Synthesis of 4-Styrylquinolines via Direct Oxidative C3-Alkenylation of Anthranils under Pd(II) Catalysis

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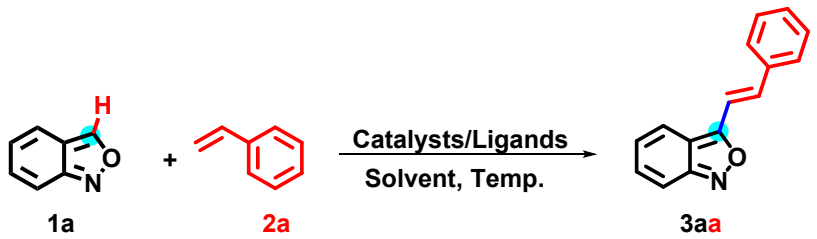
EXPERIMENTAL SECTION

General Information

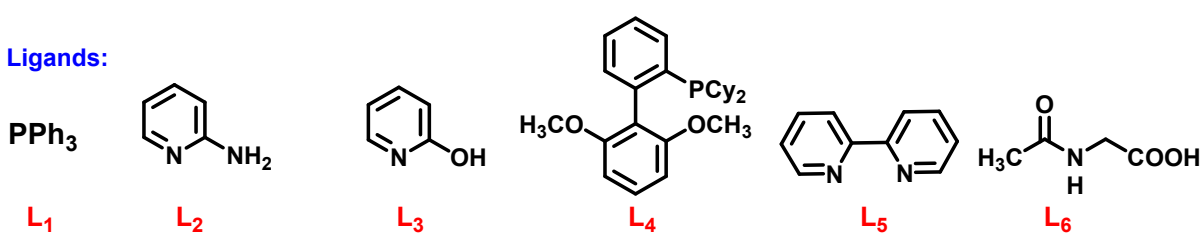
All reagents were purchased from Sigma Aldrich, Alfa Aesar, TCI, and local vendors and were used without further purification. All experiments were carried out in pressure glass sealed tube purchased from local vendors. All the solvents used for the reaction were purchased from a local vendor and used as received. The product purification by column chromatography was accomplished using silica gel 100-200 mesh. Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ^{1}H, ^{13}C NMR spectra were recorded on Avance III, and Bruker at 400 MHz, 100 MHz and 376 MHz spectrometers respectively using $CDCl_3$. In the experimental section, the ^{1}H NMR chemical shifts are expressed in the form of ppm (δ) relative to δ = 7.26 for $CDCl_3$ whereas $^{13}C\{^{1}H\}$ NMR chemical shifts are expressed relative to δ = 77.00. Multiplicities in the ^{1}H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. HRMS and Electron Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate- Mass Q-TOF LC/MS.

Optimizations of the reaction conditions for the synthesis (*E*)-3-styrylbenzo[c]isoxazoles (3aa):



1a 2a 3aa

Ligands:

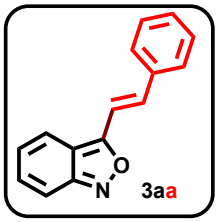


L_1 L_2 L_3 L_4 L_5 L_6

S.No.	Catalyst/Ligand	Solvent	Temp [°C]	Yield(%)[b]
1	$Pd(OAc)_2$ (10%)	Toluene	rt	trace
2	$Pd(OAc)_2$ (10%)	Toluene	60 °C	61%
3	$Pd(OAc)_2$ (10%)	Toluene	80 °C	63%
4	$Pd(OAc)_2$ (10%)	Toluene	100 °C	66%
5	$Pd(OAc)_2$ (10%)	Toluene	110 °C	78%
6	$Pd(OAc)_2$ (10%)	Toluene	120 °C	76%
7	$Pd(OAc)_2$ (20%)	Toluene	110 °C	74%
8	$Pd(OAc)_2$ (5%)	Toluene	110 °C	58%
9	$Pd(OAc)_2$ (10%)	Toluene	110 °C	48%[c]
10	$Pd(OAc)_2$ (10%)	Toluene	110 °C	69%[d]
11	$PdCl_2$, (10%)	Toluene	110 °C	trace
12	$Pd(PPh_3)_4$ (10%)	Toluene	110 °C	trace
13	$Cu(OAc)_2$ (10%)	Toluene	120 °C	n.o.
14	AgOAc (10%)	Toluene	110 °C	n.o.
15	$Pd(OAc)_2$ (10%)	DMSO	110 °C	40%[b]
16	$Pd(OAc)_2$ (10%)	CH_3CN	110 °C	39%[c]
17	$Pd(OAc)_2$ (10%)	DMF	110 °C	n.o.
18	$Pd(OAc)_2$ (10%)	Dioxane	110 °C	n.o.
19	$Pd(OAc)_2$ (10%)	Toluene	110 °C	78%[e]
20	$Pd(OAc)_2$ (10%)	Toluene	110 °C	26%[f]
20	$Pd(OAc)_2$ (10%)/ **L_1**	Toluene	110 °C	57%
21	$Pd(OAc)_2$ (10%)/ **L_2**	Toluene	110 °C	62%
22	$Pd(OAc)_2$ (10%)/ **L_3**	Toluene	110 °C	51%
23	$Pd(OAc)_2$ (10%)/ **L_4**	Toluene	110 °C	56%
24	$Pd(OAc)_2$ (10%)/ **L_5**	Toluene	110 °C	48%
25	$Pd(OAc)_2$ (10%)/ **L_6**	Toluene	110 °C	50%

[a]**Reaction conditions: 1a** (1.0 mmol), **2a** (1.1 mmol), catalyst (0.1 mmol), solvent (3.0 mL) at 110 °C, 24 h in a pressure glass-sealed tube. [b]Isolated yield; [c]when the reaction was run for 12 h.; [d]when the reaction was run for 36 h.; [e] under O_2; [f] under N_2.

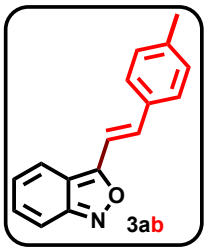
General Experimental Procedure for the synthesis of (*E*)-3-styrylbenzo[c]isoxazoles (3aa): A mixture of anthranil (**1a,** 1.0 mmol), styrene (**2a,** 1.1 mmol), $Pd(OAc)_2$ (0.1 mmol), and toluene (3.0 mL) were taken in a pressure glass sealed tube. The screw of the pressure glass tube was then tightened and allowed to stir at 110 °C for 24 h. When the reaction was completed (determined by TLC), the reaction mixture was cooled



and passed through celite, solvent was evaporated under reduced pressure to get the crude product (**3aa**) which was purified by column chromatography using 2% (ethyl acetate: hexane) on 100-200 mesh silica gel to get the product **3aa** in 78% yield (172 mg), as a yellow solid, m. p. 110 - 112 °C.; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 – 7.55 (m, 5H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.33 – 7.26 (m, 2H); 7.01 (dd, *J* = 8.6, 6.5 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 163.43, 157.33, 135.57, 135.00, 130.81, 129.31, 128.88, 127.17, 123.98, 119.76, 115.69, 115.20, 111.94; **HRMS** (ESI) m/z calcd for $C_{15}H_{12}NO$ [M+H] is 222.0913, found 222.0922.

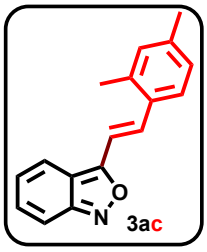
"Note: Following the same above experimental procedure all the desired products (**3ab-3at**) and (**3bc-3ef**) were prepared".

(*E*)-3-(4-methylstyryl)benzo[c]isoxazole (3ab):



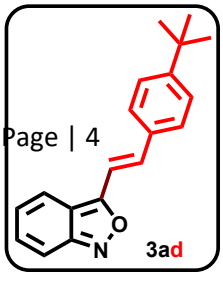
Purified by column chromatography on silica gel (4% ethyl acetate/ petroleum ether) to afford **3ab** as a yellow solid (145 mg, 61%), m. p. 113 - 115 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 16.4 Hz, 1H), 7.49 (d, *J* = 9.1 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 15.9, 7.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.95 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.80, 157.42, 139.72, 135.19, 132.95, 130.86, 129.71, 127.22, 123.86, 119.90, 115.56, 115.25, 111.12, 21.42.; **HRMS** (ESI) m/z calcd for $C_{16}H_{14}NO$ [M+H] is 236.1070, found 236.1036.

(*E*)-3-(2,4-dimethylstyryl)benzo[c]isoxazole (3ac):



Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3ac** as a yellow solid (162 mg, 65%), m. p. 68 - 70 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.87 (d, *J* = 16.3 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.31 (dd, *J* = 9.0, 6.4 Hz, 1H), 7.22 (d, *J* = 16.3 Hz, 1H), 7.09 - 7.06 m, 2H), 7.02 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.00, 157.42, 139.46, 137.00, 132.77, 131.77, 131.64, 130.87, 127.22, 125.22, 123.84, 119.87, 115.56, 115.22, 111.89, 21.28, 19.79; **HRMS** (ESI) m/z calcd for $C_{17}H_{16}NO$ [M+H] is 250.1226, found 250.1227.

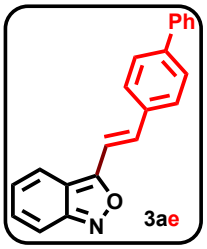
(*E*)-3-(4-(*tert*-butyl)styryl)benzo[c]isoxazole (3ad):



Purified by column chromatography on silica gel (50% ethyl acetate/ petroleum ether) to afford **3ad** as a yellow solid (168 mg, 61%), m. p. 118

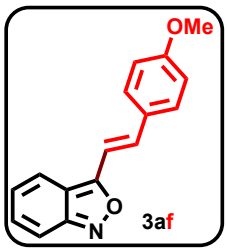
- 120 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.66 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 16.4 Hz, 1H), 7.56 (t, *J* = 8.3 Hz, 3H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.02 (dd, *J* = 8.6, 6.4 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.95, 157.56, 153.05, 135.21, 133.07, 131.01, 127.21, 126.09, 124.01, 120.07, 115.72, 115.38, 111.43, 34.99, 31.33; **HRMS** (ESI) m/z calcd for $C_{19}H_{20}NO$ [M+H] is 278.1539, found 278.1528.

(*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)benzo[c]isoxazole (3ae):



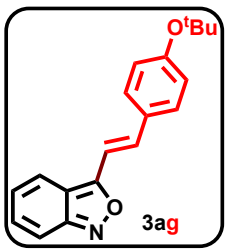
Purified by column chromatography on silica gel (4% ethyl acetate/ petroleum ether) to afford **3ae** as a yellow solid (193 mg, 65%), m. p. 132 - 134 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.74 – 7.61 (m, 8H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.29 (m, 3H), 7.08 – 7.00 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.55, 157.44, 142.11, 140.22, 134.67, 134.61, 130.90, 128.89, 127.73, 127.60, 126.98, 124.07, 119.83, 115.80, 115.32, 111.91; **HRMS** (ESI) m/z calcd for $C_{21}H_{15}NO$ [M+H] is 298.1226, found 298.1231.

(*E*)-3-(4-methoxystyryl)benzo[c]isoxazole (3af):



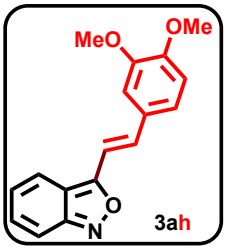
Purified by column chromatography on silica gel (5% ethyl acetate/ petroleum ether) to afford **3af** as a yellow solid (158 mg, 63%), m. p. 120 - 122 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.64 (d, *J* = 8.7 Hz, 1H), 7.59 - 7.54 (m, 4H), 7.30 (dd, *J* = 9.0, 6.5 Hz, 1H), 7.19 (d, *J* = 16.4 Hz, 1H), 7.00 (dd, *J* = 8.6, 6.6 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.97, 160.68, 157.38, 134.81, 130.82, 128.74, 128.43, 123.63, 119.93, 115.31, 115.12, 114.41, 109.88, 77.32, 77.00, 76.68, 55.37; **HRMS** (ESI) m/z calcd for $C_{16}H_{14}NO_2$ [M+H] is 252.1019, found 252.1025.

(*E*)-3-(4-(tert-butoxy)styryl)benzo[c]isoxazole (3ag):



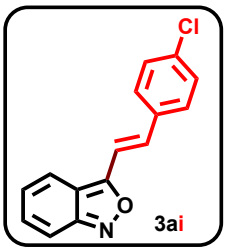
Purified by column chromatography on silica gel (2% ethyl acetate/ petroleum ether) to afford **3ag** as a yellow solid (175 mg, 60%), m. p. 156 - 158 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.64 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.47 (m, 4H), 7.30 (dd, *J* = 8.8, 6.6 Hz, 1H), 7.22 (d, *J* = 16.4 Hz, 1H), 7.07 – 6.96 (m, 3H), 1.39 (s, 9H);); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.06, 157.09, 134.98, 131.03, 130.73, 128.20, 124.20, 123.94, 120.05, 115.69, 115.30, 110.84, 79.40, 29.02; **HRMS** (ESI) m/z calcd for $C_{19}H_{20}NO_2$ [M+H] is 294.1489, found 294.1485.

(*E*)-3-(3,4-dimethoxystyryl)benzo[c]isoxazole (3ah):



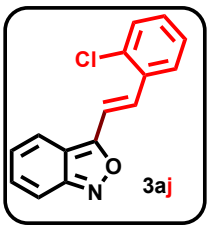
Purified by column chromatography on silica gel (15% ethyl acetate/ petroleum ether) to afford **3ah** as a yellow solid (237 mg, 80%), m. p. 105 - 107 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.64 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.21 – 7.09 (m, 3H), 7.03 – 6.94 (m, 1H), 6.89 (dd, *J* = 8.2, 3.1 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.77, 150.32, 149.19, 134.93, 130.75, 128.62, 123.59, 121.32, 119.86, 115.25, 115.01, 111.13, 110.00, 108.98, 76.68, 55.86, 55.85; **HRMS** (ESI) m/z calcd for $C_{17}H_{16}NO_3$ [M+H] is 282.1125, found 282.1123.

(*E*)-3-(4-chlorostyryl)benzo[c]isoxazole (3ai):



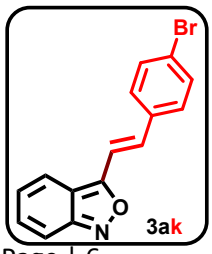
Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3ai** as a yellow solid (165 mg, 64%), m. p. 174 - 176 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.57 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.44 (m, 4H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 2H), 7.19 (d, *J* = 4.8 Hz, 1H), 6.97 (dd, *J* = 8.7, 6.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.09, 157.42, 135.11, 134.16, 133.58, 130.94, 129.20, 128.36, 124.28, 119.65, 115.94, 115.37, 112.43, 76.68; **HRMS** (ESI) m/z calcd for $C_{15}H_{11}ClNO$ [M+H] is 256.0524, found 256.0525.

(*E*)-3-(2-chlorostyryl)benzo[c]isoxazole (3aj):



Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3aj** as a yellow solid (160 mg, 63%), m. p. 90 - 92 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.05 (d, *J* = 16.5 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.41 – 7.27 (m, 4H), 7.09 (dd, *J* = 8.4, 6.7 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.25, 157.47, 134.46, 130.85, 130.23, 130.12, 127.13, 126.58, 124.52, 119.78, 116.06, 115.51, 114.58; **HRMS** (ESI) m/z calcd for $C_{15}H_{11}ClNO$ [M+H] is 256.0524, found 256.0529.

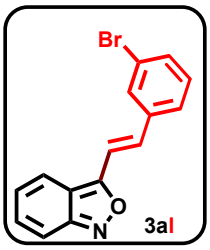
(*E*)-3-(4-bromostyryl)benzo[c]isoxazole (3ak):



Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3ak** as a yellow solid (188 mg, 63%), m. p. 180 - 182 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.66 (d, *J* = 8.8 Hz, 1H), 7.58 (dd, *J* = 17.9, 9.2 Hz, 4H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.07

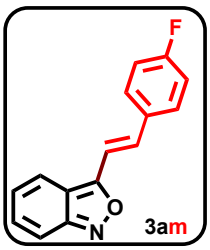
(dd, *J* = 8.6, 6.5 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.07, 157.45, 134.66, 133.62, 132.17, 130.88, 128.59, 124.30, 123.39, 119.65, 115.99, 115.42, 112.62; **HRMS** (ESI) m/z calcd for $C_{15}H_{11}BrNO$ [M+H] is 300.0019, found 300.0024.

(*E*)-3-(3-bromostyryl)benzo[c]isoxazole (3al):



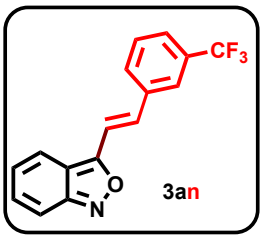
Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3al** as a yellow solid (176 mg, 59%), m. p. 144 - 146 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.75 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.50 (dd, *J* = 17.8, 9.8 Hz, 3H), 7.34 – 7.27 (m, 3H), 7.04 (dd, *J* = 8.7, 6.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 13C NMR (101 MHz, CDCl3) δ 162.79, 157.38, 137.74, 133.15, 132.05, 130.93, 130.41, 129.74, 125.95, 124.42, 123.10, 119.59, 116.12, 115.38, 113.16; **HRMS** (ESI) m/z calcd for $C_{15}H_{11}BrNO$ [M+H] is 300.0019, found 300.0022.

(*E*)-3-(4-fluorostyryl)benzo[c]isoxazole (3am):



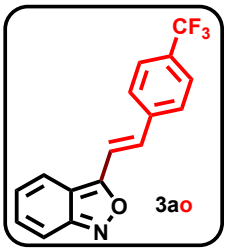
Purified by column chromatography on silica gel (2% ethyl acetate/ petroleum ether) to afford **3am** as a yellow solid (129 mg, 54%), m. p. 121 - 123 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.56 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.46 (m, 4H), 7.24 (ddd, *J* = 9.0, 6.4, 0.8 Hz, 1H), 7.15 – 7.02 (m, 3H), 6.95 (dd, *J* = 8.7, 6.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.55, 163.29, 162.06, 157.39, 133.79, 131.92, 131.89, 130.93, 129.00, 128.92, 124.12, 119.71, 116.19, 115.97, 115.74, 115.30, 111.77, 111.74; **^{19}F NMR (375 MHz, $CDCl_3$)** δ -110.86; **HRMS** (ESI) m/z calcd for $C_{15}H_{11}FNO$ [M+H] is 240.0819, found 240.0818.

(*E*)-3-(3-(trifluoromethyl)styryl)benzo[c]isoxazole (3an):



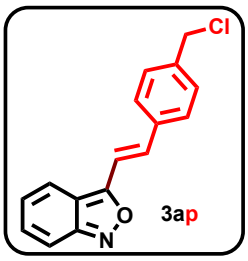
Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3an** as a yellow solid (162 mg, 56%), m. p. 127 - 129 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.78 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.58 - 7.46 (m, 4H), 7.32 (d, *J* = 16.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.99 (dd, *J* = 8.7, 6.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.69, 157.46, 136.48, 133.13, 131.68, 131.35, 130.98, 130.32, 129.50, 125.70, 125.66, 124.58, 123.67, 123.63, 120.72, 119.58, 116.26, 115.49, 115.33, 113.63; **^{19}F NMR (375 MHz, $CDCl_3$)** δ -62.83; **HRMS** (ESI) m/z calcd for $C_{16}H_{10}F_3NO$ [M+H] is 290.0787, found 290.0796.

(*E*)-3-(4-(trifluoromethyl)styryl)benzo[c]isoxazole (3ao):



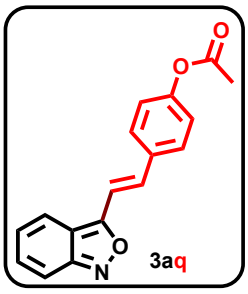
Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3ao** as a yellow solid (182 mg, 63%), m. p. 153 - 155 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.65 – 7.59 (m, 4H), 7.59 – 7.48 (m, 3H), 7.32 (d, *J* = 16.4 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.99 (dd, *J* = 8.6, 6.5 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.62, 157.43, 139.02, 133.05, 131.00, 130.93, 130.61, 127.30, 125.96, 125.92, 125.88, 125.85, 125.28, 124.66, 122.57, 119.52, 116.34, 115.49, 114.10; **^{19}F NMR (375 MHz, $CDCl_3$)** δ -62.67; **HRMS** (ESI) m/z calcd for $C_{16}H_{10}F_3NO$ [M+H] is 290.0787, found 290.0788.

(*E*)-3-(4-(chloromethyl)styryl)benzo[c]isoxazole (3ap):



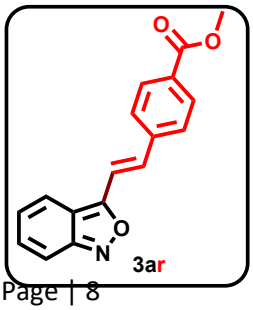
Purified by column chromatography on silica gel (4% ethyl acetate/ petroleum ether) to afford **3ap** as a yellow solid (180 mg, 67%), m. p. 148 - 150 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.72 – 7.56 (m, 5H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.30 (m, 2H), 7.06 (dd, *J* = 8.6, 6.5 Hz, 1H), 4.64 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.24, 157.42, 138.53, 135.82, 134.19, 130.92, 129.22, 127.54, 124.24, 119.73, 115.93, 115.36, 112.56, 45.78; **HRMS** (ESI) m/z calcd for $C_{16}H_{13}ClNO$ [M+H] is 270.0680, found 270.0686.

(*E*)-4-(2-(benzo[c]isoxazol-3-yl)vinyl)phenyl acetate (3aq):



Purified by column chromatography on silica gel (8% ethyl acetate/ petroleum ether) to afford **3aq** as a yellow solid (181 mg, 65%), m. p. 135 - 137 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 1H NMR (400 MHz, CDCl3) δ 7.58 - 7.49 (m, 5H), 7.25 – 7.16 (m, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.00 – 6.93 (m, 1H), 2.26 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.26, 163.30, 157.39, 151.34, 133.96, 133.42, 130.92, 128.27, 124.14, 122.19, 119.74, 115.82, 115.31, 112.14, 21.14; **HRMS** (ESI) m/z calcd for $C_{17}H_{14}NO_3$ [M+H] is 280.0968, found 280.0967.

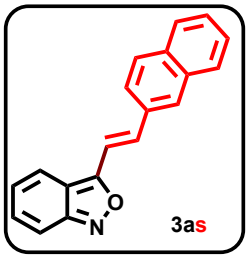
Methyl (E)-4-(2-(benzo[c]isoxazol-3-yl)vinyl)benzoate (3ar):



Purified by column chromatography on silica gel (8% ethyl acetate/ petroleum ether) to afford **3ar** as a yellow solid (175 mg, 63%), m. p. 132 - 134 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.01 (t, *J* = 8.5 Hz, 2H), 7.65 – 7.48 (m, 5H), 7.39 – 7.31 (m, 1H), 7.27 (dd, *J* = 8.4, 6.4 Hz, 1H),

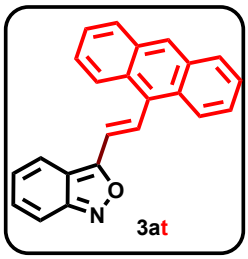
7.00 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.56, 162.81, 157.45, 139.93, 133.57, 130.99, 130.43, 130.21, 127.06, 124.61, 119.60, 116.34, 115.50, 114.04, 52.26; **HRMS** (ESI) m/z calcd for $C_{17}H_{14}NO_3$ [M+H] is 280.0968, found 280.0970.

(*E*)-3-(2-(naphthalen-2-yl)vinyl)benzo[c]isoxazole (3as):



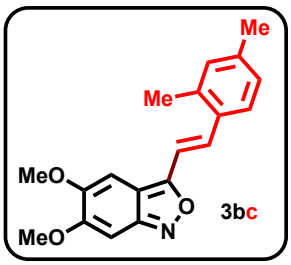
Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3as** as a yellow solid (168 mg, 62%), m. p. 174 - 176 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.88 (s, 1H), 7.81 – 7.73 (m, 3H), 7.72 – 7.64 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.35 (d, *J* = 16.4 Hz, 1H), 7.23 (dd, *J* = 9.0, 6.4 Hz, 1H), 6.95 (dd, *J* = 8.6, 6.5 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.57, 157.44, 135.15, 133.78, 133.50, 133.15, 130.88, 128.71, 128.63, 128.36, 127.77, 126.88, 126.72, 124.06, 123.01, 119.85, 115.82, 115.31, 112.18; **HRMS** (ESI) m/z calcd for $C_{19}H_{14}NO$ [M+H] is 272.1070, found 272.1084.

(*E*)-3-(2-(anthracen-9-yl)vinyl)benzo[c]isoxazole (3at):



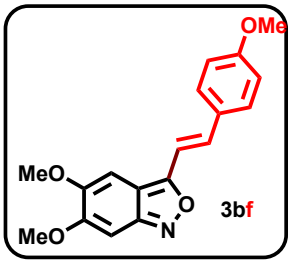
Purified by column chromatography on silica gel (4% ethyl acetate/ petroleum ether) to afford **3at** as a yellow solid (205 mg, 64%), m. p. 165 - 167 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.57 (d, *J* = 16.6 Hz, 1H), 8.50 (s, 1H), 8.43 – 8.35 (m, 2H), 8.09 – 8.06 (m, 2H), 7.68 (d, *J* = 9.5 Hz, 2H), 7.59 – 7.49 (m, 4H), 7.42 – 7.35 (m, 1H), 7.31 (d, *J* = 16.6 Hz, 1H), 7.08 (dd, *J* = 8.7, 6.8 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.03, 157.54, 132.00, 131.41, 131.02, 130.59, 129.59, 128.92, 127.93, 126.28, 125.40, 125.35, 124.43, 120.83, 119.76, 115.99, 115.40; **HRMS** (ESI) m/z calcd for $C_{23}H_{16}NO$ [M+H] is 322.1226, found 322.1220.

(*E*)-3-(2,4-dimethylstyryl)-5,6-dimethoxybenzo[*c*]isoxazole (3bc):



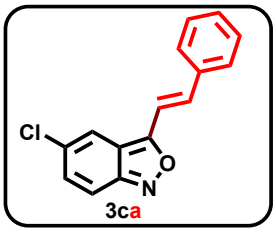
Purified by column chromatography on silica gel (30% ethyl acetate/ petroleum ether) to afford **3bc** as a yellow solid (241 mg, 78%), m. p. 80 - 82 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.63 (d, *J* = 16.2 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 16.3 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.66 (s, 1H), 6.61 (s, 1H), 3.87 (s, 3H), 3.87 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.11, 155.43, 155.05, 149.60, 138.94, 136.72, 132.00, 131.55, 131.00, 127.08, 124.99, 111.69, 111.32, 94.61, 91.44, 56.12, 55.99, 21.22, 19.76; **HRMS** (ESI) m/z calcd for $C_{19}H_{20}NO_3$ [M+H] is 310.1438, found 310.1443.

(*E*)-5,6-dimethoxy-3-(4-methoxystyryl)benzo[*c*]isoxazole (3bf):



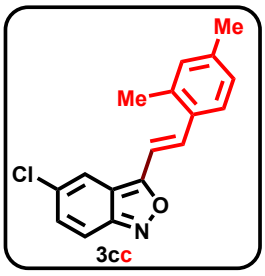
Purified by column chromatography on silica gel (30% ethyl acetate/ petroleum ether) to afford **3bf** as a yellow solid (217 mg, 70%), m. p. 154 - 156 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 16.3 Hz, 1H), 7.09 (d, *J* = 16.3 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.73 (s, 1H), 6.70 (s, 1H), 3.96 (s, 6H), 3.86 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.09, 160.33, 155.41, 155.03, 149.48, 133.08, 128.74, 128.45, 114.31, 111.01, 109.84, 94.73, 91.40, 56.10, 56.01, 55.33; **HRMS** (ESI) m/z calcd for $C_{18}H_{18}NO_4$ [M+H] is 312.1230, found 312.1198.

(*E*)-5-chloro-3-styrylbenzo[c]isoxazole (3ca):



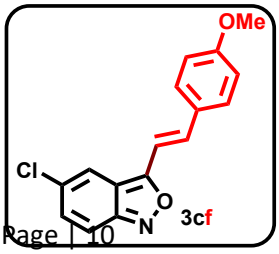
Purified by column chromatography on silica gel (2% ethyl acetate/ petroleum ether) to afford **3ca** as a yellow solid (160 mg, 63%), m. p. 144 - 146 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.59 (d, *J* = 0.8 Hz, 1H), 7.53 - 7.51 (m, 3H), 7.47 (dd, *J* = 9.4, 0.6 Hz, 1H), 7.38 - 7.29 (m, 3H), 7.23 – 7.22 - 7.15 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.31, 155.90, 135.70, 135.43, 132.71, 129.71, 129.62, 129.02, 127.32, 118.32, 116.96, 115.85, 111.57, **HRMS** (ESI) m/z calcd for $C_{15}H_{11}ClNO$ [M+H] is 256.0524, found 256.0523.

(*E*)-5-chloro-3-(2,4-dimethylstyryl)benzo[*c*]isoxazole (3cc):



Purified by column chromatography on silica gel (3% ethyl acetate/ petroleum ether) to afford **3cc** as a yellow solid (167 mg, 59%), m. p. 123 - 125 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.87 (d, *J* = 16.3 Hz, 1H), 7.65 (d, *J* = 0.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 9.4 Hz, 1H), 7.25 (dd, *J* = 9.4, 1.7 Hz, 1H), 7.17 (d, *J* = 16.3 Hz, 1H), 7.10 (d, *J* = 10.7 Hz, 2H), 2.49 (s, 3H), 2.38 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.75, 155.90, 139.75, 137.13, 133.35, 132.69, 131.70, 131.53, 129.42, 127.27, 125.28, 118.35, 116.85, 115.69, 111.32, 21.30, 19.80; **HRMS** (ESI) m/z calcd for $C_{17}H_{15}ClNO$ [M+H] is 284.0837, found 284.0844.

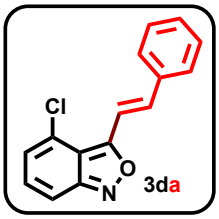
(*E*)-5-chloro-3-(4-methoxystyryl)benzo[*c*]isoxazole (3cf):



Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **3cf** as a yellow liquid (185 mg, 65%); **^{1}H NMR (400 MHz, $CDCl_3$)**: 7.67 (s, 1H), 7.62 – 7.47 (m, 4H), 7.25 (dd,

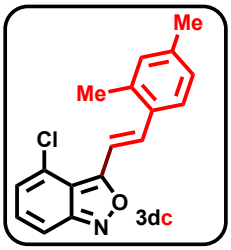
J = 9.4, 1.6 Hz, 1H), 7.15 (d, *J* = 16.4 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.81, 160.90, 155.89, 135.44, 132.64, 129.22, 128.88, 128.23, 118.46, 116.81, 115.42, 114.50, 109.43, 55.42; **HRMS** (ESI) m/z calcd for $C_{16}H_{13}ClNO_2$ [M+H] is 286.0629, found 286.0626.

(*E*)-4-chloro-3-styrylbenzo[*c*]isoxazole (3da):



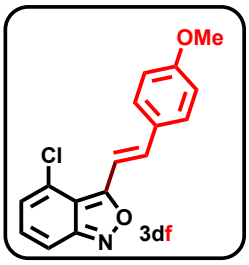
Purified by column chromatography on silica gel (2% ethyl acetate/ petroleum ether) to afford **3da** as a yellow solid (150 mg, 59%), m. p. 130 - 132 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.72 (d, *J* = 16.4 Hz, 1H), 7.63 (d, *J* = 16.4 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.27 (m, 4H), 7.12 (dd, *J* = 9.0, 7.0 Hz, 1H), 6.92 (d, *J* = 6.9 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.11, 158.22, 136.45, 135.62, 131.03, 129.60, 128.97, 127.49, 126.35, 123.76, 114.29, 114.15, 112.50; **HRMS** (ESI) m/z calcd for $C_{15}H_{11}ClNO$ [M+H] is 256.0524, found 256.0521.

(*E*)-4-chloro-3-(2,4-dimethylstyryl)benzo[c]isoxazole (3dc):



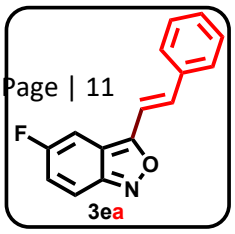
Purified by column chromatography on silica gel (2% ethyl acetate/ petroleum ether) to afford **3dc** as a yellow solid (195 mg, 69%), m. p. 137 - 139 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.95 (d, *J* = 16.2 Hz, 1H), 7.67 (d, *J* = 16.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.18 (dd, *J* = 8.9, 7.0 Hz, 1H), 7.07 (d, *J* = 10.6 Hz, 2H), 6.97 (d, *J* = 7.0 Hz, 1H), 2.48 (s, 3H), 2.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.55, 158.22, 139.68, 137.26, 134.10, 131.74, 131.66, 130.98, 127.22, 126.45, 125.58, 123.51, 114.17, 113.90, 112.45, 77.32, 77.00, 76.68, 21.30, 19.84; **HRMS** (ESI) m/z calcd for $C_{17}H_{15}ClNO$ [M+H] is 284.0837, found 284.0832.

(*E*)-4-chloro-3-(4-methoxystyryl)benzo[c]isoxazole (3df):



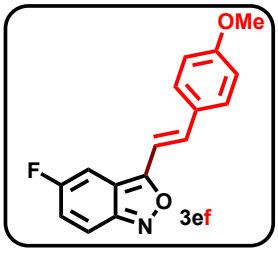
Purified by column chromatography on silica gel (4% ethyl acetate/ petroleum ether) to afford **3df** as a yellow solid (185 mg, 65%), m. p. 127 - 129 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.65 (s, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.17 (dd, *J* = 9.0, 7.0 Hz, 1H), 6.98 – 6.92 (m, 3H), 3.86 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.56, 160.87, 158.20, 136.17, 130.97, 129.06, 128.44, 126.47, 123.35, 114.42, 114.11, 113.67, 110.36, 77.32, 77.00, 76.68, 55.40; **HRMS** (ESI) m/z calcd for $C_{16}H_{13}ClNO_2$ [M+H] is 286.0629, found 286.0617.

(*E*)-5-fluoro-3-styrylbenzo[c]isoxazole (3ea):



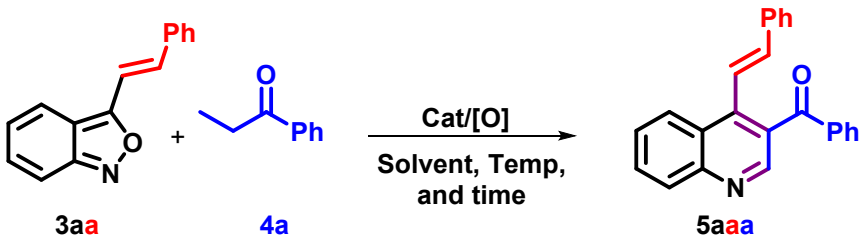
Purified by column chromatography on silica gel (2% ethyl acetate/ petroleum ether) to afford **3ea** as a yellow solid (136 mg, 57%), m. p. 137 - 139 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.52 (d, *J* = 7.3 Hz, 3H), 7.47 (d, *J* = 16.5 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.14 (dd, *J* = 16.5, 7.6 Hz, 2H), 7.10 – 7.02 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.78, 163.67, 160.14, 157.68, 155.49, 135.49, 134.88, 129.43, 128.97, 127.21, 124.06, 123.75, 117.97, 117.88, 114.84, 114.74, 111.71, 101.72, 101.47; **^{19}F NMR (375 MHz, $CDCl_3$)** δ -115.24; **HRMS** (ESI) m/z calcd for $C_{15}H_{11}FNO$ [M+H] is 240.0819, found 240.0815.

(*E*)-5-fluoro-3-(4-methoxystyryl)benzo[*c*]isoxazole (3ef):



Purified by column chromatography on silica gel (5% ethyl acetate/ petroleum ether) to afford **3ef** as a yellow solid (169 mg, 63%), m. p. 136 - 138 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.52 – 7.39 (m, 4H), 7.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.11 – 7.00 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.29, 160.75, 157.50, 155.52, 134.66, 128.75, 128.34, 123.99, 123.69, 117.83, 117.73, 114.46, 109.64, 101.85, 101.60; **^{19}F NMR (375 MHz, $CDCl_3$)** δ -115.96; **HRMS** (ESI) m/z calcd for $C_{16}H_{13}FNO_2$ [M+H] is 270.0925, found 270.0930.

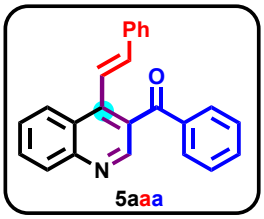
Optimizations of the reaction conditions for the synthesis of (*E*)-phenyl(4-styrylquinolin-3-yl)methanone (5aaa):



S.No.	Catalyst	Oxidant	Solvent	Temp/[°C]	Yield(%)[b]
1	CuI	TEMPO	DME	110 °C	trace
2	CuBr	TEMPO	DME	110 °C	10%
3	$Cu(OAc)_2$	TEMPO	Toluene	110 °C	50%
4	$Cu(OAc)_2$	TEMPO	Dioxane	110 °C	40%
5	$Cu(OAc)_2$	TEMPO	DMF	110 °C	55%
6	$Cu(OAc)_2$	TEMPO	DMSO	110 °C	75%
7	$Cu(OAc)_2$	TEMPO	1,2-DCB	110 °C	88%
8	$Pd(OAc)_2$	TEMPO	1,2-DCB	110 °C	n.o%
9	$Cu(OAc)_2$	TEMPO	1,2-DCB	110 °C	88%[c]
10	$Cu(OAc)_2$	TEMPO	1,2-DCB	110 °C	71%[d]

[a]**Reaction Conditions: 3aa** (1.0 mmol), **4a** (1.1 mmol), $Cu(OAc)_2$ (10 mol%), TEMPO (1.0 mmol), 1,2-DCB (3.0 mL), 24 hrs in sealed tube. [b]Yield = isolated yield, [C] When reaction was run for 36 hrs.; [d]When reaction was run for 12 hrs.

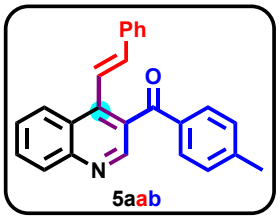
General Experimental Procedure for the synthesis of (*E*)-phenyl(4-styrylquinolin-3-yl)methanone (5aaa):



A mixture of 3-alkenylated anthranil (**3aa,** 0.22 mmol), propiophenone (**4a,** 0.22 mmol), $Cu(OAc)_2$ (0.022 mmol), TEMPO (0.22 mmol) and 1,2-dichlorobenzene (1.0 mL) in a sealed tube was stirred at 110 °C for 24 h. When the reaction was completed (determined by TLC), the reaction mixture was cooled and diluted with water (10 ml), extracted with ethyl acetate (3 x 10 ml). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, solvent was evaporate under reduced pressure to get crude product (**5aaa**) which was purified by column chromatography using 10% (ethyl acetate:hexane) on 100-200 mesh silica gel to get the product **5aaa** in 88% yield, **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.97 (s, 1H), 8.22 (dd, *J* = 8.7, 1.5 Hz, 2H), 7.86 – 7.80 (m, 1H), 7.77 – 7.71 (m, 2H), 7.67 – 7.61 (m, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.40 (dd, *J* = 19.1, 11.9 Hz, 3H), 7.28 (s, 5H), 6.82 (d, *J* = 16.3 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.18, 149.06, 148.61, 143.51, 139.76, 137.64, 136.09, 133.39, 130.65, 130.47, 130.00, 129.62, 128.79, 128.62, 127.46, 126.79, 125.99, 125.42, 122.19; **HRMS** (ESI) m/z calcd for $C_{24}H_{18}NO$ [M+H] is 336.1383, found 336.1374.

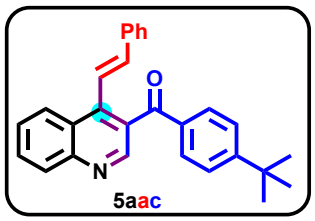
"Note: Following the same above experimental procedure all the desired products (**5aab-5aam**) were prepared".

(*E*)-(4-styrylquinolin-3-yl)(p-tolyl)methanone (5aab):



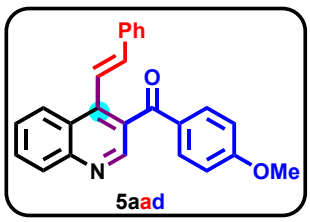
Purified by column chromatography on silica gel (15% ethyl acetate/ petroleum ether) to afford **5aab** as a brown liquid (68 mg, 86%); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.93 (s, 1H), 8.22 (t, *J* = 9.0 Hz, 2H), 7.84 – 7.79 (m, 1H), 7.68 – 7.61 (m, 3H), 7.44 (d, *J* = 16.4 Hz, 1H), 7.29 (m, *J* = 7.8, 2.6 Hz, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.71, 148.94, 148.53, 144.48, 143.18, 139.52, 136.18, 135.00, 130.73, 130.50, 129.99, 129.89, 129.35, 128.72, 128.60, 127.38, 126.82, 126.02, 125.40, 122.12, 21.66; **HRMS** (ESI) m/z calcd for $C_{25}H_{20}NO$ [M+H] is 350.1539, found 350.1535.

(*E*)-(4-(tert-butyl)phenyl)(4-styrylquinolin-3-yl)methanone (5aac):



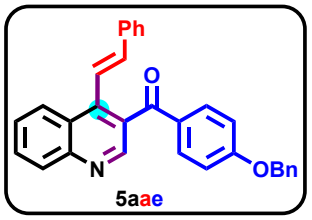
Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **5aac** as a yellow liquid (73 mg, 83%); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.96 (s, 1H), 8.22 (t, *J* = 7.3 Hz, 2H), 7.86 – 7.79 (m, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.39 (dd, *J* = 12.4, 3.9 Hz, 3H), 7.28 (d, *J* = 3.8 Hz, 5H), 6.82 (d, *J* = 16.4 Hz, 1H), 1.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ196.75, 157.28, 149.12, 148.62, 143.42, 139.47, 136.28, 135.05, 130.75, 130.55, 130.02, 129.74, 128.69, 128.56, 127.39, 126.82, 126.05, 125.60, 125.52, 122.41, 35.13, 30.97; **HRMS** (ESI) m/z calcd for $C_{28}H_{26}NO$ [M+H] is 392.2009, found 392.2013.

(*E*)-phenyl(4-styrylquinolin-3-yl)methanone (5aad):



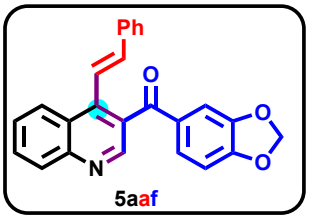
Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **5aad** as a brown liquid (70 mg, 85%); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.91 (s, 1H), 8.25 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.87 – 7.80 (m, 1H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.65 (dd, *J* = 11.2, 4.2 Hz, 1H), 7.46 (d, *J* = 16.4 Hz, 1H), 7.37 – 7.28 (m, 5H), 6.91 – 6.85 (m, 3H), 3.83 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.35, 164.15, 148.49, 140.02, 136.31, 132.42, 131.09, 130.91, 130.45, 129.69, 129.04, 128.85, 127.77, 127.09, 126.30, 125.61, 122.02, 114.15, 77.48, 77.16, 76.84, 55.68; **HRMS** (ESI) m/z calcd for $C_{25}H_{20}NO_2$ [M+H] is 366.1489, found 366.1481.

(*E*)-(4-(benzyloxy)phenyl)(4-styrylquinolin-3-yl)methanone (5aae):



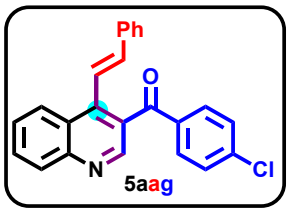
Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **5aae** as a brown liquid (87 mg, 87%); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.91 (s, 1H), 8.22 (dd, *J* = 14.9, 8.1 Hz, 2H), 7.84 – 7.80 (m, 1H), 7.77 – 7.73 (m, 2H), 7.67 – 7.61 (m, 1H), 7.45 (d, *J* = 16.4 Hz, 1H), 7.40 – 7.37 (m, 4H), 7.36– 7.30 (m, 6H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 16.4 Hz, 1H), 5.09 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.55, 163.04, 148.91, 148.56, 142.85, 139.47, 136.25, 135.94, 132.24, 130.86, 130.61, 130.42, 130.06, 128.75, 128.68, 128.66, 128.26, 127.43, 127.38, 126.87, 126.04, 125.38, 122.06, 114.77, 70.19; **HRMS** (ESI) m/z calcd for $C_{31}H_{24}NO_2$ [M+H] is 442.1802, found 442.1802.

(*E*)-benzo[d][1,3]dioxol-5-yl(4-styrylquinolin-3-yl)methanone (5aaf):



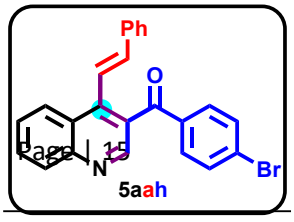
Purified by column chromatography on silica gel (15% ethyl acetate/ petroleum ether) to afford **5aaf** as a yellow solid (73 mg, 86%), m. p. 128 - 130 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.92 (s, 1H), 8.26 (dd, *J* = 8.2, 3.1 Hz, 2H), 7.85 (t, *J* = 7.3 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 16.4 Hz, 1H), 7.40 – 7.31 (m, 6H), 7.27 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.89, 152.33, 148.33, 143.31, 139.71, 136.09, 132.14, 130.69, 129.65, 128.87, 128.69, 127.57, 127.16, 126.89, 125.36, 121.79, 108.83, 107.97, 101.98; **HRMS** (ESI) m/z calcd for $C_{25}H_{18}NO_3$ [M+H] is 380.1281, found 380.1280.

(*E*)-(4-chlorophenyl)(4-styrylquinolin-3-yl)methanone (5aag):



Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **5aag** as a yellow solid (69 mg, 83%), m. p. 114 - 116 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.94 (s, 1H), 8.26 (dd, *J* = 15.6, 8.4 Hz, 2H), 7.90 – 7.84 (m, 1H), 7.70 – 7.66 (m, 3H), 7.43 (d, *J* = 16.3 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.31 (s, 5H), 6.82 (d, J = 16.3 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.15, 147.54, 141.11, 140.22, 135.70, 135.65, 131.71, 130.96, 130.00, 129.35, 129.13, 128.81, 128.76, 128.21, 126.97, 126.15, 125.55, 121.52; **HRMS** (ESI) m/z calcd for $C_{24}H_{17}ClNO$ [M+H] is 370.0993, found 370.0989.

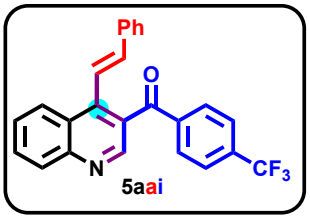
(*E*)-(4-bromophenyl)(4-styrylquinolin-3-yl)methanone (5aah):



Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **5aah** as a yellow solid (80 mg, 86%), m. p.

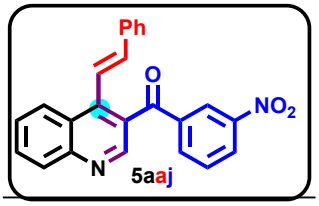
153 - 155 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.94 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 2H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 16.3 Hz, 1H), 7.30 (s, 5H), 6.80 (d, *J* = 16.3 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.09, 148.77, 148.55, 143.68, 140.17, 136.42, 135.91, 131.98, 130.99, 130.90, 129.98, 129.94, 129.03, 128.73, 128.68, 127.64, 126.82, 125.93, 125.37, 121.98; **HRMS** (ESI) m/z calcd for $C_{24}H_{17}BrNO$ [M+H] is 414.0488, found 414.0481.

(*E*)-(4-styrylquinolin-3-yl)(4-(trifluoromethyl)phenyl)methanone (5aai):



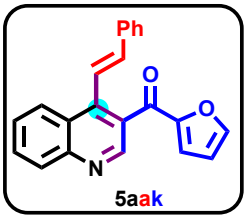
Purified by column chromatography on silica gel (12% ethyl acetate/ petroleum ether) to afford **5aai** as a yellow solid (76 mg, 84%), m. p. 100 - 102 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.00 (s, 1H), 8.21 (t, *J* = 9.4 Hz, 2H), 7.83 (ddd, *J* = 17.3, 9.2, 4.7 Hz, 3H), 7.68 – 7.58 (m, 3H), 7.38 (d, *J* = 16.3 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.23 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.75 (d, *J* = 16.3 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ196.23, 149.06, 148.85, 143.99, 140.79, 140.39, 135.76, 134.44, 134.12, 131.01, 130.11, 129.63, 129.60, 129.06, 128.66, 127.66, 126.71, 125.85, 125.64, 125.60, 125.56, 125.37, 124.76, 122.17, 122.04; **^{19}F NMR (375 MHz, $CDCl_3$)** δ-63.22; **HRMS** (ESI) m/z calcd for $C_{25}H_{17}F_3NO$ [M+H] is 404.1257, found 404.1257.

(*E*)-(3-nitrophenyl)(4-styrylquinolin-3-yl)methanone (5aaj):



Purified by column chromatography on silica gel (25% ethyl acetate/ petroleum ether) to afford **5aaj** as a yellow solid (73 mg, 86%), m. p. 144 - 146 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.01 (s, 1H), 8.54 – 8.45 (m, 1H), 8.30 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.23 (t, *J* = 9.4 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.87 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 16.3 Hz, 1H), 7.31 – 7.22 (m, 6H), 6.76 (d, *J* = 16.3 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.94, 148.75, 148.25, 141.11, 139.14, 135.47, 134.68, 131.44, 129.90, 129.33, 128.98, 128.79, 127.96, 127.32, 126.73, 125.39, 124.13, 121.80; **HRMS** (ESI) m/z calcd for $C_{24}H_{17}N_2O_3$ [M+H] is 381.1234, found 381.1227.

(*E*)-furan-2-yl(4-styrylquinolin-3-yl)methanone (5aak):

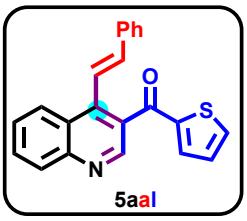


Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **5aak** as a yellow solid (57 mg, 78%), m. p. 82 - 84 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.01 (s, 1H), 8.29 – 8.17 (m,

2H), 7.87 – 7.79 (m, 1H), 7.68 – 7.62 (m, 1H), 7.60 (dd, *J* = 8.6, 7.7 Hz, 2H), 7.42 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.12 – 7.07 (m, 1H), 6.87 (d, *J* = 16.4 Hz, 1H), 6.51 (dd, *J* = 3.6, 1.7 Hz, 1H) ; **^{13}C NMR (100 MHz, $CDCl_3$):** δ183.53, 152.63, 148.50, 147.46, 144.37, 139.51, 136.10, 130.91, 129.78, 129.41, 128.87, 128.71, 127.51, 126.93, 126.06, 125.65, 121.83, 120.62, 112.72; **HRMS** (ESI) m/z calcd for $C_{22}H_{16}NO_2$ [M+H] is 326.1176, found 326.1167.

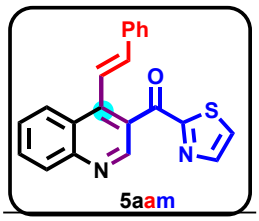
Plausible reaction mechanism for the synthesis of

(*E*)-(4-styrylquinolin-3-yl)(thiophen-2-yl)methanone (5aal):



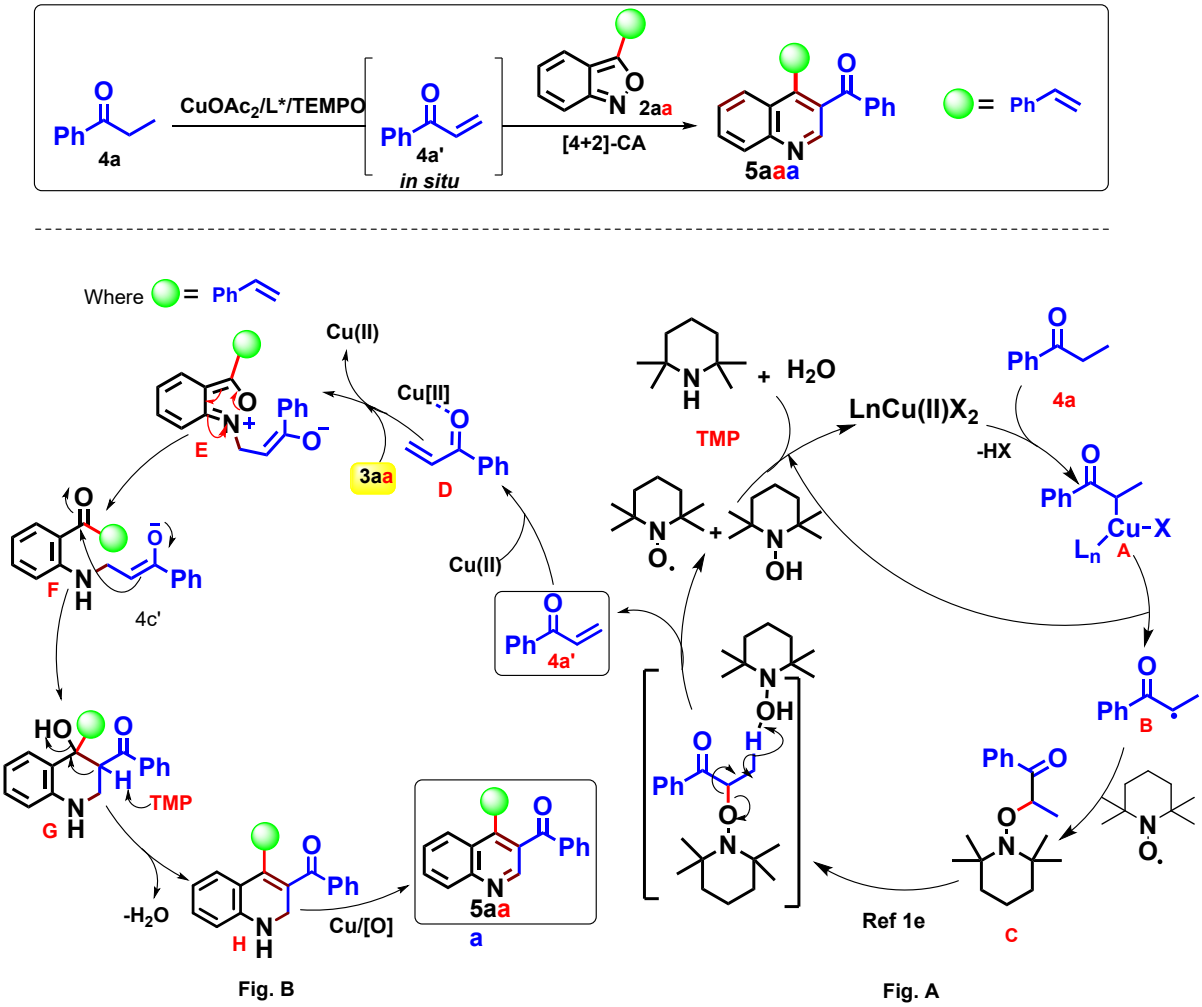
Purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) to afford **5aal** as a reddish brown liquid (58 mg, 76%); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.99 (s, 1H), 8.30 – 8.21 (m, 2H), 7.85 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.55 (d, *J* = 16.4 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.37 – 7.29 (m, 3H), 7.08 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.95 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ188.46, 148.04, 144.49, 139.80, 136.13, 135.49, 135.36, 130.92, 130.50, 129.68, 128.95, 128.74, 128.37, 127.66, 126.97, 126.13, 125.60, 121.76; **HRMS** (ESI) m/z calcd for $C_{22}H_{16}NOS$ [M+H] is 342.0947, found 342.0938.

(*E*)-(4-styrylquinolin-3-yl)(thiazol-2-yl)methanone (5aam):



Purified by column chromatography on silica gel (35% ethyl acetate/ petroleum ether) to afford **5aam** as a brown solid (56 mg, 73%), m. p. 132 - 134 °C.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 9.19 (s, 1H), 8.22 (t, *J* = 8.7 Hz, 2H), 7.99 (d, *J* = 3.0 Hz, 1H), 7.83 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.40 – 7.28 (m, 5H), 6.76 (d, *J* = 16.3 Hz, 1H).); **^{13}C NMR (100 MHz, $CDCl_3$):** δ187.94, 167.45, 149.25, 148.79, 145.68, 145.11, 139.05, 136.14, 131.18, 129.88, 128.84, 128.71, 128.52, 127.43, 126.81, 126.62, 126.13, 125.86, 123.32; **HRMS** (ESI) m/z calcd for $C_{21}H_{15}N_2OS$ [M+H] is 343.0900, found 343.0896.

Plausible reaction mechanism for the synthesis of (*E*)-phenyl(4-styrylquinolin-3-yl)methanone (5aaa):



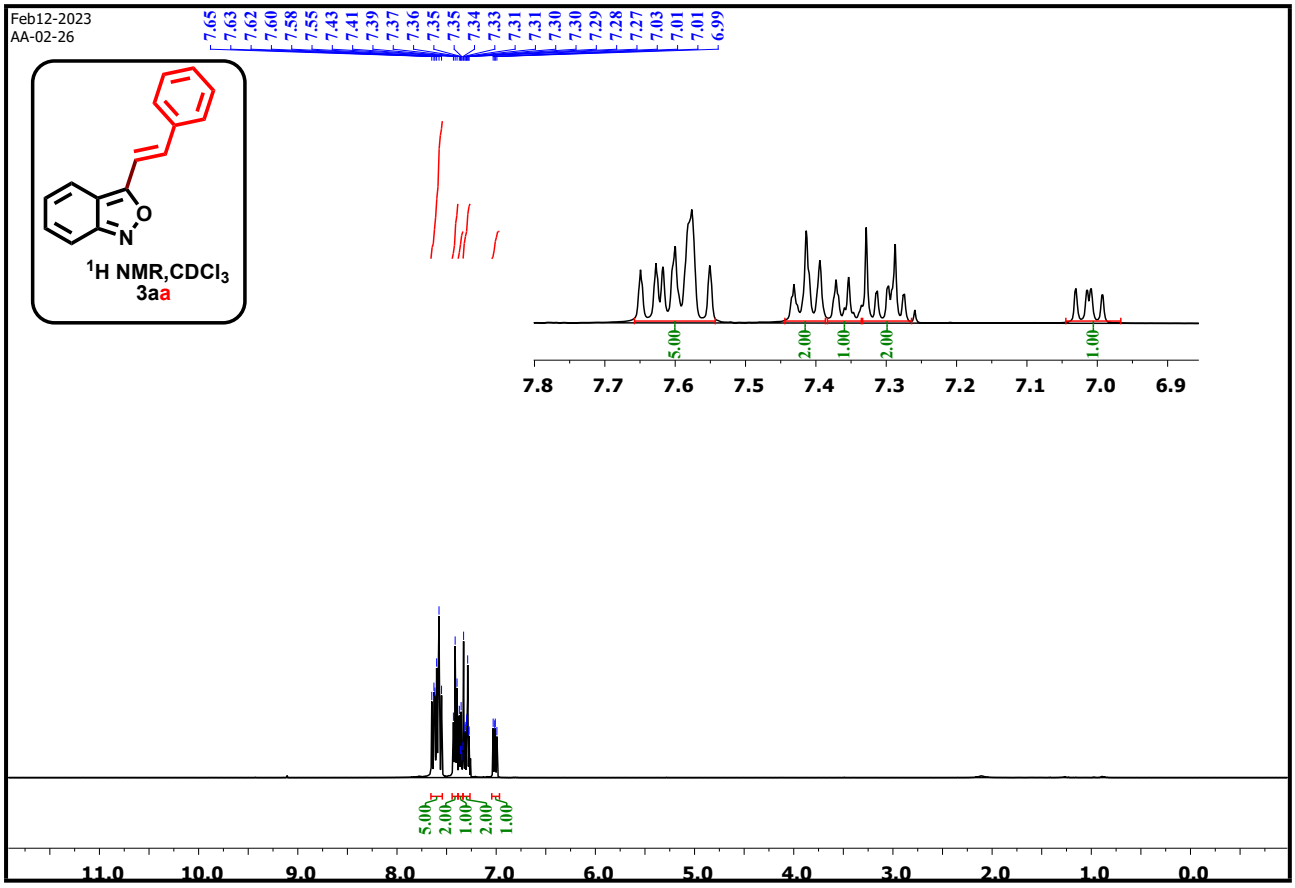
Scheme 1. Possible reaction pathways: **Fig. A:** possible catalytic cycle for in situ generation of α,β-unsaturated ketone from saturated ketone. **Fig B**: a possible route for [4+2] cycloaddition between in situ generated of α,β-unsaturated ketone and 3-styrylanthranil (**3aa**).

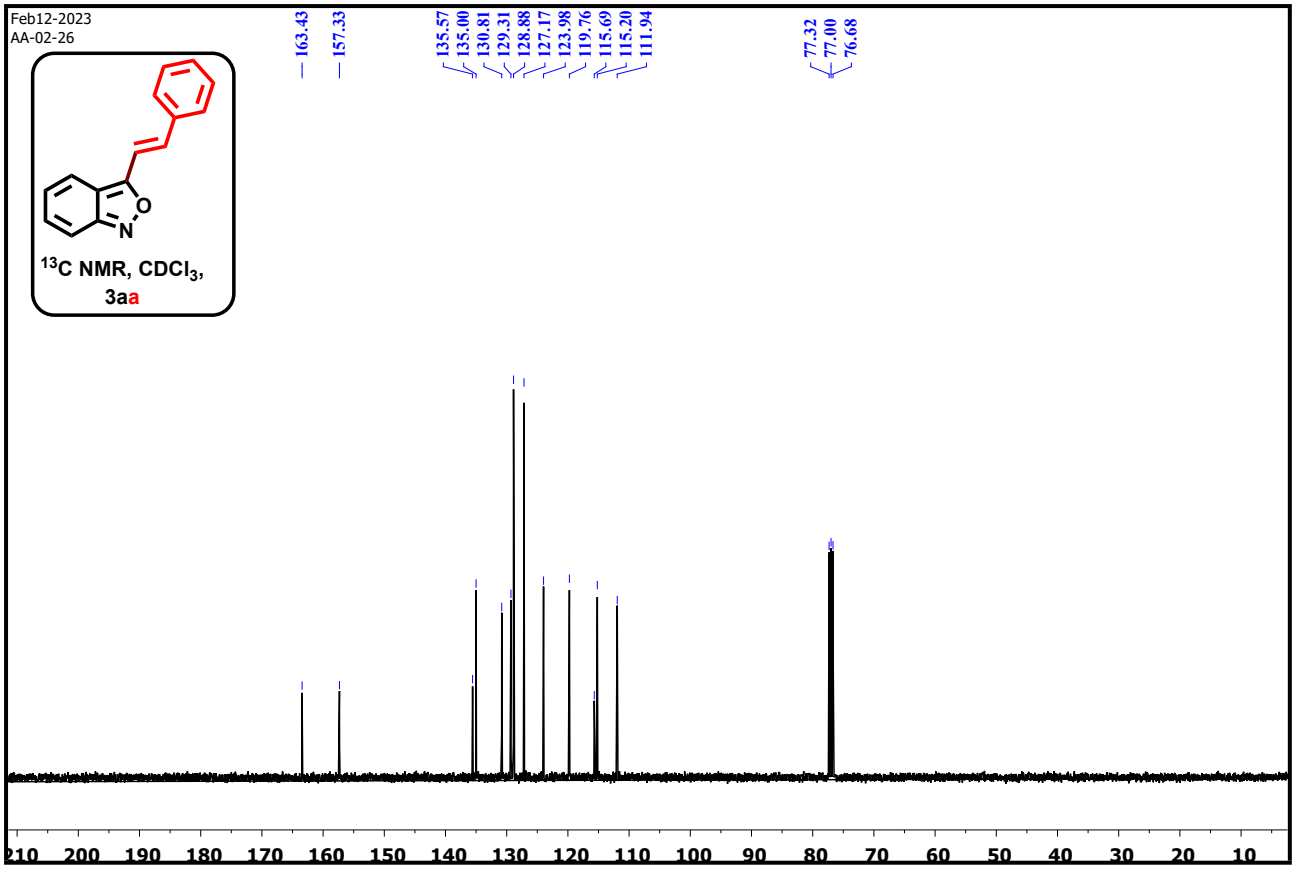
Based on the literature reports [1-2] the mechanism a plausible reaction mechanism for the synthesis of (*E*)-phenyl(4-styrylquinolin-3-yl)methanone (**5aaa**) from 3-alkenylated anthranil (**3aa**) and propiophenone (**4a**) is drawn in scheme 1.

First, $Cu(OAc)_2$ enolizes the saturated ketone (**4a**) to form complex **A**. This complex undergoes homolytic bond cleavage, generating Cu(I) species and intermediate **B**. Upon reacting with TEMPO, it produces α-TEMPO-substituted ketone **C**. Subsequently, another molecule of TEMPO abstracts the β-hydrogen of intermediate **C,** leading to the elimination of TEMPOH and the formation of the desired α,β-unsaturated ketone **4a**'. The Cu(I) species are then oxidized by either TEMPO or TEMPOH, regenerating Cu(II) species (**Fig. A**).

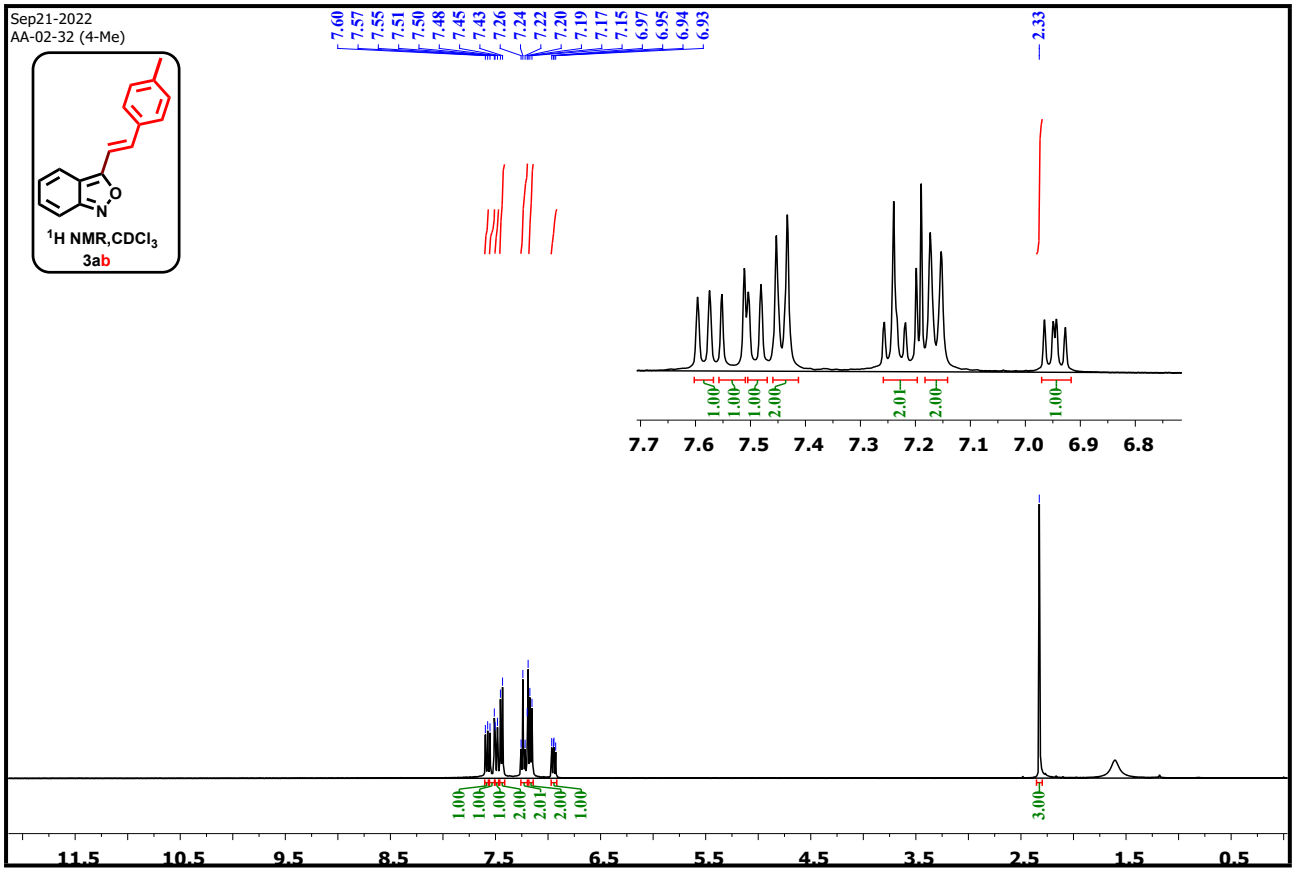
In the next step, the nitrogen atom of anthranil (**3aa**) attacks the β-position of enone (**D**), resulting in intermediate **E**. The polarized N-O bond of intermediate **E** undergoes cleavage to produce intermediate **F**. The intermediate **F** then undergoes intramolecular cyclization, followed by TMP-mediated dehydration, resulting in the dihydroquinolene **H**. Finally, intermediate **H** undergoes copper-catalyzed aerobic oxidation [O] to yield the desired **5aaa** (Fig. B).

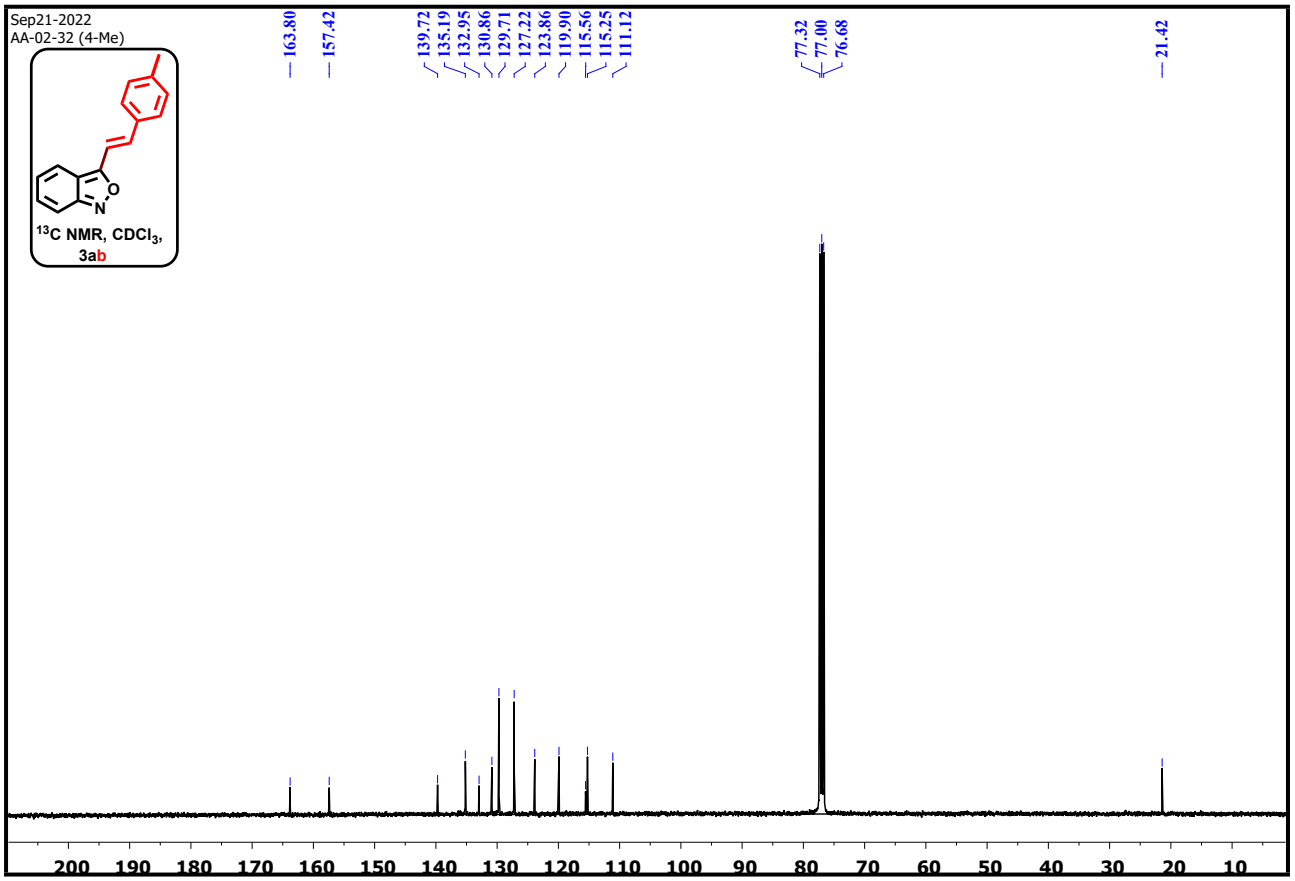
^{1}H and ^{13}C NMR spectra of **3aa**



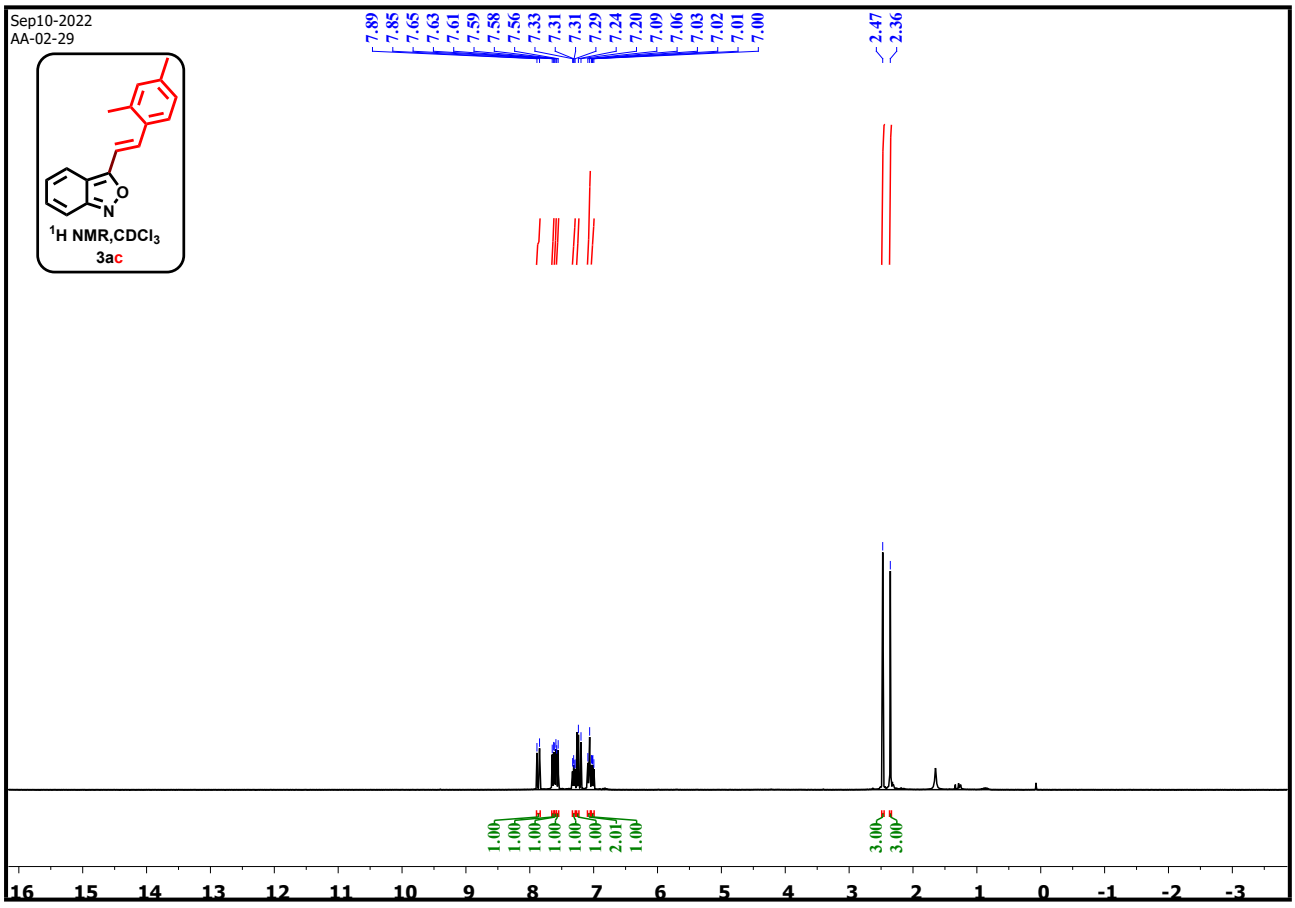


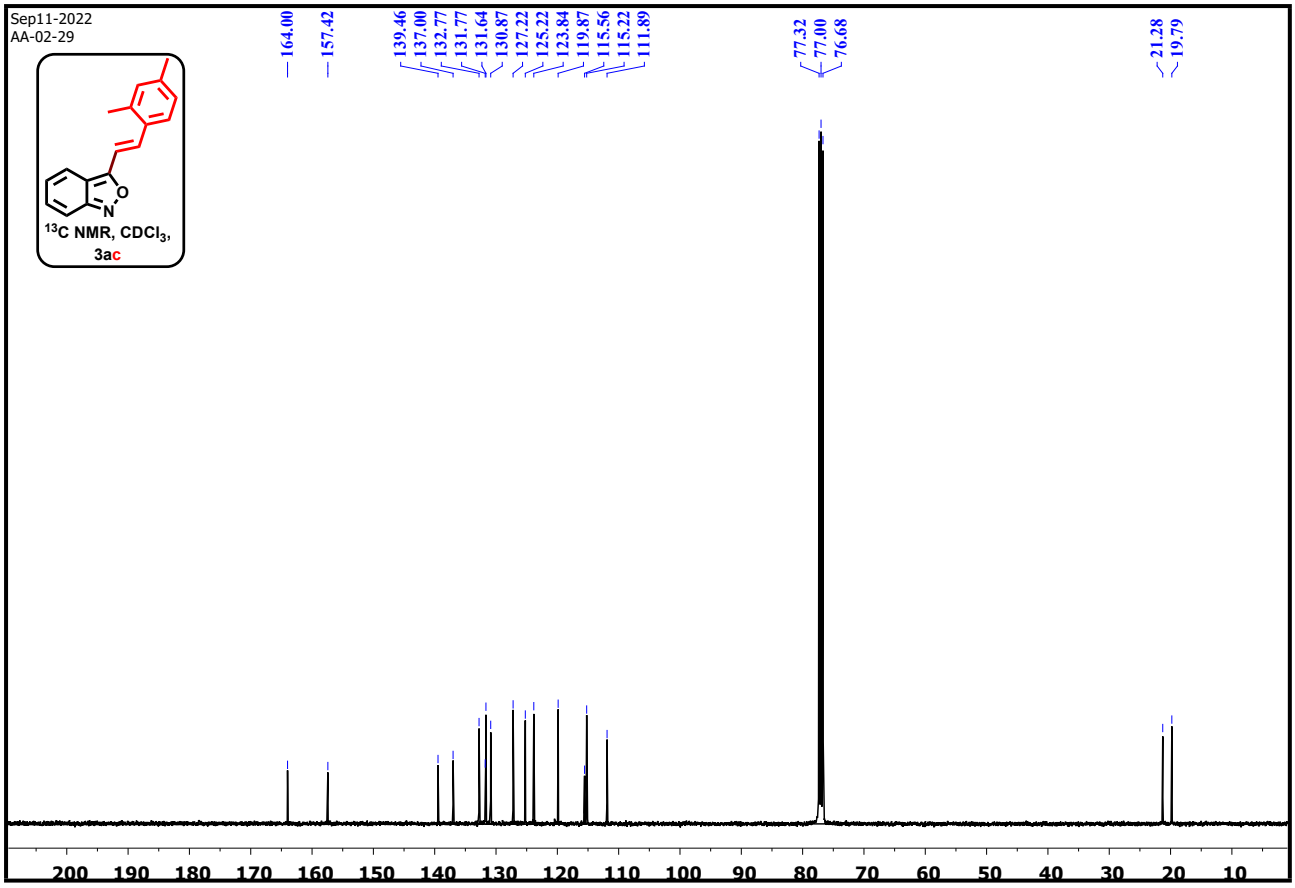
[1]H and [13]C NMR spectra of **3ab**


Sep21-2022
AA-02-32 (4-Me)
^{1}H NMR,CDCl$_3$
3ab
7.60
7.57
7.55
7.51
7.50
7.48
7.45
7.43
7.26
7.24
7.22
7.20
7.19
7.17
7.15
6.97
6.95
6.94
6.93
2.33
1.00
1.00
1.00
2.00
2.01
2.00
1.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
1.00
1.00
1.00
2.00
2.01
2.00
1.00
3.00
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5

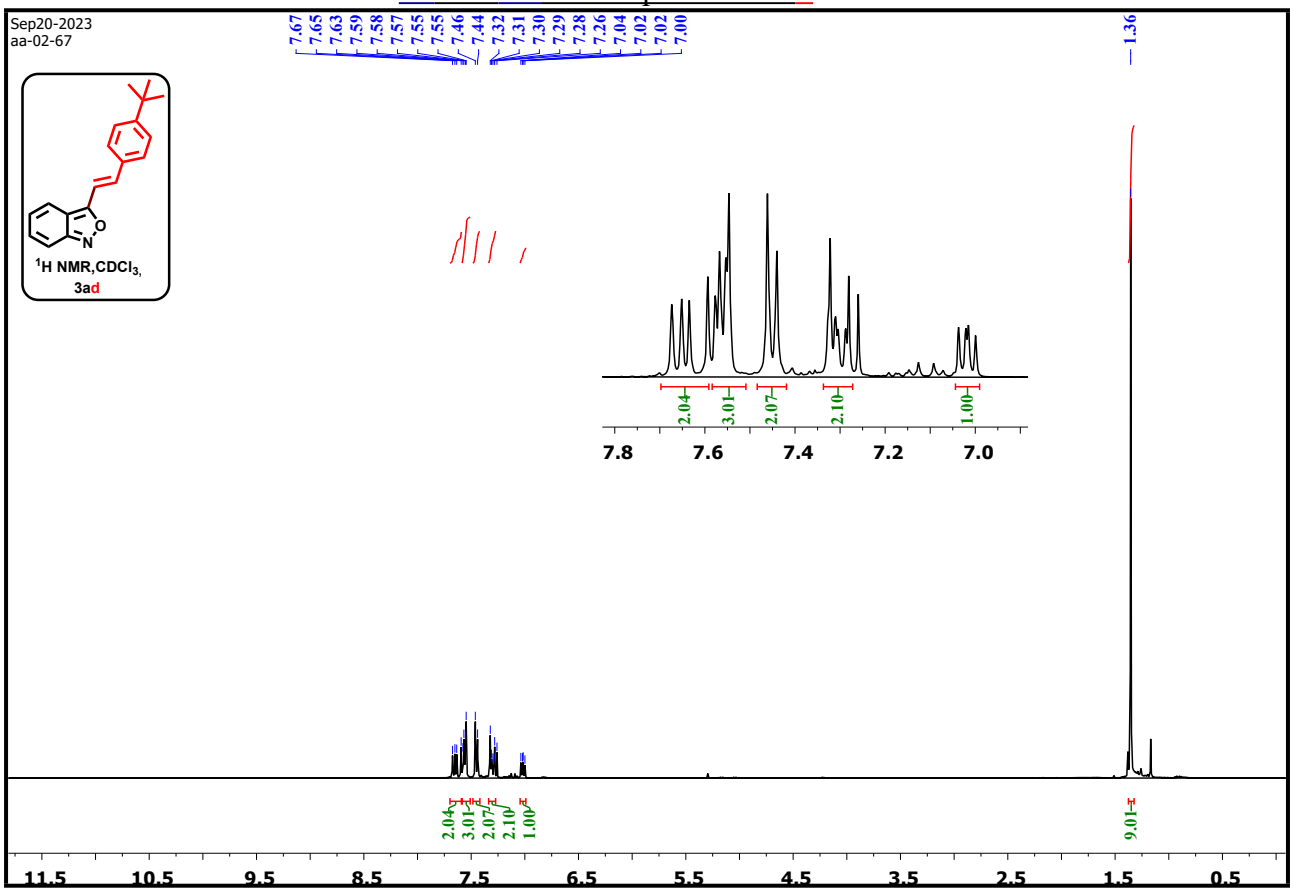

Sep21-2022
AA-02-32 (4-Me)
^{13}C NMR, CDCl$_3$,
3ab
163.80
157.42
139.72
135.19
132.95
130.86
129.71
127.22
123.86
119.90
115.56
115.25
111.12
77.32
77.00
76.68
21.42
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

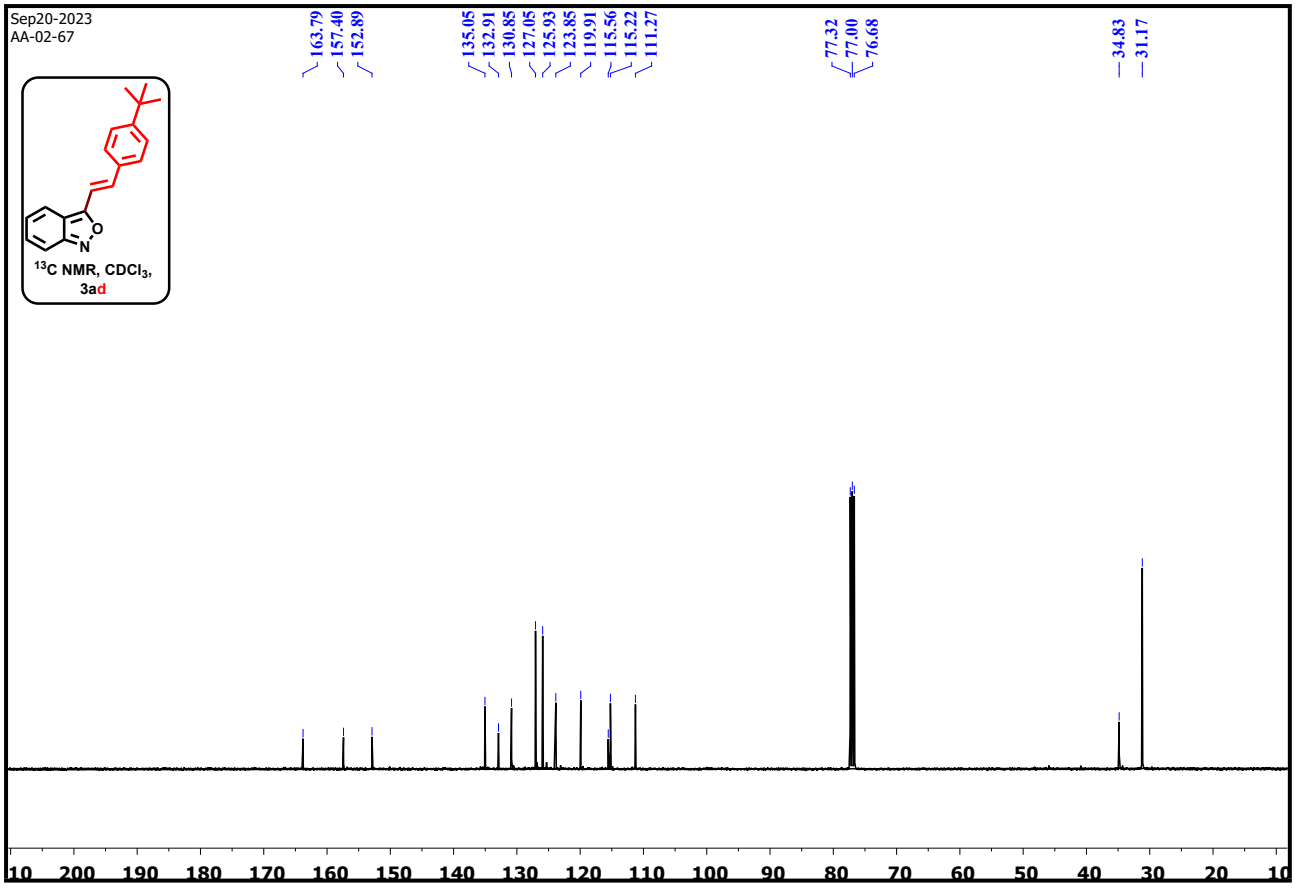
[1]H and [13]C NMR spectra of **3ac**



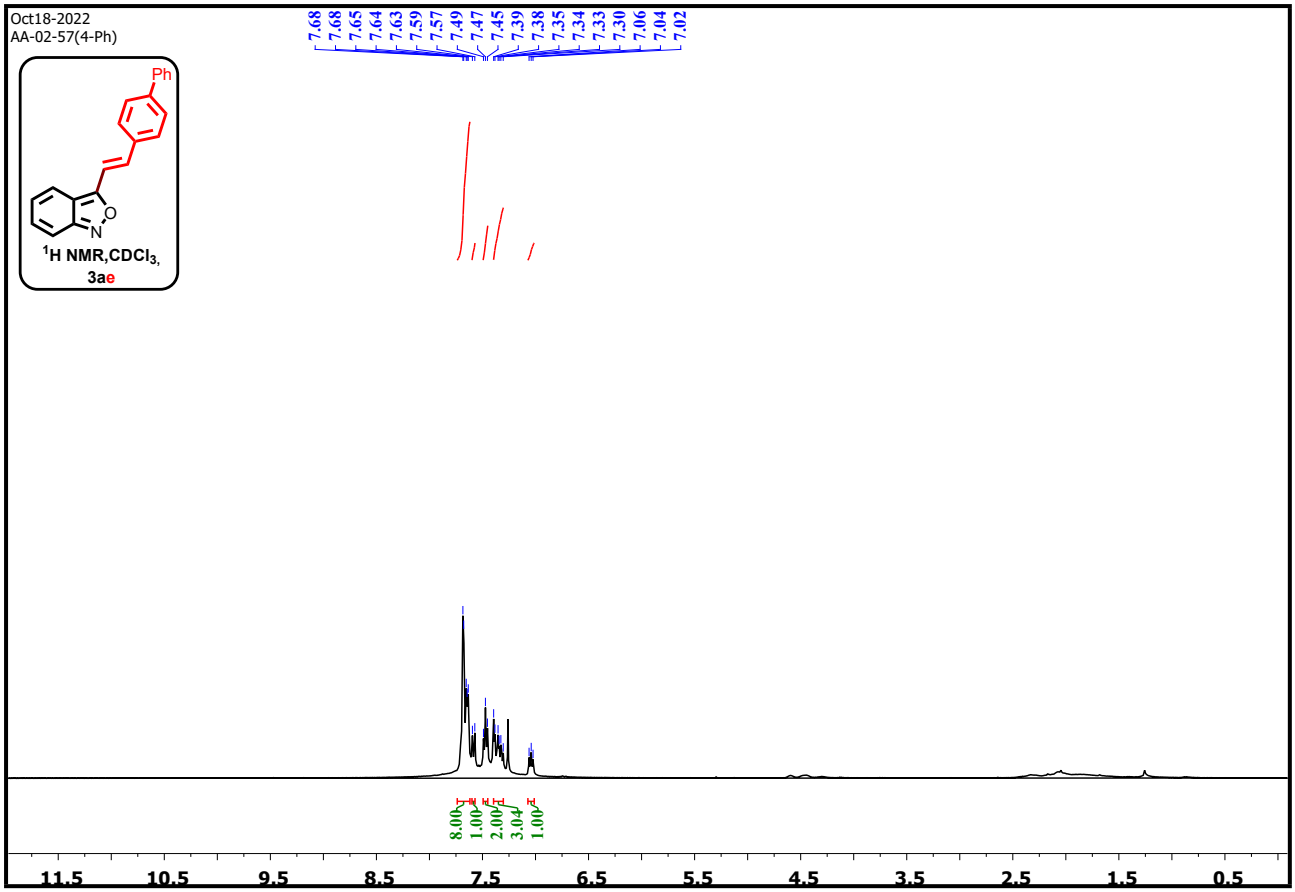


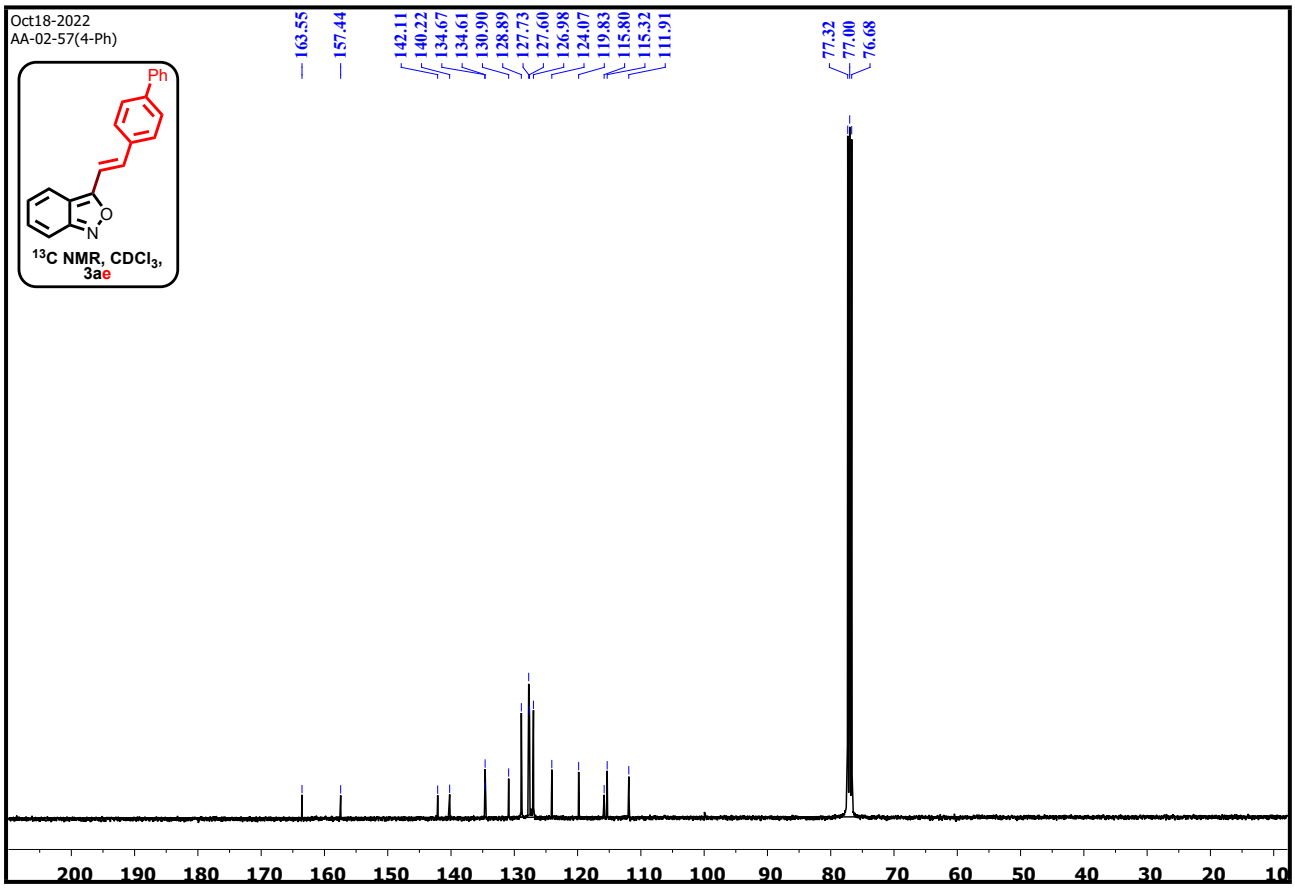
^{1}H and ^{13}C NMR spectra of **3ad**



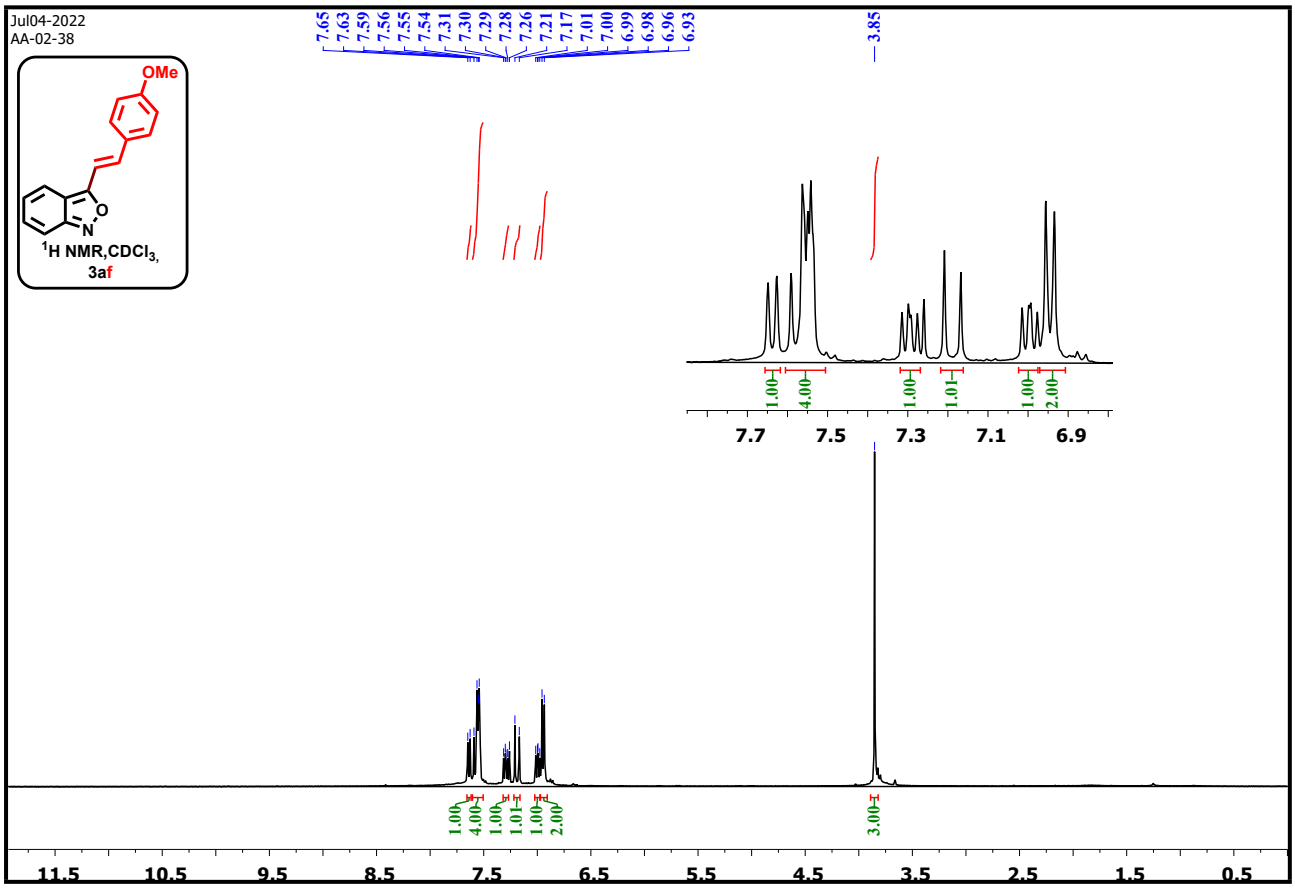


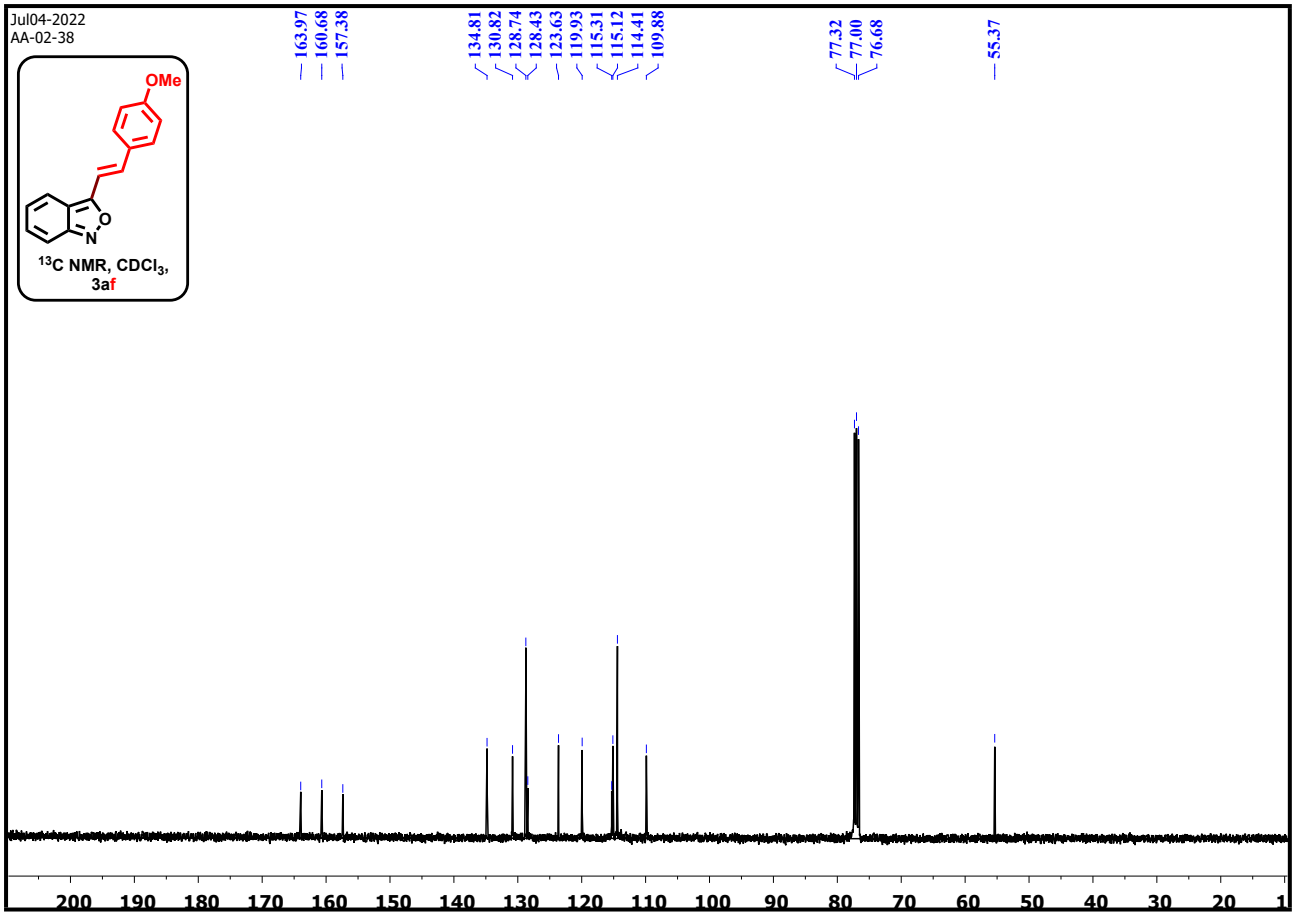
[1]H and [13]C NMR spectra of **3ae**


Oct18-2022
AA-02-57(4-Ph)
Ph
O
N
^{1}H NMR,CDCl$_3$,
3ae
7.68
7.68
7.65
7.64
7.63
7.59
7.57
7.49
7.47
7.45
7.39
7.38
7.35
7.34
7.33
7.30
7.06
7.04
7.02
8.00
1.00
2.00
3.04
1.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

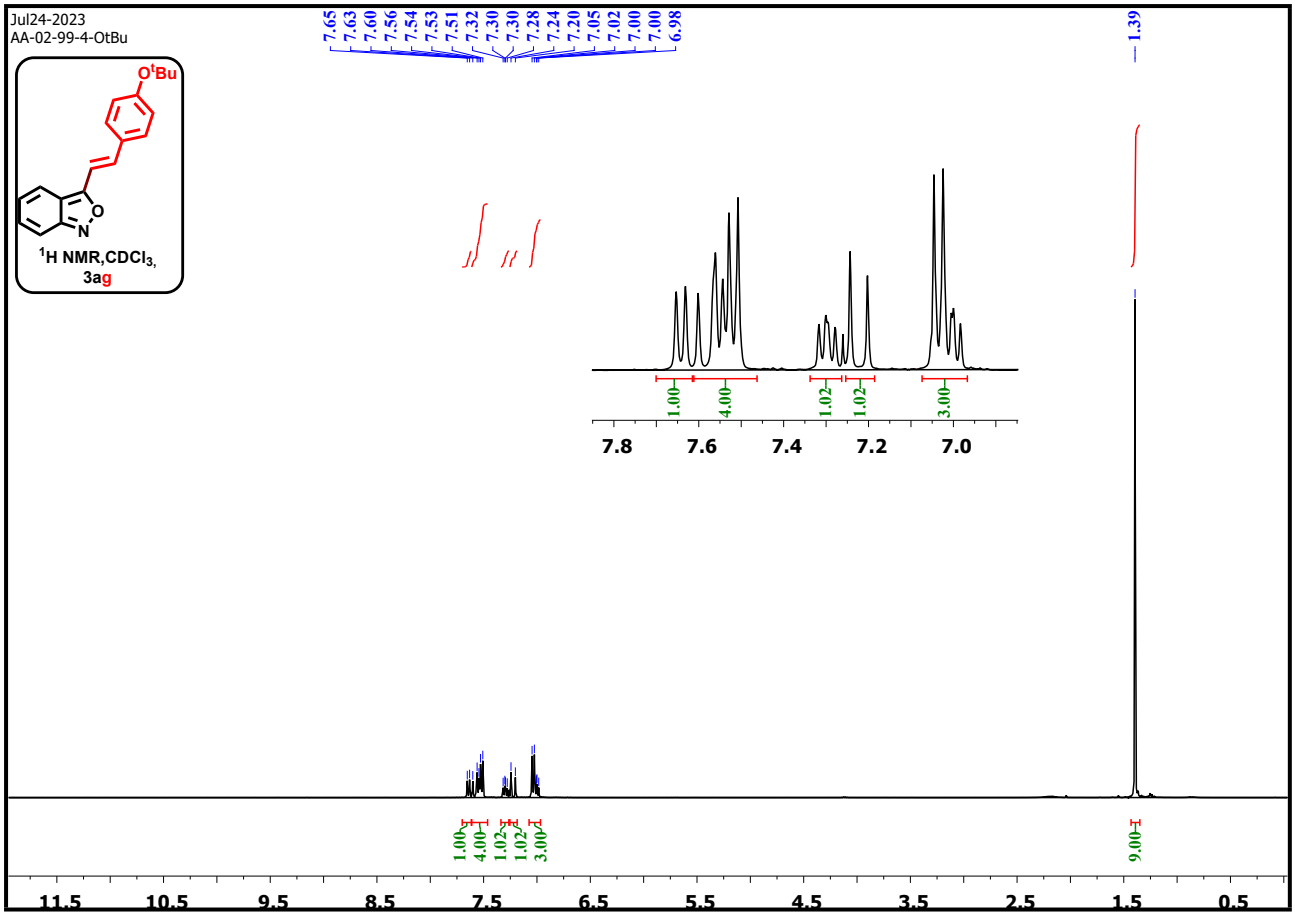

Oct18-2022
AA-02-57(4-Ph)
Ph
O
N
^{13}C NMR, CDCl$_3$,
3ae
163.55
157.44
142.11
140.22
134.67
134.61
130.90
128.89
127.73
127.60
126.98
124.07
119.83
115.80
115.32
111.91
77.32
77.00
76.68
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

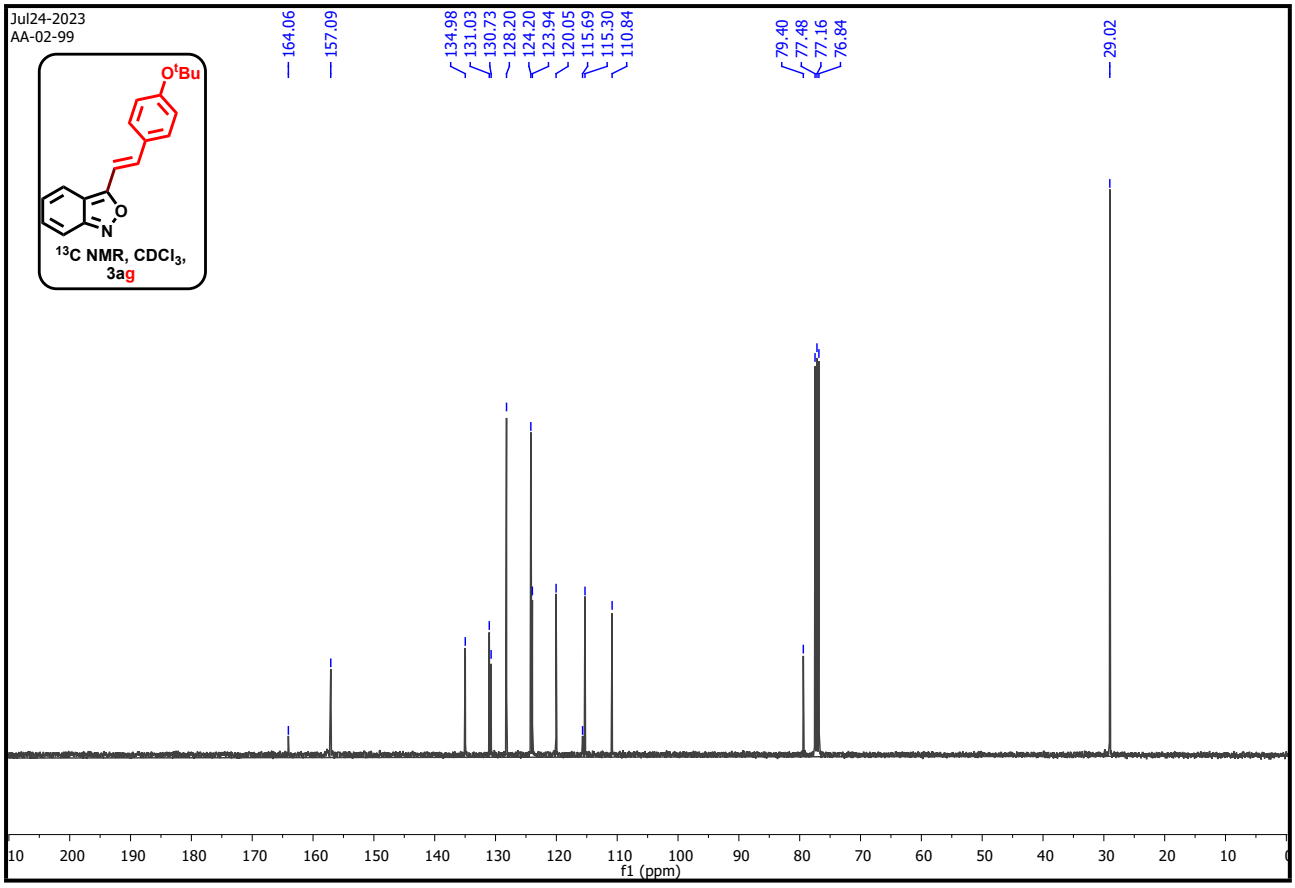
^{1}H and ^{13}C NMR spectra of **3af**



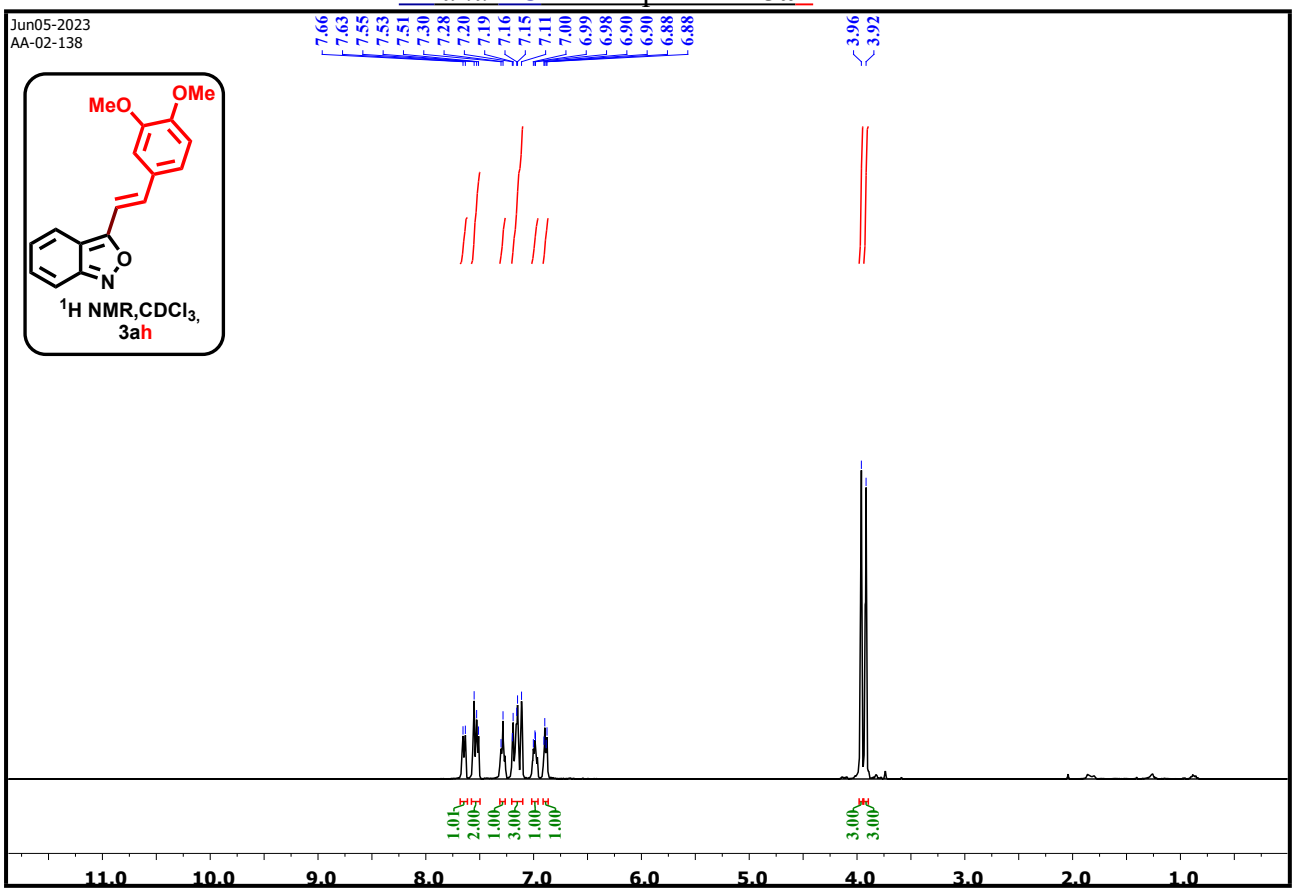


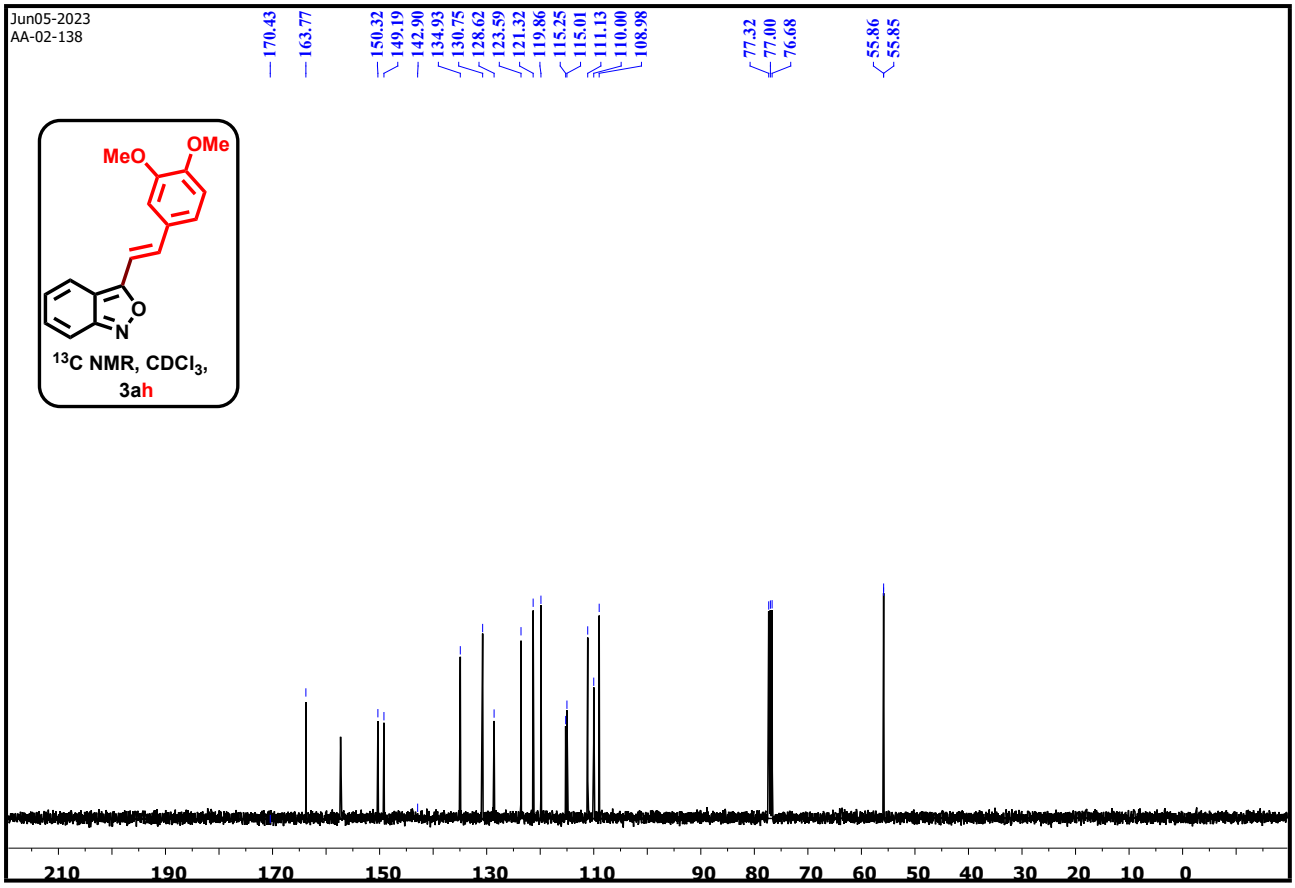
^{1}H and ^{13}C NMR spectra of **3ag**


Jul24-2023
AA-02-99-4-OtBu
OtBu
O
N
1H NMR,CDCl3,
3ag
7.65
7.63
7.60
7.56
7.54
7.53
7.51
7.32
7.30
7.30
7.28
7.24
7.20
7.05
7.02
7.00
7.00
6.98
1.39
1.00
4.00
1.02
1.02
3.00
7.8
7.6
7.4
7.2
7.0
1.00
4.00
1.02
1.02
3.00
9.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

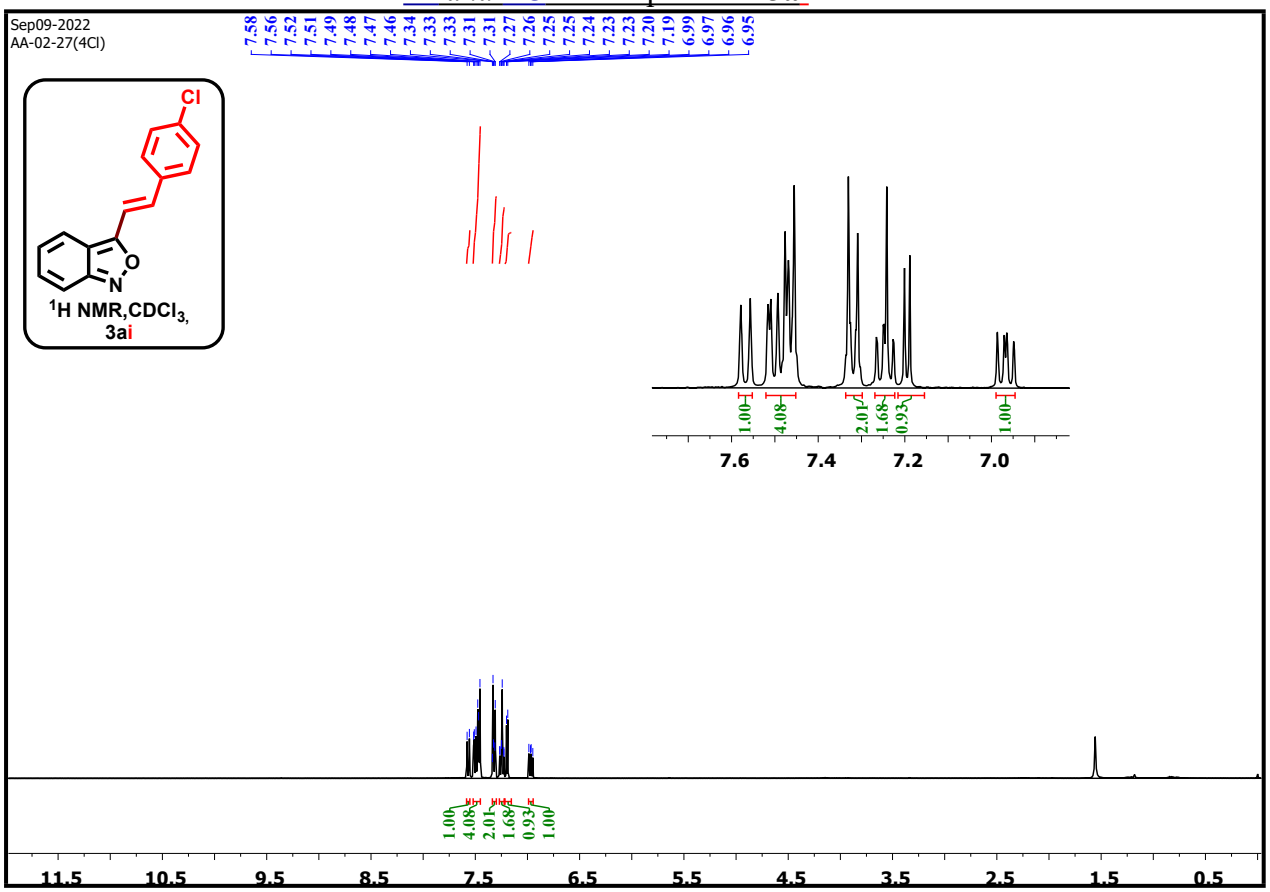

Jul24-2023
AA-02-99
O^{t}Bu
O
N
^{13}C NMR, CDCl$_3$,
3ag
164.06
157.09
134.98
131.03
130.73
128.20
124.20
123.94
120.05
115.69
115.30
110.84
79.40
77.48
77.16
76.84
29.02
f1 (ppm)

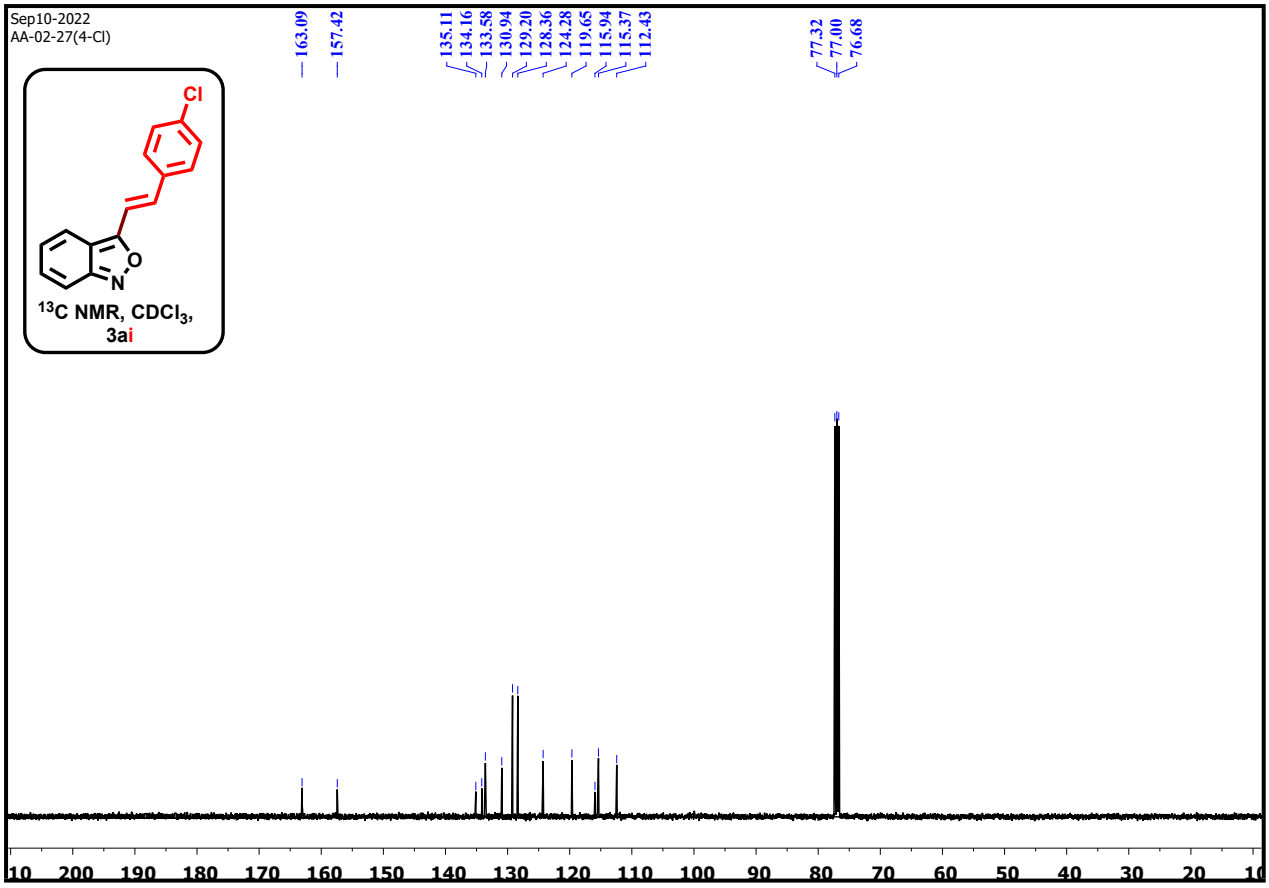
^{1}H and ^{13}C NMR spectra of **3ah**



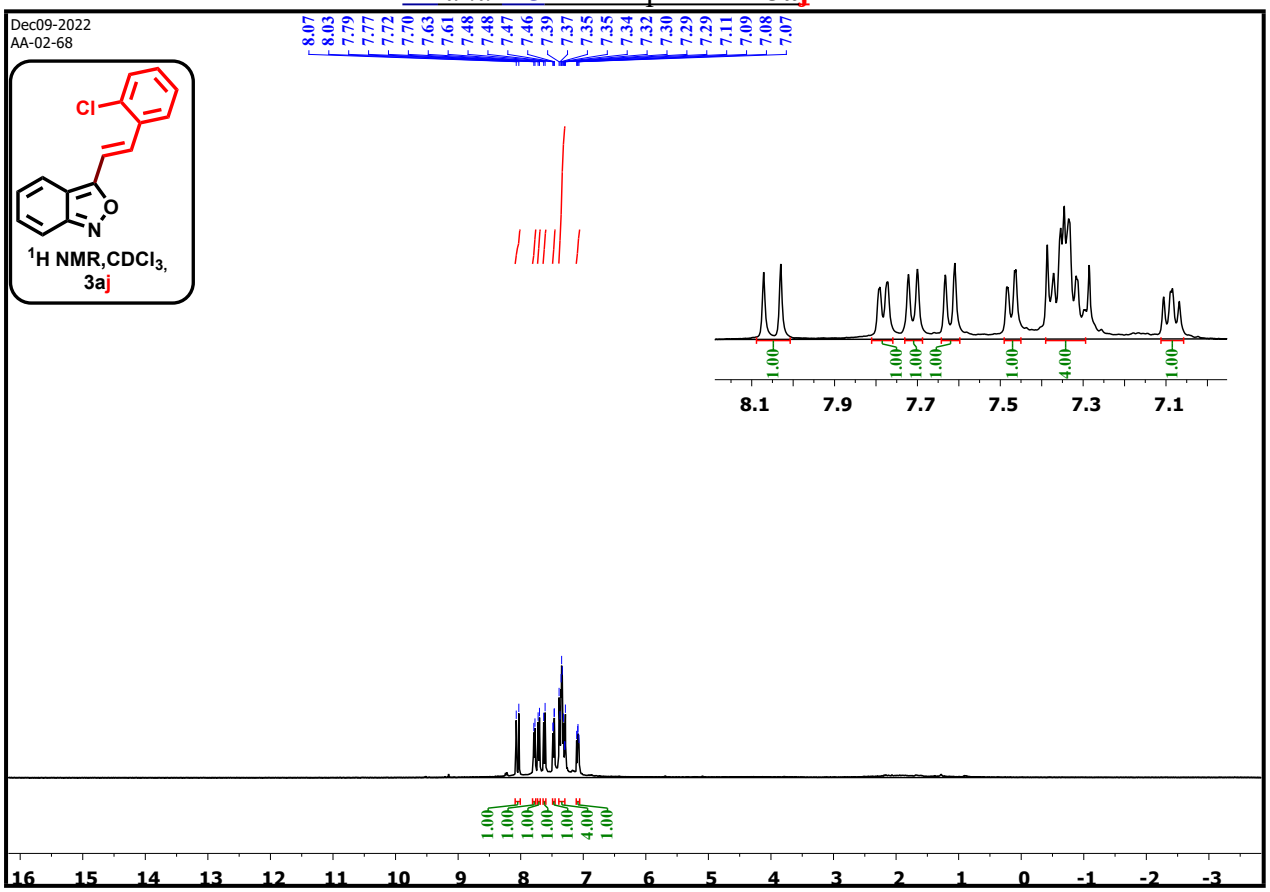

Jun05-2023
AA-02-138
170.43
163.77
150.32
149.19
142.90
134.93
130.75
128.62
123.59
121.32
119.86
115.25
115.01
111.13
110.00
108.98
77.32
77.00
76.68
55.86
55.85
MeO
OMe
O
N
13C NMR, CDCl3,
3ah
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

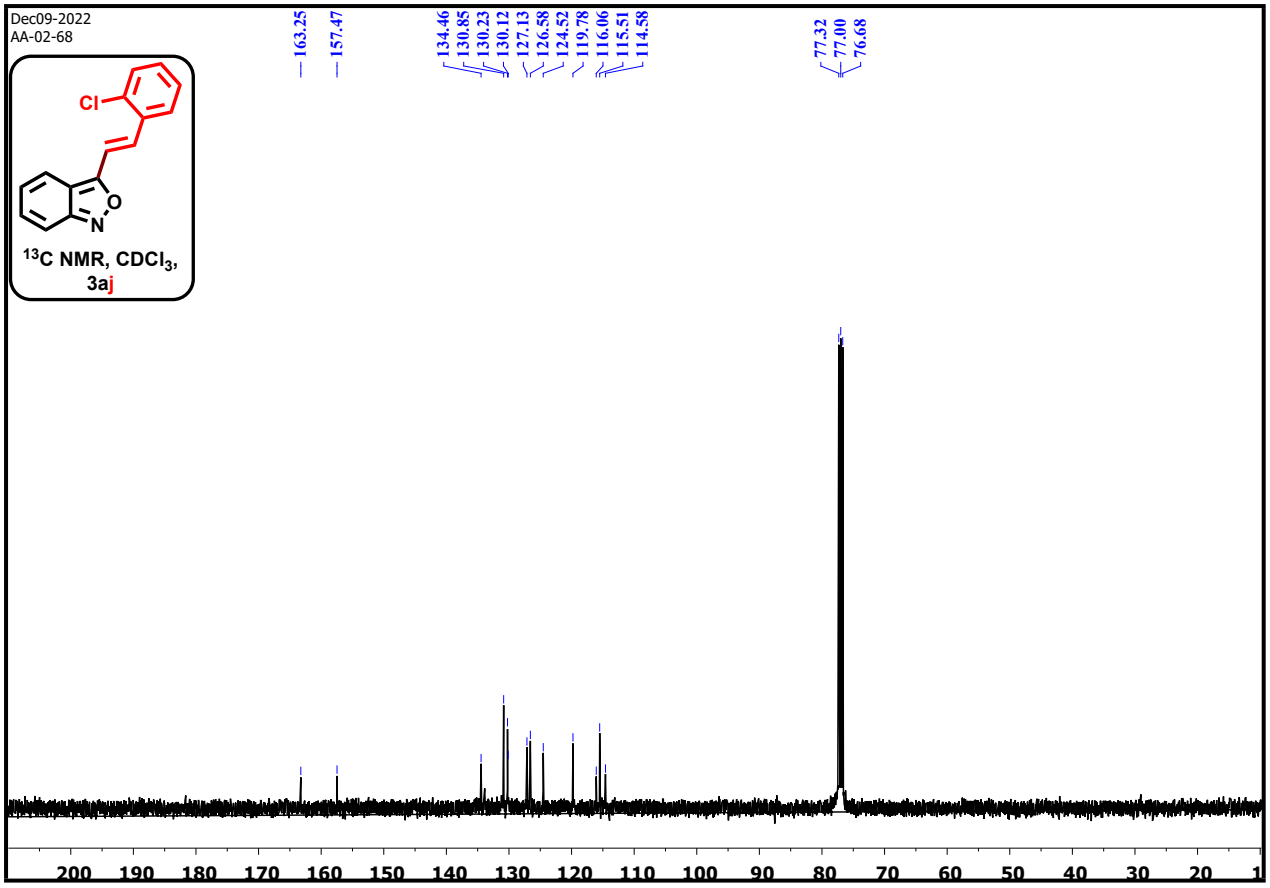
^{1}H and ^{13}C NMR spectra of **3ai**



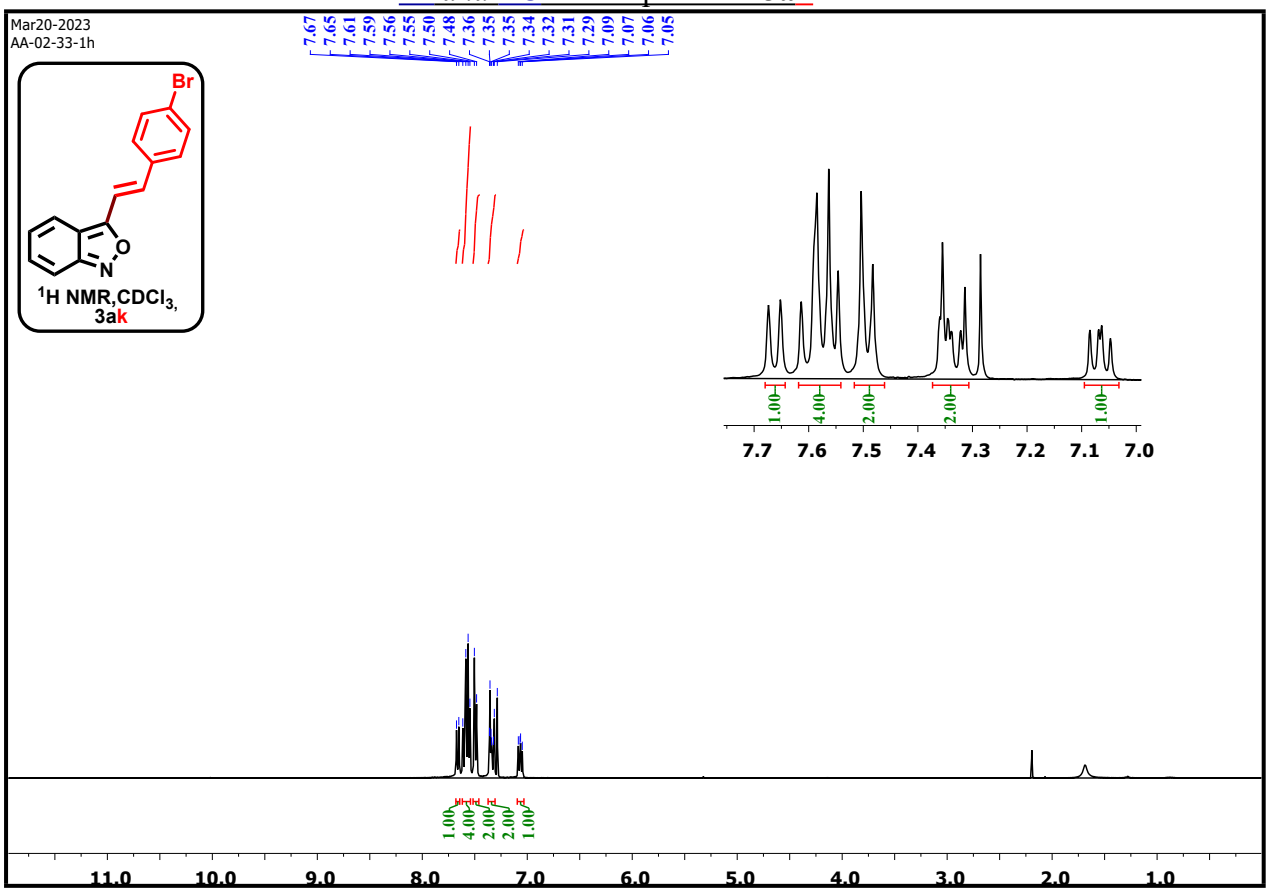

Sep10-2022
AA-02-27(4-Cl)
163.09
157.42
135.11
134.16
133.58
130.94
129.20
128.36
124.28
119.65
115.94
115.37
112.43
77.32
77.00
76.68
Cl
O
N
13C NMR, CDCl3,
3ai
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

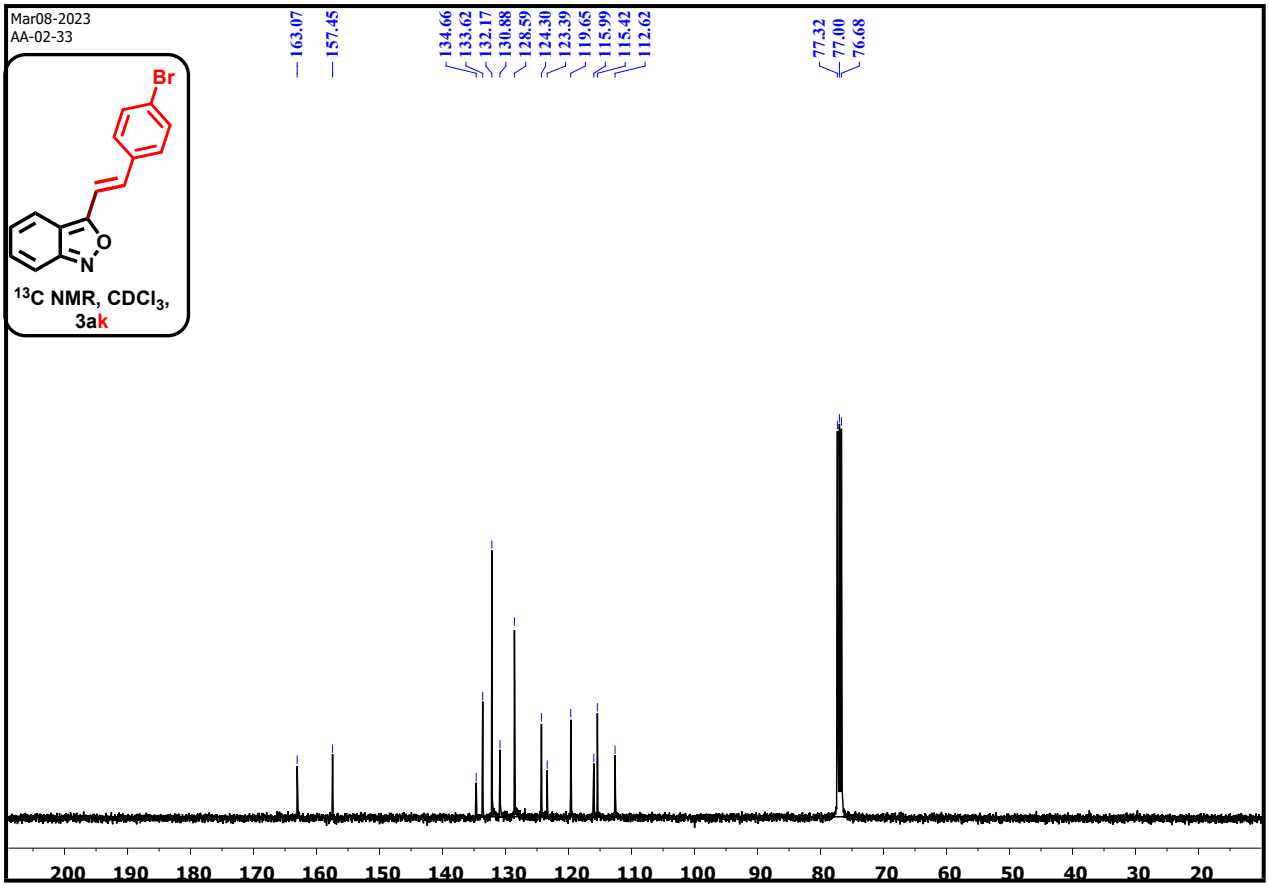
^{1}H and ^{13}C NMR spectra of **3aj**



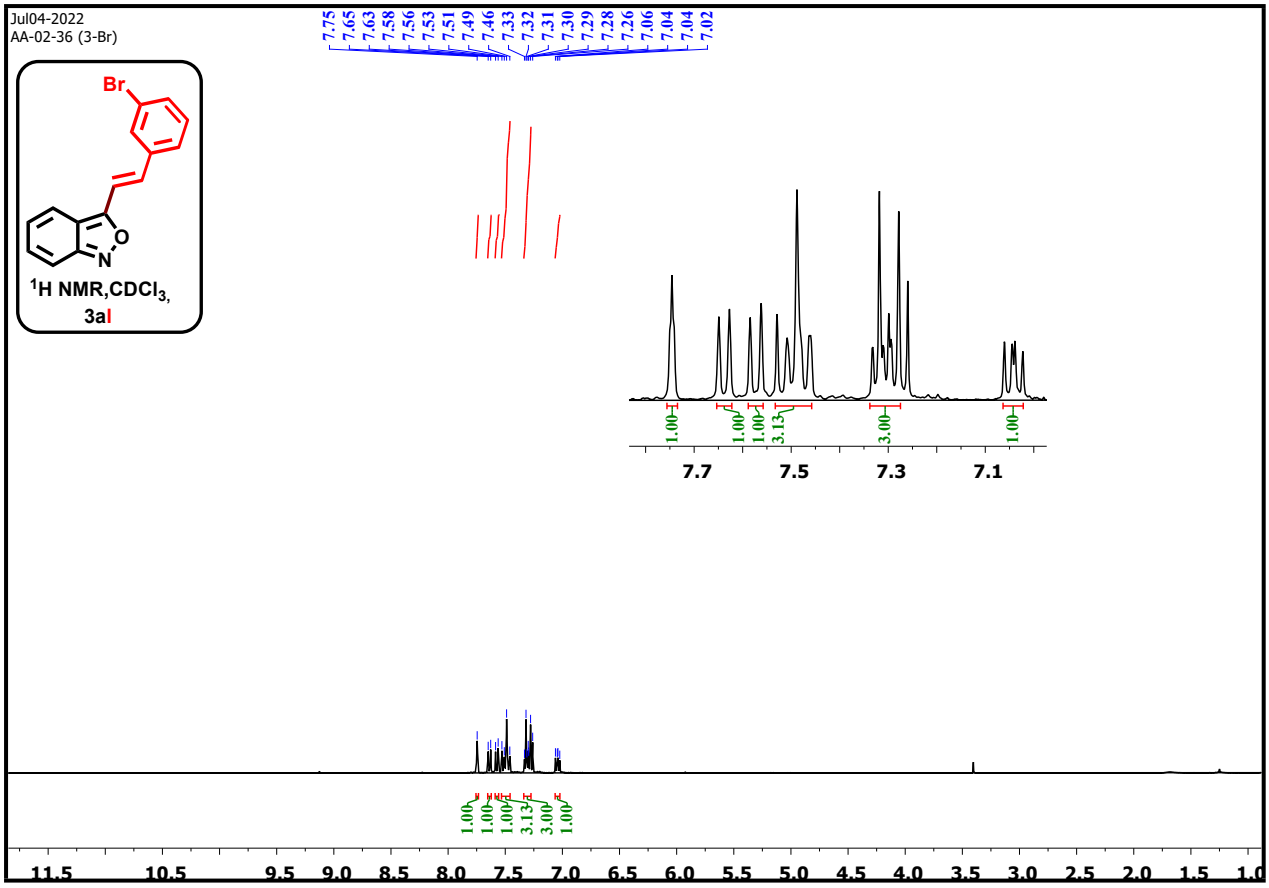

Dec09-2022
AA-02-68
Cl
O
N
^{13}C NMR, CDCl$_3$,
3aj
163.25
157.47
134.46
130.85
130.23
130.12
127.13
126.58
124.52
119.78
116.06
115.51
114.58
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1

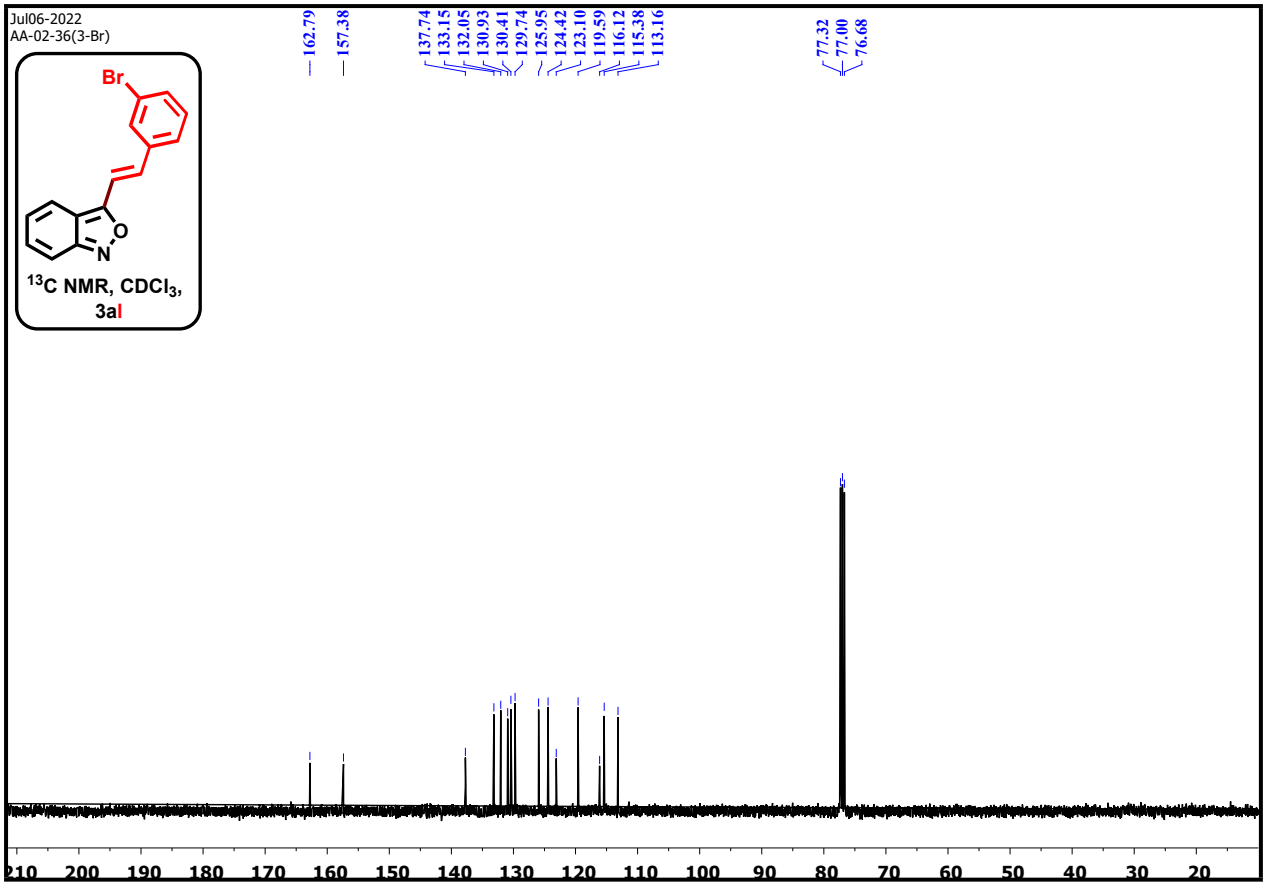
^{1}H and ^{13}C NMR spectra of **3ak**



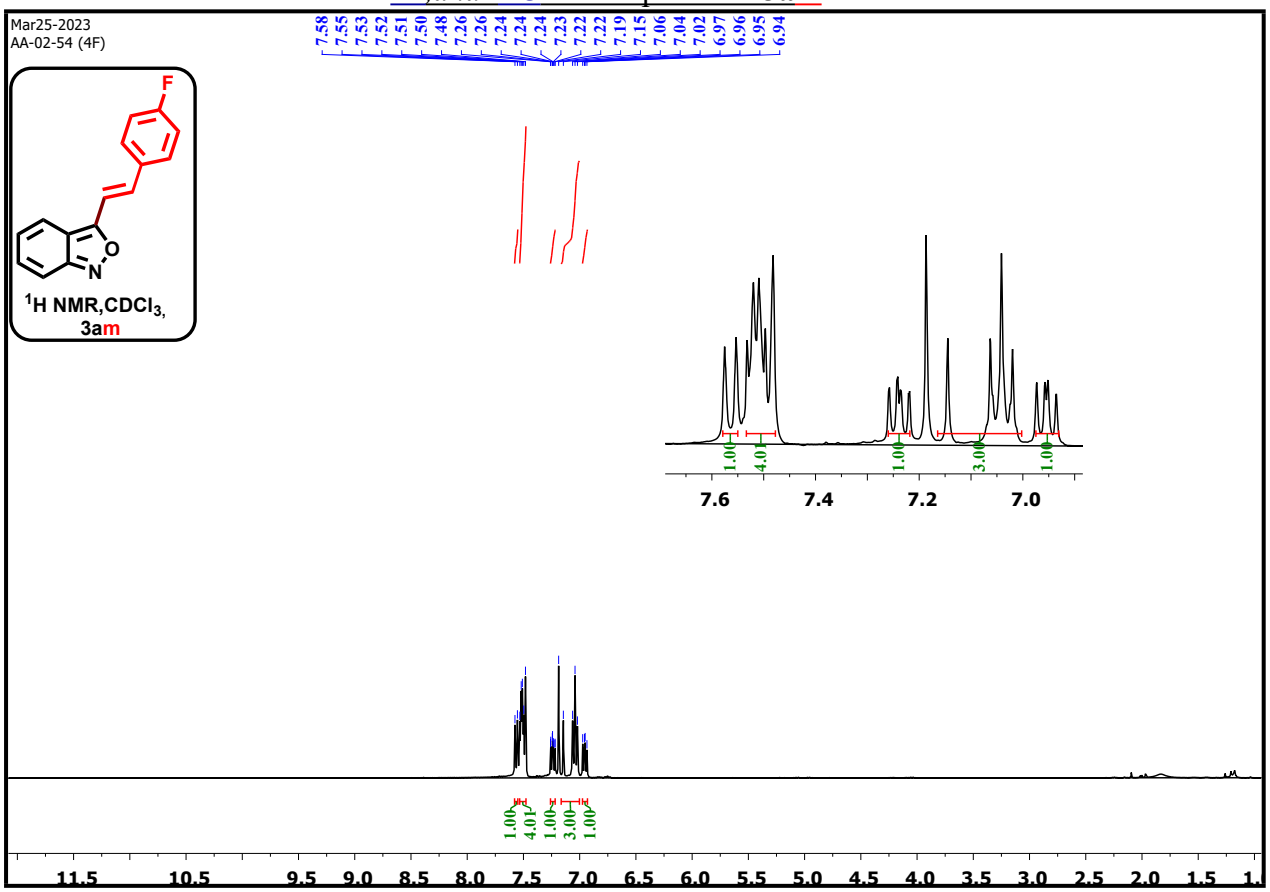


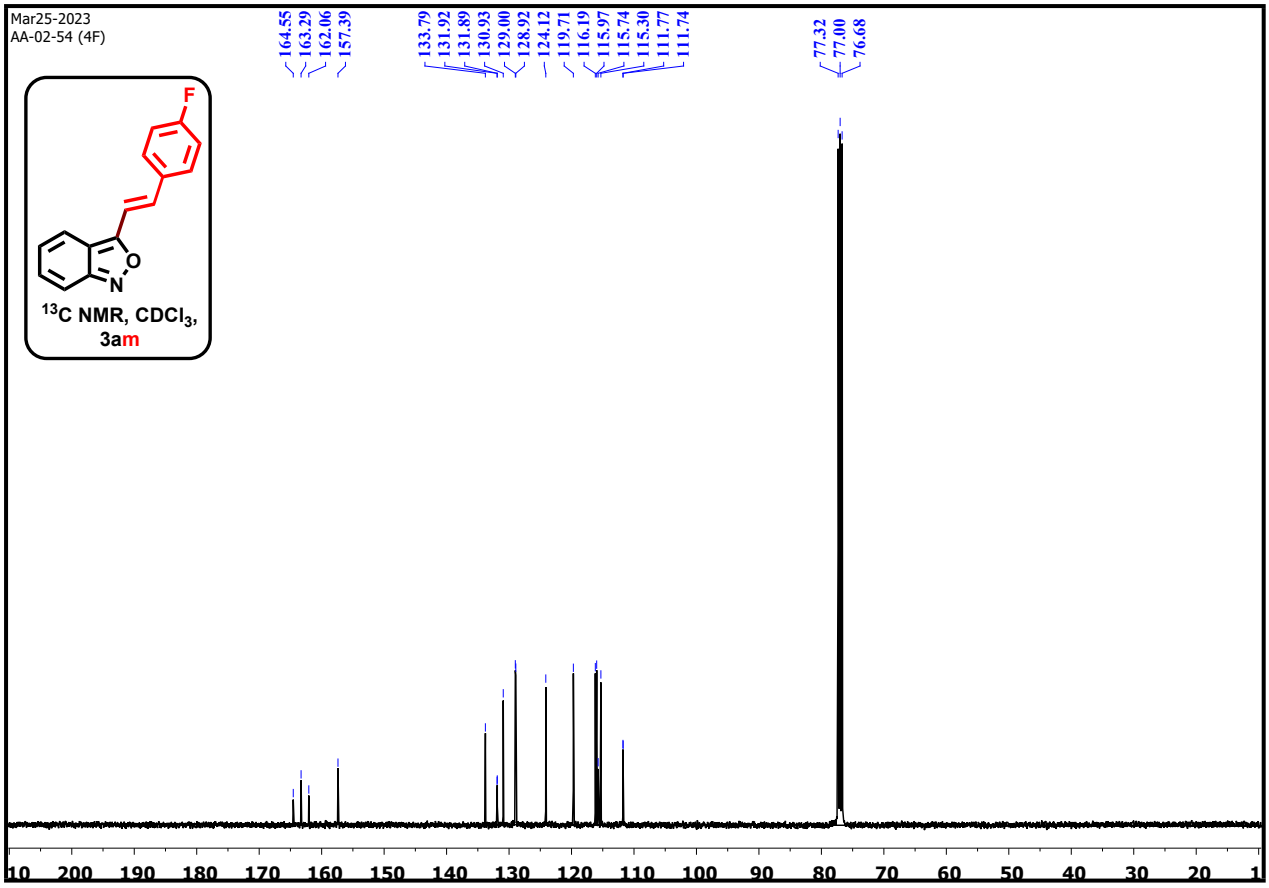
^{1}H and ^{13}C NMR spectra of **3al**


Jul04-2022
AA-02-36 (3-Br)
Br
O
N
^{1}H NMR,CDCl$_3$,
3al
7.75
7.65
7.63
7.58
7.56
7.53
7.51
7.49
7.46
7.33
7.32
7.31
7.30
7.29
7.28
7.26
7.06
7.04
7.04
7.02
1.00
1.00
1.00
3.13
3.00
1.00
7.7
7.5
7.3
7.1
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

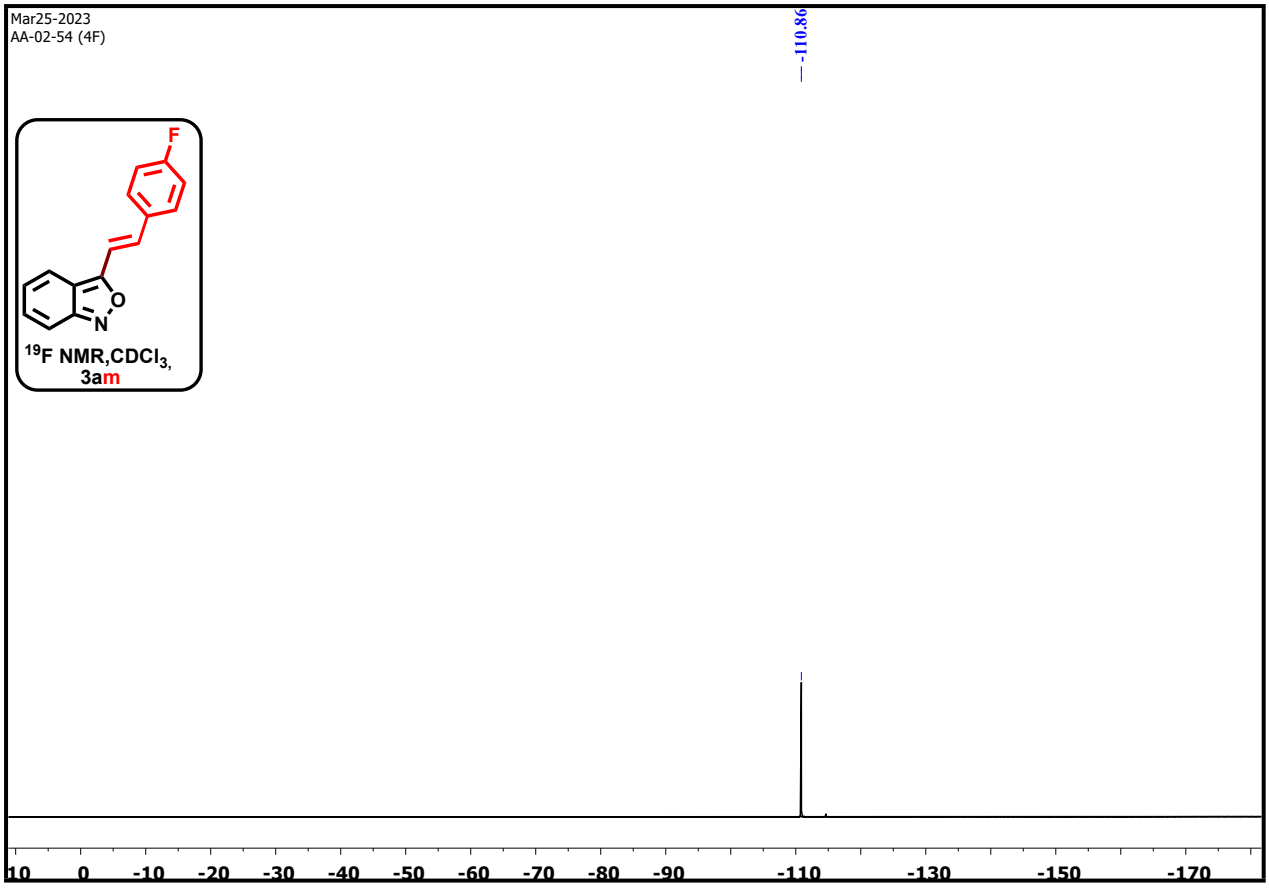

Jul06-2022
AA-02-36(3-Br)
Br
O
N
^{13}C NMR, CDCl$_3$,
3al
162.79
157.38
137.74
133.15
132.05
130.93
130.41
129.74
125.95
124.42
123.10
119.59
116.12
115.38
113.16
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

^{1}H,and ^{13}C NMR spectra of **3am**

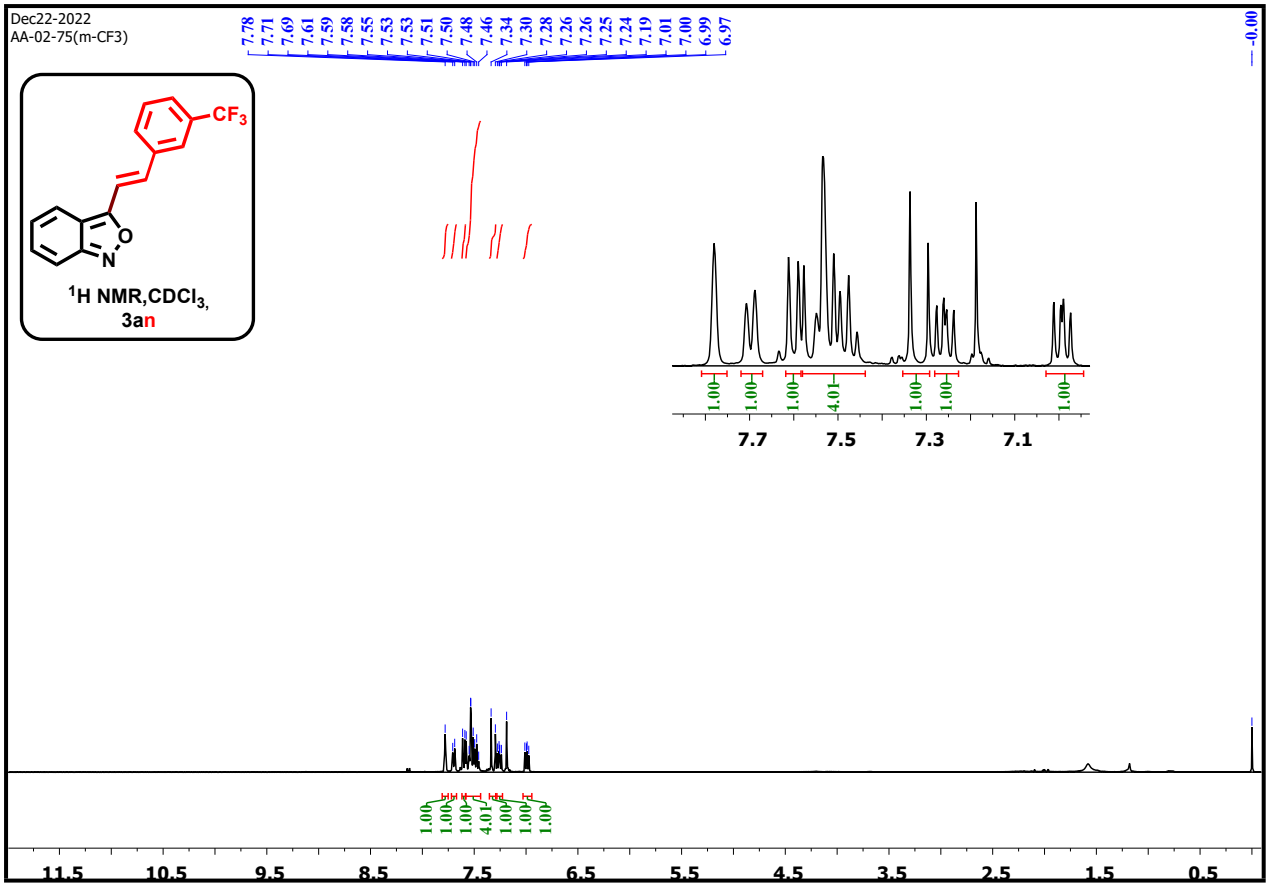


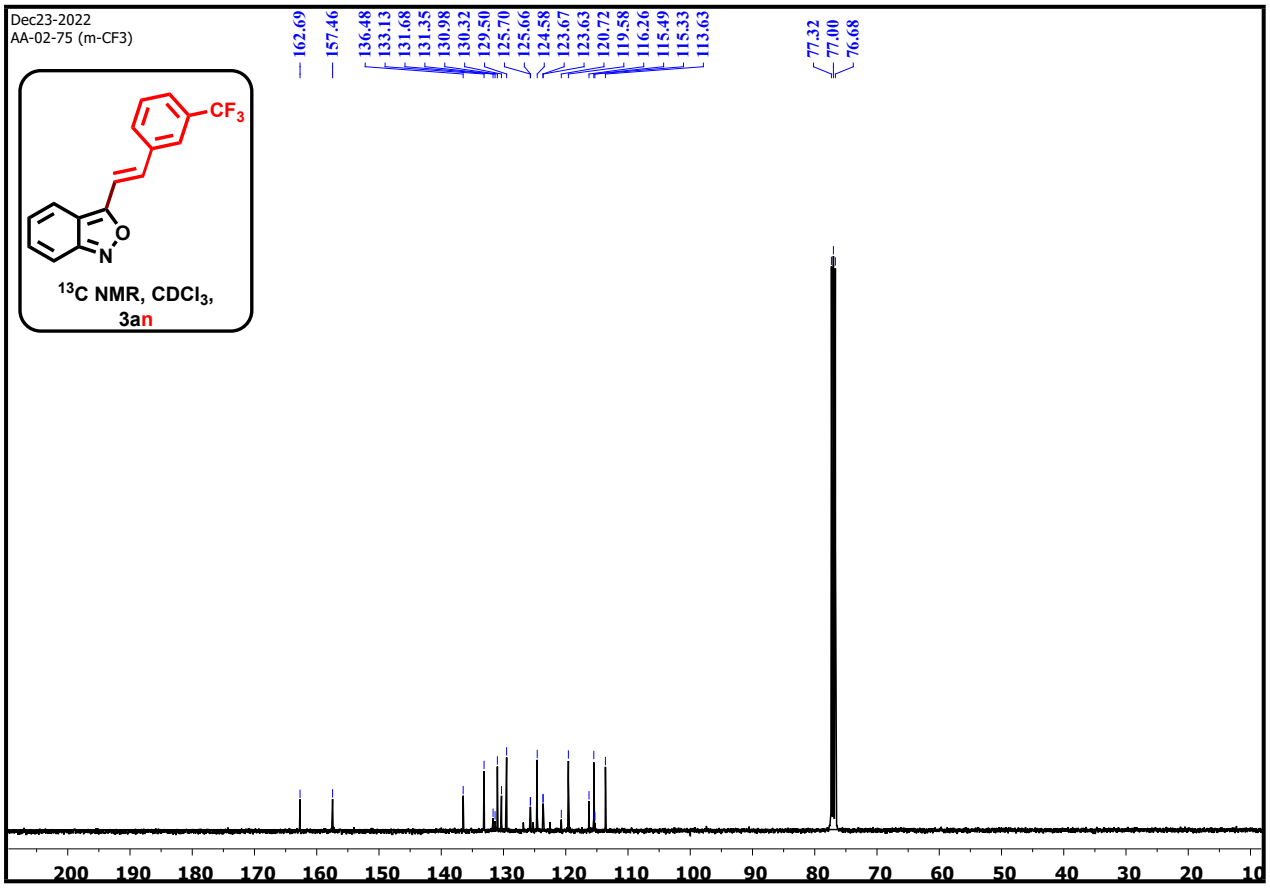


[19]F NMR spectra of **3am**

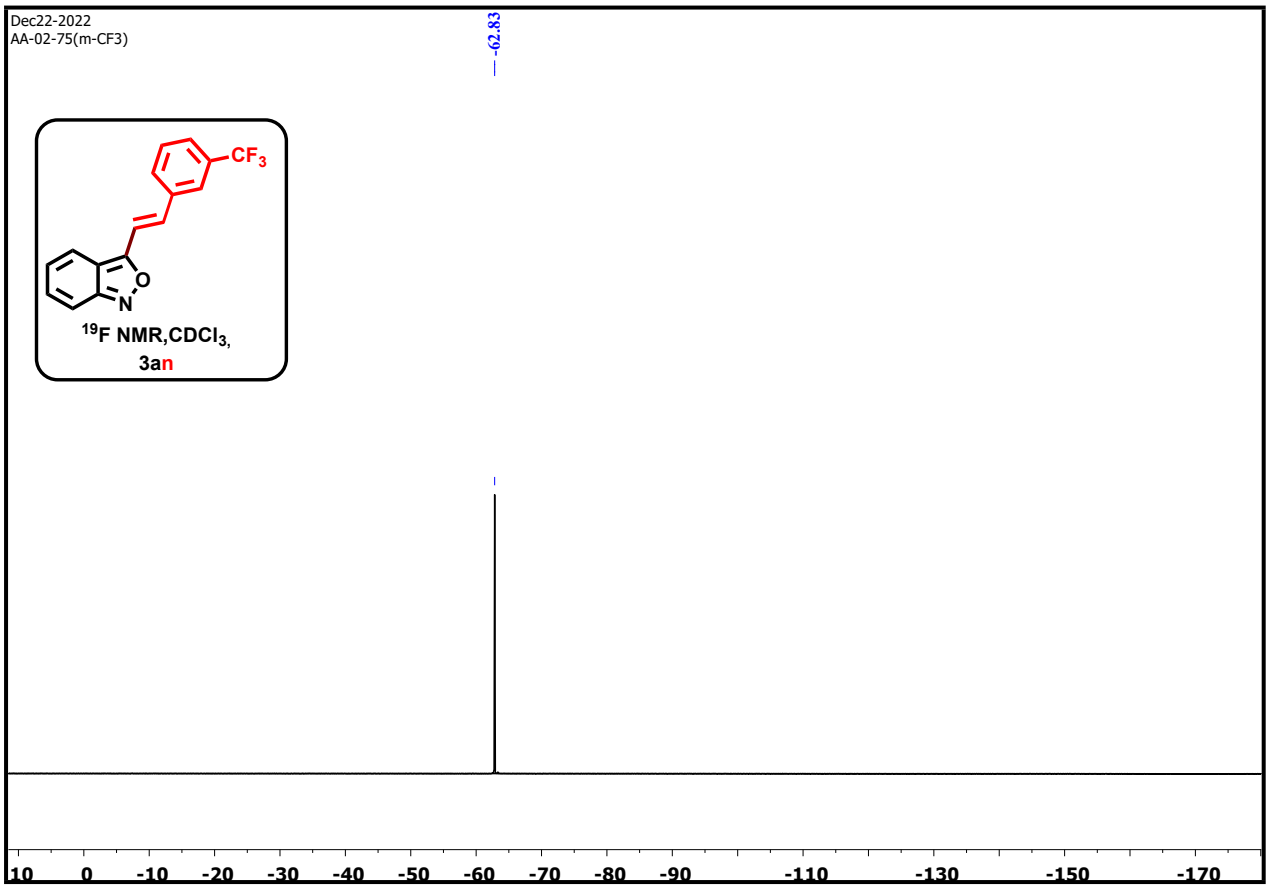


[1]H,and [13]C NMR spectra of **3an**

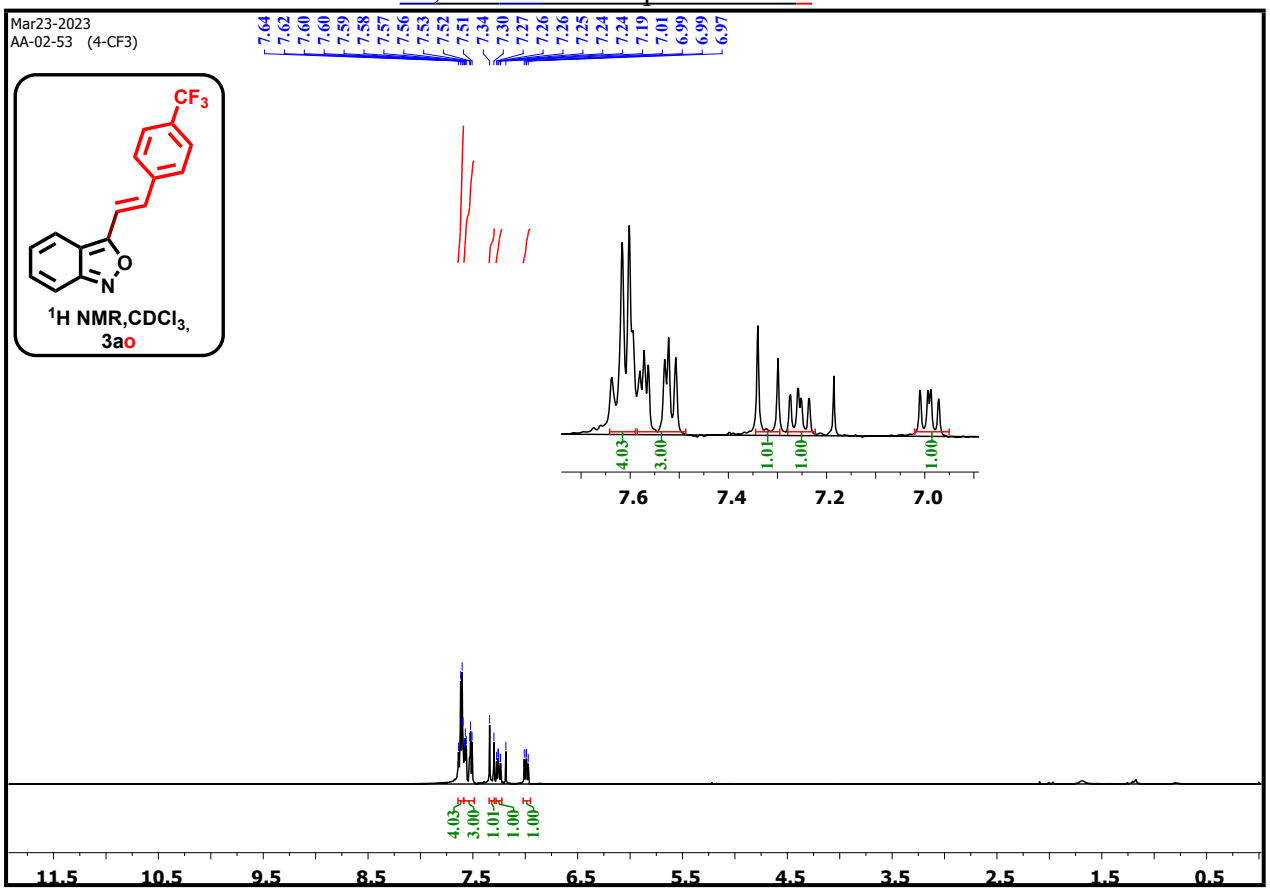

Dec22-2022
AA-02-75(m-CF3)
7.78 7.71 7.69 7.61 7.59 7.58 7.55 7.53 7.53 7.51 7.50 7.48 7.46 7.34 7.30 7.28 7.26 7.26 7.25 7.24 7.19 7.01 7.00 6.99 6.97
-0.00
CF3
O
N
1H NMR,CDCl3,
3an
1.00 1.00 1.00 4.01 1.00 1.00 1.00
7.7 7.5 7.3 7.1
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5

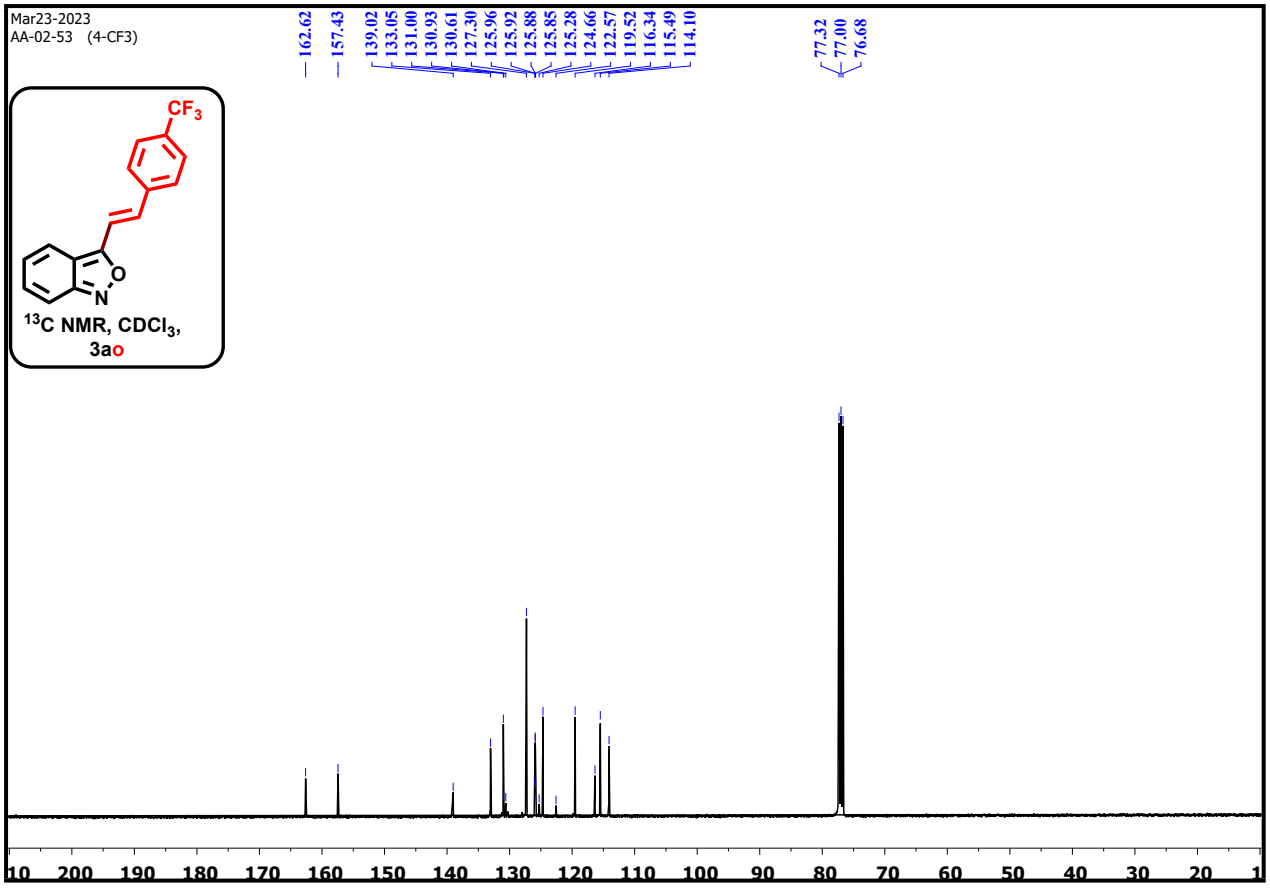

Dec23-2022
AA-02-75 (m-CF3)
162.69 157.46 136.48 133.13 131.68 131.35 130.98 130.32 129.50 125.70 125.66 124.58 123.67 123.63 120.72 119.58 116.26 115.49 115.33 113.63
77.32 77.00 76.68
CF3
O
N
13C NMR, CDCl3,
3an
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

^{19}F NMR spectra of **3an**



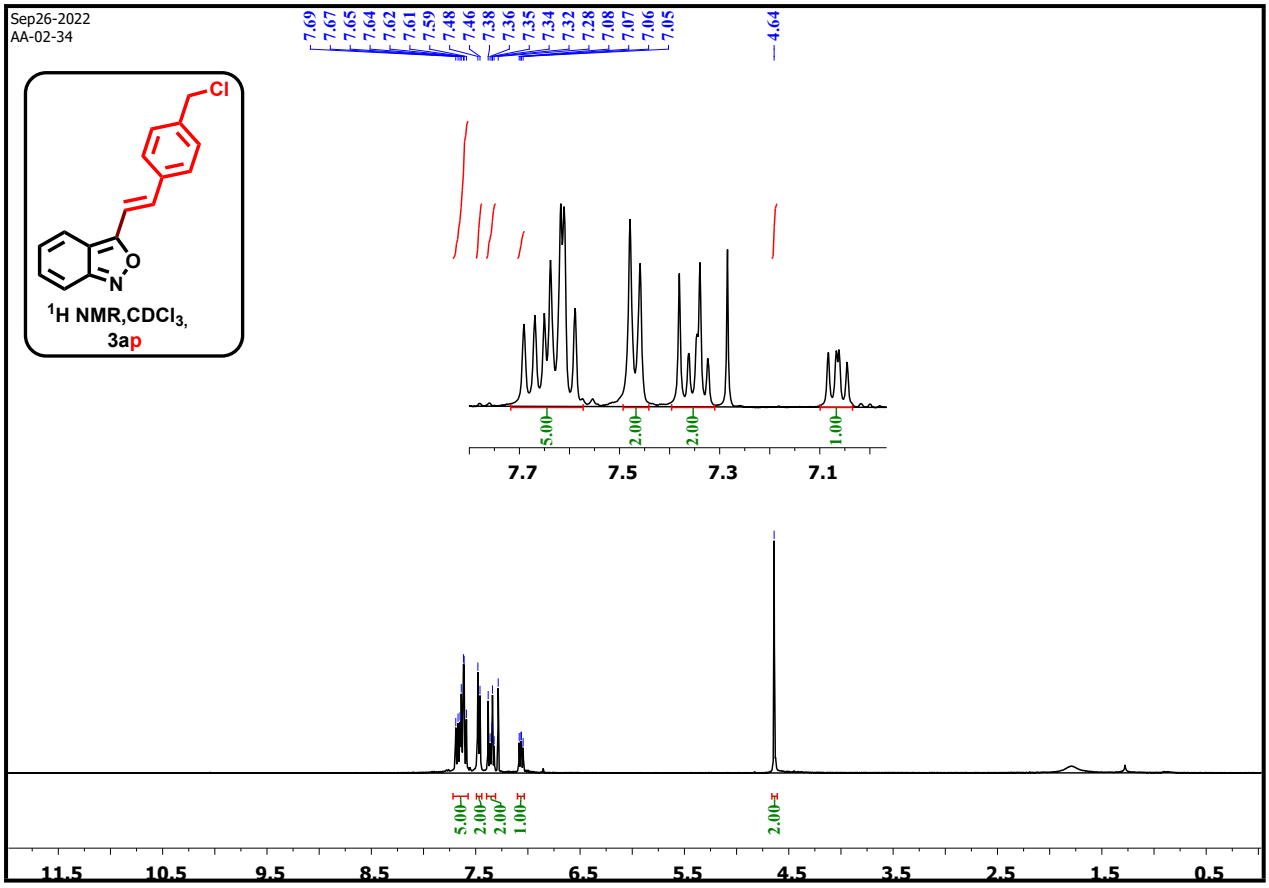
[1]H,and [13]C NMR spectra of **3ao**

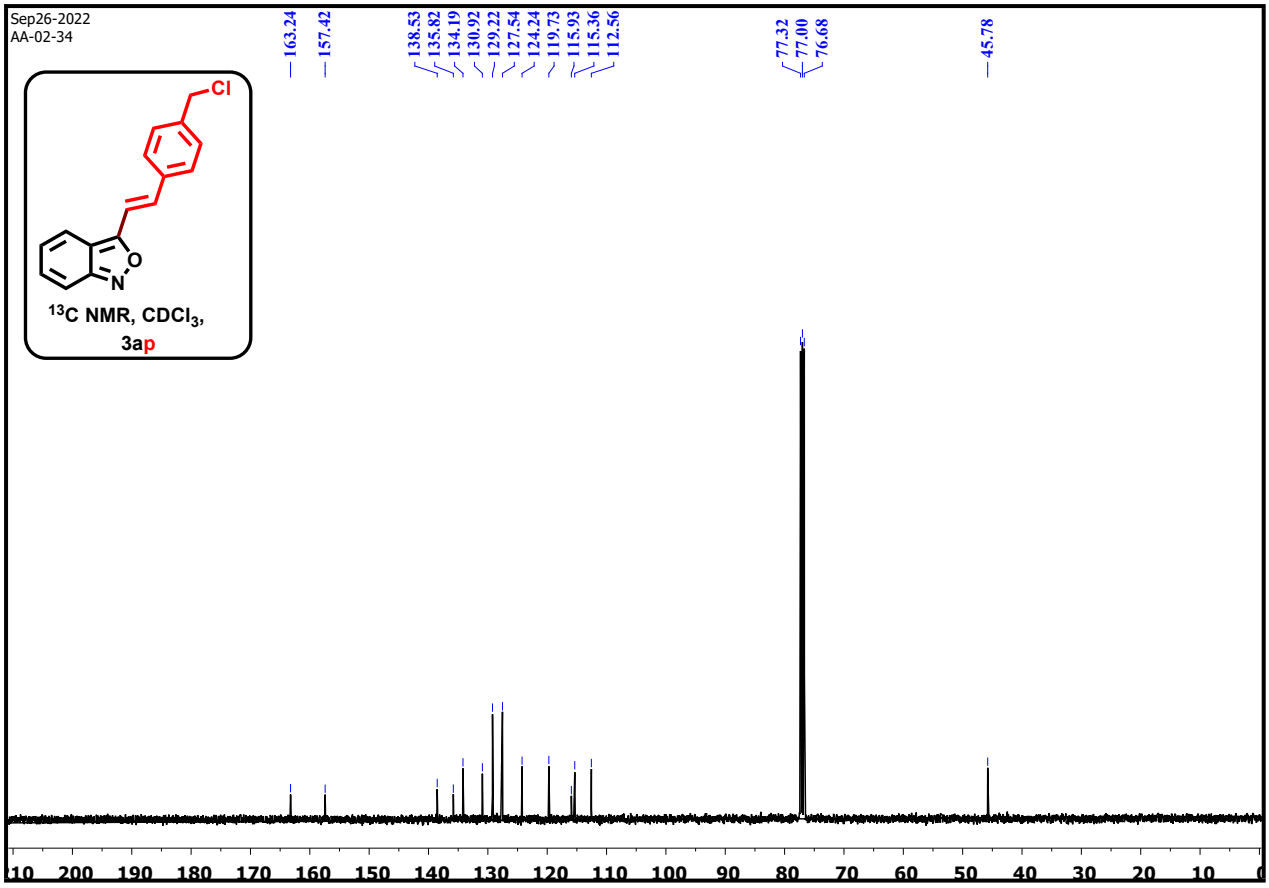




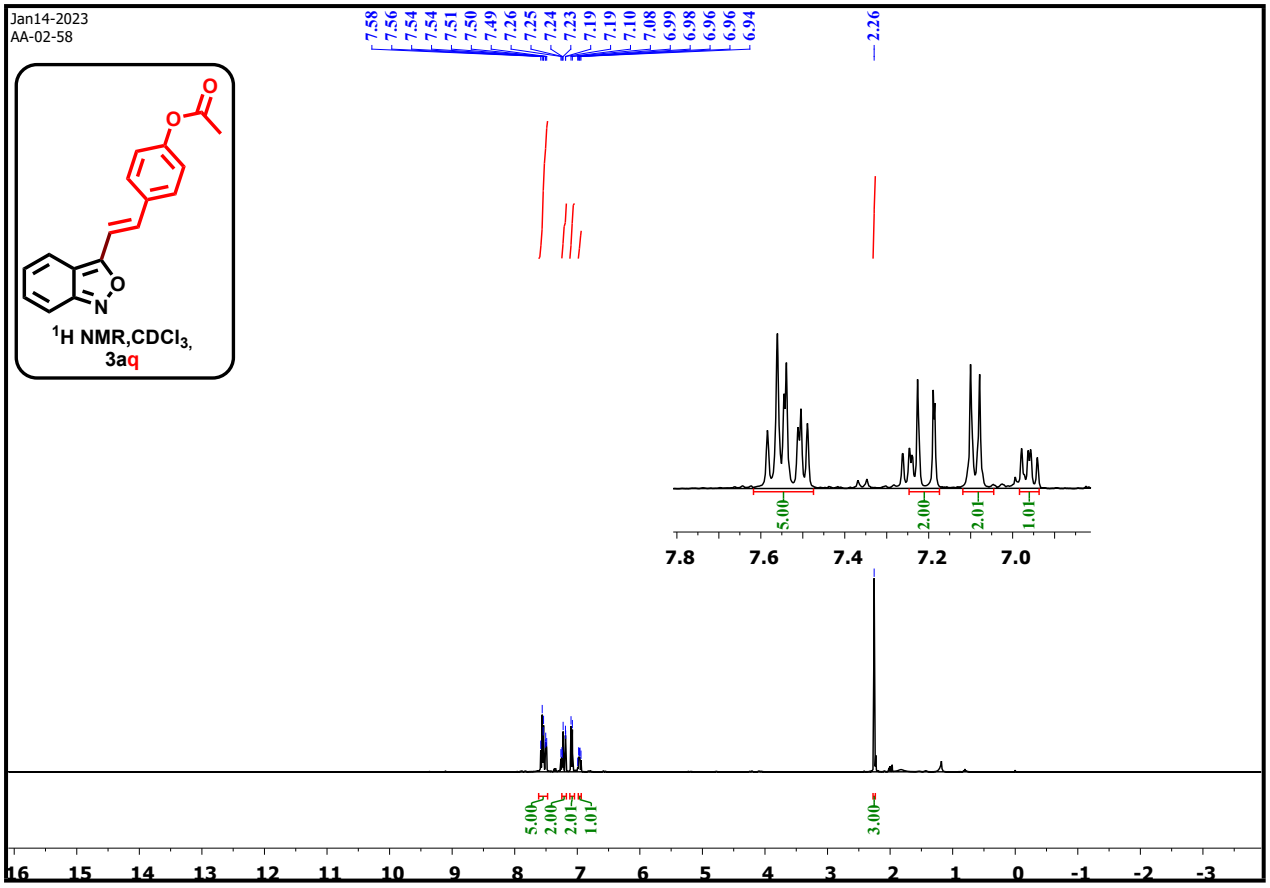
[19]F NMR spectra of **3ao**

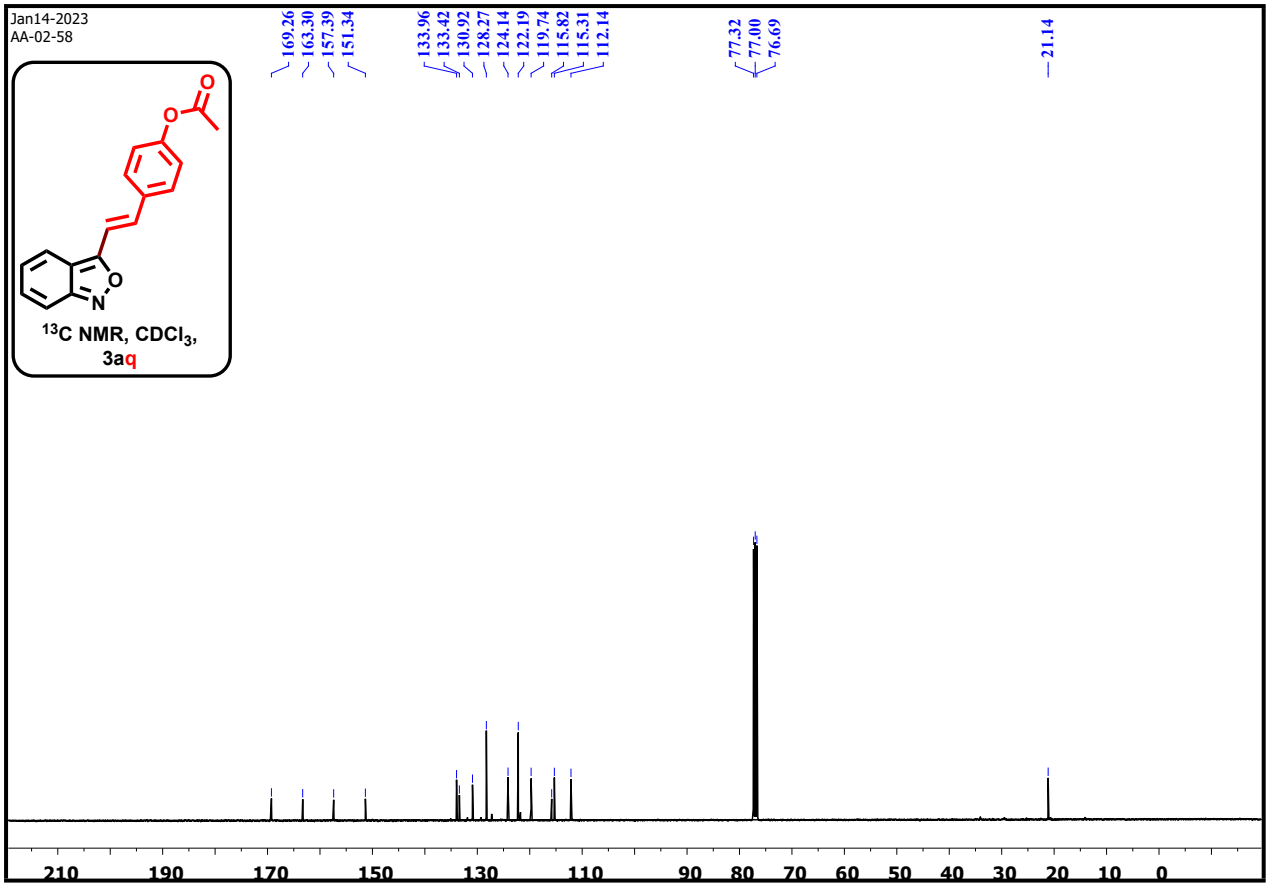
[1]H and [13]C NMR spectra of **3ap**


Sep26-2022
AA-02-34
7.69
7.67
7.65
7.64
7.62
7.61
7.59
7.48
7.46
7.38
7.36
7.35
7.34
7.32
7.28
7.08
7.07
7.06
7.05
4.64
Cl
O
N
^{1}H NMR,CDCl$_3$,
3ap
5.00
2.00
2.00
1.00
7.7
7.5
7.3
7.1
5.00
2.00
2.00
1.00
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

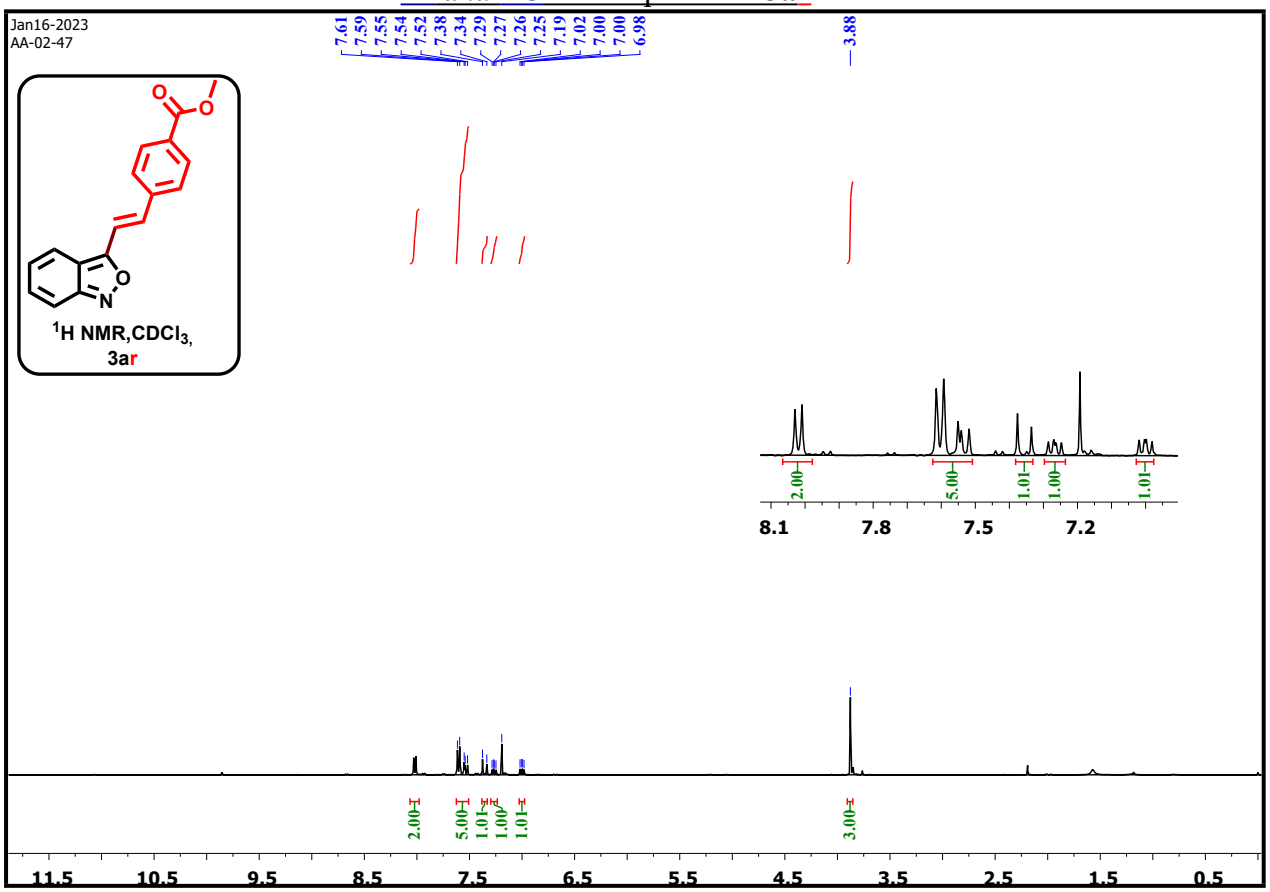


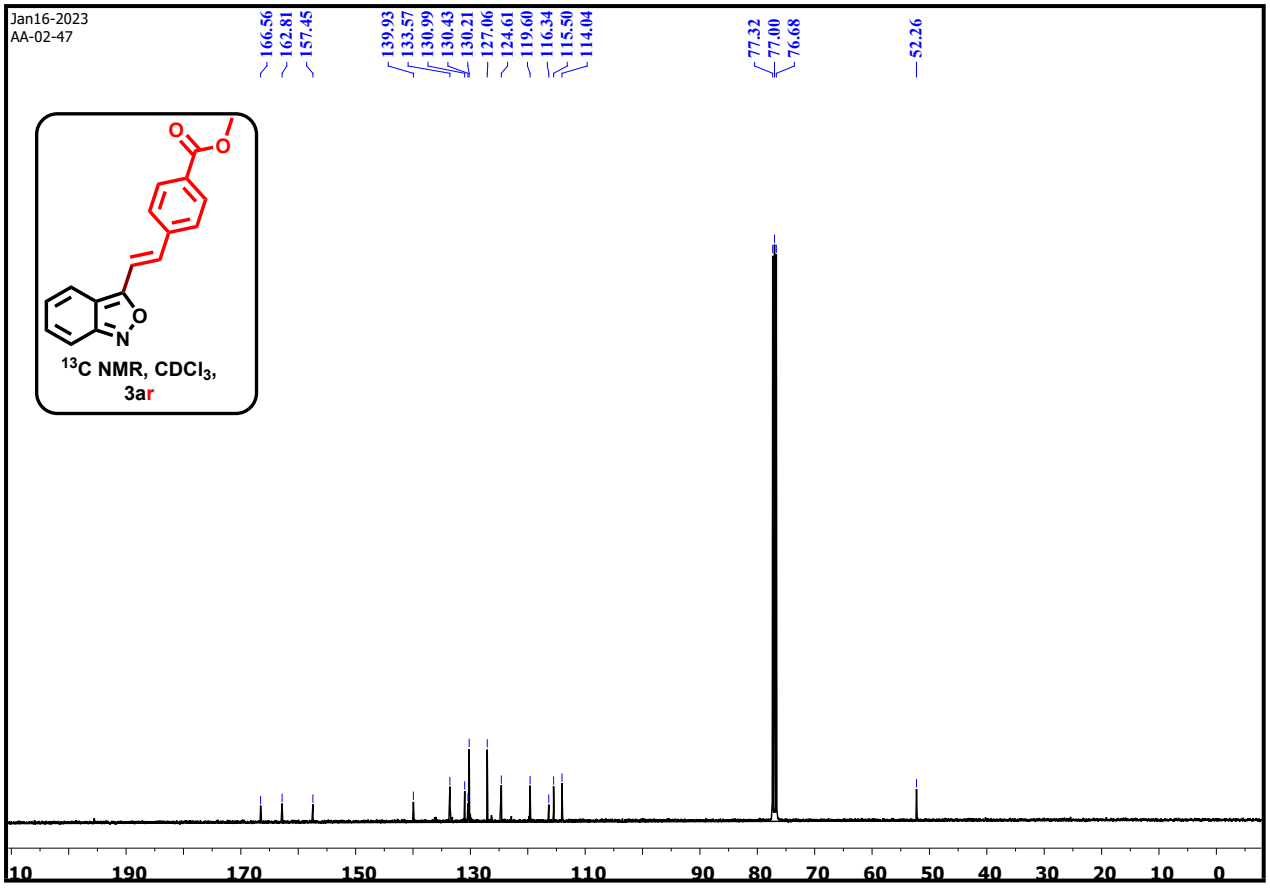
[1]H and [13]C NMR spectra of **3aq**


Jan14-2023
AA-02-58
7.58
7.56
7.54
7.54
7.51
7.50
7.49
7.26
7.25
7.24
7.23
7.19
7.19
7.10
7.08
6.99
6.98
6.96
6.96
6.94
2.26
O
O
O
N
^{1}H NMR,CDCl$_3$,
3aq
5.00
2.00
2.01
1.01
7.8
7.6
7.4
7.2
7.0
5.00
2.00
2.01
1.01
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

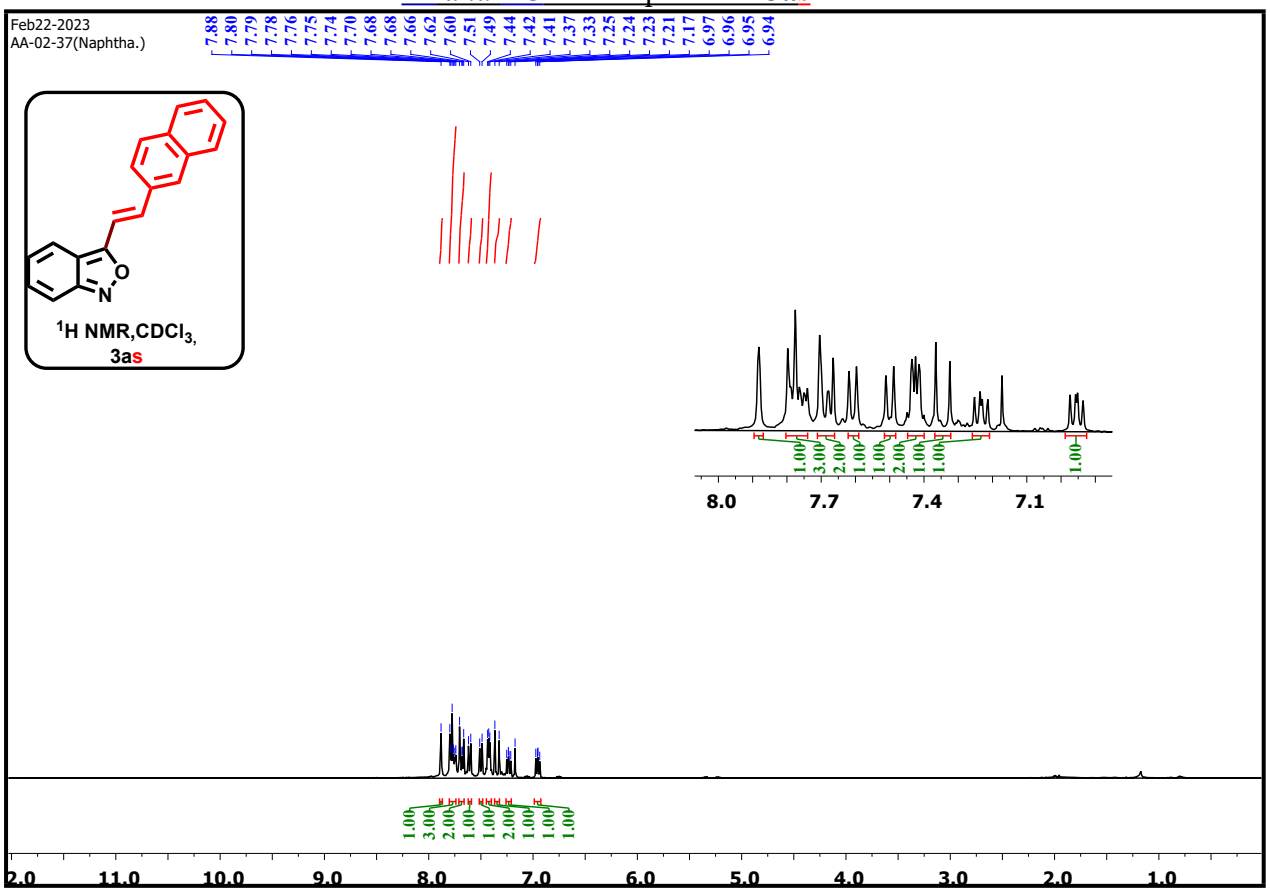

Jan14-2023
AA-02-58
169.26
163.30
157.39
151.34
133.96
133.42
130.92
128.27
124.14
122.19
119.74
115.82
115.31
112.14
77.32
77.00
76.69
21.14
13C NMR, CDCl3,
3aq
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

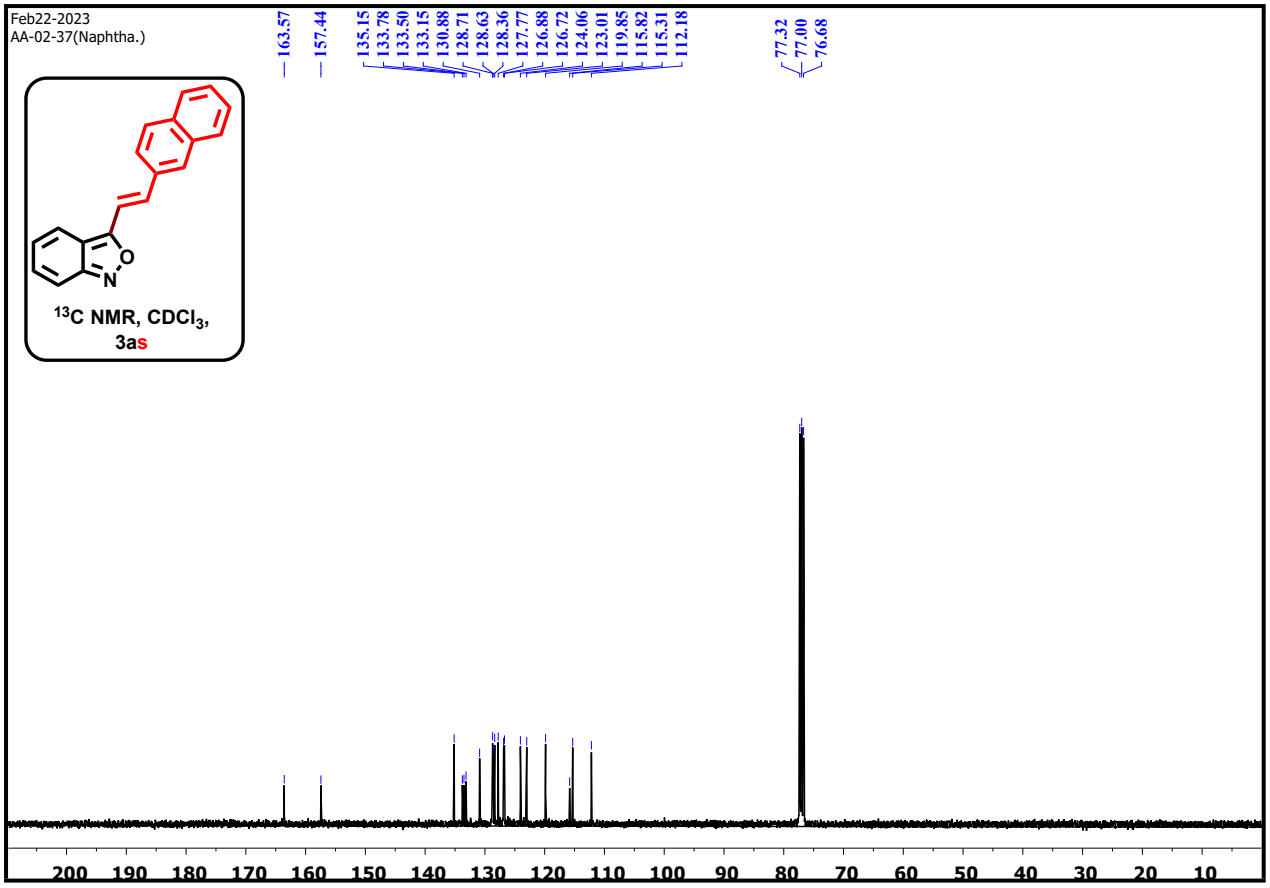
[1]H and [13]C NMR spectra of **3ar**



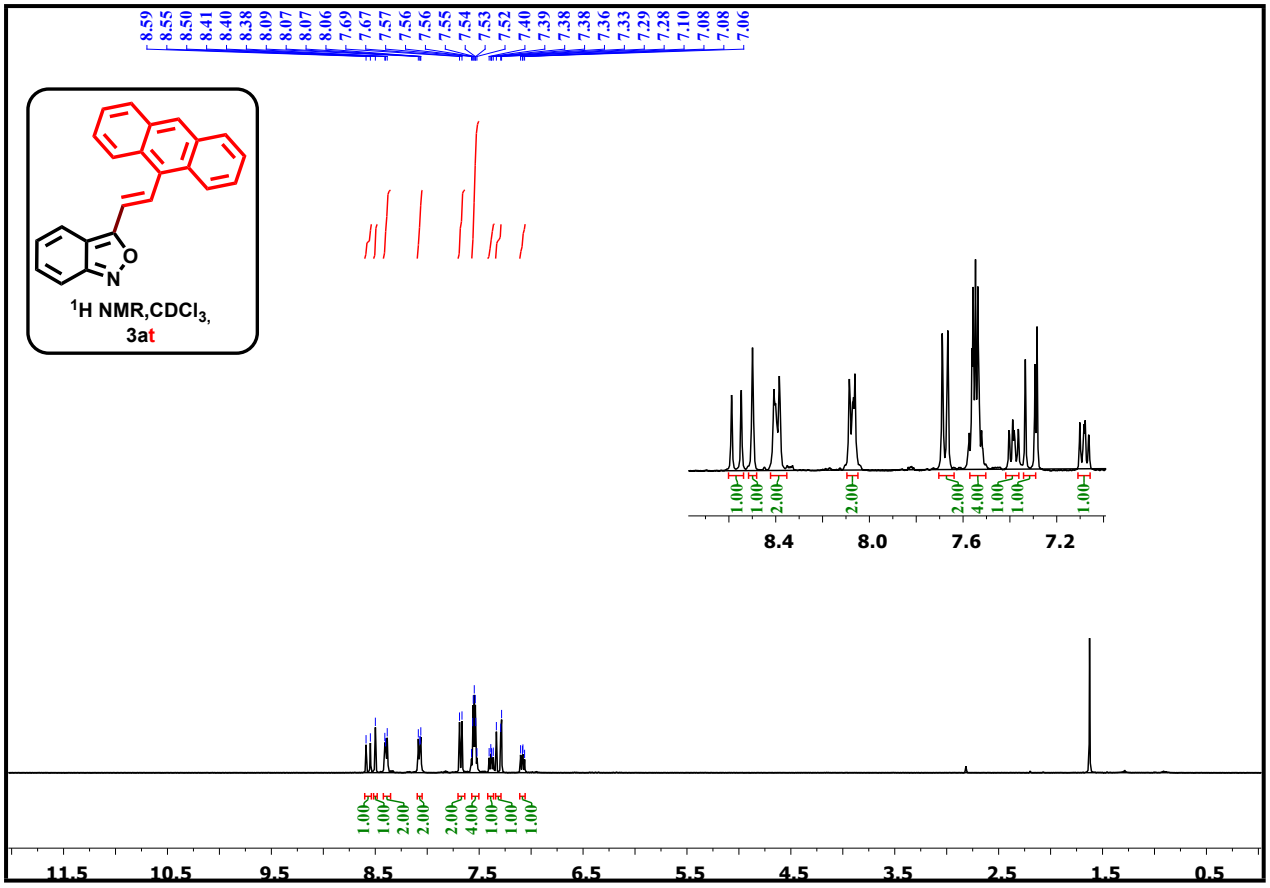

Jan16-2023
AA-02-47
166.56
162.81
157.45
139.93
133.57
130.99
130.43
130.21
127.06
124.61
119.60
116.34
115.50
114.04
77.32
77.00
76.68
52.26
13C NMR, CDCl3,
3ar
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

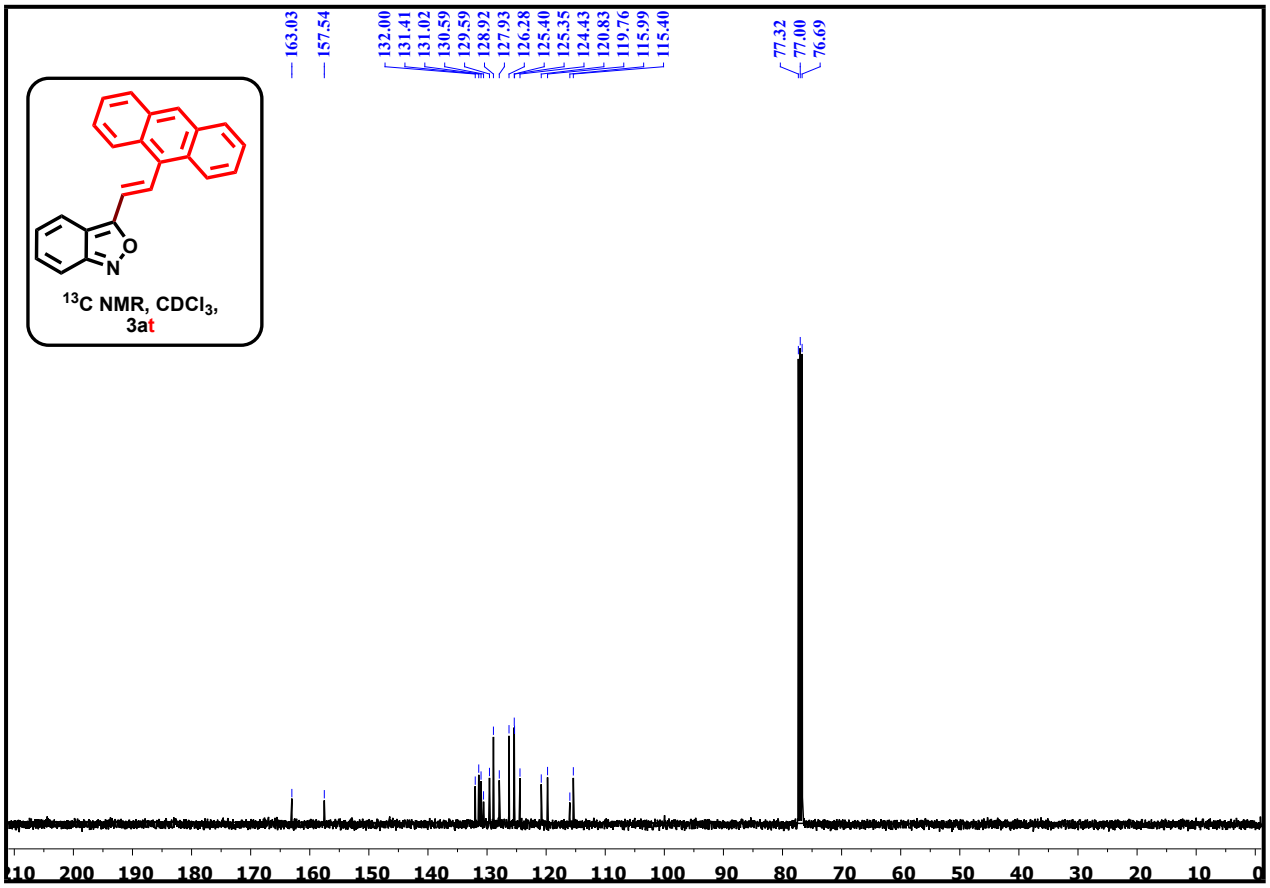
[1]H and [13]C NMR spectra of **3as**



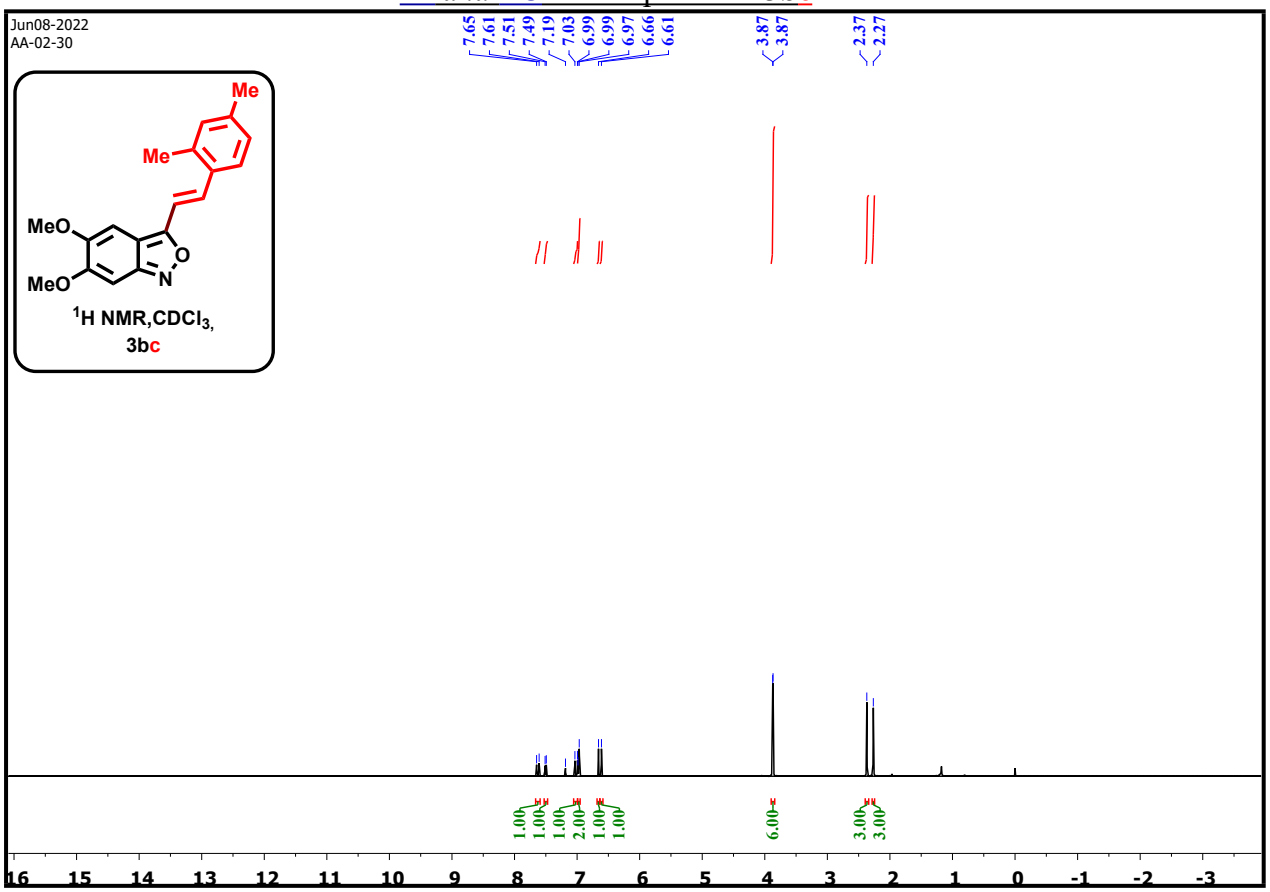


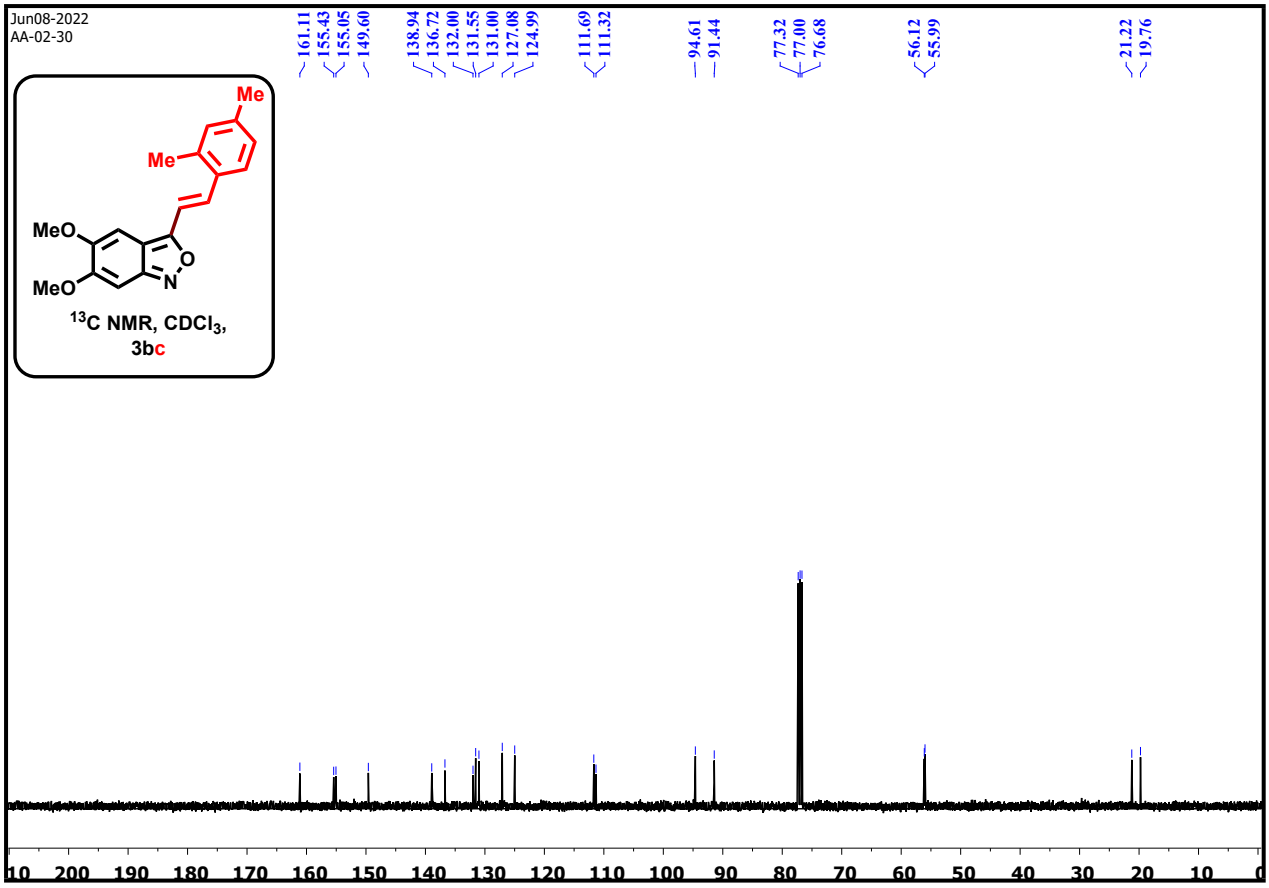
[1]H and [13]C NMR spectra of **3at**


8.59
8.55
8.50
8.41
8.40
8.38
8.09
8.07
8.07
8.06
7.69
7.67
7.57
7.56
7.56
7.55
7.54
7.53
7.52
7.40
7.39
7.38
7.38
7.36
7.33
7.29
7.28
7.10
7.08
7.08
7.06
^{1}H NMR,CDCl$_3$,
3at
1.00
1.00
2.00
2.00
2.00
4.00
1.00
1.00
1.00
8.4
8.0
7.6
7.2
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

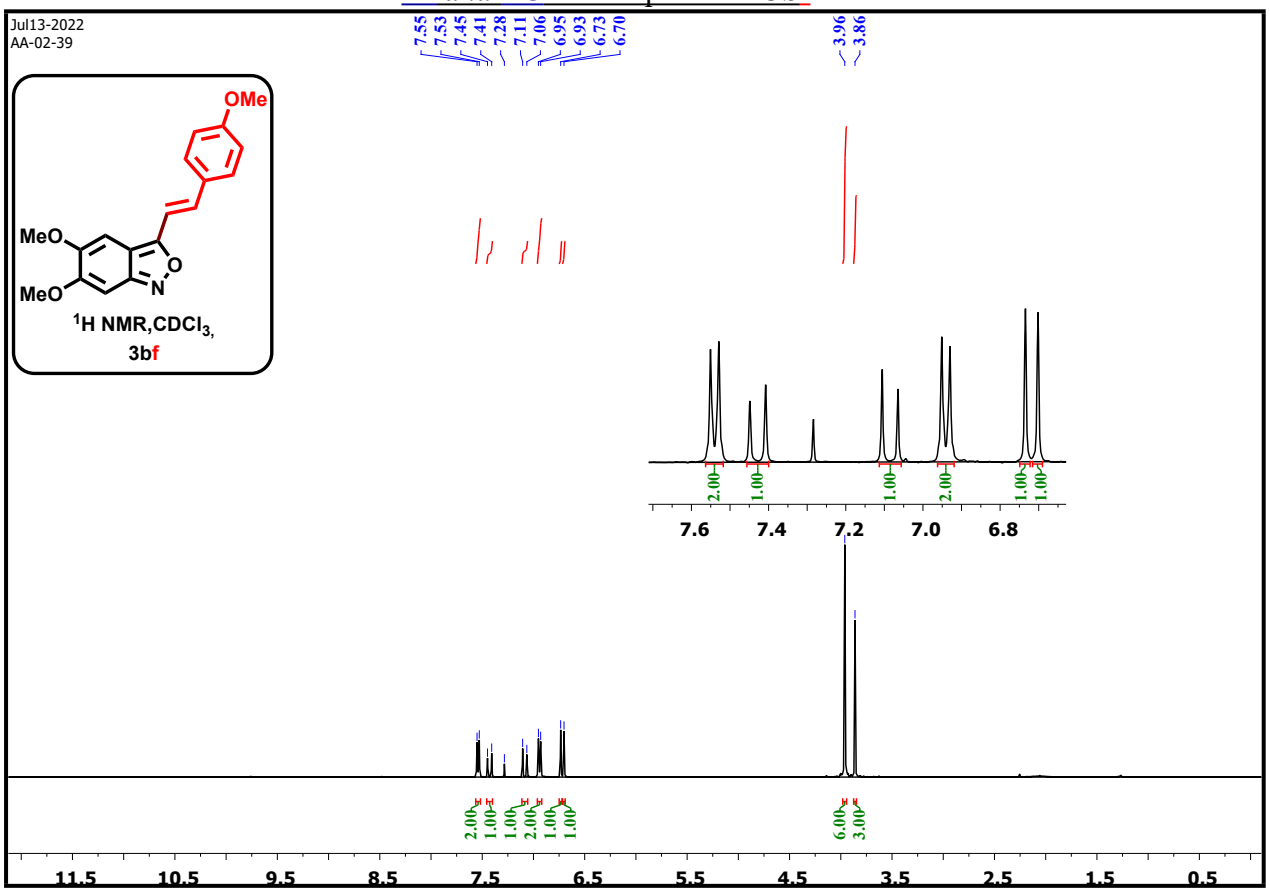

163.03
157.54
132.00
131.41
131.02
130.59
129.59
128.92
127.93
126.28
125.40
125.35
124.43
120.83
119.76
115.99
115.40
77.32
77.00
76.69
^{13}C NMR, CDCl$_3$,
3at
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

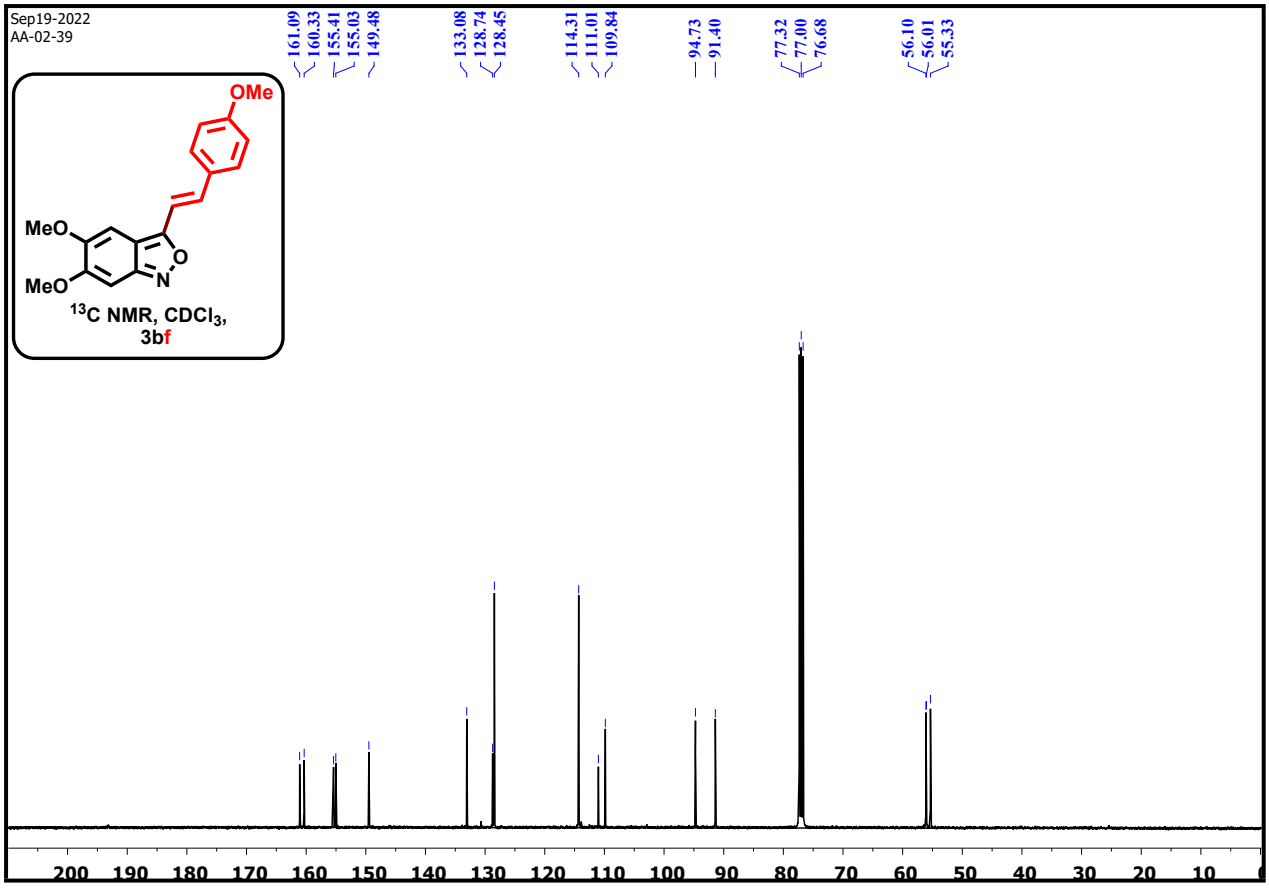
[1]H and [13]C NMR spectra of **3bc**



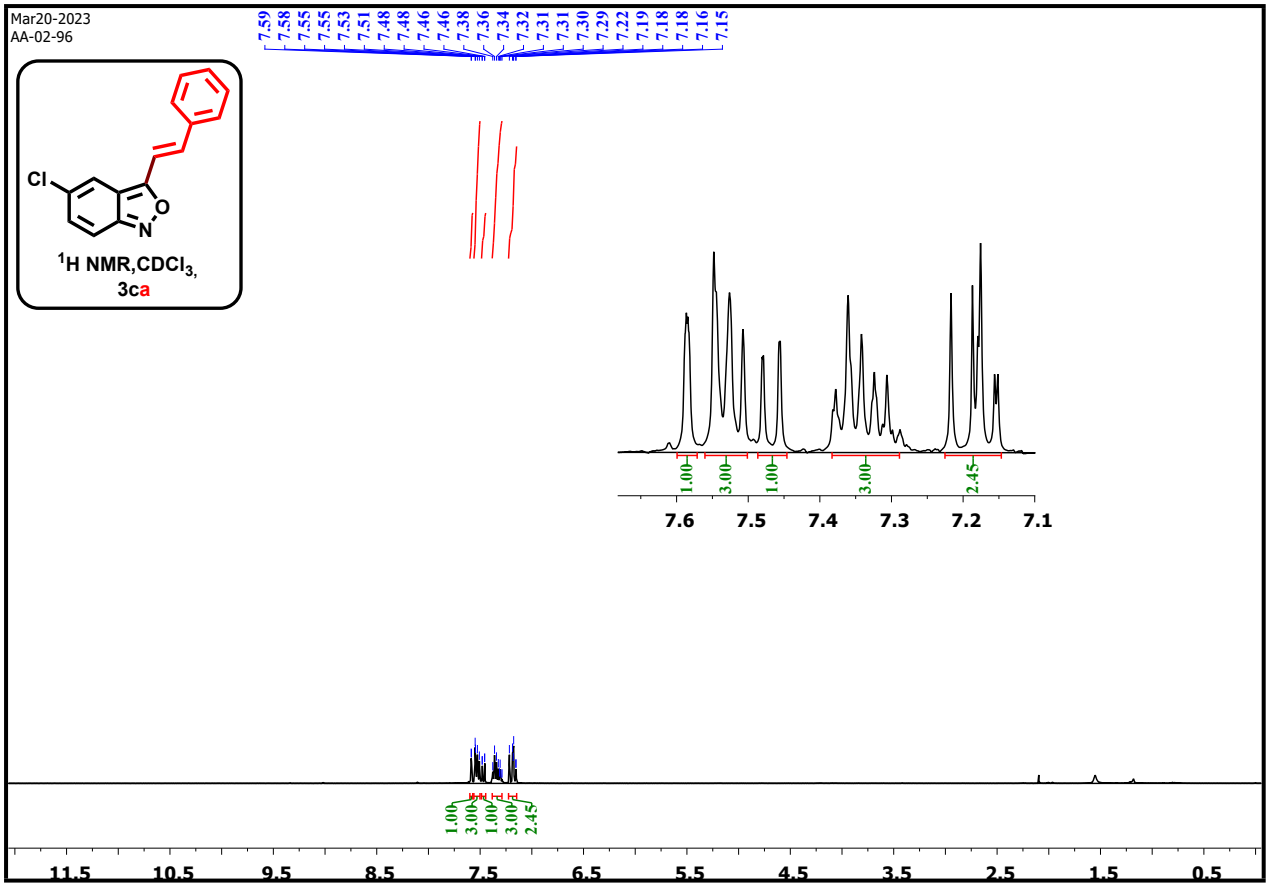

Jun08-2022
AA-02-30
161.11
155.43
155.05
149.60
138.94
136.72
132.00
131.55
131.00
127.08
124.99
111.69
111.32
94.61
91.44
77.32
77.00
76.68
56.12
55.99
21.22
19.76
Me
Me
MeO
MeO
O
N
13C NMR, CDCl3,
3bc
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

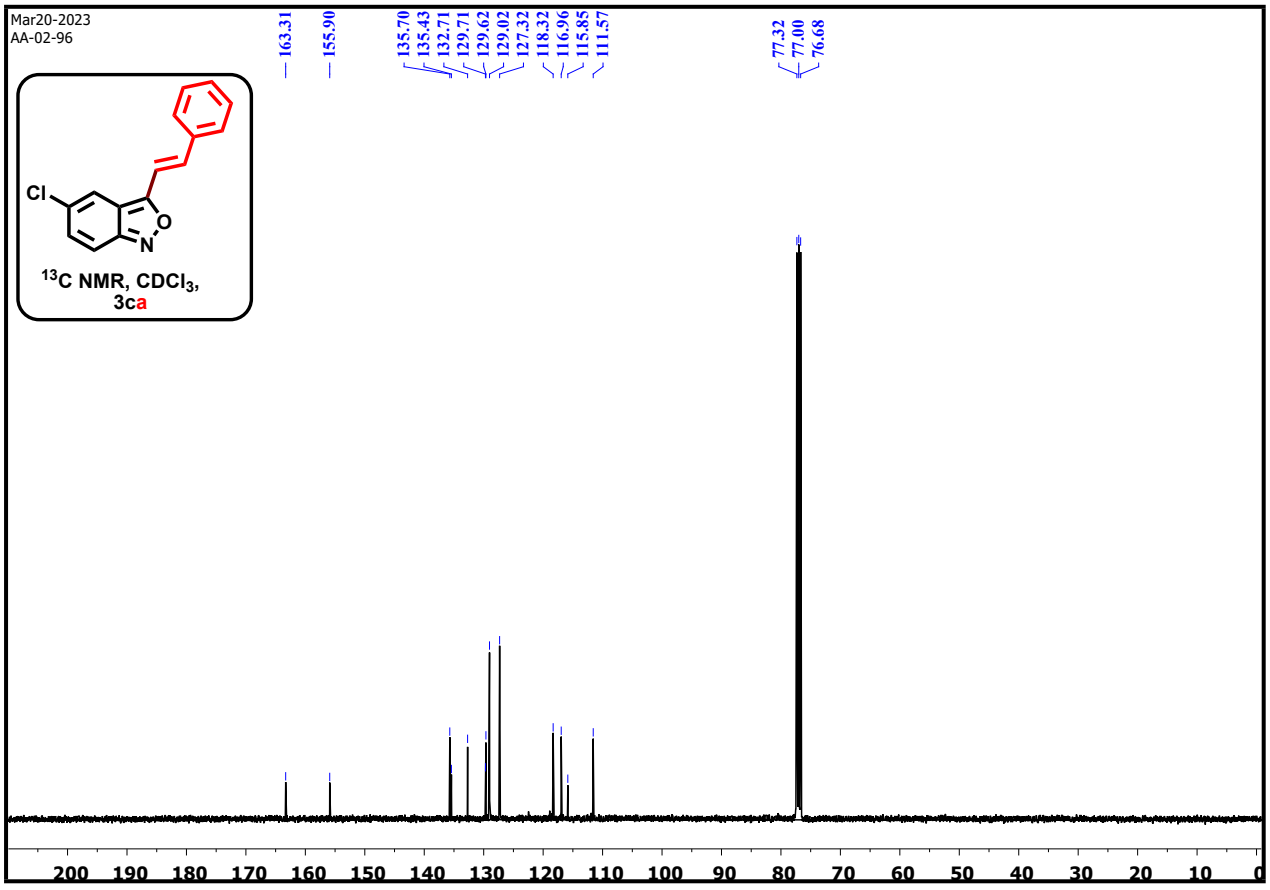
[1]H and [13]C NMR spectra of **3bf**



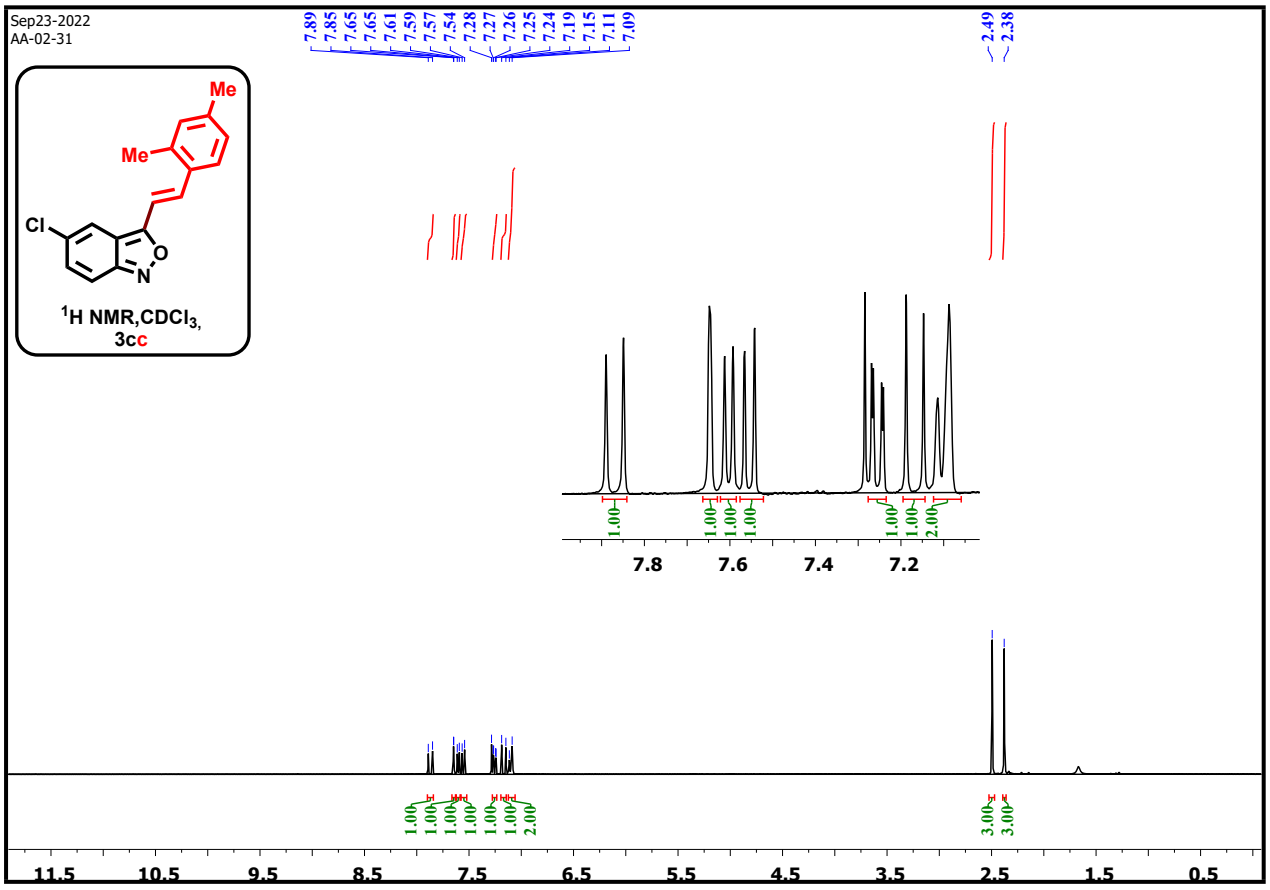


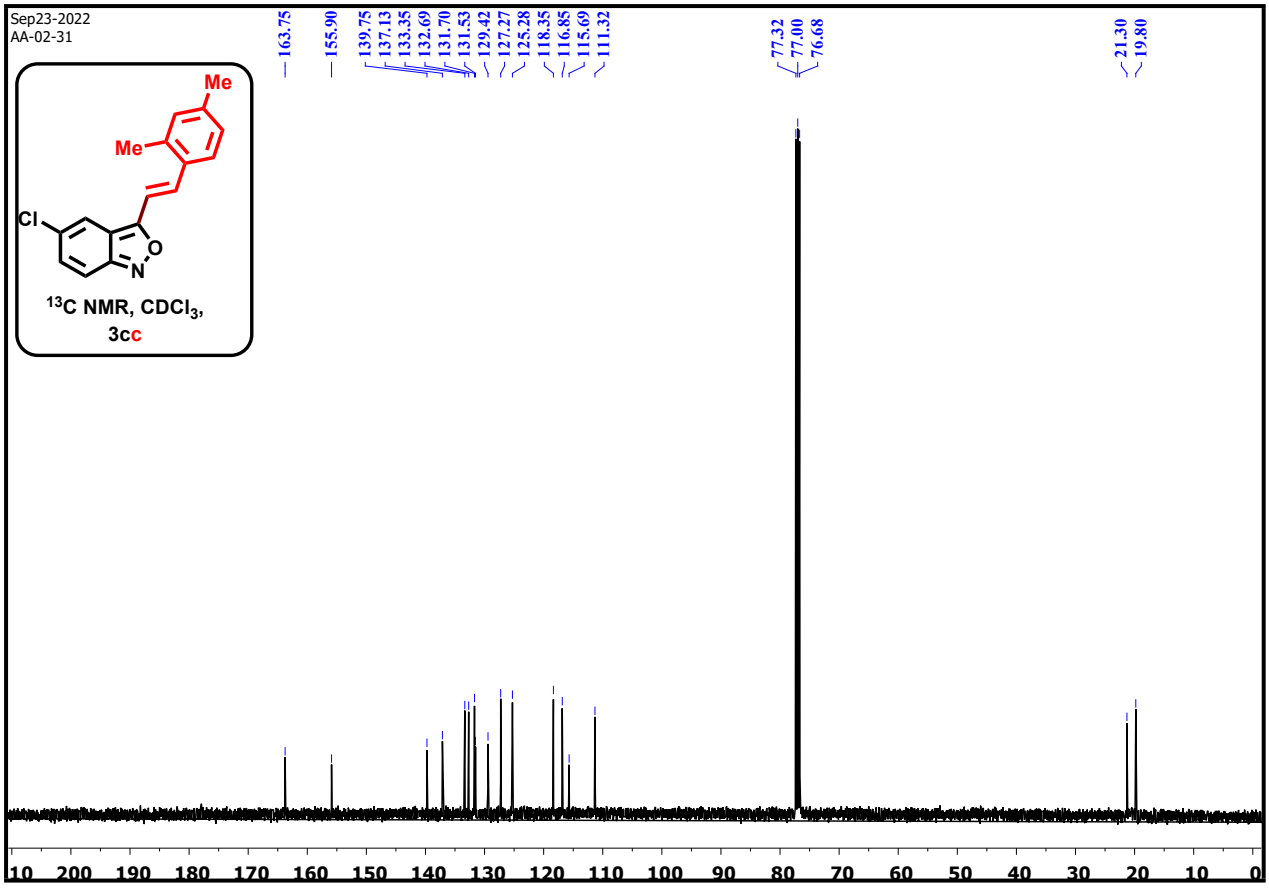
[1]H and [13]C NMR spectra of **3ca**


Mar20-2023
AA-02-96
7.59 7.58 7.55 7.55 7.53 7.51 7.48 7.48 7.46 7.46 7.38 7.36 7.34 7.32 7.31 7.31 7.30 7.29 7.22 7.19 7.18 7.18 7.16 7.15
Cl
O
N
^{1}H NMR,CDCl$_3$,
3ca
1.00 3.00 1.00 3.00 2.45
7.6 7.5 7.4 7.3 7.2 7.1
1.00 3.00 1.00 3.00 2.45
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5

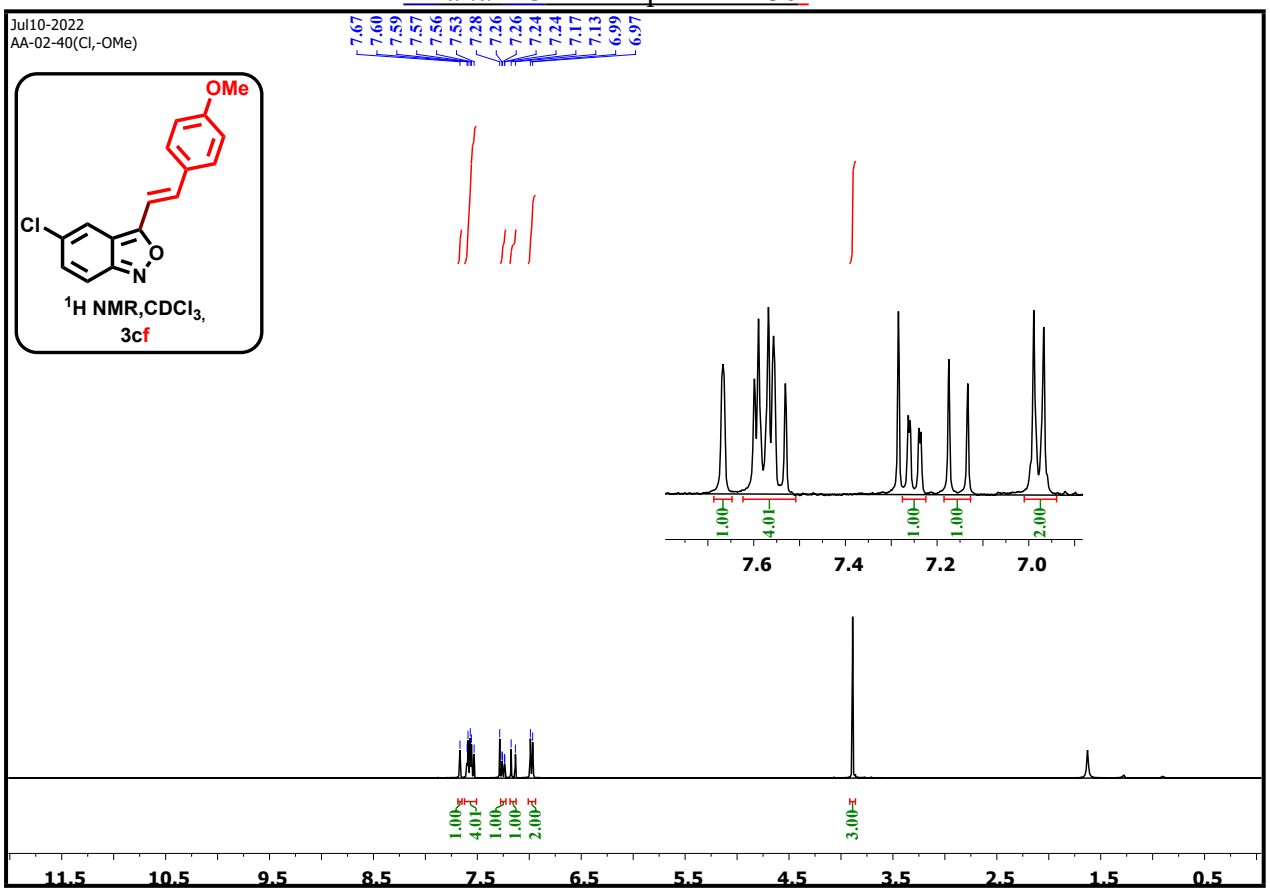

Mar20-2023
AA-02-96
163.31 155.90 135.70 135.43 132.71 129.71 129.62 129.02 127.32 118.32 116.96 115.85 111.57 77.32 77.00 76.68
Cl
O
N
^{13}C NMR, CDCl$_3$,
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

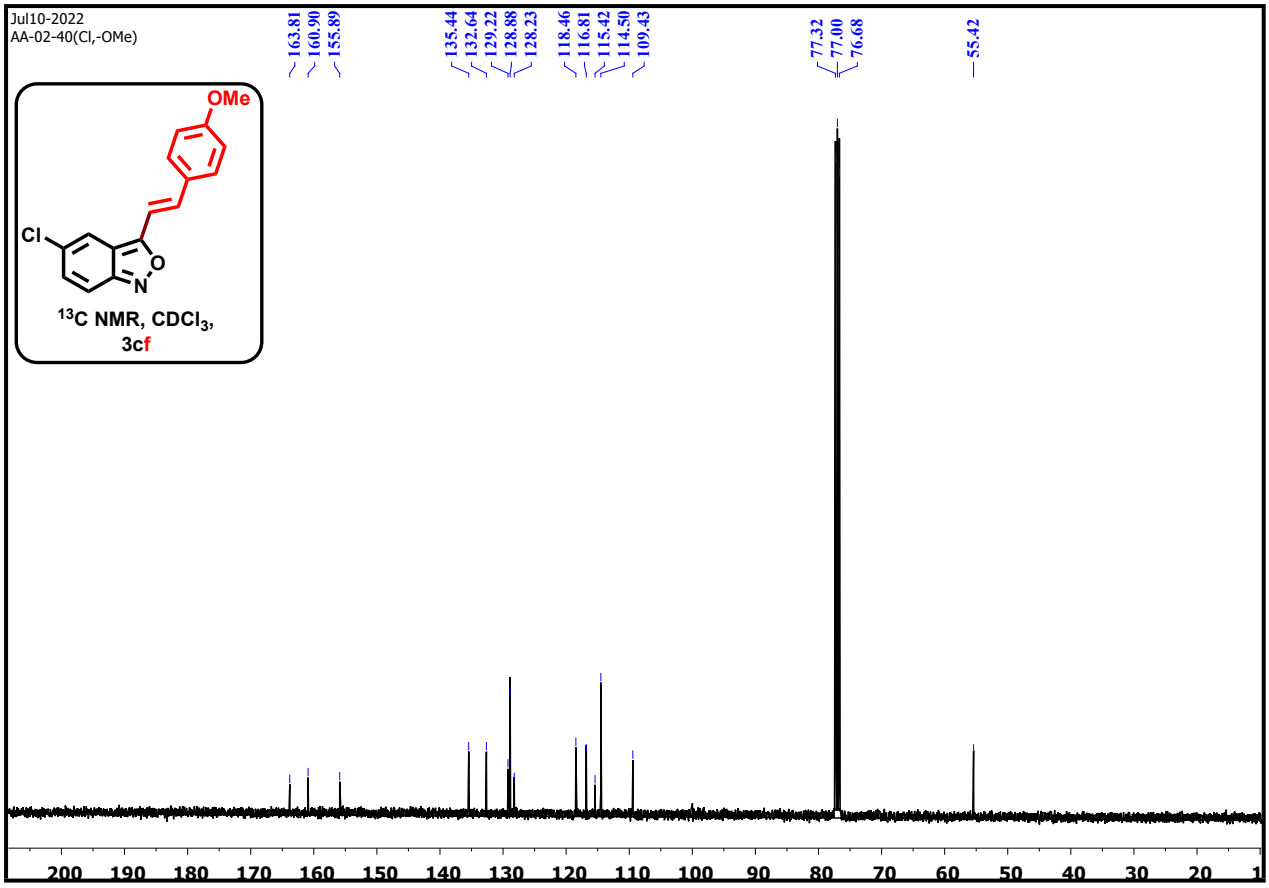
[1]H and [13]C NMR spectra of **3cc**



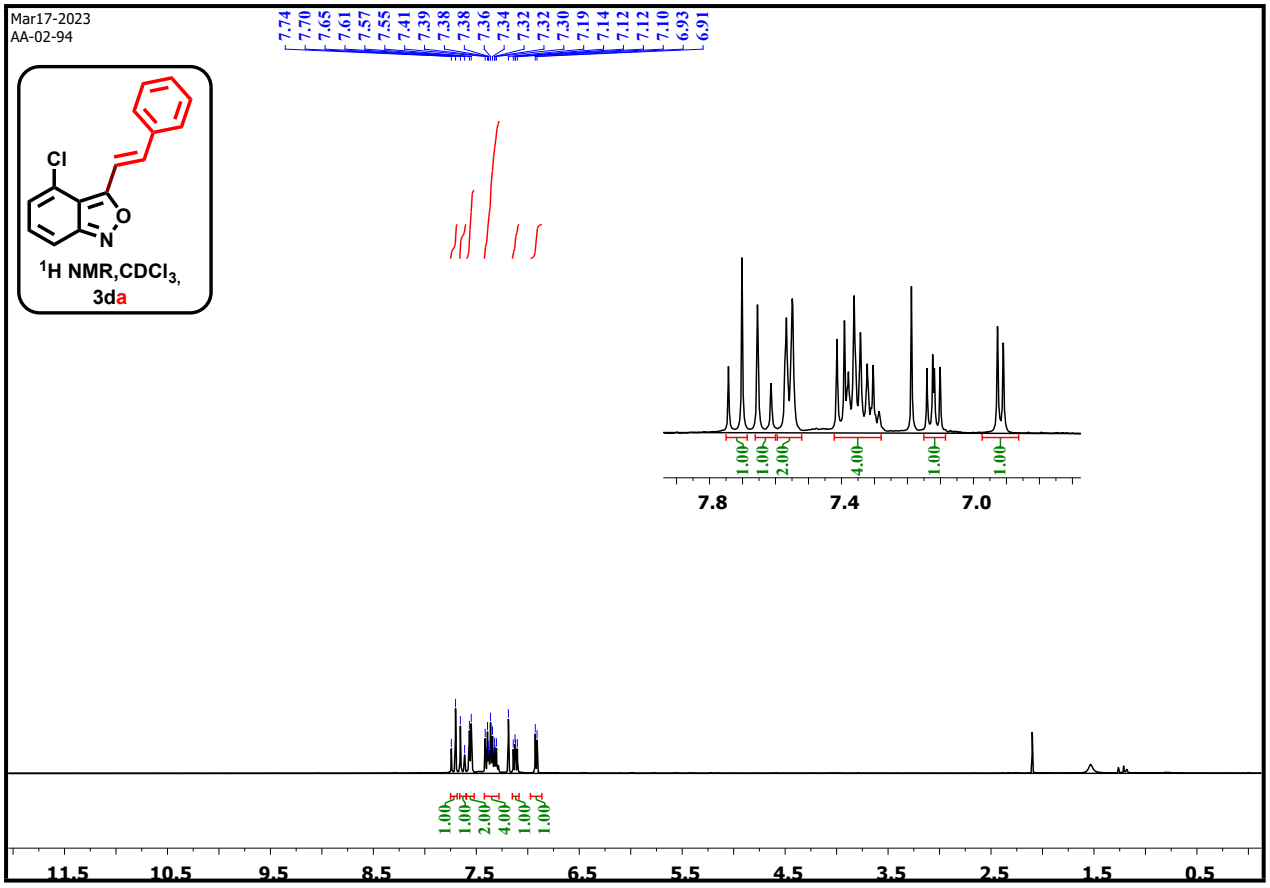

Sep23-2022
AA-02-31
163.75
155.90
139.75
137.13
133.35
132.69
131.70
131.53
129.42
127.27
125.28
118.35
116.85
115.69
111.32
77.32
77.00
76.68
21.30
19.80
Me
Me
Cl
O
N
13C NMR, CDCl3,
3cc
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

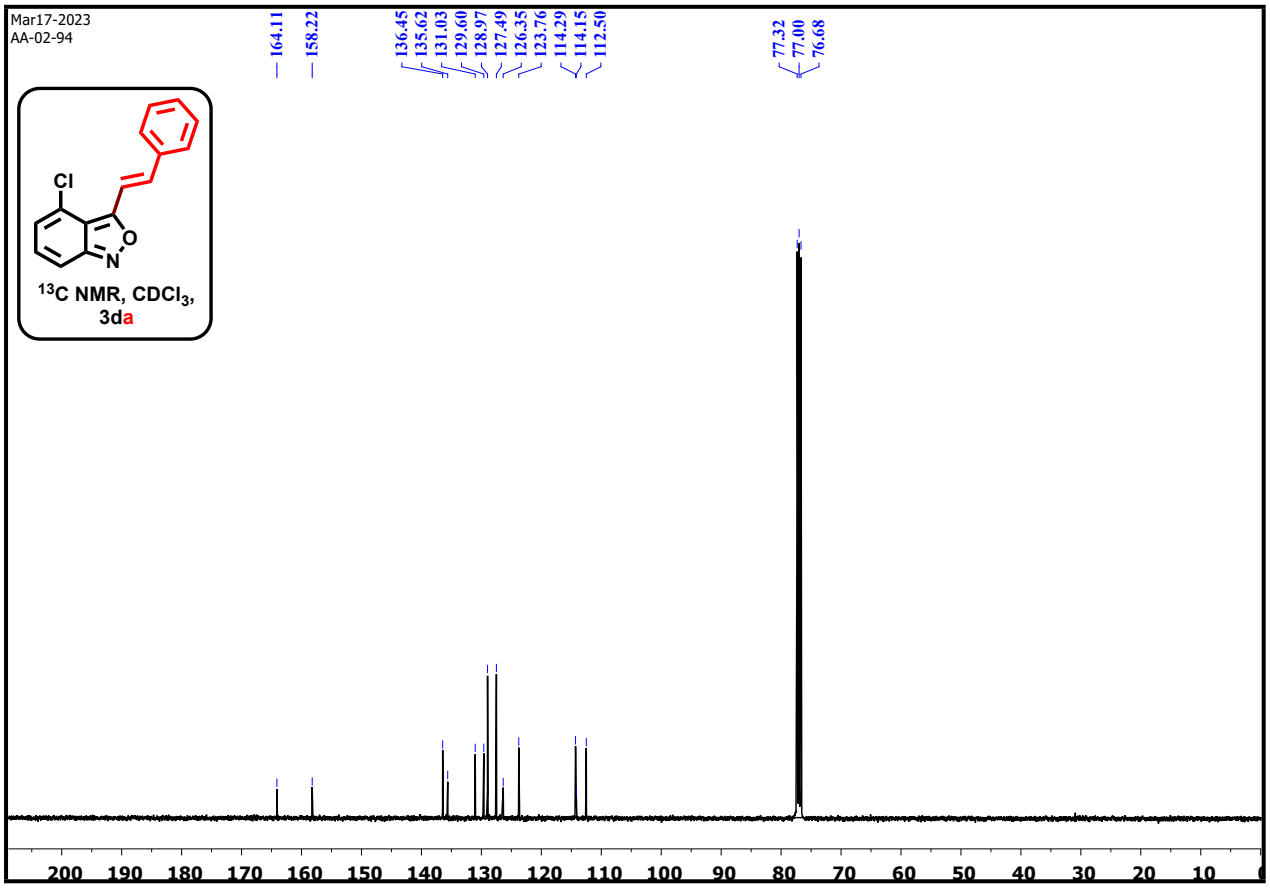
^{1}H and ^{13}C NMR spectra of **3cf**



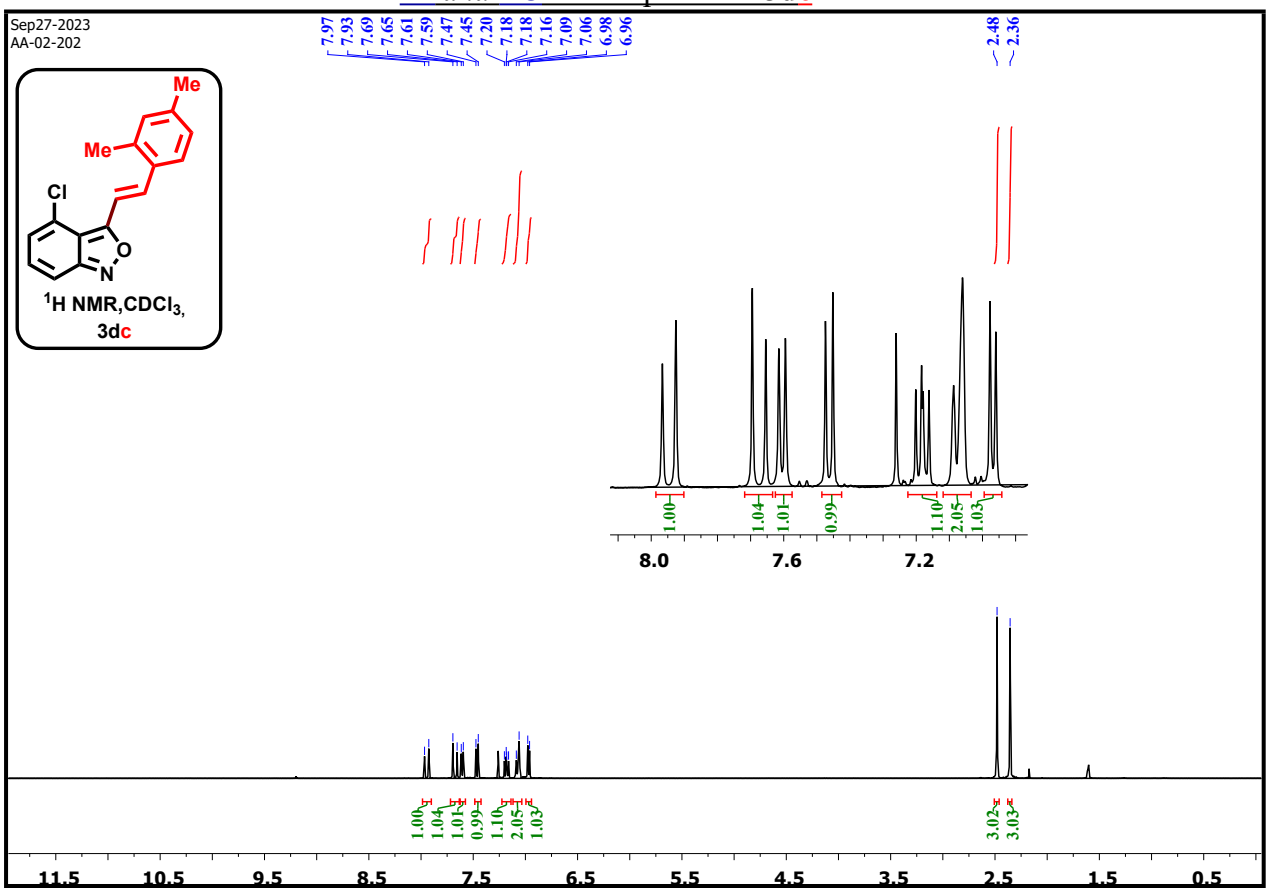


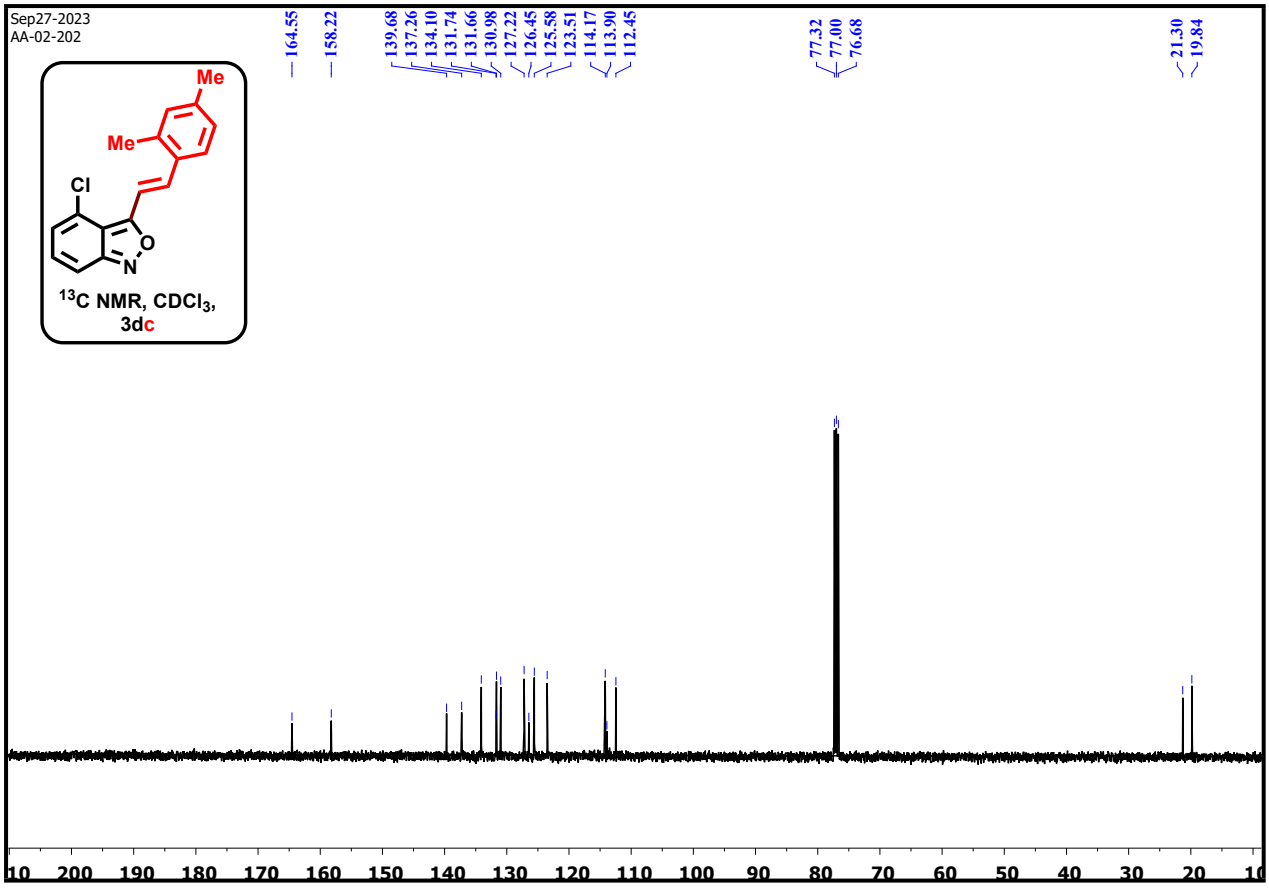
[1]H and [13]C NMR spectra of **3da**


Mar17-2023
AA-02-94
Cl
O
N
^{1}H NMR,CDCl$_3$,
3da
7.74
7.70
7.65
7.61
7.57
7.55
7.41
7.39
7.38
7.38
7.36
7.34
7.32
7.32
7.30
7.19
7.14
7.12
7.12
7.10
6.93
6.91
1.00
1.00
2.00
4.00
1.00
1.00
7.8
7.4
7.0
1.00
1.00
2.00
4.00
1.00
1.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

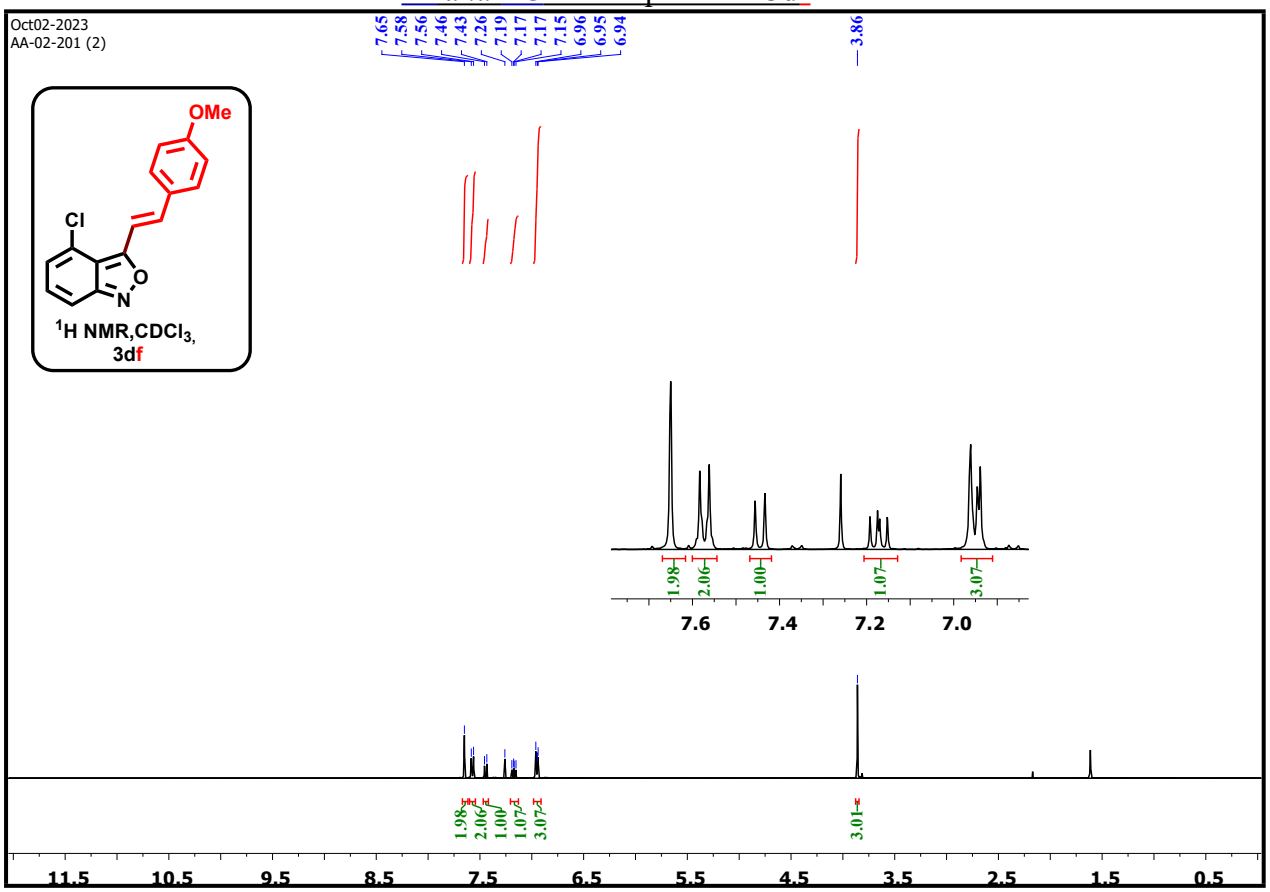

Mar17-2023
AA-02-94
Cl
O
N
^{13}C NMR, CDCl$_3$,
3da
164.11
158.22
136.45
135.62
131.03
129.60
128.97
127.49
126.35
123.76
114.29
114.15
112.50
77.32
77.00
76.68
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

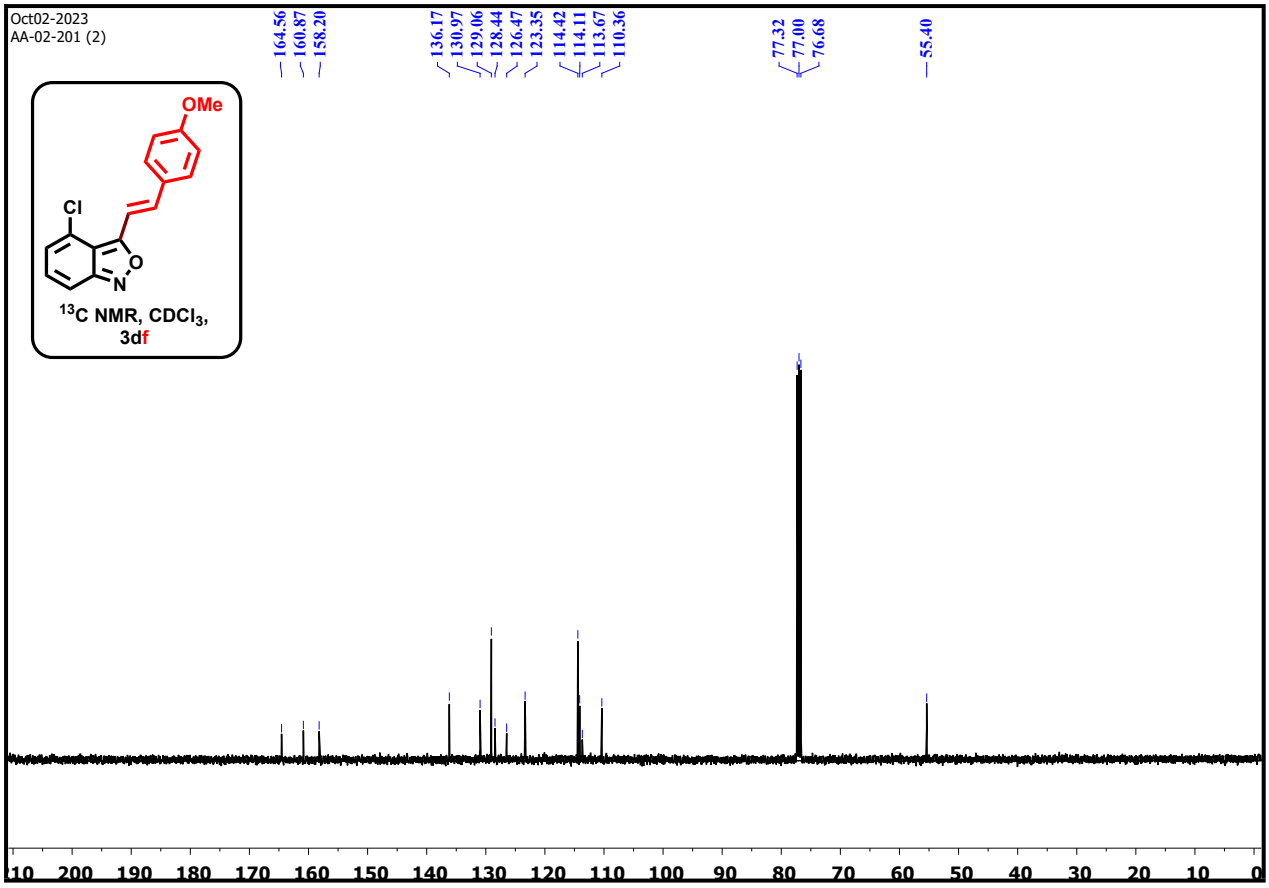
[1]H and [13]C NMR spectra of **3dc**



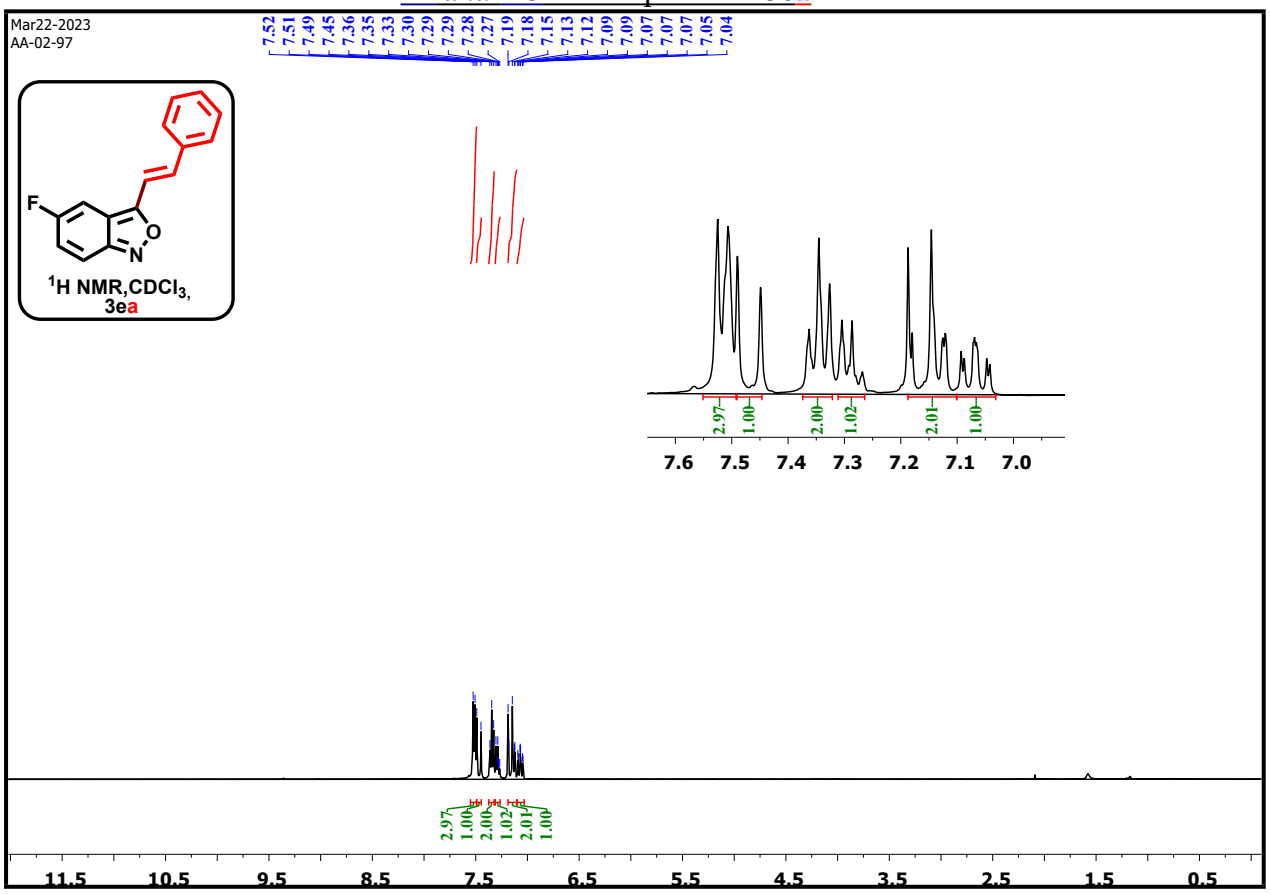

Sep27-2023
AA-02-202
164.55
158.22
139.68
137.26
134.10
131.74
131.66
130.98
127.22
126.45
125.58
123.51
114.17
113.90
112.45
77.32
77.00
76.68
21.30
19.84
Me
Me
Cl
O
N
13C NMR, CDCl3,
3dc
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

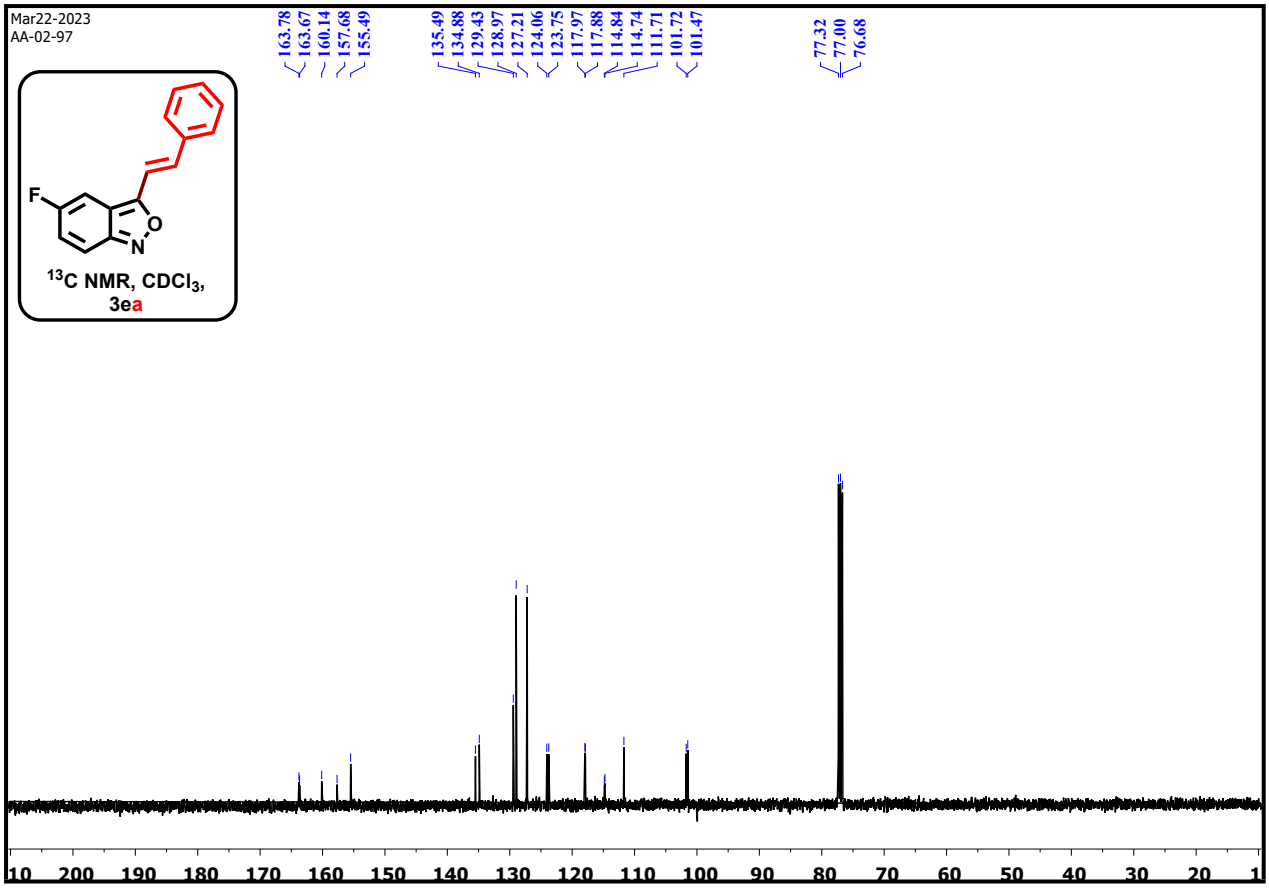
^{1}H and ^{13}C NMR spectra of **3df**



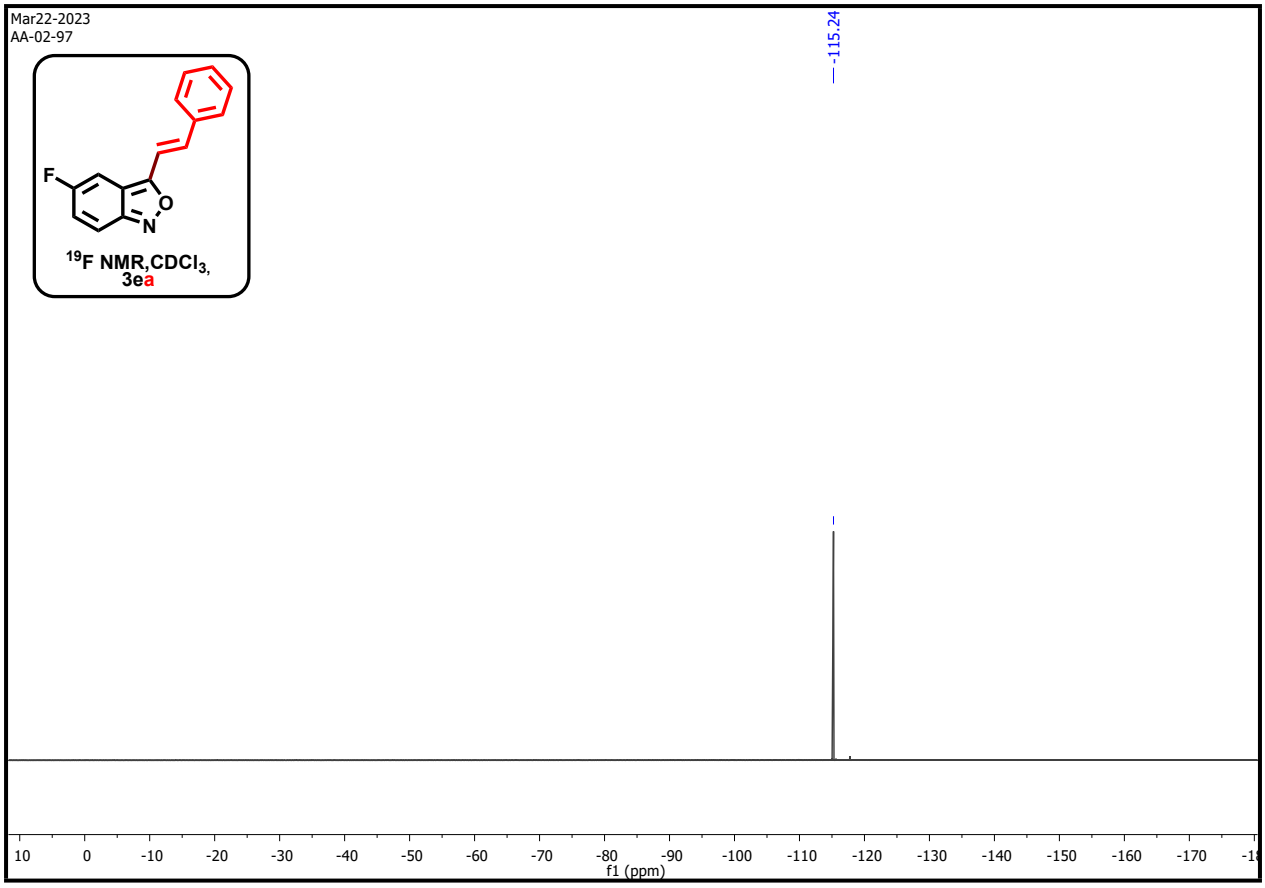

Oct02-2023
AA-02-201 (2)
164.56
160.87
158.20
136.17
130.97
129.06
128.44
126.47
123.35
114.42
114.11
113.67
110.36
77.32
77.00
76.68
55.40
OMe
Cl
O
N
13C NMR, CDCl3,
3df
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

[1]H and [13]C NMR spectra of **3ea**

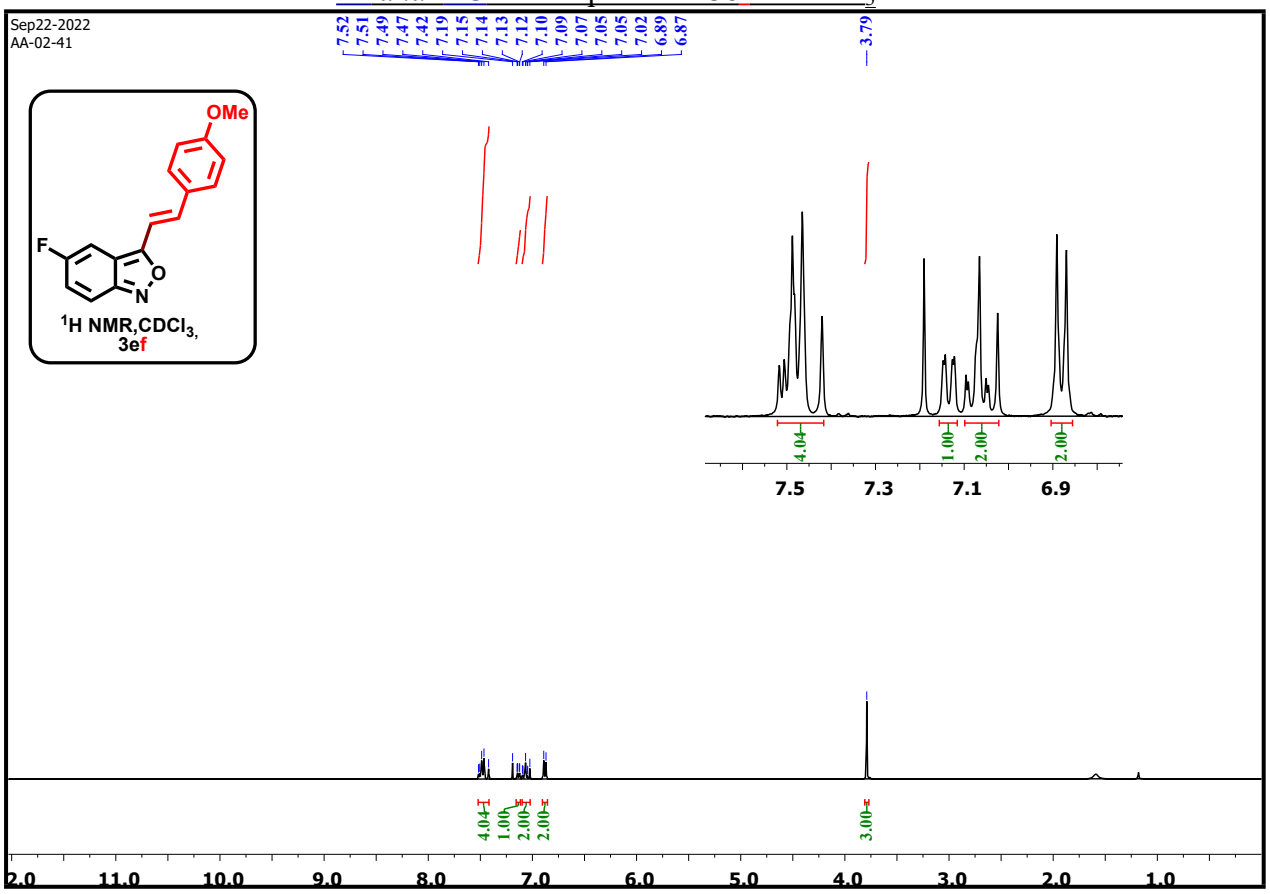


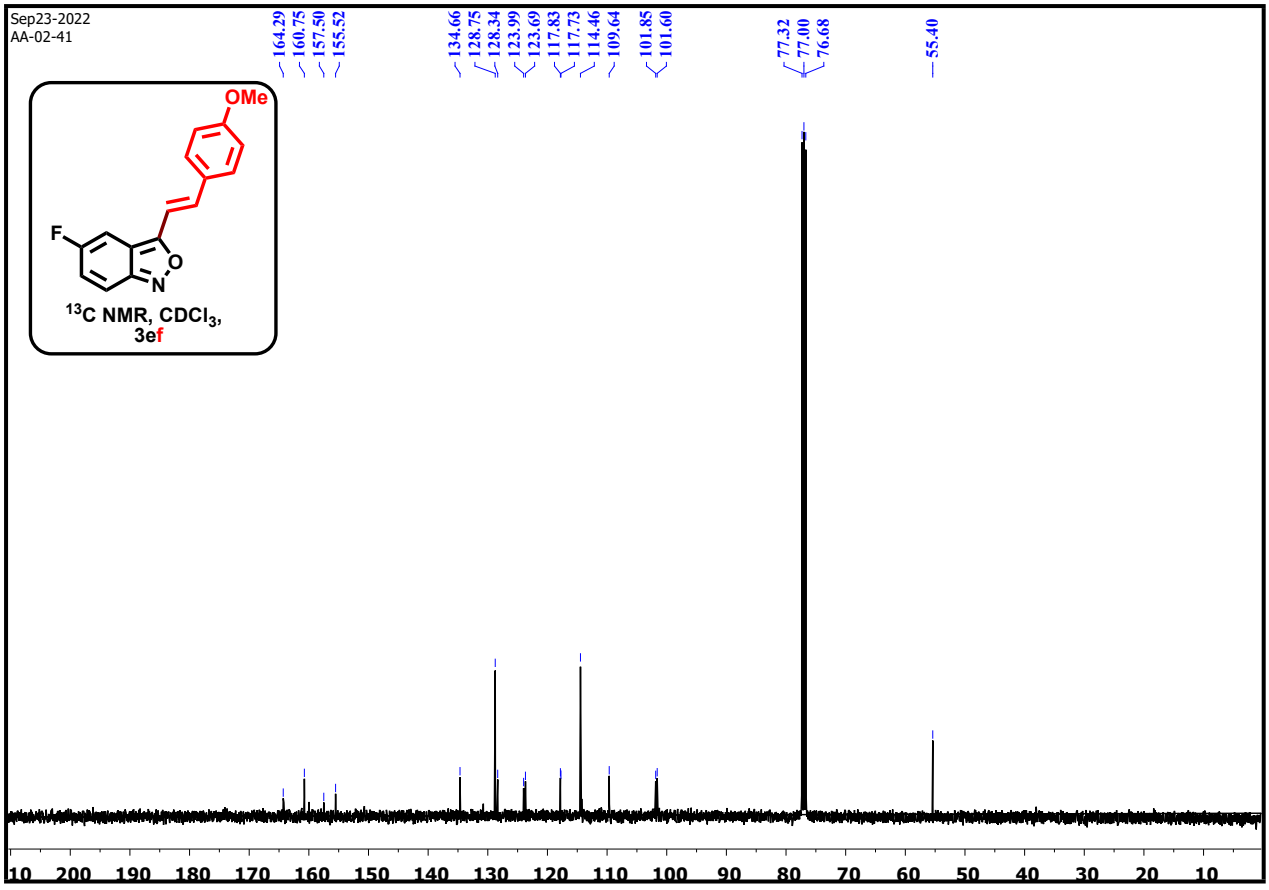


19F NMR spectra of **3ea**

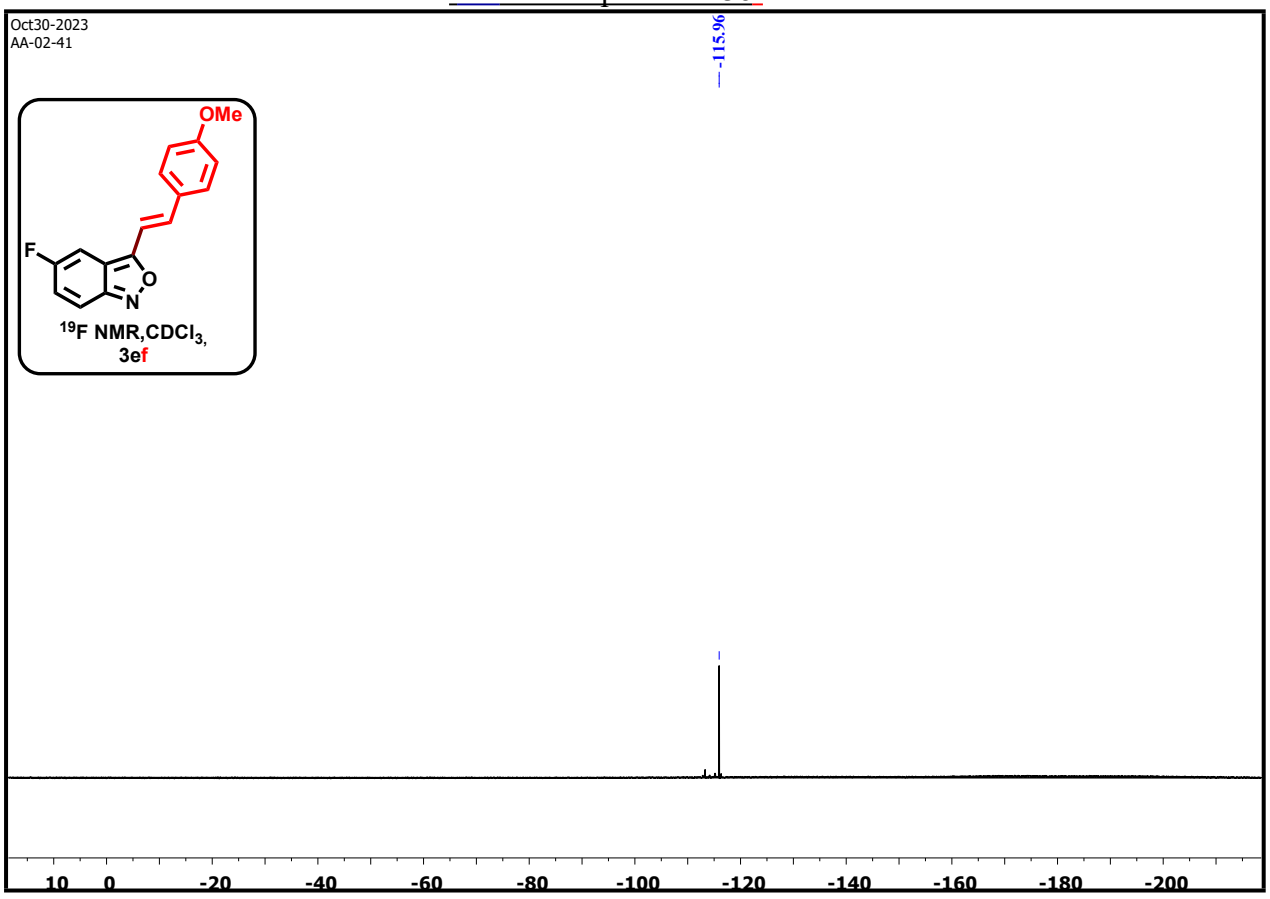

Mar22-2023
AA-02-97
-115.24
F
O
N
19F NMR,CDCl3,
3ea
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

^{1}H and ^{13}C NMR spectra of **3ef** in $CDCl_3$

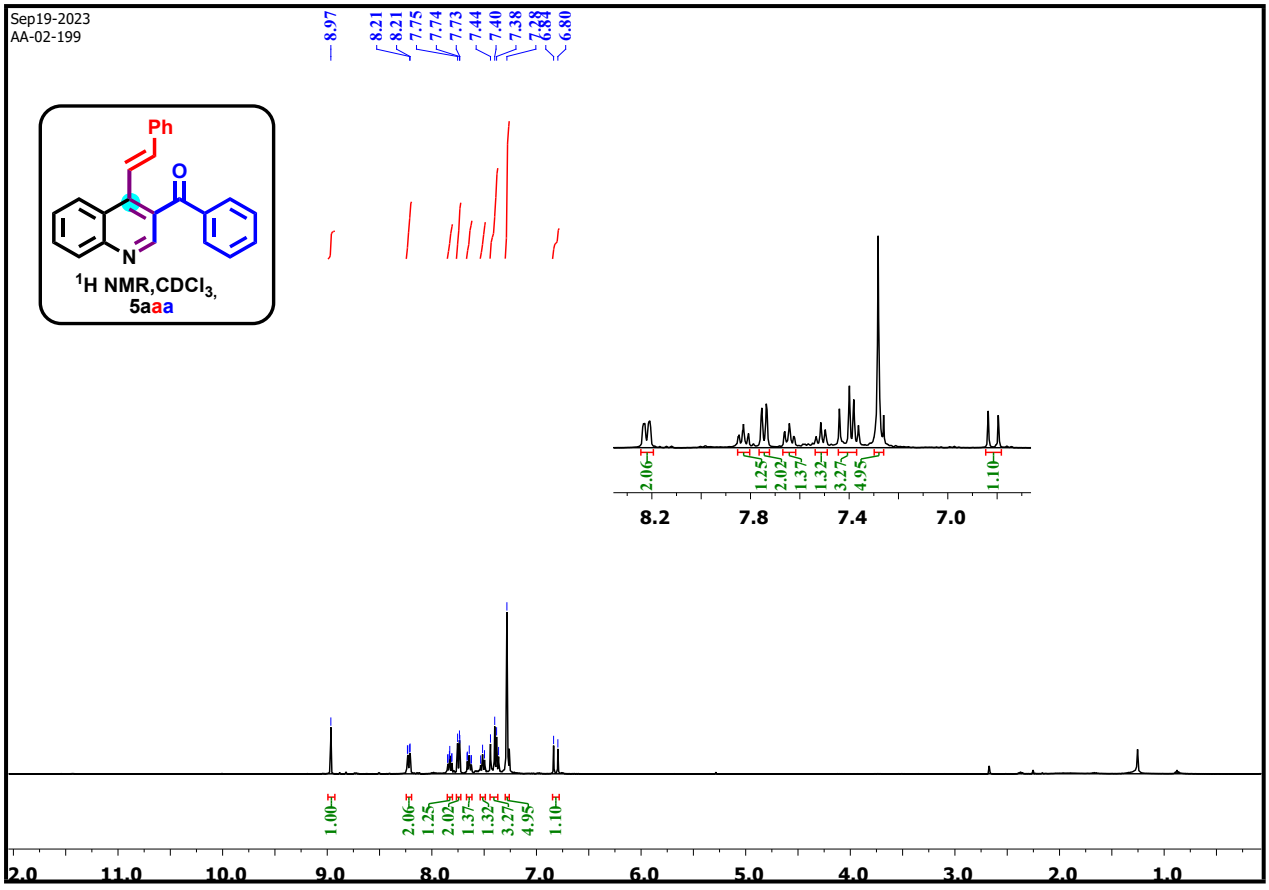


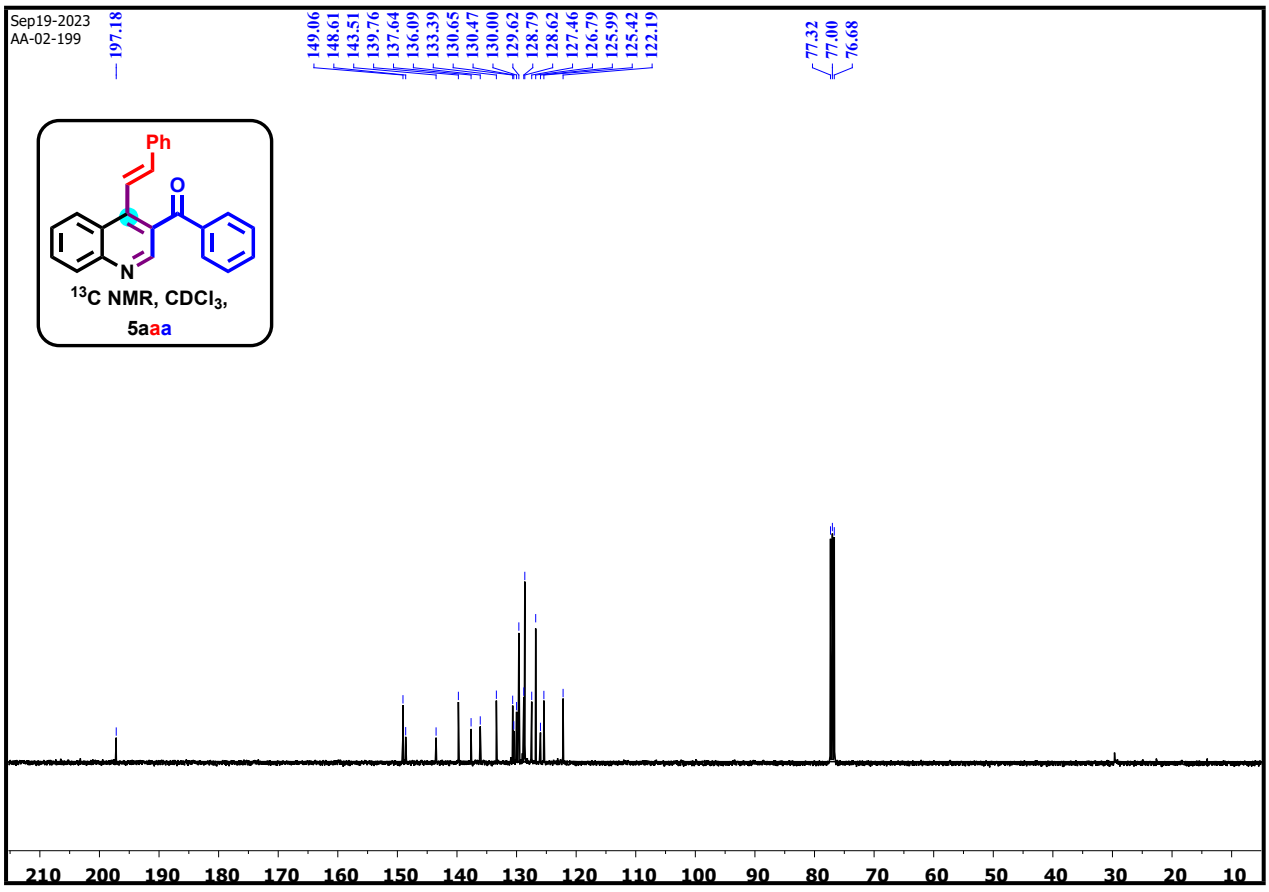

Sep23-2022
AA-02-41
164.29
160.75
157.50
155.52
134.66
128.75
128.34
123.99
123.69
117.83
117.73
114.46
109.64
101.85
101.60
77.32
77.00
76.68
55.40
OMe
F
O
N
13C NMR, CDCl3,
3ef
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

^{19}F NMR spectra of **3ef**

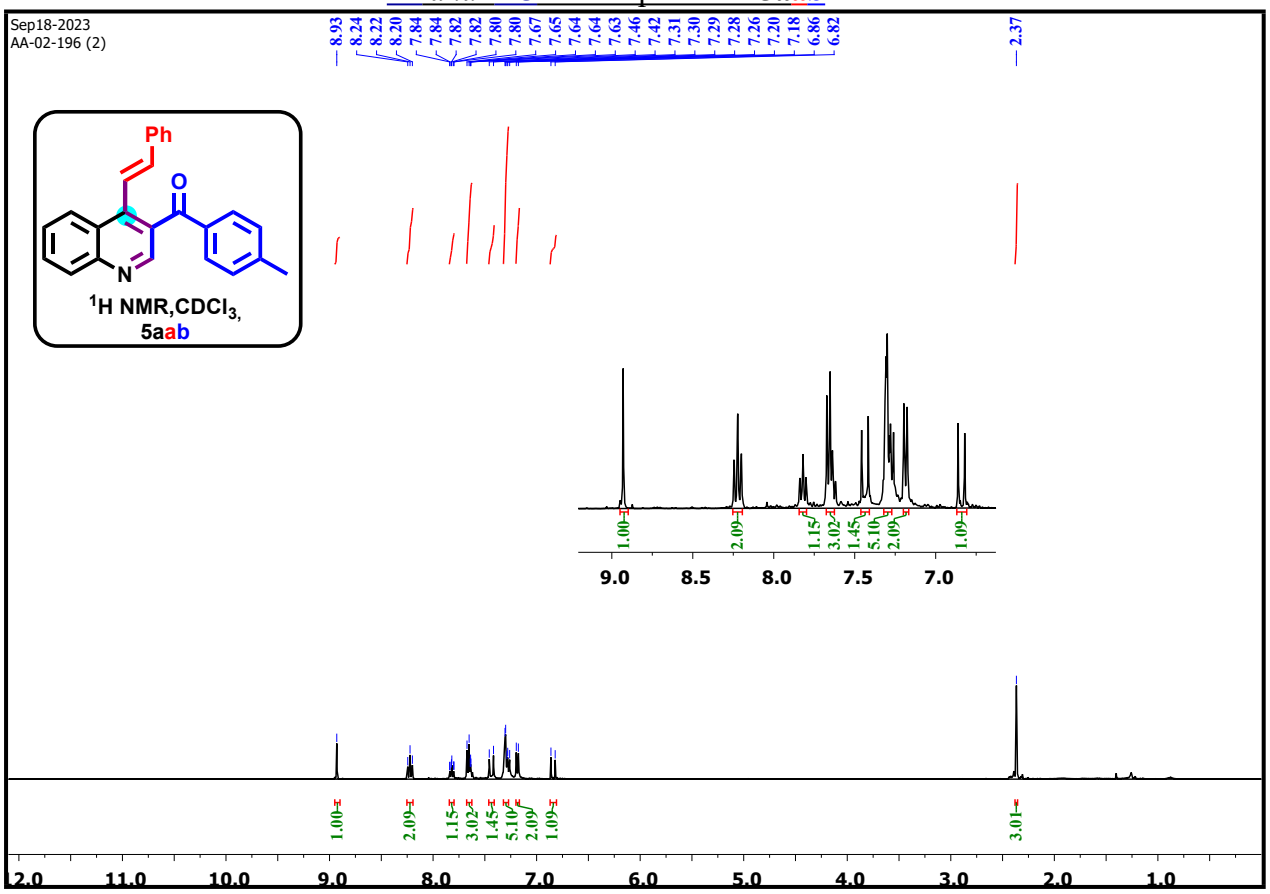


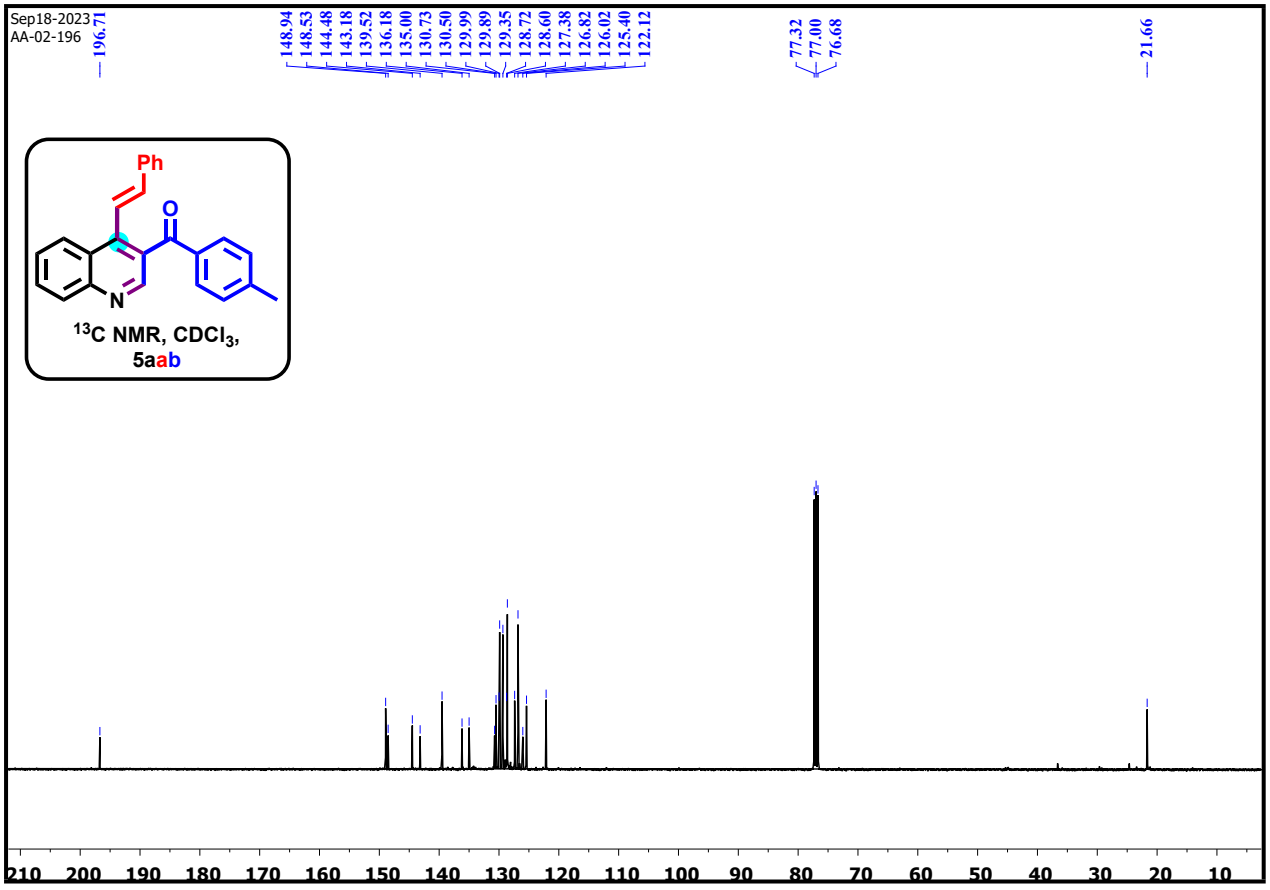
^{1}H *and* ^{13}C NMR spectra of **5aaa**


Sep19-2023
AA-02-199
8.97
8.21
8.21
7.75
7.74
7.73
7.44
7.40
7.38
7.28
6.84
6.80
Ph
O
N
^{1}H NMR,CDCl$_3$,
5aaa
2.06
1.25
2.02
1.37
1.32
3.27
4.95
1.10
8.2
7.8
7.4
7.0
1.00
2.06
1.25
2.02
1.37
1.32
3.27
4.95
1.10
2.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

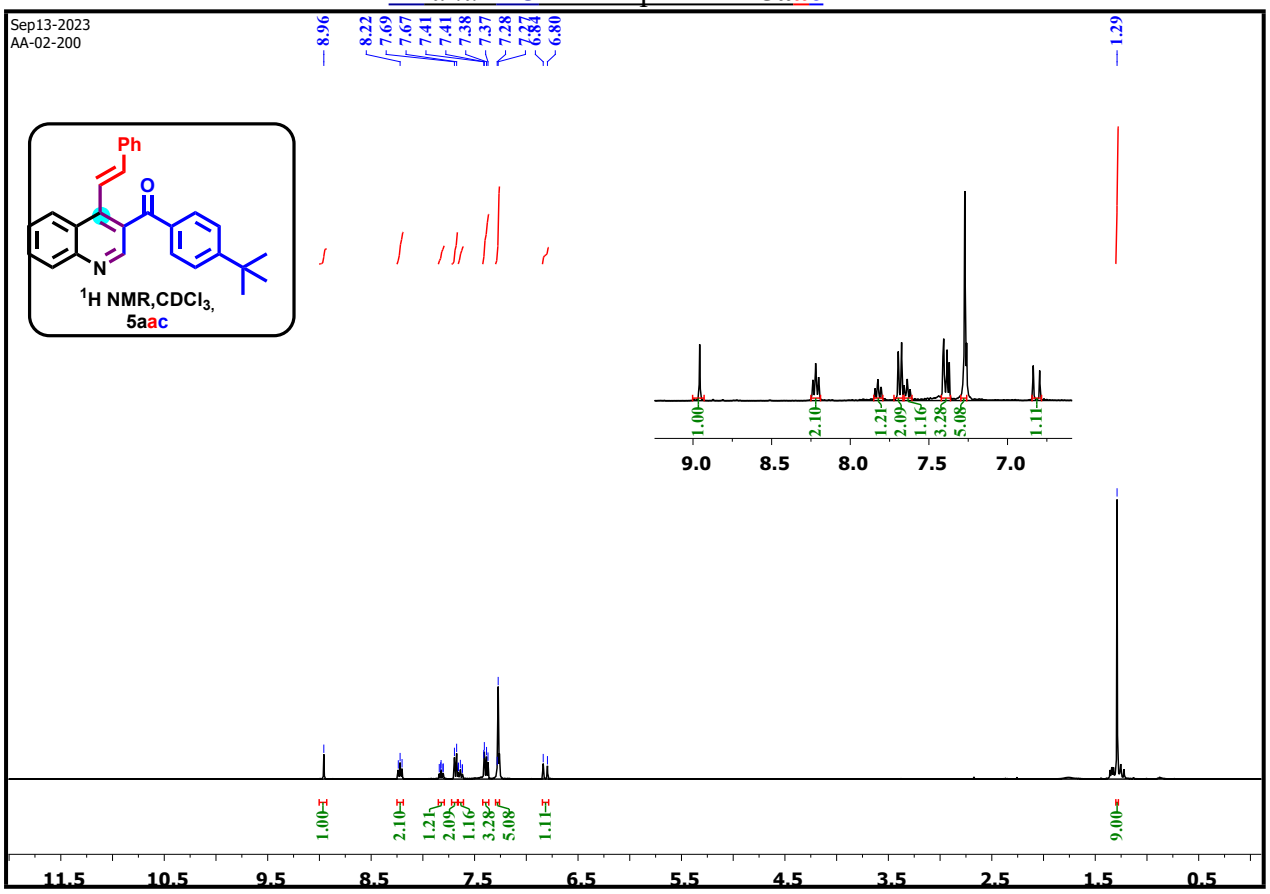

Sep19-2023
AA-02-199
197.18
149.06
148.61
143.51
139.76
137.64
136.09
133.39
130.65
130.47
130.00
129.62
128.79
128.62
127.46
126.79
125.99
125.42
122.19
77.32
77.00
76.68
Ph
O
N
^{13}C NMR, CDCl$_3$,
5aaa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

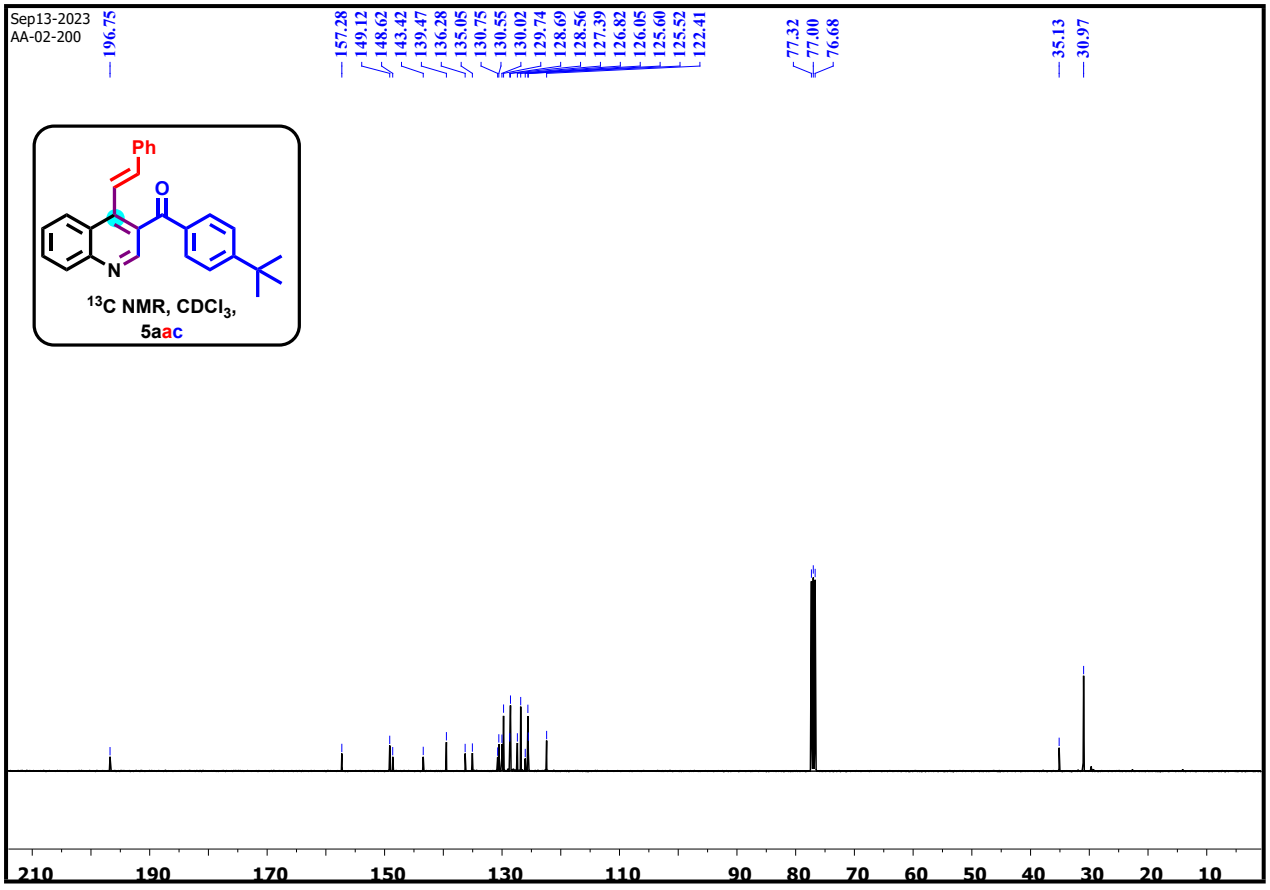
[1]H and [13]C NMR spectra of **5aab**



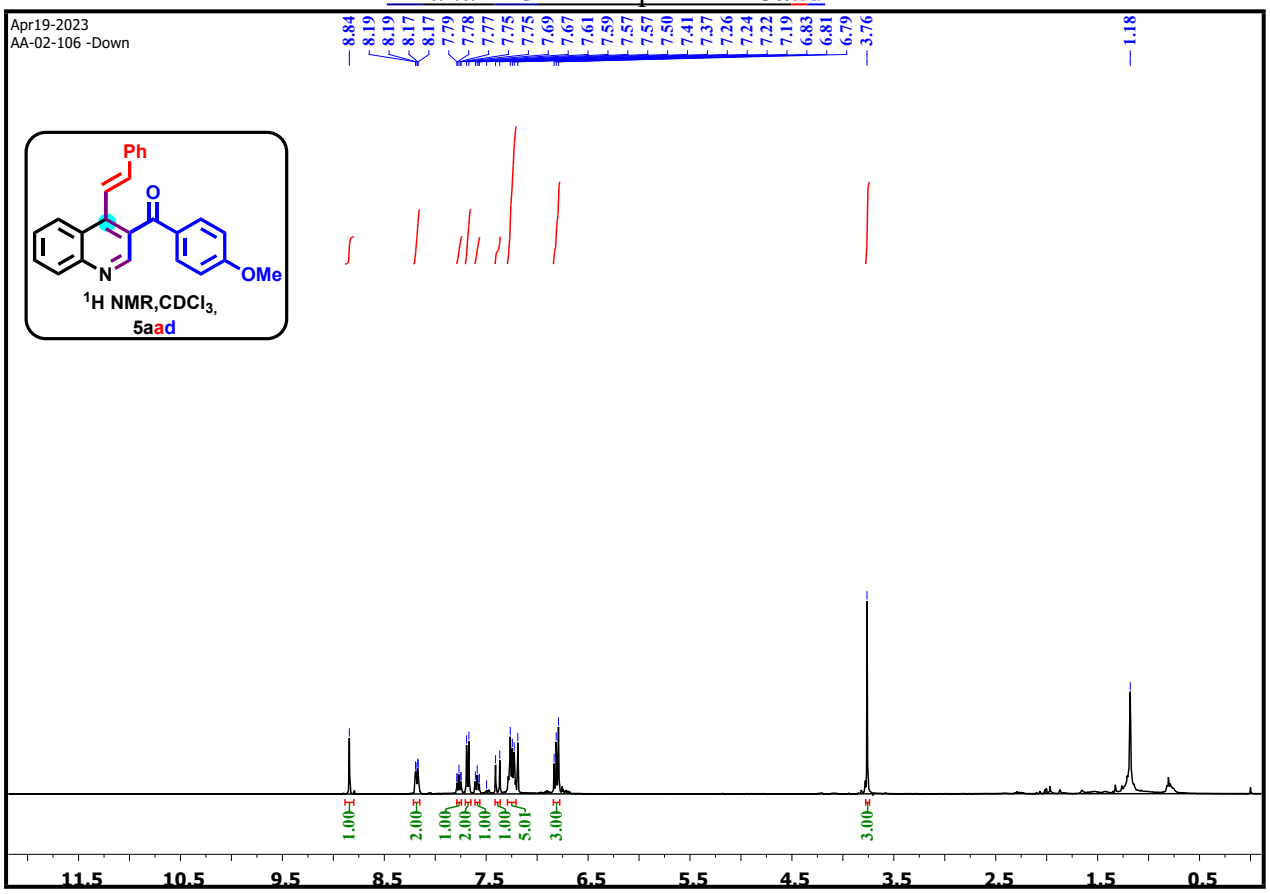

Sep18-2023
AA-02-196
196.71
148.94
148.53
144.48
143.18
139.52
136.18
135.00
130.73
130.50
129.99
129.89
129.35
128.72
128.60
127.38
126.82
126.02
125.40
122.12
77.32
77.00
76.68
21.66
Ph
O
N
13C NMR, CDCl3,
5aab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

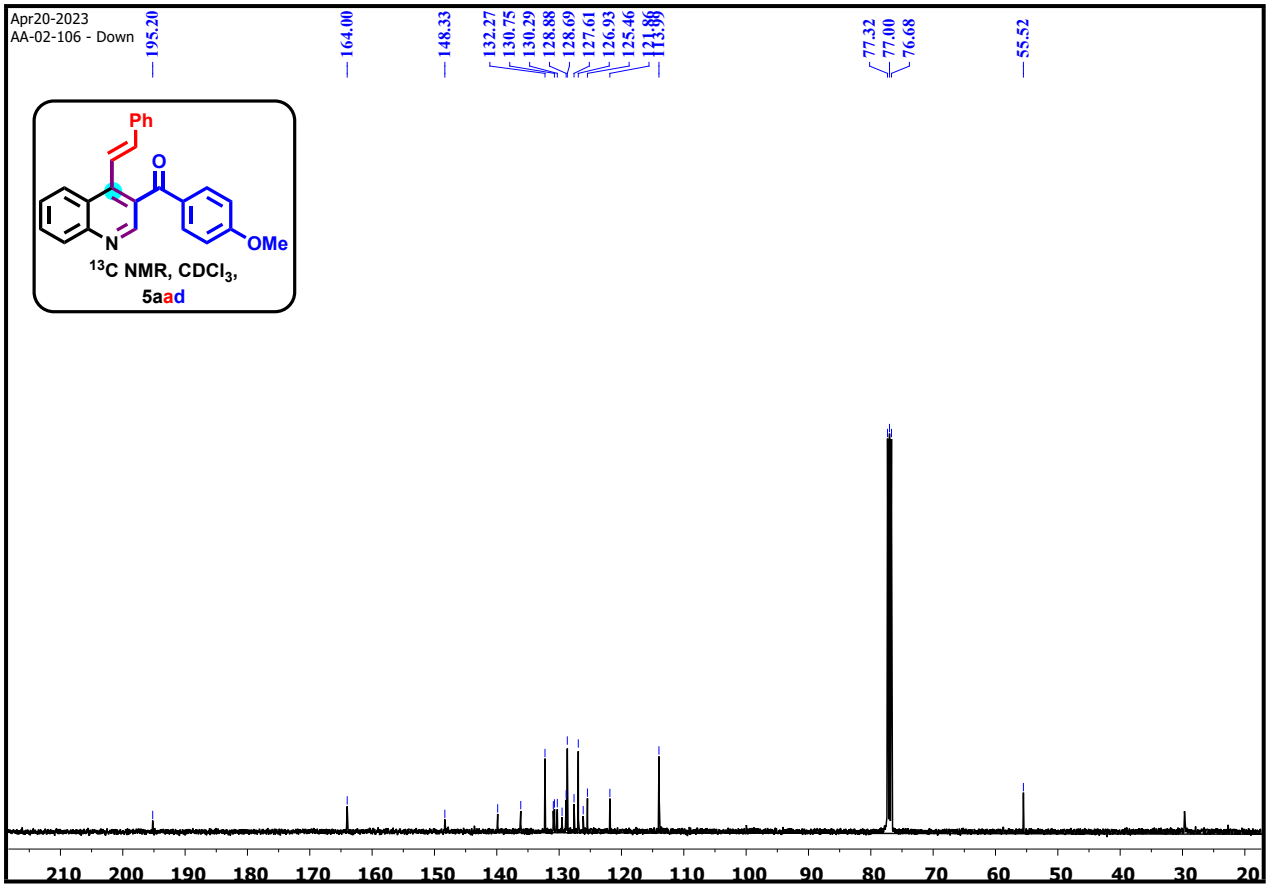
^{1}H *and* ^{13}C NMR spectra of **5aac**



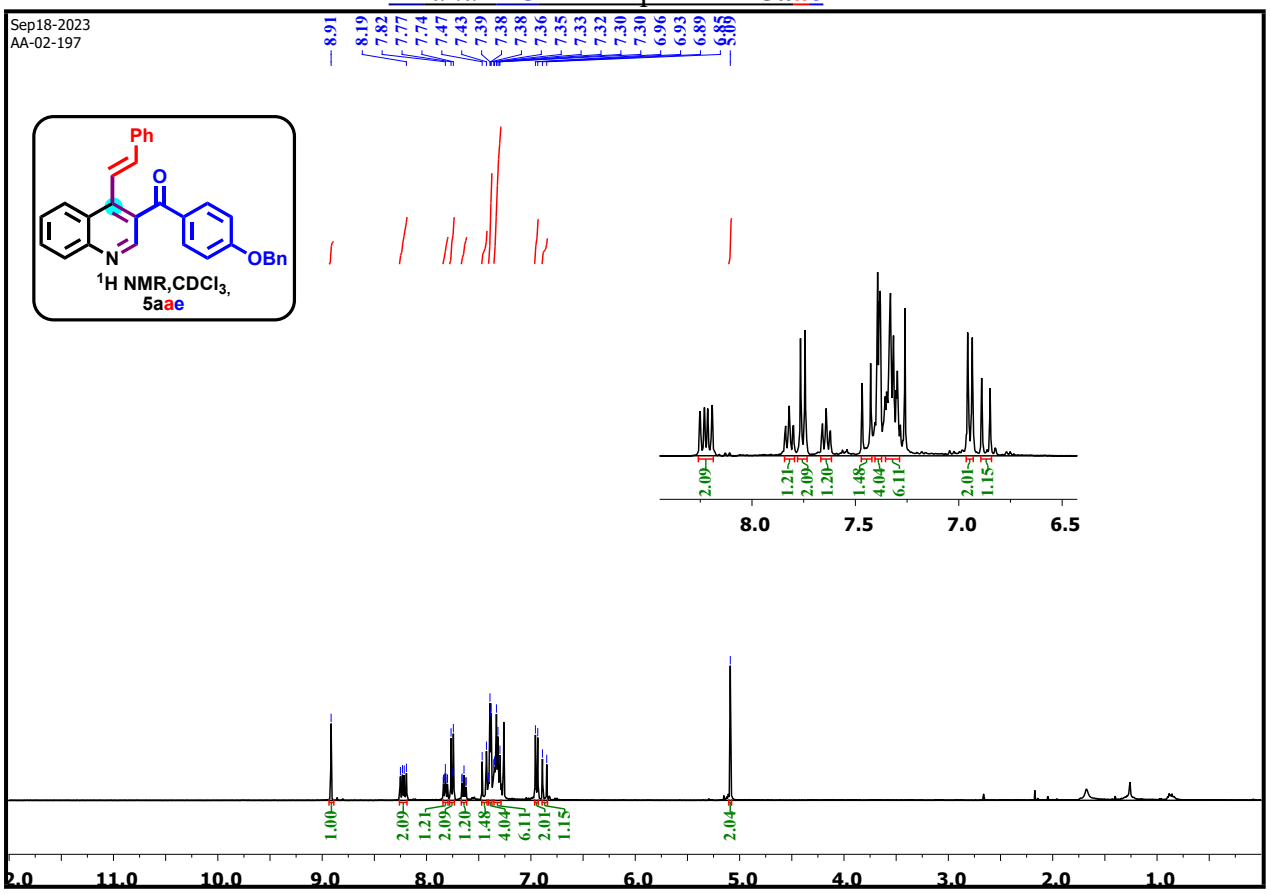

Sep13-2023
AA-02-200
196.75
157.28
149.12
148.62
143.42
139.47
136.28
135.05
130.75
130.55
130.02
129.74
128.69
128.56
127.39
126.82
126.05
125.60
125.52
122.41
77.32
77.00
76.68
35.13
30.97
Ph
O
N
13C NMR, CDCl3,
5aac
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10

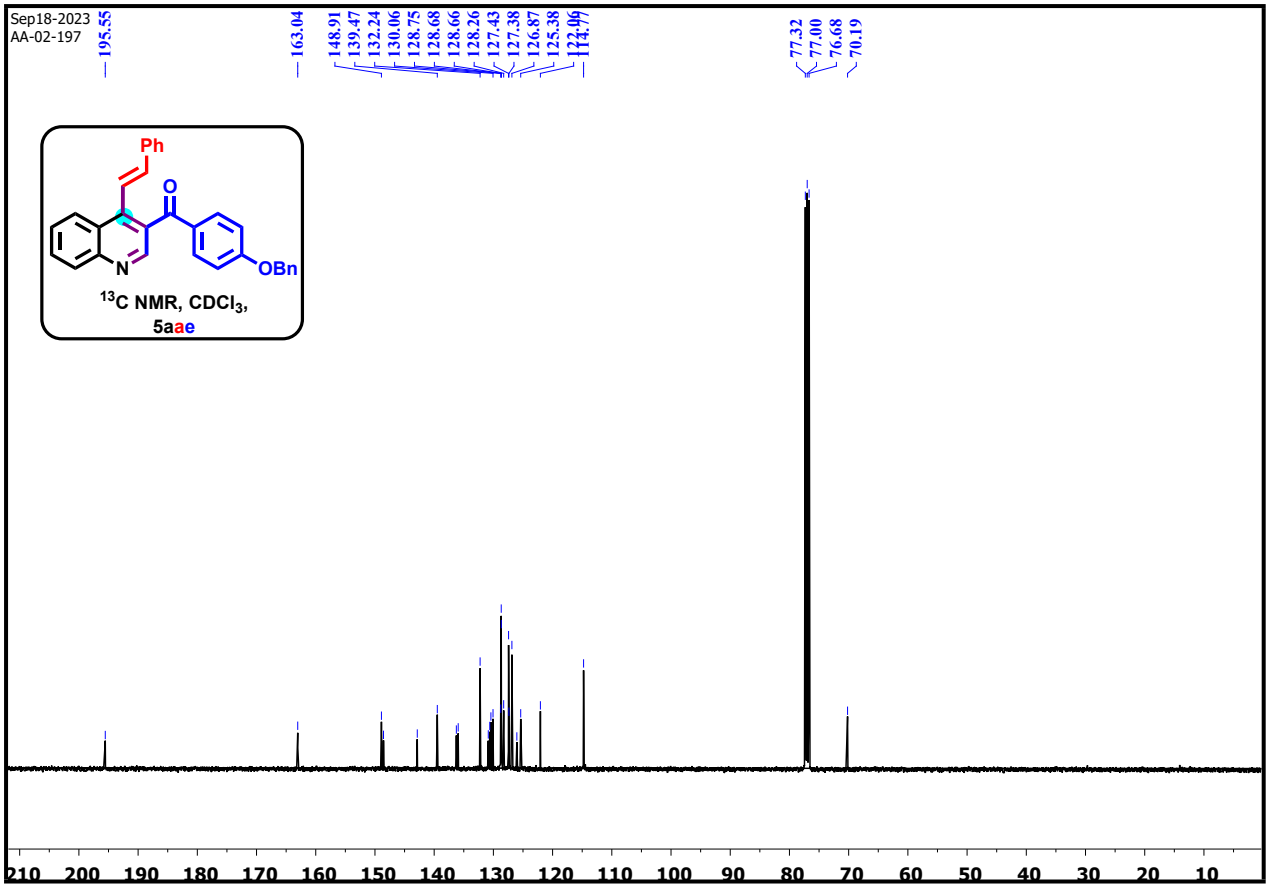
[1]H and [13]C NMR spectra of **5aad**



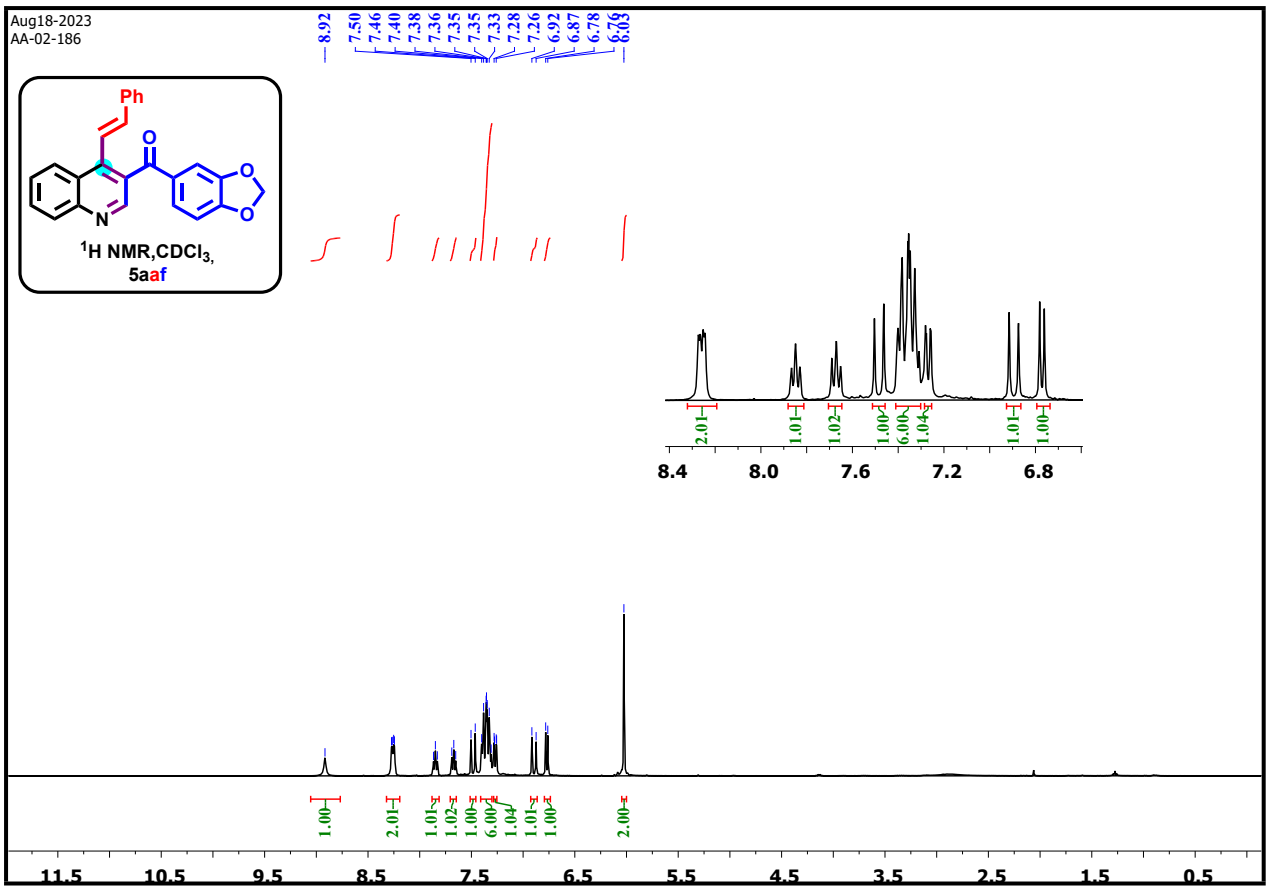

Apr20-2023
AA-02-106 - Down
195.20
164.00
148.33
132.27
130.75
130.29
128.88
128.69
127.61
126.93
125.46
121.86
113.99
77.32
77.00
76.68
55.52
Ph
O
N
OMe
13C NMR, CDCl3,
5aad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

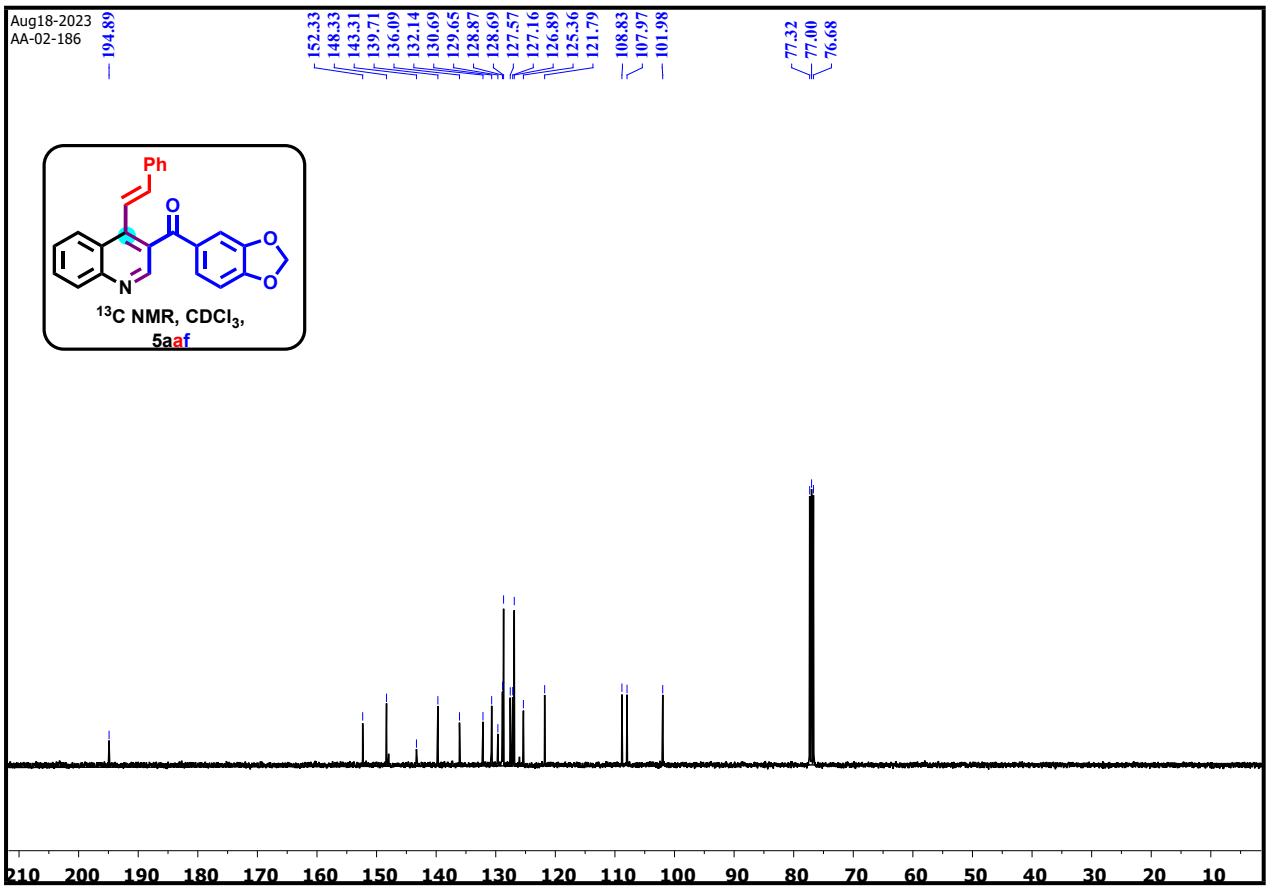
^{1}H and ^{13}C NMR spectra of **5aae**



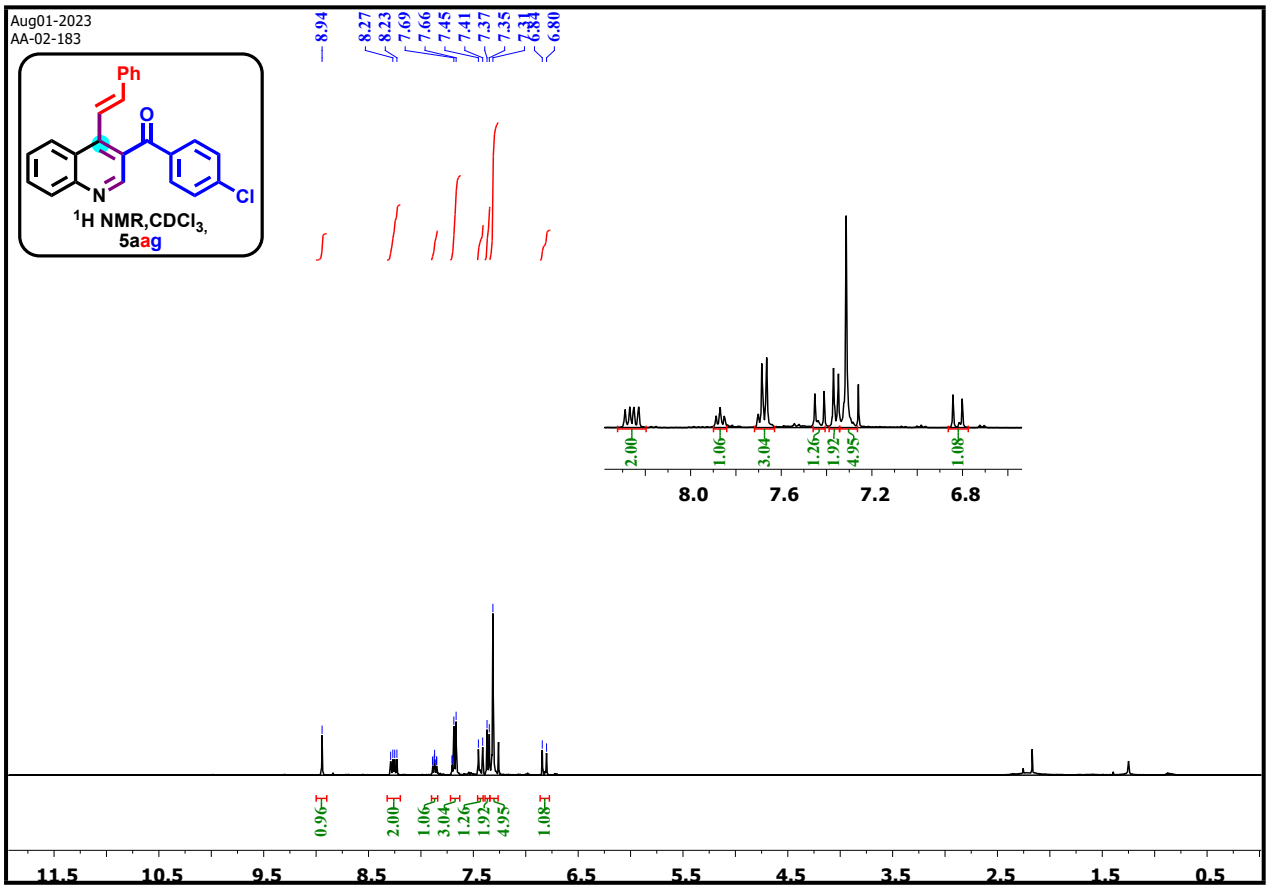


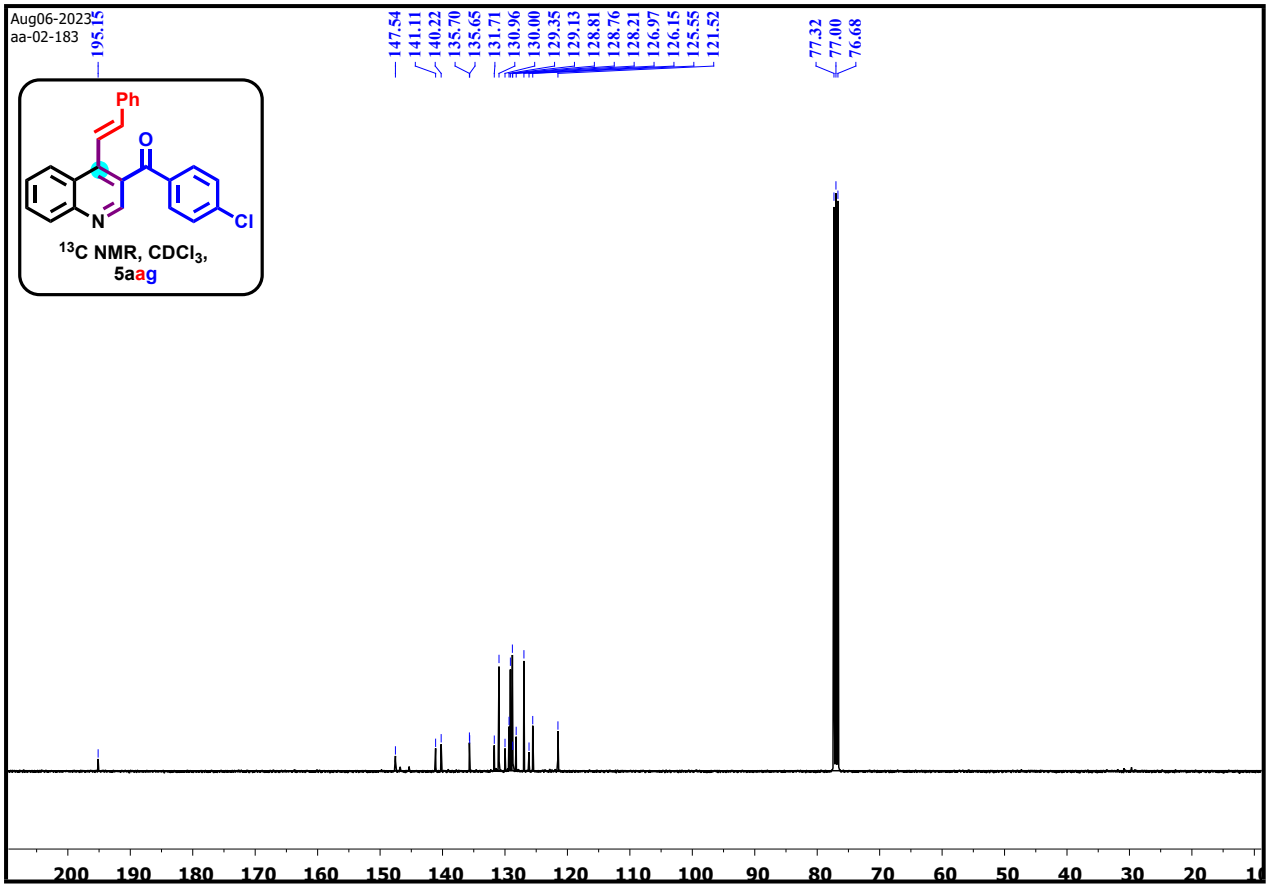
[1]H and [13]C NMR spectra of **5aaf**


Aug18-2023
AA-02-186
Ph
O
N
O
O
^{1}H NMR,CDCl$_3$,
5aaf

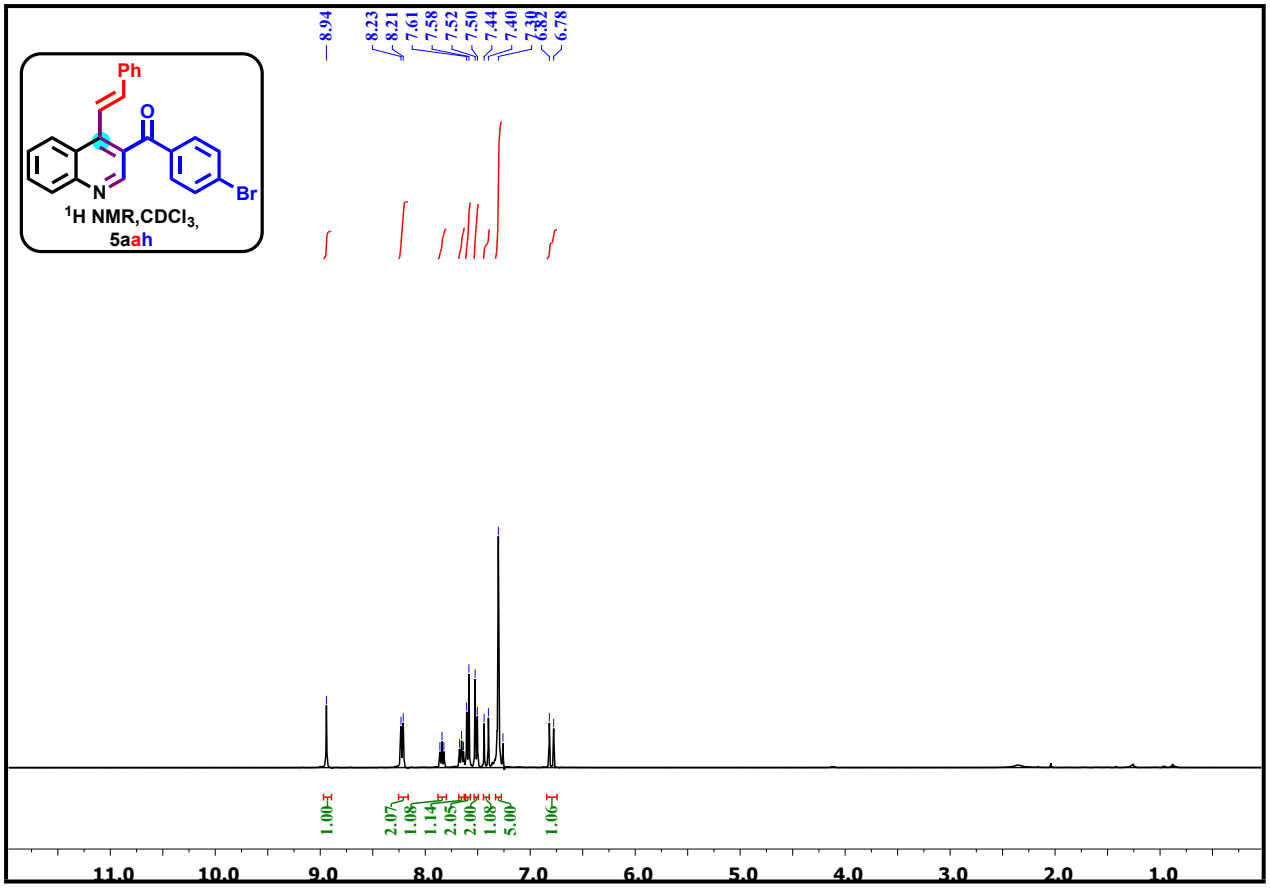

Aug18-2023
AA-02-186
Ph
O
N
O
O
^{13}C NMR, CDCl$_3$,
5aaf

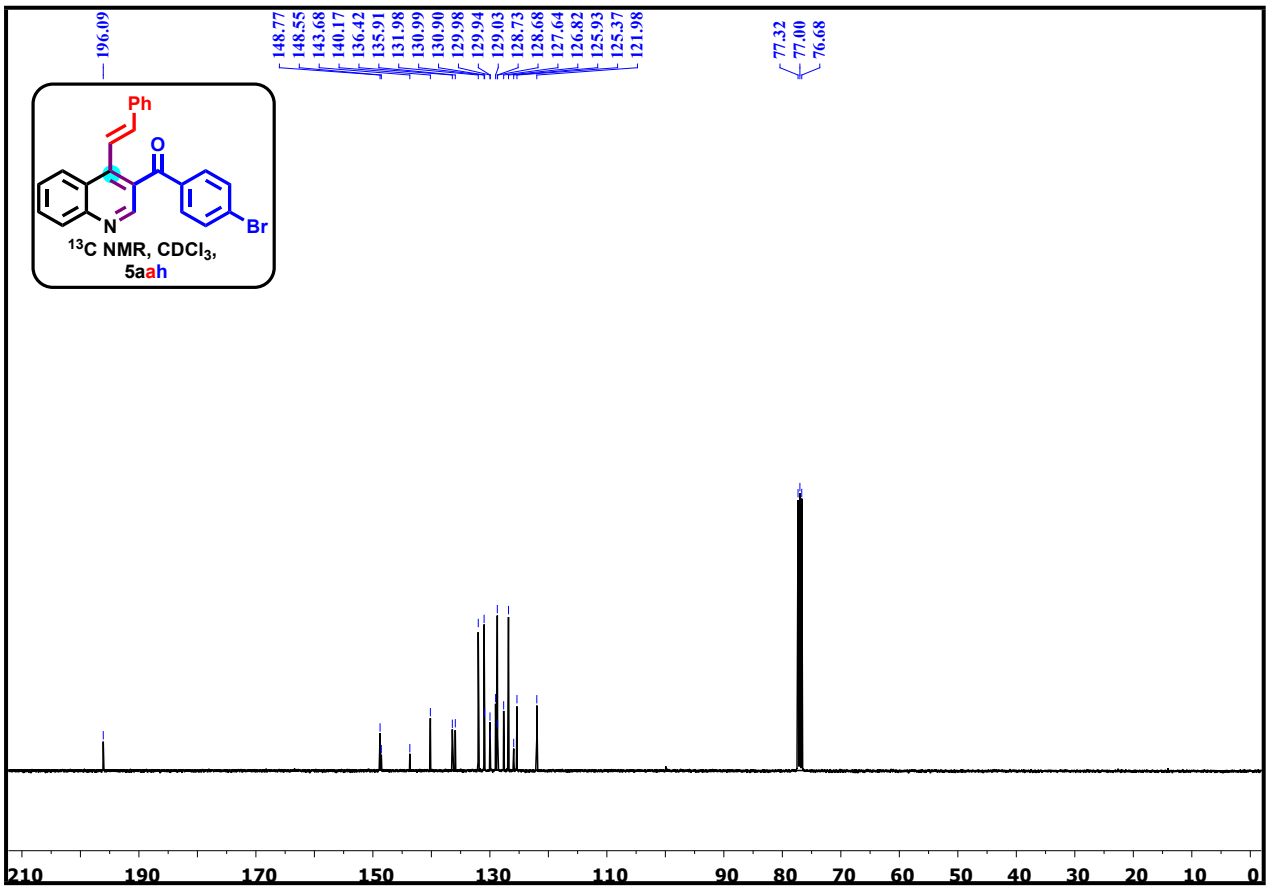
[1]H and [13]C NMR spectra of **5aag**



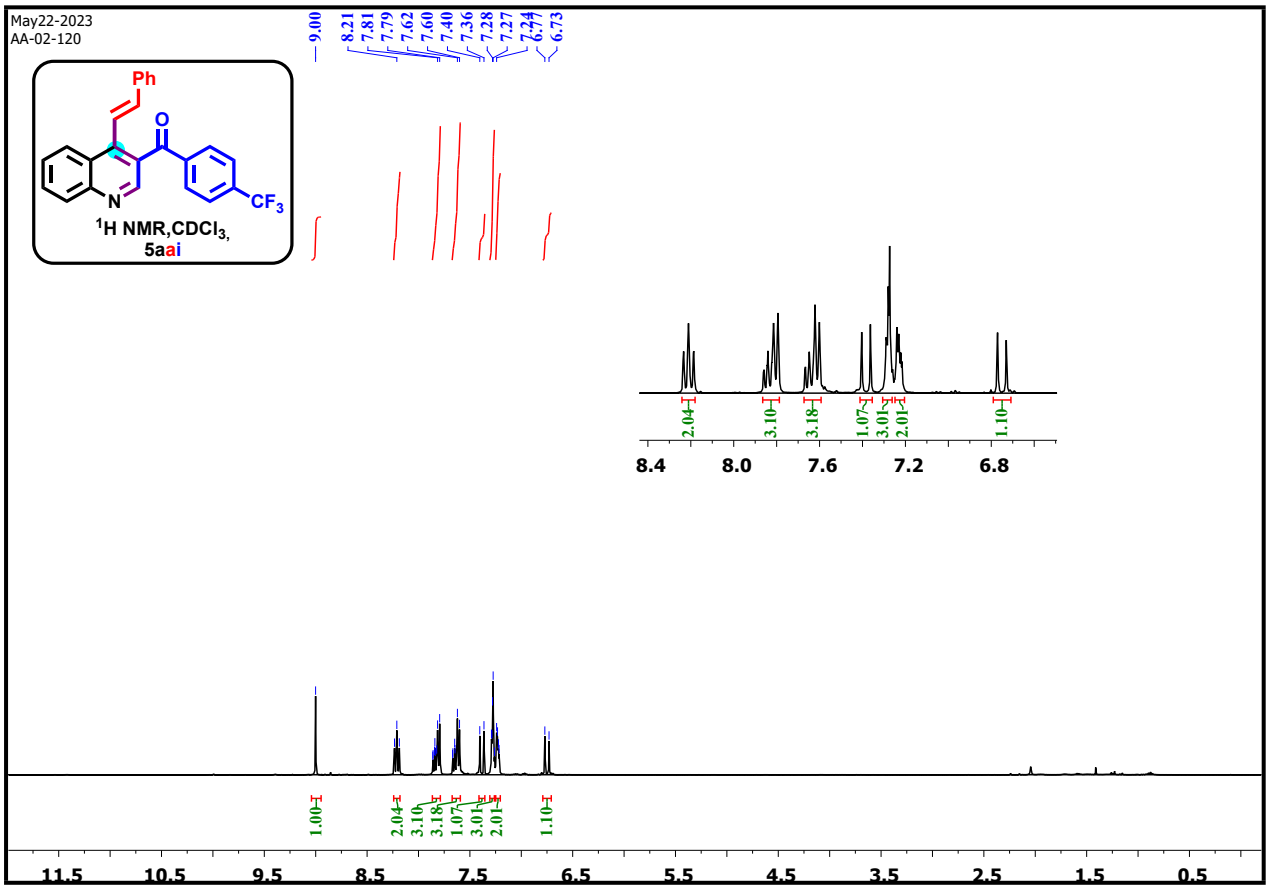


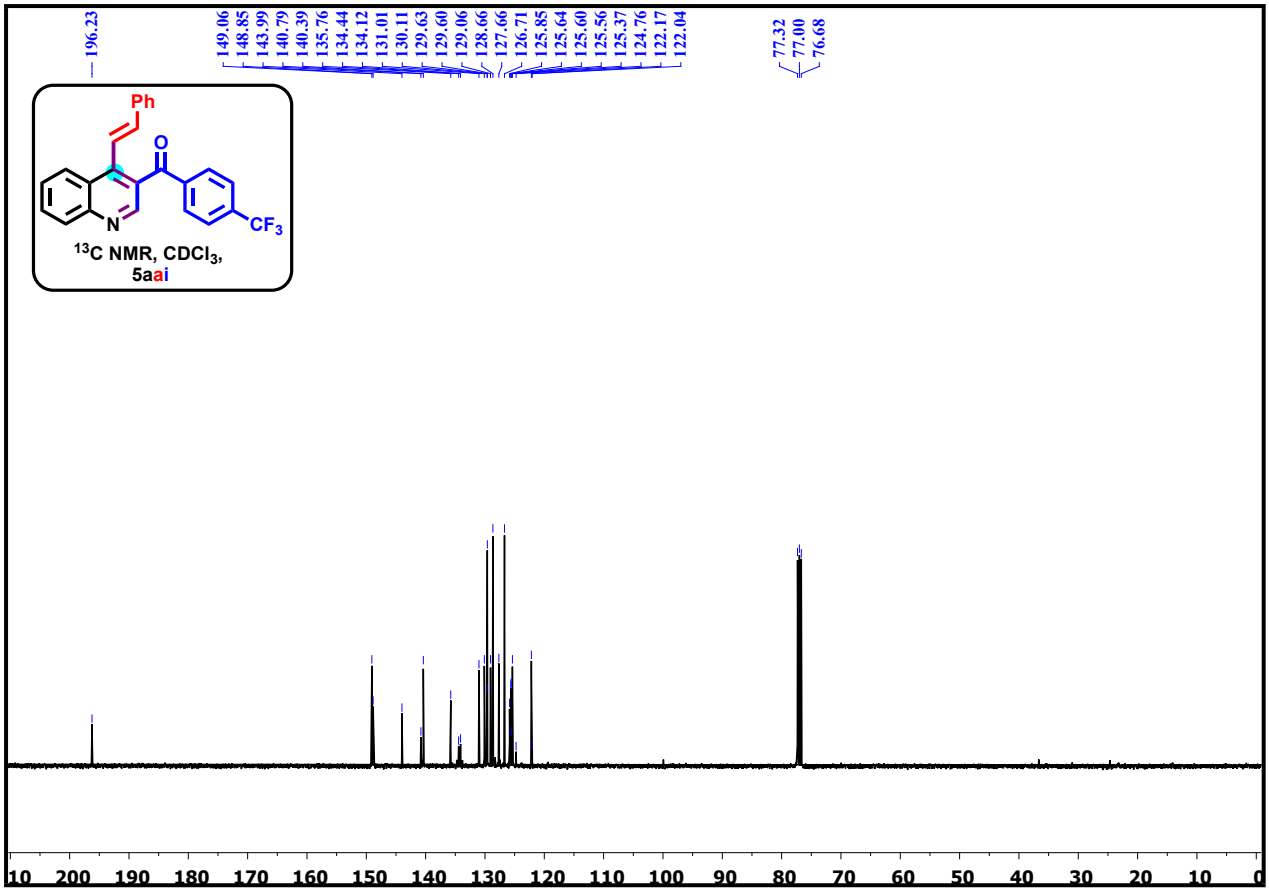
[1]H and [13]C NMR spectra of **5aah**


Ph
O
N
Br
^{1}H NMR,CDCl$_3$,
5aah
8.94
8.23
8.21
7.61
7.58
7.52
7.50
7.44
7.40
6.82
6.78
1.00
2.07
1.08
1.14
2.05
2.00
1.08
5.00
1.06
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

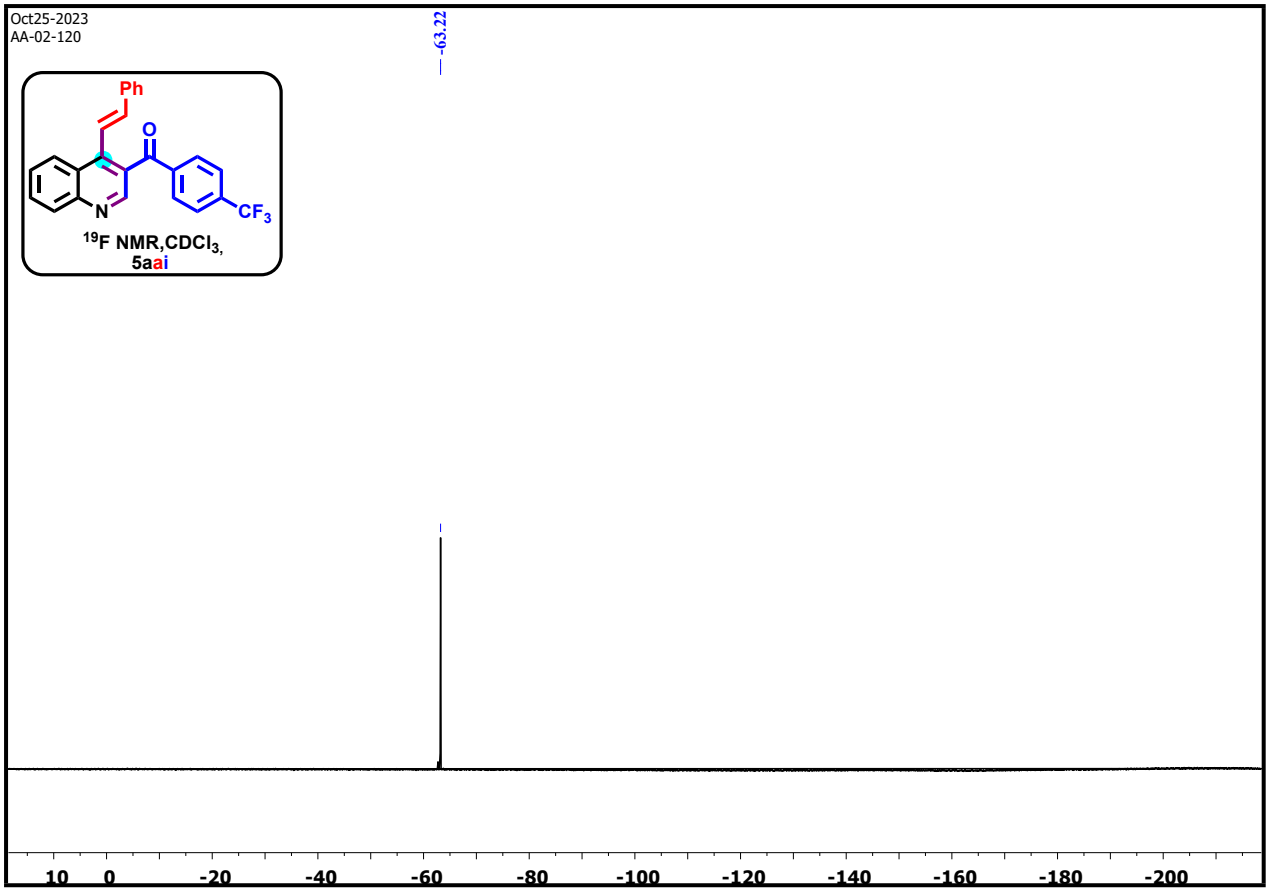

Ph
O
N
Br
^{13}C NMR, CDCl$_3$,
5aah
196.09
148.77
148.55
143.68
140.17
136.42
135.91
131.98
130.99
130.90
129.98
129.94
129.03
128.73
128.68
127.64
126.82
125.93
125.37
121.98
77.32
77.00
76.68
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

[1]H and [13]C NMR spectra of **5aai**

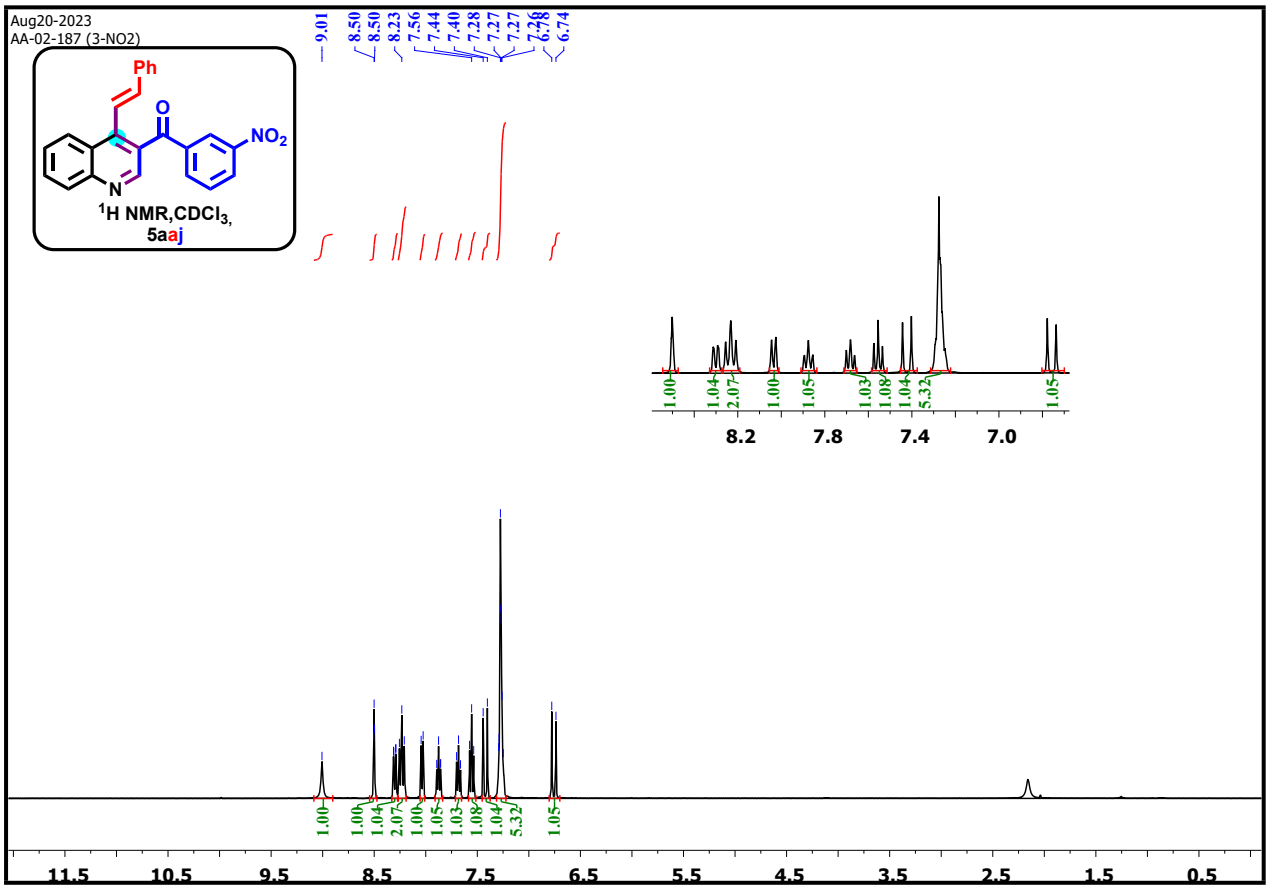


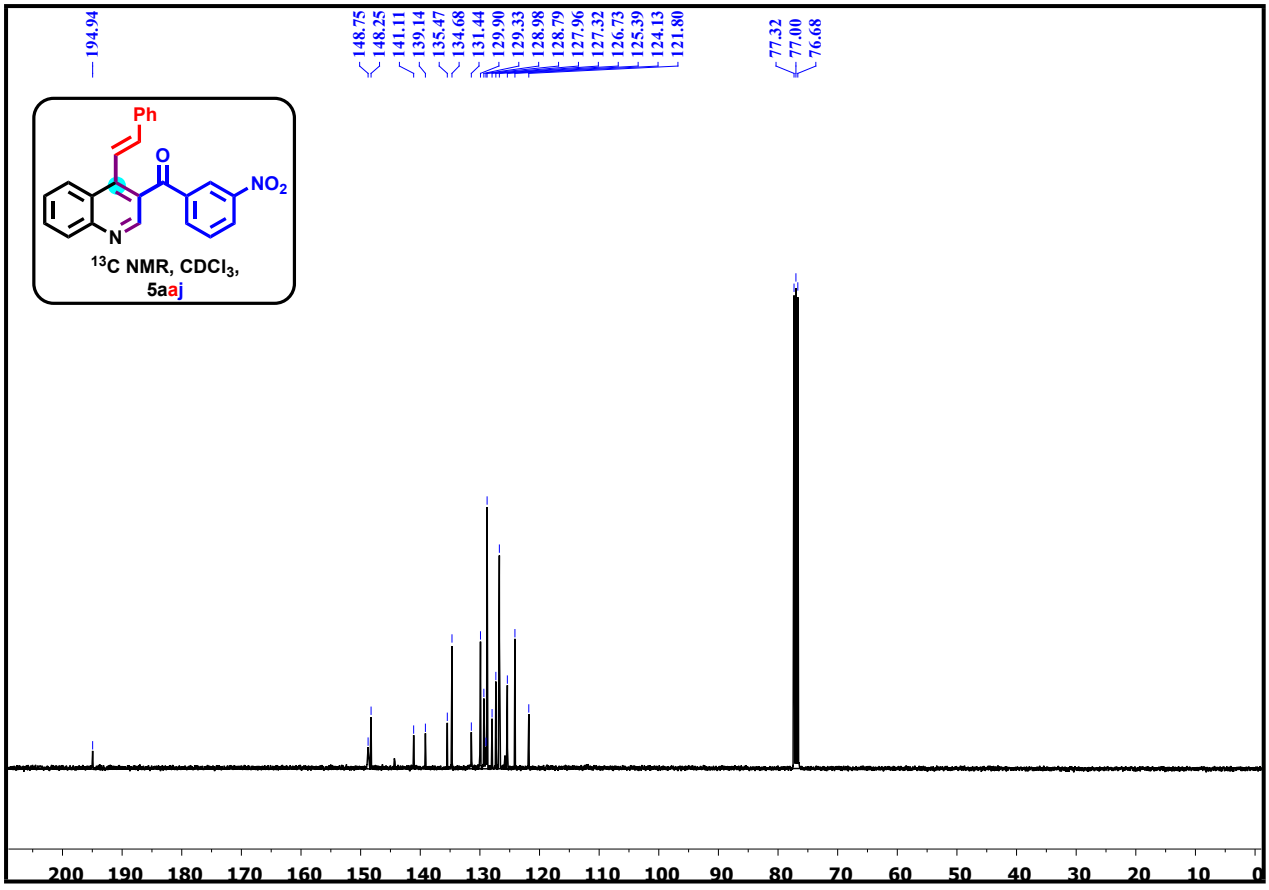


19F NMR spectra of **5aai**

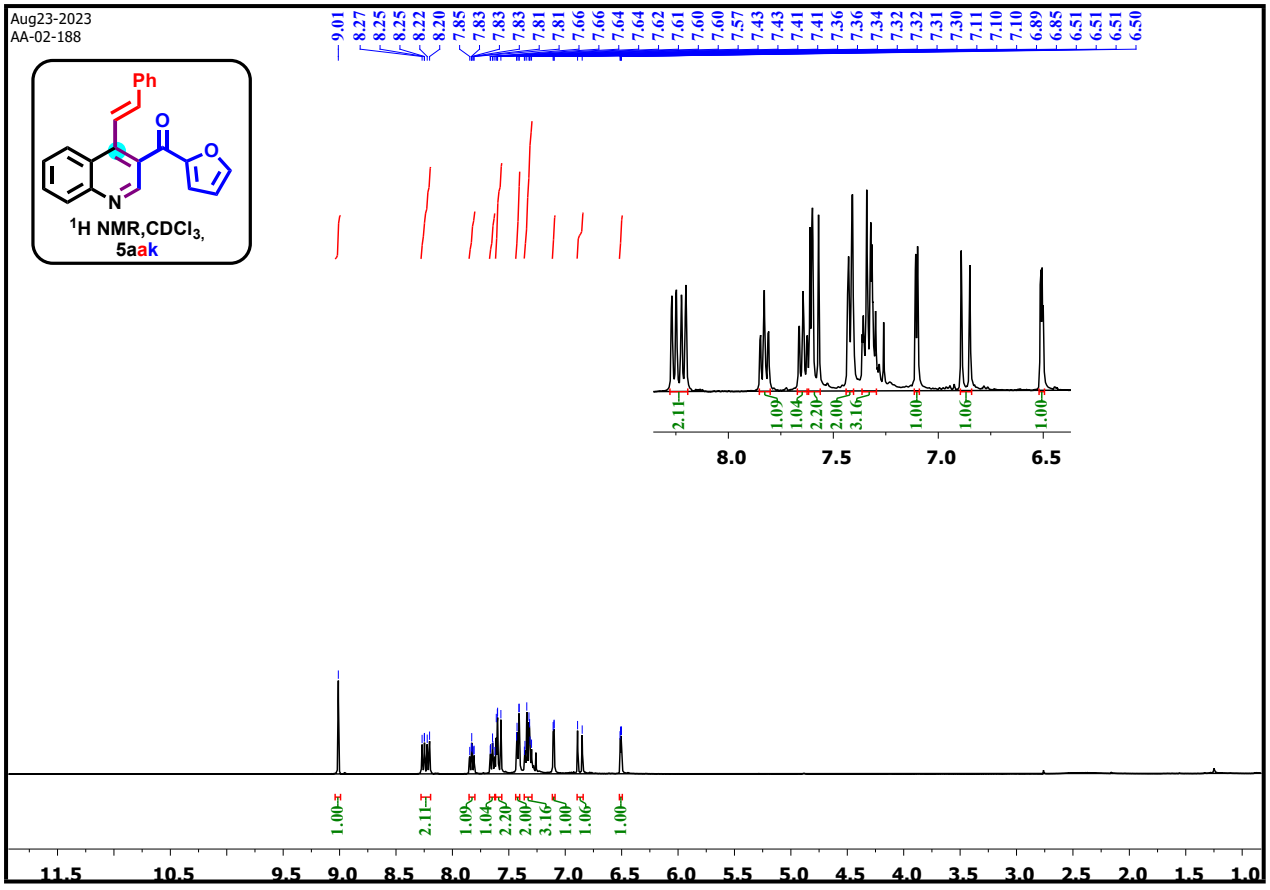

Oct25-2023
AA-02-120
-63.22
Ph
O
N
CF3
19F NMR,CDCl3,
5aai
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

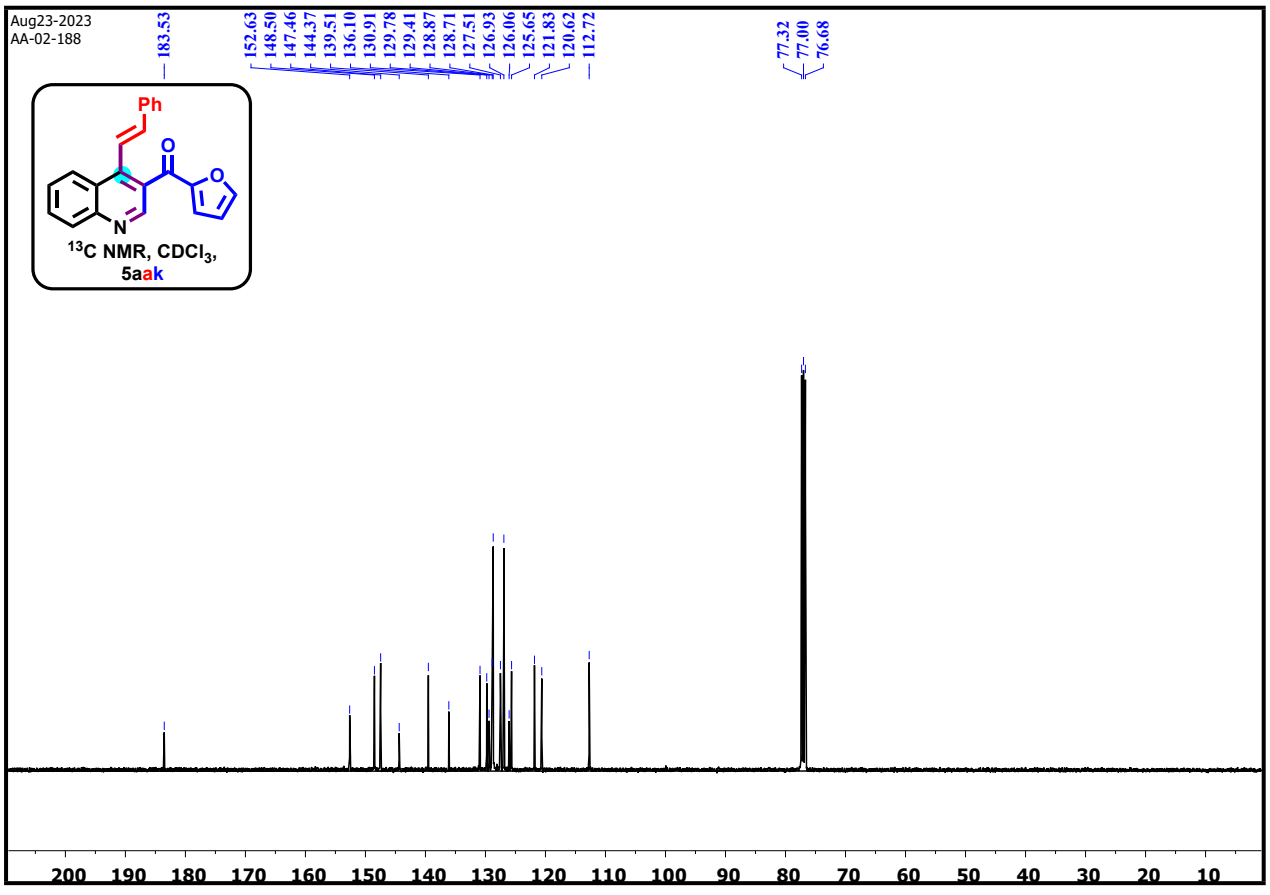
[1]H and [13]C NMR spectra of **5aaj**



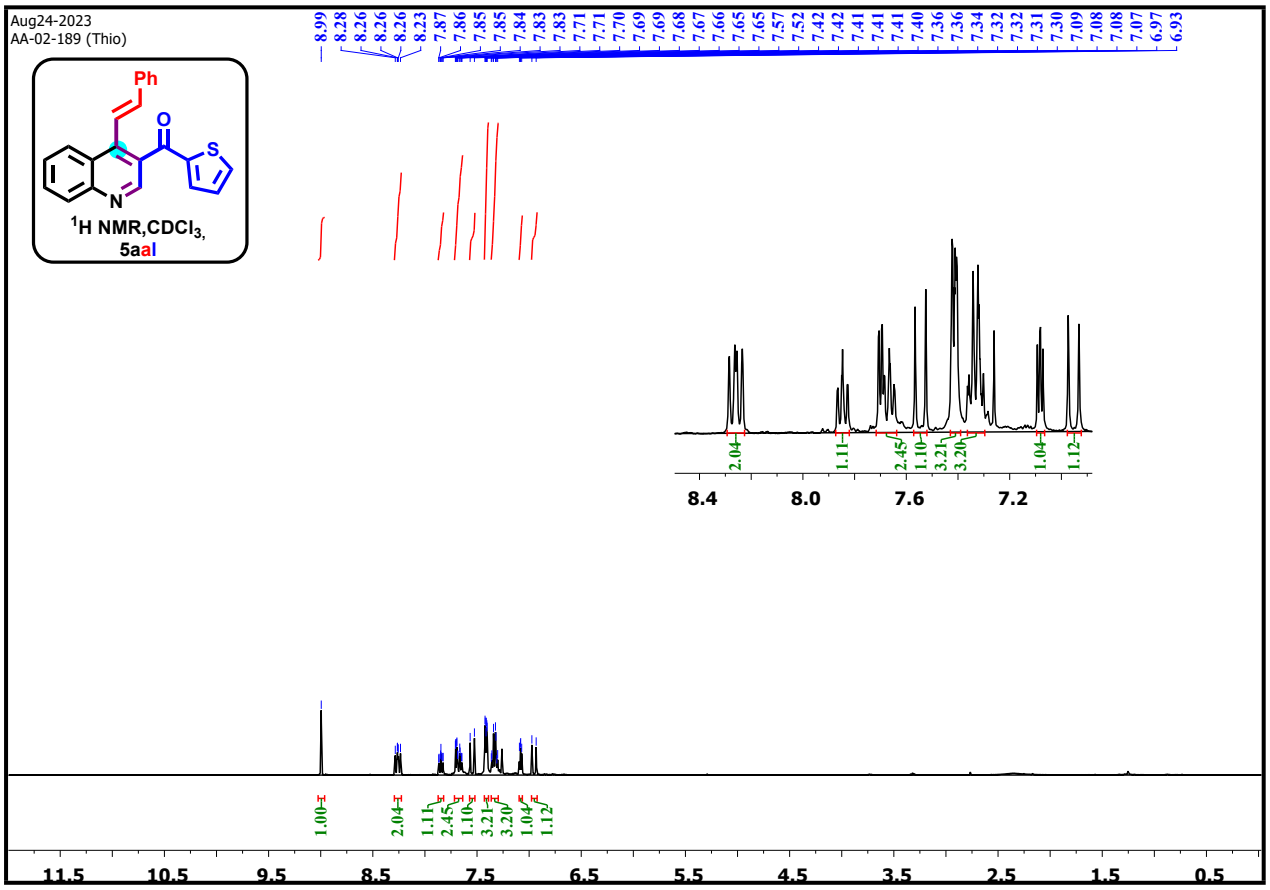


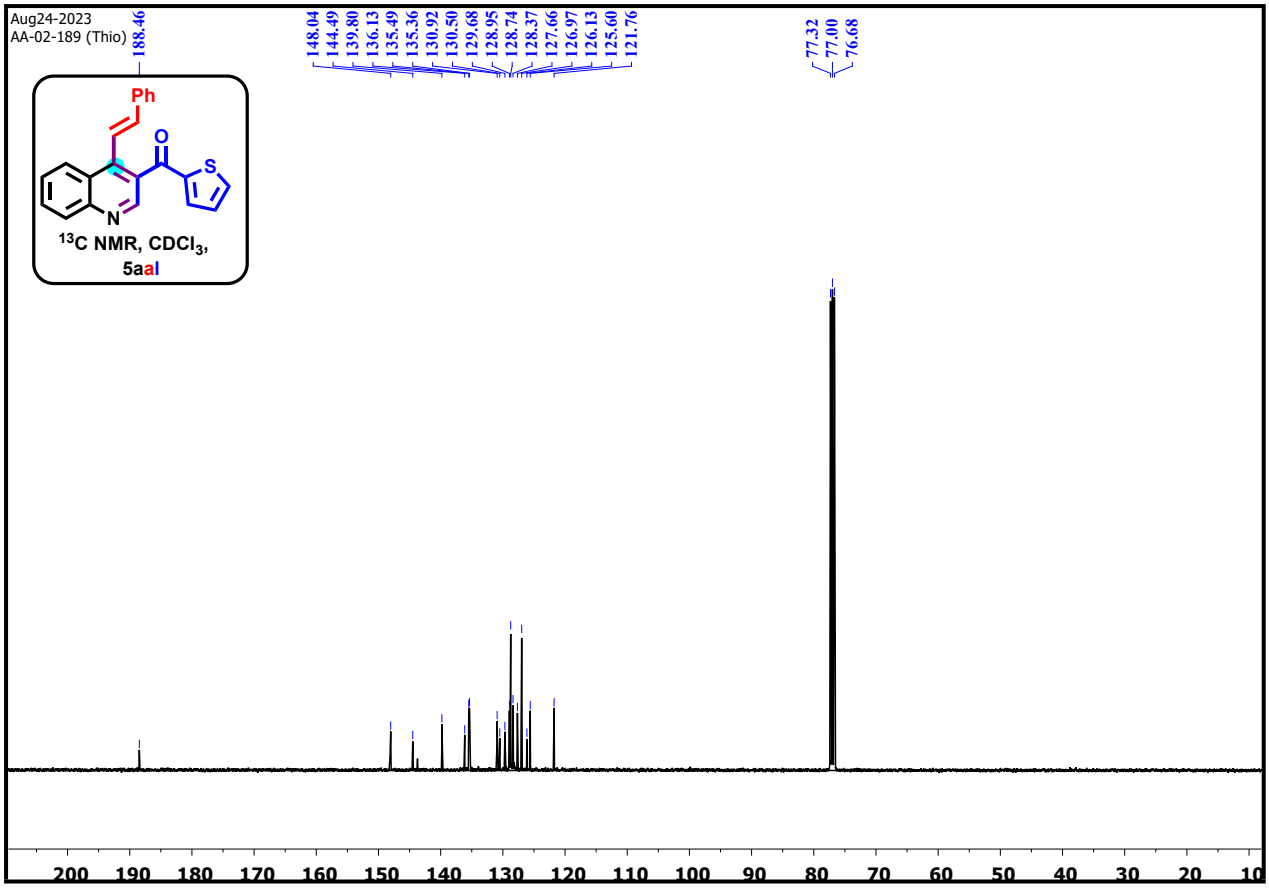
[1]H and [13]C NMR spectra of **5aak**


Aug23-2023
AA-02-188
Ph
O
O
N
^{1}H NMR,CDCl$_3$,
5aak

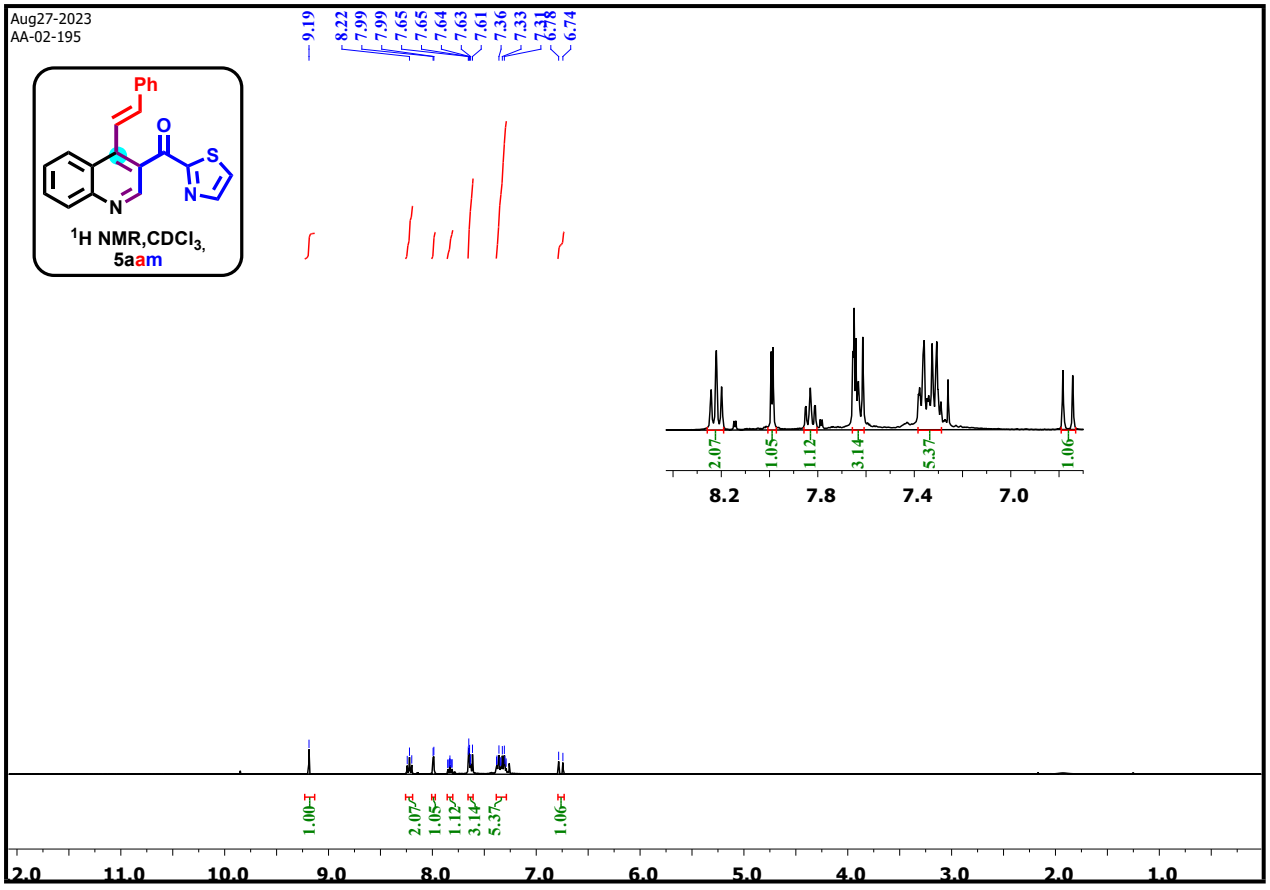

Aug23-2023
AA-02-188
Ph
O
O
N
^{13}C NMR, CDCl$_3$,
5aak

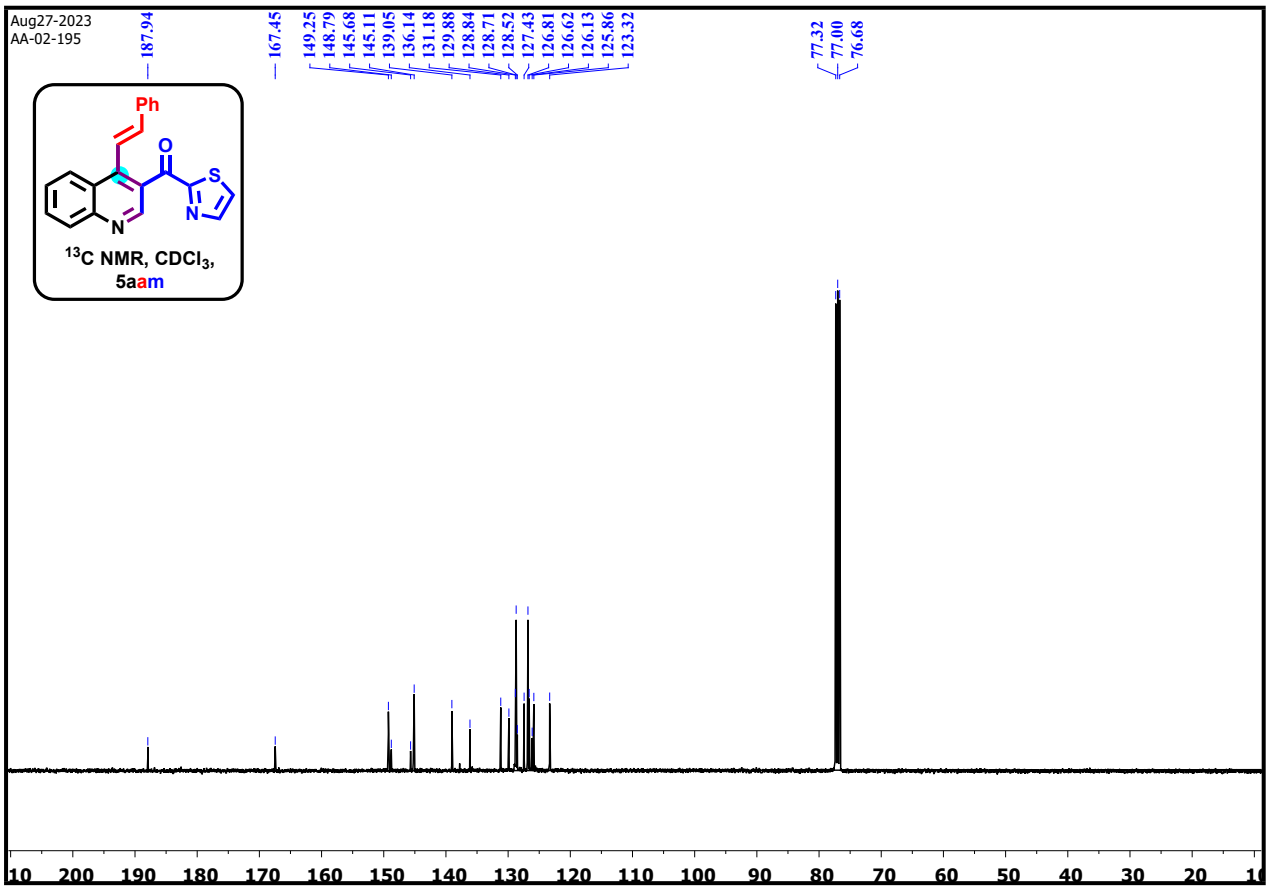
[1]H and [13]C NMR spectra of **5aal**





[1]H and [13]C NMR spectra of **5aam**


Aug27-2023
AA-02-195
Ph
O
S
N
N
^{1}H NMR,CDCl$_3$,
5aam
9.19
8.22
7.99
7.99
7.65
7.65
7.64
7.63
7.61
7.36
7.33
7.31
6.78
6.74
2.07
1.05
1.12
3.14
5.37
1.06
8.2
7.8
7.4
7.0
1.00
2.07
1.05
1.12
3.14
5.37
1.06
2.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


Aug27-2023
AA-02-195
187.94
167.45
149.25
148.79
145.68
145.11
139.05
136.14
131.18
129.88
128.84
128.71
128.52
127.43
126.81
126.62
126.13
125.86
123.32
77.32
77.00
76.68
Ph
O
S
N
N
^{13}C NMR, CDCl$_3$,
5aam
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

References:

(1) D. K. Tiwari, M. Phanindrudu, S. B. Wakade, J. B. Nanubolu, and D. K. Tiwari, *Chem. Commun.* 2017, **53**, 5302.

(2) X. Jie, Y. Shang, X. Zhang and W. Su, *J. Am. Chem. Soc.,* **2016**, *138*, 5623.