Supplementary Information

For

Visible Light-Induced Oxidative Coupling Reaction: Easy Access to Mannich-Type Product

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1. General Information.

All reagents were purchased from commercial sources unless otherwise noted. All reactions were monitored by TLC and visualized by UV lamp (254 nm). Flash column chromatography was performed using 230-400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ^{1}H NMR spectra were reported in parts per million relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR spectra were reported in parts per million relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet, respectively. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

2. General procedure for photocatalytic coupling reaction

A 10 mL round bottom flask was equipped with magnetic stir bar and was charged with tetrahydroisoquinoline **1a** (23 mg, 0.11 mmol), enol silane **2a** (64 mg, 0.33 mmol), CH_3OH (1.1 mL) and $Ru(bpy)_3Cl_2$ (4.1 mg, 0.0055 mmol). The mixture was irradiated by a blue LEDs (1 W) for 4 h. After the reaction was completed, the solvent was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (3% EtOAc in petroleum ether) to afford the desired product **3a** in 96% yield.

3. NMR analysis for photocatalytic coupling reaction

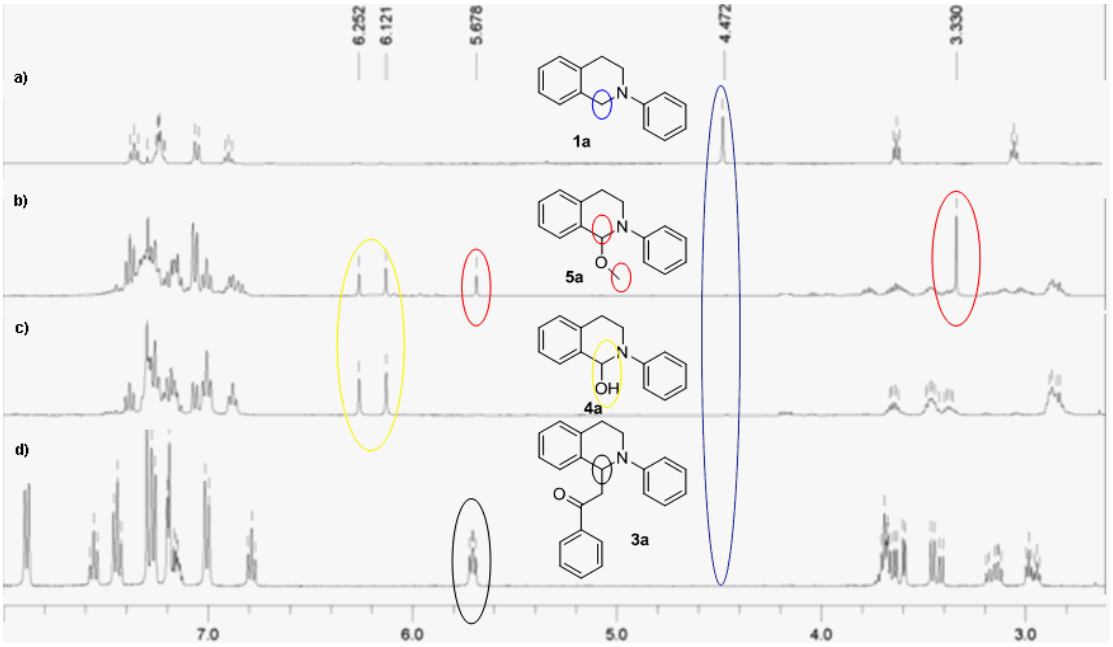
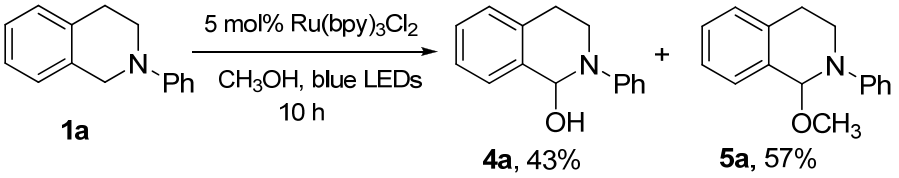
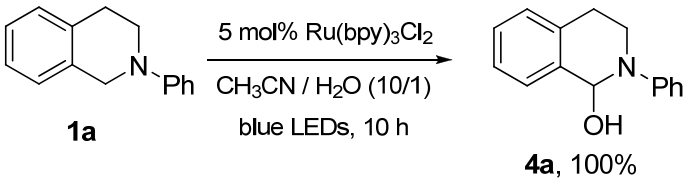


Figure 1: NMR analysis for photocatalytic reaction of the substrate **1a**. The characteristic peaks of **1a**, **4a**, **5a** and **3a** were indicated; a) substrate **1a**, b) crude products from **Reaction A**, c) crude products from **Reaction B**, d) product **3a**.



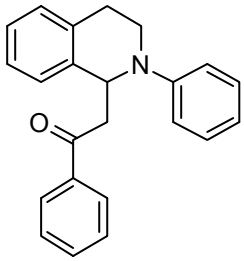
Reaction A: The tetrahydroisoquinoline **1a** (34 mg, 0.16 mmol) with $Ru(bpy)_3Cl_2$ (6.0 mg) in CH_3OH (1.6 mL) was stirred at room temperature. The mixture was irradiated using blue LEDs (1 W). After irradiation for 10h, diethyl ether (15 mL) was added to the reaction, and the solid was filtered. Then filtrate was dried with Na_2SO_4 and concentrated *in vacuo*. The crude product was directly used for NMR analysis. [see **Figure 1:** b)]



1a **4a**, 100%

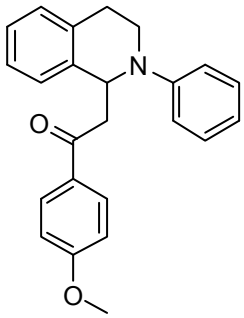
Reaction B: The tetrahydroisoquinoline **1a** (28 mg, 0.13 mmol) with $Ru(bpy)_3Cl_2$ (5.0 mg) in $CNCH_3/H_2O$ (1.3 mL, 10/1) was stirred at room temperature. The mixture was irradiated using blue LEDs (1 W). After irradiation for 10h, ethyl ester (15 mL) and H_2O (5 mL) was added to the reaction. Then organic phase was washed with brine, dried with Na_2SO_4 and concentrated *in vacuo*. The crude product was used for NMR analysis. [see **Figure 1:** c)]

4. Characterization data for compounds 3a-3o



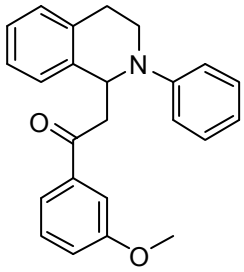
1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3a)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.29-7.13 (m, 7H), 7.00 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 7.6 Hz, 1H), 5.69 (dd, J = 6.8 Hz, 5.2 Hz, 1H), 3.70-3.65 (m, 2H), 3.61 (dd, J = 16.4, 5.2 Hz, 1H), 3.42 (dd, J = 16.8, 7.2 Hz, 1H), 3.15 (m, 1H), 2.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 148.8, 138.5, 137.3, 134.5, 133.1, 129.4, 128.6, 128.1, 127.1, 126.8, 126.3, 117.9, 114.3, 55.0, 45.4, 42.2, 27.6. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{22}NO_2$, 328.1701; found, 328.1702.



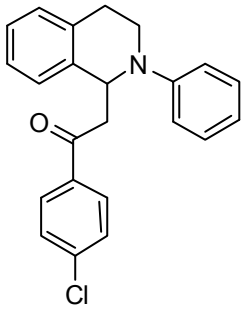
1-(4-methoxyphenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) ethanone (3b)

According to the general procedure, compound **3b** was obtained in 98% yield (4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 9.2 Hz, 1H), 7.83 (d, J = 9.2 Hz, 2H), 7.23-6.93 (m, 7H), 6.87 (d, J = 8.8 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 5.65 (dd, J = 7.2, 4.8 Hz, 1H), 3.84 (s, 3H), 3.65-3.62 (m, 2H), 3.55 (dd, J = 16.0, 5.2 Hz, 1H), 3.34 (dd, J = 16.4, 7.2 Hz, 1H), 3.11 (m, 1H), 2.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 163.5, 148.8, 138.7, 134.5, 130.6, 130.4, 129.3, 128.5, 127.2, 126.8, 126.2, 117.8, 114.2, 113.7, 55.5, 55.1, 44.9, 42.1, 27.6. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{24}NO_2$, 358.1807; found, 358.1807.



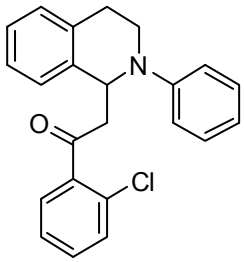
1-(3-methoxyphenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) ethanone (3c)

According to the general procedure, compound **3c** was obtained in 90% yield (4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.09 (m, 10H), 6.99 (d, J = 8.0 Hz, 2H), 6.78 (t, J = 7.2 Hz, 1H), 5.68 (dd, J = 6.8, 5.6 Hz, 1H), 3.85 (s, 3H), 3.71-3.65 (m, 2H), 3.60 (dd, J = 16.4, 5.2 Hz, 1H), 3.40 (dd, J = 16.8, 7.2 Hz, 1H), 3.14 (m, 1H), 2.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 159.8, 148.8, 138.6, 138.5, 134.5, 129.5, 129.4, 128.6, 127.1, 126.9, 126.3, 120.7, 119.7, 117.9, 114.3, 112.3, 55.4, 55.1, 45.5, 42.1, 27.5. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{24}NO_2$, 358.1807; found, 358.1806.



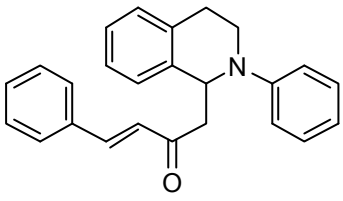
1-(4-chlorophenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) ethanone (3d)

According to the general procedure, compound **3d** was obtained in 82% yield (9 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.29-7.14 (m, 6H), 6.98 (d, J = 8.4 Hz, 2H), 6.79 (t, J = 7.6 Hz, 1H), 5.65 (dd, J = 6.8, 5.2 Hz, 1H), 3.70-3.63 (m, 2H), 3.57 (dd, J = 16.4, 4.8 Hz, 1H), 3.37 (dd, J = 16.4, 7.2 Hz, 1H), 3.14 (m, 1H), 2.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 148.7, 139.6, 138.3, 135.6, 134.5, 129.5, 129.4, 128.9, 128.6, 127.1, 126.9, 126.3, 118.1, 114.5, 55.3, 45.3, 42.2, 27.5. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{21}ClNO$, 362.1312; found, 362.1315.



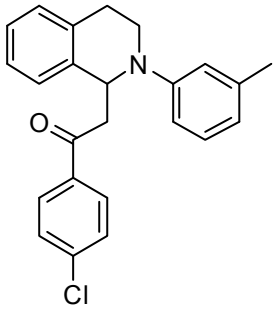
1-(2-chlorophenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) ethanone (3e)

According to the general procedure, compound **3e** was obtained in 75% yield (13 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.14 (m, 10H), 6.95 (d, J = 8.4 Hz, 2H), 6.80 (t, J = 7.2 Hz, 1H), 5.58 (t, J = 6.8 Hz, 1H), 3.67-3.56 (m, 3H), 3.42 (dd, J = 16.4, 6.8 Hz, 1H), 3.17 (m, 1H), 2.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 148.9, 139.6, 138.0, 134.6, 131.7, 130.3, 129.3, 129.2, 128.7, 127.1, 126.9, 126.3, 118.3, 114.9, 55.5, 49.7, 42.0, 27.0. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{21}ClNO$, 362.1312; found, 362.1310.



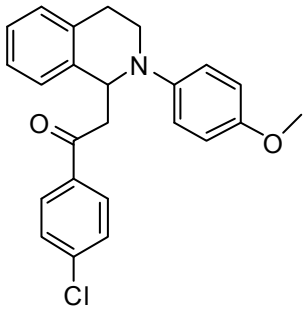
(E)-4-phenyl-1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) but-3-en-2-one (3f)

According to the general procedure, compound **3f** was obtained in 94% yield (4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.16 (m, 12H), 7.02 (d, J = 8.4 Hz, 2H), 6.80 (t, J = 7.2 Hz, 1H), 6.68 (d, J =16.4 Hz, 1H), 5.57 (dd, J = 6.8, 5.6 Hz, 1H), 3.72-3.63 (m, 2H), 3.33 (dd, J =16.0, 5.2 Hz, 1H), 3.14-3.08 (m, 2H), 2.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 148.8, 143.0, 138.4, 134.5, 134.4, 130.5, 129.4, 128.9, 128.6, 128.3, 127.1, 126.8, 126.6, 126.3, 118.1, 114.5, 55.3, 47.4, 42.1, 27.6. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{24}NO$, 354.1858; found, 354.1850.



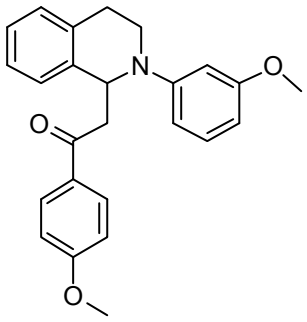
1-(4-chlorophenyl)-2-(2-m-tolyl-1,2,3,4-tetrahydroisoquinolin-1-yl) ethanone (3g)

According to the general procedure, compound **3g** was obtained in 87% yield (7 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.20-7.16 (m, 5H), 6.82-6.80 (m, 2H), 6.63 (d, J = 7.2 Hz, 1H), 5.65 (m, 1H), 3.71-3.54 (m, 3H), 3.37 (dd, J = 16.4, 7.2 Hz, 1H), 3.14 (m, 1H), 2.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 148.8, 139.5, 139.0, 138.3, 135.6, 134.5, 129.5, 129.2, 128.8, 128.6, 127.1, 126.9, 126.2, 119.1, 115.4, 111.8, 55.4, 45.2, 42.1, 27.6, 21.9. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{23}ClNO$, 376.1468; found, 376.1464.



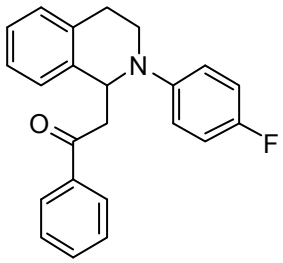
1-(4-chlorophenyl)-2-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3h)

According to the general procedure, compound **3h** was obtained in 90% yield (7 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.15-7.13 (m, 4H), 6.91 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 5.48 (t, J = 6.0 Hz, 1H), 3.73 (s, 3H), 3.56-3.49 (m, 3H), 3.23 (dd, J = 16.0, 6.4 Hz, 1H), 3.05 (m, 1H), 2.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 153.2, 143.5, 139.4, 138.3, 138.3, 135.7, 129.5, 128.9, 128.8, 127.0, 126.8, 126.2, 118.1, 114.7, 56.6, 55.6, 44.8, 42.8, 27.2. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{23}ClNO_2$, 392.1417; found, 392.1419.



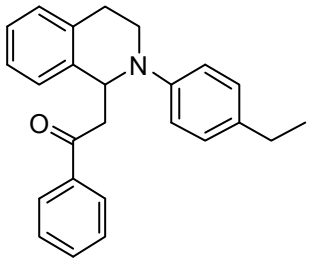
1-(4-methoxyphenyl)-2-(2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3i)

According to the general procedure, compound **3i** was obtained in 92% yield (5 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.8 Hz, 2H), 7.25-7.08 (m, 5H), 6.86 (d, J = 8.8 Hz, 2H), 6.60-6.53 (m, 2H), 6.31 (dd, J = 8.0, 2.0 Hz, 1H), 5.63 (dd, J = 7.2, 4.8 Hz, 1Hz), 3.83 (s, 3H), 3.77 (s, 3H), 3.64-3.59 (m, 2H), 3.49 (dd, J = 16.4, 4.8 Hz, 1H), 3.34 (dd, J = 16.4, 7.2 Hz, 1H), 3.10 (m, 1H), 2.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 163.5, 160.8, 150.2, 138.6, 134.5, 130.4, 130.4, 130.0, 128.5, 127.1, 126.8, 126.3, 113.7, 107.0, 103.0, 100.4, 55.5, 55.2, 45.0, 42.3, 27.7. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{26}NO_3$, 388.1913; found, 388.1910.



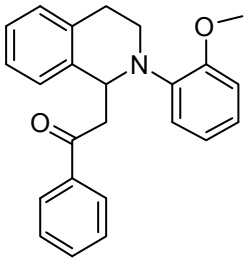
2-(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenyl ethanone (3j)

According to the general procedure, compound **3j** was obtained in 95% yield (6 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.29-7.19 (m, 4H), 6.95-6.93 (m, 4H), 5.60 (t, J = 6.0 Hz, 1H), 3.64-3.58 (m, 3H), 3.37 (dd, J = 16.8, 6.4 Hz, 1H), 3.12 (m, 1H), 2.89 (dt, J = 16.4, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 157.5, 155.2, 145.7, 138.3, 137.2, 134.3, 133.1, 128.8, 128.6, 128.1, 127.1, 126.8, 126.3, 116.7, 116.6, 115.8, 115.5, 55.9, 45.2, 42.6, 27.1. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{21}FNO$, 346.1607; found, 346.1603.



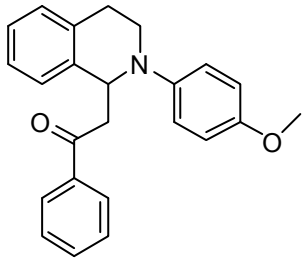
2-(2-(4-ethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenyle thanone (3k)

According to the general procedure, compound **3k** was obtained in 96% yield (4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.6 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.6 Hz, 1H), 7.14-7.09 (m, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.62 (t, J = 6.0 Hz, 1H), 3.64-3.54 (m, 3H), 3.35 (dd, J = 16.4, 7.2 Hz, 1H), 3.08 (m, 1H), 2.88 (dt, J = 16.0, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 146.9, 138.6, 137.3, 134.5, 134.1, 133.0, 128.6, 128.1, 127.1, 126.7, 126.2, 115.0, 55.4, 45.2, 42.2, 27.8, 27.5, 15.8. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{26}NO$, 356.2014; found, 356.2008.



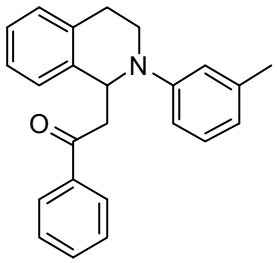
2-(2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (3l)

According to the general procedure, compound **3l** was obtained in 72% yield (8 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.15-7.12 (m, 4H), 6.93-6.76 (m, 4H), 5.59 (t, J = 5.6 Hz, 1H), 3.76 (s, 3H), 3.58-3.52 (m, 3H), 3.20 (dd, J = 15.6, 6.4 Hz, 1H), 3.07 (m, 1H), 2.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 139.1, 137.4, 134.1, 132.7, 129.1, 128.6, 128.3, 128.1, 128.1, 127.0, 126.4, 125.9, 123.3, 121.5, 120.8, 111.8, 55.6, 55.5, 44.8, 43.3, 28.0. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{24}NO_2$, 358.1807; found, 358.1804.



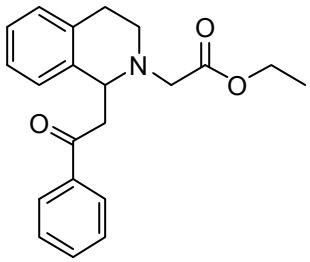
2-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (3m)

According to the general procedure, compound **3m** was obtained in 98% yield (4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.23-7.14 (m, 4H), 6.96 (d, J = 9.2 Hz, 2H), 6.82 (d, J = 9.2 Hz, 2H), 5.56 (t, J = 6.0 Hz, 1H), 3.76 (s, 3H), 3.62-3.56 (m, 3H), 3.33 (dd, J = 16.4, 6.8 Hz, 1H), 3.11 (m, 1H), 2.87 (dt, J = 16.0, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 153.0, 143.6, 138.6, 137.4, 134.3, 133.0, 128.8, 128.5, 128.1, 127.1, 126.7, 126.1, 117.8, 114.7, 56.2, 55.6, 44.9, 42.8, 27.3. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{24}NO_2$, 358.1807; found, 358.1804.



1-phenyl-2-(2-m-tolyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3n)

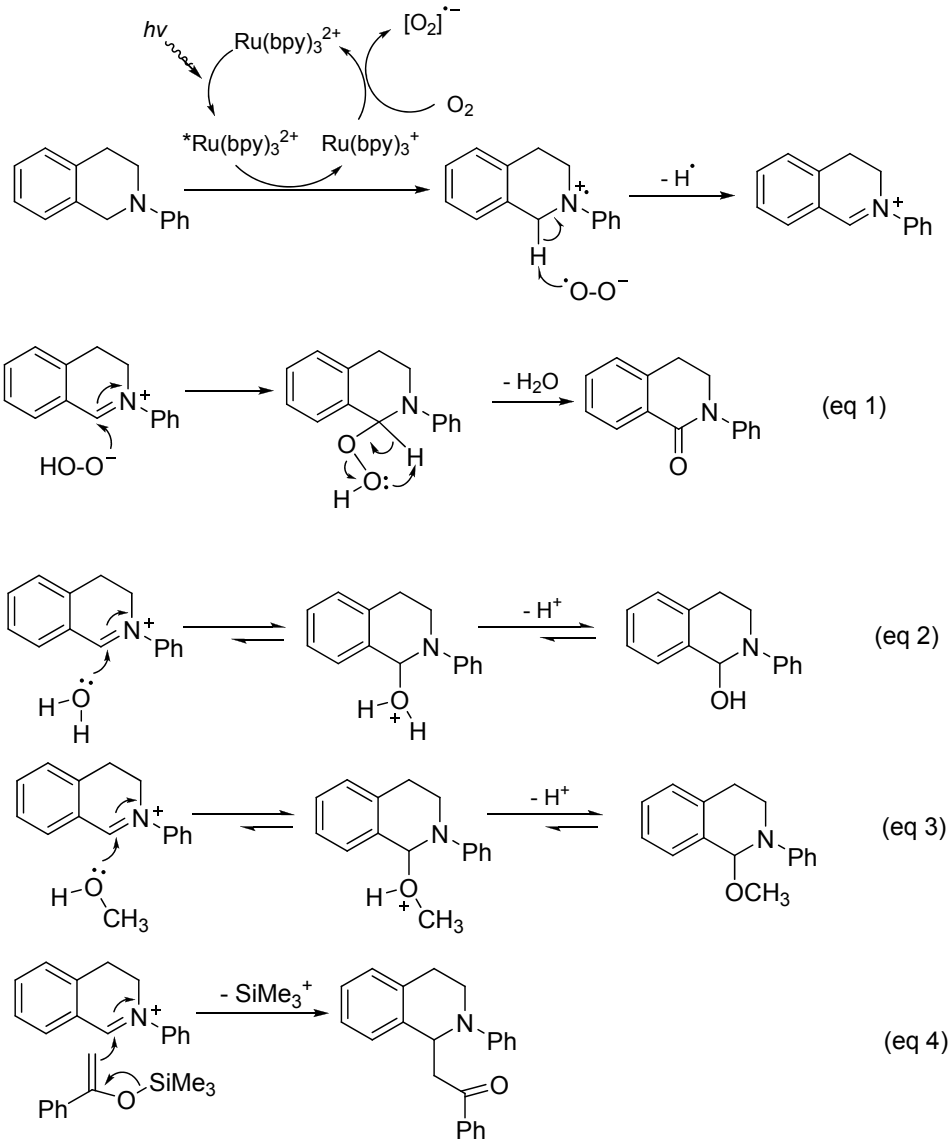
According to the general procedure, compound **3n** was obtained in 94% yield (4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.23-7.08 (m, 5H), 7.77 (d, J = 7.6 Hz, 1H), 7.76 (s, 1H), 6.57 (d, J = 7.6 Hz, 1H), 5.64 (dd, J = 6.8, 5.2 Hz, 1H), 3.66-3.60 (m, 2H), 3.55 (dd, J = 16.4, 5.2 Hz, 1H), 3.37 (dd, J = 16.4, 7.2 Hz, 1H), 3.09 (m, 1H), 2.90 (dt, J = 16.0, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 148.9, 139.0, 138.6, 137.3, 134.5, 133.1, 129.2, 128.6, 128.1, 127.2, 126.8, 126.2, 119.0, 115.2, 111.6, 55.2, 45.4, 42.2, 27.7, 22.0. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{24}NO$, 342.1858; found, 342.1856.



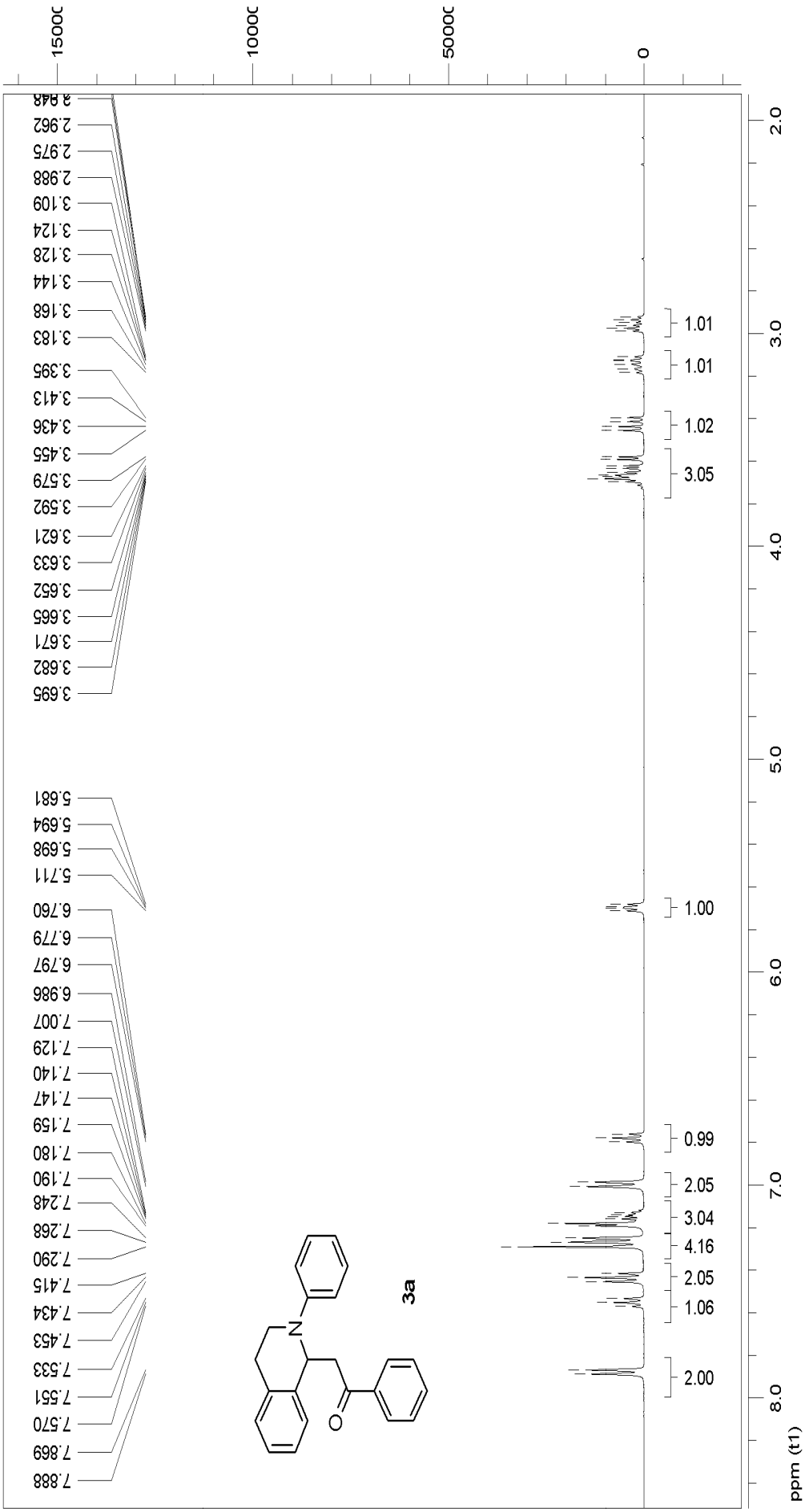
Ethyl-2-(1-(2-oxo-2-phenylethyl)-3,4-dihydroisoquinolin-2(1H)-yl)acetate (3o)

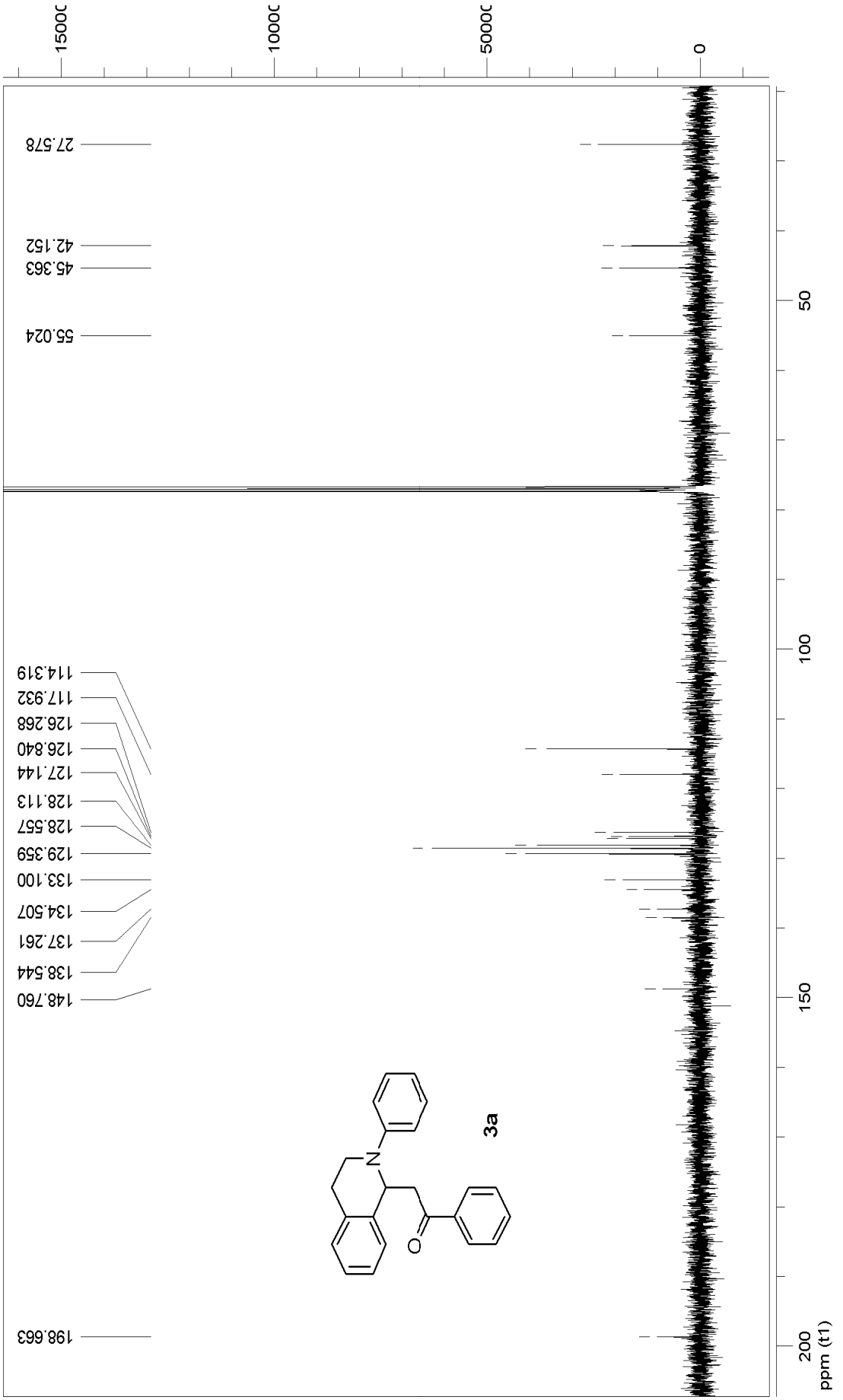
According to the general procedure, compound **3o** was obtained in 92% yield (4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.17-7.11 (m, 4H), 4.77 (t, J = 6.0 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.70 (dd, J = 16.8, 6.8 Hz, 1H), 3.57-3.43 (m, 2H), 3.34-3.21 (m, 2H), 3.09-2.96 (m, 2H), 2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 171.1, 138.2, 137.2, 134.0, 133.0, 128.9, 128.6, 128.2, 127.5, 126.4, 126.2, 60.6, 57.3, 56.0, 46.1, 45.0, 25.9, 14.2. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{21}H_{24}NO_3$, 338.1756; found, 338.1757.

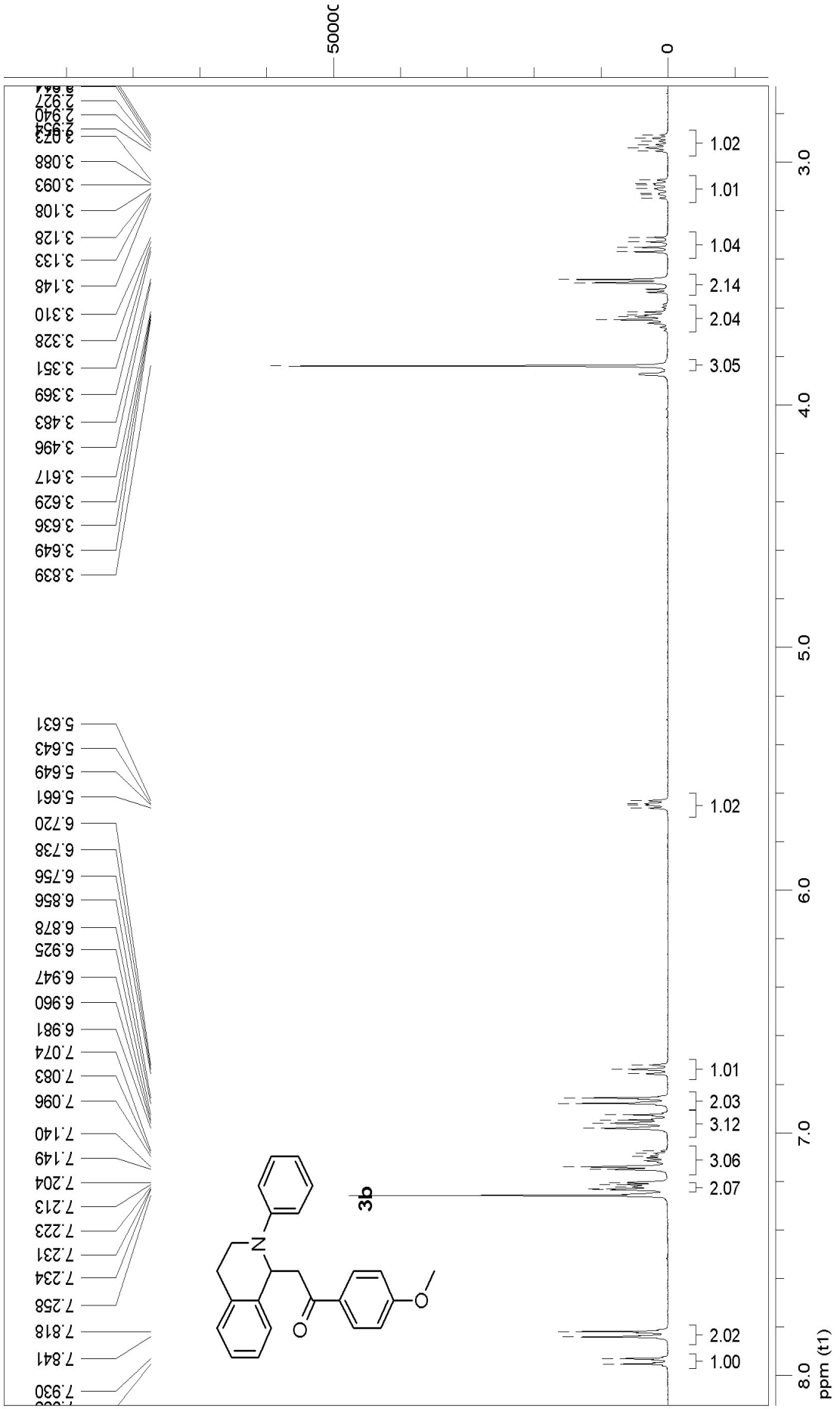
5. Plausible mechanism

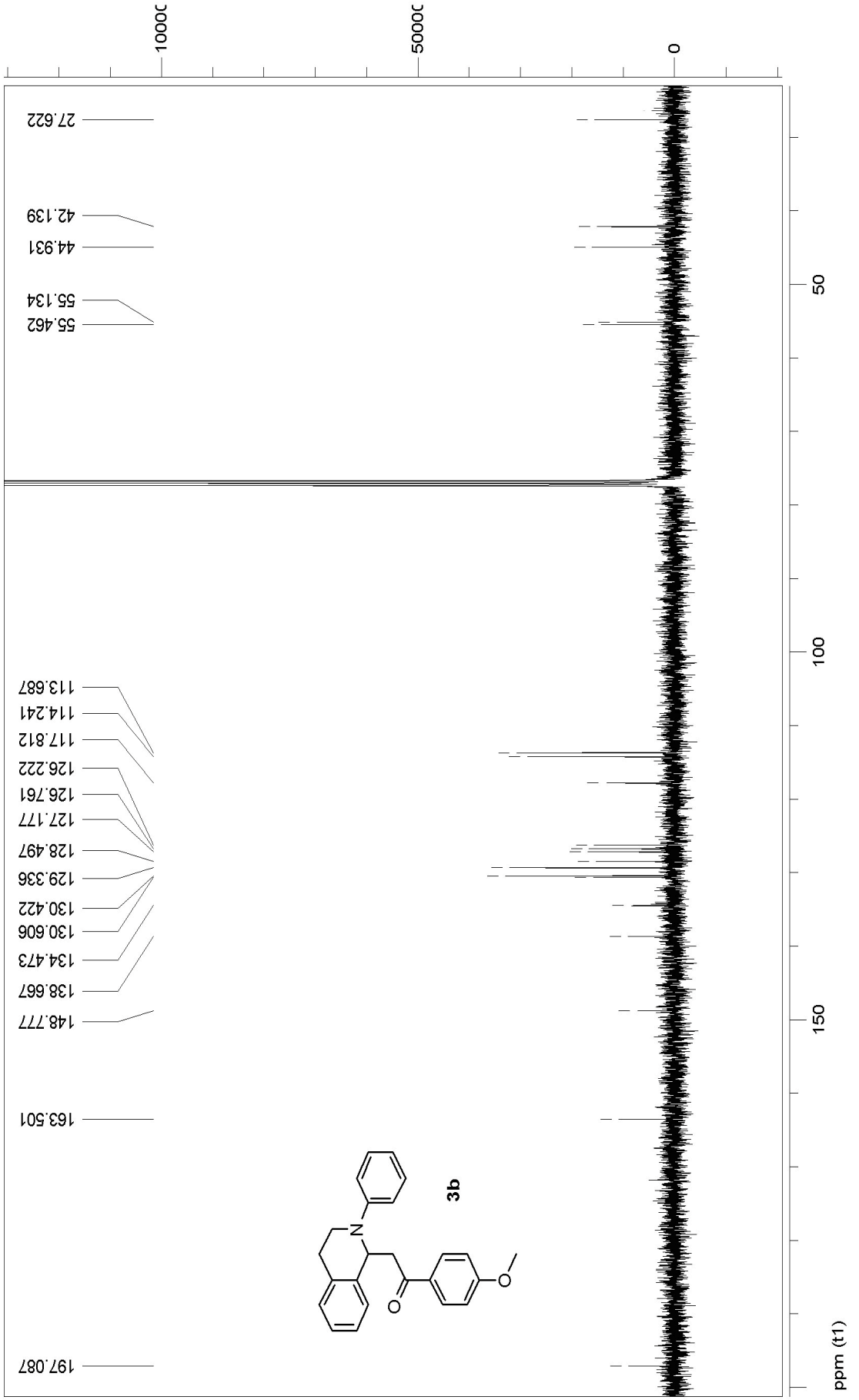


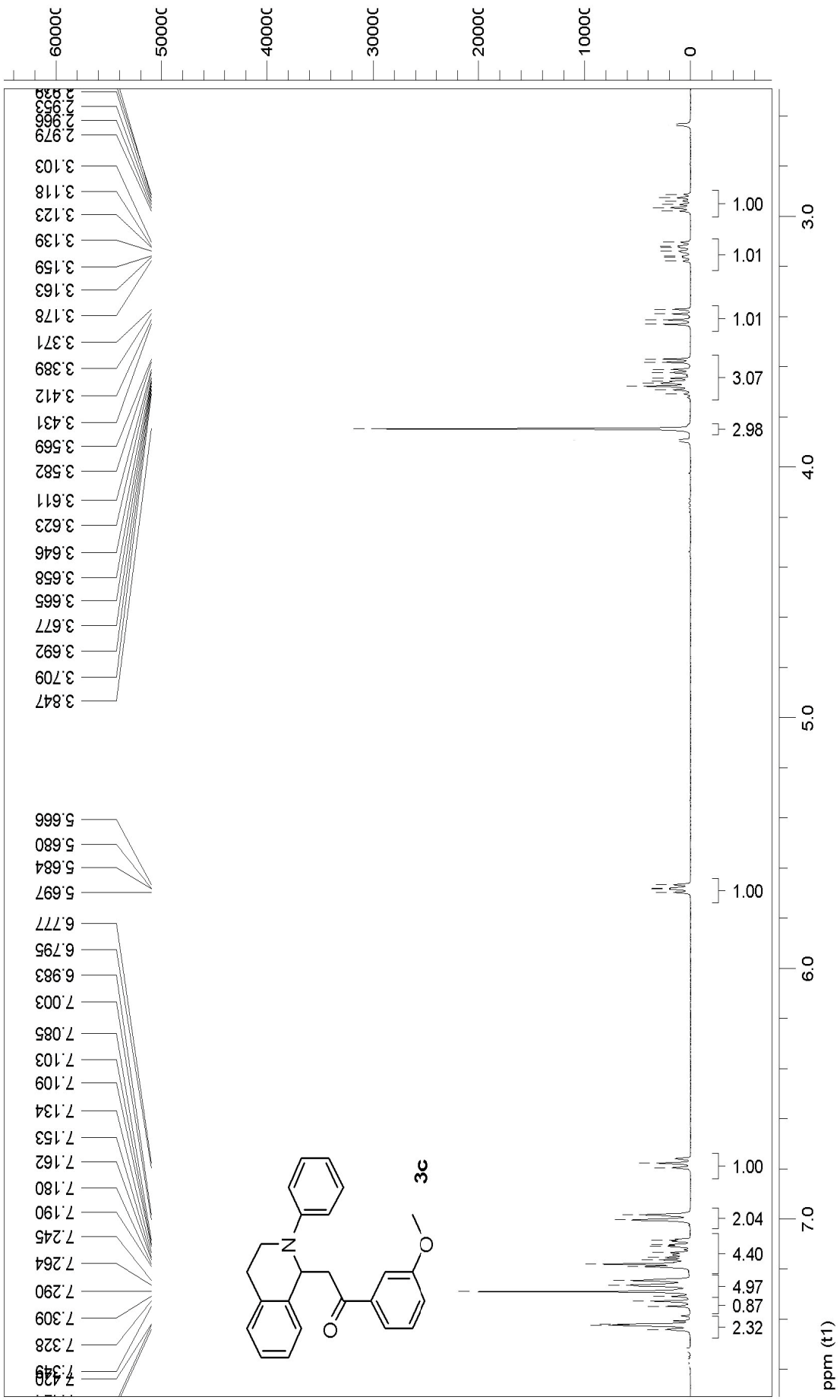
6. Copies of ^{1}H NMR and ^{13}C NMR for compounds 3a-3o

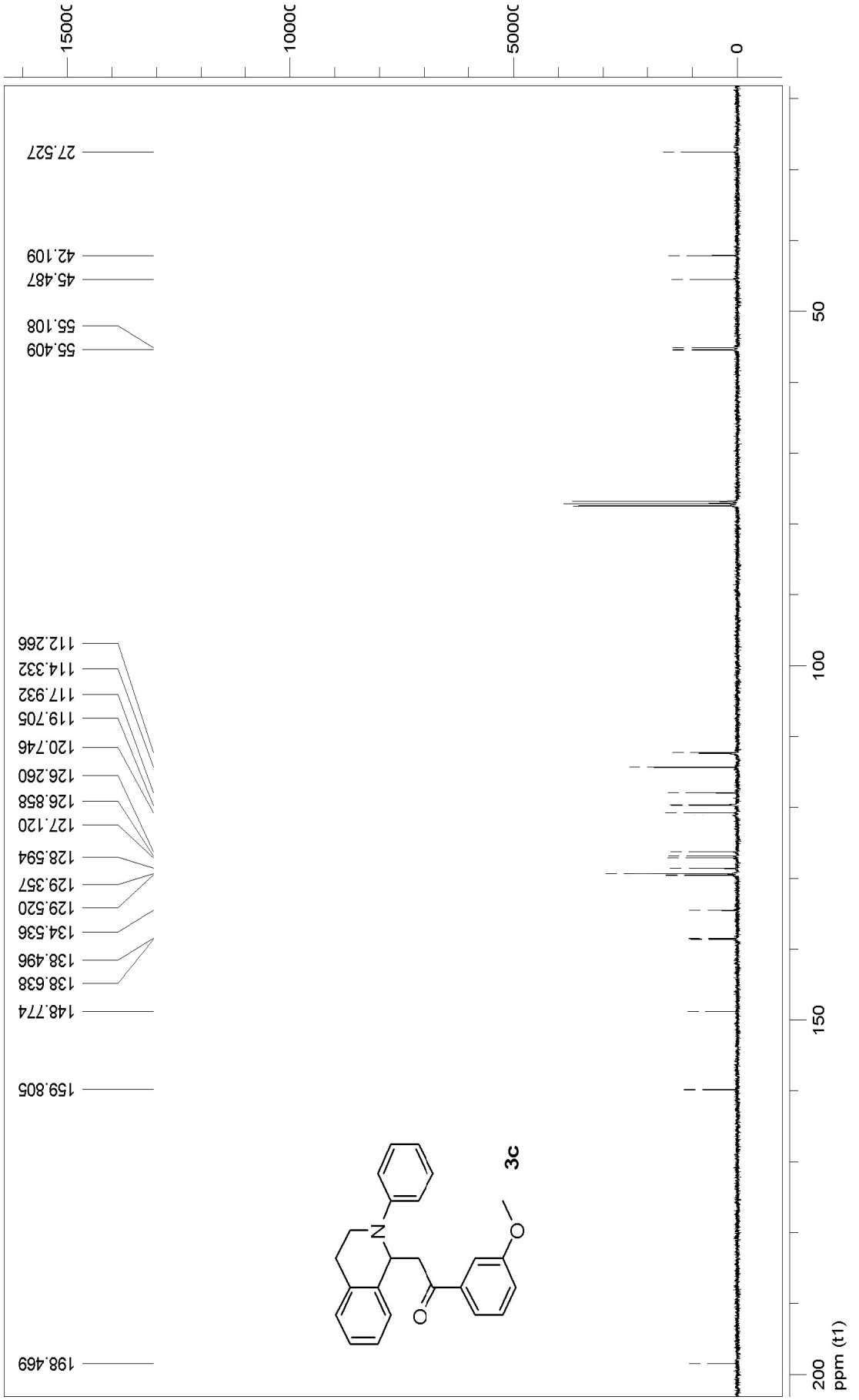


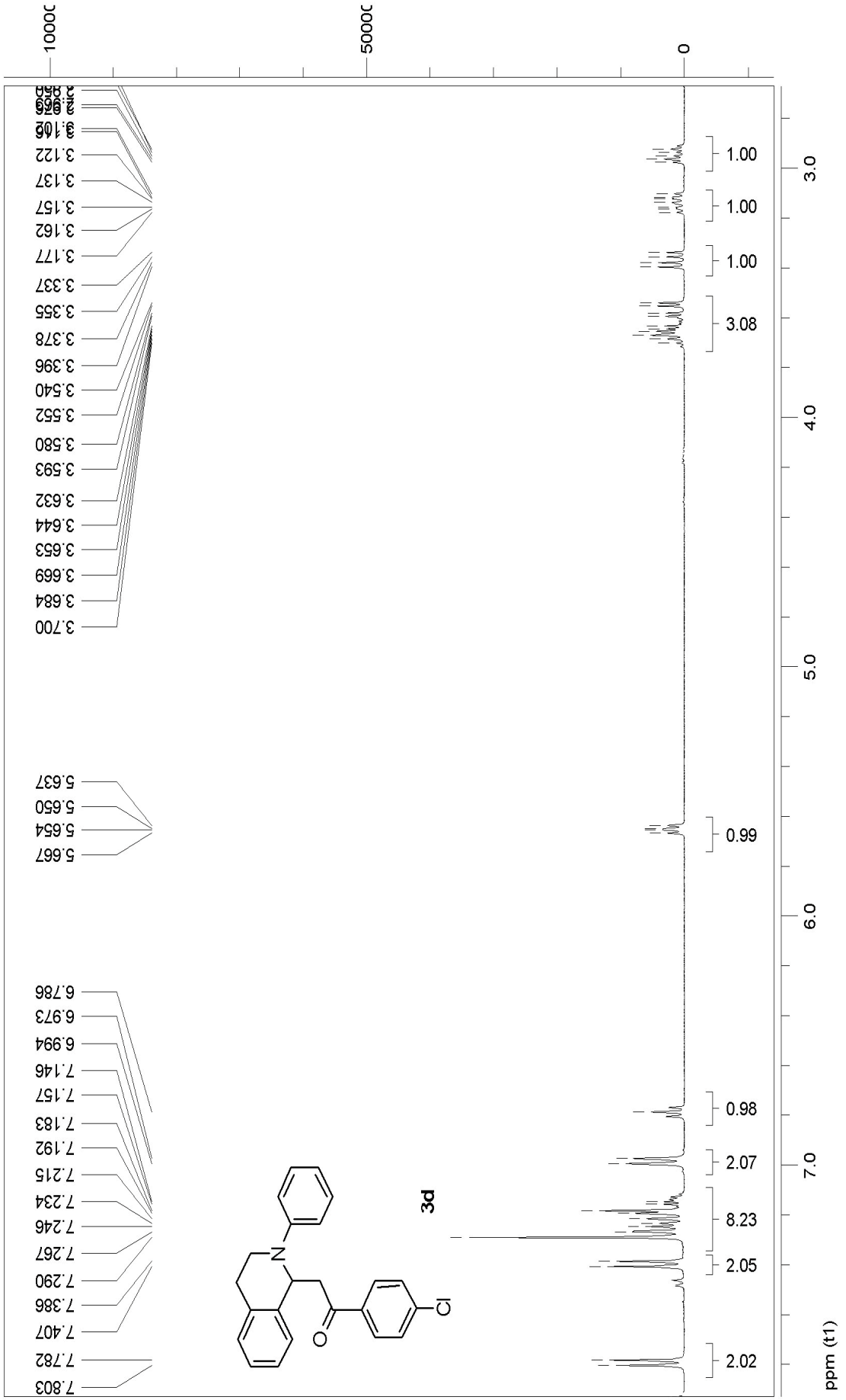


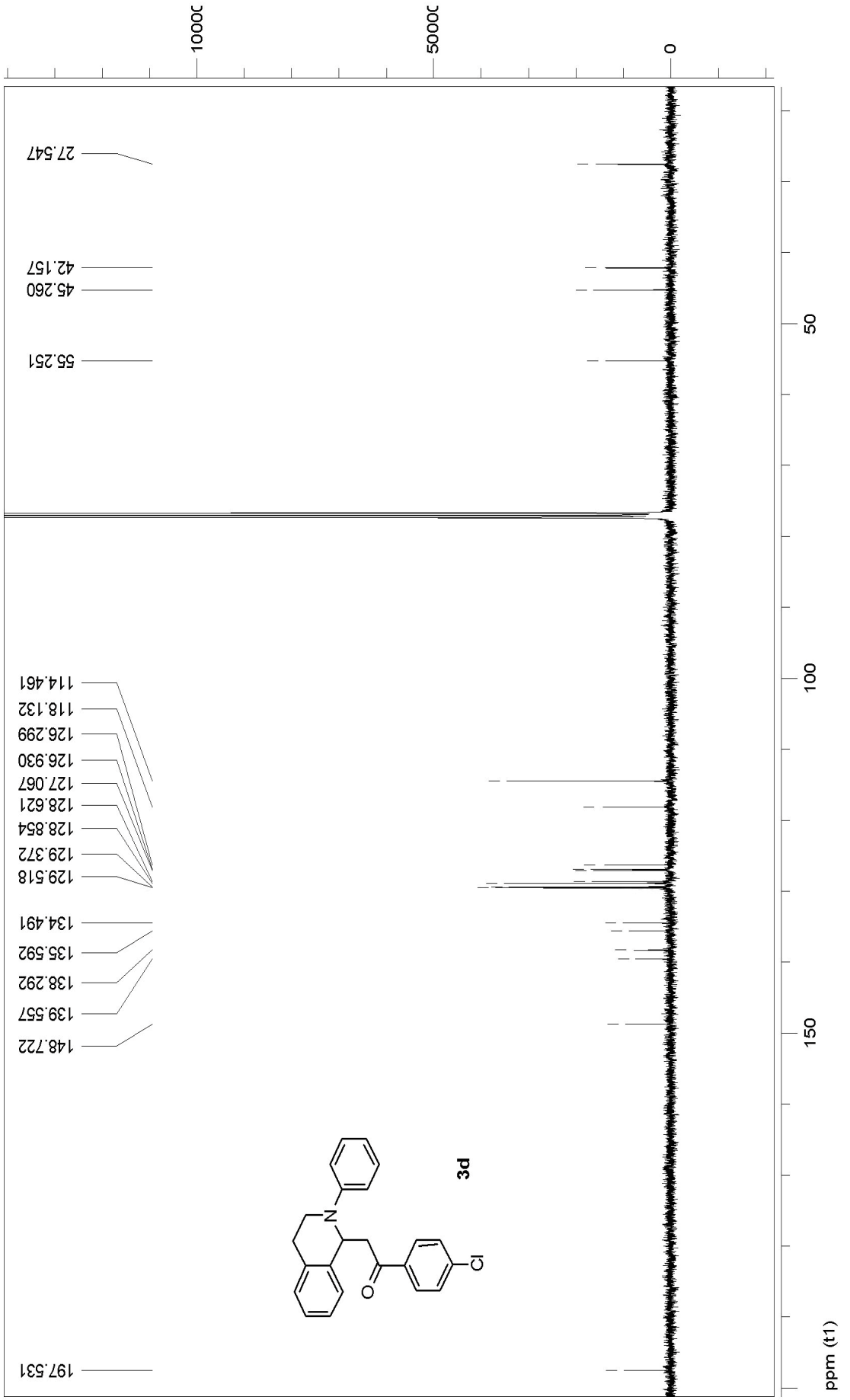


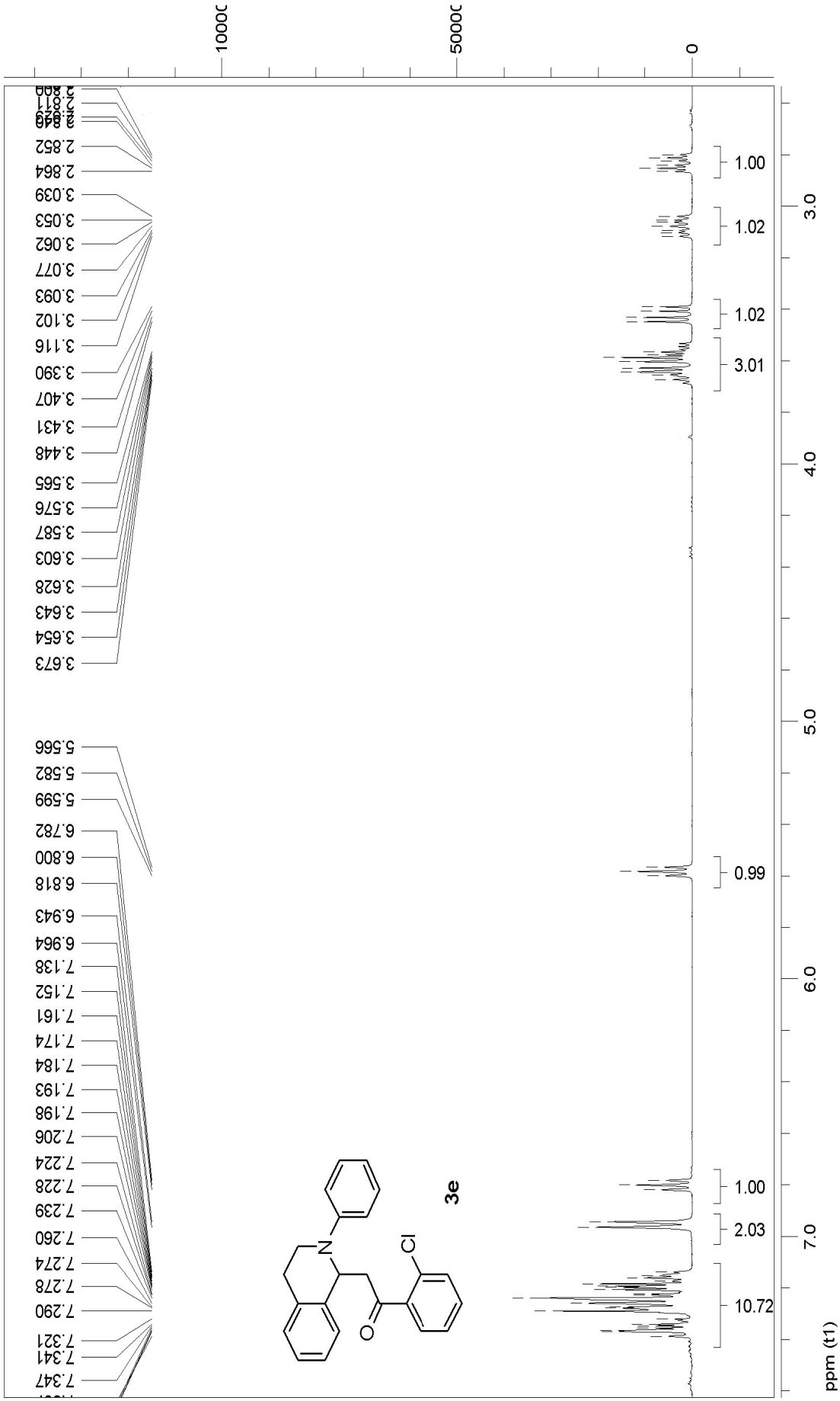








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