Electronic Supporting Information (ESI)

Copper catalyzed dehydrogenative cyclization, alkenylation towards dihydroquinolinones

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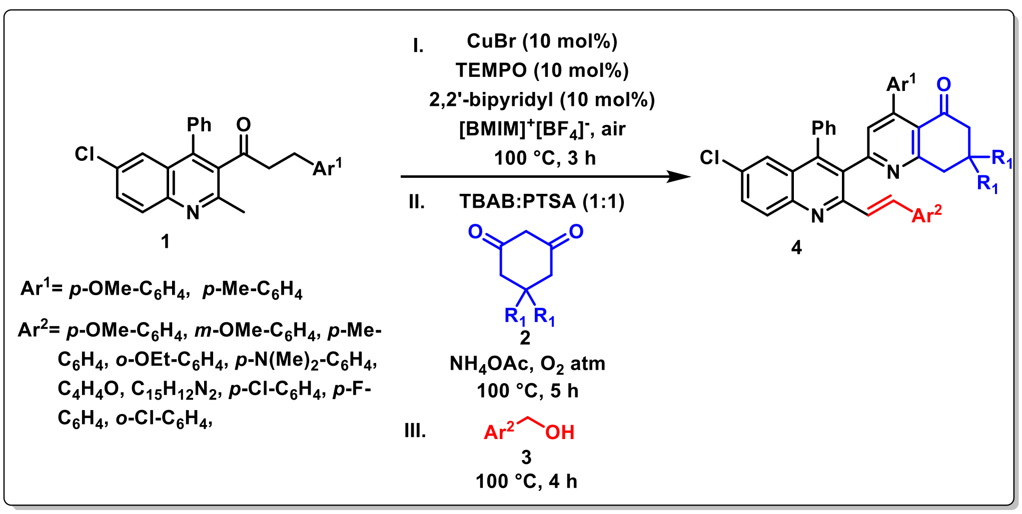
1. General Information

Chemicals were purchased from various suppliers including Sigma-Aldrich, Merck, and SRL and utilized without additional purification. Reactions were carried out in oven-dried glass containers. The progress of the reaction was monitored by thin-layer chromatography using pre-coated alumina TLC sheets (silica gel 60 F-254, Merck) and noticed using a UV detection chamber. The synthesized compounds were purified by silica gel (100-200 mesh) column chromatography. Proton (^{1}H) and carbon-13 (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded at room temperature in $CDCl_3$, utilizing a Bruker AVANCE-III spectrometer operating at 400 MHz for ^{1}H and 101 MHz for ^{13}C. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (*J*) are provided in (Hz) by referencing TMS as an internal standard. Infrared (IR) spectra were recorded using a Thermo Nicolet iS50 with an inbuilt ATR (Shimadzu IR Tracer-100) spectrometer. A positive electrospray ionization (ESI^+) mode was employed for High-resolution mass spectrometry on a WATERS-XEVO G2-XS-QToF. Single-crystal X-ray diffraction was recorded using a D8-QUEST single-crystal XRD diffractometer; all data calculations were executed using the APEX2 program package on the PC version. The UV-visible absorption and emission spectra were recorded using a JASCO V-670 PC spectrophotometer.

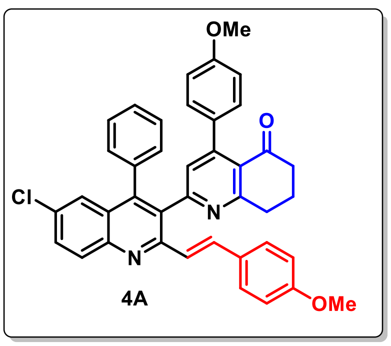
2. Experimental Procedure and Spectral Data

2.1 General procedure for the synthesis of compounds 4



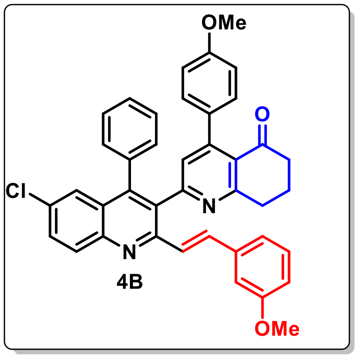
The synthesis of alkylated ketone **1** was performed according to a previously published procedure.[4] To an oven-dried reaction vial, added alkylated ketone **1** (1.0 mmol), CuBr (10 mol%), 2,2'-bipyridyl (10 mol%), TEMPO (10 mol%), $[BMIM]^+[BF_4]^-$ (1.5 ml) and the reaction mixture was stirred at 100 °C for 3 h in the air atmosphere, resulting in the formation of chalcone **1'**. Then TBAB:PTSA (1:1) (200 mg), 1,3-Cyclohexanedione **2** (1.5 mmol) and NH_4OAc (10.0 mmol) were added and the reaction was continued at 100 °C for 5 h in the O_2 atmosphere, to form the cyclized intermediate **C**. After the formation of the cyclized intermediate **C**, alcohol **3** (1.0 mmol) was added and the reaction was continued at 100 °C for 4 h to obtain C(sp^3)-H functionalized quinolinyl quinolinones **4**. The progress of the reaction was monitored by TLC. When the reaction was completed, the reaction mixture was cooled to room temperature, diluted with water (40 ml), and then extracted with DCM (50 ml x 2). The combined organic layers were dried over anhydrous $MgSO_4$, and the crude reaction mixture was purified by silica gel column chromatography using 10-15% EtOAc/Pet ether as eluent to yield 65-86% of the desired products (**4A-4P**).

(*E*)-6'-chloro-4-(4-methoxyphenyl)-2'-(4-methoxystyryl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4A). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4A** as a Pale yellow solid (84% yield) mp: 235-237 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 15.5 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.28 (s, 3H), 7.19 (s, 2H), 7.09 (s, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 6.81 (dd, *J* = 13.8, 6.7 Hz, 5H), 6.75 (d, *J* = 4.1 Hz, 1H), 3.75 (t, *J* = 5.1 Hz, 6H), 3.09 (t, *J* = 5.9 Hz, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.16 – 2.08 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 197.9, 164.1, 160.1, 159.5, 159.2, 153.6, 151.3, 146.9, 146.5, 135.8, 135.7, 132.1, 132.0, 131.6, 131.0, 130.9, 130.1, 129.7, 129.3, 128.9, 128.3, 128.2, 128.1, 126.9, 125.30, 124.4, 123.3, 114.1, 113.4, 55.3, 55.2, 40.1, 33.6, 21.6. **FT-IR**: ν = 2917, 1685, 1565, 1525, 1472, 1258, 1147, 1078, 955, 830, 702, 451 cm^{-1}. **HRMS (ESI)**: $C_{40}H_{31}ClN_2O_3$ requires 623.2101 $(M + H)^+$; found: 623.2103.



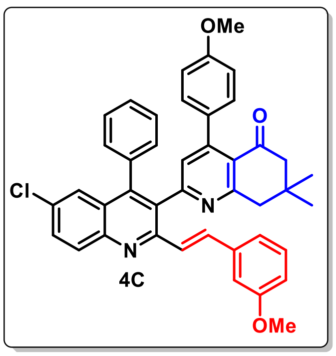
4A

(*E*)-6'-chloro-4-(4-methoxyphenyl)-2'-(3-methoxystyryl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4B). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4B** as a Pale yellow solid (86% yield); mp: 230-232°C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 15.5 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.28 (s, 3H), 7.19 (s, 2H), 7.09 (s, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 6.81 (dd, *J* = 13.8, 6.7 Hz, 5H), 6.75 (d, *J* = 4.1 Hz, 1H), 3.75 (t, *J* = 5.1

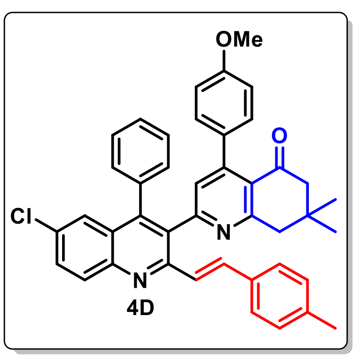

4B

Hz, 6H), 3.09 (t, J = 5.9 Hz, 2H), 2.61 (t, J = 6.4 Hz, 2H), 2.16 – 2.08 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 164.1, 159.7, 159.5, 158.9, 153.2, 151.3, 147.0, 146.4, 138.4, 135.7, 132.3, 132.2, 131.5, 131.1, 131.0, 130.1, 129.6, 129.3, 128.4, 128.3, 128.2, 127.1, 125.9, 125.3, 124.4, 124.0, 120.0, 113.9, 113.4, 113.1, 55.2, 40.1, 31.4, 30.2, 21.5. **FT-IR**: ν = 2924, 1682, 1512, 1475, 1244, 1174, 1034, 955, 826, 704, 53 cm^{-1}. **HRMS (ESI)**: $C_{40}H_{31}ClN_2O_3$ requires 623.2101 $(M + H)^+$; found: 623.2109.

(*E*)-6'-chloro-4-(4-methoxyphenyl)-2'-(3-methoxystyryl)-7,7-dimethyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4C). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **4C** as a Pale white solid (83% yield); mp: 250-252°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, J = 9.0 Hz, 1H), 7.94 (d, J = 15.6 Hz, 1H), 7.59 (dd, J = 9.0, 2.0 Hz, 1H), 7.47 (d, J = 1.9 Hz, 1H), 7.26 (s, 3H), 7.20 – 7.13 (m, 2H), 7.08 (s, 2H), 7.01 – 6.91 (m, 2H), 6.86 – 6.71 (m, 6H), 3.73 (d, J = 5.3 Hz, 6H), 2.99 (s, 2H), 2.47 (s, 2H), 1.03 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 197.90, 162.82, 159.79, 159.55, 159.27, 153.13, 151.02, 147.00, 146.42, 138.32, 135.90, 135.73, 132.32, 131.43, 131.14, 130.99, 130.12, 129.59, 129.34, 128.17, 127.06, 125.88, 125.30, 123.41, 119.92, 113.93, 113.42, 113.20, 55.26, 53.86, 47.62, 32.64, 28.11. **FT-IR**: ν = 2938, 2175, 1687, 1577, 1511, 1248, 1152, 1038, 966, 829, 705, 539 cm^{-1}. **HRMS (ESI)**: $C_{42}H_{35}ClN_2O_3$ requires 651.2414 $(M + H)^+$; found: 651.2414.

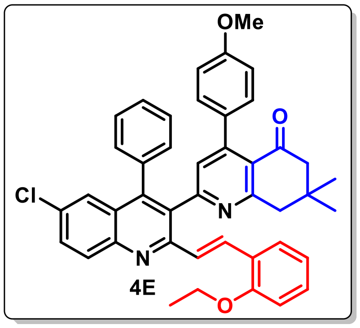

4C

(*E*)-6'-chloro-4-(4-methoxyphenyl)-7,7-dimethyl-2'-(4-methylstyryl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4D). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4D** as a White solid (85% yield); mp: 240-242°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, J = 9.0 Hz, 1H), 8.04 (d, J = 15.6 Hz, 1H), 7.69 (dd, J = 9.0, 2.2 Hz, 1H), 7.56 (d, J = 2.1 Hz, 1H), 7.38 (d, J = 8.1 Hz, 5H), 7.21 – 7.12 (m, 5H),6.98 – 6.80 (m, 5H), 3.84 (s, 3H), 3.10 (s, 2H), 2.57 (s, 2H), 2.37 (s, 3H), 1.10 (d, J = 33.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.0, 162.8, 159.5, 159.4, 153.4, 151.0, 146.9, 146.5, 138.7, 136.0, 135.8, 134.1, 132.2, 132.1, 131.4, 131.1, 130.9, 130.1, 129.4,

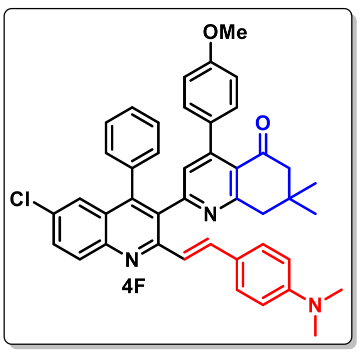

4D

129.3, 128.2, 128.2, 128.1, 127.4, 127.0, 125.3, 124.5, 123.4, 113.4, 55.3, 53.8, 47.6, 32.6, 21.4. **FT-IR**: ν = 2952, 1691, 1570, 1363, 1244, 1174, 1035, 965, 828, 699, 546 cm^{-1}. **HRMS (ESI)**: $C_{42}H_{36}ClN_2O_2$ requires 635.2465 $(M + H)^+$; found: 635.2466.

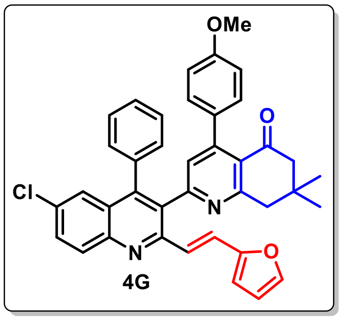
(*E*)-6'-chloro-2'-(2-ethoxystyryl)-4-(4-methoxyphenyl)-7,7-dimethyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4E). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4E** as a White solid (80% yield); mp: 255-257°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 15.7 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.44 (s, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.20 – 7.11 (m, 2H), 7.08 (s, 2H), 6.83 (d, *J* = 8.1 Hz, 2H),6.78 (t, *J* = 7.7 Hz, 4H), 3.96 (q, *J* = 6.8 Hz, 2H), 3.73 (s, 3H), 2.96 (s, 2H), 2.44 (s, 2H), 1.21 (t, *J* = 6.9 Hz, 3H), 1.01 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 162.8, 159.5, 157.5, 153.9, 150.9, 135.7, 132.5, 132.1, 131.5, 130.9, 130.1, 129.7, 129.3, 129.2, 128.1, 128.0, 127.0, 125.8, 125.2, 123.4, 120.5, 113.4, 112.0, 63.8, 55.3, 53.9, 47.6, 32.6, 14.7. **FT-IR**: ν = 2937, 1686, 1606, 1512, 1242, 1179, 1034, 962, 830, 704, 542 cm^{-1}. **HRMS (ESI)**: $C_{43}H_{38}ClN_2O_3$ requires 665.2571 $(M + H)^+$; found: 665.2578.



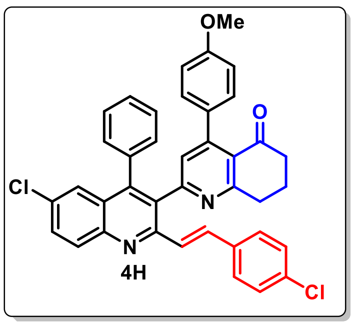
(*E*)-6'-chloro-2'-(4-(dimethylamino)styryl)-4-(4-methoxyphenyl)-7,7-dimethyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4F). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **4F** as a Pale brown solid (82% yield); mp: 262-264°C; **^{1}H NMR (400 MHz, $CDCl_3$)** 8.13 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 15.5 Hz, 1H), 7.66 (dd, J = 9.0, 2.0 Hz, 1H), 7.53 (d, J = 1.9 Hz, 1H), 7.42 – 7.32 (m, 5H), 7.19 (s, 2H), 6.96 – 6.85 (m, 6H), 6.67 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H), 3.10 (d, J = 4.2 Hz, 2H), 3.00 (s, 6H), 2.57 (s, 2H), 1.13 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.0, 162.8, 159.8, 159.5, 154.0, 150.9, 150.7, 146.7, 146.6, 136.4, 135.9, 132.1, 131.5, 130.9, 130.7, 130.1, 129.4, 128.8, 128.2, 128.1, 128.0, 126.7, 125.3, 125.0, 123.3, 120.7, 113.4, 112.0, 55.3, 53.9, 47.6, 40.3, 32.6**.** **FT-IR**: ν = 2938, 2827, 2174, 1685, 1603, 1519, 1362, 1247, 1170, 1033, 646, 831, 694, 520 cm^{-1}. **HRMS (ESI)**: $C_{43}H_{39}ClN_3O_2$ requires 664.2731 $(M + H)^+$; found: 664.2735.



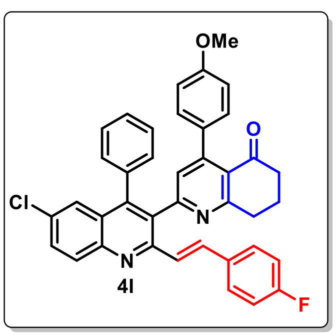
(*E*)-6'-chloro-2'-(2-(furan-2-yl)vinyl)-4-(4-methoxyphenyl)-7,7-dimethyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4G). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4G** as a Dark brown solid (78% yield); mp: 222-224 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 15.3 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.52 (s, 1H), 7.31 (t, J = 19.1 Hz, 4H), 7.15 (s, 2H), 7.00 (d, J = 15.3 Hz, 1H), 6.91 (d, J = 8.2 Hz, 2H), 6.89 – 6.78 (m, 3H), 6.46 (d, J = 29.9 Hz, 2H), 3.81 (s, 3H), 3.05 (s, 2H), 2.54 (s, 2H), 1.10 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.1, 162.9, 159.5,159.2, 153.1, 153.0, 150.9, 146.9, 146.4, 143.1, 135.8, 132.3, 132.1, 131.5, 131.0, 130.9, 130.1, 129.4, 128.1, 127.0, 125.3, 123.4, 123.3, 123.0, 113.4, 112.0, 112.0, 55.3, 53.9, 47.5, 32.6. **FT-IR**: ν = 2952, 1691, 1570, 1509, 1363, 1244, 1174, 1035, 965, 828, 699, 546 cm^{-1}. **HRMS (ESI):** $C_{39}H_{32}ClN_2O_3$ requires 611.2101 $(M + H)^+$; found: 611.2110.



(*E*)-6'-chloro-2'-(4-chlorostyryl)-4-(4-methoxyphenyl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4H). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **4H** as a White solid (76% yield); mp: 253-255 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, J = 9.0 Hz, 1H), 7.93 (d, J = 15.6 Hz, 1H), 7.60 (dd, J = 9.0, 2.1 Hz, 1H), 7.46 (t, J = 5.1 Hz, 1H), 7.36 – 7.21 (m, 7H), 7.12 – 6.99 (m, 3H), 6.84 – 6.71 (m, 5H), 3.74 (s, 3H), 3.09 (t, J = 6.0 Hz, 2H), 2.61 (t, J = 6.5 Hz, 2H), 2.18 – 2.03 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 164.1, 159.6, 158.9, 151.4, 147.1, 146.4, 135.7, 135.2, 134.3, 132.6, 132.1, 131.4, 131.0, 130.1, 129.4, 129.3, 128.6, 128.3, 128.3, 128.2, 127.4, 127.2, 126.8, 125.3, 124.5, 113.4, 55.2, 40.1, 33.6, 21.5. **FT-IR**: ν = 2941, 1685, 1569, 1510, 1472, 1240, 1175, 1036, 958, 826, 705, 659 cm^{-1}. **HRMS (ESI):** $C_{39}H_{29}Cl_2N_2O_2$ requires 627.1606 $(M + H)^+$; found: 627.1600.

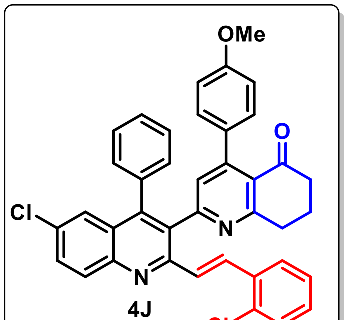


(*E*)-6'-chloro-2'-(4-fluorostyryl)-4-(4-methoxyphenyl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4I). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **4I** as a Pale yellow solid (75% yield); mp: 228-230 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, J = 9.0 Hz, 1H), 7.94 (d, J = 15.6 Hz, 1H), 7.60 (dd, J = 9.0, 2.3 Hz, 1H), 7.45 (d, J = 2.2 Hz, 1H), 7.37 (dd, J = 8.6, 5.5 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.19 (s, 2H), 7.09 (s, 2H), 6.99 (d, J = 5.0 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.83 – 6.79 (m, 2H), 6.78 (s, 1H), 6.75 (d, J = 6.7 Hz), 3.74 (s,3H), 3.09 (t, J = 6.1 Hz, 2H), 2.61 (t, J = 6.6 Hz, 2H), 2.12 (dt, J = 12.8, 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 164.1, 159.6, 158.9, 153.1, 151.3, 147.0, 146.4, 135.7, 134.8, 133.1, 132.3, 132.1, 131.5, 131.1, 131.0, 129.1, 129.0, 128.3, 128.3, 128.2, 127.1, 125.3, 125.3, 124.4,



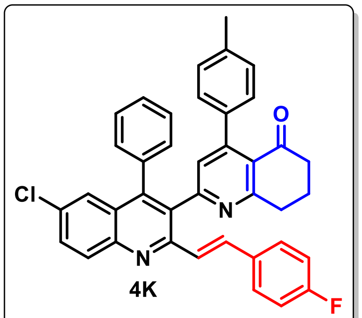
115.8, 115.6, 113.4, 55.2, 40.1, 33.6, 21.6. **FT-IR**: ν = 2924, 1677, 1503, 1307, 1227, 1142, 979, 829, 702, 607, 499 cm^{-1}. **HRMS (ESI)**: $C_{39}H_{29}ClFN_2O_2$ requires 611.1902 $(M + H)^+$; found: 611.1905.

(*E*)-6'-chloro-2'-(2-chlorostyryl)-4-(4-methoxyphenyl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4J). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4J** as a White solid (72% yield); mp: 216-218°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (d, *J* = 15.7 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 7.70 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.52 (dd, *J* = 5.2, 4.2 Hz, 1H), 7.43 – 7.38 (m, 4H), 7.25 (dd, *J* = 14.0, 9.0 Hz, 3H), 7.20 (s, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 10.4 Hz, 3H), 3.84 (s, 3H), 3.19 (t, *J* = 6.1 Hz, 2H), 2.69 (t, *J* = 6.6 Hz, 2H), 2.28 – 2.13 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.8, 164.1, 159.5, 158.9, 153.0, 151.3, 147.0, 146.3, 135.6, 135.1, 134.3, 132.5, 132.3, 132.2, 131.5, 131.4, 131.0, 130.1, 130.0, 129.3, 129.2, 128.5, 128.3, 128.2, 128.1, 127.4, 127.1, 126.8, 125.2, 124.4, 113.4, 55.2, 40.1, 33.5, 21.5. **FT-IR**: ν = 2941, 1684, 1566, 1507, 1472, 1243, 1178, 1041, 956, 830, 704, 549 cm^{-1}**.** **HRMS (ESI)**: $C_{39}H_{29}Cl_2N_2O_2$ requires 627.1606 $(M + H)^+$; found: 627.1603.



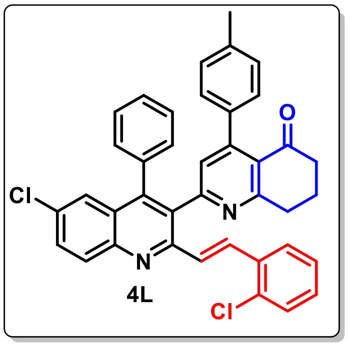
4J

(*E*)-6'-chloro-2'-(2-chlorostyryl)-4-(4-methoxyphenyl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4K). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4K** as a Pale yellow solid (79% yield); mp: 230-232°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 15.6 Hz, 1H), 7.58 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.28 (d, *J* = 3.0 Hz, 3H), 7.06 (t, *J* = 8.1 Hz, 4H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 3H), 3.09 (t, *J* = 6.1 Hz, 2H), 2.60 (t, *J* = 6.5 Hz, 2H), 2.28 (s, 3H), 2.16 – 2.06 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 164.1, 164.0, 161.7, 159.0, 153.1, 151.7, 147.1, 146.4, 137.8, 136.5, 135.7, 134.8, 133.1, 133.1, 132.3, 132.1, 131.1, 131.0, 130.1, 129.1, 129.0, 128.7, 128.3, 128.2,127.7, 127.1, 125.3, 125.3, 125.2, 124.5, 115.8, 115.6, 40.0, 33.5, 21.6, 21.3. **FT-IR**: ν = 2921, 1678, 1505, 1307, 1227, 1143, 977, 828, 704, 607, 504 cm^{-1}. **HRMS (ESI)**: $C_{39}H_{28}ClFN_2O$ requires 595.1952 $(M + H)^+$; found: 595.1962.



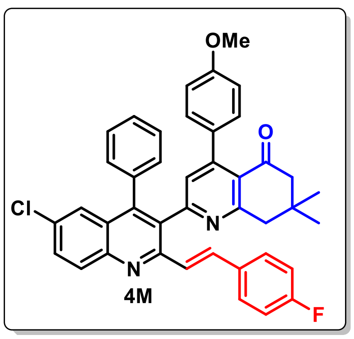
4K

(*E*)-6'-chloro-2'-(2-chlorostyryl)-4'-phenyl-4-(p-tolyl)-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4L).



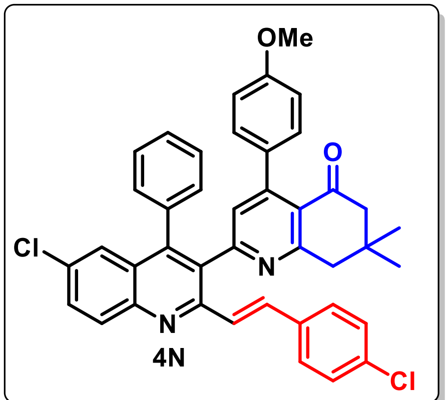
Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4L** as a White solid (65% yield); mp: 262-264 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 15.7 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.60 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.34 – 7.30 (m, 1H), 7.30 – 7.27 (m, 3H), 7.19 – 7.12 (m, 3H), 7.10 – 7.02 (m, 4H), 6.74 (d, *J* = 7.4 Hz, 3H), 3.09 (t, *J* = 6.2 Hz, 2H), 2.58 (t, *J* = 6.6 Hz, 2H), 2.28 (s, 3H), 2.15 – 2.06 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 164.0, 159.0, 153.0, 151.7, 147.1, 146.4, 137.8, 136.5, 135.6, 135.2, 134.3, 132.6, 132.4, 132.2, 131.4, 131.0, 130.1, 130.0, 129.4, 128.7, 128.6, 128.3, 128.2, 128.2, 127.7, 127.4, 127.2, 126.8, 125.3, 124.5, 40.0, 33.5, 21.6, 21.3. **FT-IR**: ν **=** 2921, 2170, 1686, 1527, 1472, 1261, 1081, 958, 826, 705, 660, 513 cm^{-1}. **HRMS (ESI):** $C_{39}H_{29}Cl_2N_2O$ requires 611.1657 $(M + H)^+$; found: 611.1665.

(*E*)-6'-chloro-2'-(4-fluorostyryl)-4-(4-methoxyphenyl)-7,7-dimethyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4M).



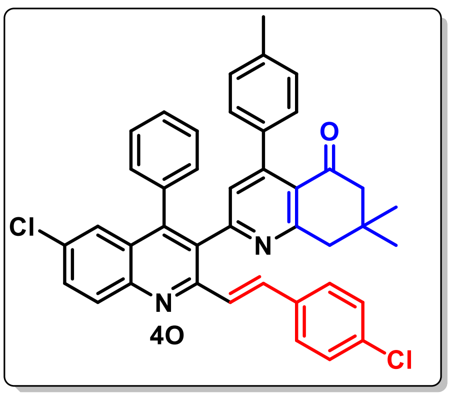
Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **4M** as a Pale white solid (78% yield) mp: 232-234°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 15.6 Hz, 1H),7.70 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.37 (s, 3H), 7.19 (s, 2H), 7.06 (dd, *J* = 12.1, 7.8 Hz, 3H), 6.94 – 6.83 (m, 5H), 3.84 (s, 3H), 3.09 (s, 2H), 2.58 (s, 2H)1.14 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 164.1, 162.8, 159.6, 159.3, 153.1, 151.0, 147.0, 146.4, 135.7, 134.7, 133.0, 132.3, 132.2, 131.3, 131.1, 131.0, 130.1, 129.3, 129.1, 129.0, 128.2, 127.0, 125.3, 125.2, 123.4, 115.8, 115.6, 113.4, 55.3, 53.8, 47.6, 32.7. **FT-IR**: ν **=** 2924, 2176, 1688, 1573, 1511, 1248, 1080, 1037, 959, 826, 701, 540 cm^{-1}. **HRMS (ESI):** $C_{41}H_{33}ClFN_2O_2$ requires 639.2215 $(M + H)^+$; found: 639.2217.

(*E*)-6'-chloro-2'-(4-chlorostyryl)-4-(4-methoxyphenyl)-7,7-dimethyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4N). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **4N** as a White solid (76% yield); mp: 244-246 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 15.6 Hz, 1H), 7.70 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.37 (s, 2H), 7.35 – 7.27 (m, 3H), 7.15 (t, *J* = 15.0 Hz, 3H), 6.89 (q, *J* = 8.8 Hz, 4H), 6.84 (s, 1H), 3.84 (s, 3H), 3.09 (s, 2H), 2.58 (s, 2H), 1.14 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 197.8, 162.8, 159.6, 159.2, 152.9, 151.1, 147.0, 146.4, 135.7, 135.4, 134.5, 134.3, 132.4, 132.3, 131.4, 131.1, 131.1, 130.1, 129.3, 128.9, 128.5, 128.2, 127.1, 126.1, 125.3, 123.4, 113.4, 55.3, 53.8, 47.6, 32.6, 28.1. **FT-IR**: ν = 2952, 1683, 1577, 1509, 1244, 1176, 1087, 1031, 963, 834, 698, 541 cm^{-1}. **HRMS (ESI)**: $C_{41}H_{33}Cl_2N_2O_2$ requires 655.1919 $(M + H)^+$; found: 655.1915.



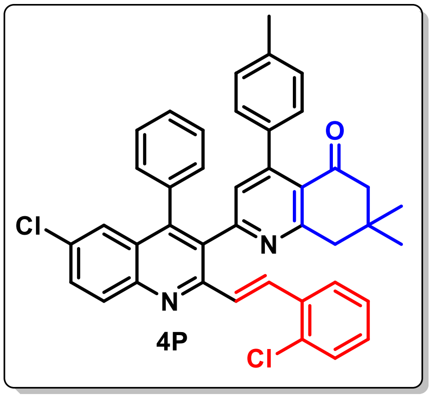
4N

(*E*)-6'-chloro-2'-(4-chlorostyryl)-7,7-dimethyl-4'-phenyl-4-(p-tolyl)-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4O). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4O** as a White solid (73% yield) mp: 236-238°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 15.6 Hz, 1H), 7.59 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 21.4, 13.0 Hz, 5H), 7.04 (t, *J* = 10.9 Hz, 5H), 6.75 (d, *J* = 9.6 Hz, 3H), 2.99 (s, 2H), 2.46 (s, 2H), 2.28 (s, 3H), 1.03 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.3, 168.0, 163.2, 158.0, 156.4, 146.0, 145.7, 136.7, 135.2, 132.5, 131.0, 130.8, 130.3, 129.5, 129.3, 128.7, 128.5, 128.5, 128.4, 126.0, 125.2, 113.8, 113.5, 61.5, 55.4, 55.2, 44.1, 43.5, 39.9, 13.6. **FT-IR**: ν = 2913, 1688, 1524, 1476, 1261, 1146, 1078, 956, 830, 747, 706, 659 cm^{-1}. **HRMS (ESI)**: $C_{41}H_{33}Cl_2N_2O$ requires 639.1970 $(M + H)^+$; found: 639.1970.

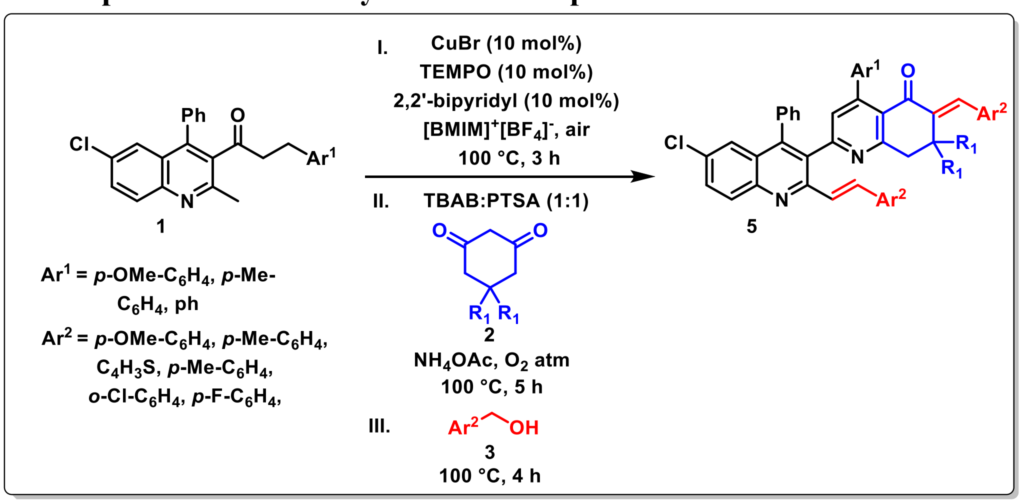


4O

(*E*)-6'-chloro-2'-(2-chlorostyryl)-7,7-dimethyl-4'-phenyl-4-(p-tolyl)-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4P). Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **4P** as a White solid (70% yield) mp: 234-236°C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 15.7 Hz, 1H), 8.20 (d, *J* = 9.0 Hz,1H), 7.70 (dd, *J* = 9.0, 2.1 Hz, 1H),7.57 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.40 (dd, *J* = 14.7, 7.8 Hz, 4H), 7.22 (d, *J* = 4.8 Hz, 3H), 7.20 – 7.12 (m, 4H), 6.85 (d, *J* = 5.3 Hz, 3H), 3.09 (s, 2H), 2.55 (s, 2H), 2.38 (s, 3H), 1.12 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 162.8, 159.3, 152.9, 151.4, 147.1, 146.4, 137.8, 136.4, 135.7, 135.1, 134.4, 132.6, 132.3, 132.2, 131.4, 131.0, 130.1, 130.0, 129.4, 128.7, 128.5, 128.2, 128.1, 127.7, 127.3, 127.1, 126.8, 125.3, 123.5, 53.7, 47.6, 32.6, 21.3. **FT-IR**: ν = 2960, 1698, 1531, 1472, 1276, 1143, 1065, 956, 824, 752, 706, 543 cm^{-1}. **HRMS (ESI)**: $C_{41}H_{33}Cl_2N_2O$ requires 639.1970 $(M + H)^+$; found: 639.1975.

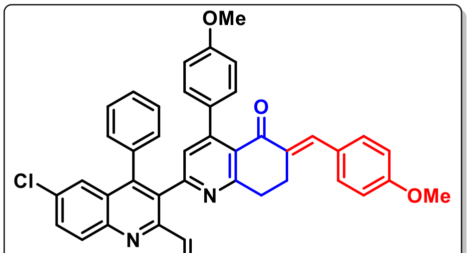


2.2 General procedure for the synthesis of compounds 5



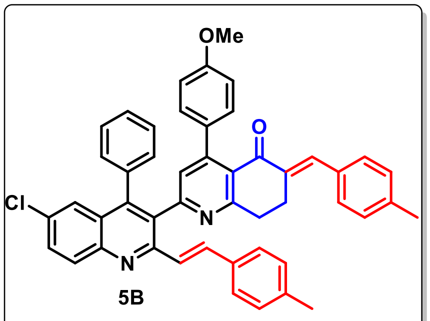
To an oven-dried reaction vial, added alkylated ketone **1** (1.0 mmol), CuBr (10 mol%), 2,2'-bipyridyl (10 mol%), TEMPO (10 mol%), and $[BMIM]^+[BF_4]^-$ (1.5 ml) and the reaction mixture was stirred at 100 °C for 3 h in the air atmosphere, resulting in the formation of chalcone **1'**. Then TBAB:PTSA (1:1) (200 mg), 1,3-Cyclohexanedione **2** (1.5 mmol) and NH_4OAc (10.0 mmol) were added and the reaction was continued at 100 °C for 5 h in the O_2 atmosphere, to form the cyclized intermediate **C**.After the formation of the cyclized intermediate **C**, alcohol **3** (3.0 mmol) was added and the reaction was continued at 100 °C for 7 h to obtain C(sp^3)-H functionalized/α-alkenylated quinolinyl quinolinones **5.** The progress of the reaction was monitored by TLC. When the reaction was completed, the reaction mixture was cooled to room temperature, diluted with water (40 ml), and then extracted with DCM (50 ml x 2). The combined organic layers were dried over anhydrous $MgSO_4$, and the crude reaction mixture was purified by silica gel column chromatography using 5-7% EtOAc/Pet ether as eluent to yield 71-83% of the desired products (**5A-5F)**.

6'-chloro-6-((*E*)-4-methoxybenzylidene)-4-(4-methoxyphenyl)-2'-((*E*)-4-methoxystyryl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (5A). Purification was carried out by column chromatography on silica gel using a 7% ethyl acetate/Pet ether mixture, resulting in the isolation of **5A** as a Pale yellow solid (79% yield); mp: 272-274 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.13 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 15.6 Hz, 1H), 7.75 (s, 1H), 7.65 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.44 (t, *J* = 8.5 Hz, 4H), 7.36 (s, 3H), 7.18 (s, 2H), 7.04-6.93 (m, 5H), 6.92-6.84 (m, 5H), 3.85 (s, 3H), 3.82 (s, 6H), 3.21 (t, *J* = 5.7 Hz, 2H), 3.12 (d, *J* = 6.0 Hz, 2H. **^{13}C NMR (101 MHz, CDCl$_3$)** δ 187.2, 162.5, 160.3, 160.1, 159.6, 158.8, 154.7, 151.4, 147.0, 137.4, 135.8, 133.3, 132.2, 132.0, 132.0, 131.4, 131.0, 130.9, 130.1, 129.7, 129.4, 128.9, 128.4, 128.2, 128.1, 128.1, 127.0, 125.4, 125.3, 123.3, 114.2, 114.1, 113.6, 55.4, 55.3, 55.2, 32.3, 25.9. **FT-IR**: ν = 2921, 1684, 1582, 1509, 1246, 1177, 1079, 1031, 832, 695, 550 cm^{-1}. **HRMS (ESI)**: $C_{48}H_{38}ClN_2O_4$ requires 741.2520 (M + H)$^+$; found: 741.2523.



5A

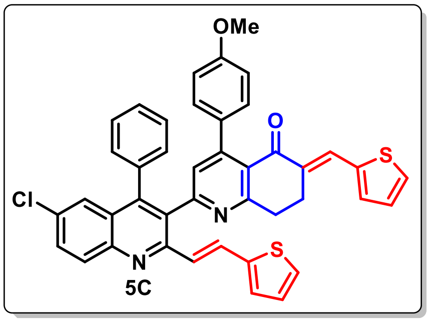
6'-chloro-4-(4-methoxyphenyl)-6-((*E*)-4-methylbenzylidene)-2'-((*E*)-4-methylstyryl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (5B). Purification was carried out by column chromatography on silica gel using a 7% ethyl acetate/Pet ether mixture, resulting in the isolation of **5B** as a Pale yellow solid (83% yield) mp: 268-270 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.13 (d, *J* = 8.9 Hz, 1H), 8.03 (d, *J* = 15.5 Hz, 1H), 7.76 (s, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.52 (s, 1H), 7.36 (s, 7H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.13 (dd, *J* = 17.3, 11.8 Hz, 5H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.92 – 6.84 (m, 3H), 3.82 (s, 3H), 3.19 (d, *J* = 5.5 Hz, 2H), 3.11 (d, *J* = 5.2 Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 187.2, 162.7, 159.6, 158.9, 153.6, 151.5, 147.0, 146.4, 139.3, 138.7, 137.6, 136.1, 135.8, 134.5, 134.2, 132.7, 132.3, 132.1, 131.4, 131.1, 130.9, 130.1, 129.4, 129.4, 129.3, 128.2, 128.1, 127.4, 127.0, 125.3, 125.3, 124.6, 113.6, 55.2, 32.4, 25.9, 21.5,



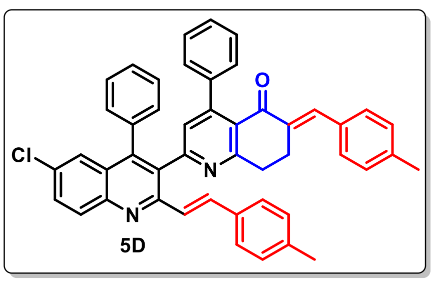
5B

21.4. **FT-IR**: ν = 2952, 1684, 1581, 1512, 1249, 1173, 1026, 966, 830, 703, 532 cm^{-1}. **HRMS (ESI)**: $C_{48}H_{38}ClN_2O_2$ requires 709.2622 $(M + H)^+$; found: 709.2621.

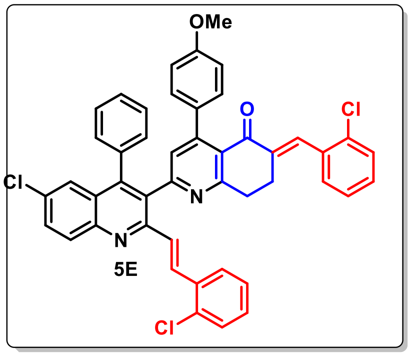
(*E*)-6'-chloro-4-(4-methoxyphenyl)-4'-phenyl-2'-((*E*)-2-(thiophen-2-yl)vinyl)-6-(thiophen-2-ylmethylene)-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (5C). Purification was carried out by column chromatography on silica gel using a 5% ethyl acetate/Pet ether mixture, resulting in the isolation of **5C** as a Pale brown solid (81% yield) mp: 274-276 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (dd, *J* = 28.7, 12.1 Hz, 2H), 7.86 (s, 1H),7.59 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.47 (dd, *J* = 9.3, 3.6 Hz, 2H), 7.30 (s, 4H), 7.19 (s, 1H), 7.14 (dd, *J* = 11.5, 4.0 Hz, 2H), 7.09 – 7.06 (m, 1H), 6.97 – 6.93 (m, 2H), 6.91 – 6.84 (m, 3H), 6.79 (d, *J* = 8.7 Hz, 3H), 3.75 (s, 3H), 3.16 (d, *J* = 4.2 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 186.9, 162.5, 159.6, 158.5, 153.1, 151.2, 146.9, 146.4, 142.6, 138.0, 135.8, 133.6, 132.2, 132.0, 131.3, 131.0, 130.2, 130.0, 130.0, 129.4, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.0, 125.9, 125.4, 125.1, 113.6, 55.2, 31.7, 25.7. **FT-IR**: ν = 2952, 1682, 1580, 1512, 1370, 1245, 1177, 1027, 968, 830, 702, 538 cm^{-1}. **HRMS (ESI)**: $C_{42}H_{30}ClN_2O_2S_2$ requires 693.1437 $(M + H)^+$; found: 693.1431.



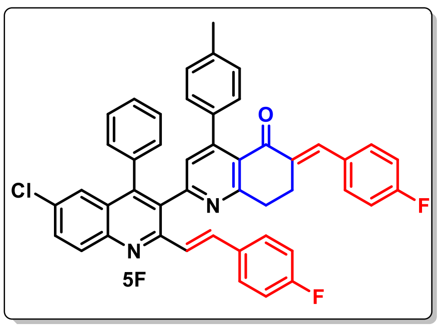
6'-chloro-6-((*E*)-4-methylbenzylidene)-2'-((*E*)-4-methylstyryl)-4,4'-diphenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (5D). Purification was carried out by column chromatography on silica gel using a 5% ethyl acetate/Pet ether mixture, resulting in the isolation of **5D** as a Pale yellow solid (74% yield) mp: 252-254 °C **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1H NMR (400 MHz, CDCl3) δ 8.14 (d, J = 9.0 Hz, 1H), 8.03 (d, J = 15.6 Hz, 1H), 7.75 (s, 1H), 7.67 (dd, J = 9.0, 2.3 Hz, 1H), 7.53 (d, J = 2.2 Hz, 1H), 7.37 (dd, J = 11.6, 5.2 Hz, 10H), 7.23 (d, J = 8.0 Hz, 3H), 7.13 (dd, J = 20.3, 11.7 Hz, 5H), 7.01 (dd, J = 6.6, 2.9 Hz, 2H), 3.21 (d, J = 6.4 Hz, 2H), 3.13 (d, J = 6.2 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 187.0, 162.6, 153.5, 151.9, 139.4, 138.8, 137.8, 136.1, 135.7, 134.3, 134.1, 132.6, 132.2, 131.1, 131.0, 130.1, 130.0, 129.4, 129.3, 128.7, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 127.0, 125.3, 125.2, 124.5, 32.4, 25.9, 21.5, 21.4. **FT-IR**: ν = 2956, 1681, 1577, 1512, 1366, 1244, 1174, 1075, 1024, 964, 830, 700, 539 cm^{-1}. **HRMS (ESI)**: $C_{47}H_{36}ClN_2O$ requires 679.2516 $(M + H)^+$; found: 679.2515.



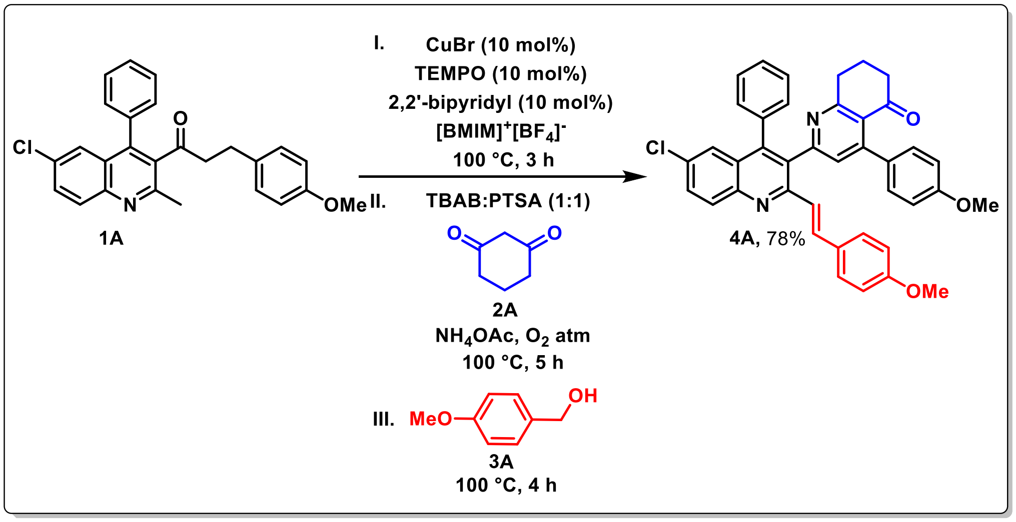
6'-chloro-6-((*E*)-2-chlorobenzylidene)-2'-((*E*)-2-chlorostyryl)-4-(4-methoxyphenyl)-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (5E). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **5E** as a White solid (71% yield); mp: 268-270 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.37 – 8.17 (m, 2H), 7.91 (s, 1H), 7.71 (s, 1H), 7.51 (d, *J* = 31.2 Hz, 4H), 7.40 (s, 4H), 7.33 (s, 2H), 7.26 (d, *J* = 12.7 Hz, 5H), 6.95 (d, *J* = 20.8 Hz, 5H), 3.85 (s, 3H), 3.11 (d, *J* = 31.8 Hz, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 186.46, 163.00, 159.65, 159.04, 153.03, 152.10, 147.11, 146.42, 136.67, 135.65, 135.16, 135.04, 134.42, 134.33, 134.10, 132.57, 132.37, 132.21, 131.45, 131.42, 131.03, 130.21, 130.11, 130.04, 129.92, 129.32, 128.61, 128.33, 128.24, 127.45, 127.16, 126.86, 126.44, 125.30, 124.89, 113.61, 55.23, 32.62, 25.96. **FT-IR**: ν = 2915, 1605, 1513, 1250, 1176, 1089, 953, 834, 704 cm^{-1}. **HRMS (ESI)**: $C_{46}H_{32}Cl_3N_2O_2$ requires 749.1529 (M + H)$^+$; found: 749.1531.



6'-chloro-6-((*E*)-4-fluorobenzylidene)-2'-((*E*)-4-fluorostyryl)-4'-phenyl-4-(p-tolyl)-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (5F). Purification was carried out by column chromatography on silica gel using a 5% ethyl acetate/Pet ether mixture, resulting in the isolation of **5F** as a Pale yellow solid (73% yield); mp: 258-620 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** 8.07 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 15.6 Hz, 1H), 7.66 (s, 1H), 7.60 (dd, J = 9.0, 2.3 Hz, 1H), 7.46 (d, J = 2.2 Hz, 1H), 7.37 (ddd, J = 8.4, 5.6, 2.2 Hz, 4H), 7.32 – 7.26 (m, 3H), 7.12 – 7.06 (m, 4H), 7.05 (s, 1H), 7.02 (d, J = 5.6 Hz, 1H), 6.97 (dd, J = 9.9, 7.5 Hz, 3H), 6.84 (d, J = 7.8 Hz, 3H), 3.10 (d, J = 5.4 Hz, 2H), 3.06 (d, J = 6.0 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 186.5, 163.0, 159.7, 159.0, 153.0, 152.1, 147.1, 146.4, 136.7, 135.7, 135.2, 135.0, 134.4, 134.3, 134.1, 132.6, 132.4, 132.2, 131.5, 131.4, 131.0, 130.2, 130.1, 130.0, 129.9, 129.3, 128.6, 128.3, 128.2, 127.5, 127.2, 126.9, 126.4, 125.3, 124.9, 113.6, 55.2, 32.6, 26.0. **FT-IR**: ν = 2933, 1686, 1529, 1478, 1243, 1157, 1076, 1071, 832, 758, 698, 653, 535 cm^{-1}. **HRMS (ESI)**: $C_{46}H_{32}ClF_2N_2O$ requires 701.2171 (M + H)$^+$; found: 701.2172.



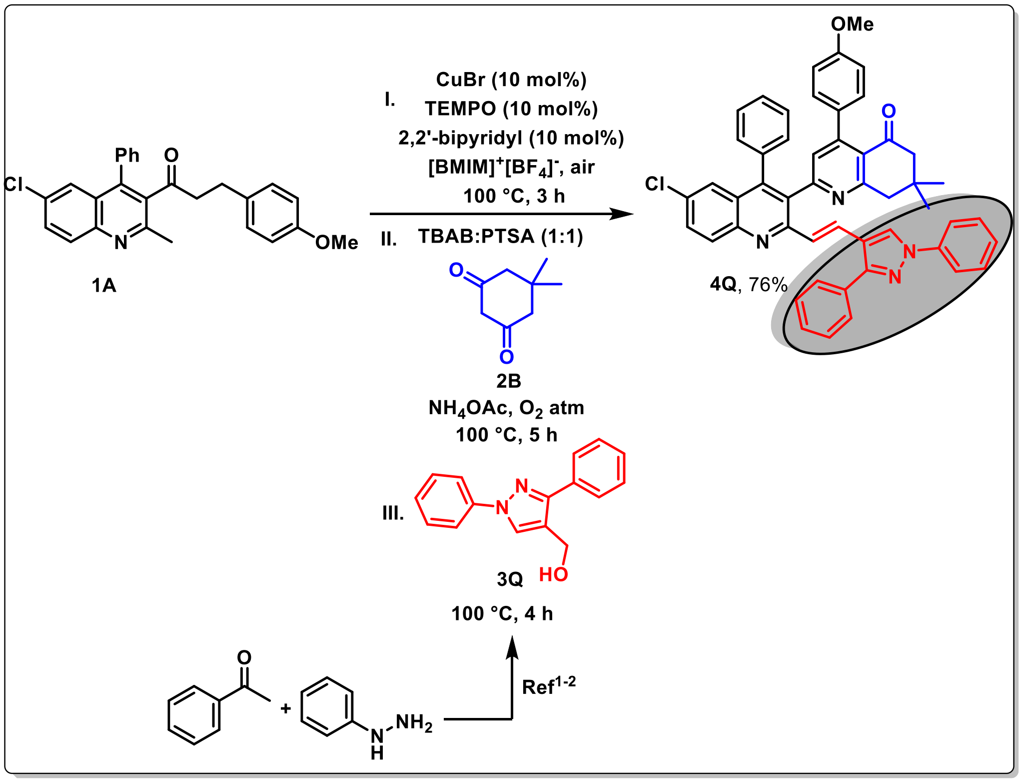
2.3 The gram-scale synthesis of 4A



To an oven-dried reaction vial, added alkylated ketone **1** (10 mmol), CuBr (10 mol%), TEMPO (10 mol%), and $[BMIM]^+[BF_4]^-$ (15 ml), and the reaction mixture was stirred at 100 °C for 3 h in the air atmosphere, resulting in the formation of chalcone **1A'**. Then TBAB:PTSA (1:1) (2000mg), 1,3-Cyclohexanedione **2A** (15 mmol) and NH_4OAc (100 mmol), were added and the reaction was continued at 100 °C for 5 h in the O_2 atmosphere, to form the cyclized intermediate **C**. After the formation of the cyclized intermediate **C**, alcohol **3A** was added and the reaction was continued at 100 °C for 4 h to obtain C(sp^3)-H functionalized quinolinyl quinolinone **4A**. The progress of the reaction was monitored using TLC. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with water (400 ml) and then extracted with DCM (500 ml x 2). The combined organic layers were dried over anhydrous $MgSO_4$, and the crude reaction mixture was purified by silica gel column chromatography using 10% EtOAc/Pet ether as eluent, to yield the desired product of C(sp^3)-H functionalized quinolinyl dihydroquinolinone **4A** in a slightly decreased yield of 78%.

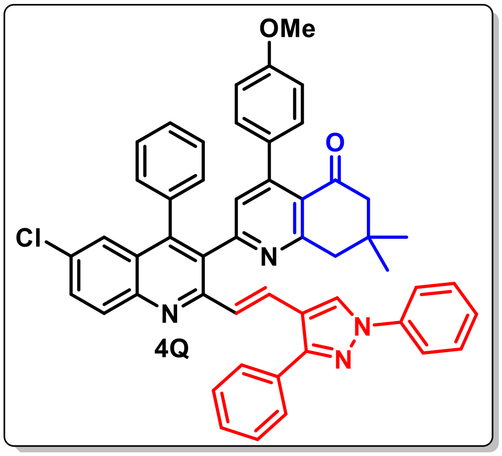
2.4 Product functionalization

2.4.1 Synthesis of the heterocyclic containing C(sp^3)-H functionalized quinolinyl quinolinone (4Q)

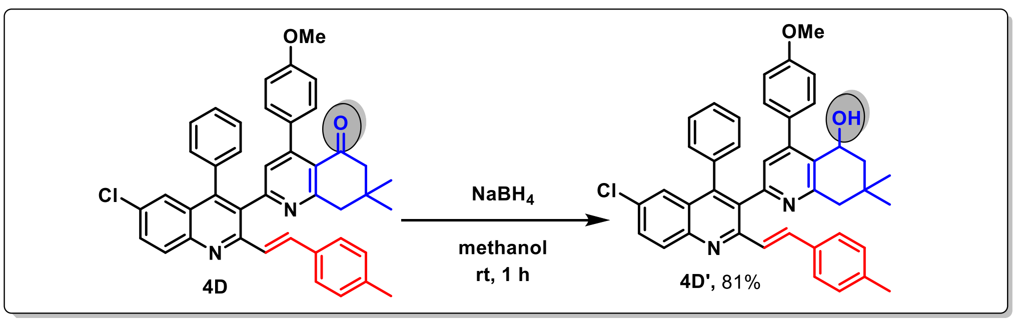


The synthesis of (1,3-diphenyl-1H-pyrazol-4-yl) methanol **3H** was performed according to previously published procedures [1,2]. To an oven-dried reaction vial, added alkylated ketone **1** (1 mmol), CuBr (10 mol%), TEMPO (10 mol%), and $[BMIM]^+[BF_4]^-$ (1.5 ml), and the reaction mixture was stirred at 100 °C for 3 h in the air atmosphere, resulting in the formation of chalcone **1A'**. Then TBAB:PTSA (1:1) (200mg), 1,3-Cyclohexanedione **2A** (1.5 mmol) and NH_4OAc (10 mmol) were added and the reaction was continued at 100 °C for 5 h in the O_2 atmosphere, to form the cyclized intermediate **C**. After the formation of the cyclized intermediate **C**, alcohol **3Q** was added and the reaction was continued at 100 °C for 4 h to obtain C(sp^3)-H functionalized quinolinyl quinolinone **4Q**. The progress of the reaction was monitored using TLC. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with water (40 ml), and then extracted with DCM (50 ml x 2). The combined organic layers were dried over anhydrous $MgSO_4$, and the crude reaction mixture was purified by silica gel column chromatography using 15% EtOAc/Pet ether as eluent, to yield the desired product of C(sp^3)-H functionalized quinolinyl quinolinone **4Q.**

(*E*)-6'-chloro-2'-(2-(1,3-diphenyl-1H-pyrazol-4-yl)vinyl)-4-(4-methoxyphenyl)-7,7-dimethyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4Q). Purification was carried out by column chromatography on silica gel using a 15% ethyl acetate/Pet ether mixture, resulting in the isolation of **4Q** as a Dark brown solid (80% yield); mp: 274-276 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 – 8.01 (m, 3H), 7.72 (t, *J* = 7.5 Hz, 4H), 7.65 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.38 (dd, *J* = 14.8, 7.4 Hz, 3H), 7.31 (dd, *J* = 13.9, 7.5 Hz, 4H), 7.13 (s, 2H), 6.90 (dt, *J* = 14.9, 12.2 Hz, 5H), 6.79 (s, 1H), 3.82 (s, 3H), 2.98 (s, 2H), 2.53 (s, 2H), 1.08 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 162.7, 159.6, 153.2, 152.5, 150.9, 139.6, 135.7, 133.1 132.2, 132.0, 131.4, 131.0, 130.0, 129.5, 129.4, 128.7, 128.5, 128.2, 128.1, 128. 0, 126.9, 126.8, 125.3, 123.4, 119.9, 119.1, 113.5, 55.3, 53.9, 47.5, 32.7, 29.7. **FT-IR**: ν = 2931, 2141, 1692, 1510, 1364, 1242, 1145, 959, 830, 701, 543 cm^{-1}. **HRMS (ESI)**: $C_{51}H_{40}ClN_3O_2$ requires 763.2840 $(M + H)^+$; found: 763.2849.

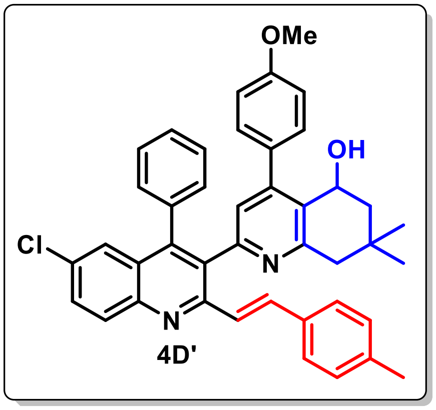


2.4.2 Selective reduction of ketone



A previously established procedure was used for the selective reduction of the keto compound **4D**.[3] In a round-bottom flask Compound **4D** (1.0 mmol) was added and dissolved using methanol (10 ml), allowed to stir at room temperature for 5 mins. Then, sodium borohydride (0.5 mmol) was slowly added to the dissolved solution of **4D**, and the reaction was continued to be stirred at RT for 1 h. The progress of the reaction was monitored using TLC. After the reaction was completed, water was added to the reaction mixture. However, a white precipitate appeared, which was then completely filtered and dried under ambient air conditions to obtain the pure product **4D'** in 81% yield.

(*E*)-6'-chloro-4-(4-methoxyphenyl)-7,7-dimethyl-2'-(4-methylstyryl)-4'-phenyl-5,6,7,8-tetrahydro-[2,3'-biquinolin]-5-ol (4D'). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **4D'** as a Dark brown solid (81% yield); mp: 256-258 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 15.6 Hz, 1H), 7.64 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.40 – 7.28 (m, 5H), 7.15 (dd, *J* = 15.4, 11.9 Hz, 4H), 7.04 (dd, *J* = 21.3, 7.0 Hz, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.67 (s, 1H), 5.11 (d, *J* = 40.0 Hz, 1H), 3.82 (s, 3H), 2.93 (d, *J* = 16.7 Hz, 1H),2.73 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H), 1.94 (dd, *J* = 13.4, 6.2 Hz, 1H), 1.71 (dd, *J* = 13.6, 6.7 Hz, 3H), 1.14 (s, 3H), 1.01 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 156.8, 155.2, 154.0, 149.3, 146.8, 146.3, 138.5, 136.2, 135.5, 134.3, 132.8, 131.9, 131.1, 130.9, 130.6, 130.4, 129.3, 129.1, 128.9, 127.8, 127.4, 127.1, 126.6, 125.3, 125.1, 114.4, 65.1, 55.3, 47.3, 44.2, 30.5, 30.1, 27.4, 21.4. **FT-IR**: ν = 2952, 1681, 1577, 1511, 1366, 1244, 1175, 1024, 834, 701, 538 cm^{-1}. **HRMS (ESI)**: $C_{42}H_{38}ClN_2O_2$ requires 637.2622 $(M + H)^+$; found: 637.2632.



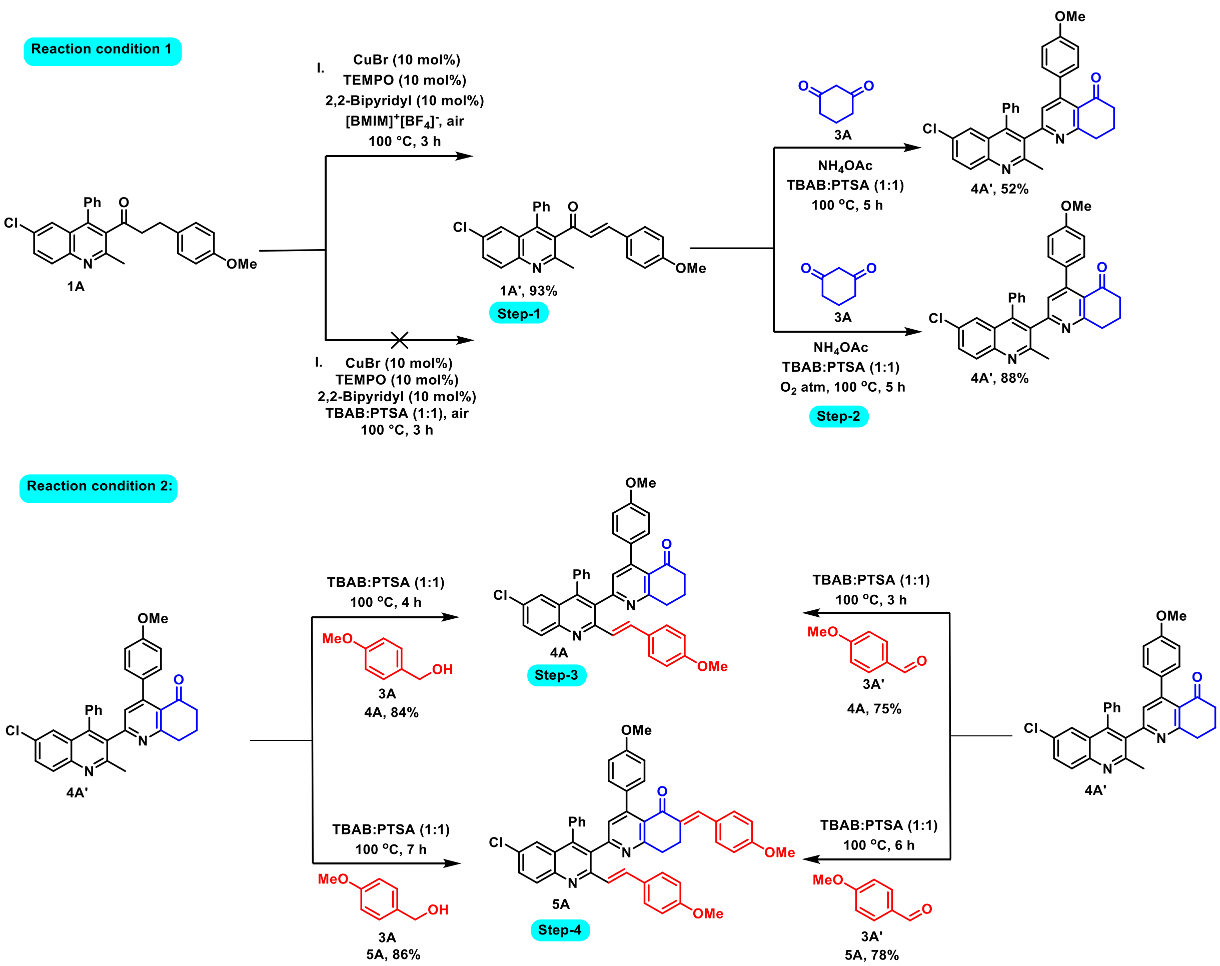
3. References

1 Y. Zhan, Q. Wei, J. Zhao and X. Zhang, *RSC Adv*, 2017, **7**, 48777–48784.

2 M. M. R. Badal, H. M. Ashekul Islam, M. Maniruzzaman and M. Abu Yousuf, *ACS Omega*, 2020, **5**, 22978–22983.

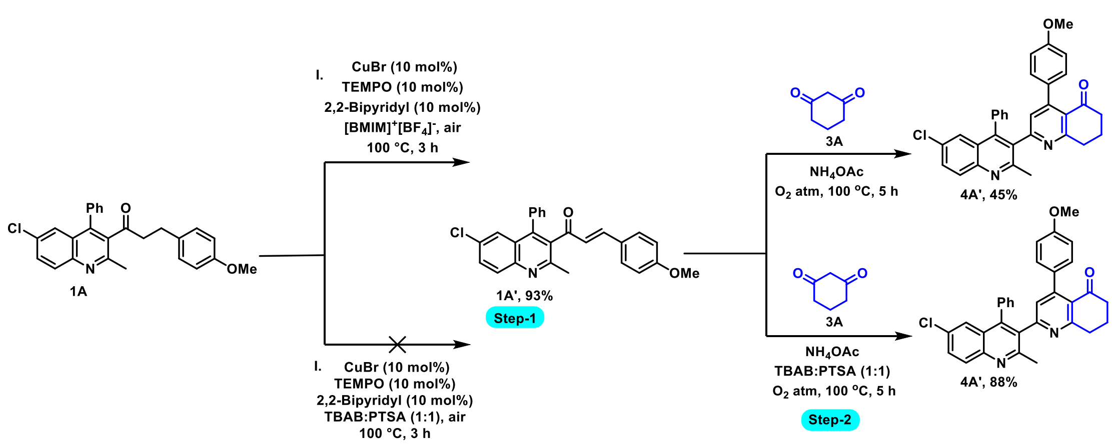
3 X. Lin, X. Wang, R. Li, Z. Wang, W. Liu, L. Chen, N. Chen, S. Sun, Z. Li, J. Hao, B. Lin and L. Xie, *ACS Omega*, 2022, **7**, 10994–11001.

4. Control Experiment



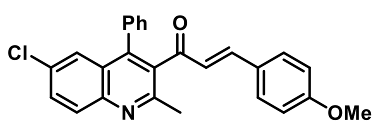
Scheme S1 Control experiment study for the synthesis of **4** and **5**

Reaction condition 1:



As illustrated in Scheme S1, a model reaction was examined using alkylated ketone **1A** as a starting material followed by the addition of CuBr (10 mol%), TEMPO (10 mol%), 2,2-bipyridyl (10 mol%), and $[BMIM]^+[BF_4]^-$ (1.5 ml) which resulted in a 93% yield of the chalcone intermediate (**1A'**) Similarly, this reaction was also conducted in a DES medium but the formation of **1A'** was unsuccessful (Reaction condition 1, Step 1). From this observation, we found the crucial role of an ionic liquid in facilitating the formation of **1A'** from the alkylated ketone **1A**. In addition, the chalcone intermediate was isolated and confirmed by ^{1}H and ^{13}C NMR (Spectra are given on page 17). However, when **1A'** was treated with, diketone **3A**, NH_4OAc in the O_2 atmosphere in the absence of DES, **4A'** was observed in a 45% yield. Conversely, when the same reaction was conducted in the presence of DES, the yield of **4A'** increased to 88%. In this context, it was found that DES significantly enhanced the reaction (Reaction condition 1, Step 2). Formation of **4A'** was characterized by ^{1}H and ^{13}C NMR (Spectra are given on page 18).

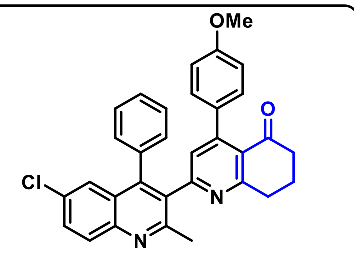
(*E*)-1-(6-chloro-2-methyl-4-phenylquinolin-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (1A'). White solid



1A'

(93% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 9.0 Hz, 1H), 7.68 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 3H), 7.30 – 7.26 (m, 4H), 7.04 (d, *J* = 16.2 Hz, 1H), 6.84 (d, *J*= 8.8 Hz, 2H), 6.49 (d, *J* = 16.2 Hz, 1H), 3.81 (s, 3H), 2.69 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.1, 162.1, 155.5, 147.0, 146.1, 144.5, 134.6, 133.6, 132.4, 130.9, 130.5, 130.23, 129.9, 128.8, 128.5, 126.6, 126.2, 125.5, 125.1, 114.5, 55.4, 23.9.

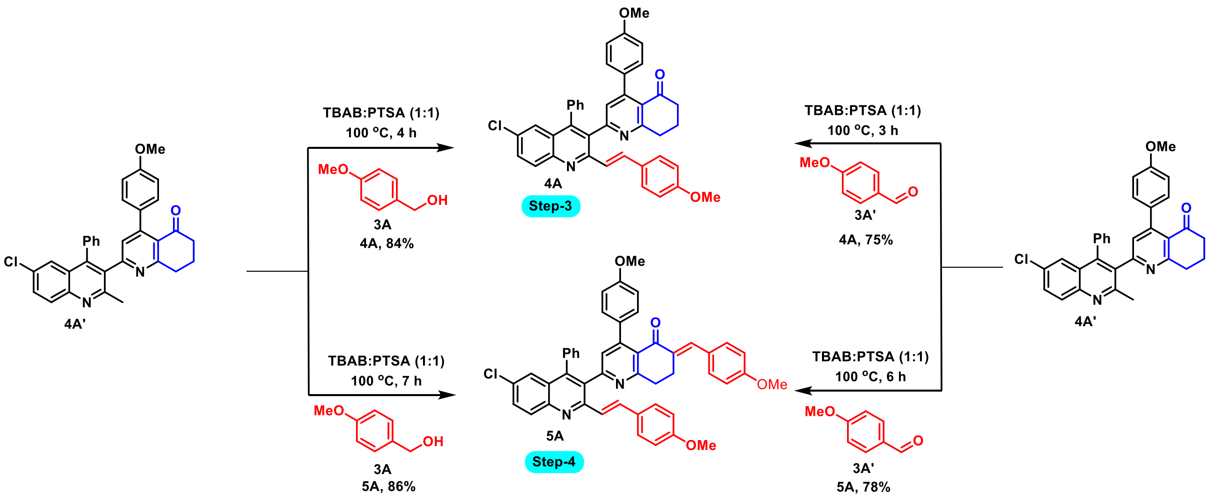
(6'-chloro-4-(4-methoxyphenyl)-2'-methyl-4'-phenyl-7,8-dihydro-[2,3'-biquinolin]-5(6H)-one (4'). Pale



4A'

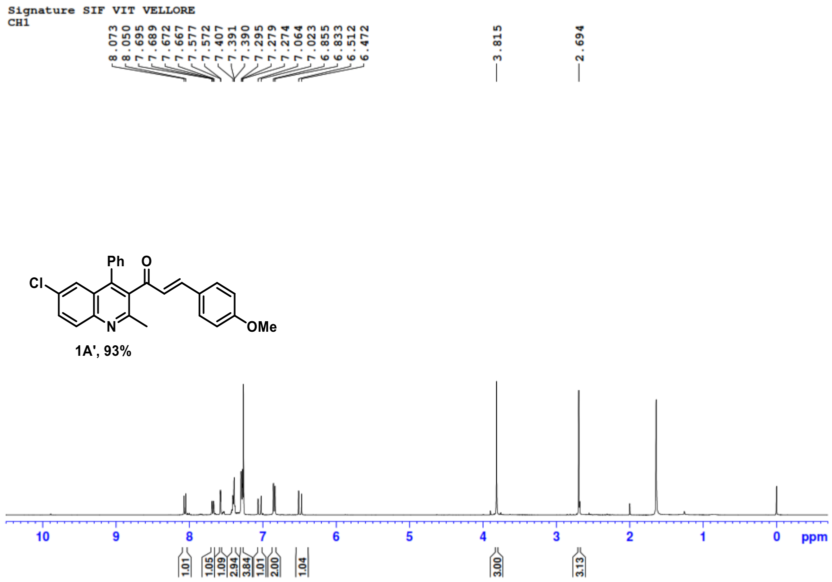
brown solid (88% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, J = 9.0 Hz, 1H), 7.57 (dd, J = 8.9, 2.3 Hz, 1H), 7.44 (d, J = 2.2 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.07 (s, 2H), 6.78 (s, 4H), 6.64 (s, 1H), 3.74 (s, 3H), 3.10 (t, J = 6.1 Hz, 2H), 2.62 – 2.56 (m, 5H), 2.17 – 2.08 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 164.1, 159.6, 159.5, 157.2, 151.5, 146.2, 145.9, 135.6, 132.8, 132.0, 131.6, 130.7, 130.5, 130.0, 129.2, 128.3, 128.2, 127.4, 126.7, 125.3, 124.5, 113.4, 55.2, 40.1, 33.5, 25.0, 21.5.

Reaction condition 2:

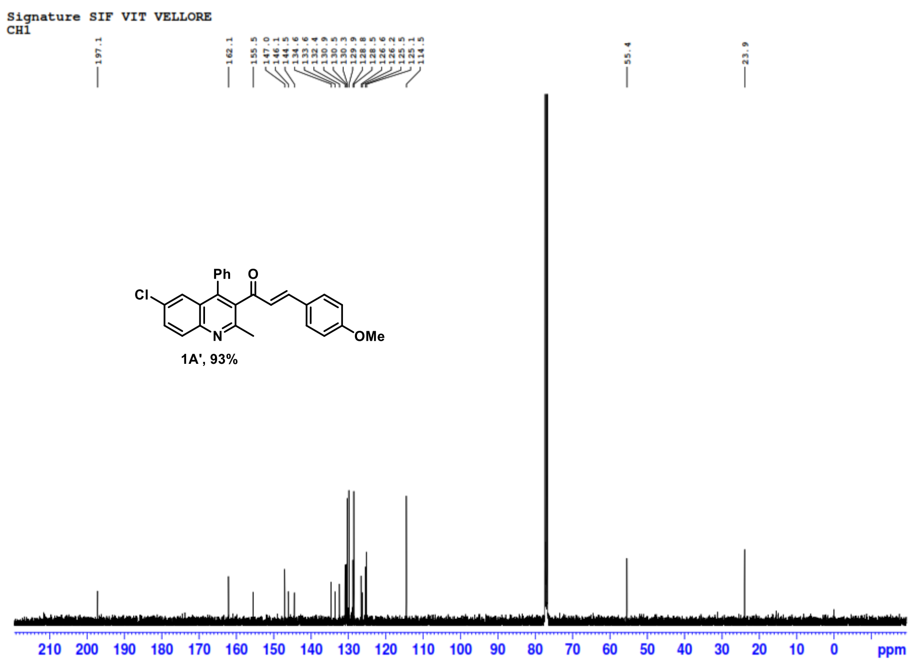


Meanwhile, the reaction was also performed by adding **3A** to intermediate **4A'** under DES condition and continued the reaction at 100 °C for 4 h, resulting in the formation of sp^3 C-H functionalized quinolinyl quinolinone **4A** in 84% yield (Reaction condition 2, Step 3). Furthermore, by adding 3.0 mmol of **3A** under the same DES condition, the α-alkenylated product **5A** was formed in 86% yield (Reaction condition 2, Step 4). Notably, when similar reactions were carried out by adding **3A'** instead of **3A**, the desired products **4A** & **5A** were obtained in 75% and 78% yields, respectively (Reaction condition 2, Steps 3 and 4).

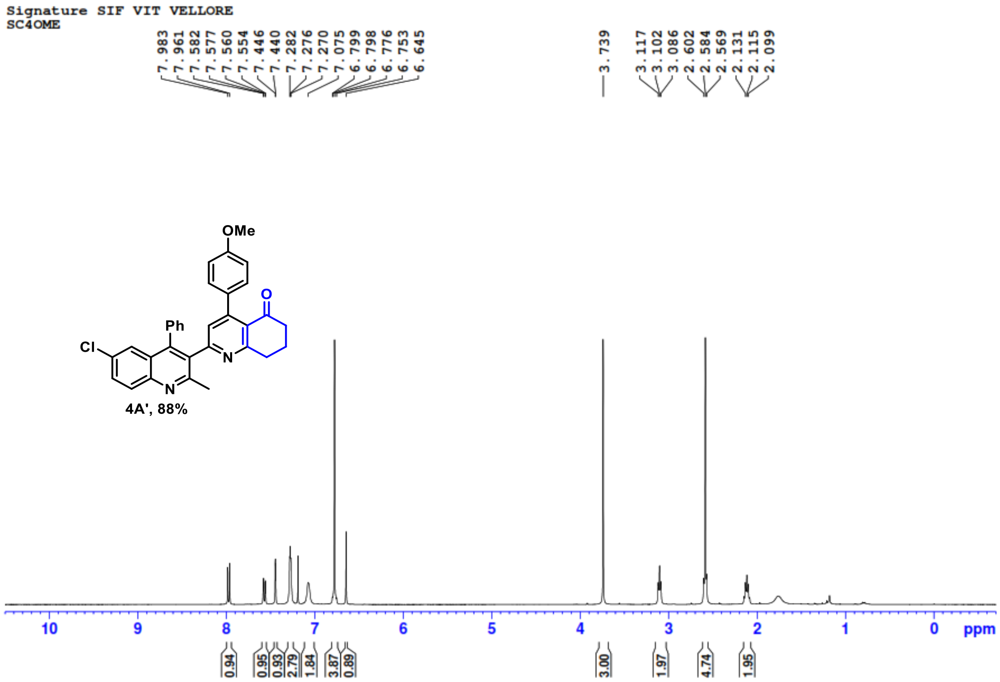
1A' ^{1}H NMR (400 MHz, CDCl$_3$)



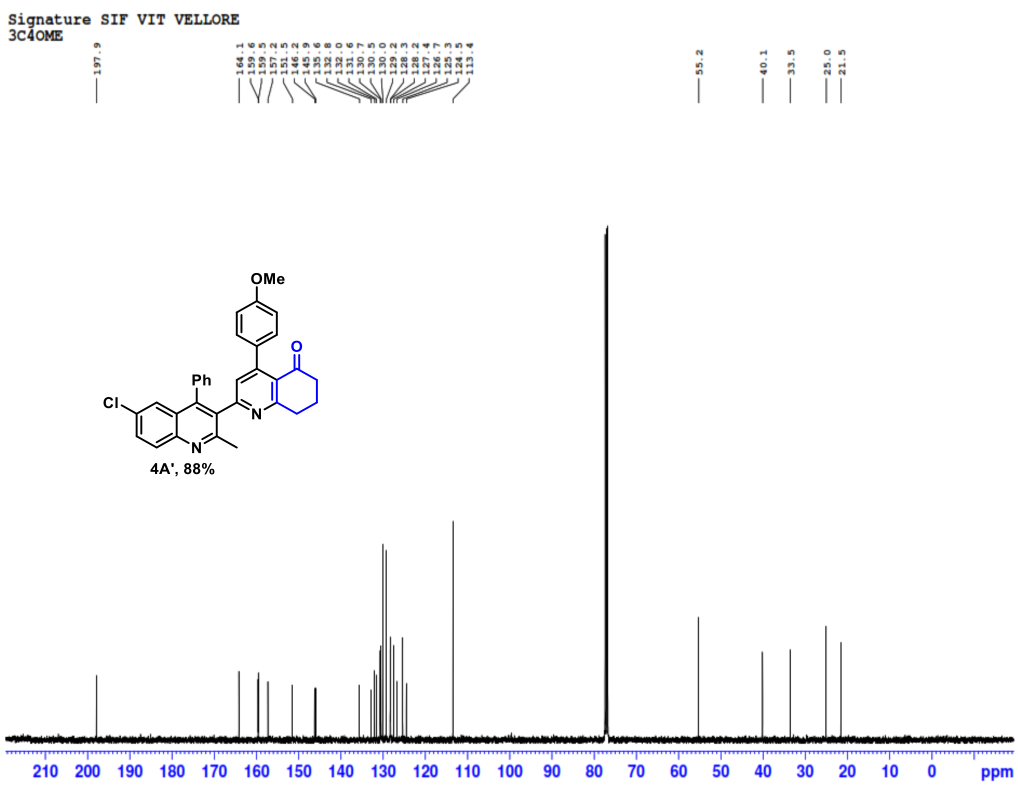
1A' ^{13}C NMR (101 MHz, CDCl$_3$)



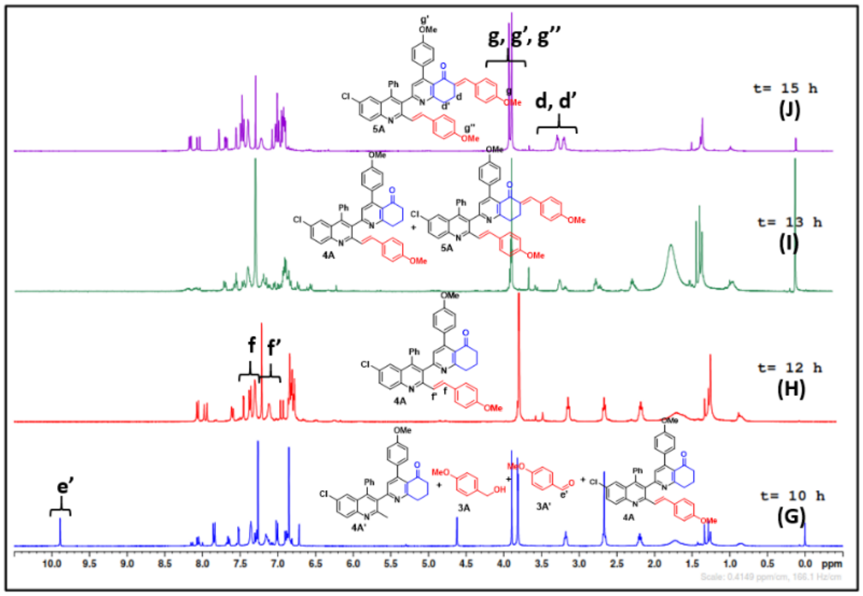
4A' ^{1}H NMR (400 MHz, $CDCl_3$)

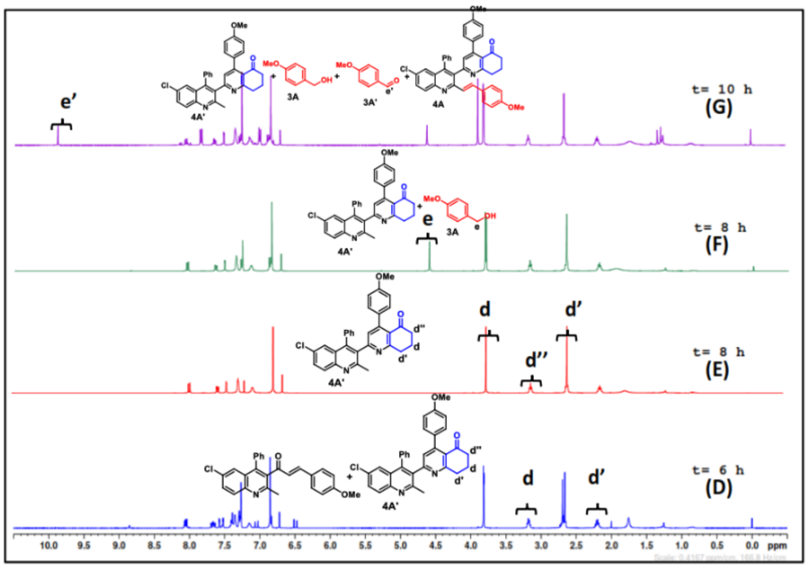


4A' ^{13}C NMR (101 MHz, $CDCl_3$)



5. Reaction Monitoring by ^{1}H NMR Analysis





5.1 Reaction monitoring by ^{1}H NMR analysis for the synthesis of 4 & 5

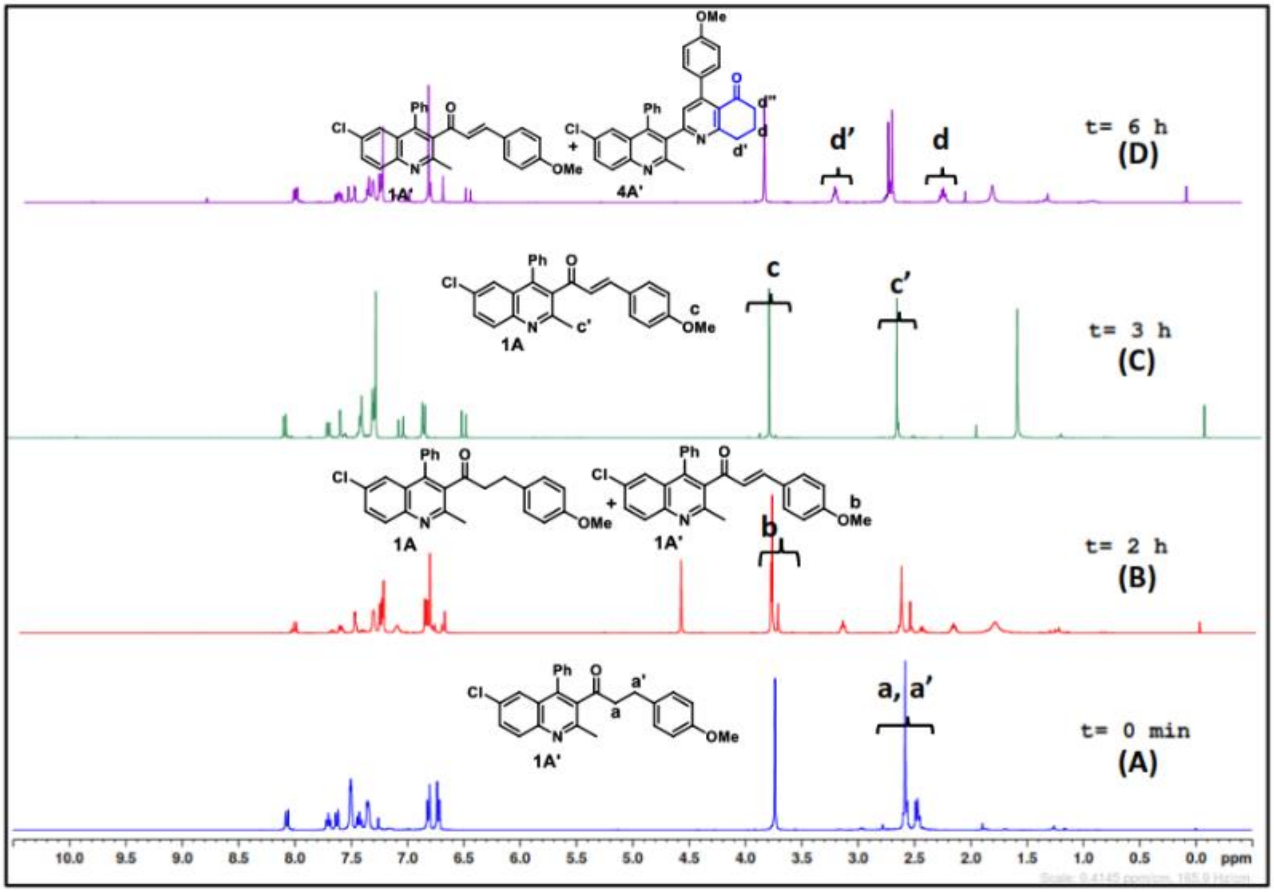


Fig S1 Reaction monitoring by ^{1}H NMR analysis in different time intervals for the synthesis of **4** & **5**

The ^{1}H NMR studies have been conducted to elucidate the mechanism of the sequential reaction in the synthesis of compounds **4** and **5**. The ^{1}H NMR spectrum of **A** was taken for the alkylated ketone **1A**, before the initiation of the reaction, revealing the aliphatic CH_2 protons in the range of 2.4-2.6 ppm. The Spectrum **B** recorded after 2 h shows the formation of the chalcone intermediate **1A'** as well as alkylated ketone **1A,** evidenced by the appearance of H-C=C-H protons at 6.8 and 7.7 ppm. The Spectrum **C,** recorded over a period of 3 h, revealed the exclusive formation of the chalcone intermediate **1A'**, confirmed by the disappearance of the aliphatic CH_2 peaks. The Spectrum **D** and Spectrum **E** were recorded at 6 h and 8 h time intervals, shows the formation of 7,8-dihydro-[2,3'-biquinolin]-5(6H)-one **4A'**, as evidenced by the appearance of aliphatic CH_2 peaks in the range of 2.0-2.1 ppm. Spectrum **F** was recorded after the addition of 4-methoxy benzyl alcohol **3A** to intermediate **4A'**, represented by the benzylic CH_2 appearing at 4.6 ppm. The spectrum **G** was recorded after 10 h, showing the formation of dehydrogenation of benzyl alcohol **3A'**. This was confirmed by the appearance of -CHO proton at 10 ppm along with C(sp^3)-H functionalized 7,8-dihydro-[2,3'-biquinolin]-5(6H)-one **4A**. Spectrum **H** was recorded over a period of 12 h, showing that the reaction was completed with the formation of C(sp^3)-H functionalized 7,8-dihydro-[2,3'-biquinolin]-5(6H)-one **4A**, confirmed by the disappearance of aliphatic methyl protons in **4A'** and the appearance of **4A** olefinic protons at 7.2 and 7.6 ppm. Similarly, by adding an excess amount (3.0 mmol) of alcohol **3A** and continuing the reaction for 15 h, the formation of the Knoevenagel product **5A** was observed. This is confirmed by the disappearance of aliphatic CH_2 protons adjacent to the keto group and the appearance of -C=C-H protons at 7.1 ppm and H-C=C-H protons at 7.3 and 7.7 ppm. All spectra (**Fig S1**) were recorded by performing the reactions according to the standard reaction procedure.

6. Optical Spectral Data of Products 4 and 5

Table S1 Photophysical properties of **4** & **5**

Compound	λ_{abs} (nm)	λ_{em} (nm)	Stoke shift (nm)	Φ_F (%)
4A	305	442	137	2.48
4B	297	426	129	1.17
4C	298	420	122	0.72
4D	303	430	127	0.33
4E	288	445	157	0.26
4F	298	528	117	1.19
4G	304	441	137	0.50
4H	302	507	205	0.23
4I	300	510	210	0.49
4J	298	439	141	2.88
4K	299	360	61	0.32
4L	297	417	120	0.53
4M	300	414	114	0.29
4N	302	414	112	0.32
4O	301	415	114	0.41
4P	297	411	114	0.31
4Q	278	448	170	0.58
5A	289	440	151	5.73
5B	329	438	109	1.36
5C	361	442	81	0.22
5D	316	438	122	0.62
5E	324	426	102	0.42
5F	317	510	193	0.15

The spectral data were measured in DCM solutions at RT, in concentrations ranging from (1.0×10^{-5} M to 5.0×10^{-6} M) for absorption and emission. The Fluorescence quantum yield (±10%) was determined relative to quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F = 0.54$) as the standard.

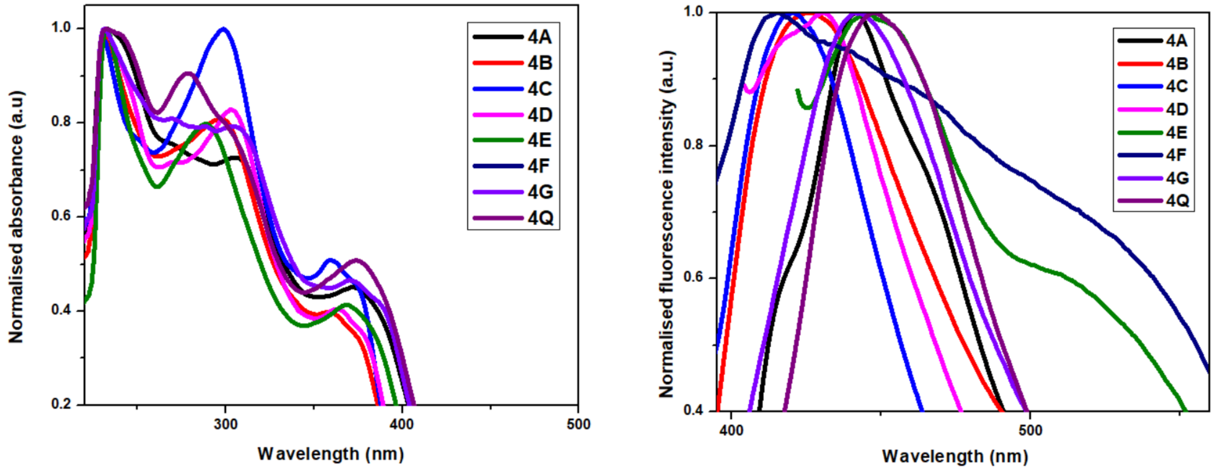


Fig S2 Normalized UV/vis and emission spectra of compounds **4A-4G** and **4Q**

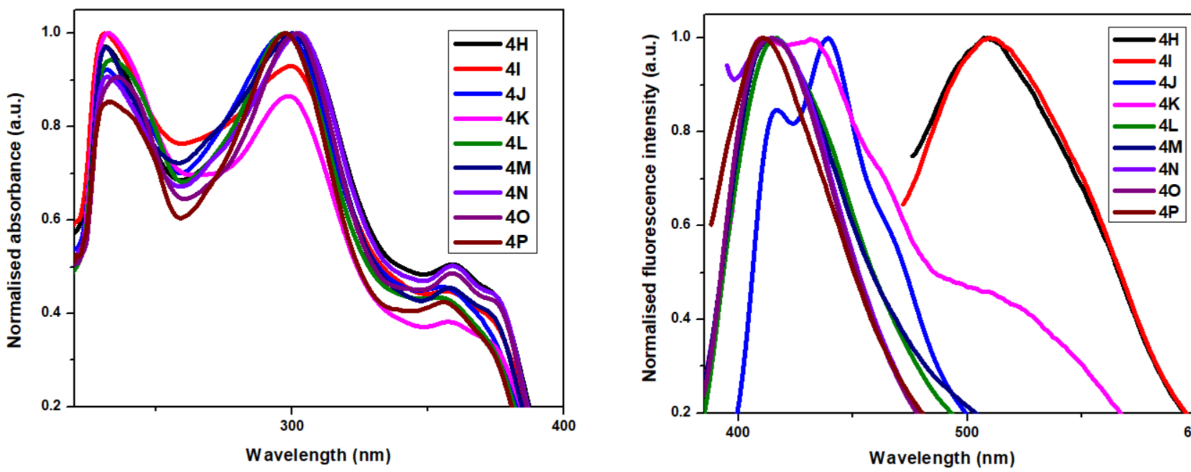


Fig S3 Normalized UV/vis and emission spectra of compounds **4H-4P**

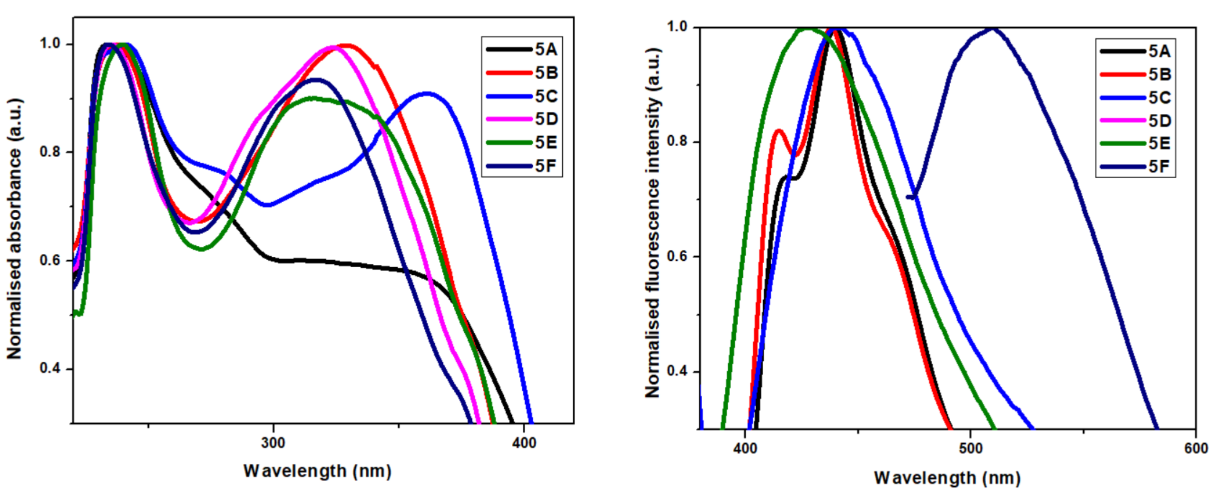
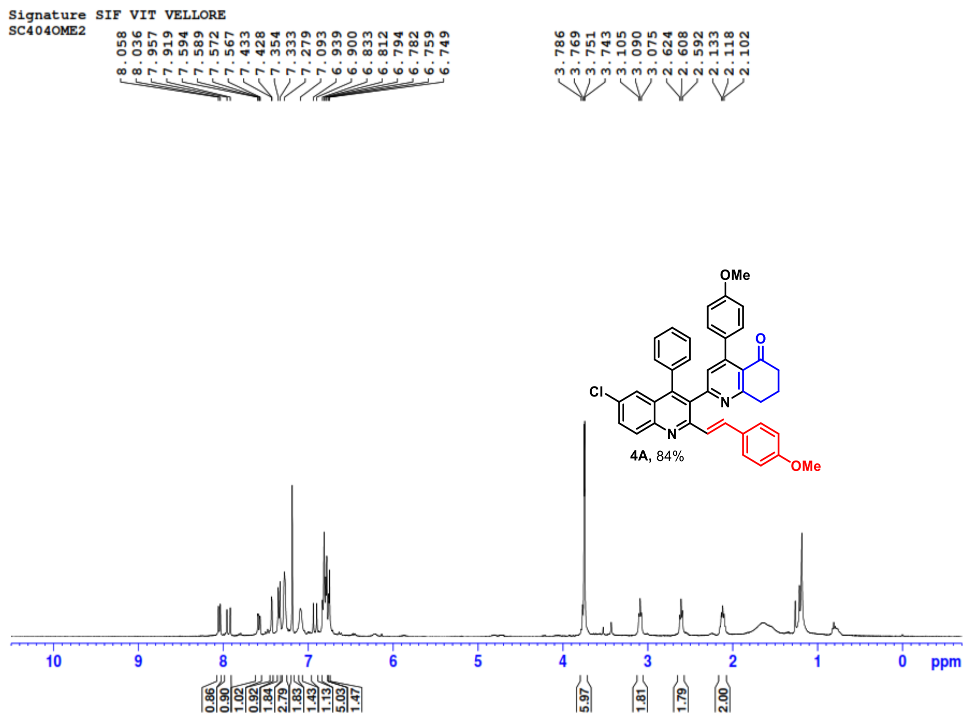


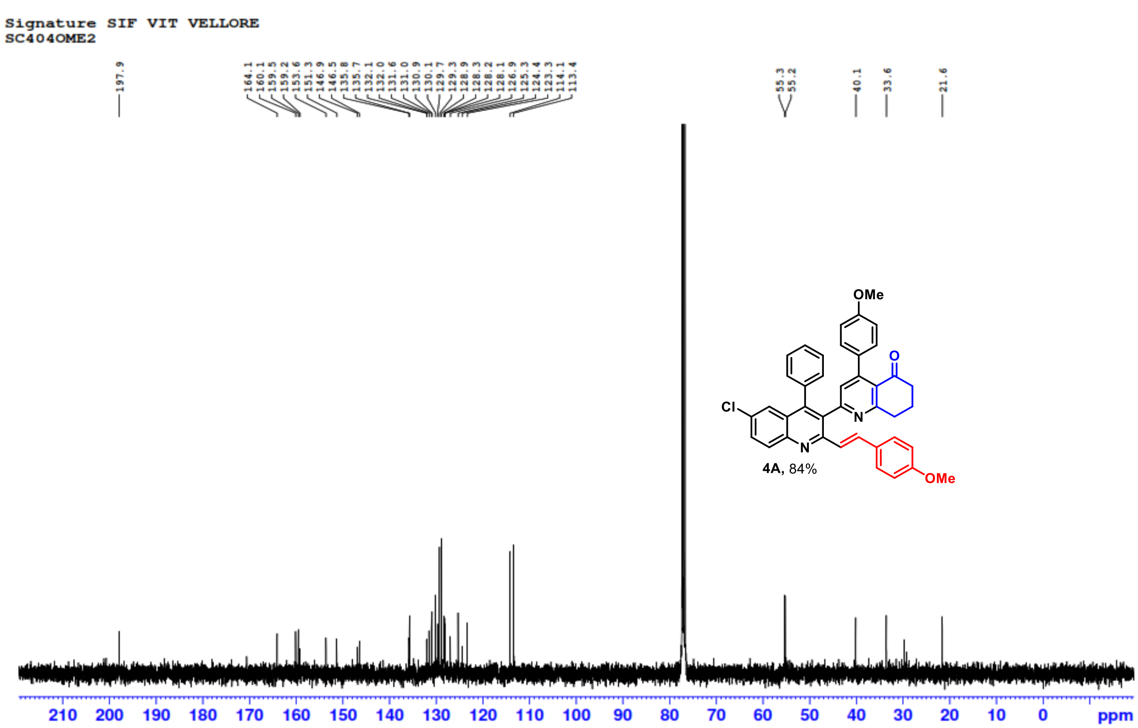
Fig S4 Normalized UV/vis and emission spectra of compounds **5A-5F**

4. Copies of NMR (^{1}H & ^{13}C), FT-IR and HRMS Spectra

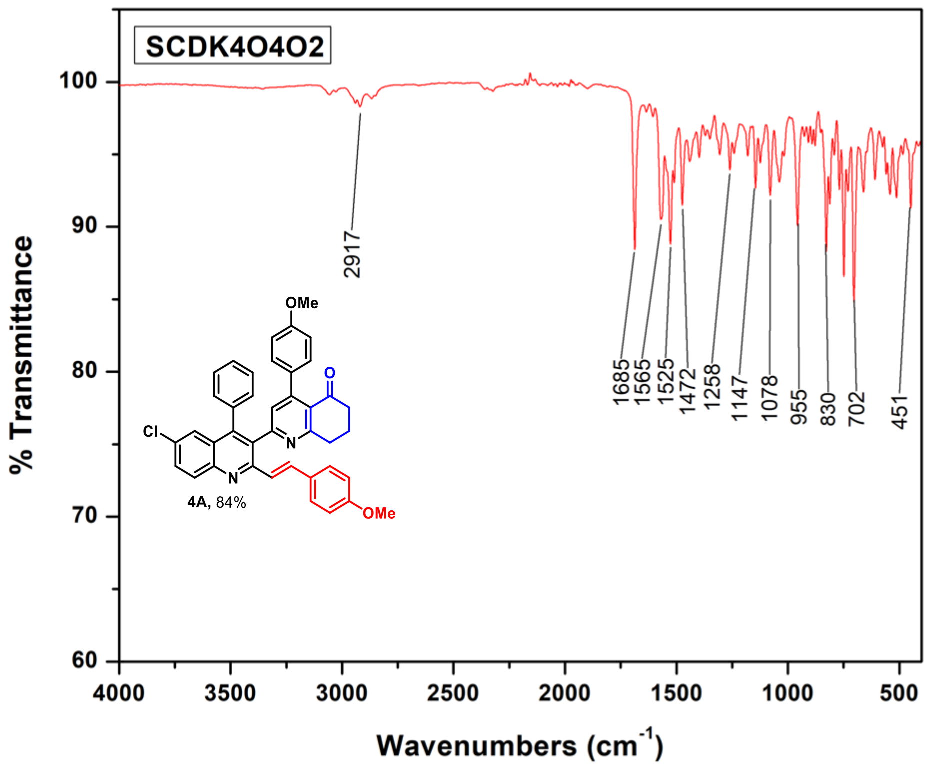
4A ^{1}H NMR (400 MHz, $CDCl_3$)



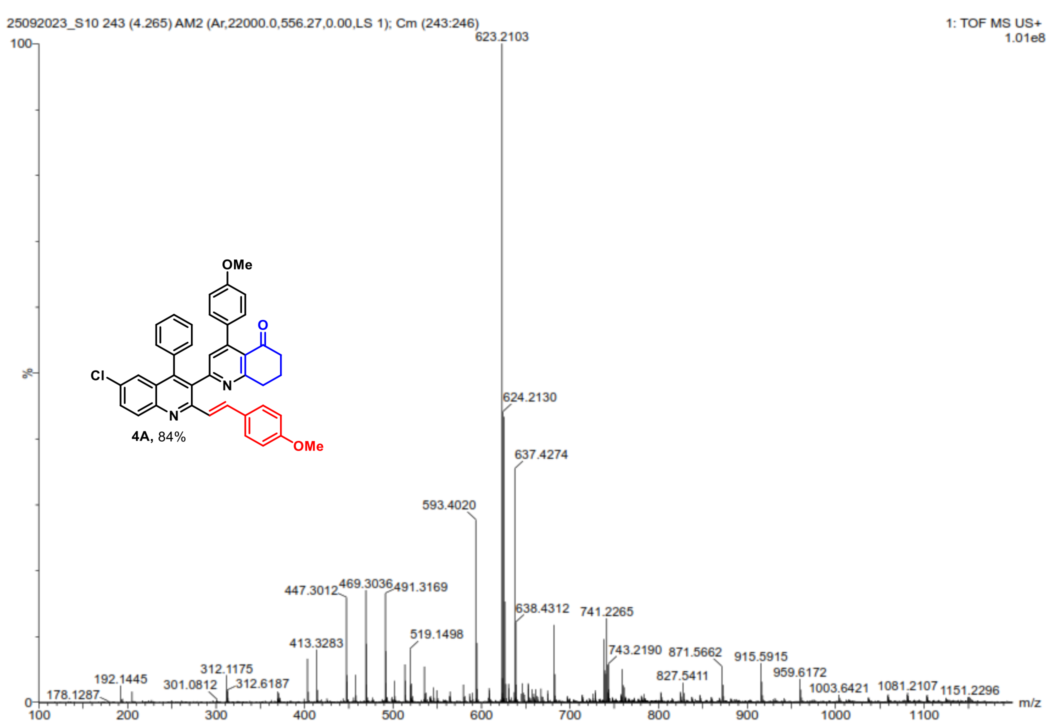
4A ^{13}C NMR (101 MHz, $CDCl_3$)



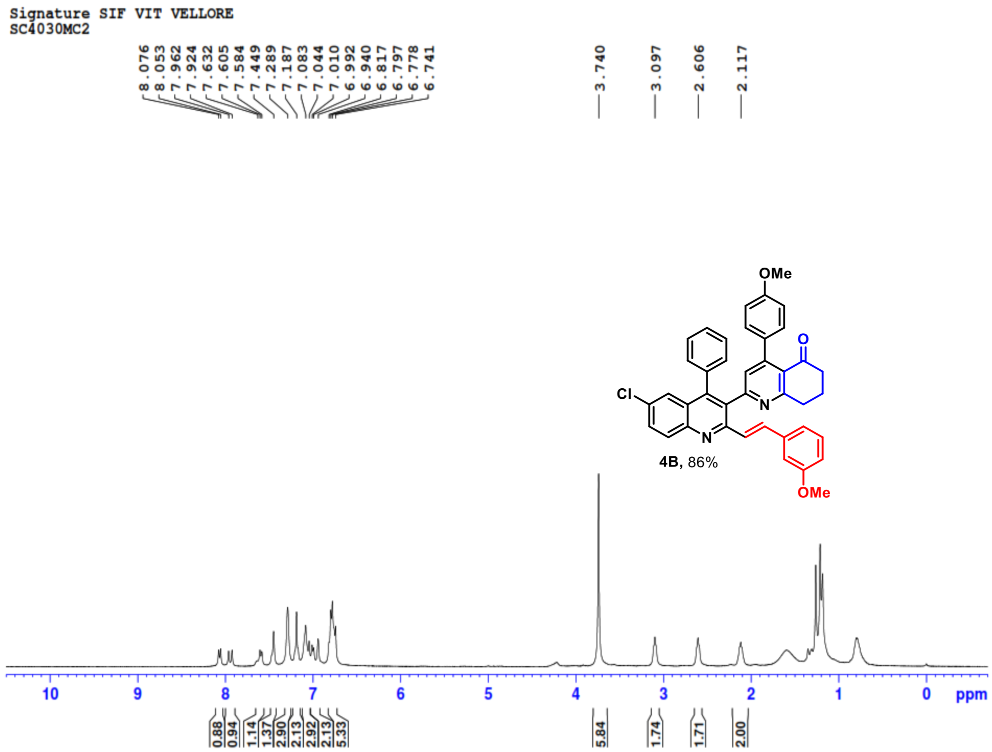
4A FTIR



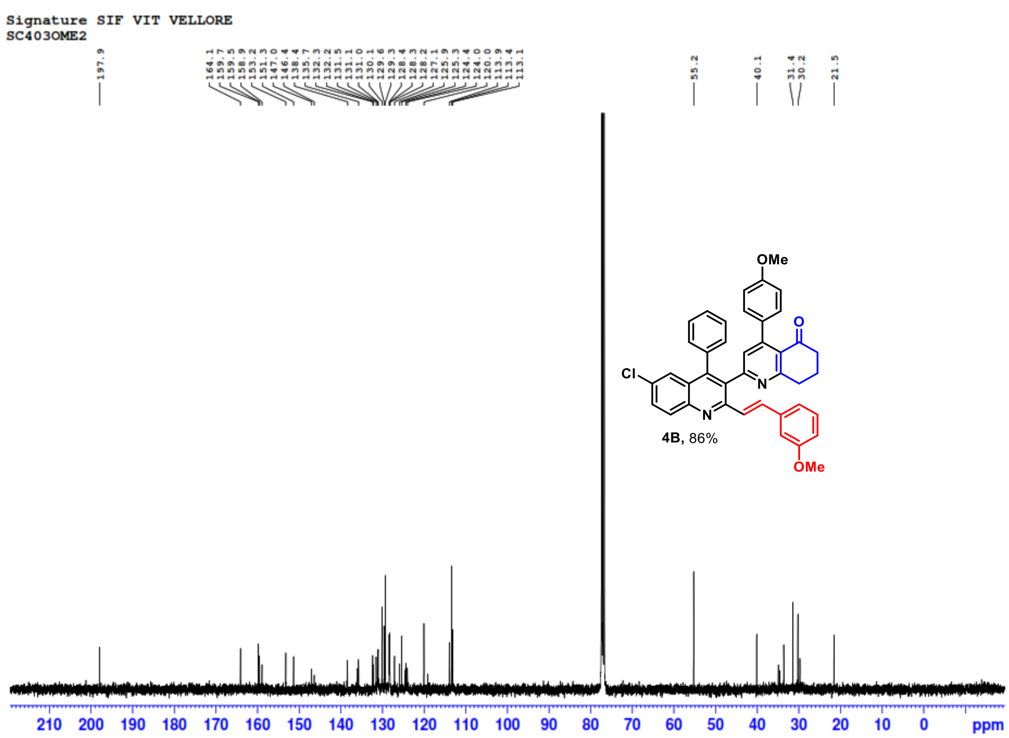
4A HRMS (ESI)



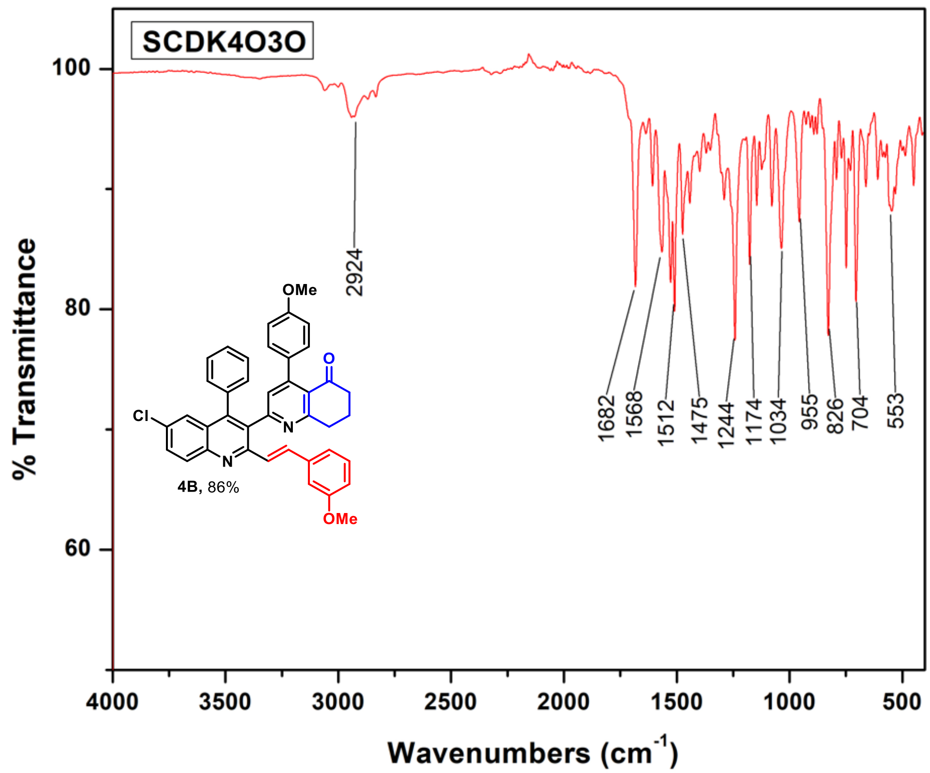
4B ^{1}H NMR (400 MHz, $CDCl_3$)



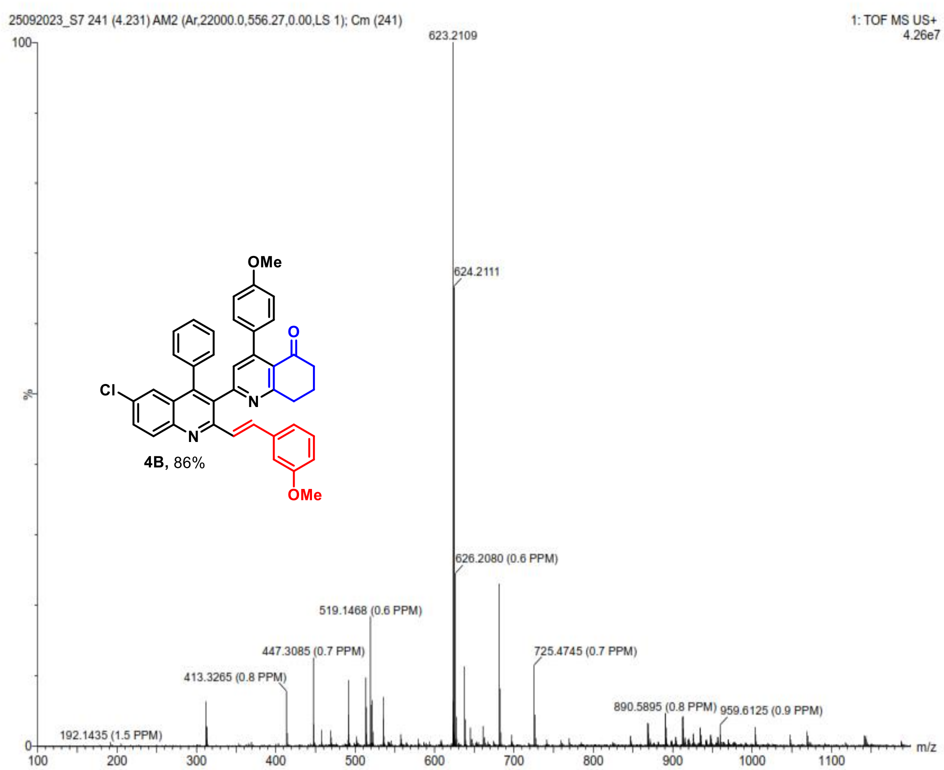
4B ^{13}C NMR (101 MHz, $CDCl_3$)



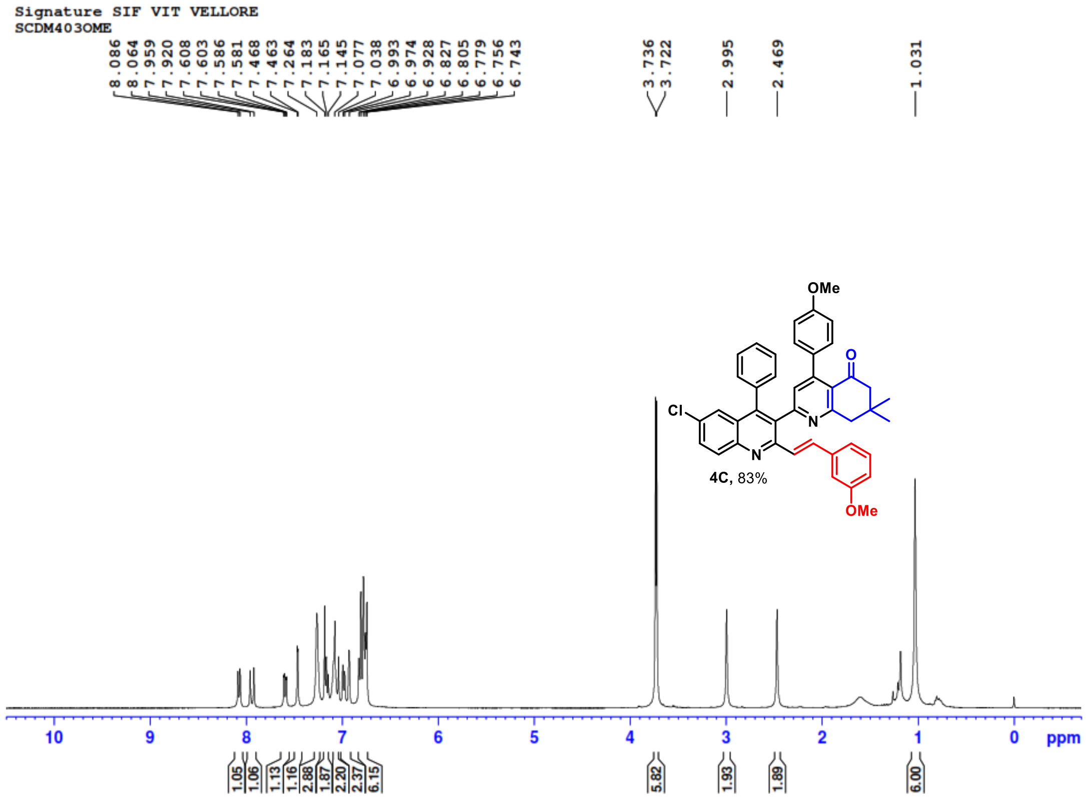
4B FTIR



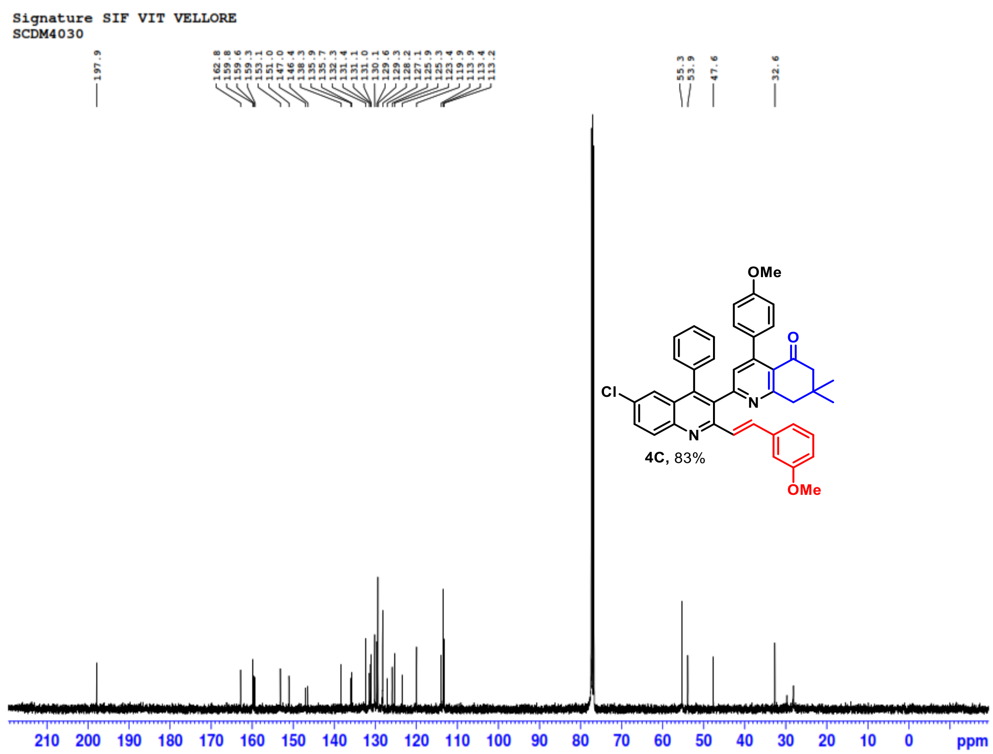
4B HRMS (ESI)



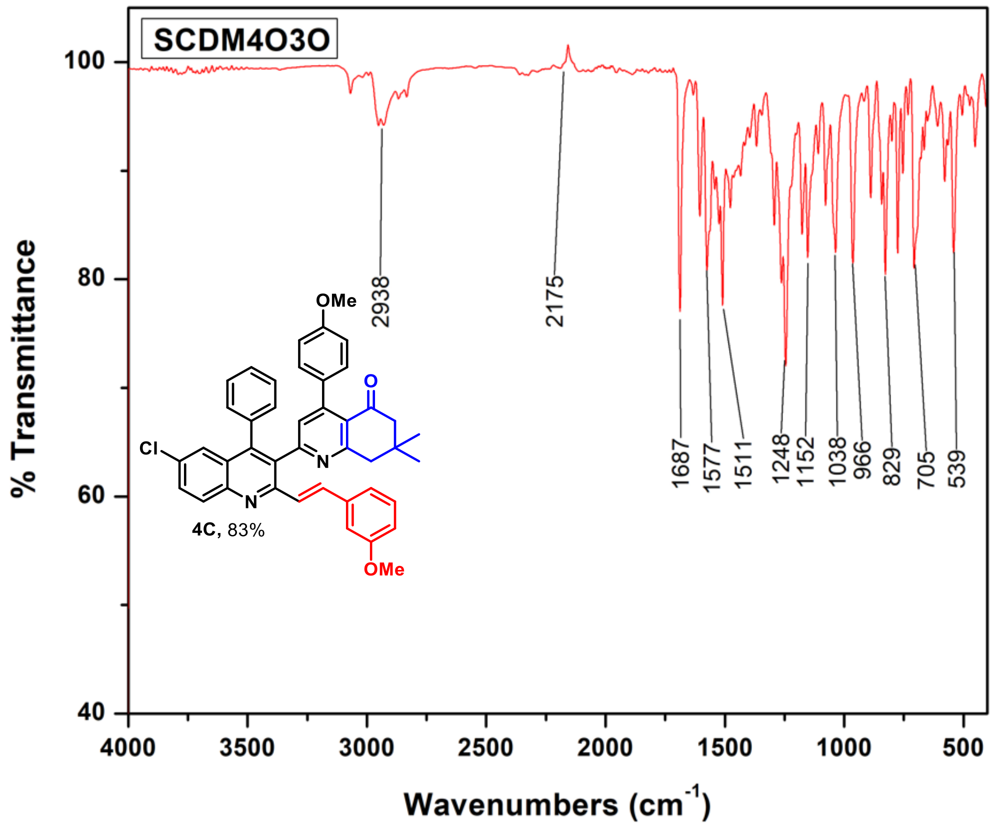
4C ^{1}H NMR (400 MHz, $CDCl_3$)



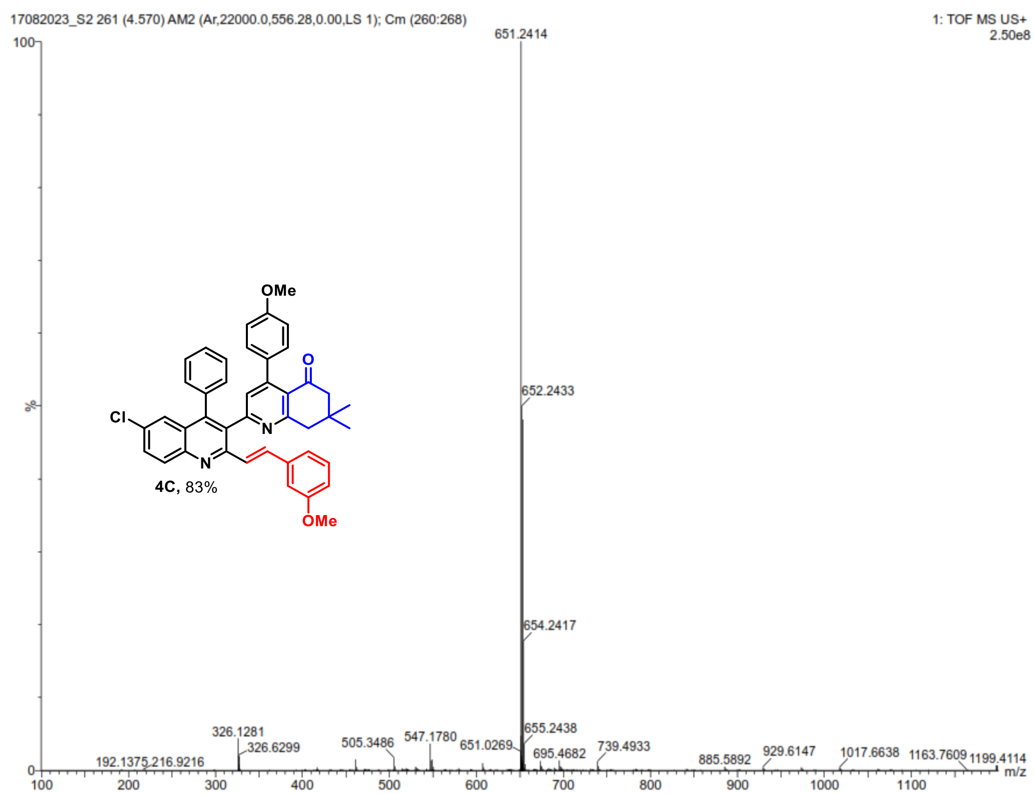
4C ^{13}C NMR (101 MHz, $CDCl_3$)



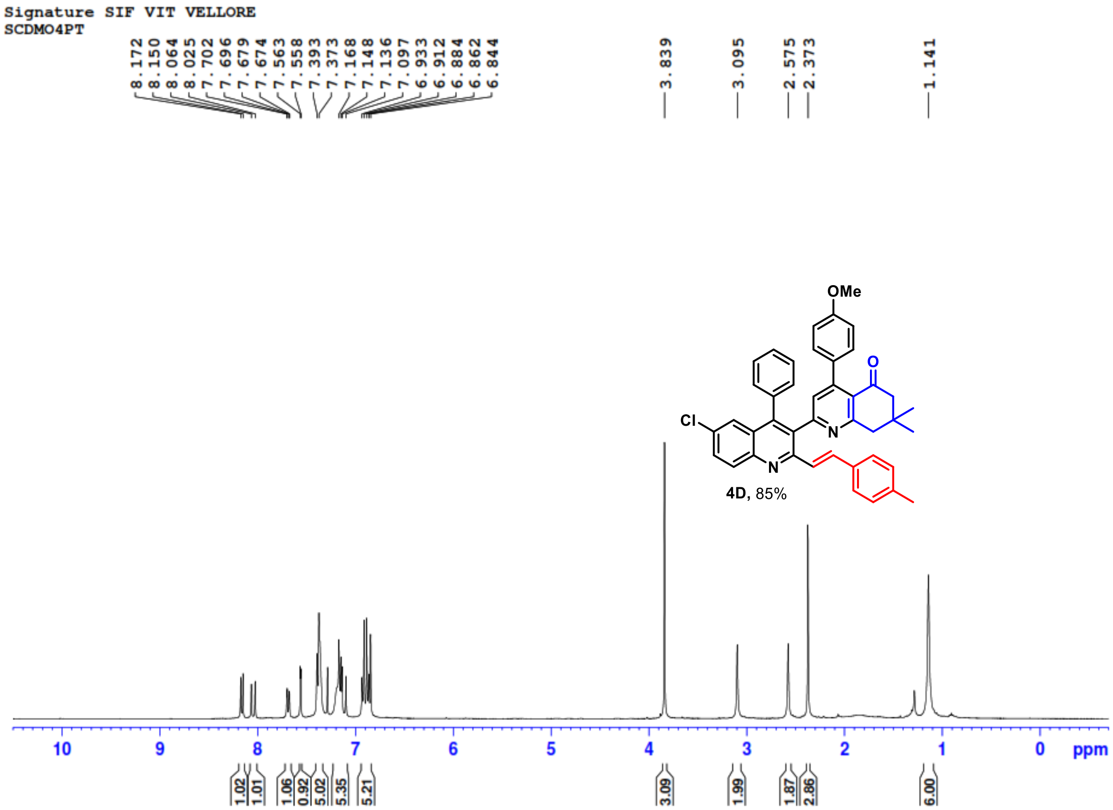
4C FTIR



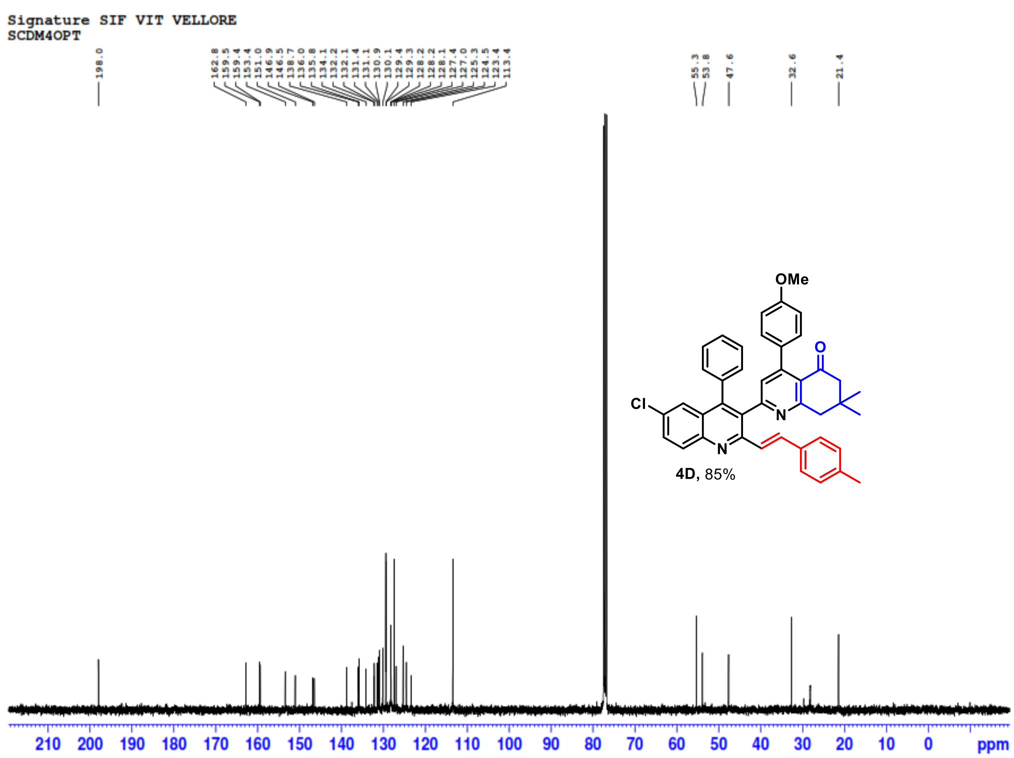
4C ESI (HRMS)



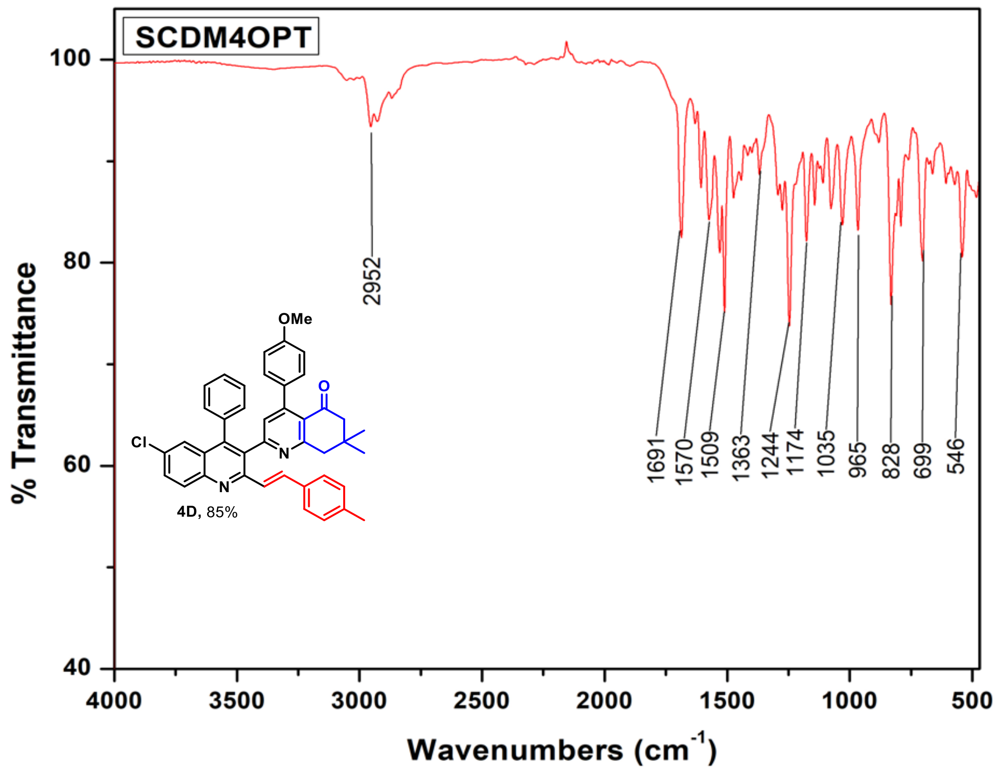
4D ^{1}H NMR (400 MHz, $CDCl_3$)



4D ^{13}C NMR (101 MHz, $CDCl_3$)



4D FTIR



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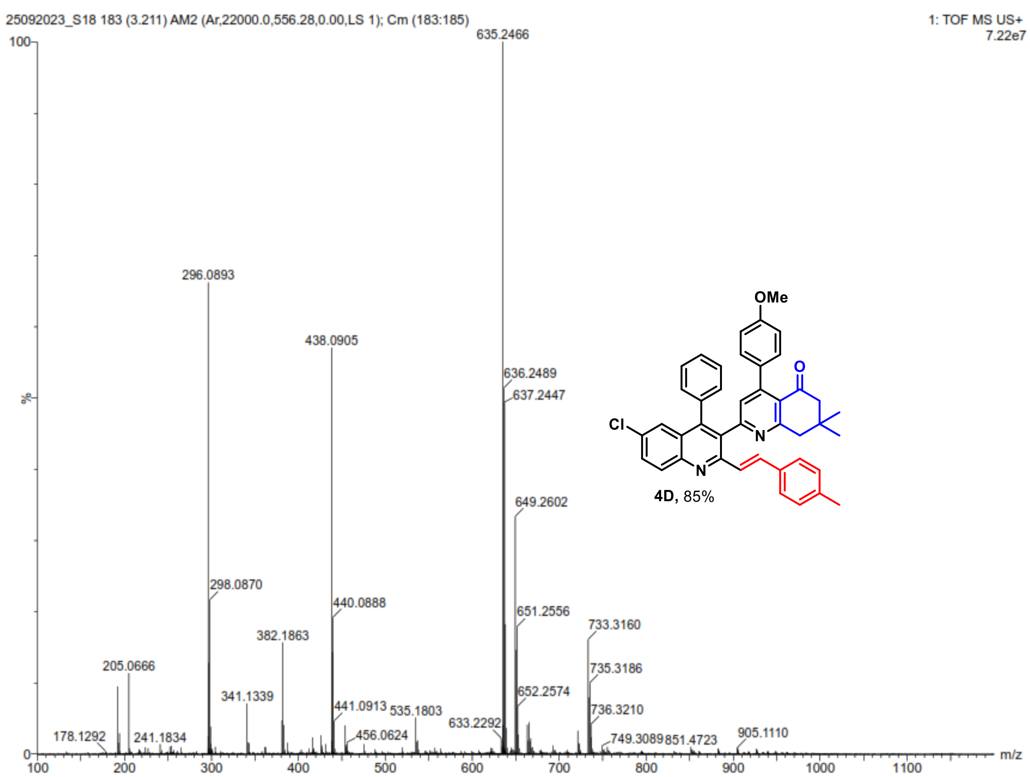
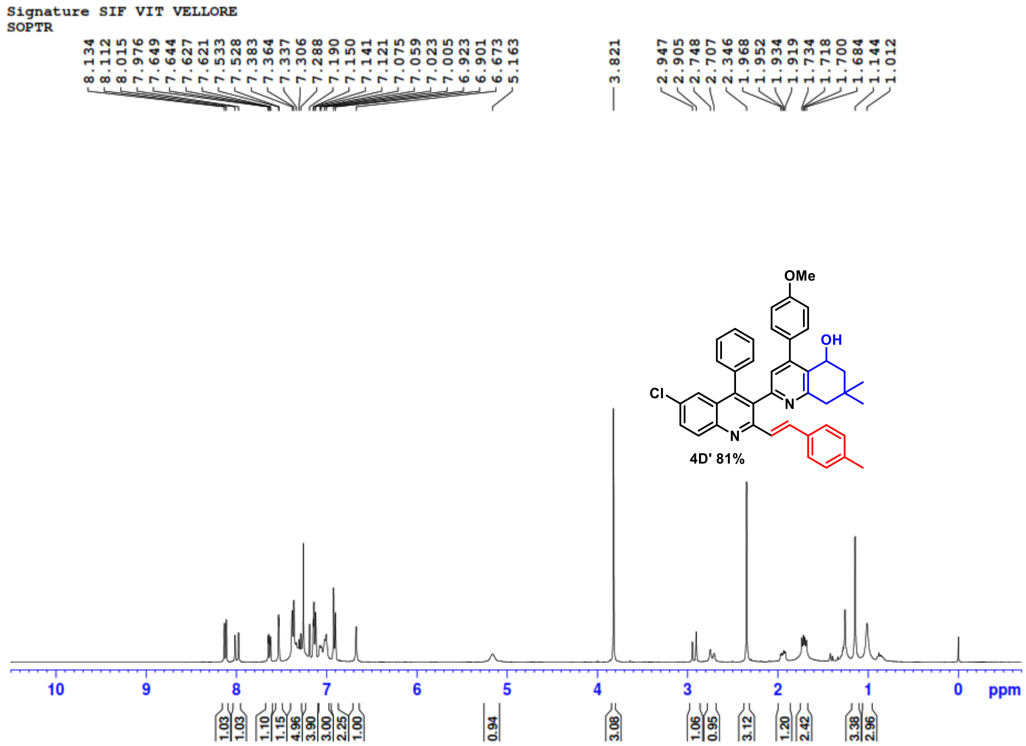
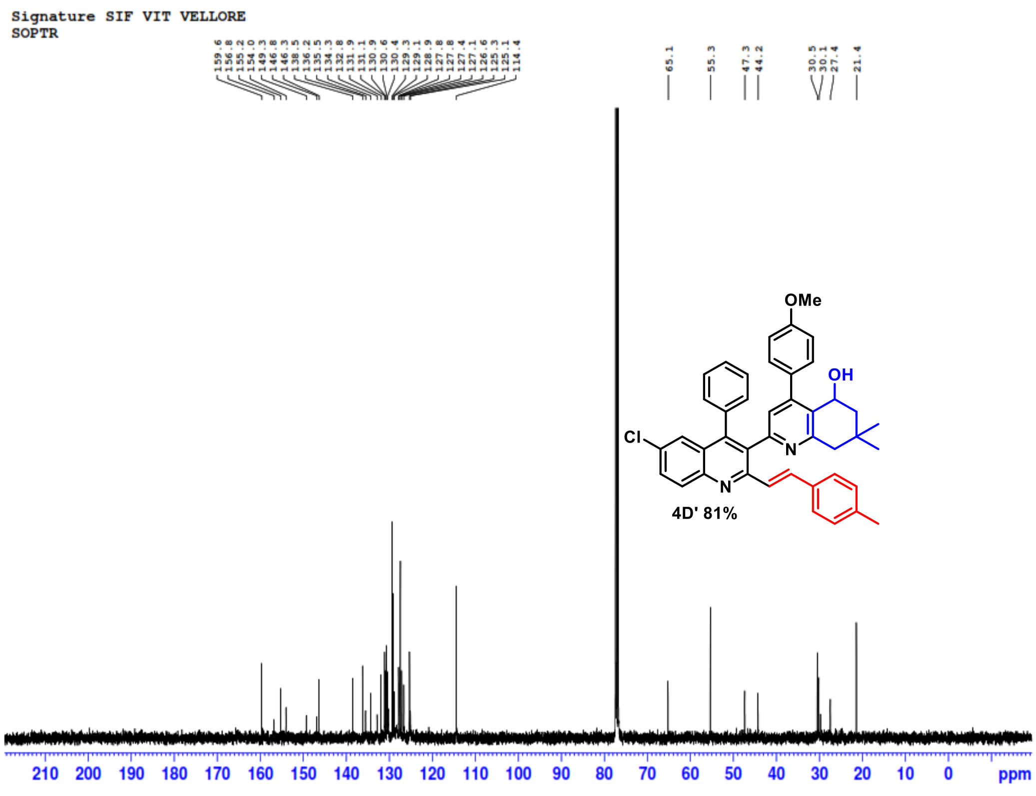


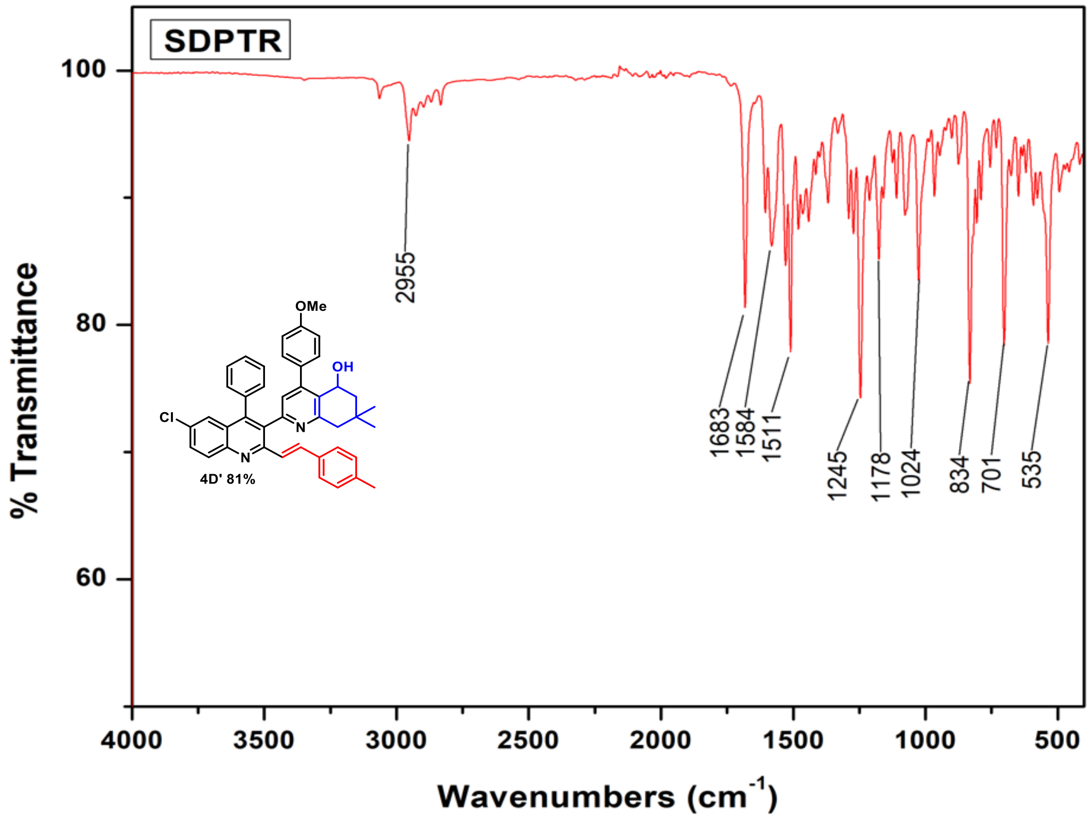
4D' ^{1}H NMR (400 MHz, $CDCl_3$)



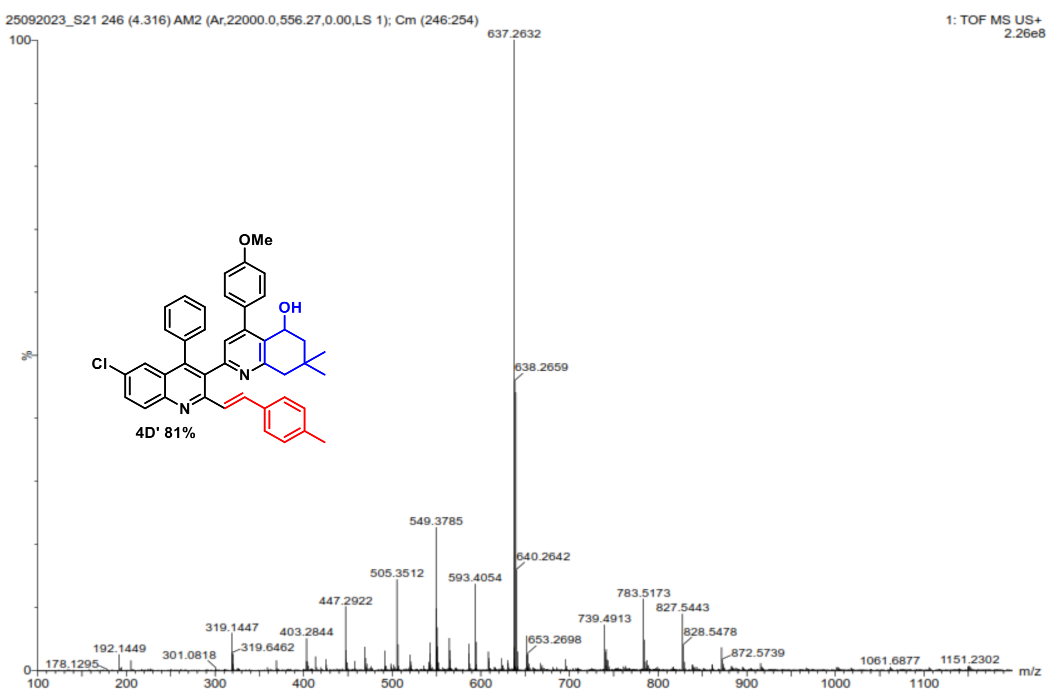
4D' ^{13}C NMR (101 MHz, $CDCl_3$)



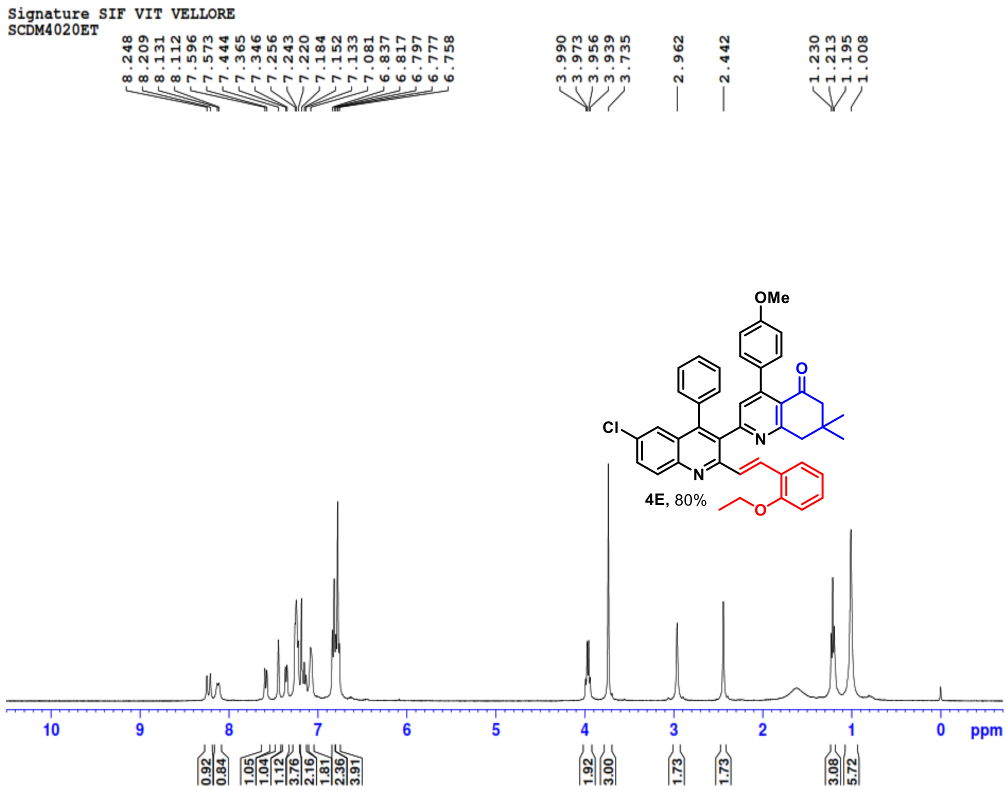
4D' FTIR



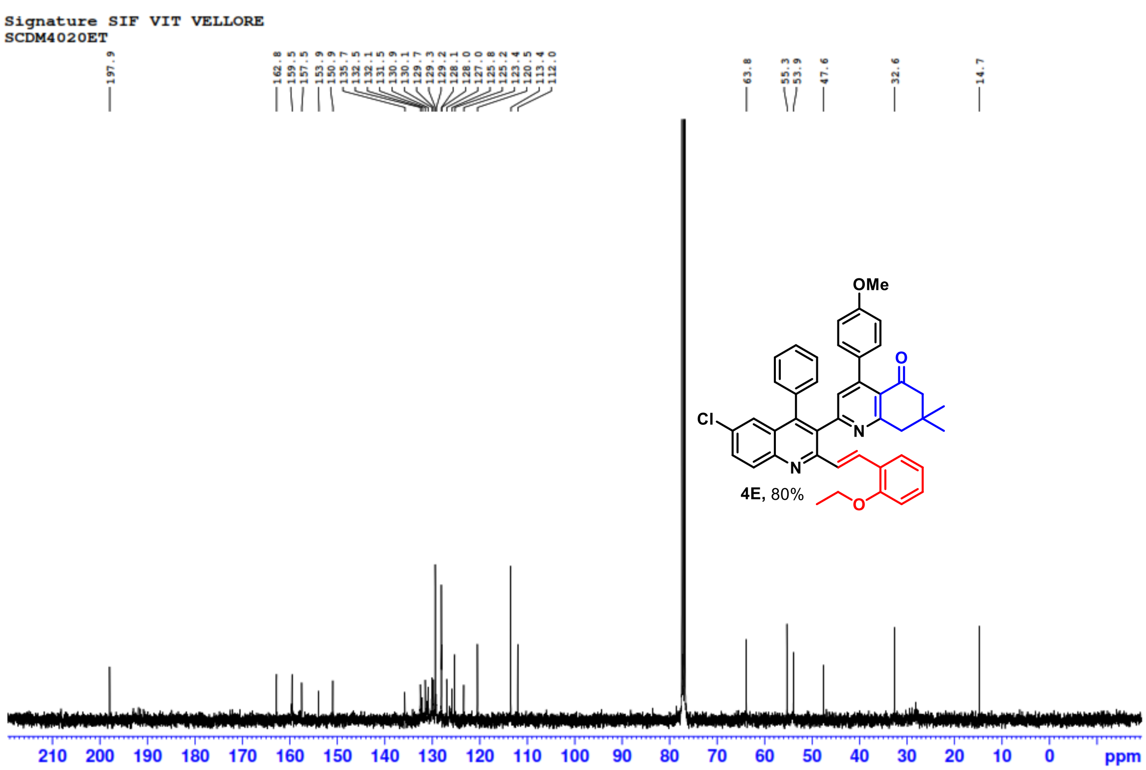
4D' HRMS (ESI)



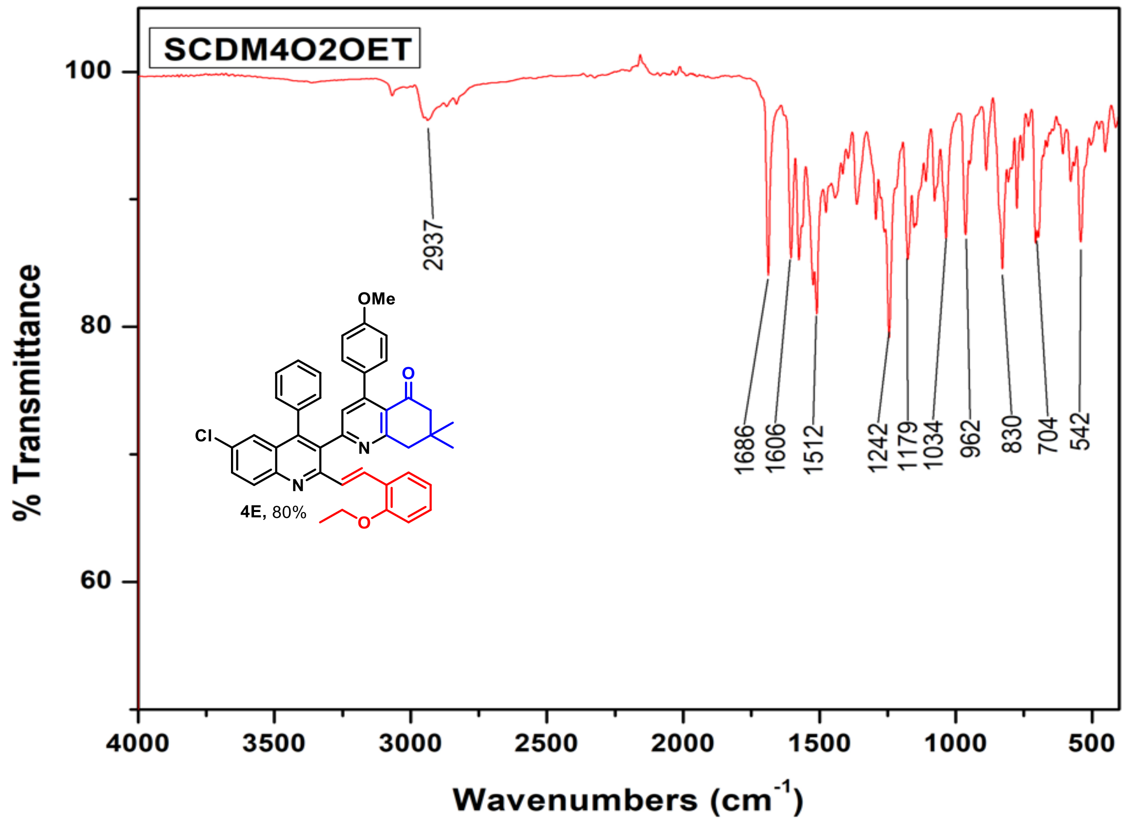
4E ^{1}H NMR (400 MHz, $CDCl_3$)



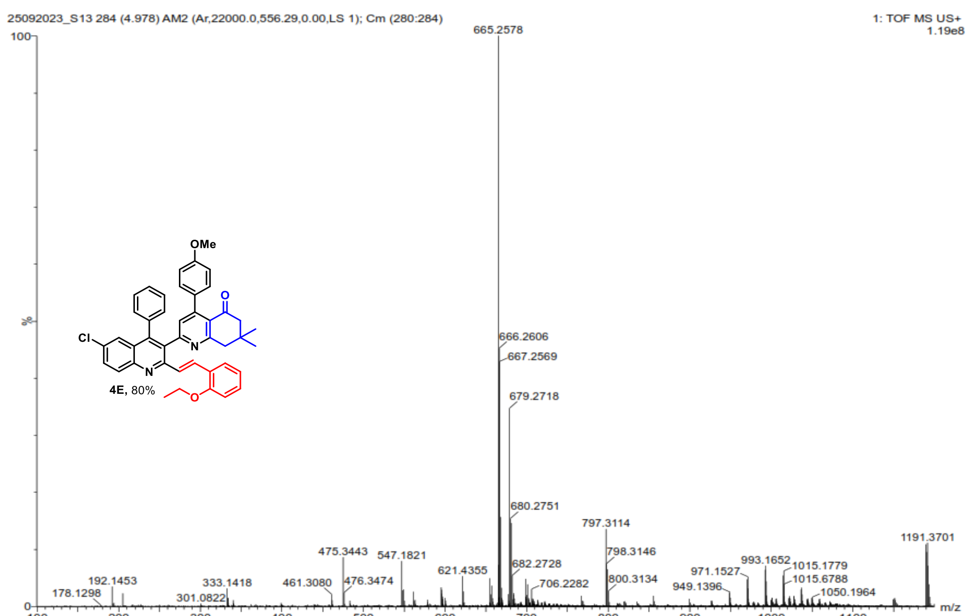
4E ^{13}C NMR (101 MHz, $CDCl_3$)



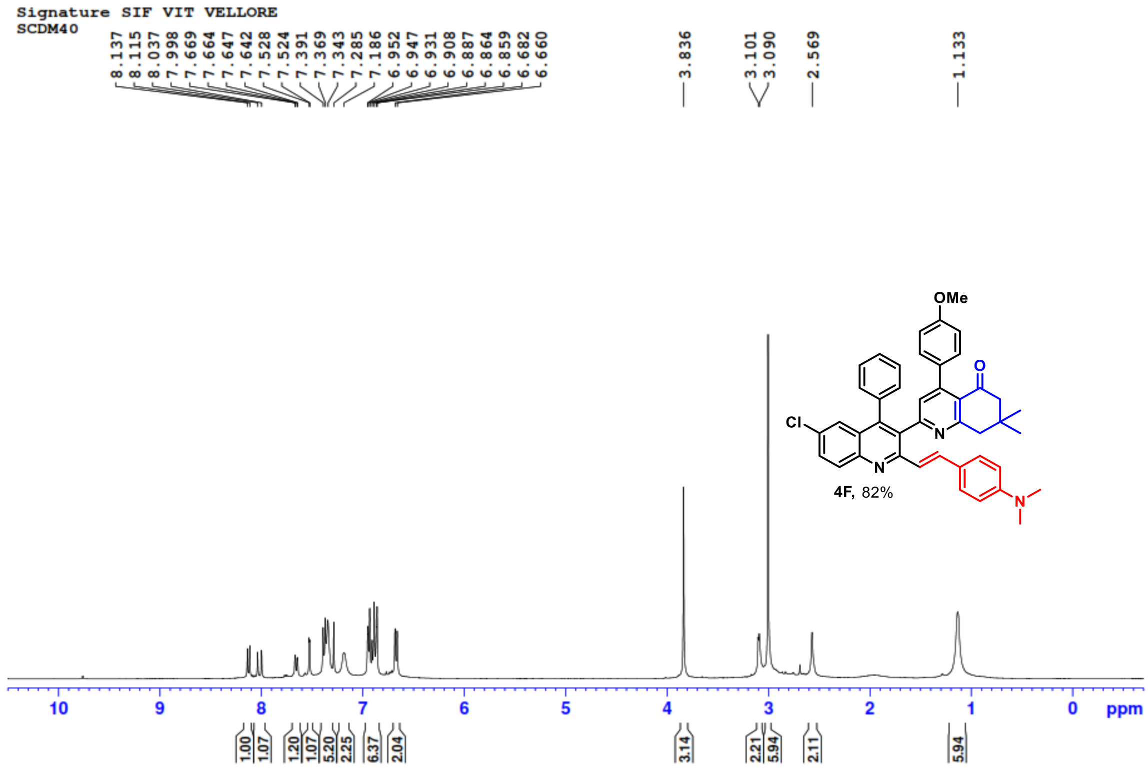
4E FTIR



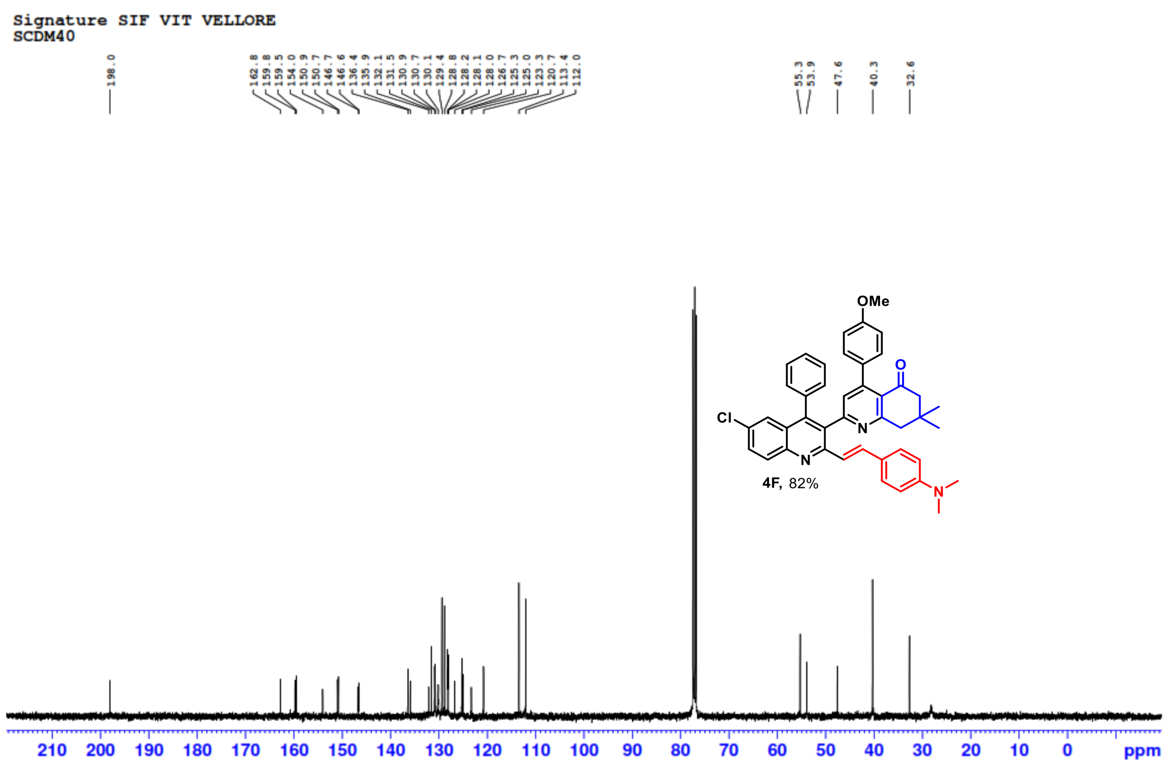
4E HRMS (ESI)



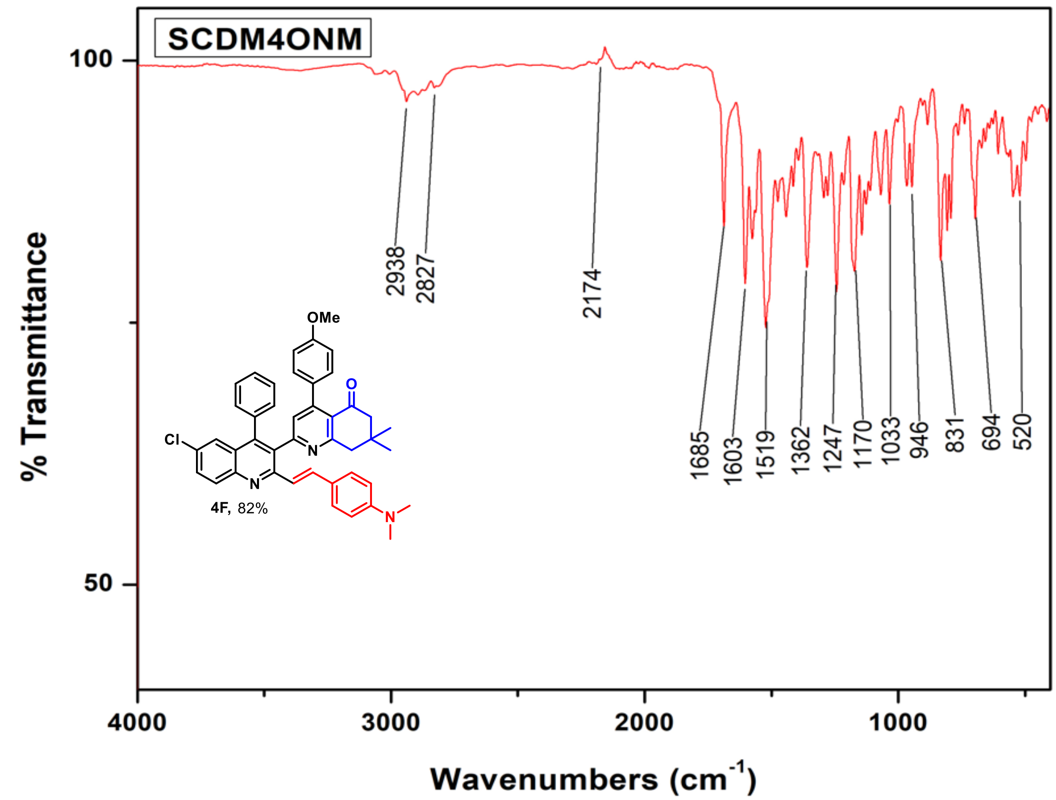
4F ^{1}H NMR (400 MHz, $CDCl_3$)



4F ^{13}C NMR (101 MHz, $CDCl_3$)



4F FTIR



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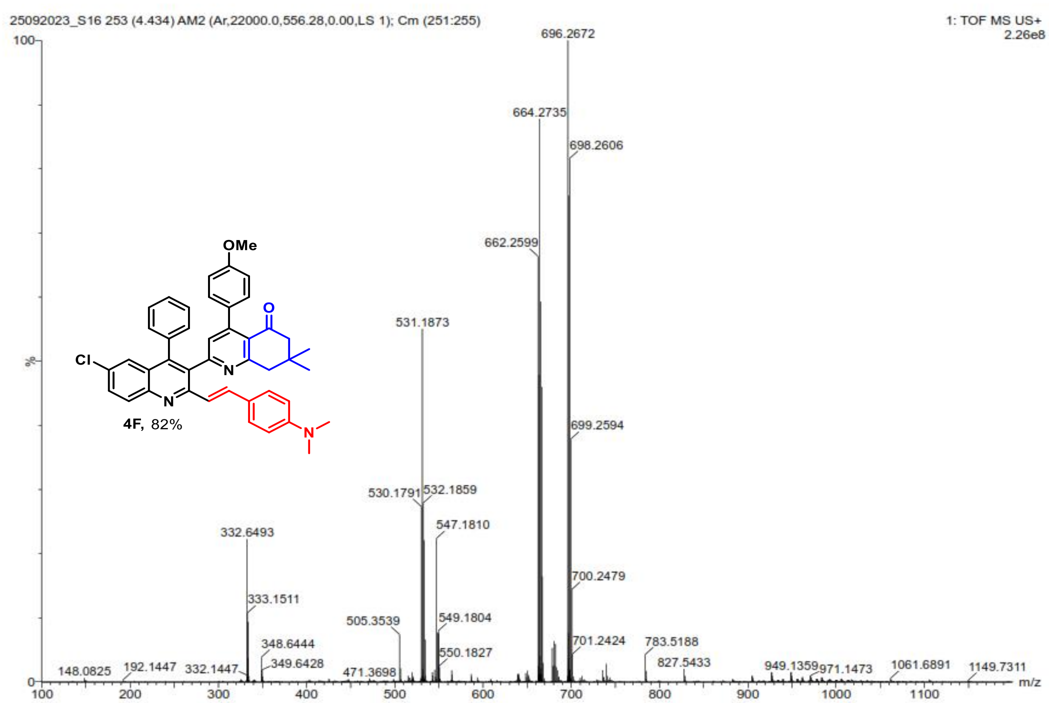
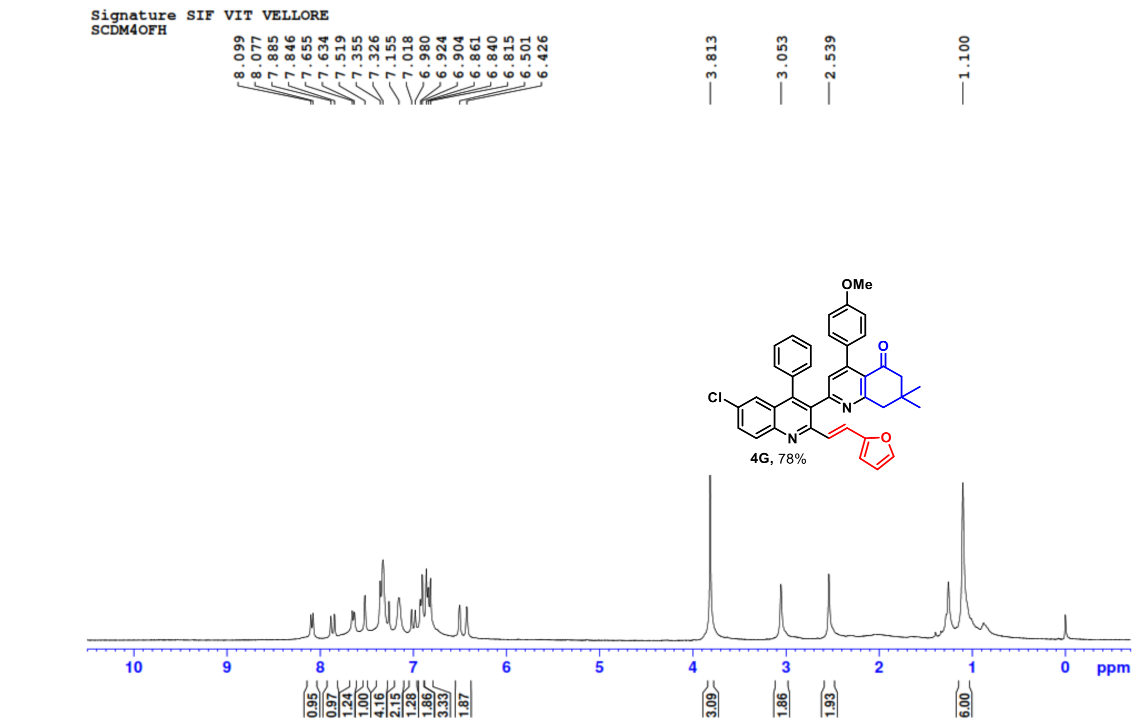
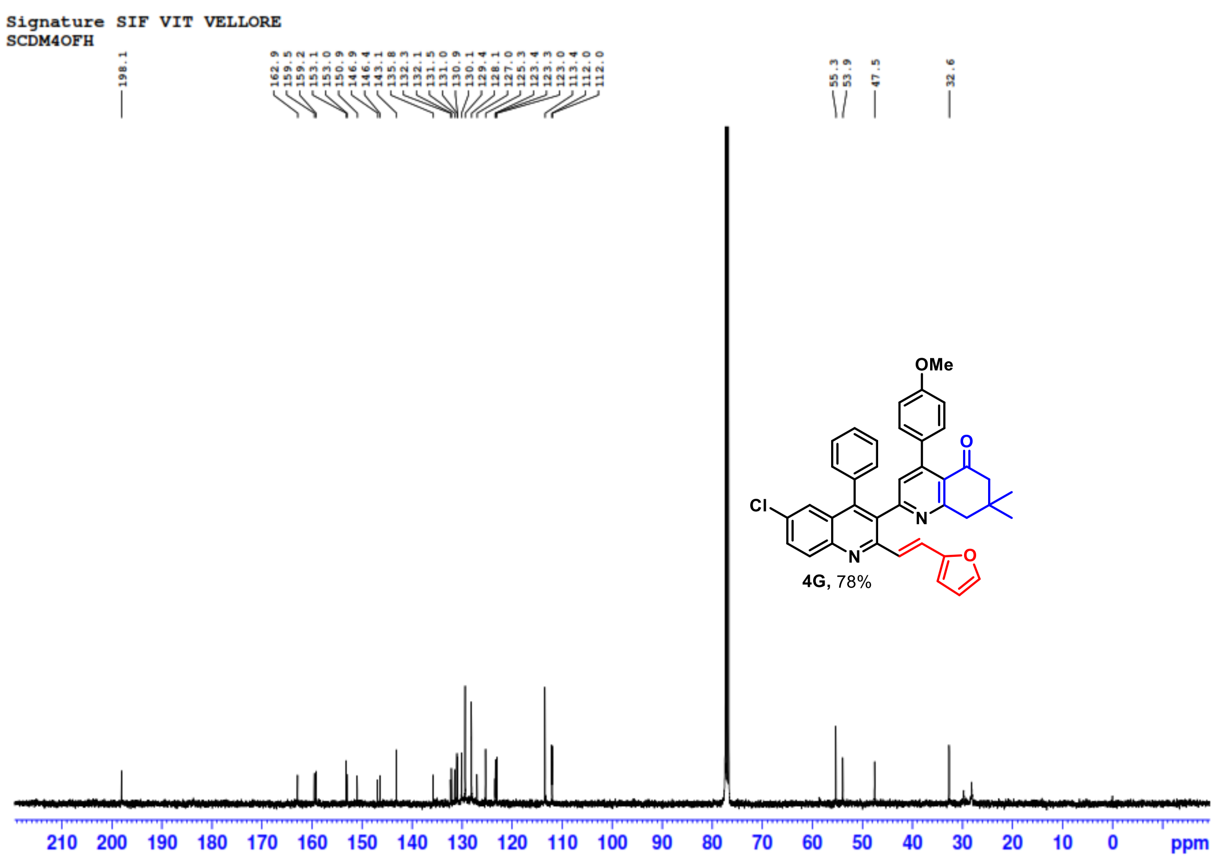


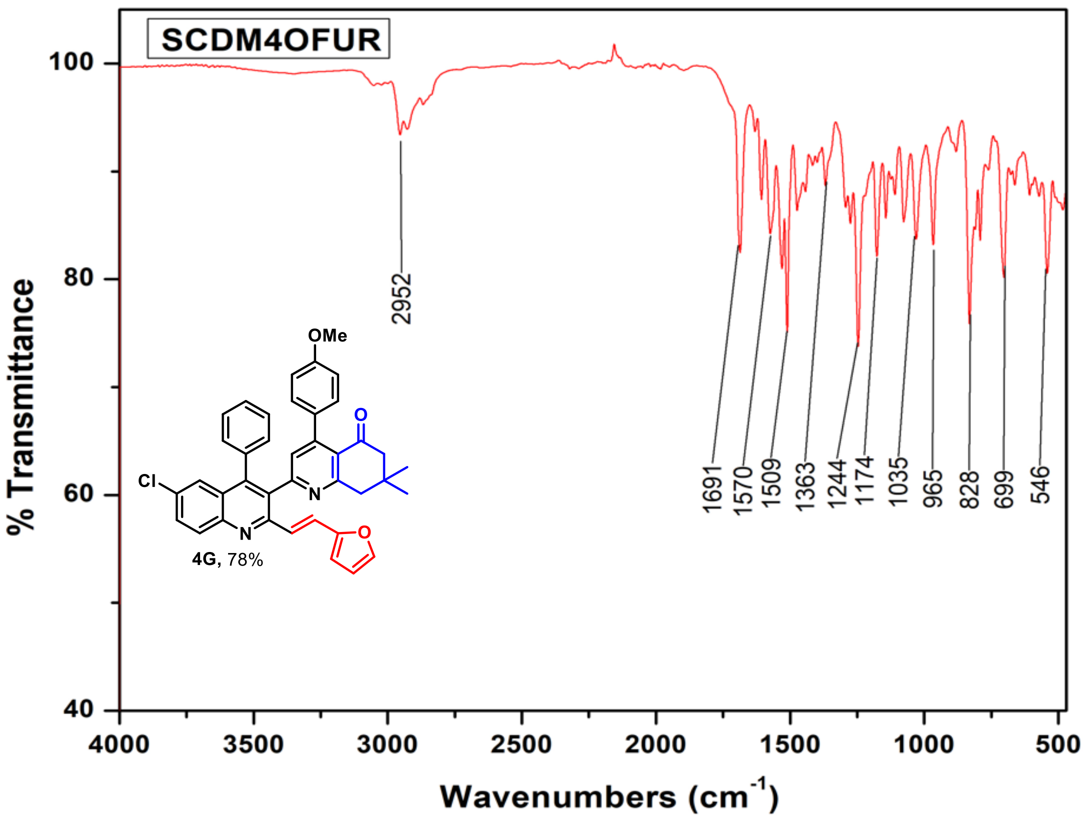
4G ^{1}H NMR (400 MHz, $CDCl_3$)



4G ^{13}C NMR (101 MHz, $CDCl_3$)



4G FTIR



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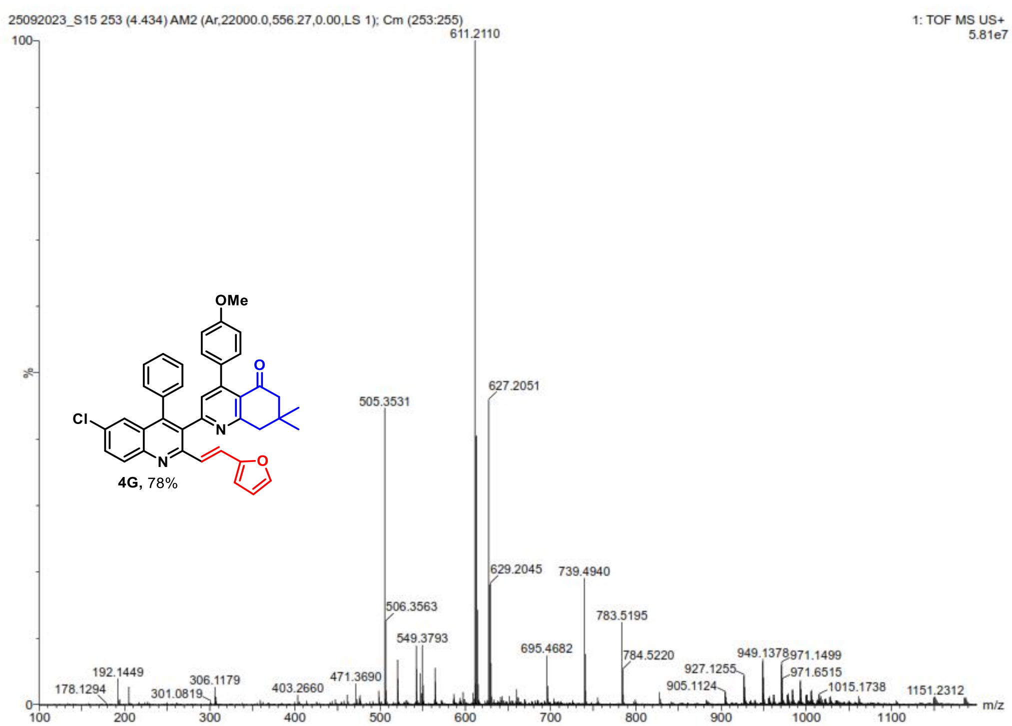
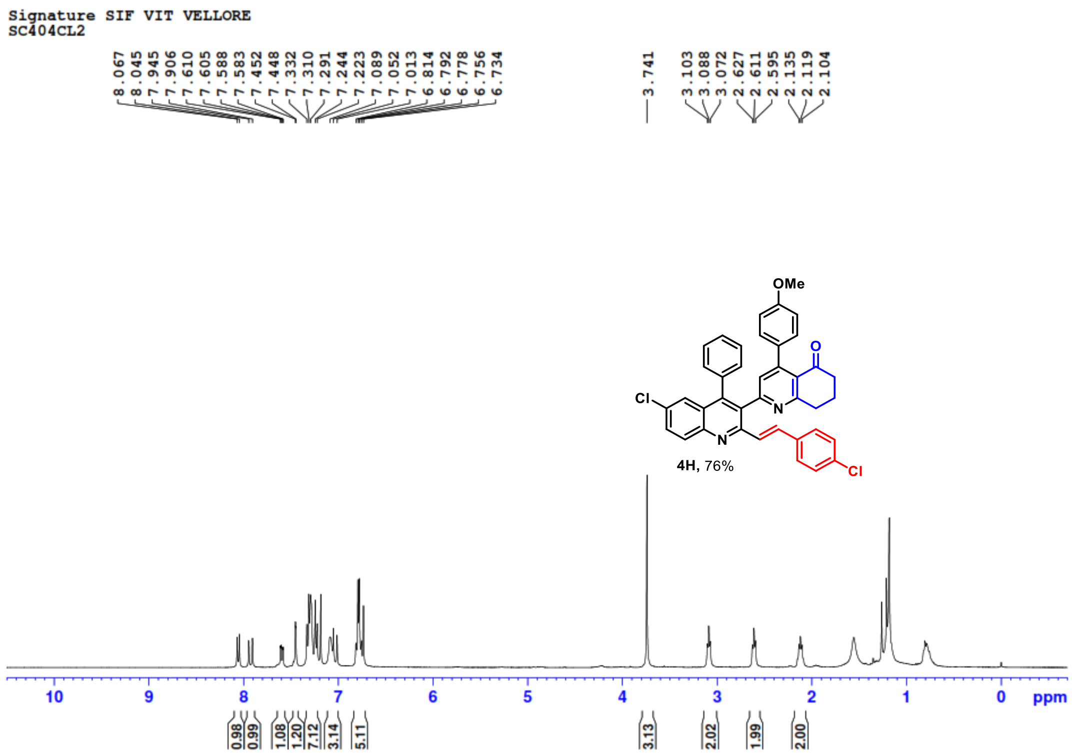
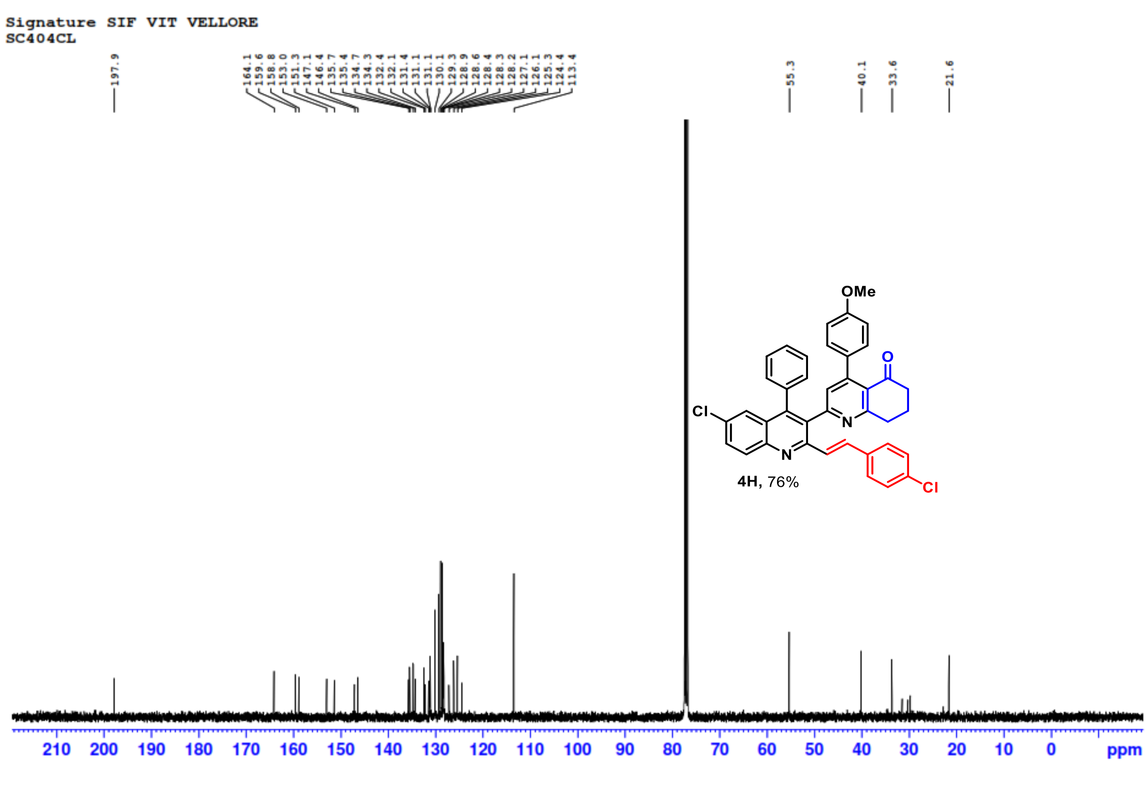


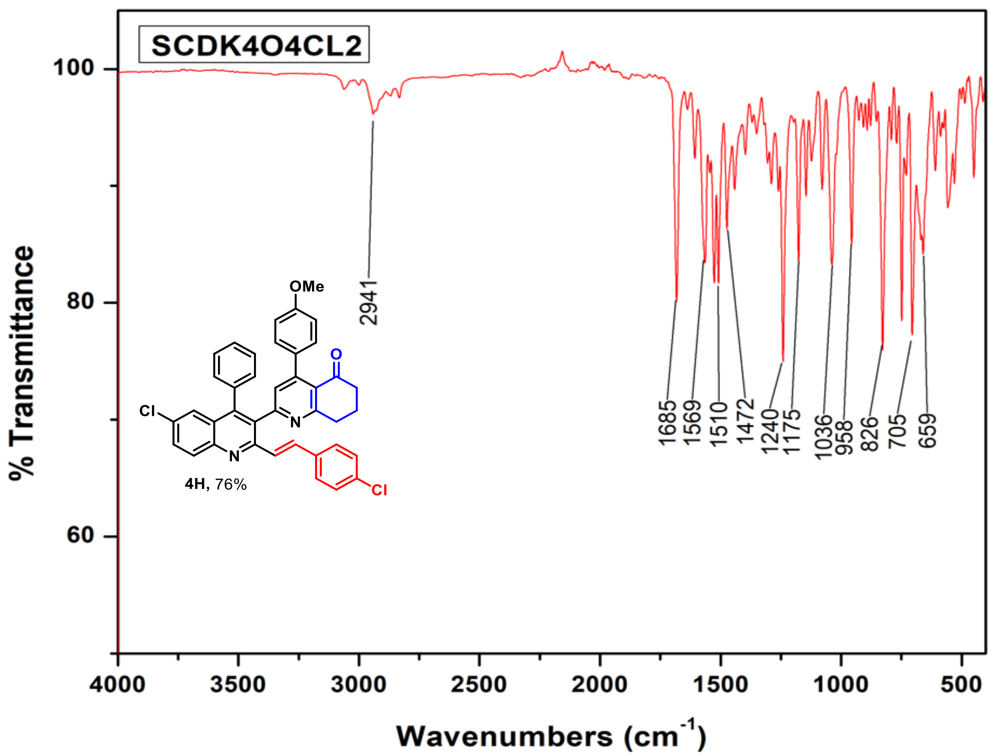
4H ^{1}H NMR (400 MHz, CDCl$_3$)



4H ^{13}C NMR (101 MHz, CDCl$_3$)



4H FTIR



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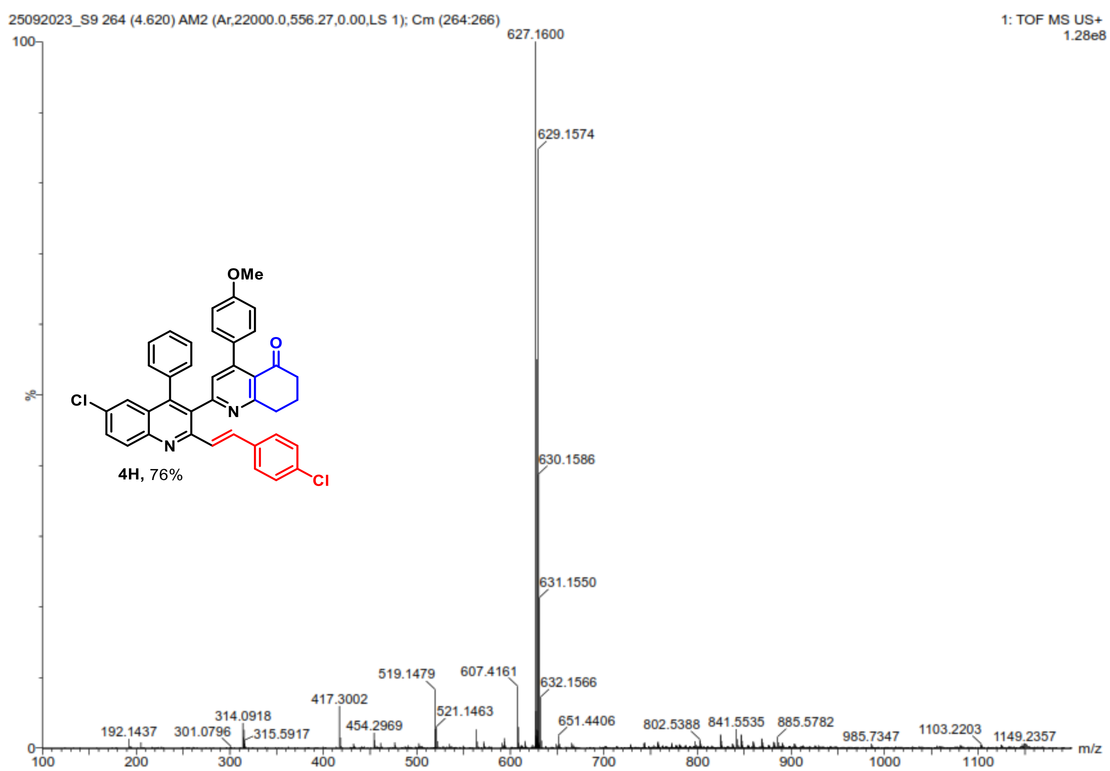
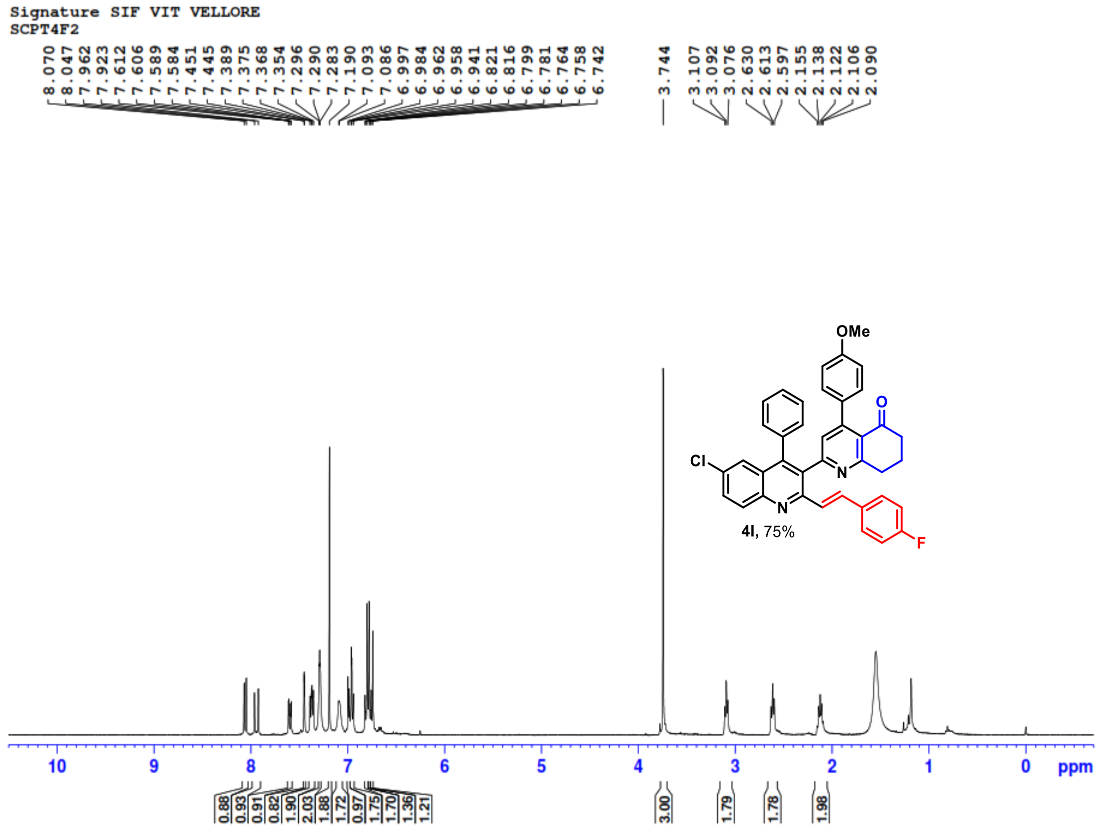
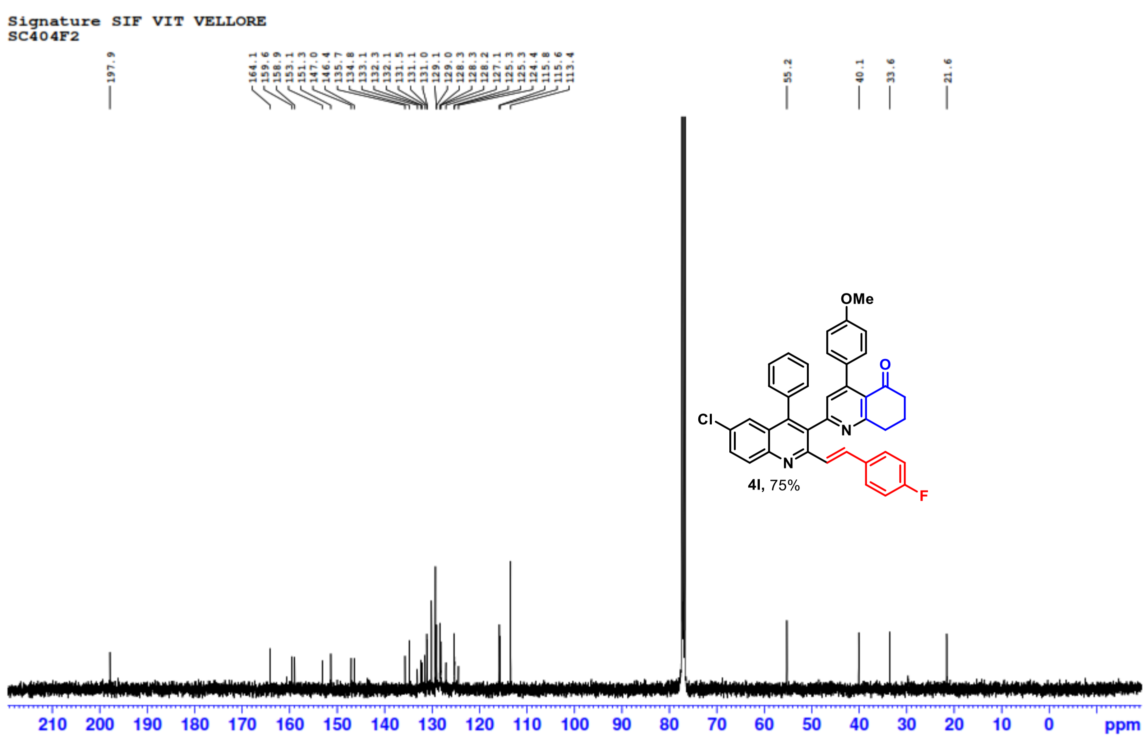


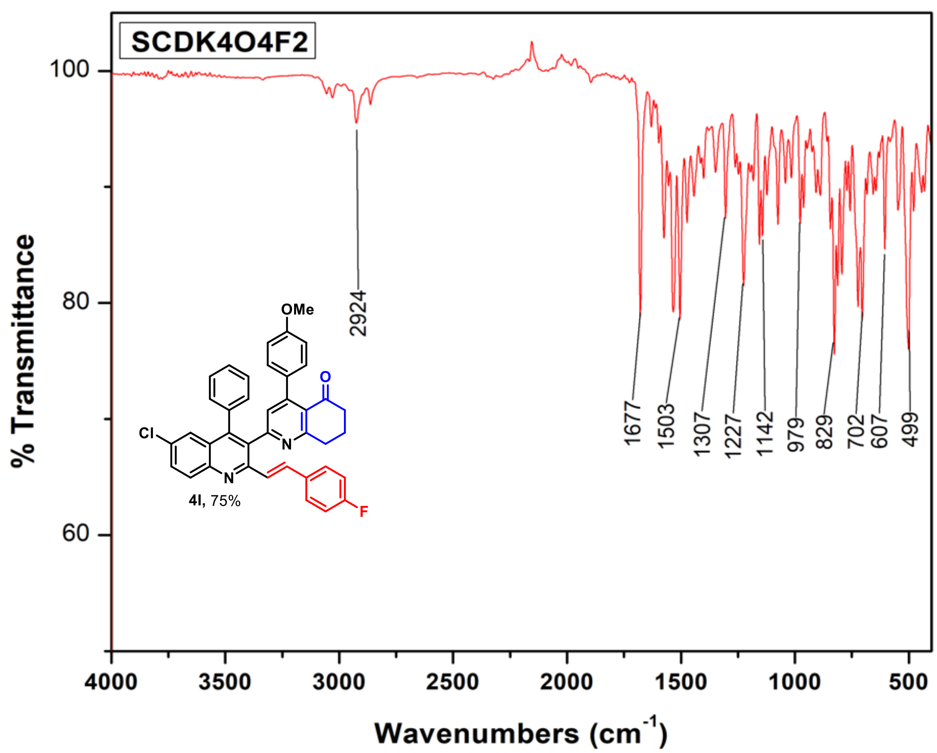
4l ^{1}H NMR (400 MHz, $CDCl_3$)



4l ^{13}C NMR (101 MHz, $CDCl_3$)



4l FTIR



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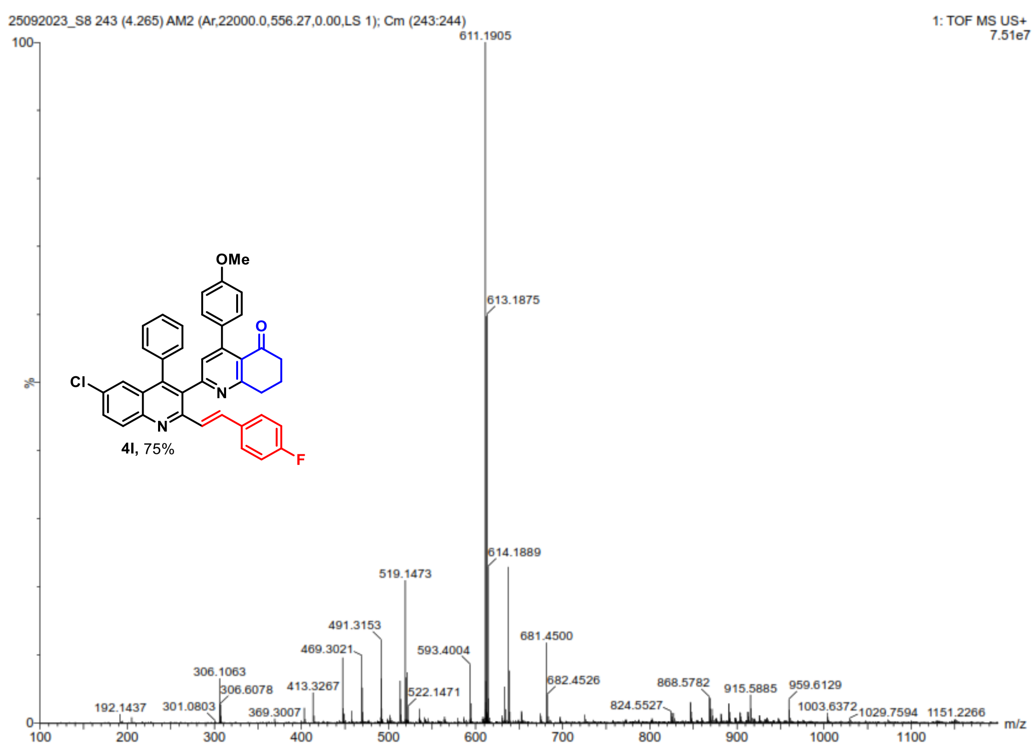
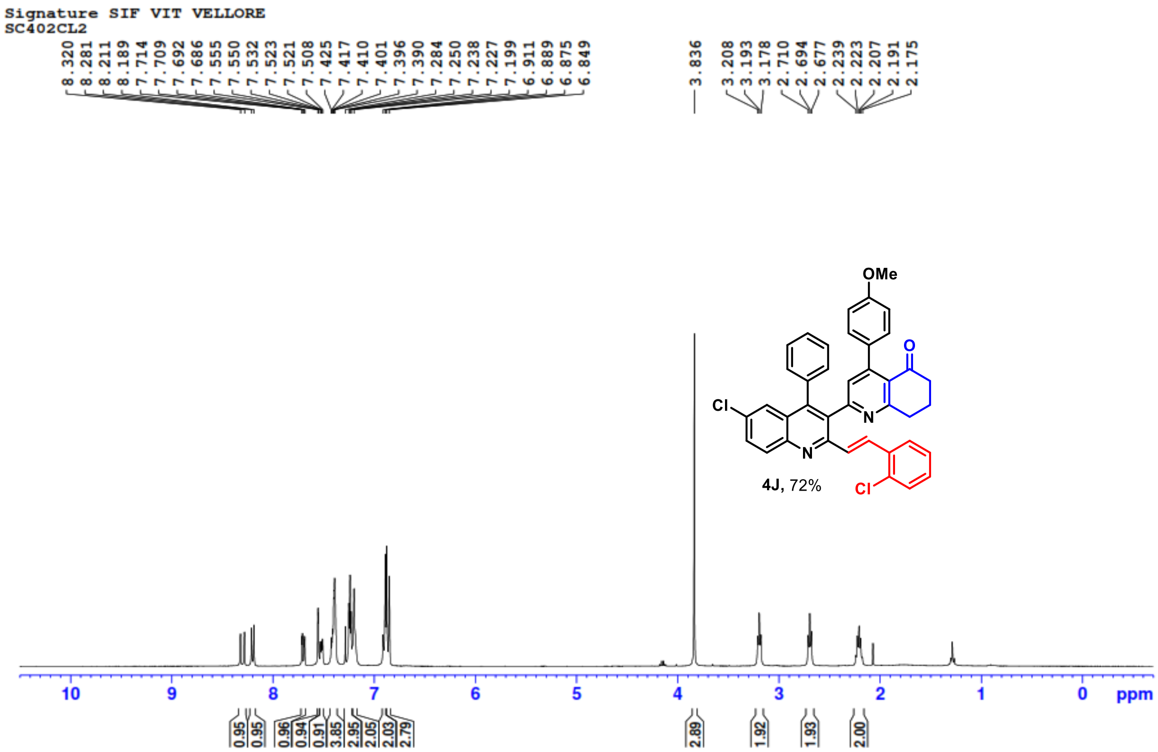
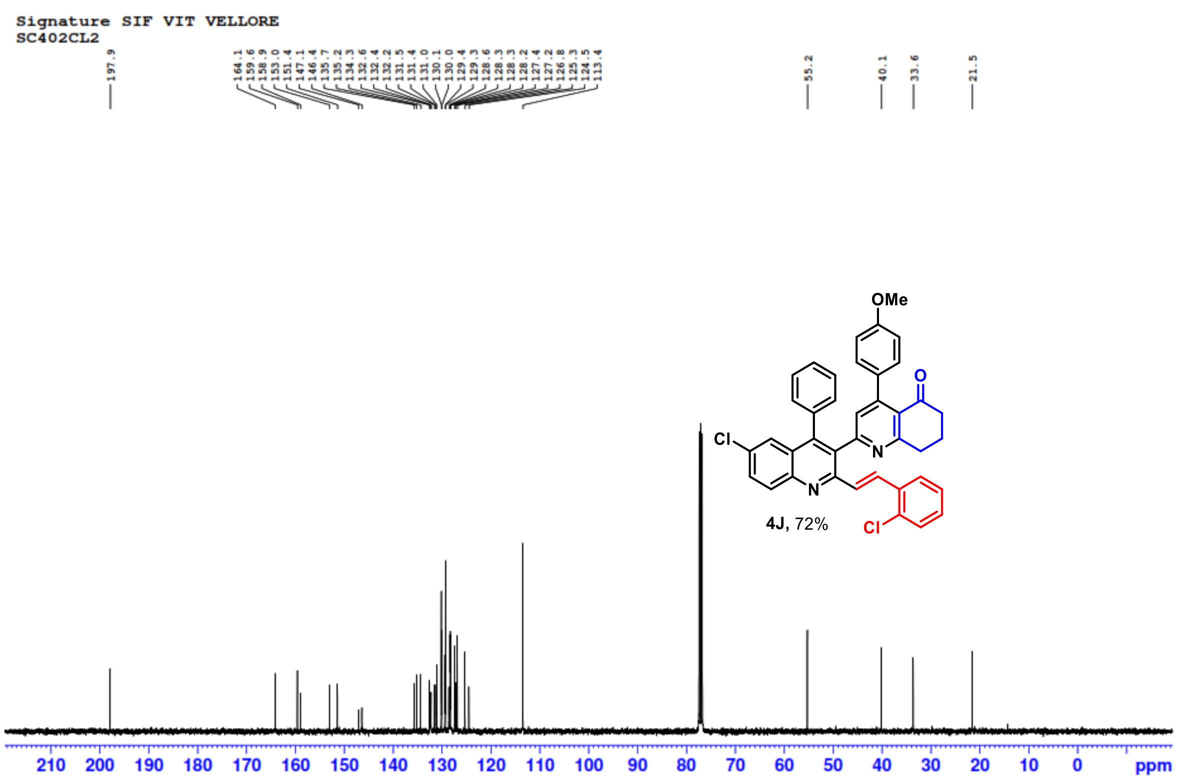


4J ^{1}H NMR (400 MHz, $CDCl_3$)



4J ^{13}C NMR (101 MHz, $CDCl_3$)



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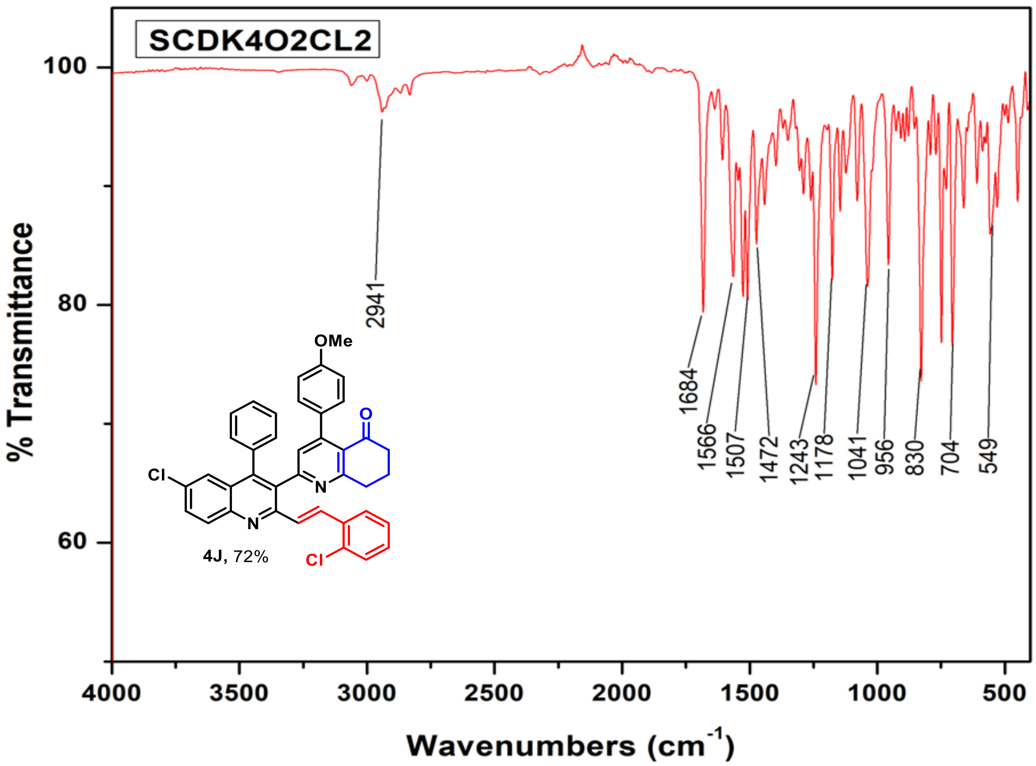

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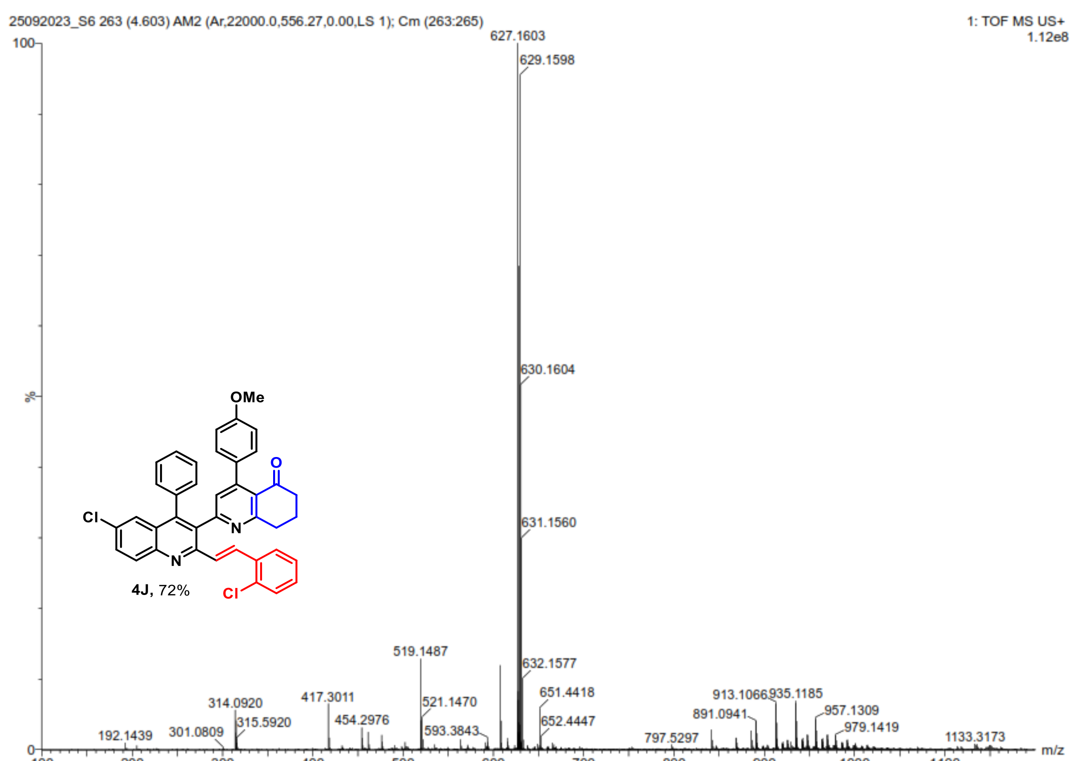
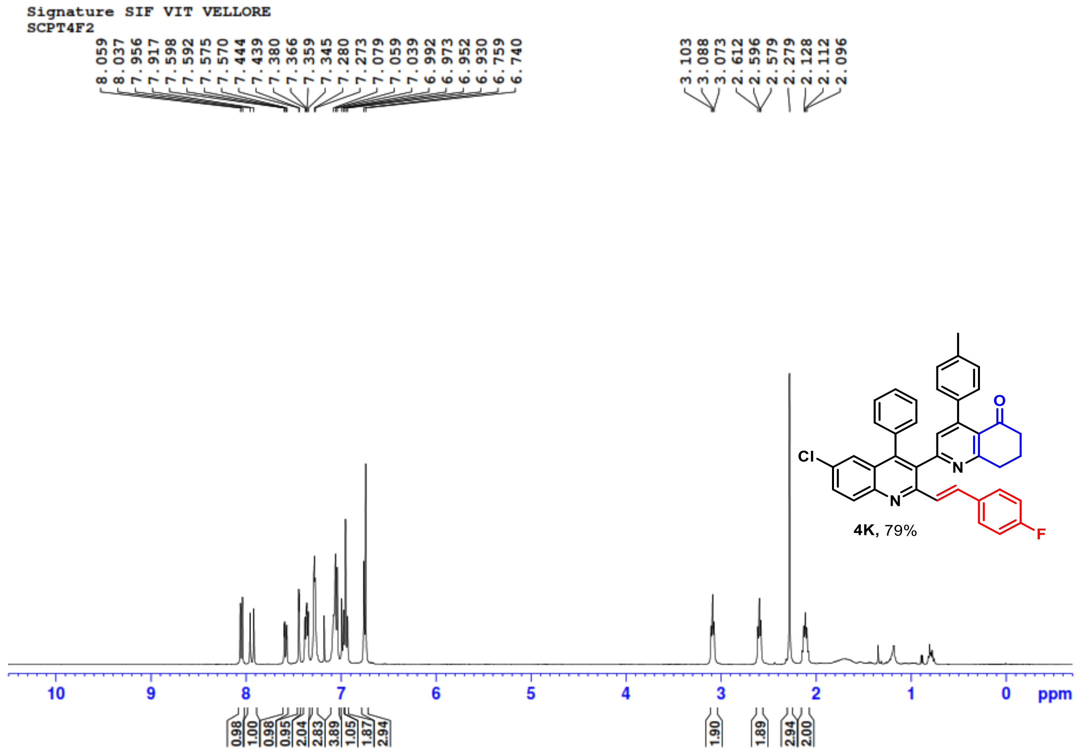
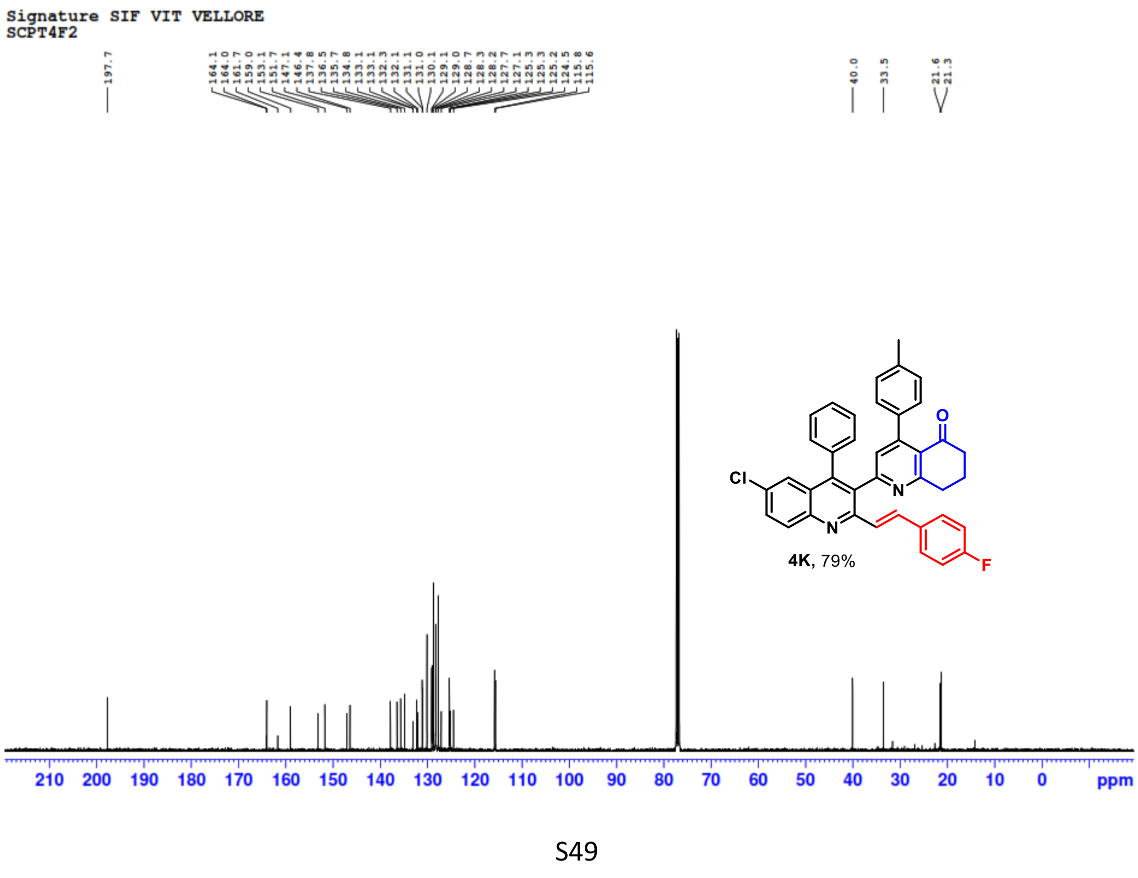


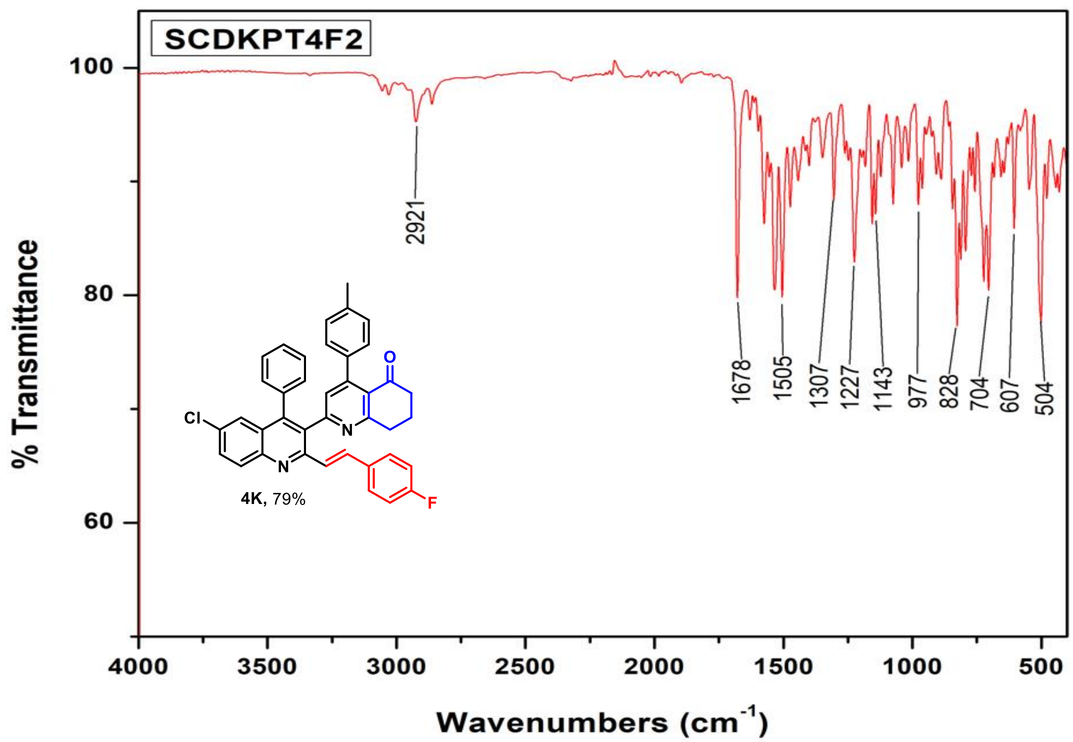
4K ^{1}H NMR (400 MHz, $CDCl_3$)



4K ^{13}C NMR (101 MHz, $CDCl_3$)



4K FTIR



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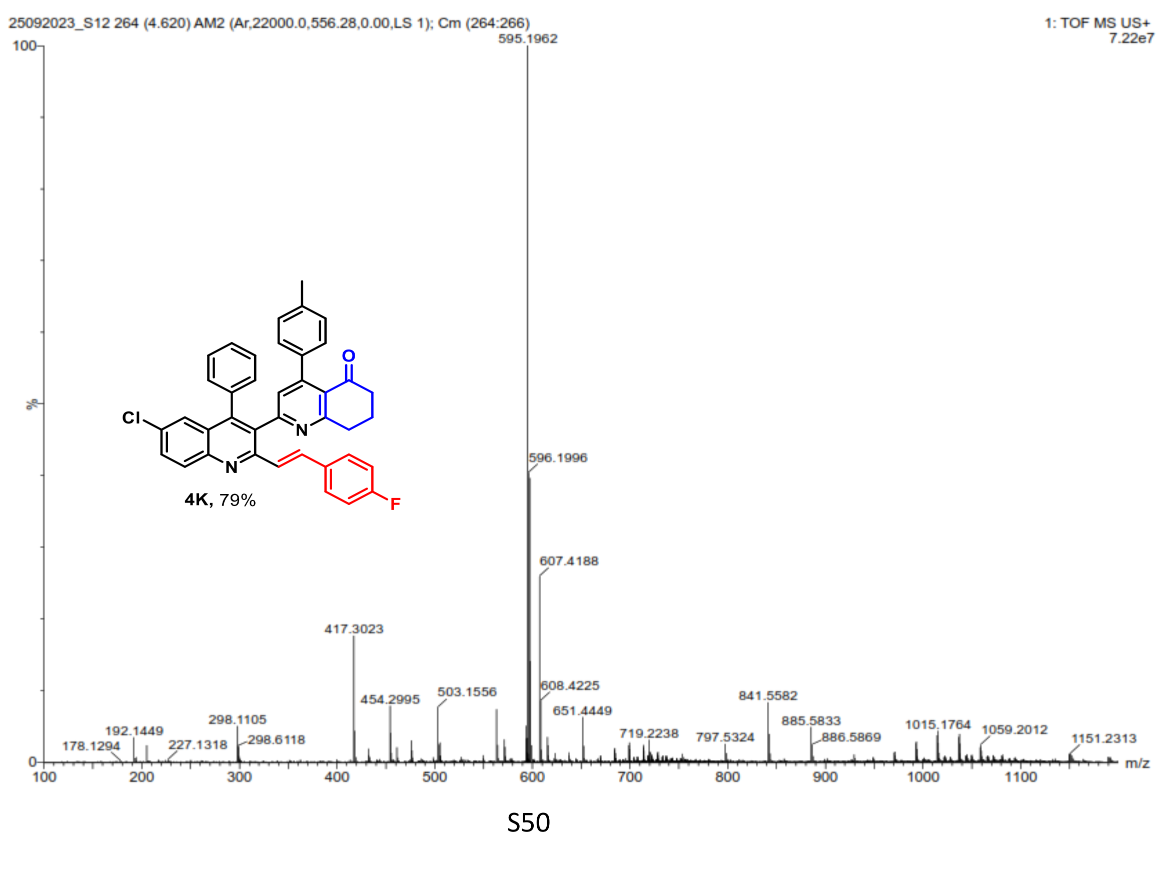
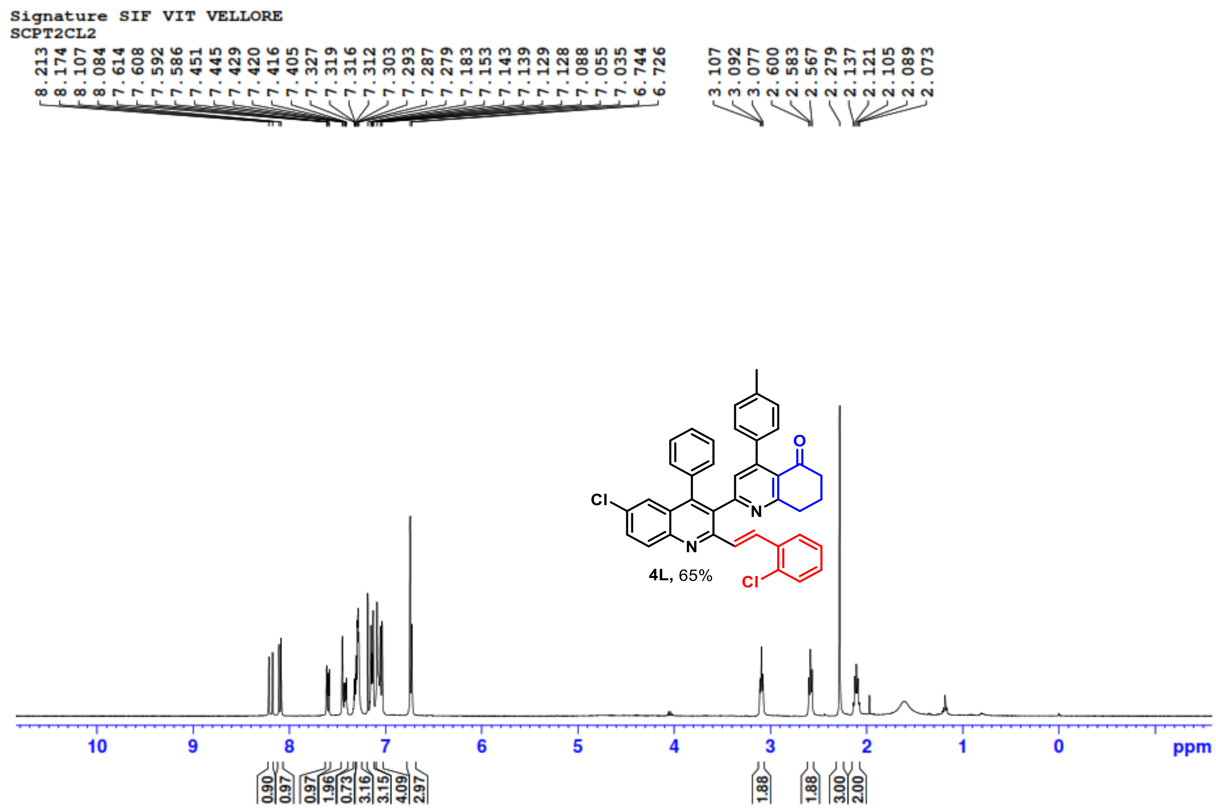
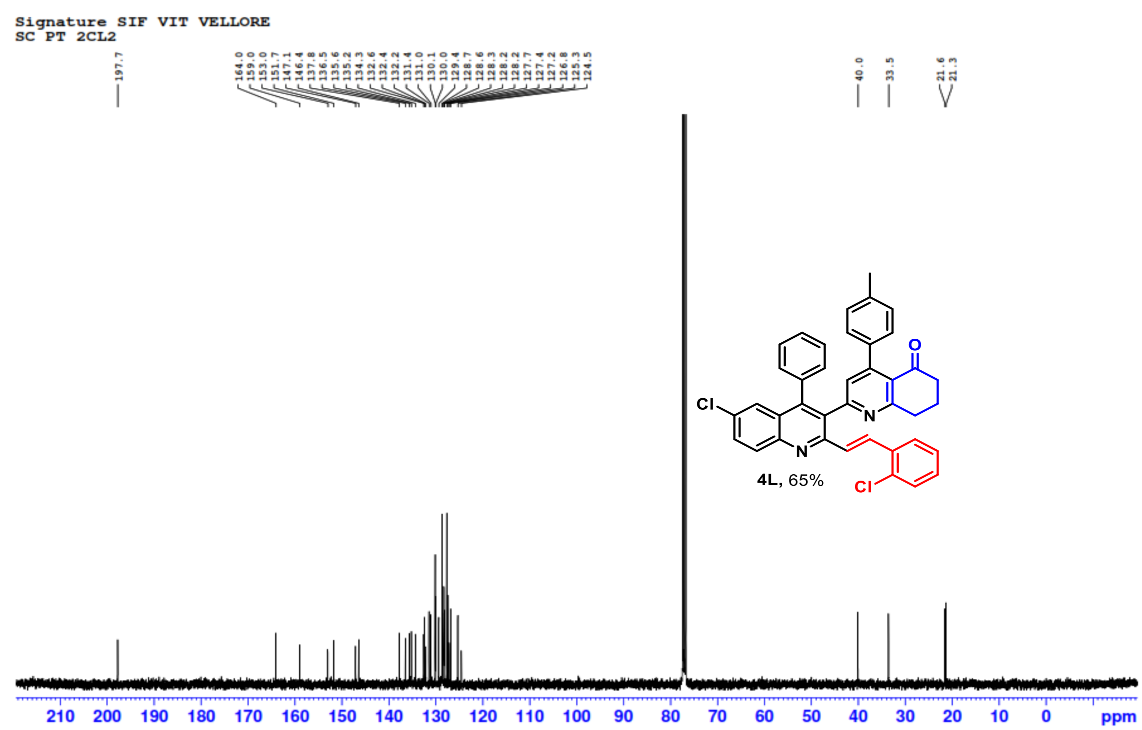


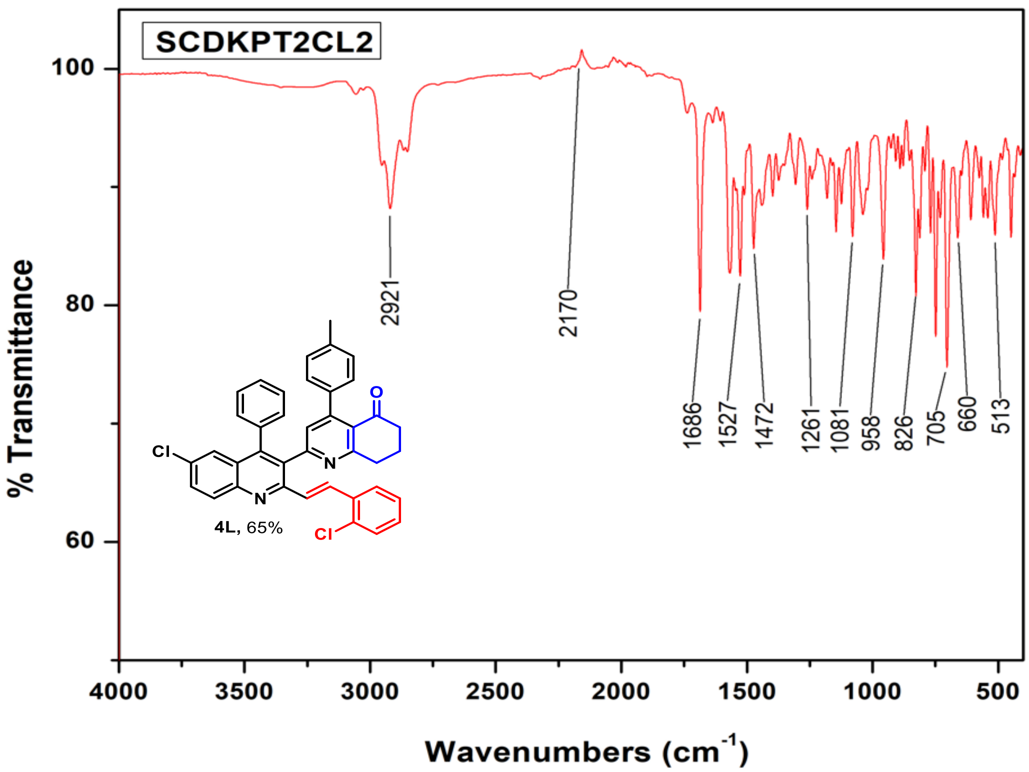
4L ^{1}H NMR (400 MHz, CDCl$_3$)



4L ^{13}C NMR (101 MHz, CDCl$_3$)



4L FTIR



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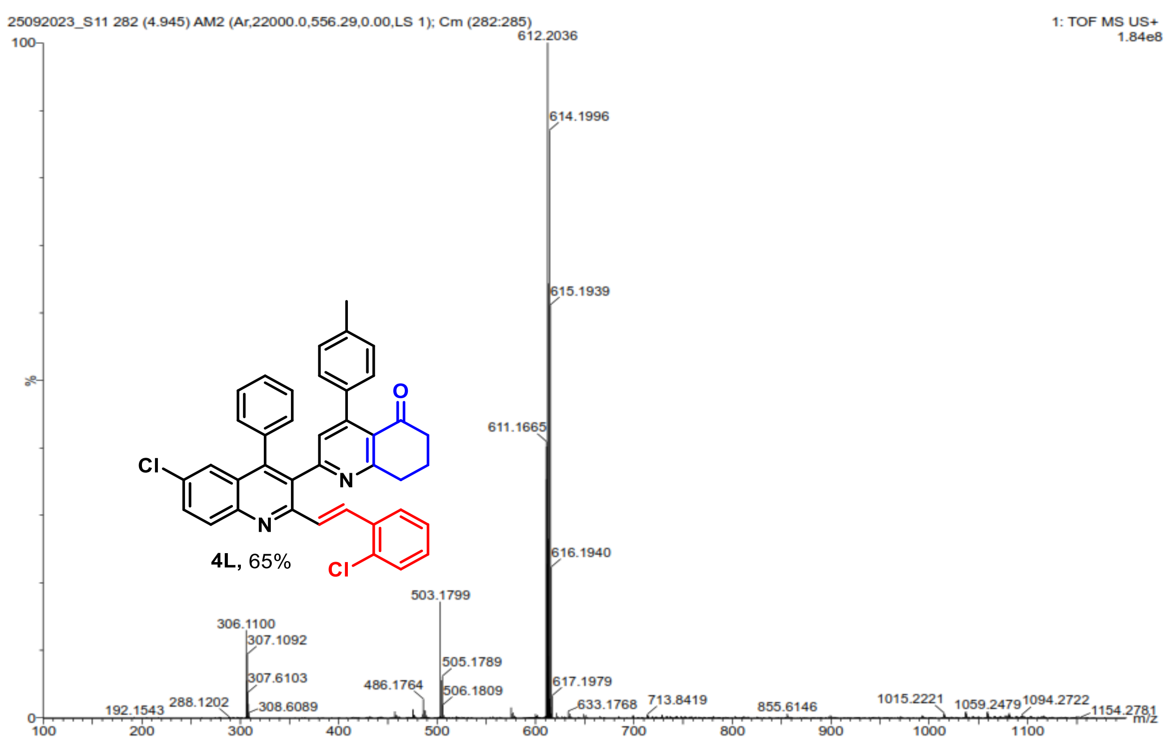
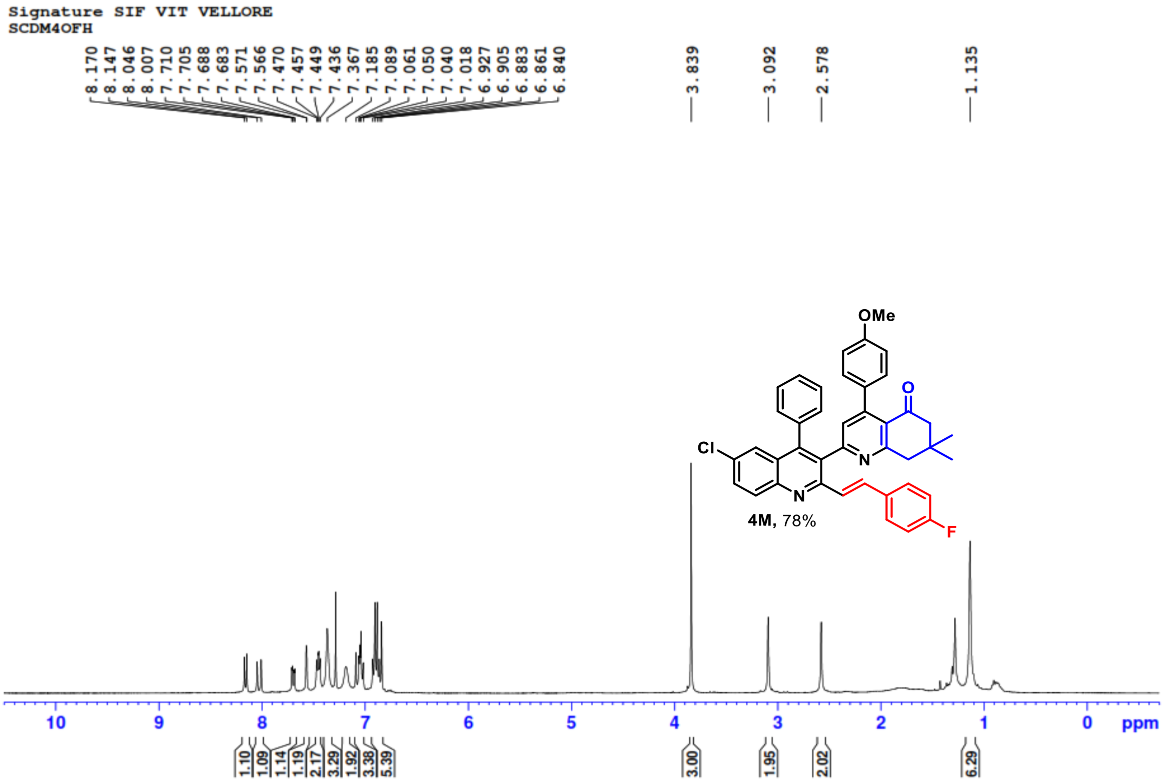
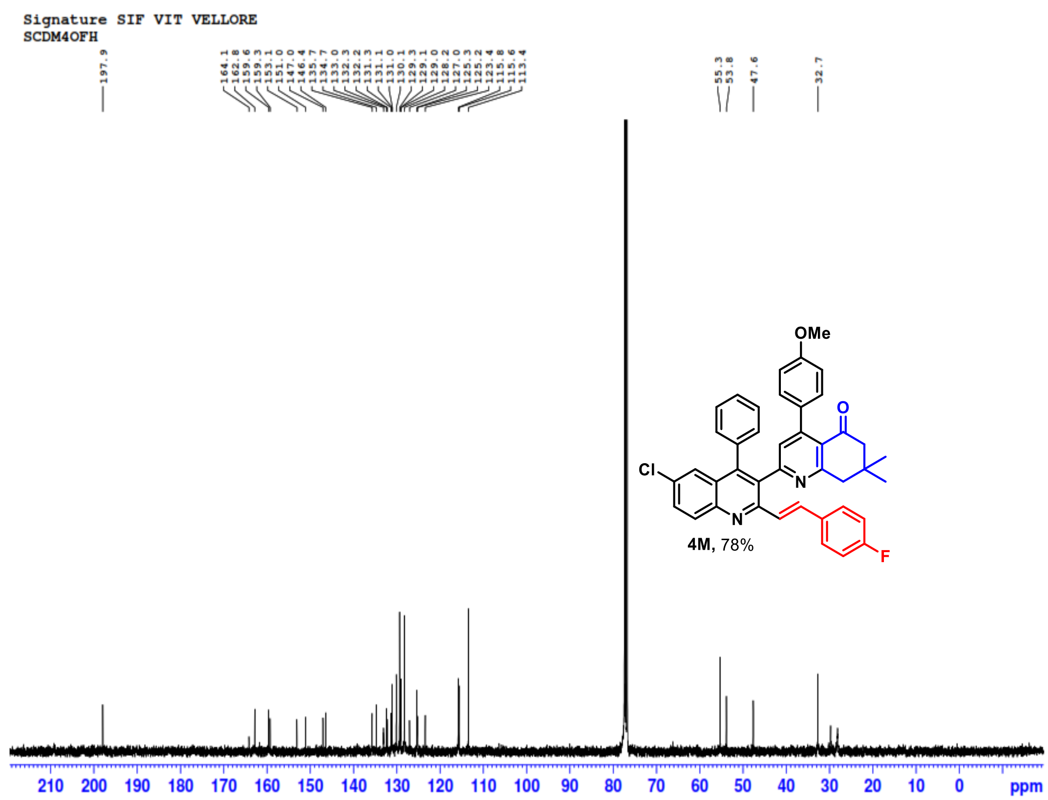


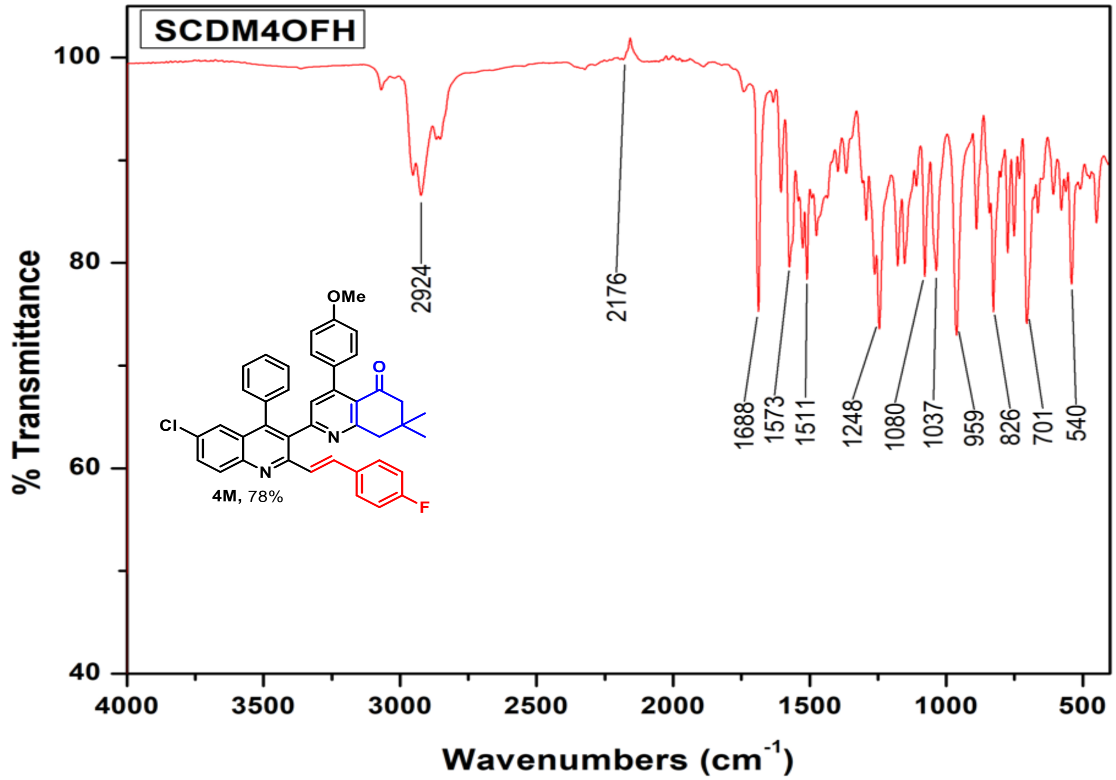
4M ^{1}H NMR (400 MHz, $CDCl_3$)



4M ^{13}C NMR (101 MHz, $CDCl_3$)



4M FTIR



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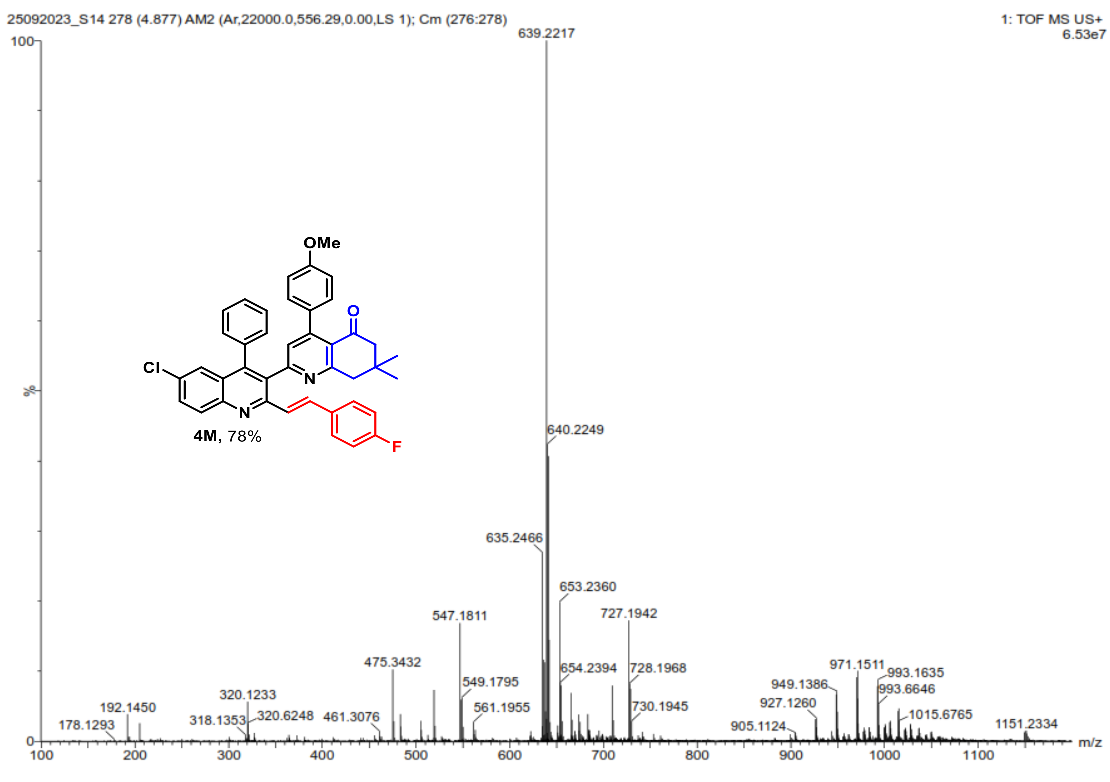
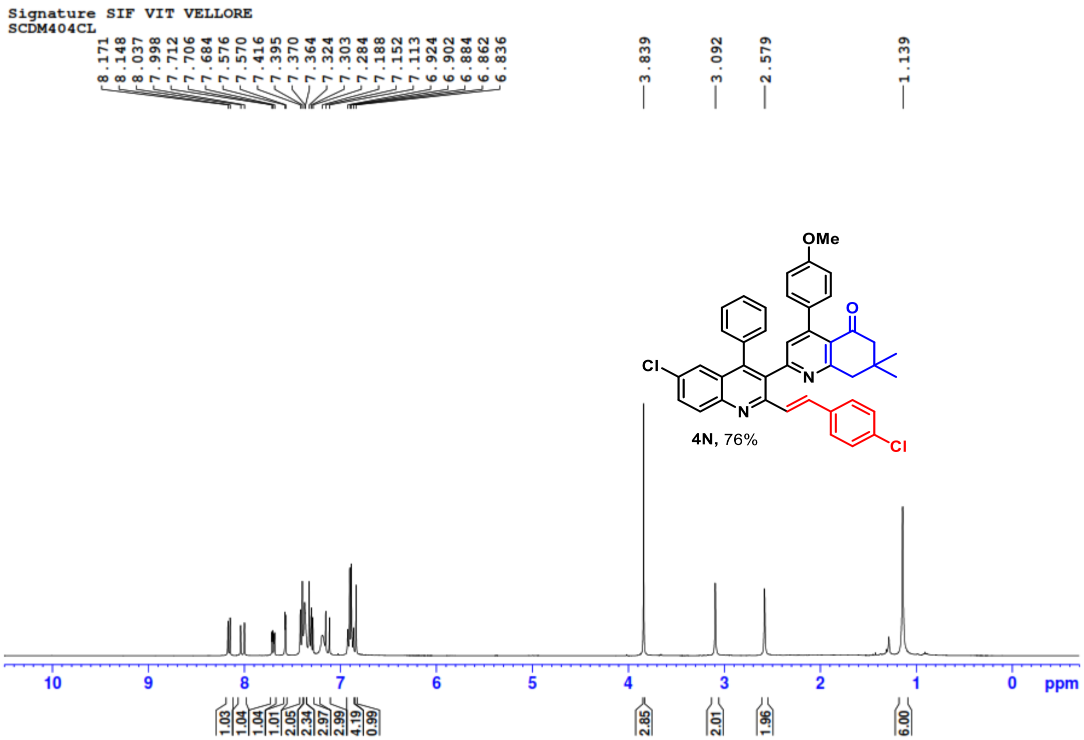
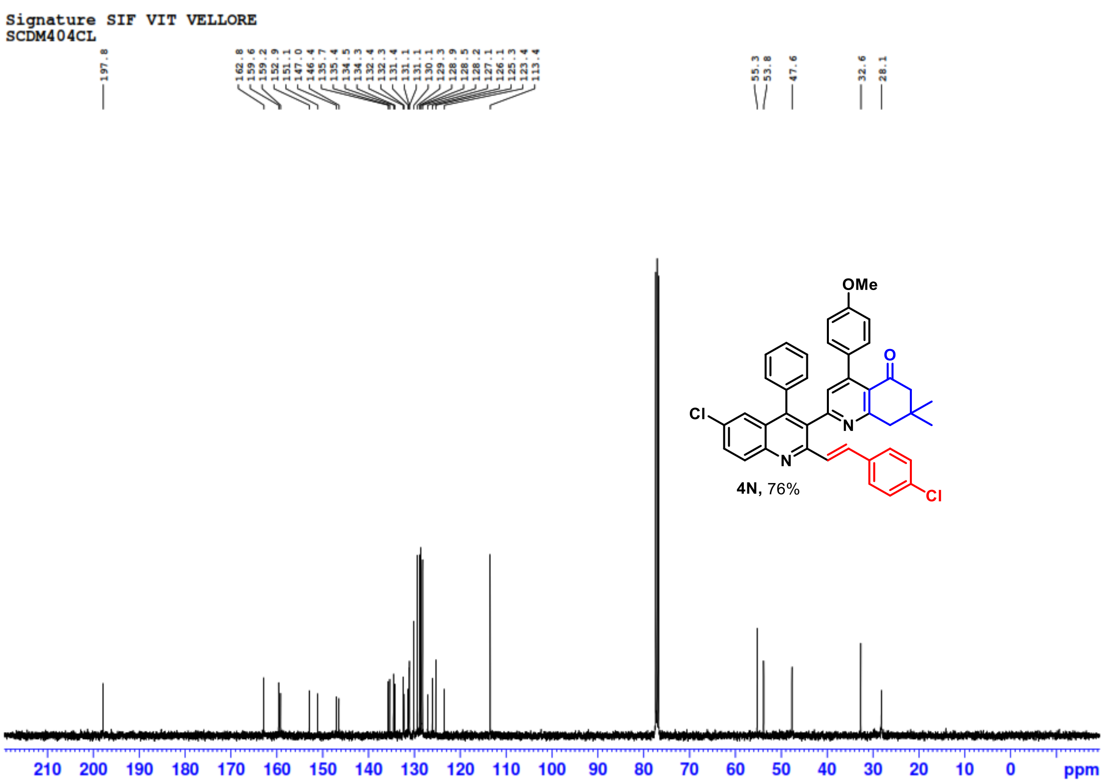


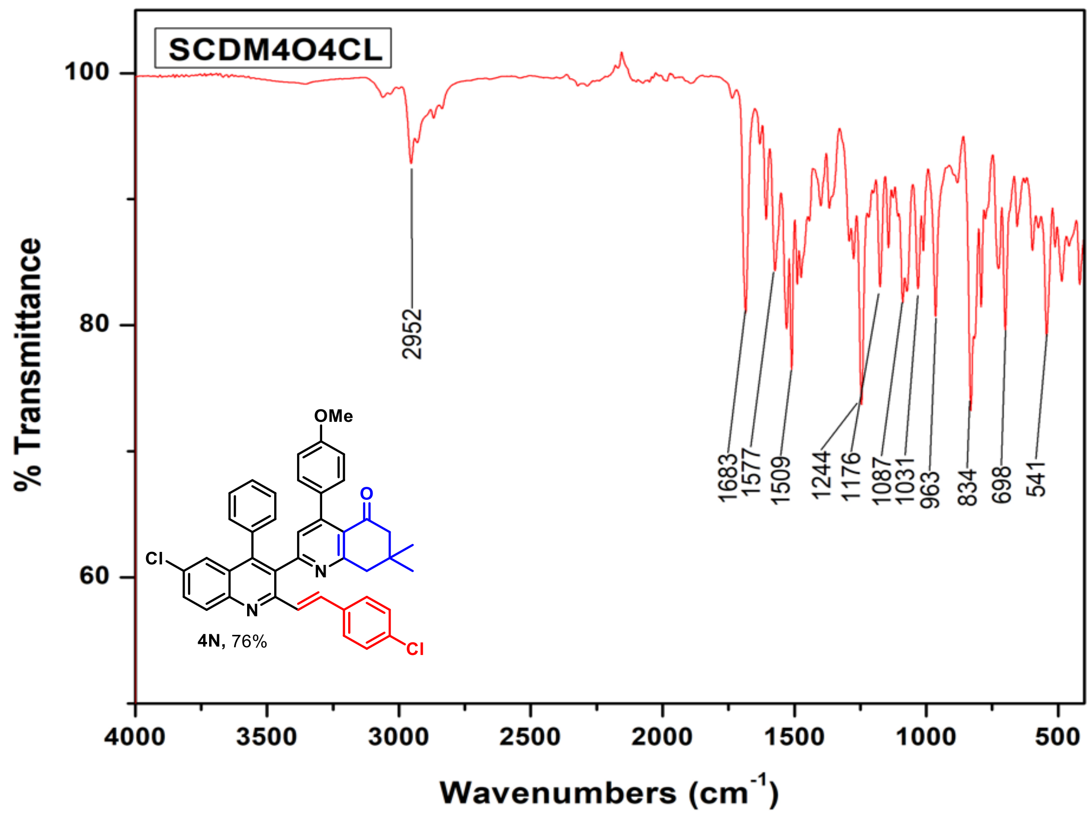
4N ^{1}H NMR (400 MHz, $CDCl_3$)



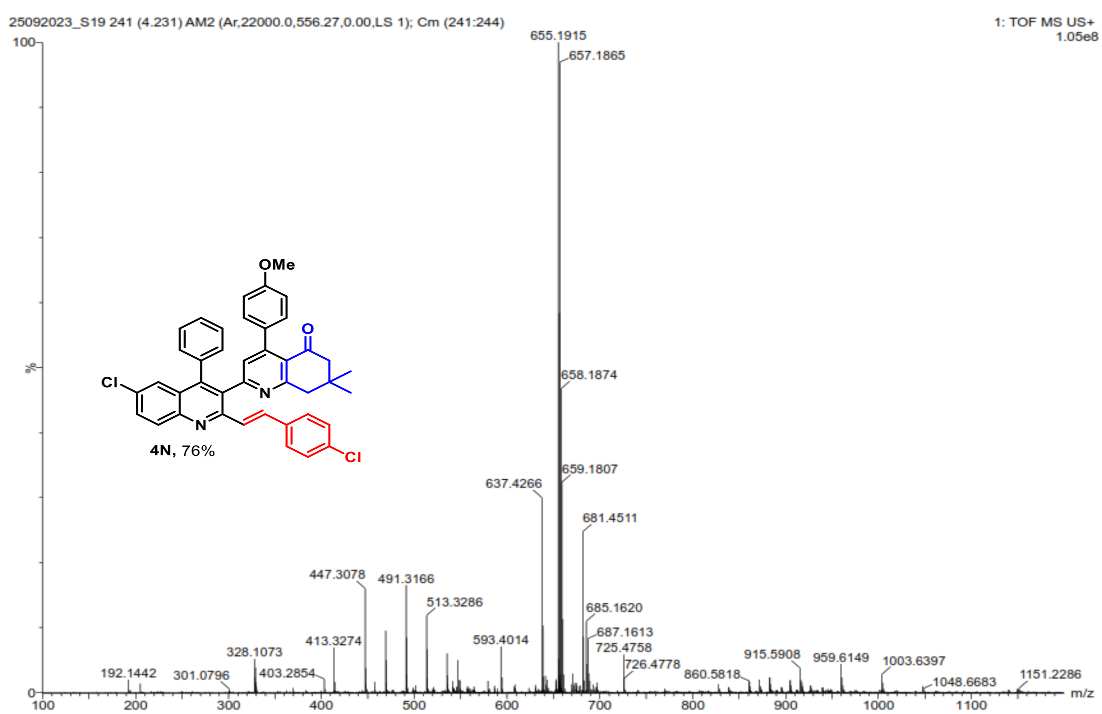
4N ^{13}C NMR (101 MHz, $CDCl_3$)



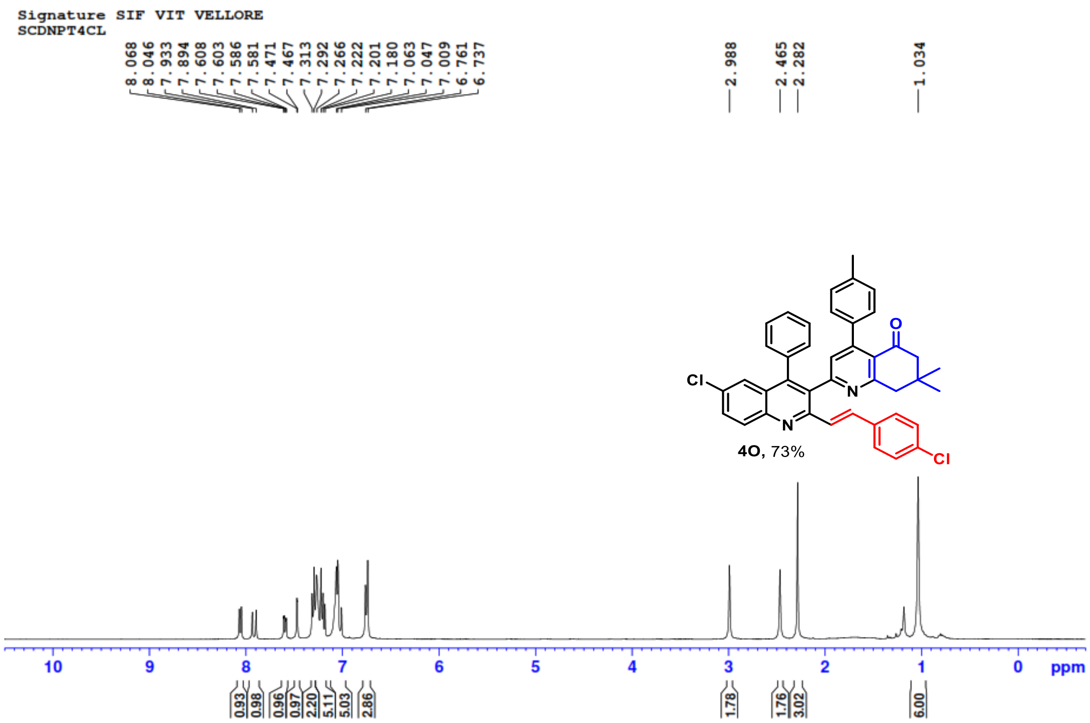
4N FTIR



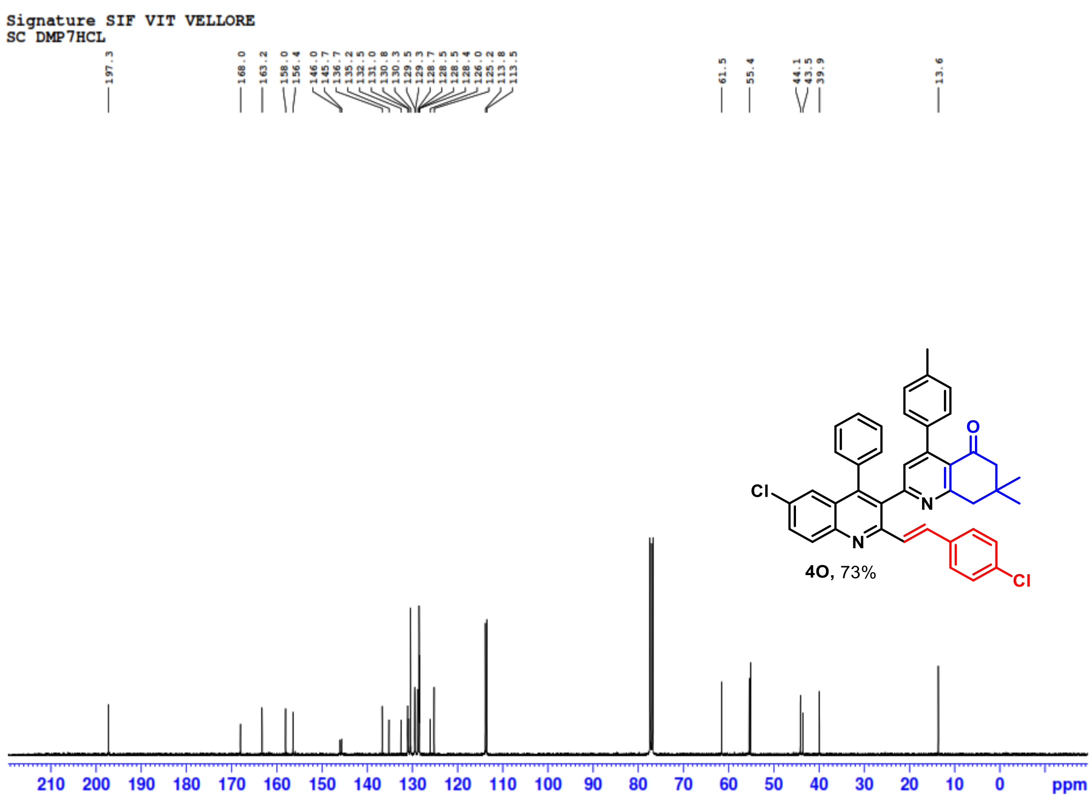
4N ESI (HRMS)



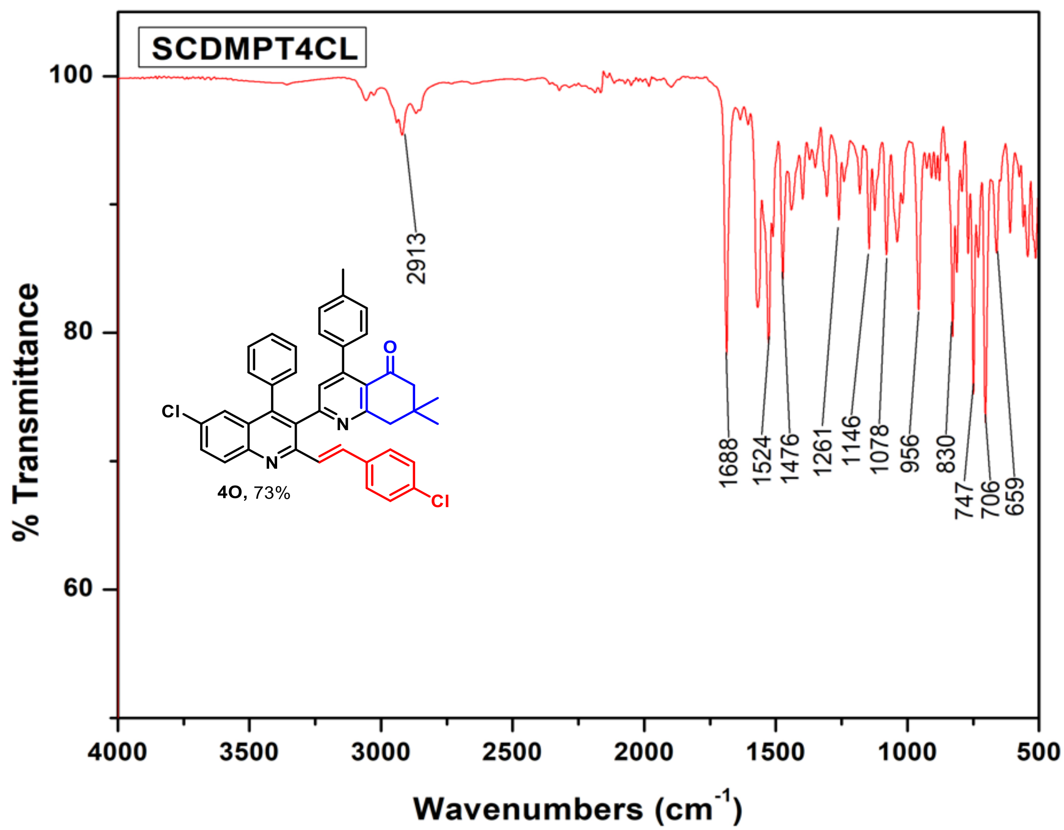
4O ^{1}H NMR (400 MHz, $CDCl_3$)



4O ^{13}C NMR (101 MHz, $CDCl_3$)



4O FTIR



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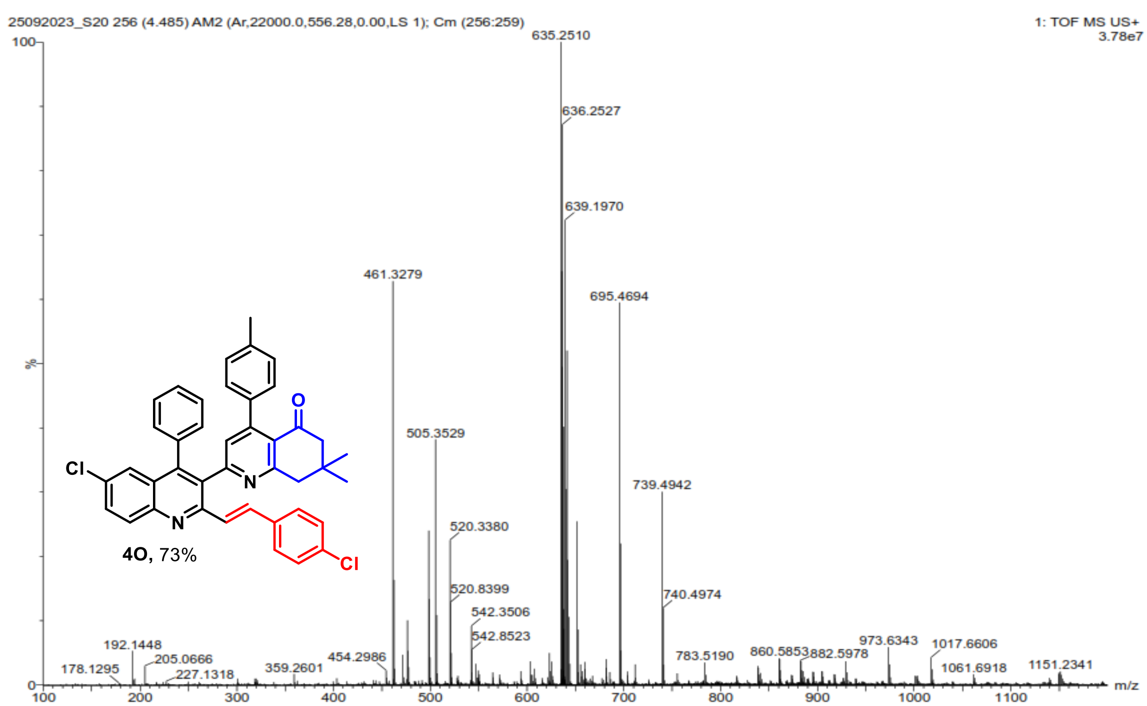
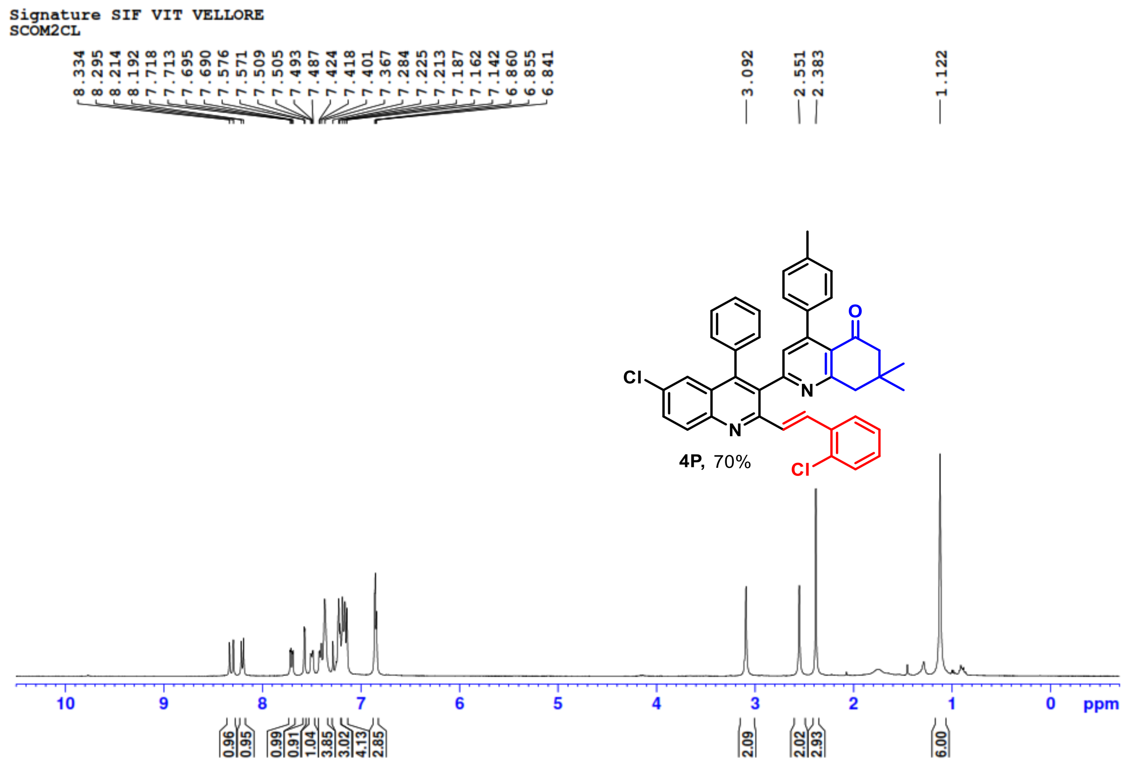
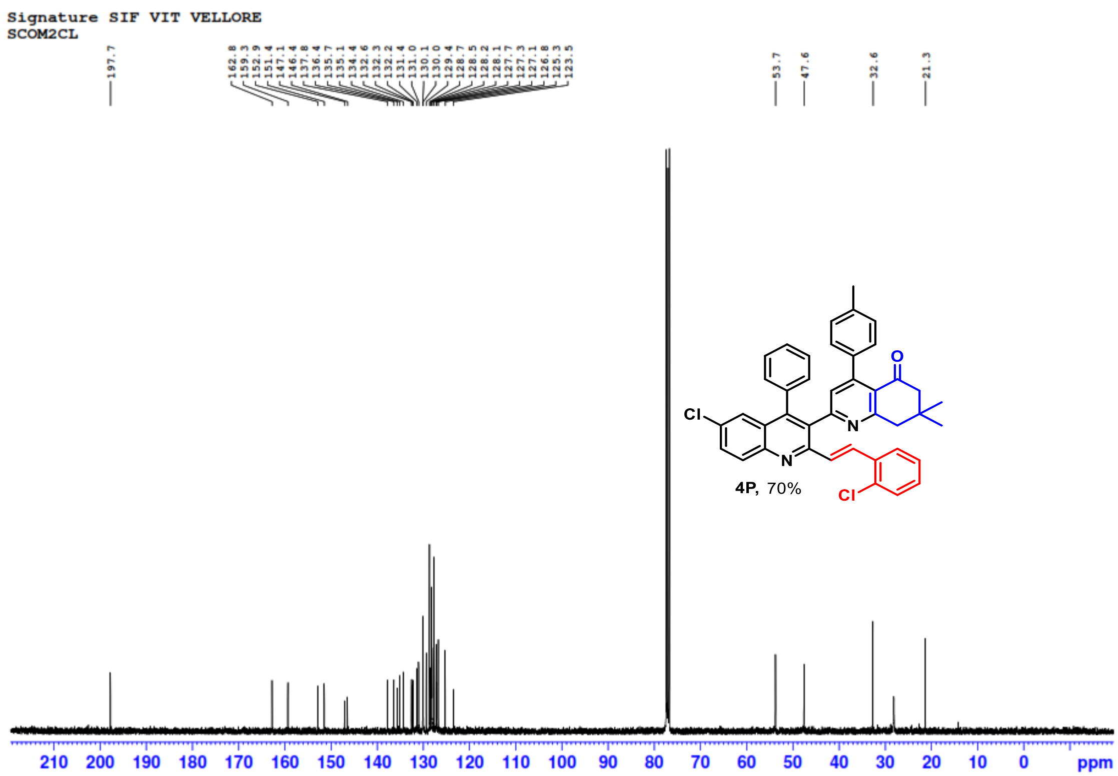


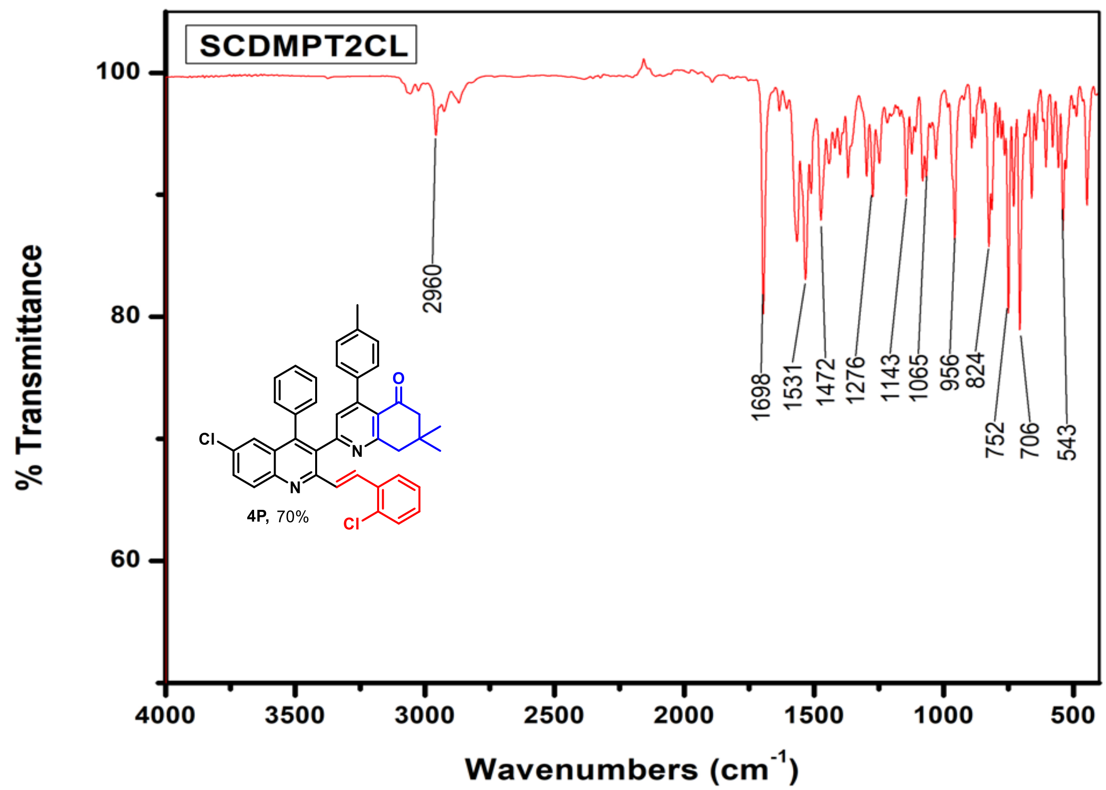
4P ^{1}H NMR (400 MHz, CDCl$_3$)



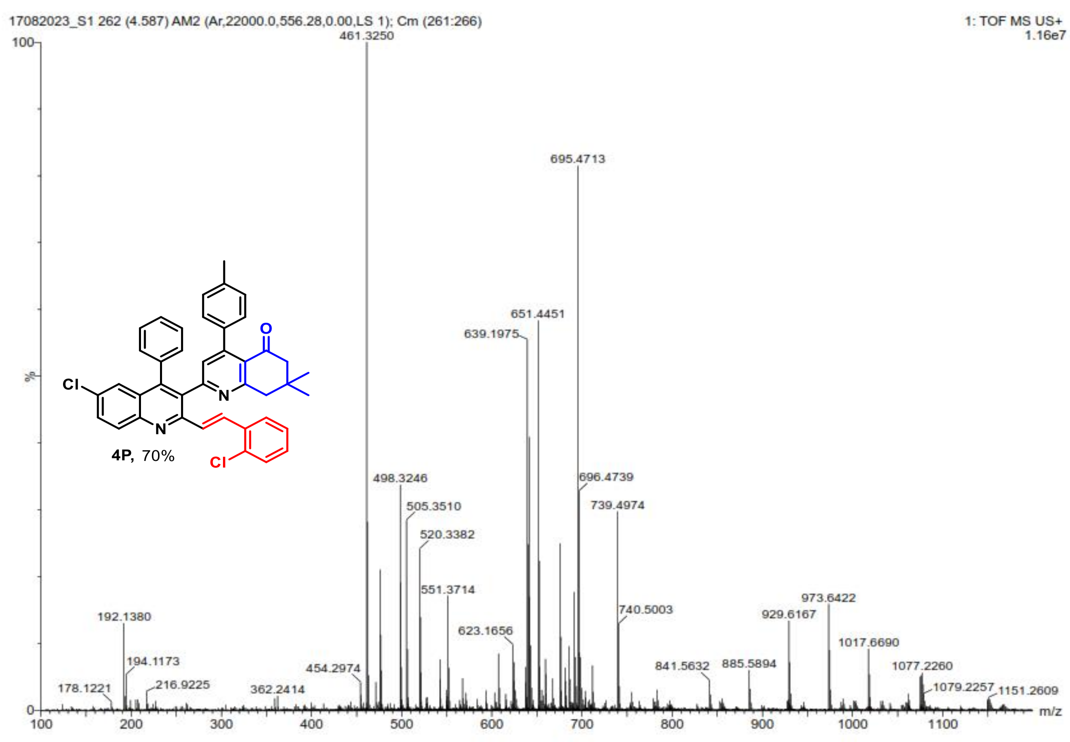
4P ^{13}C NMR (101 MHz, CDCl$_3$)



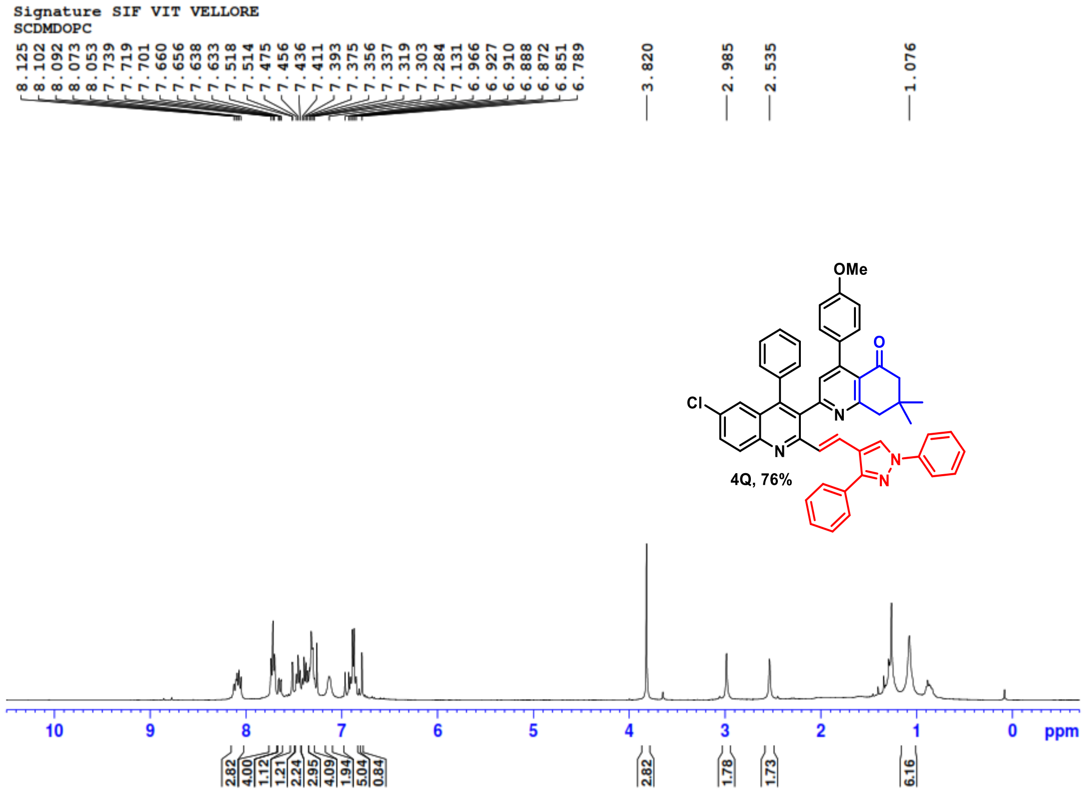
4P FTIR



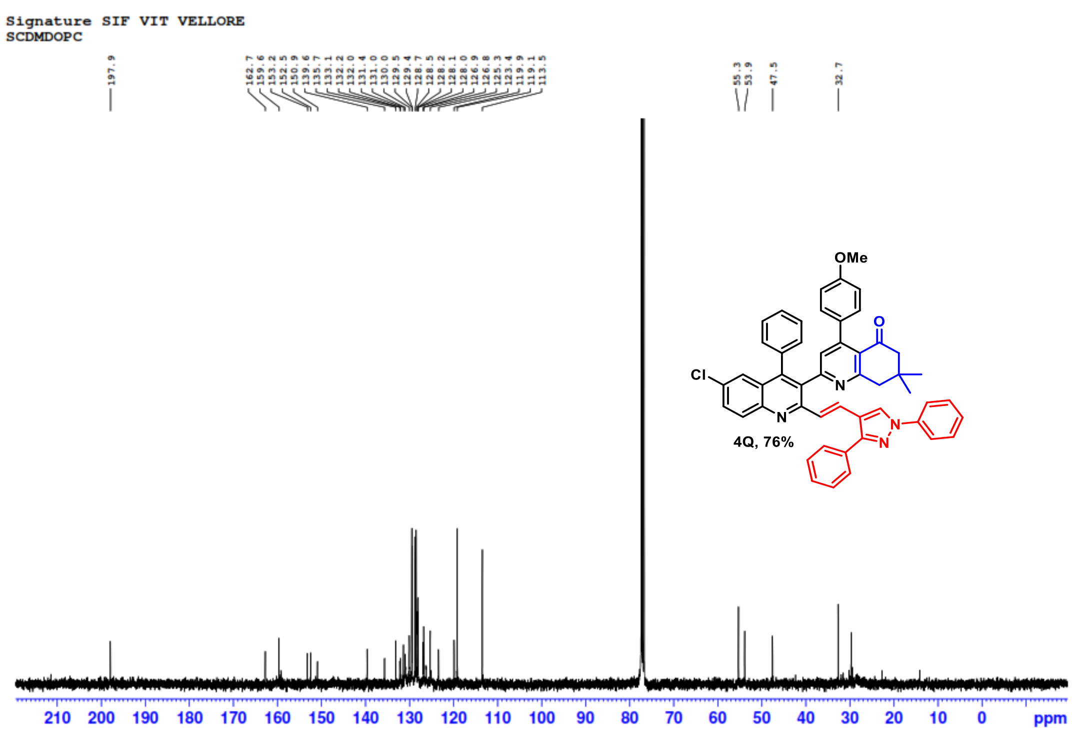
4P HRMS (ESI)



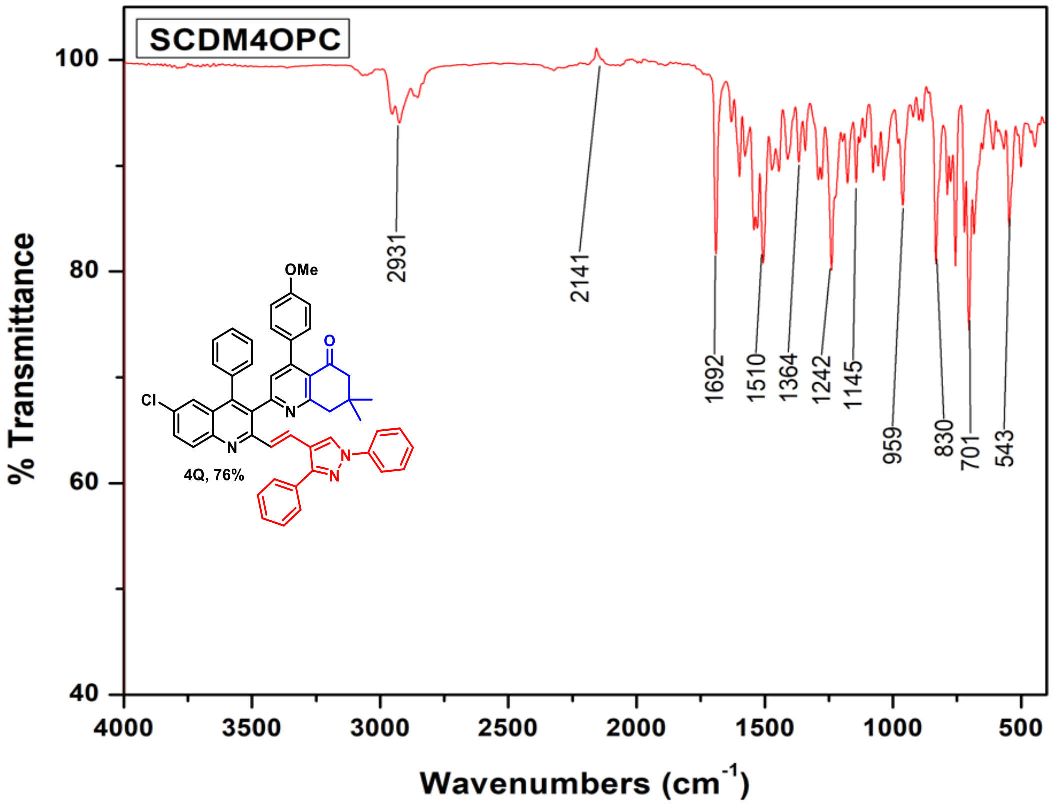
4Q ^{1}H NMR (400 MHz, $CDCl_3$)



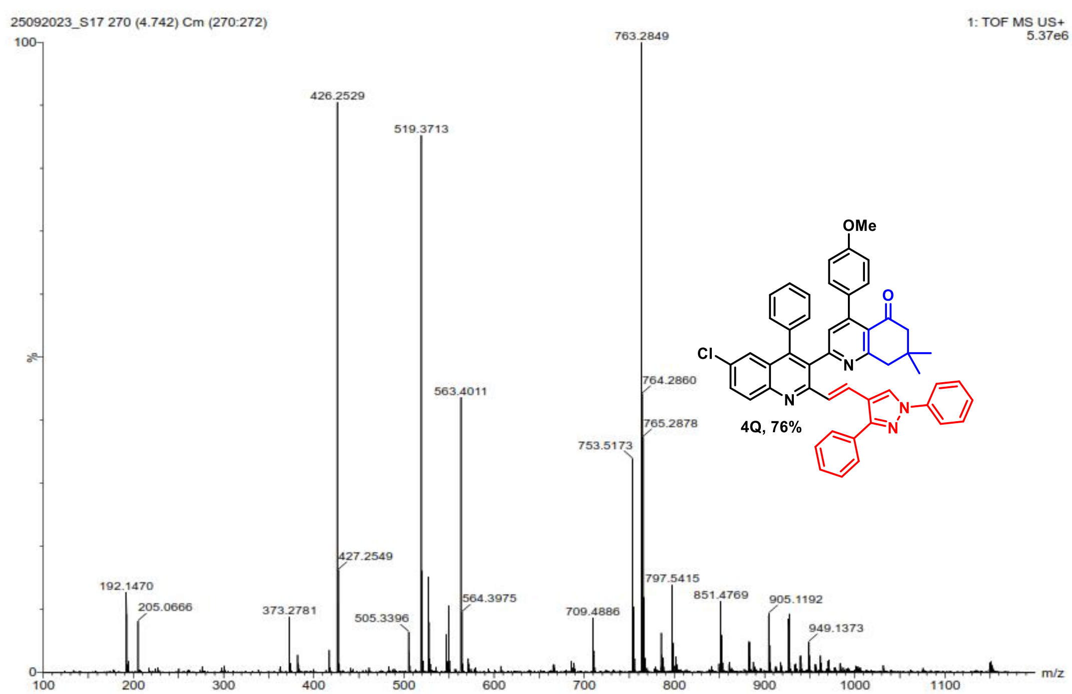
4Q ^{13}C NMR (101 MHz, $CDCl_3$)



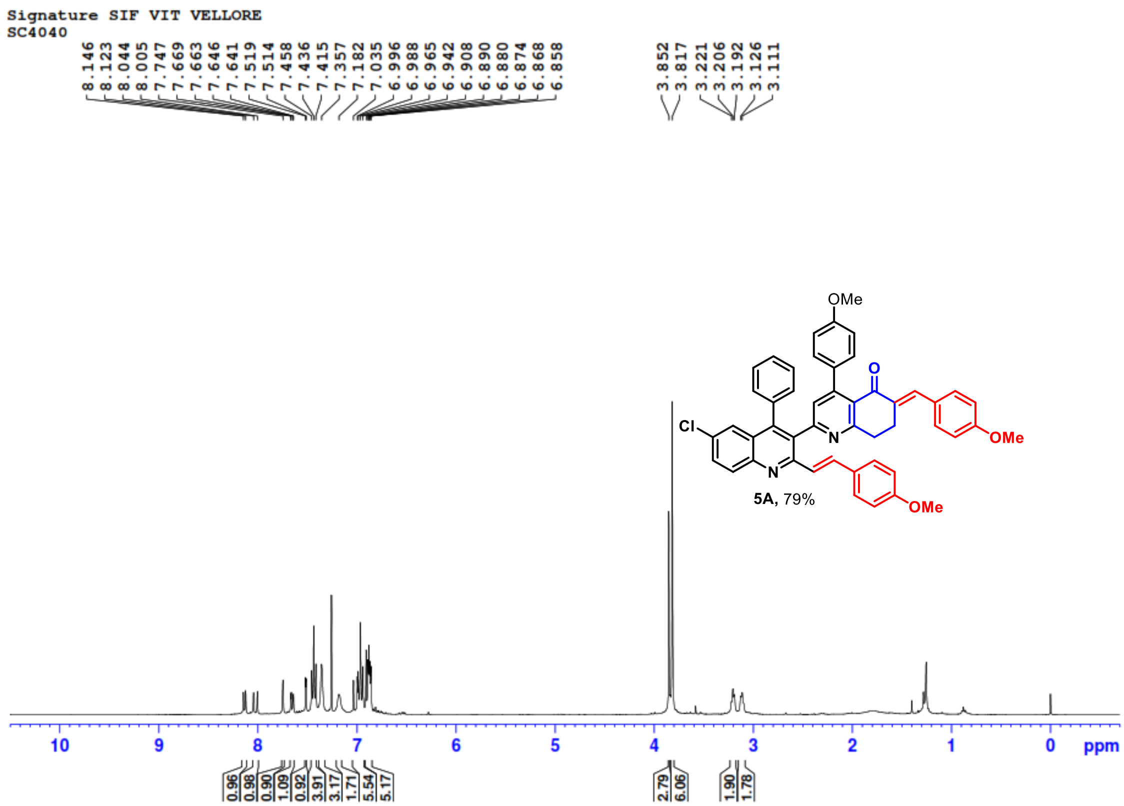
4Q FTIR



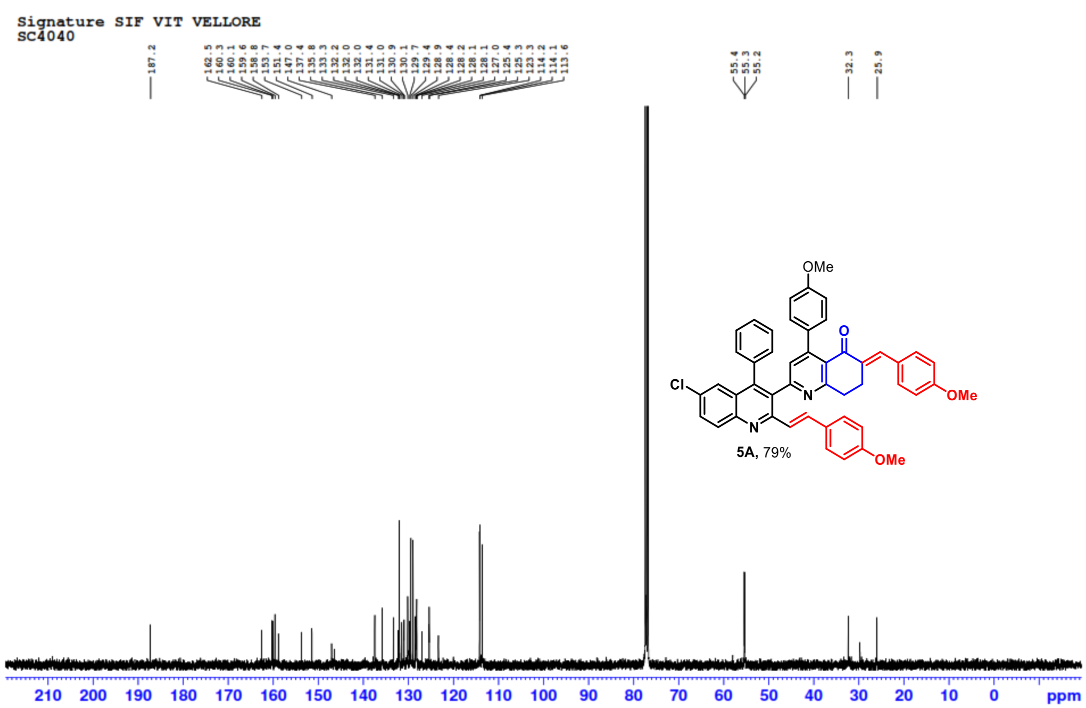
4Q HRMS (ESI)



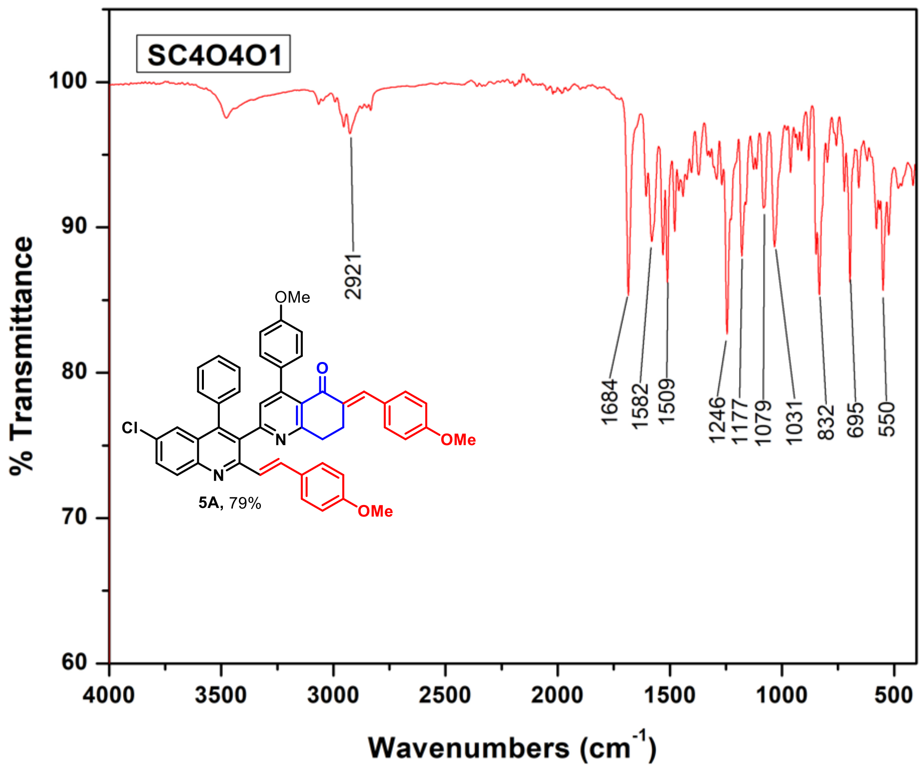
5A [1]H NMR (400 MHz, $CDCl_3$)



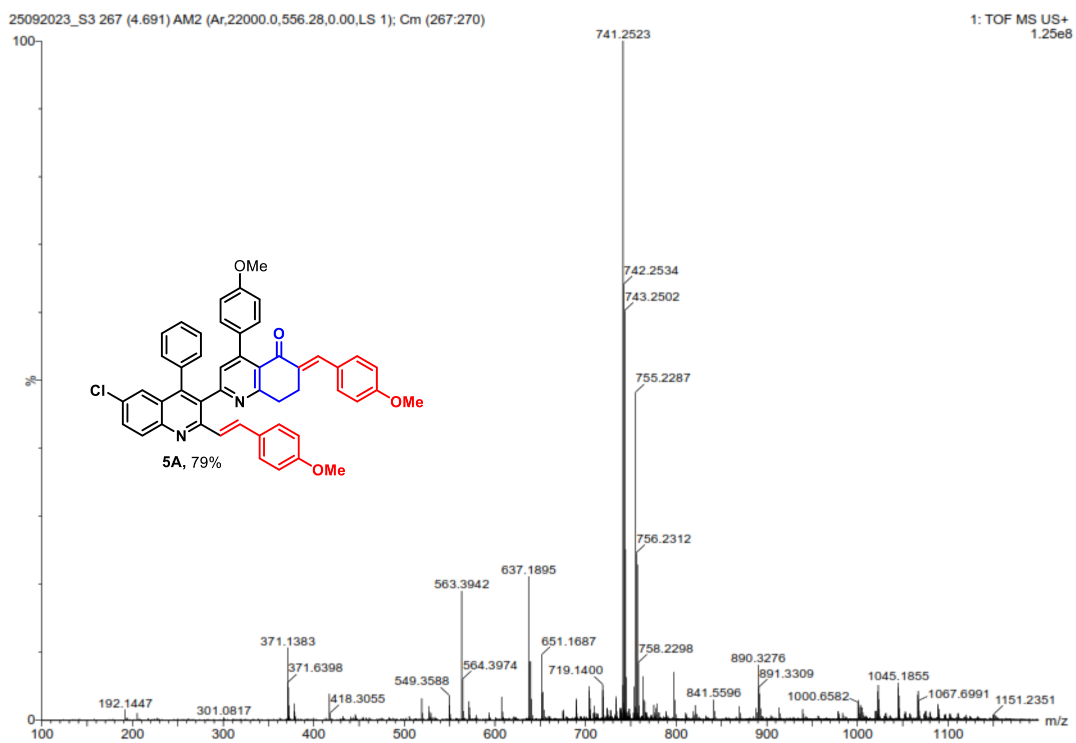
5A [13]C NMR (101 MHz, $CDCl_3$)



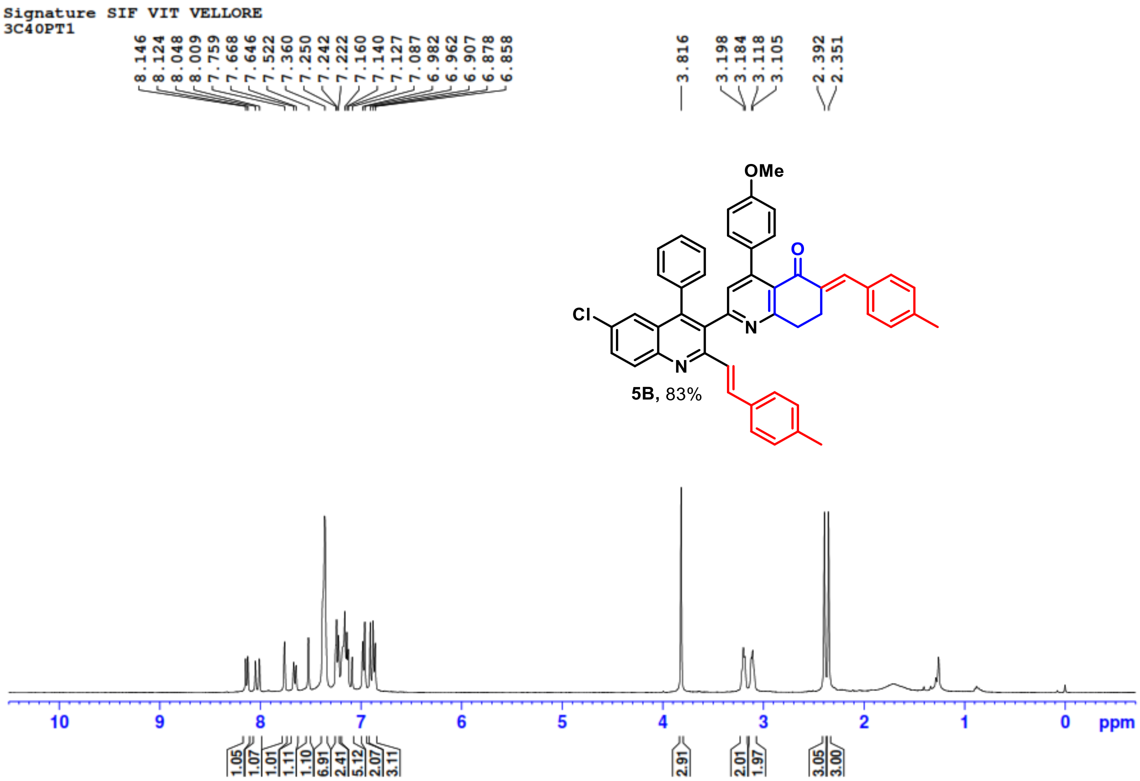
5A FTIR



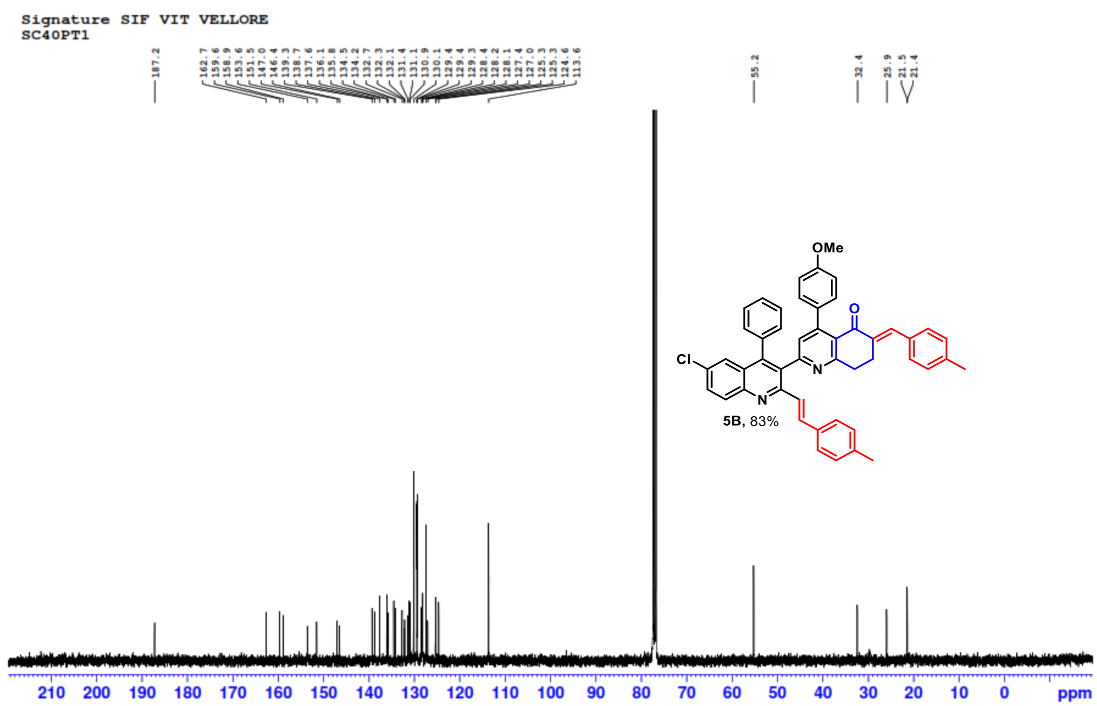
5A HRMS (ESI)



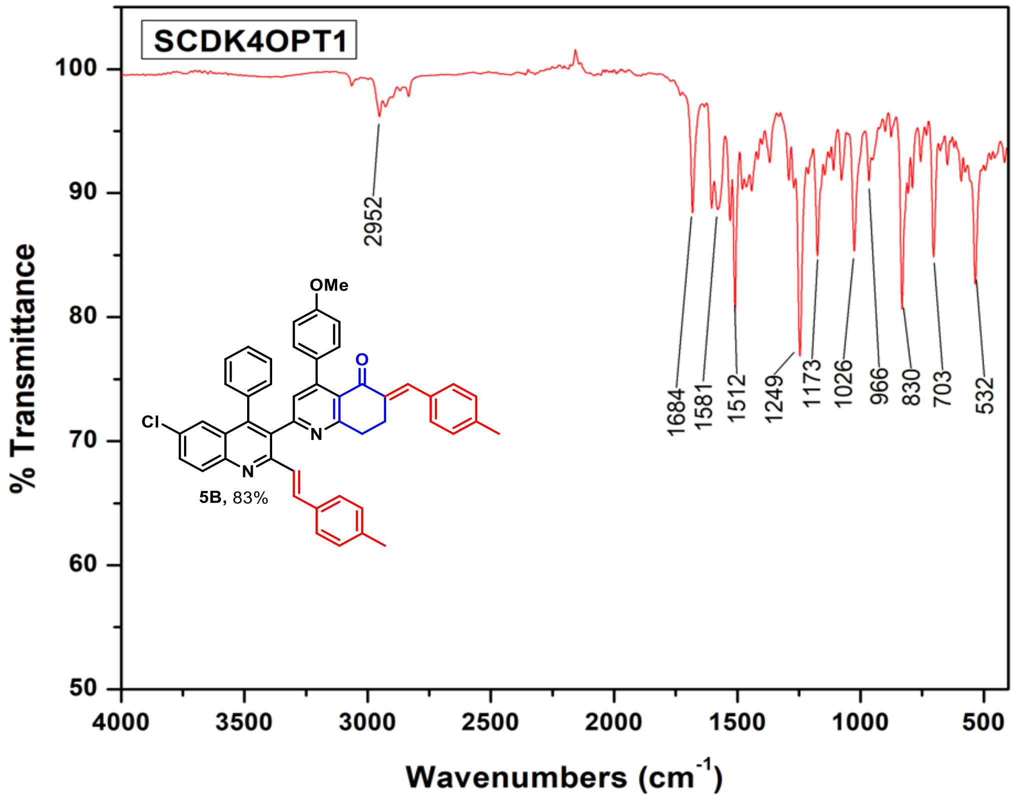
5B ^{1}H NMR (400 MHz, $CDCl_3$)



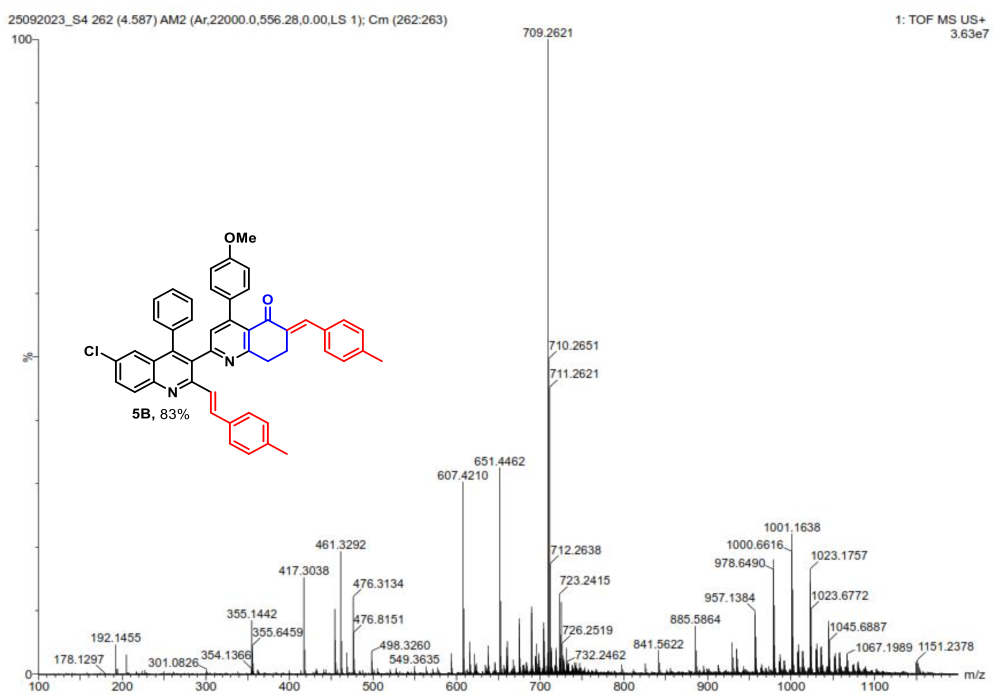
5B ^{13}C NMR (400 MHz, $CDCl_3$)



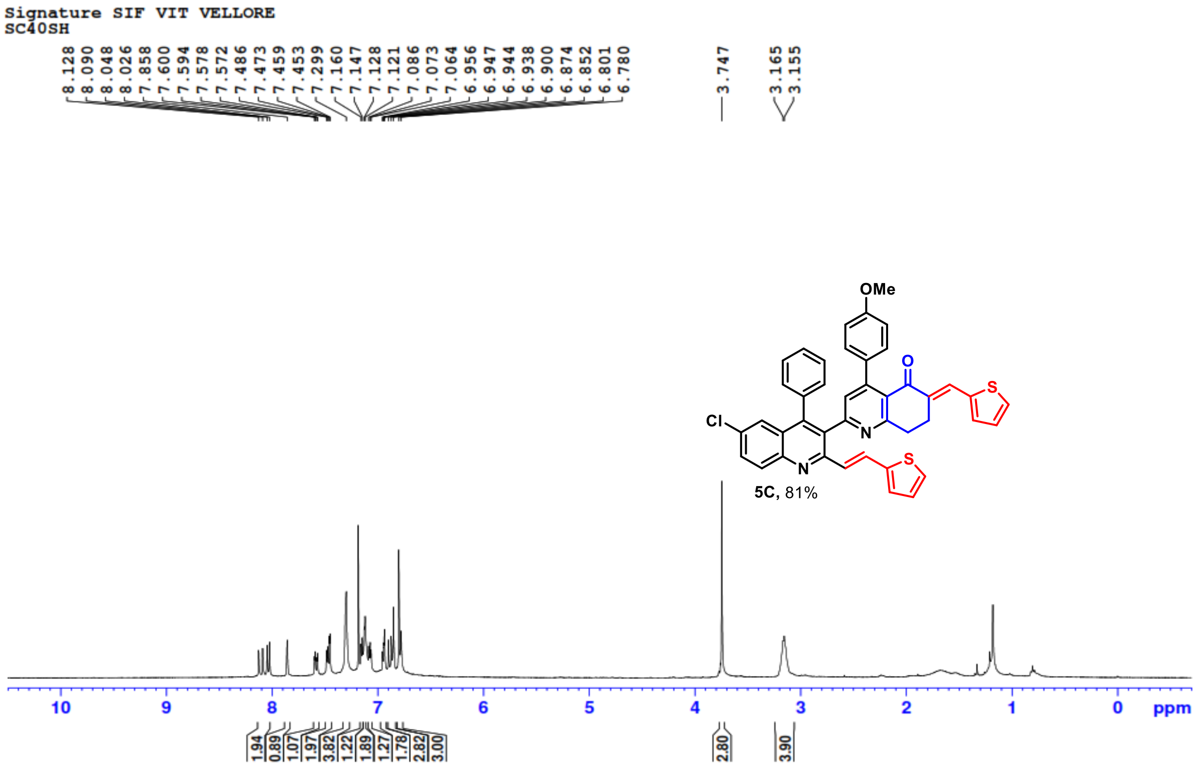
5B FTIR



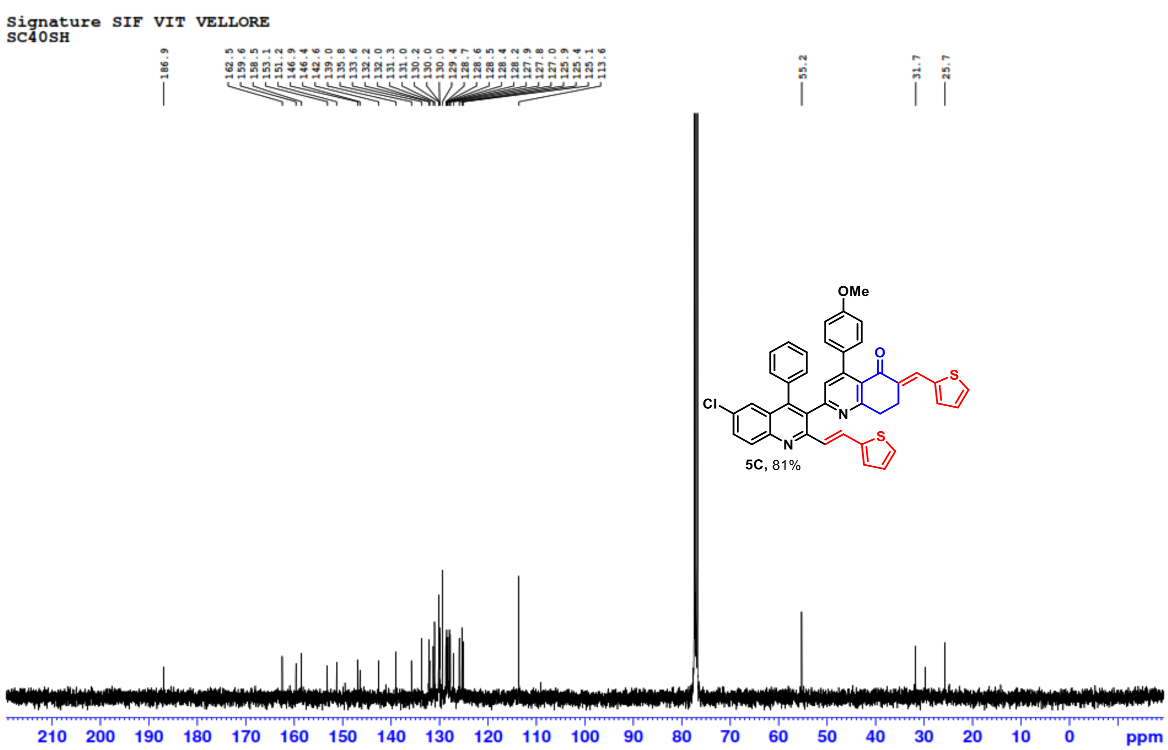
5B HRMS (ESI)

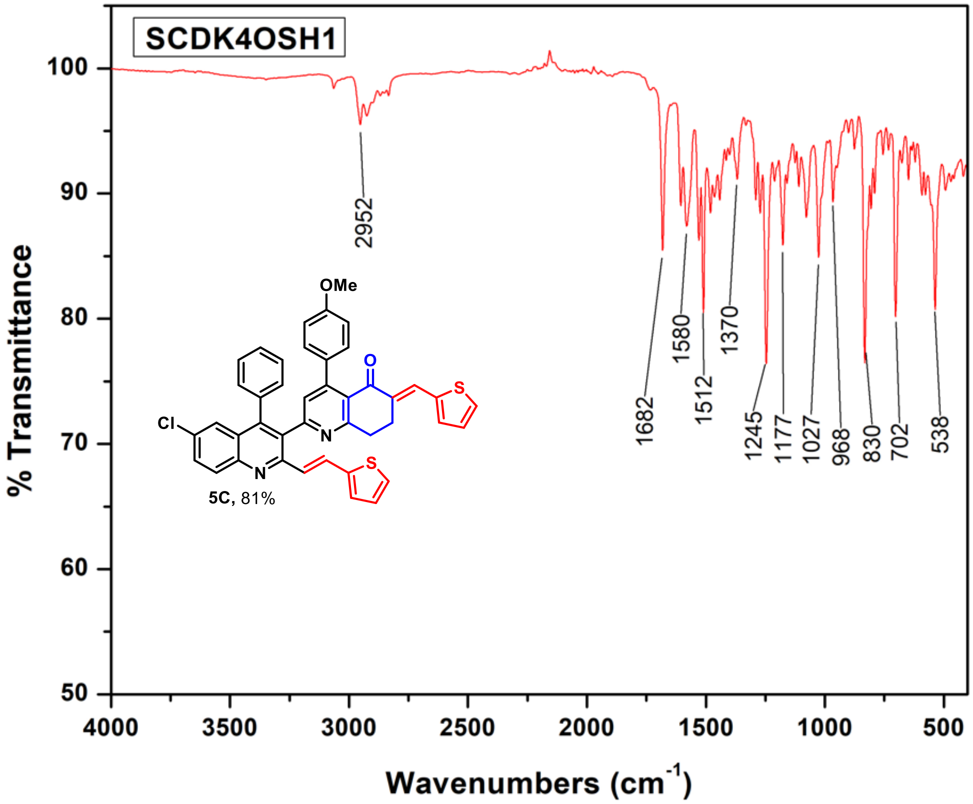


5C ^{1}H NMR (400 MHz, CDCl$_3$)

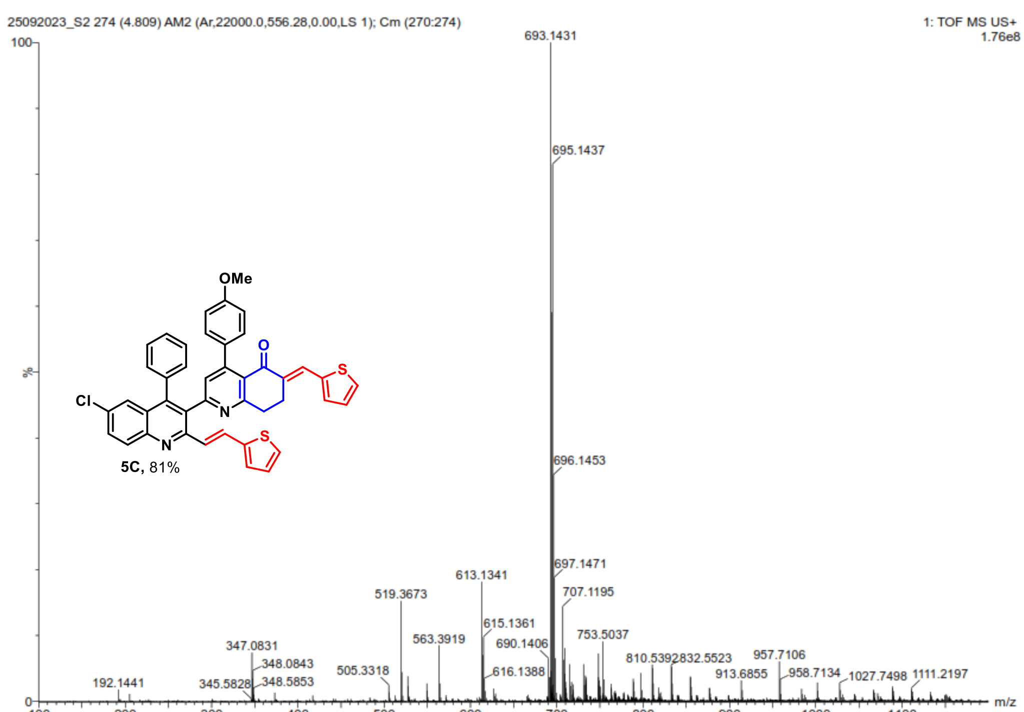


Q ^{13}C NMR (101 MHz, CDCl$_3$)




SCDK4OSH1
100
90
80
70
60
50
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
2952
1682
1580
1512
1370
1245
1177
1027
968
830
702
538
OMe
O
S
Cl
N
N
S
5C, 81%

5C HRMS (ESI)


25092023_S2 274 (4.809) AM2 (Ar,22000.0,556.28,0.00,LS 1); Cm (270:274)
1: TOF MS US+
1.76e8
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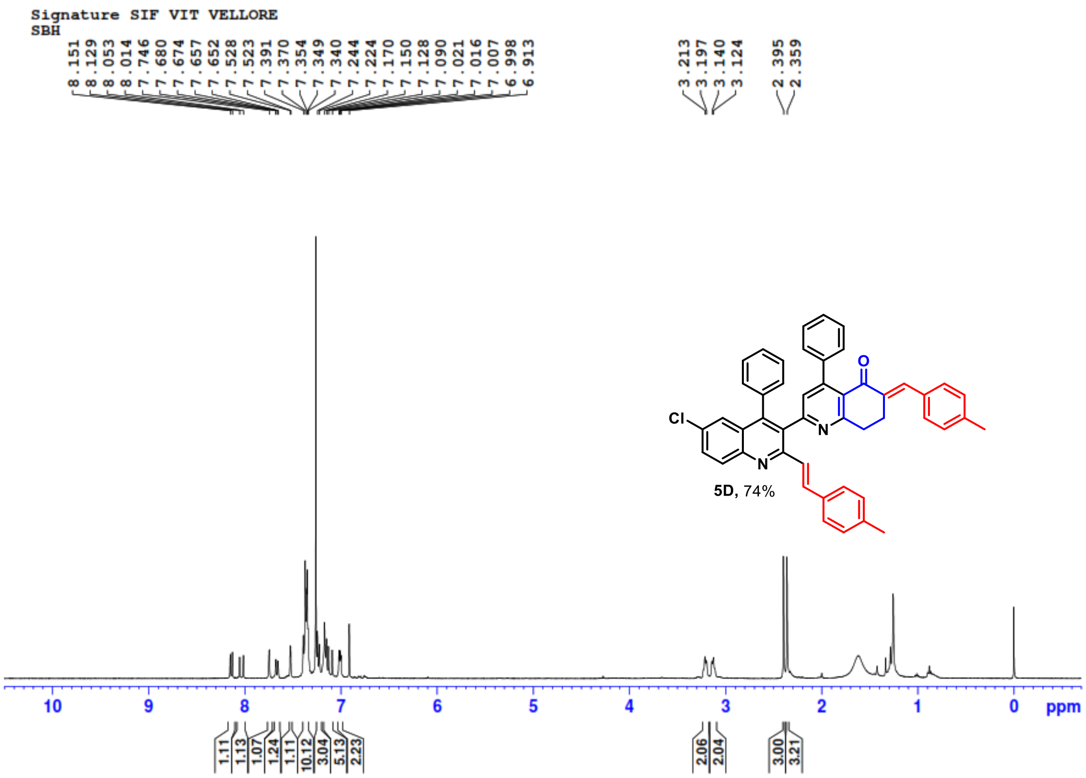
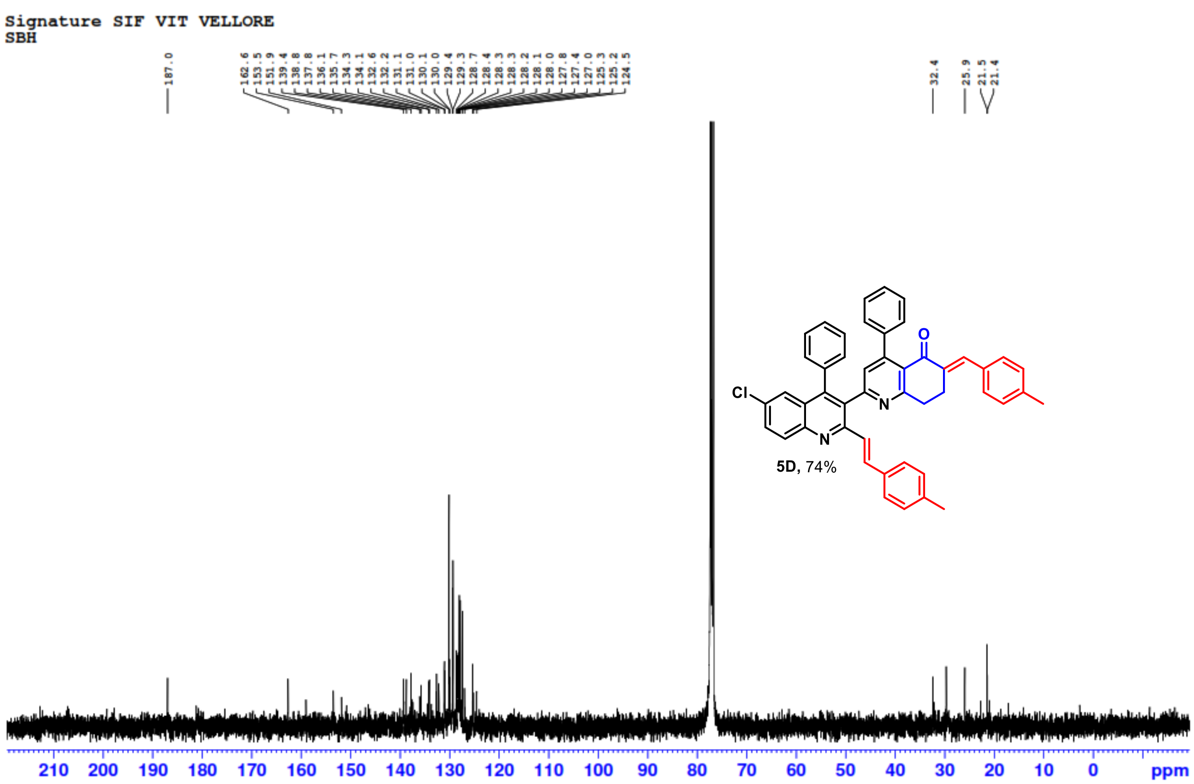
695.1437
696.1453
697.1471
707.1195
613.1341
519.3673
615.1361
753.5037
563.3919
690.1406
347.0831
810.5392
832.5523
957.7106
348.0843
505.3318
616.1388
913.6855
958.7134
1027.7498
1111.2197
192.1441
345.5828
348.5853
%
m/z
OMe
O
S
Cl
N
N
S
5C, 81%

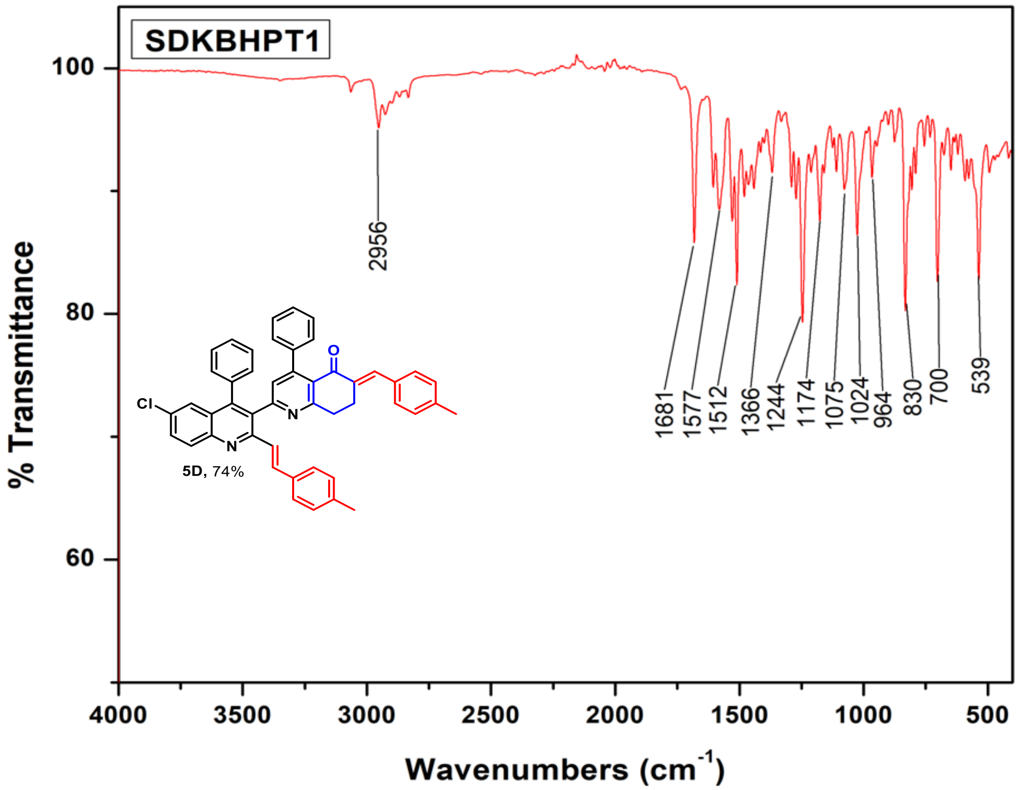
5D ^{1}H NMR (400 MHz, $CDCl_3$)



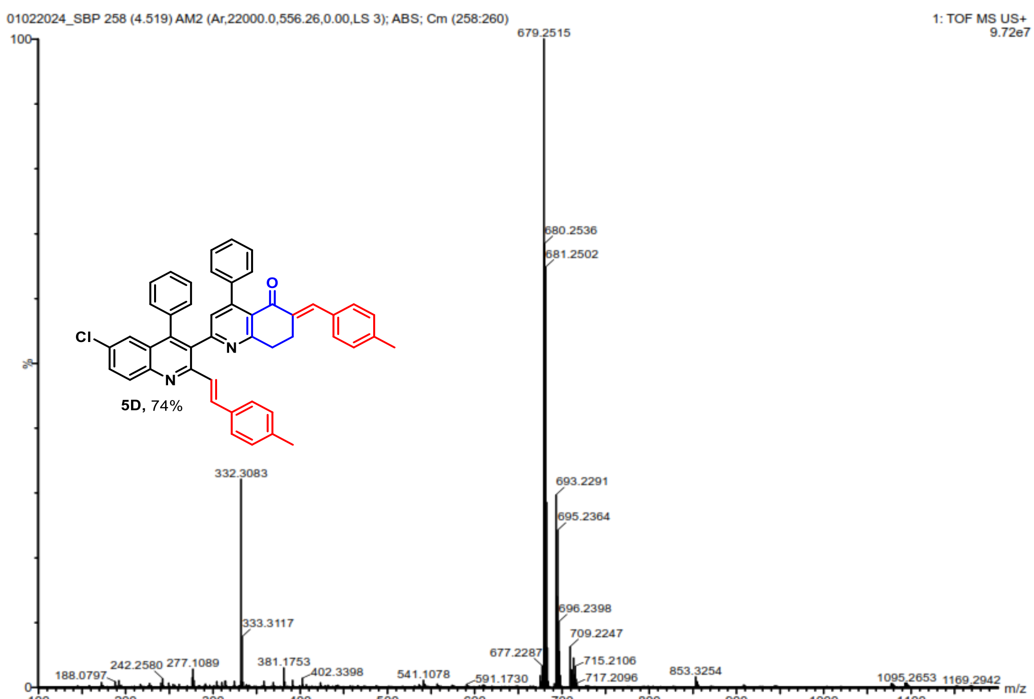
5D ^{13}C NMR (101 MHz, $CDCl_3$)



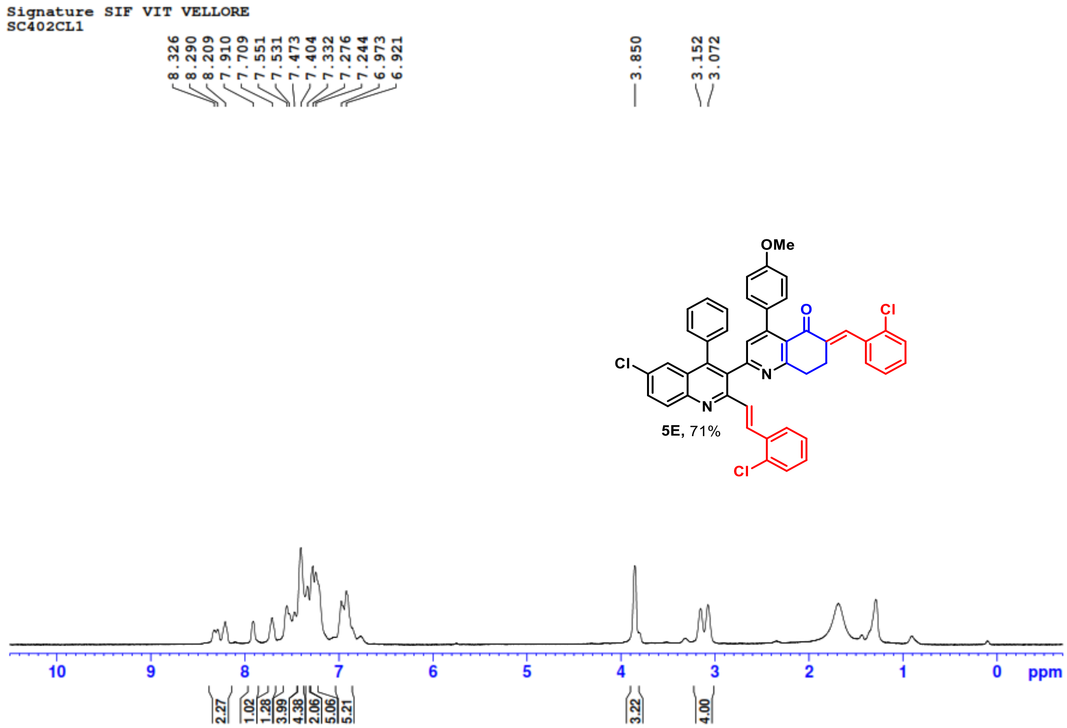
5D FTIR



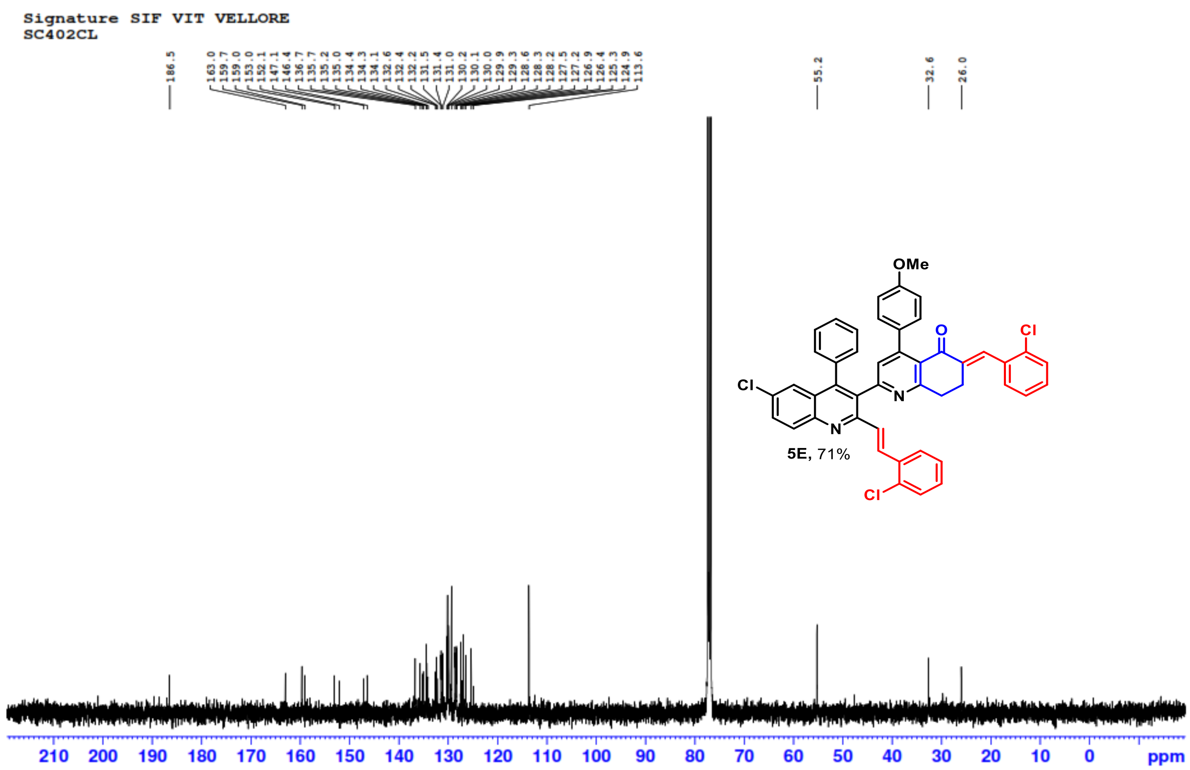
5D HRMS (ESI)



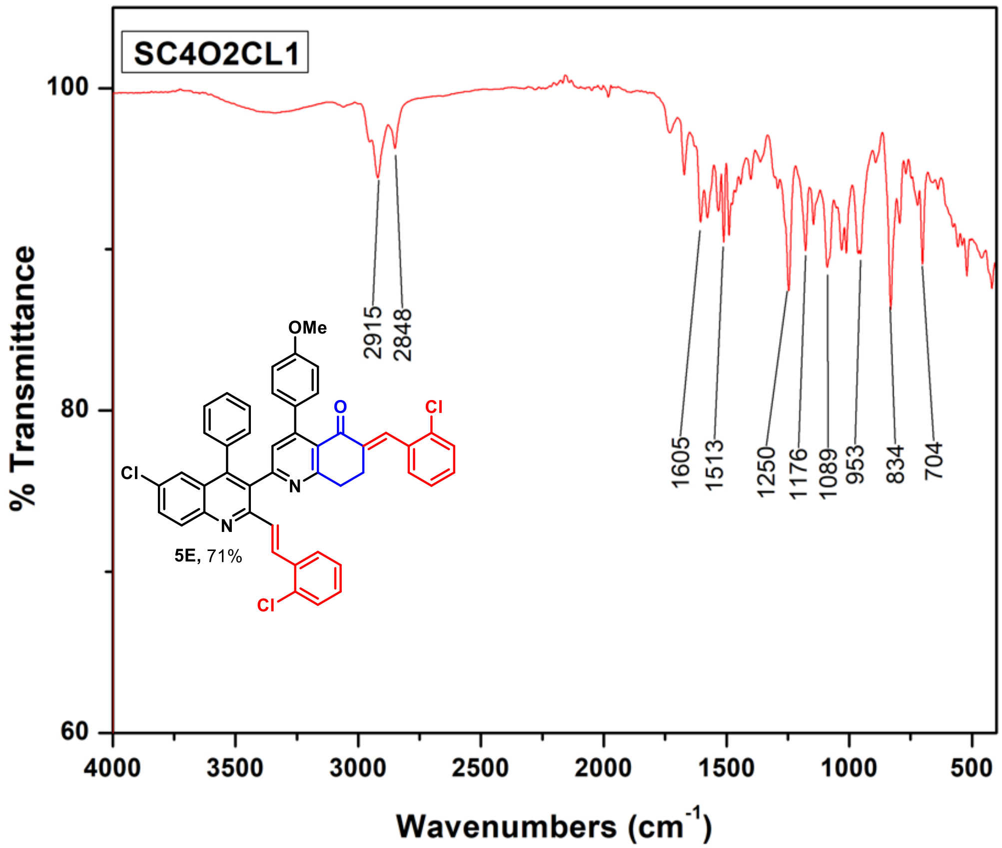
5E [1]H NMR (400 MHz, $CDCl_3$)



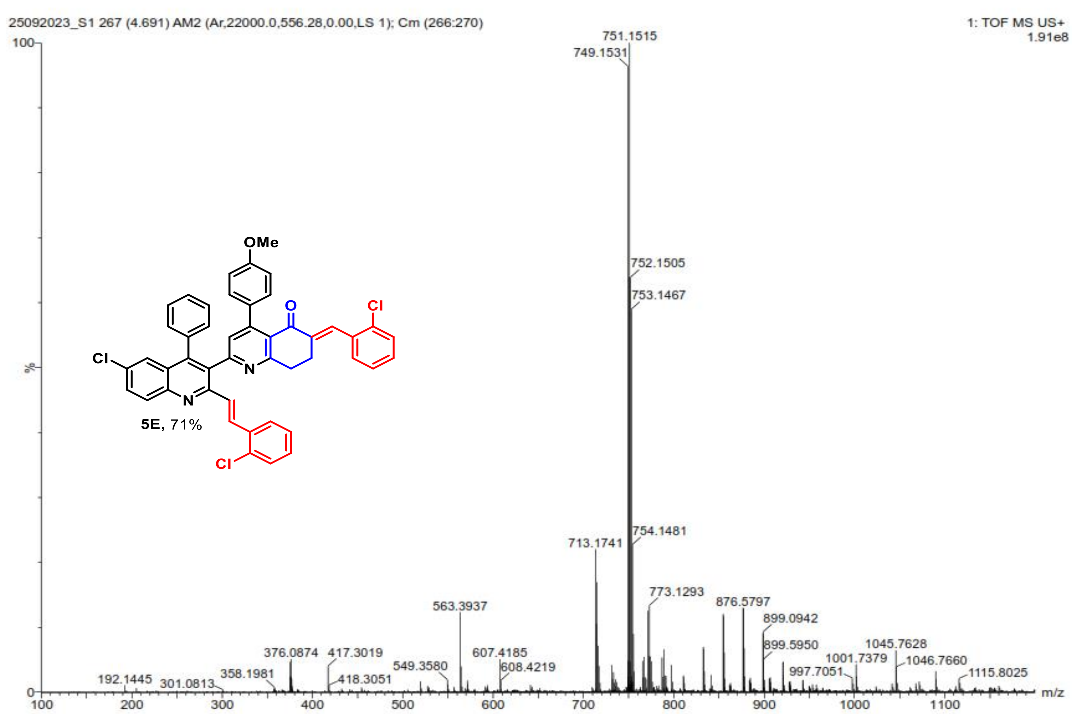
5E [13]C NMR (101 MHz, $CDCl_3$)



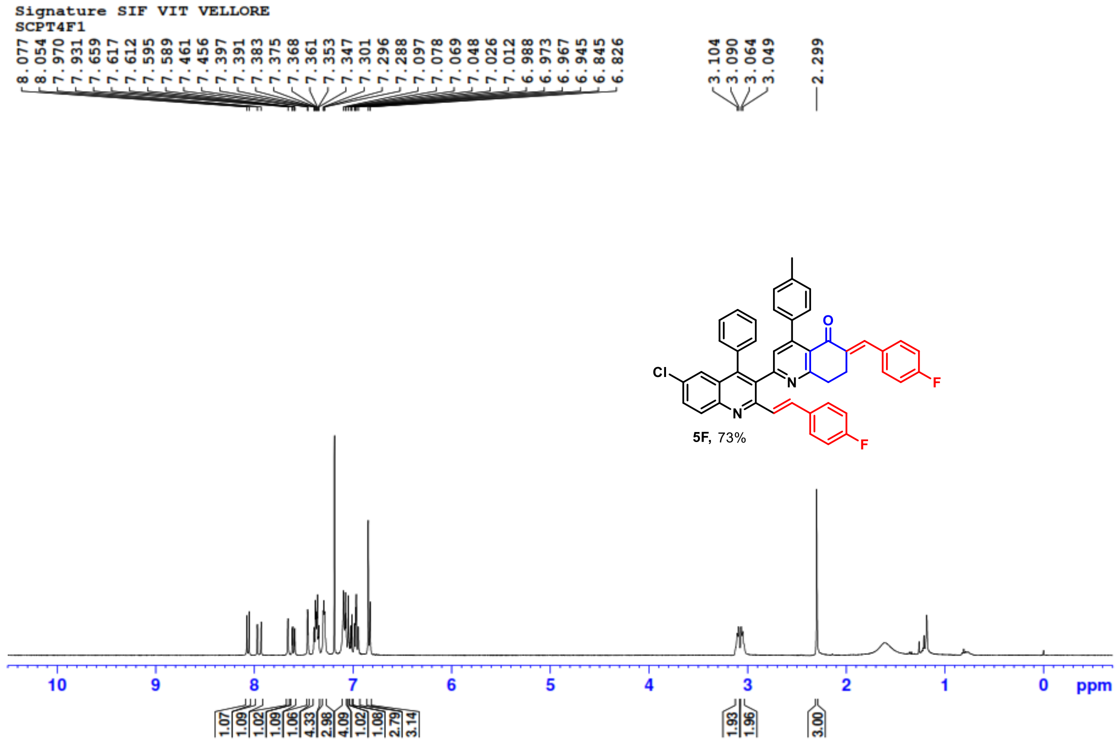
5E FTIR



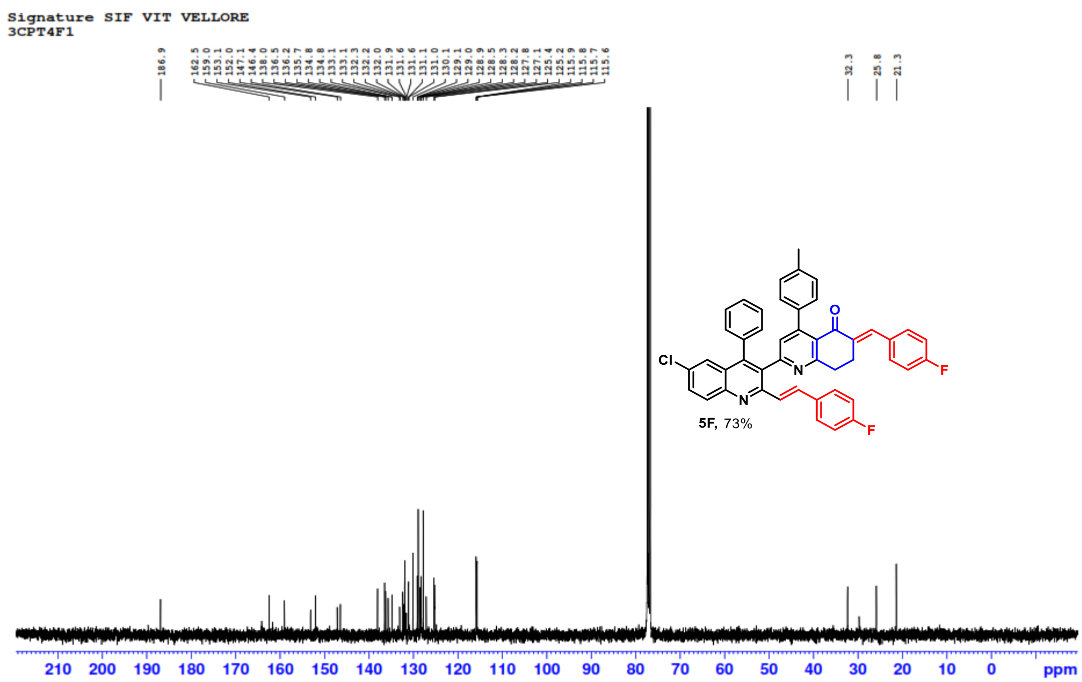
5E HRMS (ESI)



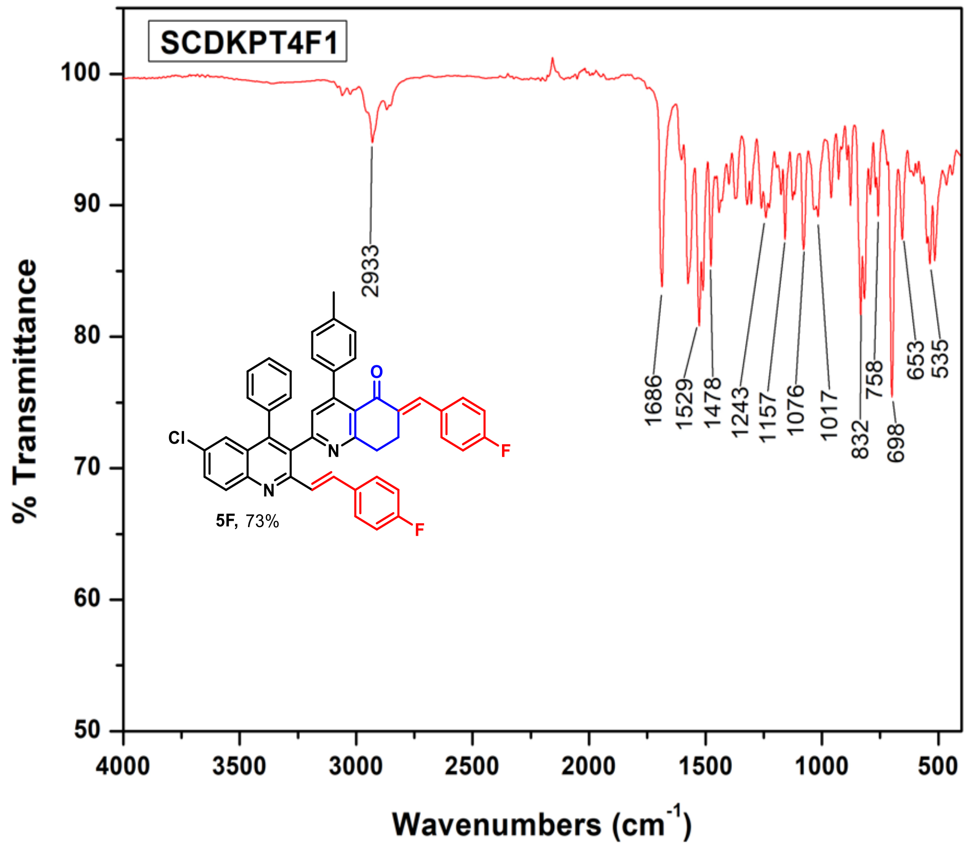
5F ^{1}H NMR (400 MHz, CDCl$_3$)



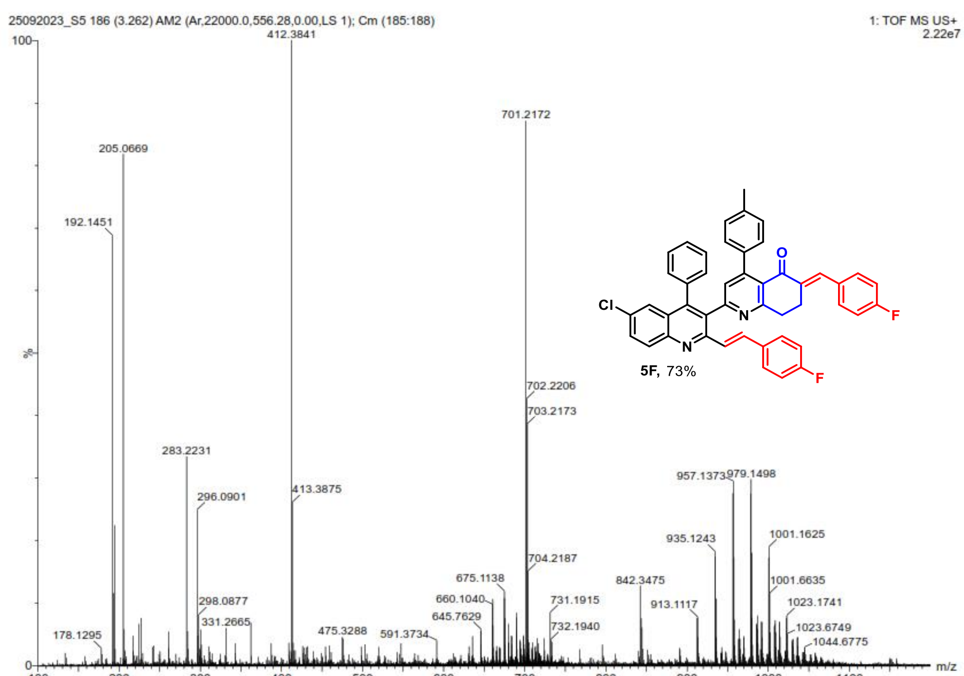
5F ^{13}C NMR (101 MHz, CDCl$_3$)



5F FTIR



5F HRMS (ESI)



3. X-Ray Crystallography for Data 4D’: (2264822)

Compound **4D’ crystals** were grown from a solution consisting of $CDCl_3$ and ethyl acetate at 25 °C. The X-ray diffraction data were collected utilizing D8- QUEST Single Crystal XRD diffractometer with X-ray intensity data were measured (λ = 0.71073 Å). A crystal **4D’** with approximate dimensions of 0.100 mm x 0.140 mm x 0.193 mm, was employed for the X-ray crystallographic analysis.

ORTEP diagram:

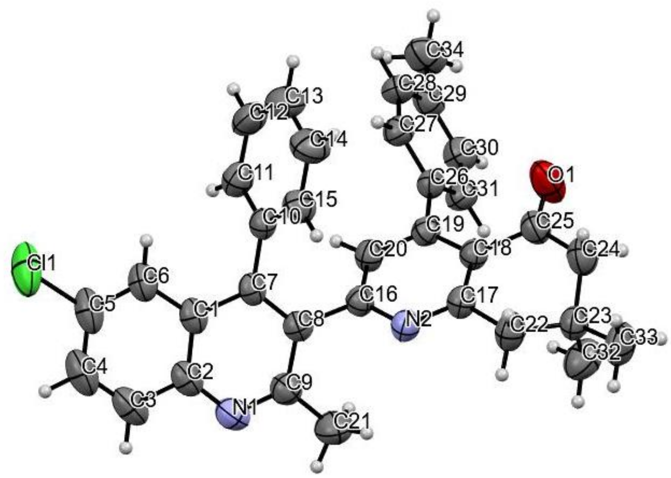


Fig S4 ORTEP diagram of the compound 4D’

Eclipsed diagram:

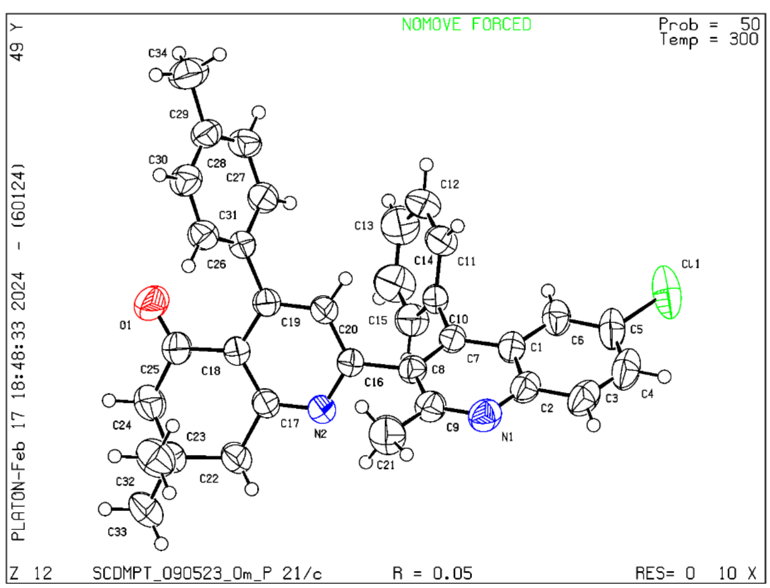


Fig S4 Eclipsed diagram of the compound 4D’

Crystal Structure Report for 4D’

A specimen of $C_{34}H_{29}ClN_2O$, approximate dimensions 0.100 mm x 0.140 mm x 0.193 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S2. Sample and crystal data for 4D’.

Identification code	SCDMPT	
Chemical formula	$C_{34}H_{29}ClN_2O$	
Formula weight	517.04 g/mol	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.140 x 0.193 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.6720(11) Å	α = 90°
	b = 11.8313(9) Å	β = 103.345(3)°
	c = 17.7342(12) Å	γ = 90°
Volume	2791.2(4) $Å^3$	
Z	4	
Density (calculated)	1.230 g/cm^3	
Absorption coefficient	0.166 mm^{-1}	
F(000)	1088	

Table S3. Data collection and structure refinement for 4D’.

Theta range for data collection	2.09 to 25.70°
Index ranges	-16<=h<=16, -14<=k<=14, -21<=l<=21
Reflections collected	32805
Independent reflections	5305 [R(int) = 0.0661]
Max. and min. transmission	0.9840 and 0.9690
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)

Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5305 / 0 / 347
Goodness-of-fit on F^2	1.030
Final R indices	2950 data; I>2σ(I) R1 = 0.0549, wR2 = 0.1147
	all data R1 = 0.1192, wR2 = 0.1524
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0511P)^2+1.4451P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.221 and -0.394 eÅ^{-3}
R.M.S. deviation from mean	0.043 eÅ^{-3}

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 4D'.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Cl1	0.48103(7)	0.08011(10)	0.24765(5)	0.1014(4)
O1	0.05683(18)	0.7240(2)	0.72289(15)	0.0933(8)
N1	0.53137(17)	0.7053(2)	0.47000(14)	0.0614(7)
N2	0.26311(17)	0.63032(18)	0.54919(12)	0.0500(6)
C1	0.4319(2)	0.8662(2)	0.40976(14)	0.0482(7)
C2	0.5133(2)	0.7911(3)	0.41707(16)	0.0542(7)
C3	0.5816(2)	0.8064(3)	0.36855(18)	0.0677(9)
C4	0.5703(3)	0.8937(3)	0.31708(18)	0.0747(10)
C5	0.4909(2)	0.9684(3)	0.31169(16)	0.0672(9)
C6	0.4224(2)	0.9564(3)	0.35621(15)	0.0576(8)
C7	0.36111(19)	0.8463(2)	0.45654(14)	0.0436(6)
C8	0.37823(19)	0.7567(2)	0.50705(14)	0.0449(6)
C9	0.4670(2)	0.6892(2)	0.51417(16)	0.0562(7)
C10	0.27065(19)	0.9196(2)	0.44884(14)	0.0452(6)
C11	0.2797(2)	0.0298(2)	0.47455(16)	0.0603(8)
C12	0.1953(3)	0.0959(3)	0.47019(19)	0.0747(10)

C13	0.1018(3)	0.0530(3)	0.4384(2)	0.0848(11)
C14	0.0921(3)	0.9439(3)	0.4119(2)	0.0827(10)
C15	0.1758(2)	0.8772(3)	0.41754(17)	0.0612(8)
C16	0.30743(19)	0.7318(2)	0.55744(14)	0.0449(6)
C17	0.1972(2)	0.6080(2)	0.59294(15)	0.0485(7)
C18	0.17264(19)	0.6849(2)	0.64554(14)	0.0461(7)
C19	0.22364(19)	0.7893(2)	0.65660(14)	0.0452(6)
C20	0.2907(2)	0.8106(2)	0.61074(14)	0.0480(7)
C21	0.4921(2)	0.5994(3)	0.57473(19)	0.0806(10)
C22	0.1501(2)	0.4922(2)	0.58065(16)	0.0629(8)
C23	0.1070(2)	0.4496(2)	0.64696(16)	0.0552(7)
C24	0.0413(2)	0.5421(3)	0.66715(19)	0.0698(9)
C25	0.0894(2)	0.6562(3)	0.68366(17)	0.0579(8)
C26	0.21388(19)	0.8780(2)	0.71370(14)	0.0442(6)
C27	0.1815(2)	0.9850(2)	0.68935(16)	0.0546(7)
C28	0.1823(2)	0.0706(2)	0.74229(18)	0.0595(8)
C29	0.2173(2)	0.0531(2)	0.82068(17)	0.0545(7)
C30	0.2494(2)	0.9467(2)	0.84463(16)	0.0587(8)
C31	0.2480(2)	0.8601(2)	0.79261(15)	0.0552(7)
C32	0.1915(3)	0.4225(3)	0.71713(19)	0.0822(10)
C33	0.0447(3)	0.3428(3)	0.6219(2)	0.0810(10)
C34	0.2201(3)	0.1491(3)	0.8771(2)	0.0818(10)

Table S5. Bond lengths (Å) for 4D'.

Cl1-C5	1.727(3)	O1-C25	1.211(3)
N1-C9	1.320(3)	N1-C2	1.366(4)
N2-C16	1.338(3)	N2-C17	1.344(3)
C1-C2	1.405(4)	C1-C6	1.415(4)
C1-C7	1.432(3)	C2-C3	1.420(4)
C3-C4	1.363(4)	C3-H3	0.930000
C4-C5	1.387(5)	C4-H4	0.930000

C5-C6	1.364(4)	C6-H6	0.930000
C7-C8	1.373(3)	C7-C10	1.490(4)
C8-C9	1.434(4)	C8-C16	1.490(3)
C9-C21	1.493(4)	C10-C11	1.378(4)
C10-C15	1.382(4)	C11-C12	1.381(4)
C11-H11	0.930000	C12-C13	1.370(5)
C12-H12	0.930000	C13-C14	1.369(5)
C13-H13	0.930000	C14-C15	1.375(4)
C14-H14	0.930000	C15-H15	0.930000
C16-C20	1.384(3)	C17-C18	1.398(3)
C17-C22	1.508(4)	C18-C19	1.410(4)
C18-C25	1.491(4)	C19-C20	1.382(3)
C19-C26	1.486(3)	C20-H20	0.930000
C21-H21A	0.960000	C21-H21B	0.960000
C21-H21C	0.960000	C22-C23	1.518(4)
C22-H22A	0.970000	C22-H22B	0.970000
C23-C24	1.509(4)	C23-C32	1.524(4)
C23-C33	1.531(4)	C24-C25	1.501(4)
C24-H24A	0.970000	C24-H24B	0.970000
C26-C27	1.377(4)	C26-C31	1.386(4)
C27-C28	1.380(4)	C27-H27	0.930000
C28-C29	1.378(4)	C28-H28	0.930000
C29-C30	1.368(4)	C29-C34	1.508(4)
C30-C31	1.376(4)	C30-H30	0.930000
C31-H31	0.930000	C32-H32A	0.960000
C32-H32B	0.960000	C32-H32C	0.960000
C33-H33A	0.960000	C33-H33B	0.960000
C33-H33C	0.960000	C34-H34A	0.960000
C34-H34B	0.960000	C34-H34C	0.960000

Table S6. Bond angles (°) for 4D'.			
C9-N1-C2	118.4(2)	C16-N2-C17	117.4(2)
C2-C1-C6	119.1(2)	C2-C1-C7	118.0(2)
C6-C1-C7	122.9(3)	N1-C2-C1	123.2(2)
N1-C2-C3	118.1(3)	C1-C2-C3	118.8(3)
C4-C3-C2	120.9(3)	C4-C3-H3	119.600000
C2-C3-H3	119.600000	C3-C4-C5	119.7(3)
C3-C4-H4	120.200000	C5-C4-H4	120.200000
C6-C5-C4	121.7(3)	C6-C5-Cl1	120.0(3)
C4-C5-Cl1	118.3(2)	C5-C6-C1	119.9(3)
C5-C6-H6	120.100000	C1-C6-H6	120.100000
C8-C7-C1	117.9(2)	C8-C7-C10	121.5(2)
C1-C7-C10	120.6(2)	C7-C8-C9	120.1(2)
C7-C8-C16	120.5(2)	C9-C8-C16	119.4(2)
N1-C9-C8	122.3(3)	N1-C9-C21	117.1(3)
C8-C9-C21	120.6(3)	C11-C10-C15	118.7(3)
C11-C10-C7	120.7(2)	C15-C10-C7	120.5(2)
C10-C11-C12	120.5(3)	C10-C11-H11	119.800000
C12-C11-H11	119.800000	C13-C12-C11	120.1(3)
C13-C12-H12	119.900000	C11-C12-H12	119.900000
C14-C13-C12	119.9(3)	C14-C13-H13	120.100000
C12-C13-H13	120.100000	C13-C14-C15	120.2(3)
C13-C14-H14	119.900000	C15-C14-H14	119.900000
C14-C15-C10	120.6(3)	C14-C15-H15	119.700000
C10-C15-H15	119.700000	N2-C16-C20	122.5(2)
N2-C16-C8	116.9(2)	C20-C16-C8	120.6(2)
N2-C17-C18	123.6(2)	N2-C17-C22	114.6(2)
C18-C17-C22	121.8(2)	C17-C18-C19	118.4(2)
C17-C18-C25	118.7(2)	C19-C18-C25	122.8(2)
C20-C19-C18	116.9(2)	C20-C19-C26	116.6(2)
C18-C19-C26	126.5(2)	C19-C20-C16	121.0(2)
C19-C20-H20	119.500000	C16-C20-H20	119.500000

C9-C21-H21A	109.500000	C9-C21-H21B	109.500000
H21A-C21-H21B	109.500000	C9-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000
C17-C22-C23	114.8(2)	C17-C22-H22A	108.600000
C23-C22-H22A	108.600000	C17-C22-H22B	108.600000
C23-C22-H22B	108.600000	H22A-C22-H22B	107.600000
C24-C23-C22	107.6(2)	C24-C23-C32	109.8(3)
C22-C23-C32	110.2(3)	C24-C23-C33	110.2(2)
C22-C23-C33	109.8(2)	C32-C23-C33	109.2(3)
C25-C24-C23	116.2(2)	C25-C24-H24A	108.200000
C23-C24-H24A	108.200000	C25-C24-H24B	108.200000
C23-C24-H24B	108.200000	H24A-C24-H24B	107.400000
O1-C25-C18	122.0(3)	O1-C25-C24	120.4(3)
C18-C25-C24	117.5(3)	C27-C26-C31	117.8(2)
C27-C26-C19	120.6(2)	C31-C26-C19	121.2(2)
C26-C27-C28	120.7(3)	C26-C27-H27	119.700000
C28-C27-H27	119.700000	C29-C28-C27	121.5(3)
C29-C28-H28	119.300000	C27-C28-H28	119.300000
C30-C29-C28	117.7(3)	C30-C29-C34	122.0(3)
C28-C29-C34	120.4(3)	C29-C30-C31	121.6(3)
C29-C30-H30	119.200000	C31-C30-H30	119.200000
C30-C31-C26	120.8(3)	C30-C31-H31	119.600000
C26-C31-H31	119.600000	C23-C32-H32A	109.500000
C23-C32-H32B	109.500000	H32A-C32-H32B	109.500000
C23-C32-H32C	109.500000	H32A-C32-H32C	109.500000
H32B-C32-H32C	109.500000	C23-C33-H33A	109.500000
C23-C33-H33B	109.500000	H33A-C33-H33B	109.500000
C23-C33-H33C	109.500000	H33A-C33-H33C	109.500000
H33B-C33-H33C	109.500000	C29-C34-H34A	109.500000
C29-C34-H34B	109.500000	H34A-C34-H34B	109.500000
C29-C34-H34C	109.500000	H34A-C34-H34C	109.500000

H34B-C34-H34C	109.500000

Table S7. Torsion angles (°) for 4D’.

C9-N1-C2-C1	2.9(4)	C9-N1-C2-C3	-178.6(2)
C6-C1-C2-N1	176.5(2)	C7-C1-C2-N1	-4.5(4)
C6-C1-C2-C3	-2.0(4)	C7-C1-C2-C3	177.1(2)
N1-C2-C3-C4	-176.9(3)	C1-C2-C3-C4	1.6(4)
C2-C3-C4-C5	-0.3(5)	C3-C4-C5-C6	-0.7(5)
C3-C4-C5-Cl1	178.3(2)	C4-C5-C6-C1	0.3(4)
Cl1-C5-C6-C1	-178.7(2)	C2-C1-C6-C5	1.1(4)
C7-C1-C6-C5	-177.9(2)	C2-C1-C7-C8	1.5(3)
C6-C1-C7-C8	-179.5(2)	C2-C1-C7-C10	-177.1(2)
C6-C1-C7-C10	1.9(4)	C1-C7-C8-C9	2.6(4)
C10-C7-C8-C9	-178.8(2)	C1-C7-C8-C16	179.9(2)
C10-C7-C8-C16	-1.5(4)	C2-N1-C9-C8	1.5(4)
C2-N1-C9-C21	-176.4(3)	C7-C8-C9-N1	-4.4(4)
C16-C8-C9-N1	178.4(2)	C7-C8-C9-C21	173.5(3)
C16-C8-C9-C21	-3.8(4)	C8-C7-C10-C11	110.8(3)
C1-C7-C10-C11	-70.7(3)	C8-C7-C10-C15	-67.6(3)
C1-C7-C10-C15	111.0(3)	C15-C10-C11-C12	1.0(4)
C7-C10-C11-C12	-177.3(3)	C10-C11-C12-C13	-1.6(5)
C11-C12-C13-C14	0.9(5)	C12-C13-C14-C15	0.4(5)
C13-C14-C15-C10	-0.9(5)	C11-C10-C15-C14	0.2(4)
C7-C10-C15-C14	178.6(3)	C17-N2-C16-C20	2.7(4)
C17-N2-C16-C8	-178.3(2)	C7-C8-C16-N2	120.3(3)
C9-C8-C16-N2	-62.4(3)	C7-C8-C16-C20	-60.7(3)
C9-C8-C16-C20	116.6(3)	C16-N2-C17-C18	0.3(4)
C16-N2-C17-C22	180.0(2)	N2-C17-C18-C19	-3.6(4)
C22-C17-C18-C19	176.8(2)	N2-C17-C18-C25	172.6(2)
C22-C17-C18-C25	-7.0(4)	C17-C18-C19-C20	3.7(4)
C25-C18-C19-C20	-172.3(2)	C17-C18-C19-C26	-175.2(2)

C25-C18-C19-C26	8.9(4)	C18-C19-C20-C16	-0.9(4)
C26-C19-C20-C16	178.0(2)	N2-C16-C20-C19	-2.4(4)
C8-C16-C20-C19	178.6(2)	N2-C17-C22-C23	158.8(2)
C18-C17-C22-C23	-21.5(4)	C17-C22-C23-C24	49.5(3)
C17-C22-C23-C32	-70.1(3)	C17-C22-C23-C33	169.5(3)
C22-C23-C24-C25	-53.3(3)	C32-C23-C24-C25	66.7(3)
C33-C23-C24-C25	-173.0(3)	C17-C18-C25-O1	-171.5(3)
C19-C18-C25-O1	4.4(4)	C17-C18-C25-C24	4.1(4)
C19-C18-C25-C24	-179.9(3)	C23-C24-C25-O1	-156.5(3)
C23-C24-C25-C18	27.8(4)	C20-C19-C26-C27	61.1(3)
C18-C19-C26-C27	-120.1(3)	C20-C19-C26-C31	-111.1(3)
C18-C19-C26-C31	67.7(4)	C31-C26-C27-C28	-0.7(4)
C19-C26-C27-C28	-173.3(3)	C26-C27-C28-C29	1.6(4)
C27-C28-C29-C30	-1.6(4)	C27-C28-C29-C34	178.2(3)
C28-C29-C30-C31	0.8(4)	C34-C29-C30-C31	-179.0(3)
C29-C30-C31-C26	0.0(4)	C27-C26-C31-C30	-0.1(4)
C19-C26-C31-C30	172.4(3)		

Table S8. Anisotropic atomic displacement parameters (Å^2) for 4D'.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	0.0916(7)	0.1387(9)	0.0777(6)	0.0373(6)	0.0274(5)	-0.0276(6)
O1	0.0937(18)	0.0846(17)	0.123(2)	-0.0346(15)	0.0686(16)	-0.0255(14)
N1	0.0516(15)	0.0656(17)	0.0690(16)	-0.0064(14)	0.0183(13)	0.0013(13)
N2	0.0594(15)	0.0448(14)	0.0485(13)	-0.0012(10)	0.0177(11)	-0.0058(11)
C1	0.0460(16)	0.0588(18)	0.0404(15)	-0.0067(13)	0.0111(13)	-0.0132(14)
C2	0.0476(17)	0.065(2)	0.0514(17)	-0.0137(15)	0.0150(14)	-0.0097(15)
C3	0.0513(19)	0.089(2)	0.069(2)	-0.0206(19)	0.0253(16)	-0.0086(17)
C4	0.063(2)	0.108(3)	0.060(2)	-0.013(2)	0.0279(17)	-0.025(2)
C5	0.060(2)	0.097(2)	0.0477(17)	0.0022(16)	0.0179(15)	-0.0264(19)

C6	0.0511(17)	0.072(2)	0.0504(16)	0.0011(15)	0.0129(14)	-0.0122(15)
C7	0.0423(15)	0.0477(16)	0.0415(14)	-0.0072(12)	0.0109(12)	-0.0097(12)
C8	0.0457(16)	0.0463(16)	0.0430(14)	-0.0047(13)	0.0109(12)	-0.0040(13)
C9	0.0554(19)	0.0559(18)	0.0585(18)	-0.0019(14)	0.0155(15)	-0.0007(15)
C10	0.0484(17)	0.0470(17)	0.0430(14)	0.0018(12)	0.0161(12)	-0.0042(13)
C11	0.070(2)	0.0486(18)	0.0625(18)	0.0005(15)	0.0164(16)	-0.0060(16)
C12	0.103(3)	0.0424(18)	0.085(2)	0.0062(16)	0.034(2)	0.007(2)
C13	0.075(3)	0.078(3)	0.106(3)	0.019(2)	0.029(2)	0.026(2)
C14	0.052(2)	0.078(3)	0.115(3)	0.000(2)	0.0143(19)	0.0053(19)
C15	0.0480(19)	0.0608(19)	0.075(2)	-0.0042(16)	0.0149(16)	-0.0033(15)
C16	0.0491(16)	0.0449(16)	0.0422(14)	0.0003(12)	0.0134(12)	-0.0018(13)
C17	0.0537(17)	0.0464(16)	0.0463(15)	0.0016(13)	0.0135(13)	-0.0064(13)
C18	0.0504(16)	0.0452(16)	0.0444(15)	0.0018(12)	0.0149(13)	-0.0031(13)
C19	0.0505(16)	0.0433(16)	0.0417(14)	0.0013(12)	0.0105(12)	0.0010(13)
C20	0.0541(17)	0.0442(16)	0.0472(15)	-0.0019(12)	0.0150(13)	-0.0075(13)
C21	0.074(2)	0.079(2)	0.090(2)	0.021(2)	0.0235(19)	0.0204(19)
C22	0.077(2)	0.0535(18)	0.0605(18)	-0.0040(15)	0.0212(16)	-0.0177(16)
C23	0.0593(18)	0.0504(18)	0.0586(18)	0.0030(14)	0.0191(15)	-0.0086(14)
C24	0.062(2)	0.067(2)	0.087(2)	0.0006(17)	0.0285(18)	-0.0135(17)
C25	0.0535(18)	0.0602(19)	0.0639(19)	-0.0012(15)	0.0216(15)	-0.0043(15)
C26	0.0457(16)	0.0415(16)	0.0477(15)	0.0006(12)	0.0154(12)	-0.0021(12)
C27	0.0599(18)	0.0500(18)	0.0544(16)	0.0074(14)	0.0144(14)	0.0080(14)
C28	0.0626(19)	0.0435(17)	0.075(2)	0.0017(15)	0.0223(16)	0.0081(14)
C29	0.0507(17)	0.0532(19)	0.0633(19)	-0.0125(15)	0.0207(14)	-0.0040(14)
C30	0.068(2)	0.061(2)	0.0476(17)	-0.0030(15)	0.0123(14)	0.0017(16)
C31	0.067(2)	0.0467(17)	0.0524(17)	0.0053(14)	0.0148(15)	0.0063(14)
C32	0.088(3)	0.073(2)	0.079(2)	0.0145(19)	0.006(2)	-0.0015(19)
C33	0.092(3)	0.060(2)	0.095(3)	0.0020(18)	0.031(2)	-0.0254(19)
C34	0.083(2)	0.072(2)	0.095(3)	-0.031(2)	0.030(2)	-0.0067(19)

Table S9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 4D'.

	x/a	y/b	z/c	U(eq)
H3	0.6348	0.7561	0.3719	0.081000
H4	0.6157	0.9031	0.2858	0.090000
H6	0.3696	1.0075	0.3514	0.069000
H11	0.3431	1.0600	0.4950	0.072000
H12	0.2020	1.1696	0.4889	0.090000
H13	0.0451	1.0978	0.4348	0.102000
H14	0.0286	0.9149	0.3901	0.099000
H15	0.1685	0.8029	0.4001	0.073000
H20	0.3252	0.8790	0.6158	0.058000
H21A	0.4924	0.6313	0.6245	0.121000
H21B	0.5572	0.5687	0.5752	0.121000
H21C	0.4427	0.5403	0.5634	0.121000
H22A	0.2004	0.4389	0.5723	0.075000
H22B	0.0967	0.4937	0.5339	0.075000
H24A	-0.0173	0.5497	0.6246	0.084000
H24B	0.0179	0.5183	0.7123	0.084000
H27	0.1590	0.9997	0.6367	0.065000
H28	0.1585	1.1418	0.7247	0.071000
H30	0.2726	0.9326	0.8973	0.070000
H31	0.2702	0.7886	0.8107	0.066000
H32A	0.1633	0.3985	0.7593	0.123000
H32B	0.2318	0.4888	0.7322	0.123000
H32C	0.2326	0.3632	0.7041	0.123000
H33A	0.0181	0.3159	0.6642	0.122000
H33B	0.0866	0.2856	0.6074	0.122000
H33C	-0.0096	0.3600	0.5785	0.122000
H34A	0.2316	1.1195	0.9288	0.123000
H34B	0.1571	1.1886	0.8649	0.123000
H34C	0.2734	1.2002	0.8735	0.123000