

Electronic Supporting Information (ESI)
for
**Facile Synthesis of Functionalized Quinolinones in
Greener Reaction Medium and Their Photophysical
Properties**

Pari Keerthana, Sundararajan Suresh, Fazhlur-Rahman Nawaz Khan*

* *Organic and Medicinal Chemistry Research Laboratory, School of Advanced Sciences, Vellore
Institute of Technology, Vellore-632 014, Tamil Nadu, India. E-mail: nawaz_f@yahoo.co.in;*

Table of Contents

1. General Information	S2
2. Experimental Procedure 2.1 General procedure for the synthesis of K ₂ CO ₃ :Ethylene glycol (DES-1) and DMU:Tartaric acid (7:3) (DES-2) 2.2 General procedure for the synthesis of compounds 5a-5l 2.3 General procedure for the synthesis of compounds 6a-6p 2.4 The gram-scale synthesis of 6a	S2-S4
3. Spectral Data for the Synthesized Compounds	S4-S18
4. Mechanistic Investigations 4.1 Control experiment study 4.2 Mass spectroscopic studies for the intermediate detection 4.3 Reaction monitoring by ¹ H NMR analysis	S18-S28
5. X-Ray Crystallography Data	S28-S29
6. Copies of NMR (¹ H & ¹³ C), FT-IR and HRMS Spectra	S30-S88
7. References	S89

1. General Information

All the reagents and chemicals were purchased from common commercial suppliers like Sigma-Aldrich, Merck, and SRL and directly used as received without any further purification unless otherwise mentioned. All the reactions were carried out under oven-dried glass containers in parallel synthesizer unless otherwise mentioned. Completion of reactions was examined by thin layer chromatography carried out on pre-coated Merck silica gel-60 F254 aluminium plates with ultraviolet light (UV) or iodine as visualizing agents. Merck silica gel 60 - 120 was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded at Bruker Advance III (^1H at 400 MHz and ^{13}C at 101 MHz) using CDCl_3 as a solvent. The Chemical shifts, δ (in ppm), are reported relative to TMS δ (^1H) 0.0 ppm, δ (^{13}C) 0.0 ppm, which was used as the internal reference. Otherwise, the solvents residual proton resonance and carbon resonance (CHCl_3 , δ (^1H) 7.26 ppm, δ (^{13}C) 77.16 ppm, were also used for calibration. Chemical shifts (δ) values were reported in ppm and spin-spin coupling constant (J) was expressed in Hz, and the following abbreviations are used to describe multiplicity: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, pent = pentate, sext = sextet. Melting points were determined using the Electrothermal IA 9200 apparatus. IR spectra were recorded on Thermo Nicolet iS50 with an inbuilt ATR (Shimadzu IR Tracer-100) spectrometer. Mass spectra were recorded on WATERS-XEVO G2-XS-QToF (A positive electrospray ionization (ESI⁺) mode). 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-vis and emission spectra were recorded with a Hitachi U-2900 apparatus JASCO V-670 PC spectrophotometer.

2. Experimental Procedure

2.1 General procedure for the synthesis of K_2CO_3 :Ethylene glycol (DES-1) and DMU:Tartaric acid (7:3) (DES-2)

A mixture of K_2CO_3 and ethylene glycol was added to an oven-dried reaction vial and heated at 100 °C for 5 mins to form the K_2CO_3 :Ethylene glycol deep Eutectic Solvent (DES-1). Similarly, the synthesis of the DMU:Tartaric acid (7:3) DES (DES-2) was carried out as per the procedure in prior literature.¹

2.2 General procedure for the synthesis of compounds 5a-5l

A mixture of substituted 2-amino benzhydrol **1**² (0.5 mmol, 1.0 equiv.), Ni(OAc)₂·4H₂O (10 mol%), 2,2'-bipyridyl (15 mol%), KO^tBu (1.0 equiv.) and K₂CO₃:Ethylene glycol (1:5) (500 mg) were added and the reaction was conducted at 100 °C for 4 h to form the benzophenone **1a**. Then, ethyl acetoacetate **2** (0.5 mmol, 1.0 equiv.) was added, and the reaction mixture was heated at 100 °C for 3 h to form the intermediate **A**. Subsequently, K₂CO₃:Ethylene glycol (1:5) (500 mg) and phenacyl bromide **3** (0.5 mmol, 1.0 equiv.) were added and continued at 100 °C for an additional 3 h to form the N-alkylated intermediate **B**. After that, DMU:Tartaric acid (7:3) (300 mg) and alcohol **4** (0.6 mmol, 1.2 equiv.) were sequentially added, and the reaction was continued at 100 °C for 4 h. The entire reaction process was monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled to RT, quenched with water (50 ml), and extracted with ethyl acetate (40 ml x 2). The combined organic layer was dried over anhydrous Na₂SO₄, and the crude reaction mixture was purified by silica gel column chromatography using 10-25% EtOAc/Pet ether as eluent, yielding a 68-81% of the desired products (**5a-5l**).

2.3 General procedure for the synthesis of compounds 6a-6p

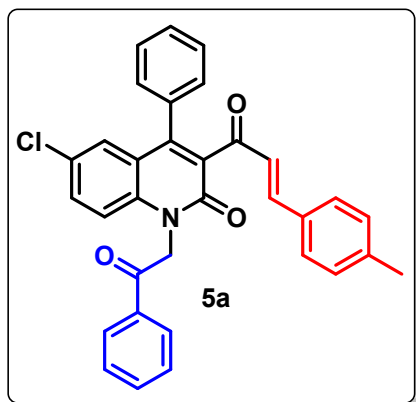
A mixture of substituted 2-amino benzhydrol **1**² (0.5 mmol, 1.0 equiv.), Ni(OAc)₂·4H₂O (10 mol%), 2,2'-bipyridyl (15 mol%), KO^tBu (1.0 equiv.) and K₂CO₃:Ethylene glycol (1:5) (500 mg) were added and the reaction was conducted at 100 °C for 4 h to form the benzophenone **1a**. Then, ethyl acetoacetate **2** (0.5 mmol, 1.0 equiv.) was added, and the reaction mixture was heated at 100 °C for 3 h to produce intermediate **A**. Subsequently, K₂CO₃:Ethylene glycol (1:5) (500 mg) and phenacyl bromide **3** (0.5 mmol, 1.0 equiv.) were added and continued at 100 °C for an additional 3 h to form the N-alkylated intermediate **B**. After that, DMU:Tartaric acid (7:3) (300 mg) and alcohol **4** (1.5 mmol, 3.0 equiv.) were sequentially added, and the reaction was continued at 100 °C for 7 h. The entire reaction process was monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled to RT, quenched with water (50 ml), and extracted with ethyl acetate (40 ml x 2). The combined organic layer was dried over anhydrous Na₂SO₄, and the crude reaction mixture was purified by silica gel column chromatography using 10-20% EtOAc/Pet ether as eluent, yielding 69-84% of the desired products (**6a-6p**).

2.4 The gram-scale synthesis of 6a

A mixture of substituted 2-amino-5-chloro benzhydrol **1a** (2.33 g, 10.0 mmol, 1.0 equiv.), Ni(OAc)₂·4H₂O (249 mg, 10 mol%), 2,2'-bipyridyl (234 mg, 15 mol%), KO^tBu (1.12 g, 10.0 mmol, 1.0 equiv.), and K₂CO₃:Ethylene glycol (1:5) (10.0 g) were added and the reaction was conducted at 100 °C for 4 h to form the benzophenone **1a**. Then, ethyl acetoacetate **2a** (1.30 g, 10.0 mmol, 1.0 equiv.) was added, and the reaction mixture was heated at 100 °C for 3 h to produce intermediate **A**. Subsequently, K₂CO₃:Ethylene glycol (1:5) (10.0 g) and phenacyl bromide **3a** (1.99 g, 10.0 mmol, 1.0 equiv.) were added and continued at 100 °C for an additional 3 h to form the N-alkylated intermediate **B**. After that, DMU:Tartaric acid (7:3) (300 mg) and alcohol **4a** (4.14 g, 30.0 mmol, 1.0 equiv.) were sequentially added, and the reaction was continued at 100 °C for 7 h. The entire reaction process was monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled to RT, quenched with water (500 ml), and extracted with ethyl acetate (300 ml x 2). The combined organic layer was dried over anhydrous Na₂SO₄, and the crude reaction mixture was purified by silica gel column chromatography using 15% EtOAc/Pet ether as eluent, yielding 78% of the desired products (**6a**).

3. Spectral Data for the Synthesized Compounds

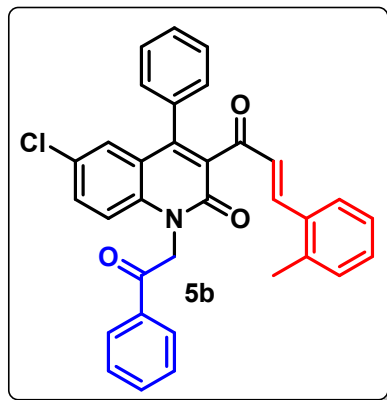
(E)-6-Chloro-1-(2-oxo-2-phenylethyl)-4-phenyl-3-(3-(p-tolyl)acryloyl)quinolin-2(1H)-one



(**5a**). Purification was carried out by column chromatography on silica gel using a 13% ethyl acetate/Pet ether mixture, resulting in the isolation of **5a** as a Pale yellow solid (81% yield) mp: 265-267 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.08 (m, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.49 – 7.40 (m, 4H), 7.36 – 7.31 (m, 6H), 7.26 (s, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.67 (d, *J* = 16.2 Hz, 1H), 5.88 (s, 2H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.1, 192.1, 159.4, 147.6, 146.0, 141.3,

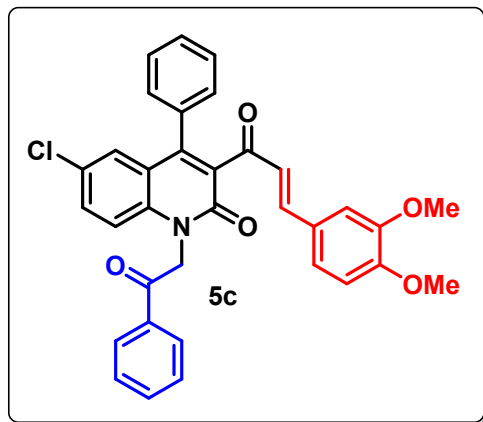
138.1, 134.7, 134.3, 133.5, 131.9, 131.6, 131.4, 129.6, 129.2, 129.1, 128.7, 128.6, 128.3, 128.2,

128.0, 126.2, 122.1, 115.9, 48.9, 21.5. **FT-IR:** $\nu = 3057, 2918, 1698, 1641, 1554, 1420, 1223, 1065, 962, 812, 754, 710, 553 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{33}\text{H}_{24}\text{ClNO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 540.1342; found: 540.1345.



(E)-6-Chloro-1-(2-oxo-2-phenylethyl)-4-phenyl-3-(3-(o-tolyl)acryloyl)quinolin-2(1H)-one (5b). Purification was carried out by column chromatography on silica gel using a 14% ethyl acetate/Pet ether mixture, resulting in the isolation of **5b** as a Pale yellow solid (76% yield) mp: 263-265 °C; **¹H NMR (400 MHz, CDCl₃)** δ 8.10 (d, $J = 7.6 \text{ Hz}$, 2H), 7.71 – 7.63 (m, 2H), 7.55 (t, $J = 7.5 \text{ Hz}$, 2H), 7.43 (d, $J = 12.1 \text{ Hz}$, 5H), 7.34 (d, $J = 5.2 \text{ Hz}$, 3H), 7.22 (d, $J = 7.4 \text{ Hz}$, 1H), 7.13 (d, $J = 6.9 \text{ Hz}$, 2H), 7.03 (d, $J = 9.0 \text{ Hz}$, 1H), 6.63 (d, $J = 16.1 \text{ Hz}$,

1H), 5.88 (s, 2H), 2.32 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 193.1, 191.9, 159.4, 147.7, 143.2, 138.2, 138.1, 134.7, 134.3, 133.5, 133.3, 131.9, 131.5, 130.7, 130.4, 129.3, 129.2, 129.1, 128.7, 128.3, 128.2, 128.1, 128.0, 126.8, 126.3, 122.1, 120.9, 115.8, 48.9, 19.8. **FT-IR:** $\nu = 1696, 1637, 1555, 1427, 1225, 1067, 960, 821, 752, 688, 541 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{33}\text{H}_{24}\text{ClNO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 540.1342; found: 540.1370.

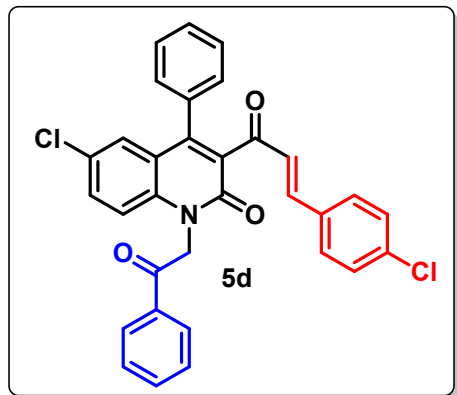


(E)-6-Chloro-3-(3-(3,4-dimethoxyphenyl)acryloyl)-1-(2-oxo-2-phenylethyl)-4-phenylquinolin-2(1H)-one (5c). Purification was carried out by column chromatography on silica gel using a 17% ethyl acetate/Pet ether mixture, resulting in the isolation of **5c**

as a Pale yellow solid (79% yield) mp: 272-274 °C; **¹H NMR (400 MHz, CDCl₃)** δ 8.03 (d, $J = 7.6 \text{ Hz}$, 2H), 7.61 (t, $J = 7.2 \text{ Hz}$, 1H), 7.49 (t, $J = 7.5 \text{ Hz}$, 3H), 7.41 – 7.34 (m, 4H), 7.25 (dd, $J = 10.7, 8.1 \text{ Hz}$, 4H), 6.95 (d, $J = 8.3 \text{ Hz}$, 2H), 6.88 (s, 1H), 6.74 (d, $J = 8.3 \text{ Hz}$, 1H), 6.53 (d, $J = 16.1 \text{ Hz}$, 1H), 5.82 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 193.0, 192.1, 151.6, 149.1, 147.6, 146.1, 138.1, 134.7, 134.4, 133.6, 131.9, 131.9, 131.4, 129.2, 129.1, 128.7, 128.3, 128.2, 128.0, 127.3, 125.2, 123.5, 122.2, 115.9, 110.9, 110.0, 56.0, 55.9, 48.9. **FT-IR:** $\nu = 1715, 1639, 1594, 1483,$

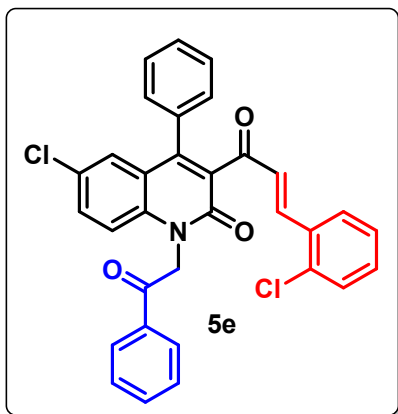
1246, 1109, 1019, 945, 750, 707, 546 cm^{-1} . **HRMS (ESI)** calcd for $\text{C}_{34}\text{H}_{26}\text{ClNO}_5\text{Na}$ requires $(\text{M} + \text{Na})^+$ 586.1397; found: 586.1397.

(E)-6-Chloro-3-(3-(4-chlorophenyl)acryloyl)-1-(2-oxo-2-phenylethyl)-4-phenylquinolin-



2(1H)-one (5d). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **5d** as a Colourless solid (77% yield) mp: 245-247 $^{\circ}\text{C}$; **^1H NMR (400 MHz, CDCl_3)** δ 8.11 (d, $J = 7.5$ Hz, 2H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.55 (t, $J = 7.3$ Hz, 2H), 7.43 (d, $J = 5.1$ Hz, 4H), 7.33 (dd, $J = 14.7, 8.2$ Hz, 8H), 7.03 (d, $J = 8.9$ Hz, 1H), 6.68 (d, $J = 16.2$ Hz, 1H), 5.87 (s, 2H). **^{13}C NMR**

(101 MHz, CDCl_3) δ 192.6, 192.0, 159.4, 148.0, 143.8, 138.1, 136.6, 134.7, 134.3, 133.5, 132.9, 131.6, 131.6, 129.6, 129.2, 129.1, 129.1, 129.1, 128.7, 128.4, 128.2, 128.1, 127.4, 122.1, 115.9, 48.9. **FT-IR:** $\nu = 1637, 1489, 1367, 1226, 1089, 958, 753, 685, 518$ cm^{-1} . **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{21}\text{Cl}_2\text{NO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 560.0796; found: 560.0796.

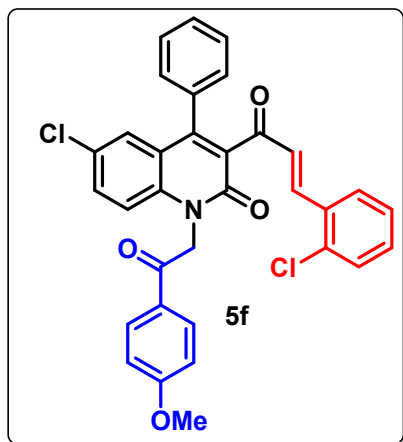


(E)-6-Chloro-3-(3-(2-chlorophenyl)acryloyl)-1-(2-oxo-2-phenylethyl)-4-phenylquinolin-2(1H)-one (5e). Purification

was carried out by column chromatography on silica gel using an 11% ethyl acetate/Pet ether mixture, resulting in the isolation of **5e** as a Colourless solid (73% yield) mp: 243-245 $^{\circ}\text{C}$; **^1H NMR (400 MHz, CDCl_3)** δ 8.10 (d, $J = 7.7$ Hz, 2H), 7.77 (d, $J = 16.3$ Hz, 1H), 7.66 (t, $J = 7.3$ Hz, 1H), 7.53 (dd, $J = 13.0, 5.2$ Hz, 3H), 7.46 (dd, $J = 14.8, 8.3$ Hz, 5H), 7.38 – 7.31 (m, 4H), 7.23 (dt, $J = 14.8, 7.9$ Hz, 3H), 7.04 (d, $J = 9.0$

Hz, 1H), 6.67 (d, $J = 16.2$ Hz, 1H), 5.87 (s, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 193.0, 191.9, 159.4, 148.0, 141.3, 138.2, 135.3, 134.7, 134.3, 133.4, 132.6, 131.6, 131.4, 131.3, 130.1, 129.4, 129.3, 129.2, 129.0, 128.7, 128.3, 128.2, 128.1, 127.9, 127.0, 122.0, 116.0, 48.9. **FT-IR:** $\nu = 1642, 1555, 1419, 1224, 1087, 959, 754, 687, 552$ cm^{-1} . **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{21}\text{Cl}_2\text{NO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 560.0796; found: 560.0797.

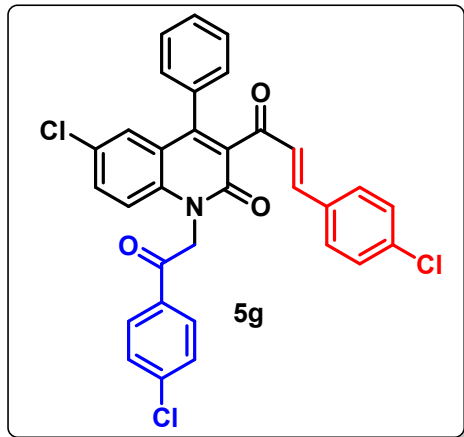
(E)-6-Chloro-3-(3-(2-chlorophenyl)acryloyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-4-



phenylquinolin-2(1H)-one (5f). Purification was carried out by column chromatography on silica gel using an 11% ethyl acetate/Pet ether mixture, resulting in the isolation of **5f** as a Colourless solid (75% yield) mp: 240-242 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.5$ Hz, 2H), 7.77 (d, $J = 16.2$ Hz, 1H), 7.51 (d, $J = 7.3$ Hz, 1H), 7.48 – 7.41 (m, 4H), 7.39 – 7.31 (m, 4H), 7.25 – 7.18 (m, 2H), 7.03 (dd, $J = 17.0, 8.8$ Hz, 3H), 6.68 (d, $J = 16.2$ Hz, 1H), 5.83 (s, 2H), 3.90 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.0, 190.2, 164.4, 159.4, 147.9, 141.2,

138.8, 135.2, 133.4, 132.6, 131.6, 131.3, 130.6, 130.0, 129.6, 129.4, 129.2, 128.7, 128.4, 128.3, 128.0, 127.9, 127.7, 127.2, 127.0, 122.0, 116.1, 114.2, 55.6, 48.6. **FT-IR:** $\nu = 1700, 1633, 1488, 1369, 1224, 1089, 960, 752, 687, 544$ cm^{-1} . **HRMS (ESI)** calcd for $\text{C}_{33}\text{H}_{23}\text{Cl}_2\text{NO}_4\text{Na}$ requires (M + Na) $^+$ 590.0902; found: 590.0903.

(E)-6-Chloro-1-(2-(4-chlorophenyl)-2-oxoethyl)-3-(3-(4-chlorophenyl)acryloyl)-4-

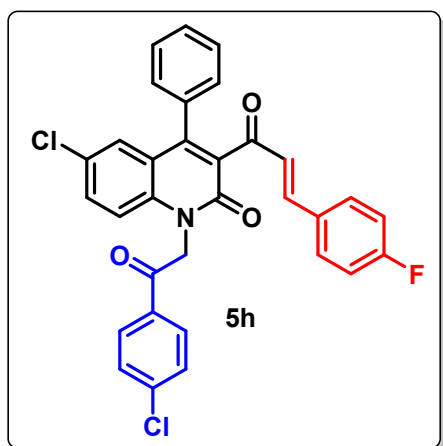


phenylquinolin-2(1H)-one (5g). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **5g** as a Colourless solid (78% yield) mp: 237-239 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (s, 2H), 7.55 (d, $J = 5.9$ Hz, 2H), 7.46 (d, $J = 3.9$ Hz, 4H), 7.39 – 7.34 (m, 4H), 7.34 – 7.30 (m, 4H), 7.28 (s, 2H), 6.69 (d, $J = 16.2$ Hz, 1H), 5.85 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 192.7, 191.1, 159.4, 148.1, 144.0, 141.0, 138.0, 136.7, 133.4,

132.9, 132.8, 131.7, 131.5, 129.7, 129.5, 129.3, 129.1, 129.1, 128.7, 128.5, 128.2, 127.31, 122.1, 115.8, 48.8. **FT-IR:** $\nu = 1700, 1637, 1594, 1427, 1366, 1224, 1085, 956, 752, 686, 550$ cm^{-1} .

HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{20}\text{Cl}_3\text{NO}_3\text{Na}$ requires (M + Na) $^+$ 594.0406; found: 594.0408.

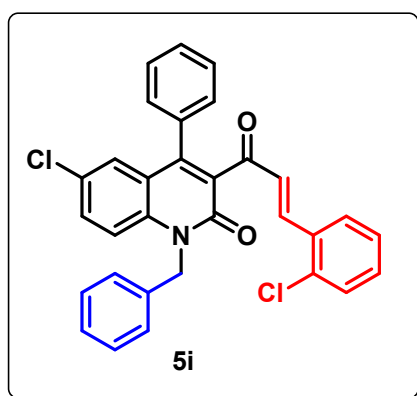
(E)-6-Chloro-1-(2-(4-chlorophenyl)-2-oxoethyl)-3-(3-(4-fluorophenyl)acryloyl)-4-



phenylquinolin-2(1H)-one (5h). Purification was carried out by column chromatography on

silica gel using an 11% ethyl acetate/Pet ether mixture, resulting in the isolation of **5h** as a Pale yellow solid (74% yield) mp: 230-232 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 9.0, 2.3 Hz, 2H), 7.45 – 7.39 (m, 5H), 7.35 – 7.29 (m, 4H), 7.02 (t, *J* = 8.5 Hz, 3H), 6.63 (d, *J* = 16.2 Hz, 1H), 5.83 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.7, 191.1, 159.4, 148.0, 144.3, 138.0 (d, *J* = 29.8 Hz), 132.9 (d, *J* = 46.8 Hz), 131.6, 130.5, 130.4, 129.6, 129.5, 129.3, 129.1 (d, *J* = 14.1 Hz), 128.5, 128.2, 126.7, 122.1, 116.15, 116.1 (d, *J* = 22.2 Hz), 115.8, 48.8. ¹⁹F NMR (377 MHz, CDCl₃) δ -108.7 (s, 1F). HRMS (ESI) calcd for C₃₂H₂₀Cl₂FNO₃Na requires (M + Na)⁺ 578.0702; found: 578.0703.

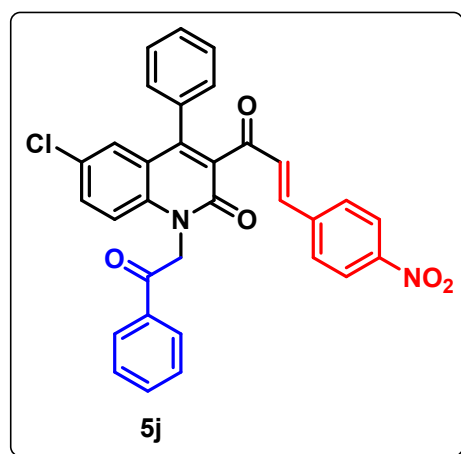
(E)-1-benzyl-6-chloro-3-(3-(2-chlorophenyl)acryloyl)-4-phenylquinolin-2(1H)-one (5i). Purification



was carried out by column chromatography on silica gel using a 13% ethyl acetate/Pet ether mixture, resulting in the isolation of **5i** as a Colourless solid (79% yield) mp: 241-243 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.39 – 8.32 (m, 2H), 8.13 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 16.3 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.51 (dd, *J* = 7.3, 3.9 Hz, 4H), 7.40 (dd, *J* = 11.6, 6.1 Hz, 3H), 7.33 – 7.30 (m, 1H), 7.23 (dd, *J* = 17.3, 8.4 Hz, 2H), 6.68 (d, *J* = 16.3 Hz, 1H),

5.96 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.4, 191.2, 159.5, 148.6, 143.5, 142.6, 141.8, 135.3, 134.6, 134.4, 132.6, 132.4, 132.1, 131.6, 130.1, 129.8, 129.3, 129.2, 129.0, 128.9, 128.3, 127.9, 127.1, 126.0, 124.9, 120.7, 115.5, 49.2. FT-IR: ν = 3060, 2931, 1697, 1637, 1553, 1485, 1418, 1227, 1090, 958, 753, 687, 548 cm⁻¹. HRMS (ESI) calcd for C₃₁H₂₂Cl₂NO₂K requires (M + K)⁺ 549.0665; found: 549.0667.

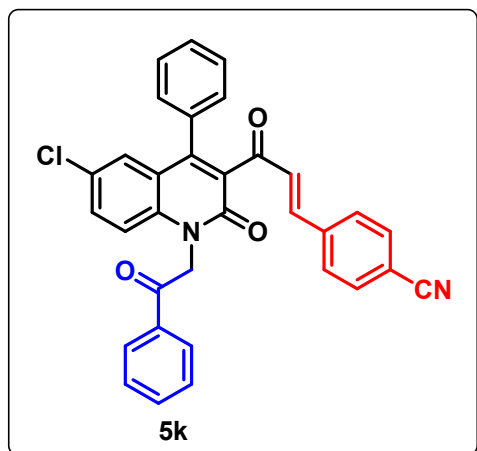
(E)-6-Chloro-3-(3-(4-nitrophenyl)acryloyl)-1-(2-oxo-2-phenylethyl)-4-phenylquinolin-



2(1H)-one (5j). Purification was carried out by column chromatography on silica gel using a 15% ethyl acetate/Pet ether mixture, resulting in the isolation of **5j** as a Yellow solid (71% yield) mp: 267-269 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 7.6 Hz, 2H), 7.70 (dd, *J* = 14.2, 7.0 Hz, 1H), 7.59 – 7.54 (m, 4H), 7.49 – 7.42 (m, 5H), 7.38 (s, 1H), 7.33 (d, *J* = 7.4

Hz, 3H), 6.84 (d, $J = 16.2$ Hz, 1H), 5.89 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.2, 191.9, 159.5, 148.7, 148.6, 141.5, 140.6, 138.2, 134.5, 134.5, 133.4, 131.9, 131.2, 130.2, 129.4, 129.1, 129.0, 128.8, 128.5, 128.2, 124.0, 122.0, 115.9, 48.9. FT-IR: $\nu = 2938, 1711, 1639, 1596, 1459, 1243, 1105, 1019, 948, 754, 709, 546$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{22}\text{ClN}_2\text{O}_5$ requires $(\text{M} + \text{H})^+$ 549.1217; found: 549.1219.

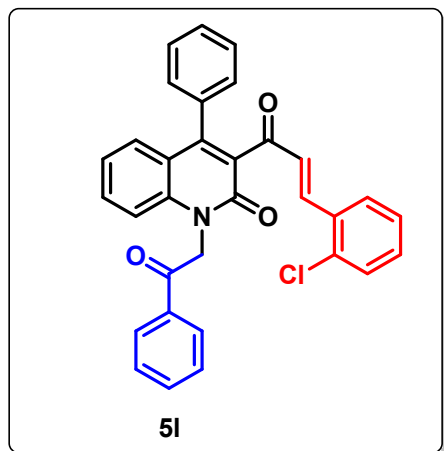
(E)-4-(3-(6-Chloro-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenyl-1,2-dihydroquinolin-3-yl)-3-



oxoprop-1-en-1-yl)benzonitrile (5k). Purification was carried out by column chromatography on silica gel using a 15% ethyl acetate/Pet ether mixture, resulting in the isolation of **5k** as a Yellow solid (68% yield) mp: 254-256 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, 2H), 7.60 (d, 1H), 7.56 (d, $J = 4.5$ Hz, 2H), 7.53 (d, $J = 6.7$ Hz, 1H), 7.49 (d, $J = 5.5$ Hz, 1H), 7.45 (d, $J = 1.9$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 2.1$ Hz, 2H), 7.31 (d, $J = 2.3$ Hz, 1H), 7.08 – 7.03 (m, 3H), 6.83 – 6.79

(m, 1H), 6.78 (d, $J = 2.2$ Hz, 1H), 5.88 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.3, 191.9, 159.4, 150.0, 148.6, 142.8, 142.2, 138.8, 138.2, 137.1, 136.6, 136.1, 135.1, 134.5, 133.4, 132.8, 132.5, 130.1, 129.6, 129.3, 129.1, 128.8, 128.2, 122.0, 118.4, 115.9, 113.5, 48.9. FT-IR: $\nu = 3372, 2227, 1696, 1634, 1447, 1366, 1227, 1073, 988, 752$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{22}\text{ClN}_2\text{O}_3$ requires $(\text{M} + \text{H})^+$ 529.1319; found: 529.1319.

(E)-3-(3-(2-Chlorophenyl)acryloyl)-1-(2-oxo-2-phenylethyl)-4-phenylquinolin-2(1H)-one

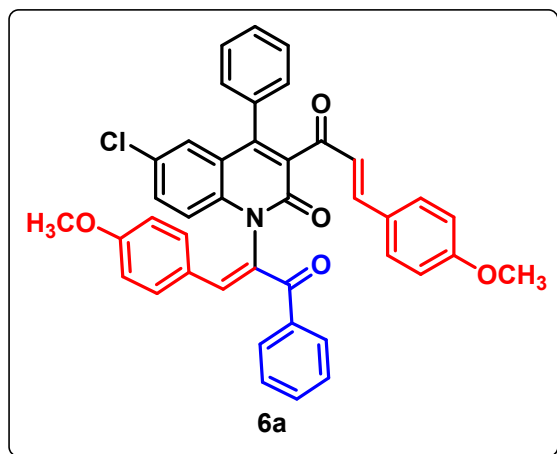


(5l). Purification was carried out by column chromatography on silica gel using a 13% ethyl acetate/Pet ether mixture, resulting in the isolation of **5l** as a Colourless solid (79% yield) mp: 215-217 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 7.4$ Hz, 2H), 7.79 (d, $J = 16.2$ Hz, 1H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.53 (dd, $J = 16.3, 8.4$ Hz, 4H), 7.38 (ddd, $J = 16.2, 11.8, 7.9$ Hz, 7H), 7.25 – 7.14 (m, 3H), 7.10 (d, $J = 8.5$ Hz, 1H), 6.70 (d, $J = 16.2$ Hz, 1H), 5.91 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.5, 192.2,

159.7, 149.2, 141.0, 139.6, 135.2, 134.8, 134.2, 134.1, 132.8, 131.6, 131.2, 130.3, 130.0, 129.5, 129.5, 129.1, 129.0, 128.9, 128.5, 128.2, 127.9, 127.0, 122.6, 120.8, 114.4, 48.8. **FT-IR:** $\nu = 1700, 1647, 1598, 1518, 1339, 1228, 1107, 849, 829, 750, 702, 537 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{23}\text{ClNO}_3$ requires $(\text{M} + \text{H})^+$ 504.1366; found: 504.1369.

6-Chloro-1-((Z)-1-(4-methoxyphenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(4-

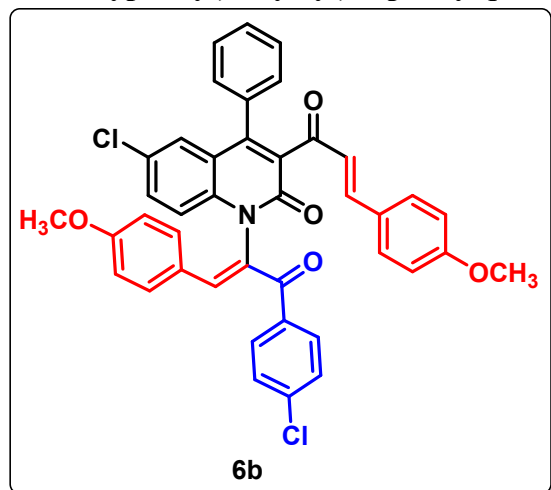
methoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6a). Purification was carried out by



column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **6a** as a Pale yellow solid (81% yield) mp: 270-272 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.6 \text{ Hz}$, 2H), 7.55 – 7.49 (m, 2H), 7.43 (d, $J = 7.5 \text{ Hz}$, 2H), 7.38 – 7.34 (m, 4H), 7.29 (d, $J = 8.9 \text{ Hz}$, 3H), 7.25 (s, 1H), 7.13 (d, $J = 8.5 \text{ Hz}$, 2H), 7.06 (d, $J = 9.6 \text{ Hz}$, 1H), 6.75 (dd, $J = 19.4, 9.5 \text{ Hz}$, 5H), 6.50 (d, $J = 16.2 \text{ Hz}$, 1H), 3.72 (s,

3H), 3.71 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.1, 192.8, 161.9, 161.7, 159.4, 148.5, 146.0, 142.5, 137.8, 137.4, 133.7, 132.4, 132.0, 131.6, 130.6, 130.4, 130.0, 129.6, 129.2, 128.8, 128.7, 128.5, 128.5, 127.8, 127.1, 125.0, 124.3, 122.1, 116.8, 114.7, 114.2, 55.4, 55.4. **FT-IR:** $\nu = 1638, 1599, 1509, 1422, 1248, 1174, 1019, 826, 709, 545 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{41}\text{H}_{30}\text{ClNO}_5\text{Na}$ requires $(\text{M} + \text{Na})^+$ 674.1710; found: 674.1715.

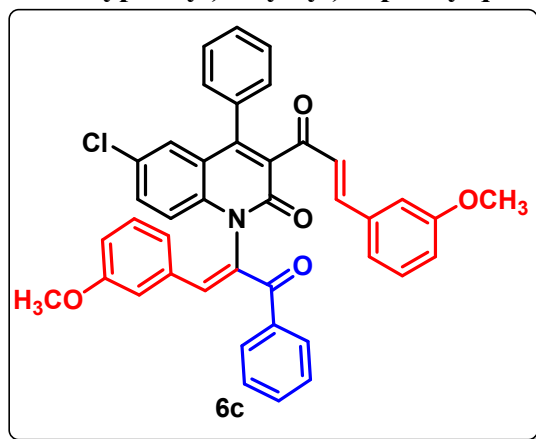
6-Chloro-1-((Z)-3-(4-chlorophenyl)-1-(4-methoxyphenyl)-3-oxoprop-1-en-2-yl)-3-((E)-3-(4-methoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6b). Purification was carried out by



column chromatography on silica gel using a 14% ethyl acetate/Pet ether mixture, resulting in the isolation of **6b** as a Pale yellow solid (79% yield) mp: 275-277 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.3 \text{ Hz}$, 2H), 7.47 (s, 1H), 7.38 (dd, $J = 10.4, 5.8 \text{ Hz}$, 6H), 7.30 – 7.23 (m, 6H), 7.12 (d, $J = 8.7 \text{ Hz}$, 2H), 7.04 (d, $J = 9.6 \text{ Hz}$, 1H), 6.73 (t, $J = 9.4 \text{ Hz}$, 4H), 6.48 (d, $J = 16.2 \text{ Hz}$, 1H), 3.72 (s, 3H), 3.70 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 192.6,

192.1, 162.0, 161.9, 159.4, 148.6, 146.1, 142.1, 138.8, 137.3, 136.1, 133.6, 132.6, 132.0, 131.7, 131.4, 130.4, 129.5, 129.2, 128.8, 128.8, 128.7, 128.7, 127.9, 127.1, 125.0, 124.1, 122.1, 116.8, 114.8, 114.3, 55.4, 55.4. **FT-IR:** $\nu = 1640, 1599, 1445, 1245, 1174, 1024, 753, 710, 549 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{41}\text{H}_{29}\text{Cl}_2\text{NO}_5\text{Na}$ requires $(\text{M} + \text{Na})^+$ 708.1320; found: 708.1321.

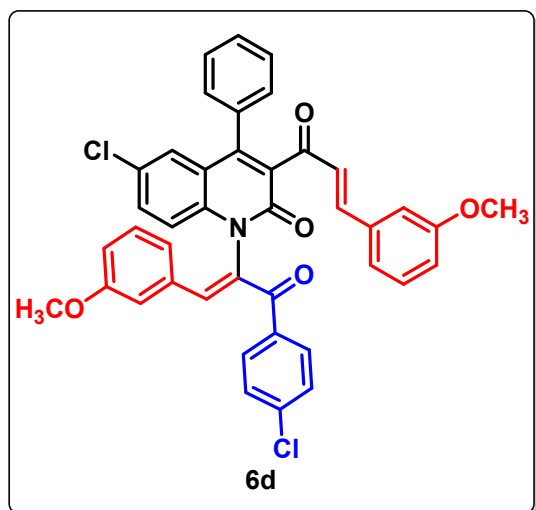
6-Chloro-1-((Z)-1-(3-methoxyphenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(3-methoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6c). Purification was carried out by



column chromatography on silica gel using a 17% ethyl acetate/Pet ether mixture, resulting in the isolation of **6c** as a Pale yellow solid (80% yield) mp: 258-260 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 78.08 (d, $J = 7.4 \text{ Hz}$, 2H), 7.92 (s, 1H), 7.70 (d, $J = 16.4 \text{ Hz}$, 1H), 7.58 (t, $J = 7.4 \text{ Hz}$, 1H), 7.48 (t, $J = 7.6 \text{ Hz}$, 2H), 7.42 – 7.33 (m, 5H), 7.28 (d, $J = 9.1 \text{ Hz}$, 2H), 7.23 (d, $J = 2.2 \text{ Hz}$, 2H), 7.13 (d, $J = 9.0$

Hz, 1H), 6.87 (t, $J = 7.6 \text{ Hz}$, 1H), 6.79 (ddd, $J = 35.3, 17.9, 9.7 \text{ Hz}$, 4H), 3.80 (d, $J = 1.4 \text{ Hz}$, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.5, 193.0, 159.8, 158.5, 157.4, 148.4, 141.9, 137.5, 133.7, 133.0, 132.7, 132.2, 132.1, 131.9, 131.3, 130.4, 129.5, 129.1, 129.1, 128.6, 128.5, 128.3, 128.2, 127.8, 127.6, 123.5, 121.9, 121.1, 121.0, 120.6, 117.0, 111.0, 110.7, 55.6, 55.4. **FT-IR:** $\nu = 1707, 1638, 1484, 1240, 1110, 1018, 943, 755, 709, 541 \text{ cm}^{-1}$. **HRMS (ESI):** $\text{C}_{41}\text{H}_{30}\text{ClNO}_5\text{Na}$ requires 674.1710 $(\text{M} + \text{Na})^+$; found: 674.1739.

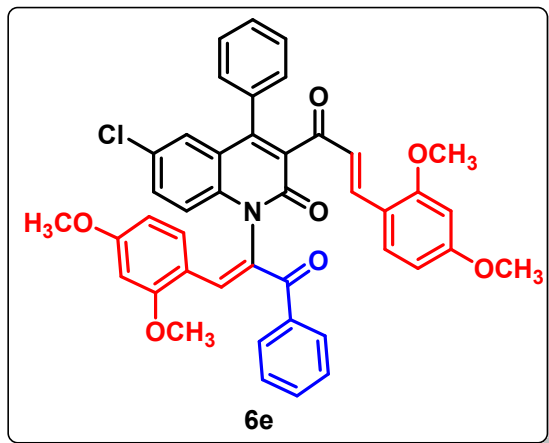
6-Chloro-1-((Z)-3-(4-chlorophenyl)-1-(3-methoxyphenyl)-3-oxoprop-1-en-2-yl)-3-((E)-3-(3-methoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6d). Purification was carried out by



column chromatography on silica gel using a 16% ethyl acetate/Pet ether mixture, resulting in the isolation of **6d** as a Pale yellow solid (76% yield) mp: 262-264 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.5 \text{ Hz}$, 2H), 7.47 (s, 1H), 7.41 (d, $J = 8.5 \text{ Hz}$, 2H), 7.36 (dd, $J = 4.8, 3.5 \text{ Hz}$, 2H), 7.28 – 7.23 (m, 4H), 7.18 (s, 1H), 7.14 (td, $J = 7.9, 4.8 \text{ Hz}$, 2H), 7.05 (d, $J = 8.9 \text{ Hz}$, 1H), 6.91 (d, $J = 7.7 \text{ Hz}$, 1H), 6.80 (ddd, $J = 12.6, 7.8, 5.5 \text{ Hz}$, 4H), 6.68 (s,

1H), 6.57 (d, $J = 16.2$ Hz, 1H), 3.69 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 192.1, 159.9, 159.8, 159.5, 148.9, 146.1, 141.7, 139.3, 137.3, 135.7, 135.6, 133.4, 132.7, 132.6, 132.2, 131.8, 131.6, 130.2, 129.7, 129.4, 129.3, 128.9, 128.8, 128.8, 128.8, 127.8, 127.3, 122.7, 121.9, 121.3, 117.6, 116.8, 116.8, 113.5, 113.2, 55.3, 55.2. FT-IR: $\nu = 1705, 1639, 1595, 1447, 1247, 1173, 1025, 830, 755, 709, 550$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{41}\text{H}_{29}\text{Cl}_2\text{NO}_5\text{Na}$ requires $(\text{M} + \text{Na})^+$ 708.1320; found: 708.1351.

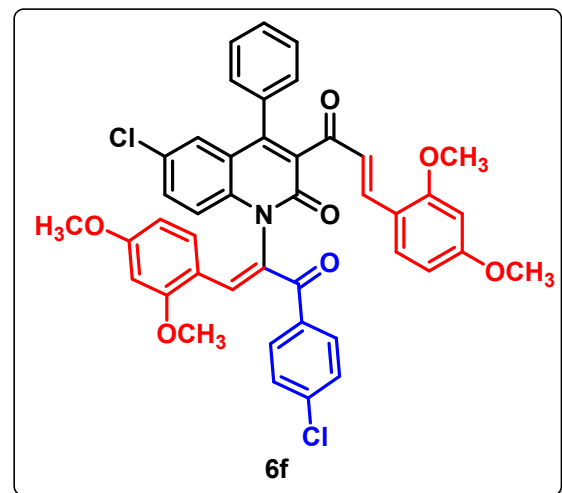
6-Chloro-1-((Z)-1-(2,4-dimethoxyphenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(2,4-dimethoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6e). Purification was carried out by



column chromatography on silica gel using a 18% ethyl acetate/Pet ether mixture, resulting in the isolation of **6e** as a Pale yellow solid (78% yield) mp: 280-282 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, $J = 29.3, 7.3$ Hz, 3H), 7.95 (s, 1H), 7.65 (d, $J = 3.3$ Hz, 1H), 7.63 – 7.54 (m, 2H), 7.48 (d, $J = 7.7$ Hz, 2H), 7.40 (dd, $J = 7.7, 4.6$ Hz, 4H), 7.35 – 7.28 (m, 4H), 7.13 (dd, $J = 8.7, 6.2$ Hz, 2H), 6.66

(d, $J = 16.3$ Hz, 1H), 6.43 – 6.30 (m, 4H), 3.77 (t, $J = 7.7$ Hz, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.5, 193.1, 163.3, 163.2, 160.1, 159.7, 159.4, 159.42, 148.0, 142.1, 138.0, 137.5, 137.1, 133.9, 132.7, 132.3, 131.3, 130.7, 130.2, 130.0, 129.6, 129.3, 128.9, 128.5, 128.4, 128.2, 128.1, 127.6, 125.7, 122.1, 117.0, 116.8, 113.9, 105.8, 105.3, 98.3, 98.2, 55.7, 55.5, 55.4, 55.4. FT-IR: $\nu = 1637, 1597, 1415, 1263, 1206, 1155, 1030, 822, 701, 554$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{34}\text{ClNO}_7\text{Na}$ requires $(\text{M} + \text{Na})^+$ 734.1921; found: 734.1949.

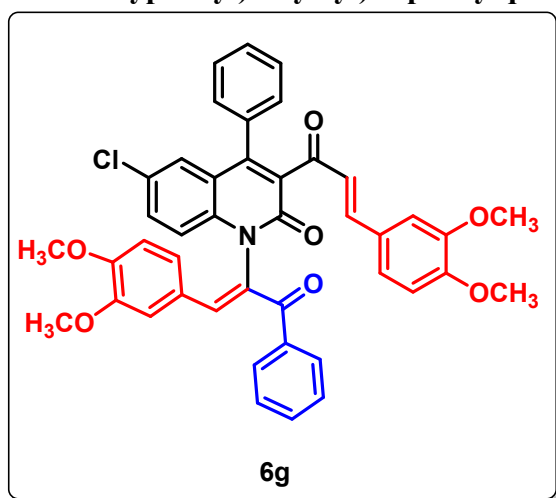
6-Chloro-1-((Z)-3-(4-chlorophenyl)-1-(2,4-dimethoxyphenyl)-3-oxoprop-1-en-2-yl)-3-((E)-3-(2,4-dimethoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6f). Purification was carried out



by column chromatography on silica gel using a 17% ethyl acetate/Pet ether mixture, resulting in the isolation of **6f** as a Pale yellow solid (75% yield) mp: 284-286 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.89 (s, 1H), 7.62 (d, $J = 16.3$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 3H), 7.43 – 7.38 (m, 4H), 7.35 – 7.28 (m, 3H), 7.10 (dd,

$J = 8.8, 5.5$ Hz, 2H), 6.66 (d, $J = 16.3$ Hz, 1H), 6.42 (dd, $J = 8.6, 2.1$ Hz, 1H), 6.36 (s, 2H), 6.31 (dd, $J = 8.7, 2.1$ Hz, 1H), 3.79 (d, $J = 2.6$ Hz, 6H), 3.77 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.4, 192.1, 163.4, 163.2, 160.1, 159.5, 148.1, 142.1, 138.7, 137.3, 136.6, 136.3, 133.8, 132.7, 131.7, 131.3, 130.7, 130.5, 130.0, 129.6, 129.1, 128.6, 128.2, 127.6, 125.6, 122.1, 117.0, 116.7, 113.7, 105.9, 105.3, 98.3, 98.2, 55.7, 55.5, 55.4. FT-IR: $\nu = 1713, 1633, 1595, 1461, 1243, 1109, 1018, 840, 754, 545$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{33}\text{Cl}_2\text{NO}_7\text{K}$ requires $(\text{M} + \text{K})^+$ 784.1271; found: 784.1273.

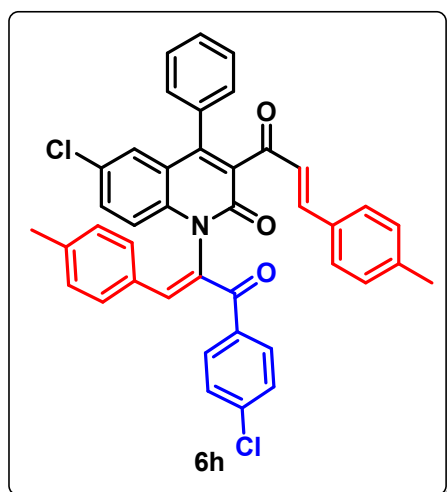
6-Chloro-1-((Z)-1-(3,4-dimethoxyphenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(3,4-dimethoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6g). Purification was carried out by



column chromatography on silica gel using a 20% ethyl acetate/Pet ether mixture, resulting in the isolation of **6g** as a Yellow solid (80% yield) mp: 271-273 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 7.3$ Hz, 2H), 7.64 (d, $J = 10.1$ Hz, 2H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.50 – 7.43 (m, 3H), 7.36 (dd, $J = 7.7, 5.5$ Hz, 3H), 7.31 (d, $J = 3.9$ Hz, 2H), 7.18 (d, $J = 8.9$ Hz, 1H), 7.02 (d, $J = 8.2$ Hz, 1H), 6.93 (d, $J = 9.7$ Hz, 2H), 6.80 (dd, $J = 8.3, 3.5$ Hz, 3H),

6.59 (d, $J = 16.1$ Hz, 1H), 3.88 (d, $J = 6.4$ Hz, 6H), 3.85 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.2, 192.6, 159.4, 151.6, 151.5, 149.1, 149.1, 148.3, 146.5, 142.6, 137.7, 137.5, 133.5, 132.8, 132.5, 131.8, 130.6, 130.1, 129.3, 129.2, 128.8, 128.7, 128.7, 128.5, 127.6, 127.3, 125.5, 125.1, 124.4, 123.5, 121.9, 116.9, 111.0, 110.9, 110.9, 110.1, 56.0, 55.9, 55.9, 55.6. FT-IR: $\nu = 2932, 2831, 1676, 1607, 1509, 1242, 1174, 1142, 1032, 827, 706, 542$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{35}\text{ClNO}_7$ requires $(\text{M} + \text{H})^+$ 712.2102; found: 712.2104.

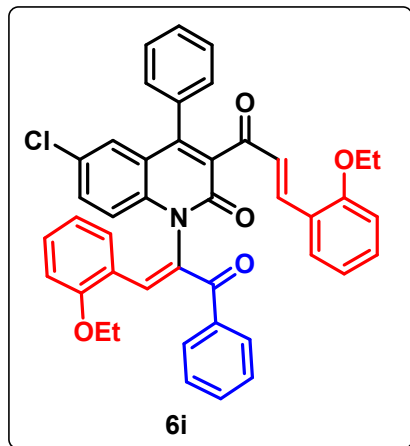
6-Chloro-1-((Z)-3-(4-chlorophenyl)-3-oxo-1-(p-tolyl)prop-1-en-2-yl)-4-phenyl-3-((E)-3-(p-



tolyl)acryloyl)quinolin-2(1H)-one (6h). Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **6h** as a Pale-yellow solid (78% yield) mp: 245-247 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.3$ Hz, 2H), 7.59 (s, 1H), 7.48 (dd, $J = 16.3, 5.3$ Hz, 6H), 7.36 –

7.28 (m, 6H), 7.19 – 7.11 (m, 7H), 6.66 (d, $J = 16.2$ Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.7, 192.2, 159.4, 148.8, 146.3, 142.2, 142.0, 141.3, 139.0, 137.3, 135.9, 133.5, 132.4, 131.7, 131.7, 131.5, 130.0, 129.9, 129.5, 129.5, 129.2, 128.9, 128.8, 128.8, 128.7, 128.6, 127.9, 126.2, 122.0, 116.8, 21.5, 21.5. FT-IR: $\nu = 3059, 2926, 1698, 1635, 1554, 1420, 1367, 1225, 1070, 961, 751, 709, 553$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{41}\text{H}_{29}\text{Cl}_2\text{NO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 676.1422; found: 676.1424.

6-Chloro-1-((Z)-1-(2-ethoxyphenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(2-

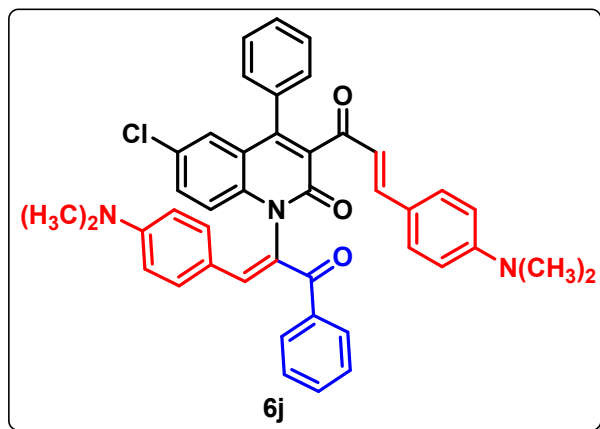


ethoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6i).

Purification was carried out by column chromatography on silica gel using a 11% ethyl acetate/Pet ether mixture, resulting in the isolation of **6i** as a Dark brown solid (76% yield) mp: 271-273 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.11 – 8.01 (m, 3H), 7.70 (d, $J = 16.4$ Hz, 1H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.43 – 7.33 (m, 5H), 7.31 (d, $J = 2.2$ Hz, 1H), 7.28 – 7.21 (m, 4H), 7.19 (dd, $J = 13.1, 6.0$ Hz, 2H), 6.89

– 6.78 (m, 4H), 6.74 (t, $J = 7.5$ Hz, 1H), 4.09 – 3.98 (m, 4H), 1.33 (dt, $J = 18.3, 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.2, 192.9, 159.7, 158.0, 157.0, 148.3, 141.8, 138.0, 137.6, 133.8, 132.6, 132.4, 132.1, 131.7, 131.2, 130.3, 129.7, 129.5, 129.2, 129.0, 128.6, 128.5, 128.4, 128.2, 128.2, 127.9, 127.6, 123.7, 121.9, 121.3, 120.9, 120.5, 117.0, 112.0, 111.7, 64.1, 64.0, 14.7, 14.6. FT-IR: $\nu = 1639, 1594, 1451, 1367, 1302, 1246, 1037, 923, 751, 711, 545$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{34}\text{ClNO}_5\text{Na}$ requires $(\text{M} + \text{Na})^+$ 702.2023; found: 702.2048.

6-Chloro-1-((Z)-1-(4-(dimethylamino)phenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(4-(dimethylamino)phenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6j).

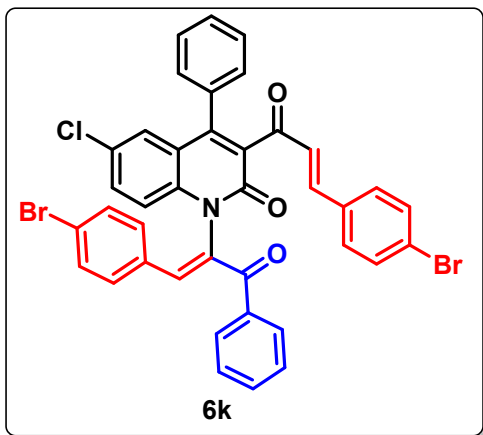


out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **6j** as a Dark brown solid (84% yield) mp: 265-267 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.1$ Hz, 2H), 7.53 (s, 1H), 7.50 – 7.44 (m, 1H), 7.39 (t, $J = 7.4$ Hz, 4H), 7.33 (dd, $J = 5.4, 2.6$ Hz, 2H), 7.29 – 7.25 (m, 2H), 7.23 (dd, $J = 9.4, 2.2$ Hz,

4H), 7.11 (d, $J = 9.6$ Hz, 1H), 7.02 (d, $J = 8.9$ Hz, 2H), 6.52 – 6.40 (m, 5H), 2.89 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.0, 192.9, 159.3, 152.1, 152.1, 147.8, 147.4, 144.0, 138.6, 137.8, 134.0, 133.3, 132.5, 131.7, 131.4, 130.6, 129.7, 129.6, 129.0, 128.9, 128.6, 128.5, 128.3, 128.1, 127.9, 127.6, 122.6, 122.3, 122.2, 119.0, 117.0, 111.9, 111.6, 40.0, 39.9. FT-IR: $\nu = 1693, 1641, 1523, 1359, 1161, 1112, 1061, 945, 812, 701, 543$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{36}\text{ClN}_3\text{O}_3\text{Na}$ requires $(\text{M} + \text{Na})^+ 700.2343$; found: 700.2371.

1-((Z)-1-(4-Bromophenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(4-

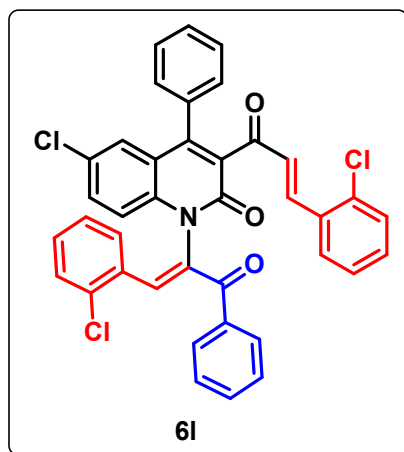
bromophenyl)acryloyl)-6-chloro-4-phenylquinolin-2(1H)-one (6k). Purification was carried



out by column chromatography on silica gel using a 11% ethyl acetate/Pet ether mixture, resulting in the isolation of **6k** as a Colourless solid (75% yield) mp: 255-257 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.91 (m, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.44 (t, $J = 7.6$ Hz, 3H), 7.38 – 7.34 (m, 6H), 7.29 – 7.23 (m, 3H), 7.19 (t, $J = 8.4$ Hz, 4H), 7.04 (dd, $J = 13.4, 8.7$ Hz, 3H), 6.57 (d, $J = 16.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ

192.8, 192.2, 159.4, 149.2, 144.3, 141.1, 137.2, 137.1, 133.3, 133.3, 133.2, 132.9, 132.5, 132.1, 131.9, 130.9, 130.7, 130.0, 129.9, 129.5, 129.4, 128.9, 128.7, 128.6, 128.1, 127.4, 125.6, 125.0, 121.9, 116.6. FT-IR: $\nu = 1701, 1637, 1418, 1370, 1227, 1064, 964, 814, 690, 553$ cm^{-1} . HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{24}\text{Br}_2\text{ClNO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+ 769.9709$; found: 769.9709.

6-Chloro-1-((Z)-1-(2-chlorophenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(2-



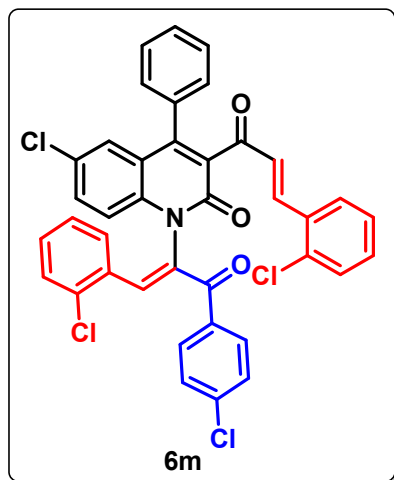
chlorophenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6l).

Purification was carried out by column chromatography on silica gel using a 12% ethyl acetate/Pet ether mixture, resulting in the isolation of **6l** as a Colourless solid (71% yield) mp: 267-269 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 7.6$ Hz, 2H), 7.85 (s, 1H), 7.74 (d, $J = 16.3$ Hz, 1H), 7.50 (t, $J = 7.9$ Hz, 3H), 7.45 – 7.36 (m, 5H), 7.35 (s, 4H), 7.28 – 7.23 (m, 3H), 7.19 (s, 1H), 7.14 (s, 1H), 6.62 (d, $J = 16.3$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 192.3, 159.9, 149.1, 141.5,

138.6, 137.5, 136.8, 135.1, 134.9, 133.9, 133.3, 133.1, 132.6, 131.7, 131.4, 131.3, 130.8, 130.3,

130.0, 129.7, 129.5, 129.4, 129.3, 128.9, 128.8, 128.6, 128.5, 128.0, 127.8, 127.4, 127.1, 121.6, 116.8. **FT-IR:** $\nu = 1637, 1489, 1367, 1226, 1089, 958, 753, 685, 518 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{39}\text{H}_{24}\text{Cl}_3\text{NO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 682.0719; found: 682.0748.

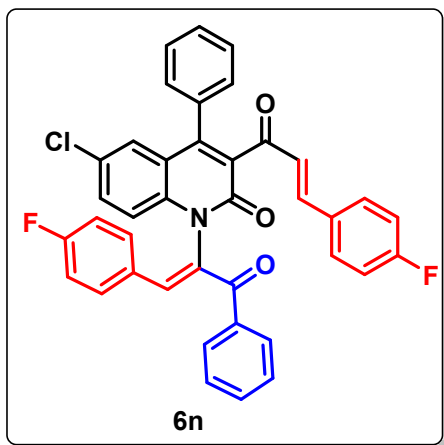
6-Chloro-1-((Z)-1-(2-chlorophenyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-3-((E)-3-(2-chlorophenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6m).



Purification was carried out by column chromatography on silica gel using a 10% ethyl acetate/Pet ether mixture, resulting in the isolation of **6m** as a Colourless solid (69% yield) mp: 271-273 °C; **¹H NMR (400 MHz, CDCl₃)** δ 7.98 (d, $J = 8.5$ Hz, 2H), 7.75 – 7.63 (m, 2H), 7.41 (d, $J = 8.5$ Hz, 3H), 7.37 – 7.32 (m, 3H), 7.30 – 7.24 (m, 6H), 7.21 (dd, $J = 7.4, 1.5$ Hz, 1H), 7.18 – 7.13 (m, 3H), 7.06 (dd, $J = 14.0, 8.2$ Hz, 2H), 6.54 (d, $J = 16.3$ Hz, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 192.6,

191.3, 159.9, 149.2, 141.7, 139.7, 138.1, 137.3, 135.1, 134.6, 133.9, 133.2, 132.5, 131.8, 131.6, 131.5, 131.2, 130.6, 130.1, 129.8, 129.4, 129.4, 129.3, 128.9, 128.8, 128.8, 128.6, 128.0, 127.8, 127.5, 127.1, 121.6, 116.7. **FT-IR:** $\nu = 1693, 1636, 1593, 1555, 1365, 1224, 1088, 752, 686, 553 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{39}\text{H}_{23}\text{Cl}_4\text{NO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 716.0303; found: 716.0305.

6-Chloro-1-((Z)-1-(4-fluorophenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(4-fluorophenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6n). Purification was carried out by

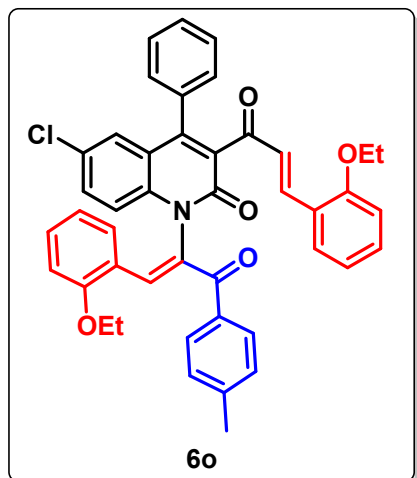


column chromatography on silica gel using a 11% ethyl acetate/Pet ether mixture, resulting in the isolation of **6n** as a Colourless solid (73% yield) mp: 280-282 °C; **¹H NMR (400 MHz, CDCl₃)** δ 8.02 (d, $J = 7.6$ Hz, 2H), 7.67 – 7.60 (m, 2H), 7.50 (dd, $J = 15.5, 7.8$ Hz, 4H), 7.40 (dd, $J = 15.0, 8.9$ Hz, 5H), 7.35 – 7.25 (m, 6H), 7.10 (d, $J = 8.7$ Hz, 1H), 7.02 – 6.96 (m, 3H), 6.60 (d, $J = 16.2$ Hz, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 192.9, 192.4, 165.2, 162.7, 162.07,

159.4, 149.1, 141.2 (d, $J = 336.3$ Hz), 137.2 (d, $J = 4.0$ Hz), 133.4, 132.8 (d, $J = 91.9$ Hz), 132.5, 132.2, 131.8 (d, $J = 2.0$ Hz), 130.6, 130.5, 130.0, 129.8, 129.3 (d, $J = 25.2$ Hz), 128.8, 128.7 (d, $J = 2.0$ Hz), 128.6, 128.0, 126.7, 126.37, 122.0, 116.7, 116.4, 115.9 (d, $J = 21.2$ Hz). **¹⁹F NMR (377 MHz, CDCl₃)** δ -107.0 (s, 1F), -108.7 (s, 1F). **FT-IR:** $\nu = 1693, 1641, 1555, 1420,$

1365, 1223, 1063, 960, 827, 687, 550 cm^{-1} . **HRMS (ESI)** calcd for $\text{C}_{39}\text{H}_{24}\text{ClF}_2\text{NO}_3\text{Na}$ requires $(\text{M} + \text{Na})^+$ 650.1310; found: 650.1337.

6-Chloro-1-((Z)-1-(2-ethoxyphenyl)-3-oxo-3-(p-tolyl)prop-1-en-2-yl)-3-((E)-3-(2-



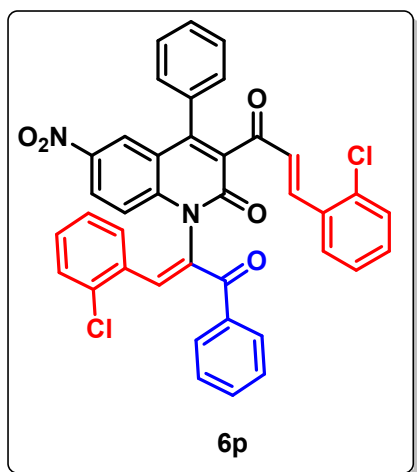
ethoxyphenyl)acryloyl)-4-phenylquinolin-2(1H)-one (6o).

Purification was carried out by column chromatography on silica gel using a 15% ethyl acetate/Pet ether mixture, resulting in the isolation of **6o** as a Colourless solid (79% yield) mp: 268-270 $^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 – 7.99 (m, 3H), 7.72 (d, $J = 16.4$ Hz, 1H), 7.55 – 7.50 (m, 1H), 7.43 (dt, $J = 6.4, 3.3$ Hz, 2H), 7.41 – 7.36 (m, 3H), 7.34 – 7.29 (m, 4H), 7.28 (s, 1H), 7.25 (d, $J = 3.9$ Hz, 1H), 7.21 (dd, $J = 10.5, 5.1$ Hz, 2H), 6.92 – 6.80 (m, 4H), 6.76 (t, $J =$

7.6 Hz, 1H), 4.06 (ddd, $J = 11.8, 9.5, 4.0$ Hz, 4H), 2.46 (s, 3H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.32 (dd, $J = 18.0, 11.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.3, 192.6, 159.7, 158.0, 156.9, 148.3, 143.3, 141.8, 137.8, 137.6, 134.8, 133.8, 132.7, 132.4, 131.9, 131.8, 131.2, 130.6, 129.7, 129.5, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.1, 127.9, 127.5, 123.6, 121.8, 121.3, 120.9, 120.4, 117.0, 111.9, 111.6, 64.0, 64.0, 21.7, 14.8, 14.6. **FT-IR:** $\nu = 2921, 2832, 1685, 1608, 1508, 1392, 1240, 1182, 1119, 997, 802, 702, 547, 492$ cm^{-1} . **HRMS (ESI)** calcd for $\text{C}_{44}\text{H}_{37}\text{ClNO}_5$ requires $(\text{M} + \text{H})^+$ 694.2360; found: 694.2362.

1-((Z)-1-(2-Chlorophenyl)-3-oxo-3-phenylprop-1-en-2-yl)-3-((E)-3-(2-

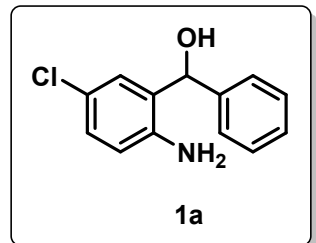
chlorophenyl)acryloyl)-6-nitro-4-phenylquinolin-2(1H)-one (6p).



by column chromatography on silica gel using a 13% ethyl acetate/Pet ether mixture, resulting in the isolation of **6p** as a Colourless solid (73% yield) mp: 245-247 $^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.28 – 8.22 (m, 2H), 8.14 (d, $J = 7.4$ Hz, 2H), 7.92 (s, 1H), 7.78 (d, $J = 16.3$ Hz, 1H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.59 – 7.48 (m, 6H), 7.36 (dd, $J = 17.8, 8.3$ Hz, 6H), 7.32 – 7.29 (m, 1H), 7.26 (dd, $J = 14.0, 6.5$ Hz, 2H), 7.17 (t, $J = 7.5$ Hz, 1H), 6.65 (d, $J = 16.3$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 192.0, 191.9, 190.3, 160.1, 149.6, 143.0,

142.8, 142.0, 139.1, 136.5, 135.2, 134.6, 133.8, 133.4, 132.5, 132.3, 132.0, 131.7, 131.7, 130.5, 130.4, 130.1, 129.9, 129.9, 129.4, 129.2, 129.1, 129.1, 128.9, 128.7, 128.6, 128.0, 127.6, 127.2, 126.0, 124.8, 120.3, 116.3. **FT-IR:** $\nu = 1700, 1641, 1557, 1420, 1374, 1226, 1089, 958, 755, 689, 553 \text{ cm}^{-1}$. **HRMS (ESI)** calcd for $\text{C}_{39}\text{H}_{25}\text{Cl}_2\text{N}_2\text{O}_5$ requires $(\text{M} + \text{H})^+$ 671.1141; found: 671.1145.

(2-amino-5-chlorophenyl) (phenyl)methanol (1a). Colourless solid (96% yield); **^1H NMR (400**

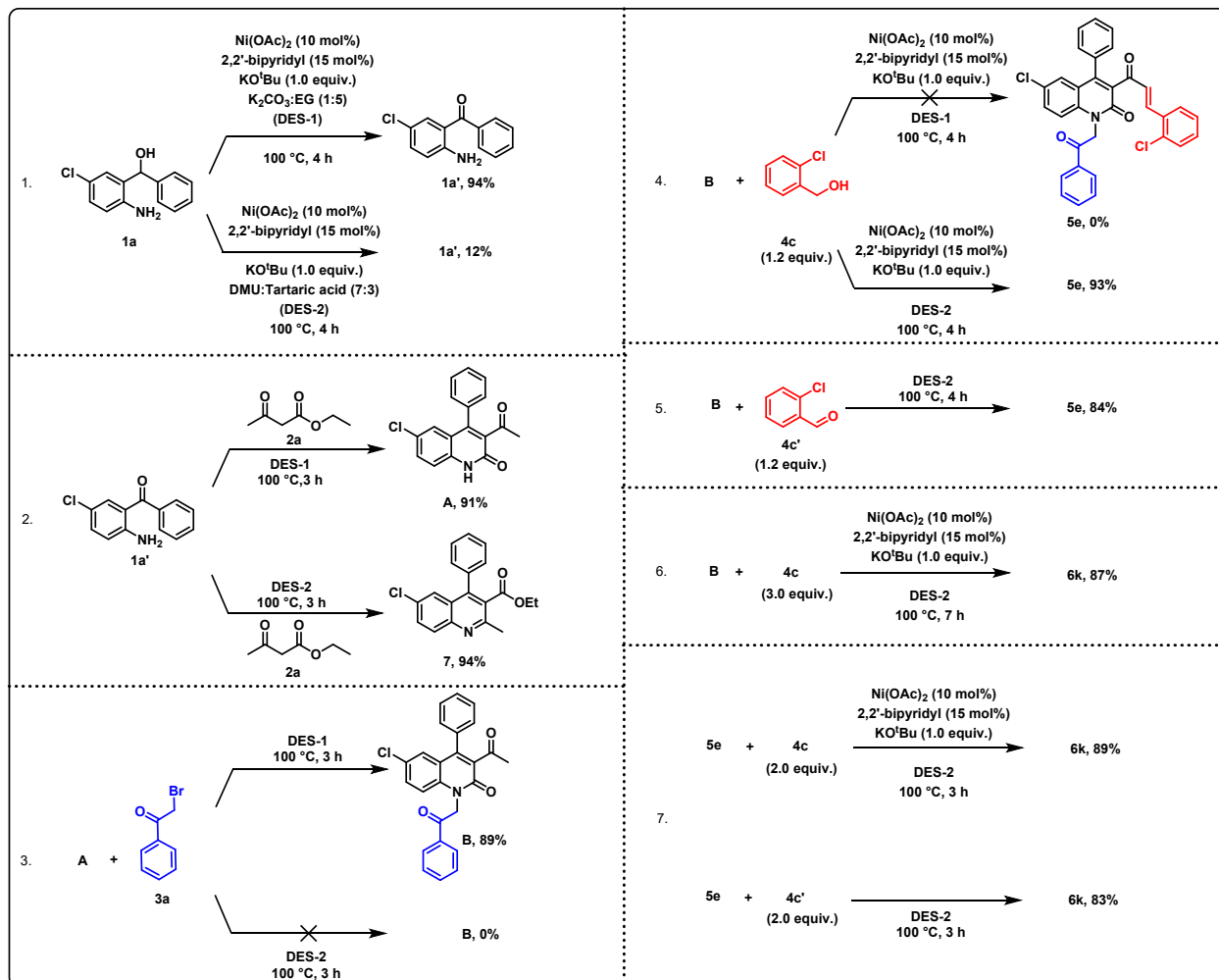


MHz, CDCl_3) δ 7.43 – 7.34 (m, 5H), 7.13 – 7.04 (m, 2H), 6.59 (d, $J = 8.4 \text{ Hz}$, 1H), 5.76 (d, $J = 3.1 \text{ Hz}$, 1H), 3.95 (s, 2H), 2.91 (d, $J = 3.5 \text{ Hz}$, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 141.1, 129.0, 128.7, 128.6, 128.2, 128.0, 126.6, 123.1, 118.1, 74.3.

4. Mechanistic Investigations

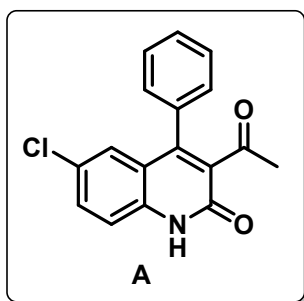
4.1 Control experiment study

As illustrated in Scheme S1, a model reaction was performed using the starting materials **1a**, **2a**, **3a** and **4c**. The formation of the intermediates **A**, **7**, and **B** was successfully isolated and characterized by ^1H and ^{13}C NMR analysis and the spectra are given below.

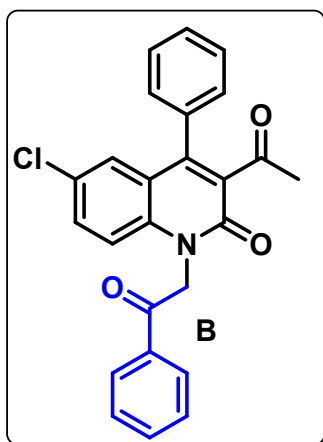


Scheme S1. Control experiment study

3-Acetyl-6-chloro-4-phenylquinolin-2(1H)-one (A). Colourless solid (93% yield); ¹H NMR



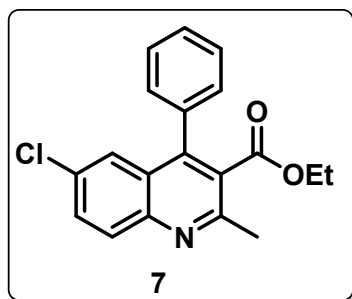
(400 MHz, CDCl₃) δ 13.20 (s, 1H), 7.52 (dd, *J* = 4.8, 1.5 Hz, 3H), 7.47 (dd, *J* = 13.0, 5.4 Hz, 2H), 7.32 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.24 (d, *J* = 2.0 Hz, 1H), 2.29 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 201.5, 161.5, 148.0, 136.7, 133.7, 133.5, 131.8, 129.4, 129.0, 128.9, 128.6, 126.7, 120.9, 118.2, 31.7.



3-Acetyl-6-chloro-1-(2-oxo-2-phenylethyl)-4-phenylquinolin-2(1H)-one (B). Colourless solid (93% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.09 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.51 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.43 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.33 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.27 – 7.26 (m, 1H), 6.98 (d, *J* =

9.0 Hz, 1H), 5.85 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.0, 191.9, 159.1, 146.3, 137.8, 134.6, 134.4, 133.6, 133.4, 131.5, 129.3, 129.1, 129.1, 128.8, 128.3, 128.2, 128.1, 122.0, 115.8, 48.9, 31.4.

Ethyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (7).



7.48 (m, 3H), 7.37 – 7.32 (s, 3H), 0.95 (t, $J = 7.1$ CDCl_3) δ 168.1, 155.0, 146.1, 145.4, 135.0, 132.4, 131.2, 130.5, 129.3, 128.8, 128.5, 128.2, 126.0, 125.2, 61.5, 23.7, 13.6.

Colourless solid (93% yield); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.9$ Hz, 1H), 7.65 (dd, $J = 8.9, 0.9$ Hz, 1H), 7.55 – 7.53 (m, 1H), 7.52 – (m, 2H), 4.07 (q, $J = 7.1$ Hz, 2H), 2.77 Hz, 3H). ^{13}C NMR (101 MHz,

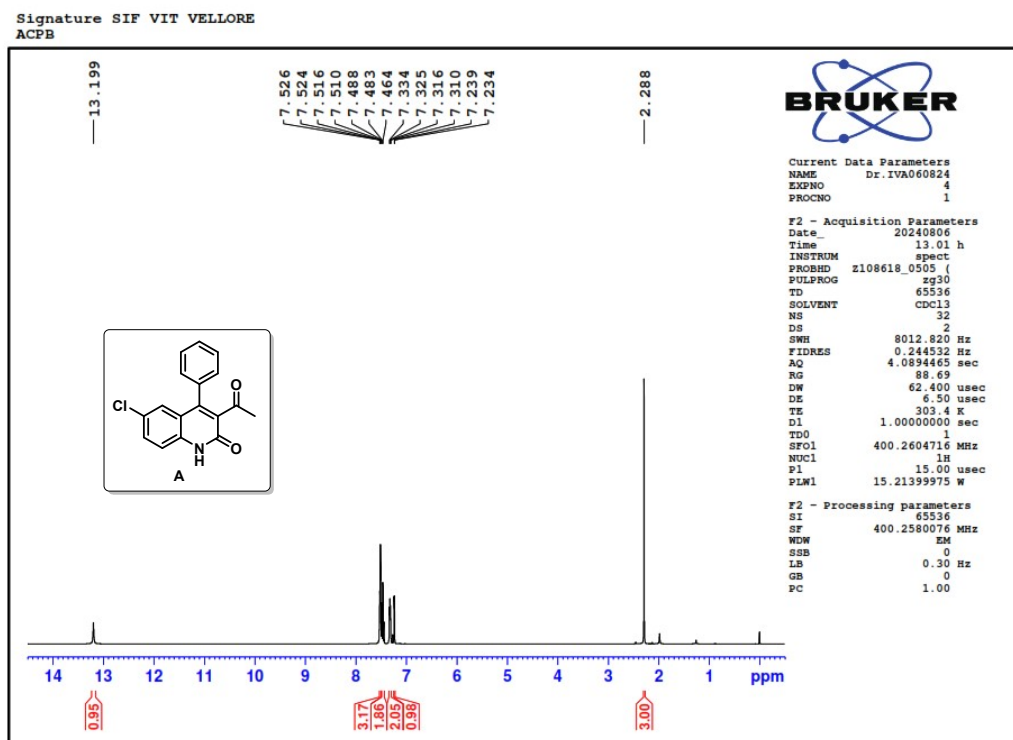


Fig. S1. ^1H NMR spectrum of A (CDCl_3 , 400 MHz)

Signature SIF VIT VELLORE
INI

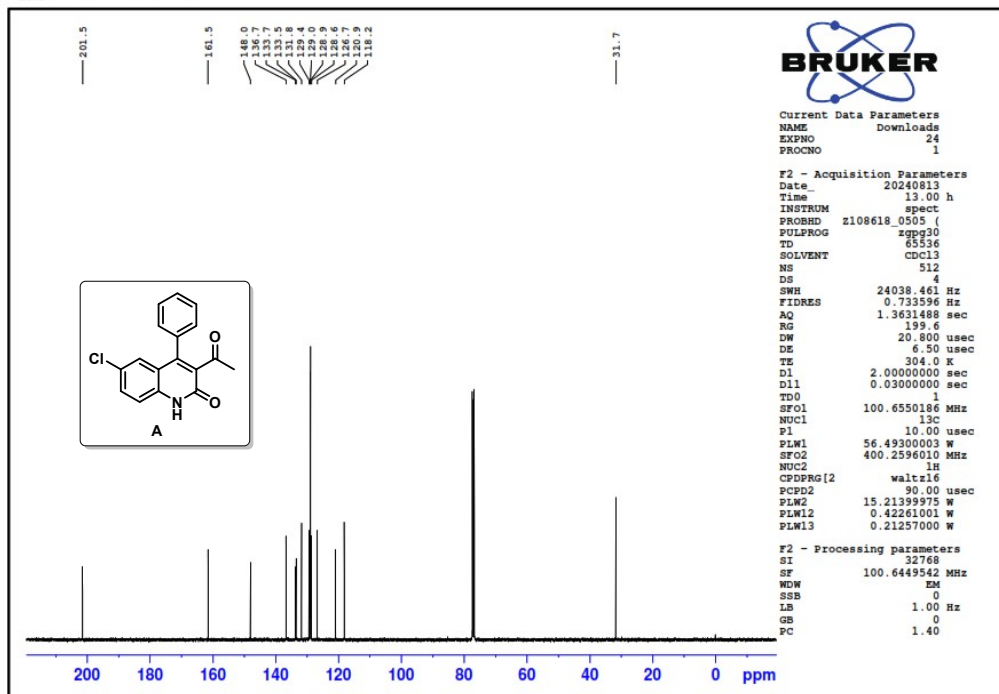


Fig. S2. ¹³C NMR spectrum of A (CDCl₃, 101 MHz)

Signature SIF VIT VELLORE
ACPB

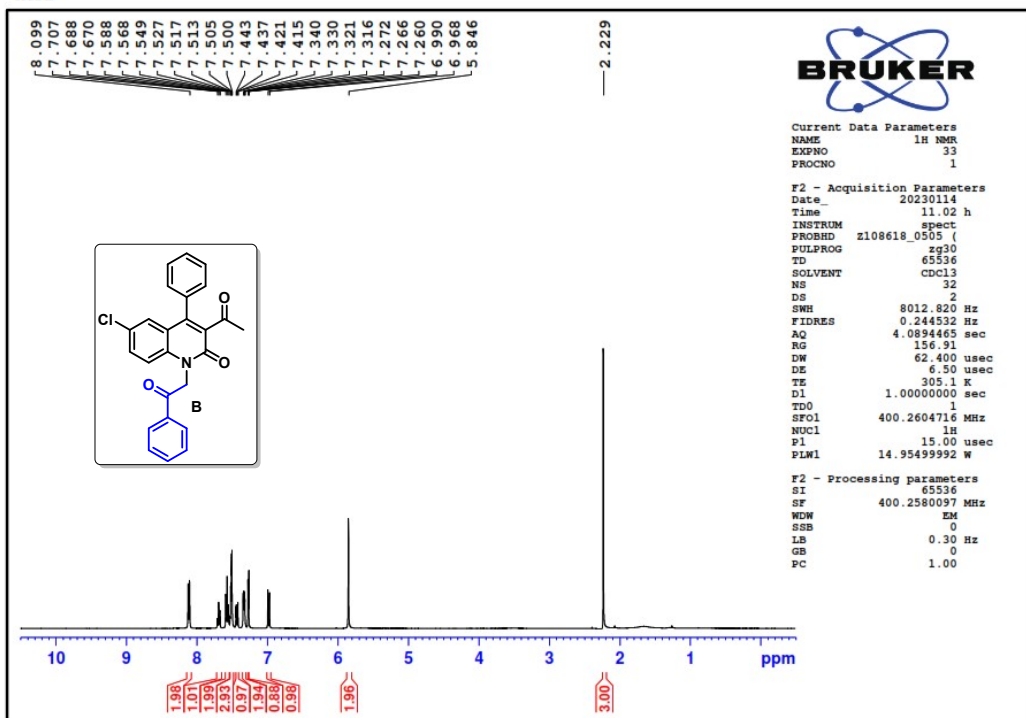


Fig. S3. ¹H NMR spectrum of B (CDCl₃, 400 MHz)

Signature SIF VIT VELLORE
ACPB

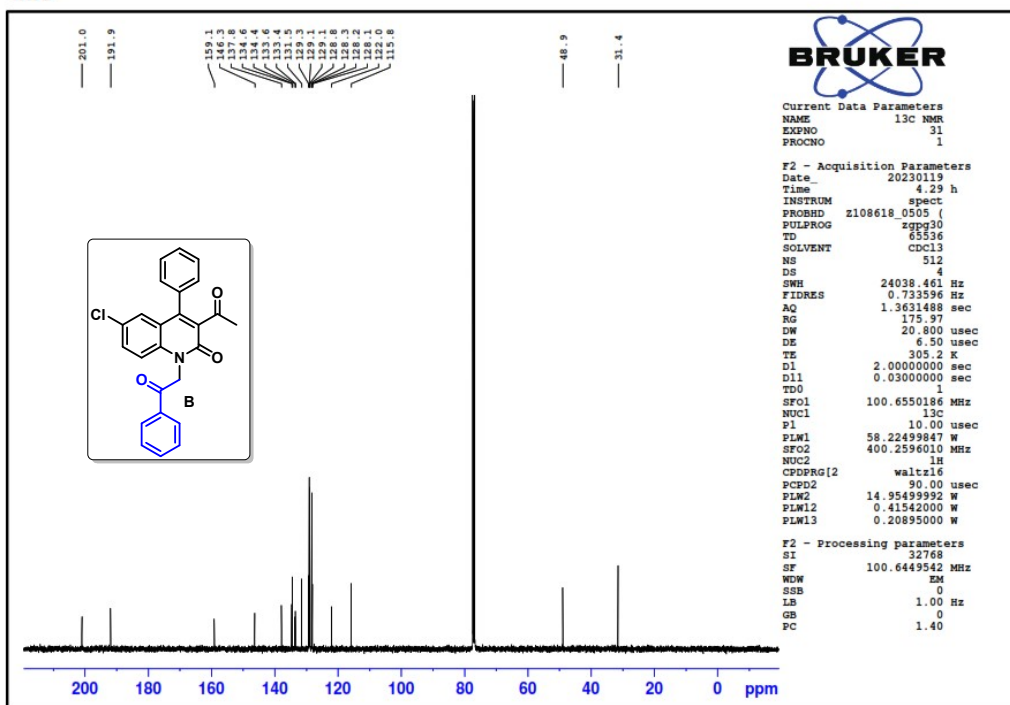


Fig S4. ¹³C NMR spectrum of **B** (CDCl₃, 101 MHz)

Signature SIF VIT VELLORE
ES

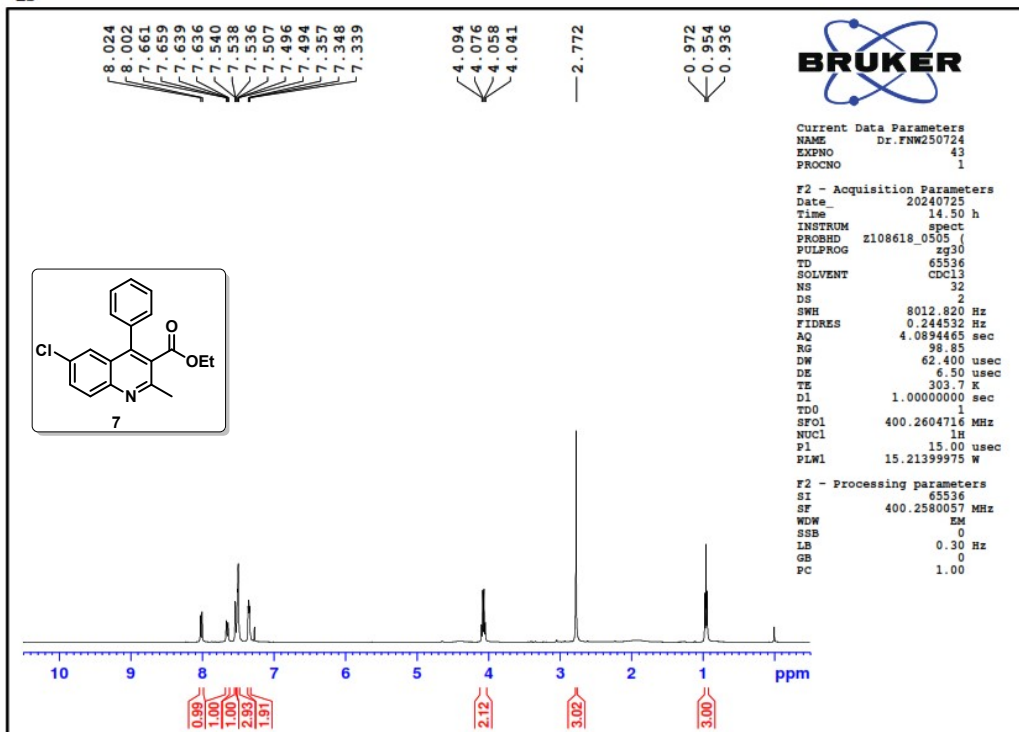


Fig. S5. ¹H NMR spectrum of **7** (CDCl₃, 400 MHz)

Signature SIF VIT VELLORE
ES

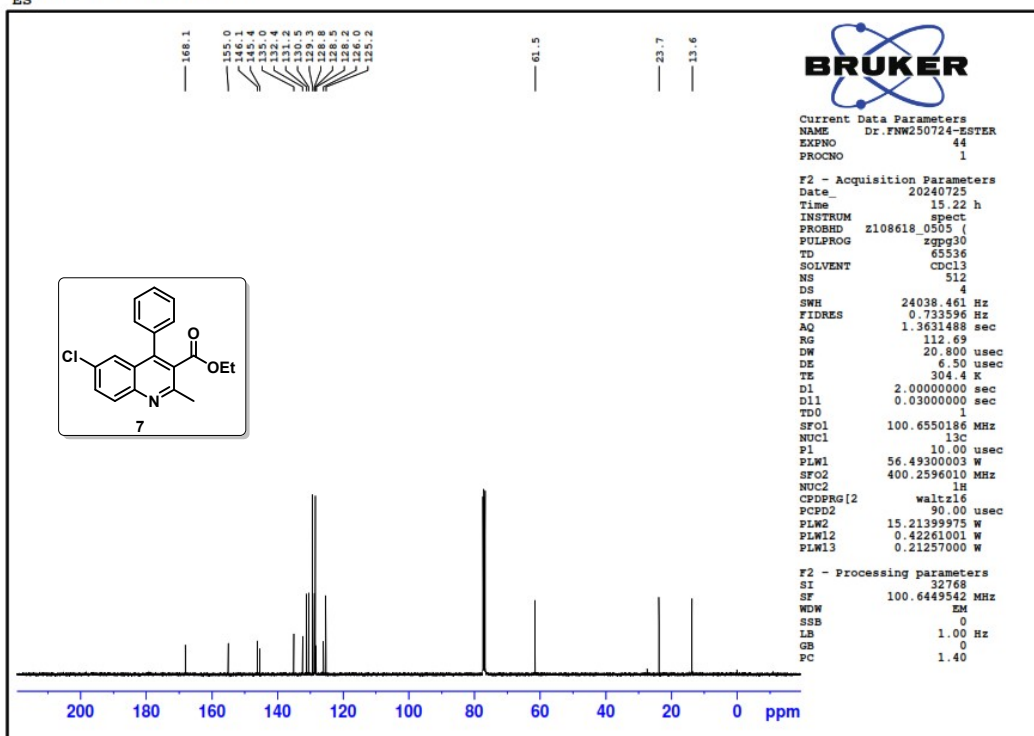


Fig. S6. ^{13}C NMR spectrum of 7 (CDCl_3 , 101 MHz)

4.2 Mass spectroscopic Studies for the intermediate detection

4.2.1 Stoichiometric studies

A mixture of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol), 2,2'-bipyridyl (1.5 mmol), KO^tBu (1.0 equiv.) and K_2CO_3 :Ethylene glycol (1:5) DES-1 were heated at 100 °C for 10 min. The reaction mixture was analyzed by HRMS (ESI) spectroscopy. The calculated mass for $\text{C}_{14}\text{H}_{14}\text{KN}_2\text{NiO}_4$ ($\text{M} + \text{K}$) $^+$ is 370.9944; found: 370.9945. Based on the HRMS result, we concluded that a nickel complex forms during the catalytic cycle. The HRMS spectrum of complex $[\text{Ni}(\text{II})\text{L}_n]$ is shown in Fig.S7

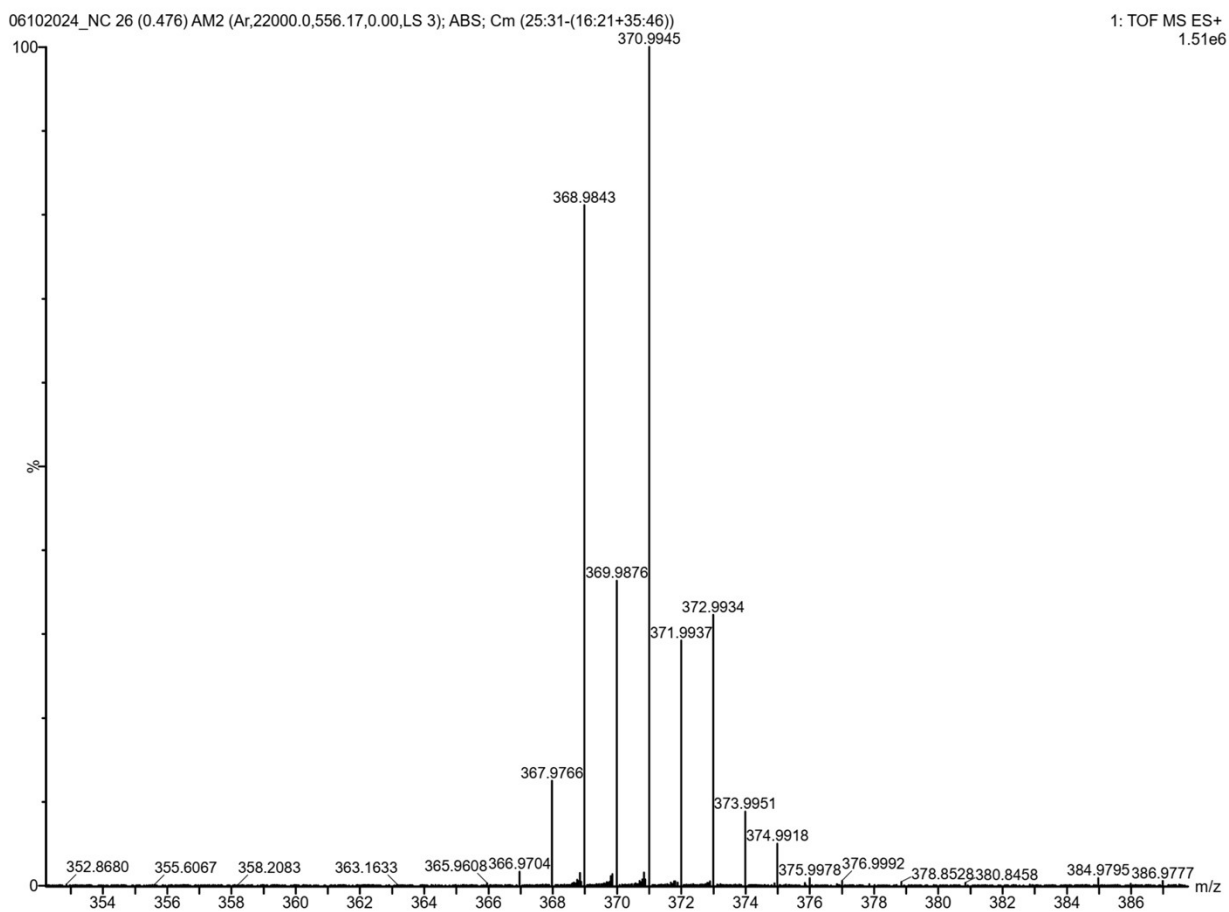
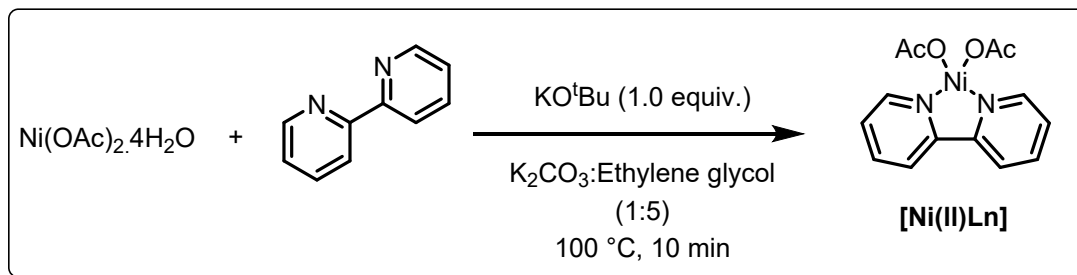
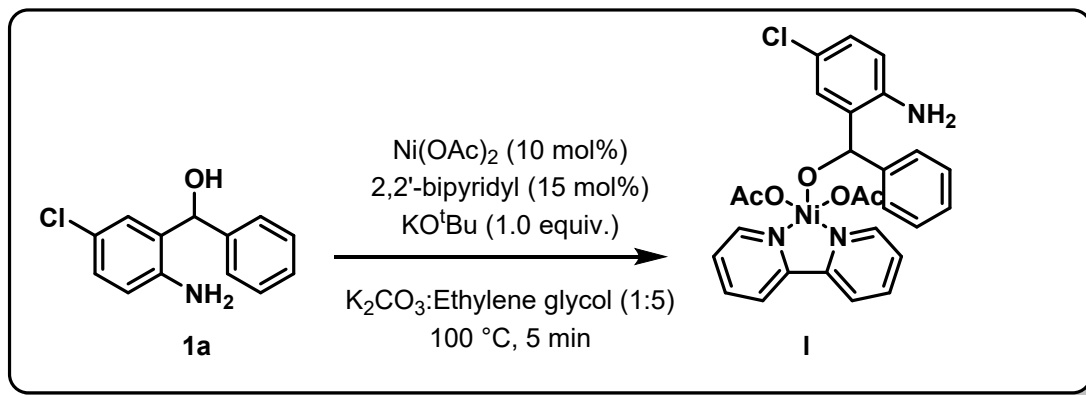


Fig. S7. HRMS spectrum of [Ni(II)L_n]

4.2.2 Nickel enolate intermediate identification study



A mixture of 2-amino benzhydrol (0.5 mmol), $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ (10 mol%), 2,2'-bipyridyl (15 mol%), KO^tBu (1.0 equiv.) and K_2CO_3 :Ethylene glycol (1:5) DES-1 were heated at $100\text{ }^\circ\text{C}$ for 5 min. The reaction mixture was analyzed by HRMS (ESI) spectroscopy. The calculated mass for $\text{C}_{27}\text{H}_{26}\text{ClN}_3\text{NiO}_5$ ($\text{M} + \text{H}$)⁺ is 565.0914; found: 565.0915.

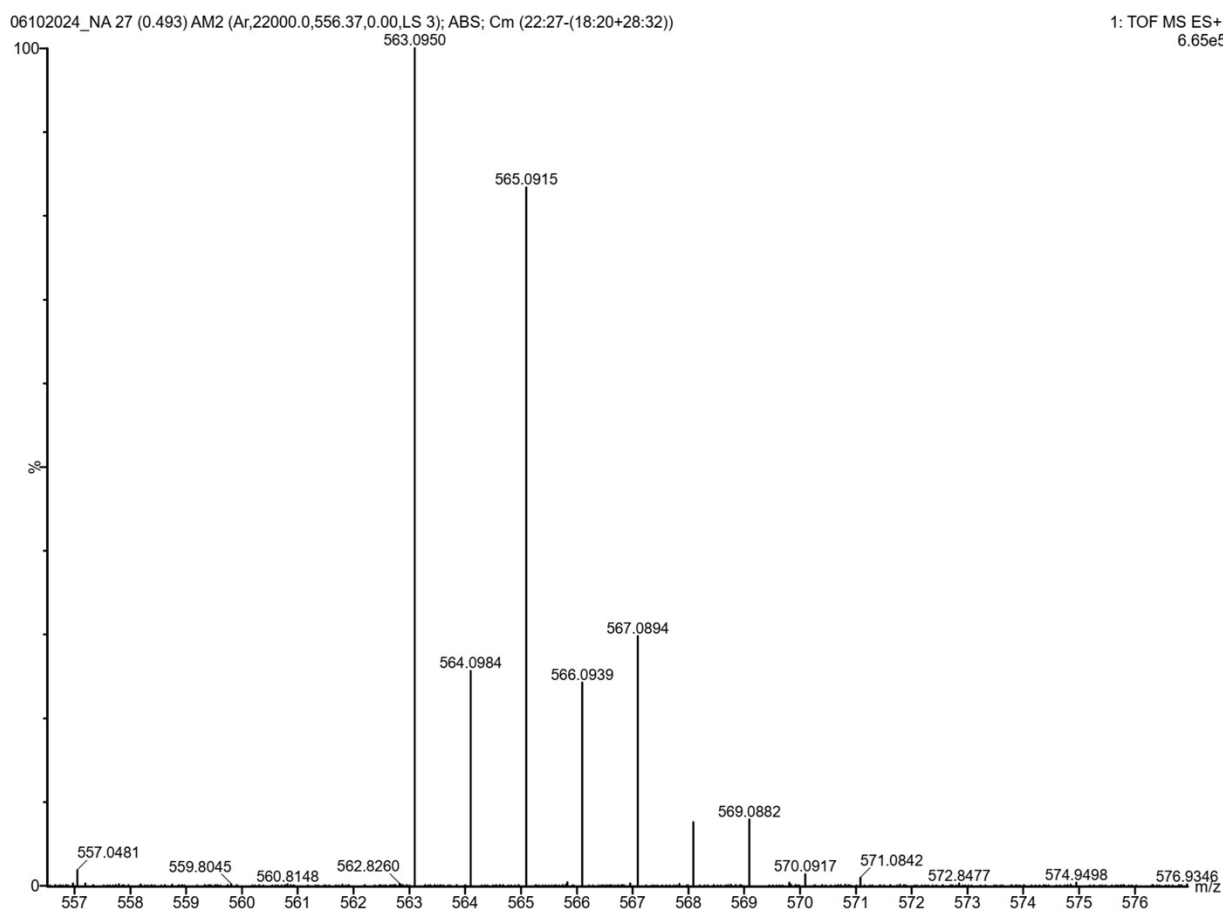
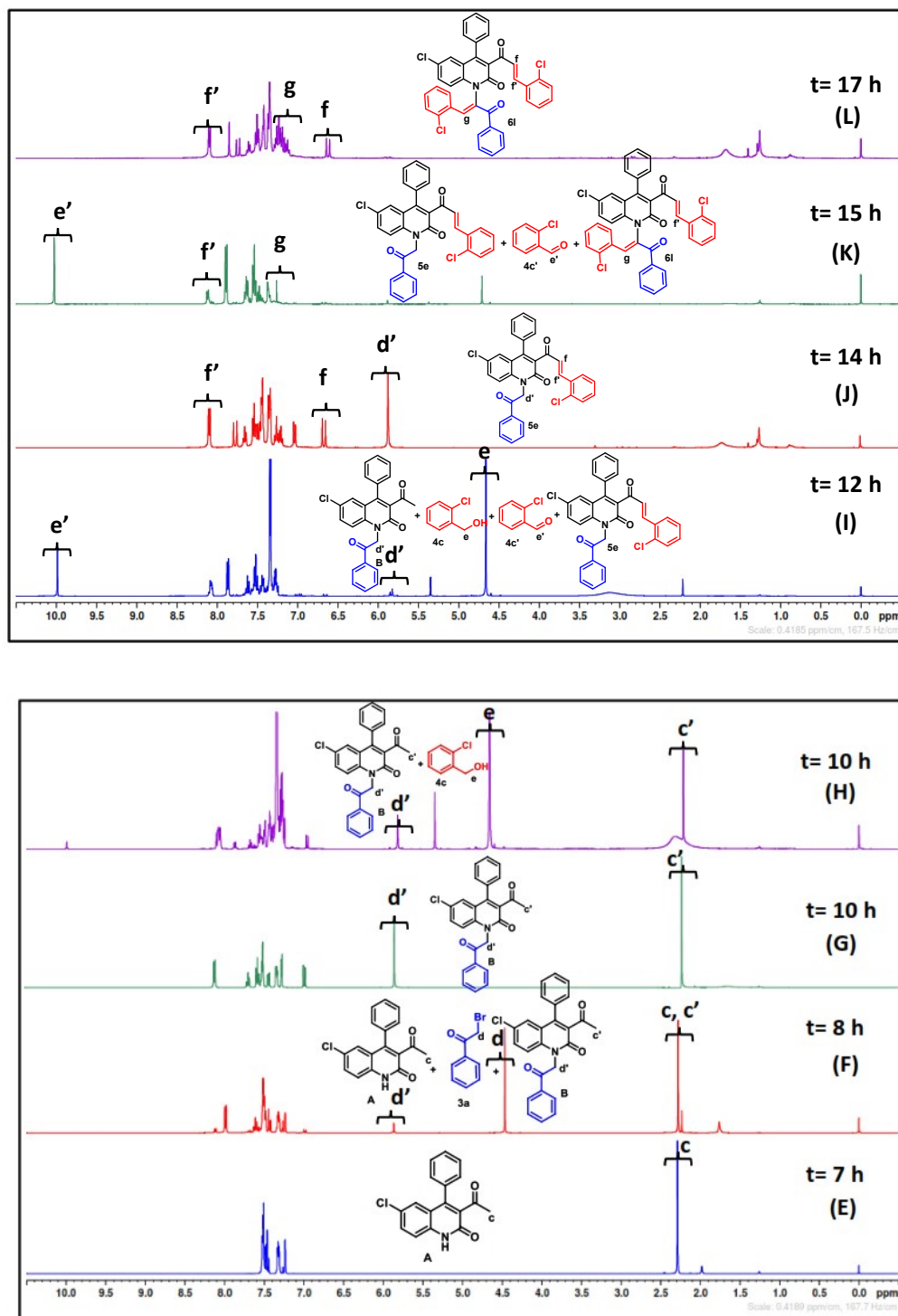


Fig. S8. HRMS spectrum of intermediate I

Based on the HRMS result, the reaction proceeds *via* metal alkoxide formation followed by a β -hydride elimination mechanism. The HRMS spectrum of intermediate I is shown in Fig. S8.

4.3 Reaction monitoring by ^1H NMR analysis for the synthesis of 5e & 6l



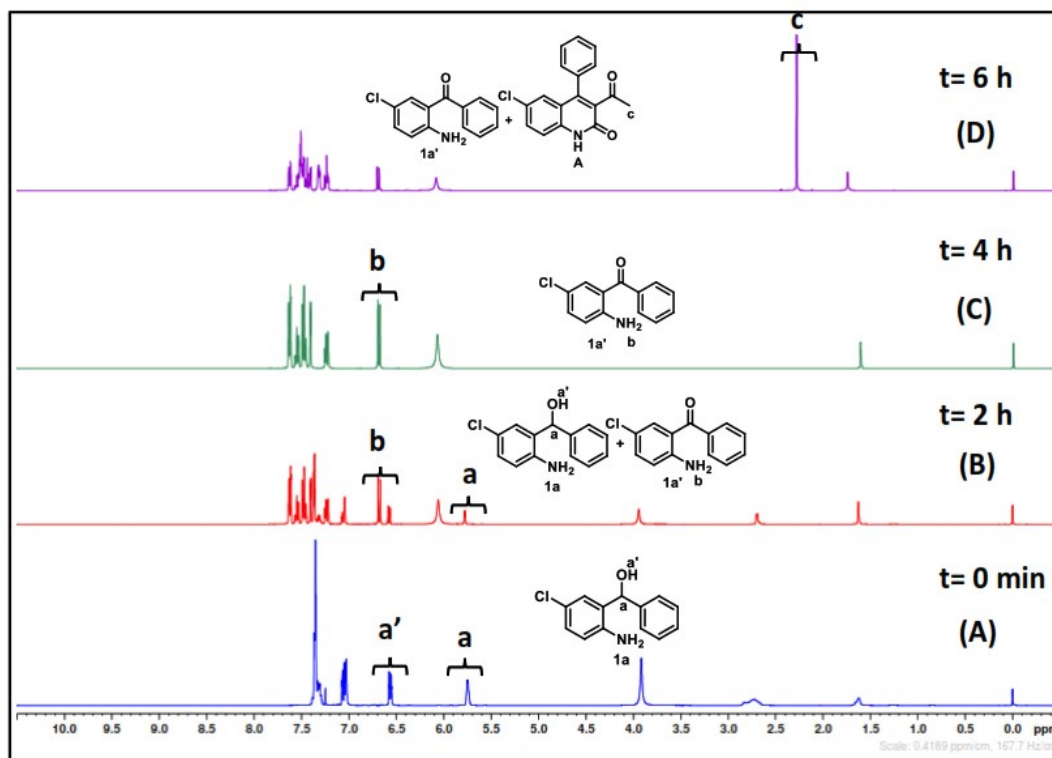


Fig. S9. Reaction monitoring by ^1H NMR analysis in different time intervals for the synthesis of **5e** & **6l**

The ^1H NMR studies were performed to propose the plausible reaction mechanism involved in the sequential synthesis of compounds **5e** and **6l**. Initially, the ^1H NMR spectrum of **A** was taken for the benzhydrol **1a**, before initiation of the reaction, showing the signal for its benzylic and alcoholic -OH protons at 5.8 ppm and 6.5 ppm respectively. Spectrum **B** was recorded after 2 h, indicating the formation of the benzophenone intermediate **1a'** along with benzhydrol **1a**, as shown by the appearance of NH_2 protons at 6.8 ppm. The Spectrum **C**, recorded after 4 h, demonstrated the exclusive formation of the benzophenone intermediate **1a'**, confirmed by the disappearance of the benzylic proton signal at 5.8 ppm. Spectrum **D** and Spectrum **E** were recorded at 6-hour and 7-hour intervals, respectively, indicating the formation of intermediate **A**, as shown by the presence of aliphatic CH_3 peaks in the range of 2.3-2.4 ppm. Spectrum **F** was recorded after the addition of phenacyl bromide **3a** to the reaction mixture, indicating the presence of benzylic CH_2 at 4.5 ppm. The spectrum **G** was recorded after 10 h, showing the formation of intermediate **B** which is confirmed by its methyl and benzylic protons appearing in 2.4 and 6.0 ppm respectively. Spectrum **H** was recorded after the addition of 2-chloro benzyl

alcohol **4c** into the reaction mixture, represented by the alcohol benzylic CH₂ appearing at 4.6 ppm. The spectrum **I** was recorded after 12 h, indicating the formation of aldehyde **4c'**, as evidenced by the appearance of -CHO proton at 10 ppm along with the formation of mono-alkenylated quinolinone **5e**. Spectrum **J** was recorded over a period of 14 h, showing that the reaction was completed with the formation of mono-alkenylated quinolinone **5e** which was confirmed by the disappearance of intermediate **B** aliphatic methyl protons in 2.4 ppm and the appearance of **5e** olefinic protons at 6.7 and 8.1 ppm. Similarly, by adding an excess of alcohol (3.0 mmol) **4c** and continuing the reaction for 17 h, the formation of the bi-alkenylated quinolinone **6l** was observed (Spectrum K and L). This was confirmed by the disappearance of the mono-alkenylated quinolinone **5e** benzylic CH₂ and the appearance of **6l** methine proton at 7.2 ppm. All spectra (**Fig. S9**) were recorded by conducting the reactions according to the standard reaction procedure.

5. X-Ray Crystallography Data

Crystallographic data and structure determination details are compiled in Table S1. The crystals were obtained by slow evaporation of compounds **B** (CCDC: 2374871) and **6m** (CCDC: 2388694) in a solution consisting of CDCl₃ and DCM at r.t. The structure was determined using direct methods employed in ShelXT,¹ OleX² and refinement was carried out using least-square minimization implemented in ShelXL.³ All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were fixed geometrically in idealized positions and were refined using a riding model.

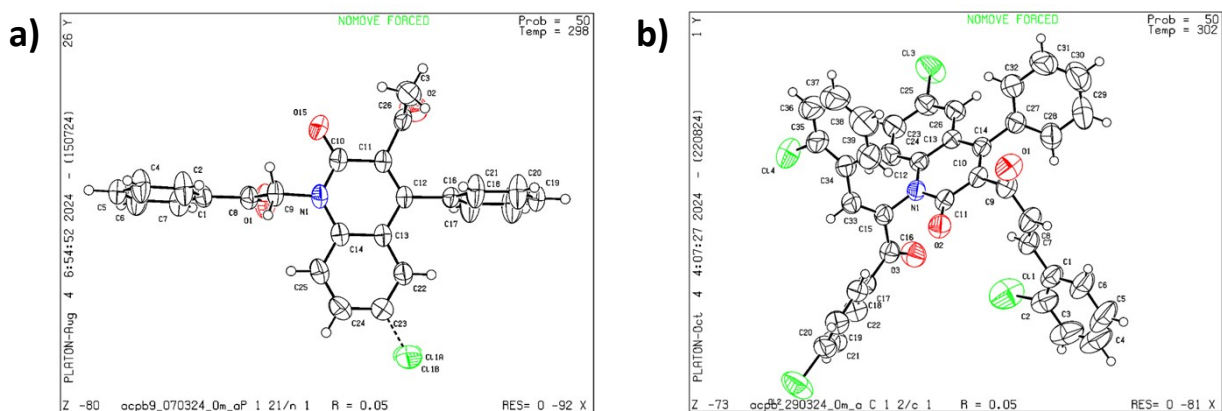
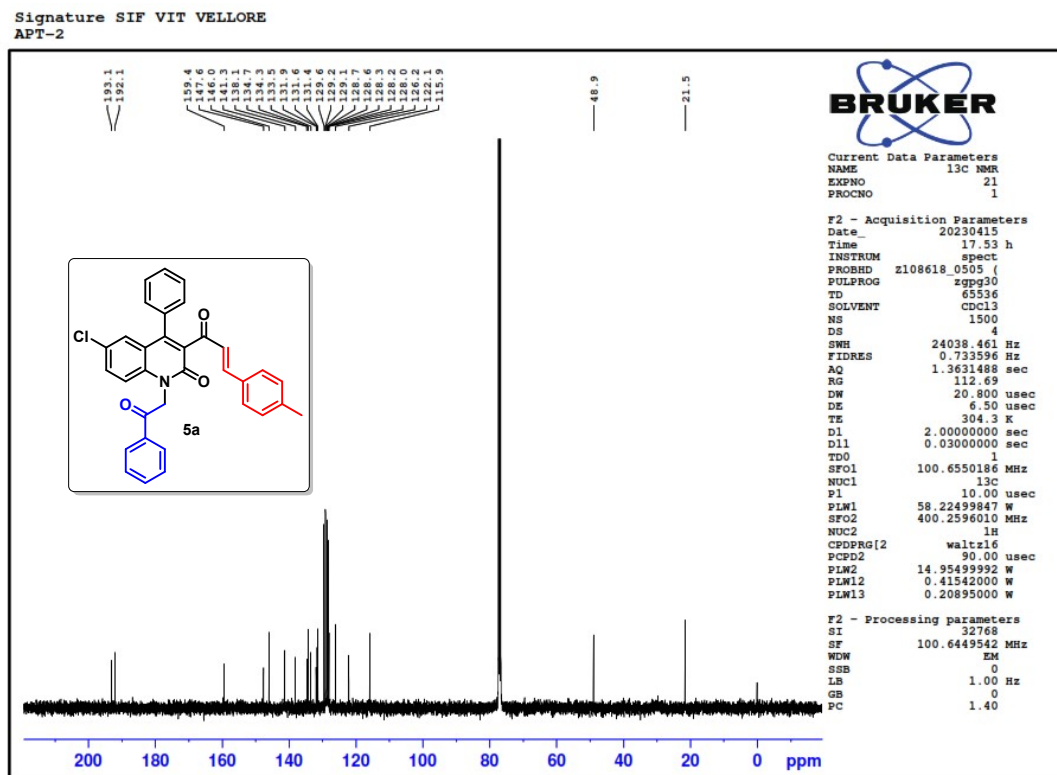
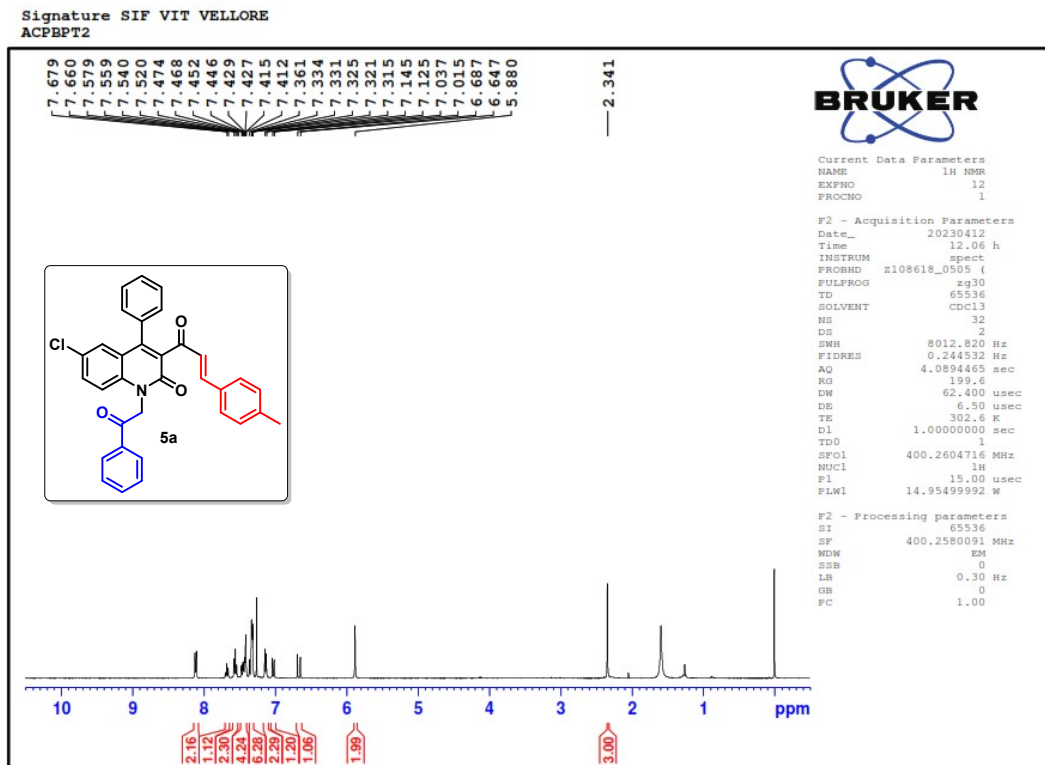


Fig 10. a) Eclipsed diagram of the compound **B**. b) Eclipsed diagram of the compound **6m**

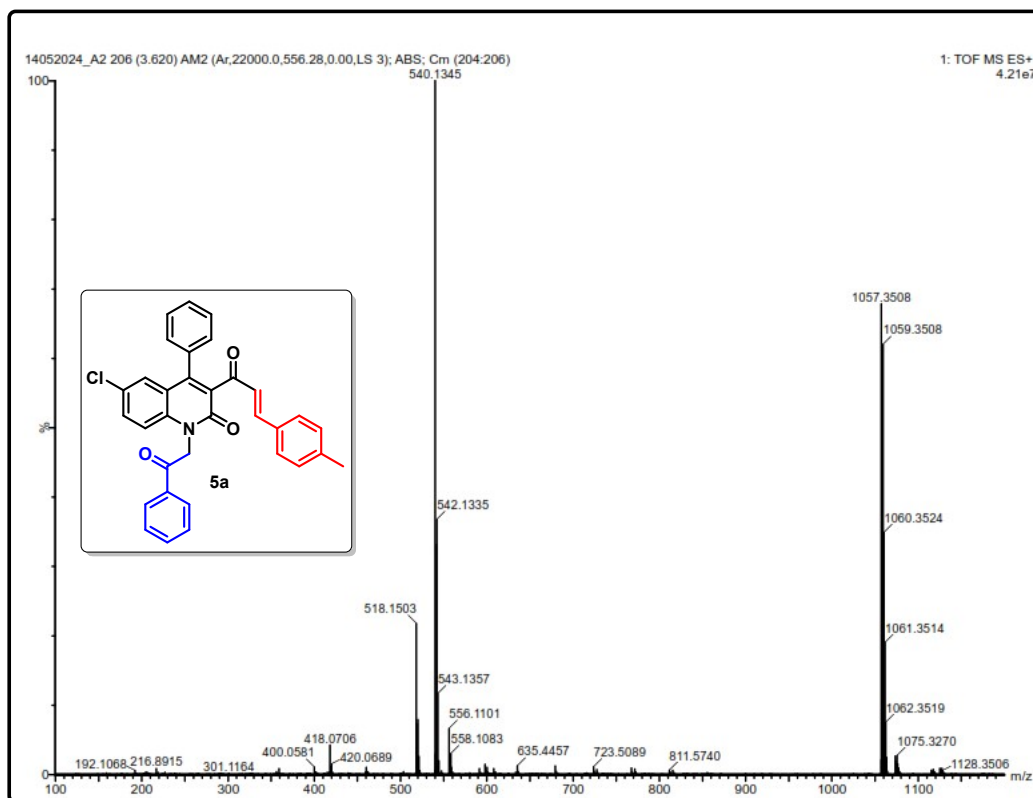
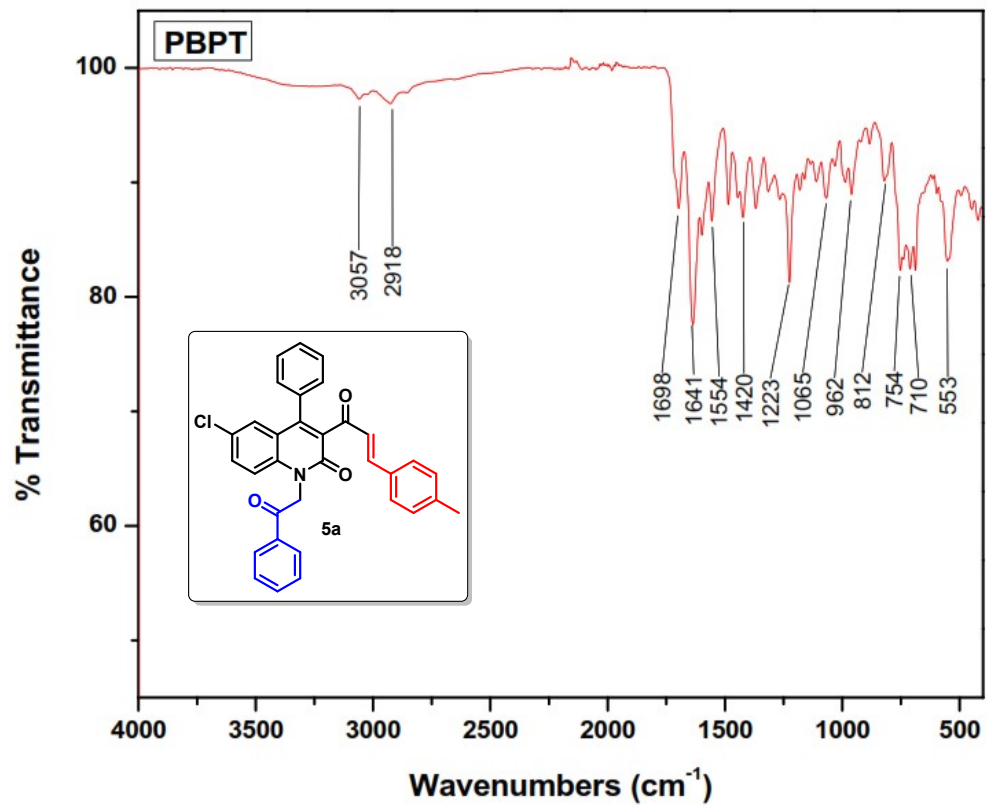
Table S1 Crystal data and structure refinement for compounds **B** (CCDC: 2374871) and **6m** (CCDC: 2388694)

Compound number	B	6m
Empirical formula	C ₂₅ H ₁₈ ClNO ₃	C ₃₉ H _{25.5} Cl ₄ NO _{4.25}
Formula weight	415.85	717.90
Temperature/K	298.00	302.00
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	C2/c
a/Å	16.624(2)	31.3651(17)
b/Å	5.2910(8)	11.6284(6)
c/Å	23.770(3)	20.2570(11)
α/°	90	90
β/°	102.602(5)	97.297(2)
γ/°	90	90
Volume/Å ³	2040.4(5)	7328.4(7)
Z	4	8
ρ _{calc} /cm ³	1.354	1.301
μ/mm ⁻¹	0.214	0.364
F(000)	864.0	2948.0
Crystal size/mm ³	0.173 × 0.168 × 0.144	0.241 × 0.179 × 0.149
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.362 to 56.562	4.054 to 56.61
Index ranges	-21 ≤ h ≤ 22, -6 ≤ k ≤ 7, -31 ≤ l ≤ 31	-31 ≤ h ≤ 41, -15 ≤ k ≤ 15, -27 ≤ l ≤ 27
Reflections collected	28713	71644
Independent reflections	5037 [R _{int} = 0.0512, R _{sigma} = 0.0431]	9085 [R _{int} = 0.0547, R _{sigma} = 0.0393]
Data/restraints/parameters	5037/0/282	9085/0/448
Goodness-of-fit on F ²	1.033	1.013
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0540, wR ₂ = 0.1314	R ₁ = 0.0541, wR ₂ = 0.1272
Final R indexes [all data]	R ₁ = 0.1107, wR ₂ = 0.1742	R ₁ = 0.1141, wR ₂ = 0.1662
Largest diff. peak/hole / e Å ⁻³	0.21/-0.21	0.30/-0.41

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

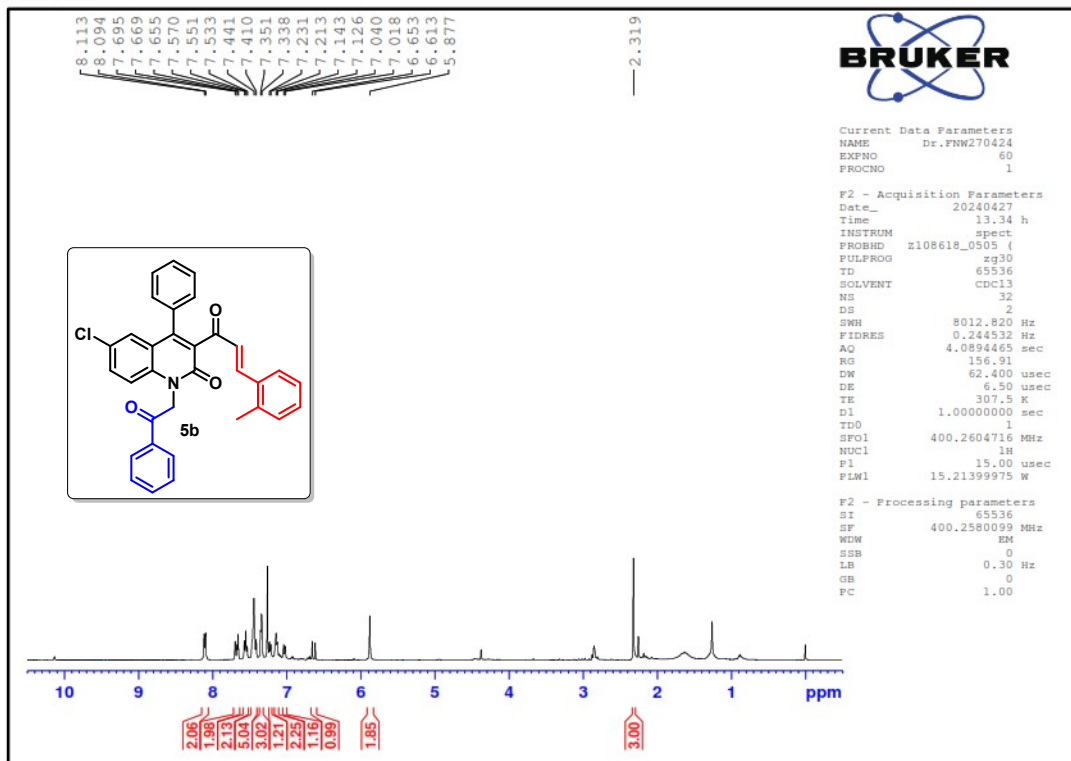


^1H and ^{13}C NMR spectra of compound **5a** in CDCl_3

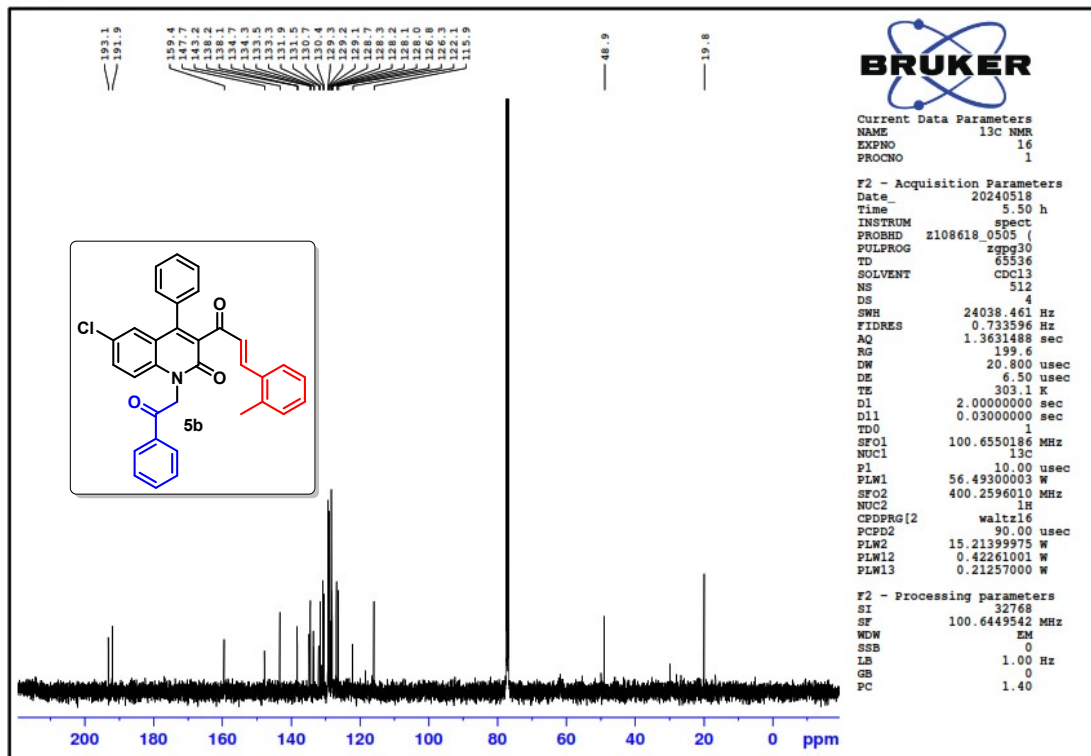


IR and HRMS spectra of compound **5a**

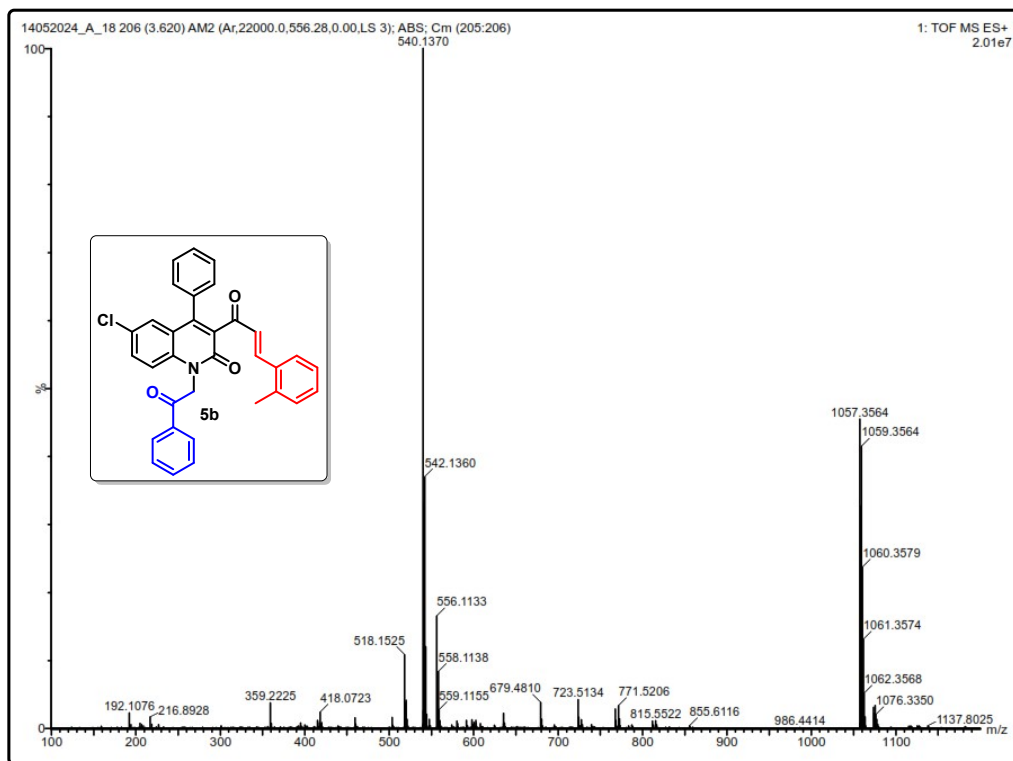
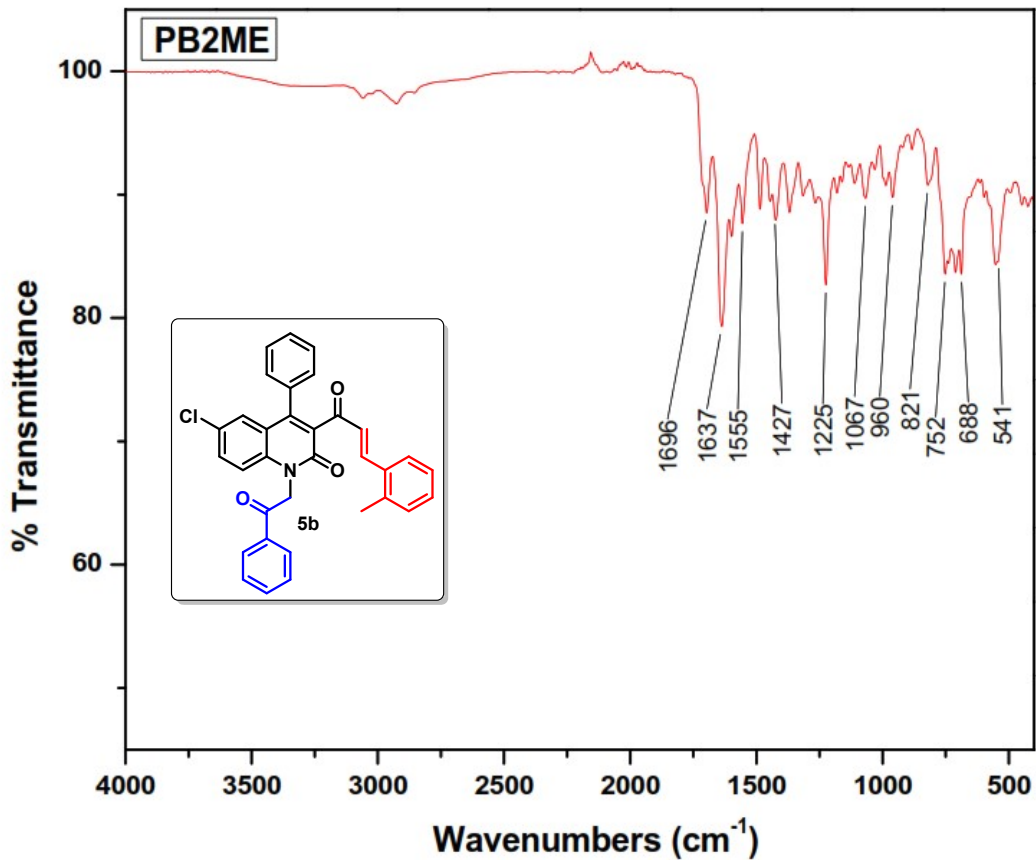
Signature SIF VIT VELLORE
ACPB2ME



Signature SIF VIT VELLORE
PB2ME

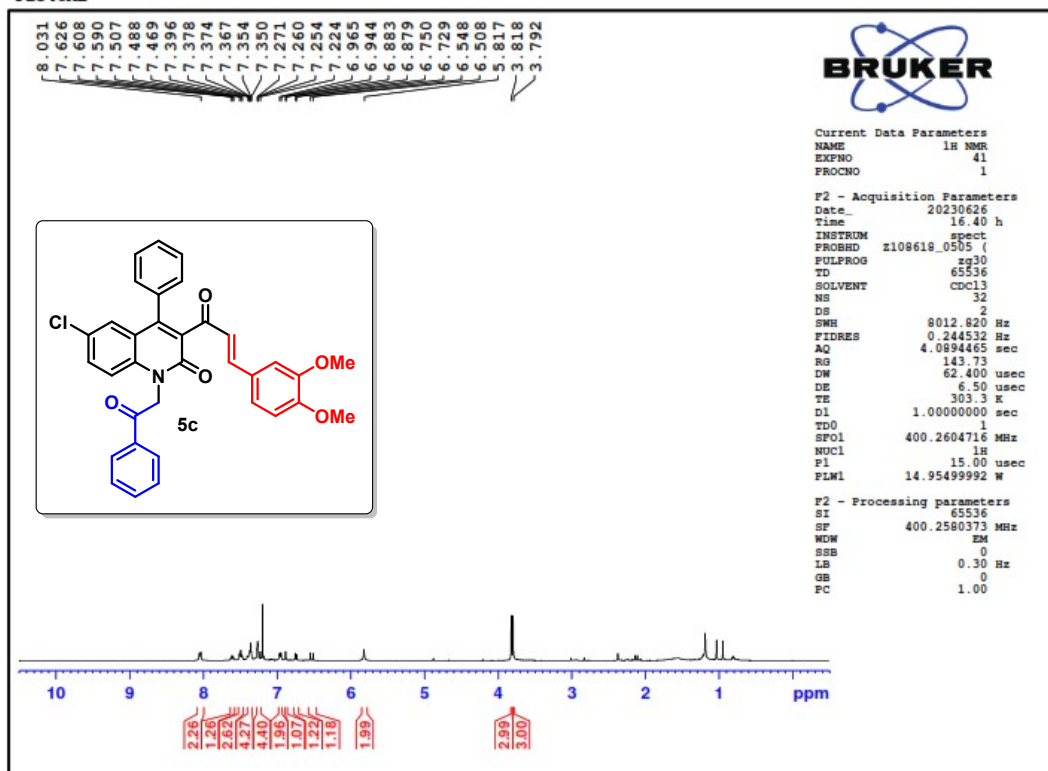


¹H and ¹³C NMR spectra of compound **5b** in CDCl₃

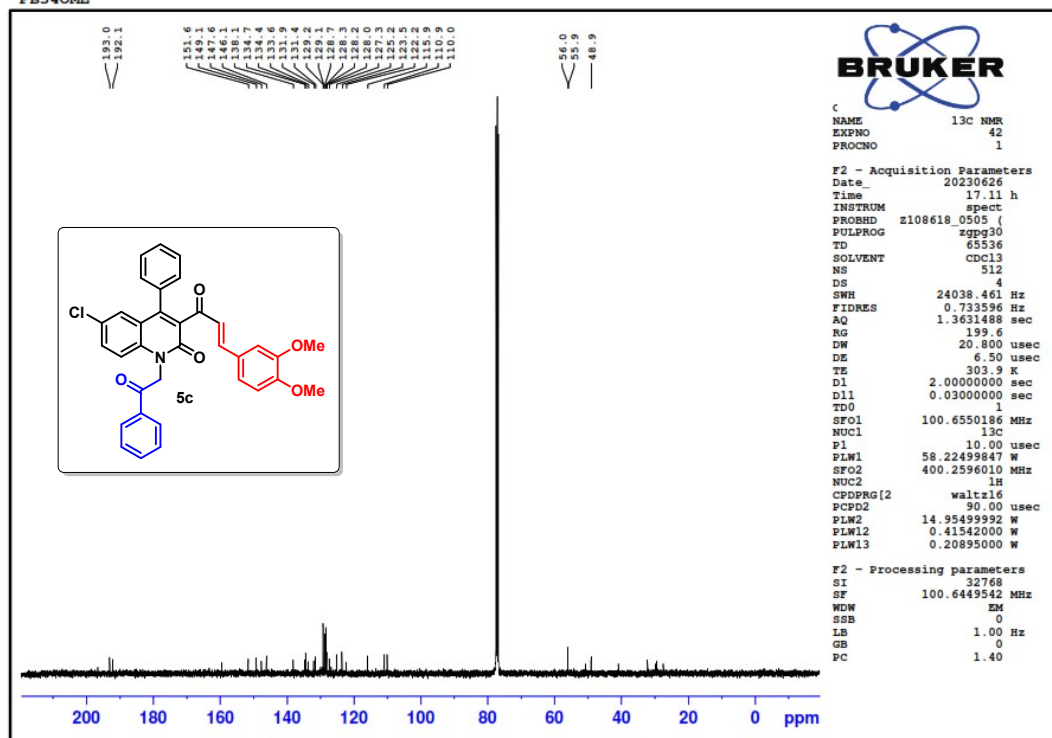


IR and HRMS spectra of compound **5b**

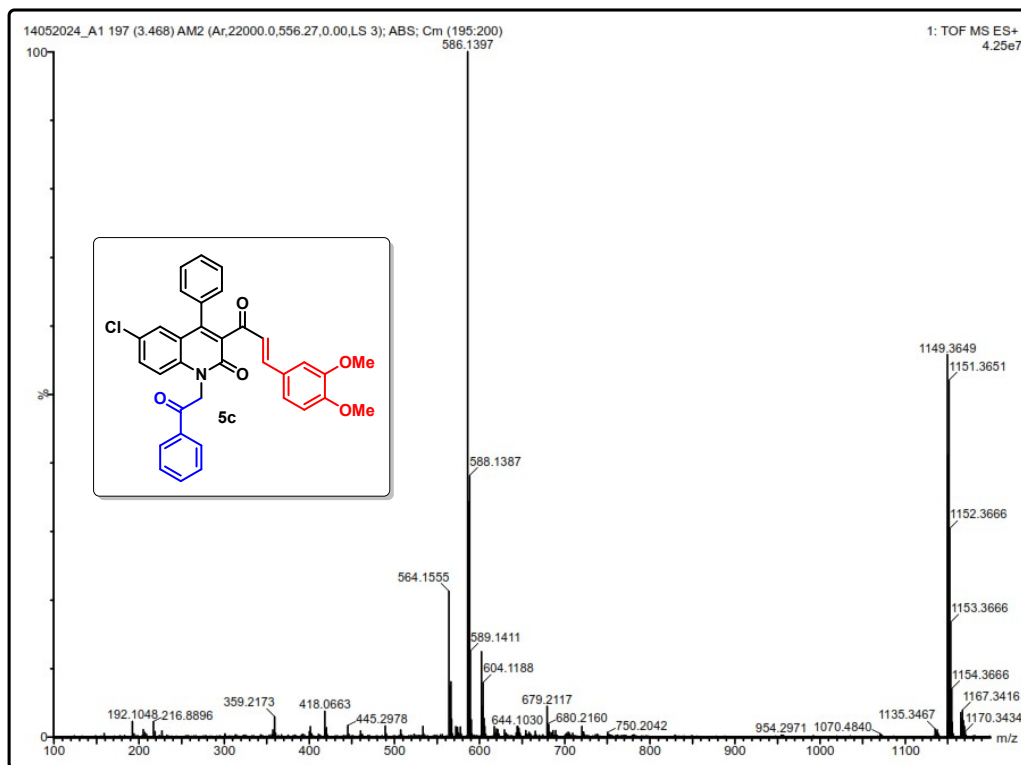
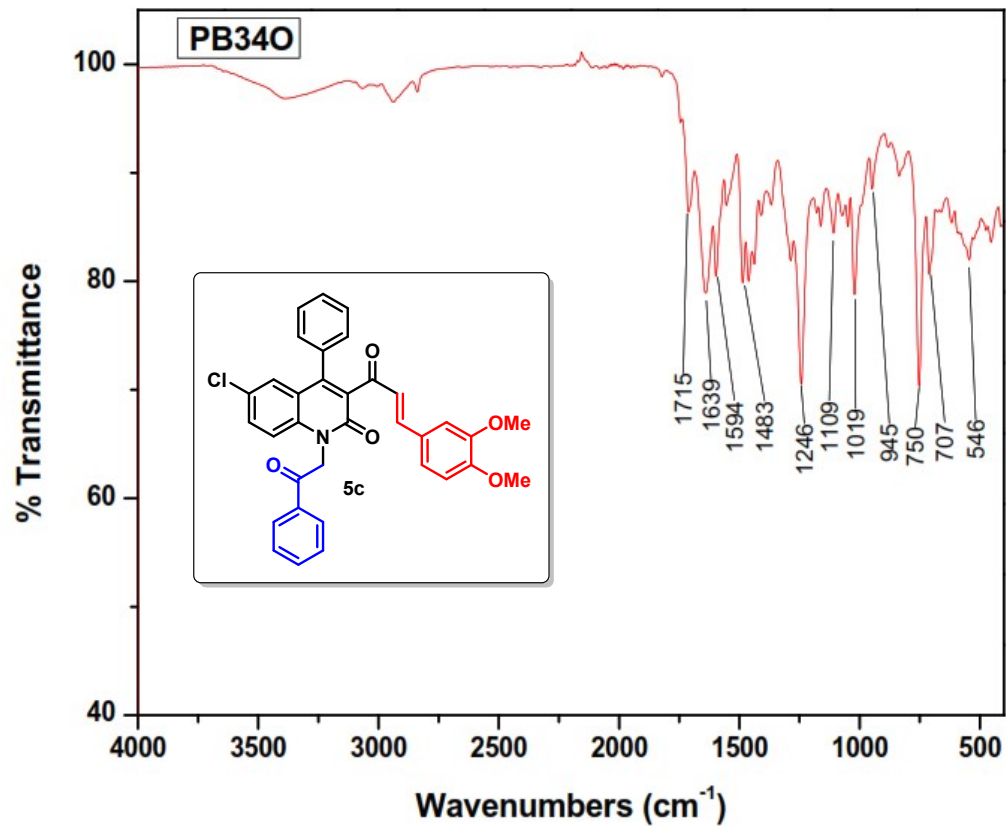
Signature SIF VIT VELLORE
PB340ME



Signature SIF VIT VELLORE
PB340ME

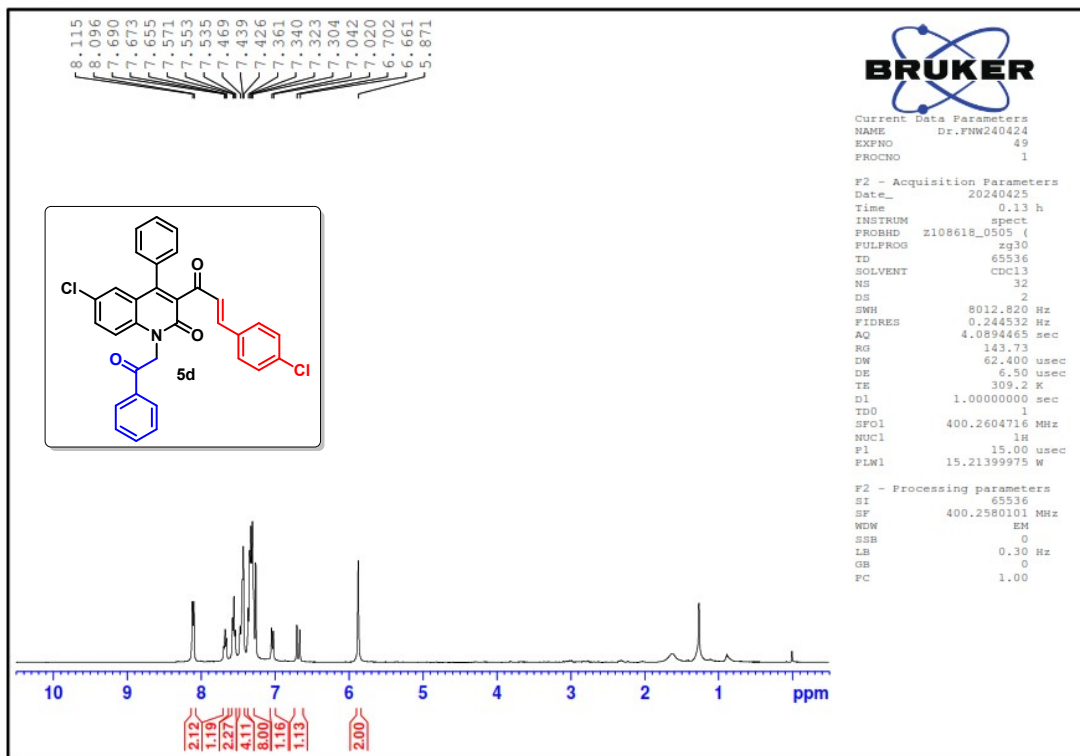


¹H and ¹³C NMR spectra of compound **5c** in CDCl₃

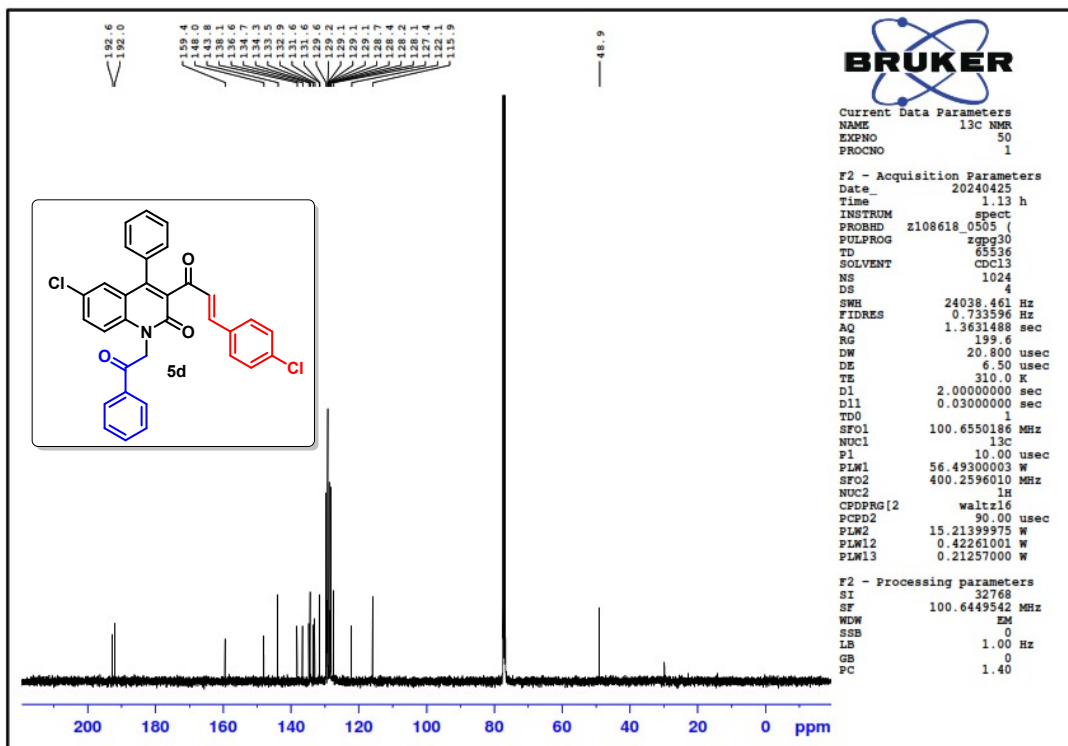


IR and HRMS spectra of compound **5c**

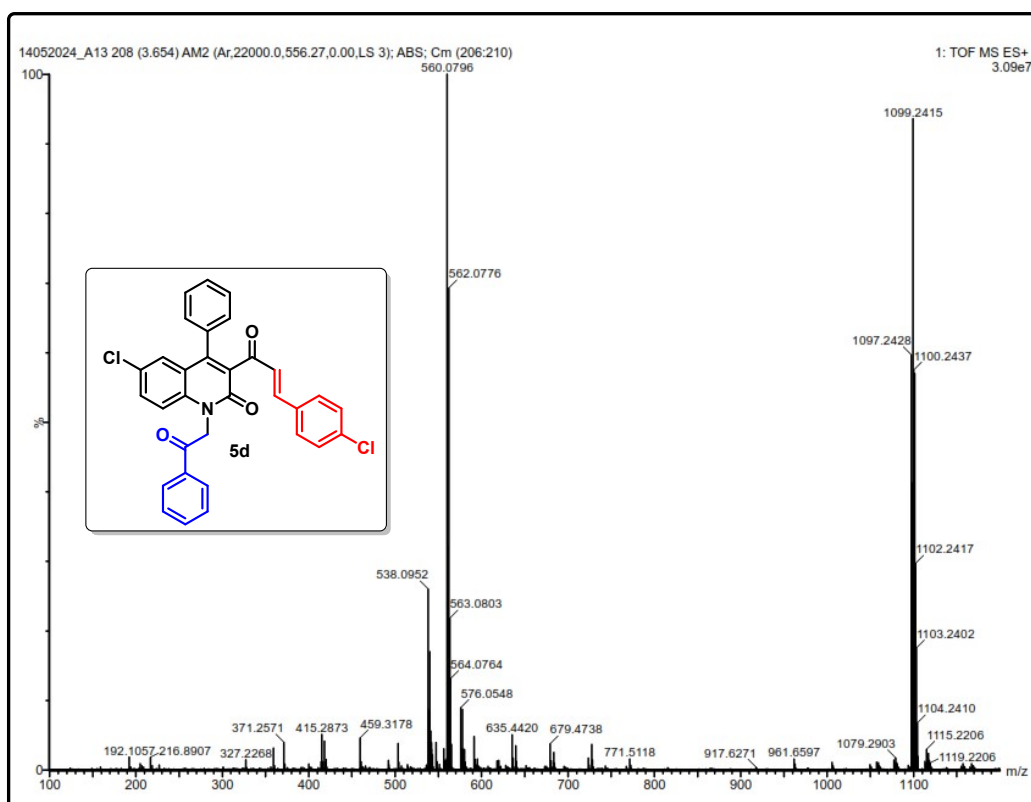
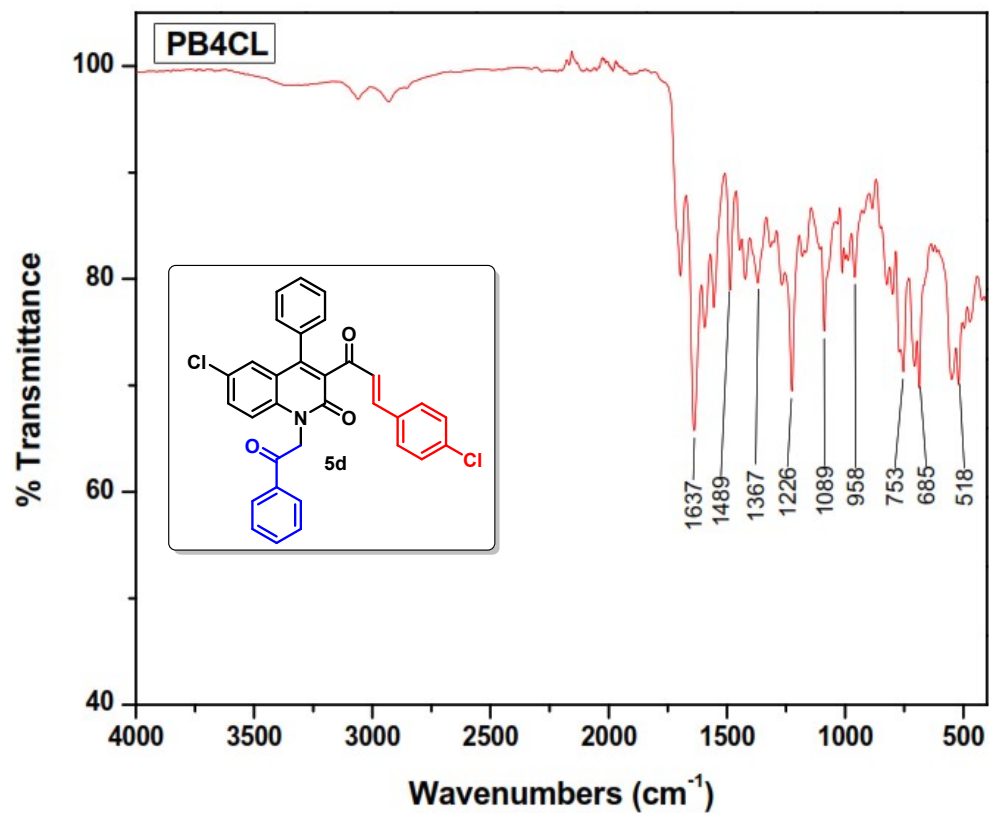
Signature SIF VIT VELLORE
ACPB4CL



Signature SIF VIT VELLORE
AC4CL

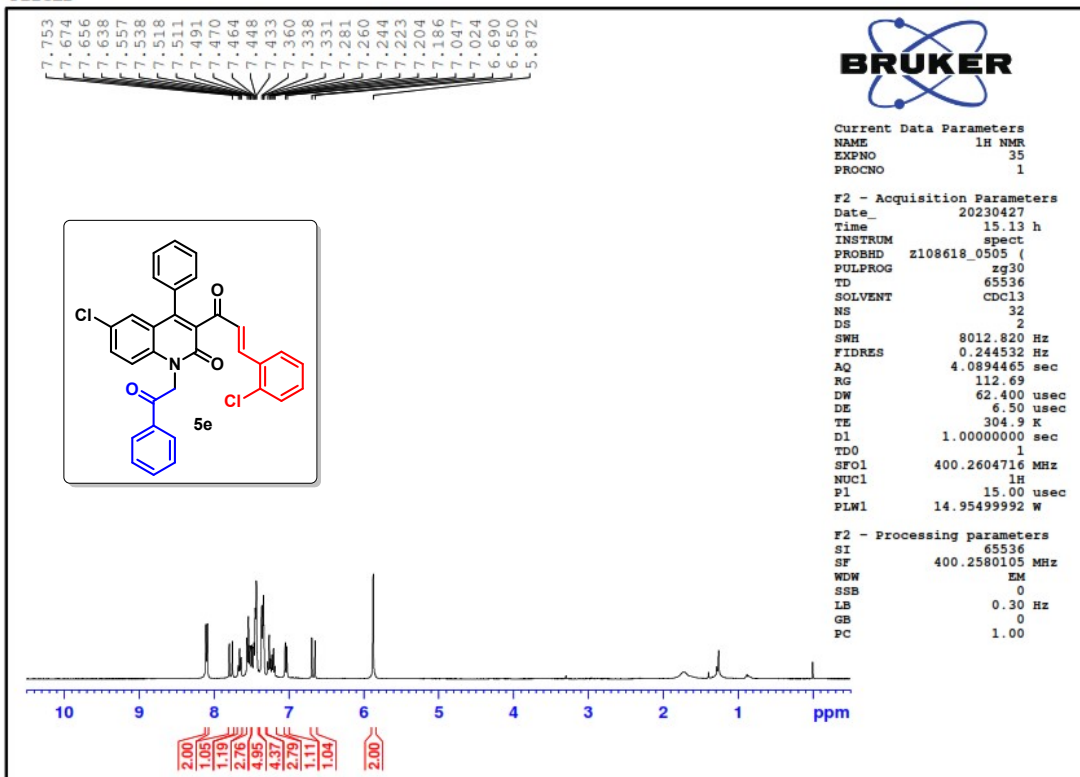


¹H and ¹³C NMR spectra of compound 5d in CDCl₃

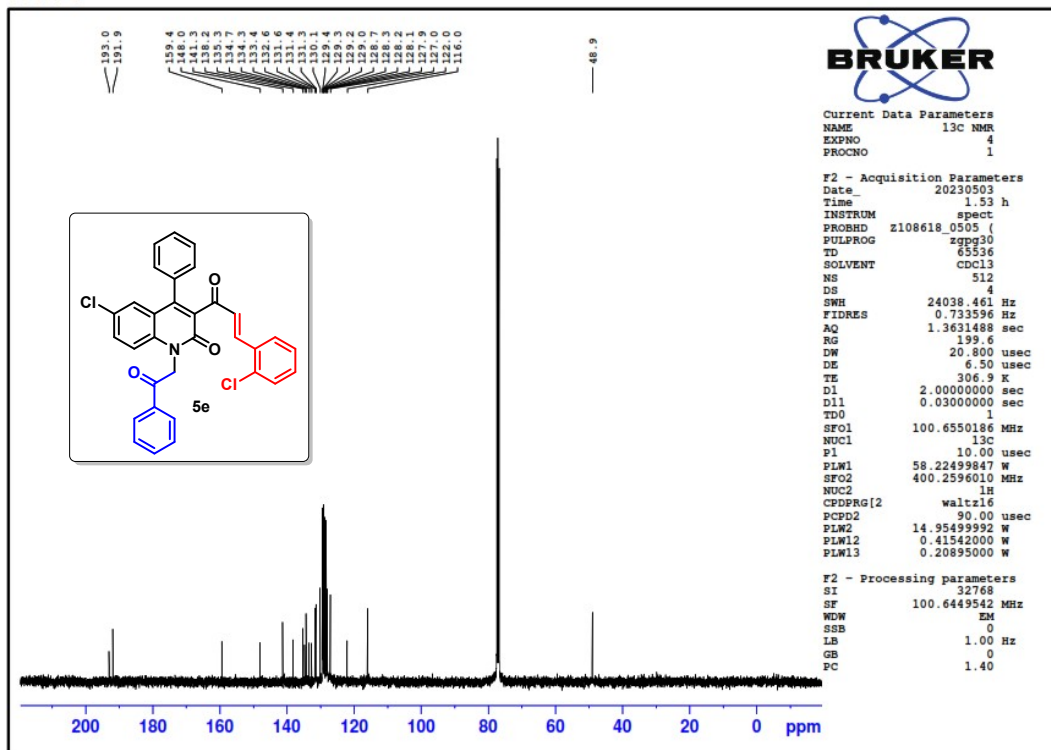


IR and HRMS spectra of compound **5d**

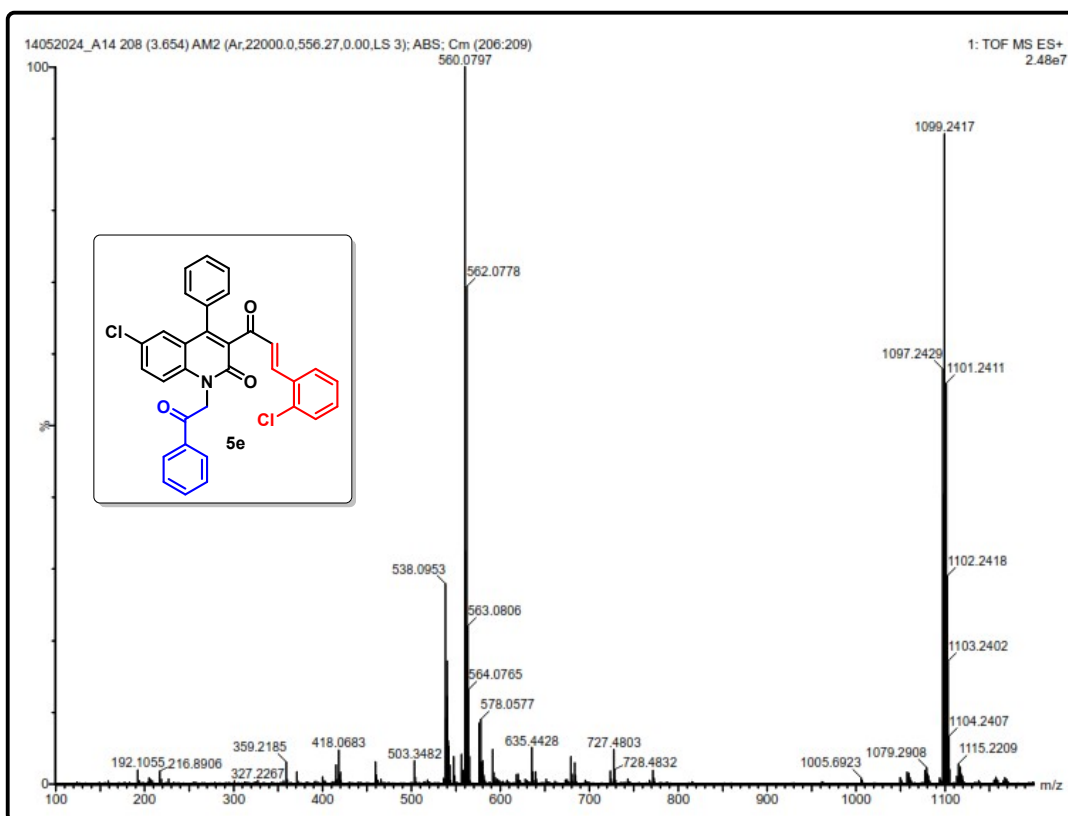
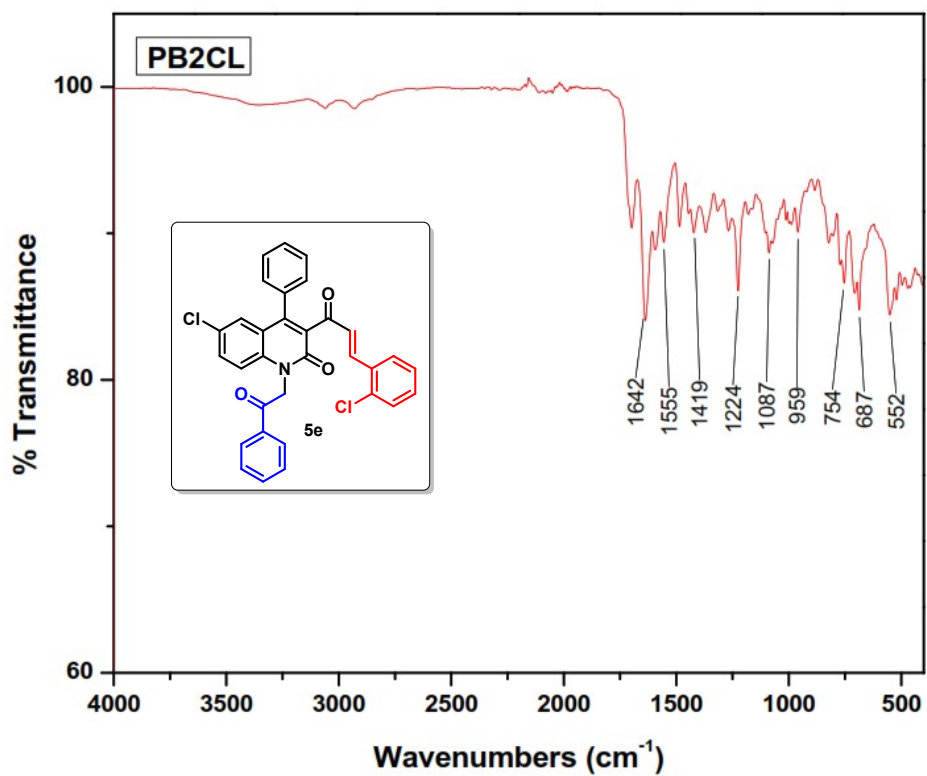
Signature SIF VIT VELLORE
PB2CL2



Signature SIF VIT VELLORE
PB2CL-2

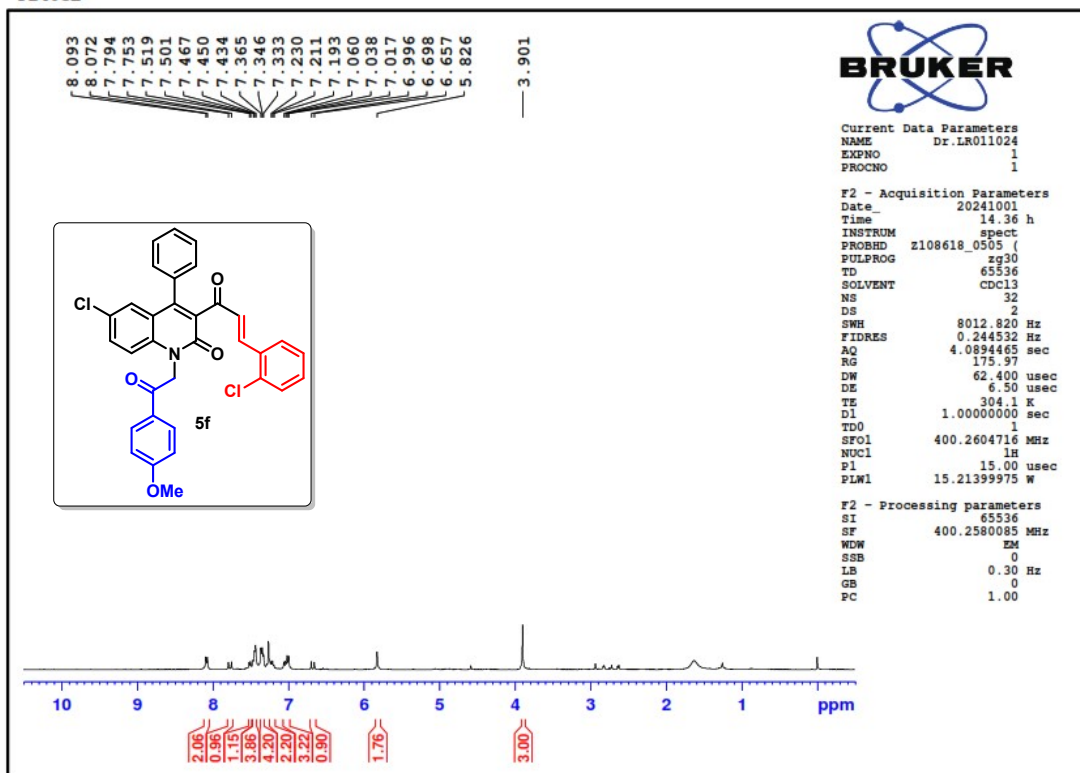


¹H and ¹³C NMR spectra of compound **5e** in CDCl₃

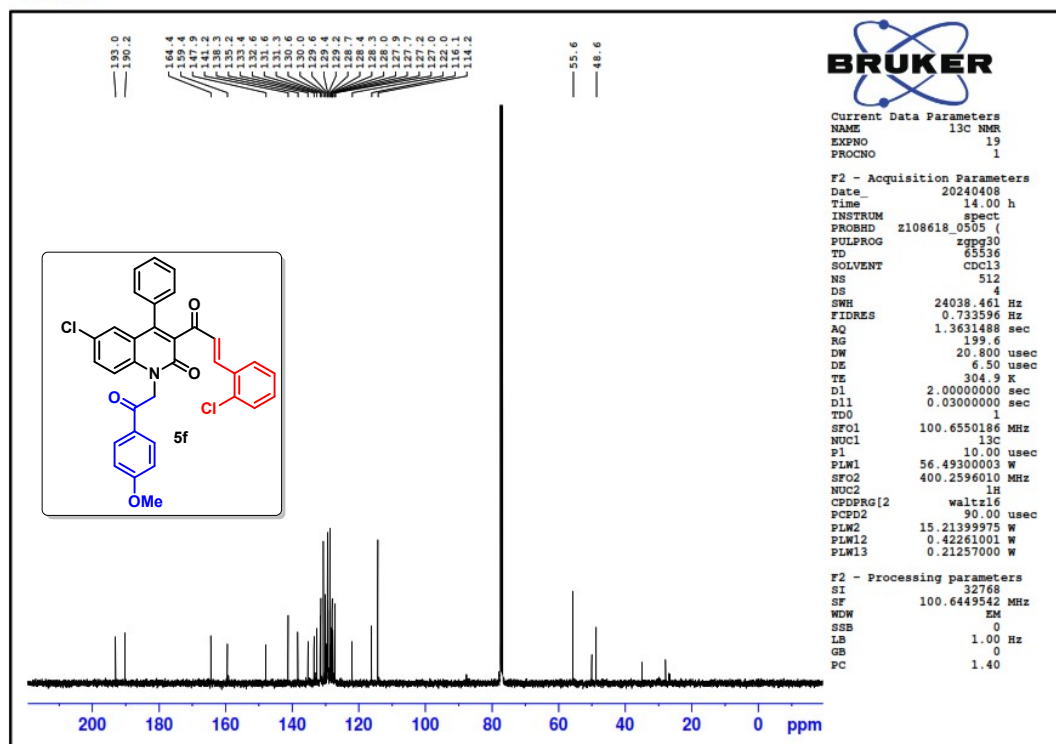


IR and HRMS spectra of compound **5e**

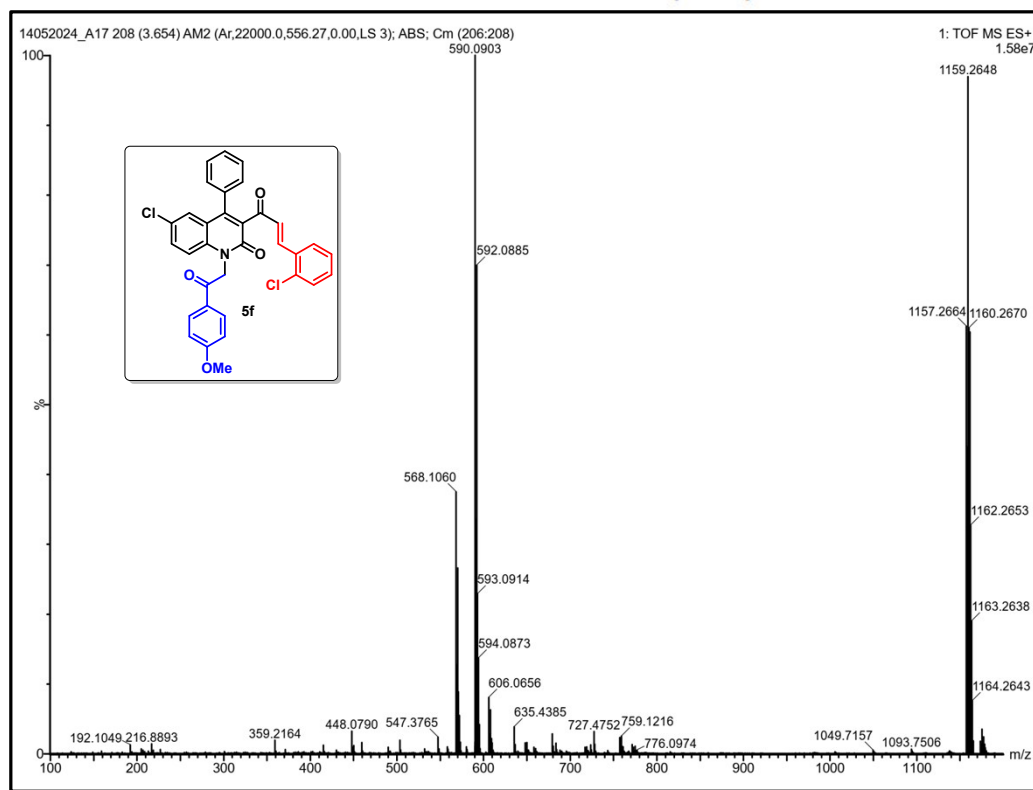
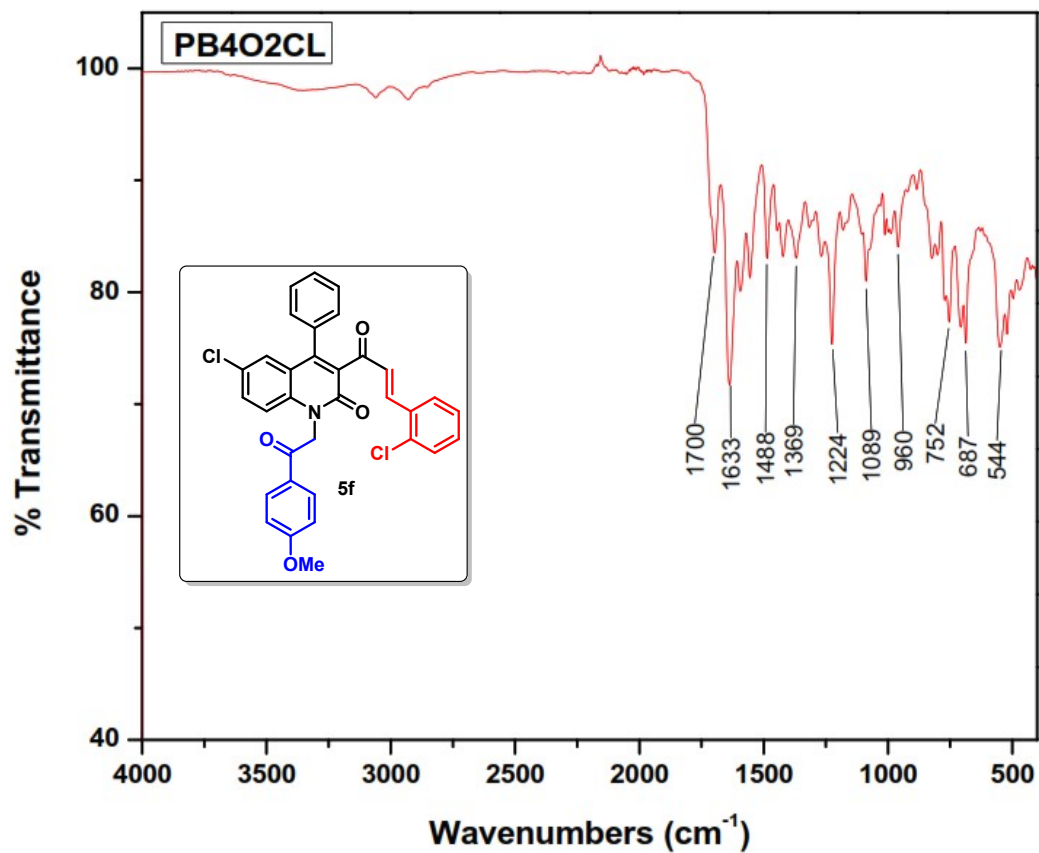
Signature SIF VIT VELLORE
PB40CL



Signature SIF VIT VELLORE
PB402CL

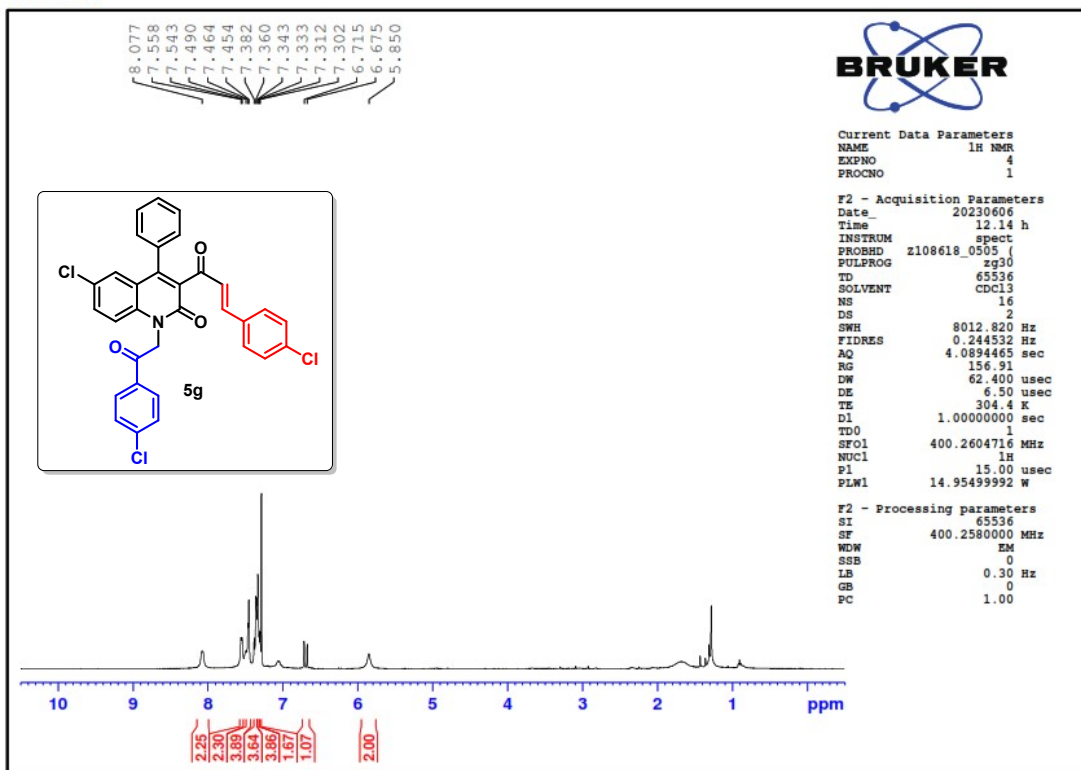


¹H and ¹³C NMR spectra of compound **5f** in CDCl₃

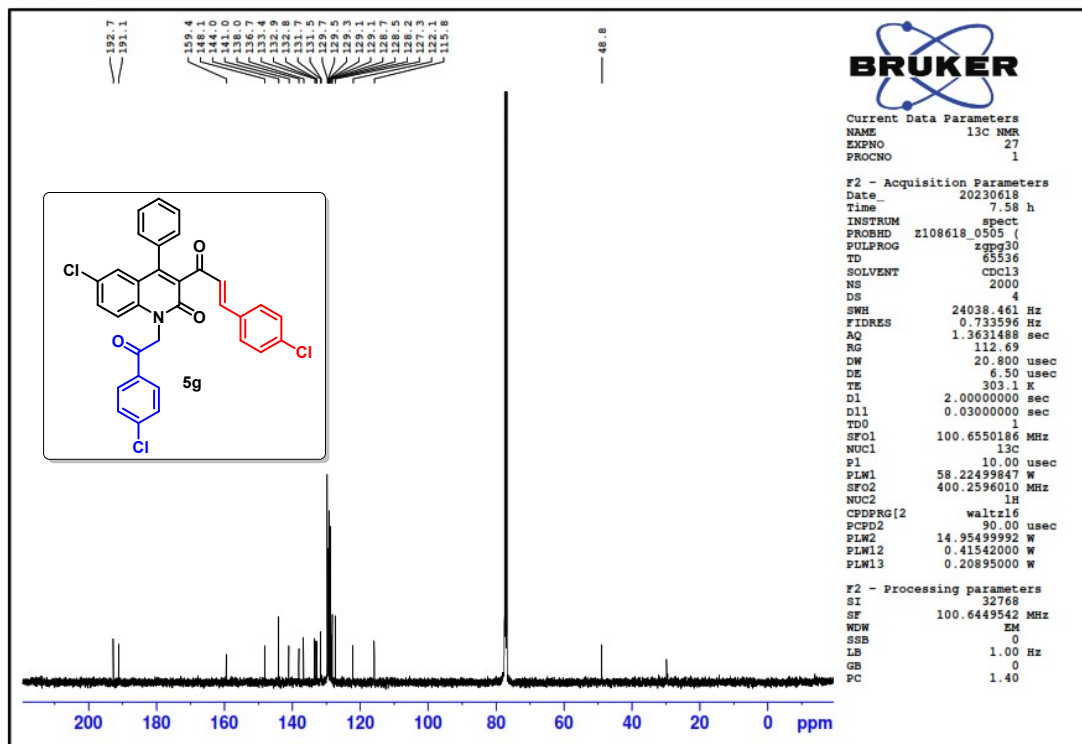


IR and HRMS spectra of compound **5f**

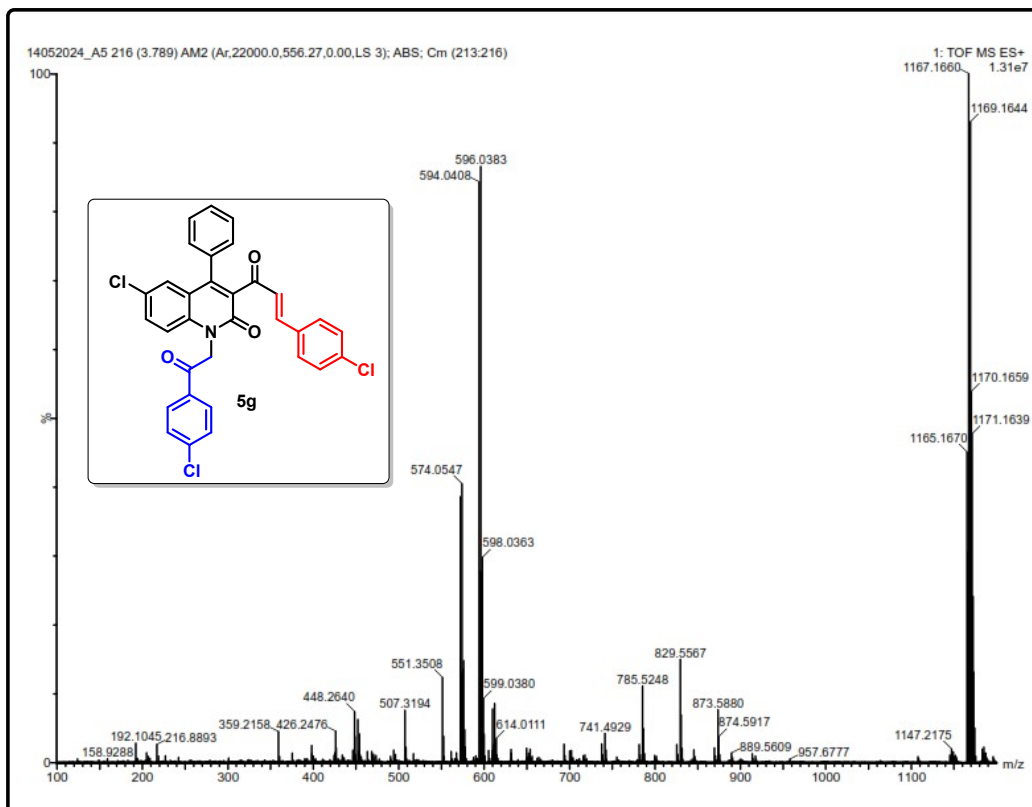
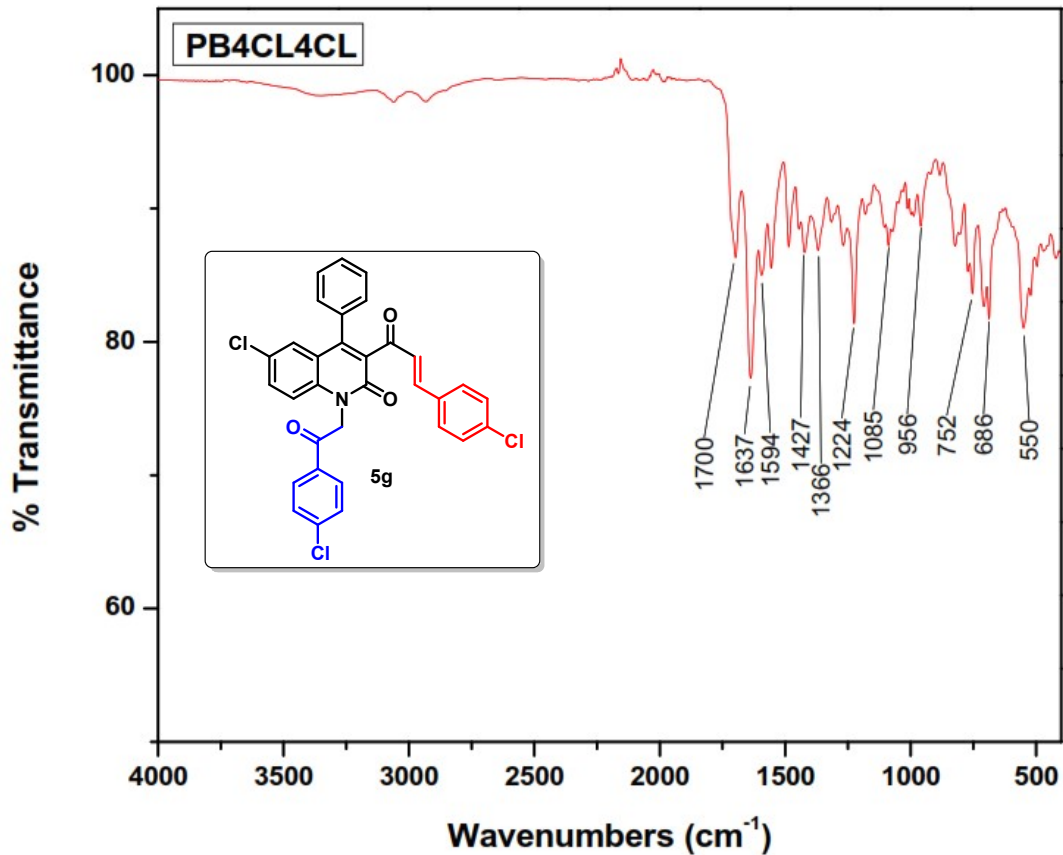
PB4CL4CL



Signature SIF VIT VELLORE
PB4CL4CL

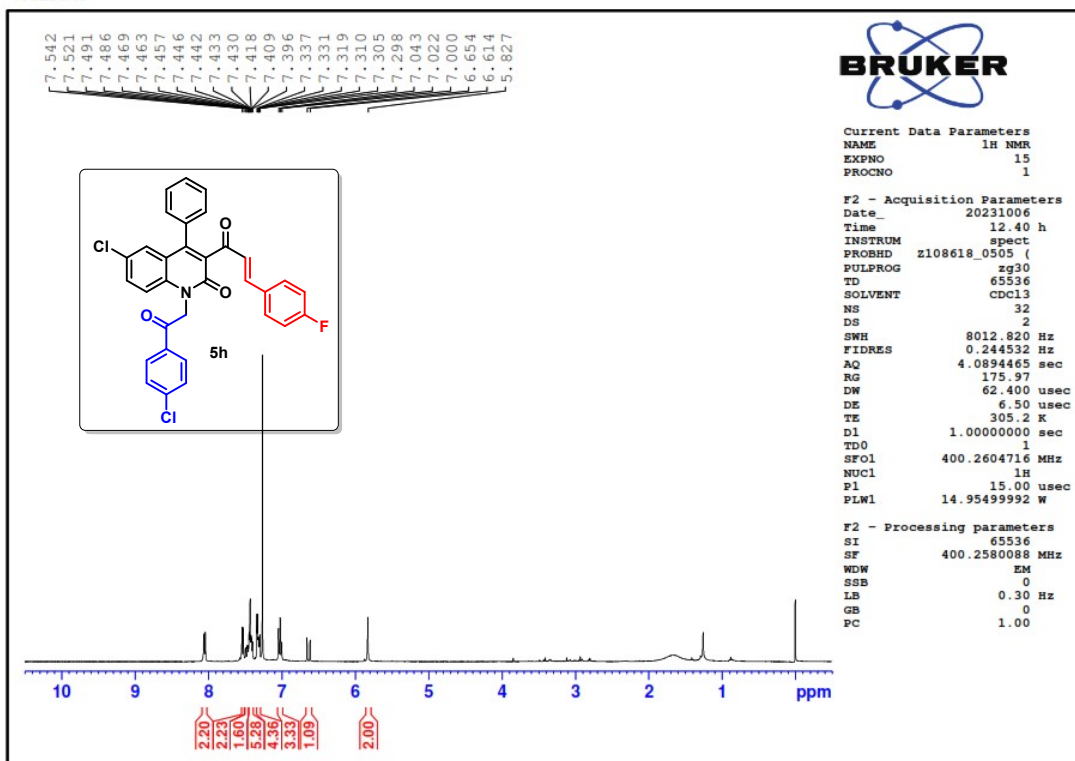


¹H and ¹³C NMR spectra of compound 5g in CDCl₃

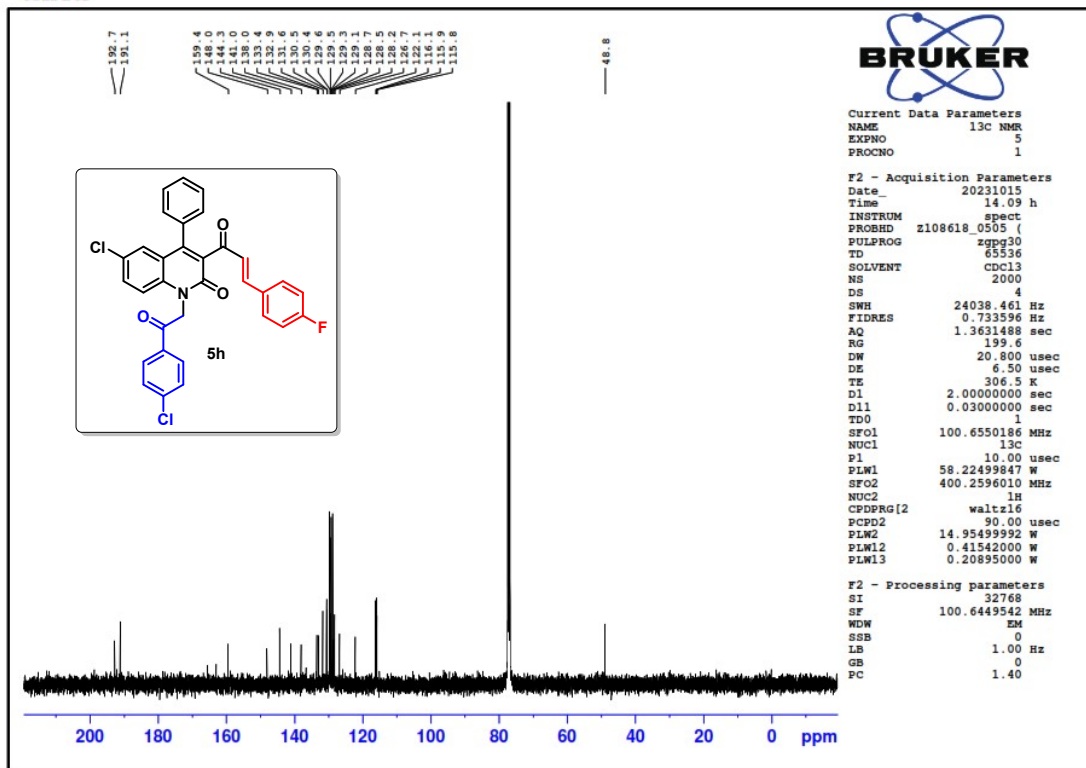


IR and HRMS spectra of compound **5g**

Signature SIF VIT VELLORE
4CLPB4F

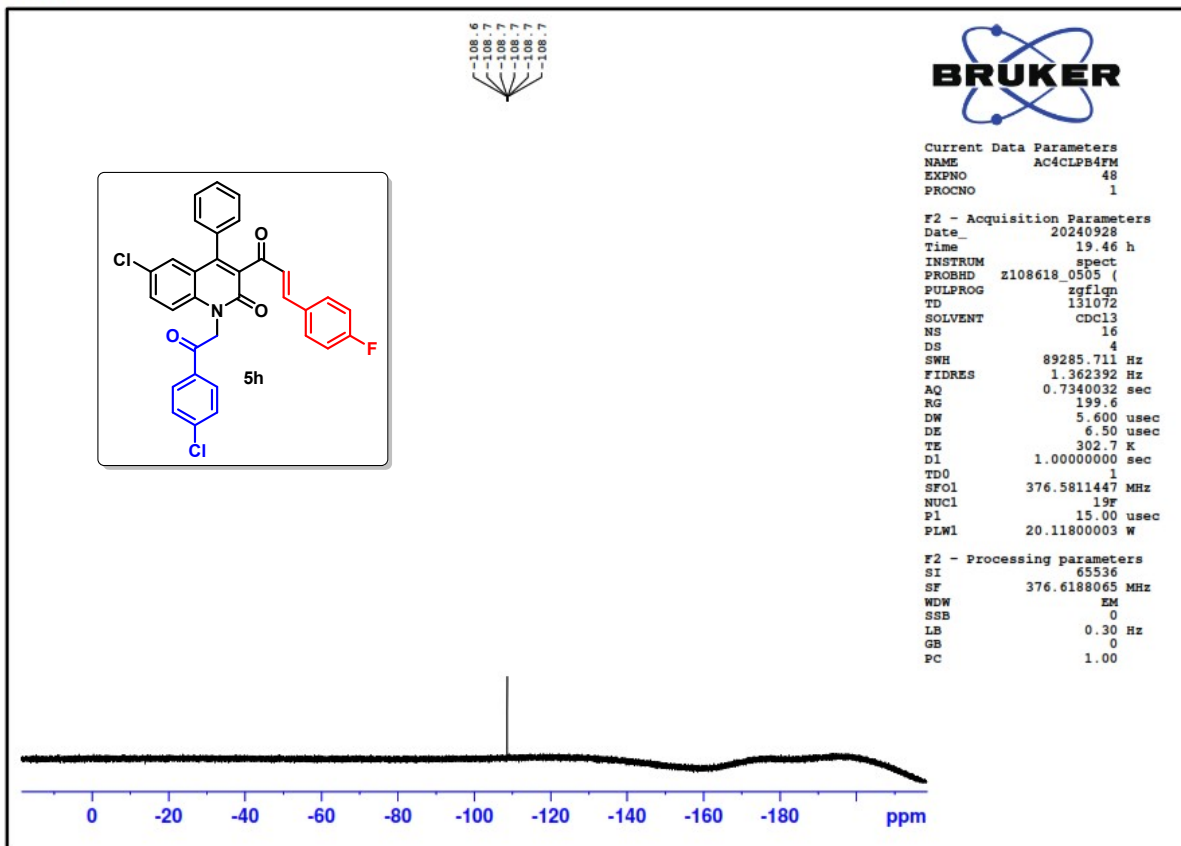


Signature SIF VIT VELLORE
4C1PB4F

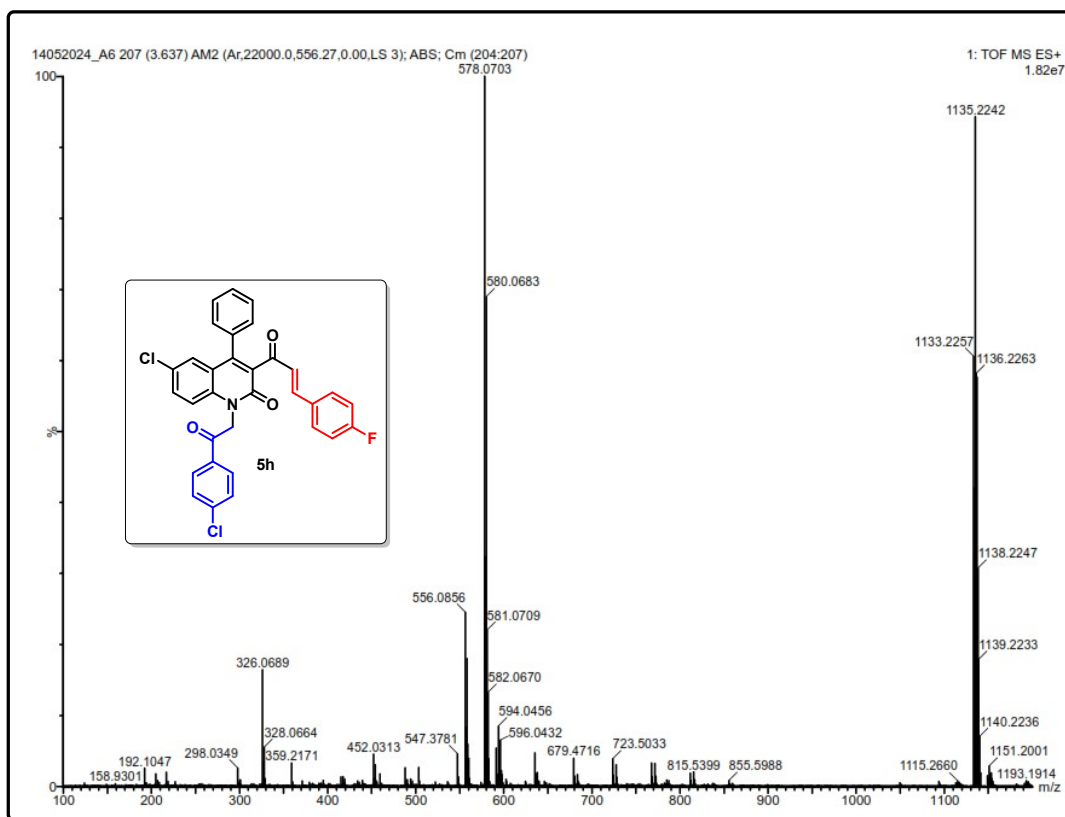
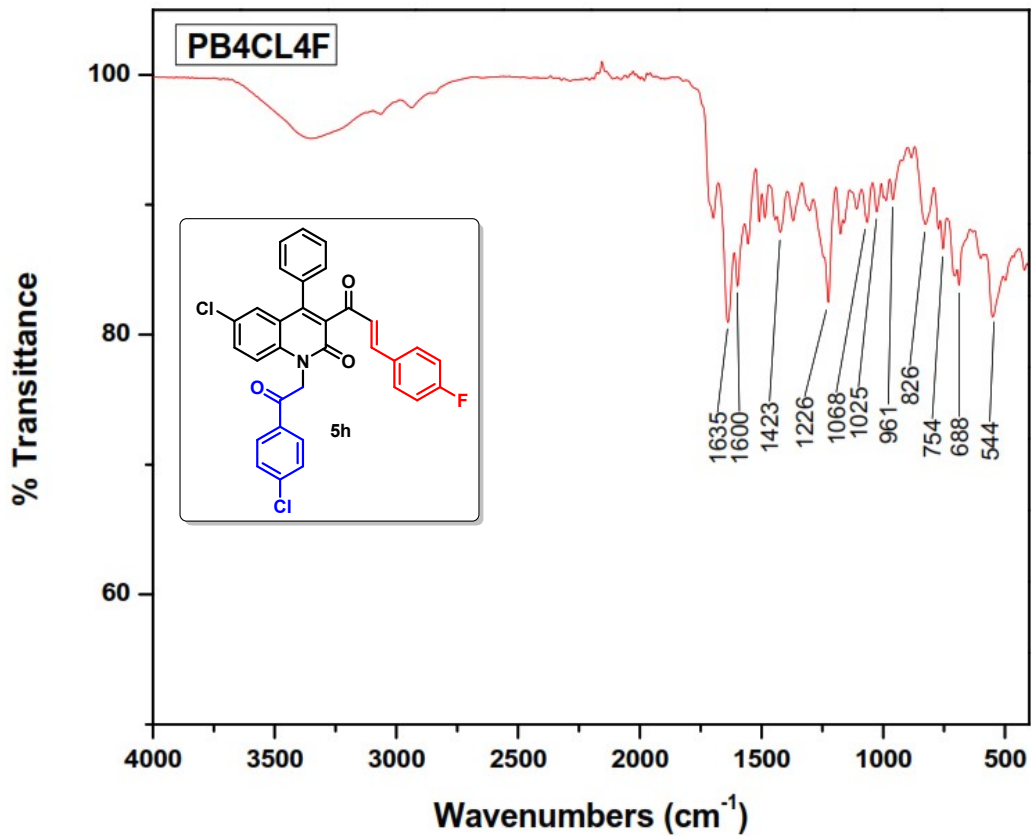


^1H and ^{13}C NMR spectra of compound **5h** in CDCl_3

Signature SIF VIT VELLORE
4CLPB4

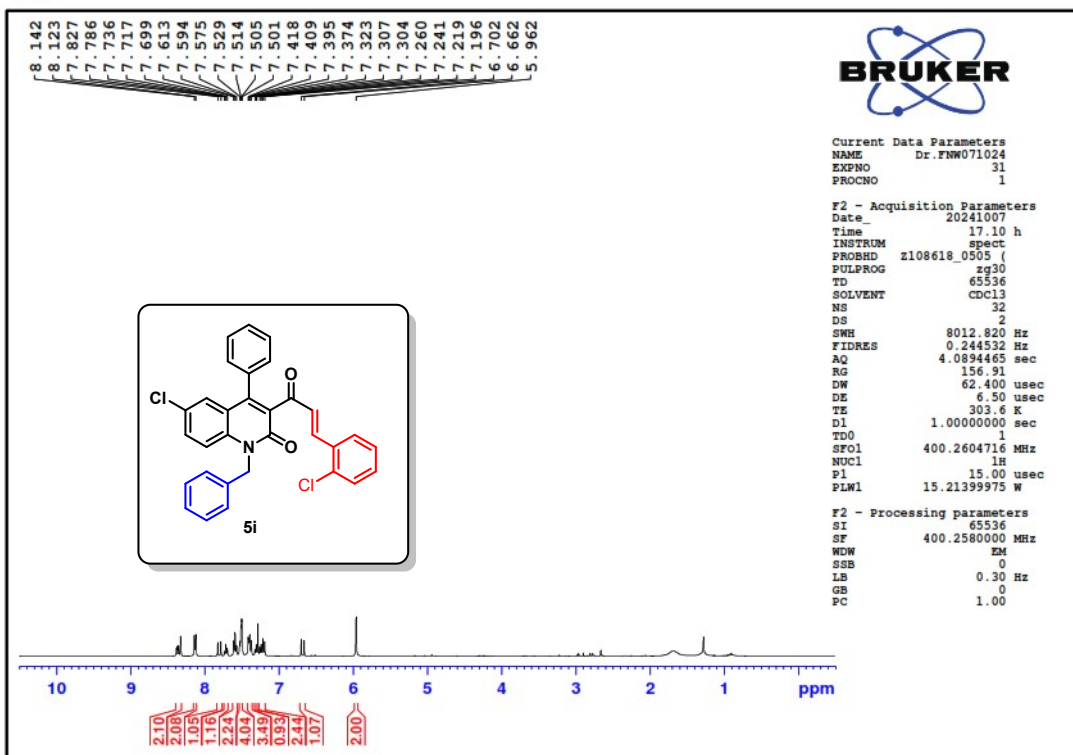


^{19}F spectra of compound **5h**

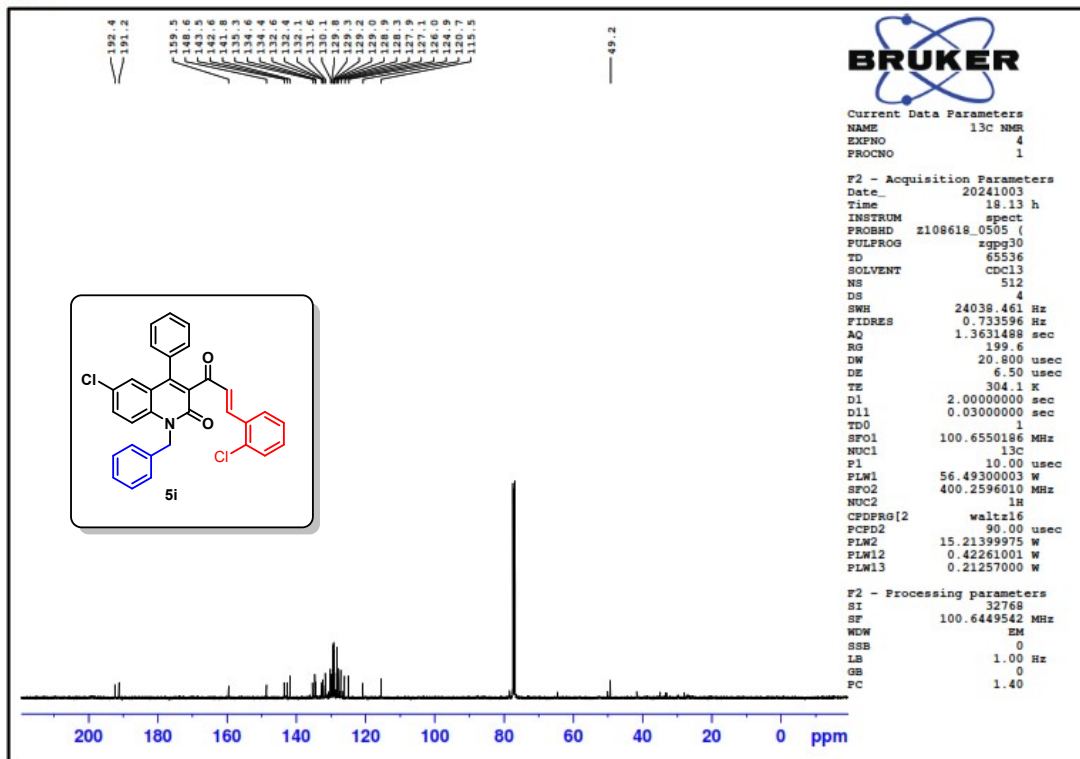


IR and HRMS spectra of compound **5h**

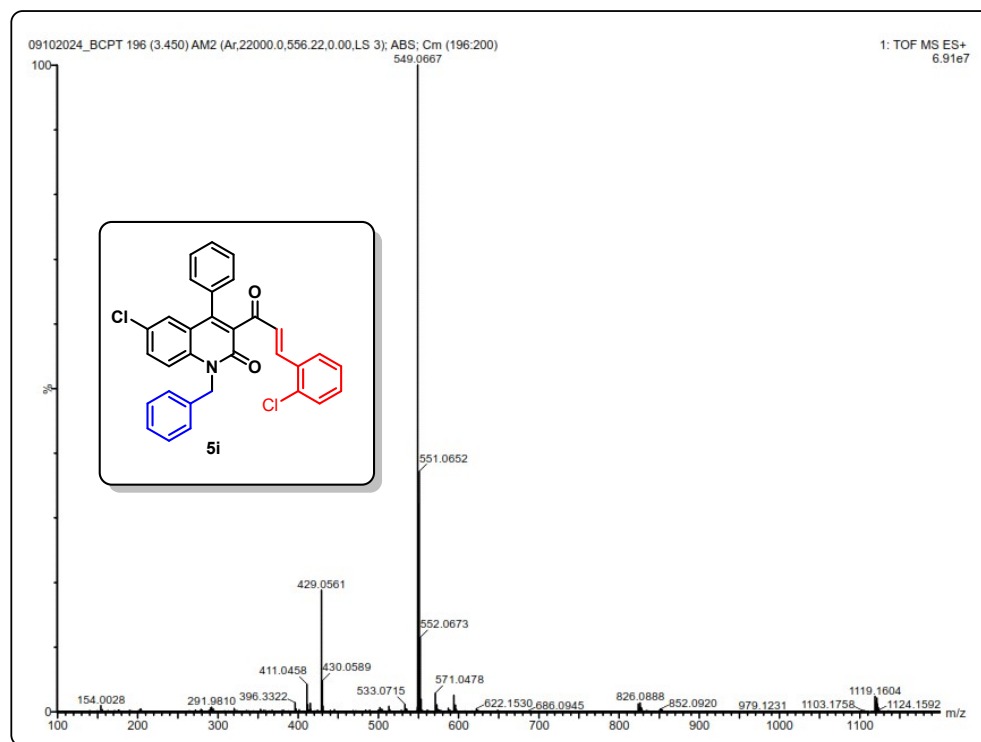
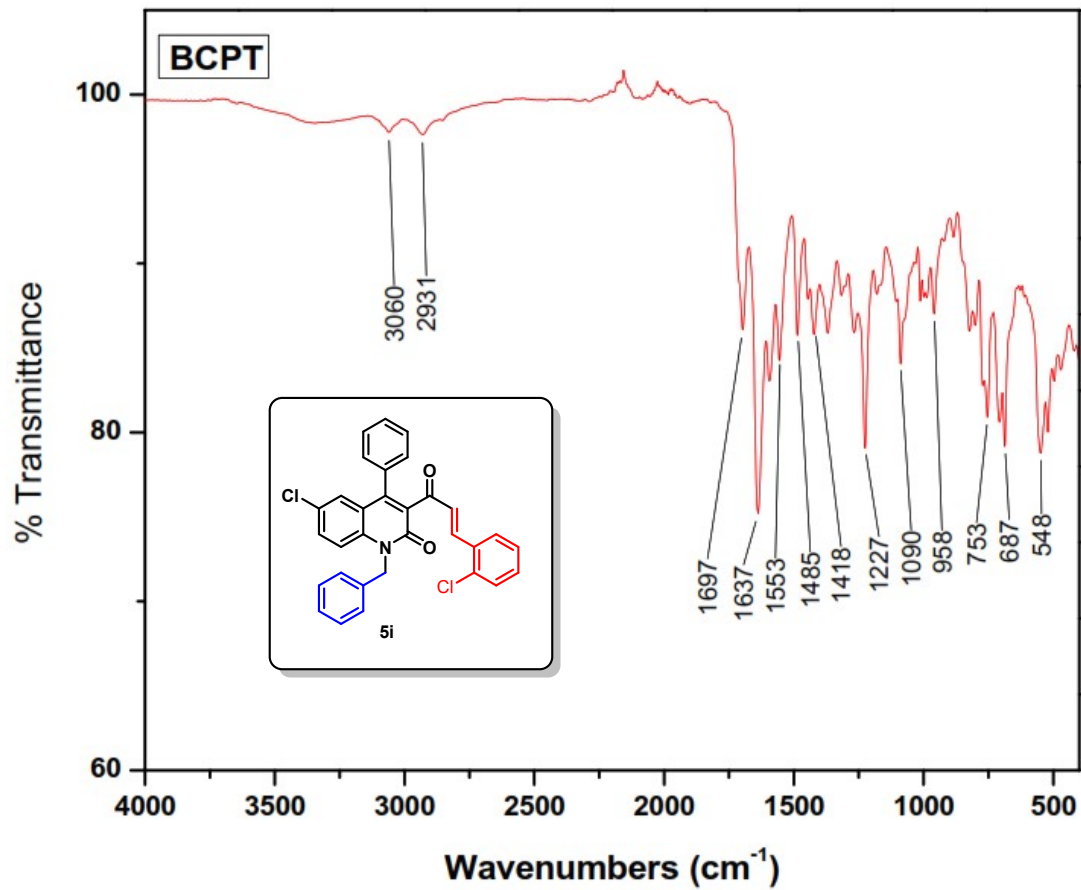
Signature SIF VIT VELLORE
BCPT



Signature SIF VIT VELLORE
BCPT

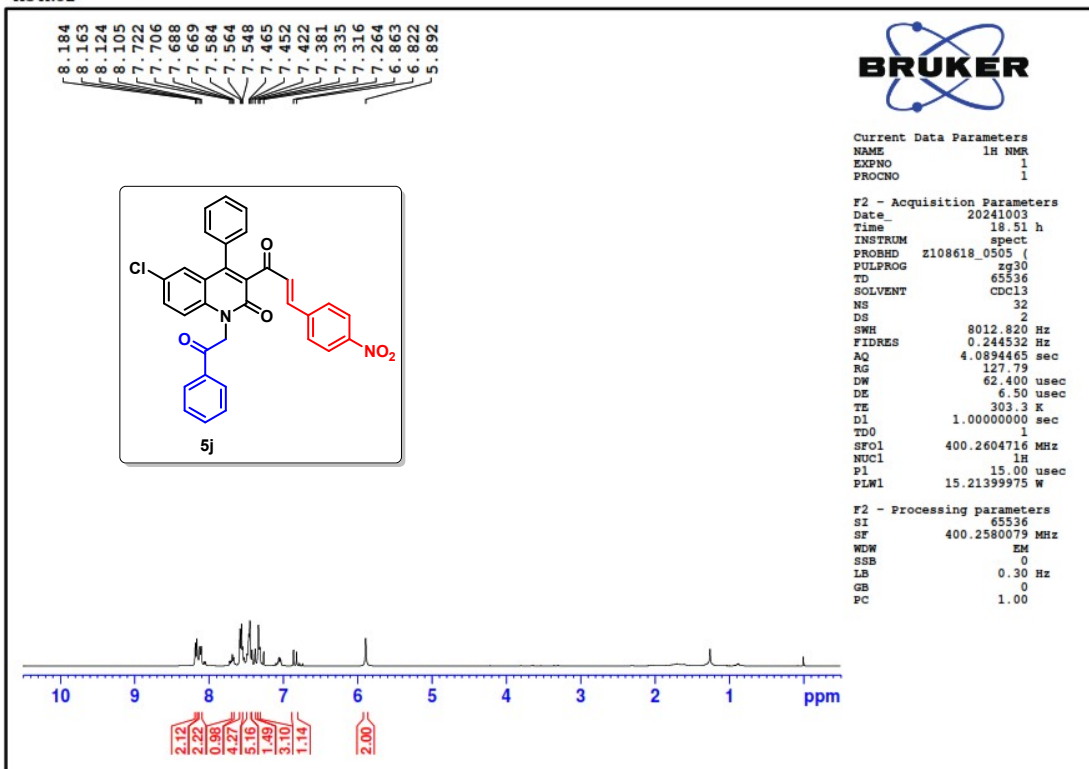


^1H and ^{13}C NMR spectra of compound **5i** in CDCl_3

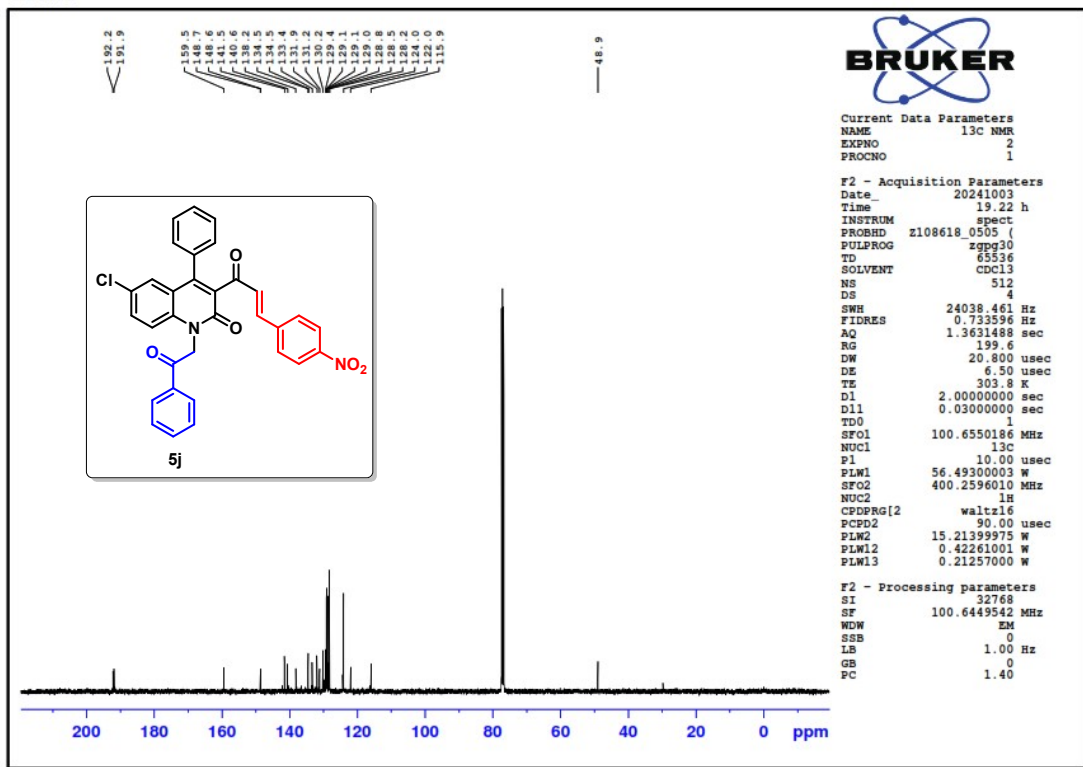


IR and HRMS spectra of compound **5i**

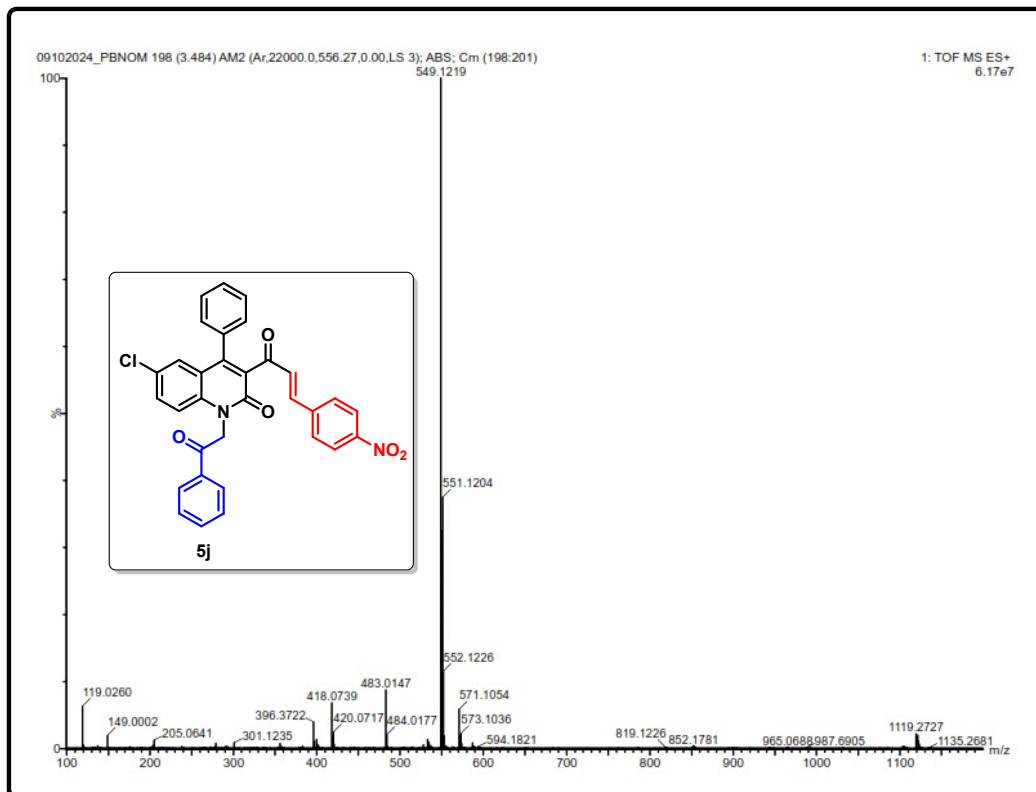
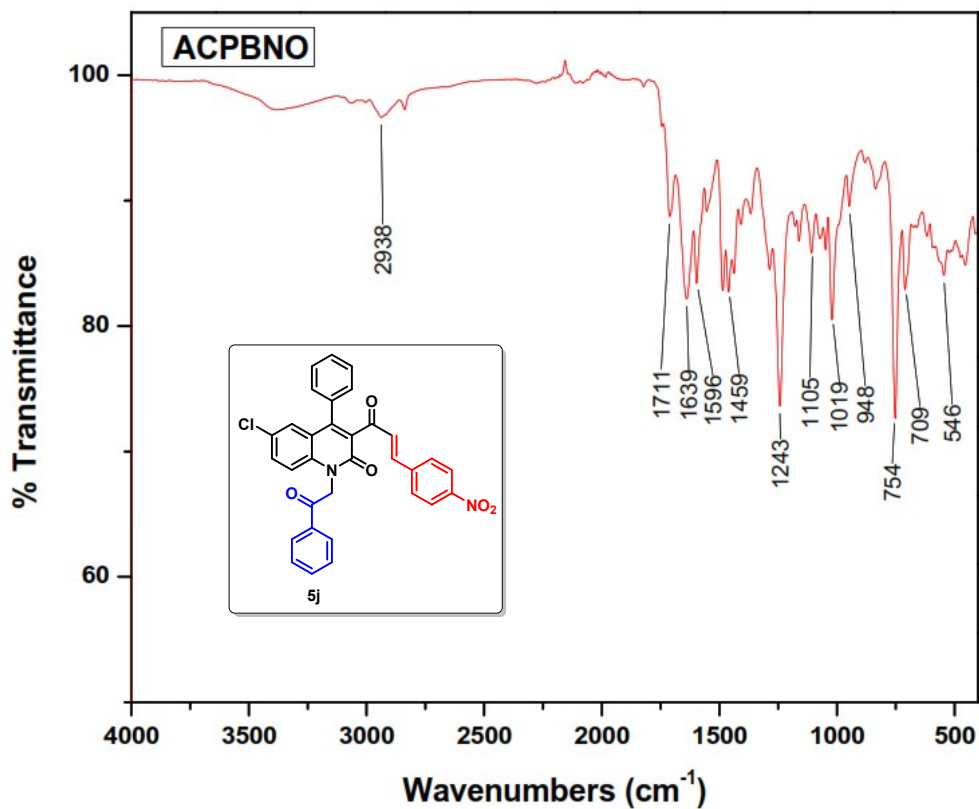
Signature SIF VIT VELLORE
AC4NO2



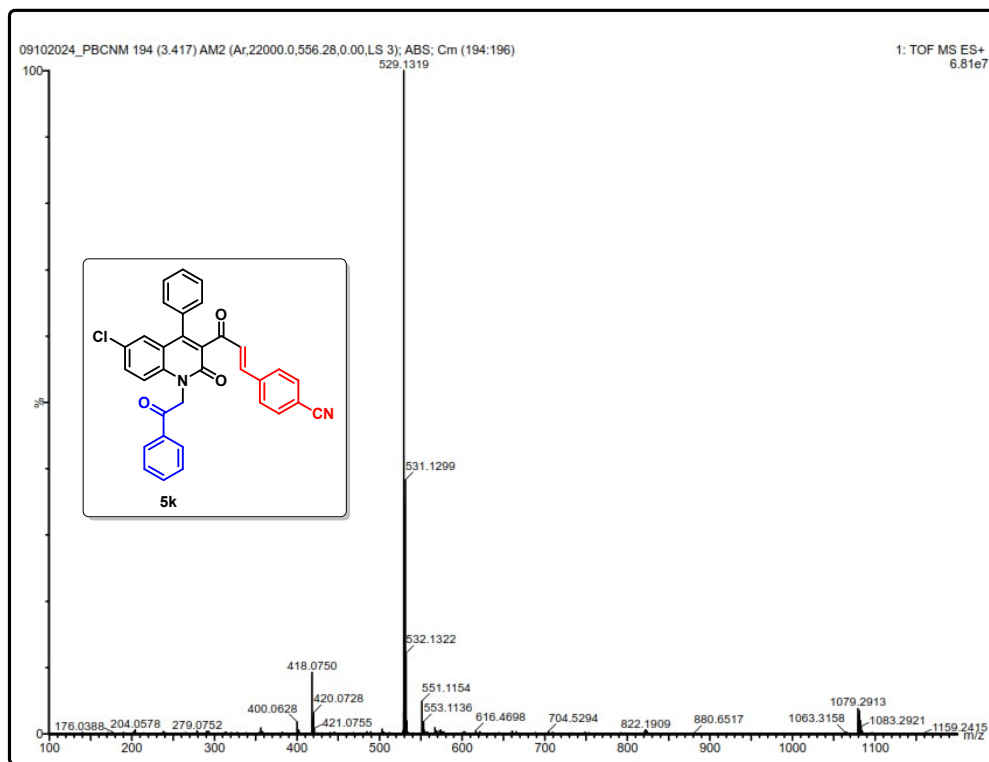
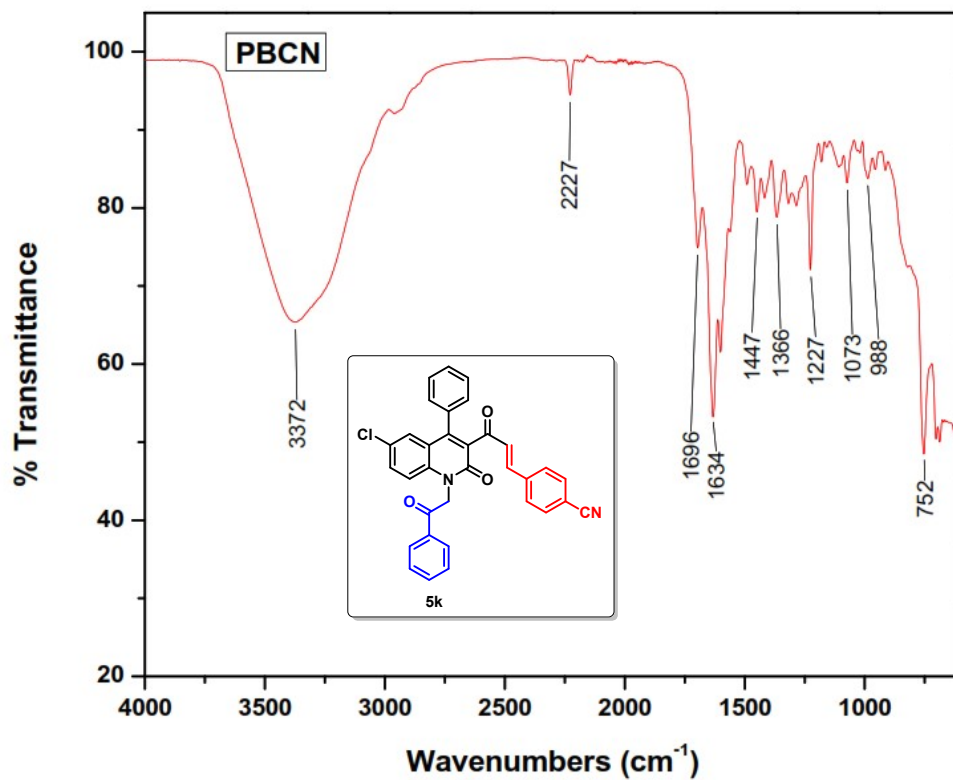
Signature SIF VIT VELLORE
AC4NO2



^1H and ^{13}C NMR spectra of compound **5j** in CDCl_3

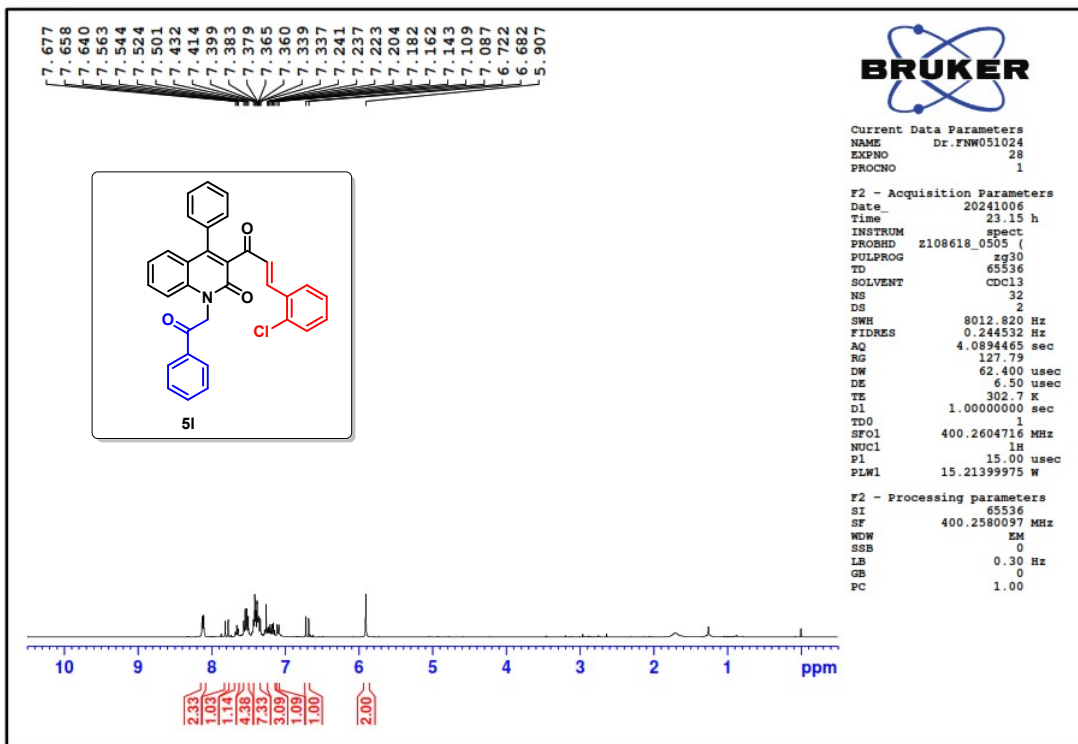


IR and HRMS spectra of compound **5j**

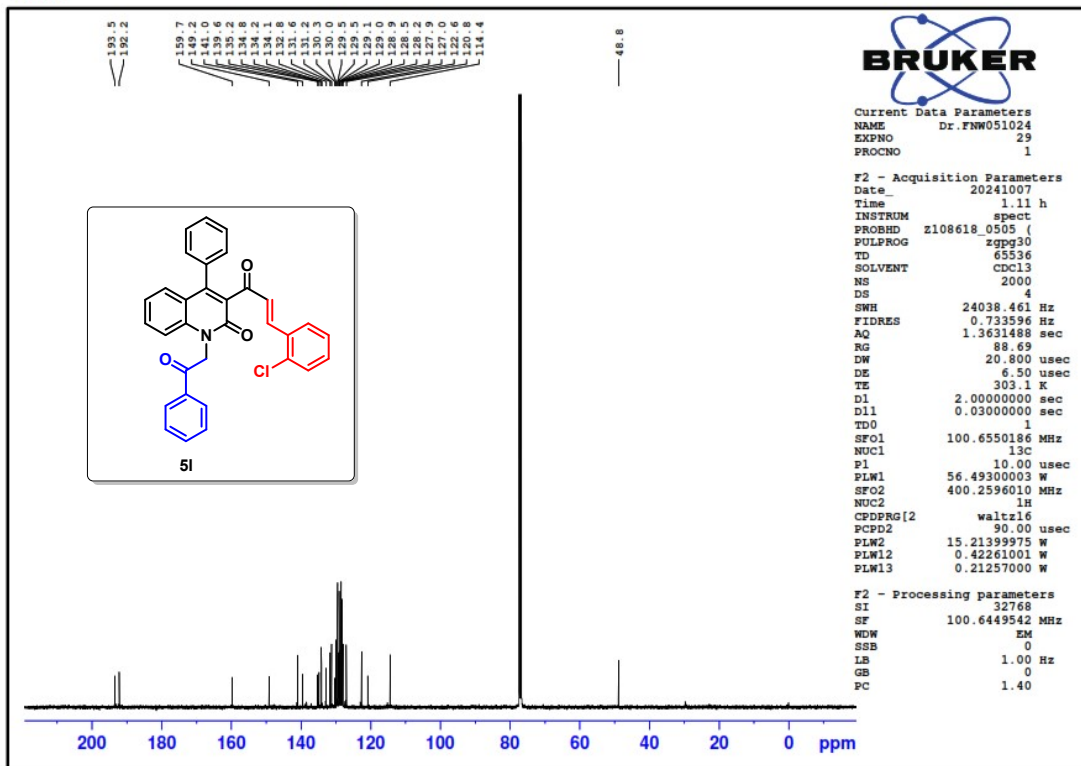


IR and HRMS spectra of compound **5k**

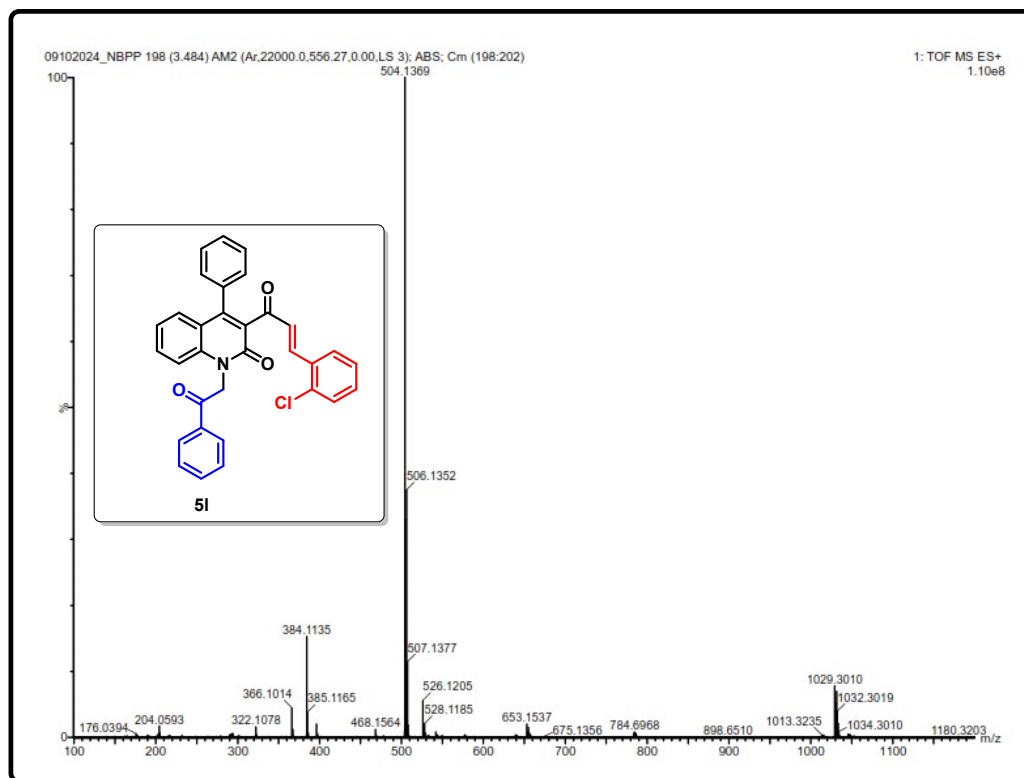
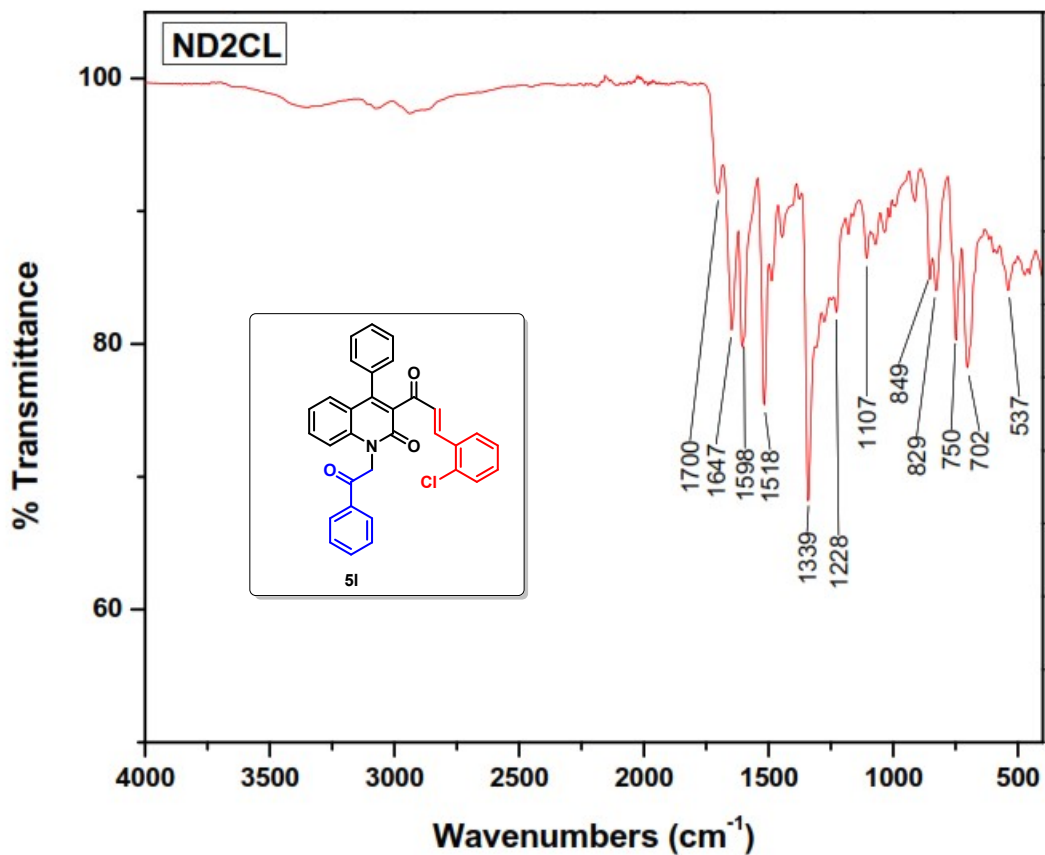
Signature SIF VIT VELLORE
NB2CL



Signature SIF VIT VELLORE
NB2CL

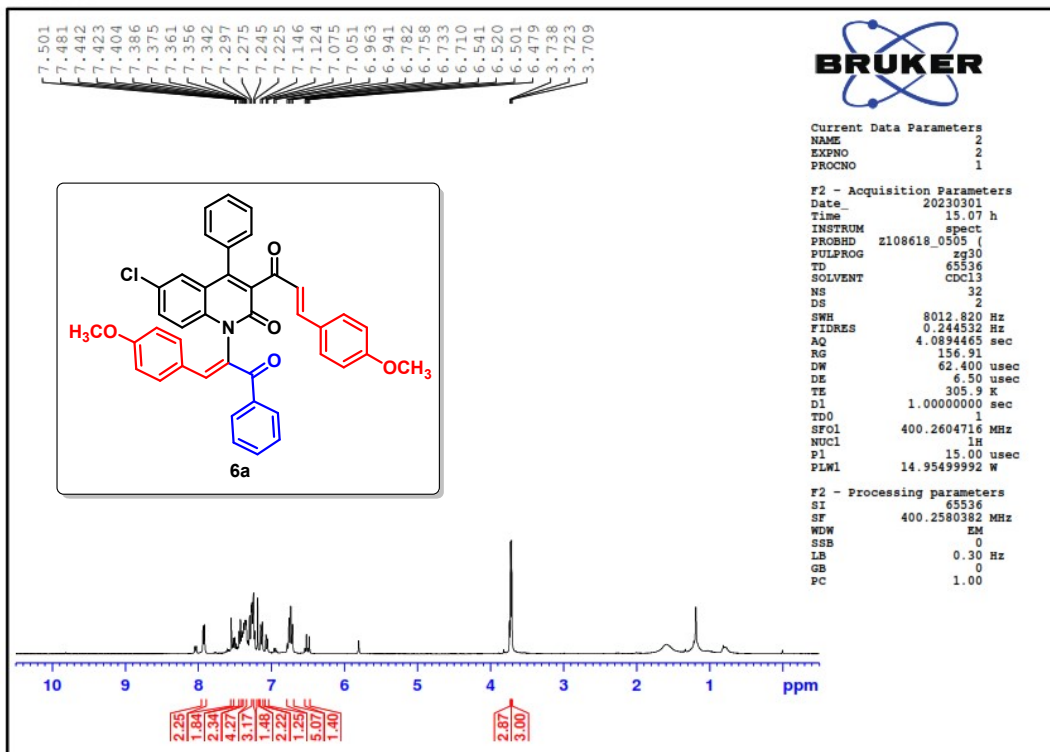


^1H and ^{13}C NMR spectra of compound **5I** in CDCl_3

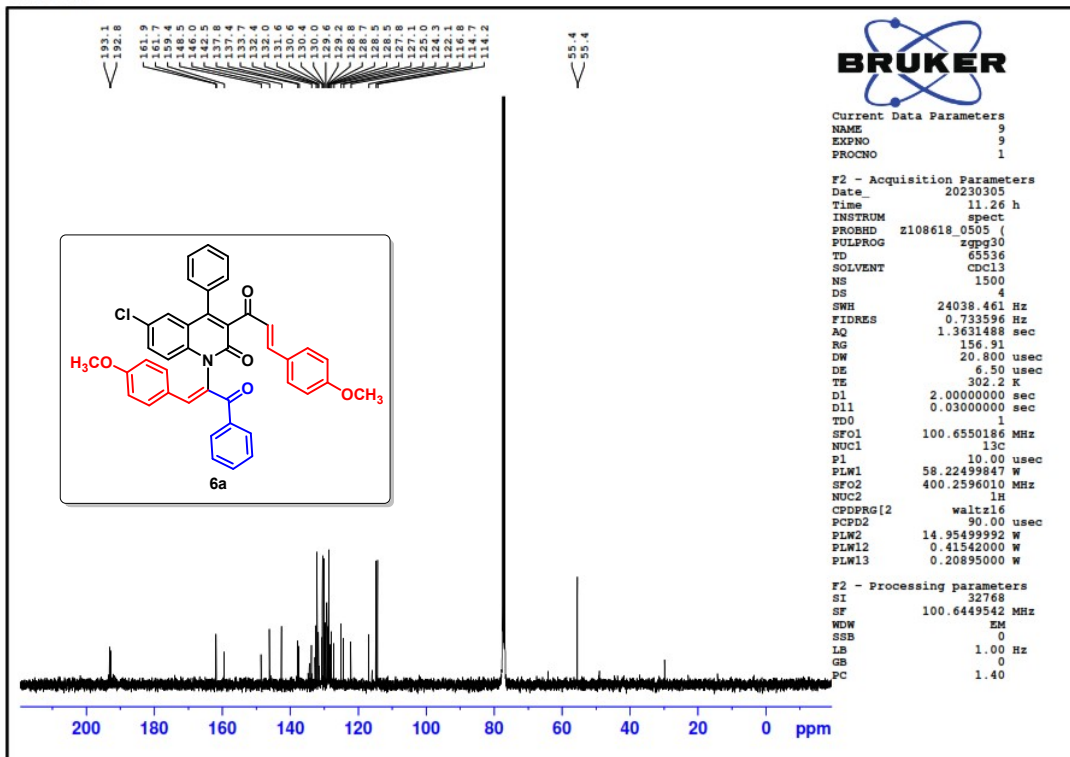


IR and HRMS spectra of compound **5I**

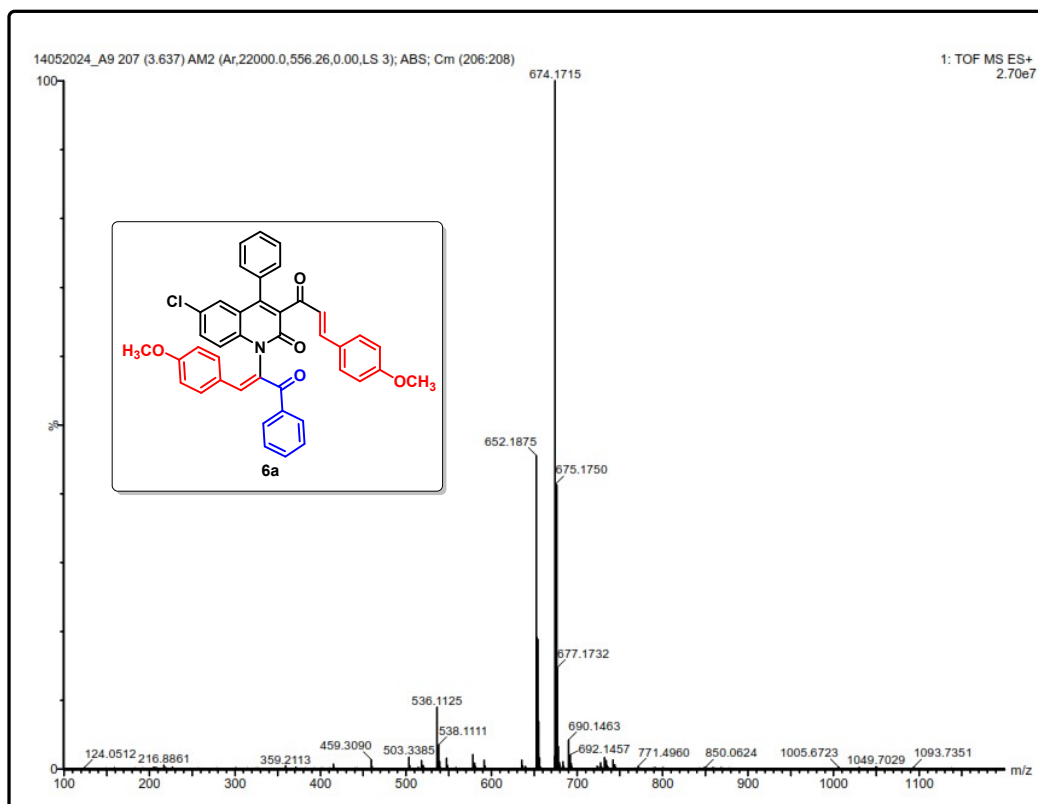
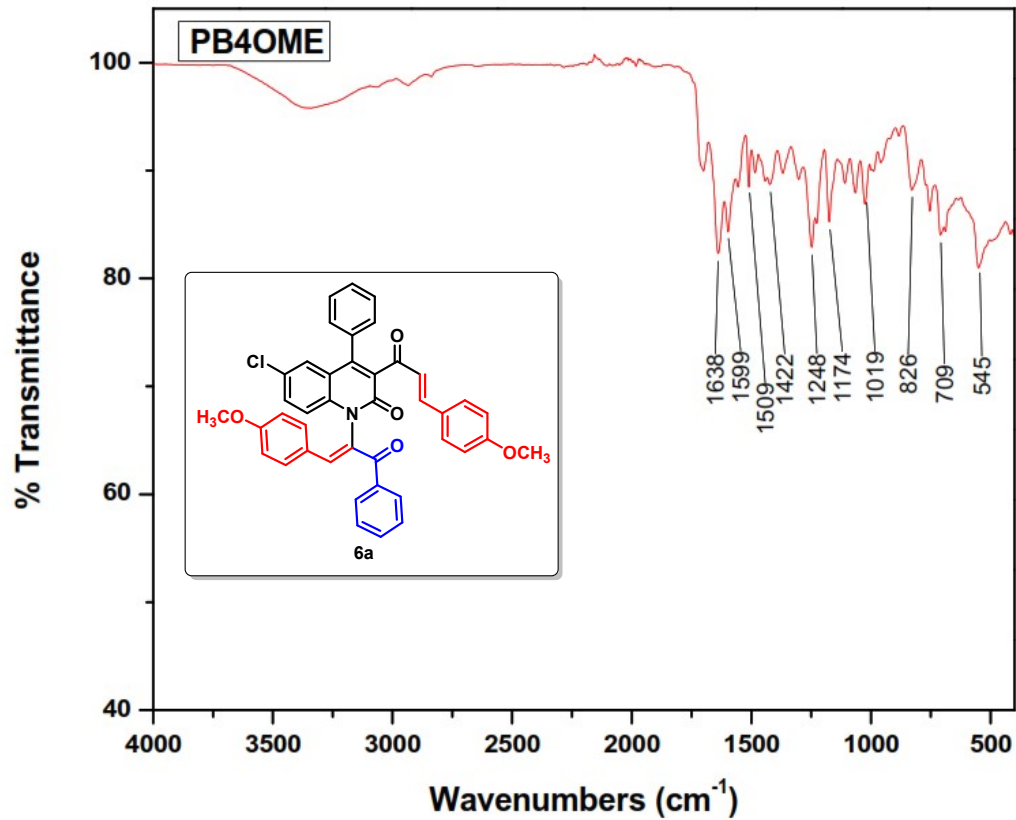
Signature SIF VIT VELLORE
ACPB40ME



Signature SIF VIT VELLORE
ACPB40ME

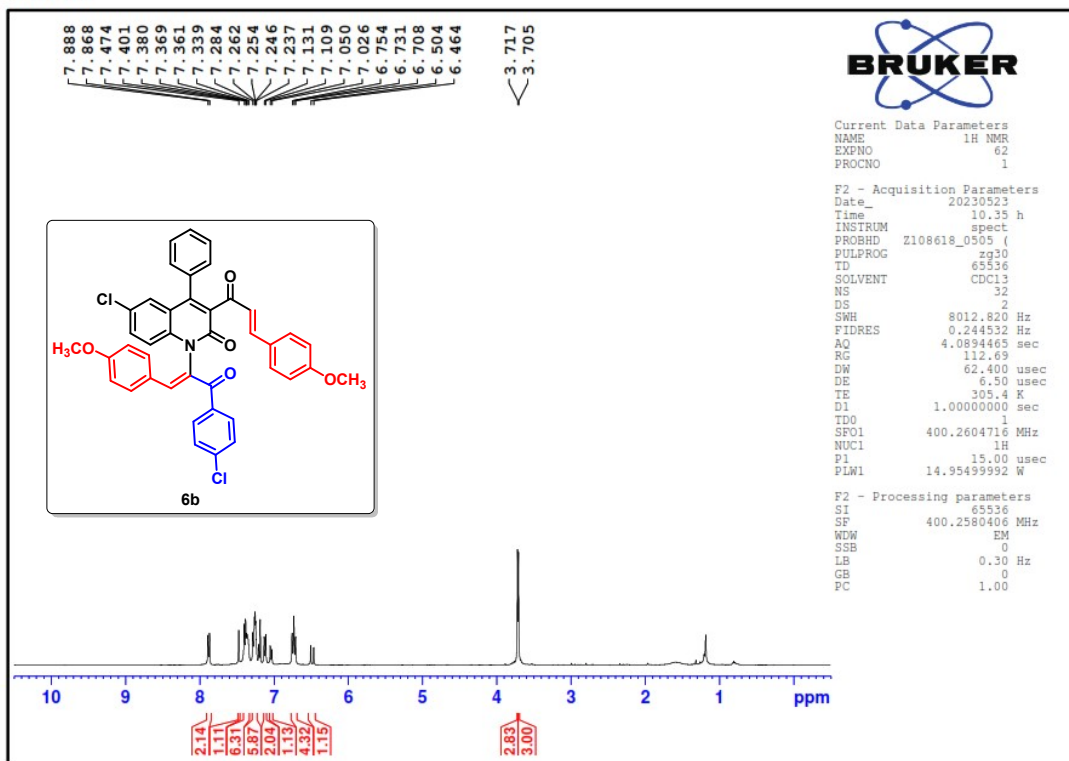


^1H and ^{13}C NMR spectra of compound **6a** in CDCl_3

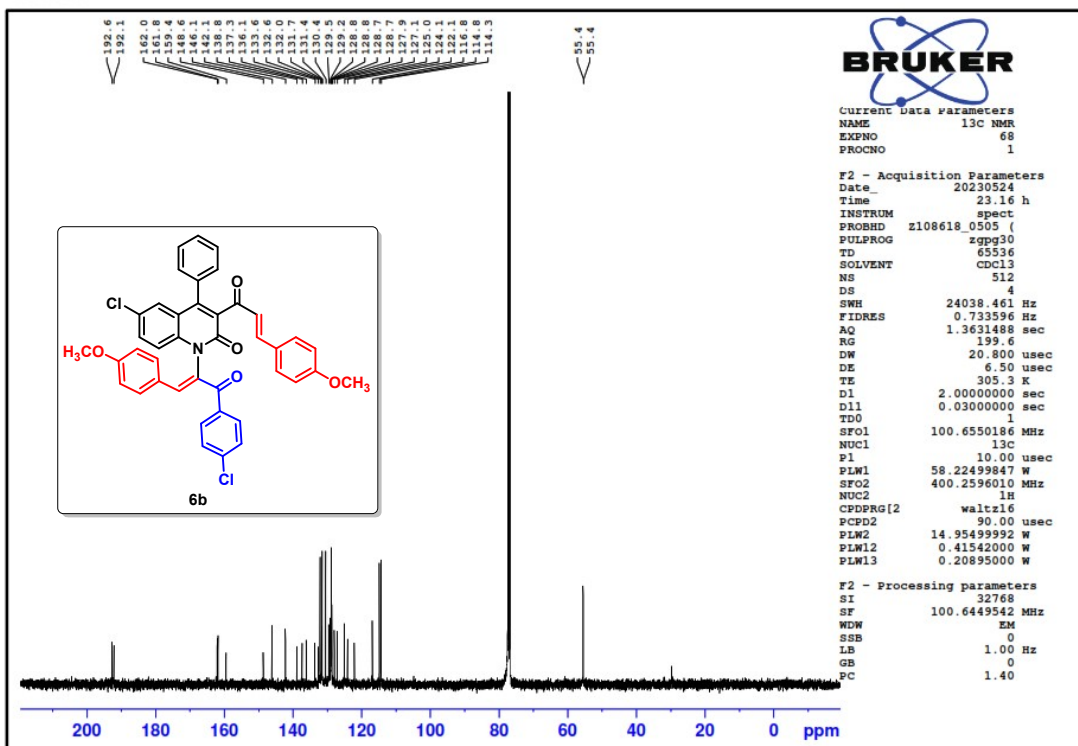


IR and HRMS spectra of compound **6a**

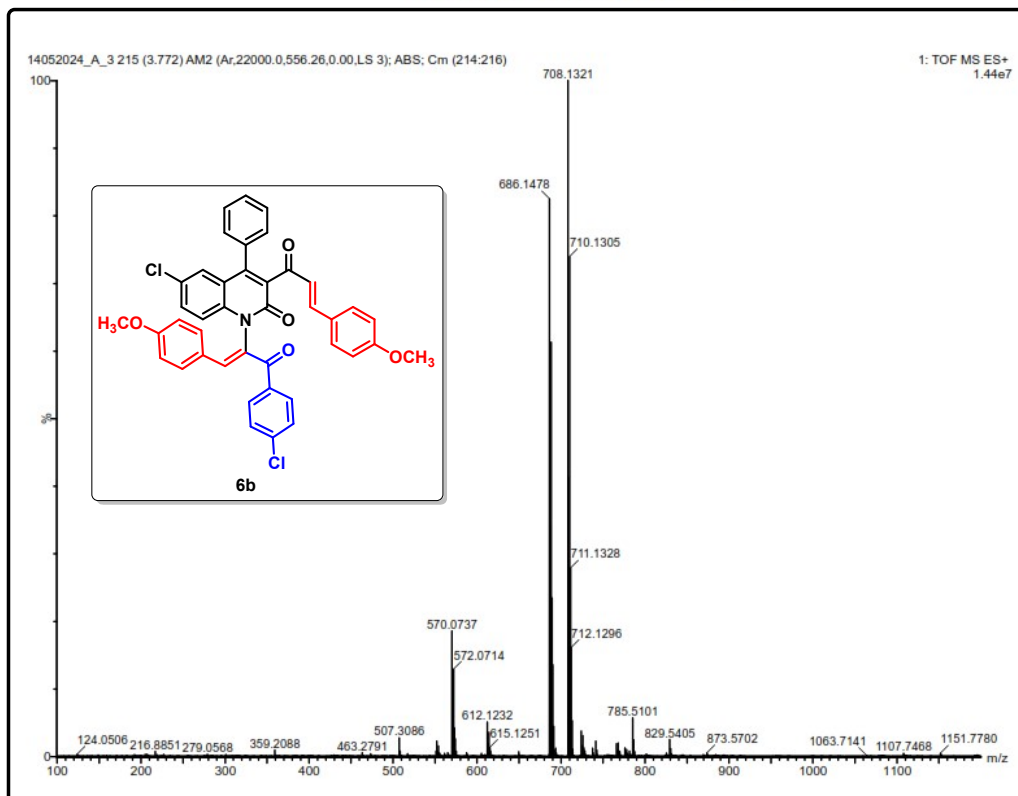
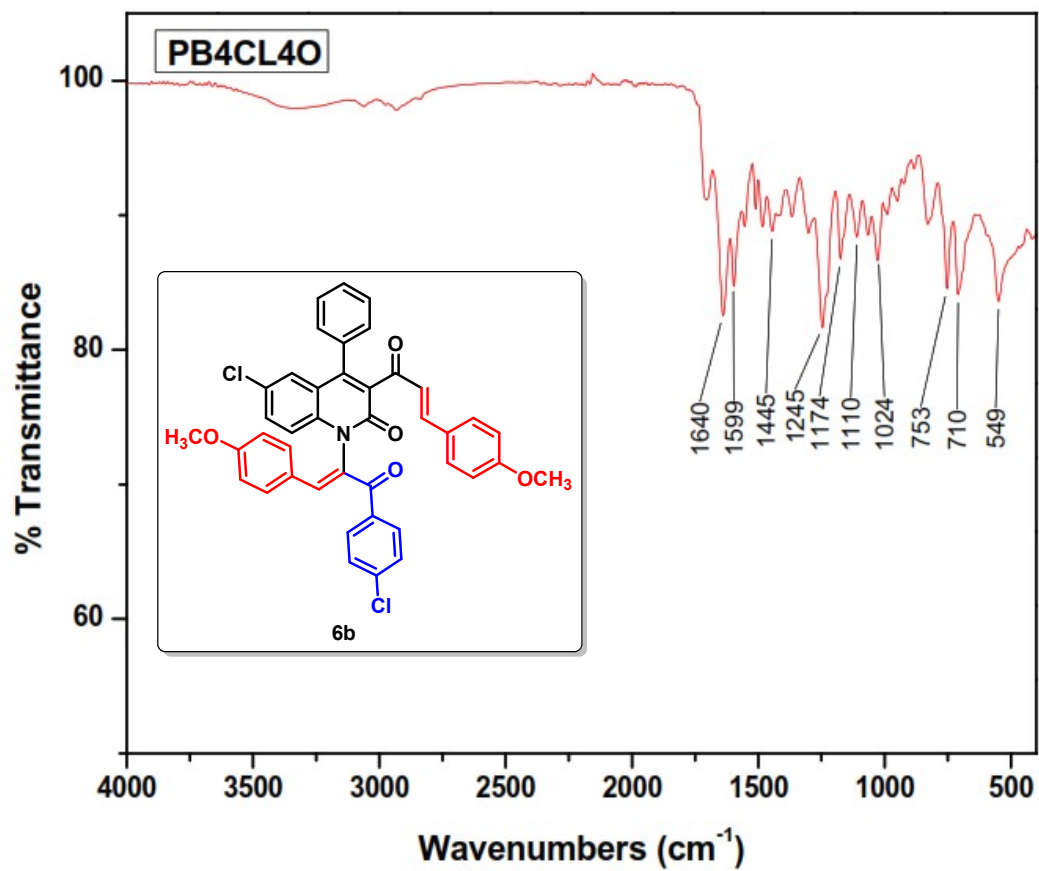
Signature SIF VIT VELLORE
PB4CL40



Signature SIF VIT VELLORE
PB4CL40

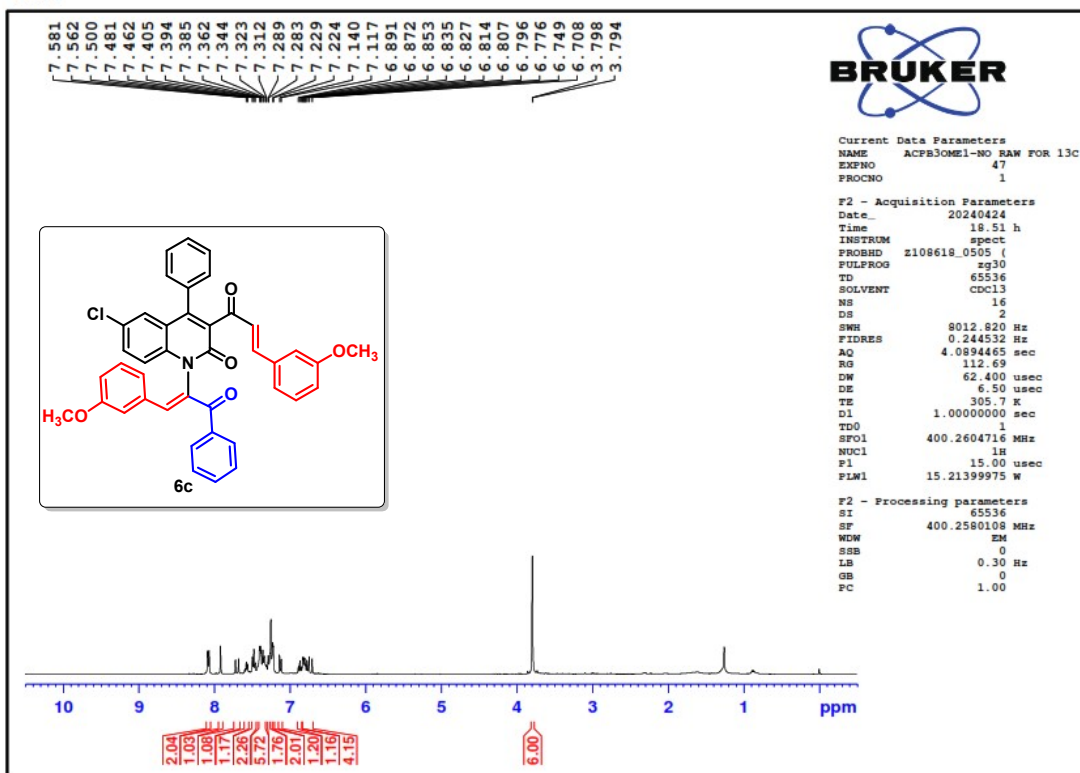


^1H and ^{13}C NMR spectra of compound **6b** in CDCl_3

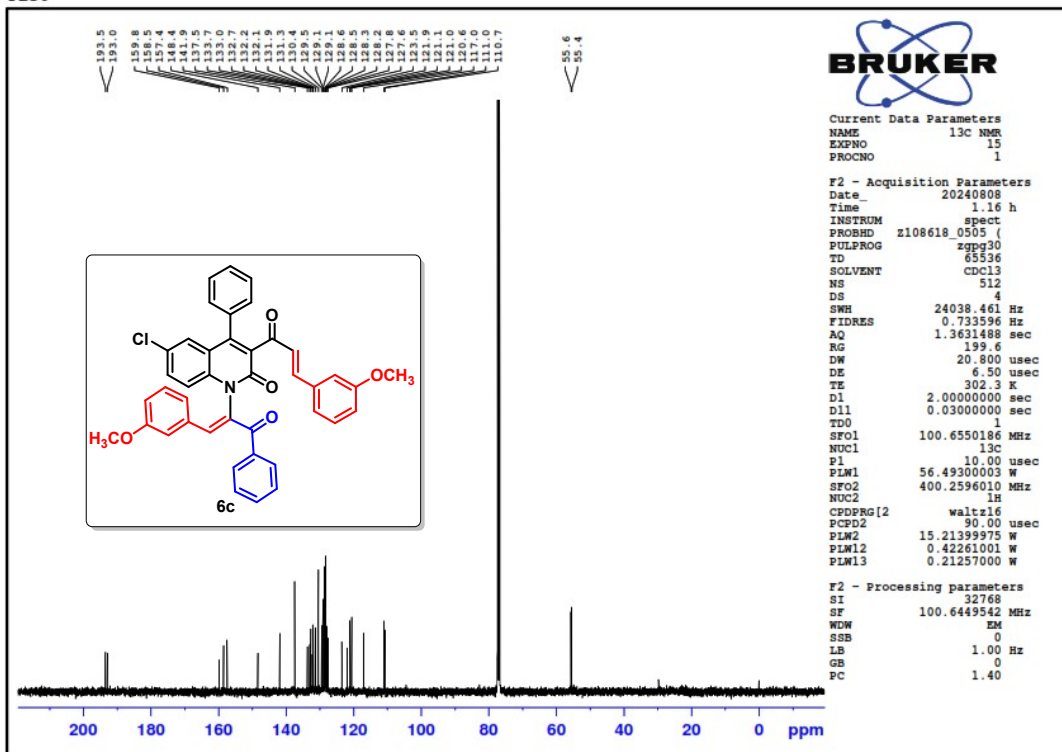


IR and HRMS spectra of compound **6b**

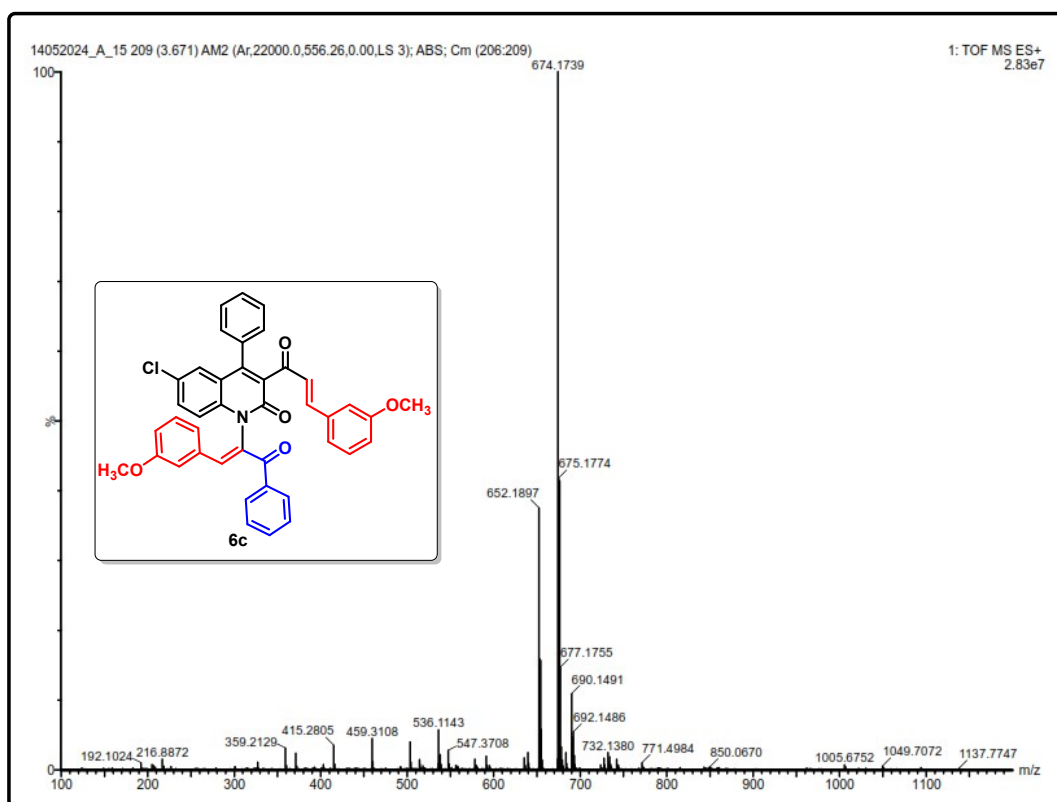
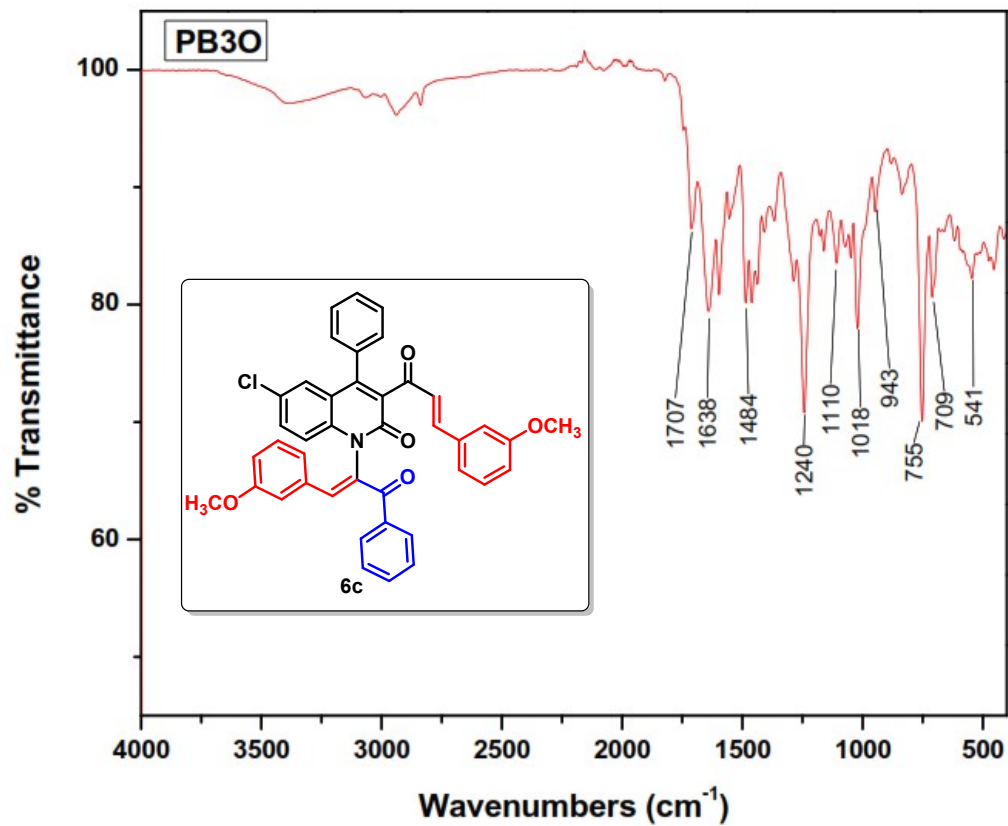
Signature SIF VIT VELLORE
PB30



Signature SIF VIT VELLORE
PB30

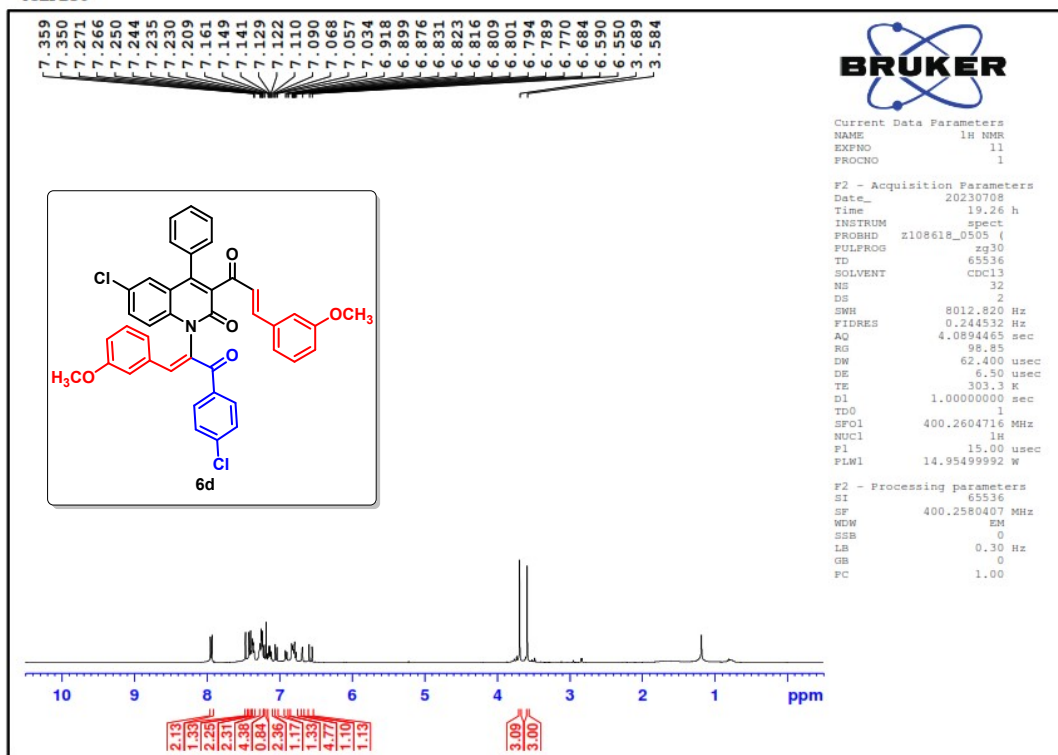


^1H and ^{13}C NMR spectra of compound **6c** in CDCl_3

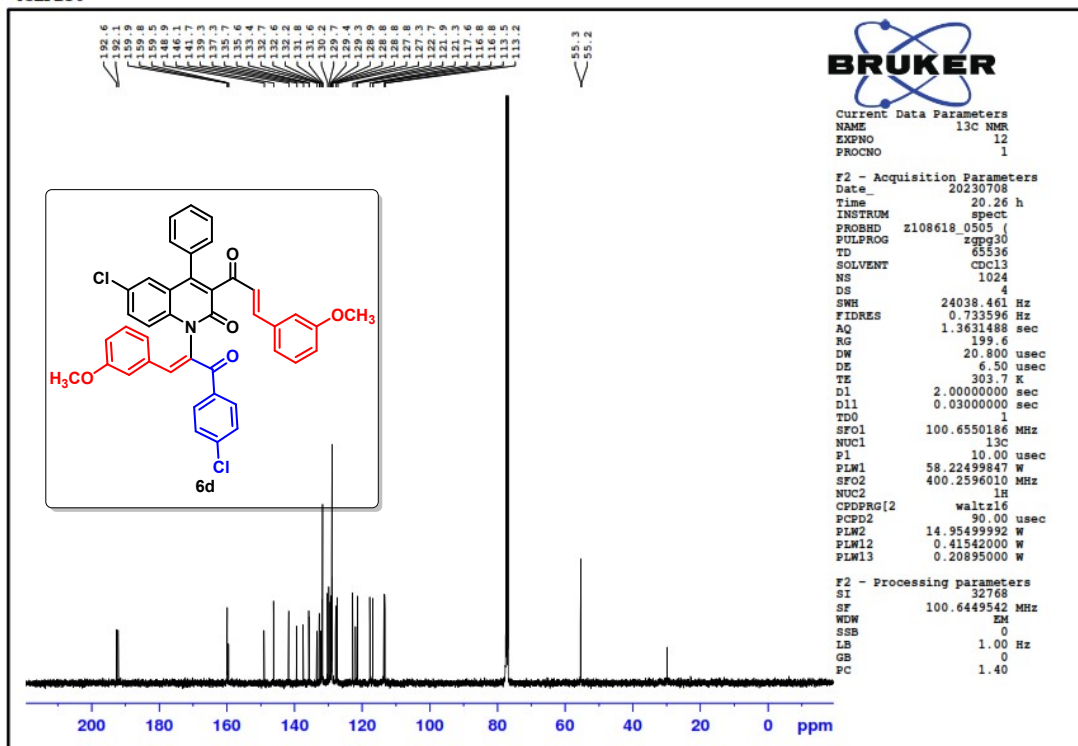


IR and HRMS spectra of compound **6c**

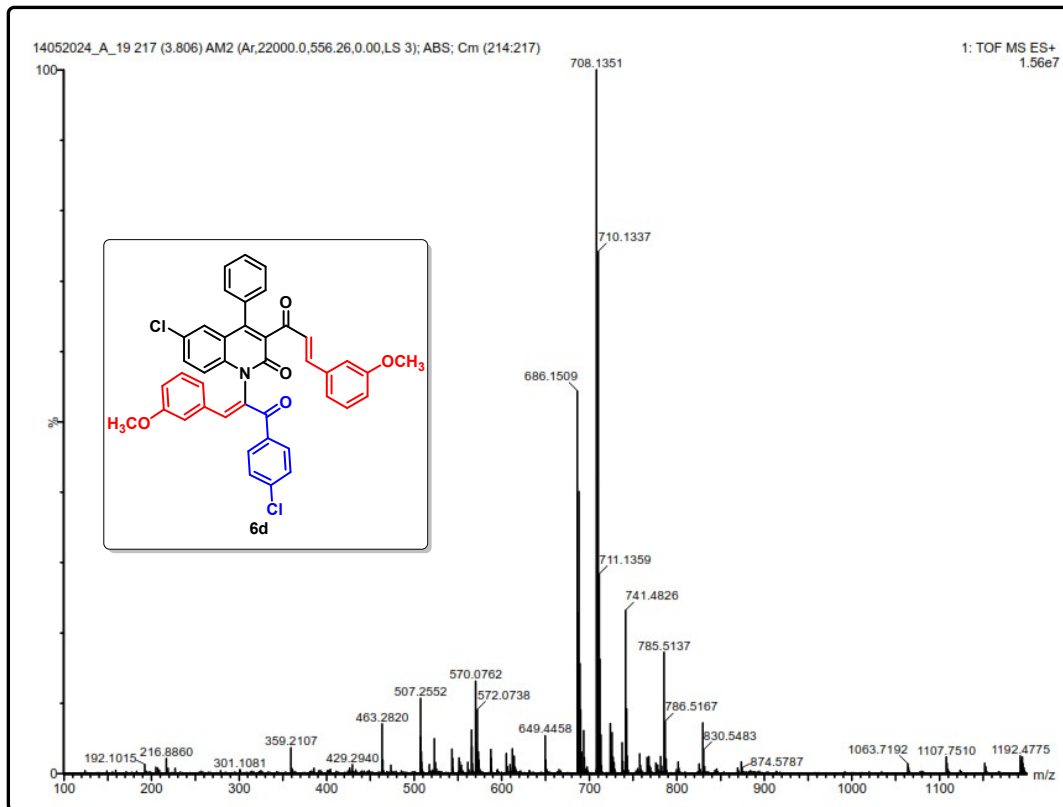
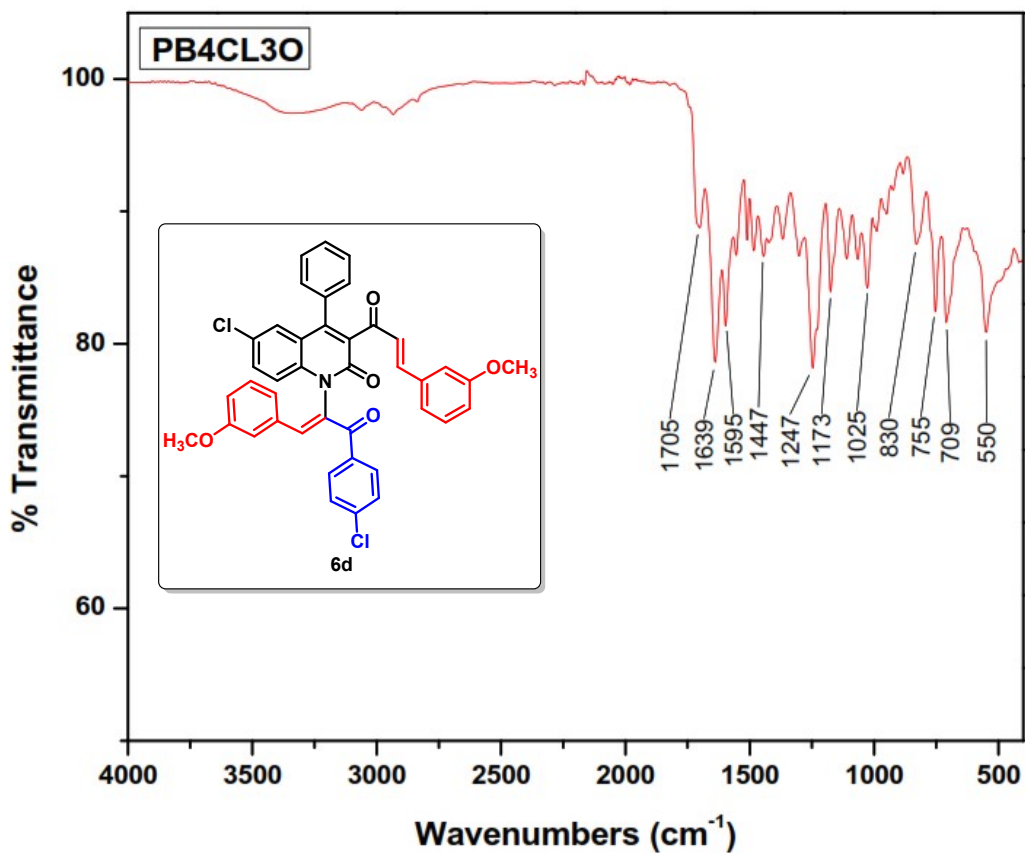
Signature SIF VIT VELLORE
4CLPB30



Signature SIF VIT VELLORE
4CLPB30

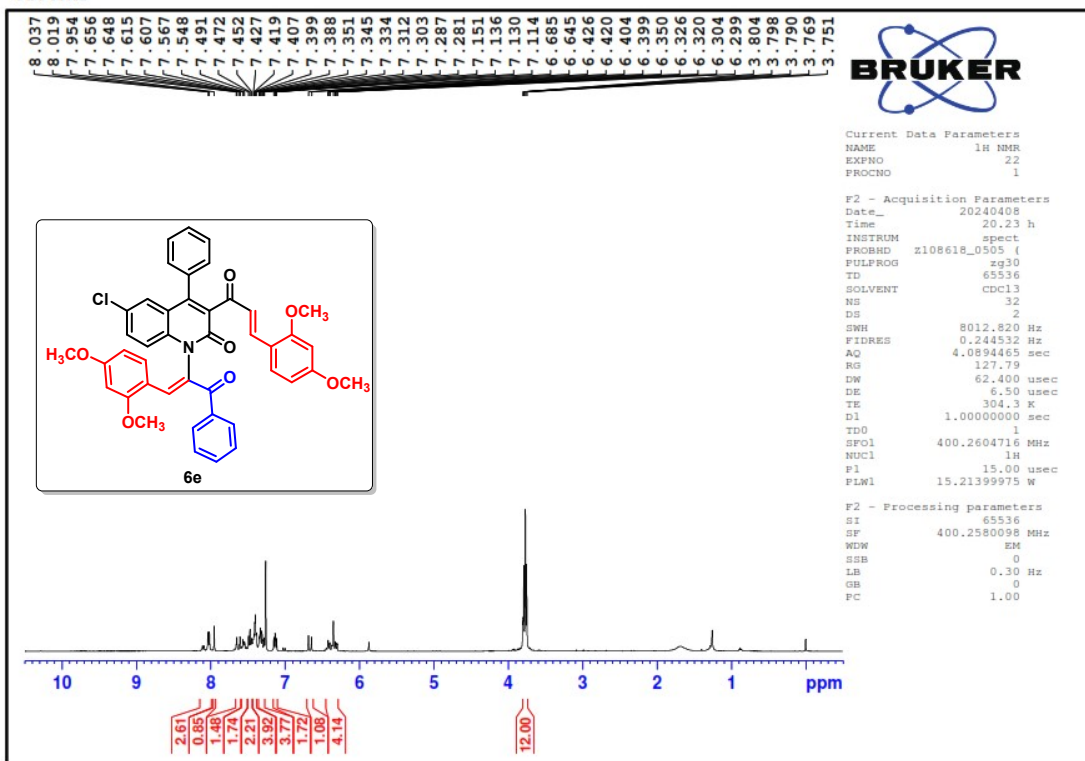


¹H and ¹³C NMR spectra of compound 6d in CDCl₃

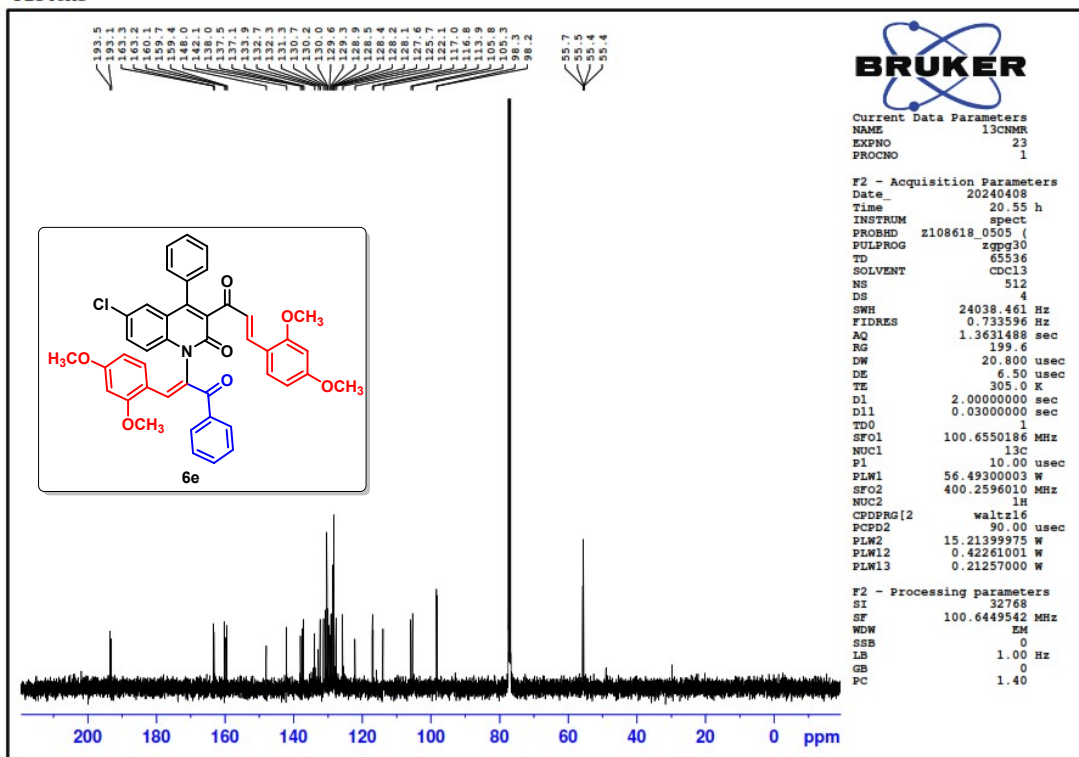


IR and HRMS spectra of compound **6d**

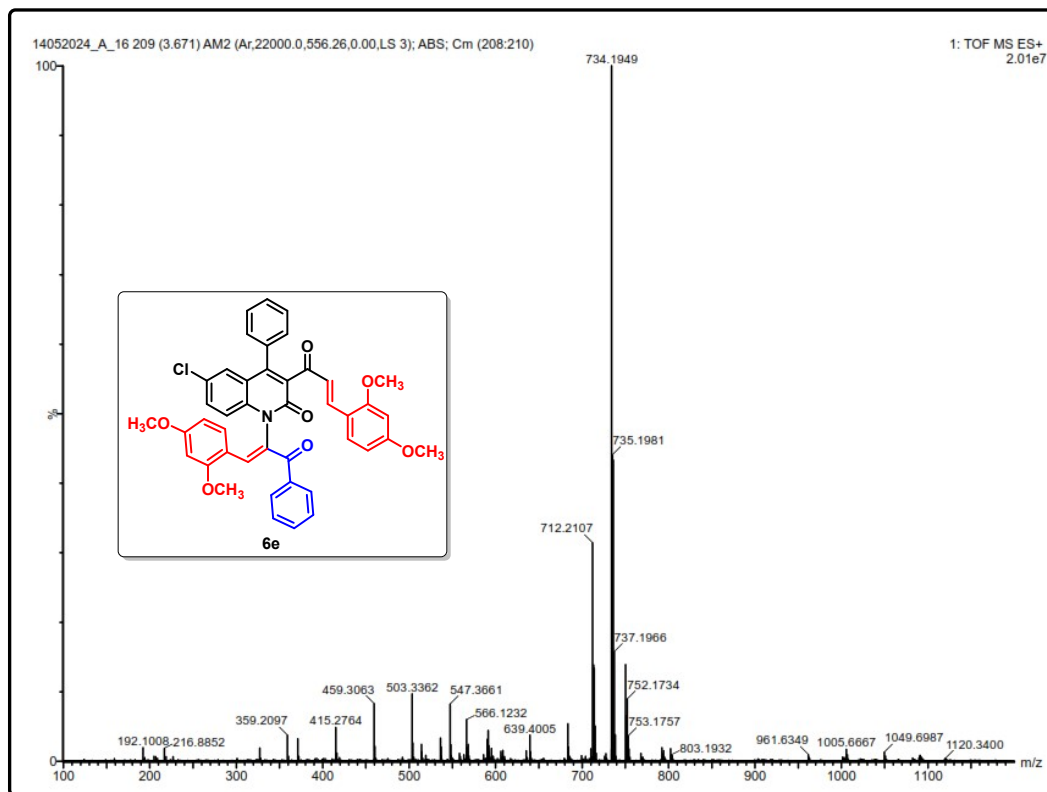
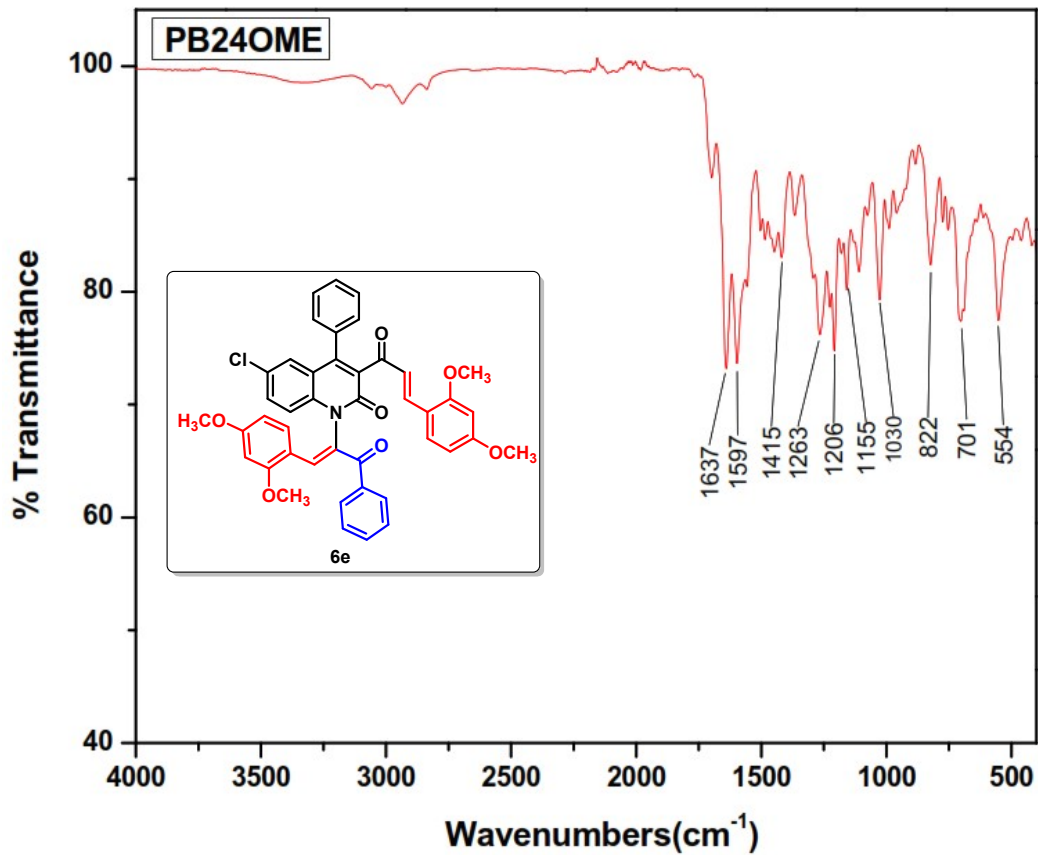
Signature SIF VIT VELLORE
PB340Me



Signature SIF VIT VELLORE
PB340Me

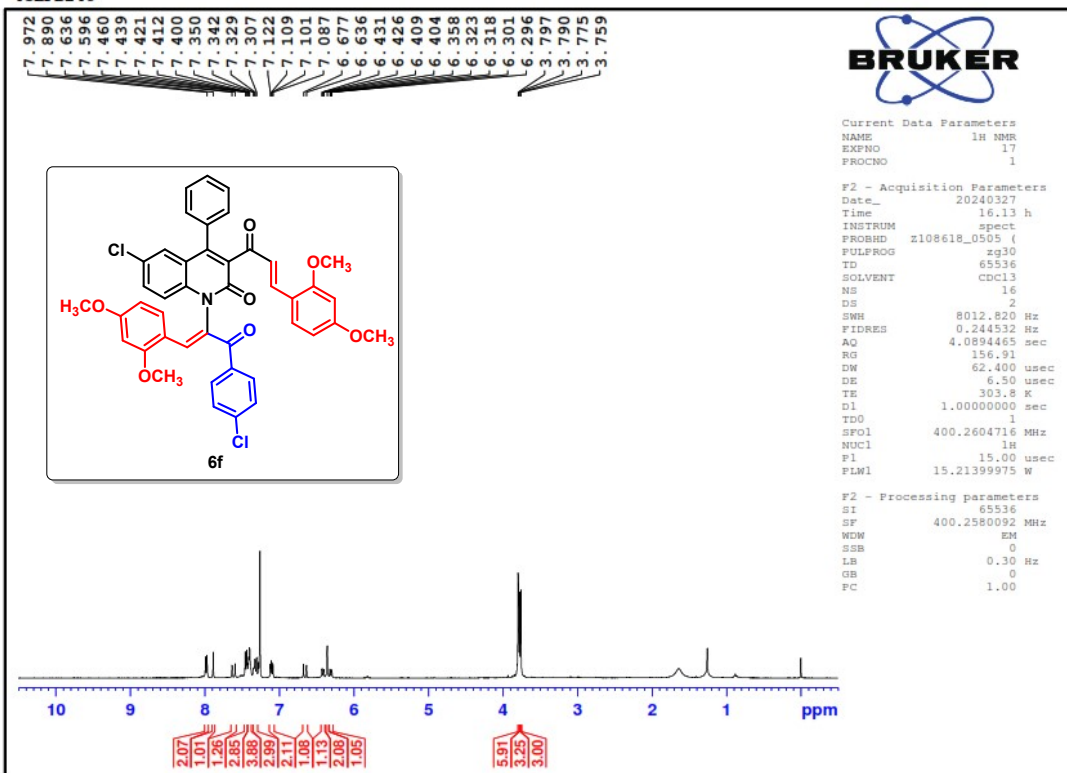


¹H and ¹³C NMR spectra of compound 6e in CDCl₃

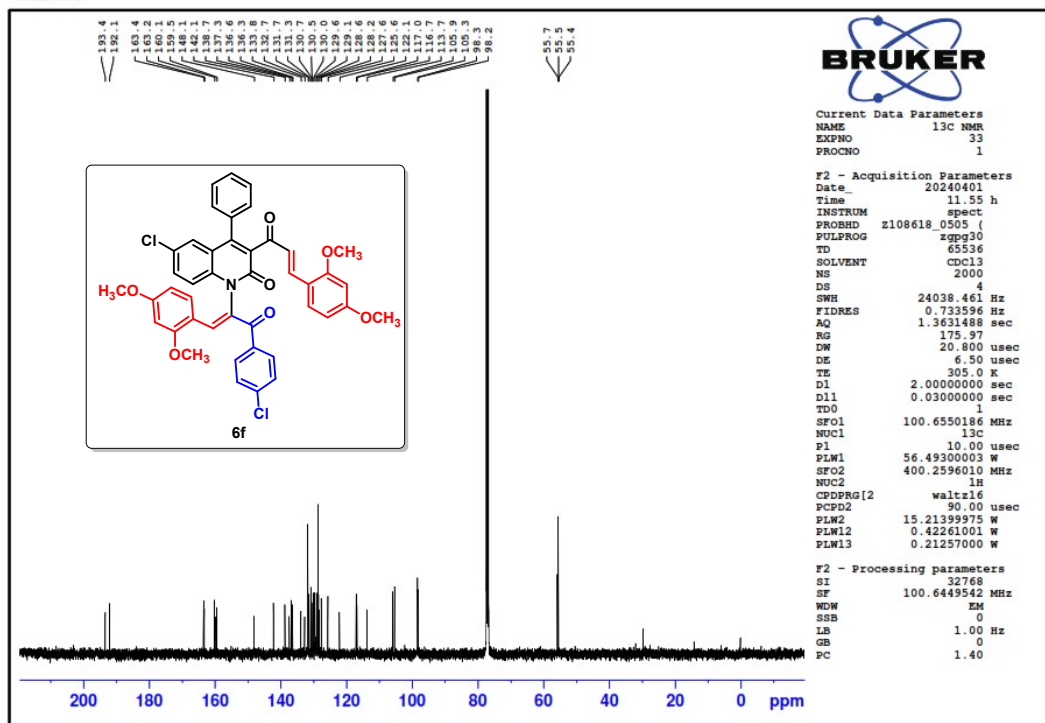


IR and HRMS spectra of compound **6e**

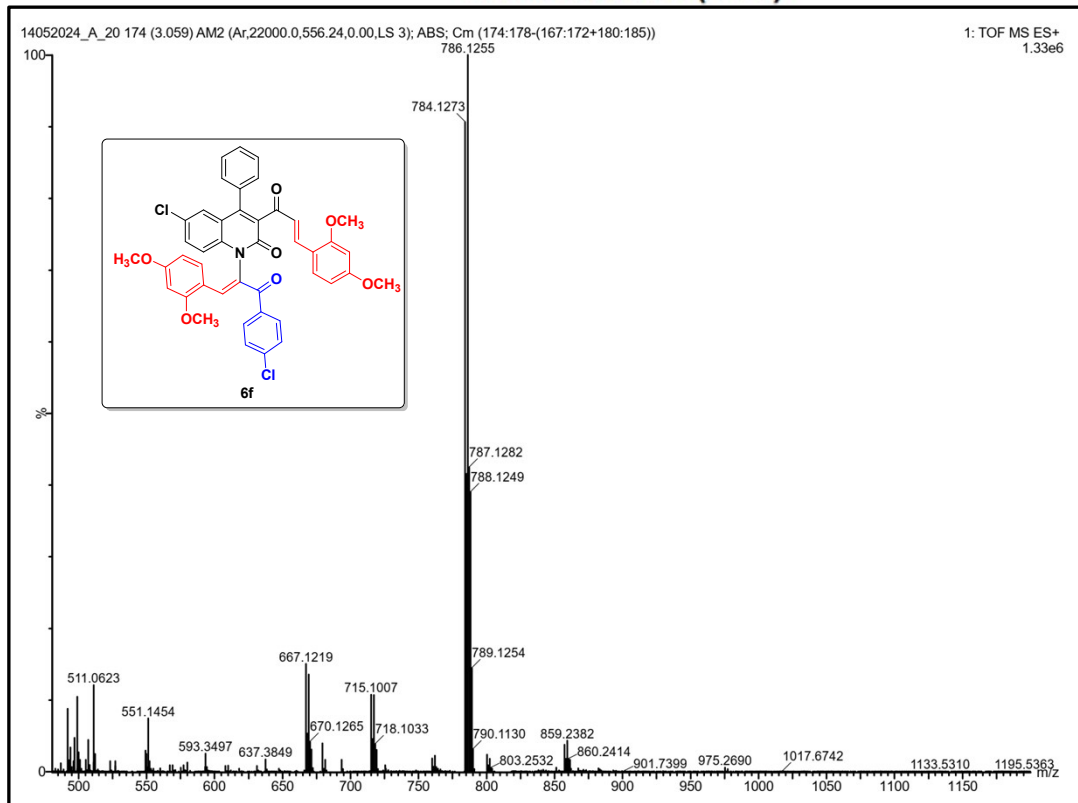
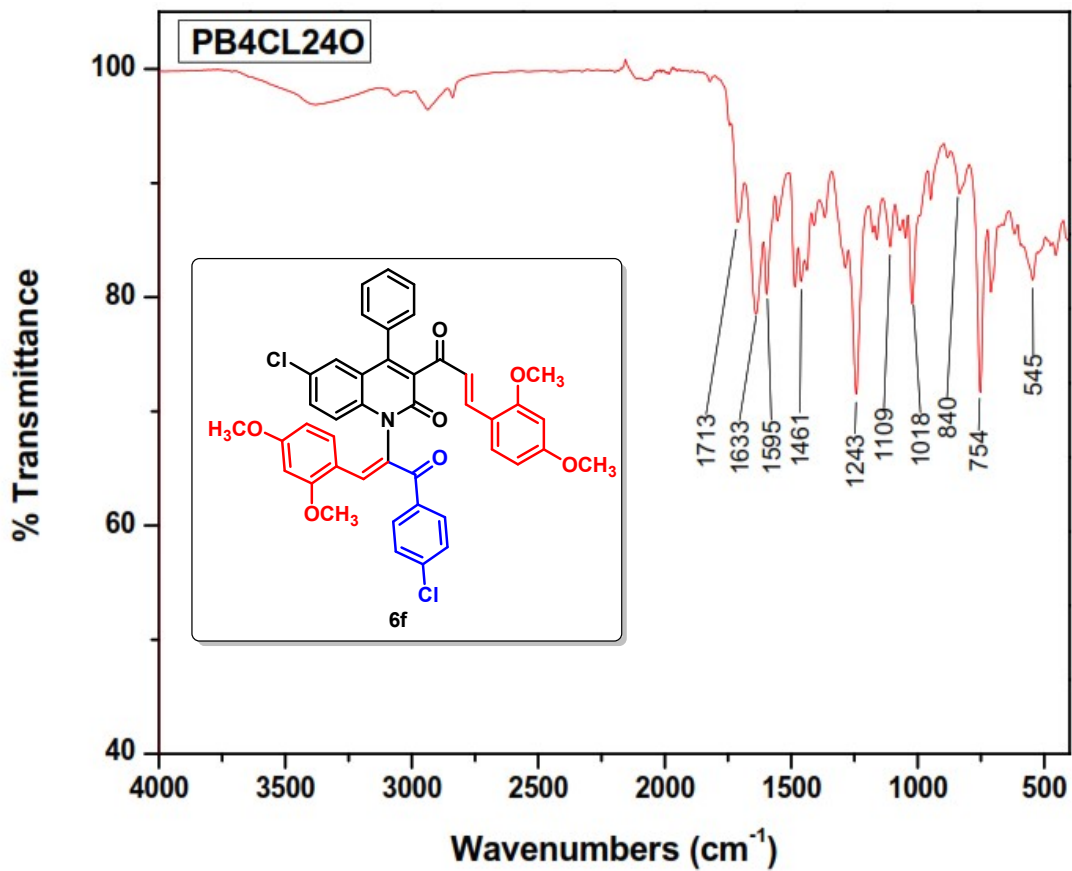
Signature SIF VIT VELLORE
4CLPB240



Signature SIF VIT VELLORE
4CLPB34

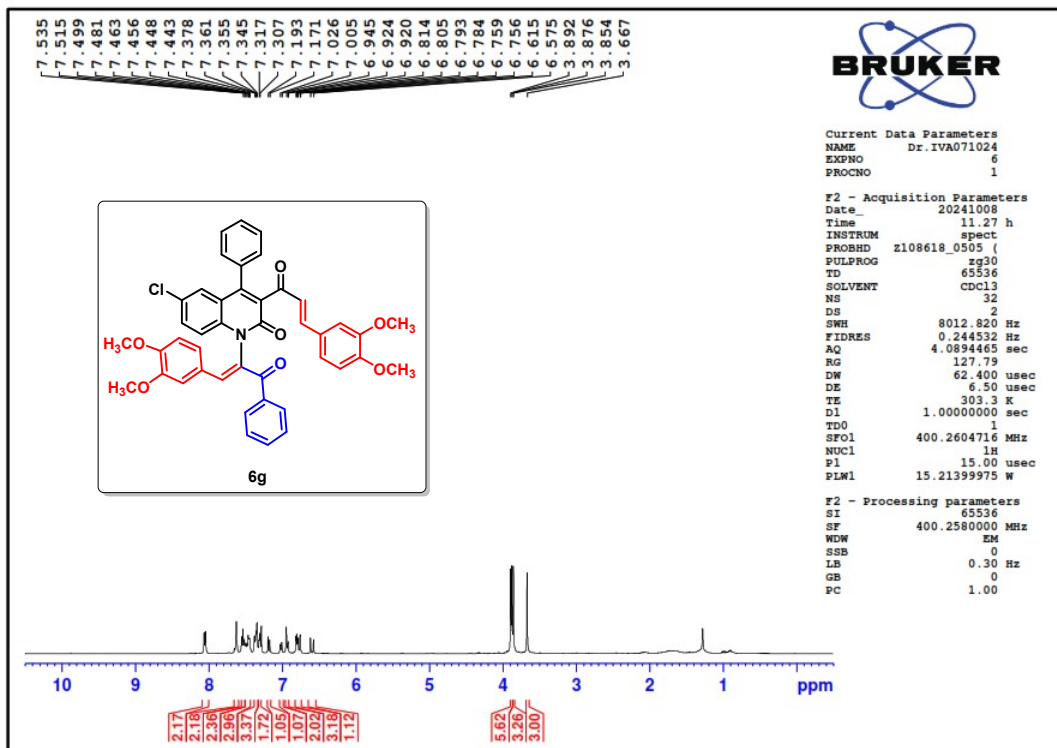


¹H and ¹³C NMR spectra of compound **6f** in CDCl₃

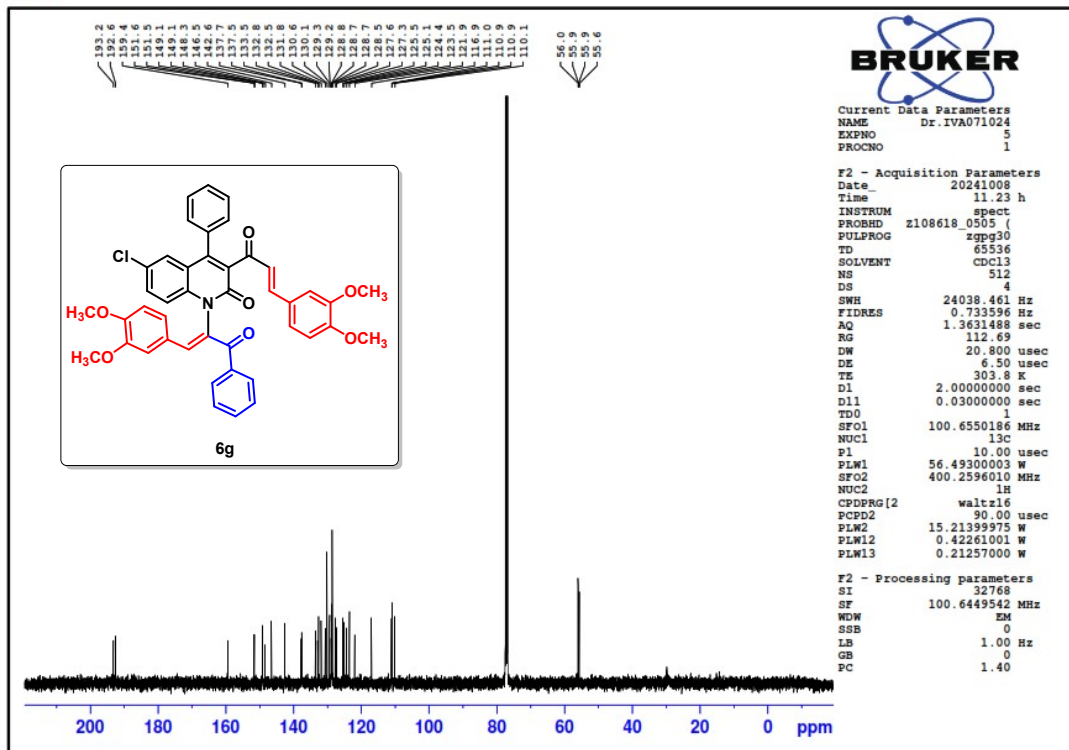


IR and HRMS spectra of compound **6f**

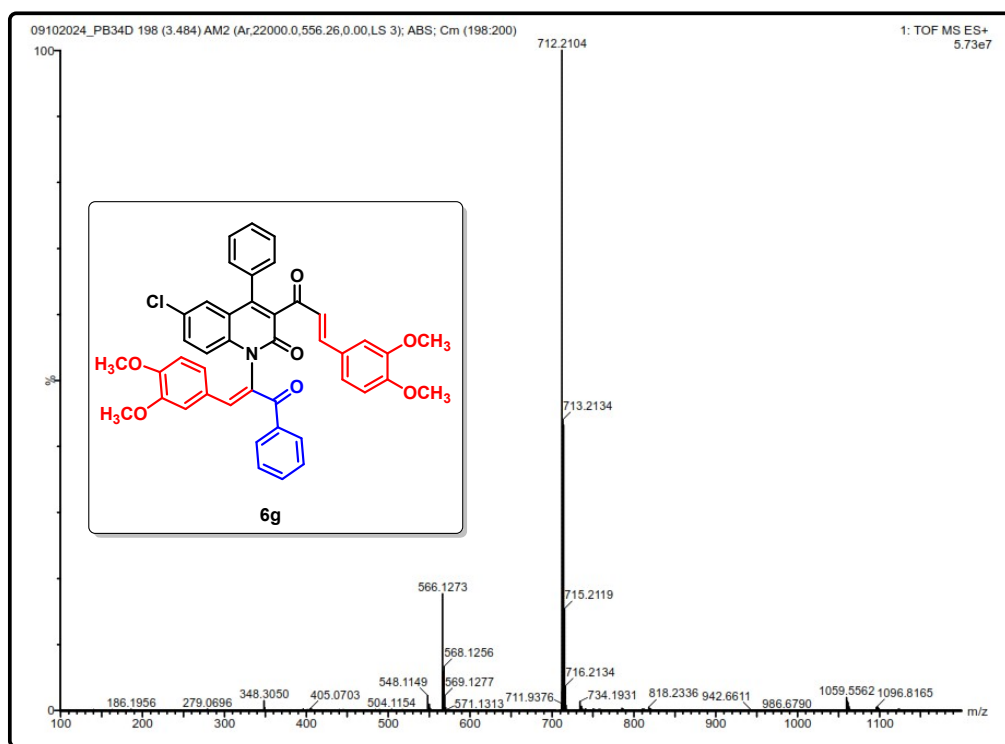
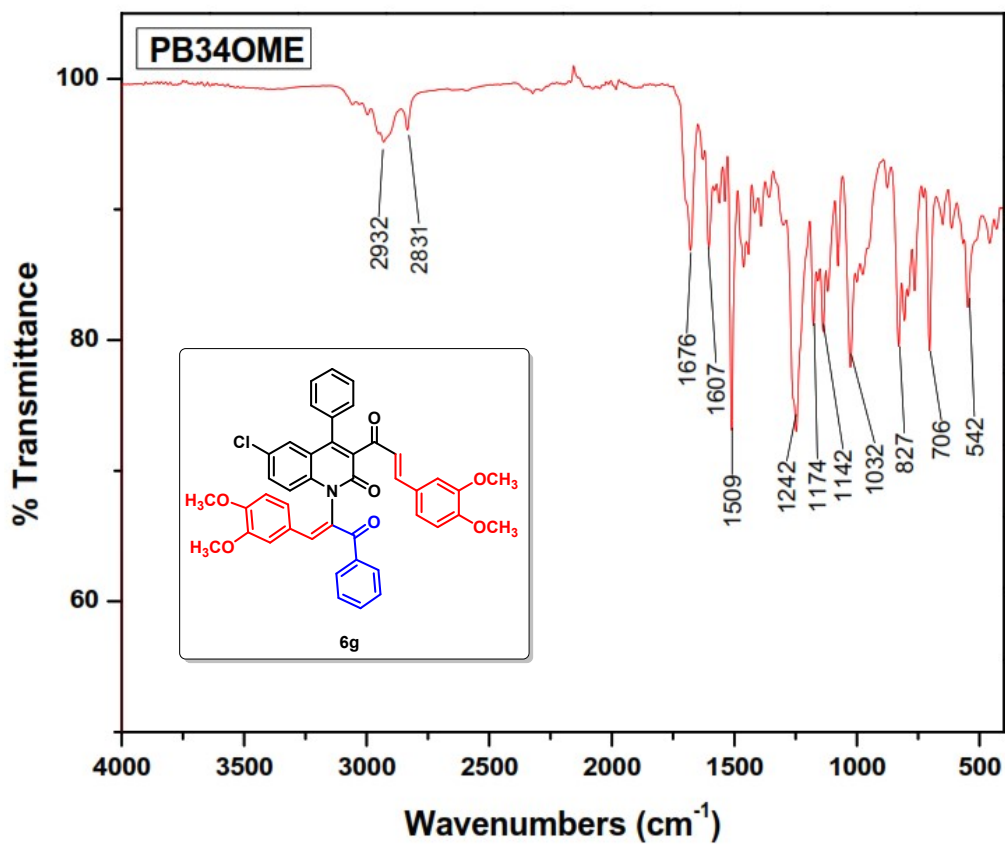
Signature SIF VIT VELLORE
PB340



Signature SIF VIT VELLORE
PB340

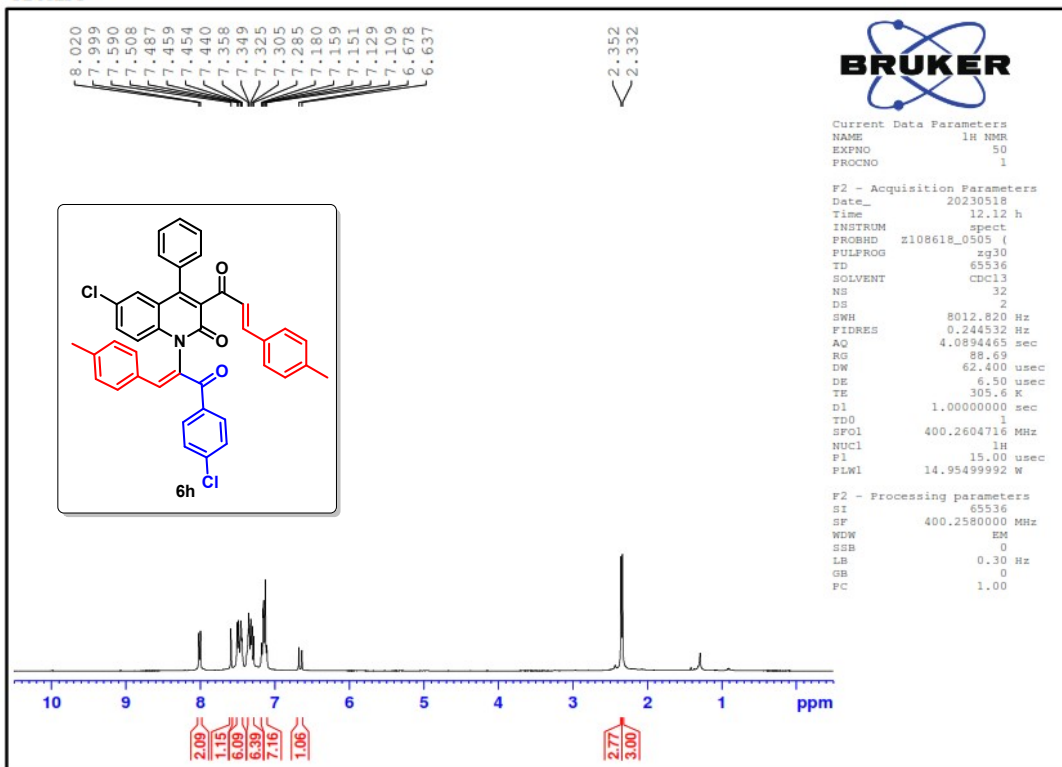


^1H and ^{13}C NMR spectra of compound **6g** in CDCl_3

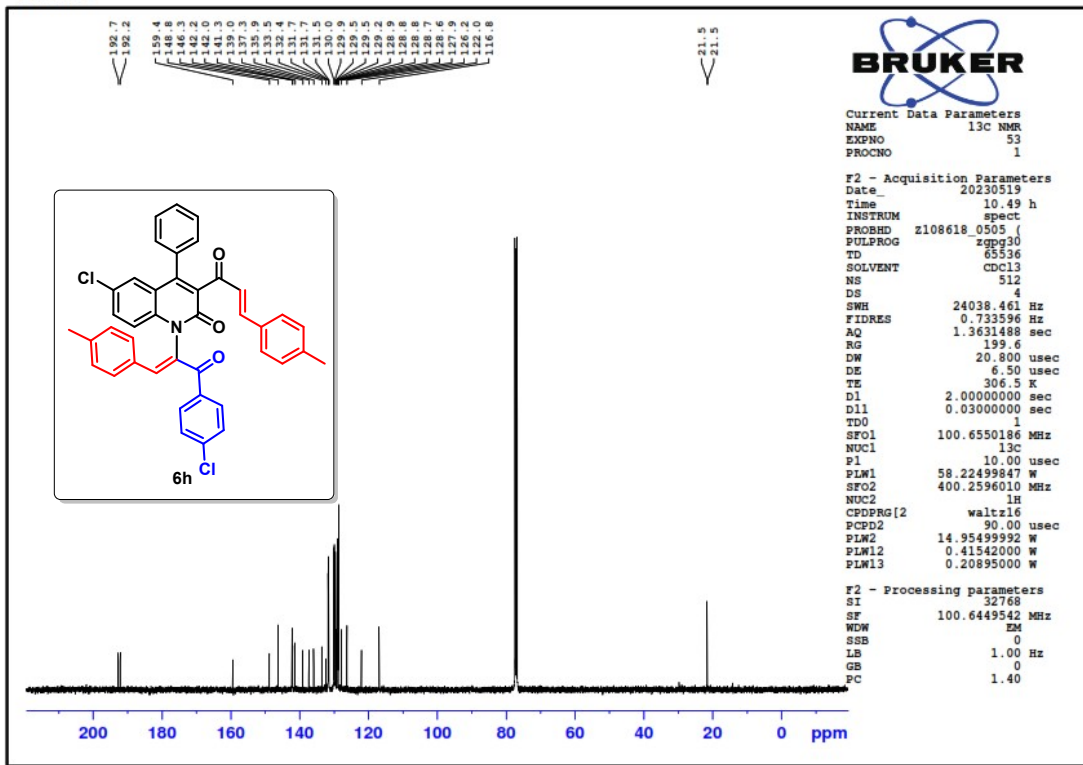


IR and HRMS spectra of compound **6g**

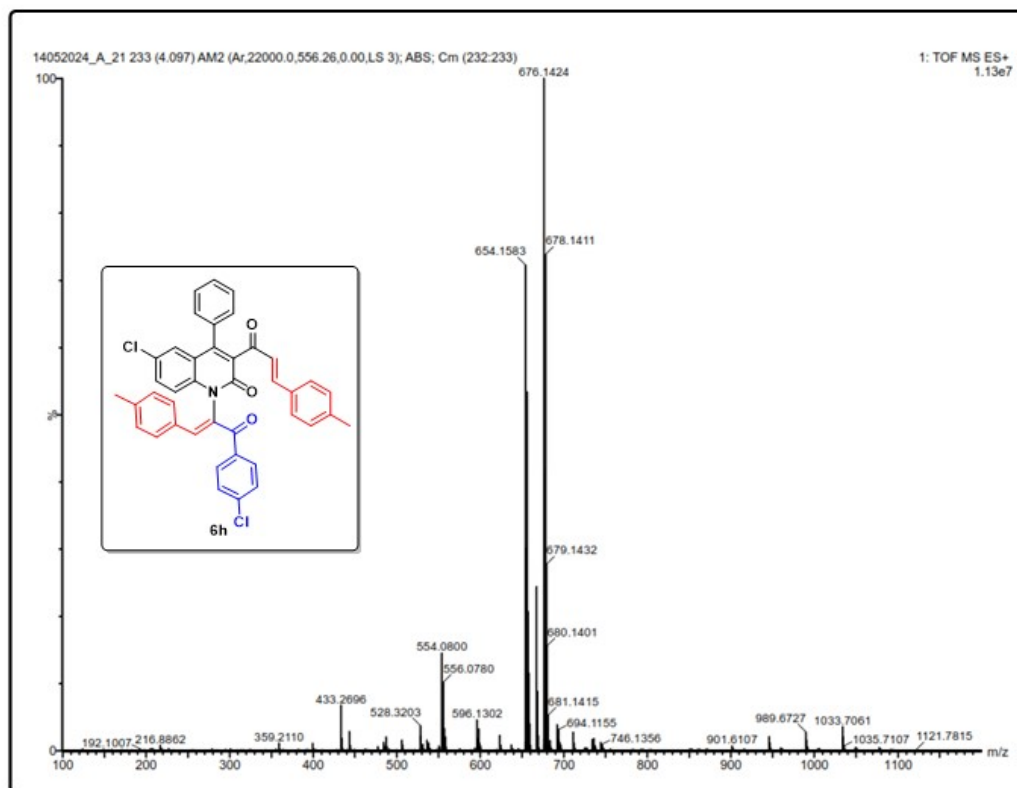
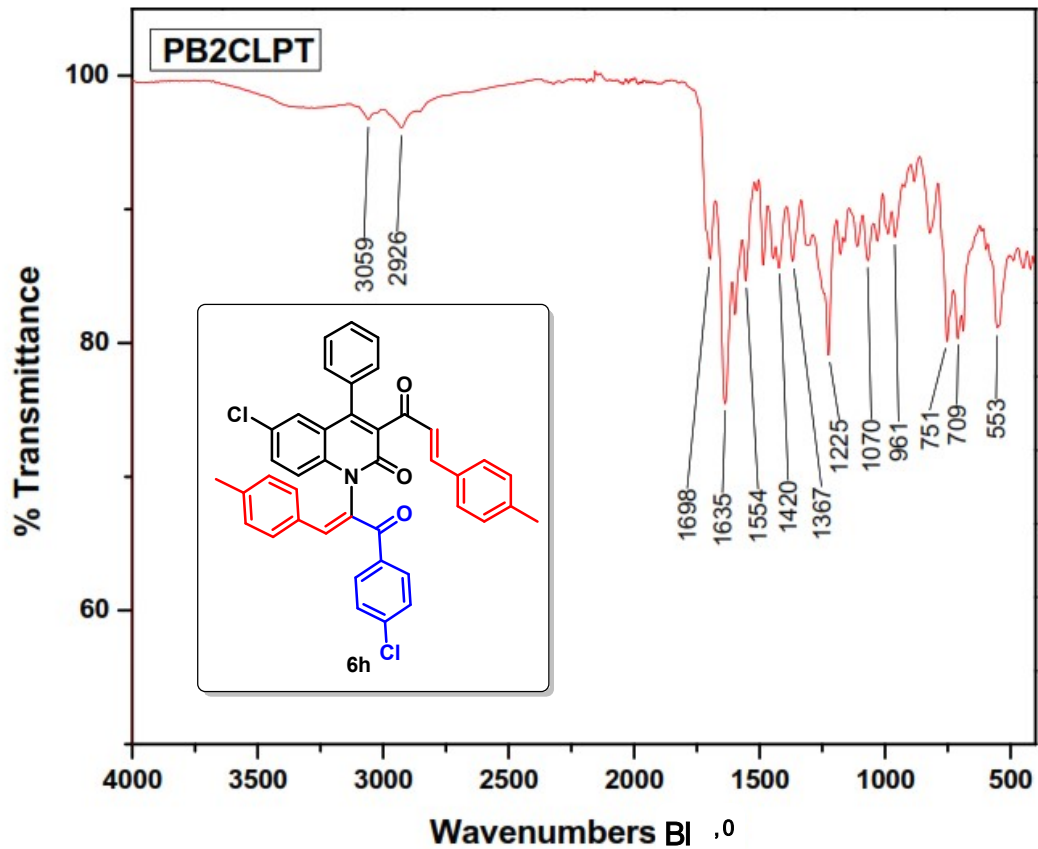
Signature SIF VIT VELLORE
PB4CLPT



Signature SIF VIT VELLORE
PB4CLPT

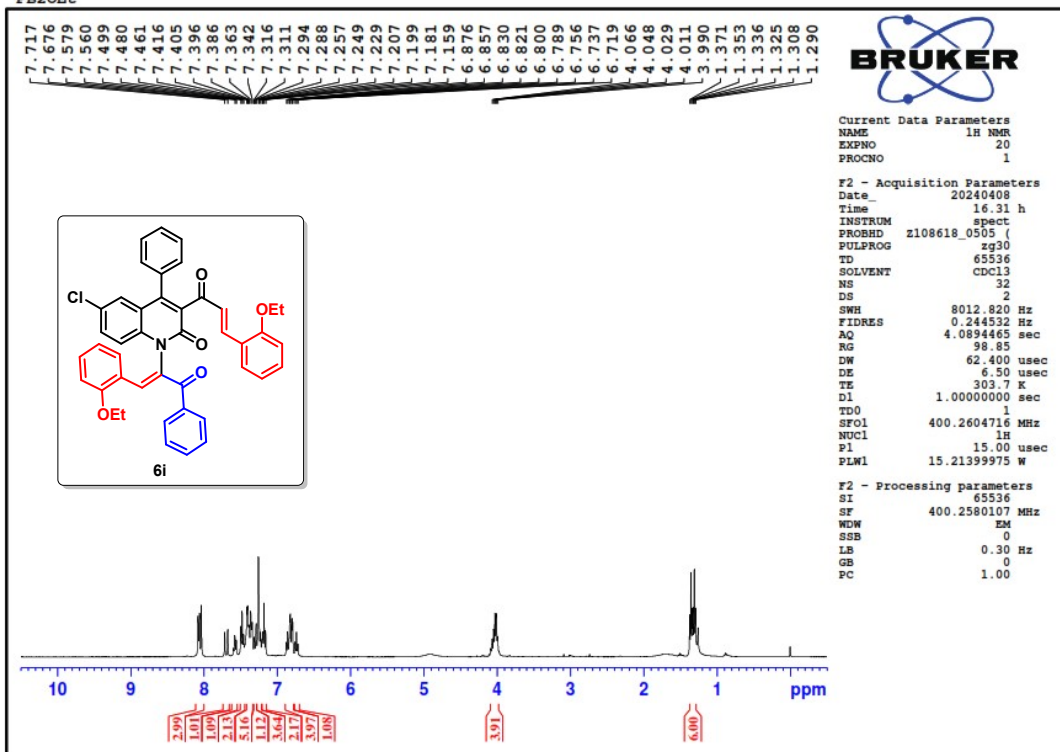


¹H and ¹³C NMR spectra of compound **6h** in CDCl₃

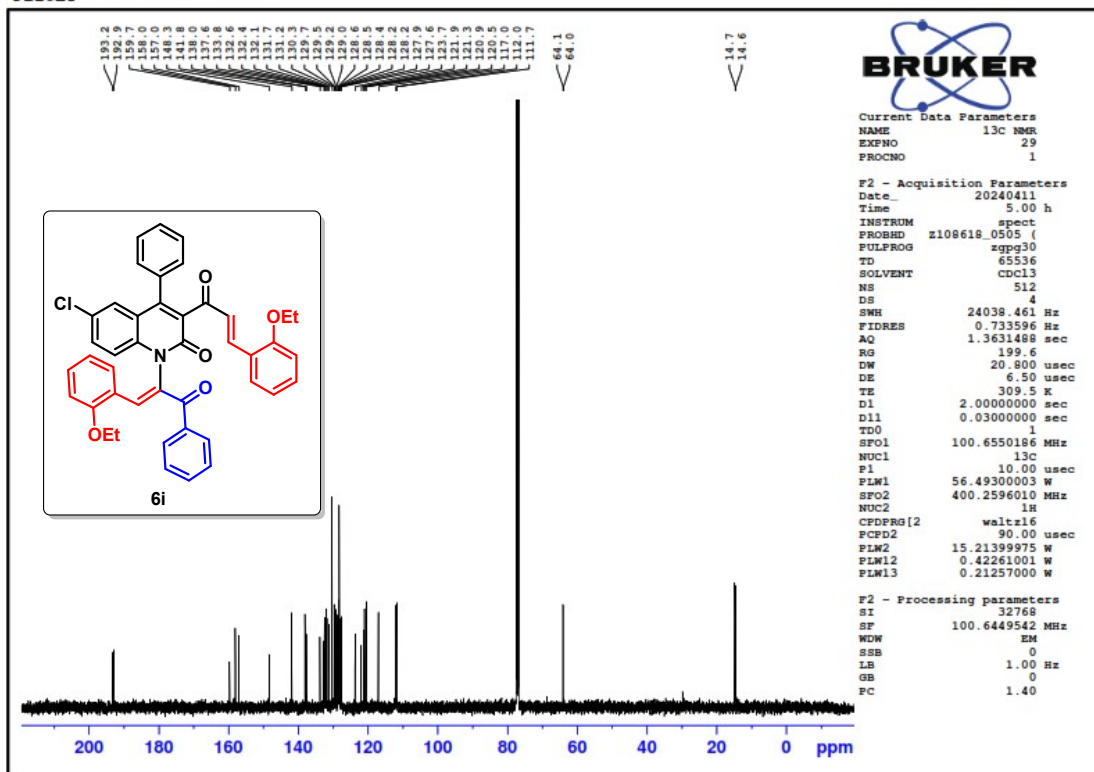


IR and HRMS spectra of compound **6h**

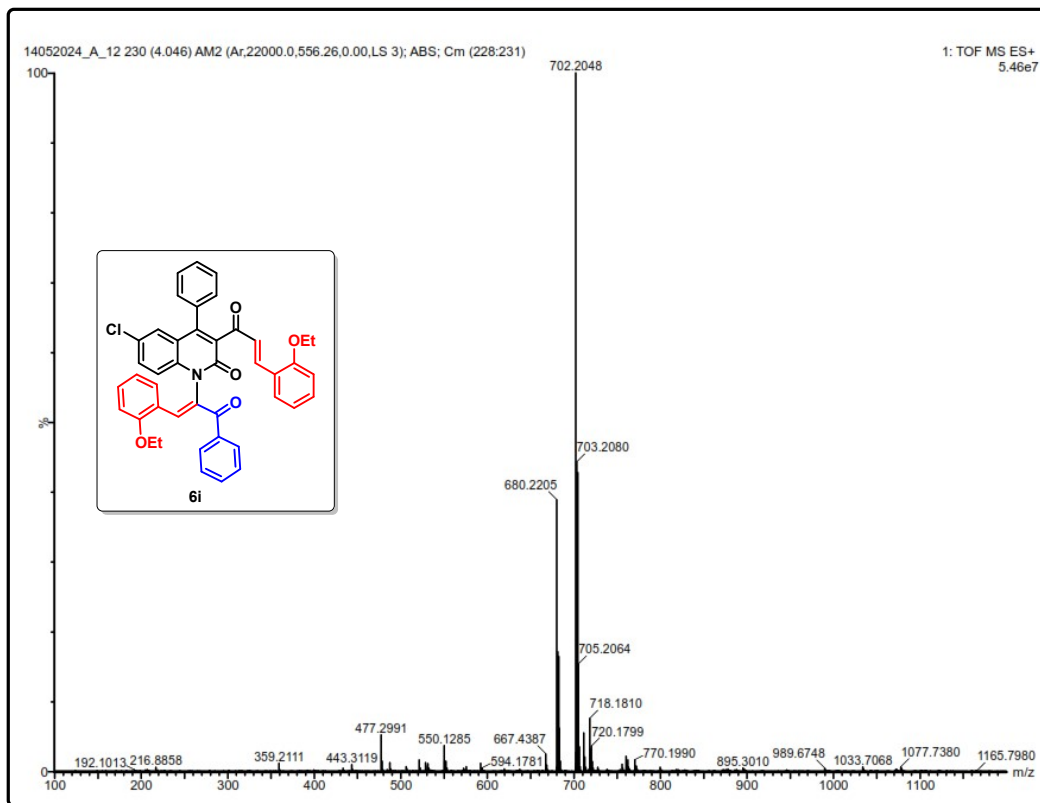
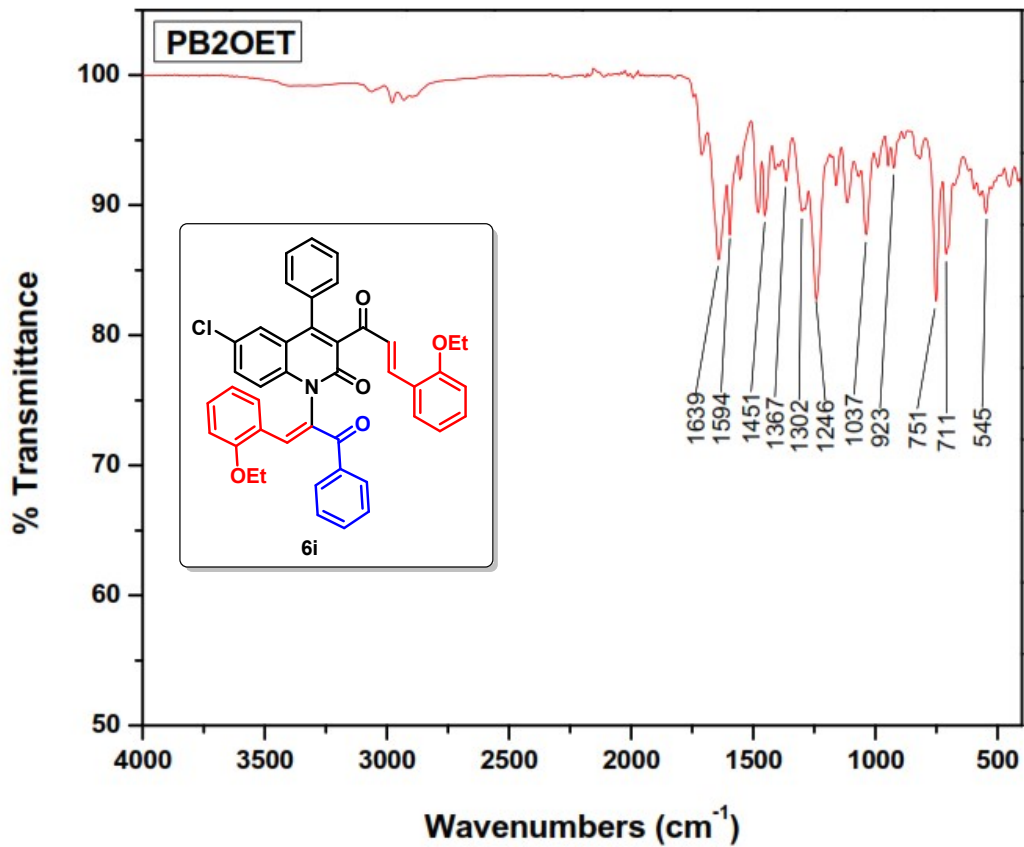
Signature SIF VIT VELLORE
PB2OEt



Signature SIF VIT VELLORE
PB2OEt

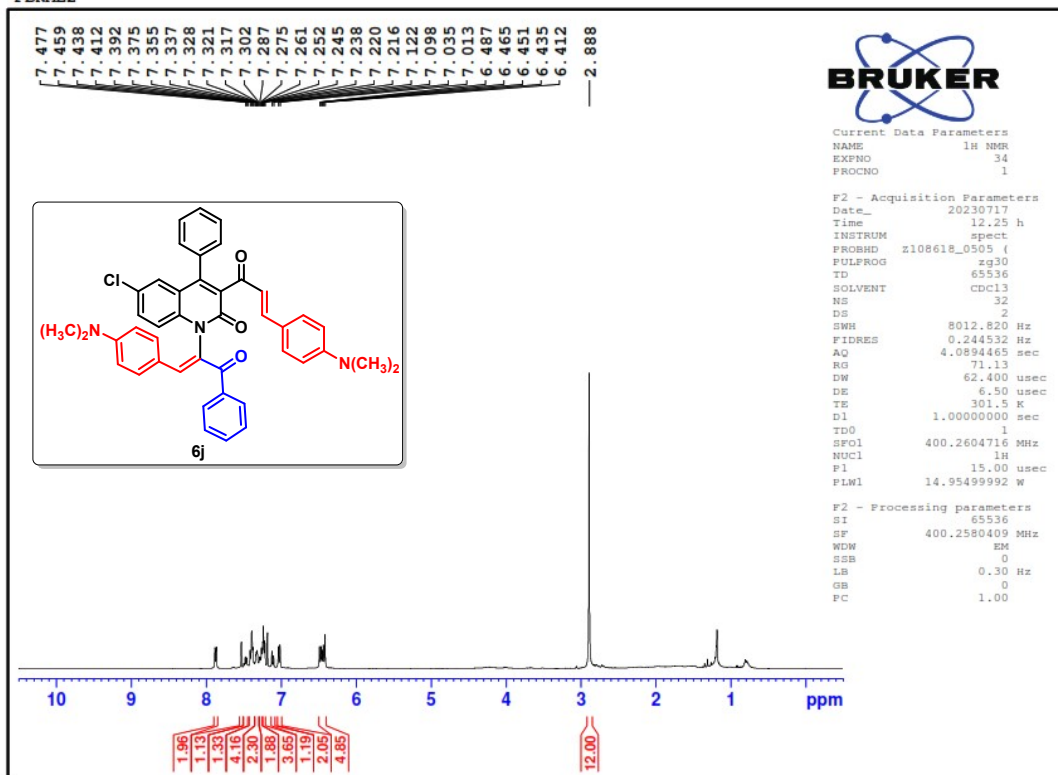


H and ¹³C NMR spectra of compound **6i** in CDCl₃

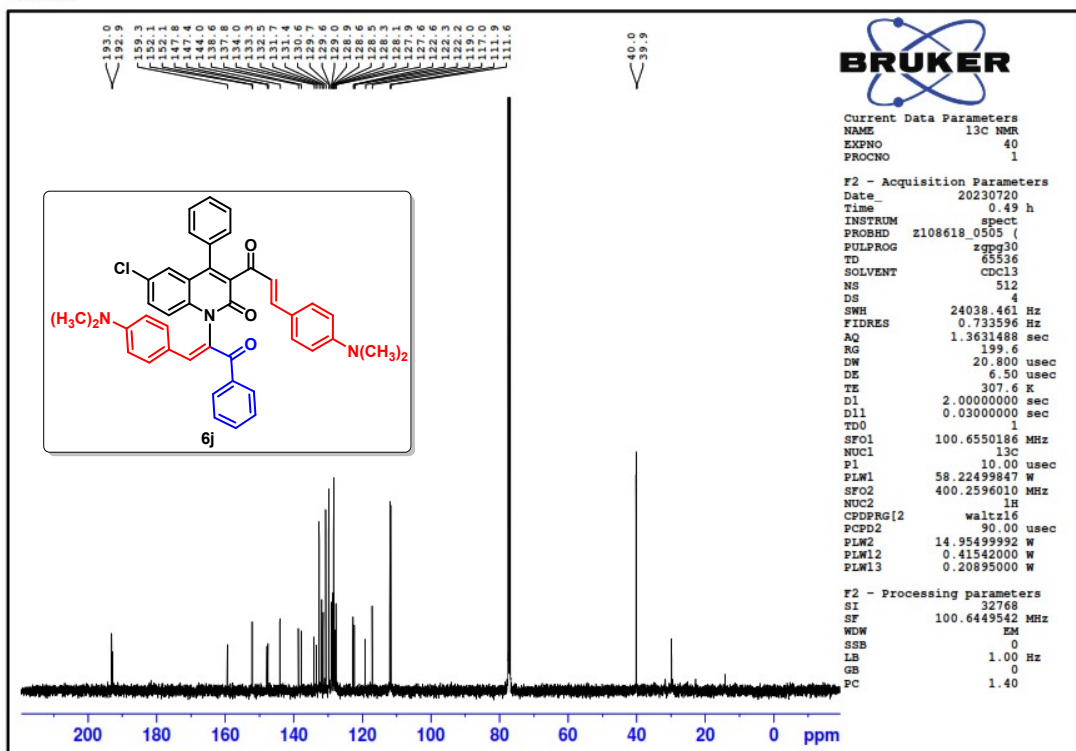


IR and HRMS spectra of compound **6i**

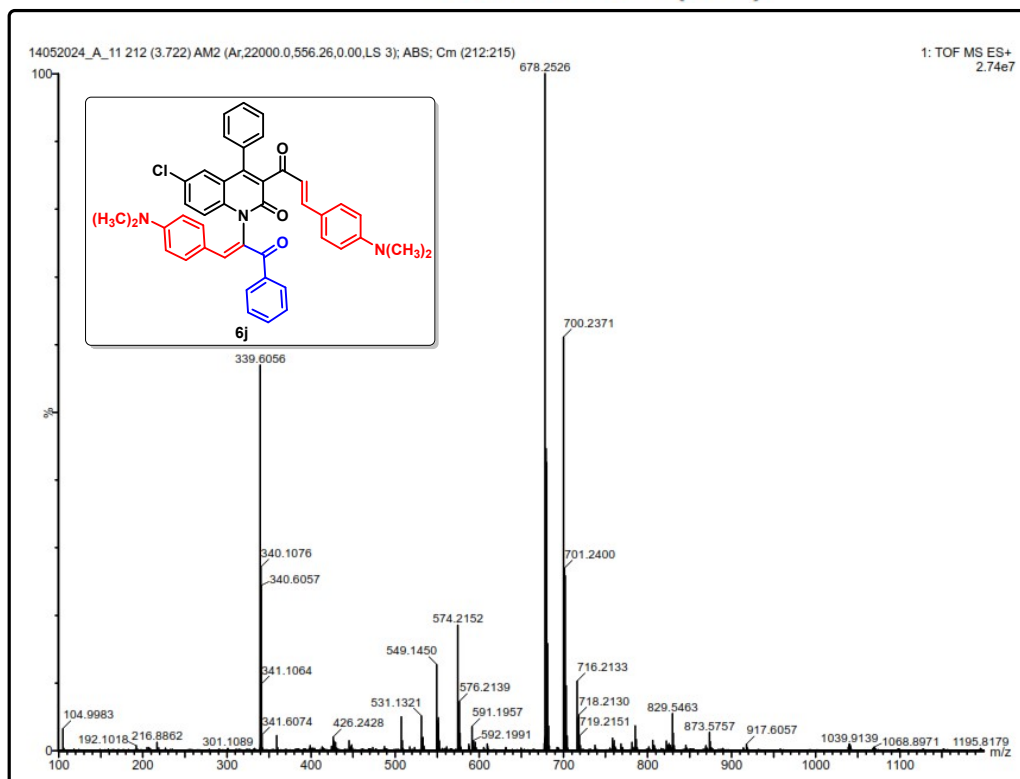
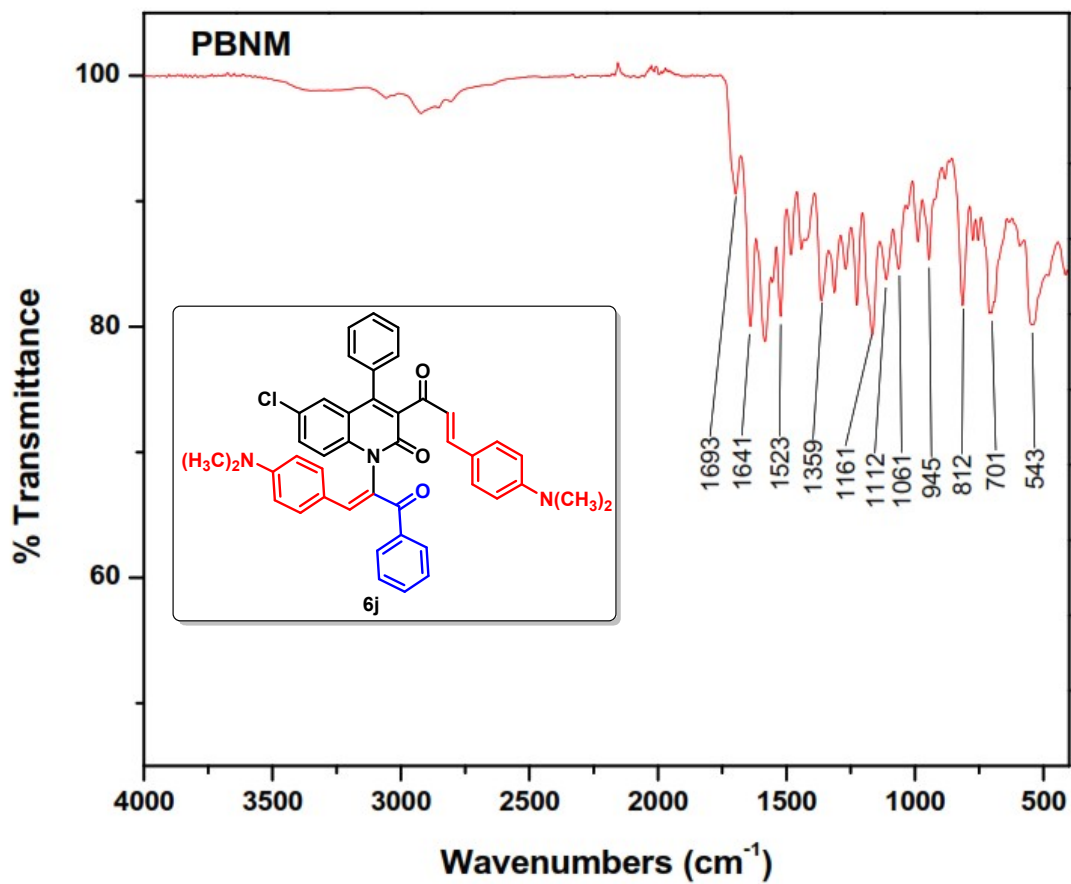
Signature SIF VIT VELLORE
PBNME2



Signature SIF VIT VELLORE
PBNME2

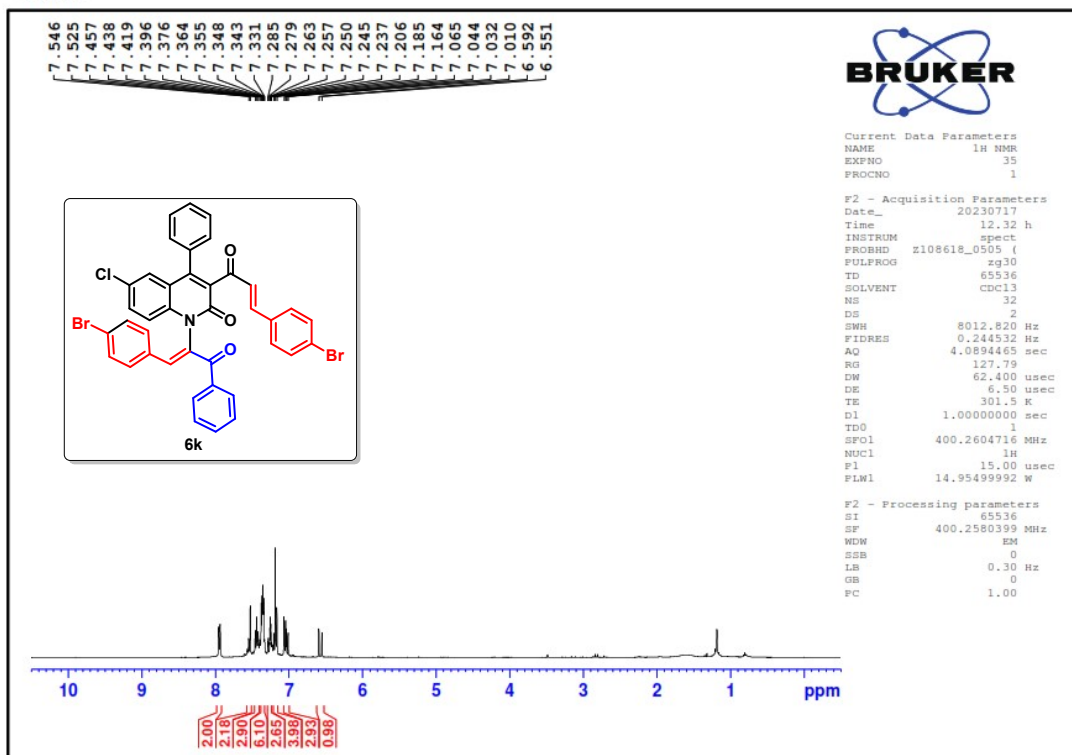


^1H and ^{13}C NMR spectra of compound **6j** in CDCl_3

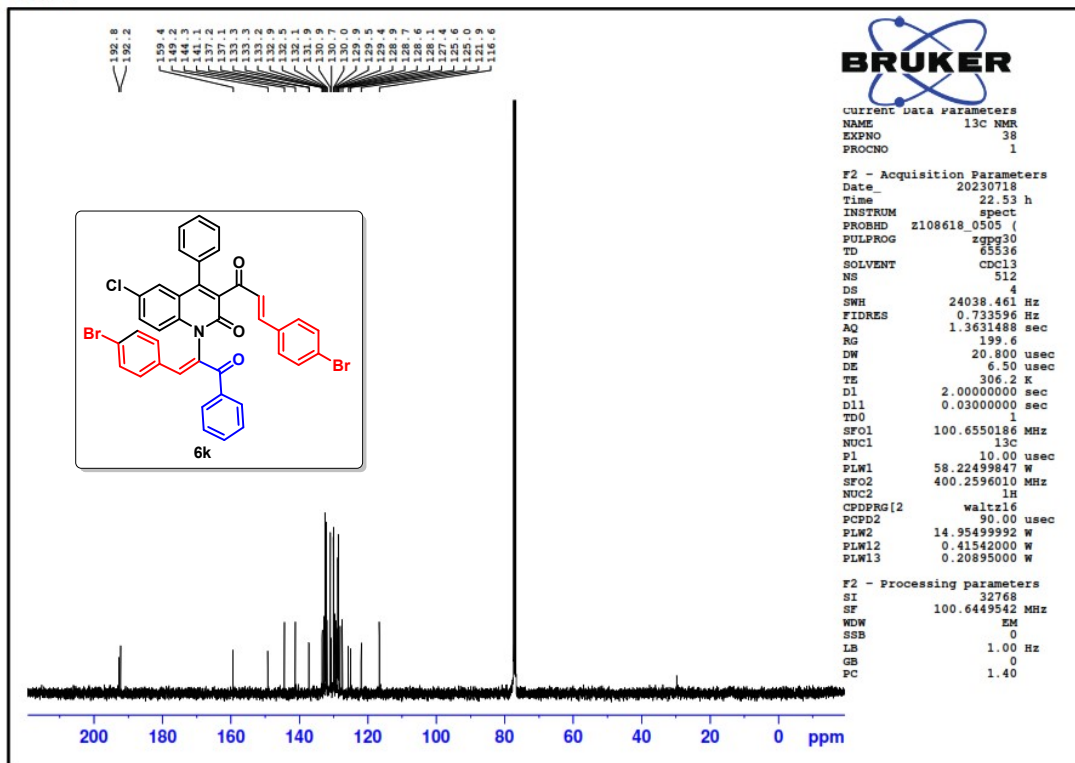


IR and HRMS spectra of compound **6j**

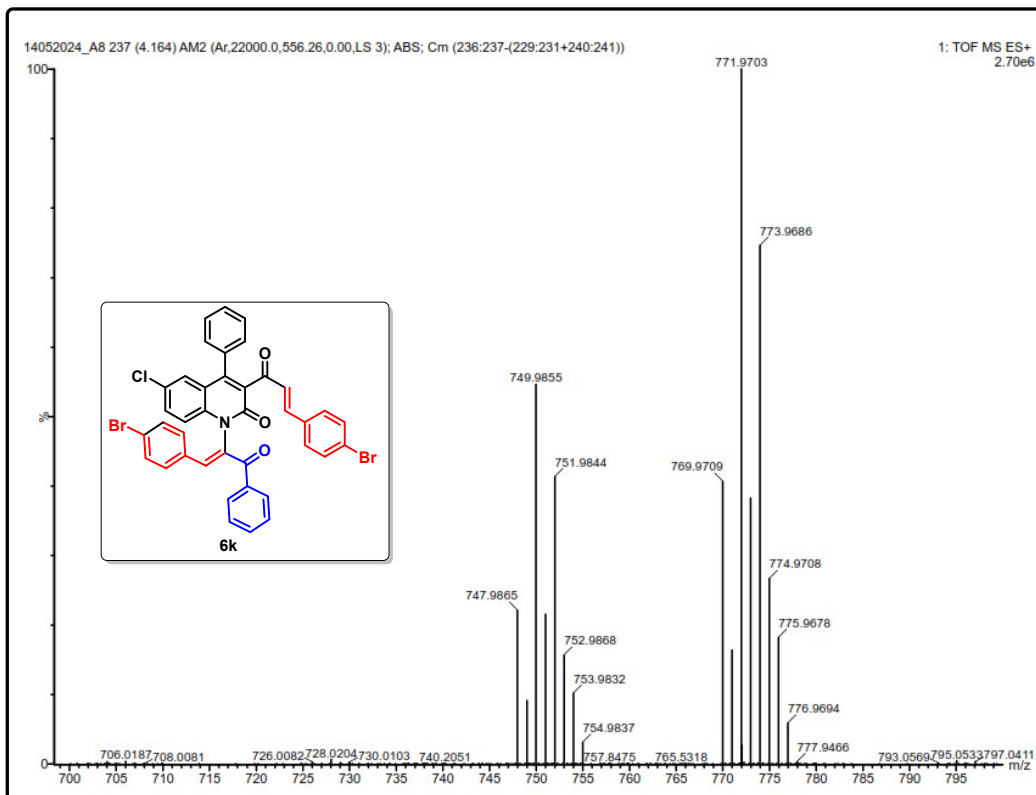
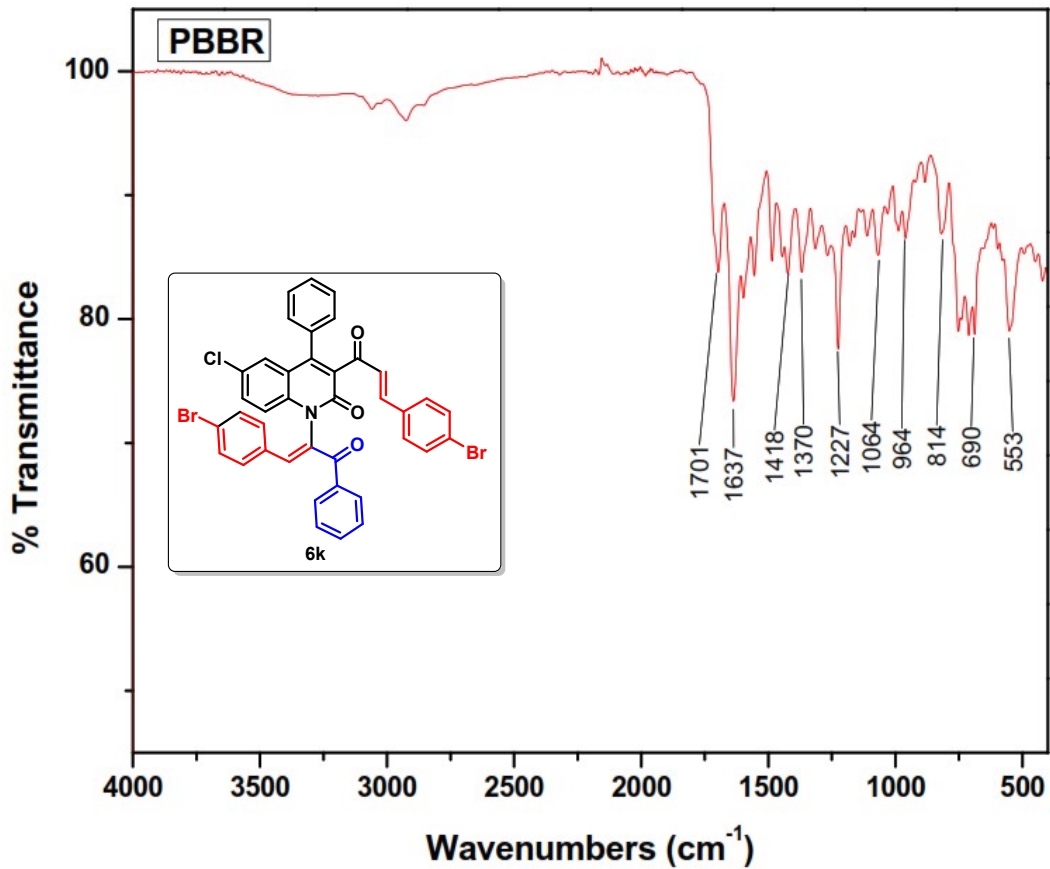
Signature SIF VIT VELLORE
PB4BR1



Signature SIF VIT VELLORE
PB4BR1

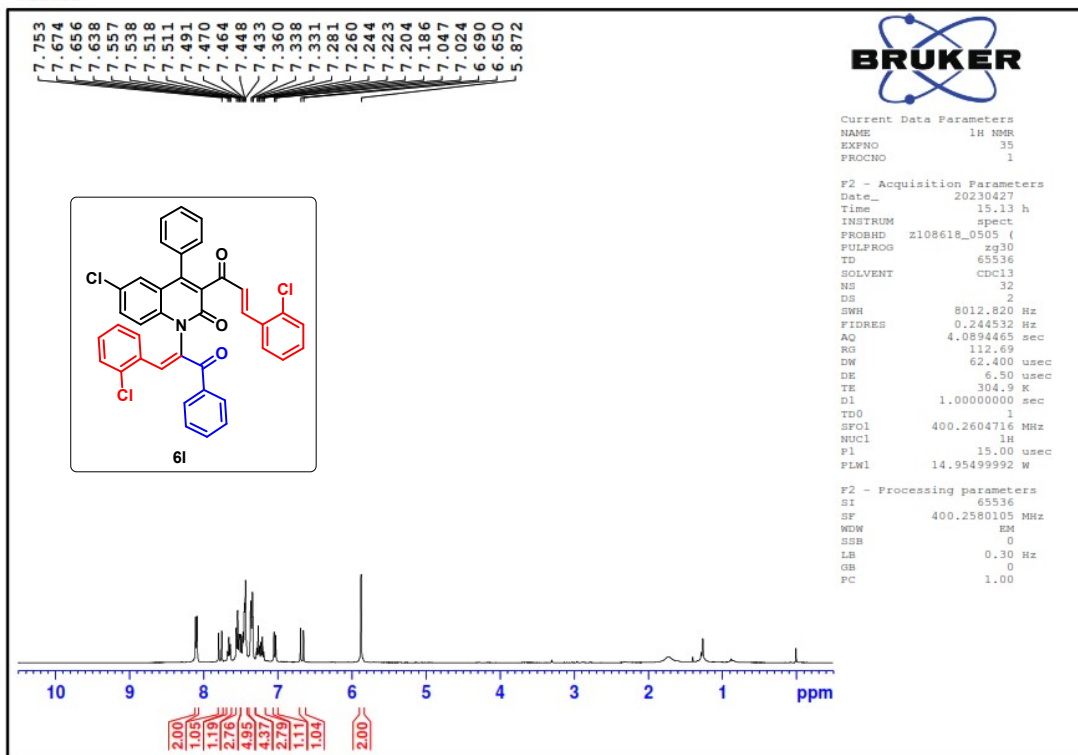


^1H and ^{13}C NMR spectra of compound **6k** in CDCl_3

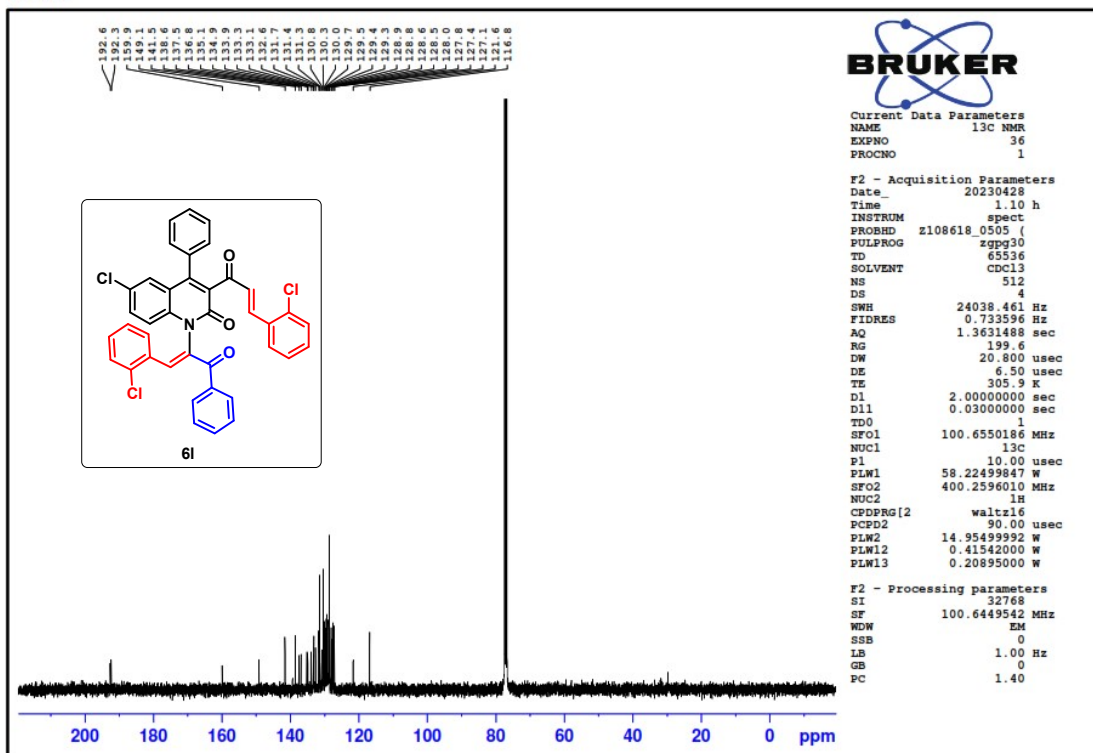


IR and HRMS spectra of compound **6k**

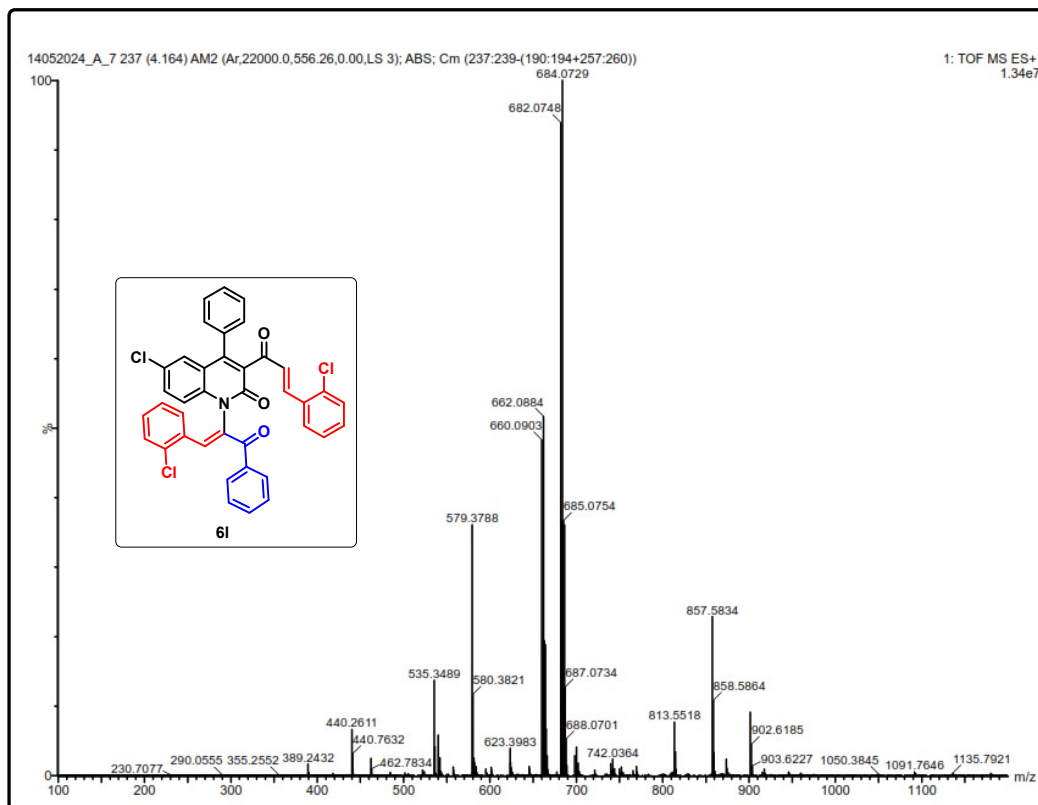
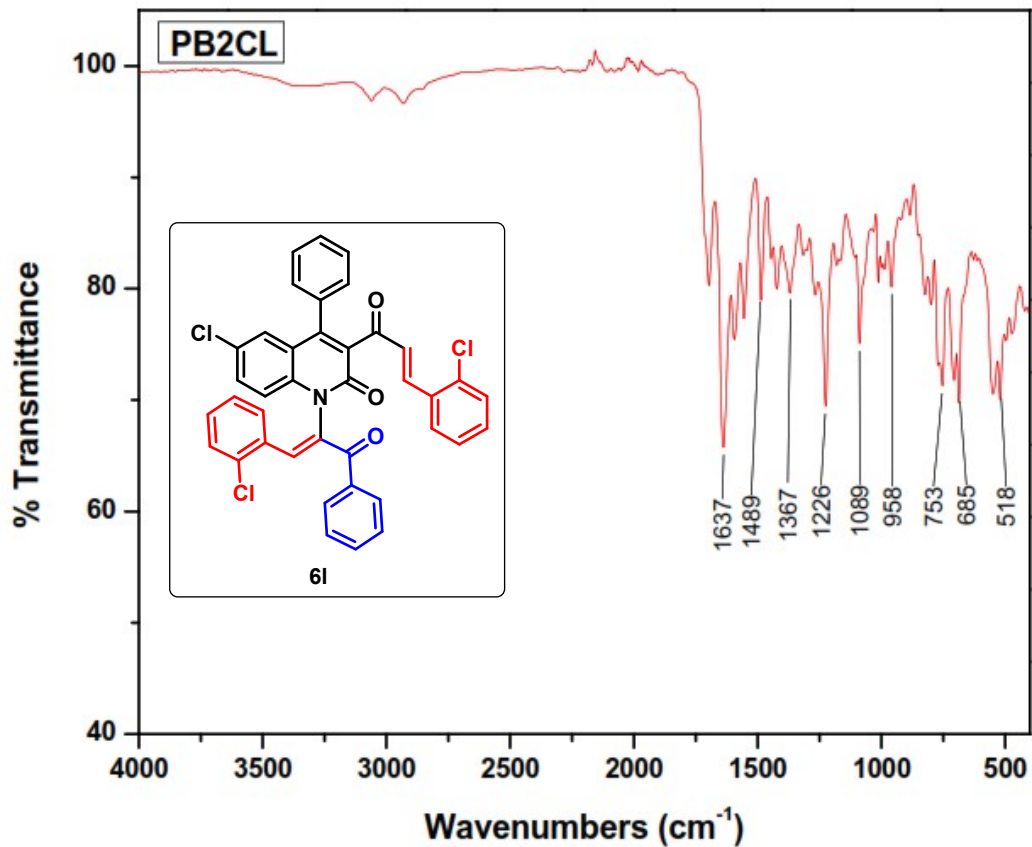
Signature SIF VIT VELLORE
PB2CL2



Signature SIF VIT VELLORE
PB2CL1

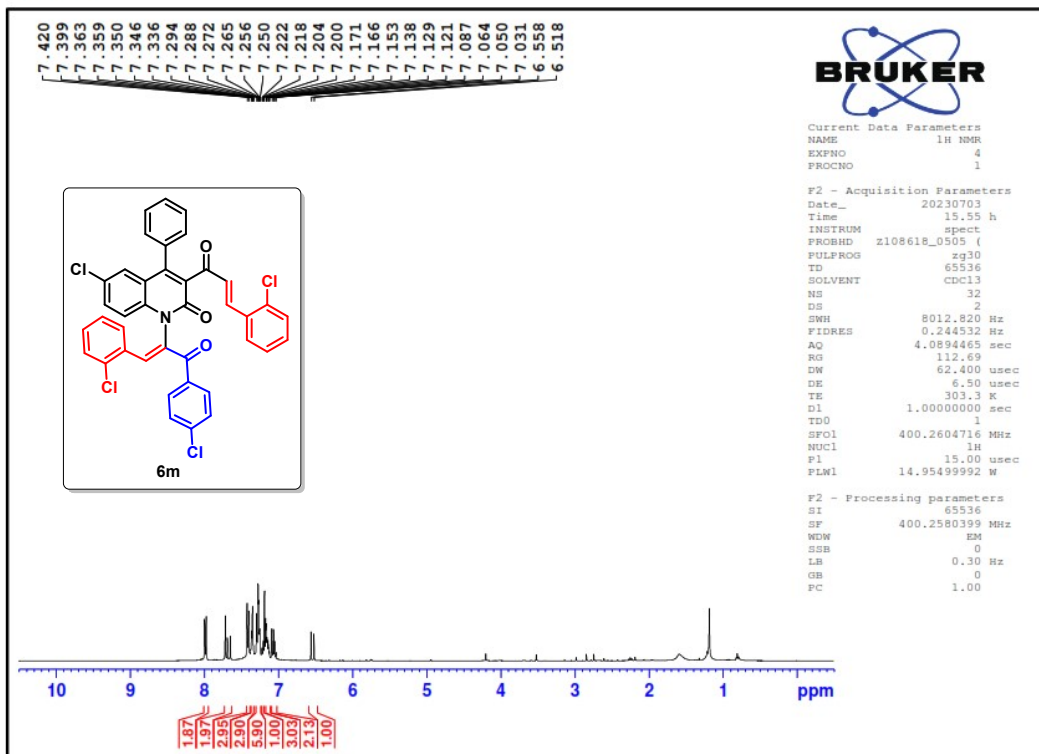


¹H and ¹³C NMR spectra of compound **6l** in CDCl₃

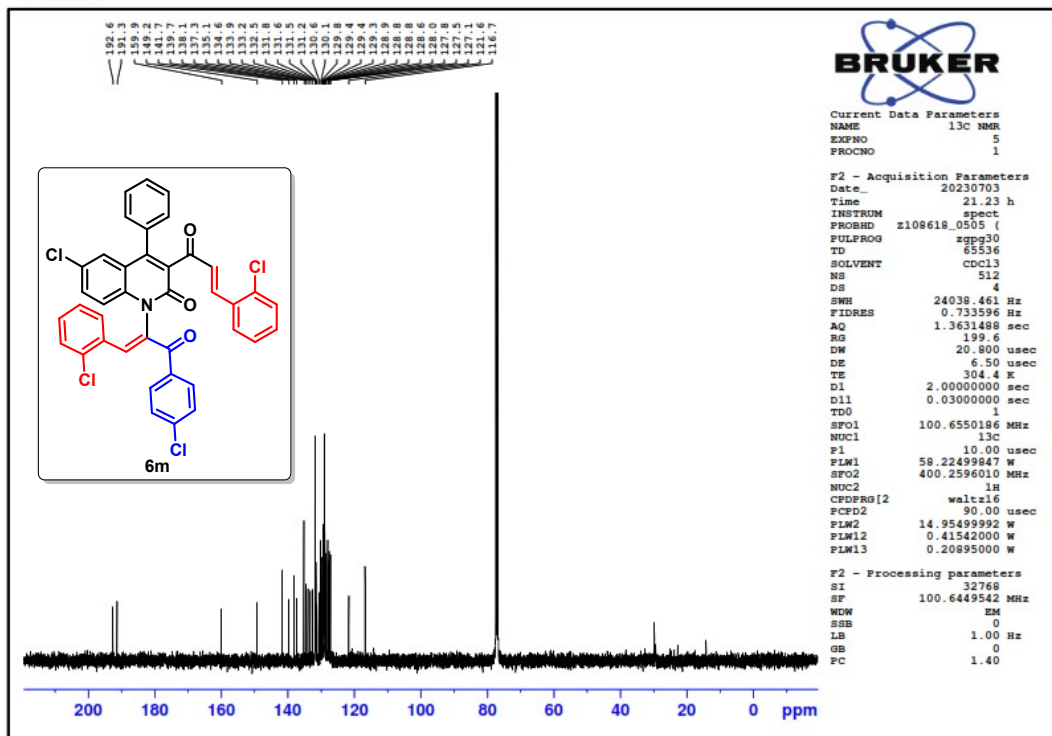


IR and HRMS spectra of compound **6l**

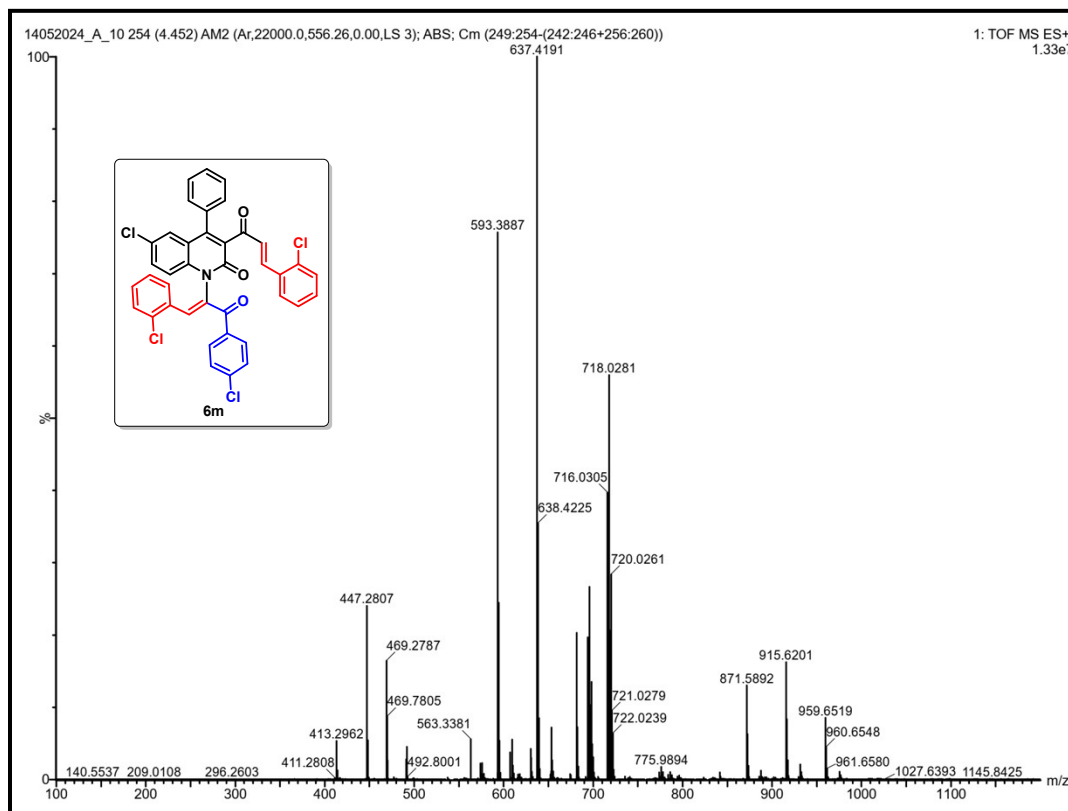
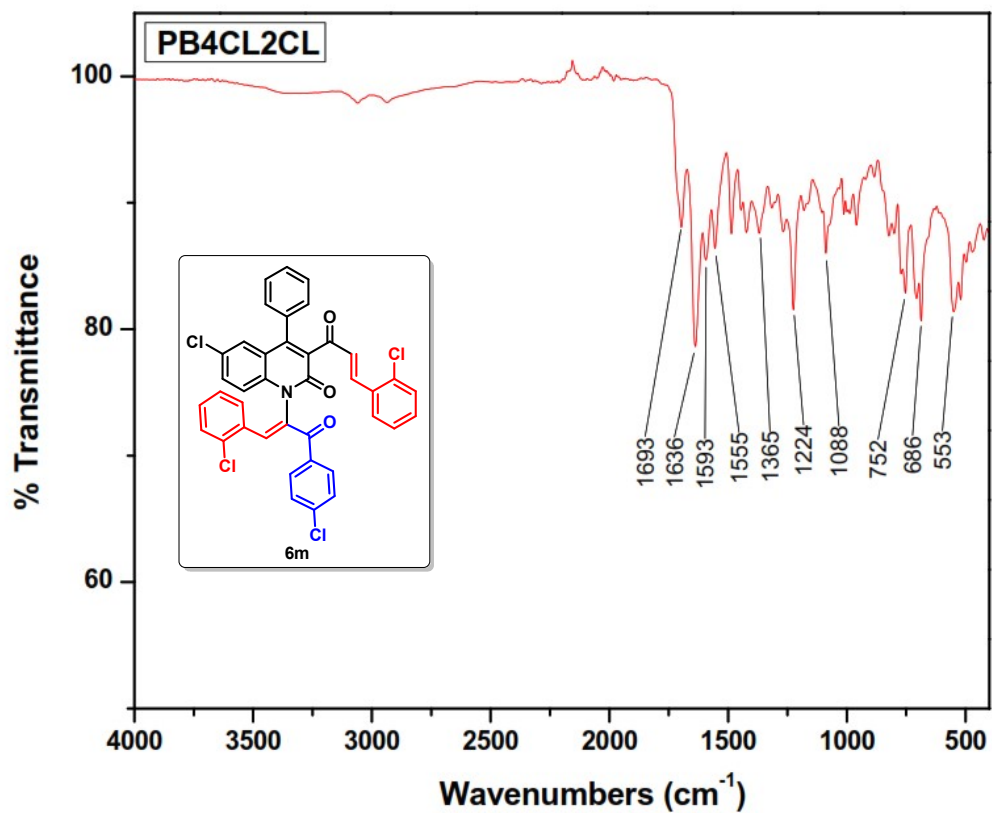
Signature SIF VIT VELLORE
4CLPB2CL



Signature SIF VIT VELLORE
4CLPB2CL

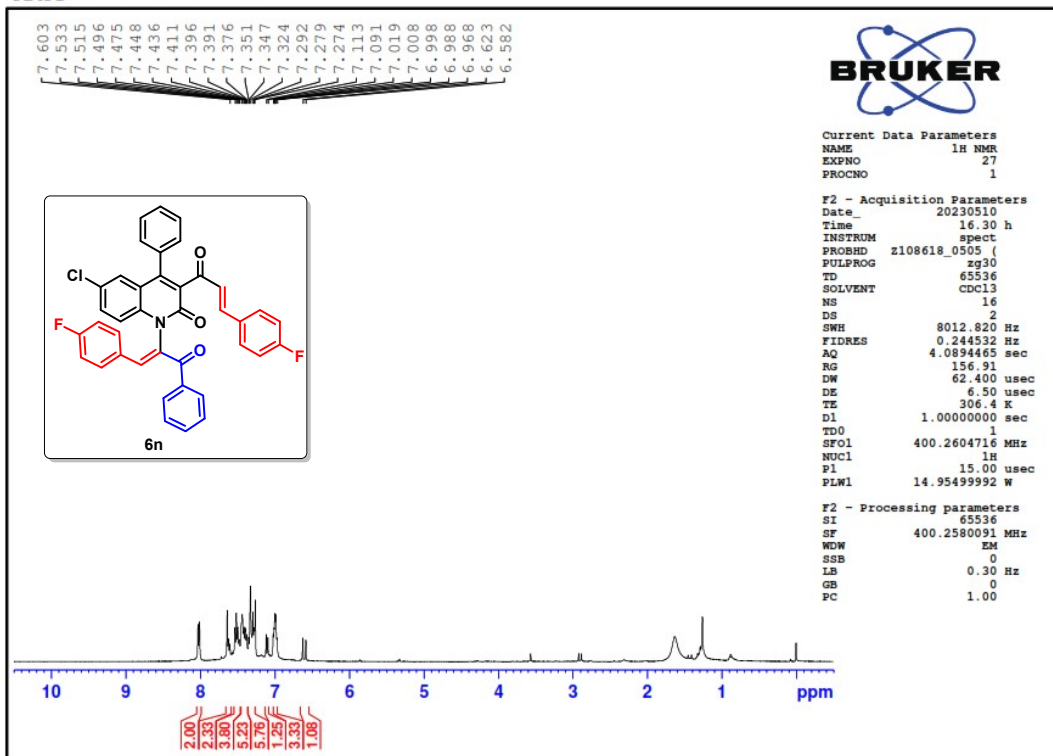


¹H and ¹³C NMR spectra of compound **6m** in CDCl₃

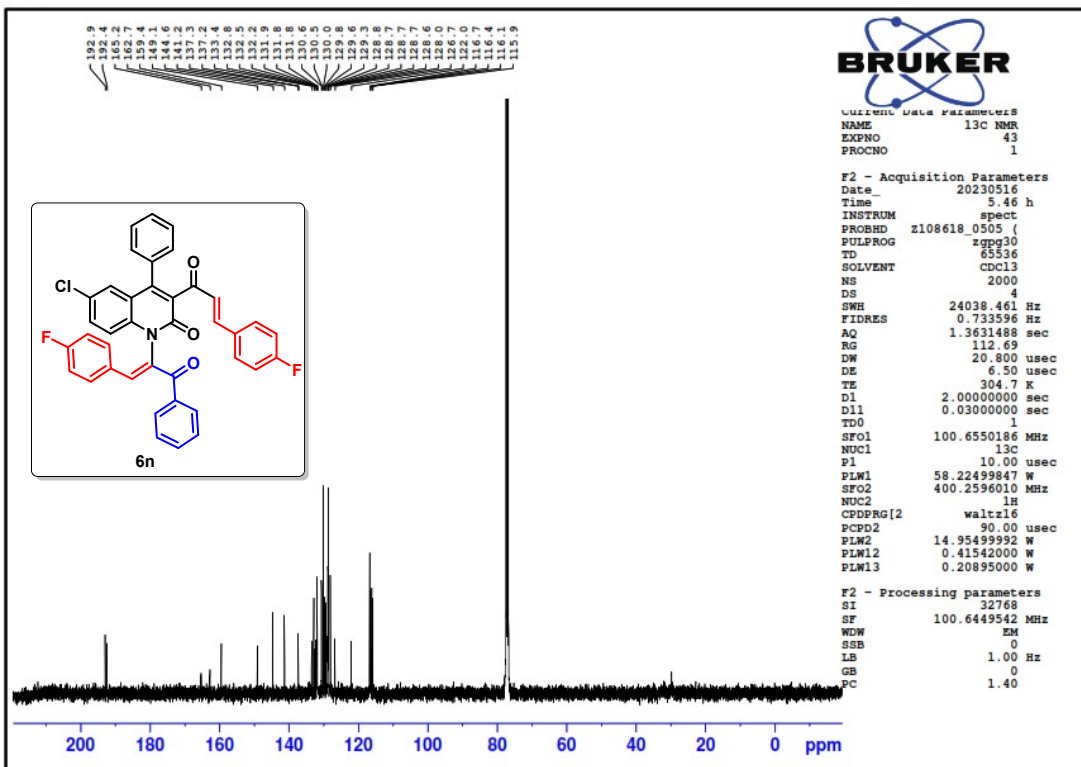


IR and HRMS spectra of compound **6m**

Signature SIF VIT VELLORE
PB4FI

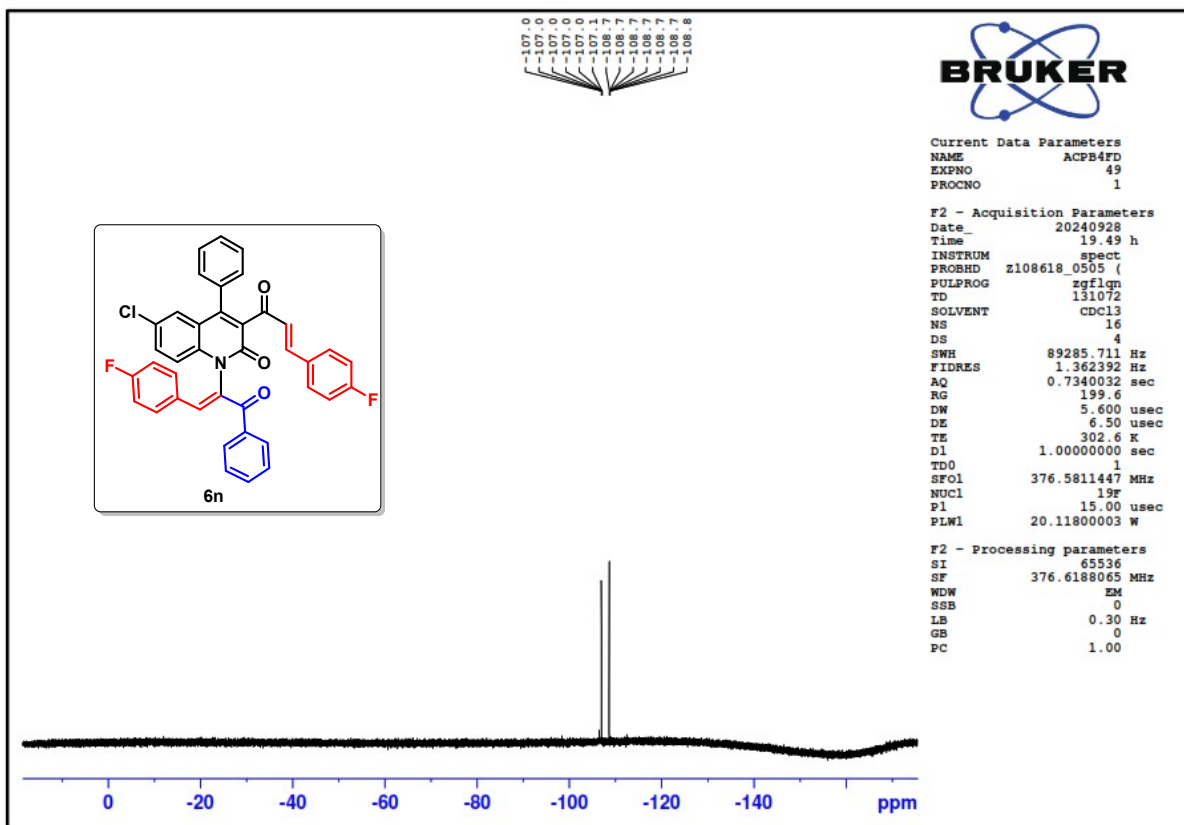


Signature SIF VIT VELLORE
PB4F7

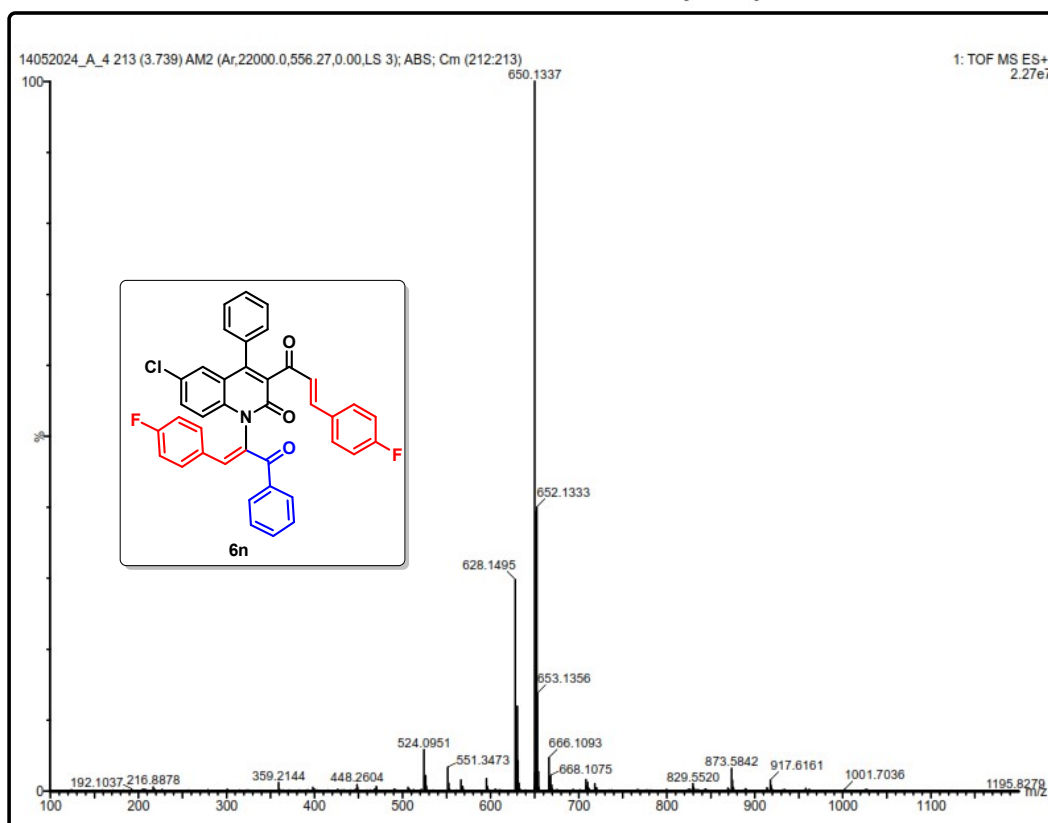
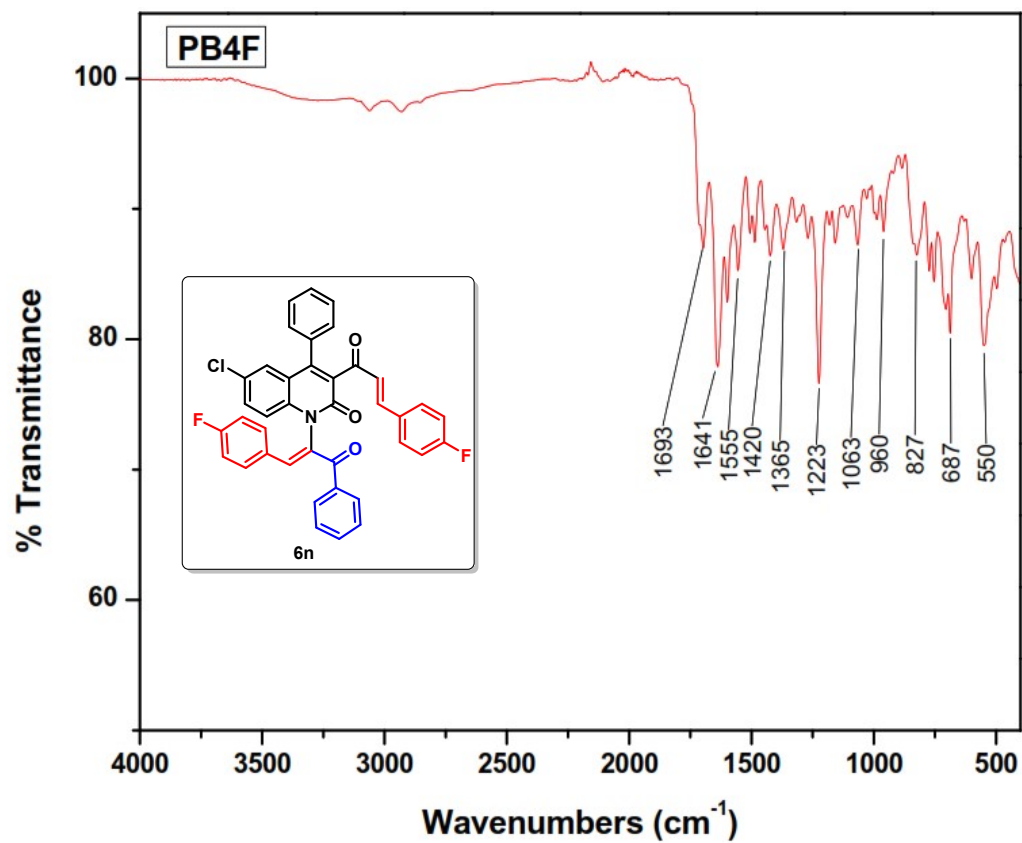


^1H and ^{13}C NMR spectra of compound **6n** in CDCl_3

Signature SIF VIT VELLORE
ACPB4F

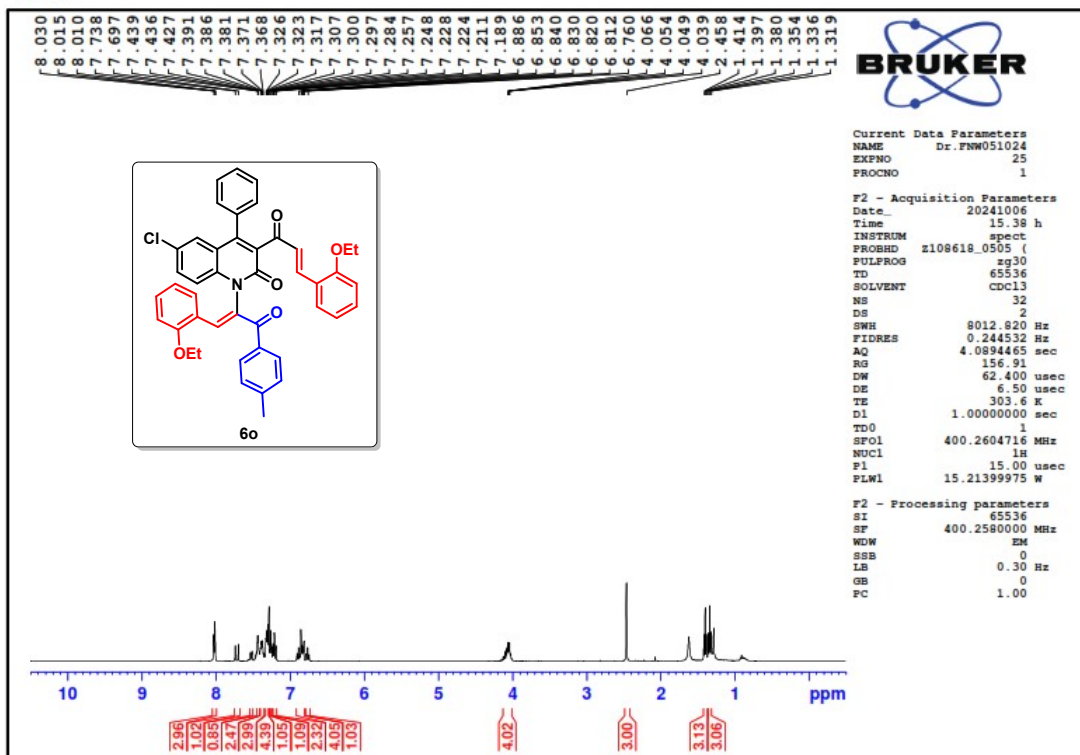


¹⁹F spectra of compound **6n**

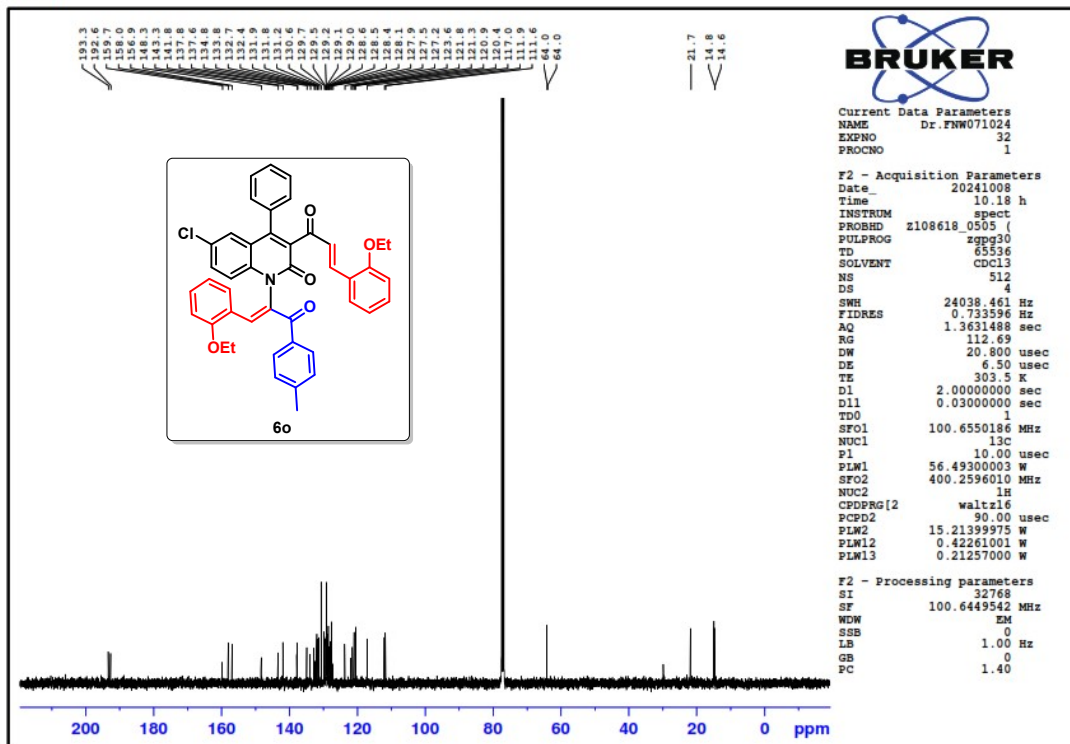


IR and HRMS spectra of compound **6n**

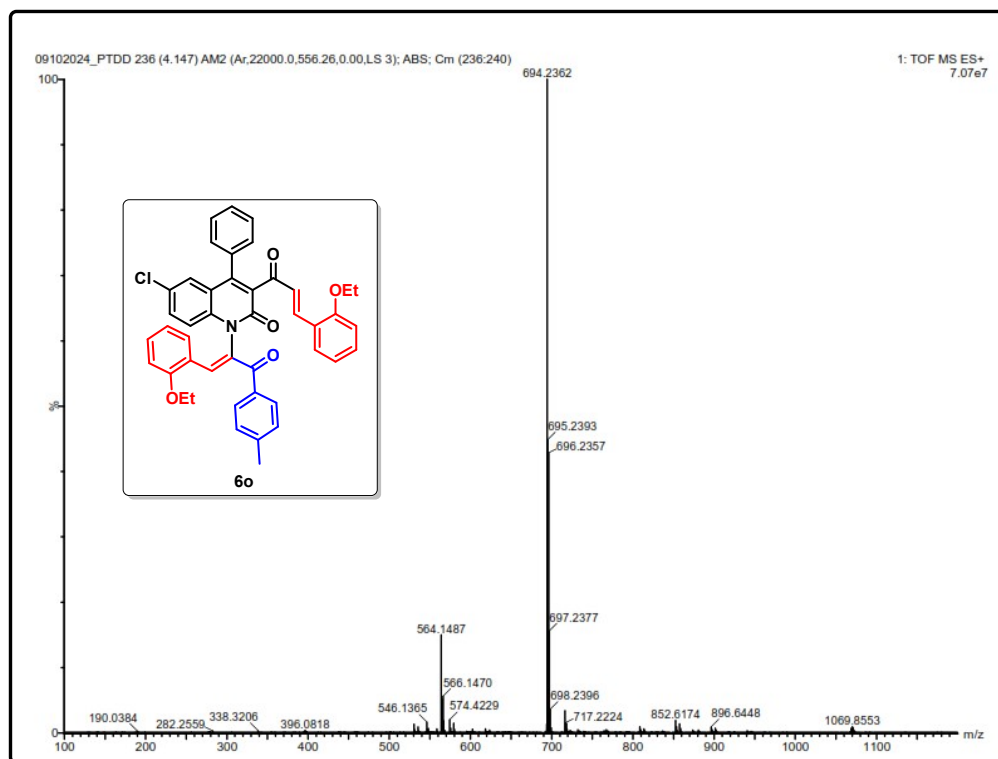
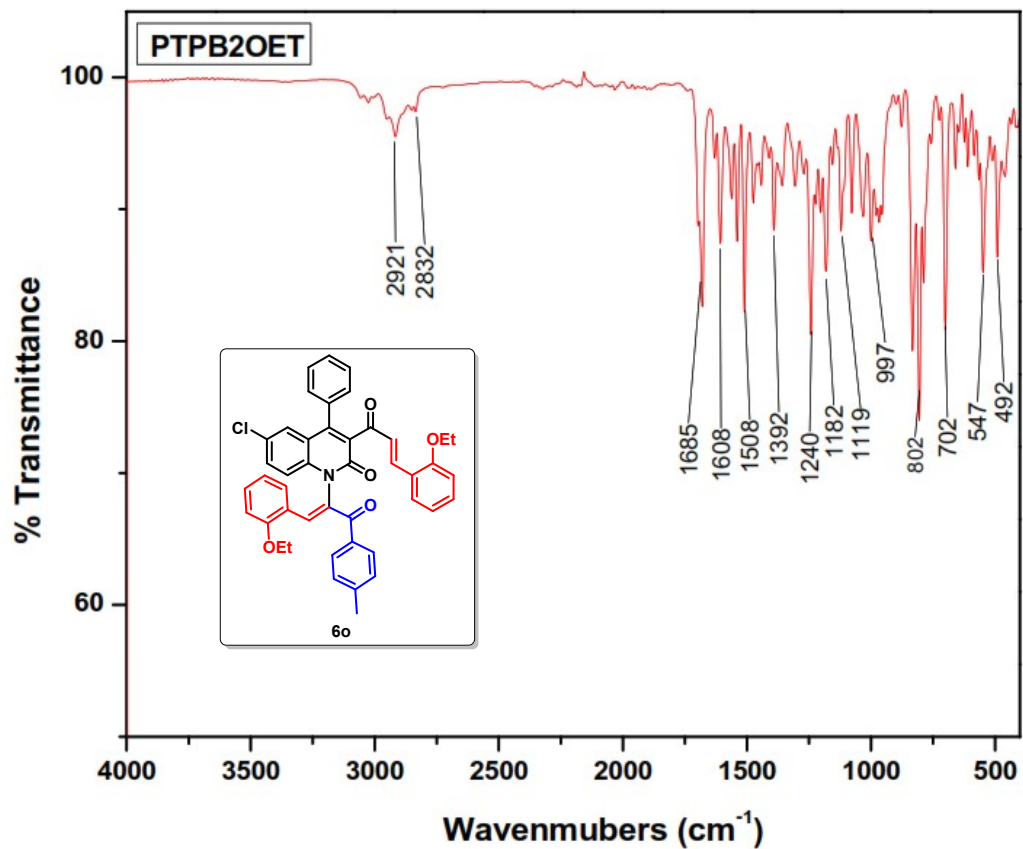
Signature SIF VIT VELLORE
PBPTP



Signature SIF VIT VELLORE
PBPTP

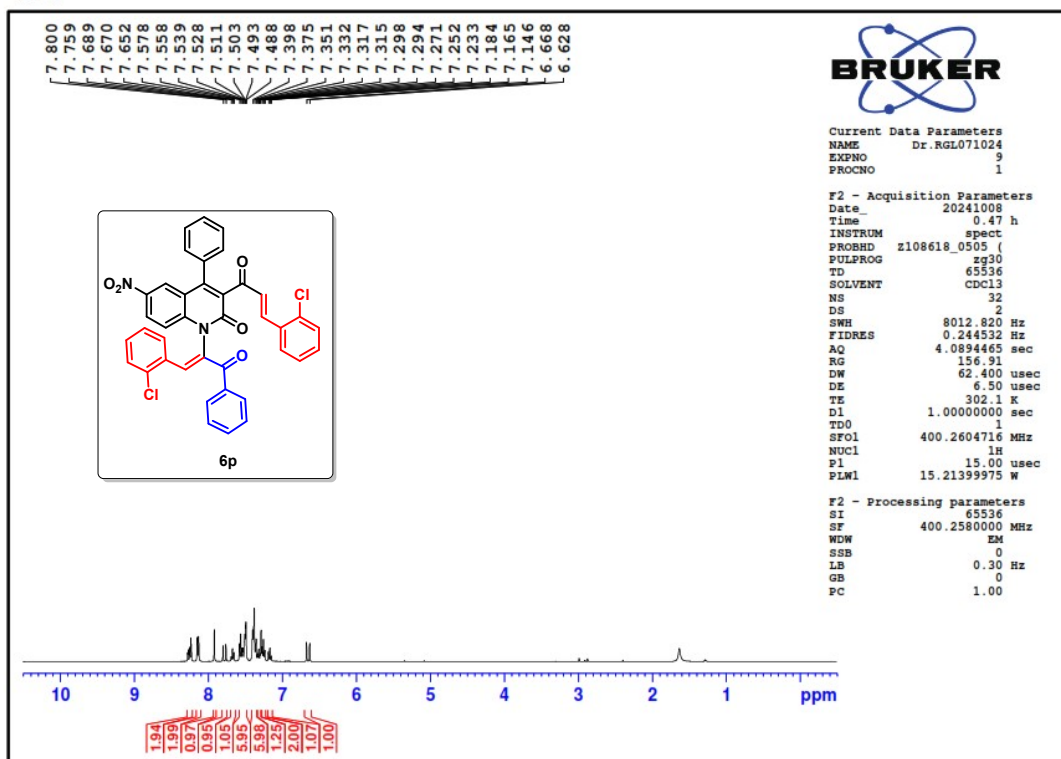


¹H and ¹³C NMR spectra of compound **6o** in CDCl₃

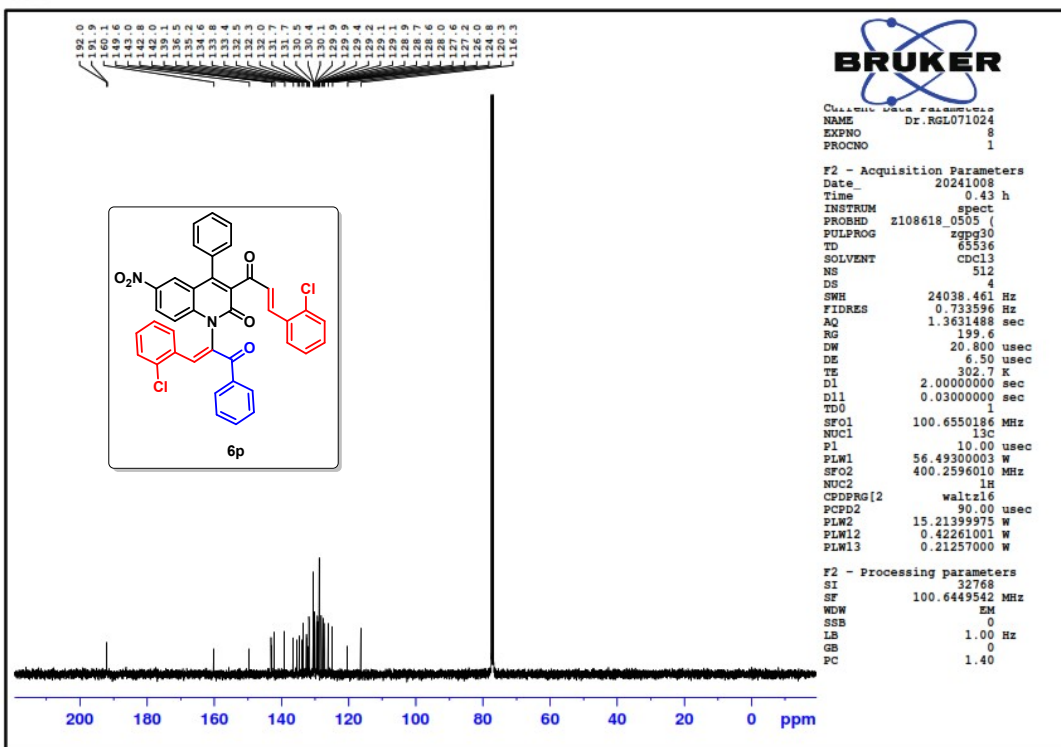


IR and HRMS spectra of compound **6o**

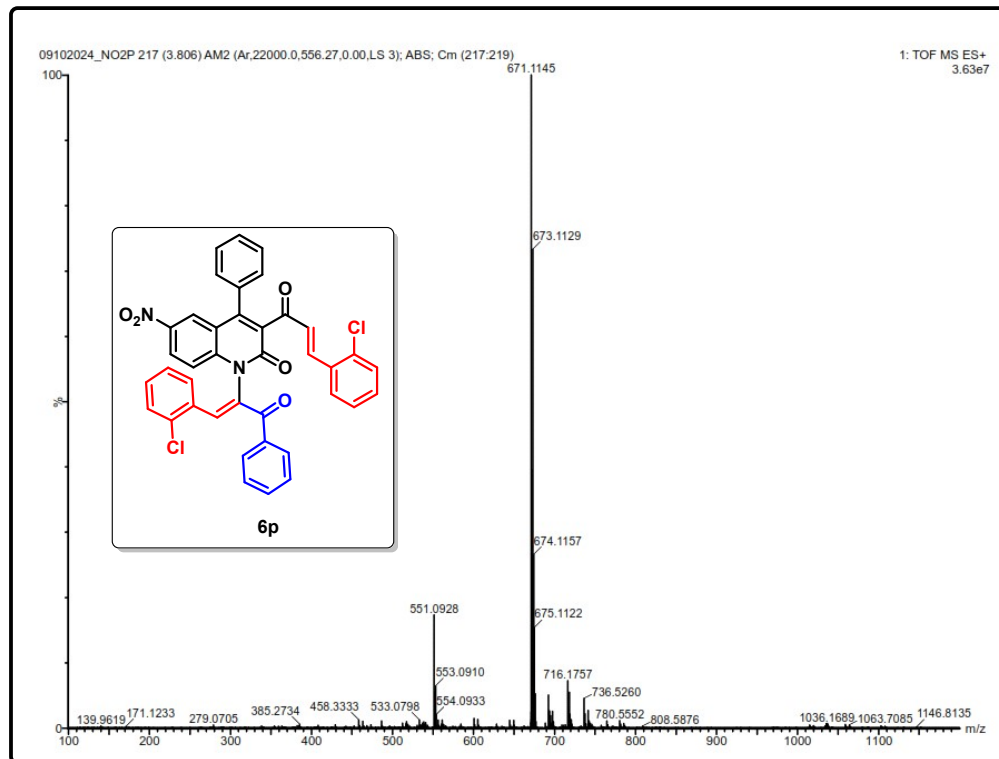
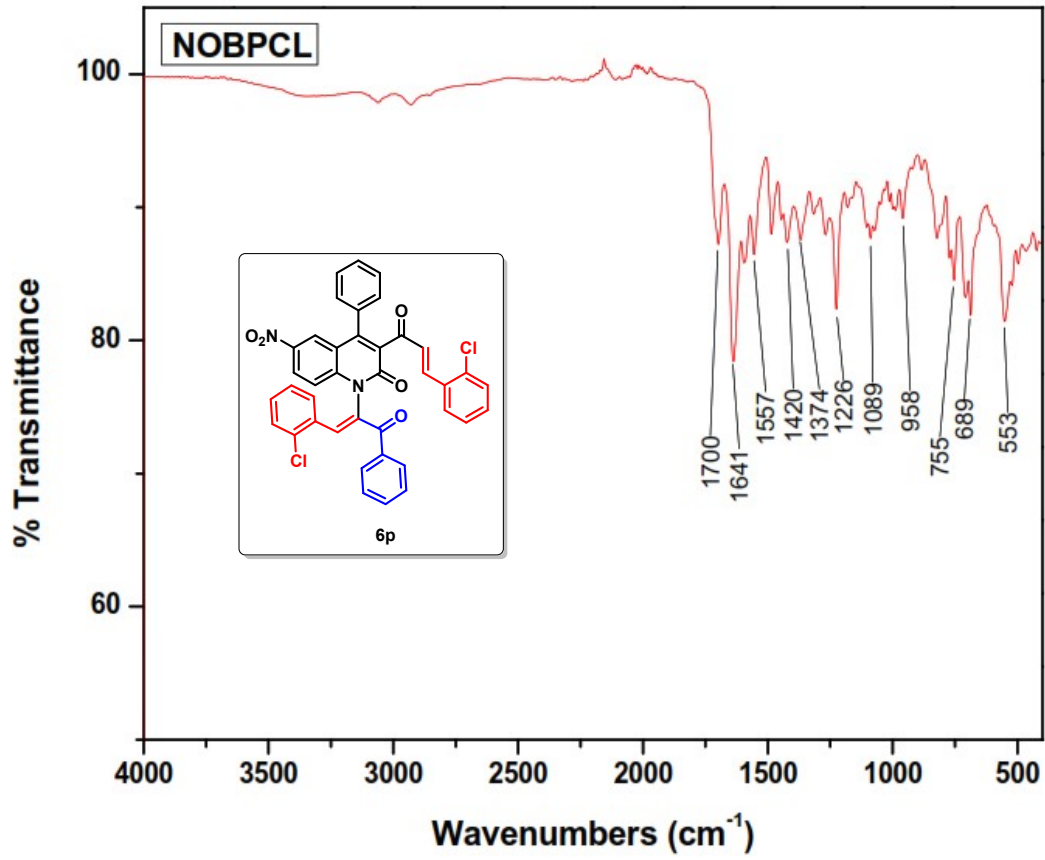
Signature SIF VIT VELLORE
NO2P



Signature SIF VIT VELLORE
NO2P

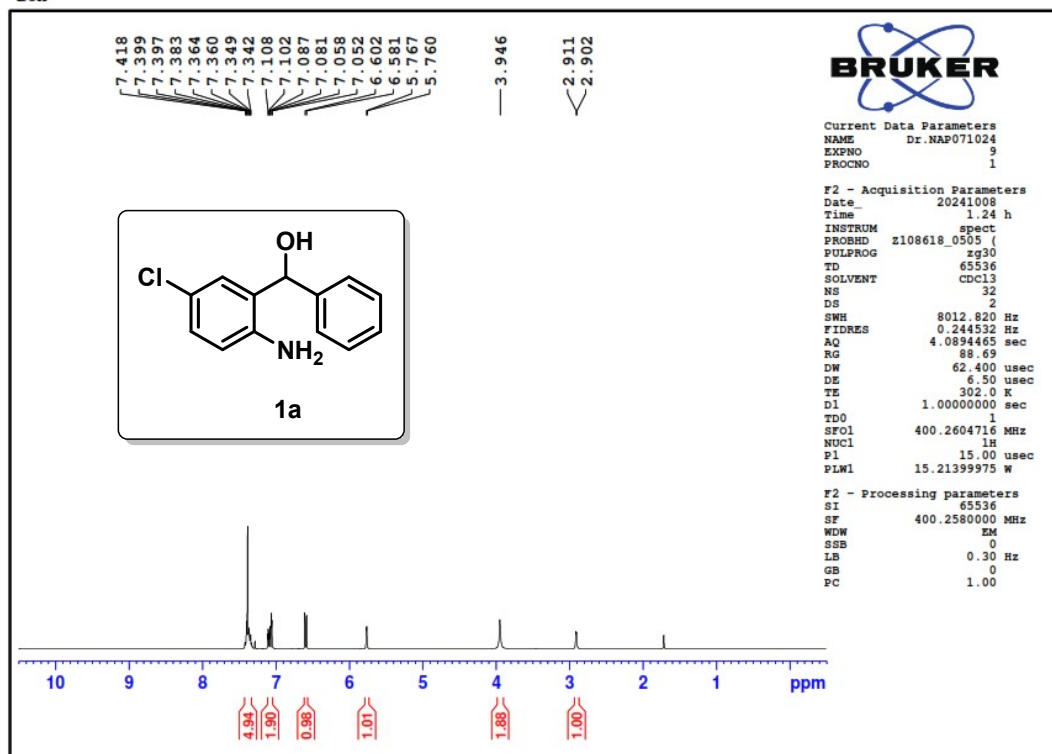


¹H and ¹³C NMR spectra of compound **6p** in CDCl₃

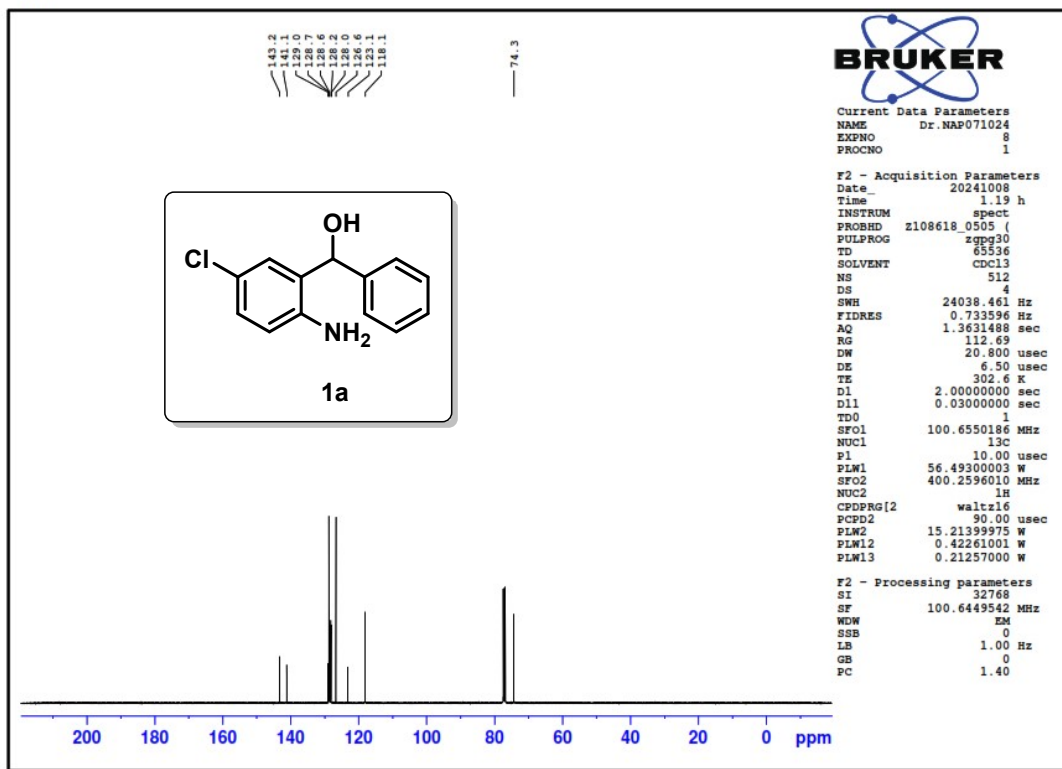


IR and HRMS spectra of compound **6p**

Signature SIF VIT VELLORE
BOH



Signature SIF VIT VELLORE
BOH



¹H and ¹³C NMR spectra of compound **1a** in CDCl₃

7. References:

1. V. Krishnakumar, N. G. Vindhya, B. K. Mandal and F.-R. Nawaz Khan, *Ind. Eng. Chem. Res.*, 2014, **53**, 10814–10819.
2. J.-C. Yang, M.-L. Liao, P.-G. Li and L.-H. Zou, *Green Chem.*, 2024, **26**, 9295–9299.