Supporting Information

The Lewis acids catalyzed aza-Diels-Alder reactions of methylenecyclopropanes with imines

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General remarks. ^1H -NMR spectra were recorded on a 300 MHz spectrometer in CDCl_3 using tetramethylsilane as the internal standard. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel.

General procedure. Under argon atmosphere, imine (0.25 mmol), MCP (0.25 mmol), catalyst (0.025 mmol) and 1,2-dichloroethane (DCE) (2.0 mL) were added into a schlaker reaction tube. The mixture was stirred at room temperature (20 °C). The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2).

7-Trifluoromethyl-4, 4-bis-(4-methoxyphenyl)-2-phenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3a**.

A white solid, Mp: 168-170 °C, ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 0.25-0.29 (m, 4H), 3.76 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.30 (s, 1H, NH), 5.11 (s, 1H), 6.70 (d, 2H, $J = 9.0$ Hz, Ar), 6.88-6.98 (m, 6H, Ar), 7.08 (d, 1H, $J = 8.4$ Hz, Ar), 7.31-7.34 (m, 5H, Ar), 7.54 (d, 2H, $J = 8.4$ Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 7.22, 25.44, 29.66, 53.39, 55.08, 55.54, 58.02, 112.19, 112.58, 114.08, 124.62 (q, $J_{\text{C-F}} = 270$ Hz), 128.24 (q, $J_{\text{C-F}} = 29.7$ Hz), 129.28, 129.70, 130.12, 130.72, 131.61, 131.64 (q, $J_{\text{C-F}} = 4.8$ Hz), 133.06, 133.41, 135.20, 139.74, 139.96, 146.32, 158.17, 158.23. IR (CH_2Cl_2) ν 3378, 3002, 2929, 2837, 1713, 1606, 1507, 1251, 831, 752, 705 cm^{-1} . MS (%) m/e 515 (M^+ , 3.73), 406 (100). HRMS calcd. for

$C_{32}H_{28}F_3NO_2$: 515.2072, Found: 515.2050. Anal. calcd. for $C_{32}H_{28}F_3NO_2$: C, 74.55%; H, 5.47%; N, 2.72%. Found: C, 74.48%; H, 5.63%; N, 2.58%.

4, 4-Bis-(4-methoxyphenyl)-2-(4-chlorophenyl)-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3c**.

A white solid, Mp: 158-160 °C, 1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.16-0.39 (m, 4H), 3.75 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.04 (s, 1H, NH), 5.05 (s, 1H), 6.64-6.72 (m, 4H, Ar), 6.91-6.98 (m, 4H, Ar), 7.10 (t, 1H, $J = 8.7$ Hz, Ar), 7.25-7.31 (m, 5H, Ar), 7.56 (d, 2H, $J = 8.7$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 7.33, 22.59, 26.01, 29.58, 55.11, 55.41, 57.47, 111.66, 113.52, 115.45, 116.48, 127.41, 128.12, 129.56, 130.36, 132.74, 132.77, 133.26, 135.40, 138.76, 140.16, 142.16, 145.58, 157.61, 157.70. IR (CH_2Cl_2) ν 3054, 2987, 1422, 1265, 896, 739 cm^{-1} . MS (%) m/e 481 (M^+ , 11.54), 372 (100). HRMS (Maldi) calcd. for $C_{31}H_{28}ClNO_2$: 481.1809, Found: 482.1885.

4, 4-Bis-(4-methoxyphenyl)-2-(4-ethoxyphenyl)-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3d**.

A white solid, Mp: 80-82 °C, 1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.23-0.38 (m, 4H), 1.35 (t, 3H, $J = 6.9$ Hz), 3.76 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87-3.93 (m, 5H, OCH_3+CH_2), 5.06 (s, 1H), 6.61-6.79 (m, 5H, Ar), 6.96-7.00 (m, 4H, Ar), 7.29-7.37 (m, 5H, Ar), 7.68 (d, 2H, $J = 9.0$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 7.77, 14.94, 26.57, 30.92, 53.45, 55.19, 55.95, 58.22, 64.16, 111.72, 113.53, 114.85, 119.41, 127.63, 127.84, 128.24, 128.30, 130.38, 132.84, 135.59, 140.13, 157.66, 157.74. IR (CH_2Cl_2) ν 3054, 2987, 1607, 1422, 1265, 740, 705 cm^{-1} . MS (%) m/e 491 (M^+ , 21.90), 382 (53.19). HRMS calcd. for $C_{33}H_{33}NO_3$ ($M-OCH_3$): 460.2277, Found: 460.2296.

4, 4-Bis-(4-methoxyphenyl)-2-(4-methoxy-phenyl)-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3e**.

A white solid, Mp: 94-96 °C. 1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.21-0.35 (m, 4H), 3.76 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.08 (s, 1H, NH), 5.05 (s, 1H), 6.64-6.71 (m, 4H, Ar), 6.85-6.88 (m, 2H, Ar), 6.92-6.99 (m, 5H, Ar), 7.09 (t, 1H, $J = 8.7$ Hz,

Ar), 7.20-7.28 (m, 2H, Ar), 7.59 (d, 2H, J = 8.4 Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 7.30, 26.08, 54.99, 55.09, 55.48, 57.35, 111.60, 113.14, 113.47, 114.20, 115.31, 116.12, 127.34, 128.04, 129.25, 130.44, 132.11, 132.76, 135.78, 140.40, 145.96, 157.54, 157.63, 158.92. IR (CH_2Cl_2) ν 3054, 1606, 1265, 896, 742 cm^{-1} . MS (%) m/e 477 (M^+ , 9.26), 368 (100). HRMS calcd. for $\text{C}_{32}\text{H}_{31}\text{NO}_3$: 477.2304, Found: 477.2289.

4, 4-Bis-(4-methoxyphenyl)-2-(4-nitrophenyl)-1, 2, 3,4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3f**.

A yellow solid, Mp: 170-172 $^\circ\text{C}$, ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 0.01-0.50 (m, 4H), 3.74 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.09 (s, 1H, NH), 5.16 (s, 1H), 6.66-6.76 (m, 4H, Ar), 6.94-6.99 (m, 5H, Ar), 7.13 (t, 1H, J = 6.9 Hz, Ar), 7.53 (t, 4H, J = 9.0 Hz, Ar), 8.17 (d, 2H, J = 9.0 Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 1.45, 7.51, 26.27, 55.04, 55.16, 55.36, 57.93, 111.79, 113.62, 115.73, 116.97, 122.99, 127.55, 128.22, 129.14, 130.35, 132.71, 132.83, 134.95, 139.85, 145.17, 147.31, 148.07, 157.75, 157.84. IR (CH_2Cl_2) ν 3055, 2988, 1712, 1422, 1363, 1266, 1223, 896, 739, 705 cm^{-1} . MS (%) m/e 492 (M^+ , 16.56), 462 (35.88), 383 (100), 367 (31.81), 338 (27.32). Anal. calcd. for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_4$: C, 75.59%; H, 5.73%; N, 5.69 %. Found: C, 75.47 %; H, 5.74 %; N, 5.43%.

4, 4-Bis-(4-methoxyphenyl)-2-phenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3g**.

A white solid, Mp: 160-162 $^\circ\text{C}$, ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 0.19-0.39 (m, 4H), 3.76 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.09-4.13 (m, 1H, NH), 5.09 (s, 1H), 6.63-6.71 (q, 4H, J = 6.9 Hz, Ar), 6.91-6.99 (m, 5H, Ar), 7.10 (t, 1H, J = 6.9 Hz, Ar), 7.23-7.35 (m, 5H, Ar), 7.60 (d, 2H, J = 8.7 Hz, Ar). ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 7.39, 26.03, 29.66, 53.41, 55.17, 55.55, 58.00, 111.66, 113.54, 115.38, 116.26, 127.41, 127.66, 127.85, 128.11, 128.37, 130.48, 132.84, 135.73, 140.26, 140.39, 145.91, 157.60, 157.69. IR (CH_2Cl_2) ν 3690, 3054, 2987, 1605, 1421, 1265, 895, 739, 705 cm^{-1} . MS (%) m/e 447 (M^+ , 2.68), 338 (21.35), 43 (100). HRMS calcd. for $\text{C}_{31}\text{H}_{29}\text{NO}_2$: 447.2198, Found: 447.2197.

7-Trifluoromethyl-2, 4, 4-triphenyl-1, 2, 3, 4-tetrahydrospiro-(3,1'-cyclopropyl)-quinoline

3h.

A white solid, Mp: 240 °C (dec.), ¹H NMR (CDCl₃, 300 MHz, TMS) δ 0.10-0.37 (m, 4H), 4.32 (s, 1H, NH), 5.13 (s, 1H), 6.91 (d, 2H, J = 7.8 Hz, Ar), 7.02-7.19 (m, 6H, Ar), 7.28-7.34 (m, 6H, Ar), 7.48 (t, 2H, J = 8.1 Hz, Ar), 7.68 (d, 2H, J = 7.2 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 7.41, 14.11, 25.30, 56.83, 57.99, 111.94, 111.97, 112.32, 126.54, 126.57, 126.64 (q, J_{C-F} = 251 Hz), 126.65, 127.96, 128.01, 128.27 (q, J_{C-F} = 30.3 Hz), 128.59, 129.46, 129.52, 131.73 (q, J_{C-F} = 6.9 Hz), 133.38, 139.51, 142.73, 146.08, 147.06. IR (CH₂Cl₂) ν 3054, 2987, 1422, 1266, 896, 739, 705 cm⁻¹. MS (%) m/e 455 (M⁺, 33.48), 376 (100). Anal. calcd. for C₃₀H₂₄F₃N · 1/2 CH₂Cl₂: C, 73.56%; H, 5.06%; N, 2.81%. Found: C, 73.30%; H, 5.15%; N, 2.47%.

4, 4-Bisphenyl-2- (4-chlorophenyl)-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline 3i.

A white solid, Mp: 244-246 °C, ¹H NMR (CDCl₃, 300 MHz, TMS) δ 0.10-0.33 (m, 4H), 4.06 (s, 1H, NH), 5.08 (s, 1H), 6.66-6.75 (m, 2H, Ar), 6.98-7.32 (m, 11H, Ar), 7.43 (t, 3H, J = 7.8 Hz, Ar), 7.71 (d, 2H, J = 7.8 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 1.21, 7.56, 25.92, 56.78, 57.51, 115.63, 116.61, 126.30, 126.35, 126.51, 127.60, 127.70, 128.09, 128.46, 129.54, 129.64, 131.82, 133.13, 133.41, 138.68, 143.31, 145.75, 147.87. IR (CH₂Cl₂) ν 3054, 1600, 1476, 1265, 753 cm⁻¹. MS (%) m/e 421 (M⁺, 46.62), 342 (100). HRMS calcd. for C₂₉H₂₄NCl: 421.1597, Found: 421.1565. Anal. calcd. for C₂₉H₂₄NCl: C, 82.55%; H, 5.73%; N, 3.32%. Found: C: 84.47%; H: 5.60%; N: 3.39%.

2, 4, 4-Triphenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline 3j.

A white solid, Mp: 230-231 °C, ¹H NMR (CDCl₃, 300 MHz, TMS) δ 0.08-0.40 (m, 4H), 4.10 (s, 1H, NH), 5.09 (s, 1H), 6.61-6.74 (m, 2H, Ar), 6.70-7.17 (m, 7H, Ar), 7.30-7.37 (m, 6H, Ar), 7.44 (t, 2H, J = 7.2 Hz, Ar), 7.76 (d, 2H, J = 7.8 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 7.59, 25.90, 29.68, 56.87, 57.98, 115.49, 116.32, 126.19, 126.24, 126.45, 127.53, 127.63, 127.72, 127.88, 128.35, 128.38, 129.58, 131.85, 133.13, 140.11, 143.56, 146.00, 148.00. IR (CH₂Cl₂) ν 3361, 3015, 1596, 1574, 1489, 1476, 1306, 1286, 780, 735 cm⁻¹. MS (%) m/e 387 (M⁺, 50.72), 308 (100), 282 (39.92). Anal. calcd. for C₂₉H₂₅N: C, 89.88%; H, 5.73%; N, 3.32%. Found: C: 89.88%; H: 5.73%; N: 3.32%.

6.46%; N, 3.62%. Found: C, 89.50%; H, 6.61%; N, 3.65%.

7-Trifluoromethyl-4, 4-bis-(4-methylphenyl)-2-phenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3k**.

A white solid, Mp: 228-230 °C. ¹H NMR (CDCl₃, 300 MHz, TMS) δ 0.24-0.28 (m, 4H), 2.25 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 4.22 (s, 1H, NH), 5.10 (s, 1H), 6.87-6.96 (m, 6H, Ar), 7.12 (d, 1H, J = 8.4 Hz, Ar), 7.24-7.34 (m, 7H, Ar), 7.55 (d, 2H, J = 8.1 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 1.25, 7.32, 20.77, 20.87, 25.20, 56.17, 57.97, 111.82, 111.88, 112.21, 112.26, 127.33, 127.87, 127.93, 128.29, 129.28, 131.61, 133.27, 135.94, 136.05, 139.64, 139.83, 144.27, 146.02. IR (CH₂Cl₂) ν 3026, 1615, 1582, 1484, 1265, 739 cm⁻¹. MS (%) m/e 483 (M⁺, 16.01), 390 (100). HRMS calcd. for C₃₂H₂₈F₃N: 483.2174, Found: 483.2132.

4, 4-Bis-(4-methylphenyl)-2-(4-ethoxyphenyl)-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3l**.

A white solid, Mp: 216-218 °C. ¹H NMR (CDCl₃, 300 MHz, TMS) δ 0.10-0.29 (m, 4H), 1.32 (t, 3H, J = 6.3 Hz), 2.25 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 3.97-4.07 (m, 3H, CH₂+NH), 5.06 (s, 1H), 6.60-6.61 (m, 2H, Ar), 6.85-6.89 (m, 1H, Ar), 7.08 (s, 4H, Ar), 7.35-7.50 (m, 7H, Ar), 7.79 (d, 2H, J = 8.1 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 1.16, 7.77, 14.93, 20.82, 26.27, 29.68, 56.55, 58.05, 64.25, 114.95, 116.43, 119.67, 127.18, 127.57, 127.80, 128.33, 128.57, 129.03, 129.15, 129.30, 131.73, 135.58, 135.70, 140.38, 140.52, 145.06, 150.14. IR (CH₂Cl₂) ν 3054, 1610, 1426, 1265, 739 cm⁻¹. MS (%) m/e 459 (M⁺, 75.97), 366 (100). HRMS calcd. for C₃₃H₃₃NO: 459.2562, Found: 459.2539.

7-Trifluoromethyl-4-(4-ethoxyphenyl)-4-methyl-2-phenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3m**.

A white solid, Mp: 80-143 °C, (*syn*-isomer) ¹H NMR (CDCl₃, 300 MHz, TMS) δ 0.00-0.24 (m, 4H), 1.43 (t, 3H, J = 7.5 Hz, CH₃), 1.49 (s, 3H, CH₃), 4.00 (q, 2H, J = 7.5 Hz), 4.31 (s, 1H), 5.05 (s, 1H), 6.73-6.89 (m, 4H, Ar), 7.05-7.08 (m, 2H, Ar), 7.26-7.37 (m, 6H, Ar). (*anti*-isomer) ¹H NMR (CDCl₃, 300 MHz, TMS) δ -0.124-0.00 (m, 4H), 1.42 (t, 3H, J = 7.5 Hz, CH₃), 1.93 (s, 3H, CH₃), 3.99-4.01 (m, 3H, CH₂+NH), 5.33 (s, 1H), 6.73-6.89 (m, 4H,

Ar), 7.05-7.08 (m, 2H, Ar), 7.26-7.37 (m, 6H, Ar). (*syn*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 5.84, 7.53, 11.78, 26.40, 30.53, 43.76, 57.63, 60.01, 110.32, 111.65, 113.72, 114.04, 114.13, 122.46 (q, $J_{\text{C-F}} = 243$ Hz), 126.59, 127.69, 127.83, 127.94, 128.12 (q, $J_{\text{C-F}} = 27.6$ Hz), 128.55, 128.98, 129.24 (q, $J_{\text{C-F}} = 7.5$ Hz), 131.23, 136.64, 140.08, 144.80, 157.11. (*anti*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 3.58, 6.25, 14.83, 27.96, 29.69, 45.99, 58.29, 63.22, 111.60, 112.69, 113.84, 114.08, 114.25, 126.07 (q, $J_{\text{C-F}} = 245$ Hz), 127.36, 127.74, 127.90, 128.02, 128.16 (q, $J_{\text{C-F}} = 28.2$ Hz), 128.76, 129.05, 131.11 (q, $J_{\text{C-F}} = 8.4$ Hz), 135.96, 139.23, 142.15, 145.88, 157.22. IR (CH_2Cl_2) ν 3054, 2987, 1422, 1265, 896, 740, 705 cm^{-1} . MS (%) m/e 437 (M^+ , 95.77), 422 (27.51), 394 (54.38), 314 (100). HRMS calcd. for $\text{C}_{27}\text{H}_{26}\text{F}_3\text{NO}$: 437.1966, Found: 437.2002.

8-Methoxy-4-(4-ethoxyphenyl)-4-methyl-2-phenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3n**.

A white solid, Mp: 74-120 °C, (*syn*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 0.25-0.33 (m, 2H), 0.52-0.60 (m, 2H), 1.40 (t, 3H, $J = 6.9$ Hz, CH_3), 1.41 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 4.02-4.06 (m, 3H, CH_2+NH), 5.03 (s, 1H), 6.60-6.87 (m, 5H, Ar), 7.11-7.12 (m, 2H, Ar), 7.14-7.51 (m, 5H, Ar). (*anti*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS) δ -0.10-0.143 (m, 4H), 1.40 (t, 3H, $J = 6.6$ Hz, CH_3), 2.00 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 4.02-4.06 (m, 3H, CH_2+NH), 4.65 (s, 1H), 6.60-6.87 (m, 5H, Ar), 7.11-7.12 (m, 2H, Ar), 7.14-7.51 (m, 5H, Ar). (*syn*-isomer) ^{13}C NMR (CDCl_3 , 75MHz, TMS) δ 1.86, 6.18, 6.28, 23.63, 28.63, 43.68, 55.32, 56.94, 63.12, 106.59, 112.45, 114.03, 116.76, 122.69, 127.53, 127.73, 128.42, 128.62, 131.15, 134.64, 137.66, 140.65, 145.88, 156.79. (*anti*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 0.99, 3.72, 14.87, 27.16, 30.48, 46.00, 55.37, 58.18, 63.18, 107.65, 113.70, 115.42, 119.90, 127.45, 127.67, 127.93, 128.51, 128.89, 132.76, 135.92, 139.87, 143.40, 146.42, 156.94. IR (CH_2Cl_2) ν 3044, 2978, 1416, 1265, 739, 705 cm^{-1} . MS (%) m/e 399 (M^+ , 29.93), 276 (72.08), 136 (100). HRMS calcd. for $\text{C}_{27}\text{H}_{29}\text{NO}_2$: 399.2198, Found: 399.2167.

6-Ethoxy-4-(4-ethoxyphenyl)-4-methyl-2-phenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3o**.

A white solid, Mp: 60-120 °C. (*syn*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 0.08-0.28

(m, 2H), 0.94-1.00 (m, 1H), 1.24-1.29 (m, 1H), 1.35-1.42 (m, 9H, 3CH₃), 3.96-4.03 (m, 5H, 2CH₂+NH), 4.57 (s, 1H), 6.56-6.82 (m, 4H, Ar), 7.05-7.39 (m, 8H, Ar). (*anti*-isomer) ¹H NMR (CDCl₃, 300 MHz, TMS) δ -0.01-0.00 (m, 3H), 0.46-0.53 (m, 1H), 1.35-1.42 (m, 6H, 2CH₃), 1.94 (s, 3H, CH₃), 3.96-4.03 (m, 5H, 2CH₂+NH), 4.96 (s, 1H), 6.56-6.82 (m, 4H, Ar), 7.05-7.39 (m, 8H, Ar). (*syn*-isomer) ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 3.90, 6.34, 14.84, 15.04, 27.39, 28.92, 43.91, 57.49, 63.13, 112.52, 113.70, 114.78, 114.93, 116.85, 127.53, 127.73, 128.44, 128.74, 131.14, 140.78, 156.81. (*anti*-isomer) ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 1.82, 6.14, 14.87, 23.62, 27.42, 29.65, 45.65, 58.73, 63.18, 64.04, 113.65, 114.87, 116.10, 127.41, 127.64, 128.36, 128.51, 129.79, 137.51, 150.94, 156.94. IR (CH₂Cl₂) ν 2979, 1506, 1248, 1049, 738 cm⁻¹. MS (%) m/e 413 (M⁺, 46.13), 290 (100). HRMS calcd. for C₂₈H₃₁NO₂: 413.2355, Found: 413.2318.

4-(4-Ethoxyphenyl)-4-methyl-2-(4-methoxyphenyl)-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3p**.

A white solid, Mp: 68-140 °C, (*syn*-isomer) ¹H NMR (CDCl₃, 300 MHz, TMS) δ 0.03-0.06 (m, 2H), 0.52-0.60 (m, 2H), 1.41-1.47 (m, 6H, 2CH₃), 3.90 (s, 3H, CH₃), 3.80-4.04 (m, 3H, CH₂+NH), 4.54 (s, 1H), 6.38-6.42 (m, 1H, Ar), 6.61-6.88 (m, 4H), 7.05-7.12 (m, 4H), 7.19-7.32 (m, 3H). (*anti*-isomer) ¹H NMR (CDCl₃, 300 MHz, TMS) δ -0.17 – 0.14 (m, 4H), 1.46 (t, 3H, J = 6.6 Hz), 1.93 (s, 3H, CH₃), 3.91 (s, 3H, OCH₃), 3.80-4.04 (m, 3H, CH₂+NH), 4.98 (s, 1H), 6.38-6.42 (m, 1H, Ar), 6.61-6.88 (m, 4H), 7.05-7.12 (m, 4H), 7.19-7.32 (m, 3H). (*syn*-isomer) ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 3.65, 6.21, 14.86, 23.44, 28.73, 43.54, 55.15, 56.92, 63.14, 112.51, 113.15, 113.96, 116.75, 126.48, 127.48, 128.34, 129.73, 131.18, 132.58, 143.25, 156.84, 158.91. (*anti*-isomer) ¹³C NMR (CDCl₃, 75 MHz, TMS) δ 1.74, 6.04, 14.89, 27.09, 30.56, 45.86, 55.19, 57.77, 63.21, 113.08, 113.80, 115.08, 117.98, 127.35, 128.19, 129.55, 130.73, 131.69, 137.77, 144.45, 156.96, 158.98. IR (CH₂Cl₂) ν 3054, 2987, 1606, 1510, 1422, 1265, 896, 742, 705 cm⁻¹. MS (%) m/e 399 (M⁺, 18.21), 276 (100). HRMS calcd. for C₂₇H₂₉NO₂: 399.2198, Found: 399.2164.

4-(4-Ethoxyphenyl)-4-methyl-2-(4-nitrophenyl)-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3q**.

A yellow solid, Mp: 220-222 °C. (*syn*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS) δ -0.17-0.08 (m, 4H), 1.36-1.43 (m, 6H, 2CH_3), 3.99 (q, 2H, $J = 6.9$ Hz, CH_2), 4.70 (s, 1H), 5.05 (s, 1H), 6.66-6.83 (m, 5H, Ar), 7.02-7.57 (m, 5H, Ar), 8.11-8.17 (m, 2H, Ar). (*anti*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 0.09-0.59 (m, 4H), 1.41 (t, 3H, $J = 6.9$ Hz, CH_3), 1.90 (s, 3H, CH_3), 3.94-4.04 (m, 3H, CH_2+NH), 5.29 (s, 1H), 6.66-6.83 (m, 5H, Ar), 7.02-7.57 (m, 5H, Ar), 8.11-8.17 (m, 2H, Ar). (*syn*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 4.13, 6.43, 14.81, 23.22, 28.51, 43.61, 57.29, 63.18, 112.62, 114.54, 117.73, 122.87, 126.73, 127.58, 128.40, 129.47, 130.99, 137.15, 142.75, 144.86, 147.76, 157.00. (*anti*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 1.79, 6.26, 14.84, 27.34, 30.20, 45.51, 58.51, 63.24, 113.91, 115.26, 118.55, 122.90, 127.53, 128.26, 129.41, 130.50, 132.21, 137.15, 143.98, 147.20, 148.54, 157.11. IR (CH_2Cl_2) ν 3054, 2987, 1606, 1524, 1265, 739 cm^{-1} . MS (%) m/e 414 (M^+ , 26.88), 291 (100). HRMS calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3$: 414.1963, Found: 414.1949. Anal. calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3$: C, 75.34%; H, 6.32%; N, 6.76%. Found: C, 75.23%; H, 6.21%; N, 6.76%.

4-(4-Ethoxyphenyl)-4-methyl-2-phenyl-1, 2, 3, 4-tetrahydrospiro-(3, 1'-cyclopropyl)-quinoline **3r**.

A white solid, Mp: 80-140 °C, (*syn*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS) δ -0.14- -0.07 (m, 2H), 0.19-0.26 (m, 2H), 1.38-1.43 (m, 6H, 2CH_3), 4.00-4.02 (m, 3H, CH_2+NH), 4.60 (s, 1H), 6.62-6.82 (m, 4H, Ar), 7.06-7.41 (m, 9H, Ar). (*anti*-isomer) ^1H NMR (CDCl_3 , 300 MHz, TMS) δ 0.06-0.13 (m, 2H), 0.45-0.52 (m, 2H), 1.41 (t, 3H, $J = 7.2$ Hz, CH_3), 1.95 (s, 3H, CH_3), 4.00-4.02 (m, 3H, CH_2+NH), 5.03 (s, 1H), 6.62-6.82 (m, 4H, Ar), 7.06-7.41 (m, 9H, Ar). (*syn*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 3.80, 6.32, 14.94, 23.50, 28.69, 43.66, 57.62, 63.20, 112.59, 114.11, 116.92, 126.59, 127.57, 127.70, 127.87, 128.42, 128.87, 131.28, 137.73, 140.76, 144.76, 156.93. (*anti*-isomer) ^{13}C NMR (CDCl_3 , 75 MHz, TMS) δ 1.86, 6.21, 14.97, 27.08, 30.64, 45.96, 58.50, 63.27, 113.88, 115.22, 118.14, 127.45, 127.61, 127.79, 128.29, 128.67, 130.81, 132.74, 139.82, 143.27, 145.91, 157.04. IR (CH_2Cl_2) ν 3054, 2987, 1422, 1265, 896, 740 cm^{-1} . MS (%) m/e 369 (M^+ , 21.08), 246 (100). HRMS calcd. for $\text{C}_{26}\text{H}_{27}\text{NO}$: 369.2093, Found: 369.2100.