Supporting Information

Iodine promoted cyclization of *N,N′*-diphenylthiocarbamides with enaminones：a protocol for the synthesis of poly-substituted 2-iminothiazolines

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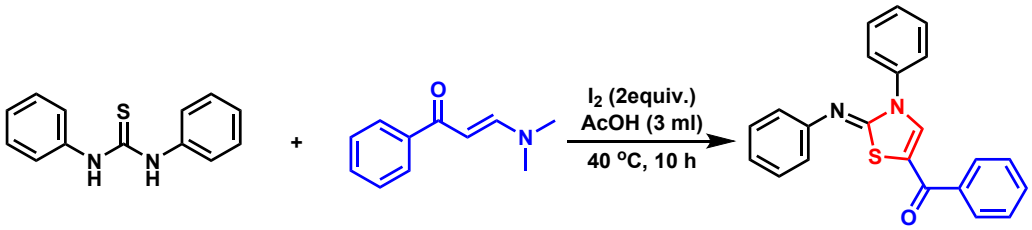
Table of Contents

1. General information

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise stated. Yields refer to isolated compounds estimated to be >95% pure as determined by ^{1}H NMR and capillary GC analysis. NMR spectra were recorded on a Bruker AM400 NMR instrument in $CDCl_3$ or DMSO-d_6 using TMS as an internal standard. Chemical shifts are given in ppm, and coupling constants (J) are given in Hz. Infrared spectra (IR) were recorded from 4000 $cm^{-1}$to 400 cm^{-1}on a Thermo Fisher Scientific spectrum Nicolet IS50 FT-IR instrument. The main absorption peaks are reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a Agilent 1290 HPLC-6545B Q-TOF mass instrument (ESI). All melting points were determined on a RY-1G melting point instrument without correction. TLC was performed using aluminum plates coated with SiO_2 (Merck 60, F-254) and visualized with UV light at 254 nm. Column chromatography was performed on silica gel (200−300 mesh) with PE (petroleum ether)/EtOAc (ethyl acetate) as eluent.

2. Scope of the [3 + 2] Cyclization Affording 2-Iminothiazoline

2.1. General Procedure for the Synthesis of 3a

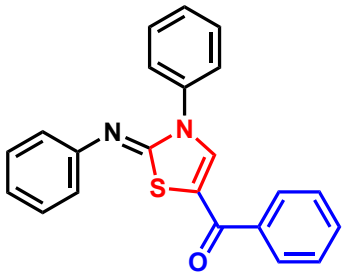


1a **2a** **3a**

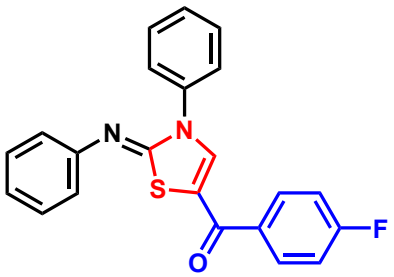
A mixture of *N,N'*-diphenylthiocarbamide **1a** (0.5 mmol, 0.114 g, 1 equiv.), enaminone **2a** (0.6 mmol, 0.105 g, 1.2 equiv.) and I_2 (1 mmol, 0.254 g, 2 equiv.) in AcOH (3.0 mL) was stirred and warmed at 40 °C using a heating mantle for 10 h, and the reaction was monitored by TLC until the starting material was consumed. The reaction was quenched with sat. $Na_2S_2O_3$ solution (3 mL) and then extracted with ethyl acetate. The crude solution was dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue

was purified by flash column chromatography to afford the desired product **3a** as a yellow solid (167.2 mg, 94% yield).

2.2. Characterization of 3

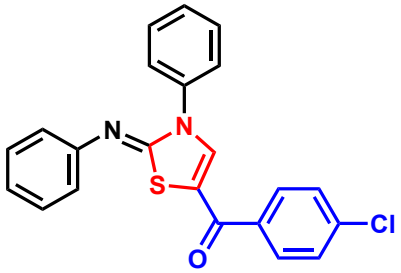


(Z)-phenyl(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3a)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3a** as a yellow solid (167.2 mg, 94% yield). mp: 164–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.4 Hz, 2H), 7.49–7.36 (m, 8H), 7.32–7.24 (m, 3H), 7.01 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.8, 155.6, 149.4, 137.5, 136.6, 136.4, 131.1, 128.6, 128.5, 127.7, 127.4, 127.2, 124.7, 123.2, 119.9, 116.8. IR (Diamond-ATR, neat): ν / cm^{-1} = 3064, 2925, 1621, 1587, 1567, 1494, 1447, 1383, 1287, 1235, 1204, 1178, 1134, 1099, 1069, 890, 825, 767, 710, 697, 683, 663, 628, 603, 528. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{22}H_{17}N_2OS^{+}$ 357.1056; Found 357.1062.

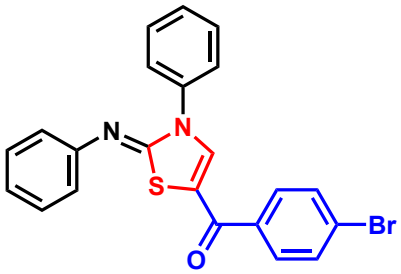


(Z)-(4-fluorophenyl)(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3b)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3b** as a yellow oil (182.7 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.34–7.30 (m, 3H), 7.25–7.17 (m, 3H), 6.99–6.93 (m, 3H), 6.90 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1,

164.0 (d, $J_{C\text{-}F}$ = 251.9 Hz), 155.3, 149.3, 137.3, 136.3, 132.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.6 (d, $J_{C\text{-}F}$ = 9.1 Hz), 128.5, 128.4, 127.4, 124.6, 123.2, 119.8, 116.4, 114.8 (d, $J_{C\text{-}F}$ = 21.5 Hz). IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 2850, 1617, 1570, 1493, 1382, 1297, 1270, 1229, 1201, 1155, 1095, 889, 848, 764, 752, 695, 589, 541. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{22}H_{16}FN_2OS^+$ 375.0962; Found 375.0969.

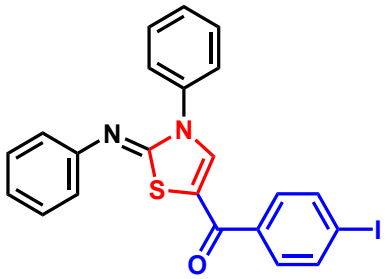


(Z)-(4-chlorophenyl)(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3c)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3c** as a yellow solid (172.2 mg, 88% yield). mp: 162–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 7.9 Hz, 2H), 7.39–7.35 (m, 3H), 7.33–7.28 (m, 3H), 7.24 (t, J = 7.9 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ183.3, 155.3, 149.3, 137.5, 137.4, 136.3, 134.8, 128.6, 128.6, 128.5, 128.0, 127.5, 124.7, 123.2, 119.8, 116.5. IR (Diamond-ATR, neat): ν / cm^{-1} = 3073, 1628, 1586, 1572, 1557, 1490, 1383, 1320, 1292, 1265, 1242, 1200, 1176, 1139, 1093, 1015, 889, 849, 824, 772, 749, 724, 699, 633, 561, 528, 492, 469. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{22}H_{16}ClN_2OS^+$ 391.0666; Found 391.0676.

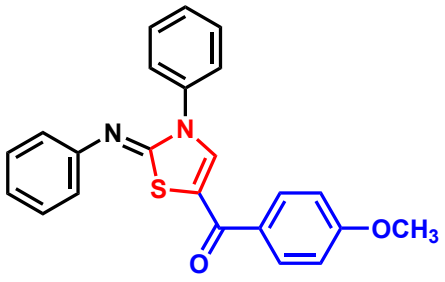


(Z)-(4-bromophenyl)(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3d)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3d** as a yellow oil (201.4 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.56–7.52 (m, 6H), 7.48–7.44 (m, 3H), 7.39–7.31 (m, 3H), 7.08 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 156.3, 150.2, 138.6, 137.1, 136.2, 131.9, 129.7, 129.6, 129.4, 128.5, 126.9, 125.6, 124.2, 120.8, 117.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 3073, 2918, 1625, 1571, 1556, 1490, 1397, 1381, 1320, 1264, 1242, 1200, 1176, 1139, 1070, 1011, 889, 846, 831, 772, 762, 747, 733, 697, 630, 526, 491. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{22}H_{16}BrN_2OS^+$ 435.0161; Found 435.0157.

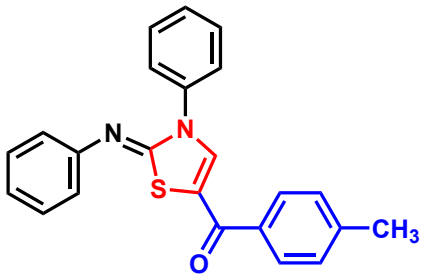


(Z)-(4-iodophenyl)(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3e)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3e** as a yellow solid (183.9 mg, 76% yield). mp: 186–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.47–7.31 (m, 8H), 7.08 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.8, 156.3, 150.3, 138.7, 138.0, 137.3, 136.9, 129.7, 129.7, 129.5, 128.6, 125.8, 124.3, 120.9, 117.5, 99.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 3068, 1625, 1585, 1568, 1490, 1378, 1321, 1264, 1244, 1200, 1176, 1139, 1008, 888, 816, 772, 761, 745, 732, 697, 630, 525. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{22}H_{16}IN_2OS^+$ 483.0023; Found 483.0015.

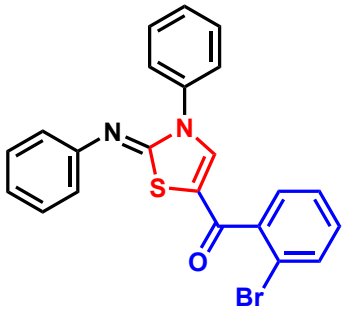


(Z)-(4-methoxyphenyl)(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3f)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target

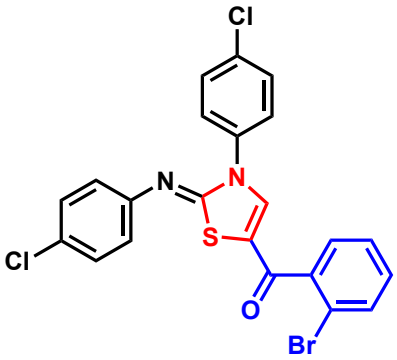
compound **3f** as a white solid (158.8 mg, 82% yield). mp: 170–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 7.9 Hz, 2H), 7.50–7.46 (m, 3H), 7.40–7.32 (m, 3H), 7.10–7.03 (m, 3H), 6.94 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 162.9, 156.6, 150.5, 137.5, 137.5, 130.4, 130.2, 129.5, 129.4, 128.3, 125.7, 124.1, 121.0, 117.8, 114.0, 55.5. IR (Diamond-ATR, neat): ν / cm^{-1} = 3073, 2919, 1616, 1584, 1492, 1370, 1324, 1255, 1199, 1167, 1138, 1095, 1032, 891, 838, 771, 756, 726, 698, 593, 496. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{23}H_{19}N_2O_2S^{+}$ 387.1162; Found 387.1175.



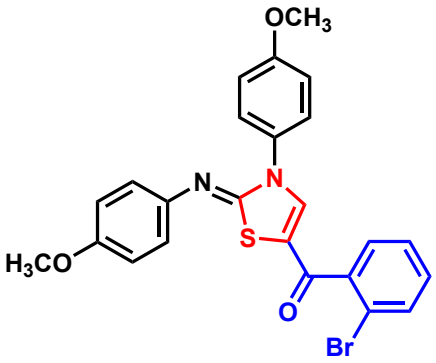
(Z)-(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)(p-tolyl)methanone ***(3g)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3g** as a white solid (169.6 mg, 92% yield). mp: 158–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.48–7.45 (m, 3H), 7.38–7.31 (m, 3H), 7.25 (d, J = 7.6 Hz, 2H), 7.09–7.03 (m, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 156.6, 150.5, 142.8, 138.1, 137.5, 134.9, 129.5, 129.4, 129.4, 128.3, 128.3, 125.7, 124.1, 120.9, 117.9, 21.6. IR (Diamond-ATR, neat): ν / cm^{-1} = 3078, 1622, 1575, 1490, 1376, 1321, 1263, 1243, 1199, 1184, 1139, 1092, 890, 834, 771, 745, 731, 697, 592, 468. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{23}H_{19}N_2OS^{+}$ 371.1213; Found 371.1202.



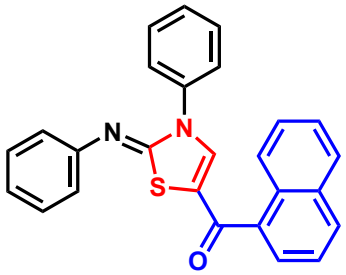
(Z)-(2-bromophenyl)(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3h)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3h** as a yellow oil (117.3 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.26–7.16 (m, 6H), 7.10 (s, 1H), 6.99 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 155.4, 149.1, 139.0, 138.2, 136.1, 132.5, 130.5, 128.5, 128.4, 127.7, 127.5, 126.3, 124.7, 123.3, 119.8, 118.6, 116.5. IR (Diamond-ATR, neat): ν / cm^{-1} = 2919, 1618, 1585, 1492, 1382, 1307, 1268, 1225, 1200, 1145, 1025, 888, 825, 761, 740, 696, 617, 532. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{22}H_{16}BrN_2OS^{+}$ 435.0161; Found 435.0175.



(Z)-(2-bromophenyl)(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)methanone ***(3i)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3i** as a yellow oil (112.4 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.36–7.28 (m, 6H), 7.25–7.19 (m, 3H), 7.09 (s, 1H), 6.87 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 155.6, 147.3, 138.1, 138.0, 134.4, 133.4, 132.6, 130.6, 128.6, 128.6, 128.4, 127.7, 126.4, 126.1, 121.2, 118.6, 117.0. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 2849, 1617, 1572, 1485, 1383, 1307, 1283, 1228, 1200, 1146, 1089, 1015, 893, 837, 770, 741, 672, 639, 475. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{22}H_{14}BrCl_2N_2OS^{+}$ 502.9382; Found 502.9369.

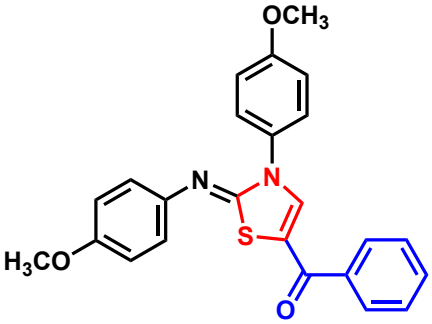


*(Z)-(2-bromophenyl)(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3j**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3j** as a yellow oil (138.6 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.9 Hz, 1H), 7.30–7.23 (m, 4H), 7.20–7.15 (m, 1H), 7.06 (s, 1H), 6.88 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.3 Hz, 2H), 3.68 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.9, 158.4, 155.3, 142.4, 139.6, 138.4, 132.5, 130.4, 128.9, 127.8, 126.3, 126.2, 120.9, 118.6, 115.8, 113.7, 113.6, 54.5, 54.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 2930, 2834, 1618, 1568, 1504, 1464, 1384, 1302, 1269, 1246, 1200, 1178, 1147, 1106, 1028, 893, 834, 778, 741, 702, 679, 639, 575, 537. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{24}H_{20}BrN_2O_3S^{+}$ 495.0373; Found 495.0364.

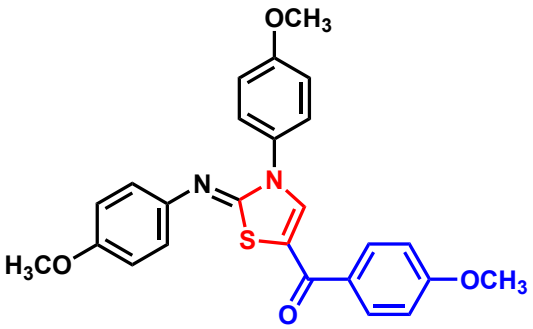


*(Z)-naphthalen-1-yl(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-5-yl)methanone (**3k**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3k** as a yellow oil (147.8 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.0 Hz, 1H), 7.43–7.41 (m, 2H), 7.38–7.35 (m, 3H), 7.32–7.22 (m, 5H), 7.18 (s, 1H),

7.02–6.95(m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 155.6, 149.3, 138.3, 136.2, 134.2, 132.8, 130.2, 129.4, 128.6, 128.3, 127.4, 127.3, 126.4, 125.7, 125.1, 124.6, 124.2, 123.3, 123.2, 119.9, 118.5. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 1618, 1567, 1493, 1383, 1296, 1270, 1227, 1200, 1148, 891, 783, 764, 697, 619. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{26}H_{19}N_2OS^+$ 407.1213; Found 407.1226.

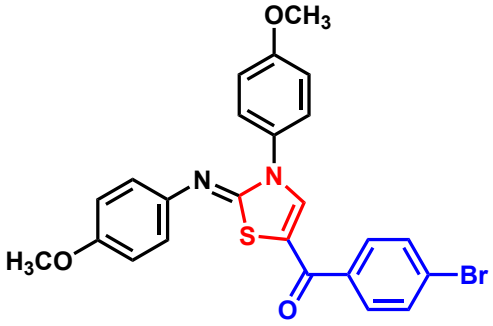


*(Z)-(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)(phenyl)methanone (**3l**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3l** as a yellow oil (202.1 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.1 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.30–7.26 (m, 5H), 6.84 (d, J = 8.9 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 6.72 (d, J = 8.9 Hz, 2H), 3.62 (s, 6H) , 3.60 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 158.2, 155.3, 155.2, 142.6, 138.0, 136.6, 130.9, 129.1, 127.6, 127.1, 126.1, 120.9, 116.0, 113.6, 113.5, 54.4, 54.3. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 1624, 1567, 1504, 1384, 1244, 1200, 1176, 1030, 891, 833, 709, 655, 574, 533. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{24}H_{21}N_2O_3S^+$ 417.1267; Found 417.1274.

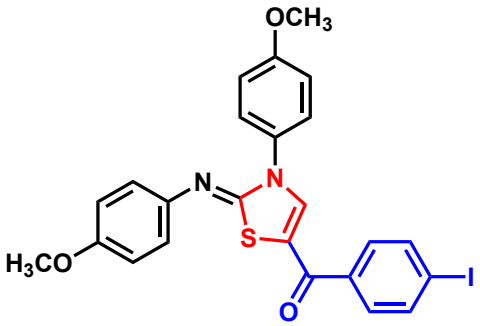


*(Z)-(4-methoxyphenyl)(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3m**).* According to the general procedure, the residue

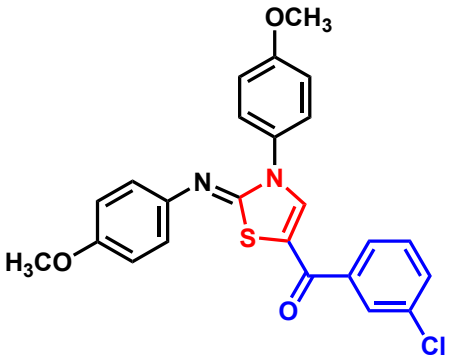
was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3m** as a yellow oil (218.1 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 2H), 7.33–7.29 (m, 3H), 6.86–6.77 (m, 6H), 6.73 (d, J = 8.9 Hz, 2H), 3.66 (s, 3H), 3.64 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.3, 161.8, 158.2, 155.5, 155.1, 142.8, 137.1, 129.4, 129.3, 129.1, 126.1, 120.9, 116.0, 113.6, 113.5, 112.9, 54.5, 54.4, 54.3. IR (Diamond-ATR, neat): ν / cm^{-1} = 2931, 2836, 1601, 1505, 1463, 1383, 1304, 1254, 1200, 1170, 1030, 893, 833, 755, 696, 608, 570, 537. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{25}H_{23}N_2O_4S^{+}$ 447.1373; Found 447.1377.



*(Z)-(4-bromophenyl)(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3n**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3n** as a yellow oil (204.3 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 4H), 7.31 (d, J = 10.0 Hz, 3H), 6.85 (t, J = 8.6 Hz, 4H), 6.76 (d, J = 8.9 Hz, 2H), 3.68 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.3, 158.4, 155.3, 155.2, 142.5, 138.1, 135.4, 130.9, 129.0, 128.7, 126.1, 125.7, 120.9, 115.7, 113.7, 113.6, 54.5, 54.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 2929, 1621, 1572, 1504, 1463, 1396, 1270, 1243, 1201, 1174, 1131, 1107, 1068, 1031, 1010, 891, 831, 745, 700, 679, 577, 537. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{24}H_{20}BrN_2O_3S^{+}$ 495.0373; Found 495.0368.

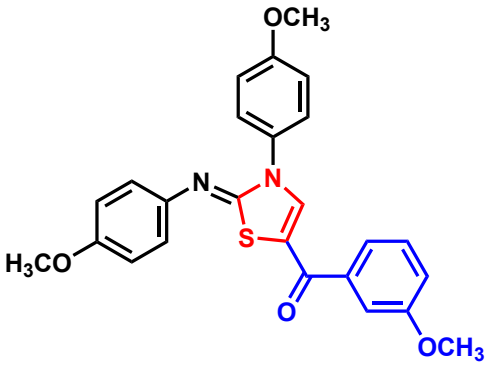


*(Z)-(4-iodophenyl)(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3o**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3o** as a yellow oil (247.4 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.32–7.28 (m, 5H), 6.86–6.781 (m, 4H), 6.75 (d, J = 8.9 Hz, 2H), 3.67 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 158.3, 155.2, 155.1, 142.5, 138.2, 136.8, 135.9, 129.0, 128.6, 126.1, 120.9, 115.7, 113.7, 113.5, 98.2, 54.5, 54.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 1571, 1504, 1392, 1244, 1201, 1178, 1031, 1006, 891, 830, 743, 676, 576, 535. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{24}H_{20}IN_2O_3S^{+}$ 543.0234; Found 543.0250.

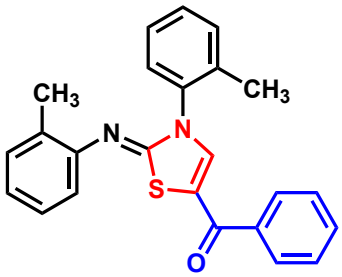


*(Z)-(3-chlorophenyl)(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3p**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3p** as a yellow solid (185.0 mg, 82% yield). mp: 162–164 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.34–7.27 (m, 4H), 7.21 (t, J = 7.8 Hz, 1H), 6.85–6.80 (m, 4H), 6.73 (d, J = 8.9 Hz, 2H), 3.64 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 158.3, 155.3, 155.0, 142.4, 138.4, 138.2, 133.8, 130.8, 129.0, 127.1, 126.1, 125.2, 120.8, 115.6, 113.7, 113.5, 54.5,

54.3. IR (Diamond-ATR, neat): ν / cm^{-1} = 2926, 1596, 1574, 1508, 1466, 1419, 1380, 1315, 1299, 1266, 1250, 1201, 1173, 1091, 1040, 1022, 913, 834, 804, 748, 707, 674, 652, 580, 535. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{24}H_{20}ClN_2O_3S^+$ 451.0878; Found 451.0868.

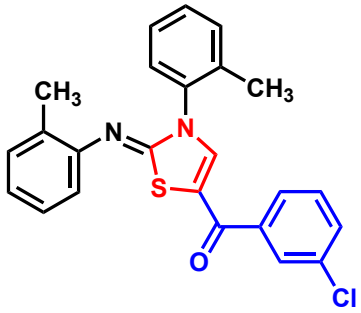


*(Z)-(3-methoxyphenyl)(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3q**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3q** as a yellow oil (205.6 mg, 92% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.21–7.14 (m, 2H), 7.10 (s, 1H), 6.92 (d, J = 7.9 Hz, 1H), 6.86–6.80 (m, 4H), 6.74 (d, J = 8.0 Hz, 2H), 3.66 (s, 3H), 3.65 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 158.7, 158.3, 155.4, 155.2, 142.6, 138.1, 137.9, 129.1, 128.6, 126.1, 120.9, 119.5, 117.0, 115.9, 113.6, 113.5, 112.1, 54.5, 54.4, 54.3. IR (Diamond-ATR, neat): ν / cm^{-1} = 3081, 2953, 2835, 1624, 1567, 1509, 1465, 1426, 1385, 1276, 1247, 1205, 1172, 1127, 1034, 867, 836, 812, 791, 762, 741, 677, 657, 606, 585, 569, 538. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_4S^+$ 447.1373; Found 447.1385.

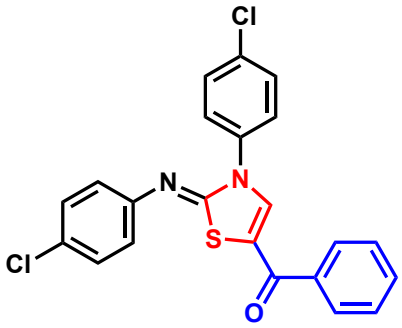


*(Z)-phenyl(3-(o-tolyl)-2-(o-tolylimino)-2,3-dihydrothiazol-5-yl)methanone (**3r**).* According to the general procedure, the residue was purified by flash chromatography

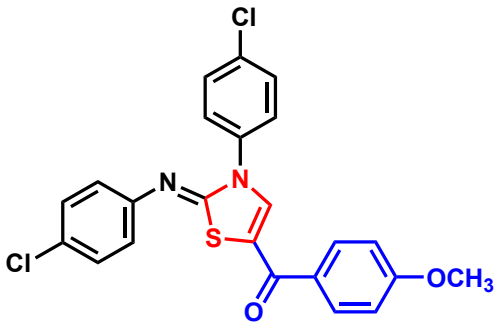
on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3r** as a yellow solid (187.8 mg, 98% yield). mp: 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.1 Hz, 2H), 7.40 (d, J = 7.3 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 7.26–7.20 (m, 5H), 7.07 (t, J = 7.8 Hz, 2H), 6.91–6.85 (m, 2H), 2.28 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 155.3, 148.4, 137.8, 136.6, 135.5, 134.9, 131.0, 130.4, 129.8, 128.9, 128.7, 127.6, 127.2, 126.9, 126.2, 126.0, 123.1, 118.4, 116.9, 16.9, 16.7. IR (Diamond-ATR, neat): ν / cm^{-1} = 3060, 2918, 1628, 1560, 1485, 1380, 1285, 1236, 1214, 1122, 894, 834, 766, 752, 724, 709, 660, 631. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{24}H_{21}N_2OS^{+}$ 385.1369; Found 385.1366.



(Z)-(3-chlorophenyl)(3-(o-tolyl)-2-(o-tolylimino)-2,3-dihydrothiazol-5-yl)methanone ***(3s)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3s** as a yellow oil (186.6 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.24–7.18 (m, 6H), 7.05 (t, J = 7.8 Hz, 2H), 6.89–6.82 (m, 2H), 2.26 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 155.0, 148.2, 138.2, 138.1, 135.3, 134.8, 133.8, 130.9, 130.4, 129.8, 129.0, 128.8, 128.8, 127.2, 126.8, 126.3, 126.0, 125.2, 123.2, 118.2, 116.5, 16.9, 16.7. IR (Diamond-ATR, neat): ν / cm^{-1} = 3058, 2918, 1609, 1559, 1492, 1421, 1376, 1295, 1273, 1231, 1212, 1188, 1115, 915, 806, 762, 744, 713, 633, 445. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{24}H_{20}ClN_2OS^{+}$ 419.0979; Found 419.0992.

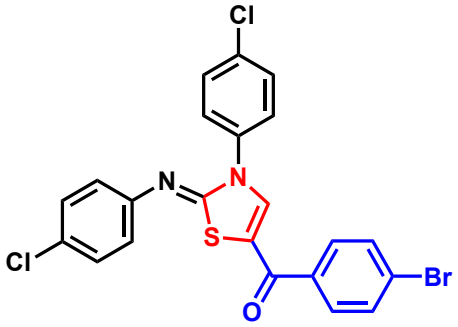


*(Z)-(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)(phenyl)methanone (**3t**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3t** as a yellow solid (180.6 mg, 85% yield). mp: 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 6.9 Hz, 2H), 7.55–7.42 (m, 8H), 7.28 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 156.7, 148.6, 137.6, 137.3, 135.6, 134.3, 132.3, 129.6, 129.3, 128.8, 128.2, 127.1, 122.3, 118.3. IR (Diamond-ATR, neat): ν / cm^{-1} = 3083, 1628, 1602, 1573, 1490, 1447, 1381, 1283, 1270, 1229, 1206, 1175, 1130, 1097, 1015, 891, 826, 790, 715, 652, 526, 490, 477. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{22}H_{15}Cl_2N_2OS^{+}$ 425.0277; Found 425.0286.

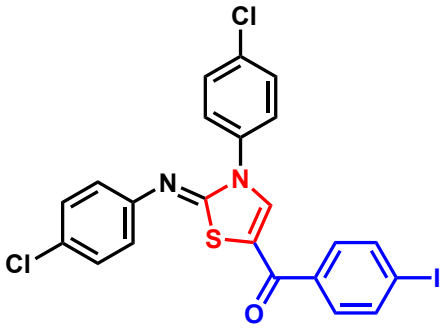


*(Z)-(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)(4-methoxyphenyl)methanone (**3u**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3u** as a yellow solid (222.2 mg, 98% yield). mp: 232–234 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (s, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.04 (t, J = 8.6 Hz, 4H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.0, 163.6, 157.3, 151.0, 140.6, 137.3, 133.5, 131.3, 130.5, 129.7, 129.4, 128.7, 128.3, 123.0, 117.0, 114.6, 56.5. IR

(Diamond-ATR, neat): ν / cm^{-1} = 3081, 2928, 1725, 1615, 1580, 1560, 1508, 1490, 1413, 1384, 1317, 1285, 1263, 1229, 1199, 1169, 1135, 1091, 1024, 894, 866, 836, 784, 757, 740, 697, 617, 602, 507, 494, 473. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{23}H_{17}Cl_2N_2O_2S^+$ 455.0382; Found 455.0390.

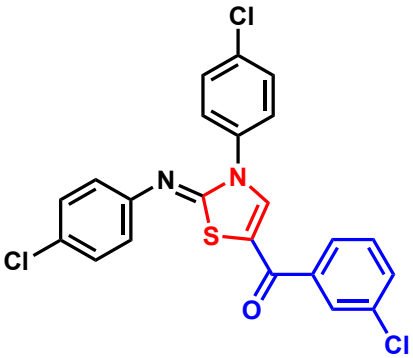


*(Z)-(4-bromophenyl)(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3v**)*. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3v** as a yellow oil (233.7 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.44 (m, 5H), 7.34 (s, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 155.3, 147.3, 136.7, 134.9, 134.5, 133.2, 131.0, 128.7, 128.6, 128.6, 128.3, 126.3, 126.0, 121.2, 116.9. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 2850, 1614, 1582, 1484, 1395, 1307, 1283, 1230, 1200, 1175, 1129, 1089, 1068, 1010, 891, 830, 745, 675, 605, 538, 475. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{22}H_{14}BrCl_2N_2OS^+$ 502.9382; Found 502.9374.

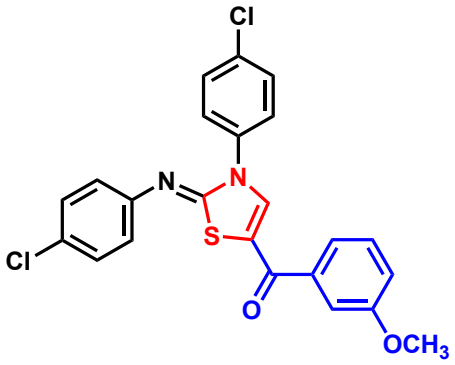


*(Z)-(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)(4-iodophenyl)methanone (**3w**)*. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to

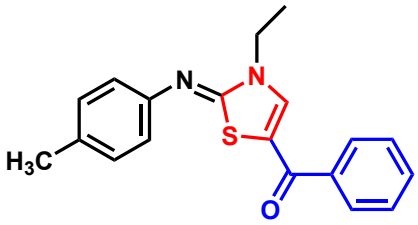
give the target compound **3w** as a yellow oil (230.4 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.35–7.28 (m, 7H), 7.16 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 156.4, 148.5, 138.1, 138.0, 137.8, 136.6, 135.6, 134.4, 129.7, 129.7, 129.4, 127.1, 122.4, 118.0, 99.8. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 2850, 1617, 1581, 1484, 1391, 1307, 1283, 1231, 1200, 1179, 1089, 1006, 890, 829, 743, 666, 474. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{22}H_{14}Cl_2IN_2OS^{+}$ 550.9243; Found 550.9251.



*(Z)-(3-chlorophenyl)(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3x**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3x** as a yellow solid (172.0 mg, 75% yield). mp: 163–165 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.45–7.36 (m, 6H), 7.32 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 155.5, 147.4, 137.9, 136.9, 134.5, 134.0, 133.5, 131.3, 129.1, 128.7, 128.7, 128.4, 127.2, 126.1, 125.2, 121.2, 116.9. IR (Diamond-ATR, neat): ν / cm^{-1} = 3082, 2917, 1619, 1581, 1557, 1491, 1413, 1384, 1310, 1286, 1269, 1228, 1202, 1164, 1143, 1091, 1015, 916, 876, 834, 801, 746, 719, 691, 649, 606, 518, 503, 487, 475, 464. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{22}H_{14}Cl_3N_2OS^{+}$ 458.9887; Found 458.9901.

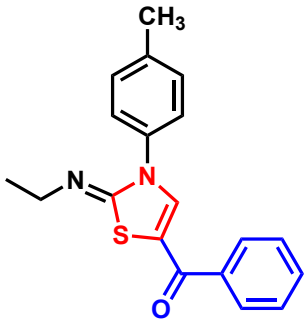


*(Z)-(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)(3-methoxyphenyl)methanone (**3y**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3y** as a yellow solid (185.9 mg, 82% yield). mp: 162–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 5H), 7.27–7.12 (m, 5H), 6.98 (d, J = 7.2 Hz, 1H), 6.85 (d, J = 8.2 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 158.9, 155.7, 147.5, 137.5, 136.7, 134.6, 133.2, 128.8, 128.6, 128.6, 128.2, 126.0, 121.3, 119.5, 117.3, 117.2, 112.2, 54.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 3084, 1617, 1566, 1492, 1449, 1429, 1381, 1310, 1288, 1267, 1247, 1227, 1199, 1089, 1047, 1015, 931, 837, 824, 773, 744, 656, 519, 509, 487, 472. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{23}H_{17}Cl_2N_2O_2S^{+}$ 455.0382; Found 455.0395.

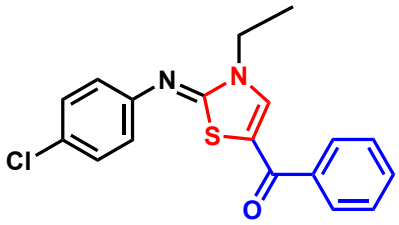


*(Z)-(3-ethyl-2-(p-tolylimino)-2,3-dihydrothiazol-5-yl)(phenyl)methanone (**3aa**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3aa** as a yellow oil (129.1 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 4.8 Hz, 2H), 7.51 (d, J = 7.3 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.41 (s, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.23 (s, 1H), 7.02–6.91 (m, 1H), 3.23 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 157.4, 141.7, 138.6, 137.9, 135.0, 132.6, 130.0, 128.6, 128.2, 125.9, 114.2, 50.2, 24.7, 14.9. IR (Diamond-ATR,

neat): ν / cm^{-1} = 2918, 2850, 1635, 1566, 1512, 1446, 1384, 1317, 1249, 1177, 1134, 888, 819, 711, 653, 607, 524. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{19}H_{19}N_2OS^{+}$ 323.1213; Found 323.1204.

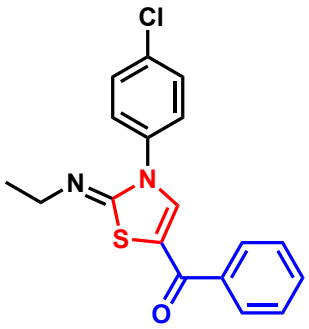


(Z)-(2-(ethylimino)-3-(p-tolyl)-2,3-dihydrothiazol-5-yl)(phenyl)methanone ***(3ab)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3ab** as a yellow oil (23.8 mg, 15% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.0 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.38 (s, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 4.01 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 155.3, 146.7, 137.3, 137.0, 132.4, 130.8, 129.1, 127.6, 127.2, 119.8, 115.3, 42.2, 19.2, 13.2. IR (Diamond-ATR, neat): ν / cm^{-1} = 3072, 2918, 1741, 1620, 1602, 1559, 1505, 1447, 1414, 1379, 1340, 1301, 1260, 1220, 1194, 1177, 1131, 1102, 932, 872, 840, 827, 792, 715, 674, 655, 623, 543, 527, 506. HRMS (ESI) *m/z* [M + H] $^{+}$ Calcd for $C_{19}H_{19}N_2OS^{+}$ 323.1213; Found 323.1216.

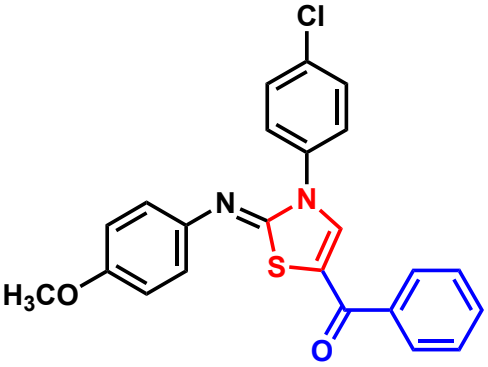


(Z)-(2-((4-chlorophenyl)imino)-3-ethyl-2,3-dihydrothiazol-5-yl)(phenyl)methanone ***(3ac)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3ac** as a yellow oil (123.5 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.1 Hz, 2H), 7.45–7.26 (m, 8H), 3.11 (q, J = 7.2 Hz, 2H), 1.15 (t, J = 7.2

Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 153.4, 137.5, 136.7, 135.0, 132.6, 130.9, 128.4, 127.7, 127.1, 125.8, 116.9, 49.1, 14.0. IR (Diamond-ATR, neat): ν / cm^{-1} = 2969, 2853, 1744, 1635, 1613, 1594, 1565, 1494, 1447, 1414, 1385, 1354, 1315, 1282, 1256, 1231, 1176, 1128, 1083, 1054, 1016, 889, 840, 789, 709, 651, 605, 525, 496, 470. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{18}H_{16}ClN_2OS^+$ 343.0666; Found 343.0660.

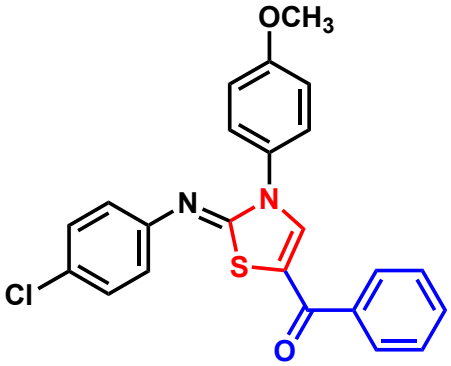


(Z)-(3-(4-chlorophenyl)-2-(ethylimino)-2,3-dihydrothiazol-5-yl)(phenyl)methanone ***(3ad)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3ad** as a yellow oil (42.7 mg, 25% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 7.3 Hz, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 4.6 Hz, 1H), 7.29 (s, 1H), 7.25 (s, 1H), 6.95 (d, J = 8.7 Hz, 2H), 3.91 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 156.0, 147.7, 137.1, 131.0, 128.6, 127.9, 127.7, 127.1, 125.8, 121.5, 115.6, 41.5, 13.1. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 1604, 1560, 1485, 1413, 1342, 1306, 1259, 1218, 1194, 1133, 1099, 870, 840, 711, 661, 622, 523. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{18}H_{16}ClN_2OS^+$ 343.0666; Found 343.0673.

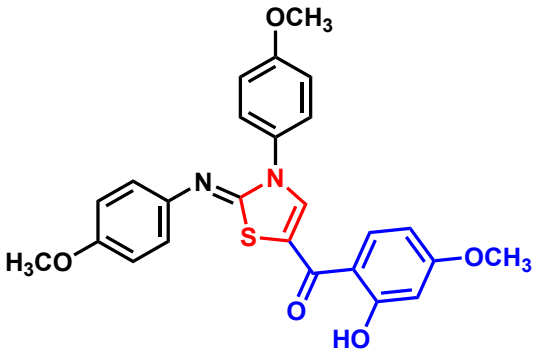


(Z)-(3-(4-chlorophenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)(phenyl)methanone ***(3ae)***. According to the general procedure, the residue was

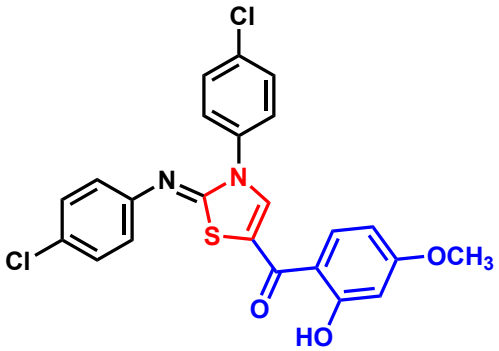
purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3ae** as a yellow solid (106.9 mg, 51% yield). mp: 149–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 6.9 Hz, 2H), 7.56–7.48 (m, 4H), 7.46 (s, 1H), 7.44 (d, J = 2.7 Hz, 2H), 7.42 (s, 1H), 6.98 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 156.4, 155.0, 146.8, 137.8, 137.5, 135.9, 134.0, 132.6, 129.6, 128.8, 128.2, 127.0, 122.7, 118.0, 115.2, 54.3. IR (Diamond-ATR, neat): ν / cm^{-1} = 2961, 1723, 1619, 1588, 1566, 1505, 1492, 1466, 1382, 1306, 1282, 1267, 1243, 1201, 1179, 1108, 1085, 1029, 1014, 890, 829, 792, 714, 704, 678, 654, 527, 474. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{23}H_{18}ClN_2O_2S^+$ 421.0772; Found 421.0785.



(Z)-(2-((4-chlorophenyl)imino)-3-(4-methoxyphenyl)-2,3-dihydrothiazol-5-yl)(phenyl)methanone ***(3af)***. According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3af** as a yellow oil (84.6 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.46–7.41 (m, 5H), 7.27 (d, J = 8.7 Hz, 2H), 6.98–6.95 (m, 4H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 145.3, 143.3, 134.9, 124.6, 123.3, 118.0, 115.8, 115.4, 114.8, 114.6, 114.0, 113.0, 108.3, 103.3, 100.5, 41.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 2918, 1627, 1609, 1574, 1511, 1480, 1382, 1303, 1268, 1249, 1231, 1195, 1138, 1091, 1030, 891, 844, 827, 791, 719, 659, 575, 509. HRMS (ESI) *m/z* [M + H] $^+$ Calcd for $C_{23}H_{18}ClN_2O_2S^+$ 421.0772; Found 421.0780.



*(Z)-(2-hydroxy-4-methoxyphenyl)(3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-2,3-dihydrothiazol-5-yl)methanone (**3ag**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3ag** as a yellow solid (67.2 mg, 29% yield). mp: 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (s, 1H), 7.58 (d, J = 8.9 Hz, 1H), 7.52 (s, 1H), 7.39 (d, J = 8.9 Hz, 2H), 6.92–6.89 (m, 4H), 6.80 (d, J = 8.9 Hz, 2H), 6.39–6.34 (m, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 164.6, 163.8, 158.4, 155.3, 155.1, 142.7, 136.8, 130.2, 129.2, 126.2, 120.9, 114.1, 113.7, 113.6, 112.0, 106.6, 100.5, 54.6, 54.4. IR (Diamond-ATR, neat): ν / cm^{-1} = 3432, 2958, 2835, 1623, 1563, 1506, 1467, 1397, 1339, 1322, 1296, 1269, 1242, 1199, 1183, 1168, 1109, 1083, 1036, 883, 860, 832, 821, 802, 765, 731, 693, 652, 624, 575, 536, 521, 459. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_5S^+$ 463.1322; Found 463.1310.

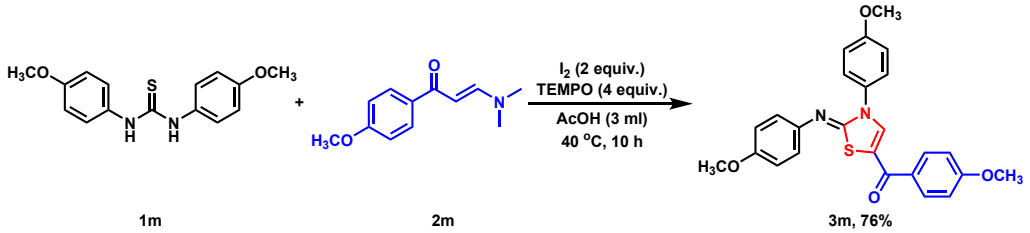


*(Z)-(3-(4-chlorophenyl)-2-((4-chlorophenyl)imino)-2,3-dihydrothiazol-5-yl)(2-hydroxy-4-methoxyphenyl)methanone (**3ah**).* According to the general procedure, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target compound **3ah** as a yellow solid (81.8 mg, 35% yield).

mp: 190–192 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.27 (s, 1H), 8.19 (s, 1H), 7.79 (d, J = 8.6 Hz, 3H), 7.63 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.56 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 185.6, 164.8, 161.6, 156.9, 149.5, 139.4, 136.3, 133.1, 132.7, 130.0, 129.5, 128.6, 128.2, 123.0, 116.6, 115.1, 107.2, 101.9, 56.0. IR (Diamond-ATR, neat): ν / cm^{-1} = 3423, 2924, 1639, 1610, 1578, 1560, 1490, 1412, 1384, 1351, 1303, 1283, 1261, 1235, 1198, 1159, 1096, 1031, 1017, 860, 825, 768, 732, 691, 626, 578, 519, 506, 478, 419. HRMS (ESI) *m/z* [M + H]$^{+}$ Calcd for $C_{23}H_{17}Cl_2N_2O_3S^{+}$ 471.0331; Found 471.0340.

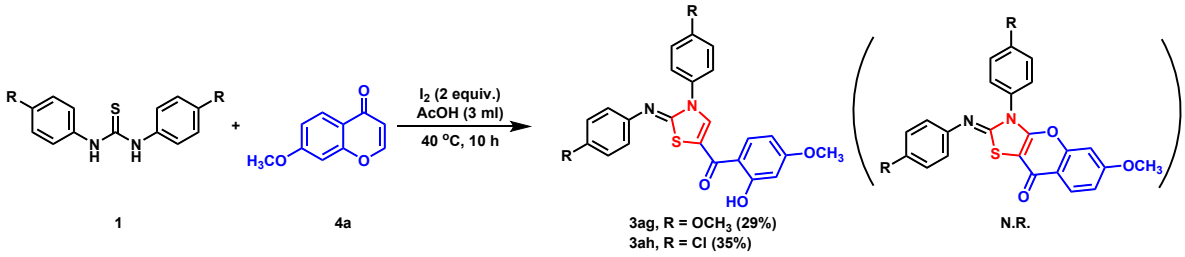
3. Control Experiments

3.1. Reaction with Radical Trapping Agent TEMPO



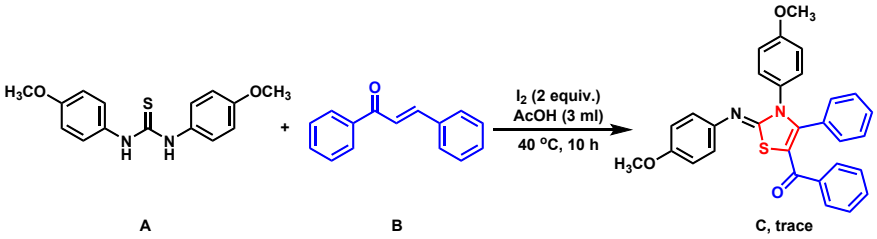
A mixture of **1m** (0.5 mmol, 1 equiv.), **2m** (0.6 mmol, 1.2 equiv.), I_2 (1 mmol, 2 equiv.) and TEMPO (2 mmol, 4 equiv.) in AcOH (3.0 mL) was stirred and warmed at 40 °C, using a heating mantle, for 10 h, and the reaction was monitored by TLC until the starting material was consumed. The reaction was quenched with sat. $Na_2S_2O_3$ solution (3 mL) and then extracted with ethyl acetate. The crude solution was dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography to afford the desired product **3m** as a yellow solid (170.1 mg, 76% yield).

3.2. Reaction with 7-Methoxy-4H-Chromen-4-One



A mixture of **1** (0.5 mmol, 1 equiv.), **4a** (0.6 mmol, 1.2 equiv.) and I_2 (1 mmol, 2 equiv.) in AcOH (3.0 mL) was stirred and warmed at 40 °C, using a heating mantle, for 10 h, and the reaction was monitored by TLC until the starting material was consumed. The reaction was quenched with sat. $Na_2S_2O_3$ solution (3 mL) and then extracted with ethyl acetate. The crude solution was dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography to afford the desired products **3ag** (67.2 mg, 29% yield) and **3ah** (81.8 mg, 35% yield) as two yellow solids.

3.3. Reaction with Chalcone



A B C, trace

A mixture of **A** (0.5 mmol, 1 equiv.), **B** (0.6 mmol, 1.2 equiv.) and I_2 (1 mmol, 2 equiv.) in AcOH (3.0 mL) was stirred and warmed at 40 °C, using a heating mantle, for 10 h, and the reaction was monitored by TLC until the starting material was consumed, while the desired compound was not detected.

4. Crystallographic Data of Compound 3a

The method for crystal growth is slow volatilization using DCM (dichloromethane) as a solvent. Crystallography data and structure refinement for **3a** (CCDC 2162042) (**Figure S1.**).

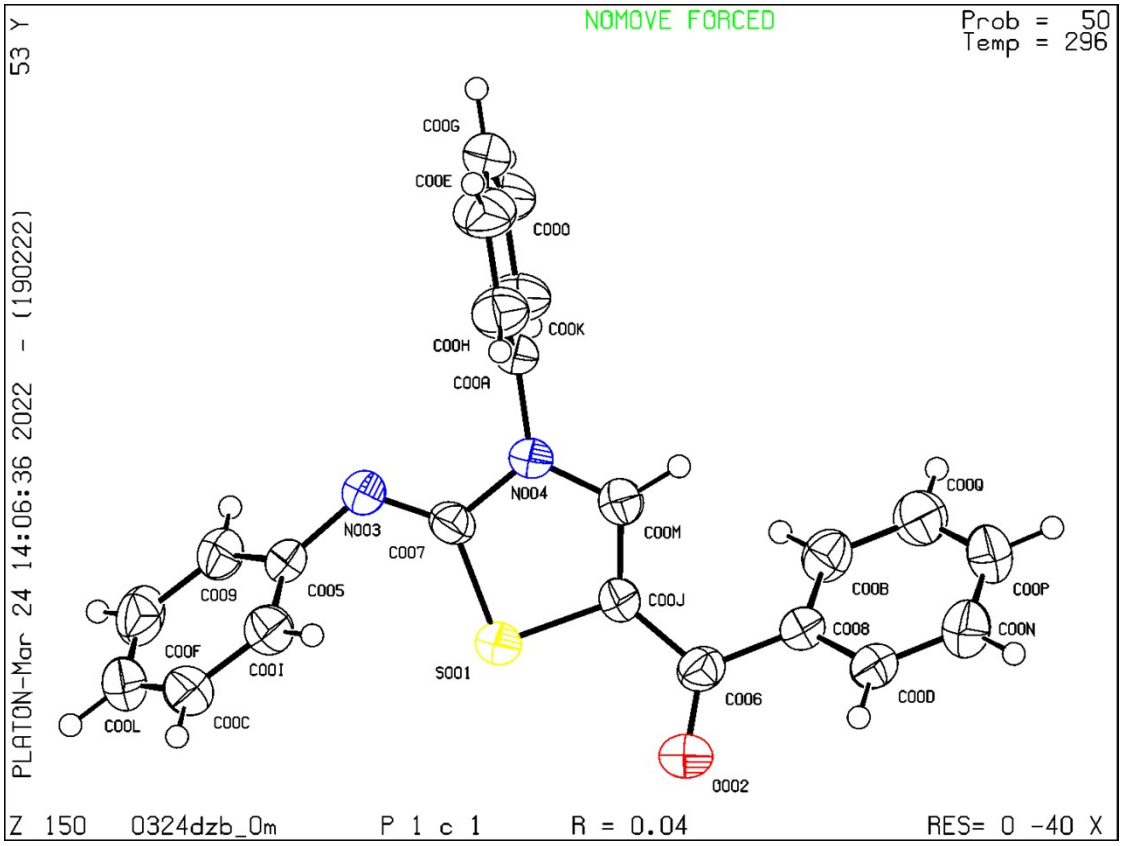


Figure S1. X-ray crystallography of product **3a**

Bond precision: C-C = 0.0077 A Wavelength=0.71073

Cell: a=5.8239(14) b=15.770(4) c=9.954(3)
alpha=90 beta=98.110(6) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	905.1(4)	905.0(4)
Space group	P c	P 1 c 1
Hall group	P -2yc	P -2yc
Moiety formula	C22 H16 N2 O S	C22 H16 N2 O S
Sum formula	C22 H16 N2 O S	C22 H16 N2 O S
Mr	356.43	356.43
Dx,g cm-3	1.308	1.308
Z	2	2
Mu (mm-1)	0.192	0.192
F000	372.0	372.0
F000'	372.38	
h,k,lmax	6,18,11	6,18,11
Nref	3196[1607]	2760
Tmin,Tmax		0.669,0.745
Tmin'		

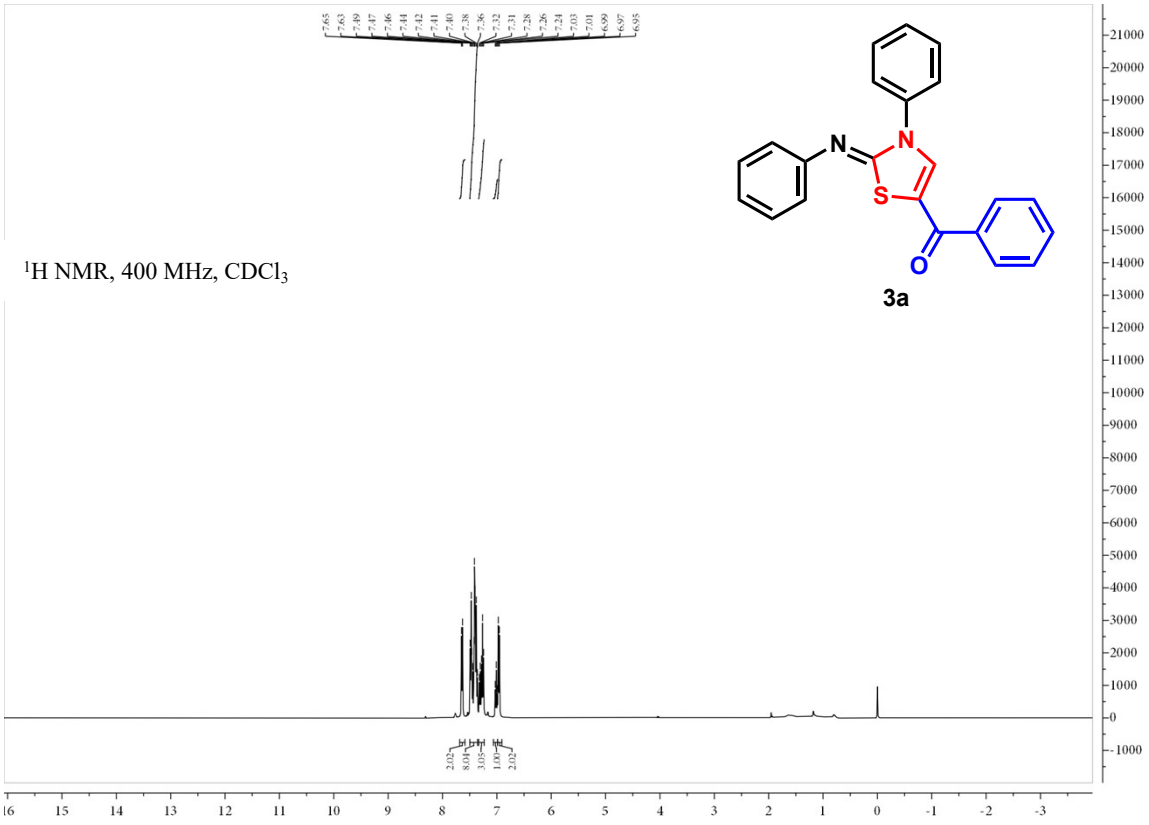
Correction method= # Reported T Limits: Tmin=0.669 Tmax=0.745 AbsCorr = NONE

Data completeness= 1.72/0.86 Theta(max)= 25.046

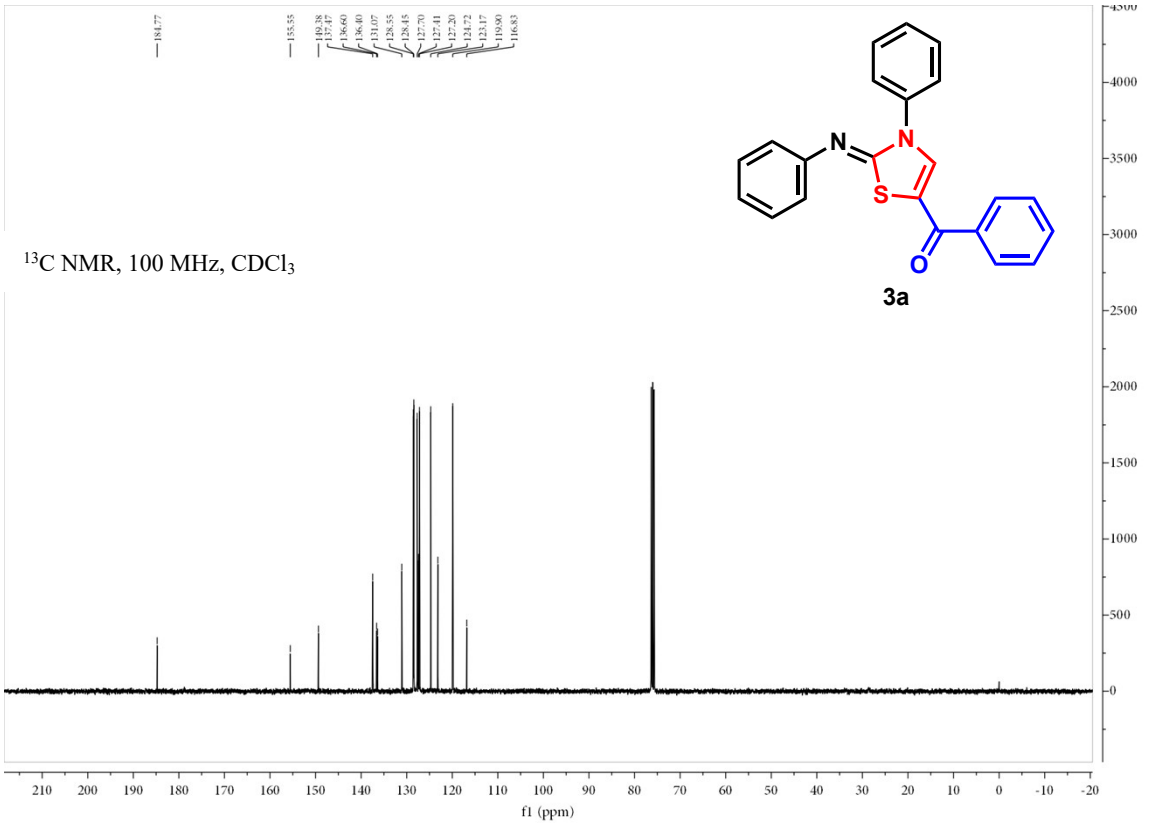
R(reflections)= 0.0436(2037) wR2(reflections)= 0.0886(2760)

S = 1.076 Npar= 235

5. ^{1}H NMR and ^{13}C NMR Spectra of 3a-3ah

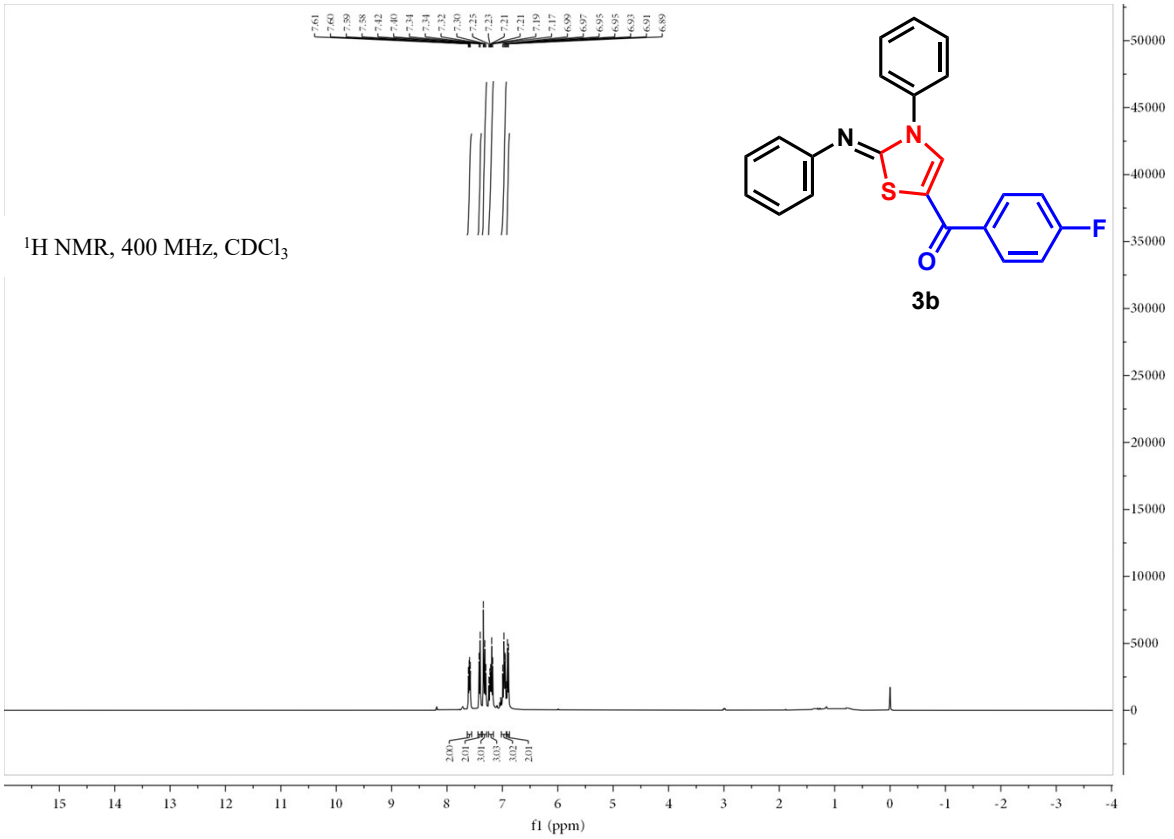


^{1}H NMR, 400 MHz, $CDCl_3$

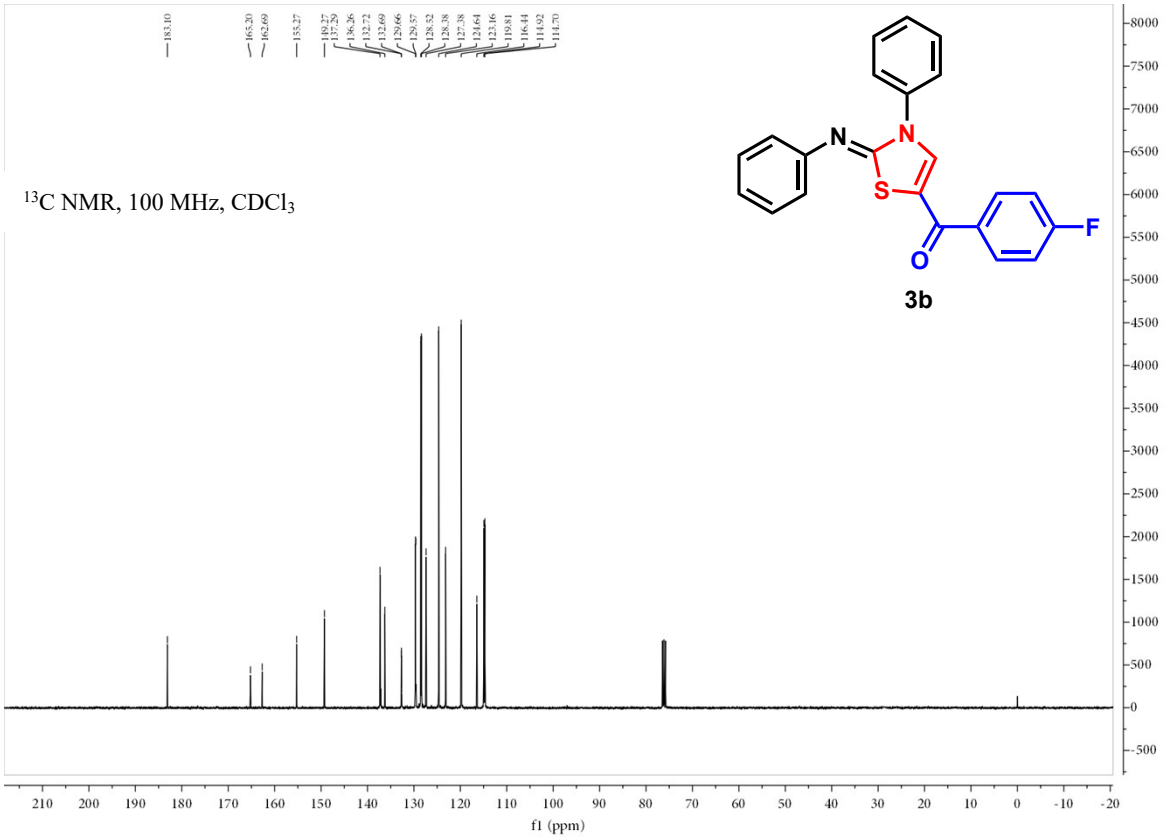


^{13}C NMR, 100 MHz, $CDCl_3$

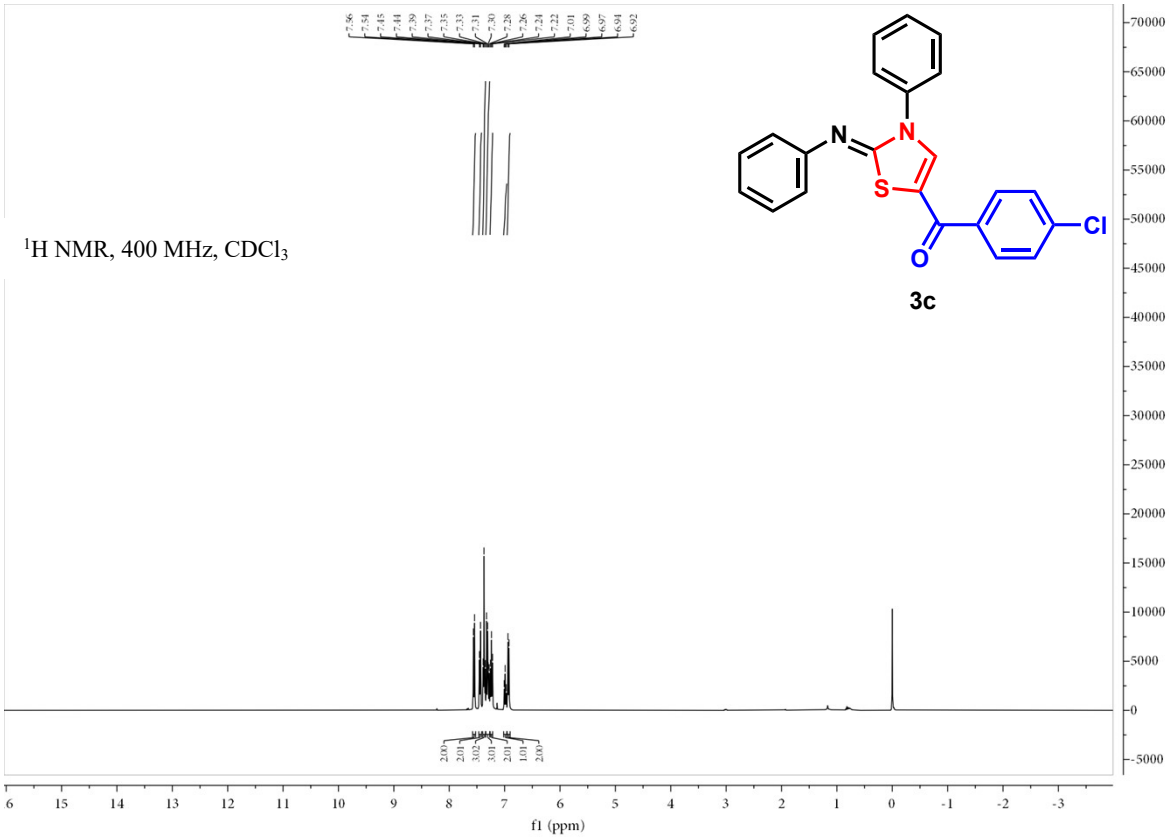
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$

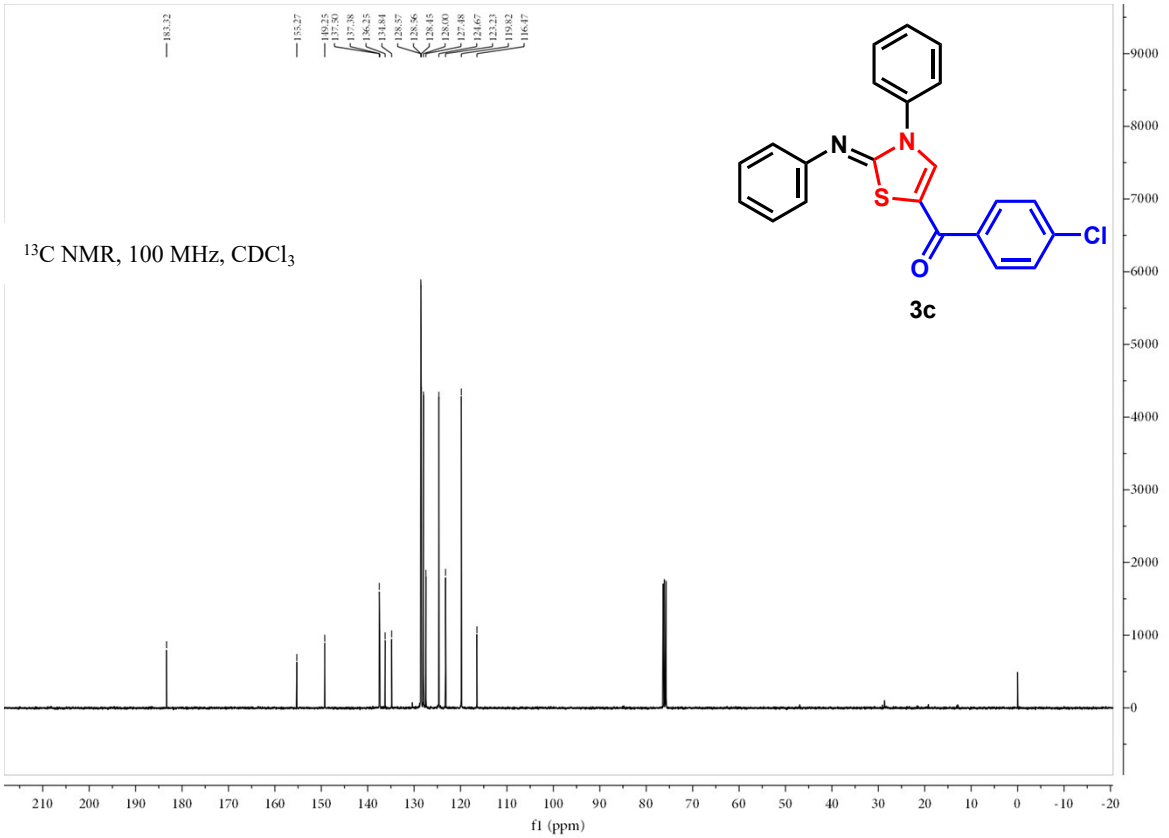


^{1}H NMR, 400 MHz, $CDCl_3$



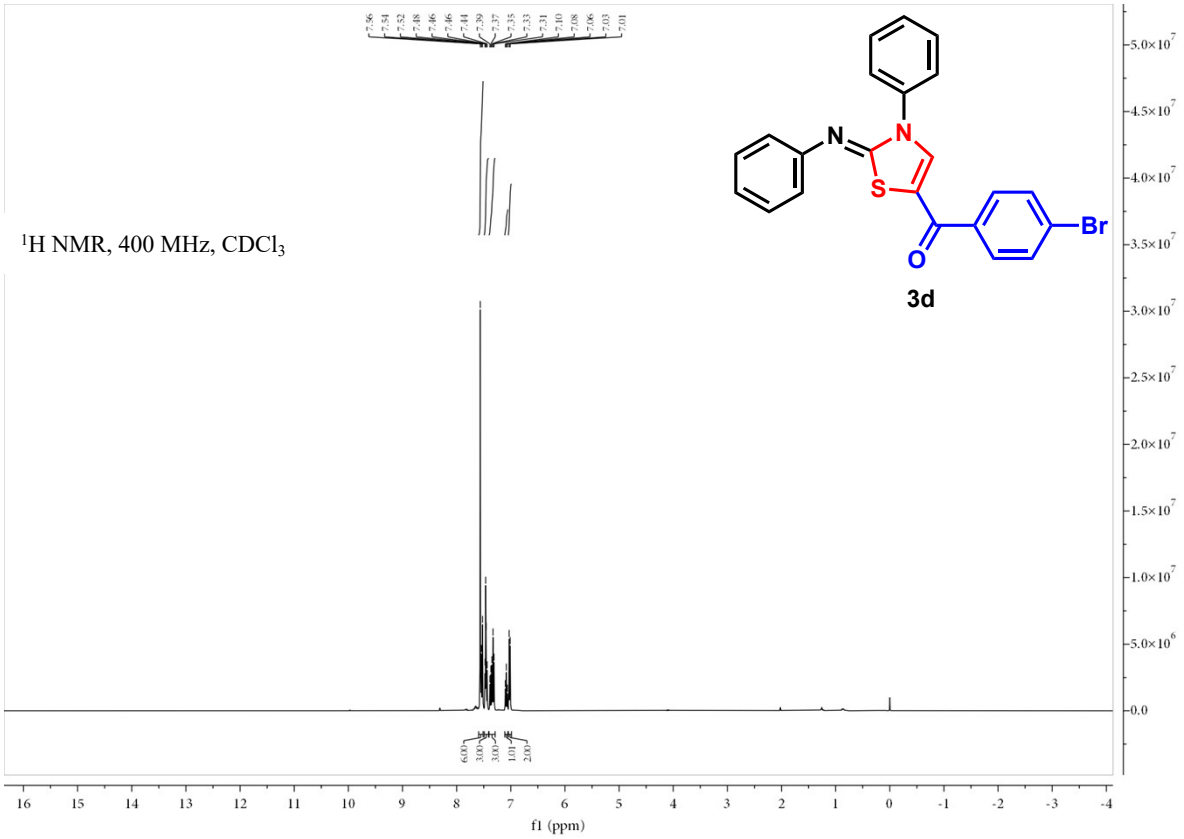
3c

^{13}C NMR, 100 MHz, $CDCl_3$



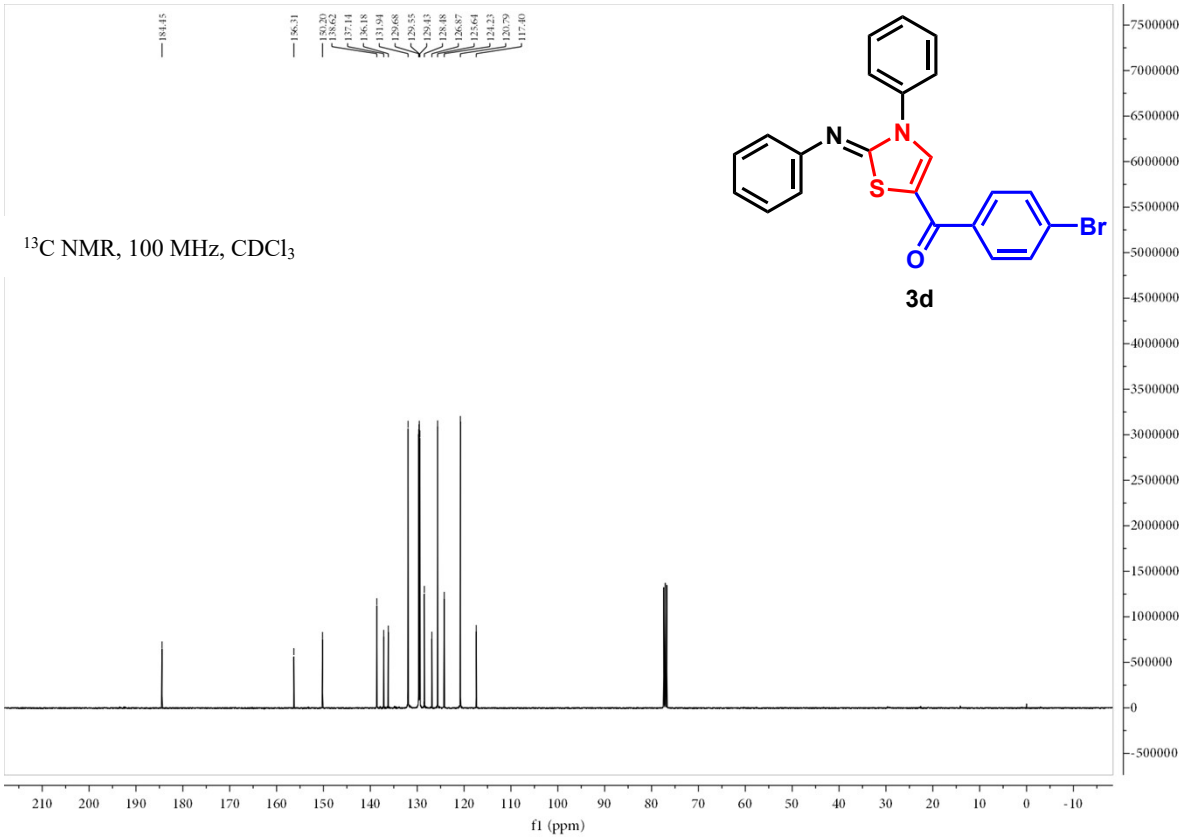
3c

^{1}H NMR, 400 MHz, $CDCl_3$



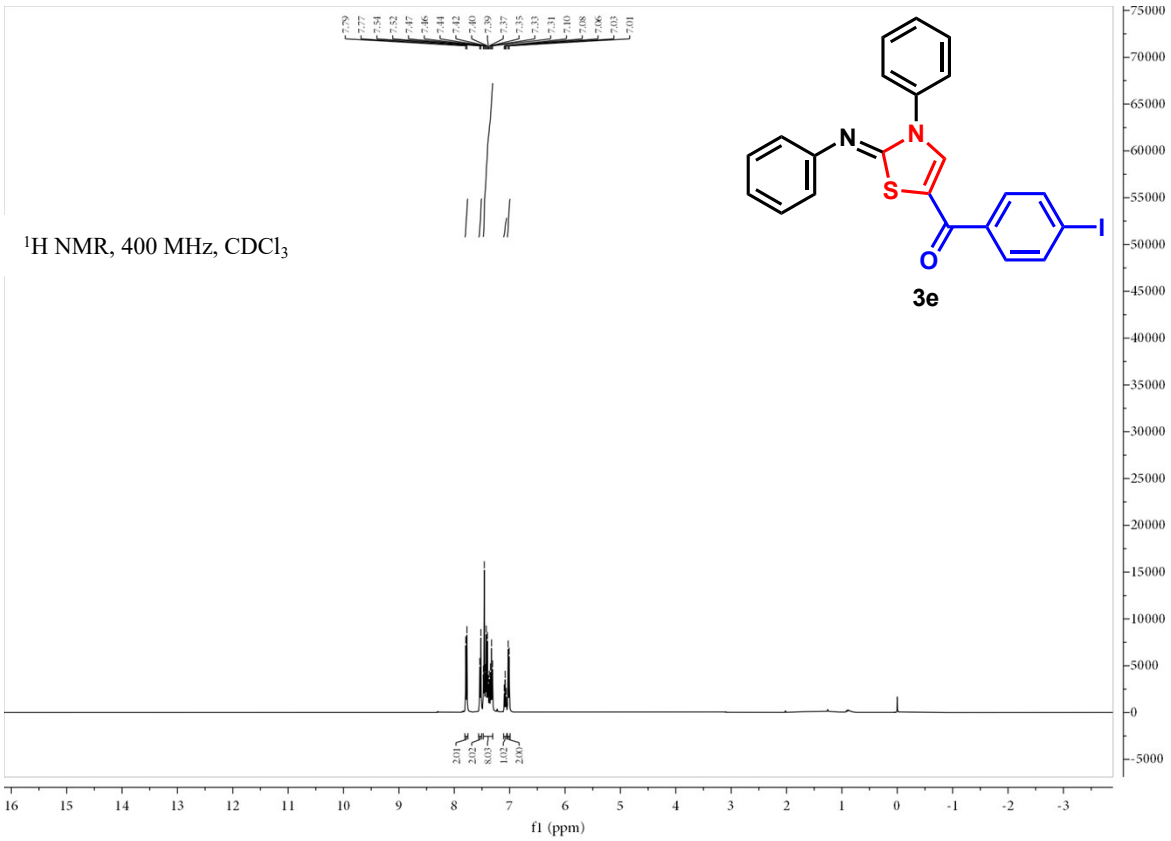
3d

^{13}C NMR, 100 MHz, $CDCl_3$



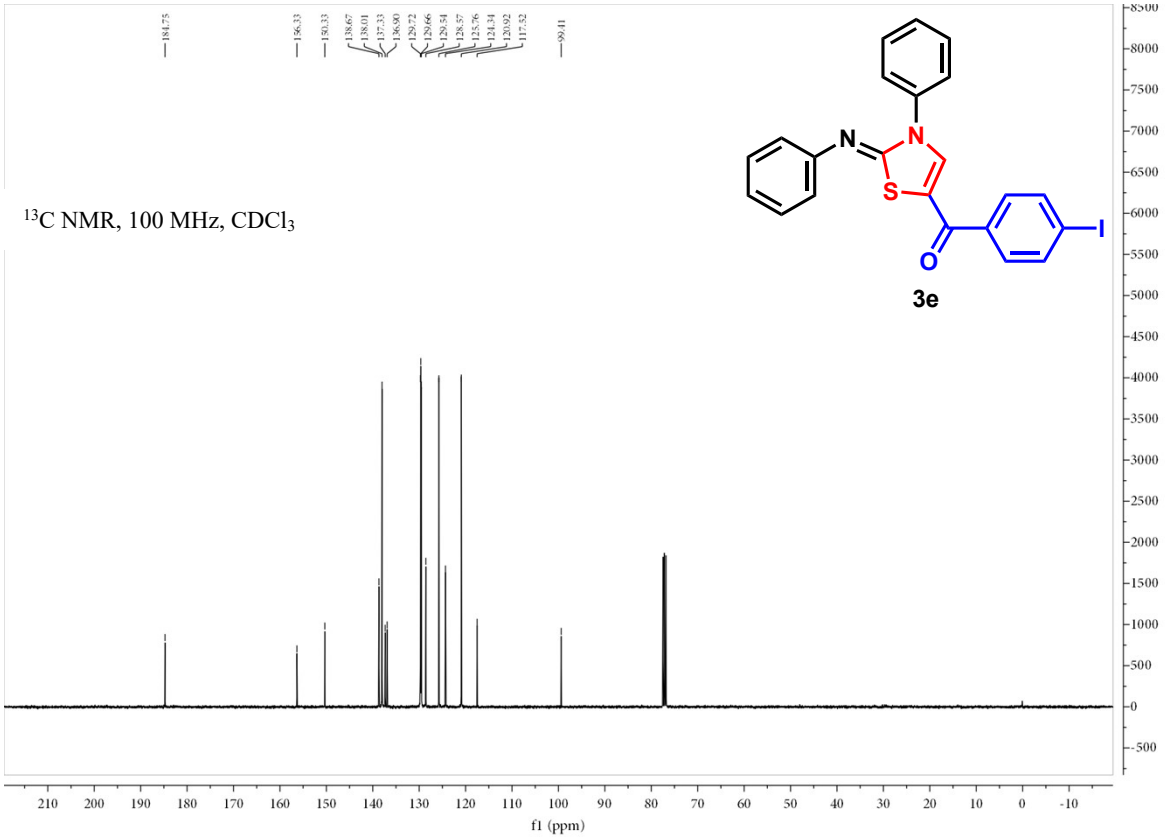
3d

^{1}H NMR, 400 MHz, $CDCl_3$

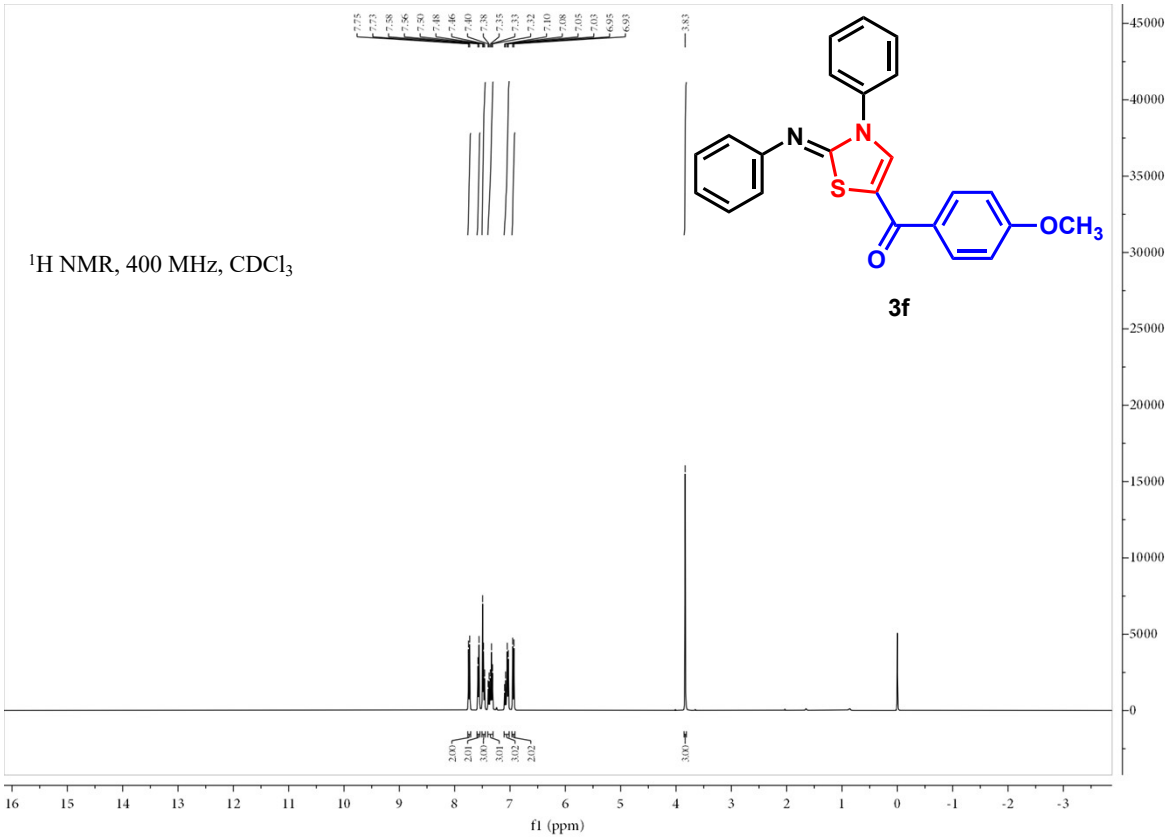


3e

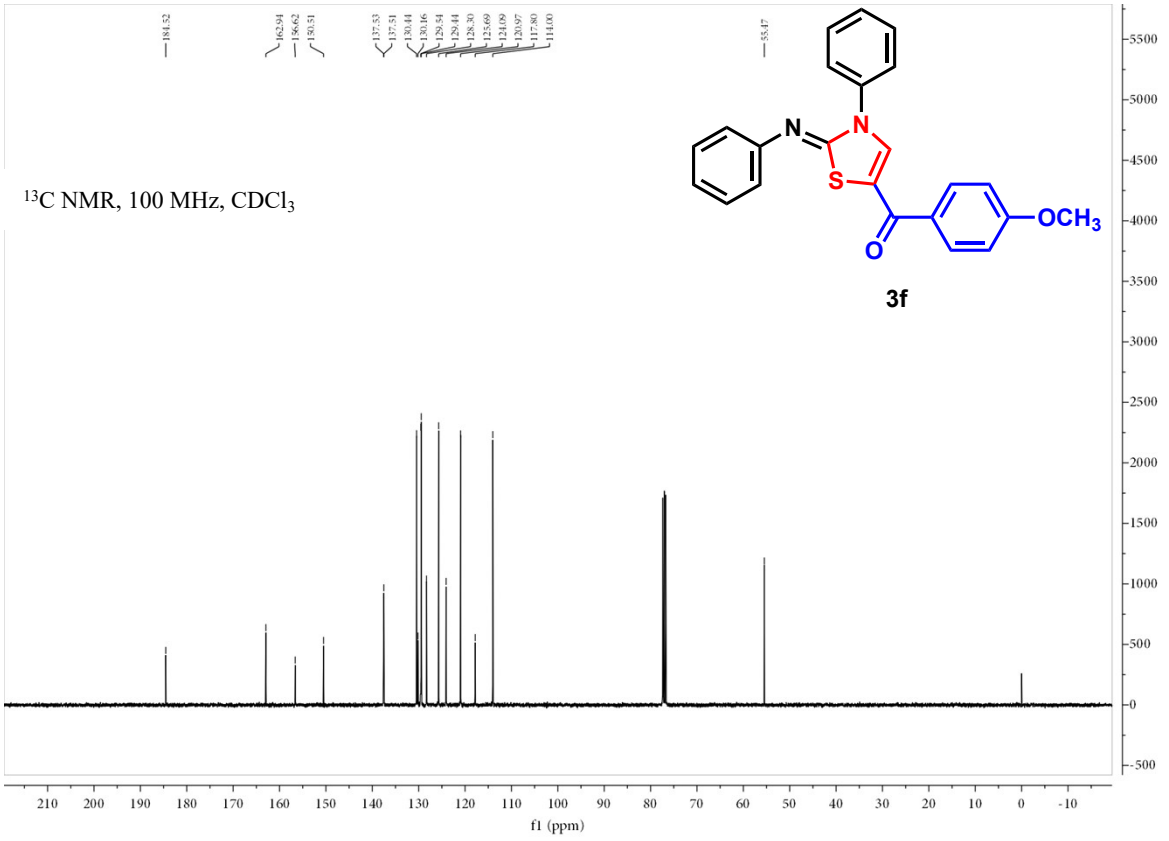
^{13}C NMR, 100 MHz, $CDCl_3$



3e

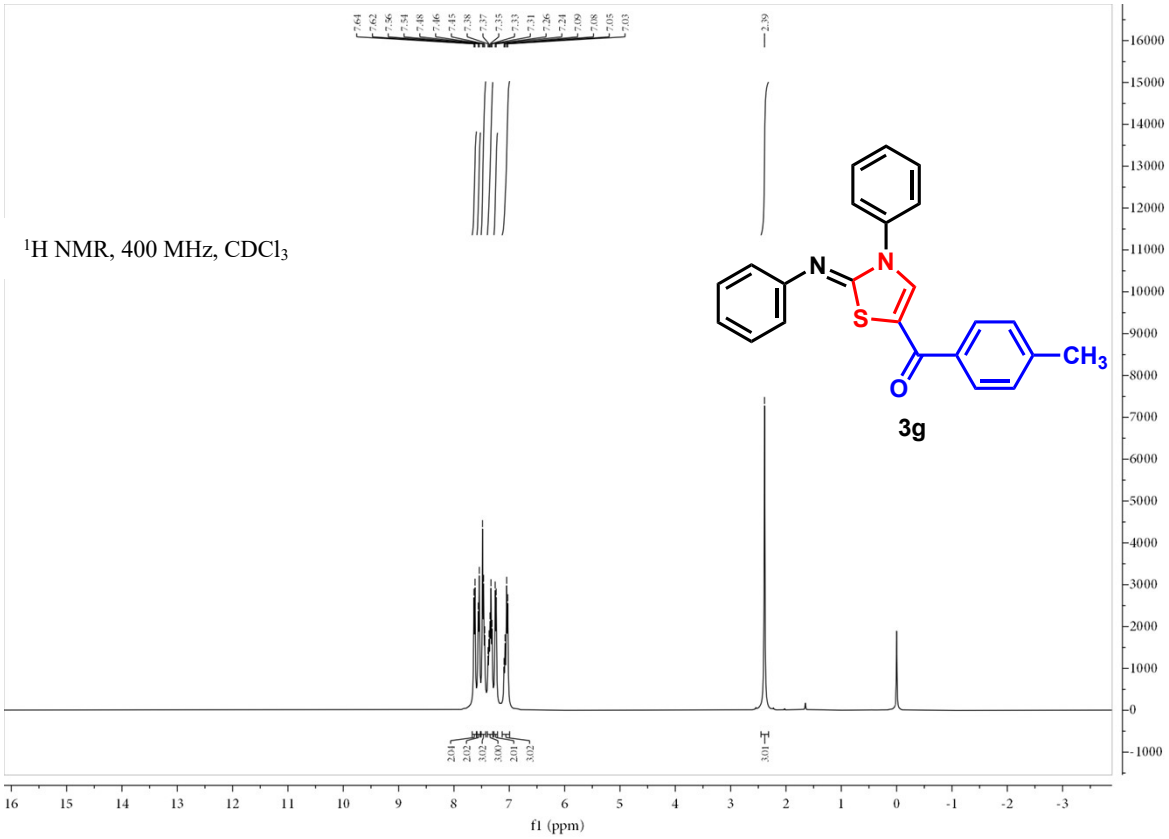


^{1}H NMR, 400 MHz, $CDCl_3$

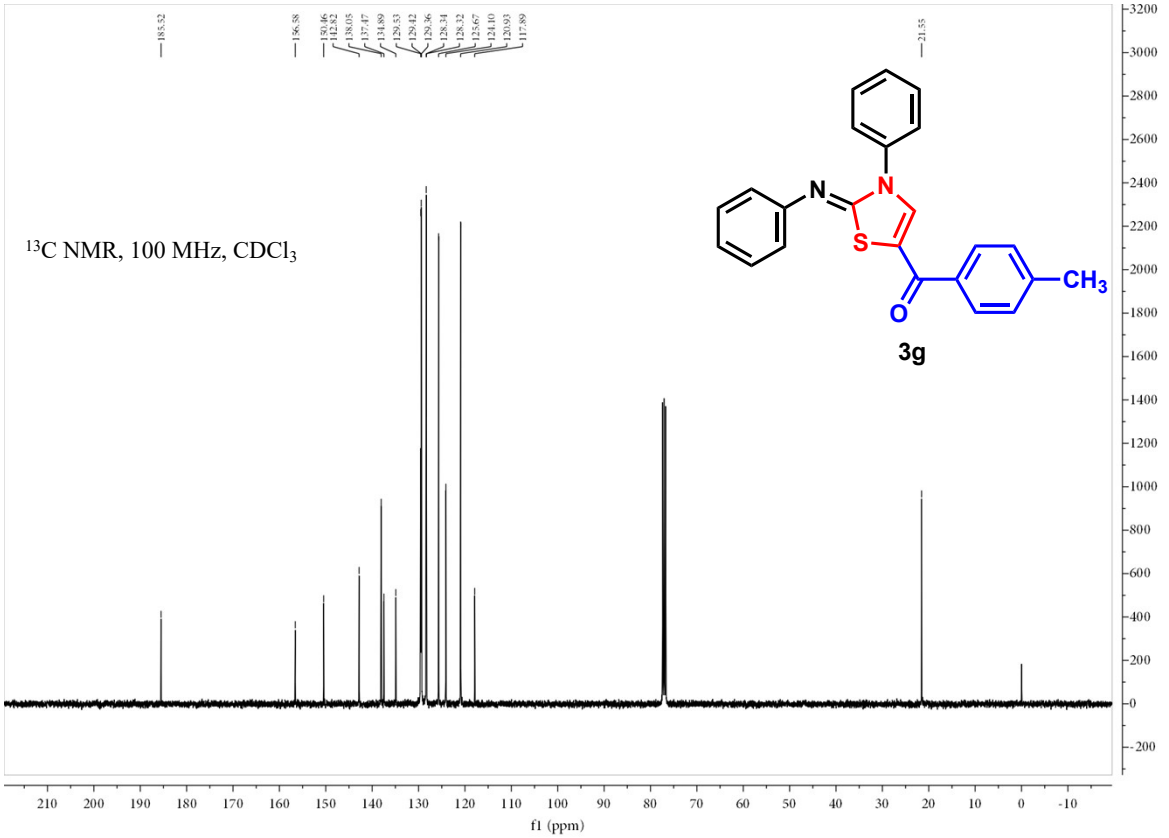


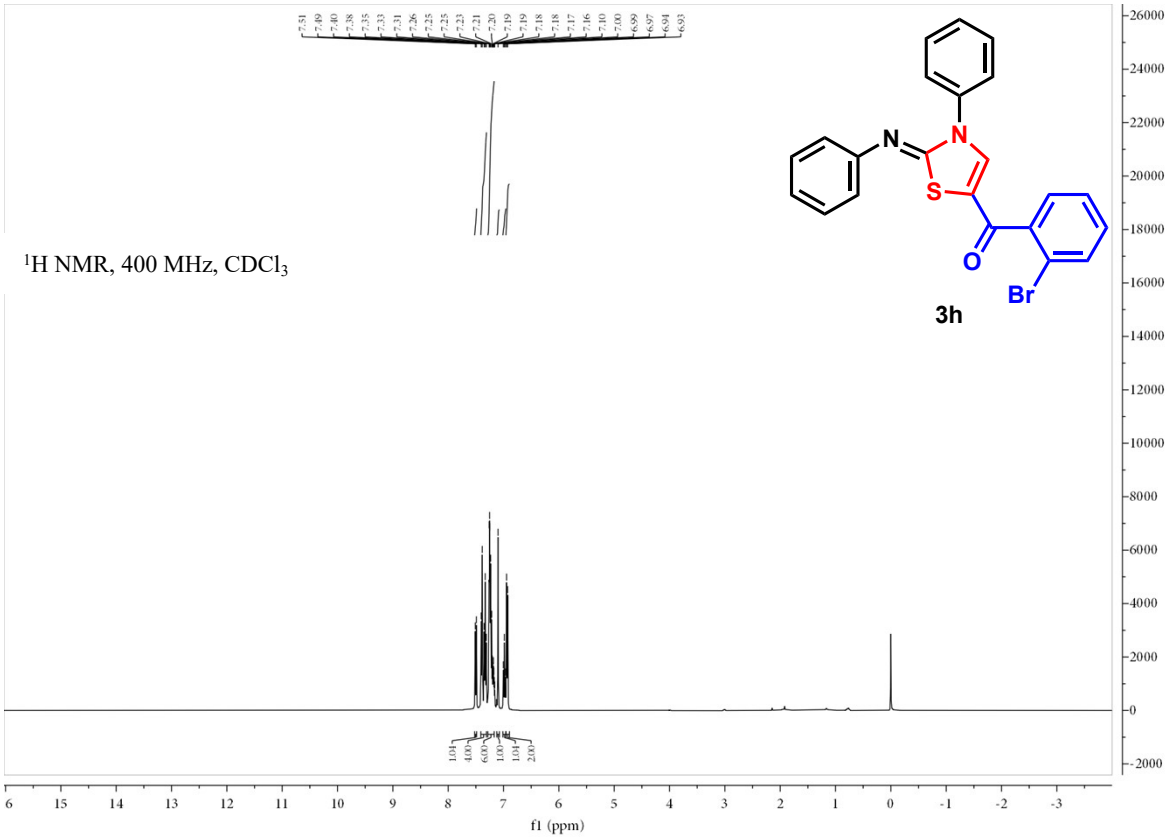
^{13}C NMR, 100 MHz, $CDCl_3$

^{1}H NMR, 400 MHz, $CDCl_3$

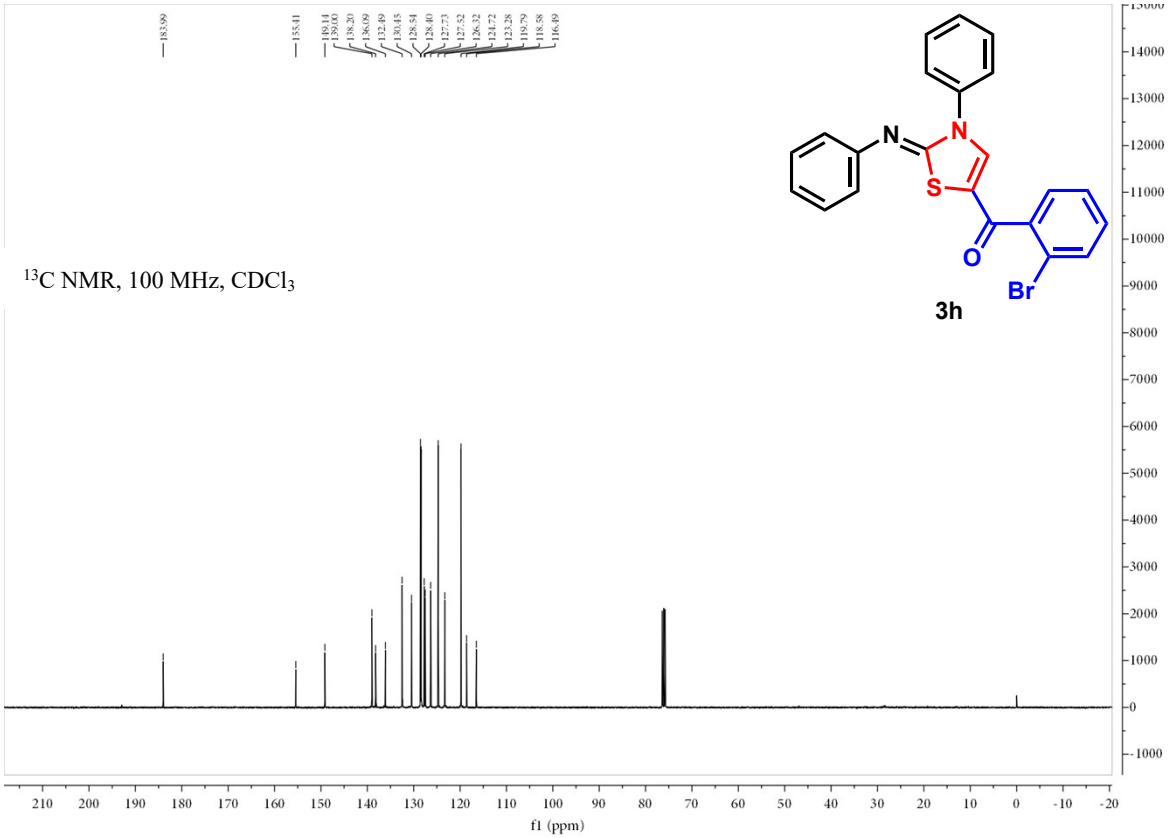


^{13}C NMR, 100 MHz, $CDCl_3$



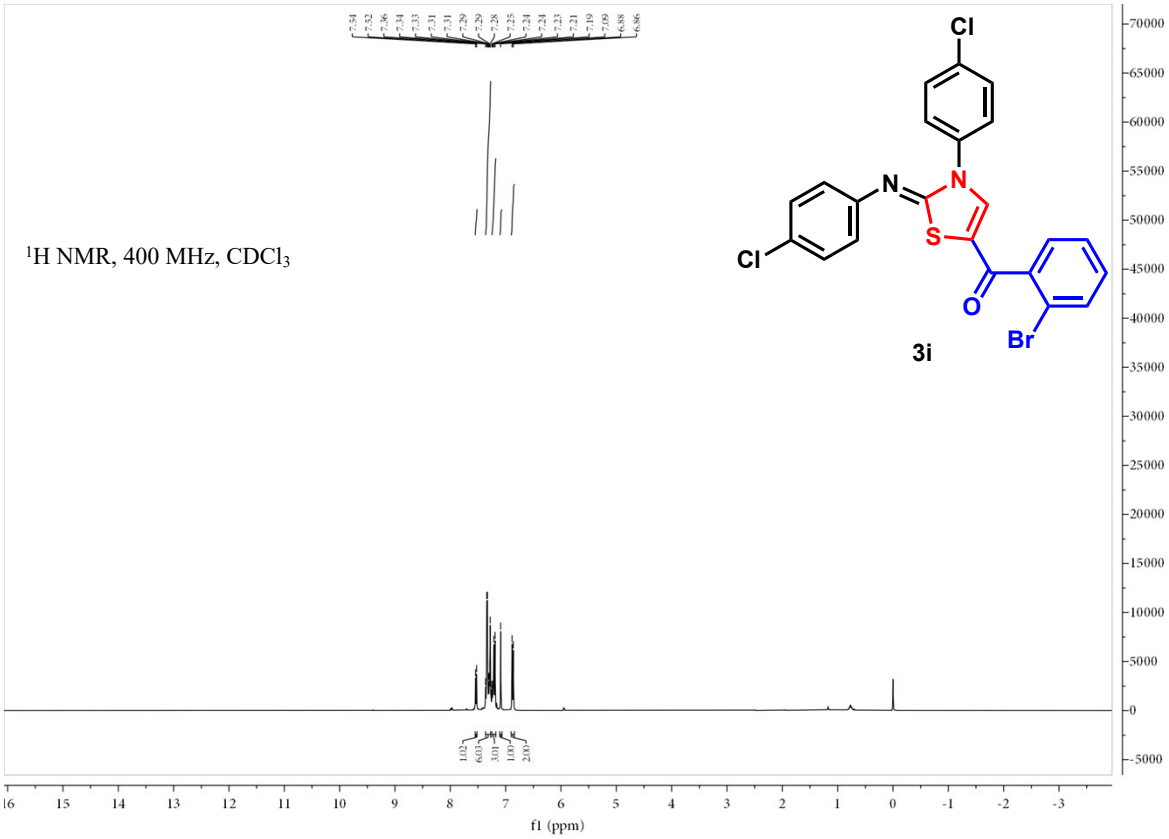


^{1}H NMR, 400 MHz, $CDCl_3$

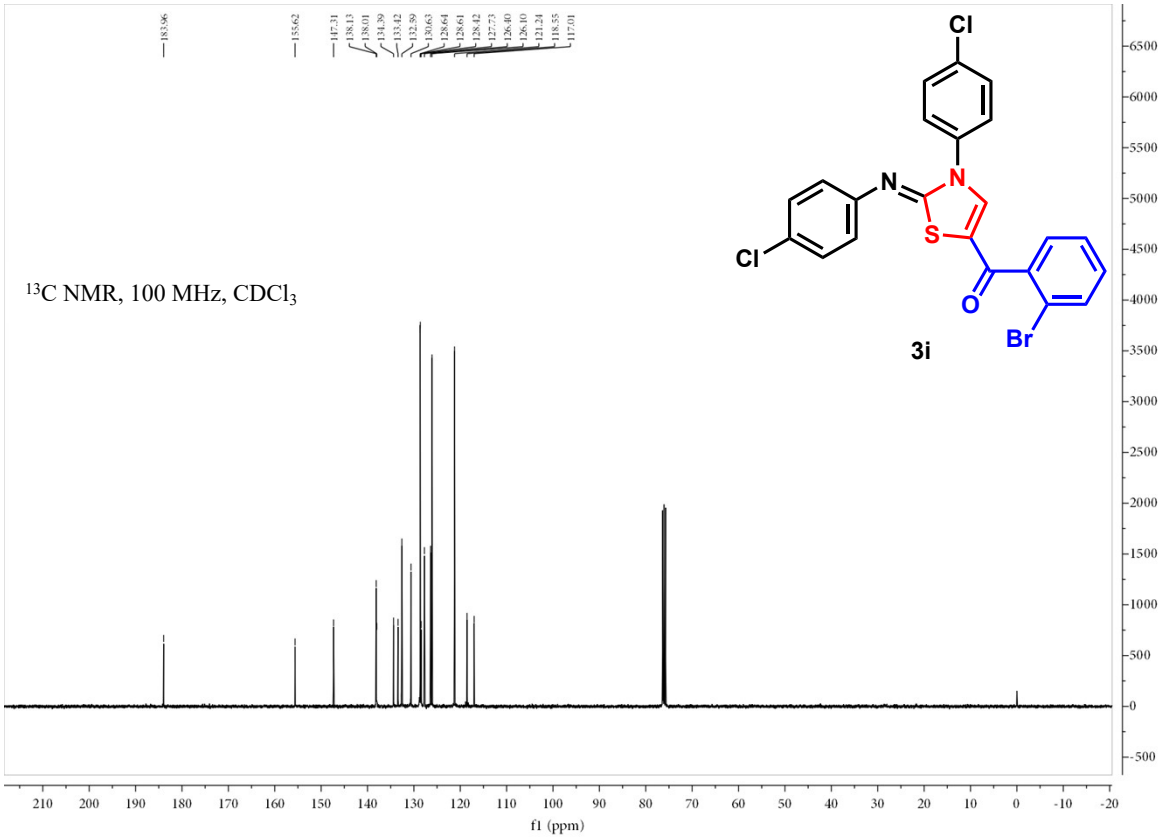


^{13}C NMR, 100 MHz, $CDCl_3$

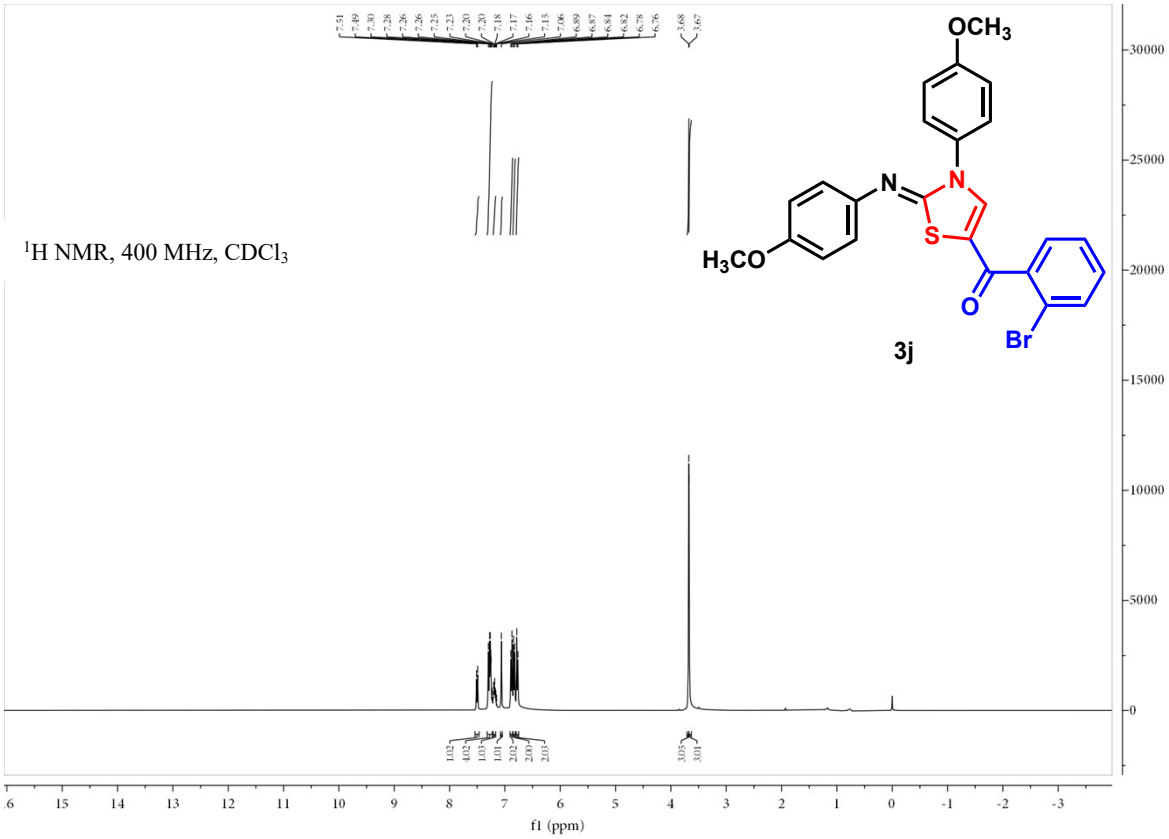
^{1}H NMR, 400 MHz, $CDCl_3$



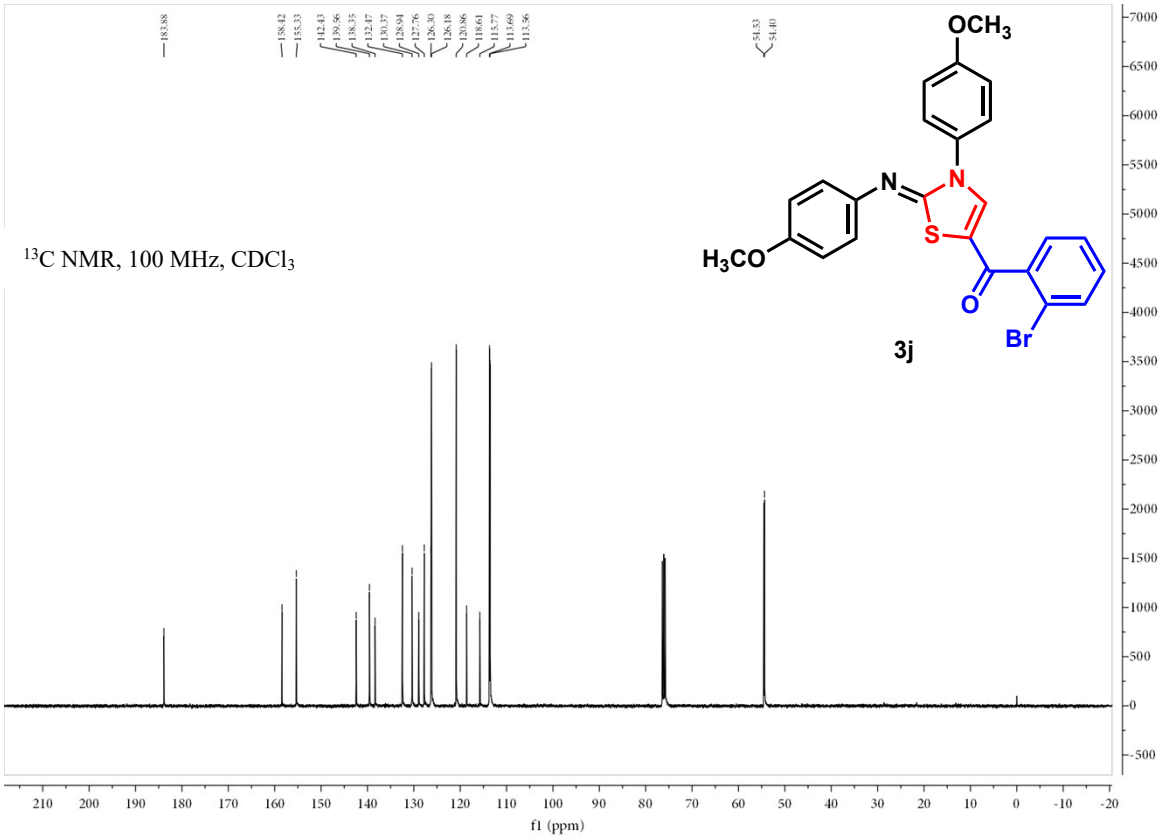
^{13}C NMR, 100 MHz, $CDCl_3$

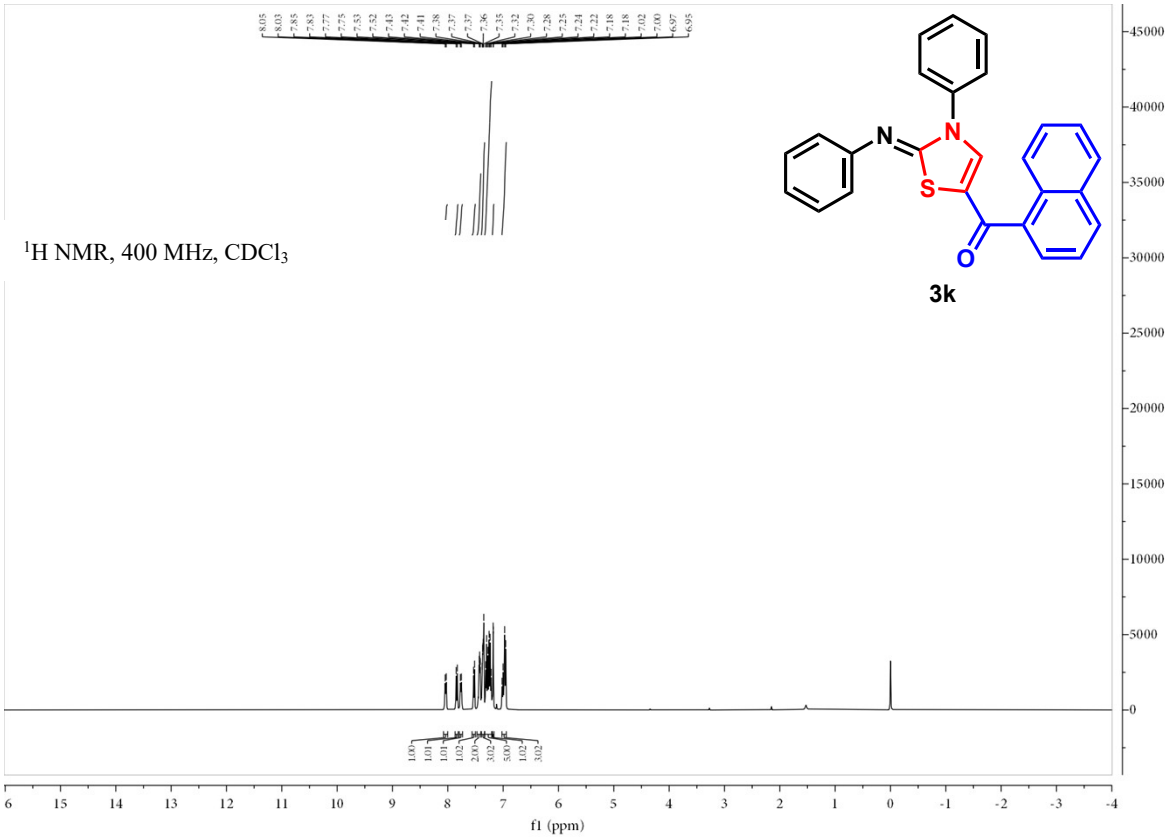


^{1}H NMR, 400 MHz, $CDCl_3$



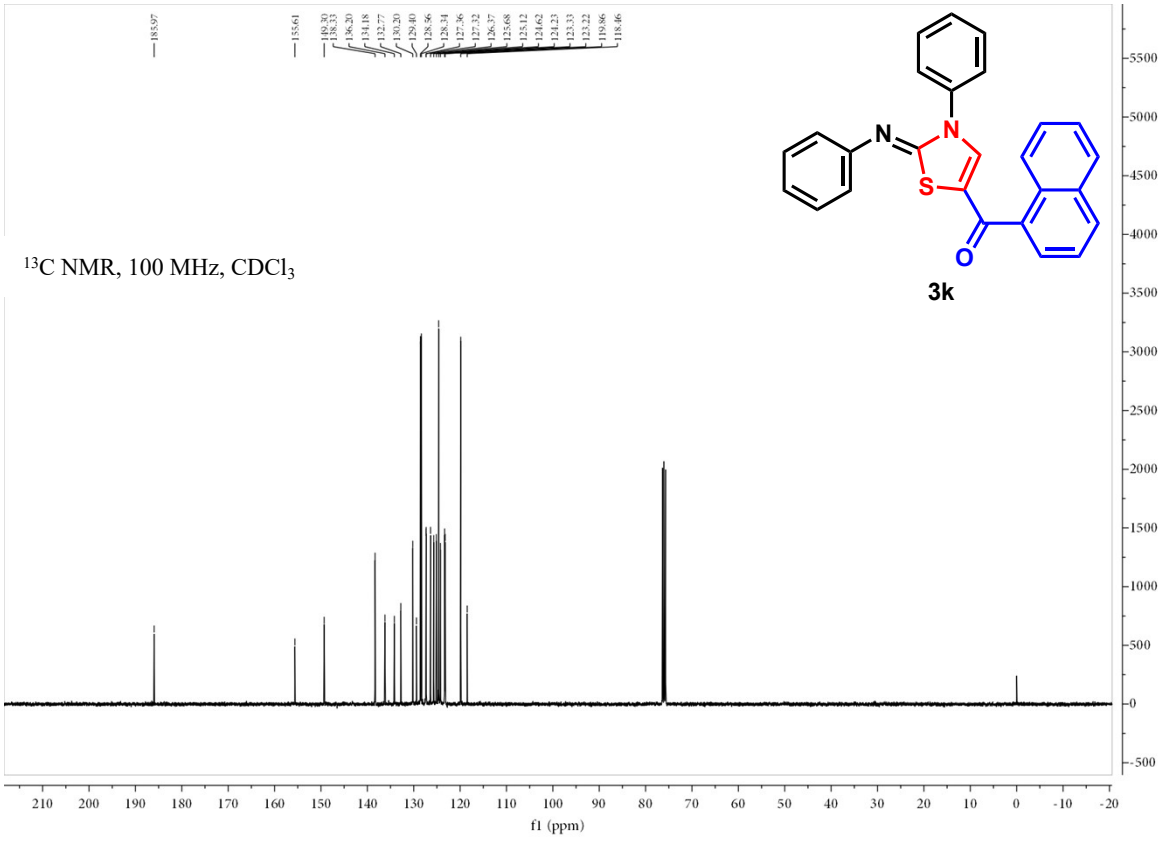
^{13}C NMR, 100 MHz, $CDCl_3$





^{1}H NMR, 400 MHz, $CDCl_3$

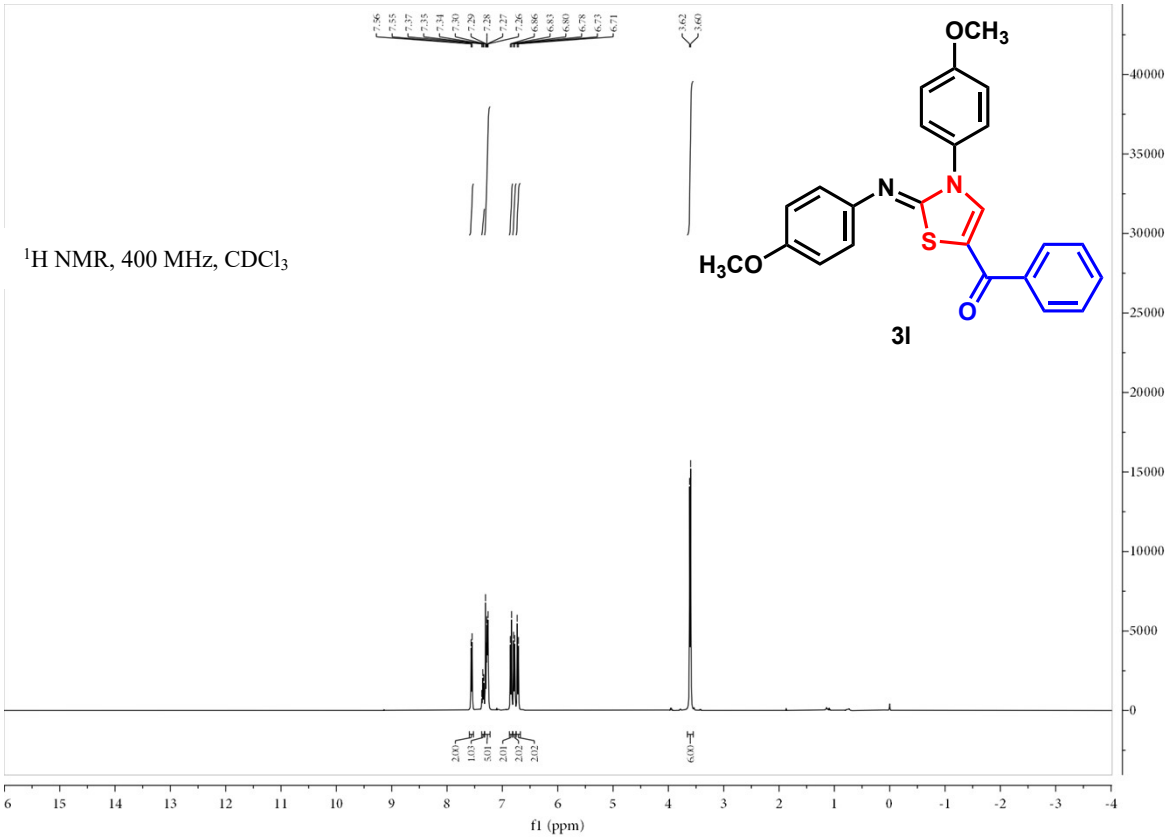
3k



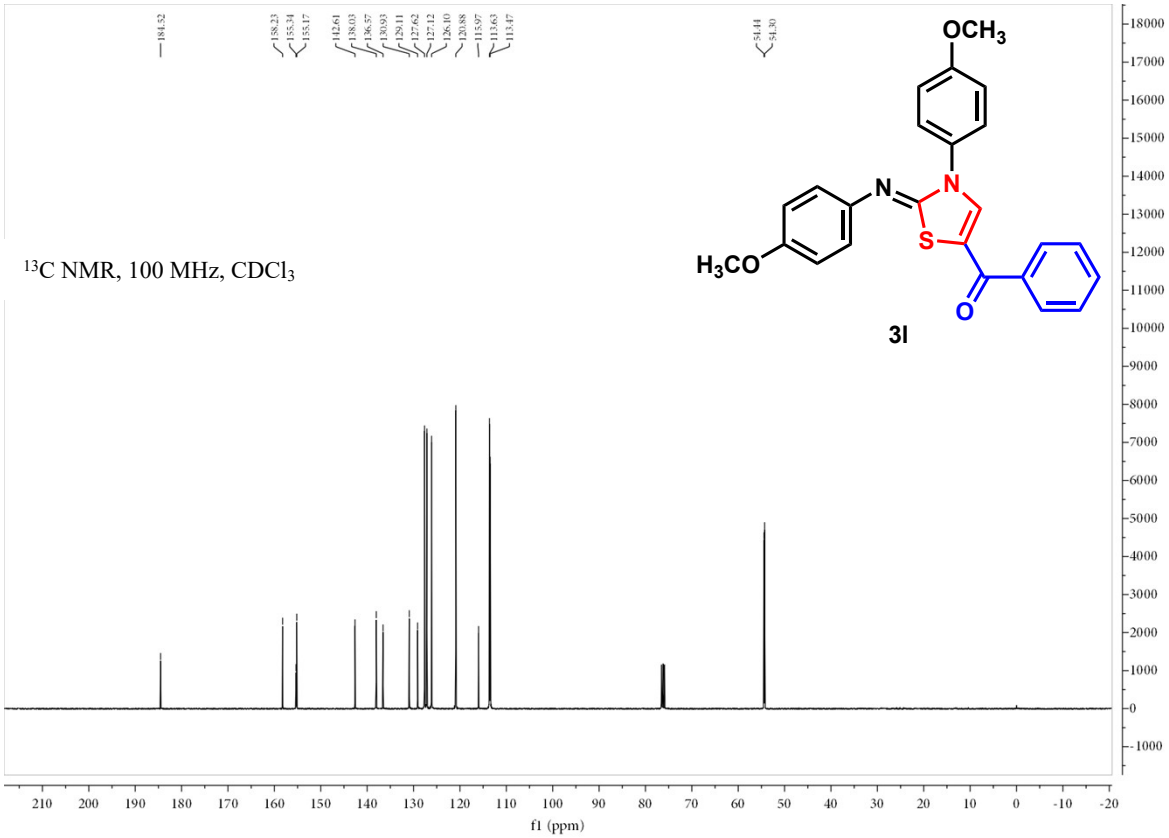
^{13}C NMR, 100 MHz, $CDCl_3$

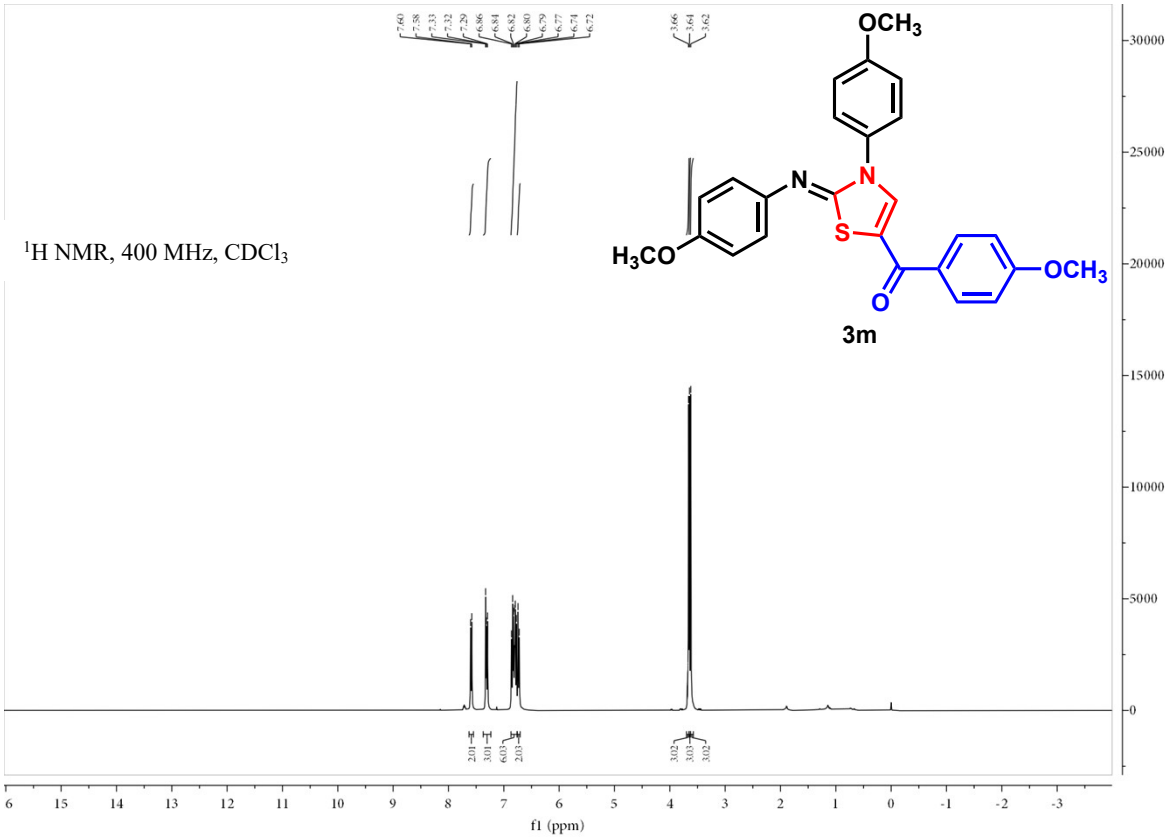
3k

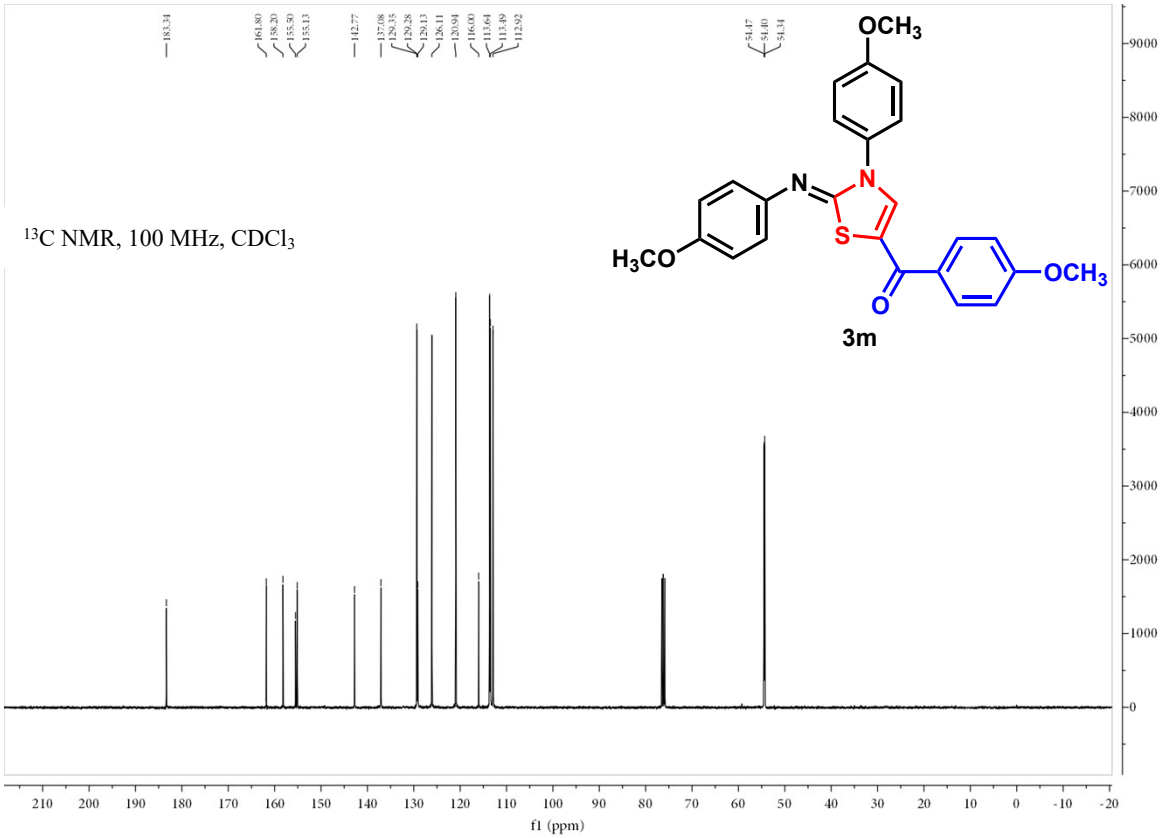
^{1}H NMR, 400 MHz, $CDCl_3$



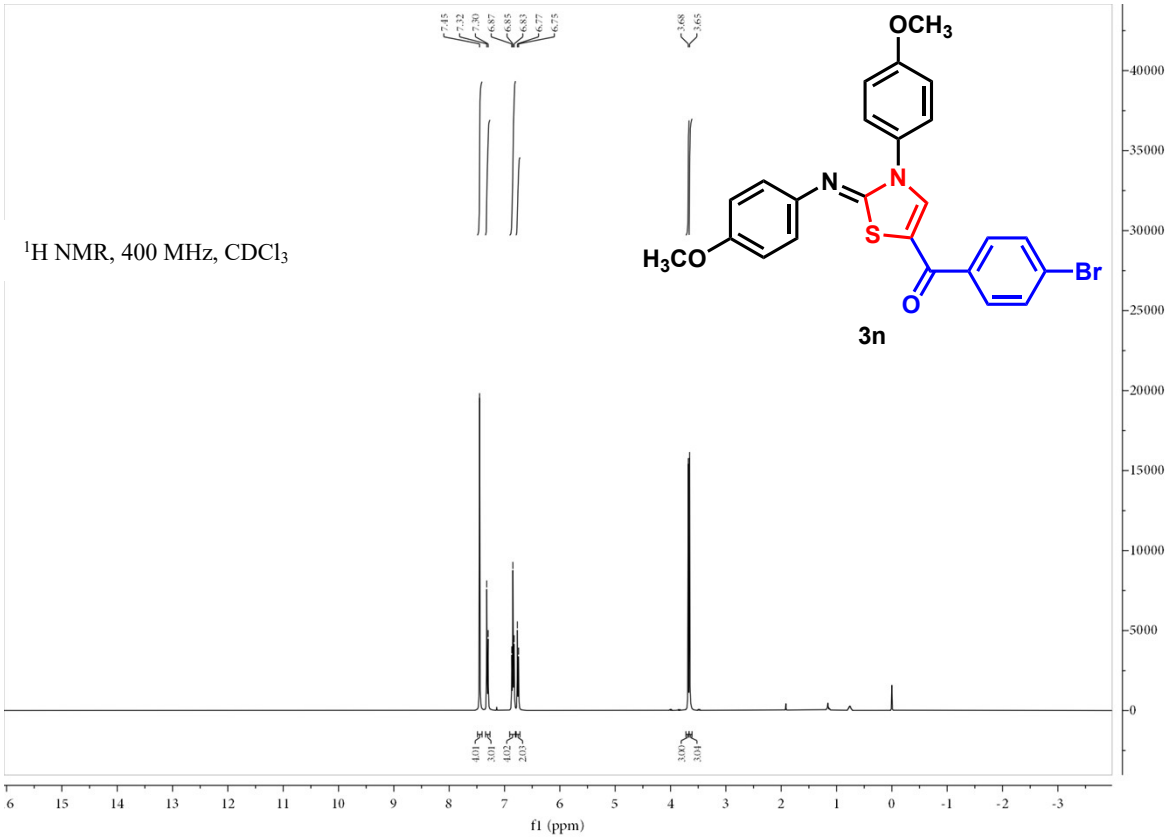
^{13}C NMR, 100 MHz, $CDCl_3$



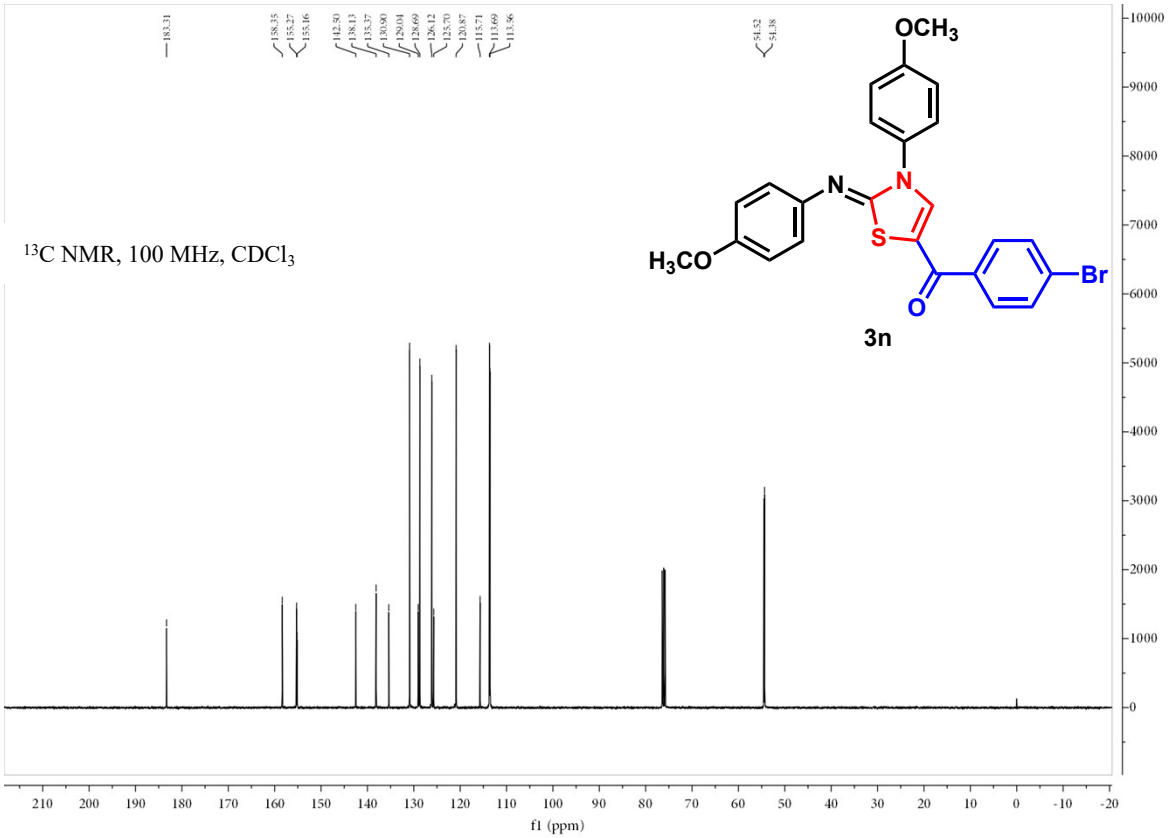

^{1}H NMR, 400 MHz, $CDCl_3$
OCH3
N
S
O
H3CO
OCH3
3m
f1 (ppm)


^{13}C NMR, 100 MHz, $CDCl_3$
OCH3
N
S
O
H3CO
OCH3
3m
f1 (ppm)

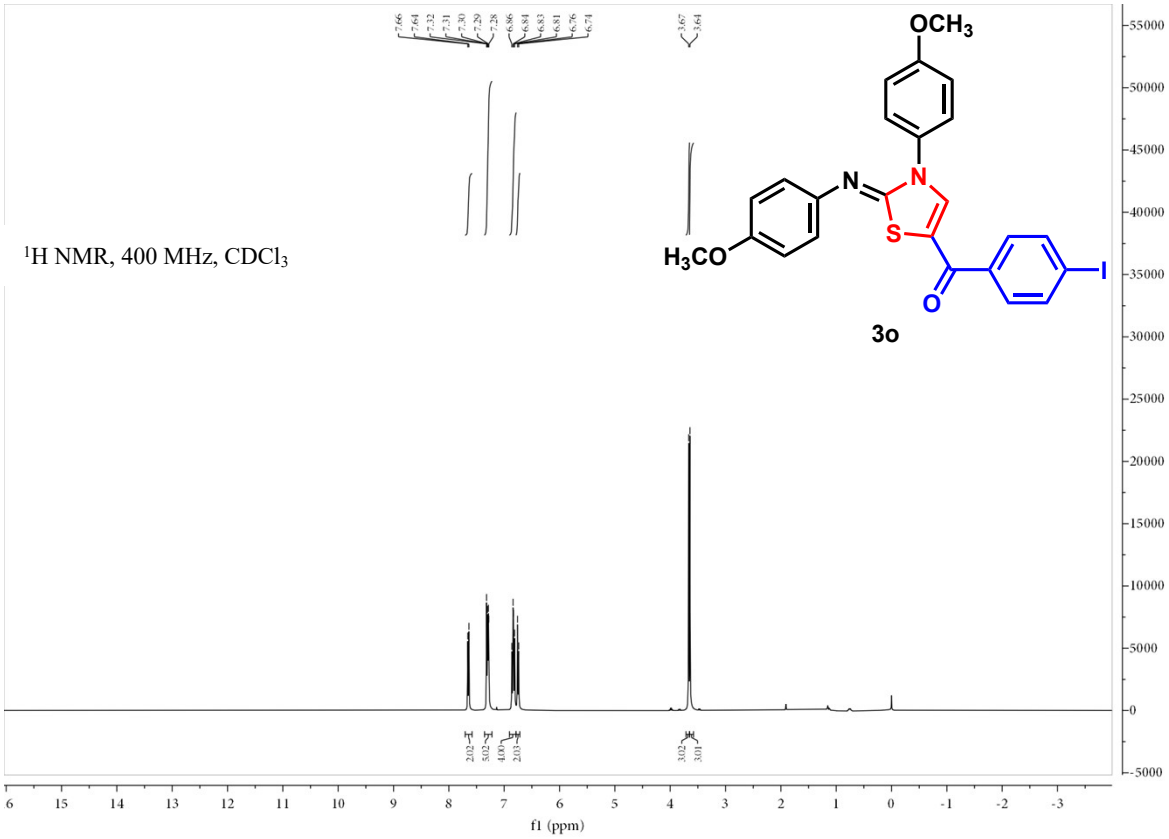
^{1}H NMR, 400 MHz, $CDCl_3$



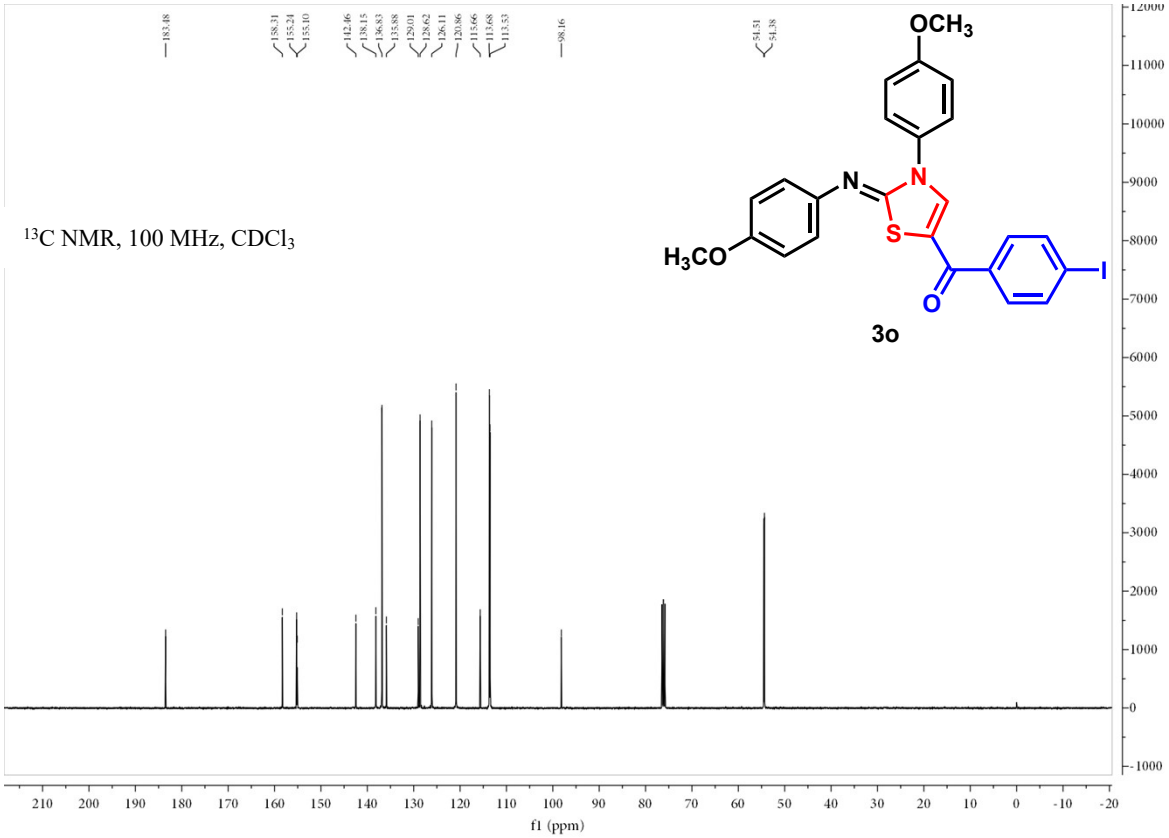
^{13}C NMR, 100 MHz, $CDCl_3$

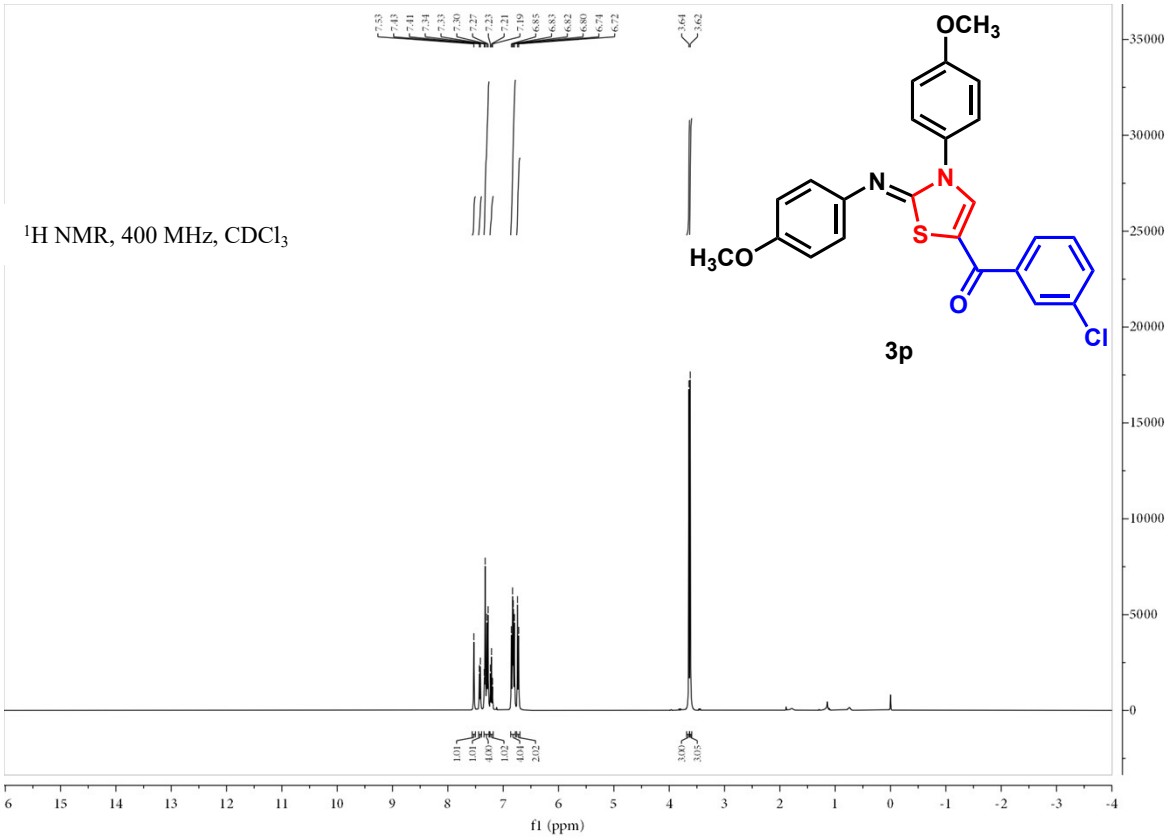


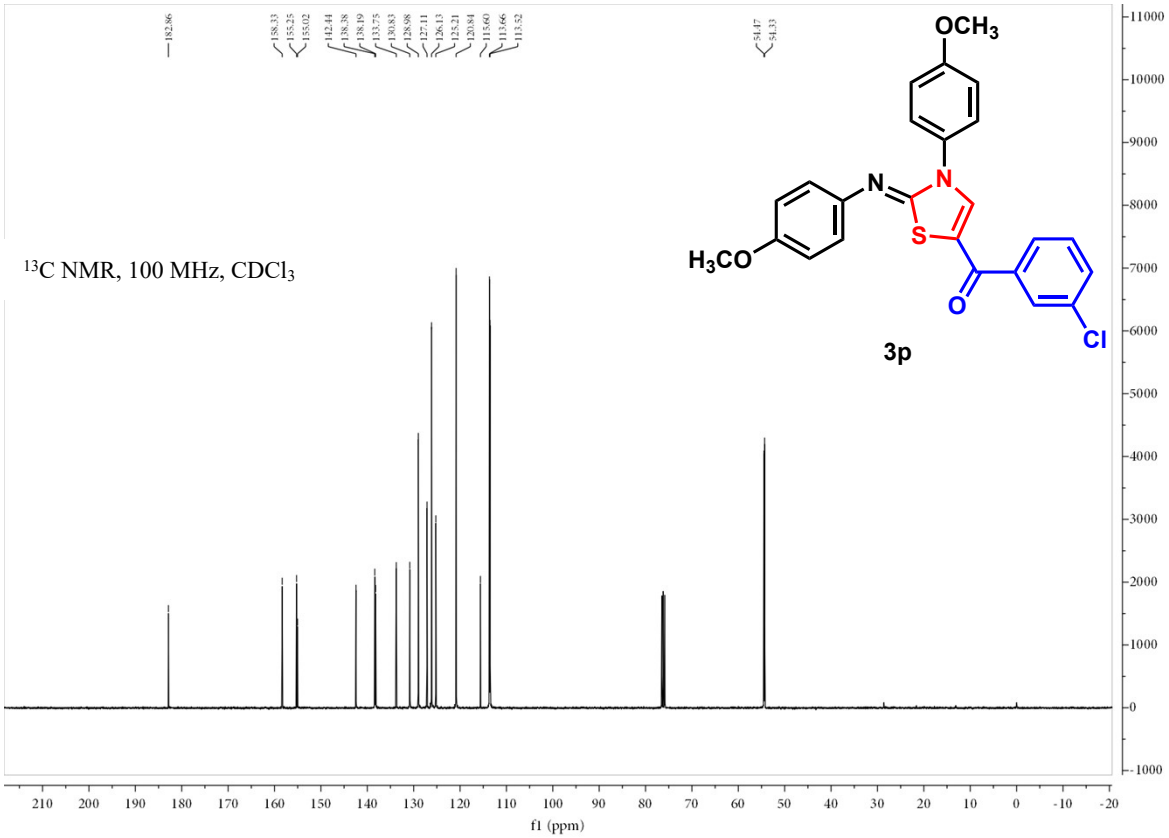
^{1}H NMR, 400 MHz, $CDCl_3$

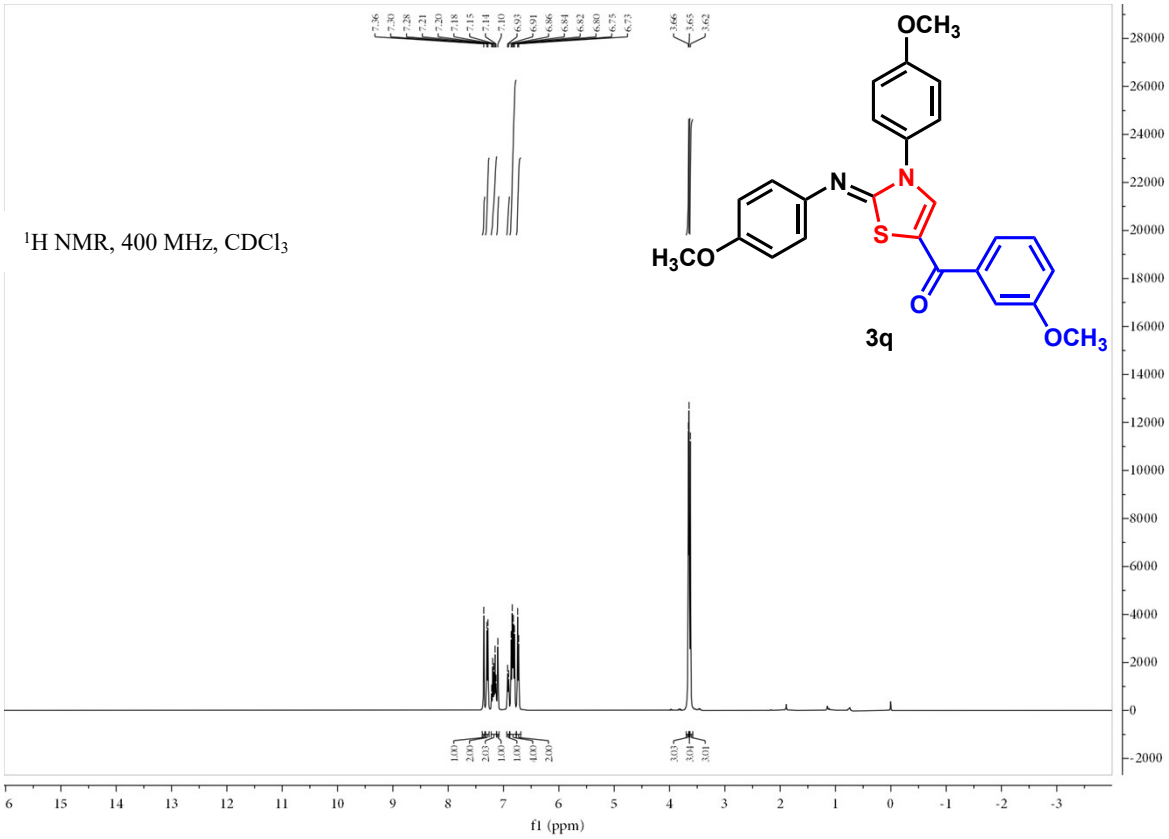


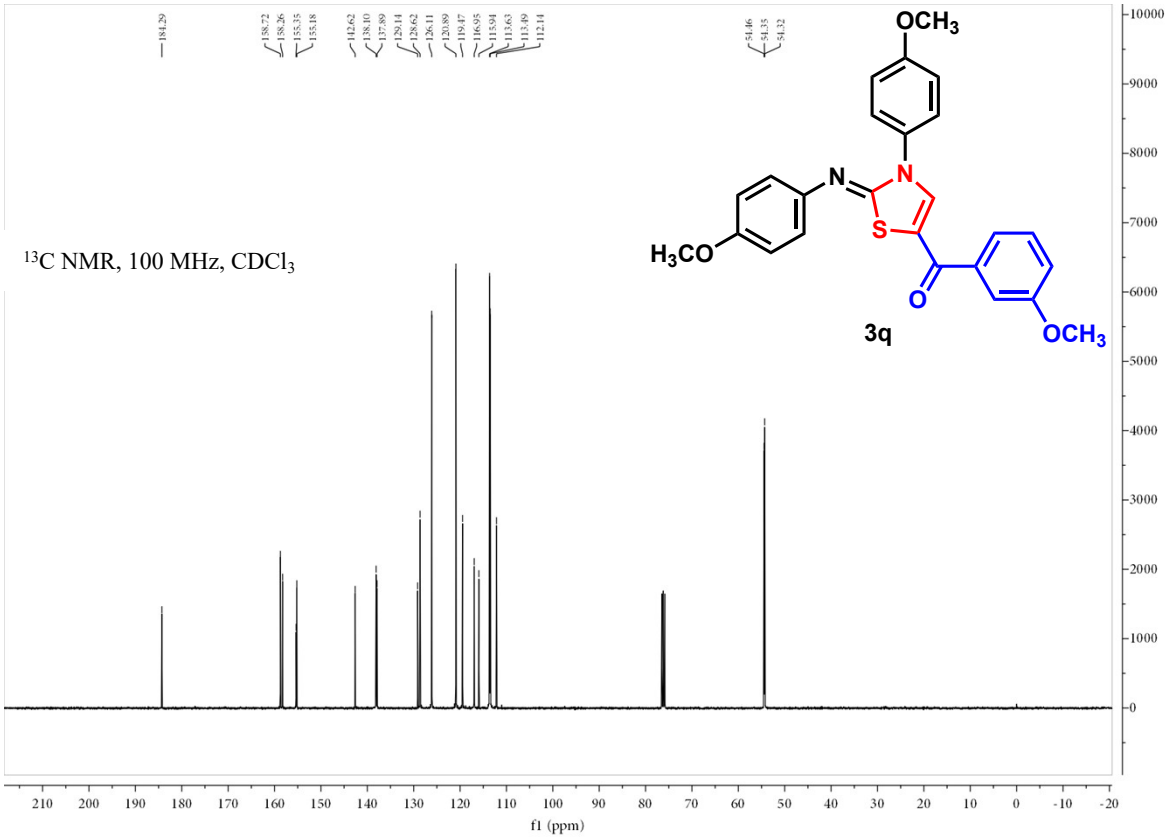
^{13}C NMR, 100 MHz, $CDCl_3$



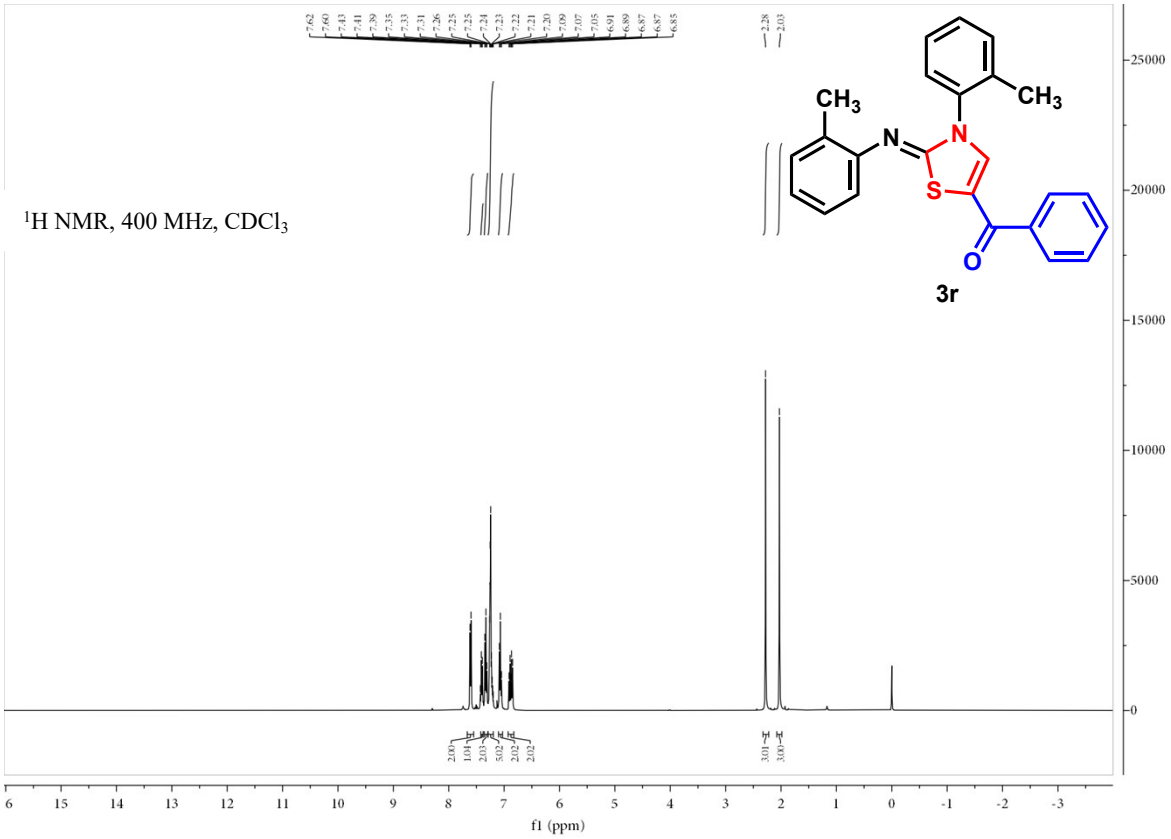

^{1}H NMR, 400 MHz, $CDCl_3$
OCH3
H3CO
N
S
O
Cl
3p
f1 (ppm)


^{13}C NMR, 100 MHz, $CDCl_3$
OCH3
H3CO
N
S
O
Cl
3p
f1 (ppm)

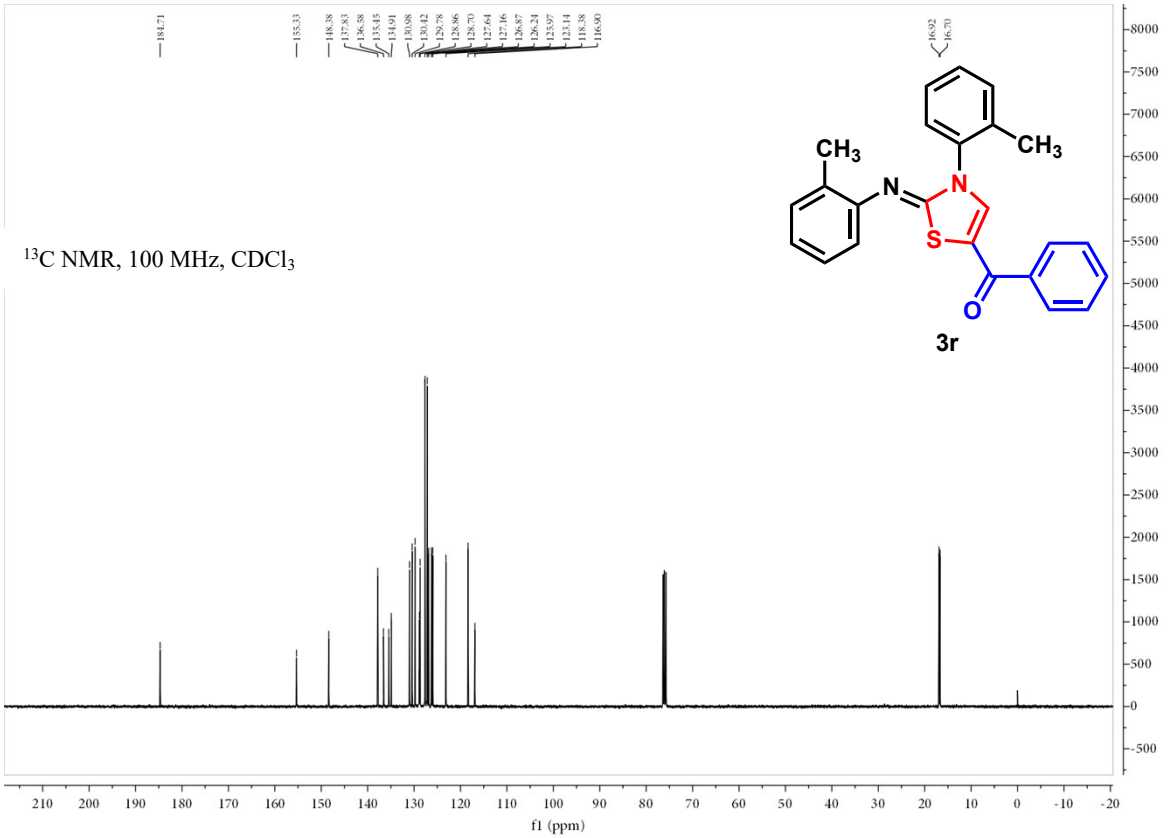

^{1}H NMR, 400 MHz, $CDCl_3$
OCH_3
N
S
O
H_3CO
OCH_3
3q
f1 (ppm)


^{13}C NMR, 100 MHz, $CDCl_3$
OCH_3
N
S
O
H_3CO
OCH_3
3q
f1 (ppm)

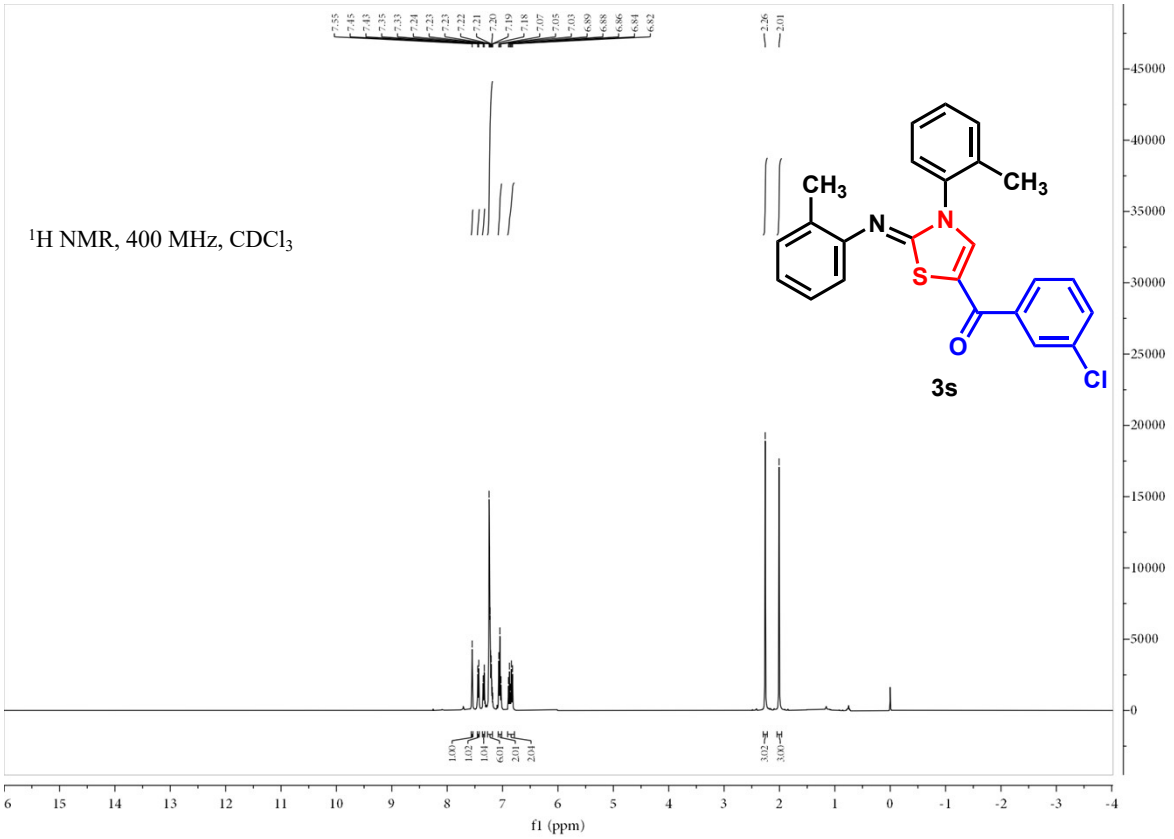
^{1}H NMR, 400 MHz, $CDCl_3$



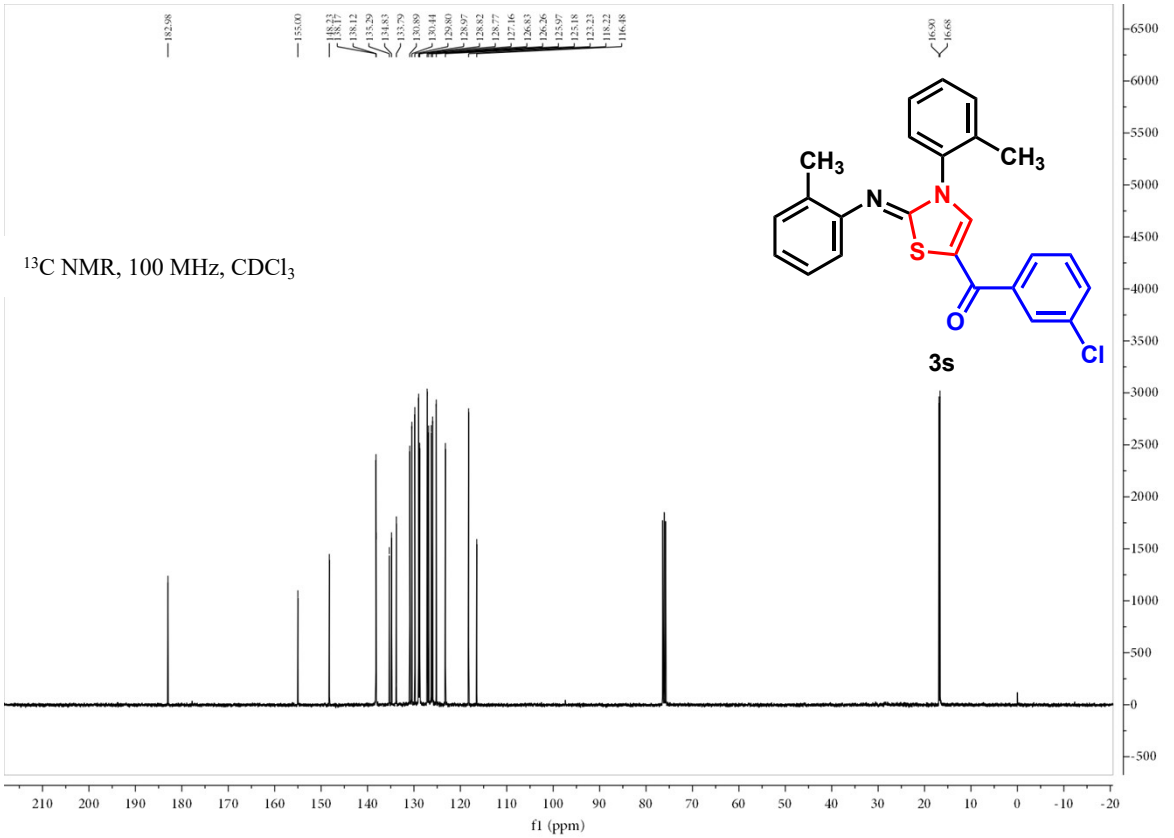
^{13}C NMR, 100 MHz, $CDCl_3$

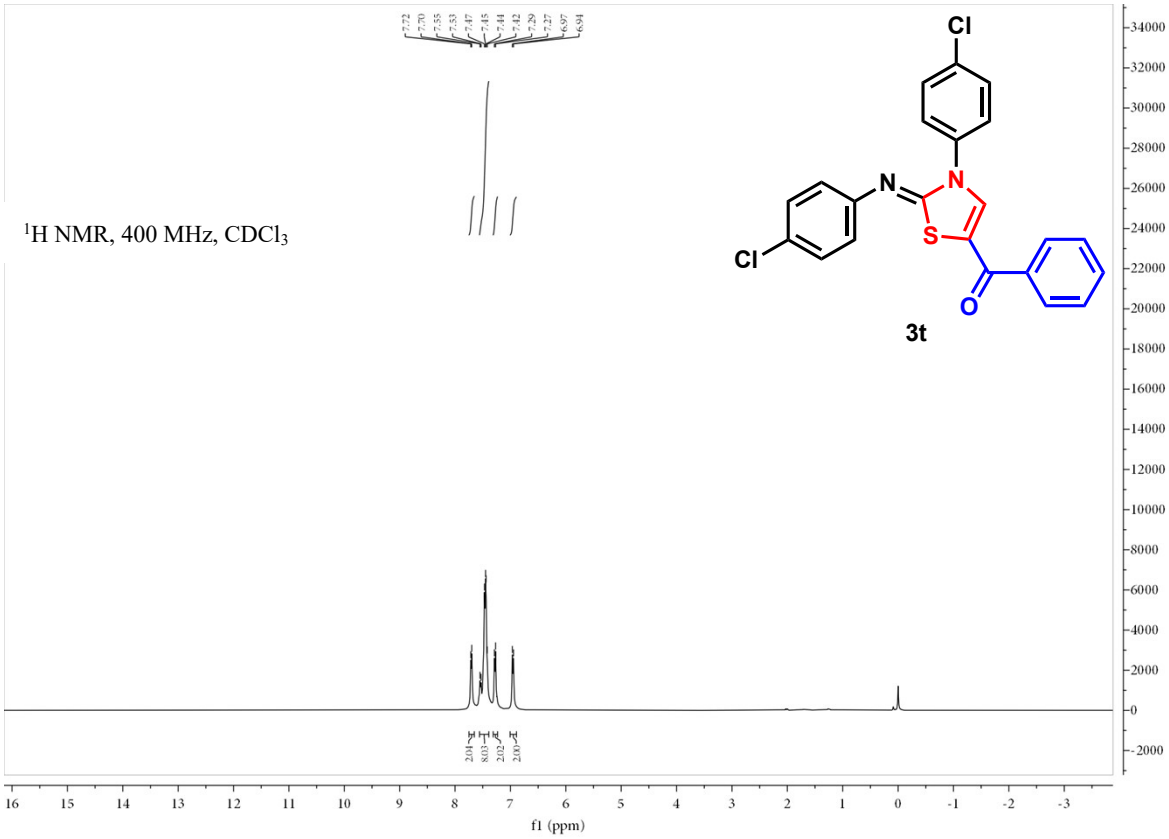


^{1}H NMR, 400 MHz, $CDCl_3$

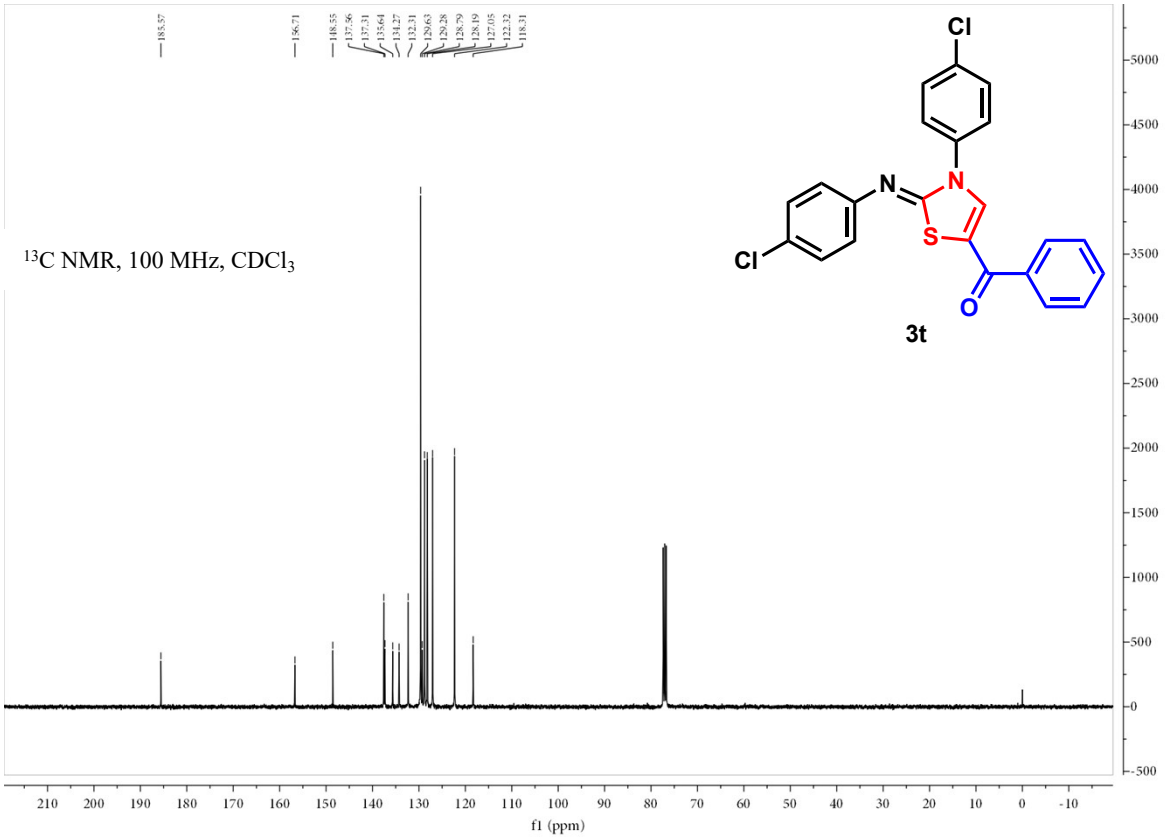


^{13}C NMR, 100 MHz, $CDCl_3$

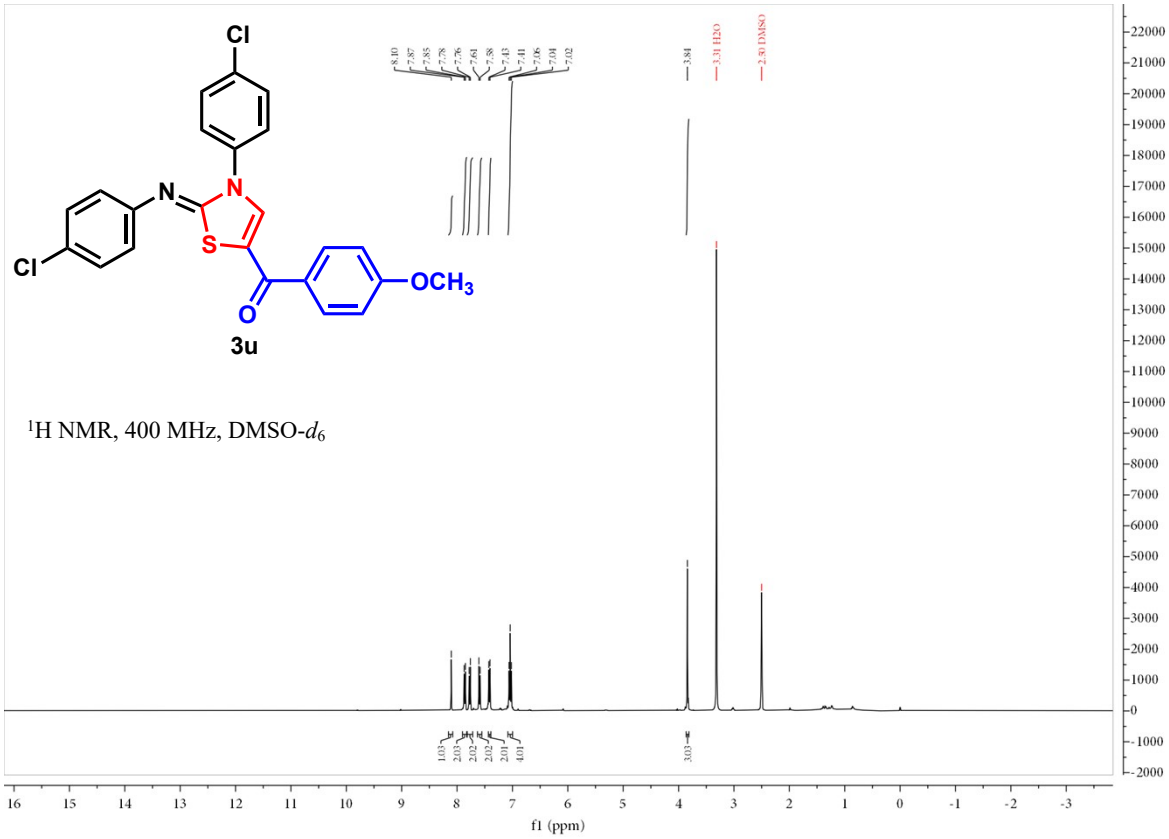




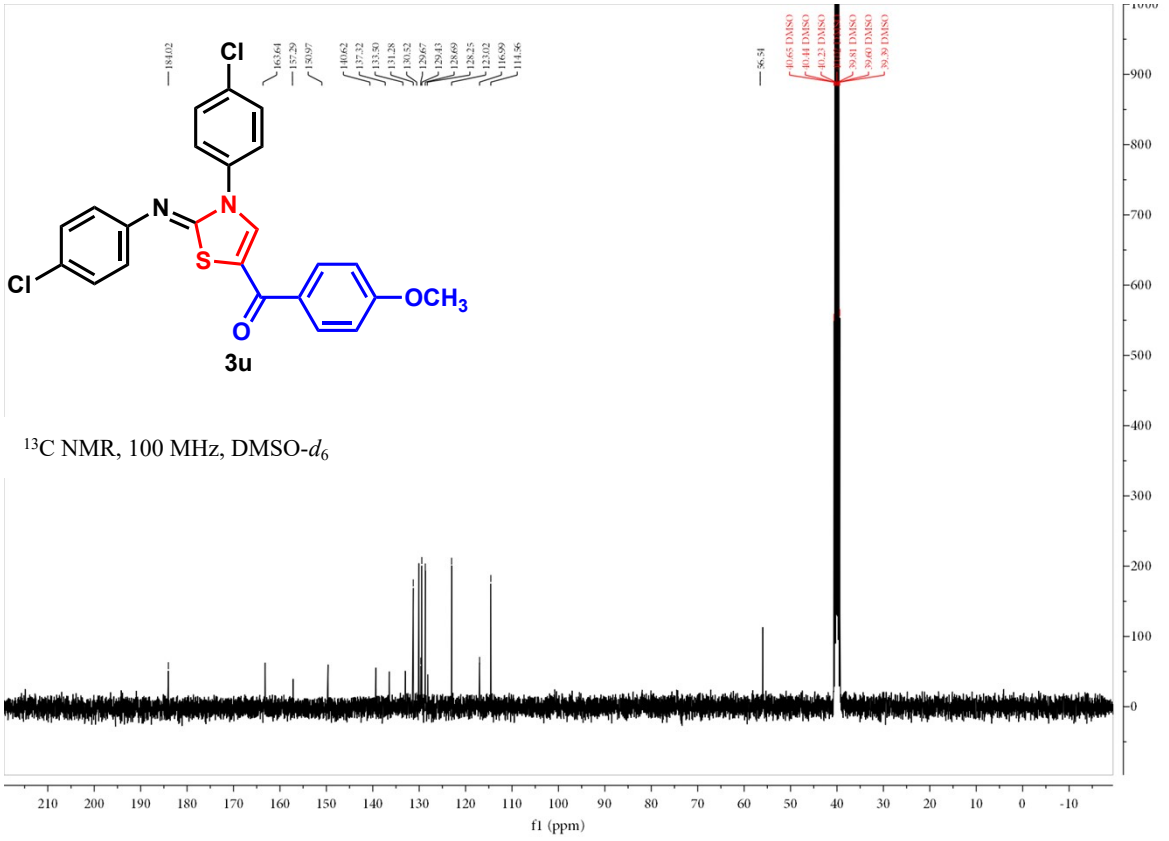
^{1}H NMR, 400 MHz, $CDCl_3$



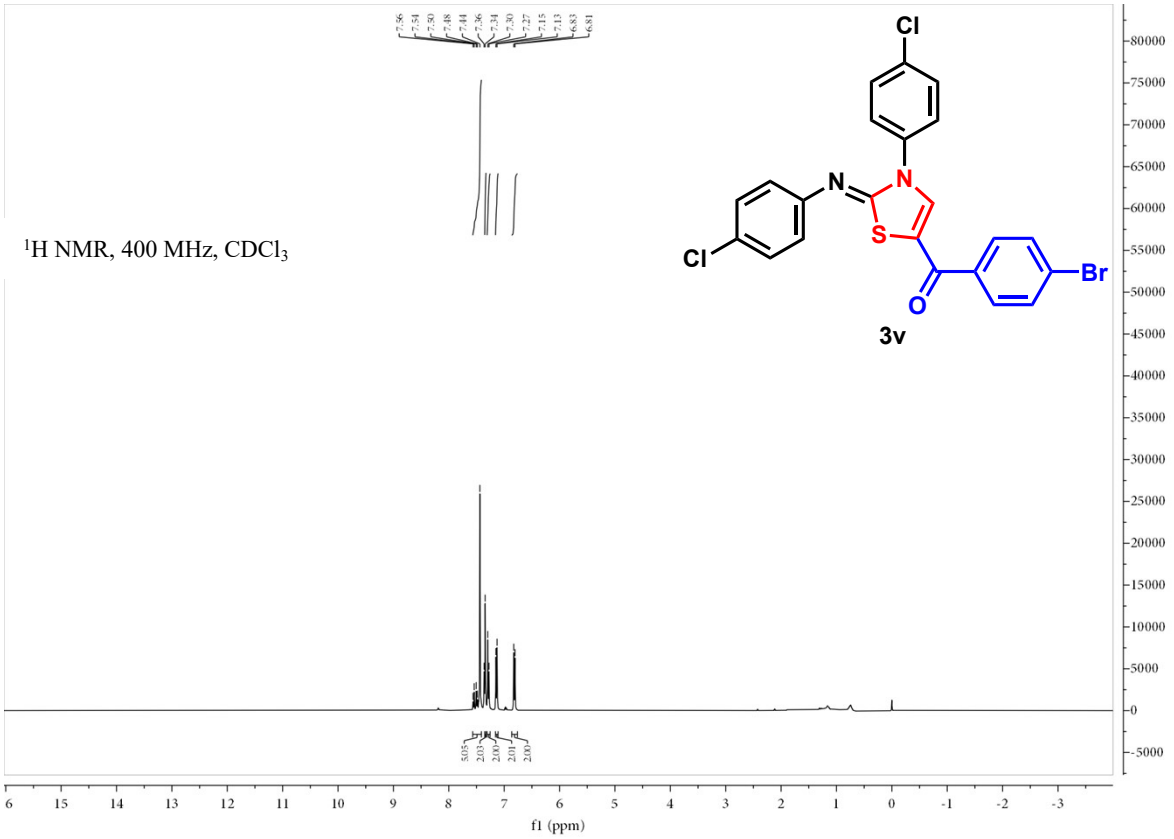
^{13}C NMR, 100 MHz, $CDCl_3$



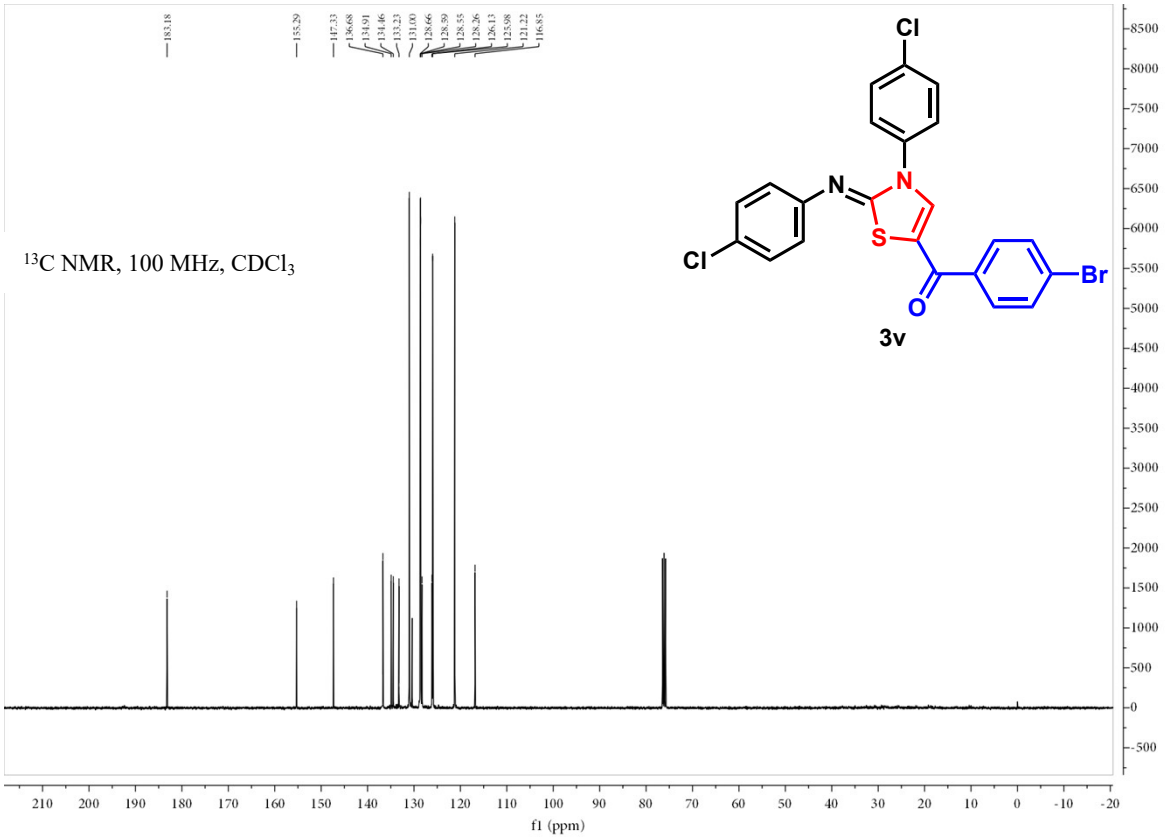
^{1}H NMR, 400 MHz, DMSO-d_6



^{13}C NMR, 100 MHz, DMSO-d_6

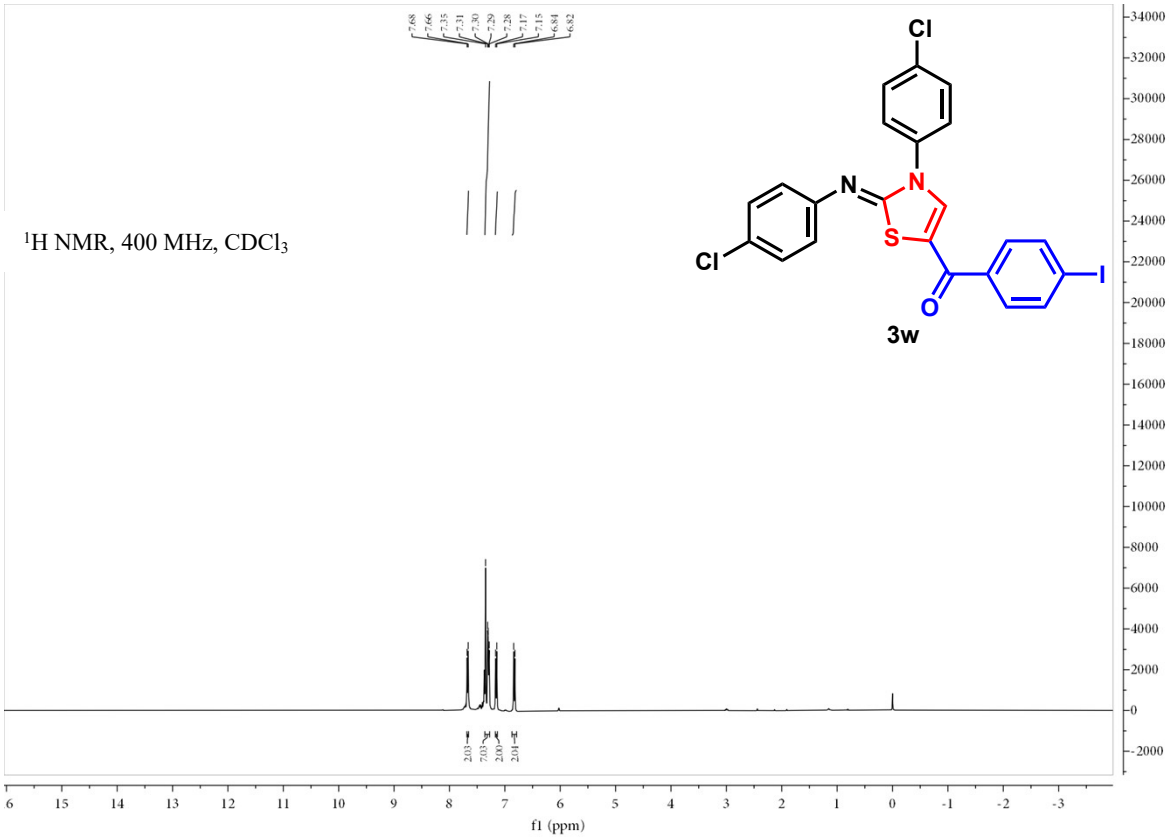


^{1}H NMR, 400 MHz, $CDCl_3$

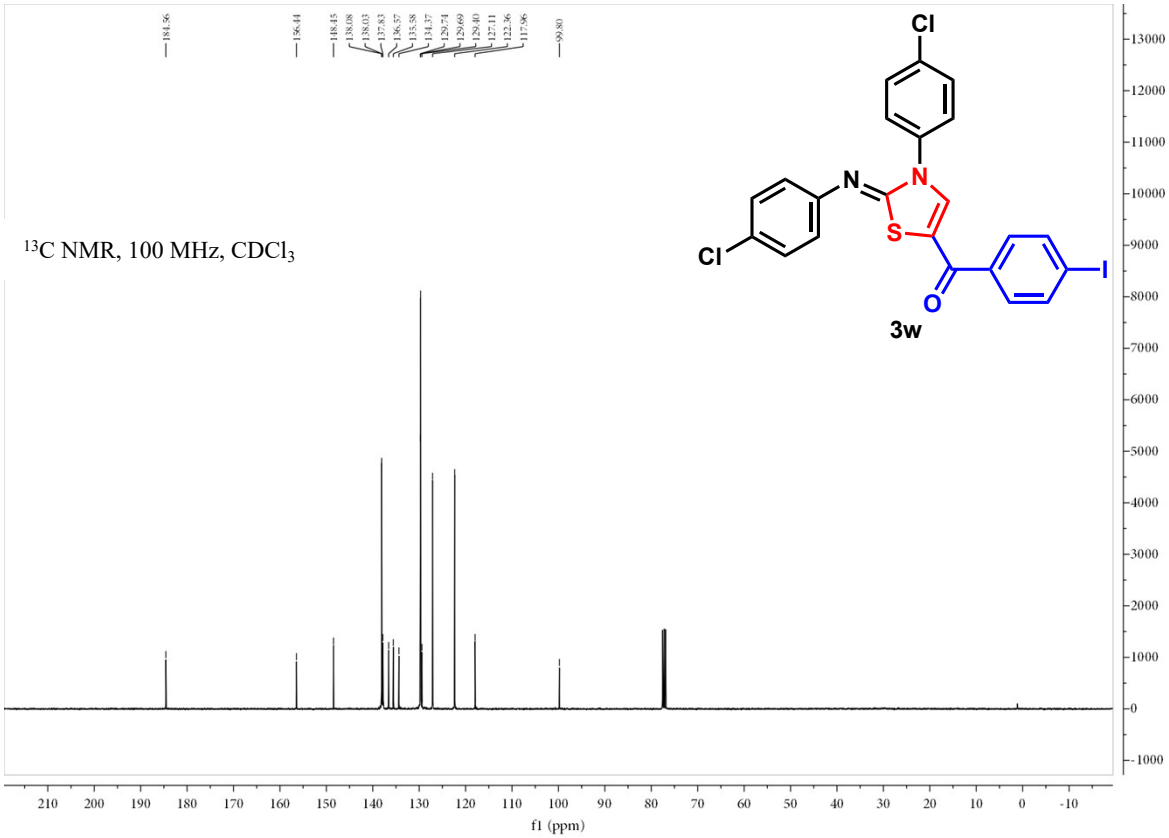


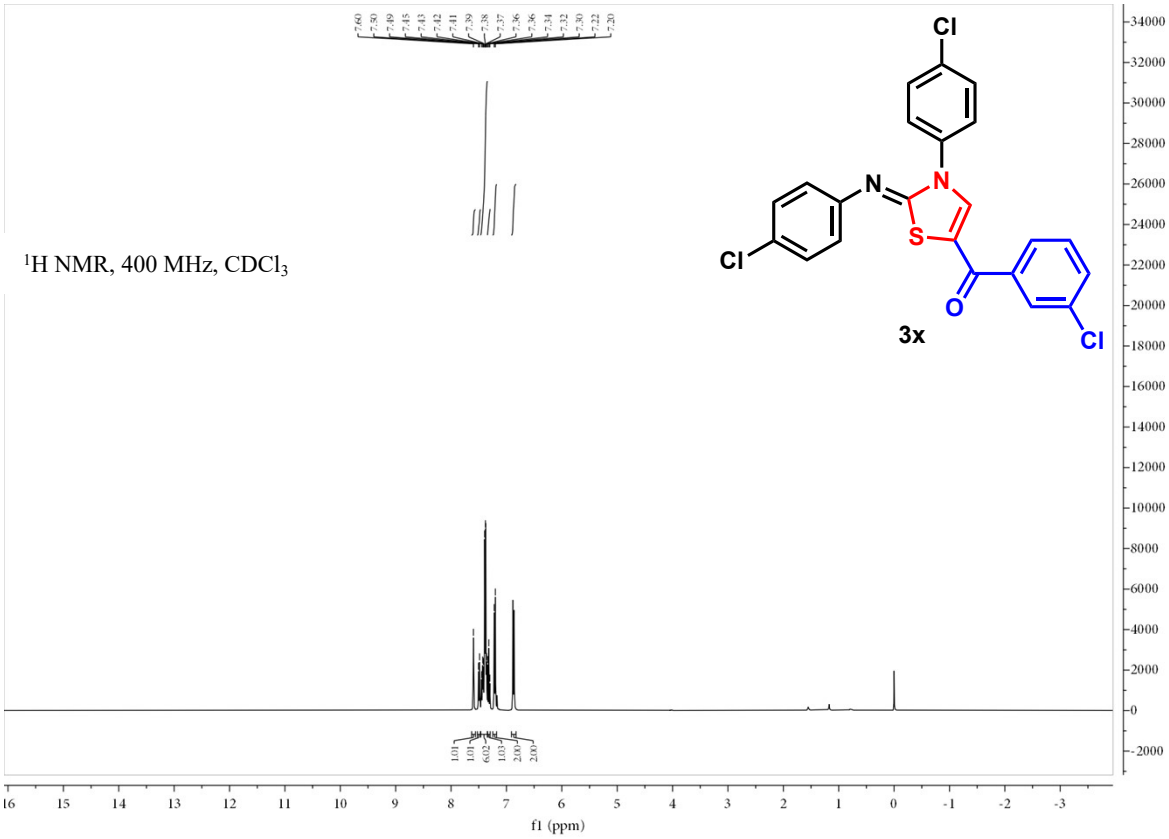
^{13}C NMR, 100 MHz, $CDCl_3$

^{1}H NMR, 400 MHz, $CDCl_3$

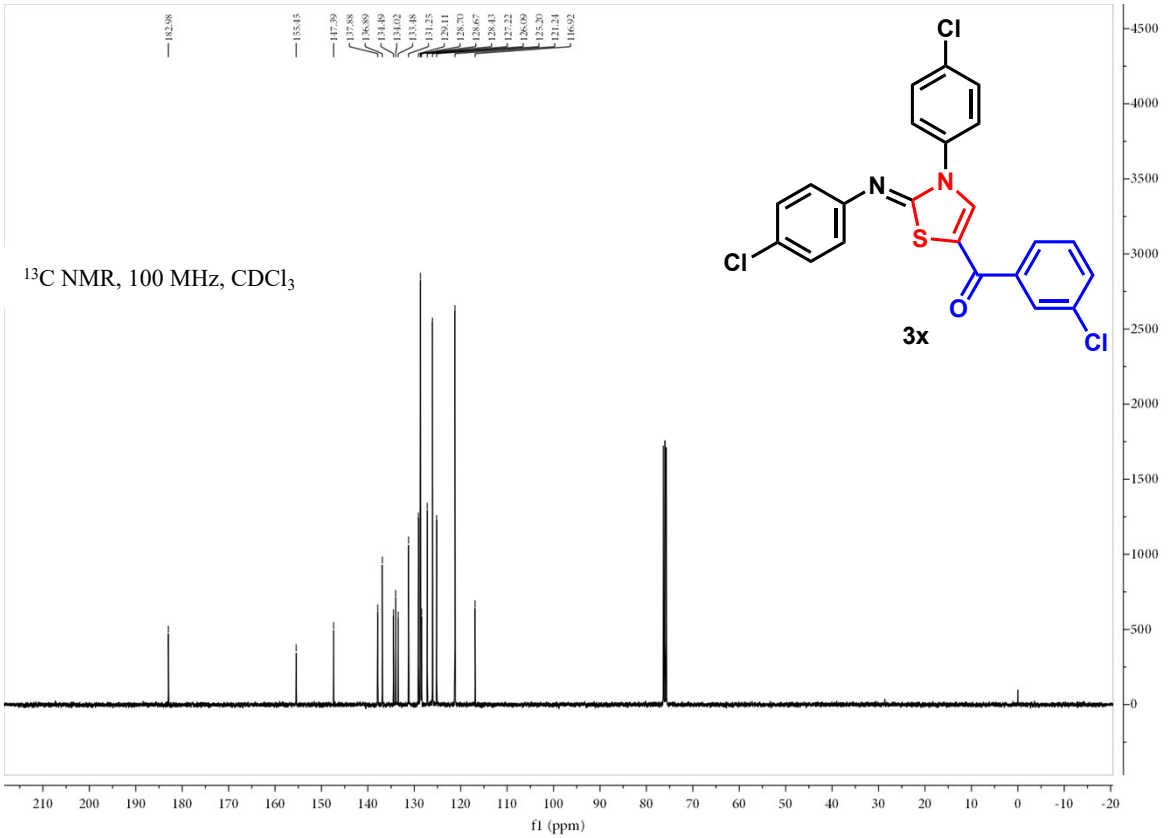


^{13}C NMR, 100 MHz, $CDCl_3$

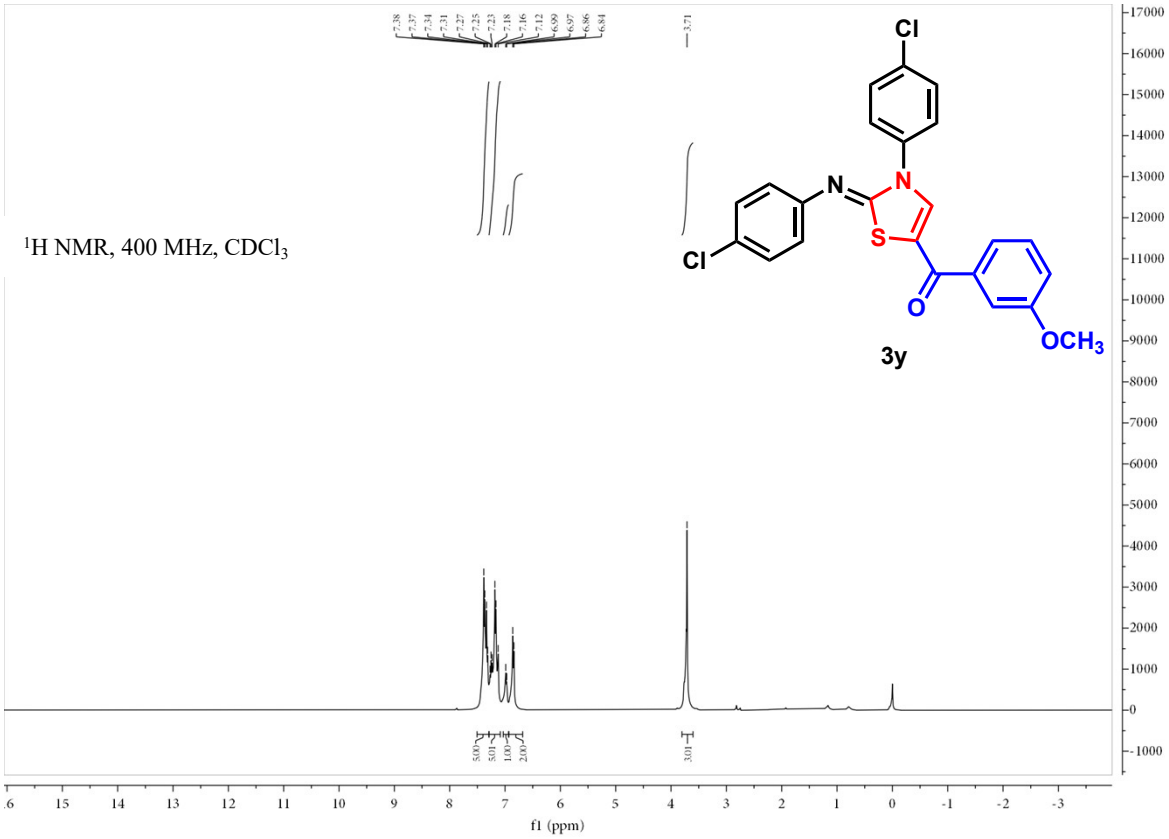


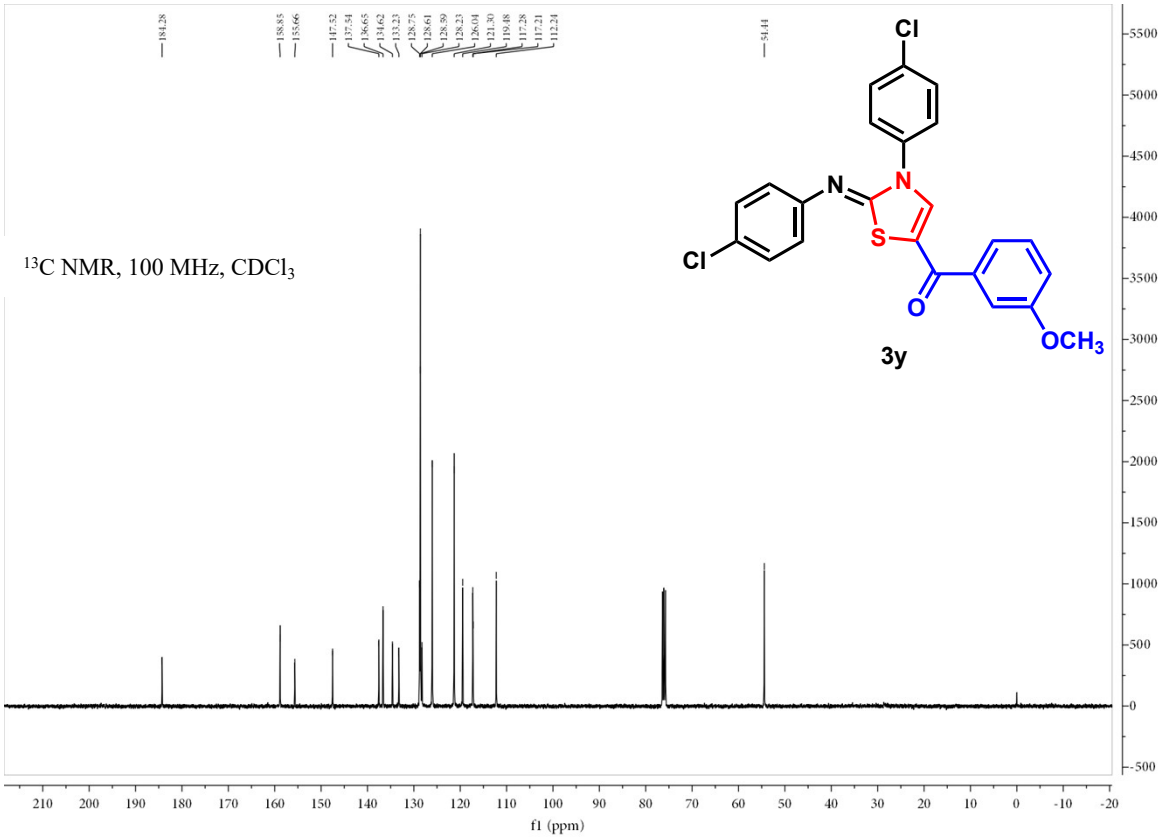


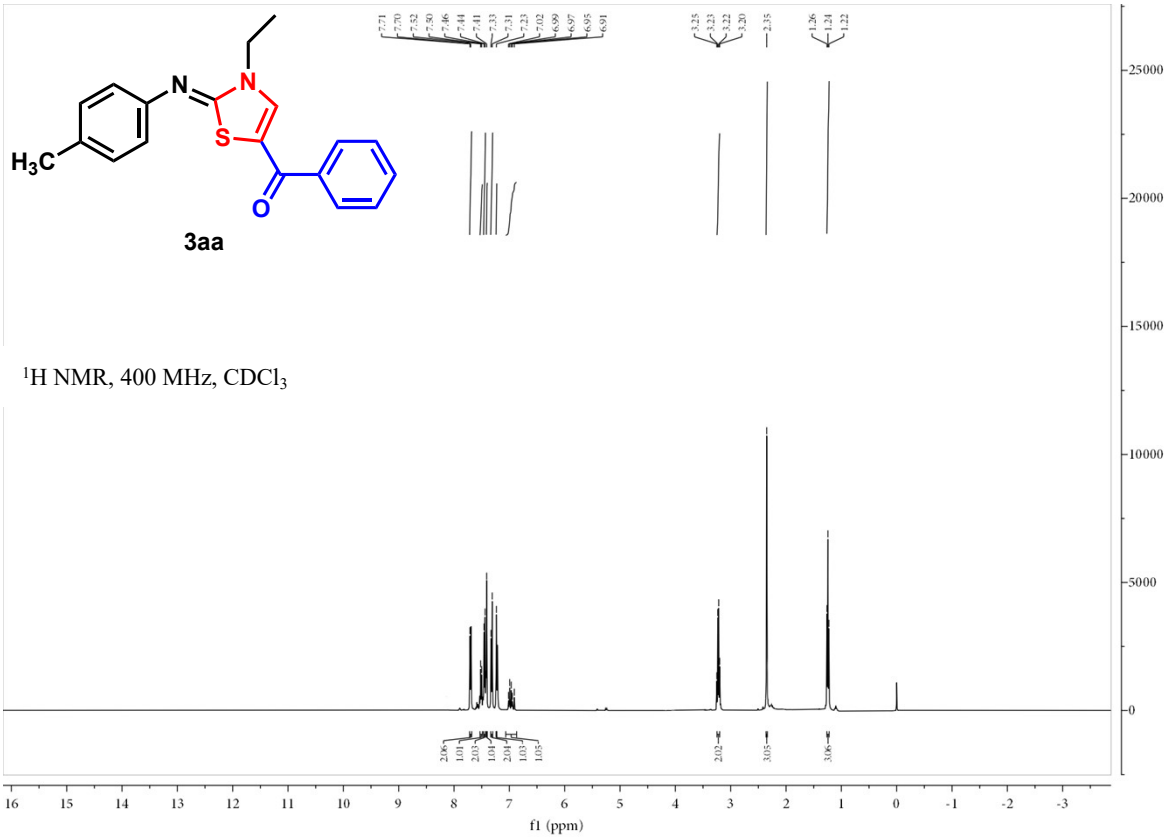
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$

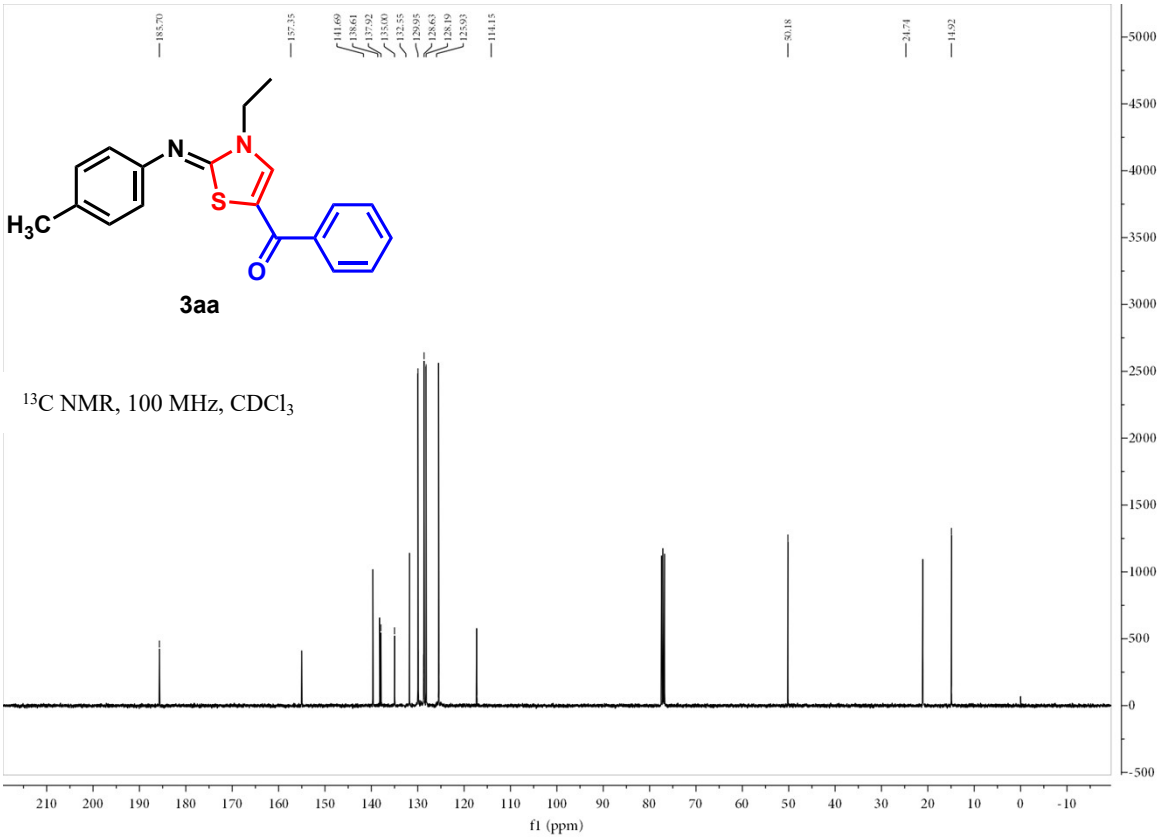

^{1}H NMR, 400 MHz, $CDCl_3$
Cl
N
S
O
OCH_3
3y
f1 (ppm)


^{13}C NMR, 100 MHz, $CDCl_3$
Cl
N
S
O
OCH_3
3y
f1 (ppm)



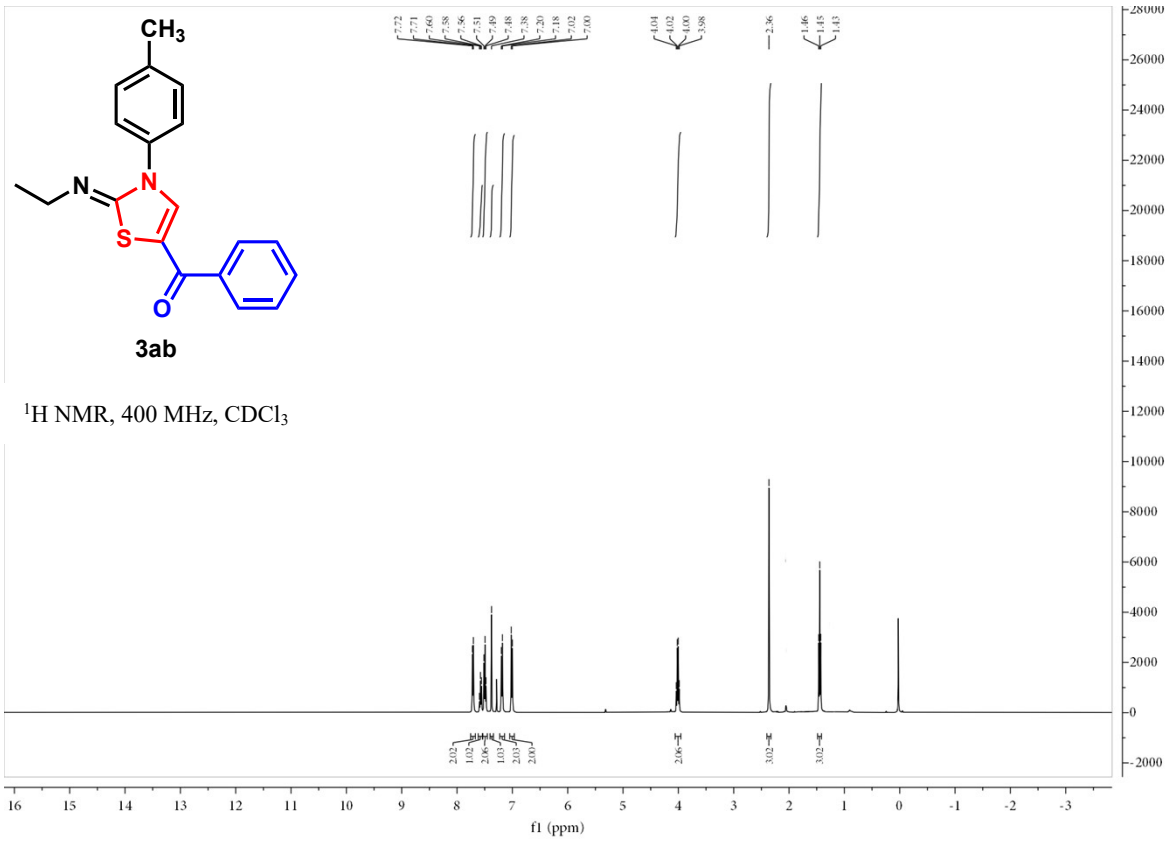
3aa

^{1}H NMR, 400 MHz, $CDCl_3$

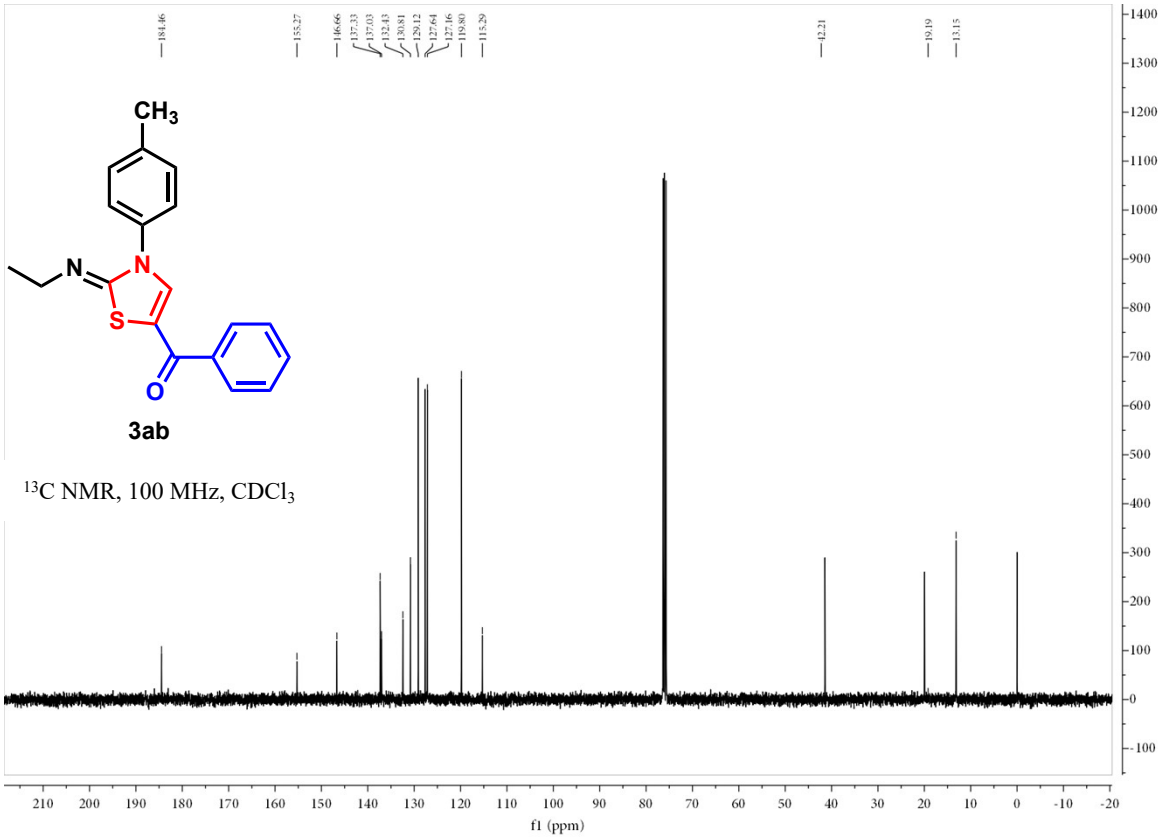


3aa

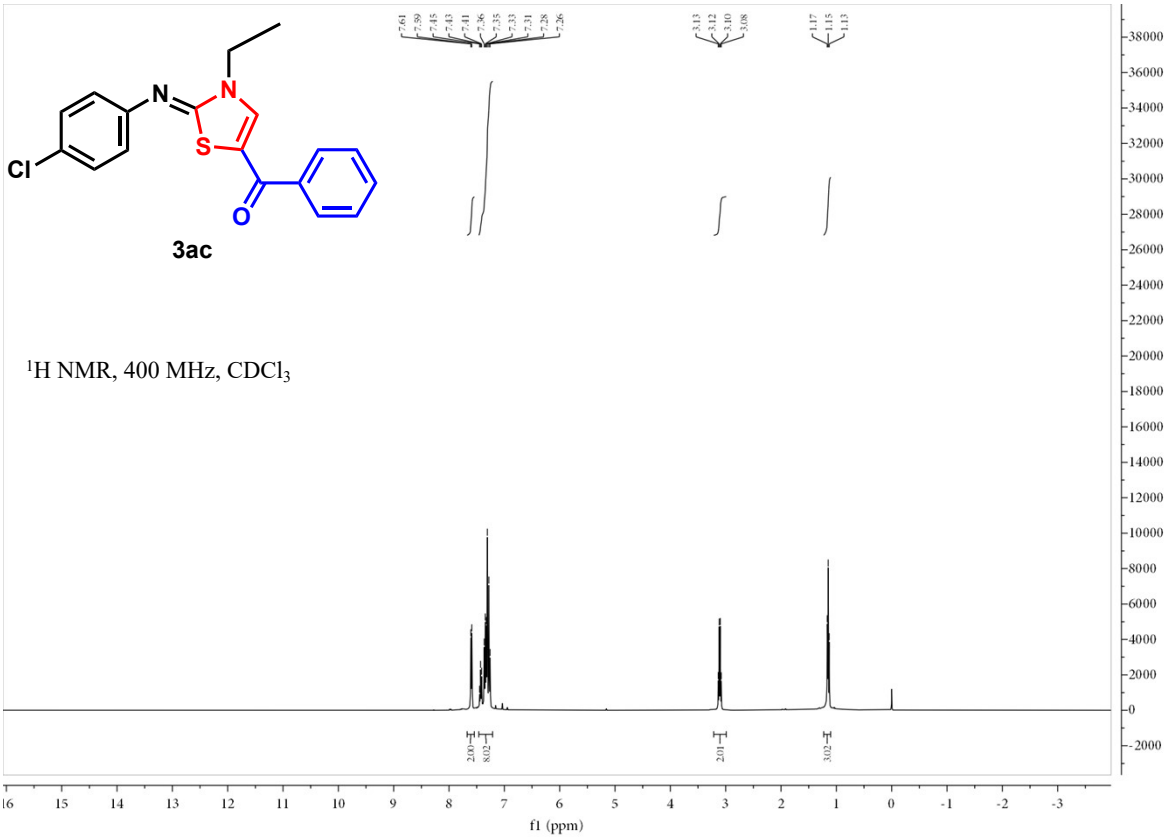
^{13}C NMR, 100 MHz, $CDCl_3$



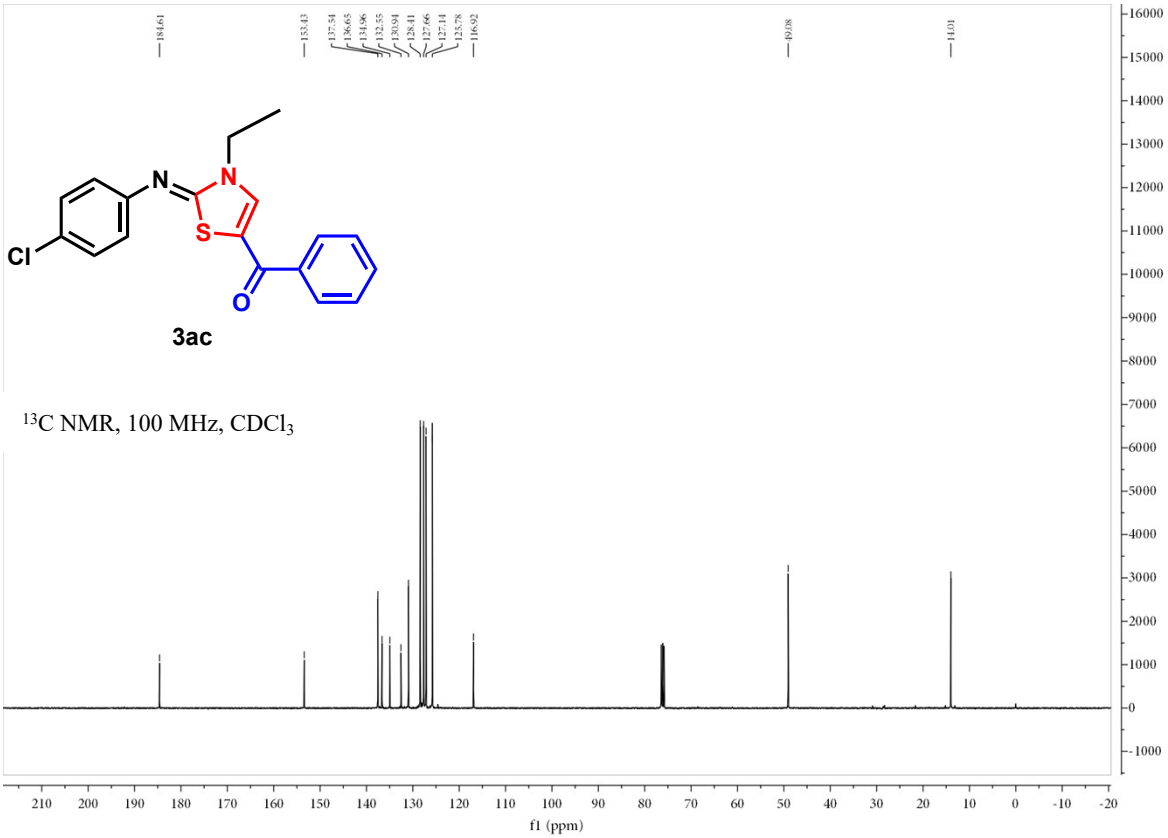
^{1}H NMR, 400 MHz, $CDCl_3$



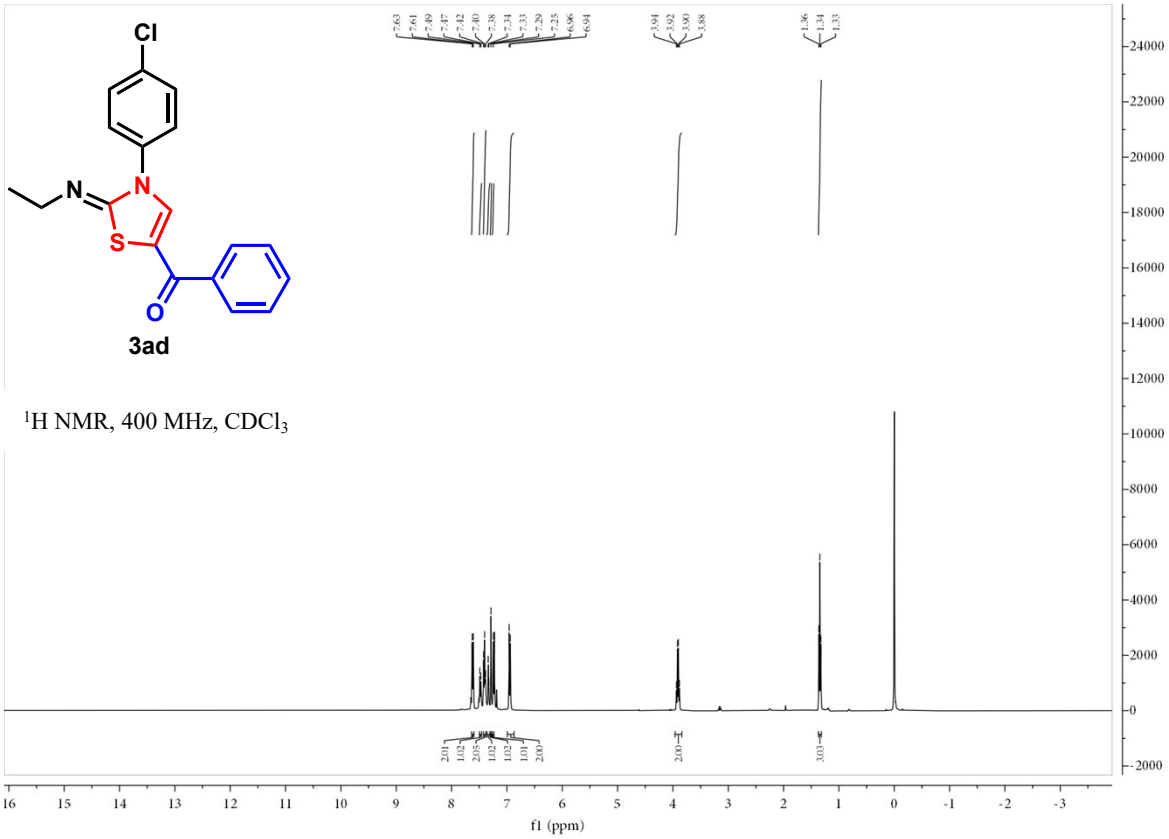
^{13}C NMR, 100 MHz, $CDCl_3$



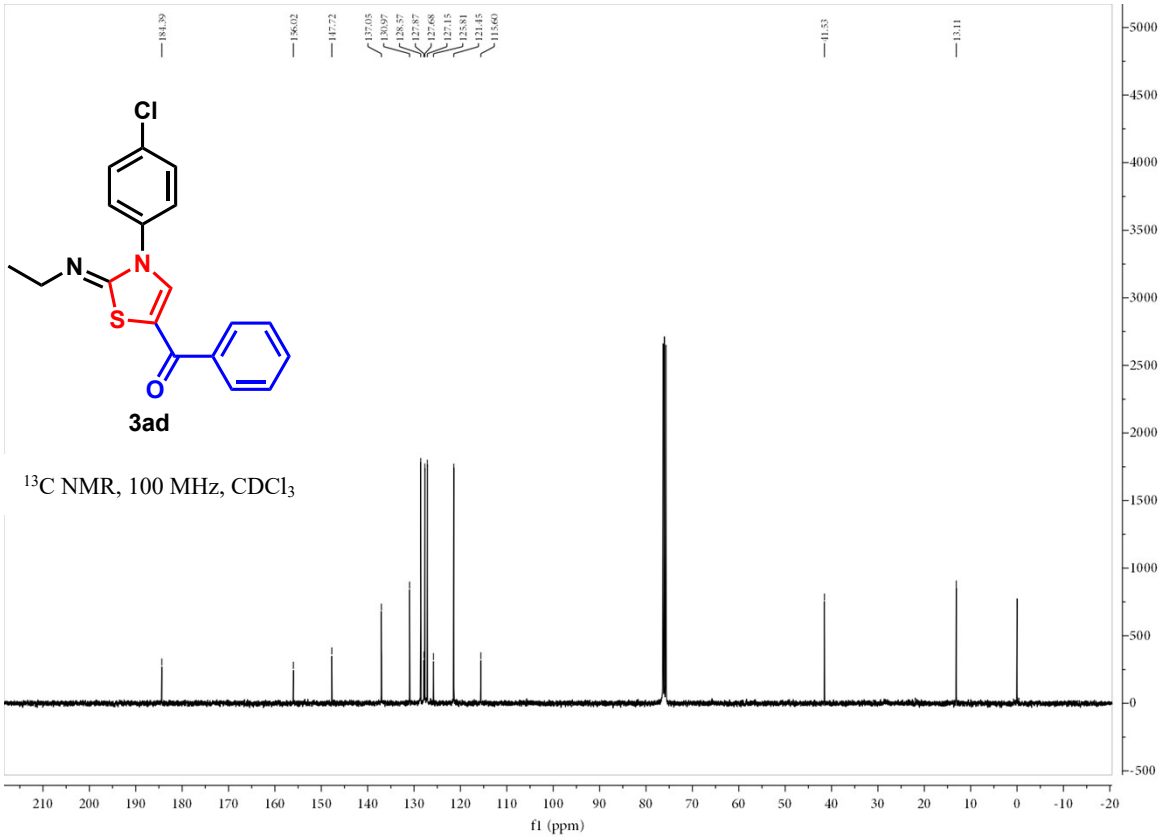
^{1}H NMR, 400 MHz, $CDCl_3$



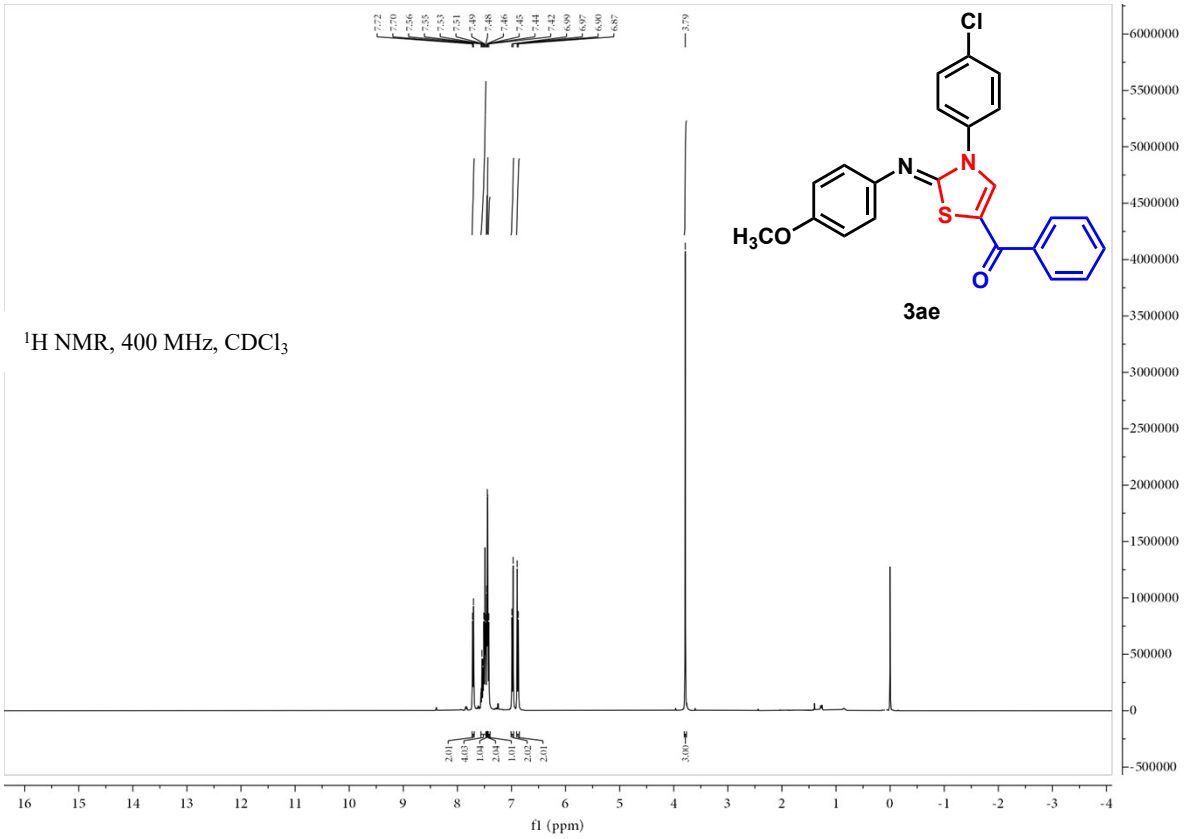
^{13}C NMR, 100 MHz, $CDCl_3$



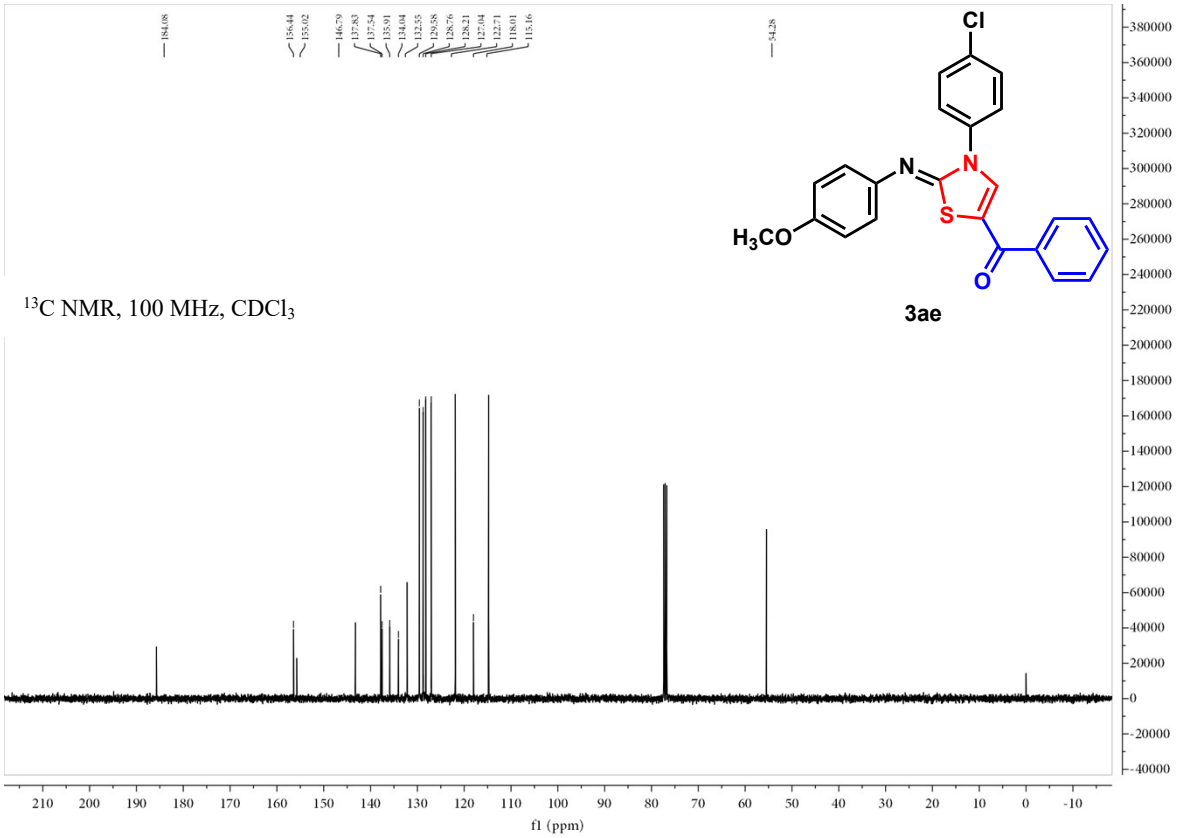
^{1}H NMR, 400 MHz, $CDCl_3$



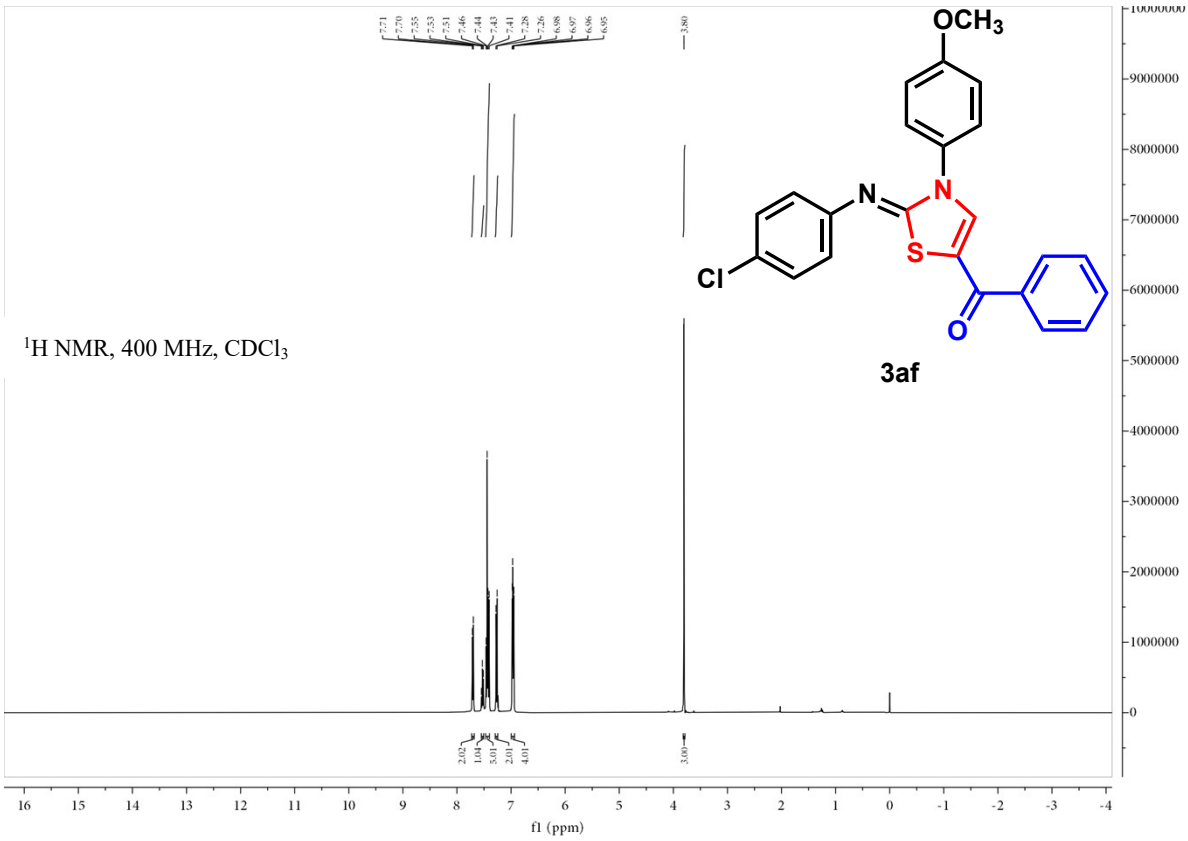
^{13}C NMR, 100 MHz, $CDCl_3$

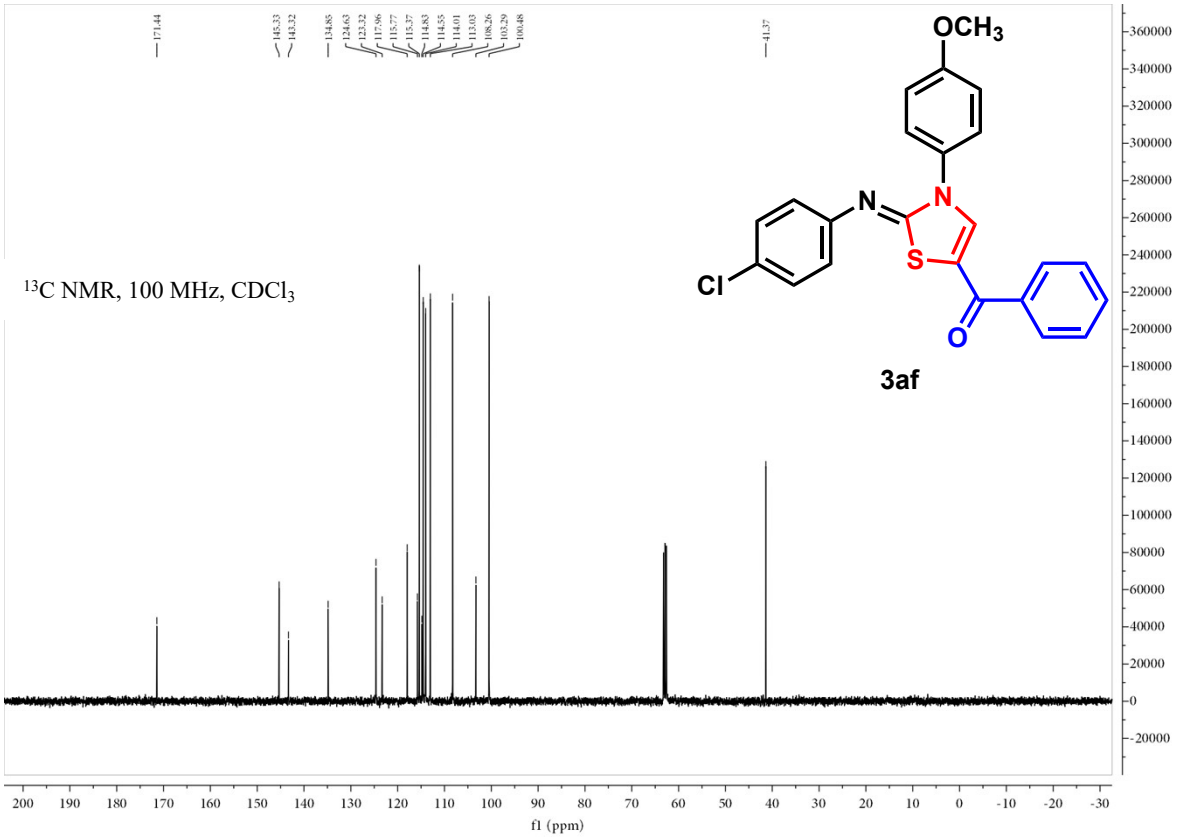


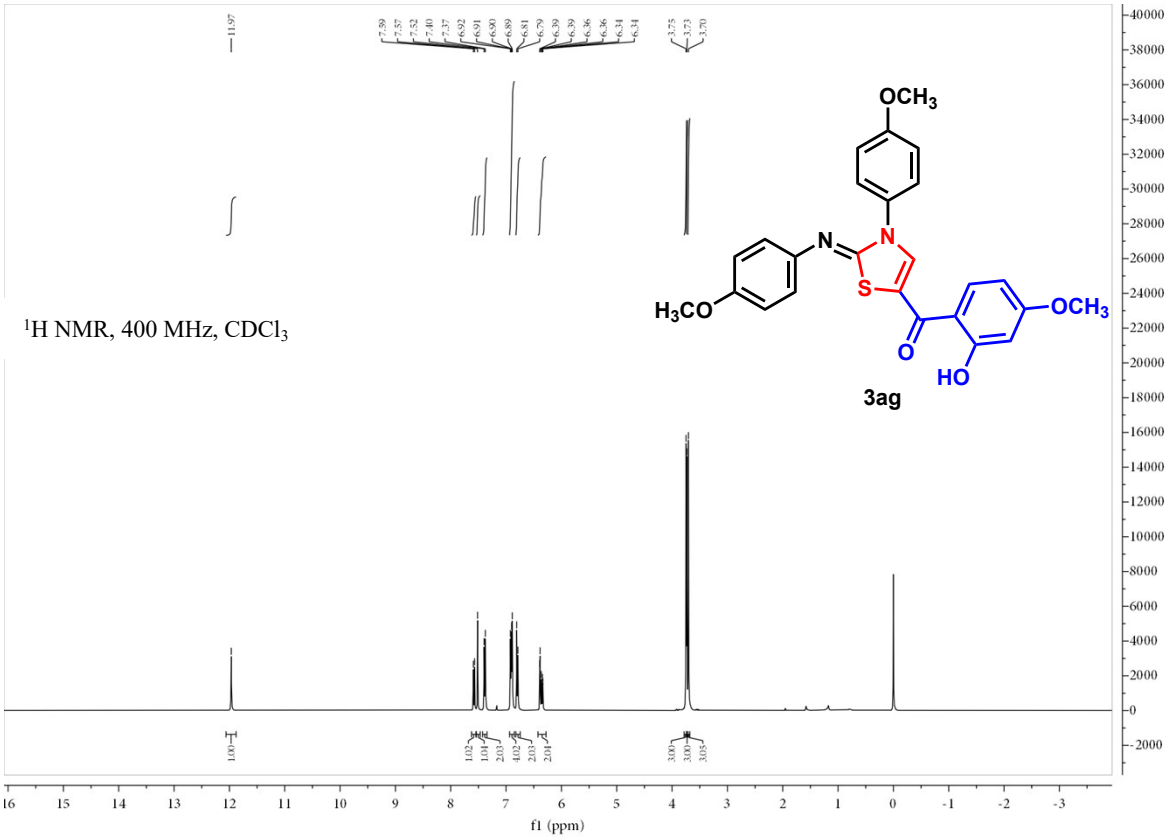
^{1}H NMR, 400 MHz, $CDCl_3$

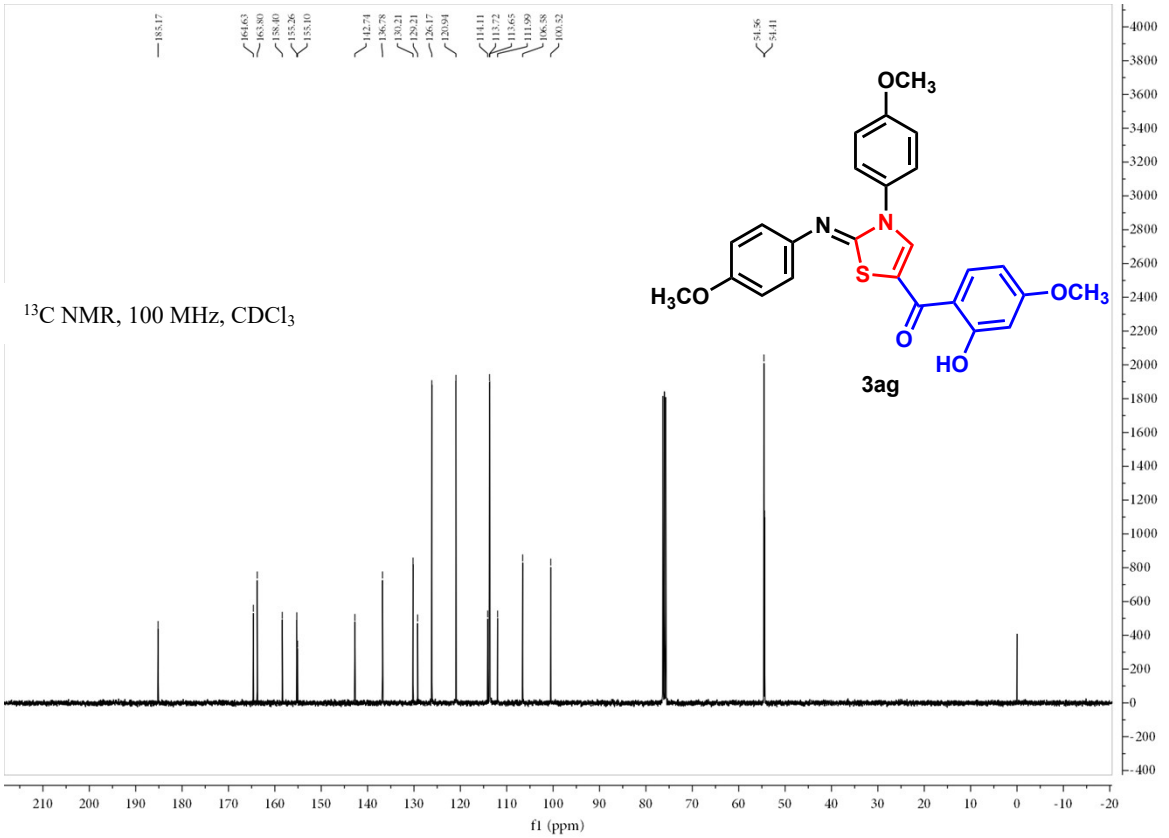


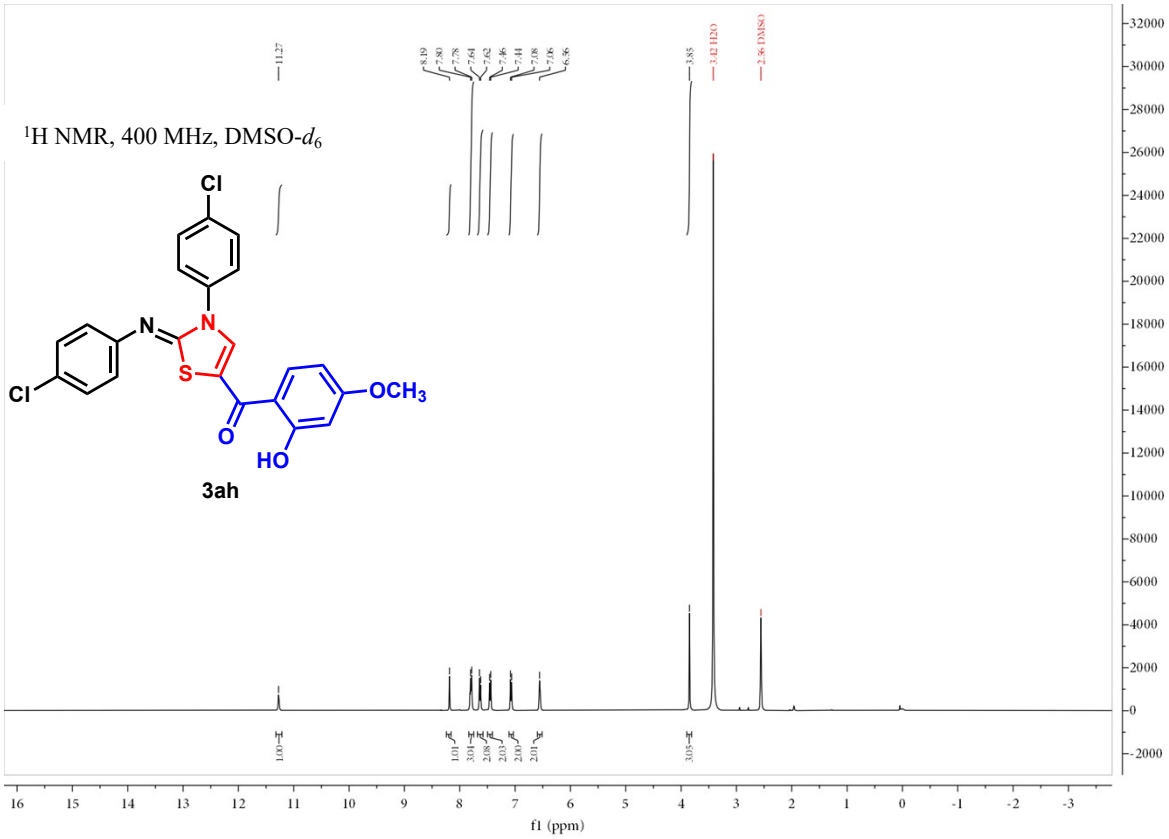
^{13}C NMR, 100 MHz, $CDCl_3$

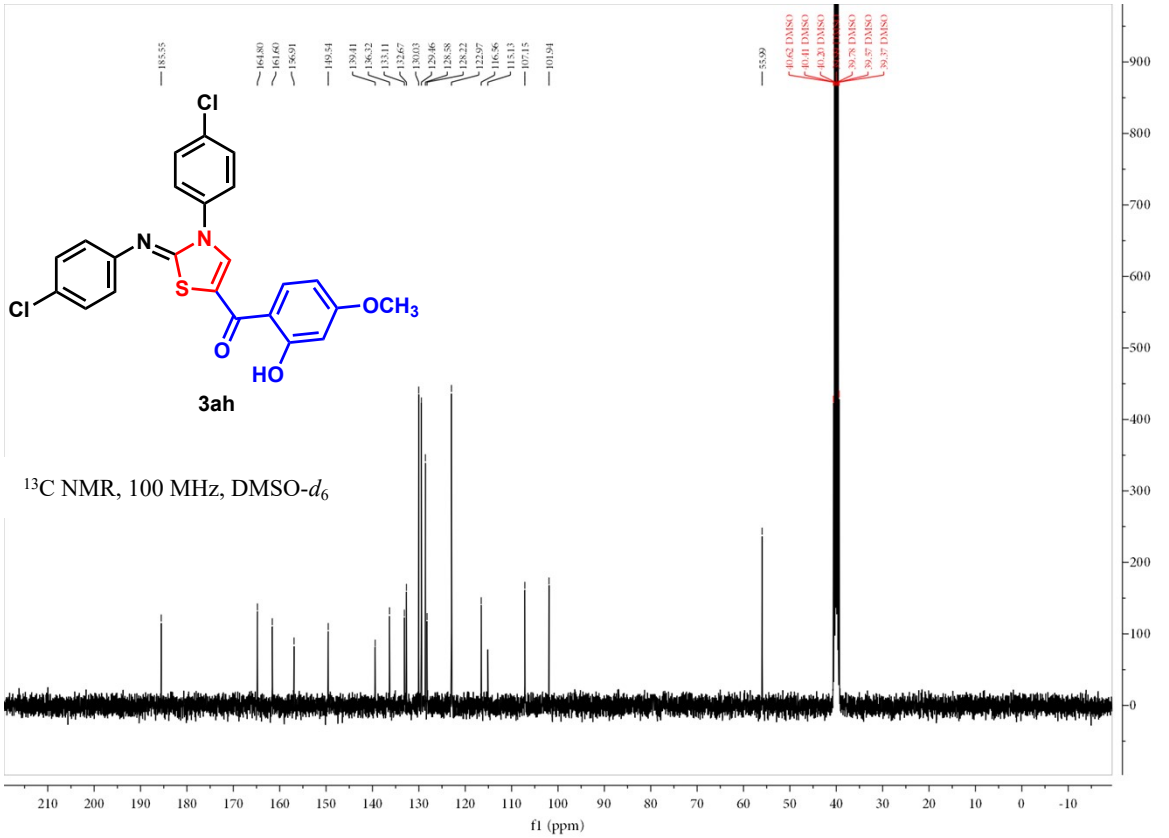

^{1}H NMR, 400 MHz, $CDCl_3$
OCH3
N
S
Cl
O
3af
f1 (ppm)


^{13}C NMR, 100 MHz, $CDCl_3$
OCH3
N
S
Cl
O
3af
f1 (ppm)


^{1}H NMR, 400 MHz, $CDCl_3$
3ag
f1 (ppm)


^{13}C NMR, 100 MHz, $CDCl_3$
3ag
f1 (ppm)


^{1}H NMR, 400 MHz, DMSO-d_6
Cl
N
S
N
Cl
O
HO
OCH$_3$
3ah
f1 (ppm)


Cl
N
S
N
Cl
O
HO
OCH$_3$
3ah
^{13}C NMR, 100 MHz, DMSO-d_6
f1 (ppm)