Supporting Information

Rongalite-mediated hydride-free chemoselective reduction of C=C bond of isatin-derived Michael acceptors

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1. General information:

All reactions were performed in either 10 mL reaction tubes or 50 mL pear-shaped round-bottom flasks. The progress of the reaction was monitored by analytical thin-layer chromatography (TLC) on pre-coated silica gel plate (silica gel 60 F 254). After development, TLC plate was visualized under UV light (254 nm) and further developed by staining with a basic $KMnO_4$ solution or exposure to iodine (I_2) vapor. ^{1}H, ^{13}C, DEPT-135, and ^{19}F NMR spectra were recorded at room temperature on Bruker Avance Ultrashield 400 or 500 MHz spectrometer operating at 400/500 MHz for ^{1}H, 101 MHz for ^{13}C, and 376 MHz ^{19}F nuclei. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard for ^{1}H NMR and to the residual solvent peak for ^{13}C NMR. ^{1}H NMR data is reported as follows: chemical shift (δ, ppm), multiplicity, coupling constant, and integration. ^{13}C NMR data is reported as chemical shifts (δ, ppm). High-resolution mass spectra (HRMS) was obtained on a Thermo Scientific Q-Exactive mass spectrometer equipped with an Accela 1250 pump and an ESI-TOF mass analyzer. All commercially available analytical grades solvents and reagents were used as received without further purification unless otherwise stated.

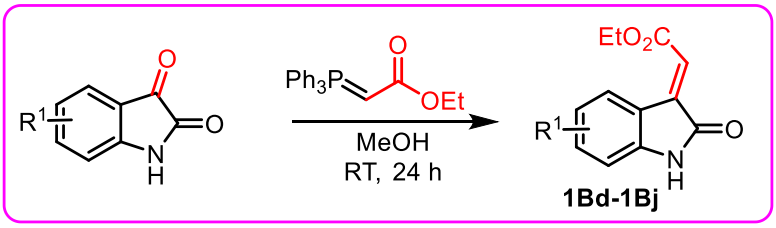
2. Experimental Procedure:

3. General procedure for synthesis of Michael Acceptor [Starting material]

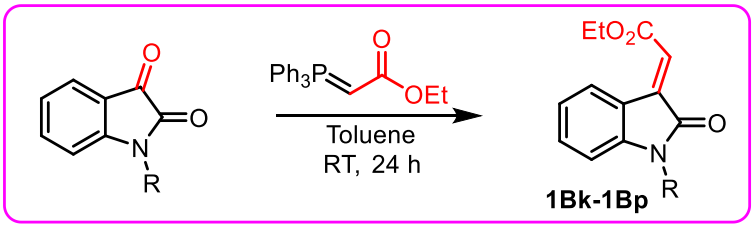
All isatin derivatives (**1Aa-1Ao**) commercially available of analytical grade were used as received without further purifications.

General procedure for synthesis of Isatyledene acetates/ Cyanoacetate/ malonate:[1]

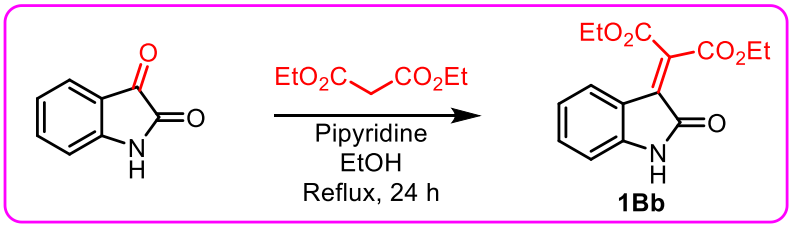
To a solution of the corresponding substituted isatin (0.5 mmol, 1equiv.) in methanol (5 mL) was added phosphonium ylide (1.2 equiv.) and the mixture was stirred at room temperature. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% ethyl acetate/ petroleum ether) directly to afford the purified product. (**1Ba, & 1Bd-1Bj**)



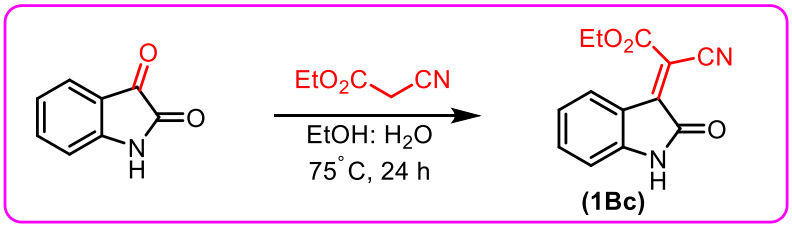
To a solution of the corresponding *N*-substituted isatin (0.5 mmol, 1equiv.) in toluene solvent, added phosphonium ylide (1.2 equiv.) and stirred at room temperature for 24 hrs. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (10% ethyl acetate/ petroleum ether) directly to afford a purified product. (**1Bk-1Bp**)



To a (25 ml) pair-shaped round bottom flask was sequentially added corresponding substituted isatin (0.5 mmol, 1equiv.), EtOH (5 mL), diethyl malonate (0.5 mmol) and piperidine (1.0 mmol). The mixture was stirred under reflux condition for overnight. The resulting dark red mixture was evaporated to dryness under reduced pressure and the residue was directly purified by column chromatography on silica gel (Pet ether/Ethyl acetate = 10/1) to afford the purified product. (**1Bb**)

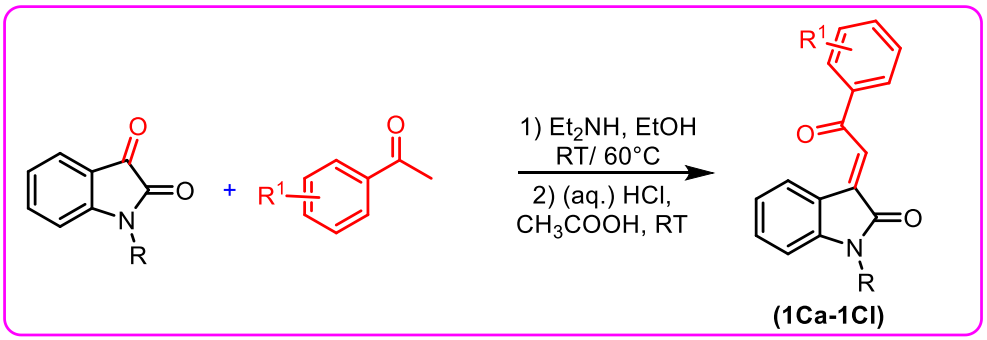


A mixture of isatin/substituted isatin (0.5 mmol, 1 equiv.), ethyl cyanoacetate (0.51 mmol, 1.01 equiv.) in Ethanol: H_2O (3:7) solvent (2 mL) was stirred at 75° C until the starting material was completely converted to product (monitored by TLC). After completion of reaction solvent was removed under low pressure. Obtained product was used for next step without any further purification. (**1Bc**)



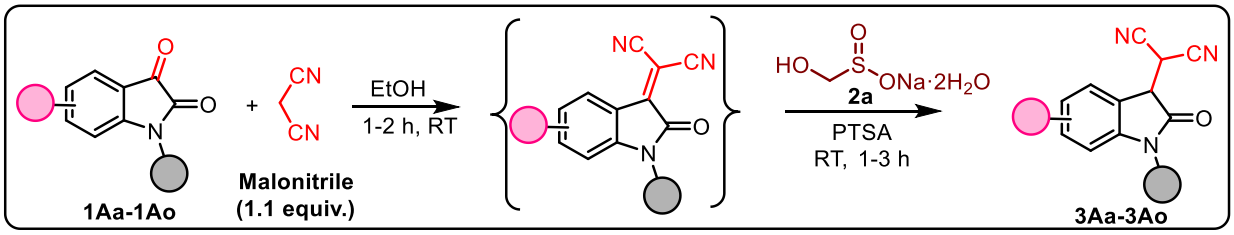
General procedure for synthesis of 3-Acylidene oxindole:[2]

N-methylisatin (1 equiv.), substituted acetophenone (1.5 equiv.) and diethylamine as a base in MeOH solvent were stirred at room temperature or 60° C to give the intermediate crude aldol addition product. This intermediate was dehydrated in EtOH solvent using (aq.) HCl and glacial ethanoic acid and stirred at room temperature for 24 h. After in that ethyl acetate and water was added to the reaction mixture and organic layer was washed with H_2O and saturated aqueous $NaHCO_3$ solution. The crude reaction mixture was further purified by column chromatography to provide 3-phenacylidene oxindole. (**1Ca-1Cl**)



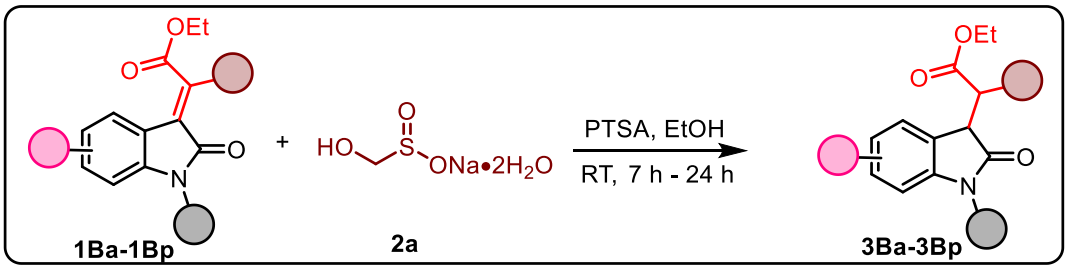
4. General procedure (A) for one-pot reduction of Isatyledene malononitriles:

In 10 mL reaction tube, the corresponding substituted isatin (0.3 mmol, 1.0 equiv.) and malonitrile (1.1 equiv.) were dissolved in ethanol (2 mL) and stirred at room temperature for 1-2 h until the starting isatin derivative completely converted to the isatyledene malonitrile (monitored by TLC). Subsequently p-toluenesulfonic acid (*P*-TSA), rongalite (**2a** 1.5 equiv.) and additional ethanol (1 mL) were added and the reaction mixture was stirred at room temperature for 1-3 h. Upon completion of reaction (monitored by TLC), in crude reaction mixture ethyl acetate and water was added and the layers was separated. The organic layer was collected, dried and concentrated to afford product **(3Aa-3Ao).**



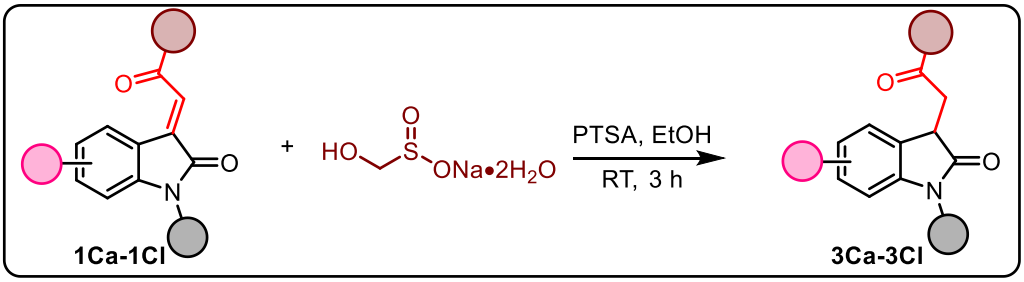
General procedure (B) for reduction of Isatyledene acetates/ malonate/ Cyanoacetate:

In 10 mL reaction tube, added the corresponding substituted Isatyledene acetates/ malonate/ Cyanoacetate (0.3 mmol, 1.0 equiv.), *p*-toluenesulfonic acid (*P*-TSA) and rongalite (**2a** 1.5 equiv.) and stirred in ethanol (3 mL) solvent at room temperature for 7-24 hours. Upon completion of reaction (monitored by TLC), in the crude reaction mixture ethyl acetate and water was added and the layers was separated. The organic layer was collected and purified by column chromatography on silica gel using Petroleum ether/ethyl acetate (8:2) as the eluent to afford the desired product **(3Ba-3Bp).**



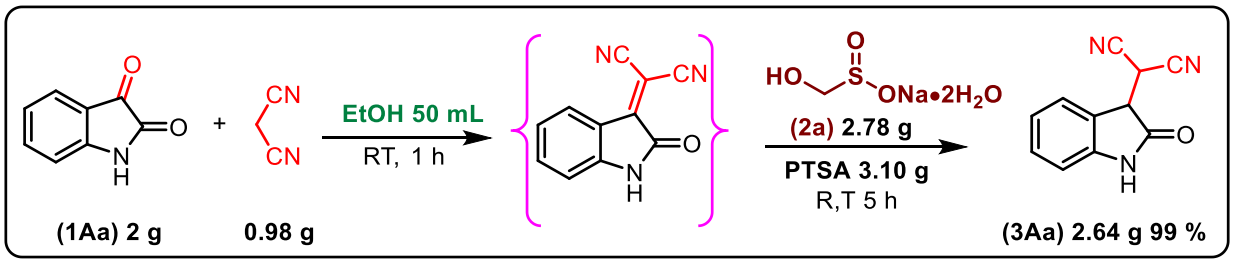
General procedure (C) for reduction of Isatyledene aryl ketone:

In 10 mL reaction tube, added the corresponding substituted Isatyledene aryl ketone (0.3 mmol, 1.0 equiv.), p-toluenesulfonic acid (PTSA) and rongalite (**2a** 1.5 equiv.) and stirred in ethanol (3 mL) solvent at room temperature for 7-24 hours. Upon completion of reaction (monitored by TLC), precipitate was observed and then it was filter to collect solid compound. In the crude reaction mixture ethyl acetate and water was added and the layers was separated. The organic layer was collected and purified by column chromatography on silica gel using Petroleum ether/ethyl acetate (8:2) as the eluent to afford the desired product **(3Ca-3Cl).**

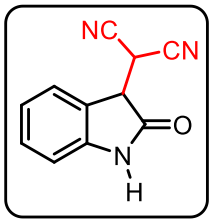


5. Procedure for one-pot multi-gram-scale synthesis of 3Aa:

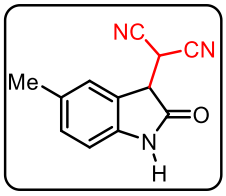
In 100 mL reaction tube, the corresponding substituted isatin (2 g; 1.0 equiv.) and malonitrile (0.98 g; 1.1 equiv.) were dissolved in ethanol (30 mL) and stirred at room temperature for 1 h until the starting isatin derivative was completely converted to the isatyledene malonitrile, as monitored by TLC. Subsequently p-toluenesulfonic acid (3.1 g; *P*-TSA), **2a** rongalite (2.78 g; 1.5 equiv.) and additional ethanol (20 mL) were added and Tte reaction mixture was stirred at room temperature for 5 h. Upon completion of reaction (monitored by TLC), the ethanol solvent was removed under the vacuum. The residue was then diluted with ethyl acetate and water and the layers was separated. The organic layer was collected, dried and concentrated to afford compound **3Aa** in 99% yield.



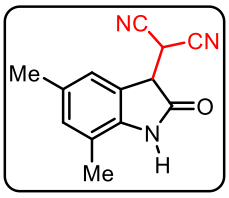
6. Characterization data:



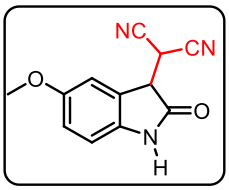
[3Aa] **2-(2-oxoindolin-3-yl)malononitrile**, the titled compound was prepared by General Procedure-A, obtained as a solid, 99% yield, **^{1}H NMR** (400MHz ,DMSO-d_6) δ = 10.92 (s, 1 H), 7.46 (d, *J* = 7.5 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 10 H), 7.16 - 7.03 (m, 9 H), 6.94 (d, *J* = 7.9 Hz, 10 H), 5.65 (d, *J* = 4.4 Hz, 9 H), 4.45 (d, *J* = 4.5 Hz, 9 H); **^{13}C NMR** (101MHz ,DMSO-d_6) δ = 173.7, 143.1, 129.8, 124.6, 123.7, 122.2, 112.7, 112.4, 110.2, 44.0, 23.8; **HRMS:** (ESI) m/z calculated for $C_{11}H_7N_3O$ $[M+H]^+$, 198.0667 found: 198.0671



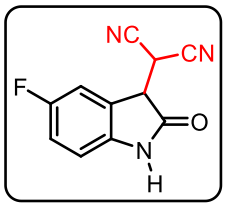
[3Ab] **2-(5-methyl-2-oxoindolin-3-yl)malononitrile**, the titled compound was prepared by General Procedure-A, obtained as a solid, 97% yield, **^{1}H NMR** (400MHz ,DMSO-d_6) δ = 10.83 (s, 1 H), 7.24 (s, 1 H), 7.12 (d, *J* = 7.1 Hz, 1 H), 6.84 (d, *J* = 7.9 Hz, 1 H), 5.47 (d, *J* = 4.4 Hz, 1 H), 4.31 (d, *J* = 4.1 Hz, 1 H), 2.25 (s, 3 H); **^{13}C NMR** (101MHz ,DMSO-d_6) d = 174.2, 140.9, 132.0, 130.7, 125.5, 124.0, 113.1, 112.7, 110.6, 44.6, 24.4, 21.1; **HRMS:** (ESI) m/z calculated for $C_{12}H_9N_3O$ $[M+H]^+$, 212.0824 found: 212.0830



[3Ac] **2-(5,7-dimethyl-2-oxoindolin-3-yl)malononitrile**, the titled compound was prepared by General Procedure-A, obtained as a solid, 97% yield, **^{1}H NMR** (400MHz, DMSO-d_6) δ = 10.86 (s, 1 H), 7.09 (s, 1 H), 6.96 (d, *J* = 0.8 Hz, 1 H), 5.59 (d, *J* = 4.3 Hz, 1 H), 4.38 (d, *J* = 4.3 Hz, 1 H), 2.25 (s, 3 H), 2.19 (s, 3 H); **^{13}C NMR** (101MHz ,DMSO-d_6) δ = 174.1, 139.2, 131.5, 131.1, 123.4, 122.3, 119.4, 112.8, 112.5, 44.3, 23.9, 20.7, 16.4; **HRMS:** (ESI) m/z calculated for $C_{13}H_{11}N_3O$ $[M+H]^+$, 226.0980 found: 226.0985

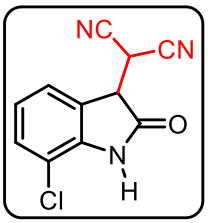


[3Ad] **2-(5-methoxy-2-oxoindolin-3-yl)malononitrile,** the titled compound was prepared by General Procedure-A, obtained as a solid, 98% yield, **^{1}H NMR** (400MHz, DMSO-d_6) δ = 10.74 (s, 1 H), 7.10 (d, *J* = 1.5 Hz, 1 H), 6.95 - 6.89 (m, 1 H), 6.88 - 6.82 (m, 1 H), 5.65 (d, *J* = 4.4 Hz, 1 H), 4.41 (d, *J* = 4.3 Hz, 1 H), 3.73 (s, 3 H); **^{13}C NMR** (101MHz, DMSO-d_6) δ = 173.6, 155.1, 136.2, 124.9, 114.3, 112.7, 112.4, 111.8, 110.7, 55.5, 44.4, 23.8; **HRMS:** (ESI) m/z calculated for $C_{12}H_9N_3O_2$ $[M+H]^+$, 228.0773 found: 228.0771

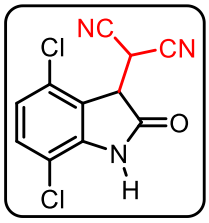


[3Ae] **2-(5-fluoro-2-oxoindolin-3-yl)malononitrile,** the titled compound was prepared by General Procedure-A, obtained as a solid, 93% yield, **^{1}H NMR** (400MHz, DMSO-d_6) δ = 10.94 (s, 1 H), 7.31 (dd, *J* = 1.9, 8.4 Hz, 1 H), 7.24 - 7.13 (m, 1 H), 6.93 (dd, *J* = 4.4, 8.6 Hz, 1 H), 5.69 (d, *J* = 4.4 Hz, 1 H), 4.49 (d, *J* = 3.8 Hz, 1 H); **^{13}C NMR** (101MHz ,DMSO-d_6) δ = 173.7, 159.1, 156.7, 139.4, 125.3, 125.2, 116.4, 116.1, 112.6, 112.4, 112.4, 112.3,

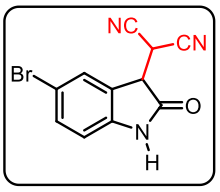
111.1, 111.0, 44.4, 23.6; **^{19}F NMR** (377 MHz, DMSO-d_6) δ -120.99; **HRMS:** (ESI) m/z calculated for $C_{11}H_6FN_3O$ $[M+H]^+$, 216.0573 found:216.0577



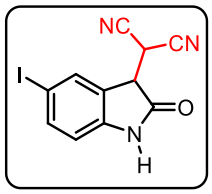
[3Af] 2-(5-fluoro-2-oxoindolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a solid, 94% yield, **^{1}H NMR** (500MHz, DMSO-d$_6$) δ = 11.37 (s, 1 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.17 - 7.05 (m, 1 H), 5.69 (d, *J* = 4.5 Hz, 1 H), 4.59 (d, *J* = 4.5 Hz, 1 H); **^{13}C NMR** (126MHz ,DMSO-d$_6$) δ = 173.6, 140.8, 129.8, 125.5, 123.5, 123.2, 114.3, 112.5, 112.2, 44.7, 23.7 **HRMS:** (ESI) m/z calculated for $C_{11}H_6ClN_3O$ $[M+H]^+$, 232.0278 found: 232.0283



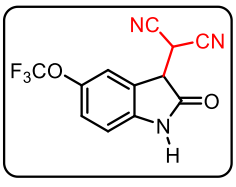
[3Ag] 2-(4,7-dichloro-2-oxoindolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a solid, 95% yield, **^{1}H NMR** (500MHz ,DMSO-d$_6$) δ = 11.69 (s, 1 H), 7.49 (d, *J* = 8.8 Hz, 1 H), 7.16 (d, *J* = 8.8 Hz, 1 H), 5.74 (d, *J* = 3.8 Hz, 1 H), 4.81 (d, *J* = 3.7 Hz, 1 H); **^{13}C NMR** (126MHz ,DMSO-d$_6$) d = 173.2, 142.8, 132.0, 129.1, 123.9, 122.6, 113.7, 112.3, 112.0, 45.5, 22.9; **HRMS:** (ESI) m/z calculated for $C_{11}H_5Cl_2N_3O$ $[M+H]^+$, 265.9888 found: 265.9883



[3Ah] 2-(5-bromo-2-oxoindolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a solid, 92% yield, **^{1}H NMR** (400MHz ,DMSO-d$_6$) δ = 11.05 (s, 1 H), 7.62 (s, 1 H), 7.52 (dd, *J* = 1.6, 8.4 Hz, 1 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 5.70 (d, *J* = 4.4 Hz, 1 H), 4.50 (d, *J* = 4.4 Hz, 1 H); **^{13}C NMR** (101MHz ,DMSO-d$_6$) δ = 173.4, 142.4, 132.5, 127.5, 126.1, 113.6, 112.4, 112.3, 112.1, 44.0, 23.5; **HRMS:** (ESI) m/z calculated for $C_{11}H_6BrN_3O$ $[M+H]^+$, 275.9772 found: 275.9775

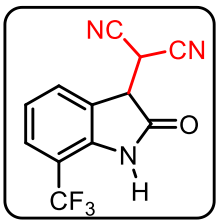


[3Ai] 2-(5-iodo-2-oxoindolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a solid, 94% yield, **^{1}H NMR** (400MHz ,DMSO-d$_6$) δ = 11.02 (s, 1 H), 7.76 (s, 1 H), 7.67 (d, *J* = 8.1 Hz, 1 H), 6.78 (d, *J* = 8.1 Hz, 1 H), 5.68 (d, *J* = 4.4 Hz, 1 H) 4.46 (d, J = 4.4 Hz, 1 H); **^{13}C NMR** (101MHz ,DMSO-d$_6$) δ = 173.2, 142.8, 138.3, 133.0, 126.3, 112.5, 112.4, 112.3, 84.7, 43.8, 23.5; **HRMS:** (ESI) m/z calculated for $C_{11}H_6IN_3O$ $[M+H]^+$, 323.9634 found: 323.9637

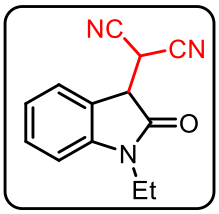


[3Aj] 2-(2-oxo-5-(trifluoromethoxy)indolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a solid, 85% yield, Rf (Ethyl acetate/Pet. ether; 20:60) = 0.20, **^{1}H NMR** (400MHz ,DMSO-d$_6$) δ = 11.10 (s, 1 H), 7.48 (s, 1 H), 7.35 (d, *J* = 11.0 Hz, 1 H), 7.02 (d, *J* = 8.5 Hz, 1 H), 5.74 (d, *J* = 4.5 Hz, 1 H), 4.54 (d, *J* = 4.5 Hz, 1 H); **^{13}C NMR** (101MHz ,DMSO-d$_6$) δ = 173.8, 143.1, 142.3, 125.3, 123.1, 121.4, 118.9, 118.4, 112.4, 112.2, 112.1, 111.1, 44.2, 23.5; **^{19}F NMR** (377

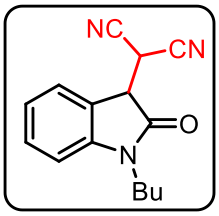
MHz, DMSO-d_6) δ -57.38 (1 F); **HRMS:** (ESI) m/z calculated for $C_{12}H_6F_3N_3O_2$ $[M+H]^+$, 282.0490 found: 282.0494



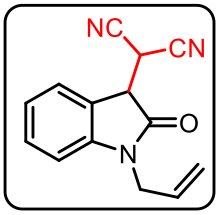
[3Ak] 2-(2-oxo-7-(trifluoromethyl)indolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a solid, 85% yield, **^{1}H NMR** (400MHz ,DMSO-d_6) δ = 11.42 (s, 1 H), 7.74 (d, *J* = 7.5 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 5.75 (d, *J* = 4.5 Hz, 1 H), 4.59 (d, *J* = 4.5 Hz, 1 H); **^{13}C NMR** (101MHz ,DMSO-d_6) δ = 174.4, 140.3, 128.6, 126.2, 125.7, 124.6, 122.3, 122.0, 112.4, 112.2, 111.4, 111.1, 43.2, 23.6; **^{19}F NMR** (377 MHz, DMSO-d_6) δ -60.24 (1 F); **HRMS:** (ESI) m/z calculated for $C_{12}H_6F_3N_3O_2$ $[M+H]^+$, 282.0490 found: 282.0494



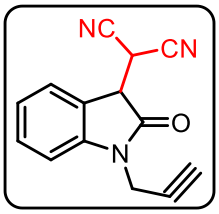
[3Al] 2-(1-ethyl-2-oxoindolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a liquid 81% yield, **^{1}H NMR** (400MHz ,$CDCl_3$) δ = 7.65 (d, *J* = 7.5 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 6.97 (d, *J* = 7.9 Hz, 1 H), 4.61 (d, *J* = 3.8 Hz, 1 H), 3.94 (d, *J* = 3.9 Hz, 1 H), 3.85 (td, *J* = 7.2, 14.3 Hz, 1 H), 3.75 (td, *J* = 7.1, 14.2 Hz, 1 H), 1.29 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 170.6, 143.5, 130.6, 124.8, 123.5, 121.7, 111.6, 109.6, 109.4, 44.7, 35.3, 24.6, 12.3; **HRMS:** (ESI) m/z calculated for $C_{13}H_{11}N_3O$ $[M+H]^+$, 226.0980 found: 226.0985



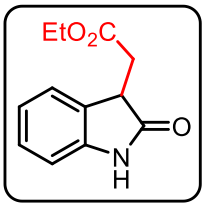
[3Am] 2-(1-butyl-2-oxoindolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a liquid, 94% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.65 (d, *J* = 7.5 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 1 H), 7.19 (t, *J* = 7.3 Hz, 1 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 4.58 (d, *J* = 3.8 Hz, 1 H), 3.93 (d, *J* = 3.8 Hz, 1 H), 3.87 - 3.76 (m, 1 H), 3.68 (td, *J* = 7.2, 14.1 Hz, 1 H), 1.68 (quin, *J* = 7.5 Hz, 2 H), 1.45 - 1.35 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR** (101MHz ,CHLOROFORM-d) δ = 170.8, 144.0, 130.6, 124.8, 123.6, 121.6, 111.6, 109.6, 44.9, 40.4, 29.2, 24.6, 20.0, 13.6; **HRMS:** (ESI) m/z calculated for $C_{15}H_{15}N_3O$ $[M+H]^+$, 254.1293 found: 254.1285



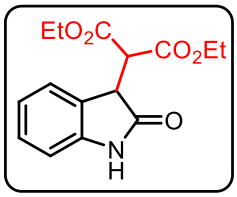
[3An] 2-(1-allyl-2-oxoindolin-3-yl)malononitrile, the titled compound was prepared by General Procedure-A, obtained as a solid 97% yield, **^{1}H NMR** (500MHz ,DMSO-d_6) δ = 7.52 (d, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.7 Hz, 1 H), 7.16 (t, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 7.9 Hz, 1 H), 5.87 - 5.78 (m, 1 H), 5.74 (d, *J* = 4.4 Hz, 1 H), 5.22 - 5.14 (m, 2 H), 4.61 (d, *J* = 4.3 Hz, 1 H), 4.44 - 4.38 (m, 1 H), 4.34 - 4.27 (m, 1 H); **^{13}C NMR** (126MHz ,DMSO-d_6) δ = 171.7, 143.4, 131.2, 129.8, 124.3, 122.8, 122.8, 116.8, 112.6, 112.3, 109.8, 43.5, 41.7, 23.9; **HRMS:** (ESI) m/z calculated for $C_{14}H_{11}N_3O$ $[M+H]^+$, 238.0980 found: 238.0971



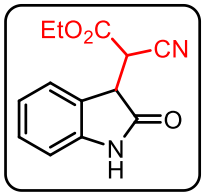
[3Ao] **2-(2-oxo-1-(prop-2-yn-1-yl)indolin-3-yl)malononitrile**, the titled compound was prepared by General Procedure-A, obtained as a liquid 95% yield, **^{1}H NMR** (500MHz ,DMSO-d_6) δ = 7.55 (d, *J* = 7.4 Hz, 1 H), 7.50 - 7.44 (m, 1 H), 7.25 - 7.18 (m, 2 H), 5.74 (d, *J* = 4.5 Hz, 1 H), 4.64 (d, *J* = 4.7 Hz, 1 H), 4.60 (t, *J* = 2.6 Hz, 2 H), 3.30 (d, *J* = 1.0 Hz, 1 H); **^{13}C NMR** (126MHz ,DMSO-d_6) δ = 171.3, 142.5, 129.9, 124.5, 123.2, 122.7, 112.4, 112.1, 110.0, 77.4, 74.7, 43.3, 29.1, 23.8; **HRMS:** (ESI) m/z calculated for $C_{14}H_9N_3O$ $[M+H]^+$, 236.0824 found: 236.0831



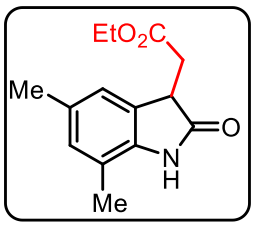
[3Ba] **Ethyl 2-(2-oxoindolin-3-yl)acetate**, the titled compound was prepared by General Procedure-B, obtained as a solid, 91% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.25, **^{1}H NMR** (400MHz ,$CDCl_3$) δ = 9.18 (br. s., 1 H), 7.18 - 7.08 (m, 2 H), 6.97 - 6.89 (m, 1 H), 6.84 (d, *J* = 7.8 Hz, 1 H), 4.15 - 3.97 (m, 2 H), 3.74 (dd, *J* = 4.6, 7.8 Hz, 1 H), 3.00 (dd, *J* = 4.6, 16.8 Hz, 1 H), 2.76 (dd, *J* = 7.9, 16.9 Hz, 1 H), 1.12 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 179.6, 171.0, 141.7, 128.7, 128.2, 124.0, 122.3, 109.9, 60.9, 42.4, 34.7, 14.0; **HRMS:** (ESI) m/z calculated for $C_{12}H_{13}NO_3$ $[M+H]^+$, 220.0974 found:220.0981



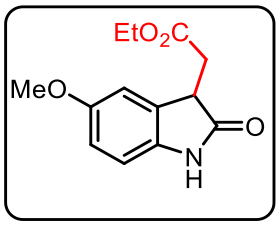
[3Bb] **diethyl 2-(2-oxoindolin-3-yl)malonate**, the titled compound was prepared by General Procedure-B, obtained as a thick oil, 90% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.20, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 9.33 (br. s., 1 H), 7.29 (d, *J* = 7.5 Hz, 1 H), 7.18 - 7.04 (m, 1 H), 6.91 (t, *J* = 7.6 Hz, 1 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 4.30 - 4.16 (m, 2 H), 4.14 (d, *J* = 3.8 Hz, 1 H), 3.99 (d, *J* = 3.6 Hz, 1 H), 3.97 - 3.81 (m, 2 H), 1.21 (t, *J* = 7.1 Hz, 3 H), 0.93 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 178.0, 167.9, 166.9, 142.1, 128.5, 126.1, 125.0, 122.3, 109.9, 61.8, 61.7, 52.1, 45.1, 13.9, 13.5; **HRMS:** (ESI) m/z calculated for $C_{15}H_{17}NO_5$ $[M+H]^+$, 292.1185 found: 292.1181



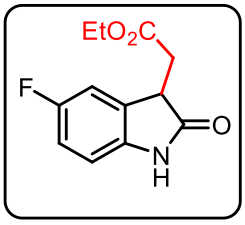
[3Bc] **ethyl 2-cyano-2-(2-oxoindolin-3-yl)acetate,** the titled compound was prepared by General Procedure-A, obtained as a mixture of diastereomer (6:4) solid, 91% yield, [Major diastereomer, **^{1}H NMR** (400MHz ,$CDCl_3$) δ = 9.21 (br. s., 1 H), 7.42 (d, *J* = 7.5 Hz, 1 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 6.98 - 6.94 (m, 1 H), 6.87 (t, *J* = 8.3 Hz, 1 H), 4.36 (d, *J* = 3.3 Hz, 1 H), 4.33 - 4.27 (m, 2 H), 3.91 (d, *J* = 3.2 Hz, 1 H), 1.00 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 175.7, 164.5, 142.0, 129.4, 124.6, 124.0, 122.8, 115.3, 110.4, 63.2, 45.2, 38.8, 13.5]; **HRMS:** (ESI) m/z calculated for $C_{13}H_{12}N_2O_3$ $[M+H]^+$, 245.0926 found: 245.0930



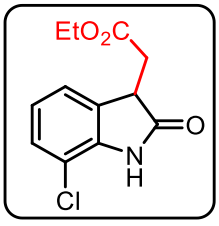
[3Bd], **ethyl 2-(5,7-dimethyl-2-oxoindolin-3-yl)acetate**, the titled compound was prepared by General Procedure-B, obtained as a solid, 89% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.20, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 9.70 (br. s., 1 H), 6.87 (d, *J* = 11.6 Hz, 2 H), 4.28 - 4.03 (m, 2 H), 3.82 (dd, *J* = 4.5, 8.1 Hz, 1 H), 3.05 (dd, *J* = 4.6, 16.7 Hz, 1 H), 2.78 (dd, *J* = 8.1, 16.8 Hz, 1 H), 2.27 (d, *J* = 3.6 Hz, 6 H), 1.22 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz ,$CDCl_3$) δ = 180.0, 171.2, 138.0, 131.8, 130.0, 128.5, 122.1, 119.0, 119.0, 60.9, 42.8, 35.0, 21.0, 16.3, 14.0; **HRMS:** (ESI) m/z calculated for $C_{14}H_{17}NO_3$ $[M+H]^+$, 248.1287 found: 248.1297



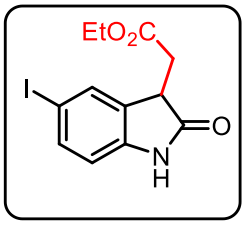
[3Be] **ethyl 2-(5-methoxy-2-oxoindolin-3-yl)acetate**, the titled compound was prepared by General Procedure-B, obtained as a solid, 93% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.25, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 9.19 (br. s., 1 H), 6.85 (d, *J* = 1.3 Hz, 1 H), 6.83 - 6.77 (m, 1 H), 6.76 - 6.70 (m, 1 H), 4.15 (dq, *J* = 2.6, 7.1 Hz, 2 H), 3.86 - 3.78 (m, 1 H), 3.75 (s, 3 H), 3.06 (dd, *J* = 4.4, 16.9 Hz, 1 H), 2.81 (dd, *J* = 8.1, 16.9 Hz, 1 H), 1.21 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 179.4, 171.0, 155.7, 135.1, 130.1, 112.7, 111.3, 110.2, 61.0, 55.7, 42.8, 34.7, 14.0 **HRMS:** (ESI) m/z calculated for $C_{13}H_{15}NO_4$ $[M+H]^+$, 250.1079 found: 250.1070



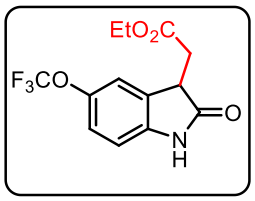
[3Bf] **ethyl 2-(5-fluoro-2-oxoindolin-3-yl)acetate**, the titled compound was prepared by General Procedure-B, obtained as a solid, 91% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.20, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 8.88 (br. s., 1 H), 7.01 (d, *J* = 8.0 Hz, 1 H), 6.97 - 6.88 (m, 1 H), 6.87 - 6.75 (m, 1 H), 4.16 (dq, *J* = 2.6, 7.1 Hz, 2 H), 3.81 (dd, *J* = 4.2, 7.8 Hz, 1 H), 3.08 (dd, *J* = 4.3, 17.1 Hz, 1 H), 2.84 (dd, *J* = 8.1, 17.1 Hz, 1 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 178.8, 170.5, 159.9, 157.5, 137.2, 130.1, 130.0, 114.4, 114.2, 112.1, 111.8, 110.1, 110.0, 60.8, 42.4, 34.2, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.5; **HRMS:** (ESI) m/z calculated for $C_{12}H_{12}FNO_3$ $[M+H]^+$, 238.0179 found: 238.0187



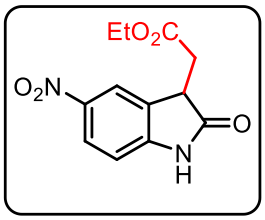
[3Bg] **ethyl 2-(7-chloro-2-oxoindolin-3-yl)acetate**, the titled compound was prepared by General Procedure-B, obtained as a solid, 92% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.20, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 8.71 (br. s., 1 H), 7.21 (d, *J* = 8.3 Hz, 1 H), 7.14 (d, *J* = 7.4 Hz, 1 H), 7.01 - 6.90 (m, 1 H), 4.23 - 4.07 (m, 2 H), 3.89 (dd, *J* = 4.4, 7.9 Hz, 1 H), 3.10 (dd, *J* = 4.4, 17.0 Hz, 1 H), 2.86 (dd, *J* = 7.9, 17.1 Hz, 1 H), 1.20 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 178.0, 170.7, 139.4, 130.1, 128.3, 128.2, 123.3, 122.3, 115.0, 61.1, 43.2, 34.7, 14.0; **HRMS:** (ESI) m/z calculated for $C_{12}H_{12}ClNO_3$ $[M+H]^+$, 254.0584 found:254.0590



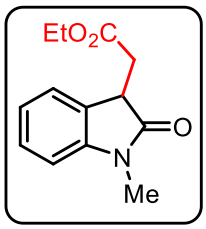
[3Bh] ethyl 2-(5-iodo-2-oxoindolin-3-yl)acetate, the titled compound was prepared by General procedure-B, obtained as a solid 84% yield, Rf (Ethyl acetate/Pet. ether; 20:80) = 0.20, **^{1}H NMR** (400MHz , $CDCl_3$) d = 9.02 (br. s., 1 H), 7.60 - 7.33 (m, 2 H), 6.62 (d, *J* = 8.6 Hz, 1 H), 4.19 - 3.99 (m, 2 H), 3.70 (dd, *J* = 4.3, 7.6 Hz, 1 H), 2.98 (dd, *J* = 4.3, 17.1 Hz, 1 H), 2.77 (dd, *J* = 7.8, 17.1 Hz, 1 H), 1.16 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) d = 178.7, 170.7, 141.4, 137.1, 132.9, 131.2, 111.9, 84.9, 61.2, 42.2, 34.4, 14.0; **HRMS**: (ESI) m/z calculated for $C_{12}H_{12}INO_3$ $[M+H]^+$, 345.9940 found: 345.9949



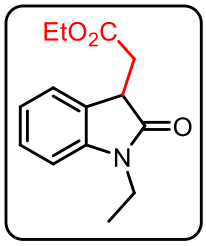
[3Bi] ethyl 2-(2-oxo-5-(trifluoromethoxy)indolin-3-yl)acetate, the titled compound was prepared by General Procedure-B, obtained as a solid, 84% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.20, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 9.15 (br. s., 1 H), 7.11 - 6.93 (m, 2 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 4.08 (dq, *J* = 3.3, 7.1 Hz, 2 H), 3.75 (dd, *J* = 4.3, 7.5 Hz, 1 H), 3.01 (dd, *J* = 4.4, 17.0 Hz, 1 H), 2.78 (dd, *J* = 7.9, 17.1 Hz, 1 H), 1.14 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 179.3, 170.7, 144.5, 140.4, 130.2, 121.5, 118.1, 110.4, 61.2, 42.6, 34.5, 34.5, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.40; **HRMS:** (ESI) m/z calculated for $C_{13}H_{12}F_3NO_4$ $[M+H]^+$, 304.0797 found: 304.0791



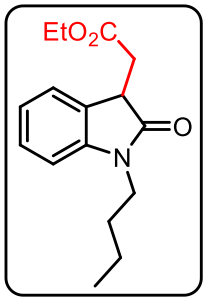
[3Bj] ethyl 2-(5-nitro-2-oxoindolin-3-yl)acetate, the titled compound was prepared by General Procedure-B, obtained as a solid, 81% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.15, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 9.44 (br. s., 1 H), 8.13 (d, *J* = 8.6 Hz, 1 H), 8.07 (s, 1 H), 6.96 (d, *J* = 8.6 Hz, 1 H), 4.10 - 4.03 (m, 2 H), 3.81 - 3.72 (m, 1 H), 3.14 - 3.05 (m, 1 H), 2.99 - 2.89 (m, 1 H), 1.17 - 1.12 (m, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 179.4, 170.4, 147.8, 143.3, 129.5, 125.5, 119.9, 109.6, 61.4, 42.1, 34.0, 29.6, 14.0; **HRMS:** (ESI) m/z calculated for $C_{12}H_{12}N_2O_5$ $[M+H]^+$, 265.0824 found: 265.0832



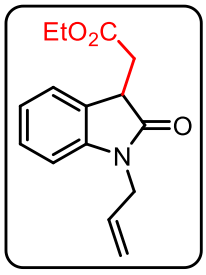
[3Bk] ethyl 2-(1-methyl-2-oxoindolin-3-yl) acetate, the titled compound was prepared by General procedure-B, obtained as a thick oil 87% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.15, **^{1}H NMR** (400MHz ,$CDCl_3$) δ = 7.32 - 7.24 (m, 2 H), 7.07 - 7.00 (m, 1 H), 6.84 (d, J = 7.9 Hz, 1 H), 4.13 (ttd, J = 3.5, 7.0, 10.6 Hz, 2 H), 3.79 (dd, J = 4.4, 8.0 Hz, 1 H), 3.23 (s, 3 H), 3.08 (dd, J = 4.4, 16.9 Hz, 1 H), 2.79 (dd, J = 8.1, 16.8 Hz, 1 H), 1.20 (t, J = 7.1 Hz, 3 H); **13C NMR** (101MHz ,$CDCl_3$) δ = 176.8, 171.0, 144.4, 128.3, 128.2, 123.8, 122.5, 108.0, 60.9, 41.9, 35.0, 26.3, 14.1; **HRMS**: (ESI) m/z calculated for $C_{13}H_{15}NO_3$ $[M+H]^+$, 234.1130 found: 234.1127



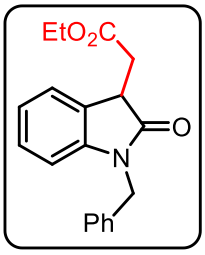
[3Bl] ethyl 2-(1-ethyl-2-oxoindolin-3-yl)acetate, the titled compound was prepared by General procedure-B, obtained as a thick oil 90% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.15, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.24 - 7.14 (m, 2 H), 7.02 - 6.90 (m, 1 H), 6.78 (d, *J* = 7.9 Hz, 1 H), 4.13 - 3.95 (m, 2 H), 3.78 - 3.62 (m, 3 H), 3.00 (dd, *J* = 4.5, 16.8 Hz, 1 H), 2.72 (dd, *J* = 8.0, 16.8 Hz, 1 H), 1.20 (t, *J* = 7.2 Hz, 3 H), 1.11 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 176.3, 171.0, 143.4, 128.4, 128.2, 123.9, 122.2, 108.1, 60.8, 41.8, 34.9, 34.7, 14.0, 12.5; **HRMS**: (ESI) m/z calculated for $C_{14}H_{17}NO_3$ $[M+H]^+$, 248.1287 found:0248.1295



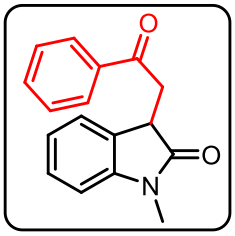
[3Bm] ethyl 2-(1-butyl-2-oxoindolin-3-yl)acetate, the titled compound was prepared by General procedure-B, obtained as a thick oil 84% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.15, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.23 - 7.13 (m, 2 H), 6.98 - 6.89 (m, 1 H), 6.77 (d, *J* = 7.8 Hz, 1 H), 4.14 - 3.94 (m, 2 H), 3.74 - 3.67 (m, 1 H), 3.67 - 3.53 (m, 2 H), 2.99 (dd, *J* = 4.6, 16.8 Hz, 1 H), 2.70 (dd, *J* = 8.0, 16.8 Hz, 1 H), 1.59 (quin, *J* = 7.5 Hz, 2 H), 1.40 - 1.26 (m, 2 H), 1.11 (t, *J* = 7.1 Hz, 3 H), 0.88 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 176.6, 171.0, 143.7, 128.3, 128.1, 123.9, 122.1, 108.2, 60.8, 41.8, 39.8, 34.9, 29.3, 20.1, 14.0, 13.7; **HRMS**: (ESI) m/z calculated for $C_{16}H_{21}NO_3$ $[M+H]^+$, 276.1600 found: 276.1611



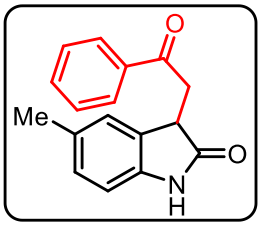
[3Bn] ethyl 2-(1-allyl-2-oxoindolin-3-yl)acetate, the titled compound was prepared by General procedure-B, obtained as a thick oil 84% yield, Rf (Ethyl acetate/Pet. ether; 20:80) = 0.20, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.27 - 7.21 (m, 2 H), 7.07 - 6.97 (m, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 5.94 - 5.76 (m, 1 H), 5.33 - 5.16 (m, 2 H), 4.44 - 4.30 (m, 2 H), 4.22 - 4.04 (m, 2 H), 3.82 (dd, *J* = 4.5, 8.0 Hz, 1 H), 3.09 (dd, *J* = 4.5, 16.9 Hz, 1 H), 2.82 (dd, *J* = 7.9, 16.9 Hz, 1 H), 1.20 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 176.5, 170.9, 143.5, 131.3, 128.2, 123.8, 122.4, 117.6, 109.0, 60.9, 42.5, 41.8, 34.9, 14.1; **HRMS**: (ESI) m/z calculated for $C_{15}H_{17}NO_3$ $[M+H]^+$, 260.1287 found: 260.1281



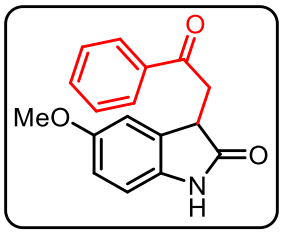
[3Bo] ethyl 2-(1-benzyl-2-oxoindolin-3-yl)acetate, the titled compound was prepared by General procedure-B, obtained as a thick oil 81% yield, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.23, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.38 - 7.29 (m, 4 H), 7.29 - 7.26 (m, 1 H), 7.25 - 7.23 (m, 1 H), 7.20 - 7.13 (m, 1 H), 6.99 (dt, *J* = 0.9, 7.6 Hz, 1 H), 6.72 (d, *J* = 7.9 Hz, 1 H), 4.93 (d, *J* = 3.5 Hz, 2 H), 4.20 - 4.05 (m, 2 H), 3.94 - 3.83 (m, 1 H), 3.13 (dd, *J* = 4.6, 16.8 Hz, 1 H), 2.87 (dd, *J* = 7.9, 16.8 Hz, 1 H), 1.17 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 176.8, 170.9, 143.4, 135.8, 128.7, 128.2, 128.1, 127.6, 127.3, 123.8, 122.5, 109.1, 60.9, 43.9, 41.9, 35.0, 14.0; **HRMS**: (ESI) m/z calculated for $C_{19}H_{19}NO_3$ $[M+H]^+$, 310.1443 found: 310.1450



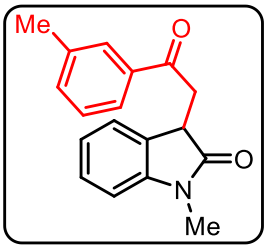
[3Ca] 1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one, the titled compound was prepared by General Procedure-C, obtained as a solid, 92% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 7.8 Hz, 2 H), 7.56 - 7.46 (m, 1 H), 7.45 - 7.31 (m, 2 H), 7.25 - 7.11 (m, 2 H), 7.00 - 6.86 (m, 1 H), 6.78 (d, *J* = 7.8 Hz, 1 H), 4.01 (d, *J* = 9.0 Hz, 1 H), 3.76 (d, *J* = 18.3 Hz, 1 H), 3.40 - 3.25 (m, 1 H), 3.25 - 3.09 (m, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 197.0, 177.8, 144.3, 136.3, 133.4, 129.1, 128.7, 128.1, 128.1, 124.4, 122.5, 108.0, 41.2, 40.0, 26.4; **HRMS** (ESI) m/z calculated for $C_{17}H_{15}NO_2$ $[M+H]^+$, 266.1181 found: 266.1176



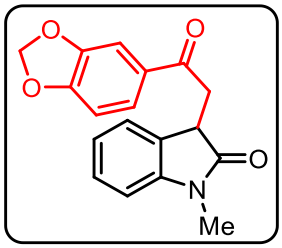
[3Cb] 5-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one, the titled compound was prepared by General Procedure-C, obtained as a solid, 90% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 8.09 (br. s., 1 H), 7.93 (d, *J* = 7.3 Hz, 2 H), 7.59 - 7.47 (m, 1 H), 7.46 - 7.34 (m, 2 H), 7.00 - 6.89 (m, 2 H), 6.72 (d, *J* = 7.9 Hz, 1 H), 4.00 (dd, *J* = 2.6, 8.9 Hz, 1 H), 3.75 (dd, *J* = 3.0, 18.3 Hz, 1 H), 3.38 (dd, *J* = 8.9, 18.3 Hz, 1 H), 2.19 (s, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) d = 196.9, 179.8, 138.8, 136.3, 133.5, 132.0, 129.7, 128.7, 128.3, 128.2, 125.4, 109.3, 41.5, 39.9, 21.1; **HRMS** (ESI) m/z calculated for $C_{17}H_{15}NO_2$ $[M+H]^+$, 266.1181 found: 266.1174



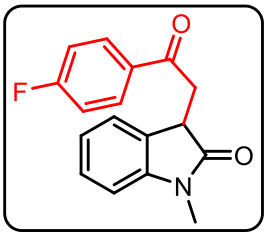
[3Cc] 5-methoxy-3-(2-oxo-2-phenylethyl)indolin-2-one, the titled compound was prepared by General Procedure-C, obtained as a solid, 92% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 8.82 (br. s., 1 H), 7.90 (d, *J* = 8.5 Hz, 2 H), 7.54 - 7.46 (m, 1 H), 7.42 - 7.35 (m, 2 H), 6.78 - 6.72 (m, 2 H), 6.64 (d, *J* = 10.8 Hz, 1 H), 4.00 (dd, *J* = 2.6, 8.7 Hz, 1 H), 3.74 (dd, *J* = 3.0, 18.4 Hz, 1 H), 3.64 (s, 3 H), 3.42 - 3.31 (m, 1 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 196.9, 180.3, 180.2, 155.7, 136.2, 135.0, 133.5, 131.0, 128.7, 128.1, 112.6, 111.8, 110.1, 110.1, 55.7, 42.1, 39.8; **HRMS** (ESI) m/z calculated for $C_{17}H_{15}NO_3$ $[M+H]^+$, 282.1130 found: 282.1134



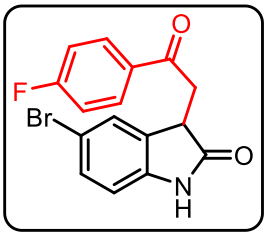
[3Cd] **1-methyl-3-(2-oxo-2-(m-tolyl)ethyl)indolin-2-one**, the titled compound was prepared by General Procedure-C, obtained as a solid, 91% yield, **^{1}H NMR** (500MHz , $CDCl_3$) δ = 7.78 - 7.62 (m, 2 H), 7.35 - 7.24 (m, 2 H), 7.23 - 7.13 (m, 2 H), 6.91 (t, *J* = 8.0 Hz, 1 H), 6.78 (d, *J* = 7.8 Hz, 1 H), 4.01 (dd, *J* = 2.8, 9.3 Hz, 1 H), 3.75 (dd, *J* = 3.0, 18.2 Hz, 1 H), 3.31 (dd, *J* = 9.3, 18.2 Hz, 1 H), 3.19 (s, 3 H), 2.32 (s, 3 H); **^{13}C NMR** (126MHz , $CDCl_3$) δ = 197.2, 177.8, 144.3, 138.5, 136.4, 134.2, 129.2, 128.7, 128.5, 128.0, 125.3, 124.4, 122.5, 107.9, 41.2, 40.1, 26.4, 21.3; **HRMS** (ESI) m/z calculated for $C_{18}H_{17}NO_2$ $[M+H]^+$, 280.1338 found: 280.1345



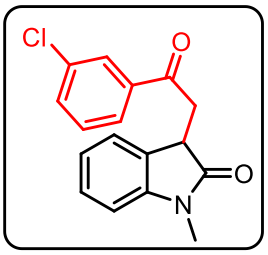
[3Ce] **3-(2-(benzo[d][1,3]dioxol-5-yl)-2-oxoethyl)-1-methylindolin-2-one**, the titled compound was prepared by General Procedure-C, obtained as a solid, 89% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.57 (dd, *J* = 1.4, 8.2 Hz, 1 H), 7.45 (d, *J* = 1.4 Hz, 1 H), 7.33 - 7.27 (m, 1 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.09 - 6.93 (m, 1 H), 6.85 (dd, *J* = 4.0, 7.9 Hz, 2 H), 6.04 (s, 2 H), 4.05 (dd, *J* = 2.4, 9.1 Hz, 1 H), 3.74 (dd, *J* = 3.0, 18.0 Hz, 1 H), 3.38 - 3.27 (m, 1 H), 3.26 (s, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 194.9, 177.7, 152.0, 148.2, 144.2, 131.2, 129.1, 128.0, 124.5, 124.4, 122.5, 108.0, 107.9, 107.9, 101.9, 41.3, 39.8, 26.4; **HRMS** (ESI) m/z calculated for $C_{18}H_{15}NO_4$ $[M+H]^+$, 310.1079 found: 310.1085



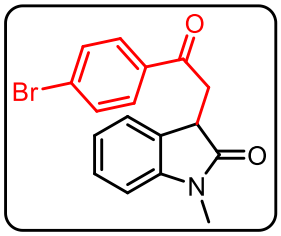
[3Cf] **3-(2-(4-fluorophenyl)-2-oxoethyl)-1-methylindolin-2-one**, the titled compound was prepared by General Procedure-C, obtained as a solid, 92% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 8.00 (dd, *J* = 5.4, 9.0 Hz, 2 H), 7.34 - 7.27 (m, 1 H), 7.24 (d, *J* = 7.4 Hz, 1 H), 7.14 (t, *J* = 8.6 Hz, 2 H), 7.00 (t, *J* = 7.6 Hz, 1 H), 6.86 (d, *J* = 7.8 Hz, 1 H), 4.07 (dd, *J* = 2.8, 9.1 Hz, 1 H), 3.80 (dd, *J* = 3.1, 18.1 Hz, 1 H), 3.43 - 3.32 (m, 1 H), 3.27 (s, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 195.4, 177.6, 167.2, 164.6, 144.3, 132.8, 132.8, 130.8, 130.7, 129.0, 128.1, 124.3, 122.5, 115.9, 115.7, 108.0, 41.1, 39.9, 26.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.46 (1 F); **HRMS** (ESI) m/z calculated for $C_{17}H_{14}FNO_2$ $[M+H]^+$, 284.1087 found: 284.1087



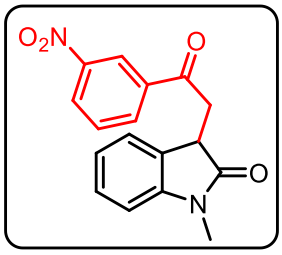
[3Cg] 5-bromo-3-(2-(4-fluorophenyl)-2-oxoethyl)indolin-2-one, the titled compound was prepared by General Procedure-C, obtained as a solid, 87% yield, **^{1}H NMR** (400MHz ,DMSO-d_6) δ = 10.56 (s, 1 H), 8.06 (dd, *J* = 5.6, 8.9 Hz, 2 H), 7.51 - 7.25 (m, 4 H), 6.80 (d, *J* = 8.3 Hz, 1 H), 3.96 (dd, *J* = 3.9, 18.7 Hz, 1 H), 3.89 - 3.79 (m, 1 H), 3.65 (dd, *J* = 6.2, 18.7 Hz, 1 H); **^{13}C NMR** (101MHz ,DMSO-d_6) δ = 195.8, 178.3, 166.4, 163.9, 142.4, 132.8, 132.7, 132.5, 131.1, 131.0, 130.0, 126.3, 115.9, 115.6, 112.7, 110.9, 41.4, 38.0; **^{19}F NMR** (377 MHz, DMSO-*d*$_6$) δ -105.52 (1 F); **HRMS** (ESI) m/z calculated for $C_{16}H_{11}BrFNO_2$ $[M+H]^+$, 384.0035 found: 384.0040



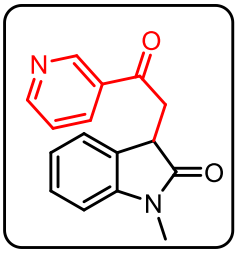
[3Ch] 3-(2-(3-chlorophenyl)-2-oxoethyl)-1-methylindolin-2-one, the titled compound was prepared by General Procedure-C, obtained as a solid, 85% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.88 (s, 1 H), 7.77 (d, *J* = 7.8 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.39 - 7.29 (m, 1 H), 7.27 - 7.19 (m, 1 H), 7.16 (d, *J* = 7.4 Hz, 1 H), 6.99 - 6.87 (m, 1 H), 6.79 (d, *J* = 7.8 Hz, 1 H), 3.99 (dd, *J* = 2.6, 8.9 Hz, 1 H), 3.73 (dd, *J* = 3.1, 18.3 Hz, 1 H), 3.30 (dd, *J* = 9.0, 18.3 Hz, 1 H), 3.19 (s, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 195.8, 177.5, 144.3, 137.8, 135.1, 133.4, 130.0, 128.8, 128.3, 128.2, 126.2, 124.3, 122.6, 108.1, 41.0, 40.1, 26.4; **HRMS** (ESI) m/z calculated for $C_{17}H_{14}ClNO_2$ $[M+H]^+$, 300.0791 found: 300.0795



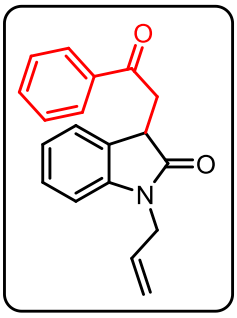
[3Ci] 3-(2-(4-bromophenyl)-2-oxoethyl)-1-methylindolin-2-one, the titled compound was prepared by General Procedure-C, obtained as a solid, 88% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 8.80 (t, *J* = 1.9 Hz, 1 H), 8.44 (dd, *J* = 3.2, 8.2 Hz, 1 H), 8.30 (d, *J* = 7.9 Hz, 1 H), 7.70 (t, *J* = 8.0 Hz, 1 H), 7.36 - 7.27 (m, 1 H), 7.26 - 7.21 (m, 1 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 6.88 (d, *J* = 7.9 Hz, 1 H), 4.09 (dd, *J* = 3.1, 8.6 Hz, 1 H), 3.88 (dd, *J* = 3.4, 18.4 Hz, 1 H), 3.47 (dd, *J* = 8.8, 18.4 Hz, 1 H), 3.28 (s, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 194.9, 177.2, 148.5, 144.3, 137.5, 133.6, 130.0, 128.5, 128.4, 127.7, 124.2, 123.1, 122.6, 108.2, 41.0, 40.2, 26.4; **HRMS** (ESI) m/z calculated for $C_{17}H_{14}BrNO_2$ $[M+H]^+$, 344.0286 found: 344.0290



[3Cj] **1-methyl-3-(2-(3-nitrophenyl)-2-oxoethyl)indolin-2-one**, the titled compound was prepared by General Procedure-C, obtained as a solid, 84% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 8.80 (t, *J* = 1.9 Hz, 1 H), 8.44 (dd, *J* = 2.2, 8.2 Hz, 1 H), 8.30 (d, *J* = 9.0 Hz, 1 H), 7.70 (t, *J* = 8.0 Hz, 1 H), 7.35 - 7.27 (m, 1 H), 7.25 (d, *J* = 7.5 Hz, 1 H), 7.08 - 6.97 (m, 1 H), 6.88 (d, *J* = 7.9 Hz, 1 H), 4.09 (dd, *J* = 3.1, 8.6 Hz, 1 H), 3.88 (dd, *J* = 3.4, 18.4 Hz, 1 H), 3.47 (dd, *J* = 8.8, 18.4 Hz, 1 H), 3.28 (s, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 194.9, 177.2, 148.5, 144.3, 137.5, 133.6, 130.0, 128.5, 128.4, 127.7, 124.2, 123.1, 122.6, 108.2, 41.0, 40.2, 26.4; **HRMS** (ESI) m/z calculated for $C_{17}H_{14}N_2O_4$ $[M+H]^+$, 311.1032 found: 311.1037



[3Ck] **1-methyl-3-(2-oxo-2-(pyridin-3-yl)ethyl)indolin-2-one**, the titled compound was prepared by General Procedure-C, obtained as a solid, 81% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 10.69 - 8.42 (m, 2 H), 8.27 (d, *J* = 7.9 Hz, 1 H), 7.38 - 7.14 (m, 2 H), 7.07 - 6.95 (m, 1 H), 6.87 (d, *J* = 7.8 Hz, 1 H), 4.08 (dd, *J* = 2.4, 8.6 Hz, 1 H), 3.84 (dd, *J* = 3.1, 18.3 Hz, 1 H), 3.43 (dd, *J* = 8.8, 18.3 Hz, 1 H), 3.28 (s, 3 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 196.0, 177.3, 153.5, 149.3, 144.3, 135.4, 128.6, 128.3, 128.3, 124.2, 122.6, 108.1, 108.1, 40.9, 40.2, 26.4; **HRMS** (ESI) m/z calculated for $C_{16}H_{14}N_2O_2$ $[M+H]^+$, 267.1134 found: 267.1141



[3Cl] **1-allyl-3-(2-oxo-2-phenylethyl)indolin-2-one**, the titled compound was prepared by General Procedure-C, obtained as a solid, 80% yield, **^{1}H NMR** (400MHz , $CDCl_3$) δ = 7.90 (d, *J* = 7.6 Hz, 2 H), 7.54 - 7.46 (m, 1 H), 7.44 - 7.35 (m, 2 H), 7.18 - 7.11 (m, 2 H), 6.99 - 6.86 (m, 1 H), 6.78 (d, *J* = 7.8 Hz, 1 H), 5.97 - 5.69 (m, 1 H), 5.32 - 5.11 (m, 2 H), 4.33 (d, *J* = 5.3 Hz, 2 H), 4.10 - 3.95 (m, 1 H), 3.78 (dd, *J* = 3.0, 18.1 Hz, 1 H), 3.36 (dd, *J* = 9.0, 18.3 Hz, 1 H); **^{13}C NMR** (101MHz , $CDCl_3$) δ = 196.8, 177.4, 143.4, 136.3, 133.4, 131.4, 129.0, 128.6, 128.1, 127.9, 124.3, 122.4, 117.5, 108.9, 42.5, 41.1, 40.0 **HRMS** (ESI) m/z calculated for $C_{19}H_{17}NO_2$ $[M+H]^+$, 292.1338 found: 292.1342

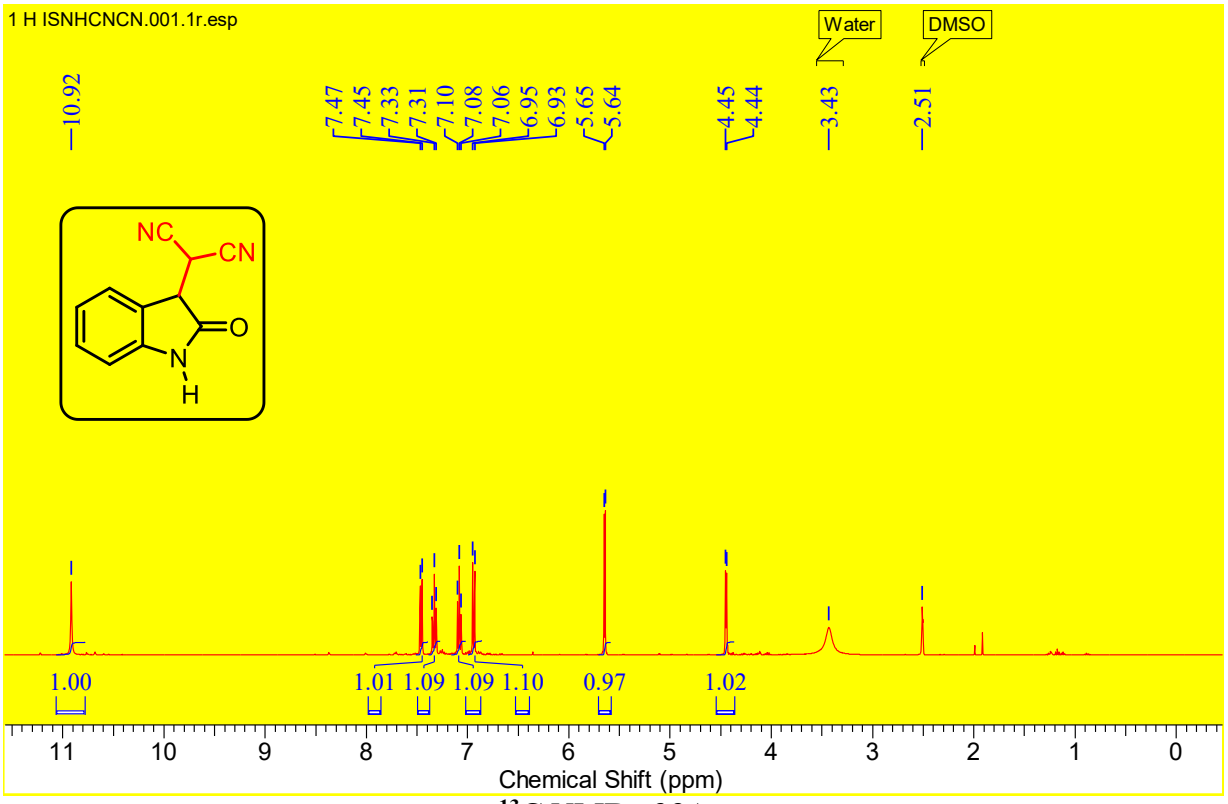
7. References:

1] (a) J.M.G.D.O. Ferreira, G.A. da Silva, M.C. Coelho, C.G.L. Junior and J.A. Vale, *Results Chem*. **2021**, *3*, 100135.; (b) A. M. Shelke and G. Suryavanshi *Org. Biomol. Chem.*, **2015**, *13*, 8669-8675.; (c) X. Zhang, S. Cao, Y. Wei, M. Shi, *Org. Lett.* **2011**, *13*, 1142-1145.

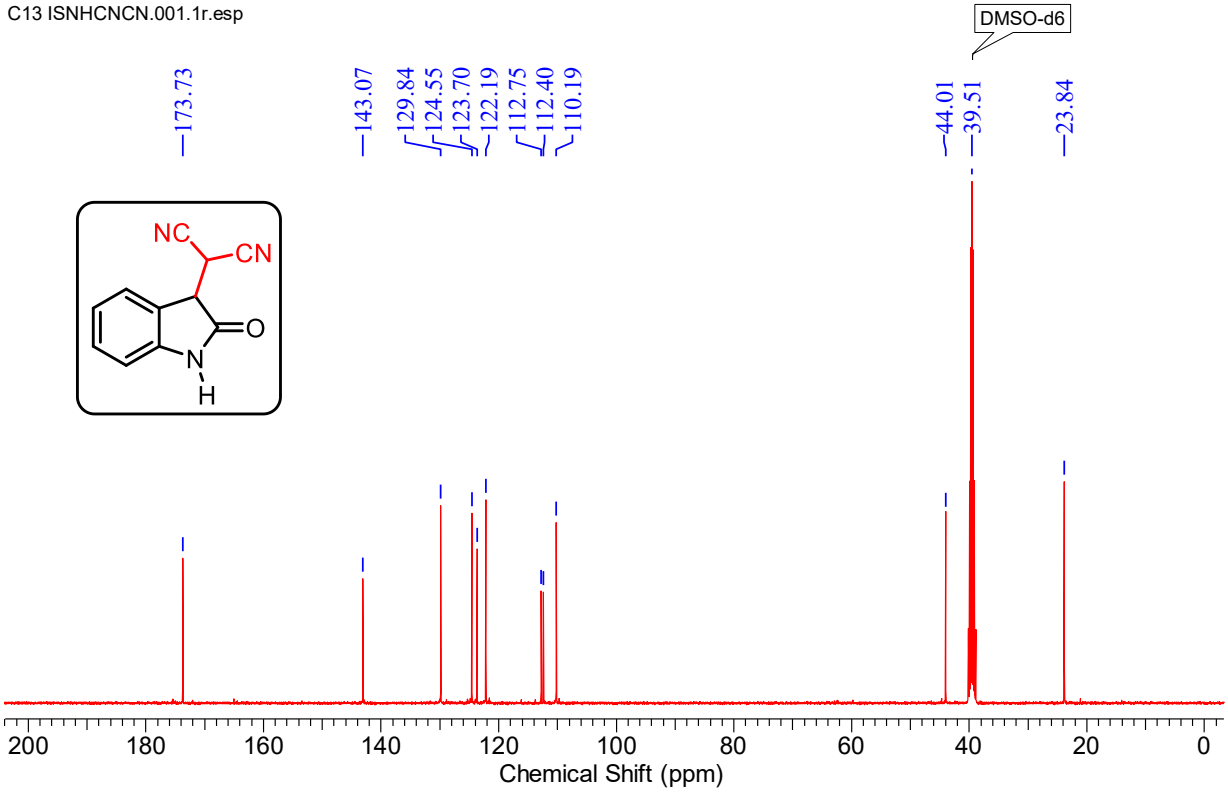
2] (a) S. J. Edeson, J. L. Jiang, S. Swanson, P. A. Procopiou, Adams, H.; Meijer, A.; Harrity, J. Studies on the stereochemical assignment of 3-acylidene 2-oxindoles. *Org. Biomol. Chem*. **2014**, *12*, 3201.; (b) P. Tehri, R. K. Peddinti, DBU-catalyzed [3+2] cycloaddition and Michael addition reactions of 3-benzylidenesuccinimides with 3-ylidene oxindoles and chalcones. *Org. Biomol.Chem.* **2019**, *17*, 3964.

8. NMR spectra of compounds

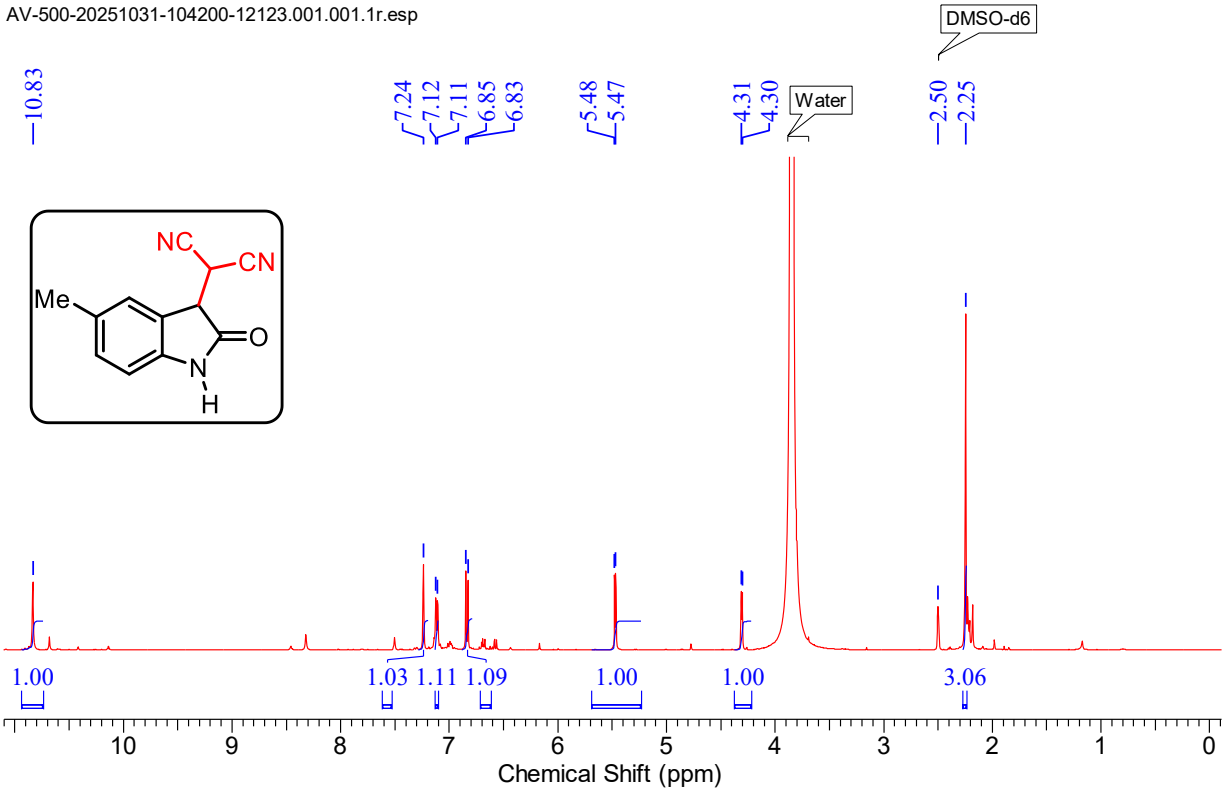
^{1}H NMR of 3Aa



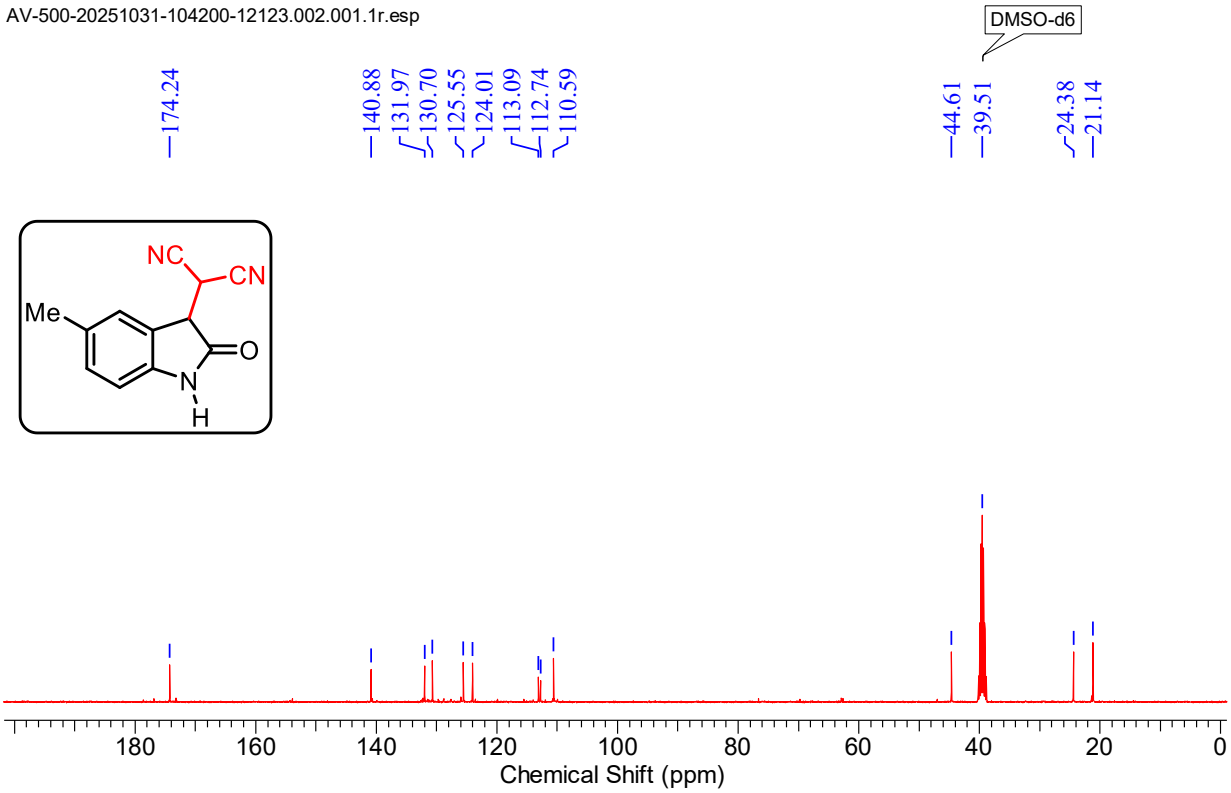
^{13}C NMR of 3Aa



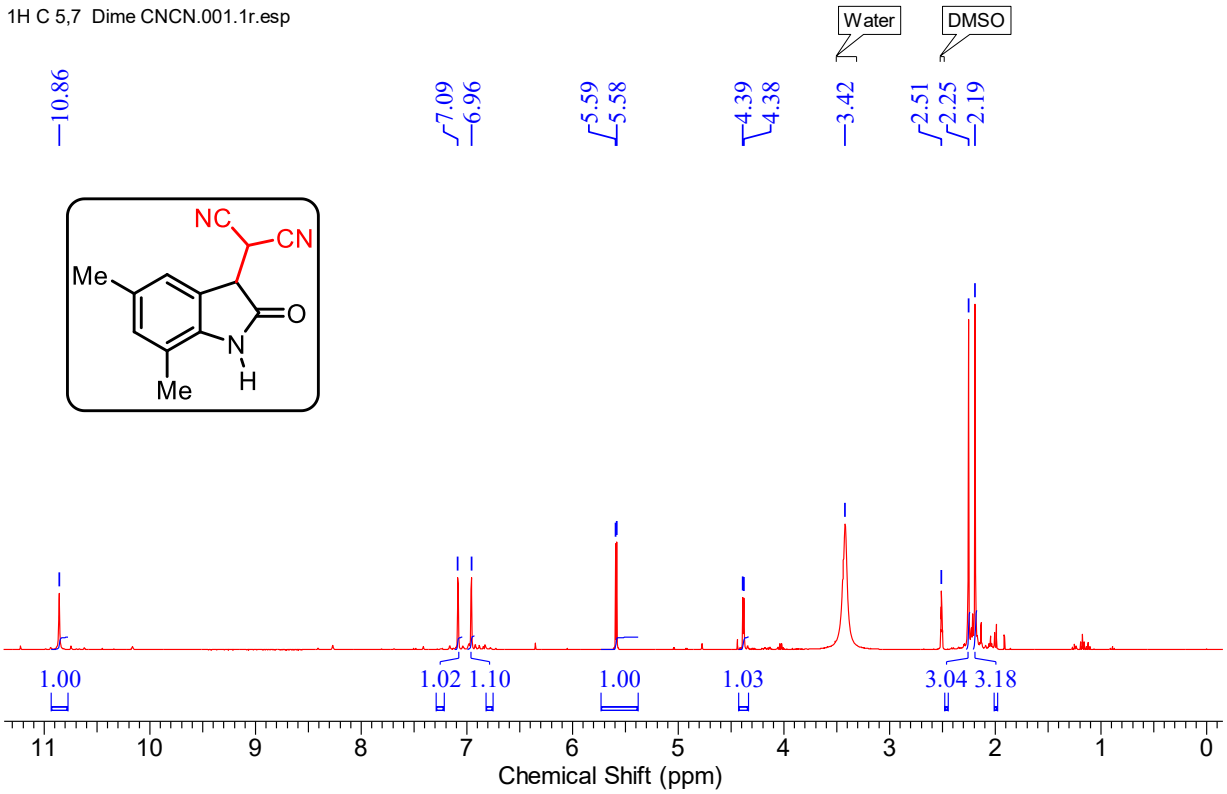
^{1}H NMR of 3Ab



^{13}C NMR of 3Ab



^{1}H NMR of 3Ac



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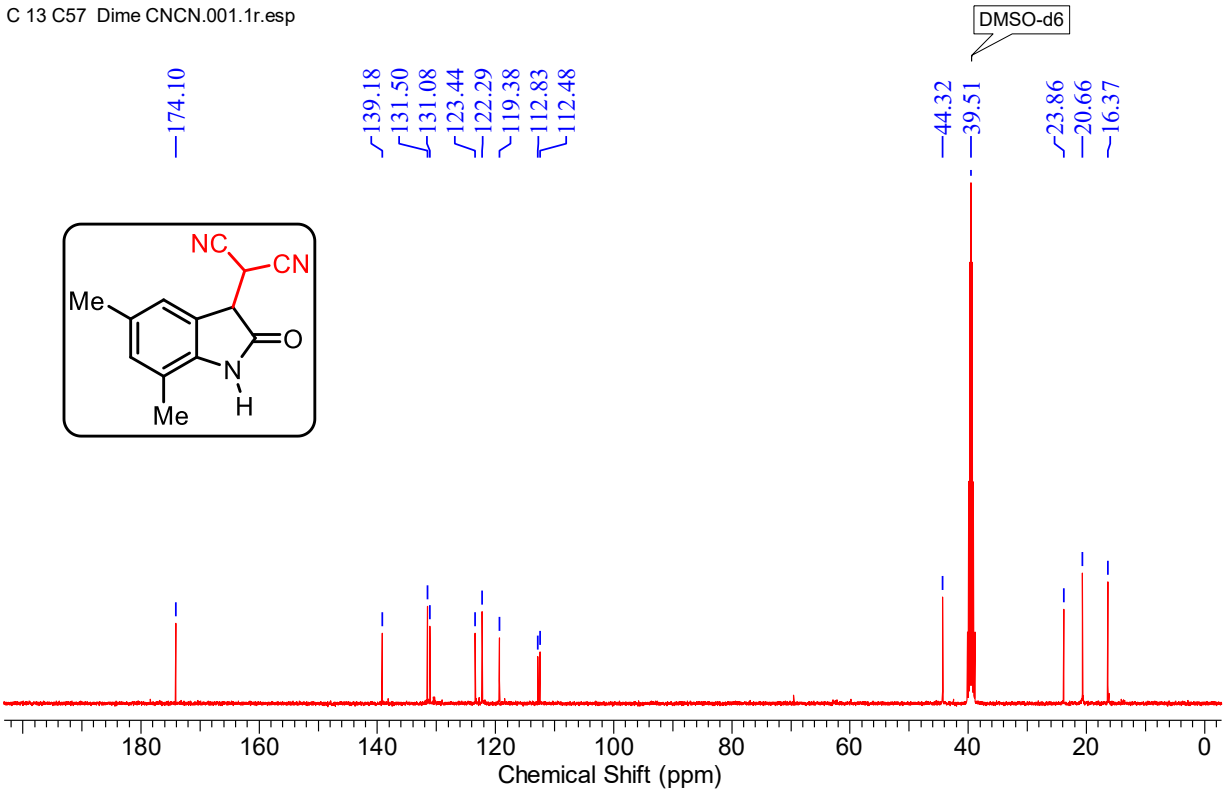
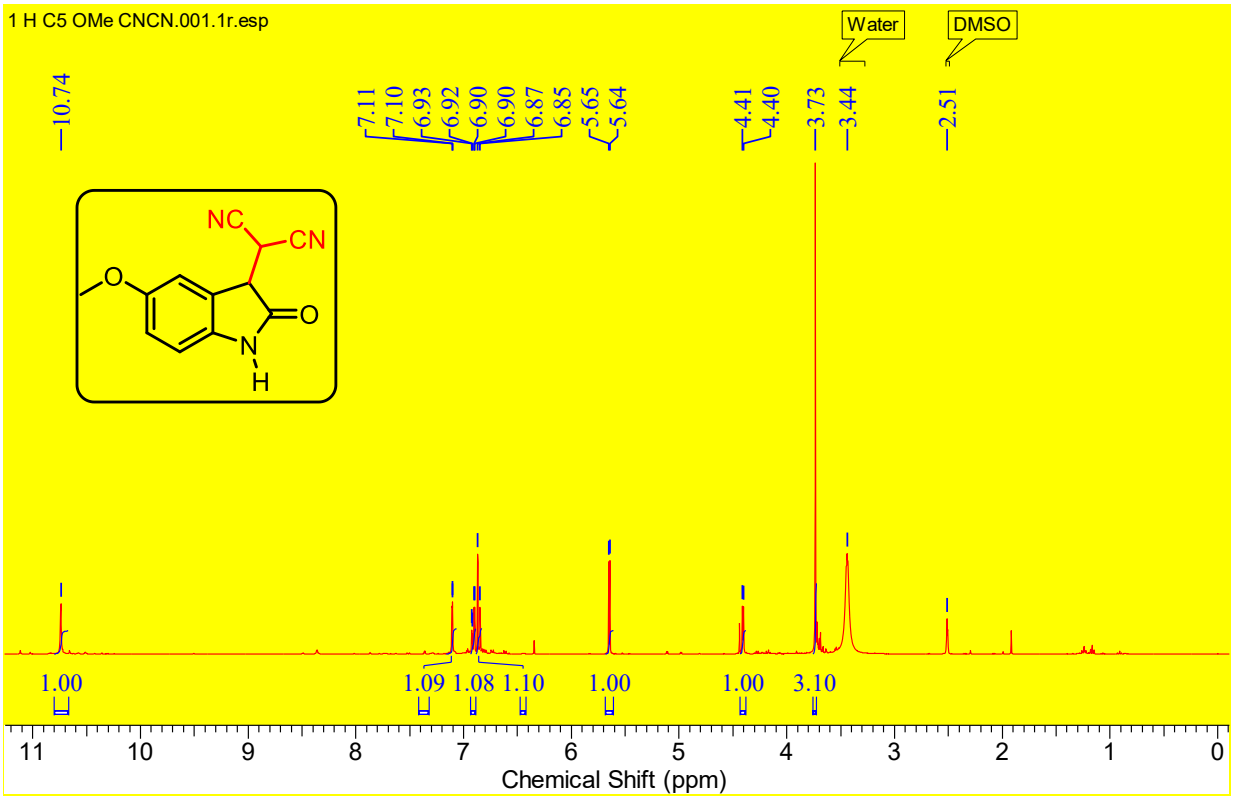


^{1}H NMR of 3Ad



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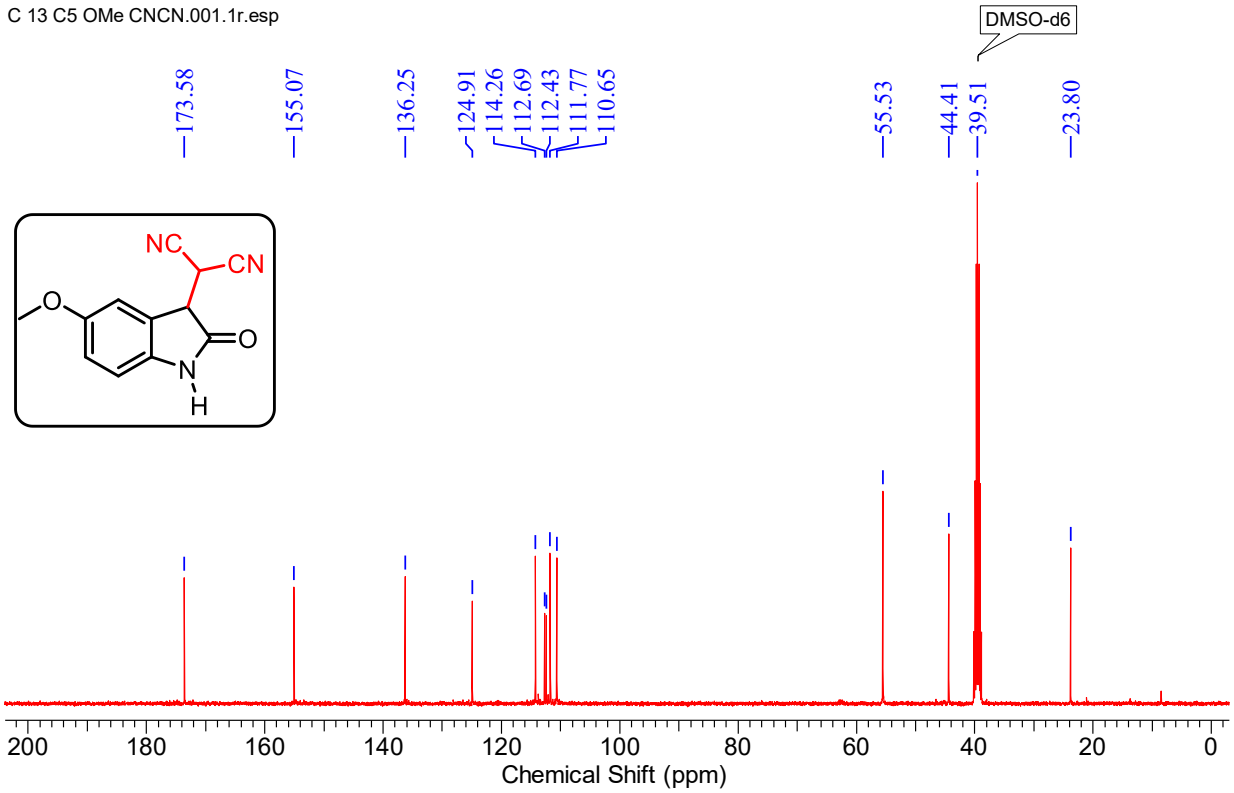
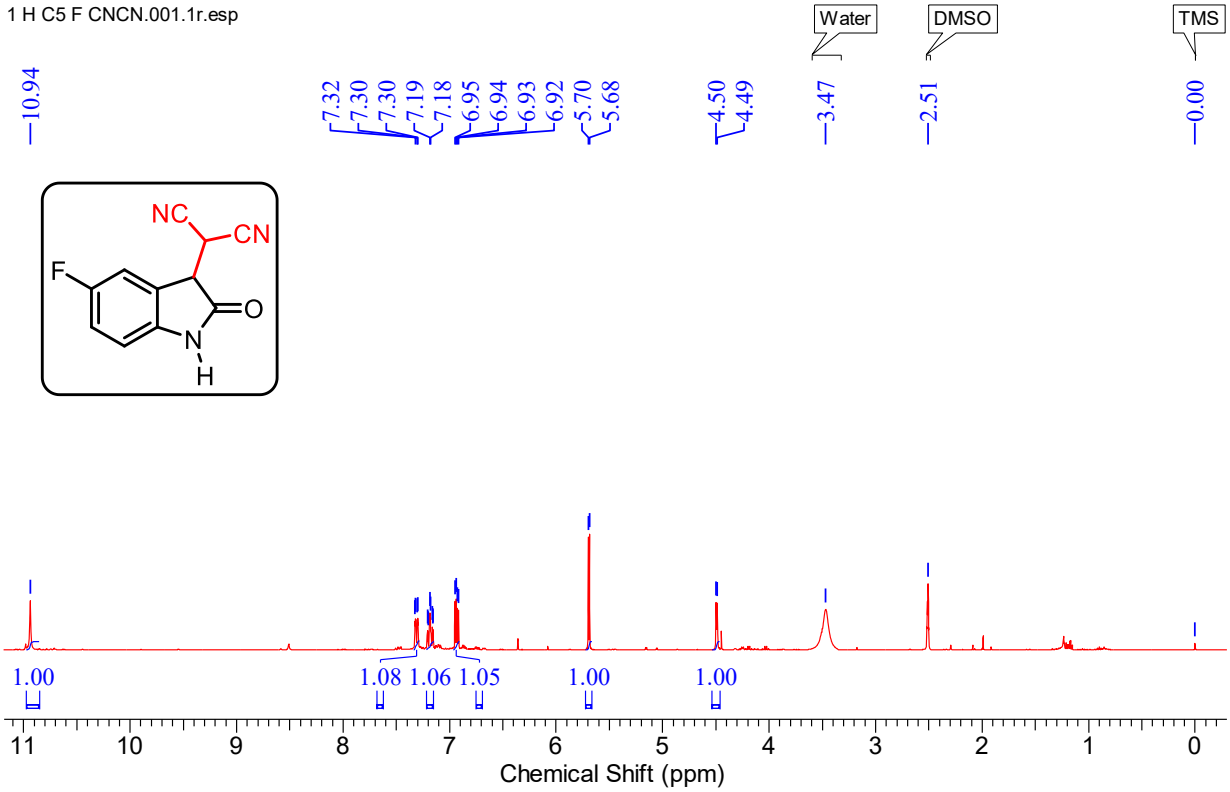
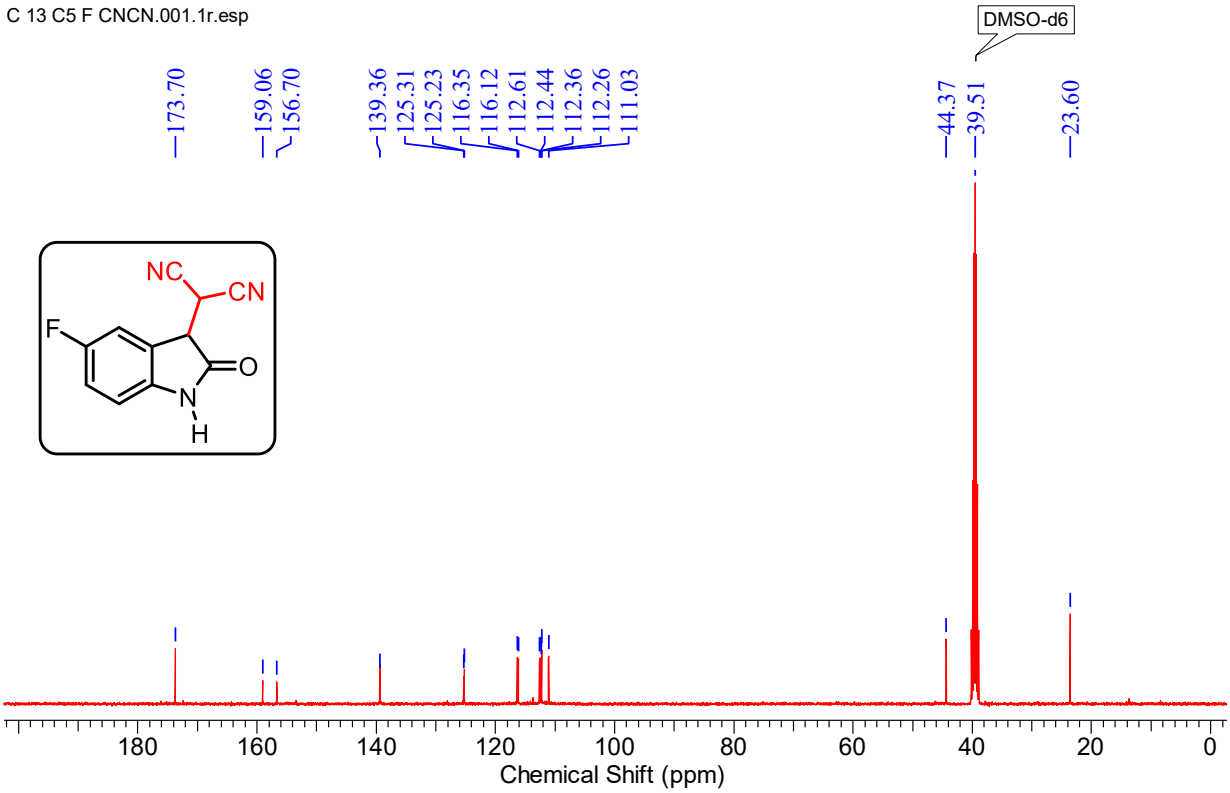


^{1}H NMR of 3Ae



^{13}C NMR of 3Ae



^{19}F NMR of 3Ae

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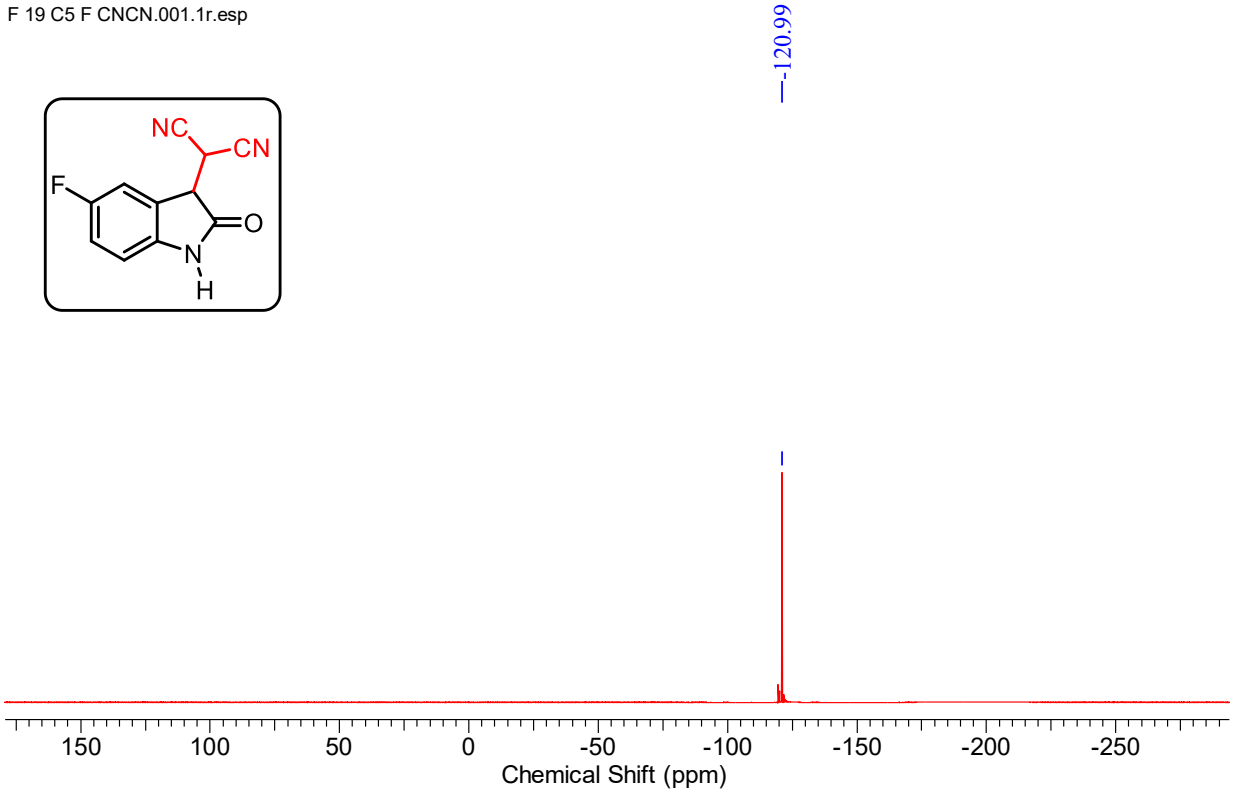
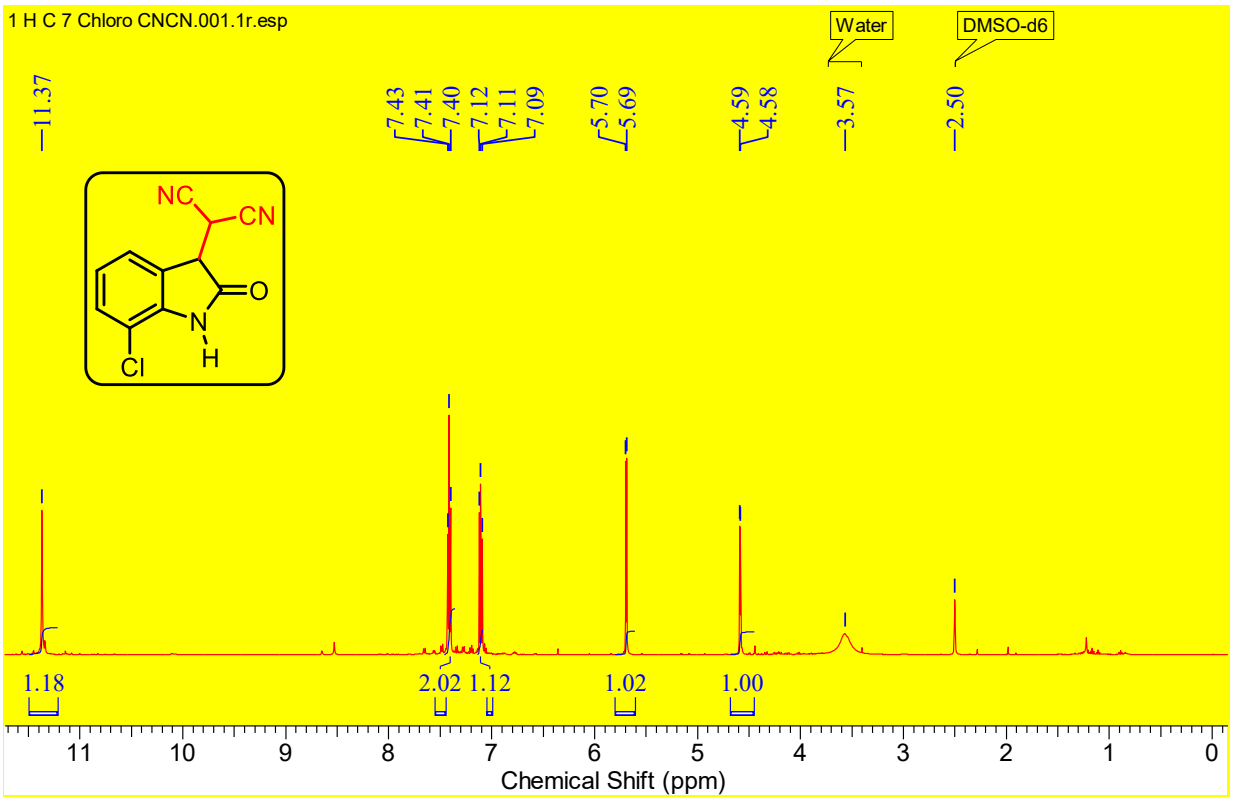
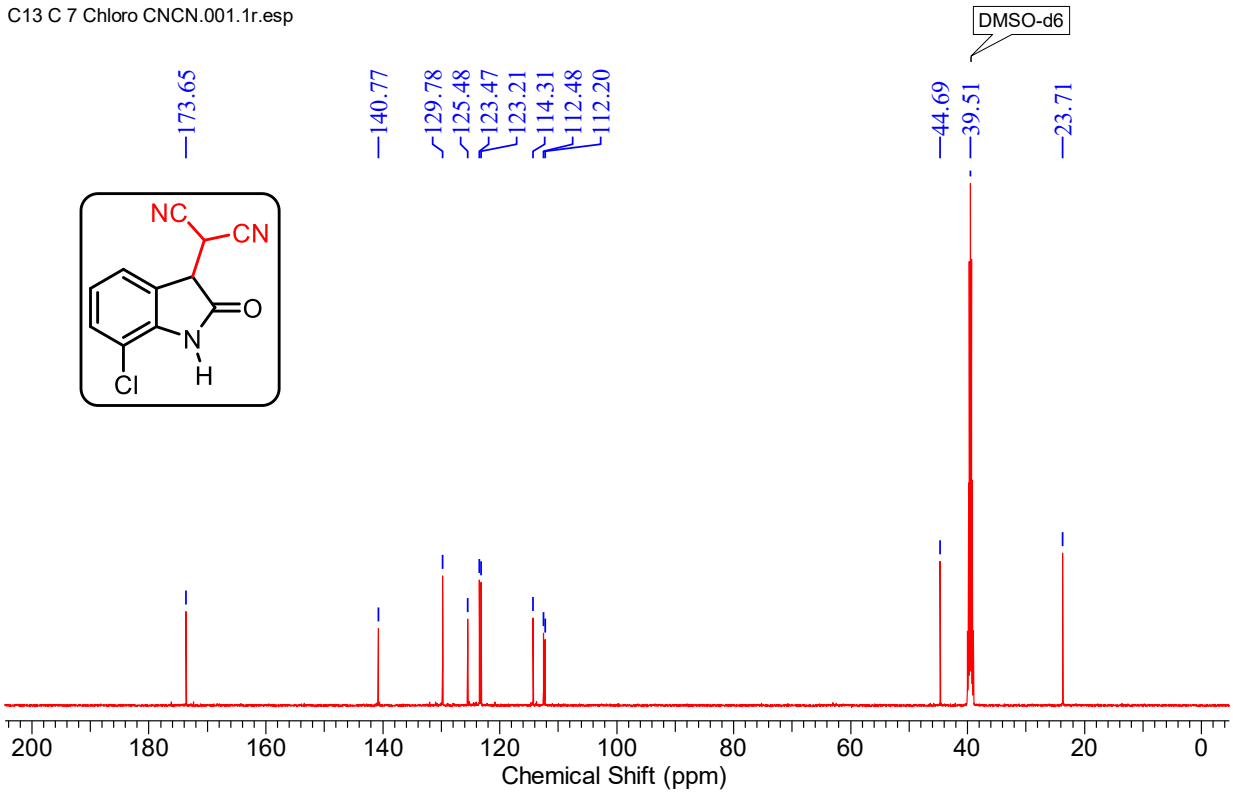


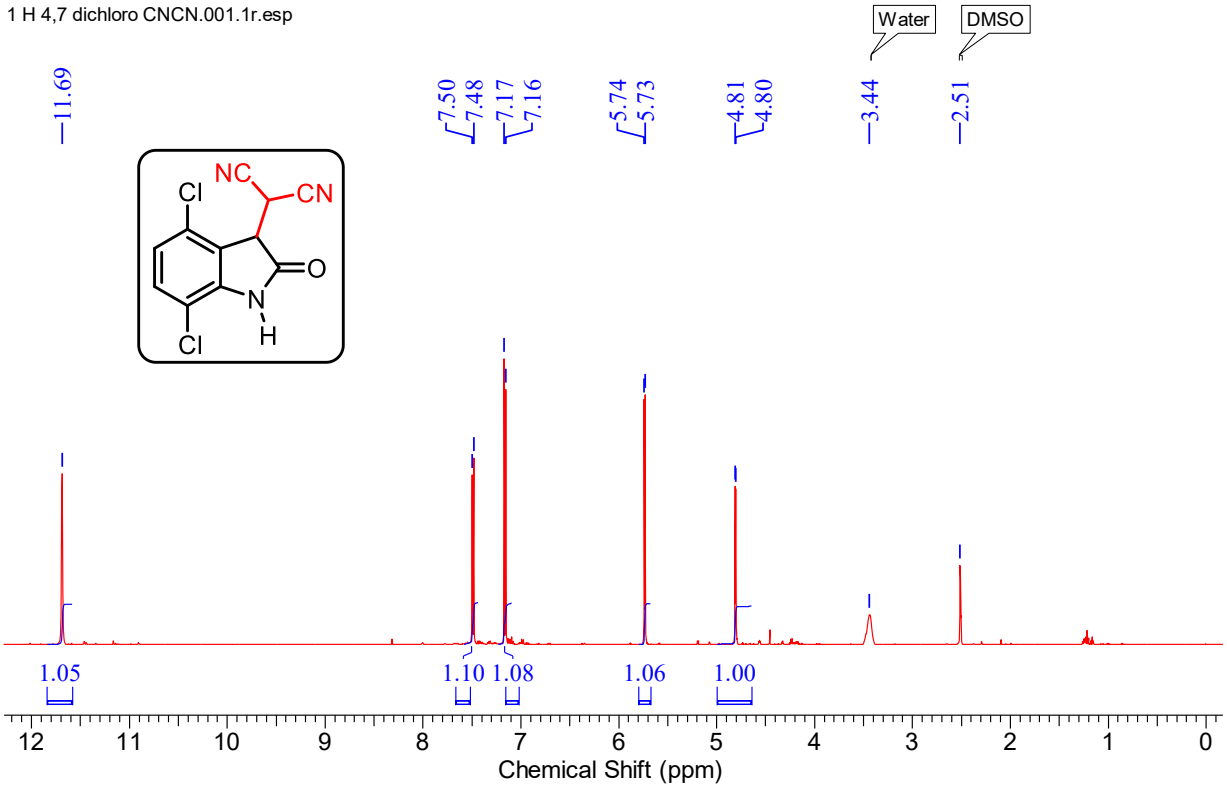
^{1}H NMR of 3Af



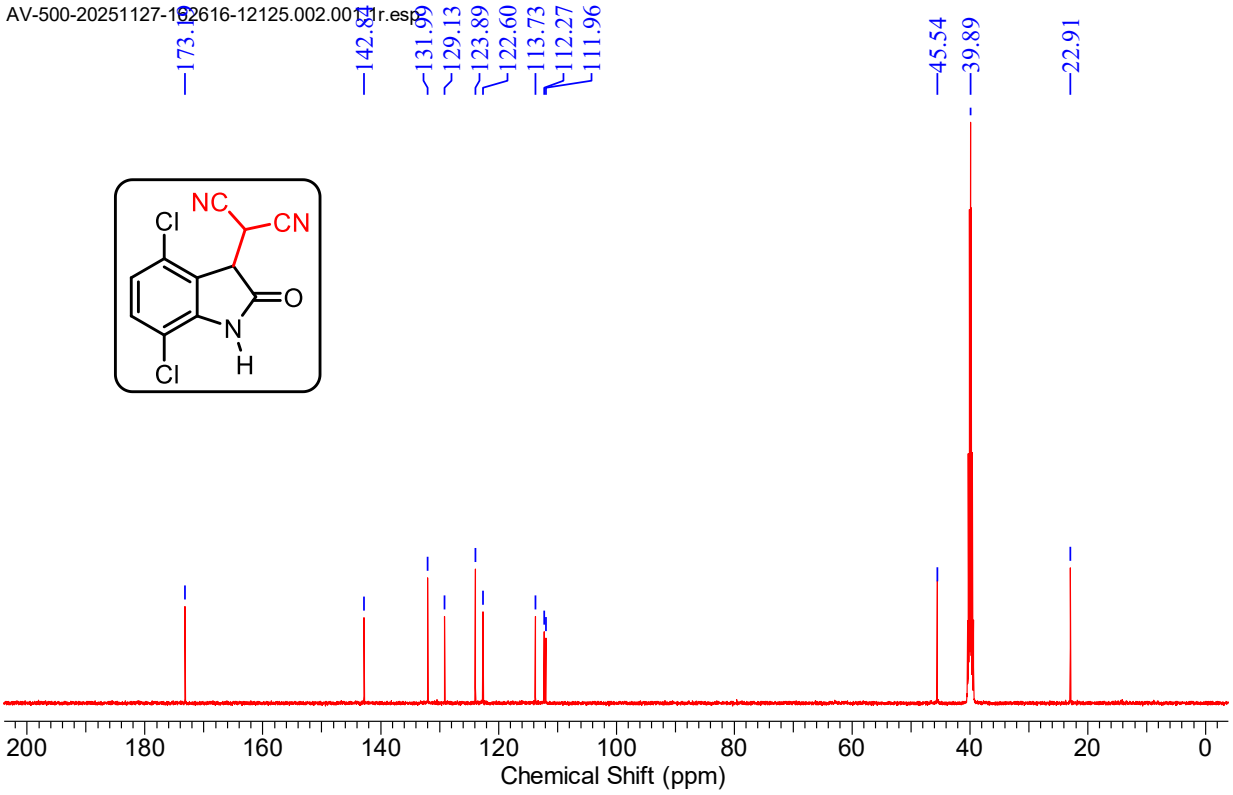
^{13}C NMR of 3Af



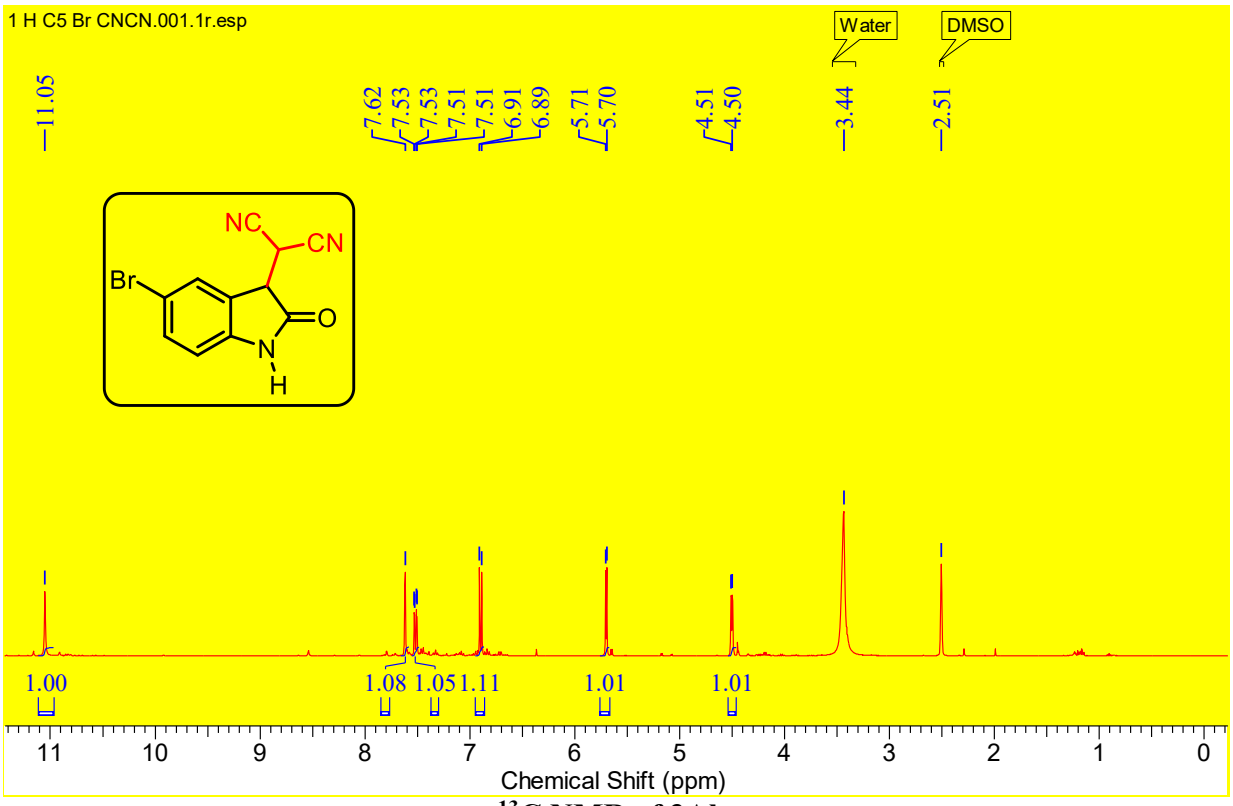
^{1}H NMR of 3Ag



^{13}C NMR of 3Ag



^{1}H NMR of 3Ah



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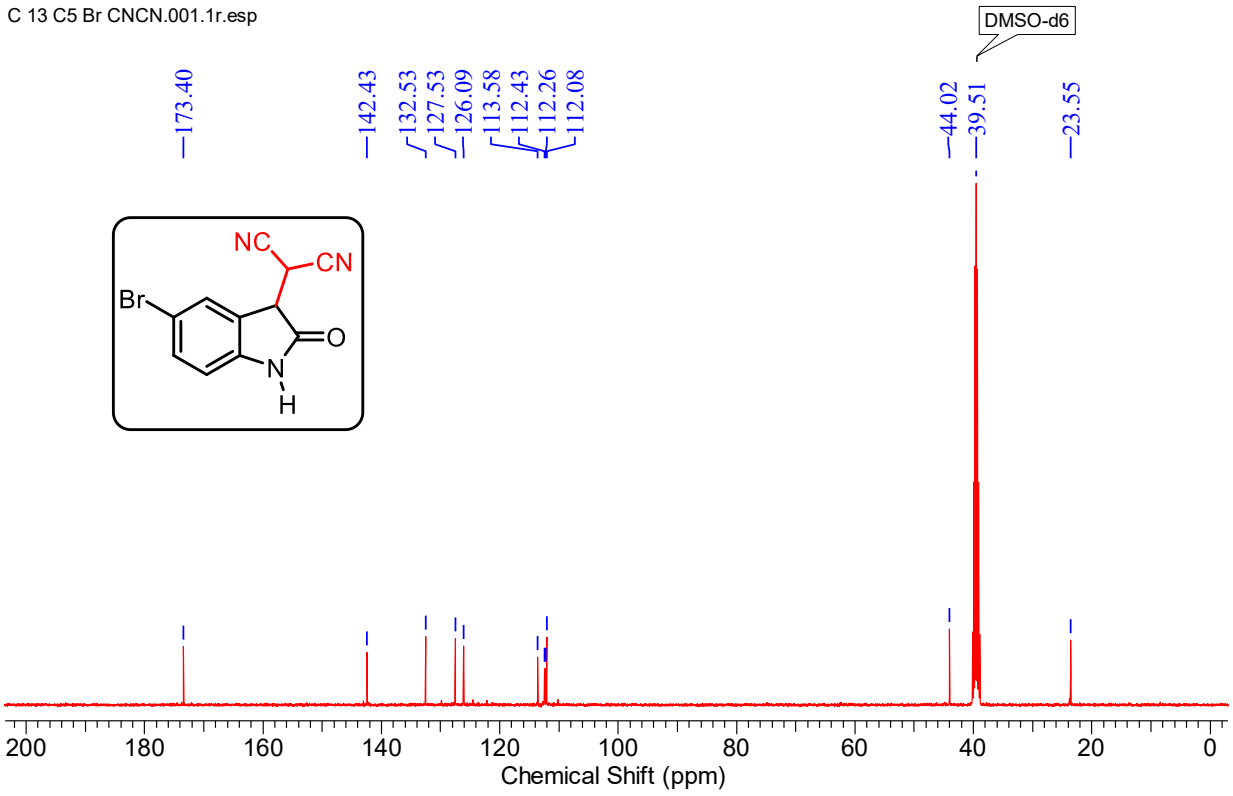
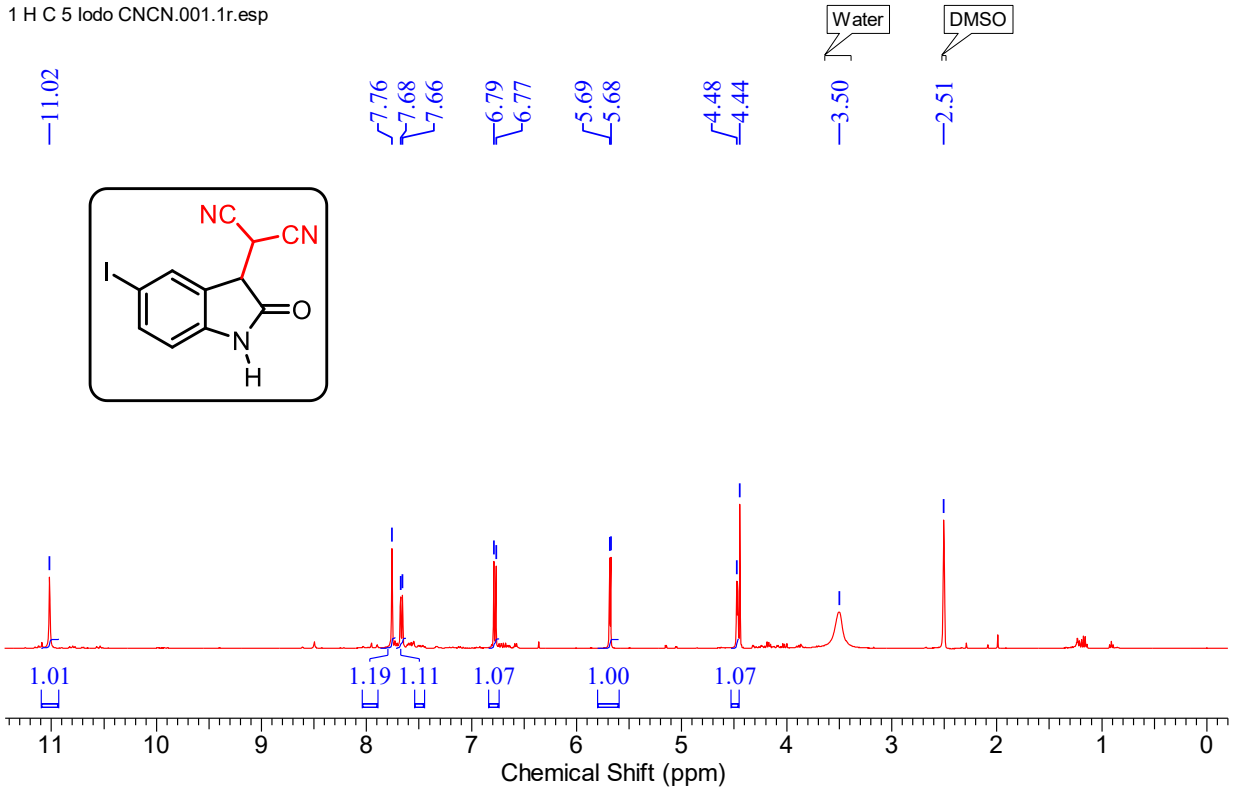
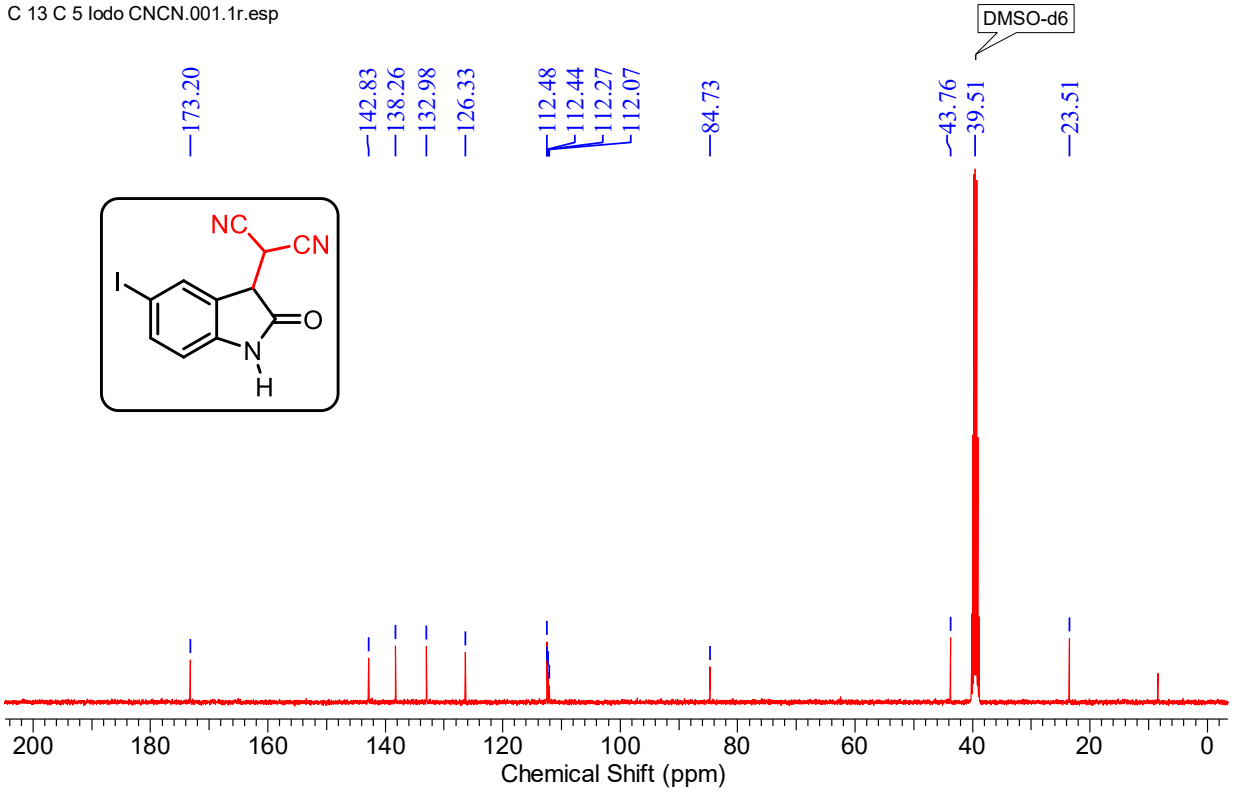


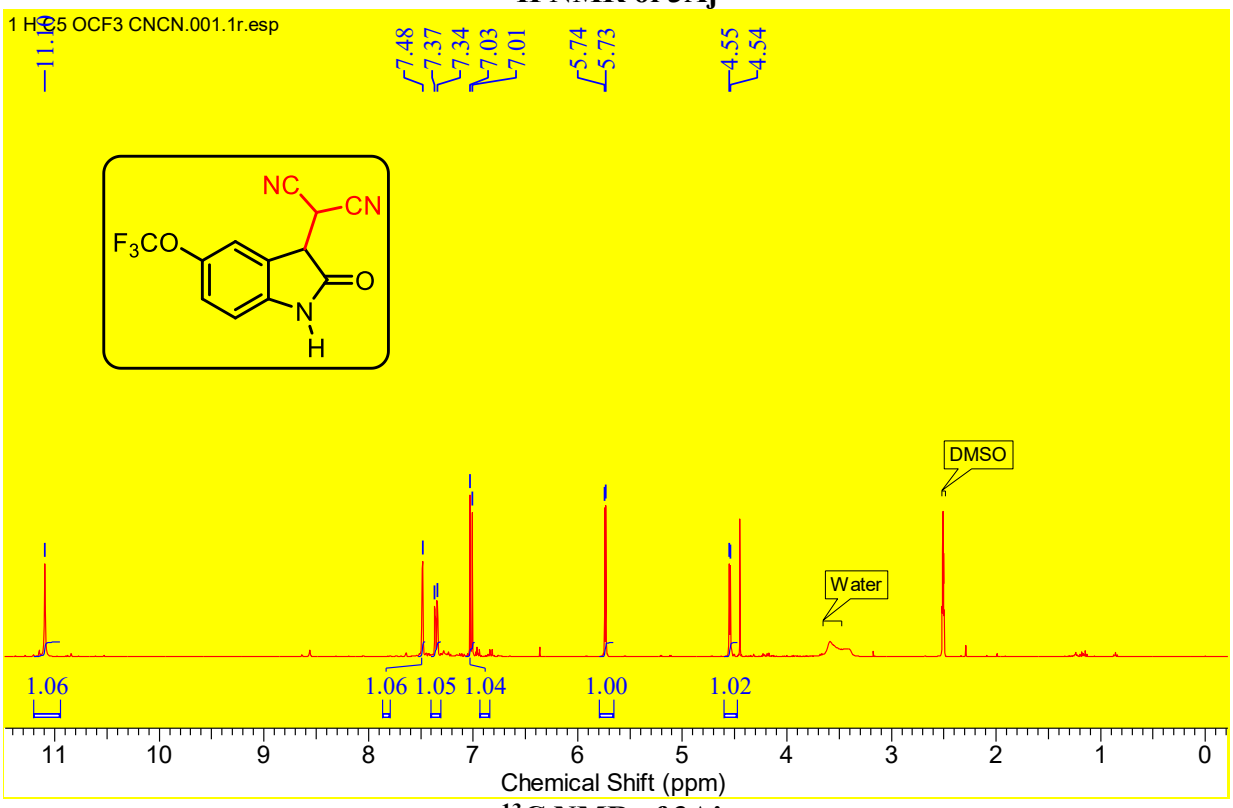
^{1}H NMR of 3Ai



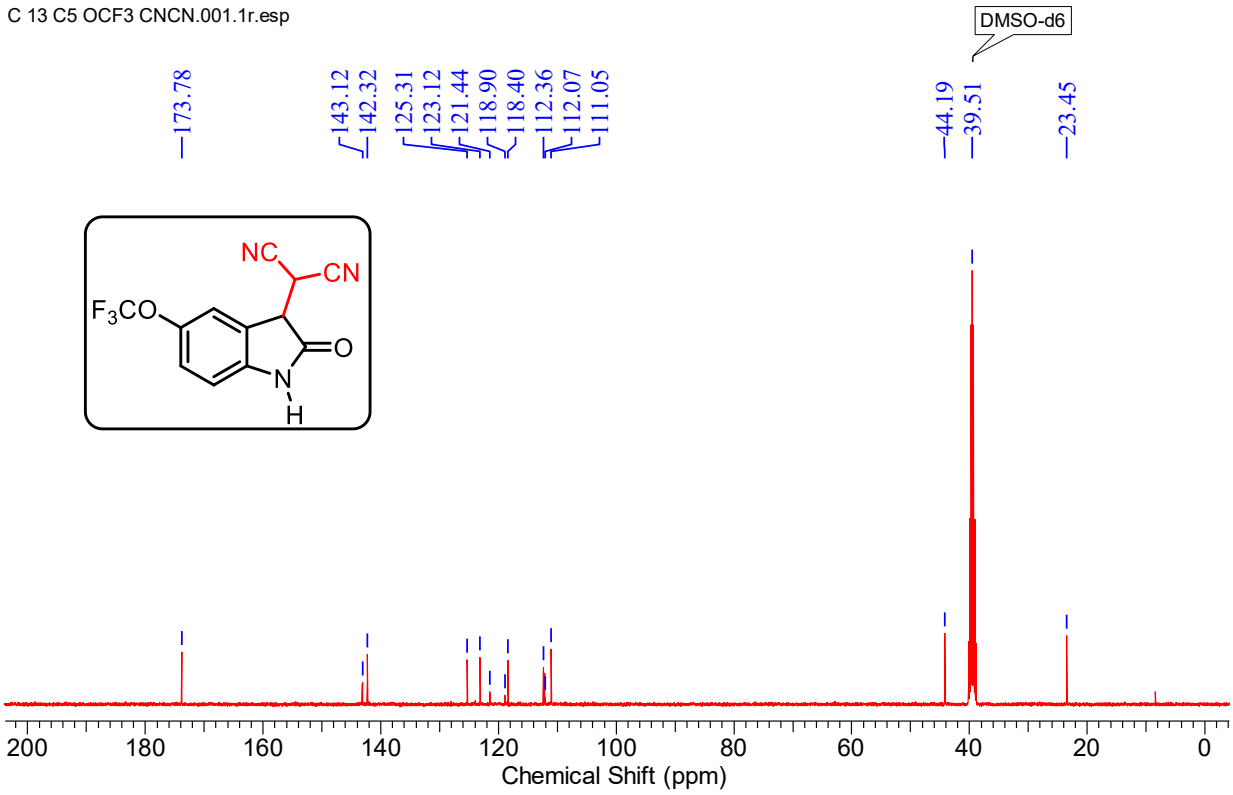
^{13}C NMR of 3Ai



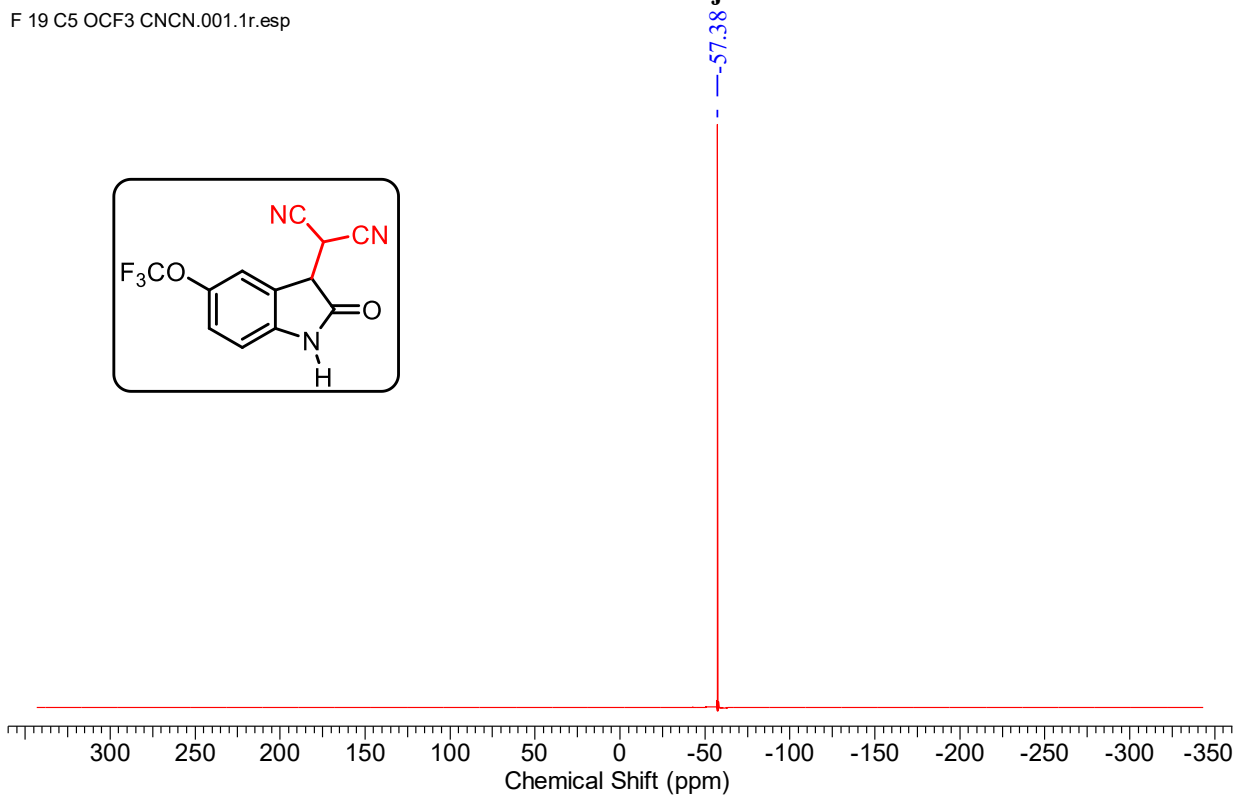
^{1}H NMR of 3Aj



^{13}C NMR of 3Aj



^{19}F NMR of 3Aj



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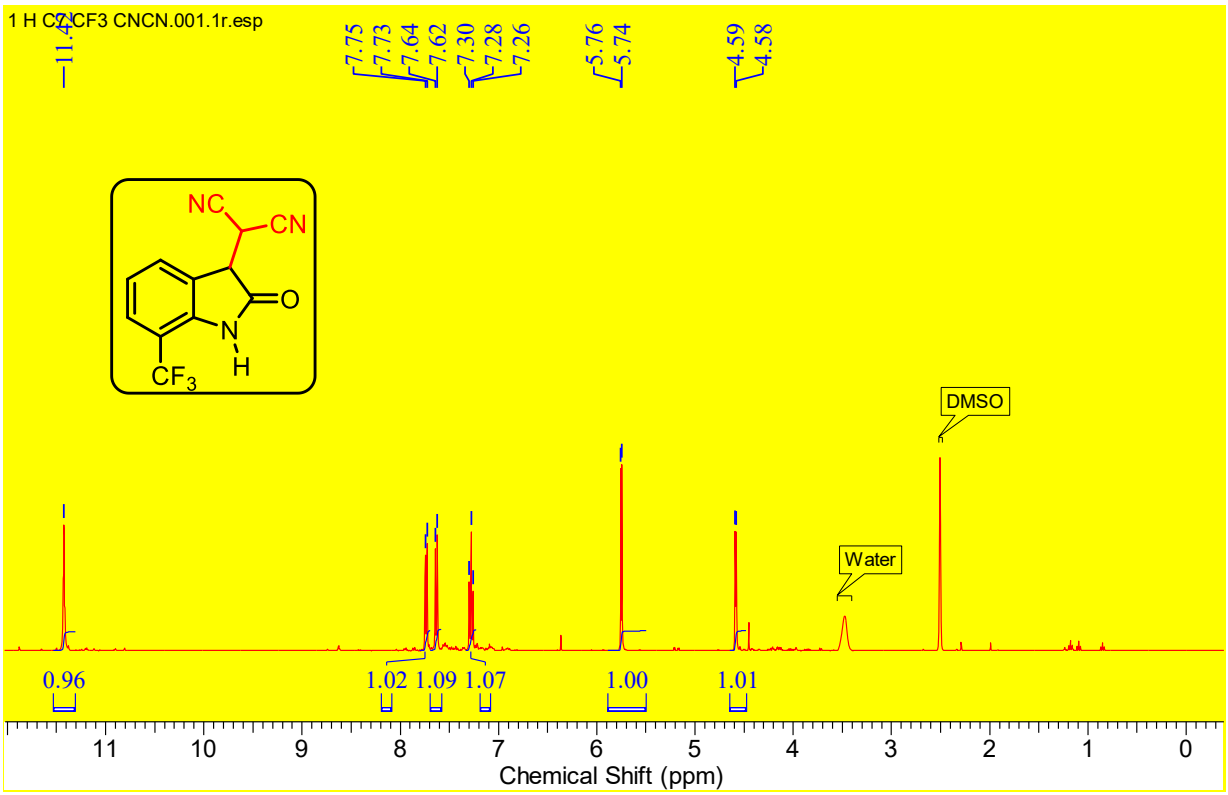

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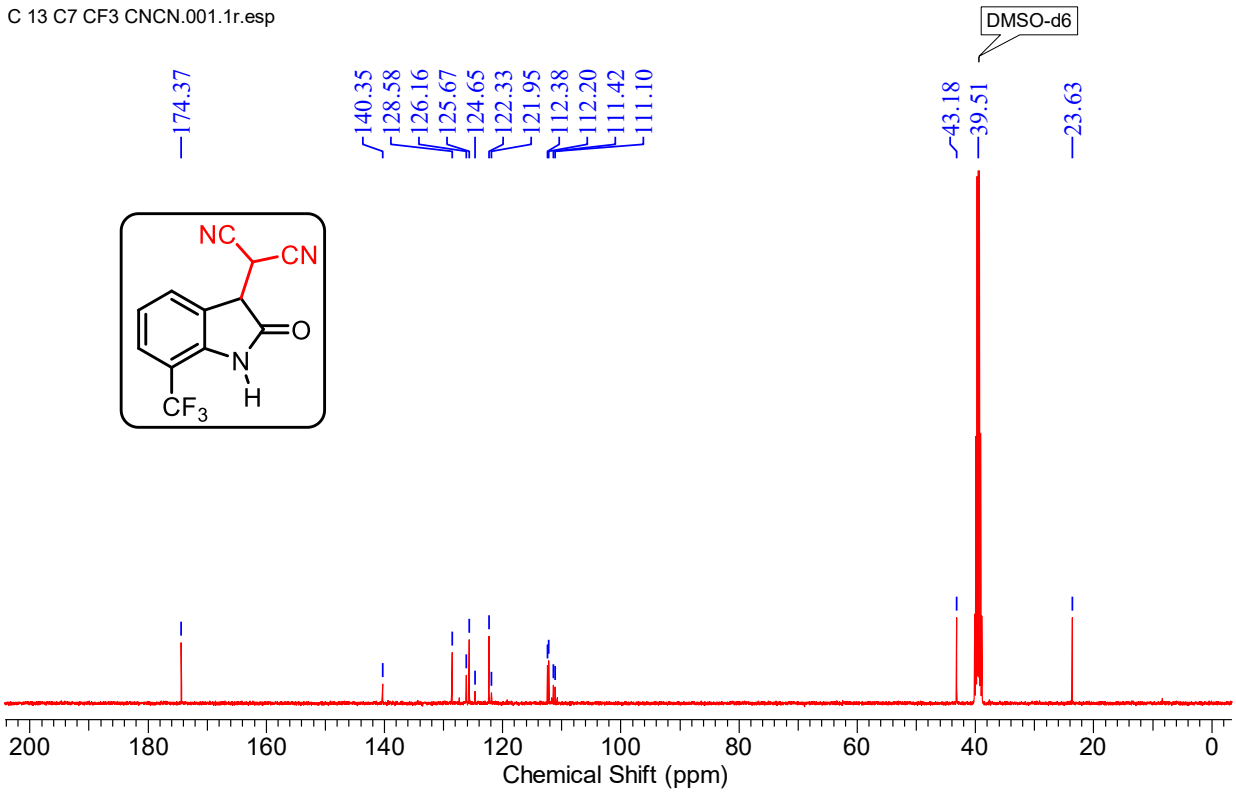

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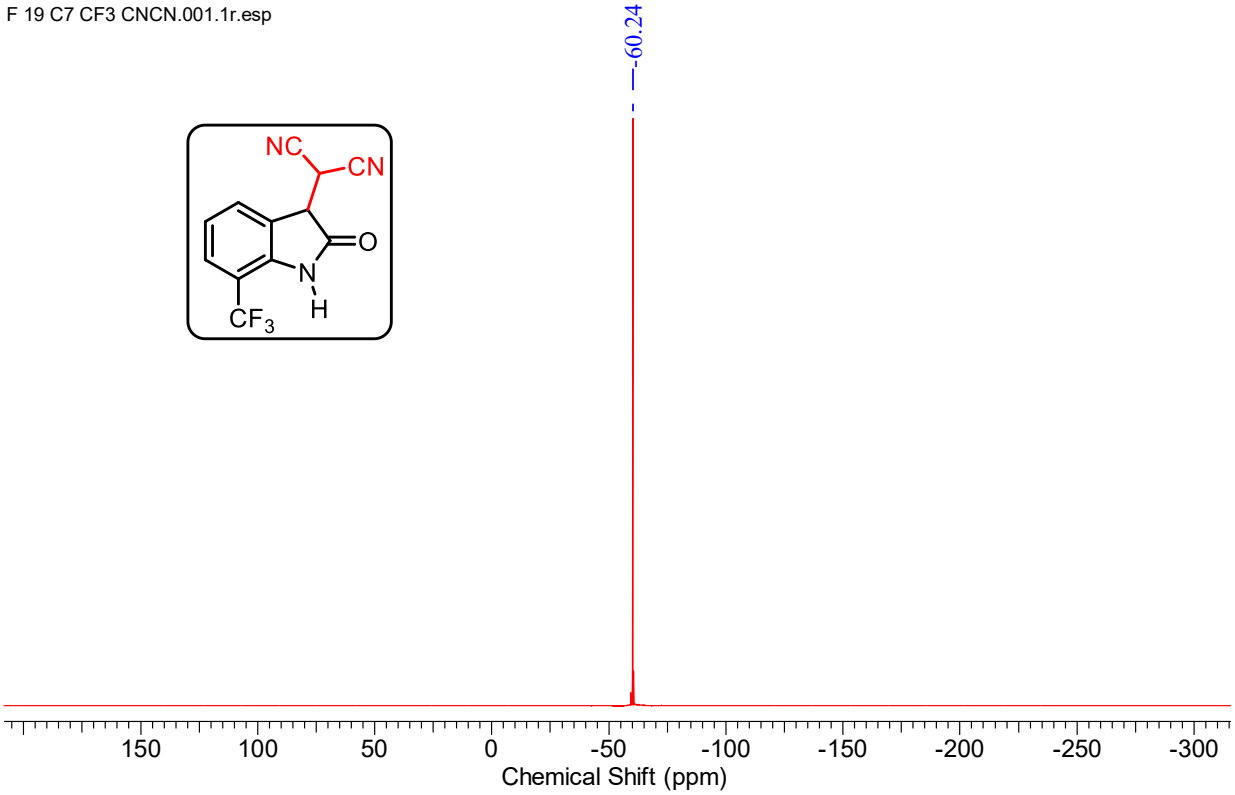
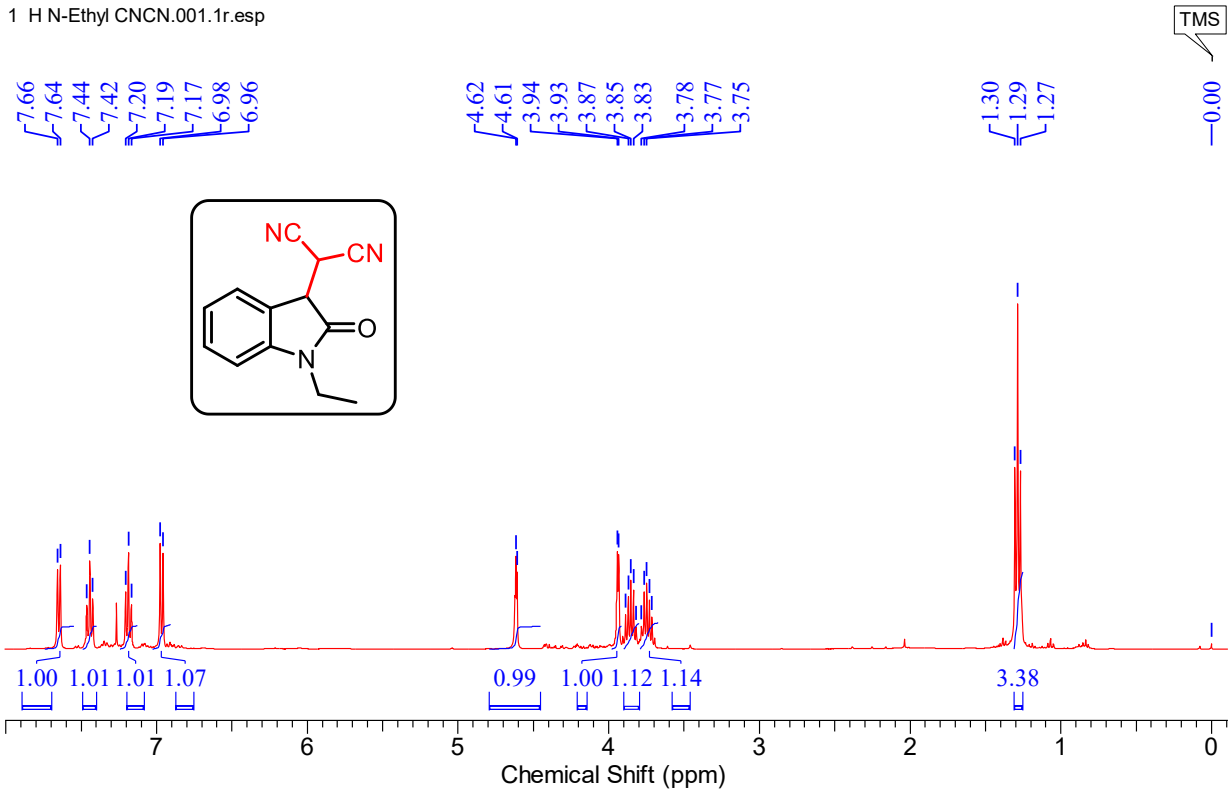
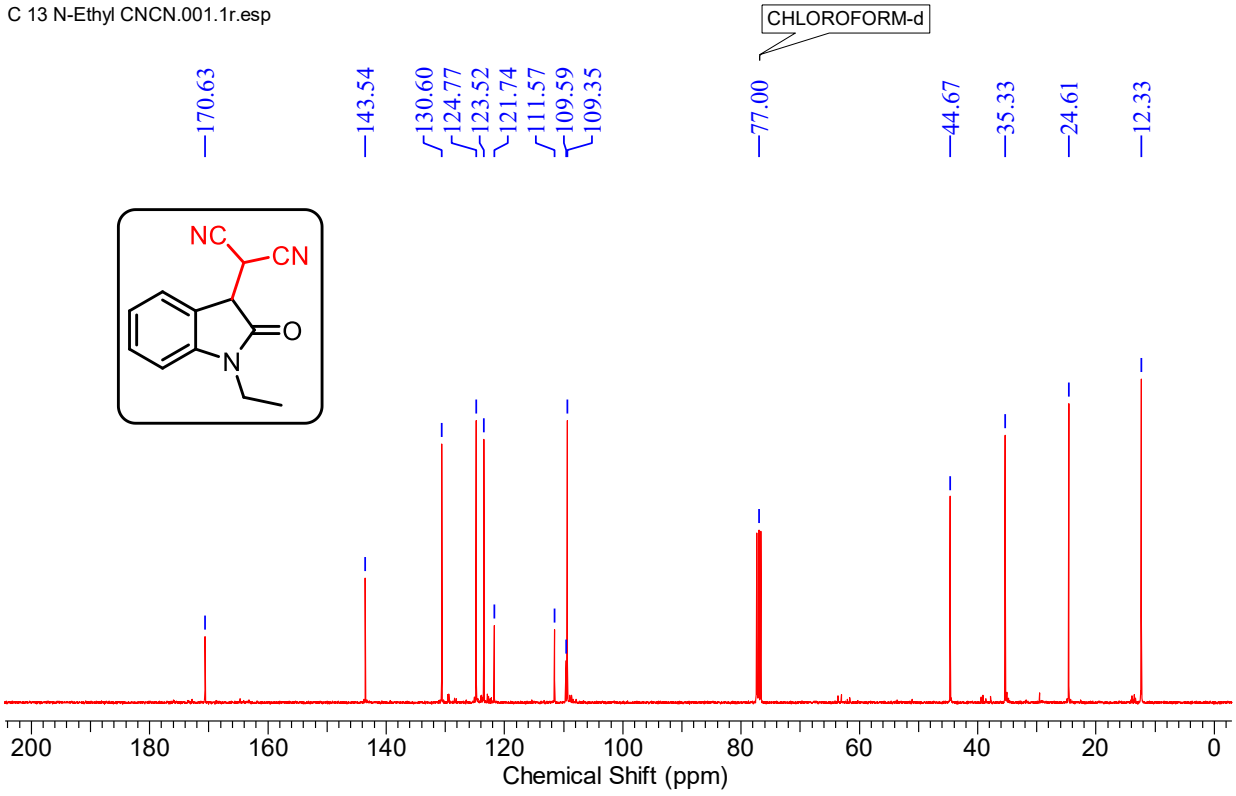


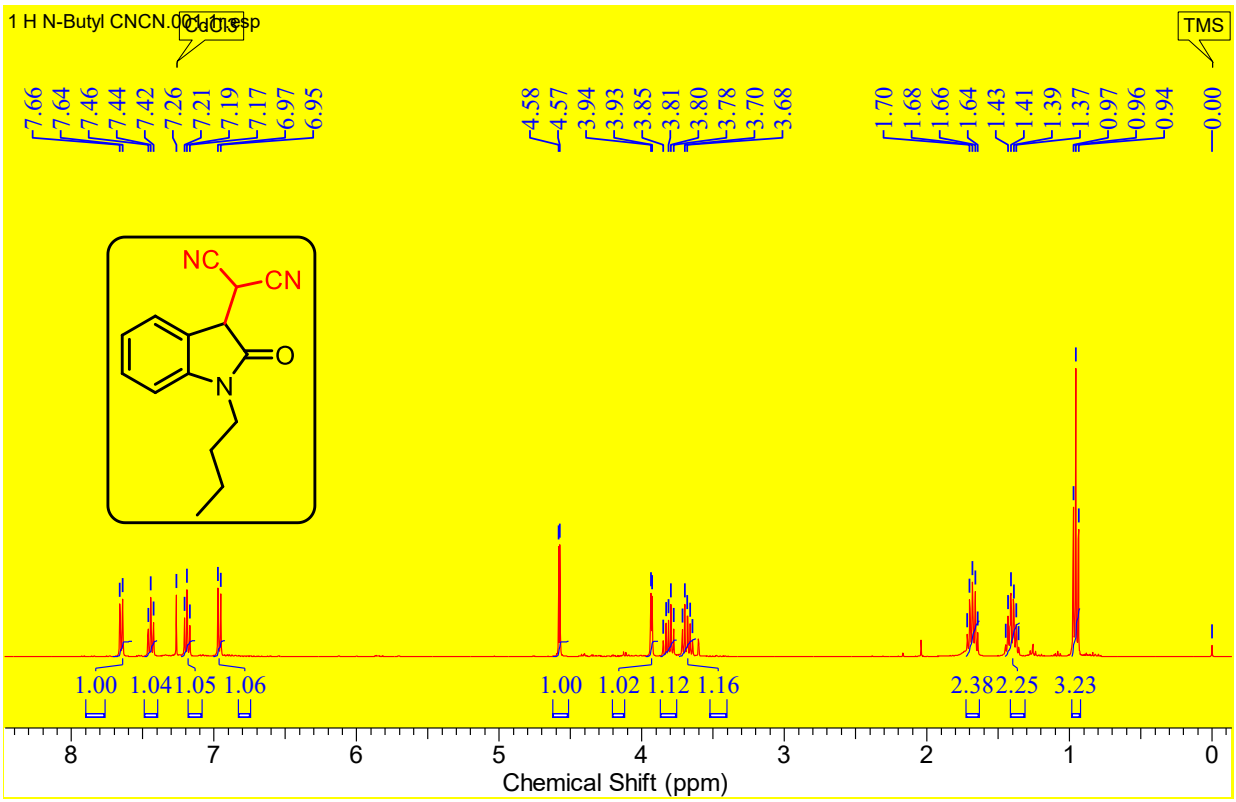
^{1}H NMR of 3Al



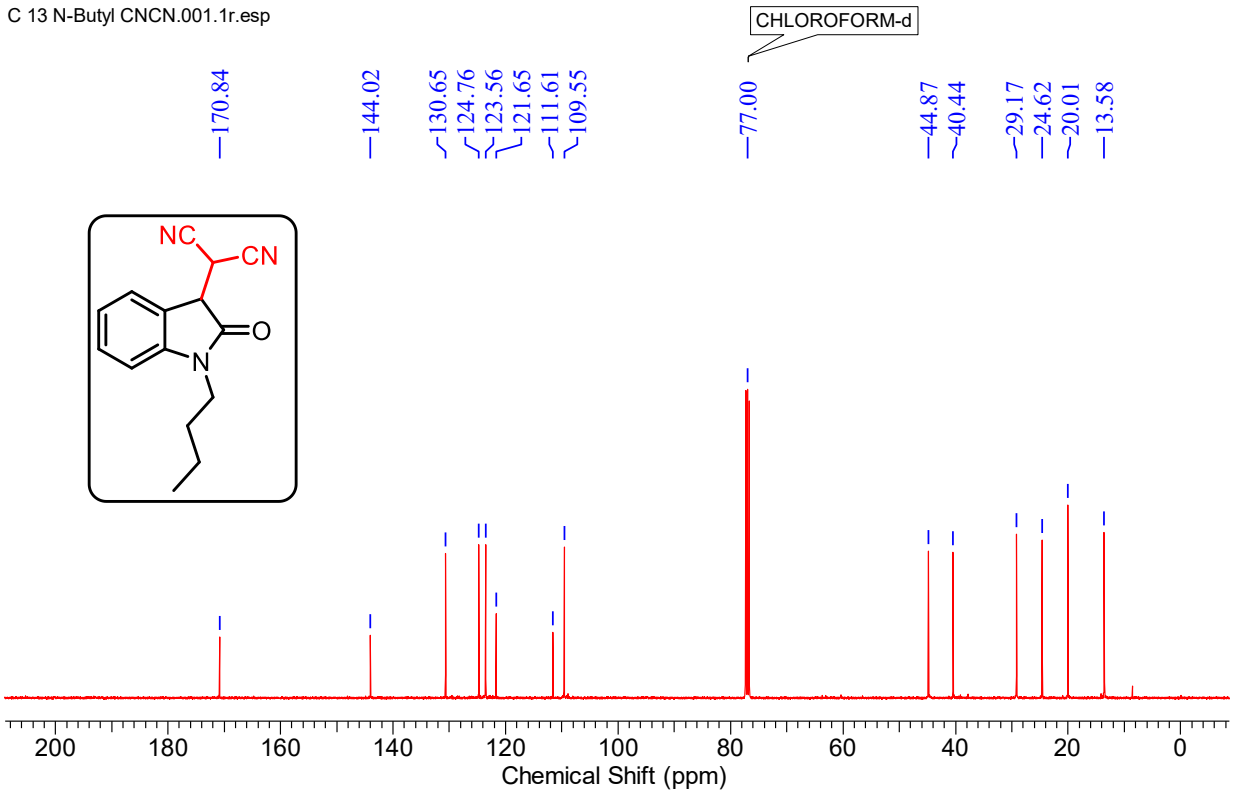
^{13}C NMR of 3Al



^{1}H NMR of 3Am



^{13}C NMR of 3Am



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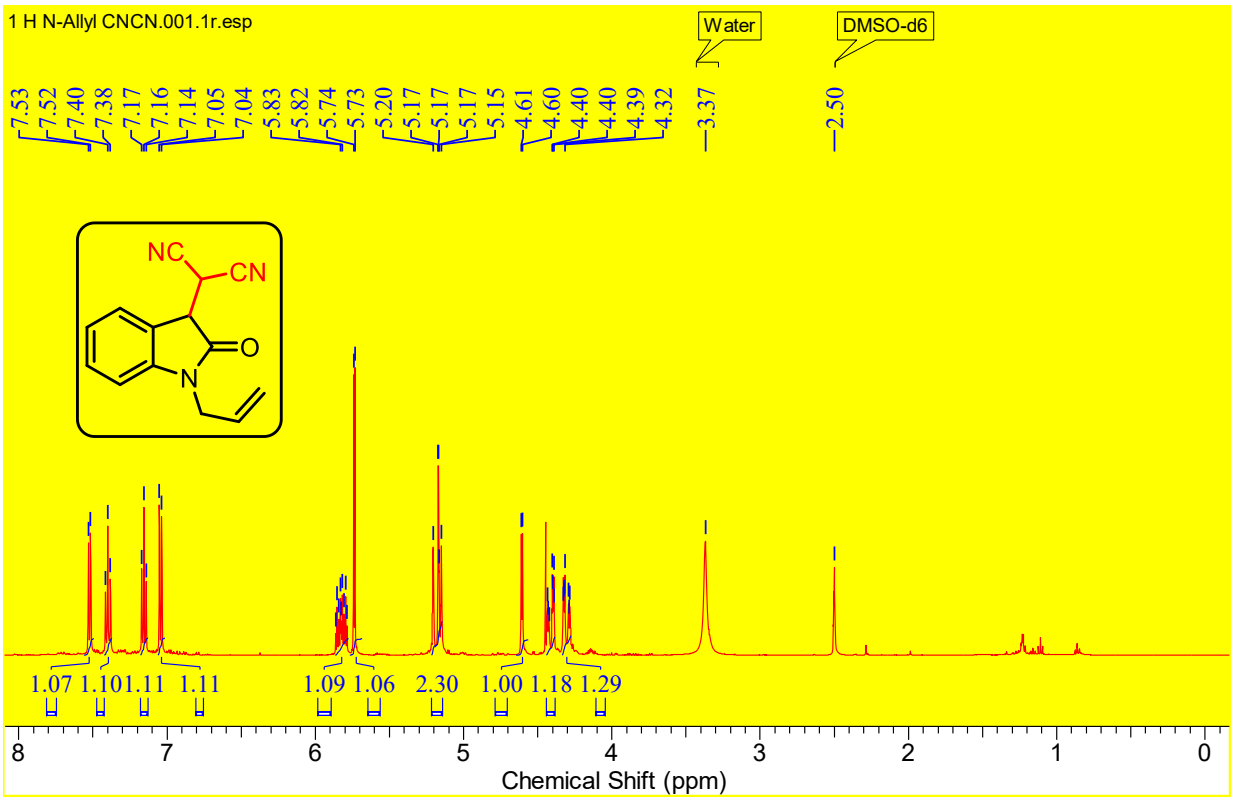

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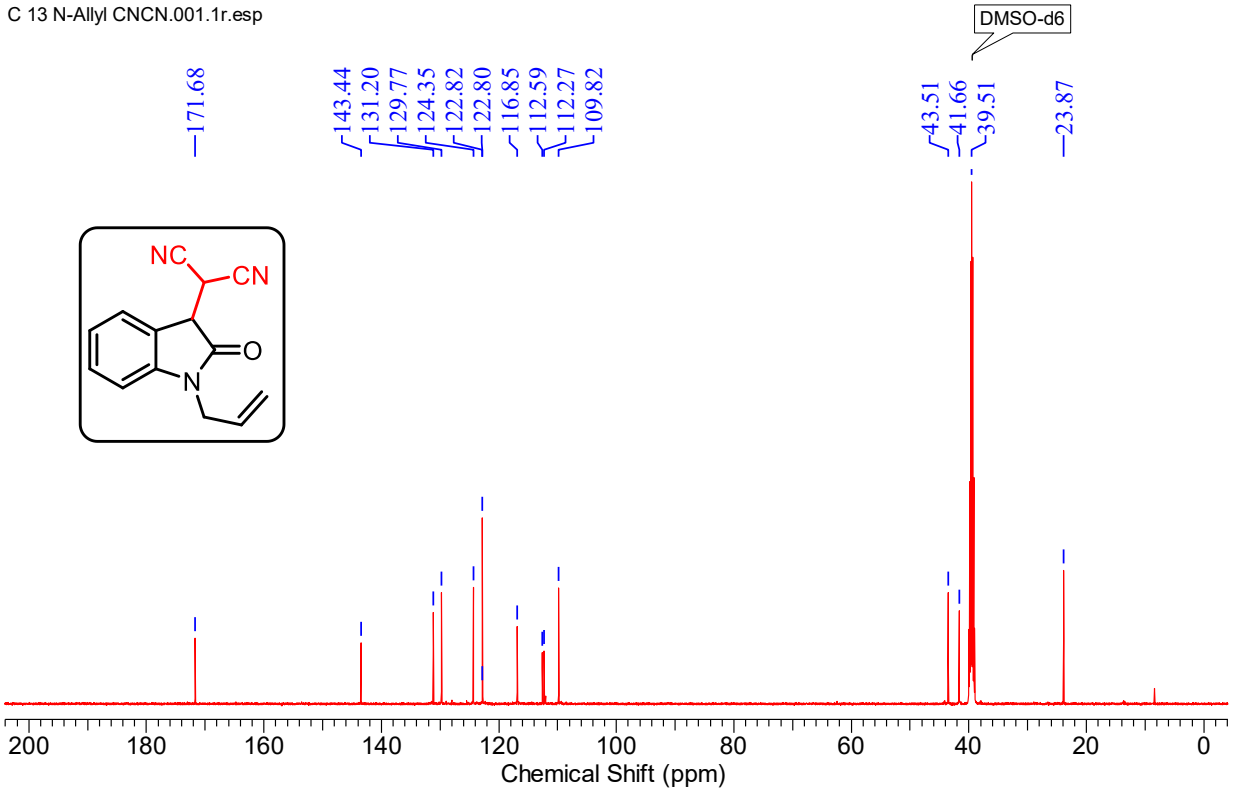

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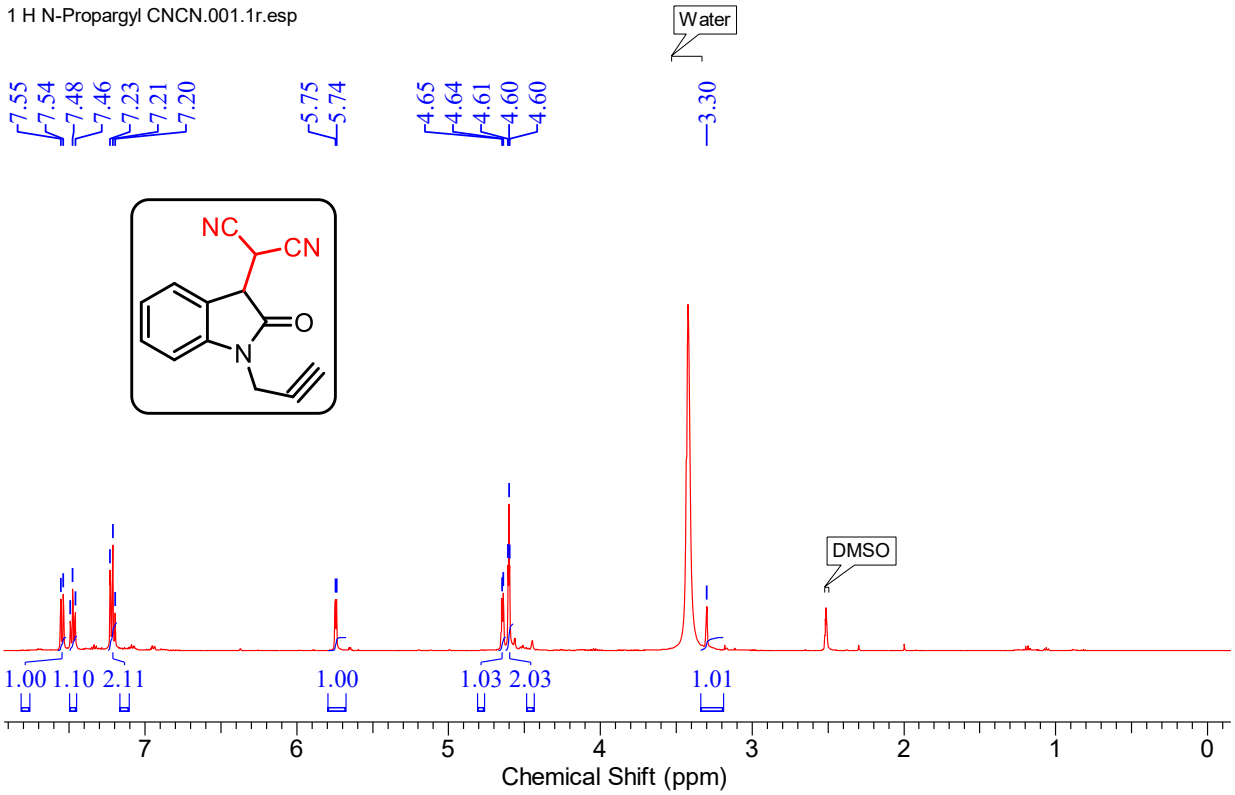

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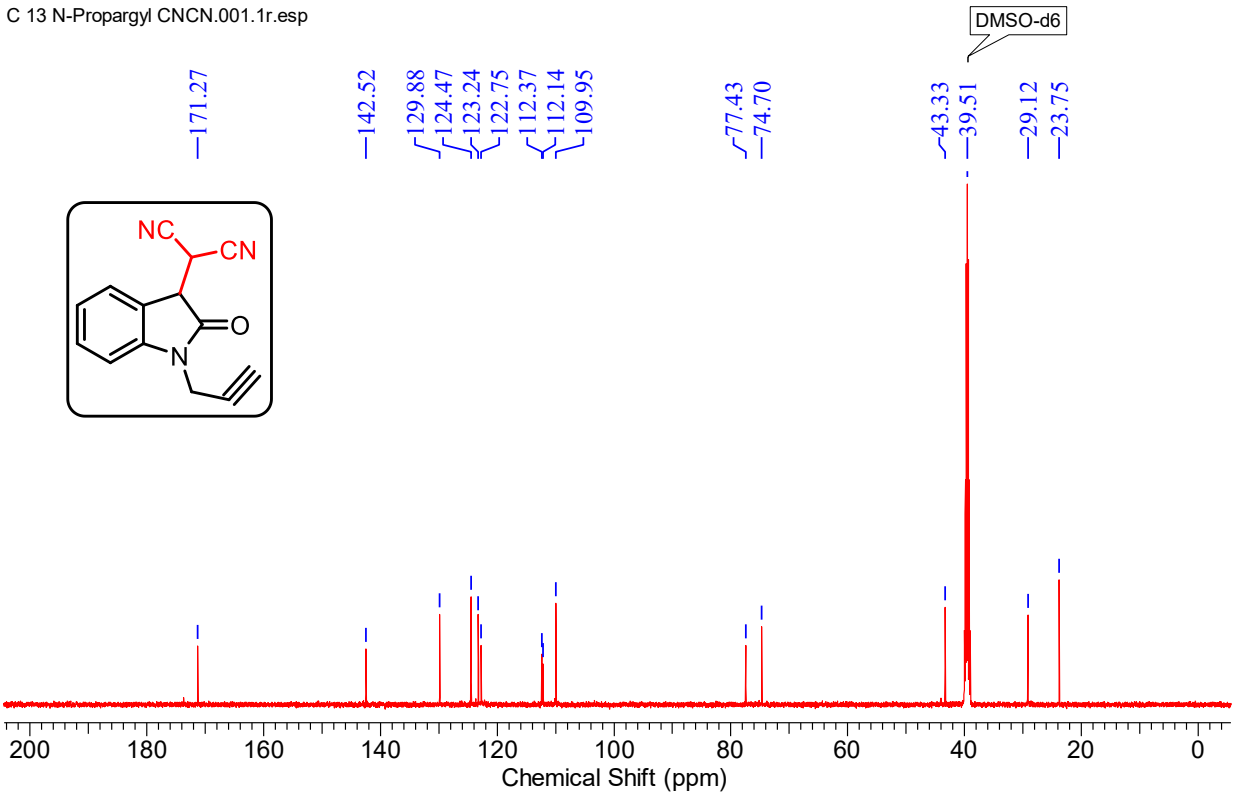
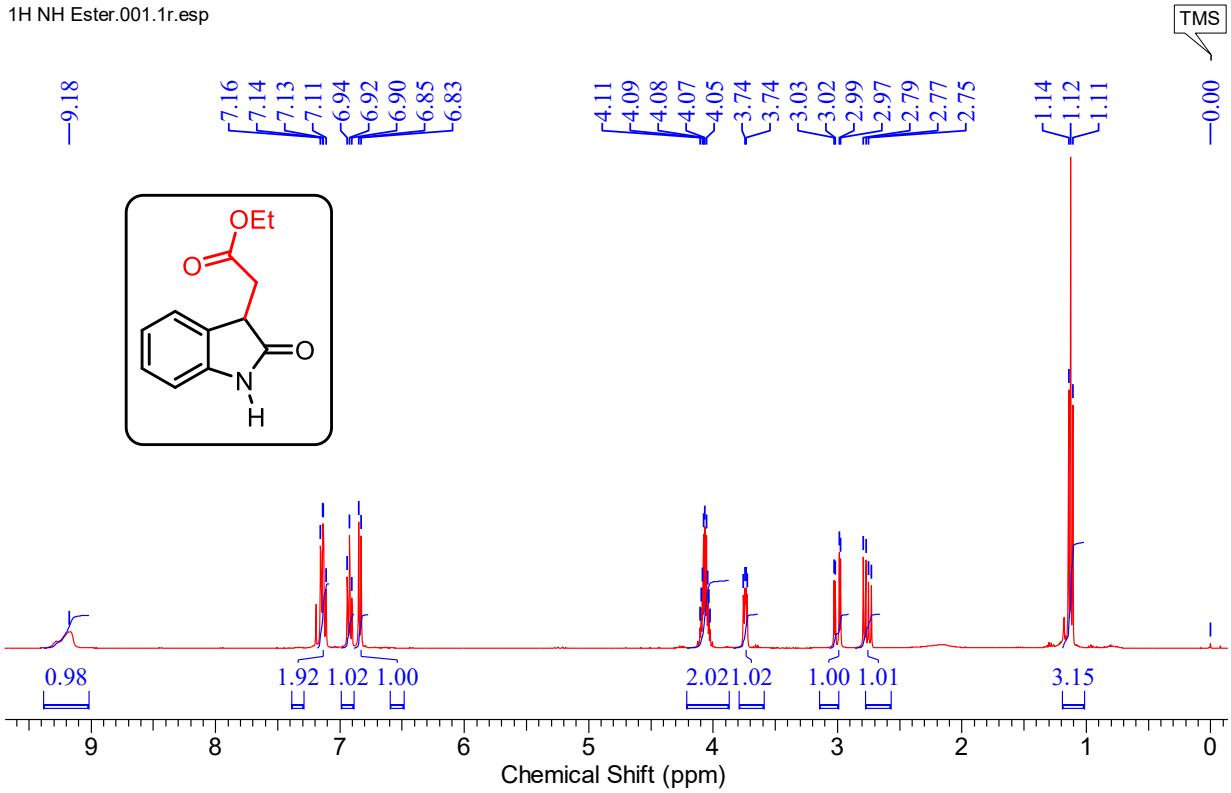
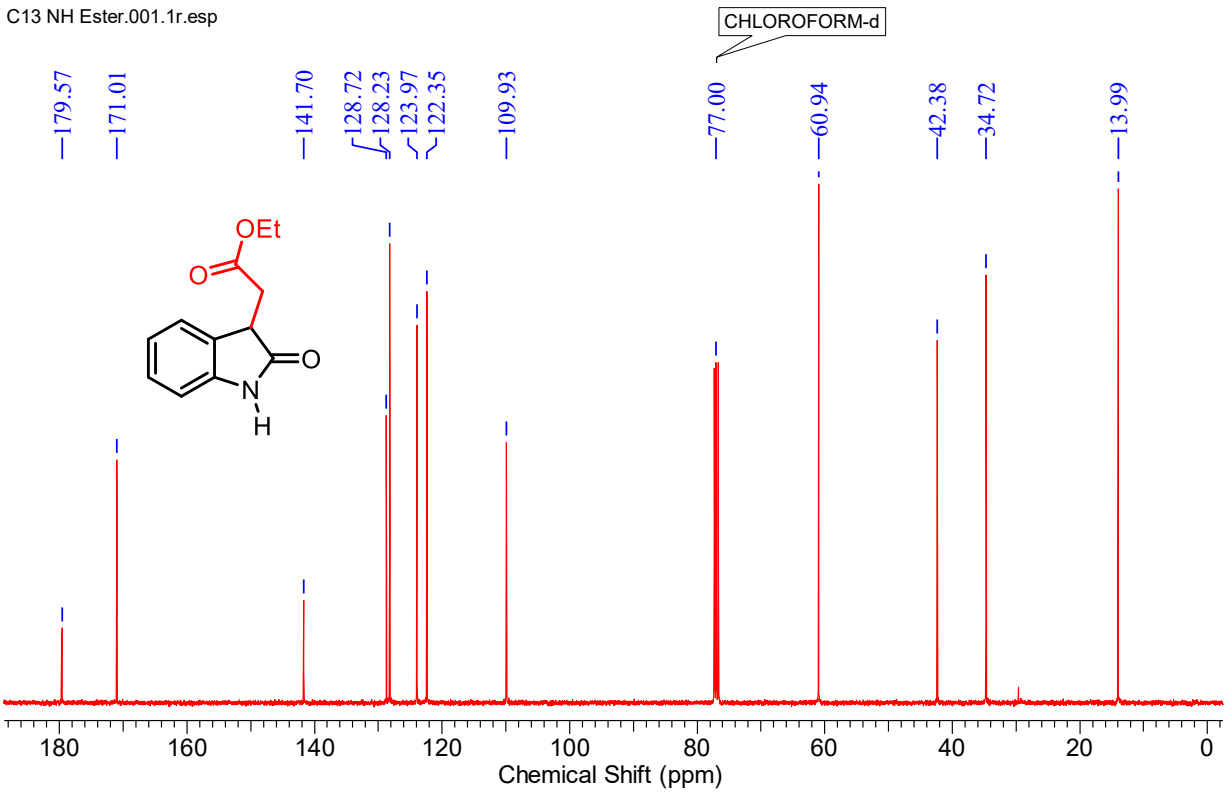


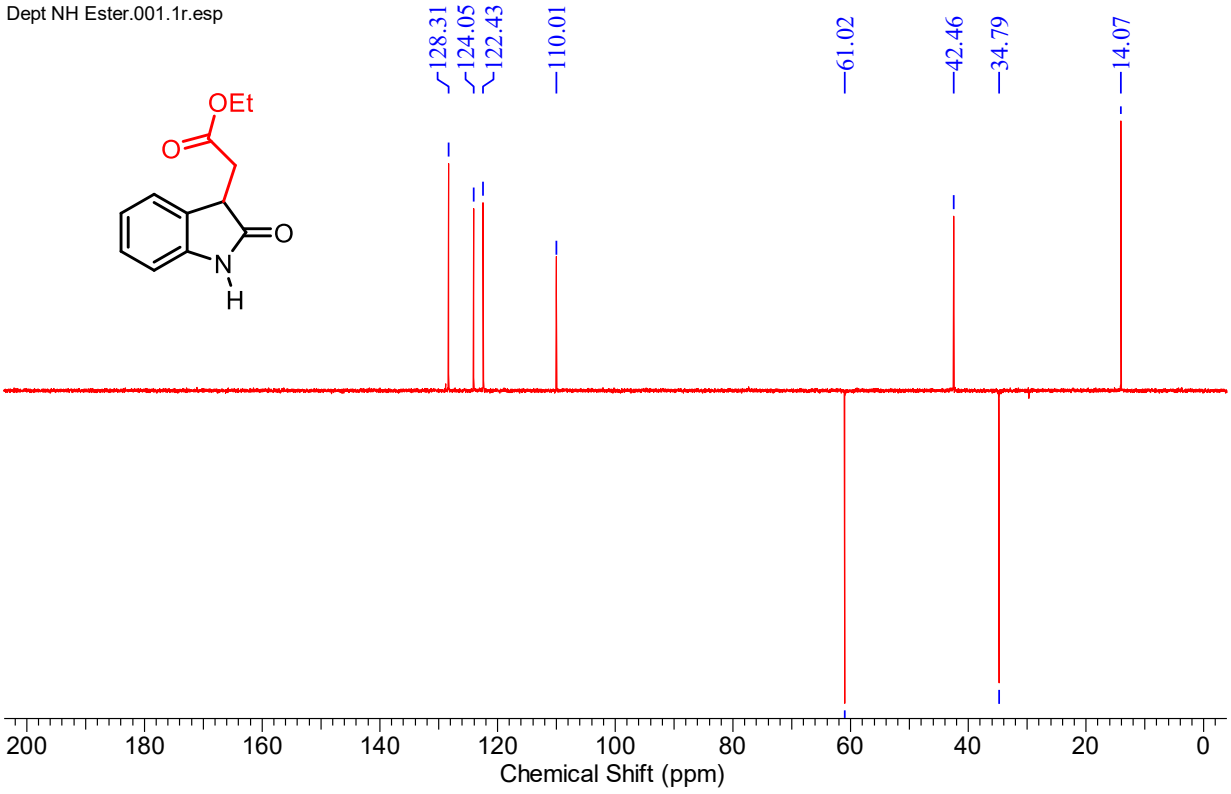
^{1}H NMR of 3Ba



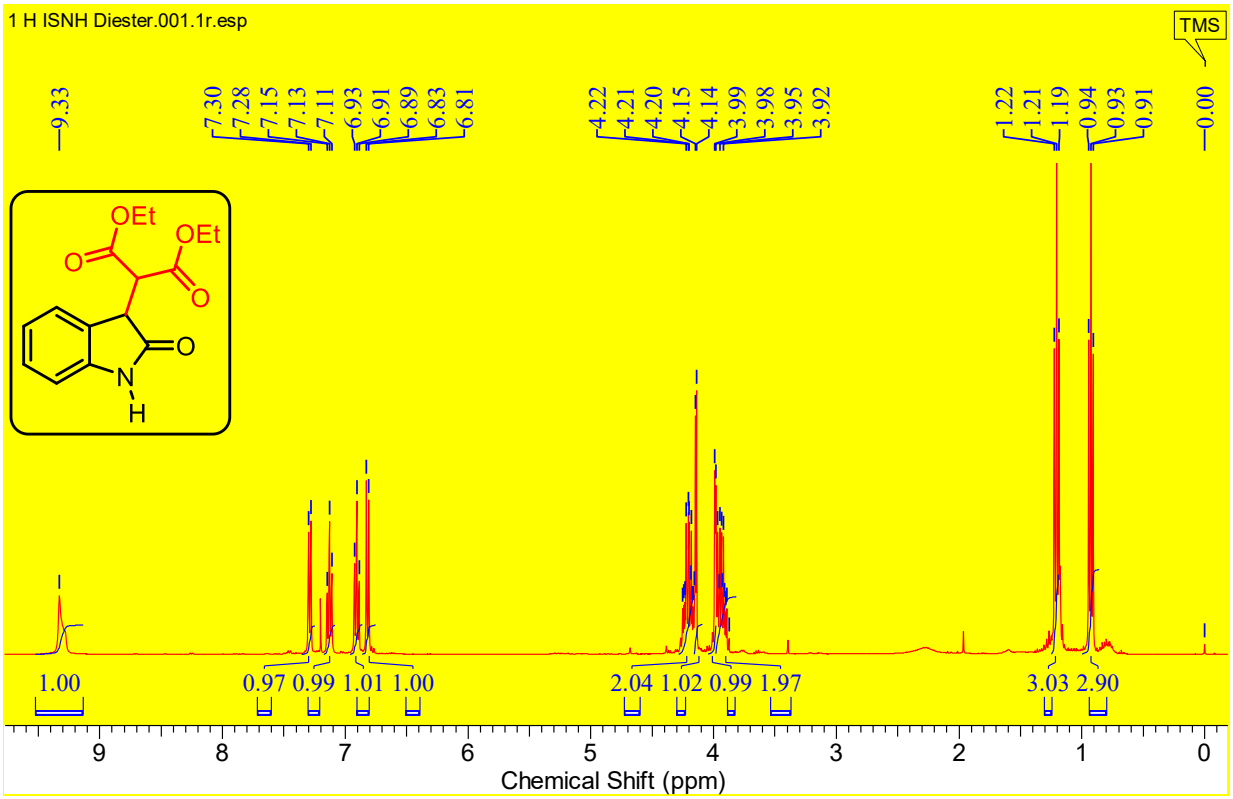
^{13}C NMR of 3Ba



135 DEPT of 3Ba



^{1}H NMR of 3Bb



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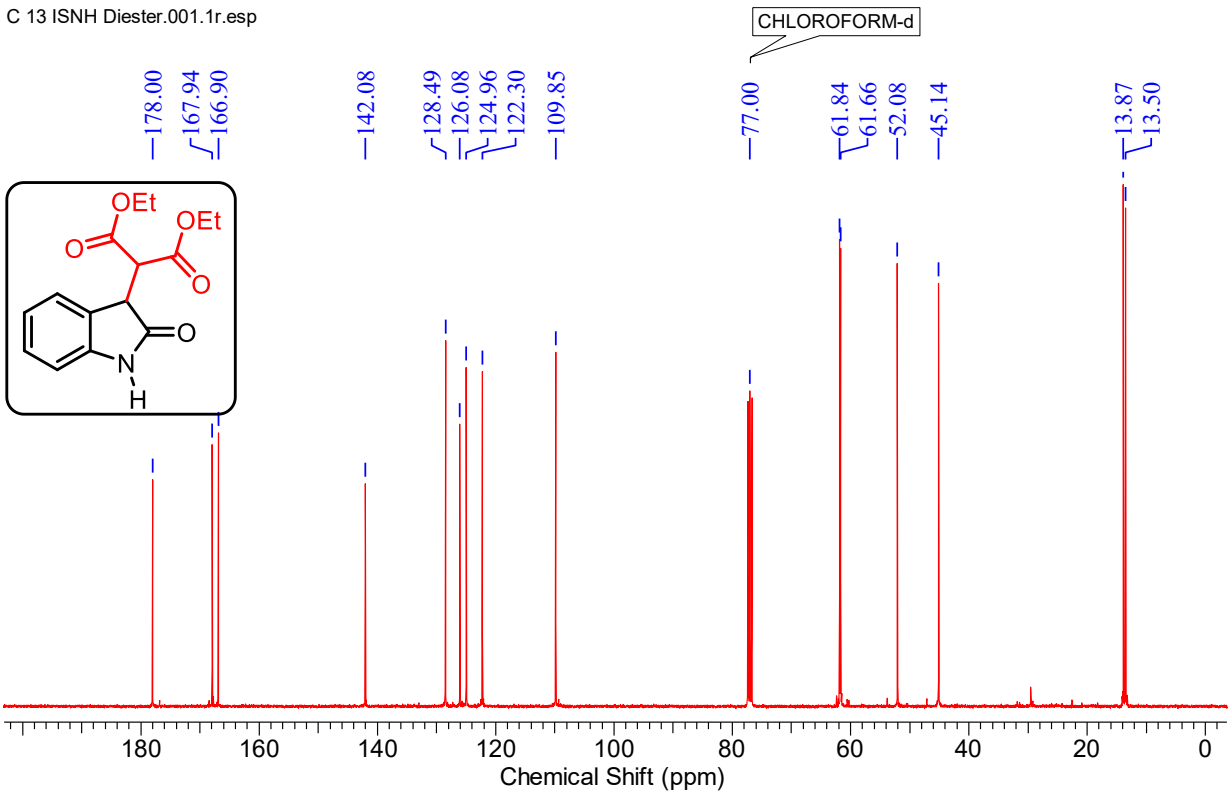
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13.87
13.50
OEt
OEt
O
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O
N
H
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140
120
100
80
60
40
20
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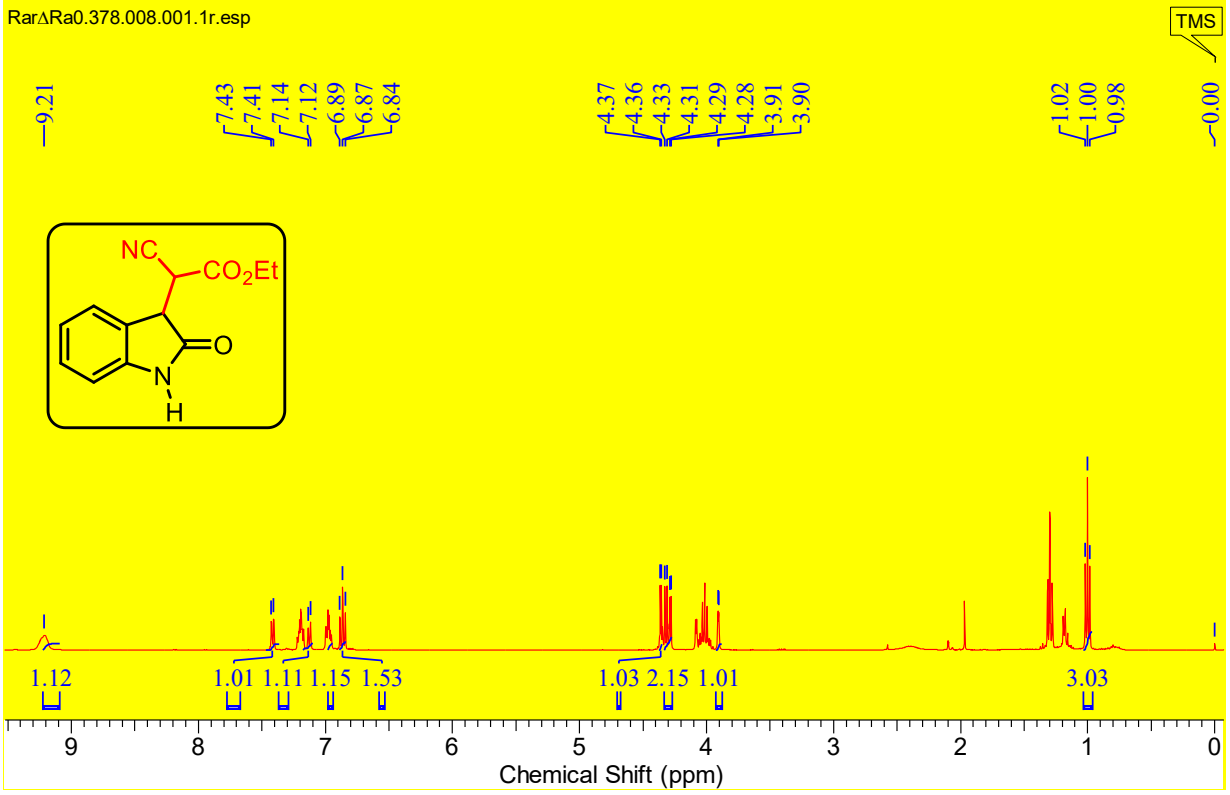
Chemical Shift (ppm)

^{1}H NMR of 3Bc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1.11
1.15
1.53
1.03
2.15
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3.03
9
8
7
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5
4
3
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1
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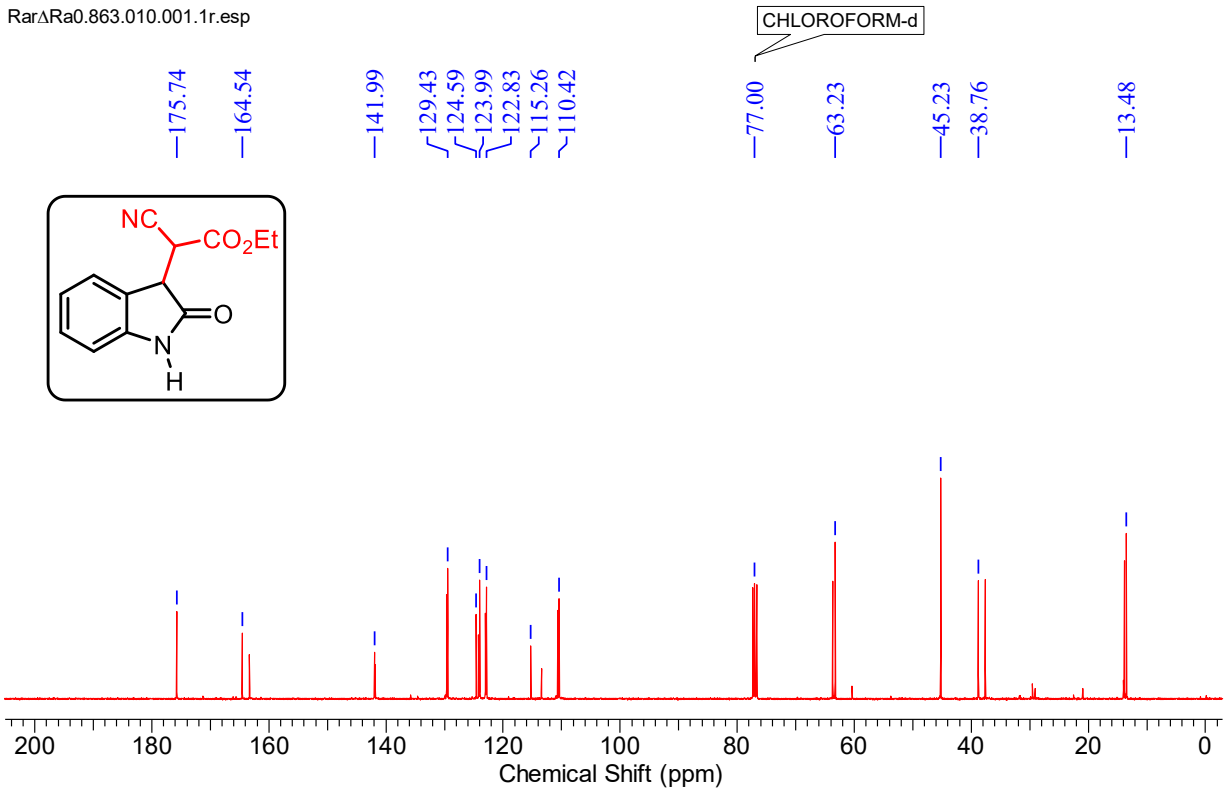
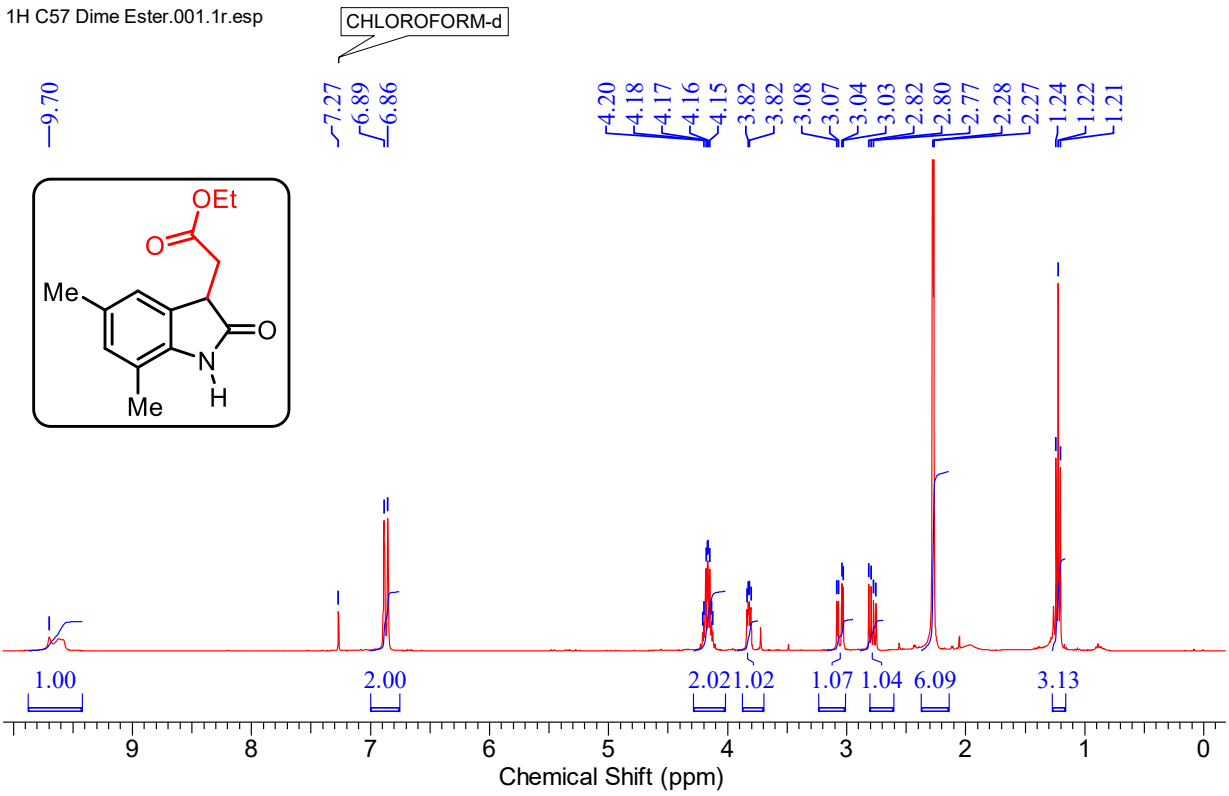
Chemical Shift (ppm)

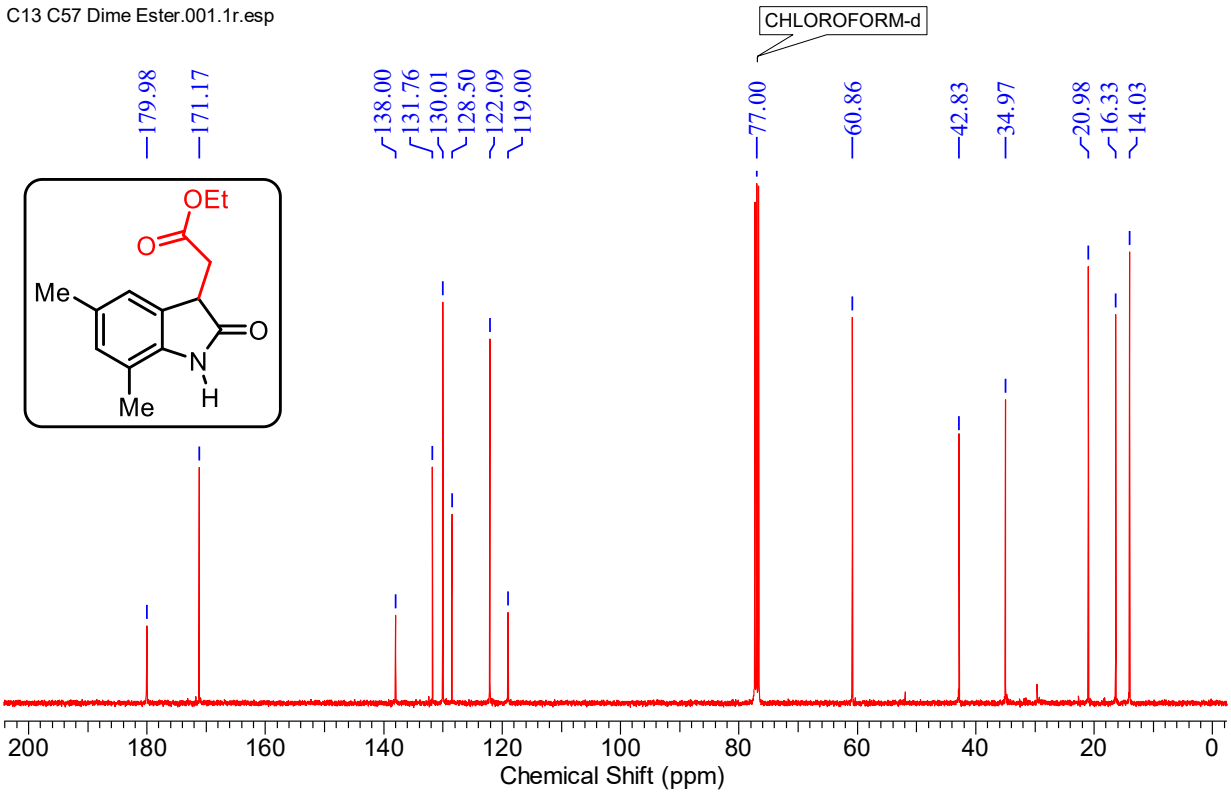
^{13}C NMR of 3Bc



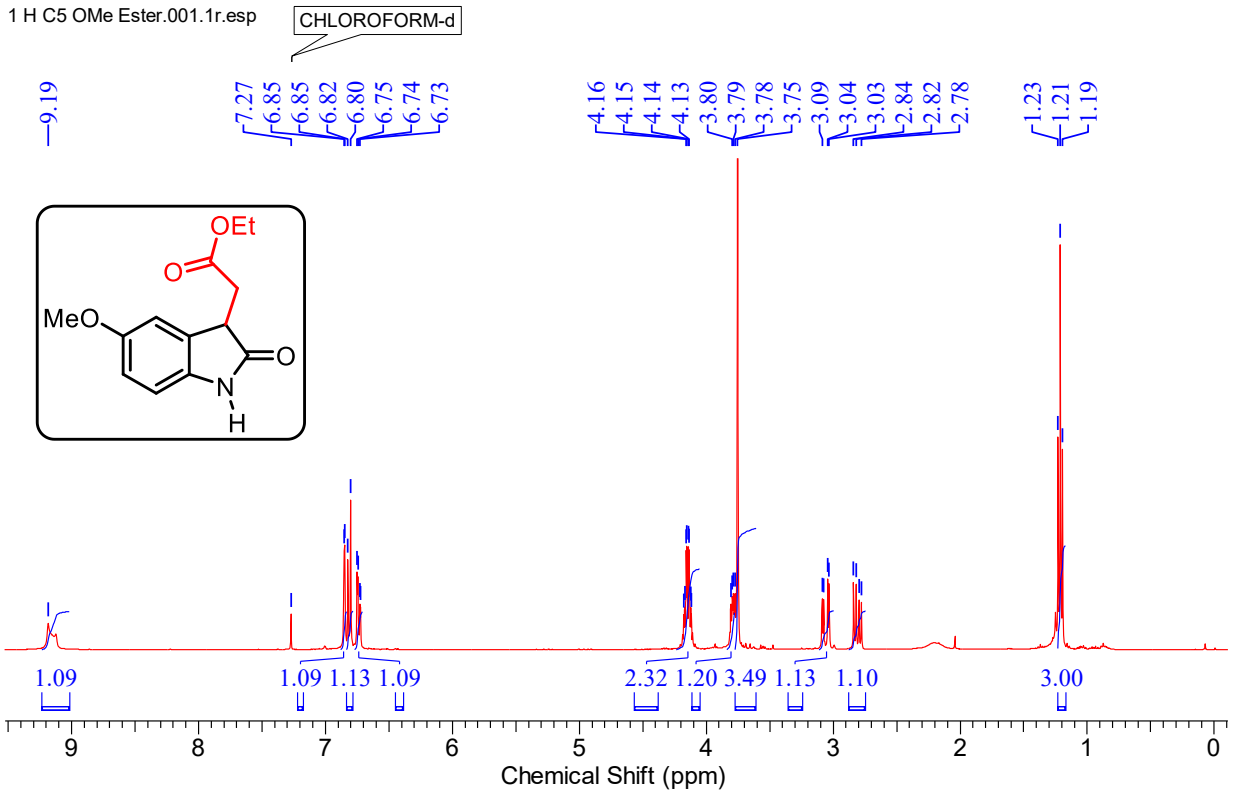
^{1}H NMR of 3Bd



^{13}C NMR of 3Bd



^{1}H NMR of 3Be



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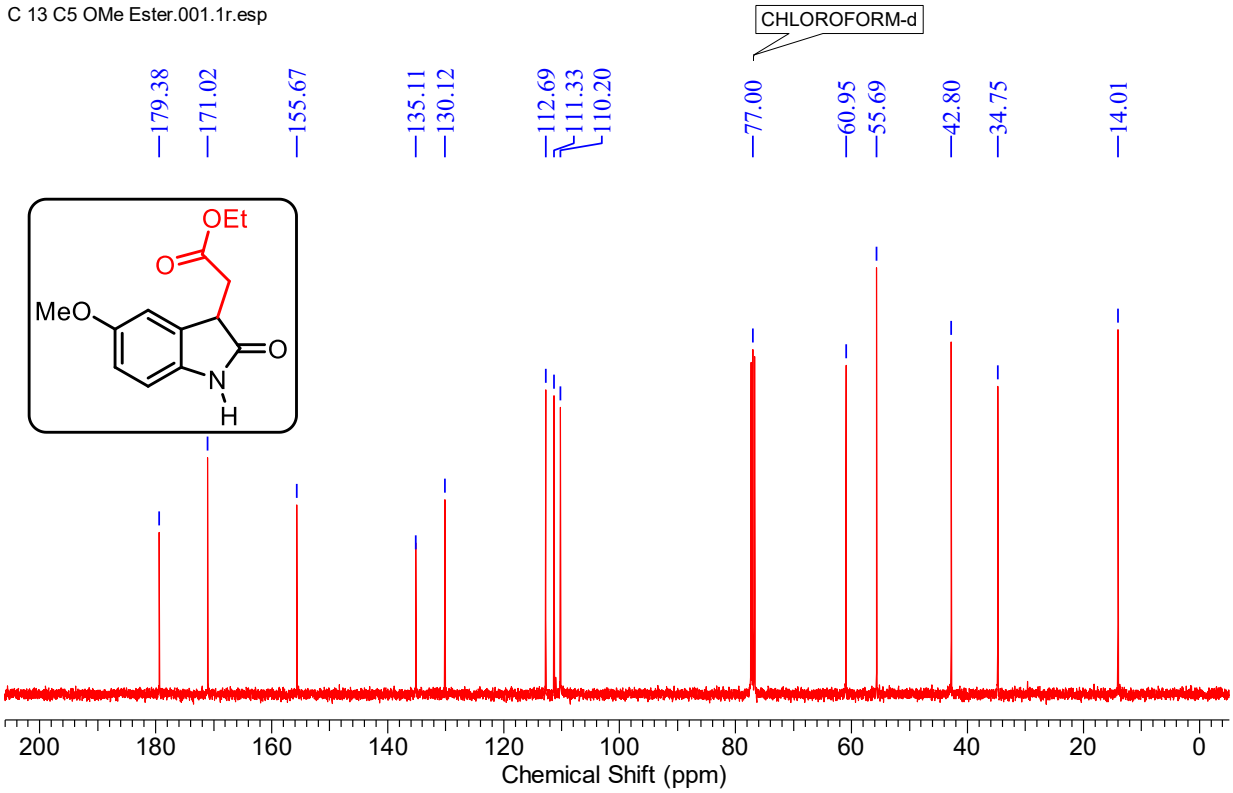
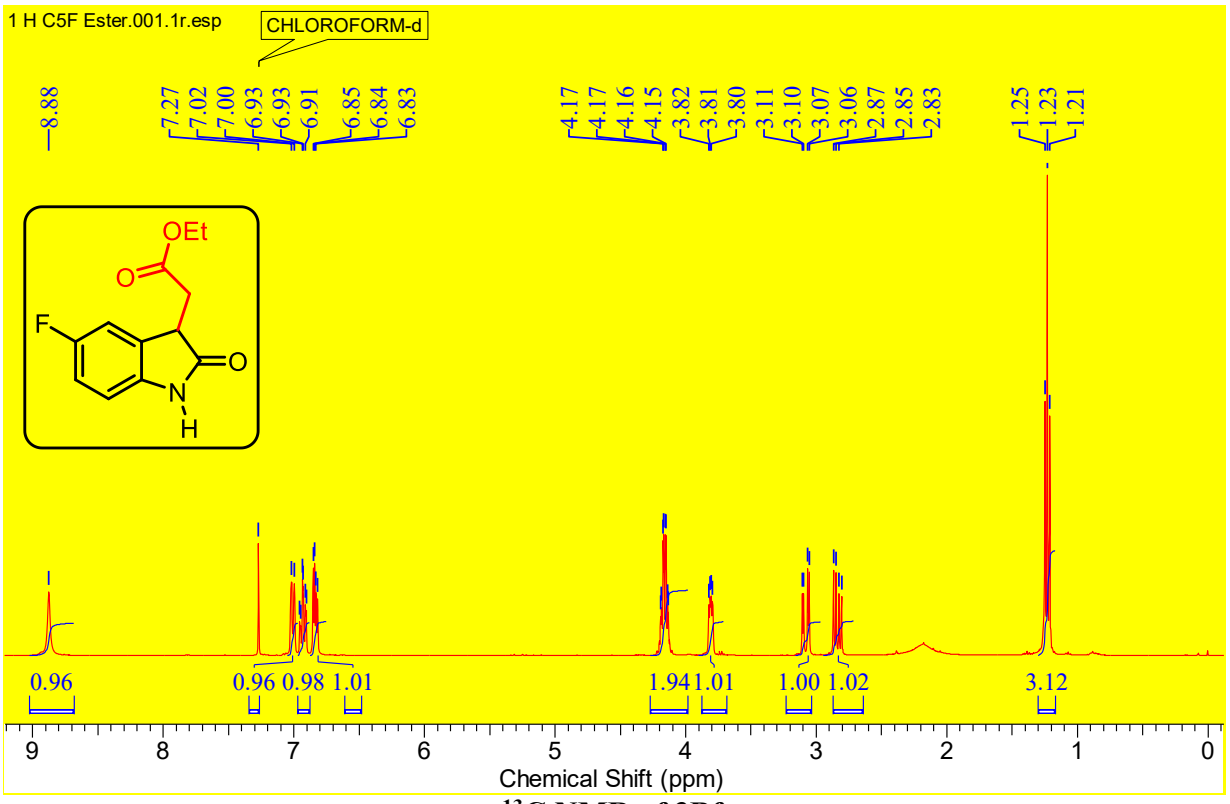


^{1}H NMR of 3Bf



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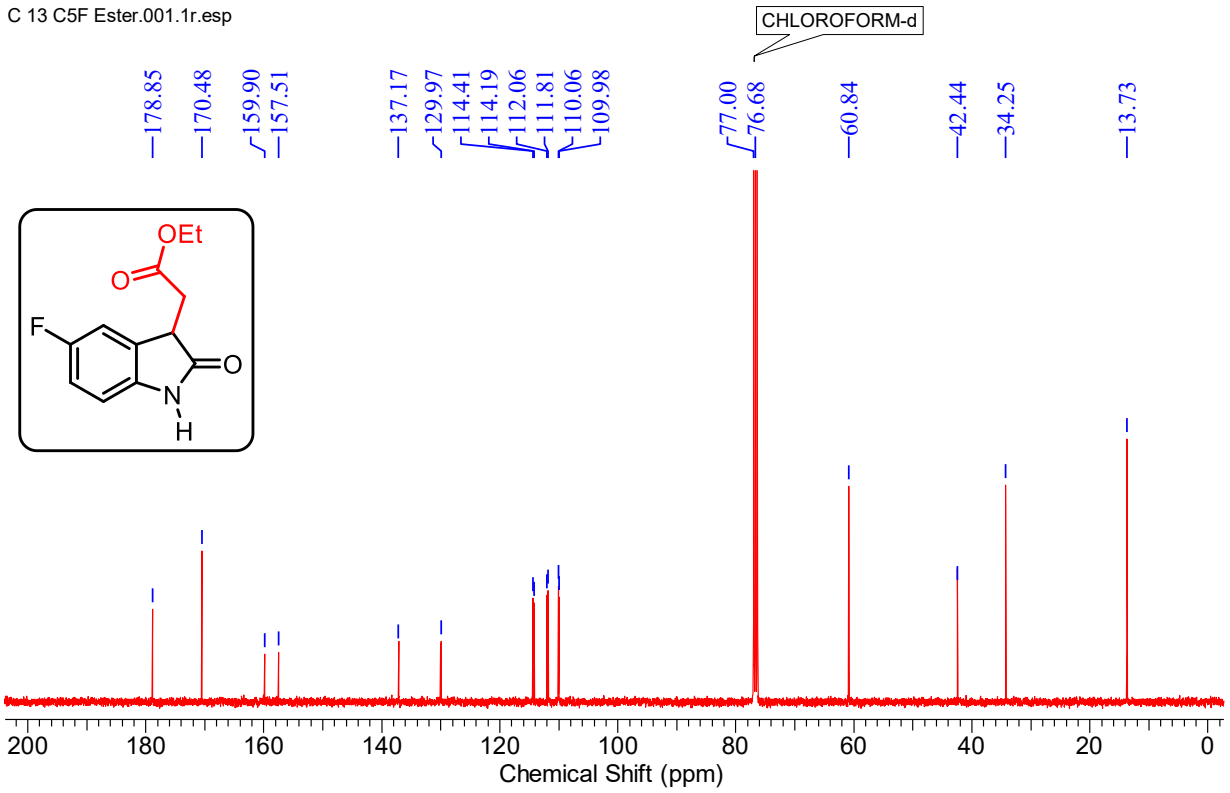
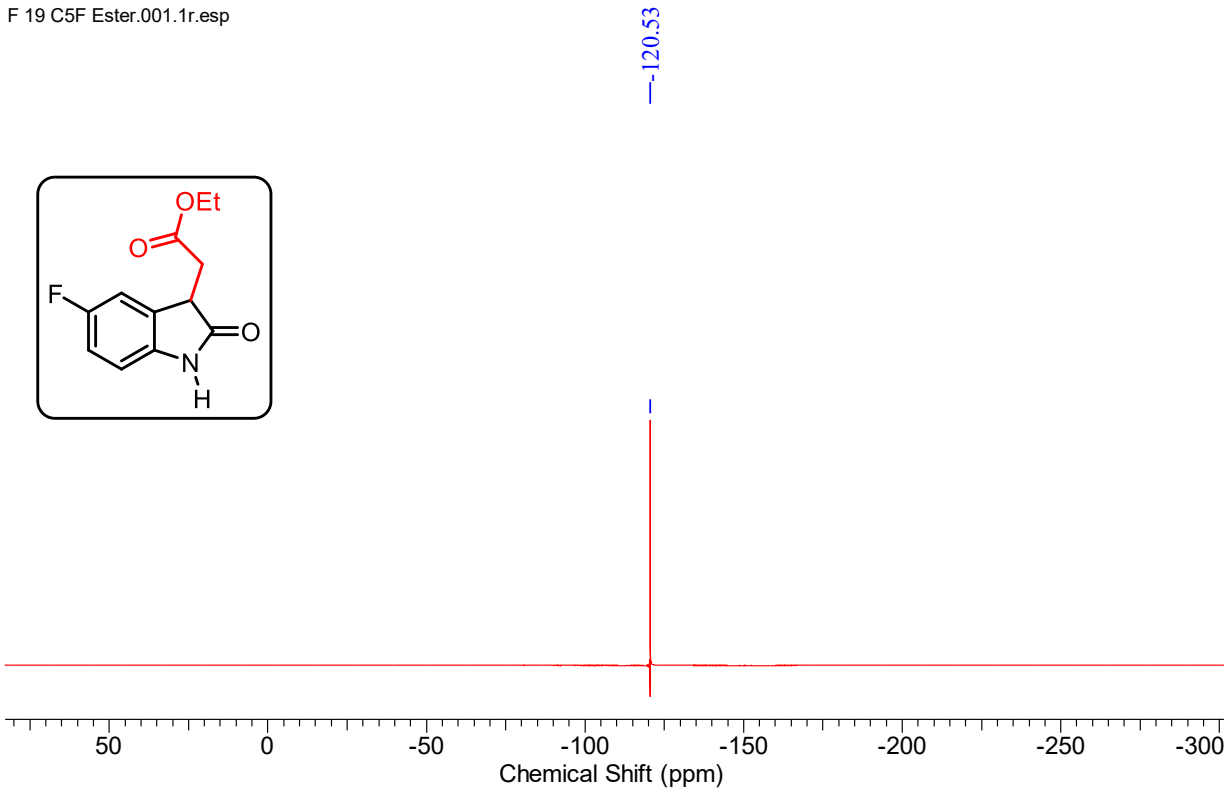
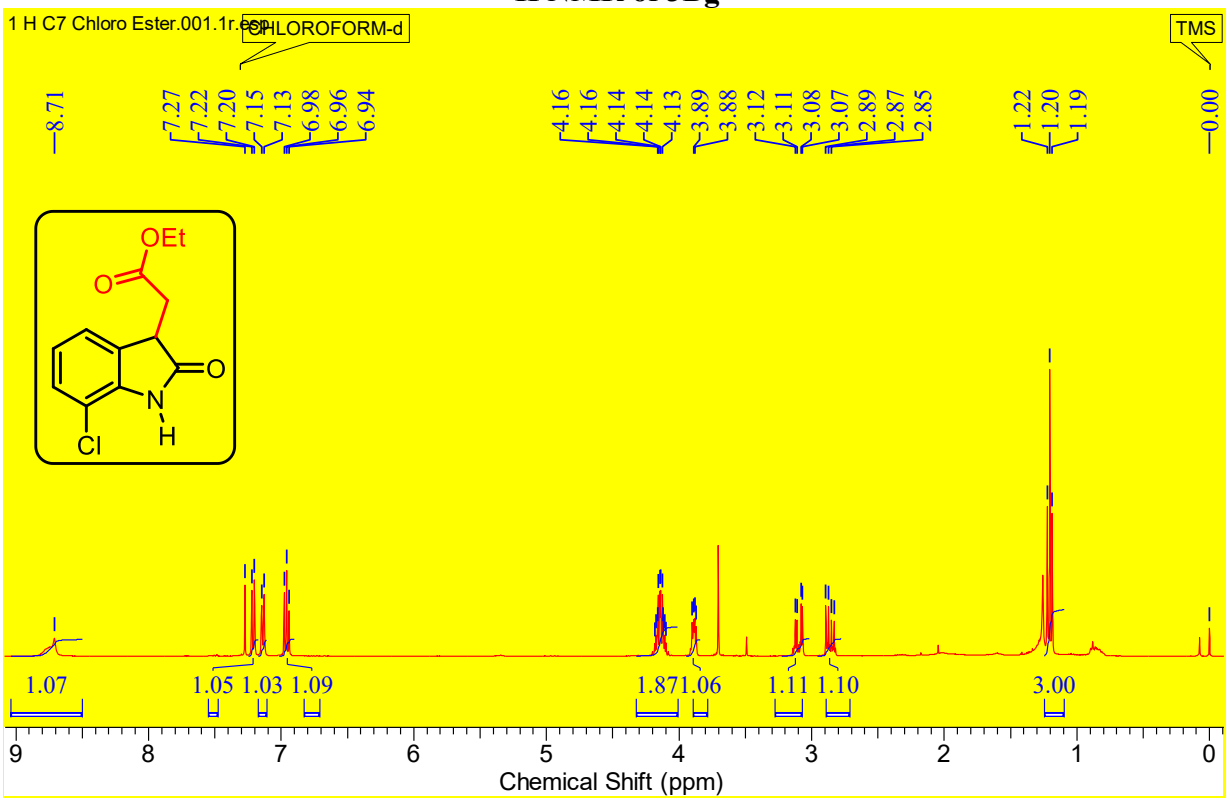


^{19}F NMR of 3Bf

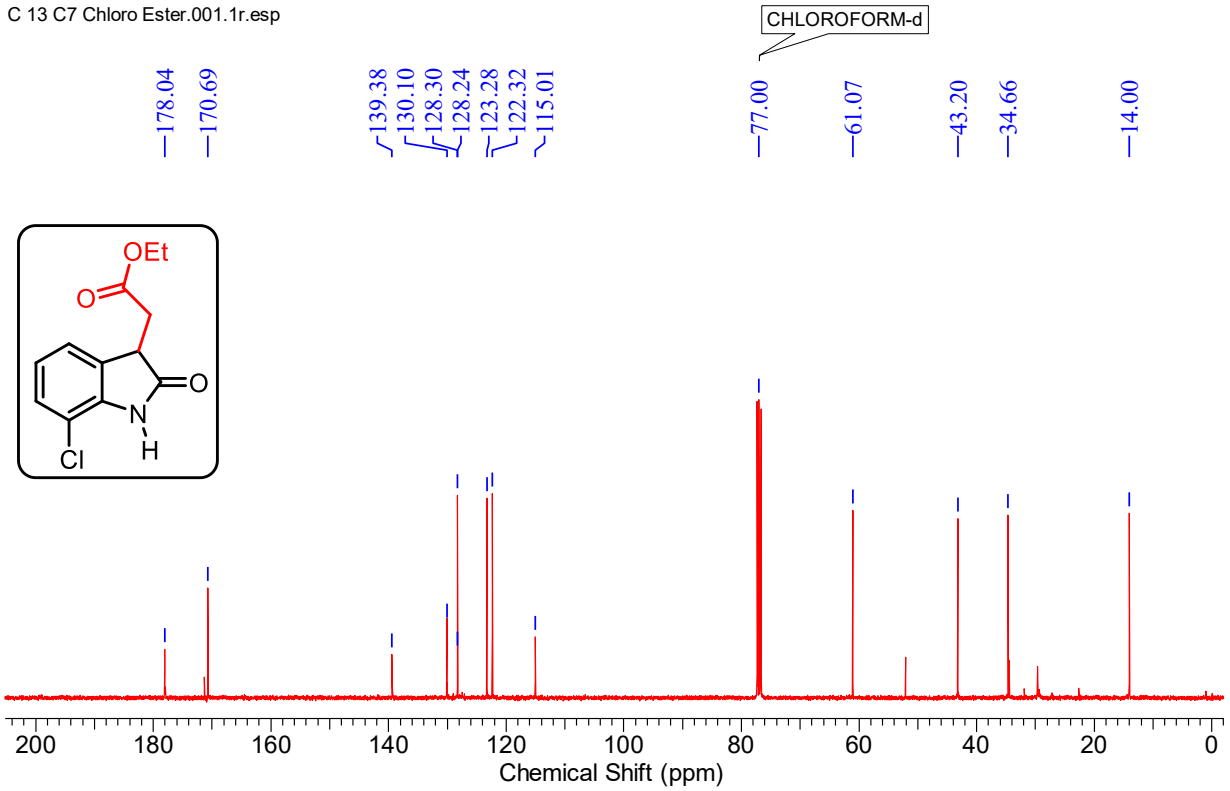
F 19 C5F Ester.001.1r.esp



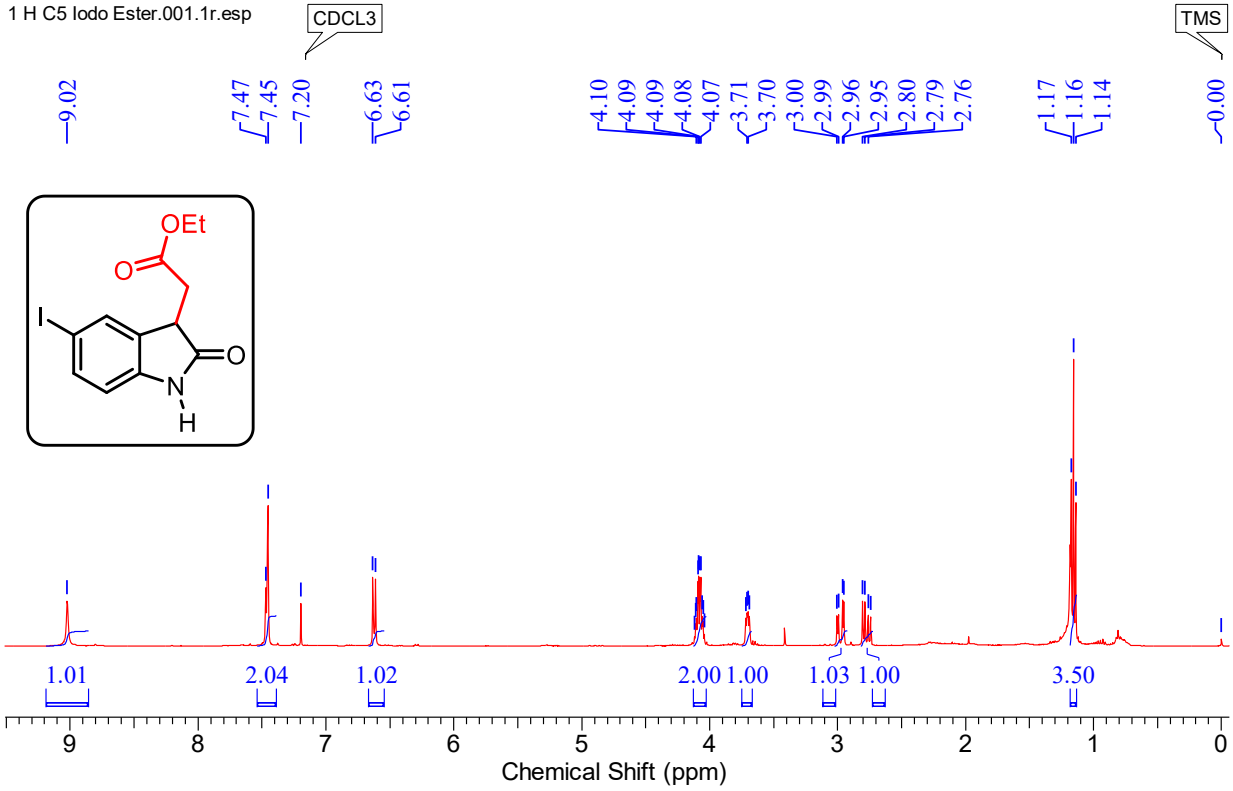
^{1}H NMR of 3Bg



^{13}C NMR of 3Bg



^{1}H NMR of 3Bh



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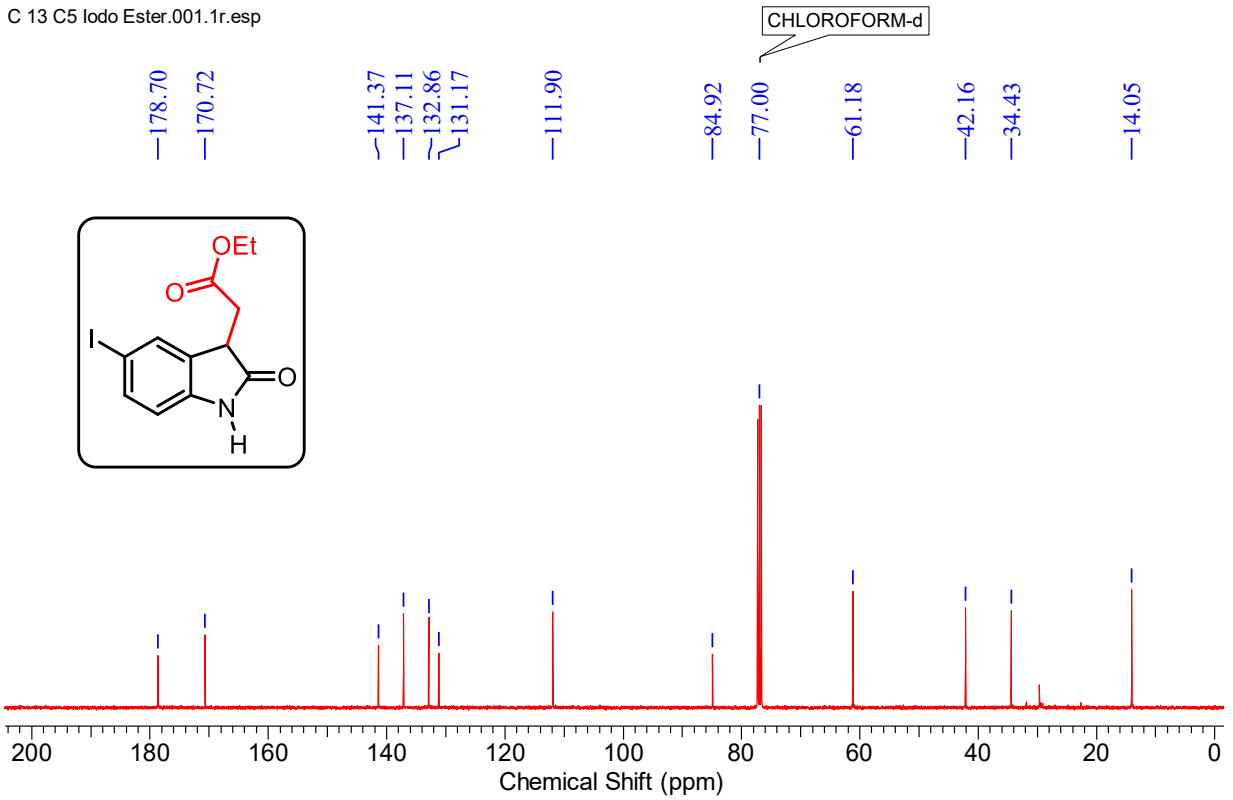

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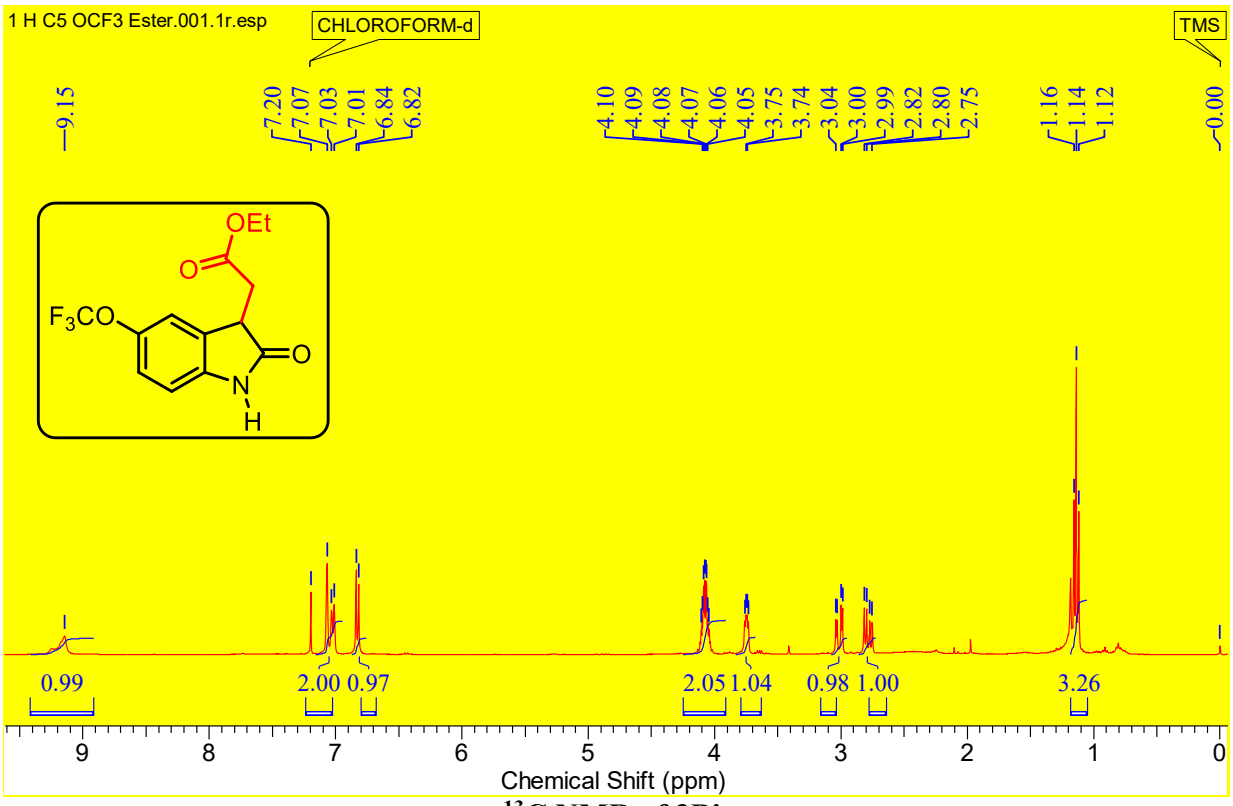

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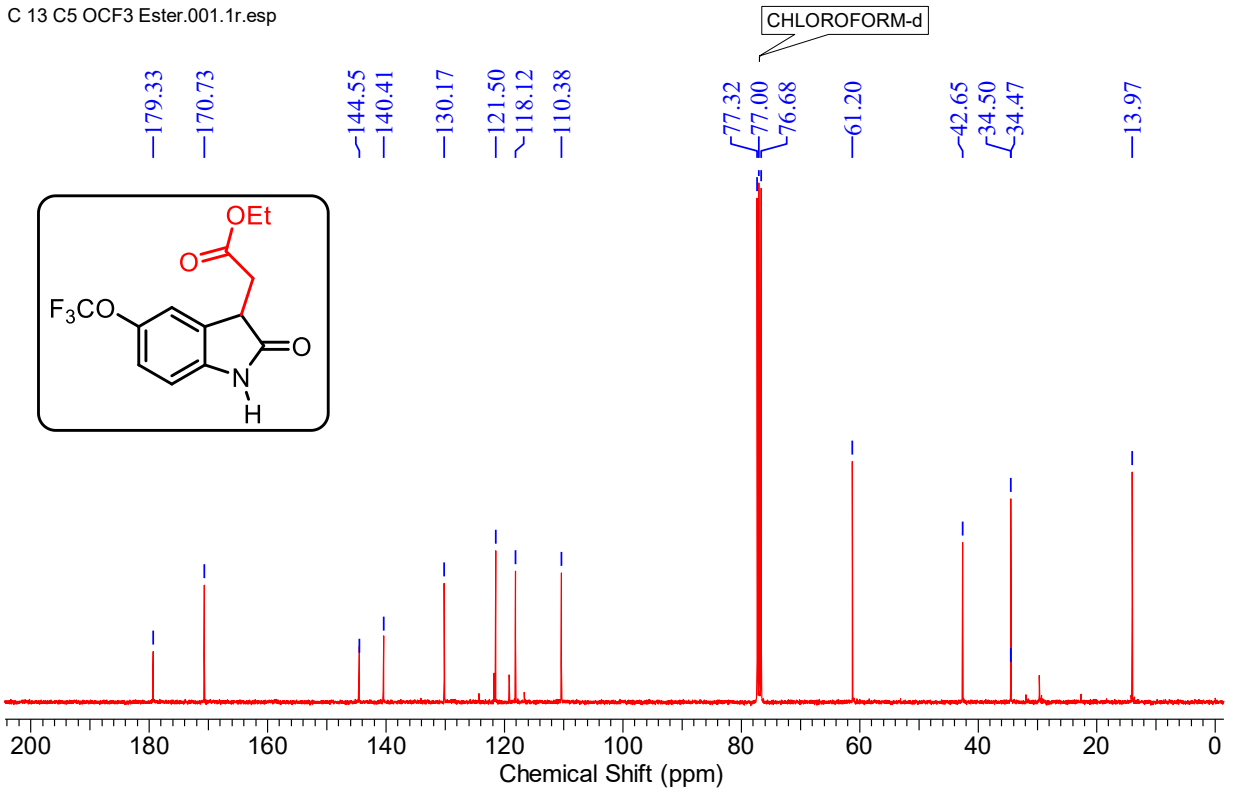
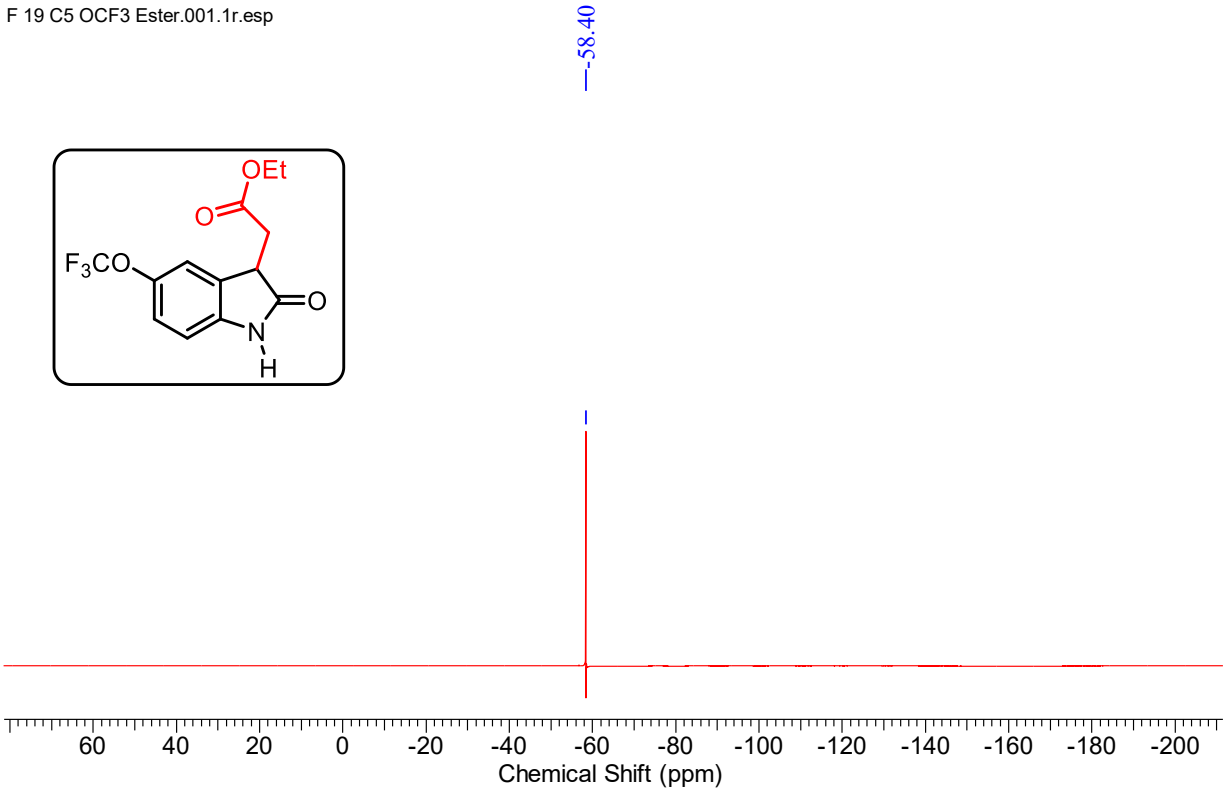
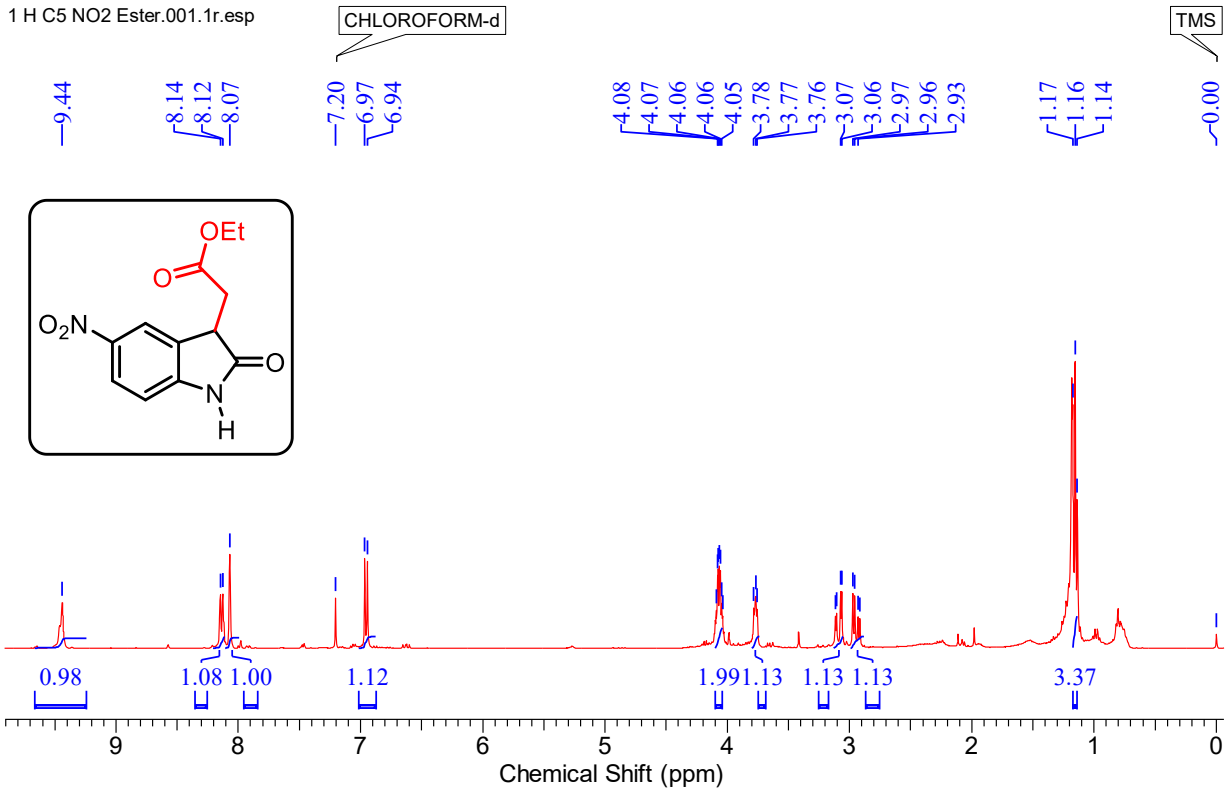


^{19}F NMR of 3Bi

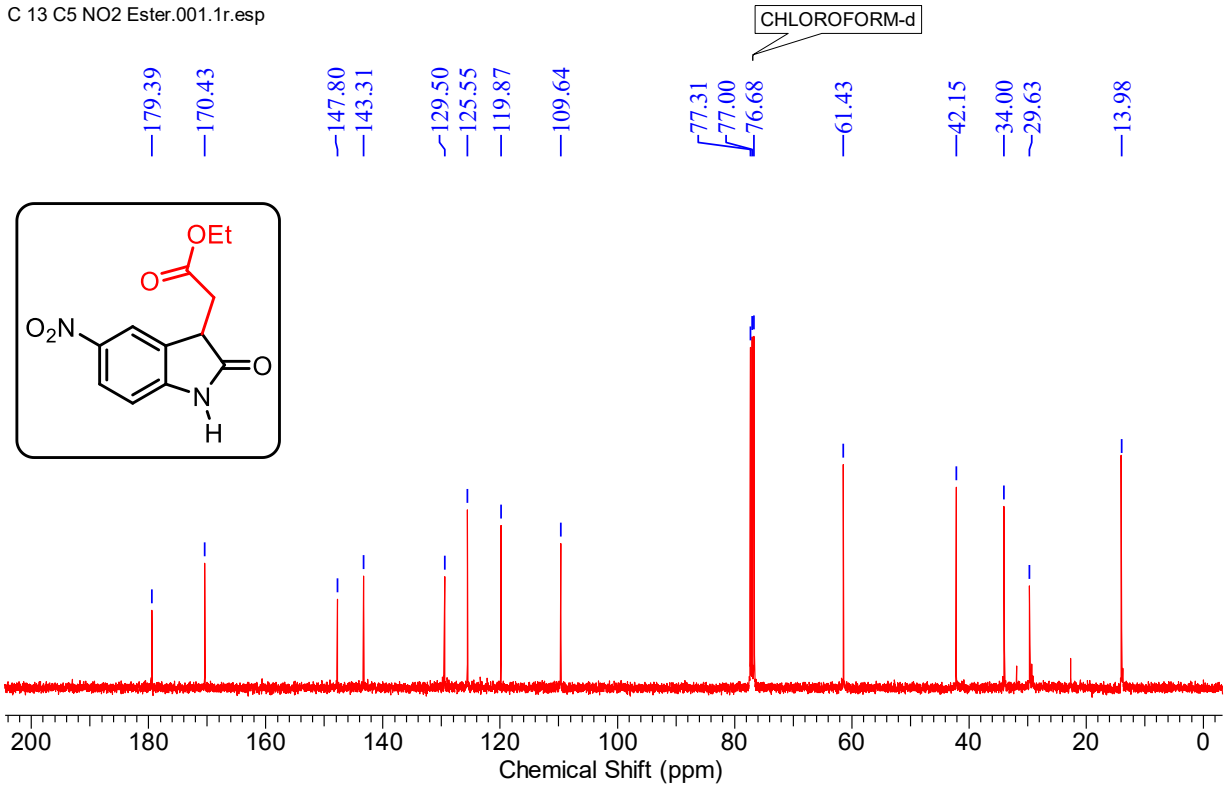
F 19 C5 OCF3 Ester.001.1r.esp



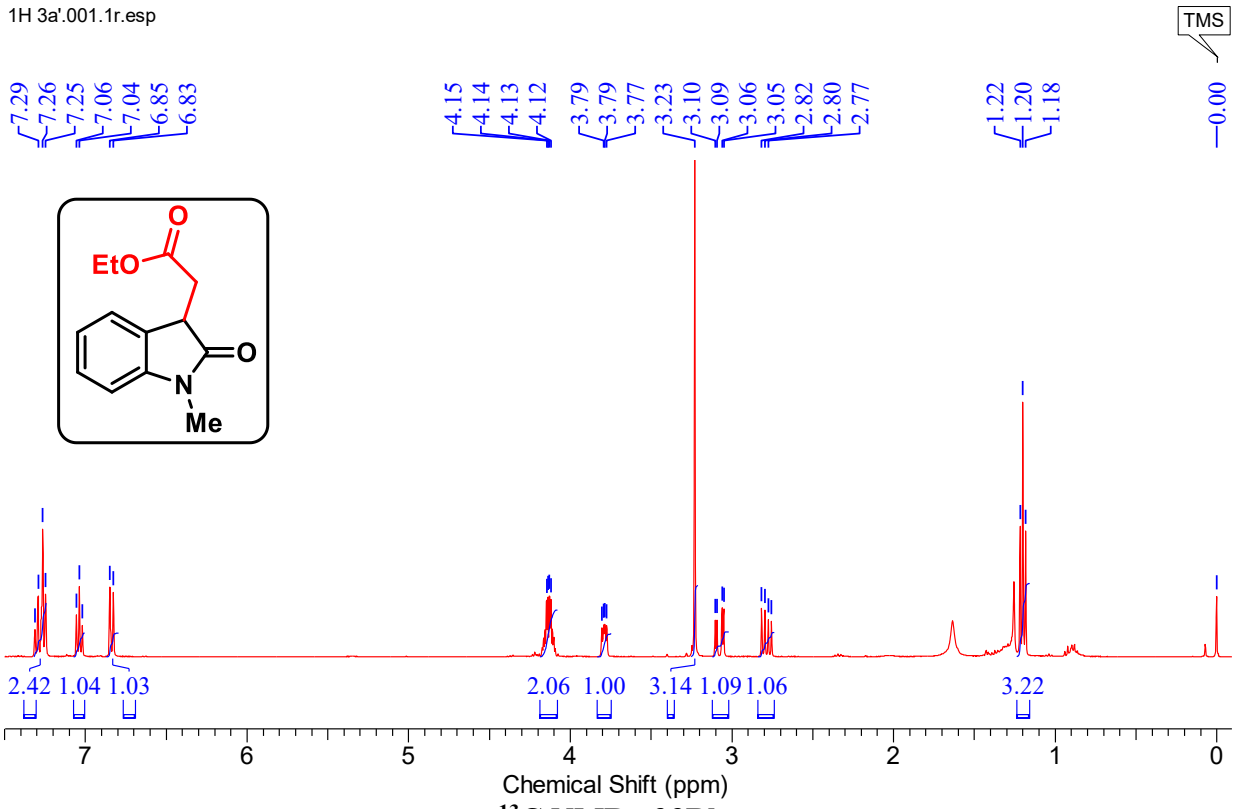
^{1}H NMR of 3Bj



^{13}C NMR of 3Bj



^{1}H NMR of 3Bk



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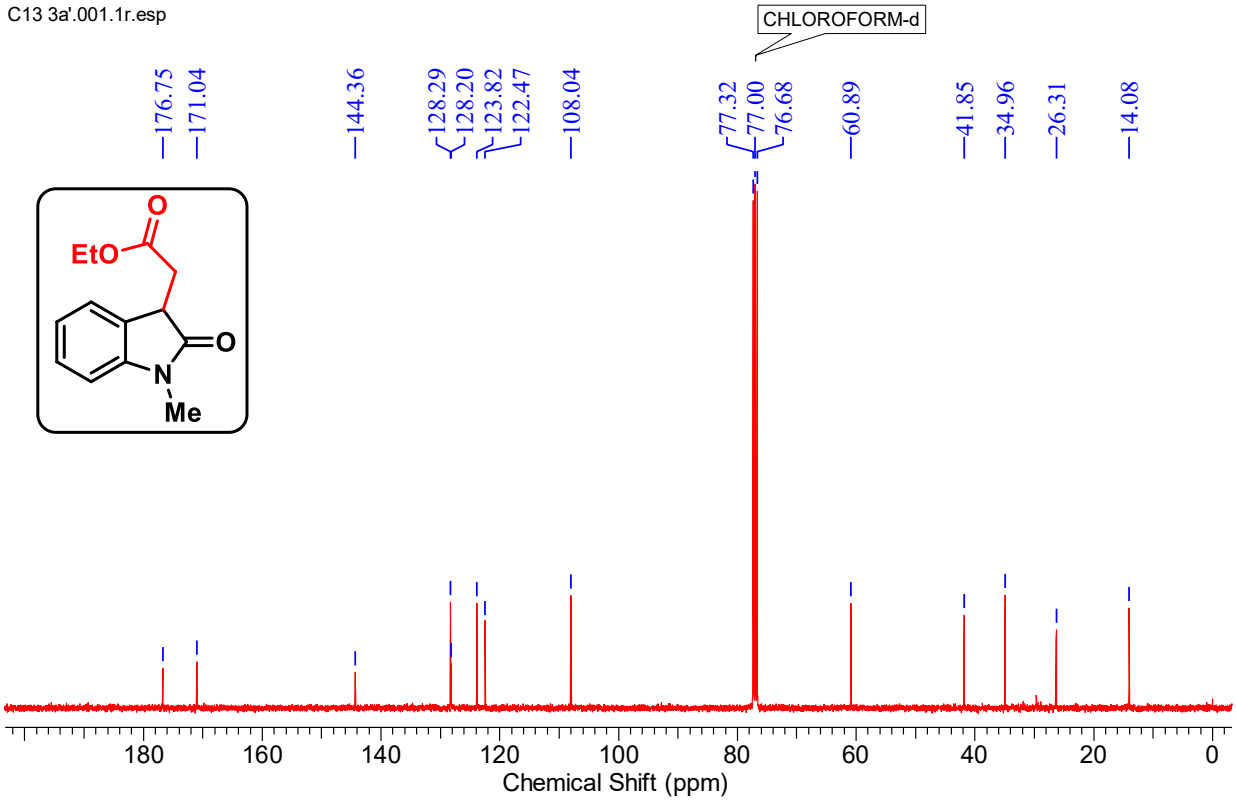
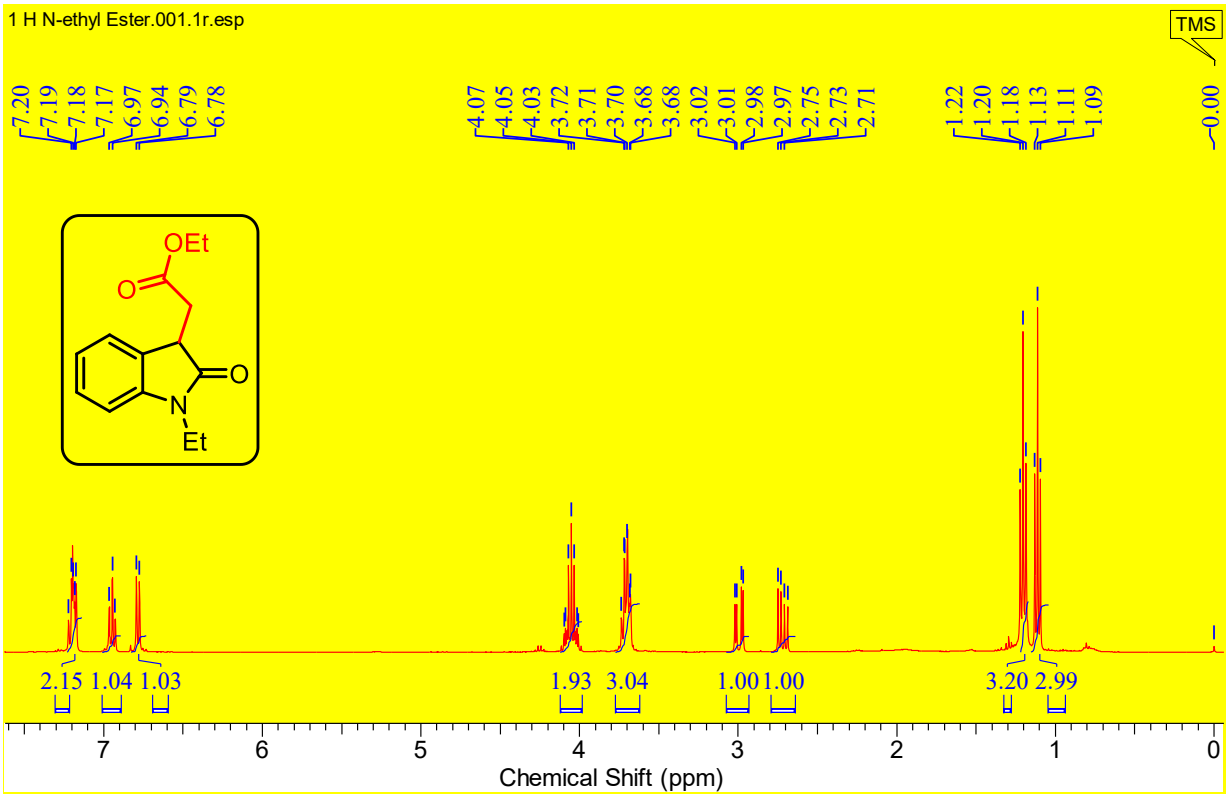
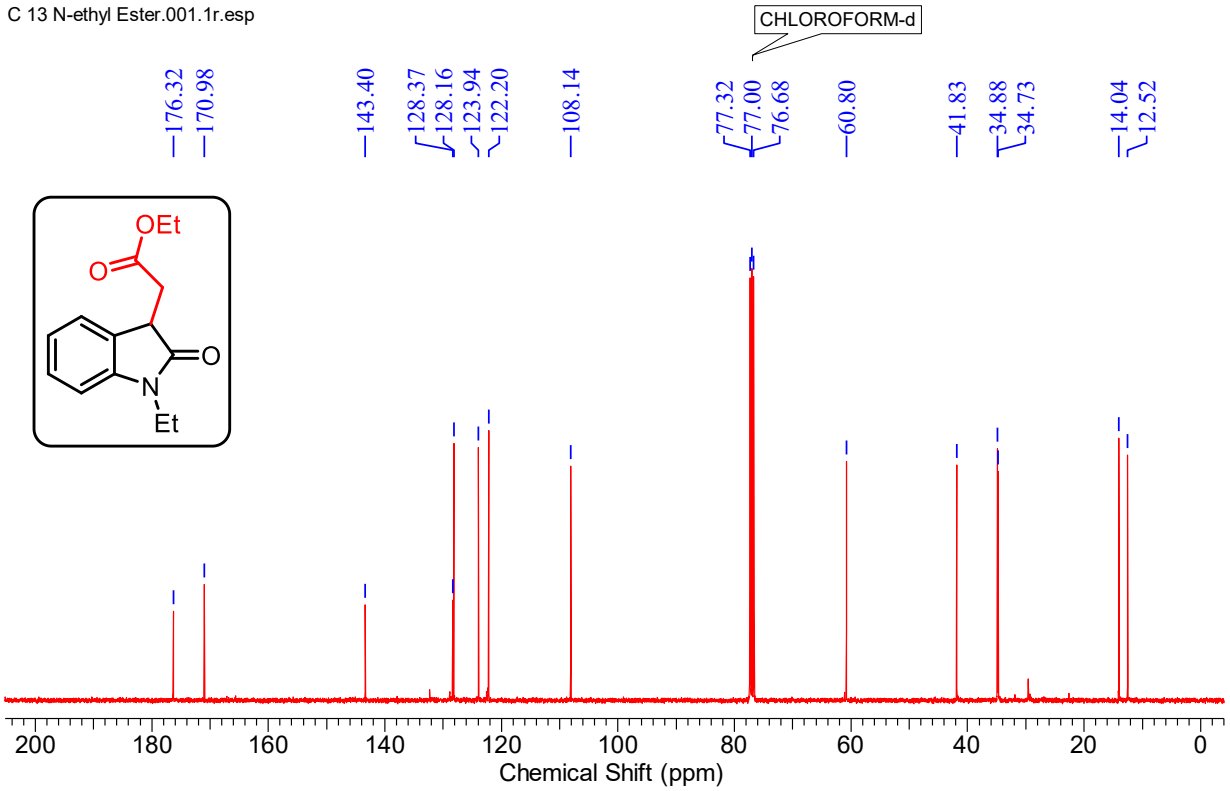


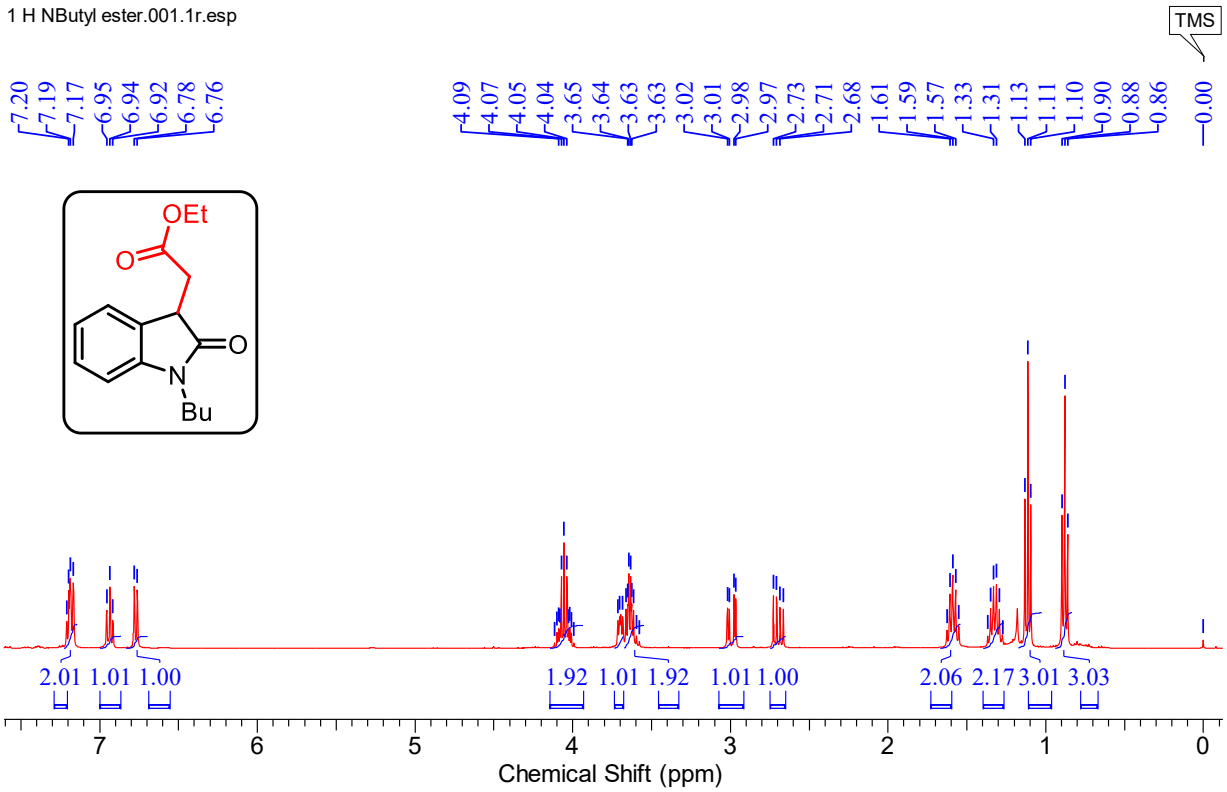
^{1}H NMR of 3Bl



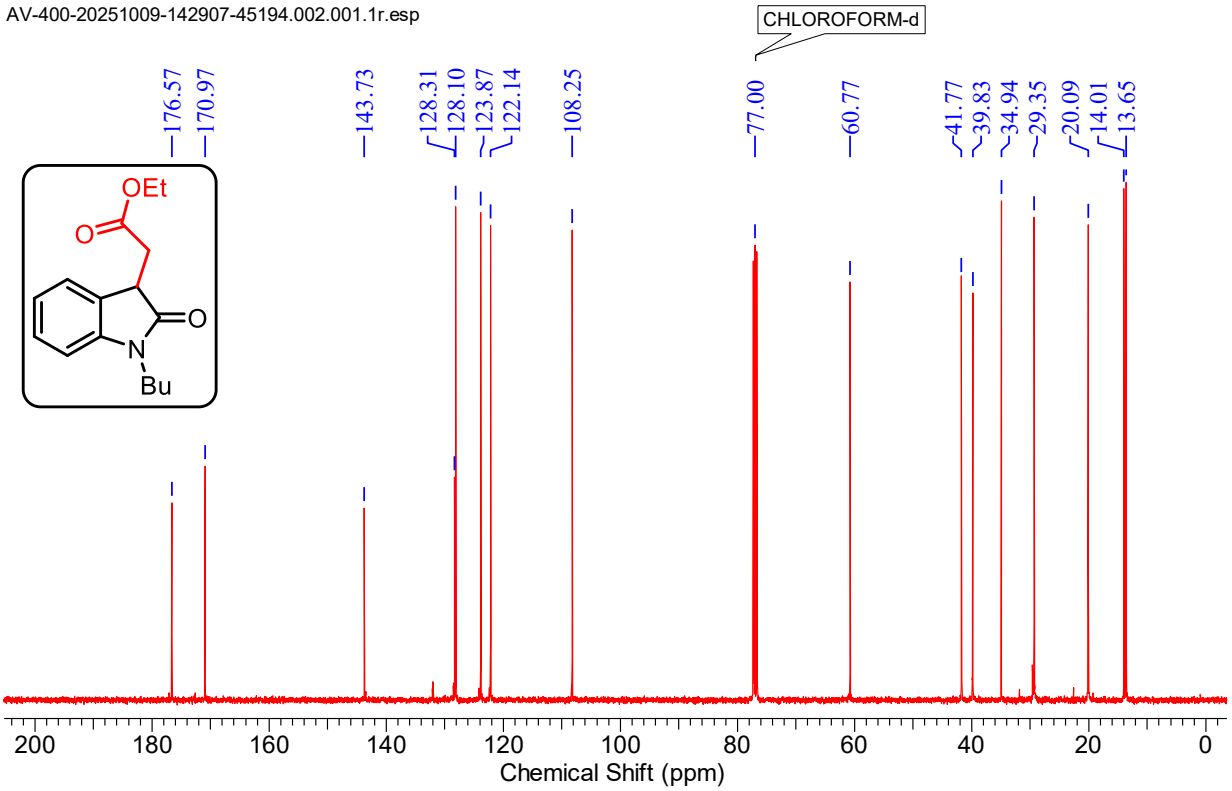
^{13}C NMR of 3Bl



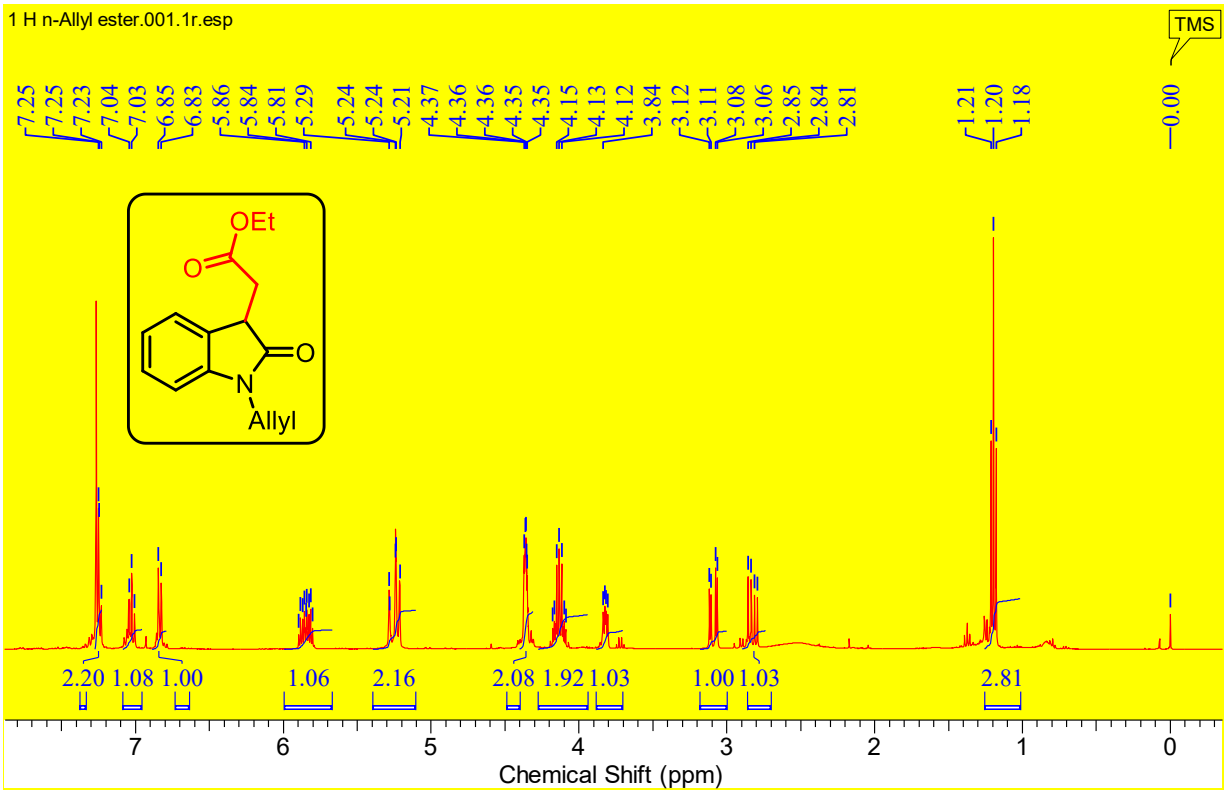
^{1}H NMR of 3Bm



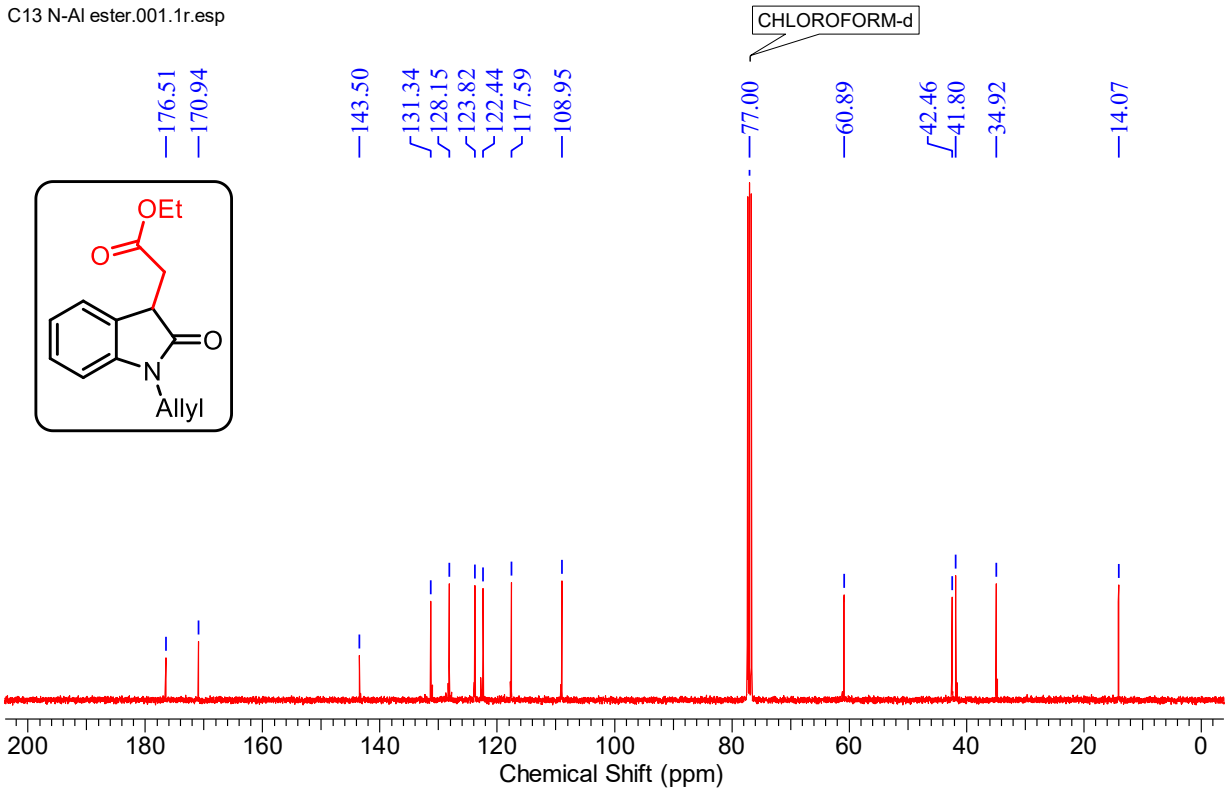
^{13}C NMR of 3Bm



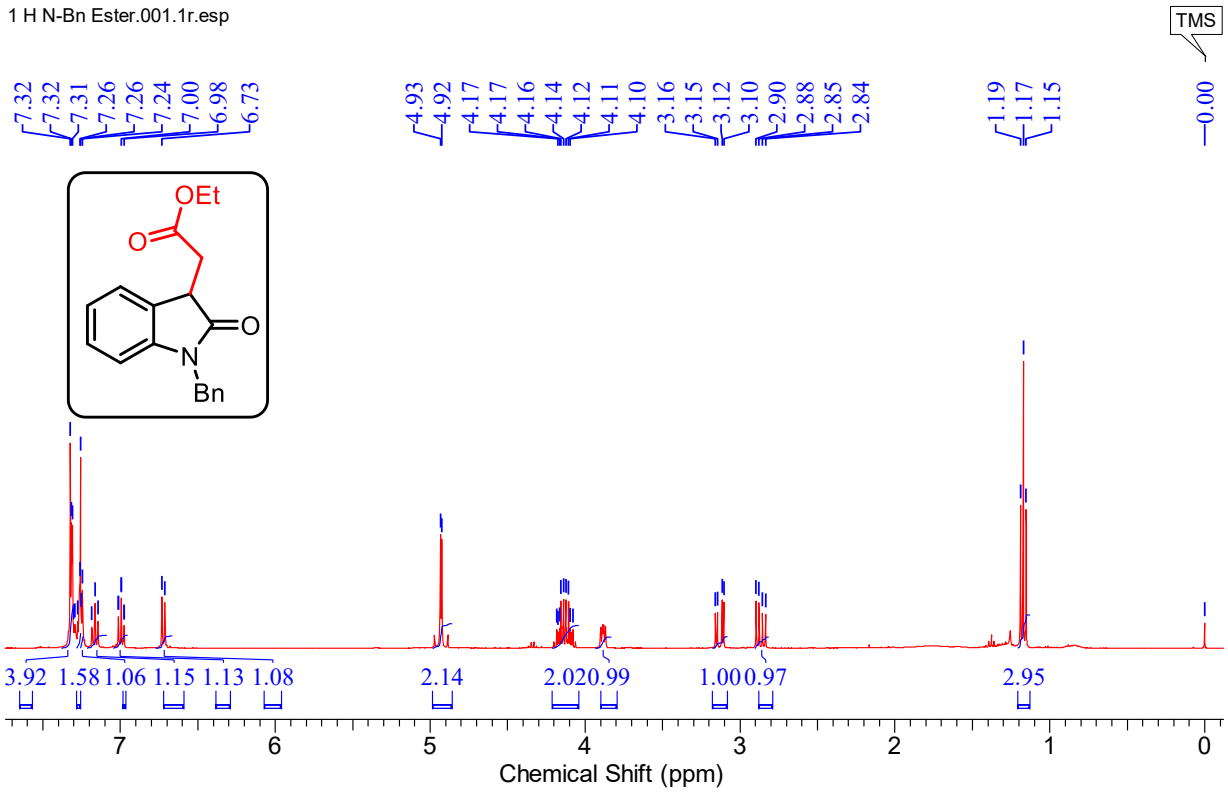
^{1}H NMR of 3Bn



^{13}C NMR of 3Bn



^{1}H NMR of 3Bo



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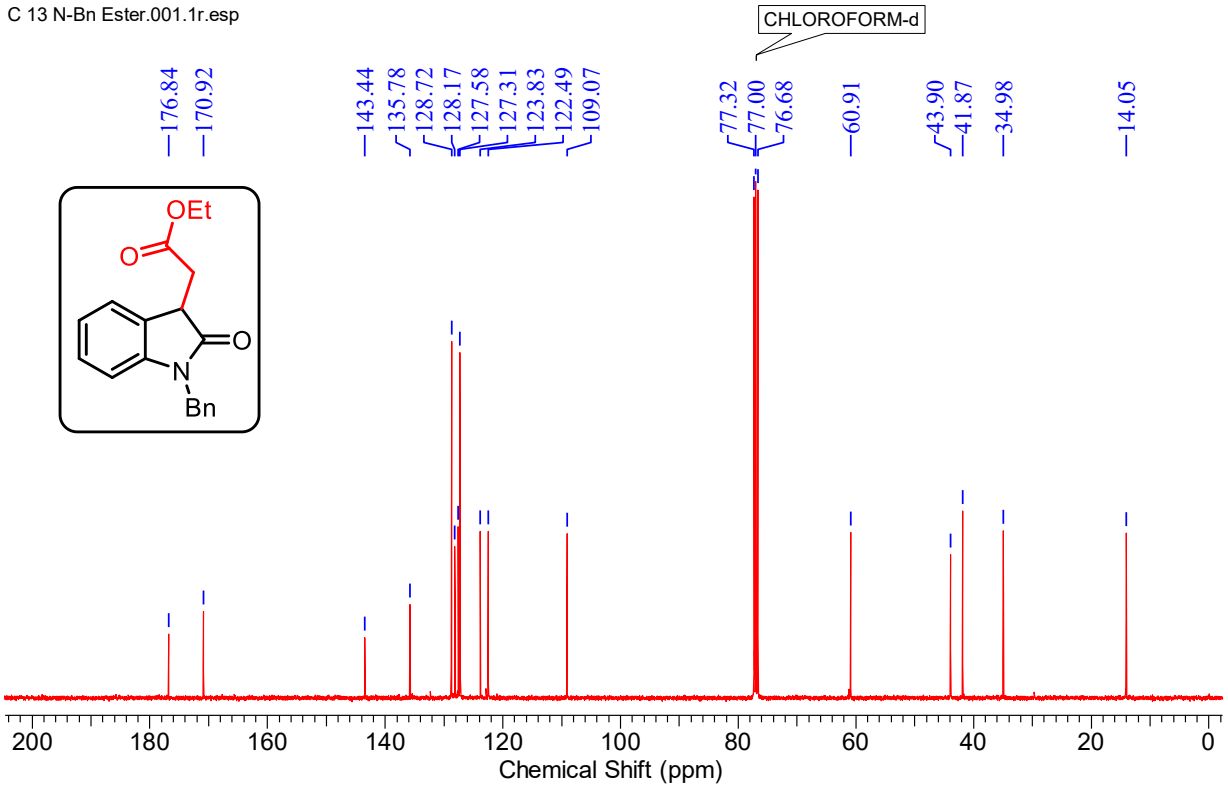
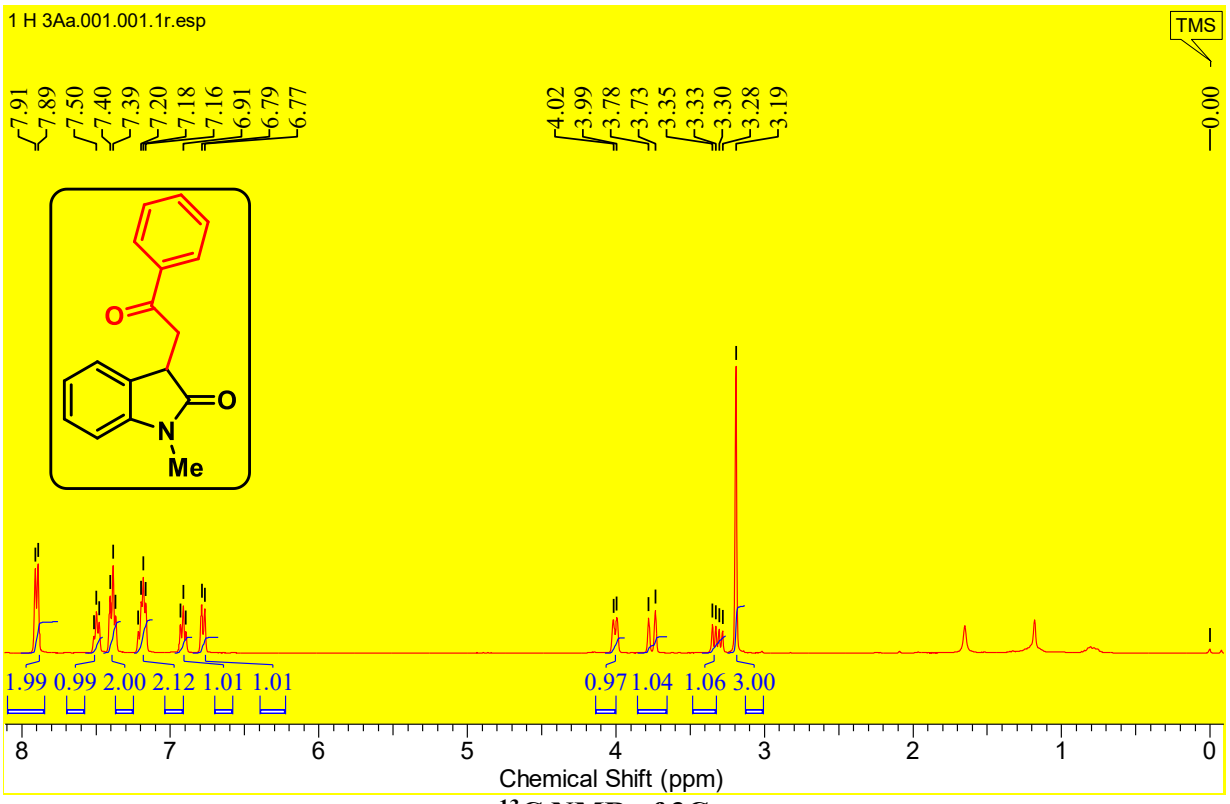
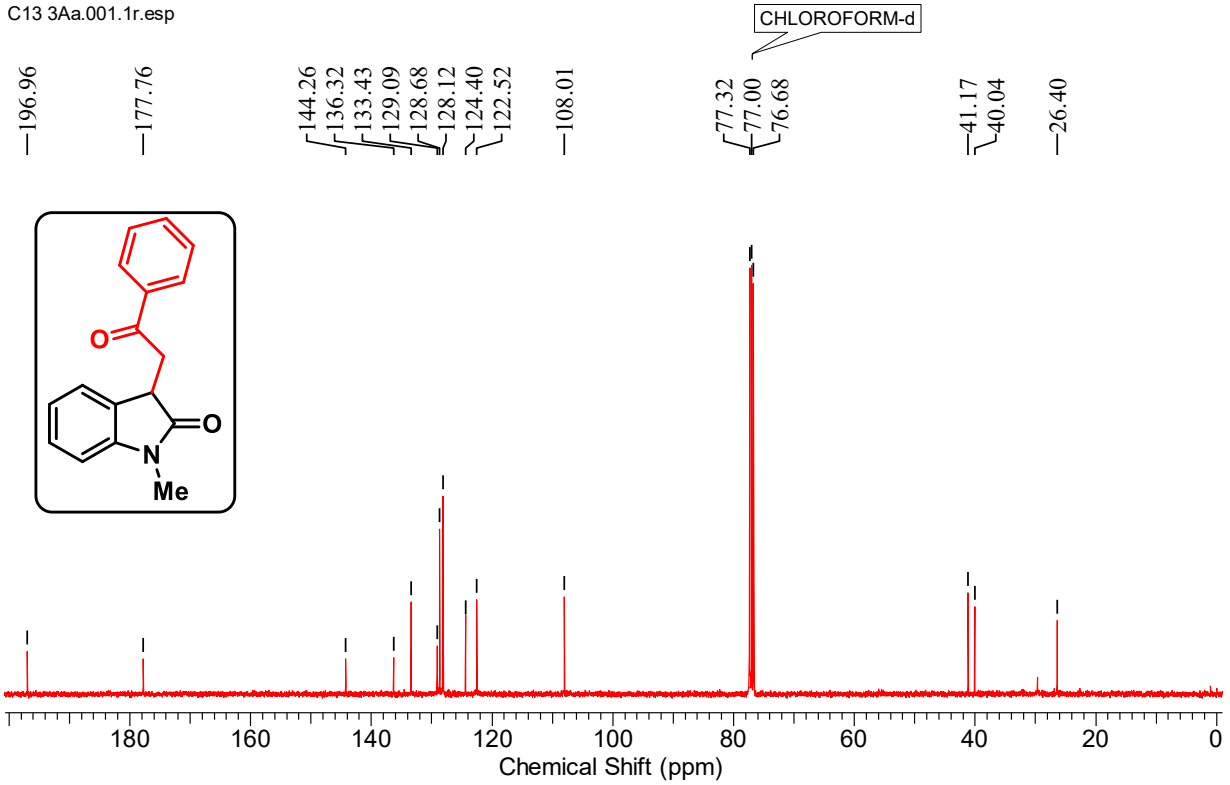


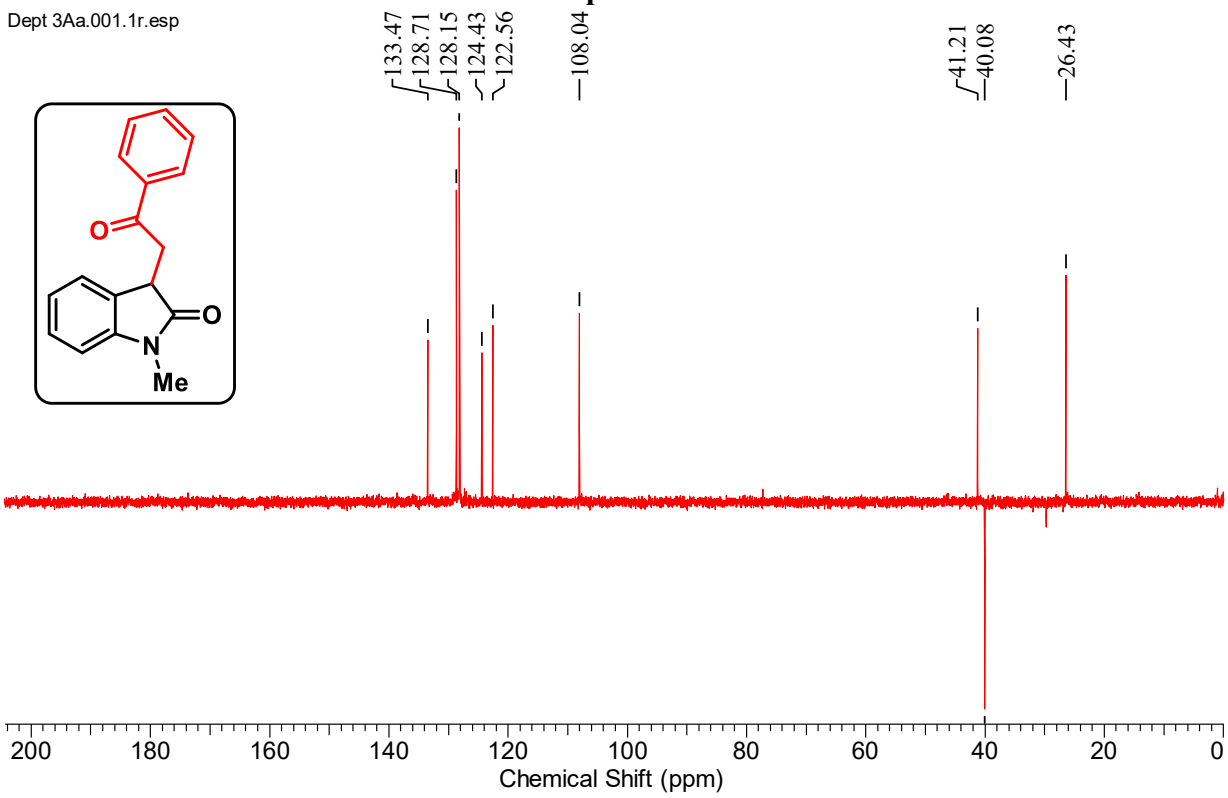
^{1}H NMR of 3Ca



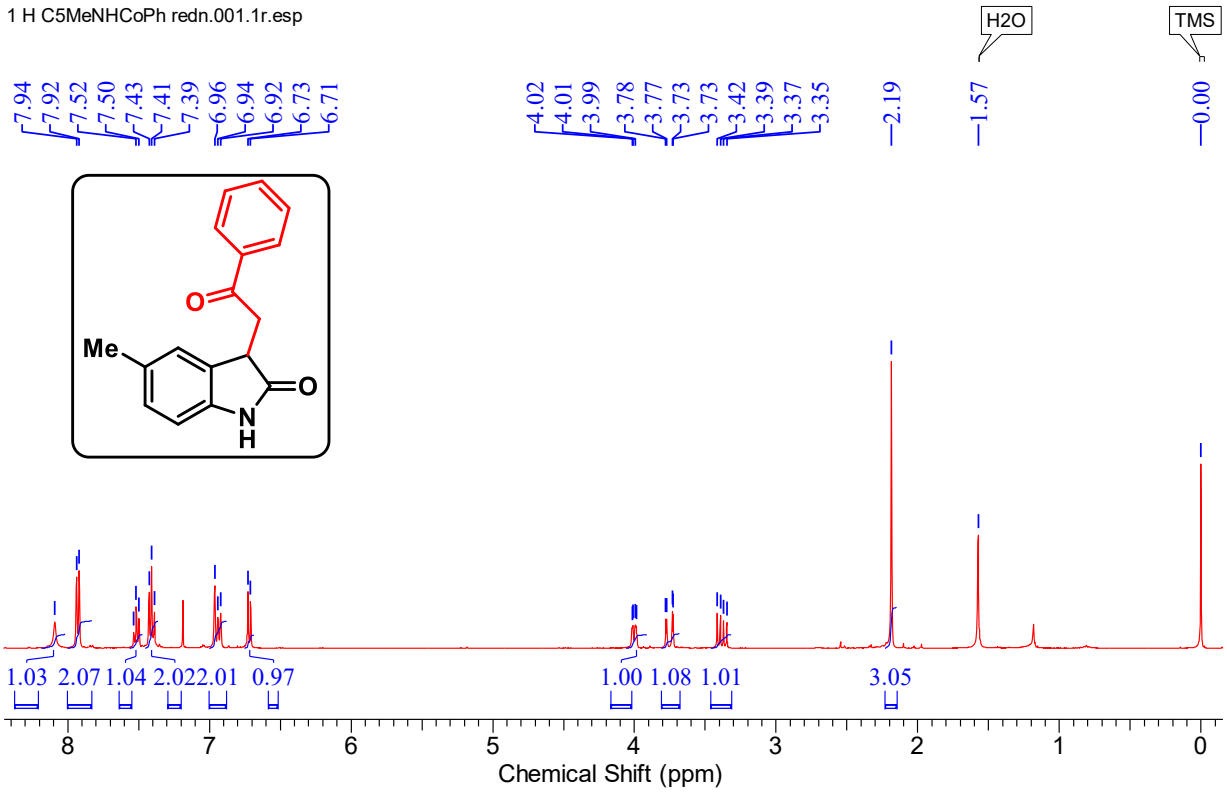
^{13}C NMR of 3Ca



135 DEPT spectrum of 3Ca



^{1}H NMR of 3Cb



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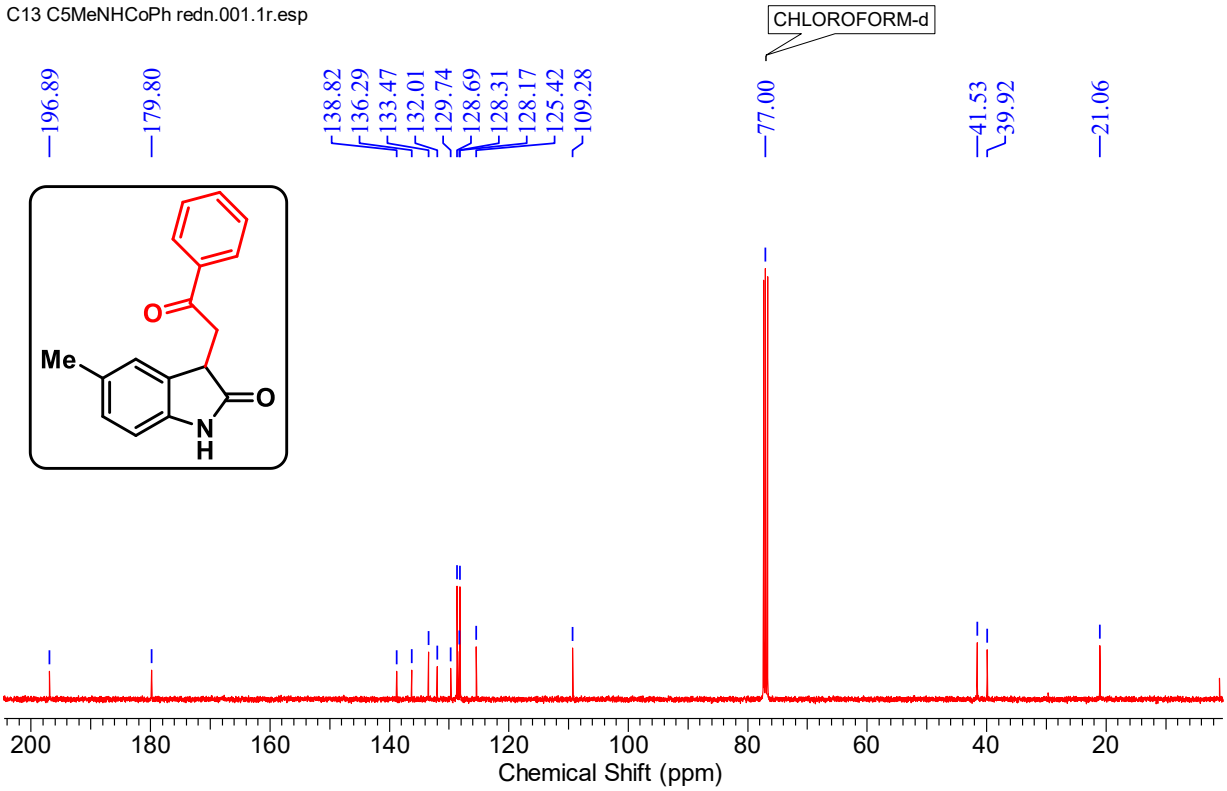
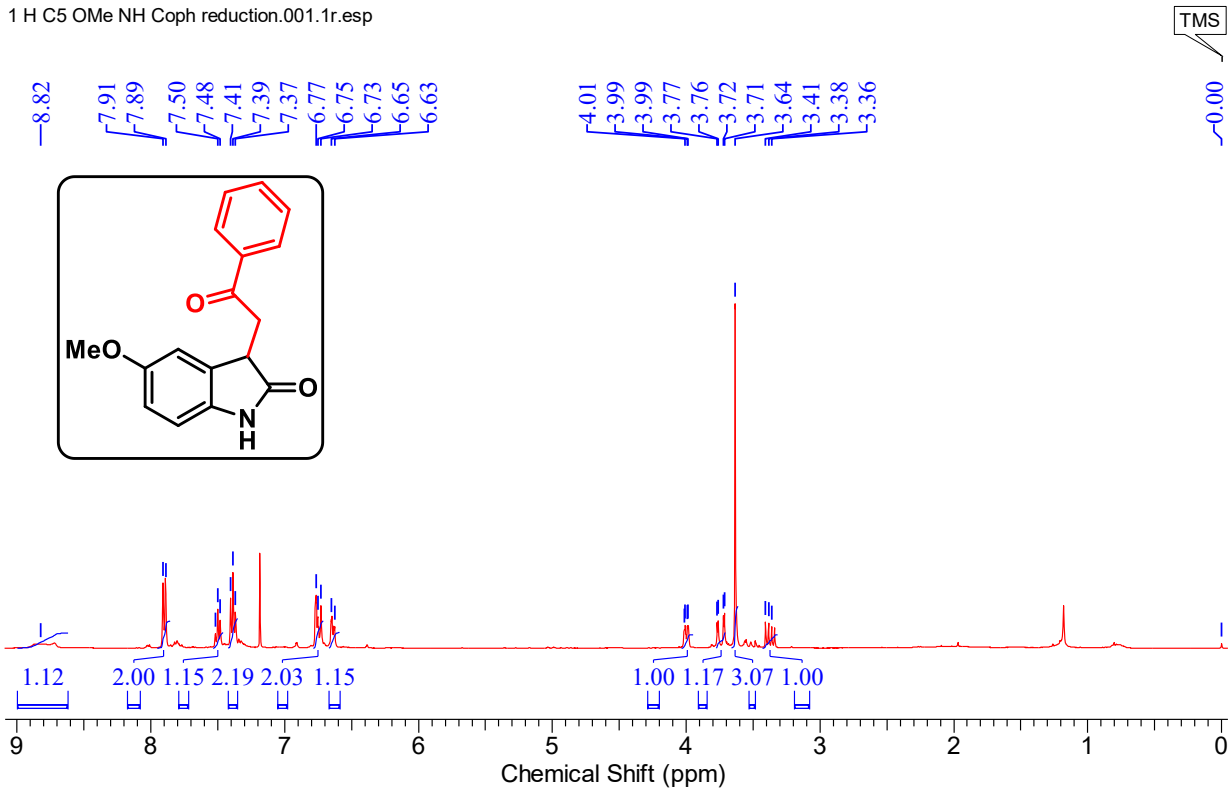


^{1}H NMR of 3Cc



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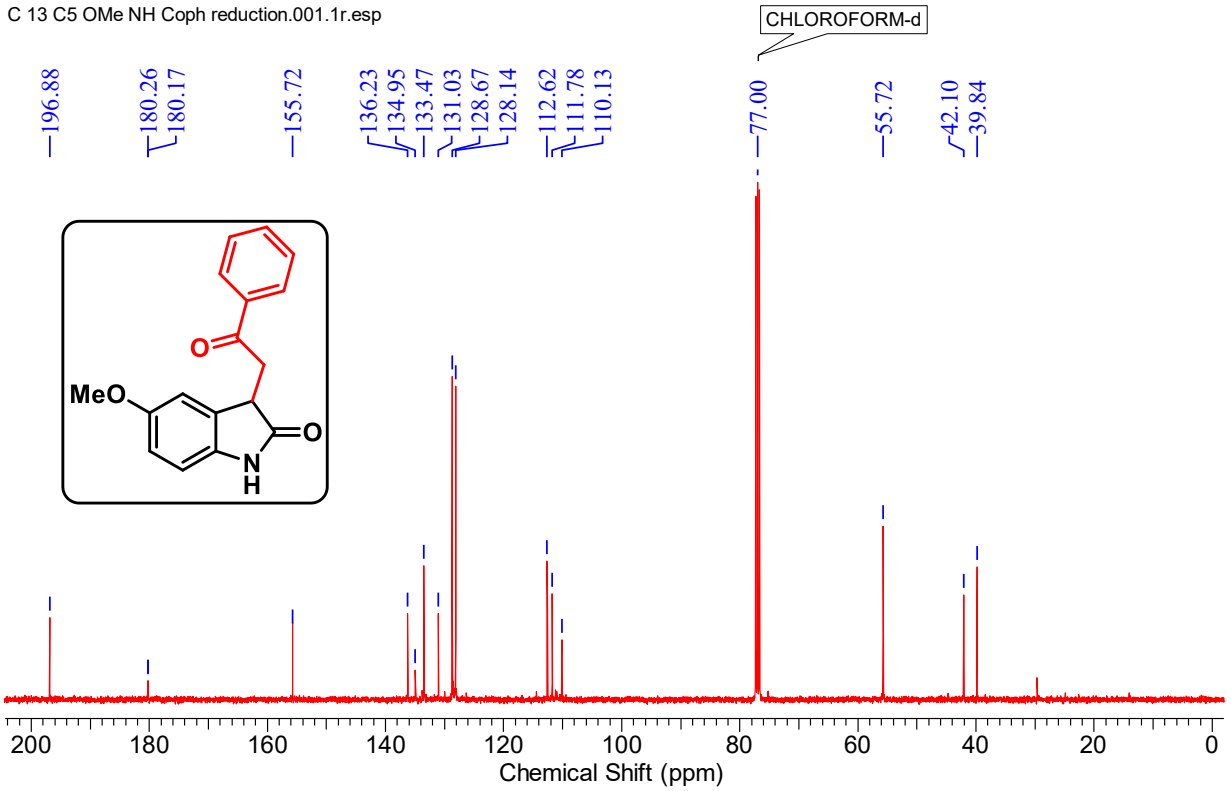
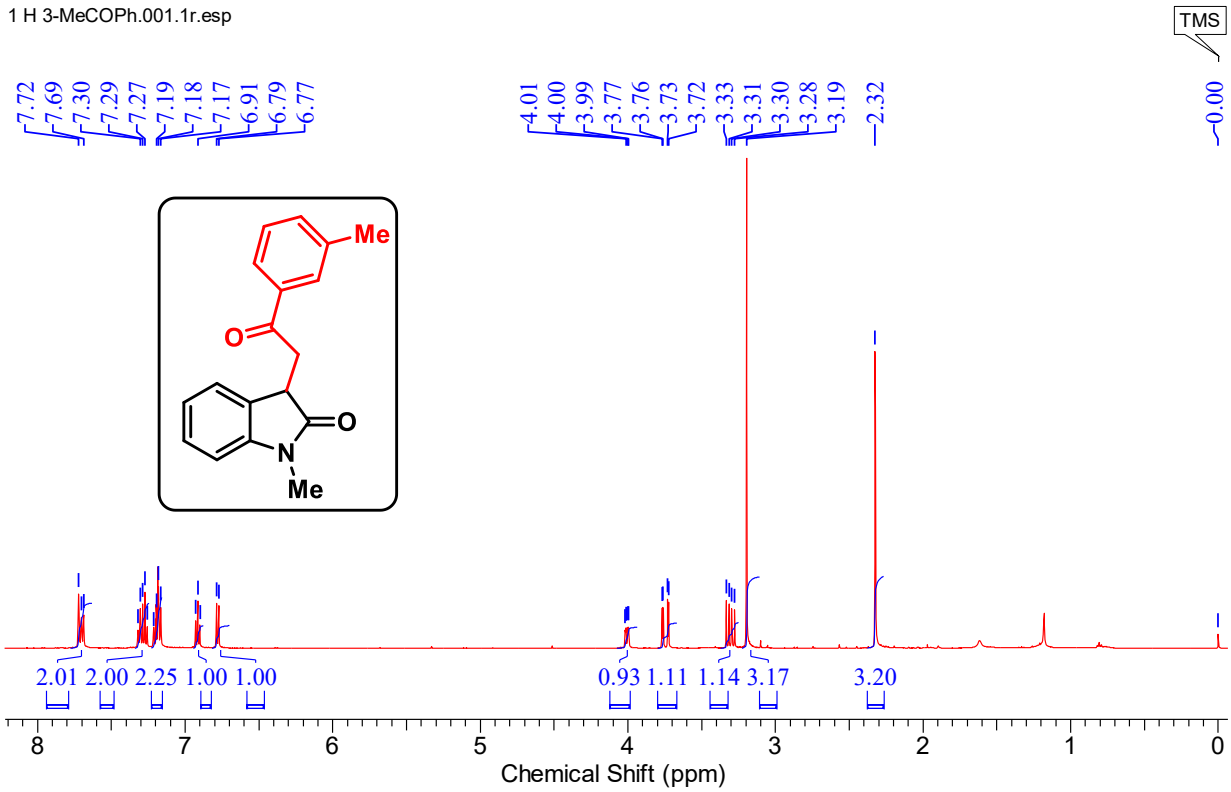


^{1}H NMR of 3Cd



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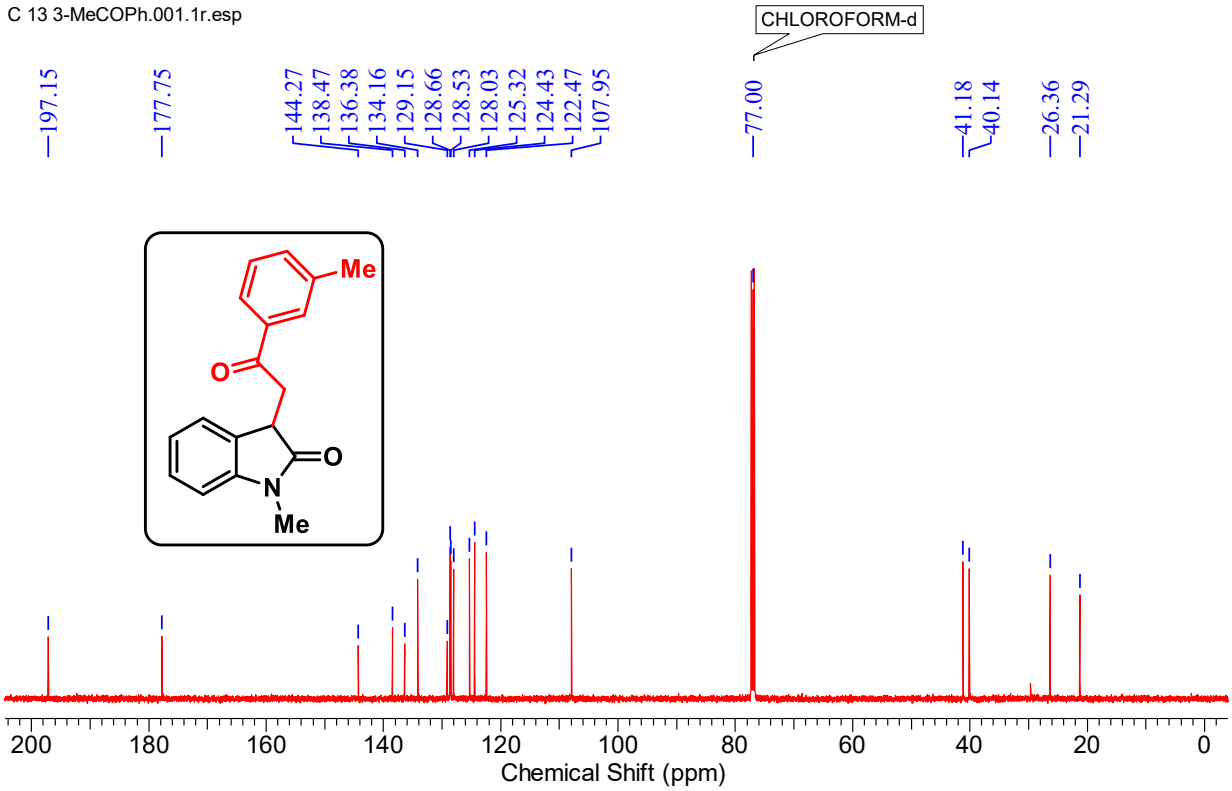
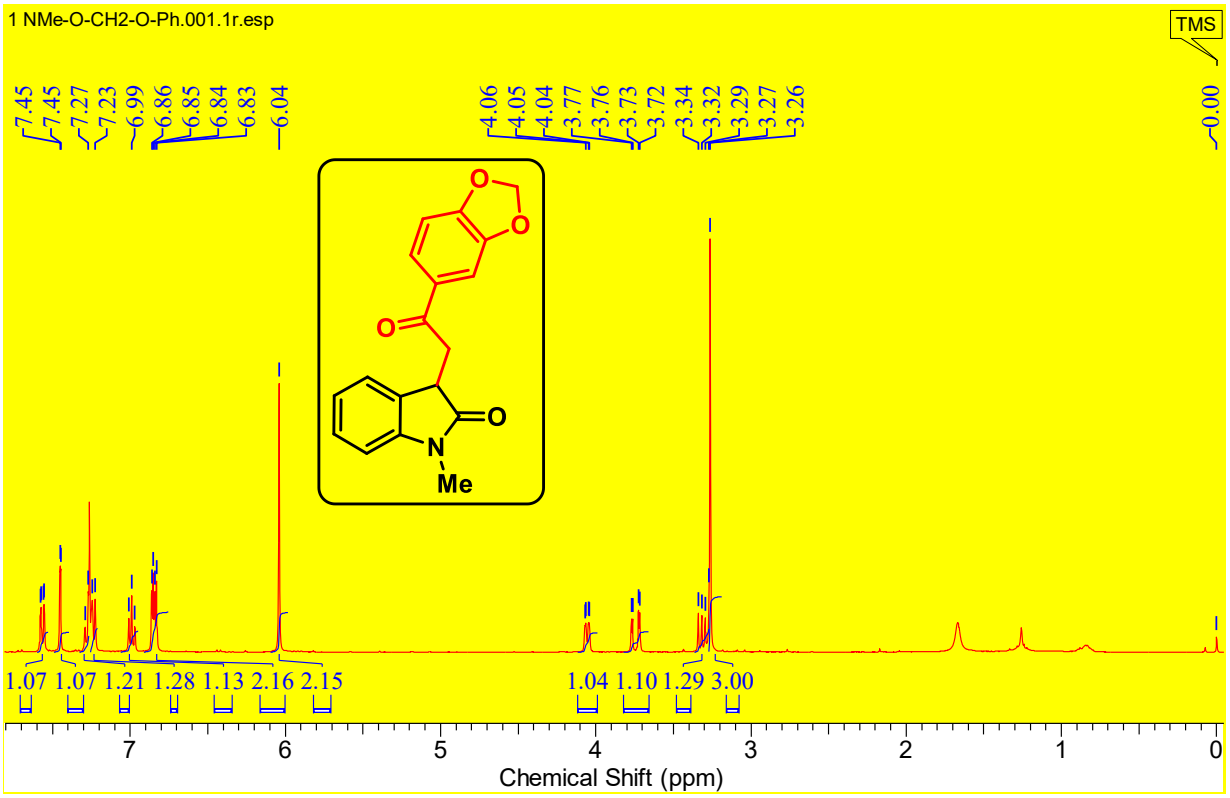


^{1}H NMR of 3Ce



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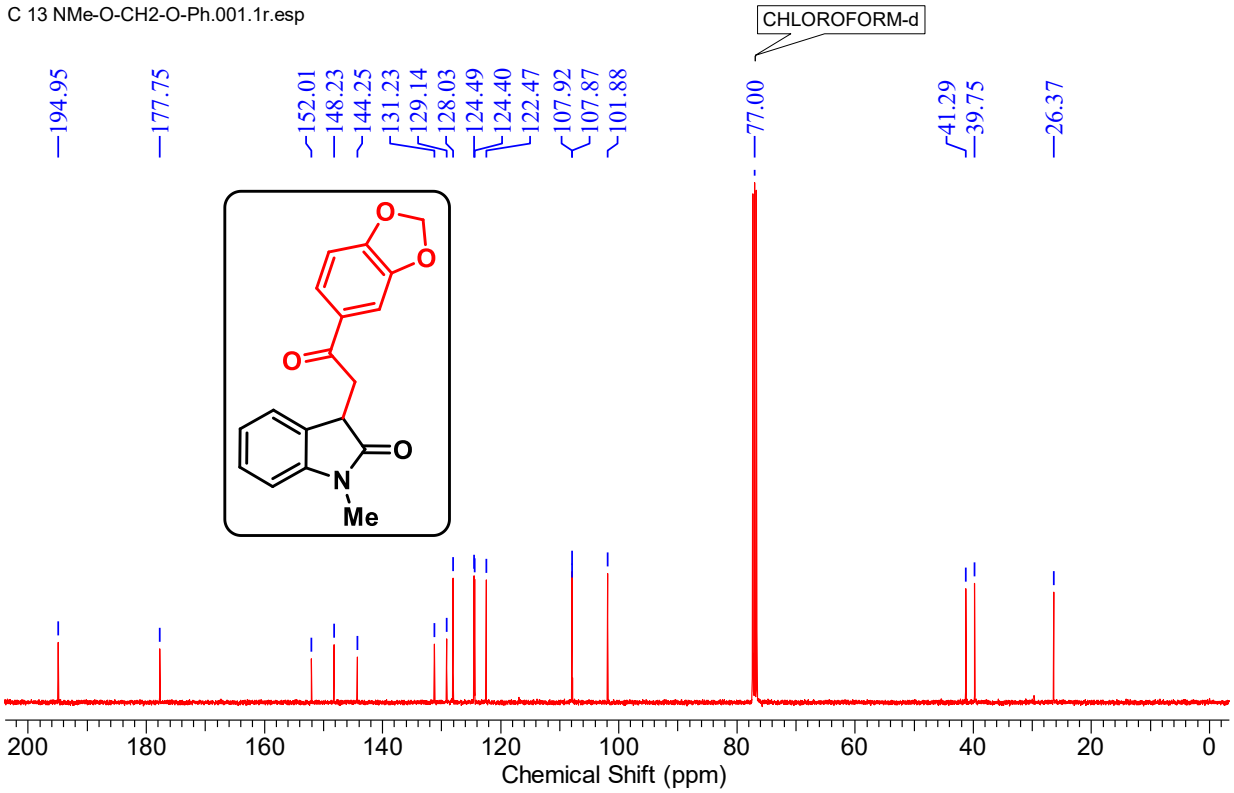
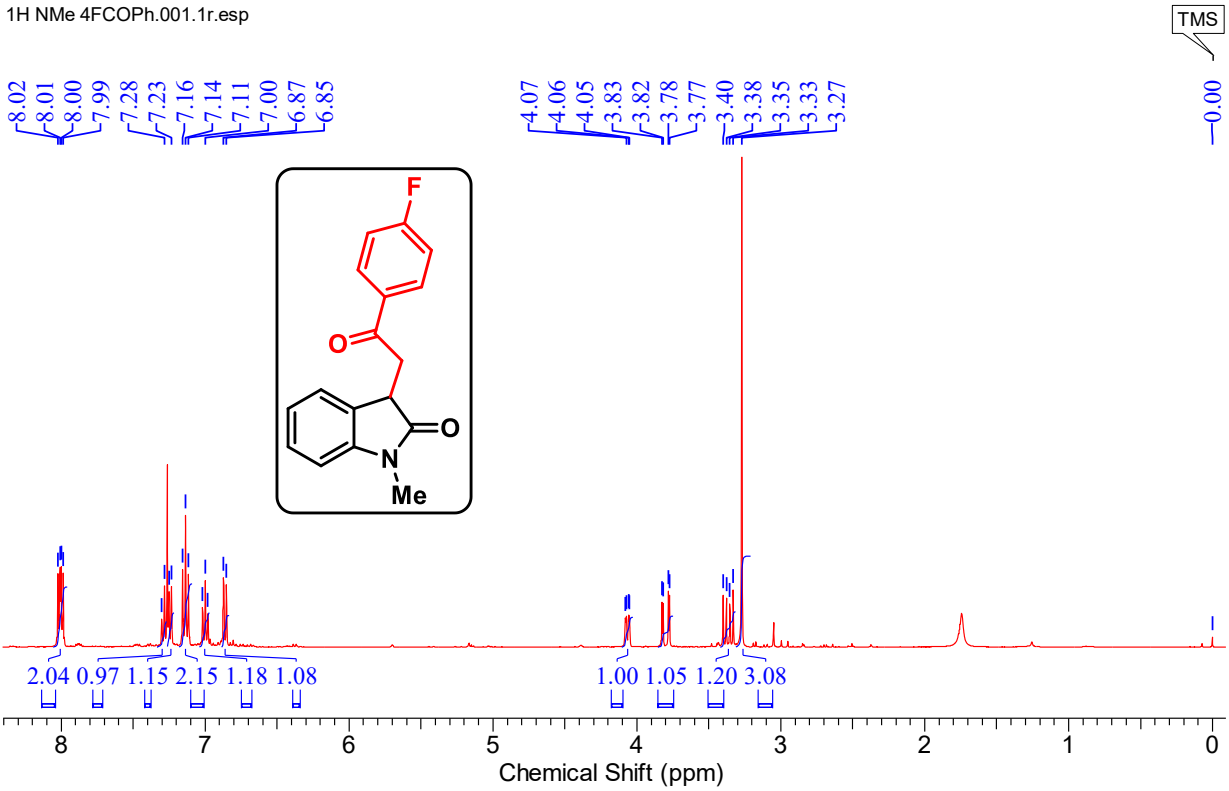


^{1}H NMR of 3Cf



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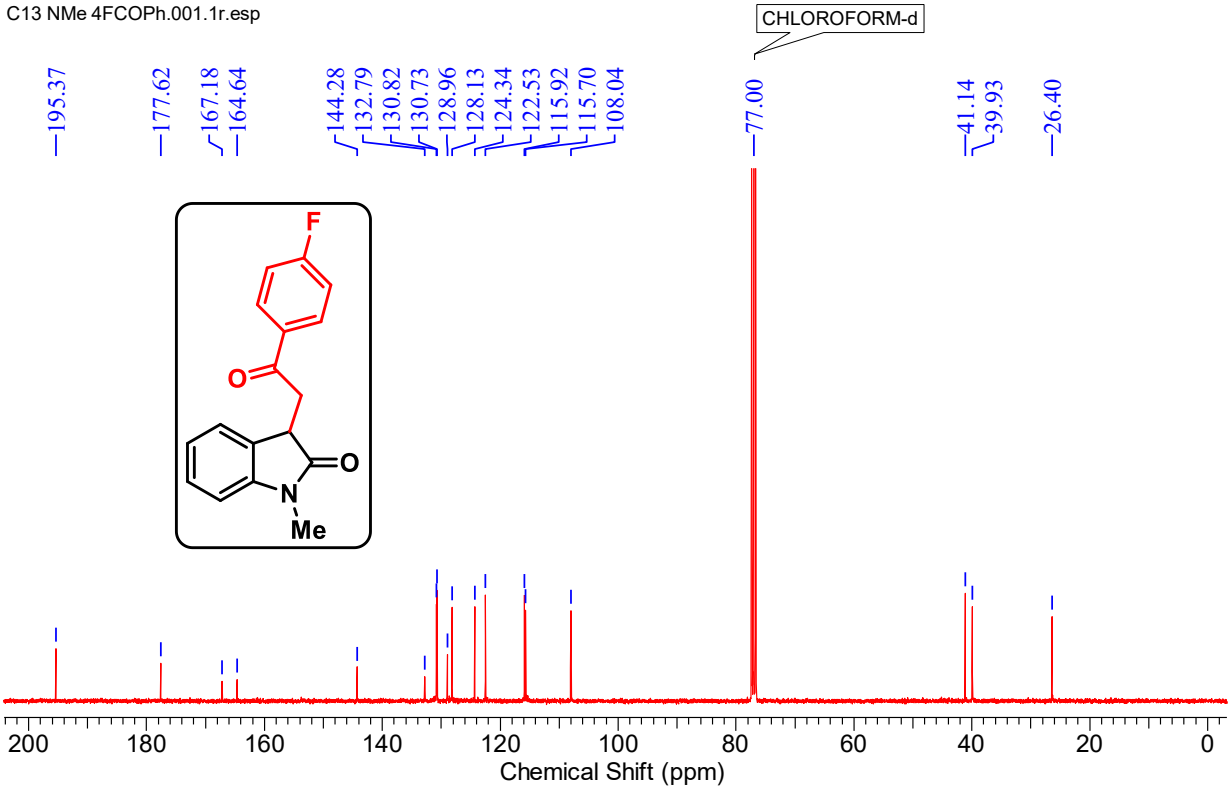

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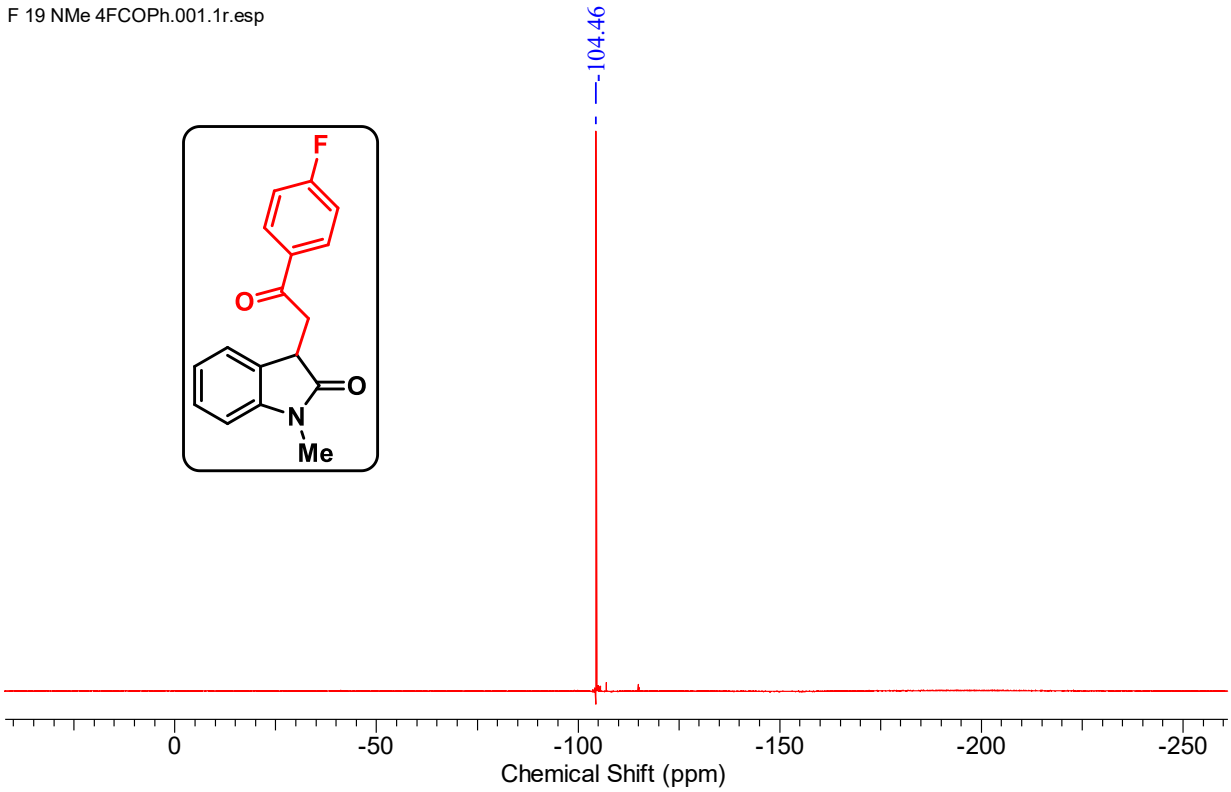
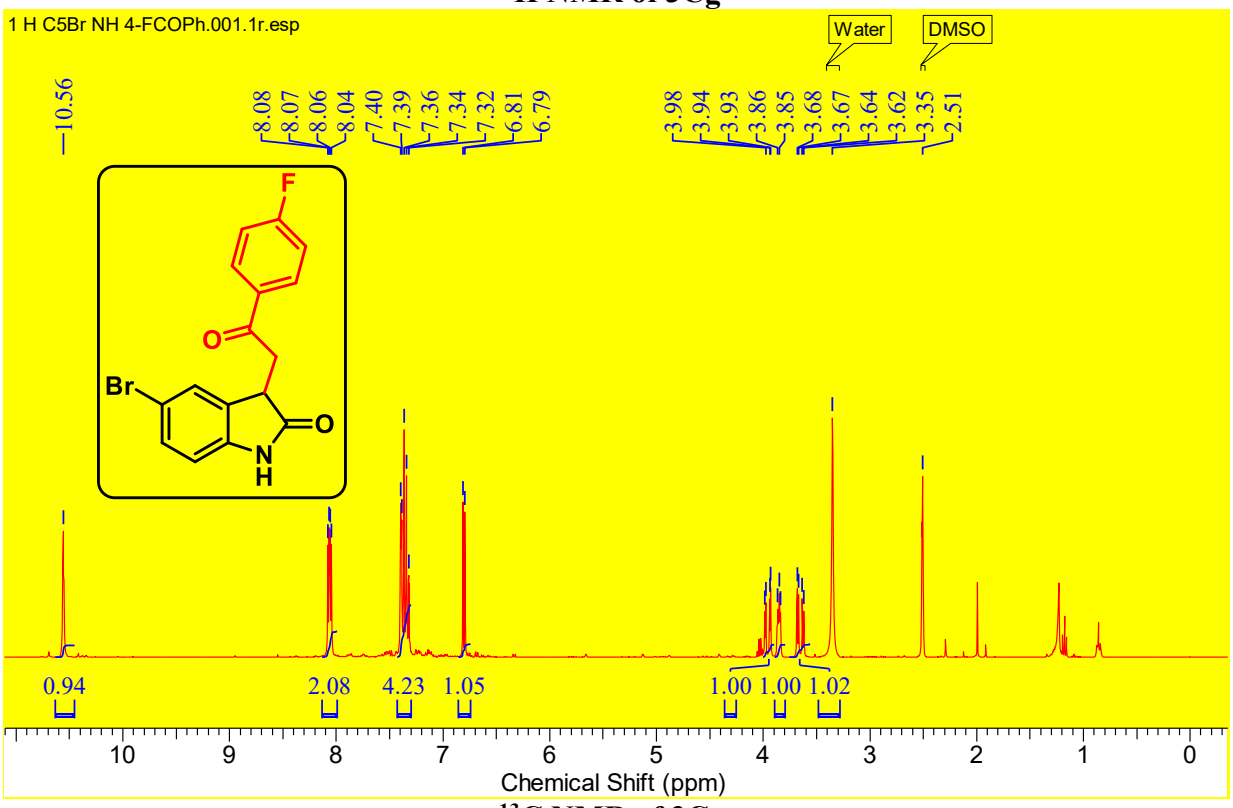
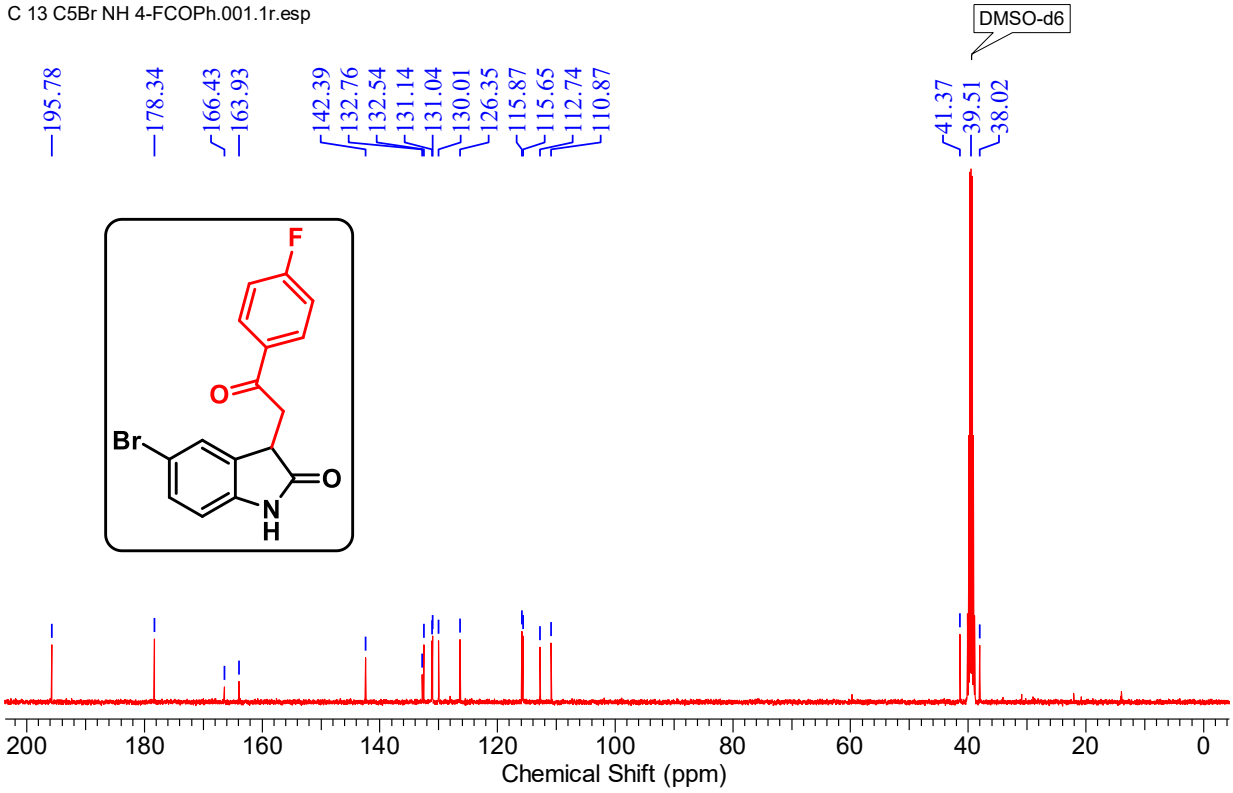


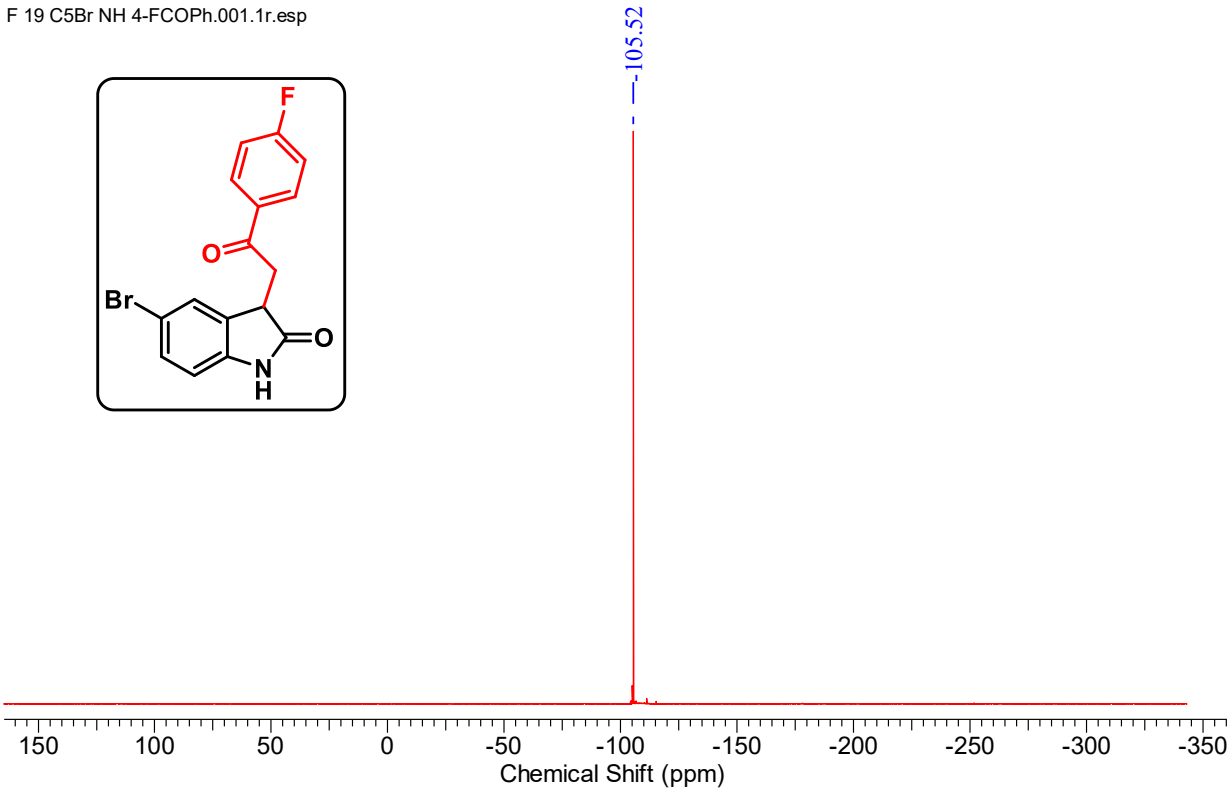
^{1}H NMR of 3Cg



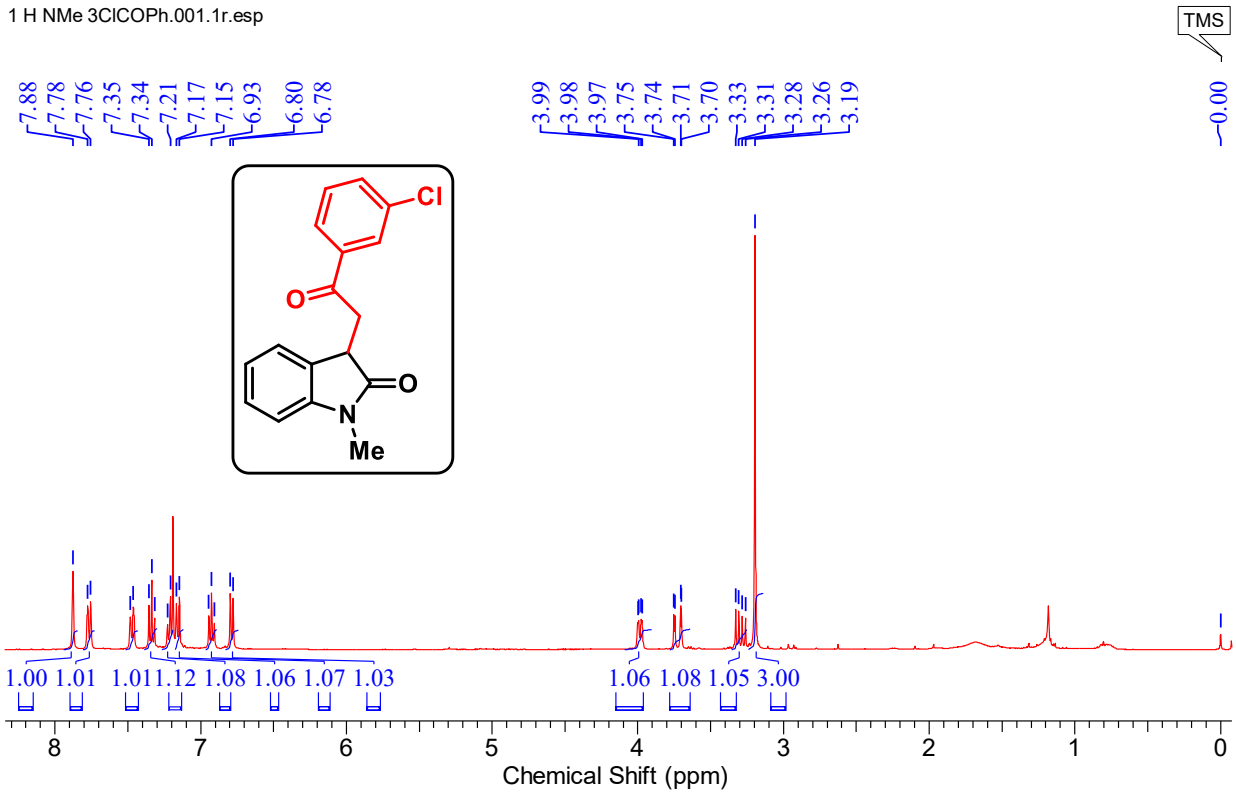
^{13}C NMR of 3Cg



^{19}F NMR of 3Cg



^{1}H NMR of 3Ch



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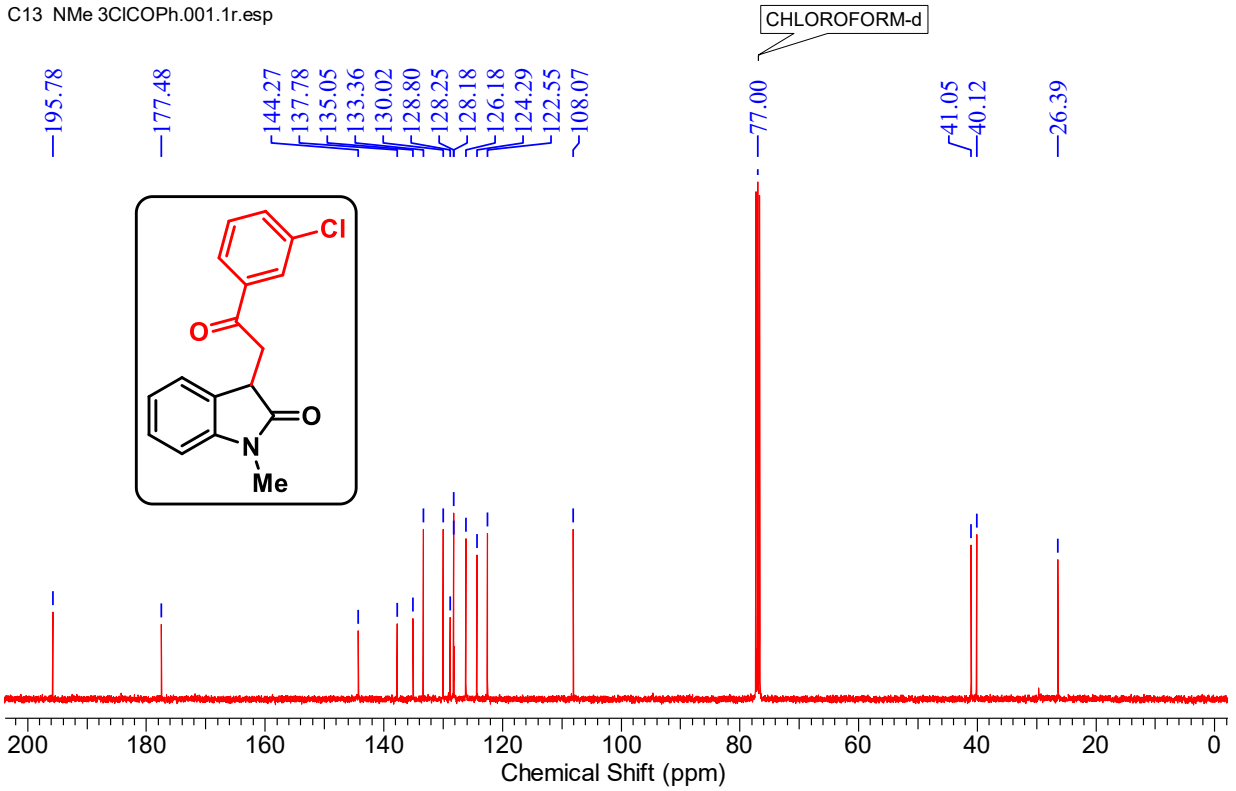
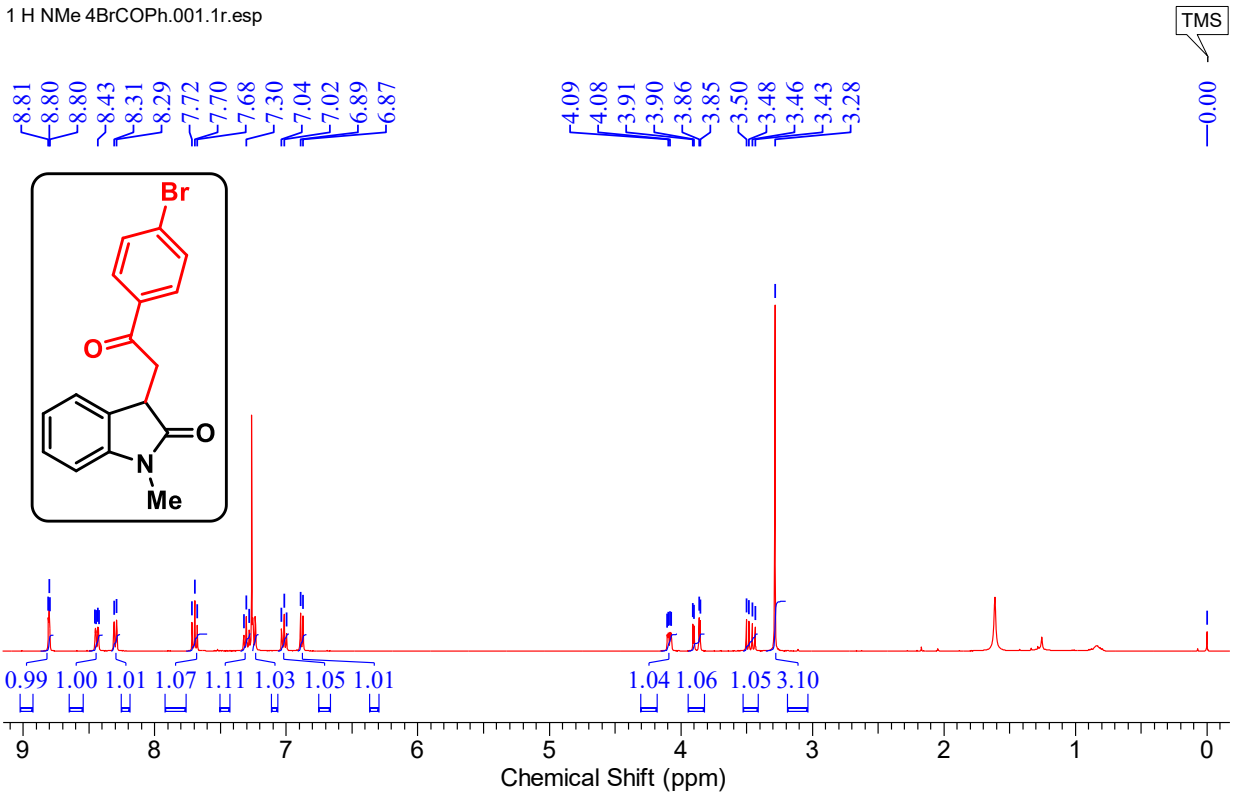


^{1}H NMR of 3Ci



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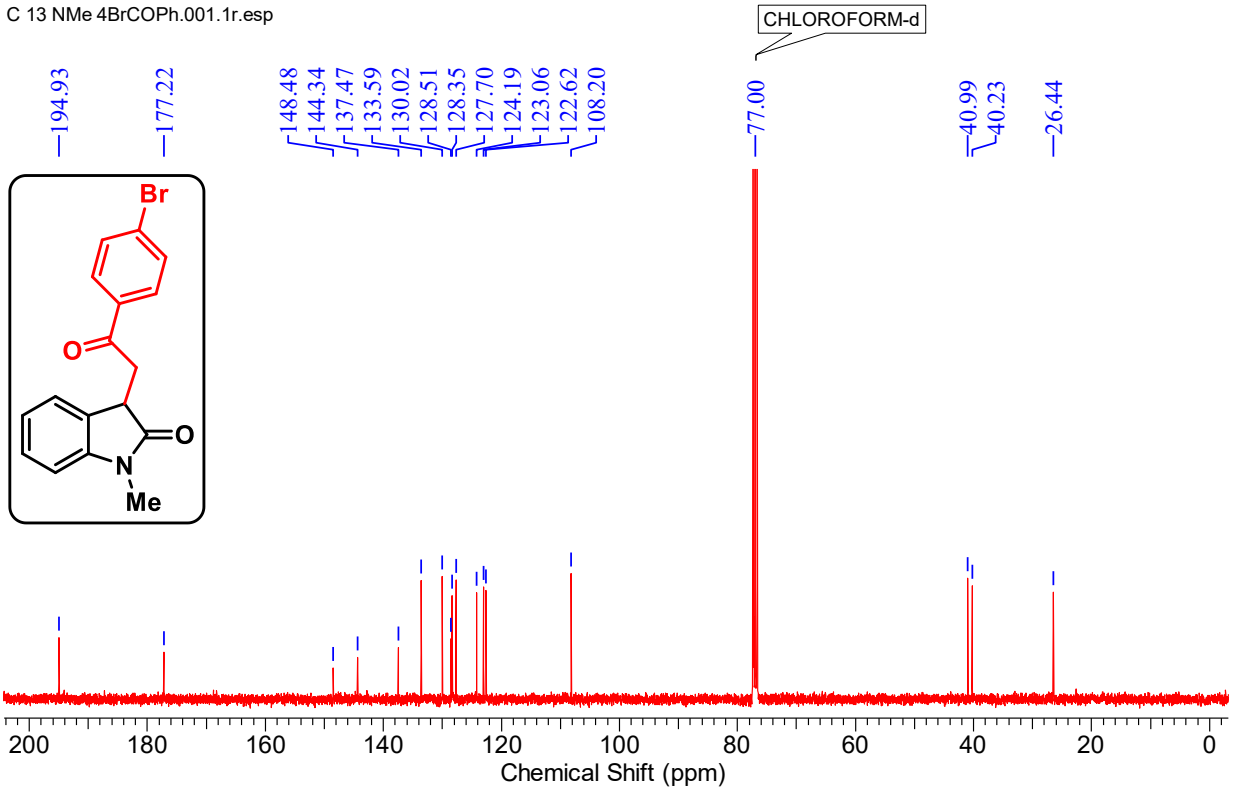
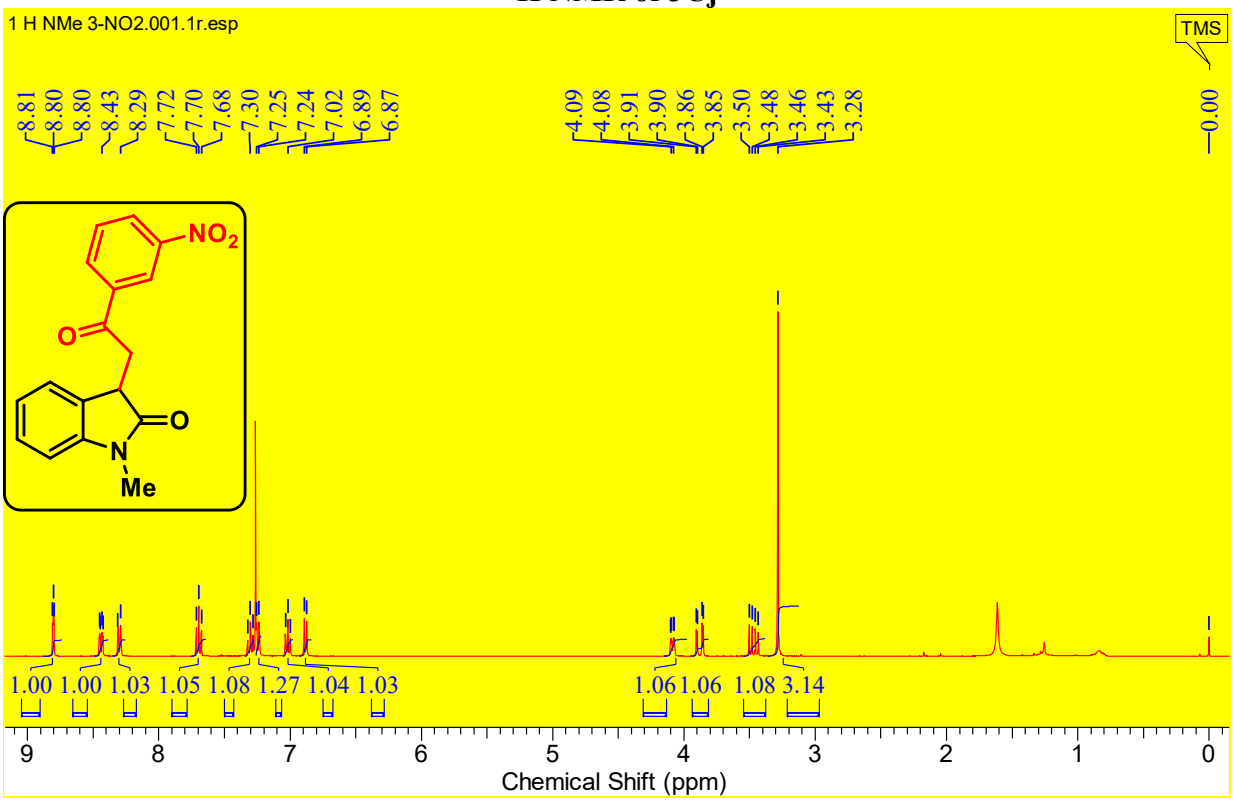


^{1}H NMR of 3Cj



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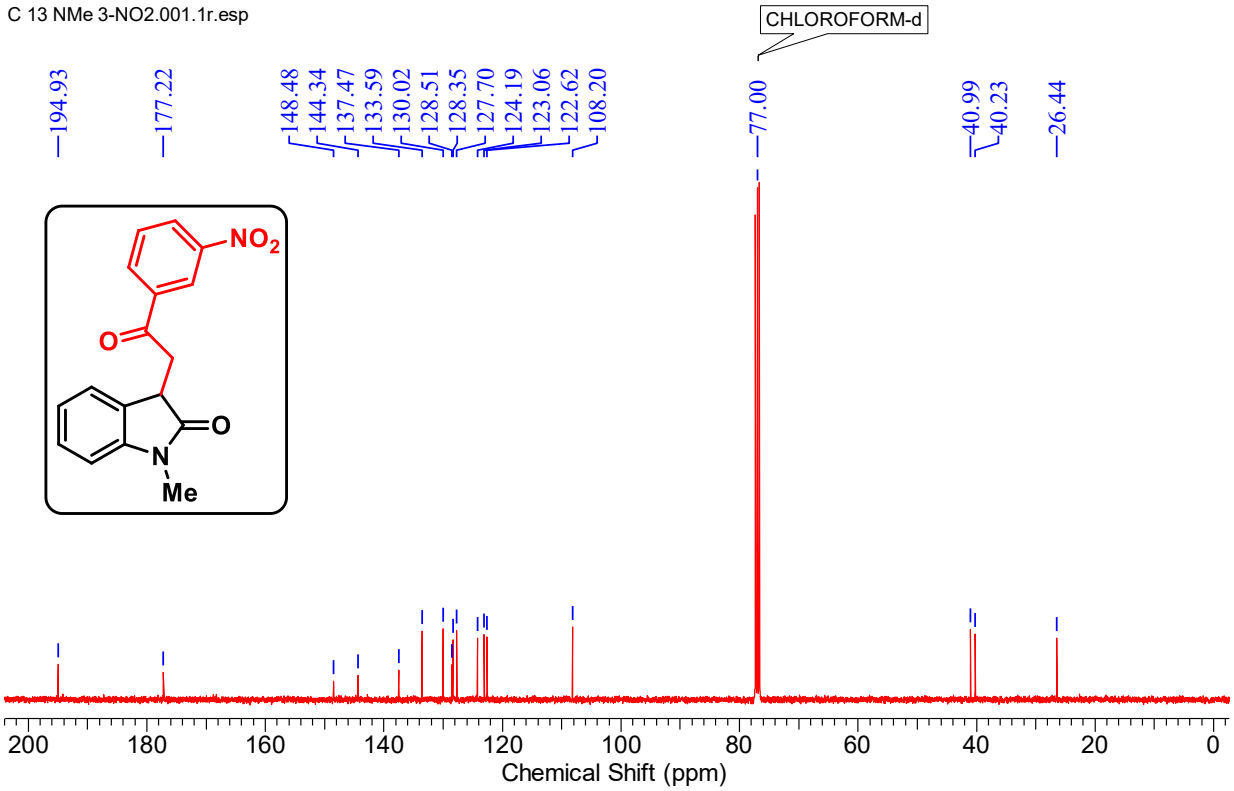
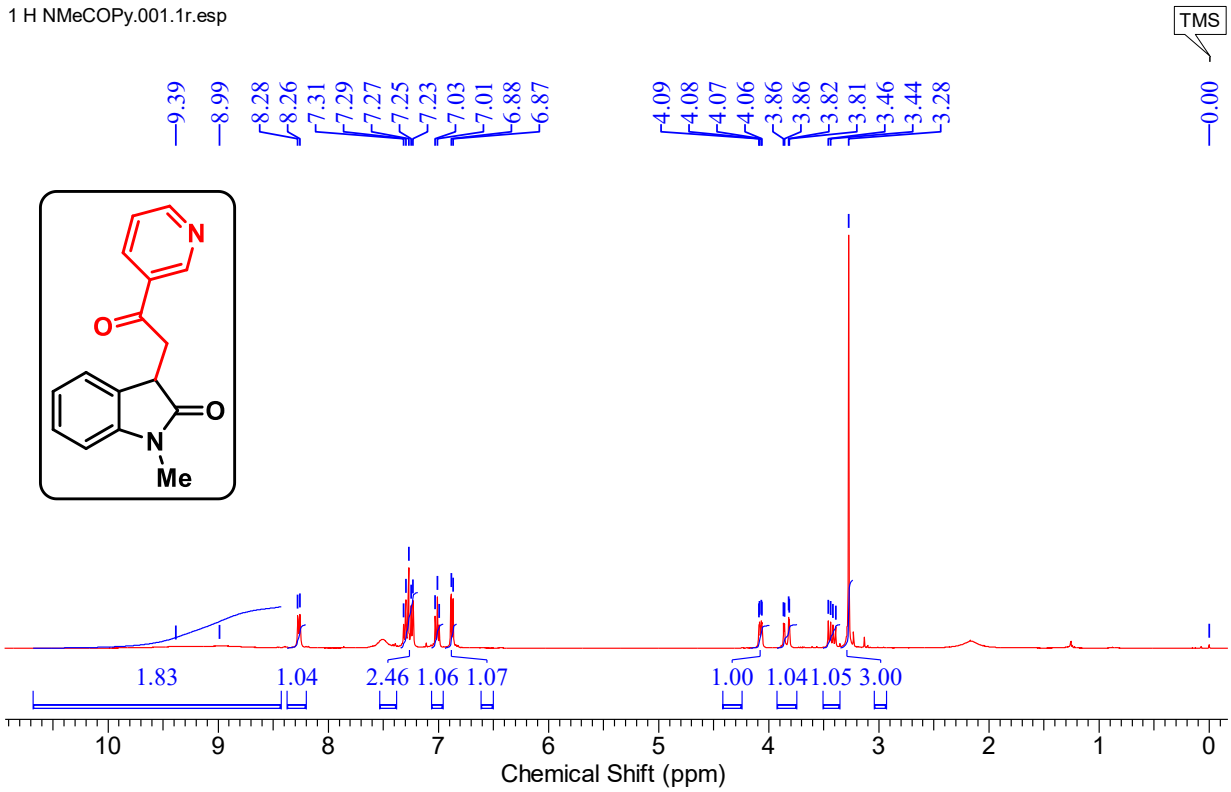
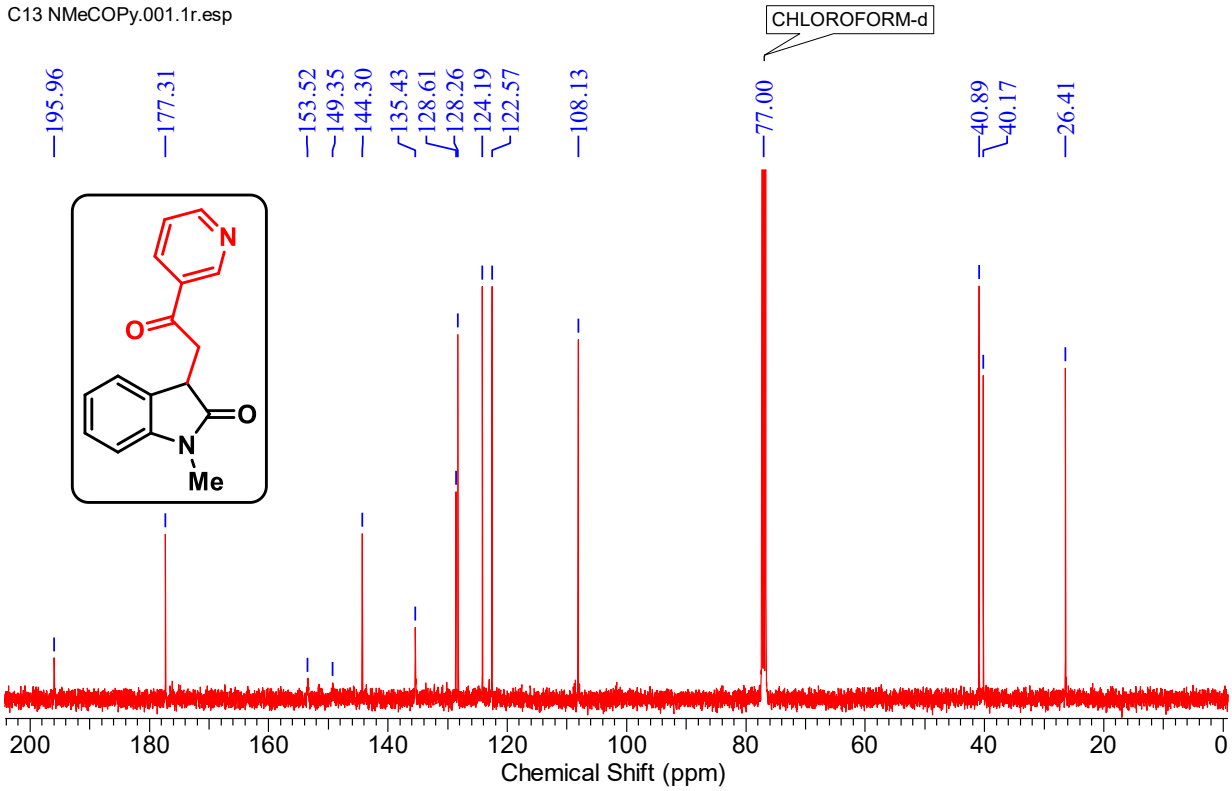


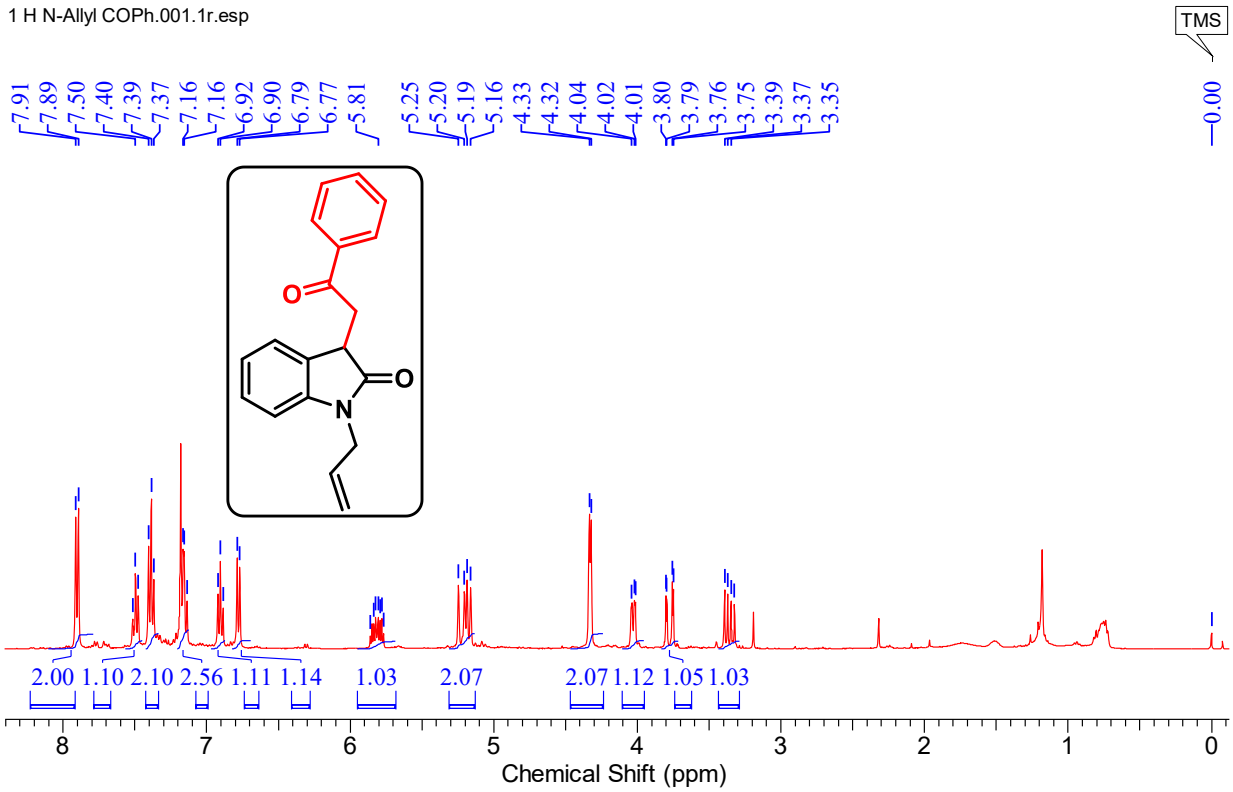
^{1}H NMR of 3Ck



^{13}C NMR of 3Ck



^{1}H NMR of 3Cl



^{13}C NMR of 3Cl