Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting Information

Highly Efficient and Selective Au(I)-Catalyzed Tandem Synthesis of Diversely Substituted Pyrrolo[1,2-*α*]quinolines in Aqueous Medium

Xin-Yuan Liu and Chi-Ming Che*

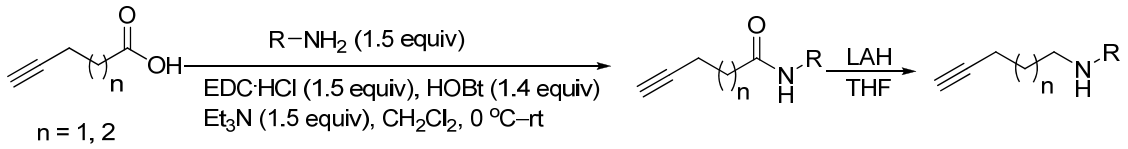
Department of Chemistry and Open Laboratory of Chemical Biology, Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong (P. R. China)

Table of Contents

Experimental Section

General Methods. All manipulations with air-sensitive reagents were carried out under a dry argon atmosphere. Unless otherwise stated, all commercial reagents were used without additional purification. Solvents were dried using standard methods and distilled before use. The $Au(PPh_3)Cl$,[S1] (IPr)AuCl,[S2] Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl,[S1,S3] Au[P(Cy)$_2$(2',4',6'-triisopropyl-*o*-biphenyl)]Cl,[S1,S3] and Au[P(*t*-Bu)$_2$(2',4',6'-triisopropyl-*o*-biphenyl)]Cl[S1,S3] catalysts were prepared following literature procedures. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on a Bruker DPX-300/400 spectrometer at 300/400 MHz for ^{1}H NMR and 75/100 MHz for ^{13}C NMR in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a Bio-RAD PTS-165 spectrometer; frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. Mass spectra were determined on a Finnigan MAT 95 mass spectrometer.

Typical Experimental Procedures for the Syntheses of Aminoalkyne Substrates

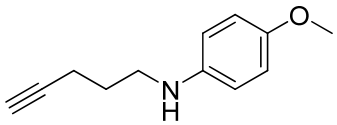


To a solution of EDC·HCl (2.3 g, 12 mmol) and HOBt (1.5 g, 11.2 mmol) in CH_2Cl_2 (20 mL) was added a solution of 4-pentynoic acid (785 mg, 8 mmol) or 5-hexynoic acid (897 mg, 8 mmol) in CH_2Cl_2 (10 mL) followed by addition of a solution of amines (12 mmol) in CH_2Cl_2 (10 mL). The mixture was cooled to 0 ^oC and Et_3N (1.2 mL, 12 mmol) was added dropwise. After being slowly warmed to room temperature and stirred overnight, the reaction mixture was diluted with CH_2Cl_2, washed successively with water, aqueous HCl 5%, saturated $NaHCO_3$, and brine, and dried over Na_2SO_4. Evaporation of the solvent followed by column chromatography on silica gel with EtOAc/Hx (1:2) as eluent afforded substituted 4-pentynoylamide or 5-hexynoylamide in good to excellent yields.

To a solution of substituted 4-pentynoylamide or 5-hexynoylamide (4 mmol) in THF (30 mL) was slowly added lithium aluminum hydride (642 mg, 16 mmol) at 0 ^oC. The reaction mixture was slowly warmed to room temperature and stirred for 24-30 h, and then quenched with Baechströms reagent ($Na_2SO_4 \cdot 10H_2O$) and stirred for 30 min. After filtration, the filtrate was evaporated and chromatographed on silica gel column with EtOAc/Hx (1:20) as eluent to afford substituted aminoalkynes in good to excellent yields.

***N*-(4-methoxyphenyl)pent-4-ynamide**[S4] and ***N*-benzylpent-4-yn-1-amine (1K)**[S5] were prepared following literature procedures.

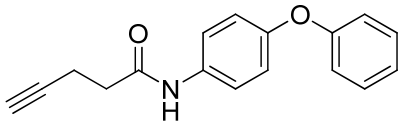
4-Methoxy-*N*-(pent-4-ynyl)aniline (1A):



1A

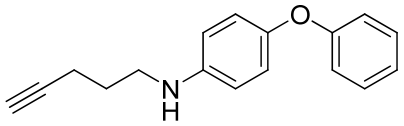
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 6.83 (m, 2H), 6.63 (m, 2H), 3.78 (s, 3H), 3.52 (br, 1H), 3.23 (t, J = 6.8 Hz, 2H), 2.34 (m, 2H), 2.06 (t, J = 2.6 Hz, 1H), 1.85 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 152.0, 142.5, 114.9, 114.1, 83.9, 69.1, 55.8, 43.7, 28.1, 16.2. IR (film): ν 3305, 3056, 2950, 1603, 1509 cm^{-1}. MS: *m/z* (% relative intensity) 189(M^+, 69), 188(17), 174(9), 136(100); HRMS: *m/z* calcd for $C_{12}H_{15}NO$ (M^+) 189.1154, found 189.1145.

***N*-(4-phenoxyphenyl)pent-4-ynamide:**



^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 8.26 (s, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 6.96 (m, 4H), 2.59 (s, 4H), 2.04 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 169.8, 157.4, 153.6, 133.3, 129.8, 123.2, 122.2, 119.5, 118.5, 82.8, 69.7, 36.0, 14.9. IR (film): ν 3434, 3304, 3056, 1684, 1590, 1509 cm^{-1}. MS: *m/z* (% relative intensity) 265(M^+, 61), 186(12), 185(100), 108(29); HRMS: *m/z* calcd for $C_{17}H_{15}NO_2$ (M^+) 265.1103, found 265.1105.

***N*-(pent-4-ynyl)-4-phenoxyaniline (1B):**

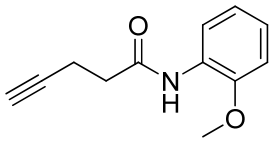


1B

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.34 (m, 2H), 7.02 (m, 5H), 6.66 (m, 2H), 3.72 (br, 1H), 3.29 (t, J = 6.8 Hz, 2H), 2.37 (m, 2H), 2.08 (t, J = 2.6 Hz, 1H), 1.88 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.2, 147.6, 144.9, 129.6, 122.0, 121.4, 117.1, 113.8, 83.8, 69.2, 43.4, 28.1, 16.2. IR (film): ν 3299, 3056, 1597, 1509, 1484 cm^{-1}. MS: *m/z* (%

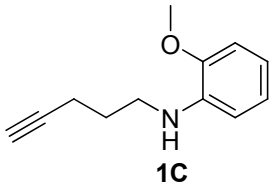
relative intensity) 251(M^+, 100), 250(23), 198(100), 157(11); HRMS: *m/z* calcd for $C_{17}H_{17}NO$ (M^+) 251.1310, found 251.1308.

***N*-(2-methoxyphenyl)pent-4-ynamide:**



^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 8.31 (d, J = 7.0 Hz, 1H), 7.96 (s, 1H), 6.89 (m, 3H), 3.77 (s, 3H), 2.53 (s, 4H), 2.02 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 169.0, 147.9, 127.5, 123.8, 120.9, 119.9, 110.0, 82.9, 69.5, 55.6, 36.4, 14.7. IR (film): ν 3421, 3305, 2842, 1684, 1603, 1522, 1484 cm^{-1}. MS: *m/z* (% relative intensity) 203(M^+, 66), 123(100), 108(37); HRMS: *m/z* calcd for $C_{12}H_{13}NO_2$ (M^+) 203.0946, found 203.0939.

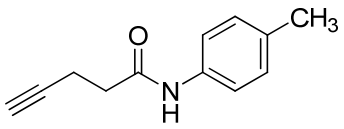
2-Methoxy-*N*-(pent-4-ynyl)aniline (1C):



1C

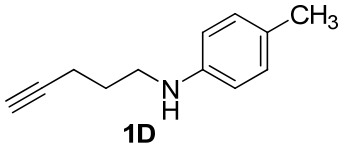
^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.03 (m, 1H), 6.89 (m, 1H), 6.80 (m, 2H), 4.42 (br, 1H), 3.94 (s, 3H), 3.39 (t, J = 6.9 Hz, 2H), 2.43 (m, 2H), 2.14 (t, J = 2.6 Hz, 1H), 1.97 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 146.9, 138.3, 121.5, 116.5, 109.8, 109.6, 83.9, 69.2, 55.5, 42.5, 28.3, 16.3. IR (film): ν 3305, 2950, 1597, 1516, 1354 cm^{-1}. MS: *m/z* (% relative intensity) 189(M^+, 21), 153(55), 136(53), 77(100); HRMS: *m/z* calcd for $C_{12}H_{15}NO$ (M^+) 189.1154, found 189.1159.

***N*-p-tolylpent-4-ynamide:**



^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 8.00 (s, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 2.56 (s, 4H), 2.30 (s, 3H), 2.03 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 169.5, 135.2, 134.0, 129.4, 120.3, 82.9, 69.6, 36.1, 20.8, 14.8. IR (film): ν 3426, 3305, 3064, 2988, 1684, 1603, 1516 cm^{-1}. MS: *m/z* (% relative intensity) 187(M^+, 30), 153(15), 107(100), 106(34); HRMS: *m/z* calcd for $C_{12}H_{13}NO$ (M^+) 187.0997, found 187.0999.

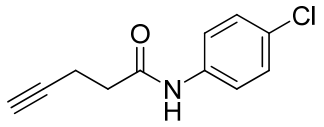
4-Methyl-*N*-(pent-4-ynyl)aniline (1D):



1D

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.13 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 3.68 (br, 1H), 3.34 (t, J = 6.8 Hz, 2H), 2.43 (m, 2H), 2.39 (s, 3H), 2.14 (t, J = 2.7 Hz, 1H), 1.92 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 146.1, 129.9, 126.5, 113.1, 84.0, 69.2, 43.2, 28.2, 20.5, 16.3. IR (film): ν 3305, 3056, 2988, 1611, 1509, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 173(M^+, 39), 172(15), 120(100); HRMS: *m/z* calcd for $C_{12}H_{15}N$ (M^+) 173.1204, found 173.1197.

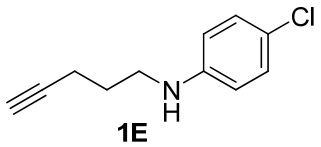
***N*-(4-chlorophenyl)pent-4-ynamide:**



^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 9.33 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 2.57 (m, 4H), 2.35 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 205.6, 169.4, 138.1, 128.6, 120.7, 83.0, 69.5, 35.7, 14.1. IR (film): ν 3421, 3299, 3050, 1692,

1590, 1509 cm^{-1}. MS: *m/z* (% relative intensity) 209(M^++2, 8), 207(M^+, 24), 129(30), 127(100); HRMS: *m/z* calcd for $C_{11}H_{10}NOCl$ (M^+) 207.0451, found 207.0449.

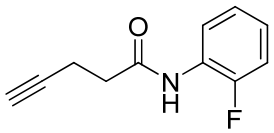
4-Chloro-*N*-(pent-4-ynyl)aniline (1E):



1E

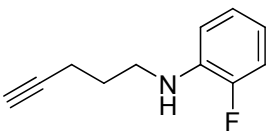
^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.14 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.8 Hz, 2H), 3.78 (br, 1H), 3.22 (t, J = 6.8 Hz, 2H), 2.32 (m, 2H), 2.09 (t, J = 2.6 Hz, 1H), 1.83 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 146.9, 129.1, 121.6, 113.9, 83.8, 69.4, 42.9, 27.9, 16.2. IR (film): ν 3305, 3064, 2983, 1603, 1495, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 195(M^++2, 12), 193(M^+, 34), 142(32), 140(100); HRMS: *m/z* calcd for $C_{11}H_{12}NCl$ (M^+) 193.0658, found 193.0653.

***N*-(2-Fluorophenyl)pent-4-ynamide:**



^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 8.13 (m, 2H), 7.01 (m, 3H), 2.56 (m, 4H), 2.05 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 169.9, 154.1, 151.7, 124.7 (d, J_{CF} = 7.5 Hz), 124.4, 124.3, 122.6, 114.9 (d, J_{CF} = 19.1 Hz), 82.7, 69.7, 36.0, 14.6. IR (film): ν 3434, 3305, 1698, 1617, 1522, 1457 cm^{-1}. MS: *m/z* (% relative intensity) 191(M^+, 17), 112(7), 111(100); HRMS: *m/z* calcd for $C_{11}H_{10}FNO$ (M^+) 191.0746, found 191.0752.

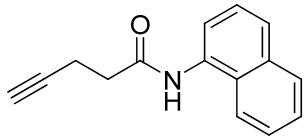
2-Fluoro-*N*-(pent-4-ynyl)aniline (1F):



1F

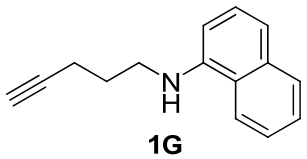
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.02 (m, 2H), 6.77 (m, 1H), 6.68 (m, 1H), 4.04 (br, 1H), 3.34 (s, 2H), 2.37 (m, 2H), 2.07 (t, J = 2.7 Hz, 1H), 1.89 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 152.8, 150.4, 136.6 (d, J_{CF} = 11.4 Hz), 124.6 (d, J_{CF} = 3.5 Hz), 116.5 (d, J_{CF} = 6.9 Hz), 114.4 (d, J_{CF} = 18.4 Hz), 111.9 (d, J_{CF} = 3.3 Hz), 83.5, 69.2, 42.3, 28.0, 16.0. IR (film): ν 3305, 2950, 1617, 1516, 1335 cm^{-1}. MS: *m/z* (% relative intensity) 177(M^+, 27), 153(8), 124(100); HRMS: *m/z* calcd for $C_{11}H_{12}FN$ (M^+) 177.0954, found 177.0946.

***N*-(naphthanlen-1-yl)pent-4-ynamide:**



^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 8.15 (s, 1H), 7.84 (t, J = 9.8 Hz, 2H), 7.74 (d, J = 7.4 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.40 (m, 3H), 2.62 (m, 4H), 2.10 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 170.3, 134.0, 132.2, 128.6, 127.6, 126.2, 126.1, 125.9, 125.6, 121.6, 121.2, 83.1, 69.8, 36.0, 15.0. IR (film): ν 3426, 3305, 3042, 2929, 1684, 1522, 1495 cm^{-1}. MS: *m/z* (% relative intensity) 223(M^+, 19), 153(82), 143(70), 77(100); HRMS: *m/z* calcd for $C_{15}H_{13}NO$ (M^+) 223.0997, found 223.0997.

***N*-(pent-4-ynyl)naphthalene-1-amine (1G):**

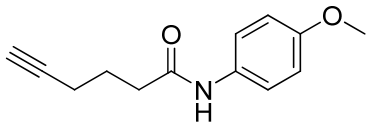


1G

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.96 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.56 (m, 3H), 7.42 (d, J = 8.1 Hz, 1H), 6.75 (d, J = 7.4 Hz, 1H), 4.53 (br, 1H), 3.47 (t, J = 6.8 Hz, 2H), 2.47 (m, 2H), 2.24 (t, J = 2.6 Hz, 1H), 2.03 (m, 2H). ^{13}C NMR ($CDCl_3$,

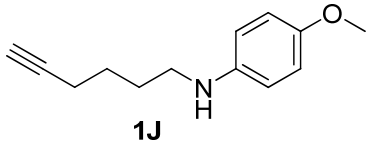
TMS, 75 MHz): δ 143.5, 134.5, 128.8, 126.9, 125.9, 124.8, 123.6, 120.1, 117.5, 104.4, 84.2, 69.5, 43.3, 27.9, 16.6. IR (film): ν 3305, 3064, 2988, 1576, 1522, 1484 cm^{-1}. MS: *m/z* (% relative intensity) 209(M^+, 96), 208(51), 156(100), 129(42); HRMS: *m/z* calcd for $C_{15}H_{15}N$ (M^+) 209.1204, found 209.1197.

***N*-(4-methoxyphenyl)hex-5-ynamide:**



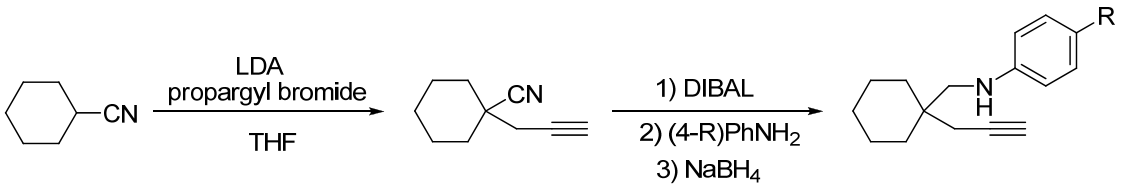
^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.86 (br, 1H), 7.38 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 3.75 (s, 3H), 2.44 (t, J = 7.3 Hz, 2H), 2.26 (m, 2H), 1.99 (t, J = 2.6 Hz, 1H), 1.90 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 170.8, 156.4, 131.0, 122.0, 114.0, 83.5, 69.3, 55.4, 35.7, 24.1, 17.9. IR (film): ν 3426, 3305, 3056, 1684, 1590, 1509, 1408 cm^{-1}. MS: *m/z* (% relative intensity) 217(M^+, 31), 153(21), 123(100), 108(61); HRMS: *m/z* calcd for $C_{13}H_{15}NO_2$ (M^+) 217.1103, found 217.1102.

***N*-(hex-5-ynyl)-4-methoxyaniline (1J):**



1J

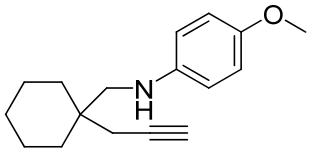
^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.82 (m, 2H), 6.59 (m, 2H), 3.76 (s, 3H), 3.39 (br, 1H), 3.09 (t, J = 6.7 Hz, 2H), 2.26 (m, 2H), 2.06 (t, J = 2.6 Hz, 1H), 1.69 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 152.0, 142.8, 114.9, 114.0, 84.3, 68.9, 55.7, 44.4, 28.7, 26.1, 18.3. IR (film): ν 3303, 3052, 2934, 2864, 1707, 1507 cm^{-1}. MS: *m/z* (% relative intensity) 203(M^+, 47), 202(14), 136(100); HRMS: *m/z* calcd for $C_{13}H_{17}NO$ (M^+) 203.1310, found 203.1297.



To a solution of diisopropylamine (1821 mg, 18 mmol) in THF (25 mL) was added dropwise *n*BuLi (7.2 mL, 2.5 M solution in hexanes) at 0 ^{o}C under Ar atmosphere. The resulting solution was stirred for 30 min before cooling to -78 ^{o}C. To this freshly prepared LDA solution, a solution of cyanocyclohexane (1635 mg, 15 mmol) was added dropwise at -78 ^{o}C and stirred for 1 h at -78 ^{o}C followed by the addition of propargyl bromide (1840 µL, 80 wt% solution in toluene). The reaction mixture was stirred for 1 h at -78 ^{o}C and then warmed to room temperature. Saturated aq NH_4Cl (30 mL) was added, followed by addition of diethyl ether (60 mL) and extraction with diethyl ether (60 mL × 3). The organic layer was dried (Na_2SO_4), filtered, evaporated, and purified by a silica gel chromatography (EtOAc/Hx, 1:50) to afford propargylated cyclohexanenitrile (1.98 g).[S5] To a solution of the above obtained nitrile (441 mg, 3 mmol) in diethyl ether (30 mL) was added dropwise diisobutylaluminum hydride (6 mL, 1.0 M solution in toluene) under Ar atmosphere at -78 ^{o}C. After stirring for 5 h at -30 to -78 ^{o}C, MeOH (6 mL) was added, followed by addition of aromatic amines (4.5 mmol). The reaction mixture was warmed to room temperature and heated at 60 ^{o}C for 8 h. Rubber septum was removed and sodium borohydride (378 mg, 15 mmol) was added. The reaction mixture was stirred overnight at room temperature. The organic solvent was removed under reduced pressure and the residue was re-dissolved in dichloromethane (60 mL). The resulting slurry was washed with saturated aqueous sodium bicarbonate solution, water and brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed and the

residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:40) to give the desired product in good yield.[S5]

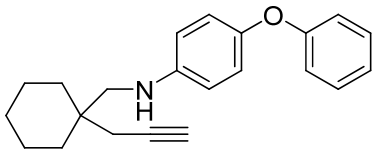
4-Methoxy-*N*-((1-(prop-2-ynyl)cyclohexyl)methyl)aniline (1H):



1H

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.82 (m, 2H), 6.68 (m, 2H), 3.77 (s, 3H), 3.51 (br, 1H), 3.12 (s, 2H), 2.34 (d, J = 2.6 Hz, 2H), 2.08 (t, J = 2.7 Hz, 1H), 1.51 (m, 10H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 151.9, 143.5, 114.9, 114.3, 82.0, 70.7, 55.8, 52.5, 37.0, 33.4, 26.1, 25.8, 21.7. IR (film): ν 3070, 2929, 2855, 1603, 1509 cm^{-1}. MS: *m/z* (% relative intensity) 257(M^+, 100), 256(100), 214(70), 201(43); HRMS: *m/z* calcd for $C_{17}H_{23}NO$ (M^+) 257.1780, found 257.1770.

4-Phenoxy-*N*-((1-(prop-2-ynyl)cyclohexyl)methyl)aniline (1I):



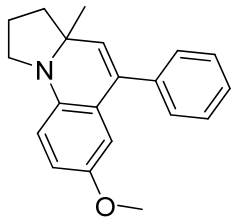
1I

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.37 (m, 2H), 7.05 (m, 5H), 6.76 (d, J = 8.9 Hz, 2H), 3.79 (br, 1H), 3.22 (s, 2H), 2.41 (d, J = 2.7 Hz, 2H), 2.16 (t, J = 2.7 Hz, 1H), 1.57 (m, 10H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.3, 147.4, 146.0, 129.6, 122.0, 121.4, 117.1, 114.0, 82.0, 71.0, 52.2, 37.1, 33.4, 26.2, 25.9, 21.8. IR (film): ν 2929, 2848, 1603, 1516, 1484 cm^{-1}. MS: *m/z* (% relative intensity) 319(M^+, 100), 318(67), 262(53), 153(58); HRMS: *m/z* calcd for $C_{22}H_{25}NO$ (M^+) 319.1936, found 319.1927.

General Procedure for Au(I)-Catalyzed Tandem Synthesis of Diversely Substituted Pyrrolo[1,2-α]quinolines in Water

A mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.005 or 0.002 mmol), $AgSbF_6$ (0.005 or 0.002 mmol), alkyne (0.4 or 0.3 mmol) and 1,4-aminoalkyne (0.1 mmol) in water (0.4 mL) was stirred at 75 ^oC for 24-45 h under Ar atmosphere. Water was removed under reduced pressure, and the residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:100) to give the desired product.

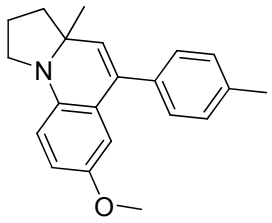
7-Methoxy-3a-methyl-5-phenyl-1,2,3,3a-tetrahydropyrrolo[1,2-α]quinoline (3Aa):



3Aa

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.37 (m, 5H), 6.77 (dd, J = 8.6, 2.9 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 6.47 (d, J = 7.5 Hz, 1H), 5.73 (s, 1H), 3.67 (s, 3H), 3.42 (m, 2H), 2.05 (m, 4H), 1.13 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 150.7, 139.9, 138.3, 135.8, 129.3, 129.1, 128.2, 127.3, 123.4, 114.1, 112.9, 112.8, 60.9, 55.9, 45.9, 38.0, 22.6, 20.7. IR (film): ν 2969, 2834, 1603, 1563, 1489, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 291(M^+, 1), 277(12), 276(100), 153(42); HRMS: *m/z* calcd for $C_{20}H_{21}NO$ (M^+) 291.1623, found 291.1615.

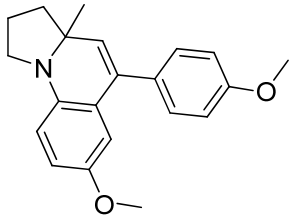
7-Methoxy-3a-methyl-5-*p*-tolyl-1,2,3,3a-tetrahydropyrrolo[1,2-α]quinoline (3Ab):



3Ab

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.26 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.76 (dd, J = 8.6, 2.9 Hz, 1H), 6.63 (d, J = 2.5 Hz, 1H), 6.48 (s, 1H), 5.71 (s, 1H), 3.67 (s, 3H), 3.43 (s, 2H), 2.40 (s, 3H), 2.03 (m, 4H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 150.7, 138.2, 137.0, 136.9, 135.6, 129.1, 129.0, 128.8, 123.5, 114.1, 112.9, 112.8, 60.9, 55.9, 45.8, 38.0, 22.5, 21.2, 20.7. IR (film): ν 2961, 2927, 1491, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 305(M^+, 4), 291(20), 290(100), 247(10); HRMS: *m/z* calcd for $C_{21}H_{23}NO$ (M^+) 305.1780, found 305.1782.

7-Methoxy-5-(4-methoxyphenyl)-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ac):

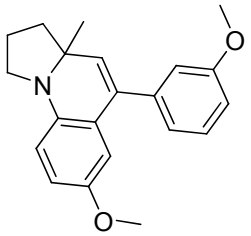


3Ac

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.28 (m, 2H), 6.92 (m, 2H), 6.75 (dd, J = 8.6, 2.9 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 6.45 (d, J = 8.5 Hz, 1H), 5.68 (s, 1H), 3.85 (s, 3H), 3.66 (s, 3H), 3.41 (m, 2H), 2.02 (m, 4H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 158.9, 150.7, 138.3, 135.2, 132.3, 130.2, 128.9, 123.6, 114.1, 113.6, 112.8, 112.7, 60.8, 55.9, 55.3, 45.8, 38.0, 22.4, 20.7. IR (film): ν 2963, 2842, 1603, 1503, 1416 cm^{-1}. MS: *m/z* (% relative intensity) 321(M^+, 5), 307(16), 306(100), 153(33); HRMS: *m/z* calcd for

$C_{21}H_{23}NO_2$ (M^+) 321.1729, found 321.1726.

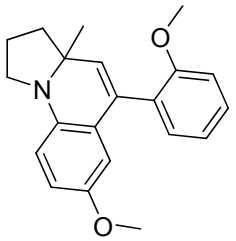
7-Methoxy-5-(3-methoxyphenyl)-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ad):



3Ad

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.27 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.88 (m, 2H), 6.74 (dd, J = 8.6, 2.9 Hz, 1H), 6.60 (d, J = 2.8 Hz, 1H), 6.44 (d, J = 8.6 Hz, 1H), 5.70 (s, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 3.40 (m, 2H), 2.01 (m, 4H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 159.4, 150.7, 141.4, 138.2, 135.6, 129.2, 129.1, 123.2, 121.6, 114.5, 114.3, 113.0, 112.8, 112.7, 60.8, 55.9, 55.2, 45.8, 38.0, 22.6, 20.7. IR (film): ν 2963, 2834, 1603, 1484, 1457, 1282 cm^{-1}. MS: *m/z* (% relative intensity) 321(M^+, 5), 307(18), 306(100), 153(52); HRMS: *m/z* calcd for $C_{21}H_{23}NO_2$ (M^+) 321.1729, found 321.1733.

7-Methoxy-5-(2-methoxyphenyl)-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ae):

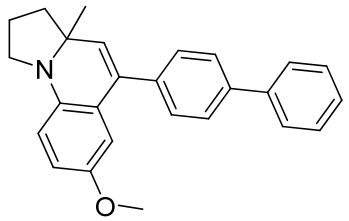


3Ae

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.30 (m, 1H), 7.16 (br, 1H), 6.95 (m, 2H), 6.68 (dd, J = 8.6, 2.9 Hz, 1H), 6.39 (d, J = 8.6 Hz, 1H), 6.28 (d, J = 2.4 Hz, 1H), 5.66 (s, 1H), 3.71

(s, 3H), 3.60 (s, 3H), 3.41 (m, 2H), 2.00 (m, 4H), 1.12 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 157.5, 150.7, 137.9, 131.4, 130.0, 128.9, 128.7, 123.5, 120.6, 113.6, 112.8, 112.3, 111.2, 61.1, 55.9, 55.7, 46.1, 38.0, 23.2, 20.6. IR (film): ν 2963, 2929, 2842, 1597, 1495, 1457, 1416 cm^{-1}. MS: *m/z* (% relative intensity) 321(M^+, 4), 307(23), 306(100), 153(24); HRMS: *m/z* calcd for $C_{21}H_{23}NO_2$ (M^+) 321.1729, found 321.1735.

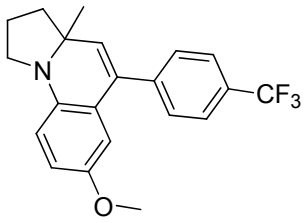
5-(Biphenyl-4-yl)-7-methoxy-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Af):



3Af

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.63 (m, 4H), 7.45 (m, 5H), 6.78 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.66 (d, *J* = 2.9 Hz, 1H), 6.47 (d, *J* = 8.6 Hz, 1H), 5.77 (s, 1H), 3.67 (s, 3H), 3.44 (m, 2H), 2.04 (m, 4H), 1.12 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 150.7, 140.9, 140.1, 139.0, 138.3, 135.4, 129.5, 129.4, 128.8, 127.2, 127.1, 126.9, 123.2, 114.2, 112.9, 112.8, 60.9, 56.0, 45.8, 38.0, 22.6, 20.7. IR (film): ν 2961, 1603, 1491, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 367(M^+, 3), 353(19), 352(67), 149(100); HRMS: *m/z* calcd for $C_{26}H_{25}NO$ (M^+) 367.1936, found 367.1940.

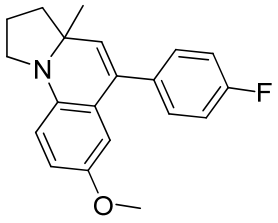
7-Methoxy-3a-methyl-5-(4-(trifluoromethyl)phenyl)-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ag):



3Ag

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.63 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.7 Hz, 2H), 6.76 (dd, J = 8.6, 2.6 Hz, 1H), 6.48 (s, 1H), 6.47 (d, J = 8.2 Hz, 1H), 5.71 (s, 1H), 3.66 (s, 3H), 3.41 (m, 2H), 2.06 (m, 4H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 150.7, 143.8, 138.2, 134.8, 130.1, 129.4, 127.7, 126.3, 125.1 (m, CF_3), 122.6, 114.4, 113.0, 112.6, 60.9, 55.9, 45.8, 38.0, 22.6, 20.7. IR (film): ν 3064, 2983, 2842, 1603, 1563, 1489, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 359(M^+, 7), 345(21), 344(100), 301(10); HRMS: *m/z* calcd for $C_{21}H_{20}NOF_3$ (M^+) 359.1497, found 359.1493.

5-(4-Fluorophenyl)-7-methoxy-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ah):

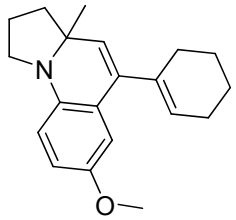


3Ah

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.30 (m, 2H), 7.06 (m, 2H), 6.75 (dd, J = 8.6, 2.9 Hz, 1H), 6.52 (d, J = 2.9 Hz, 1H), 6.45 (d, J = 8.6 Hz, 1H), 5.68 (s, 1H), 3.66 (s, 3H), 3.40 (m, 2H), 2.02 (m, 4H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 163.8, 160.6, 150.7, 138.2, 135.9 (d, J_{CF} = 3.3 Hz), 134.8, 130.7 (d, J_{CF} = 7.8 Hz), 129.4, 123.2, 115.1, 114.9, 114.2, 112.8 (d, J_{CF} = 6.5 Hz), 60.8, 55.9, 45.8, 38.0, 22.5, 20.7. IR (film): ν 2969, 2844, 1603, 1499, 1498 cm^{-1}. MS: *m/z* (% relative intensity) 309(M^+, 4), 295(14),

294(100), 251(19); HRMS: *m/z* calcd for $C_{20}H_{20}NOF$ (M^+) 309.1529, found 309.1525.

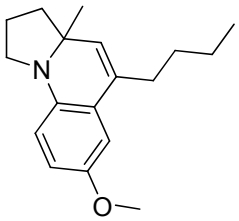
5-Cyclohexenyl-7-methoxy-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ai):



3Ai

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.69 (m, 2H), 6.37 (m, 1H), 5.69 (s, 1H), 5.55 (s, 1H), 3.74 (s, 3H), 3.33 (m, 2H), 2.07 (m, 8H), 1.65 (m, 4H), 0.98 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 150.7, 138.2, 137.8, 137.1, 126.9, 126.2, 123.0, 113.3, 112.4, 60.6, 55.9, 45.6, 37.9, 29.1, 25.4, 23.0, 22.3, 22.2, 20.6. IR (film): ν 2942, 2848, 1611, 1489, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 295(M^+, 5), 281(20), 280(100), 153(7); HRMS: *m/z* calcd for $C_{20}H_{25}NO$ (M^+) 295.1936, found 295.1940.

5-Butyl-7-methoxy-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Aj):

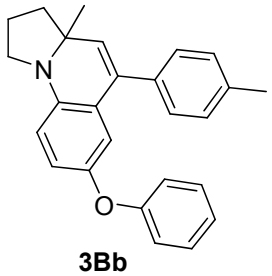


3Aj

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.80 (d, J = 2.8 Hz, 1H), 6.71 (dd, J = 8.5, 2.8 Hz, 1H), 6.37 (d, J = 8.6 Hz, 1H), 5.56 (s, 1H), 3.79 (s, 3H), 3.36 (m, 2H), 2.37 (m, 2H), 1.94 (m, 4H), 1.54 (m, 2H), 1.41 (m, 2H), 1.02 (s, 3H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 150.8, 138.2, 132.3, 127.1, 123.4, 113.1, 112.3, 110.7, 60.6, 56.0, 46.1, 38.2, 31.8, 30.6, 23.3, 22.7, 20.6, 14.0. IR (film): ν 3064, 2988, 2963, 2929,

1603, 1563, 1495 cm^{-1}. MS: *m/z* (% relative intensity) 271(M^+, 7), 257(20), 256(100); HRMS: *m/z* calcd for $C_{18}H_{25}NO$ (M^+) 271.1936, found 271.1935.

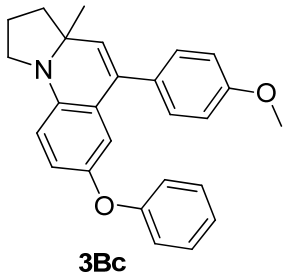
3a-Methyl-7-phenoxy-5-*p*-tolyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Bb):



3Bb

^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.22 (m, 6H), 6.92 (m, 4H), 6.79 (d, J = 2.7 Hz, 1H), 6.47 (d, J = 8.5 Hz, 1H), 5.69 (s, 1H), 3.48 (m, 2H), 2.37 (s, 3H), 2.06 (m, 4H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.5, 145.6, 140.5, 137.0, 136.7, 135.4, 129.4, 129.0, 128.9, 128.5, 123.3, 121.5, 120.9, 119.0, 116.5, 112.4, 61.1, 45.6, 38.1, 23.1, 21.1, 20.6. IR (film): ν 3056, 2983, 2929, 1597, 1484, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 367(M^+, 3), 353(25), 352(100); HRMS: *m/z* calcd for $C_{26}H_{25}NO$ (M^+) 367.1936, found 367.1938.

5-(4-Methoxyphenyl)-3a-methyl-7-phenoxy-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Bc):

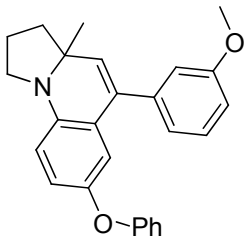


3Bc

^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.25 (m, 4H), 6.90 (m, 6H), 6.77 (d, J = 2.7 Hz, 1H), 6.47 (d, J = 8.5 Hz, 1H), 5.68 (s, 1H), 3.82 (s, 3H), 3.47 (m, 2H), 2.04 (m, 4H), 1.16 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.4, 159.0, 145.7, 140.5, 135.0, 132.0,

130.1, 129.4, 128.3, 123.4, 121.5, 120.9, 118.9, 116.5, 113.6, 112.4, 61.1, 55.3, 45.6, 38.1, 23.1, 20.7. IR (film): ν 3056, 2963, 2848, 1603, 1516, 1484, 1430 cm^{-1}. MS: *m/z* (% relative intensity) 383(M^+, 4), 369(30), 368(100), 352(33); HRMS: *m/z* calcd for $C_{26}H_{25}NO_2$ (M^+) 383.1885, found 383.1884.

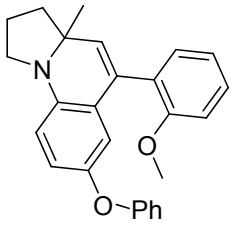
5-(3-Methoxyphenyl)-3a-methyl-7-phenoxy-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Bd):



3Bd

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.21 (m, 3H), 6.87 (m, 7H), 6.76 (d, J = 2.7 Hz, 1H), 6.45 (d, J = 8.6 Hz, 1H), 5.70 (s, 1H), 3.75 (s, 3H), 3.45 (m, 2H), 2.04 (m, 4H), 1.14 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 159.4, 145.7, 141.1, 140.4, 135.4, 129.3, 129.2, 128.7, 123.0, 121.5, 121.4, 121.0, 118.9, 116.5, 114.4, 113.2, 112.5, 61.1, 55.2, 45.6, 38.1, 23.1, 20.5. IR (film): ν 2969, 2842, 1597, 1484, 1430, 1287 cm^{-1}. MS: *m/z* (% relative intensity) 383(M^+, 2), 369(25), 368(100), 153(26); HRMS: *m/z* calcd for $C_{26}H_{25}NO_2$ (M^+) 383.1885, found 383.1889.

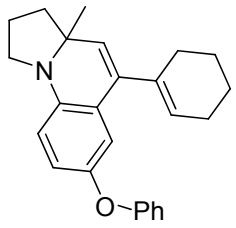
5-(2-Methoxyphenyl)-3a-methyl-7-phenoxy-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Be):



3Be

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.22 (m, 4H), 6.86 (m, 6H), 6.40 (m, 2H), 5.67 (s, 1H), 3.68 (s, 3H), 3.46 (m, 2H), 2.10 (m, 4H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 159.6, 157.0, 145.5, 140.0, 131.6, 130.9, 129.5, 129.2, 129.0, 128.9, 128.5, 123.1, 121.3, 120.6, 118.9, 116.4, 112.0, 110.8, 61.3, 55.5, 45.5, 38.0, 23.2, 20.4. IR (film): ν 3056, 2983, 2842, 1603, 1489, 1422, 1281 cm^{-1}. MS: *m/z* (% relative intensity) 383(M^+, 4), 369(28), 368(100), 352(37); HRMS: *m/z* calcd for $C_{26}H_{25}NO_2$ (M^+) 383.1885, found 383.1889.

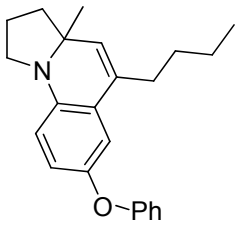
5-Cyclohexenyl-3a-methyl-7-phenoxy-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Bi):



3Bi

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.26 (m, 2H), 6.96 (m, 3H), 6.79 (m, 2H), 6.38 (dd, J = 9.0, 1.7 Hz, 1H), 5.66 (m, 1H), 5.54 (s, 1H), 3.38 (m, 2H), 2.03 (m, 8H), 1.62 (m, 4H), 1.03 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.3, 146.0, 140.3, 137.7, 136.9, 129.4, 126.4, 126.3, 122.7, 121.6, 120.2, 118.0, 116.8, 112.3, 60.8, 45.4, 38.0, 29.1, 25.3, 22.9, 22.2, 20.5. IR (film): ν 3056, 2983, 2929, 2855, 1611, 1570, 1484, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 357(M^+, 3), 343(28), 342(100), 153(22); HRMS: *m/z* calcd for $C_{25}H_{27}NO$ (M^+) 357.2093, found 357.2093.

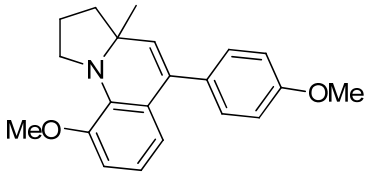
5-Butyl-3a-methyl-7-phenoxy-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Bj):



3Bj

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.27 (m, 2H), 6.94 (m, 4H), 6.80 (dd, J = 8.5, 2.7 Hz, 1H), 6.36 (d, J = 8.6 Hz, 1H), 5.54 (s, 1H), 3.39 (m, 2H), 2.30 (m, 2H), 2.01 (m, 4H), 1.50 (m, 2H), 1.32 (m, 2H), 1.04 (s, 3H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.5, 145.8, 140.3, 132.2, 129.4, 126.5, 123.2, 121.5, 120.3, 116.7, 116.3, 112.1, 60.9, 45.8, 38.3, 31.7, 30.5, 23.8, 22.6, 20.4, 14.0. IR (film): ν 2963, 2929, 2869, 1597, 1563, 1484, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 333(M^+, 4), 319(25), 318(100), 274(21); HRMS: *m/z* calcd for $C_{23}H_{27}NO$ (M^+) 333.2093, found 333.2092.

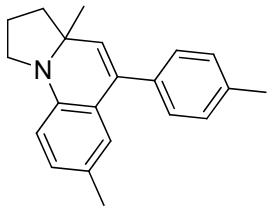
9-Methoxy-5-(4-methoxyphenyl)-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Cc):



3Cc

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.25 (d, J = 8.3 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 6.75 (m, 3H), 5.48 (s, 1H), 3.93 (m, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.11 (m, 1H), 2.03 (m, 2H), 1.90 (m, 1H), 1.66 (m, 1H), 1.20 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 158.8, 152.1, 135.3, 134.5, 132.8, 130.3, 130.0, 126.4, 119.4, 119.0, 113.4, 110.8, 60.7, 55.8, 55.3, 54.3, 40.4, 27.4, 24.9. IR (film): ν 2969, 2848, 1603, 1503, 1457, 1349 cm^{-1}. MS: *m/z* (% relative intensity) 321(M^+, 5), 307(17), 306(100), 153(30); HRMS: *m/z* calcd for $C_{21}H_{23}NO_2$ (M^+) 321.1729, found 321.1742.

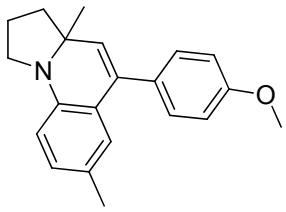
3a,7-Dimethyl-5-*p*-tolyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Db):



3Db

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.23 (m, 4H), 6.94 (dd, J = 8.0, 1.5 Hz, 1H), 6.78 (d, J = 1.6 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 5.63 (s, 1H), 3.45 (m, 2H), 2.41 (s, 3H), 2.16 (s, 3H), 2.02 (m, 4H), 1.12 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 141.3, 137.4, 136.7, 135.7, 129.2, 129.1, 128.8, 128.0, 126.8, 124.4, 122.2, 111.8, 60.9, 45.5, 38.1, 23.0, 21.2, 20.6. IR (film): ν 3056, 2983, 2923, 2861, 1611, 1495, 1416, 1362 cm^{-1}. MS: *m/z* (% relative intensity) 289(M^+, 3), 275(20), 274(100), 153(29); HRMS: *m/z* calcd for $C_{21}H_{23}N$ (M^+) 289.1830, found 289.1828.

5-(4-Methoxyphenyl)-3a,7-dimethyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Dc):

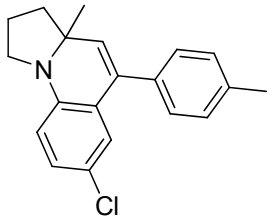


3Dc

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.28 (m, 2H), 6.93 (m, 3H), 6.77 (d, J = 1.5 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 5.61 (s, 1H), 3.86 (s, 3H), 3.44 (m, 2H), 2.16 (s, 3H), 2.02 (m, 4H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 158.8, 141.3, 135.3, 132.7, 130.3, 129.2, 127.8, 126.7, 124.4, 122.3, 113.5, 111.8, 60.9, 55.3, 45.4, 38.1, 23.0, 20.6. IR (film): ν 3056, 2969, 2855, 1603, 1509, 1362 cm^{-1}. MS: *m/z* (% relative intensity)

305(M^+, 4), 291(18), 290(100), 275(9); HRMS: *m/z* calcd for $C_{21}H_{23}NO$ (M^+) 305.1780, found 305.1777.

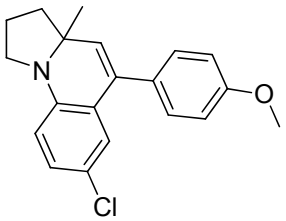
7-Chloro-3a-methyl-5-*p*-tolyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Eb):



3Eb

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.22 (s, 4H), 7.05 (dd, J = 8.5, 2.4 Hz, 1H), 6.91 (d, J = 2.4 Hz, 1H), 6.39 (d, J = 8.5 Hz, 1H), 5.66 (s, 1H), 3.44 (m, 2H), 2.41 (s, 3H), 2.07 (m, 4H), 1.13 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 141.9, 137.2, 136.5, 135.0, 129.0, 128.9, 128.5, 128.3, 125.9, 123.5, 120.3, 112.7, 61.2, 45.5, 38.1, 23.5, 21.2, 20.4. IR (film): ν 3029, 2969, 2855, 1590, 1484, 1416 cm^{-1}. MS: *m/z* (% relative intensity) 309(M^+, 4), 296(32), 295(19), 294(100); HRMS: *m/z* calcd for $C_{20}H_{20}NCl$ (M^+) 309.1284, found 309.1280.

7-Chloro-5-(4-methoxyphenyl)-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ec):

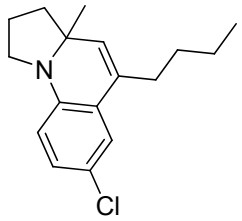


3Ec

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.25 (m, 2H), 7.05 (dd, J = 8.5, 2.4 Hz, 1H), 6.92 (m, 3H), 6.38 (d, J = 8.5 Hz, 1H), 5.64 (s, 1H), 3.86 (s, 3H), 3.43 (m, 2H), 2.03 (m, 4H), 1.12 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.1, 141.9, 134.6, 131.8, 130.2, 128.4, 128.3, 125.8, 123.6, 120.3, 113.7, 112.7, 61.1, 55.3, 45.4, 38.1, 23.5, 20.5. IR

(film): ν 3064, 2963, 2842, 1603, 1509, 1476 cm^{-1}. MS: *m/z* (% relative intensity) 325(M^+, 3), 312(30), 311(20), 310(100); HRMS: *m/z* calcd for $C_{20}H_{20}NOCl$ (M^+) 325.1233, found 325.1231.

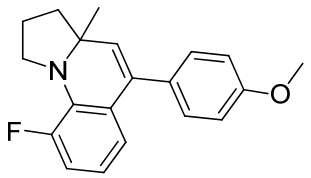
5-Butyl-7-chloro-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Ej):



3Ej

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.07 (d, J = 2.4 Hz, 1H), 7.00 (dd, J = 8.5, 2.4 Hz, 1H), 6.28 (d, J = 8.5 Hz, 1H), 5.52 (s, 1H), 3.40 (m, 1H), 3.30 (m, 1H), 2.31 (m, 2H), 2.00 (m, 4H), 1.51 (m, 2H), 1.40 (m, 2H), 1.01 (s, 3H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 141.9, 131.7, 127.8, 126.5, 123.3, 123.2, 120.2, 112.3, 60.9, 45.6, 38.2, 31.5, 30.4, 24.1, 22.6, 20.3, 14.0. IR (film): ν 2963, 2923, 2861, 1603, 1484, 1416, 1368 cm^{-1}. MS: *m/z* (% relative intensity) 275(M^+, 5), 262(32), 261(17), 260(100); HRMS: *m/z* calcd for $C_{17}H_{22}NCl$ (M^+) 275.1441, found 275.1440.

9-Fluoro-5-(4-methoxyphenyl)-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline (3Fc):

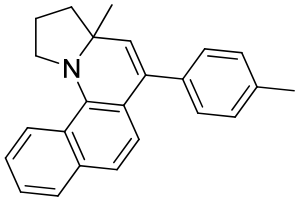


3Fc

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.24 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.82 (m, 2H), 6.56 (m, 1H), 5.53 (s, 1H), 3.96 (m, 1H), 3.83 (s, 3H), 3.45 (m, 1H), 1.97 (m, 3H), 1.79 (m, 1H), 1.19 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.0, 155.2,

152.0, 134.6 (d, J_{CF} = 3.4 Hz), 132.3, 130.3, 129.6, 126.6 (d, J_{CF} = 4.7 Hz), 121.8 (d, J_{CF} = 2.6 Hz), 117.3 (d, J_{CF} = 7.7 Hz), 115.0 (d, J_{CF} = 20.4 Hz), 113.5, 61.0, 55.3, 52.6 (d, J_{CF} = 7.5 Hz), 39.8, 27.3, 23.4 (d, J_{CF} = 1.1 Hz). IR (film): ν 2969, 1603, 1503, 1462, 1349 cm^{-1}. ESI, MS: *m/e* 310 ($[M+H]^+$); HRMS: *m/z* calcd for $C_{20}H_{20}FNO$ (M^+) 309.1529, found 309.1536.

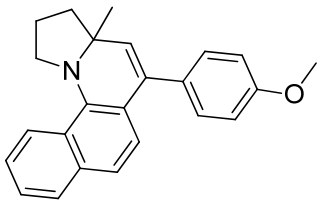
3a-Methyl-5-*p*-tolyl-1,2,3,3a-tetrahydrobenzo[*h*]pyrrolo[1,2-a]quinoline (3Gb):



3Gb

^1H NMR ($CDCl_3$, TMS, 400 MHz): δ 8.28 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.35 (m, 8H), 5.55 (s, 1H), 4.03 (m, 1H), 3.34 (m, 1H), 2.43 (s, 3H), 2.16 (m, 2H), 2.00 (m, 1H), 1.77 (m, 1H), 1.25 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 142.0, 137.8, 137.3, 137.1, 134.5, 130.1, 129.5, 129.3, 128.4, 127.6, 125.9, 125.4, 125.3, 124.9, 122.7, 121.2, 61.6, 57.6, 41.6, 27.0, 26.6, 21.6. IR (film): ν 2975, 2926, 2871, 1512, 1381 cm^{-1}. MS: *m/z* (% relative intensity) 325(M^+, 5), 311(20), 310(100), 153(58); HRMS: *m/z* calcd for $C_{24}H_{23}N$ (M^+) 325.1830, found 325.1825.

5-(4-Methoxyphenyl)-3a-methyl-1,2,3,3a-tetrahydrobenzo[h]pyrrolo[1,2-a]quinoline (3Gc):

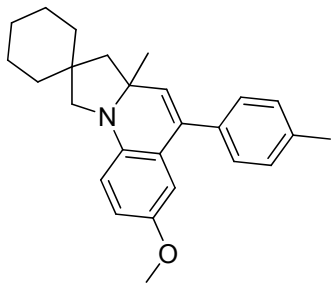


3Gc

^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 8.28 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H),

7.34 (m, 6H), 6.93 (d, J = 8.7 Hz, 2H), 5.50 (s, 1H), 3.99 (m, 1H), 3.84 (s, 3H), 3.31 (m, 1H), 2.13 (m, 2H), 1.97 (m, 1H), 1.74 (m, 1H), 1.21 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 158.9, 141.6, 136.3, 134.0, 132.7, 130.3, 129.8, 129.4, 128.0, 125.5, 125.0, 124.9, 124.4, 122.3, 120.8, 113.6, 61.1, 57.1, 55.3, 41.2, 26.6, 26.2. IR (film): ν 2963, 2861, 1603, 1509, 1422, 1389 cm^{-1}. MS: *m/z* (% relative intensity) 341(M^+, 5), 327(23), 326(100), 282(12); HRMS: *m/z* calcd for $C_{24}H_{23}NO$ (M^+) 341.1780, found 341.1778.

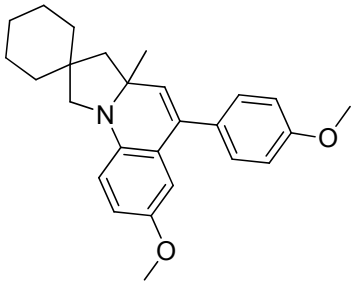
7'-Methoxy-3a'-methyl-5'-*p*-tolyl-3',3a'-dihydro-1'*H*-spiro[cyclohexane-1,2'-pyrrolo[1,2-a]quinoline] (3Hb):



3Hb

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.25 (d, J = 7.5 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.76 (dd, J = 8.5, 2.9 Hz, 1H), 6.64 (d, J = 2.8 Hz, 1H), 6.50 (d, J = 8.6 Hz, 1H), 5.68 (s, 1H), 3.67 (s, 3H), 3.27 (dd, J = 40.9, 9.6 Hz, 2H), 2.42 (s, 3H), 1.92 (dd, J = 48.2, 12.5 Hz, 2H), 1.55 (m, 10H), 1.12 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 150.9, 138.4, 137.1, 136.8, 134.8, 130.9, 129.0, 128.8, 123.7, 114.1, 113.6, 112.7, 60.7, 58.8, 55.9, 52.1, 40.3, 38.8, 38.7, 25.8, 24.0, 23.7, 21.2. IR (film): ν 3056, 2988, 2923, 2861, 1603, 1489, 1416 cm^{-1}. MS: *m/z* (% relative intensity) 373(M^+, 2), 359(26), 358(100); HRMS: *m/z* calcd for $C_{26}H_{31}NO$ (M^+) 373.2406, found 373.2389.

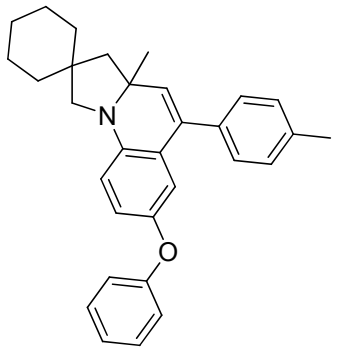
7'-Methoxy-5'-(4-methoxyphenyl)-3a'-methyl-3',3a'-dihydro-1'*H*-spiro[cyclohexane-1,2'-pyrrolo[1,2-a]quinoline] (3Hc):



3Hc

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.27 (m, 2H), 6.90 (m, 2H), 6.75 (dd, J = 8.6, 2.9 Hz, 1H), 6.62 (d, J = 2.8 Hz, 1H), 6.48 (d, J = 8.6 Hz, 1H), 5.65 (s, 1H), 3.85 (s, 3H), 3.67 (s, 3H), 3.26 (dd, J = 41.9, 9.6 Hz, 2H), 1.91 (dd, J = 48.3, 12.5 Hz, 2H), 1.54 (m, 10H), 1.10 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 158.9, 150.9, 138.4, 134.4, 132.4, 130.7, 130.2, 123.8, 114.0, 113.6, 113.5, 112.6, 60.7, 58.7, 55.9, 55.3, 52.1, 40.3, 38.8, 38.7, 25.8, 24.0, 23.9, 23.7. IR (film): ν 3056, 2929, 2855, 1603, 1509, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 375(23), 374(100), 153(30), 136(28); HRMS: *m/z* calcd for $C_{26}H_{31}NO_2$ (M^+) 389.2355, found 389.2348.

3a'-Methyl-7'-phenoxy-5'-*p*-tolyl-3',3a'-dihydro-1'*H*-spiro[cyclohexane-1,2'-pyrrolo[1,2-a]quinoline] (3Ib):

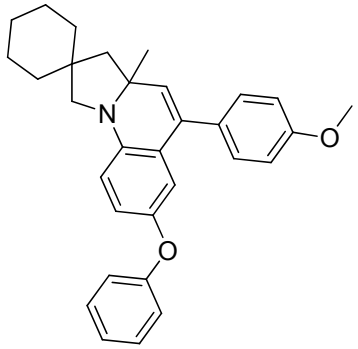


3Ib

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.19 (m, 6H), 6.89 (m, 4H), 6.78 (d, J = 2.5 Hz, 1H), 6.49 (d, J = 8.5 Hz, 1H), 5.67 (s, 1H), 3.31 (dd, J = 49.6, 9.7 Hz, 2H), 2.35 (s, 3H),

1.94 (dd, J = 48.3, 12.6 Hz, 2H), 1.55 (m, 10H), 1.16 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.4, 145.8, 140.6, 136.9, 136.8, 134.7, 130.4, 129.3, 128.9, 128.8, 123.6, 121.5, 120.6, 118.8, 116.5, 113.1, 60.9, 58.3, 52.1, 40.2, 38.9, 38.7, 25.8, 24.2, 24.0, 23.7, 21.1. IR (film): ν 2929, 2855, 1597, 1484, 1416 cm^{-1}. MS: *m/z* (% relative intensity) 435(M^+, 3), 422(31), 421(100), 153(17); HRMS: *m/z* calcd for $C_{31}H_{33}NO$ (M^+) 435.2562, found 435.2541.

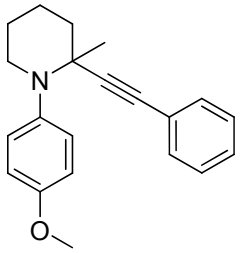
5'-(4-Methoxyphenyl)-3a'-methyl-7'-phenoxy-3',3a'-dihydro-1'*H*-spiro[cyclohexane-1,2'-pyrrolo[1,2-a]quinoline] (3Ic):



3Ic

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.25 (m, 4H), 6.92 (m, 6H), 6.78 (d, J = 2.4 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 5.66 (s, 1H), 3.82 (s, 3H), 3.32 (dd, J = 50.5, 9.7 Hz, 2H), 1.95 (dd, J = 48.5, 12.6 Hz, 2H), 1.56 (m, 10H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.4, 159.0, 145.9, 140.6, 134.3, 132.1, 130.2, 130.1, 129.4, 123.8, 121.5, 120.6, 118.8, 116.6, 113.6, 113.1, 60.9, 58.3, 55.3, 52.1, 40.2, 38.9, 38.7, 25.8, 24.1, 24.0, 23.7. IR (film): ν 2934, 2850, 1596, 1507, 1486 cm^{-1}. MS: *m/z* (% relative intensity) 437(23), 281(22), 199(14), 198(100); HRMS: *m/z* calcd for $C_{31}H_{33}NO_2$ (M^+) 451.2511, found 451.2499.

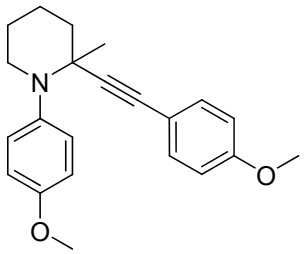
1-(4-Methoxyphenyl)-2-methyl-2-(phenylethynyl)piperidine (5Ja):



5Ja

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.47 (m, 2H), 7.34 (m, 5H), 6.83 (dd, J = 12.3, 3.3 Hz, 2H), 3.80 (s, 3H), 3.42 (m, 1H), 2.85 (d, J = 11.6 Hz, 1H), 1.89 (m, 2H), 1.69 (m, 4H), 1.28 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 157.0, 143.7, 131.6, 128.4, 128.2, 127.7, 123.7, 113.2, 91.6, 86.1, 56.1, 55.3, 51.6, 41.1, 29.7, 26.8, 22.2. IR (film): ν 3002, 2942, 1603, 1509, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 305(M^+, 44), 291(21), 290(100), 136(68); HRMS: *m/z* calcd for $C_{21}H_{23}NO$ (M^+) 305.1780, found 305.1782.

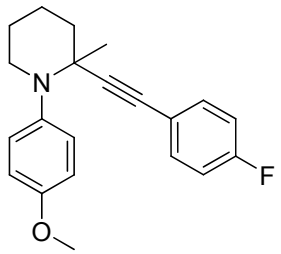
1-(4-Methoxyphenyl)-2-((4-methoxyphenyl)ethynyl)-2-methylpiperidine (5Jc):



5Jc

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.38 (dd, J = 6.8, 2.1 Hz, 2H), 7.31 (dd, J = 7.0, 2.1 Hz, 2H), 6.83 (m, 4H), 3.81 (s, 3H), 3.78 (s, 3H), 3.40 (m, 1H), 2.82 (d, J = 13.2 Hz, 1H), 1.90 (m, 2H), 1.68 (m, 4H), 1.25 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 159.2, 157.0, 143.8, 132.9, 128.4, 115.9, 113.9, 113.2, 89.9, 85.9, 56.1, 55.3, 55.2, 51.6, 41.1, 29.8, 26.8, 22.2. IR (film): ν 3056, 2936, 1603, 1503, 1416 cm^{-1}. MS: *m/z* (% relative intensity) 335(M^+, 87), 334(23), 320(100), 153(74); HRMS: *m/z* calcd for $C_{22}H_{25}NO_2$ (M^+) 335.1885, found 335.1878.

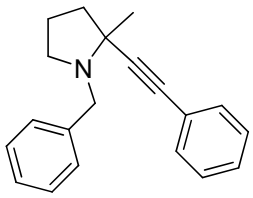
2-((4-Fluorophenyl)ethynyl)-1-(4-methoxyphenyl)-2-methylpiperidine (5Jh):



5Jh

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.44 (m, 2H), 7.31 (m, 2H), 7.02 (m, 2H), 6.83 (m, 2H), 3.80 (s, 3H), 3.40 (m, 1H), 2.85 (m, 1H), 1.90 (m, 2H), 1.68 (m, 4H), 1.27 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 163.4, 160.9, 157.0, 143.7, 133.3 (d, J_{CF} = 8.2 Hz), 128.4, 119.7 (d, J_{CF} = 3.4 Hz), 115.4 (d, J_{CF} = 21.8 Hz), 113.2, 91.2, 85.0, 56.1, 55.3, 51.5, 41.0, 29.7, 26.7, 22.2. IR (film): ν 2990, 2940, 1603, 1507, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 323(M^+, 51), 322(27), 309(23), 308(100); HRMS: *m/z* calcd for $C_{21}H_{22}NOF$ (M^+) 323.1685, found 323.1676.

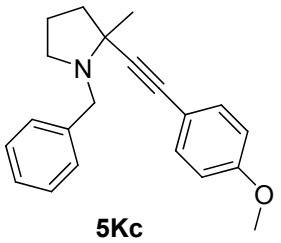
1-Benzyl-2-methyl-2-(phenylethynyl)pyrrolidine (5Ka):



5Ka

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.49 (m, 2H), 7.36 (m, 8H), 4.03 (d, J = 13.1 Hz, 1H), 3.41 (d, J = 13.1 Hz, 1H), 2.93 (m, 1H), 2.51 (m, 1H), 2.25 (m, 1H), 1.86 (m, 3H), 1.55 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 140.3, 131.7, 128.8, 128.2, 128.1, 127.8, 126.7, 123.6, 91.0, 84.7, 60.2, 54.8, 51.7, 40.6, 26.1, 20.5. IR (film): ν 2975, 2940, 1603, 1485, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 275(M^+, 2), 261(20), 260(100); HRMS: *m/z* calcd for $C_{20}H_{21}N$ (M^+) 275.1674, found 275.1663.

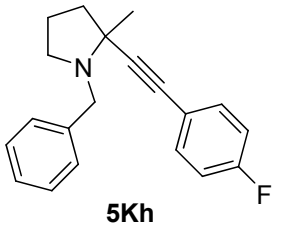
1-Benzyl-2-((4-methoxyphenyl)ethynyl)-2-methylpyrrolidine (5Kc):



5Kc

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.41 (m, 4H), 7.33 (m, 2H), 7.26 (m, 1H), 6.87 (m, 2H), 4.01 (d, J = 13.1 Hz, 1H), 3.84 (s, 3H), 3.40 (d, J = 13.1 Hz, 1H), 2.93 (m, 1H), 2.50 (m, 1H), 2.23 (m, 1H), 1.85 (m, 3H), 1.54 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 159.2, 140.4, 133.1, 128.8, 128.2, 126.7, 115.8, 113.9, 89.4, 84.4, 60.2, 55.3, 54.8, 51.7, 40.6, 26.1, 20.5. IR (film): ν 3064, 2977, 2936, 2834, 1603, 1503, 1416 cm^{-1}. MS: *m/z* (% relative intensity) 305(M^+, 3), 291(21), 290(100); HRMS: *m/z* calcd for $C_{21}H_{23}NO$ (M^+) 305.1780, found 305.1765.

1-Benzyl-2-((4-fluorophenyl)ethynyl)-2-methylpyrrolidine (5Kh):

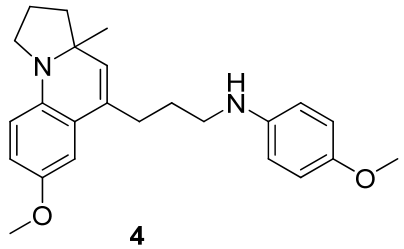


5Kh

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.36 (m, 7H), 7.02 (m, 2H), 4.01 (d, J = 13.1 Hz, 1H), 3.38 (d, J = 13.1 Hz, 1H), 2.91 (m, 1H), 2.48 (m, 1H), 2.21 (m, 1H), 1.85 (m, 3H), 1.53 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 163.9, 160.6, 140.2, 133.5 (d, J_{CF} = 8.1 Hz), 128.8, 128.3, 126.7, 119.6 (d, J_{CF} = 3.5 Hz), 115.4 (d, J_{CF} = 21.8 Hz), 90.6, 83.6, 60.2, 54.7, 51.7, 40.6, 26.0, 20.5. IR (film): ν 2975, 2940, 2815, 1597, 1499 cm^{-1}. MS: *m/z* (% relative intensity) 293(M^+, 3), 279(19), 278(100); HRMS: *m/z* calcd for $C_{20}H_{20}NF$ (M^+) 293.1580, found 293.1573.

Procedure for the Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/AgSbF$_6$-Catalyzed Reaction of 4-Methoxy-*N*-(pent-4-ynyl)aniline (1A). A mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.01 mmol), $AgSbF_6$ (0.01 mmol) and 4-methoxy-*N*-(pent-4-ynyl)aniline (0.2 mmol) in CH_3CN (1.0 mL) was stirred at 80 ^oC for 36 h under Ar atmosphere. Solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:15) to give the product **4** in 43% yield.

4-Methoxy-*N*-(3-(7-methoxy-3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-α]quinolin-5-yl)propyl)aniline (4):



4

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.74 (m, 4H), 6.56 (dd, J = 10.0, 3.3 Hz, 2H), 6.37 (d, J = 8.5 Hz, 1H), 5.57 (s, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.35 (m, 2H), 3.14 (t, J = 6.9 Hz, 2H), 2.49 (m, 2H), 1.91 (m, 6H), 0.99 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 152.0, 150.8, 142.7, 138.2, 131.5, 127.6, 122.9, 114.9, 114.0, 113.5, 112.5, 110.6, 60.6, 56.0, 55.8, 46.1, 44.7, 38.2, 29.7, 28.2, 23.2, 20.6. IR (film): ν 2961, 2836, 1506, 1422 cm^{-1}. MS: *m/z* (% relative intensity) 378(M^+, 13), 364(24), 363(100), 240(38); HRMS: *m/z* calcd for $C_{24}H_{30}N_2O_2$ (M^+) 378.2307, found 378.2303.

Gram-Scale Catalytic Synthesis of 7-Methoxy-3a-methyl-5-phenyl-1,2,3,3a-tetrahydropyrrolo[1,2-α]quinoline (3Aa) Using Gold(I) Complexes. A mixture of

Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.125 mmol), $AgSbF_6$ (0.125 mmol), phenylacetylene (20 mmol) and 4-methoxy-*N*-(pent-4-ynyl)aniline (5 mmol) in water (2 mL) was stirred at 75 ^oC under Ar atmosphere. After stirring for 26 h, Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.125 mmol) and $AgSbF_6$ (0.125 mmol) were added to this mixture, and the resulting mixture was stirred for 30 h at the same temperature. Water was removed under reduced pressure. The residue was purified by vacuum distillation at 120-140 ^oC to give the product **3Aa** (1.3 g) in 91% yield.

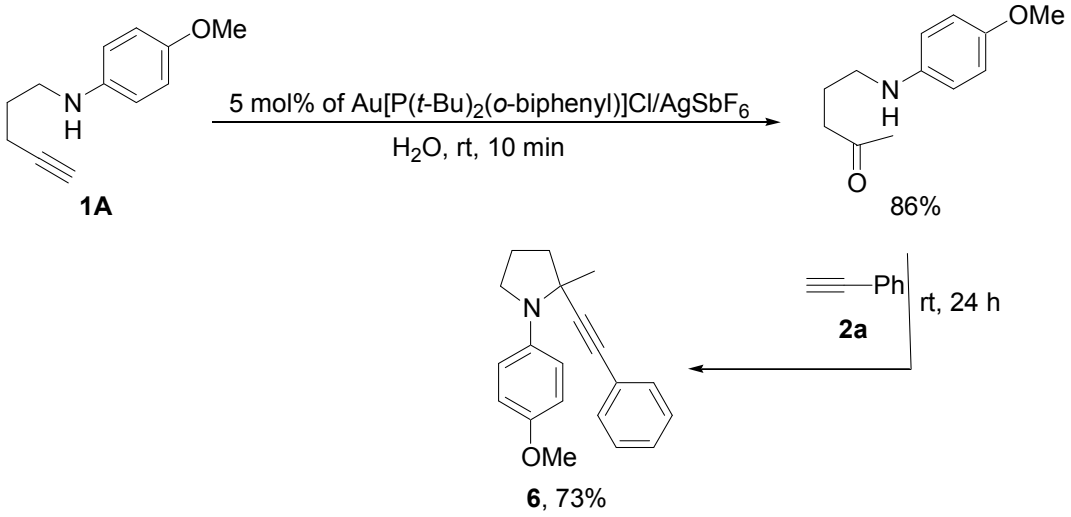
A mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.33 mmol), $AgSbF_6$ (0.33 mmol), phenylacetylene (66 mmol) and 4-methoxy-*N*-(pent-4-ynyl)aniline (22 mmol) in water (2 mL) was stirred at 75 ^oC under Ar atmosphere. After stirring for 48 h, Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.22 mmol) and $AgSbF_6$ (0.22 mmol) were added to this mixture and the resulting mixture was stirred for 60 h at the same temperature. Water was removed under reduced pressure, and the residue was purified by flash chromatography to give the product **3Aa** (5.5 g) in 91% yield.

Procedure for the Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/$AgSbF_6$-Catalyzed Reaction of 4-Methoxy-*N*-(pent-4-ynyl)aniline with Phenylacetylene at Room Temperature.

To a mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.01 mmol) and $AgSbF_6$ (0.01 mmol) in H_2O (1.0 mL) was added 4-methoxy-*N*-(pent-4-ynyl)aniline (0.2 mmol) with stirring. The reaction mixture was capped and stirred for 10 min at room temperature. *N*-(4-methoxyphenyl)-5-aminopentan-2-one[S6] was obtained in 86% yield.

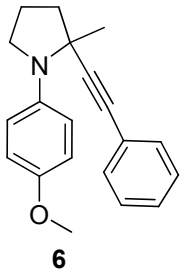
To a mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.01 mmol) and $AgSbF_6$ (0.01 mmol) in H_2O (1.0 mL) was added *N*-(4-methoxyphenyl)-5-aminopentan-2-one (0.2 mmol) and

phenylacetylene (0.8 mmol) with stirring. The reaction mixture was capped and stirred for 24 h at room temperature. Solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:100) to give the product **6** in 73% yield.



To a mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.01 mmol) and $AgSbF_6$ (0.01 mmol) in H_2O (1.0 mL) was added 4-methoxy-*N*-(pent-4-ynyl)aniline (0.2 mmol) and phenylacetylene (0.8 mmol) with stirring. The reaction mixture was capped and stirred for 24 h at room temperature. Solvent was removed under reduced pressure. The residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:100) to give the product **6** in 74% yield.

1-(4-Methoxyphenyl)-2-methyl-2-(phenylethynyl)pyrrolidine (6):



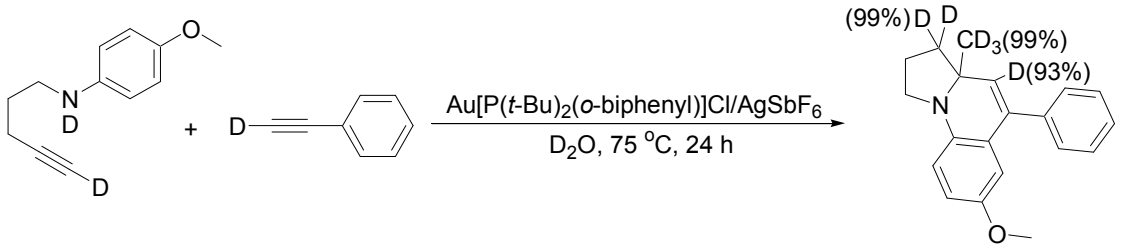
6

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.39 (m, 2H), 7.28 (m, 3H), 7.05 (m, 2H), 6.88 (m, 2H), 3.78 (s, 3H), 3.45 (m, 2H), 2.50 (m, 1H), 2.09 (m, 3H), 1.65 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 152.0, 140.4, 131.6, 128.1, 127.8, 123.4, 116.9, 114.2, 93.2, 83.3, 57.6, 55.7, 50.5, 44.0, 26.2, 22.5. IR (film): ν 2969, 2948, 2844, 1507, 1485 cm^{-1}. MS: *m/z* (% relative intensity) 291(M^+, 18), 276(75), 153(38), 149(100); HRMS: *m/z* calcd for $C_{20}H_{21}NO$ (M^+) 291.1623, found 291.1617.

Procedure for the Conversion of 1-(4-Methoxyphenyl)-2-methyl-2-(phenylethynyl)pyrrolidine (6) to 3Aa Catalyzed by Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/AgSbF$_6$. To a mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.005 mmol) and $AgSbF_6$ (0.005 mmol) in H_2O (0.5 mL) was added **6** (0.1 mmol) with stirring. The reaction mixture was capped and stirred for 8 h at 60 ^{o}C. Solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:100) to give the product **3Aa** in 96% yield.

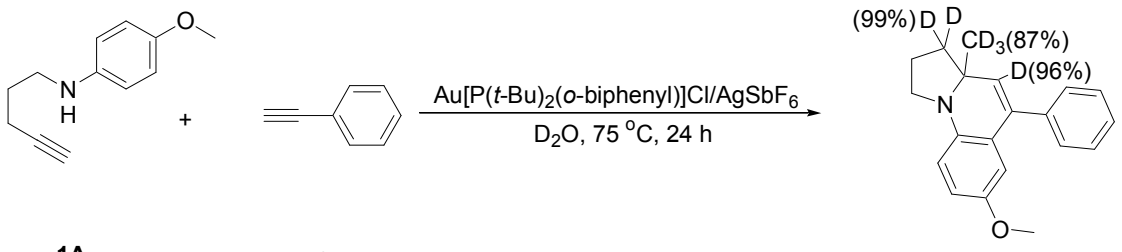
Procedure for the Isotope Studies. Deuterated amionalkyne **1L**-*d*$_2$ was prepared by deprotonation of **1A** using *n*BuLi (2.2 equiv) at -78 ^{o}C followed by quenching with D_2O in 76% yield with >98% deuterium incorporation at both terminal alkynyl and amino sites. A mixture of Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl (0.005 mmol), $AgSbF_6$ (0.005 mmol), phenylacetylene-*d* (0.4 mmol) and amionalkyne **1L**-*d*$_2$ (0.1 mmol) in D_2O (0.4 mL) was stirred at 75 ^{o}C for 24 h under Ar atmosphere. D_2O was removed under reduced pressure, and the residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:100) to give the product **3Lk** in 85% yield, which was analyzed using ^{1}H NMR spectroscopy to determine the content of the deuterium incorporation. ^{1}H NMR ($CDCl_3$, TMS, 300

MHz): δ 7.34 (m, 5H), 6.74 (dd, J = 8.6, 2.9 Hz, 1H), 6.58 (d, J = 2.9 Hz, 1H), 6.44 (d, J = 8.6 Hz, 1H), 3.64 (s, 3H), 3.40 (m, 2H), 2.02 (t, J = 6.9 Hz, 2H).



1L **2k** **3Lk**, 85%

A mixture of Au[P(t-Bu)$_2$(o-biphenyl)]Cl (0.005 mmol), $AgSbF_6$ (0.005 mmol), phenylacetylene (0.4 mmol) and amionalkyne **1A** (0.1 mmol) in D_2O (0.4 mL) were stirred at 75 ^oC for 24 h under Ar atmosphere. D_2O was removed under reduced pressure, and the residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:100) to give the product **7** in 89% yield, which was analyzed using ^1H NMR spectroscopy to determine the content of the deuterium incorporation. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 7.34 (m, 5H), 6.74 (dd, J = 8.6, 2.9 Hz, 1H), 6.58 (d, J = 2.9 Hz, 1H), 6.44 (d, J = 8.6 Hz, 1H), 3.64 (s, 3H), 3.40 (m, 2H), 2.02 (t, J = 6.9 Hz, 2H), 1.00 (m, 0.4H).



1A **2a** **7**, 89%

Cytotoxicity Studies (MTT Assay)

Cervical epithelioid carcinoma (HeLa) cell line and normal lung fibroblast (CCD-19Lu) cell line were maintained in a minimum essential medium with Earle's balanced salts (MEM), respectively. The medium for HeLa was supplemented with 2 mM *L*-glutamine, 1% sodium pyruvate, and 10% fetal bovine serum; and the medium for CCD-19Lu was supplemented with 2 mM *L*-glutamine and 10% fetal bovine serum. Penicillin (100 U/mL) and Streptomycin (100 μg/mL) were added to all media. Cultures were incubated at 37 °C in a 5% CO_2/95% air humidified atmosphere.

Assays on the cytotoxic effects were conducted in 96-well flat-bottomed microtitre plates. The supplemented culture medium (100 μL) with cells (6×10^4 cells/mL) was added into each well and was incubated (37 °C, 5% CO_2/95% air) for 24 h. All the media were then removed and fresh supplemented medium (100 μL) was added into each well. Compound **3Bc** dissolved in the culture medium (100 μL + < 1 % DMSO) was added into a set of wells. After mixing, the sample-containing media (100 μL) were drawn and added to another set of wells. Such processes were repeated to provide a set of two-fold dilution series. Controlled wells only contained 100 μL of supplemented media. Microtitre plates were incubated at 37 °C in a 5% CO_2/95% air humidified atmosphere for further 3 days. All the cytotoxicity assays were run in parallel with a negative control (i.e., untreated population). Assessment of the cytotoxicity was carried out using a modified method of Mosmann based 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) Assay [T. Mosmann, *J. Immunol. Methods* **1983**, 65, 55–63.]. At the end of each incubation period, 10 μL of the MTT solution (Cell Proliferation Kit I, Roche) were added into each well and the cultures were further incubated for 4 h at 37 ^{o}C in a 5%

CO_2/95% air humidified atmosphere. Then 100 μL of the solubilization solution was added into the wells to lyse the cells and solubilize the formazan complex formed. The microtitre plates were maintained in a dark and humidified chamber overnight. The formation of formazan was measured with a microtitre plate reader at 550 nm, and the percentages of cell survival were determined. The cytotoxicity was evaluated based on the percentage cell survival in a dosedependence manner relative to the negative control.

References:

[S1] A. K. Al-Sa'Ady, C. A. McAuliffe, R. V. Parish, J. A. Sandeank, *Inorg. Synth.* **1985**, 191.

[S2] P. de Frémont, N. M. Scott, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 2411.

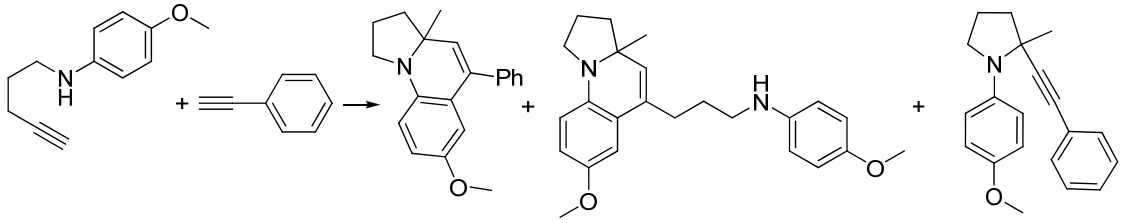
[S3] C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178.

[S4] S. Serna, I. Tellitu, E. Domínguez, I. Moreno, R. SanMartín, *Org. Lett.* **2005**, *7*, 3073.

[S5] S. Chang, M. Lee, D. Y. Jung, E. J. Yoo, S. H. Cho, S. K. Han, *J. Am. Chem. Soc.* **2006**, *128*, 12366.

[S6] A. J. Duplantier, C. J. Andresen, J. B. Cheng, V. L. Cohan, C. Decker, F. M. DiCapua, K. G. Kraus, K. L. Johnson, C. R. Turner, J. P. UmLand, J. W. Watson, R. T. Wester, A. S. Williams, J. A. Williams, *J. Med. Chem.* **1998**, *41*, 2268.

Table S1. Effect of catalyst, solvent and temperature on tandem synthesis of pyrrolo[1,2-α]quinoline **3Aa**.[a]

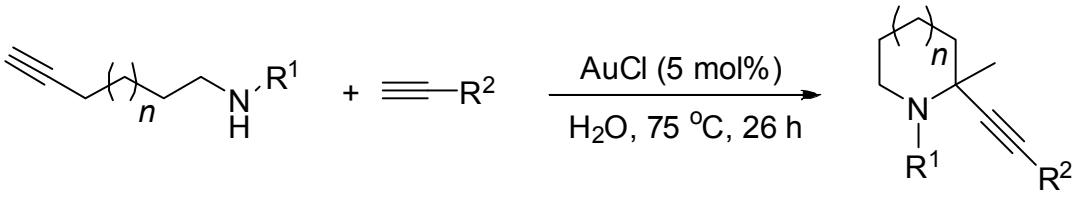


1A **2a** **3Aa** **4** **6**

Entry	Catalyst	Solvent	Temperature [°C]	Time [h]	Yield of **3Aa** [%][b]	Yield of **4** [%][b]	Yield of **6** [%][b]
1	$AgSbF_6$	CH_3NO_2	60	24	0	0	0
2	$AuCl_3$	CH_3NO_2	60	24	0	0	0
3	$AuCl/AgSbF_6$	CH_3NO_2	60	24	3	12	0
4	$(IPr)AuCl^{[c]}/AgSbF_6$	CH_3NO_2	60	24	0	0	0
5	$Ph_3PAuCl/AgSbF_6$	CH_3NO_2	60	24	3	12	0
6	Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/$AgSbF_6$	CH_3NO_2	60	24	36	14	0
7	Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/$AgBF_4$	CH_3NO_2	60	24	0	0	0
8	Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/$AgPF_6$	CH_3NO_2	60	24	6	0	0
9	Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/AgOTf	CH_3NO_2	60	24	0	0	0
10[d]	CF_3SO_3H	H_2O	75	26	0	0	0
11[d]	$AgSbF_6$	H_2O	75	26	0	0	0
12[d]	AuCl	H_2O	75	26	30	0	60
13[d]	Au[P(Cy)$_2$(2',4',6'-triisopropyl-*o*-biphenyl)]Cl/$AgSbF_6$	H_2O	75	26	13	0	74
14[d]	Au[P(*t*-Bu)$_2$(2',4',6'-triisopropyl-*o*-biphenyl)]Cl/$AgSbF_6$	H_2O	75	26	53	0	26

[a] Reaction conditions: **1A**/**2a**/catalyst = 1:2:0.05. [b] Determined by ^{1}H NMR with 0.005 mol of trimethyl(phenyl)silane as an internal standard. [c] IPr = *N*,*N*'-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene. [d] Reaction conditions: **1A**/**2a**/catalyst = 1:4:0.05.

Scheme S1. Reactions of 1,5-aminoalkyne **1J** and *N*-benzylpent-4-yn-1-amine (**1K**) with alkynes **2a**, **2c**, and **2h** catalyzed by AuCl.



n = 1, R^1 = 4-CH_3OPh (**1J**):	R^2 = Ph (**2a**),	66% (**5Ja**)
	R^2 = 4-CH_3OPh (**2c**),	83% (**5Jc**)
	R^2 = 4-FPh (**2h**),	77% (**5Jh**)
n = 0, R^1 = CH_2Ph (**1K**):	R^2 = Ph (**2a**),	95% (**5Ka**)
	R^2 = 4-CH_3OPh (**2c**),	97% (**5Kc**)
	R^2 = 4-FPh (**2h**),	92% (**5Kh**)

Scheme S2.

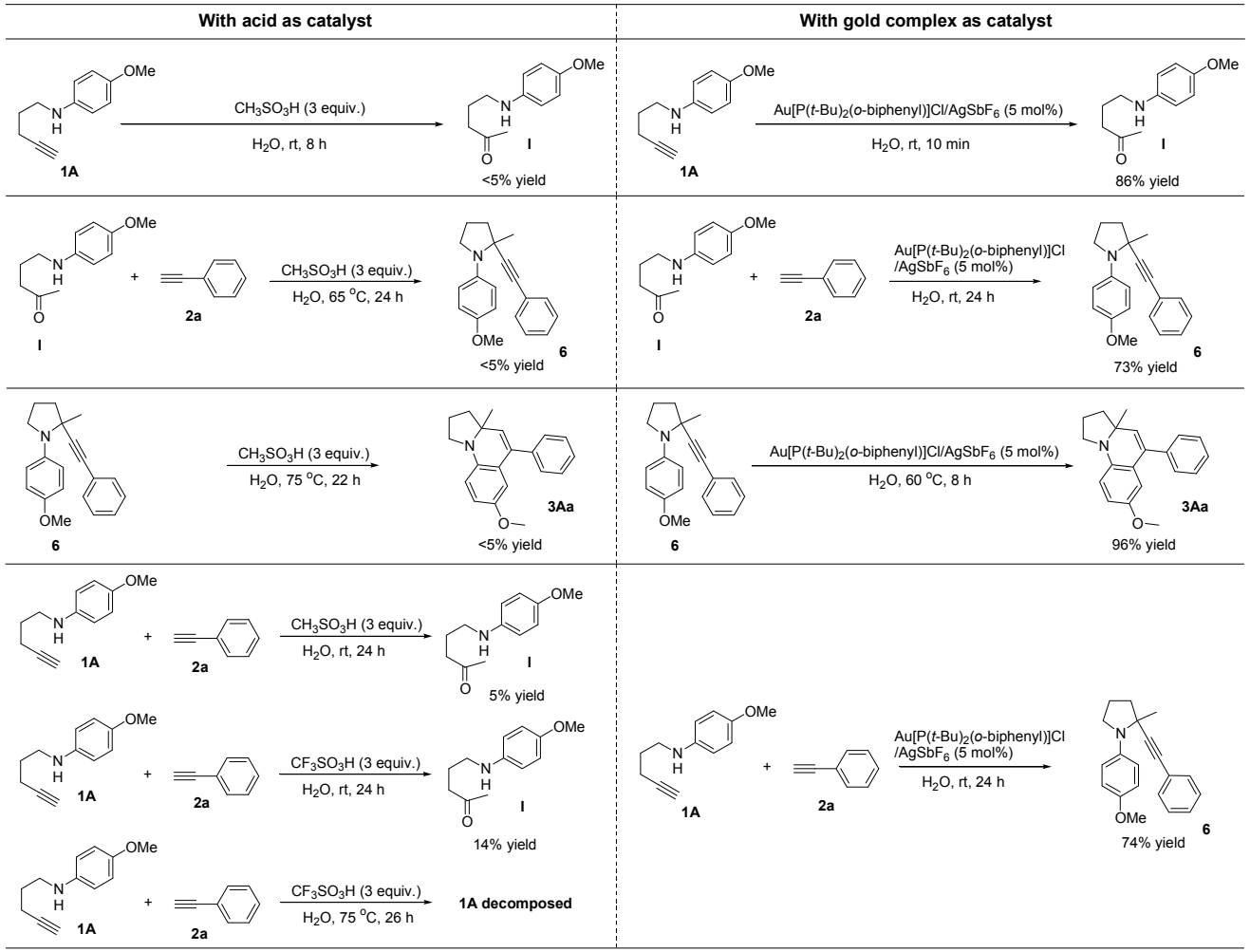
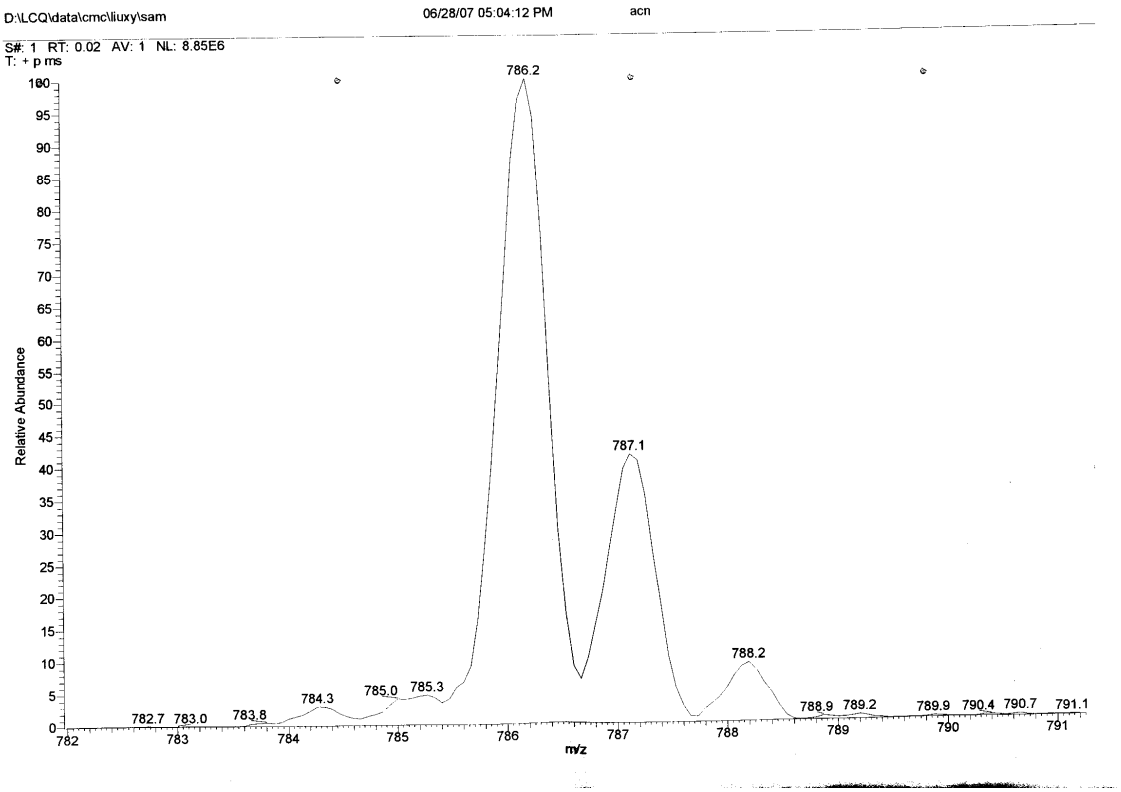
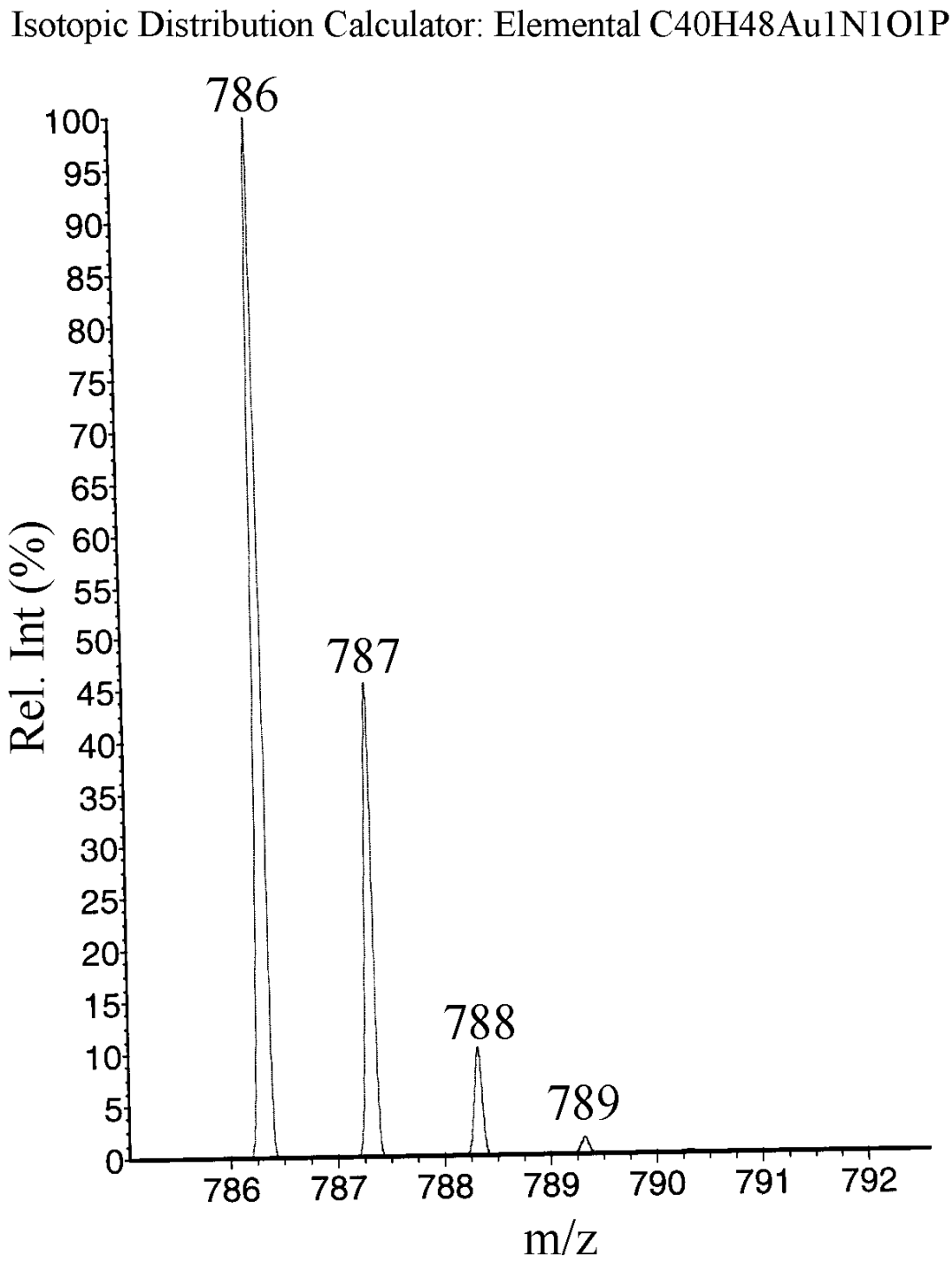

With acid as catalyst
With gold complex as catalyst
OMe
N
H
1A
CH3SO3H (3 equiv.)
H2O, rt, 8 h
O
I
<5% yield
Au[P(t-Bu)2(o-biphenyl)]Cl/AgSbF6 (5 mol%)
H2O, rt, 10 min
86% yield
2a
CH3SO3H (3 equiv.)
H2O, 65 °C, 24 h
6
<5% yield
Au[P(t-Bu)2(o-biphenyl)]Cl
/AgSbF6 (5 mol%)
H2O, rt, 24 h
73% yield
CH3SO3H (3 equiv.)
H2O, 75 °C, 22 h
3Aa
<5% yield
Au[P(t-Bu)2(o-biphenyl)]Cl/AgSbF6 (5 mol%)
H2O, 60 °C, 8 h
96% yield
CH3SO3H (3 equiv.)
H2O, rt, 24 h
5% yield
CF3SO3H (3 equiv.)
H2O, rt, 24 h
14% yield
CF3SO3H (3 equiv.)
H2O, 75 °C, 26 h
1A decomposed
74% yield

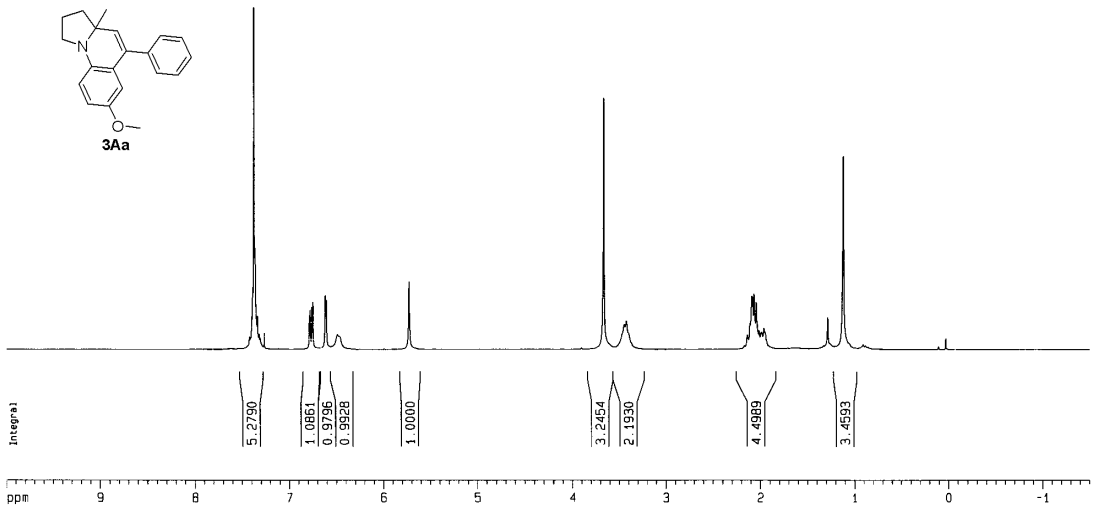
Figure S1. ESI MS spectrum of a solution of **6** and Au[P(*t*-Bu)$_2$(*o*-biphenyl)]SbF$_6$ (20 mol%) in CH_3CN (spectrum **a**) showing a cluster peak at *m/z* 786 which can be attributed to the adduct formed between Au^+[P(*t*-Bu)$_2$(*o*-biphenyl)] and **6**. The observed isotopic distribution well matches the calculated one (spectrum **b**)

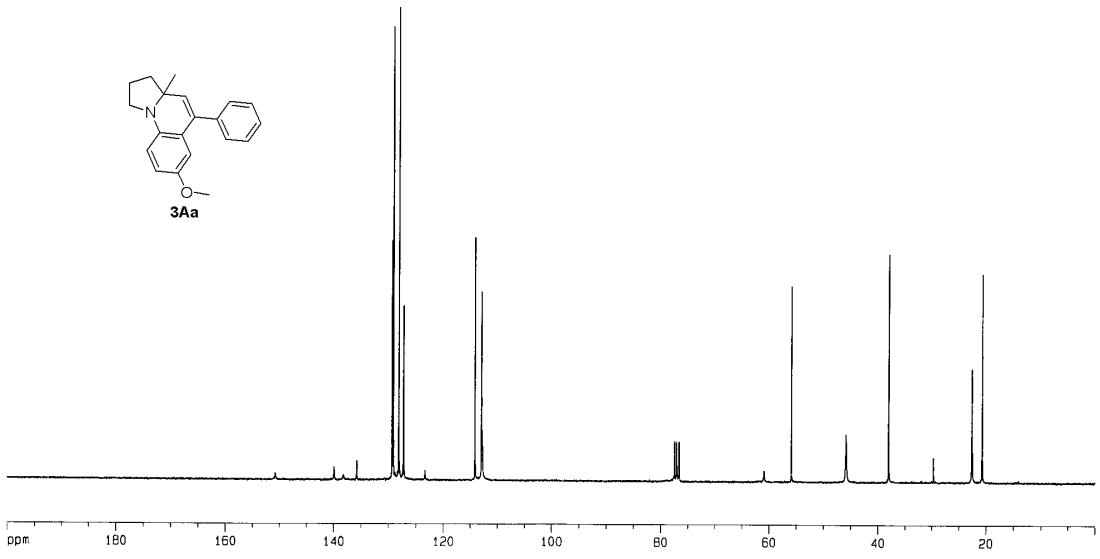
Spectrum a

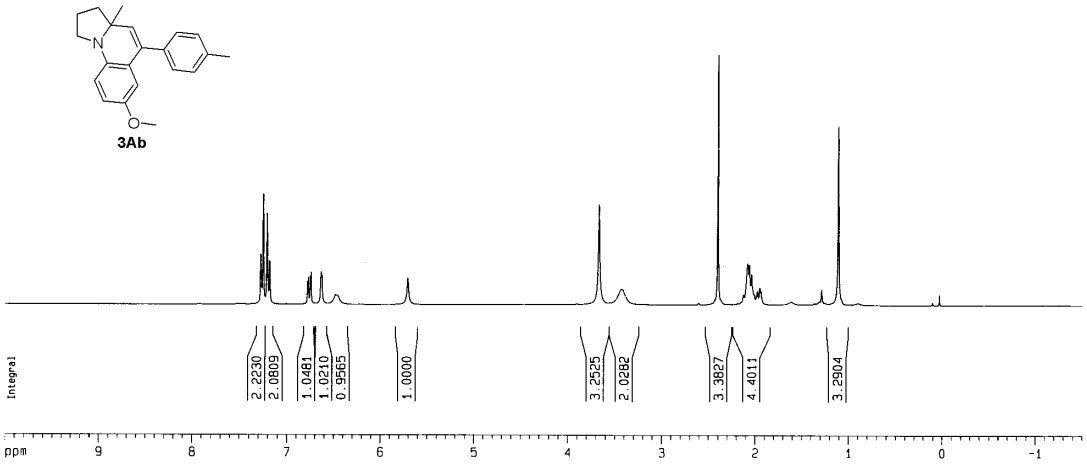


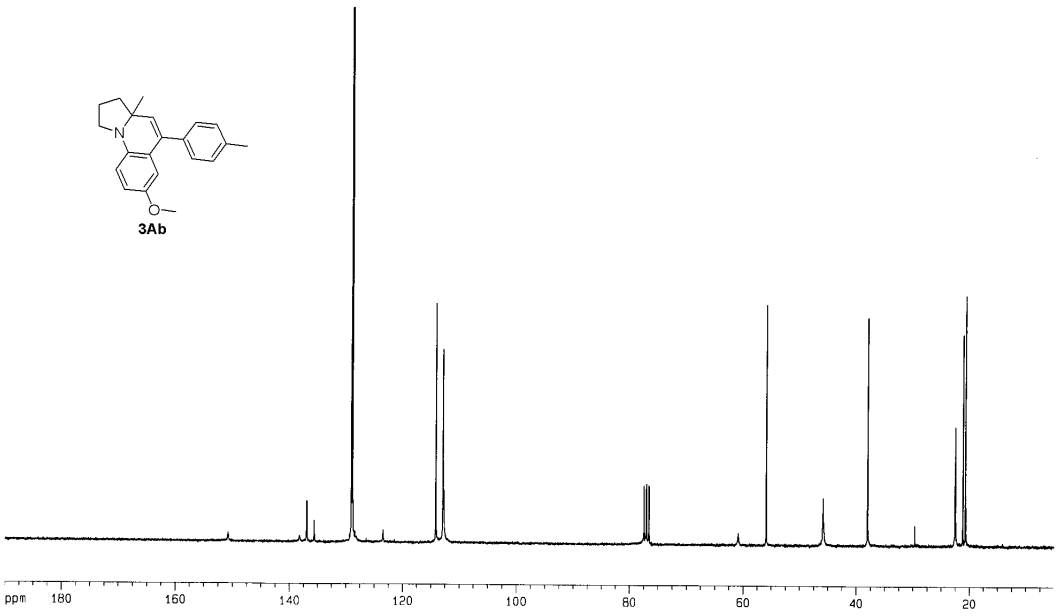
Spectrum b

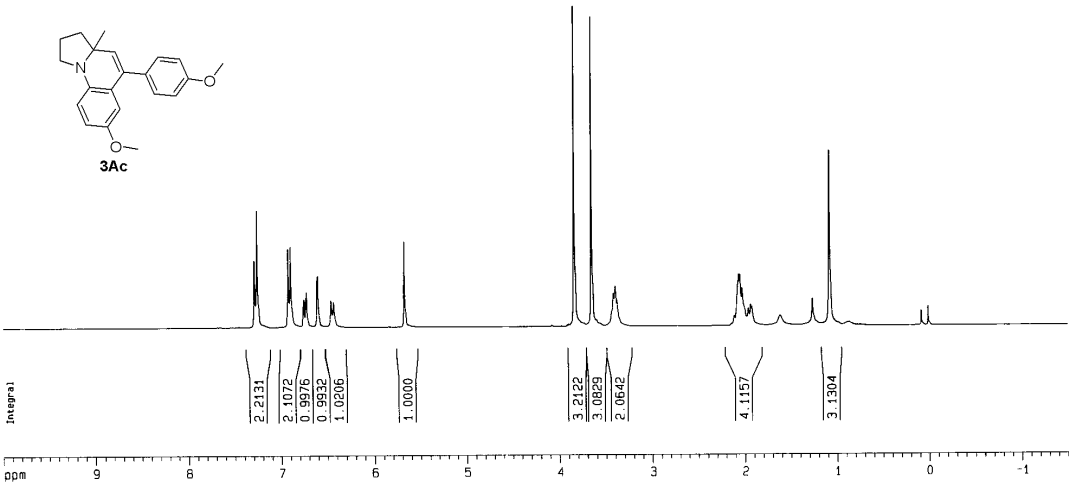

Isotopic Distribution Calculator: Elemental C40H48Au1N1O1P1
786
787
788
789
Rel. Int (%)
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
786
787
788
789
790
791
792
m/z

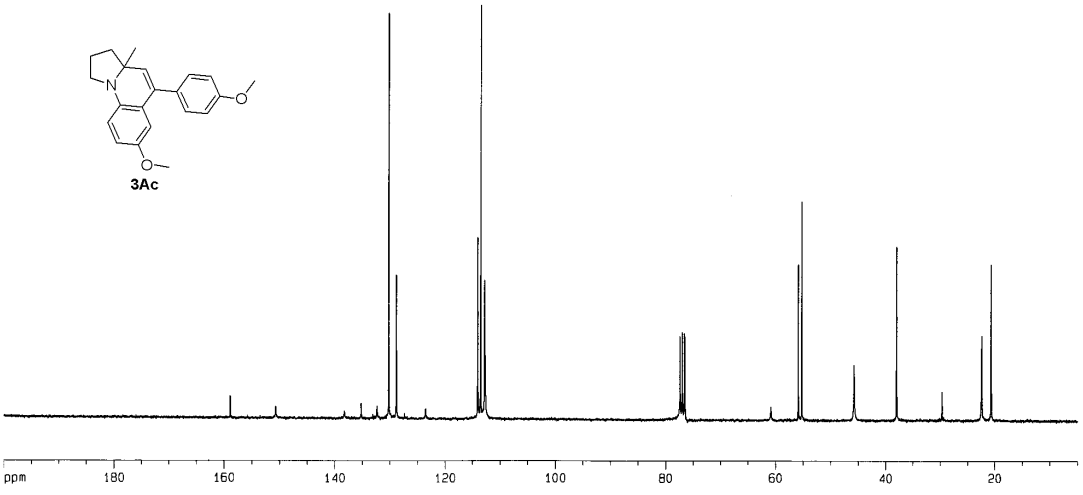

3Aa
Integral
5.2790
1.0861
0.9796
0.9928
1.0000
3.2454
2.1930
4.4989
3.4593
ppm
9
8
7
6
5
4
3
2
1
0
-1

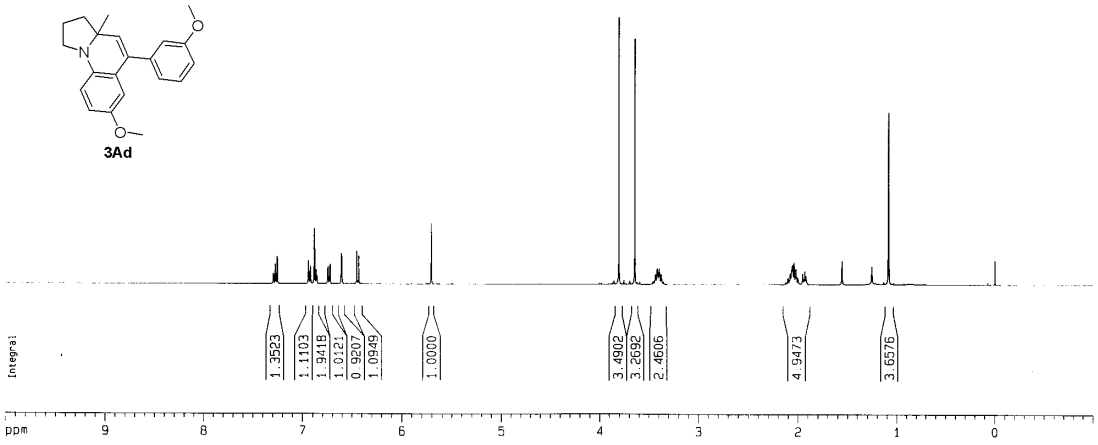

3Aa
ppm
180
160
140
120
100
80
60
40
20

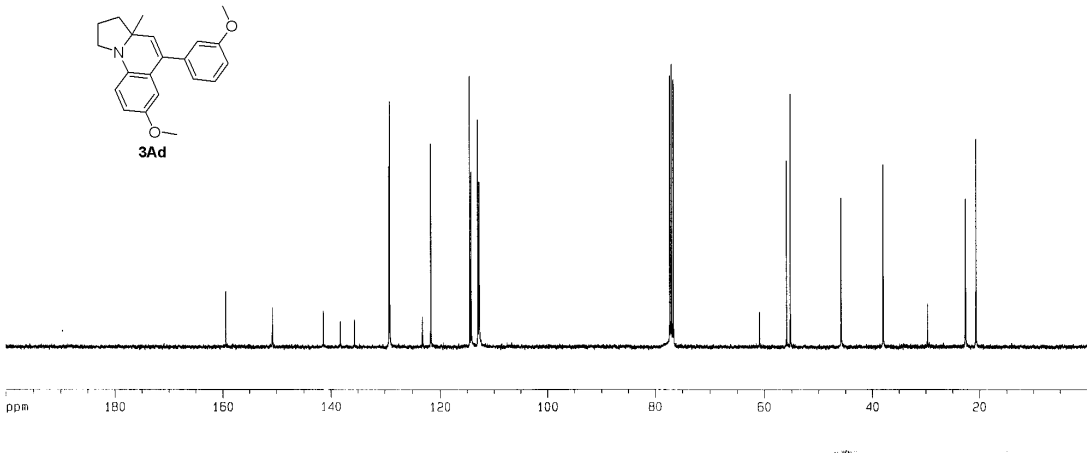

3Ab
Integral
2.2230
2.0809
1.0481
1.0210
0.9565
1.0000
3.2525
2.0282
3.3827
4.4011
3.2904
ppm
9
8
7
6
5
4
3
2
1
0
-1

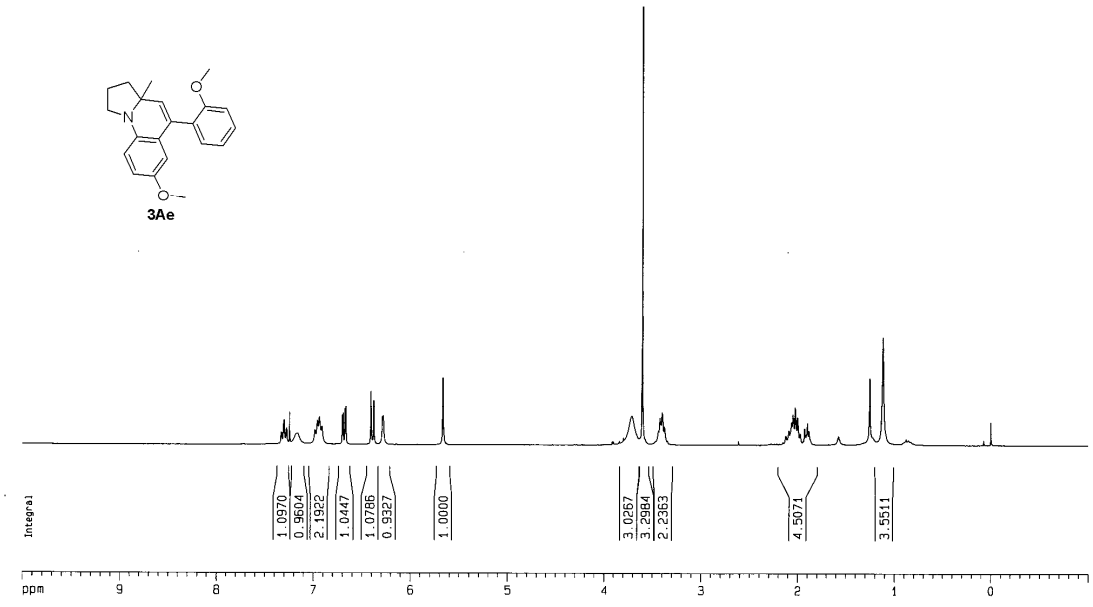

3Ab
ppm
180
160
140
120
100
80
60
40
20

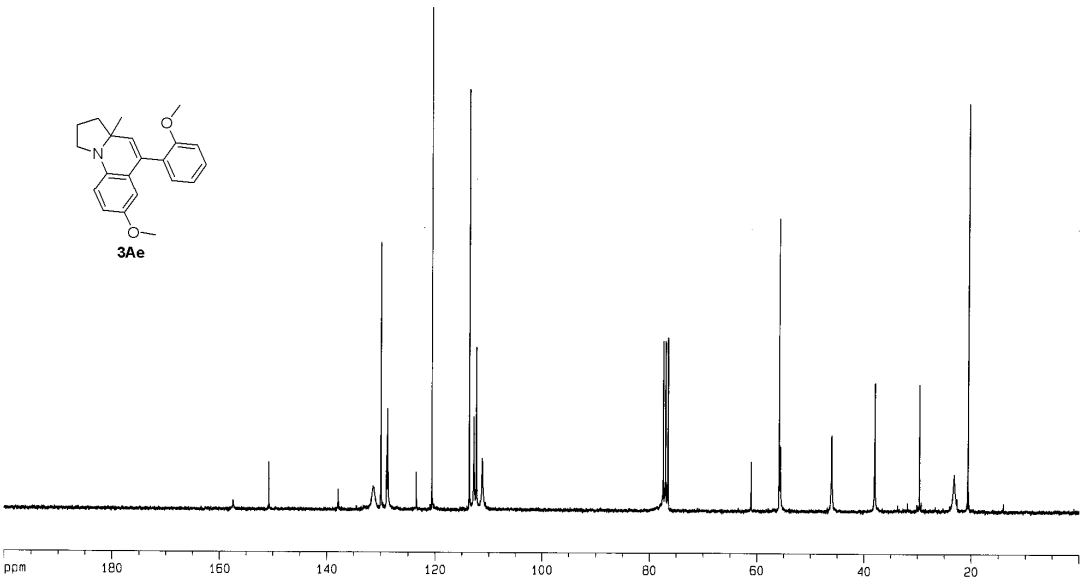

3Ac
Integral
2.2131
2.1072
0.9976
0.9932
1.0206
1.0000
3.2122
3.0829
2.0642
4.1157
3.1304
ppm
9
8
7
6
5
4
3
2
1
0
-1

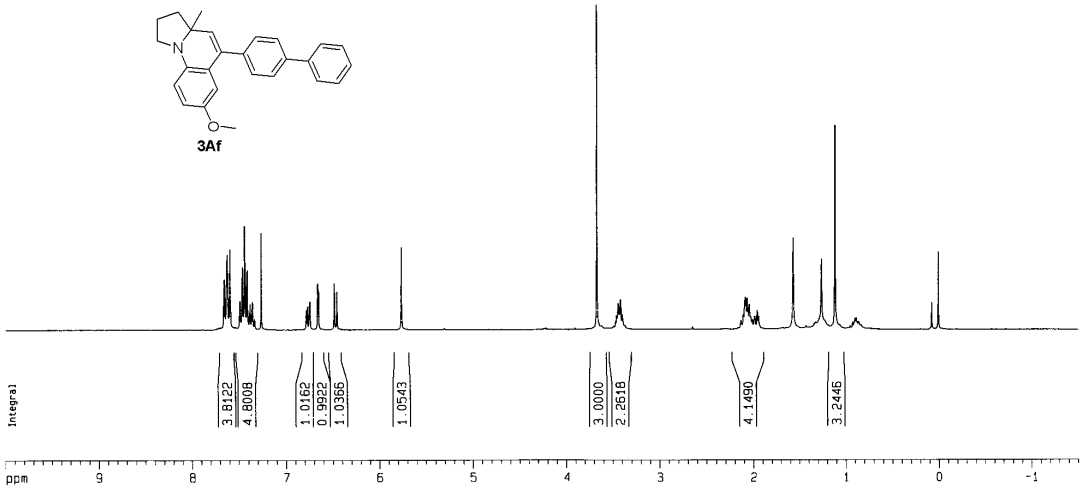

3Ac
ppm
180
160
140
120
100
80
60
40
20

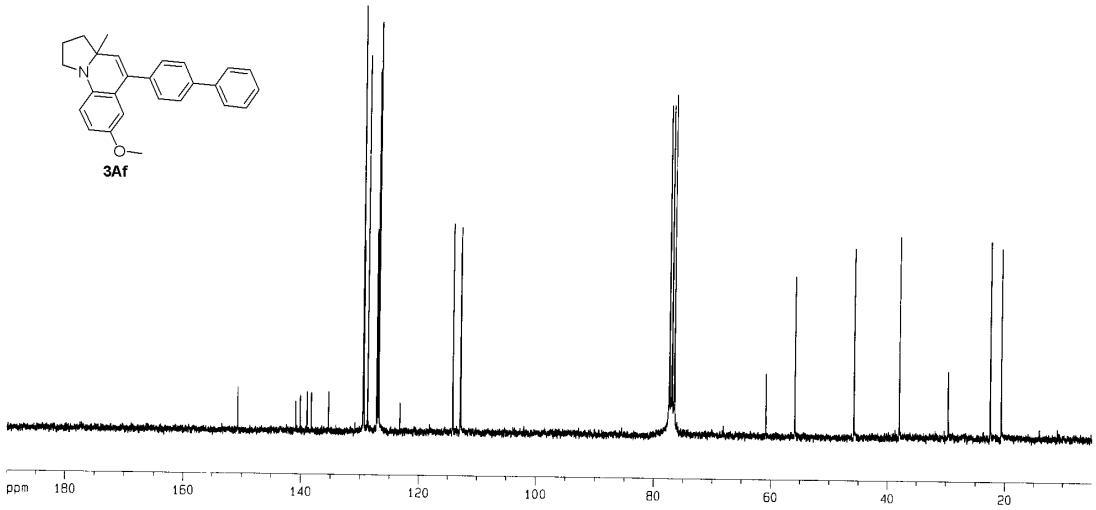

3Ad
Integral
1.3523
1.1103
1.9418
1.0121
0.9207
1.0949
1.0000
3.4902
3.2692
2.4606
4.9473
3.6576
ppm
9
8
7
6
5
4
3
2
1
0

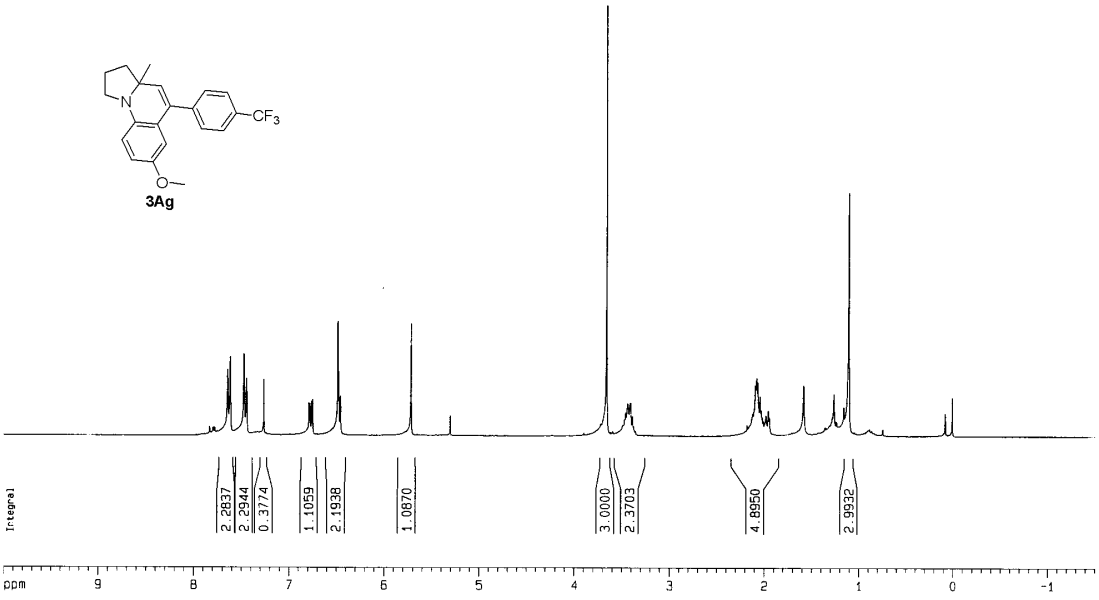

3Ad
ppm
180
160
140
120
100
80
60
40
20

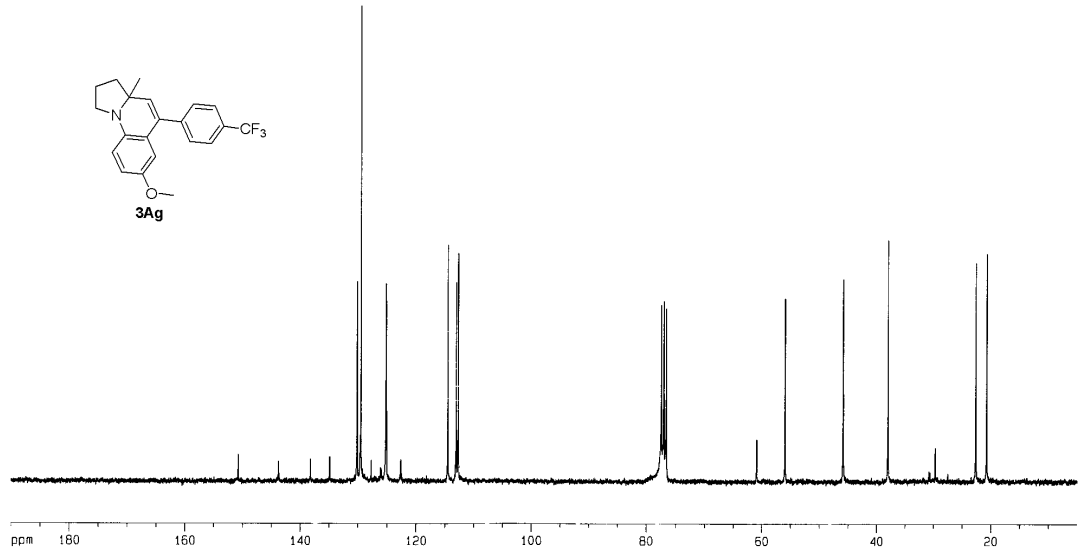

3Ae
Integral
1.0970
0.9604
2.1922
1.0447
1.0786
0.9327
1.0000
3.0267
3.2984
2.2363
4.5071
3.5511
ppm
9
8
7
6
5
4
3
2
1
0

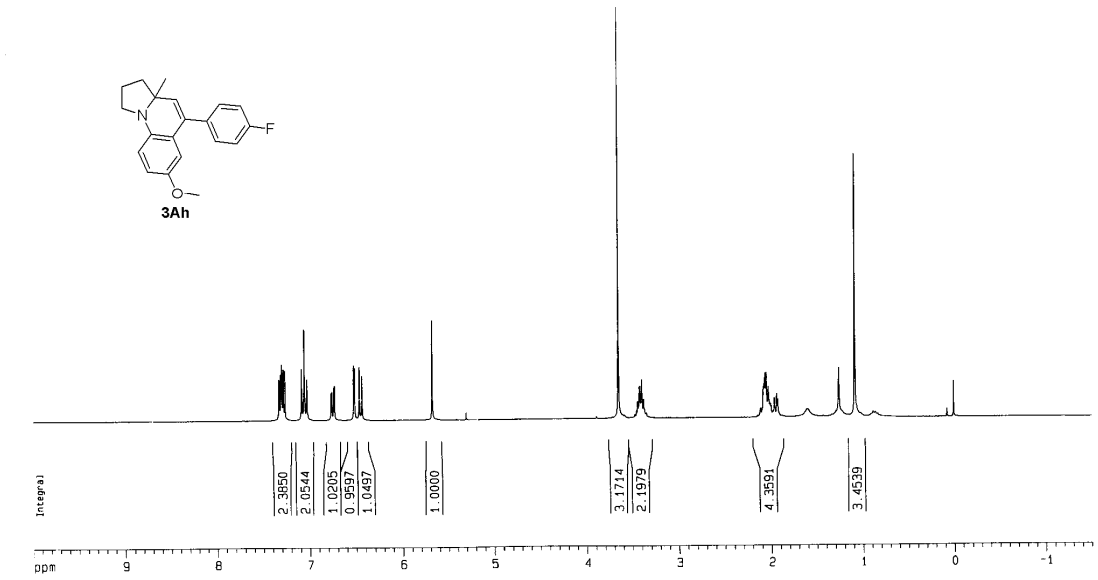

3Ae
ppm
180
160
140
120
100
80
60
40
20

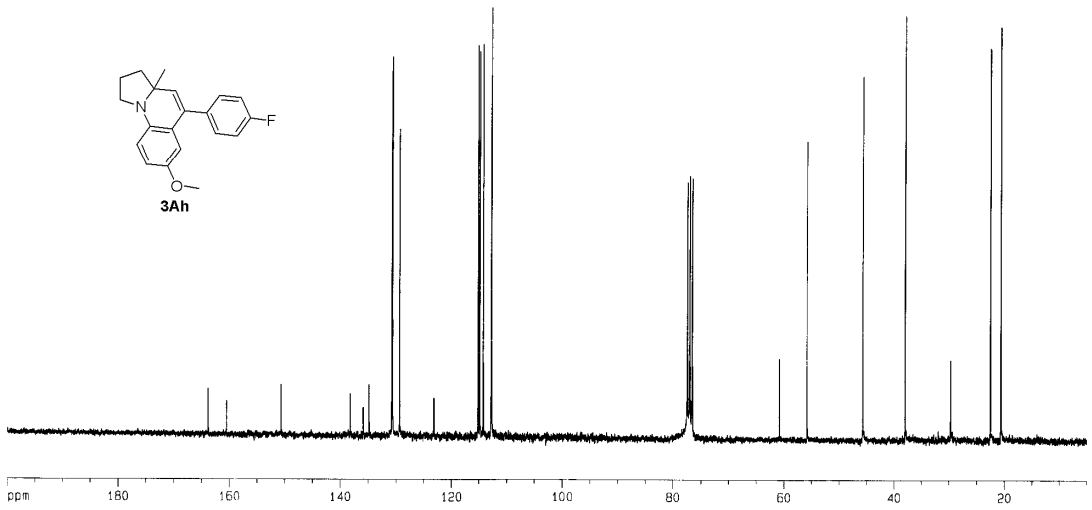

3Af
Integral
3.8122
4.8008
1.0162
0.9922
1.0366
1.0543
3.0000
2.2618
4.1490
3.2446
ppm
9
8
7
6
5
4
3
2
1
0
-1

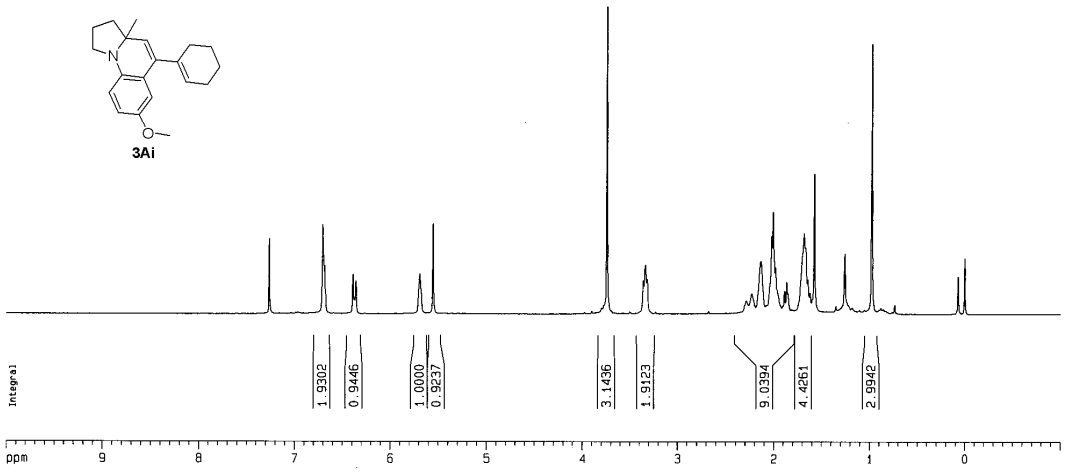

3Af
ppm
180
160
140
120
100
80
60
40
20

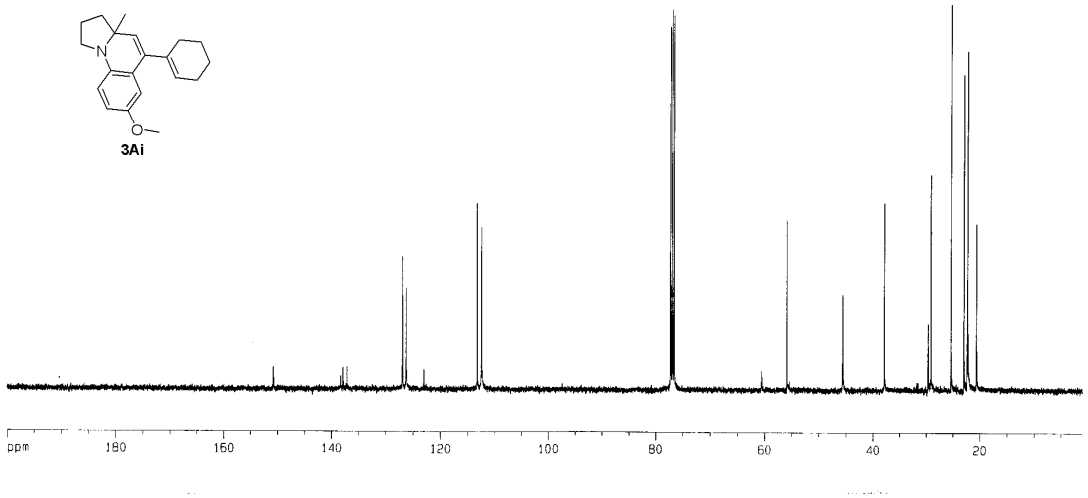

3Ag
Integral
2.2837
2.2944
0.3774
1.1059
2.1938
1.0870
3.0000
2.3703
4.8950
2.9932
ppm

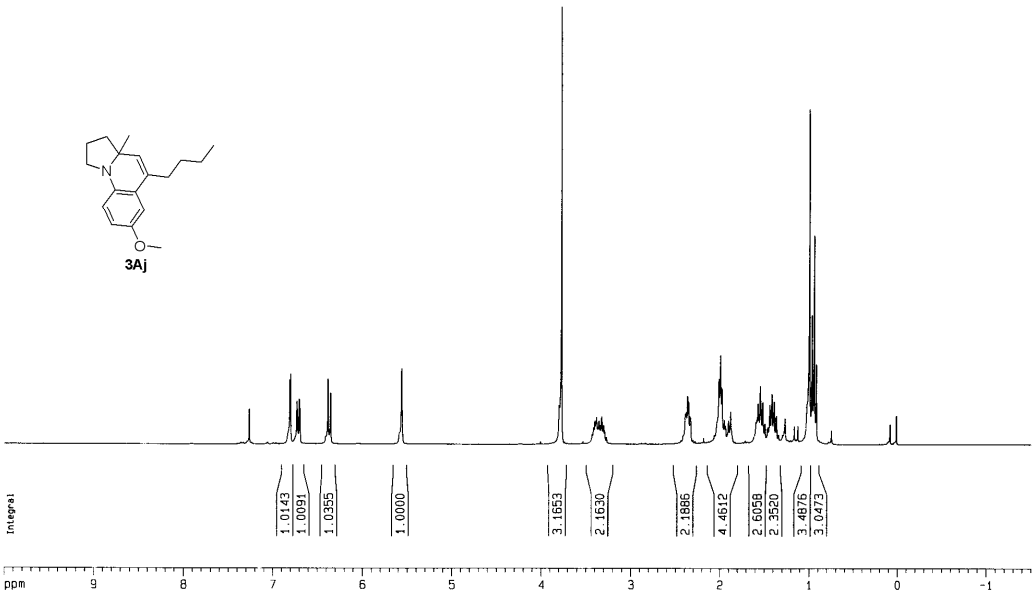

3Ag
ppm

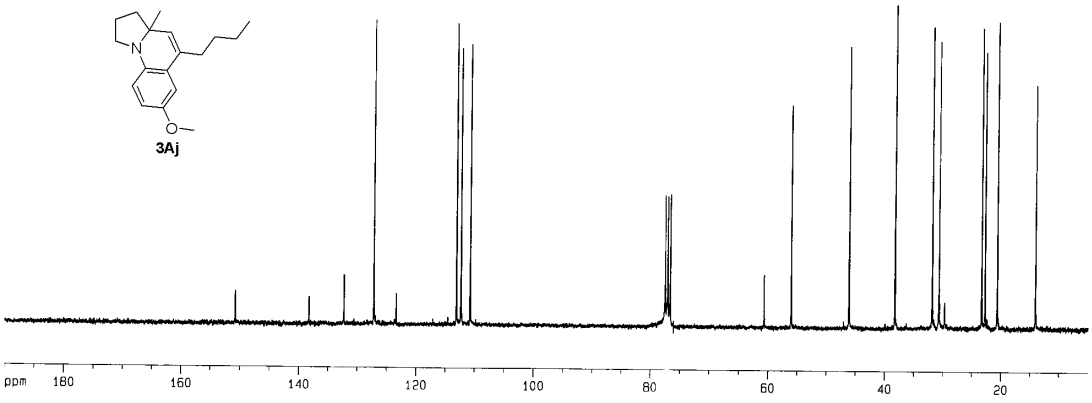

3Ah
F
Integral
2.3850
2.0544
1.0205
0.9597
1.0497
1.0000
3.1714
2.1979
4.3591
3.4539
ppm
9
8
7
6
5
4
3
2
1
0
-1

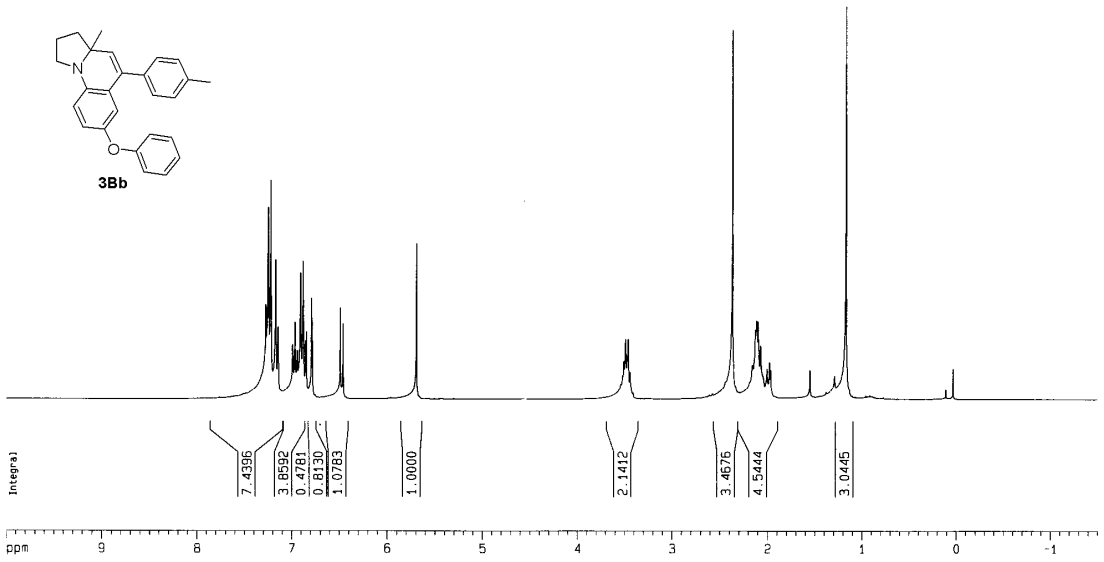

3Ah
F
ppm
180
160
140
120
100
80
60
40
20

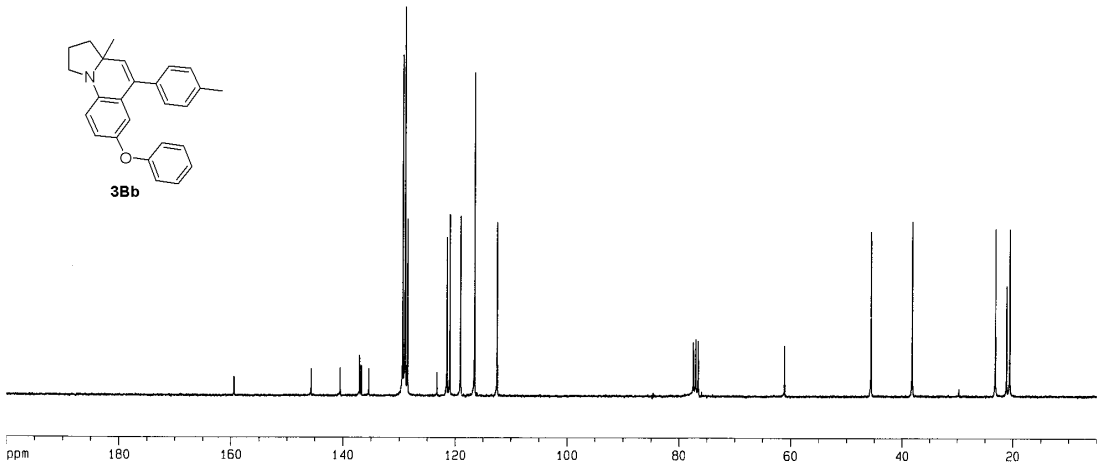

3Ai
Integral
1.9302
0.9446
1.0000
0.9237
3.1436
1.9123
9.0394
4.4261
2.9942
ppm
9
8
7
6
5
4
3
2
1
0

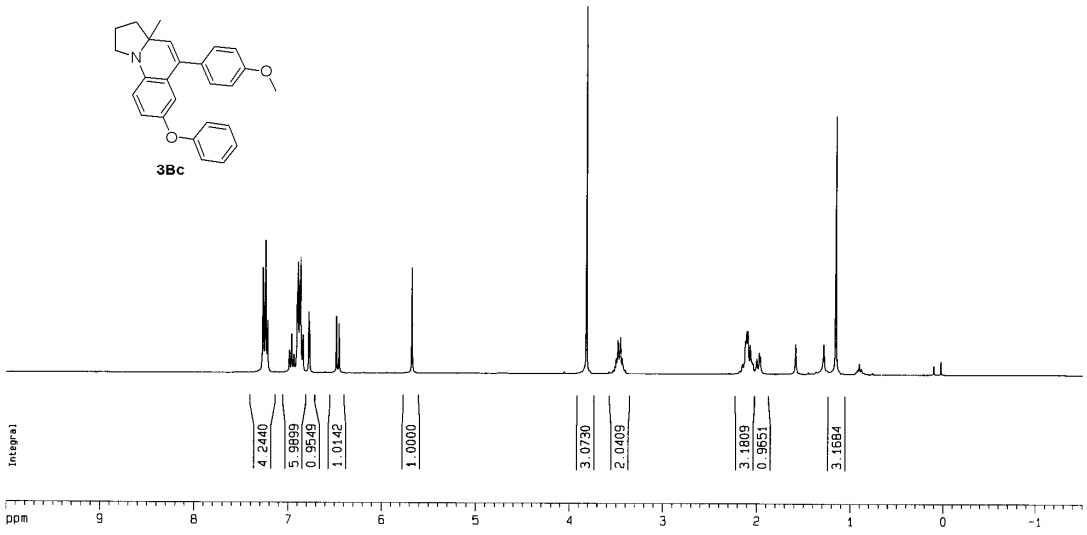

3Ai
ppm
180
160
140
120
100
80
60
40
20

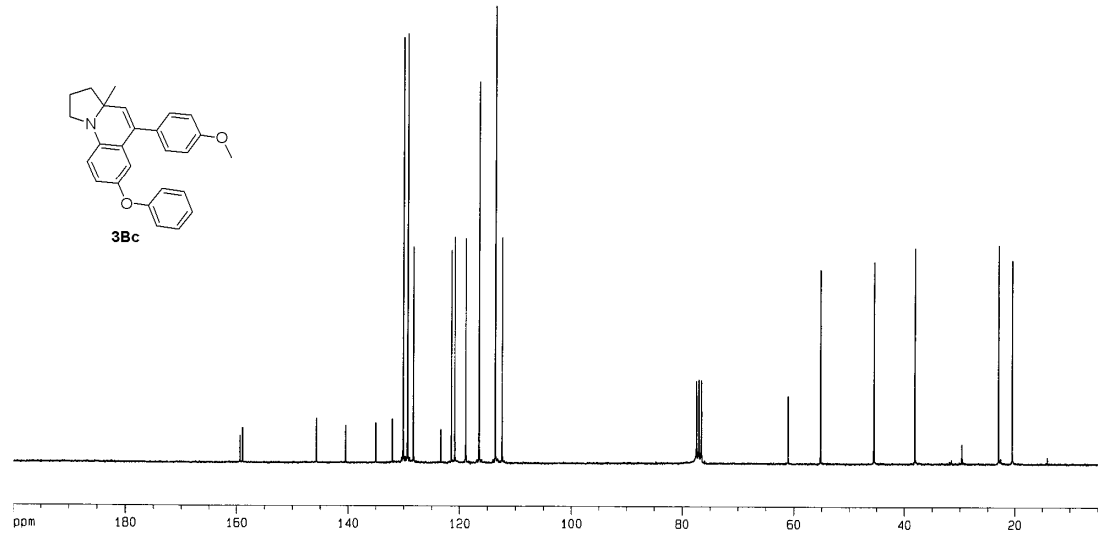

3Aj
Integral
1.0143
1.0091
1.0355
1.0000
3.1653
2.1630
2.1886
4.4612
2.6056
2.3520
3.4876
3.0473
ppm
9
8
7
6
5
4
3
2
1
0
-1

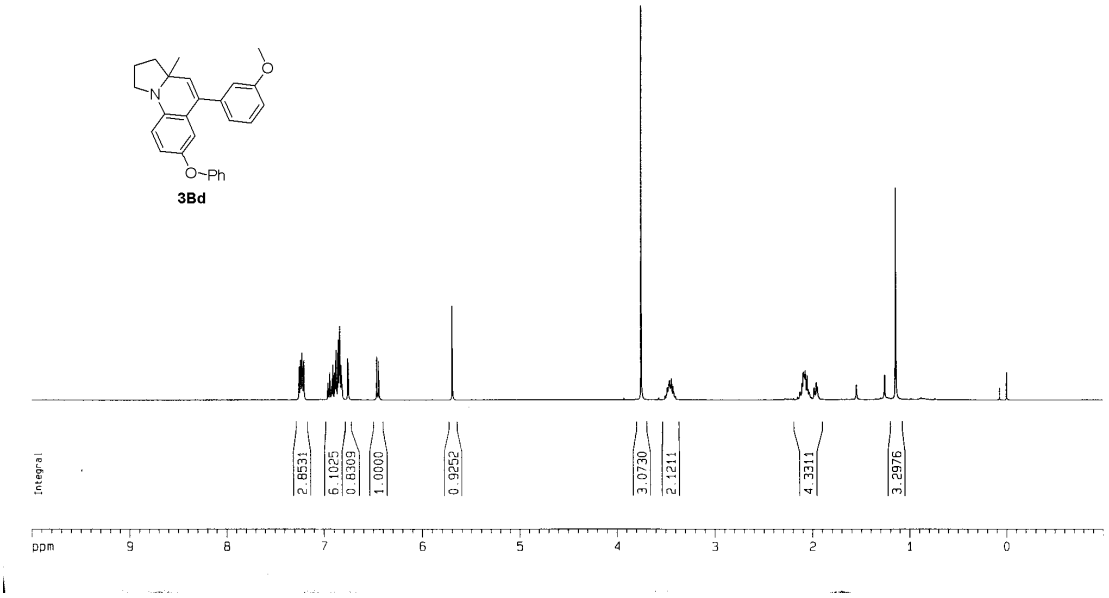

3Aj
ppm
180
160
140
120
100
80
60
40
20

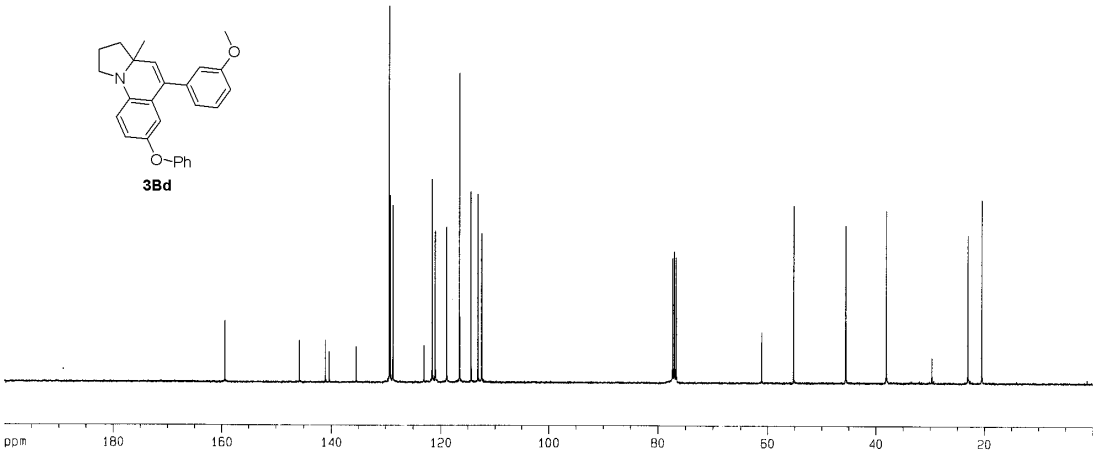

3Bb
Integral
7.4396
3.8592
0.4781
0.8130
1.0783
1.0000
2.1412
3.4676
4.5444
3.0445
ppm
9
8
7
6
5
4
3
2
1
0
-1

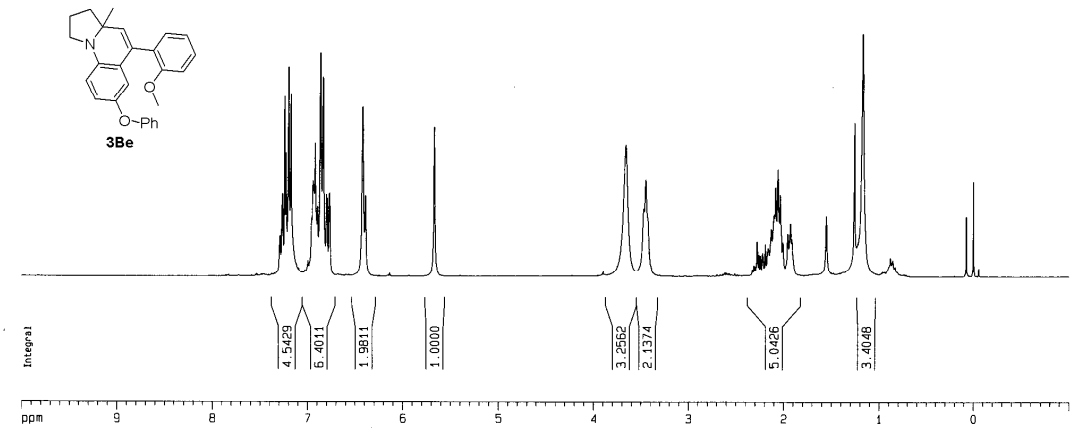

3Bb
ppm
180
160
140
120
100
80
60
40
20

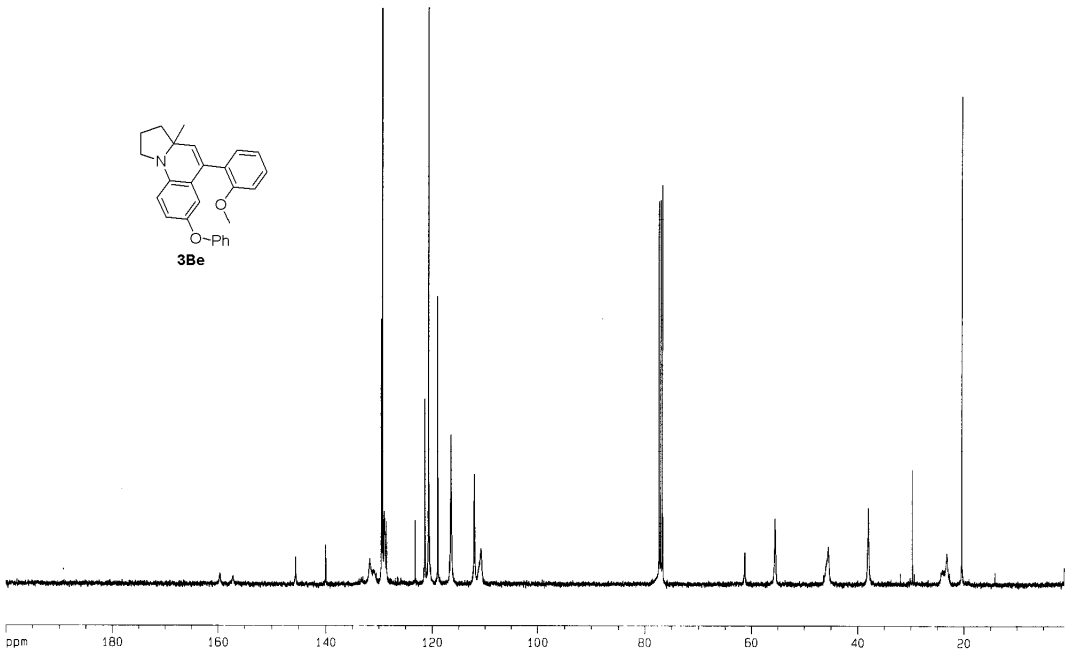

3Bc
Integral
4.2440
5.9899
0.9549
1.0142
1.0000
3.0730
2.0409
3.1809
0.9651
3.1684
ppm
9
8
7
6
5
4
3
2
1
0
-1

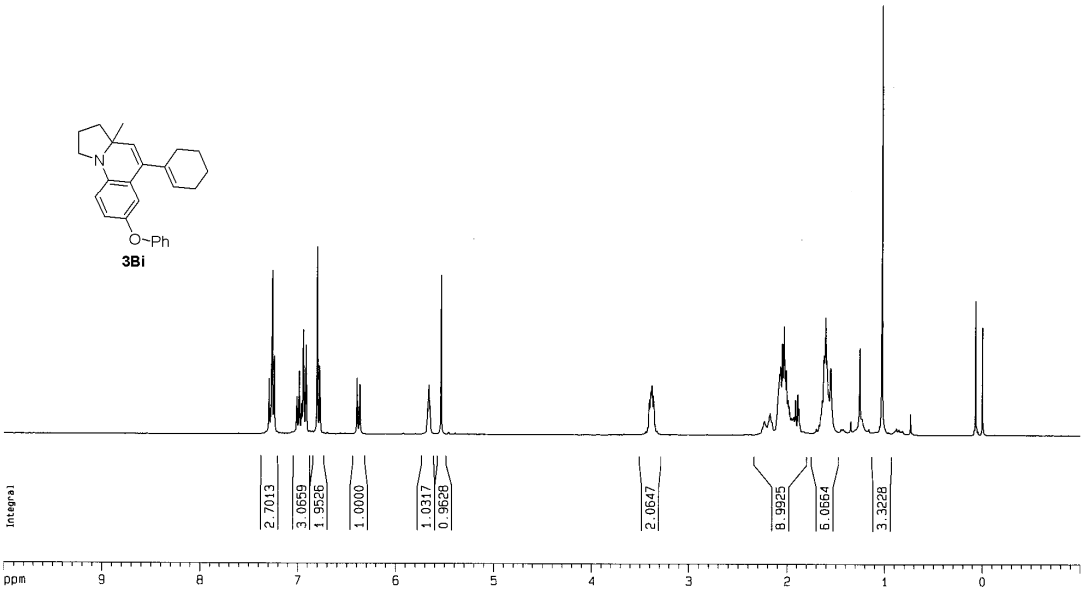

3Bc
ppm
180
160
140
120
100
80
60
40
20

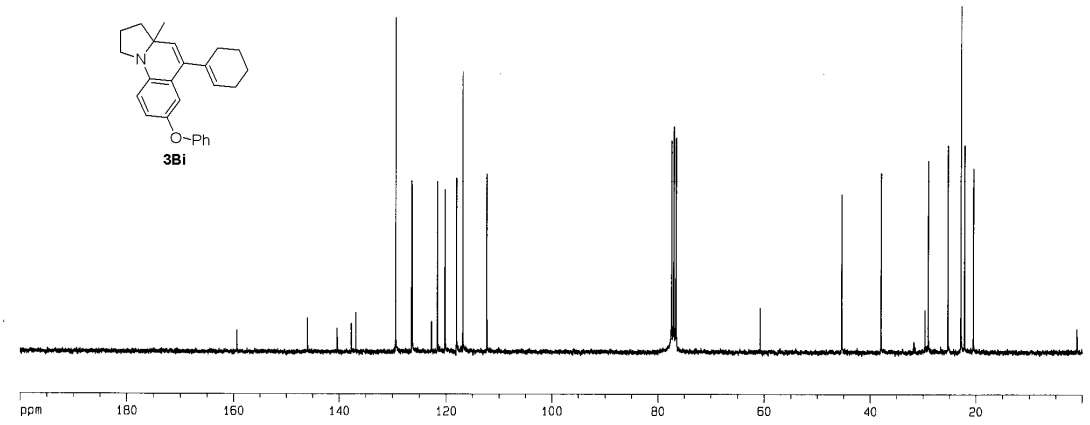

O
N
O~Ph
3Bd
Integral
2.8531
6.1025
0.8309
1.0000
0.9252
3.0730
2.1211
4.3311
3.2976
ppm
9
8
7
6
5
4
3
2
1
0

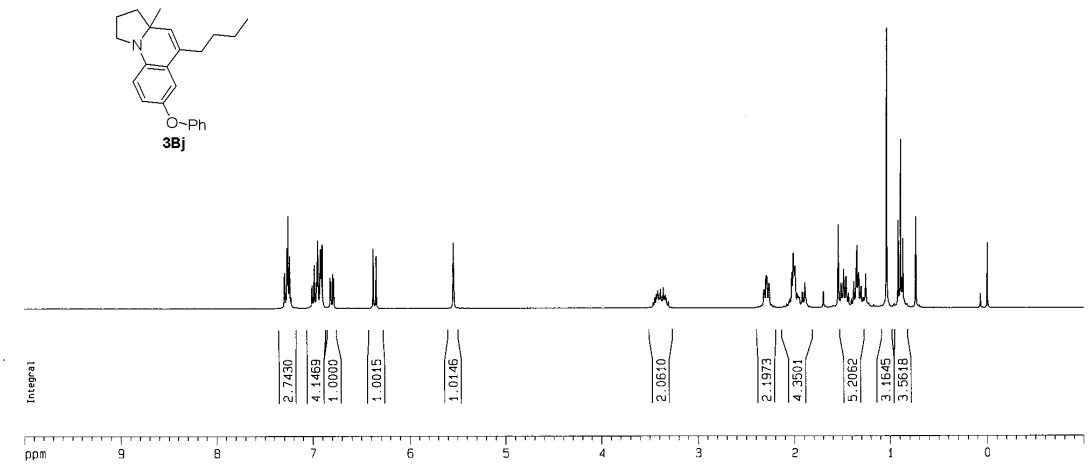

O
N
O~Ph
3Bd
ppm
180
160
140
120
100
80
50
40
20

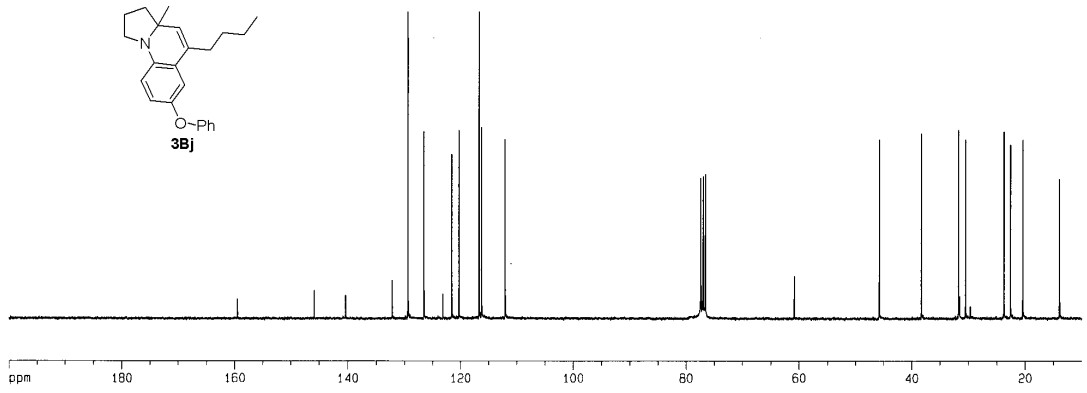

3Be
Integral
4.5429
6.4011
1.9811
1.0000
3.2562
2.1374
5.0426
3.4048
ppm
9
8
7
6
5
4
3
2
1
0

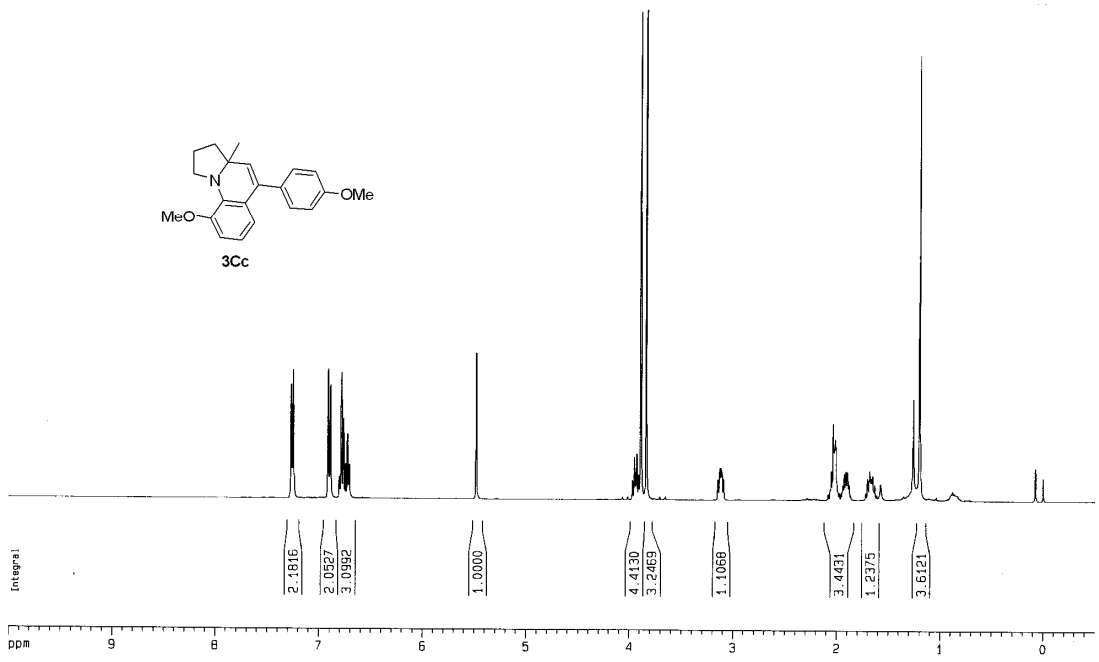

3Be
ppm
180
160
140
120
100
80
60
40
20

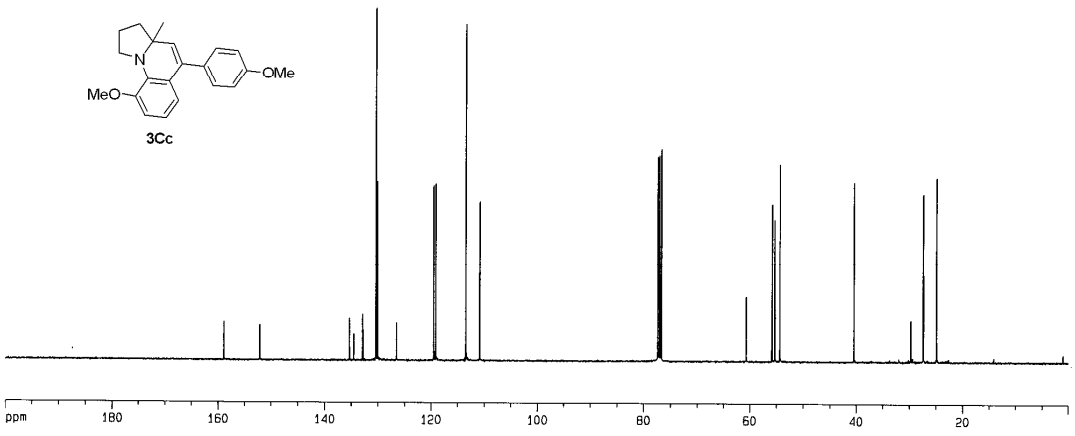

O~Ph
3Bi
Integral
2.7013
3.0659
1.9526
1.0000
1.0317
0.9628
2.0647
8.9925
5.0664
3.3228
ppm
9
8
7
6
5
4
3
2
1
0

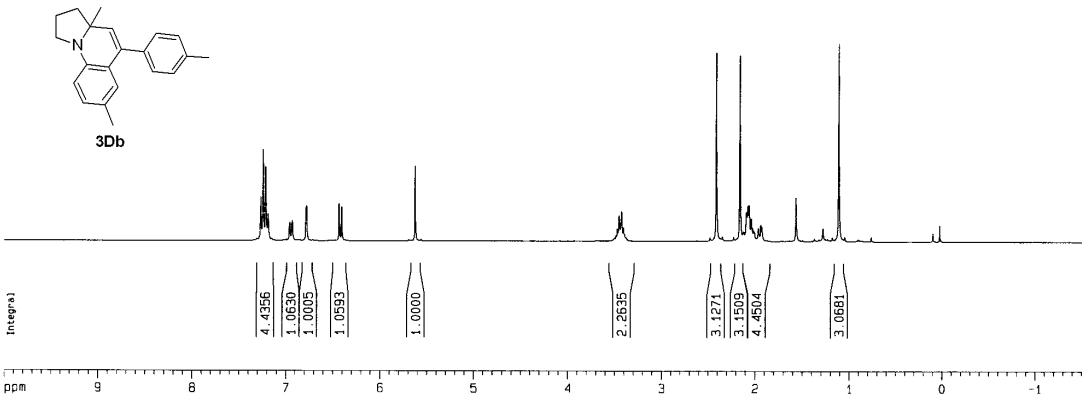

O~Ph
3Bi
ppm
180
160
140
120
100
80
60
40
20

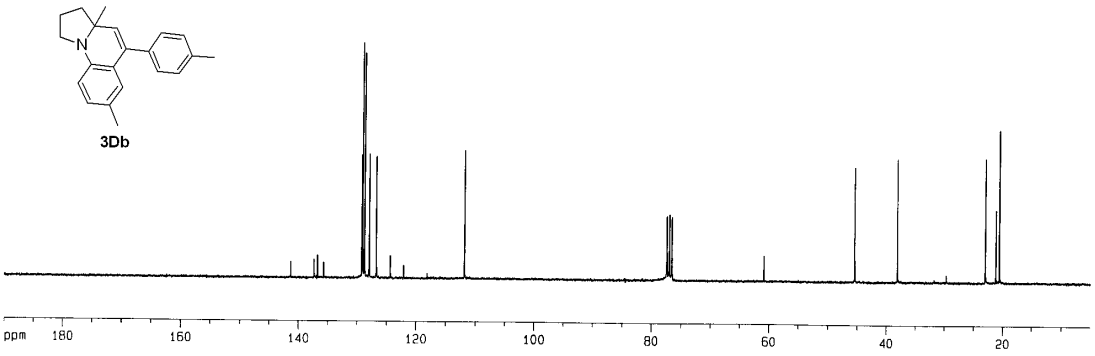

O~Ph
3Bj
Integral
2.7430
4.1469
1.0000
1.0015
1.0146
2.0610
2.1973
4.3501
5.2062
3.1645
3.5618
ppm
9
8
7
6
5
4
3
2
1
0

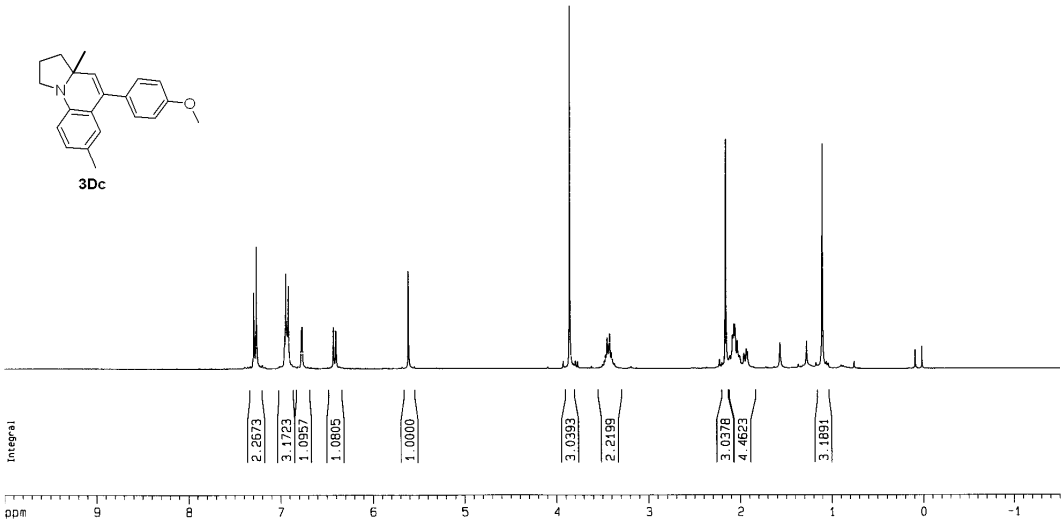

O~Ph
3Bj
ppm
180
160
140
120
100
80
60
40
20

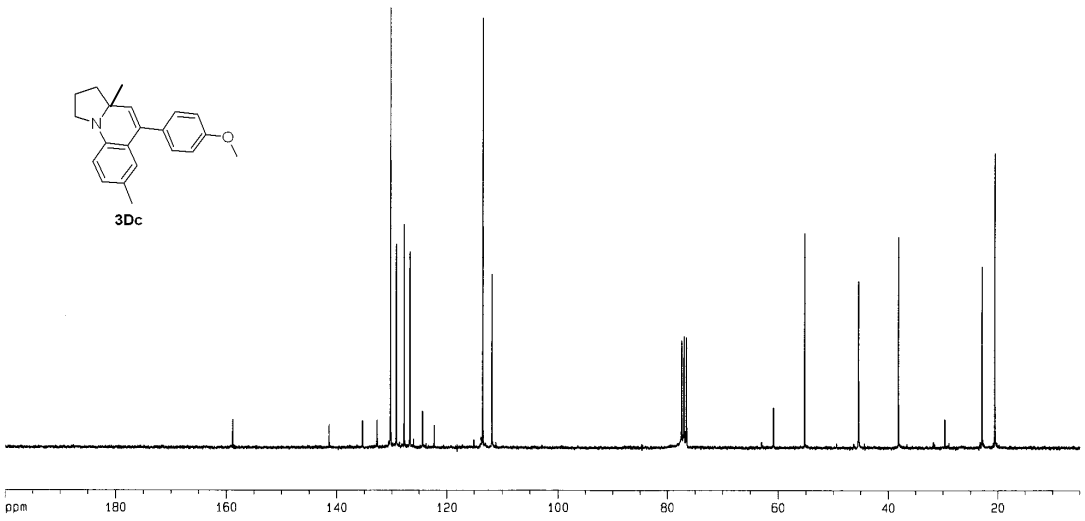

OMe
MeO
3Cc
Integral
2.1816
2.0527
3.0992
1.0000
4.4130
3.2469
1.1068
3.4431
1.2375
3.6121
ppm
9
8
7
6
5
4
3
2
1
0

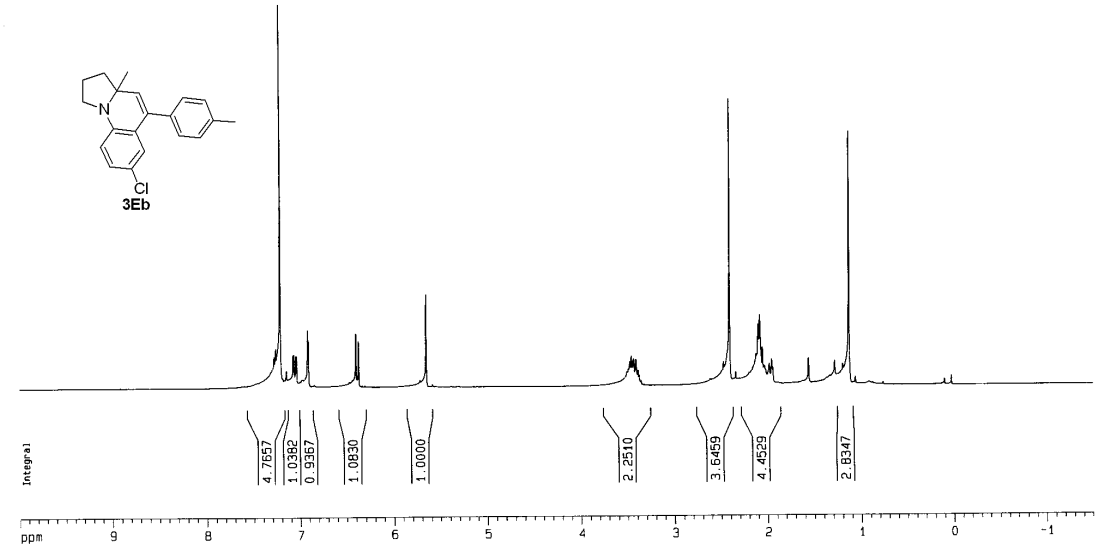

OMe
MeO
3Cc
ppm
180
160
140
120
100
80
60
40
20

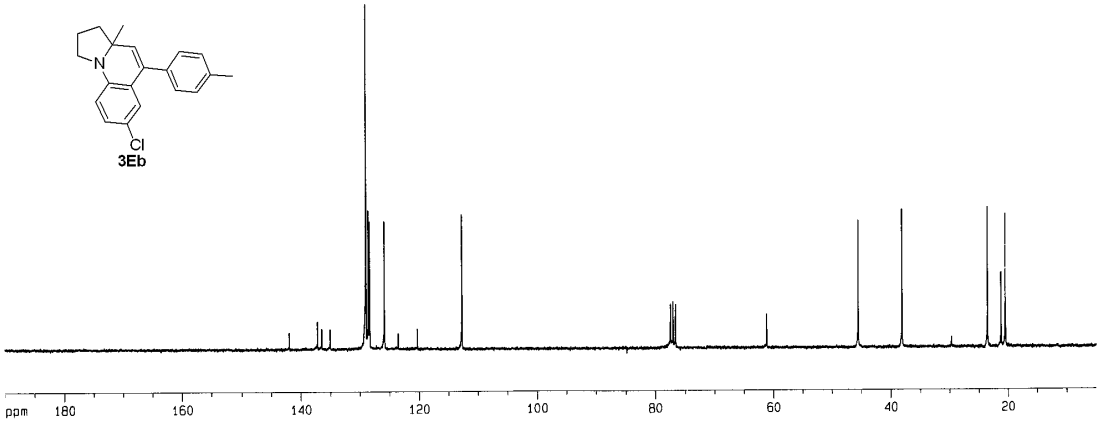

3Db
Integral
4.4356
1.0630
1.0005
1.0593
1.0000
2.2635
3.1271
3.1509
4.4504
3.0681
ppm
9
8
7
6
5
4
3
2
1
0
-1

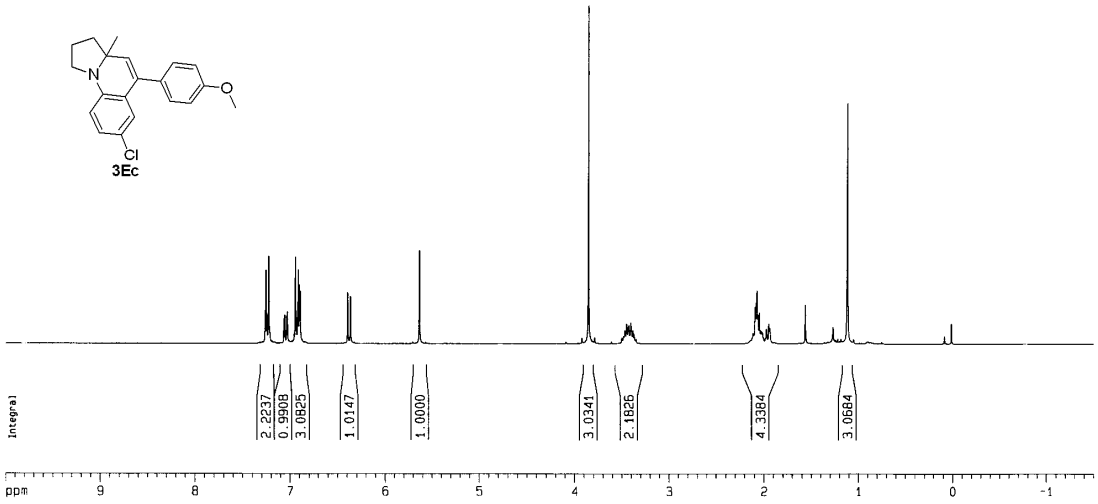

3Db
ppm
180
160
140
120
100
80
60
40
20

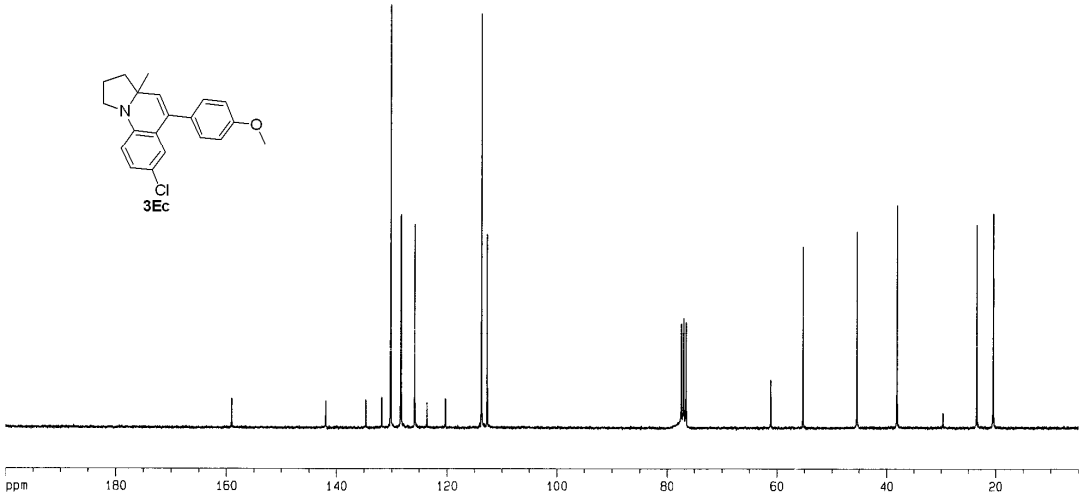

3Dc
Integral
2.2673
3.1723
1.0957
1.0805
1.0000
3.0393
2.2199
3.0378
4.4623
3.1891
ppm
9
8
7
6
5
4
3
2
1
0
-1

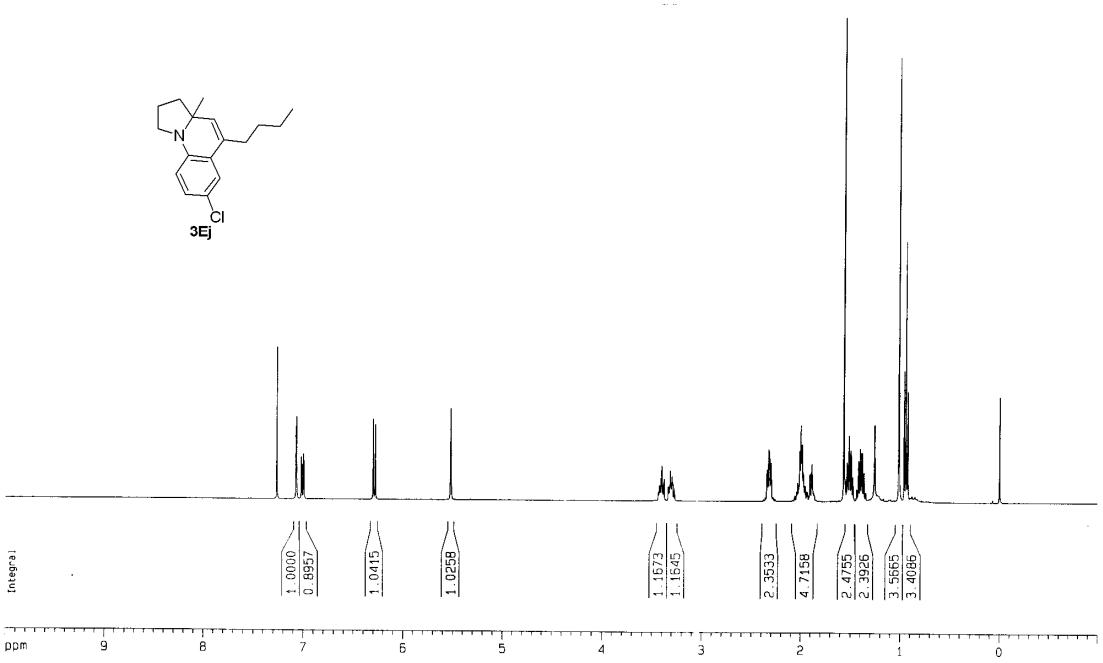

3Dc
ppm
180
160
140
120
100
80
60
40
20

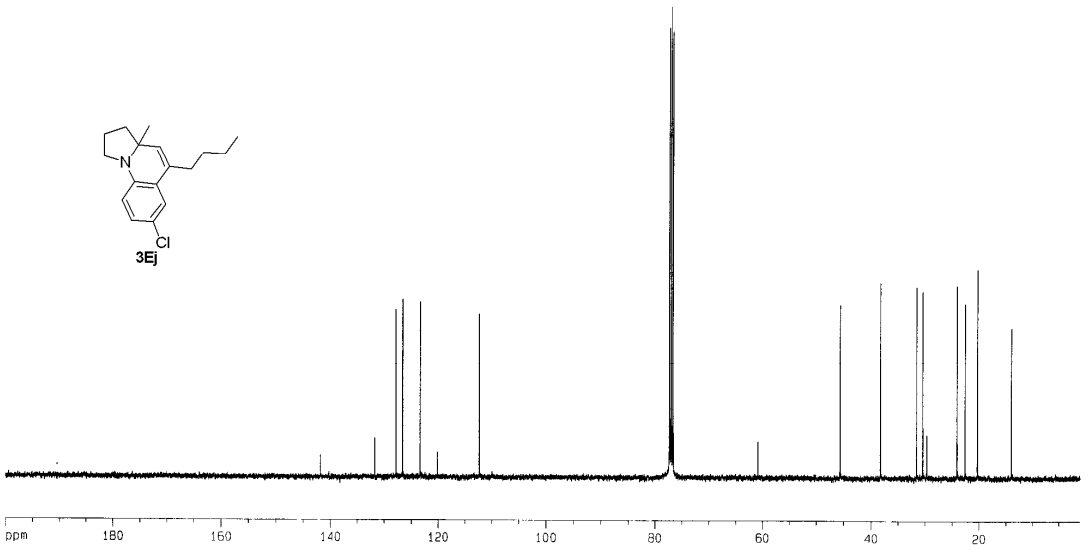

N
Cl
3Eb
Integral
4.7657
1.0382
0.9367
1.0830
1.0000
2.2510
3.6459
4.4529
2.8347
ppm
9
8
7
6
5
4
3
2
1
0
-1

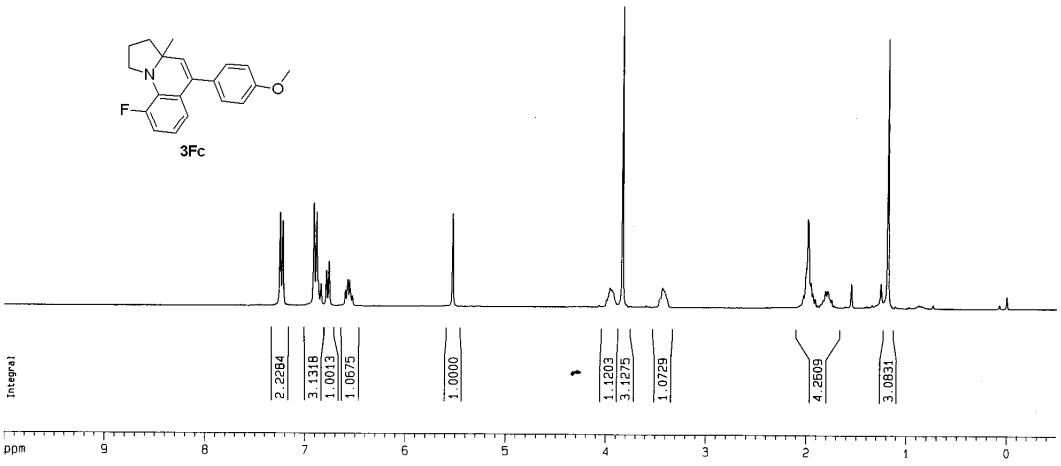

N
Cl
3Eb
ppm
180
160
140
120
100
80
60
40
20

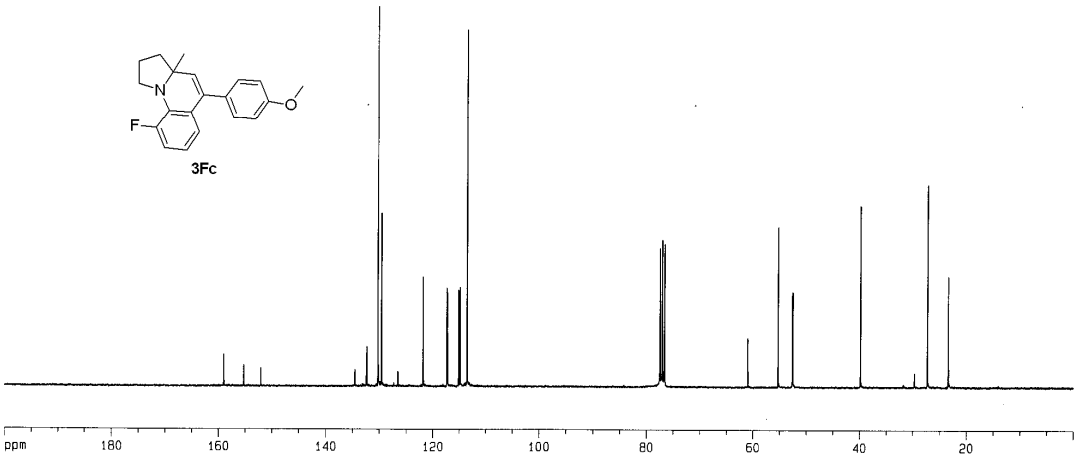

3Ec
Integral
2.2237
0.9908
3.0825
1.0147
1.0000
3.0341
2.1826
4.3384
3.0684
ppm
9
8
7
6
5
4
3
2
1
0
-1

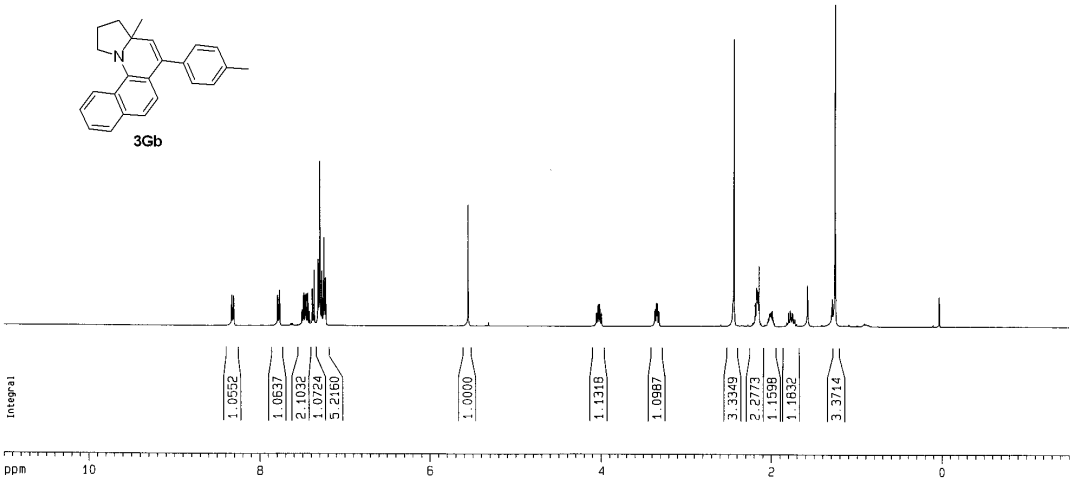

3Ec
ppm
180
160
140
120
100
80
60
40
20

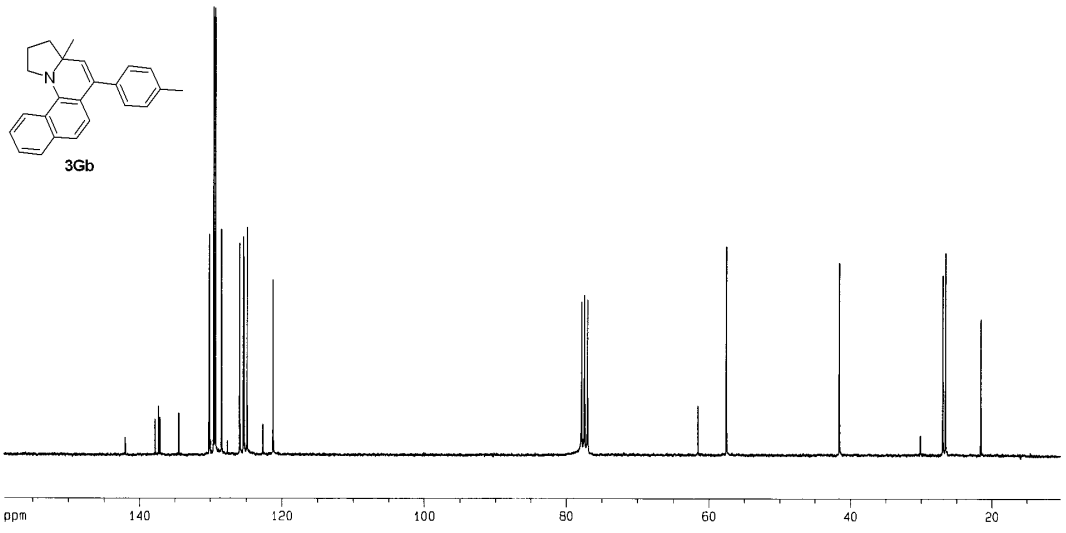

3Ej
Integral
1.0000
0.8957
1.0415
1.0258
1.1673
1.1645
2.3533
4.7158
2.4755
2.3926
3.5665
3.4086
ppm
9
8
7
6
5
4
3
2
1
0

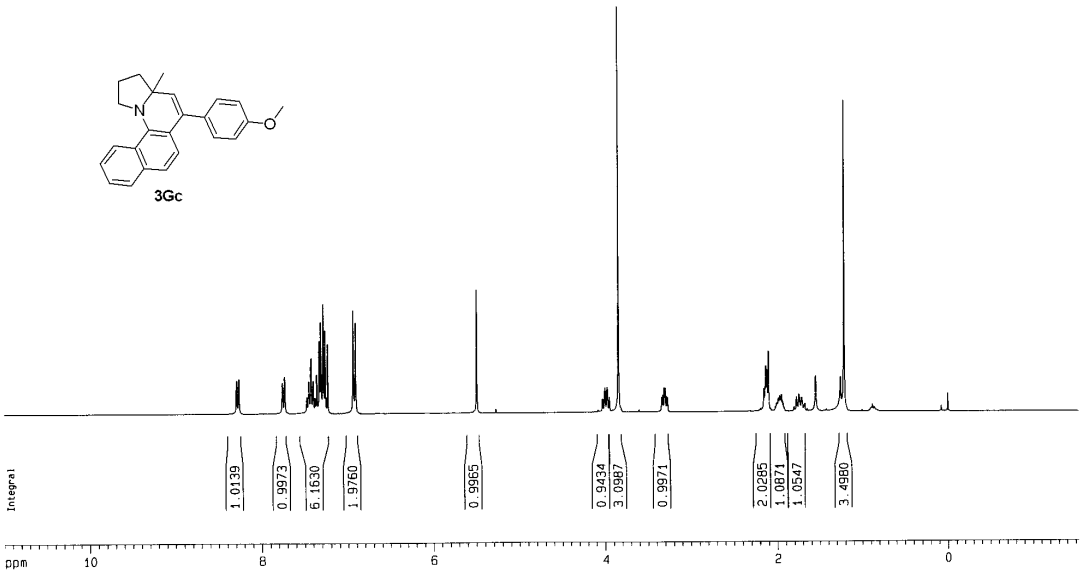

3Ej
ppm
180
160
140
120
100
80
60
40
20

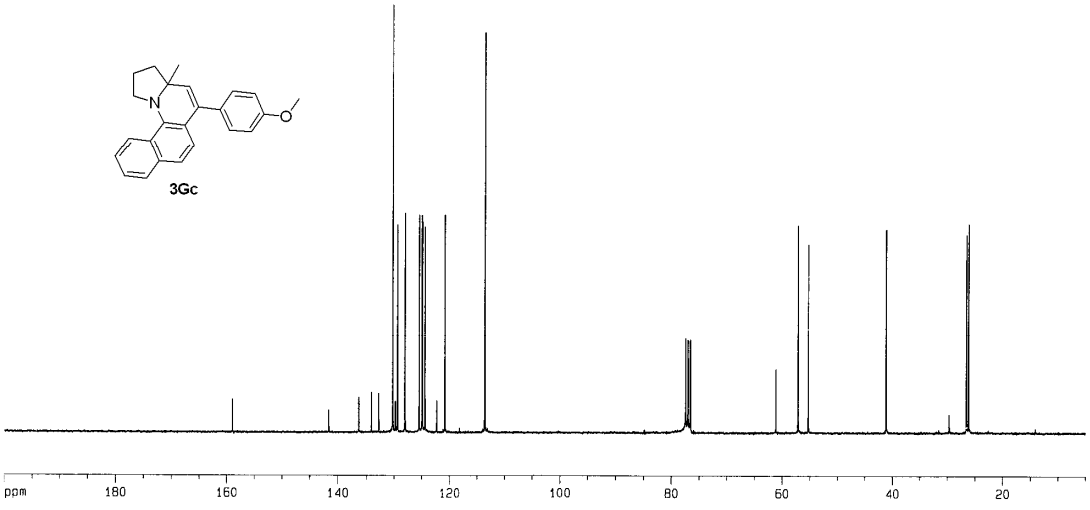

3Fc
Integral
2.2284
3.1318
1.0013
1.0675
1.0000
1.1203
3.1275
1.0729
4.2609
3.0831
ppm
9
8
7
6
5
4
3
2
1
0

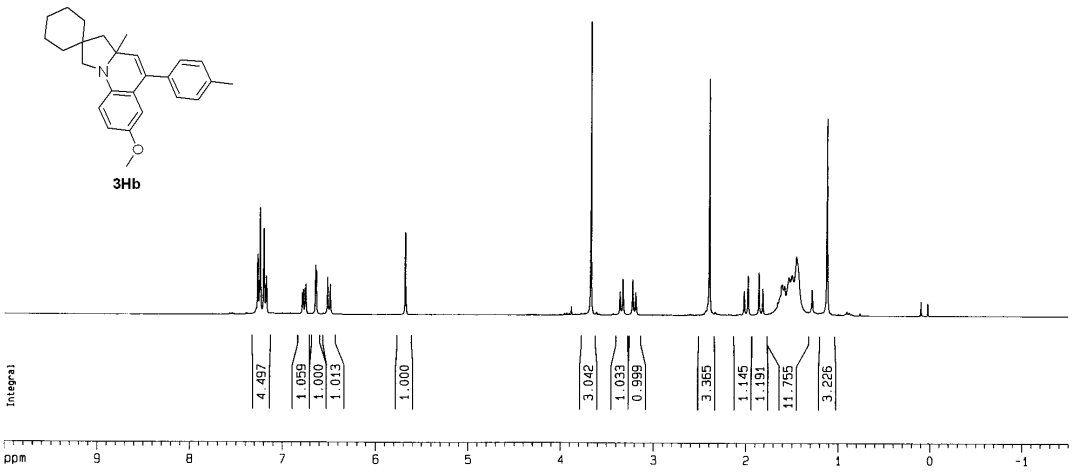

3Fc
ppm
180
160
140
120
100
80
60
40
20

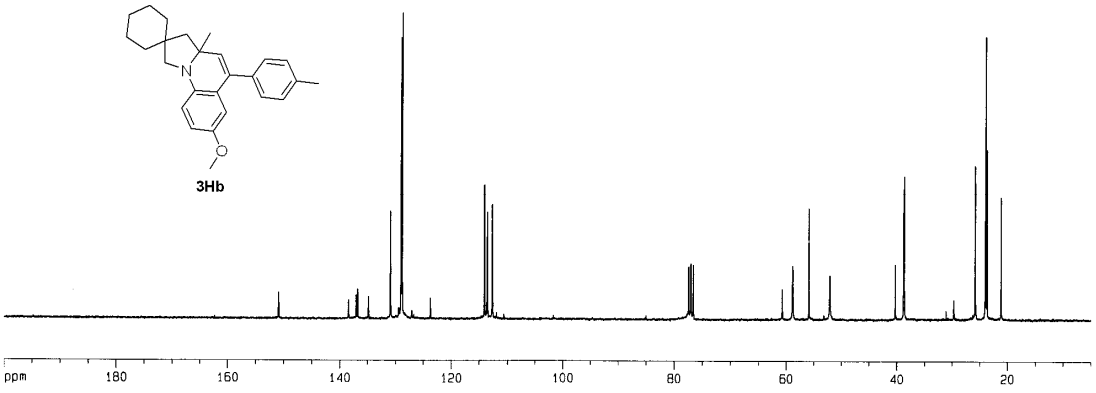

3Gb
Integral
1.0552
1.0637
2.1032
1.0724
5.2160
1.0000
1.1318
1.0987
3.3349
2.2773
1.1598
1.1832
3.3714
ppm
10
8
6
4
2
0

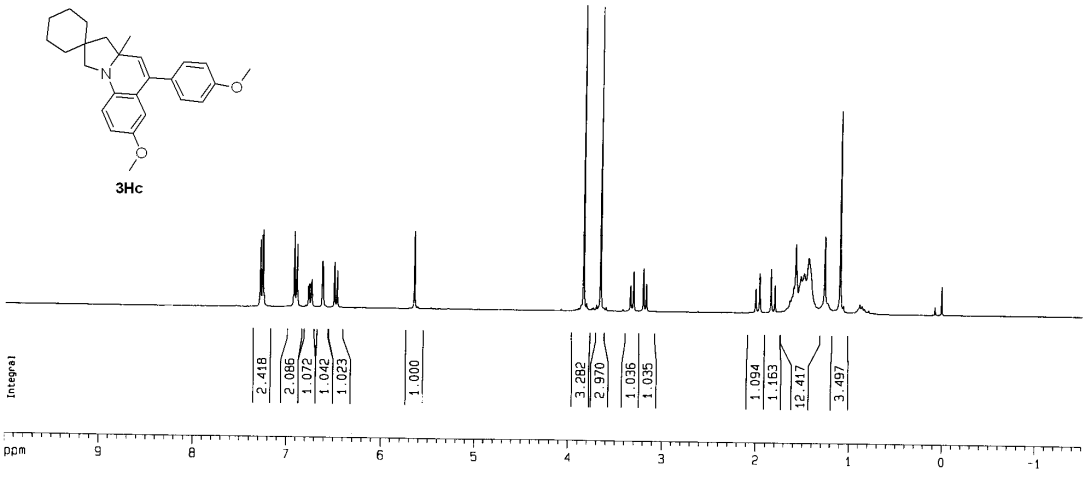

3Gb
ppm
140
120
100
80
60
40
20

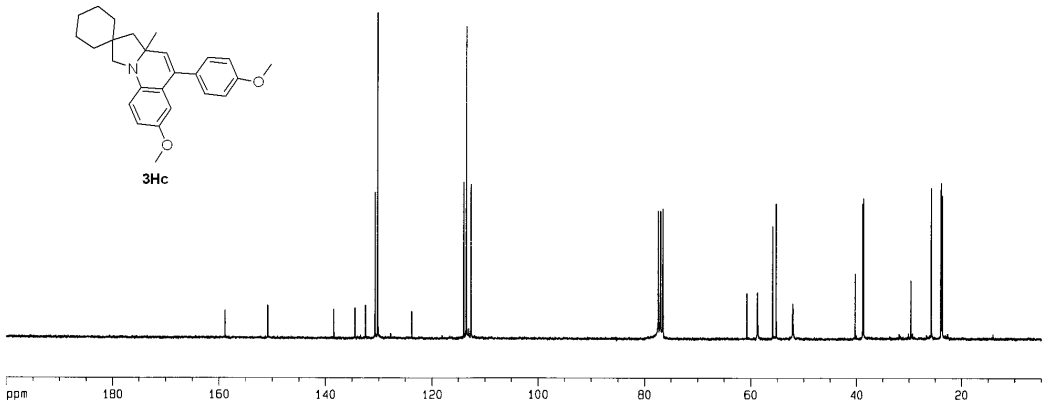

3Gc
Integral
1.0139
0.9973
6.1630
1.9760
0.9965
0.9434
3.0987
0.9971
2.0285
1.0871
1.0547
3.4980
ppm
10
8
6
4
2
0

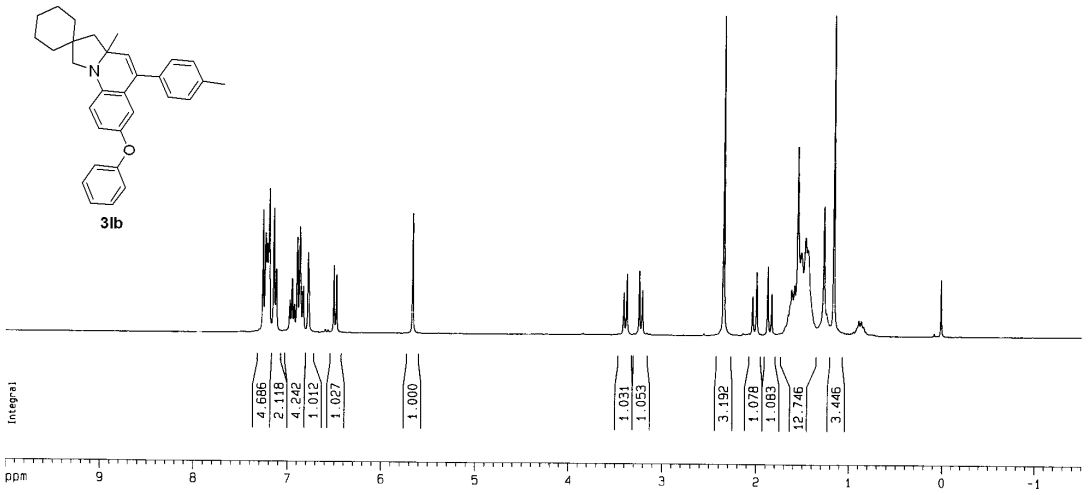

3Gc
ppm
180
160
140
120
100
80
60
40
20

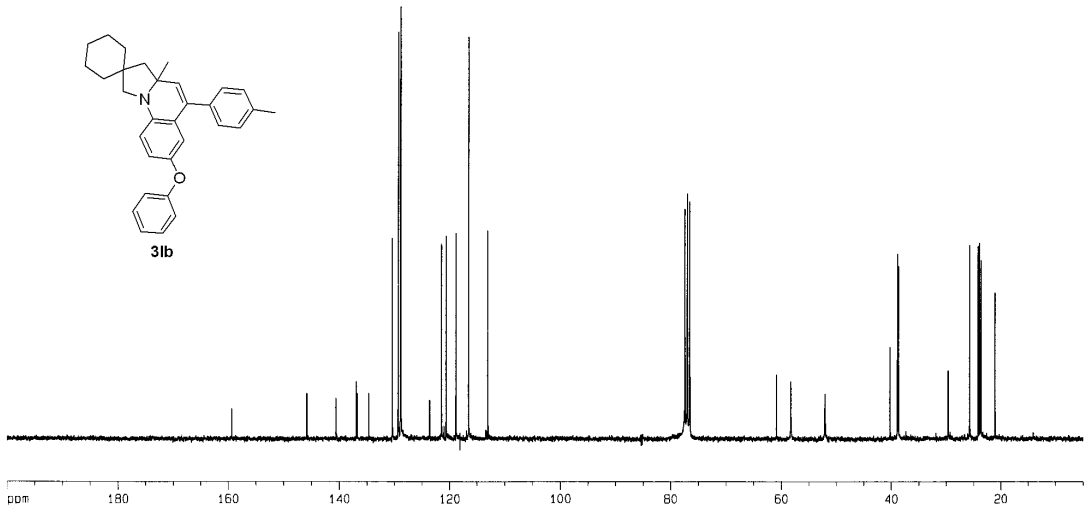

3Hb
Integral
4.497
1.059
1.000
1.013
1.000
3.042
1.033
0.999
3.365
1.145
1.191
11.755
3.226
ppm
9
8
7
6
5
4
3
2
1
0
-1

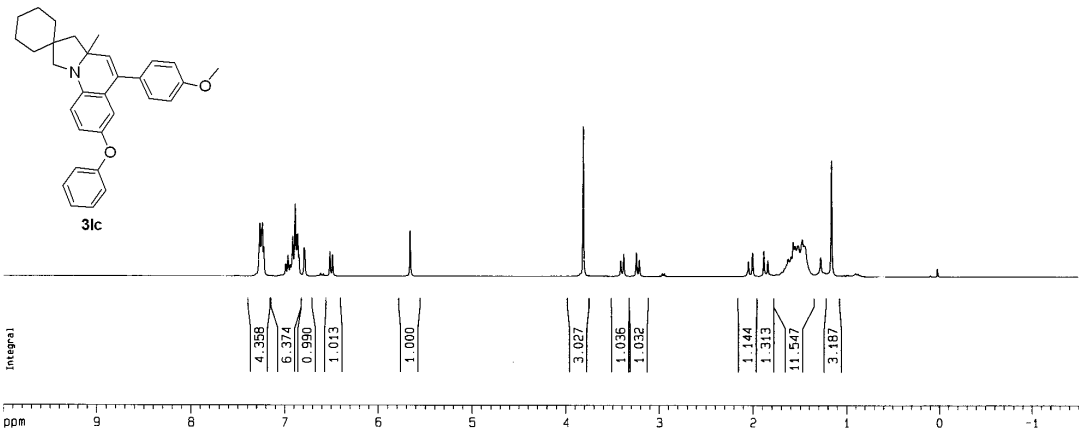

3Hb
ppm
180
160
140
120
100
80
60
40
20

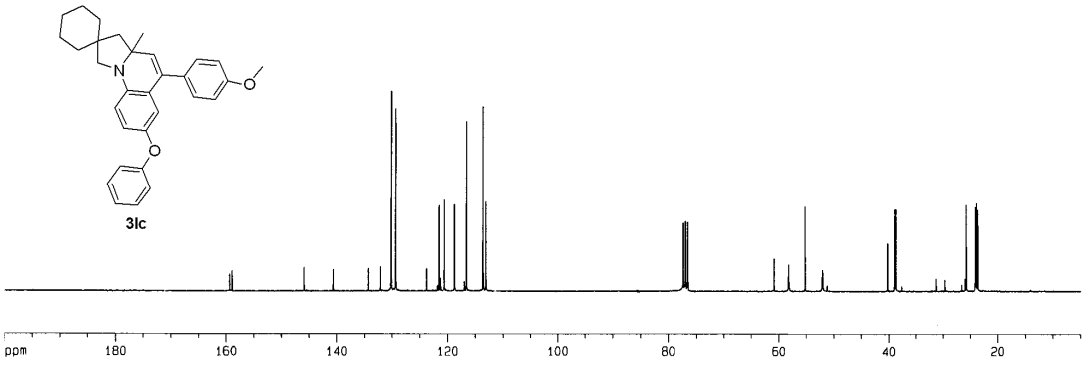

3Hc
Integral
2.418
2.086
1.072
1.042
1.023
1.000
3.282
2.970
1.036
1.035
1.094
1.163
12.417
3.497
ppm

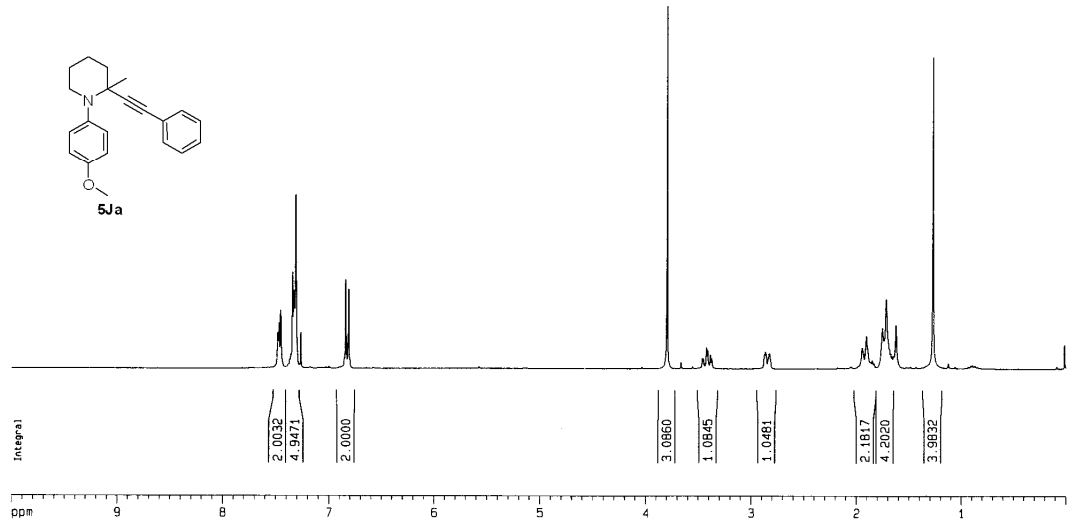

3Hc
ppm

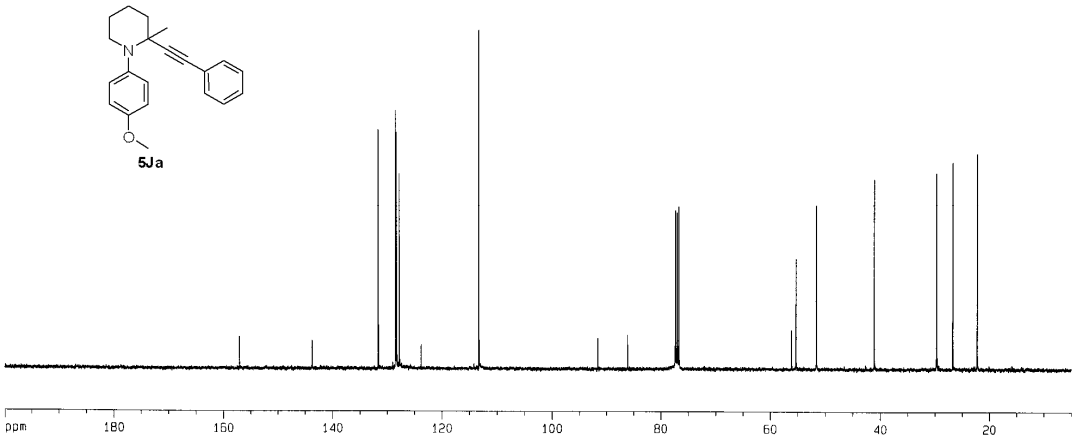

3Ib
Integral
4.686
2.118
4.242
1.012
1.027
1.000
1.031
1.053
3.192
1.078
1.083
12.746
3.446
ppm
9
8
7
6
5
4
3
2
1
0
-1

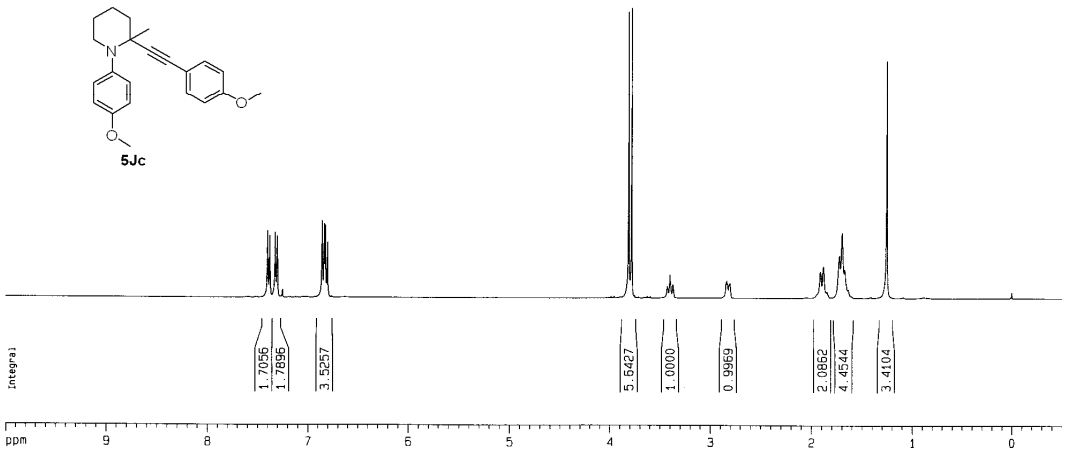

3Ib
ppm
180
160
140
120
100
80
60
40
20

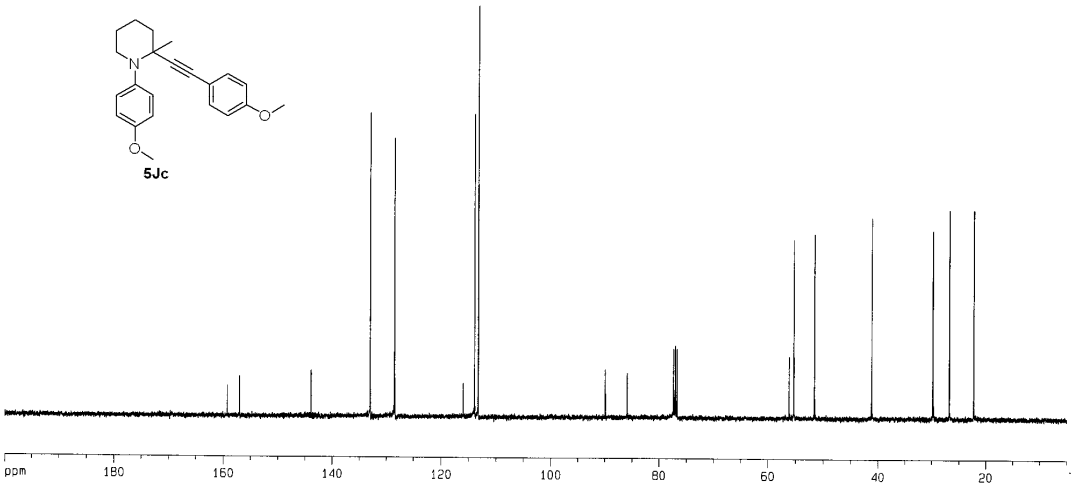

3Ic
Integral
4.358
6.374
0.990
1.013
1.000
3.027
1.036
1.032
1.144
1.313
11.547
3.187
ppm
9
8
7
6
5
4
3
2
1
0
-1

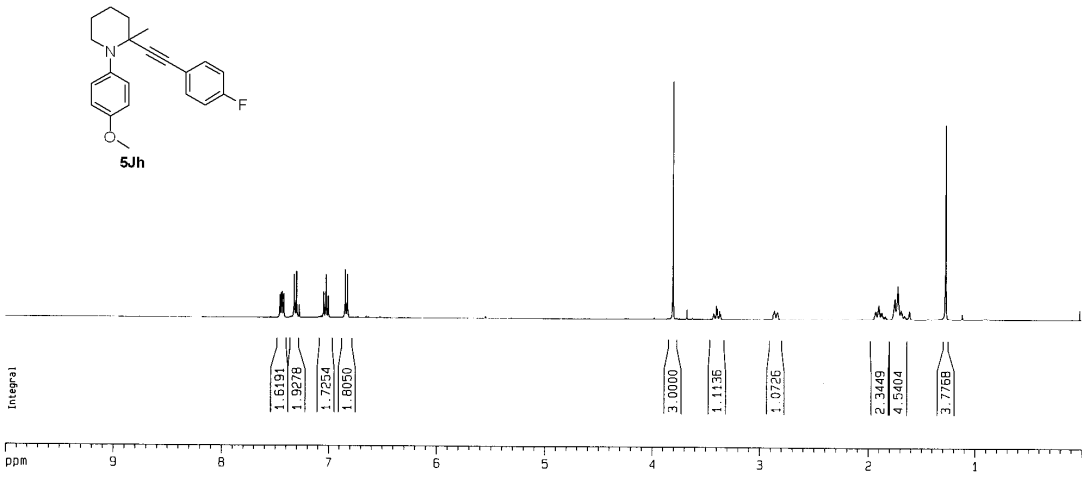

3Ic
ppm
180
160
140
120
100
80
60
40
20

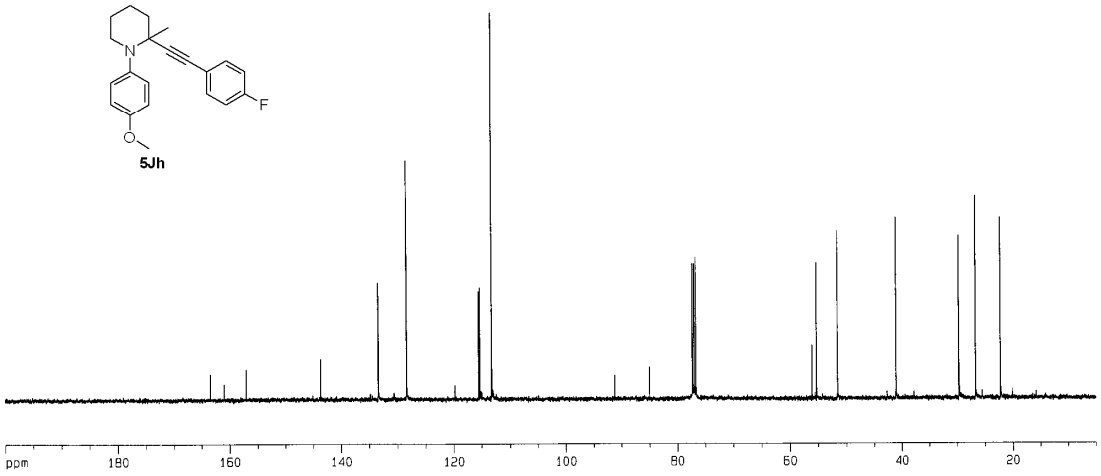

5Ja
Integral
2.0032
4.9471
2.0000
3.0860
1.0845
1.0481
2.1817
4.2020
3.9832
ppm
9
8
7
6
5
4
3
2
1

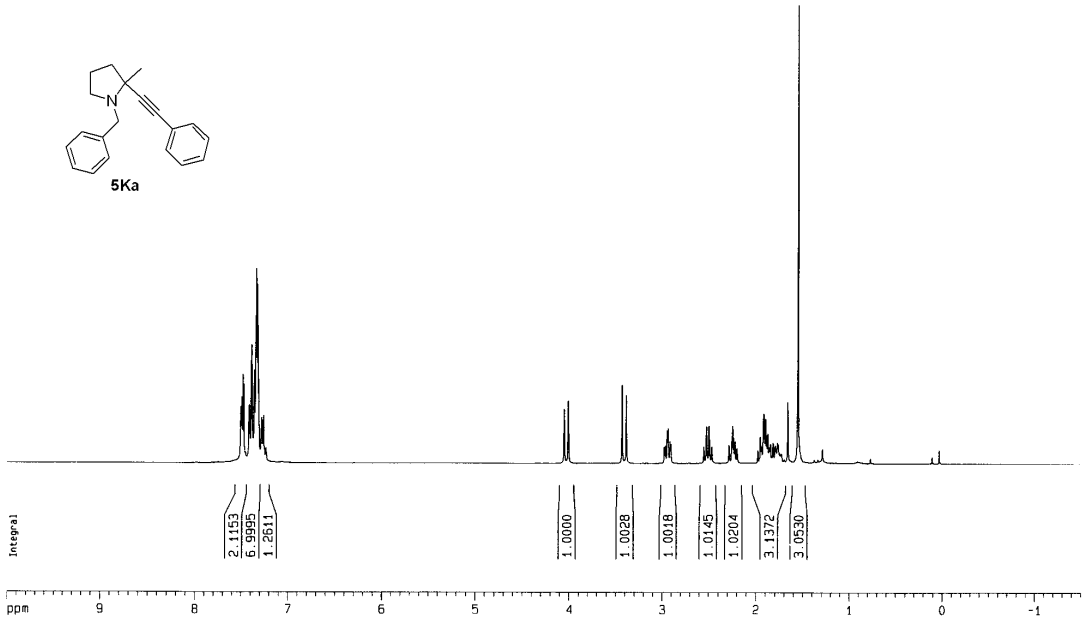

5Ja
ppm
180
160
140
120
100
80
60
40
20

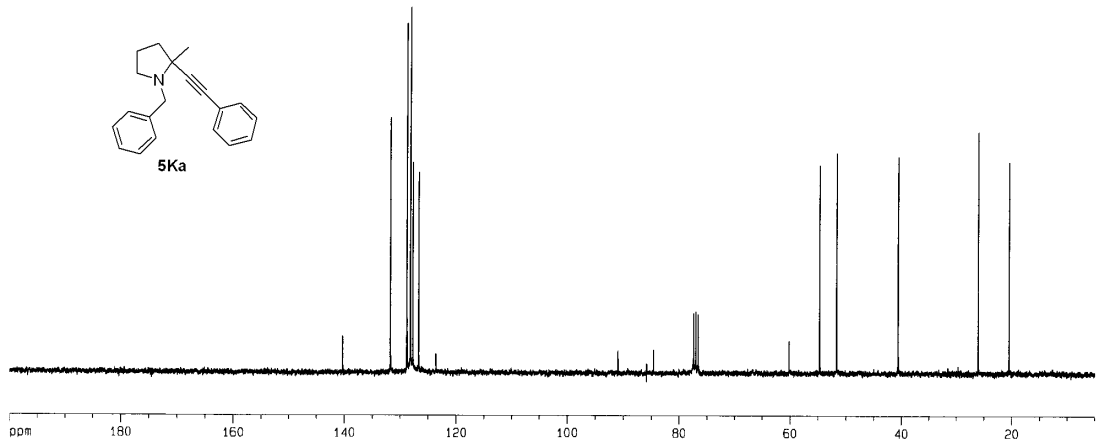

5Jc
Integral
1.7056
1.7896
3.5257
5.6427
1.0000
0.9969
2.0862
4.4544
3.4104
ppm
9
8
7
6
5
4
3
2
1
0

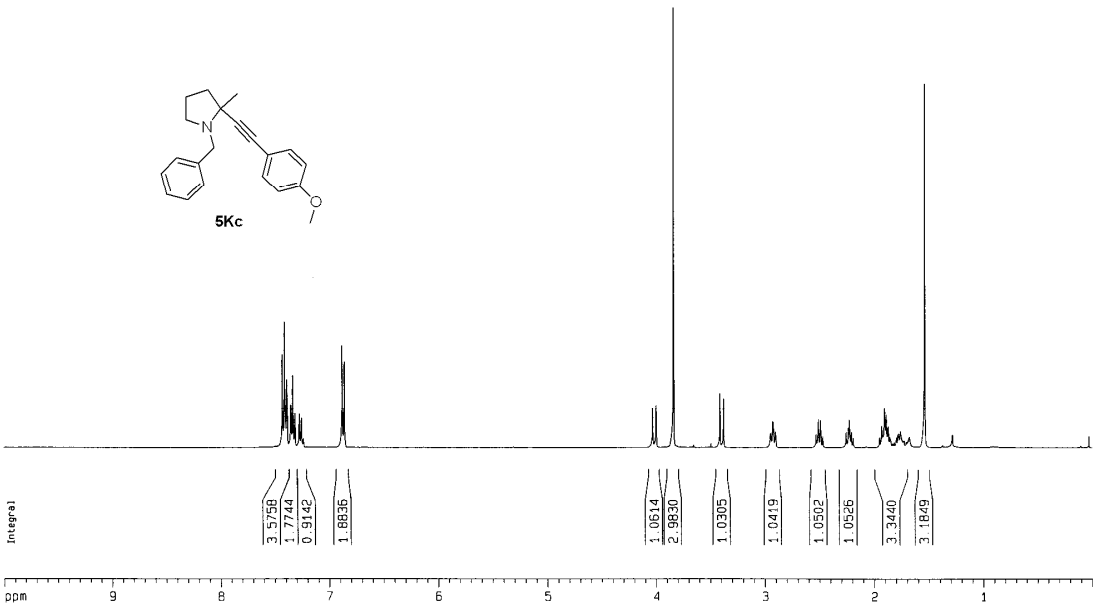

5Jc
ppm
180
160
140
120
100
80
60
40
20

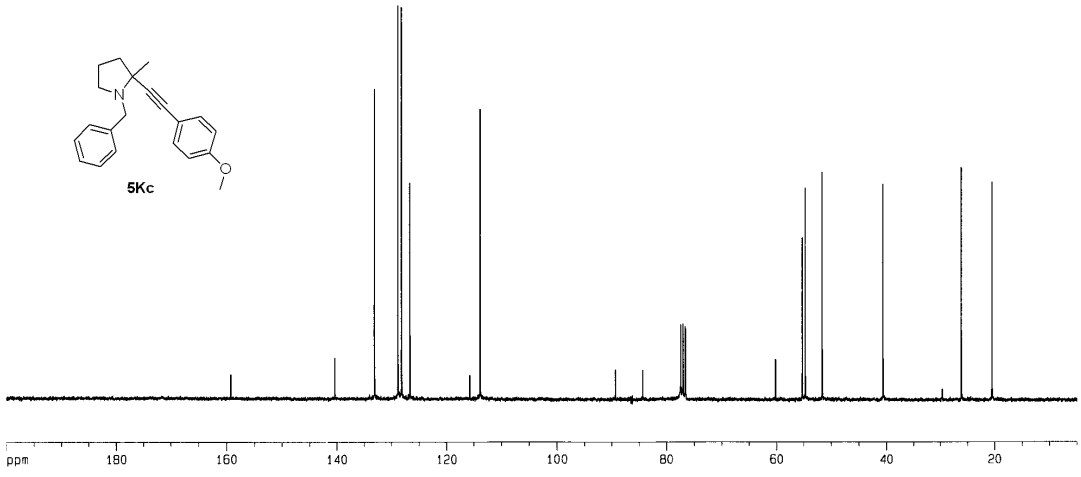

5Jh
F
Integral
1.6191
1.9278
1.7254
1.8050
3.0000
1.1136
1.0726
2.3449
4.5404
3.7768
ppm
9
8
7
6
5
4
3
2
1

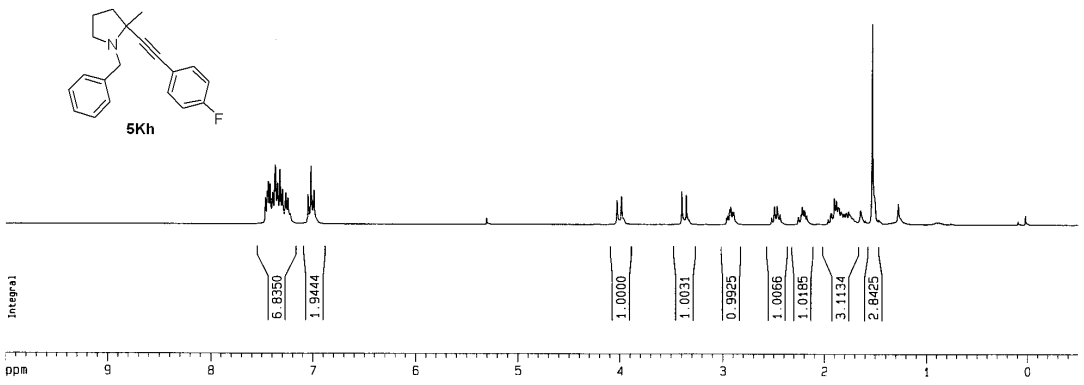

5Jh
F
ppm
180
160
140
120
100
80
60
40
20

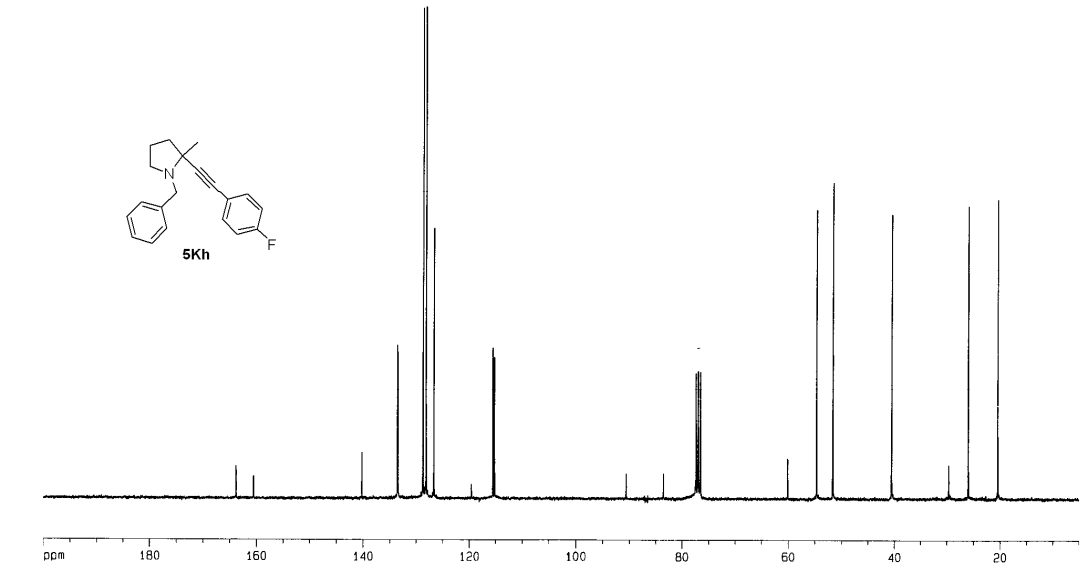

5Ka
Integral
2.1153
6.9995
1.2611
1.0000
1.0028
1.0018
1.0145
1.0204
3.1372
3.0530
ppm
9
8
7
6
5
4
3
2
1
0
-1

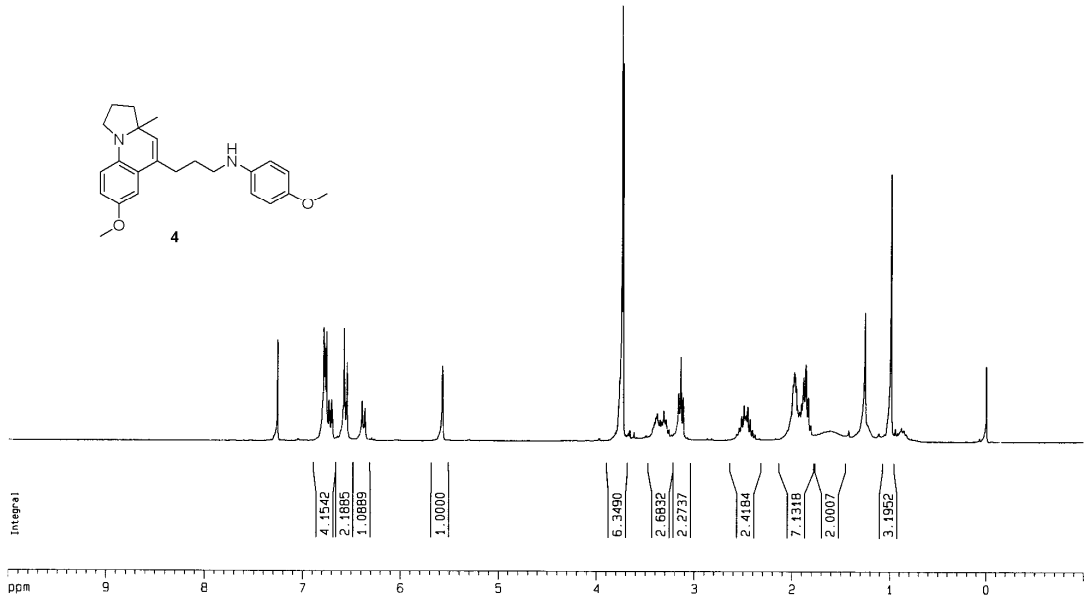

5Ka
ppm
180
160
140
120
100
80
60
40
20

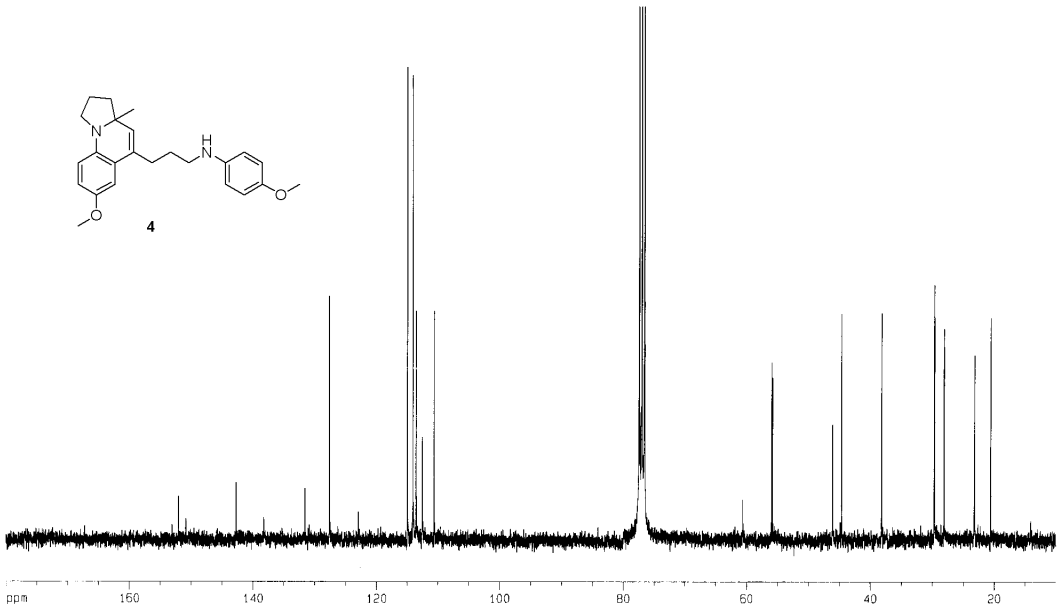

5Kc
Integral
3.5758
1.7744
0.9142
1.8836
1.0614
2.9830
1.0305
1.0419
1.0502
1.0526
3.3440
3.1849
ppm
9
8
7
6
5
4
3
2
1

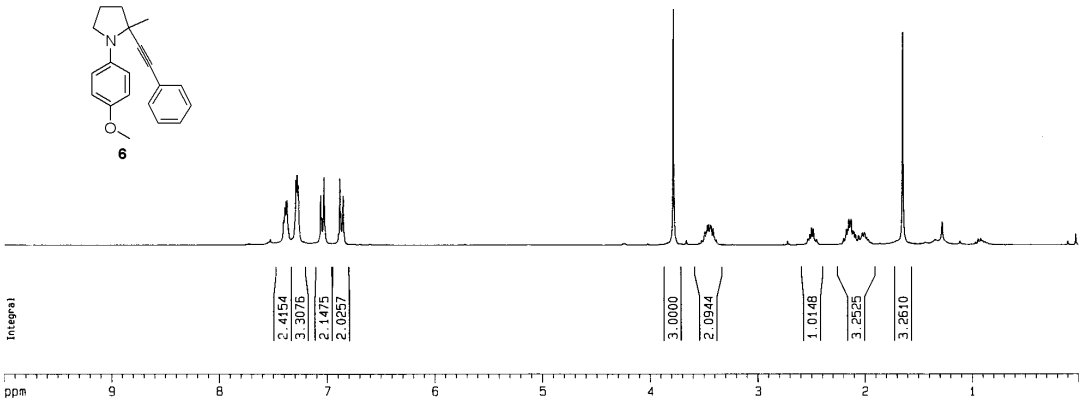

5Kc
ppm
180
160
140
120
100
80
60
40
20

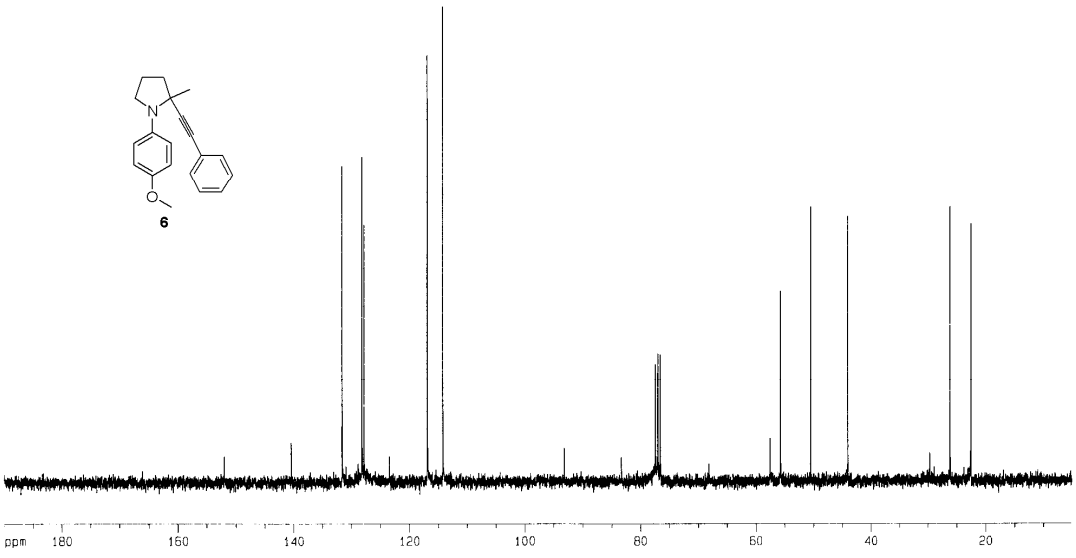

5Kh
Integral
6.8350
1.9444
1.0000
1.0031
0.9925
1.0066
1.0185
3.1134
2.8425
ppm
9
8
7
6
5
4
3
2
1
0

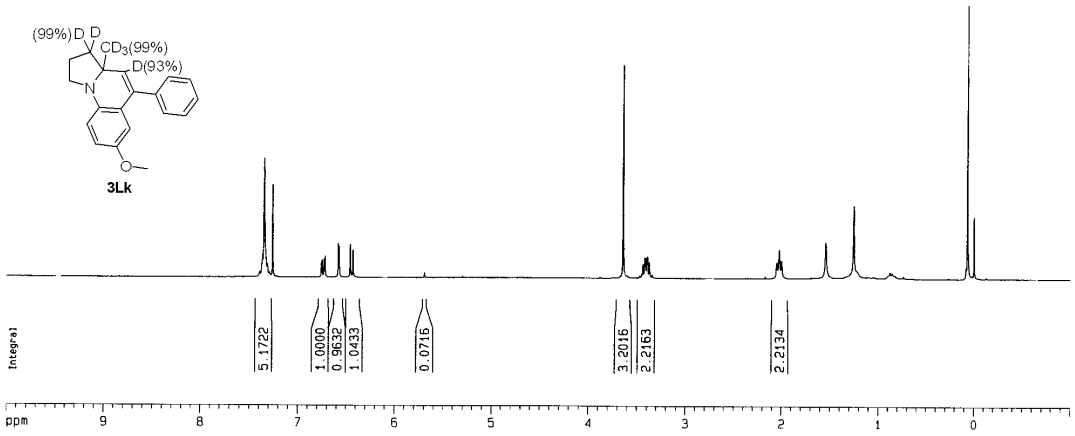

5Kh
ppm
180
160
140
120
100
80
60
40
20

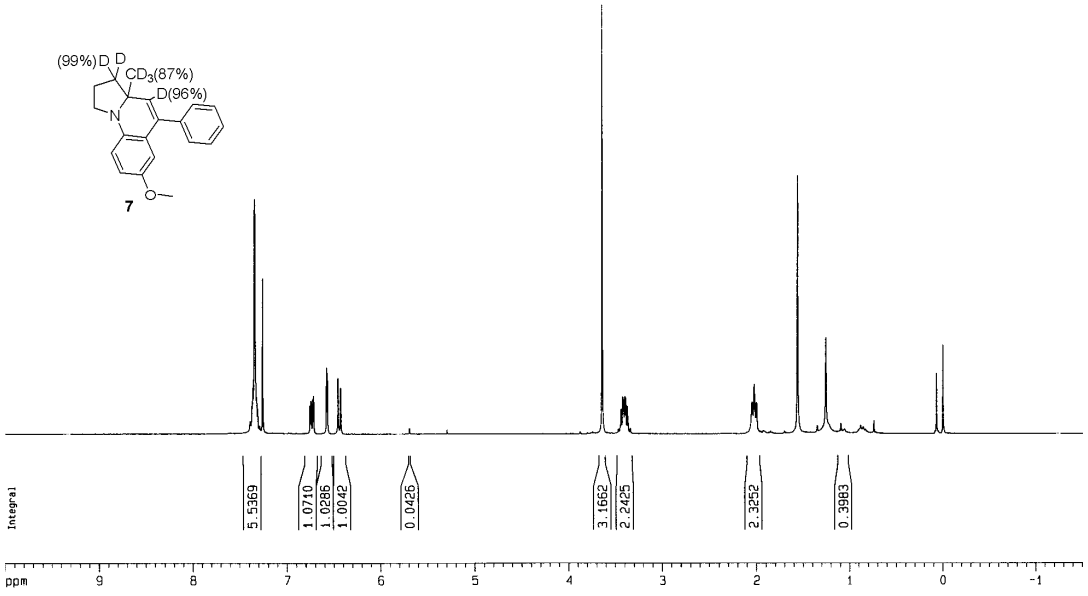

4
Integral
4.1542
2.1885
1.0889
1.0000
6.3490
2.6832
2.2737
2.4184
7.1318
2.0007
3.1952
ppm
9
8
7
6
5
4
3
2
1
0


4
ppm
160
140
120
100
80
60
40
20


6
Integral
2.4154
3.3076
2.1475
2.0257
3.0000
2.0944
1.0148
3.2525
3.2610
ppm
9
8
7
6
5
4
3
2
1


6
ppm
180
160
140
120
100
80
60
40
20


(99%)D D
CD3(99%)
D(93%)
N
O
3Lk
Integral
5.1722
1.0000
0.9632
1.0433
0.0716
3.2016
2.2163
2.2134
ppm
9
8
7
6
5
4
3
2
1
0


(99%)D D
CD3(87%)
D(96%)
N
O
7
Integral
5.5369
1.0710
1.0286
1.0042
0.0426
3.1662
2.2425
2.3252
0.3983
ppm
9
8
7
6
5
4
3
2
1
0
-1