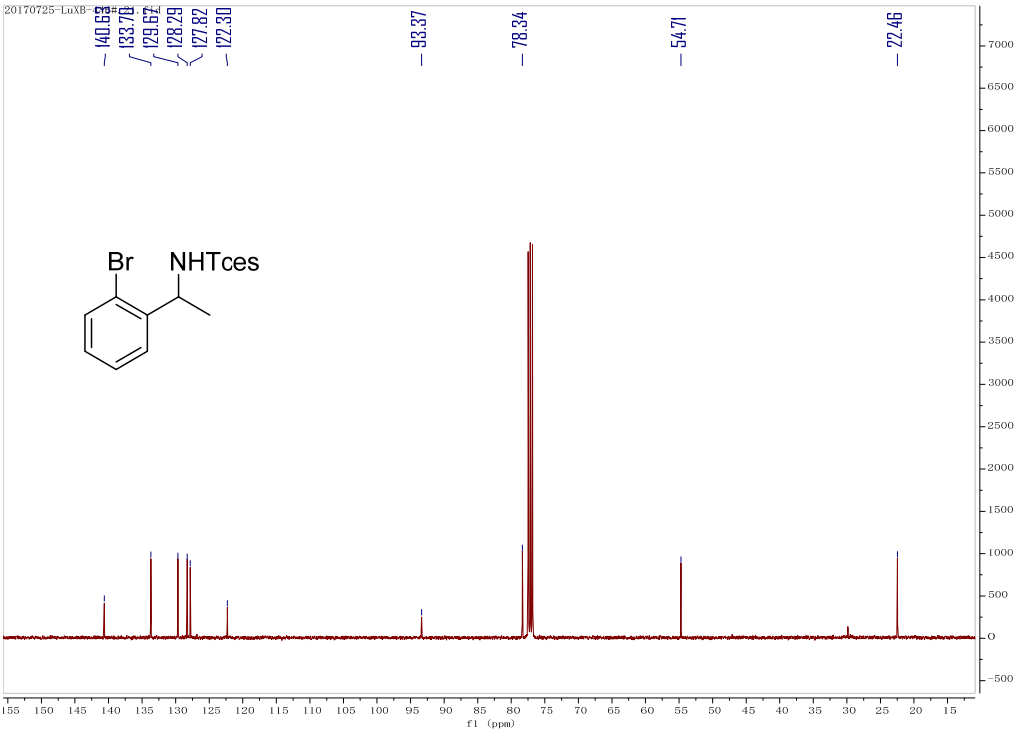

NHTces
Br
7.46
7.45
7.44
7.43
7.30
7.29
7.28
7.27
7.26
5.13
5.11
4.74
4.72
4.70
4.69
4.67
4.51
4.48
4.45
1.62
1.60
1.00
1.00
2.50
0.99
1.08
0.91
1.18
3.26
f1 (ppm)

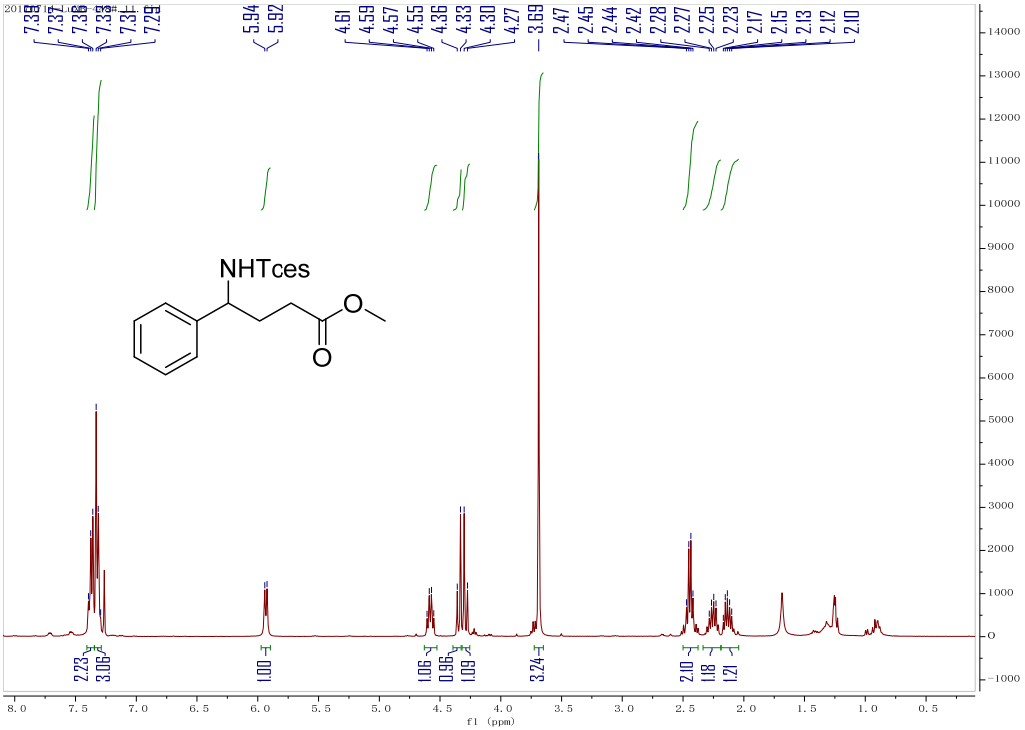

20170829-LuXB-506#.21.fid
NHTces
Br
143.79
131.50
130.69
129.55
125.10
123.15
93.38
78.26
54.47
23.01
f1 (ppm)

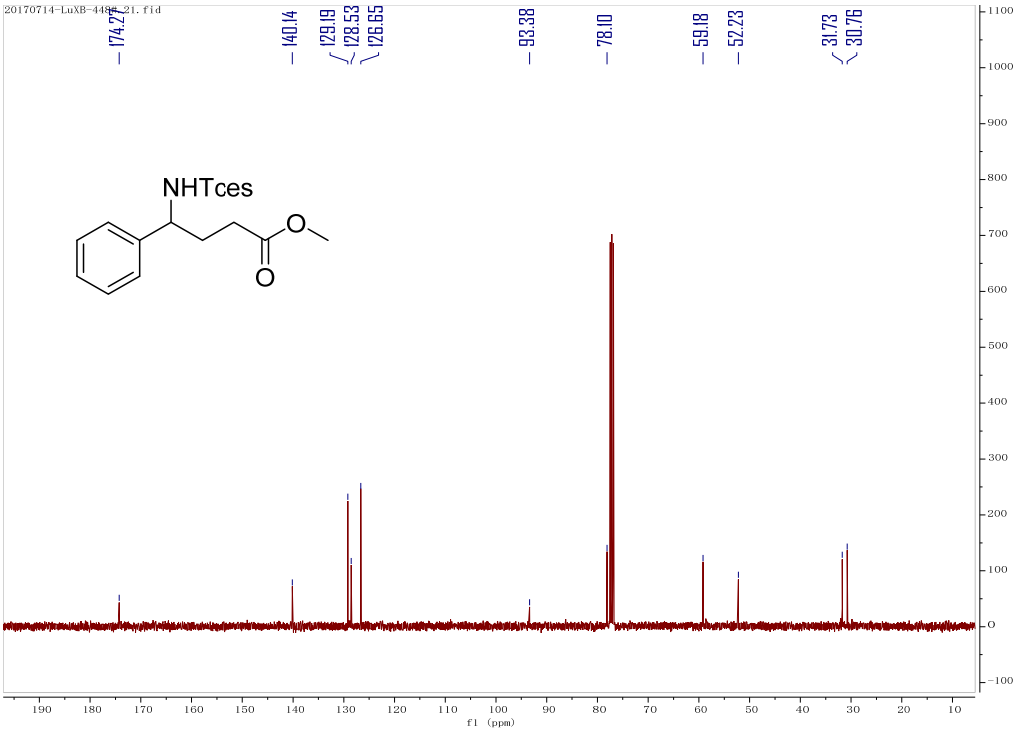

449/1
7.36
7.35
7.34
7.33
7.29
7.29
7.28
7.28
7.25
7.24
7.24
7.22
7.22
7.21
5.04
5.02
5.01
5.00
4.45
4.43
4.41
4.39
2.45
1.63
1.63
NHTces
1.09
0.49
2.35
1.97
1.03
1.00
3.00
3.09
f1 (ppm)

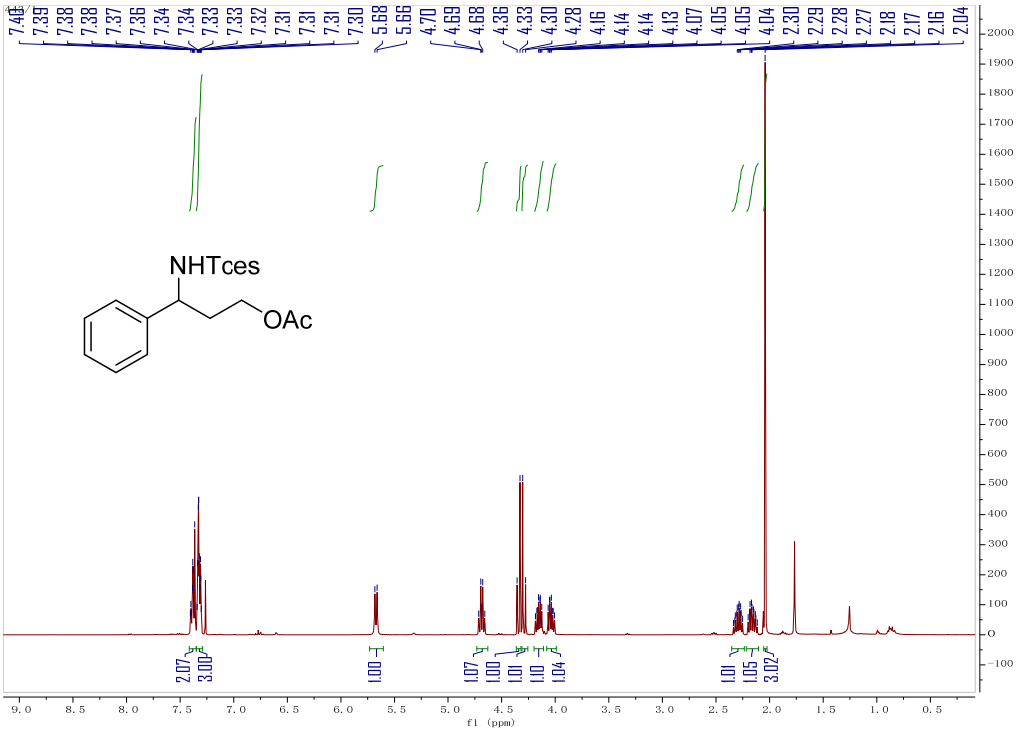

139.77
135.28
131.14
128.26
126.89
125.09
93.46
78.22
51.18
22.58
19.29
NHTces
f1 (ppm)

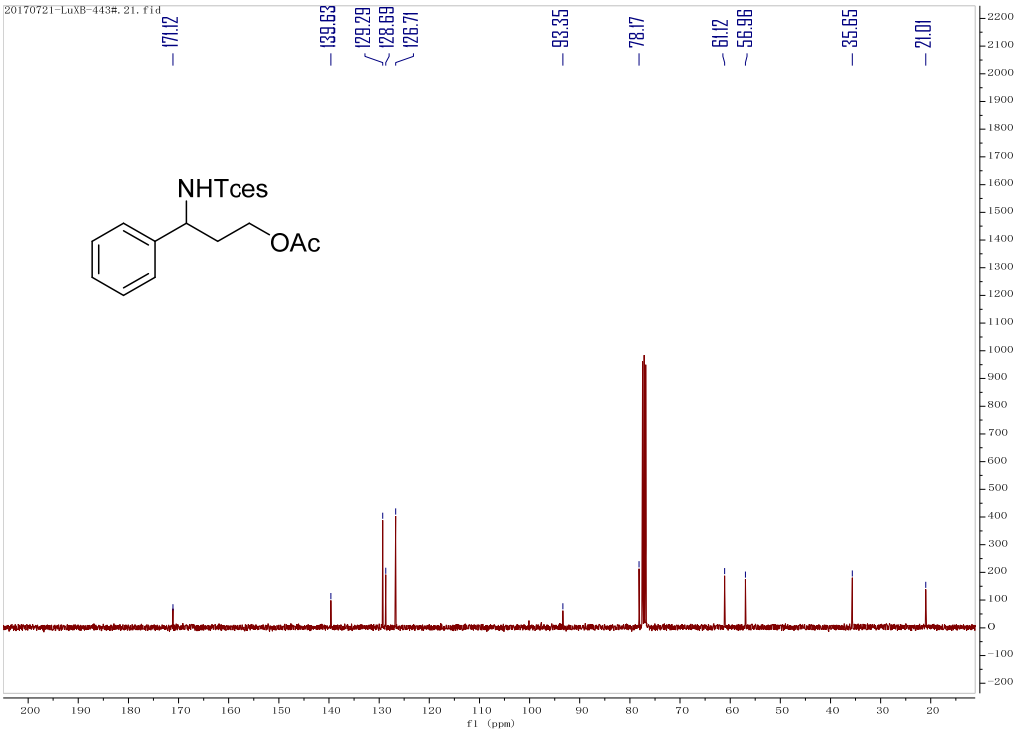

446/1
7.61
7.60
7.59
7.58
7.43
7.43
7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.17
5.32
5.30
5.18
5.16
5.15
5.13
5.11
4.53
4.51
4.50
4.47
1.65
1.63
Br
NHTces
0.93
2.01
1.00
0.93
1.01
1.00
0.96
2.95
f1 (ppm)

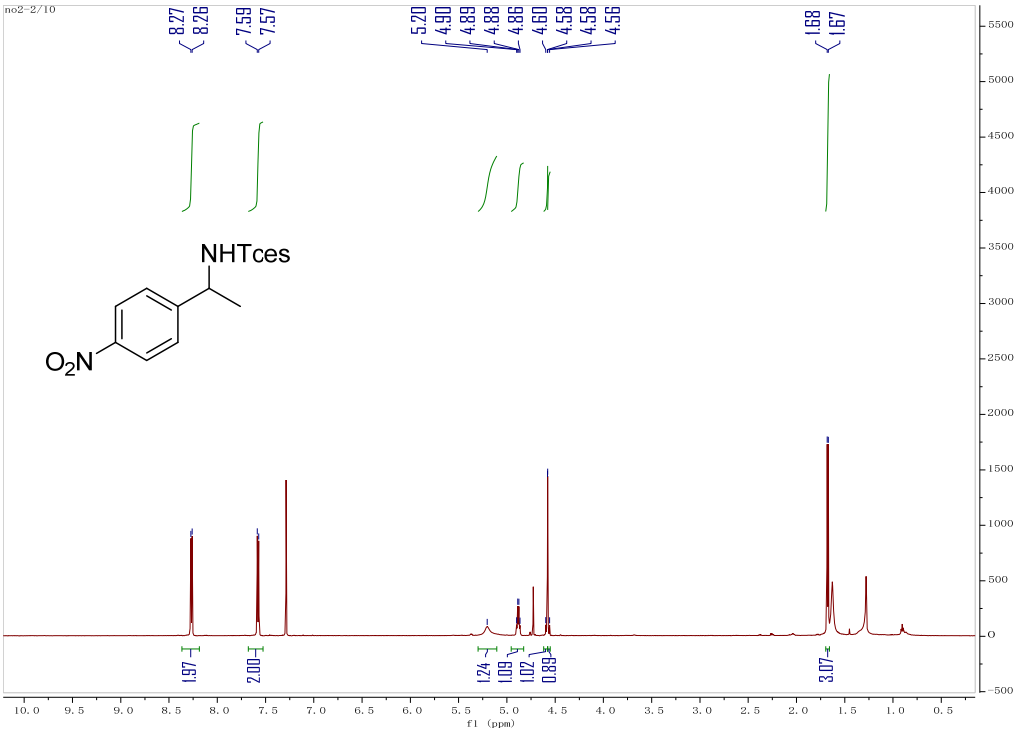

20170725-LuXB-
140.63
133.76
129.62
128.29
127.82
122.30
93.37
78.34
54.71
22.46
Br
NHTces
f1 (ppm)

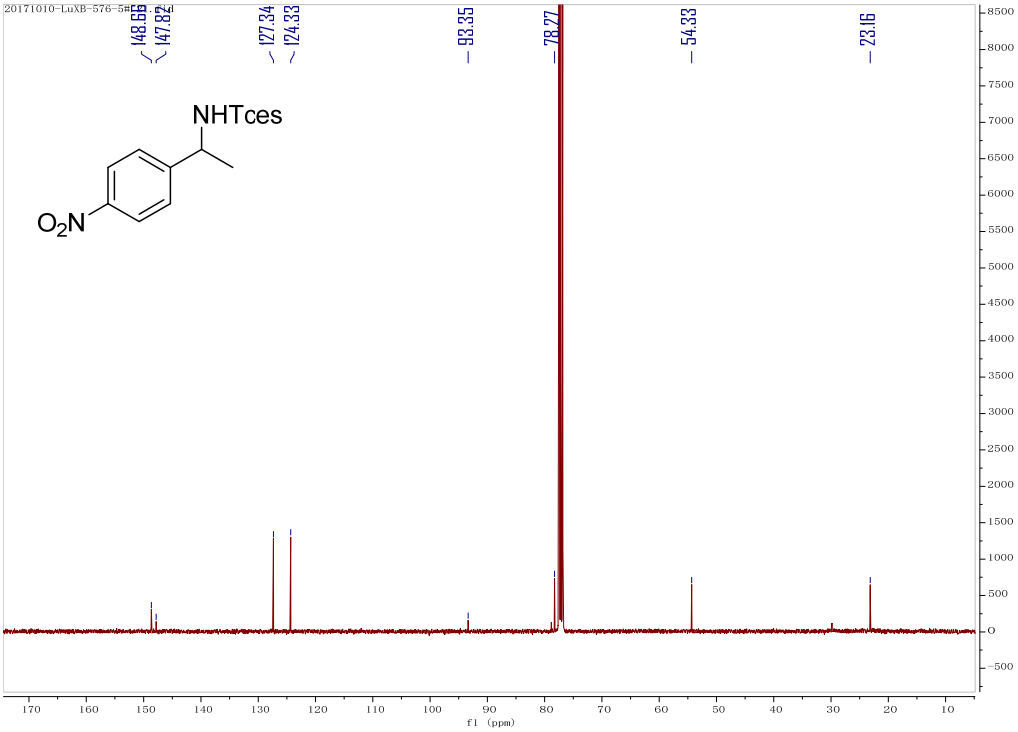

NHTces
O
O
7.33
7.32
7.31
7.29
5.94
5.92
4.61
4.59
4.57
4.55
4.36
4.33
4.30
4.27
3.69
2.47
2.45
2.44
2.42
2.28
2.27
2.25
2.23
2.17
2.15
2.13
2.12
2.10
2.23
3.06
1.00
1.06
0.96
1.09
3.24
2.10
1.18
1.21
f1 (ppm)

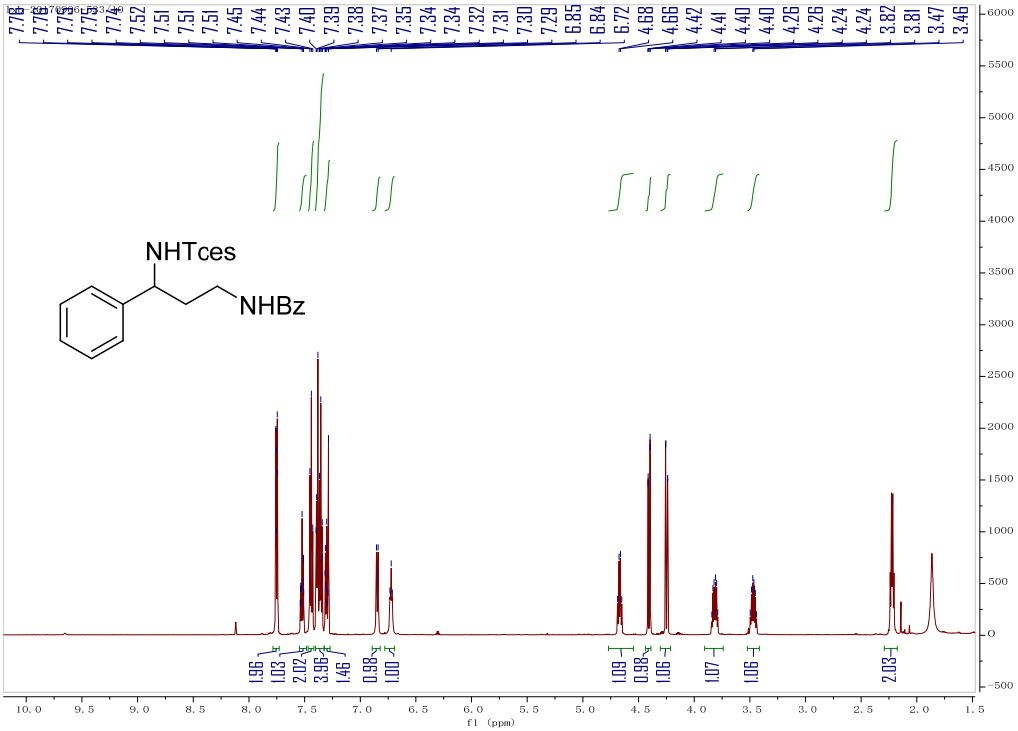

NHTces
O
O
174.27
140.14
129.19
128.53
126.65
93.38
78.10
59.18
52.23
31.73
30.76
f1 (ppm)

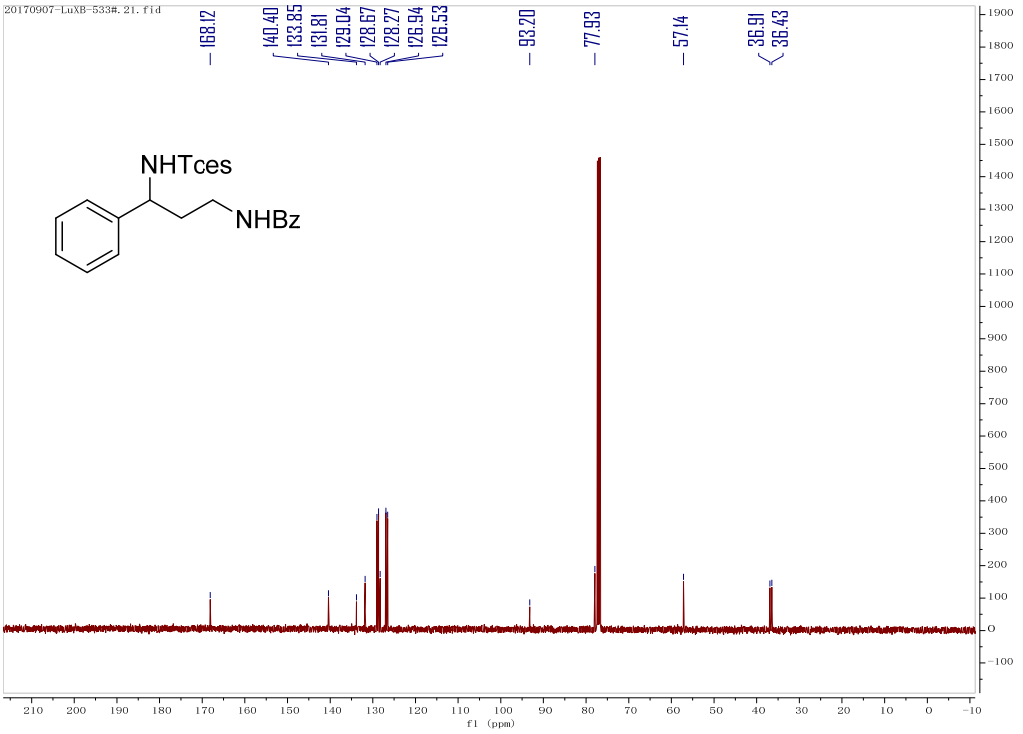

NHTces
OAc
f1 (ppm)

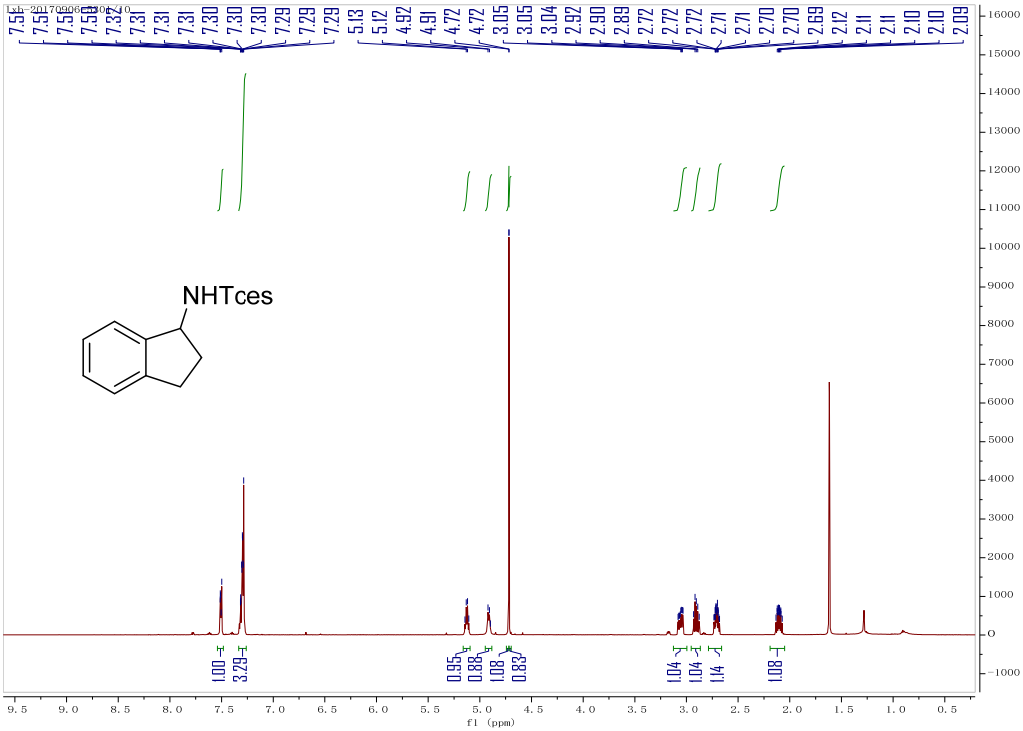

20170721-LuXB-443#.21.fid
NHTces
OAc
f1 (ppm)

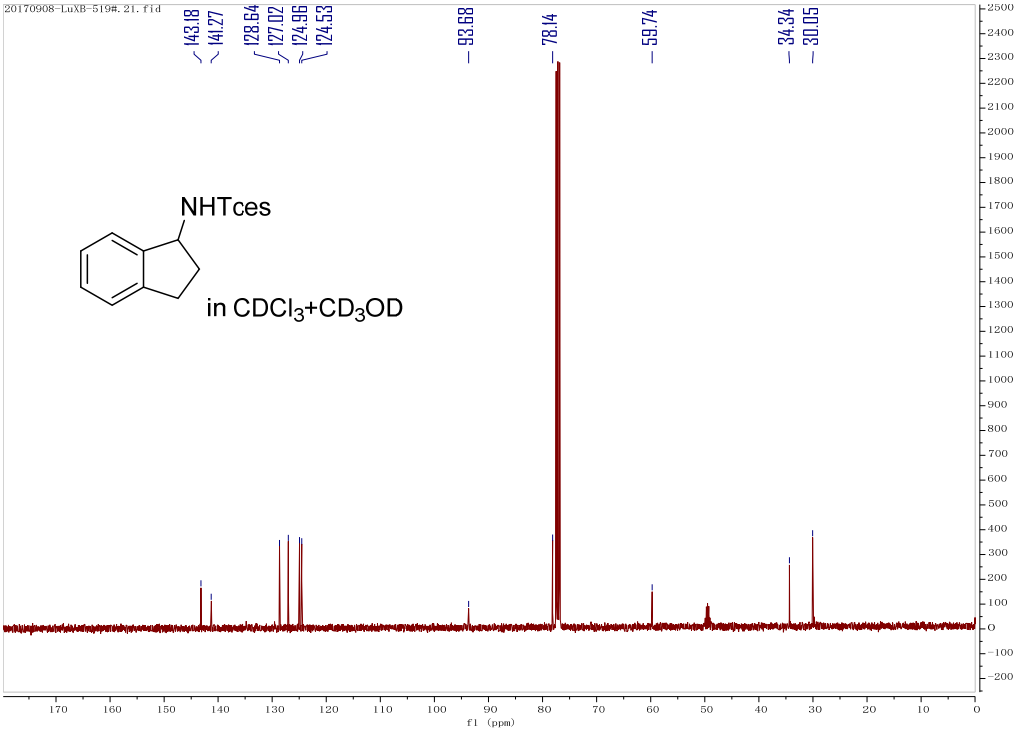

no2-2/10
8.27
8.26
7.59
7.57
5.20
4.90
4.89
4.88
4.86
4.60
4.58
4.58
4.56
1.68
1.67
NHTces
O2N
1.97
2.00
1.24
1.09
1.02
0.89
3.07
f1 (ppm)

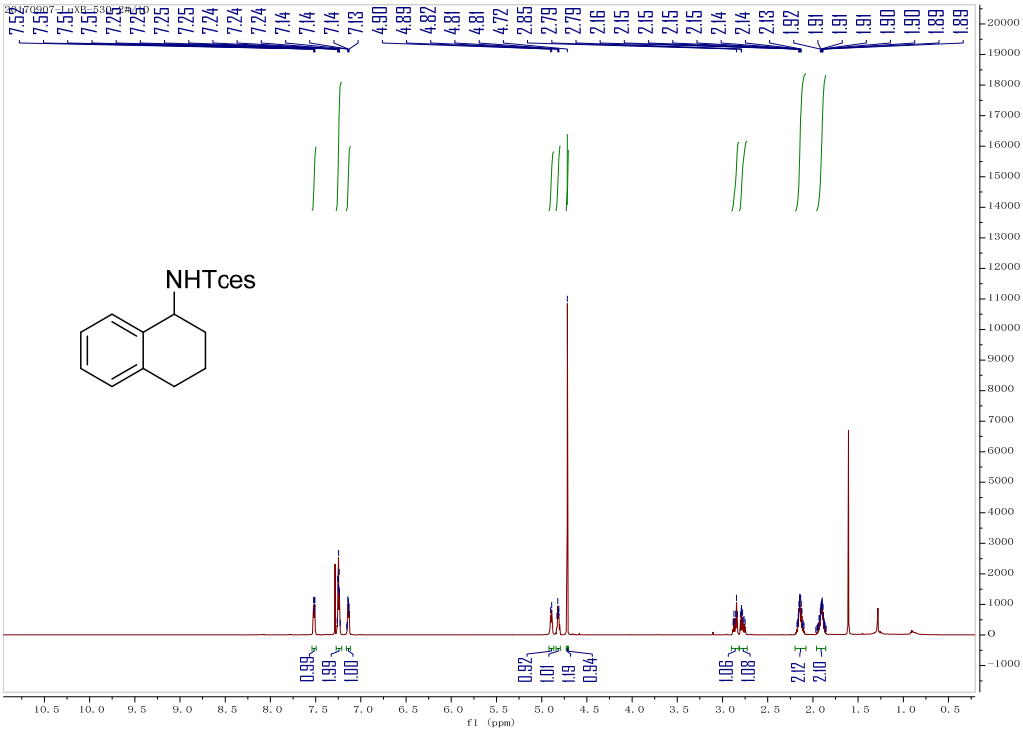

148.66
147.82
127.34
124.33
93.35
78.77
54.33
23.16
NHTces
O_2N
f1 (ppm)

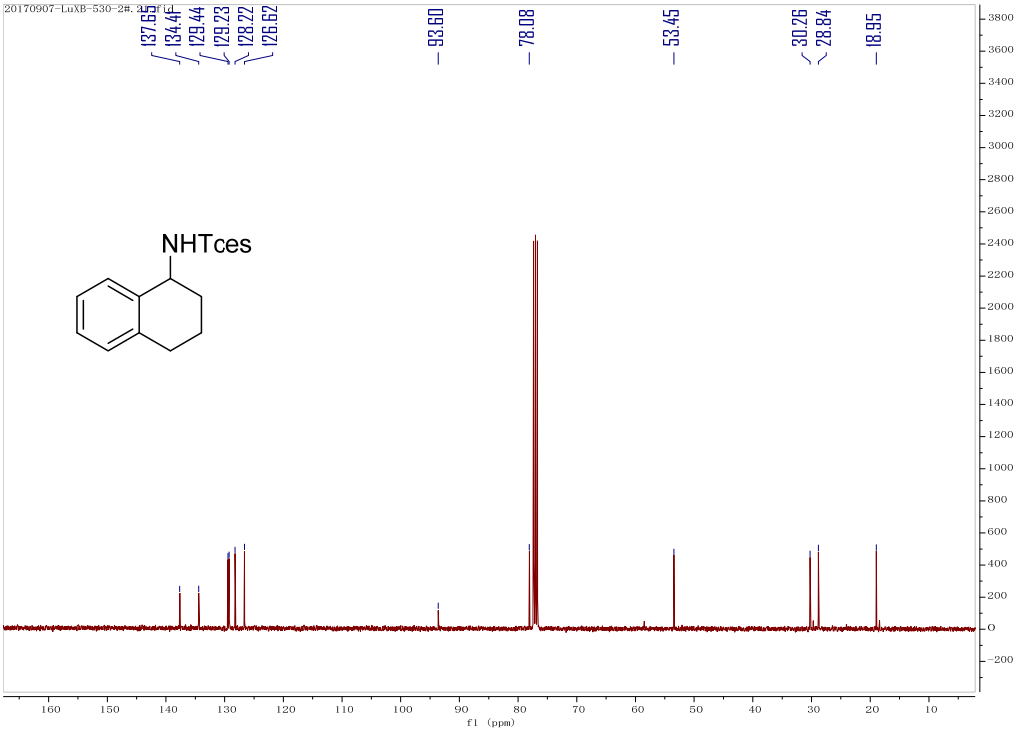

NHTces
NHBz
1.96
1.03
2.02
3.96
1.46
0.98
1.00
1.09
0.98
1.06
1.07
1.06
2.03
f1 (ppm)

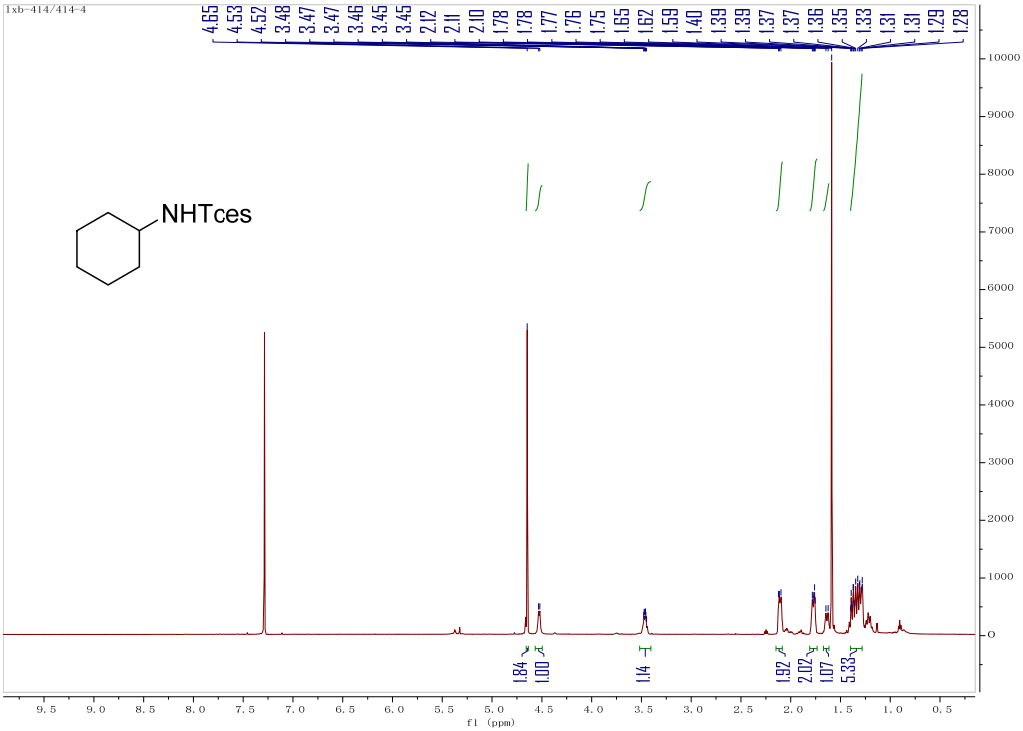

20170907-LuXB-533#.21.fid
168.12
140.40
133.85
131.81
129.04
128.67
128.27
126.94
126.53
93.20
77.93
57.14
36.91
36.43
NHTces
NHBz
f1 (ppm)

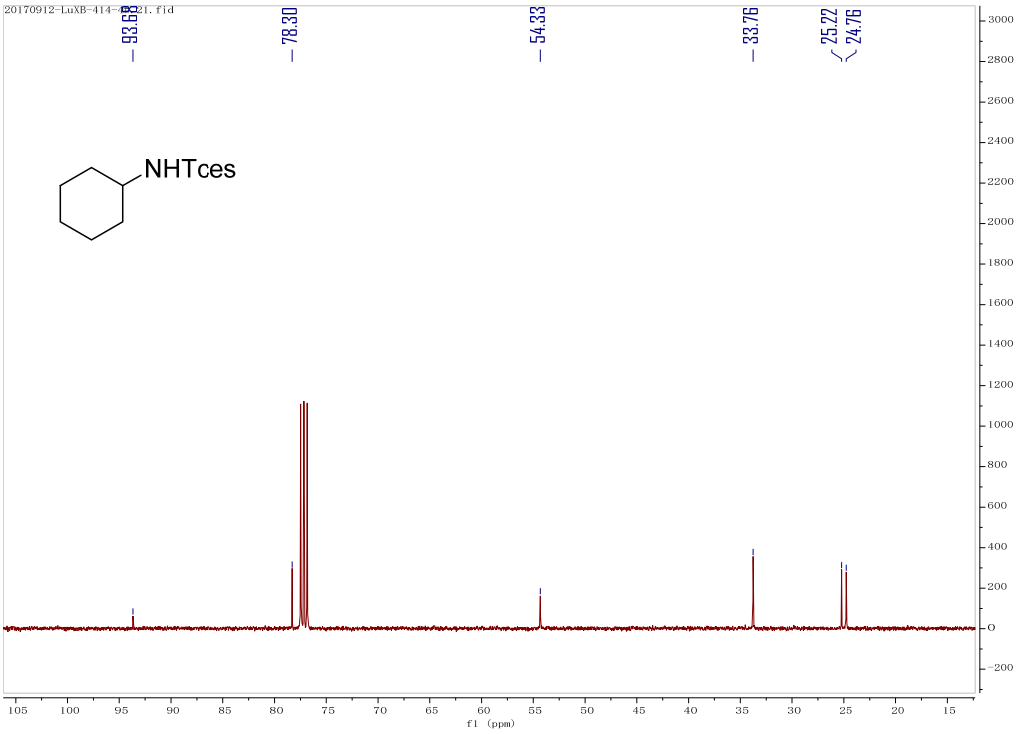

7.56
7.55
7.55
7.54
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.30
7.29
7.29
7.29
5.13
5.12
4.92
4.91
4.72
4.72
3.05
3.05
3.04
2.92
2.90
2.89
2.72
2.72
2.72
2.71
2.71
2.70
2.70
2.69
2.12
2.11
2.11
2.10
2.10
2.09
NHTces
1.00
3.29
0.95
0.88
1.08
0.83
1.04
1.04
1.14
1.08
f1 (ppm)

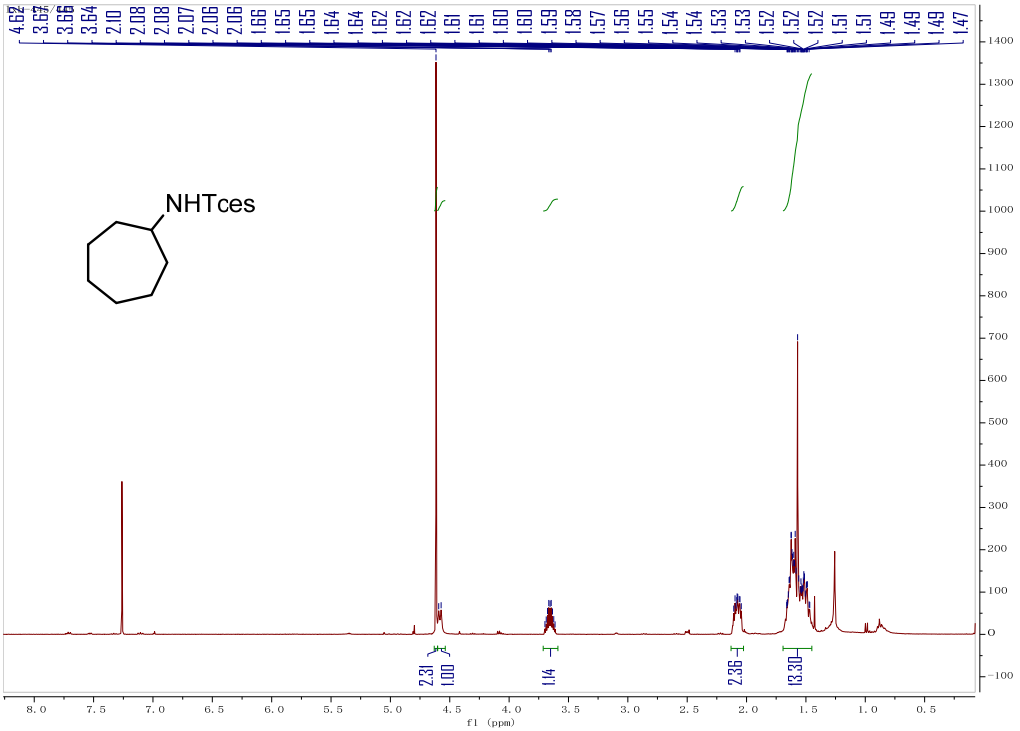

20170908-LuXB-519#.21.fid
143.18
141.27
128.64
127.02
124.96
124.53
93.68
78.14
59.74
34.34
30.05
NHTces
in CDCl3+CD3OD
f1 (ppm)

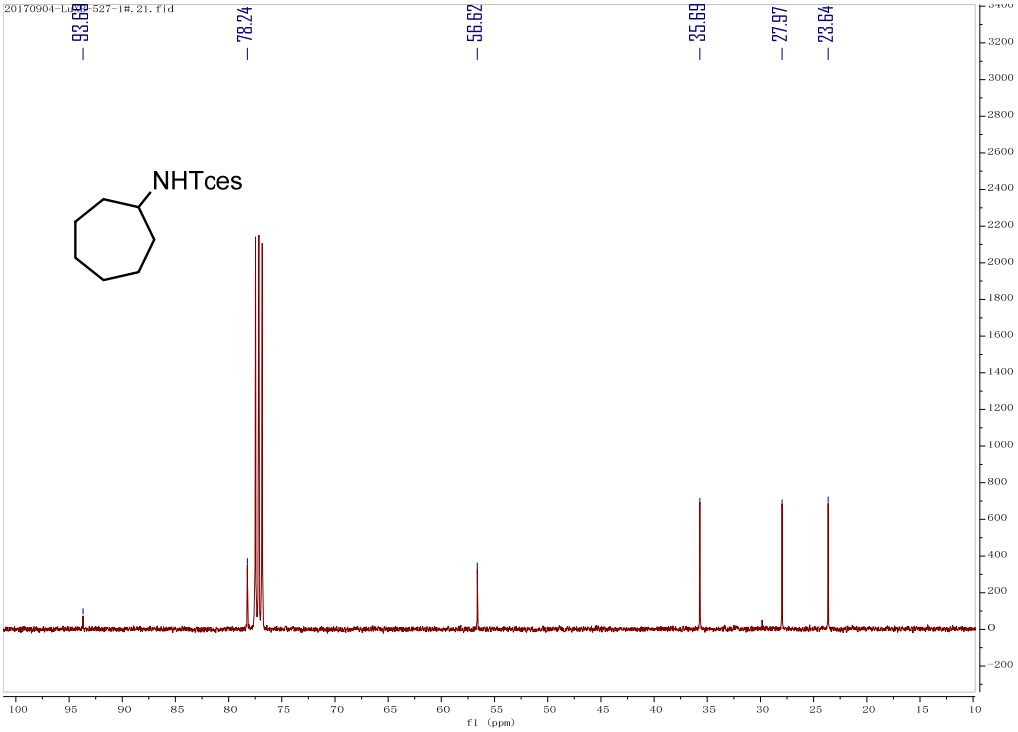

7.52
7.51
7.51
7.50
7.25
7.24
7.14
7.13
4.90
4.89
4.82
4.81
4.72
2.85
2.79
2.16
2.15
2.14
2.13
1.92
1.91
1.90
1.89
NHTces
0.99
1.99
1.00
0.92
1.01
1.19
0.94
1.06
1.08
2.12
2.10
f1 (ppm)

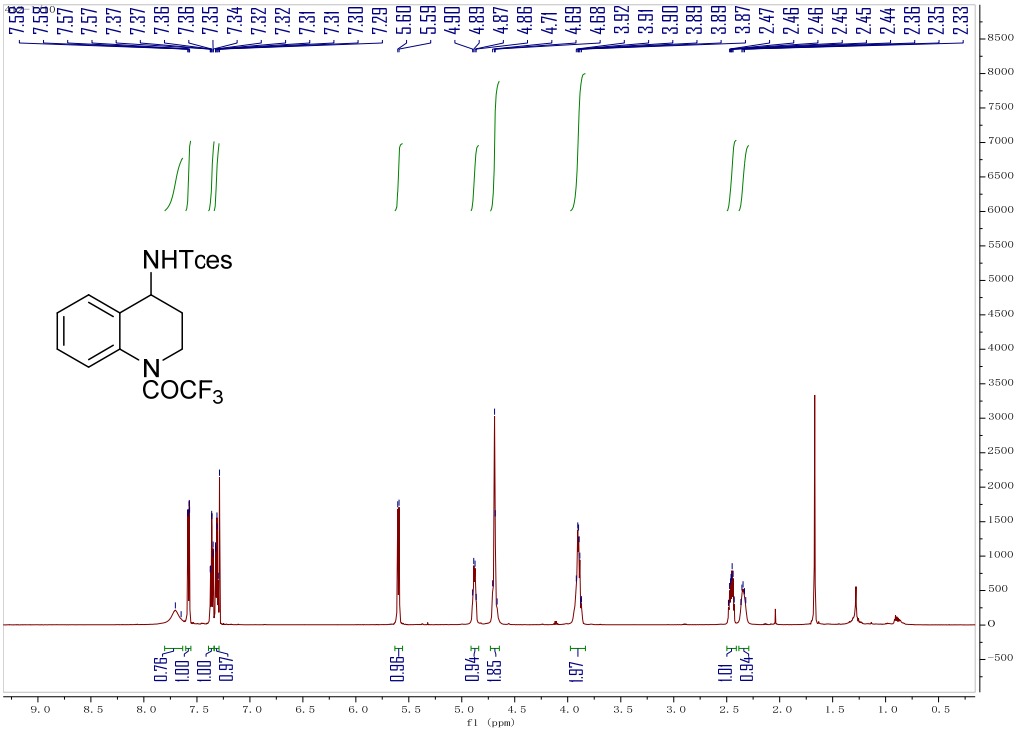

137.65
134.46
129.44
129.23
128.22
126.62
93.60
78.08
53.45
30.26
28.84
18.95
NHTces
f1 (ppm)

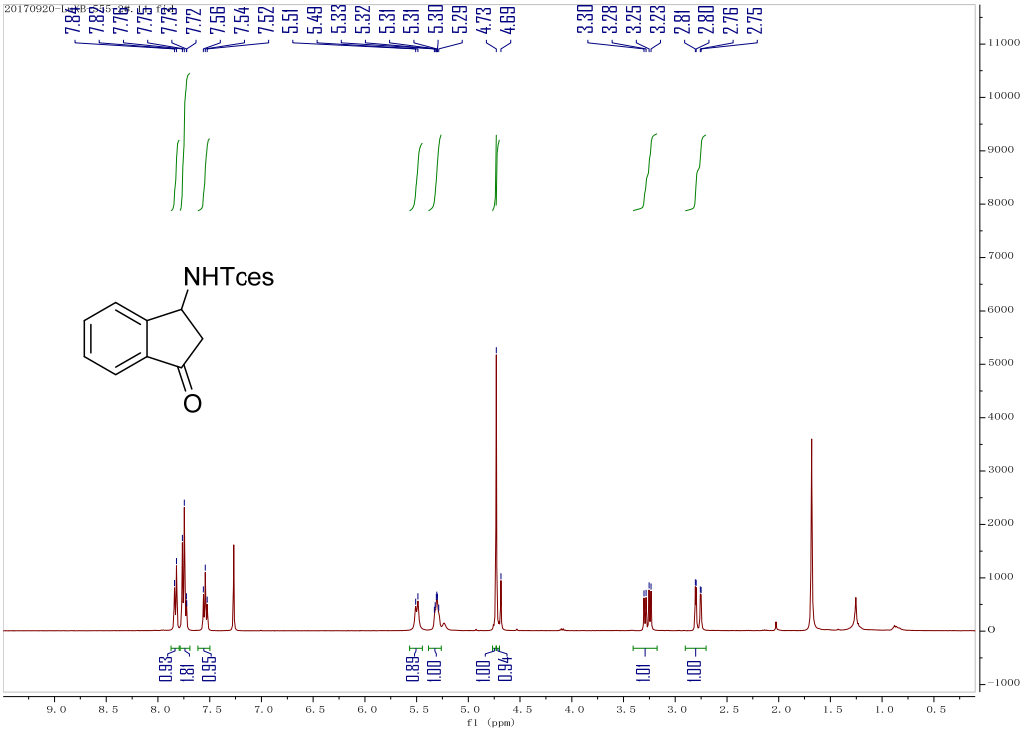

lxb-414/414-4
4.55
4.53
4.52
3.48
3.47
3.47
3.46
3.45
3.45
2.12
2.11
2.10
1.78
1.78
1.77
1.76
1.75
1.65
1.62
1.59
1.40
1.39
1.39
1.37
1.37
1.36
1.35
1.33
1.31
1.31
1.29
1.28
NHTces
1.84
1.00
1.14
1.92
2.02
1.07
5.33
f1 (ppm)

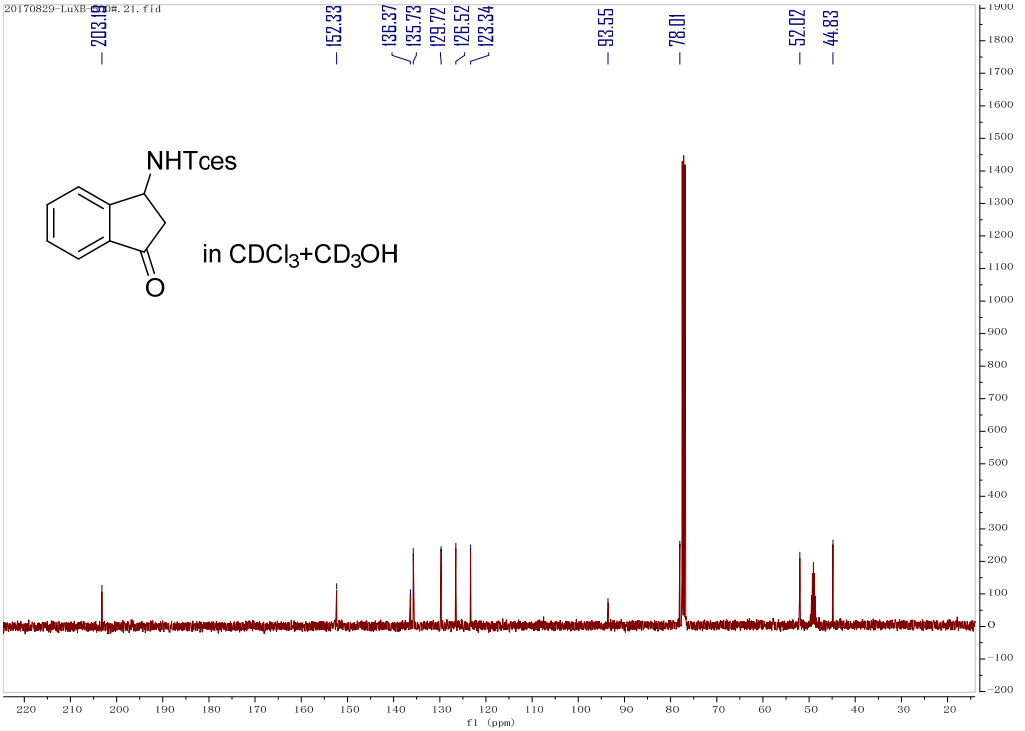

93.68
78.30
54.33
33.76
25.22
24.76
NHTces
f1 (ppm)

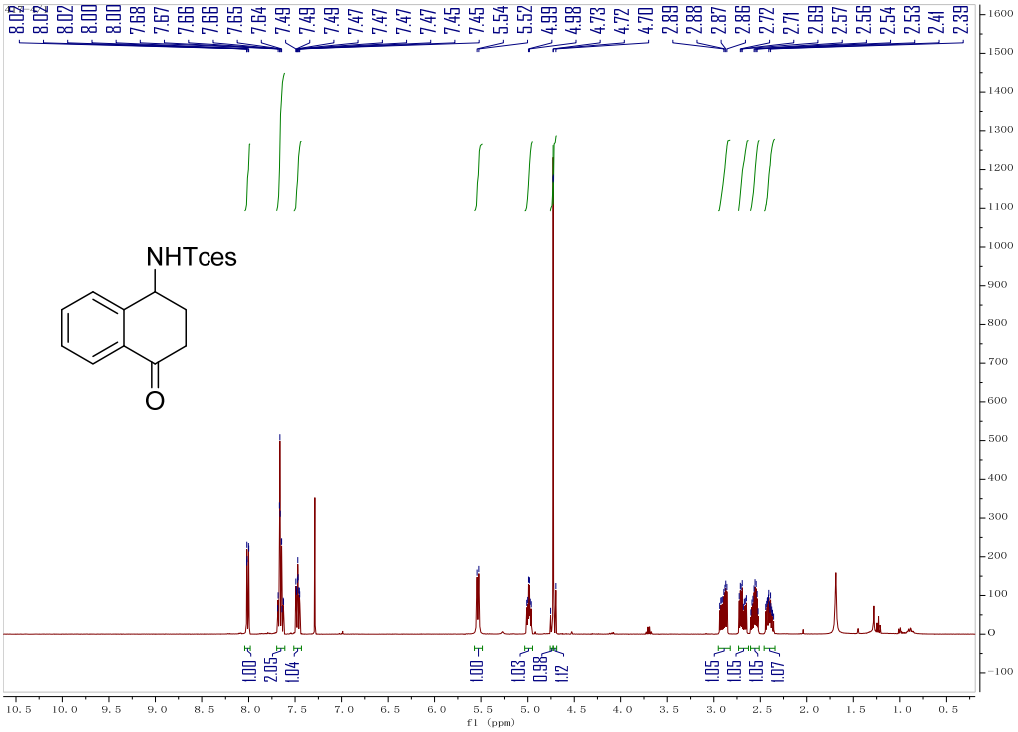

NHTces
2.31
1.00
1.14
2.36
13.30
f1 (ppm)

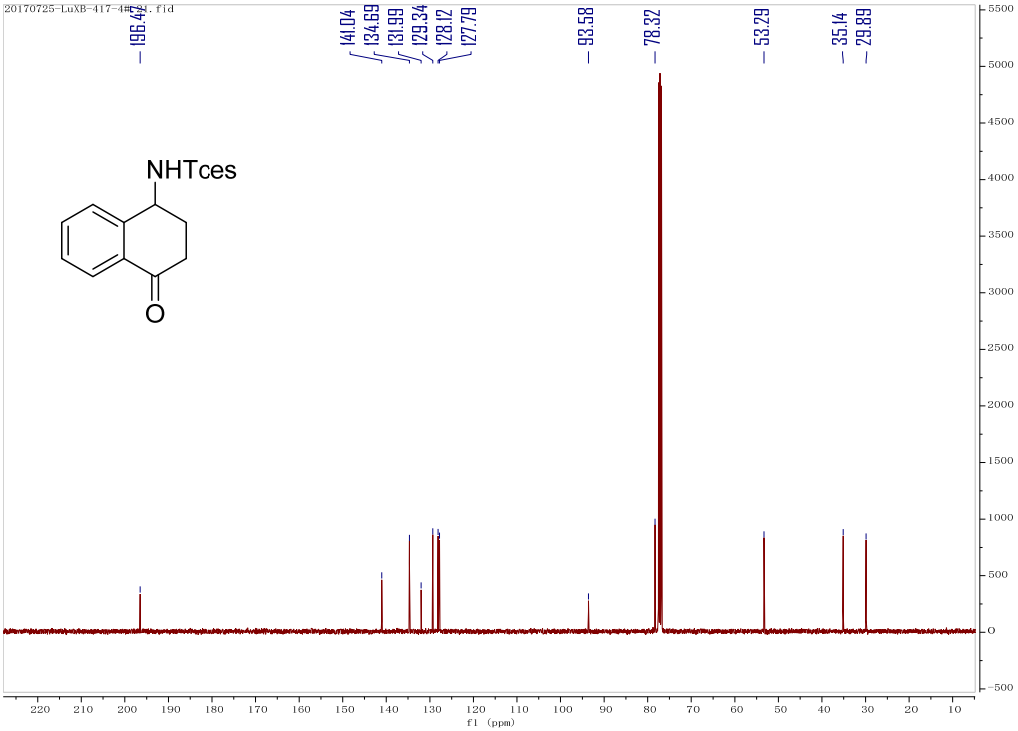

93.68
78.24
56.62
35.69
27.97
23.64
NHTces
f1 (ppm)

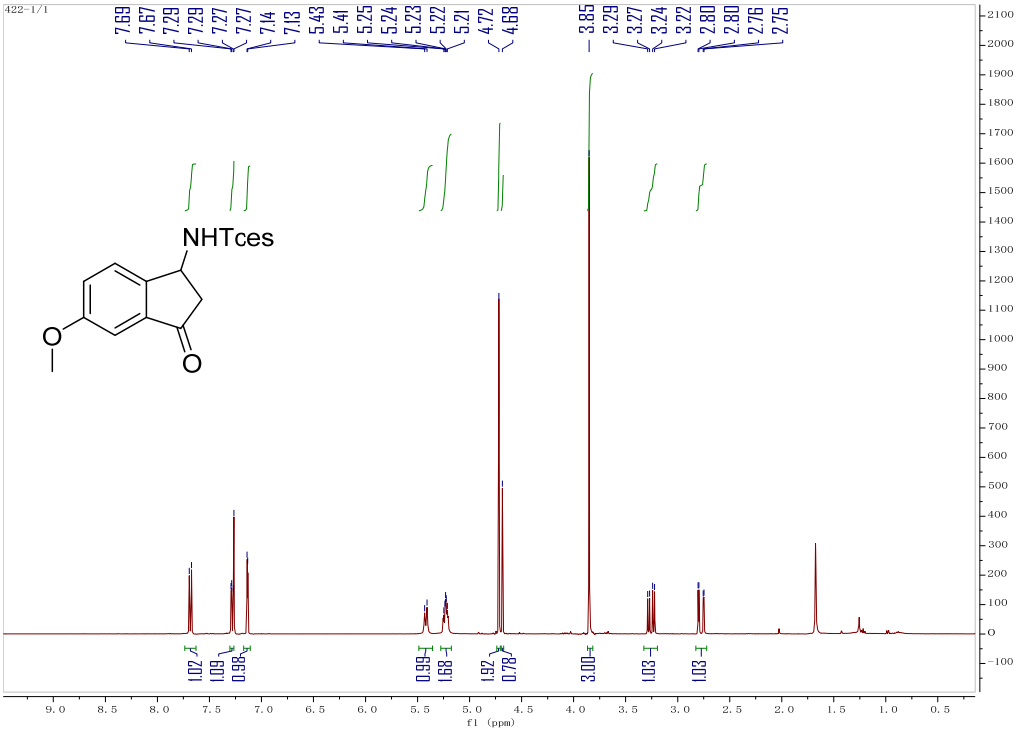

7.58
7.57
7.37
7.36
7.35
7.34
7.32
7.31
7.30
7.29
5.60
5.59
4.90
4.89
4.87
4.86
4.71
4.69
4.68
3.92
3.91
3.90
3.89
3.87
2.47
2.46
2.45
2.44
2.36
2.35
2.33
NHTces
N
COCF3
0.76
1.00
1.00
0.97
0.96
0.94
1.85
1.97
1.01
0.94
f1 (ppm)

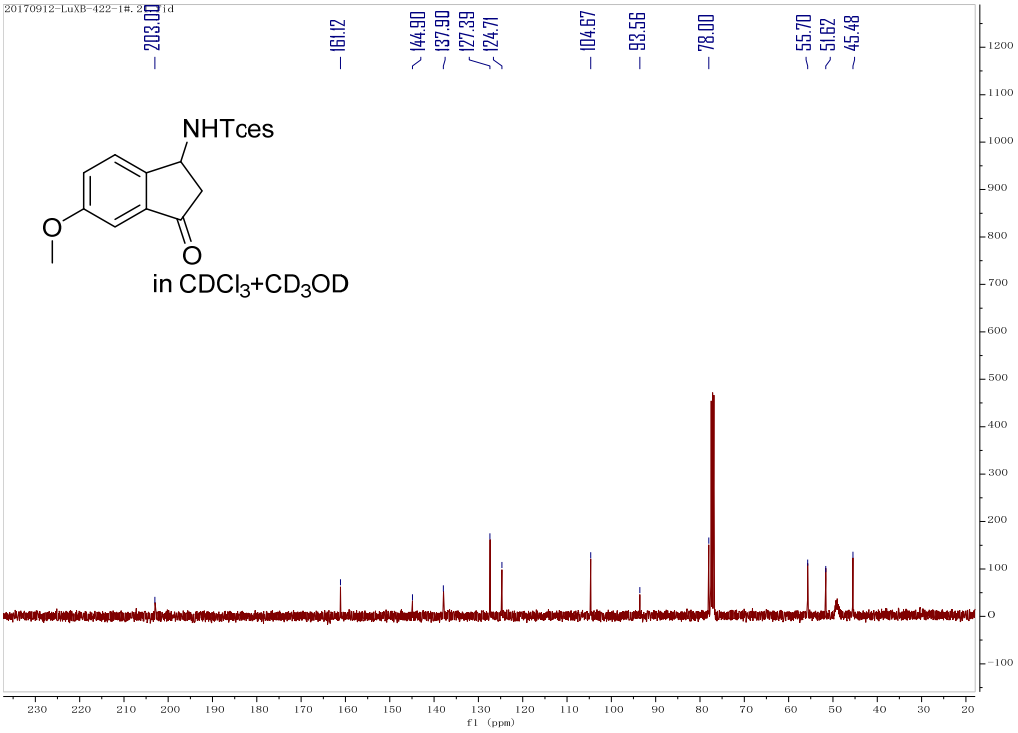

7.84
7.82
7.78
7.75
7.73
7.72
7.56
7.54
7.52
5.51
5.49
5.33
5.32
5.31
5.31
5.30
5.29
4.73
4.69
3.30
3.28
3.25
3.23
2.81
2.80
2.76
2.75
NHTces
O
0.93
1.81
0.95
0.89
1.00
1.00
0.94
1.01
1.00
f1 (ppm)

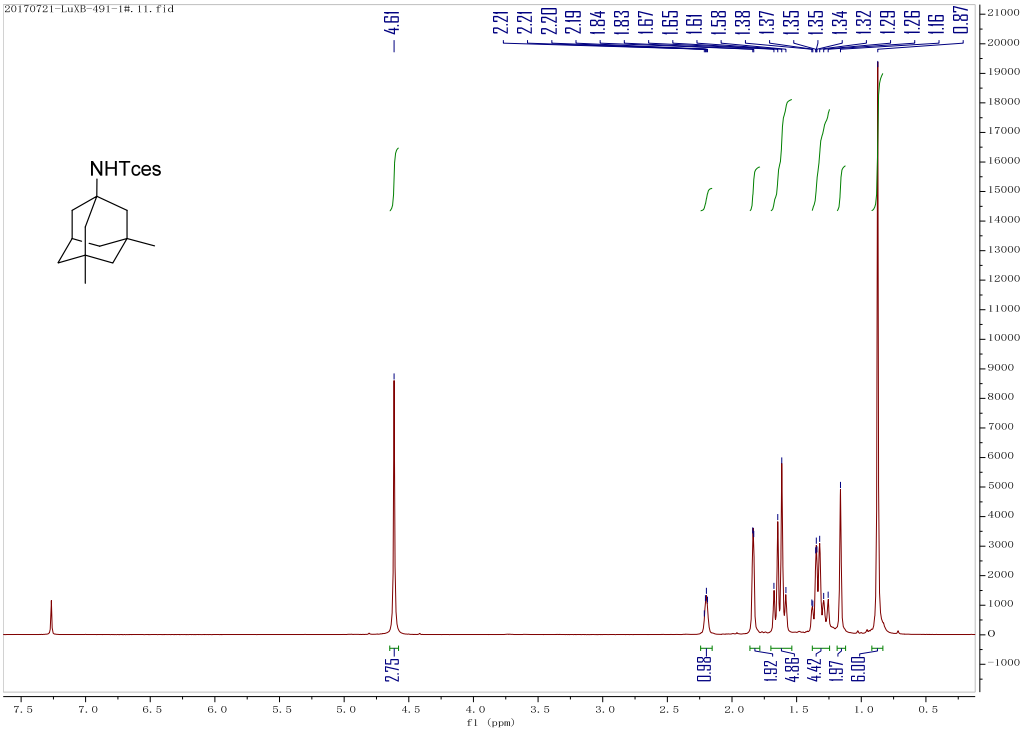

203.19
152.33
136.37
135.73
129.72
126.52
123.34
93.55
78.01
52.02
44.83
NHTces
O
in CDCl3+CD3OH
f1 (ppm)

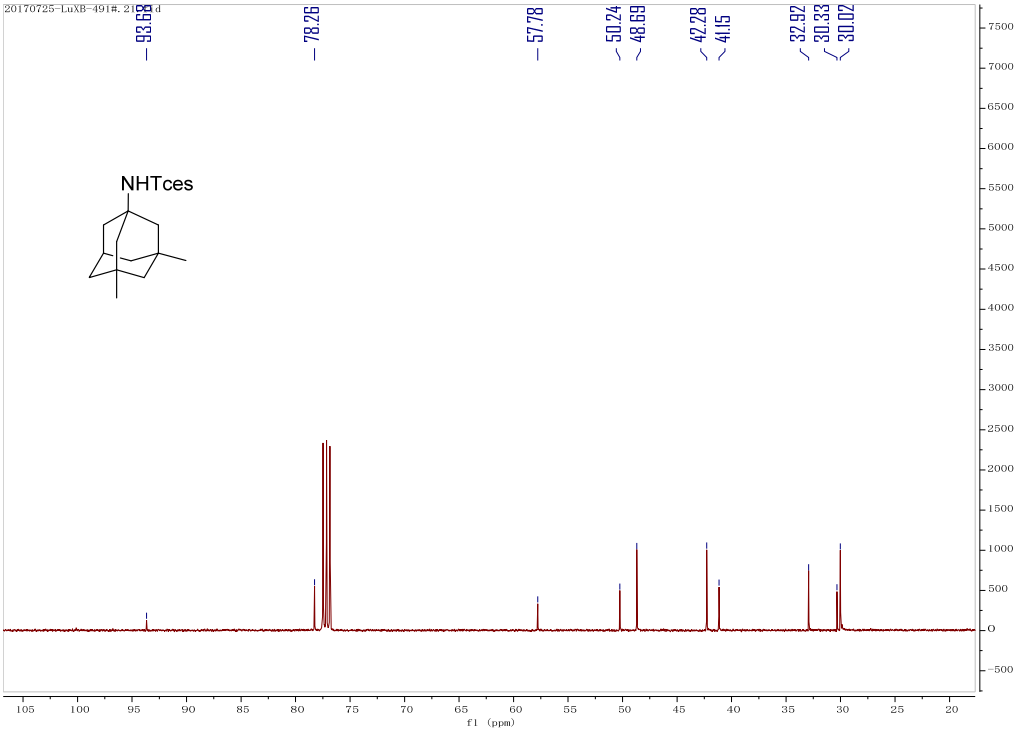

8.02
8.02
8.02
8.00
8.00
7.68
7.67
7.66
7.66
7.65
7.64
7.49
7.49
7.49
7.47
7.47
7.47
7.47
7.45
7.45
5.54
5.52
4.99
4.98
4.73
4.72
4.70
2.89
2.88
2.87
2.86
2.72
2.71
2.69
2.57
2.56
2.54
2.53
2.41
2.39
NHTces
O
1.00
2.05
1.04
1.00
1.03
0.98
1.12
1.05
1.05
1.05
1.07
f1 (ppm)

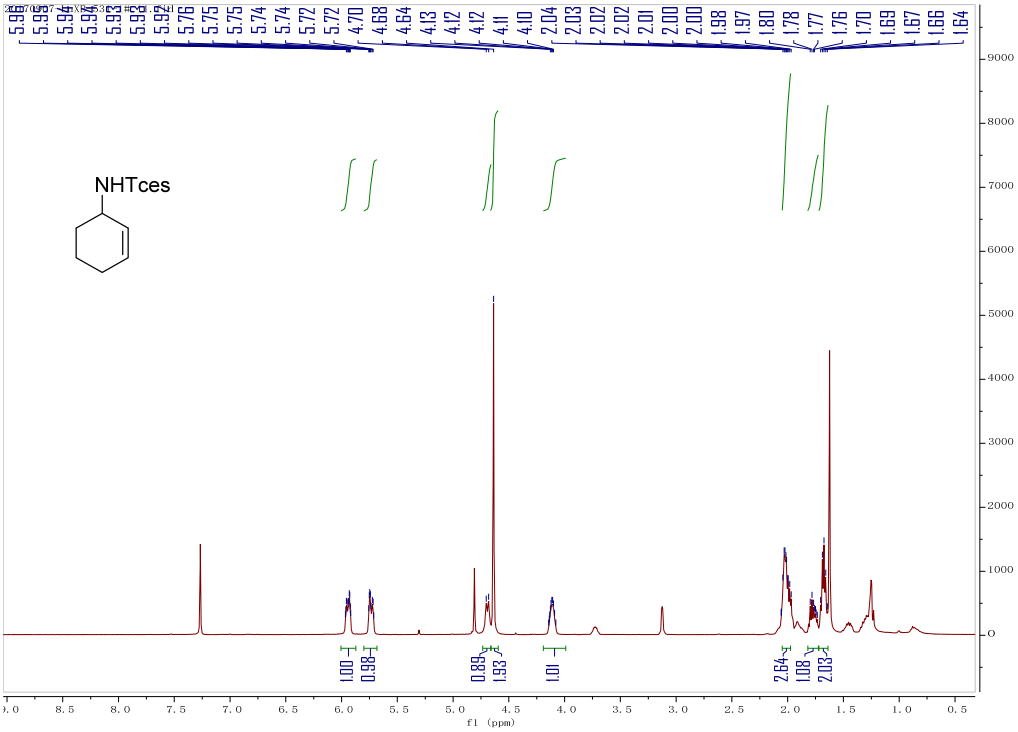

20170725-LuXB-417-4B-2.fid
196.42
141.04
134.69
131.99
129.34
128.12
127.79
93.58
78.32
53.29
35.14
29.89
NHTces
O
f1 (ppm)

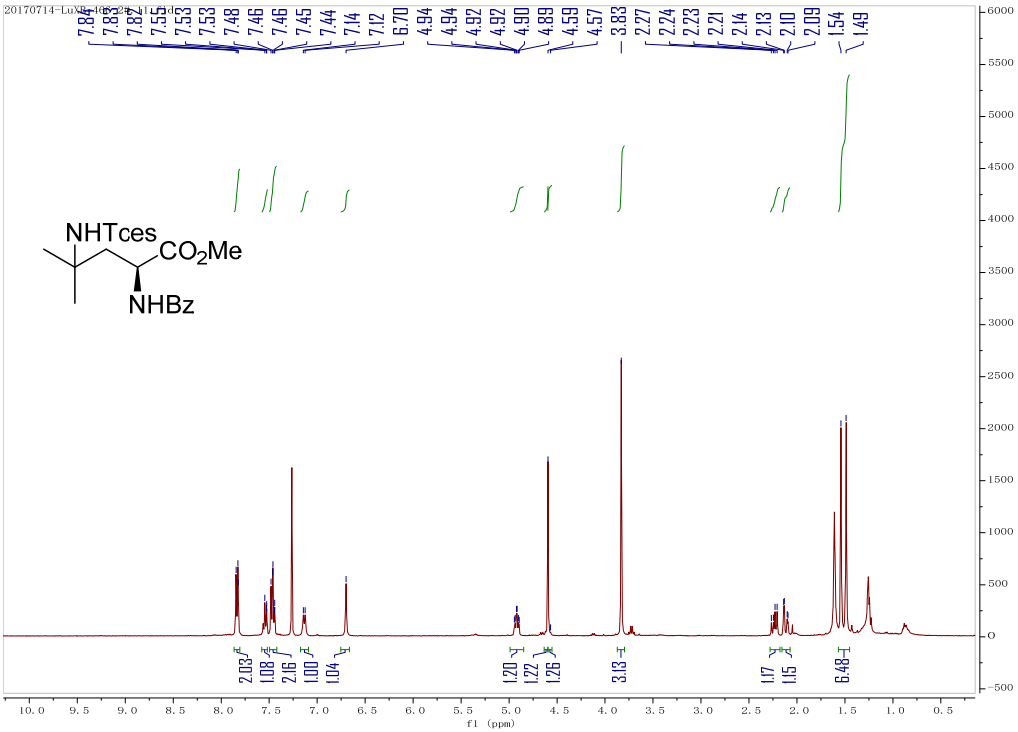

422-1/1
7.69
7.67
7.29
7.29
7.27
7.27
7.14
7.13
5.43
5.41
5.25
5.24
5.23
5.22
5.21
4.72
4.68
3.85
3.29
3.27
3.24
3.22
2.80
2.80
2.76
2.75
NHTces
O
O
1.02
1.09
0.98
0.99
1.68
1.92
0.78
3.00
1.03
1.03
f1 (ppm)

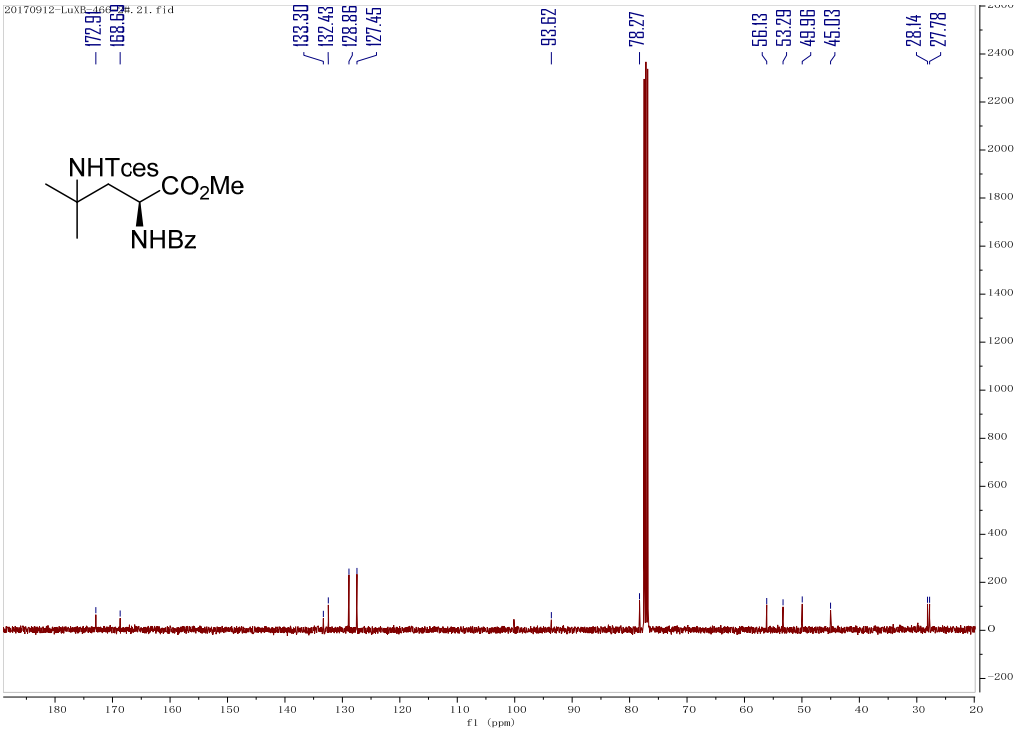

20170912-LuXB-422-1#.2.fid
203.00
161.12
144.90
137.90
127.39
124.71
104.67
93.56
78.00
55.70
51.62
45.48
NHTces
O
O
in CDCl3+CD3OD
f1 (ppm)

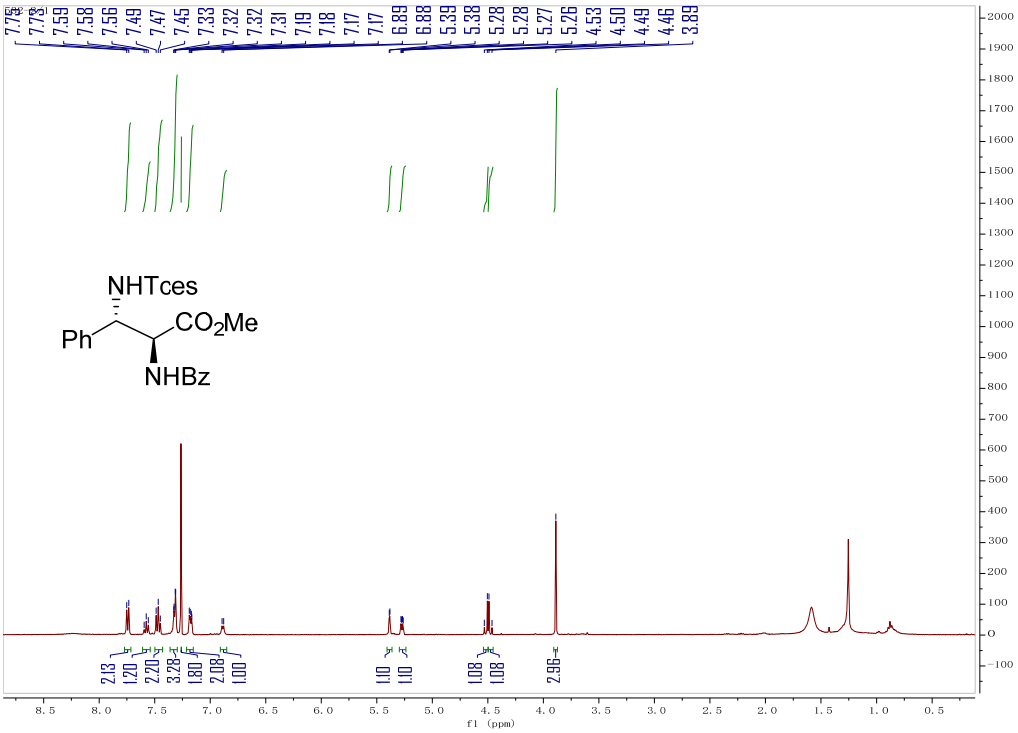

NHTces

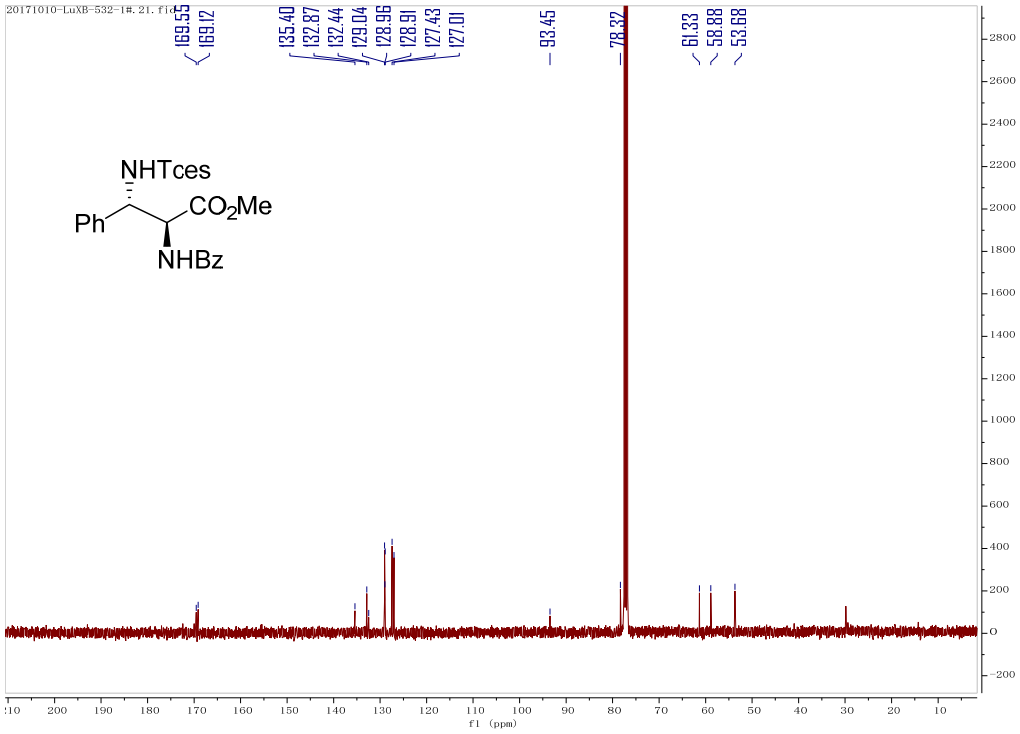

NHTces

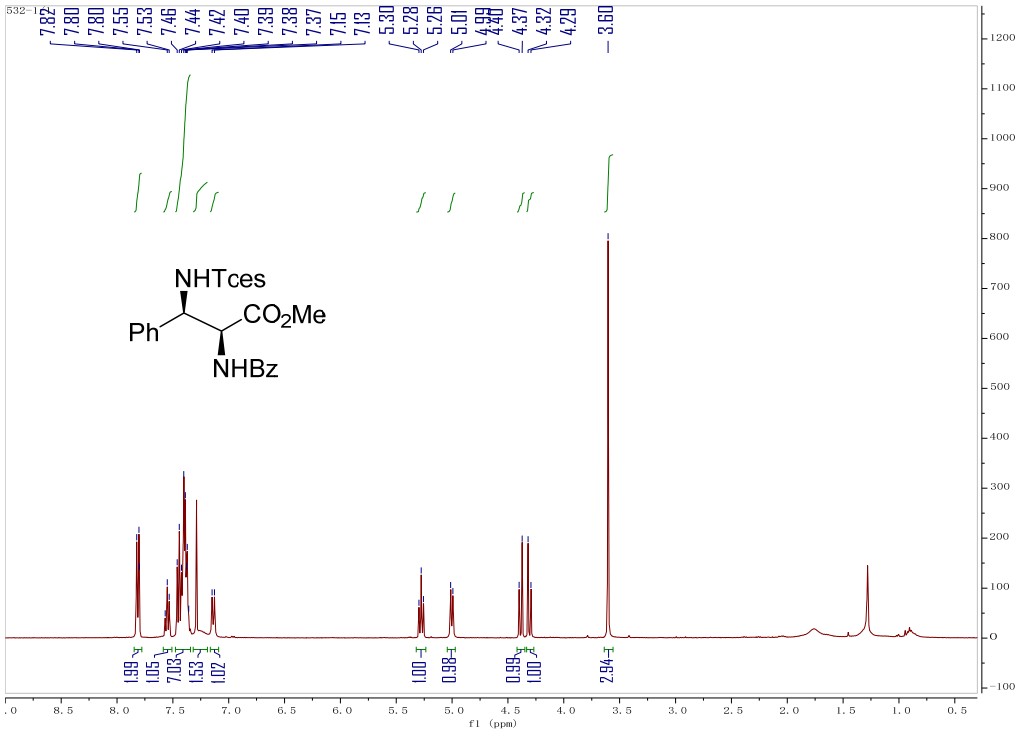

NHTces
f1 (ppm)

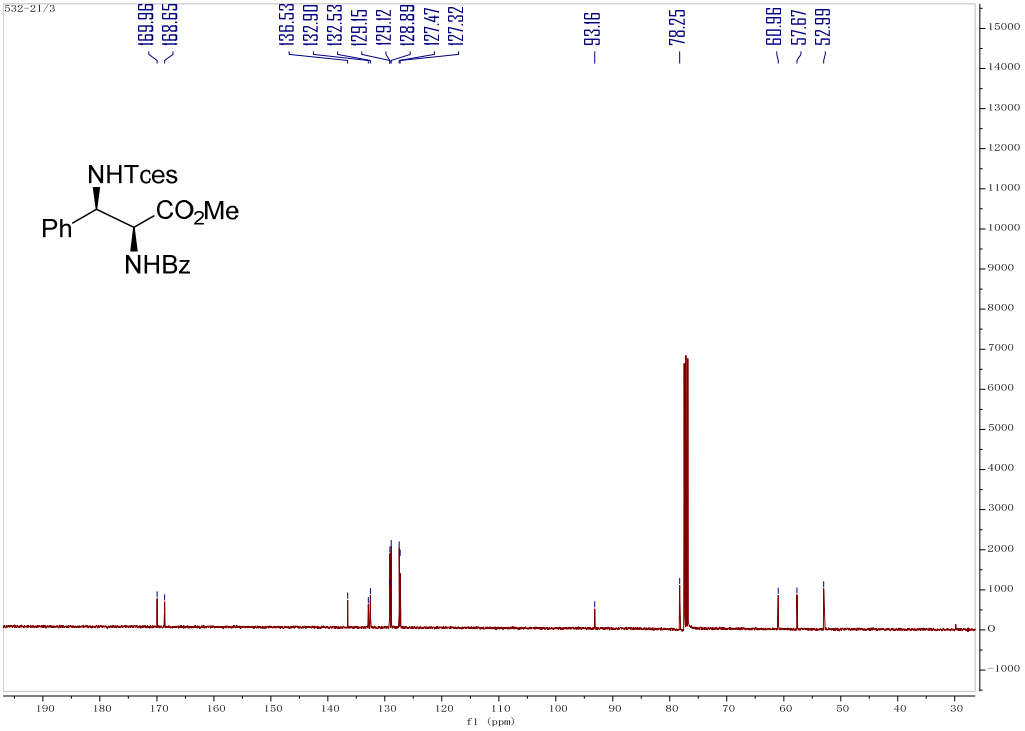

NHTces
CO2Me
NHBz
f1 (ppm)

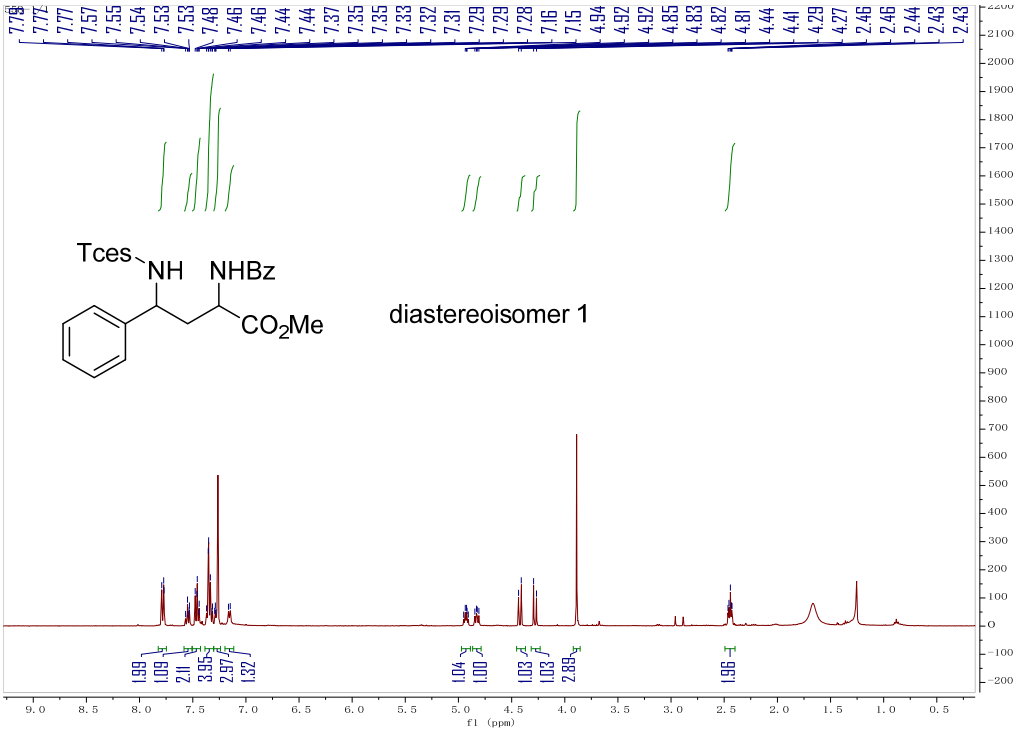

20170912-LuXB-166-28.21.fid
172.91
168.69
133.30
132.43
128.86
127.45
93.62
78.27
56.13
53.29
49.96
45.03
28.14
27.78
NHTces
CO2Me
NHBz
f1 (ppm)

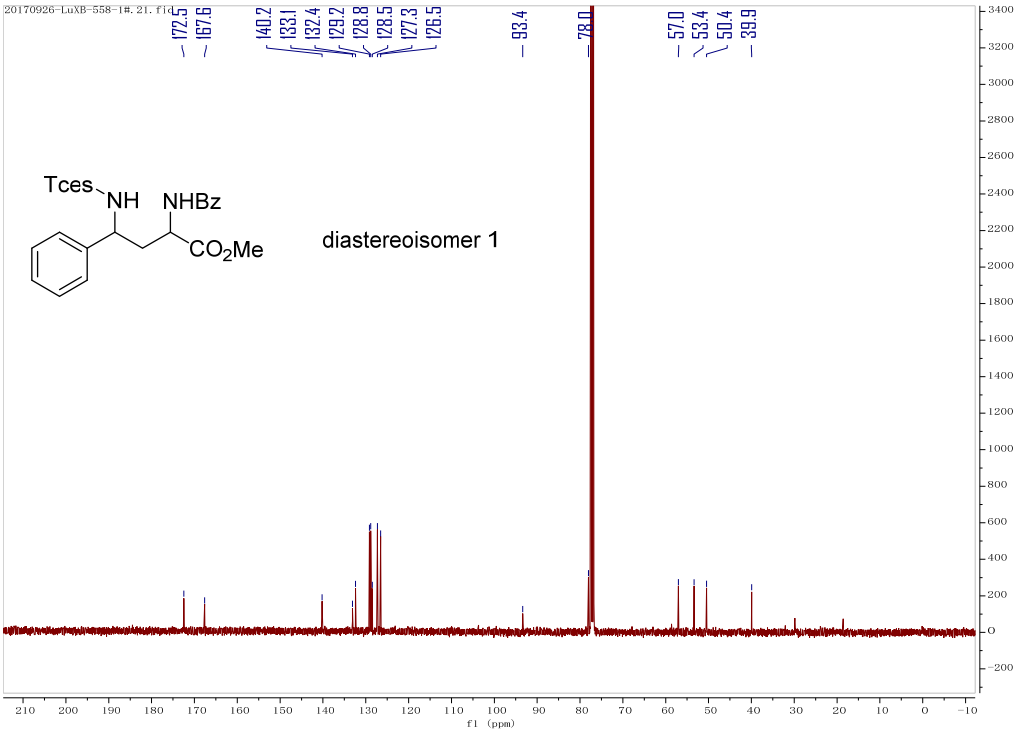

7.76
7.73
7.59
7.58
7.56
7.49
7.47
7.45
7.33
7.32
7.32
7.31
7.19
7.18
7.17
7.17
6.89
6.88
5.39
5.38
5.28
5.28
5.27
5.26
4.53
4.50
4.49
4.46
3.89
NHTces
CO2Me
Ph
NHBz
2.13
1.20
2.20
3.28
1.80
2.08
1.00
1.10
1.10
1.08
1.08
2.96
f1 (ppm)

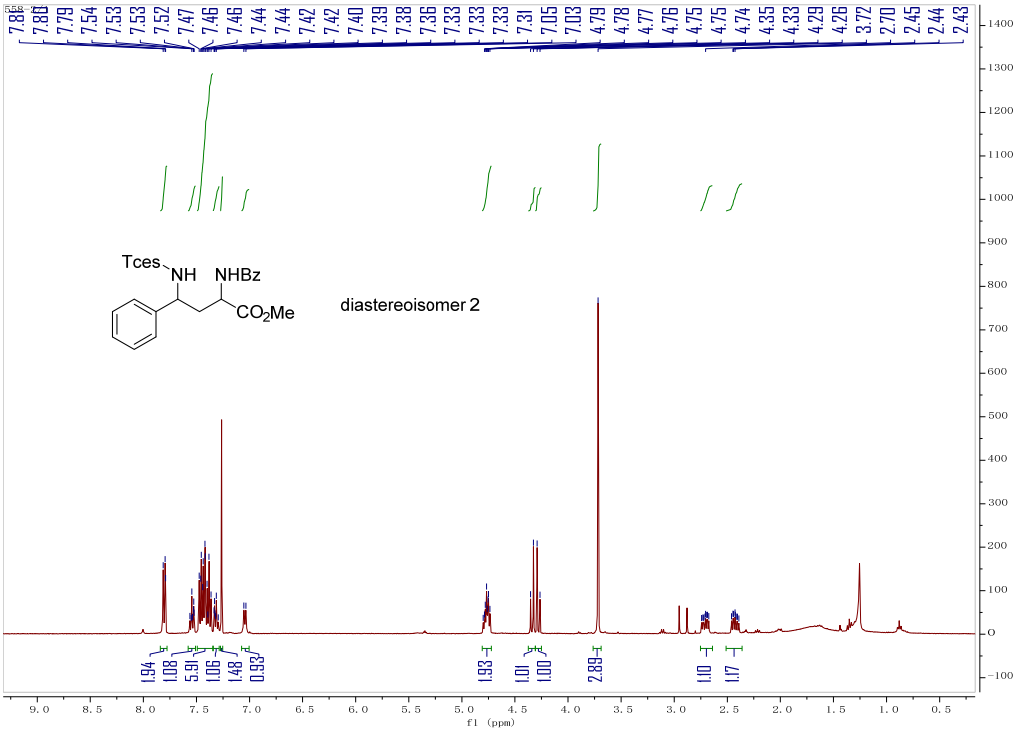

20171010-LuXB-532-1#.21.fid
169.55
169.12
135.40
132.87
132.44
129.04
128.96
128.91
127.43
127.01
93.45
78.32
61.33
58.88
53.68
NHTces
Ph
CO2Me
NHBz
f1 (ppm)

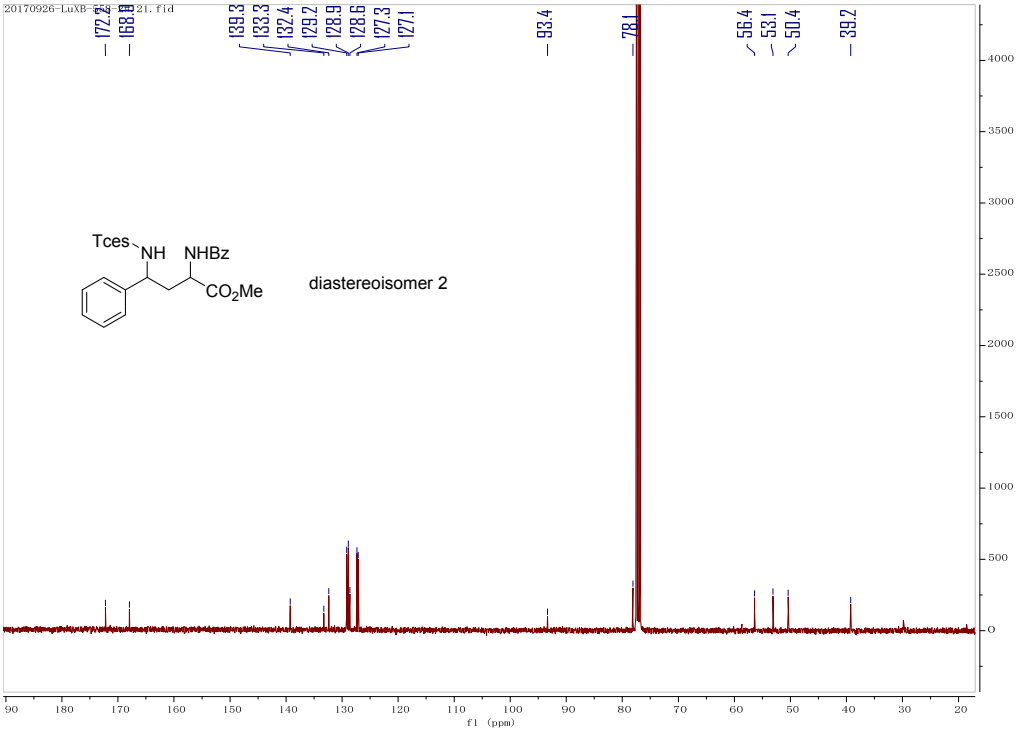

532-1
7.82
7.80
7.80
7.55
7.53
7.46
7.44
7.42
7.40
7.39
7.38
7.37
7.15
7.13
5.30
5.28
5.26
5.01
4.99
4.40
4.37
4.32
4.29
3.60
NHTces
Ph
CO2Me
NHBz
1.99
1.05
7.03
1.53
1.02
1.00
0.98
0.99
1.00
2.94
f1 (ppm)

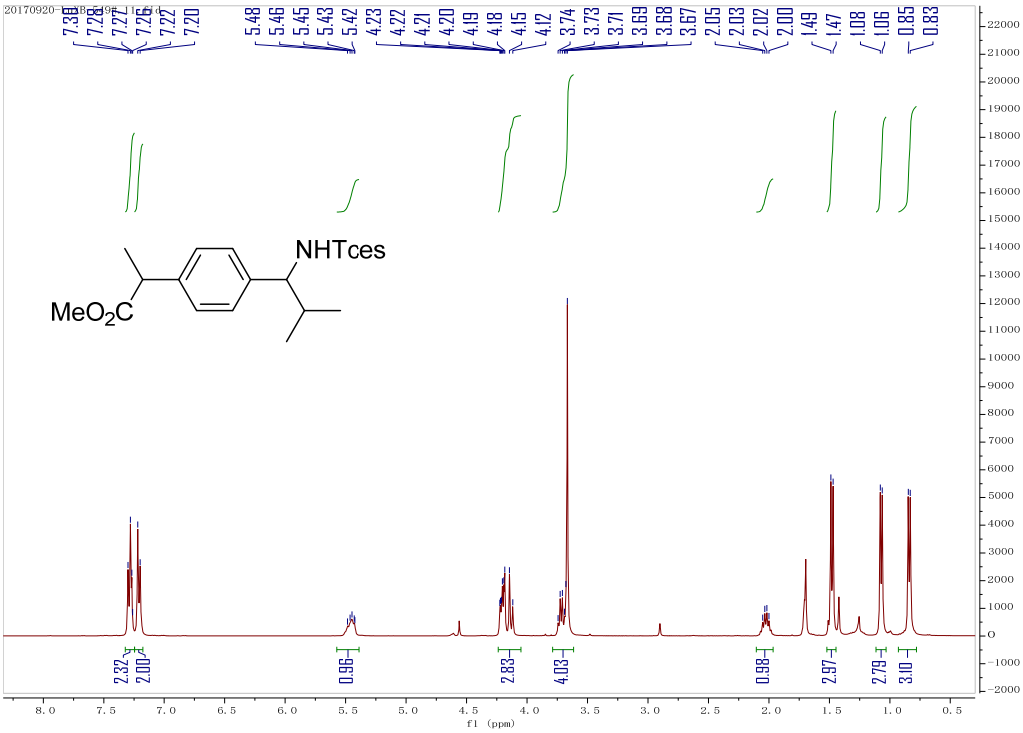

532-21/3
169.96
168.85
136.53
132.90
132.53
129.15
129.12
128.89
127.47
127.32
93.16
78.25
60.96
57.67
52.99
NHTces
Ph
CO2Me
NHBz
f1 (ppm)

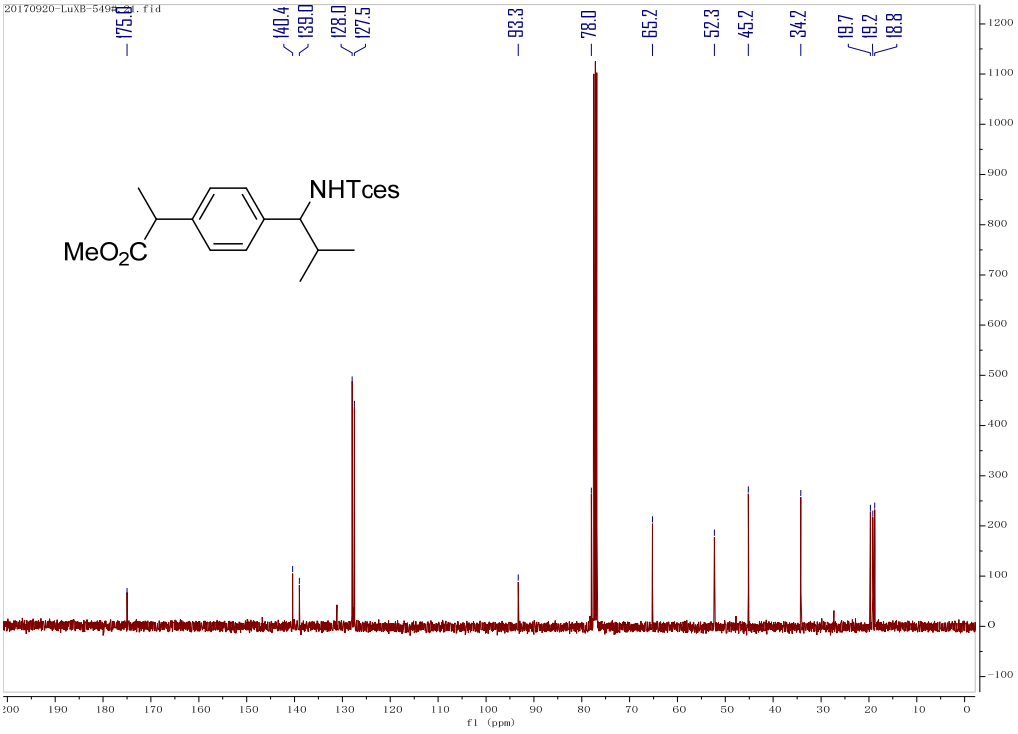

7.78
7.77
7.77
7.57
7.55
7.54
7.53
7.53
7.48
7.46
7.46
7.44
7.44
7.37
7.35
7.35
7.33
7.32
7.31
7.29
7.29
7.28
7.16
7.15
4.94
4.92
4.92
4.85
4.83
4.82
4.81
4.44
4.41
4.29
4.27
2.46
2.46
2.44
2.43
2.43
Tces
NH
NHBz
CO2Me
diastereoisomer 1
1.99
1.09
2.11
3.95
2.97
1.32
1.04
1.00
1.03
1.03
2.89
1.96
f1 (ppm)


20170926-LuXB-558-1#.21.fid
172.5
167.6
140.2
133.1
132.4
129.2
128.8
128.5
127.3
126.5
93.4
78.0
57.0
53.4
50.4
39.9
Tces
NH
NHBz
CO2Me
diastereoisomer 1
f1 (ppm)


7.81
7.80
7.79
7.54
7.53
7.53
7.52
7.47
7.46
7.46
7.44
7.44
7.42
7.42
7.40
7.39
7.38
7.36
7.33
7.33
7.33
7.31
7.05
7.03
4.79
4.78
4.77
4.76
4.75
4.75
4.74
4.35
4.33
4.29
4.26
3.72
2.70
2.45
2.44
2.43
Tces
NH
NHBz
CO2Me
diastereoisomer 2
1.94
1.08
5.91
1.06
1.48
0.93
1.93
1.01
1.00
2.89
1.10
1.17
f1 (ppm)


172.2
168.8
139.3
133.3
132.4
129.2
128.9
128.6
127.3
127.1
93.4
78.1
56.4
53.1
50.4
39.2
Tces
NH
NHBz
CO2Me
diastereoisomer 2
f1 (ppm)


7.36
7.28
7.27
7.26
7.22
7.20
5.48
5.46
5.45
5.43
5.42
4.23
4.22
4.21
4.20
4.19
4.18
4.15
4.12
3.74
3.73
3.71
3.69
3.68
3.67
2.05
2.03
2.02
2.00
1.49
1.47
1.08
1.06
0.85
0.83
NHTces
MeO2C
2.32
2.00
0.96
2.83
4.03
0.98
2.97
2.79
3.10
f1 (ppm)


20170920-LuXB-5498-1D.fid
175.6
140.4
139.0
128.0
127.5
93.3
78.0
65.2
52.3
45.2
34.2
19.7
19.2
18.8
NHTces
MeO2C
f1 (ppm)