Anti-Markovnikov Rearrangement in Sulfur Mediated Allyllic C-H Amination of Olefins

Zhong Zhang, Hongguang Du*, Jiaxi Xu* and Pingfan Li*

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, China

Email: dhg@mail.buct.edu.cn, jxxu@mail.buct.edu.cn, lipf@mail.buct.edu.cn

Supporting Information

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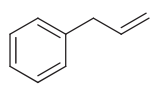
I. General Information

Unless otherwise noted, all materials were purchased from commercial suppliers. Dichloromethane was refluxed over CaH_2, and freshly distilled prior to use. Tetrahydrofuran (THF) was refluxed with sodium/benzophenone, and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200-300 mesh) from Branch of Qingdao Haiyang Chemical. Petroleum ether used for column chromatography were 60-90 ^{o}C fraction, and the removal of residue solvent was accomplished under rotovap with repeated azeotrope with chloroform, and then evaporation under vacuum (< 1 mmHg pressure). Reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates from Yantai Chemical Industry Research Institute. The plates were visualized under UV light, as well as other TLC stains (phosphomolybdic acid: 10% in ethanol; potassium permanganate: 1% in water; iodine: 10 g iodine absorbed on 30g silica gel). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer, usually in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) were reported in parts per million (ppm). The IR spectra (KBr pellets, ν [cm^{-1}]) were taken on a Nicolet 5700 FTIR spectrometer. HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. The thin layer chromatography silica gel preparative plates were brought from Anhui LiangChen Silicon Material Co. Ltd.

II. Compounds Chart



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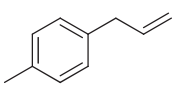

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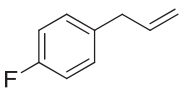

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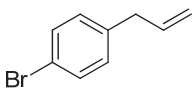

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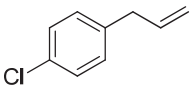

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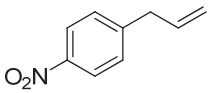

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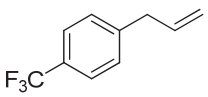

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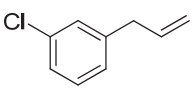

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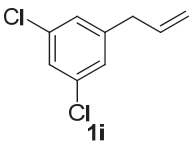

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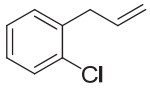

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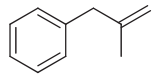

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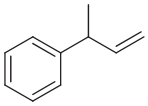

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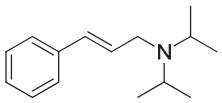
[a] commerically available, used as received



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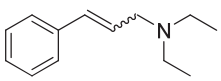

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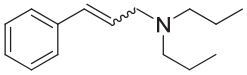

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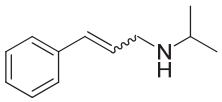

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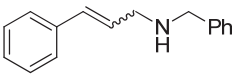

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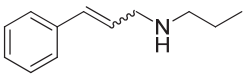

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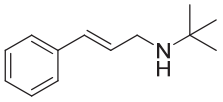

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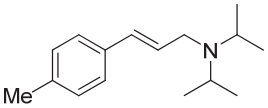

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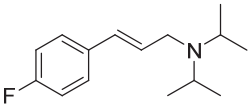

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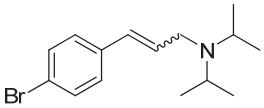

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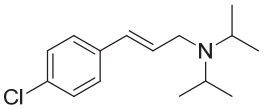

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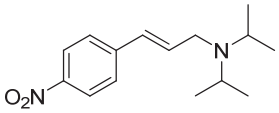

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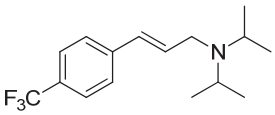

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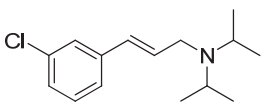

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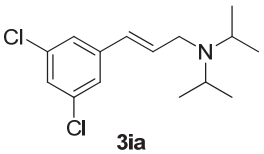

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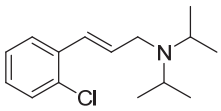

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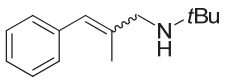

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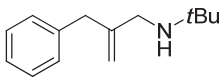

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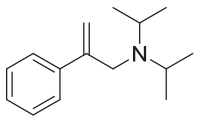

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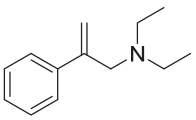

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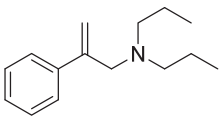

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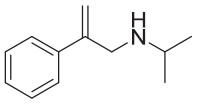

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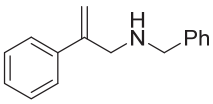

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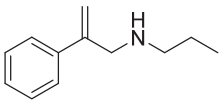

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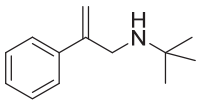

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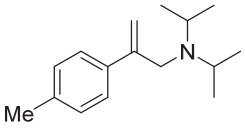

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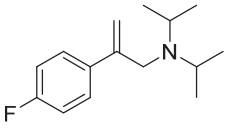

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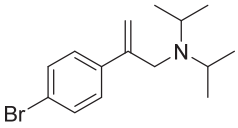

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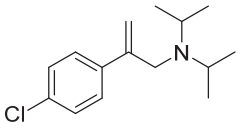

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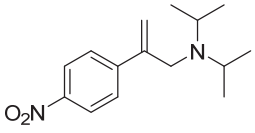

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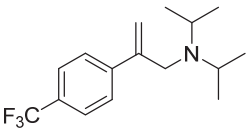

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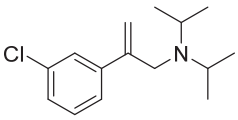

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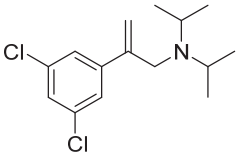

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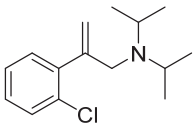

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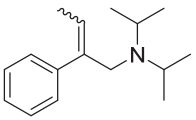

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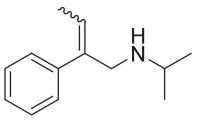

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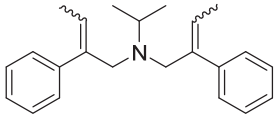

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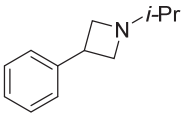

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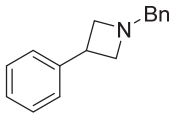

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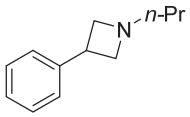

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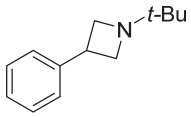


5ag

III. Experimental Procedures and Characterization Data

Preparation of alkene substrates

(1) General Procedure 1 for preparation of alkenes **1b – 1e**, **1g – 1h**: [1]

Under a N_2 atmosphere, a dry 100 mL three-necked flask, fitted with a reflux condenser, and pressure-equalizing dropping funnel, was charged with a magnetic stirring bar and magnesium turnings (1.2 equiv.). Aryl bromide (1 equiv.) and an iodide grain were dissolved in Et_2O (1.6 M, for **1b**, **1d**) or THF (1.6 M, for **1c**, **1e**, **1g-1h**) in the funnel. Part of the solution (~2 mL) was added to the flask and stirred. After the color of the mixture suddenly faded, the rest solution was added dropwise *via* the dropping funnel. Then the mixture was refluxed for 2h. The reaction solution was decanted into another dry flask and allylbromide (1.5 equiv.) was added at ice bath temperature. When the mixture had reached room temperature, it was carefully hydrolyzed with aqueous saturated NH_4Cl solution. The aqueous phase was removed and extracted with Et_2O. The combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was applied to flash column chromatography afford pure allyl arene.

[1] Lin, S.; Song, C.-X.; Cai, G.-X.; Wang, W.-H.; Shi, Z.-J. *J. Am. Chem. Soc*. **2008**, *130*, 12901.

(2) General Procedure 2 for preparation of alkenes **1f** and **1i**: [2]

The arylamine (3.0 mmol) was added during 20 min to a solution of *tert*-butyl nitrite (535 μL, 4.5 mmol) and allyl bromide (1.9 mL, 22.5 mmol) in dry and degassed CH_3CN (3 mL) under argon atmosphere while maintaining the specified temperature (**1f** in 50 ºC and **1i** in 30 ºC). At the end of the addition of arylamine, extra *tert*-butyl nitrite (180 μL, 1.5 mmol) was added. The reaction mixture was then stirred at a temperature specified in Table 1 for 1 h. The volatile material in the reaction mixture was then removed at reduced pressure. The crude product was applied to flash column chromatography afford pure allyl arene.

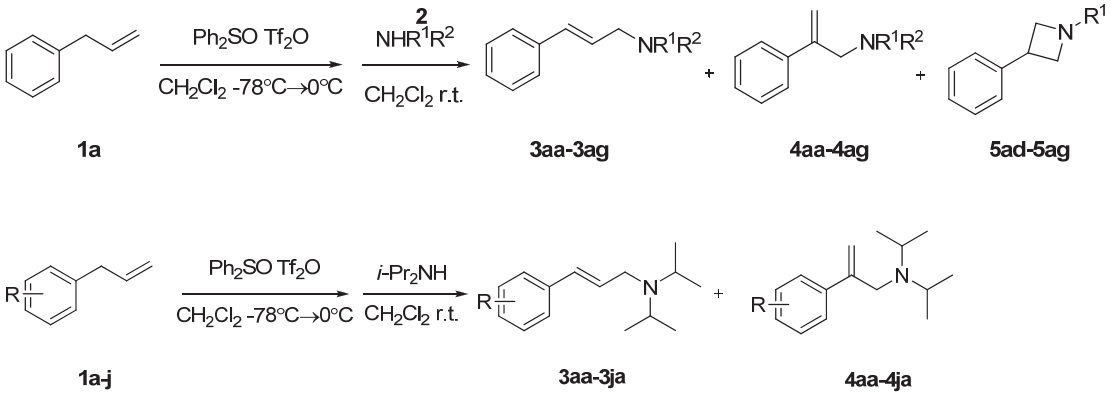
[2] Ek, F.; Axelsson, O.; Wistrand, L-G.; Frejd, T. *J. Org. Chem*. **2002**, *67*, 6376.

(3) General Procedure 3 for preparation of alkene **1j**: [3]

To a solution of tetrakis(triphenylphosphine)palladium (11.6 mg, 0.01 mmol), sodium carbonate (252 mg, 3 mmol), and *o*-methylphenylboronic acid (136 mg, 1 mmol) in a mixed solvent (dimethoxyethane/H_2O = 1/1, 5 mL), allyl bromide (260 mL, 3 mmol) was added. The resultant mixture was heated under reflux for 6 hours. The mixture was dissolved into dichloromethane (30 mL), and washed with water (20 mL). Furthermore, the aqueous layer was extracted with dichloromethane (30 mL x 3). The combined organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel) using petroleum ether.

[3] Nishiwaki, N.; Kamimura, R.; Shono, K.; Kawakami, T.; Nakayama, K.; Nishino, K.; Nakayama, T.; Takahashi, K.; Nakamura, A.; Hosokawa, T. *Tetrahedron Letters*. **2010**, *51*, 3590.

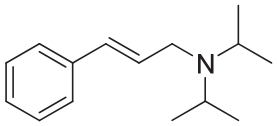
Sulfur mediated allylic amination reactions



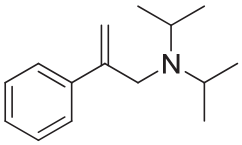
General Procedure

To a flame-dried Schlenk tube, 1 eq alkene (**1a**) (47 mg, 0.4 mmol) and 1.2 eq diphenyl sulfoxide (97 mg, 0.48 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -78 ºC (liquid nitrogen/ethyl acetate bath). 1.2 eq Tf_2O (81 µL, 0.48 mmol) were added dropwise, and then gradually warmed up to 0 ºC. And a solution of 5 eq diisopropylamine (**2a**) (202 mg, 2.0 mmol) in 1 mL CH_2Cl_2 was added. After 12 hours of reaction at room temperature, the solution was quenched by 10 mL 0.1 M aqueous solution of sodium hydroxide. The aqueous phase extracted with CH_2Cl_2 (10 mL×3). The combined organic phases were dried with Na_2SO_4 and concentrated under reduced pressure to give the crude amine products. Crude ^1H NMR was taken for determination of isomer ratio. The crude product was then purified by repeated flash column chromatography and preparative thin layer chromatography to give pure isolated pruducts.

Characterization data of new compounds



3aa



4aa

N,N-diisopropyl-2-phenylprop-2-en-1-amine (**4aa**) and (*E*)-*N,N*-diisopropyl-3-phenylprop-2-en-1-amine (**3aa**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/5/1, to give 61 mg product **4aa** as a yellow oil in 70% yield and 10 mg product **3aa** as a yellow oil in 12% yield.

3aa: R_f = 0.39 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 2H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.24 (dt, *J* = 15.6, 6.0 Hz, 1H), 3.29 (d, *J* = 6.0 Hz, 2H), 3.10 (hept, *J* = 6.8, 2H), 1.04 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 131.7, 130.0, 128.5, 127.0, 126.1, 48.4, 47.7, 20.7.

IR (KBr) ν (cm^{-1}) 2962, 2924, 1495, 1382, 1362, 1178, 965, 748, 691.

HRMS (ESI) calcd for $C_{15}H_{24}N^+$ $(M+H)^+$ *m/z*: 218.1903, found: 218.1908.

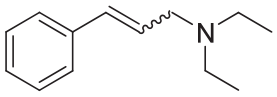
4aa: R_f = 0.38 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.32 – 7.22 (m, 3H), 5.42 (d, *J* = 2.0 Hz, 1H), 5.36 (d, *J* = 1.2 Hz, 1H), 3.43 (s, 2H), 3.07 (hept, *J* = 6.4 Hz, 2H), 0.99 (d, *J* = 6.4 Hz, 12H).

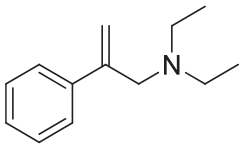
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.3, 127.9, 127.1, 126.4, 113.5, 49.3, 47.7, 20.6.

IR (KBr) ν (cm^{-1}) 2963, 2927, 1629, 1600, 1464, 1179, 1026, 902, 778, 700.

HRMS (ESI) calcd for $C_{15}H_{24}N^+$ $(M+H)^+$ *m/z*: 218.1903, found: 218.1903.



3ab



4ab

N,N-diethyl-2-phenylprop-2-en-1-amine (**4ab**) and (*E/Z*)-*N,N*-diethyl-3-phenylprop-2-en-1-amine (**3ab**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/5/1, to give 36 mg product **4ab** as a yellow oil in 47% yield and 12 mg product **3ab** as a yellow oil in 16% yield (*E/Z* = 95:5 according to the NMR).

3ab: R_f = 0.39 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 16.0, 6.8 Hz, 1H, major), 5.81 (dt, *J* = 12.4, 6.4 Hz, 1H, ninor),3.39 (dd, *J* = 6.4, 1.9 Hz, 2H, ninor), 3.26 (dd, *J* = 6.8, 1.2 Hz, 2H, major), 2.59 (q, *J* = 7.2 Hz, 4H), 1.07 (t, *J* = 7.2 Hz, 6H).

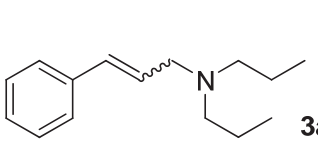
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 132.2, 128.5, 127.6, 127.3, 126.2, 55.6, 46.7, 11.7.

IR (KBr) ν (cm^{-1}) 2965, 2920, 1659, 1623, 1469, 1383, 965. 735, 691.

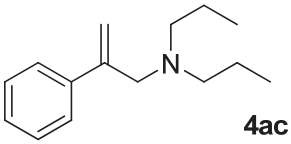
HRMS (ESI) calcd for $C_{13}H_{20}N^+$ $(M+H)^+$ *m/z*: 190.1590, found: 190.1591.

4ab: R_f = 0.20 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.33 – 7.24 (m, 3H), 5.41 (d, *J* = 1.6 Hz, 1H), 5.27 (d, *J* = 1.6 Hz, 1H), 3.41 (s, 2H), 2.53 (q, *J* = 7.0 Hz, 4H), 1.00 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 140.8, 128.1, 127.3, 126.4, 114.7, 57.7, 46.8, 11.5.
IR (KBr) ν (cm^{-1}) 2968, 2930, 1628, 1494, 1384, 1169, 1061, 904, 777, 705.
HRMS (ESI) calcd for $C_{13}H_{20}N^+$ $(M+H)^+$ *m/z*: 190.1590, found: 190.1593.



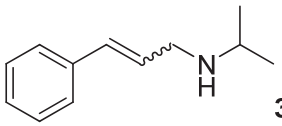
3ac



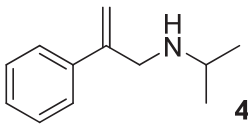
4ac

2-phenyl-*N,N*-dipropylprop-2-en-1-amine (**4ac**) and (*E/Z*)-3-phenyl-*N,N*-dipropylprop-2-en-1-amine (**3ac**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/5/1, to give 49 mg product **4ac** as a yellow oil in 56% yield and 26 mg product **3ac** as a yellow oil in 18% yield (*E/Z* = 95:5 according to the NMR).
3ac: R_f = 0.43 ($CHCl_3$/MeOH = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.6 Hz, 1H, major), 5.81 (dt, *J* = 15.7, 6.4 Hz, 1H, minor),3.38 (d, *J* = 6.4 Hz, 2H, minor),3.25 (d, *J* = 6.6 Hz, 2H, major), 2.43 (t, *J* = 7.6 Hz,4H), 1.50 (sext, *J* = 7.6 Hz, 4H), 0.88 (t, *J* = 7.6 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 131.9, 128.5, 128.1, 127.2, 126.2, 56.7, 56.0, 20.2, 12.0.
IR (KBr) ν (cm^{-1}) 2956, 2920, 1658, 1632, 1469, 1380, 1180, 1141, 1075, 967.
HRMS (ESI) calcd for $C_{15}H_{24}N^+$ $(M+H)^+$ *m/z*: 218.1903, found: 218.1896 .

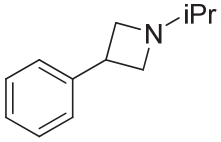
4ac: R_f = 0.22 (petroleum ether/ethyl acetate = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.40 (s, 1H), 5.27 (s, 1H), 3.39 (s, 2H), 2.38 (t, *J* = 7.2 Hz, 4H), 1.44 (sext, *J* = 7.2 Hz, 4H), 0.80 (t, *J* = 7.2 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 140.8, 128.0, 127.2, 126.5, 114.5, 59.2, 55.9, 20.0, 11.9.
IR (KBr) ν (cm^{-1}) 2958, 2925, 1725, 1510, 1407, 1384, 1295, 1259, 1180, 1075, 829.
HRMS (ESI) calcd for $C_{15}H_{24}N^+$ $(M+H)^+$ *m/z*: 218.1903, found: 218.1900.



3ad



4ad



5ad

N-isopropyl-2-phenylprop-2-en-1-amine (**4ad**), (*E/Z*)-*N*-isopropyl-3-phenylprop-2-en-1-amine (**3ad**) and 1-isopropyl-3-phenylazetidine (**5ad**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 10/1 to petroleum ether/ethyl acetate/triethylamine = 100/30/1, to give 35 mg product **4ad** as a yellow oil in 50% yield and 18 mg product **3ad**/**5ad** as a colorless oil in 26% mixture yield (NMR yield for **3ad** is 8%, its *E/Z* ratio is 92:8, NMR yield for **5ad** is 18%). Then the mixture was purified by preparative TLC. Only the pure **3ad** were got and **5ad** were mixed with **3ad**.
3ad: R_f = 0.27 ($CHCl_3$/MeOH = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.32 (dt, *J* = 12.4, 6.4 Hz, 1H, major), 5.77 (dt, *J* = 12.4, 6.4 Hz, 1H,

minor), 3.55 (d, J = 6.4 Hz, 2H, minor), 3.43 (d, J = 6.4 Hz, 2H, major), 2.91 (hept, J = 6.2 Hz, 1H), 1.11 (d, J = 6.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 131.4, 128.5, 128.3, 127.4, 126.3, 49.3, 48.2, 22.7.

IR (KBr) ν (cm^{-1}) 3360, 2956, 2921, 1660, 1632, 1470, 1383, 1138, 1074, 748.

HRMS (ESI) calcd for $C_{12}H_{18}N^+$ $(M+H)^+$ *m/z*: 176.1434, found: 176.1431.

4ad: R_f = 0.27 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.29 (d, J = 6.8 Hz, 1H), 5.39 (s, 1H), 5.39 (s, 1H), 5.24 (d, J = 0.8 Hz, 1H), 3.66 (s, 2H), 2.85 (hept, J = 6.2 Hz, 1H), 1.60 (br, 1H), 1.06 (d, J = 6.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 140.0, 128.5, 127.6, 126.2, 113.2, 51.0, 47. 9, 22.8.

IR (KBr) ν (cm^{-1}) 3354, 2957, 2921, 1659, 1632, 1469, 1383, 1180, 1141, 1075, 901, 777, 703, 617.

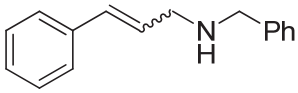
HRMS (ESI) calcd for $C_{12}H_{18}N^+$ $(M+H)^+$ *m/z*: 176.1434, found: 176.1434.

5ad: R_f = 0.27 ($CHCl_3$/MeOH = 10:1). (Mixed with **3ad**)

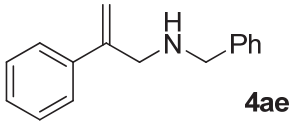
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.19 (m, 5H), 3.81 – 3.77 (m, 2H), 3.70 (quint, J = 15.6 Hz, 1H), 3.10 – 3.06(m, 2H), 2.36 (hept, J = 6.2 Hz, 1H), 0.97 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) mixture δ 137.1, 131.2, 128.7, 128.5, 128.3, 128.2, 127.3, 127.0, 126.3, 126.2, 60.1, 58.6, 49.4, 48.1, 34.4, 23.5, 22.8, 19.5.

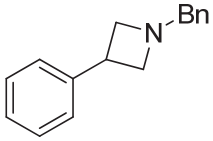
HRMS (ESI) calcd for $C_{12}H_{18}N^+$ $(M+H)^+$ *m/z*: 176.1434, mixture found: 176.1432 .



3ae



4ae



5ae

N-benzyl-2-phenylprop-2-en-1-amine (**4ae**), (*E*)-*N*-benzyl-3-phenylprop-2-en-1-amine (**3ae**) and 1-benzyl-3-phenylazetidine (**5ae**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 10/1 to petroleum ether/ethyl acetate/triethylamine = 100/30/1, to give product **4ae**/**5ae** mixture and 8 mg product **3ae** as a yellow oil in 9% yield. The mixture of **4ae**/**5ae** was purified by preparative TLC to give 23 mg **4ae** as a yellow oil in 26% yield and 29 mg **5ae** as a yellow oil in 32% yield (*E/Z* = 92:8 according to the NMR).

3ae: R_f = 0.34 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 10H), 6.55 (d, J = 15.9 Hz, 1H), 6.32 (dt, J = 15.9, 6.0 Hz, 1H, major),5.81 (dt, J = 12.4, 6.6 Hz, 1H, minor), 3.85 (s, 2H, major), 3.79 (s, 1H, minor), 3.57 (dd, J = 6.6, 1.4 Hz, 1H, minor), 3.45 (d, J = 6.0 Hz, 2H, major), 2.19 (br, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 137.1, 131.7, 128.53, 128.46, 128.3, 128.1, 127.4, 127.1, 126.3, 53.2, 51.1.

IR (KBr) ν (cm^{-1}) 3356, 2921, 2850, 1659, 1494, 1452, 1383, 1141, 966, 736, 696.

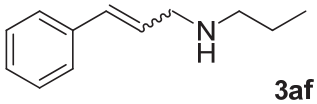
HRMS (ESI) calcd for $C_{16}H_{18}N^+$ $(M+H)^+$ *m/z*: 224.1434, found: 224.1438.

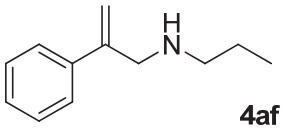
4ae: R_f = 0.34 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.22 (m, 8H), 5.42 (s, 1H), 5.26 (d, J = 1.2 Hz, 1H), 3.80 (s, 2H), 3.67 (s, 2H), 1.55 (br, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 140.2, 139.9, 128.4, 128.3, 128.2, 127.6, 126.9, 126.2, 113.5, 53.0, 52.7.
IR (KBr) ν (cm^{-1}) 3359, 2953, 2920, 1632, 1494, 1453, 1180, 1027, 903, 778, 698.
HRMS (ESI) calcd for $C_{16}H_{18}N^+$ $(M+H)^+$ *m/z*: 224.1434, found: 224.1433.

5ae: R_f = 0.34 ($CHCl_3$/MeOH = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32– 7.19 (m, 10H), 3.78 – 3.72 (m, 3H), 3.67 (s, 2H), 3.23 – 3.16 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.2, 128.5, 128.4, 128.3, 126.98, 126.93, 126.3, 63.8, 61.5, 35.8.
IR (KBr) ν (cm^{-1}) 2957, 2920, 1725, 1462, 1408, 1383, 1259, 1180, 1074, 806.
HRMS (ESI) calcd for $C_{16}H_{18}N^+$ $(M+H)^+$ *m/z*: 224.1434, found: 224.1437.


3af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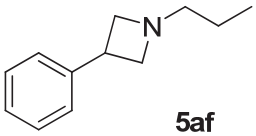
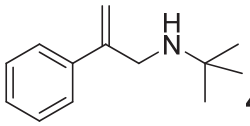

5af

2-phenyl-N-propylprop-2-en-1-amine (**4af**), (*E/Z*)-3-phenyl-N-propylprop-2-en-1-amine (**3af**) and 3-phenyl-1-propylazetidine (**5af**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 10/1 to petroleum ether/ethyl acetate/triethylamine = 100/30/1, to give 35 mg product **4af** as a yellow oil in 50% yield and mixture **3af**/**5af**. The mixture of **3af**/**5af** was purified by preparative TLC to give 6 mg **3af** as a yellow oil in 9% yield (*E/Z* = 93:7 according to the NMR) and 25 mg **5af** as a yellow oil in 35% yield.
3af: R_f = 0.29 ($CHCl_3$/MeOH = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.4 Hz, 1H, major), 5.78 (dt, *J* = 12.0, 6.4 Hz, 1H, minor), 3.55 (d, *J* = 6.4 Hz, 2H, minor), 3.43 (d, *J* = 6.4 Hz, 2H, major), 2.64 (t, *J* = 7.2 Hz, 2H, major), 2.59 (t, *J* = 7.2 Hz, 2H, minor), 1.55 (sext, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 131.6, 128.5, 128.0, 127.4, 126.3, 51.7, 51.2, 23.0, 11.8.
IR (KBr) ν (cm^{-1}) 3345, 2956, 2853, 1460, 1377, 1260, 1029, 801, 693.
HRMS (ESI) calcd for $C_{12}H_{18}N^+$ $(M+H)^+$ *m/z*: 176.1434, found: 176.1429.

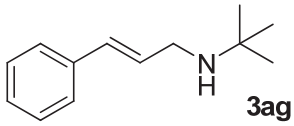
4af: R_f = 0.29 ($CHCl_3$/MeOH = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 – 7.27 (m, 3H), 5.40 (s, 1H), 5.25 (s, 1H), 3.68 (s, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 1.50 (sext, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 139.9, 128.4, 127.6, 126.2, 113.3, 53.3, 51.0, 23.0, 11.7.
IR (KBr) ν (cm^{-1}) 3357, 2957, 2928, 1723, 1632, 1460, 1295, 1075, 1046.
HRMS (ESI) calcd for $C_{12}H_{18}N^+$ $(M+H)^+$ *m/z*: 176.1434, found: 176.1435.

5af: R_f = 0.29 ($CHCl_3$/MeOH = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 5H), 3.85 – 3.73 (m, 3H), 3.18 – 3.09 (m, 2H), 2.48 (t, *J* = 7.4 Hz, 2H), 1.42 (sext, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.4, 127.0, 126.4, 61.7, 61.6, 35.8, 20.8, 11.8.
IR (KBr) ν (cm^{-1}) 2955, 2923, 1631, 1462, 1383, 1141, 1075, 699.

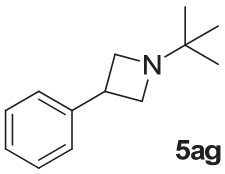
HRMS (ESI) calcd for $C_{12}H_{18}N^+$ $(M+H)^+$ *m/z*: 176.1434, found: 176.1435.



4ag



3ag



5ag

N-tert-butyl-2-phenylprop-2-en-1-amine (**4ag**), (*E*)-*N*-tert-butyl-3-phenylprop-2-en-1-amine (**3ag**) and 1-tert-butyl-3-phenylazetidine(**5ag**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 10/1 to petroleum ether/ethyl acetate/triethylamine = 100/30/1, to give 36 mg product **4ag** as a yellow oil in 48% yield and 26 mg product **3ag**/**5ag** as a yellow oil in 34% mixture yield (NMR yield for **3ag** is 14%, NMR yield for **5ag** is 20%).

Mixture of **3ag** and **5ag**: R_f = 0.32 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ **3ag**: 7.37 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.4 Hz, 1H), 3.38 (d, *J* = 6.4 Hz, 2H), 1.17 (s, 9H). **5ag**: 7.33 – 7.18 (m, *J* = 7.3 Hz, 5H), 3.70 (quint, *J* = 7.6 Hz, 1H), 3.60 (t, *J* = 7.6 Hz, 2H), 3.33 (t, *J* = 7.6 Hz, 2H), 1.02 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 137.2, 130.7, 129.4, 128.5, 128.3, 127.2, 127.0, 126.3, 126.2, 53.6, 52.0, 50.4, 45.2, 33.7, 29.1, 24.2.

HRMS (ESI) calcd for $C_{13}H_{20}N^+$ $(M+H)^+$ *m/z*: 190.1590, mixture found: 190.1590.

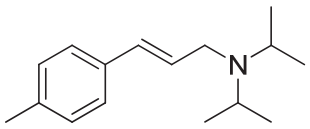
4ag: R_f = 0.32 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 5.38 (s, 1H), 5.28 (d, *J* = 1.2 Hz, 1H), 3.62 (s, 2H), 1.15 (s, 9H).

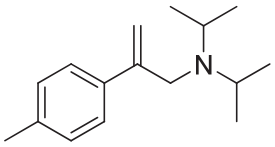
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 140.2, 128.4, 127.6, 126.2, 113.0, 50.5, 46.6, 29.0.

IR (KBr) ν (cm^{-1}) 3353, 2959, 2921, 1631, 1469, 1361, 1229, 901, 778, 704.

HRMS (ESI) calcd for $C_{13}H_{20}N^+$ $(M+H)^+$ *m/z*: 190.1590, found: 190.1590.



3ba



4ba

N,N-diisopropyl-2-p-tolylprop-2-en-1-amine (**4ba**) and (*E*)-*N,N*-diisopropyl-3-p-tolylprop-2-en-1-amine (**3ba**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 54 mg product **4ba** as a yellow oil in 58% yield and 8mg product **3ba** as a yellow oil in 9% yield.

3ba: R_f = 0.39 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.18 (dt, *J* = 16,0 6.6 Hz, 1H), 3.27 (d, *J* = 6.6 Hz, 2H), 3.09 (hept, *J* = 6.6 Hz, 2H), 2.32 (s, 3H), 1.04 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 134.8, 130.8, 129.9, 129.2, 126.0, 48.3, 47.7, 21.1, 20.7.

IR (KBr) ν (cm^{-1}) 2960, 2919, 1658, 1632, 1470, 1380, 1174, 967, 793.

HRMS (ESI) calcd for $C_{16}H_{26}N^+$ $(M+H)^+$ *m/z*: 232.2060, found: 232.2063.

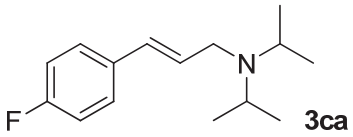
4ba: R_f = 0.30 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.38 (d, *J* = 2.0 Hz, 1H), 5.33 (d, *J* = 2.0 Hz, 1H), 3.41 (s, 2H), 3.07 (hept, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 0.99 (d, *J* = 6.6 Hz, 12H).

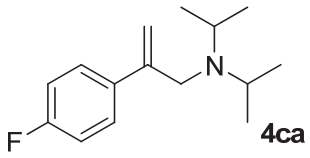
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 138.4, 136.8, 128.6, 126.2, 112.8, 49.3, 47.8, 21.1, 20.6.

IR (KBr) ν (cm^{-1}) 2963, 2925, 1630, 1513, 1463, 1362, 1179, 1118, 900, 823, 740.

HRMS (ESI) calcd for $C_{16}H_{26}N^+$ $(M+H)^+$ *m/z*: 232.2060, found: 232.2063.



3ca



4ca

2-(4-fluorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**4ca**) and (*E*)-3-(4-fluorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**3ca**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 35 mg product **4ca** as a yellow oil in 38% yield and 16 mg product **3ca** as a yellow oil in 17% yield.

3ca: R_f = 0.39 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 6.98 (t, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, *J* = 15.8, 5.8 Hz, 1H), 3.27 (d, *J* = 5.8 Hz, 2H), 3.09 (hept, *J* = 6.6 Hz, 2H), 1.04 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 243 Hz, 1C), 133.8 (d, *J* = 3 Hz, 1C), 131.6, 128.8, 127.5 (d, *J* = 2 Hz, 1C), 115.3 (d, *J* = 22 Hz, 1C), 48.3, 47.5, 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.65.

IR (KBr) ν (cm^{-1}) 2962, 2925, 1601, 1508, 1461, 1380, 1231, 1156, 966, 845, 774.

HRMS (ESI) calcd for $C_{15}H_{23}FN^+$ $(M+H)^+$ *m/z*: 236.1809, found: 236.1811.

4ca: R_f = 0.42 (petroleum ether/ethyl acetate = 5:1).

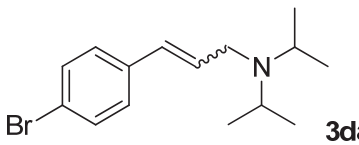
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.01 – 6.94 (m, 2H), 5.37 (s, 1H), 5.30 (s, 1H), 3.41 (s, 2H), 3.05 (hept, *J* = 6.6 Hz, 2H), 0.98 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244 Hz, 12H), 147.11, 137.2 (d, *J* = 3, 1C), 128.0 (d, *J* = 7 Hz, 1C), 114.6 (d, *J* = 21 Hz, 1C), 113.7, 49.5, 47.5, 20.5.

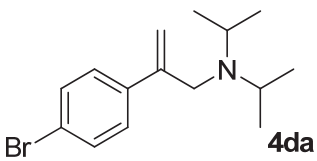
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.78.

IR (KBr) ν (cm^{-1}) 2962, 2925, 1633, 1603, 1509, 1463, 1383, 1117, 837, 618.

HRMS (ESI) calcd for $C_{15}H_{23}FN^+$ $(M+H)^+$ *m/z*: 236.1809, found: 236.1811.



3da



4da

2-(4-bromophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**4da**) and (*E/Z*)-3-(4-bromophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**3da**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 79 mg product **4da** as a yellow oil in 67% yield and 24 mg product **3da** as a yellow oil in 20% yield (*E/Z* = 89:11 according to the NMR).

3da: R_f = 0.39 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7. 62 (m, 2H, minor), 7.46 – 7.44 (m, 2H, minor), 7.41 – 7.36 (m, 2H, major) 7.24 – 7.20 (m, 2H, major), 6.81 (d, *J* = 15.8 Hz, 1H, minor), 6.44 (d, *J* = 15.8 Hz, 1H, major), 6.23 (dt, *J* = 15.8, 6.4 Hz, 1H), 3.30 (dd, *J* = 6.4, 1.6 Hz, 2H, minor), 3.26 (dd, *J* = 6.4, 1.6 Hz, 2H, major), 3.08 (hept, *J* = 6.6, 1H), 1.04 (d, *J* = 6.6, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 134.0, 132.8, 131.5, 131.0, 130.9, 129.8, 129.3, 128.8, 127.7, 124.8, 120.6, 48.6, 48.4, 47.5, 47.3, 20.8, 20.7.

IR (KBr) ν (cm^{-1}) 2963, 2923, 1632, 1487, 1463, 1382, 1175, 1072, 1008, 967.

HRMS (ESI) calcd for $C_{15}H_{23}BrN^+$ $(M+H)^+$ *m/z*: 296.1008, found: 296.1014.

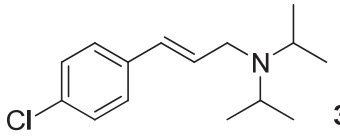
4da: R_f = 0.36 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.36 – 7.27 (m, 2H), 5.40 (d, *J* = 1.1 Hz, 1H), 5.35 (d, *J* = 1.1 Hz, 1H), 3.41 (s, 1H), 3.05 (hept, *J* = 6.6 Hz, 2H), 0.98 (d, *J* = 6.6 Hz, 12H).

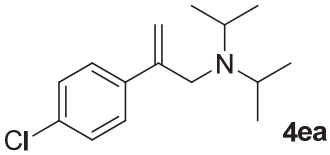
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 140.0, 131.0, 128.2, 121.0, 114.5, 49.3, 47.6, 20.5.

IR (KBr) ν (cm^{-1}) 2963, 2926, 1728, 1588, 1488, 1383, 1179, 1072, 1009, 905, 829.

HRMS (ESI) calcd for $C_{15}H_{23}BrN^+$ $(M+H)^+$ *m/z*: 296.1008, found: 296.1016.



3ea



4ea

2-(4-chlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**4ea**) and (*E*)-3-(4-chlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**3ea**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 50 mg product **4ea** as a yellow oil in 50% yield and 22 mg product **3ea** as a yellow oil in 22% yield.

3ea: R_f = 0.39 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 4H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 5.8 Hz, 1H), 3.27 (d, *J* = 5.8 Hz, 2H), 3.14 – 3.02 (hept, *J* = 6.4 Hz, 2H), 1.04 (d, *J* = 6.4 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 132.7, 132.5, 128.7, 128.6, 127.3, 48.4, 47.5, 20.7.

IR (KBr) ν (cm^{-1}) 2962, 2924, 1491, 1384, 1180, 1091, 1012, 967.

HRMS (ESI) calcd for $C_{15}H_{23}ClN^+$ $(M+H)^+$ *m/z*: 252.1514, found: 252.1514.

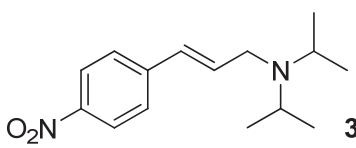
4ea: R_f = 0.45 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.40 (s, 1H), 5.34 (s, 1H), 3.41 (s, 2H), 3.05 (hept, *J* = 6.7 Hz, 2H), 0.98 (d, *J* = 6.7 Hz, 12H).

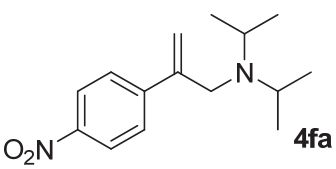
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 139.5, 132.9, 128.0, 127.8, 114.3, 77.3, 47.5, 20.5.

IR (KBr) ν (cm^{-1}) 2963, 2926, 1676, 1592, 1491, 1381, 1208, 1179, 1140, 1092, 1013, 832.

HRMS (ESI) calcd for $C_{15}H_{23}ClN^+$ $(M+H)^+$ *m/z*: 252.1514, found: 252.1513 .



3fa



4fa

N,N-diisopropyl-2-(4-nitrophenyl)prop-2-en-1-amine (**4fa**) and (*E*)-*N,N*-diisopropyl-3-(4-nitro phenyl)prop-2-en-1-amine (**3fa**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 25 mg product **4fa** as a bright yellow oil in 24% yield and 21 mg product **3fa** as a bright yellow oil in 20% yield.

3fa: R_f = 0.38 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 15.6 Hz, 1H), 6.46 (dt, *J* = 15.6, 5.4 Hz, 1H), 3.32 (d, *J* = 5.4 Hz, 2H), 3.08 (hept, *J* = 12.9, 6.4 Hz, 2H), 1.05 (d, *J* = 6.4 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 144.2, 137.9, 127.8, 126.5, 123.9, 48.6, 47.5, 20.8.

IR (KBr) ν (cm^{-1}) 2964, 2927, 1596, 1517, 1383, 1342, 1180, 1109, 859.

HRMS (ESI) calcd for $C_{15}H_{23}N_2O_2^+$ $(M+H)^+$ *m/z*: 263.1754, found: 263.1754.

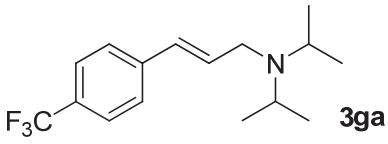
4fa: R_f = 0.42 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 5.54 (d, *J* = 1.2 Hz, 1H), 5.49 (s, 2H), 3.48 (s, 2H), 3.04 (hept, *J* = 6.6 Hz, 2H), 0.98 (d, *J* = 6.6 Hz, 12H).

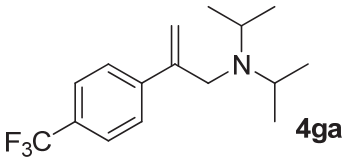
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.9, 146.6, 127.3, 123.2, 117.3, 49.3, 47.4, 20.4.

IR (KBr) ν (cm^{-1}) 2965, 2927, 1596, 1518, 1343, 1178, 1110, 856, 712.

HRMS (ESI) calcd for $C_{15}H_{23}N_2O_2^+$ $(M+H)^+$ *m/z*: 263.1754, found: 263.1754.



3ga



4ga

N,N-diisopropyl-2-(4-(trifluoromethyl)phenyl)prop-2-en-1-amine (**4ga**) and (*E*)-*N,N*-diisopropyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-amine (**3ga**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 25 mg product **4ga** as a yellow oil in 22% yield and 46 mg product **3ga** as a yellow oil in 40% yield.

3ga: R_f = 0.39 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8, 5.6 Hz, 1H), 3.29 (dd, *J* = 5.6, 0.8 Hz, 2H), 3.08 (hept, *J* = 6.6 Hz, 2H), 1.04 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 135.1, 128.7 (q, *J* = 32 Hz, 1C), 128.5, 126.2, 125.4 (q, *J* = 4 Hz, 1C), 124.3 (q, *J* = 270 Hz, 1C), 48.49, 47.49, 20.71.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.42.

IR (KBr) ν (cm^{-1}) 2962, 2923, 1616, 1467, 1382, 1326, 1165, 1126, 1068, 1017, 969, 856.

HRMS (ESI) calcd for $C_{16}H_{23}F_3N^+$ $(M+H)^+$ *m/z*: 286.1777, found: 236.1784.

4ga: R_f = 0.42 (petroleum ether/ethyl acetate = 5:1).

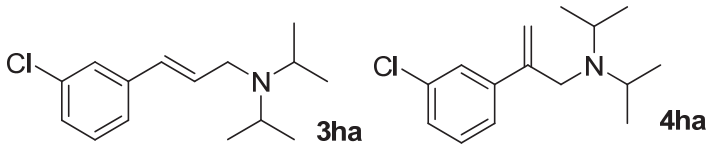
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 4H), 5.48 (d, *J* = 1.3 Hz, 1H), 5.41 (s, 1H), 3.45 (s, 2H), 3.05 (hept, *J* = 6.6 Hz, 2H), 0.98 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 144.8, 129.1 (q, *J* = 32 Hz, 1C), 124.4 (q, *J* = 270 Hz, 1C), 126.8, 124.8 (q, *J* = 4 Hz, 1C), 115.7, 49.3, 47.5, 20.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.42.

IR (KBr) ν (cm^{-1}) 2965, 2927, 1617, 1383, 1364, 1165, 1126, 1067, 1016, 847, 617.

HRMS (ESI) calcd for $C_{16}H_{23}F_3N^+$ $(M+H)^+$ *m/z*: 286.1777, found: 236.1781.



2-(3-chlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**4ha**) and (*E*)-3-(3-chlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**3ha**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 43 mg product **4ha** as a yellow oil in 43% yield and 26 mg product **3ha** as a yellow oil in 26% yield.

3ha: R_f = 0.44 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.22 – 7.18 (m, 2H), 7.18 – 7.12 (m, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.25 (dt, *J* = 16.0, 6.0 Hz, 1H), 3.27 (dd, *J* = 6.0, 0.4 Hz, 2H), 3.08 (hept, *J* = 6.6 Hz, 2H), 1.04 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 134.4, 133.7, 129.6, 128.6, 126.8, 126.1, 124.3, 48.4, 47.4, 20.7.

IR (KBr) ν (cm^{-1}) 2963, 2920, 1658, 1632, 1470, 1384, 1180, 1141, 1076, 1049.

HRMS (ESI) calcd for $C_{15}H_{23}ClN^+$ $(M+H)^+$ *m/z*: 252.1514, found: 252.1514.

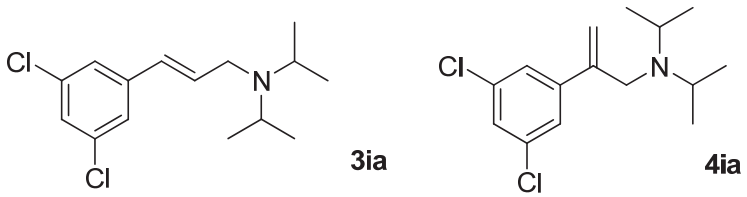
4ha: R_f = 0.48 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.33 (t, *J* = 4.2 Hz, 1H), 7.23 (d, *J* = 4.2 Hz, 2H), 5.44 (s, 1H), 5.38 (s, 1H), 3.41 (s, 2H), 3.06 (hept, *J* = 6.6 Hz, 2H), 0.99 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 133.8, 129.10, 127.1, 126.7, 124.6, 114.9, 49.3, 47.6, 20.5.

IR (KBr) ν (cm^{-1}) 2963, 2926, 1593, 1562, 1465, 1383, 1207, 1180, 1141, 787.

HRMS (ESI) calcd for $C_{15}H_{23}ClN^+$ $(M+H)^+$ *m/z*: 252.1514, found: 252.1514 .



2-(3,5-dichlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**4ia**) and (*E*)-3-(3,5-dichlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**3ia**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 27 mg product **4ia** as a yellow oil in 24% yield and 53 mg product **3ia** as a yellow oil in 46% yield.

3ia: R_f = 0.27 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.21 (s, 1H), 7.17 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.27 (dt, *J* = 15.8, 5.7 Hz, 1H), 3.26 (d, *J* = 5.7 Hz, 2H), 3.06 (hept, *J* = 6.6 Hz, 2H), 1.03 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 135.5, 135.0, 127.3, 126.6, 124.5, 48.5, 47.3, 20.7.

IR (KBr) ν (cm^{-1}) 2960, 2922, 1585, 1560, 1416, 1205, 1141, 1179, 1116, 1075, 799.

HRMS (ESI) calcd for $C_{15}H_{22}Cl_2N^+$ $(M+H)^+$ *m/z*: 286.1124, found: 286.1118.

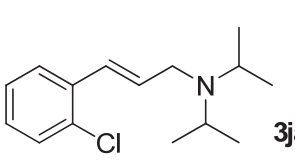
4ia: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 7.24 (s, 1H), 5.44 (s, 1H), 5.39 (s, 1H), 3.38 (s, 2H), 3.05 (hept, *J* = 6.4 Hz, 2H), 0.99 (d, *J* = 6.4 Hz, 12H).

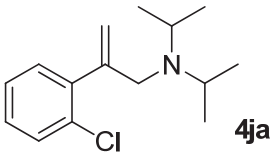
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 144.0, 134.4, 126.9, 125.1, 116.0, 77.3, 47.5, 20.4.

IR (KBr) ν (cm^{-1}) 2963, 2925, 1583, 1558, 1383, 1363, 1207, 1180, 1141, 1095, 801.

HRMS (ESI) calcd for $C_{15}H_{22}Cl_2N^+$ $(M+H)^+$ *m/z*: 286.1124, found: 286.1118.



3ja



4ja

2-(2-chlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**4ja**) and (*E*)-3-(2-chlorophenyl)-*N,N*-diisopropylprop-2-en-1-amine (**3ja**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 4 mg product **4ja** as a yellow oil in 4% yield and 44 mg product **3ja** as a yellow oil in 44% yield.

3ja: R_f = 0.33 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 6.22 (dt, *J* = 15.6, 6.0 Hz, 1H), 3.32 (d, *J* = 6.0 Hz, 2H), 3.16 – 3.04 (hept, *J* = 6.4 Hz, 2H), 1.05 (d, *J* = 6.4 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.0, 132.7, 129.5, 127.9, 126.8, 126.7, 126.1, 48.5, 47.7, 20.8.

IR (KBr) ν (cm^{-1}) 2962, 2923, 1469, 1440, 1382, 1204, 1180, 1075, 1033, 749.

HRMS (ESI) calcd for $C_{15}H_{23}ClN^+$ $(M+H)^+$ *m/z*: 252.1514, found: 252.1519.

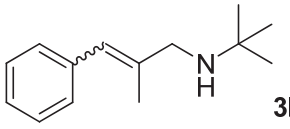
4ja: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 7.21 – 7.13 (m, 3H), 5.55 (s, 1H), 5.05 (s, 1H), 3.31 (s, 2H), 3.07 (hept, *J* = 6.6 Hz, 2H), 0.95 (d, *J* = 6.6 Hz, 12H).

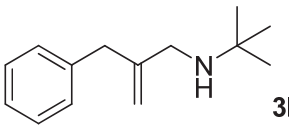
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 141.6, 132.1, 130.9, 129.2, 128.0, 126.2, 115.3, 50.1, 47.6, 20.7.

IR (KBr) ν (cm^{-1}) 2962, 2924, 1456, 1363, 1331, 1207, 1179, 1147, 1046, 160.

HRMS (ESI) calcd for $C_{15}H_{23}ClN^+$ $(M+H)^+$ *m/z*: 252.1514, found: 252.1514 .



3kg



3kg'

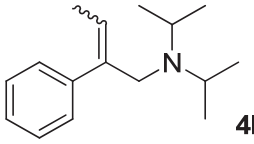
(*E/Z*)-*N*-tert-butyl-2-methyl-3-phenylprop-2-en-1-amine (**3kg**) and 2-benzyl-*N*-tert-butylprop-2-en-1-amine (**3kg'**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to give 30 mg mixture product **3kg** and **3kg'** as a yellow oil in 37 % yield (**3kg**: **3kg'** = 1:0.3 according to the NMR, for **3kg**, the *E/Z* ratio is 89:11).

Mixtureof **3kg** and **3kg'**: R_f= 0.29 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ (**3kg**) 7.34 – 7.16 (m, 5H), 6.45 (s, 1H, major), 6.38 (s, 1H, minor), 3.28 (s, 2H, major), 3.26 (s, 2H, major), 1.96 (d, *J* = 1.6 Hz, 3H, minor), 1.91 (s, 3H, major), 1.16 (s, 9H, major), 1.08 (s, 9H, major); (**3kg'**) 7.34 – 7.16 (m, 5H), 5.02 (s, 1H), 4.82 (s, 1H), 3.42 (s, 2H), 3.08 (s, 2H), 1.06 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 139. 7, 138.3, 138.0, 131.0, 129.3, 129.0, 128.9, 128.5, 128.2, 128.02, 127.97, 127.4, 126.2, 126.03, 126.00, 125.1, 124.8, 111.5, 51.3, 50.5, 50.4, 46.8, 44.0, 41.6, 29.7, 29.3, 29.1, 29.0, 23.4, 17.1.

HRMS (ESI) calcd for $C_{14}H_{22}N^+$ $(M+H)^+$ *m/z*: 204.1747, mixture found: 204.1747.



4la

(*E*/*Z*)-*N*,*N*-diisopropyl-2-phenylbut-2-en-1-amine (**4la**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/ triethylamine = 100/10/1, to give 49 mg product **4la** as a yellow oil in 53% yield (*E*/*Z* = 3:1 according to the NMR).

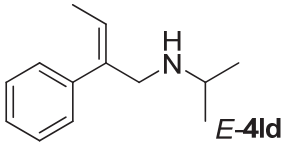
4la: R_f = 0.27 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.20 (m, 5H), 5.87 (q, *J* = 7.0 Hz, 1H, major), 5.82 (q, *J* = 6.8 Hz, 1H, minor), 3.55 (s, 2H, major), 3.29 (s, 2H, minor), 3.20 – 2.96 (m, 2H), 1.91 (d, *J* = 7.0 Hz, 3H, major, *E* product), 1.64 (dd, *J* = 6.8, 1.2 Hz, 3H, minor, *Z* product), 1.02 – 0.97 (m, *J* = 7.2 Hz, 12H).

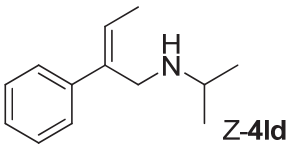
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.0, 140.0, 128.8, 127.6, 127.4, 127.1, 126.2, 126.1, 126.0, 122.1, 52.2, 47.1, 46.1, 42.7, 20.5, 14.5, 14.0.

IR (KBr) ν (cm^{-1}) 2962, 2925, 1463, 1380, 1361, 1179, 1116, 1029, 698.

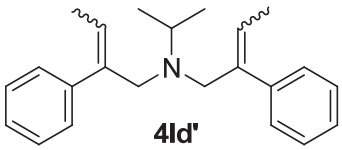
HRMS (ESI) calcd for $C_{16}H_{26}N^+$ $(M+H)^+$ *m/z*: 232.2060, found: 232.2060.



E-**4ld**



Z-**4ld**



4ld'

(*E*/*Z*)-*N*-isopropyl-2-phenyl-*N*-((*E*/*Z*)-2-phenylbut-2-enyl)but-2-en-1-amine (**4ld'**) and (*E*/*Z*)-*N*-isopropyl-2-phenylbut-2-en-1-amine (*E*/*Z*-**4ld**) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 18 mg product **4ld'** as a yellow oil in 28 % yield and 54 mg product *E*/*Z*-**4ld** as a yellow oil in 71% yield (*E*/*Z* = 3:1 according to the NMR). The mixture *E*/*Z*-**4ld** was purified by preparative TLC.

E-**4ld**: R_f = 0.29 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.31 (m, 2H), 7.23 (m, 1H), 5.87 (q, *J* = 7.0 Hz, 1H), 3.67 (s, 2H), 2.79 (hept, *J* = 6.2 Hz, 1H), 1.86 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 139.1, 128.4, 126.7, 126.2, 125.2, 48.1, 45.0, 22.9, 14.1.

IR (KBr) ν (cm^{-1}) 3361, 2960, 2926, 2854, 1725, 1599, 1462, 1378, 1179, 1074, 760, 698.

HRMS (ESI) calcd for $C_{13}H_{20}N^+$ $(M+H)^+$ *m/z*: 190.1590, found: 190.1590.

Z-**4ld**: R_f = 0.29 ($CHCl_3$/MeOH = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.26 (m, 1H), 7.20 (m, 2H), 5.72 (q, *J* = 6.8 Hz, 1H), 3.48 (s, 2H), 2.80 (hept, *J* = 6.2 Hz, 1H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 139.4, 128.6, 128.2, 126.8, 123.0, 54.2, 47.3, 22.7, 14.5.

IR (KBr) ν (cm^{-1}) 2956, 2925, 1494, 1463, 1378, 1179, 1074, 768, 701.

HRMS (ESI) calcd for $C_{13}H_{20}N^+$ $(M+H)^+$ *m/z*: 190.1590, found: 190.1594.

4ld': R_f = 0.43 (petroleum ether/ethyl acetate = 5:1)

^1H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.00 (m, 10H), 5.94 (q, *J* = 7.0 Hz, 0.8H), 5.85 (q, *J* = 7.0 Hz, 0.5H), 5.60 (q, *J* = 7.0 Hz, 0.5H), 5.54 (q, *J* = 7.0 Hz, 0.2H), 3.43 (s, 1.6H), 3.41 (s, 1H), 3.21 (s, 1H), 3.18 (s, 0.4H), 3.13 – 2.89 (m, 1H), 1.83 (d, *J* = 7.0 Hz, 2.4H), 1.79 (d, *J* = 7.0 Hz, 1.5H), 1.59 (d, *J* = 7.0 Hz, 1.5H), 1.53 (d, *J* = 7.0 Hz, 0.6H), 0.93 (d, *J* = 6.7 Hz, 2.4H), 0.87 (d, *J* = 6.7 Hz, 3.0H), 0.83 (d, *J* = 6.7 Hz, 0.6H).

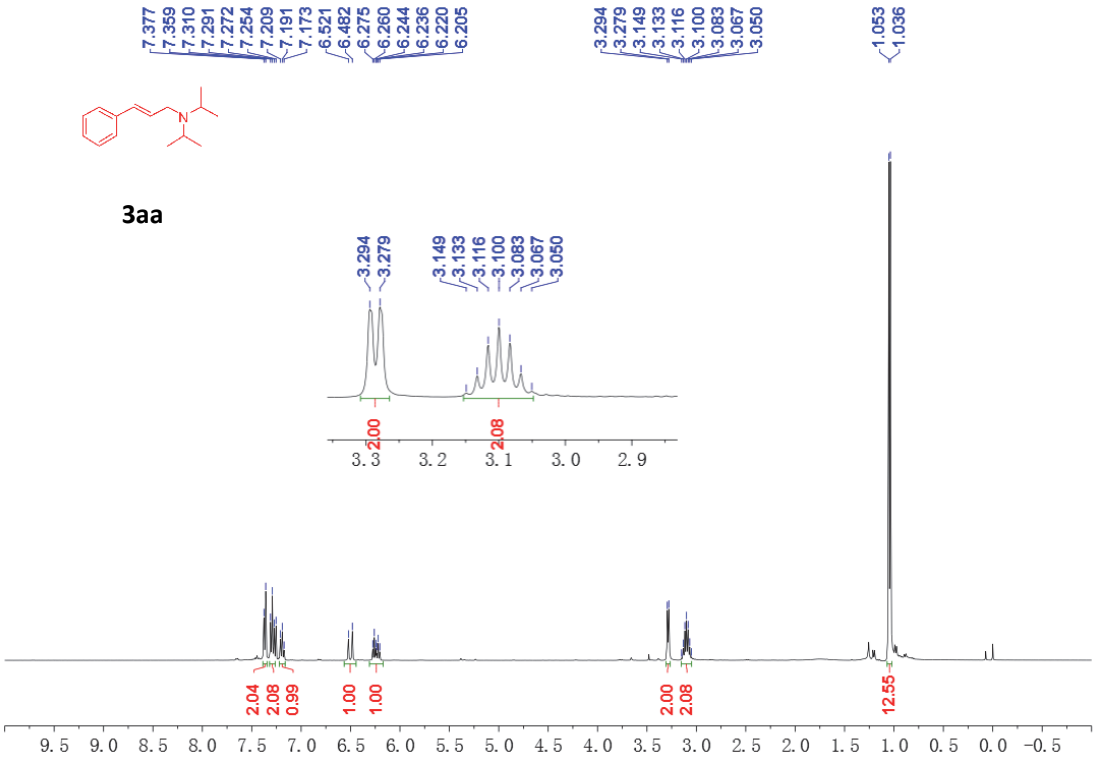
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.9, 140.1, 139.4, 138.8, 138.4, 128.83, 128.81, 127.6, 127.50, 127.48, 126.9, 126.8, 126.6, 126.5, 126.1, 126.04, 126.00, 123.8, 123.3, 56.4, 47.5, 47.4, 47.0, 46.5, 17.2, 17.1, 14.65, 14.23, 14.15.

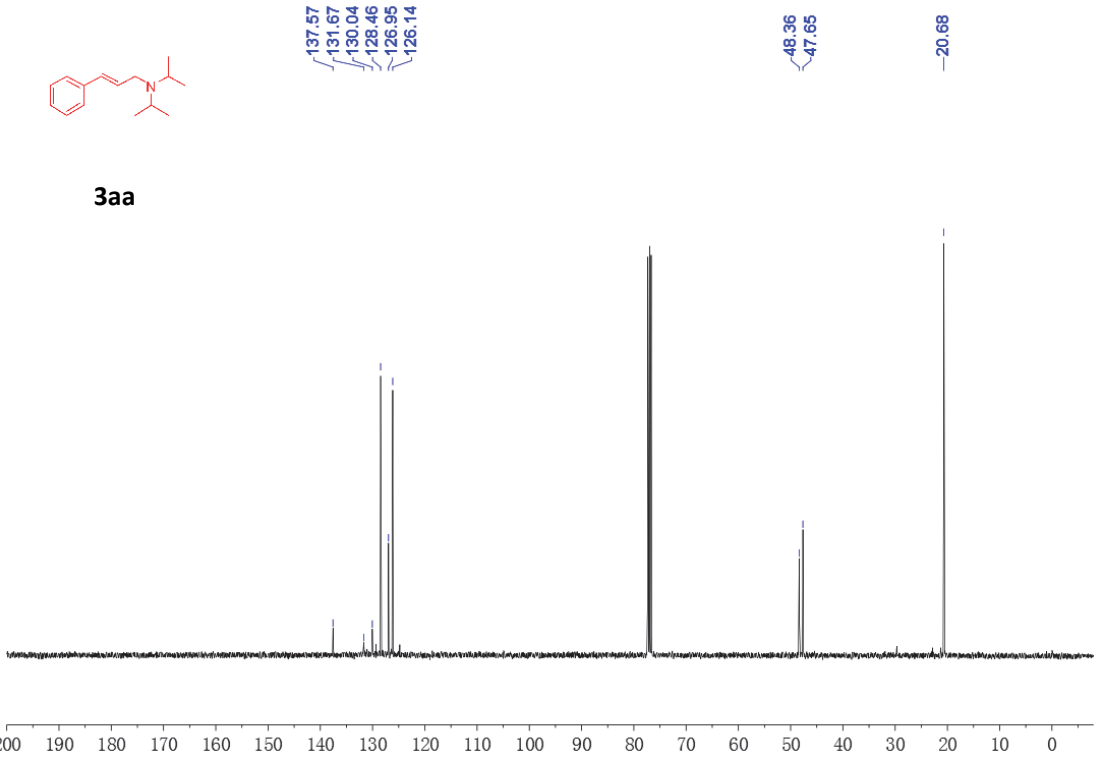
IR (KBr) ν (cm^{-1}) 2959, 2924, 1494, 1462, 1383, 1260, 1166, 1098, 1021, 750, 698.

HRMS (ESI) calcd for $C_{23}H_{30}N^+$ $(M+H)^+$ *m/z*: 320.2373, found: 320.2375.

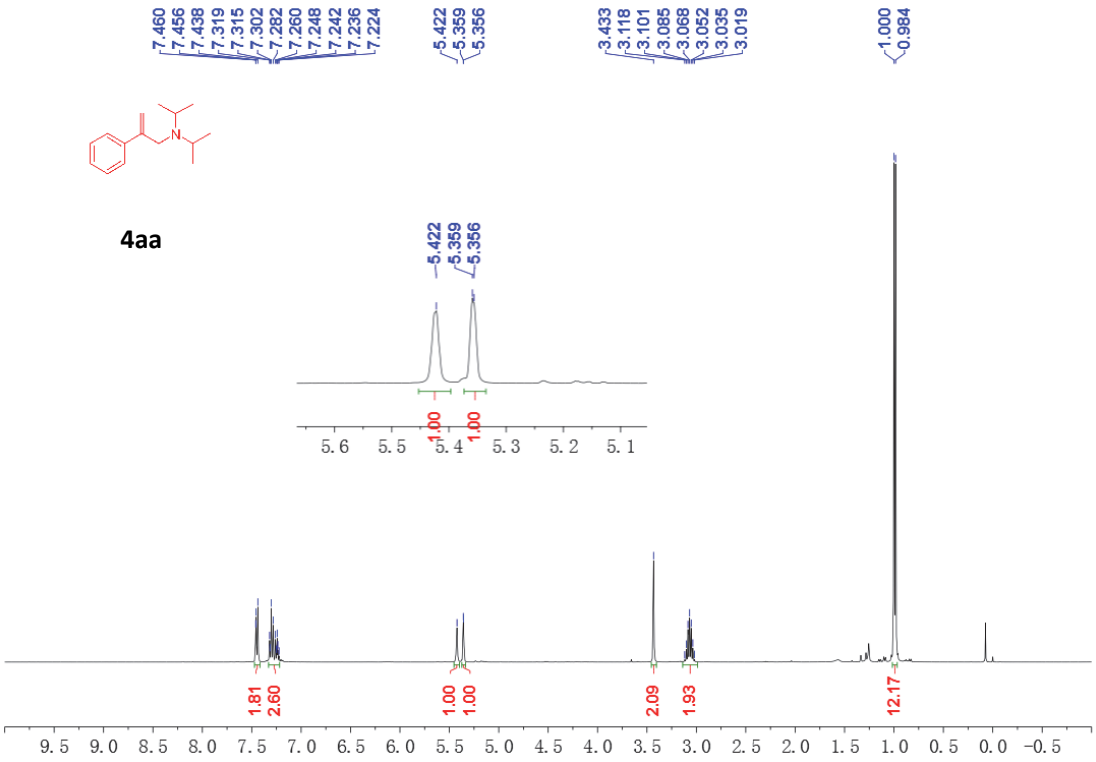
IV. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

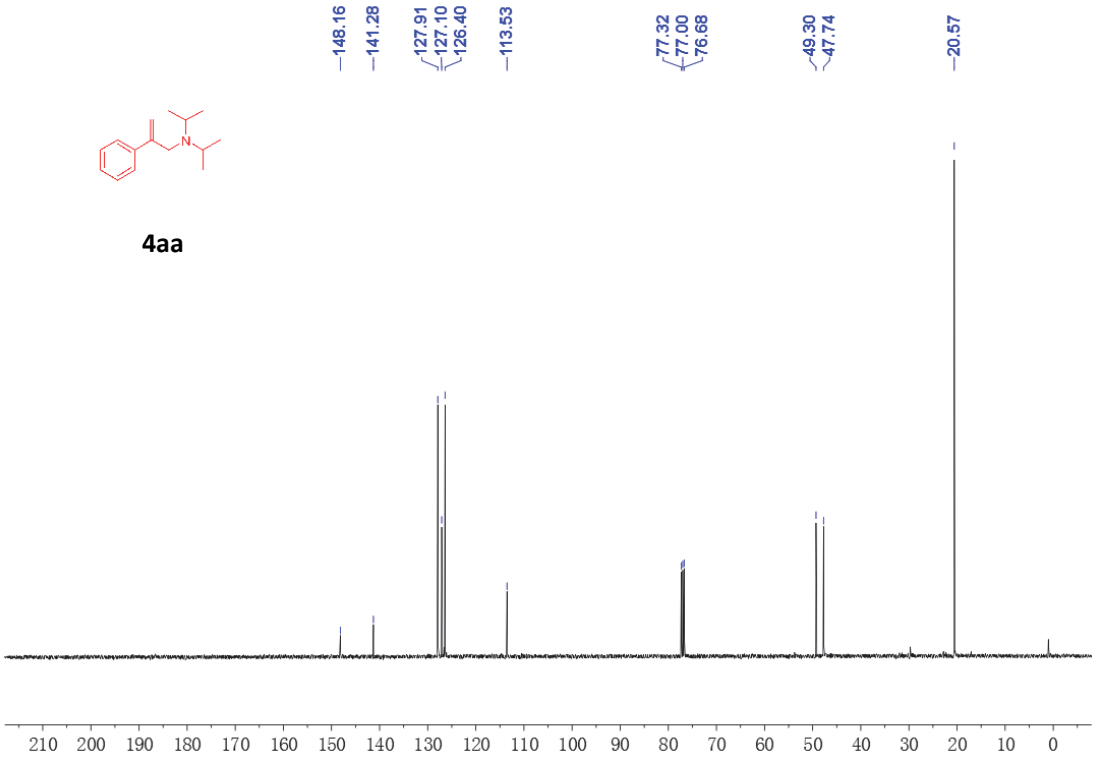
the ^{1}H and ^{13}C NMR spectra of **3aa**



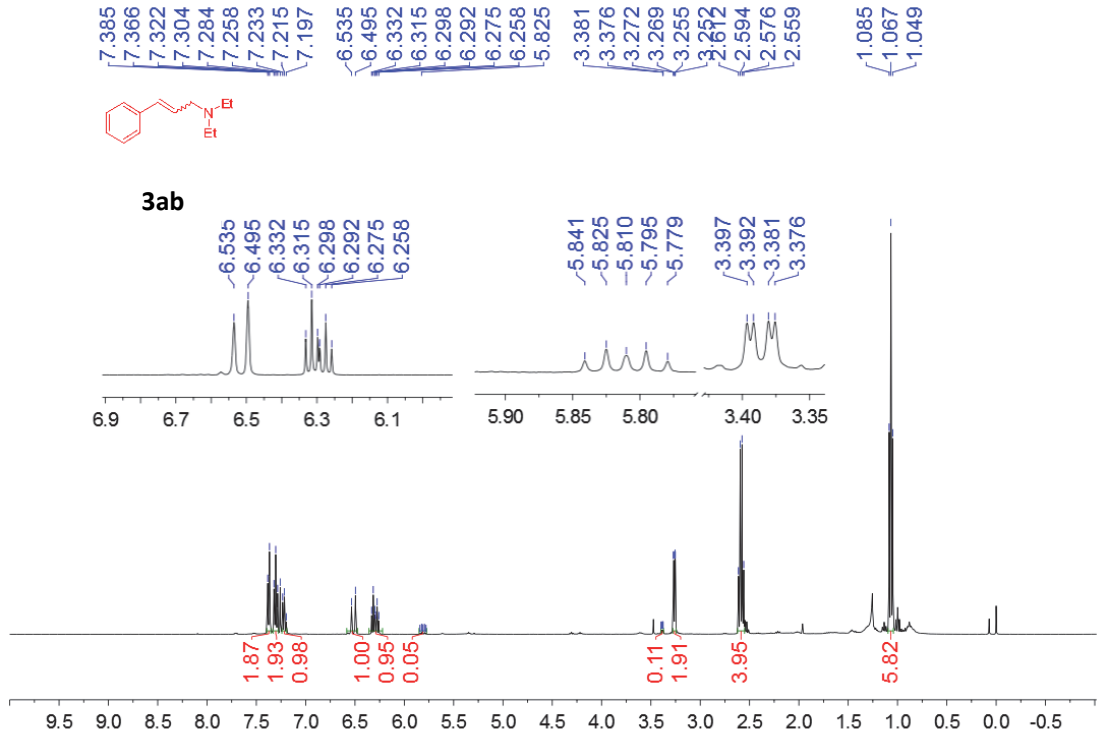


the ^{1}H and ^{13}C NMR spectra of **4aa**



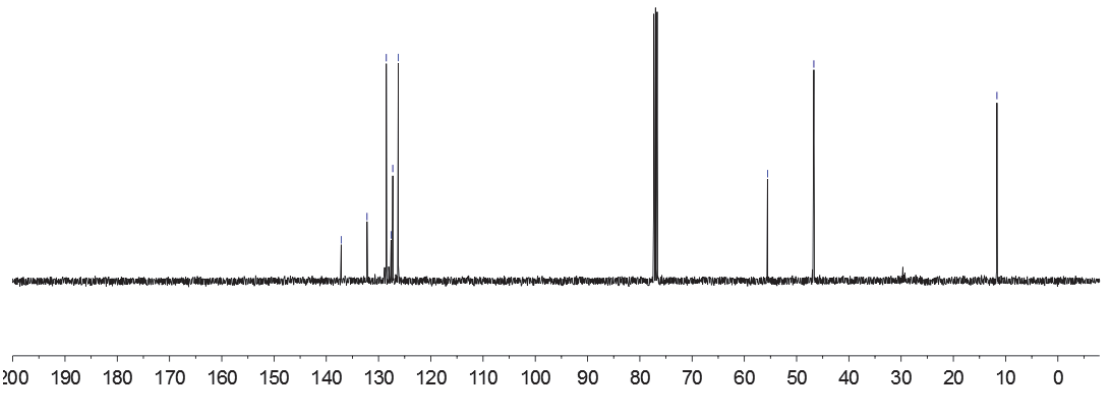


the ^{1}H and ^{13}C NMR spectra of **3ab**

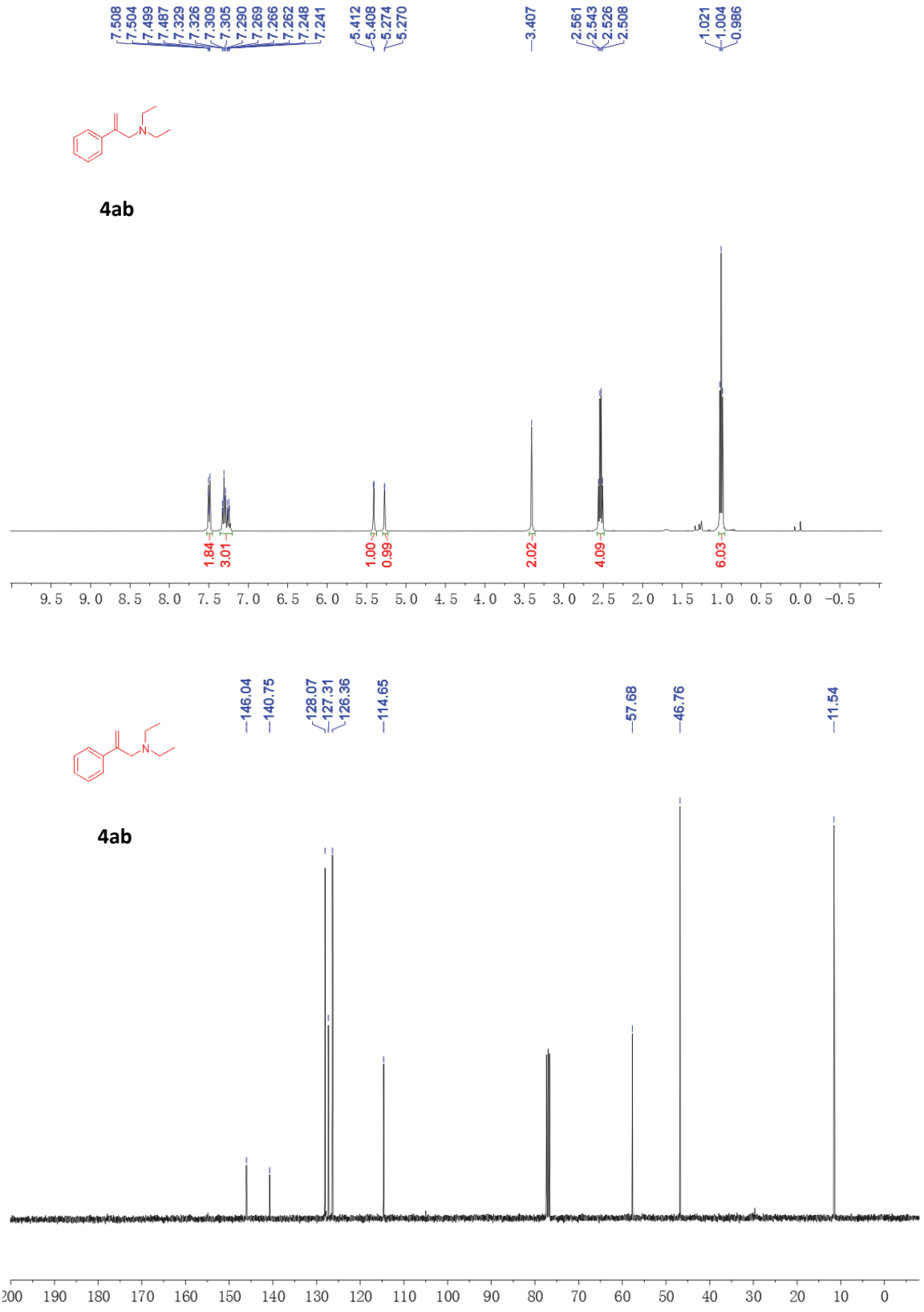


3ab

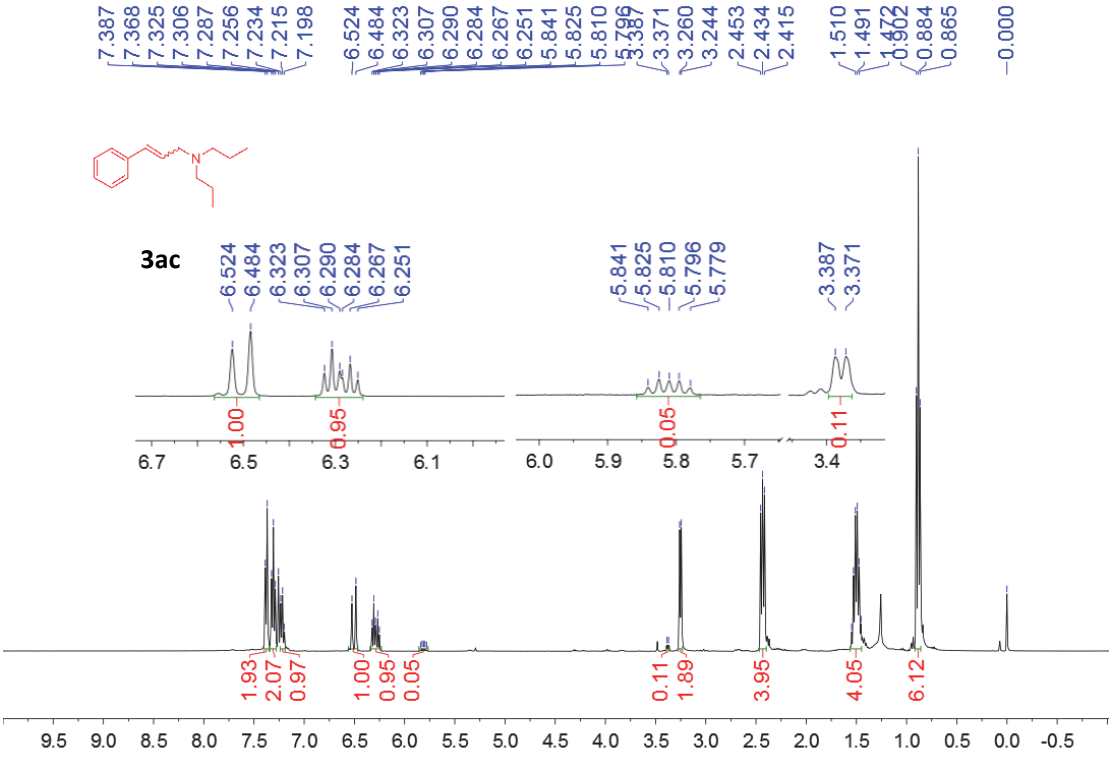
3ab

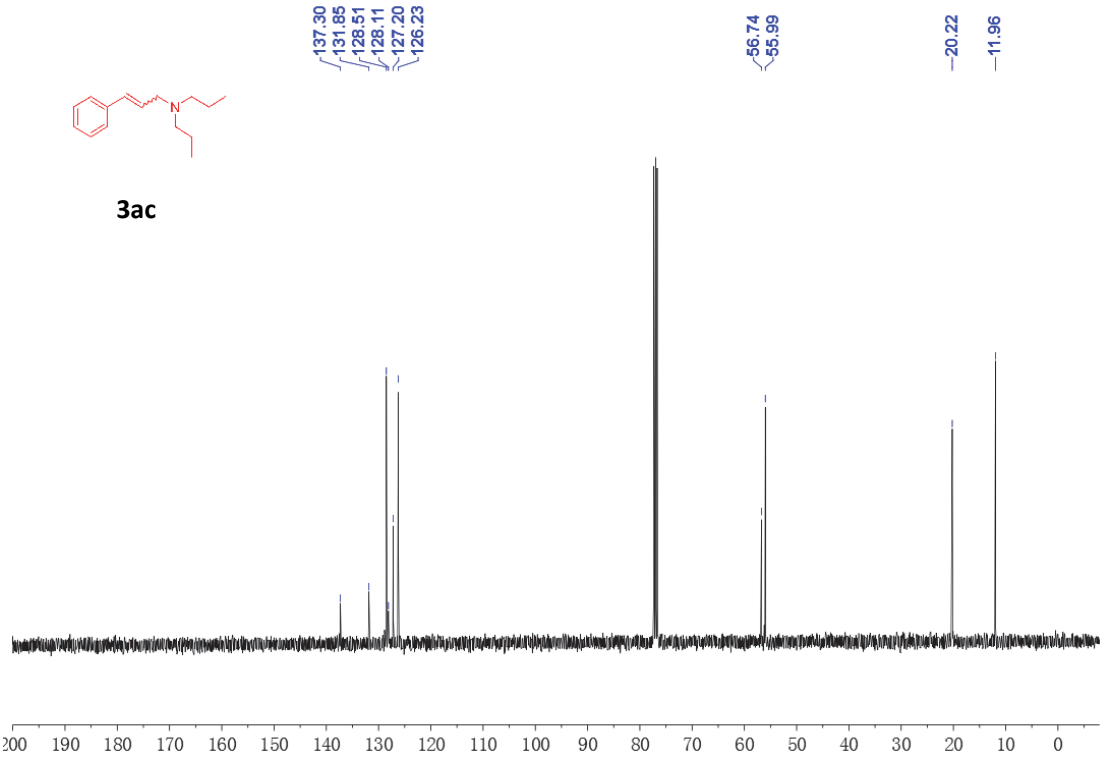


the ^{1}H and ^{13}C NMR spectra of **4ab**

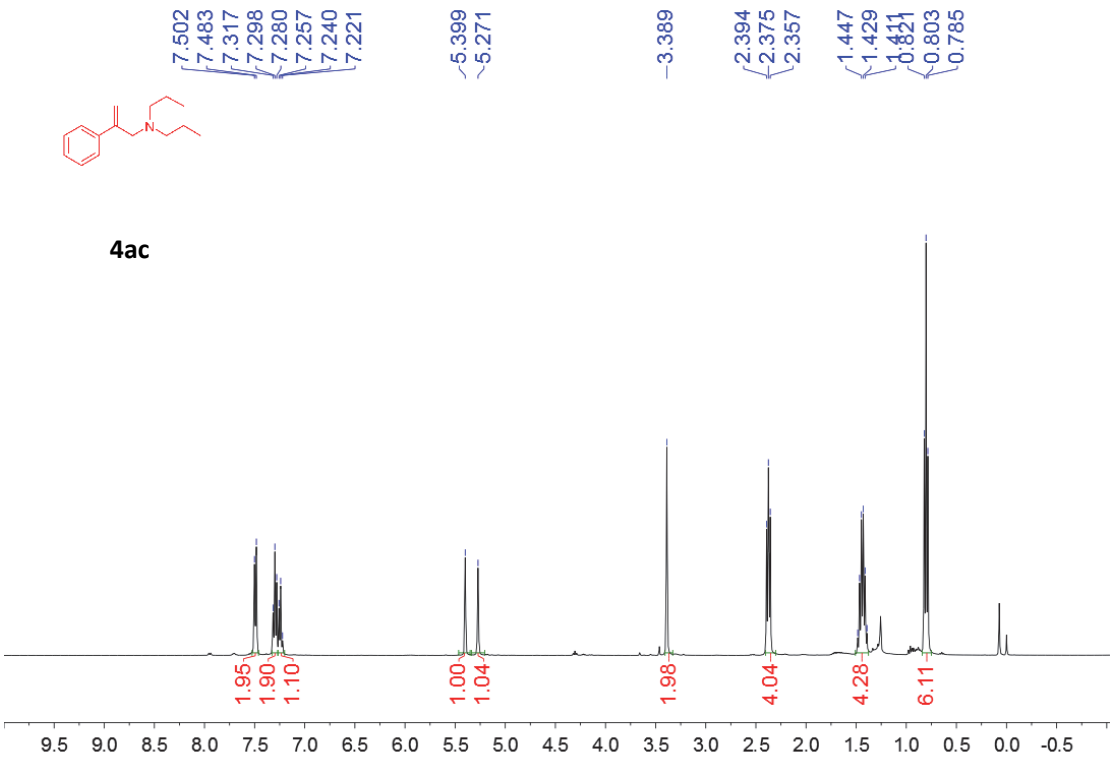


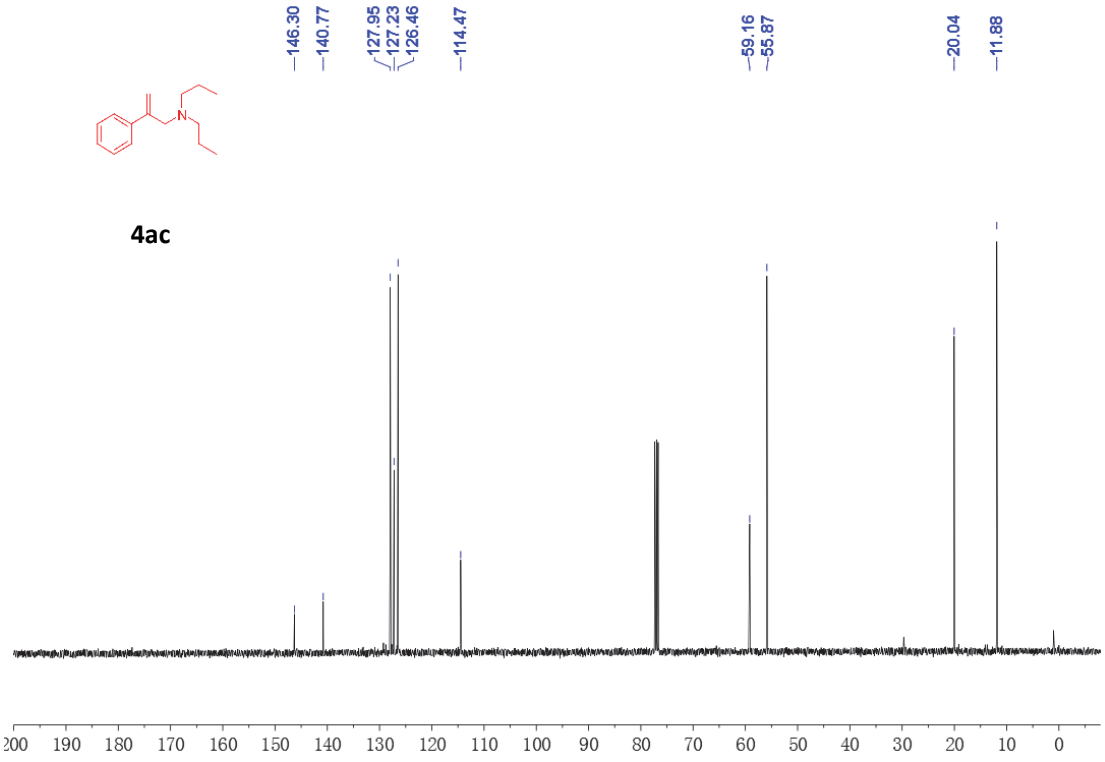
the ^{1}H and ^{13}C NMR spectra of **3ac**



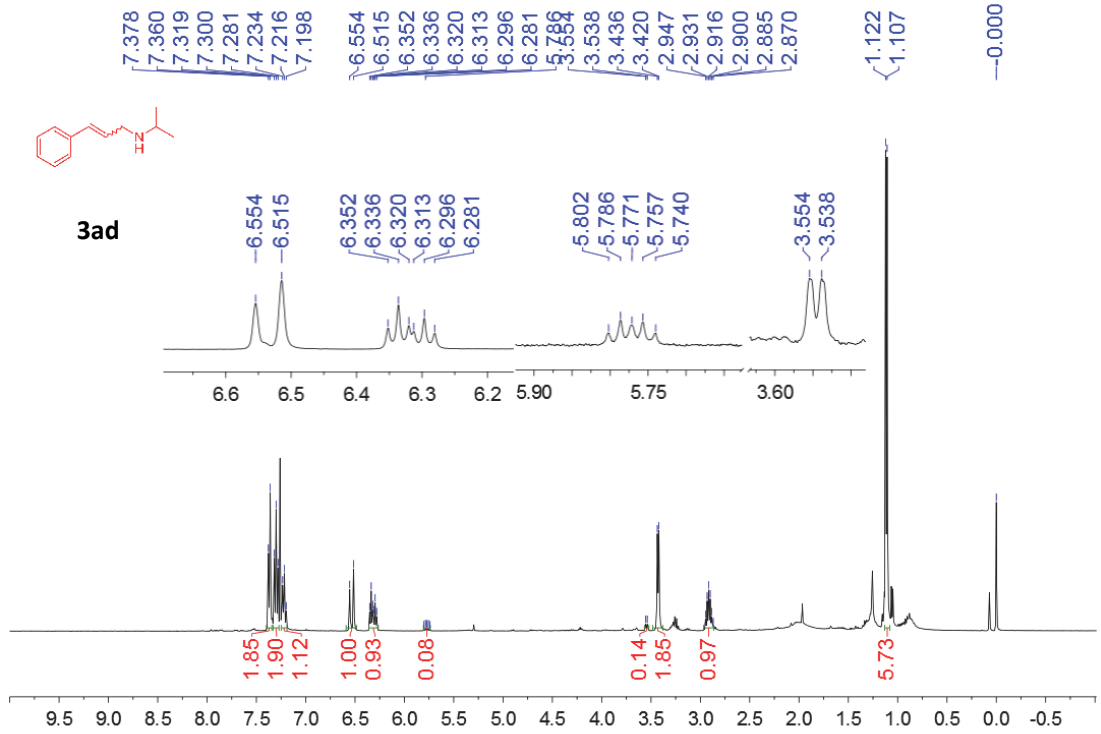


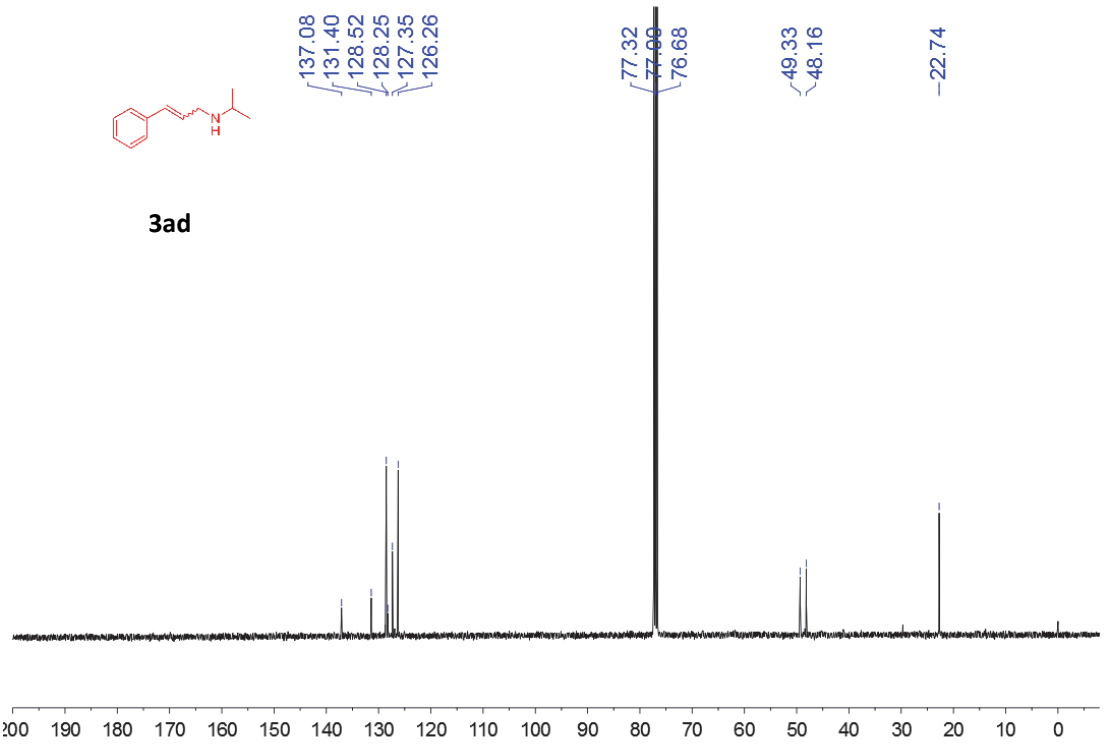
the ^{1}H and ^{13}C NMR spectra of **4ac**



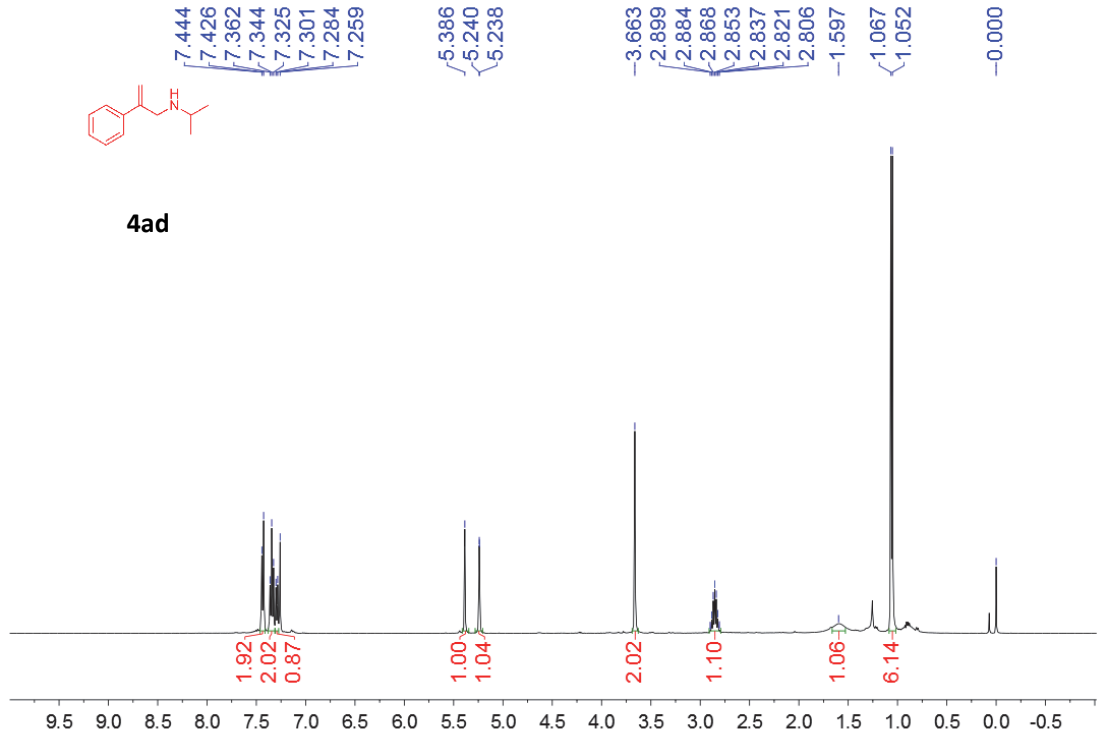


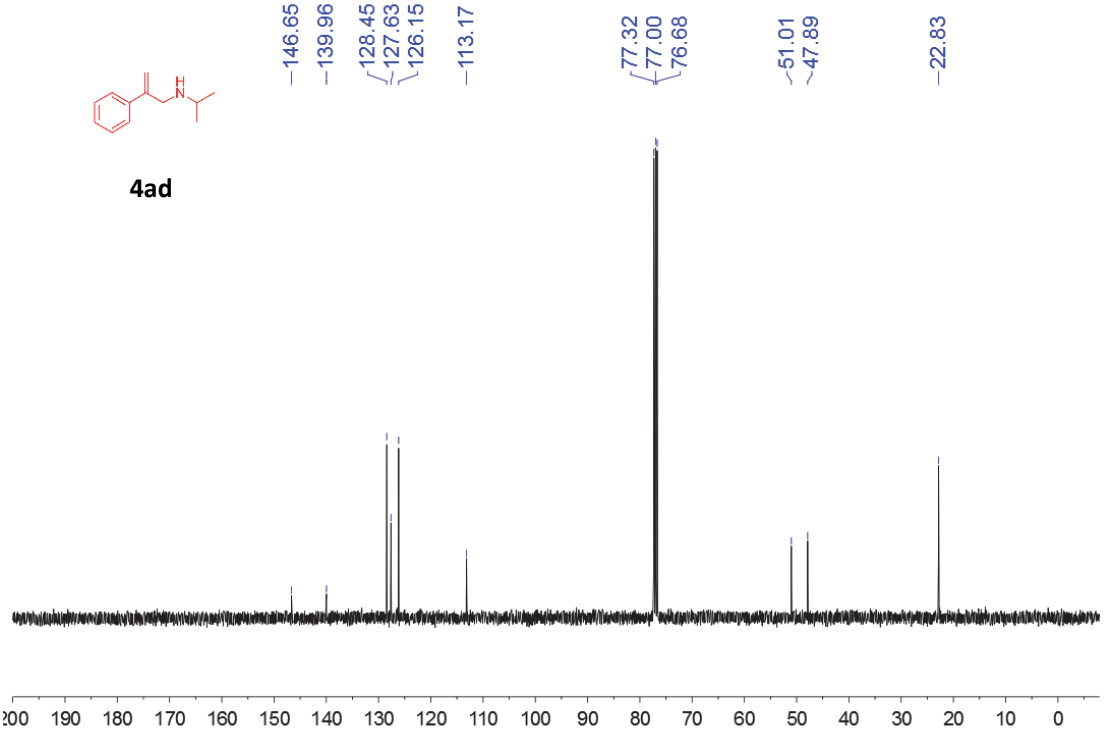
the ^{1}H and ^{13}C NMR spectra of **3ad**



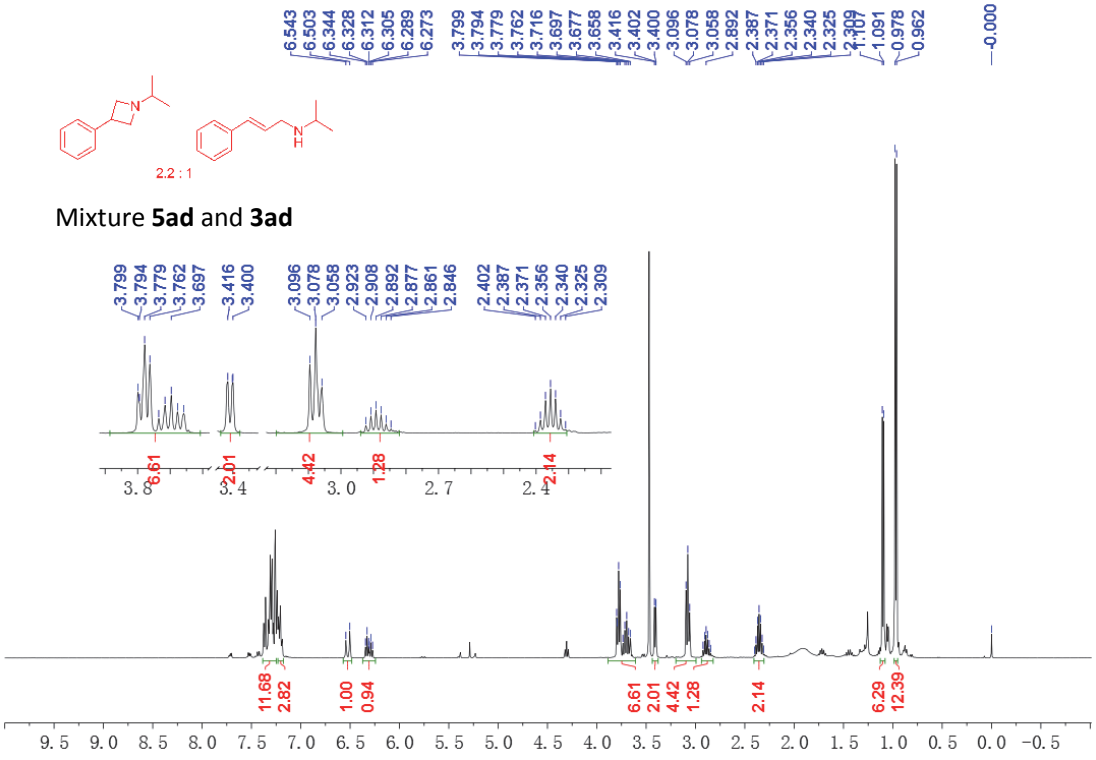


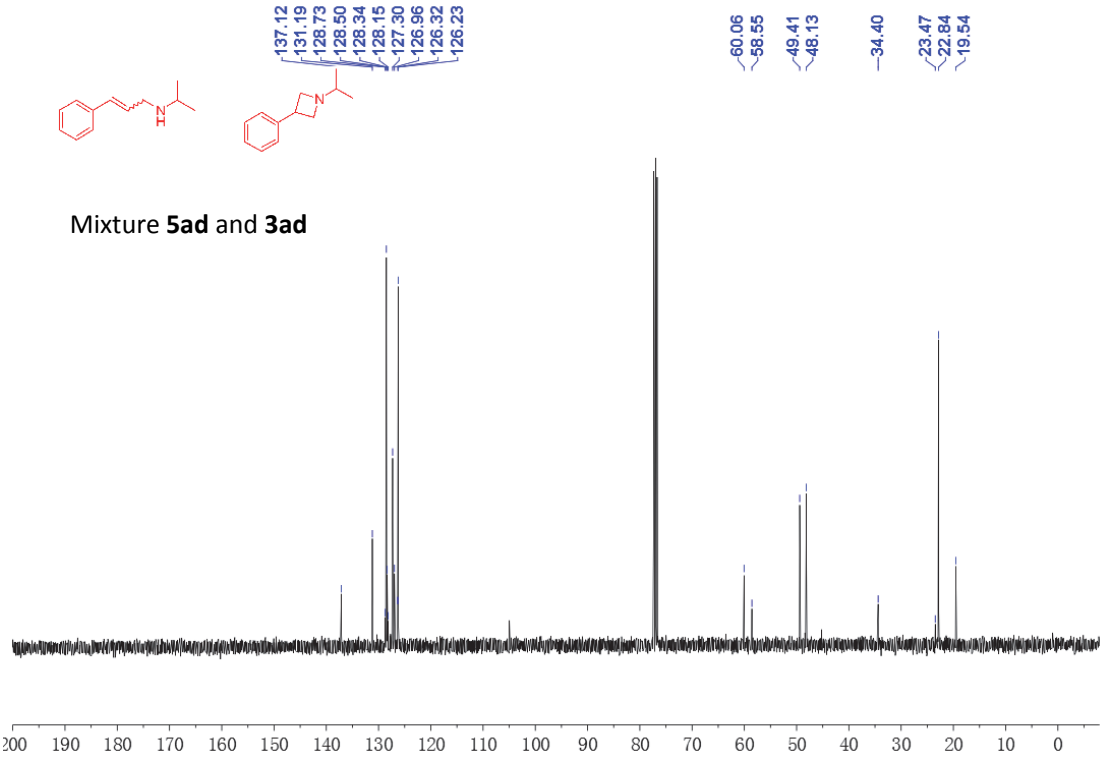
the ^{1}H and ^{13}C NMR spectra of **4ad**



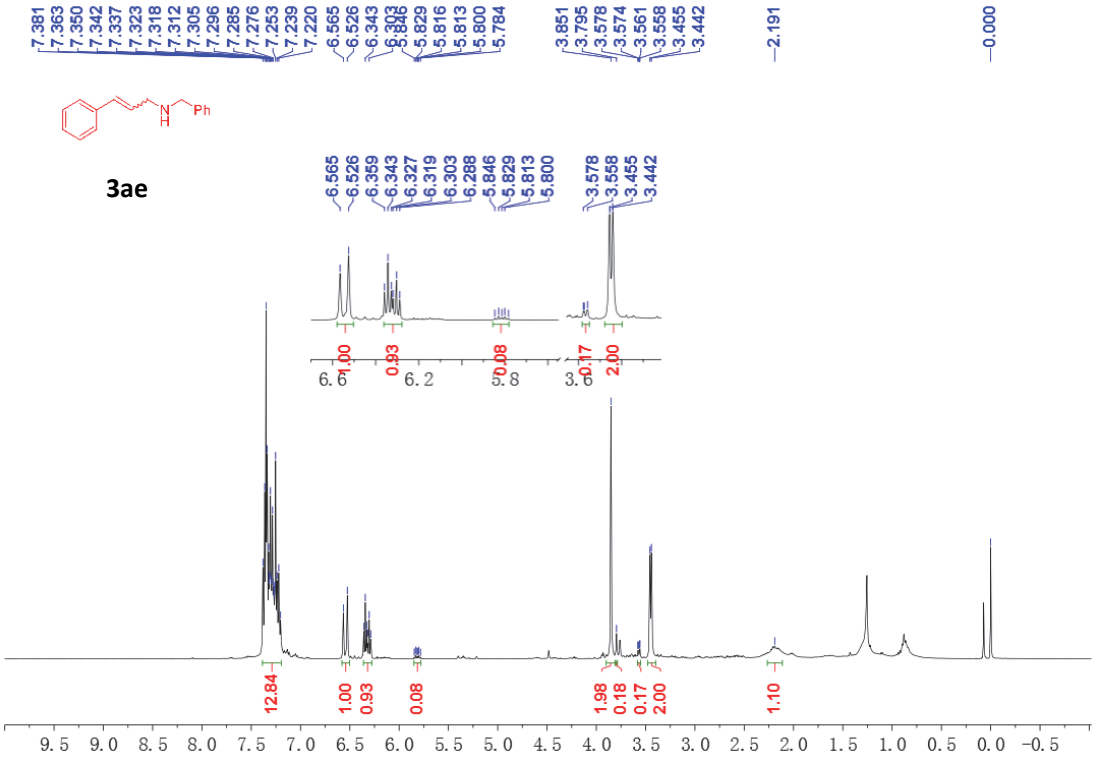


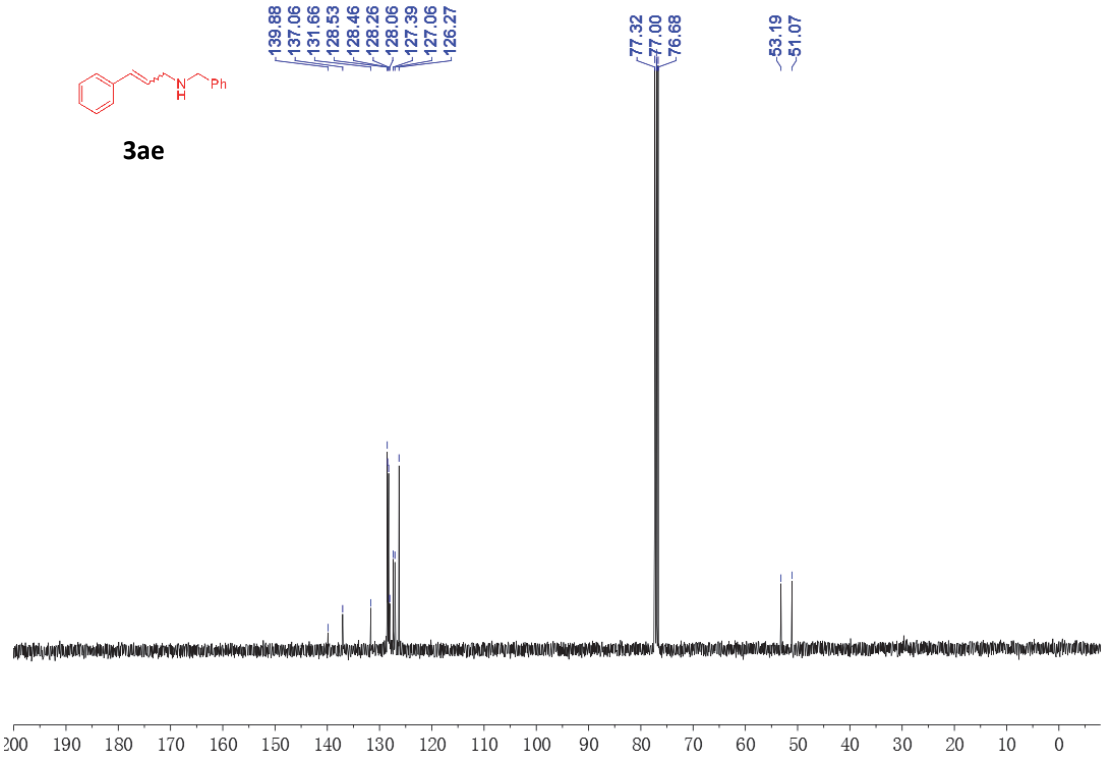
the ^{1}H and ^{13}C NMR spectra of mixture **5ad** and **3ad**



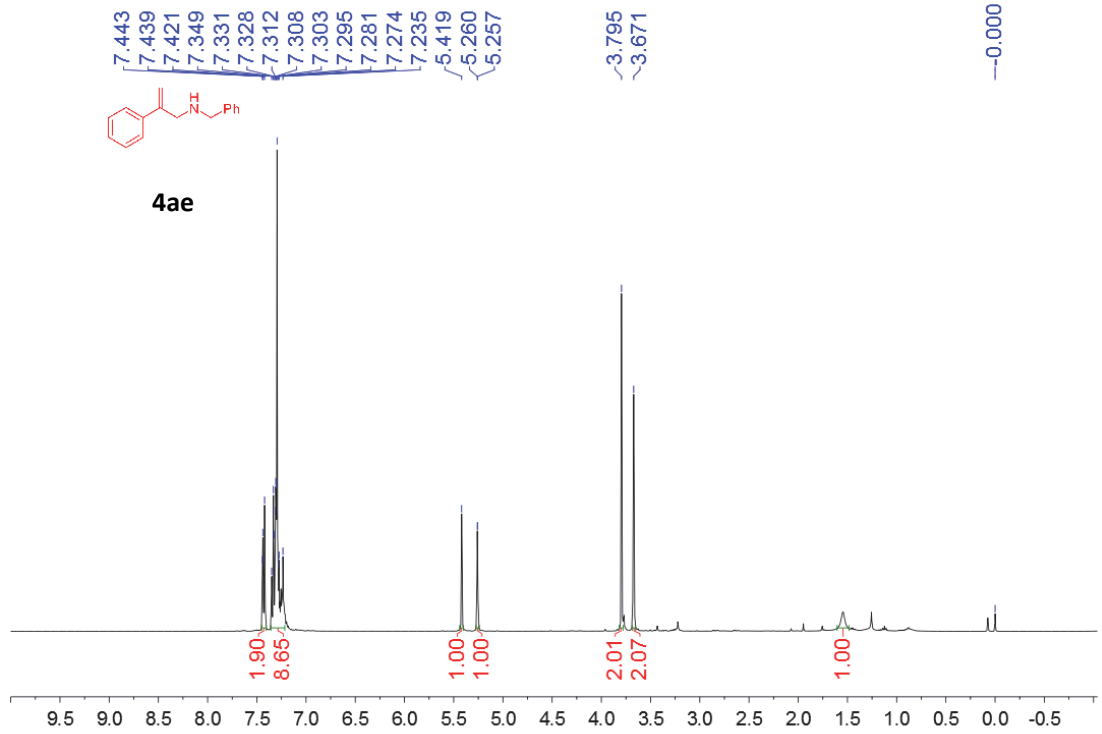


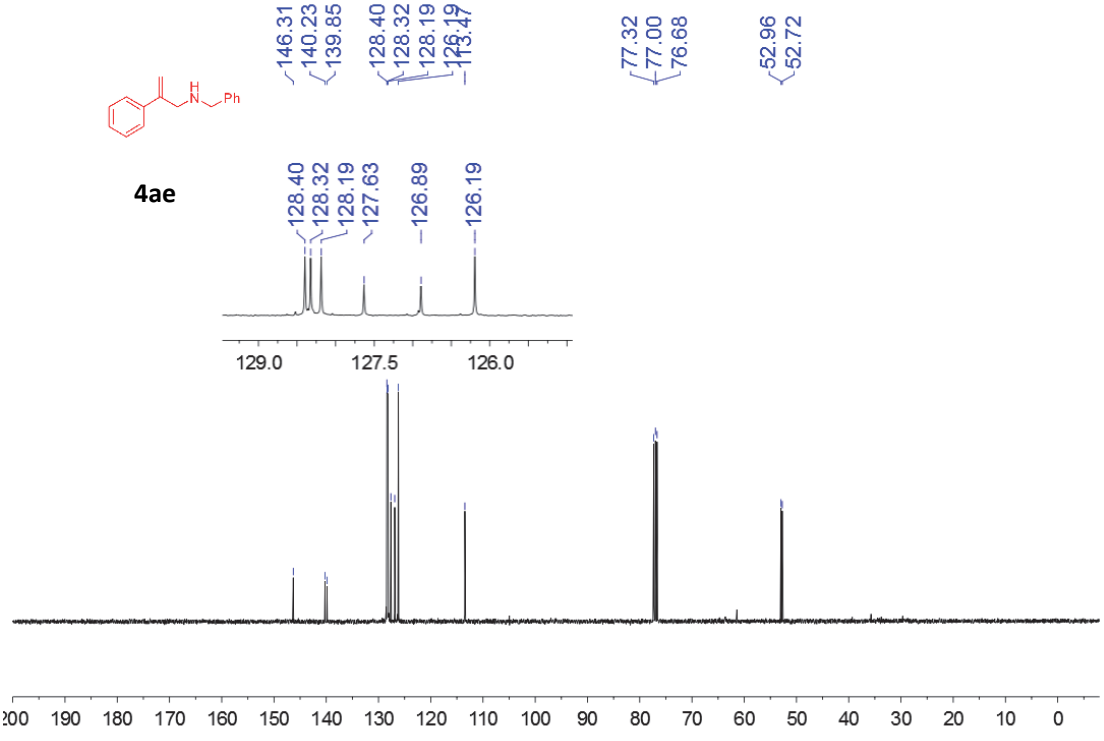
the ^{1}H and ^{13}C NMR spectra of **3ae**



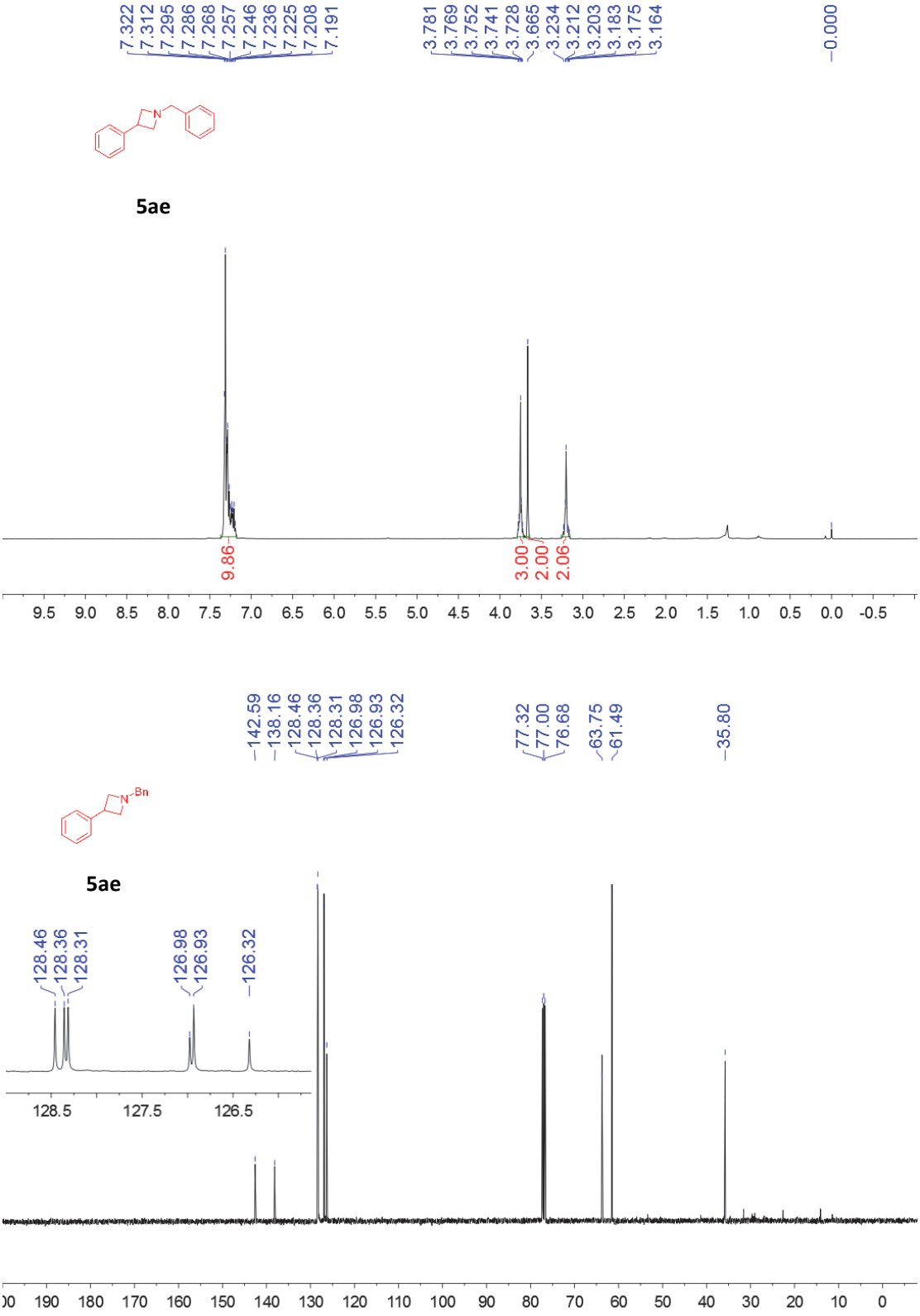


the ^{1}H and ^{13}C NMR spectra of **4ae**

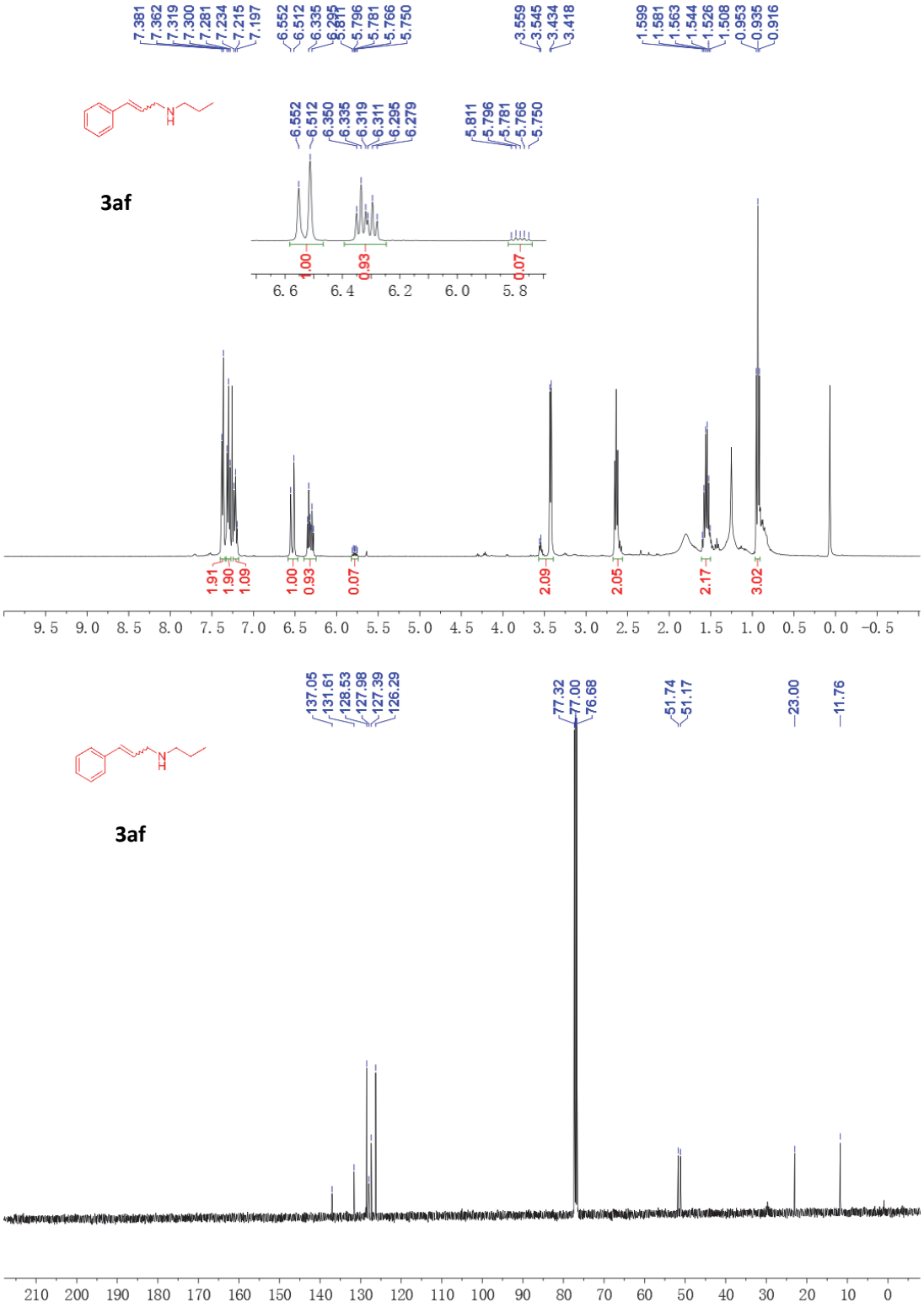




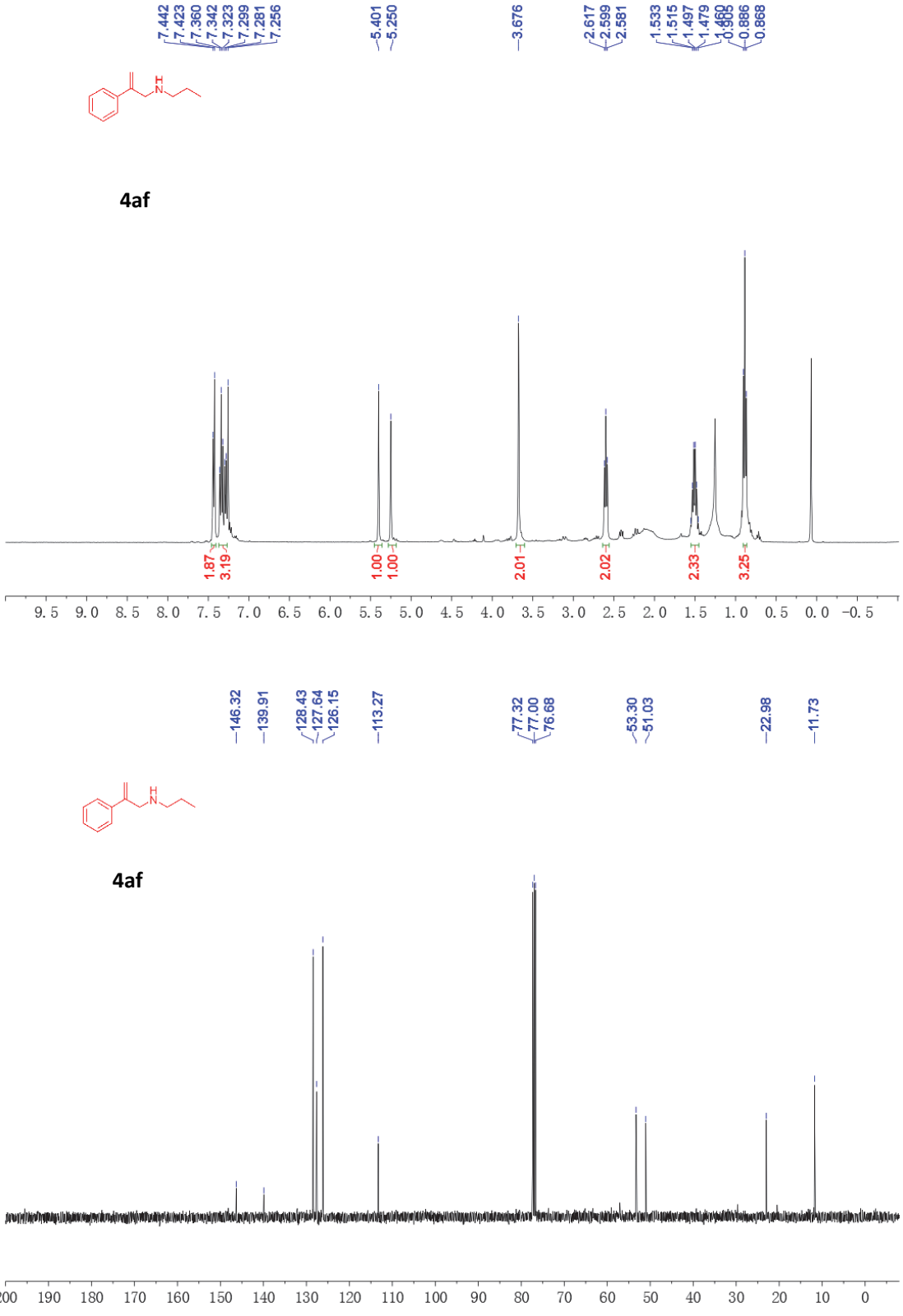
the ^{1}H and ^{13}C NMR spectra of **5ae**



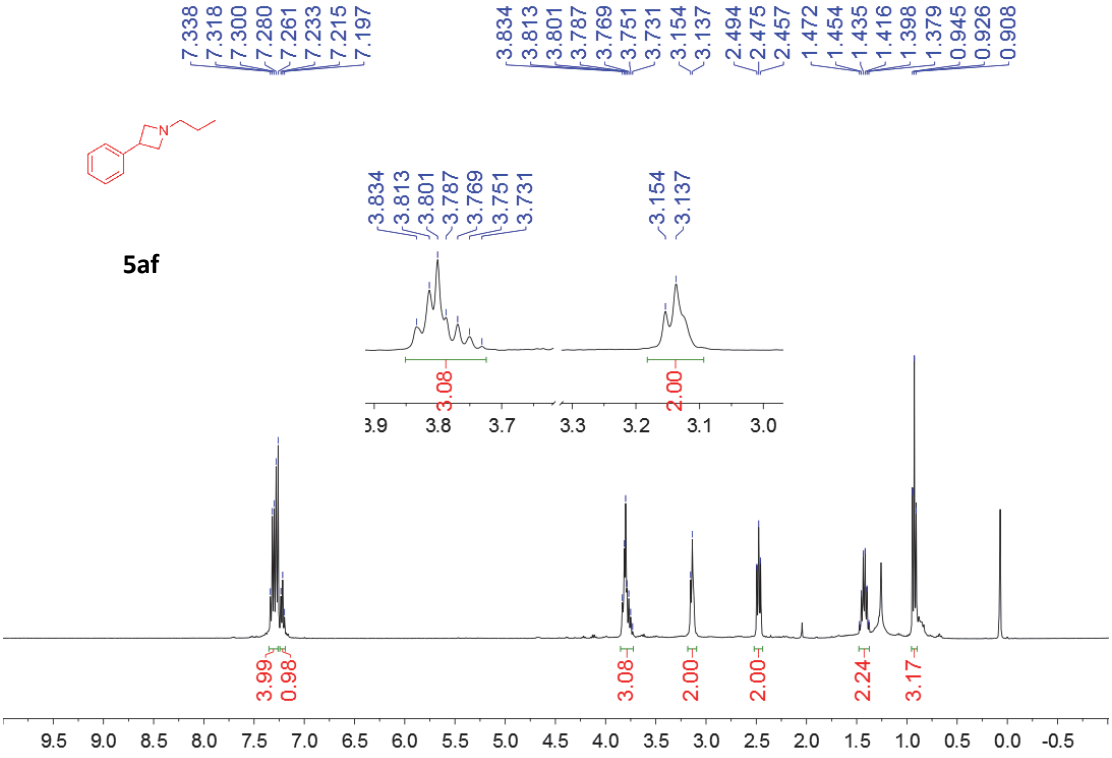
the ^{1}H and ^{13}C NMR spectra of **3af**

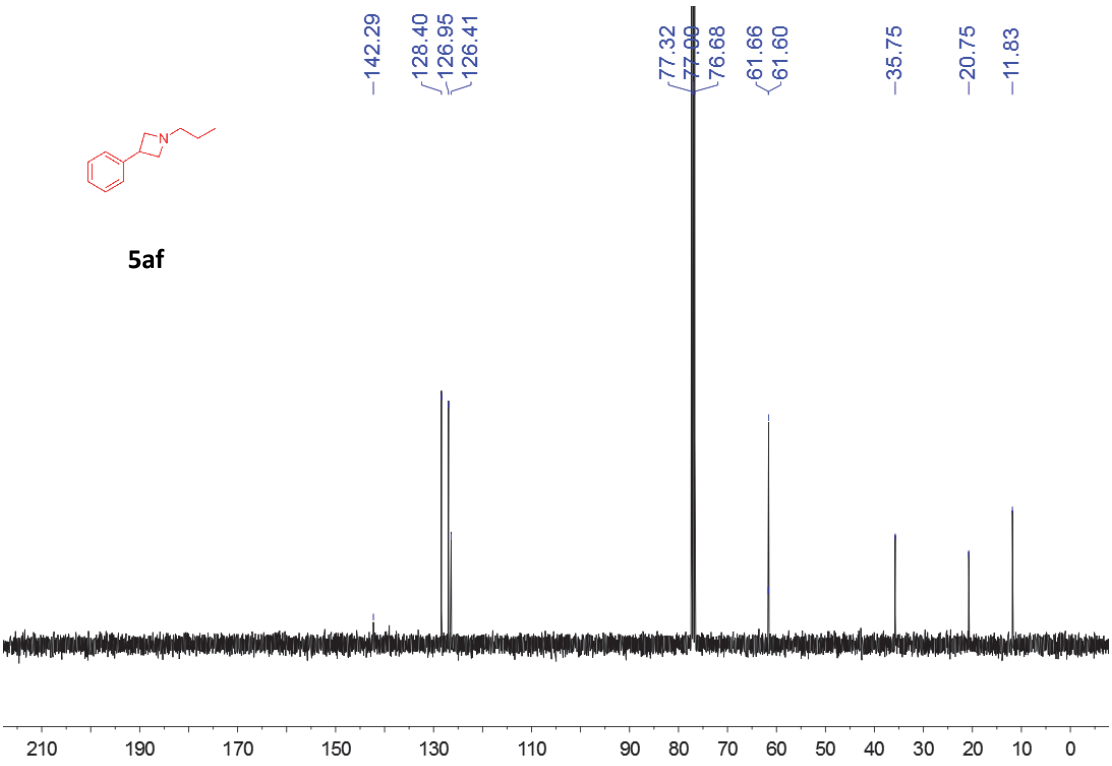


the ^{1}H and ^{13}C NMR spectra of **4af**

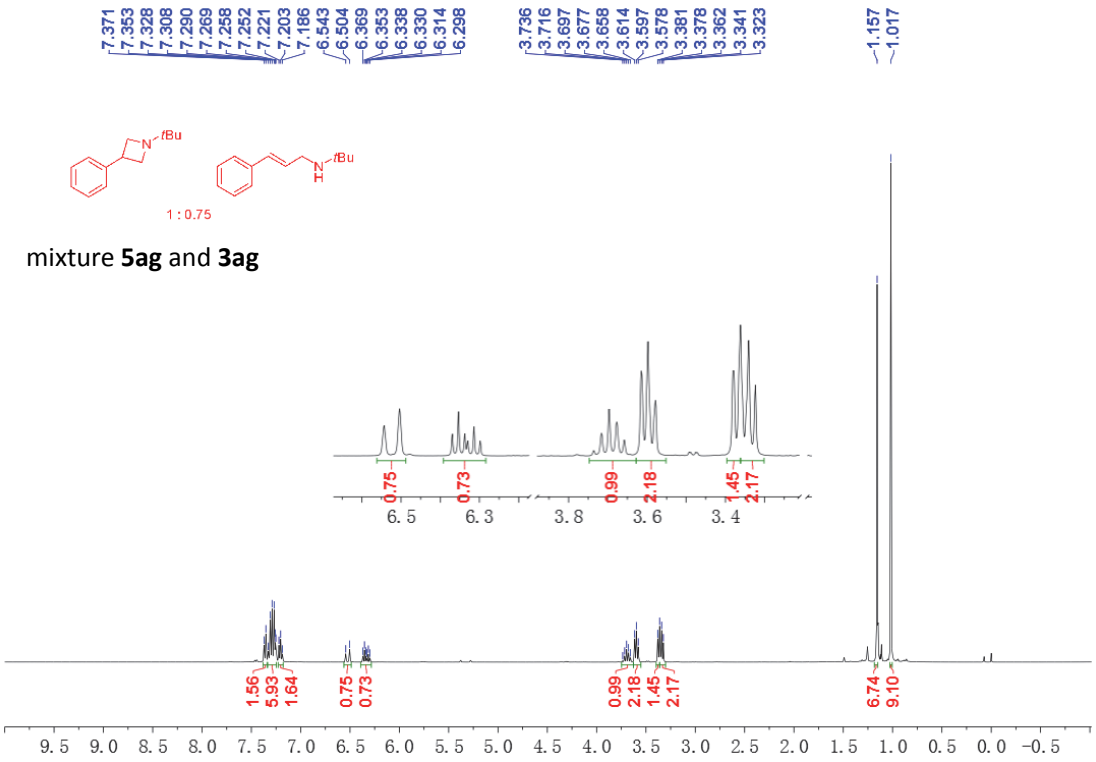


the ^{1}H and ^{13}C NMR spectra of **5af**

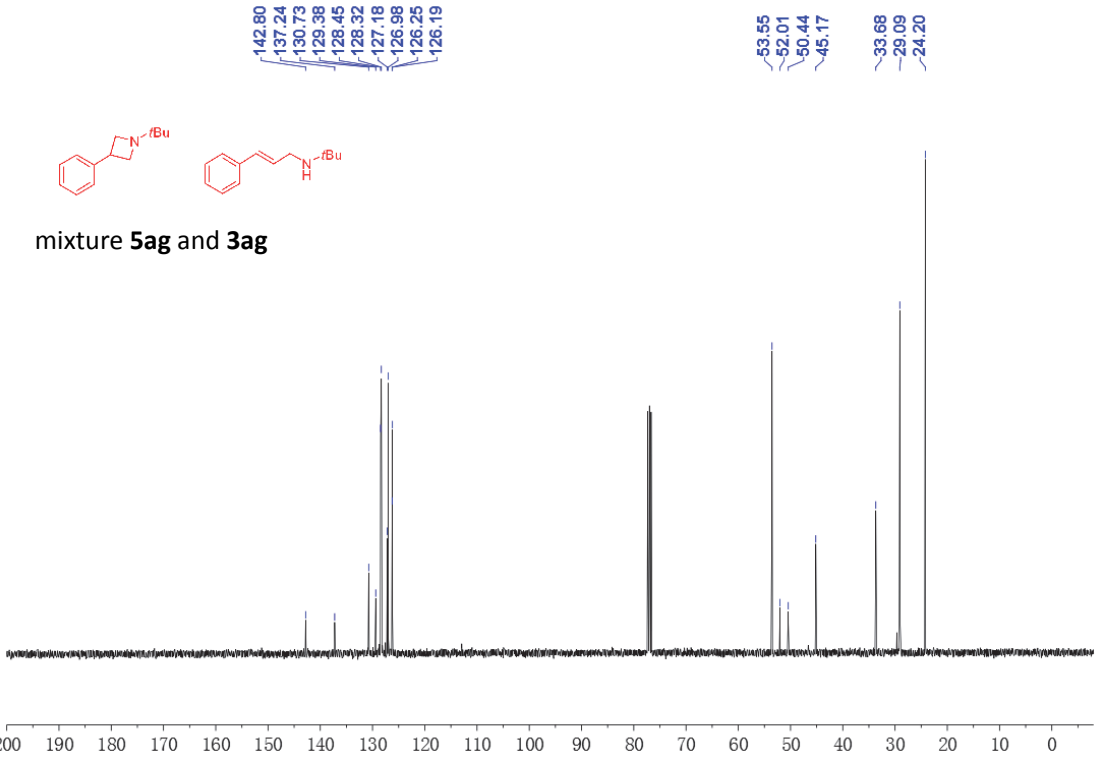




the ^{1}H and ^{13}C NMR spectra of mixture **5ag** and **3ag**

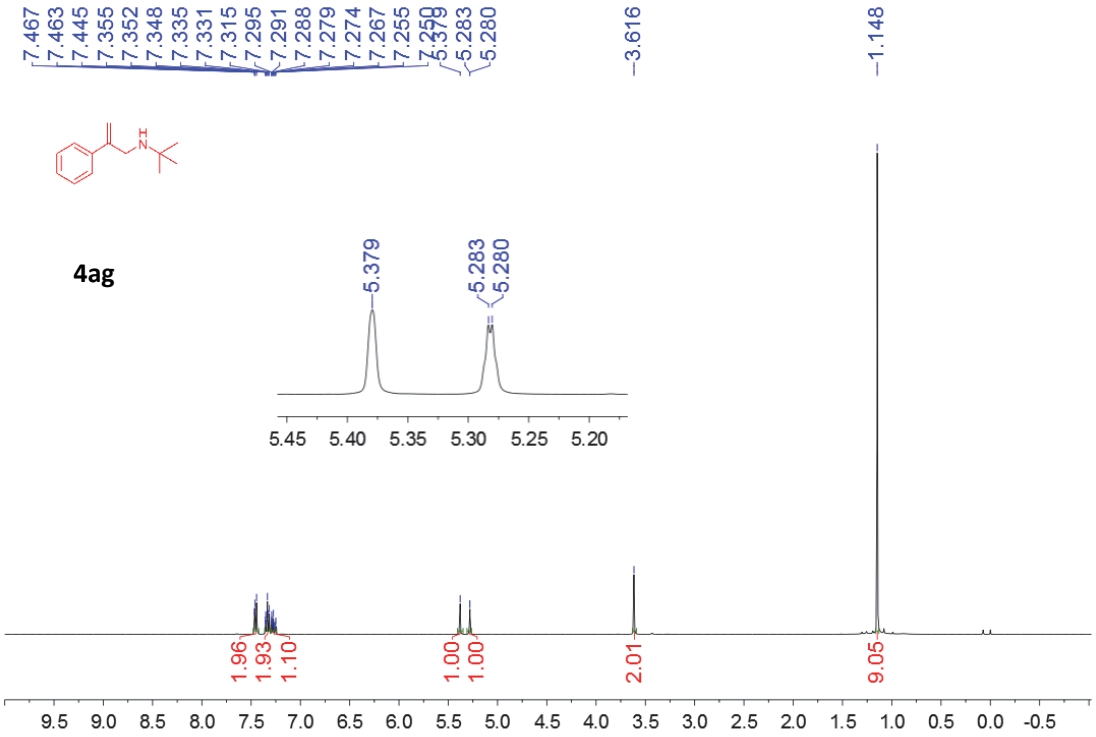


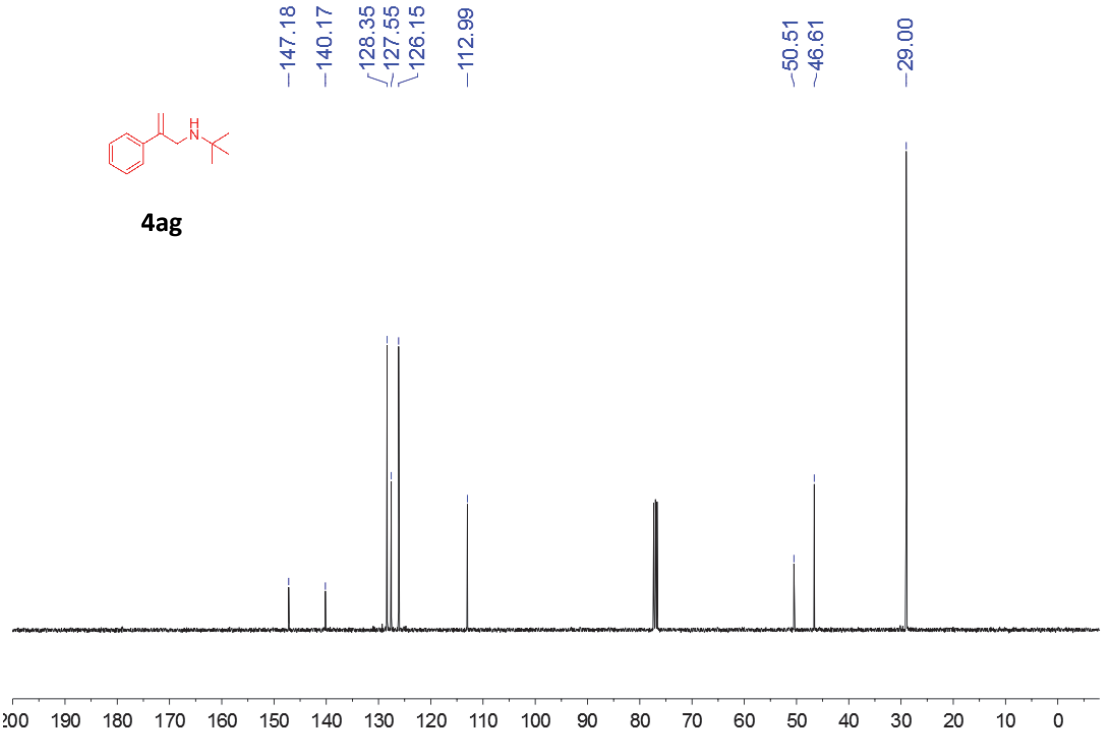
mixture **5ag** and **3ag**



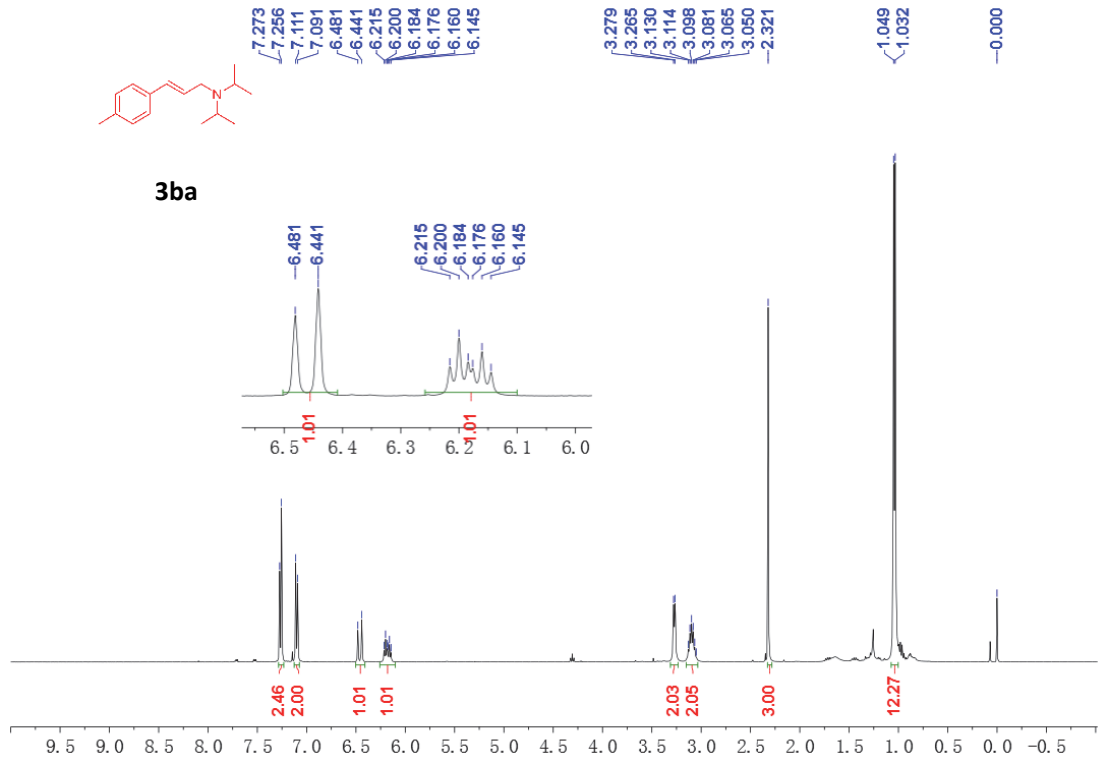
mixture **5ag** and **3ag**

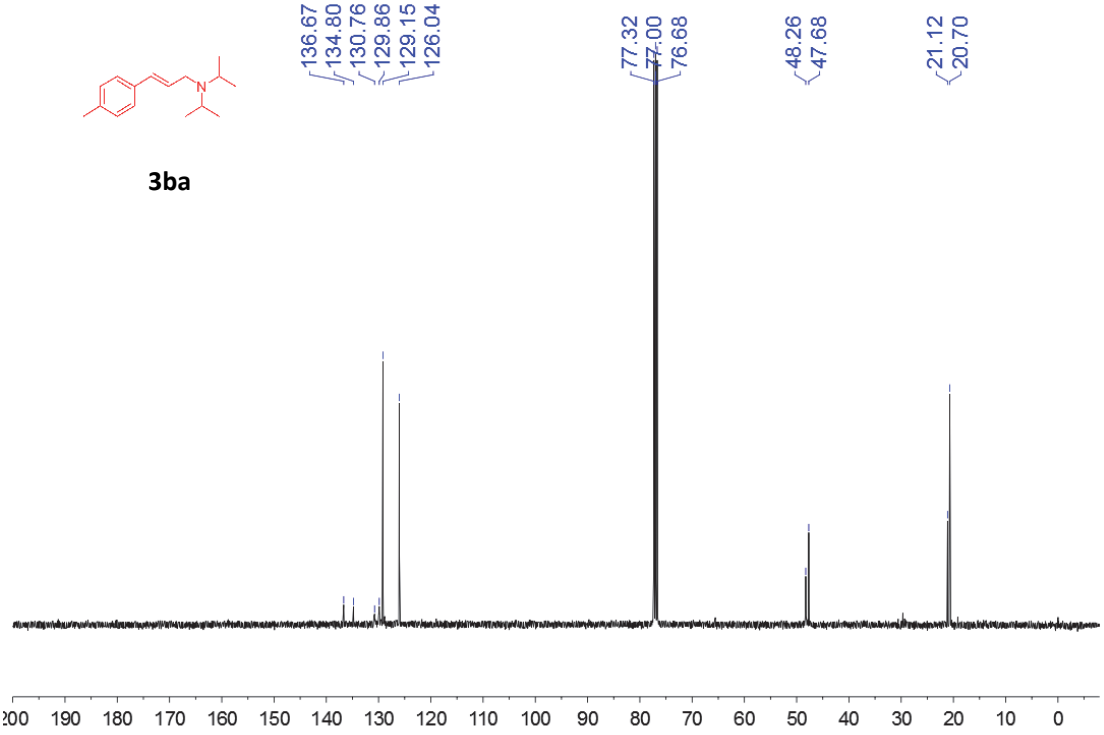
the ^{1}H and ^{13}C NMR spectra of **4ag**



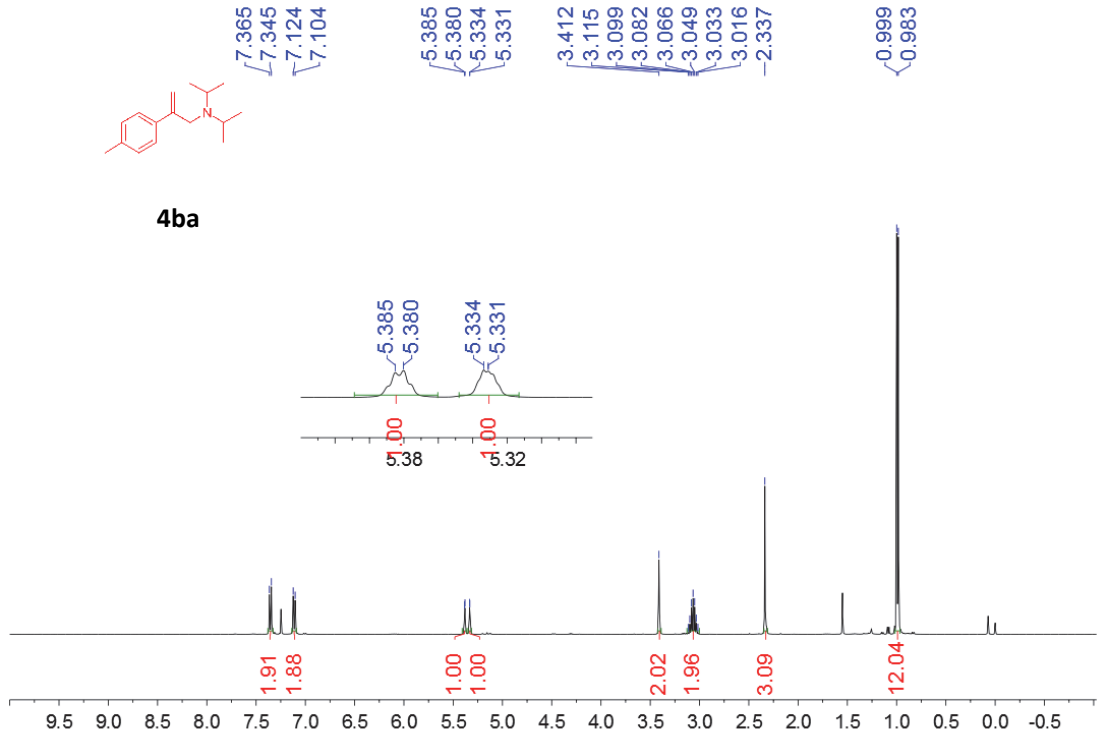


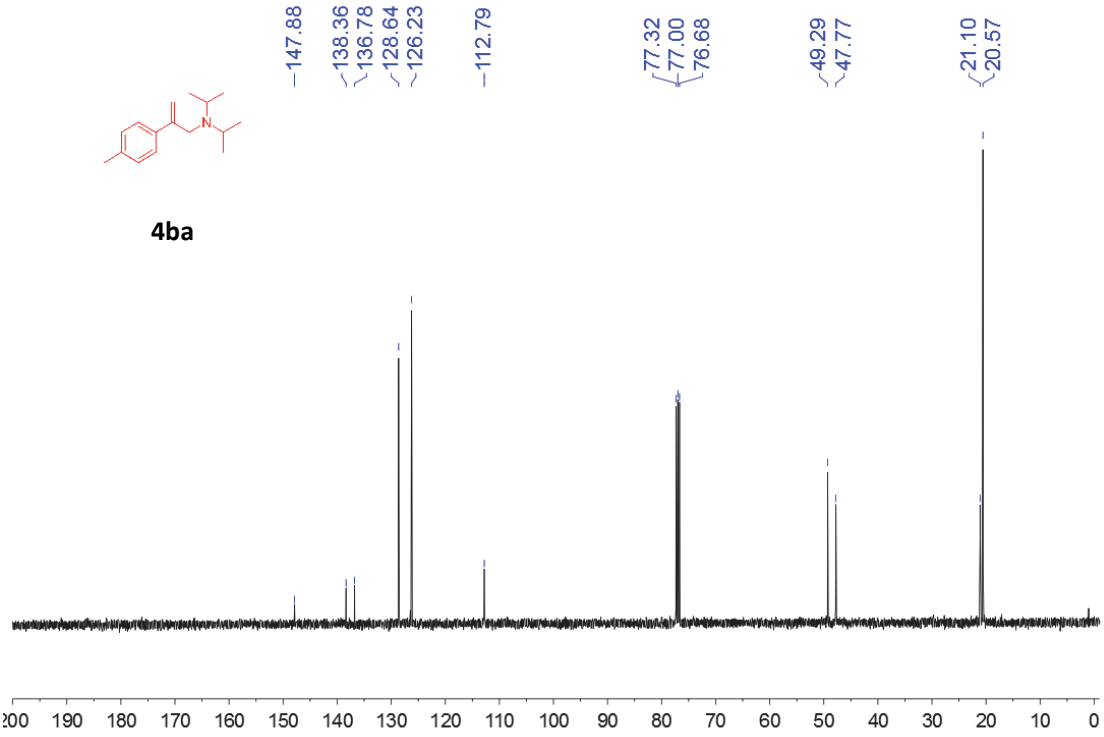
the ^{1}H and ^{13}C NMR spectra of **3ba**



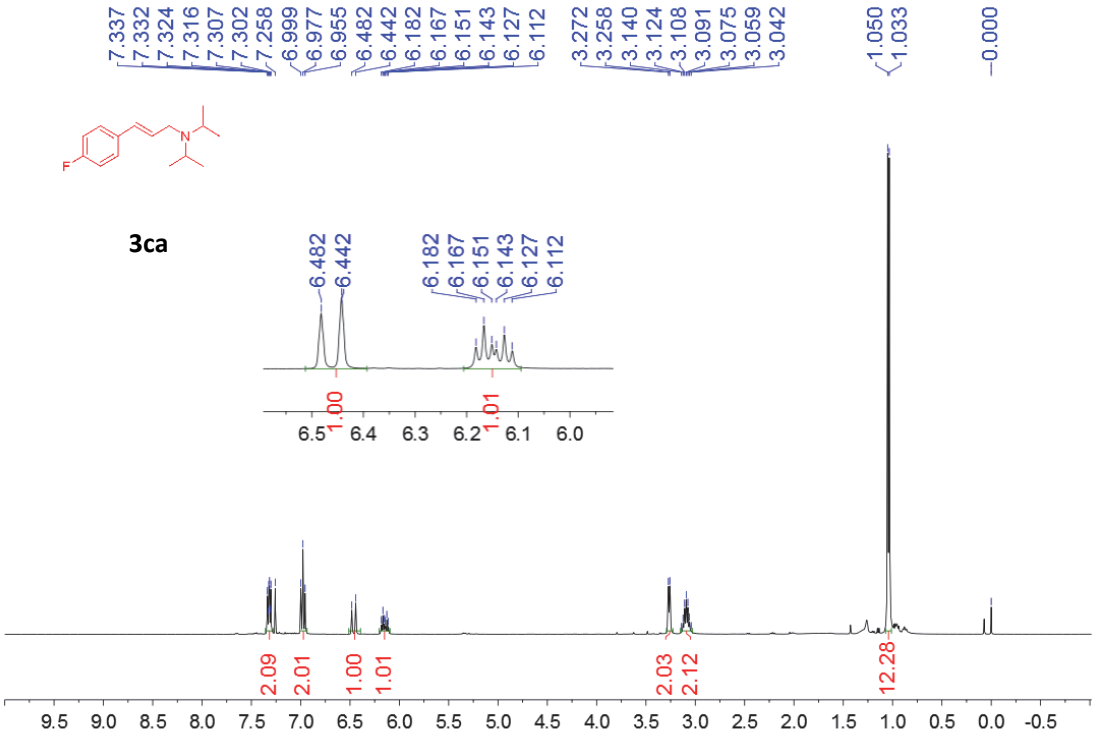


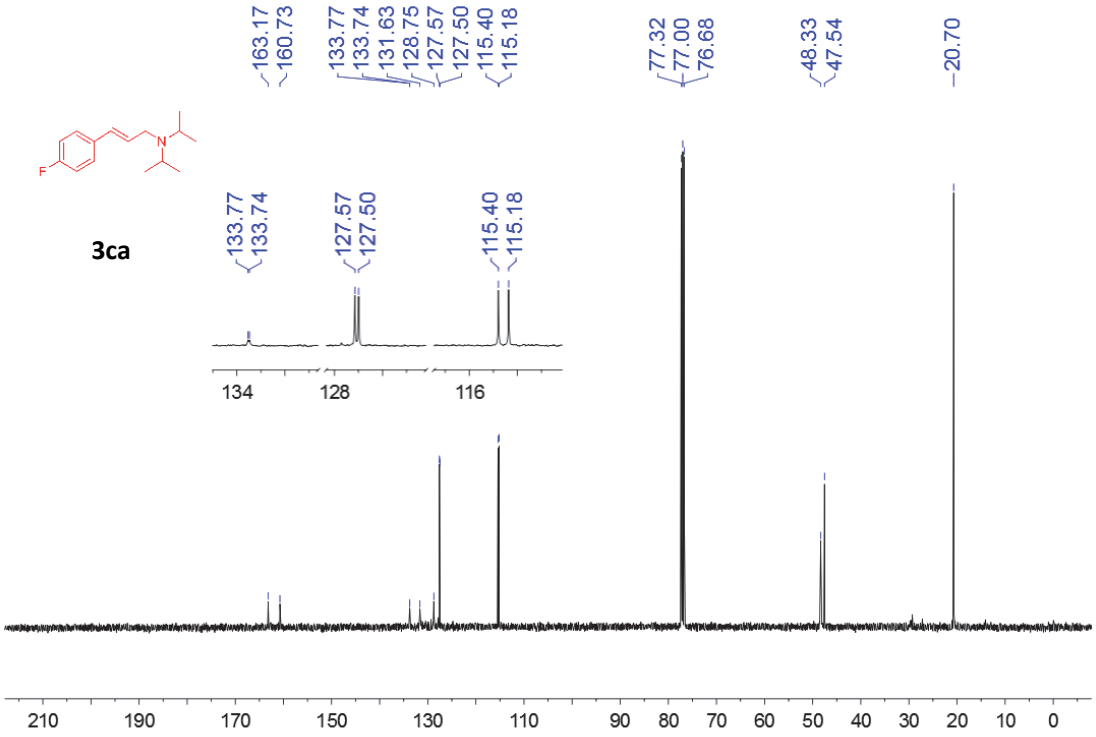
the ^{1}H and ^{13}C NMR spectra of **4ba**

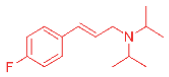




the ^{1}H, ^{13}C and ^{19}F NMR spectra of **3ca**

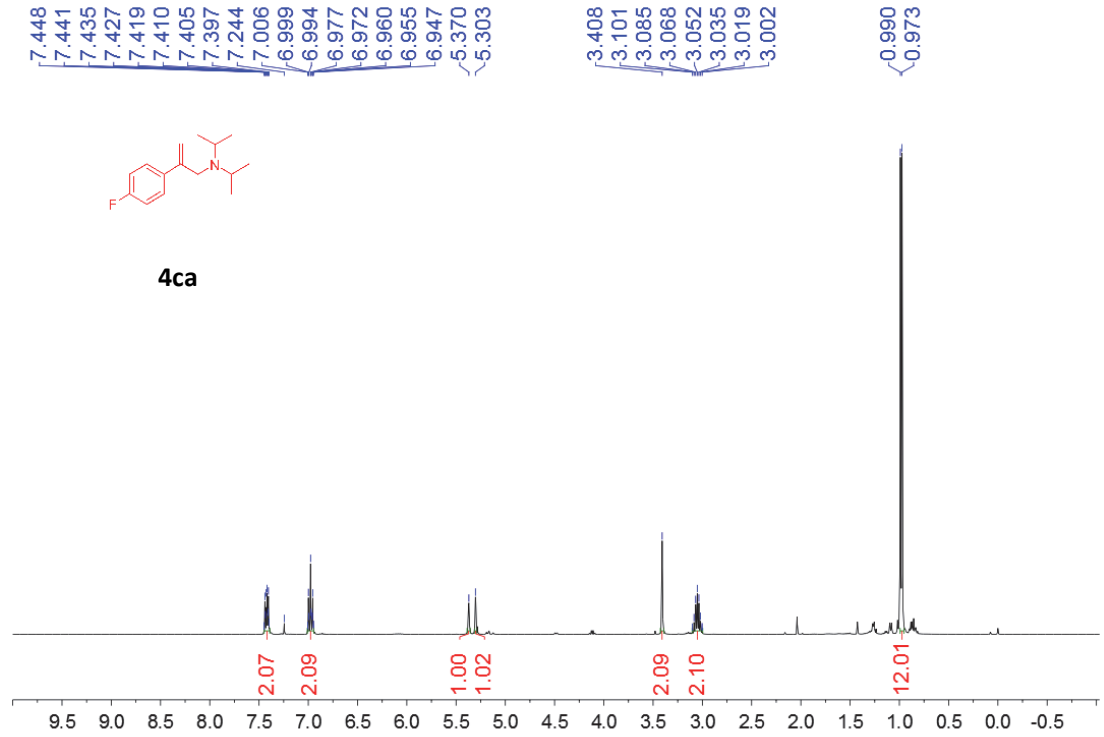


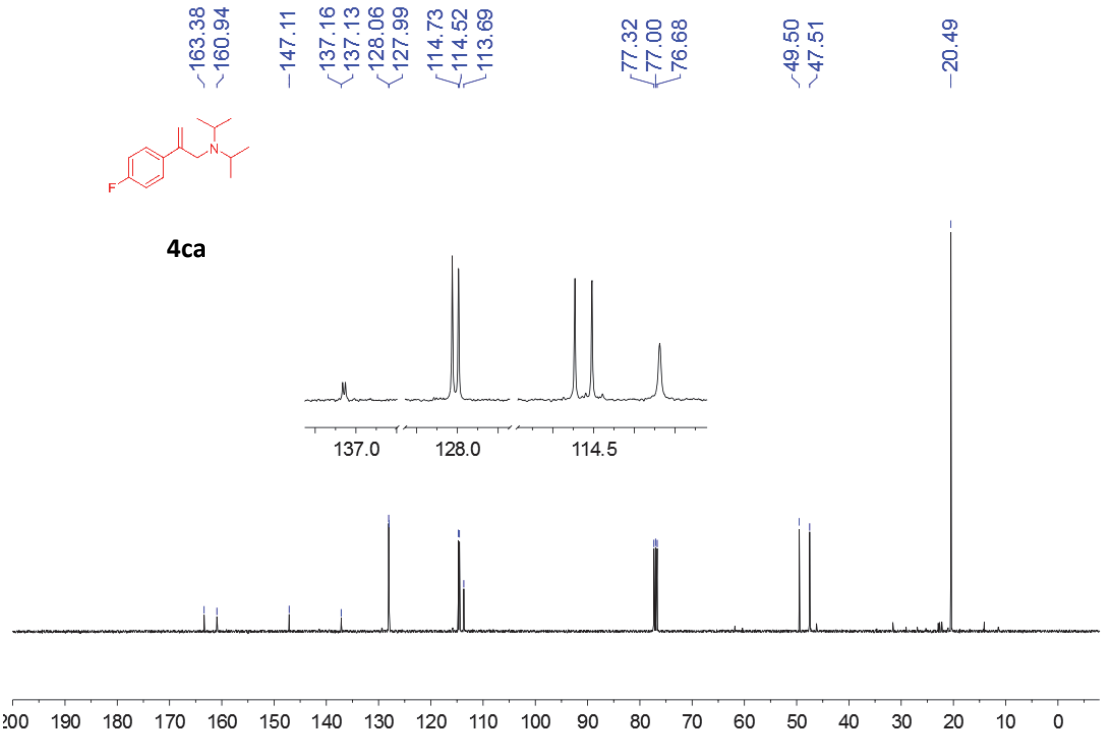


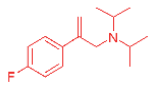


3ca

the ^{1}H, ^{13}C and ^{19}F NMR spectra of **4ca**

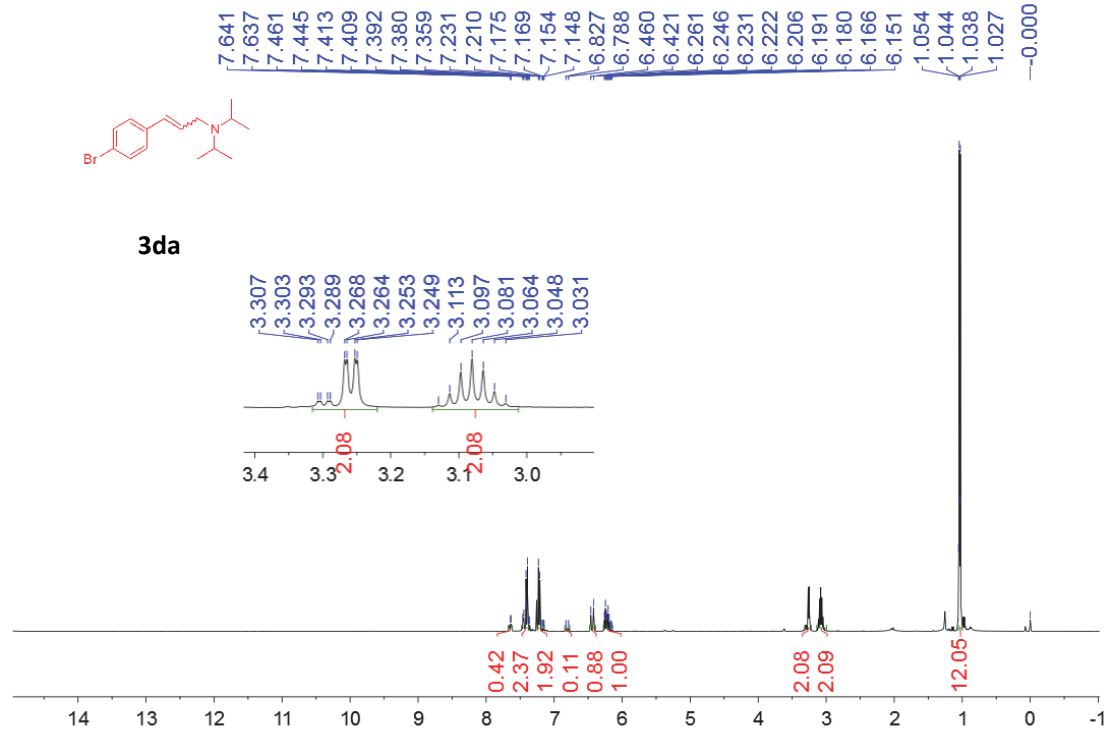


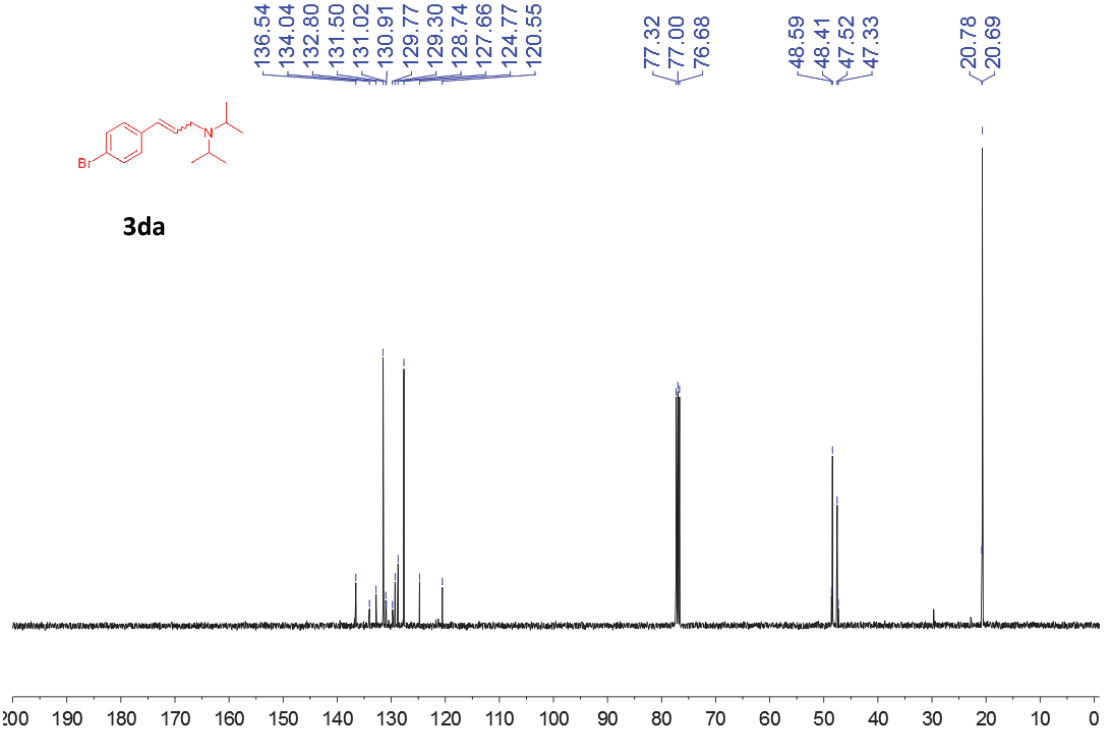




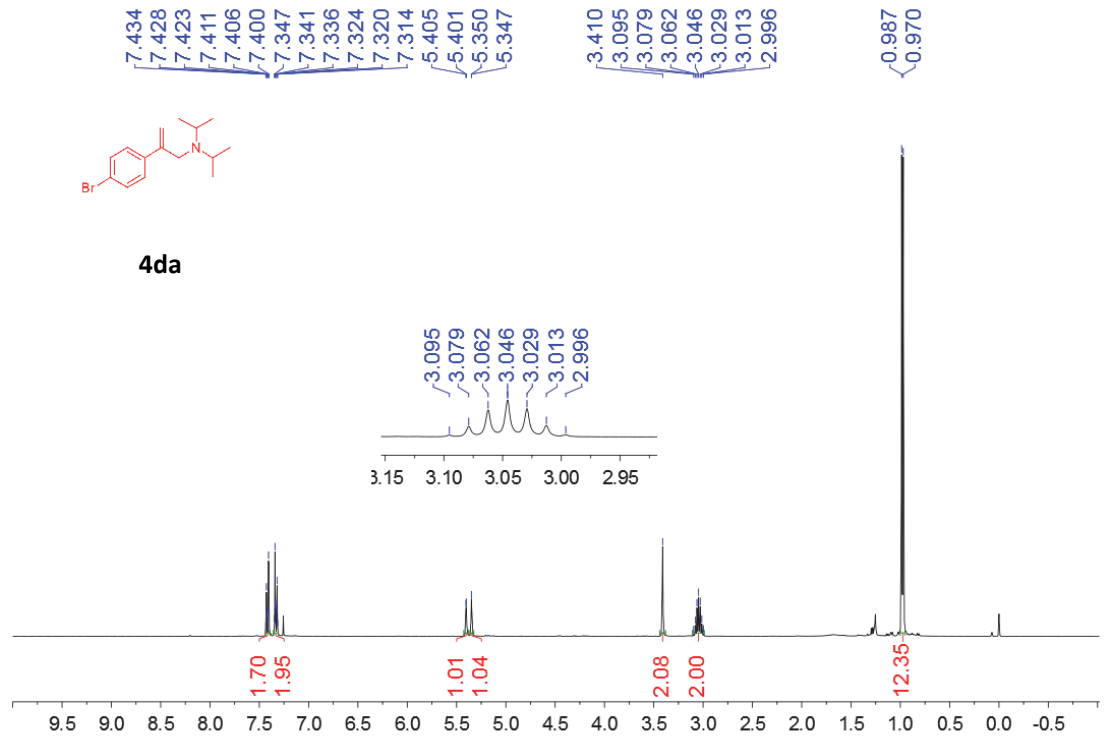
4ca

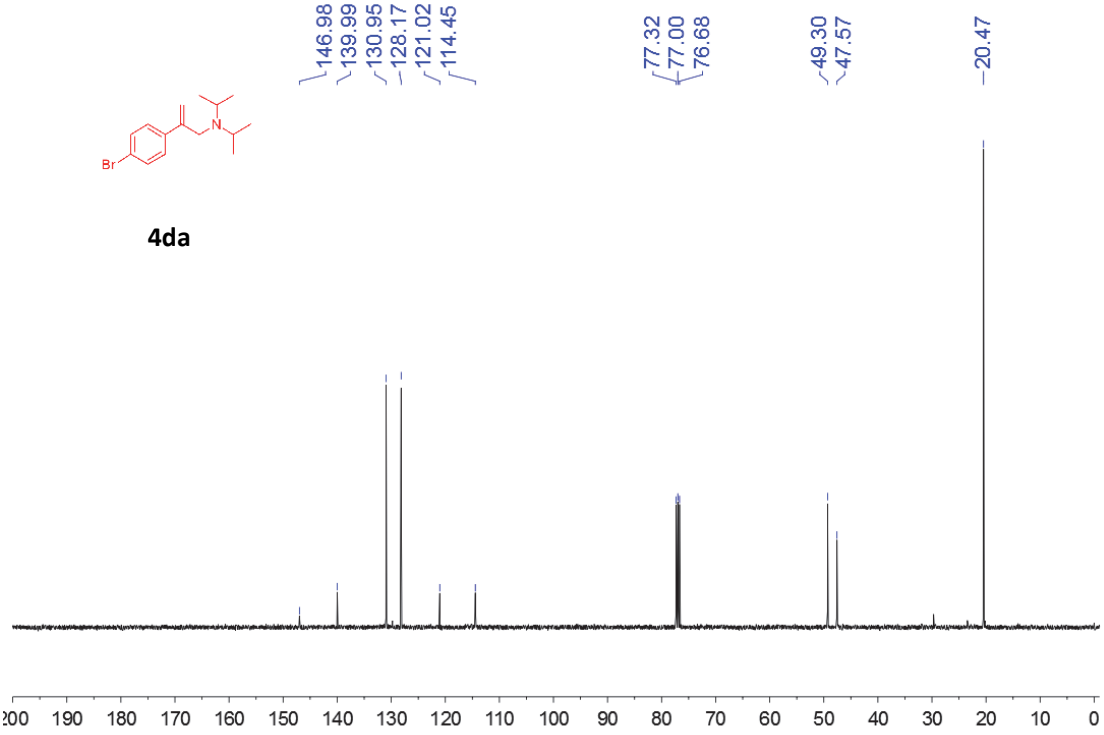
the ^{1}H and ^{13}C NMR spectra of **3da**



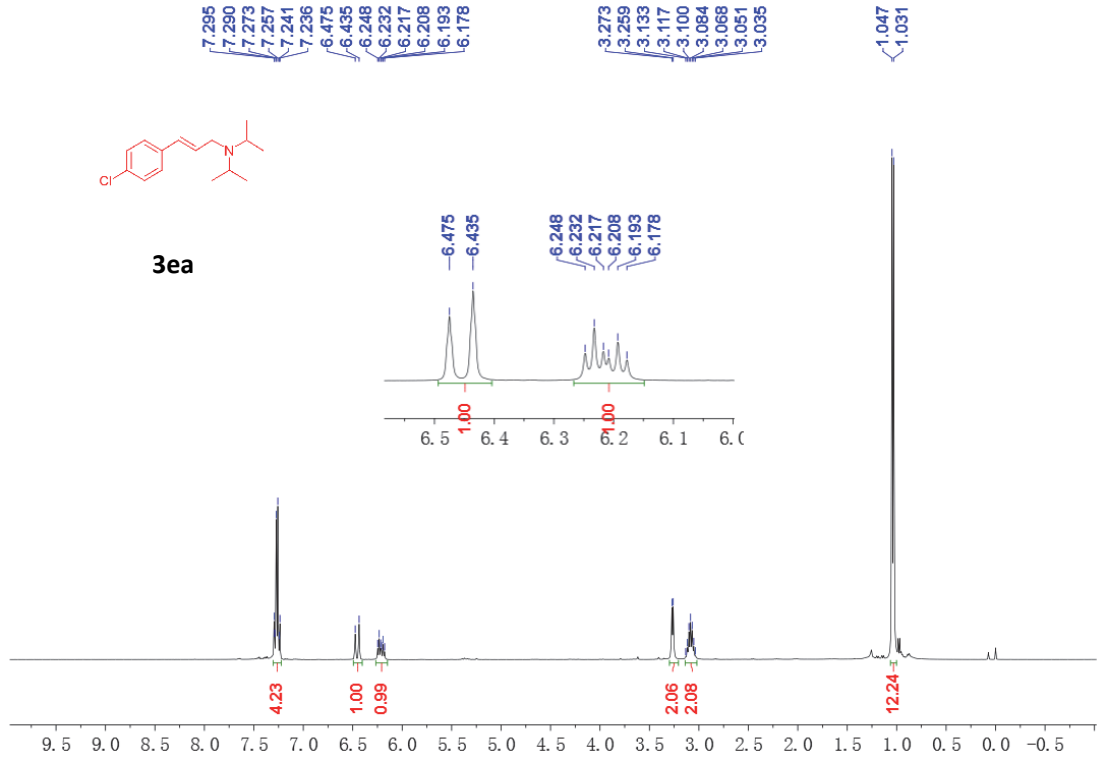


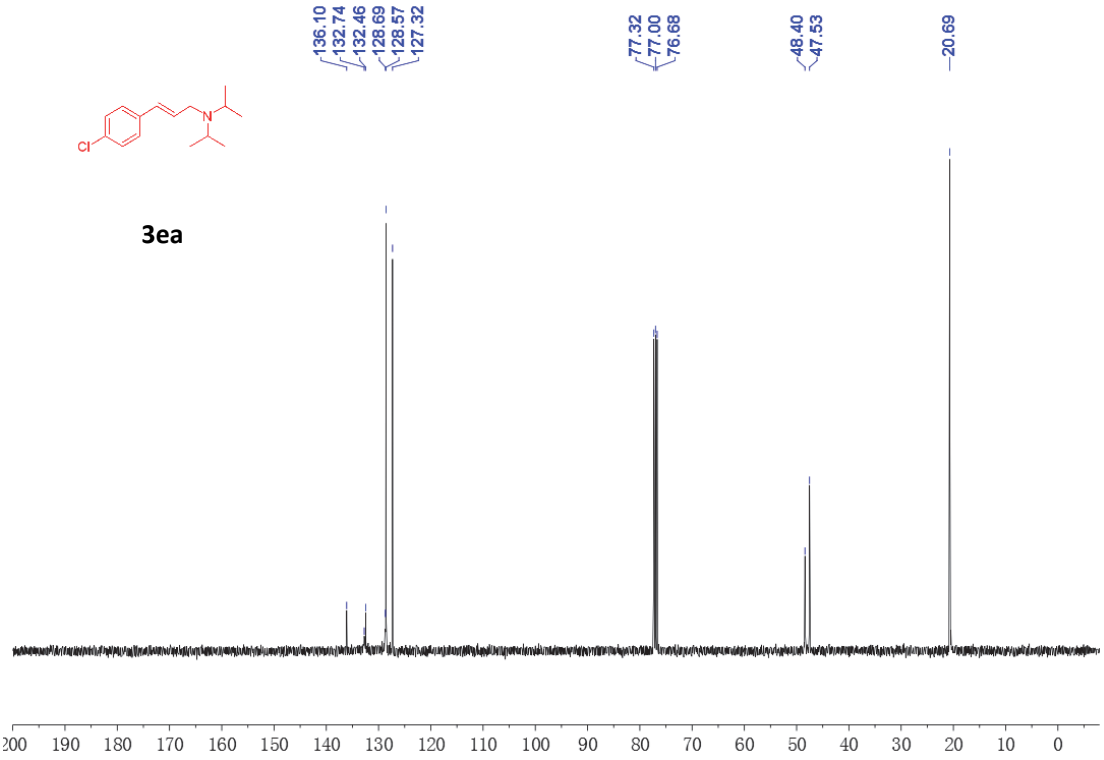
the ^{1}H and ^{13}C NMR spectra of **4da**



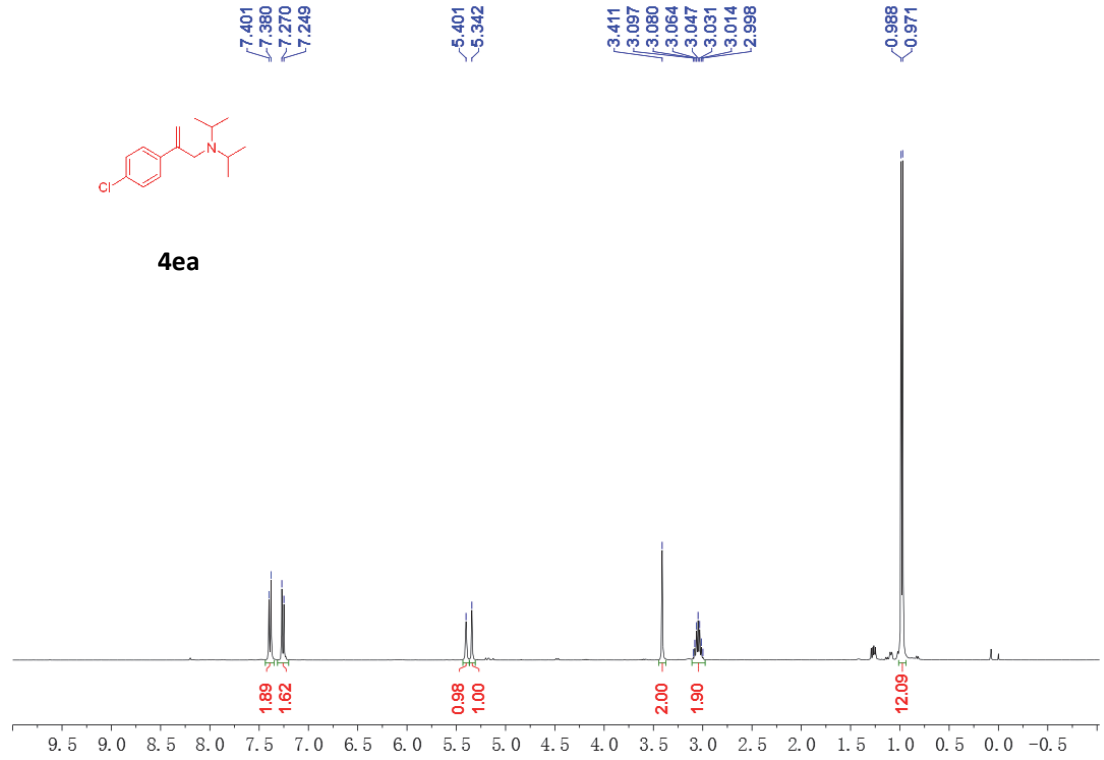


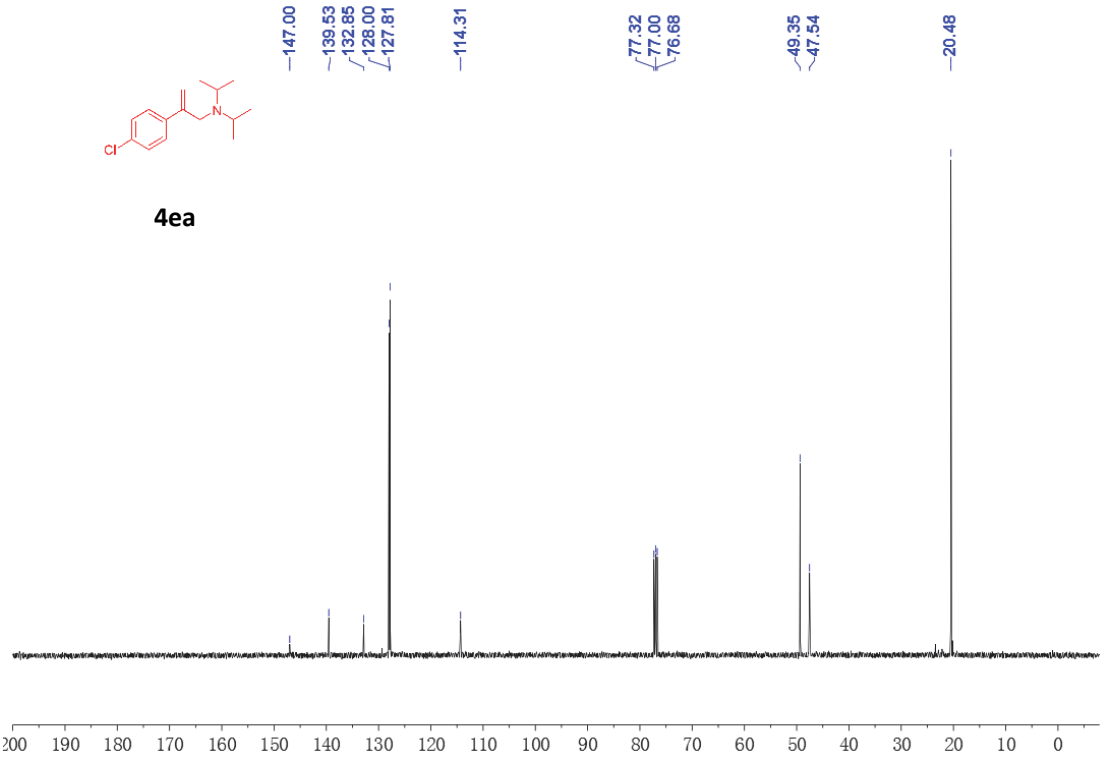
the ^{1}H and ^{13}C NMR spectra of **3ea**



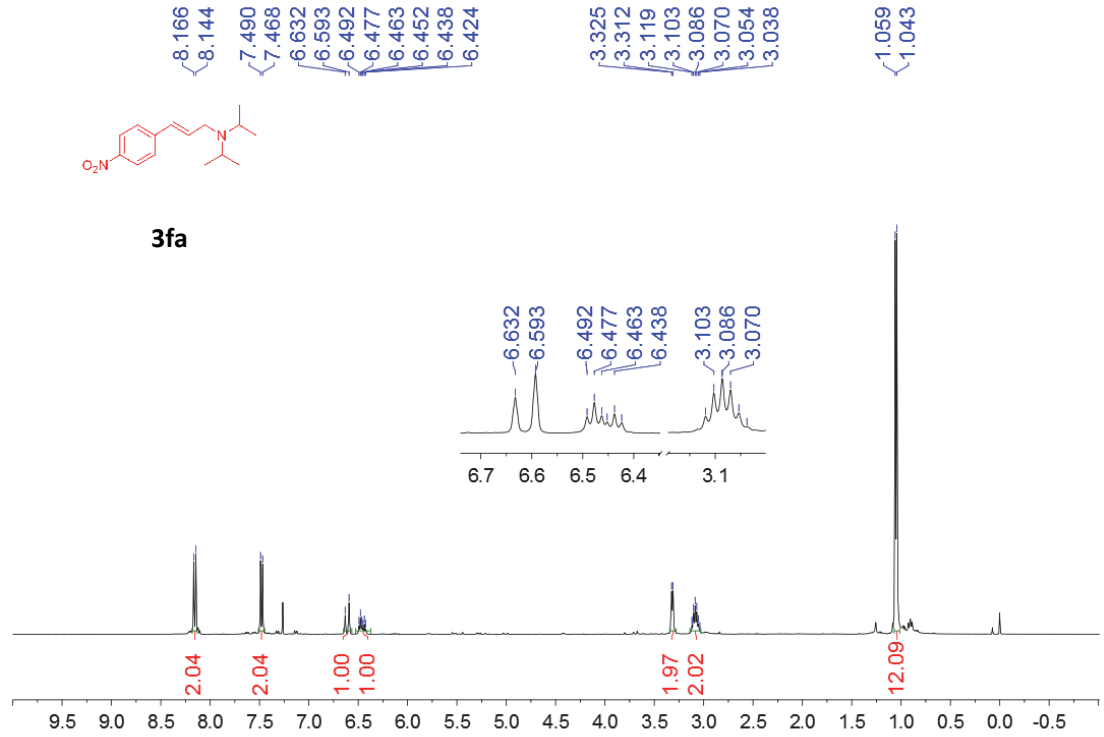


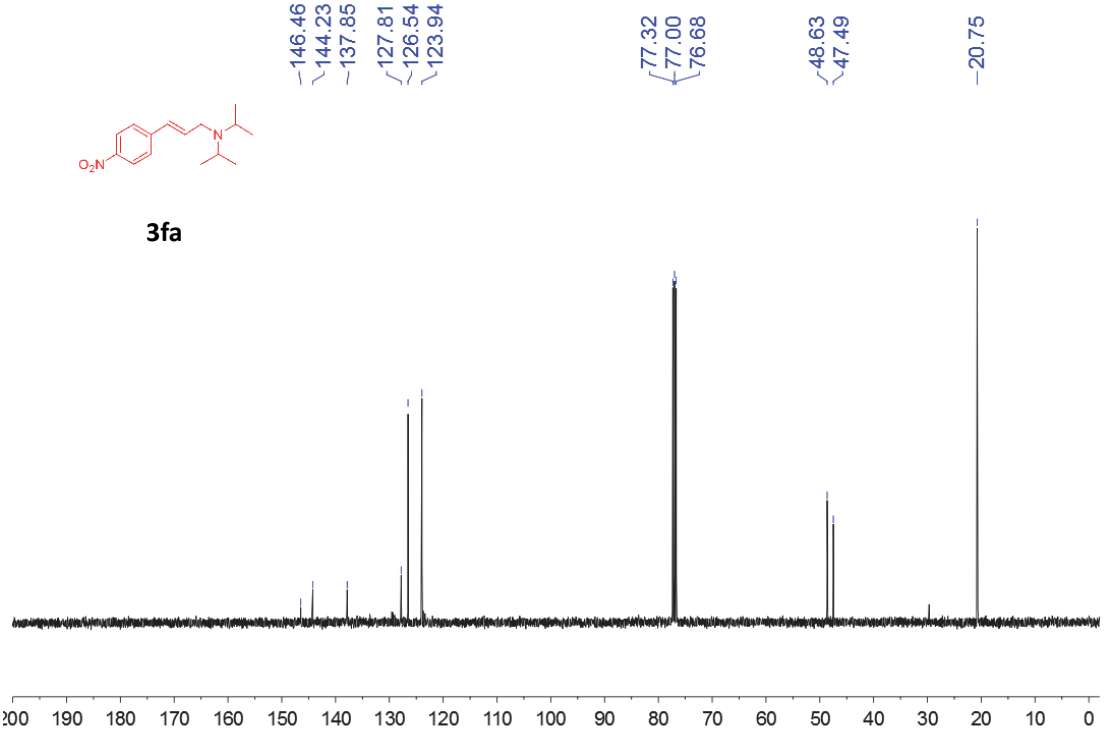
the ^{1}H and ^{13}C NMR spectra of **4ea**



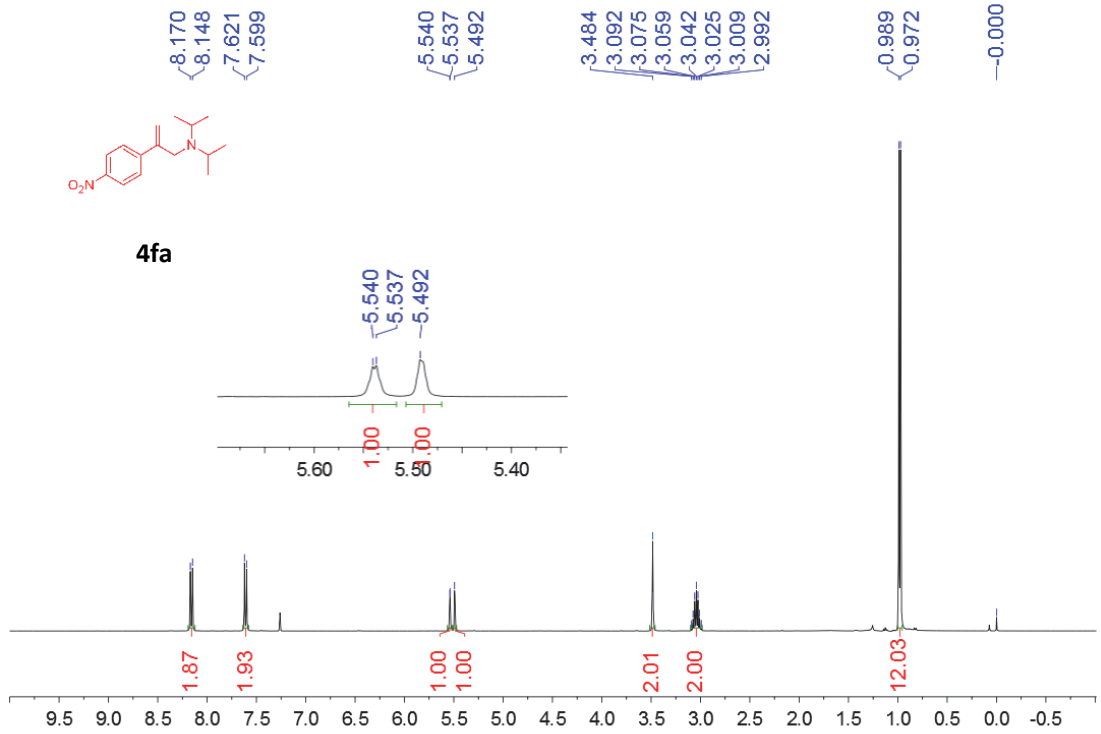


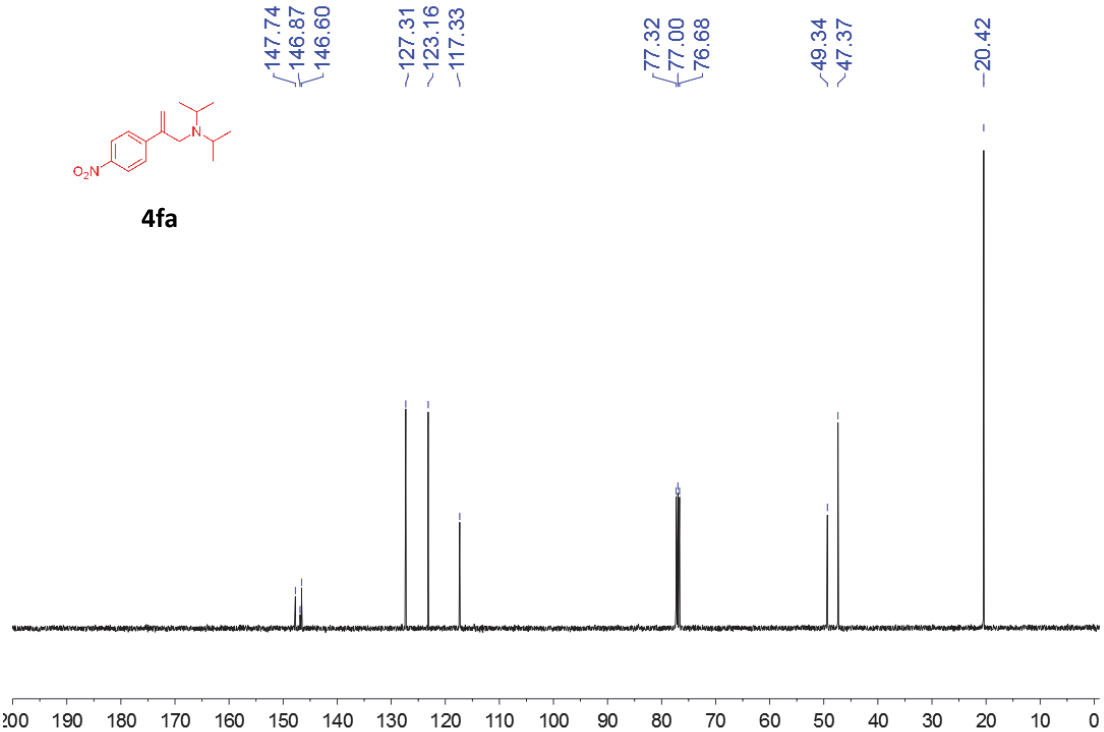
the ^{1}H and ^{13}C NMR spectra of **3fa**



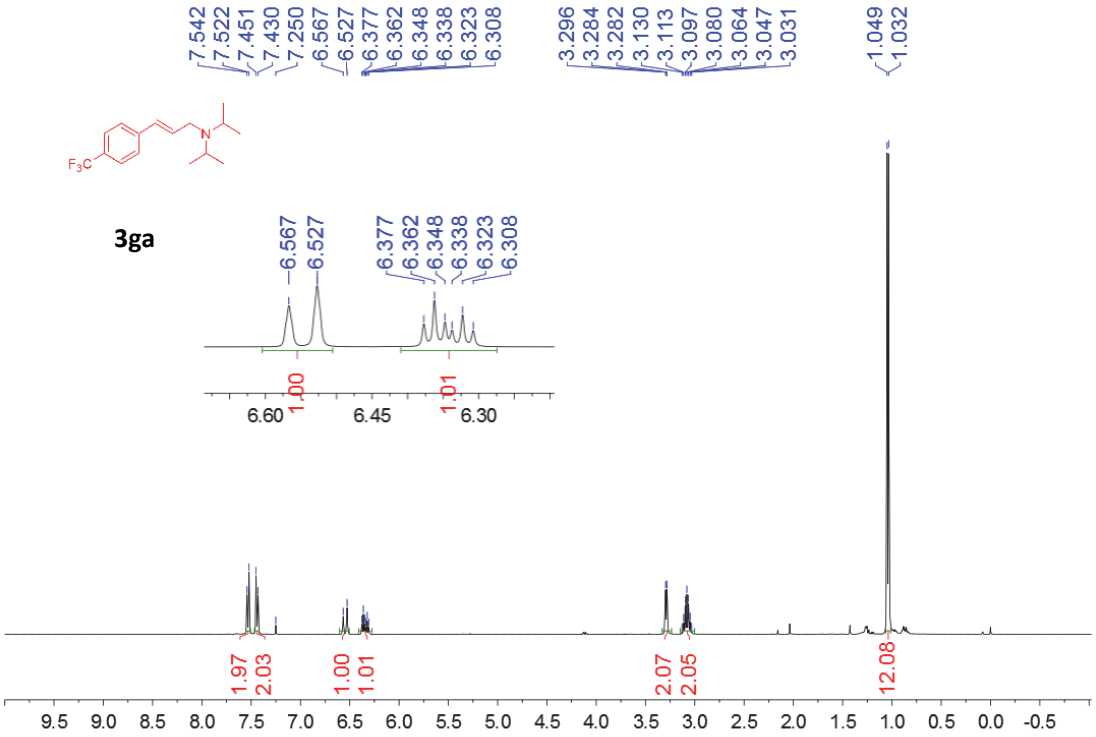


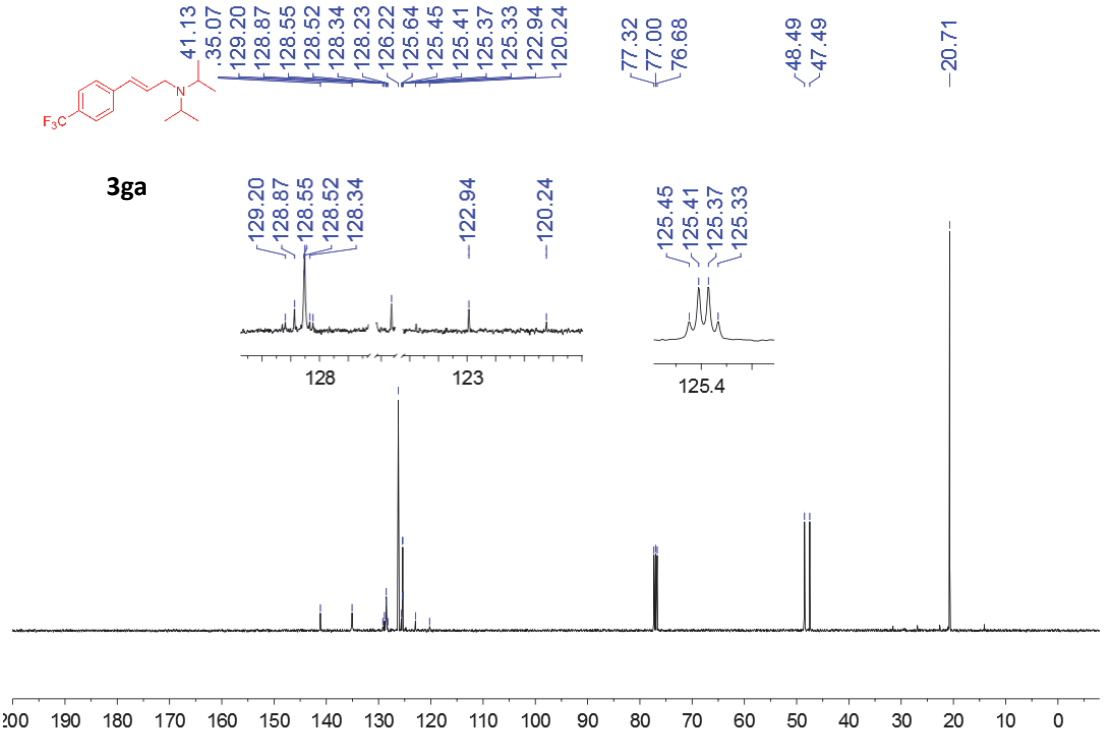
the ^{1}H and ^{13}C NMR spectra of **4fa**

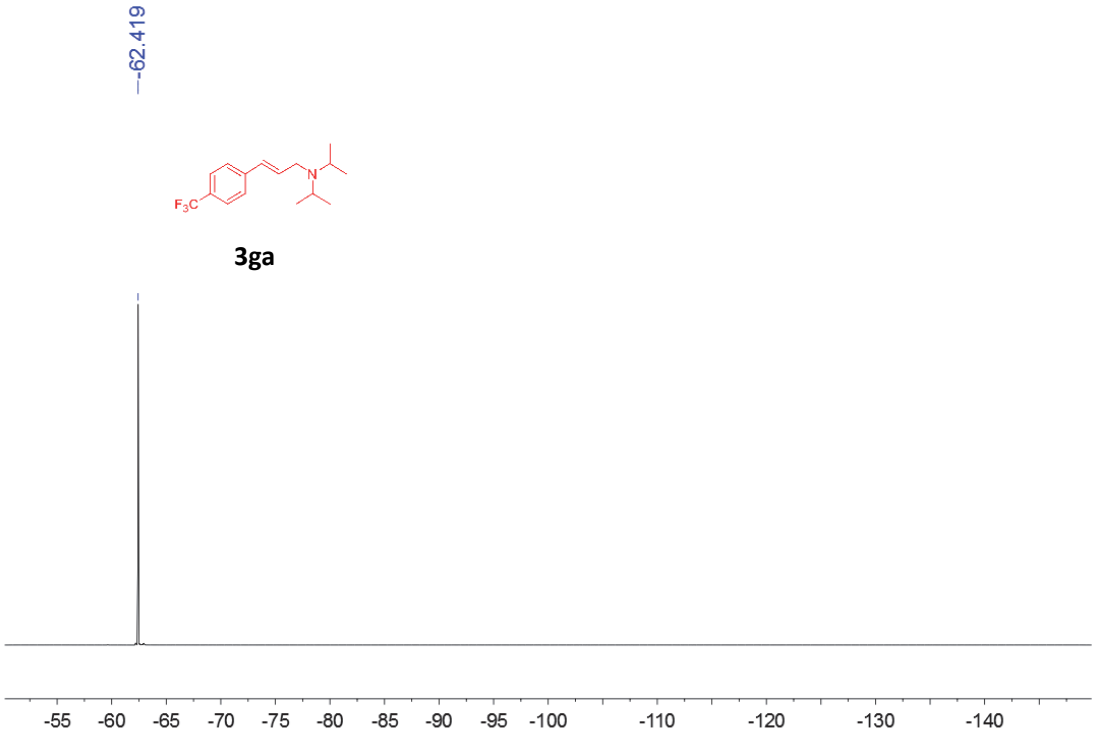




the ^{1}H, ^{13}C and ^{19}F NMR spectra of **3ga**

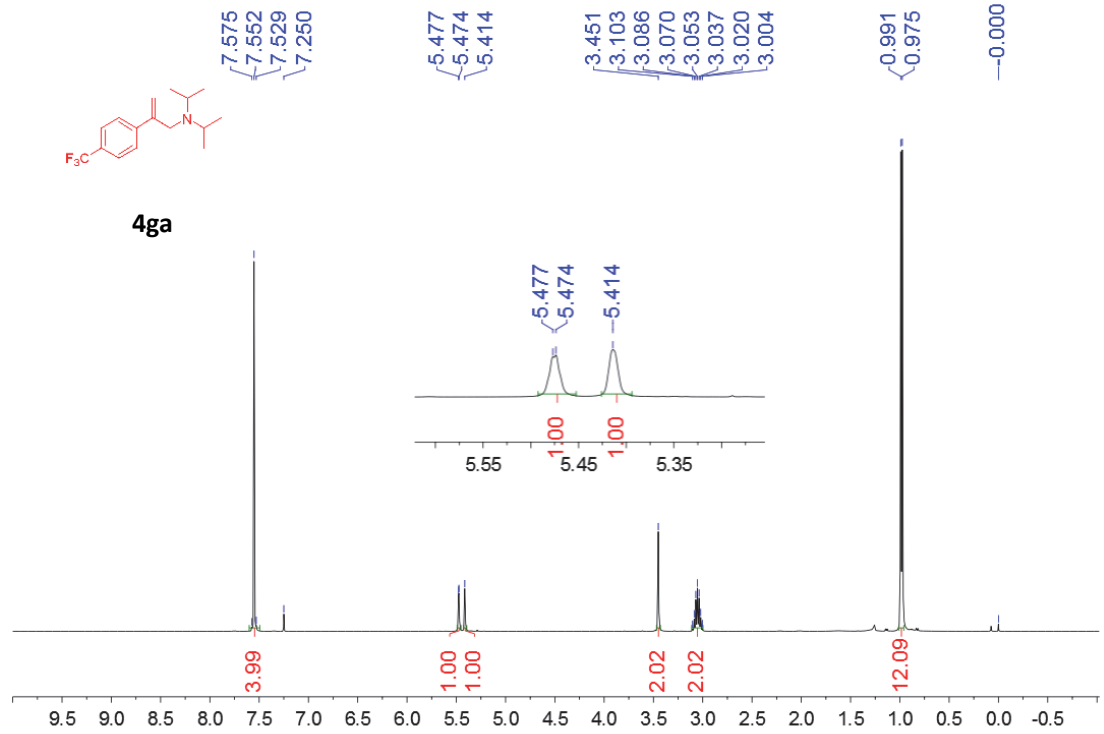


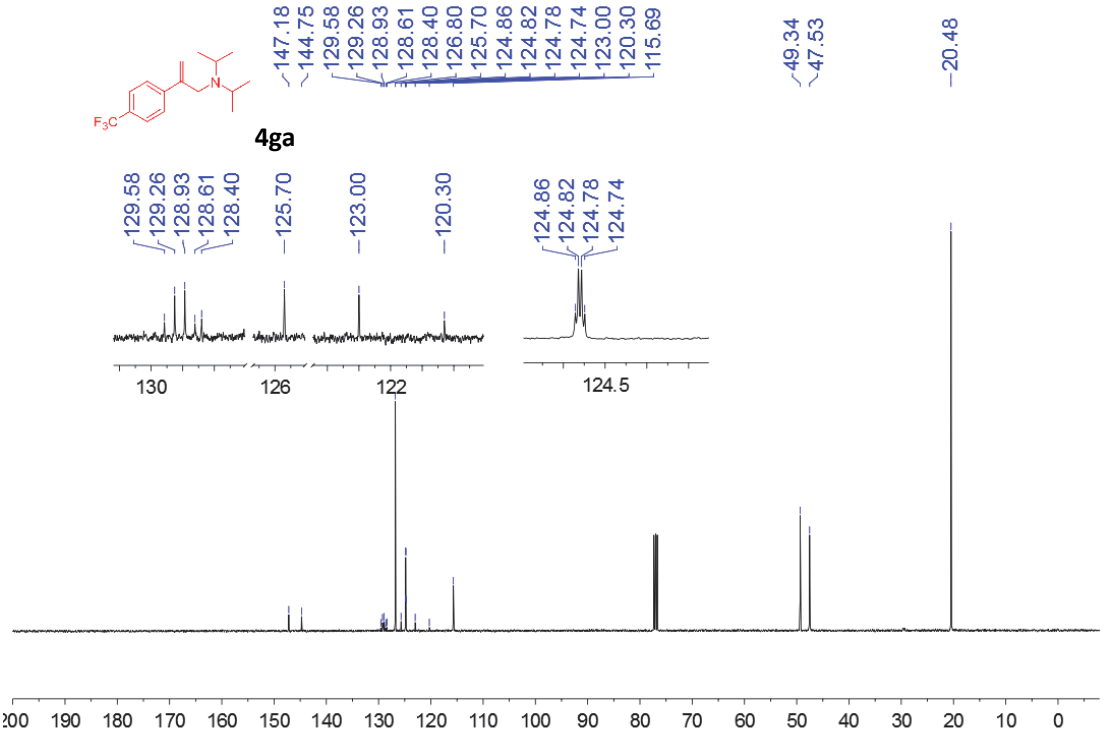


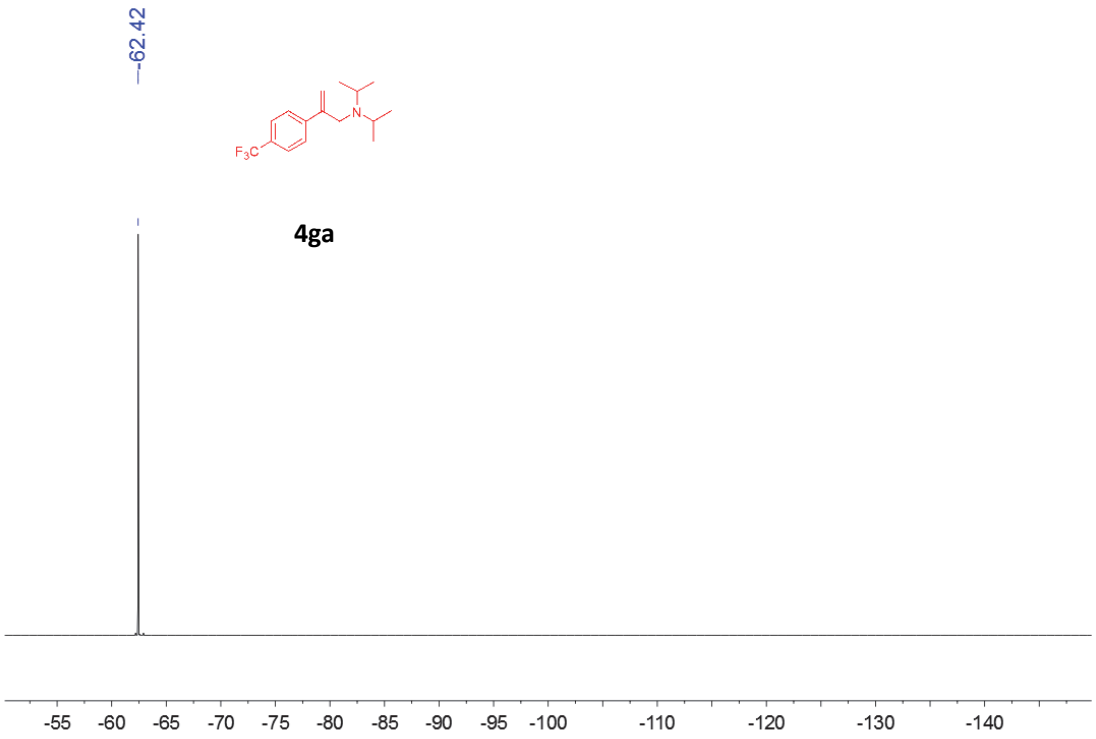


3ga

the ^{1}H, ^{13}C and ^{19}F NMR spectra of **4ga**

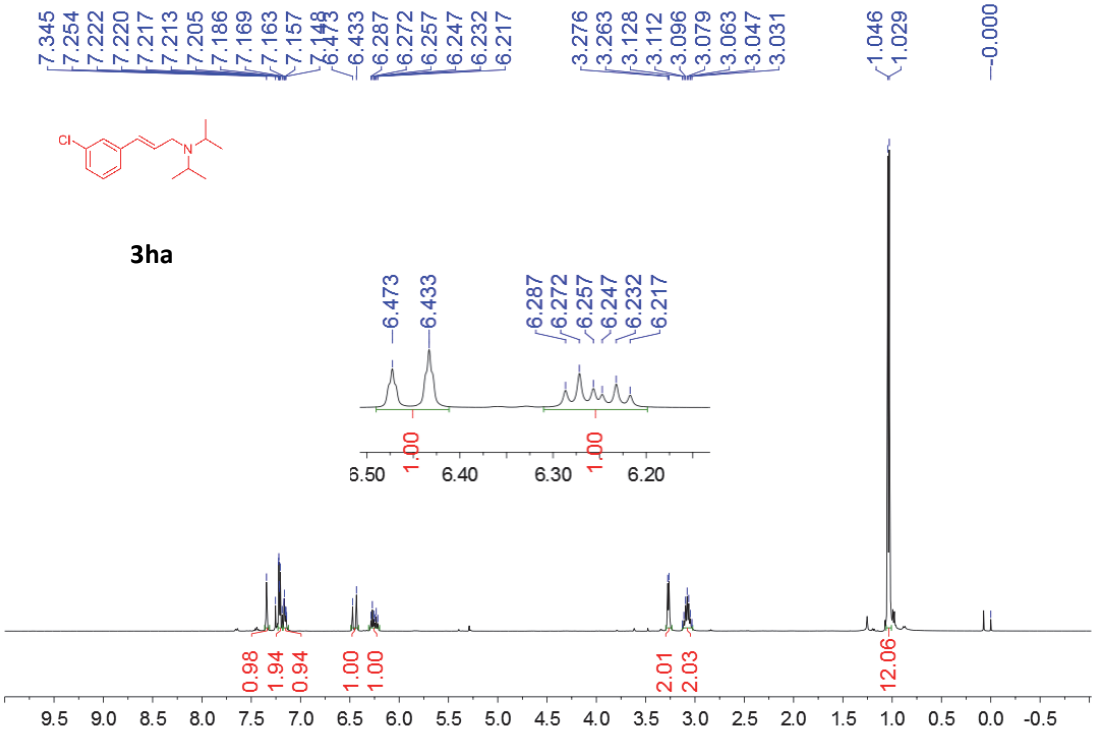


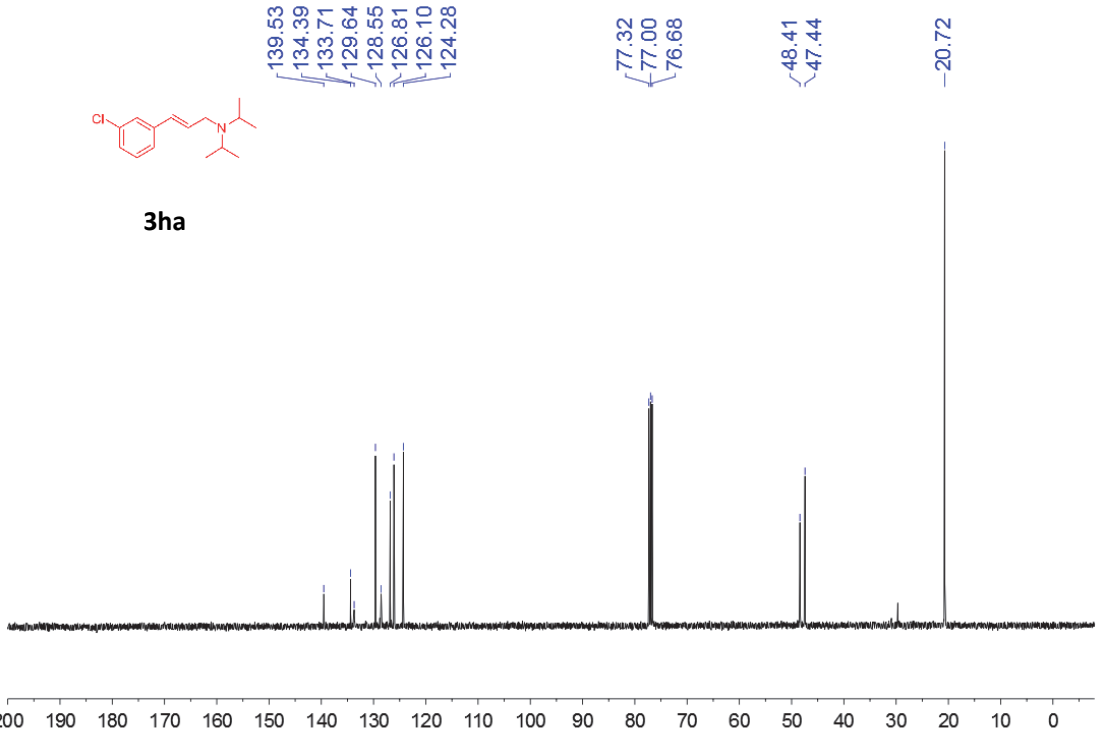




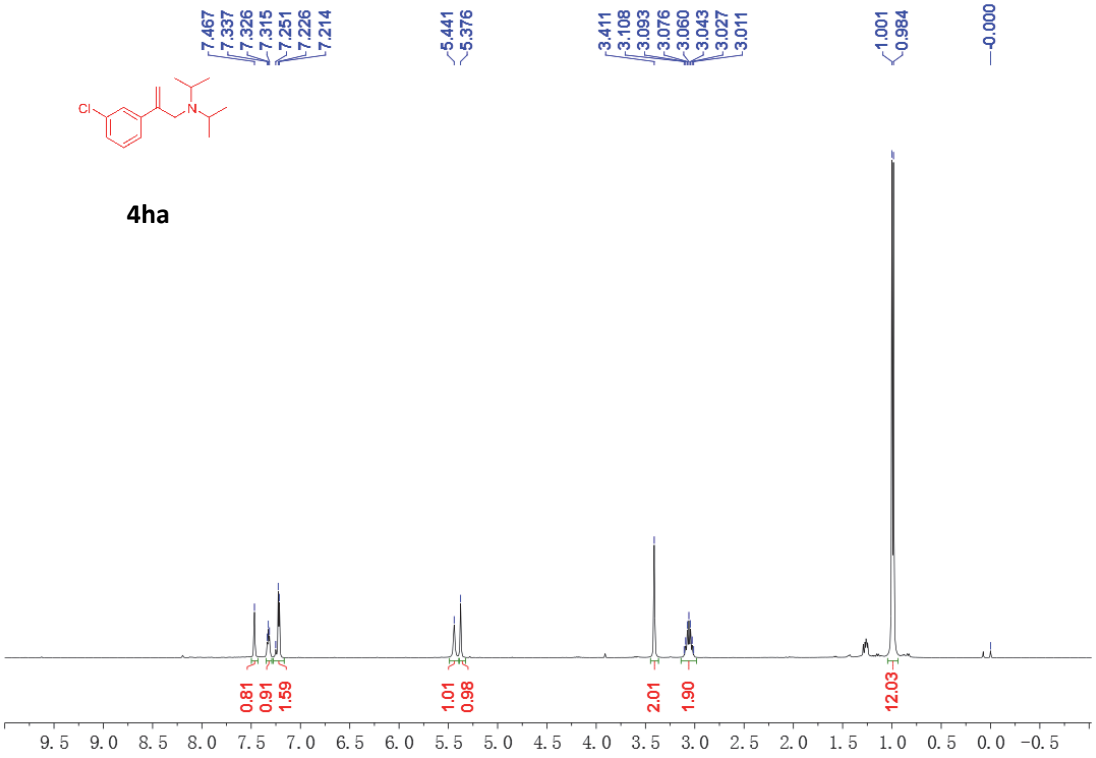
4ga

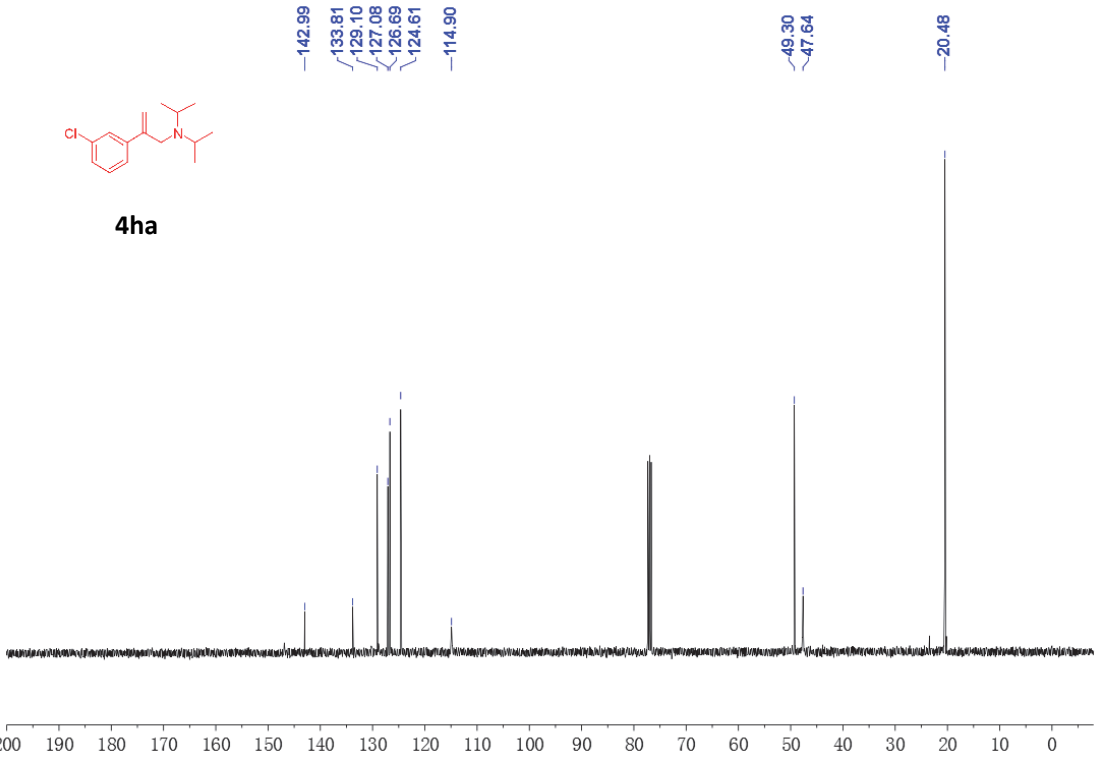
the ^{1}H and ^{13}C NMR spectra of **3ha**



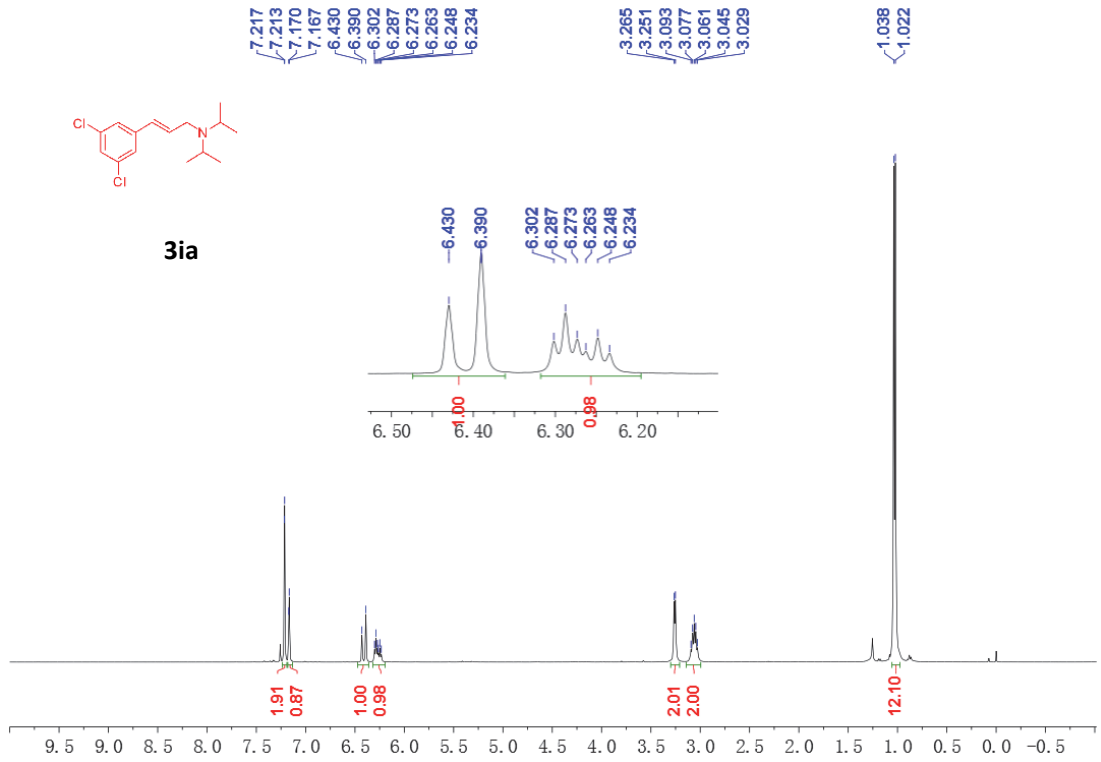


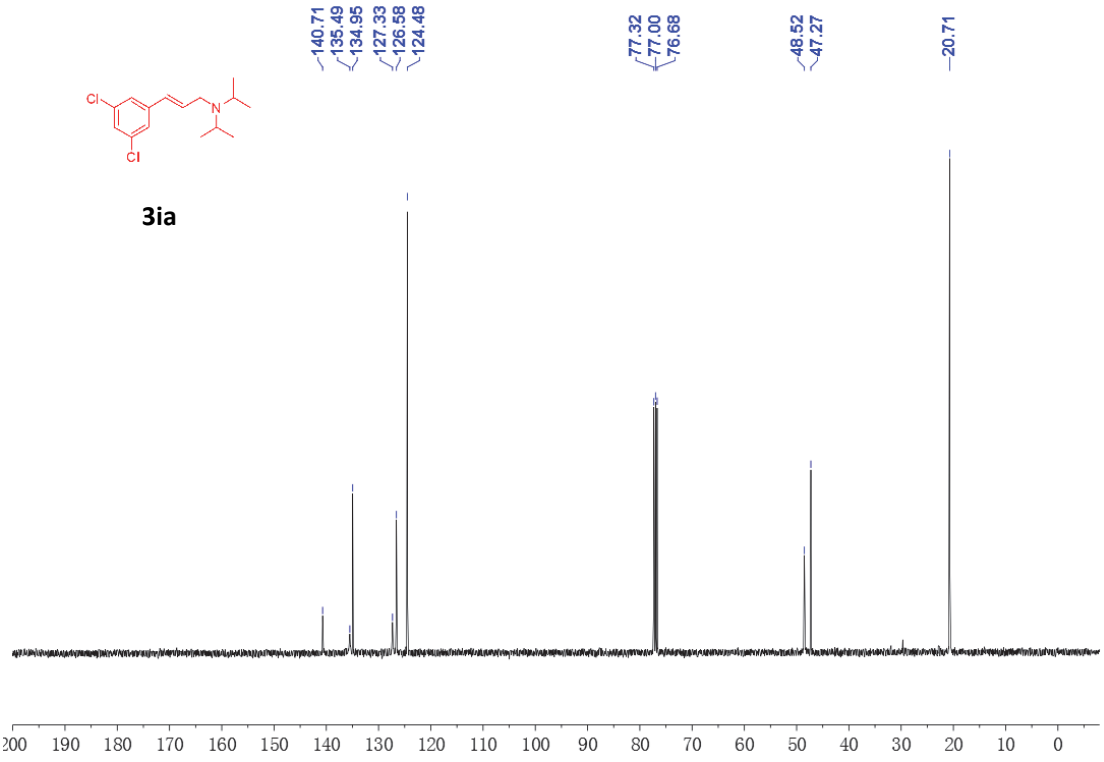
the ^{1}H and ^{13}C NMR spectra of **4ha**



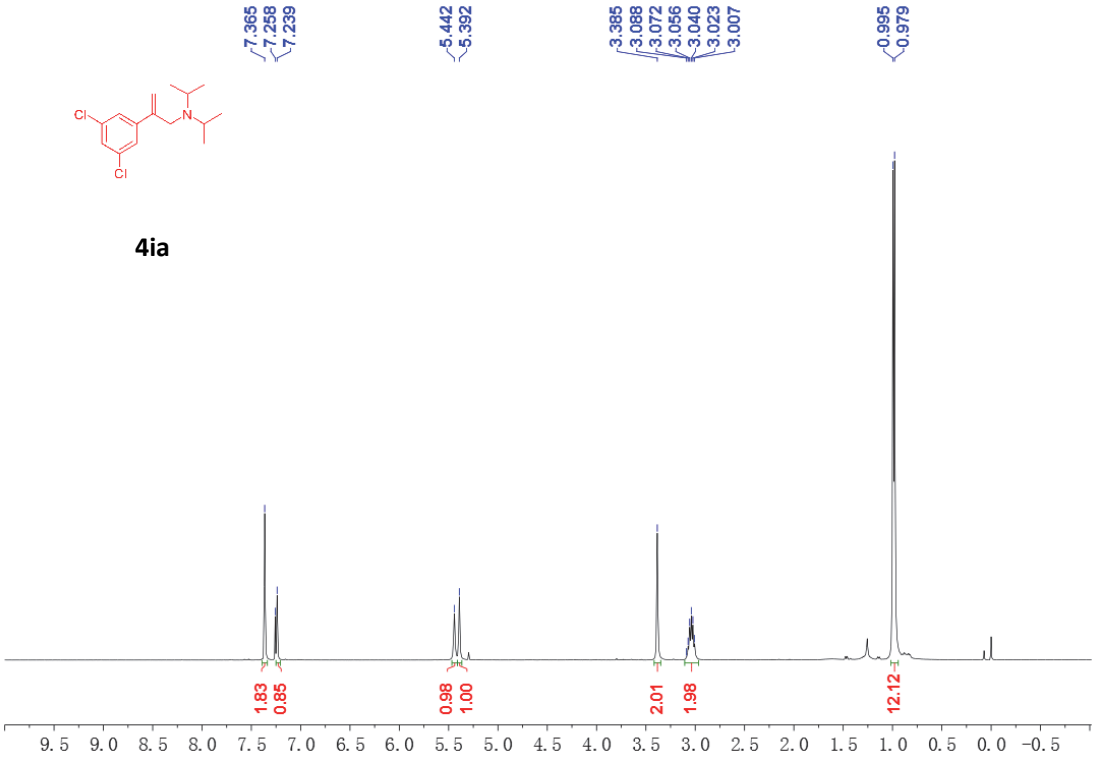


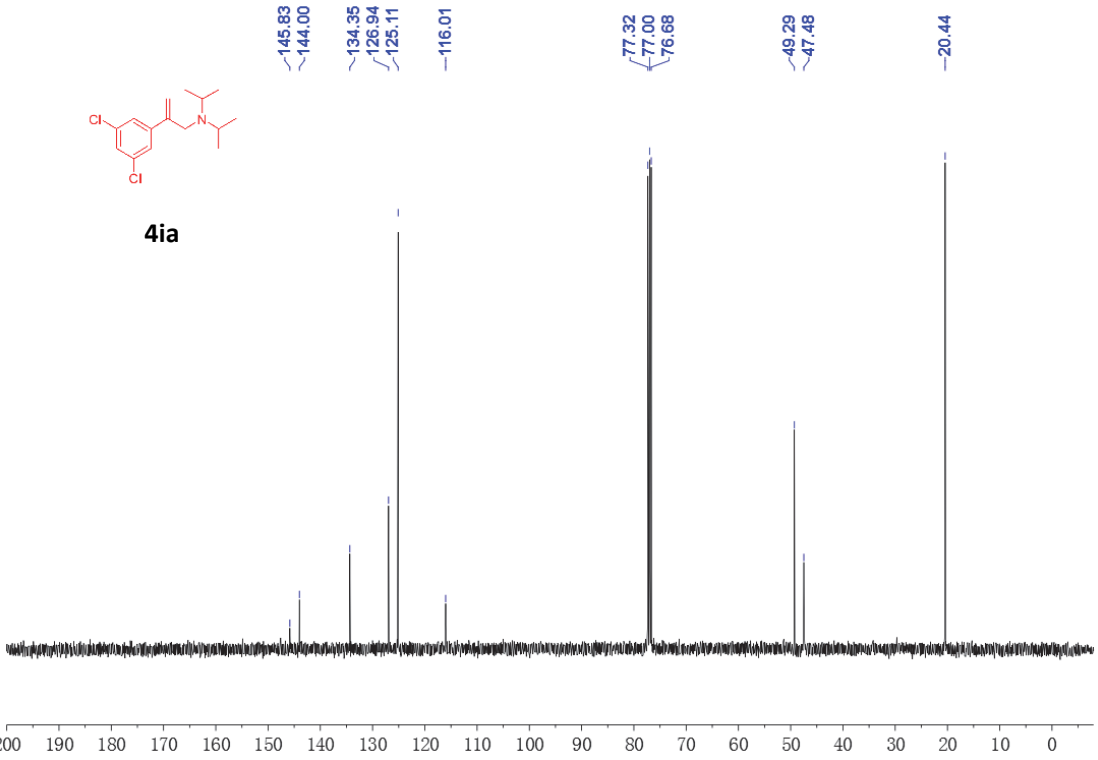
the ^{1}H and ^{13}C NMR spectra of **3ia**



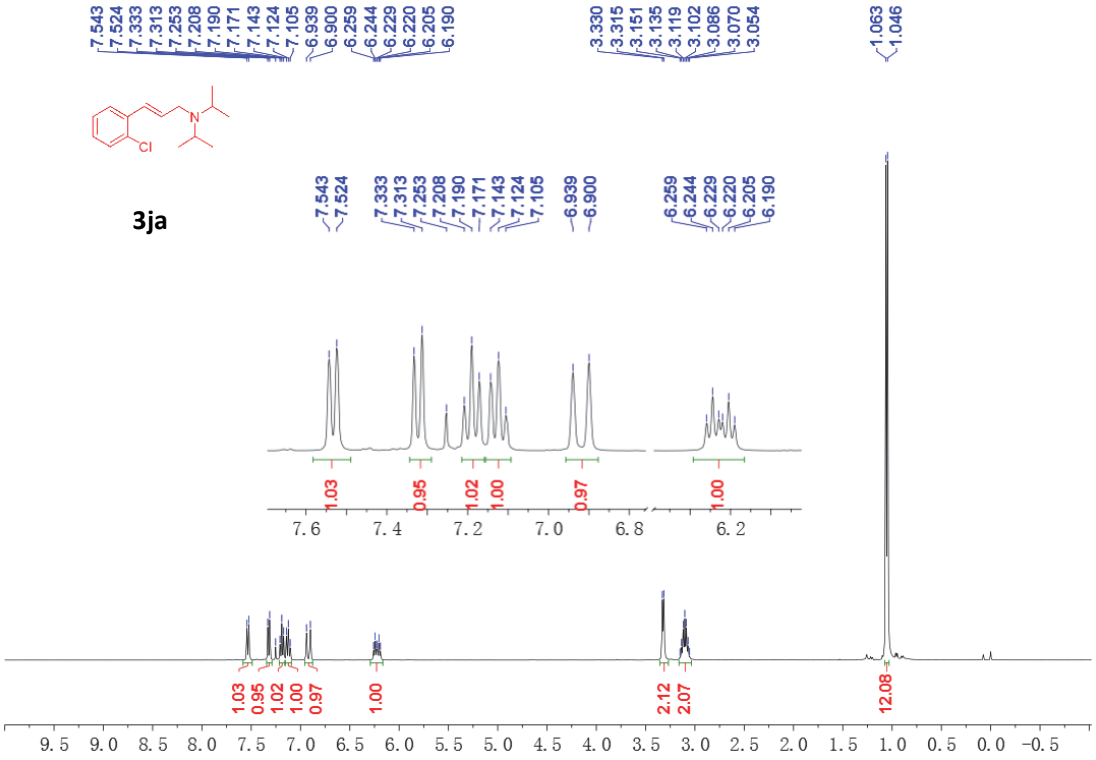


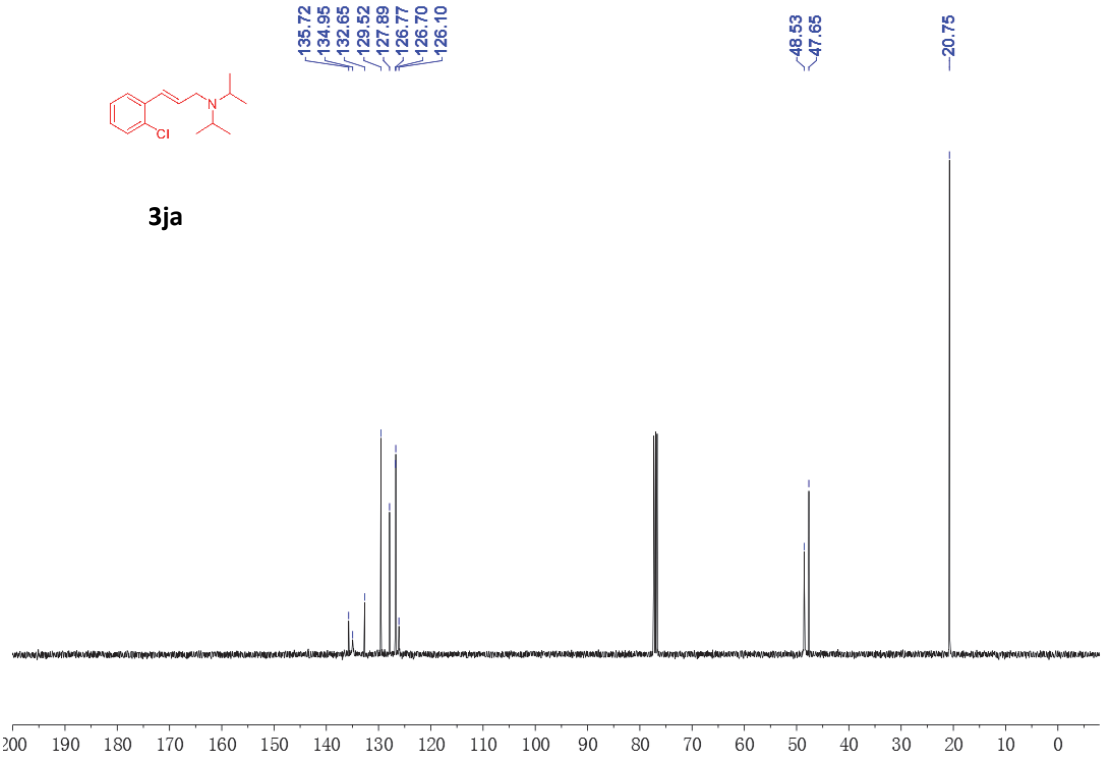
the ^{1}H and ^{13}C NMR spectra of **4ia**



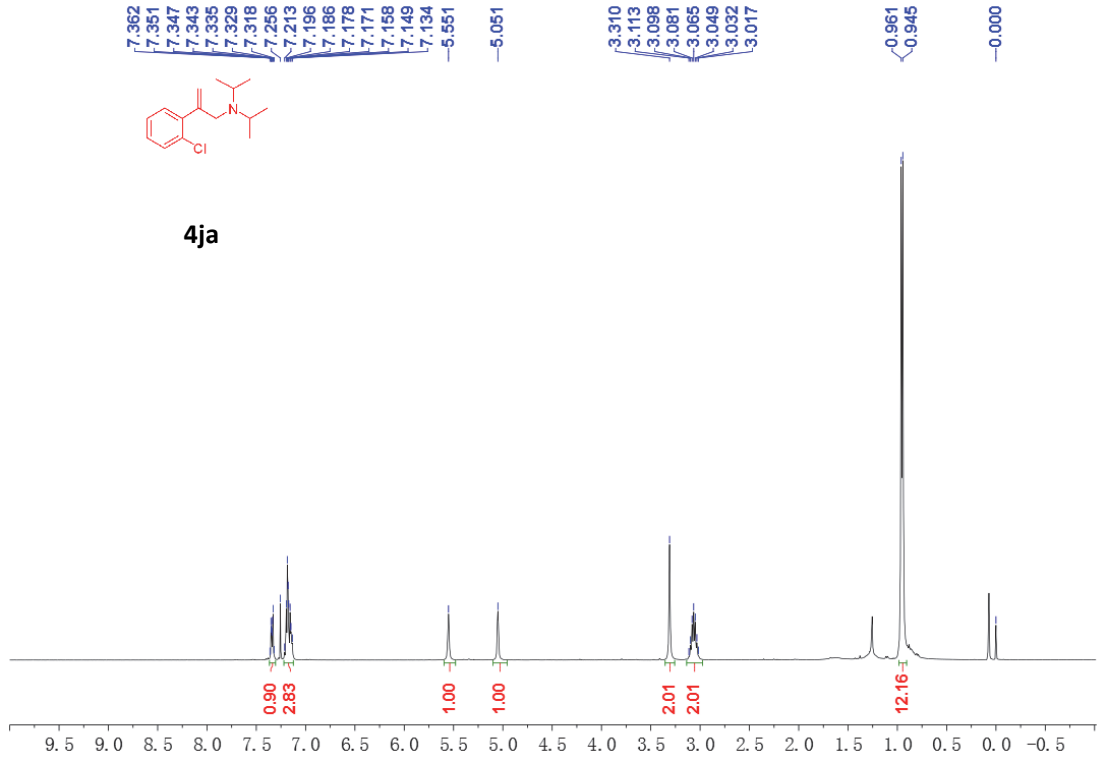


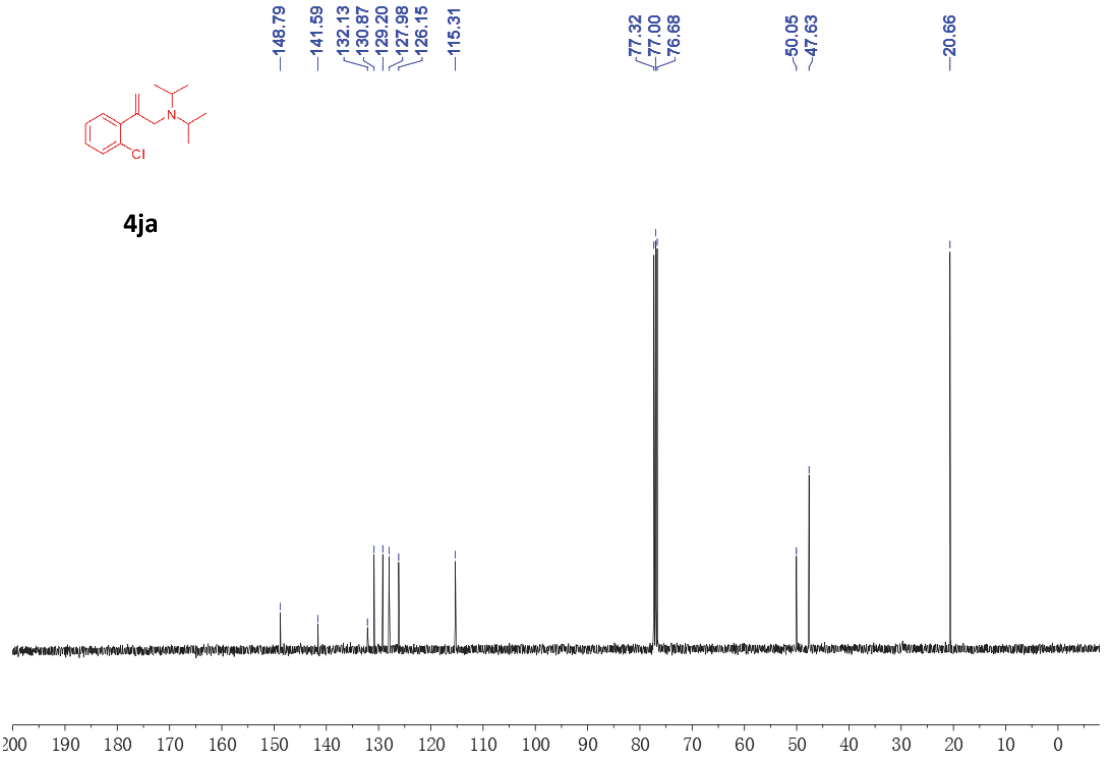
the ^{1}H and ^{13}C NMR spectra of **3ja**





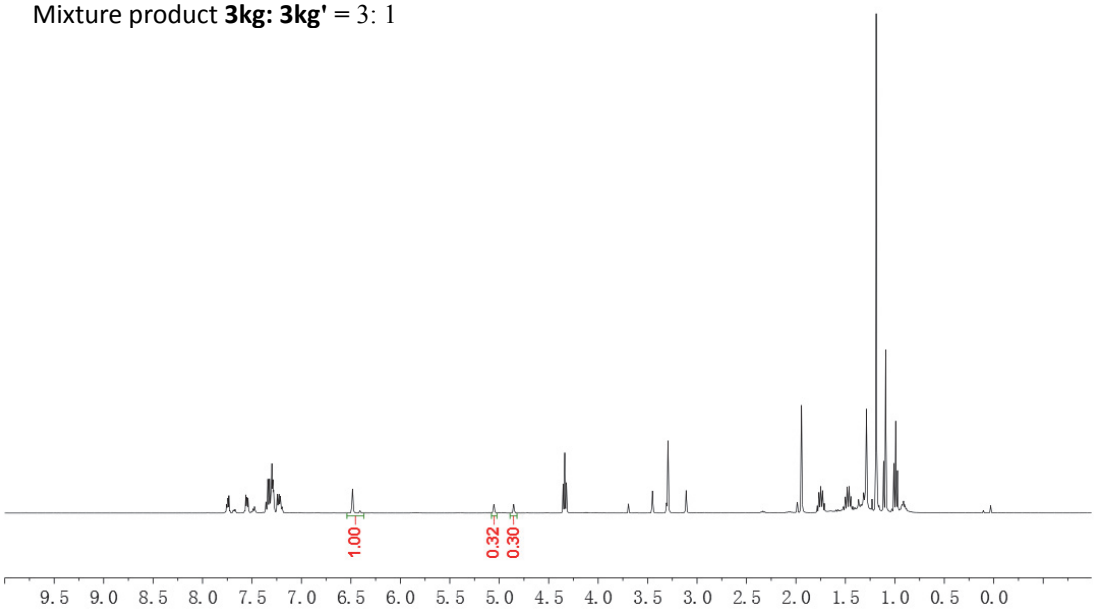
the ^{1}H and ^{13}C NMR spectra of **4ja**



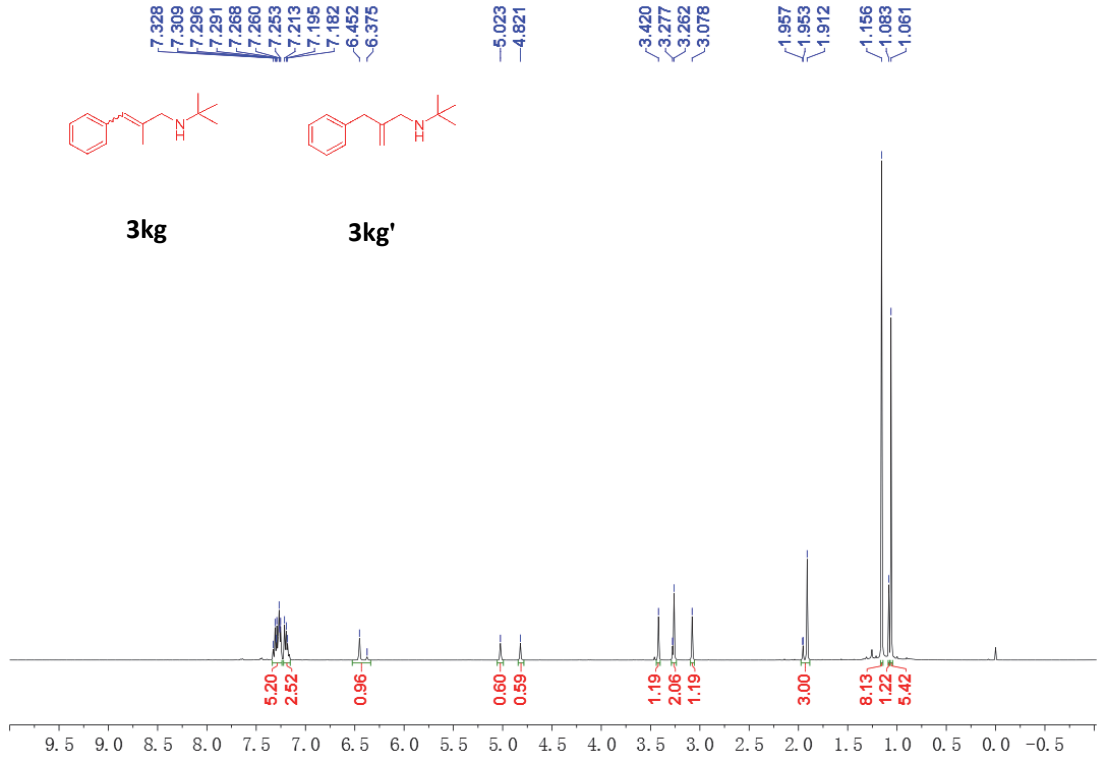


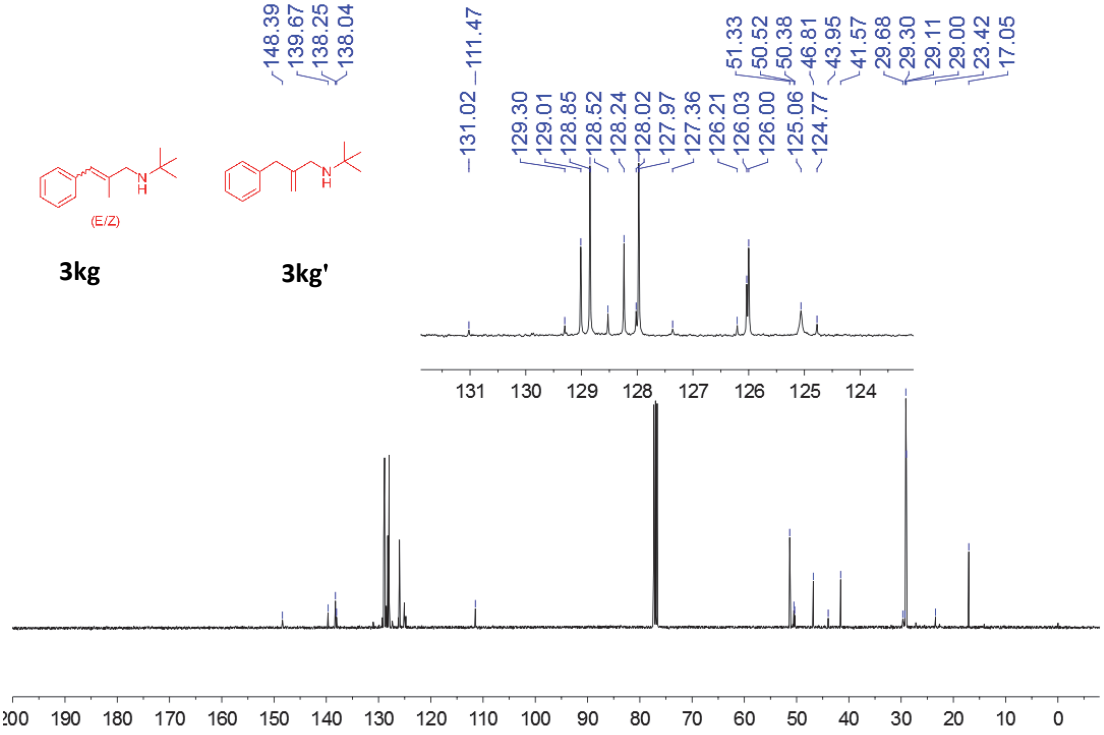
the ^{1}H NMR spectra of crude mixture to determine the ratio of **3kg** and **3kg'**

Mixture product **3kg: 3kg'** = 3: 1

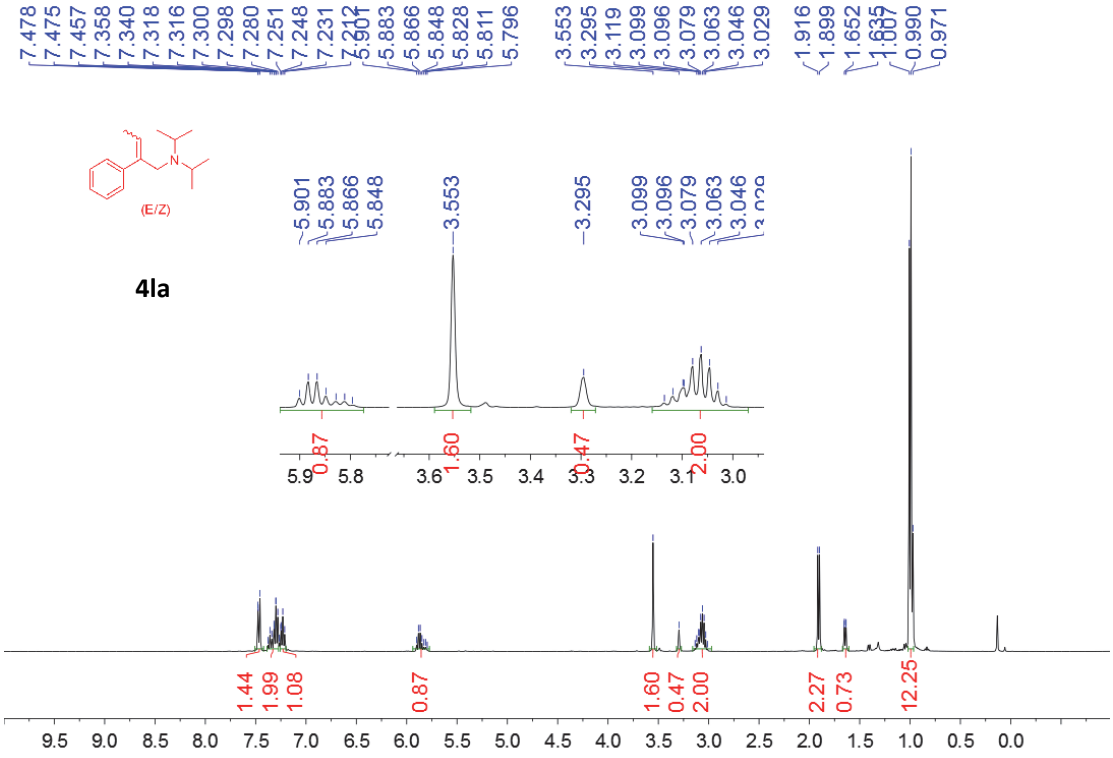


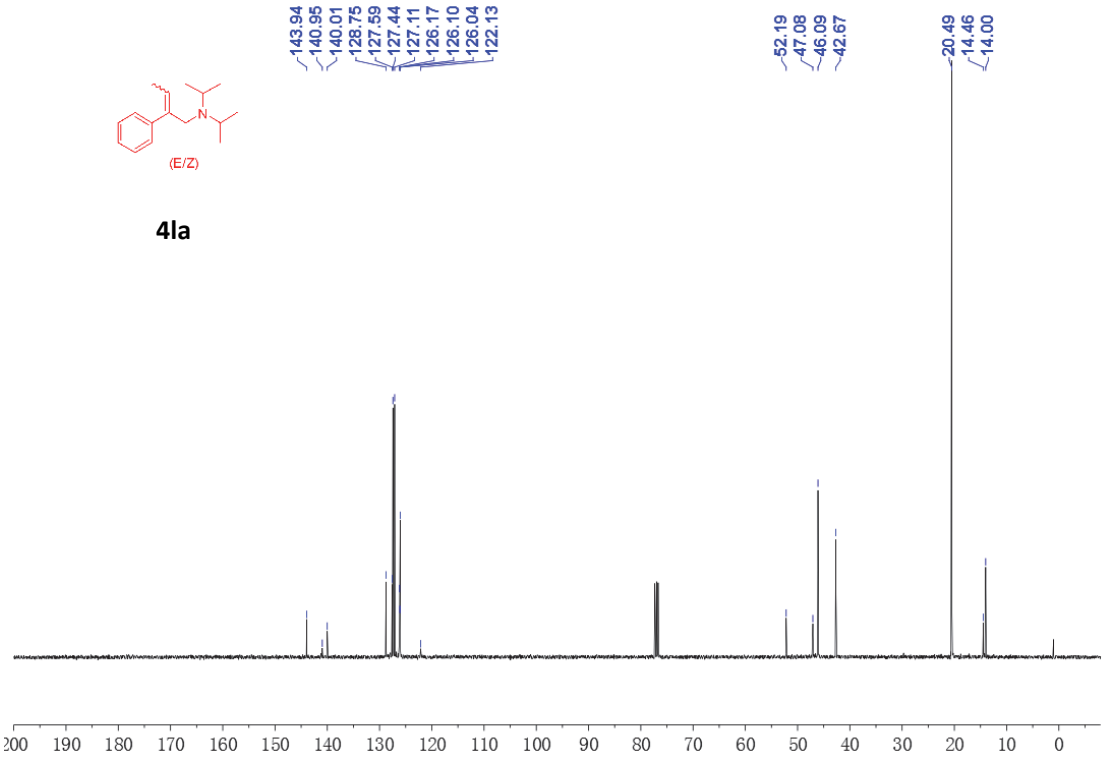
the ^{1}H and ^{13}C NMR spectra of mixture **3kg** and **3kg'**



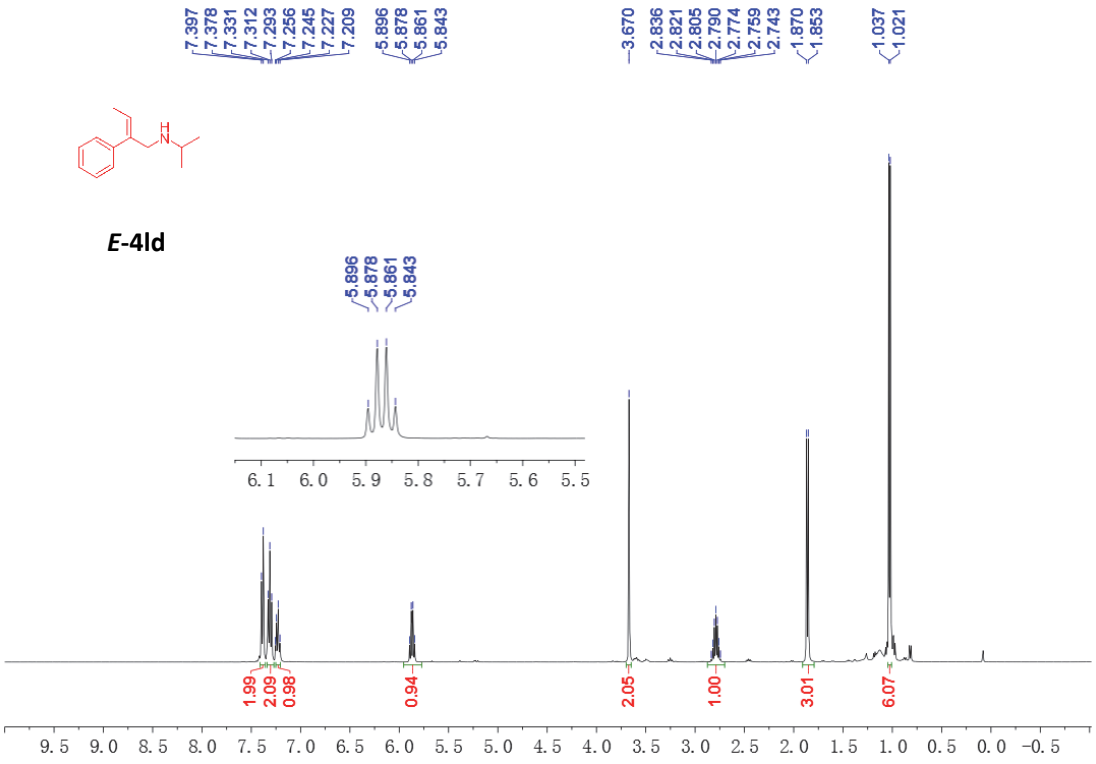


the ^{1}H and ^{13}C NMR spectra of **4la**

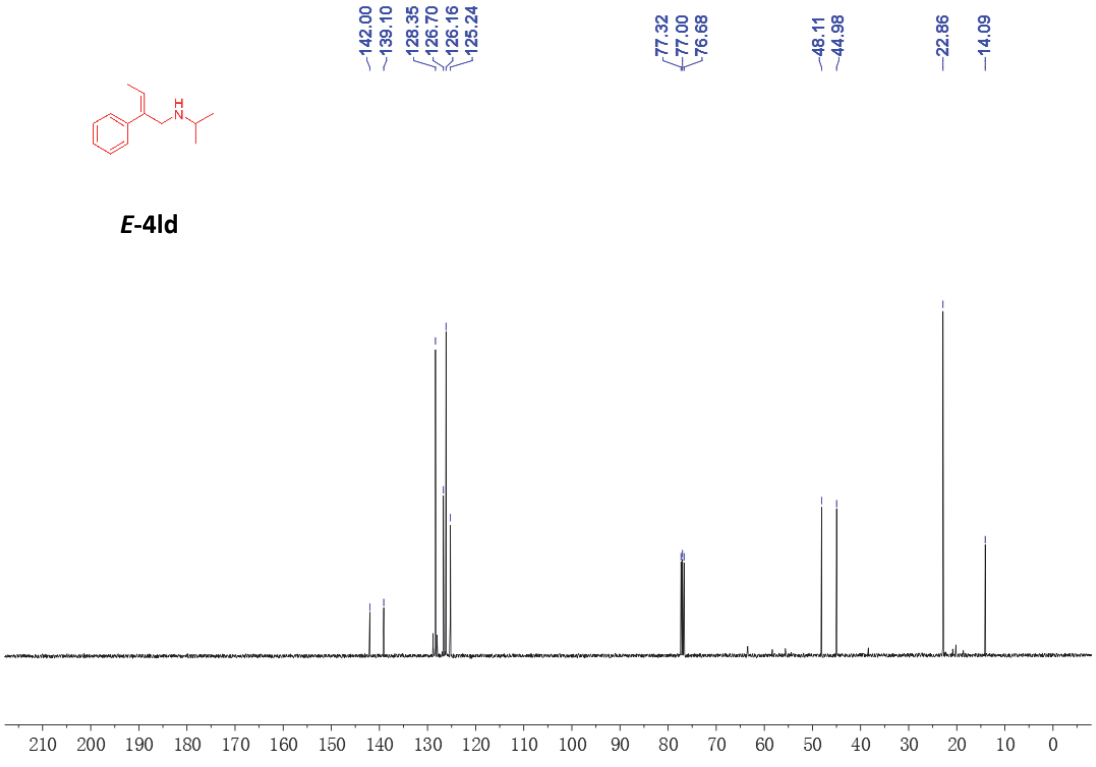




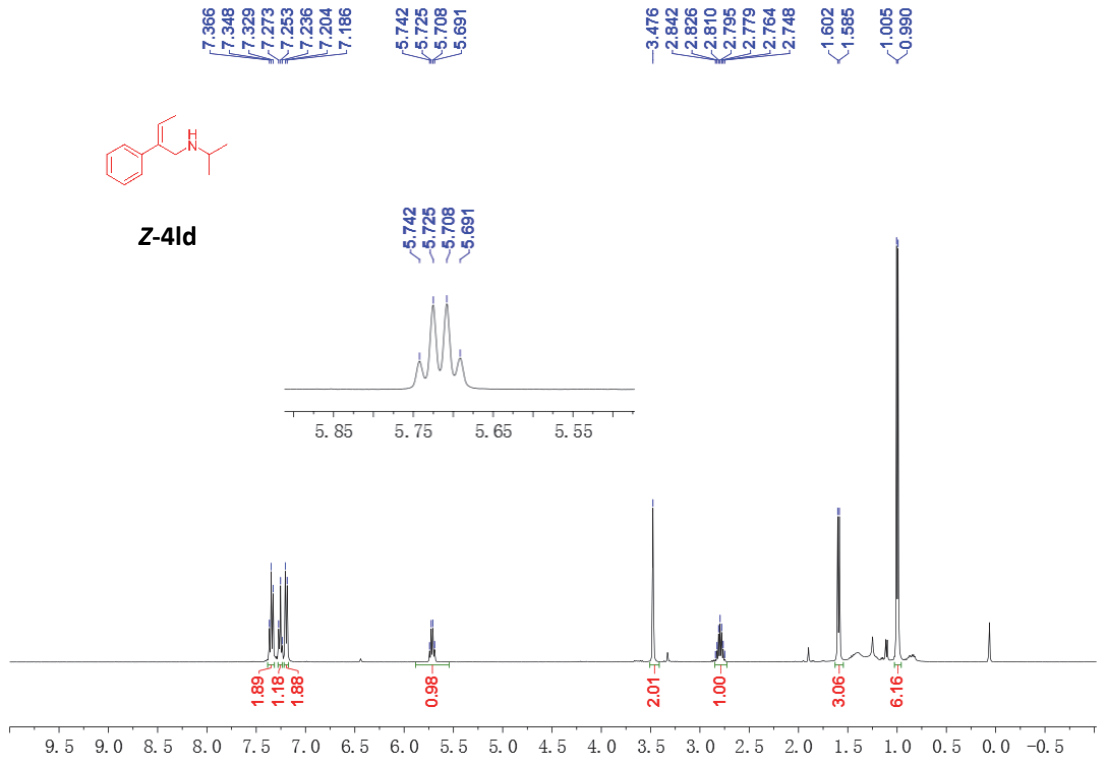
the ^{1}H and ^{13}C NMR spectra of ***E*-4ld**

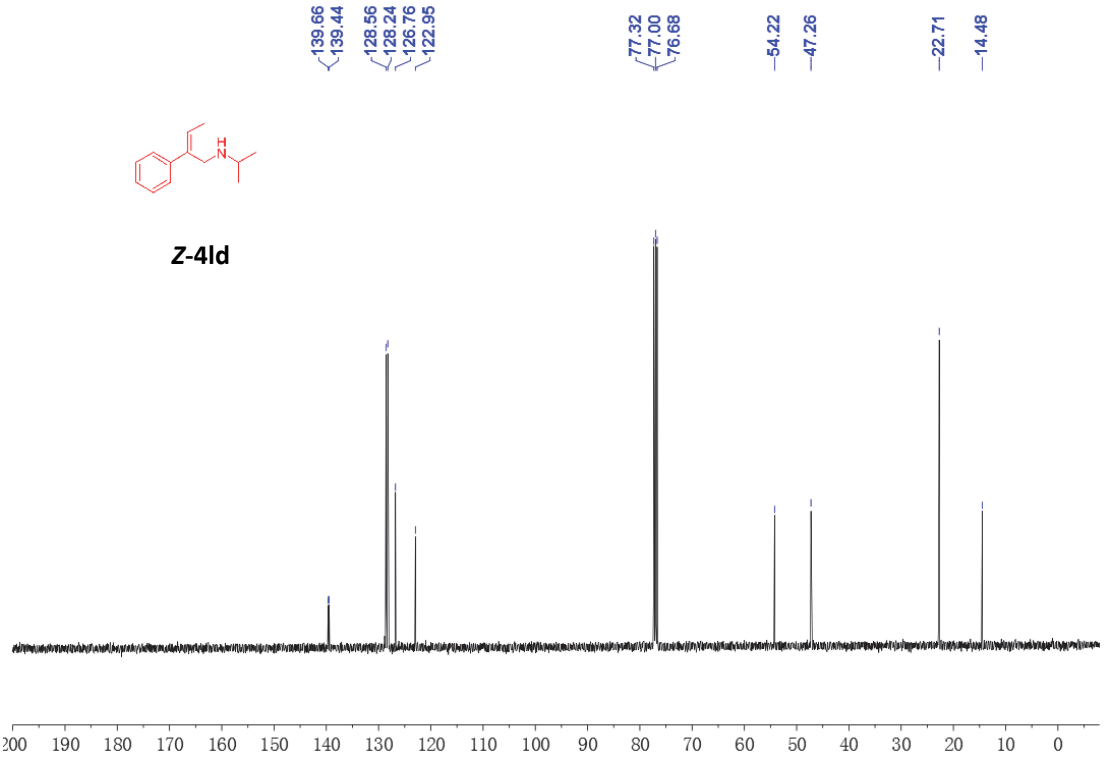


***E*-4ld**

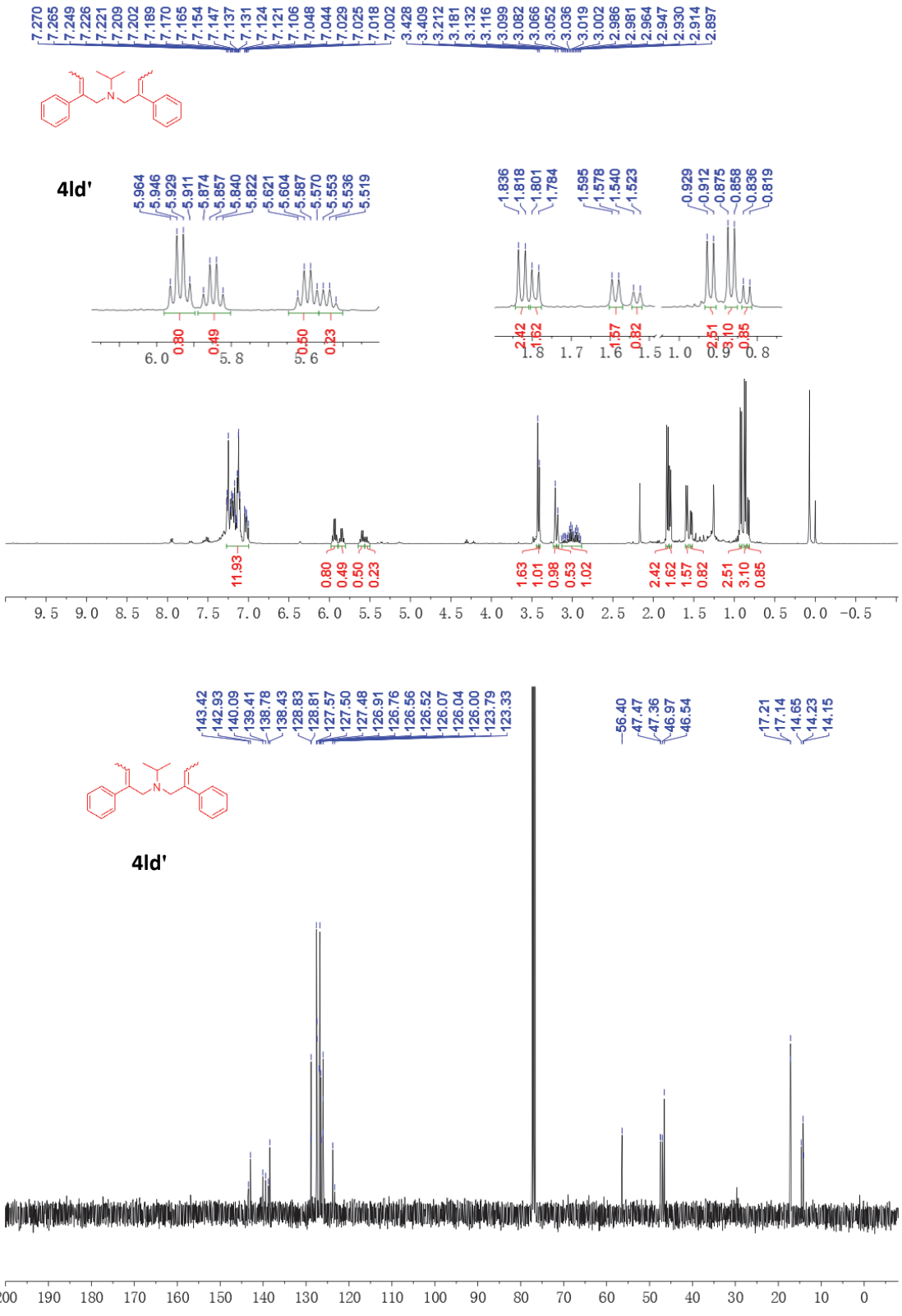


the ^{1}H and ^{13}C NMR spectra of ***Z*-4ld**

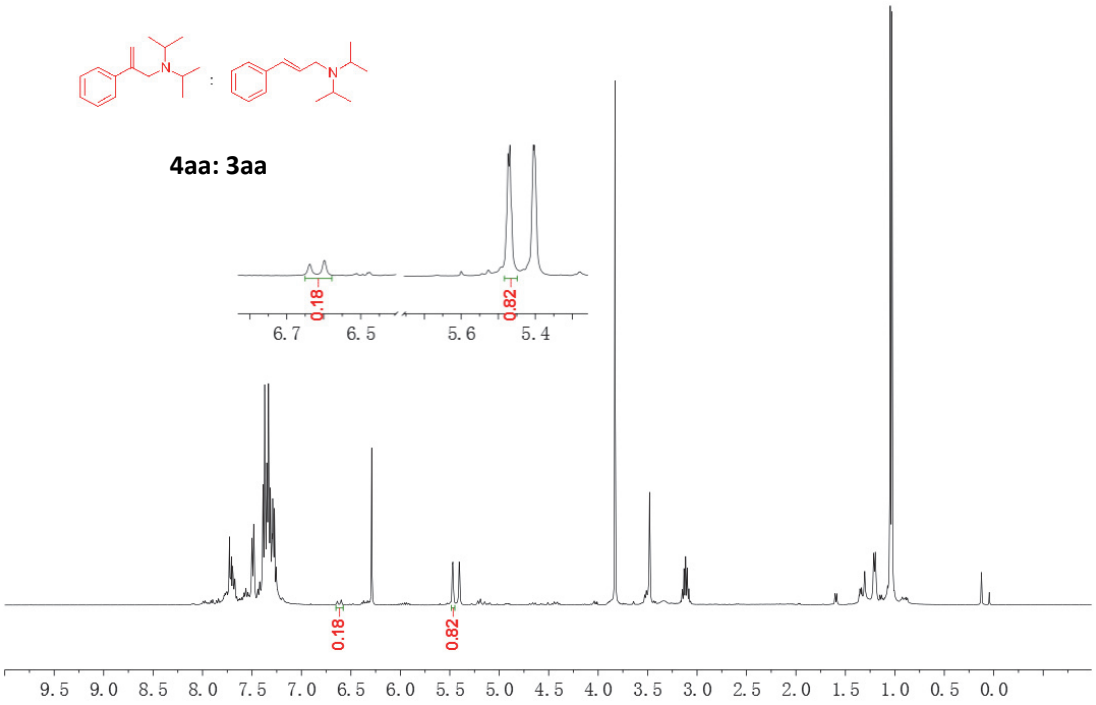


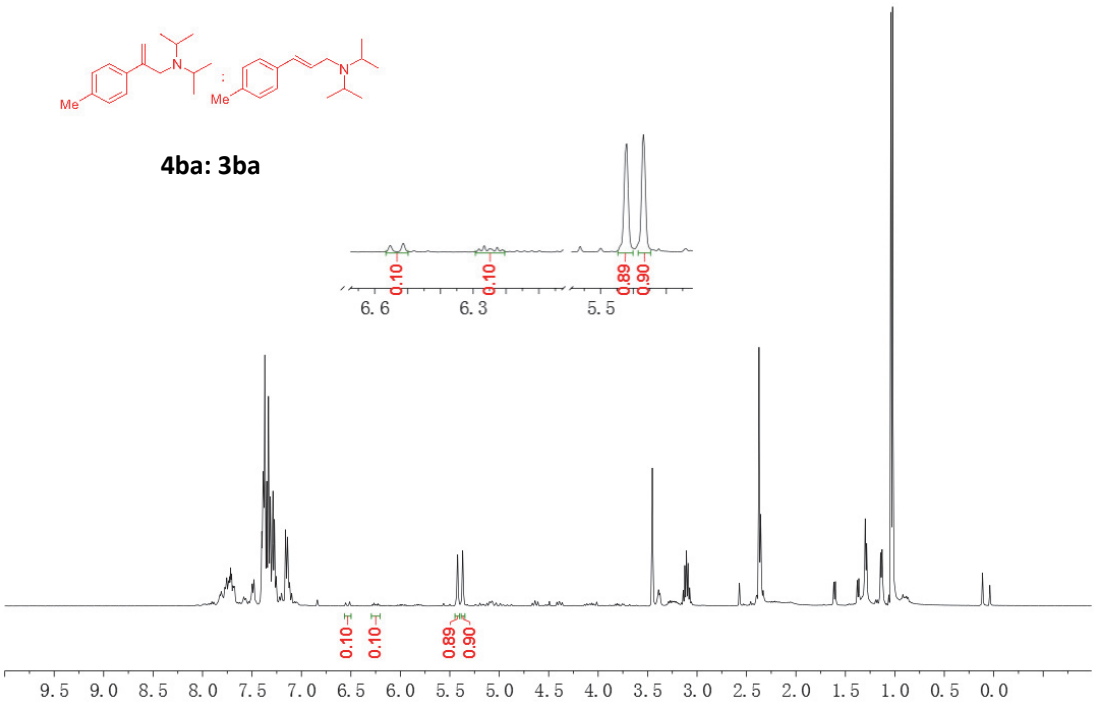


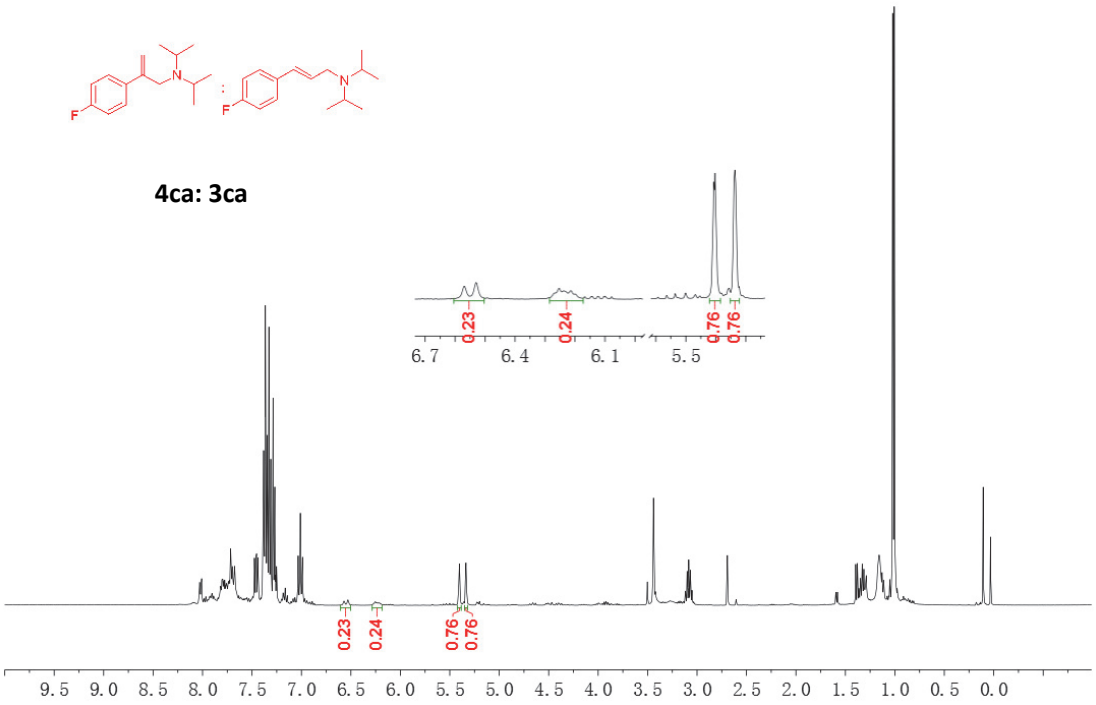
the ^{1}H and ^{13}C NMR spectra of **4ld'**

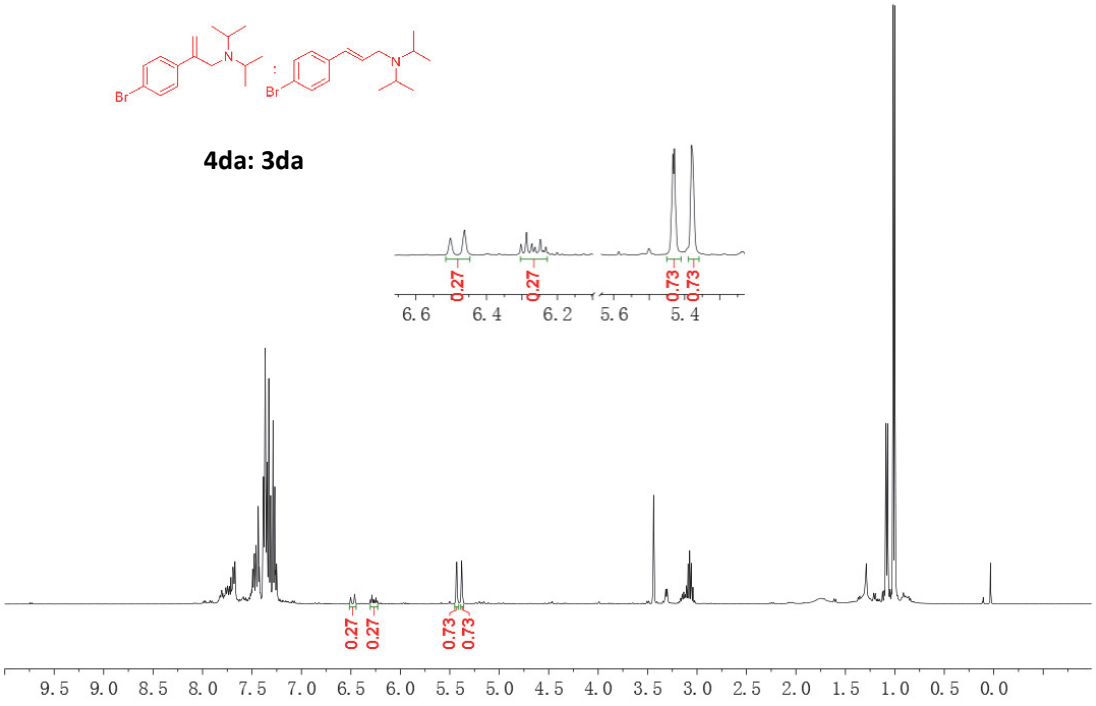


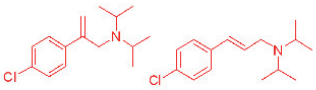
V. Copies of crude ^{1}H NMR spectra for determination of the product ratio (**3**: **4**) in **Table 2**



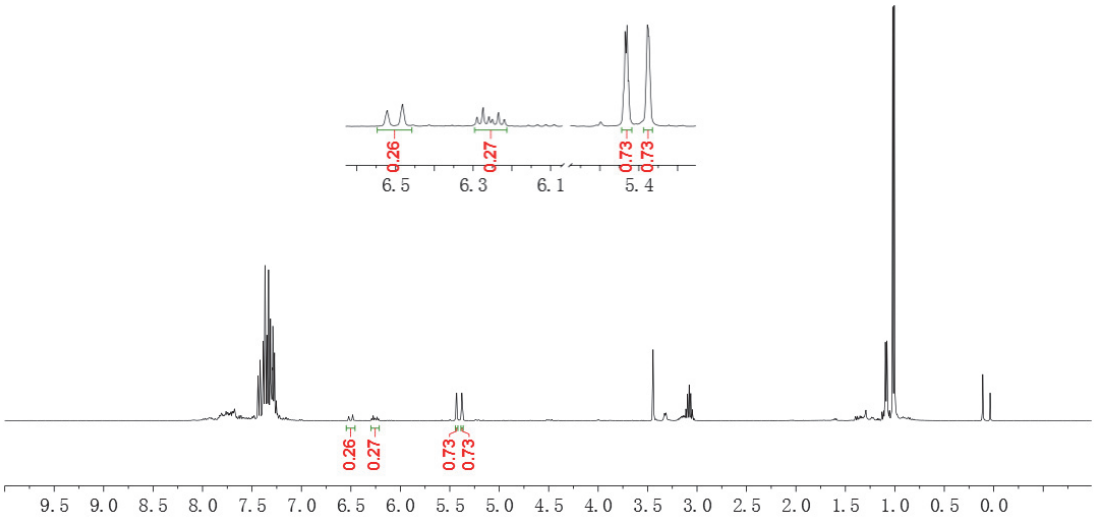


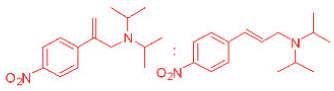

4ca: 3ca
0.23
0.24
0.76
0.76
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


4da: 3da
0.27
0.27
0.73
0.73
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

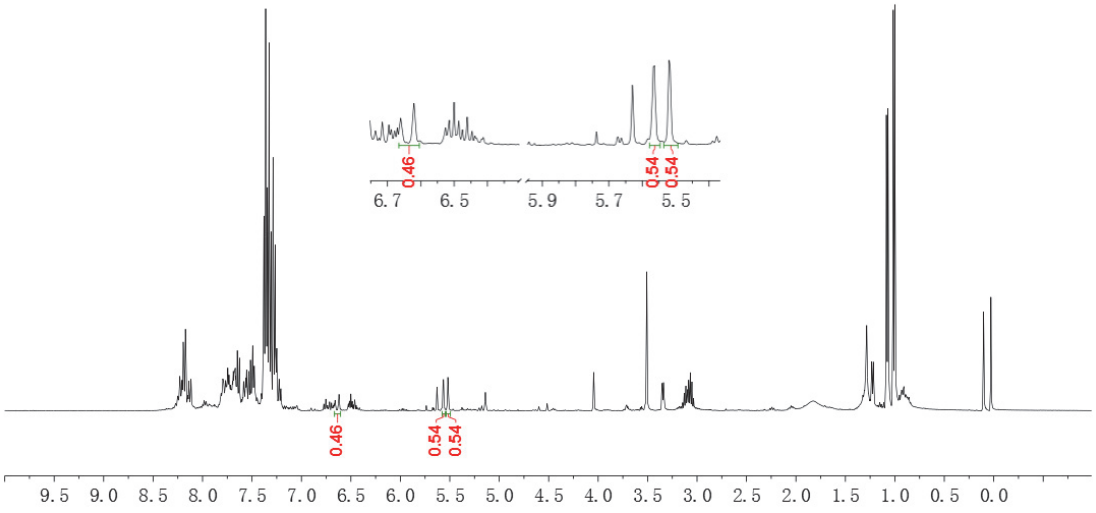


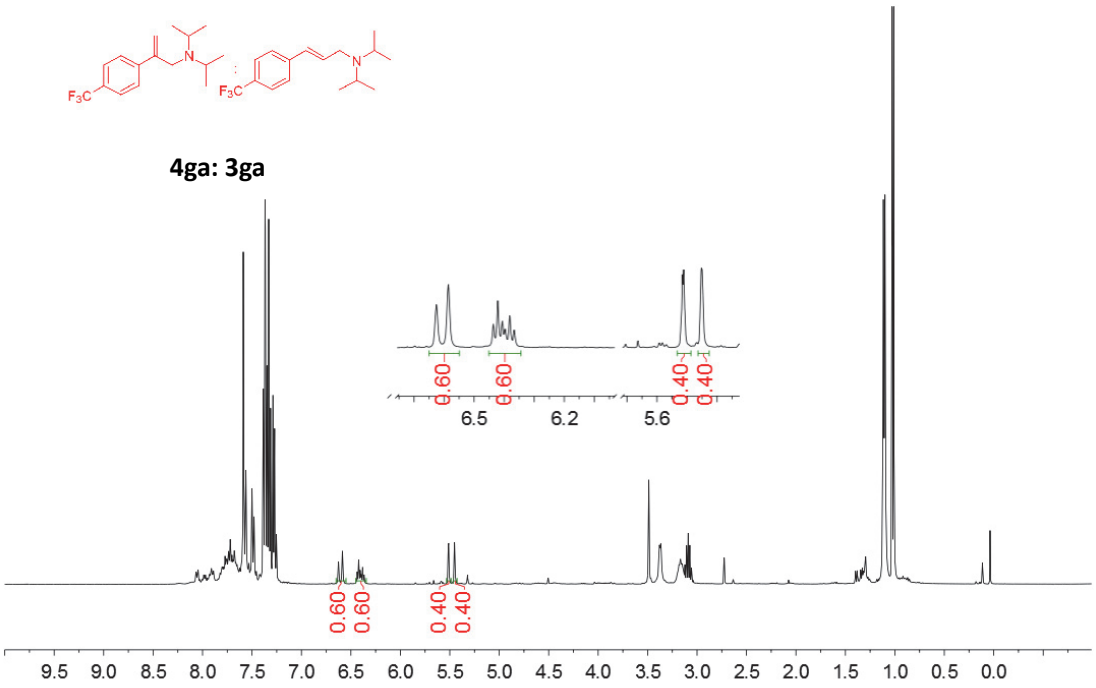
4ea: 3ea

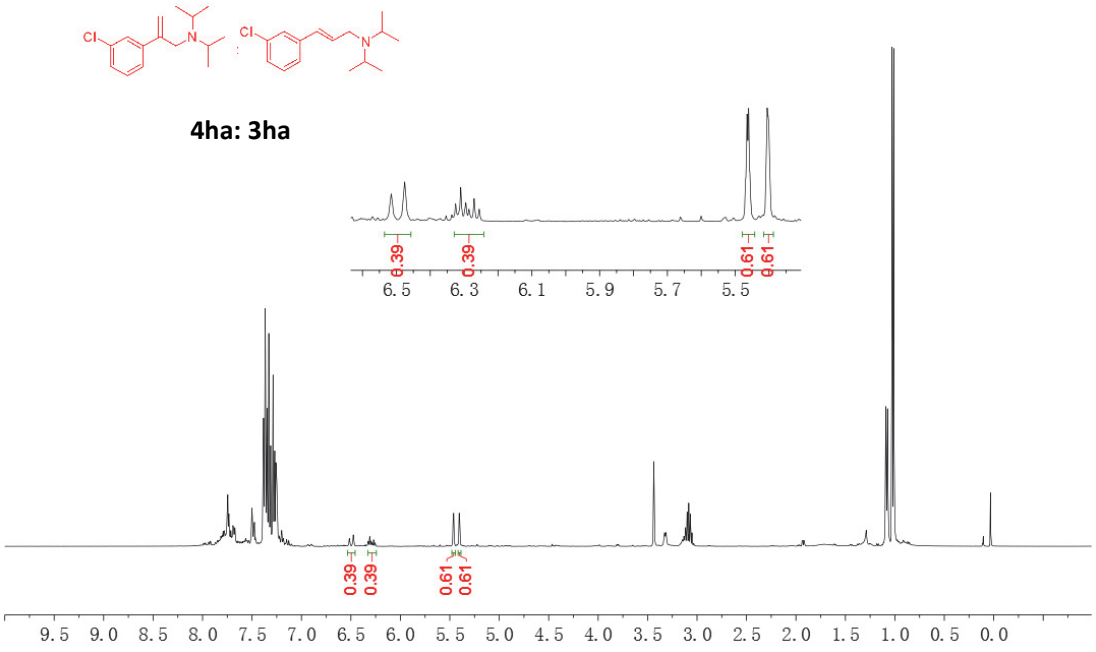


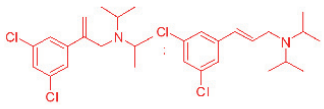


4fa: 3fa

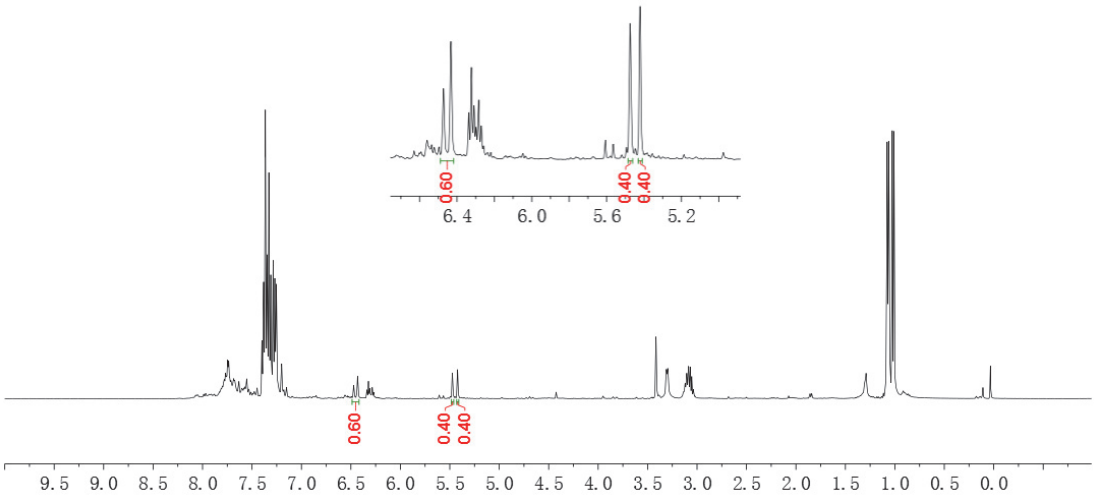


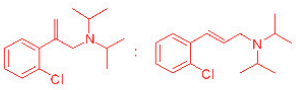

4ga: 3ga
0.60
0.60
0.40
0.40
6.5
6.2
5.6
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


4ha: 3ha
0.39
0.39
0.61
0.61
6.5 6.3 6.1 5.9 5.7 5.5
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



4ia: 3ia





4ja: 3ja