Supporting Information

Synthesis of Substituted 1,2-Dihydroquinolines and Quinolines from Aromatic Amines and Alkynes by Gold(I)-Catalyzed Tandem Hydroamination-Hydroarylation under Microwave-Assisted Conditions

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Contents

Experimental Section

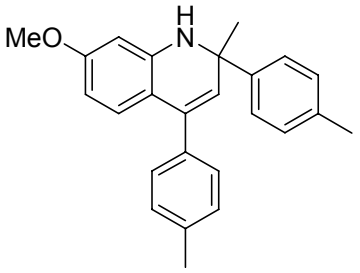
General. All manipulations with air-sensitive reagents were carried out under a dry nitrogen atmosphere. Solvents were dried using standard methods and distilled before use. Amine and alkyne substrates were received from commercial sources and used without further purification. Unless otherwise noted, all reactions were prepared in flame or oven-dried glassware in a nitrogen-filled Vacuum Atmospheres inert atmosphere box and performed in sealed vessels. The reactions under microwave-assisted conditions were conducted on a CEM Focused instrument. NMR spectra were recorded on Bruker AMX-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 obtained with a Nicolet AV-360 spectrophotometer. Lower resolution mass spectra or high-resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 or a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 ev), respectively. Thin-layer chromatography (TLC) was carried out on glass supported plate and compounds were visualized by iodine or UV light.

General Procedure of the Catalytic Reactions under Thermal Conditions. To a mixture of gold catalyst (0.025 mmol) and NH_4PF_6 (0.075 mmol) in dry solvent (1.0 mL) was added *m*-anisidine (0.5 mmol) and phenylacetylene (2.5 mmol) with stirring. The reaction mixture was capped and stirred for 12–24 h at 80–100 °C. The product **4Aa** was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 4:1 or 2:1).

Typical Procedure for the Synthesis of 1,2-Dihydroquinoline Derivatives under Microwave-Assisted Conditions. To a mixture of **1c** (15.6 mg, 0.025 mmol) and silver triflate (6.5 mg, 0.025 mmol) in acetonitrile (1.0 mL) in a microwave reaction vessel was

added amine (0.5 mmol) and alkyne (2.5 mmol). The vessel was sealed and subjected to microwave-irradiation at a power of 19–47 W for 25–70 min. The product **4** was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 4:1 or 2:1).

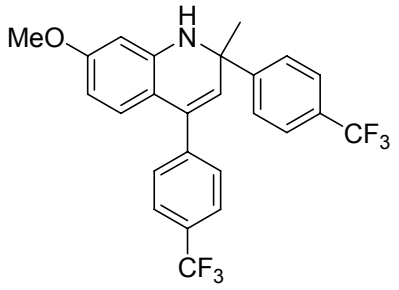
7-Methoxy-2-methyl-2,4-di-*p*-tolyl-1,2-dihydroquinoline (4Ab):



4Ab

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.79 (s, 3H), 2.37 (s, 3H), 2.43 (s, 3H), 3.80 (s, 3H), 4.24 (br, 1H), 5.54 (s, 1H), 6.16 (s, 1H), 6.17 (d, 1H, J = 9.2 Hz), 6.89 (d, 1H, J = 9.2 Hz), 7.21 (m, 4H), 7.30 (d, 2H, J = 8.1 Hz), 7.48 (d, 2H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.4, 21.6, 30.6, 55.5, 57.3, 99.2, 102.9, 114.6, 125.7, 127.0, 127.6, 127.7, 129.3, 129.5, 135.5, 136.8, 137.2, 137.4, 145.1, 146.5, 160.9. IR (film): ν 3382, 2962, 2924, 1613, 1515, 1168, 815 cm^{-1}. MS: *m/z* (% relative intensity) 355(M^+, 2), 340(100), 297(13), 264(25), 163(14); HRMS: *m/z* calcd for $C_{24}H_{22}NO$ (M^+ - CH_3) 340.1701, found 340.1701.

7-Methoxy-2-methyl-2,4-di-(4-trifluoromethyl-phenyl)-1,2-dihydroquinoline (4Ac):

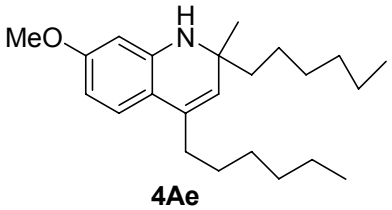


4Ac

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.80 (s, 3H), 3.78 (s, 3H), 4.28 (br, 1H), 5.53 (s, 1H), 6.18 (d, 1H, J = 8.3 Hz), 6.21 (s, 1H), 6.75 (d, 1H, J = 8.3 Hz), 7.45 (d, 2H, J = 7.9 Hz), 7.64 (q, 6H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.1, 55.2, 57.1, 99.1, 103.2, 113.4, 125.2 (m), 125.5 (m), 125.7, 126.3, 127.3, 129.2, 135.3, 143.1, 144.3, 152.5,

161.0. IR (film): ν 3380, 2966, 2932, 1615, 1326, 1168, 840 cm^{-1}. MS: *m/z* (% relative intensity) 463(M^+, 3), 450(30), 449(100), 403(16), 316(44); HRMS: *m/z* calcd for $C_{24}H_{16}NOF_6$ (M^+ - CH_3) 448.1136, found 448.1141.

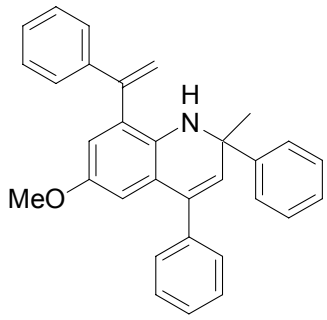
2,4-Dihexyl-7-methoxy-2-methyl-1,2-dihydroquinoline (4Ae):



4Ae

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 0.91 (m, 6H), 1.24 (s, 3H), 1.44 (m, 18H), 2.34 (m, 2H), 3.63 (br, 1H), 3.77 (s, 3H), 5.11 (s, 1H), 6.01 (d, 1H, J = 2.9 Hz), 6.18 (d, 1H, J = 8.4 Hz), 7.01 (d, 1H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 14.5, 23.1, 24.7, 28.8, 29.7, 30.2, 30.4, 32.2, 32.3, 32.5, 44.7, 55.0, 55.4, 98.8, 102.2, 114.7, 124.5, 124.8, 133.1, 145.7, 160.4. IR (film): ν 3381, 2955, 2928, 1613, 1465, 1166, 823 cm^{-1}. MS: *m/z* (% relative intensity) 343(M^+, 1), 328(9), 259(18), 258(100), 187(26); HRMS: *m/z* calcd for $C_{23}H_{37}NO$ (M^+) 343.2875, found 343.2881.

6-Methoxy-2-methyl-2.4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (4'Ba):

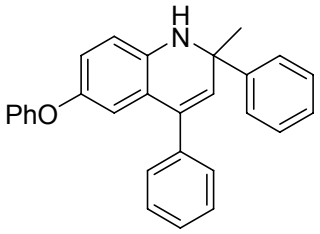


4'Ba

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.55 (s, 3H), 3.64 (s, 3H), 4.24 (br, 1H), 5.42 (s, 1H), 5.76 (s, 1H), 5.88 (s, 1H), 6.59 (s, 1H), 6.61 (s, 1H), 7.32 (m, 15H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 29.9, 55.8, 56.8, 112.1, 115.8, 116.6, 122.2, 124.3, 125.2, 126.5, 126.9, 127.5, 128.1, 128.2, 128.6, 128.8, 129.0, 130.4, 134.9, 136.4, 139.5, 139.7, 146.4, 148.2, 151.0. IR (film): ν 3390, 3057, 2929, 1597, 1463, 1223, 698 cm^{-1}. MS: *m/z* (% relative intensity) 429(M^+, 3), 415(29), 414(100), 350(19), 84(79); HRMS: *m/z* calcd

for $C_{30}H_{24}NO$ (M^+) 414.1858, found 414.1862.

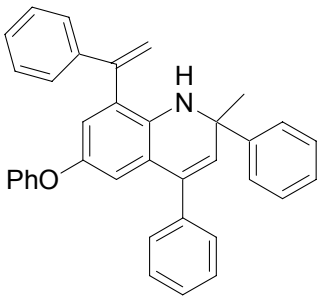
2-Methyl-6-phenoxy-2,4-diphenyl-1,2-dihydroquinoline (4Ca):



4Ca

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.81 (s, 3H), 4.21 (br, 1H), 5.75 (s, 1H), 6.59 (d, 1H, J = 7.9 Hz), 6.76 (m, 2H), 6.89 (d, 2H, J = 7.9 Hz), 6.91 (m, 1H), 7.30 (m, 10H), 7.60 (d, 2H, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.0, 57.2, 114.1, 116.7, 118.5, 121.0, 121.5, 121.8, 125.4, 126.9, 127.6, 128.3, 128.5, 128.9, 129.4, 130.0, 135.5, 138.9, 139.9, 147.2, 148.6, 159.1. IR (film): ν 3390, 3057, 3027, 1596, 1488, 1224, 699 cm^{-1}. MS: *m/z* (% relative intensity) 389(M^+, 1), 375(17), 374(44), 312(19), 84(100); HRMS: *m/z* calcd for $C_{27}H_{20}NO$ (M^+ - CH_3) 374.1545, found 374.1536.

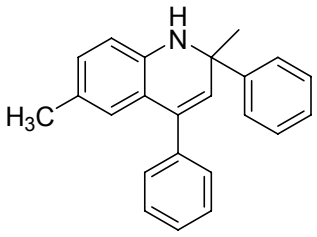
2-Methyl-6-phenoxy-2,4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (4'Ca):



4'Ca

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.58 (s, 3H), 4.36 (br, 1H), 5.44 (s, 1H), 5.74 (s, 1H), 5.86 (s, 1H), 6.77 (s, 2H), 6.94 (m, 3H), 7.28 (m, 17H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.1, 57.0, 116.6, 117.0, 118.1, 121.7, 121.9, 122.4, 125.2, 126.6, 126.8, 127.0, 127.6, 128.2, 128.3, 128.4, 128.6, 128.9, 129.4, 130.0, 135.9, 137.3, 139.2, 139.5, 145.9, 146.3, 148.2, 159.0. IR (film): ν 3408, 3058, 2924, 1586, 1490, 1445, 1223, 697 cm^{-1}. MS: *m/z* (% relative intensity) 477(7), 449(23), 341(35), 84(88), 57(100); HRMS: *m/z* calcd for $C_{36}H_{29}NO$ (M^+) 491.2249, found 491.2271.

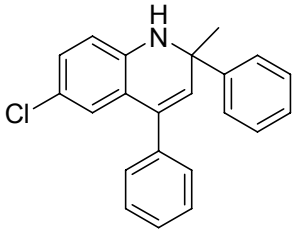
2,6-Dimethyl-2,4-diphenyl-1,2-dihydroquinoline (4Da):



4Da

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.80 (s, 3H), 2.17 (s, 3H), 4.15 (br, 1H), 5.69 (s, 1H), 6.53 (d, 1H, J = 7.9 Hz), 6.76 (s, 1H), 6.89 (d, 1H, J = 7.9 Hz), 7.31 (m, 1H), 7.39 (m, 7H), 7.61 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.0, 30.4, 57.4, 113.7, 120.8, 125.8, 126.8, 126.9, 127.2, 127.7, 128.6, 128.8, 129.4, 129.8, 129.9, 136.3, 140.0, 141.3, 149.3. IR (film): ν 3381, 3022, 1631, 1493, 1443, 699 cm^{-1}. MS: *m/z* (% relative intensity) 311(M^+, 3), 297(26), 296(100), 234(36), 141(15); HRMS: *m/z* calcd for $C_{23}H_{21}N$ (M^+) 311.1674, found 311.1665.

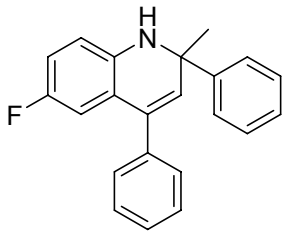
6-Chloro-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (4Ga):



4Ga

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.80 (s, 3H), 4.23 (br, 1H), 5.70 (s, 1H), 6.51 (d, 1H, J = 8.4 Hz), 6.89 (s, 1H), 6.90 (d, 1H, J = 7.9 Hz), 7.29 (m, 1H), 7.39 (m, 7H), 7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.4, 57.6, 114.6, 122.1, 122.3, 125.7, 126.1, 127.4, 128.1, 128.8, 128.9, 129.0, 129.3, 130.5, 135.4, 139.1, 142.1, 148.7. IR (film): ν 3393, 3057, 2923, 1598, 1484, 699 cm^{-1}. MS: *m/z* (% relative intensity) 331(M^+, 4), 318(29), 317(22), 316(100), 254(41), 201(47); HRMS: *m/z* calcd for $C_{22}H_{18}NCl$ (M^+) 331.1128, found 331.1124.

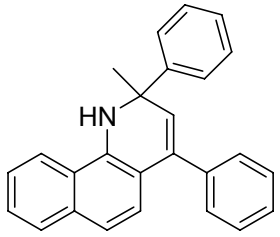
6-Fluoro-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (4Ha):



4Ha

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.79 (s, 3H), 4.16 (br, 1H), 5.77 (s, 1H), 6.53 (m, 1H), 6.68 (m, 1H), 6.77 (m, 1H), 7.27 (m, 1H), 7.39 (m, 7H), 7.56 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 29.9, 57.1, 112.5 (d, J_{CF} = 23.9 Hz), 113.7 (d, J_{CF} = 7.6 Hz), 115.2 (d, J_{CF} = 22.8 Hz), 125.3, 126.9, 127.7, 128.4, 128.5, 128.9, 130.5, 135.3, 138.8, 139.4, 148.4, 154.1, 157.2. IR (film): ν 3397, 3059, 2925, 1491, 1445, 699 cm^{-1}. MS: *m/z* (% relative intensity) 315(M^+, 3), 301(18), 300(100), 238(34), 222(15); HRMS: *m/z* calcd for $C_{21}H_{15}NF$ (M^+ - CH_3) 300.1189, found 300.1190.

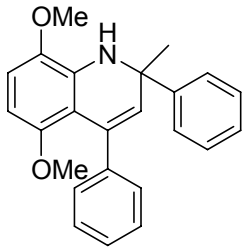
2-Methyl-2,4-diphenyl-1,2-dihydro-benzo[*h*]quinoline (4Ia):



4Ia

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.93 (s, 3H), 5.03 (br, 1H), 5.80 (s, 1H), 7.16 (m, 2H), 7.28 (m, 1H), 7.41 (m, 9H), 7.65 (m, 2H), 7.79 (m, 1H), 7.90 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.9, 57.7, 115.1, 116.9, 120.2, 122.3, 125.0, 125.4, 125.8, 126.3, 127.3, 127.7, 127.8, 128.7, 128.9, 129.2, 129.6, 134.7, 137.0, 138.5, 140.3, 149.5. IR (film): ν 3424, 3055, 2923, 1515, 1398, 699 cm^{-1}. MS: *m/z* (% relative intensity) 347(M^+, 5), 333(24), 332(100), 270(31), 254(19); HRMS: *m/z* calcd for $C_{25}H_{18}N$ (M^+ - CH_3) 332.1439, found 332.1433.

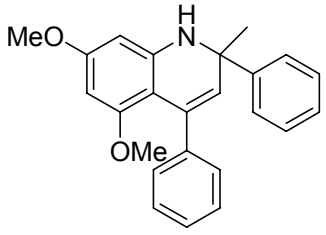
5,8-Dimethoxy-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (4Ja):



4Ja

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.73 (s, 3H), 3.28 (s, 3H), 3.89 (s, 3H), 5.08 (br, 1H), 5.75 (s, 1H), 6.12 (d, 1H, J = 8.8 Hz), 6.69 (d, 1H, J = 8.8 Hz), 7.30 (m, 8H), 7.51 (d, 2H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.1, 55.5, 55.9, 56.1, 100.1, 110.2, 110.8, 125.2, 126.1, 126.6, 127.1, 127.4, 128.2, 130.7, 135.1, 135.4, 141.1, 142.6, 148.5, 151.2. IR (film): ν 3399, 2934, 2832, 1606, 1494, 1247, 699 cm^{-1}. MS: *m/z* (% relative intensity) 357(M^+, 2), 343(12), 342(47), 312(23), 84(100); HRMS: *m/z* calcd for $C_{23}H_{20}NO_2$ (M^+ - CH_3) 342.1494, found 342.1497.

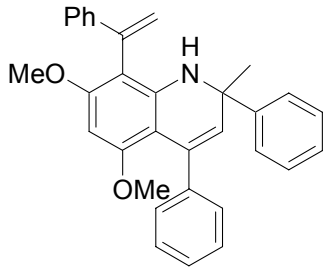
5,7-Dimethoxy-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (4Ka):



4Ka

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.70 (s, 3H), 3.32 (s, 3H), 3.79 (s, 3H), 4.38 (br, 1H), 5.56 (s, 1H), 5.82 (s, 1H), 5.93 (s, 1H), 7.27 (m, 8H), 7.52 (d, 2H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 29.5, 55.0, 55.1, 56.2, 89.9, 92.1, 103.9, 125.3, 126.1, 126.6, 127.1, 127.3, 128.0, 128.2, 134.8, 142.8, 146.5, 148.3, 158.0, 161.2. IR (film): ν 3399, 2934, 2832, 1606, 1494, 1247, 699 cm^{-1}. MS: *m/z* (% relative intensity) 357(M^+, 1), 342(19), 84(55), 57(43), 43(100); HRMS: *m/z* calcd for $C_{23}H_{20}NO_2$ (M^+ - CH_3) 342.1494, found 342.1488.

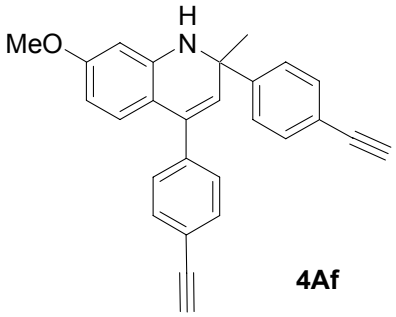
5,7-Dimethoxy-2-methyl-2,4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (4'Ka):



4'Ka

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.60 (s, 3H), 3.39 (s, 3H), 3.64 (s, 3H), 4.91 (br, 1H), 5.43 (s, 1H), 5.65 (s, 1H), 5.90 (s, 1H), 6.12 (s, 1H), 7.29 (m, 15H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 29.7, 55.2, 55.6, 56.1, 87.0, 104.6, 108.6, 117.7, 125.3, 126.1, 126.2, 126.4, 127.2, 127.3, 127.7, 128.1, 128.3, 128.5, 135.6, 140.0, 142.3, 143.0, 143.9, 148.0, 157.1, 158.2. IR (film): ν 3392, 3055, 2957, 1593, 1328, 1142, 699 cm^{-1}. MS: *m/z* (% relative intensity) 446(43), 444(100), 429(21), 379(28), 213(27); HRMS: *m/z* calcd for $C_{32}H_{29}NO_2$ (M^+) 459.2198, found 459.2187.

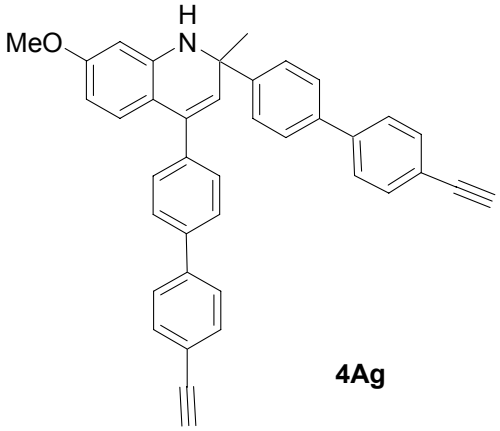
2,4-Bis(4-ethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (4Af):



4Af

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.75 (s, 3H), 3.06 (s, 1H), 3.11 (s, 1H), 3.77 (s, 3H), 4.22 (br, 1H), 5.48 (s, 1H), 6.16 (m, 2H), 6.78 (d, 1H, J = 9.1 Hz), 7.28 (m, 2H), 7.46 (m, 6H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.0, 55.2, 57.1, 76.6, 77.4, 83.4, 83.6, 98.9, 102.9, 113.6, 120.6, 121.1, 125.3, 126.2, 127.2, 128.9, 132.0, 132.2, 135.3, 140.1, 144.4, 149.4, 160.8. IR (film): ν 3393, 3272, 2955, 1603, 1502, 1273, 1167 cm^{-1}. MS: *m/z* (% relative intensity) 375(M^+, 3), 361(20), 360(100), 274(22), 153(44), 136(47); HRMS: *m/z* calcd for $C_{27}H_{21}NO$ (M^+) 375.1623, found 375.1618.

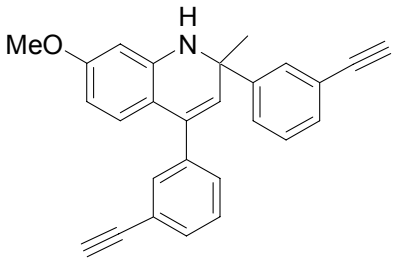
2,4-Bis(4'-ethynylbiphenyl-4-yl)-7-methoxy-2-methyl-1,2-dihydroquinoline (4Ag):



4Ag

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.82 (s, 3H), 3.13 (s, 1H), 3.15 (s, 1H), 3.78 (s, 3H), 4.28 (br, 1H), 5.60 (s, 1H), 6.17 (m, 2H), 6.90 (d, 1H, J = 9.2 Hz), 7.45 (d, 2H, J = 8.1 Hz), 7.60 (m, 14H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.2, 55.2, 57.1, 77.8, 83.5, 83.6, 98.9, 102.8, 113.9, 121.0, 125.9, 126.5, 126.8, 126.9, 127.1, 127.2, 127.3, 129.5, 132.5, 132.6, 135.2, 138.7, 139.1, 139.3, 141.1, 141.2, 144.6, 148.4, 160.7. IR (film): ν 3393, 3295, 3044, 1612, 1490, 1266, 738 cm^{-1}. MS: *m/z* (% relative intensity) 513(18), 512(80), 153(98), 136(91), 106(100); HRMS: *m/z* calcd for $C_{39}H_{29}NO$ (M^+) 527.2249, found 527.2236.

2,4-Bis(3-ethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (4Ah):

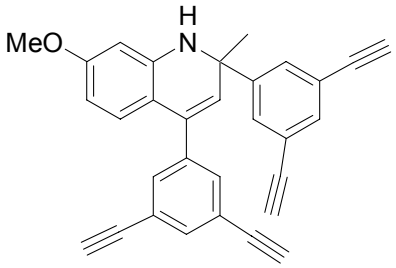


4Ah

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 1.76 (s, 3H), 3.10 (s, 2H), 3.78 (s, 3H), 4.22 (br, 1H), 5.48 (s, 1H), 6.18 (m, 2H), 6.79 (d, 1H, J = 8.9 Hz), 7.34 (m, 4H), 7.48 (m, 1H), 7.51 (s, 1H), 7.56 (d, 1H, J = 7.8 Hz), 7.68 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 30.0, 55.1, 57.1, 77.0, 77.3, 83.5, 83.8, 98.9, 102.9, 113.5, 122.0, 122.1, 126.2, 126.3, 127.2, 128.2, 128.5, 129.0, 129.5, 130.6, 131.1, 132.5, 134.9, 139.7, 144.3, 149.0,160.8. IR (film): ν 3383, 3289, 2966, 1614, 1514, 1166, 797 cm^{-1}. MS: *m/z* (% relative intensity) 375(M^+, 3), 360(100), 274(22), 149(30), 136(15); HRMS: *m/z* calcd for $C_{27}H_{21}NO$ (M^+)

375.1623, found 375.1614.

2,4-Bis(3,5-diethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (4Ai):

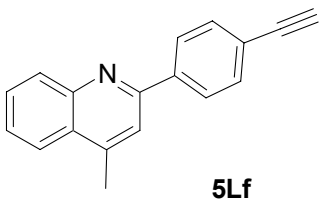


4Ai

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 1.74 (s, 3H), 3.10 (s, 4H), 3.78 (s, 3H), 4.16 (br, 1H), 5.42 (s, 1H), 6.18 (m, 2H), 6.75 (d, 1H, J = 8.4 Hz), 7.45 (s, 2H), 7.50 (s, 1H), 7.59 (s, 1H), 7.65 (s, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 29.8, 55.2, 57.1, 78.0, 78.1, 82.5, 82.7, 99.0, 103.2, 113.0, 122.5, 122.6, 125.0, 126.0, 127.2, 129.6, 132.8, 134.1, 134.6, 139.9, 144.0, 149.2, 161.0. IR (film): ν 3392, 3290, 2915, 1614, 1167, 883 cm^{-1}. MS: *m/z* (% relative intensity) 408(94), 298(25), 186(31), 171(100), 149(46); HRMS: *m/z* calcd for $C_{31}H_{21}NO$ (M^+) 423.1623, found 423.1621.

Typical Procedure for the Synthesis of Quinoline Derivatives under Microwave-Assisted Conditions. To a mixture of **1c** (15.6 mg, 0.025 mmol) and silver triflate (6.5 mg, 0.025 mmol) in acetonitrile (1.0 mL) in a microwave reaction vessel was added 2-aminoacetophenone or 2-aminobenzophenone (0.5 mmol) and alkyne (1 mmol). The vessel was sealed and subjected to microwave-irradiation at a power of 20–30 W for 30 min. The product **5** was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 4:1).

2-(4-Ethynylphenyl)-4-methylquinoline (5Lf):

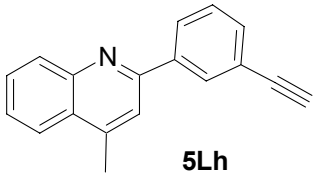


5Lf

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 2.78 (s, 3H), 3.20 (s, 1H), 7.57 (m, 1H), 7.66 (m, 2H), 7.74 (m, 2H), 8.02 (d, 1H, J = 8.3 Hz), 8.16(m, 3H). ^{13}C NMR ($CDCl_3$, TMS, 75

MHz): δ 19.0, 78.4, 83.6, 119.5, 122.9, 123.6, 126.3, 127.3, 129.5, 130.3, 132.5, 140.0, 145.0, 148.1, 155.9. IR (film): ν 3288, 3063, 2357, 1599, 1504, 1417, 758 cm^{-1}. MS: *m/z* (% relative intensity) 243(M^+, 100), 228(48), 153(54), 136(51), 106(42); HRMS: *m/z* calcd for $C_{18}H_{13}N$ (M^+) 248.1048, found 243.1043.

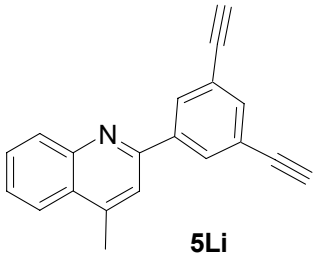
2-(3-Ethynylphenyl)-4-methylquinoline (5Lh):



5Lh

^1H NMR ($CDCl_3$, TMS, 400 MHz): δ 2.77 (s, 3H), 3.16 (s, 1H), 7.50 (m, 1H), 7.57 (m, 2H), 7.72 (m, 2H), 8.00 (d, 1H, J = 9.1 Hz), 8.19 (m, 2H), 8.31 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 19.0, 77.4, 83.6, 119.5, 122.6, 123.6, 126.2, 127.3, 127.9, 128.8, 129.4, 130.3, 131.2, 132.7, 140.0, 145.0, 148.1, 155.9. IR (film): ν 3293, 3058, 2918, 1598, 1508, 758 cm^{-1}. MS: *m/z* (% relative intensity) 243(M^+, 100), 228(50), 153(70), 136(51), 106(48); HRMS: *m/z* calcd for $C_{18}H_{13}N$ (M^+) 243.1048, found 243.1045.

2-(3,5-Diethynylphenyl)-4-methylquinoline (5Li):



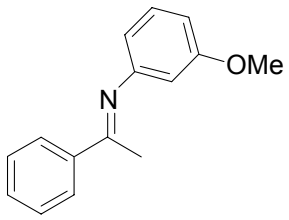
5Li

^1H NMR ($CDCl_3$, TMS, 400 MHz): δ 2.78 (s, 3H), 3.16 (s, 2H), 7.59 (m, 1H), 7.70 (s, 2H), 7.75 (m, 1H), 8.02 (d, 1H, J = 8.3 Hz), 8.18 (d, 1H, J = 8.4 Hz), 8.29 (s, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 19.0, 78.1, 82.6, 119.3, 123.0, 123.6, 126.5, 127.5, 129.6, 130.4, 131.4, 135.9, 140.3, 145.3, 148.1, 154.8. IR (film): ν 3292, 2922, 2855, 1600, 1549, 1273, 759 cm^{-1}. MS: *m/z* (% relative intensity) 267(M^+, 100), 252(31), 153(13), 106(10); HRMS: *m/z* calcd for $C_{20}H_{13}N$ (M^+) 267.1048, found 267.1041.

Gram-Scale Catalytic Synthesis of Quionline Derivative (5La) Using Gold(I) Complexes. To a mixture of **1c** (0.6 mmol), silver triflate (0.6 mmol), and 4 A MS (0.4 g) in toluene (15 mL) was added 2-aminoacetophenone (2.7 g, 20 mmol) and phenylacetylene (4.1 g, 40 mmol) with stirring. The reaction mixture was capped and stirred for 36 h at 100 °C. The product **5La** was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 4:1).

Procedure for the 1a/AgOTf-Catalyzed Reaction of *m*-Anisidine with Phenylacetylene at Room Temperature. To a mixture of **1a** (0.025 mmol) and AgOTf (0.025 mmol) in CH_3NO_2 (1.0 mL) was added *m*-anisidine (0.5 mmol) and phenylacetylene (1 mmol) with stirring. The reaction mixture was capped and stirred for 30 min at room temperature. The product **6Aa** was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 40:1).

(*E*)-3-Methoxy-*N*-(1-phenylethylidene)aniline (6Aa):



6Aa

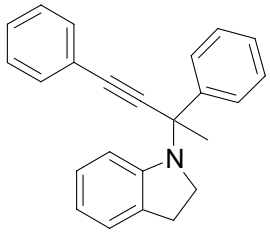
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 2.27 (s, 3H), 3.83 (s, 3H), 6.41 (m, 2H), 6.66 (m, 1H), 7.26 (m, 1H), 7.47 (m, 3H), 8.00 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 17.4, 55.2, 105.0, 108.9, 111.7, 127.2, 128.4, 129.8, 130.5, 139.4, 153.1, 160.3, 165.6. IR (film): ν 2835, 1684, 1598, 1497cm^{-1}. MS: *m/z* (% relative intensity) 225(M^+, 12), 210(15), 123(100), 94(19); HRMS: *m/z* calcd for $C_{15}H_{15}NO$ (M^+) 225.1154, found 225.1154.

Procedure for the Reaction of (*E*)-3-Methoxy-*N*-(1-phenylethylidene)aniline (6Aa) with Phenylacetylene Catalyzed by 1a/AgOTf. To a mixture of **1a** (0.025 mmol) and AgOTf (0.025 mmol) in CH_3NO_2 (1.0 mL) was added **6Aa** (0.5 mmol) and phenylacetylene (1 mmol) with stirring. The reaction mixture was capped and stirred for

4 h at 35 ^{o}C. The product **4Aa** was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 4:1).

Typical Procedure for 1a/$AgSbF_6$-Catalyzed Reactions of Indoline (2N) with Alkynes at Room Temperature. To a mixture of **1a** (0.025 mmol) and $AgSbF_6$ (0.025 mmol) in dry solvent (1.0 mL) was added indoline (0.5 mmol) and alkyne (2.5 mmol) with stirring. The reaction mixture was capped and stirred at room temperature. The product was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 4:1).

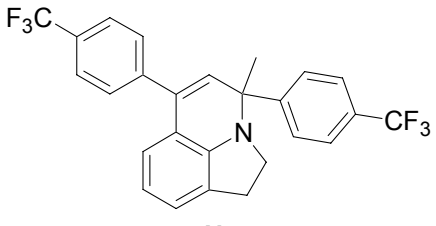
1-(2,4-Diphenylbut-3-yn-2-yl)indoline (7Na):



7Na

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.84 (s, 3H), 3.02 (m, 2H), 3.53 (m, 1H), 3.79 (m, 1H), 5.95 (d, 1H, J = 7.9 Hz), 6.64 (t, 1H, J = 7.9 Hz), 6.74 (t, 1H, J = 7.9 Hz), 7.09 (d, 1H, J = 7.9 Hz), 7.30 (m, 8H), 7.82 (d, 2H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 28.3, 33.2, 50.6, 60.5, 85.1, 89.9, 112.7, 118.5, 123.1, 123.9, 125.9, 126.1, 127.2, 128.0, 128.1, 128.6, 131.5, 131.9, 145.6, 150.2. IR (film): ν 2923, 2848, 1604, 1482 cm^{-1}. MS: *m/z* (% relative intensity) 325(M^+, 11), 205(100), 202(38), 119(56); HRMS: *m/z* calcd for $C_{24}H_{21}N$ (M^+) 323.1674, found 323.1666.

4-Methyl-4,6-bis(4-(trifluoromethyl)phenyl)-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (4Nc):

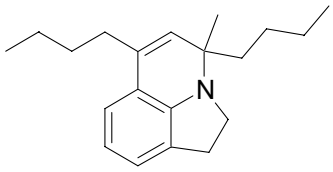


4Nc

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.85 (s, 3H), 3.06 (m, 3H), 3.49 (m, 1H), 5.29 (s,

1H), 6.51 (t, 1H, J = 7.5 Hz), 6.72 (d, 1H, J = 7.5 Hz), 6.97 (d, 1H, J = 7.5 Hz), 7.47 (d, 2H, J = 8.0 Hz), 7.62 (d, 4H, J = 8.6 Hz), 7.71 (d, 2H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 23.3, 28.0, 46.4, 61.2, 115.3, 117.1, 122.3, 125.1, 125.3 (m), 125.4 (m), 126.0, 126.6, 127.0, 128.3, 128.9, 129.2, 129.6, 129.9, 133.8, 142.0, 148.0, 149.3. MS: *m/z* (% relative intensity) 459(M^+, 11), 444(100), 314(49), 153(15); HRMS: *m/z* calcd for $C_{26}H_{19}NF_6$ (M^+) 459.1422, found 459.1419.

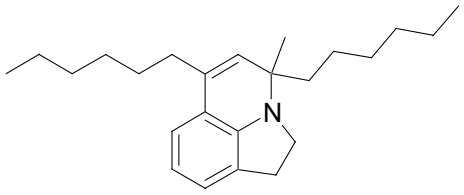
4, 6-Dibutyl-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (4Nd):



4Nd

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.00 (m, 6H), 1.27 (s, 3H), 1.43 (m, 7H), 1.62 (m, 2H), 1.80 (m, 1H), 2.41 (m, 2H), 3.05 (m, 2H), 3.52 (m, 2H), 5.06 (s, 1H), 6.53 (t, 1H, J = 7.5 Hz), 6.91 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 14.1, 14.3, 22.7, 23.3, 25.2, 27.5, 28.3, 30.8, 31.0, 40.5, 45.3, 58.3, 115.9, 117.2, 120.4, 123.6, 125.8, 126.4, 133.3, 149.2. MS: *m/z* (% relative intensity) 283(M^+, 5), 268(11), 227(17), 226(100), 183(13); HRMS: *m/z* calcd for $C_{20}H_{29}N$ (M^+) 283.2300, found 283.2295.

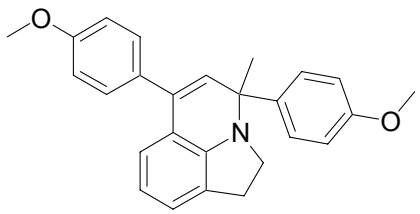
4, 6-Dihexyl-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (4Ne):



4Ne

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.89 (m, 6H), 1.20 (s, 3H), 1.35 (m, 15H), 1.54 (m, 2H), 1.72 (m, 1H), 2.33 (m, 2H), 2.98 (m, 2H), 3.46 (m, 2H), 4.99 (s, 1H), 6.46 (t, 1H, J = 7.4 Hz), 6.85 (t, 2H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): δ 14.2, 22.8, 25.2, 25.4, 28.3, 28.7, 29.3, 29.9, 31.4, 31.8, 32.0, 40.8, 45.3, 58.3, 115.9, 117.2, 120.4, 123.6, 125.8, 126.4, 133.3, 149.2. MS: *m/z* (% relative intensity) 339(M^+, 2), 255(20), 254(100), 252(31), 183(14); HRMS: *m/z* calcd for $C_{24}H_{37}N$ (M^+) 339.2926, found 339.2913.

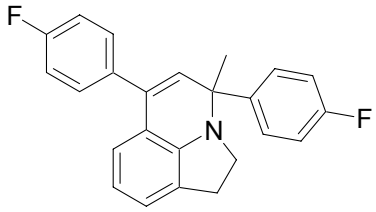
4, 6-Bis(4-methoxyphenyl)-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (4Nj):



4Nj

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.83 (s, 3H), 2.99 (m, 2H), 3.10 (m, 1H), 3.51 (d, 1H, J = 8.4 Hz), 3.83 (s, 3H), 3.85 (s, 3H), 5.34 (s, 1H), 6.51 (t, 1H, J = 7.5 Hz), 6.84 (d, 1H, J = 7.7 Hz), 6.93 (m, 5H), 7.35 (d, 2H, J = 8.5 Hz), 7.52 (d, 2H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 24.0, 28.1, 46.3, 55.2, 55.3, 60.5, 113.5, 113.6, 116.4, 122.5, 124.3, 126.3, 128.0, 129.7, 129.8, 131.1, 133.4, 137.8, 148.4, 158.5, 159.0. MS: *m/z* (% relative intensity) 383(M^+, 7), 369(26), 368(100), 276(30), 149(22); HRMS: *m/z* calcd for $C_{26}H_{25}NO_2$ (M^+) 383.1885, found 383.1881.

4, 6-Bis(4-fluorophenyl)-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (4Nk):



4Nk

^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.85 (s, 3H), 3.07 (m, 3H), 3.51 (d, 1H, J = 8.6 Hz), 5.31 (s, 1H), 6.56 (t, 1H, J = 7.6 Hz), 6.77 (d, 1H, J = 7.7 Hz), 6.97 (d, 1H, J = 7.7 Hz), 7.08 (m, 4H), 7.38 (m, 2H), 7.58 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 23.7, 28.0, 46.3, 60.7, 115.1 (m), 115.6, 116.7, 122.4, 124.7, 126.4, 129.3 (m), 129.9, 133.3, 134.4, 141.5, 148.2, 160.2, 160.7, 163.5, 164.0. MS: *m/z* (% relative intensity) 359(M^+, 7), 345(25), 344(100), 264(44), 262(10); HRMS: *m/z* calcd for $C_{24}H_{19}NF_2$ (M^+) 359.1486, found 359.1480.

Procedure for the Conversion of 1-(2,4-Diphenylbut-3-yn-2-yl)indoline (7Na) to 4Na Catalyzed by 1a/$AgSbF_6$. To a mixture of **1a** (5 mol %) and $AgSbF_6$ (5 mol %) in CH_3NO_2 (0.5 mL) was added **7Na** (0.1 mmol) with stirring. The reaction mixture was

capped and stirred for 2 h at room temperature. The product **4Na** was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride = 4:1).

For characterization of **4Aa**,[S1] **4Ad**,[S2] **4Ea**,[S1] **4″Ea**,[S1] **4Fa**,[S3] **4Na**,[S4] **4Nb**,[S4] **5La**,[S5] **5Lb**,[S5] **5Lc**,[S6] **5Le**,[S7] **5Ma**,[S8] and **5Mb**,[S8] see the reference indicated specifically.

References:

(S1) Arduini, A.; Bigi, F.; Casiraghi, G.; Casnati, G.; Sartori, G. *Synthesis* **1981**, 975.

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(S5) Molina, P.; Alajarín, M.; Sánchez-Andrada, P. *Synthesis* **1993**, 225.

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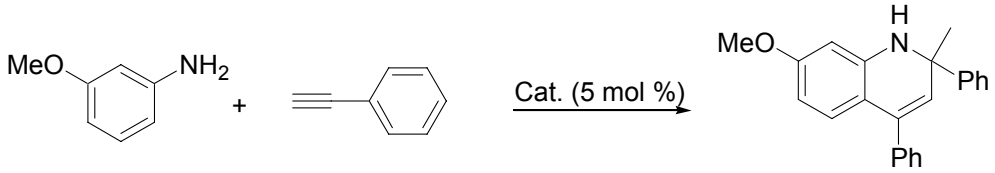
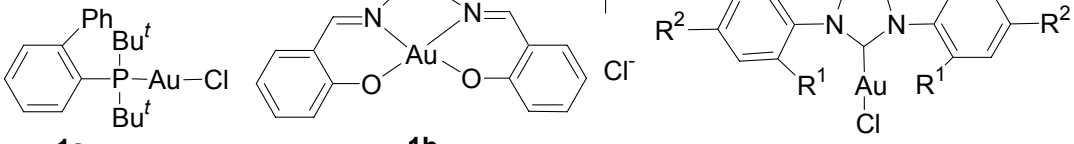
(S8) Kobayashi, K.; Yoneda, K.; Miyamoto, K.; Morikawa, O.; Konishi, H. *Tetrahedron* **2004**, *60*, 11639.

Table S1. Catalyst Activity of Selected Gold Complexes.[a]



2A **3a** **4Aa**



1a **1b**

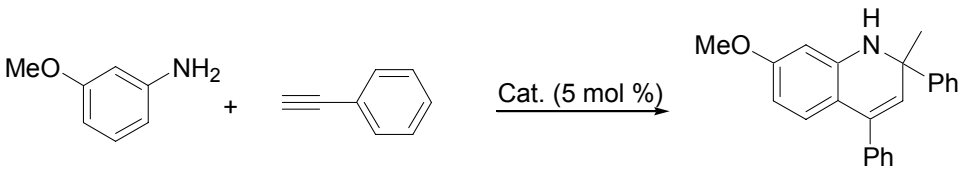
1c: $R^1 = Pr^i$, $R^2 = H$

1d: R^1,$R^2 = CH_3$

entry	catalyst	additive	solvent	time (h)	T (^{o}C)	yield (%)[b]
1	$AuCl_3$	NH_4PF_6	toluene	24	100	11
2	AgOTf	none	toluene	24	100	35
3	$(PPh_3)AuOTf$	none	toluene	24	100	76
4	**1b**	NH_4PF_6	toluene	24	100	80
5	**1b**	HBF_4	toluene	24	100	56
6	***1c**/AgOTf*	*none*	*toluene*	*12*	*80*	*80*
7	**1c**	NH_4PF_6	toluene	12	80	61
8	**1b**	NH_4PF_6	CH_3CN	24	100	51
9	**1b**	NH_4PF_6	CH_3CN	24	80	62
10	**1b**	NH_4PF_6	DMF	24	80	12
11	**1b**	NH_4PF_6	MeOH	24	100	53

[a] Reactions conditions: *m*-anisidine (0.5 mmol), alkyne (2.5 mmol), catalyst (0.025 mmol), NH_4PF_6 (0.075 mmol). [b] Isolated yield based on *m*-anisidine.

Table S2. Catalyst Activity of Selected Gold Complexes under Microwave Irradiation.[a]

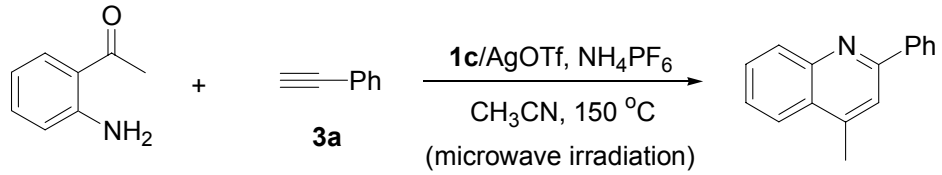


2A **3a** **4Aa**

entry	catalyst	yield (%)[b]
1	Ph_3PAuCl/AgOTf	66
2	**1a**/AgOTf	86
3	**1b**	43
4	**1c**/AgOTf	90(82[c])
5	**1d**/AgOTf	69
6	(tetrahydrothiophene)AuCl	76

[a] Reaction conditions: catalyst (5 mol %), NH_4PF_6 (15 mol %), CH_3CN (1 mL), 150 ^oC with microwave irradiation, 25 min. [b] Determined by ^1H NMR. [c] Isolated yield based on *m*-anisidine.

Table S3. Formation of Quinoline Derivative **5La** from **1c**/AgOTf-Catalyzed Reaction of **2L** and **3a** at Different Catalyst Loadings.[a]

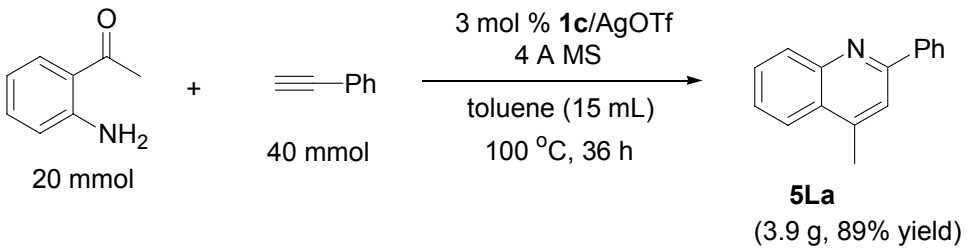


2L **3a** **5La**

entry	catalyst loading	time (min)	yield (%)[b]
1	5	30	93
2	2	30	92[c]
3	1	40	84[c]
4	0.5	40	53[c]
5	0.1	40	9[c]

[a] Reaction conditions: CH_3CN (1 mL), 150 °C with microwave irradiation. [b] Isolated yield based on 2-aminoacetophenone. [c] Determined by ^1H NMR.

Scheme S1. Gram-Scale Synthesis of Quinoline Derivative **5La**



5La
(3.9 g, 89% yield)

Figure S1. ^{1}H NMR spectrum of 7-methoxy-2-methyl-2,4-di-*p*-tolyl-1,2-dihydroquinoline (**4Ab**)

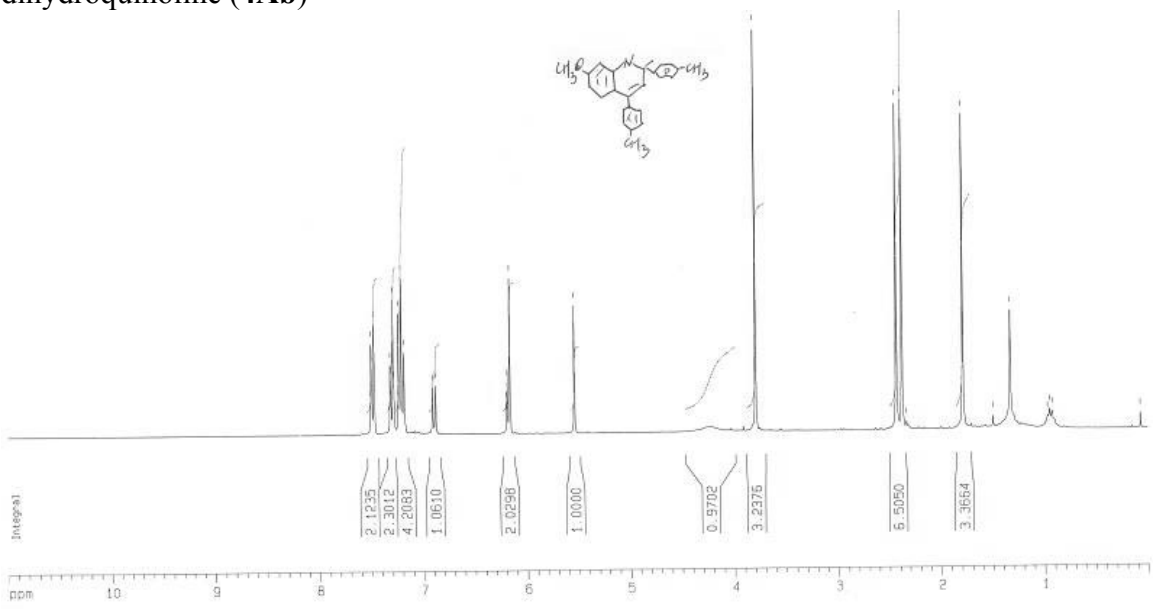


Figure S2. ^{13}C NMR spectrum of 7-methoxy-2-methyl-2,4-di-*p*-tolyl-1,2-dihydroquinoline (**4Ab**)

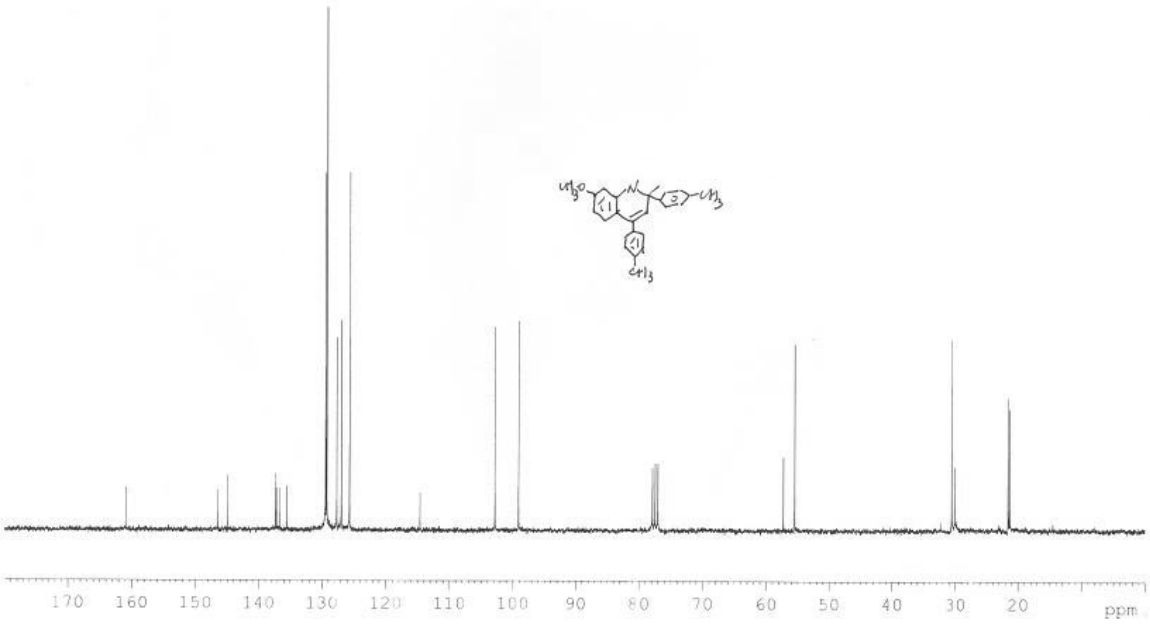


Figure S3. ^{1}H NMR spectrum of 7-methoxy-2-methyl-2,4-di-(4-trifluoromethyl-phenyl)-1,2-dihydroquinoline(**4Ac**)

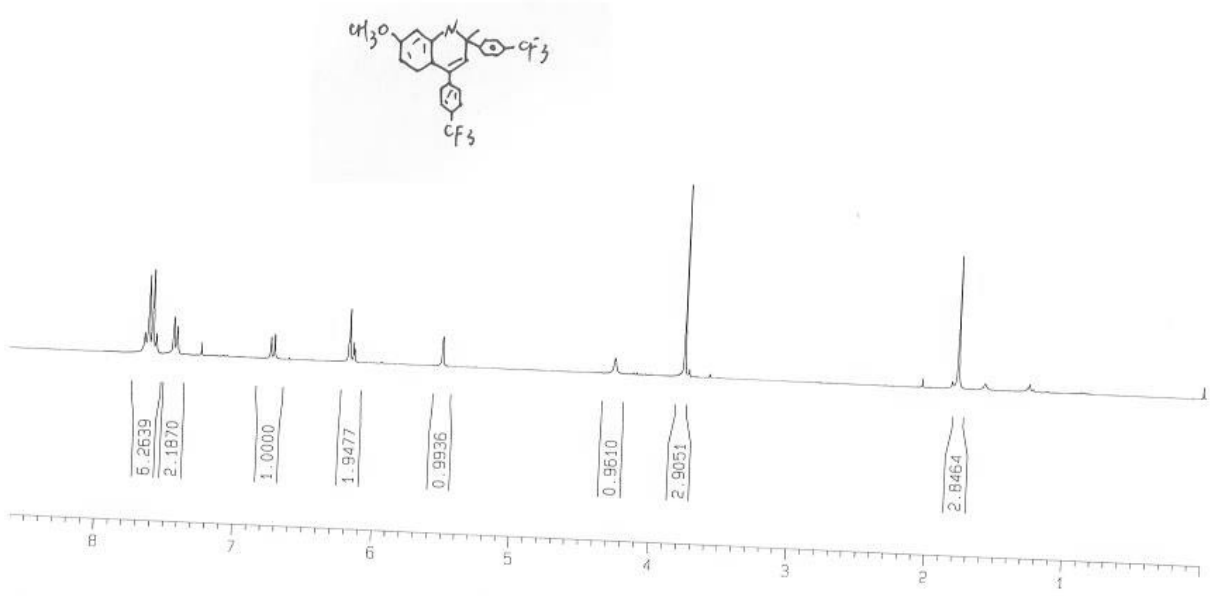


Figure S4. ^{13}C NMR spectrum of 7-methoxy-2-methyl-2,4-di-(4-trifluoromethyl-phenyl)-1,2-dihydroquinoline (**4Ac**)

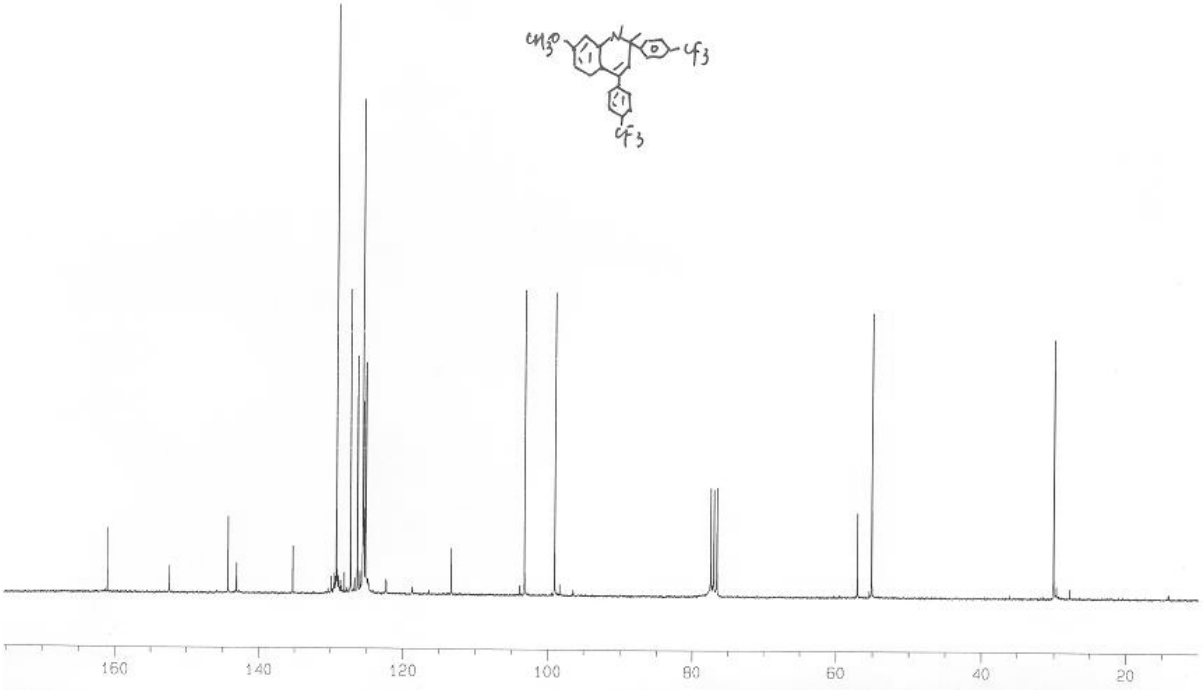


Figure S5. ^{1}H NMR spectrum of 2,4-dihexyl-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Ae**)

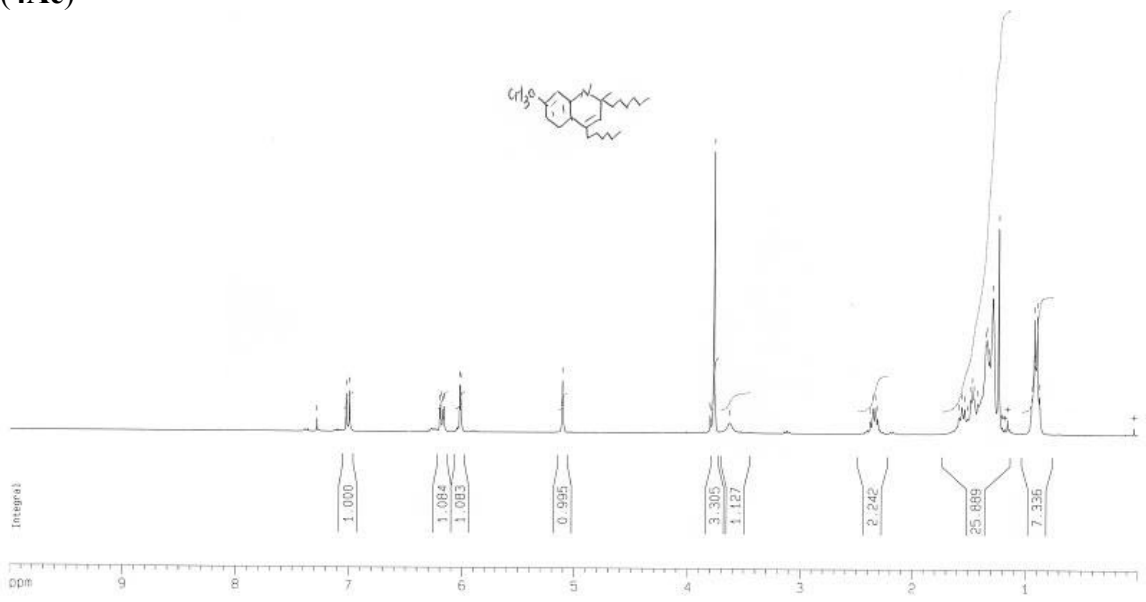


Figure S6. ^{13}C NMR spectrum of 2,4-dihexyl-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Ae**)

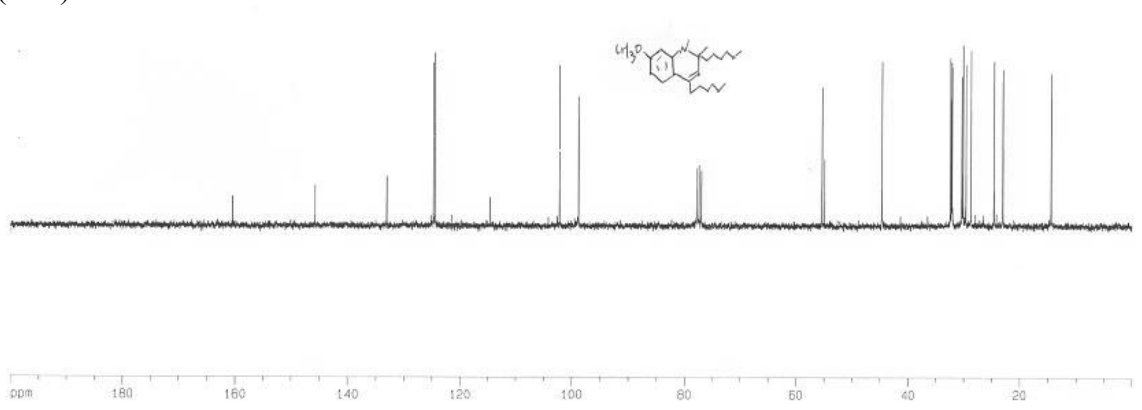


Figure S7. ^{1}H NMR spectrum of 6-methoxy-2-methyl-2.4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (**4'Ba**)

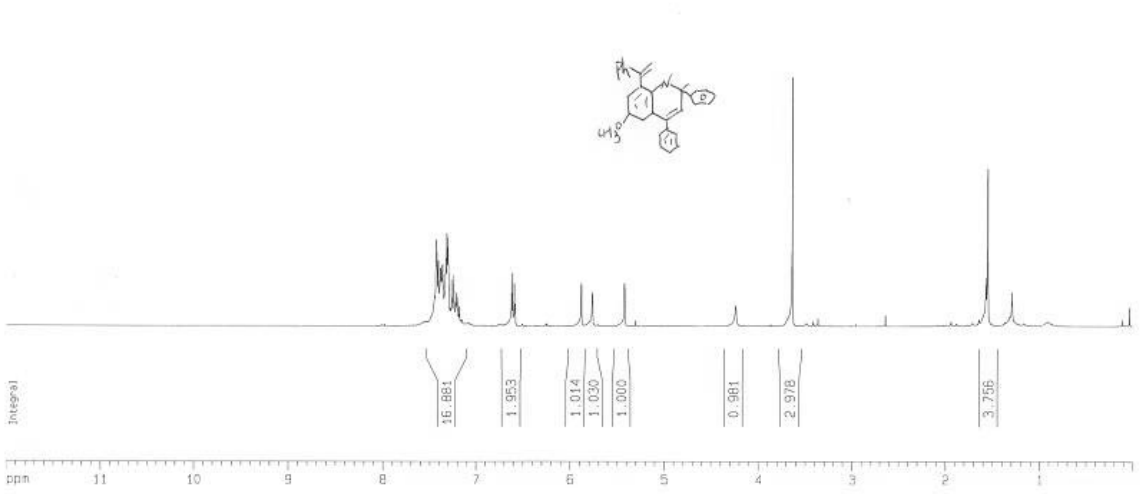


Figure S8. ^{13}C NMR spectrum of 6-methoxy-2-methyl-2.4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (**4'Ba**)

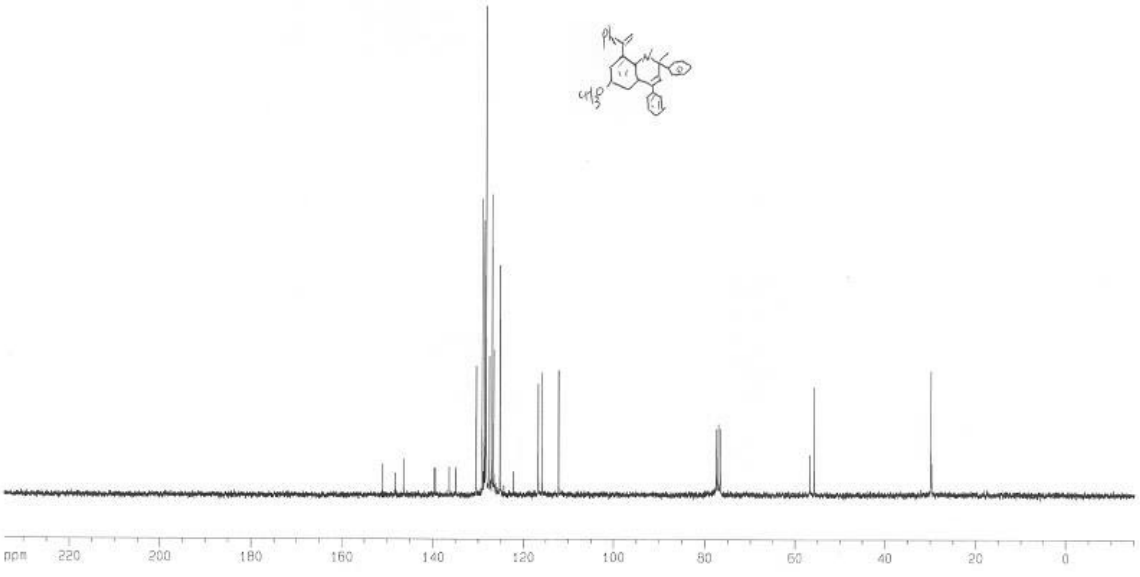


Figure S9. ^{1}H NMR spectrum of 2-methyl-6-phenoxy-2,4-diphenyl-1,2-dihydroquinoline (**4Ca**)

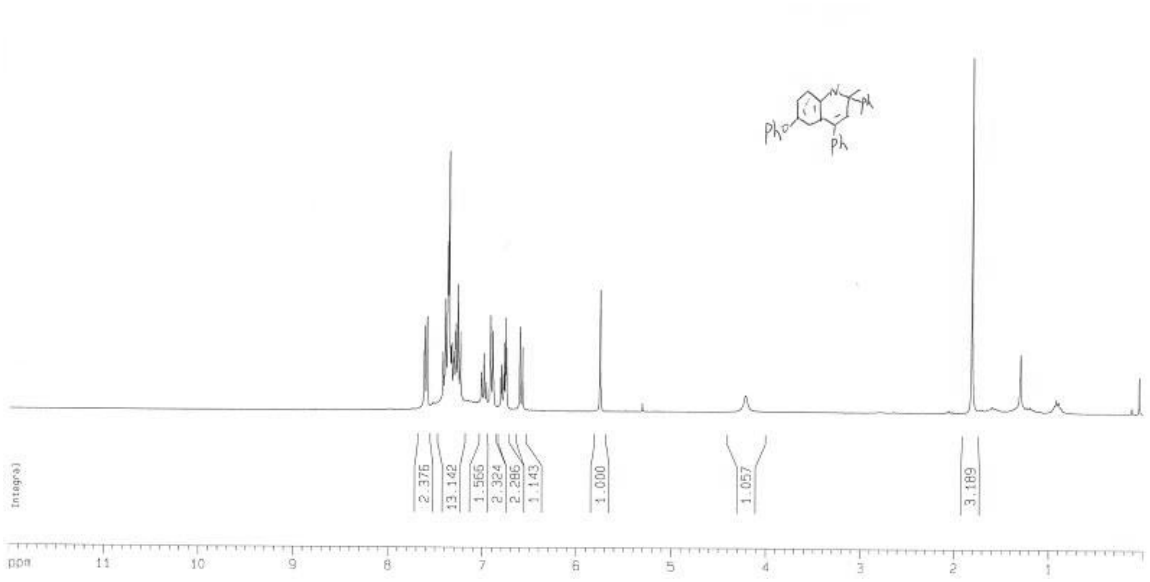


Figure S10. ^{13}C NMR of 2-methyl-6-phenoxy-2,4-diphenyl-1,2-dihydroquinoline (**4Ca**)

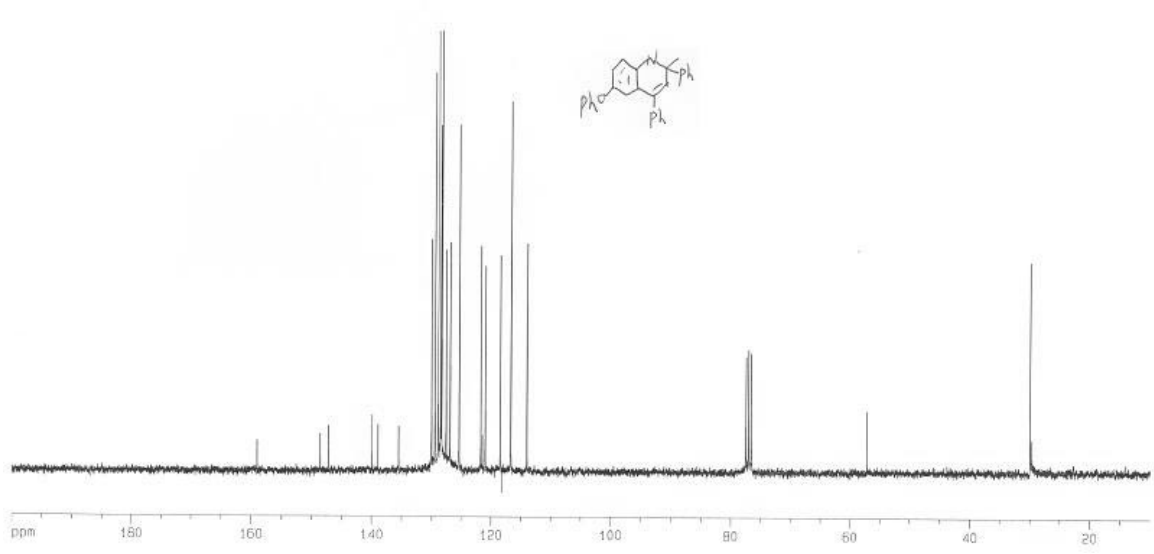


Figure S11. ^{1}H NMR spectrum of 2-methyl-6-phenoxy-2,4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (**4'Ca**)

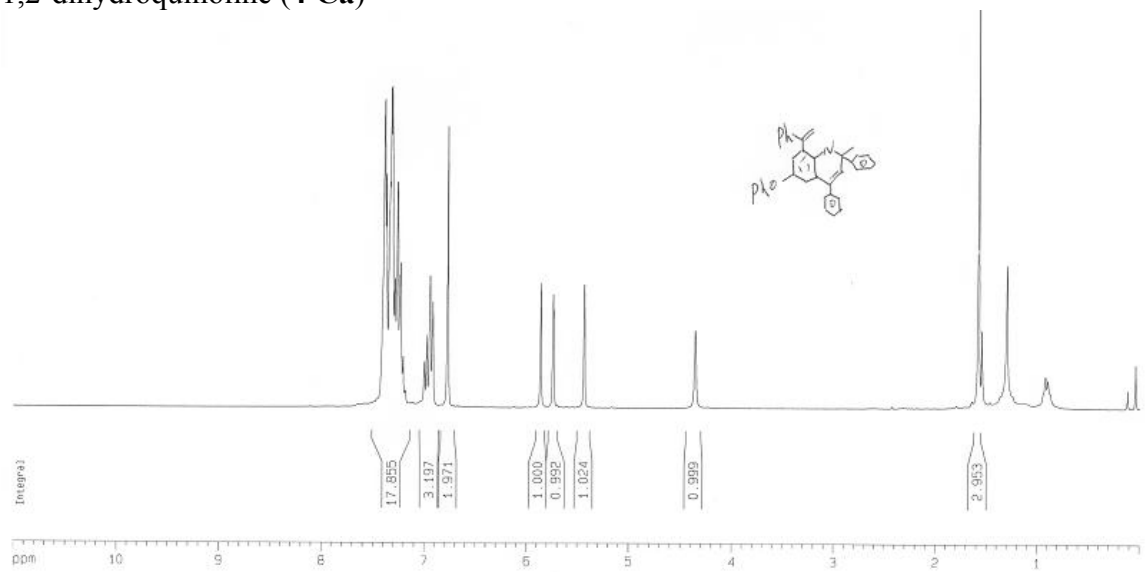


Figure S12. ^{13}C NMR spectrum of 2-methyl-6-phenoxy-2,4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (**4'Ca**)

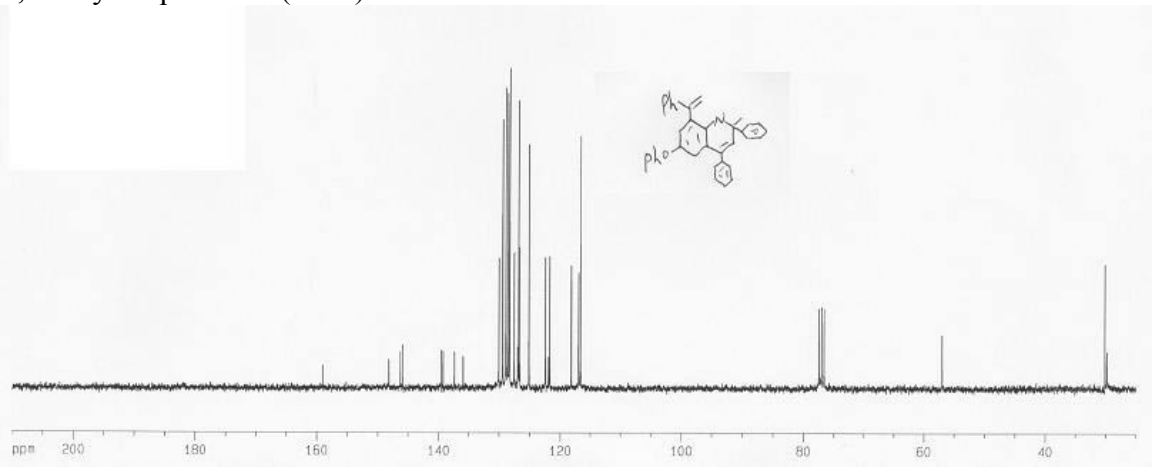


Figure S13. [1]H NMR spectrum of 2,6-dimethyl-2,4-diphenyl-1,2-dihydroquinoline (**4Da**)

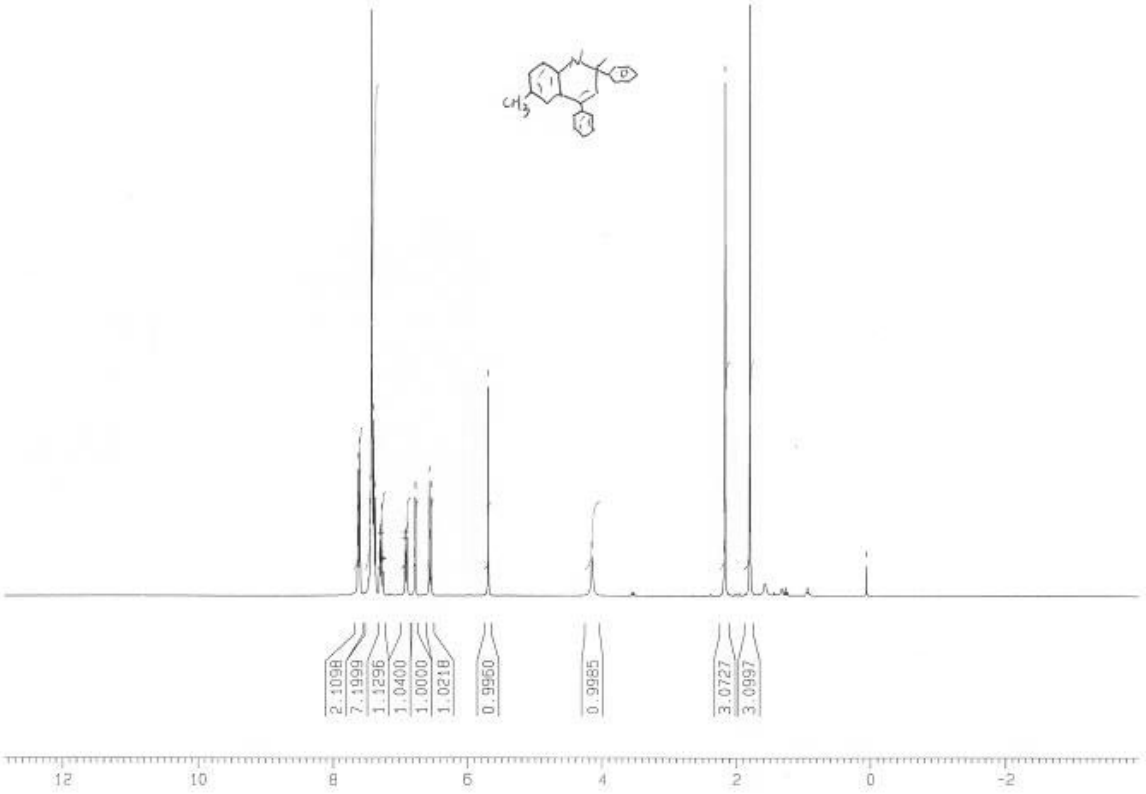


Figure S14. [13]C NMR spectrum of 2,6-dimethyl-2,4-diphenyl-1,2-dihydroquinoline (**4Da**)

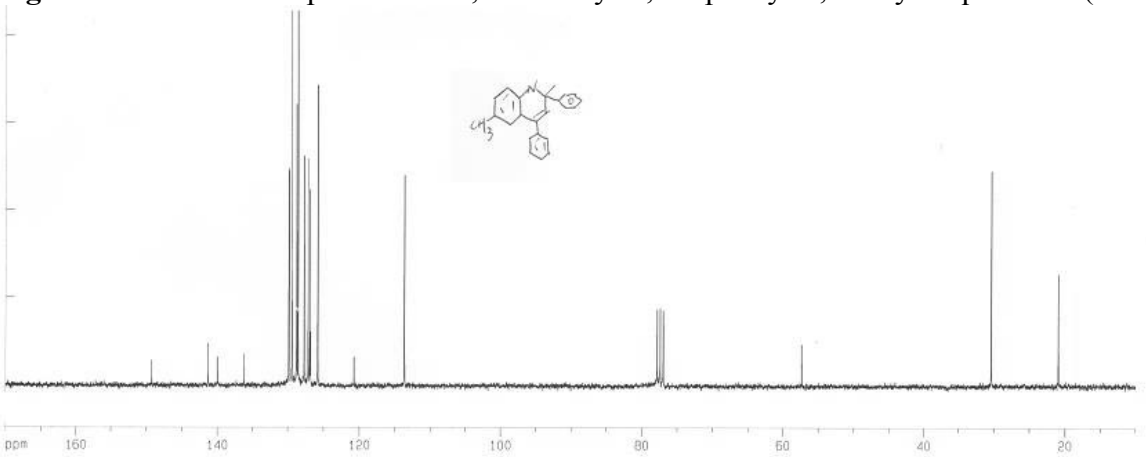


Figure S15. ^{1}H NMR spectrum of 6-chloro-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ga**)

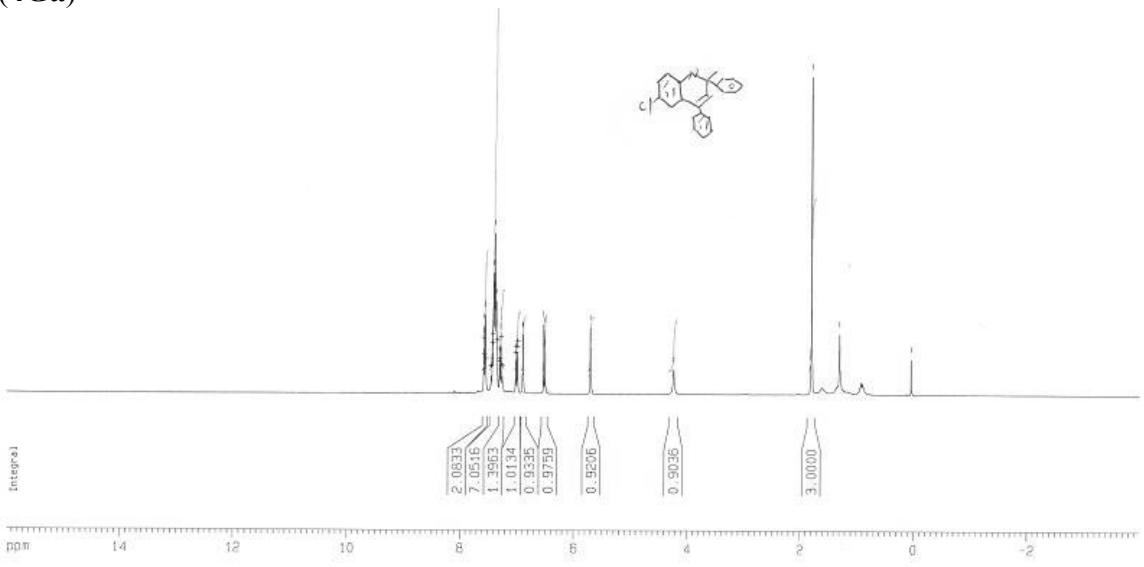


Figure S16. ^{13}C NMR spectrum of 6-chloro-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ga**)

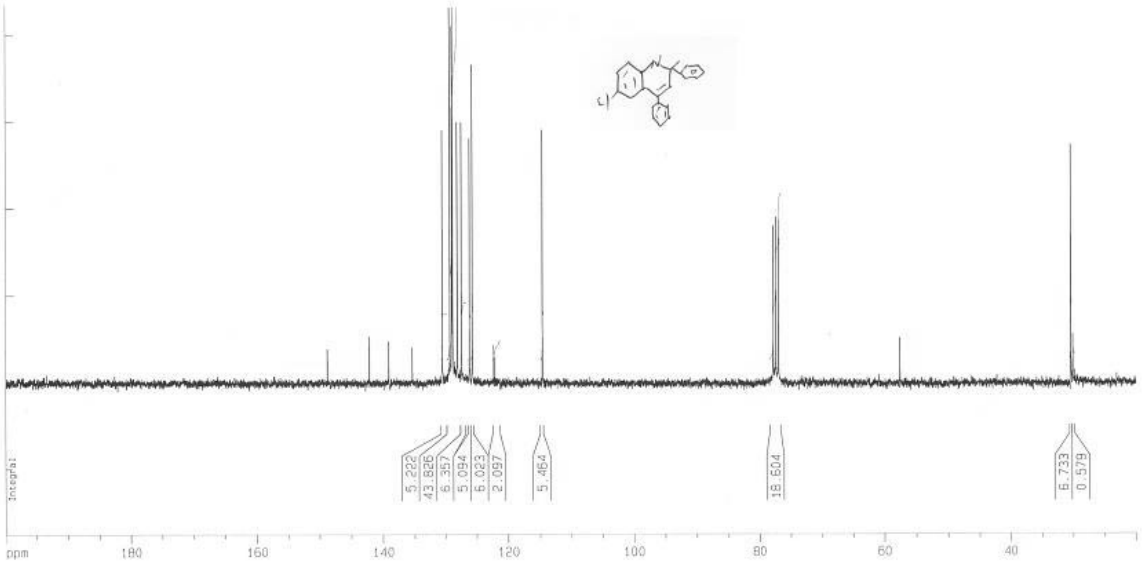


Figure S17. [1]H NMR spectrum of 6-fluoro-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ha**)

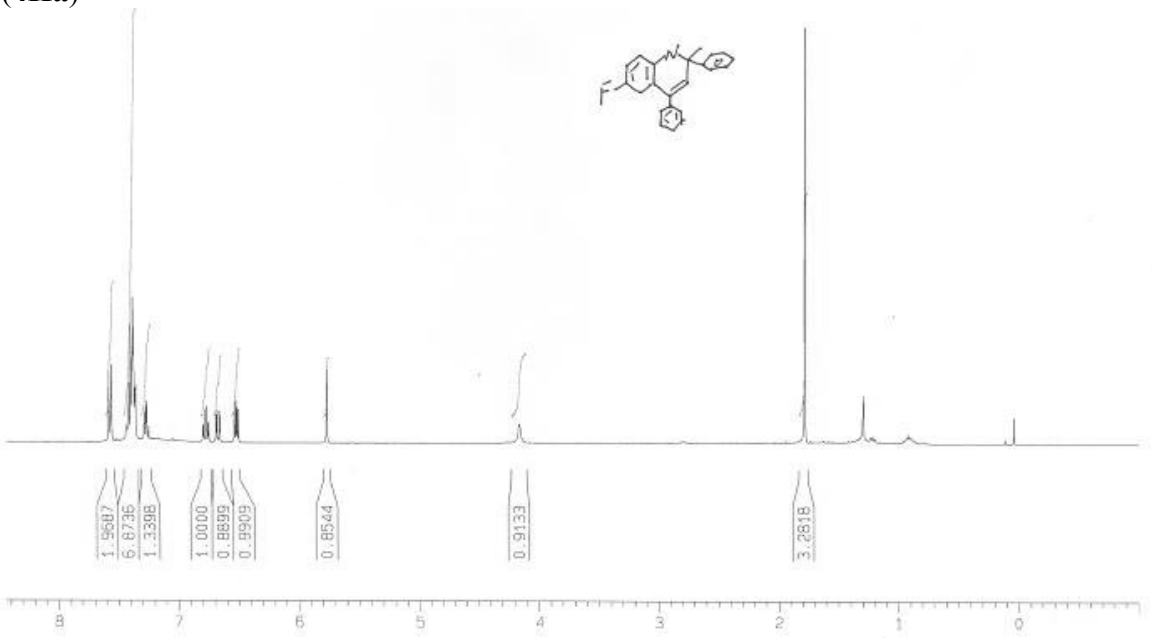


Figure S18. [13]C NMR spectrum of 6-fluoro-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ha**)

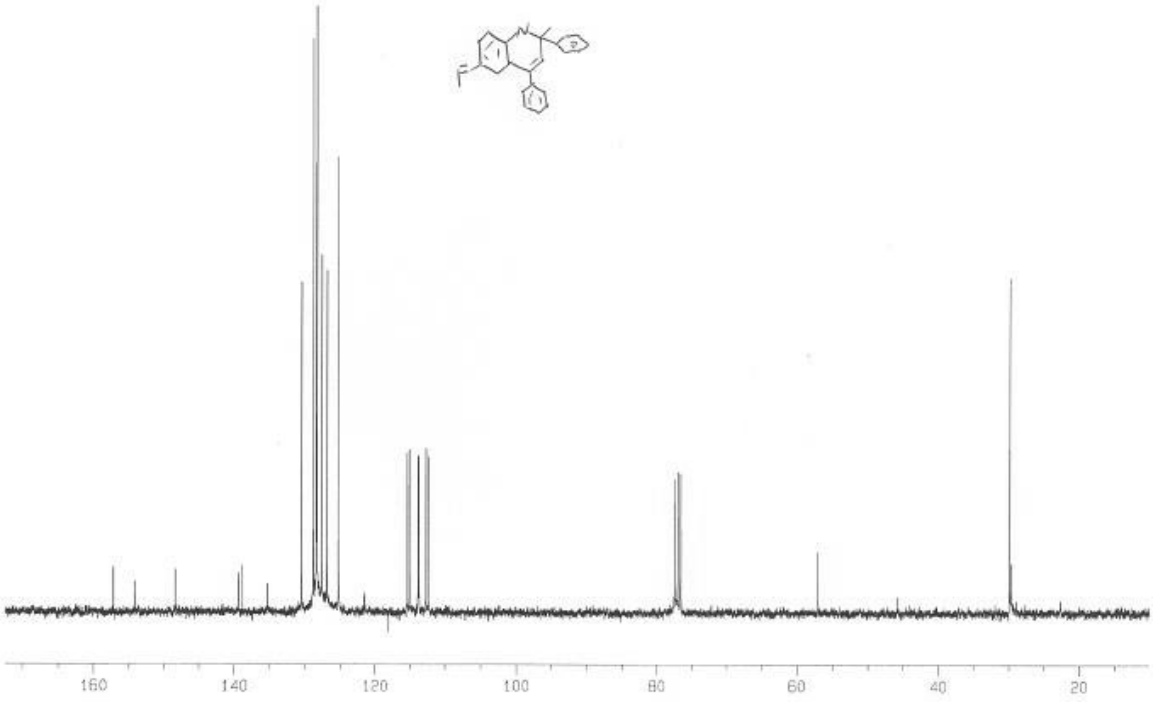


Figure S19. ^{1}H NMR spectrum of 2-methyl-2,4-diphenyl-1,2-dihydro-benzo[*h*]quinoline (**4Ia**)

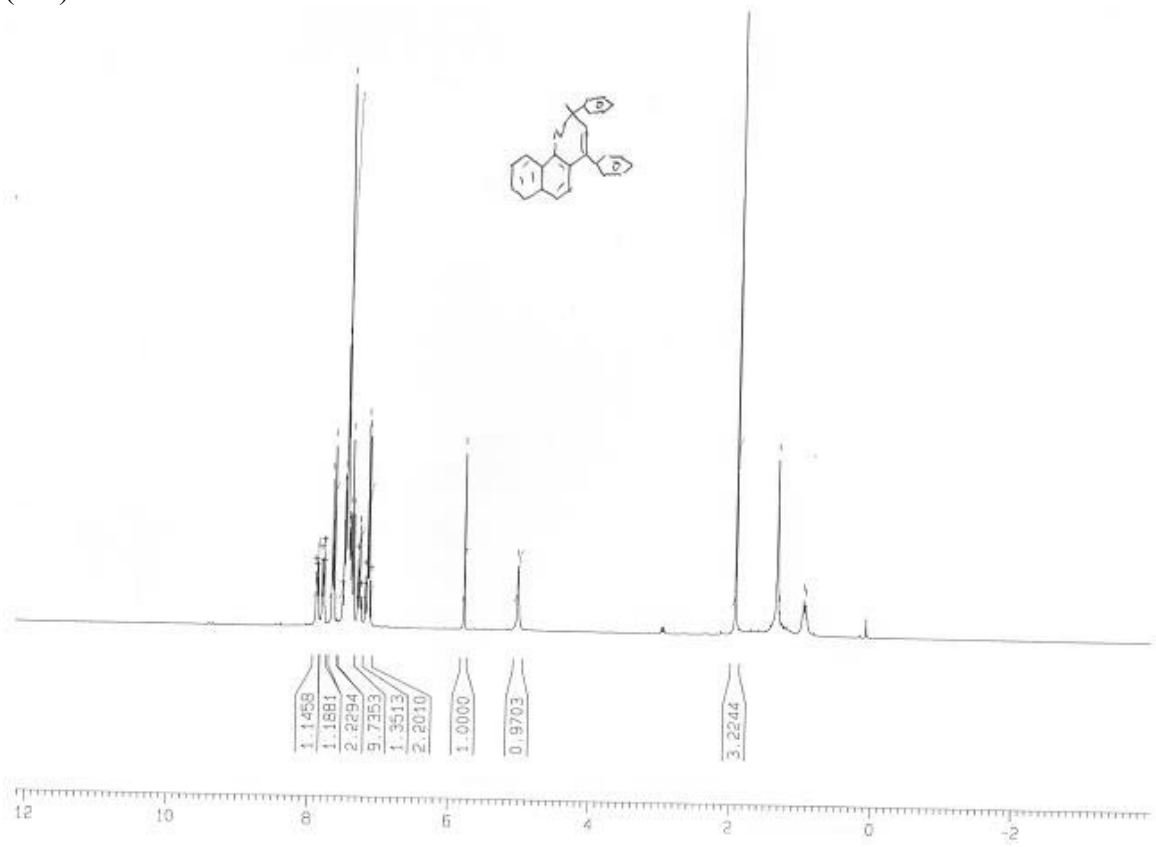


Figure S20. ^{13}C NMR spectrum of 2-methyl-2,4-diphenyl-1,2-dihydro-benzo[*h*]quinoline (**4Ia**)

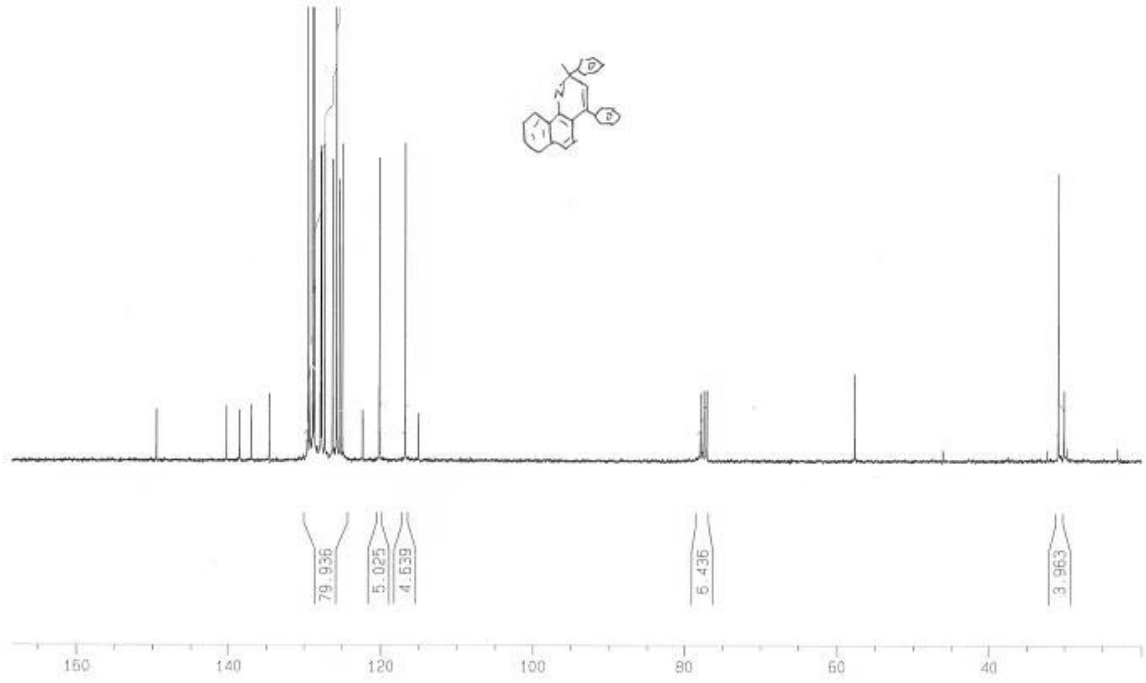


Figure S21. ^{1}H NMR spectrum of 5,8-dimethoxy-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ja**)

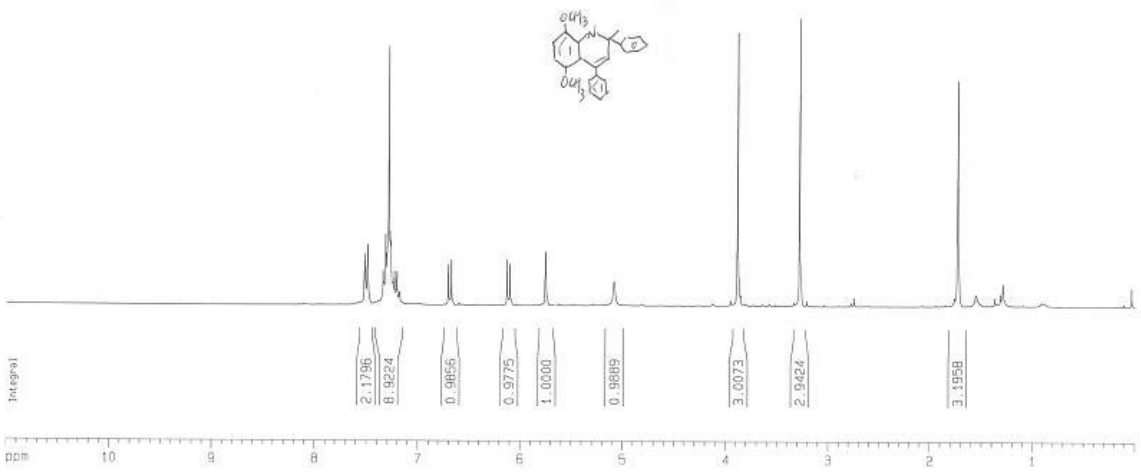


Figure S22. ^{13}C NMR spectrum of 5,8-dimethoxy-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ja**)

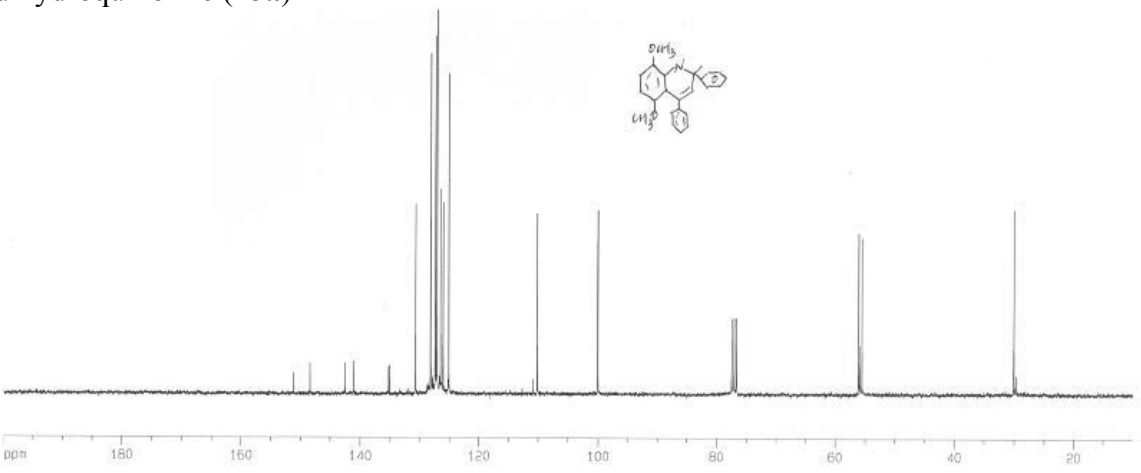


Figure S23. ^{1}H NMR spectrum of 5,7-dimethoxy-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ka**)

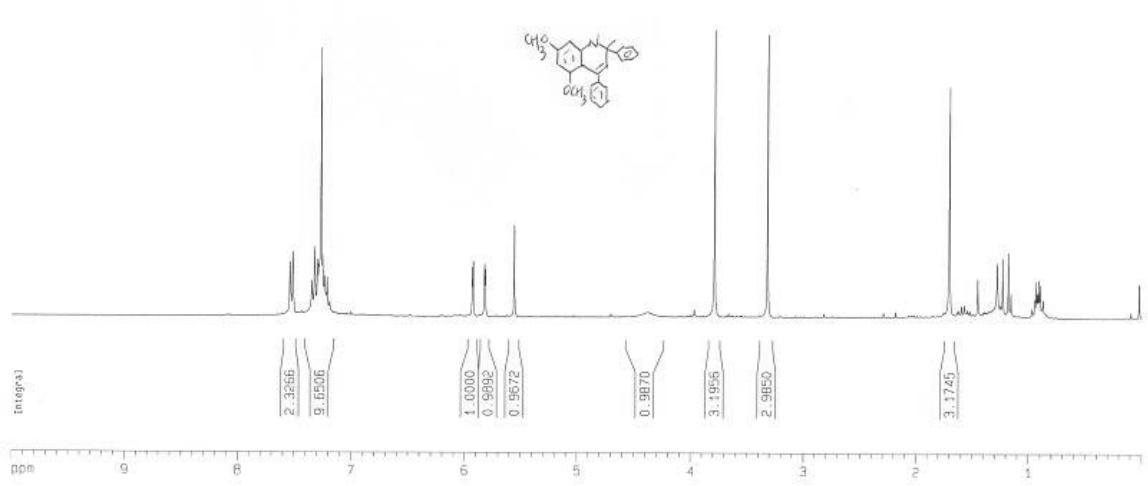


Figure S24. ^{13}C NMR spectrum of 5,7-dimethoxy-2-methyl-2,4-diphenyl-1,2-dihydroquinoline (**4Ka**)

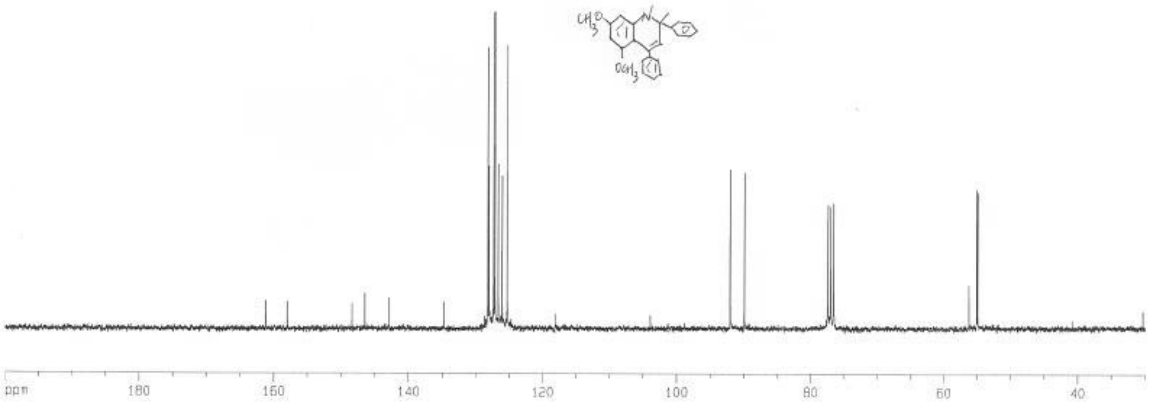


Figure S25. ^{1}H NMR spectrum of 5,7-dimethoxy-2-methyl-2,4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (**4'Ka**)

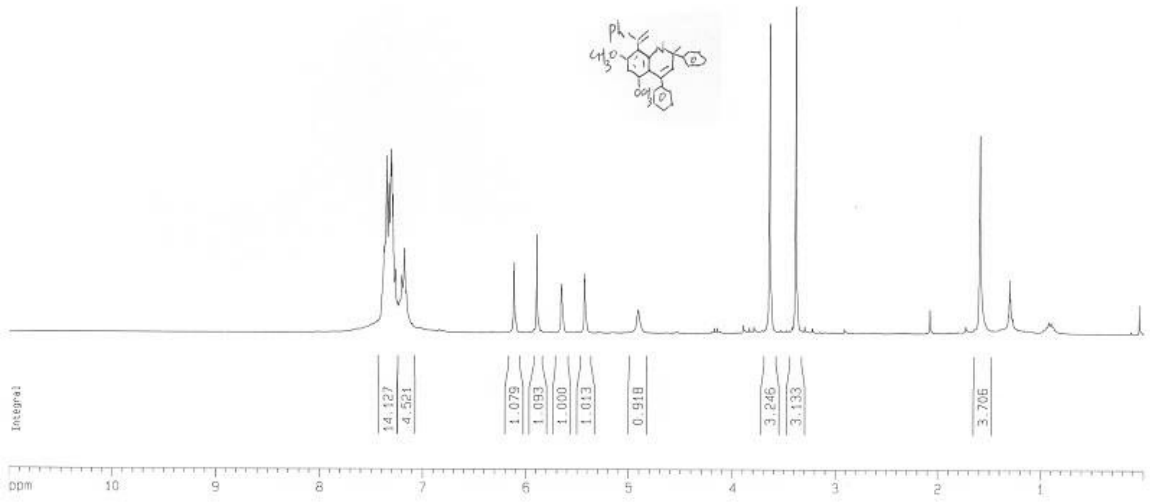


Figure S26. ^{13}C NMR spectrum of 5,7-dimethoxy-2-methyl-2,4-diphenyl-8-(1-phenylvinyl)-1,2-dihydroquinoline (**4'Ka**)

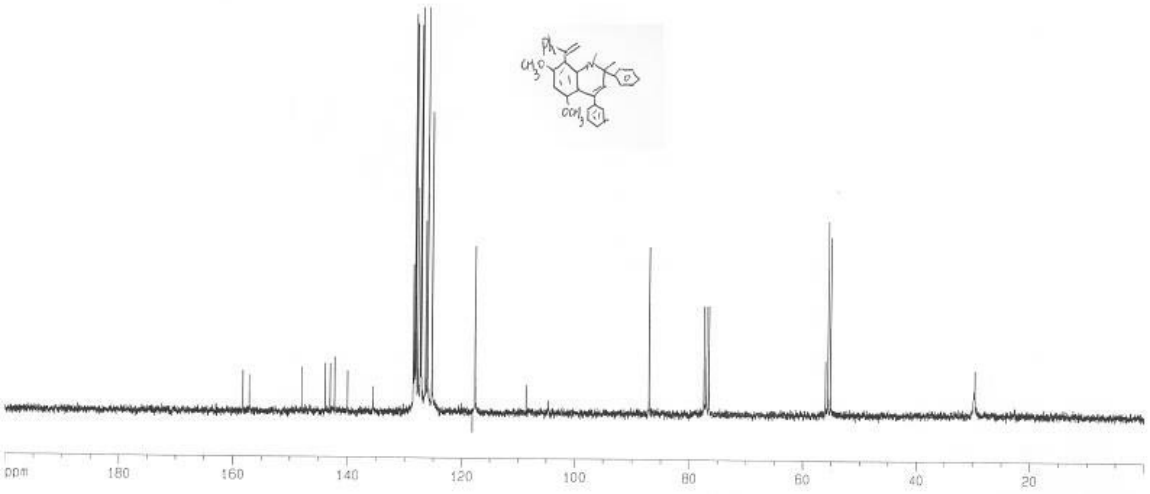


Figure S27. ^{1}H NMR spectrum of 2,4-bis(4-ethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Af**)

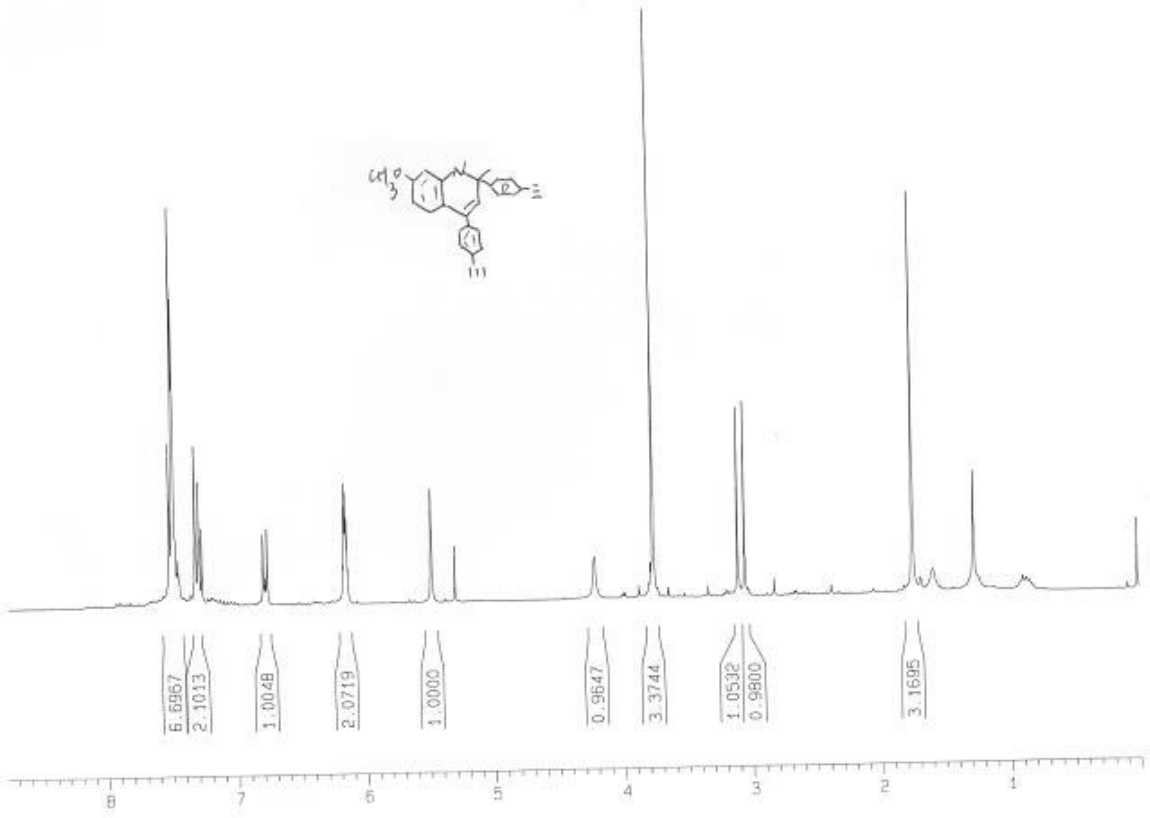


Figure S28. ^{13}C NMR spectrum of 2,4-bis(4-ethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Af**)

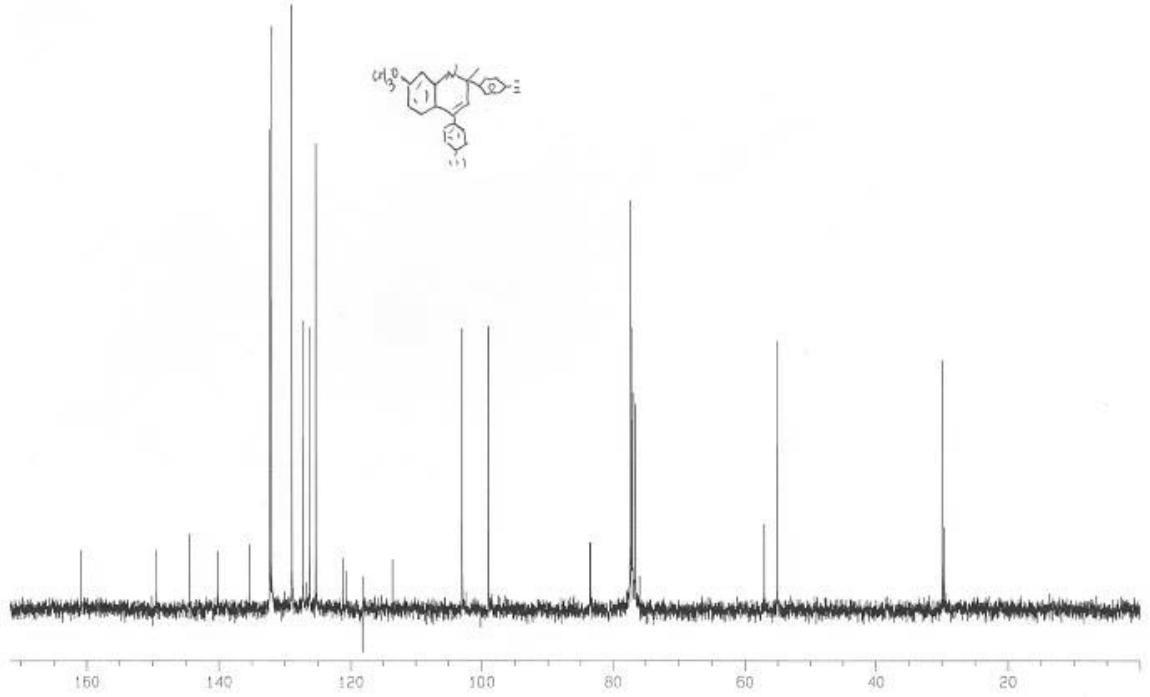


Figure S29. ^{1}H NMR spectrum of 2,4-bis(4'-ethynylbiphenyl-4-yl)-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Ag**)

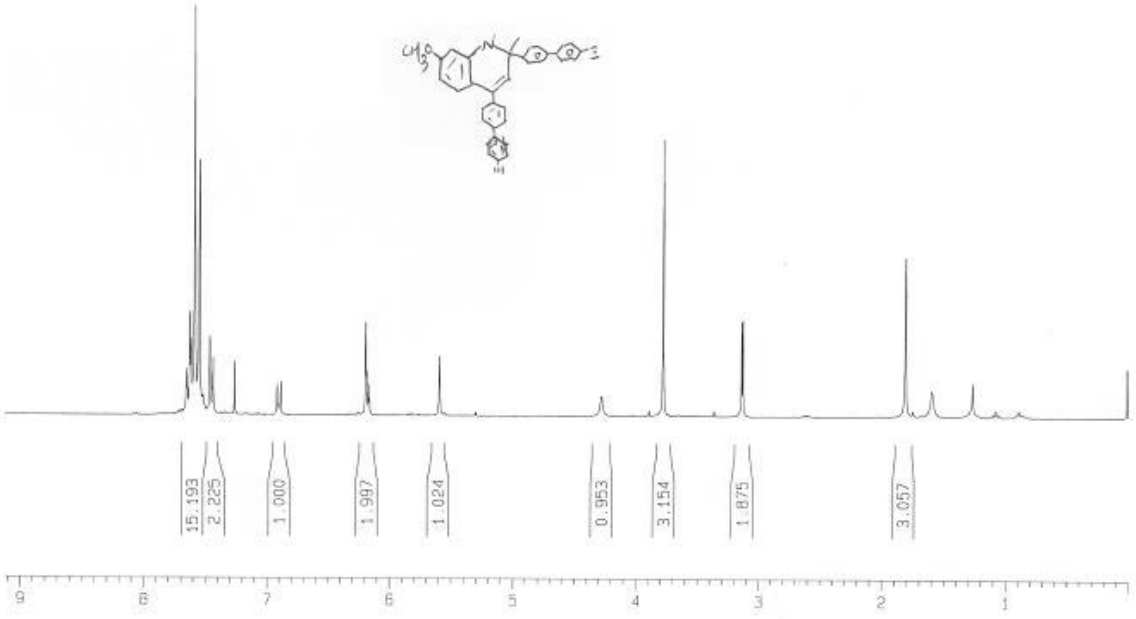


Figure S30. ^{13}C NMR spectrum of 2,4-bis(4'-ethynylbiphenyl-4-yl)-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Ag**)

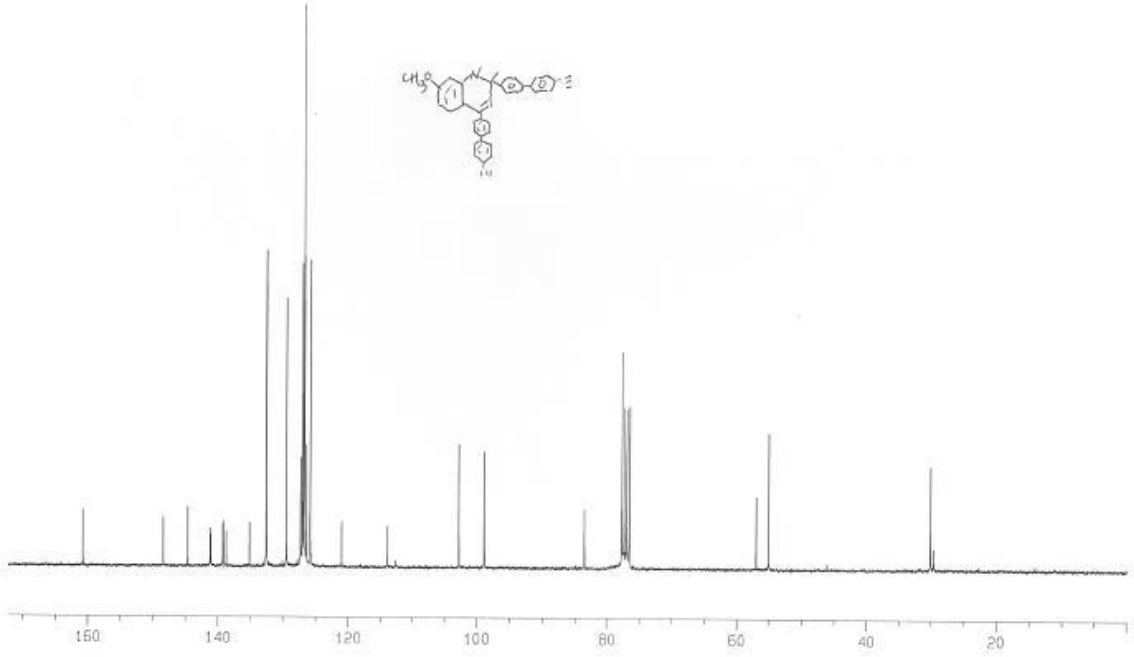


Figure S31. ^{1}H NMR spectrum of 2,4-bis(3-ethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Ah**)

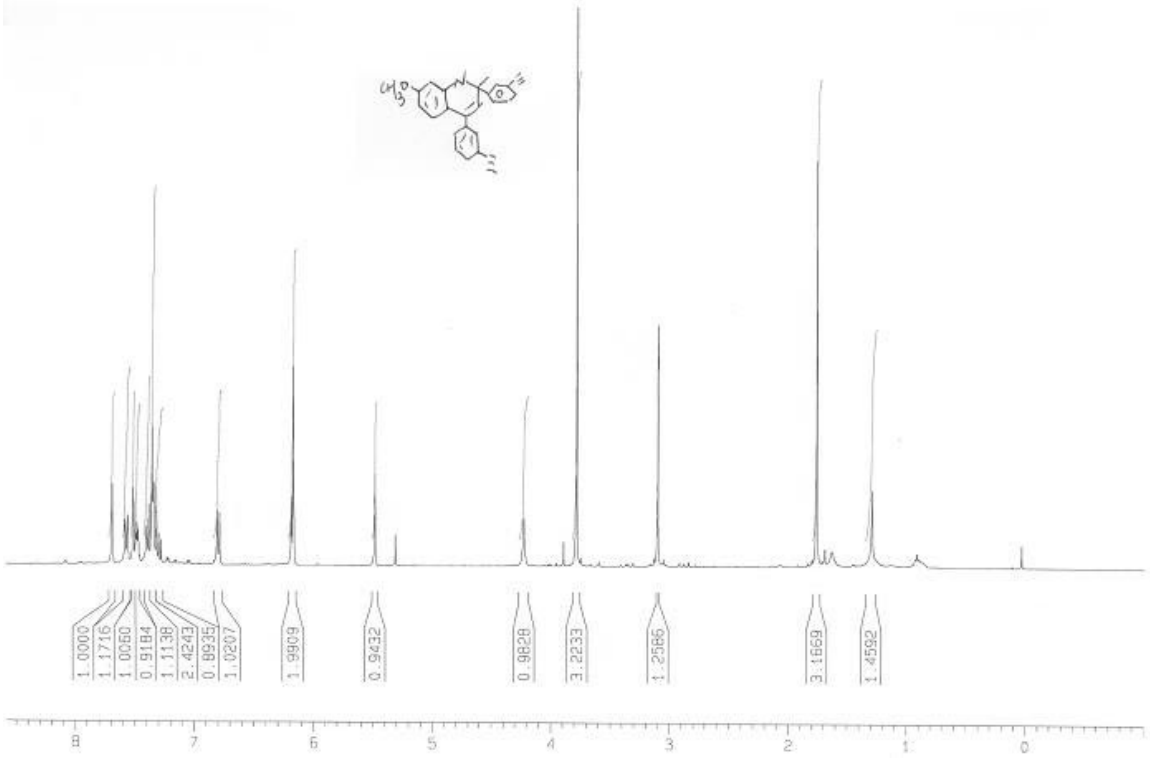


Figure S32. ^{13}C NMR spectrum of 2,4-bis(3-ethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Ah**)

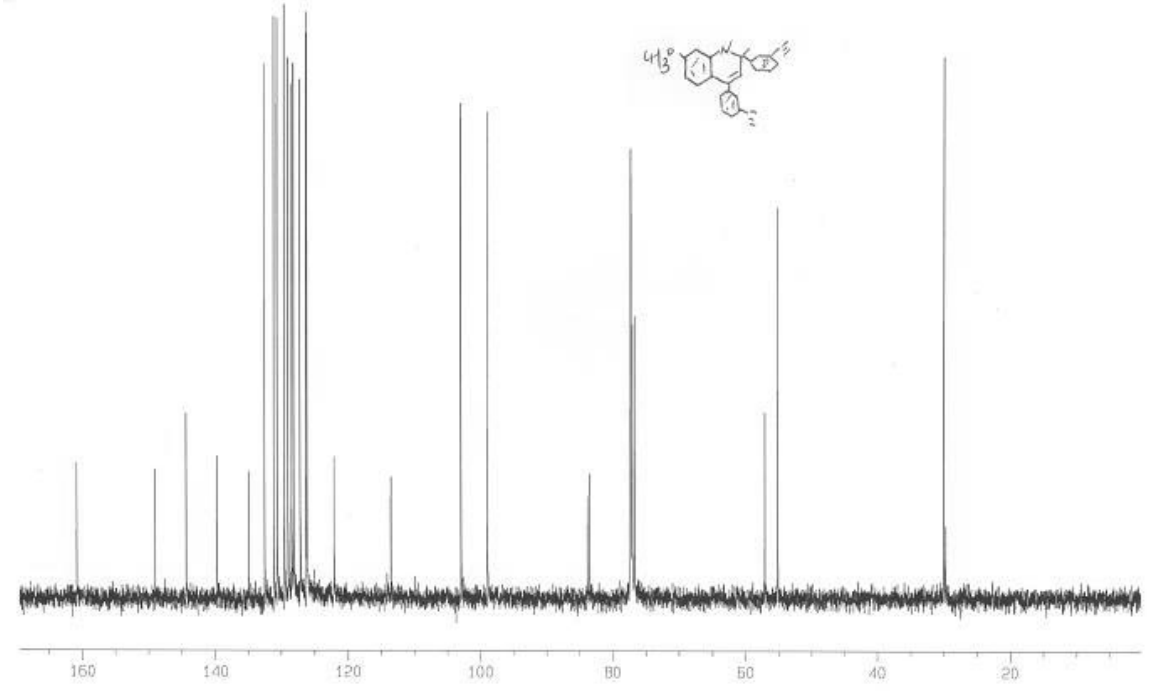


Figure S33. ^{1}H NMR spectrum of 2,4-bis(3,5-diethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline (**4Ai**)

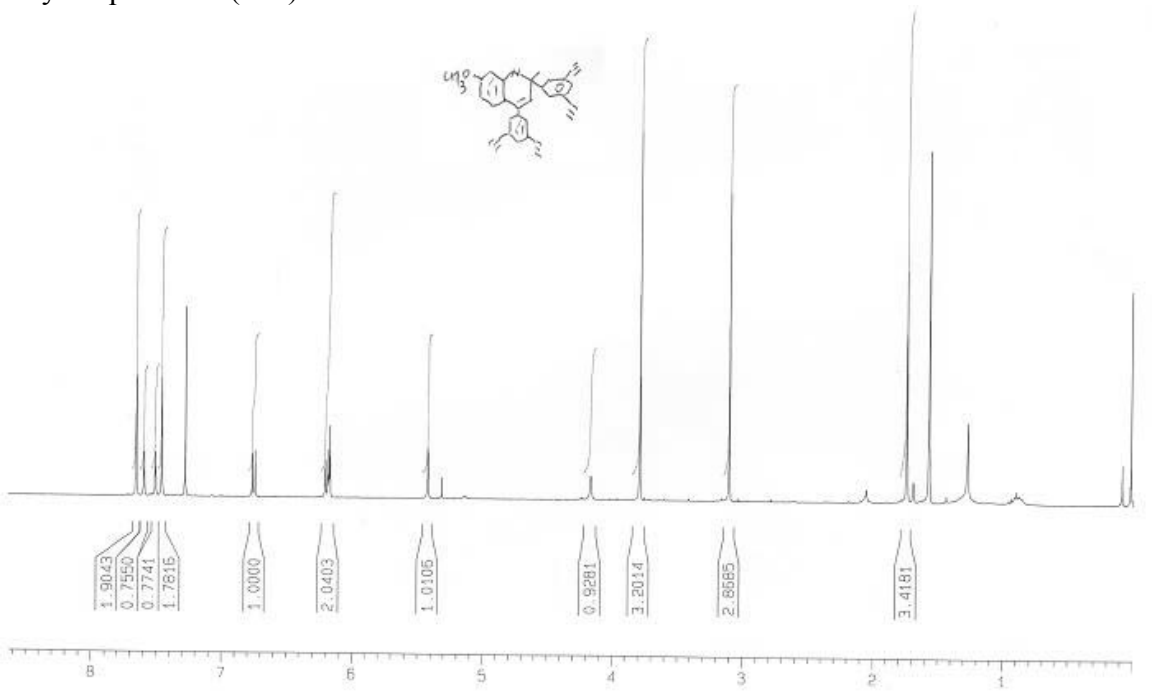


Figure S34. ^{13}C NMR spectrum of 2,4-bis(3,5-diethynylphenyl)-7-methoxy-2-methyl-1,2-dihydroquinoline(**4Ai**)

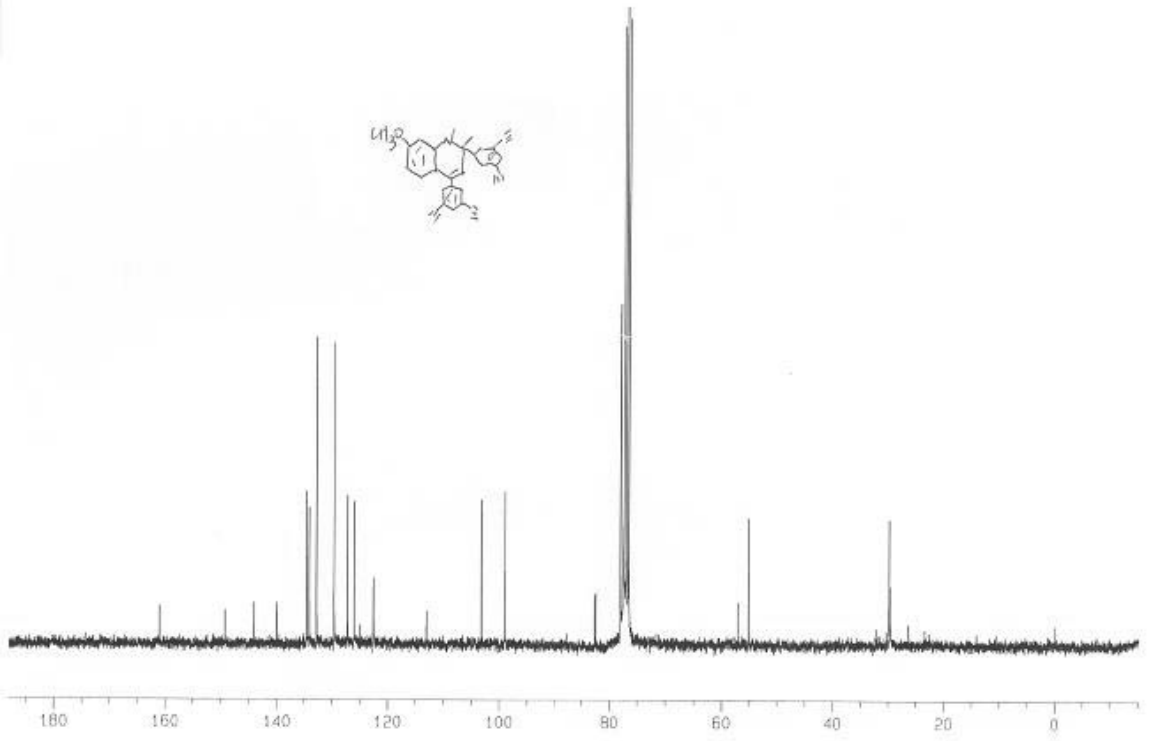


Figure S35. ^{1}H NMR spectrum of 2-(4-ethynylphenyl)-4-methylquinoline (**5Lf**)

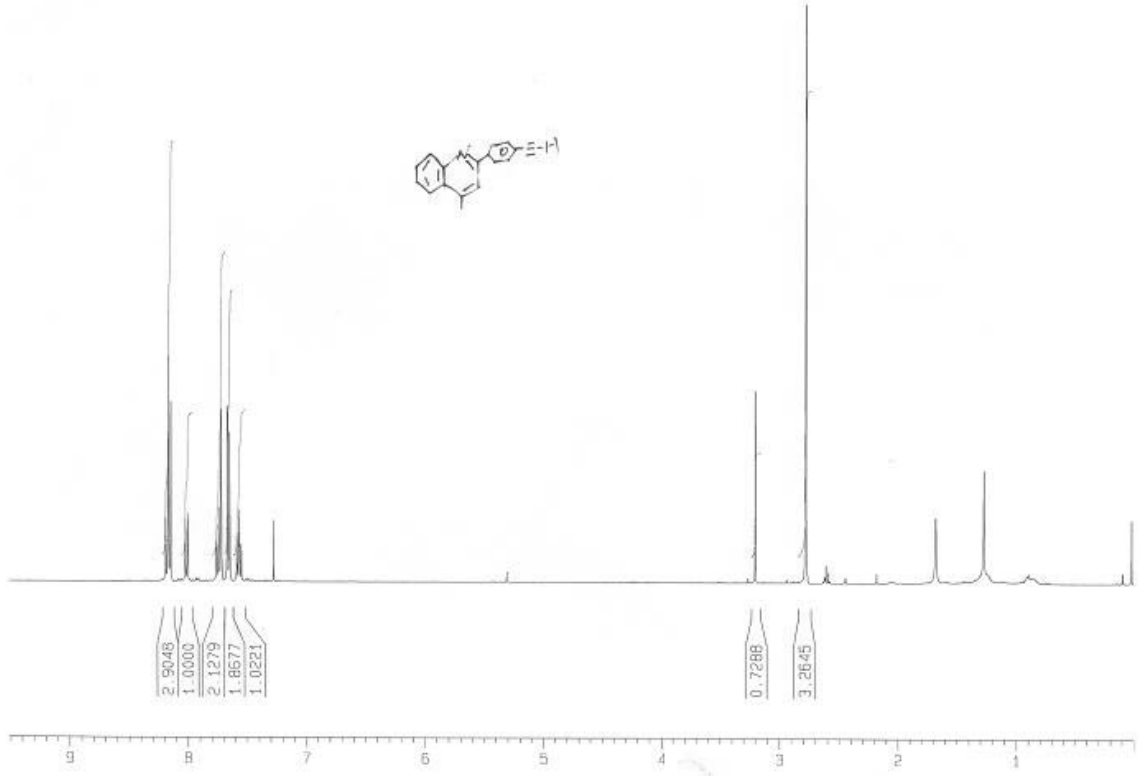


Figure S36. ^{13}C NMR spectrum of 2-(4-ethynylphenyl)-4-methylquinoline (**5Lf**)

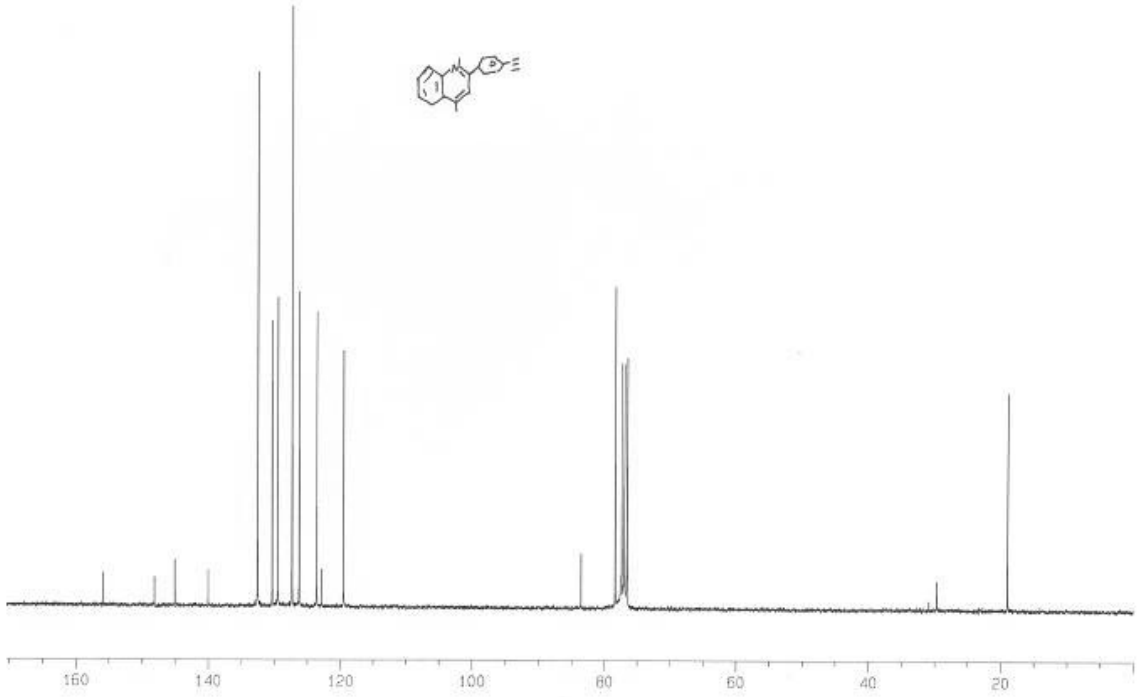


Figure S37. ^{1}H NMR spectrum of 2-(3-ethynylphenyl)-4-methylquinoline (**5Lh**)

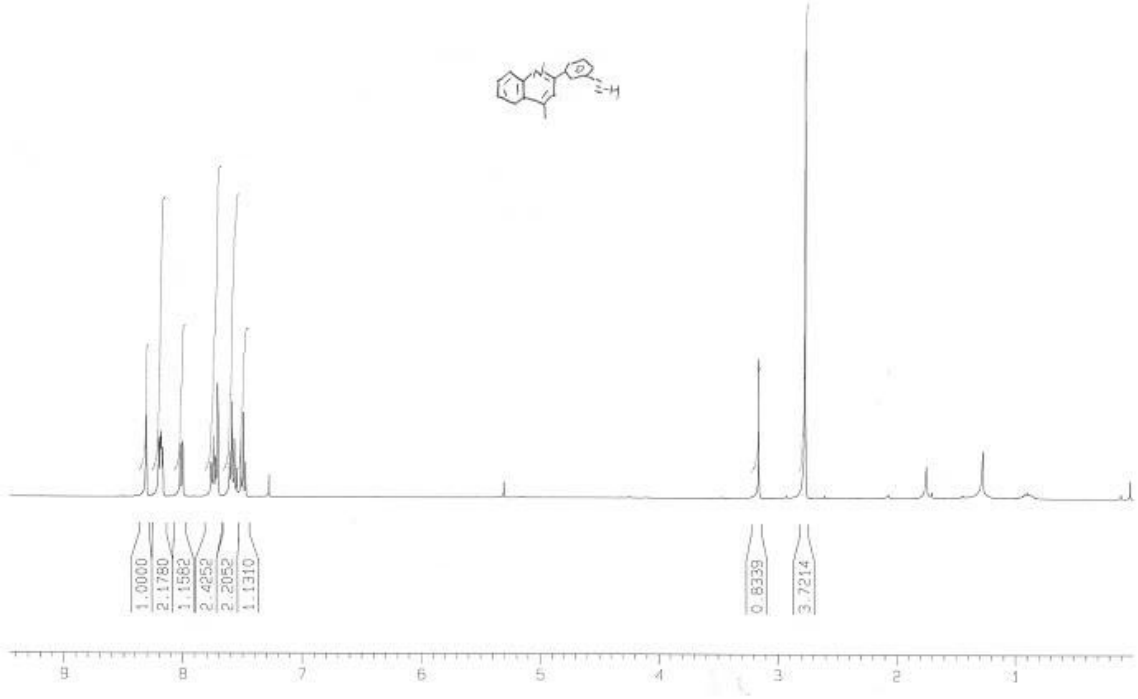


Figure S38. ^{13}C NMR spectrum of 2-(3-ethynylphenyl)-4-methylquinoline (**5Lh**)

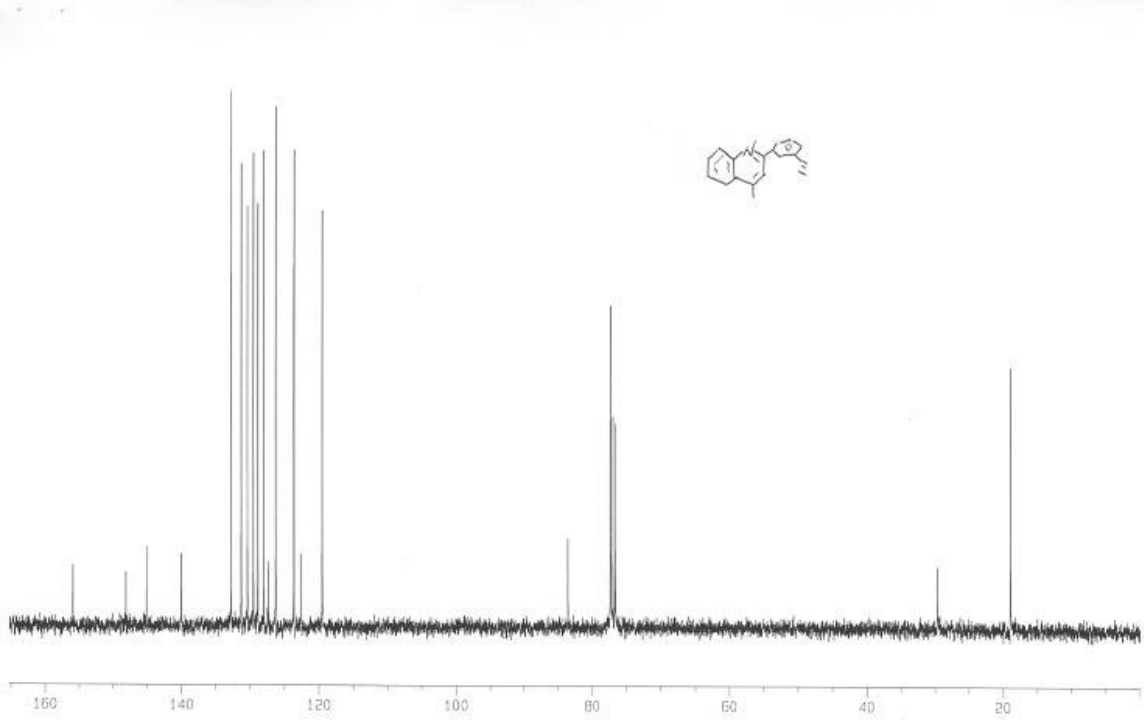


Figure S39. ^{1}H NMR spectrum of 2-(3,5-diethynylphenyl)-4-methylquinoline (**5Li**)

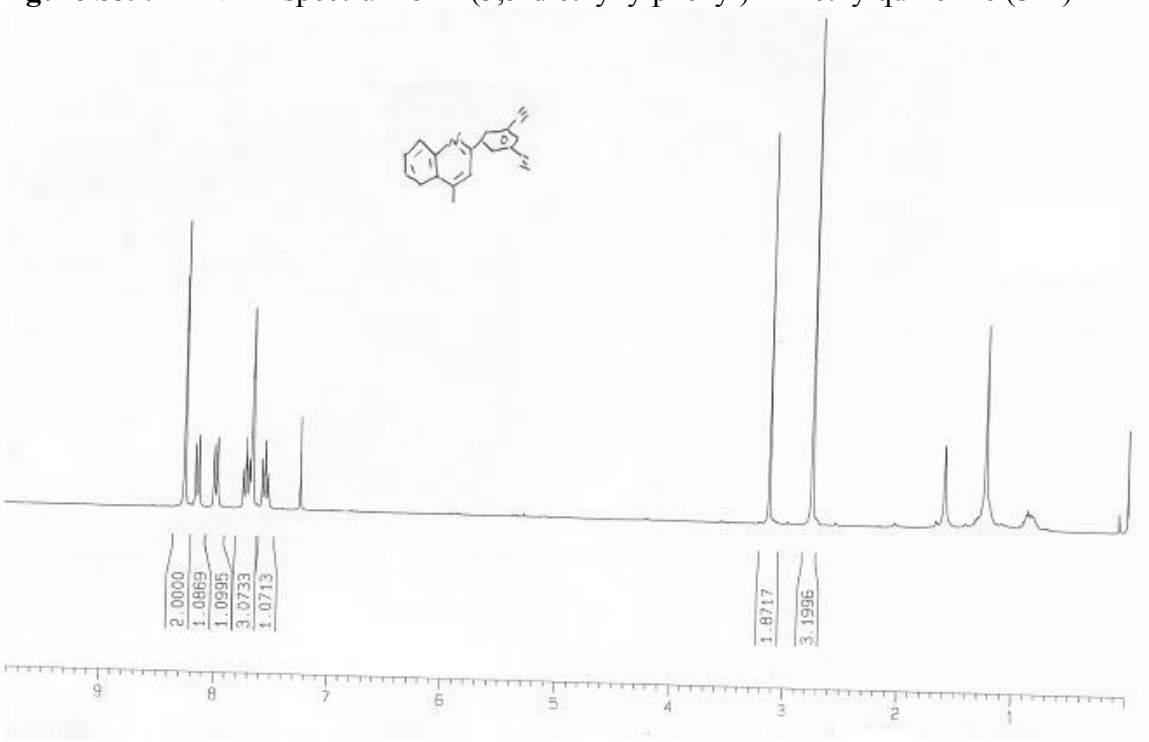


Figure S40. ^{13}C NMR spectrum of 2-(3,5-diethynylphenyl)-4-methylquinoline (**5Li**)

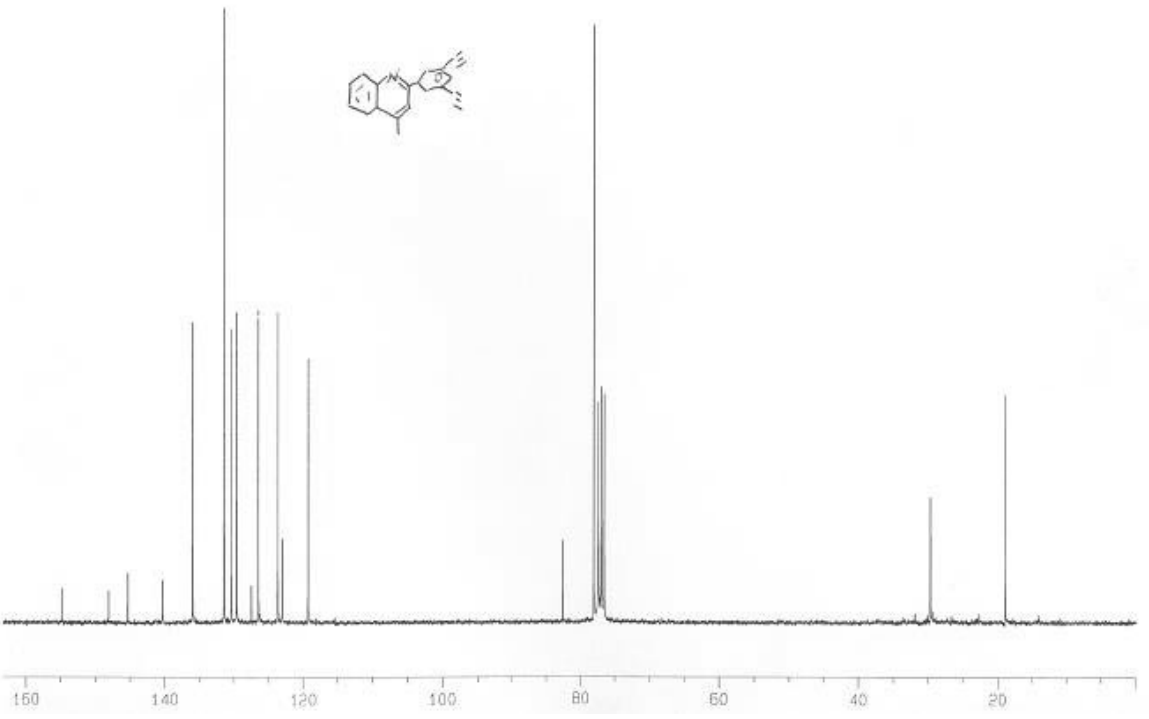


Figure S41. [1]H NMR spectrum of (*E*)-3-methoxy-*N*-(1-phenylethylidene)aniline (**6Aa**)

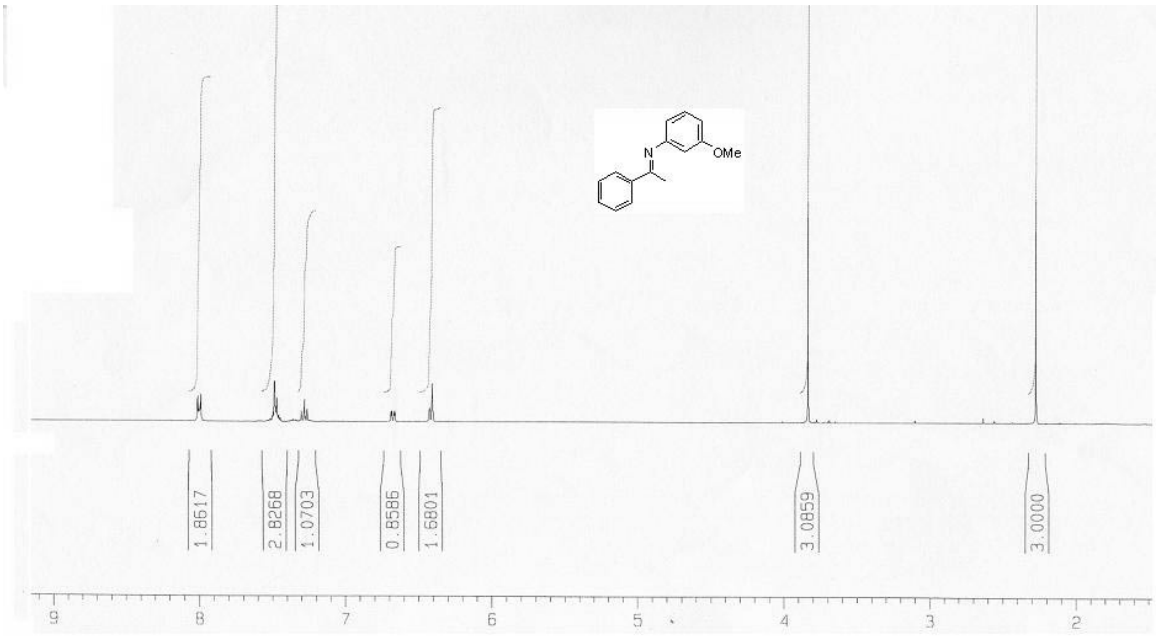


Figure S42. [13]C NMR spectrum of (*E*)-3-methoxy-*N*-(1-phenylethylidene)aniline (**6Aa**)

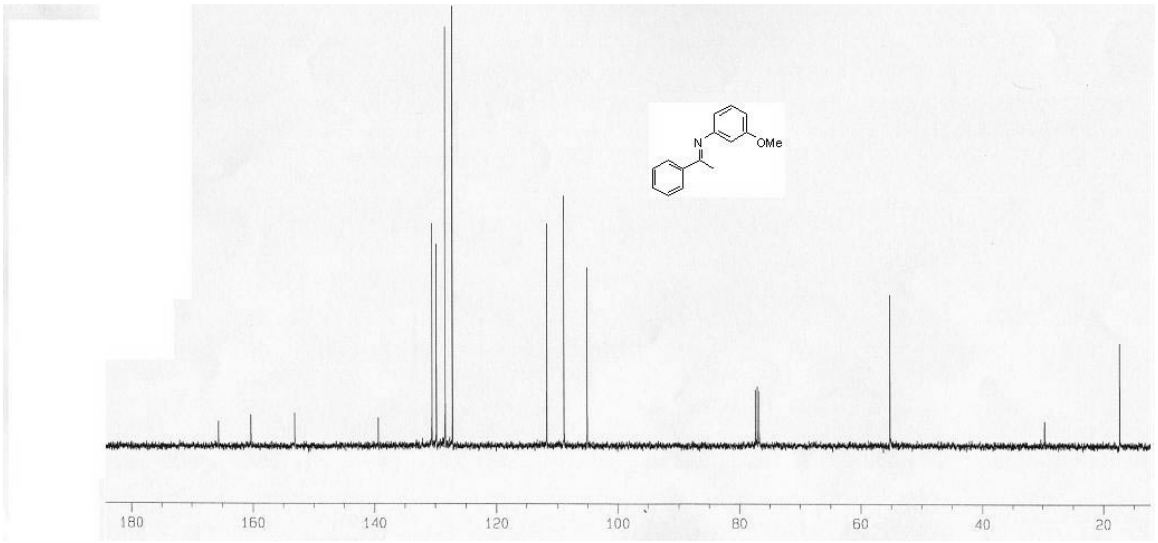


Figure S43. ^{1}H NMR spectrum of 1-(2,4-diphenylbut-3-yn-2-yl)indoline (**7Na**)

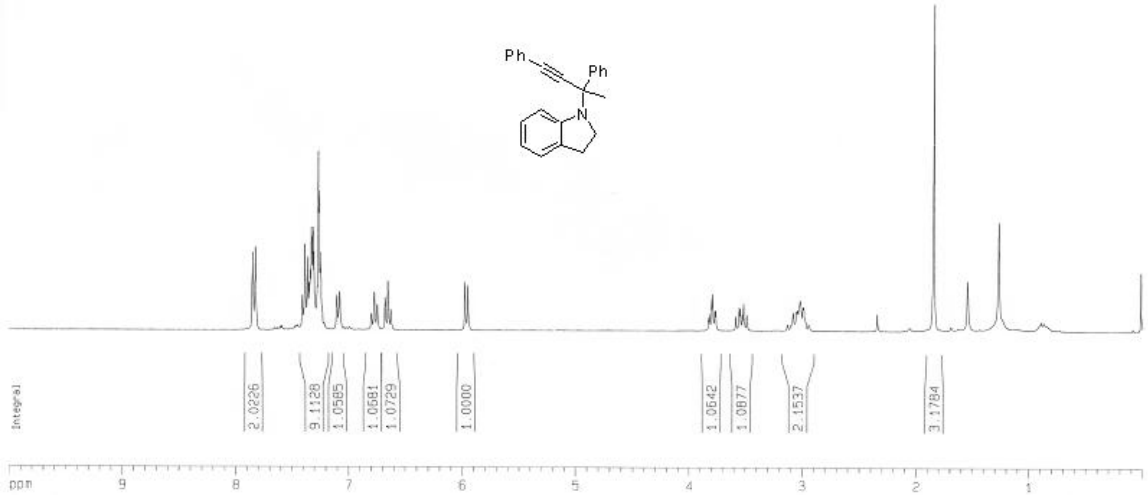


Figure S44. ^{13}C NMR spectrum of 1-(2,4-diphenylbut-3-yn-2-yl)indoline (**7Na**)

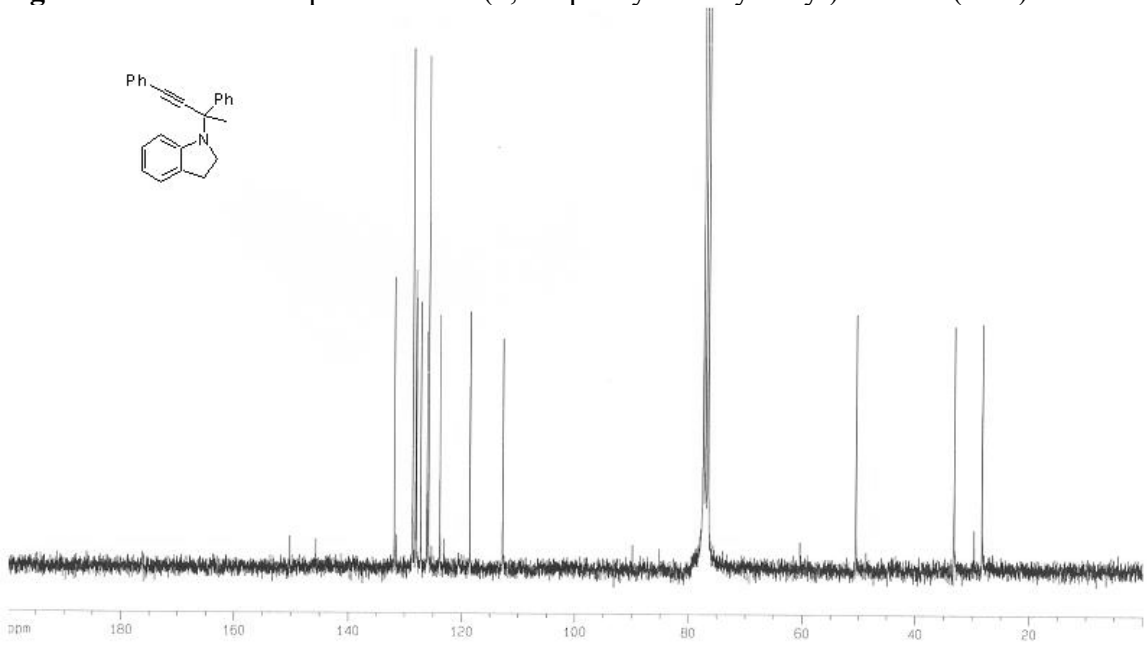


Figure S45. ^{1}H NMR spectrum of 4-methyl-4,6-bis(4-(trifluoromethyl)phenyl)-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nc**)

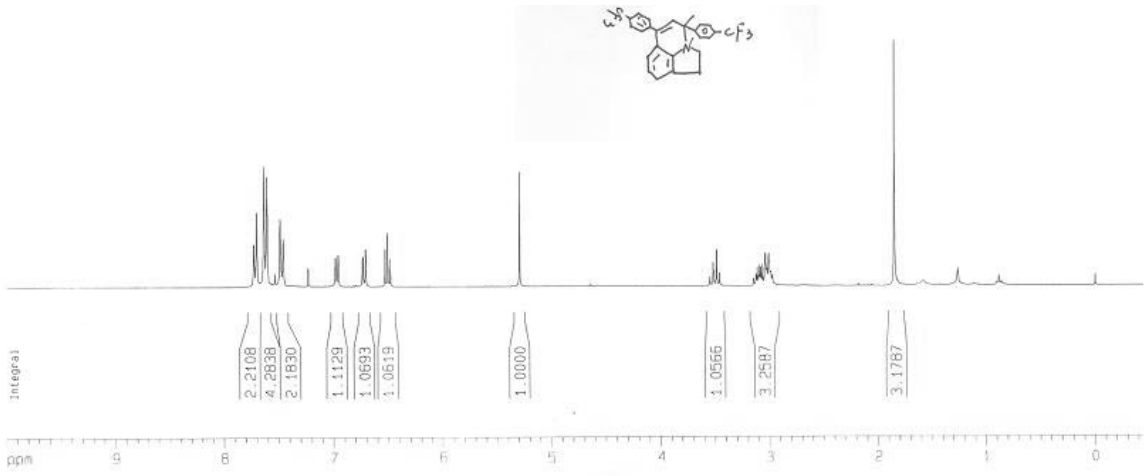


Figure S46. ^{13}C NMR spectrum of 4-methyl-4,6-bis(4-(trifluoromethyl)phenyl)-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nc**)

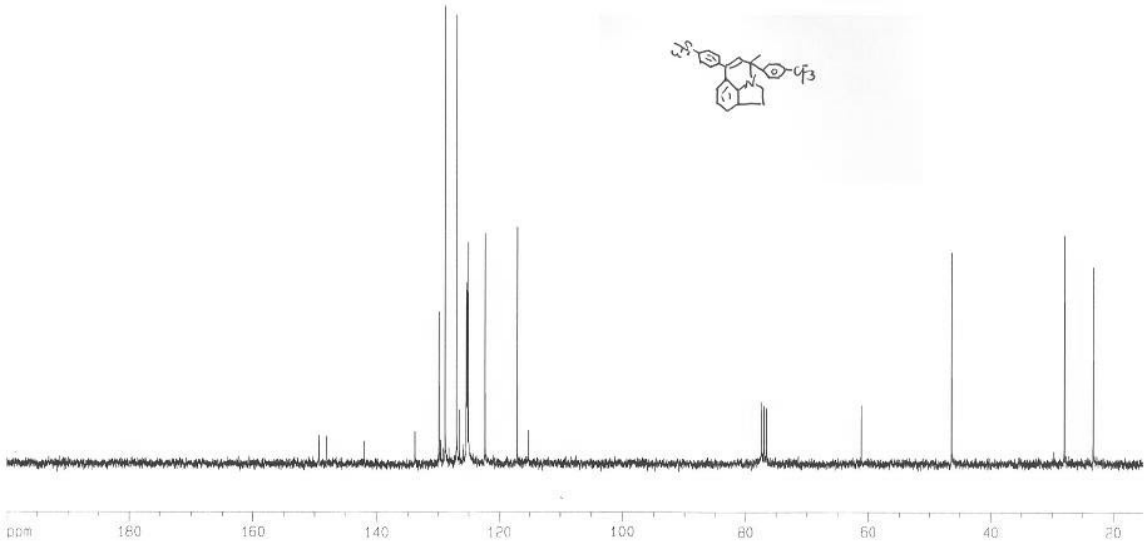


Figure S47. ^{1}H NMR spectrum of 4, 6-dibutyl-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nd**)

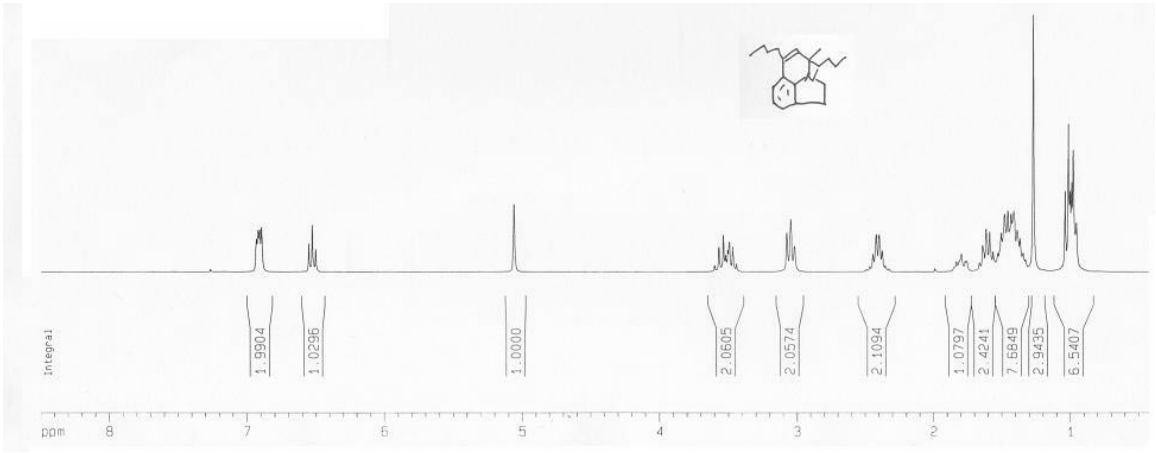


Figure S48. ^{13}C NMR spectrum of 4, 6-dibutyl-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nd**)

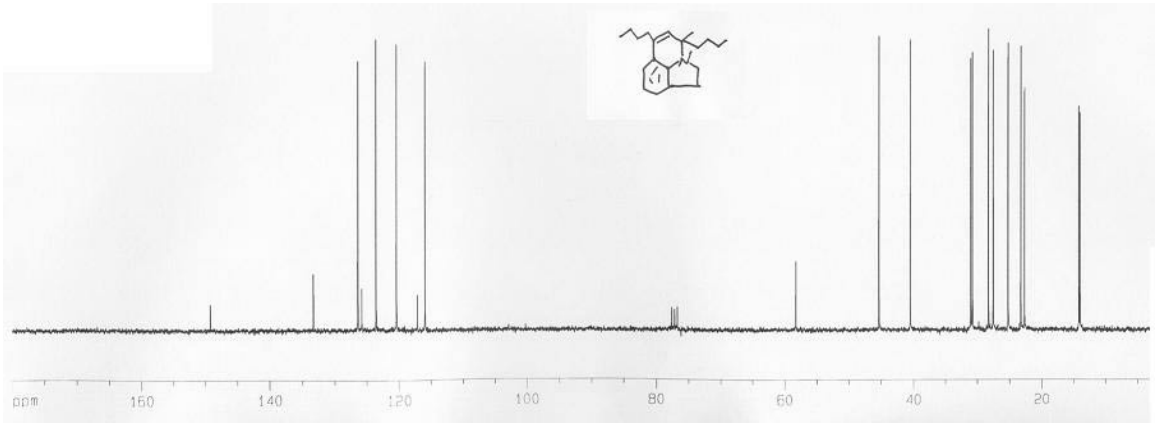


Figure S49. ^{1}H NMR spectrum of 4, 6-dihexyl-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Ne**)

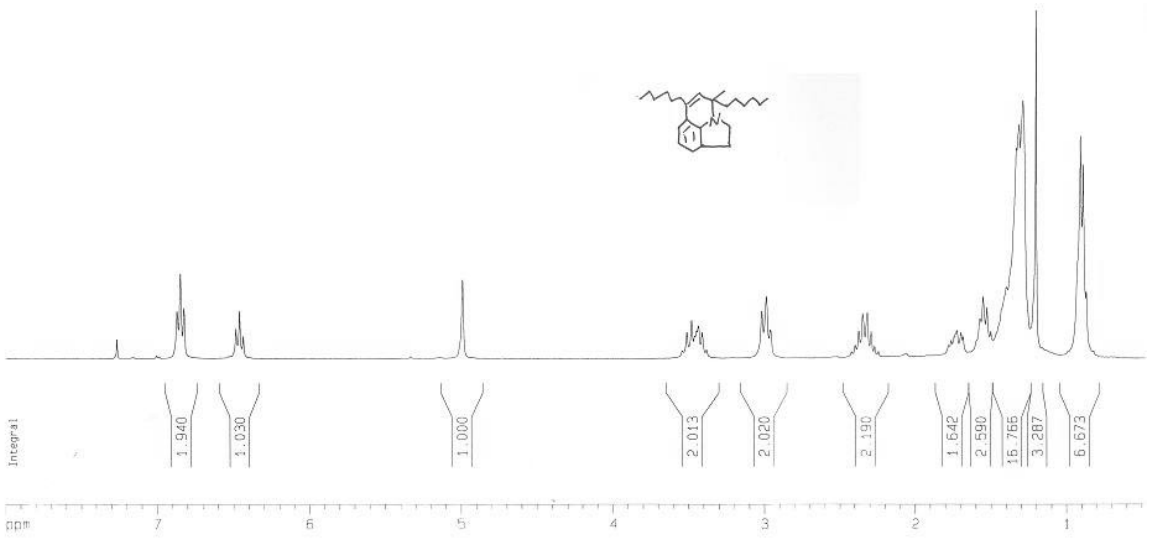


Figure S50. ^{13}C NMR spectrum of 4, 6-dihexyl-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Ne**)

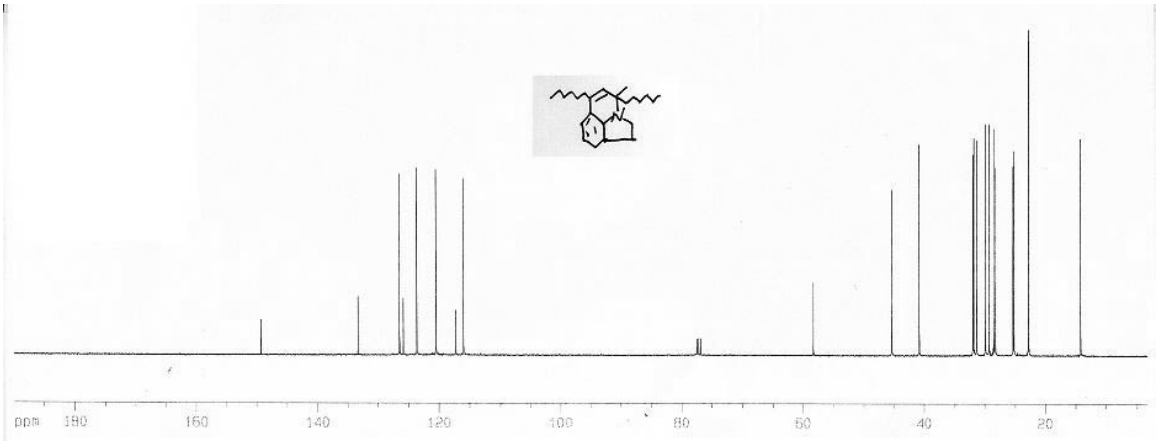


Figure S51. ^{1}H NMR spectrum of 4, 6-bis(4-methoxyphenyl)-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nj**)

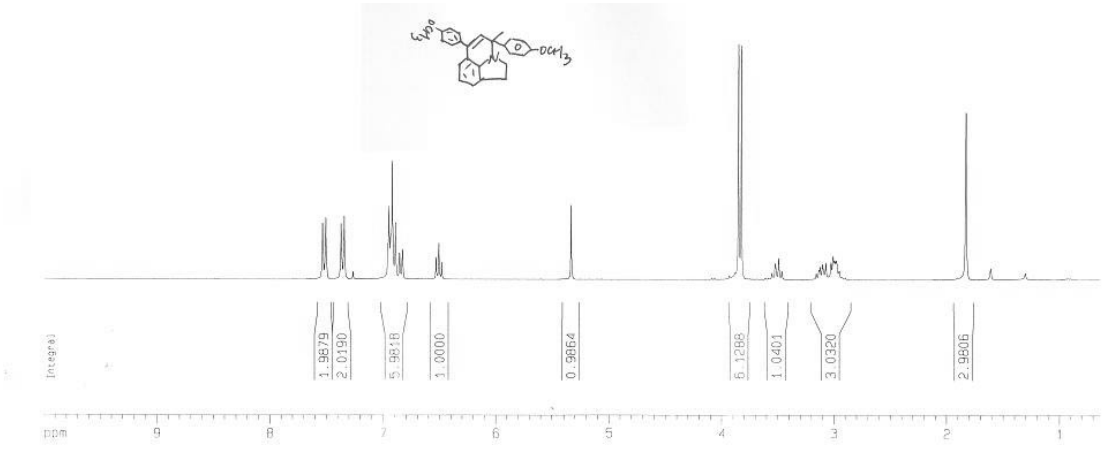


Figure S52. ^{13}C NMR spectrum of 4, 6-bis(4-methoxyphenyl)-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nj**)

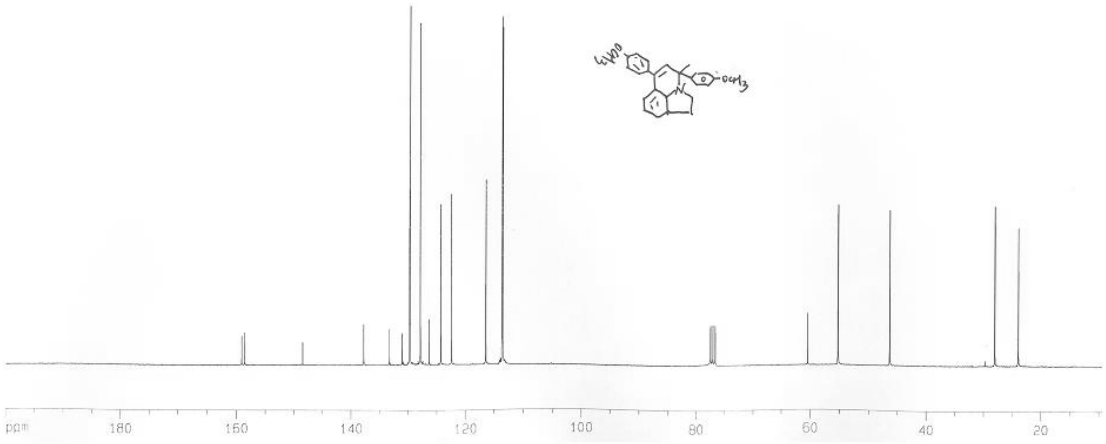


Figure S53. ^{1}H NMR spectrum of 4, 6-bis(4-fluorophenyl)-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nk**)

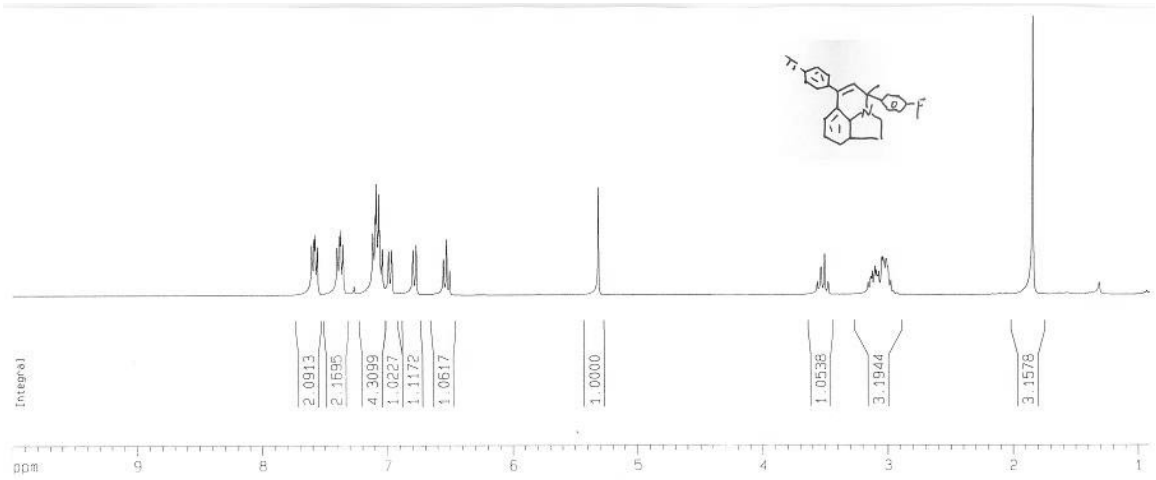


Figure S54. ^{13}C NMR spectrum of 4, 6-bis(4-fluorophenyl)-4-methyl-2,4-dihydro-*1H*-pyrrolo[3,2,1-*ij*]quinoline (**4Nk**)