Supporting Information for

Fragile Intermediate Identification and Reactivity Elucidation in Electrochemical Oxidative α-C(sp^3)-H Functionalization of Tertiary Amines

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1. Experimental methods

1.1 Fabrication of the bipolar ultramicroelectrode (BPE) onto a nanopipette

The method for the fabrication of the BPE was adopted from a previous study[1] and is only briefly introduced here. A bare nanopipette was made from a quartz capillary (QF100-50-10, Sutter Instrument) using a laser-based P-2000 pipette puller (Sutter Instrument Co., Novato, CA, USA). The resulting nanopipette had an opening of ~500 nm. Method for depositing a thin layer of carbon into the nanopipette is based on the pyrolysis of butane. In brief, butane gas passes (~30 kPa) through the nanopipette from its rear end and heated by a butane fire under a nitrogen atmosphere by inserting the nanopipette into a thicker quartz tube (O.D. 3.0 mm and I.D. 1.5 mm) fed with ~5 kPa N_2. Typically, a pyrolysis time of 10 s is enough for depositing sufficient carbon into the tip, and the carbon film was measured to be around 150 nm thick.

1.2 Mass spectrometry

All the mass spectrometry experiments were carried out in the atmosphere. Mass spectra were acquired using an LTQ-XL mass spectrometer (Thermo-Fisher, Waltham, MA). The inlet capillary temperature of the mass spectrometer was maintained at 275 °C. The tube lens voltage on the LTQ-XL was set to be 0 V to avoid in-source fragmentation of the fragile radicals. The applied positive voltage was set to be 650-700 V in this study to trigger both the electrospray and oxidation reactions. Solutions of 1-phenylpyrrolidine (10 μM), mixture of 1-phenylpyrrolidine (10 μM) and phenyl *trans*-styryl sulfone (50 μM), tri-*n*-propylamine (50 μM), and mixture of tri-*n*-propylamine (50 μM) and phenyl *trans*-styryl sulfone (50 μM) filled in the BPE nanopipette were sprayed for mass analysis.

1.3 General procedure for electrochemical experiments

All glasswares were oven dried at 110 ℃ for hours and cooled down under vacuum. Vinyl sulfones were prepared according to reported procedures.[2] Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrochemical reaction is dual display potentiostat (DJS-292B) (Shanghai Xinrui Instruments & Meters Co., Ltd., China). Cyclic voltammograms were obtained on a CorrTest® CS2350H

bipotentiostat. The anode electrode is carbon felt electrode (15 mm × 10 mm × 3 mm) and the cathode electrode is platinum plate electrode (15 mm × 15 mm × 0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp.60-90℃). ^{1}H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.16 ppm for ^{13}C), respectively. High resolution mass spectra (HRMS) were measured with Thermo Orbitrap Elite, accurate masses were reported for the molecular ion + proton $(M+H)^+$.

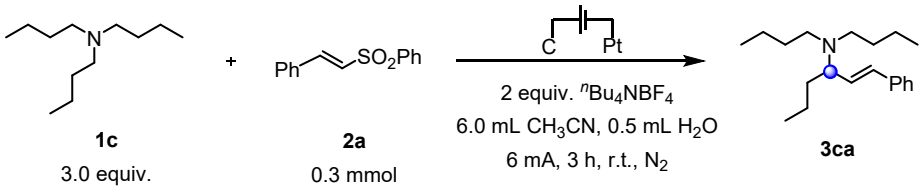
The synthesis of **3ca** is representative for the synthesis of allylic alkylamines: In an oven-dried undivided three-necked bottle (6 mL) equipped with a stir bar. The bottle was equipped with carbon felt anode (15 mm × 10 mm × 3 mm) and platinum plate cathode (15 mm × 15 mm × 0.3 mm). Tributylamine (**1c**, 0.9 mmol, 3 equiv.), phenyl *trans*-styryl sulfone (**2a**, 0.3 mmol, 1 equiv.), $^{n}Bu_4NBF_4$ (0.6 mmol, 2 equiv.) in acetonitrile (MeCN, 6 mL) and H_2O (0.5 mL) were stirred and electrolyzed at a constant current of 6 mA under nitrogen atmosphere at room temperature for 3 h. After completion of the reaction, the reaction mixture was extracted with DCM for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The pure product was obtained by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (250/5/3).

The synthesis of **3ra** is representative for the synthesis of allylic arylamines: In an oven-dried undivided three-necked bottle (6 mL) equipped with a stir bar. The bottle was equipped with carbon felt anode (15 mm × 10 mm × 3 mm) and platinum plate cathode (15 mm × 15 mm × 0.3 mm). 1-Phenylpyrrolidine (**1r**, 0.6 mmol, 2 equiv.), phenyl *trans*-styryl sulfone (**2a**, 0.3 mmol, 1 equiv.), CsOAc (0.9 mmol, 3 equiv.), $^{n}Bu_4NBF_4$ (0.6 mmol, 2 equiv.) in *N*, *N*-dimethylformamide (DMF, 6 mL) and H_2O (0.5 mL) were stirred and electrolyzed at a constant current of 6 mA under nitrogen atmosphere at room temperature for 3 h. After completion of the reaction, the reaction mixture was extracted with DCM for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. Purification by removal of excess 1-phenylpyrrolidine by heating to 120

℃ under vacuum. The pure product was obtained by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (250/1/1).

1.4 Optimization of reaction conditions

Table S1. Optimization of reaction conditions.



1c 3.0 equiv. | **2a** 0.3 mmol | **3ca**

Entry	Variation from the standard conditions	Yield [%][b]
1	None	74[a]
2	No H_2O	21
3	THF (6 mL), H_2O (0.5 mL)	50
4	Nickel plate instead of platinum plate	70
5	Carbon felt instead of platinum plate	41
6	$^nBu_4NPF_6$ instead of $^nBu_4NBF_4$	63
7	2.0 equiv. **1c**	54
8	10 mA, 1.8 h	68
9	6 mA, 3.5 h	70
10	Under air atmosphere	52
11	No electricity	n.d.

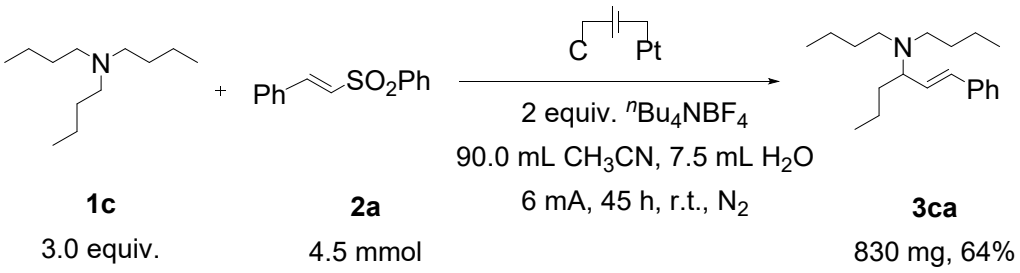
Standard conditions: Carbon felt anode (15 mm × 10 mm × 3 mm), platinum plate cathode (15 mm × 15 mm × 0.3 mm), constant current = 6 mA, **1c** (0.9 mmol, 3.0 equiv. based on **2a**), **2a** (0.3 mmol), $^nBu_4NBF_4$ (2 equiv. based on **2a**), CH_3CN (6.0 mL), H_2O (0.5 mL), room temperature, N_2 atmosphere, 3 h, undivided cell. [a]Isolated yields were shown. [b]Yields were determined by ^1H NMR, calibrated using CH_2Br_2 as the internal standard.

1.5 Cyclic voltammetry (CV) measurements

Cyclic voltammetry measurements were performed in a three-electrode cell connected to a Schlenk line under air atmosphere at room temperature. The working electrode was a glass carbon electrode, the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. Commercially available MeCN (6 mL) containing $^nBu_4NBF_4$ (0.1 M) was poured into the electrochemical cell in

all experiments. The concentration of substrates is 0.01 M. The scan rate is 0.1 V/s.

1.6 Scale-up experiments



In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar. The bottle was equipped with carbon felt anode (15 mm × 10 mm × 3 mm) and platinum plate cathode (15 mm × 15 mm × 0.3 mm). Tributylamine (**1c**, 13.5 mmol, 3 equiv.), phenyl *trans*-styryl sulfone (**2a**, 4.5 mmol, 1 equiv.), $^{n}Bu_4NBF_4$ (9 mmol, 2 equiv.) in acetonitrile (MeCN, 90 mL) and H_2O (7.5 mL) were stirred and electrolyzed at a constant current of 6 mA under nitrogen atmosphere at room temperature for 45 h. After completion of the reaction, the reaction mixture was extracted with DCM for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The pure product (830 mg, 64%) was obtained by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (250/5/3).

2. Supporting experimental results

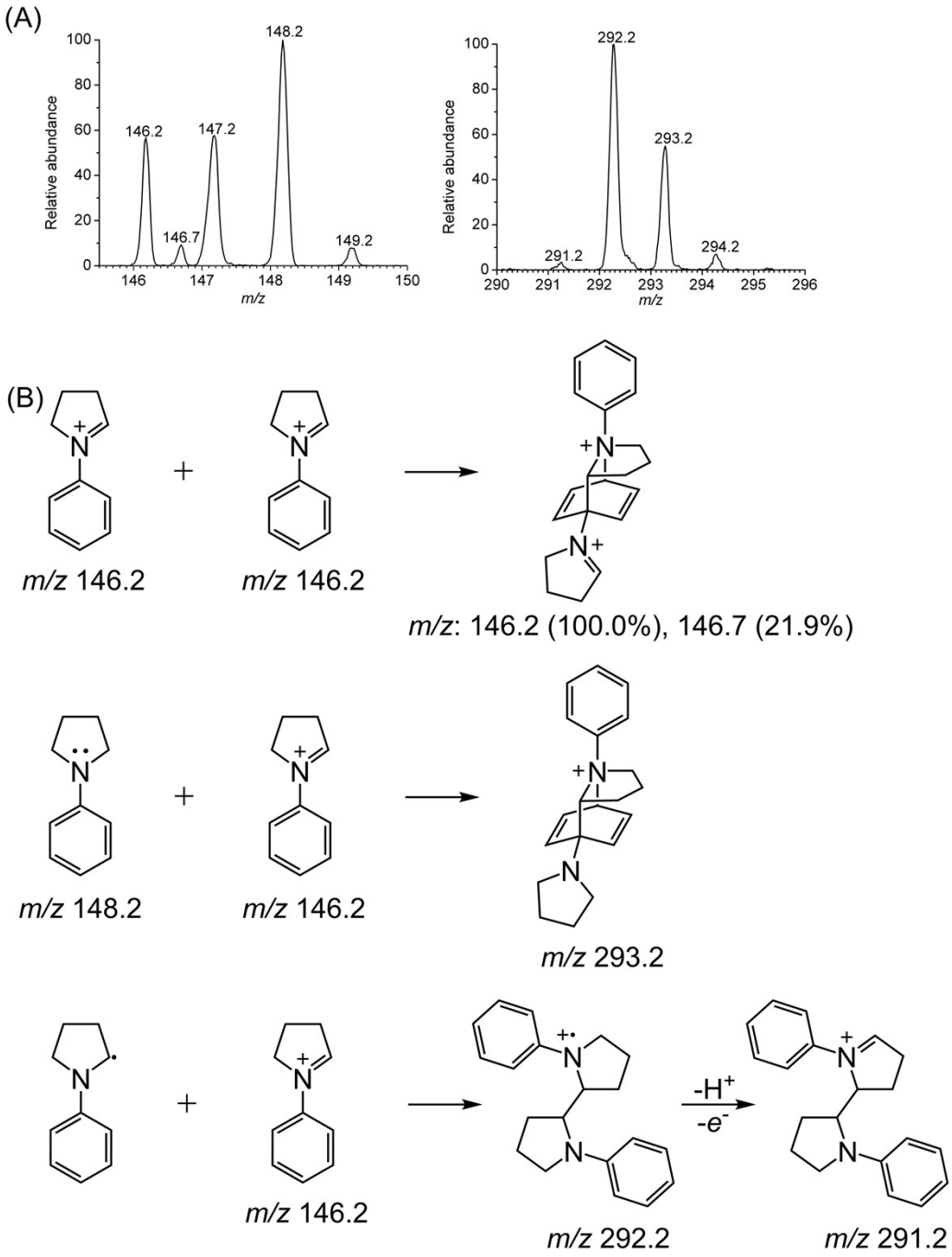
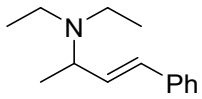
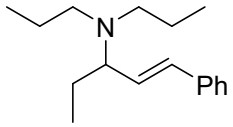


Figure S1. (A) Typical mass spectra showing the dimerization of the reactive species generated from 1-phenylpyrrolidine; **(B)** Possible structures accountable for the mass peaks from the dimerization.

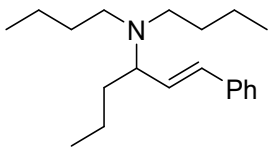
3. Analytical data of products



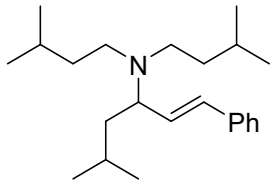
***(E)-N, N*-diethyl-4-phenylbut-3-en-2-amine (3aa)**: isolated yield (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.27 – 6.20 (m, 1H), 3.45 – 3.42 (m, 1H), 2.68 – 2.51 (m, 4H), 1.22 (dd, *J* = 6.7, 1.7 Hz, 3H), 1.05 (td, *J* = 7.1, 1.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.46, 133.37, 130.05, 128.64, 127.28, 126.31, 57.56, 43.53, 17.49, 13.12. HRMS (ESI) calculated for $C_{14}H_{22}N^+$ $(M+H)^+$: 204.1747; found: 204.1743.



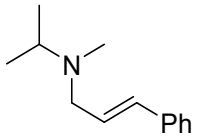
***(E)*-1-phenyl-*N, N*-dipropylpent-1-en-3-amine (3ba):** isolated yield (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.0 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.06 – 3.00 (m, 1H), 2.53 – 2.46 (m, 2H), 2.39 – 2.32 (m, 2H), 1.72 – 1.62 (m, 1H), 1.55 – 1.36 (m, 5H), 0.93 – 0.85 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.58, 131.75, 130.31, 128.62, 127.21, 126.32, 65.17, 52.83, 25.85, 21.96, 12.08, 11.59. HRMS (ESI) calculated for $C_{17}H_{28}N^+$ $(M+H)^+$: 246.2216; found: 246.2213.



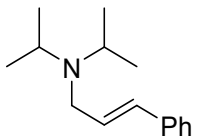
***(E)-N, N*-dibutyl-1-phenylhex-1-en-3-amine (3ca):** isolated yield (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.18 – 3.13 (m, 1H), 2.58 – 2.51 (m, 2H), 2.43 – 2.27 (m, 2H), 1.70 – 1.54 (m, 1H), 1.52 – 1.22 (m, 11H), 0.93 – 0.89 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.60, 131.65, 130.48, 128.63, 127.21, 126.33, 62.93, 50.49, 35.26, 31.16, 20.81, 20.13, 14.33, 14.30. HRMS (ESI) calculated for $C_{20}H_{34}N^+$ $(M+H)^+$: 288.2686; found: 288.2679.



***(E)-N, N*-diisopentyl-5-methyl-1-phenylhex-1-en-3-amine (3da):** ^{1}H NMR yield (80%), calibrated using CH_2Br_2 as the internal standard. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.14 (m, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.12 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.28 – 3.33 (m, 1H), 2.63 – 2.50 (m, 2H), 2.37 – 2.30 (m, 2H), 1.72 – 1.64 (m, 1H), 1.62 – 1.54 (m, 2H), 1.53 – 1.44 (m, 1H), 1.42 – 1.28 (m, 5H), 0.96 – 0.82 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.59, 131.65, 130.43, 128.64, 127.24, 126.35, 60.63, 48.70, 42.16, 38.06, 26.44, 24.91, 23.38, 23.24, 22.76, 22.67. HRMS (ESI) calculated for $C_{23}H_{40}N^+$ $(M+H)^+$: 330.3155; found: 330.3148.

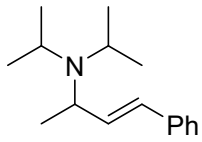


***(E)-N*-isopropyl-*N*-methyl-3-phenylprop-2-en-1-amine (3ea):** isolated yield (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.20 (dd, *J* = 6.7, 1.4 Hz, 2H), 2.96 – 2.86 (m, 1H), 2.22 (s, 3H), 1.05 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.28, 132.12, 128.64, 128.45, 127.41, 126.38, 56.44, 52.97, 36.66, 18.08. HRMS (ESI) calculated for $C_{13}H_{20}N^+$ $(M+H)^+$: 190.1590; found: 190.1586.

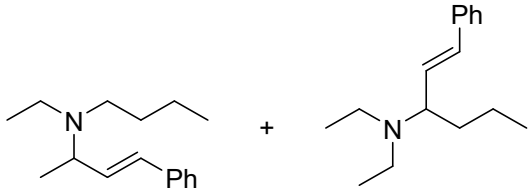


***(E)-N, N*-diisopropyl-3-phenylprop-2-en-1-amine (3fa):** isolated yield (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.15 (m, 1H), 6.50 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.2 Hz, 1H), 3.28 (dd, *J* = 6.2, 1.6 Hz, 2H), 3.14 – 3.05 (m, 2H), 1.04 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.74, 131.98, 130.10, 128.60, 127.07,

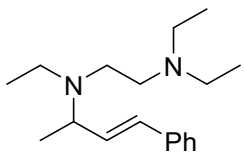
126.27, 48.41, 47.79, 20.85. HRMS (ESI) calculated for $C_{15}H_{24}N^+$ $(M+H)^+$: 218.1903; found: 218.1896.



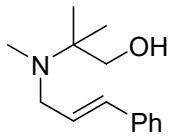
***(E)-N, N*-diisopropyl-4-phenylbut-3-en-2-amine (3ga):** isolated yield (43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 7.21 – 7.14 (m, 1H), 6.40 (dd, *J* = 16.1, 1.5 Hz, 1H), 6.28 (dd, *J* = 16.1, 5.1 Hz, 1H), 3.71 – 3.65 (m, 1H), 3.19-3.09 (m, 2H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.05 (dd, *J* = 6.7, 2.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.16, 136.81, 128.62, 127.63, 126.89, 126.20, 50.44, 45.16, 23.20, 20.19. HRMS (ESI) calculated for $C_{16}H_{26}N^+$ $(M+H)^+$: 232.2060; found: 232.2056.



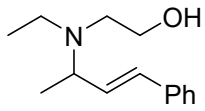
***(E)-N*-butyl-*N*-ethyl-4-phenylbut-3-en-2-amine + *(E)-N, N*-diethyl-1-phenylhex-1-en-3-amine (3ha):** isolated yield (64%, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.17 (m, 1H), 6.42 (dd, *J* = 16.0, 9.3 Hz, 1H), 6.24 (dd, *J* = 16.0, 7.2 Hz, 0.81H), 6.12 (dd, *J* = 15.9, 8.9 Hz, 0.15H), 3.49 – 3.42 (m, 0.83H), 3.23 – 3.17 (m, 0.16H), 2.75 – 2.32 (m, 4H), 1.51 – 1.38 (m, 2H), 1.36 – 1.19 (m, 5H), 1.07 – 1.03 (m, 3H), 0.94 – 0.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.56, 133.33, 130.06, 128.65, 127.26, 126.33, 62.89, 57.69, 49.78, 44.28, 43.82, 35.17, 30.60, 20.90, 20.12, 17.27, 14.30, 14.25, 13.65, 13.38. HRMS (ESI) calculated for $C_{16}H_{26}N^+$ $(M+H)^+$: 232.2060; found: 232.2055.



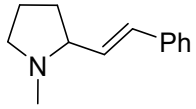
***(E)*-N_1, N_1, N_2-triethyl-N_2-(4-phenylbut-3-en-2-yl) ethane-1,2-diamine (3ia):** isolated yield (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.50 – 3.42 (m, 1H), 2.71 – 2.48 (m, 10H), 1.23 (d, *J* = 6.7 Hz, 3H), 1.08 – 1.00 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.45, 132.75, 130.36, 128.63, 127.30, 126.33, 58.27, 52.78, 48.32, 47.68, 45.47, 17.32, 13.60, 11.87. HRMS (ESI) calculated for $C_{18}H_{31}N_2^+$ $(M+H)^+$: 275.2482; found: 275.2477.



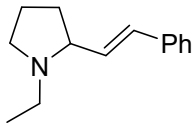
2-(Cinnamyl(methyl)amino)-2-methylpropan-1-ol (3ja): isolated yield (43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.19 (m, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.9, 6.5 Hz, 1H), 3.37 (s, 2H), 3.19 (dd, *J* = 6.6, 1.4 Hz, 2H), 2.22 (s, 3H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.17, 131.82, 128.94, 128.68, 127.50, 126.36, 68.40, 57.74, 52.64, 34.28, 20.87. HRMS (ESI) calculated for $C_{14}H_{22}NO^+$ $(M+H)^+$: 220.1696; found: 220.1690.



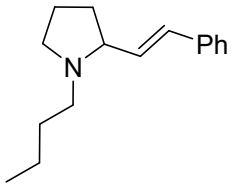
***(E)*-2-(ethyl(4-phenylbut-3-en-2-yl)amino)ethan-1-ol (3ka):** isolated yield (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.27 – 7.18 (m, 1H), 6.43 (dd, *J* = 16.1, 1.2 Hz, 1H), 6.20 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.64 – 3.34 (m, 3H), 2.76 – 2.67 (m, 1H), 2.65 – 2.52 (m, 3H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.17, 131.55, 130.95, 128.68, 127.51, 126.37, 58.56, 56.87, 50.91, 44.05, 17.06, 14.14. HRMS (ESI) calculated for $C_{14}H_{22}NO^+$ $(M+H)^+$: 220.1696; found: 220.1692.



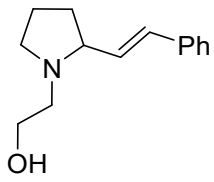
***(E)*-1-methyl-2-styrylpyrrolidine (3la)[3]:** isolated yield (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.9 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.10 (dd, *J* = 15.8, 8.4 Hz, 1H), 3.15 (td, *J* = 8.0, 4.0 Hz, 1H), 2.68 (q, *J* = 8.2 Hz, 1H), 2.30 (s, 3H), 2.22 (q, *J* = 9.0 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.94 – 1.84 (m, 1H), 1.82 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.13, 132.12, 131.84, 128.67, 127.51, 126.43, 69.81, 56.88, 40.48, 32.28, 22.45.



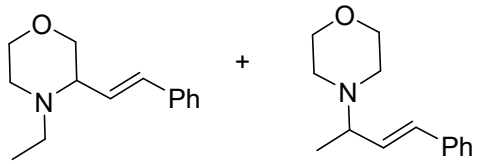
***(E)*-1-ethyl-2-styrylpyrrolidine (3ma):** isolated yield (66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.30 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.25 – 7.15 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 8.5 Hz, 1H), 3.26 (td, *J* = 8.5, 2.6 Hz, 1H), 2.96 – 2.77 (m, 2H), 2.19 – 1.95 (m, 3H), 1.95 – 1.66 (m, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.15, 132.42, 131.73, 128.66, 127.47, 126.41, 68.67, 53.13, 48.26, 31.92, 22.22, 13.83. HRMS (ESI) calculated for $C_{14}H_{20}N^+$ $(M+H)^+$: 202.1590; found: 202.1584.



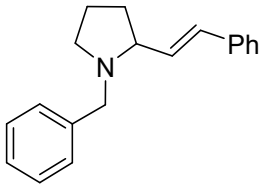
***(E)*-1-butyl-2-styrylpyrrolidine (3na)[4]:** isolated yield (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.34 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.28 – 7.23 (m, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.16 (dd, *J* = 15.8, 8.3 Hz, 1H), 3.27 (td, *J* = 8.6, 2.6 Hz, 1H), 2.87 – 2.79 (m , 2H), 2.16 (q, *J* = 8.8 Hz, 1H), 2.10 – 1.69 (m, 5H), 1.57 – 1.47 (m, 2H), 1.39 – 1.27 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.30, 132.86, 131.45, 128.67, 127.41, 126.42, 68.86, 54.50, 53.77, 31.93, 31.16, 22.39, 21.03, 14.22.



***(E)*-2-(2-styrylpyrrolidin-1-yl)ethan-1-ol (3oa):** isolated yield (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.05 (dd, *J* = 15.8, 8.5 Hz, 1H), 3.70 – 3.54 (m, 2H), 3.24 (td, *J* = 8.5, 3.1 Hz, 1H), 3.06 – 2.93 (m, 2H), 2.72 (s, 1H), 2.30 (dt, *J* = 12.4, 3.8 Hz, 1H), 2.26 – 2.17 (m, 1H), 2.05 – 2.97 (m, 1H), 1.92 – 1.76 (m, 2H), 1.72 – 1.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.93, 132.08, 131.93, 128.60, 127.52, 126.41, 68.39, 59.96, 55.47, 53.34, 31.90, 22.50. HRMS (ESI) calculated for $C_{14}H_{20}NO^+$ $(M+H)^+$: 218.1539; found: 218.1533.

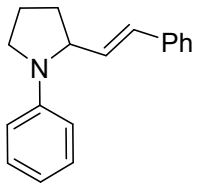


***(E)*-4-(4-phenylbut-3-en-2-yl)morpholine + (*E*)-4-ethyl-3-styrylmorpholine (3pa):** ^{1}H NMR yield (33%, 3:1), calibrated using CH_2Br_2 as the internal standard. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.28 – 7.21 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 0.73H), 6.47 (d, *J* = 15.9 Hz, 0.21H), 6.17 (dd, *J* = 15.9, 8.2 Hz, 0.23H),6.05 (dd, *J* = 16.0, 8.8 Hz, 0.72H), 3.92 – 3.87 (m, 0.79H), 3.78 – 3.70 (m, 2H), 3.48 – 3.43 (m, 0.77H), 3.06 – 2.97 (m, 1H), 2.94 – 2.86 (m, 1.48H), 2.62 – 2.54 (m, 1H), 2.34 – 2.20 (m, 2H), 1.29 – 1.24 (m, 0.77H), 1.05 (t, *J* = 7.2 Hz, 2.18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.63, 133.94, 131.55, 128.76, 128.72, 127.93, 127.64, 126.48, 126.41, 71.38, 67.35, 67.25, 64.77, 63.31, 50.86, 50.45, 49.11, 17.86, 11.11. HRMS (ESI) calculated for $C_{14}H_{20}NO^+$ $(M+H)^+$: 218.1539; found: 218.1532.

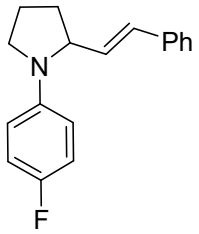


***(E)*-1-benzyl-2-styrylpyrrolidine (3qa)[5]:** isolated yield (45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.34 – 7.26 (m, 6H), 7.25 – 7.18 (m, 2H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 3.13 (d, *J* = 13.0 Hz, 1H), 2.98 (t, *J* = 8.3 Hz, 2H), 2.17 (q, *J* = 8.8 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.87 – 1.69 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.51,

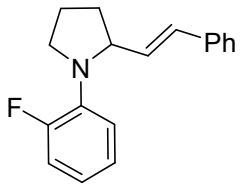
137.25, 132.72, 131.84, 129.16, 128.67, 128.27, 127.48, 126.89, 126.44, 68.03, 58.47, 53.50, 31.92, 22.27. HRMS (ESI) calculated for $C_{19}H_{22}N^+$ $(M+H)^+$: 264.1747; found: 264.1740.



***(E)*-1-phenyl-2-styrylpyrrolidine (3ra)[1]:** isolated yield (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.21 - 7.18 (m, 3H), 6.67 – 6.63 (m, 3H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 5.2 Hz, 1H), 4.32 – 4.30 (m, 1H), 3.54 (t, *J* = 7.2 Hz, 1H), 3.27 (q, *J* = 8.0 Hz, 1H), 2.17 – 1.89 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.65, 137.13, 131.76, 129.55, 129.14, 128.60, 127.34, 126.46, 115.84, 112.30, 60.84, 48.85, 33.10, 23.49.

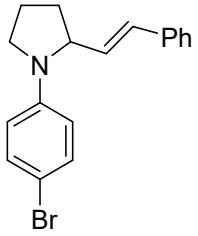


***(E)*-1-(4-fluorophenyl)-2-styrylpyrrolidine (3sa)[1]:** isolated yield (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 4H), 7.23 – 7.09 (m, 1H), 6.98 – 6.78 (m, 2H), 6.61 – 6.49 (m, 2H), 6.43 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.19 (dd, *J* = 15.8, 5.5 Hz, 1H), 4.25 – 4.20 (m, 1H), 3.54 – 3.49 (m, 1H), 3.25 – 3.19 (m, 1H), 2.25 – 1.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.06 (d, *J* = 234.3 Hz), 144.34 (d, *J* = 2.0 Hz), 137.03, 131.72, 129.67, 128.64, 127.43, 126.45, 115.47 (d, *J* = 22.2 Hz), 112.70 (d, *J* = 7.1 Hz), 61.29, 49.37, 33.23, 23.60. ^{19}F NMR (377 MHz, $CDCl_3$) δ -130.46.

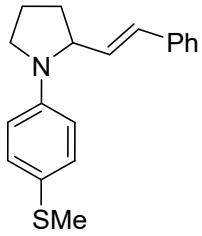


***(E)*-1-(2-fluorophenyl)-2-styrylpyrrolidine (3ta):** isolated yield (44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 4H), 7.21 – 7.13 (m, 1H), 6.99 – 6.89 (m, 2H), 6.78 – 6.73 (m, 1H), 6.67

– 6.62 (m, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 6.7 Hz, 1H), 4.45 (q, *J* = 6.4 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.43 – 3.29 (m, 1H), 2.22 – 2.16 (m, 1H), 2.09 – 1.98 (m, 1H), 1.96 – 1.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.62 (d, *J* = 242.4 Hz), 137.15, 136.69 (d, *J* = 9.1 Hz), 131.97, 130.19, 128.59, 127.36, 126.42, 124.28 (d, *J* = 3.0 Hz), 117.92 (d, *J* = 7.1 Hz), 116.80 (d, *J* = 5.1 Hz), 116.26 (d, *J* = 21.2 Hz), 61.83 (d, J = 3.0 Hz), 51.41 (d, J = 7.1 Hz), 33.30, 23.90 (d, J = 2.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -125.14. HRMS (ESI) calculated for $C_{18}H_{19}FN^+$ $(M+H)^+$: 268.1496; found: 268.1488.

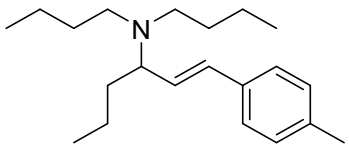


***(E)*-1-(4-bromophenyl)-2-styrylpyrrolidine (3ua)[1]:** ^{1}H NMR yield (70%), calibrated using CH_2Br_2 as the internal standard. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.14 (m, 7H), 6.57 – 6.46 (m, 2H), 6.39 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.17 (dd, *J* = 15.9, 5.3 Hz, 1H), 4.29 – 4.24 (m, 1H), 3.53 – 3.48 (m, 1H), 3.24 (td, *J* = 9.0, 6.8 Hz, 1H), 2.22 – 2.15 (m, 1H), 2.11 – 1.96 (m, 2H), 1.94 – 1.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.49, 136.90, 131.73, 131.00, 129.86, 128.66, 127.51, 126.47, 113.94, 107.70, 60.89, 48.92, 33.12, 23.47.

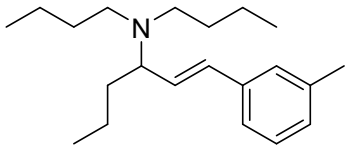


***(E)*-1-(4-(methylthio)phenyl)-2-styrylpyrrolidine (3va):** ^{1}H NMR yield (75%), calibrated using CH_2Br_2 as the internal standard.. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.13 (m, 7H), 6.64 – 6.53 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 15.9, 5.4 Hz, 1H), 4.29 (td, *J* = 7.4, 6.9, 2.2 Hz, 1H), 3.54 (ddd, *J* = 9.6, 7.3, 2.6 Hz, 1H), 3.27 (td, *J* = 9.0, 6.7 Hz, 1H), 2.39 (s, 3H), 2.23 – 1.88 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.61, 136.97, 131.96, 131.31, 129.73, 128.63, 127.44,

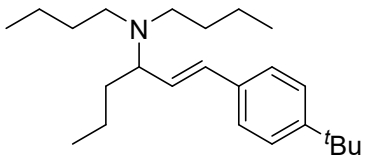
126.46, 122.33, 112.95, 60.87, 48.89, 33.09, 23.46, 19.75. HRMS (ESI) calculated for $C_{19}H_{22}NS^+$ $(M+H)^+$: 296.1467; found: 296.1461.



***(E)-N, N*-dibutyl-1-(*p*-tolyl)hex-1-en-3-amine (3ab):** isolated yield (65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.07 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.16 – 3.11 (m, 1H), 2.57 – 2.50 (m, 2H), 2.41 – 2.28 (m, 5H), 1.67 – 1.55 (m, 1H), 1.48 – 1.21 (m, 11H), 0.91 (t, *J* = 7.2 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.98, 134.79, 131.57, 129.32, 126.23, 63.00, 50.48, 35.27, 31.09, 21.27, 20.82, 20.14, 14.32, 14.29. HRMS (ESI) calculated for $C_{21}H_{36}N^+$ $(M+H)^+$: 302.2842; found: 302.2834.

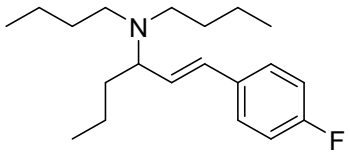


***(E)-N, N*-dibutyl-1-(*m*-tolyl)hex-1-en-3-amine (3ac):** isolated yield (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 3H), 7.06 – 6.97 (m, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.17 – 3.11 (m, 1H), 2.58 – 2.51 (m, 2H), 2.40 – 2.30 (m, 5H), 1.65 – 1.57 (m, 1H), 1.49 – 1.22 (m, 11H), 0.91 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.17, 137.52, 131.77, 130.18, 128.54, 128.01, 127.02, 123.50, 62.95, 50.49, 35.31, 31.16, 21.53, 20.81, 20.14, 14.32, 14.30. HRMS (ESI) calculated for $C_{21}H_{36}N^+$ $(M+H)^+$: 302.2842; found: 302.2834.

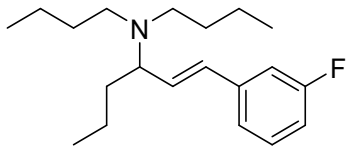


***(E)-N, N*-dibutyl-1-(4-(*tert*-butyl)phenyl)hex-1-en-3-amine (3ad):** isolated yield (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 4H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.22 – 3.17 (m, 1H), 2.67 – 2.52 (m, 2H), 2.43 – 2.37 (m, 2H), 1.78 – 1.60 (m, 1H), 1.55 – 1.25 (m, 20H), 0.96 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.32, 134.80, 131.47, 129.58,

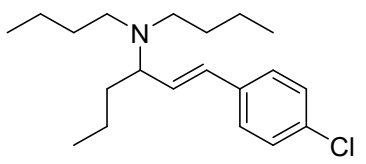
126.05, 125.57, 63.05, 50.50, 35.35, 34.66, 31.45, 31.08, 20.83, 20.13, 14.32, 14.30. HRMS (ESI) calculated for $C_{24}H_{42}N^+$ $(M+H)^+$: 344.3312; found: 344.3303.



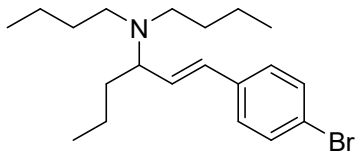
***(E)-N, N*-dibutyl-1-(4-fluorophenyl)hex-1-en-3-amine (3ae):** isolated yield (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.17 – 3.11 (m, 1H), 2.57 – 2.50 (m, 2H), 2.38 – 2.31 (m, 2H), 1.65 – 1.57 (m, 1H), 1.49 – 1.23 (m, 11H), 0.93 – 0.89 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.18 (d, *J* = 249.5 Hz), 133.73 (d, *J* = 3.0 Hz), 130.47, 130.20, 127.75 (d, *J* = 8.1 Hz), 115.47 (d, *J* = 21.2 Hz), 62.87, 50.46, 35.15, 31.13, 20.79, 20.13, 14.31, 14.28. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.28. HRMS (ESI) calculated for $C_{20}H_{33}FN^+$ $(M+H)^+$: 306.2592; found: 306.2584.



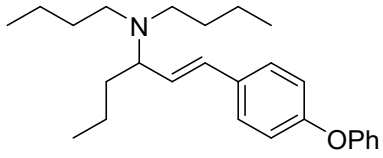
***(E)-N, N*-dibutyl-1-(3-fluorophenyl)hex-1-en-3-amine (3af):** isolated yield (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (q, *J* = 7.7 Hz, 1H), 7.09 (dd, *J* = 20.1, 9.0 Hz, 2H), 6.92 – 6.87 (m, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.9, 8.6 Hz, 1H), 3.16 (q, *J* = 7.6 Hz, 1H), 2.58 – 2.50 (m, 2H), 2.38 – 2.31 (m, 2H), 1.64 – 1.57 (m, 1H), 1.52 – 1.21 (m, 11H), 0.91 (t, *J* = 7.2 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.28 (d, *J* = 246.4 Hz), 139.95 (d, *J* = 7.1 Hz), 131.98, 130.60, 130.03 (d, *J* = 8.1 Hz), 122.23 (d, *J* = 2.0 Hz), 113.99 (d, *J* = 22.2 Hz), 112.72 (d, *J* = 22.2 Hz), 62.79, 50.47, 35.04, 31.12, 20.78, 20.11, 14.30, 14.28. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.72. HRMS (ESI) calculated for $C_{20}H_{33}FN^+$ $(M+H)^+$: 306.2592; found: 306.2583.



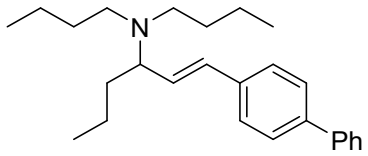
***(E)-N, N*-dibutyl-1-(4-chlorophenyl)hex-1-en-3-amine (3ag):** isolated yield (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 4H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 8.6 Hz, 1H), 3.17 – 3.12 (m, 1H), 2.57 – 2.50 (m, 2H), 2.37 – 2.31 (m, 2H), 1.68 – 1.56 (m, 1H), 1.49 – 1.20 (m, 11H), 0.91 (td, *J* = 7.2, 2.4 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.05, 132.77, 131.29, 130.41, 128.74, 127.52, 62.84, 50.46, 35.05, 31.13, 20.78, 20.12, 14.31, 14.28. HRMS (ESI) calculated for $C_{20}H_{33}ClN^+$ $(M+H)^+$: 322.2296; found: 322.2293.



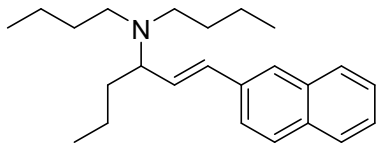
***(E)*-1-(4-bromophenyl)-*N, N*-dibutylhex-1-en-3-amine (3ah):** isolated yield (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 8.6 Hz, 1H), 3.17 – 3.11 (m, 1H), 2.57 – 2.50 (m, 2H), 2.37 – 2.31 (m, 2H), 1.69 – 1.55 (m, 1H), 1.50 – 1.21 (m, 11H), 0.91 (td, *J* = 7.2, 2.4 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.49, 131.69, 131.47, 130.44, 127.87, 120.87, 62.84, 50.46, 35.02, 31.13, 20.78, 20.11, 14.31, 14.28. HRMS (ESI) calculated for $C_{20}H_{33}BrN^+$ $(M+H)^+$: 366.1791; found: 366.1790.



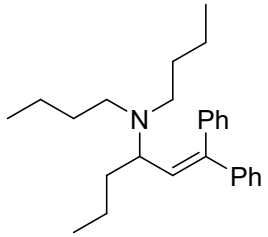
***(E)-N, N*-dibutyl-1-(4-phenoxyphenyl)hex-1-en-3-amine (3ai):** isolated yield (59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 4H), 7.12 – 7.05 (m, 1H), 7.03 – 6.98 (m, 2H), 6.97 – 6.92 (m, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.05 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.17 – 3.12 (m, 1H), 2.63 – 2.47 (m, 2H), 2.39 – 2.32 (m, 2H), 1.64 – 1.57 (m, 1H), 1.53 – 1.21 (m, 11H), 0.91 (td, *J* = 7.2, 1.9 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.47, 156.43, 132.93, 130.83, 129.85, 129.57, 127.62, 123.29, 119.18, 118.83, 62.94, 50.48, 35.27, 31.14, 20.81, 20.15, 14.33, 14.30. HRMS (ESI) calculated for $C_{26}H_{38}NO^+$ $(M+H)^+$: 380.2948; found: 380.2940.



***(E)*-1-([1,1'-biphenyl]-4-yl)-*N, N*-dibutylhex-1-en-3-amine (3aj):** isolated yield (49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 4H), 7.43 (dd, *J* = 10.4, 7.9 Hz, 4H), 7.37 – 7.28 (m, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.21 – 3.15 (m, 1H), 2.60 – 2.53 (m, 2H), 2.40 – 2.34 (m, 2H), 1.68 – 1.59 (m, 1H), 1.54 – 1.22 (m, 11H), 0.94 – 0.90 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.96, 140.07, 136.58, 131.27, 130.63, 128.90, 127.37, 127.34, 127.05, 126.75, 63.03, 50.51, 35.22, 31.10, 20.82, 20.15, 14.33, 14.30. HRMS (ESI) calculated for $C_{26}H_{38}N^+$ $(M+H)^+$: 364.2999; found: 364.2995.

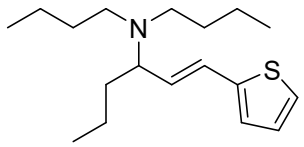


***(E)*-*N, N*-dibutyl-1-(naphthalen-2-yl)hex-1-en-3-amine (3ak):** isolated yield (49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.3 Hz, 3H), 7.70 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.50 – 7.34 (m, 2H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.24 – 3.19 (m, 1H), 2.61 – 2.54 (m, 2H), 2.42 – 2.36 (m, 2H), 1.69 – 1.61 (m, 1H), 1.56 – 1.23 (m, 11H), 1.02 – 0.80 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.99, 133.81, 132.93, 131.84, 130.89, 128.22, 127.99, 127.77, 126.32, 125.93, 125.74, 123.80, 63.09, 50.52, 35.21, 31.12, 20.82, 20.18, 14.35, 14.31. HRMS (ESI) calculated for $C_{24}H_{36}N^+$ $(M+H)^+$: 338.2842; found: 338.2837.

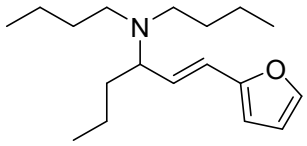


***N, N*-dibutyl-1,1-diphenylhex-1-en-3-amine (3al):** isolated yield (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.10 (m, 10H), 6.03 (d, *J* = 10.4 Hz, 1H), 3.29 – 3.23 (m, 1H), 2.56 – 2.49 (m, 2H), 2.31 – 2.24 (m, 2H), 1.61 – 1.57 (m, 1H), 1.49 – 1.39 (m, 1H), 1.35 (q, *J* = 7.3 Hz, 2H), 1.29 – 1.05

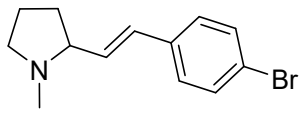
(m, 8H), 0.86 – 0.80 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70, 142.92, 140.38, 130.10, 130.05, 128.23, 128.15, 127.39, 127.16, 127.03, 57.25, 50.14, 35.94, 31.07, 20.72, 19.92, 14.38, 14.23. HRMS (ESI) calculated for $C_{26}H_{38}N^+$ $(M+H)^+$: 364.2999; found: 364.2992.



***(E)-N, N*-dibutyl-1-(thiophen-2-yl)hex-1-en-3-amine (3am):** isolated yield (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 5.1 Hz, 1H), 7.01 – 6.82 (m, 2H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.8, 8.6 Hz, 1H), 3.14 – 3.09 (m, 1H), 2.56 – 2.49 (m, 2H), 2.43 – 2.28 (m, 2H), 1.64 – 1.55 (m, 1H), 1.50 – 1.23 (m, 11H), 0.91 (t, *J* = 7.1 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.87, 130.44, 127.41, 124.91, 124.80, 123.59, 62.82, 50.47, 35.06, 31.16, 20.79, 20.14, 14.30. HRMS (ESI) calculated for $C_{18}H_{32}NS^+$ $(M+H)^+$: 294.2250; found: 294.2245.

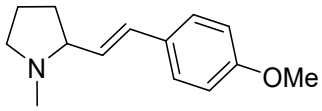


***(E)-N, N*-dibutyl-1-(furan-2-yl)hex-1-en-3-amine (3an):** isolated yield (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 1.8 Hz, 1H), 6.36 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.28 – 6.14 (m, 2H), 6.07 (dd, *J* = 15.9, 8.6 Hz, 1H), 3.11 (td, *J* = 8.3, 5.8 Hz, 1H), 2.56 – 2.49 (m, 2H), 2.36 – 2.30 (m, 2H), 1.66 – 1.53 (m, 1H), 1.48 – 1.22 (m, 11H), 0.90 (t, *J* = 7.2 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.07, 141.54, 129.25, 120.19, 111.29, 106.82, 62.68, 50.49, 35.17, 31.27, 20.79, 20.14, 14.29. HRMS (ESI) calculated for $C_{18}H_{32}NO^+$ $(M+H)^+$: 278.2478; found: 278.2472.

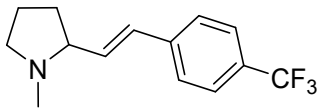


***(E)*-2-(4-bromostyryl)-1-methylpyrrolidine (3ao):** isolated yield (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.09 (dd, *J* = 15.8, 8.3 Hz, 1H), 3.17 – 3.12 (m, 1H), 2.67 (q, *J* = 8.2 Hz, 1H), 2.29 (s, 3H), 2.22 (q, *J* = 9.0 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.96 – 1.84 (m, 1H), 1.84 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

136.07, 132.97, 131.73, 130.62, 127.95, 121.18, 69.63, 56.85, 40.49, 32.21, 22.48. HRMS (ESI) calculated for $C_{13}H_{17}BrN^+$ $(M+H)^+$: 266.0539; found: 266.0539.

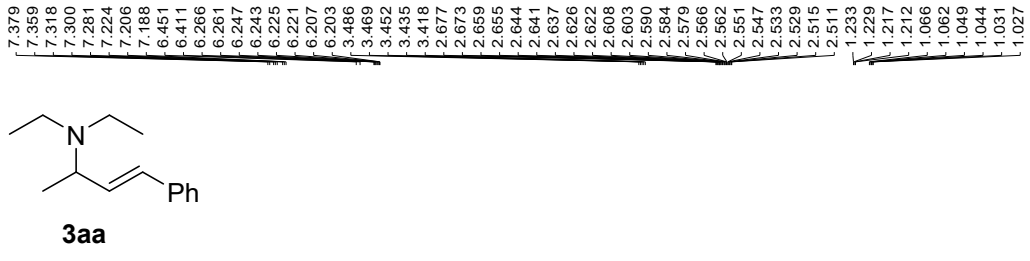


***(E)*-2-(4-methoxystyryl)-1-methylpyrrolidine (3ap):** isolated yield (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 6.91 – 6.78 (m, 2H), 6.45 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.8, 8.5 Hz, 1H), 3.80 (s, 3H), 3.19 – 3.15 (m, 1H), 2.71 – 2.65 (m, 1H), 2.31 (s, 3H), 2.24 (q, *J* = 9.0 Hz, 1H), 2.08 – 1.98 (m, 1H), 1.95 – 1.83 (m, 1H), 1.82 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.23, 131.59, 129.88, 129.41, 127.62, 114.10, 70.00, 56.74, 55.43, 40.33, 32.26, 22.37. HRMS (ESI) calculated for $C_{14}H_{20}NO^+$ $(M+H)^+$: 218.1539; found: 218.1533.

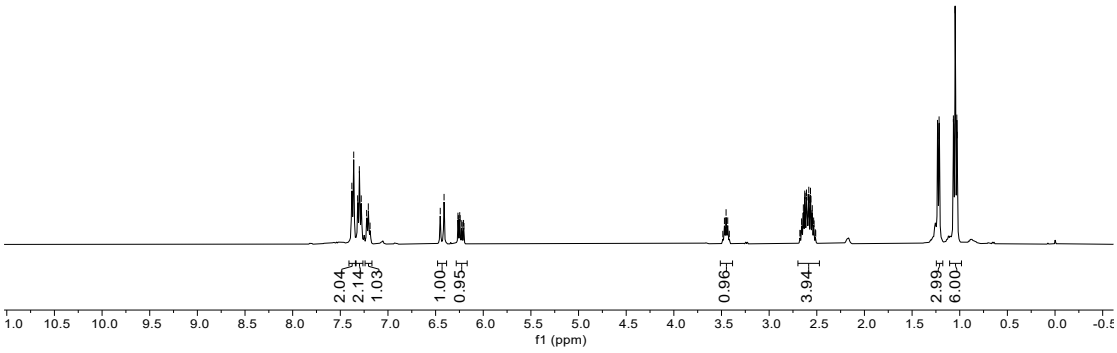


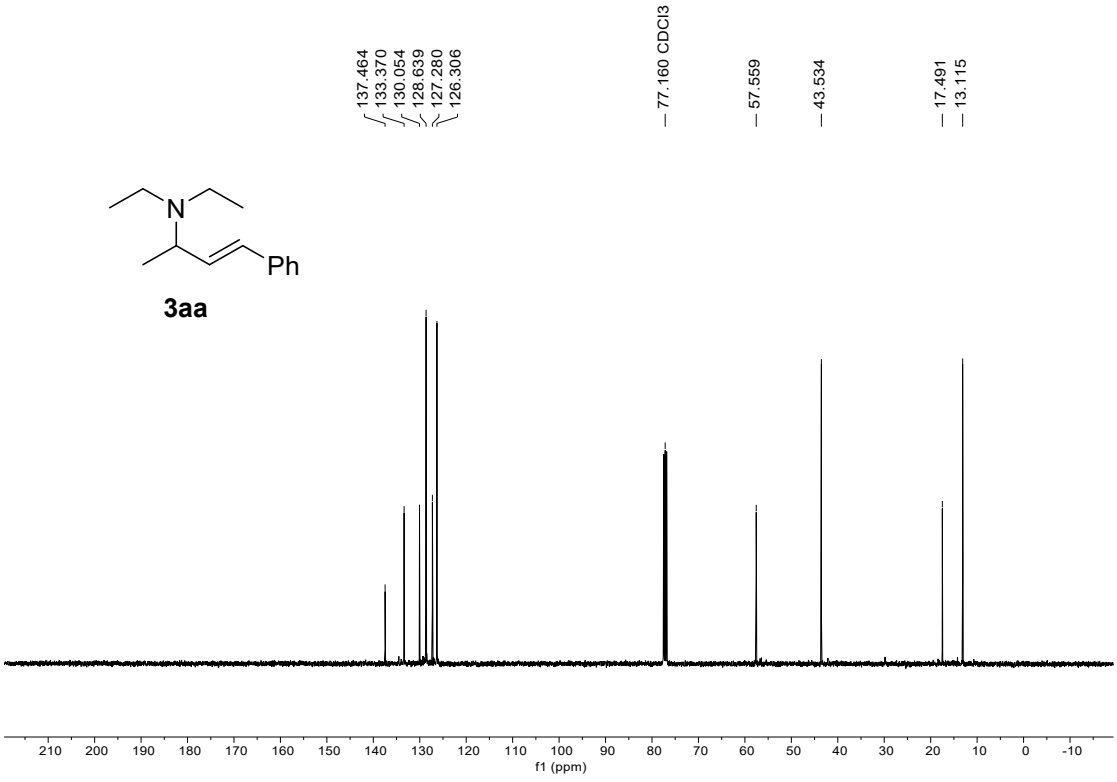
***(E)*-1-methyl-2-(4-(trifluoromethyl)styryl)pyrrolidine (3aq):** isolated yield (32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.9, 8.3 Hz, 1H), 3.18 – 3.13 (m, 1H), 2.71 (q, *J* = 8.2 Hz, 1H), 2.31 (s, 3H), 2.28 – 2.20 (m, 1H), 2.10 – 2.01 (m, 1H), 1.96 – 1.85 (m, 1H), 1.85 – 1.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.67, 135.14, 130.36, 129.29 (q, *J* = 32.3 Hz), 126.56, 125.64 (q, *J* = 4.0 Hz), 124.35 (d, *J* = 271.7 Hz), 69.52, 56.94, 40.57, 32.29, 22.58. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.47. HRMS (ESI) calculated for $C_{14}H_{17}F_3N^+$ $(M+H)^+$: 256.1308; found: 256.1300.

4. NMR spectra of products



3aa





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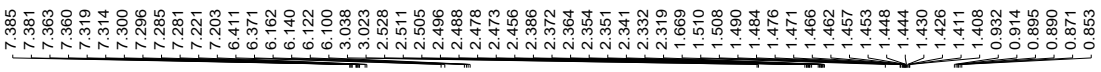
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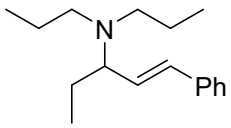
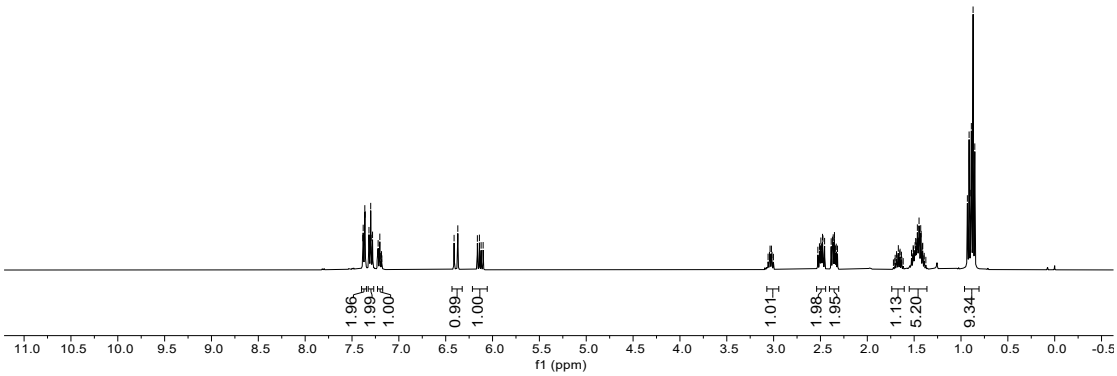
0.853


N
Ph

3ba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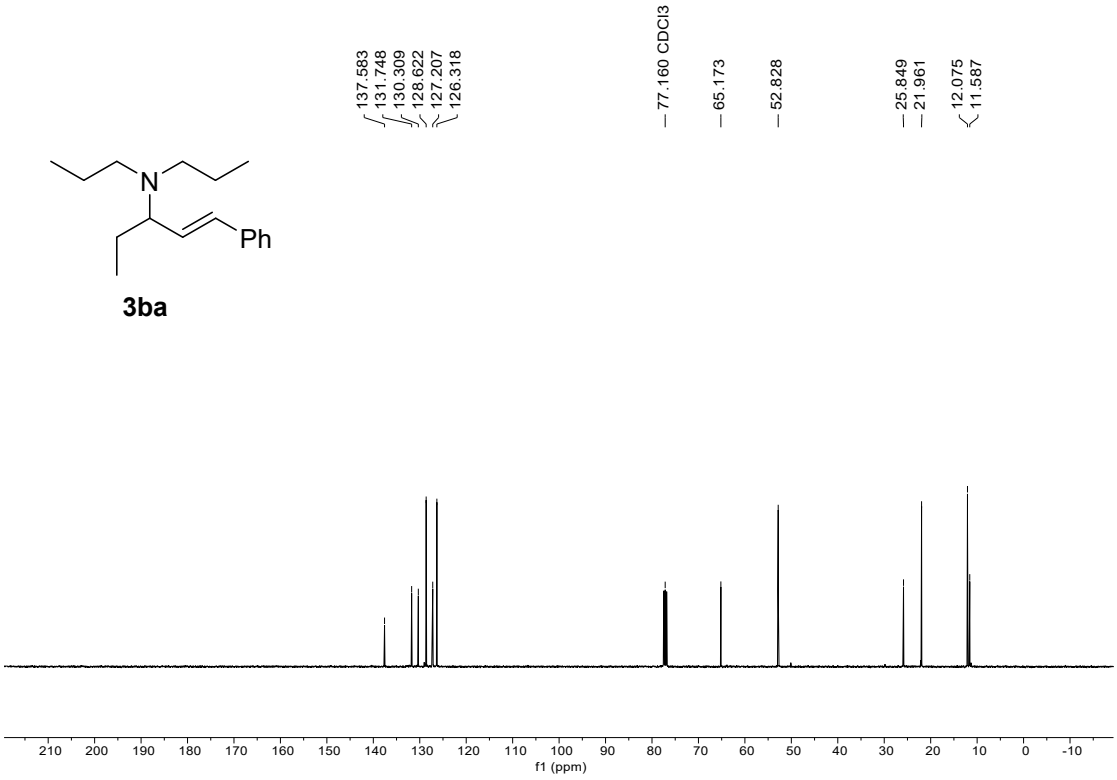
1.99
1.00
0.99
1.00
1.01
1.98
1.95
1.13
5.20
9.34
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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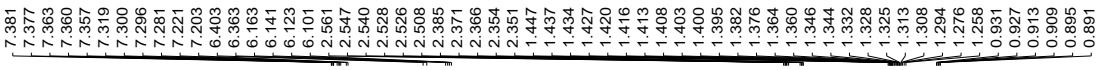
f1 (ppm)

N
Ph

3ba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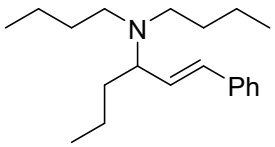
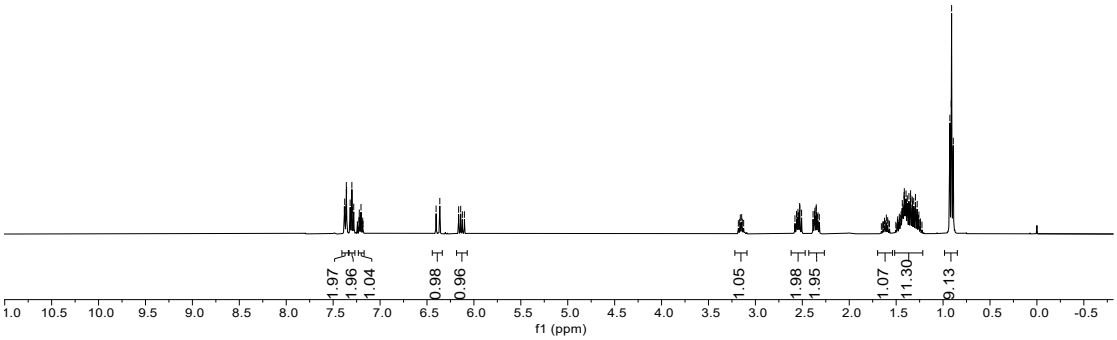
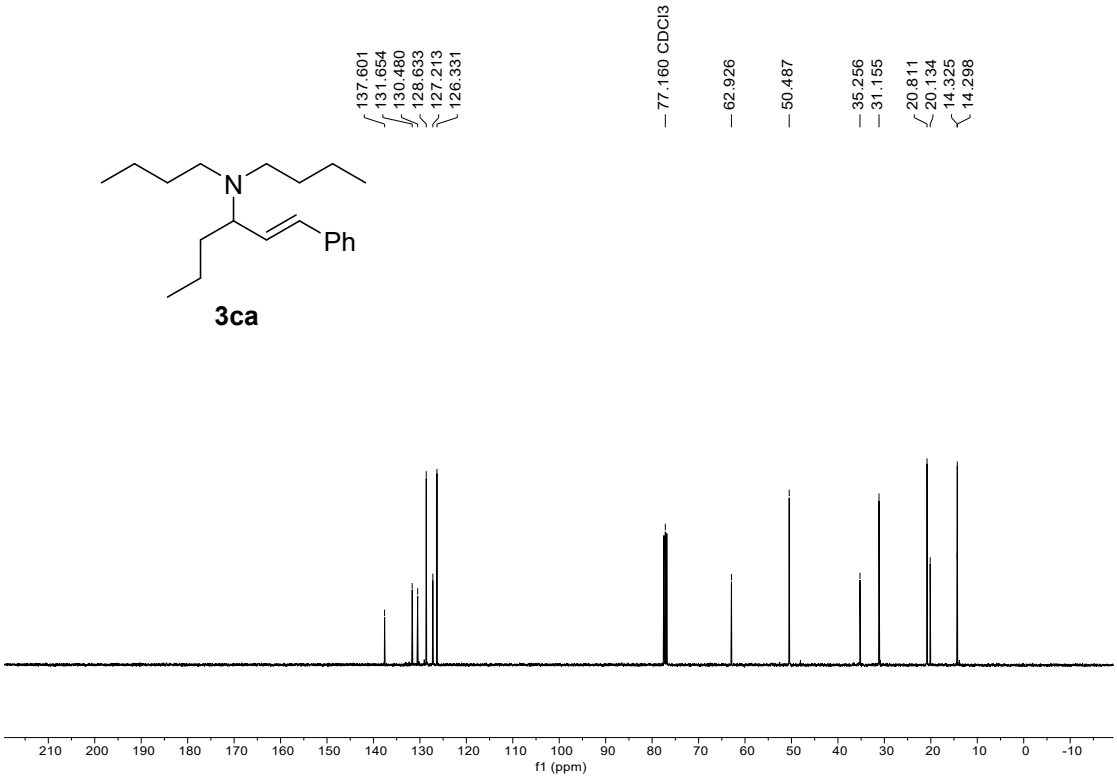
0.895
0.891


N
Ph

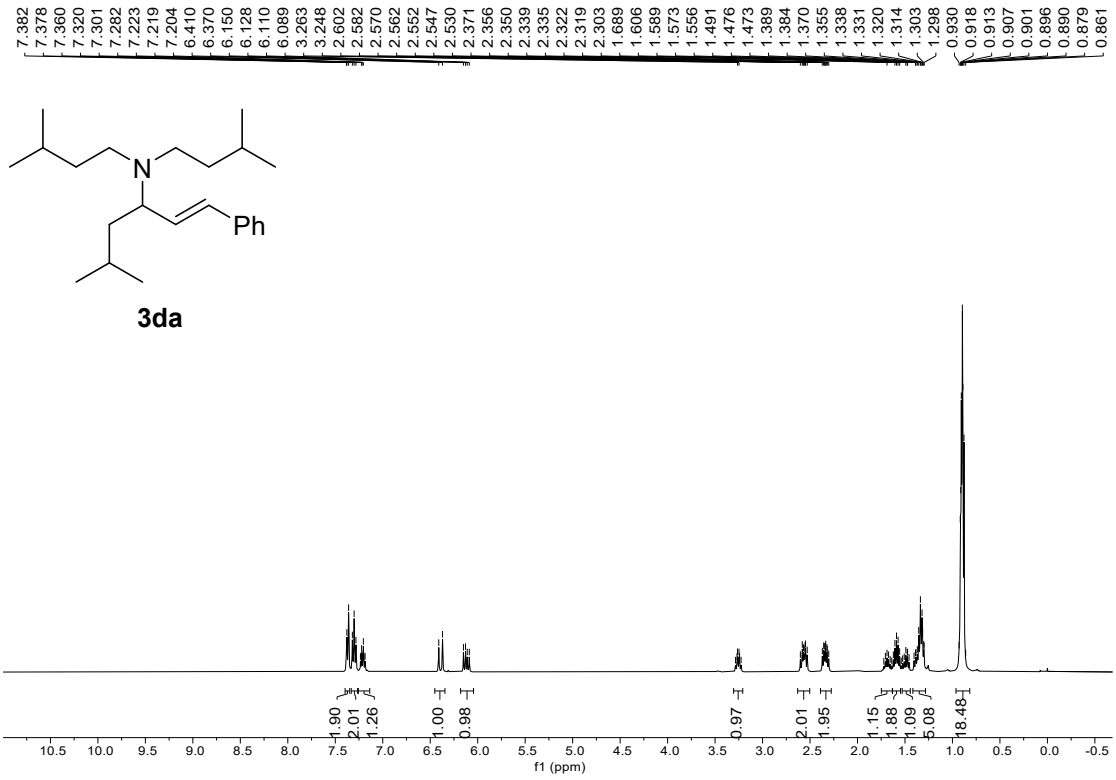
3ca


1.97
1.96
1.04
0.98
0.96
1.05
1.98
1.95
1.07
11.30
9.13
f1 (ppm)

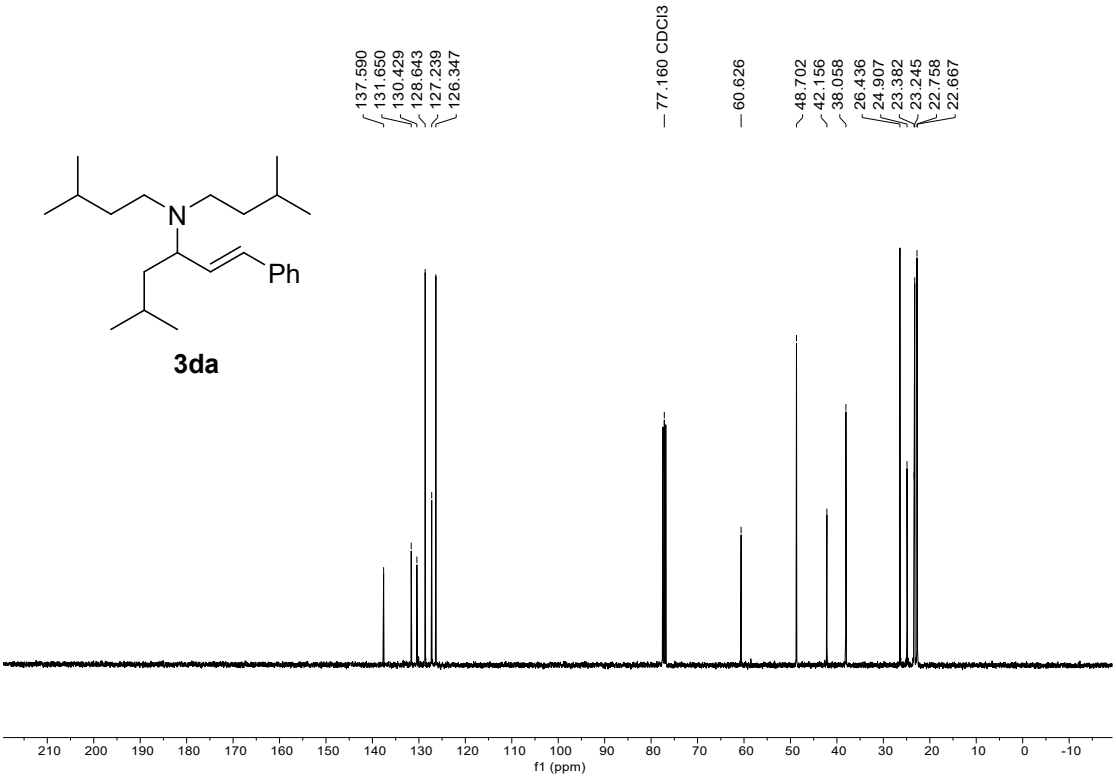

137.601
131.654
130.480
128.633
127.213
126.331
77.160 CDCl3
62.926
50.487
35.256
31.155
20.811
20.134
14.325
14.298
f1 (ppm)

N
Ph

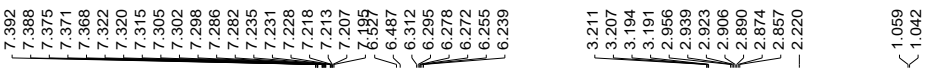
3ca


7.382
7.378
7.360
7.320
7.301
7.282
7.223
7.219
7.204
6.410
6.370
6.150
6.128
6.110
6.089
3.263
3.248
2.602
2.582
2.570
2.562
2.552
2.547
2.530
2.371
2.356
2.350
2.339
2.335
2.322
2.319
2.303
1.689
1.606
1.589
1.573
1.556
1.491
1.476
1.473
1.389
1.384
1.370
1.355
1.338
1.331
1.320
1.314
1.303
1.298
0.930
0.918
0.913
0.907
0.901
0.896
0.890
0.879
0.861
N
Ph
1.90
2.01
1.26
1.00
0.98
0.97
2.01
1.95
1.15
1.88
1.09
5.08
18.48
f1 (ppm)

3da


137.590
131.650
130.429
128.643
127.239
126.347
77.160 CDCl3
60.626
48.702
42.156
38.058
26.436
24.907
23.382
23.245
22.758
22.667
N
Ph
f1 (ppm)

3da


7.392
7.388
7.375
7.371
7.368
7.322
7.320
7.315
7.305
7.302
7.298
7.286
7.282
7.235
7.231
7.228
7.218
7.213
7.207
7.195
6.527
6.487
6.312
6.295
6.278
6.272
6.255
6.239
3.211
3.207
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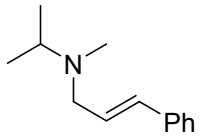
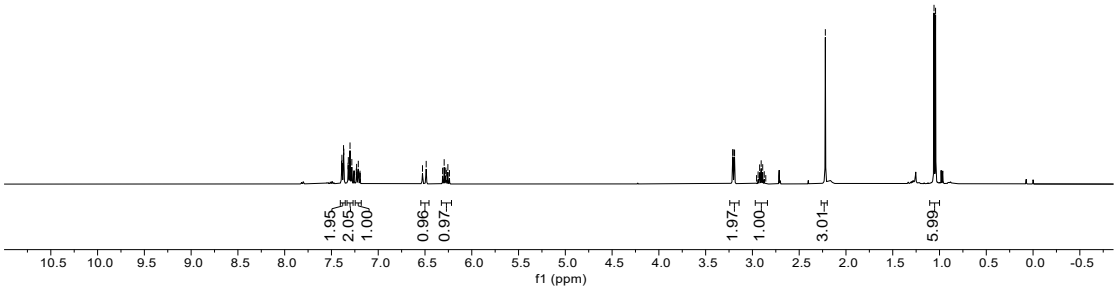
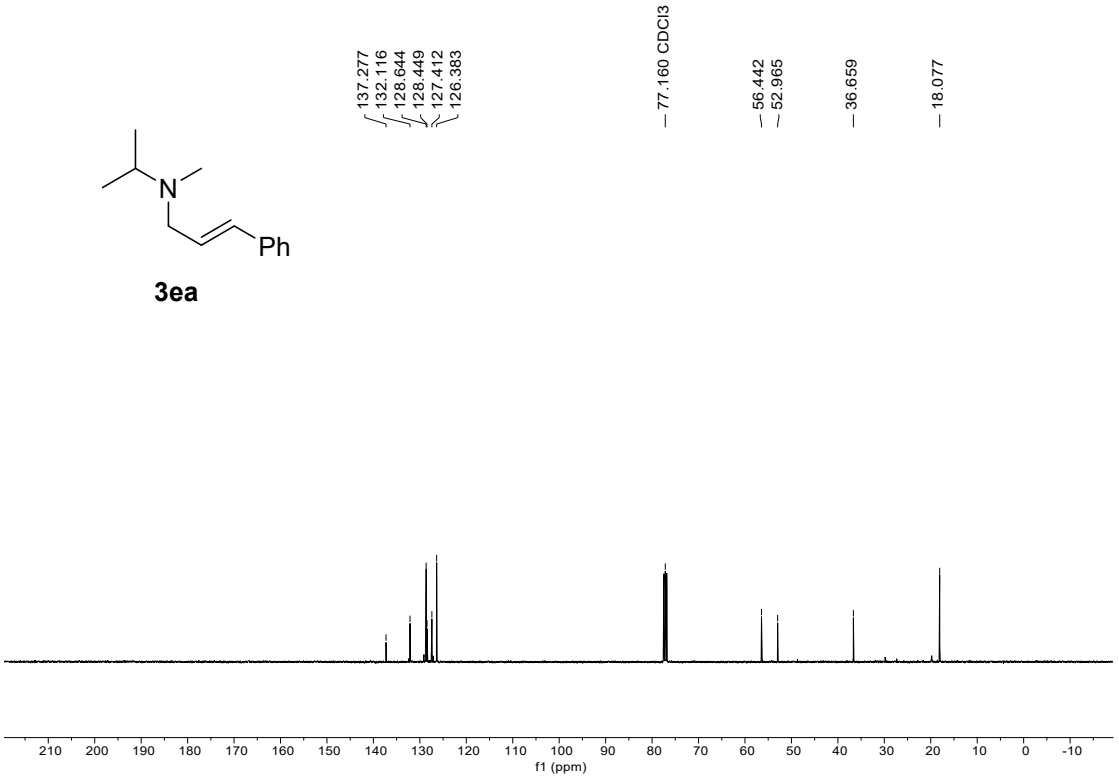
2.874
2.857
2.220
1.059
1.042


N
Ph

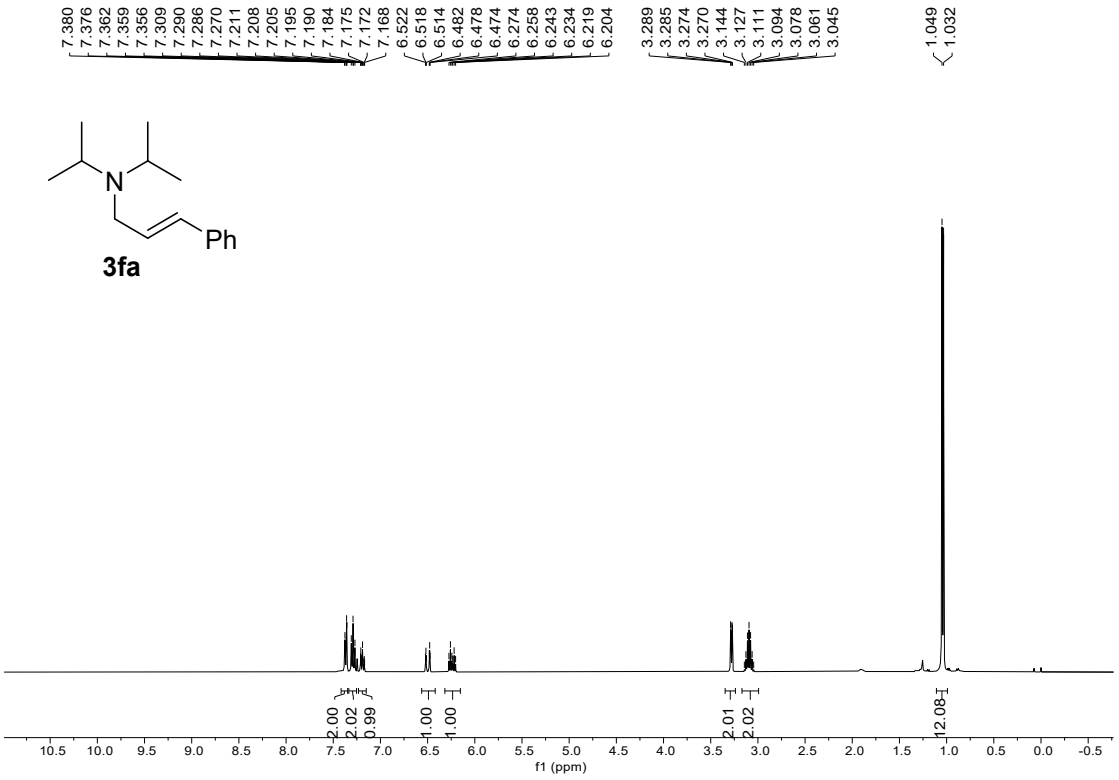
3ea

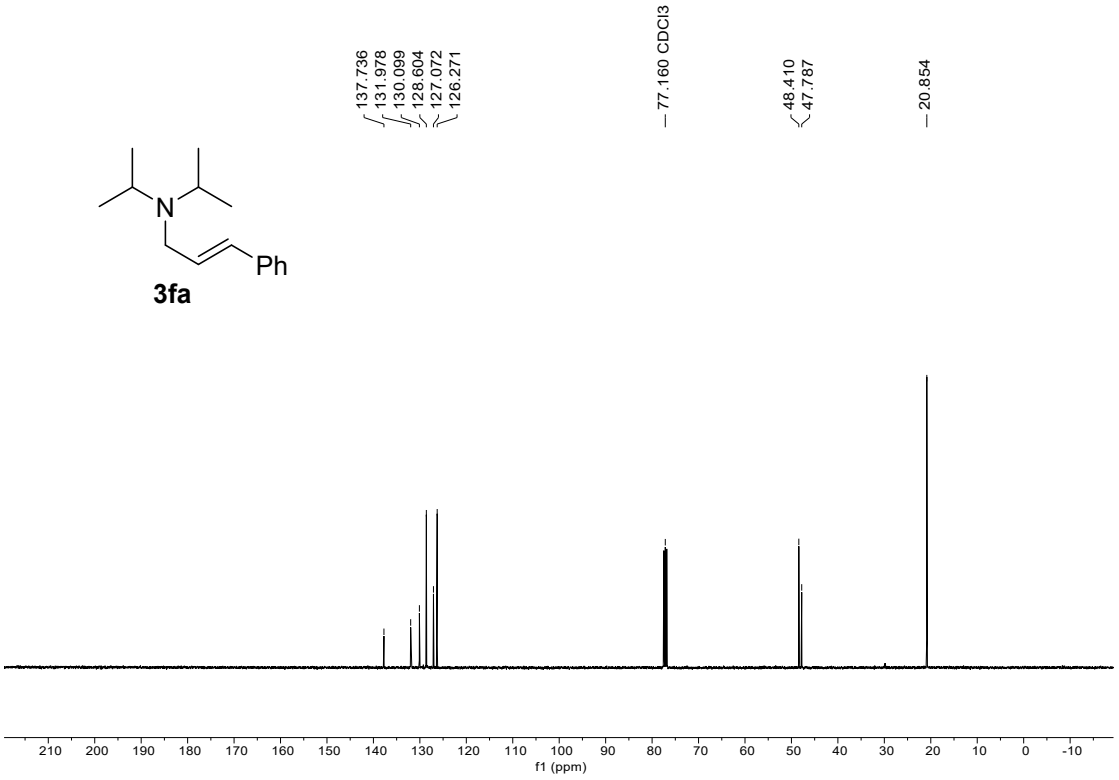

1.95
2.05
1.00
0.96
0.97
1.97
1.00
3.01
5.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

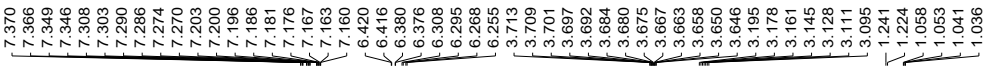

137.277
132.116
128.644
128.449
127.412
126.383
77.160 CDCl3
56.442
52.965
36.659
18.077
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

N
Ph

3ea


7.380
7.376
7.362
7.359
7.356
7.309
7.290
7.286
7.270
7.211
7.208
7.205
7.195
7.190
7.184
7.175
7.172
7.168
6.522
6.518
6.514
6.482
6.478
6.474
6.274
6.258
6.243
6.234
6.219
6.204
3.289
3.285
3.274
3.270
3.144
3.127
3.111
3.094
3.078
3.061
3.045
1.049
1.032
N
Ph
3fa
2.00
2.02
0.99
1.00
1.00
2.01
2.02
12.08
f1 (ppm)


137.736
131.978
130.099
128.604
127.072
126.271
77.160 CDCl3
48.410
47.787
20.854
N
Ph
3fa
f1 (ppm)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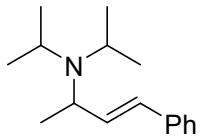
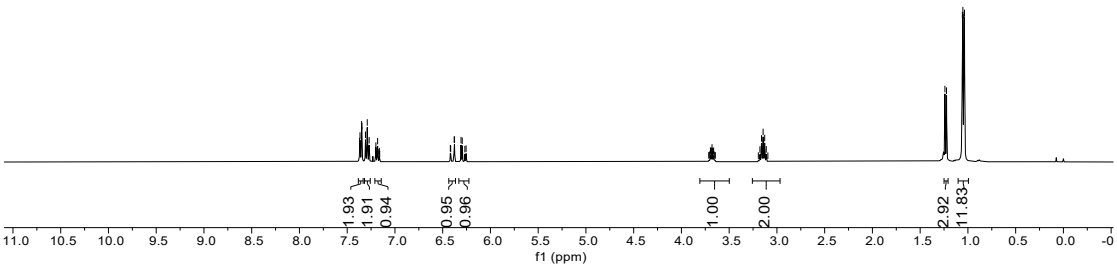
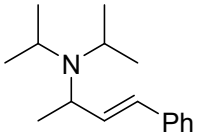
7.366
7.349
7.346
7.308
7.303
7.290
7.286
7.274
7.270
7.203
7.200
7.196
7.186
7.181
7.176
7.167
7.163
7.160
6.420
6.416
6.380
6.376
6.308
6.295
6.268
6.255
3.713
3.709
3.701
3.697
3.692
3.684
3.680
3.675
3.667
3.663
3.658
3.650
3.646
3.195
3.178
3.161
3.145
3.128
3.111
3.095
1.241
1.224
1.058
1.053
1.041
1.036


N
Ph

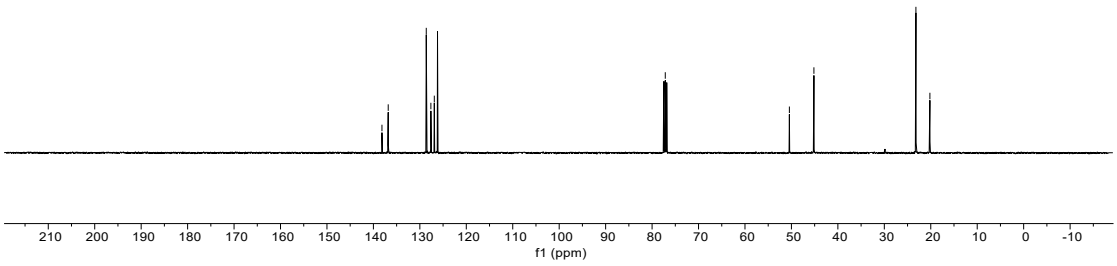
3ga

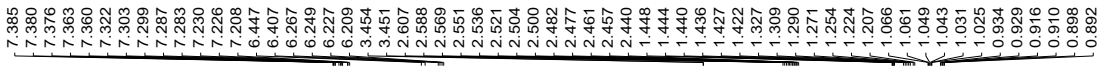

1.93
1.91
0.94
0.95
0.96
1.00
2.00
2.92
11.83
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

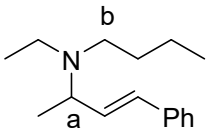

138.158
136.810
128.619
127.626
126.887
126.198
77.160 CDCl3
50.440
45.158
23.198
20.187


N
Ph

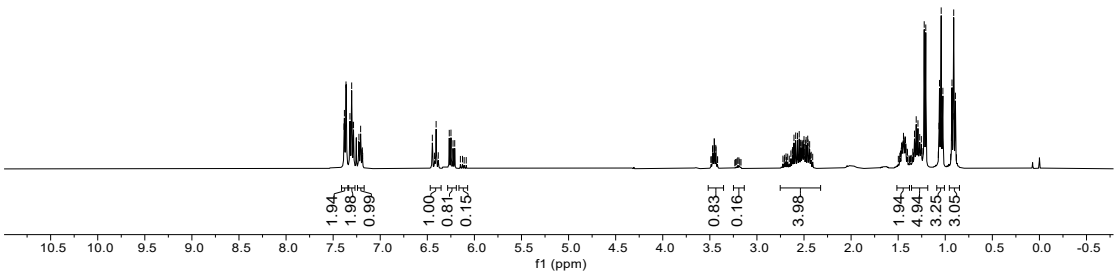
3ga

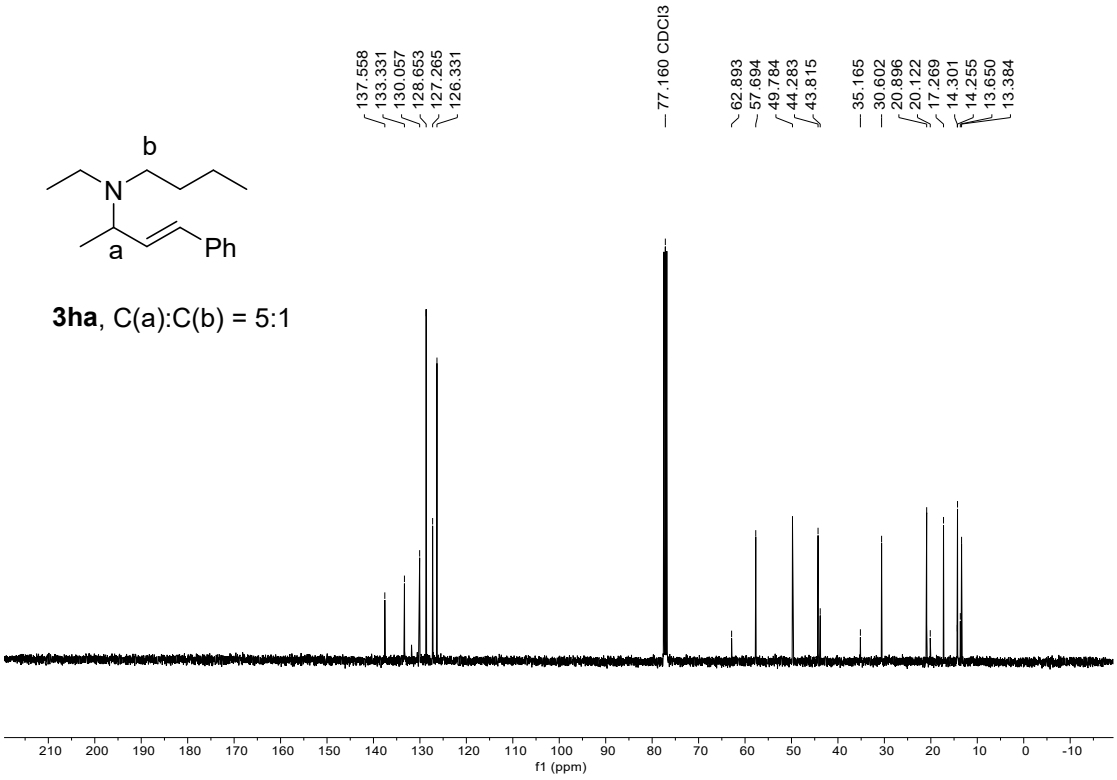

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



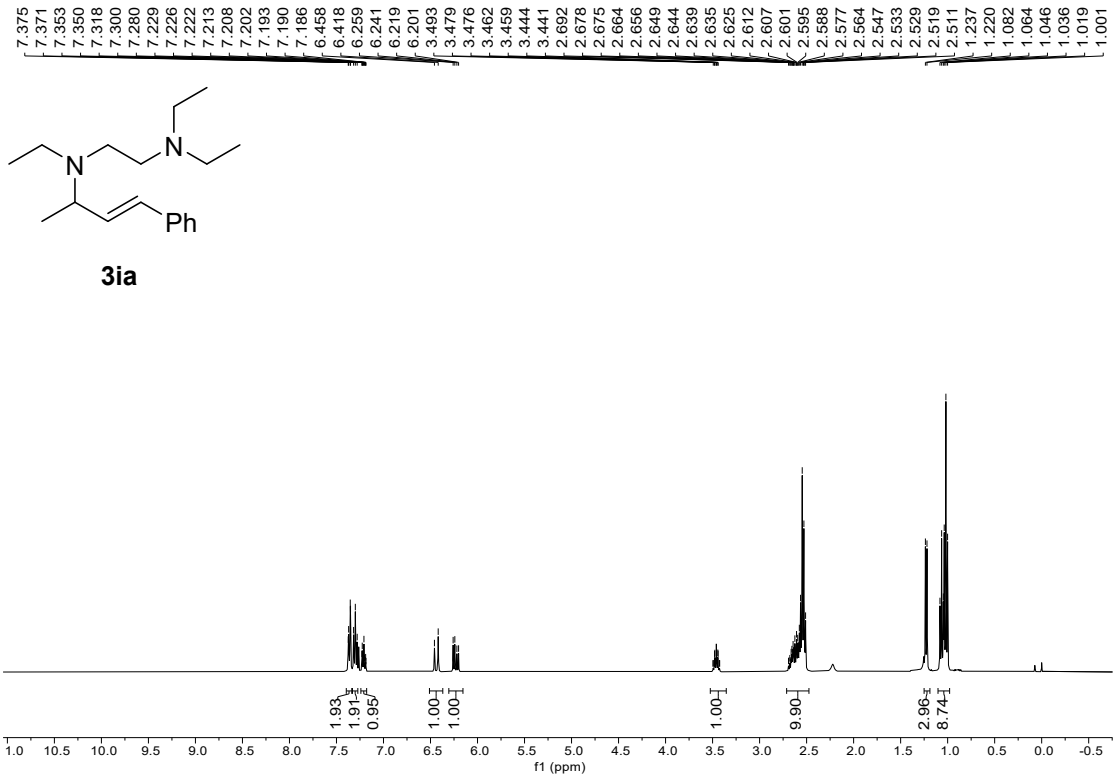


3ha, C(a):C(b) = 5:1





3ha, C(a):C(b) = 5:1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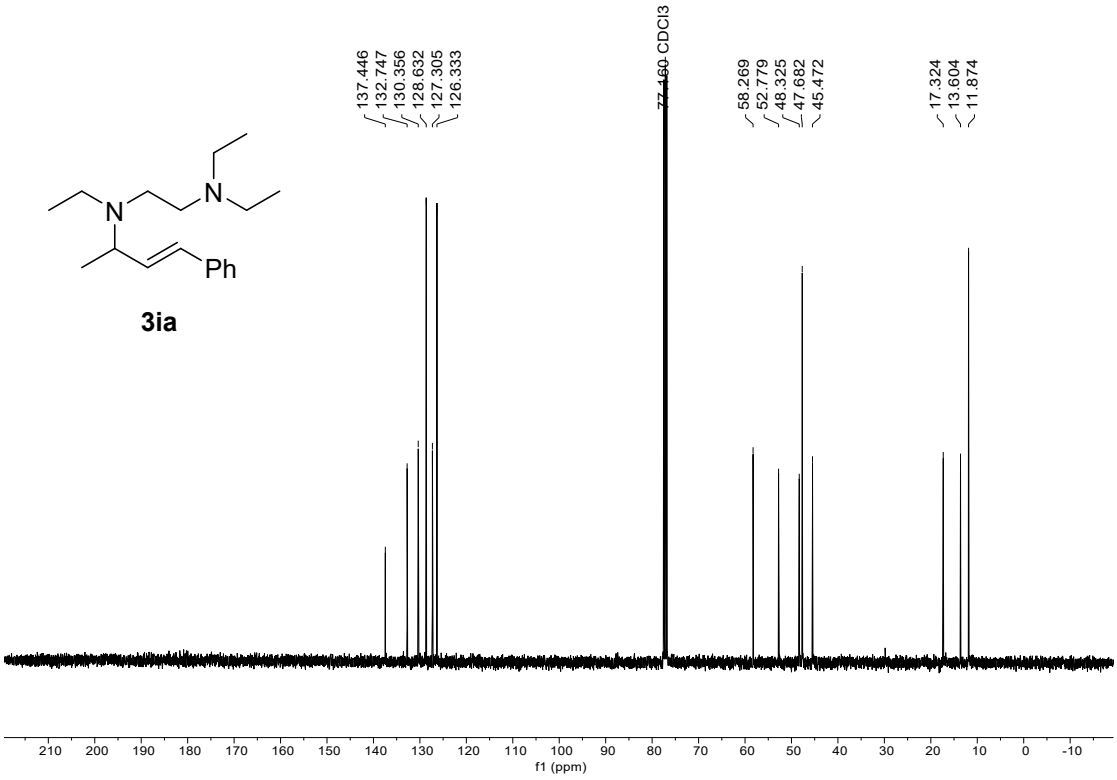
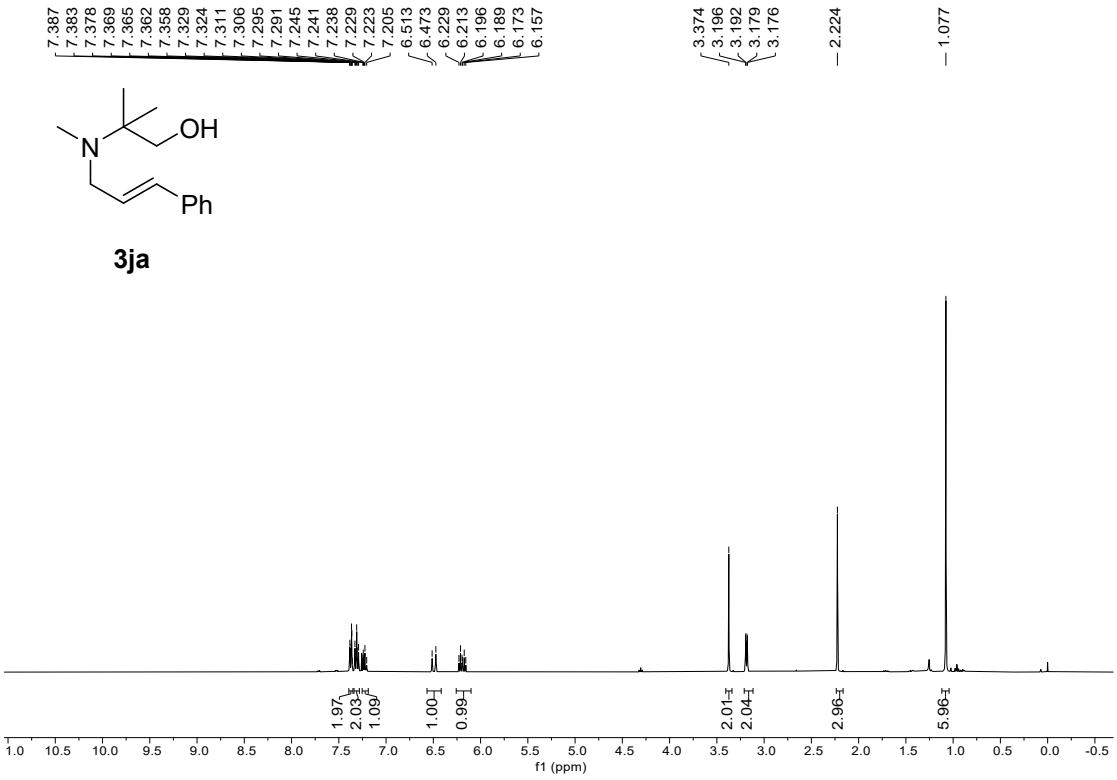
7.371
7.353
7.350
7.318
7.300
7.280
7.229
7.226
7.222
7.213
7.208
7.202
7.193
7.190
7.186
6.458
6.418
6.259
6.241
6.219
6.201
3.493
3.479
3.476
3.462
3.459
3.444
3.441
2.692
2.678
2.675
2.664
2.656
2.649
2.644
2.639
2.635
2.625
2.612
2.607
2.601
2.595
2.588
2.577
2.564
2.547
2.533
2.529
2.519
2.511
1.237
1.220
1.082
1.064
1.046
1.036
1.019
1.001
N
N
Ph

3ia

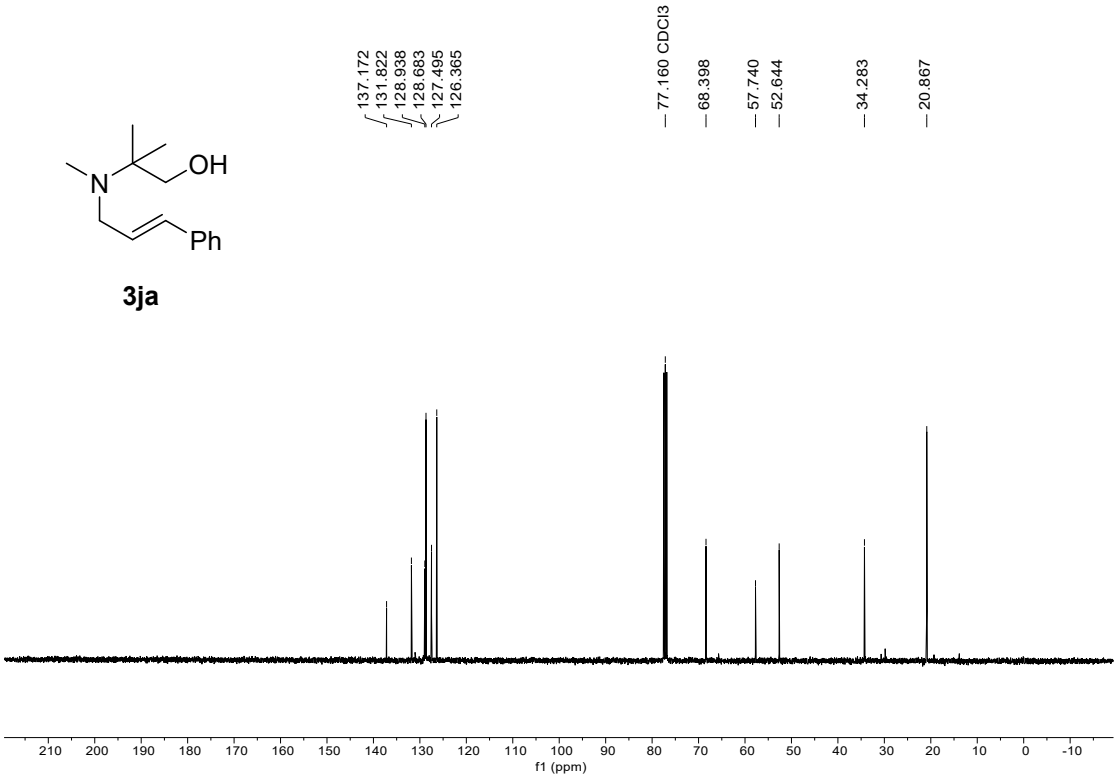
1.93
1.91
0.95
1.00
1.00
1.00
9.90
2.96
8.74
f1 (ppm)


137.446
132.747
130.356
128.632
127.305
126.333
77.160 CDCl3
58.269
52.779
48.325
47.682
45.472
17.324
13.604
11.874
N
N
Ph
f1 (ppm)

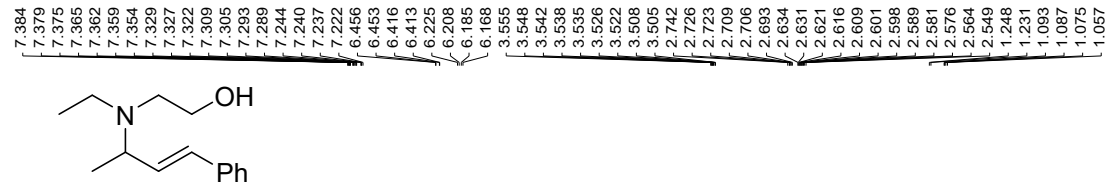
3ia


7.387
7.383
7.378
7.369
7.365
7.362
7.358
7.329
7.324
7.311
7.306
7.295
7.291
7.245
7.241
7.238
7.229
7.223
7.205
6.513
6.473
6.229
6.213
6.196
6.189
6.173
6.157
3.374
3.196
3.192
3.179
3.176
2.224
1.077
OH
N
Ph
1.97
2.03
1.09
1.00
0.99
2.01
2.04
2.96
5.96
f1 (ppm)

3ja


137.172
131.822
128.938
128.683
127.495
126.365
77.160 CDCl3
68.398
57.740
52.644
34.283
20.867
OH
N
Ph
f1 (ppm)

3ja


7.384
7.379
7.375
7.365
7.362
7.359
7.354
7.329
7.327
7.322
7.309
7.305
7.293
7.289
7.244
7.240
7.237
7.222
6.456
6.453
6.416
6.413
6.225
6.208
6.185
6.168
3.555
3.548
3.542
3.538
3.535
3.526
3.522
3.508
3.505
2.742
2.726
2.723
2.709
2.706
2.693
2.634
2.631
2.621
2.616
2.609
2.601
2.598
2.589
2.581
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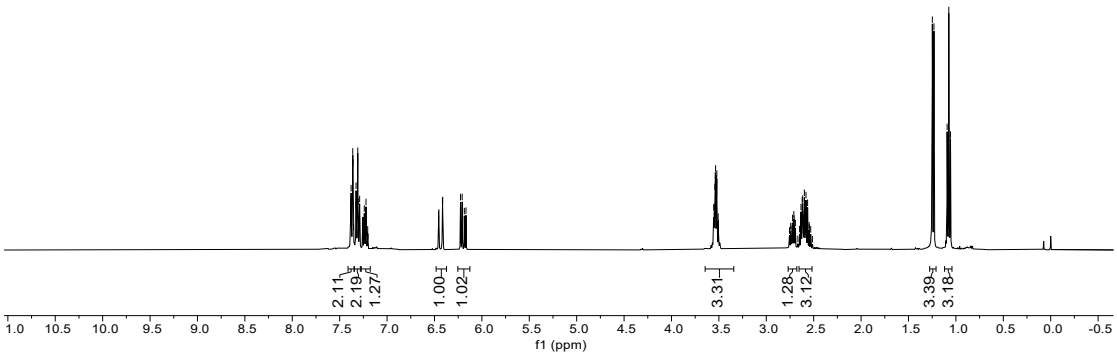
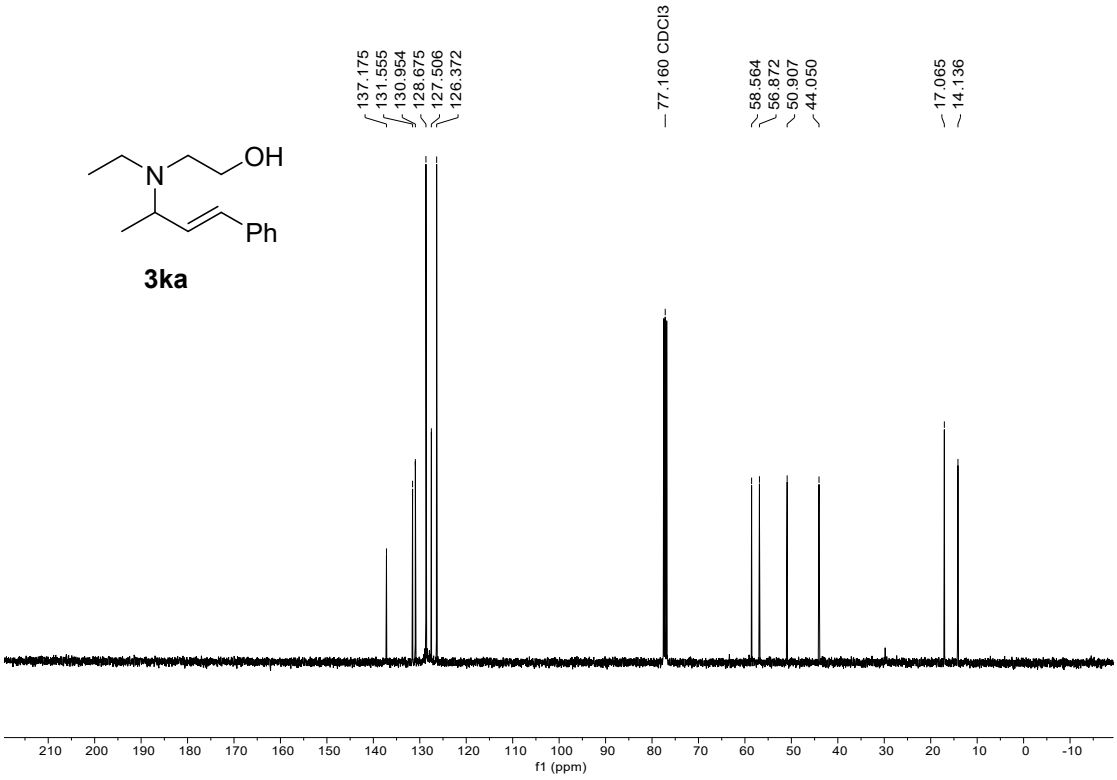
2.549
1.248
1.231
1.093
1.087
1.075
1.057

N
OH
Ph

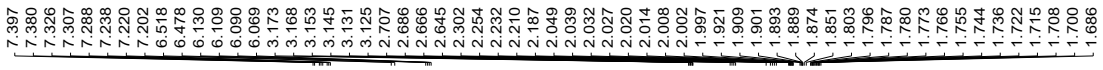
3ka


2.11
2.19
1.27
1.00
1.02
3.31
1.28
3.12
3.39
3.18
1.0 10.5 10.0 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 -0.5
f1 (ppm)


137.175
131.555
130.954
128.675
127.506
126.372
77.160 CDCl3
58.564
56.872
50.907
44.050
17.065
14.136
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

N
OH
Ph

3ka


7.397
7.380
7.326
7.307
7.288
7.238
7.220
7.202
6.518
6.478
6.130
6.109
6.090
6.069
3.173
3.168
3.153
3.145
3.131
3.125
2.707
2.686
2.666
2.645
2.302
2.254
2.232
2.210
2.187
2.049
2.039
2.032
2.027
2.020
2.014
2.008
2.002
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1.921
1.909
1.901
1.893
1.889
1.874
1.851
1.803
1.796
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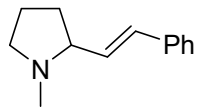
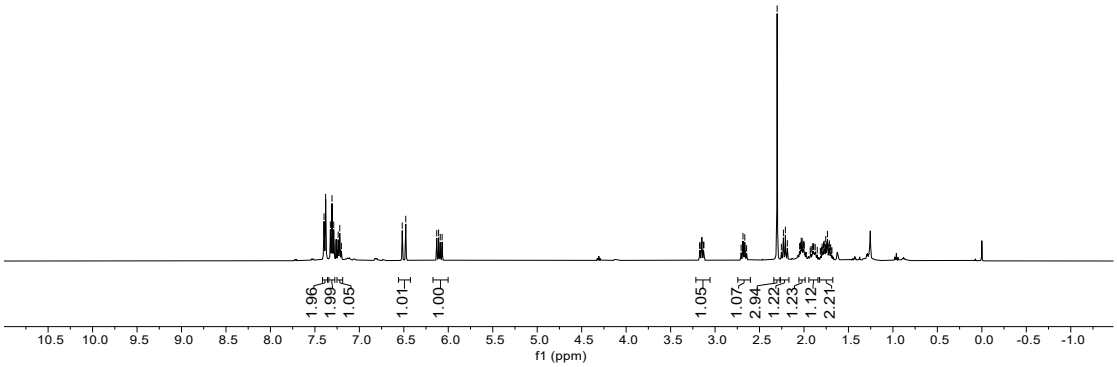
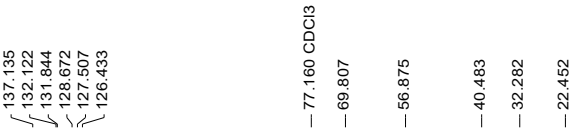
1.736
1.722
1.715
1.708
1.700
1.686


N
Ph

3la


1.96
1.99
1.05
1.01
1.00
1.05
1.07
2.94
1.22
1.23
1.12
2.21
10.5 10.0 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 -0.5 -1.0
f1 (ppm)


137.135
132.122
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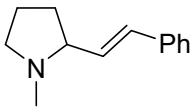
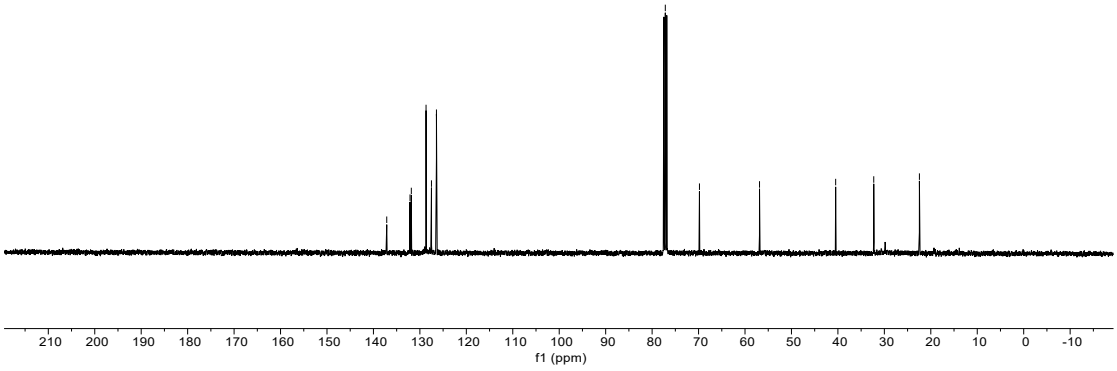
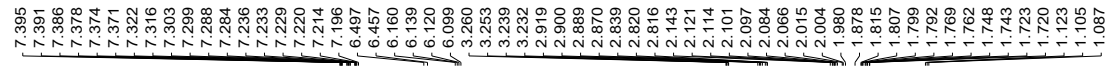
127.507
126.433
77.160 CDCl3
69.807
56.875
40.483
32.282
22.452


N
Ph

3la


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.236
7.233
7.229
7.220
7.214
7.196
6.497
6.457
6.160
6.139
6.120
6.099
3.260
3.253
3.239
3.232
2.919
2.900
2.889
2.870
2.839
2.820
2.816
2.143
2.121
2.114
2.101
2.097
2.084
2.066
2.015
2.004
1.980
1.878
1.815
1.807
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1.723
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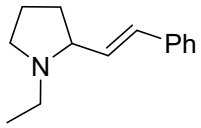
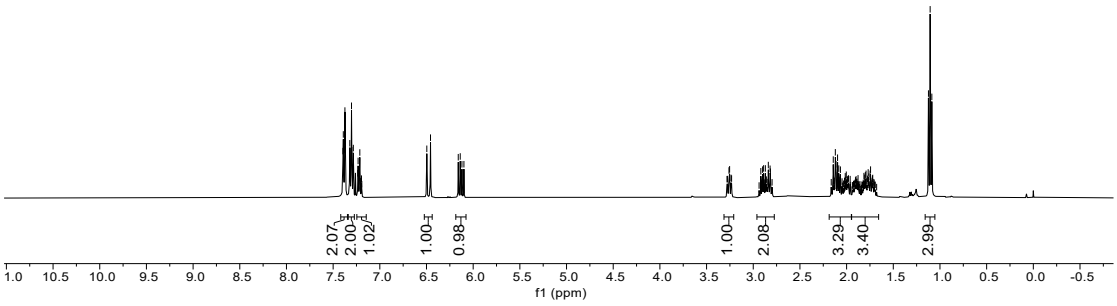
1.123
1.105
1.087


N
Ph

3ma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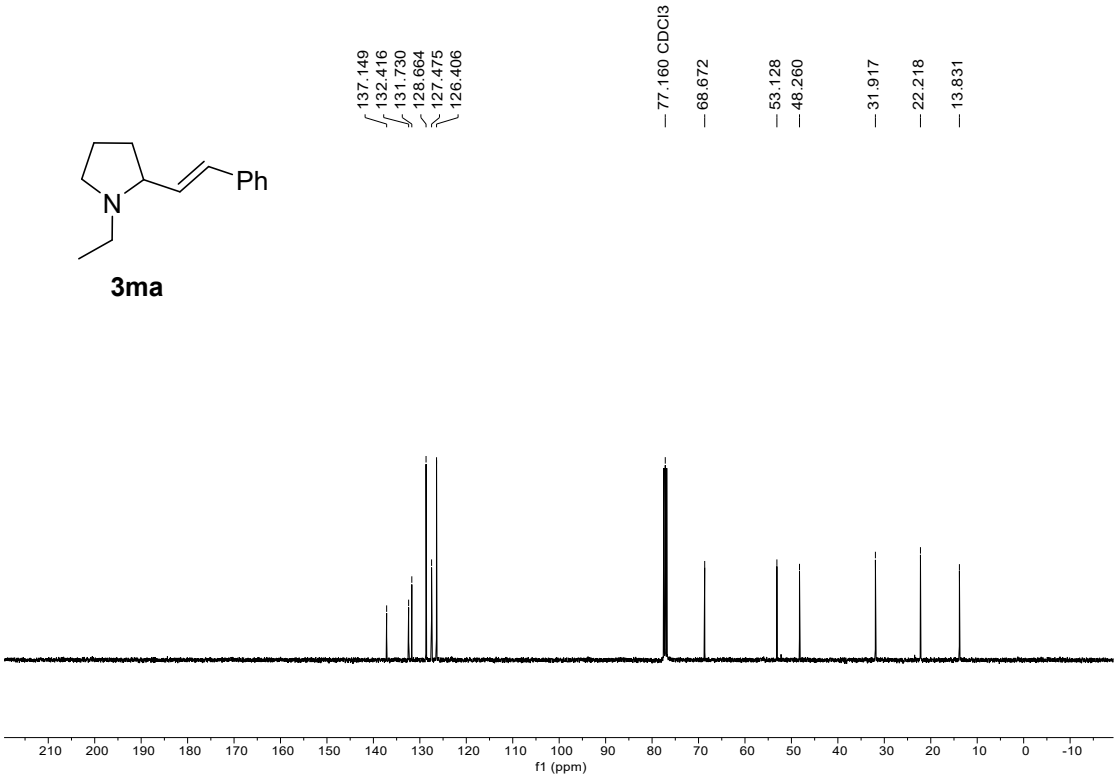
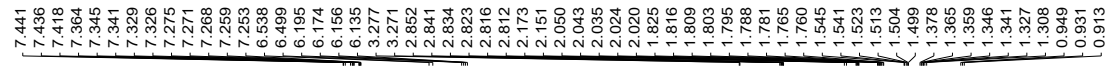
1.00
0.98
1.00
2.08
3.29
3.40
2.99
f1 (ppm)


137.149
132.416
131.730
128.664
127.475
126.406
77.160 CDCl3
68.672
53.128
48.260
31.917
22.218
13.831
f1 (ppm)

N
Ph

3ma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7.436
7.418
7.364
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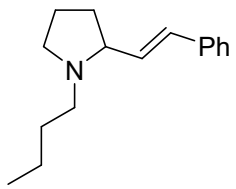
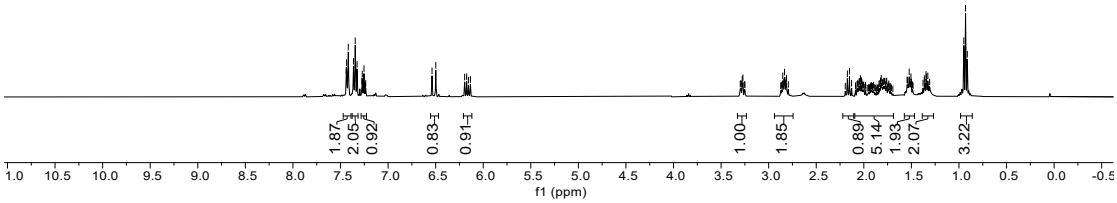
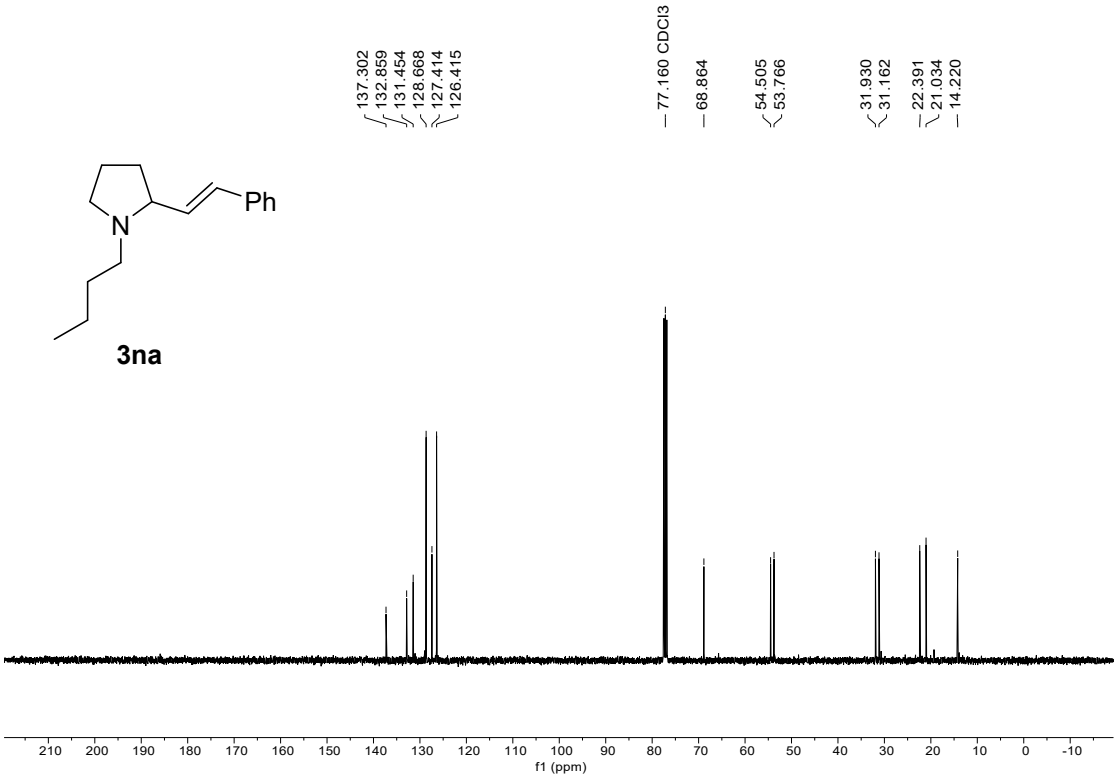
7.341
7.329
7.326
7.275
7.271
7.268
7.259
7.253
6.538
6.499
6.195
6.174
6.156
6.135
3.277
3.271
2.852
2.841
2.834
2.823
2.816
2.812
2.173
2.151
2.050
2.043
2.035
2.024
2.020
1.825
1.816
1.809
1.803
1.795
1.788
1.781
1.765
1.760
1.545
1.541
1.523
1.513
1.504
1.499
1.378
1.365
1.359
1.346
1.341
1.327
1.308
0.949
0.931
0.913


N
Ph

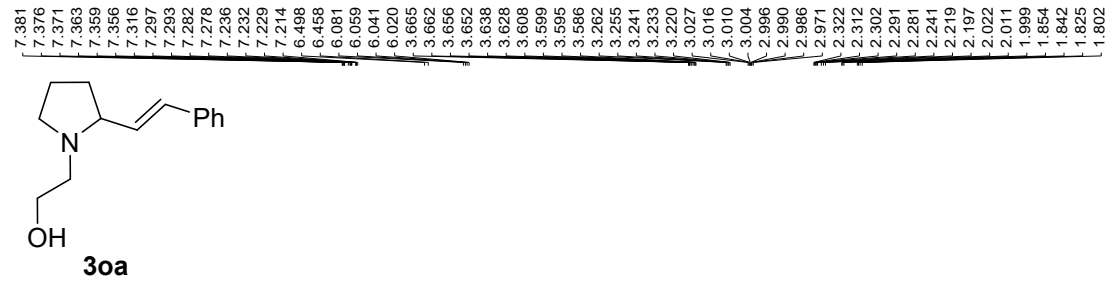
3na


1.87
2.05
0.92
0.83
0.91
1.00
1.85
0.89
5.14
1.93
2.07
3.22
f1 (ppm)


137.302
132.859
131.454
128.668
127.414
126.415
77.160 CDCl3
68.864
54.505
53.766
31.930
31.162
22.391
21.034
14.220
f1 (ppm)

N
Ph

3na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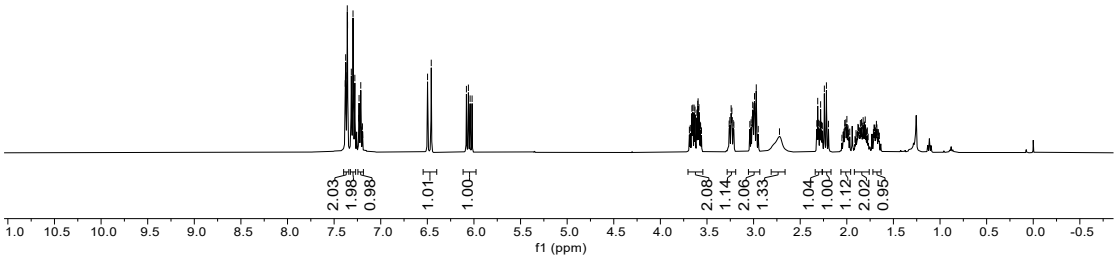
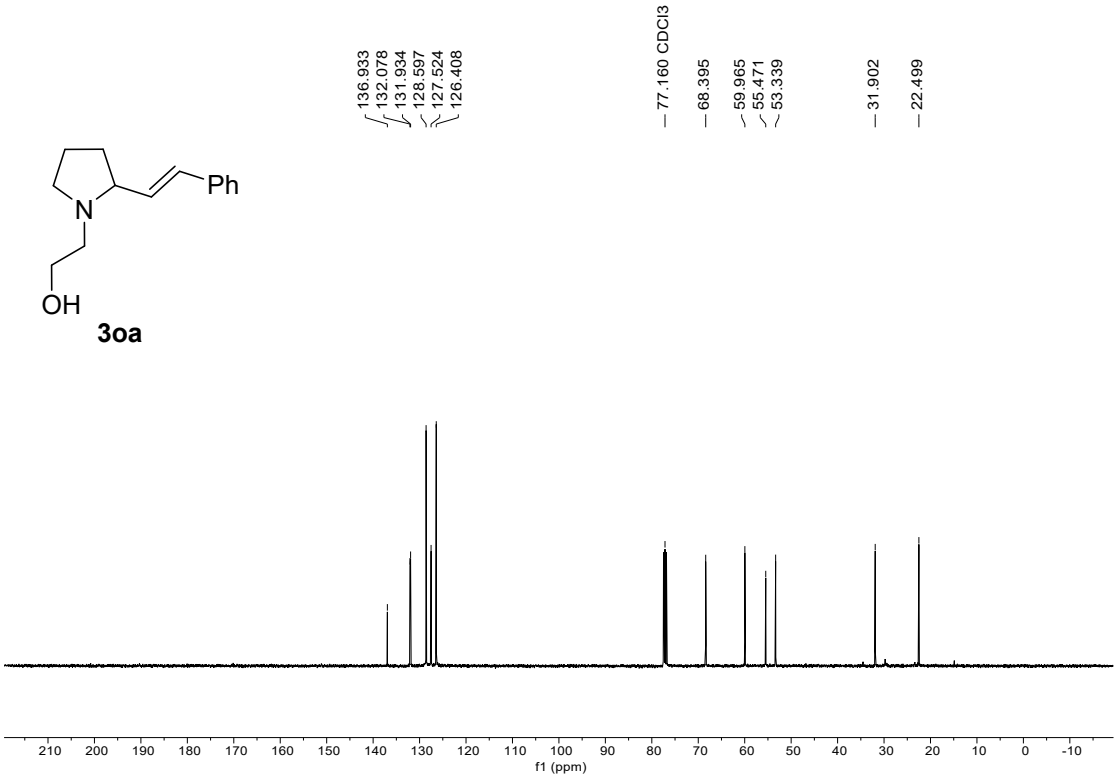
7.371
7.363
7.359
7.356
7.316
7.297
7.293
7.282
7.278
7.236
7.232
7.229
7.214
6.498
6.458
6.081
6.059
6.041
6.020
3.665
3.662
3.656
3.652
3.638
3.628
3.608
3.599
3.595
3.586
3.262
3.255
3.241
3.233
3.220
3.027
3.016
3.010
3.004
2.996
2.990
2.986
2.971
2.322
2.312
2.302
2.291
2.281
2.241
2.219
2.197
2.022
2.011
1.999
1.854
1.842
1.825
1.802

Ph
N
OH

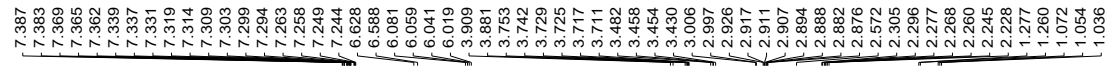
3oa


2.03
1.98
0.98
1.01
1.00
2.08
1.14
2.06
1.33
1.04
1.00
1.12
2.02
0.95
f1 (ppm)


136.933
132.078
131.934
128.597
127.524
126.408
77.160 CDCl3
68.395
59.965
55.471
53.339
31.902
22.499
f1 (ppm)

Ph
N
OH

3oa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7.383
7.369
7.365
7.362
7.339
7.337
7.331
7.319
7.314
7.309
7.303
7.299
7.294
7.263
7.258
7.249
7.244
6.628
6.588
6.081
6.059
6.041
6.019
3.909
3.881
3.753
3.742
3.729
3.725
3.717
3.711
3.482
3.458
3.454
3.430
3.006
2.997
2.926
2.917
2.911
2.907
2.894
2.888
2.882
2.876
2.572
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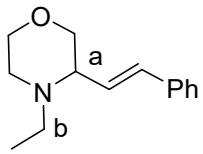
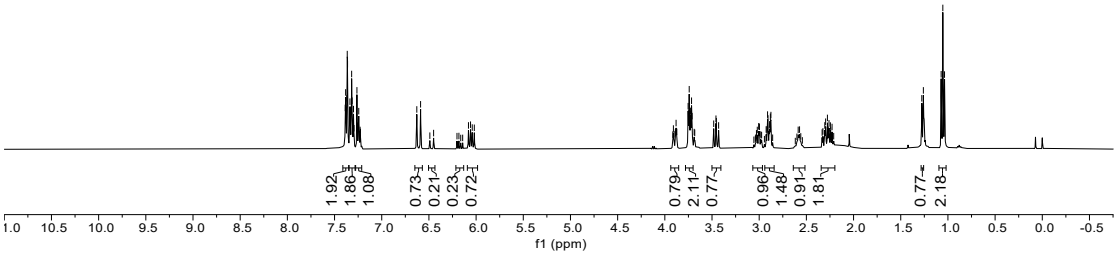
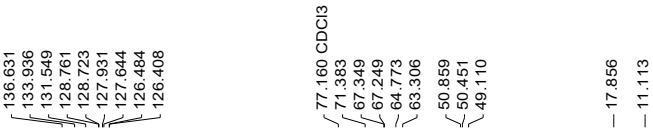
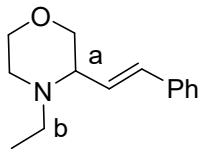
2.228
1.277
1.260
1.072
1.054
1.036


O
a
N
Ph
b

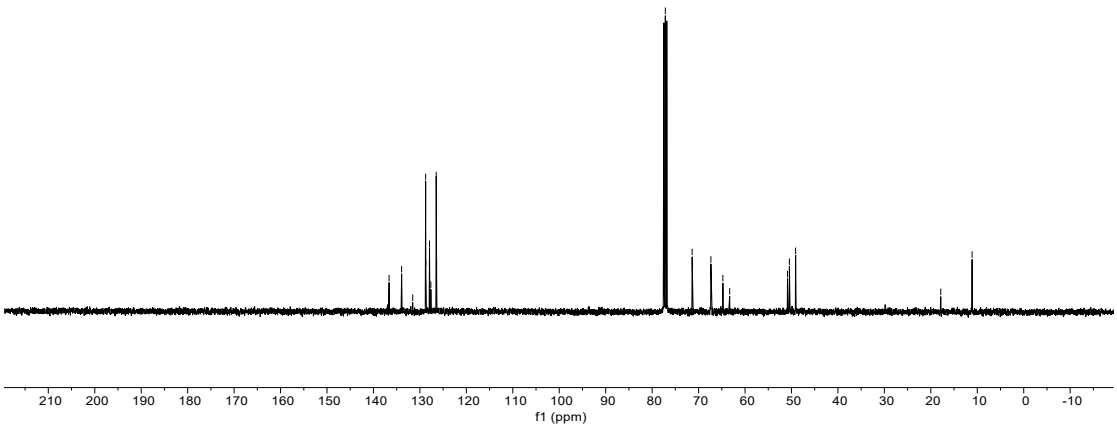
3pa

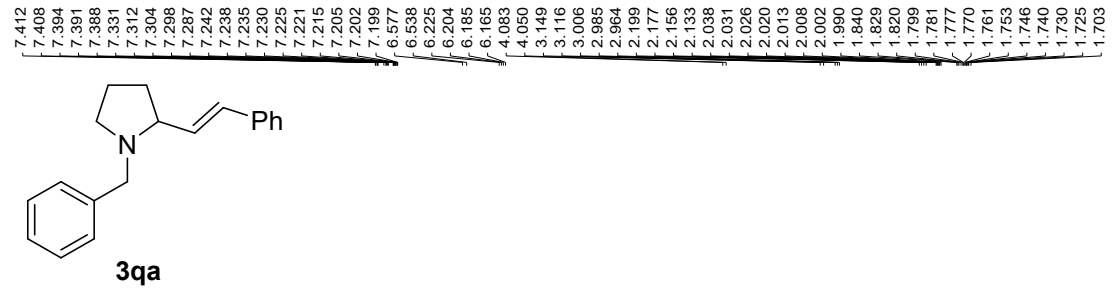

1.92
1.86
1.08
0.73
0.21
0.23
0.72
0.79
2.11
0.77
0.96
1.48
0.91
1.81
0.77
2.18
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


136.631
133.936
131.549
128.761
128.723
127.931
127.644
126.484
126.408
77.160 CDCl3
71.383
67.349
67.249
64.773
63.306
50.859
50.451
49.110
17.856
11.113


O
a
N
Ph
b

3pa


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.388
7.331
7.312
7.304
7.298
7.287
7.242
7.238
7.235
7.230
7.225
7.221
7.215
7.205
7.202
7.199
6.577
6.538
6.225
6.204
6.185
6.165
4.083
4.050
3.149
3.116
3.006
2.985
2.964
2.199
2.177
2.156
2.133
2.038
2.031
2.026
2.020
2.013
2.008
2.002
1.990
1.840
1.829
1.820
1.799
1.781
1.777
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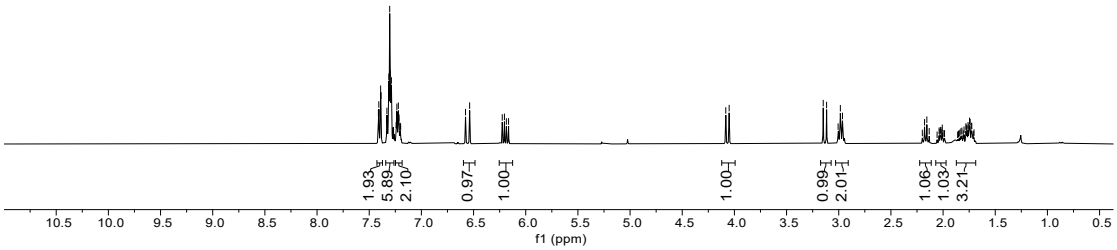
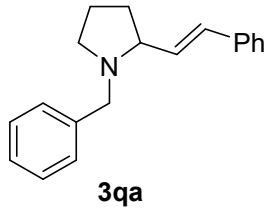
1.761
1.753
1.746
1.740
1.730
1.725
1.703
N
Ph

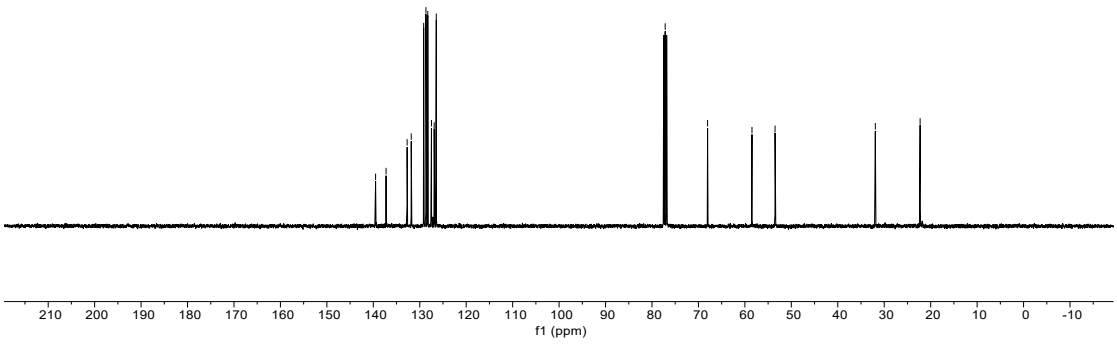
3qa

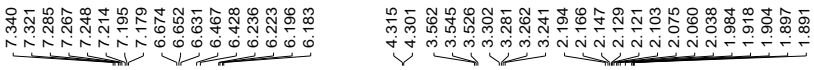

1.93
5.89
2.10
0.97
1.00
1.00
0.99
2.01
1.06
1.03
3.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


139.510
137.251
132.721
131.835
129.158
128.668
128.271
127.480
126.894
126.444
77.160 CDCl3
68.033
58.473
53.503
31.919
22.274


N
Ph

3qa


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


7.340
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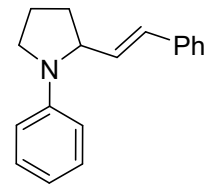
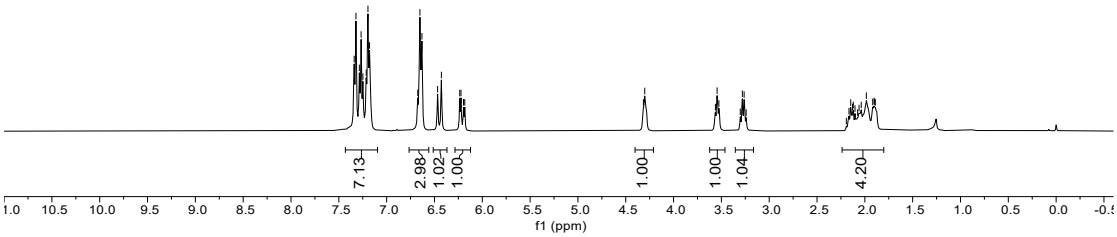
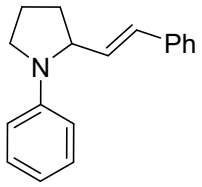
7.267
7.248
7.214
7.195
7.179
6.674
6.652
6.631
6.467
6.428
6.236
6.223
6.196
6.183
4.315
4.301
3.562
3.545
3.526
3.302
3.281
3.262
3.241
2.194
2.166
2.147
2.129
2.121
2.103
2.075
2.060
2.038
1.984
1.918
1.904
1.897
1.891


N
Ph

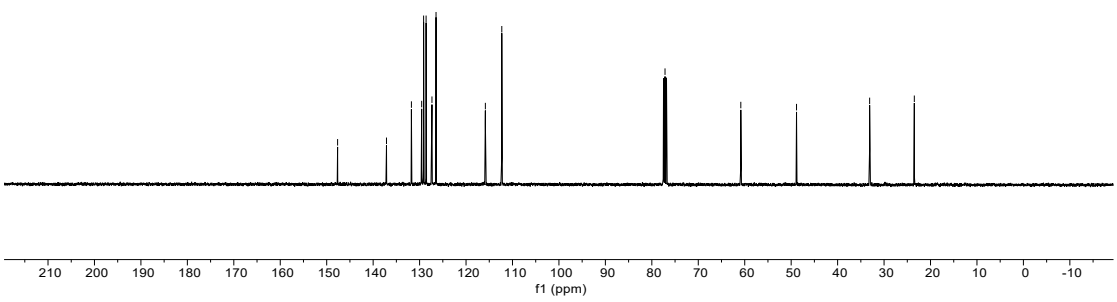
3ra

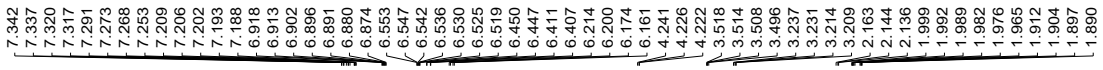

7.13
2.98
1.02
1.00
1.00
1.00
1.04
4.20
f1 (ppm)


147.653
137.127
131.762
129.554
129.135
128.600
127.338
126.460
115.839
112.302
77.160 CDCl3
60.842
48.847
33.105
23.487


N
Ph

3ra


f1 (ppm)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7.317
7.291
7.273
7.268
7.253
7.209
7.206
7.202
7.193
7.188
6.918
6.913
6.902
6.896
6.891
6.880
6.874
6.553
6.547
6.542
6.536
6.530
6.525
6.519
6.450
6.447
6.411
6.407
6.214
6.200
6.174
6.161
4.241
4.226
4.222
3.518
3.514
3.508
3.496
3.237
3.231
3.214
3.209
2.163
2.144
2.136
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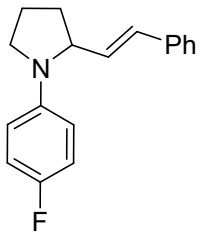
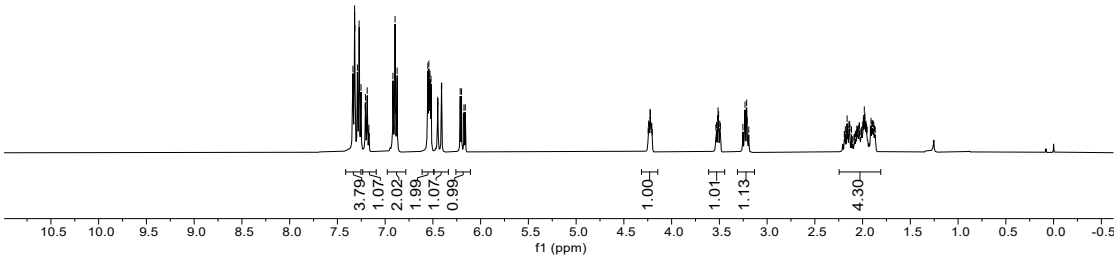
1.989
1.982
1.976
1.965
1.912
1.904
1.897
1.890


Ph
N
F

3sa


3.79
1.07
2.02
1.99
1.07
0.99
1.00
1.01
1.13
4.30
10.5 10.0 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 -0.5
f1 (ppm)


156.222
153.901
144.347
144.332
137.026
131.715
129.673
128.642
127.431
126.454
115.575
115.357
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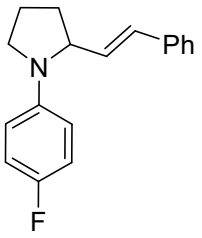
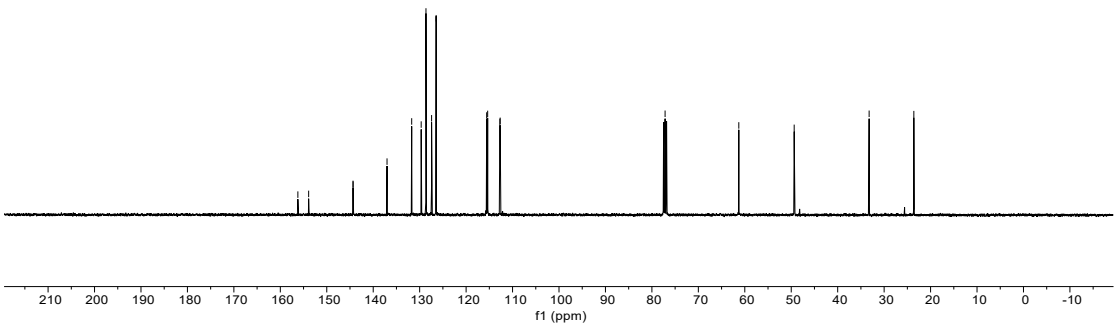
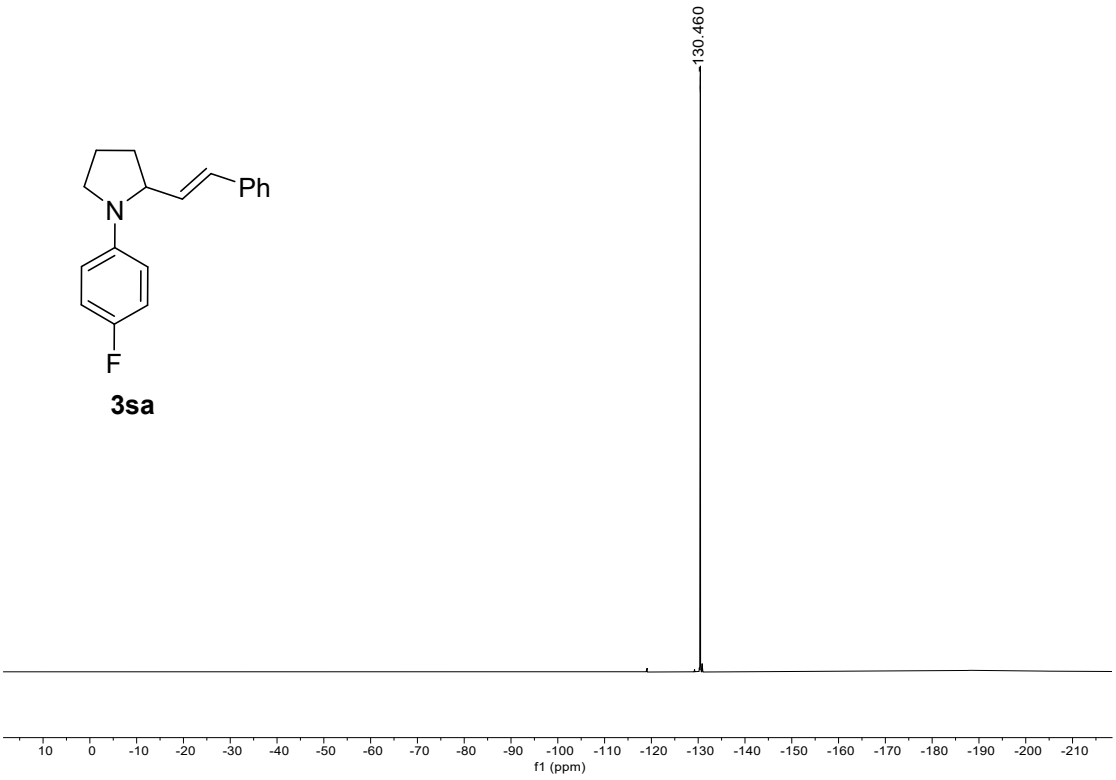
77.160 CDCl3
61.289
49.366
33.229
23.604


Ph
N
F

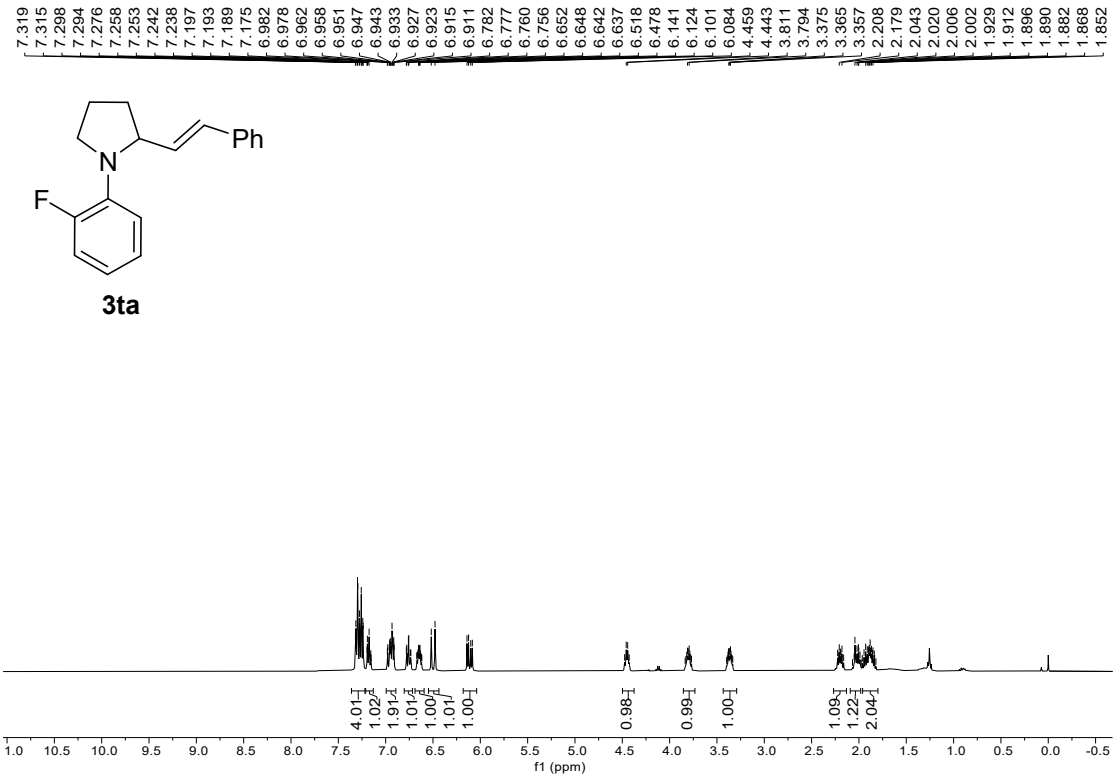
3sa


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


130.460
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

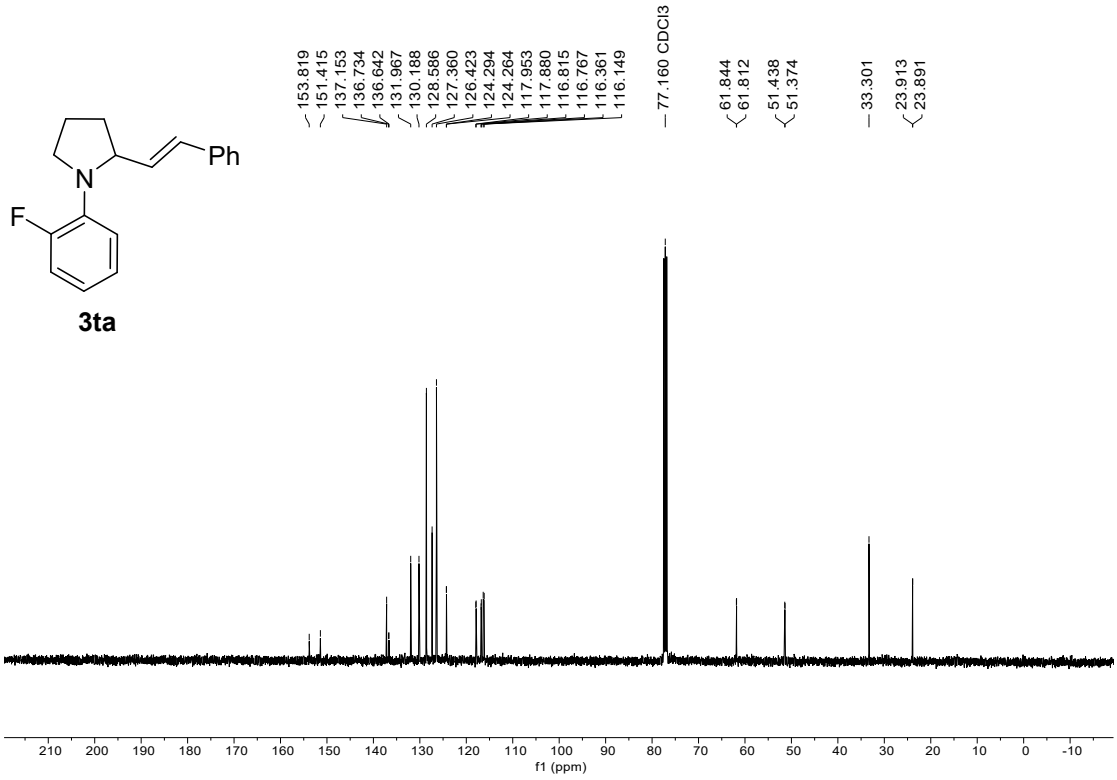
Ph
N
F

3sa


7.319
7.315
7.298
7.294
7.276
7.258
7.253
7.242
7.238
7.197
7.193
7.189
7.175
6.982
6.978
6.962
6.958
6.951
6.947
6.943
6.933
6.927
6.923
6.915
6.911
6.782
6.777
6.760
6.756
6.652
6.648
6.642
6.637
6.518
6.478
6.141
6.124
6.101
6.084
4.459
4.443
3.811
3.794
3.375
3.365
3.357
2.208
2.179
2.043
2.020
2.006
2.002
1.929
1.912
1.896
1.890
1.882
1.868
1.852
4.01
1.02
1.91
1.01
1.00
1.01
1.00
0.98
0.99
1.00
1.09
1.22
2.04
1.0 10.5 10.0 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 -0.5
f1 (ppm)

Ph
N
F

3ta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137.153
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128.586
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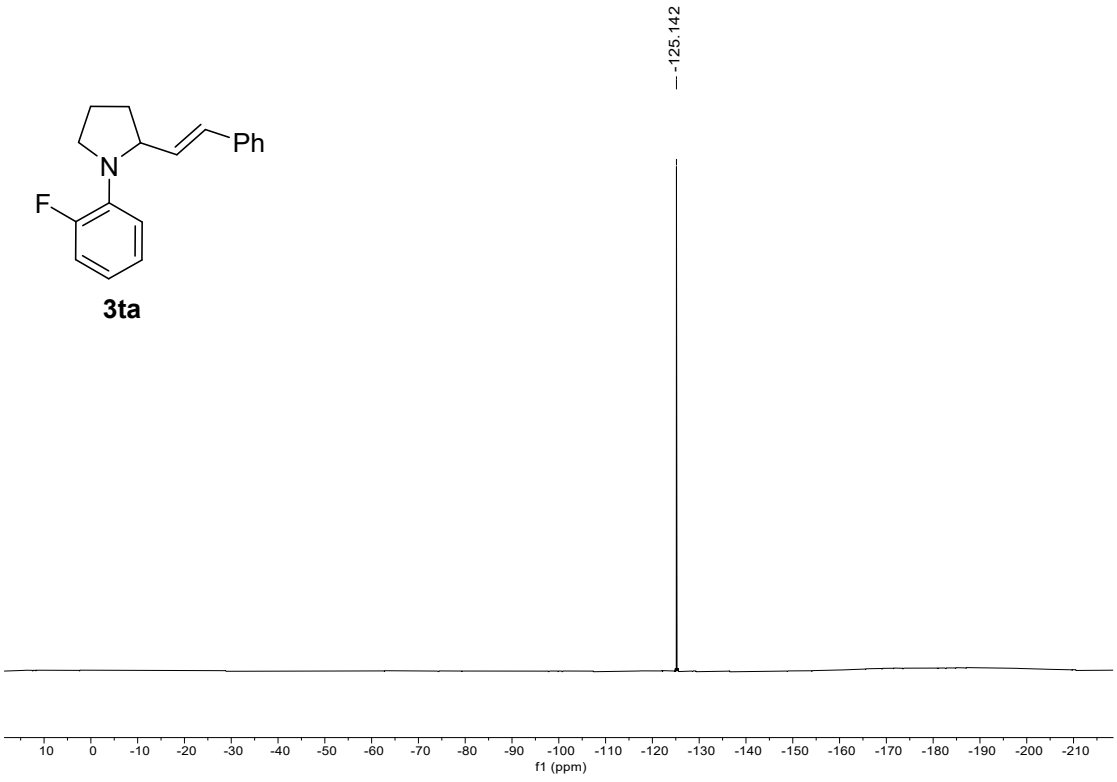
124.294
124.264
117.953
117.880
116.815
116.767
116.361
116.149
77.160 CDCl3
61.844
61.812
51.438
51.374
33.301
23.913
23.891
Ph
N
F
3ta
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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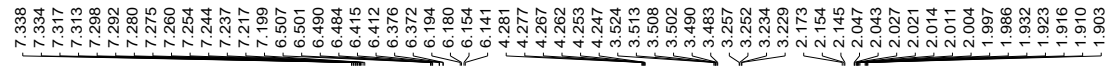
f1 (ppm)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7.275
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7.237
7.217
7.199
6.507
6.501
6.490
6.484
6.415
6.412
6.376
6.372
6.194
6.180
6.154
6.141
4.281
4.277
4.267
4.262
4.253
4.247
3.524
3.513
3.508
3.502
3.490
3.483
3.257
3.252
3.234
3.229
2.173
2.154
2.145
2.047
2.043
2.027
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2.011
2.004
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1.923
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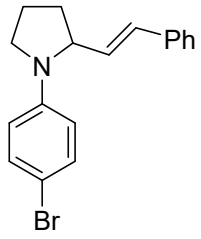
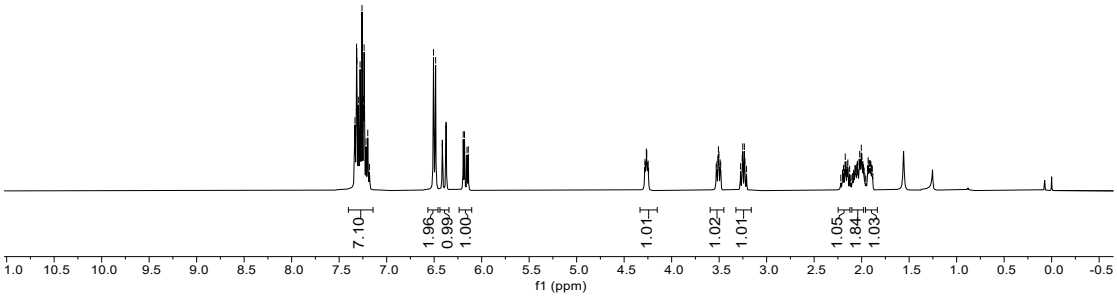
1.903


N
Ph
Br

3ua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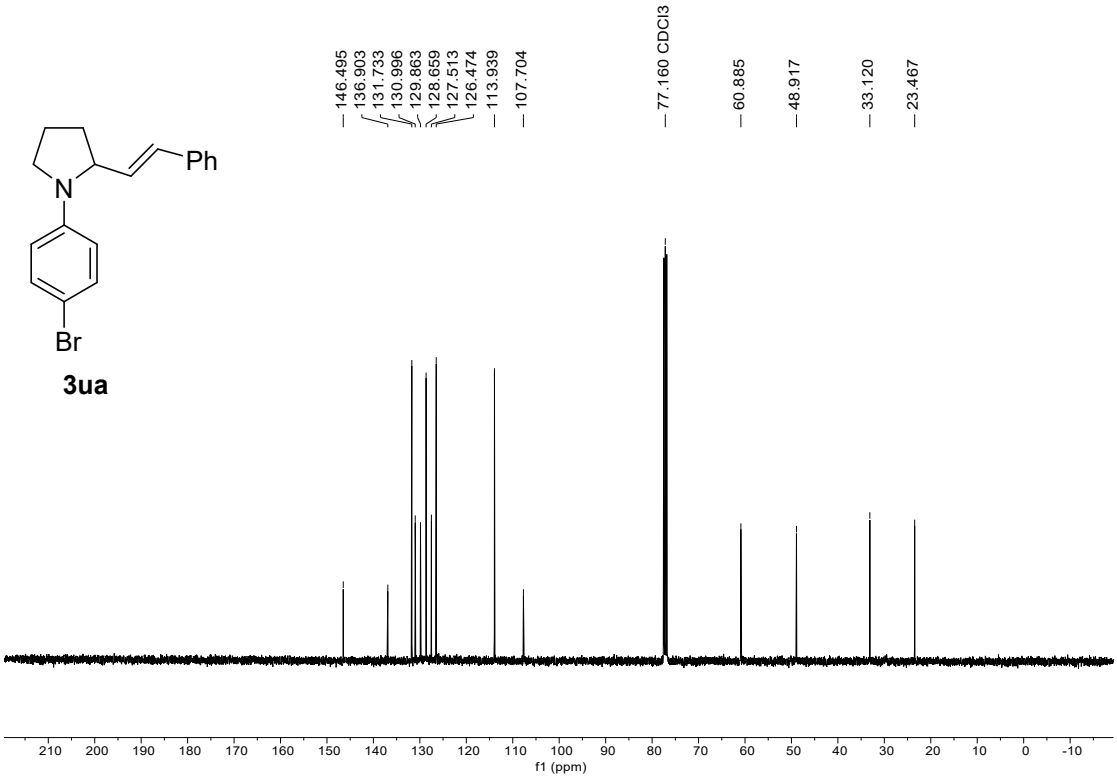
0.99
1.00
1.01
1.02
1.01
1.05
1.84
1.03
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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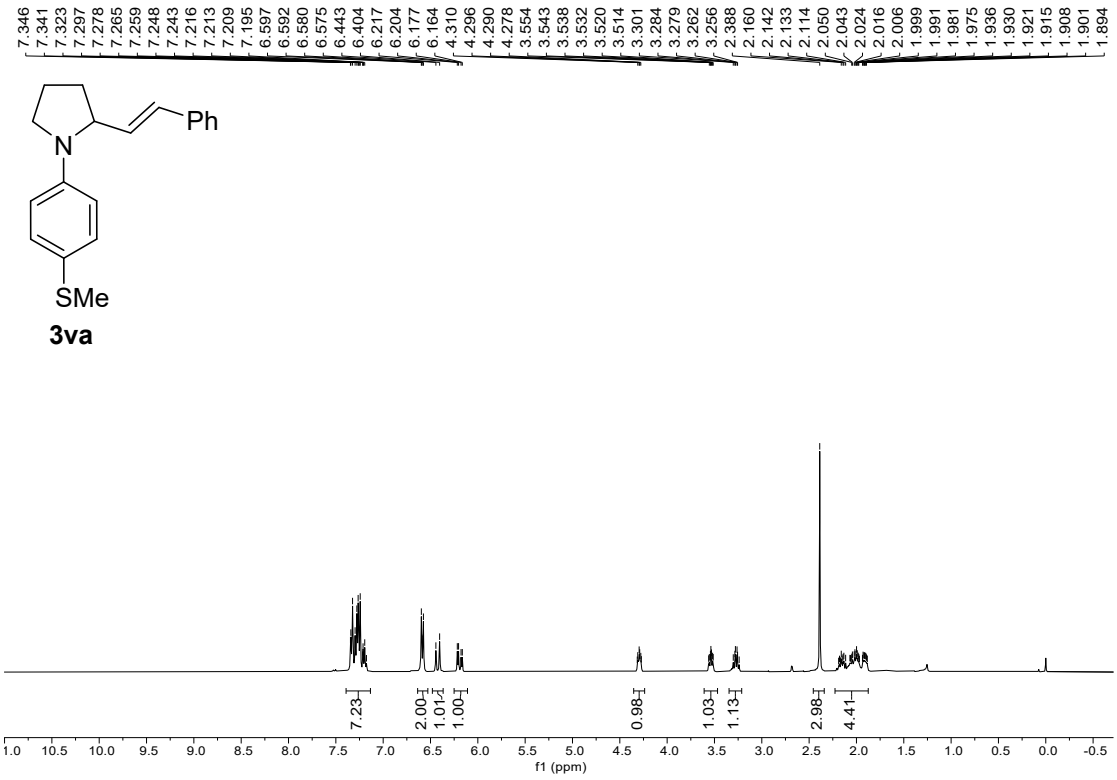
136.903
131.733
130.996
129.863
128.659
127.513
126.474
113.939
107.704
77.160 CDCl3
60.885
48.917
33.120
23.467
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

N
Ph
Br

3ua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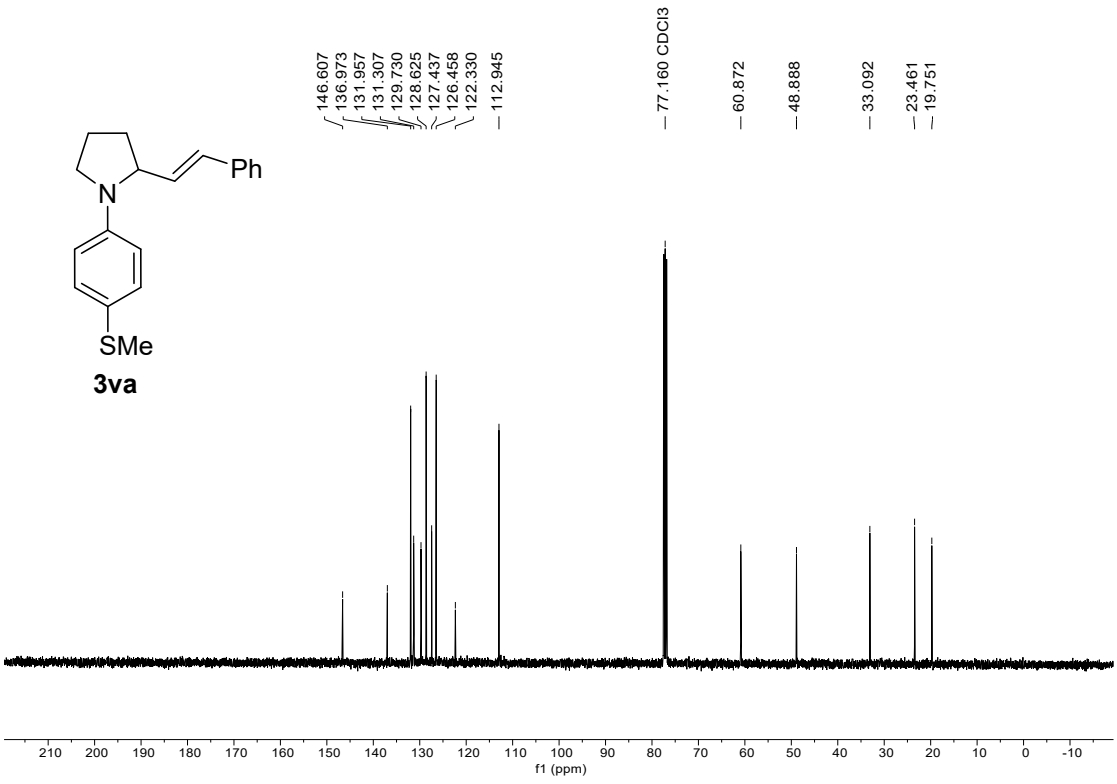
7.341
7.323
7.297
7.278
7.265
7.259
7.248
7.243
7.216
7.213
7.209
7.195
6.597
6.592
6.580
6.575
6.443
6.404
6.217
6.204
6.177
6.164
4.310
4.296
4.290
4.278
3.554
3.543
3.538
3.532
3.520
3.514
3.301
3.284
3.279
3.262
3.256
2.388
2.160
2.142
2.133
2.114
2.050
2.043
2.024
2.016
2.006
1.999
1.991
1.981
1.975
1.936
1.930
1.921
1.915
1.908
1.901
1.894
Ph
N
SMe
3va
7.23
2.00
1.01
1.00
0.98
1.03
1.13
2.98
4.41
f1 (ppm)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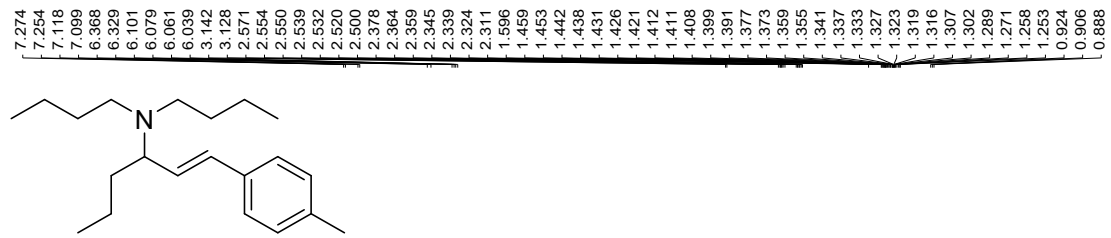
129.730
128.625
127.437
126.458
122.330
112.945
77.160 CDCl3
60.872
48.888
33.092
23.461
19.751
Ph
N
SMe
3va
f1 (ppm)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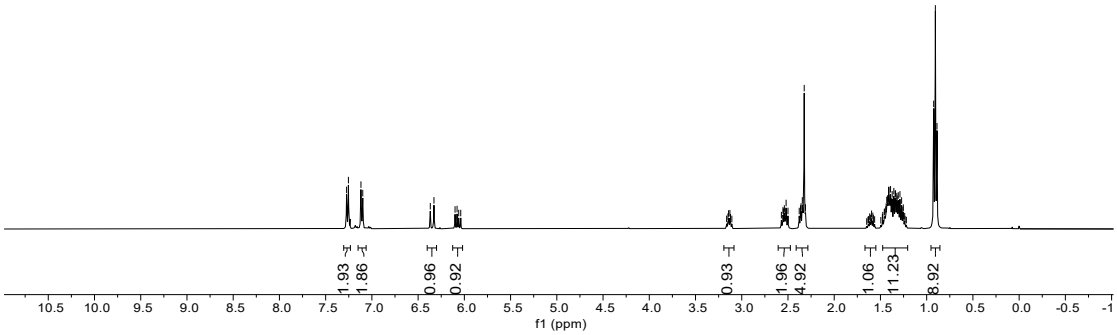
7.254
7.118
7.099
6.368
6.329
6.101
6.079
6.061
6.039
3.142
3.128
2.571
2.554
2.550
2.539
2.532
2.520
2.500
2.378
2.364
2.359
2.345
2.339
2.324
2.311
1.596
1.459
1.453
1.442
1.438
1.431
1.426
1.421
1.412
1.411
1.408
1.399
1.391
1.377
1.373
1.359
1.355
1.341
1.337
1.333
1.327
1.323
1.319
1.316
1.307
1.302
1.289
1.271
1.258
1.253
0.924
0.906
0.888

3ab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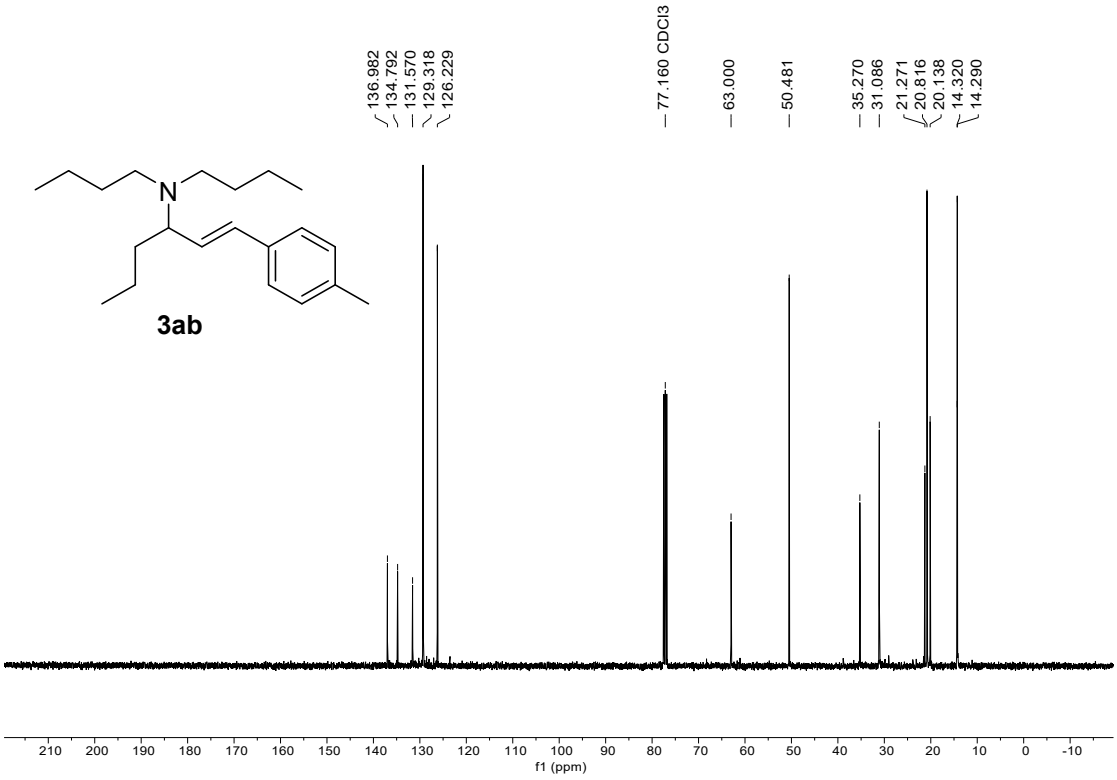
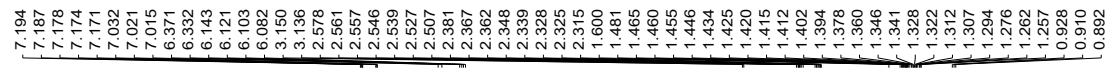
1.86
0.96
0.92
0.93
1.96
4.92
1.06
11.23
8.92
f1 (ppm)


136.982
134.792
131.570
129.318
126.229
77.160 CDCl3
63.000
50.481
35.270
31.086
21.271
20.816
20.138
14.320
14.290
f1 (ppm)

3ab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7.187
7.178
7.174
7.171
7.032
7.021
7.015
6.371
6.332
6.143
6.121
6.103
6.082
3.150
3.136
2.578
2.561
2.557
2.546
2.539
2.527
2.507
2.381
2.367
2.362
2.348
2.339
2.328
2.325
2.315
1.600
1.481
1.465
1.460
1.455
1.446
1.434
1.425
1.420
1.415
1.412
1.402
1.394
1.378
1.360
1.346
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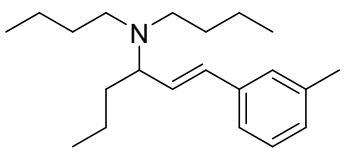
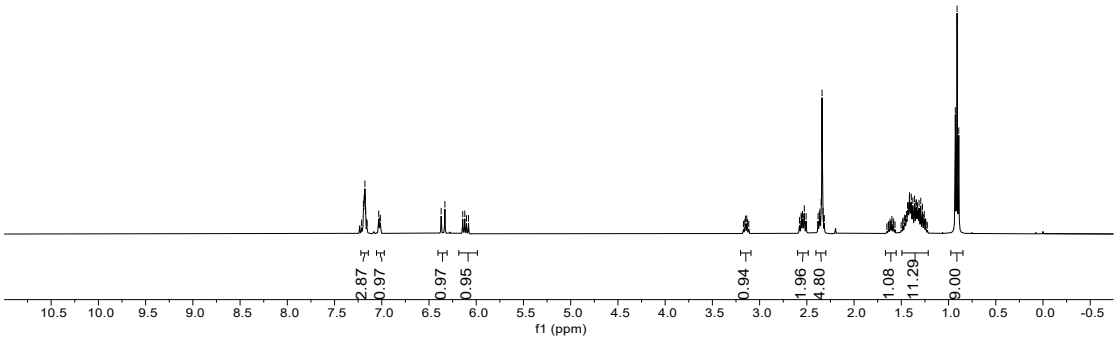
1.312
1.307
1.294
1.276
1.262
1.257
0.928
0.910
0.892



3ac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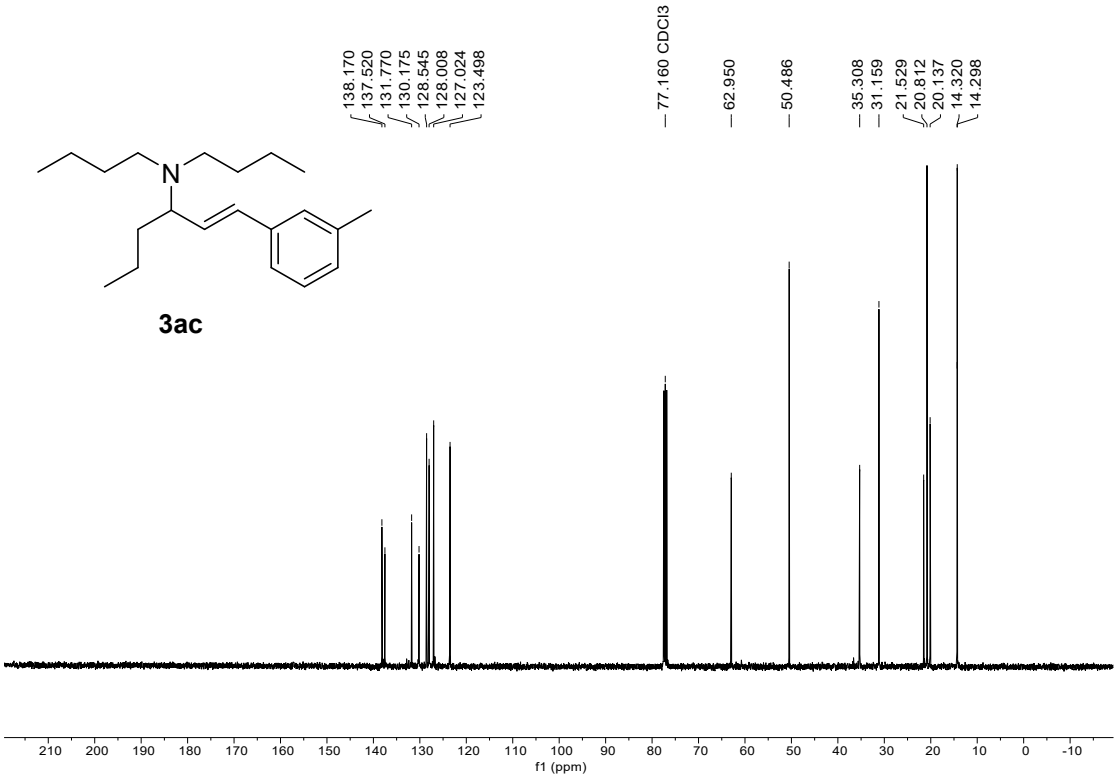
0.97
0.97
0.95
0.94
1.96
4.80
1.08
11.29
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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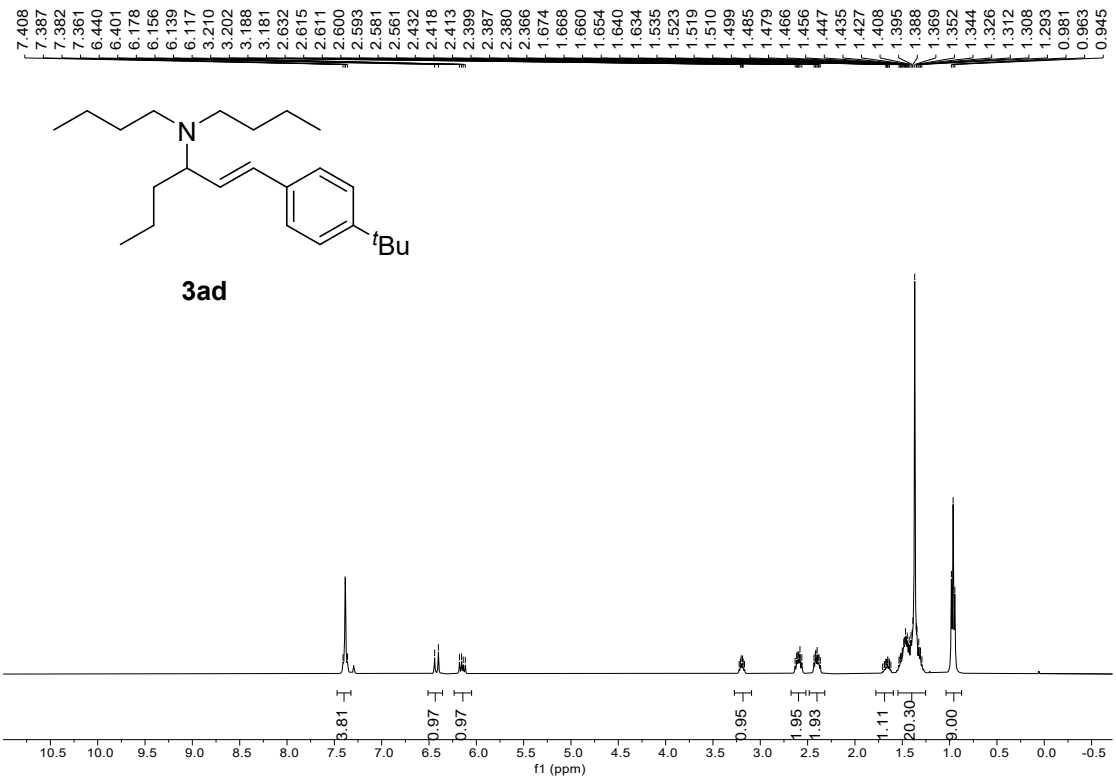
137.520
131.770
130.175
128.545
128.008
127.024
123.498
77.160 CDCl3
62.950
50.486
35.308
31.159
21.529
20.812
20.137
14.320
14.298
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ac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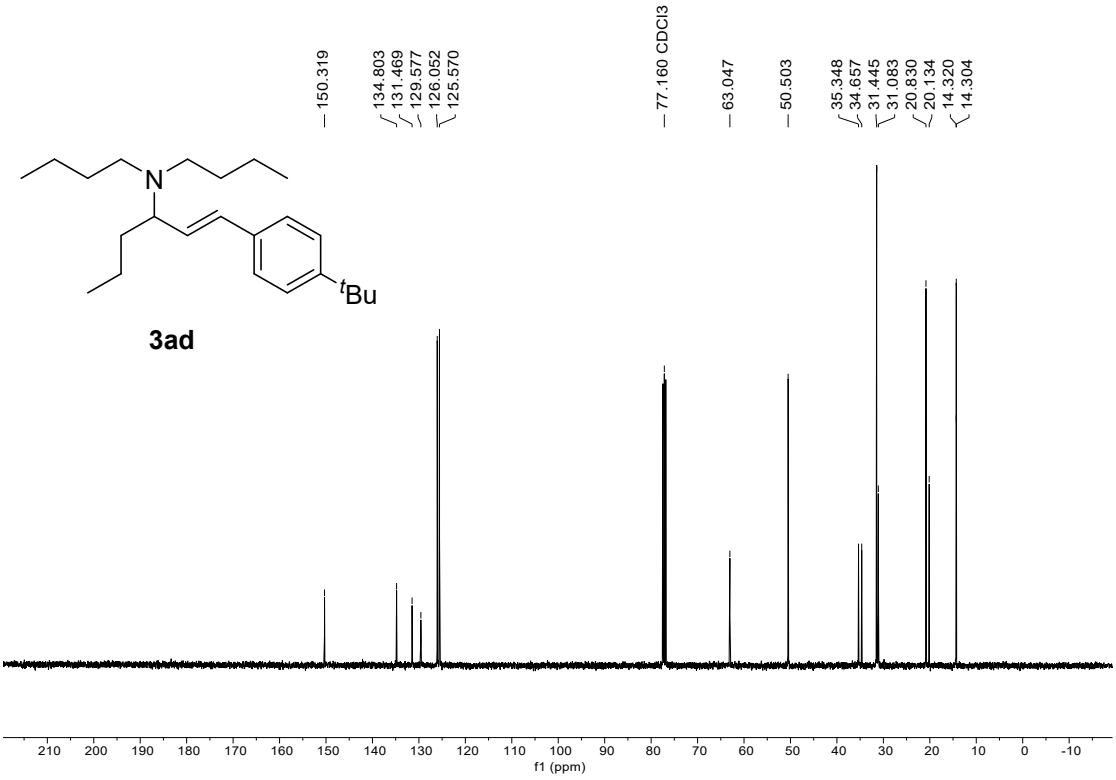
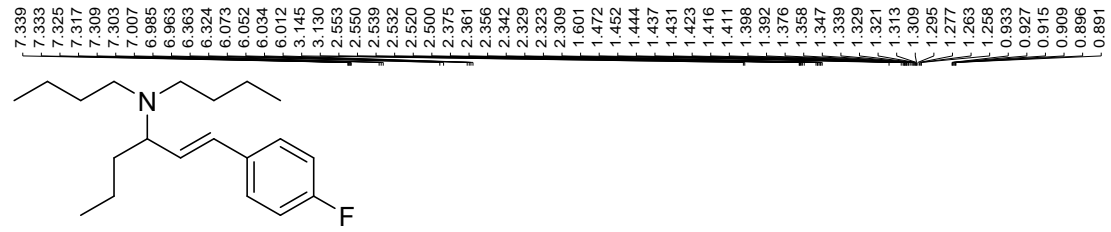
7.361
6.440
6.401
6.178
6.156
6.139
6.117
3.210
3.202
3.188
3.181
2.632
2.615
2.611
2.600
2.593
2.581
2.561
2.432
2.418
2.413
2.399
2.387
2.380
2.366
1.674
1.668
1.660
1.654
1.640
1.634
1.535
1.523
1.519
1.510
1.499
1.485
1.479
1.466
1.456
1.447
1.435
1.427
1.408
1.395
1.388
1.369
1.352
1.344
1.326
1.312
1.308
1.293
0.981
0.963
0.945
N
tBu
3ad
3.81
0.97
0.97
0.95
1.95
1.93
1.11
20.30
9.00
f1 (ppm)


150.319
134.803
131.469
129.577
126.052
125.570
77.160 CDCl3
63.047
50.503
35.348
34.657
31.445
31.083
20.830
20.134
14.320
14.304
N
tBu
3ad
f1 (ppm)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6.963
6.363
6.324
6.073
6.052
6.034
6.012
3.145
3.130
2.553
2.550
2.539
2.532
2.520
2.500
2.375
2.361
2.356
2.342
2.329
2.323
2.309
1.601
1.472
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1.444
1.437
1.431
1.423
1.416
1.411
1.398
1.392
1.376
1.358
1.347
1.339
1.329
1.321
1.313
1.309
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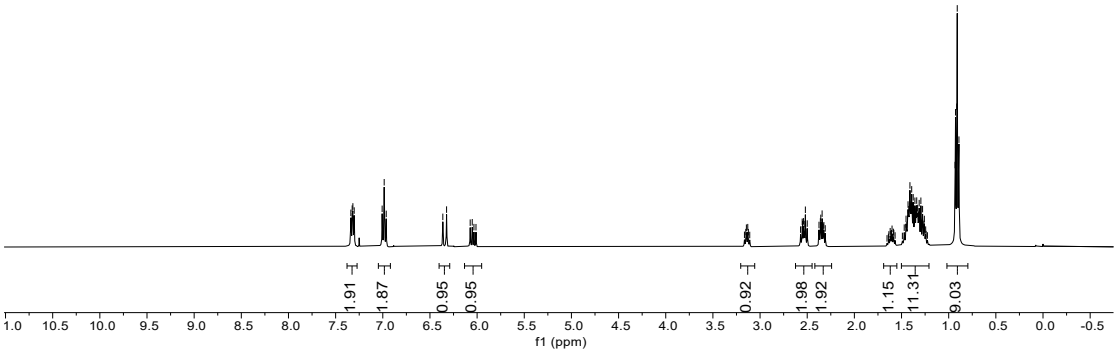
1.258
0.933
0.927
0.915
0.909
0.896
0.891
N
F

3ae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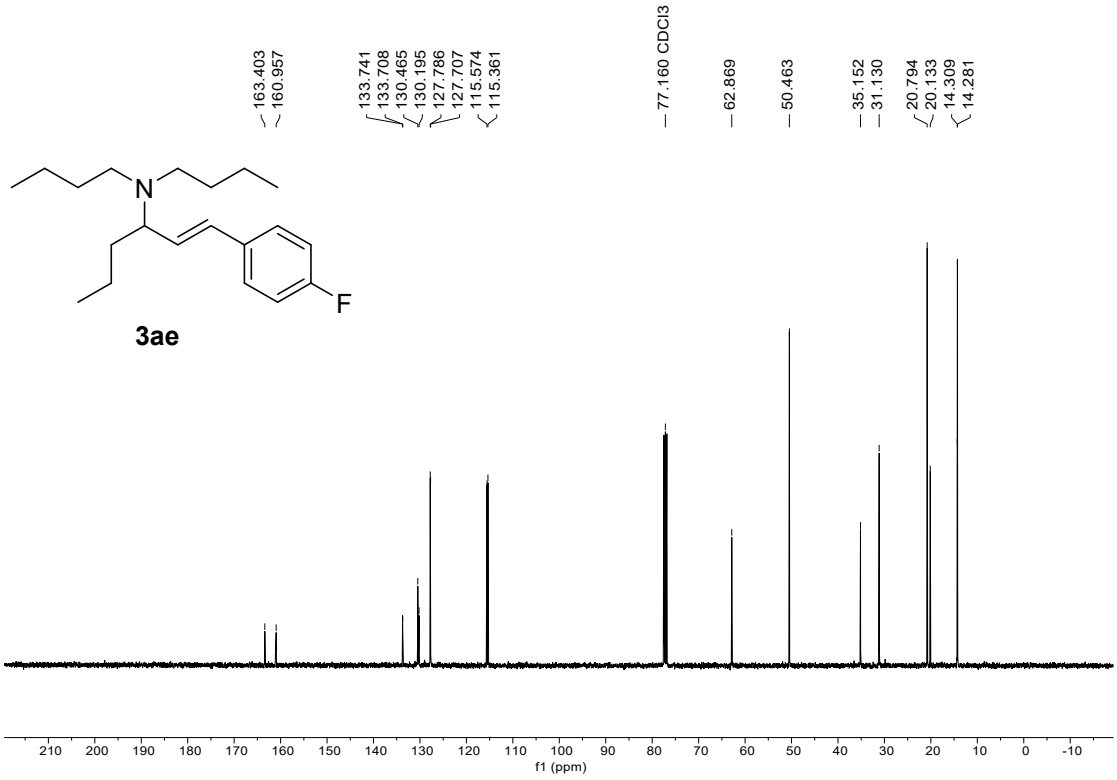
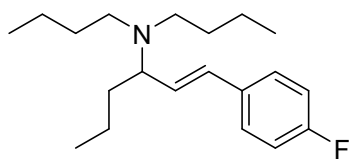
0.95
0.95
0.92
1.98
1.92
1.15
11.31
9.03
f1 (ppm)

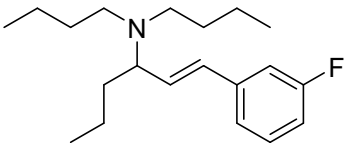

163.403
160.957
133.741
133.708
130.465
130.195
127.786
127.707
115.574
115.361
77.160 CDCl3
62.869
50.463
35.152
31.130
20.794
20.133
14.309
14.281
N
F
f1 (ppm)

3ae



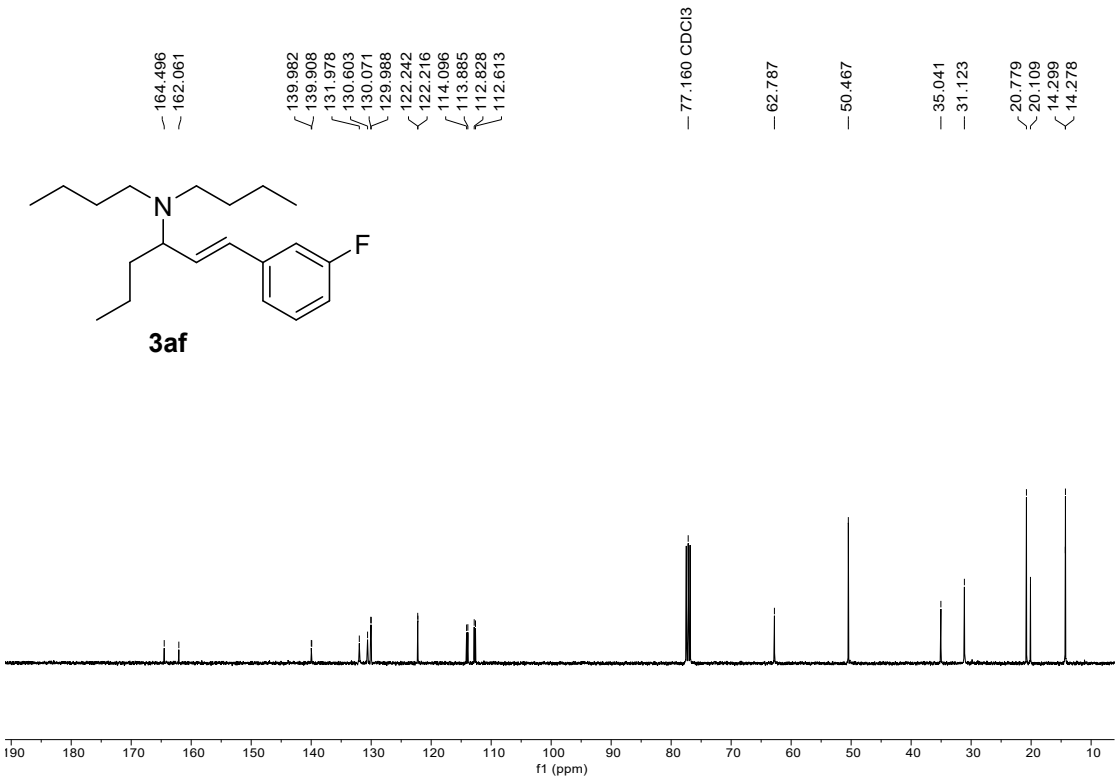
3ae

-115.277
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



3af

7.279 7.259 7.243 7.224 7.126 7.106 7.079 7.053 6.921 6.915 6.900 6.894 6.879 6.873 6.373 6.334 6.179 6.158 6.140 6.118
3.184 3.164 3.146 3.128 2.576 2.557 2.542 2.525 2.505 2.378 2.361 2.345 2.329 2.312
1.430 1.411 1.394 1.377 1.359 1.340 1.329 1.314 1.296 1.279 1.261 0.930 0.911
1.14 1.88 0.91 0.98 0.90 0.94 1.93 1.93 1.21 11.25 8.93
1.0 10.5 10.0 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 -0.5
f1 (ppm)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122.216
114.096
113.885
112.828
112.613
77.160 CDCl3
62.787
50.467
35.041
31.123
20.779
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14.299
14.278
N
F
3af
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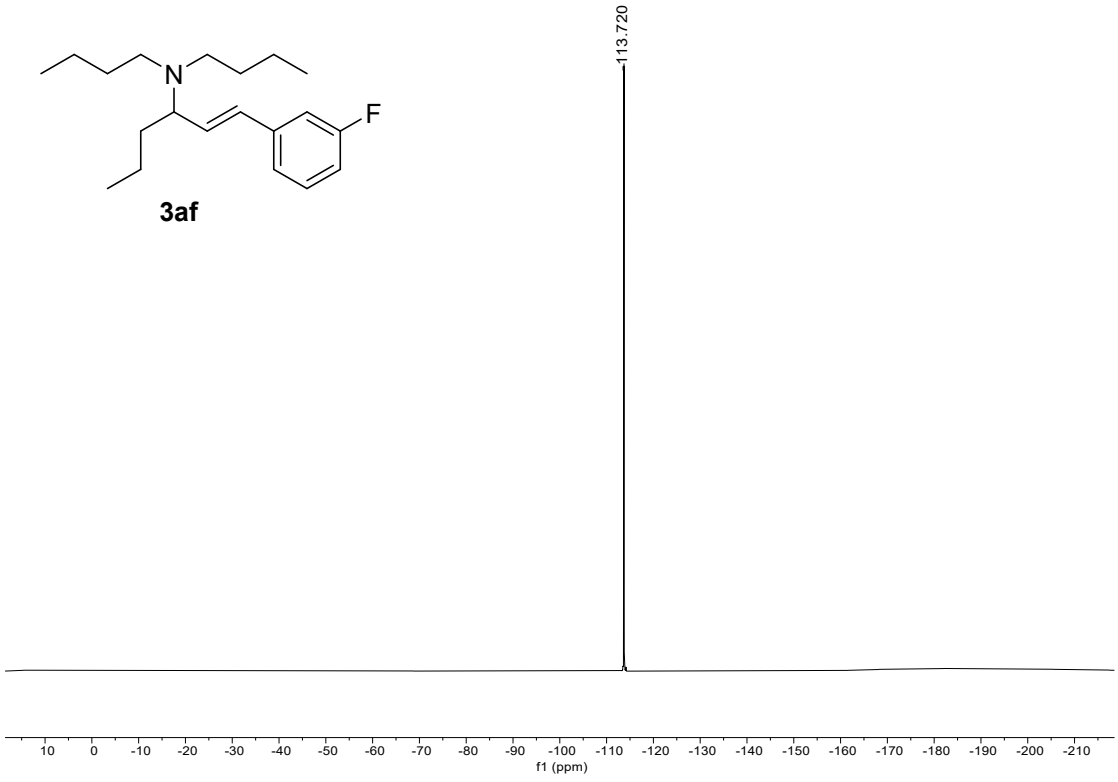
f1 (ppm)


113.720
N
F
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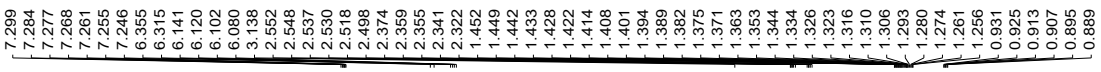
f1 (ppm)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6.141
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6.102
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3.138
2.552
2.548
2.537
2.530
2.518
2.498
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2.355
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1.452
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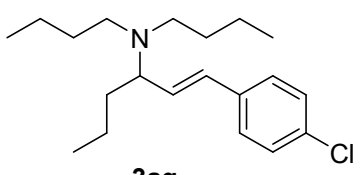
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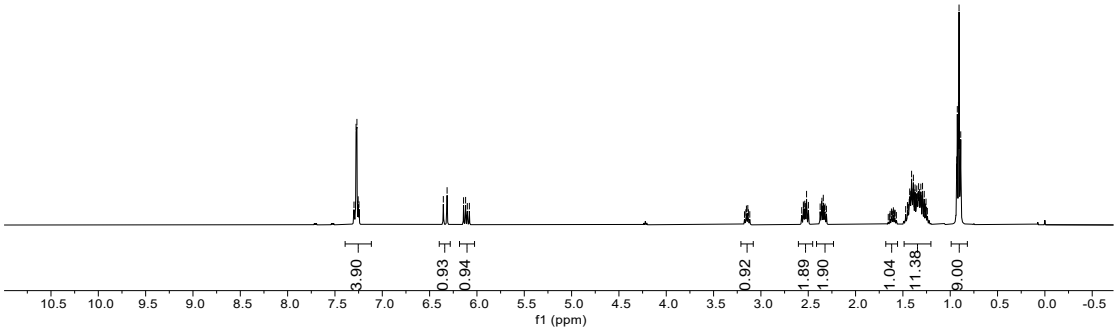
Cl

3ag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0.92
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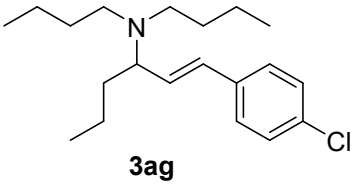
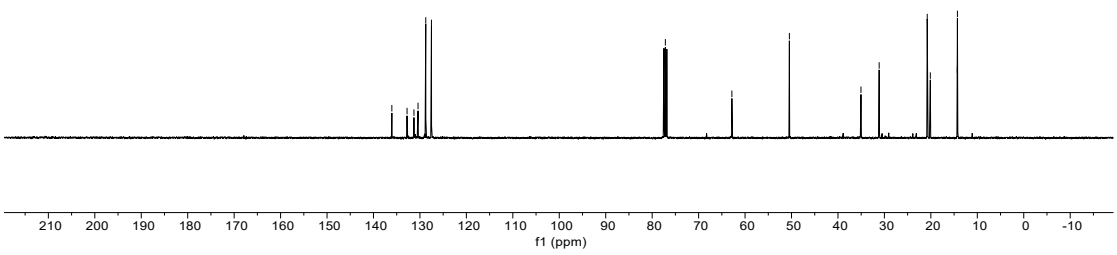
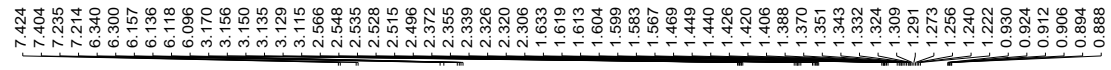
1.90
1.04
11.38
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


136.045
132.772
131.289
130.406
128.745
127.519
77.160 CDCl3
62.839
50.458
35.048
31.129
20.780
20.116
14.307
14.280


N
Cl

3ag


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.235
7.214
6.340
6.300
6.157
6.136
6.118
6.096
3.170
3.156
3.150
3.135
3.129
3.115
2.566
2.548
2.535
2.528
2.515
2.496
2.372
2.355
2.339
2.326
2.320
2.306
1.633
1.619
1.613
1.604
1.599
1.583
1.567
1.469
1.449
1.440
1.426
1.420
1.406
1.388
1.370
1.351
1.343
1.332
1.324
1.309
1.291
1.273
1.256
1.240
1.222
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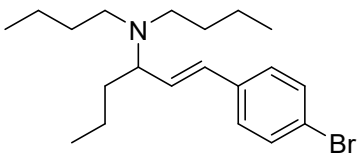
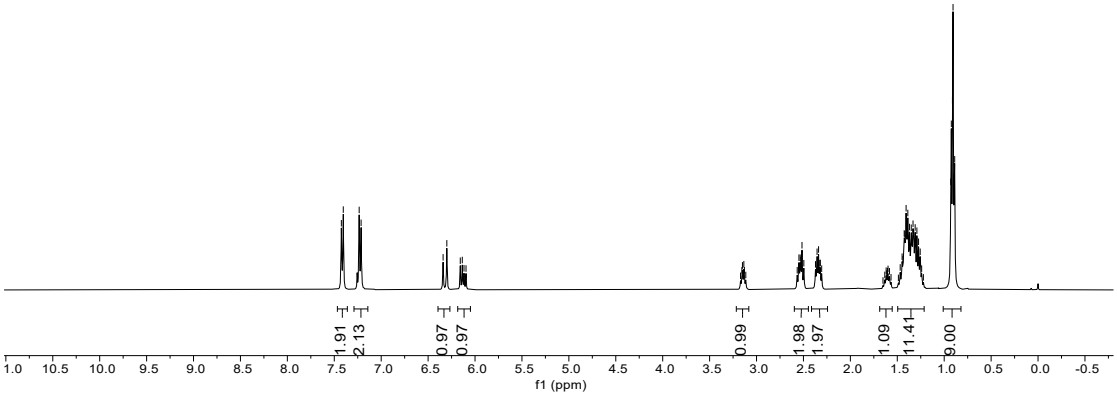
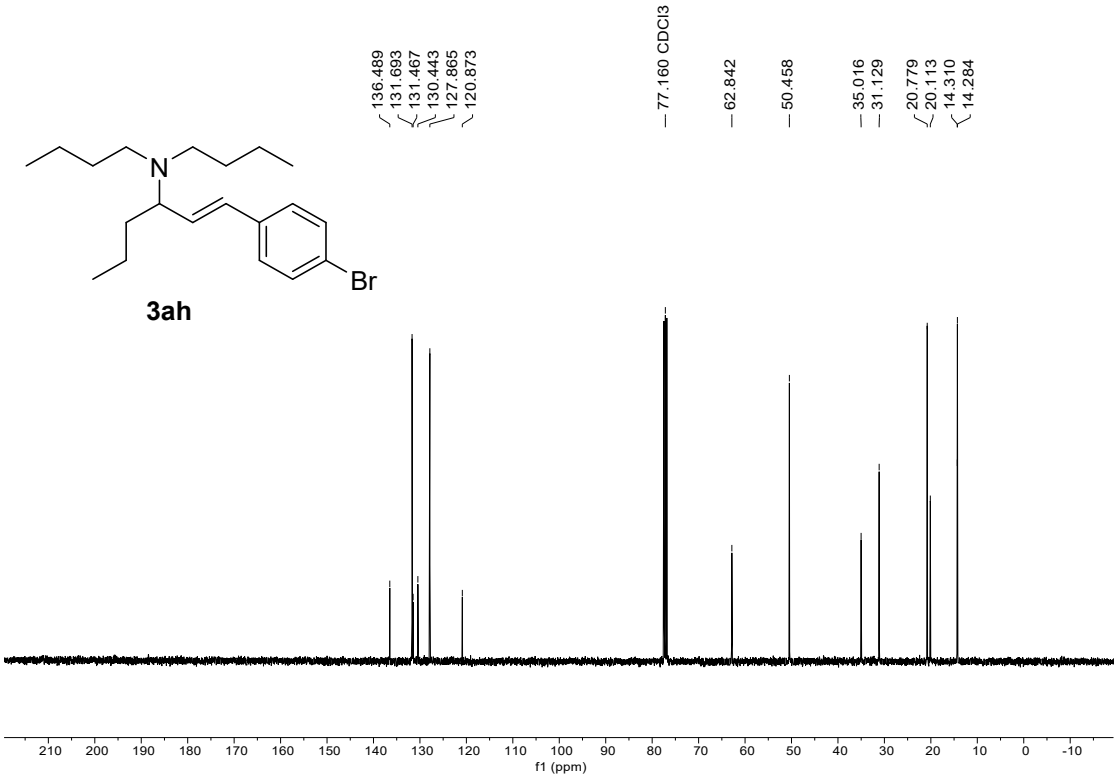
0.924
0.912
0.906
0.894
0.888


N
Br

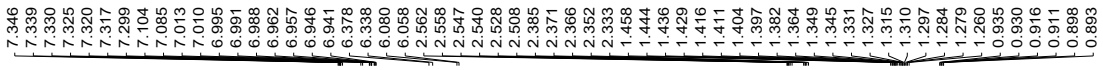
3ah

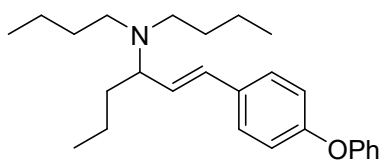

1.91
2.13
0.97
0.97
0.99
1.98
1.97
1.09
11.41
9.00
f1 (ppm)


136.489
131.693
131.467
130.443
127.865
120.873
77.160 CDCl3
62.842
50.458
35.016
31.129
20.779
20.113
14.310
14.284
f1 (ppm)

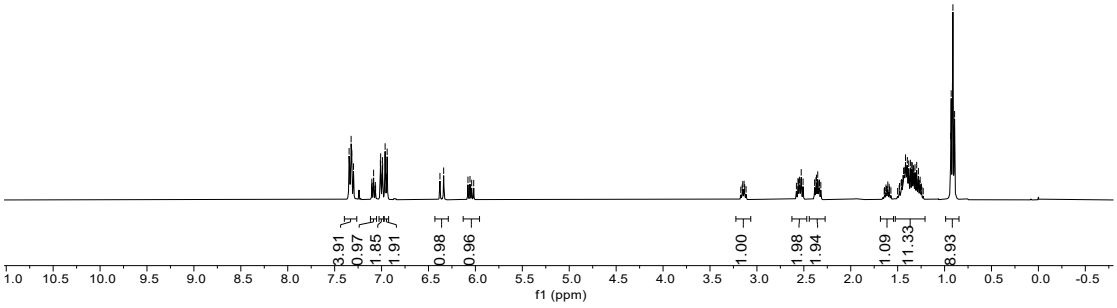
N
Br

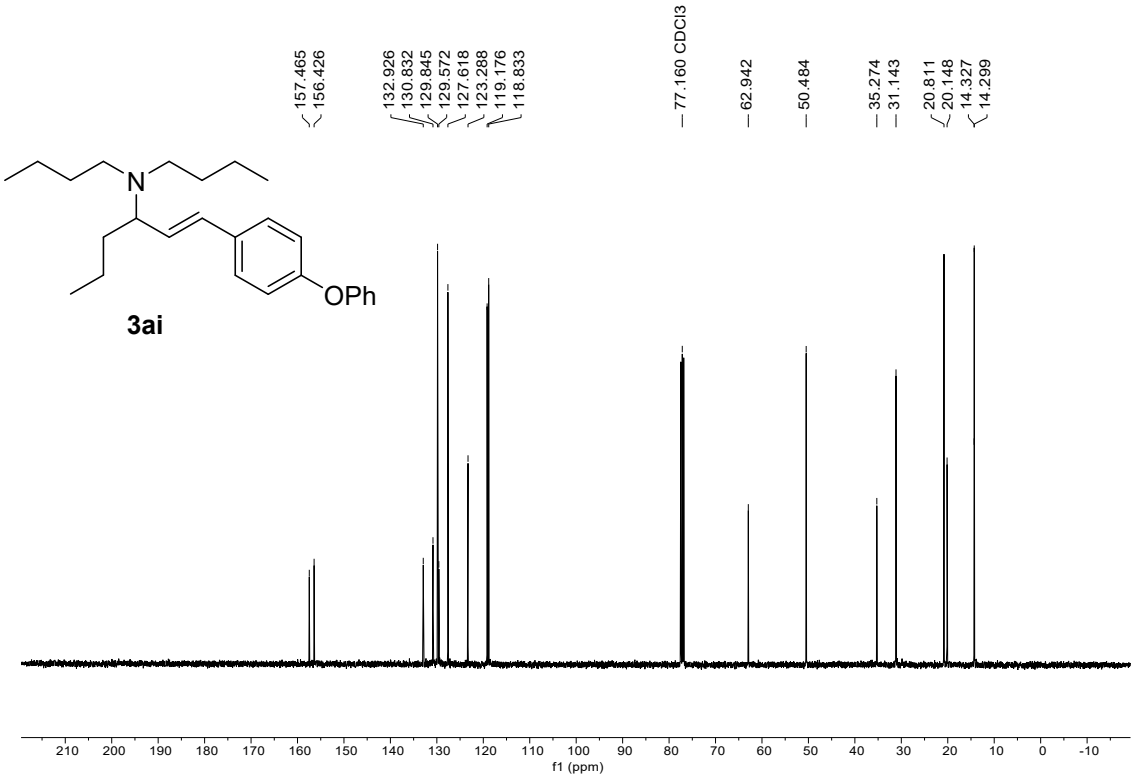
3ah


7.346
7.339
7.330
7.325
7.320
7.317
7.299
7.104
7.085
7.013
7.010
6.995
6.991
6.988
6.962
6.957
6.946
6.941
6.378
6.338
6.080
6.058
2.562
2.558
2.547
2.540
2.528
2.508
2.385
2.371
2.366
2.352
2.333
1.458
1.444
1.436
1.429
1.416
1.411
1.404
1.397
1.382
1.364
1.349
1.345
1.331
1.327
1.315
1.310
1.297
1.284
1.279
1.260
0.935
0.930
0.916
0.911
0.898
0.893

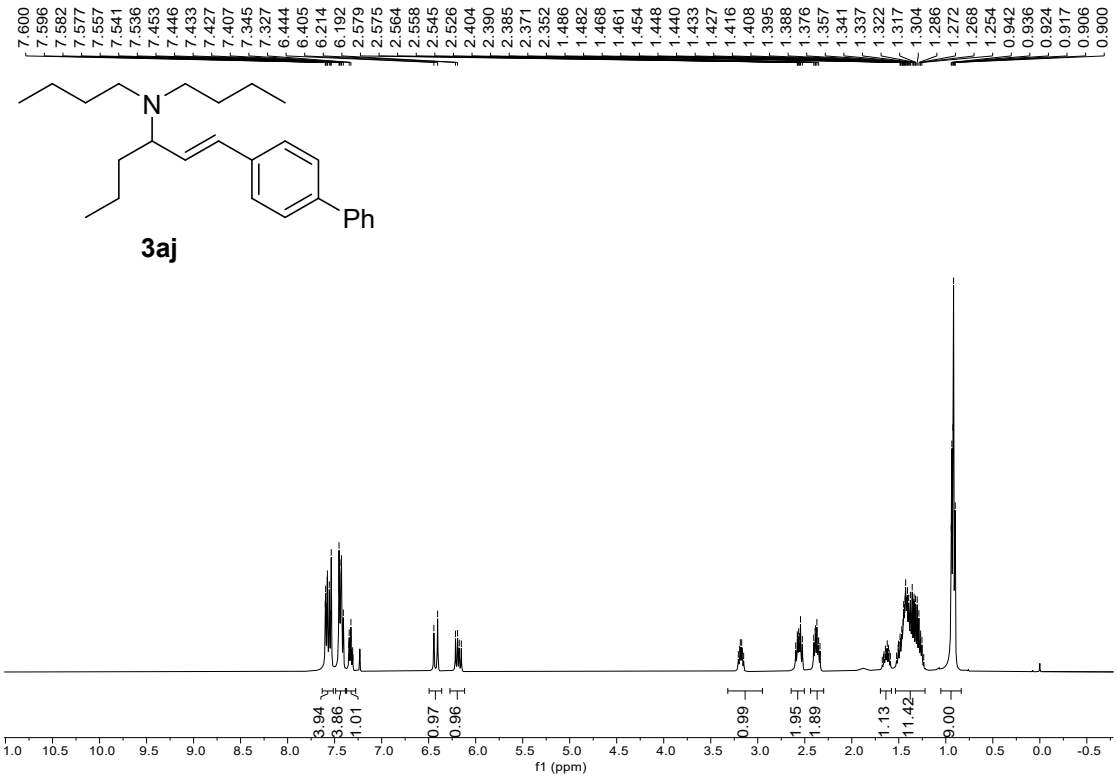

N
OPh

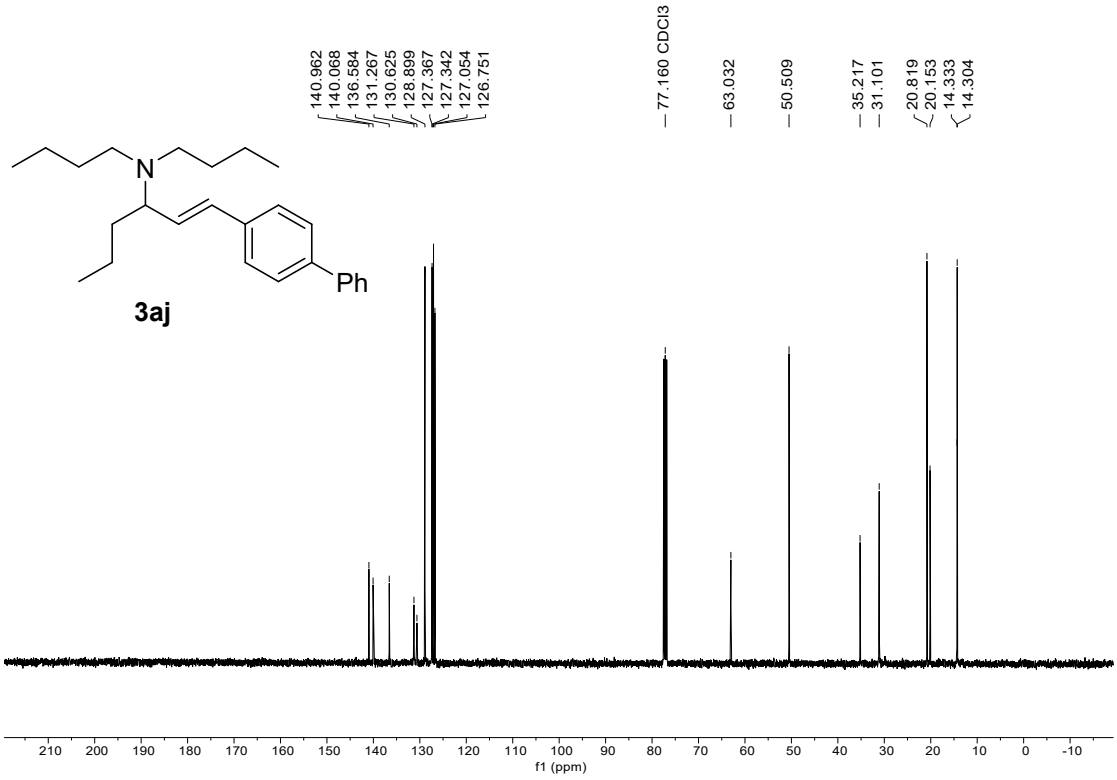
3ai

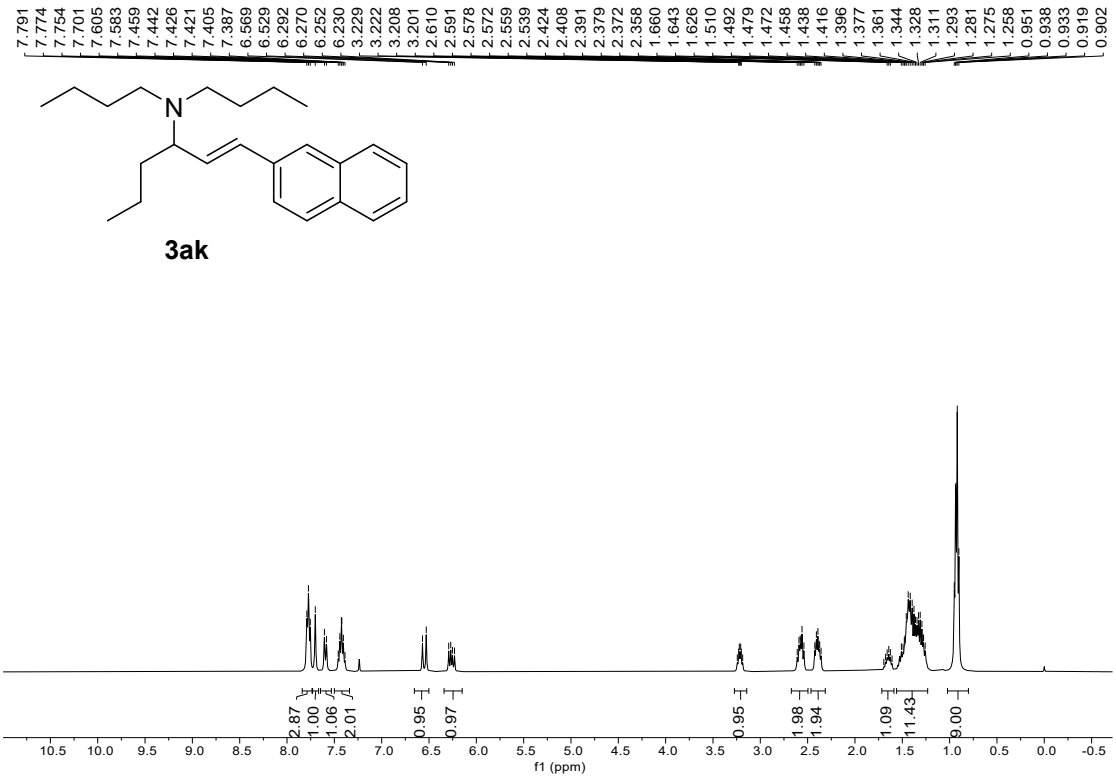

3.91
0.97
1.85
1.91
0.98
0.96
1.00
1.98
1.94
1.09
11.33
8.93
f1 (ppm)

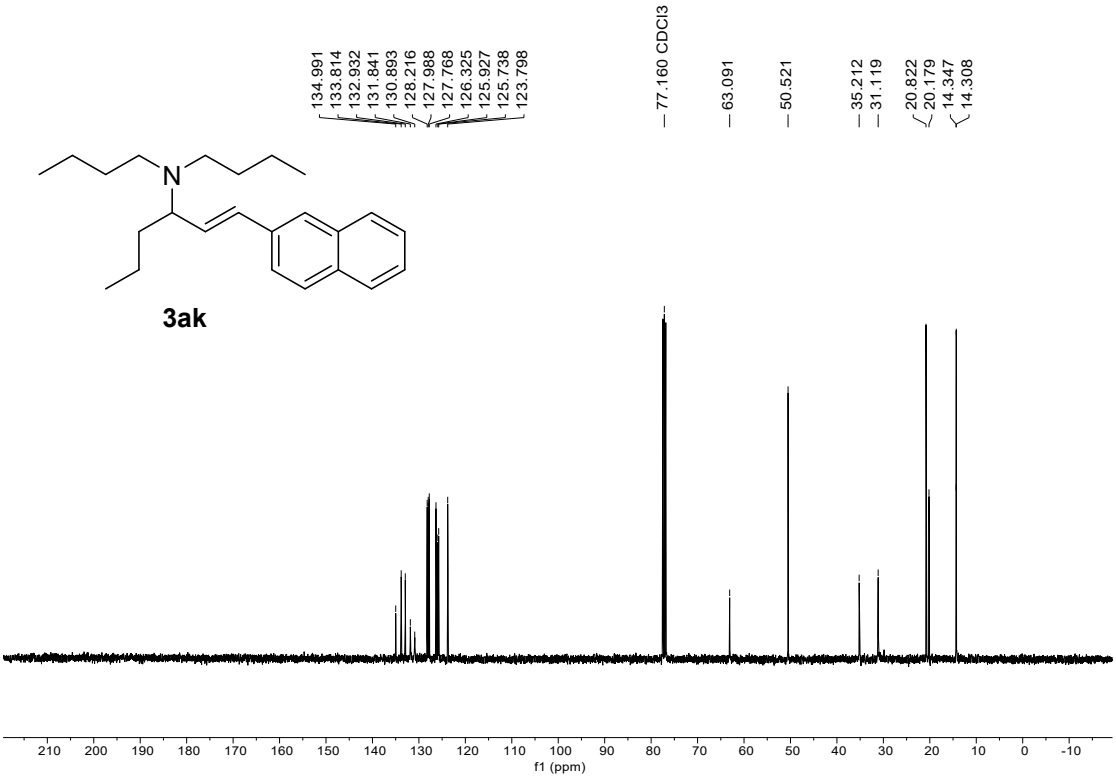

157.465
156.426
132.926
130.832
129.845
129.572
127.618
123.288
119.176
118.833
77.160 CDCl3
62.942
50.484
35.274
31.143
20.811
20.148
14.327
14.299
N
OPh
f1 (ppm)

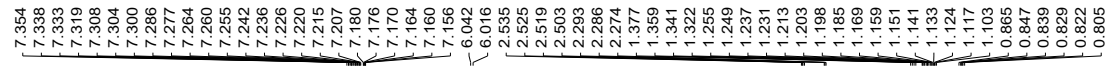
3ai

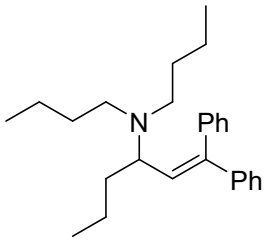

7.600
7.596
7.582
7.577
7.557
7.541
7.536
7.453
7.446
7.433
7.427
7.407
7.345
7.327
6.444
6.405
6.214
6.192
2.579
2.575
2.564
2.558
2.545
2.526
2.404
2.390
2.385
2.371
2.352
1.486
1.482
1.468
1.461
1.454
1.448
1.440
1.433
1.427
1.416
1.408
1.395
1.388
1.376
1.357
1.341
1.337
1.322
1.317
1.304
1.286
1.272
1.268
1.254
0.942
0.936
0.924
0.917
0.906
0.900
N
Ph
3aj
3.94
3.86
1.01
0.97
0.96
0.99
1.95
1.89
1.13
11.42
9.00
f1 (ppm)


140.962
140.068
136.584
131.267
130.625
128.899
127.367
127.342
127.054
126.751
77.160 CDCl3
63.032
50.509
35.217
31.101
20.819
20.153
14.333
14.304
N
Ph
3aj
f1 (ppm)

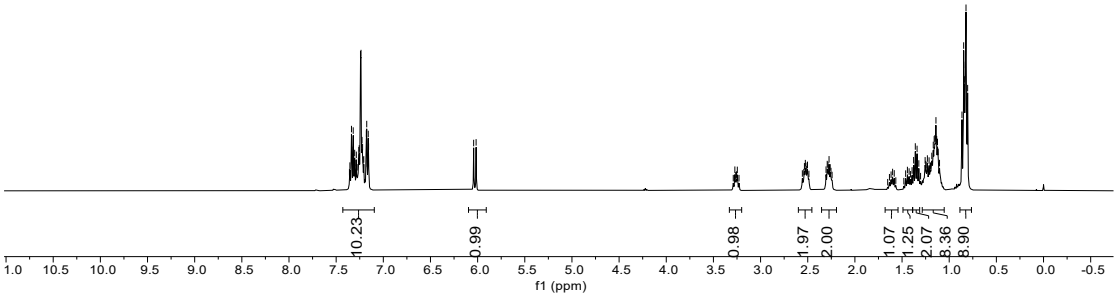

7.791
7.774
7.754
7.701
7.605
7.583
7.459
7.442
7.426
7.421
7.405
7.387
6.569
6.529
6.292
6.270
6.252
6.230
3.229
3.222
3.208
3.201
2.610
2.591
2.578
2.572
2.559
2.539
2.424
2.408
2.391
2.379
2.372
2.358
1.660
1.643
1.626
1.510
1.492
1.479
1.472
1.458
1.438
1.416
1.396
1.377
1.361
1.344
1.328
1.311
1.293
1.281
1.275
1.258
0.951
0.938
0.933
0.919
0.902
N
3ak
2.87
1.00
1.06
2.01
0.95
0.97
0.95
1.98
1.94
1.09
11.43
9.00
f1 (ppm)

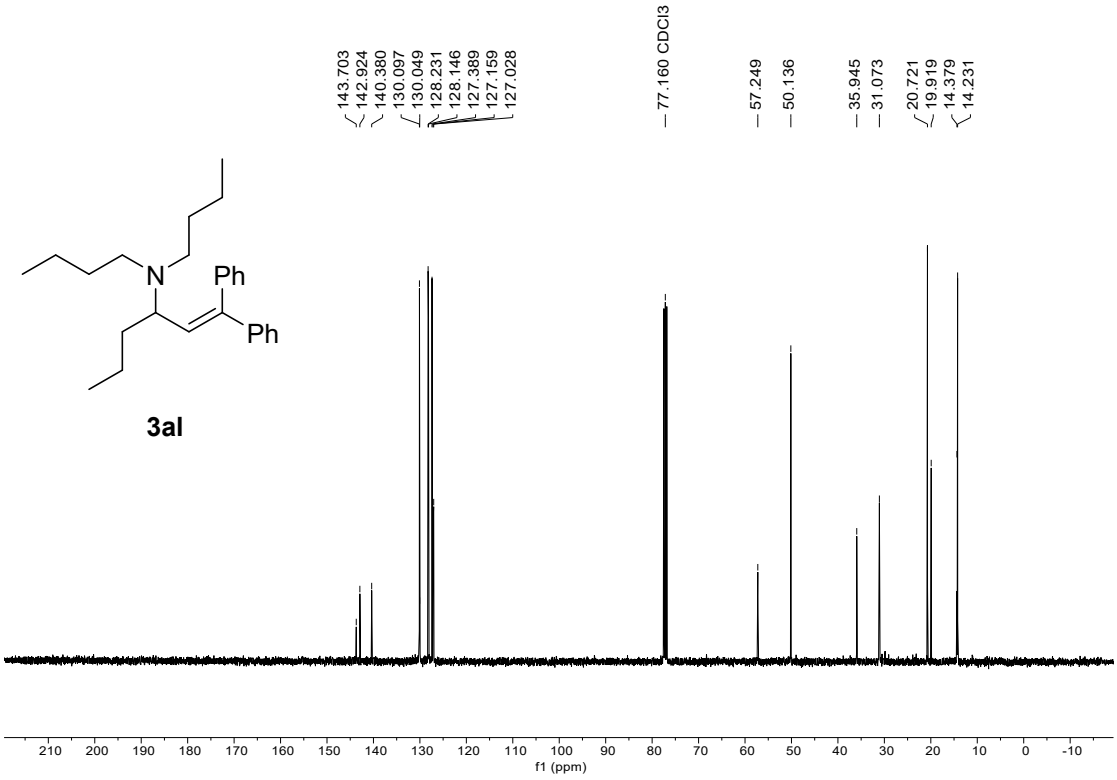

134.991
133.814
132.932
131.841
130.893
128.216
127.988
127.768
126.325
125.927
125.738
123.798
77.160 CDCl3
63.091
50.521
35.212
31.119
20.822
20.179
14.347
14.308
N
3ak
f1 (ppm)


7.354
7.338
7.333
7.319
7.308
7.304
7.300
7.286
7.277
7.264
7.260
7.255
7.242
7.236
7.226
7.220
7.215
7.207
7.180
7.176
7.170
7.164
7.160
7.156
6.042
6.016
2.535
2.525
2.519
2.503
2.293
2.286
2.274
1.377
1.359
1.341
1.322
1.255
1.249
1.237
1.231
1.213
1.203
1.198
1.185
1.169
1.159
1.151
1.141
1.133
1.124
1.117
1.103
0.865
0.847
0.839
0.829
0.822
0.805


N
Ph
Ph

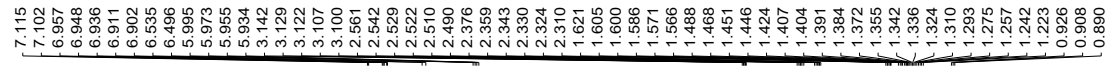
3al

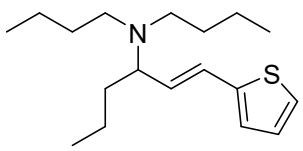

10.23
0.99
0.98
1.97
2.00
1.07
1.25
2.07
3.36
8.90
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


143.703
142.924
140.380
130.097
130.049
128.231
128.146
127.389
127.159
127.028
77.160 CDCl3
57.249
50.136
35.945
31.073
20.721
19.919
14.379
14.231
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

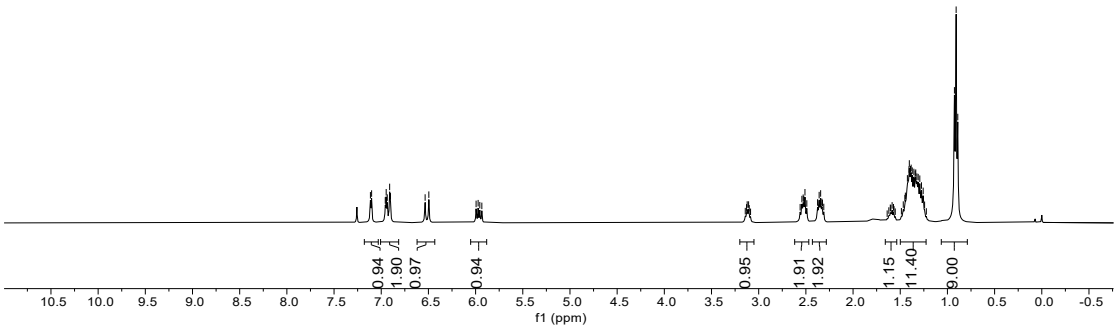
N
Ph
Ph

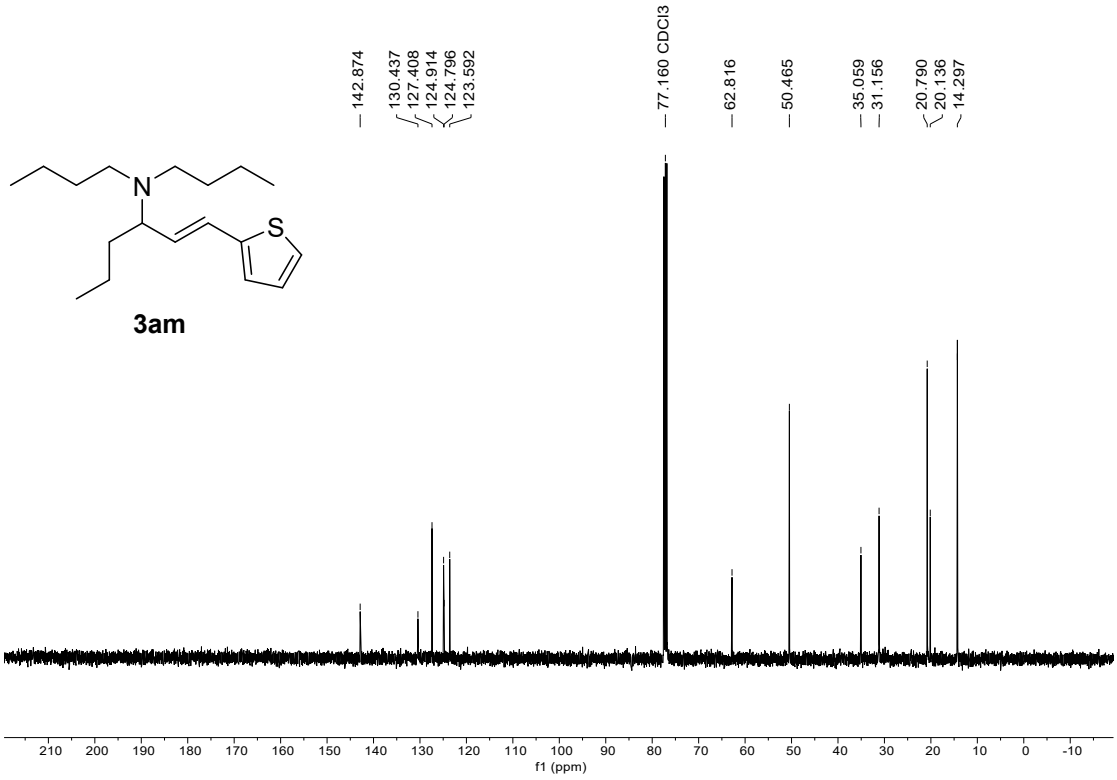
3al


7.115
7.102
6.957
6.948
6.936
6.911
6.902
6.535
6.496
5.995
5.973
5.955
5.934
3.142
3.129
3.122
3.107
3.100
2.561
2.542
2.529
2.522
2.510
2.490
2.376
2.359
2.343
2.330
2.324
2.310
1.621
1.605
1.600
1.586
1.571
1.566
1.488
1.468
1.451
1.446
1.424
1.407
1.404
1.391
1.384
1.372
1.355
1.342
1.336
1.324
1.310
1.293
1.275
1.257
1.242
1.223
0.926
0.908
0.890


N
S

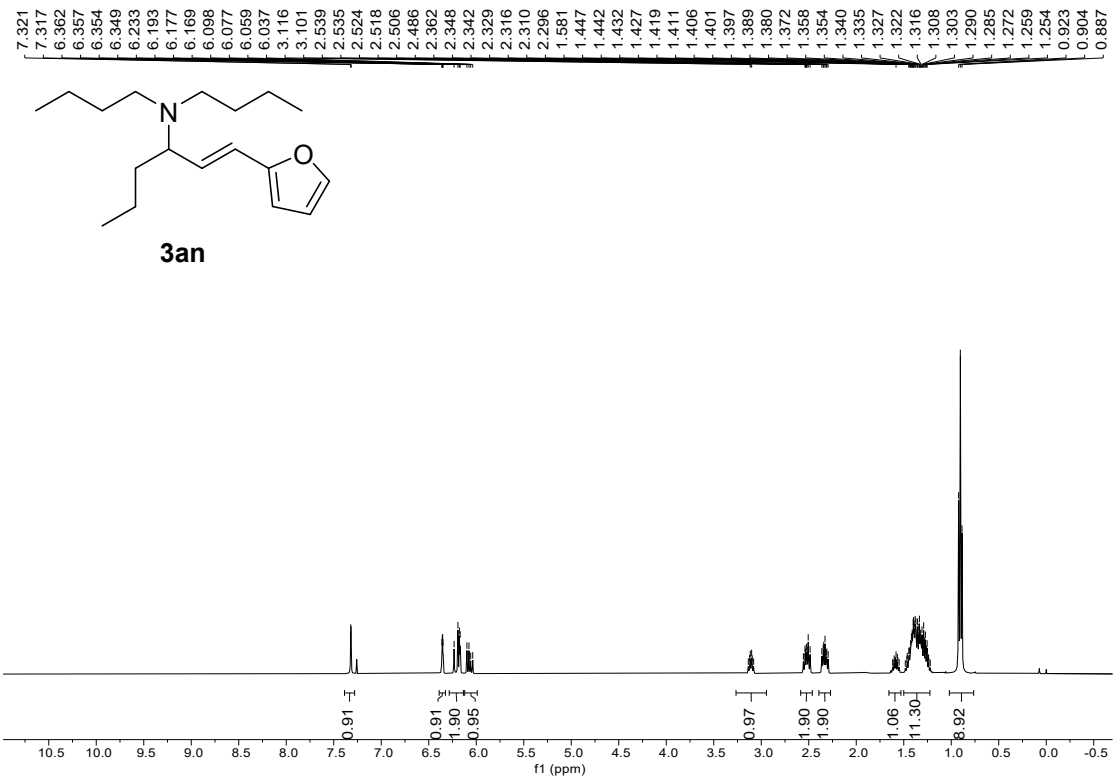
3am


0.94
1.90
0.97
0.94
0.95
1.91
1.92
1.15
11.40
9.00
10.5 10.0 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 -0.5
f1 (ppm)


142.874
130.437
127.408
124.914
124.796
123.592
77.160 CDCl3
62.816
50.465
35.059
31.156
20.790
20.136
14.297
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

N
S

3am


7.321
7.317
6.362
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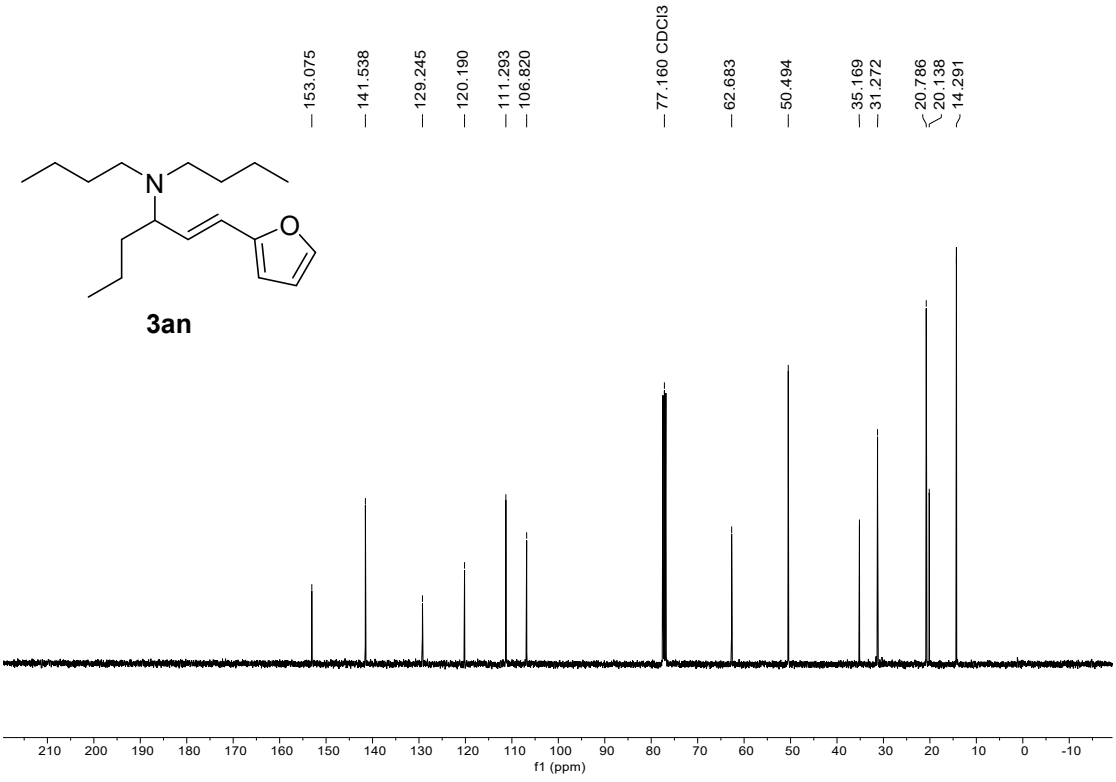
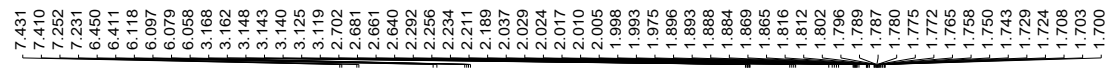
6.354
6.349
6.233
6.193
6.177
6.169
6.098
6.077
6.059
6.037
3.116
3.101
2.539
2.535
2.524
2.518
2.506
2.486
2.362
2.348
2.342
2.329
2.316
2.310
2.296
1.581
1.447
1.442
1.432
1.427
1.419
1.411
1.406
1.401
1.397
1.389
1.380
1.372
1.358
1.354
1.340
1.335
1.327
1.322
1.316
1.308
1.303
1.290
1.285
1.272
1.259
1.254
0.923
0.904
0.887
N
O
3an
0.91
0.91
1.90
0.95
0.97
1.90
1.90
1.06
11.30
8.92
f1 (ppm)


153.075
141.538
129.245
120.190
111.293
106.820
77.160 CDCl3
62.683
50.494
35.169
31.272
20.786
20.138
14.291
N
O
3an
f1 (ppm)


7.431
7.410
7.252
7.231
6.450
6.411
6.118
6.097
6.079
6.058
3.168
3.162
3.148
3.143
3.140
3.125
3.119
2.702
2.681
2.661
2.640
2.292
2.256
2.234
2.211
2.189
2.037
2.029
2.024
2.017
2.010
2.005
1.998
1.993
1.975
1.896
1.893
1.888
1.884
1.869
1.865
1.816
1.812
1.802
1.796
1.789
1.787
1.780
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1.765
1.758
1.750
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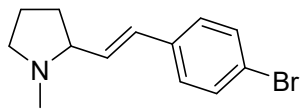
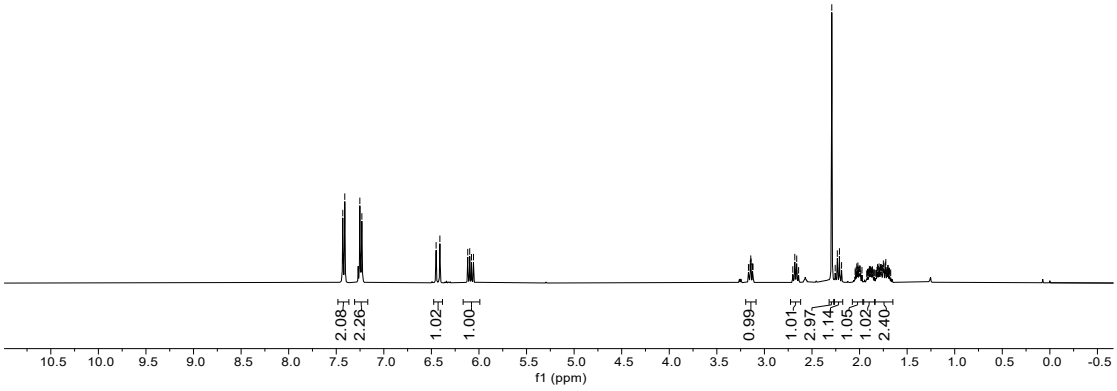
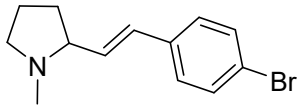
1.703
1.700


N
Br

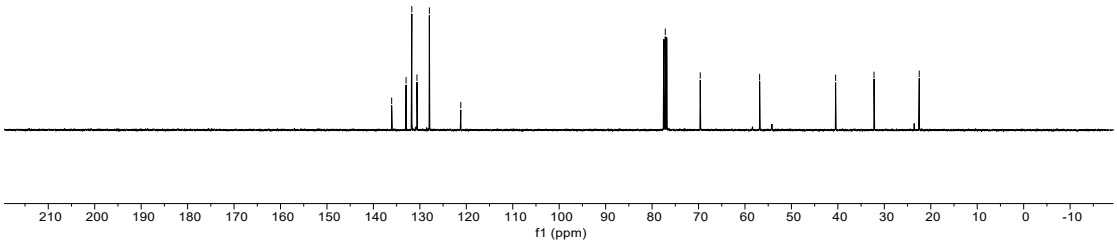
3ao

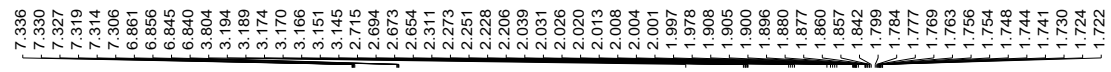

2.08
2.26
1.02
1.00
0.99
1.01
2.97
1.14
1.05
1.02
2.40
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

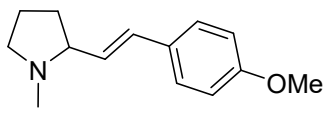

136.066
132.969
131.730
130.622
127.954
121.184
77.160 CDCl3
69.630
56.845
40.486
32.214
22.476


N
Br

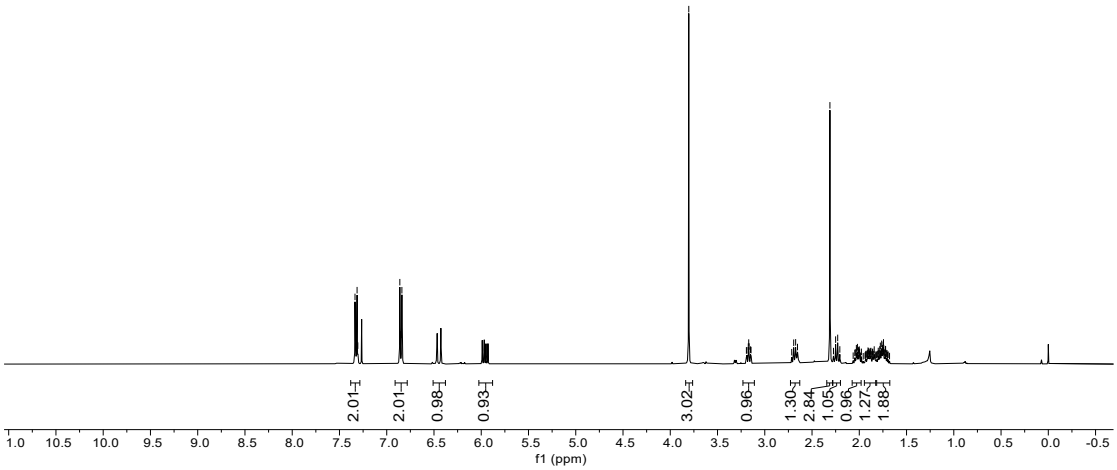
3ao

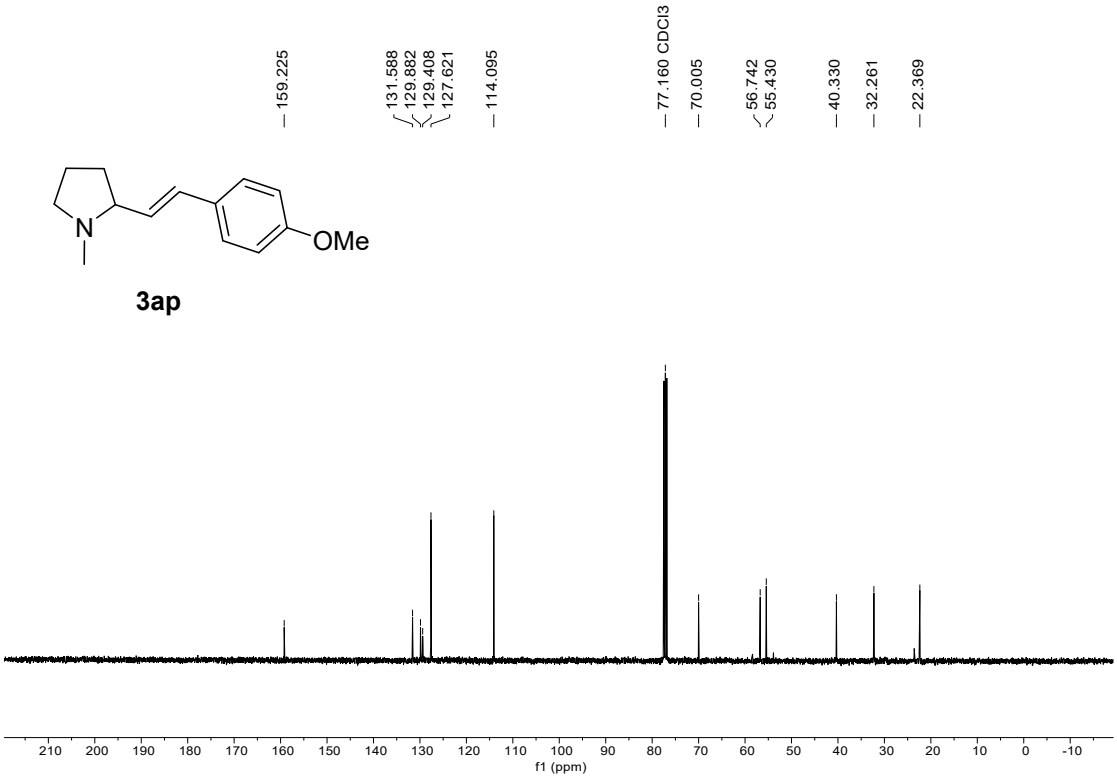

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.336
7.330
7.327
7.319
7.314
7.306
6.861
6.856
6.845
6.840
6.804
3.194
3.189
3.174
3.170
3.166
3.151
3.145
2.715
2.694
2.673
2.654
2.311
2.273
2.251
2.228
2.206
2.039
2.031
2.026
2.020
2.013
2.008
2.004
2.001
1.997
1.978
1.908
1.905
1.900
1.896
1.880
1.877
1.860
1.857
1.842
1.799
1.784
1.777
1.769
1.763
1.756
1.754
1.748
1.744
1.741
1.730
1.724
1.722


N
OMe

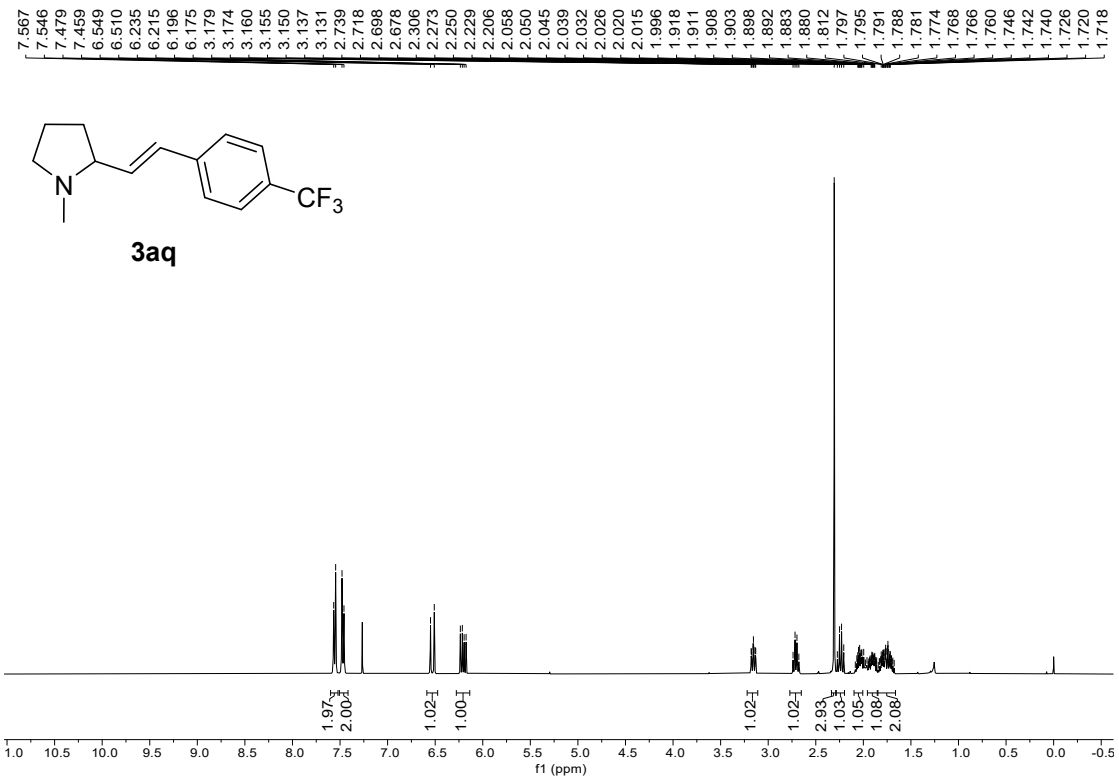
3ap

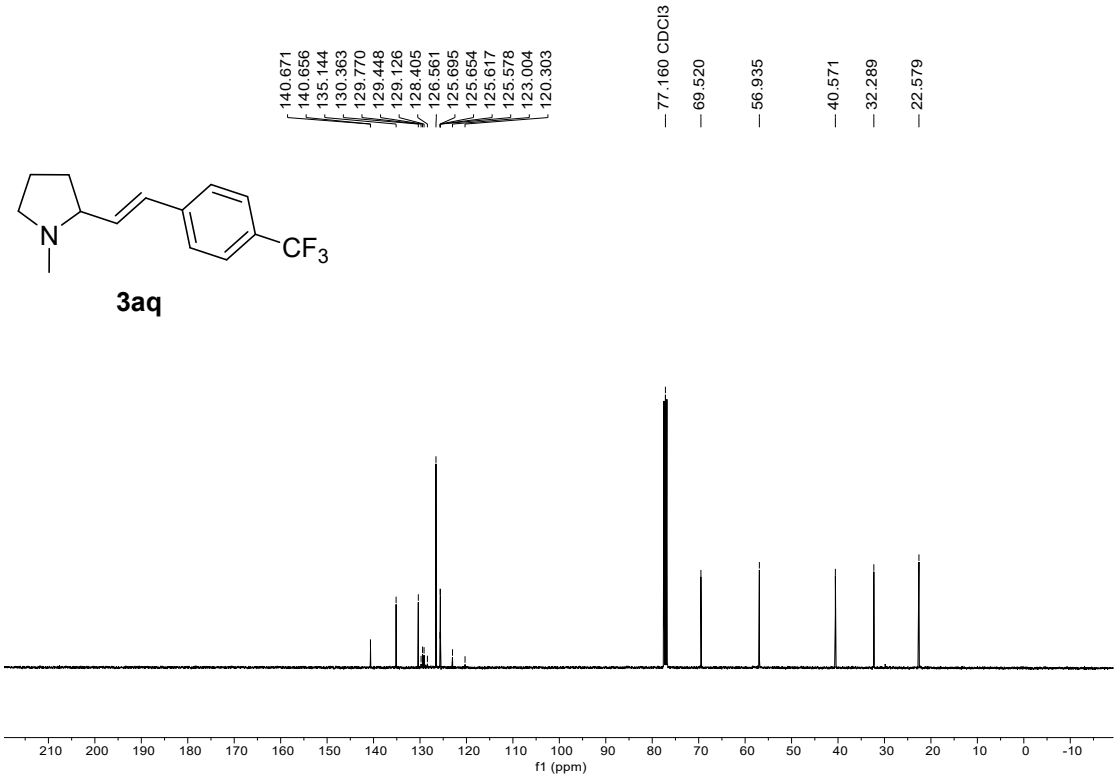

2.01
2.01
0.98
0.93
3.02
0.96
1.30
2.84
1.05
0.96
1.27
1.88
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.225
131.588
129.882
129.408
127.621
114.095
77.160 CDCl3
70.005
56.742
55.430
40.330
32.261
22.369
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

N
OMe

3ap


7.567
7.546
7.479
7.459
7.549
6.510
6.235
6.215
6.196
6.175
3.179
3.174
3.160
3.155
3.150
3.137
3.131
2.739
2.718
2.698
2.678
2.306
2.273
2.250
2.229
2.206
2.058
2.050
2.045
2.039
2.032
2.026
2.020
2.015
1.996
1.918
1.911
1.908
1.903
1.898
1.892
1.883
1.880
1.812
1.797
1.795
1.791
1.788
1.781
1.774
1.768
1.766
1.760
1.746
1.742
1.740
1.726
1.720
1.718
N
CF3
3aq
1.97
2.00
1.02
1.00
1.02
1.02
2.93
1.03
1.05
1.08
2.08
f1 (ppm)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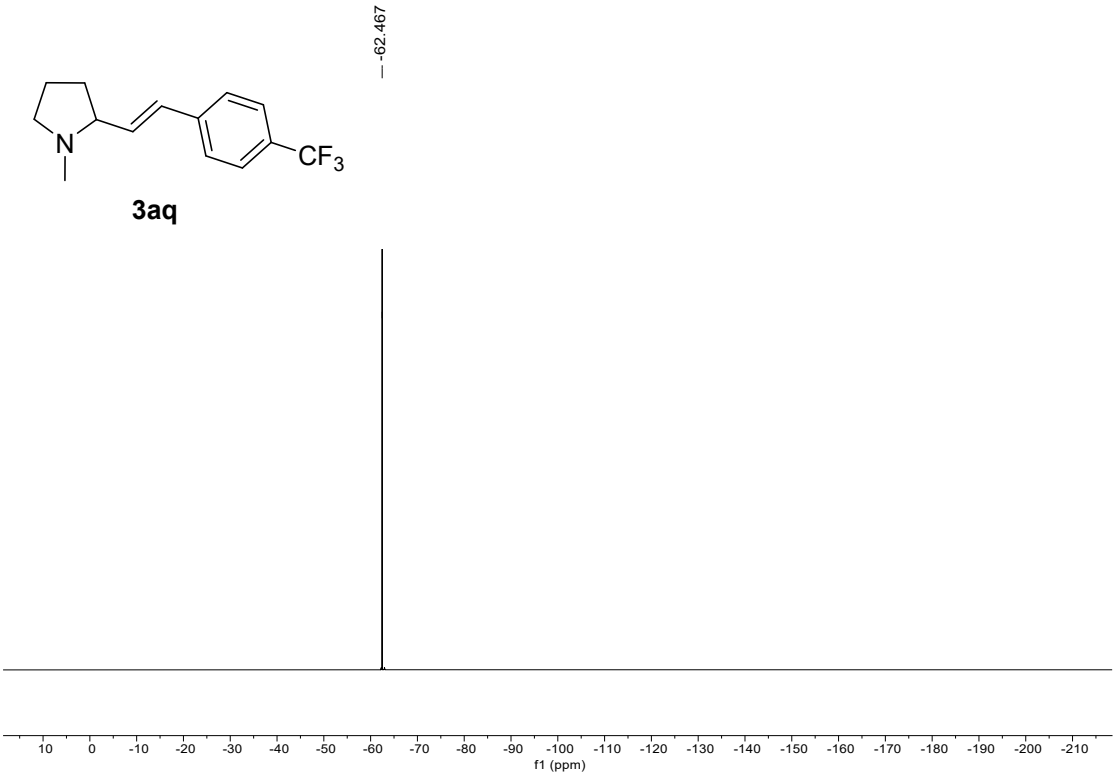
140.656
135.144
130.363
129.770
129.448
129.126
128.405
126.561
125.695
125.654
125.617
125.578
123.004
120.303
77.160 CDCl3
69.520
56.935
40.571
32.289
22.579
N
CF3
3aq
f1 (ppm)



5. References

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