

BF₃·Et₂O Catalysed Transannulation Reaction of Pyridotriazoles with Isothiocyanate Synthesis of Thiazolo[3,4-a] pyridin-3-imine

Rahul Kumar^a, Vaibhavkumar Ginoya^a, Rashmi Semwal^a and Subbarayappa Adimurthy^{*a}

Academy of Scientific & Innovative Research, Ghaziabad, CSIR–Central Salt & Marine Chemicals Research Institute, G.B. Marg, Bhavnagar-364 002. Gujarat (INDIA).

* E-mail: adimurthy@csmcri.org

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Experimental section

General information

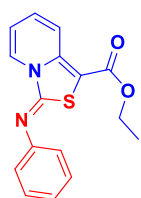
All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ¹H and ¹³C NMR spectra were recorded at 500, 600 and 150, 125 MHz respectively. The spectra were recorded in deuterated chloroform (CDCl₃) and DMSO-d₆ as solvent. Multiplicity was indicated as follows: singlet (s); doublet (d); triplet (t); multiplet (m); doublet of doublets (dd) etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of ¹H NMR (7.26), and ¹³C NMR (77.15) are correspond to deuterated solvent chloroform ¹H NMR (2.50) and ¹³C NMR (39.43) are correspond to deuterated solvent DMSO respectively. Mass spectra were obtained using electron impact (EI) ionization method. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane/ethyl acetate as eluent unless otherwise indicated.

Experimental procedure for the synthesis of ethyl (Z)-3-(phenylimino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate

To a reaction tube equipped with a magnetic stir bar, added ethyl [1,2,3]thiazolo[1,5-a]pyridine-3-carboxylate **11** (38.2 mg, 0.2 mmol), phenyl isothiocyanate **2a** (29.7 mg, 0.22 mmol), and BF₃·Et₂O 25% mol% with combination of DCB (0.5mL)/DCE (0.5mL) in 24h. The mixture was heated in an oil bath at 120 °C in a closed tube. Reaction was monitored by TLC, after completion of the reaction, it was allowed to attain room temperature. Then the mixture was poured into 30 mL of sodium chloride solution. The product was extracted with EtOAc (15 mL X 3) and dried with anhydrous Na₂SO₄. Removal of the solvent under reduced pressure the left out residue was purified by column chromatography using silica gel (5% EtOAc/hexane) to afford **3** (44.1 mg; 74% yield).

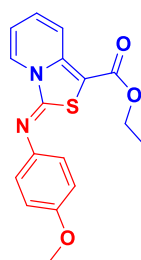
Characterization data

ethyl (Z)-3-(phenylimino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (**3a**)⁽¹⁾



(Eluent: 5% EtOAc/hexane); 74% yield (44.1 mg); Orange solid m.p; 115-120°C ¹H NMR (600 MHz, CDCl₃) δ 8.38 (d, J = 7.1 Hz, 1H), 8.02 (d, J = 9.4 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.16 – 7.10 (m, 2H), 6.47 (t, J = 6.8 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.02, 153.36, 148.96, 148.73, 142.15, 131.74, 129.77, 125.80, 124.58, 121.17, 120.08, 111.04, 60.52, 14.61.

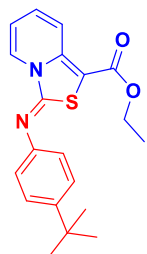
ethyl (Z)-3-((4-methoxyphenyl)imino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (**3b**)



(Eluent: 5% EtOAc/hexane); 70% yield (45.9 mg); Orange solid; m.p; 121-126°C ¹H NMR (600 MHz, CDCl₃) δ 8.36 (d, J = 6.7 Hz, 1H), 8.01 (d, J = 9.4 Hz, 1H), 7.16 – 7.13 (m, 2H), 7.12 – 7.10 (m, 1H), 6.95 (d, J = 8.3 Hz, 2H), 6.45 (t, J = 6.8 Hz, 1H), 4.28 (d, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.32 (t, J = 7.3 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.10, 156.55, 152.42, 147.32, 142.23, 141.82, 131.80, 125.86, 122.26, 120.04, 114.88,

110.84, 60.45, 55.57, 14.63. HRMS(ESI-TOF)m/z: calcd for $C_{17}H_{16}N_2O_3S[M+Na]^+$: 351.0774 ; found: 351.0754.

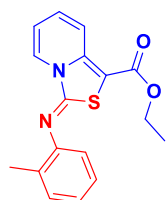
ethyl (Z)-3-((4-(tert-butyl)phenyl)imino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (3c)



(Eluent: 5% EtOAc/hexane); 72 % yield (50.9 mg); Orange solid; m.p; 160-165°C 1H NMR (600 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.96 (d, $J = 9.4$ Hz, 1H), 7.36 – 7.34 (m, 2H), 7.08 (d, $J = 8.1$ Hz, 2H), 7.05 (dd, $J = 9.3, 6.7$ Hz, 1H), 6.40 (t, $J = 6.7$ Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 1.27 (s, 9H), 1.25 (t, $J = 6.0$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$)

δ 162.03, 150.22, 148.74, 142.16, 131.74, 126.54, 125.99, 125.42, 120.76, 120.04, 114.65, 111.03, 60.51, 34.56, 31.51, 14.64. HRMS(ESI-TOF)m/z: calcd for $C_{20}H_{22}N_2O_2S[M+Na]^+$: 377.1294 ; found: 377.1296.

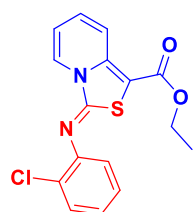
ethyl (Z)-3-(o-tolylimino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (3d)



(Eluent: 5% EtOAc/hexane); 71% yield (44.3 mg); Orange solid; m.p; 114-119°C 1H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, $J = 6.0$ Hz, 1H), 7.96 (d, $J = 9.4$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.03 (ddd, $J = 25.3, 13.1, 7.0$ Hz, 3H), 6.40 (t, $J = 6.7$ Hz, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.17 (s, 3H), 1.24 (t, $J = 6.0$ Hz, 3H), ^{13}C

NMR (150 MHz, $CDCl_3$) δ 162.05, 142.33, 134.91, 131.69, 131.16, 130.96, 130.78, 128.88, 127.22, 125.79, 124.69, 120.18, 119.12, 111.05, 60.48, 17.79, 14.60. HRMS(ESI-TOF)m/z: calcd for $C_{17}H_{16}N_2O_2S[M+Na]^+$: 335.0825 ; found: 335.0824.

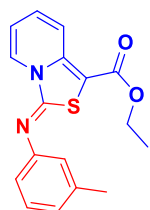
ethyl (Z)-3-((2-chlorophenyl)imino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (3e)



(Eluent: 5% EtOAc/hexane); 68% yield (45.1 mg); Orange solid; m.p; 110-115 °C 1H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, $J = 7.3$ Hz, 1H), 7.97 (d, $J = 9.5$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.23 (dd, $J = 11.5, 4.8$ Hz, 1H), 7.15 (d, $J = 8.1$ Hz, 1H), 7.07 (dd, $J = 9.5, 6.2$ Hz, 1H), 7.02 (t, $J = 8.4$ Hz, 1H), 6.44 (t, $J = 6.9$ Hz, 1H), 4.20 (q, $J =$

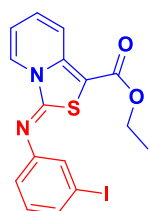
7.0 Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.91, 159.49, 154.58, 146.89, 131.66, 130.61, 128.24, 128.07, 127.42, 125.79, 125.33, 121.08, 120.11, 111.36, 60.60, 14.59. HRMS(ESI-TOF)m/z: calcd for $C_{16}H_{13}N_2O_2SCl [M+Na]^+$: 355.0278 ; found: 355.0430.

ethyl (Z)-3-(m-tolylimino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (3f)



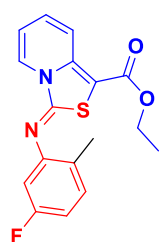
(Eluent: 5% EtOAc/hexane); 68 % yield (42.4 mg); Orange solid; m.p; 90-95°C ¹H NMR (600 MHz, CDCl₃) δ 8.78 (d, J = 7.0 Hz, 1H), 8.20 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.20 (d, J = 7.8 Hz, 2H), 7.10 (t, J = 6.8 Hz, 1H), 4.47 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 161.52, 143.55, 139.28, 135.16, 129.73, 129.57, 129.32, 128.37, 126.46, 126.05, 125.39, 122.89, 119.45, 116.54, 61.30, 21.58, 14.52. HRMS(ESI-TOF)m/z: calcd for C₁₇H₁₆N₂O₂S[M+Na]⁺: 335.0825 ; found: 335.0974.

ethyl (Z)-3-((3-iodophenyl)imino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (3g)



(Eluent: 5% EtOAc/hexane); 61% yield (51.6 mg); Orange solid; m.p; 135-140°C ¹H NMR (600 MHz, CDCl₃) δ 8.30 (d, J = 7.1 Hz, 1H), 7.97 (d, J = 9.4 Hz, 1H), 7.48 (s, 1H), 7.41 (d, J = 7.3 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 8.0 Hz, 2H), 6.43 (t, J = 6.9 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 161.84, 154.21, 148.10, 143.95, 141.96, 133.49, 131.68, 131.21, 130.45, 125.65, 120.51, 120.12, 111.45, 94.99, 60.72, 14.61. HRMS(ESI-TOF)m/z: calcd for C₁₆H₁₃N₂O₂SI[M+Na]⁺: 446.9635 ; found: 446.9638.

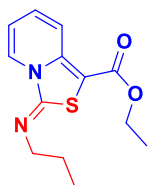
ethyl (Z)-3-((5-fluoro-2-methylphenyl)imino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (3h)



(Eluent: 5% EtOAc/hexane); 62% yield (40.9 mg); Orange solid; m.p; 116-121°C ¹H NMR (600 MHz, CDCl₃) δ 8.28 (d, J = 7.1 Hz, 1H), 7.97 (d, J = 9.4 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.06 (dd, J = 9.5, 6.1 Hz, 1H), 6.78 (dd, J = 9.8, 2.6 Hz, 1H), 6.69 (td, J = 8.4, 2.6 Hz, 1H), 6.42 (t, J = 6.9 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.11 (s, 3H), 1.24 (d, J = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.72, 161.52 (d, J_{C-F} = 126 Hz), 142.19, 133.92, 131.88 (d, J_{C-F} = 9.0 Hz, 2C), 131.65, 126.47, 125.61, 120.20, 111.13 (d, J_{C-F} = 28.5 Hz, 2C), 110.90, 106.29 (d, J_{C-F} = 22.5 Hz, 2C), 60.59, 17.14, 14.59. ¹⁹F NMR (564 MHz,

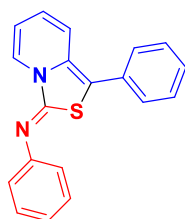
CDCl₃) δ -115.62 to -115.66 ppm. HRMS(ESI-TOF)m/z: calcd for C₁₇H₁₅N₂O₂SF[M+Na]⁺: 353.0730 ; found: 353.0729.

ethyl (Z)-3-(propylimino)-3H-thiazolo[3,4-a]pyridine-1-carboxylate (3i)



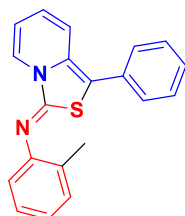
(Eluent: 5% EtOAc/hexane); 60% yield (31.6 mg); Orange solid; m.p; 95-100°C ¹H NMR (600 MHz, CDCl₃) δ 8.35 – 8.12 (m, 1H), 7.97 (d, J = 9.2 Hz, 1H), 7.08 (dd, J = 8.9, 6.5 Hz, 1H), 6.38 (s, 1H), 4.32 – 4.28 (m, 2H), 3.17 (t, J = 6.9 Hz, 2H), 1.78 – 1.75 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.26, 142.83, 140.35, 132.00, 130.86, 125.95, 119.98, 110.20, 60.33, 56.05, 23.66, 14.68, 12.14. HRMS(ESI-TOF)m/z: calcd for C₁₃H₁₆N₂O₂S[M+Na]⁺: 287.0825; found: 287.1062.

(Z)-N,1-diphenyl-3H-thiazolo[3,4-a]pyridin-3-imine (5a)



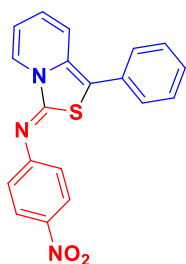
(Eluent: 5% EtOAc/hexane); 61% yield (36.8 mg); Orange solid; m.p; 92-97°C ¹H NMR (500 MHz, CDCl₃) δ 7.98 (dd, J = 7.5, 0.7 Hz, 1H), 7.36 (ddd, J = 9.8, 6.9, 3.3 Hz, 6H), 7.23 – 7.17 (m, 3H), 7.09 (d, J = 8.4 Hz, 2H), 6.53 (dd, J = 9.6, 6.0 Hz, 1H), 6.02 (dd, J = 7.2, 6.3 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 152.40, 149.17, 131.40, 129.69, 128.50, 127.88, 126.45, 125.59, 125.20, 124.09, 122.42, 120.10, 117.28, 107.47, 99.52. HRMS(ESI-TOF)m/z: calcd for C₁₉H₁₄N₂S[M+K]⁺: 341.0509 ; found: 341.0505.

(Z)-1-phenyl-N-(o-tolyl)-3H-thiazolo[3,4-a]pyridin-3-imine (5b)



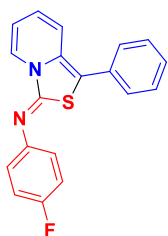
(Eluent: 5% EtOAc/hexane); 55% yield (34.7 mg); Orange solid; m.p; 85-90°C ¹H NMR (600 MHz, CDCl₃) δ 7.93 (d, J = 7.5 Hz, 1H), 7.28 – 7.25 (m, 4H), 7.18 (d, J = 7.5 Hz, 1H), 7.13 (s, 2H), 7.06 – 7.01 (m, 2H), 6.94 (td, J = 7.4, 1.0 Hz, 1H), 6.47 (ddd, J = 9.6, 6.0, 0.9 Hz, 1H), 5.98 – 5.94 (m, 1H), 2.18 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 153.19, 149.21, 133.02, 132.69, 130.99, 129.01, 128.25, 127.53, 127.05, 126.67, 126.32, 125.32, 124.72, 123.72, 119.16, 118.54, 108.48, 17.89. HRMS(ESI-TOF)m/z: calcd for C₂₀H₁₆N₂S[M+H]⁺: 317.1107 ; found: 317.1117.

(Z)-N-(4-nitrophenyl)-1-phenyl-3H-thiazolo[3,4-a]pyridin-3-imine (5c)



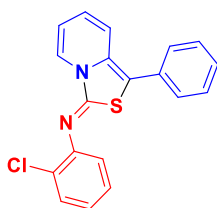
(Eluent: 5% EtOAc/hexane); 45% yield (31.2 mg); Orange solid; m.p; 80-85°C ¹H NMR (600 MHz, CDCl₃) δ 8.25 (t, J = 5.7 Hz, 2H), 8.10 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 4.5 Hz, 4H), 7.32 (d, J = 9.0 Hz, 3H), 7.21 (d, J = 9.4 Hz, 1H), 6.67 (dd, J = 9.6, 6.1 Hz, 1H), 6.22 (t, J = 6.8 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 155.60, 153.06, 133.02, 131.67, 131.07, 129.28, 128.03, 127.53, 126.40, 125.70, 125.04, 121.36, 118.57, 115.95, 110.07. HRMS(ESI-TOF)m/z: calcd for C₁₉H₁₃N₃O₂S[M+H]⁺: 348.0801; found: 348.0950.

(Z)-N-(4-fluorophenyl)-1-phenyl-3H-thiazolo[3,4-a]pyridin-3-imine (5d)



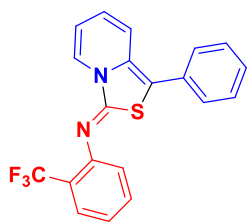
(Eluent: 5% EtOAc/hexane); 52% yield (33.2 mg); Orange solid; m.p; 101-106°C ¹H NMR (600 MHz, CDCl₃) δ 7.93 (d, J = 7.3 Hz, 1H), 7.29 (d, J = 4.4 Hz, 4H), 7.16 (dd, J = 8.2, 4.0 Hz, 1H), 7.09 – 7.05 (m, 3H), 6.99 (t, J = 8.6 Hz, 2H), 6.50 (dd, J = 9.5, 5.9 Hz, 1H), 6.00 (t, J = 6.7 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 159.17(d, J_{C-F} = 181.0 Hz), 153.98, 146.51, 132.47, 130.91, 129.08, 127.65, 126.62(d, J_{C-F} = 69 Hz, 2C), 125.15, 122.51(d, J_{C-F} = 9.0 Hz, 2C), 118.49, 116.27(d, J_{C-F} = 22.5 Hz, 2C), 108.73, 100.68. ¹⁹F NMR (564 MHz, CDCl₃) δ -111.54 ppm. HRMS(ESI-TOF)m/z: calcd for C₁₉H₁₃N₂FS[M+H]⁺: 321.0856 ; found: 321.0825.

(Z)-N-(2-chlorophenyl)-1-phenyl-3H-thiazolo[3,4-a]pyridin-3-imine (5e)



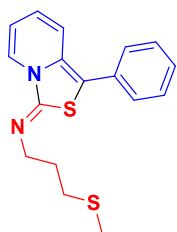
(Eluent: 5% EtOAc/hexane); 65% yield (43.6 mg); Orange solid; m.p; 110-115°C ¹H NMR (600 MHz, CDCl₃) δ 8.06 (d, J = 7.5 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.37 – 7.35 (m, 4H), 7.25 (ddd, J = 9.0, 6.3, 2.1 Hz, 3H), 7.13 (d, J = 9.6 Hz, 1H), 7.02 (ddd, J = 8.2, 6.4, 2.5 Hz, 1H), 6.59 (ddd, J = 9.6, 6.1, 0.9 Hz, 1H), 6.10 (ddd, J = 7.2, 6.2, 0.8 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 157.42, 150.11, 135.12, 133.72, 133.28, 131.87, 130.72, 130.51, 129.73, 129.09, 128.07, 127.15, 123.91, 121.27, 111.90, 104.34. HRMS(ESI-TOF)m/z: calcd for C₁₉H₁₂N₂ClS[M+H]⁺: 337.0561; found: 337.1260.

(Z)-1-phenyl-N-(2-(trifluoromethyl)phenyl)-3H-thiazolo[3,4-a]pyridin-3-imine (5f)



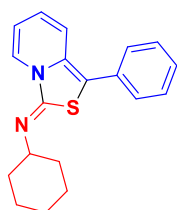
(Eluent: 5% EtOAc/hexane); 55% yield (40.7 mg); sticky Orange ^1H NMR (600 MHz, CDCl_3) δ 8.00 -7.97 (m, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.44 (dd, $J = 16.3, 7.9$ Hz, 2H), 7.31 (t, $J = 8.4$ Hz, 5H), 7.06 (dd, $J = 14.8, 7.8$ Hz, 2H), 6.54 (dd, $J = 9.4, 6.1$ Hz, 1H), 6.05 (t, $J = 6.2$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 153.56, 148.42, 133.02, 132.27, 130.91, 129.11, 127.28 (q, $J_{\text{CF}_3} = 85.5$ Hz), 126.46, 125.30, 123.54 (q, $J_{\text{CF}_3} = 18.0$ Hz, 2C), 122.71, 119.89, 118.39, 109.31, 101.37. ^{19}F NMR (564 MHz, CDCl_3) δ -52.46 to -62.56 ppm. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{13}\text{N}_2\text{F}_3\text{S}[\text{M}+\text{Na}]^+$: 393.0644 ; found: 393.0646.

(Z)-N-(2-(methylthio)ethyl)-1-phenyl-3H-thiazolo[3,4-a]pyridin-3-imine (5g)



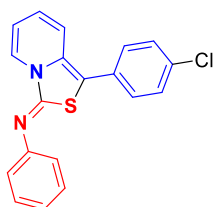
(Eluent: 5% EtOAc/hexane); 58% yield (34.8 mg); Orange solid; m.p; 105-110°C ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 7.1$ Hz, 1H), 7.40 – 7.36 (m, 4H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.05 (d, $J = 9.4$ Hz, 1H), 6.50 (dd, $J = 9.5, 6.0$ Hz, 1H), 5.92 (t, $J = 6.5$ Hz, 1H), 3.26 (t, $J = 6.6$ Hz, 2H), 2.68 (t, $J = 7.1$ Hz, 2H), 2.13 (s, 3H), 2.06 – 2.01 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 153.68, 137.14, 131.41, 129.00, 127.32, 126.59, 126.37, 125.41, 118.27, 107.54, 99.98, 53.08, 32.35, 30.28, 15.70. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{S}_2[\text{M}+\text{Na}]^+$: 337.0804 ; found: 337.0822.

(Z)-N-cyclohexyl-1-phenyl-3H-thiazolo[3,4-a]pyridin-3-imine (5h)



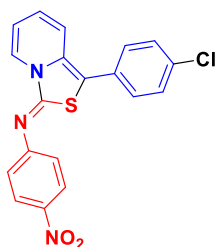
(Eluent: 5% EtOAc/hexane); 40% yield (24.6 mg); Orange solid; m.p; 95-100°C ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 7.3$ Hz, 1H), 7.37 (q, $J = 8.4$ Hz, 4H), 7.21 (t, $J = 6.8$ Hz, 1H), 7.02 (d, $J = 9.6$ Hz, 1H), 6.48 (dd, $J = 9.5, 6.0$ Hz, 1H), 5.87 (s, 1H), 2.94 (td, $J = 9.3, 4.3$ Hz, 1H), 1.88 (s, 2H), 1.85 – 1.79 (m, 2H), 1.61 (s, 2H), 1.40 (dd, $J = 17.1, 10.0$ Hz, 4H). ^{13}C NMR (150 MHz, CDCl_3) δ 140.28, 133.30, 131.86, 131.24, 128.86, 127.13, 126.61, 126.10, 125.71, 118.08, 63.94, 33.06, 25.90, 25.07. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{S}[\text{M}+\text{H}]^+$: 309.1420 ; found: 309.1408.

(Z)-1-(4-chlorophenyl)-N-phenyl-3H-thiazolo[3,4-a]pyridin-3-imine (5i)



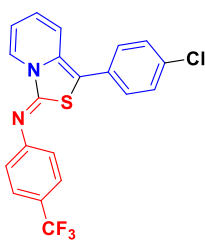
(Eluent: 5% EtOAc/hexane); 65% yield (43.6 mg); Orange solid; m.p; 115-120°C ^1H NMR (500 MHz, CDCl_3) δ 8.04 – 7.97 (m, 1H), 7.38 (t, $J = 7.5$ Hz, 2H), 7.33 – 7.24 (m, 4H), 7.18 (s, 2H), 7.09 (dd, $J = 7.8, 6.9$ Hz, 1H), 7.08 – 7.01 (m, 1H), 6.57 (dd, $J = 9.6, 6.1$ Hz, 1H), 6.05 (dd, $J = 7.3, 6.3$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.07, 149.02, 131.04, 130.05, 129.95, 128.53, 128.04, 127.47, 125.73, 124.21, 122.57, 120.03, 116.91, 107.55, 98.02. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{19}\text{H}_{13}\text{N}_2\text{ClS}$ [$\text{M}+\text{H}$] $^+$: 337.0561 ; found: 337.0554.

(Z)-1-(4-chlorophenyl)-N-(4-nitrophenyl)-3H-thiazolo[3,4-a]pyridin-3-imine (5j)



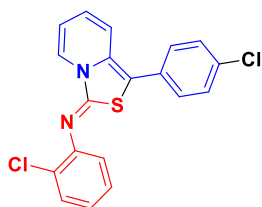
(Eluent: 5% EtOAc/hexane); 50% yield (38.1 mg); Orange solid; m.p; 65-70°C ^1H NMR (500 MHz, CDCl_3) δ 8.72 (d, $J = 4.3$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 4H), 7.91 (d, $J = 7.7$ Hz, 1H), 7.51 (dd, $J = 7.5, 4.8$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 3H), 7.34 (dd, $J = 19.6, 10.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 153.57, 147.42, 138.31, 136.10, 133.47, 131.39, 128.29, 128.09, 127.90, 127.71, 127.37, 125.33, 124.52, 123.59, 120.19. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{19}\text{H}_{12}\text{N}_3\text{ClSO}_2$ [$\text{M}+\text{Na}$] $^+$: 404.0231; found: 404.0742.

(Z)-1-(4-chlorophenyl)-N-(4-(trifluoromethyl)phenyl)-3H-thiazolo[3,4-a]pyridin-3-imine (5k)



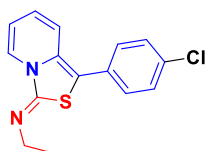
(**5k**) (Eluent: 5% EtOAc/hexane); 48% yield (38.7 mg); Orange solid; m.p; 135-140°C ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 7.5$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.39 – 7.25 (m, 6H), 7.09 (d, $J = 9.6$ Hz, 1H), 6.64 (dd, $J = 9.6, 6.1$ Hz, 1H), 6.14 (t, $J = 6.8$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.26 (q, $J_{\text{CF}_3} = 31.5$ Hz), 131.50, 130.02, 129.51 (d, $J_{\text{C-F}} = 76.5$ Hz, 2C), 128.15, 127.66 (d, $J_{\text{C-F}} = 73.5$ Hz, 2C), 125.70, 124.03, 120.18, 116.98, 108.13, 98.69. ^{19}F NMR (564 MHz, CDCl_3) δ -63.60 ppm. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{ClSF}_3$ [$\text{M}+\text{H}$] $^+$: 405.0435 ; found: 405.0706.

(Z)-N-(2-chlorophenyl)-1-(4-chlorophenyl)-3H-thiazolo[3,4-a]pyridin-3-imine (5l)



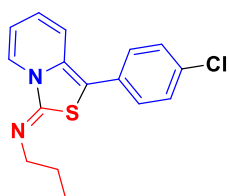
(Eluent: 5% EtOAc/hexane); 68% yield (50.3 mg); Orange solid; m.p; 105-110°C ^1H NMR (600 MHz, CDCl_3) δ 8.06 (s, 1H), 7.40 (d, $J = 8.1$ Hz, 1H), 7.25 (d, $J = 1.8$ Hz, 1H), 7.24 – 7.20 (m, 3H), 7.18 (dd, $J = 9.9, 6.0$ Hz, 2H), 7.02 (d, $J = 9.5$ Hz, 1H), 7.00 – 6.97 (m, 1H), 6.57 (dd, $J = 9.6, 6.1$ Hz, 1H), 6.09 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 136.11, 132.62, 131.38, 130.70, 130.57, 129.30, 128.84, 128.02, 127.68, 126.82, 125.47, 124.79, 122.15, 121.45, 120.19, 118.15, 109.49. HRMS(ESI-TOF)m/z: calcd for $\text{C}_{19}\text{H}_{12}\text{N}_2\text{Cl}_2\text{S}[\text{M}+\text{H}]^+$: 371.0171 ; found: 371.0171.

(Z)-1-(4-chlorophenyl)-N-ethyl-3H-thiazolo[3,4-a]pyridin-3-imine (5m)



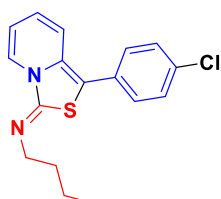
(Eluent: 5% EtOAc/hexane); 55% yield (31.6 mg); Orange solid; m.p; 120-125°C ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 7.4$ Hz, 1H), 7.36 – 7.31 (m, 4H), 7.01 (dd, $J = 9.6, 0.9$ Hz, 1H), 6.57 – 6.52 (m, 1H), 5.95 (t, $J = 6.8$ Hz, 1H), 3.23 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 151.73, 130.59, 128.77, 128.56, 127.94, 127.15, 125.95, 124.38, 116.69, 106.41, 47.83, 14.45. HRMS(ESI-TOF)m/z: calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{ClS}[\text{M}+\text{H}]^+$: 289.0561 ; found: 289.0581.

(Z)-1-(4-chlorophenyl)-N-propyl-3H-thiazolo[3,4-a]pyridin-3-imine (5n)



(Eluent: 5% EtOAc/hexane); 53% yield (32.0 mg); Orange solid; m.p; 125-130°C ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 7.4$ Hz, 1H), 7.32 (d, $J = 2.4$ Hz, 4H), 6.99 (d, $J = 9.7$ Hz, 1H), 6.57 – 6.50 (m, 1H), 5.93 (t, $J = 6.7$ Hz, 1H), 3.13 (t, $J = 7.0$ Hz, 2H), 1.75 (dt, $J = 14.5, 7.3$ Hz, 2H), 1.02 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 154.65, 135.37, 130.62, 130.47, 127.94, 127.13, 125.97, 124.45, 120.69, 116.69, 106.35, 55.39, 22.79, 11.01. HRMS(ESI-TOF)m/z: calcd for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{ClS}[\text{M}+\text{H}]^+$: 303.0717 ; found: 303.0749.

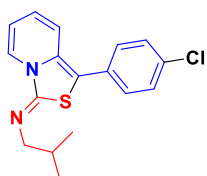
(Z)-N-butyl-1-(4-chlorophenyl)-3H-thiazolo[3,4-a]pyridin-3-imine (5o)



(Eluent: 5% EtOAc/hexane); 56% yield (35.3 mg); Orange solid; m.p; 135-140°C ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.4$ Hz, 1H), 7.32 (d, $J = 2.0$ Hz, 4H), 6.99 (d, $J = 9.7$ Hz, 1H), 6.53 (dd, $J = 15.0, 6.0$ Hz, 1H), 5.92 (t, $J =$

6.7 Hz, 1H), 3.17 (t, J = 7.0 Hz, 2H), 1.72 (dt, J = 14.7, 7.2 Hz, 2H), 1.47 (dd, J = 15.0, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 151.55, 139.40, 130.66, 130.61, 130.44, 127.93, 127.11, 125.98, 124.46, 116.68, 106.30, 53.30, 31.64, 19.61, 12.88. HRMS(ESI-TOF)m/z: calcd for C₁₇H₁₇N₂ClS[M+H]⁺: 317.0878; found: 317.0876.

(Z)-1-(4-chlorophenyl)-N-isobutyl-3H-thiazolo[3,4-a]pyridin-3-imine (5p)



(Eluent: 5% EtOAc/hexane); 60% yield (37.9 mg); Orange solid; m.p; 95-100°C

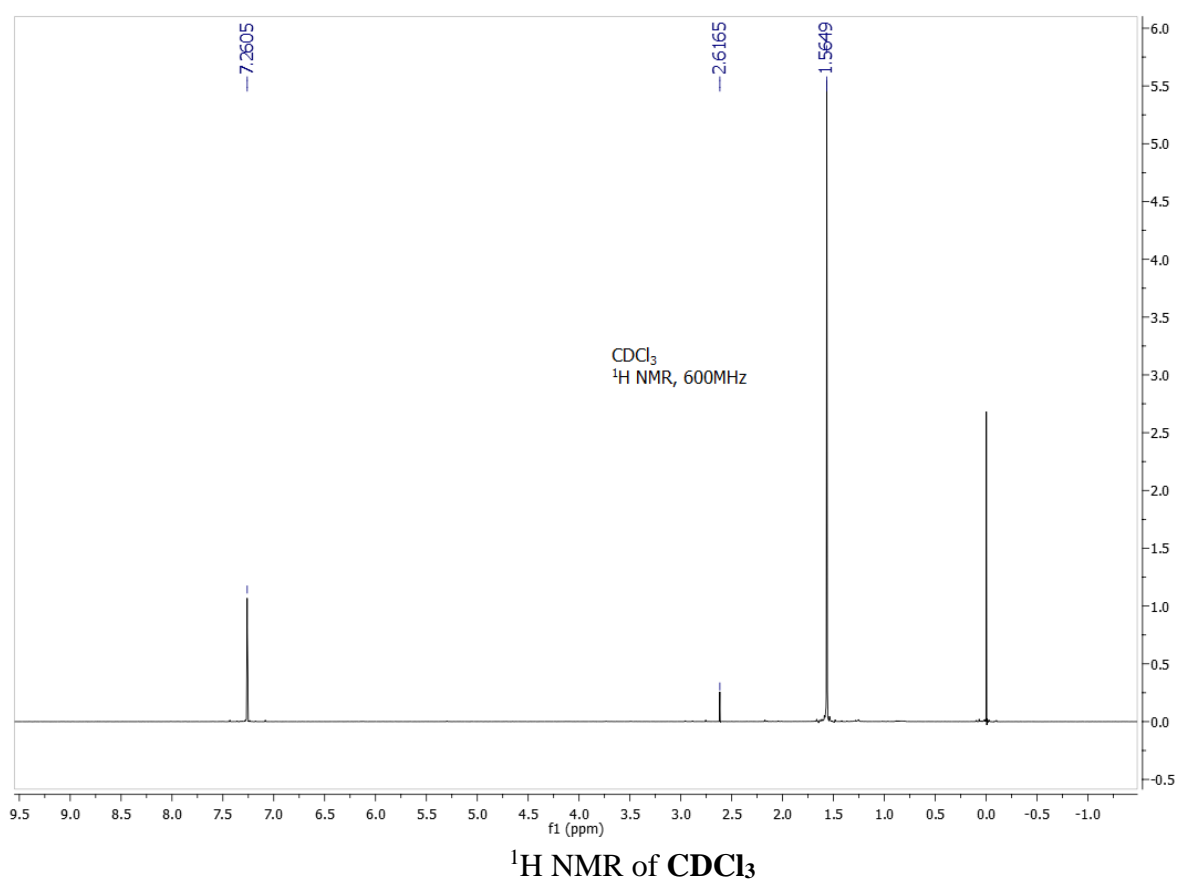
¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 7.4 Hz, 1H), 7.31 (d, J = 2.1 Hz, 4H), 6.99 (d, J = 9.6 Hz, 1H), 6.53 (dd, J = 9.3, 6.2 Hz, 1H), 5.92 (t, J = 6.7 Hz, 1H),

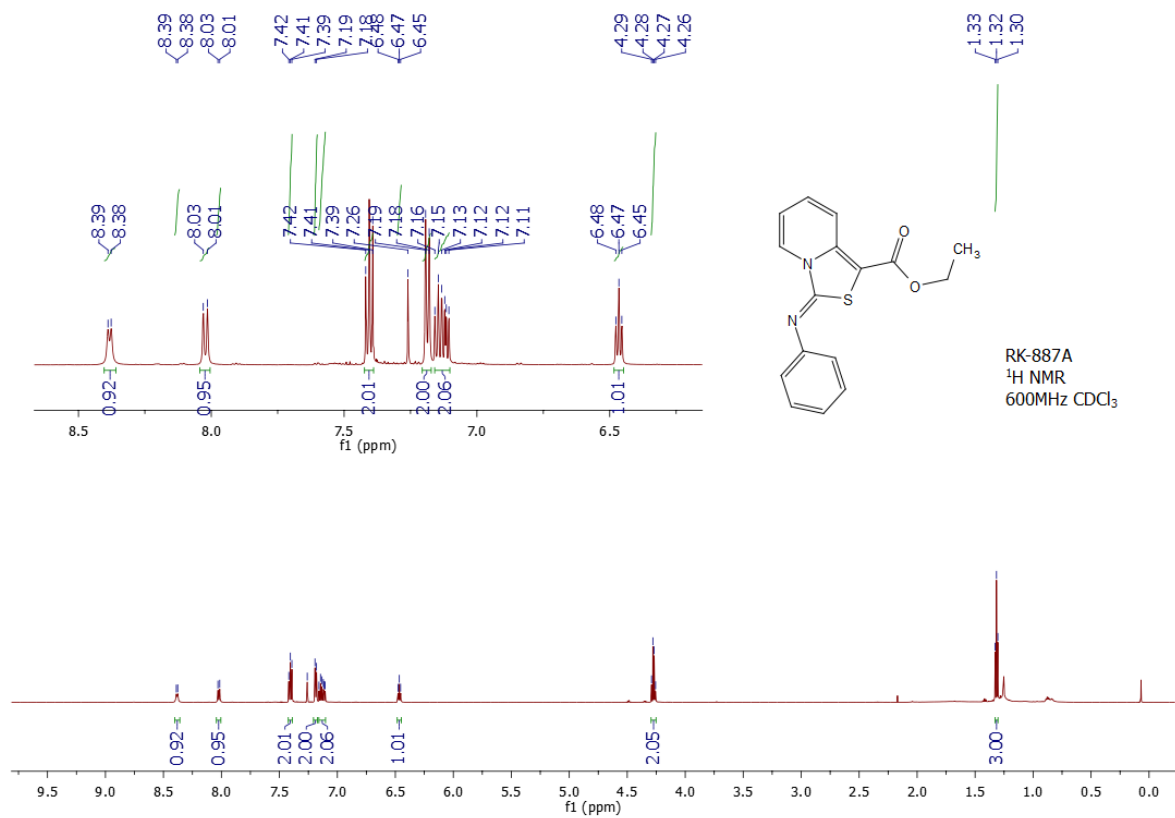
2.96 (d, J = 6.7 Hz, 2H), 2.01 (dd, J = 13.3, 6.7 Hz, 1H), 1.02 (s, 3H), 1.00 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 156.27, 151.26, 130.72, 130.61, 130.39, 127.92, 127.07, 126.01, 116.67, 106.21, 96.98, 61.53, 21.54, 19.68, 13.00. HRMS(ESI-TOF)m/z: calcd for C₁₇H₁₇N₂ClS[M+H]⁺: 317.0878; found: 317.0872.

Reference

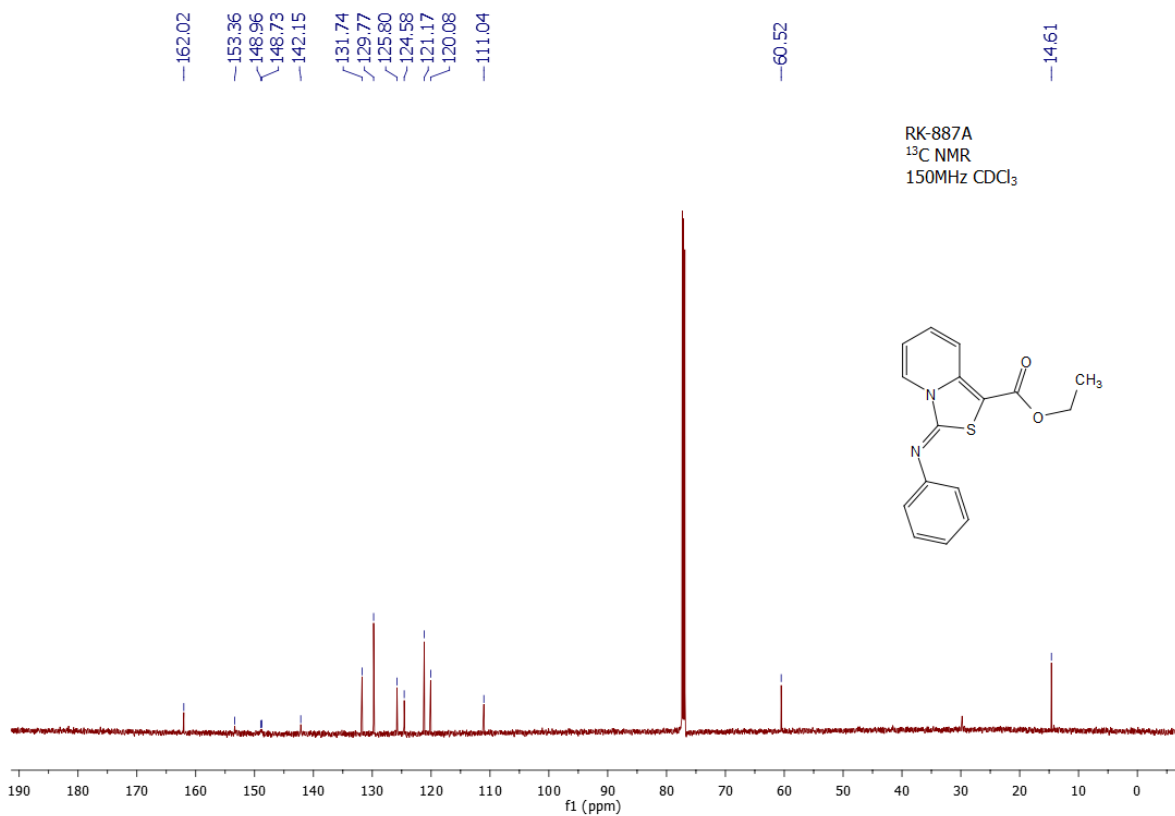
(1). Z. Zhang, V. G evorgyan, Co-Catalyzed Transannulation of Pyridotriazoles with Isothiocyanates and Xanthate Esters, *Org. Lett.*, 2020, **22**, 8500.

Copies of ^1H and ^{13}C NMR spectra

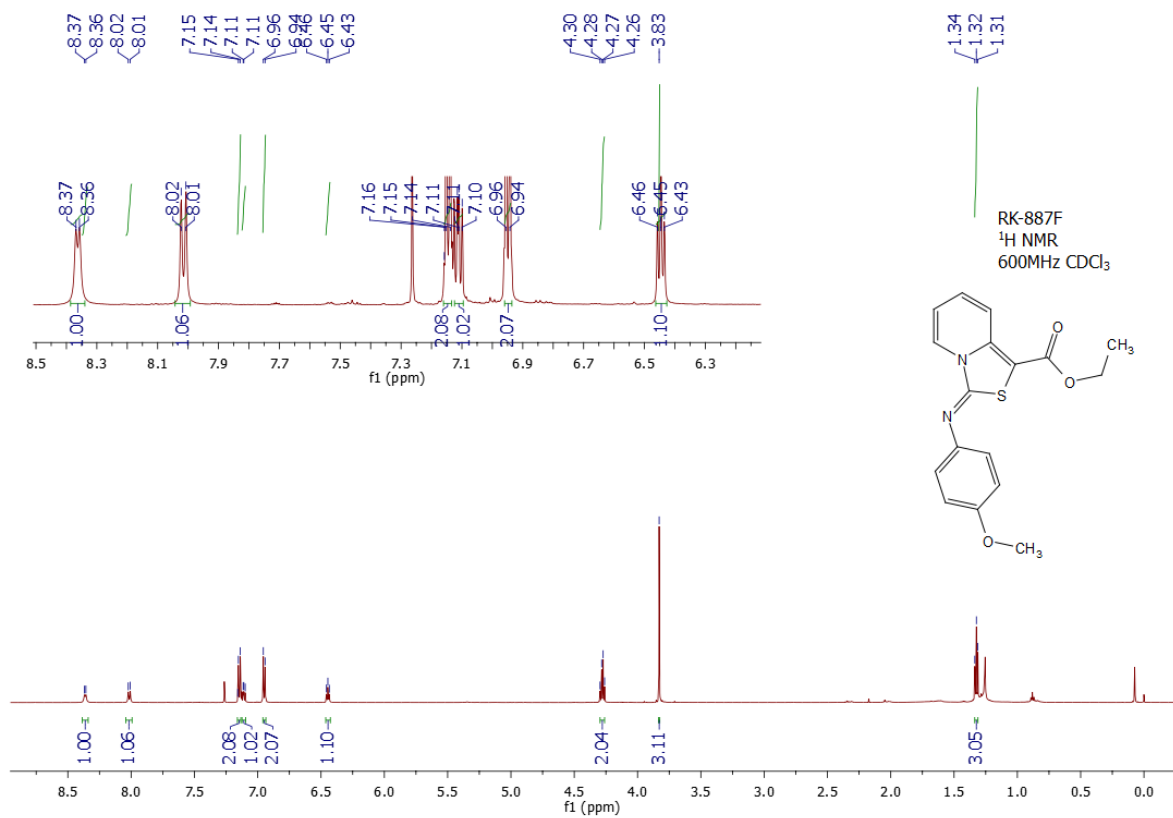




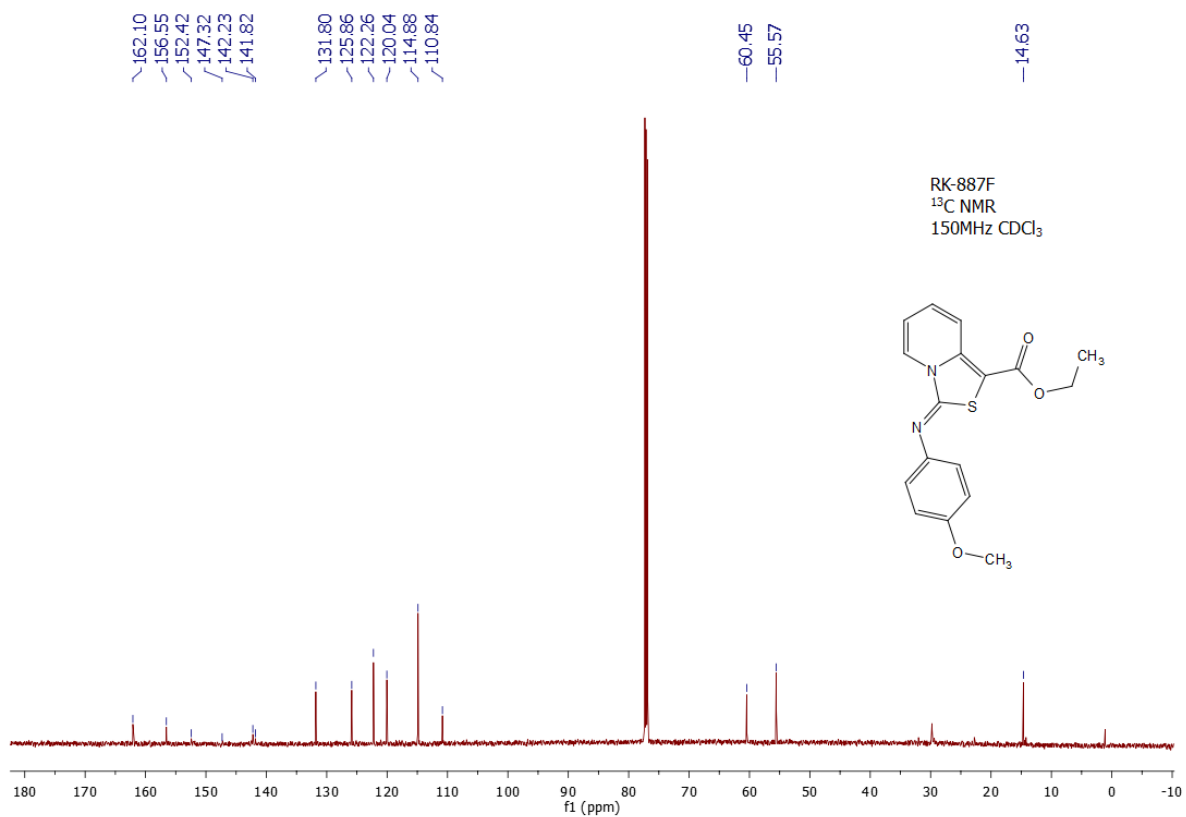
¹H NMR of 3a



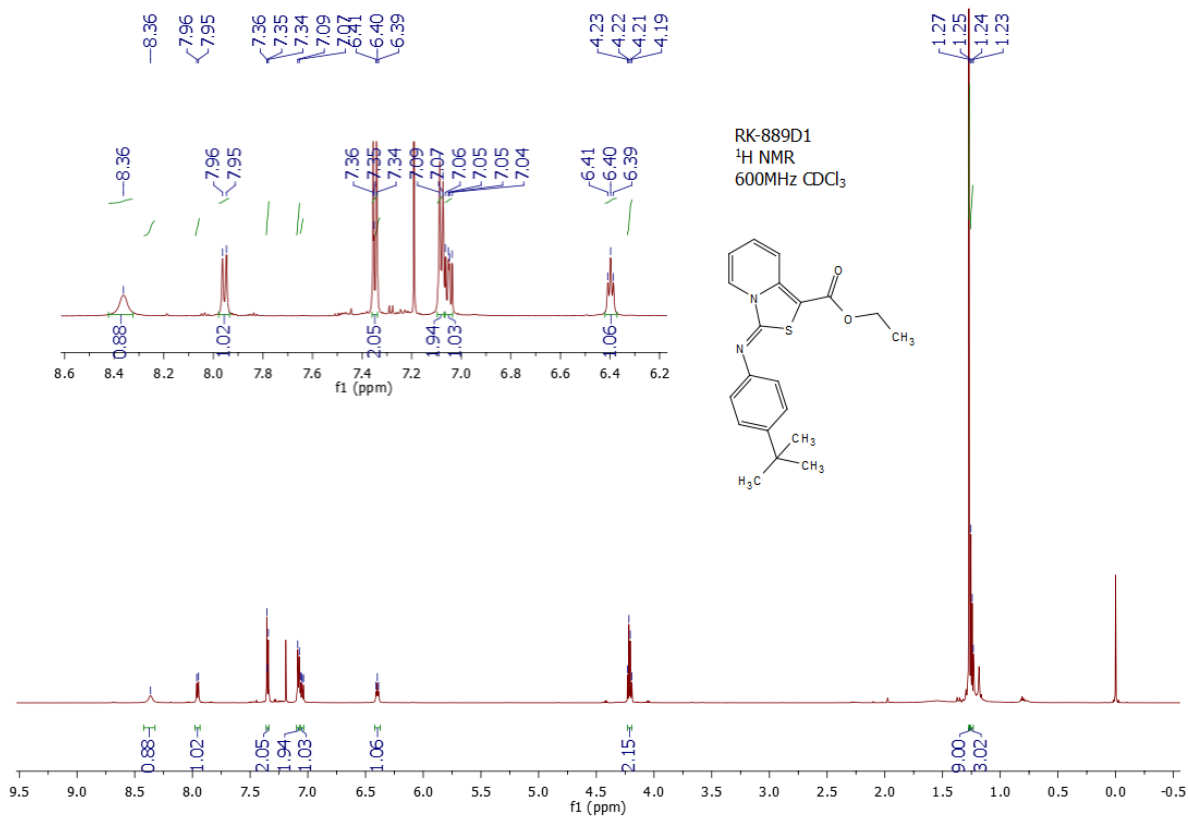
¹³C NMR of 3a



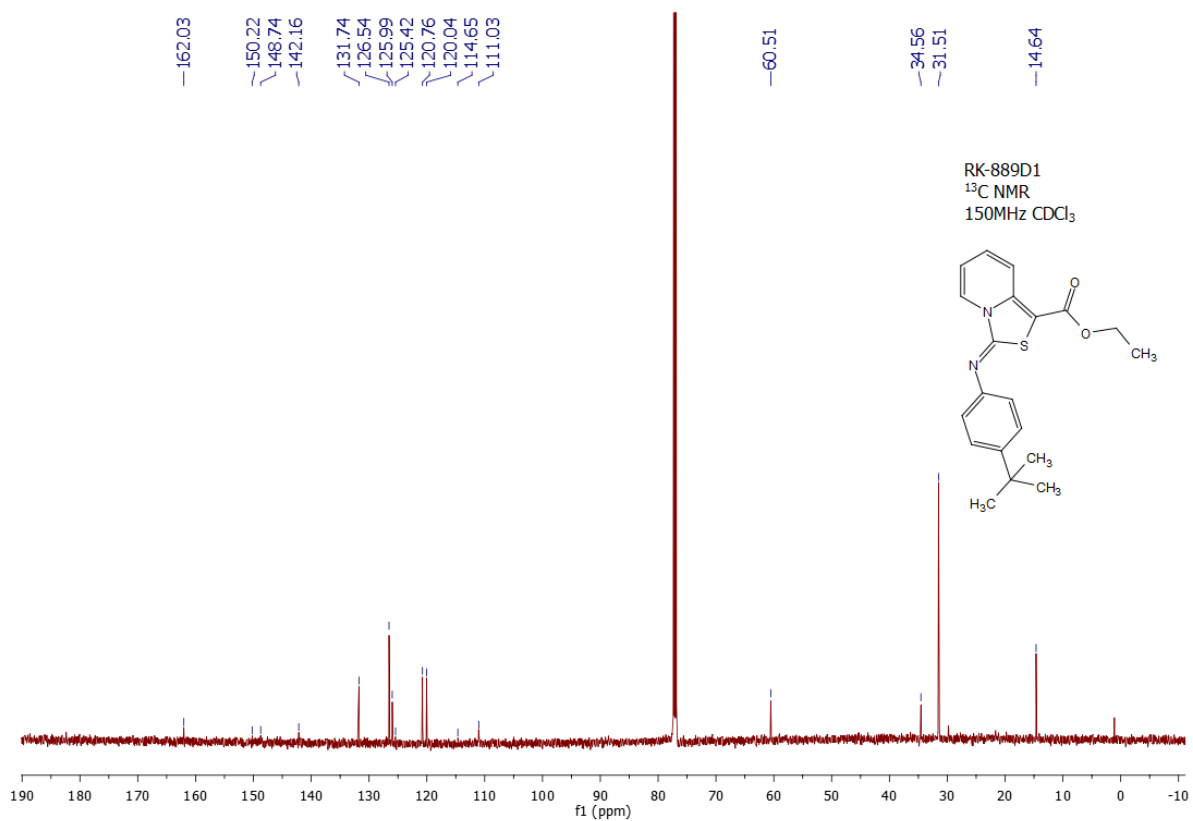
¹H NMR of **3b**



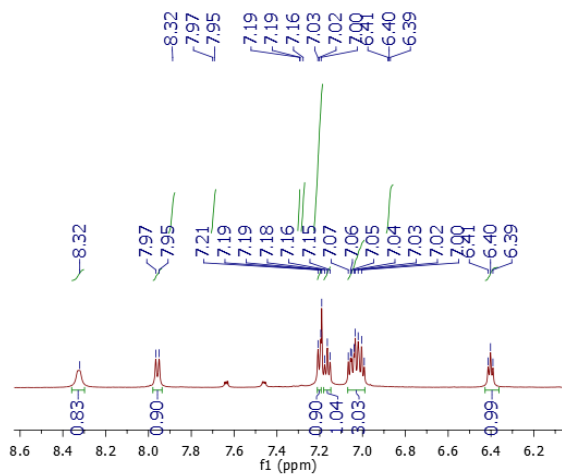
¹³C NMR of **3b**



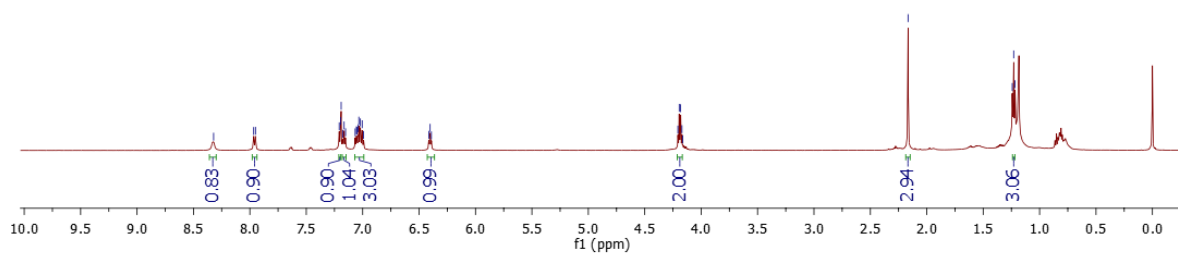
¹H NMR of **3c**



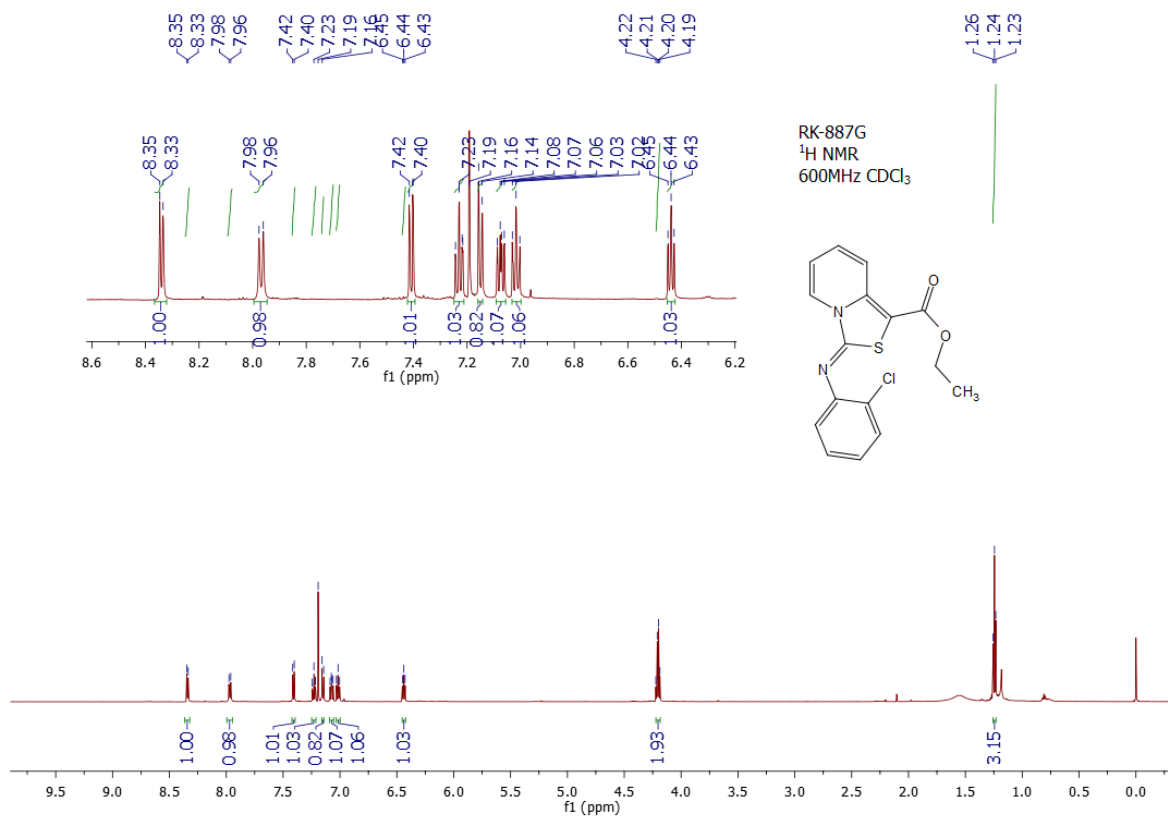
¹³C NMR of **3c**



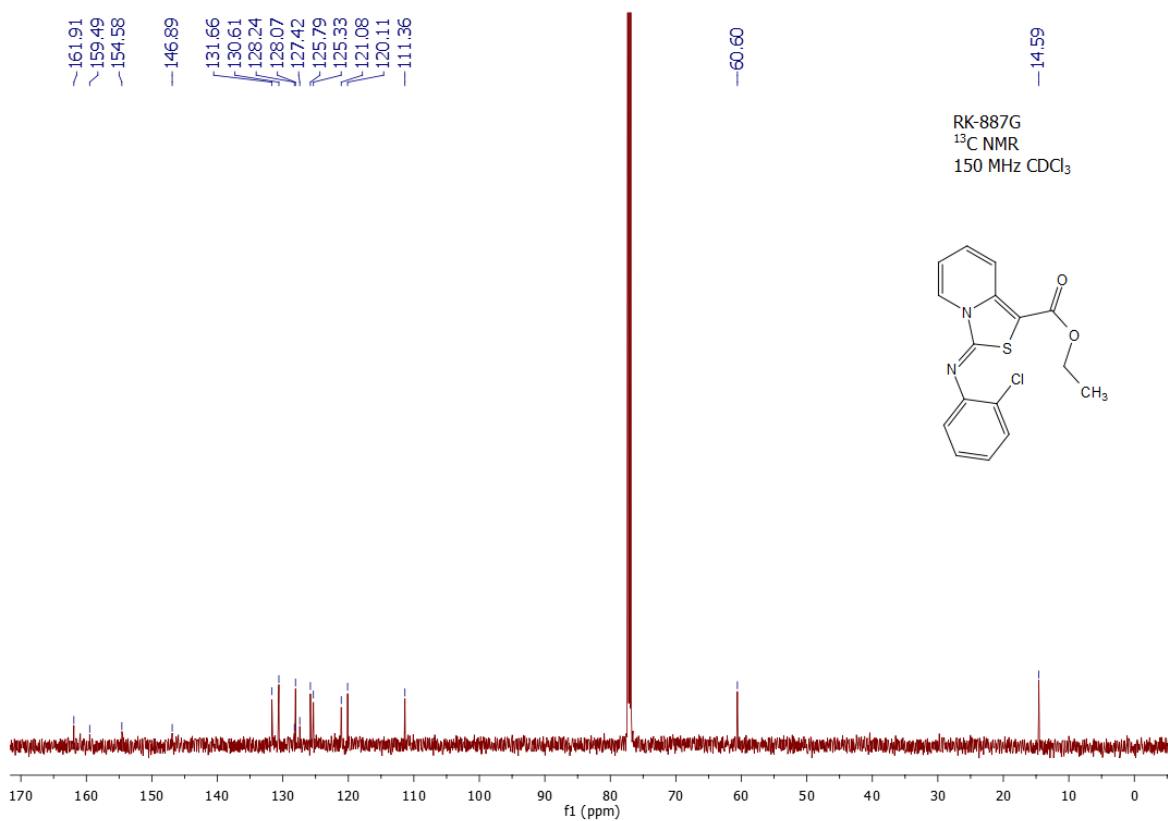
¹H NMR of **3d**



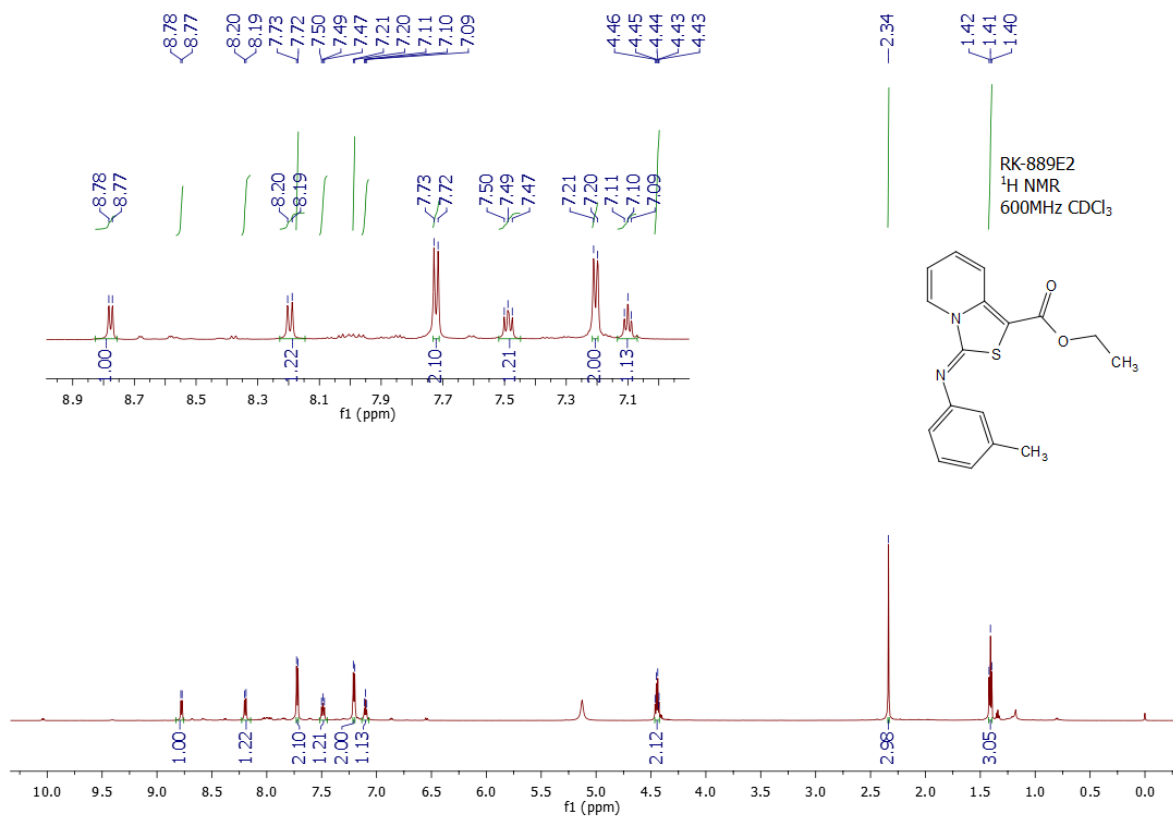
¹³C NMR of **3d**



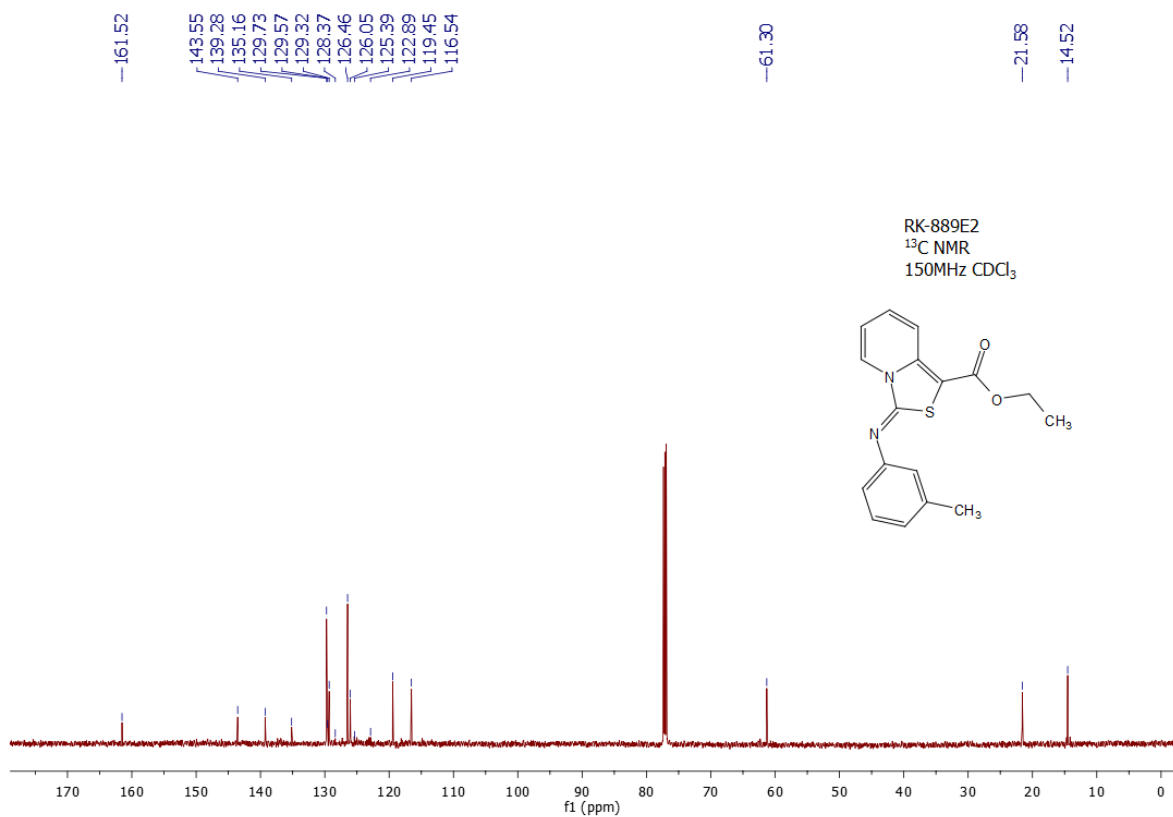
¹H NMR of 3e



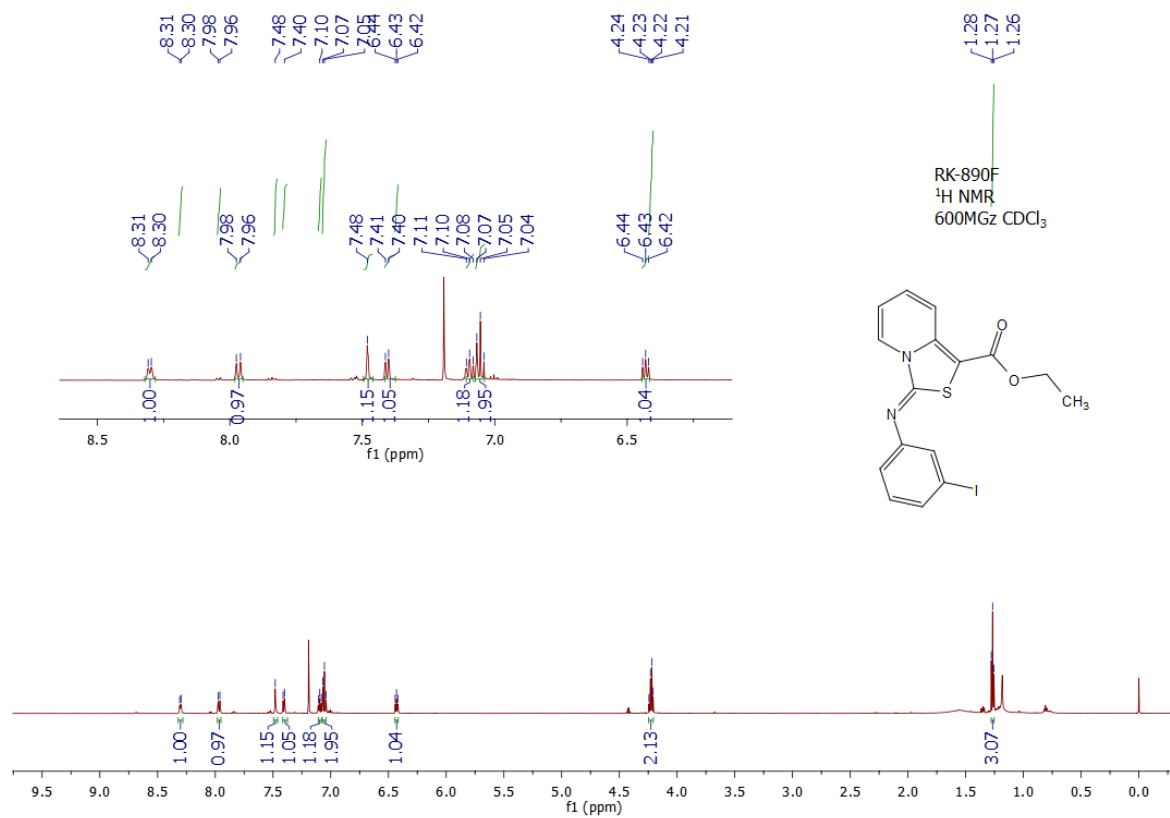
¹³C NMR of 3e



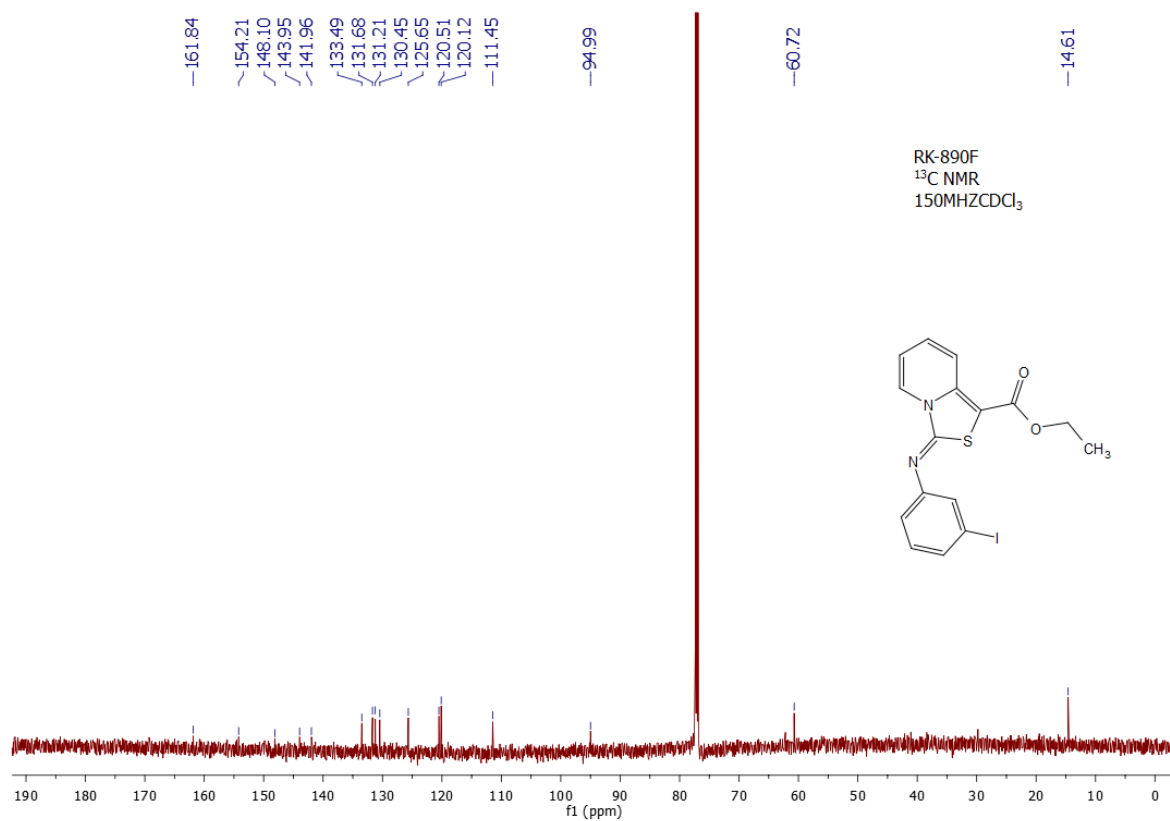
$^1\text{H NMR}$ of **3f**



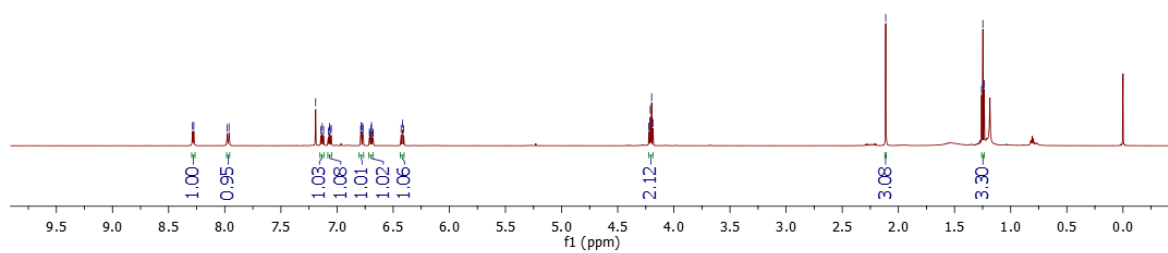
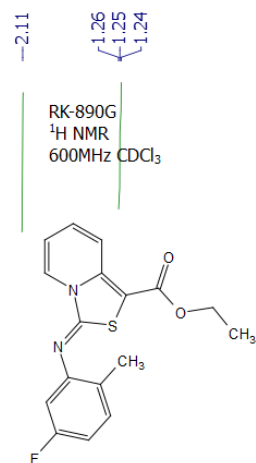
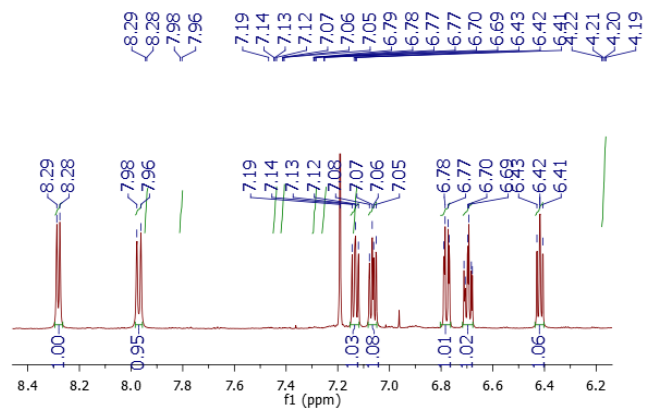
$^{13}\text{C NMR}$ of **3f**



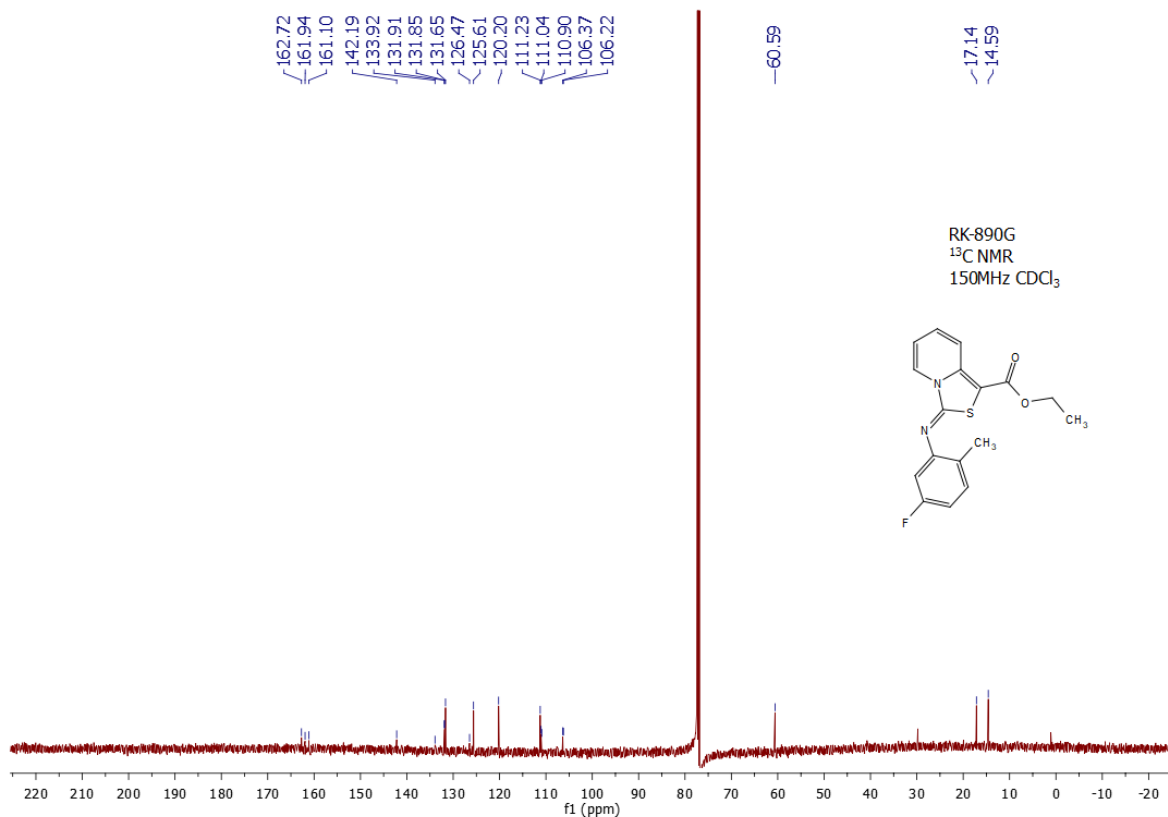
¹H NMR of **3g**



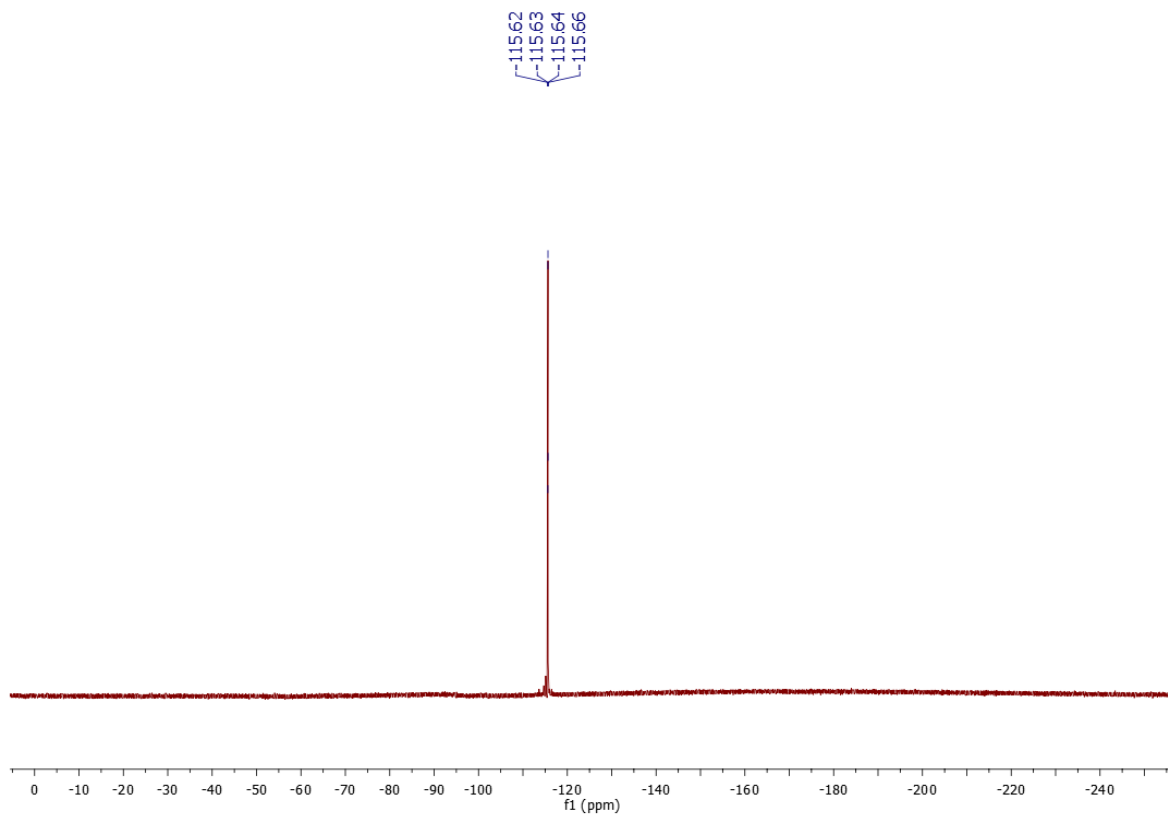
¹³C NMR of **3g**



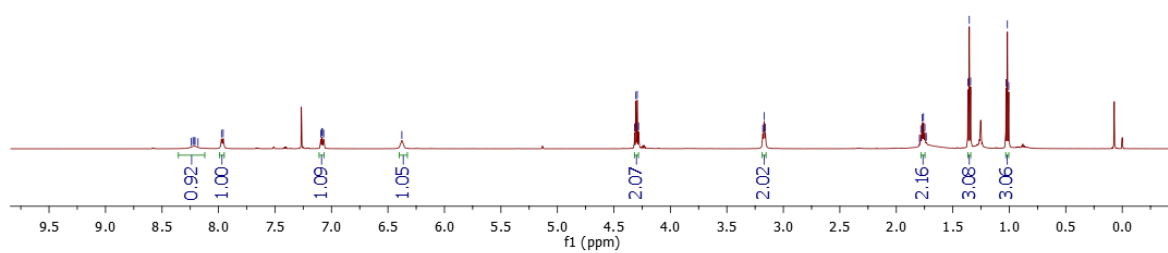
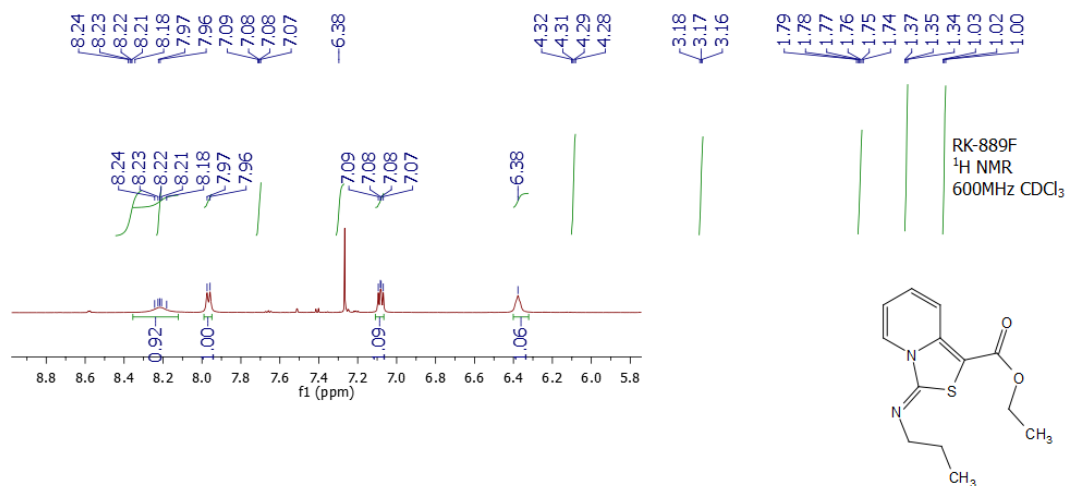
¹H NMR of 3h



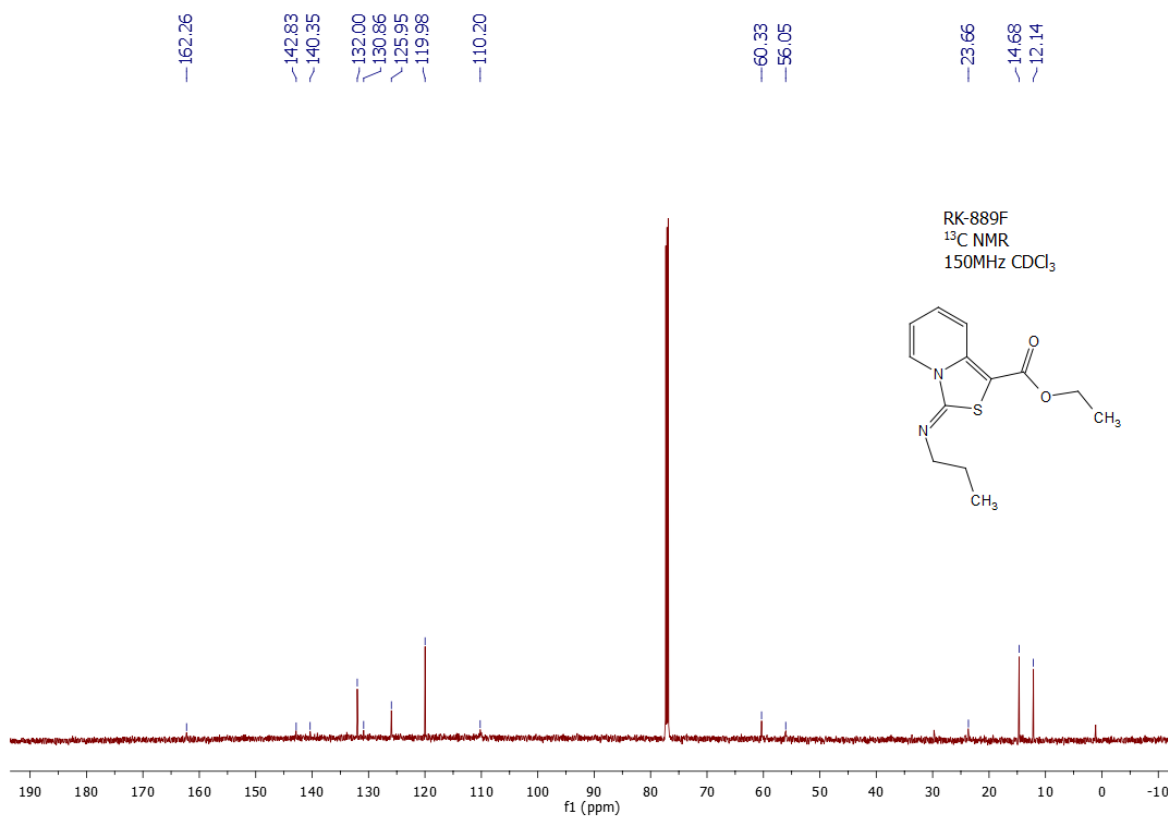
¹³C NMR of 3h



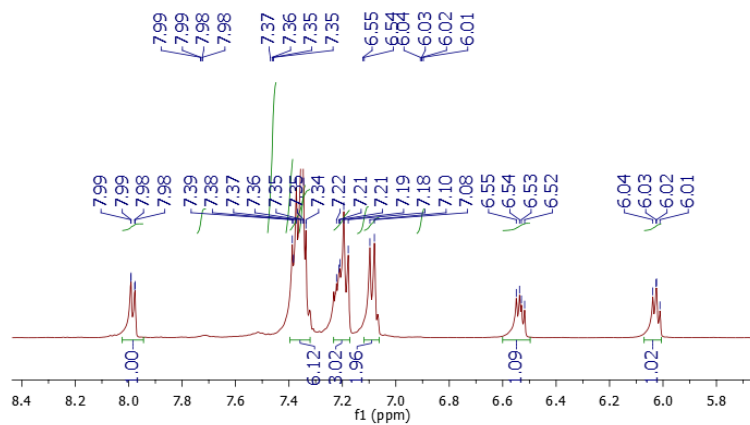
^{19}F NMR of **3h**



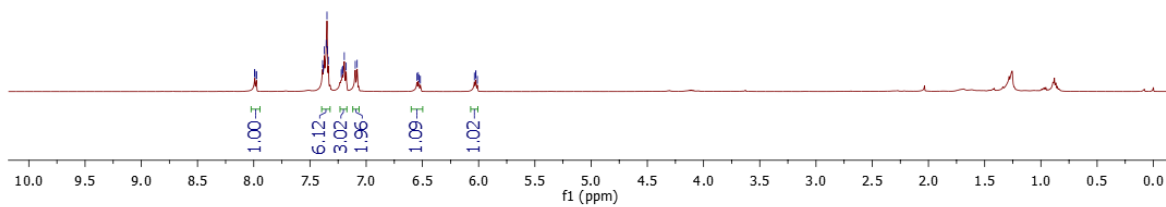
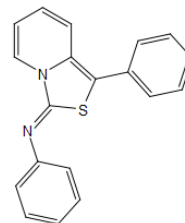
¹H NMR of **3i**



¹³C NMR of **3i**



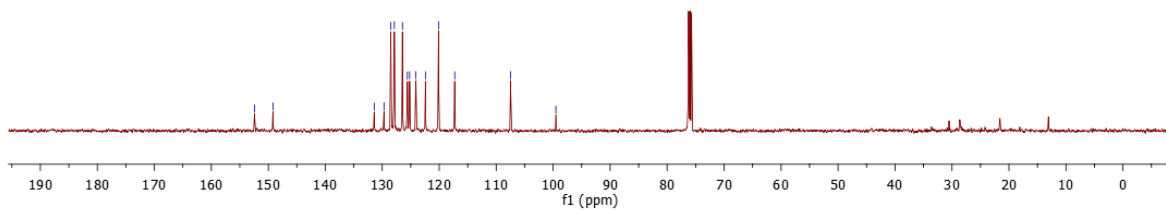
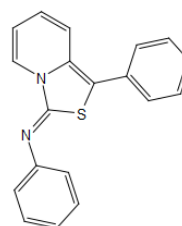
RK-845
¹H NMR
 500MHz CDCl₃



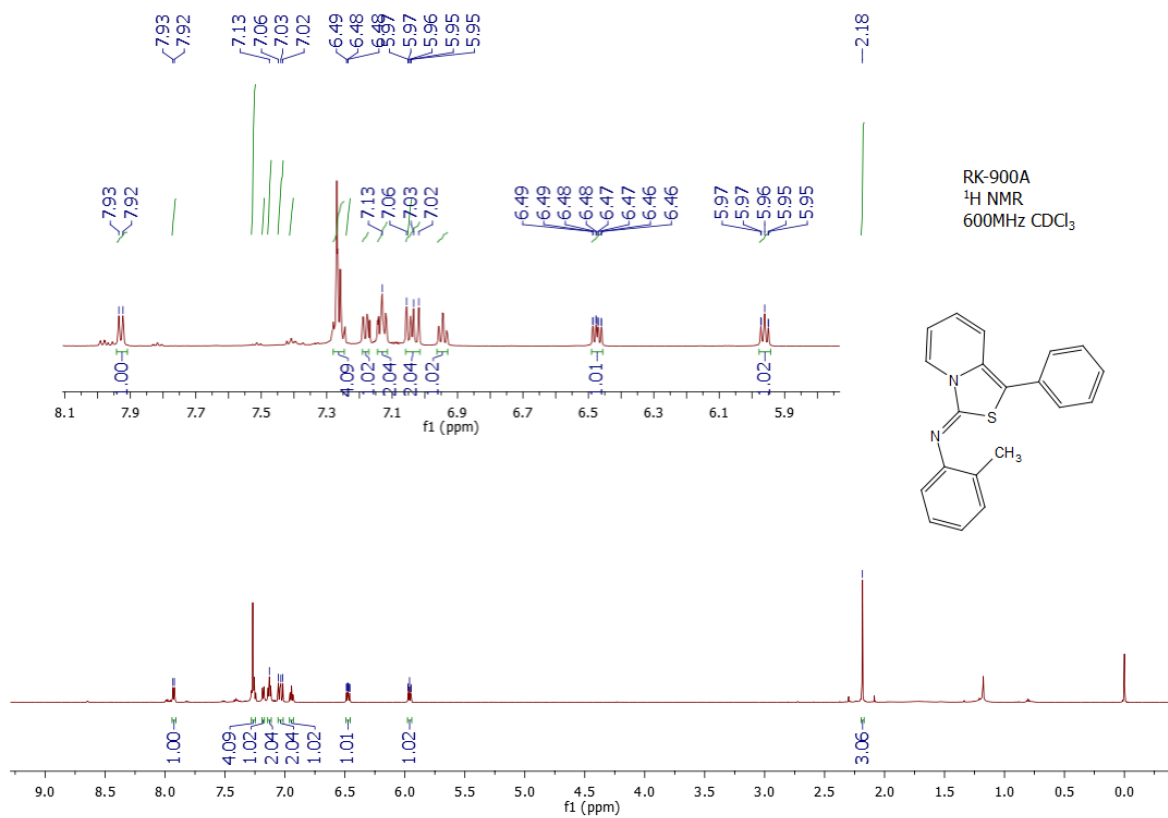
¹H NMR of **5a**

Peak labels (ppm): 152.40, 149.17, 129.69, 128.50, 127.88, 126.45, 125.59, 124.09, 122.42, 120.10, 117.39, 99.52.

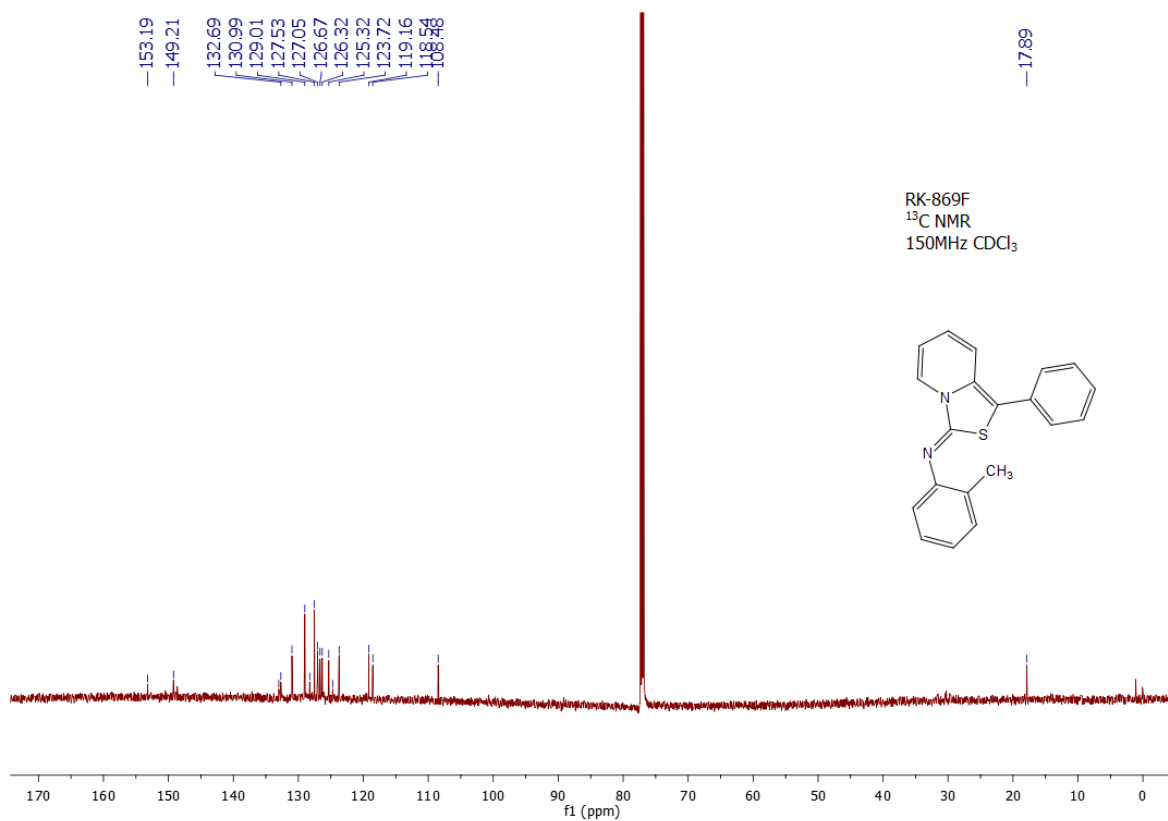
RK-845
¹³C NMR
 125MHz CDCl₃



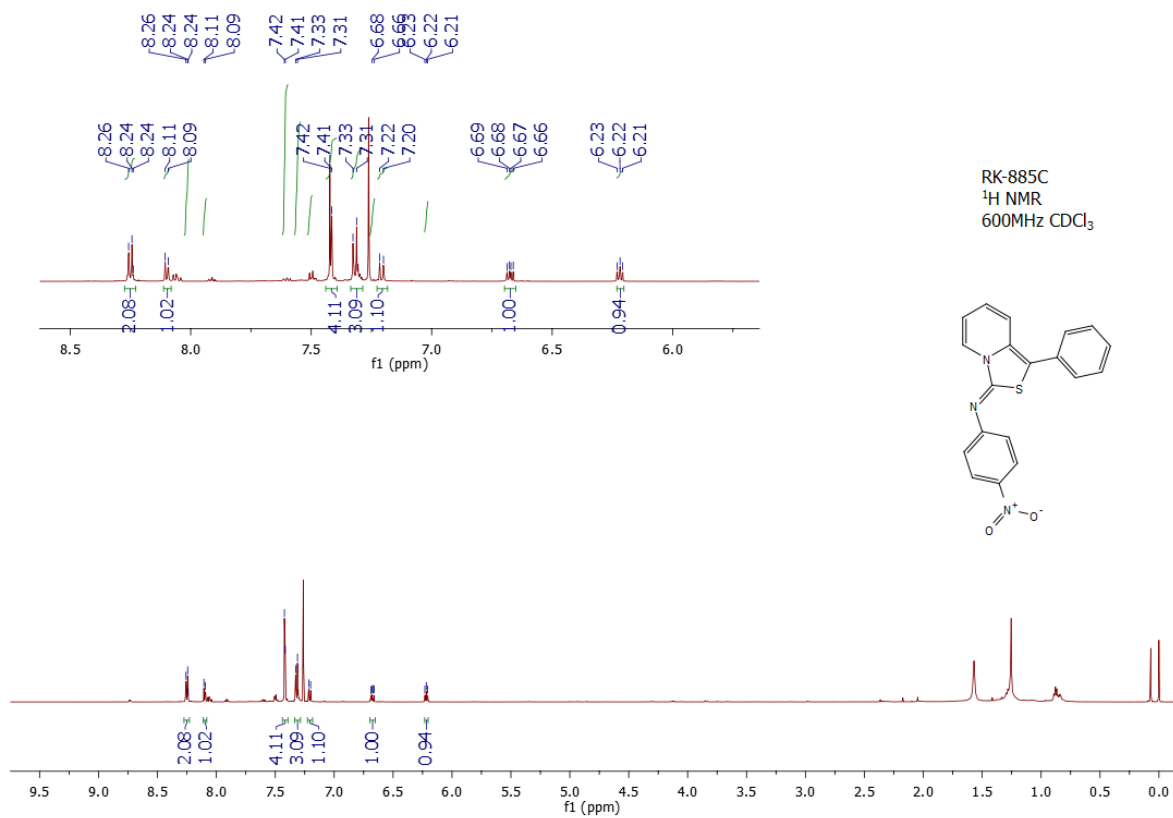
¹³C NMR of **5a**



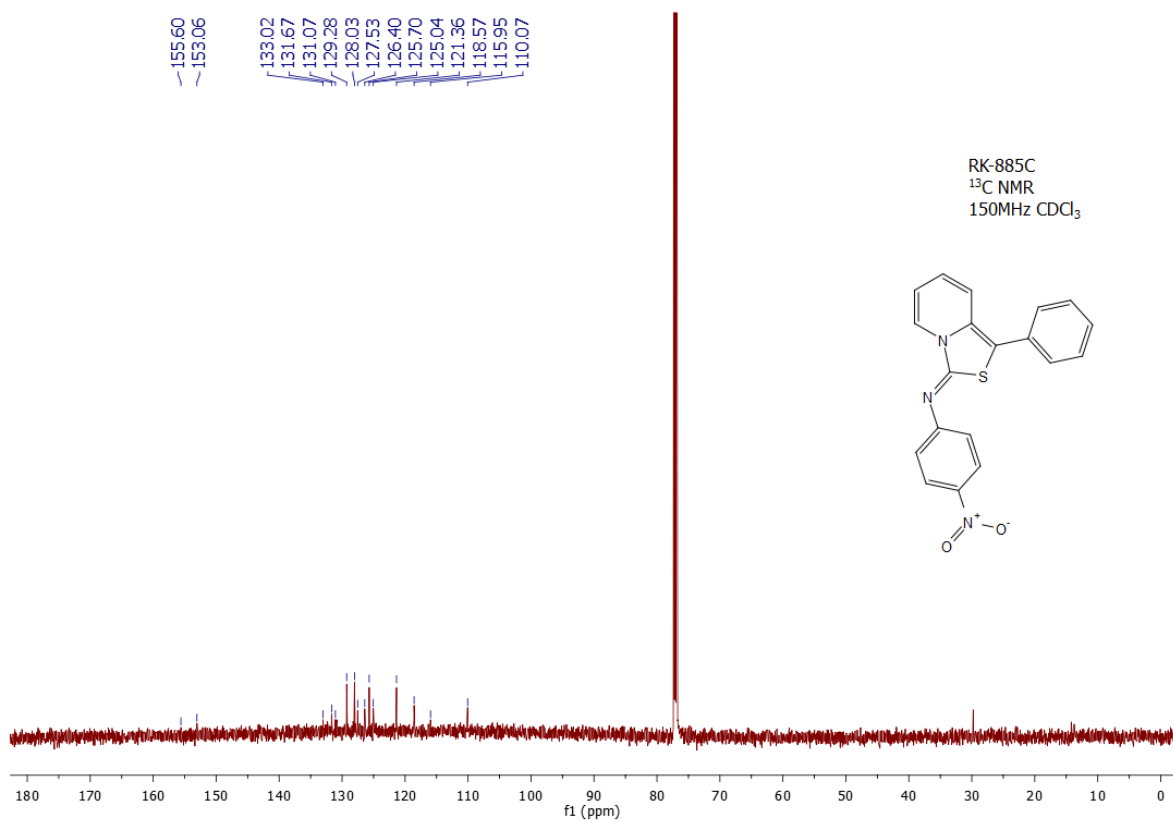
¹H NMR of **5b**



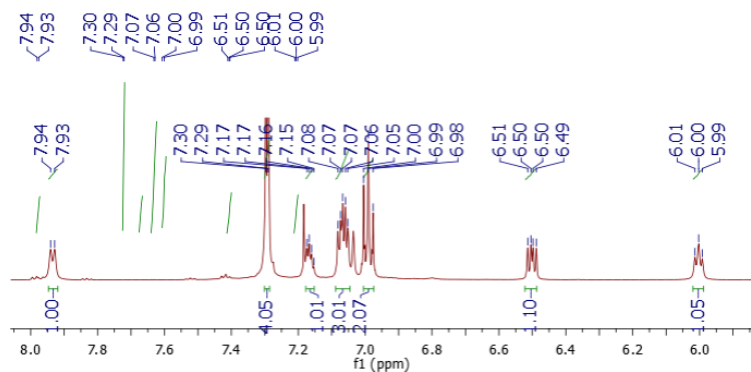
¹³C NMR of **5b**



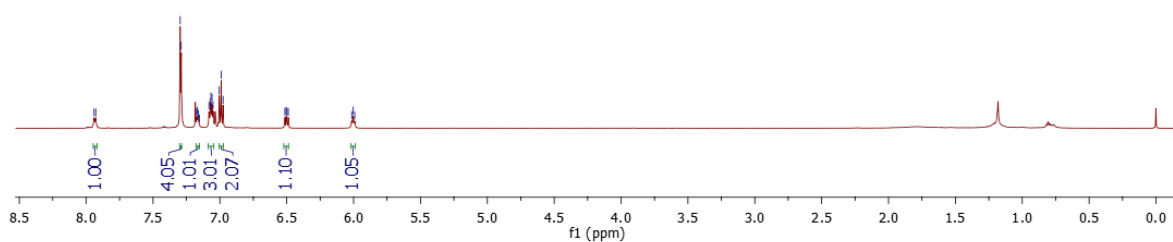
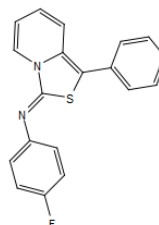
¹H NMR of 5c



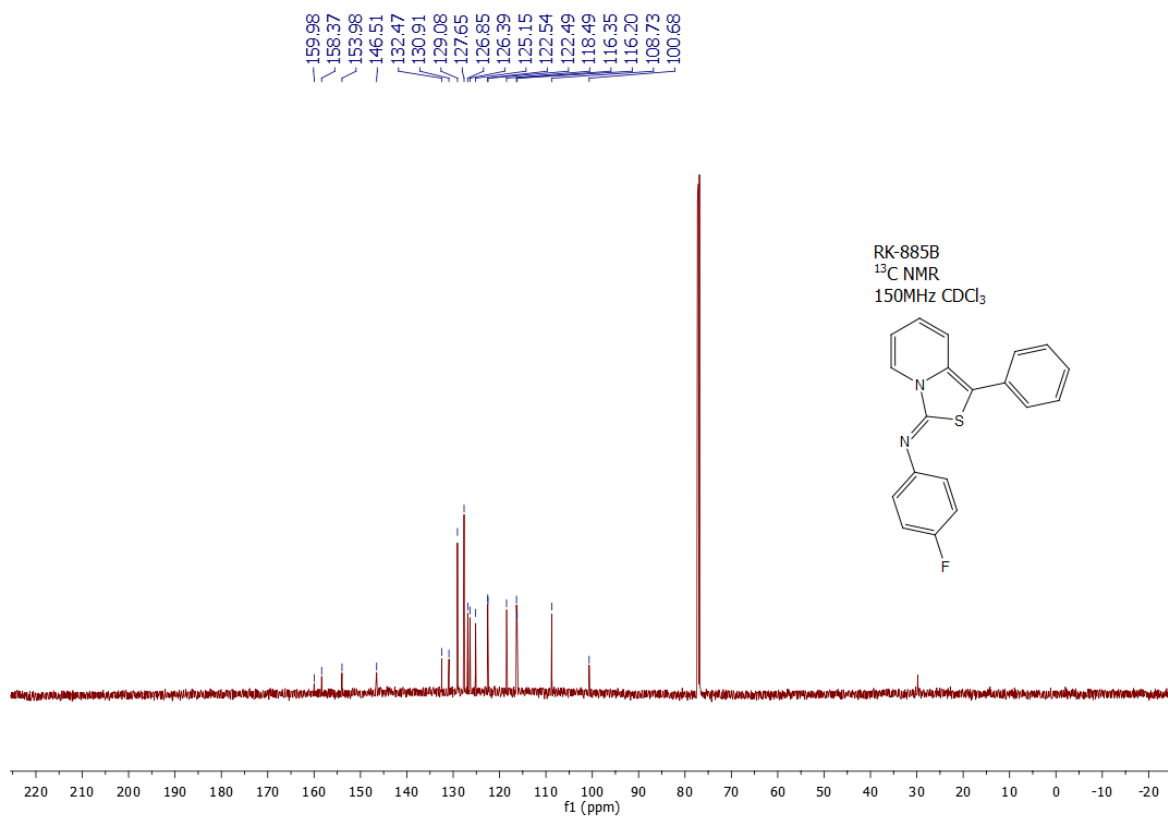
¹³C NMR of 5c



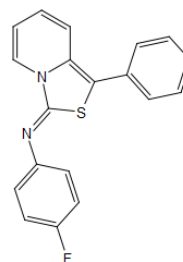
RK-885B
¹H NMR
 600MHz CDCl₃



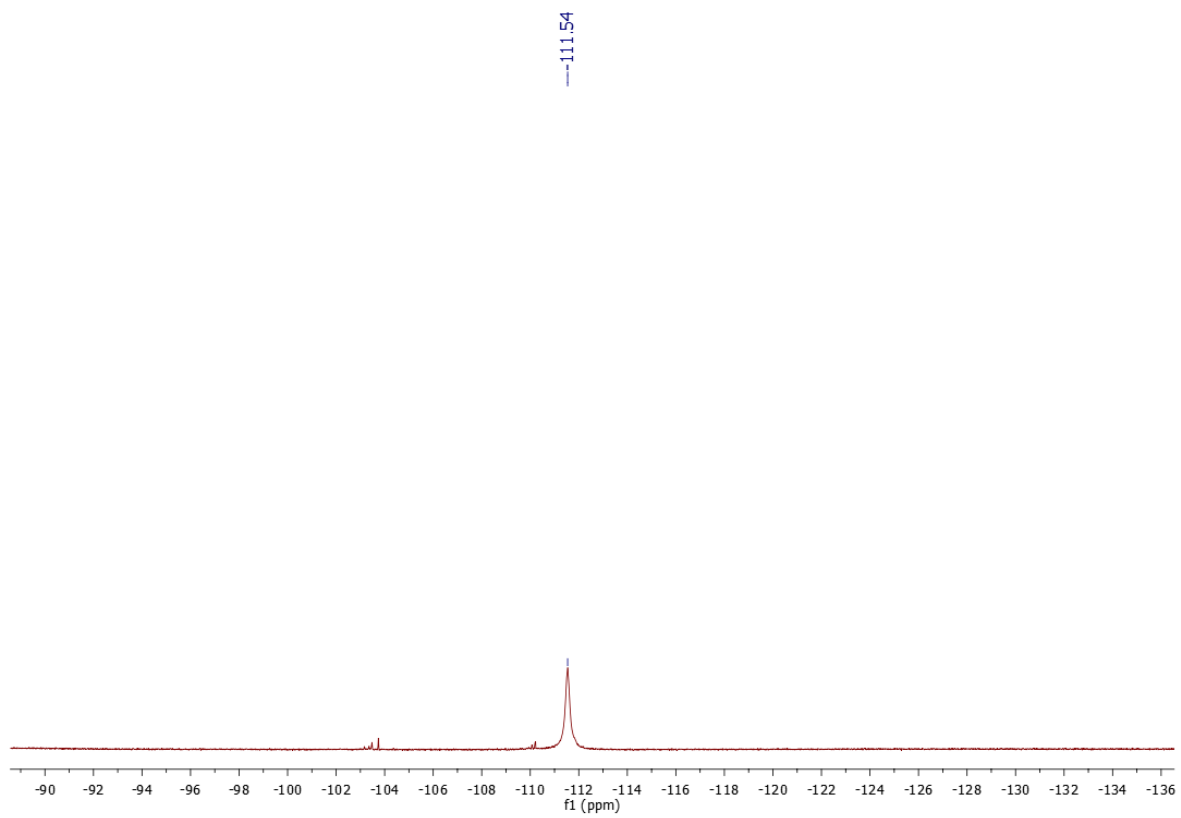
¹H NMR of **5d**



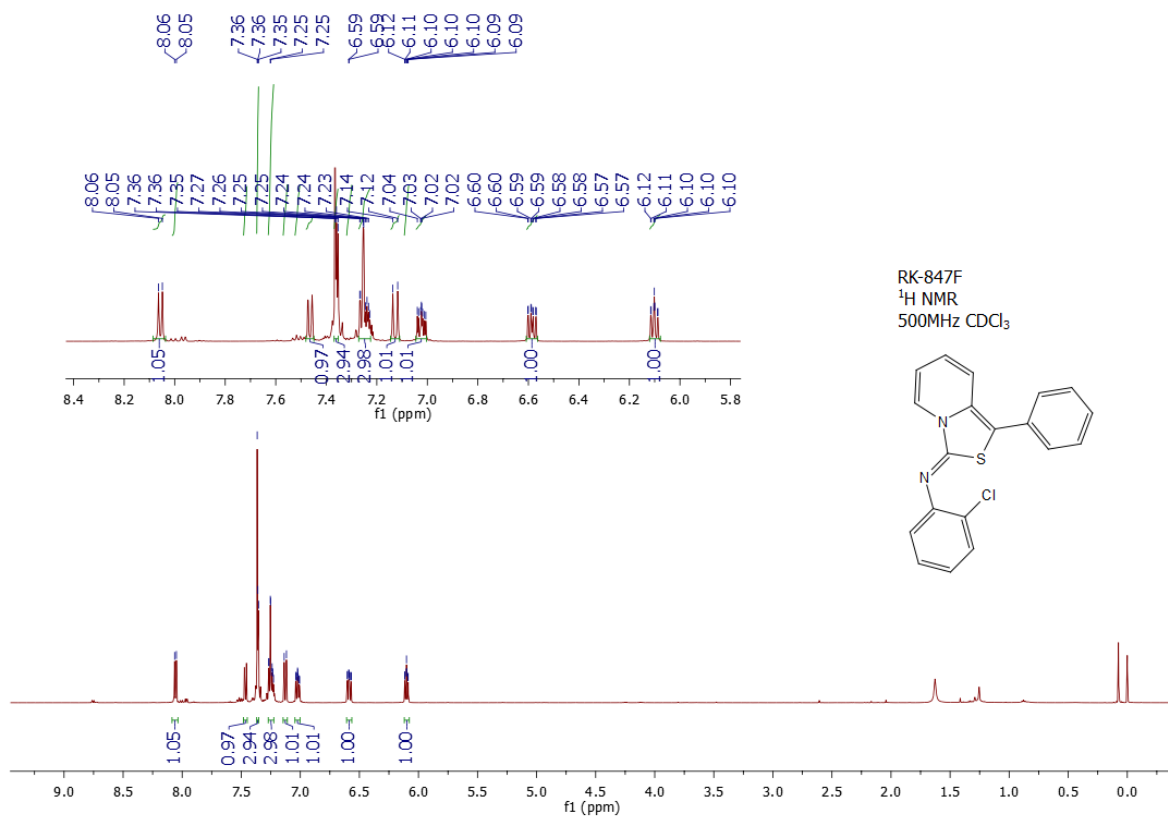
RK-885B
¹³C NMR
 150MHz CDCl₃



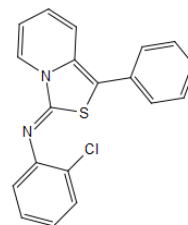
¹³C NMR of **5d**



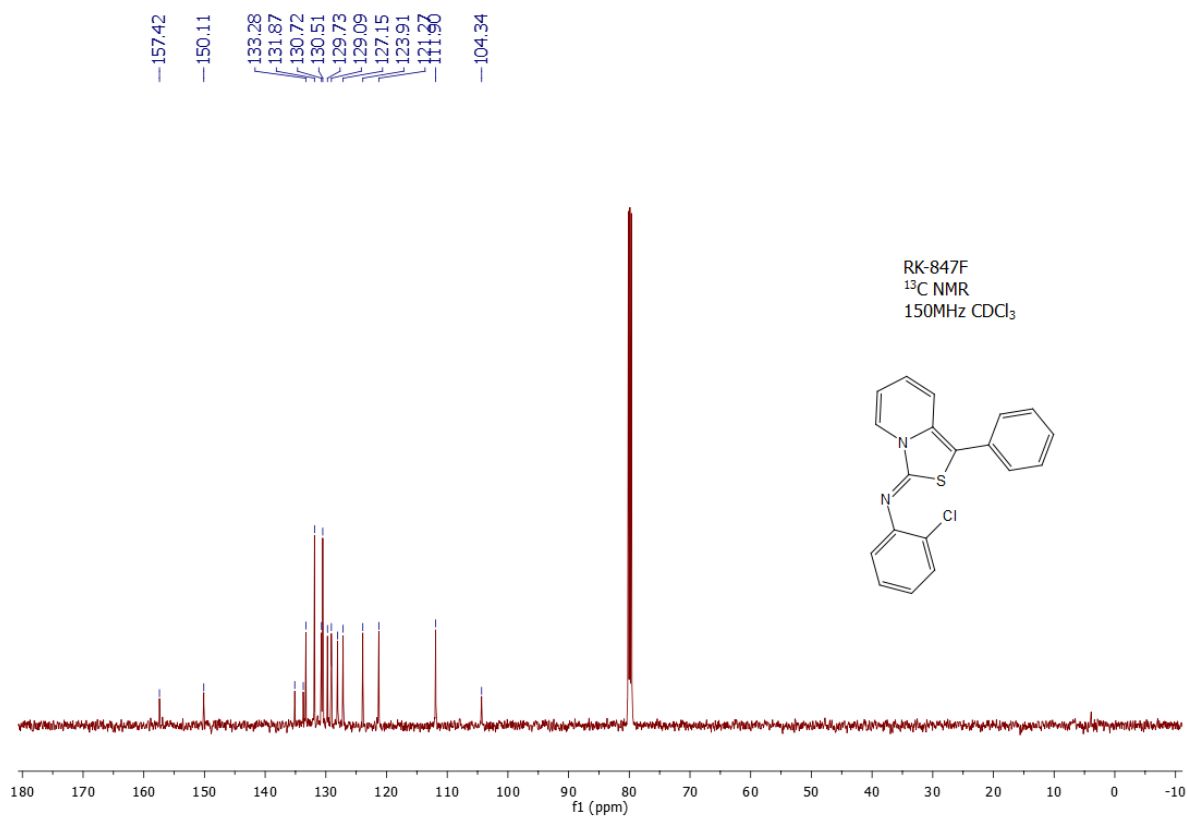
^{19}F NMR of **5d**



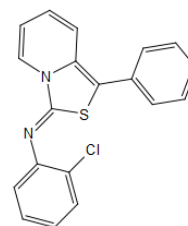
RK-847F
¹H NMR
 500MHz CDCl₃



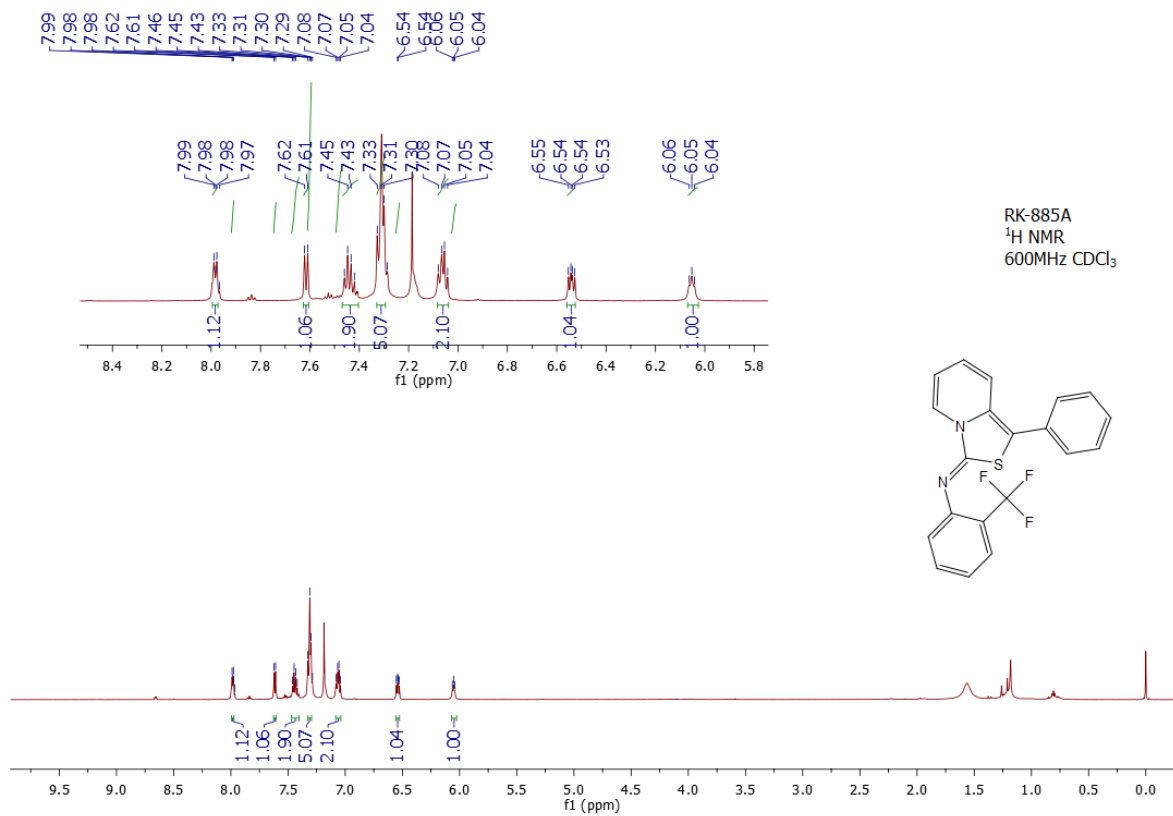
¹H NMR of **5e**



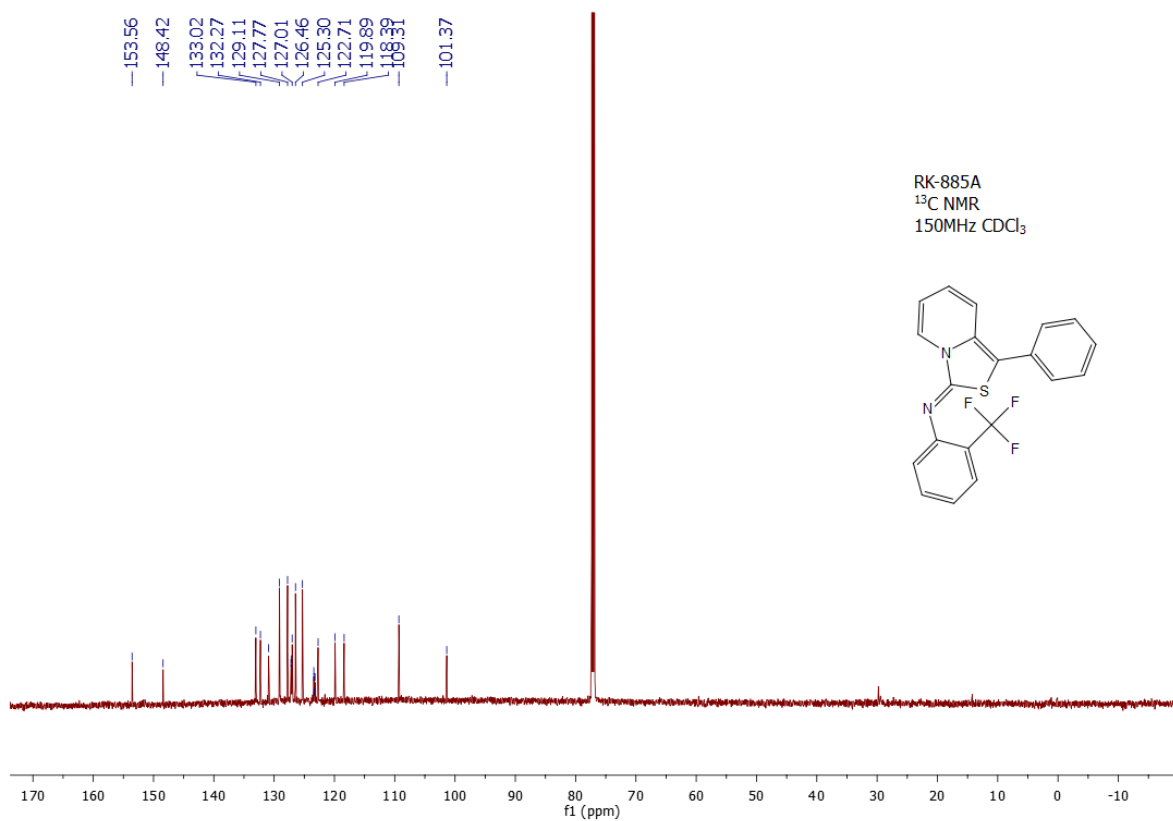
RK-847F
¹³C NMR
 150MHz CDCl₃



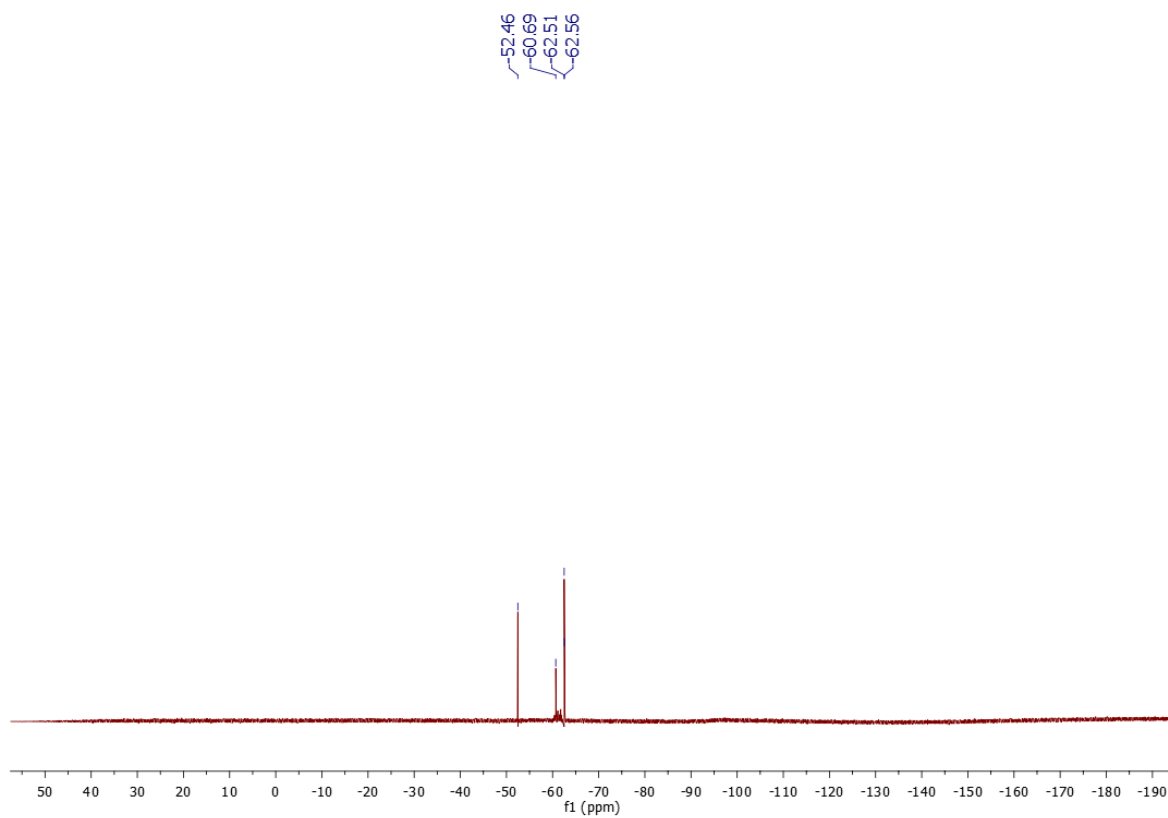
¹³C NMR of **5e**



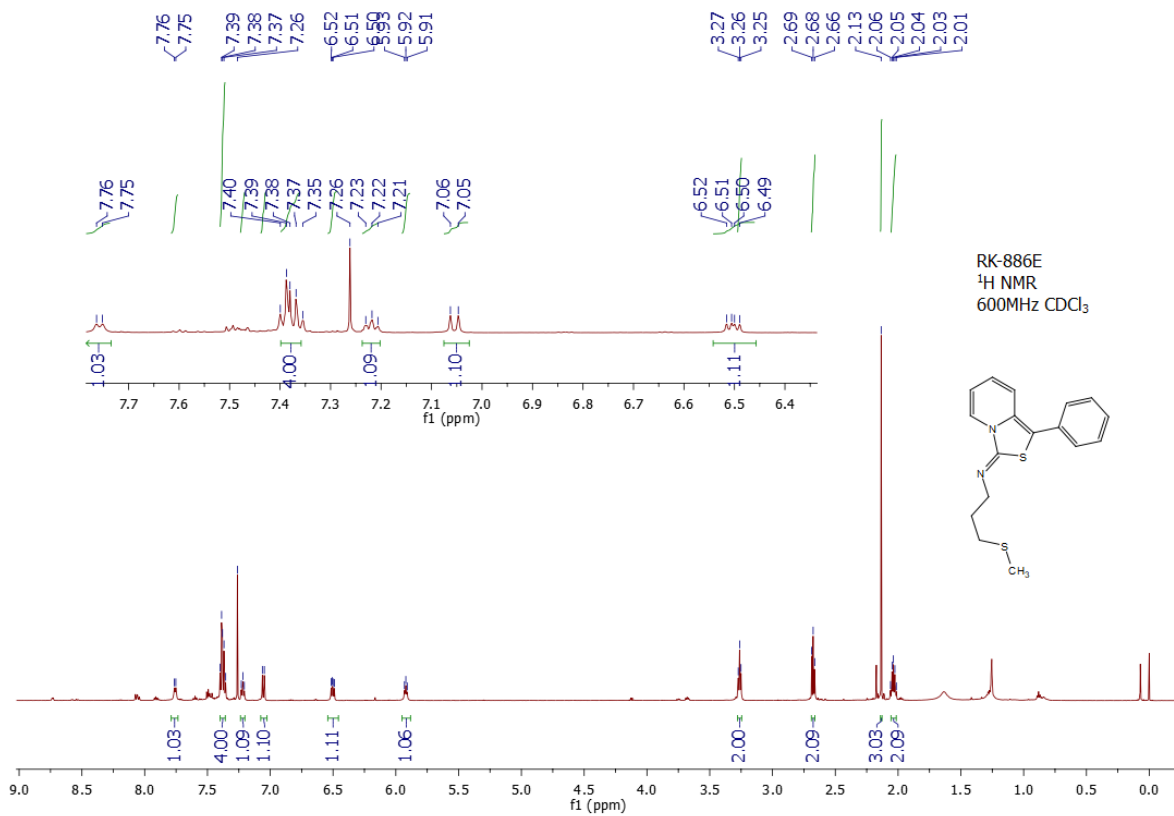
¹H NMR of **5f**



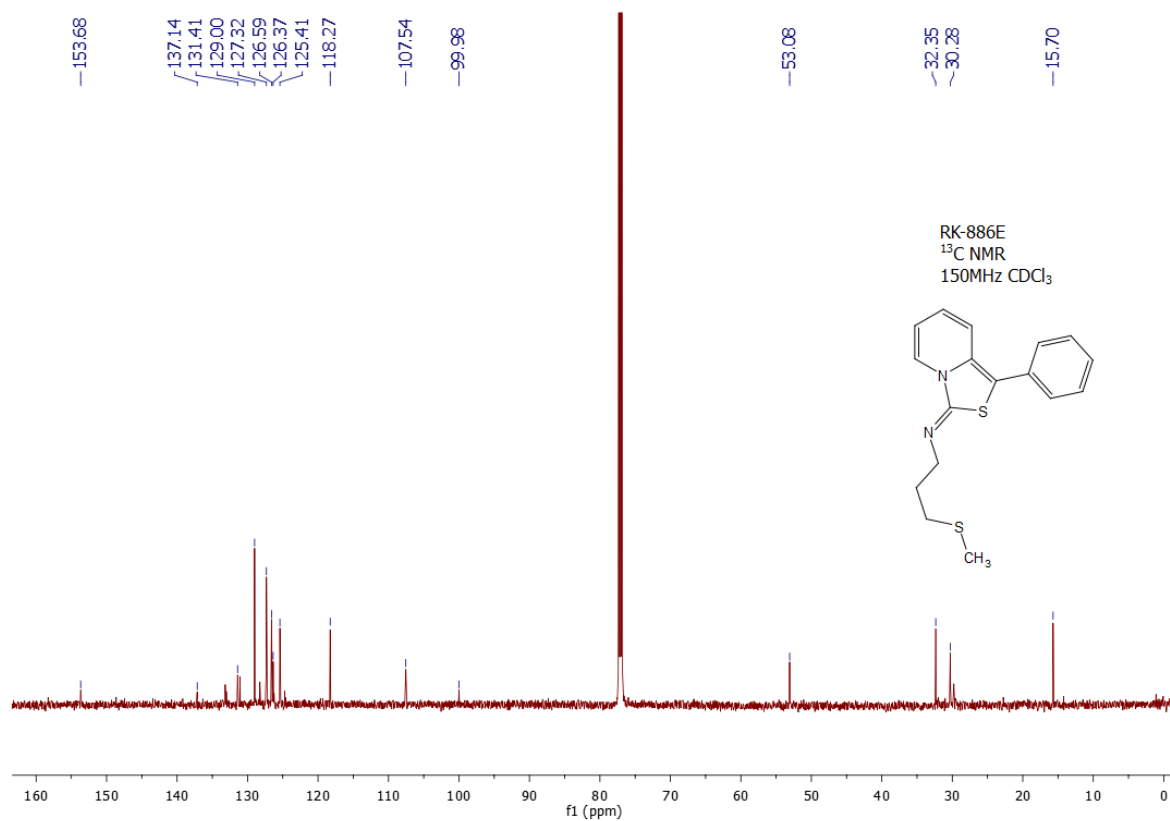
¹³C NMR of **5f**



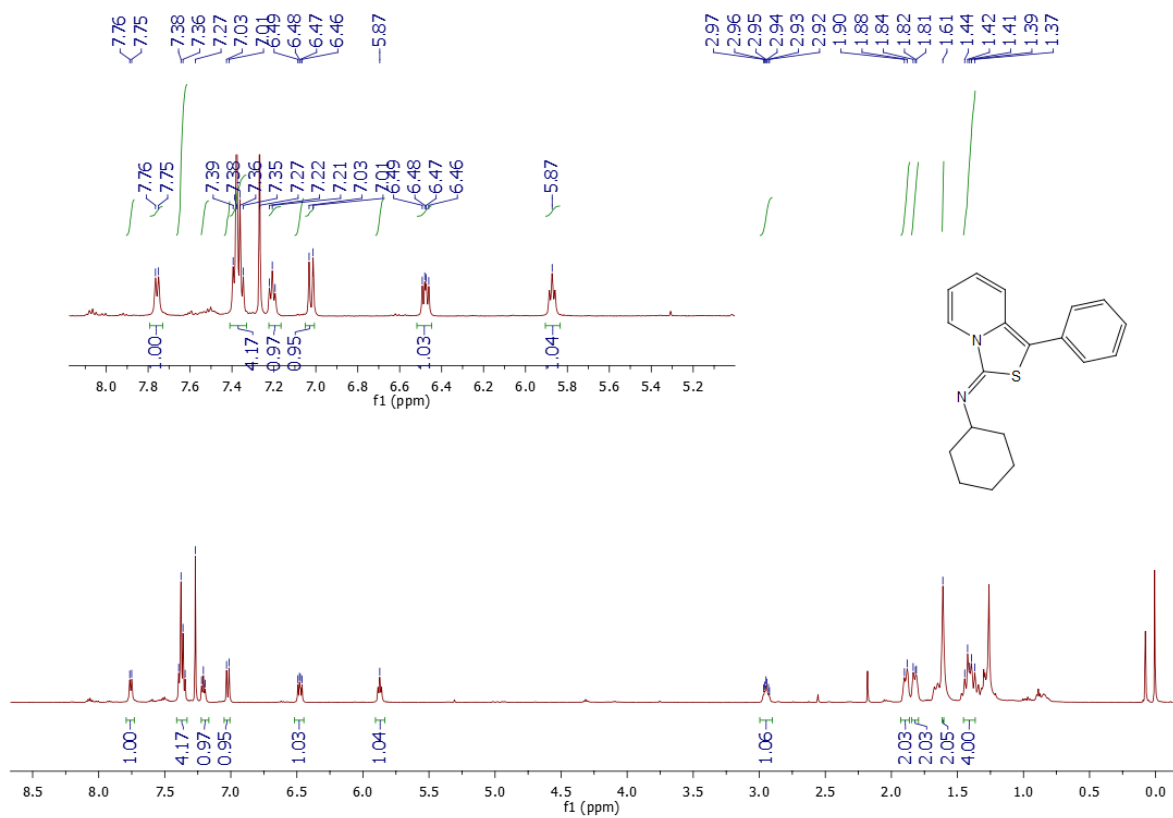
^{19}F NMR of **5f**



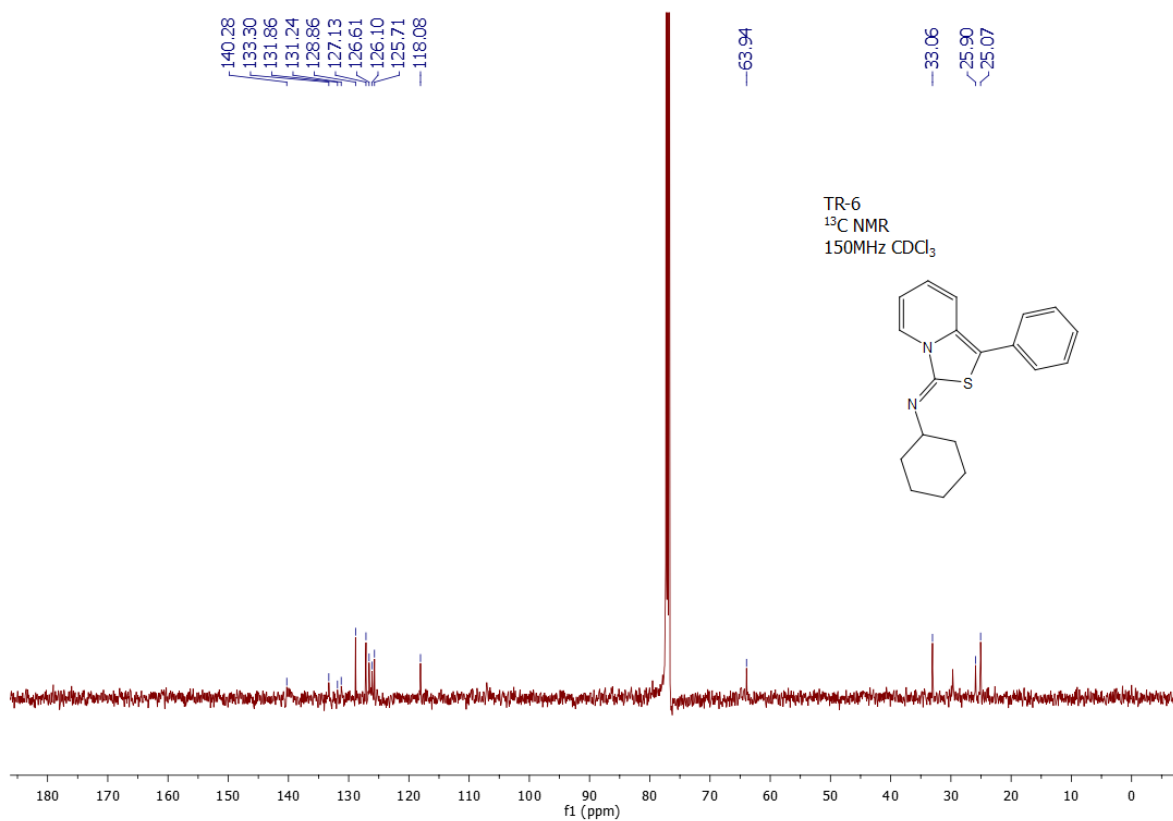
¹H NMR of **5g**



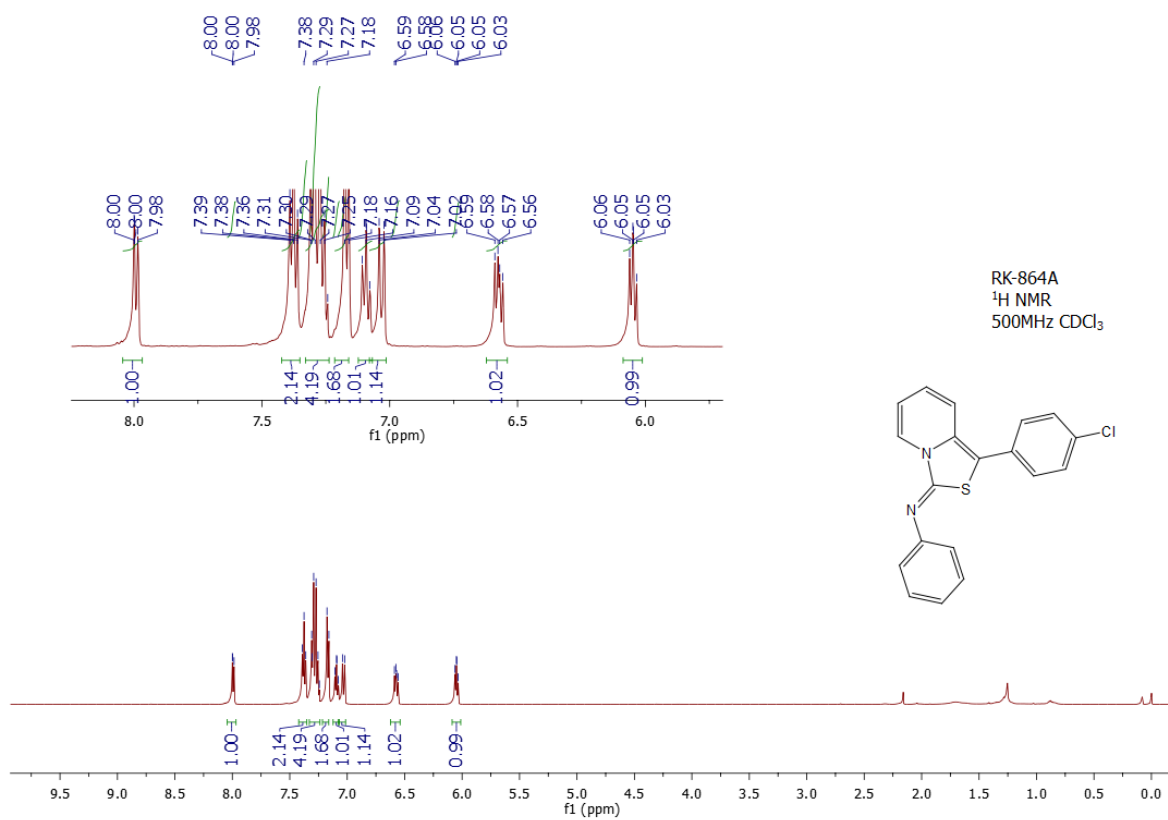
¹³C NMR of **5g**



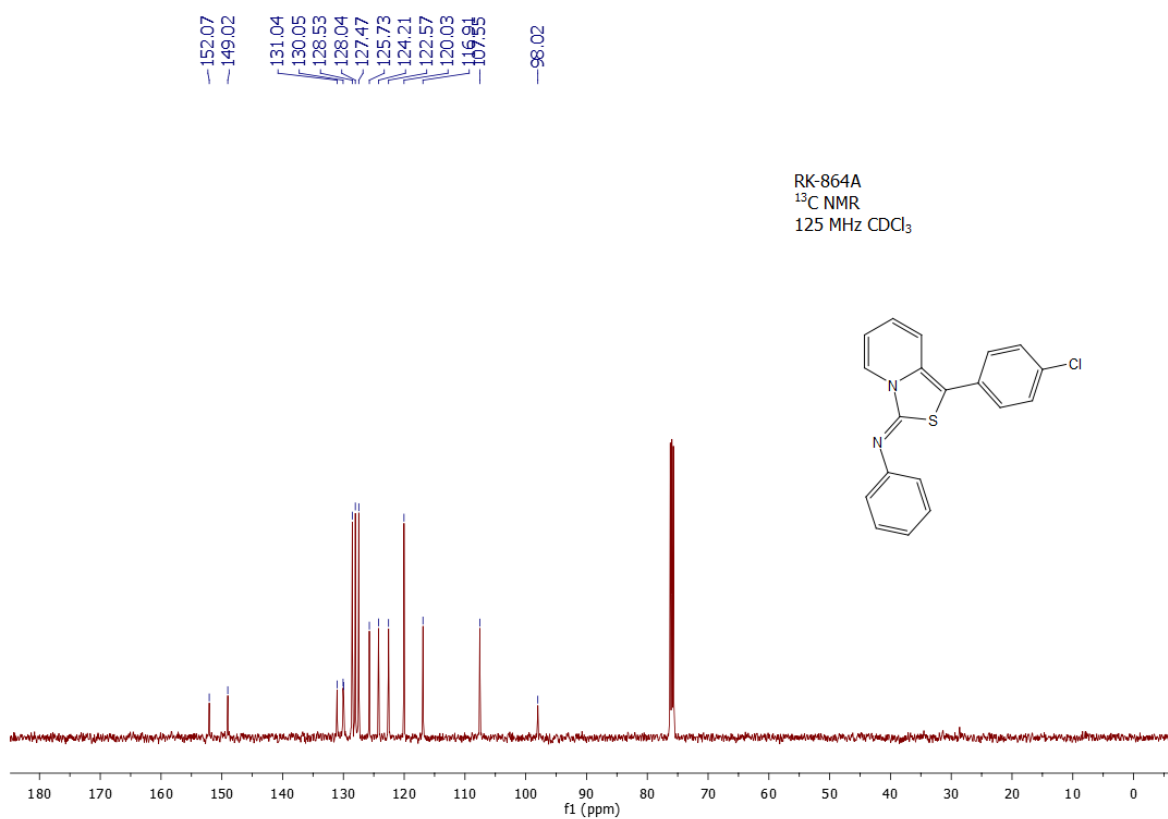
¹H NMR of 5h



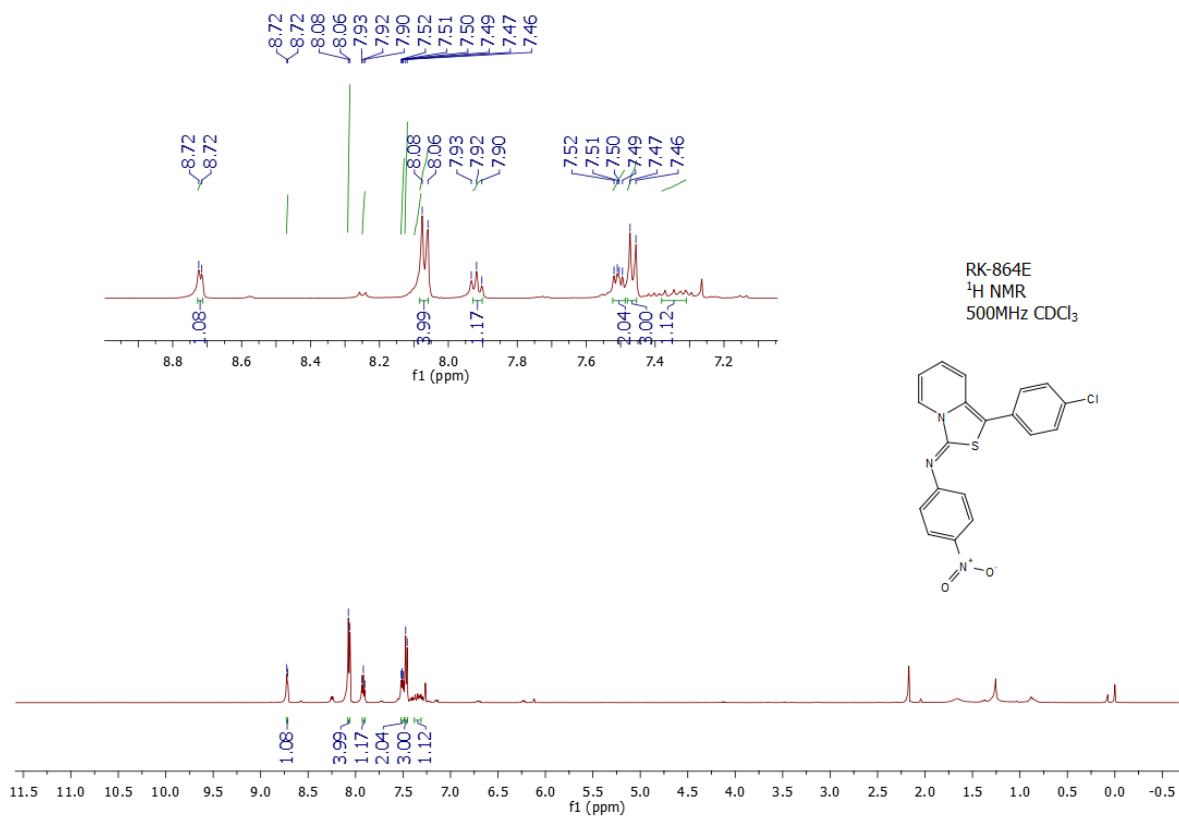
¹³C NMR of 5h



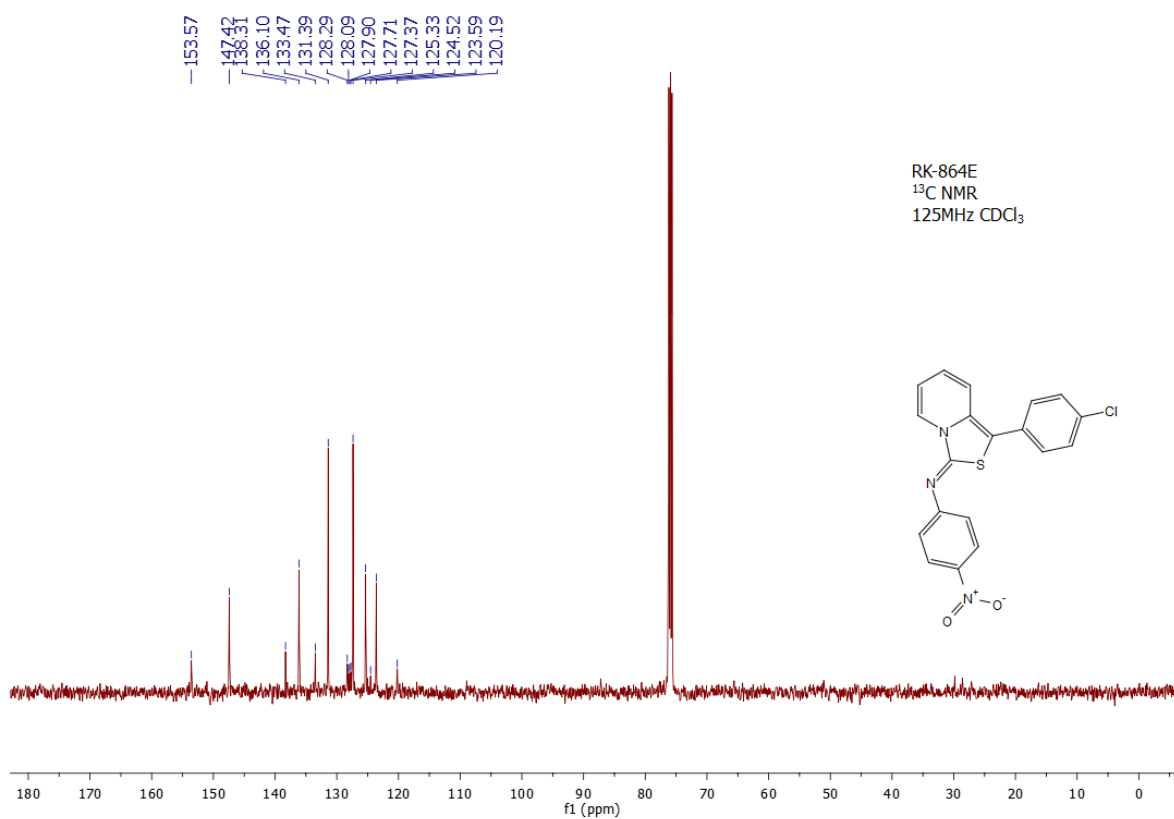
¹H NMR of **5i**



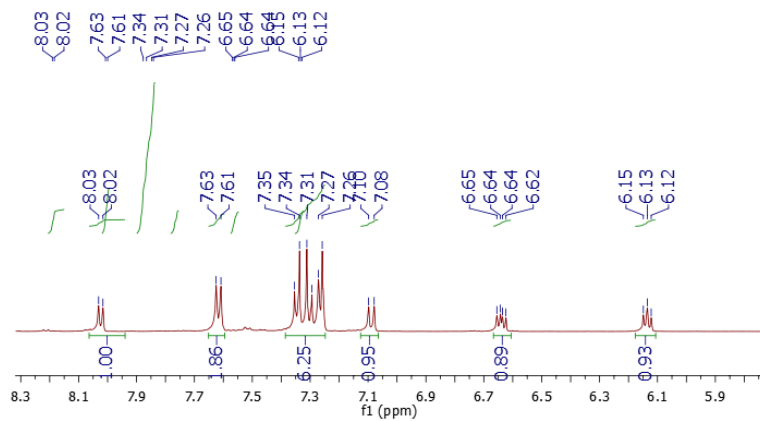
¹³C NMR of **5i**



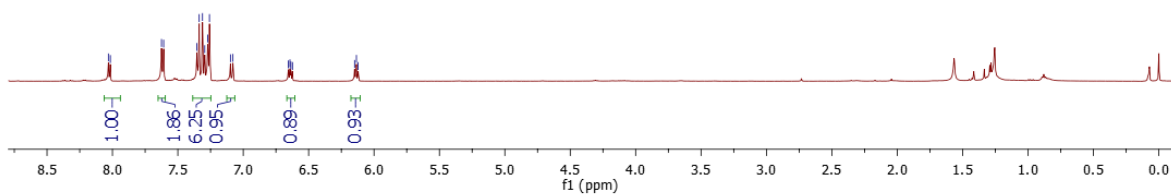
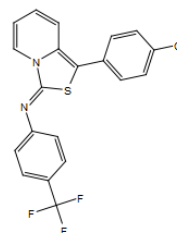
¹H NMR of **5j**



¹³C NMR of **5j**

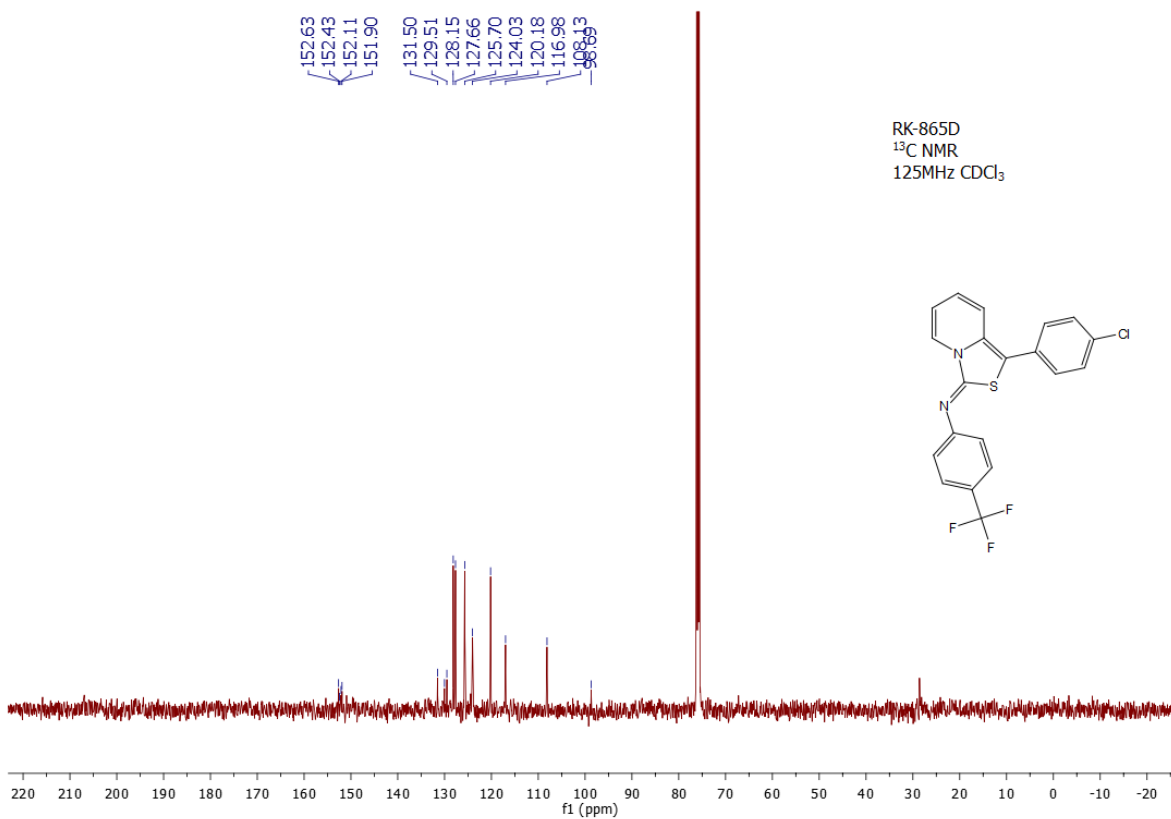
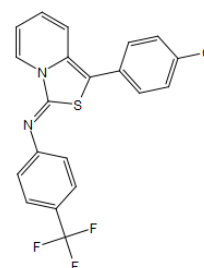


RK-865D
¹H NMR
 500MHz CDCl₃

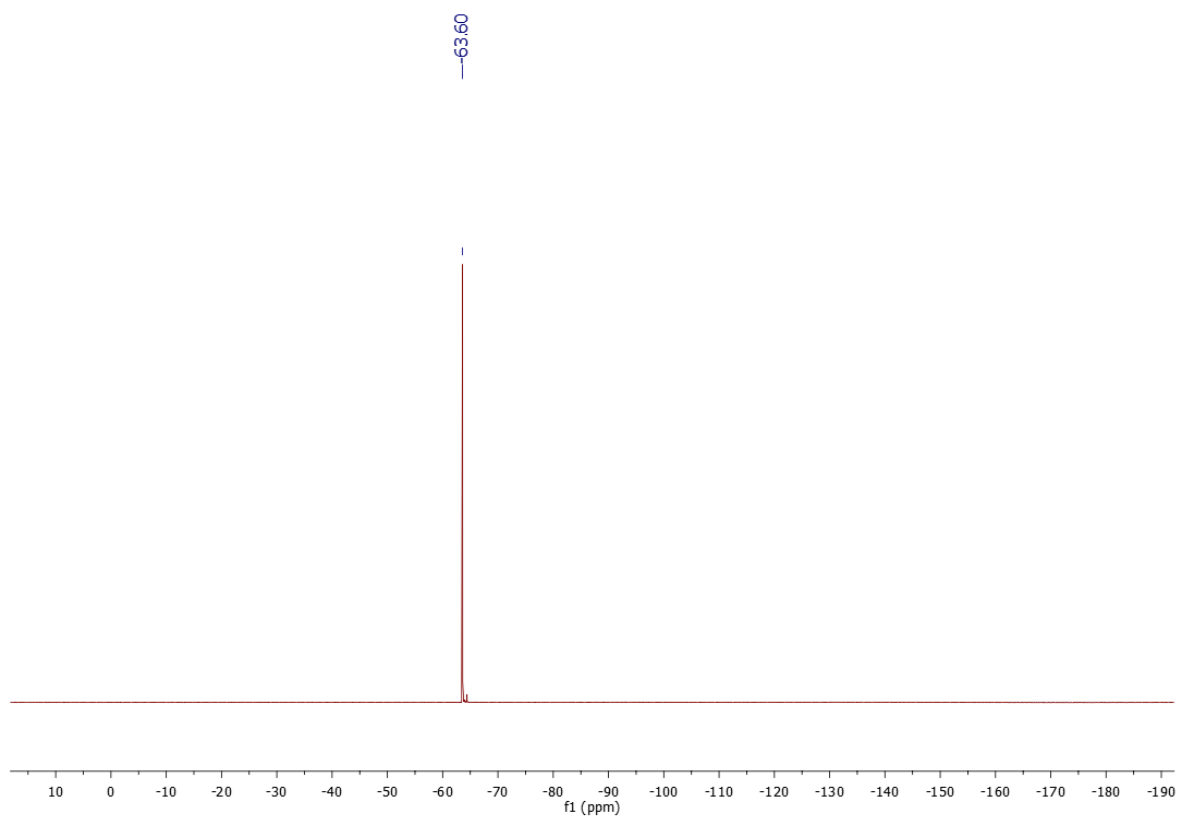


¹H NMR of **5k**

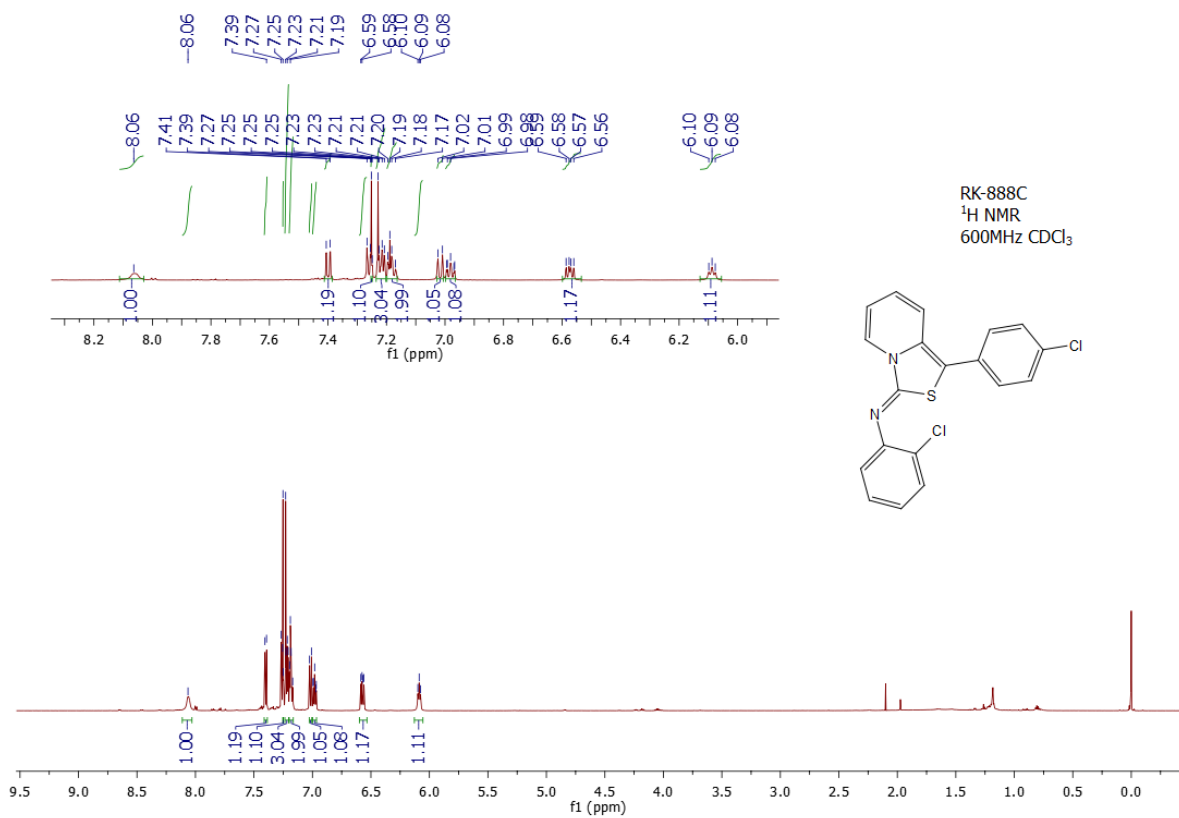
RK-865D
¹³C NMR
 125MHz CDCl₃



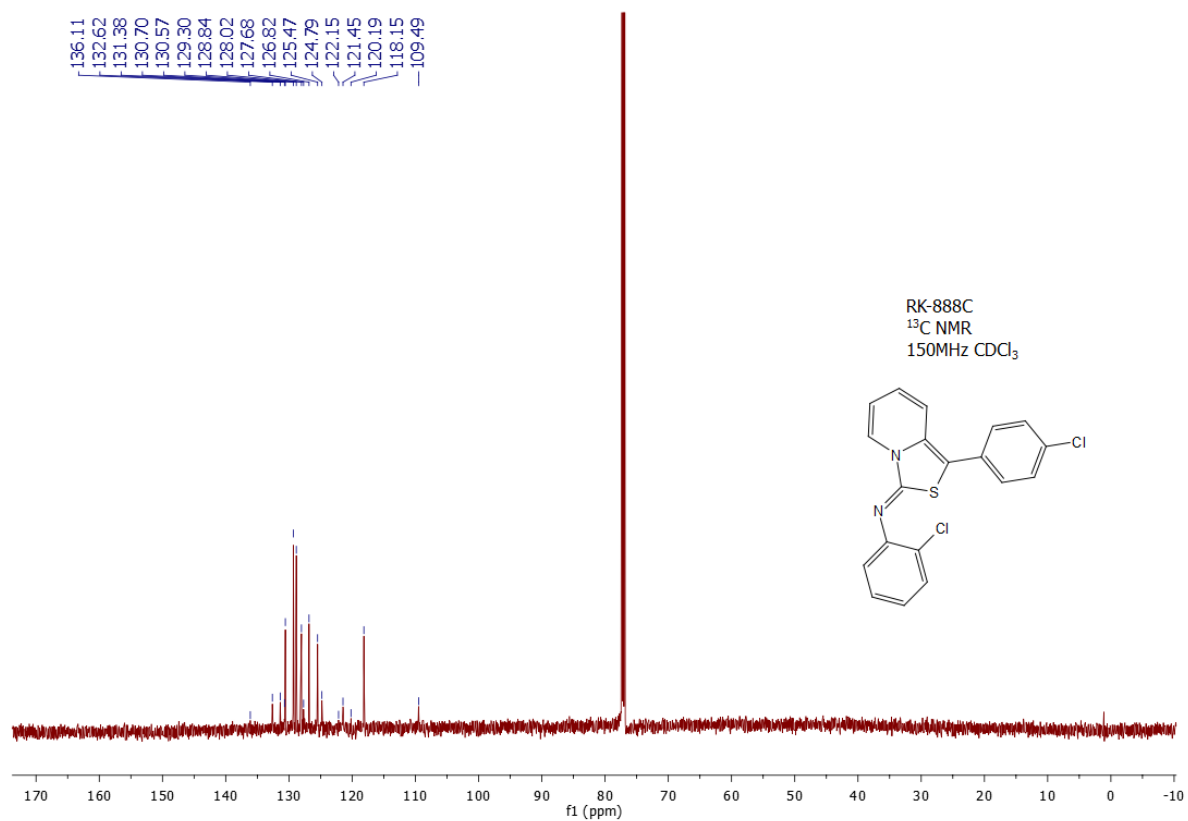
¹³C NMR of **5k**



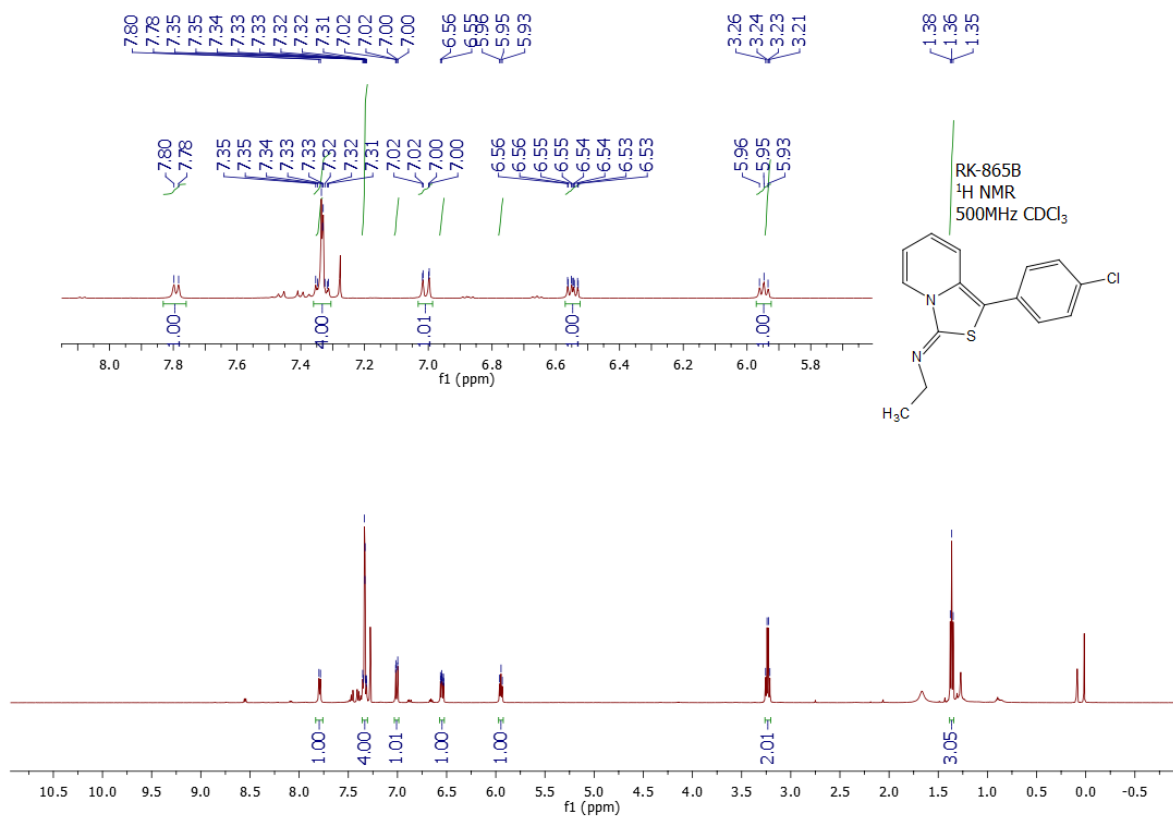
^{19}F NMR of **5k**



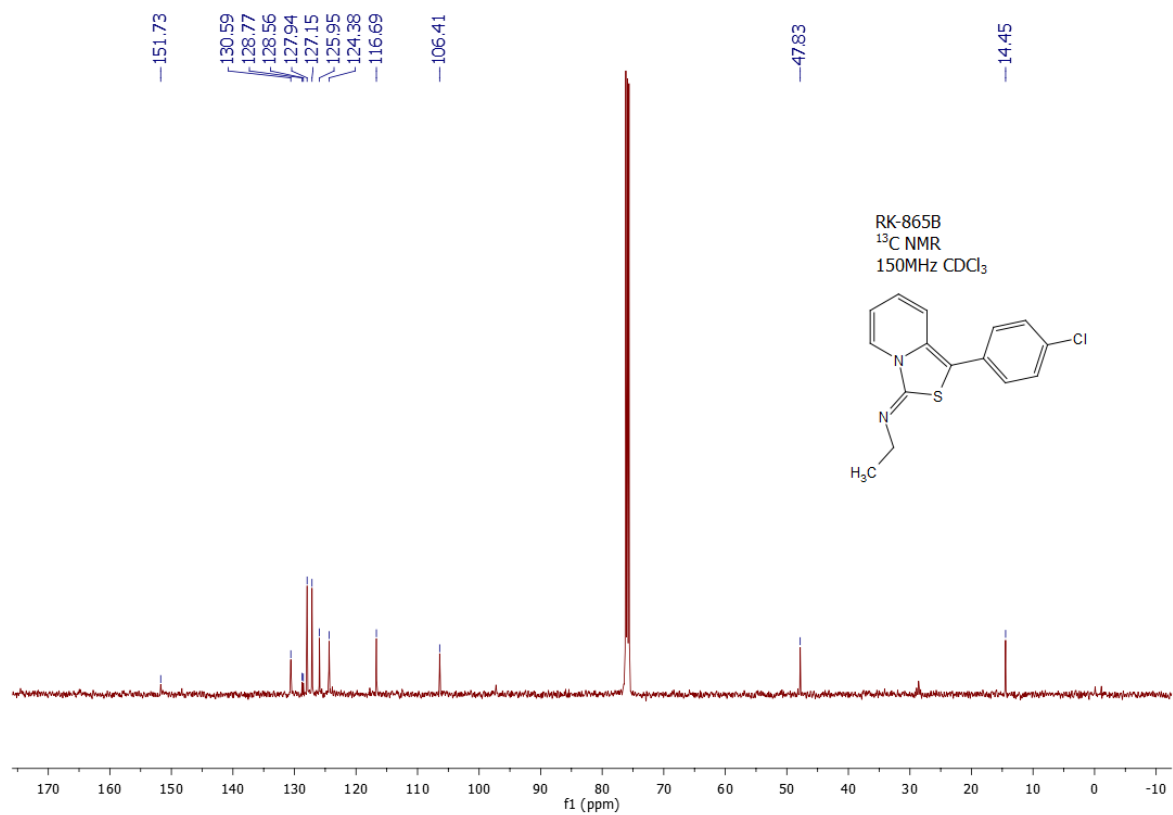
¹H NMR of **51**



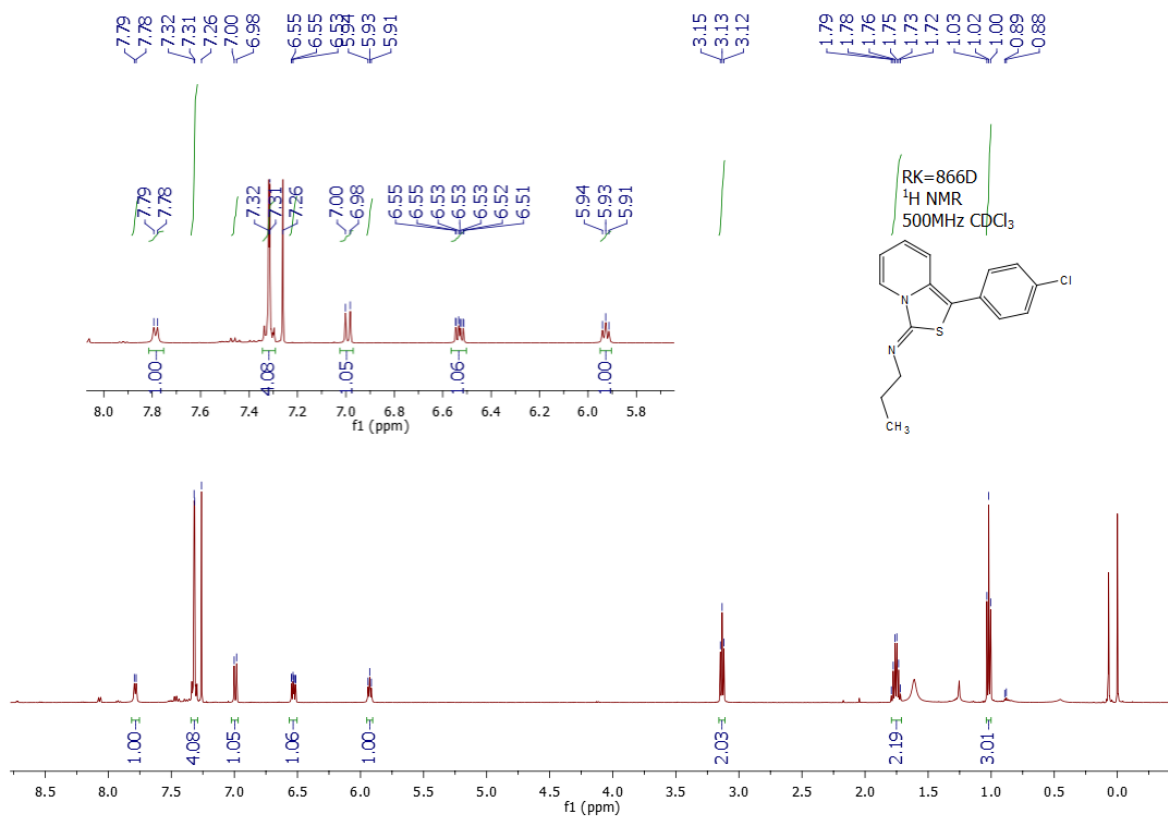
¹³C NMR of **51**



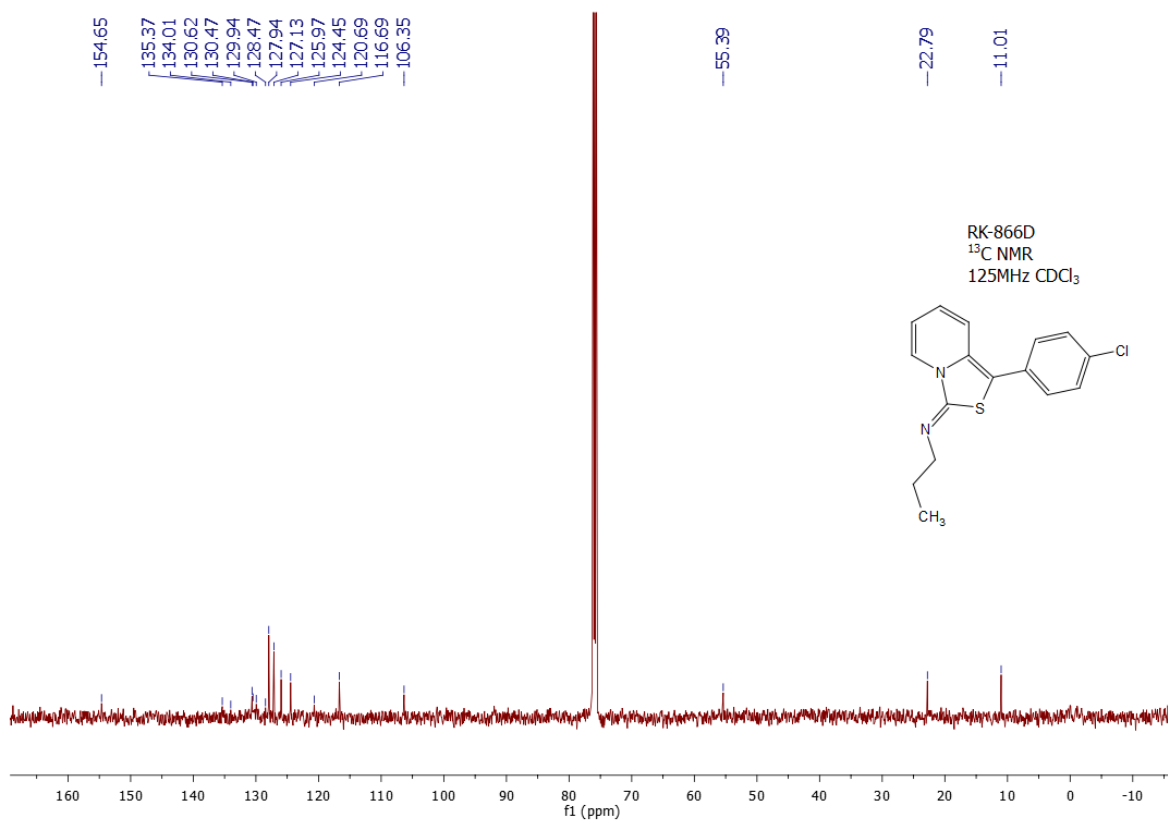
¹H NMR of 5m



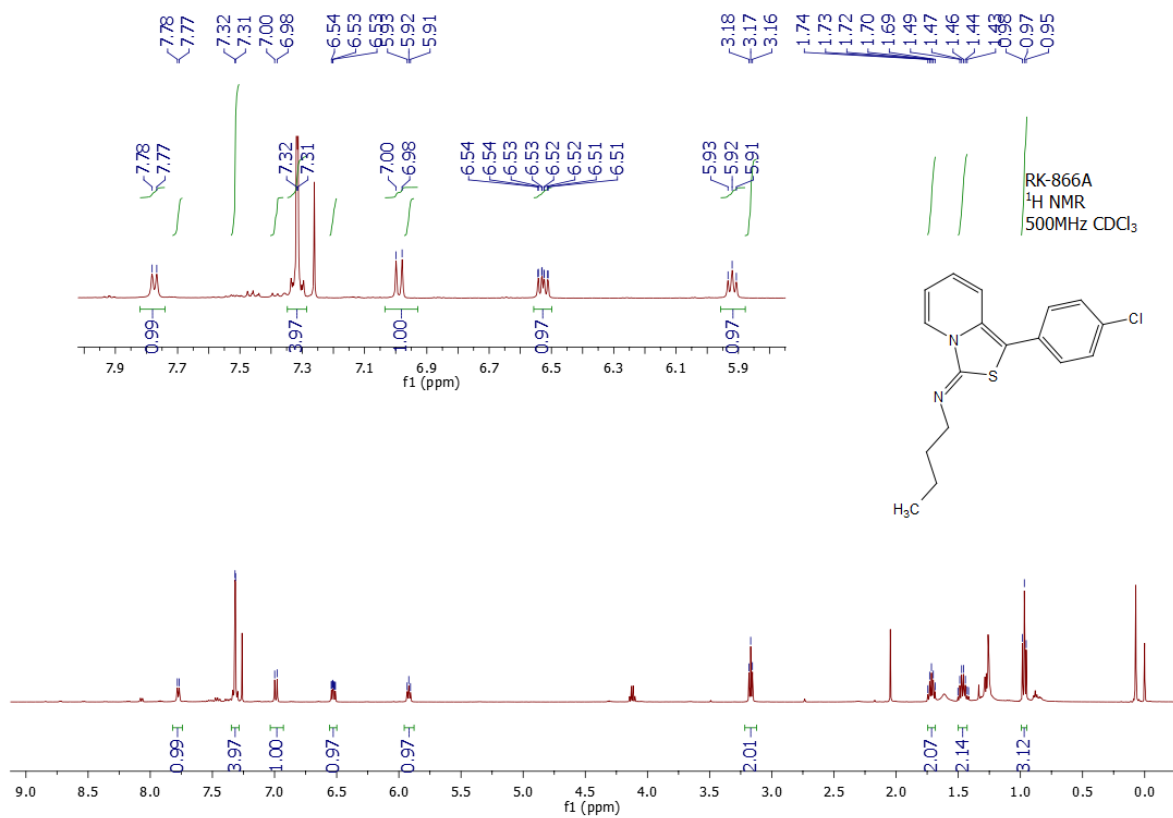
¹³C NMR of 5m



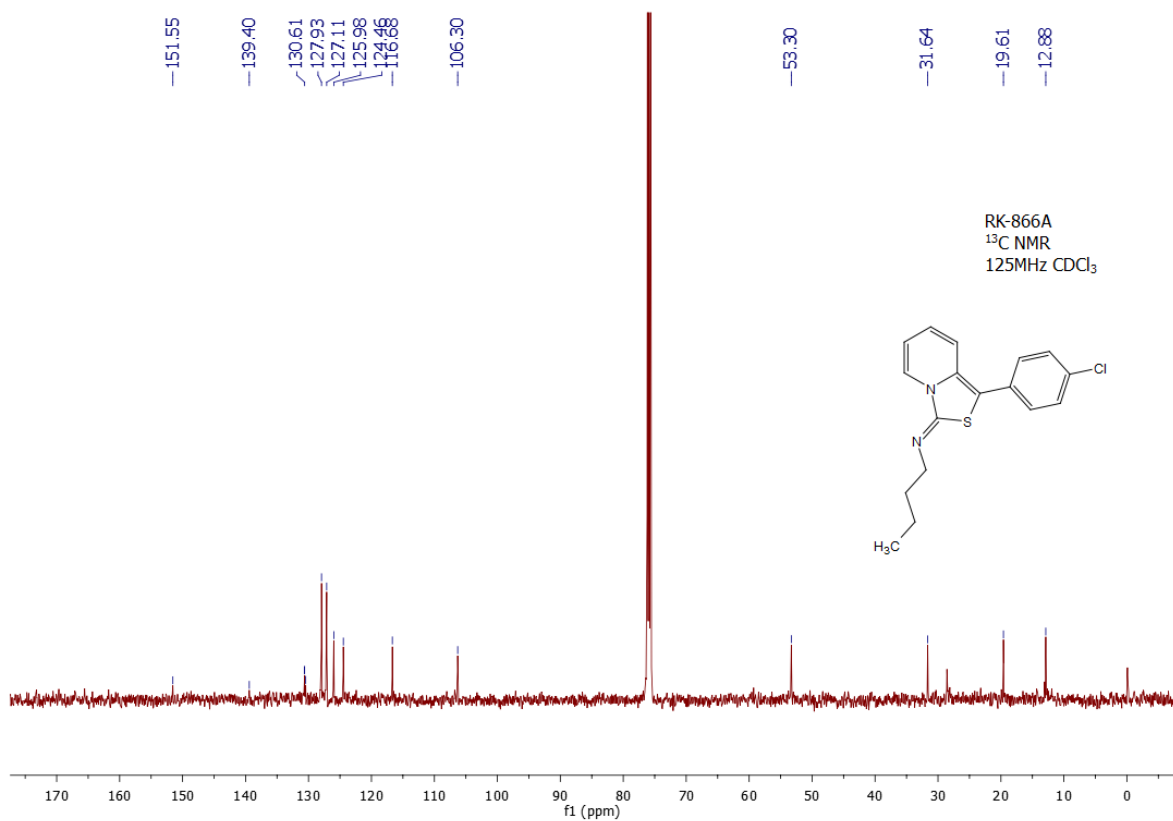
¹H NMR of **5n**



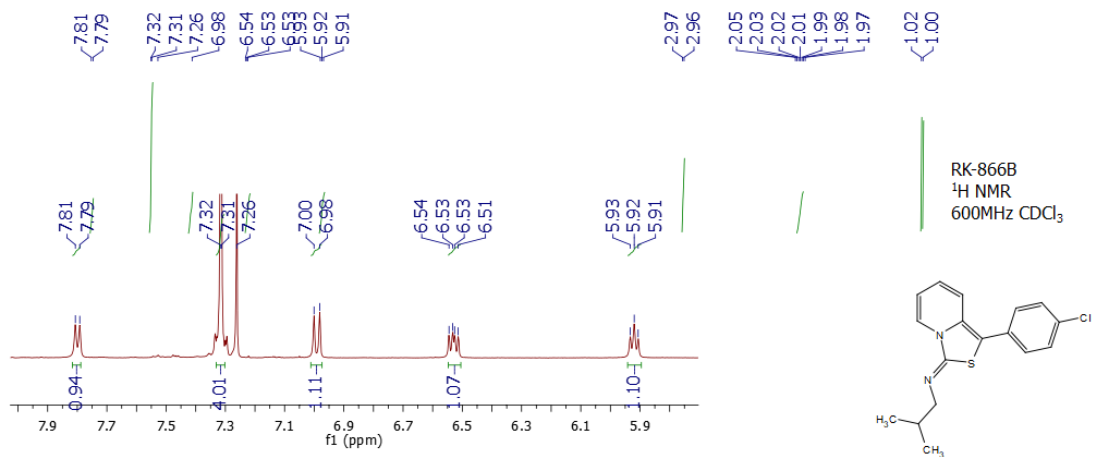
¹³C NMR of **5n**



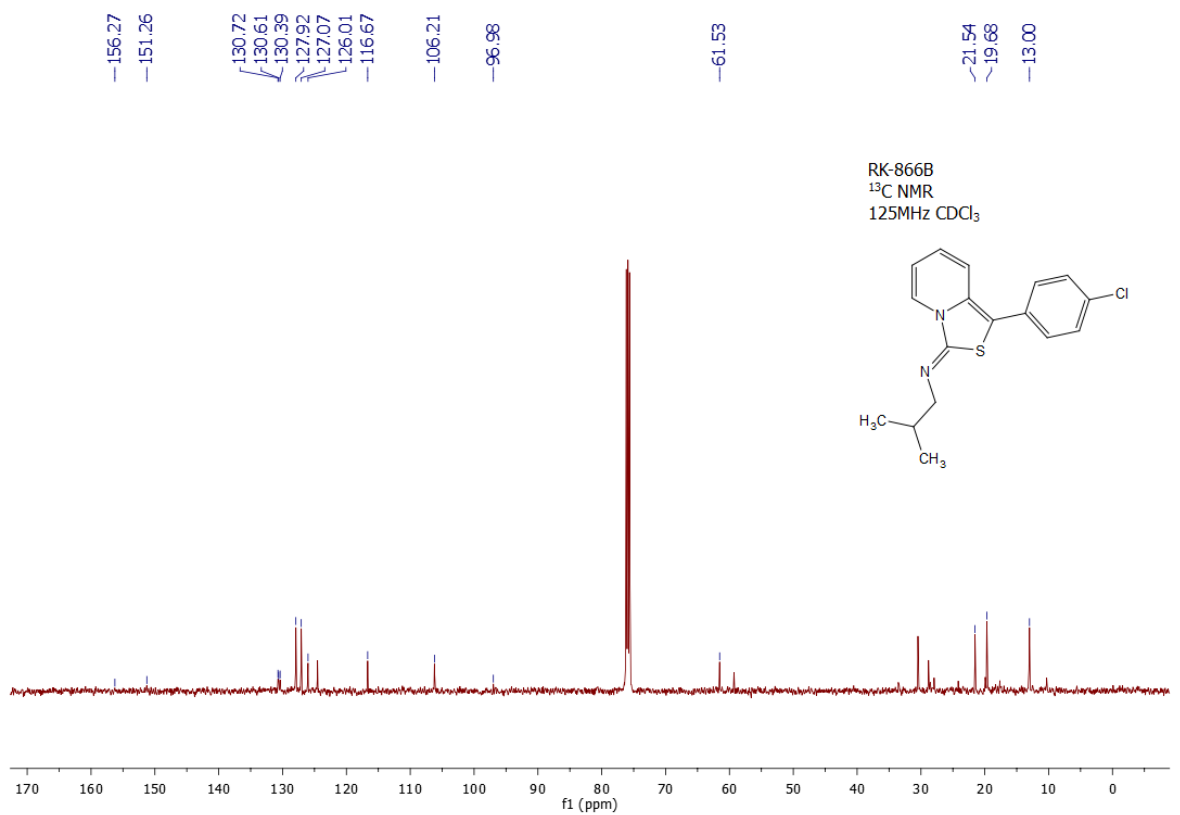
¹H NMR of **5o**



¹³C NMR of **5o**

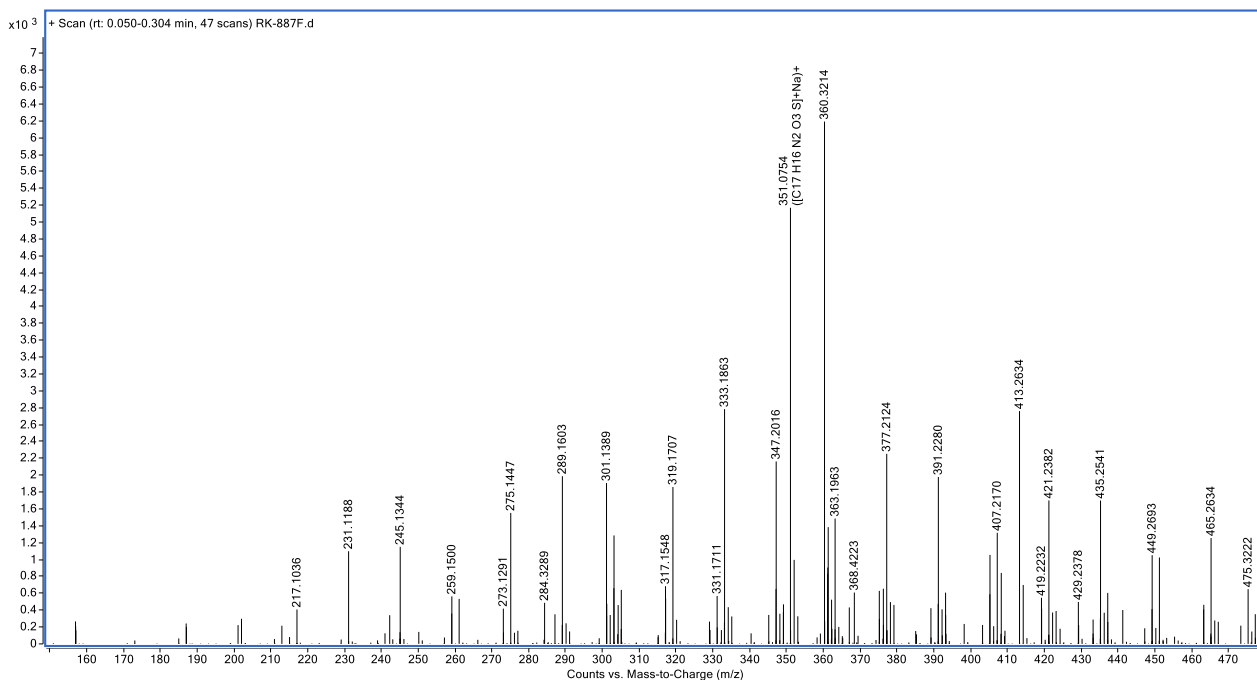


¹H NMR of **5p**

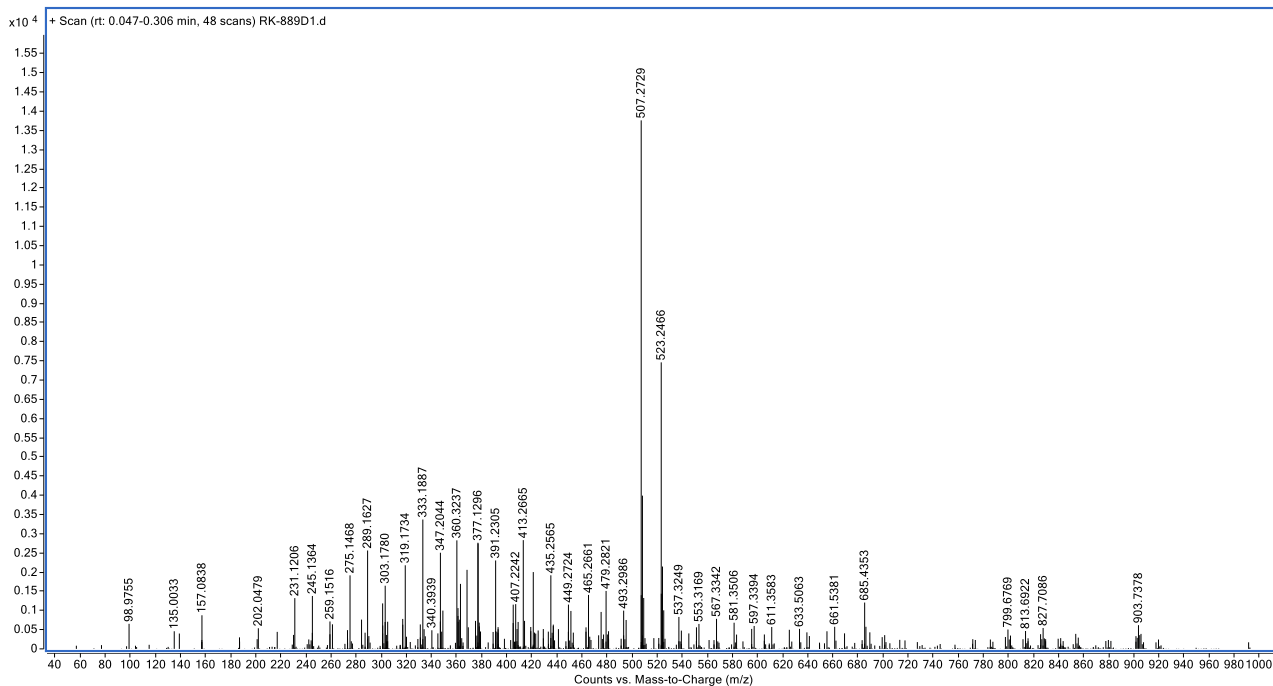


¹³C NMR of **5p**

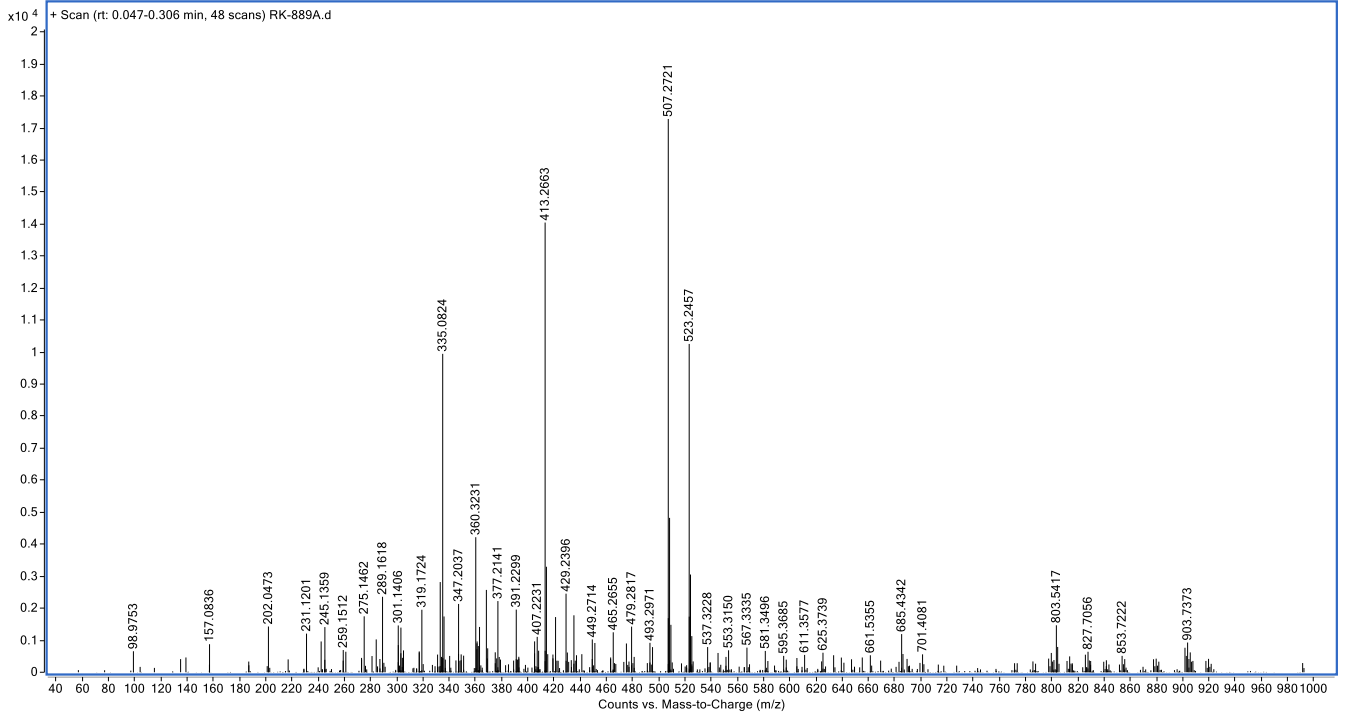
Copy of HRMS spectra of compounds



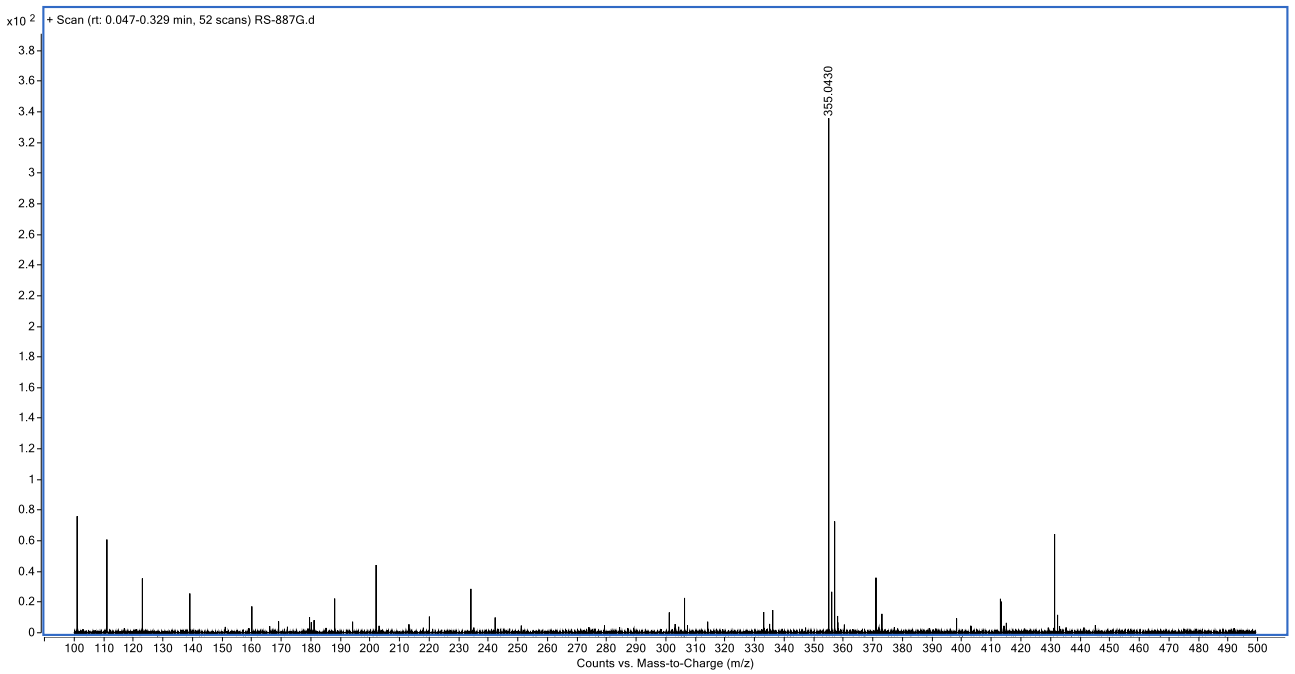
3b



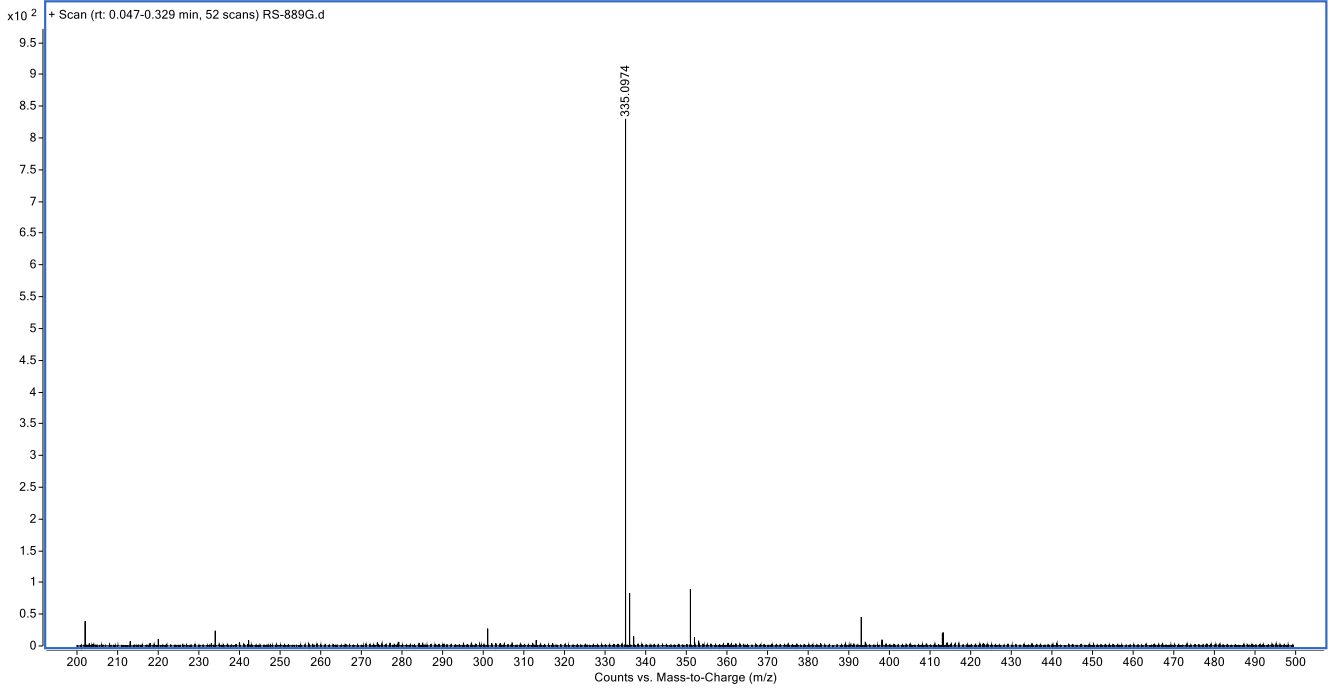
3c



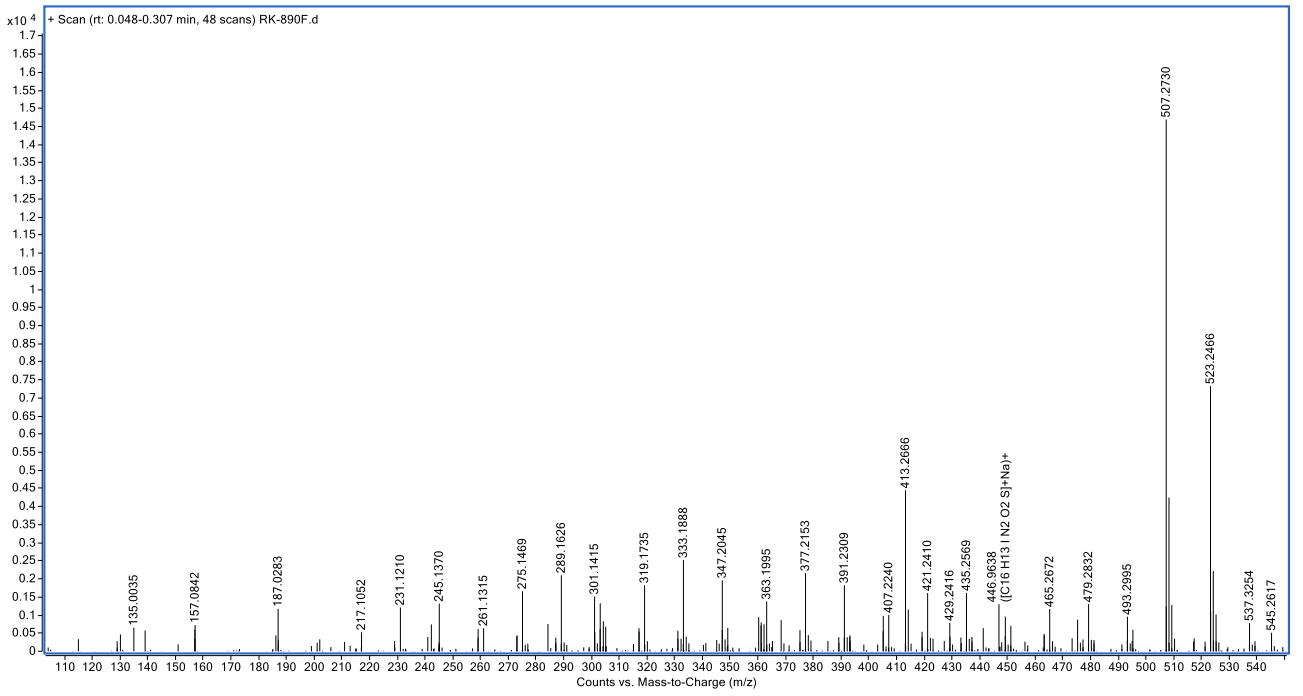
3d



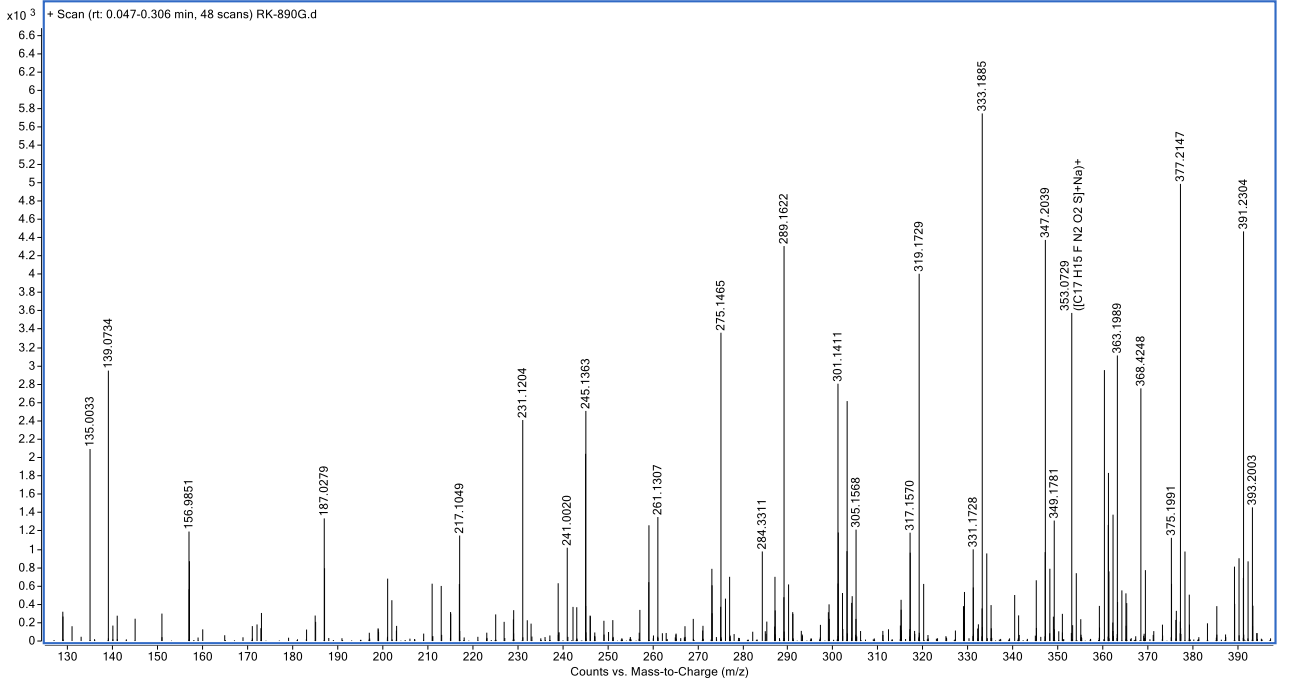
3e



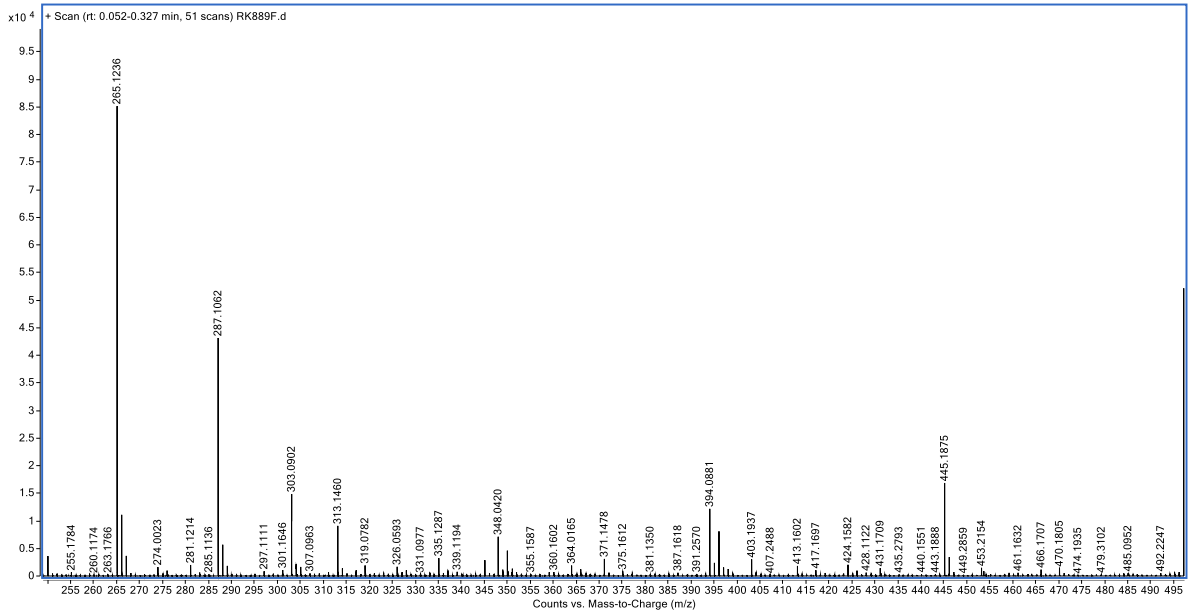
3f



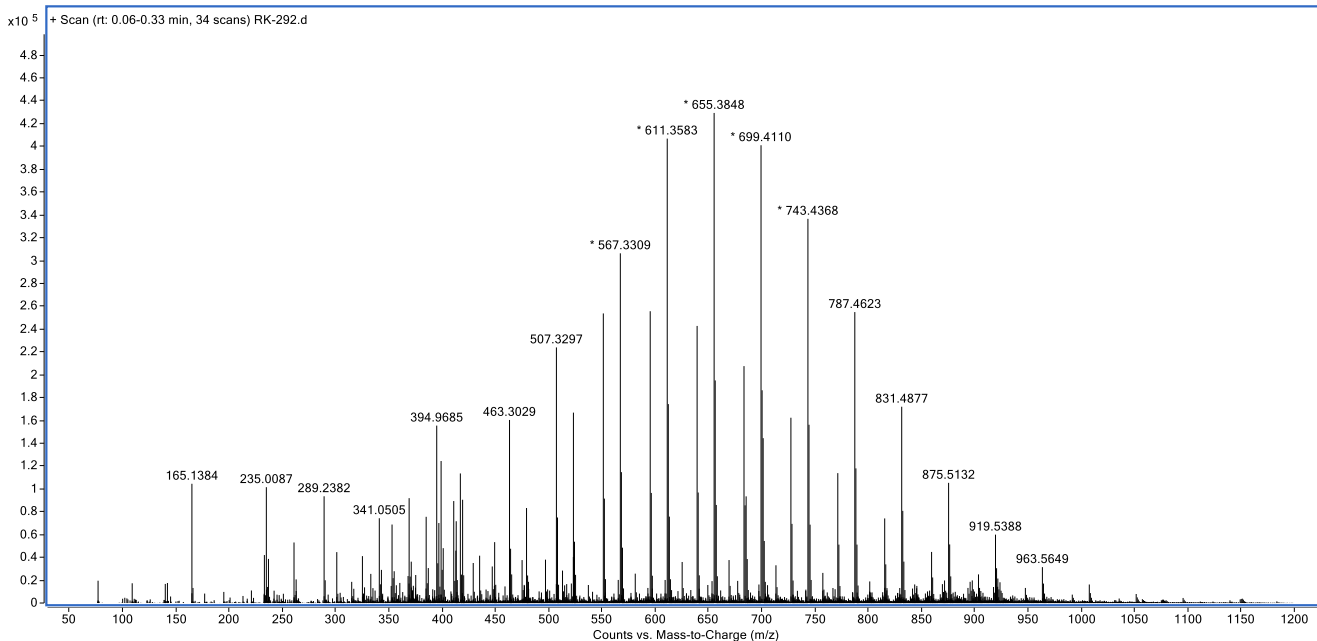
3g



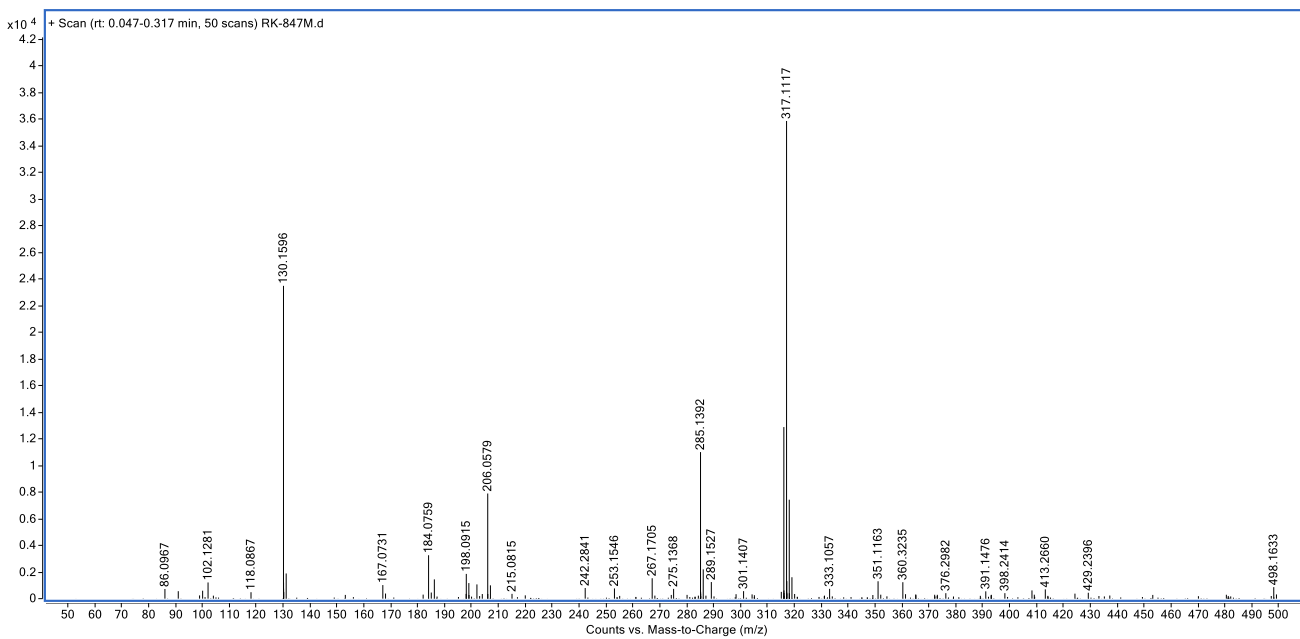
3h



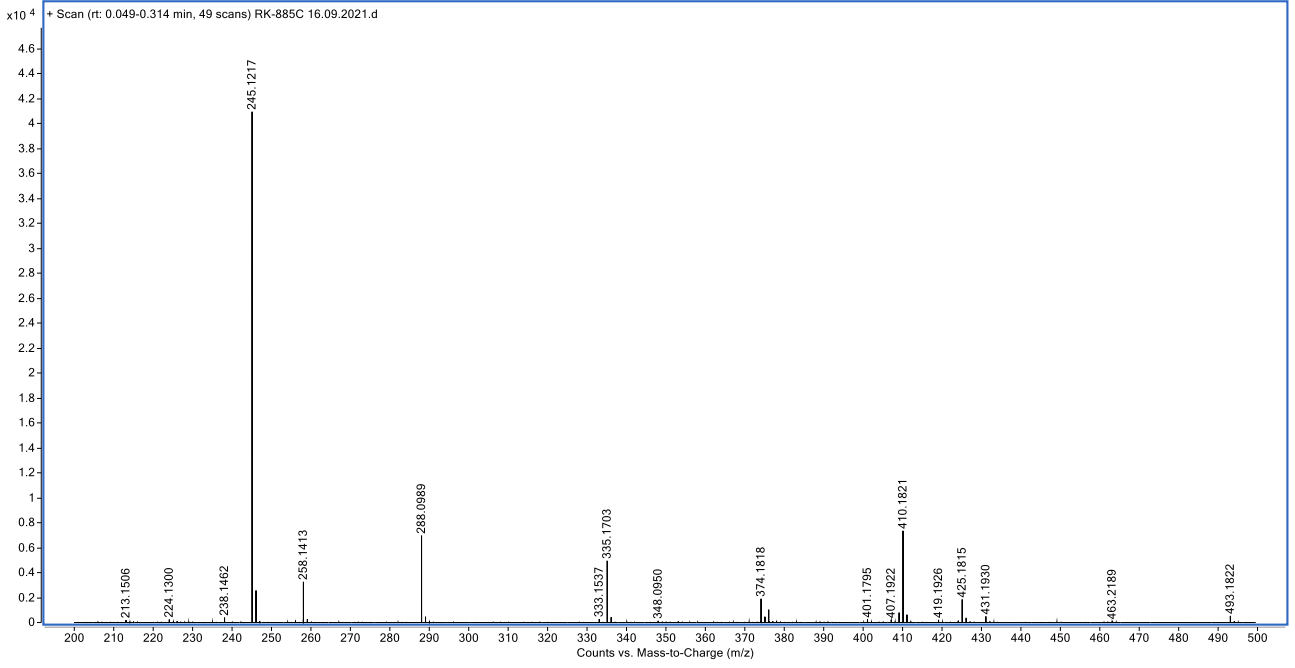
3i



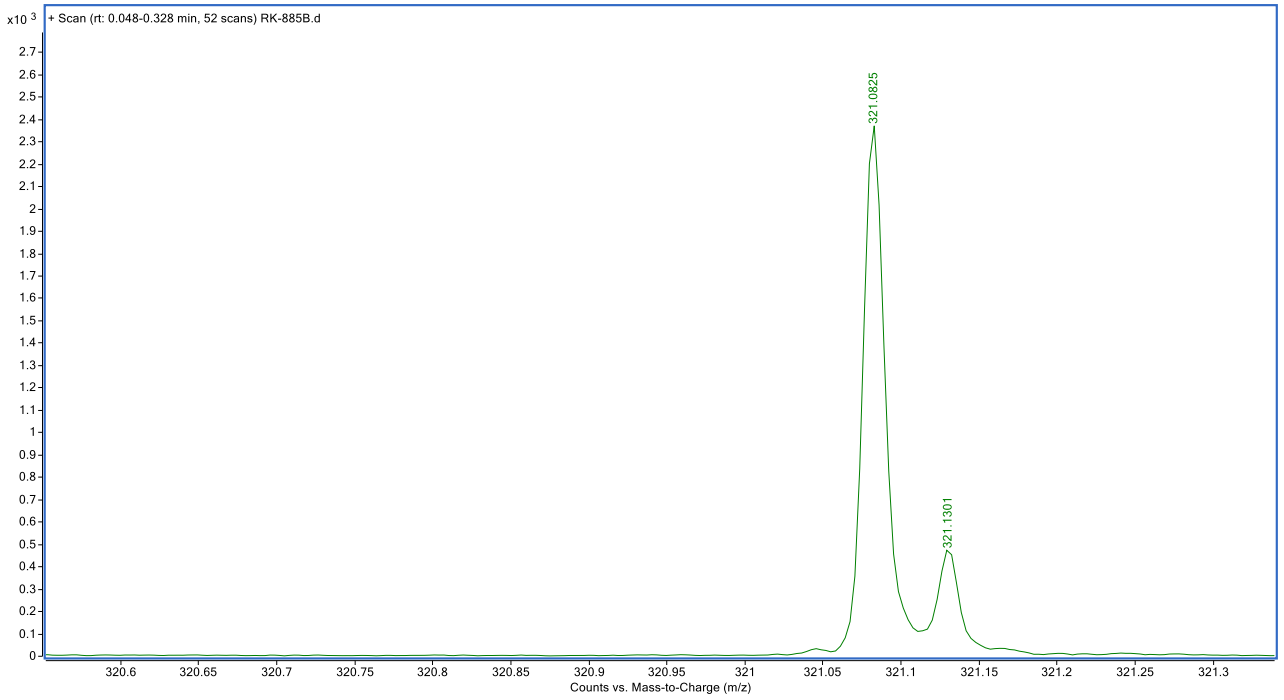
5a



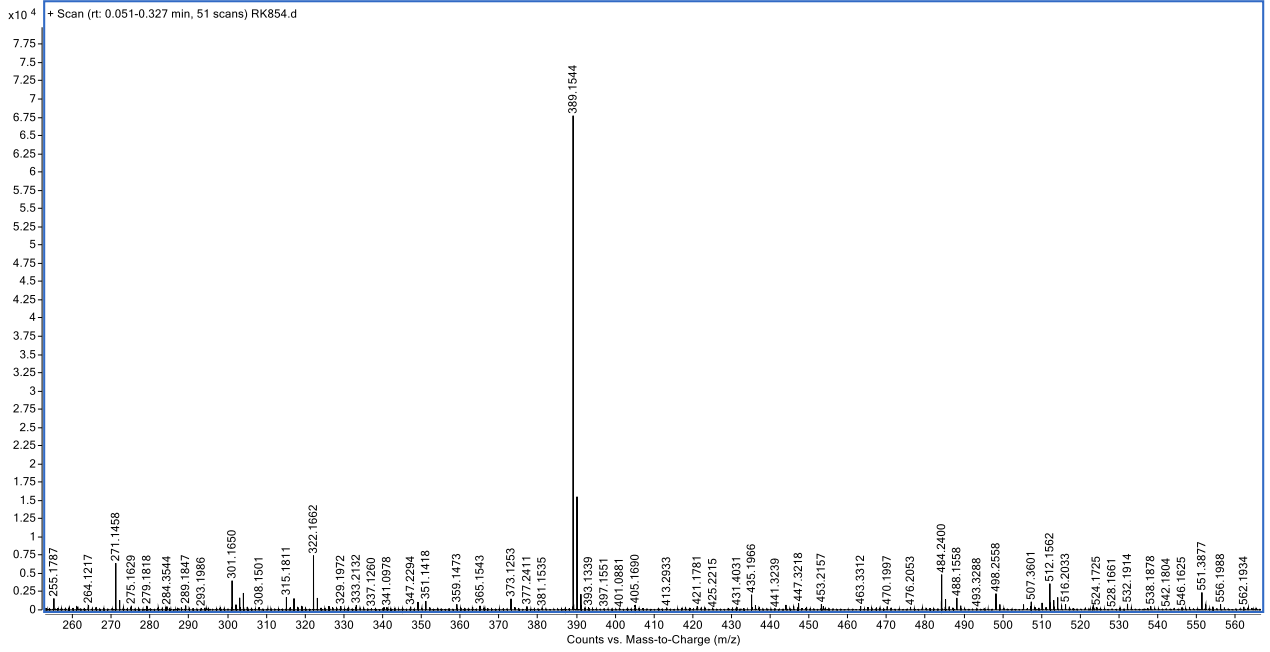
5b



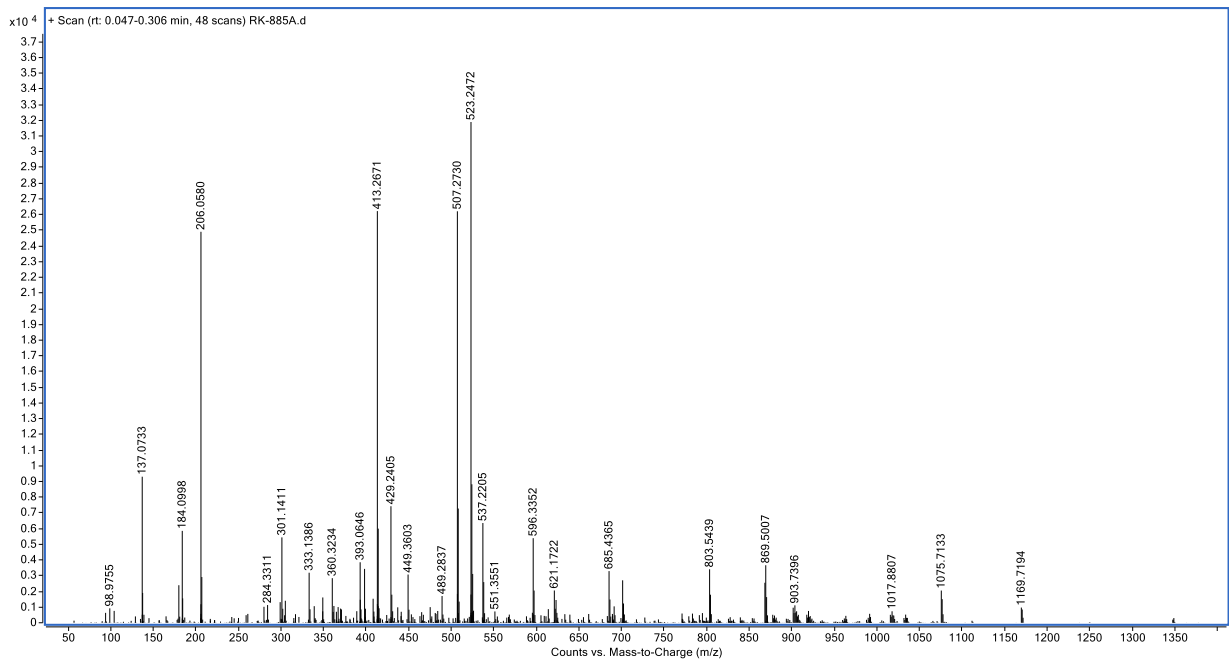
5c



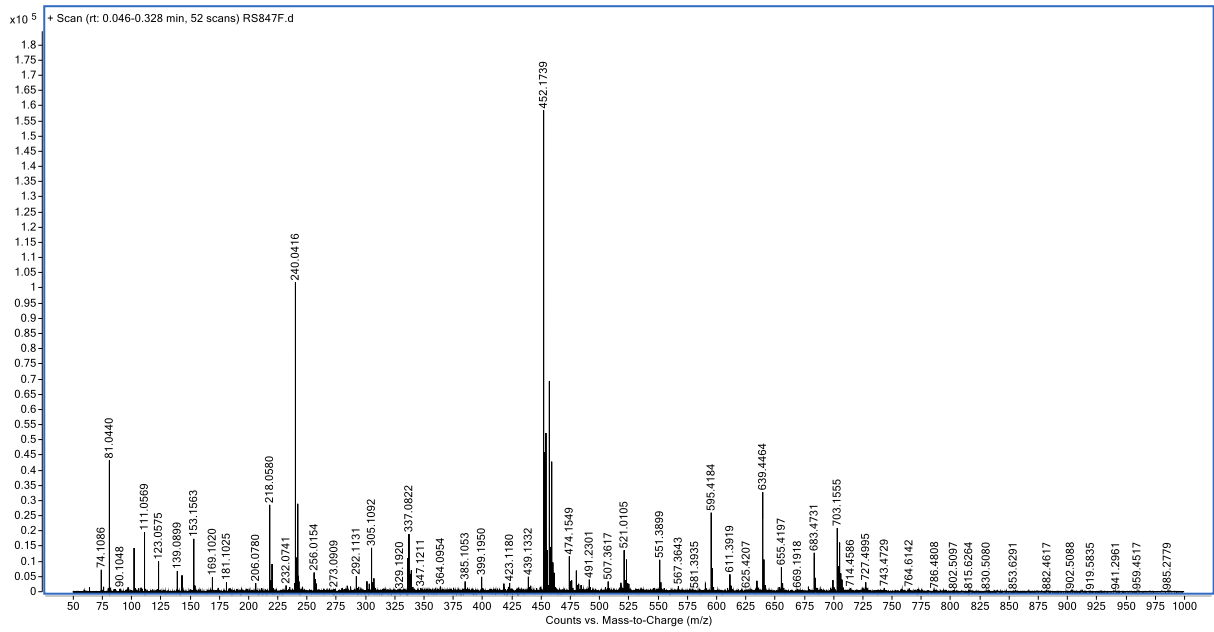
5d



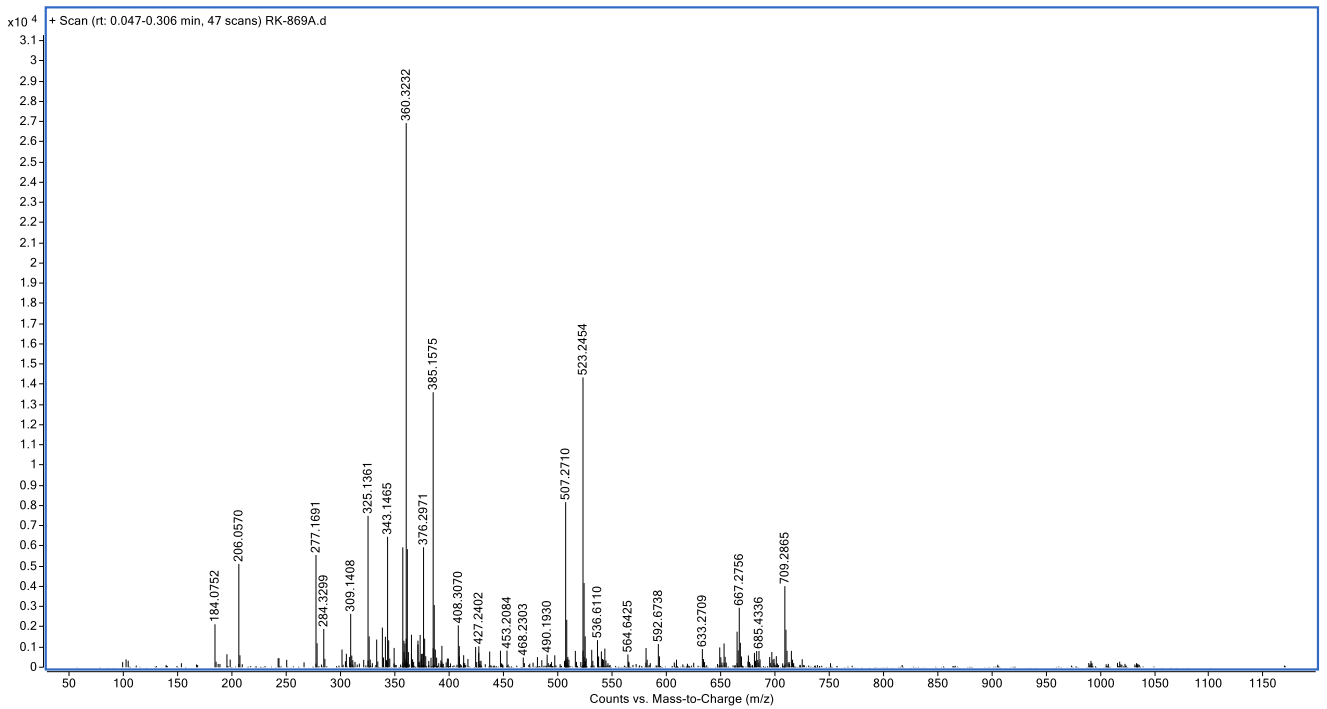
5e



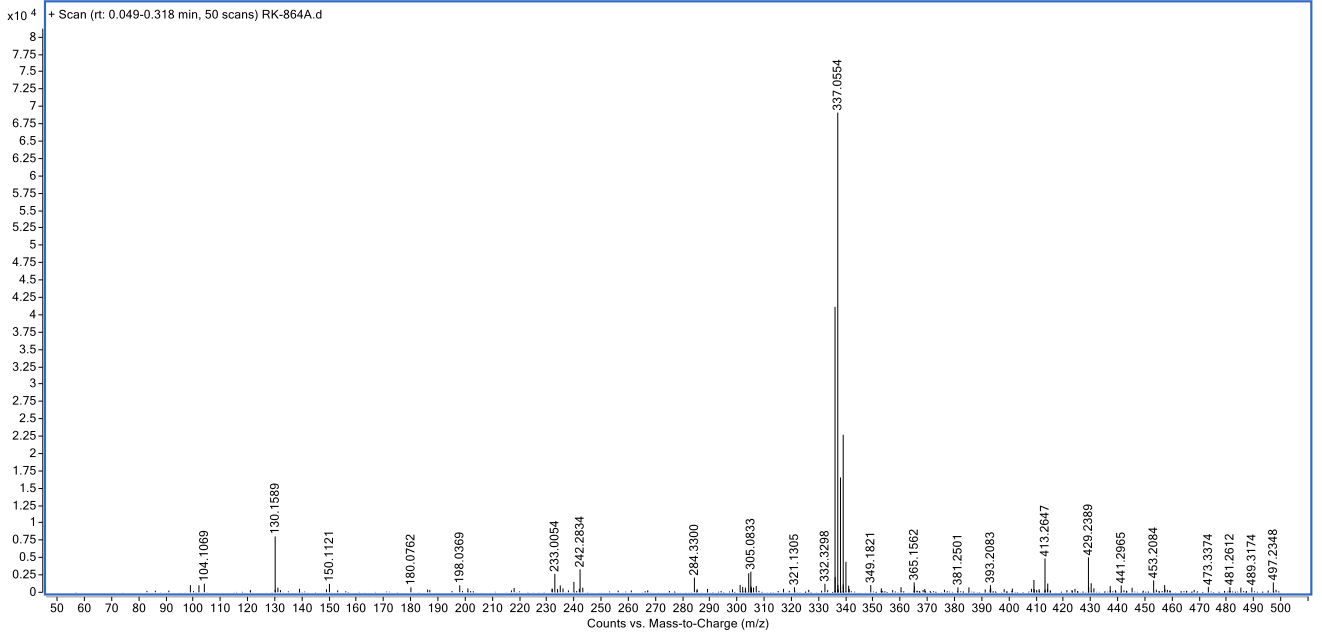
5f



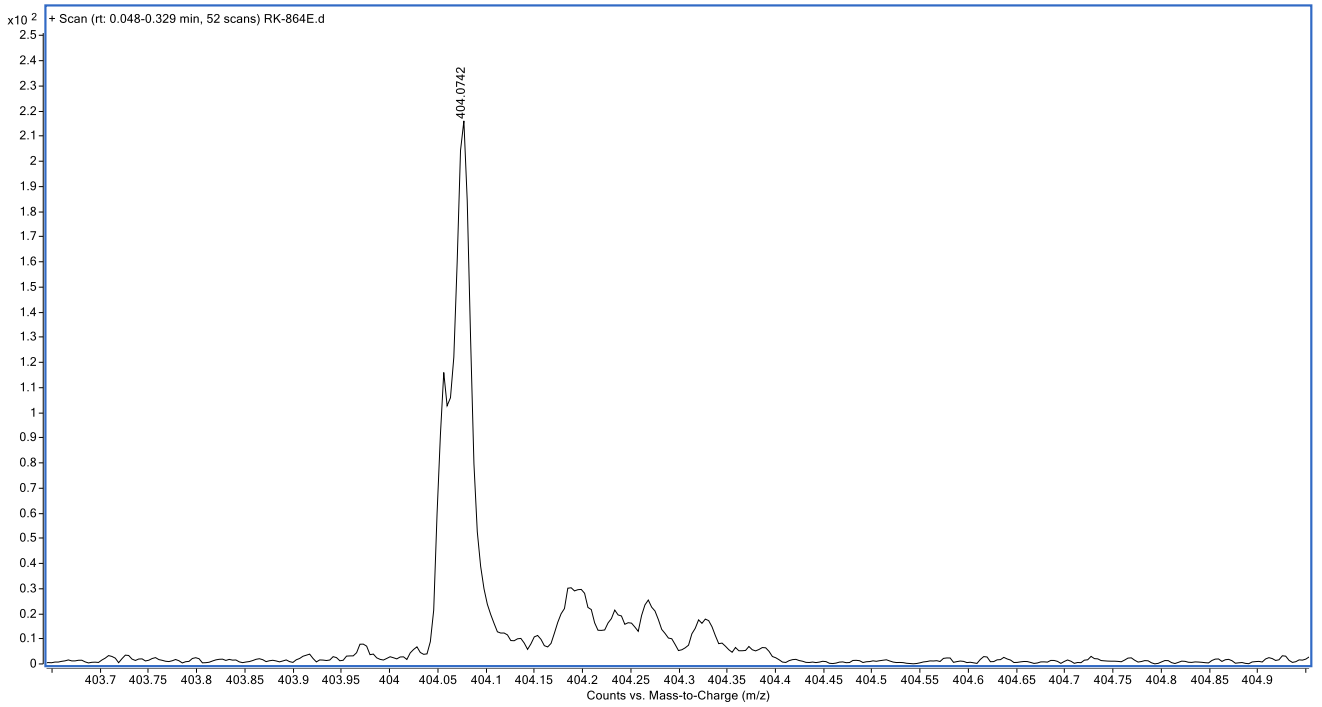
5g



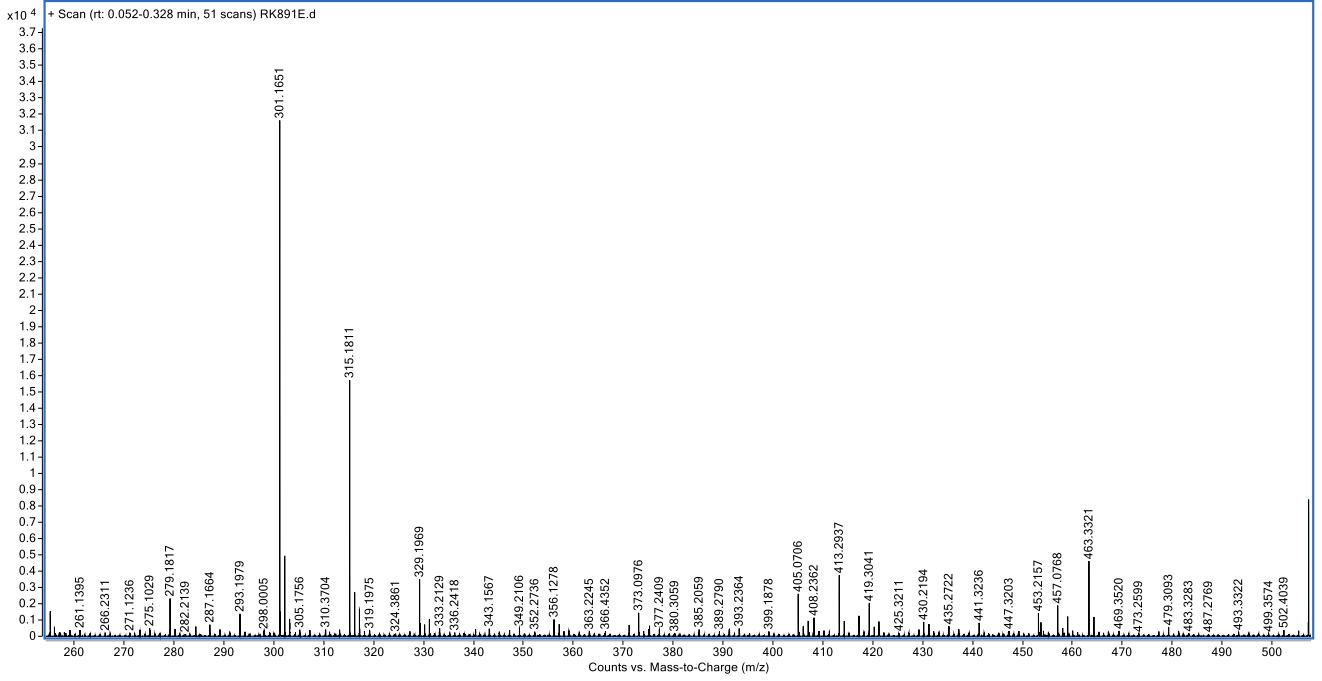
5h



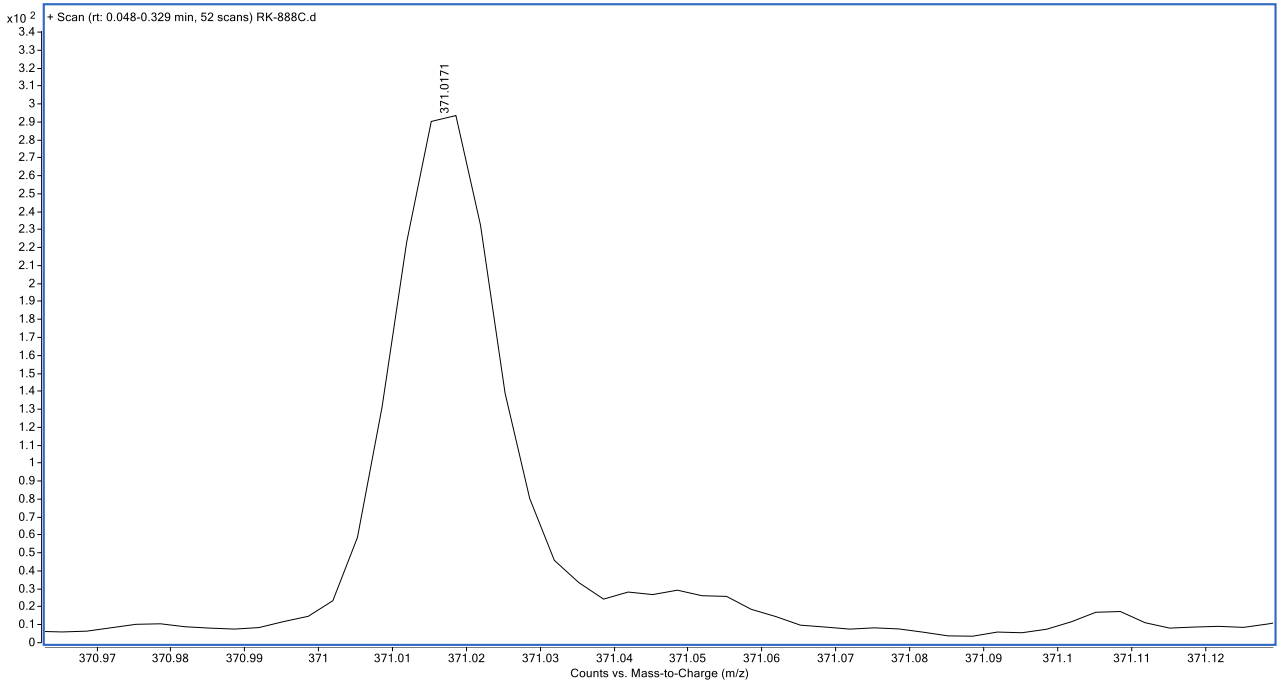
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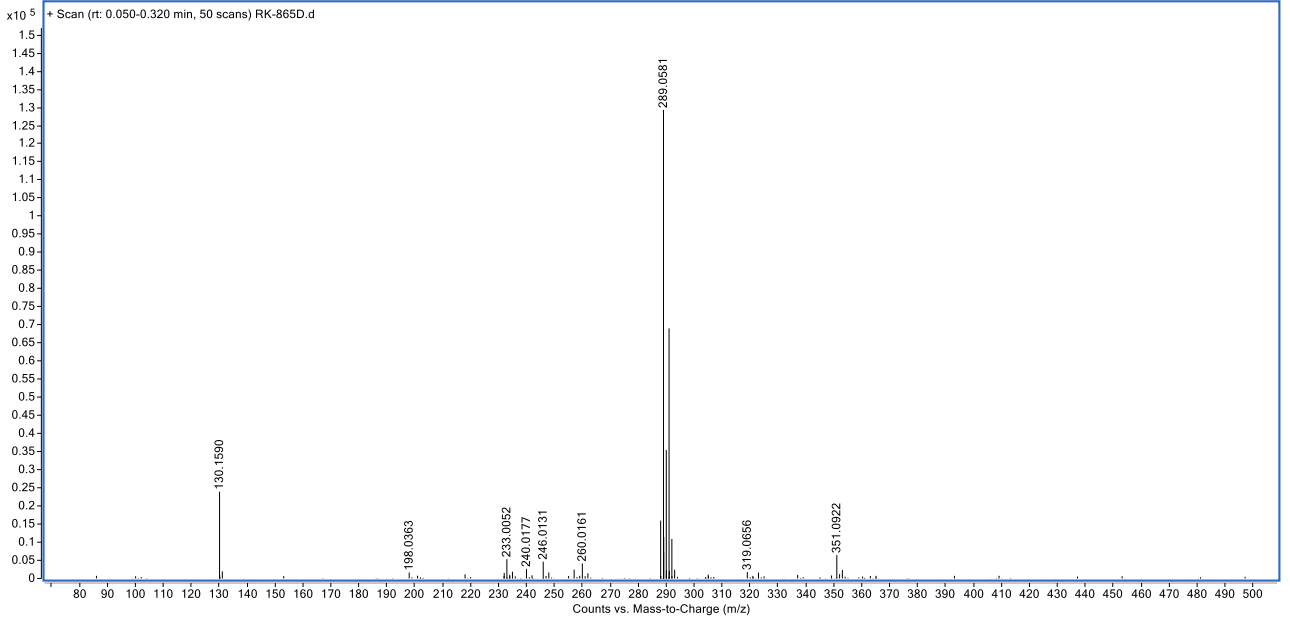
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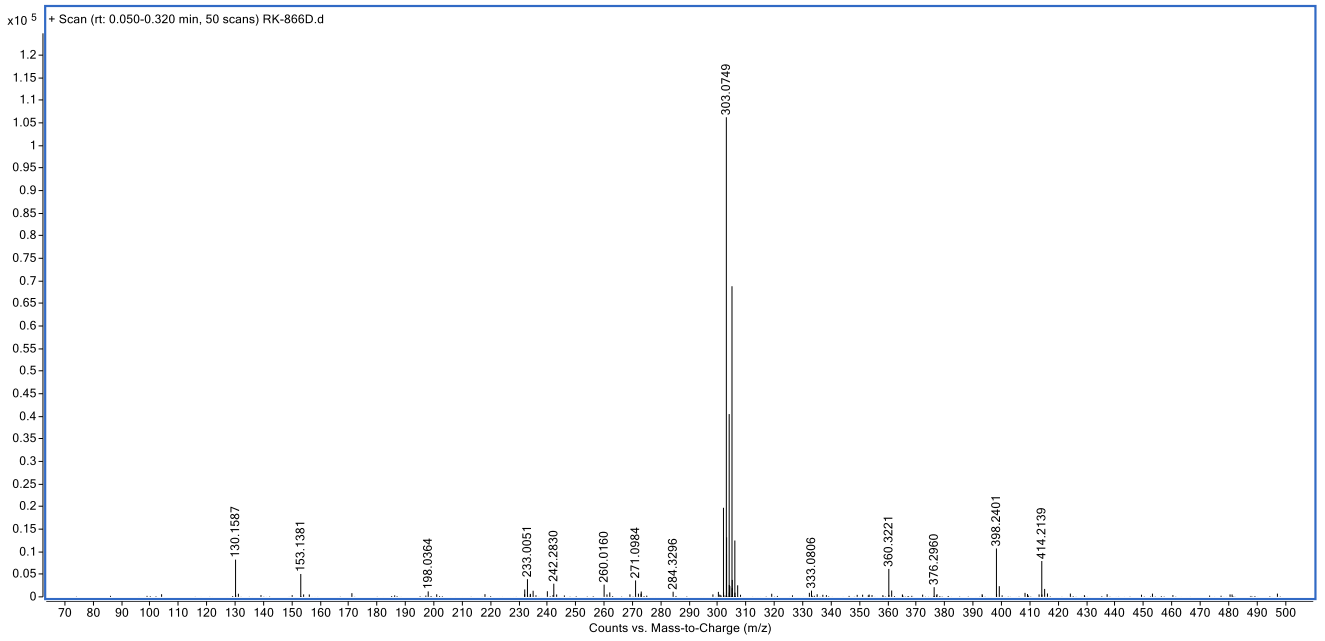
5k



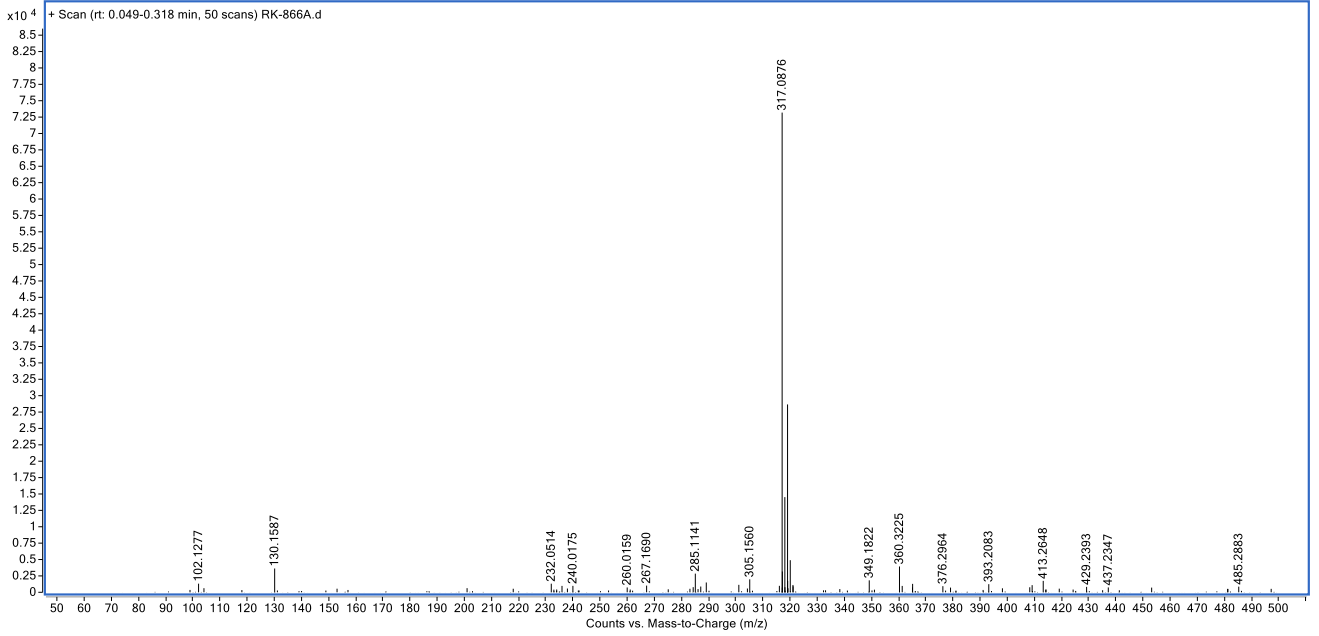
51



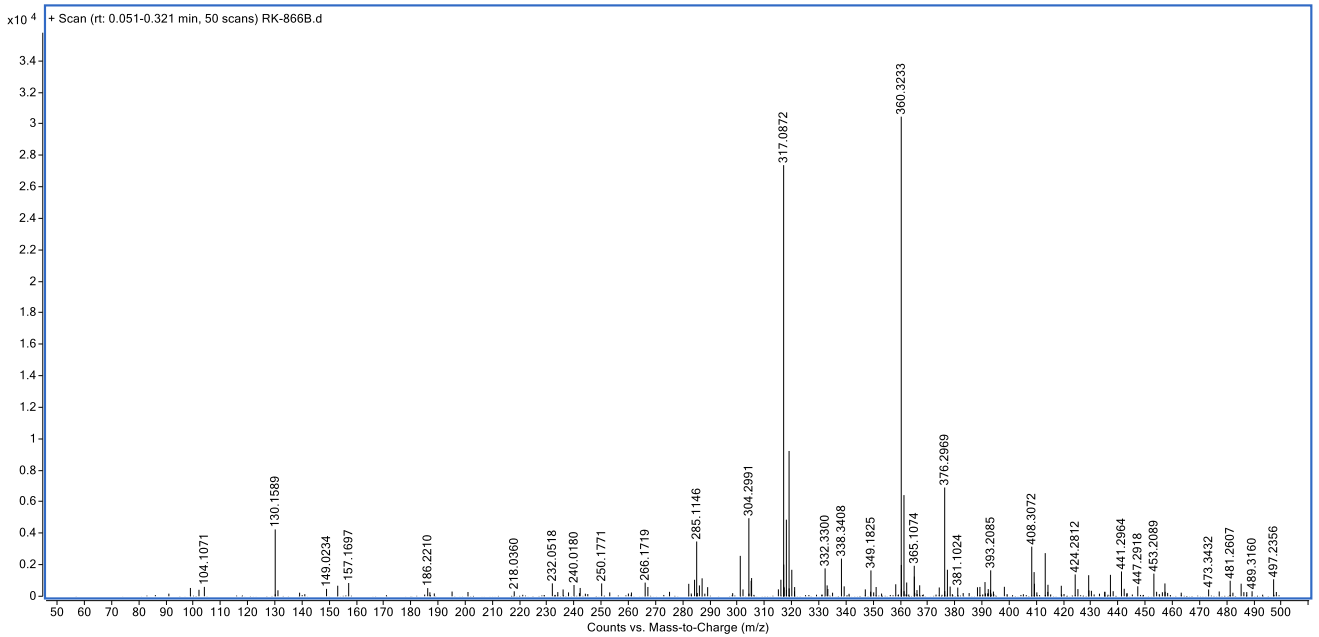
5m



5n



5o



5p