CuBr-Catalyzed Reaction of *N*,*N*-Dimethylanilines and Silyl Enol Ethers: An Alternative Route to β-Amino Ketones

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Supporting Information

Content

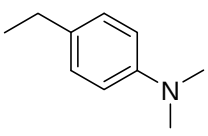
General: All reactions were carried out in air in oven-dried flask. CH_3CN were distilled from Na using benzophenone as the indicator. *N,N*-Dimethylaniline compounds **2d**, **2e**, **2g**, and **2j** were prepared by known methods (ref. 1). [1] Silyl Enol Ether compounds **1c**, **1d**, **1g** were prepared according to the method of reference 2, [2] **1a**, **1f** were prepared by the method of reference 3. [3] Other materials were purchased from common commercial sources and used without additional purification. The gas chromatography analysis was performed on a GC instrument. ^{1}H NMR spectra were recorded at 400 MHz using TMS as internal standard. ^{13}C NMR spectra were recorded at 100 MHz using TMS as internal standard. Mass spectroscopy data were collected on an HRMS-EI instrument.

Preparation and Characterization of Starting Materials:

Method A: The preparation of *N,N*-Dimethylaniline (2d, 2e, 2j, and 2g).[1]

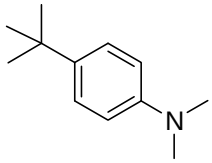
A mixture of trimethyl phosphate 8.4 g (60 mmol) and aniline (40 mmol) was stirring at 110 °C for 2 hr and then cooled to room temperature. The solution was neutralized with 25 mL NaOH (20%) and stirred at 110 °C for another 12 hr. After the reaction, water was added to dissolve the resulted Na_3PO_4 and the organic layer was collected. The aqueous phase was extracted with diethyl ether (3×50 mL). The combined organic phase was dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure afforded the crude *N,N*-Dimethylanilines, which was further purified on a silica gel column.

4-ethyl-*N,N*-dimethylbenzenamine (Compound **2d**)



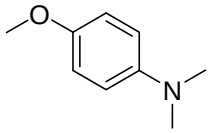
A red oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (d, J = 7.6 Hz, 2 H), 6.86 (d, J = 6.8 Hz, 2 H), 3.04 (s, 6 H), 2.73 (q, J = 7.1 Hz, 2 H), 1.37 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 132.4, 128.2, 113.0, 40.8, 27.7, 15.8.

4-*tert*-butyl-*N*,*N*-di- methylbenzenamine (Compound **2e**)



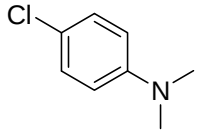
A red oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36 (dd, *J* = 8.8, 2.4 Hz, 2 H), 6.80 (dd, *J* = 9.2, 2.8 Hz, 2 H), 2.99 (d, *J* = 2.8 Hz, 6 H), 1.38 (d, *J* = 2.4 Hz, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.2, 125.6, 112.5, 40.6, 33.5, 31.3.

4-methoxy-*N*,*N*-dimethylbenzenamine (Compound **2j**)



A light yellow solid after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.85 (d, *J* = 9.2 Hz, 2 H), 6.76 (d, *J* = 9.2 Hz, 2 H), 3.77 (s, 3 H), 2.87 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 145.5, 114.7, 114.4, 55.5, 41.6.

4-chloro-*N*,*N*-dimethylbenzenamine (Compound **2g**)



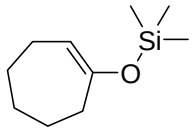
A yellow solide after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.20 (d, *J* = 9.6 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 2.94 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 128.5, 121.1, 113.4, 40.3.

Method B: The preparation of Silyl Enol Ether (1c, 1d and 1g).[2]

Triethylamine 16.6 mL (120 mmol) and chlorotrimethylsilane 15.2 mL (120 mmol) was added in a solution of ketone (100 mmol), pre-dried sodium iodide 18.0 g (120 mmol), and 100 mL dried CH_3CN. The reaction mixture was stirred for 12 hr and subsequently treated with prechilled (~0 °C) hexane (100 mL) and saturated aqueous ammonium chloride (100 mL). The organic phase was

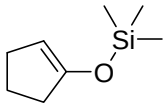
collected and the aqueous phase was extracted with hexane (2×50 mL). The combined organic phase was washed with ice-water (2×50 mL) as well as saturated ammonium chloride (100 mL), and then dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure afforded the crude enol silyl ether, which was further purified by fractional distillation under reduced pressure.

Cycloheptenyloxytrimethylsilane (Compound **1c**)



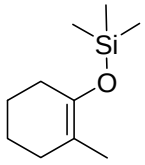
A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.94 (t, *J* = 6.6 Hz, 1 H), 2.16 (t, *J* = 5.8 Hz, 2 H), 1.92 (q, *J* = 5.7 Hz, 2 H), 1.52-1.43 (m, 6 H), 0.10 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 108.2, 35.2, 31.2, 27.5, 25.0, 24.9, -0.14.

Cyclopentenyloxytrimethylsilane (Compound **1d**)



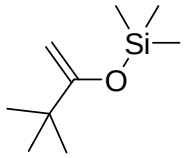
A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.59 (t, *J* = 1.6 Hz, 1 H), 2.27-2.20 (m, 4 H), 1.83 (qui, *J* = 7.4 Hz, 2 H), 0.18 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 101.7, 33.2, 28.4, 21.0, -0.34.

Trimethyl(2-methylcyclohex-1-enyloxy)silane (Compound **1g**)



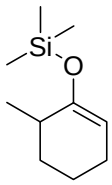
A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ1.99-1.94 (m, 2 H), 1.91-1.88 (m, 2 H), 1.62-1.56 (m, 2 H), 1.52-1.46 (m, 5 H), 0.12 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 111.4, 30.0, 29.8, 23.5, 22.7, 16.0, 0.32.

Method C: The preparation of (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (1a):[3]



3,3-Dimethylbutan-2-one (27.9 mL, 0.223 mol) was added in a solution of DMF (75 mL), chlorotrimethylsilane (34.0 mL, 0.268 mol), and 1,4-diazabicyclo[2.2.2] octane (39.2 g, 0.35 mol). The resulted mixture was refluxed with stirring for 24 hr and then cooled to room temperature. After the filtration, the filtrate was diluted with 150 mL of hexane, and washed with cold aqueous $NaHCO_3$ (3×100 mL). The aqueous phase was extracted by hexane. The organic layer was combined with the hexane extract and washed rapidly in succession with portions of cold aqueous 1.5 *M* HCl and cold aqueous $NaHCO_3$. The resulting organic phase was dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure afforded the crude enol silyl ether as a light yellow oil, which was further purified by fractional distillation under reduced pressure. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.08 (d, *J* = 0.8 Hz, 1 H), 3.92 (d, *J* = 1.2 Hz, 1 H), 1.04 (s, 9 H), 0.2 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 85.4, 36.1, 27.7, -0.2.

Method D: The preparation of trimethyl(6-methylcyclohex-1-enyloxy)silane (1f):[3]



2-Methylcyclohexanone 12.2 mL **(**100 mmol) in 50 mL of l,2-dimethoxyethane was added in a solution of lithium diiiopropylamide 50 mL **(**2 M) dropwise and with stirring over a 10-min period until the red color of the triphenylmethide indicator was almost completely discharged at -5 ^{o}C. Meanwhile a quenching solution, prepared from 50 mL of l,2-dimethoxyethane, 5.0 mL (36 mmol) of triethylamine, and 20 ml (157 mmol) of chlorotrimethylsilane was centrifuged to remove any of the insoluble triethylamine hydrochloride. This chlorotrimethylsilane solution was added, rapidly and with stirring, to a cold (0 ^{o}C) solution of the lithium enolate. After the addition was complete, a white solid (LiCl) began to separate after 15 sec. The resulting mixture was stirred at room temperature for 2 hr and then partitioned between hexane and cold aqueous $NaHCO_3$. The organic

layer was dried over anhydrous magnesium sulfate and concentrated to leave the crude silyl ether as a light yellow oil, which was further purified by fractional distillation under reduced pressure. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.77 (dt, *J* = 4.0, 0.8 Hz, 1 H), 2.14-2.08 (m, 1 H), 2.00-1.95 (m, 2 H), 1.80-1.73 (m, 1 H), 1.62-1.52 (m, 1 H), 1.48-1.30 (m, 2 H), 1.00 (d, *J* = 7.2 Hz, 3 H), 0.16 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 103.1, 33.3, 31.3, 24.0, 20.0, 18.3, -0.02.

A typical procedure for the product

Method E: A typical procedure for the preparation of β-arylamino ketones: To a mixture of *N*,*N*-dimethylanilines (1.5 mmol), CuBr (4 mg, 0.025 mmol), silyl enol ethers (0.5 mmol) and CH_3CN (5 mL), *tert*-butyl hydroperoxide (0.10 mL, 5-6 M in decane) was added dropwise at room temperature. The resulting mixture was stirred at 50 ^{o}C for 12 hr. After the reaction, the mixture was filtered through a pad of cellite, and the solvent was removed under reduced pressure. The residue was purified on a silica gel column to afford the desired product.

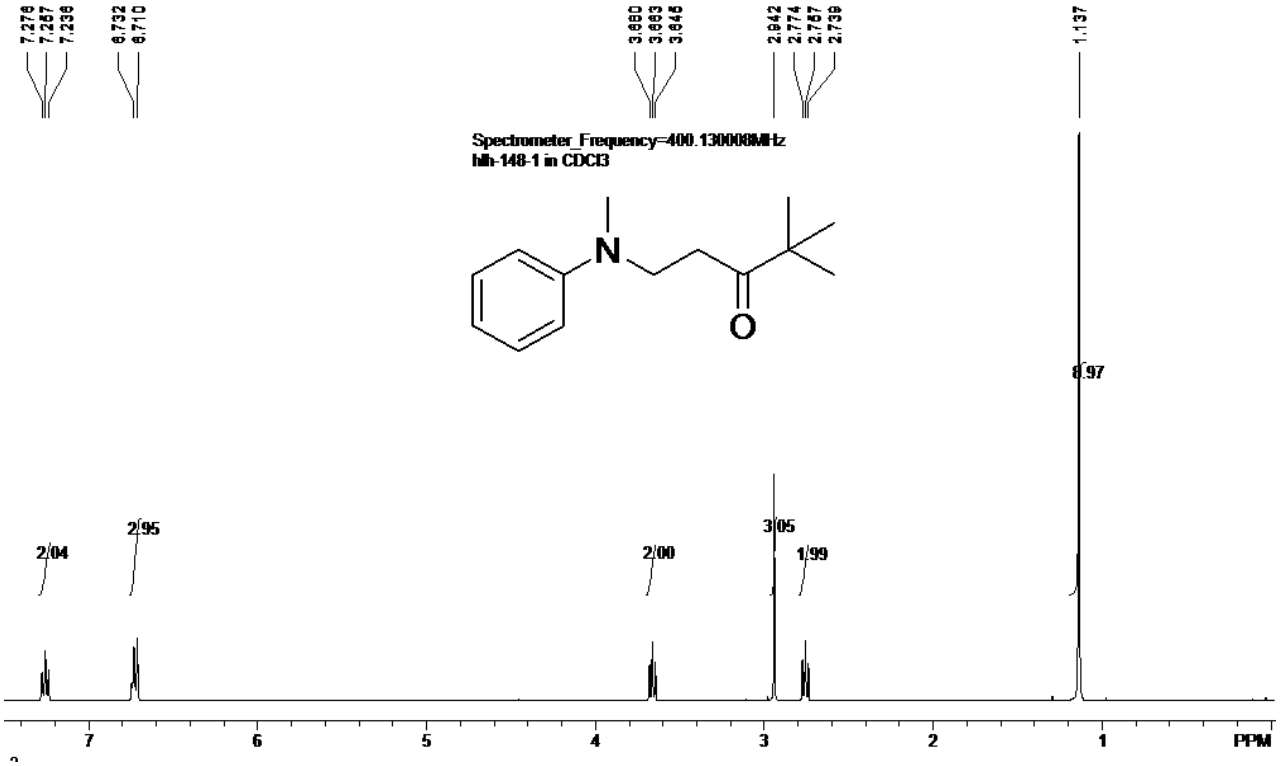
Method F: A typical procedure for the preparation of hexahydrofuro[3,2-c]quinoline: To a mixture of *N*,*N*-dimethylbenzenamine (2.0 mmol), CuBr (7 mg, 0.05 mmol), 2,3-dihydrofuran (70 mg, 1.0 mmol) and CH_3CN (2.5 mL), *tert*-butyl hydroperoxide (0.20 mL, 5-6 M in decane) was added dropwise at room temperature. The resulting mixture was stirred at 50 ^{o}C for 12 hr. After the reaction, the mixture was filtered through a pad of cellite, and the solvent was removed under reduced pressure. The residue was purified on a silica gel column to afford the desired product.

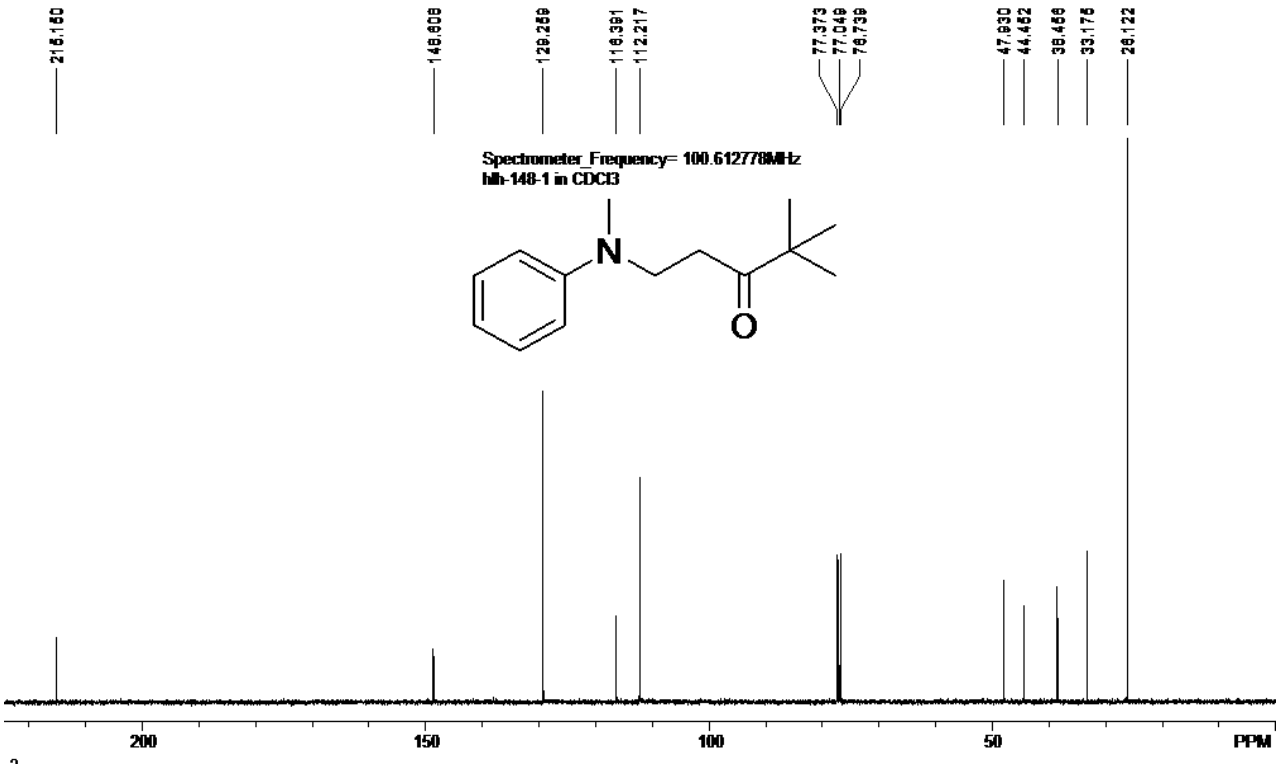
Characterization data of the product

Compound **3a** (4,4-dimethyl-1-(methyl(phenyl)amino)pentan-3-one, new compound)

Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 82 mg (75% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.26 (t, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 3 H), 3.66 (t, *J* = 7.0 Hz, 2 H), 2.94 (s, 3 H), 2.76 (t, *J* = 7.0 Hz, 2 H), 1.14 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.2, 148.6, 129.3, 116.4, 112.2, 47.9, 44.5, 38.5, 33.2, 26.1. HRMS (EI) Calcd for $C_{14}H_{21}NO$: $[M]^+$ 219.1623; Found, 219.1626.

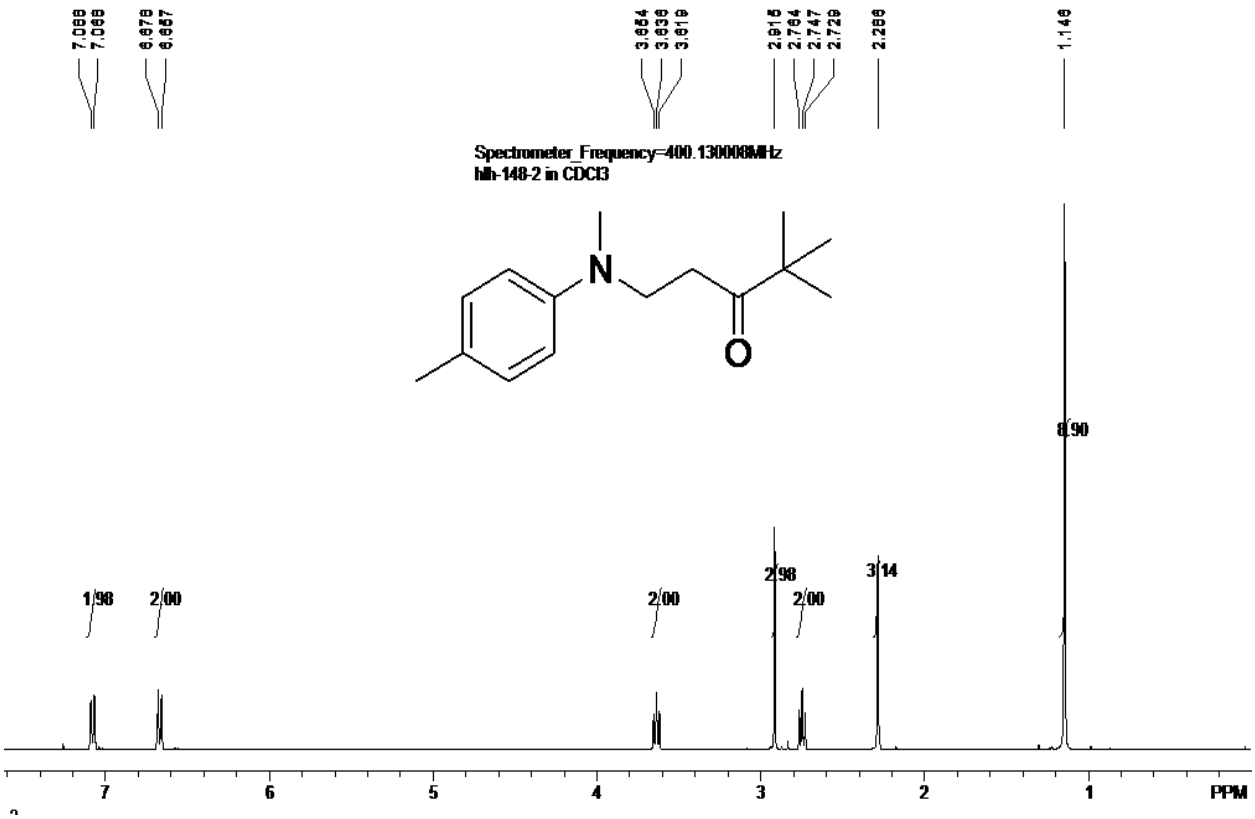




Compound **3b** (4,4-dimethyl-1-(methyl(p-tolyl)amino)pentan-3-one, new compound)

Following the typical procedure **E** using *N*,*N*,4-trimethylbenzenamine (203 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 100 mg (86% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.08 (d, *J* = 8.0 Hz, 2 H), 6.67 (d, *J* = 8.4 Hz, 2 H), 3.64 (t, *J* = 7.0 Hz, 2 H), 2.92 (s, 3 H), 2.75 (t, *J* = 7.0 Hz, 2 H), 2.29 (s, 3 H), 1.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.2, 146.7, 129.8, 125.7, 112.7, 48.3, 44.5, 38.6, 33.0, 26.1, 20.2. HRMS (EI) Calcd for $C_{15}H_{23}NO$: $[M]^+$ 233.1780; Found, 233.1781.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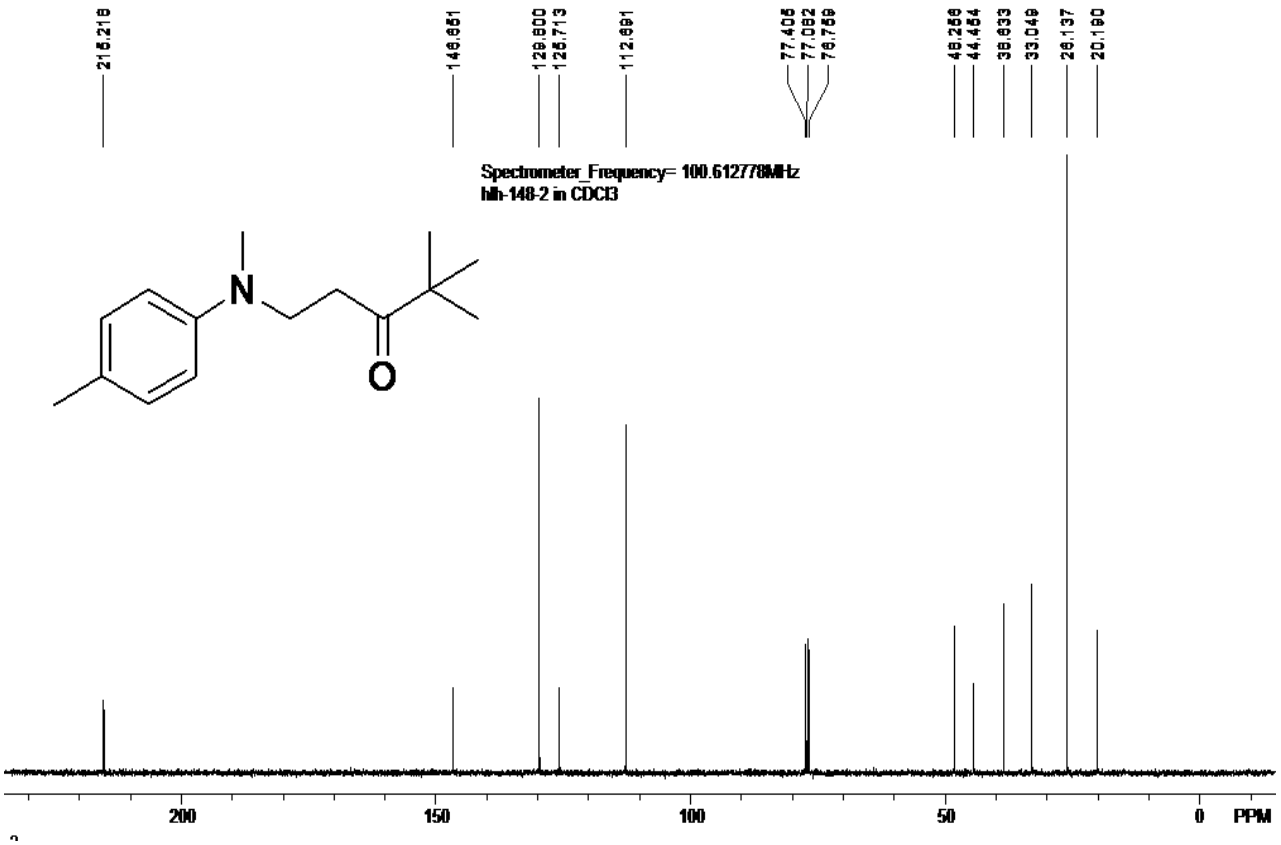
7
6
5
4
3
2
1
PPM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O
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50
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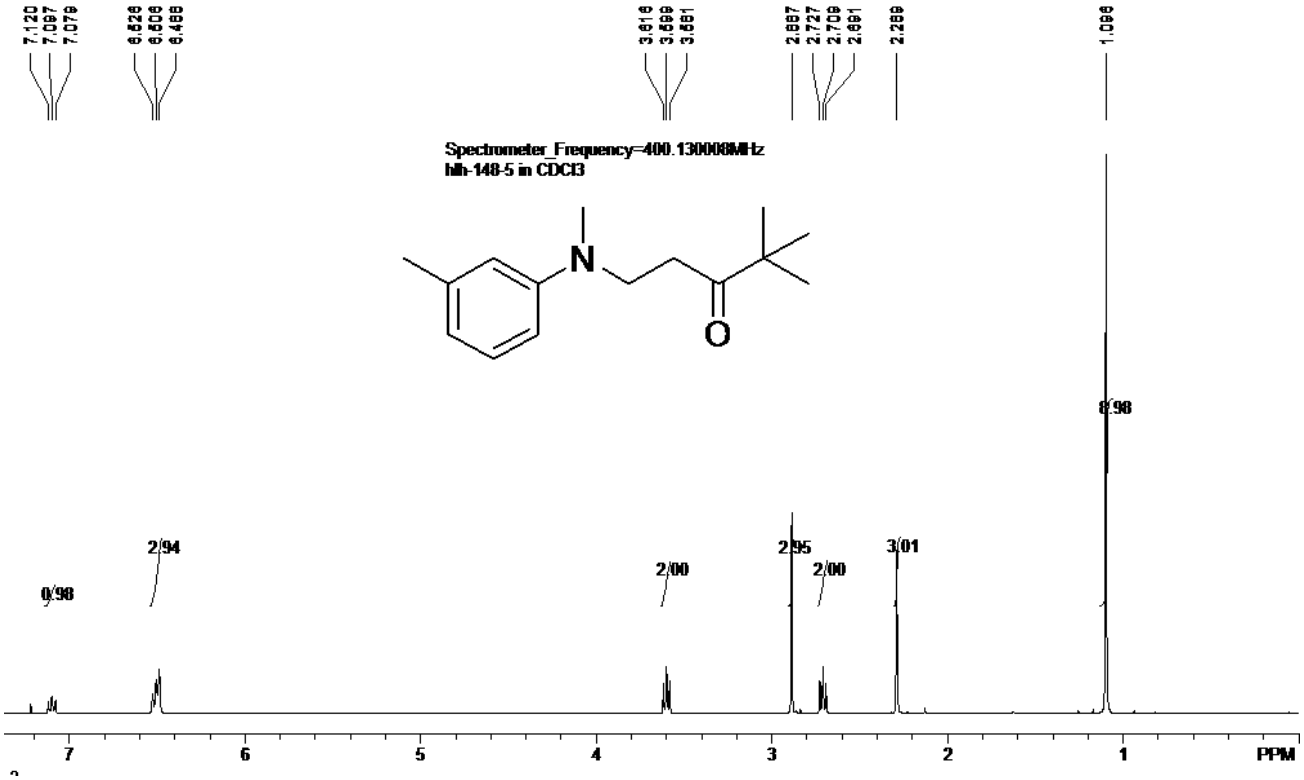
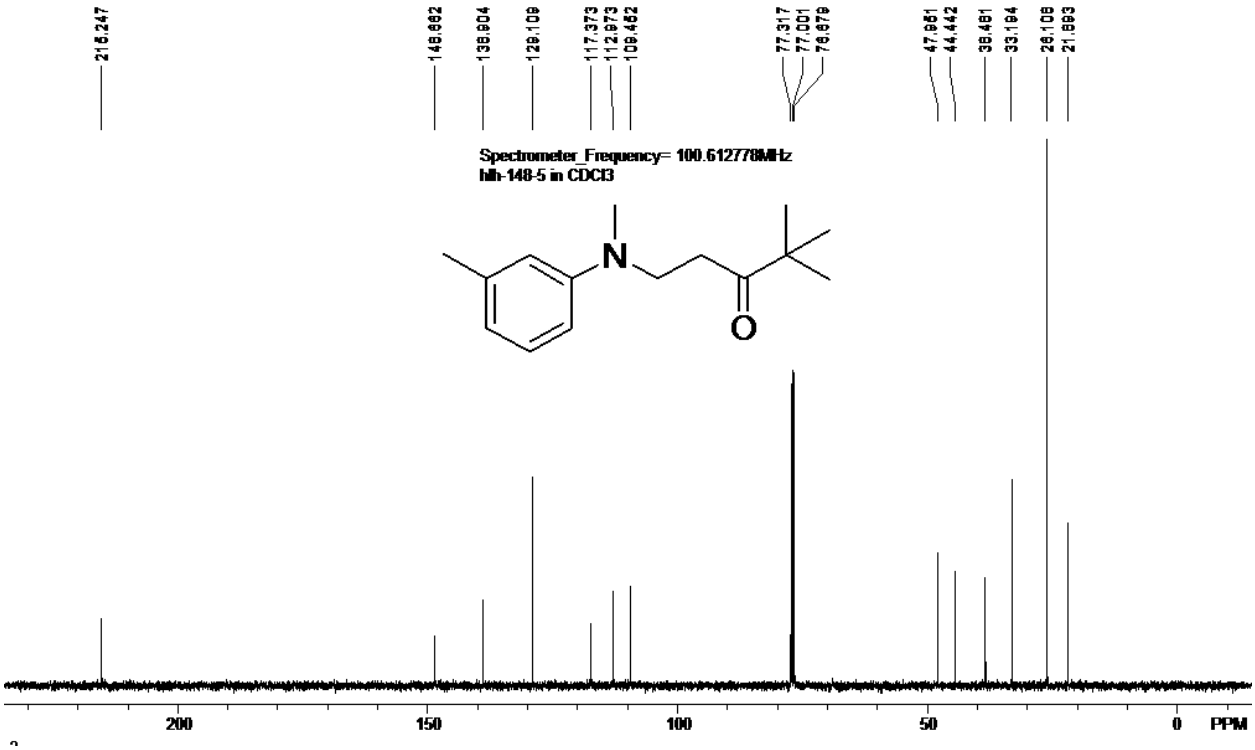
PPM

Compound **3c** (4,4-dimethyl-1-(methyl(m-tolyl)amino)pentan-3-one, new compound)

Following the typical procedure **E** using *N*,*N*,3-trimethylbenzenamine (203 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 70 mg (60% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.10 (t, *J* = 8.2 Hz, 1 H), 6.53-6.49 (m, 3 H), 3.60 (t, *J* = 7.0 Hz, 2 H), 2.89 (s, 3 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.10 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.2, 148.7, 138.9, 129.1, 117.4, 113.0, 109.5, 48.0, 44.4, 38.5, 33.2, 26.1, 21.9. HRMS (EI) Calcd for $C_{15}H_{23}NO$: $[M]^+$ 233.1780; Found, 233.1774.

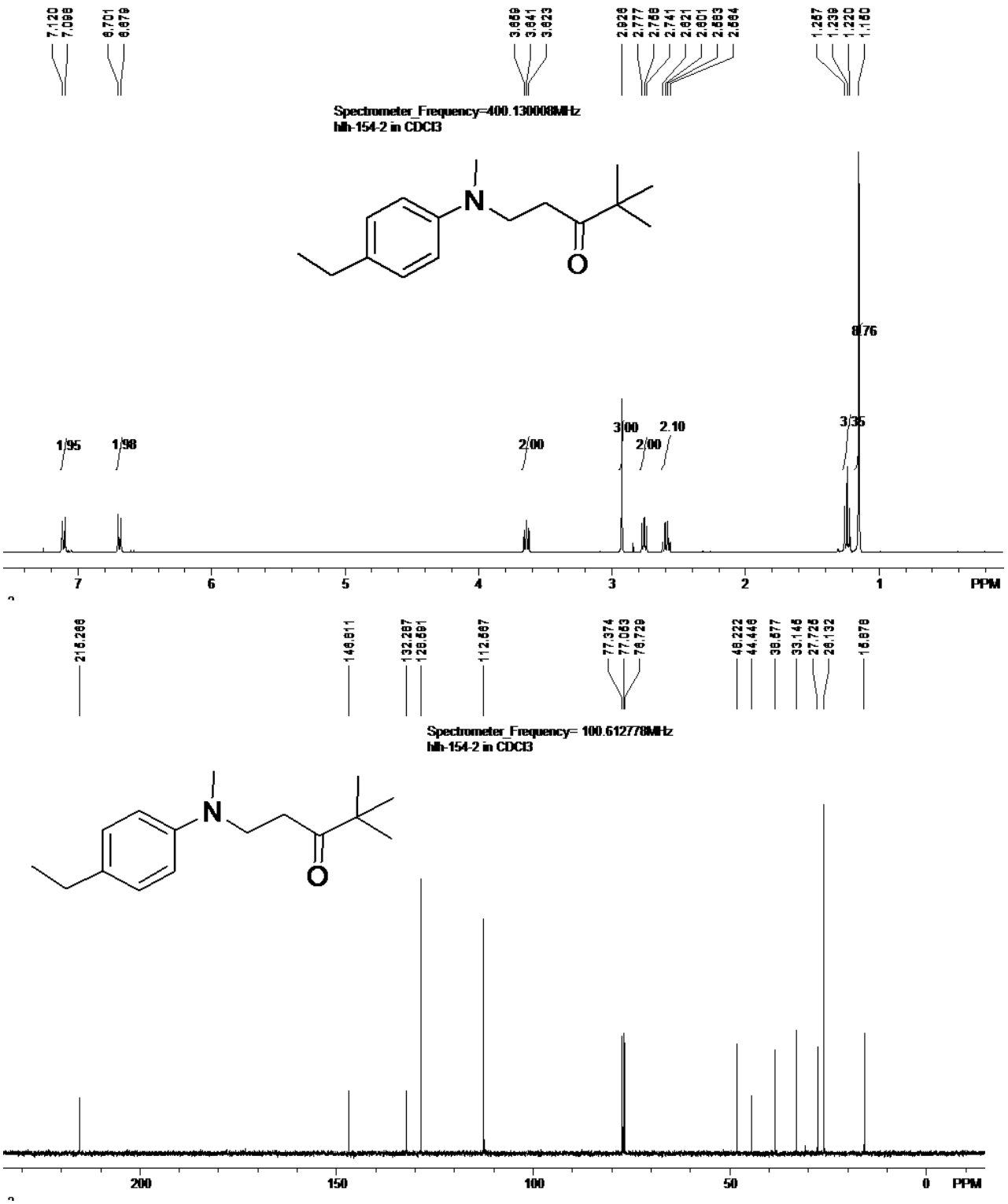




Compound **3d** (1-((4-ethylphenyl)(methyl)amino)-4,4-dimethylpentan-3-one, new compound)

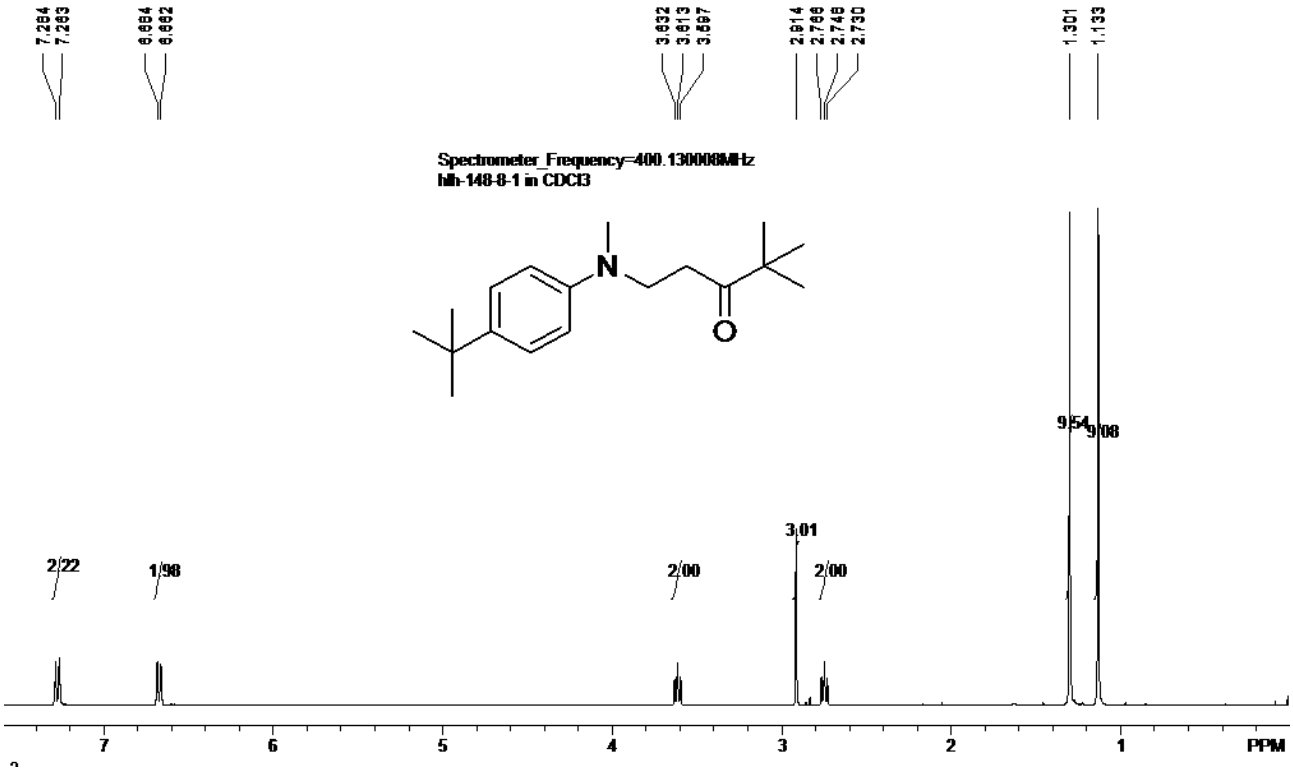
Following the typical procedure **E** using 4-ethyl-*N*,*N*-dimethylbenzenamine (223 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 101 mg (82% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

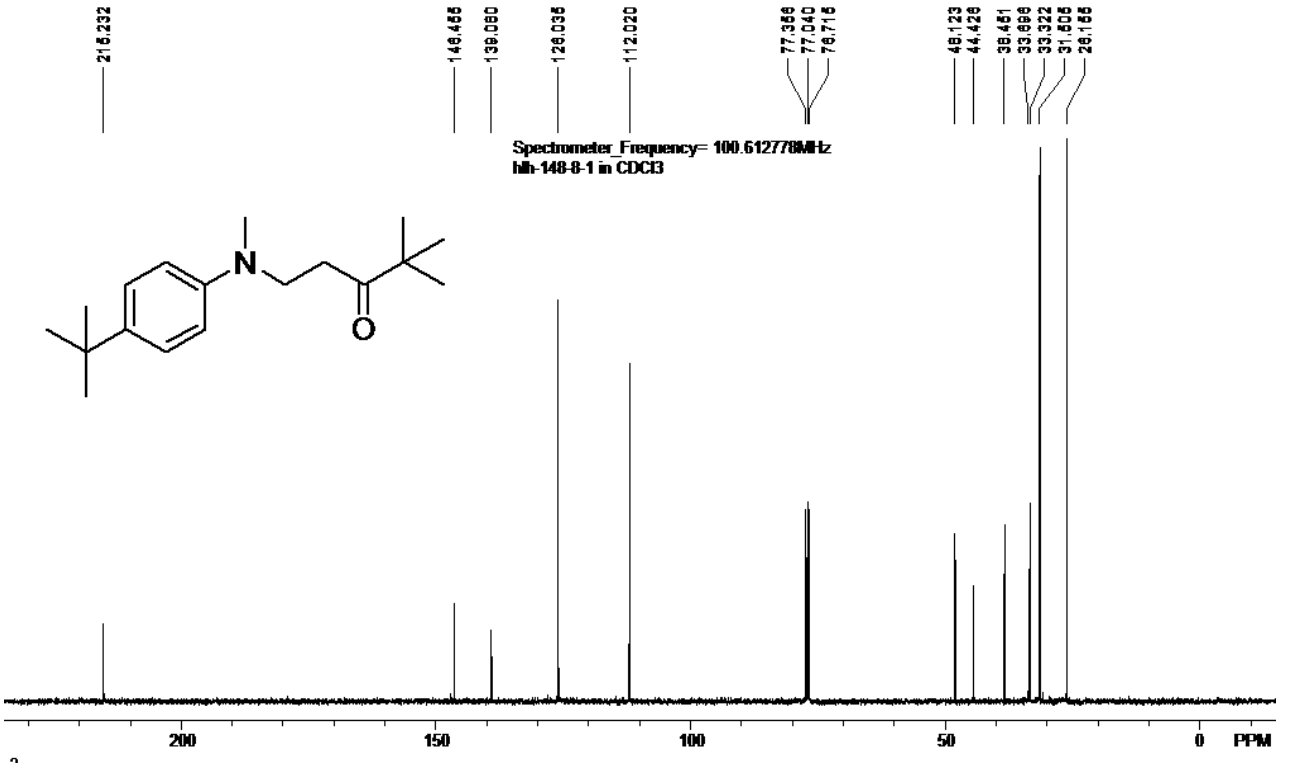
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.11 (d, *J* = 8.8 Hz, 2 H), 6.69 (d, *J* = 8.8 Hz, 2 H), 3.64 (t, *J* = 7.2 Hz, 2 H), 2.93 (s, 3 H), 2.76 (t, *J* = 7.2 Hz, 2 H), 2.59 (q, *J* = 7.6 Hz, 2 H), 1.24 (t, *J* = 7.4 Hz, 3 H), 1.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 146.8, 132.3, 128.6, 112.6, 48.2, 44.4, 38.6, 33.1, 27.7, 26.1, 15.9. HRMS (EI) Calcd for $C_{16}H_{25}NO$: $[M]^+$ 247.1936; Found, 247.1930.



Compound **3e** 1-((4-tert-butylphenyl)(methyl)amino)-4,4-dimethylpentan-3-one, new compound) Following the typical procedure **E** using 4-tert-butyl-*N*,*N*-dimethylbenzenamine (266 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 117 mg (85% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.27 (d, *J* = 8.4 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 3.61 (t, *J* = 7.0 Hz, 2 H), 2.91 (s, 3 H), 2.75 (t, *J* = 7.2 Hz, 2 H), 1.30 (s, 9 H), 1.13 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.2, 146.5, 139.1, 126.0, 112.0, 48.1, 44.4, 38.5, 33.7, 33.3, 31.5, 26.2. HRMS (EI) Calcd for $C_{18}H_{29}NO$: $[M]^+$ 275.2249; Found, 275.2247.

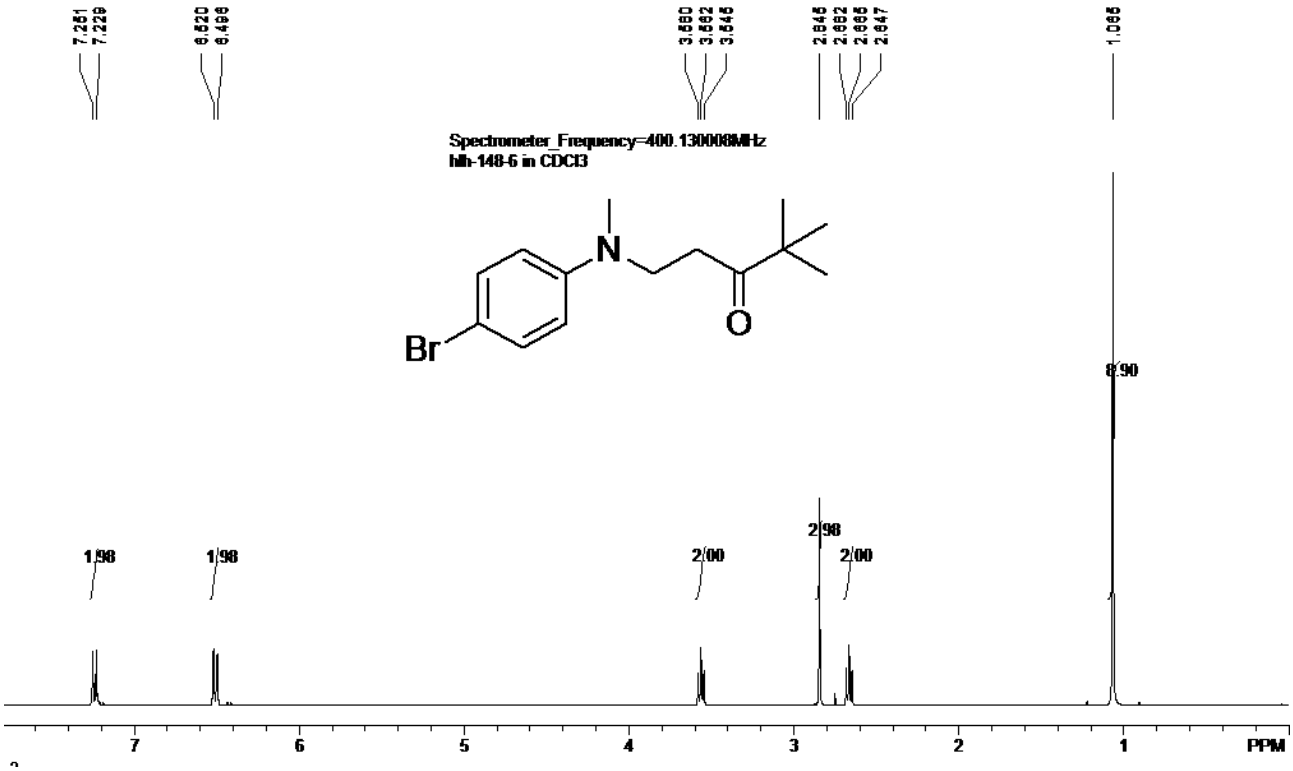


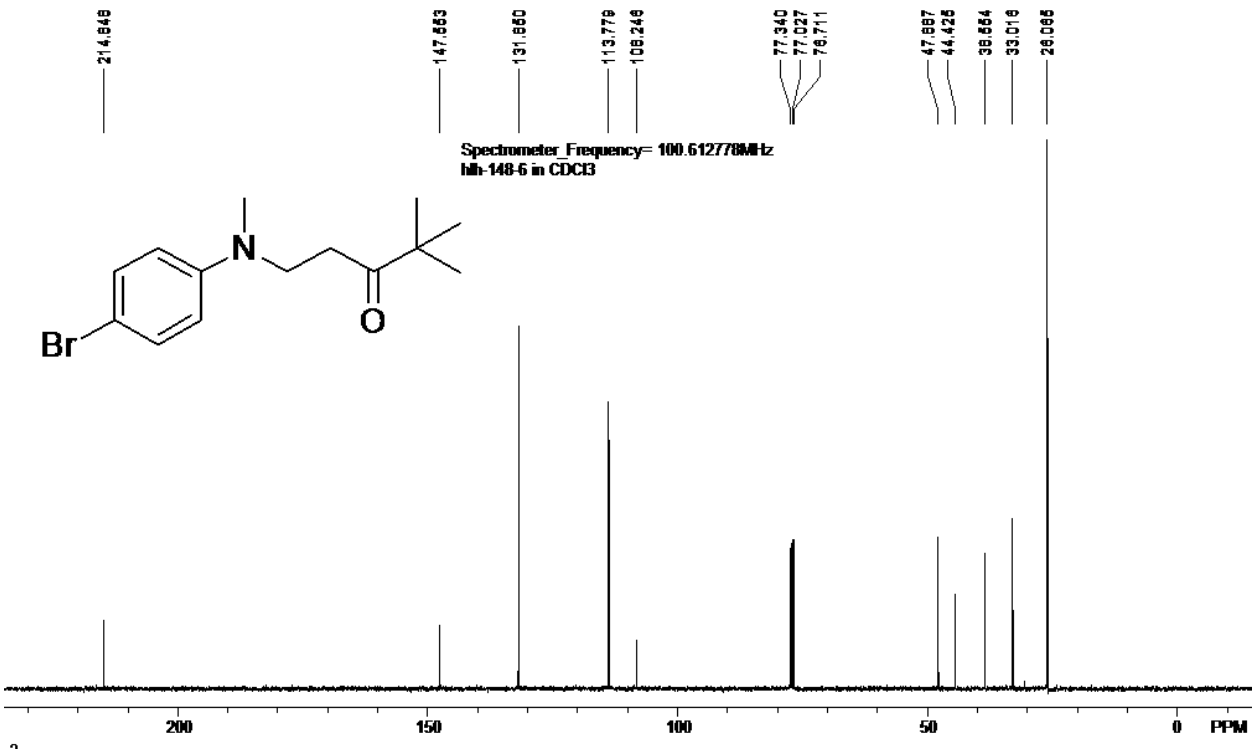


Compound **3f** 1-((4-bromophenyl)(methyl)amino)-4,4-dimethylpentan-3-one, new compound)

Following the typical procedure **E** using 4-bromo-*N*,*N*-dimethylbenzenamine (300 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 95 mg (64% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (d, *J* = 8.8 Hz, 2 H), 6.51 (d, *J* = 9.6 Hz, 2 H), 3.56 (t, *J* = 7.0 Hz, 2 H), 2.85 (s, 3 H), 2.66 (t, *J* = 7.0 Hz, 2 H), 1.07 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.8, 147.6, 131.9, 113.8, 108.2, 47.9, 44.4, 38.6, 33.0, 26.1. HRMS (EI) Calcd for $C_{14}H_{20}BrNO$: $[M]^+$ 297.0728; Found, 297.0721.

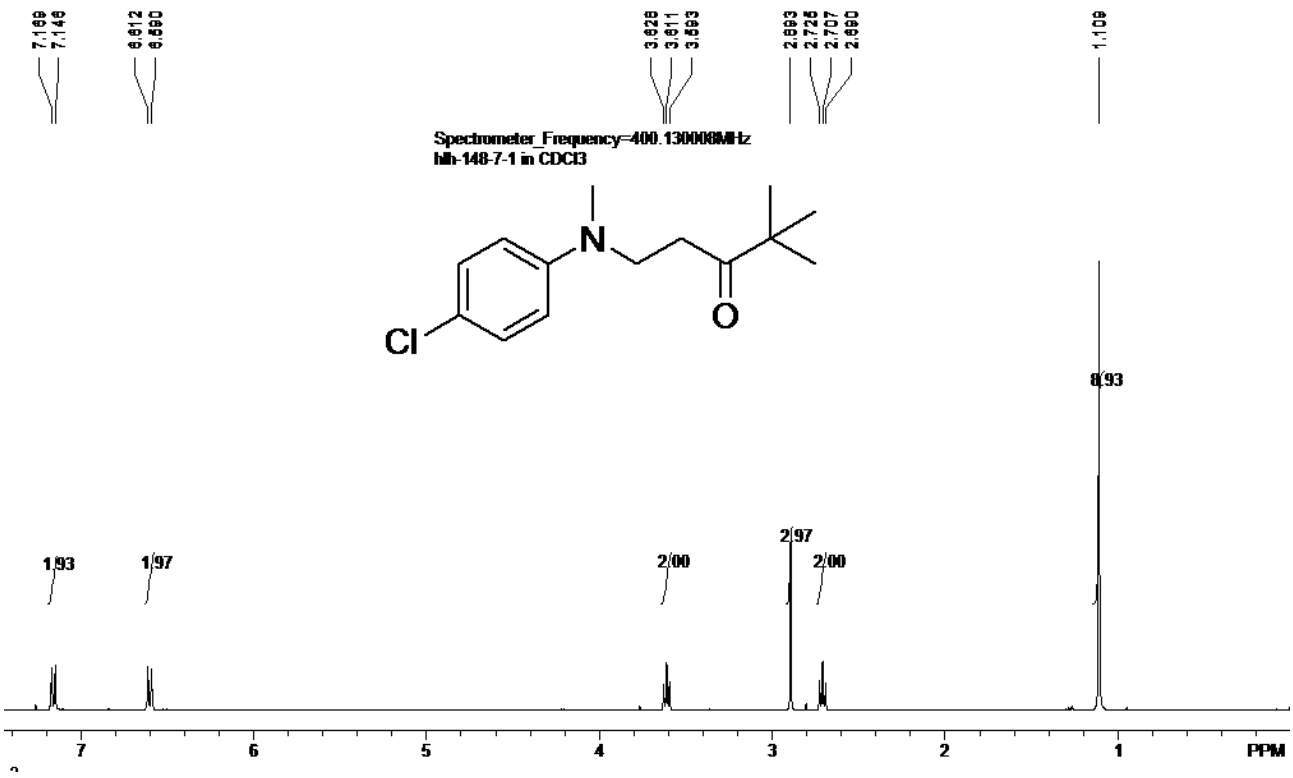


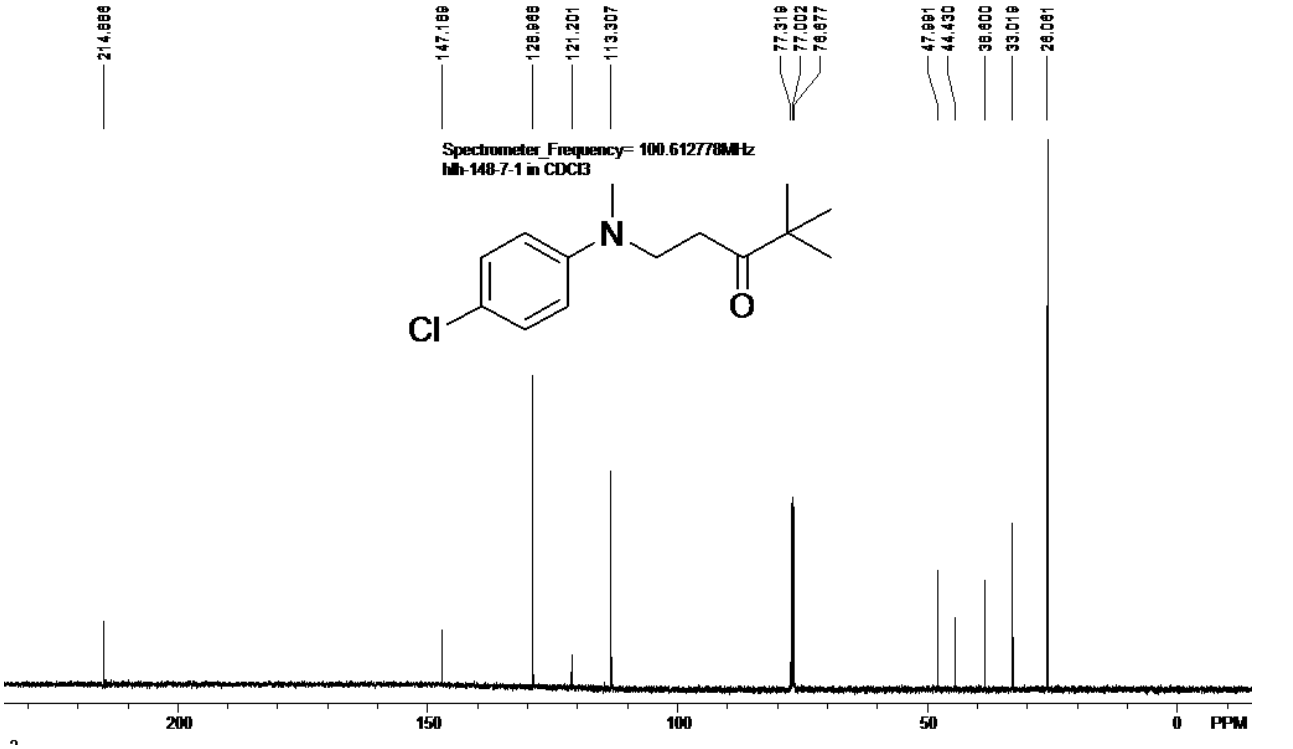


Compound **3g** (1-((4-chlorophenyl)(methyl)amino)-4,4-dimethylpentan-3-one, new compound)

Following the typical procedure **E** using 4-chloro-*N*,*N*-dimethylbenzenamine (234 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 95 mg (75% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.16 (d, J = 9.2 Hz, 2 H), 6.60 (d, J = 8.8 Hz, 2 H), 3.61 (t, J = 7.0 Hz, 2 H), 2.89 (s, 3 H), 2.71 (t, J = 7.0 Hz, 2 H), 1.11 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.9, 147.2, 129.0, 121.2, 113.3, 48.0, 44.4, 38.6, 33.0, 26.1. HRMS (EI) Calcd for $C_{14}H_{20}ClNO$: $[M]^+$ 253.1233; Found, 253.1228.

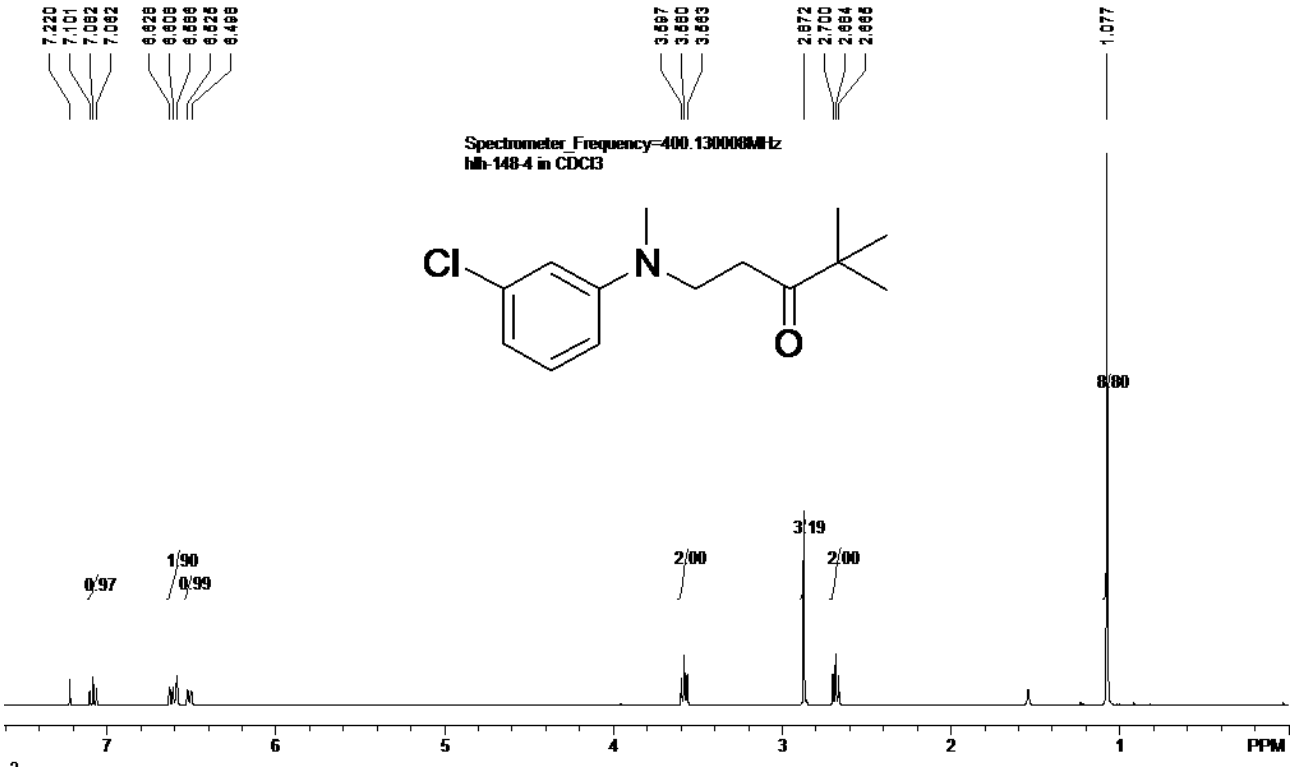


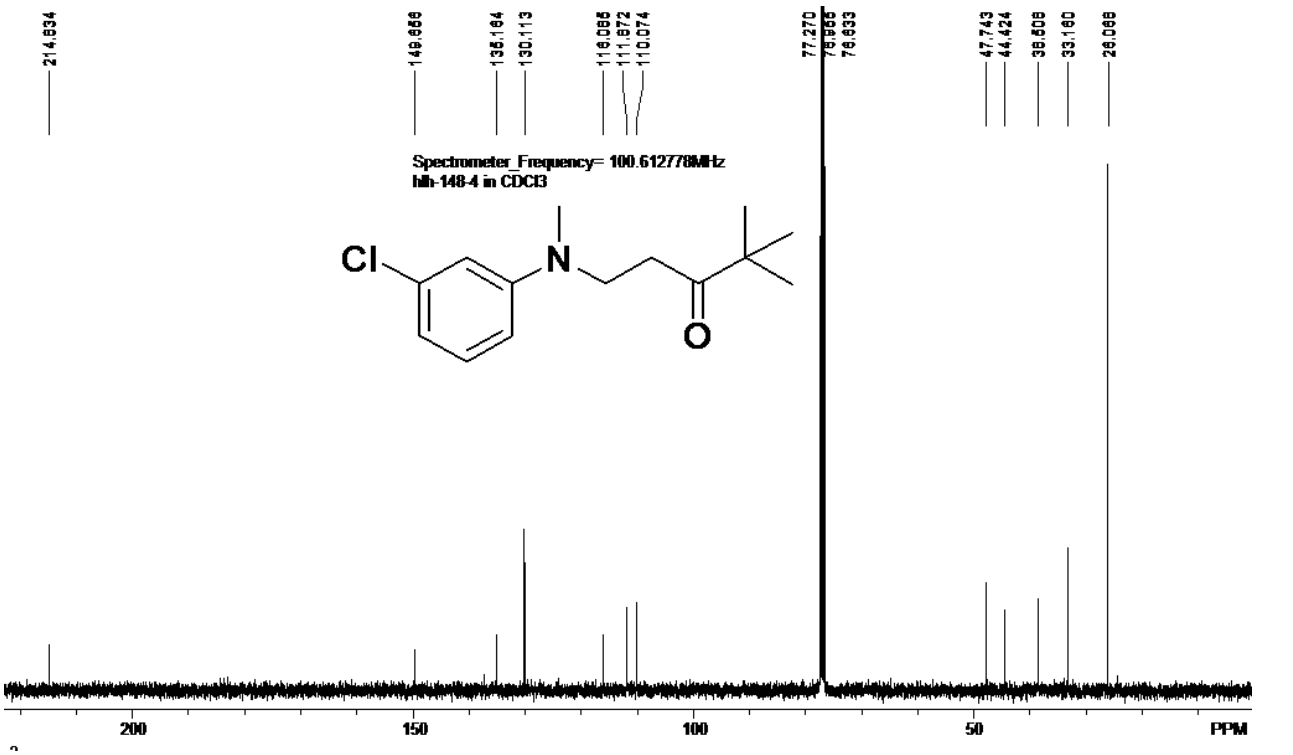


Compound **3h** 1-((3-chlorophenyl)(methyl)amino)-4,4-dimethylpentan-3-one, new compound)

Following the typical procedure **E** using 3-chloro-*N*,*N*-dimethylbenzenamine (234 mg, 1.5 mmol), (3,3-dimethylbut-1-en-2-yloxy)trimethylsilane (86 mg, 0.5 mmol) provided 76 mg (60% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/80).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.08 (t, *J* = 7.8 Hz, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 6.59 (s, 1 H),6.51 (d, *J* = 10.8 Hz, 1 H), 3.58 (t, *J* = 6.8 Hz, 2 H), 2.87 (s, 3 H), 2.68 (t, *J* = 7.0 Hz, 2 H), 1.08 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.8, 149.7, 135.2, 130.1, 116.1, 111.9, 110.1, 47.7, 44.4, 38.5, 33.2, 26.1. HRMS (EI) Calcd for $C_{14}H_{20}ClNO$: $[M]^+$ 253.1233; Found, 253.1231.

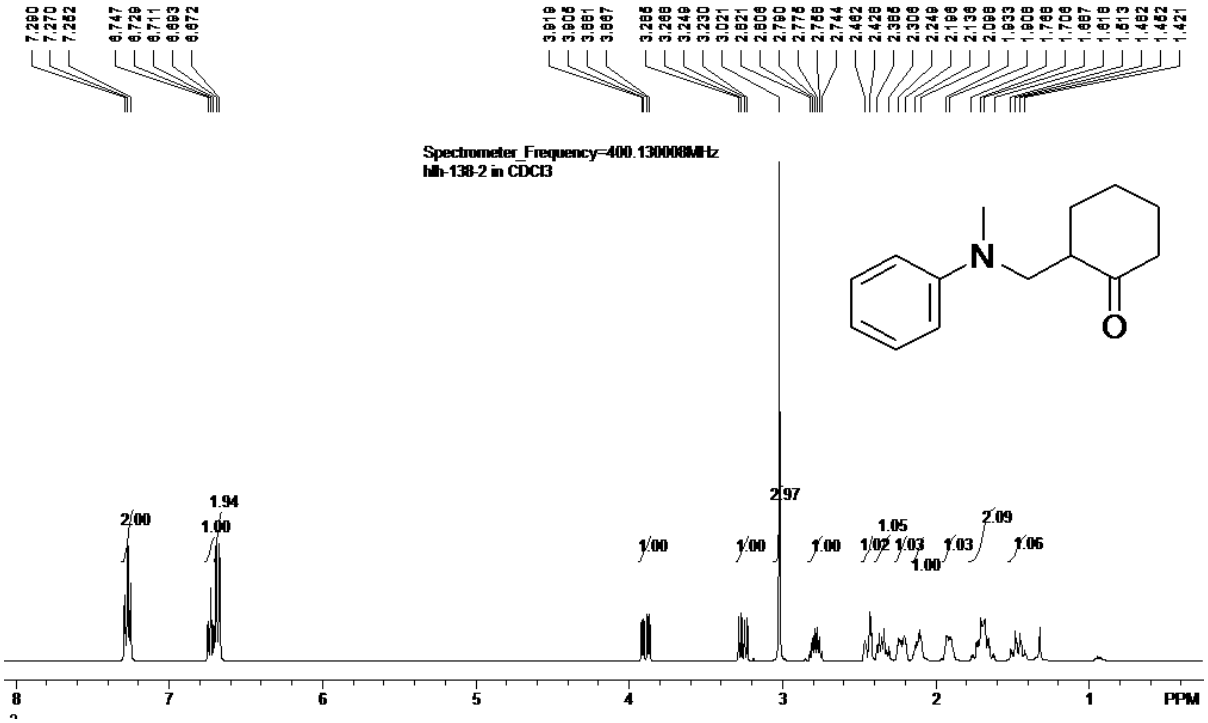


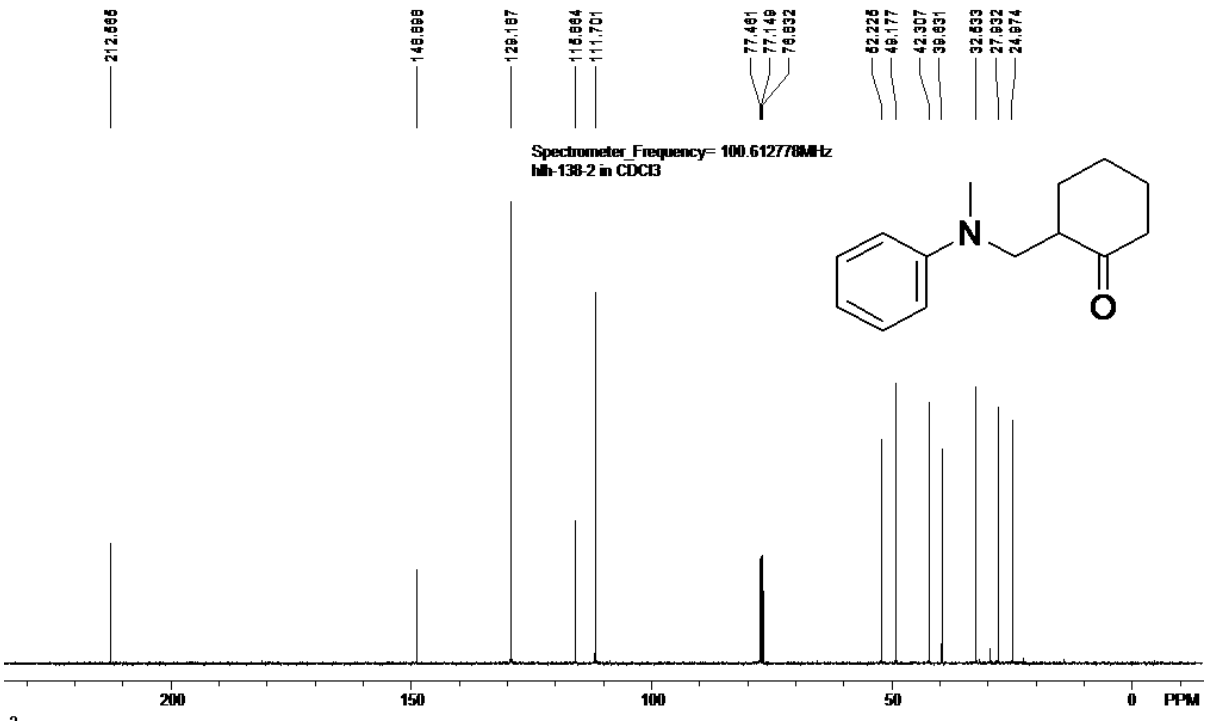


Compound **3i** (2-((methyl(phenyl)amino)methyl)cyclohexanone)[4]

Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 76 mg (70% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.27 (t, *J* = 7.6 Hz, 2 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 3.89 (dd, *J* = 15.2, 5.6 Hz, 1 H), 3.26 (dd, *J* = 14.4, 6.8 Hz, 1 H), 3.02 (s, 3 H), 2.78 (sxt, *J* = 6.2 Hz, 1 H), 2.46-2.43 (m, 1 H), 2.39-2.31 (m, 1 H), 2.25-2.20 (m, 1 H), 2.14-2.10 (m, 1 H), 1.93-1.91 (m, 1 H), 1.77-1.62 (m, 2 H), 1.51-1.42 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 148.9, 129.2, 115.9, 111.7, 52.2, 49.2, 42.3, 39.6, 32.5, 27.9, 25.0.

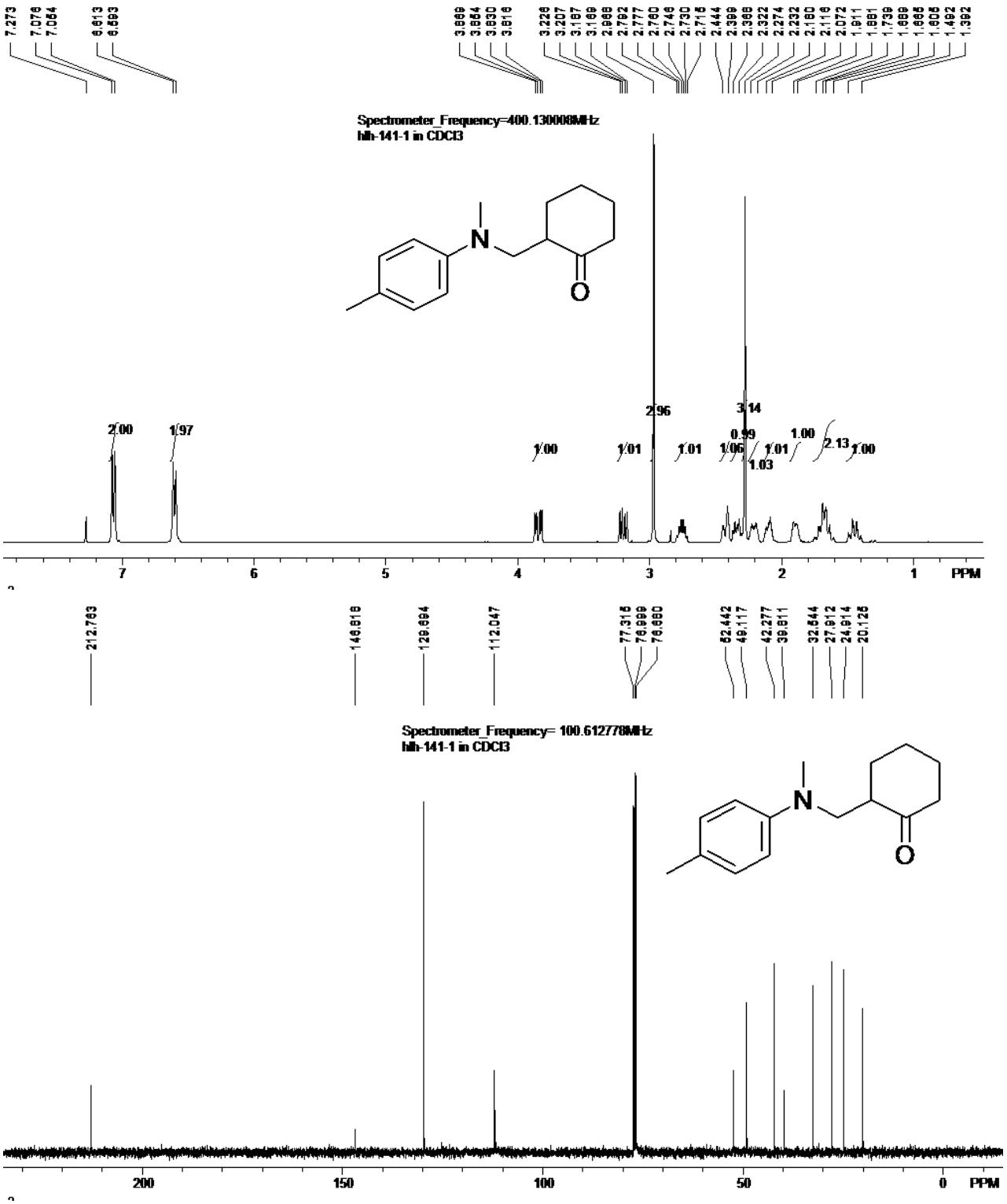




Compound **3j** (2-((methyl(p-tolyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using *N*,*N*,4-trimethylbenzenamine (203 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 67 mg (58% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.07 (d, *J* = 8.8 Hz, 2 H), 6.60 (d, *J* = 8.0 Hz, 2 H), 3.84 (dd, *J* = 15.6, 6.0 Hz, 1 H), 3.20 (dd, *J* = 15.6, 7.6 Hz, 1 H), 2.97 (s, 3 H), 2.75 (sxt, *J* = 6.2 Hz, 1 H), 2.44-2.40 (m, 1 H), 2.37-2.32 (m, 1 H), 2.27 (s, 3 H), 2.23-2.18 (m, 1 H), 2.12-2.07 (m, 1 H), 1.91-1.89 (m, 1 H), 1.74-1.61 (m, 2 H), 1.49-1.39 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.8, 146.8, 129.7, 112.0, 52.4, 49.1, 42.3, 39.8, 32.5, 27.9, 24.9, 20.1. HRMS (EI) Calcd for $C_{15}H_{21}NO$: $[M]^+$ 231.1623; Found, 231.1620.



Compound **3k** (2-((methyl(m-tolyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using *N*,*N*,3-trimethylbenzenamine (203 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 67 mg (58% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

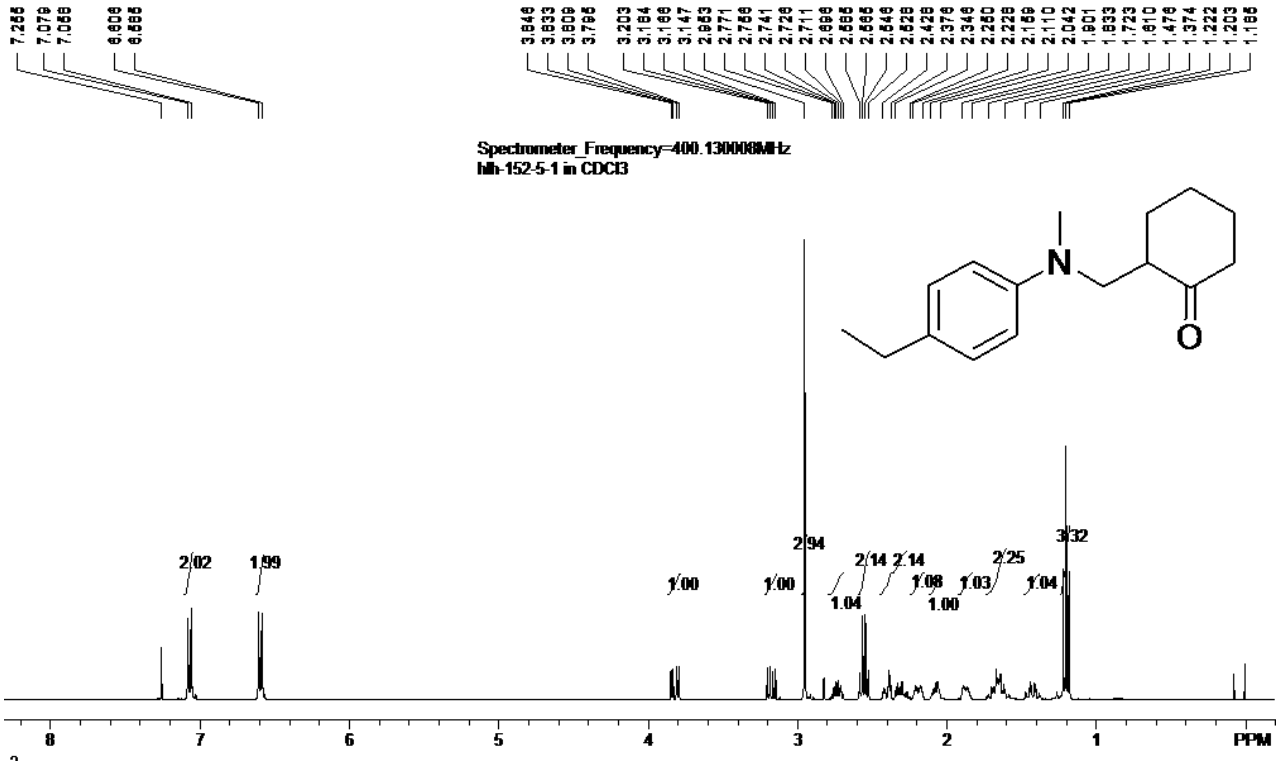
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.13 (t, *J* =8.0 Hz, 1 H), 6.53 (d, *J* = 7.2 Hz, 1 H), 6.47 (s, 2 H), 3.85 (dd, *J* = 14.8, 5.2 Hz, 1 H), 3.22 (dd, *J* = 15.2, 7.2 Hz, 1 H), 2.98 (s, 3 H), 2.75 (sxt, *J* = 6.2 Hz, 1 H), 2.44-2.40 (m, 1 H), 2.36-2.29 (m, 1 H), 2.32 (s, 3 H), 2.22-2.18 (m, 1 H), 2.11-2.08 (m, 1 H), 1.90-1.88 (m, 1 H), 1.74-1.60 (m, 2 H), 1.49-1.39 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 149.1, 138.9, 129.1, 116.9, 112.5, 109.0, 52.2, 49.3, 42.3, 39.7, 32.5, 27.9, 25.0, 22.0. HRMS (EI) Calcd for $C_{15}H_{21}NO$: $[M]^+$ 231.1623; Found, 231.1619.

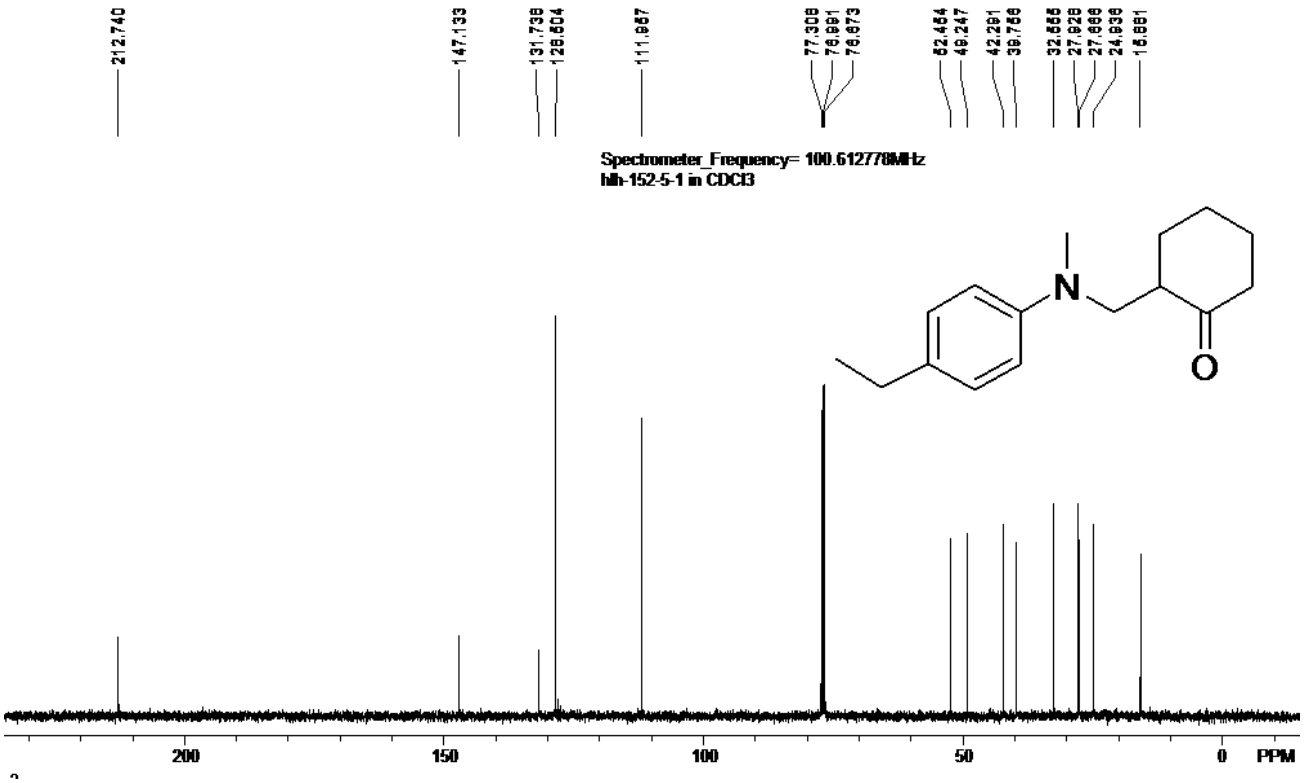
Compound **3m** (2-(((4-ethylphenyl)(methyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using 4-ethyl-*N*,*N*-dimethylbenzenamine (223 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 61 mg (50% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.07 (d, *J* = 8.4 Hz, 2 H), 6.60 (d, *J* = 8.4 Hz, 2 H), 3.82 (dd, *J* = 14.8, 5.2 Hz, 1 H), 3.18 (dd, *J* = 14.8, 7.6 Hz, 1 H), 2.95 (s, 3 H), 2.73 (sxt, *J* = 6.0 Hz, 1 H), 2.56 (q, *J* = 7.6 Hz, 2 H), 2.43-2.38 (m, 1 H), 2.35-2.25 (m, 1 H), 2.23-2.16 (m, 1 H), 2.11-2.04 (m, 1 H), 1.90-1.83 (m, 1 H), 1.72-1.61 (m, 2 H), 1.48-1.37 (m, 1 H), 1.20 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 147.1, 131.7, 128.5, 112.0, 52.5, 49.2, 42.3, 39.8, 32.6, 27.9, 27.7, 24.9, 15.9.

HRMS (EI) Calcd for $C_{16}H_{23}NO$: $[M]^+$ 245.1780; Found, 245.1776.

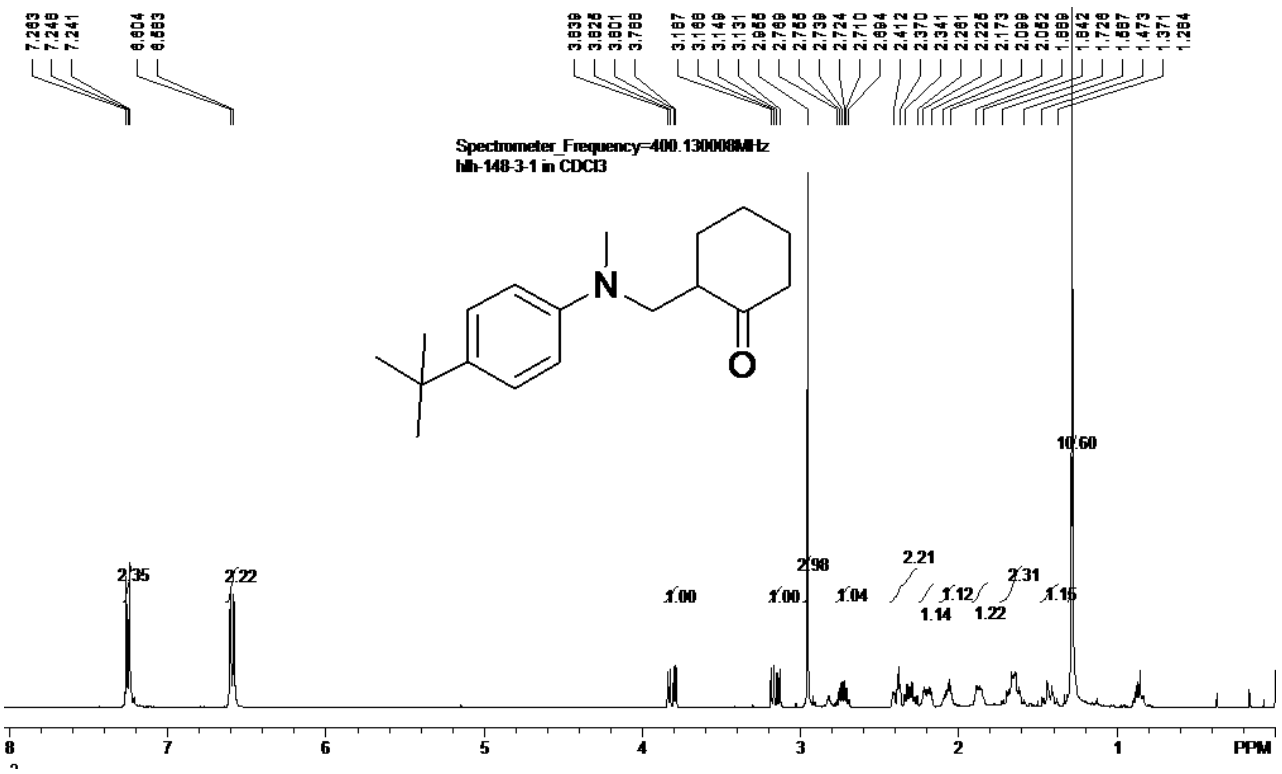




Compound **3n** (2-(((4-tert-butylphenyl)(methyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using 4-tert-butyl-*N*,*N*-dimethylbenzenamine (266 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 91 mg (67% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

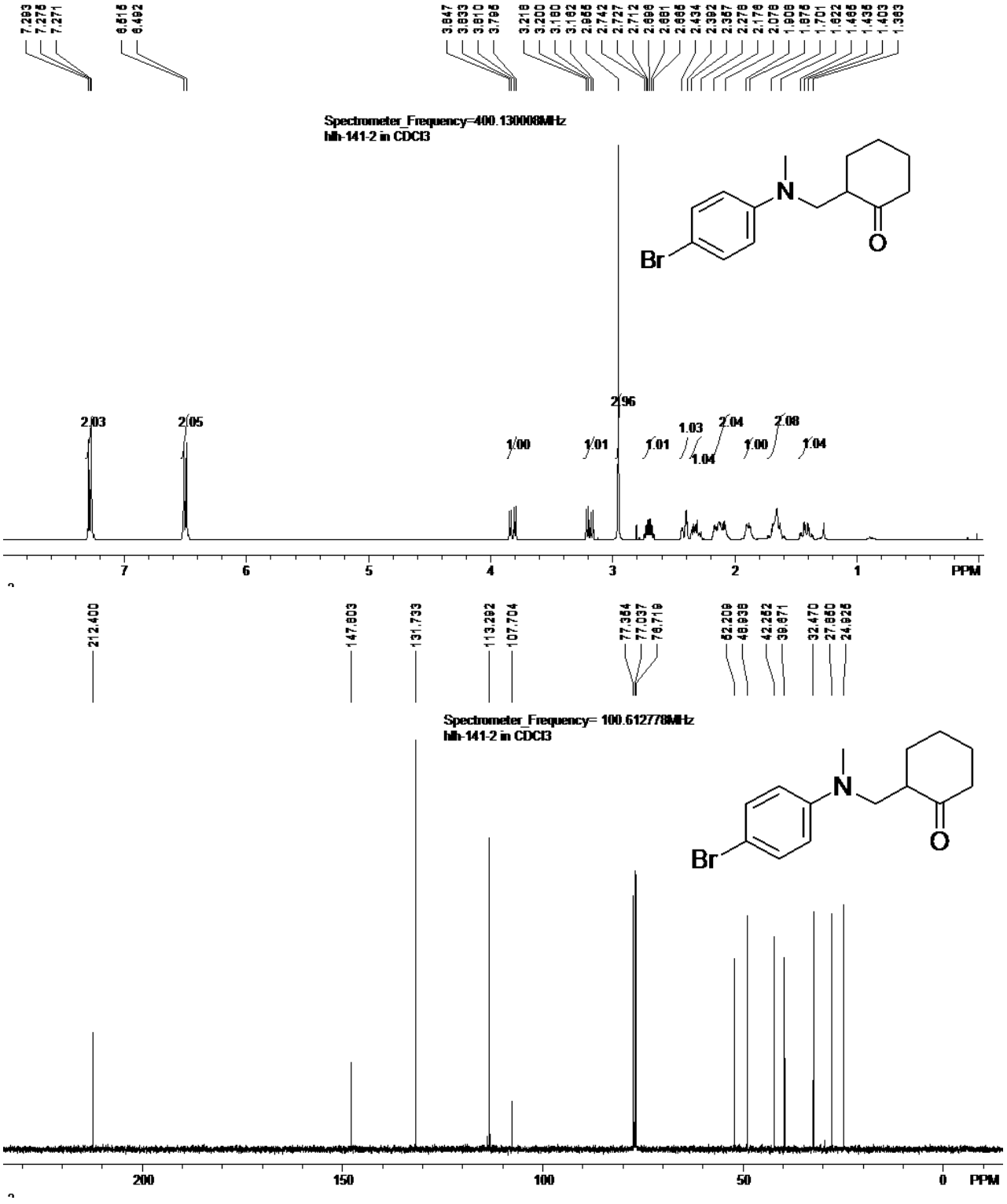
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.25 (d, *J* = 8.8 Hz, 2 H), 6.59 (d, *J* = 8.4 Hz, 2 H), 3.81 (dd, *J* = 15.2, 5.6 Hz, 1 H), 3.16 (dd, *J* = 15.2, 7.6 Hz, 1 H), 2.96 (s, 3 H), 2.73 (sxt, *J* = 6.0 Hz, 1 H), 2.41-2.37 (m, 1 H), 2.34-2.26 (m, 1 H), 2.23-2.17 (m, 1 H), 2.10-2.05 (m, 1 H), 1.90-1.84 (m, 1 H), 1.73-1.59 (m, 2 H), 1.47-1.37 (m, 1 H), 1.28 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 146.7, 138.6, 126.0, 111.4, 52.4, 49.3, 42.3, 39.7, 33.6, 32.6, 31.5, 27.9, 24.9. HRMS (EI) Calcd for $C_{18}H_{27}NO$: $[M]^+$ 273.2093; Found, 273.2101.



Compound **3o** (2-(((4-bromophenyl)(methyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using 4-bromo-*N*,*N*-dimethylbenzenamine (300 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 86 mg (58% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

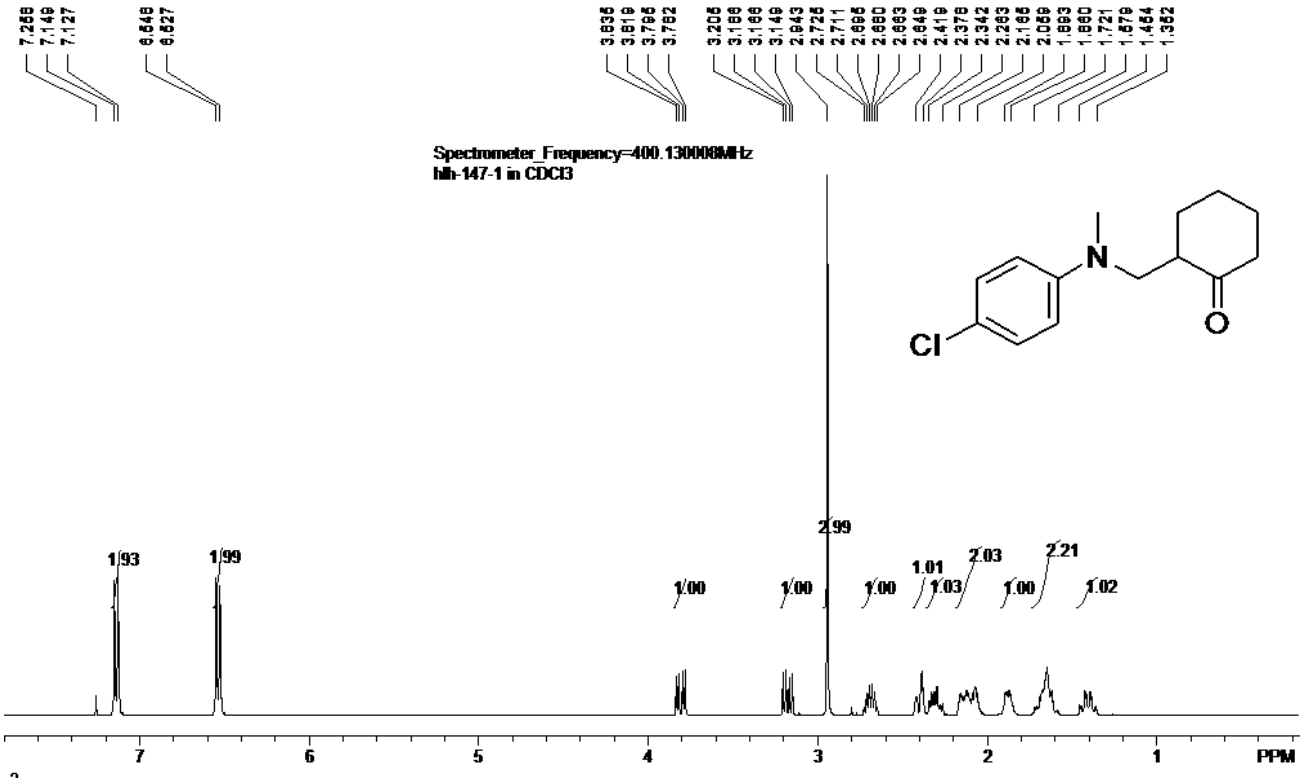
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.28 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 9.2 Hz, 2 H), 3.82 (dd, *J* = 14.8, 5.6 Hz, 1 H), 3.19 (dd, *J* = 15.2, 7.2 Hz, 1 H), 2.96 (s, 3 H), 2.70 (sxt, *J* = 6.2 Hz, 1 H), 2.43-2.39 (m, 1 H), 2.36-2.28 (m, 1 H), 2.18-2.08 (m, 2 H), 1.91-1.88 (m, 1 H), 1.70-1.62 (m, 2 H), 1.47-1.36 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 147.8, 131.7, 113.3, 107.7, 52.2, 48.9, 42.3, 39.7, 32.5, 27.9, 24.9. HRMS (EI) Calcd for $C_{14}H_{18}BrNO$: $[M]^+$ 295.0572; Found, 295.0565.

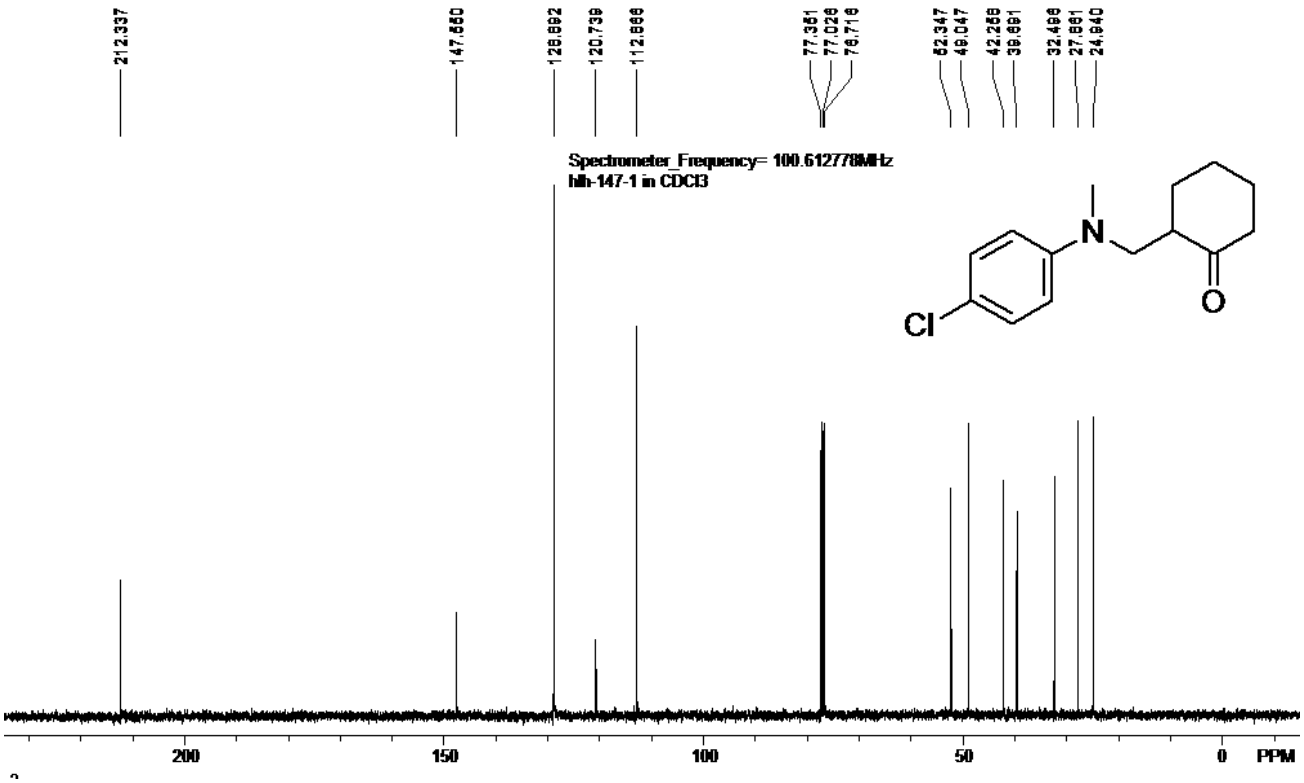


Compound **3p** (2-(((4-chlorophenyl)(methyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using 4-chloro-*N*,*N*-dimethylbenzenamine (234 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 75 mg (60% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.14 (d, *J* = 8.8 Hz, 2 H), 6.54 (d, *J* = 8.4 Hz, 2 H), 3.81 (dd, *J* = 14.8, 5.2 Hz, 1 H), 3.18 (dd, *J* = 14.8, 6.8 Hz, 1 H), 2.94 (s, 3 H), 2.69 (sxt, *J* = 6.0 Hz, 1 H), 2.42-2.38 (m, 1 H), 2.34-2.26 (m, 1 H), 2.17-2.06 (m, 2 H), 1.89-1.86 (m, 1 H), 1.72-1.58 (m, 2 H), 1.45-1.35 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 147.6, 128.9, 120.7, 112.9, 52.3, 49.0, 42.3, 39.7, 32.5, 27.9, 24.9. HRMS (EI) Calcd for $C_{14}H_{18}ClNO$: $[M]^+$ 251.1077; Found, 251.1075.

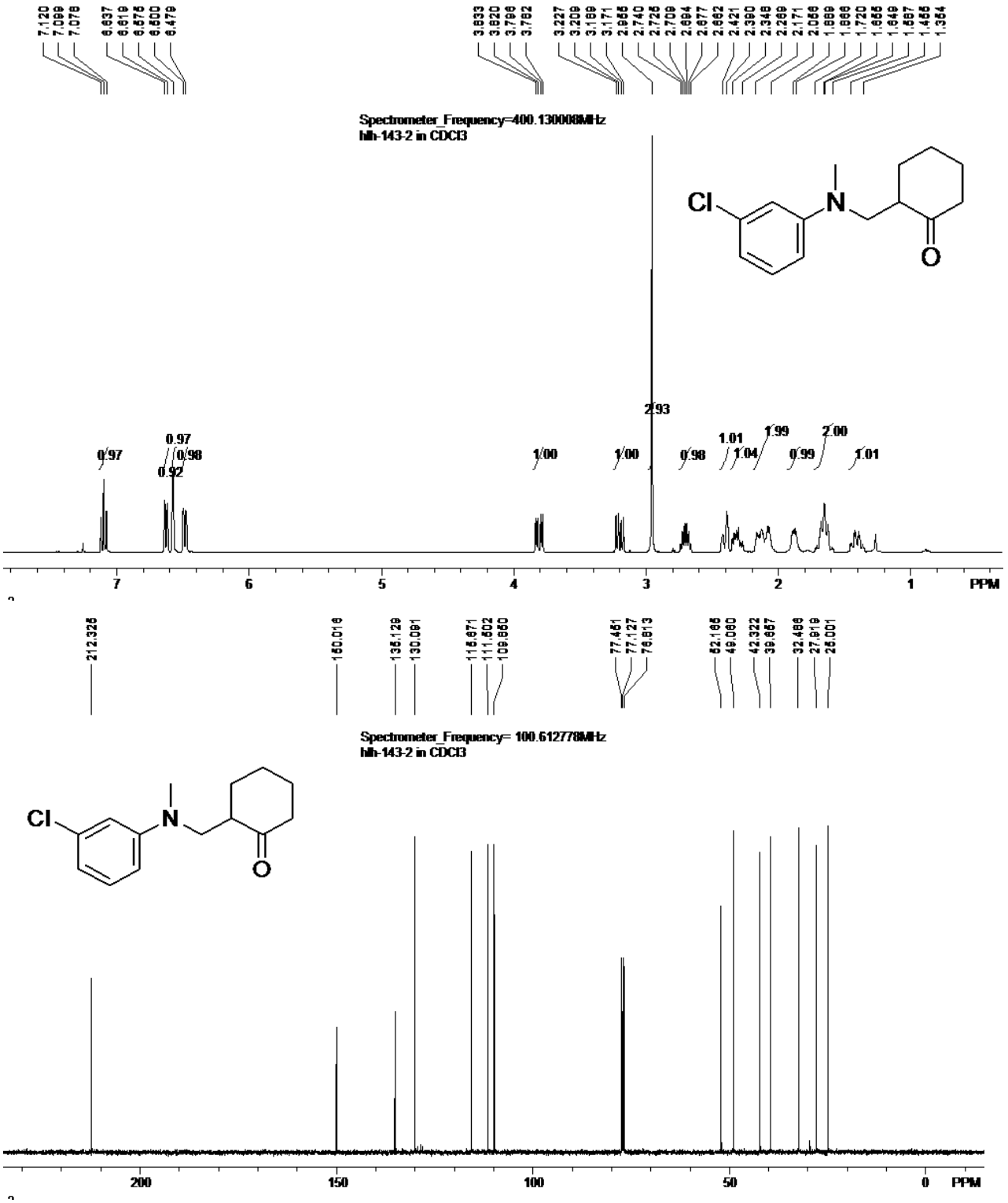




Compound **3q** (2-(((3-chlorophenyl)(methyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using 3-chloro-*N*,*N*-dimethylbenzenamine (234 mg, 1.5 mmol), cyclohexenyloxytrimethylsilane (85 mg, 0.5 mmol) provided 75 mg (60% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

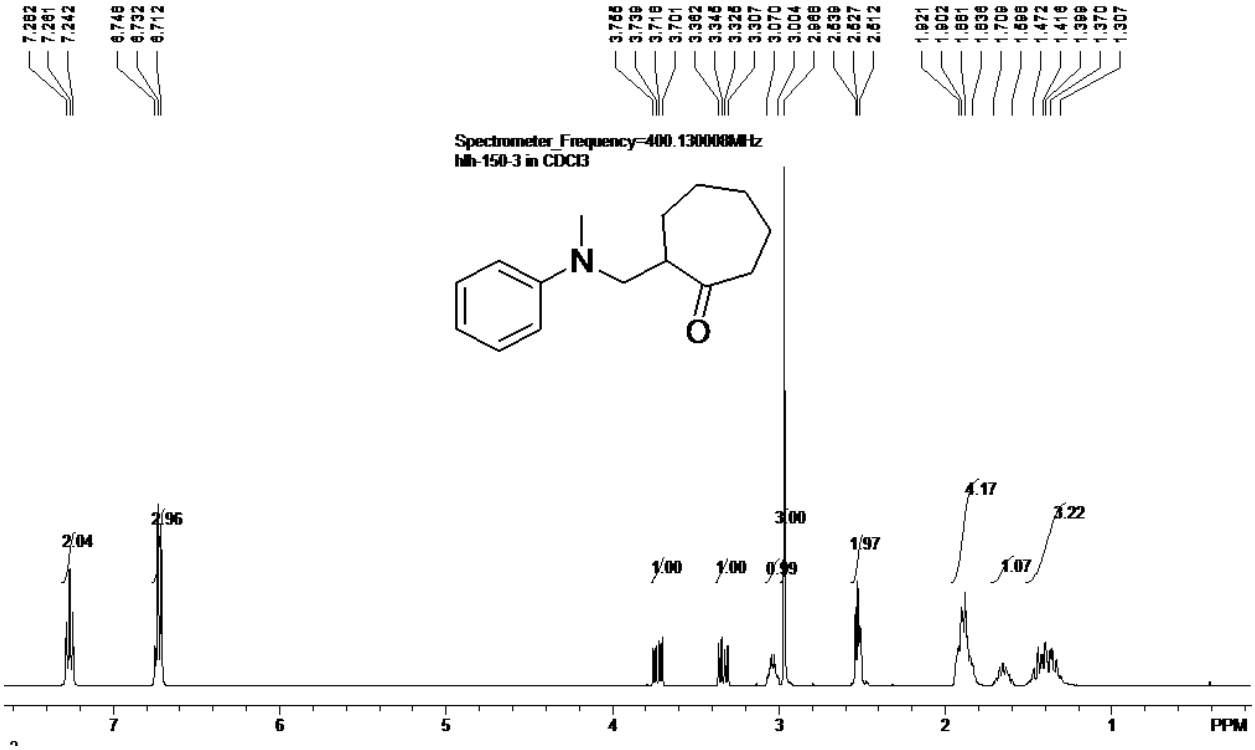
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.10 (t, *J* =8.4 Hz, 1 H), 6.63 (d, *J* = 7.2 Hz, 1 H), 6.58 (s, 1 H), 6.56 (d, *J* = 8.4 Hz, 1 H), 3.81 (dd, *J* = 14.8, 5.2 Hz, 1 H), 3.20 (dd, *J* = 15.2, 7.2 Hz, 1 H), 2.96 (s, 3 H), 2.70 (sxt, *J* = 6.2 Hz, 1 H), 2.42-2.40 (m, 1 H), 2.35-2.27 (m, 1 H), 2.17-2.06 (m, 2 H), 1.89-1.87 (m, 1 H), 1.72-1.59 (m, 2 H), 1.46-1.35 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 150.0, 135.1, 130.1, 115.7, 111.5, 109.9, 52.2, 49.1, 42.3, 39.7, 32.5, 27.9, 25.0. HRMS (EI) Calcd for $C_{14}H_{18}ClNO$: $[M]^+$ 251.1077; Found, 251.1073.

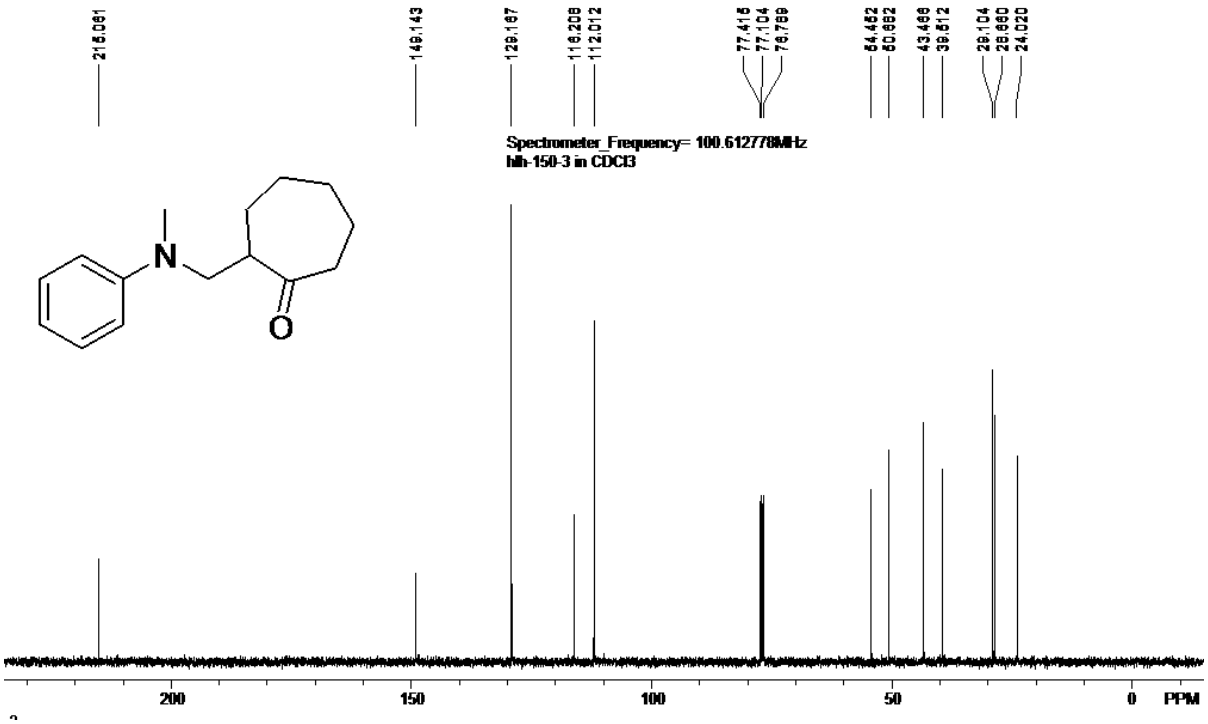


Compound **3r** (2-((methyl(phenyl)amino)methyl)cycloheptanone, new compound)

Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), (E)-cycloheptenyloxytrimethylsilane (92 mg, 0.5 mmol) provided 91 mg (79% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.26 (t, *J* = 8.0 Hz, 2 H), 6.75-6.71 (m, 3 H), 3.73 (dd, *J* = 14.8, 6.4 Hz, 1 H), 3.33 (dd, *J* = 14.8, 6.8 Hz, 1 H), 3.07-3.00 (m, 1 H), 2.97 (s, 3 H), 2.54-2.51 (m, 2 H), 1.92-1.84 (m, 4 H), 1.71-1.60 (m, 1 H), 1.47-1.31 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 149.1, 129.2, 116.2, 112.0, 54.5, 50.7, 43.5, 39.5, 29.1, 28.7, 24.0. HRMS (EI) Calcd for $C_{15}H_{21}NO$: $[M]^+$ 231.1623; Found, 231.1626.

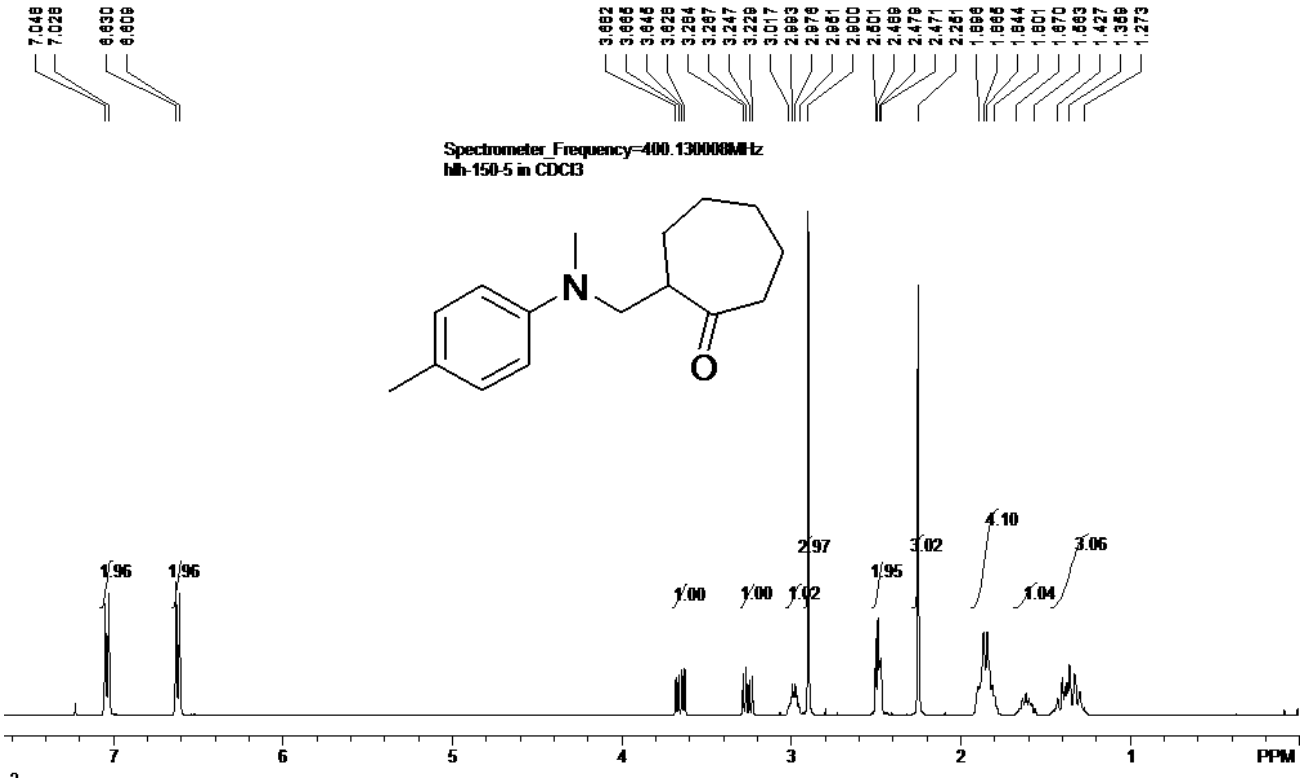


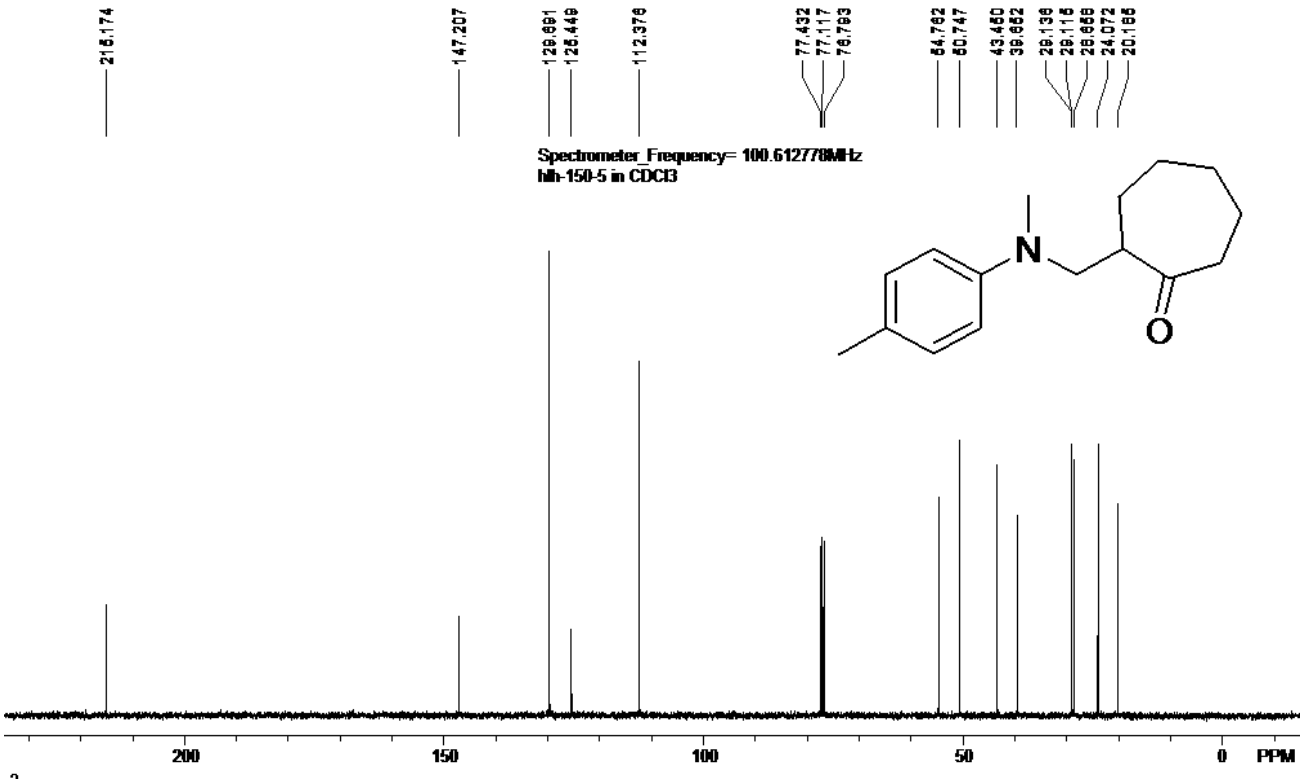


Compound **3s** (2-((methyl(p-tolyl)amino)methyl)cycloheptanone, new compound)

Following the typical procedure **E** using *N*,*N*,4-trimethylbenzenamine (135 mg, 1.0 mmol), (E)-cycloheptenyloxytrimethylsilane (92 mg, 0.5 mmol) provided 81 mg (66% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.04 (d, *J* = 8.0 Hz, 2 H), 6.62 (d, *J* = 8.4 Hz, 2 H), 3.66 (dd, *J* = 14.8, 6.8 Hz, 1 H), 3.26 (dd, *J* = 14.8, 6.8 Hz, 1 H), 3.02-2.96 (m, 1 H), 2.90 (s, 3 H), 2.50-2.47 (m, 2 H), 2.25 (s, 3 H), 1.90-1.80 (m, 4 H), 1.67-1.56 (m, 1 H), 1.43-1.27 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.2, 147.2, 129.7, 125.4, 112.4, 54.8, 50.7, 43.5, 39.7, 29.2, 29.1, 28.7, 24.1, 20.2. HRMS (EI) Calcd for $C_{16}H_{23}NO$: $[M]^+$ 245.1780; Found, 245.1777.

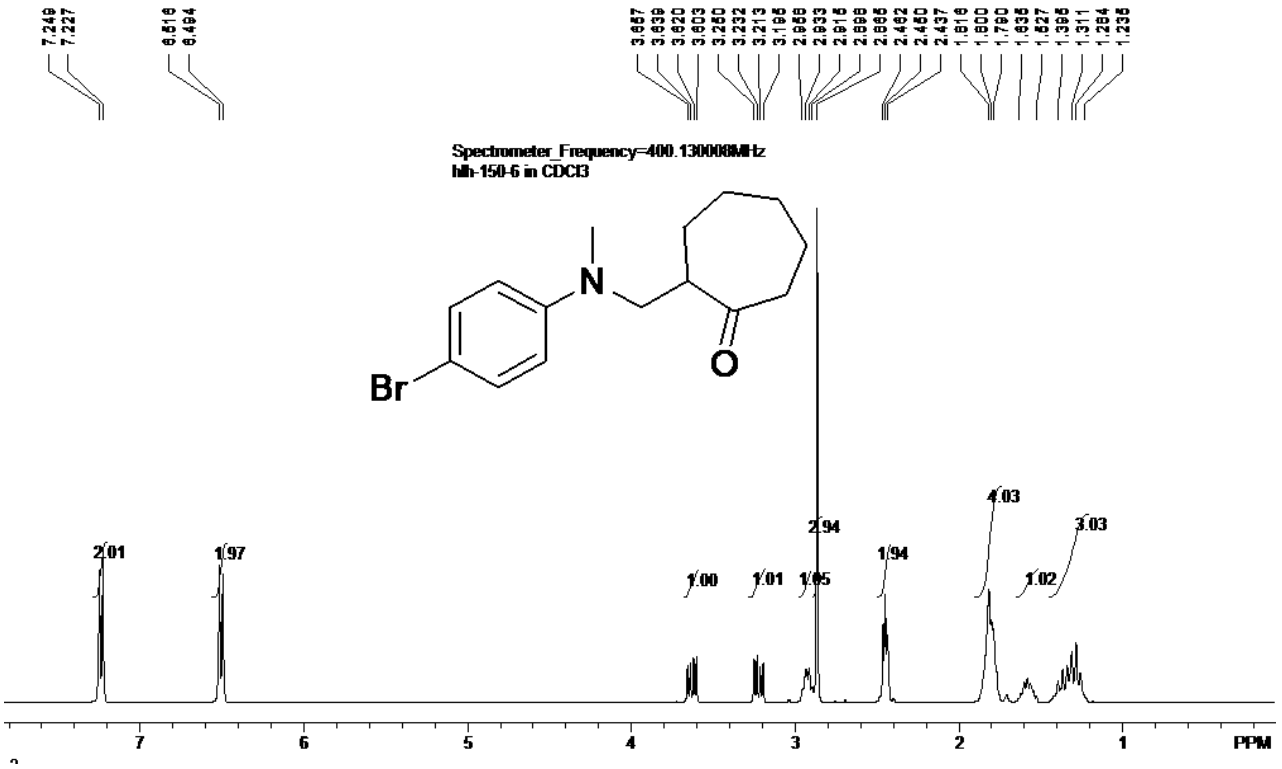


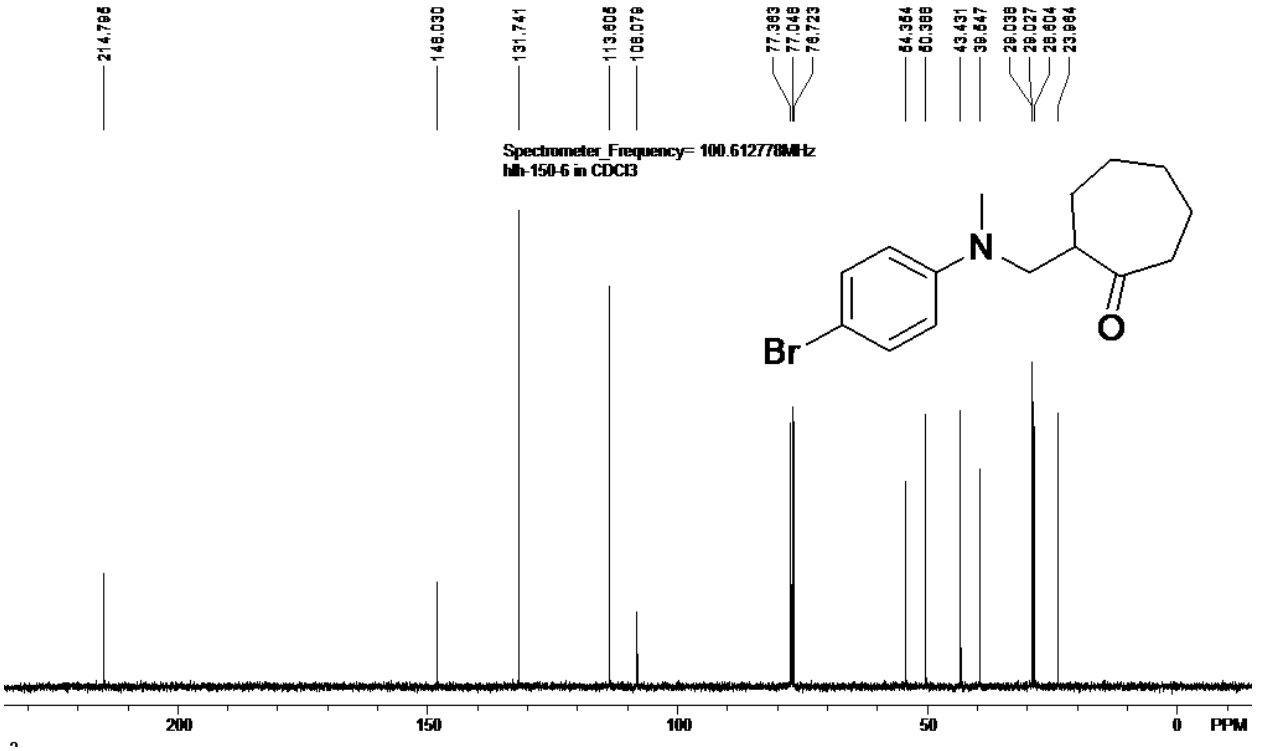


Compound **3t** (2-(((4-bromophenyl)(methyl)amino)methyl)cycloheptanone, new compound)

Following the typical procedure **E** using 4-bromo-*N*,*N*-dimethylbenzenamine (300 mg, 1.5 mmol), (E)-cycloheptenyloxytrimethylsilane (92 mg, 0.5 mmol) provided 98 mg (64% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (d, *J* = 8.8 Hz, 2 H), 6.51 (d, *J* = 8.8 Hz, 2 H), 3.63 (dd, *J* = 14.8, 7.2 Hz, 1 H), 3.22 (dd, *J* = 14.8, 7.2 Hz, 1 H), 2.96-2.90 (m, 1 H), 2.87 (s, 3 H), 2.46-2.44 (m, 2 H), 1.82-1.80 (m, 4 H), 1.64-1.53 (m, 1 H), 1.40-1.24 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.8, 148.0, 131.7, 113.6, 108.1, 54.4, 50.4, 43.4, 39.5, 29.1, 29.0, 28.6, 24.0. HRMS (EI) Calcd for $C_{15}H_{20}BrNO$: $[M]^+$ 309.0728; Found, 309.0724.





Compound **3u** (2-((methyl(phenyl)amino)methyl)cyclopentanone, new compound)

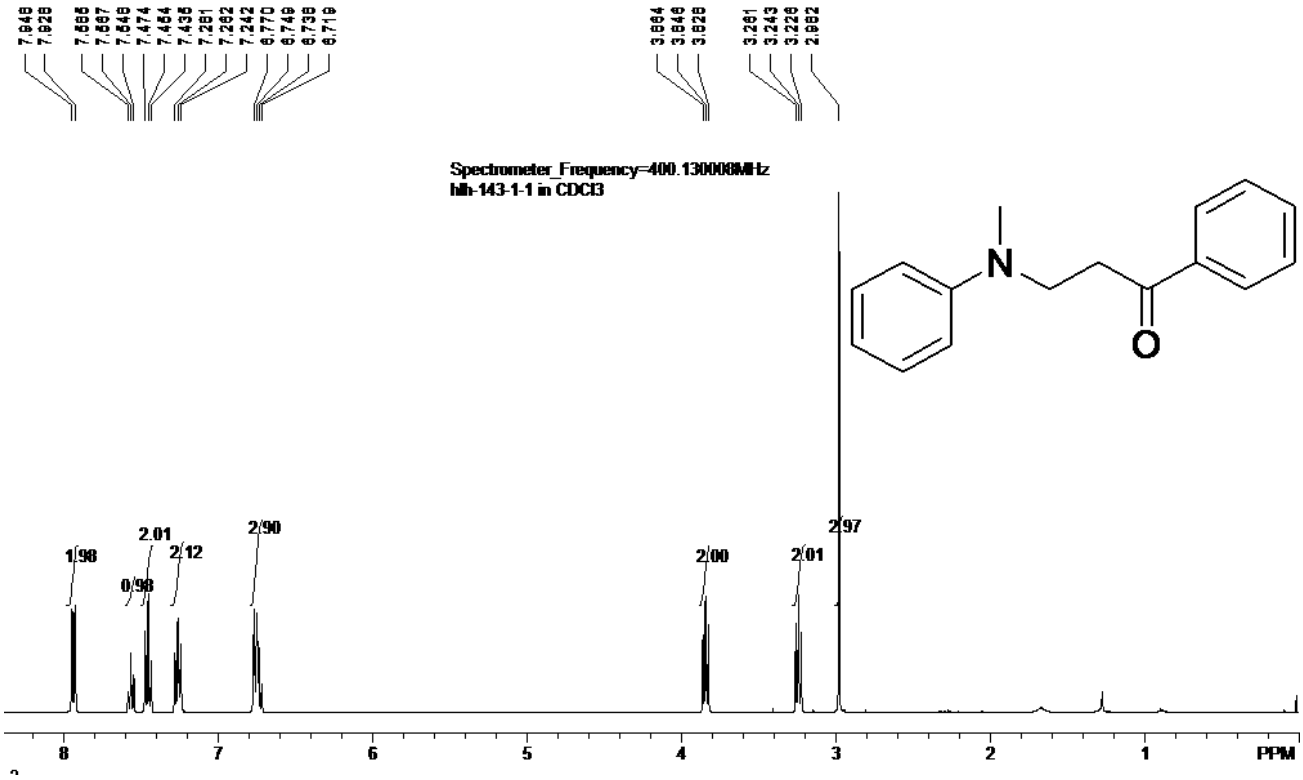
Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), cyclopentenyloxytrimethylsilane (78 mg, 0.5 mmol) provided 21 mg (21% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

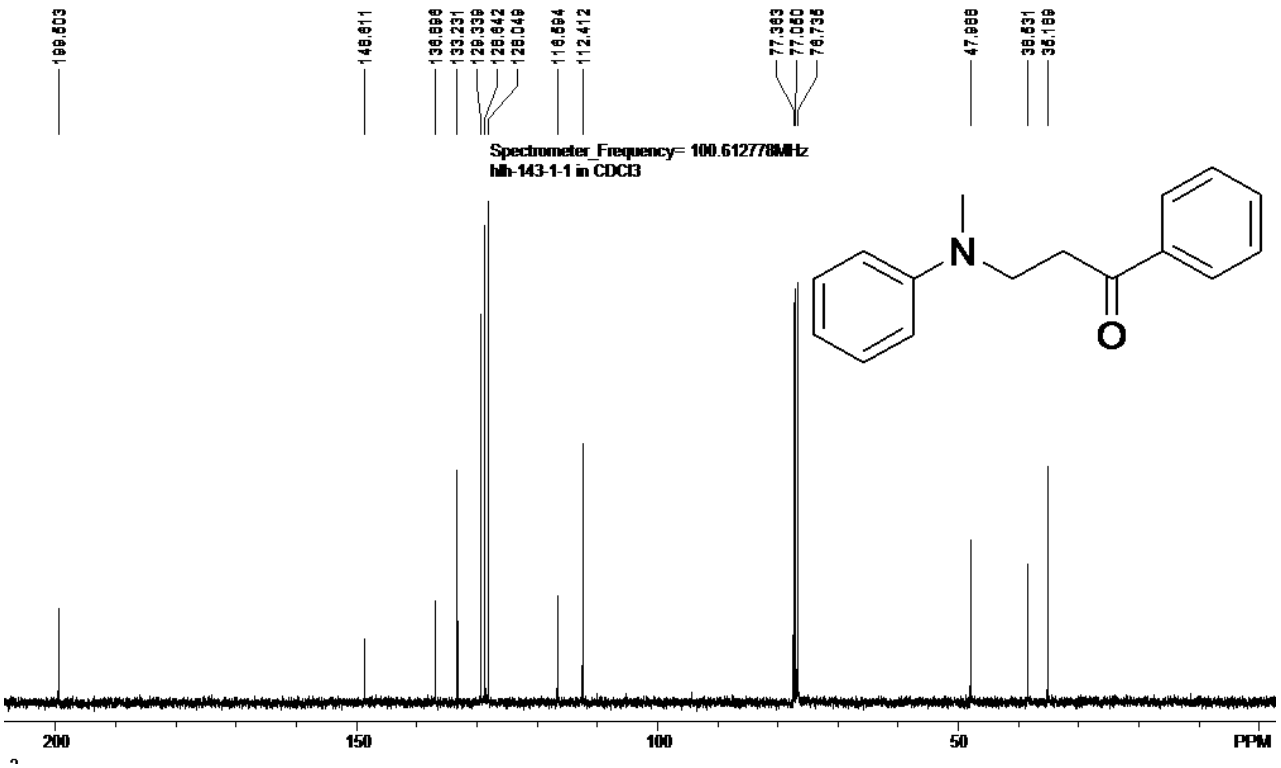
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (dd, *J* = 8.4, 6.8 Hz, 2 H), 6.75-6.70 (m, 3 H), 3.89 (dd, *J* = 14.4, 4.4 Hz, 1 H), 3.28 (dd, *J* = 14.8, 7.6 Hz, 1 H), 2.96 (s, 3 H), 2.53-2.45 (m, 1 H), 2.37-2.29 (m, 1 H), 2.25-2.19 (m, 1 H), 2.18-2.08 (m, 1 H), 2.06-2.00 (m, 1 H), 1.81-1.63 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.2, 148.7, 129.2, 116.4, 112.2, 52.5, 48.4, 39.2, 38.1, 29.2, 20.7. HRMS (EI) Calcd for $C_{13}H_{17}NO$: $[M]^+$ 203.1310; Found, 203.1302.

Compound **3v** (3-(methyl(phenyl)amino)-1-phenylpropan-1-one, new compound)

Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), trimethyl(1-phenylvinyloxy)silane (96 mg, 0.5 mmol) provided 80 mg (67% yield) of the desired product as a light yellow solid after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (d, *J* = 8.0 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.26 (t, *J* = 7.8 Hz, 2 H), 6.77-6.72 (m, 3 H), 3.85 (t, *J* = 7.2 Hz, 2 H), 3.24 (t, *J* = 7.0 Hz, 2 H), 2.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 148.6, 136.9, 133.2, 129.3, 128.6, 128.0, 116.6, 112.4, 48.0, 38.5, 35.2. HRMS (EI) Calcd for $C_{16}H_{17}NO$: $[M]^+$ 239.1310; Found, 239.1309.

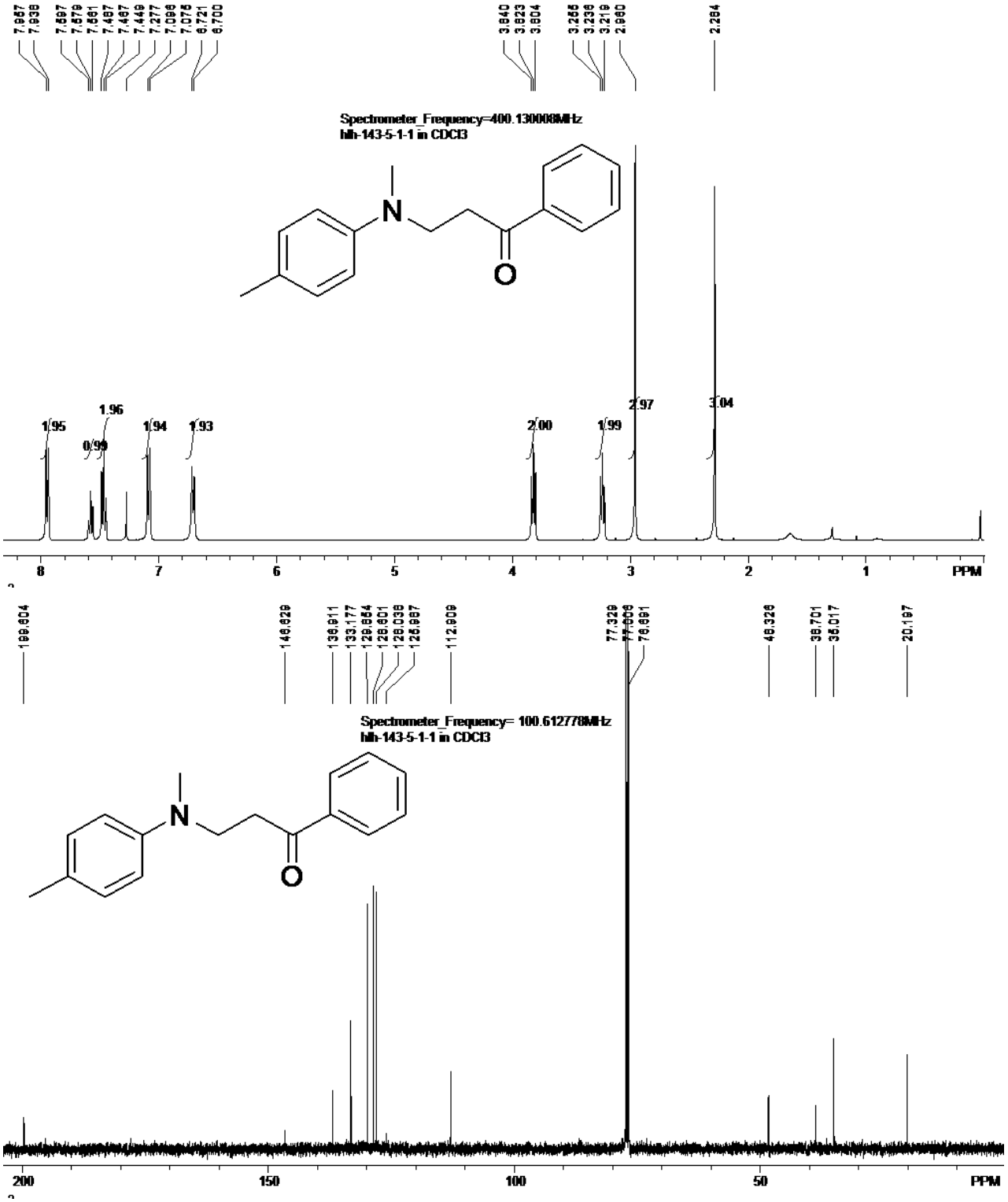




Compound **3w** (3-(methyl(p-tolyl)amino)-1-phenylpropan-1-one, new compound)

Following the typical procedure **E** using *N*,*N*,4-trimethylbenzenamine (203 mg, 1.5 mmol), trimethyl(1-phenylvinyloxy)silane (96 mg, 0.5 mmol) provided 82 mg (65% yield) of the desired product as a light yellow solid after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

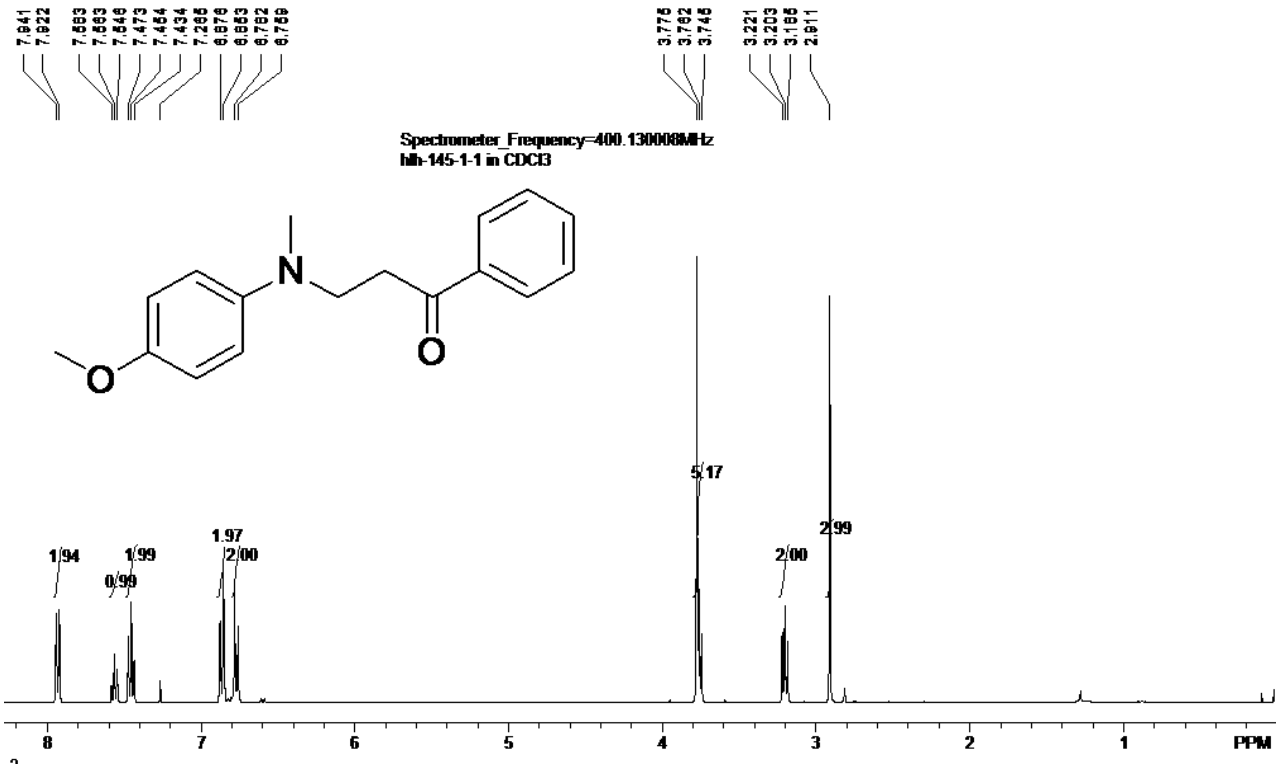
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (d, *J* = 7.6 Hz, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 3.82 (t, *J* = 7.2 Hz, 2 H), 3.24 (t, *J* = 7.2 Hz, 2 H), 2.96 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 146.6, 136.9, 133.2, 129.9, 128.6, 128.0, 126.0, 112.9, 48.3, 38.7, 35.0, 20.2. HRMS (EI) Calcd for $C_{17}H_{19}NO$: $[M]^+$ 253.1467; Found, 253.1462.

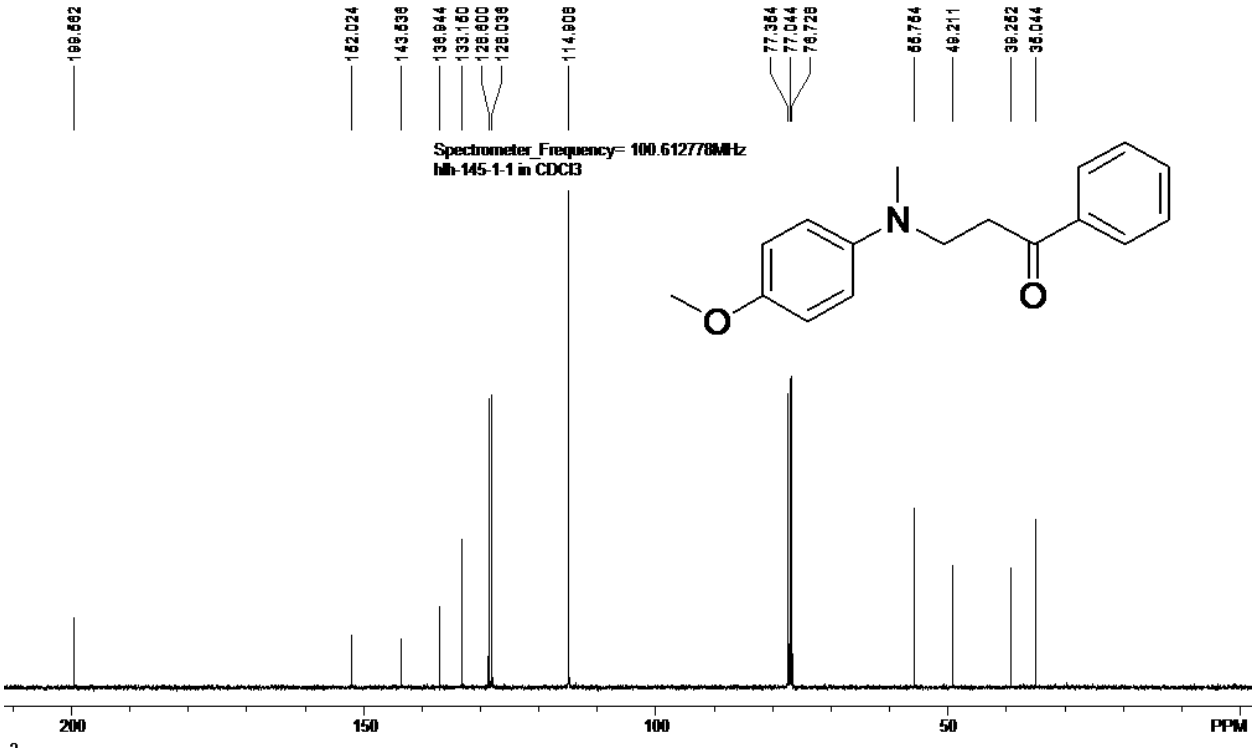


Compound **3y** (3-((4-methoxyphenyl)(methyl)amino)-1-phenylpropan-1-one, new compound)

Following the typical procedure **E** using 4-methoxy-*N*,*N*-dimethylbenzenamine (227 mg, 1.5 mmol), trimethyl(1-phenylvinyloxy)silane (96 mg, 0.5 mmol) provided 91 mg (68% yield) of the desired product as a light yellow solid after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.93 (d, *J* = 7.6 Hz, 2 H), 7.56 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 6.86 (d, *J* = 9.2 Hz, 2 H), 6.77 (d, *J* = 9.2 Hz, 2 H), 3.78 (s, 3 H), 3.76 (t, *J* = 6.8 Hz, 2 H), 3.20 (t, *J* = 7.2 Hz, 2 H), 2.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 152.0, 143.5, 136.9, 133.2, 128.6, 128.0, 114.9, 55.8, 49.2, 39.3, 35.0. HRMS (EI) Calcd for $C_{17}H_{19}NO_2$: $[M]^+$ 269.1416; Found, 269.1411.

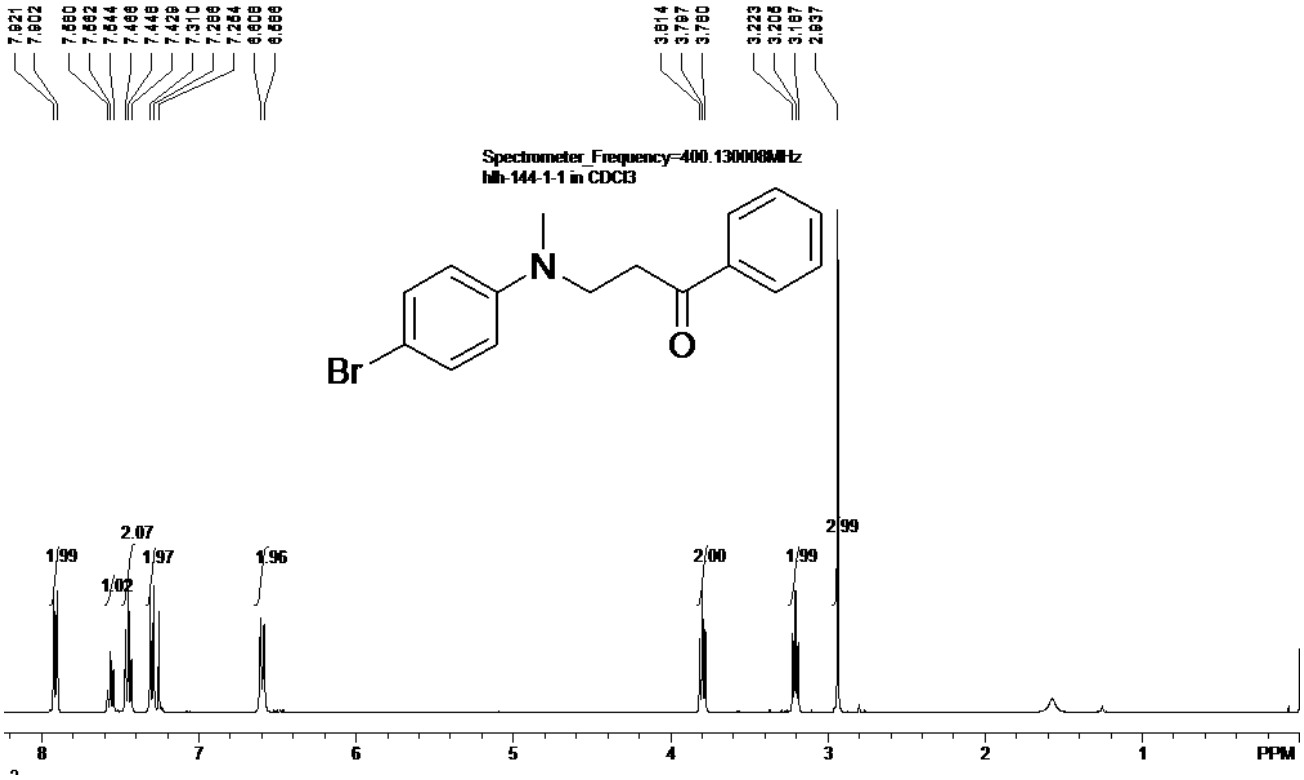


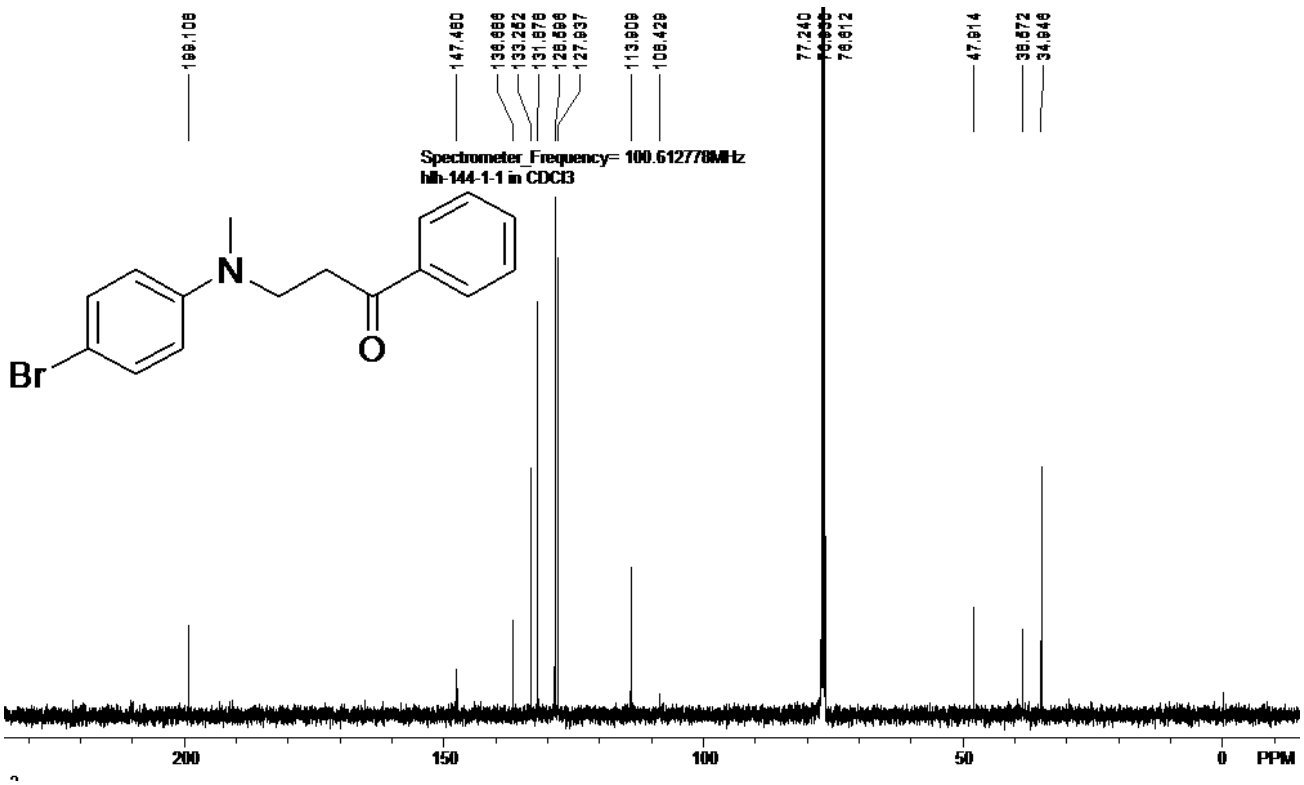


Compound **3x** (3-((4-bromophenyl)(methyl)amino)-1-phenylpropan-1-one, new compound)

Following the typical procedure **E** using 4-bromo-*N*,*N*-dimethylbenzenamine (300 mg, 1.5 mmol), trimethyl(1-phenylvinyloxy)silane (96 mg, 0.5 mmol) provided 99 mg (63% yield) of the desired product as a light yellow solid after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.91 (d, *J* = 7.6 Hz, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 2 H), 7.30 (d, *J* = 9.6 Hz, 2 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 3.80 (t, *J* = 6.8 Hz, 2 H), 3.21 (t, *J* = 7.2 Hz, 2 H), 2.94 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 147.5, 136.7, 133.3, 131.9, 128.6, 128.0, 113.9, 108.4, 47.9, 38.6, 35.0. HRMS (EI) Calcd for $C_{16}H_{16}BrNO$: $[M]^+$ 317.0415; Found, 317.0422.

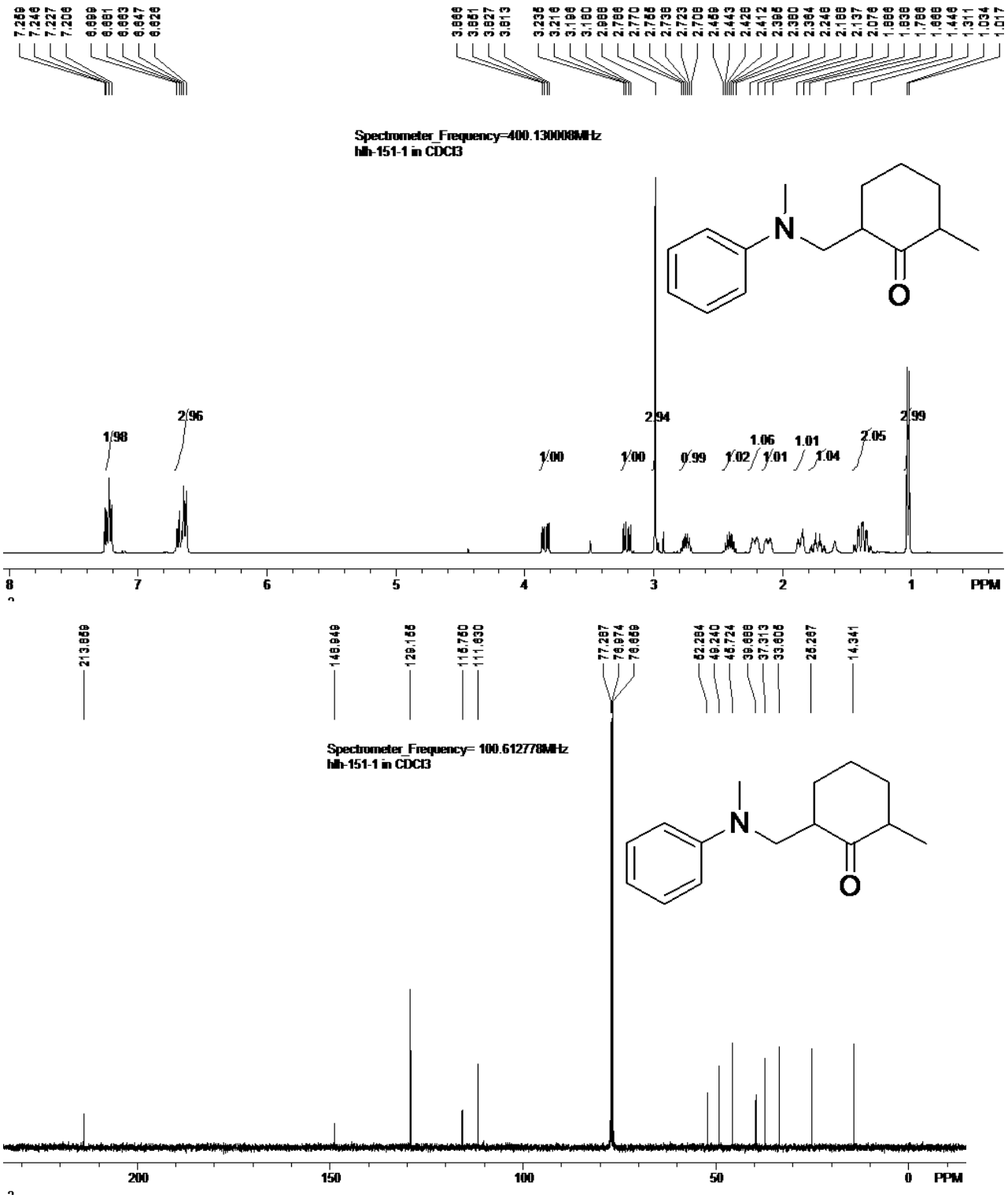




Compound **4a$_1$** (2-methyl-6-((methyl(phenyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), trimethyl(6-methylcyclohex-1-enyloxy)silane (92 mg, 0.5 mmol) provided 39 mg (34% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

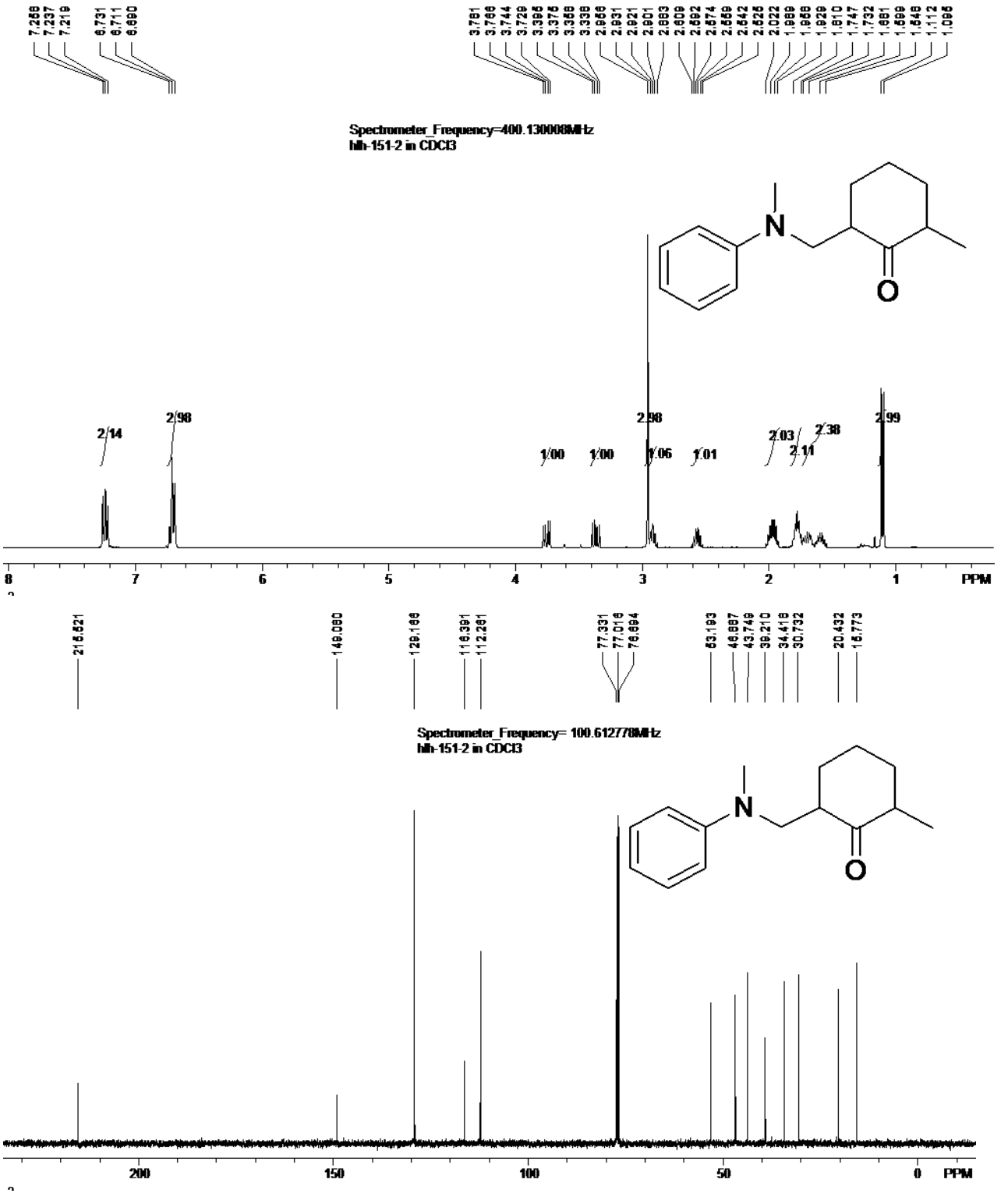
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23 (t, *J* = 8.0 Hz, 2 H), 6.68 (t, *J* = 7.2 Hz, 1 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 3.84 (dd, *J* = 15.6, 6.0 Hz, 1 H), 3.21 (dd, *J* = 15.6, 7.6 Hz, 1 H), 2.99 (s, 3 H), 2.75 (sxt, *J* = 6.2 Hz, 1 H), 2.46-2.36 (m, 1 H), 2.25-2.19 (m, 1 H), 2.14-2.08 (m, 1 H), 1.89-1.84 (m, 1 H), 1.79-1.67 (m, 1 H), 1.45-1.31 (m, 2 H), 1.03 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.9, 148.9, 129.2, 115.8, 111.6, 52.3, 49.2, 45.7, 39.7, 37.3, 33.6, 25.3, 14.3. HRMS (EI) Calcd for $C_{15}H_{21}NO$: $[M]^+$ 231.1623; Found, 231.1629.



Compound **4a$_2$** (2-methyl-6-((methyl(phenyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), trimethyl(6-methylcyclohex-1-enyloxy)silane (92 mg, 0.5 mmol) provided 38 mg (33% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

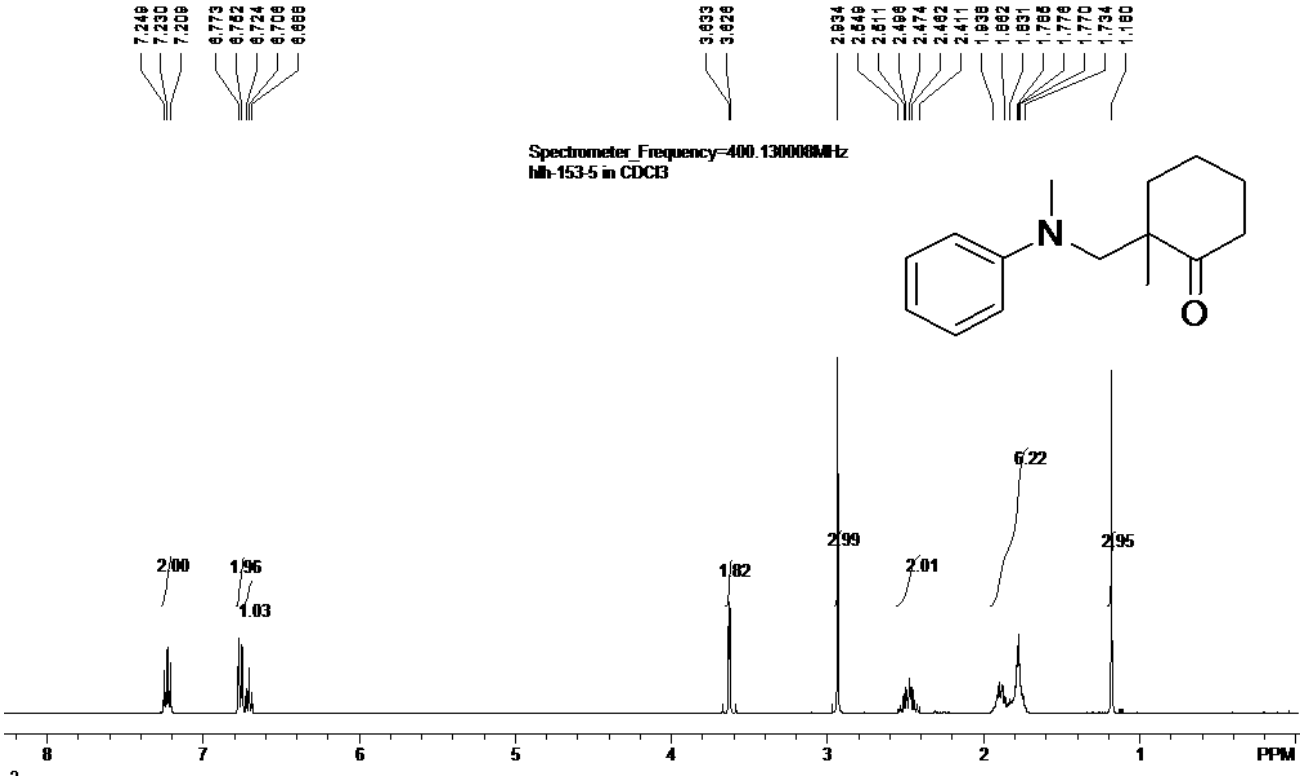
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (t, *J* = 7.8 Hz, 2 H), 6.73-6.69 (m, 3 H), 3.76 (dd, *J* = 14.8, 6.0 Hz, 1 H), 3.37 (dd, *J* = 14.8, 8.0 Hz, 1 H), 2.96 (s, 3 H), 2.93-2.88 (m, 1 H), 2.57 (sxt, *J* = 6.7 Hz, 1 H), 2.01-1.93 (m, 2 H), 1.81-1.55 (m, 4 H), 1.10 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 149.1, 129.2, 116.4, 112.3, 53.2, 46.9, 43.7, 39.2, 34.4, 30.7, 20.4, 15.8. HRMS (EI) Calcd for $C_{15}H_{21}NO$: $[M]^+$ 231.1623; Found, 231.1629.

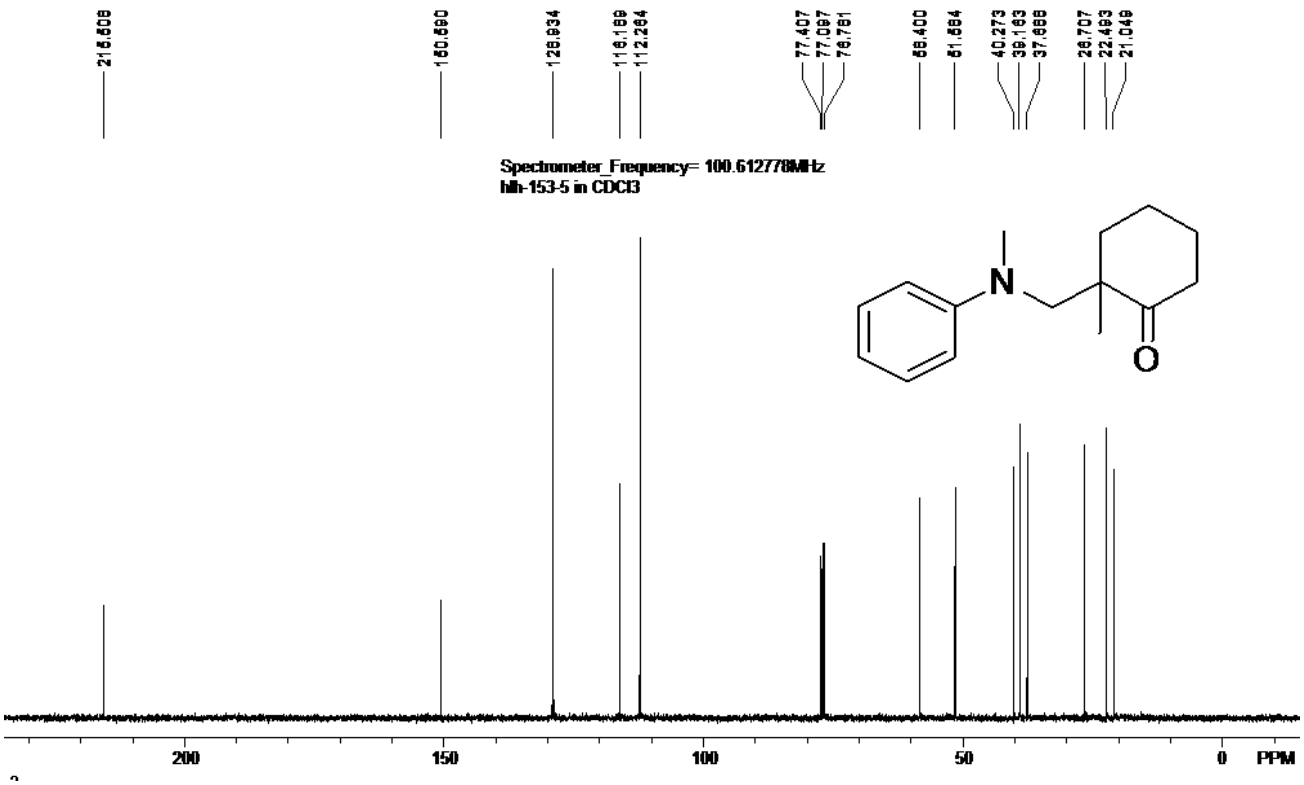


Compound **4b** (2-methyl-2-((methyl(phenyl)amino)methyl)cyclohexanone, new compound)

Following the typical procedure **E** using *N*,*N*-dimethylbenzenamine (182 mg, 1.5 mmol), trimethyl(2-methylcyclohex-1-enyloxy)silane (92 mg, 0.5 mmol) provided 67 mg (58% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23 (t, *J* = 8.0 Hz, 2 H), 6.76 (d, *J* = 8.4 Hz, 2 H), 6.71 (t, *J* = 7.2 Hz, 1 H), 3.63 (d, *J* = 2.8 Hz, 2 H), 2.93 (s, 3 H), 2.55-2.41 (m, 2 H), 1.94-1.73 (m, 6 H), 1.18 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 150.6, 128.9, 116.2, 112.3, 58.4, 51.6, 40.3, 39.2, 37.7, 26.7, 22.5, 21.0. HRMS (EI) Calcd for $C_{15}H_{21}NO$: $[M]^+$ 231.1623; Found, 231.1624.

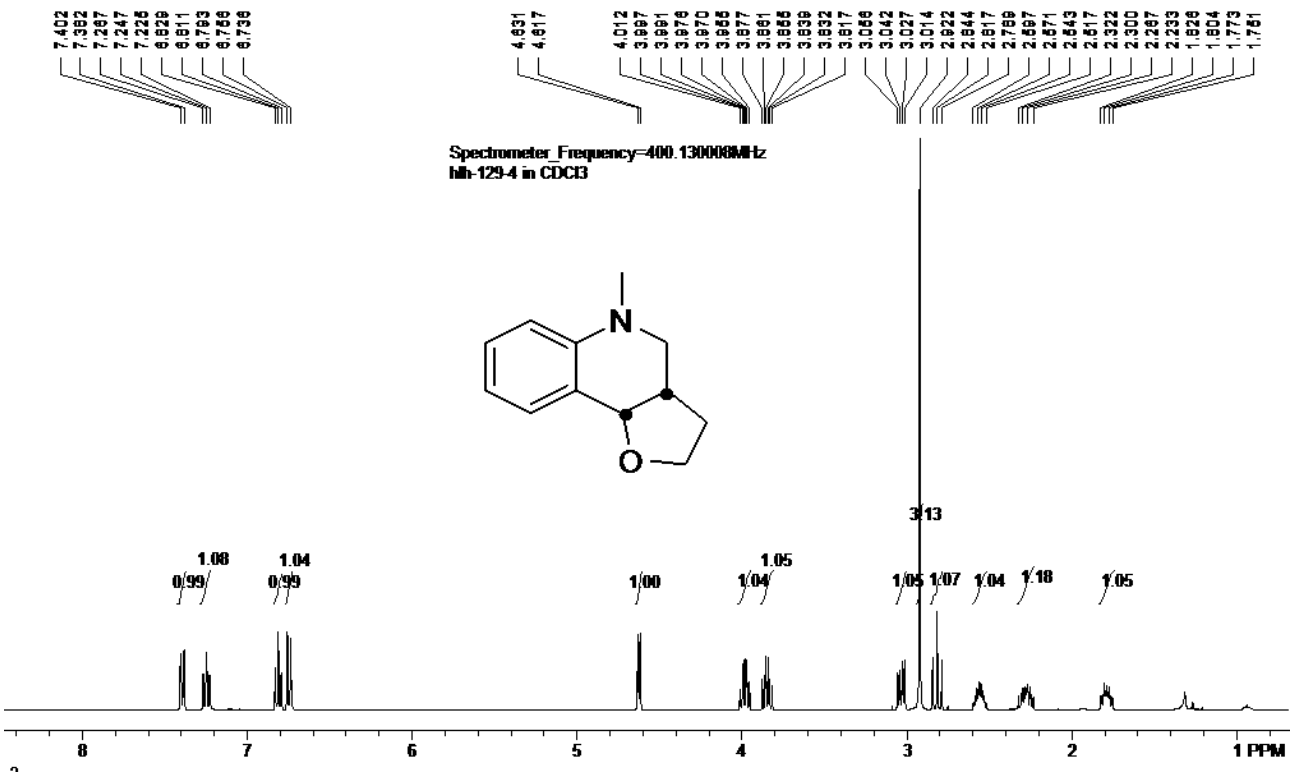


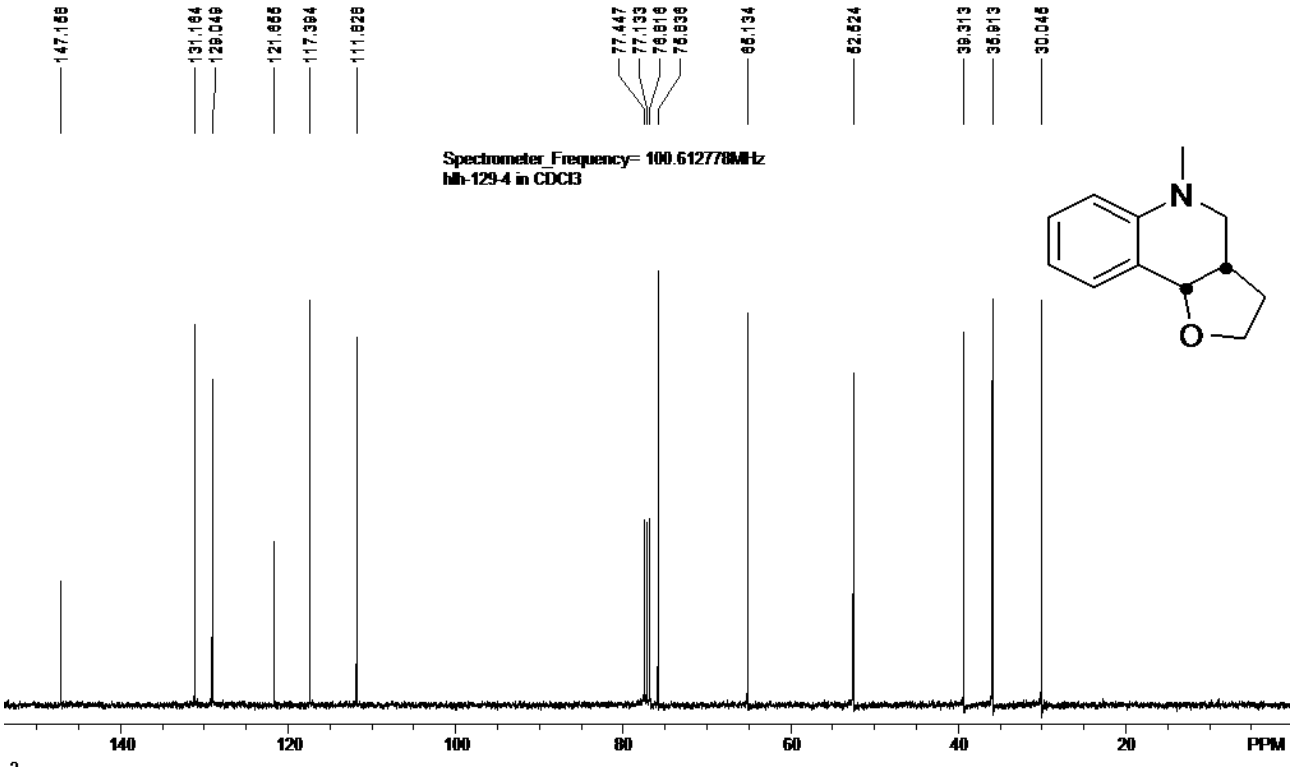


Compound **4c** (5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline, new compound)

Following the typical procedure **F** using *N*,*N*-dimethylbenzenamine (242 mg, 2.0 mmol), 2,3-dihydrofuran (70 mg, 1.0 mmol) provided 56 mg (30% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39 (d, *J* =8.0 Hz, 1 H), 7.25 (t, *J* = 8.4 Hz, 1 H), 6.81 (t, *J* = 7.2 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 4.62 (d, *J* = 5.6 Hz, 1 H), 3.98 (dt, *J* = 8.4, 6.0 Hz, 1 H), 3.85 (dt, *J* = 8.8, 6.4 Hz, 1 H), 3.04 (dd, *J* = 11.6, 5.6 Hz, 1 H), 2.92 (s, 3 H), 2.82 (t, *J* = 11.0 Hz, 1 H), 2.60-2.52 (m, 1 H), 2.32-2.23 (m, 1 H), 1.83-1.75 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 131.2, 129.0, 121.7, 117.4, 111.8, 75.8, 65.1, 52.5, 39.3, 35.9, 30.0. HRMS (EI) Calcd for $C_{12}H_{15}NO$: $[M]^+$ 189.1154; Found, 189.1151.

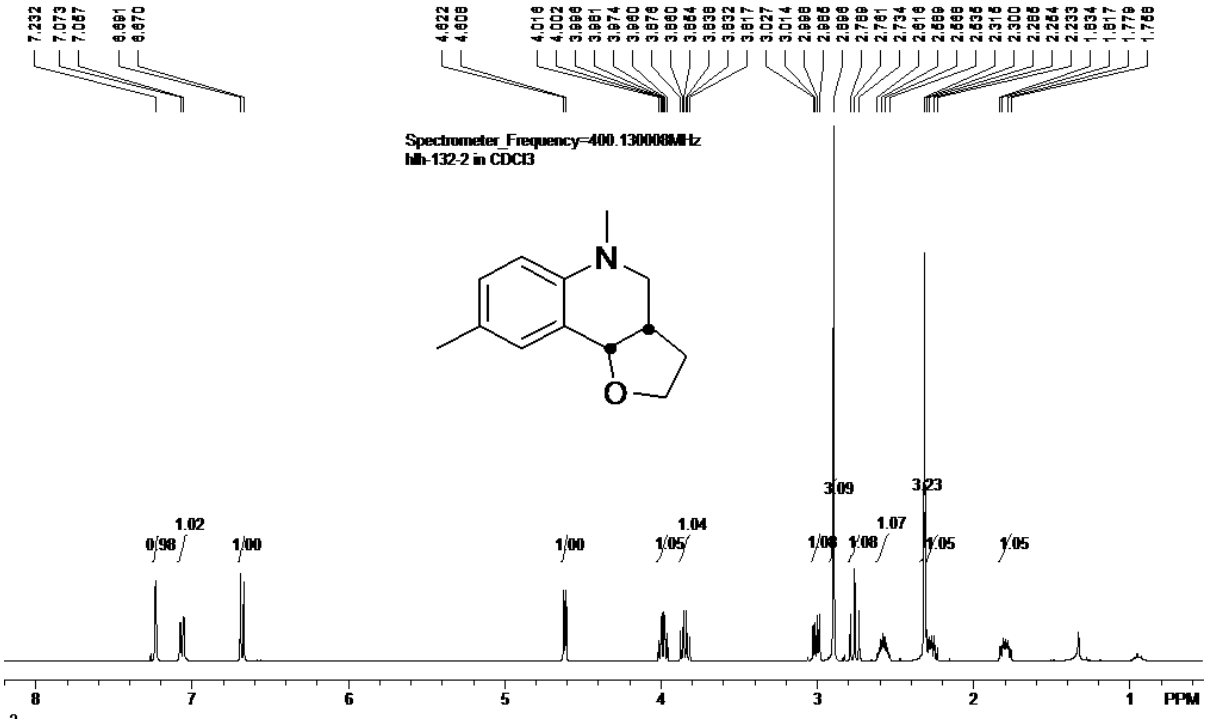


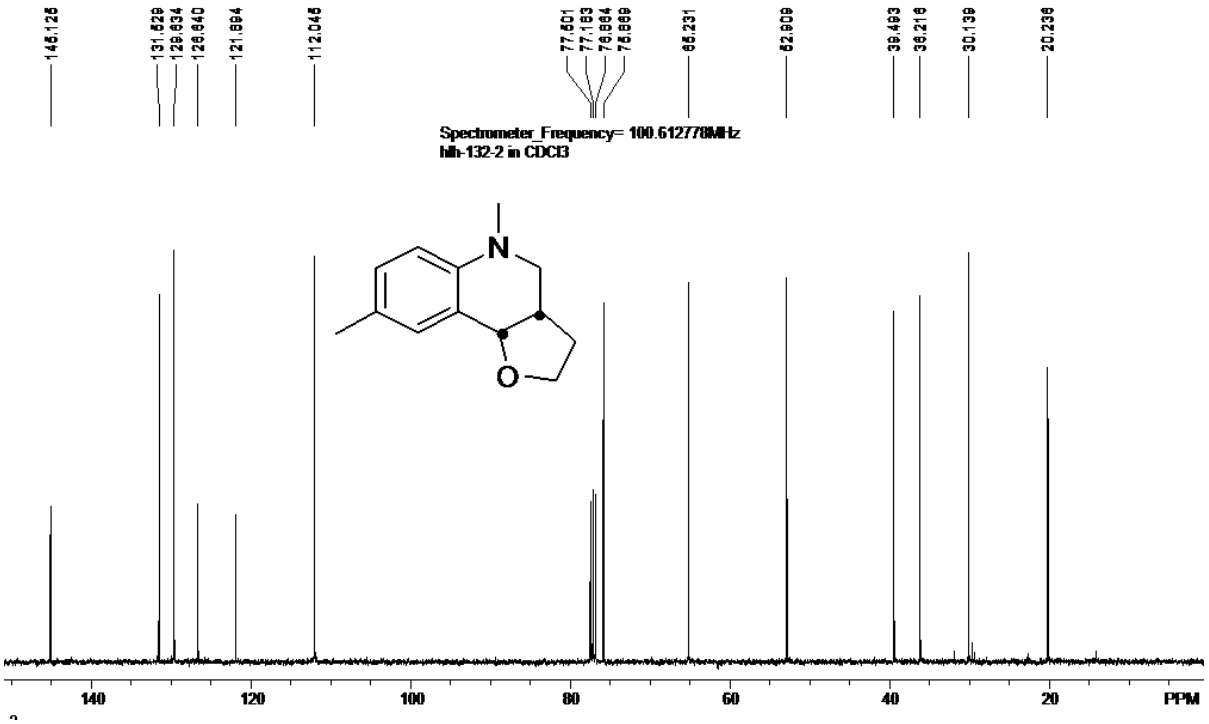


Compound **4d** (5,8-dimethyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline, new compound)

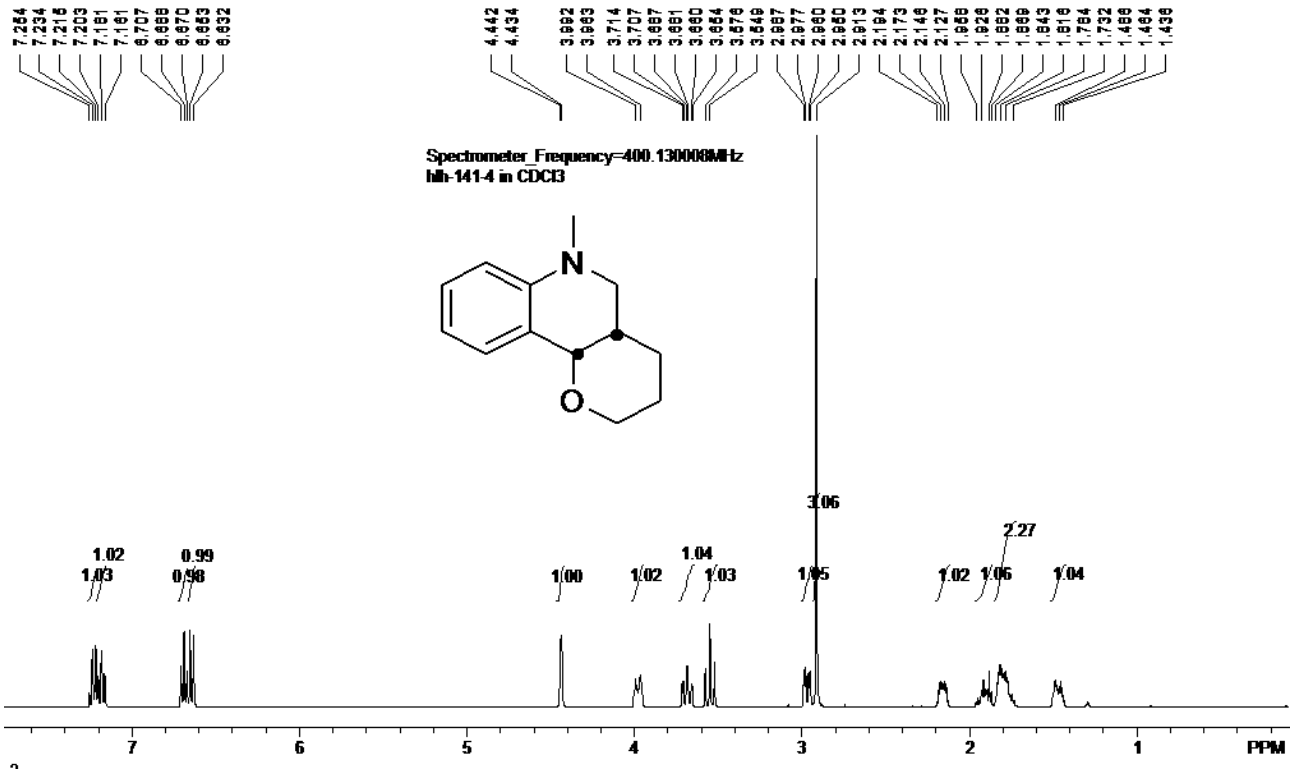
Following the typical procedure **F** using *N*,*N*,4-trimethylbenzenamine (270 mg, 2.0 mmol), 2,3-dihydrofuran (70 mg, 1.0 mmol) provided 81 mg (40% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40).

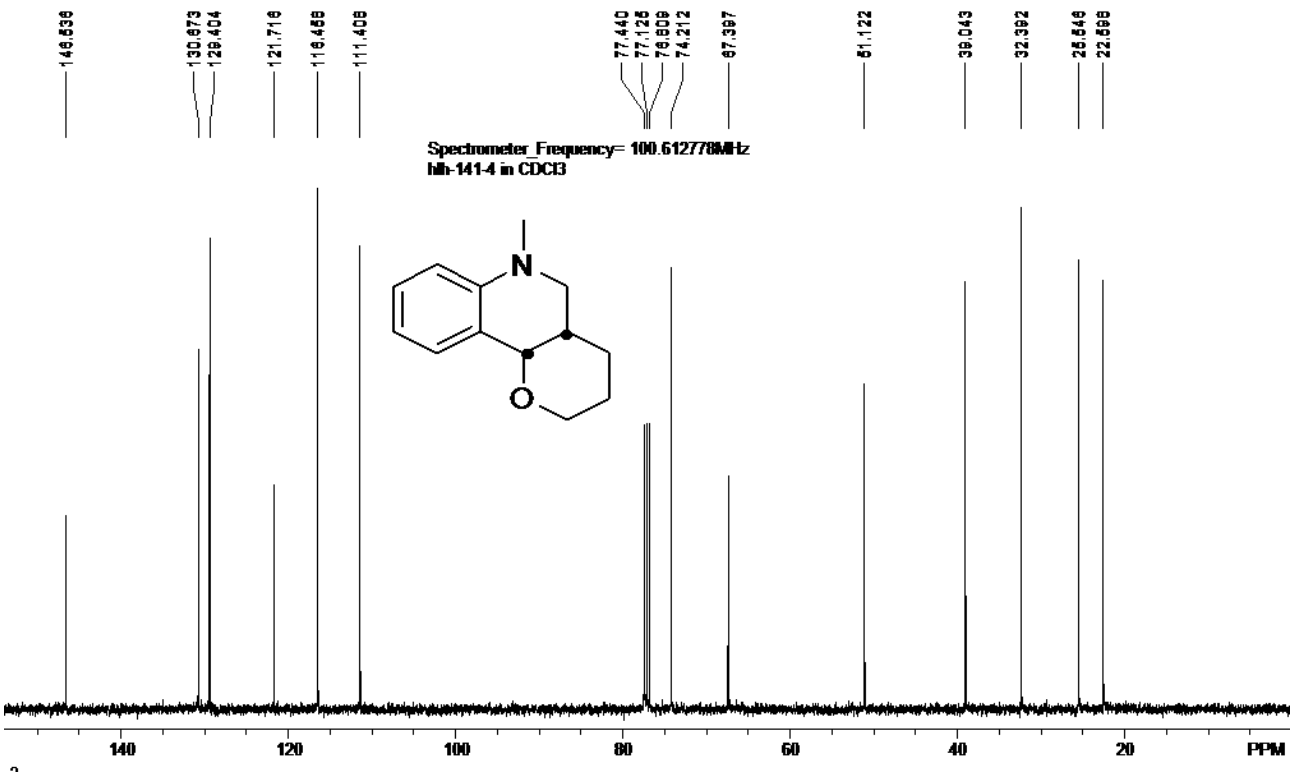
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23 (s, 1 H), 7.06 (d, *J* = 8.4 Hz, 1 H), 6.68 (d, *J* = 8.4 Hz, 1 H), 4.62 (d, *J* = 5.6 Hz, 1 H), 3.99 (dt, *J* = 8.0, 5.6 Hz, 1 H), 3.85 (dt, *J* = 8.8, 6.4 Hz, 1 H), 3.01 (dd, *J* = 11.6, 5.2 Hz, 1 H), 2.90 (s, 3 H), 2.76 (t, *J* = 11.0 Hz, 1 H), 2.62-2.54 (m, 1 H), 2.32 (s, 3 H), 2.30-2.23 (m, 1 H), 1.83-1.76 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 131.5, 129.6, 126.6, 121.9, 112.0, 75.9, 65.2, 52.9, 39.5, 36.2, 30.1, 20.2. HRMS (EI) Calcd for $C_{13}H_{17}NO$: $[M]^+$ 203.1310; Found, 203.1305.





Compound **4e** (6-methyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline, new compound) Following the typical procedure **F** using *N*,*N*-dimethylbenzenamine (242 mg, 2.0 mmol), 3,4-dihydro-2H-pyran (84 mg, 1.0 mmol) provided 50 mg (25% yield) of the desired product as a light yellow oil after purification by flash chromatography (eluent: ethyl acetate/petrol ether =1/40). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.22 (d, *J* =7.6 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 6.69 (t, *J* = 7.4 Hz, 1 H), 6.64 (d, *J* = 8.4 Hz, 1 H), 4.44 (d, *J* = 3.2 Hz, 1 H), 3.98 (d, *J* = 11.6 Hz, 1 H), 3.68 (dt, *J* = 10.8, 2.8 Hz, 1 H), 3.55 (t, *J* = 11.0 Hz, 1 H), 2.97 (dd, *J* = 10.8, 4.0 Hz, 1 H), 2.91 (s, 3 H), 2.19-2.13 (m, 1 H), 1.96-1.87 (m, 1 H), 1.84-1.73 (m, 2 H), 1.49-1.44 (m, 1 H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 130.7, 129.4, 121.7, 116.5, 111.4, 74.2, 67.4, 51.1, 39.0, 32.4, 25.5, 22.6. HRMS (EI) Calcd for $C_{13}H_{17}NO$: $[M]^+$ 203.1310; Found, 203.1302.





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