Supporting Information

A Three Component Iodine-Catalyzed Oxidative Coupling Reaction: A Heterodifunctionality of 3-Methylindole

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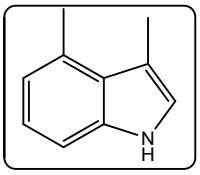
1. Experimental Section

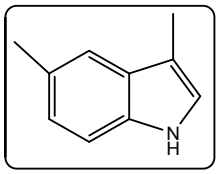
Chemicals. Unless otherwise stated, commercial grade chemicals were used without further purification. All solvents were distilled over sodium under N_2. Volume reduction and drying steps were performed *in vacuo*. The starting material 3-methylindole derivatives were synthesized according to the literature procedure.[1-5]

General Physical Measurements: ^{1}H NMR spectra were recorded on Bruker Avance III (400 MHz) and chemical shifts were expressed in δ ppm values with reference to tetramethylsilane (TMS) as internal standard. HR-MS (ESI) spectra were obtained using a Bruker Impact II quardrupole time of flight mass spectrometer. The single crystal data were collected on an Oxford Diffraction Supernova dual diffractometer equipped with an Oxford Cryostream 700 low-temperature apparatus.

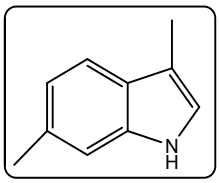
1.1 *^{1}H NMR data of 3-Methylindole derivatives*



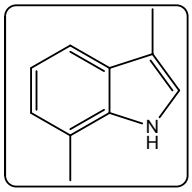
3,4-dimethyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.59 (s, 1H), 7.16 (d, J = 17.7, 8.1 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.91 (s, J = 6.4 Hz, 1H), 6.88 (d, J = 7.0 Hz, 1H), 2.78 (s, 3H), 2.57 (s, 3H).



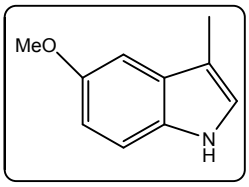
3,5-dimethyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.38 (s, J = 0.6 Hz, 1H), 7.28 – 7.21 (d, 2H), 7.03 (d, J = 8.2, 1.2 Hz, 1H), 6.94 (s, J = 1.0 Hz, 1H), 2.49 (s, 3H), 2.33 (s, J = 1.0 Hz, 3H).



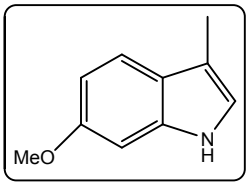
3,6-dimethyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.60 (s, 1H), 7.14 (d, J = 4.9 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.91 (s, 1H), 2.61 (s, 3H), 2.46 (s, 3H).



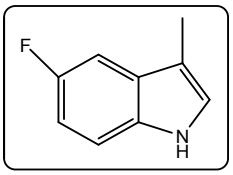
3,7-dimethyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.0 Hz, 1H), 6.98 (d, J = 0.7 Hz, 1H), 2.51 (s, 3H), 2.40 (s, 3H).



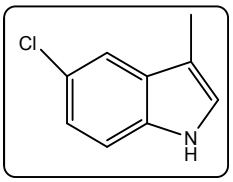
5-methoxy-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.24 (d, J = 8.8 Hz, 1H), 7.11 (s, 1H), 6.96 (s, 1H), 3.95 (s, 3H), 2.38 (s, 3H).



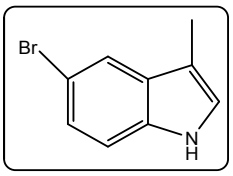
6-methoxy-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, J = 28.6 Hz, 1H), 7.47 (d, J = 9.4 Hz, 1H), 6.87 – 6.80 (m, 3H), 3.86 (s, 3H), 2.33 (s, 3H).



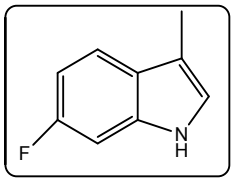
5-fluoro-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDC1_3$) δ 6 7.30-7.23 (m, 2H), δ 7.04 (s, 1H), δ 6.97 (td, J = 9.0, 2.0 Hz, 1H), δ 2.33 (s, 3H)



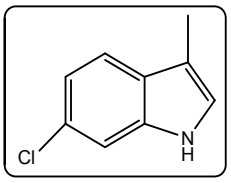
5-chloro-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, J = 1.3 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.6, 1.8 Hz, 1H), 6.99 (s, 1H), 2.30 (s, 3H).



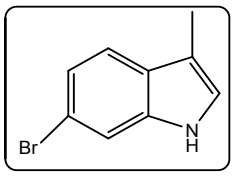
5-bromo-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, J = 46.7 Hz, 1H), 7.73 (s, J = 1.1 Hz, 1H), 7.28 (d, J = 8.6, 1.7 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 6.96 (s, 1H), 2.31 (s, 3H).



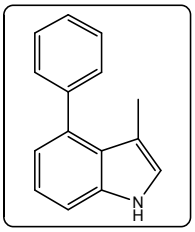
6-fluoro-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.53 (dd, J = 8.6, 5.4 Hz, 1H), 7.03 (dd, J = 9.8, 2.2 Hz, 1H), 7.01 – 6.91 (m, 2H), 2.37 (s, 3H).



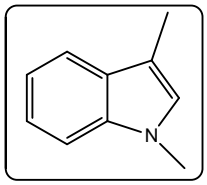
6-chloro-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 1.2 Hz, 1H), 7.12 (d, J = 8.4, 1.5 Hz, 1H), 6.95 (s, 1H), 2.34 (s, 3H).



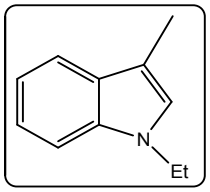
6-bromo-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 1.3 Hz, 1H), 7.28 (d, 1H), 6.91 (s, 1H), 2.35 (s, J = 2.9 Hz, 3H).



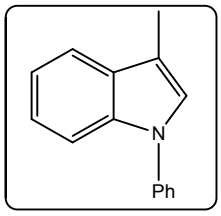
3-methyl-4-phenyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.55 – 7.40 (m, 6H), 7.30 (dt, J = 15.3, 4.7 Hz, 1H), 7.05 (d, J = 7.6 Hz, 2H), 1.93 (s, 3H).



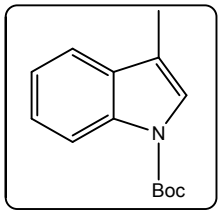
1, 3-dimethyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 16.1, 7.9 Hz, 1H), 7.37 – 7.21 (m, 2H), 7.21 – 7.09 (m, 1H), 6.85 (d, J = 7.6 Hz, 1H), 3.84 – 3.70 (m, 3H), 2.45 – 2.31 (m, 3H).



1-ethyl-3-methyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.7 Hz), 7.25 (d, J = 8.1 Hz), 7.18 (t, J = 7.4 Hz), 7.09 (d, J = 7.6 Hz), 6.82 (s), 4.15 – 3.93 (m), 2.31 (s), 1.36 (t, J = 6.8 Hz).

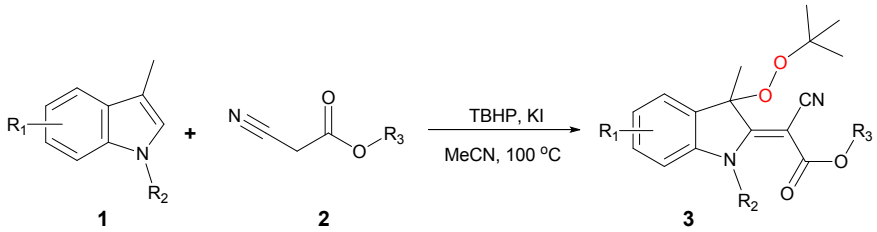


3-methyl-1-phenyl-1H-indole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 4.4 Hz, 4H), 7.34 – 7.26 (m, 1H), 7.25 – 7.10 (m, 3H), 2.38 (s, 3H).



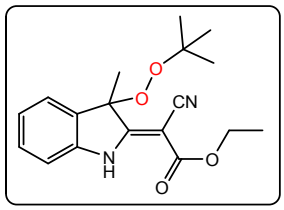
tert-butyl 3-methyl-1H-indole-1-carboxylate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.43 (s, 1H), 7.39 (t, 1H), 7.35 – 7.28 (t, 1H), 2.33 (d, J = 1.3 Hz, 3H), 1.73 (s, 9H).

1.2 Synthetic Route for *Heterodifunctionality of 3-Methylindole*



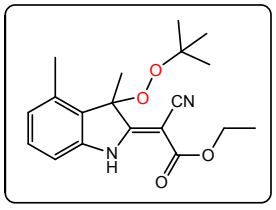
A solution of compound **1** (0.2 mmol), compound **2** (1.0 mmol), *tert*-butyl hydroperoxide (1.0 mmol) and potassium iodide (0.02 mmol) in MeCN (0.5 mL) was stirred for 12 h at 100 °C under N_2 atmosphere. The mixture was diluted with dichlormethane (5 mL) and filtered. The solvent of filtrate was removed in *vacuo* to leave an oily residue, which was purified on a silica gel column eluted with petroleum ether/ethyl acetate (4:1 v/v) to afford the product **3** as solid (compounds **3p** and **3q** are oily).

(Z)-ethyl 2-(3-(tert-butylperoxy)-3-methylindolin-2-ylidene)-2-cyanoacetate:



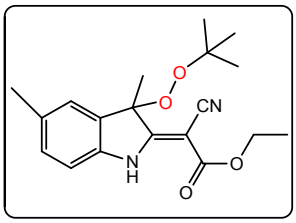
Yield 85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.29 (t, J = 11.9, 5.3 Hz, 1H), 7.10 (t, J = 7.5, 0.7 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 4.30 (qq, J = 10.7, 7.1 Hz, 2H), 1.80 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.43, 167.95, 140.81, 131.93, 129.75, 123.74, 123.61, 116.09, 110.70, 88.01, 80.58, 71.76, 61.28, 26.44, 21.46, 14.33. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{18}H_{22}N_2O_4Na$, 353.1477; found: 353.1472.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3,4-dimethylindolin-2-ylidene)-2-cyanoacetate:



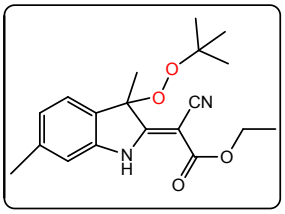
Yield 75%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.16 (t, J = 7.7 Hz, 1H), 6.85 (t, J = 7.7 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 4.38 – 4.22 (m, 2H), 2.44 (s, 3H), 1.85 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.21, 168.18, 140.60, 135.55, 129.41, 128.73, 126.19, 116.46, 108.34, 88.86, 80.40, 70.68, 61.19, 26.65, 19.58, 16.90, 14.34. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{19}H_{24}N_2O_4Na$: 367.1634; found: 367.1628.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3,5-dimethylindolin-2-ylidene)-2-cyanoacetate:



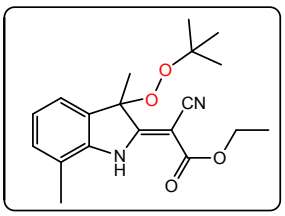
Yield 70%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.16 (s, 1H), 7.07 (d, J = 7.9 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 4.29 (qq, J = 10.8, 7.1 Hz, 2H), 2.35 (s, 3H), 1.78 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.46, 168.07, 138.56, 133.41, 132.08, 130.07, 124.43, 116.30, 110.36, 88.02, 80.53, 71.15, 61.17, 26.46, 21.49, 21.19, 14.34. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{19}H_{24}N_2O_4Na$: 367.1634; found: 367.1631.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3,6-dimethylindolin-2-ylidene)-2-cyanoacetate:



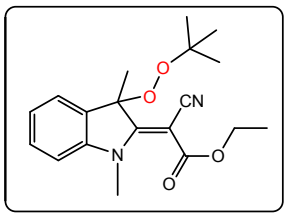
Yield 71%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.72 (s, 1H), 4.30 (qq, J = 10.7, 7.1 Hz, 2H), 2.36 (s, 3H), 1.77 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.79, 168.00, 141.05, 140.13, 129.05, 124.28, 123.45, 116.17, 111.46, 87.84, 80.48, 71.63, 61.22, 26.46, 21.67, 21.49, 14.34. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{19}H_{24}N_2O_4Na$: 367.1634; found: 367.1629.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3,7-dimethylindolin-2-ylidene)-2-cyanoacetate:



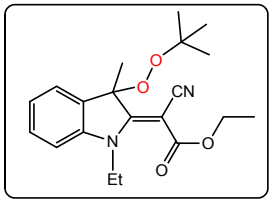
Yield 73%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.20 (d, J = 7.3 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 4.31 (qq, J = 10.7, 7.1 Hz, 2H), 2.32 (d, J = 5.6 Hz, 3H), 1.78 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.49, 168.20, 139.46, 131.61, 131.04, 123.62, 121.21, 119.96, 116.14, 88.35, 80.56, 71.67, 61.26, 26.48, 21.63, 15.93, 14.36. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{19}H_{24}N_2O_4Na$: 367.1634; found: 367.1630.

(Z)-ethyl 2-(3-(tert-butylperoxy)-1,3-dimethylindolin-2-ylidene)-2-cyanoacetate:



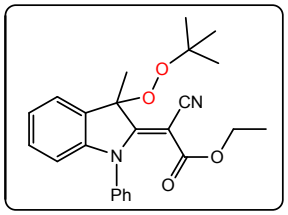
Yield 63%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 8.1 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.37 (s, 3H), 1.81 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.14 (s, 9H); 13C NMR (101 MHz, $CDCl_3$) δ 172.32, 164.05, 144.92, 132.55, 129.66, 124.07, 123.27, 118.30, 109.60, 88.36, 80.42, 72.25, 61.02, 36.87, 26.47, 22.09, 14.36. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{19}H_{24}N_2O_4Na$: 367.1634; found: 367.1632.

(Z)-ethyl 2-(3-(tert-butylperoxy)-1-ethyl-3-methylindolin-2-ylidene)-2-cyanoacetate:



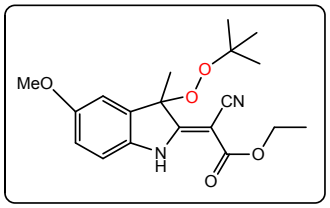
Yield 26%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 8.5 Hz), 7.13 (t, J = 7.3 Hz), 6.96 (d, J = 7.9 Hz), 4.27 (q, J = 7.1 Hz), 4.21 (dd, J = 13.4, 6.1 Hz), 1.80 (s), 1.36 (t, J = 7.1 Hz), 1.21 (t, J = 7.1 Hz), 1.13 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.33, 164.32, 143.93, 132.90, 129.53, 123.82, 123.44, 118.12, 110.10, 88.54, 80.43, 73.22, 61.19, 42.33, 26.46, 22.16, 14.43, 11.86. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{20}H_{26}N_2O_4Na$: 381.1790; found: 381.1786.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3-methyl-1-phenylindolin-2-ylidene)-2-cyanoacetate:



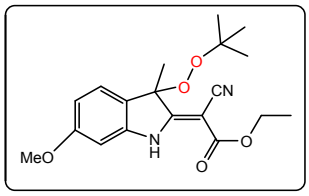
Yield 41%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, J = 7.5 Hz), 7.41 (dd, J = 7.3, 0.9 Hz), 7.39 – 7.33 (m), 7.31 (s), 7.20 (td, J = 7.7, 1.3 Hz), 7.14 – 7.09 (m), 6.69 (t, J = 7.3 Hz), 3.84 – 3.66 (m), 1.93 (s), 1.19 (s), 1.04 (t, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.76, 162.45, 145.34, 139.56, 131.46, 129.91, 129.57, 128.18, 123.93, 123.69, 123.01, 117.36, 110.16, 87.95, 80.60, 76.24, 61.16, 26.56, 22.10, 14.25. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{24}H_{26}N_2O_4Na$: 429.1790; found: 429.1786.

(Z)-ethyl 2-(3-(tert-butylperoxy)-5-methoxy-3-methylindolin-2-ylidene)-2-cyanoacetate:



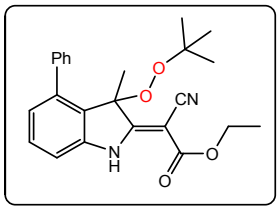
Yield 74%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.26 (s, 1H), 6.93 (t, J = 3.1 Hz, 1H), 6.81 (d, J = 2.2 Hz, 1H), 4.37 – 4.17 (m, 2H), 3.81 (s, 3H), 1.78 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.45, 168.14, 156.79, 134.31, 133.61, 116.34, 114.30, 111.10, 110.48, 88.15, 80.64, 70.81, 61.15, 55.87, 26.47, 21.59, 14.35. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{19}H_{24}N_2O_5Na$: 383.1583; found: 383.1577.

(Z)-ethyl 2-(3-(tert-butylperoxy)-6-methoxy-3-methylindolin-2-ylidene)-2-cyanoacetate:



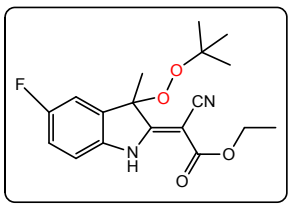
Yield 72%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.23 (d, J = 8.2 Hz, 1H), 6.60 (d, J = 10.4 Hz, 1H), 6.48 (t, J = 5.4 Hz, 1H), 4.36 – 4.22 (m, 2H), 3.81 (s, 3H), 1.78 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.15, 167.90, 161.34, 142.19, 124.41, 123.78, 116.04, 108.19, 97.80, 87.55, 80.44, 72.06, 61.29, 55.63, 26.46, 21.47, 14.32. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{19}H_{24}N_2O_5Na$: 383.1583; found: 383.1578.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3-methyl-4-phenylindolin-2-ylidene)-2-cyanoacetate:



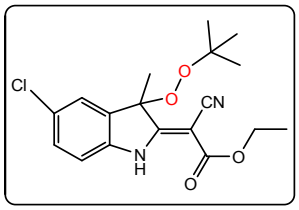
Yield 44%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.61 (dd, J = 6.6, 3.0 Hz, 2H), 7.40 (dd, J = 5.0, 1.7 Hz, 3H), 7.34 (t, J = 7.8 Hz, 1H), 7.02 (d, J = 6.2, 5.1, 1.0 Hz, 1H), 6.92 (d, J = 6.0, 5.0, 0.9 Hz, 1H), 4.31 (qdd, J = 9.5, 6.6, 3.0 Hz, 2H), 1.47 (s, 3H), 1.37 (t, J = 8.7, 5.6 Hz, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.91, 168.23, 141.34, 141.07, 138.39, 129.89, 129.52, 127.92, 127.82, 127.69, 126.26, 116.84, 109.81, 89.12, 81.16, 71.18, 61.28, 26.96, 18.26, 14.36. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{24}H_{26}N_2O_4Na$: 429.1790; found: 429.1786.

(Z)-ethyl 2-(3-(tert-butylperoxy)-5-fluoro-3-methylindolin-2-ylidene)-2-cyanoacetate:



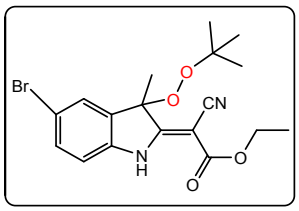
Yield 85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.08 (dd, J = 7.6, 2.4 Hz, 1H), 6.98 (td, J = 8.8, 4.4 Hz, 1H), 6.85 (dd, J = 8.5, 4.0 Hz, 1H), 4.30 (qq, J = 10.7, 7.2 Hz, 2H), 1.79 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.58, 167.83, 159.76, 136.72, 133.94, 116.26, 115.87, 111.63, 111.30, 87.95, 80.88, 71.96, 61.36, 26.43, 21.44, 14.31. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{18}H_{21}FN_2O_4Na$: 371.1383; found: 371.1382.

(Z)-ethyl 2-(3-(tert-butylperoxy)-5-chloro-3-methylindolin-2-ylidene)-2-cyanoacetate:



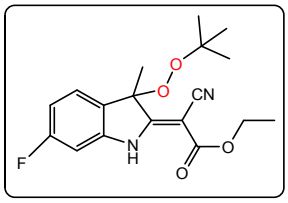
Yield 86%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s), 7.32 (d, J = 1.5 Hz), 7.25 (dd, J = 7.9, 2.0 Hz), 6.84 (d, J = 8.3 Hz), 4.30 (qdd, J = 14.3, 8.9, 5.4 Hz), 1.79 (s), 1.37 (t, J = 7.2 Hz), 1.17 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.07, 167.72, 139.37, 133.80, 129.76, 129.06, 124.19, 115.68, 111.58, 87.82, 80.93, 72.45, 61.45, 26.43, 21.43, 14.30. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ calcd. for $C_{18}H_{21}ClN_2O_4Na$: 387.1087; found: 387.1081.

(Z)-ethyl 2-(5-bromo-3-(tert-butylperoxy)-3-methylindolin-2-ylidene)-2-cyanoacetate:



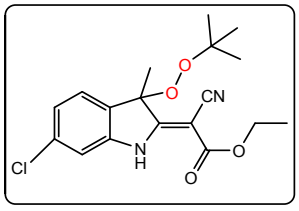
Yield 89%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s), 7.44 (dd, J = 8.3, 1.5 Hz), 7.29 (d, J = 10.2 Hz), 6.83 (d, J = 8.3 Hz), 4.41 – 4.26 (m), 1.83 (s), 1.41 (t, J = 7.1 Hz), 1.21 (d, J = 6.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.90, 167.69, 139.86, 134.12, 127.01, 124.57, 121.49, 116.34, 112.44, 87.79, 80.96, 72.49, 61.49, 26.44, 21.45, 14.30. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ calcd. for $C_{18}H_{21}BrN_2O_4Na$: 431.0582; found, 431.0577.

(Z)-ethyl 2-(3-(tert-butylperoxy)-6-fluoro-3-methylindolin-2-ylidene)-2-cyanoacetate:



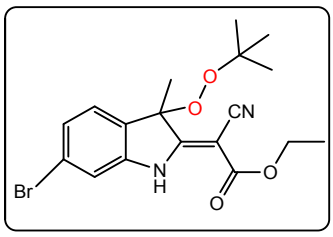
Yield 86%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.29 (dd, J = 8.2, 5.2 Hz, 1H), 6.78 (td, J = 9.3, 2.1 Hz, 1H), 6.64 (dd, J = 8.5, 2.0 Hz, 1H), 4.39 – 4.23 (m, 2H), 1.79 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.80, 167.62, 163.83, 142.15, 127.38, 124.72, 115.63, 110.02, 99.23, 87.32, 80.69, 72.93, 61.47, 26.42, 21.44, 14.28. HRMS (ESI-TOF) m/z [M + Na]$^{+}$ calcd. for $C_{18}H_{21}FN_2O_4Na$: 371.1383; found, 371.1382.

(Z)-ethyl 2-(3-(tert-butylperoxy)-6-chloro-3-methylindolin-2-ylidene)-2-cyanoacetate:



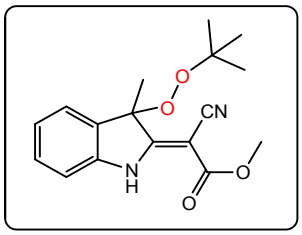
Yield 84%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.09 (d, J = 7.9 Hz, 1H), 6.94 (d, J = 1.3 Hz, 1H), 4.39 – 4.28 (m, 2H), 1.81 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 167.60, 141.91, 135.41, 130.38, 124.51, 123.56, 115.58, 111.31, 87.44, 80.79, 72.96, 61.49, 26.40, 21.38, 14.26. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{18}H_{21}ClN_2O_4Na$: 387.1087; found: 387.1081.

(Z)-ethyl 2-(6-bromo-3-(tert-butylperoxy)-3-methylindolin-2-ylidene)-2-cyanoacetate:



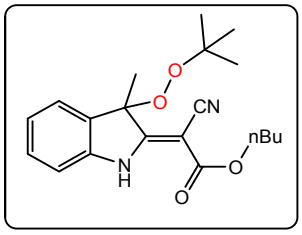
Yield 93%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s), 7.25 – 7.18 (m), 7.07 (d, J = 0.9 Hz), 4.31 (qq, J = 10.7, 7.1 Hz), 1.78 (s), 1.37 (t, J = 7.1 Hz), 1.16 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.24, 167.59, 142.09, 130.97, 126.48, 124.88, 123.18, 115.55, 114.12, 87.53, 80.82, 73.01, 61.50, 26.42, 21.36, 14.29. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{18}H_{21}BrN_2O_4Na$: 431.0582; found: 431.0577.

(Z)-methyl 2-(3-(tert-butylperoxy)-3-methylindolin-2-ylidene)-2-cyanoacetate:



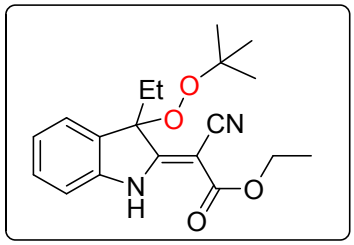
Yield 69%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (d, J = 48.9 Hz, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.11 (dd, J = 10.9, 4.2 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 3.85 (d, J = 2.1 Hz, 3H), 1.79 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.63, 168.38, 140.81, 131.99, 129.86, 123.80, 116.19, 110.86, 100.00, 88.08, 80.68, 71.46, 52.30, 26.51, 21.55. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{17}H_{20}N_2O_4Na$: 339.1321; found: 339.1315.

(Z)-butyl 2-(3-(tert-butylperoxy)-3-methylindolin-2-ylidene)-2-cyanoacetate:



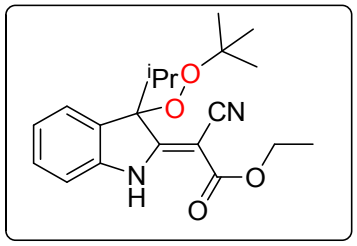
Yield 66%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s), 7.36 (d, J = 7.4 Hz), 7.28 (t), 7.10 (t, J = 7.5 Hz), 6.91 (d, J = 7.8 Hz), 4.29 – 4.20 (m), 1.81 (d, J = 6.7 Hz), 1.72 (dd, J = 15.1, 6.6 Hz), 1.46 (dd, J = 15.1, 7.5 Hz), 1.15 (d, J = 5.9 Hz), 0.96 (t, J = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.44, 168.07, 140.85, 131.95, 129.79, 123.77, 123.64, 116.08, 110.75, 88.03, 80.61, 71.77, 65.14, 30.72, 26.46, 21.47, 19.16, 13.82. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{20}H_{26}N_2O_4Na$: 381.1790; found: 381.1785.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3-ethylindolin-2-ylidene)-2-cyanoacetate:



Yield 63%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.28 (dd, J = 12.9, 5.2 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 4.36 – 4.25 (m, 2H), 2.47 – 2.08 (m, 2H), 1.38 (t, J = 7.0 Hz, 3H), 1.16 (s, 9H), 0.66 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.86, 167.98, 141.61, 130.15, 129.73, 124.09, 123.48, 115.96, 110.55, 92.22, 80.52, 71.81, 61.26, 27.58, 26.47, 14.32, 7.35. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{20}H_{26}N_2O_4Na$: 381.1790; found: 381.1786.

(Z)-ethyl 2-(3-(tert-butylperoxy)-3-isopropylindolin-2-ylidene)-2-cyanoacetate:



Yield 27%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.29 (tt, J = 4.6, 2.3 Hz, 1H), 7.08 (td, J = 7.5, 0.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 4.36 – 4.25 (m, 2H), 2.87 (dt, J = 13.5, 6.8 Hz, 1H), 1.38 (t, J = 7.1 Hz, 3H), 1.21 (d, J = 6.7 Hz, 3H), 1.18 (s, 9H), 0.54 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.55, 168.15, 141.91, 129.62, 128.10, 125.68, 122.88, 116.10, 110.62, 94.43, 80.59, 71.25, 61.24, 33.55, 26.51, 16.66, 16.30, 14.33. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{20}H_{26}N_2O_4Na$: 381.1790; found: 381.1785.

1.3 *Experimental procedure for the reactions shown in the Scheme 2.*

(a) A mixture of 3-methylindole (1.50 g, 11.5 mmol), ethyl cyanoacetate (6.45 g, 57.5 mmol), *tert*-butyl hydroperoxide (5.19 g, 57.5 mmol) and potassium iodide (0.16 g, 1.15 mmol) in MeCN (35 mL) was stirred at 100 °C for 12 h under N_2 atmosphere. After cooling to room temperature, the mixture was diluted with dichlormethane (20 mL) and the solution was filtered. The solvent of filtrate was removed in *vacuo* to leave an oily residue, which was purified on a silica gel column eluted with petroleum ether/acetone (4:1 v/v) to afford the product **3a** in yield 78% (2.94 g).

(b) A mixture of compound **3a** (66 mg, 0.2 mmol) and Zn powder (65 mg, 1.0 mmol) in AcOH (0.5 mL) was stirred at 70 °C for 6 h in air. After cooling to room temperature, the mixture was diluted with water (5 mL) and the pH value of solution was adjusted to *ca*. 8 by NaOH (1 M). The resultant solution was extracted with Et_2O (3 × 20 mL). The solvent of filtrate was removed *in vacuo* to leave an oily residue, which was purified on a silica gel column eluted with petroleum ether/ acetone (2:1 v/v) to afford the compound **3b** as solid (31g, 60%). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 10.62 – 10.34 (m, 1H), 7.45 (d, J = 7.4 Hz, 1H), 7.29 (tt, J = 5.9, 3.0 Hz, 1H), 7.13 (t, J = 7.3 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 4.33 – 4.22 (m, 2H), 3.31 (s, 1H), 1.89 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.15, 167.52, 140.19, 133.51, 130.18, 124.33, 123.57, 116.75, 111.06, 80.62, 71.05, 61.43, 25.85, 14.32. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd. for $C_{14}H_{14}N_2O_3Na$: 281.0902; found: 281.0899.

(c) A mixture of 3-methylindole (26.2 mg, 0.2 mmol), *tert*-butyl hydroperoxide (5 M in decane, 0.12 mL, 0.6 mmol) and potassium iodide (3.3 mg, 0.02 mmol) in MeCN/$MeNO_2$ (1 mL/0.1 mL) was stirred for 24 h at 100 °C under N_2 atmosphere. After cooling to room temperature, the reaction mixture was diluted with dichlormethane (5 mL), filtered and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/acetone (2:1 v/v) to afford the compound **3c** as solid (17.4 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 48.0 Hz, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 1.54 (s, 3H), 1.11 (d, J = 4.6 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.63, 140.72, 130.05, 129.39, 124.26, 122.43, 110.08, 82.25, 80.41, 26.44, 20.31. A mixture of compound **3c** (47 mg, 0.2 mmol) and Zn powder (65 mg, 1.0 mmol) in AcOH (0.5 mL) was stirred at 70 °C for 6 h in air. After cooling to room temperature, the mixture was diluted with water (5 mL) and the pH value of solution was adjusted to *ca*. 8 by NaOH (1 M). The resultant solution was extracted with Et_2O (3 × 20 mL). The solvent of filtrate was removed *in vacuo* to leave an oily residue, which was purified on a silica gel column eluted with petroleum ether/acetone (2:1 v/v) to afford the compound **3d** as solid (20.6 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s), 7.37 (d, J = 7.3 Hz), 7.25 – 7.18 (m), 7.06 (t, J = 7.5 Hz), 6.88 (d, J = 7.7 Hz), 3.87 (d, J = 38.0 Hz), 1.58 (d, J = 7.8 Hz); 13C NMR (101 MHz, CDCl3) δ 181.36, 139.86, 132.01, 129.59, 123.80, 123.26, 110.57, 74.13, 24.69.

(d) To a solution of **1a** (26.2 mg, 0.2 mmol), **2a** (113 mg, 1.0 mmol), *tert*-butyl hydroperoxide (5 M in decane, 0.2 mL, 1.0 mmol), and potassium iodide (3.3 mg, 0.02 mmol) in MeCN (0.5 mL) was added TEMPO (94 mg, 0.6 mmol). The mixture was stirred for 12 h at 100 °C under N_2 atmosphere. The mixture was diluted with dichlormethane (5 mL) and filtered. No signal of the target compound **3a** could be found on the TLC plate of mother solution.

(e) A solution of 3-methylindole (26.2 mg, 0.2 mmol), *tert*-butyl hydroperoxide (5 M in decane, 0.2 mL, 1.0 mmol), and potassium iodide (3.3 mg, 0.02 mmol) in MeCN (0.5 mL) was stirred for 12 h at 100 °C under N_2 atmosphere. The mixture was diluted with dichlormethane (5 mL) and filtered. The solvent of filtrate was removed in *vacuo* to leave an oily residue, which was purified on a silica gel column eluted with petroleum ether/ethyl acetate (4:1 v/v) to afford the compound **3e** as solid (15.3 mg, 47%). ^{1}H NMR (400 MHz, CDCl3) δ 11.62 (s, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.50 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 2.68 (s, 3H).

(f) A solution of ethyl cyanoacetate (113 mg, 1.0 mmol), *tert*-butyl hydroperoxide (5 M in decane, 0.2 mL, 1.0 mmol), and potassium iodide (3.3 mg, 0.02 mmol) in MeCN (0.5 mL) was stirred for 12 h at 100 °C under N_2 atmosphere. The mixture was diluted with dichlormethane (5 mL) and filtered. No signal of any new compound could be found on the TLC plate of mother solution. The starting material ethyl cyanoacetate was recovered.

2. X-ray Structure Determinations

Diffraction data were collected on an Oxford Diffraction Supernova dual diffractometer equipped with an Oxford Cryostream 700 low-temperature apparatus. Cu K\a radiation source (λ = 1.54184 Å) was used for the data collection. Single crystals were coated with paratone-N oil and mounted on a nylon loop for diffraction. The data reduction and cell refinement were processed using CrysAlisPro software.[6] Structures were solved by direct methods using the SHELXTL program packages.[7] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added geometrically. Crystal data and refinement details were given in Table S1. Other refinement details and explanations were included in individual CIF files.

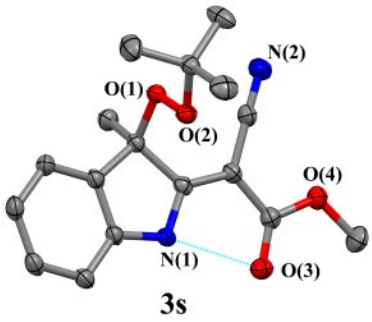


Figure S1. Crystal structure of compound **3s** with all non-hydrogen atoms shown as 50% probability ellipsoids.

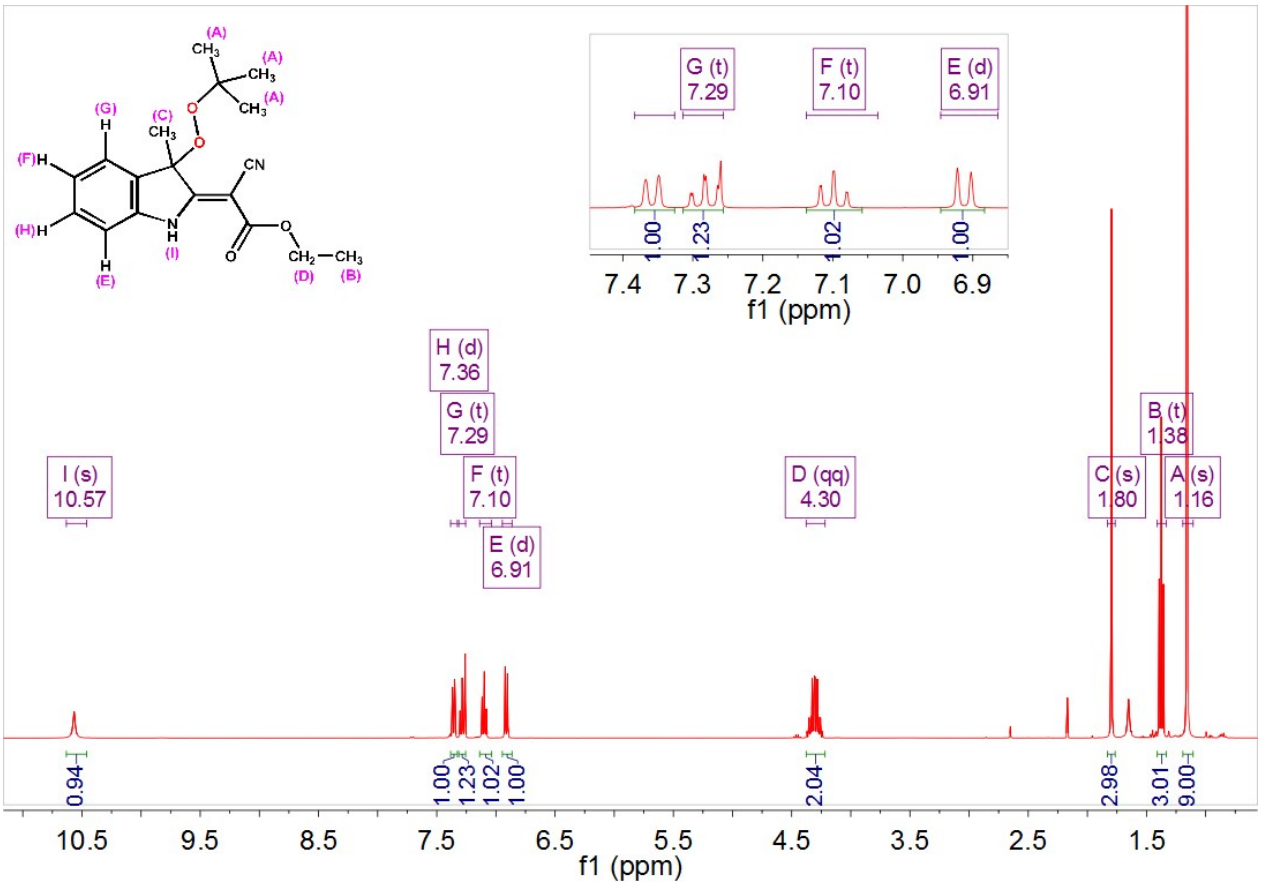
Table S1. Crystallographic data[a] for compounds **3a** (CCDC: 2064845), **3o** (CCDC: 2067966) and **3s** (CCDC: 2064846).

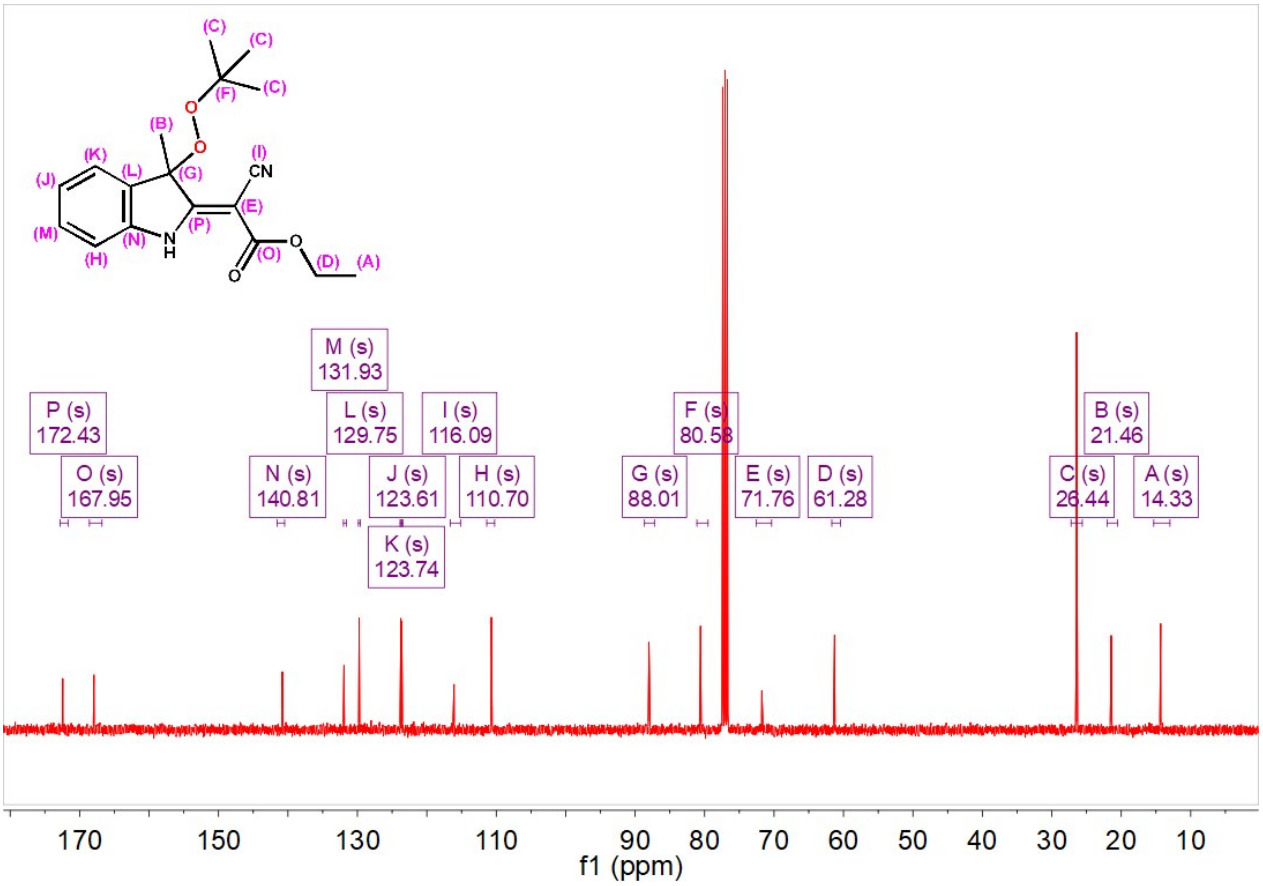
	3a	**3o**[b]	**3s**
formula	$C_{18}H_{22}N_2O_4$	$C_{19}H_{24}N_2O_4$	$C_{17}H_{20}N_2O_4$
M	330.38	344.40	316.35
crystal system	Monoclinic	triclinic	Monoclinic
space group	P21/n	P-1	P21/n
a, Å	9.0953(3)	9.9866(6)	8.7888(4)
b, Å	19.6563(5)	10.4170(6)	19.6193(8)
c, Å	10.0974(4)	10.4938(8)	10.0883(4)
α , deg	90.00	101.921(6)	90.00
β , deg	109.550(4)	111.131(7)	109.798(5)
γ , deg	90.00	105.454(5)	90.00
V, Å^3	1701.14(10)	924.17(11)	1636.71(12)
Z	4	2	4
μ, mm^{-1}	0.751	0.711	0.758
independent data	3204	3569	3082
refined parameters	217	226	208

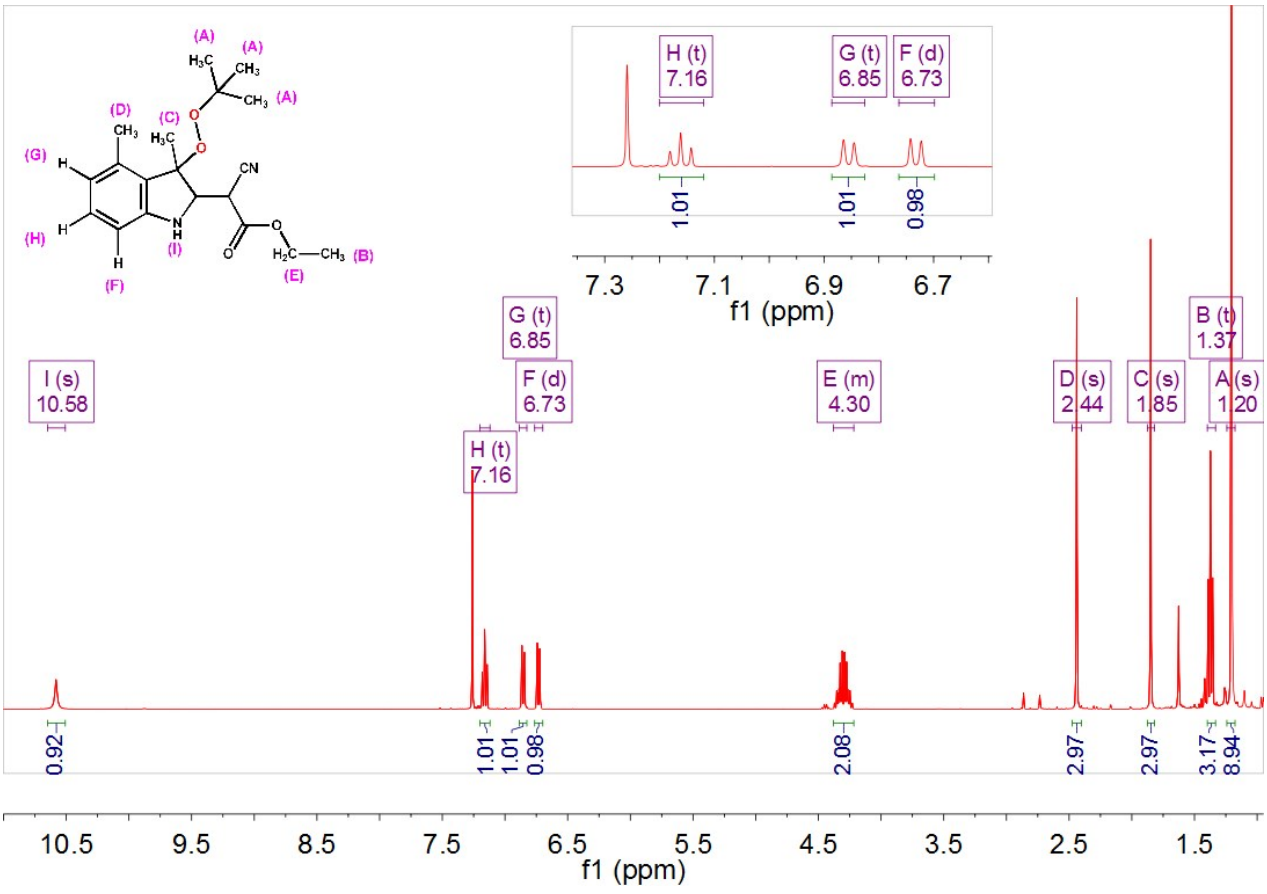
R_1[c], wR_2[d] ($I > 2\sigma(I)$)	0.0396, 0.0941	0.0615, 0.1605	0.0439, 0.1155
R_1, wR_2 (all data)	0.0524, 0.1008	0.0748, 0.1738	0.0565, 0.1228

[a]T = 150(2) K, Cu Kα radiation (λ = 1.54184 Å). [b]T = 293(2) K. [c]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d]$wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

3. ^{1}H NMR and ^{13}C NMR spectra of compounds




P (s) 172.43
O (s) 167.95
M (s) 131.93
L (s) 129.75
I (s) 116.09
N (s) 140.81
J (s) 123.61
H (s) 110.70
K (s) 123.74
F (s) 80.58
G (s) 88.01
E (s) 71.76
D (s) 61.28
B (s) 21.46
C (s) 26.44
A (s) 14.33
170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)


H (t) 7.16
G (t) 6.85
F (d) 6.73
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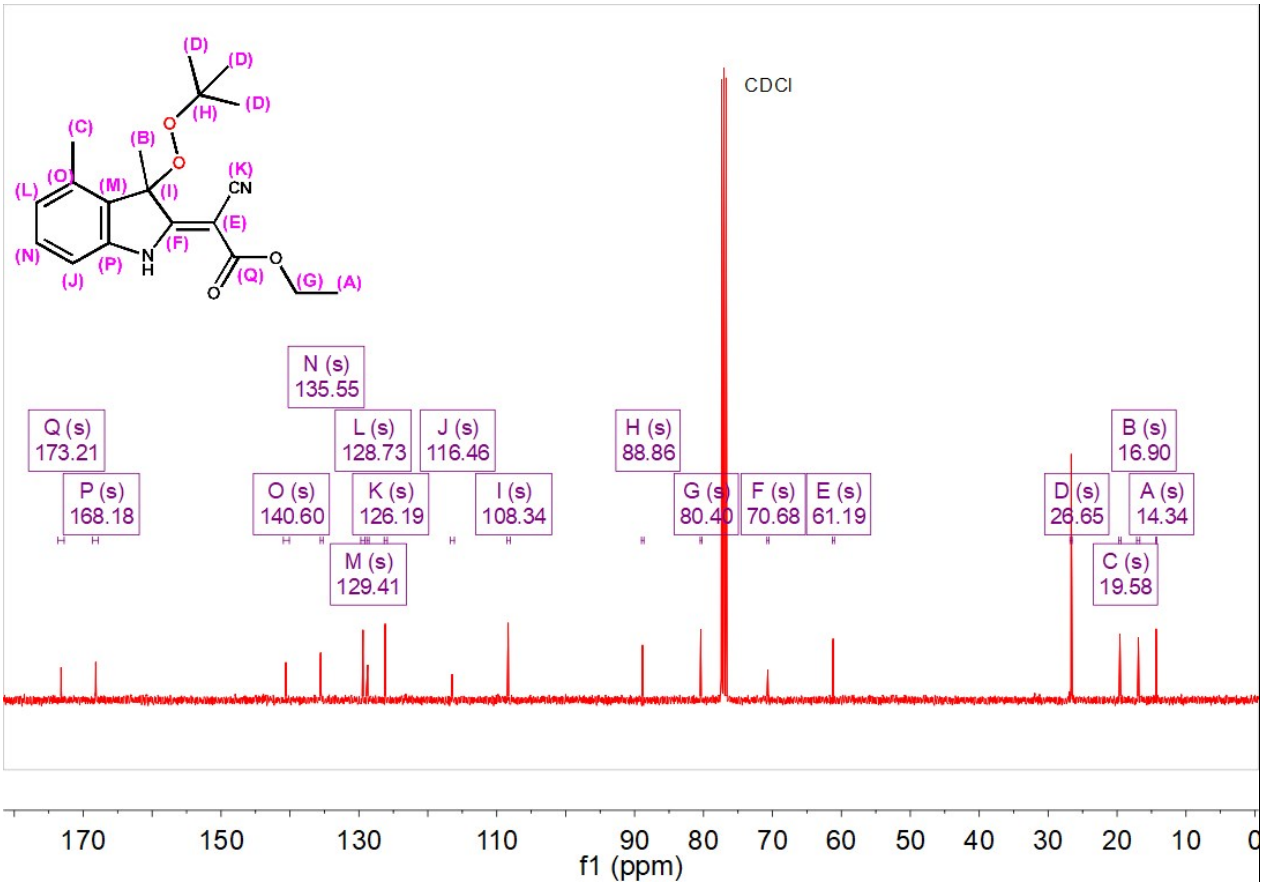
1.01
0.98
7.3 7.1 6.9 6.7
f1 (ppm)
I (s) 10.58
G (t) 6.85
F (d) 6.73
H (t) 7.16
E (m) 4.30
D (s) 2.44
C (s) 1.85
B (t) 1.37
A (s) 1.20
0.92
1.01
1.01
0.98
2.08
2.97
2.97
3.17
8.94
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)


CDCl
N (s) 135.55
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J (s) 116.46
H (s) 88.86
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P (s) 168.18
O (s) 140.60
K (s) 126.19
I (s) 108.34
G (s) 80.40
F (s) 70.68
E (s) 61.19
D (s) 26.65
A (s) 14.34
M (s) 129.41
C (s) 19.58
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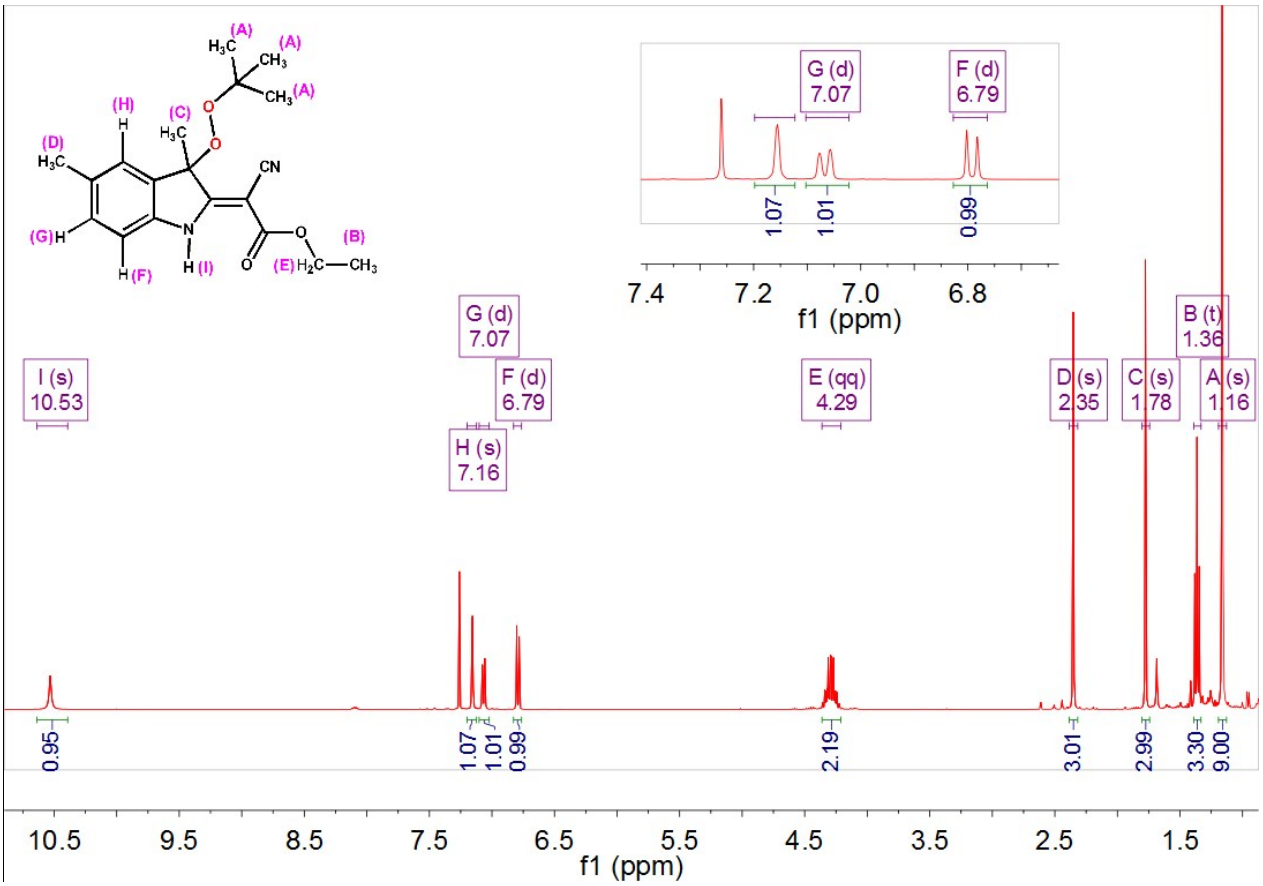
f1 (ppm)


G (d) 7.07
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1.01
0.99
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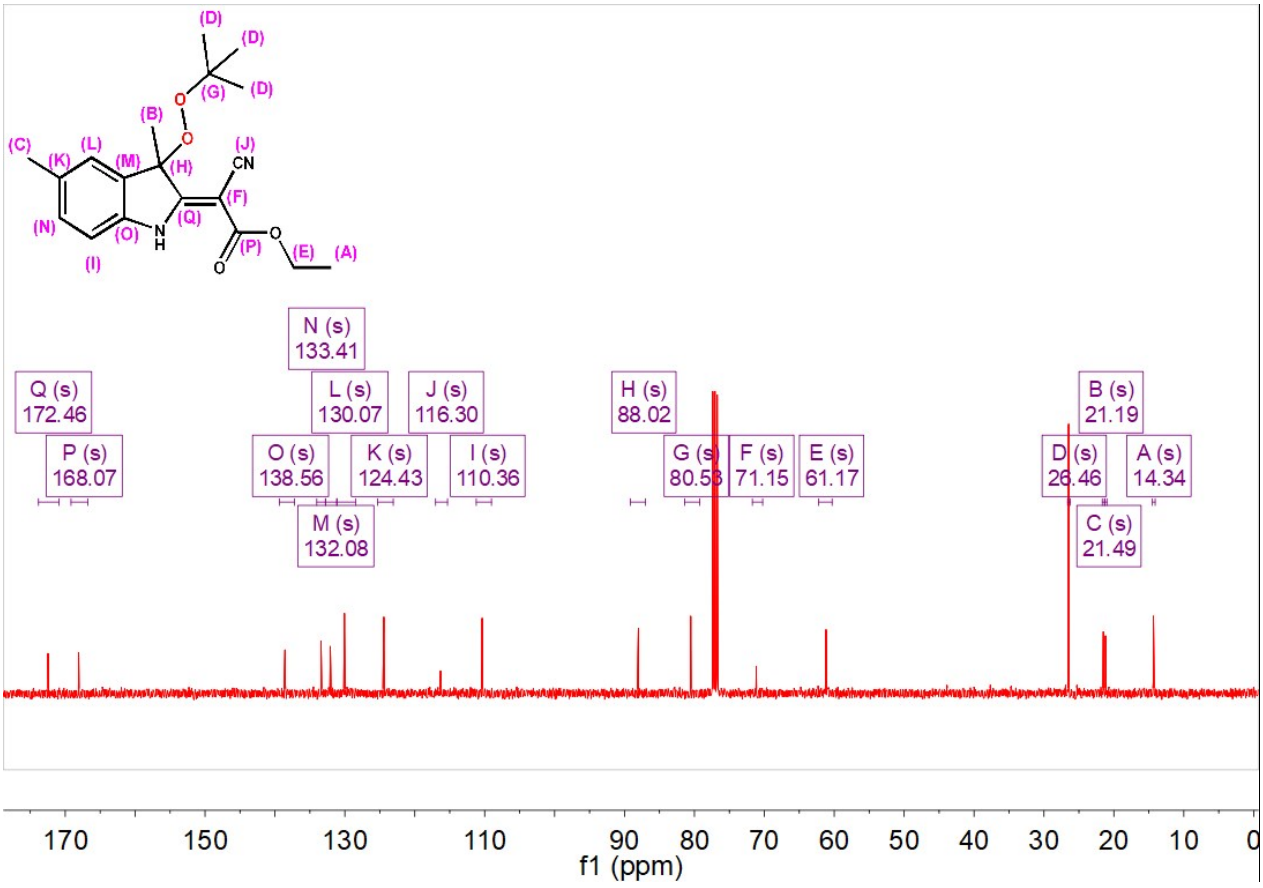
f1 (ppm)
I (s) 10.53
G (d) 7.07
F (d) 6.79
H (s) 7.16
E (qq) 4.29
D (s) 2.35
C (s) 1.78
B (t) 1.36
A (s) 1.16
0.95
1.07
1.01
0.99
2.19
3.01
2.99
3.30
9.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)


N (s)
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Q (s)
172.46
L (s)
130.07
J (s)
116.30
H (s)
88.02
B (s)
21.19
P (s)
168.07
O (s)
138.56
K (s)
124.43
I (s)
110.36
G (s)
80.53
F (s)
71.15
E (s)
61.17
D (s)
26.46
A (s)
14.34
M (s)
132.08
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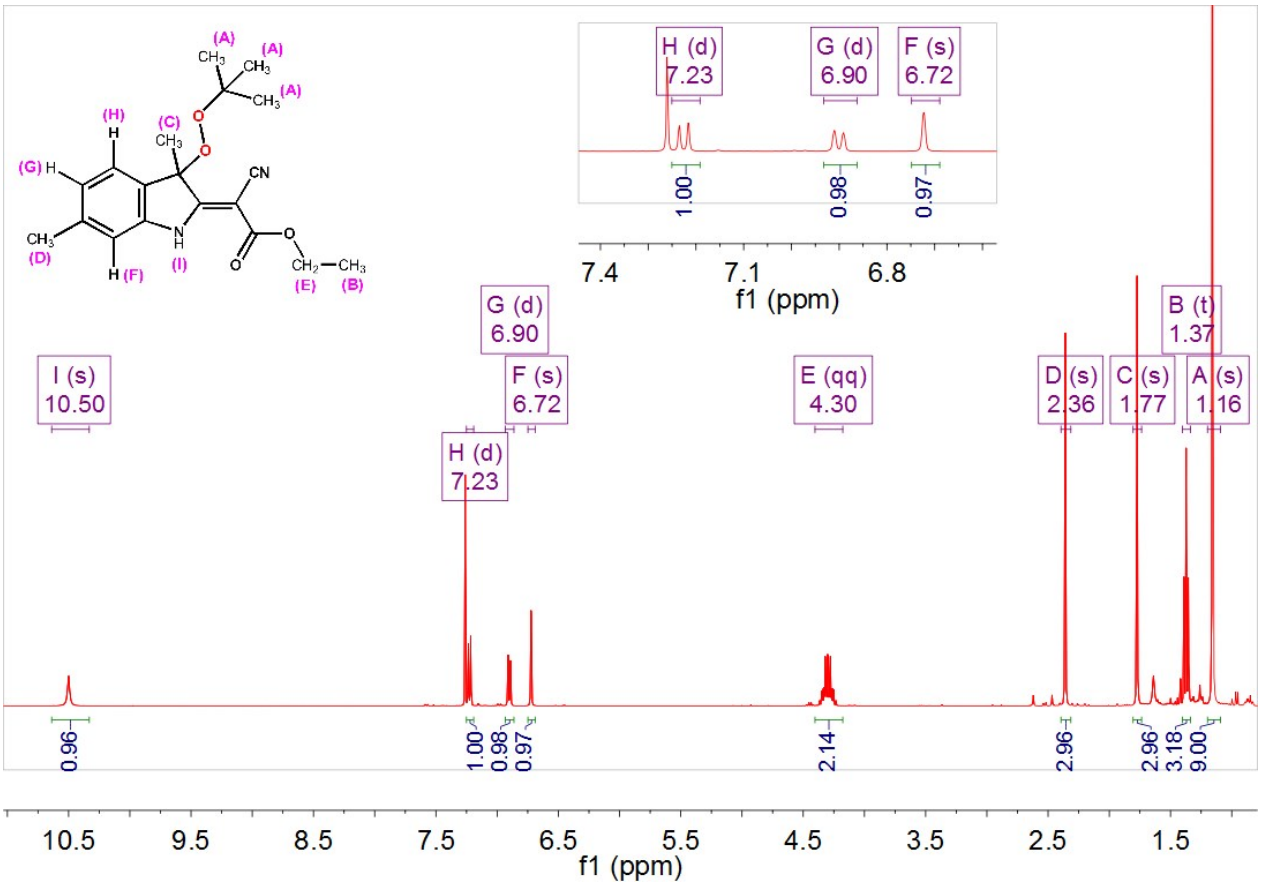
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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F (s)
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0.97
7.4
7.1
6.8
f1 (ppm)
G (d)
6.90
B (t)
1.37
I (s)
10.50
F (s)
6.72
E (qq)
4.30
D (s)
2.36
C (s)
1.77
A (s)
1.16
H (d)
7.23
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1.00
0.98
0.97
2.14
2.96
2.96
3.18
9.00
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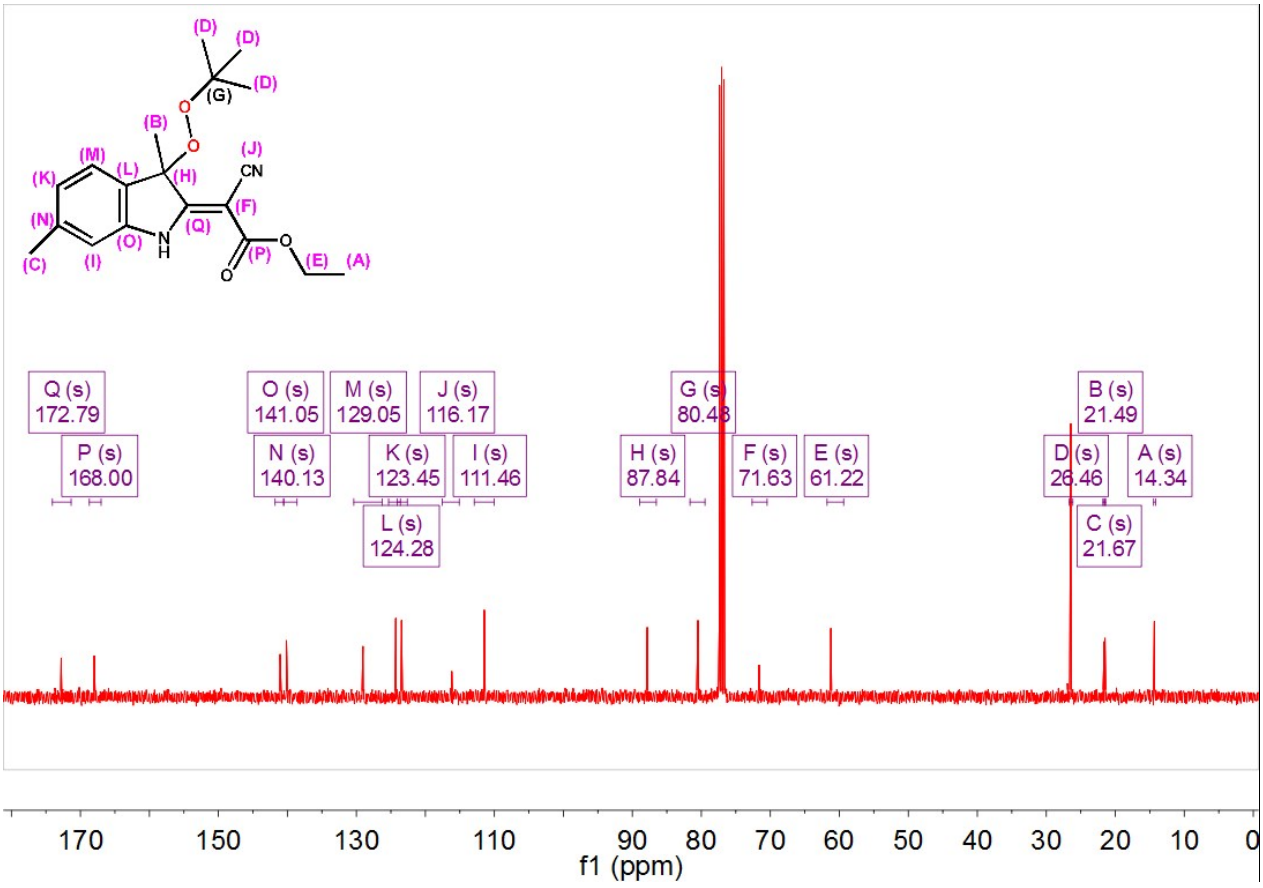
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
f1 (ppm)


Q (s) 172.79
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O (s) 141.05
N (s) 140.13
M (s) 129.05
K (s) 123.45
L (s) 124.28
J (s) 116.17
I (s) 111.46
G (s) 80.48
H (s) 87.84
F (s) 71.63
E (s) 61.22
B (s) 21.49
D (s) 26.46
C (s) 21.67
A (s) 14.34
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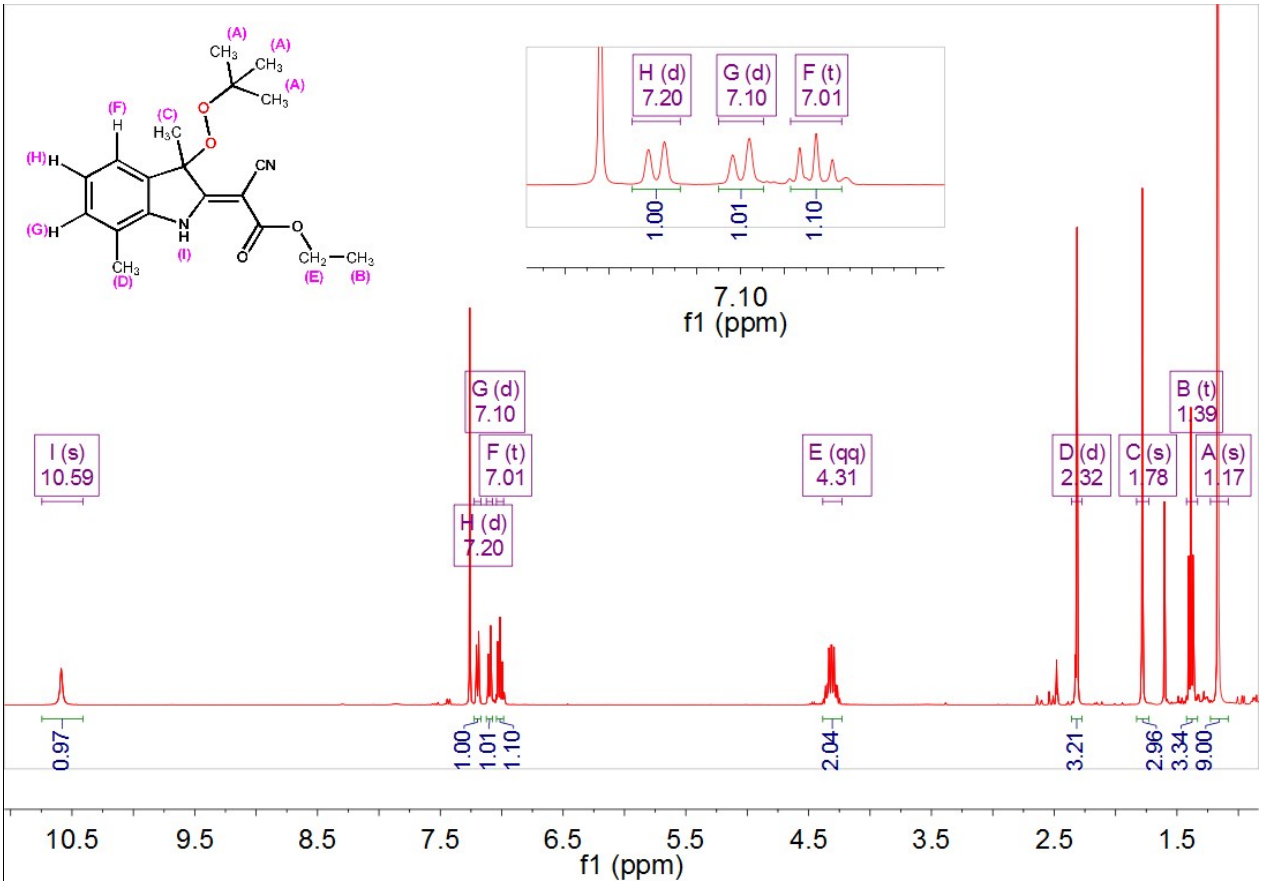
f1 (ppm)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G (d) 7.10
F (t) 7.01
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1.01
1.10
7.10
f1 (ppm)
I (s) 10.59
G (d) 7.10
F (t) 7.01
H (d) 7.20
E (qq) 4.31
D (d) 2.32
C (s) 1.78
B (t) 1.39
A (s) 1.17
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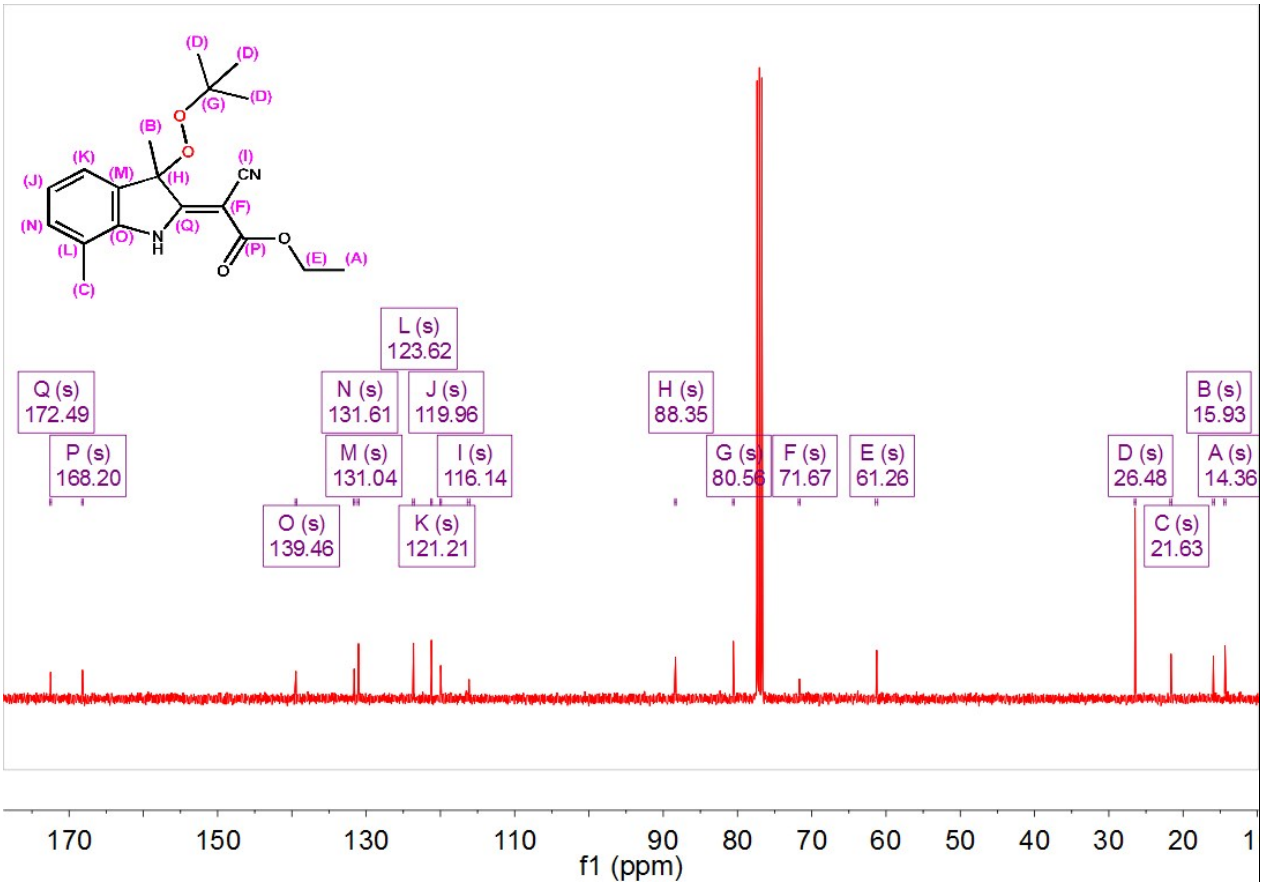
1.00
1.01
1.10
2.04
3.21
2.96
3.34
9.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)


(D)
(D)
(D)
(G)
(B)
O
O
(K)
(M)
(H)
(I)
CN
(J)
(F)
(N)
(O)
N
H
(Q)
(L)
O
(P)
(E)
(A)
(C)
L (s)
123.62
Q (s)
172.49
N (s)
131.61
J (s)
119.96
H (s)
88.35
B (s)
15.93
P (s)
168.20
M (s)
131.04
I (s)
116.14
G (s)
80.56
F (s)
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E (s)
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D (s)
26.48
A (s)
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O (s)
139.46
K (s)
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C (s)
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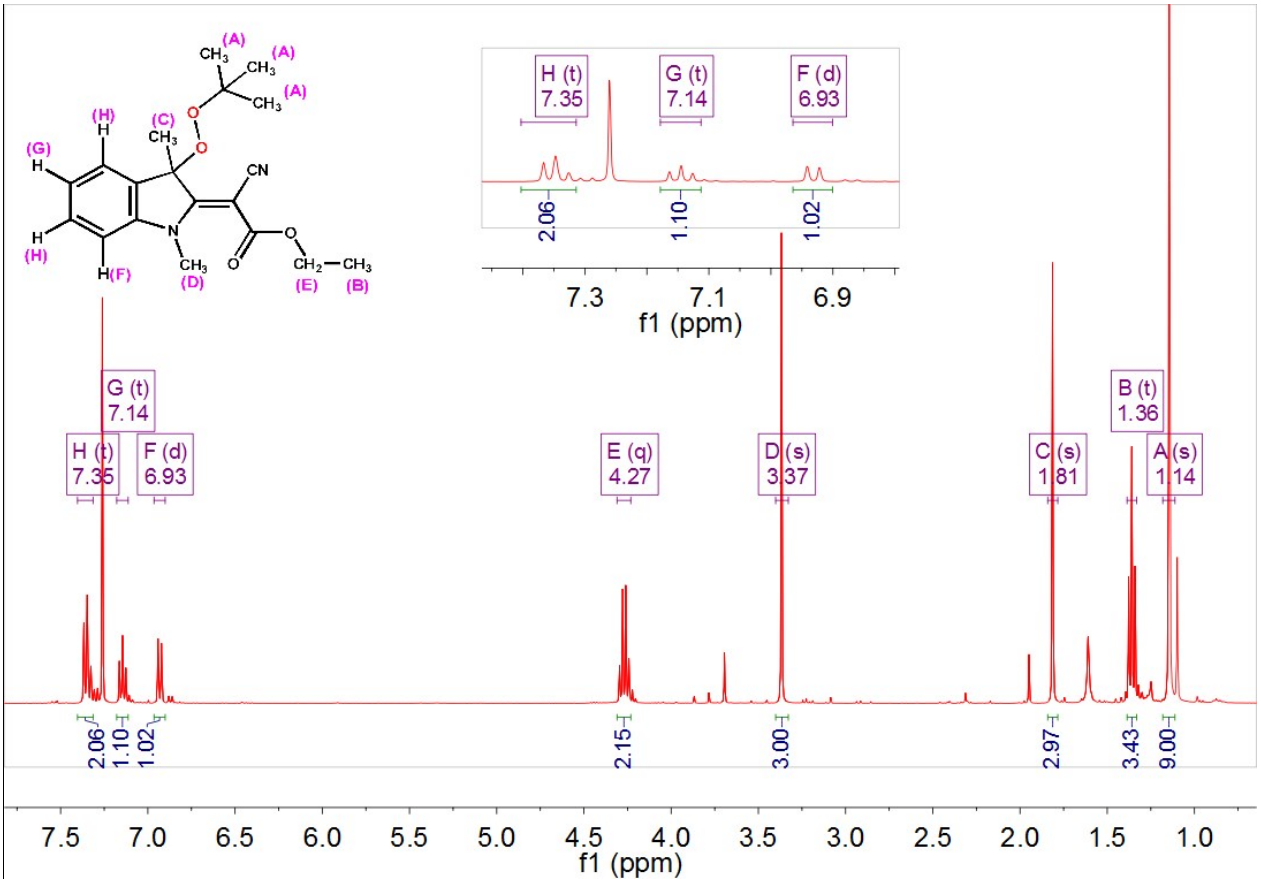
150
130
110
90
80
70
60
50
40
30
20
1
f1 (ppm)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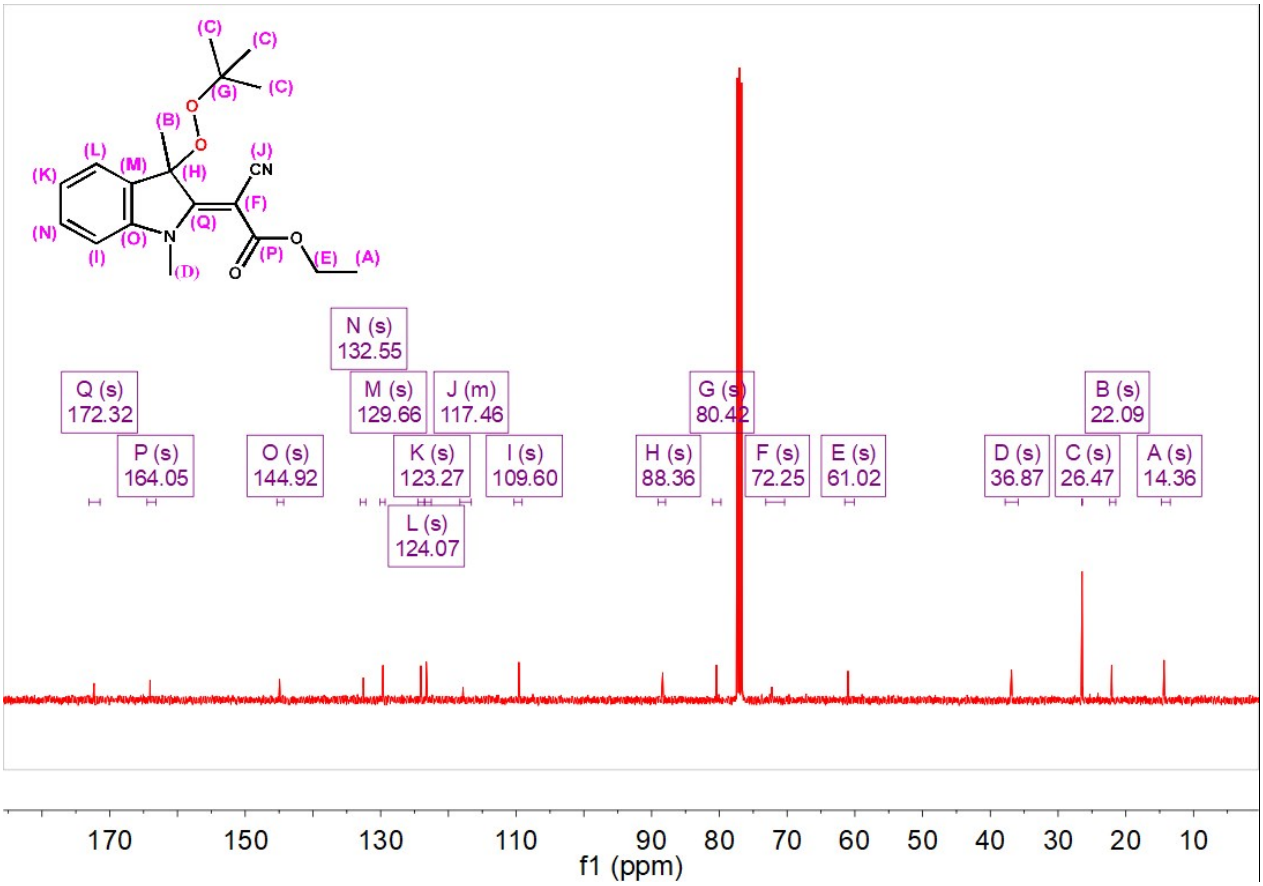
CH3
(A)
CH3
(A)
(H)
H
(C)
CH3
O
O
(G)
H
CN
N
O
H
(H)
CH3
(D)
O
CH2
CH3
(E)
(B)
H(F)
H (t)
7.35
G (t)
7.14
F (d)
6.93
2.06
1.10
1.02
7.3
7.1
6.9
f1 (ppm)
G (t)
7.14
H (t)
7.35
F (d)
6.93
E (q)
4.27
D (s)
3.37
B (t)
1.36
C (s)
1.81
A (s)
1.14
2.06
1.10
1.02
2.15
3.00
2.97
3.43
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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M (s) 129.66
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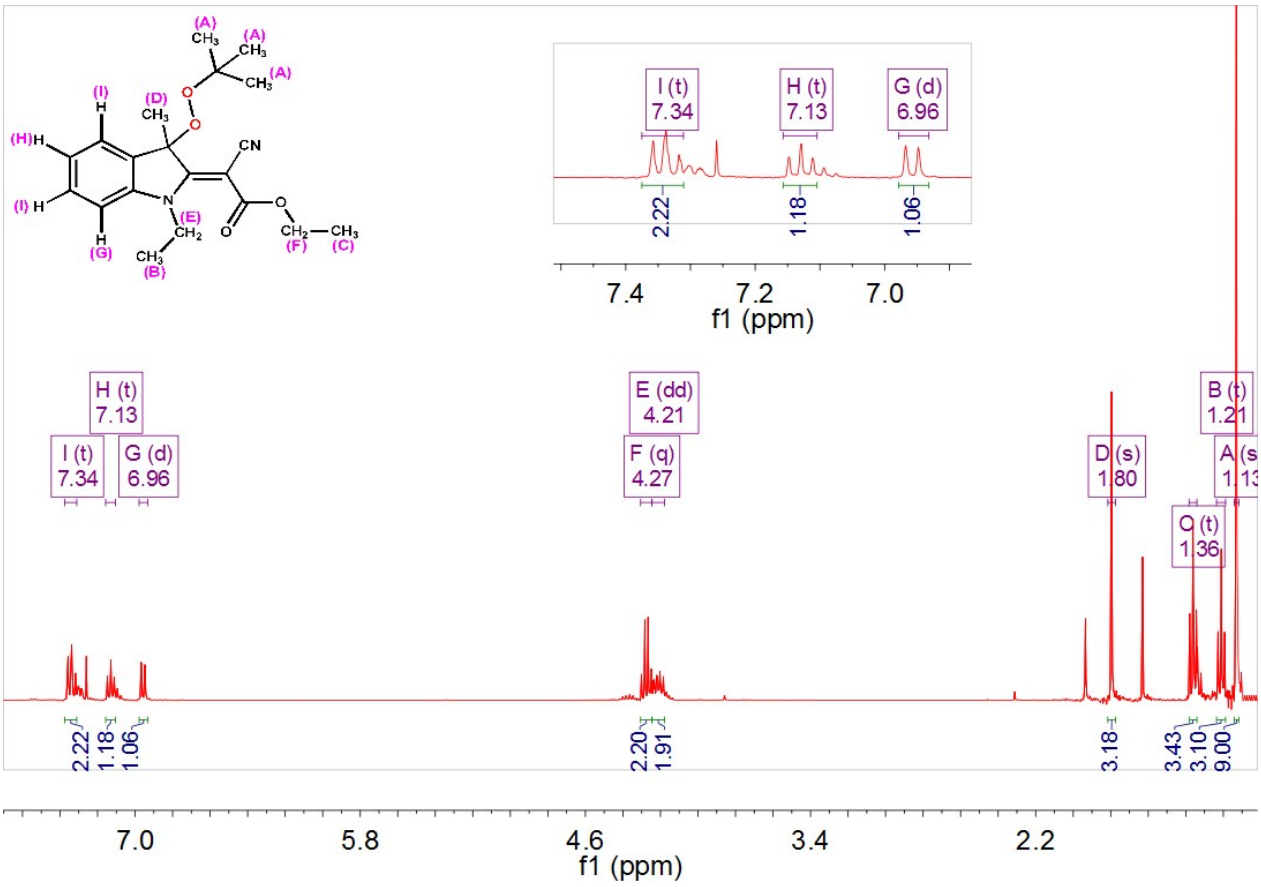
G (s) 80.42
B (s) 22.09
P (s) 164.05
O (s) 144.92
K (s) 123.27
I (s) 109.60
H (s) 88.36
F (s) 72.25
E (s) 61.02
D (s) 36.87
C (s) 26.47
A (s) 14.36
L (s) 124.07
170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)


I (t) 7.34
H (t) 7.13
G (d) 6.96
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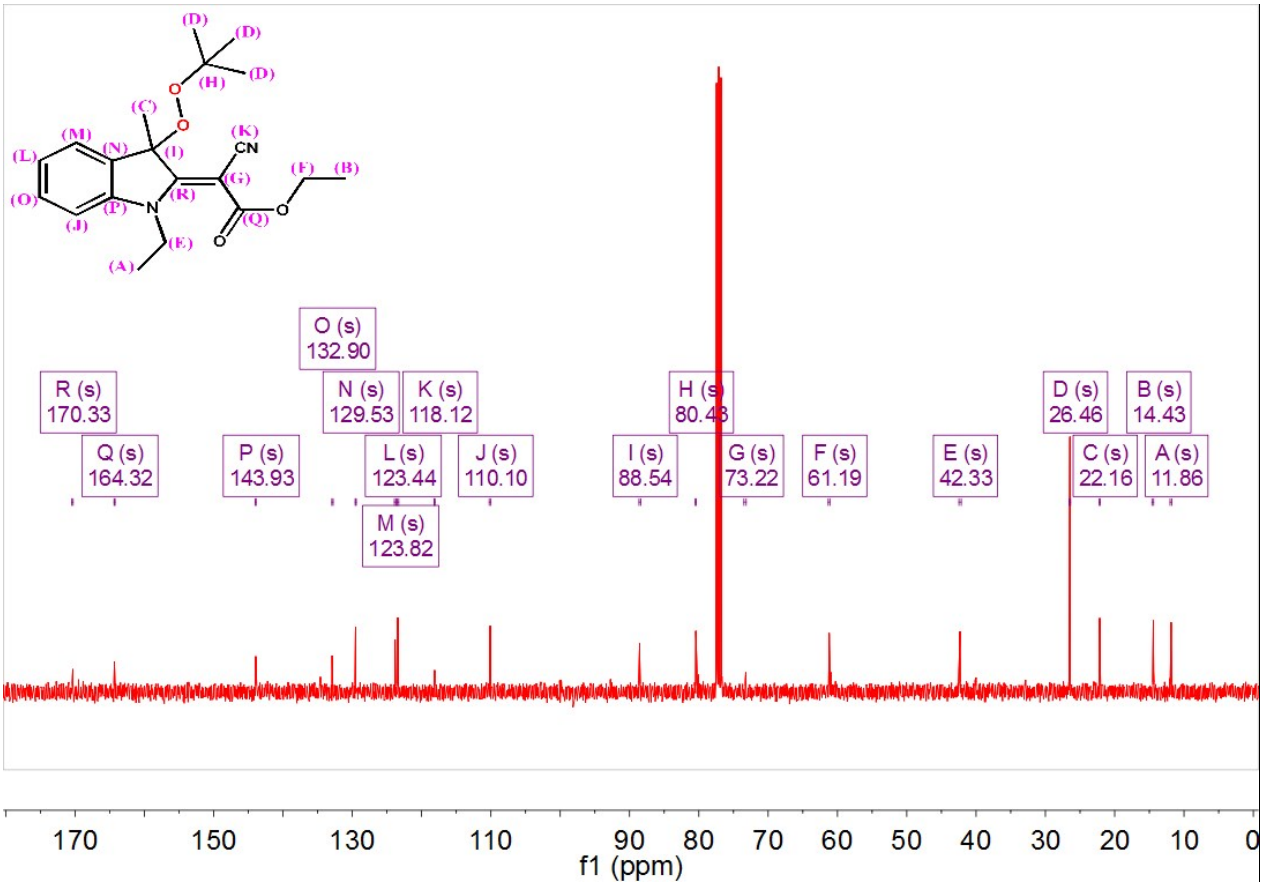
1.18
1.06
7.4 7.2 7.0
f1 (ppm)
H (t) 7.13
I (t) 7.34
G (d) 6.96
E (dd) 4.21
F (q) 4.27
D (s) 1.80
B (t) 1.21
Q (t) 1.36
2.22
1.18
1.06
2.20
1.91
3.18
3.43
3.10
9.00
7.0 5.8 4.6 3.4 2.2
f1 (ppm)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Q (s) 164.32
P (s) 143.93
O (s) 132.90
N (s) 129.53
K (s) 118.12
L (s) 123.44
M (s) 123.82
J (s) 110.10
I (s) 88.54
H (s) 80.48
G (s) 73.22
F (s) 61.19
E (s) 42.33
D (s) 26.46
C (s) 22.16
B (s) 14.43
A (s) 11.86
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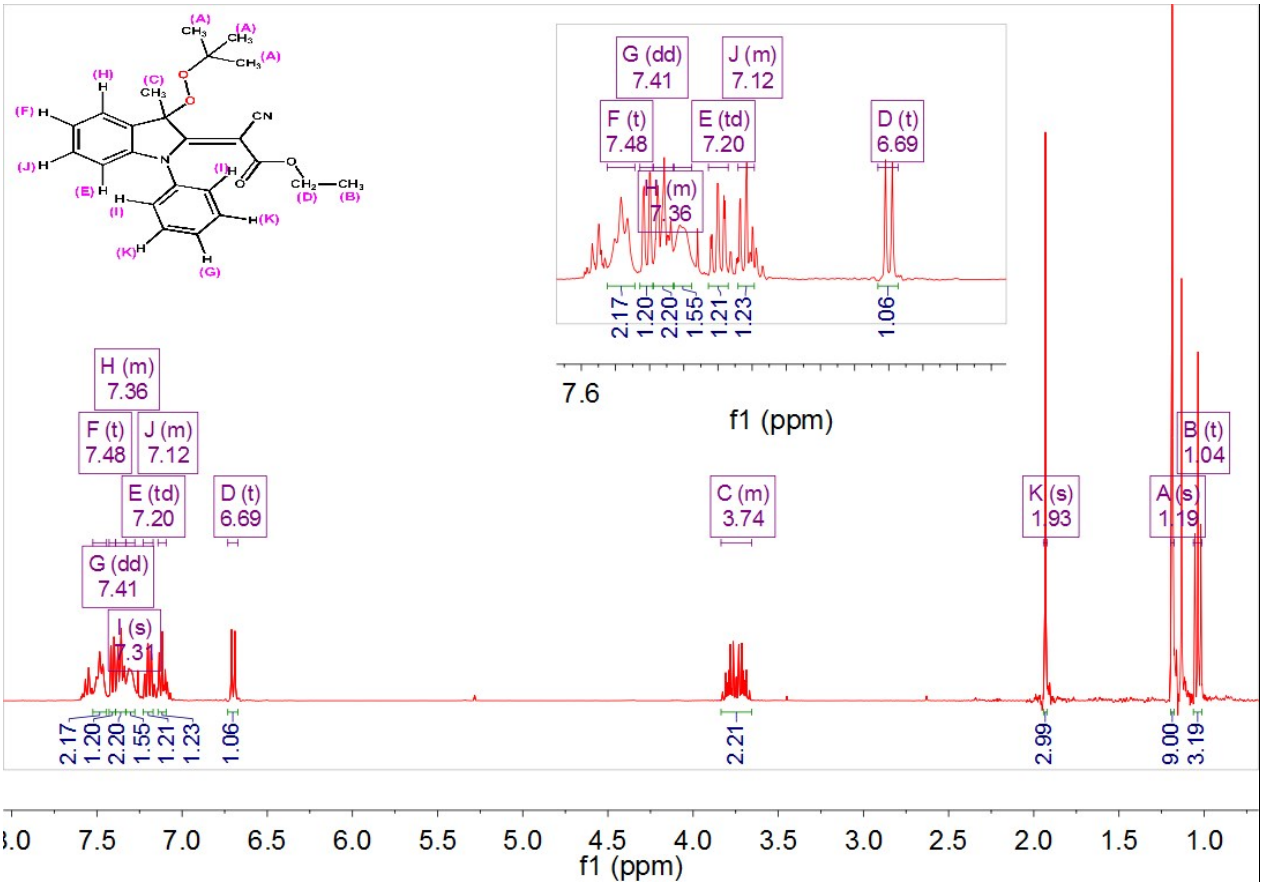
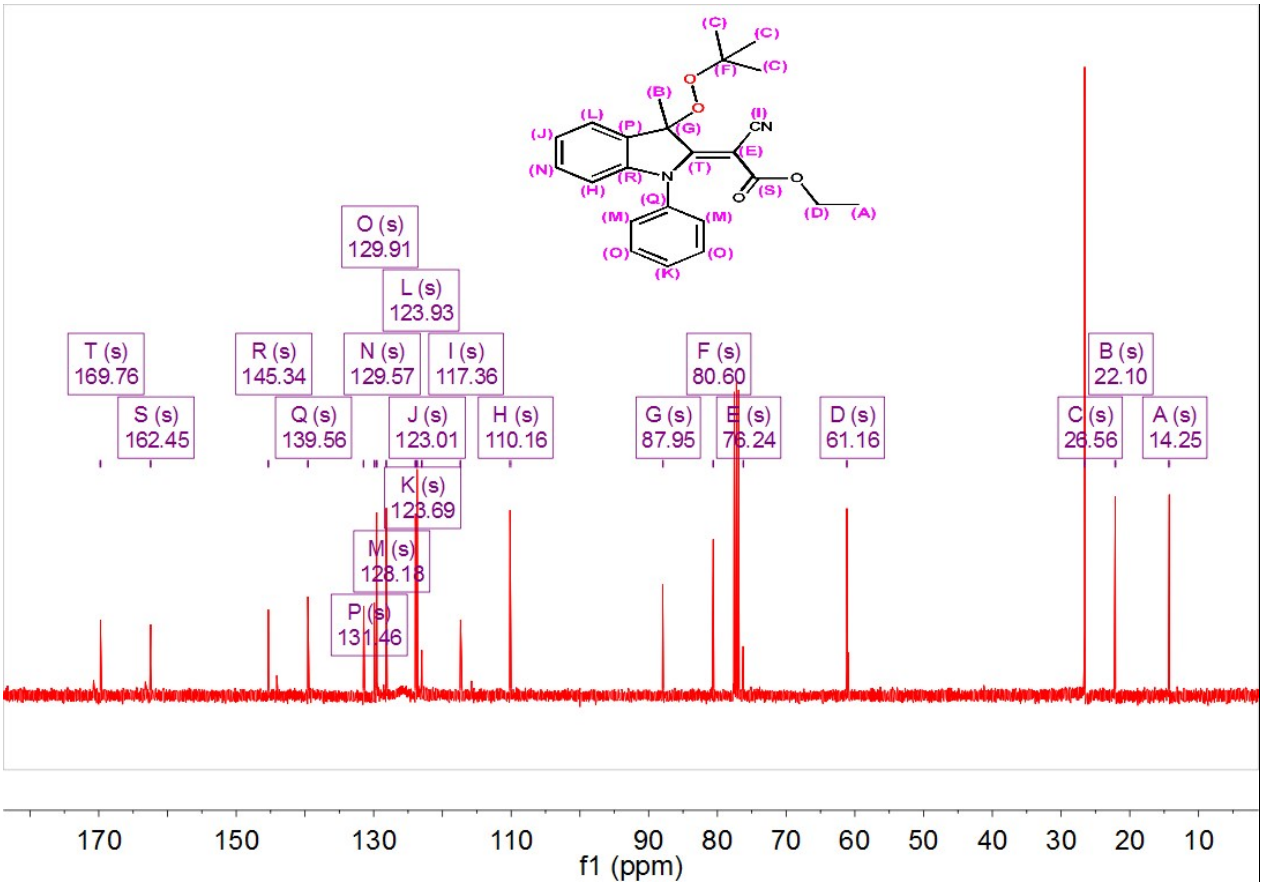
f1 (ppm)


G (dd) 7.41
J (m) 7.12
F (t) 7.48
E (td) 7.20
H (m) 7.36
D (t) 6.69
2.17 1.20 2.20 1.55 1.21 1.23 1.06
7.6
f1 (ppm)
H (m) 7.36
F (t) 7.48
J (m) 7.12
E (td) 7.20
D (t) 6.69
G (dd) 7.41
I (s) 7.3
C (m) 3.74
K (s) 1.93
B (t) 1.04
A (s) 1.19
2.17 1.20 2.20 1.55 1.21 1.23 1.06 2.21 2.99 9.00 3.19
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
f1 (ppm)


O (s) 129.91
L (s) 123.93
T (s) 169.76
R (s) 145.34
N (s) 129.57
I (s) 117.36
F (s) 80.60
B (s) 22.10
S (s) 162.45
Q (s) 139.56
J (s) 123.01
H (s) 110.16
G (s) 87.95
E (s) 76.24
D (s) 61.16
C (s) 26.56
A (s) 14.25
K (s) 123.69
M (s) 128.18
P (s) 131.46
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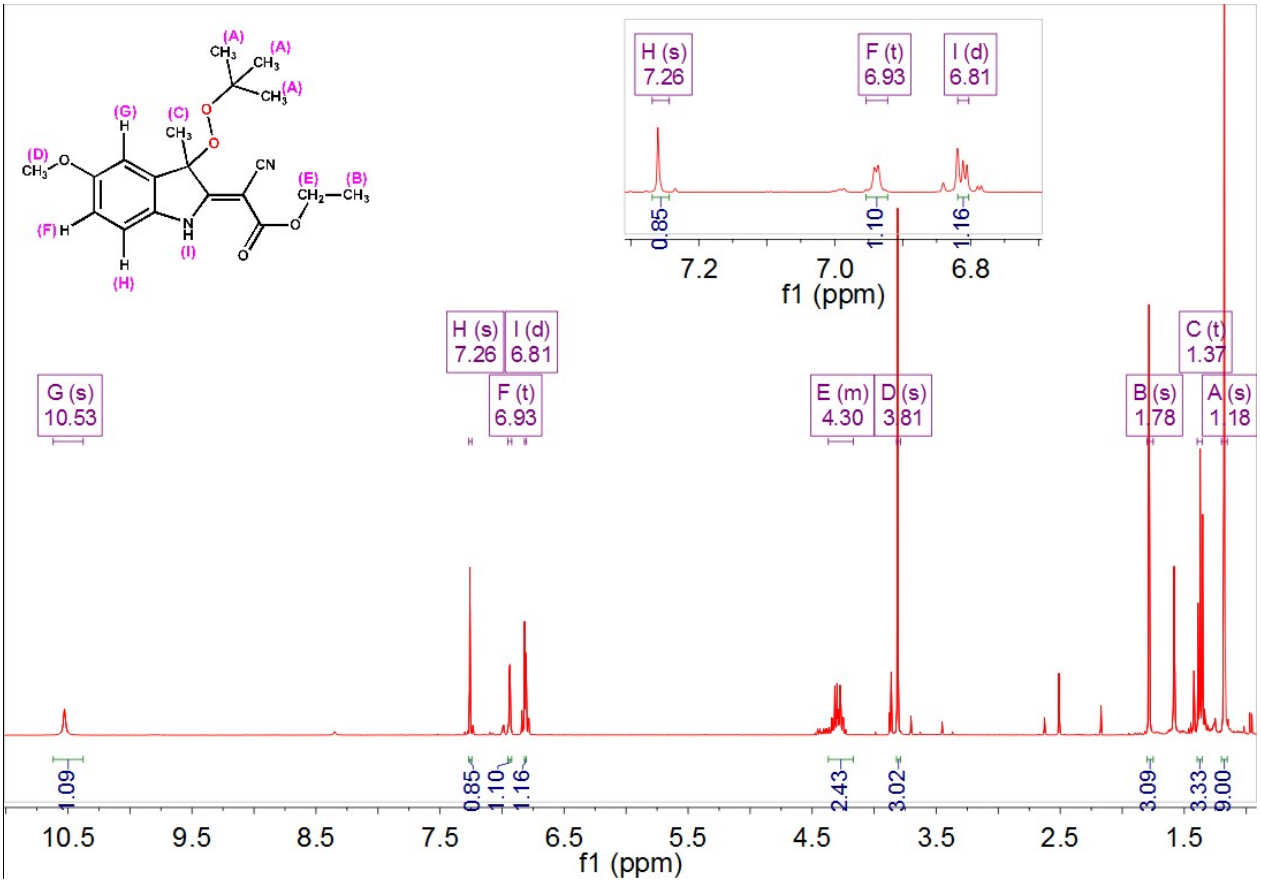
f1 (ppm)


H (s) 7.26
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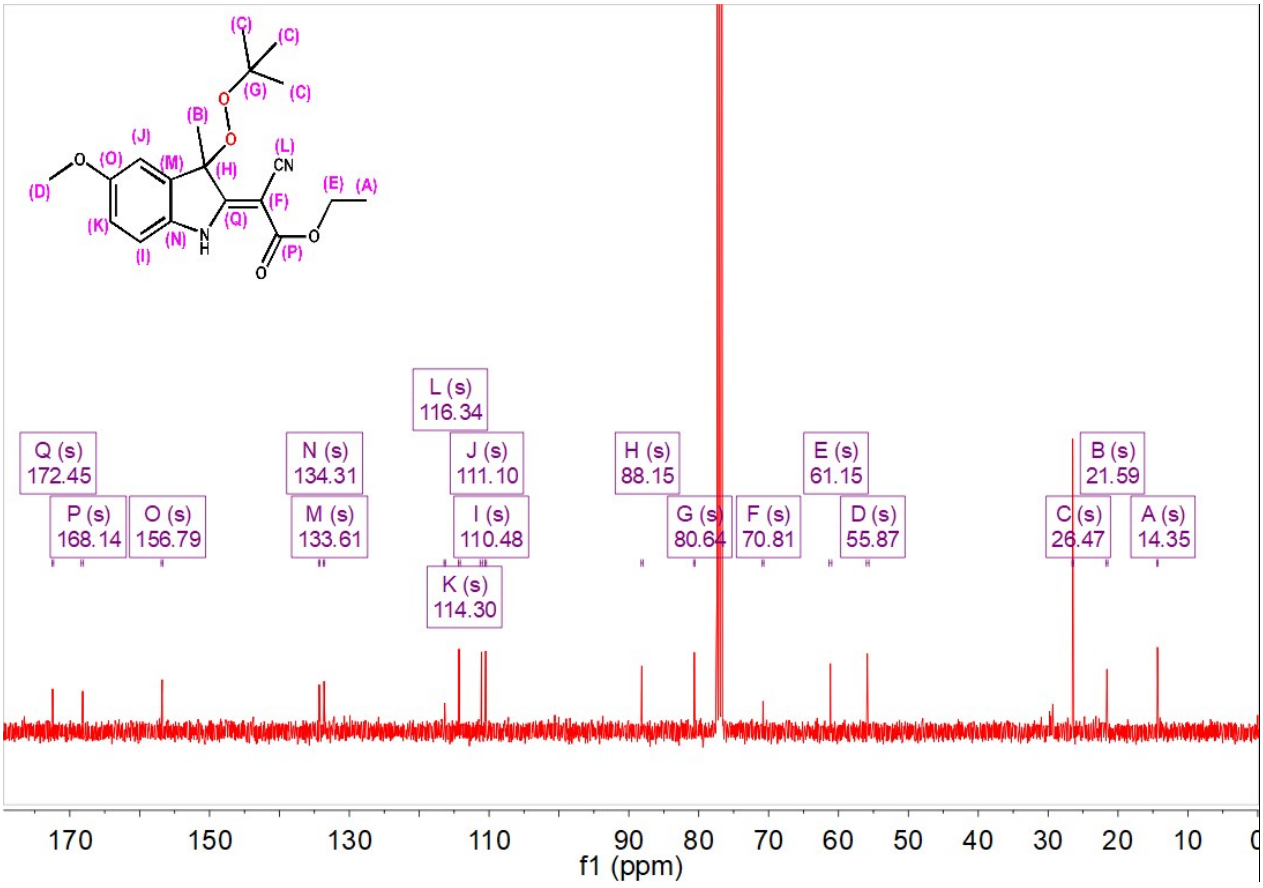
I (d) 6.81
0.85
1.10
1.16
7.2 7.0 6.8
f1 (ppm)
H (s) 7.26
I (d) 6.81
F (t) 6.93
G (s) 10.53
E (m) 4.30
D (s) 3.81
C (t) 1.37
B (s) 1.78
A (s) 1.18
1.09
0.85
1.10
1.16
2.43
3.02
3.09
3.33
9.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)


Q (s) 172.45
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O (s) 156.79
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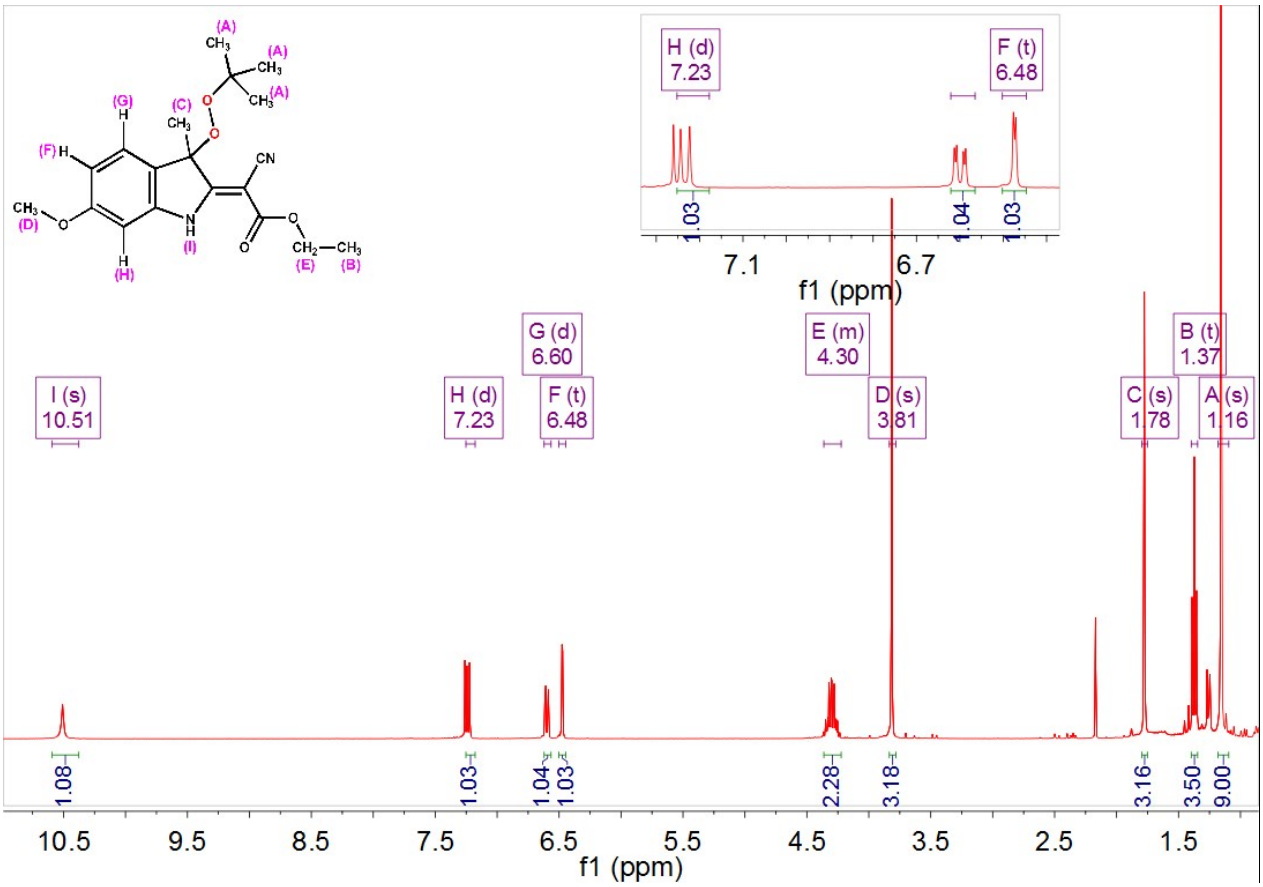
M (s) 133.61
L (s) 116.34
J (s) 111.10
I (s) 110.48
K (s) 114.30
H (s) 88.15
G (s) 80.64
F (s) 70.81
E (s) 61.15
D (s) 55.87
B (s) 21.59
C (s) 26.47
A (s) 14.35
170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)


H (d) 7.23
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1.04
1.03
7.1
6.7
f1 (ppm)
I (s) 10.51
H (d) 7.23
G (d) 6.60
F (t) 6.48
E (m) 4.30
D (s) 3.81
C (s) 1.78
B (t) 1.37
A (s) 1.16
1.08
1.03
1.04
1.03
2.28
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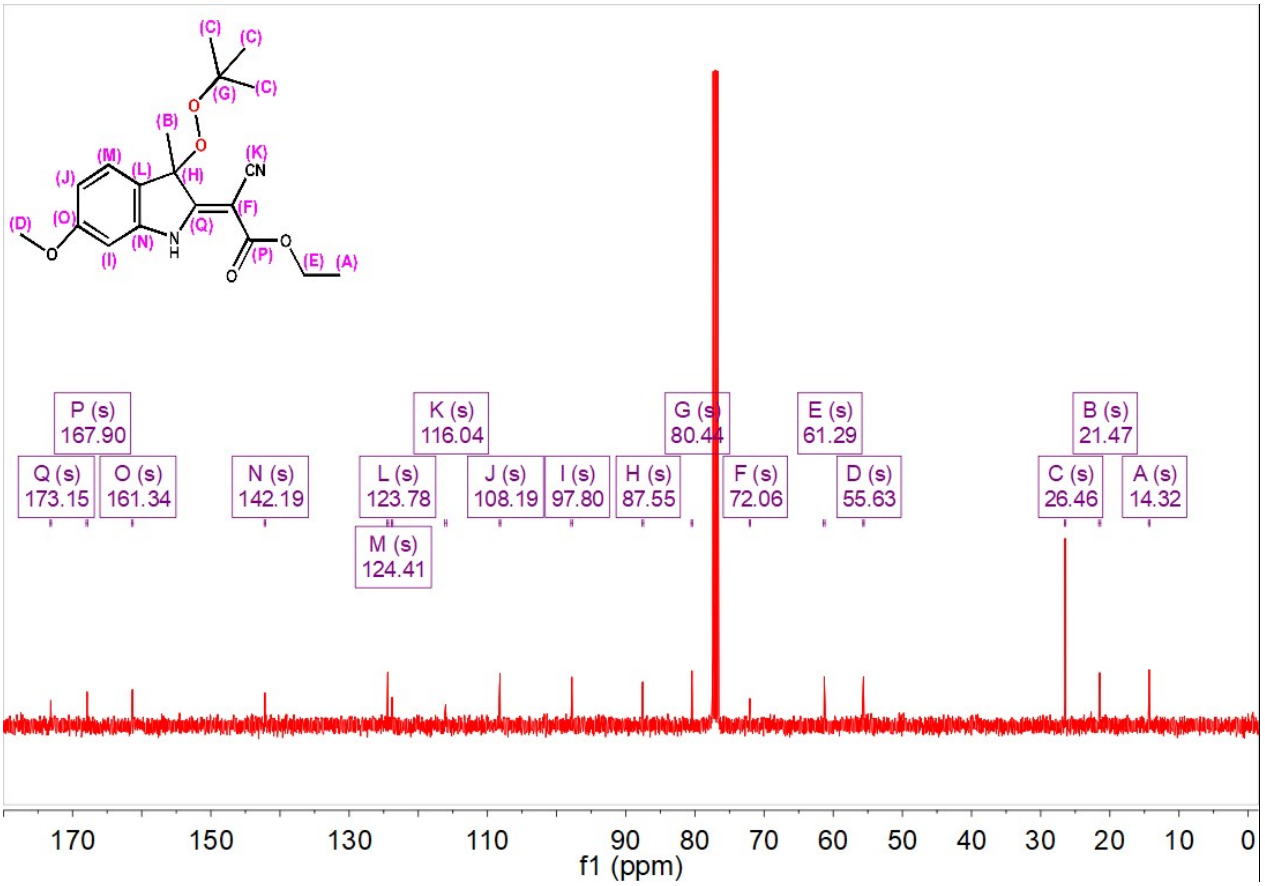
3.50
9.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)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K (s) 116.04
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J (s) 108.19
I (s) 97.80
H (s) 87.55
G (s) 80.44
F (s) 72.06
E (s) 61.29
D (s) 55.63
B (s) 21.47
C (s) 26.46
A (s) 14.32
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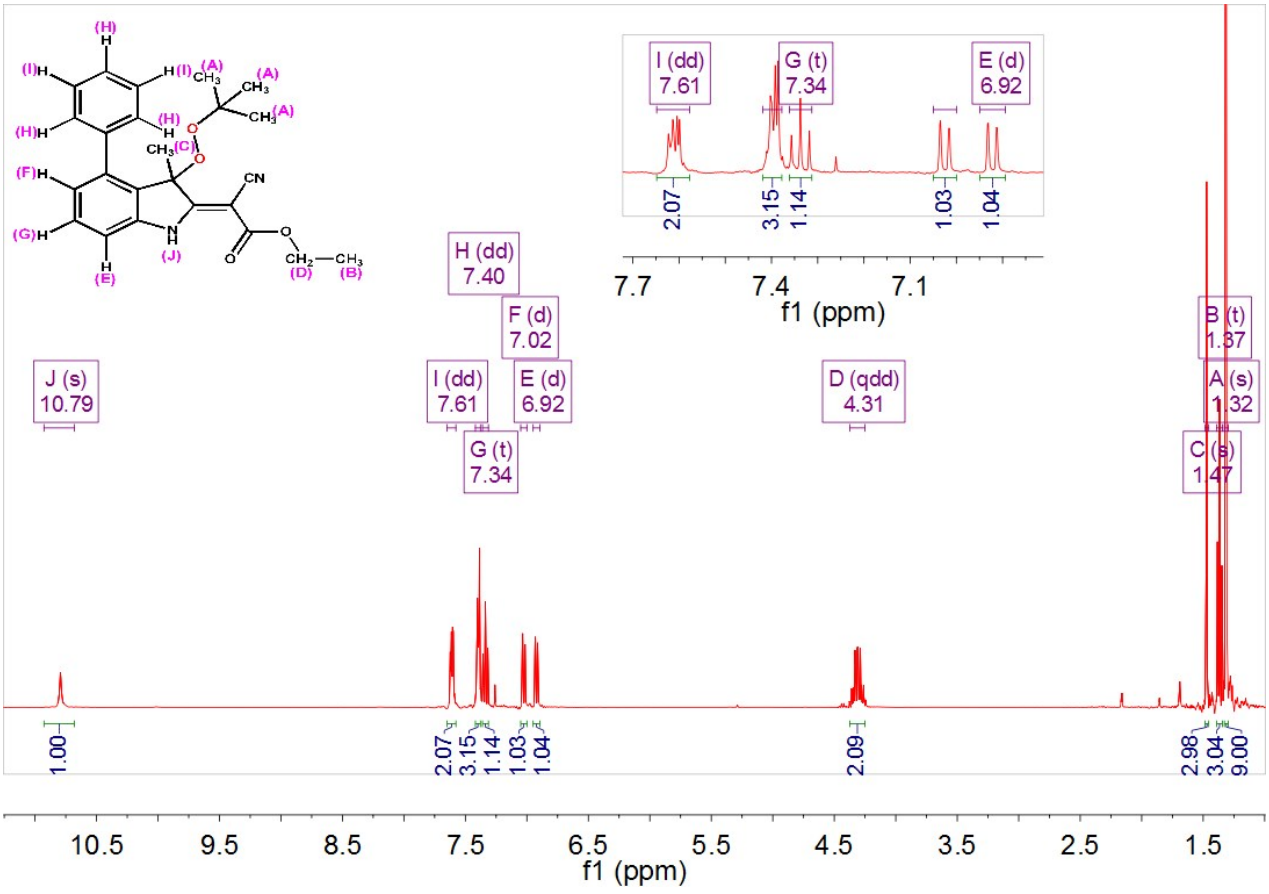
f1 (ppm)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G (t) 7.34
E (d) 6.92
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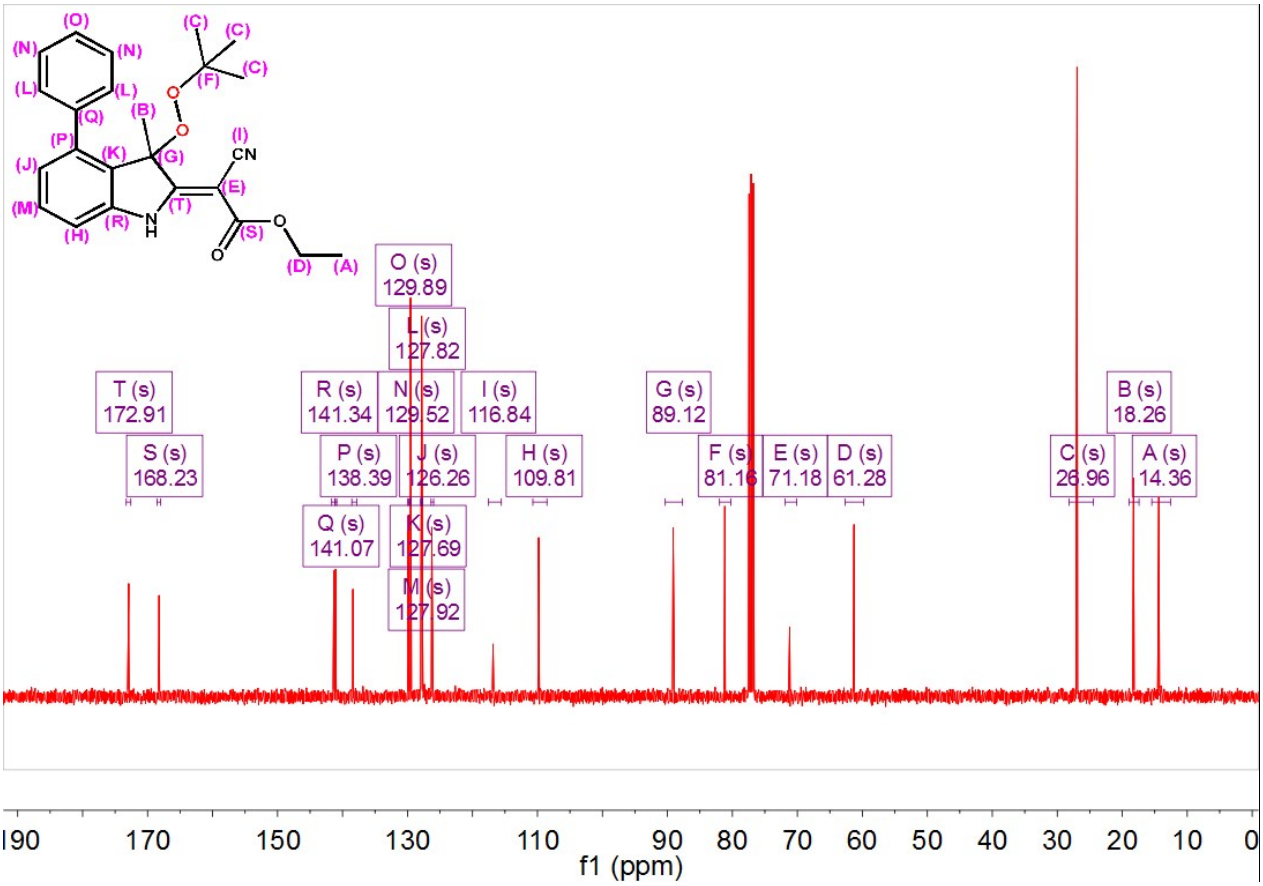
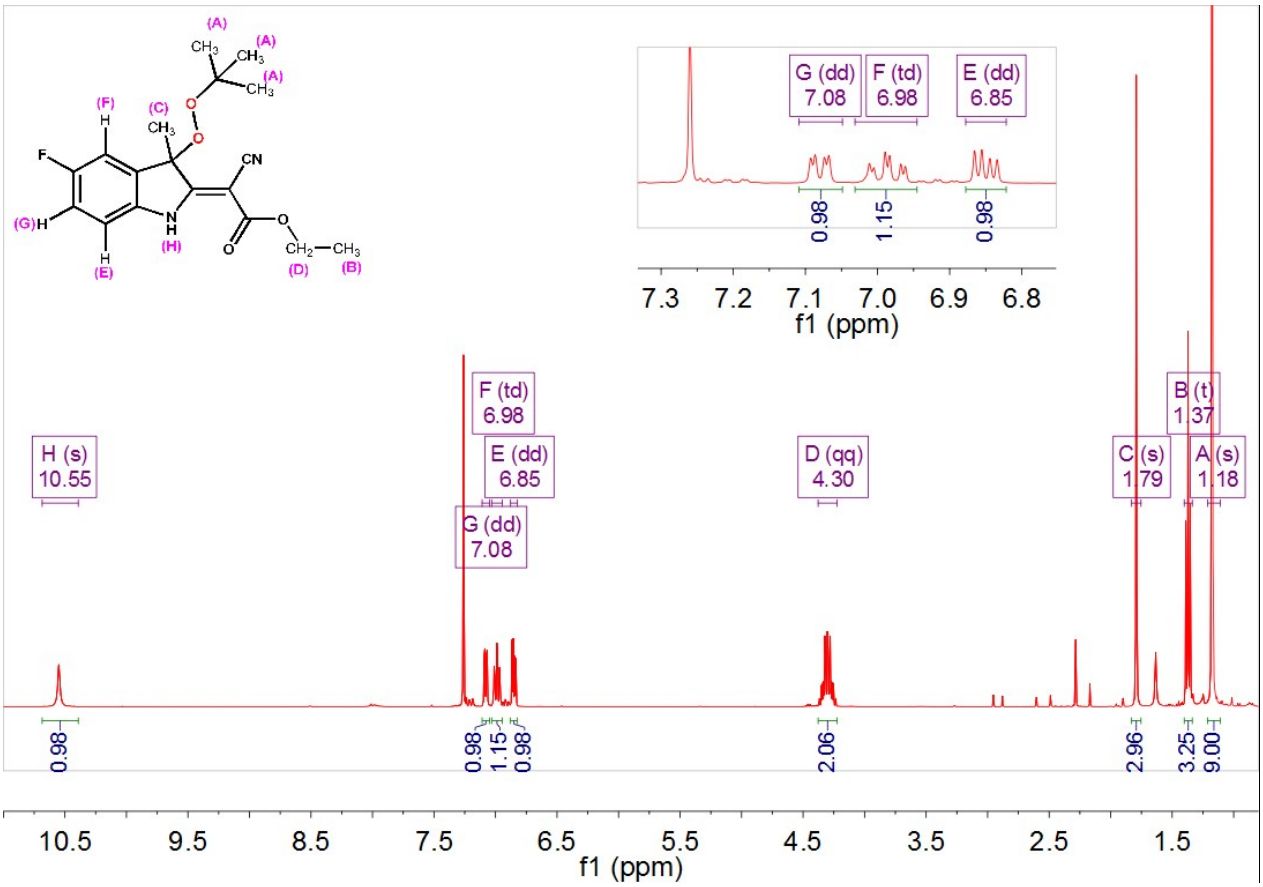
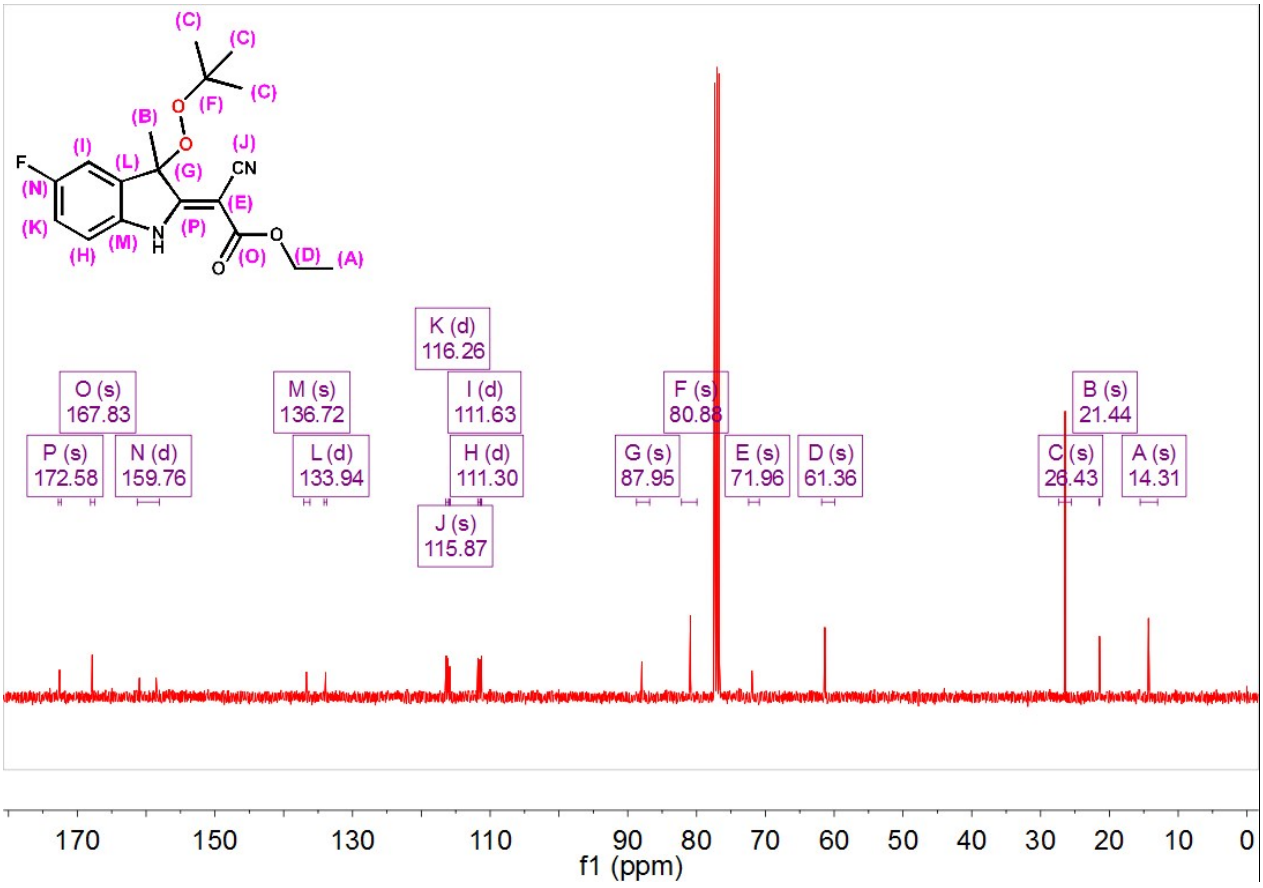
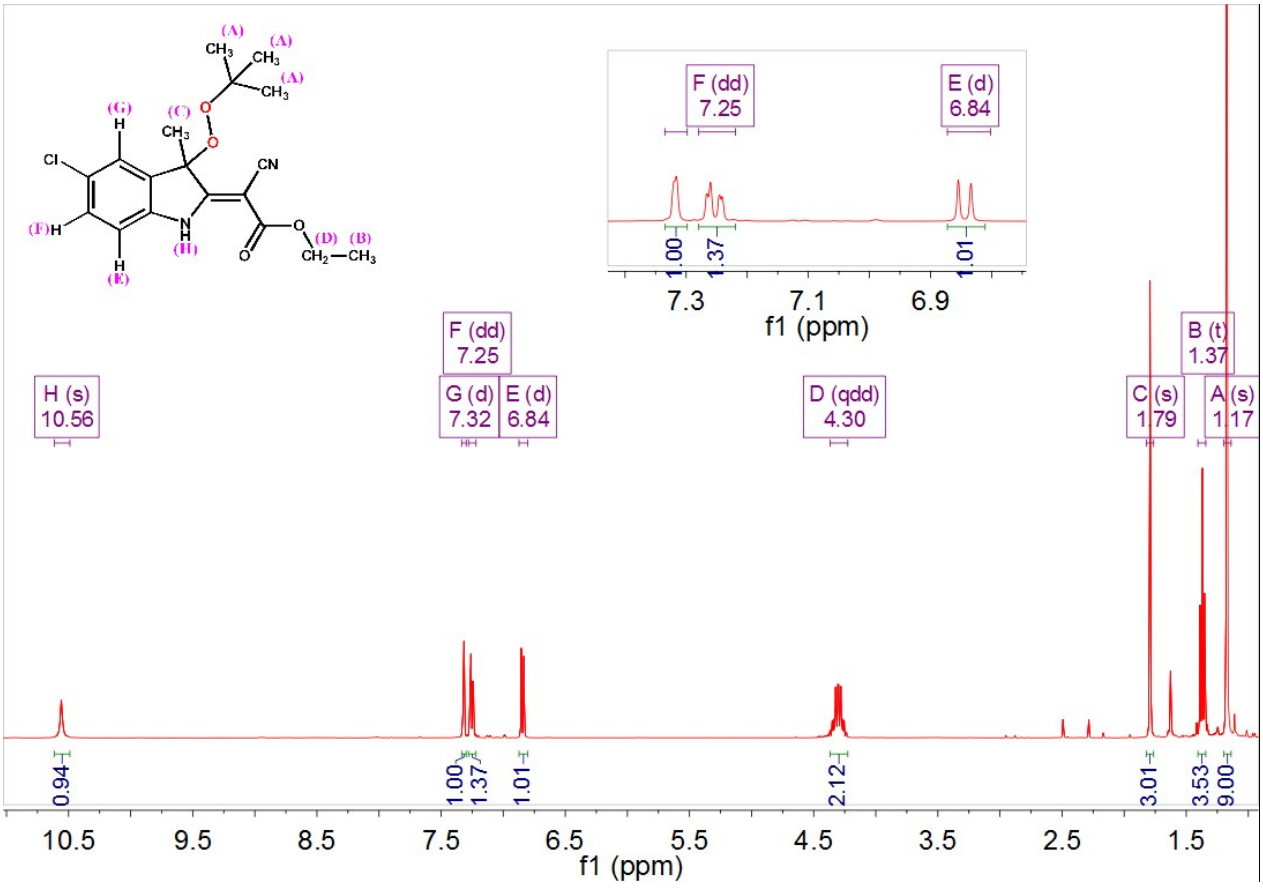
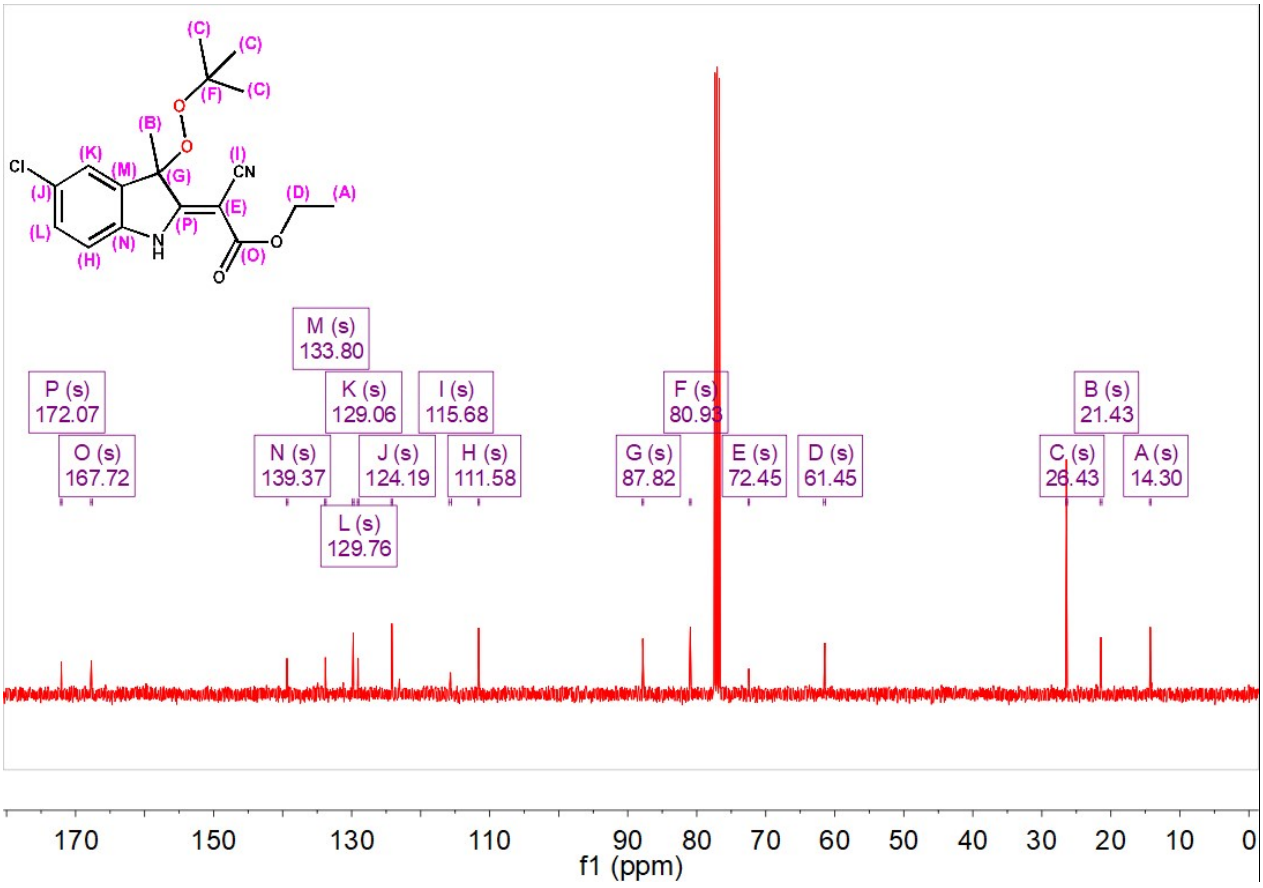
3.15
1.14
1.03
1.04
7.7 7.4 7.1
f1 (ppm)
H (dd) 7.40
F (d) 7.02
I (dd) 7.61
E (d) 6.92
G (t) 7.34
J (s) 10.79
D (qdd) 4.31
B (t) 1.37
A (s) 1.32
C (s) 1.47
1.00
2.07
3.15
1.14
1.03
1.04
2.09
2.98
3.04
9.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)

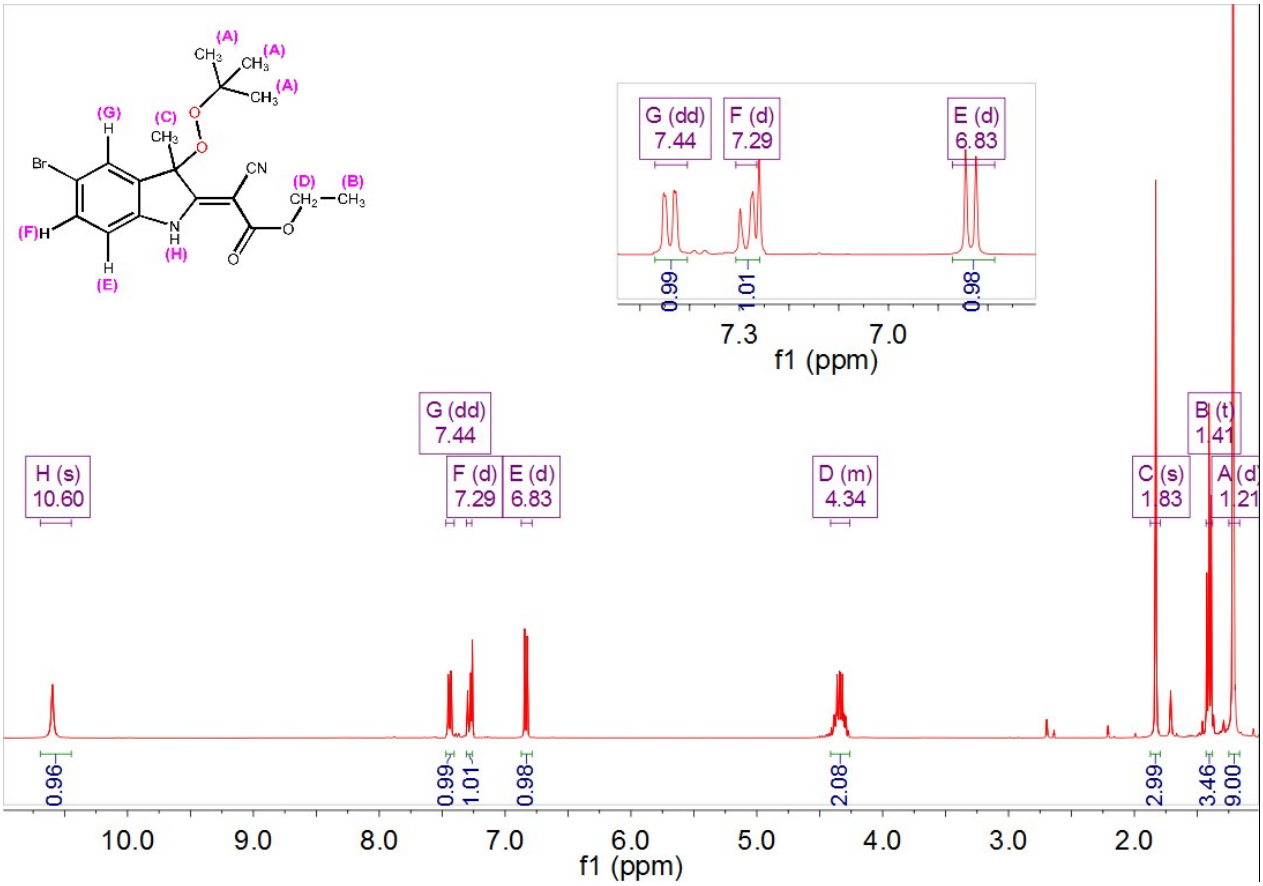

O (s) 129.89
L (s) 127.82
T (s) 172.91
R (s) 141.34
N (s) 129.52
I (s) 116.84
G (s) 89.12
B (s) 18.26
S (s) 168.23
P (s) 138.39
J (s) 126.26
H (s) 109.81
F (s) 81.16
E (s) 71.18
D (s) 61.28
C (s) 26.96
A (s) 14.36
Q (s) 141.07
K (s) 127.69
M (s) 127.92
f1 (ppm)

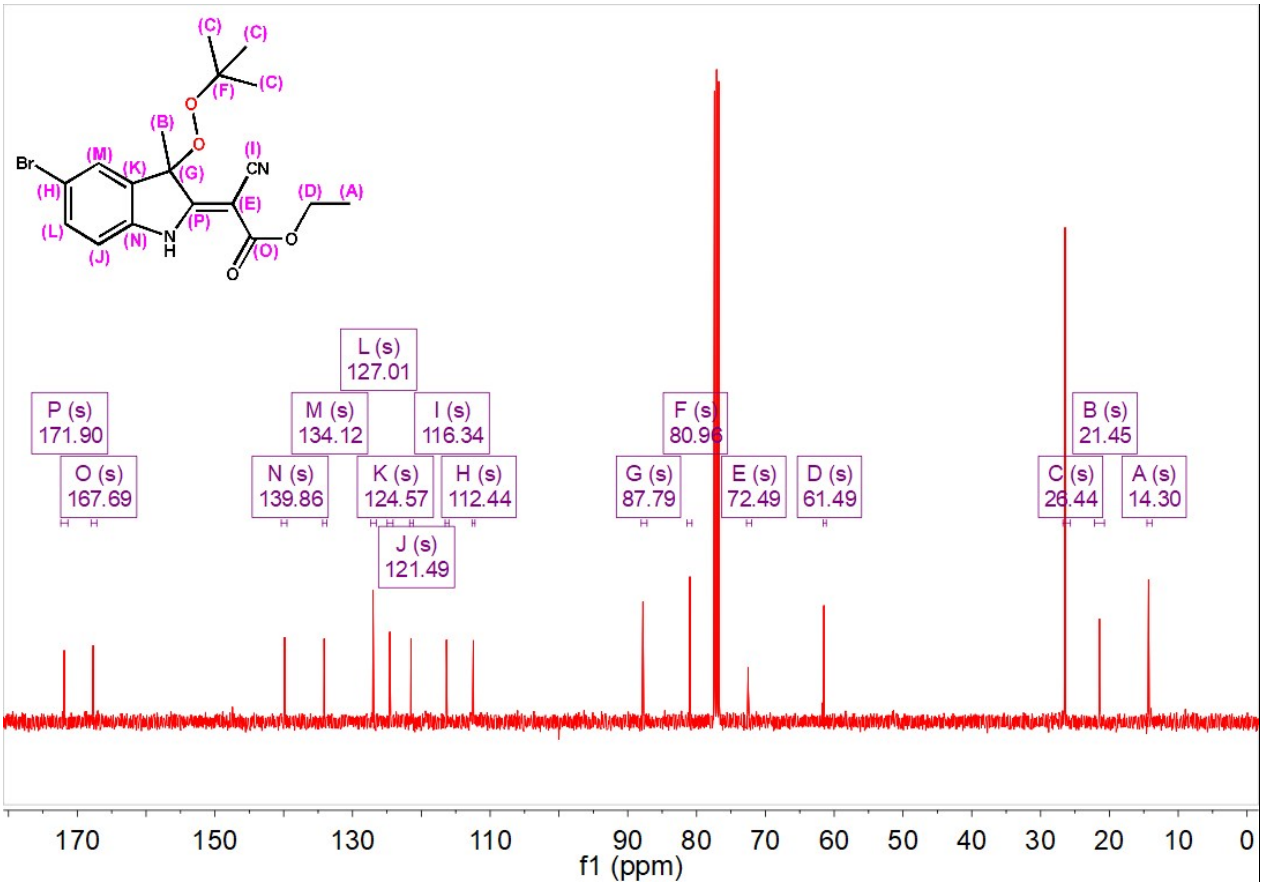

G (dd) 7.08
F (td) 6.98
E (dd) 6.85
0.98
1.15
0.98
f1 (ppm)
F (td) 6.98
E (dd) 6.85
G (dd) 7.08
H (s) 10.55
D (qq) 4.30
B (t) 1.37
C (s) 1.79
A (s) 1.18
0.98
0.98
1.15
0.98
2.06
2.96
3.25
9.00
f1 (ppm)

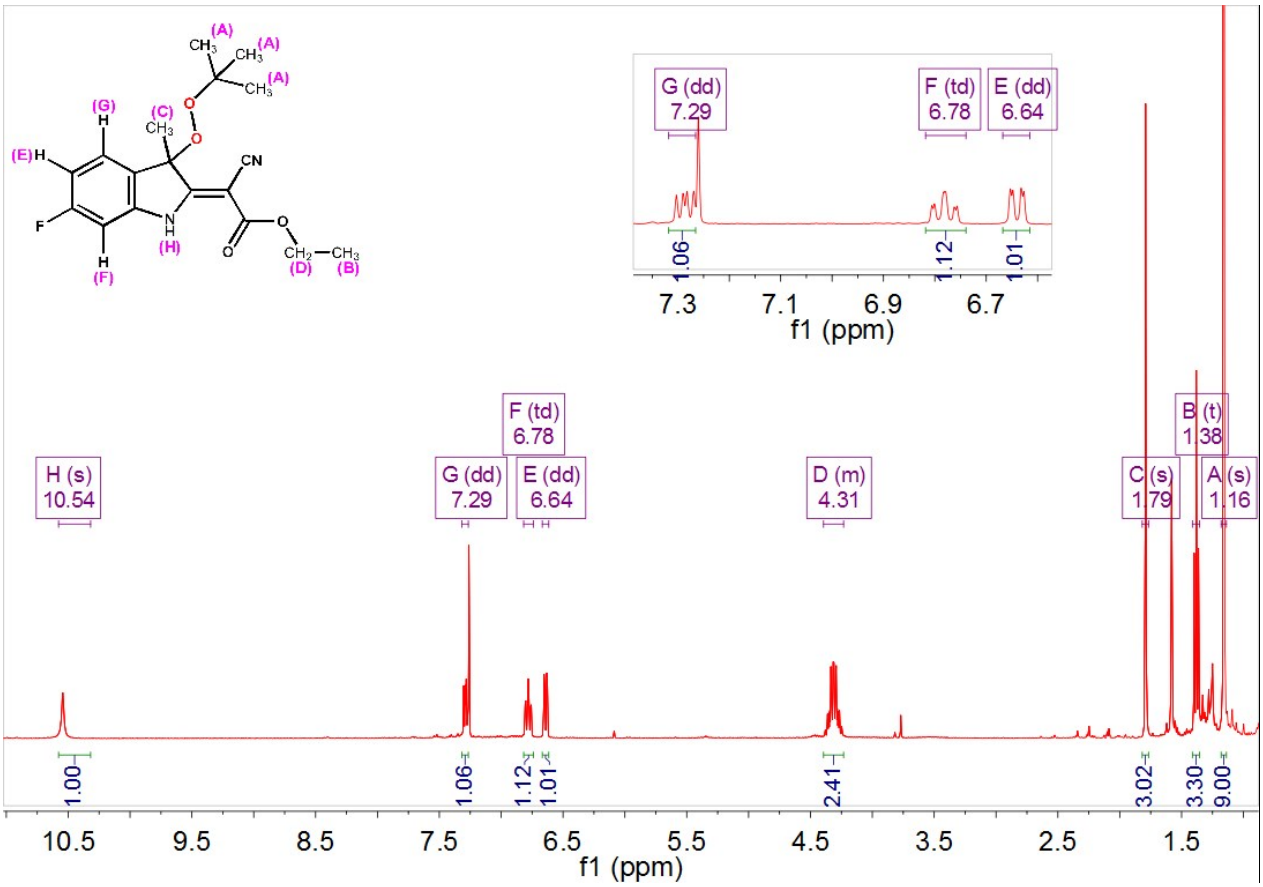

O (s) 167.83
P (s) 172.58
N (d) 159.76
M (s) 136.72
L (d) 133.94
K (d) 116.26
I (d) 111.63
H (d) 111.30
J (s) 115.87
F (s) 80.88
G (s) 87.95
E (s) 71.96
D (s) 61.36
B (s) 21.44
C (s) 26.43
A (s) 14.31
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

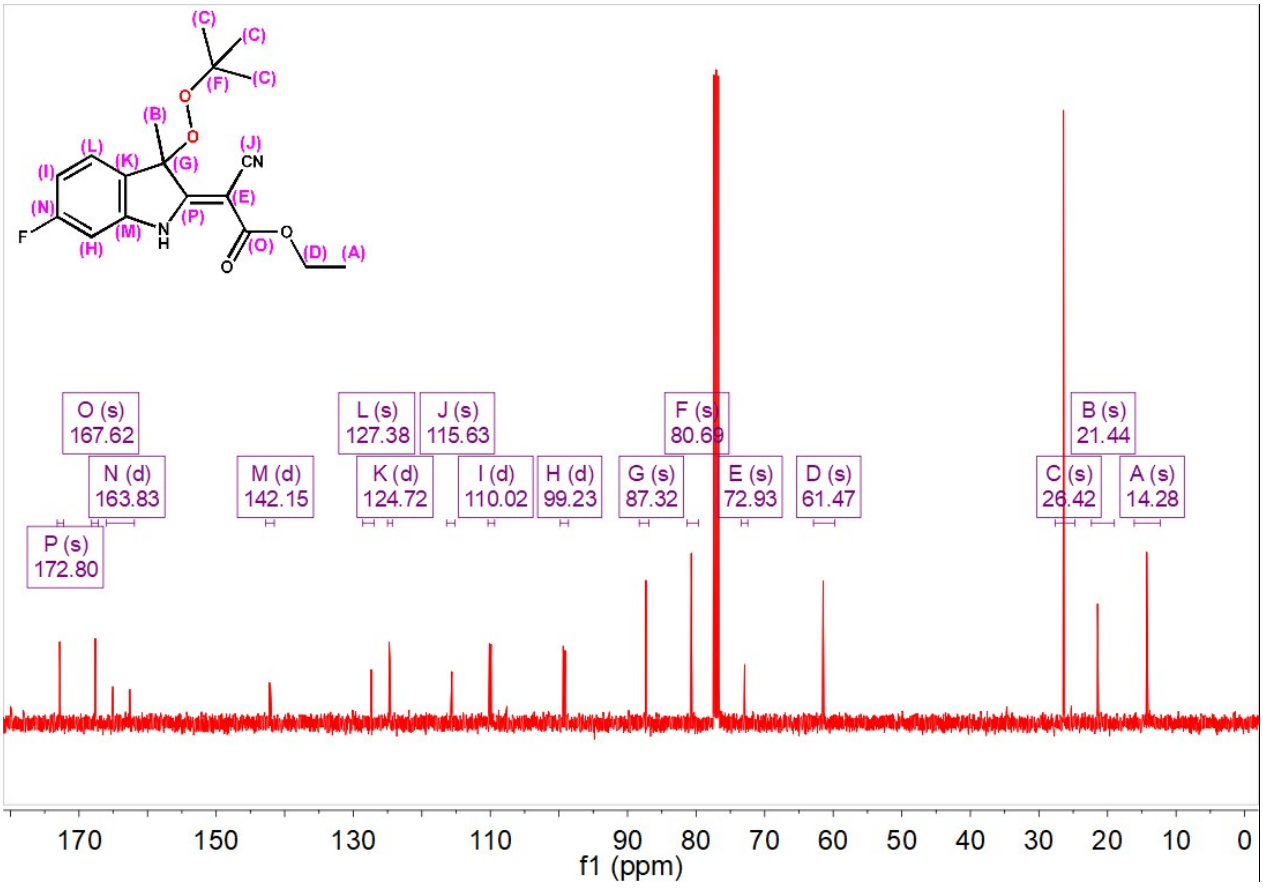

F (dd) 7.25
E (d) 6.84
1.00
1.37
1.01
7.3 7.1 6.9
f1 (ppm)
H (s) 10.56
F (dd) 7.25
G (d) 7.32
E (d) 6.84
D (qdd) 4.30
B (t) 1.37
C (s) 1.79
A (s) 1.17
0.94
1.00
1.37
1.01
2.12
3.01
3.53
9.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)

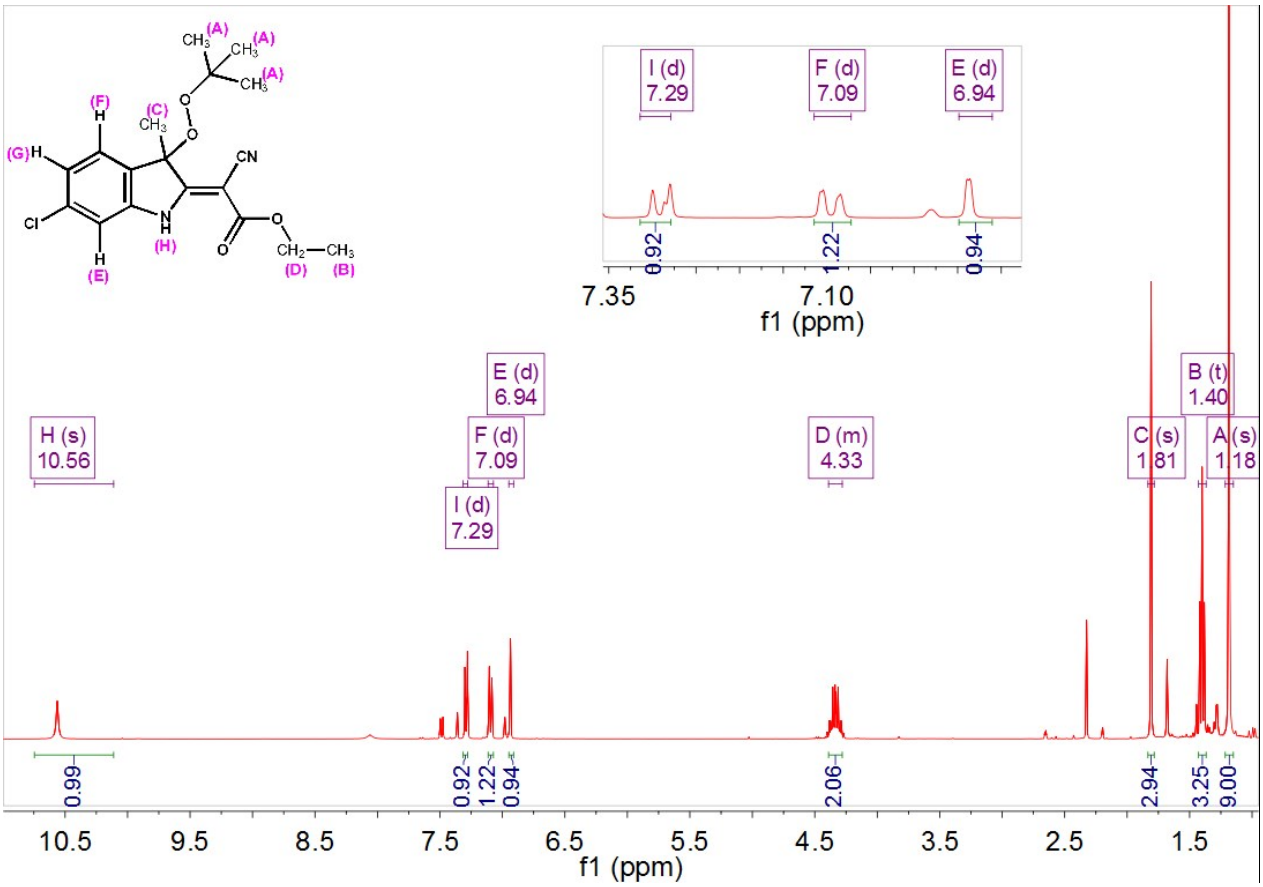

P (s) 172.07
O (s) 167.72
M (s) 133.80
K (s) 129.06
N (s) 139.37
J (s) 124.19
L (s) 129.76
I (s) 115.68
H (s) 111.58
F (s) 80.93
G (s) 87.82
E (s) 72.45
D (s) 61.45
B (s) 21.43
C (s) 26.43
A (s) 14.30
f1 (ppm)

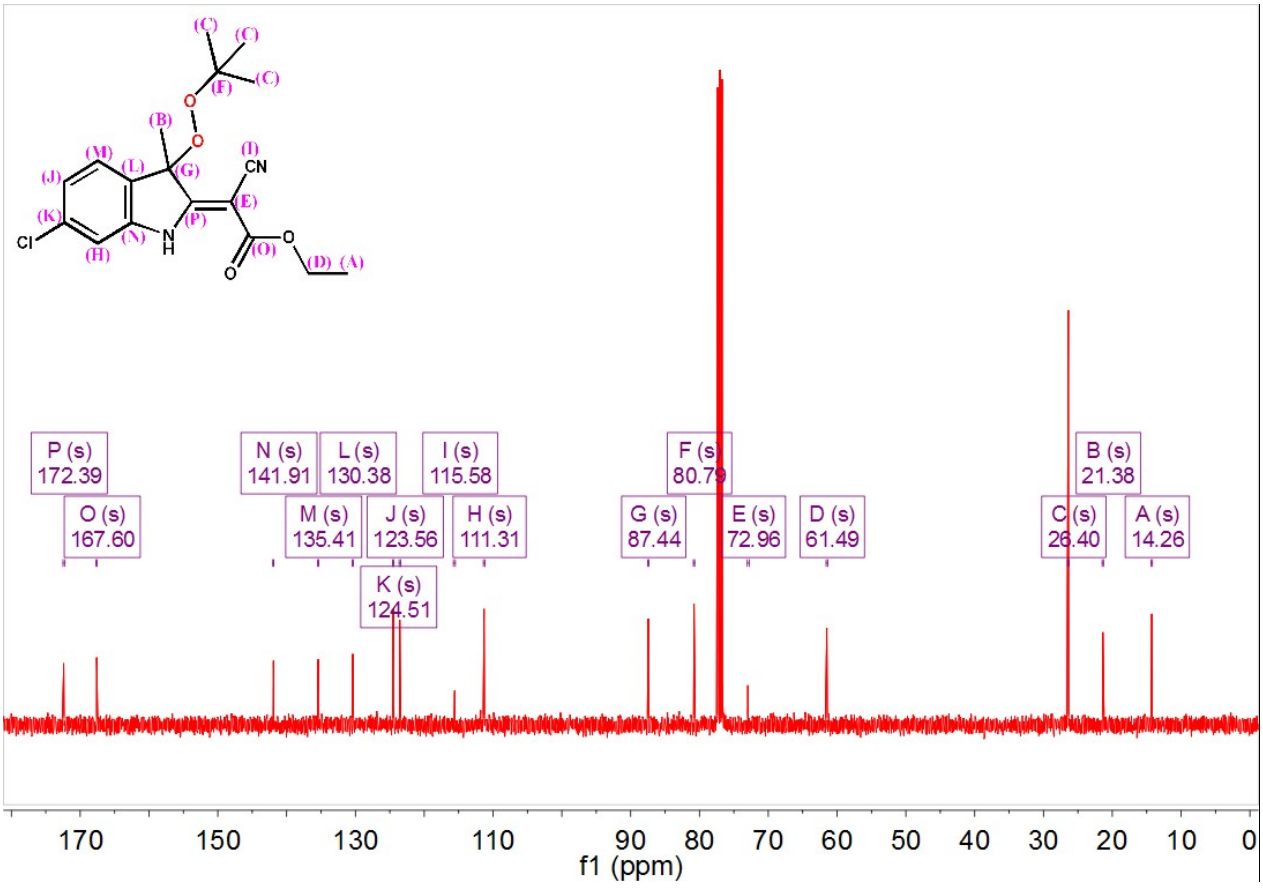

G (dd) 7.44
F (d) 7.29
E (d) 6.83
0.99
1.01
0.98
f1 (ppm)
H (s) 10.60
G (dd) 7.44
F (d) 7.29
E (d) 6.83
D (m) 4.34
B (t) 1.41
C (s) 1.83
A (d) 1.21
0.96
0.99
1.01
0.98
2.08
2.99
3.46
9.00
f1 (ppm)

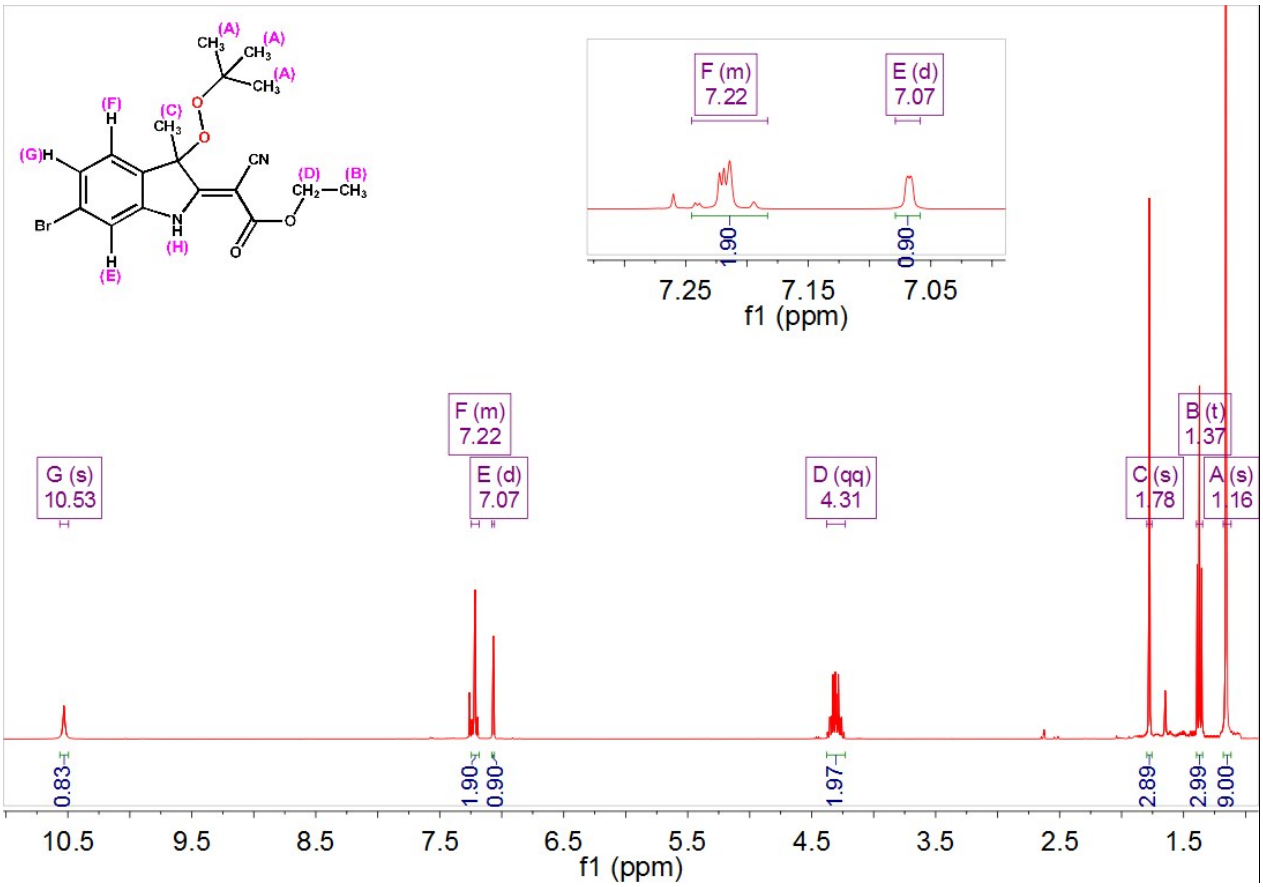

P (s) 171.90
O (s) 167.69
L (s) 127.01
M (s) 134.12
I (s) 116.34
N (s) 139.86
K (s) 124.57
H (s) 112.44
J (s) 121.49
F (s) 80.96
G (s) 87.79
E (s) 72.49
D (s) 61.49
B (s) 21.45
C (s) 26.44
A (s) 14.30
f1 (ppm)

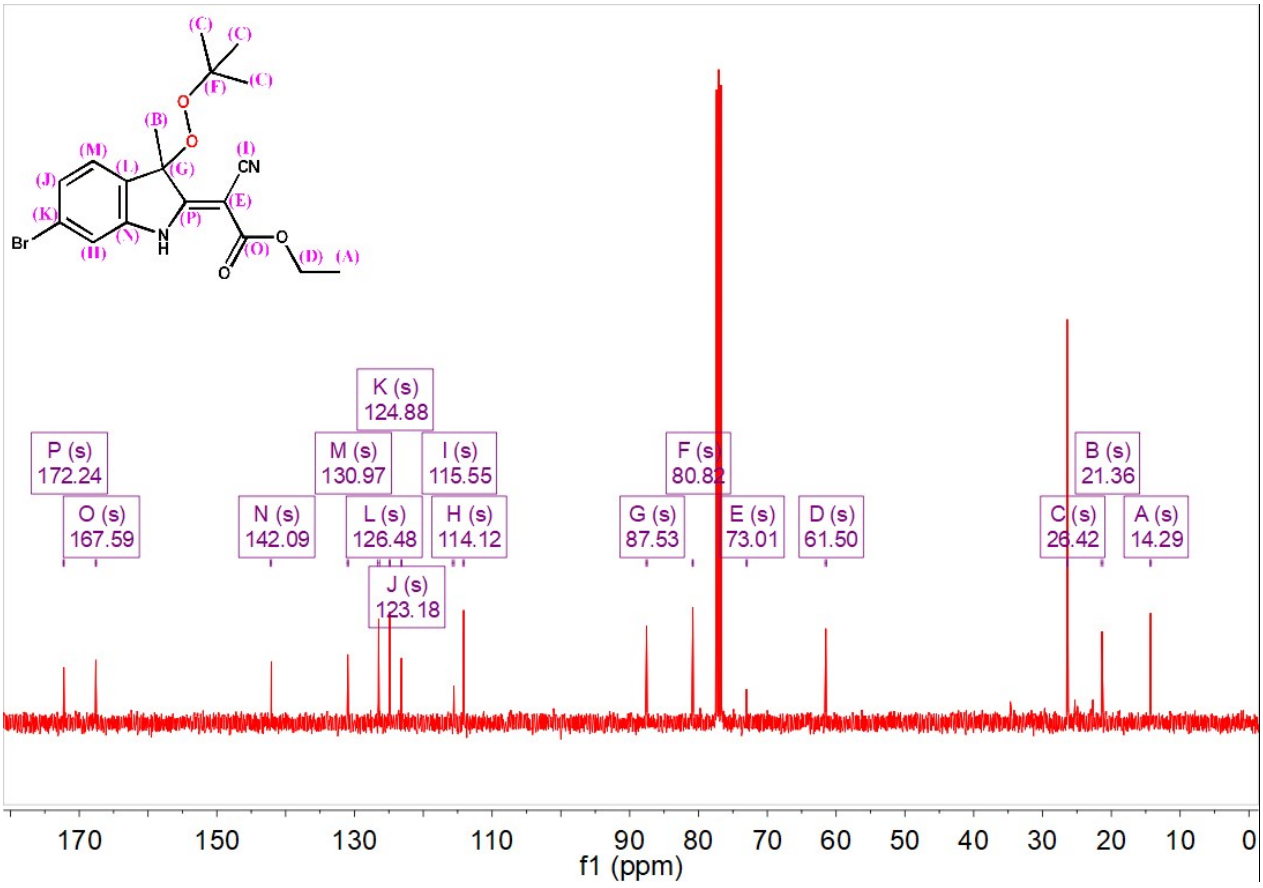

G (dd) 7.29
F (td) 6.78
E (dd) 6.64
1.06
1.12
1.01
f1 (ppm)
H (s) 10.54
G (dd) 7.29
F (td) 6.78
E (dd) 6.64
D (m) 4.31
B (t) 1.38
C (s) 1.79
A (s) 1.16
1.00
1.06
1.12
1.01
2.41
3.02
3.30
9.00
f1 (ppm)

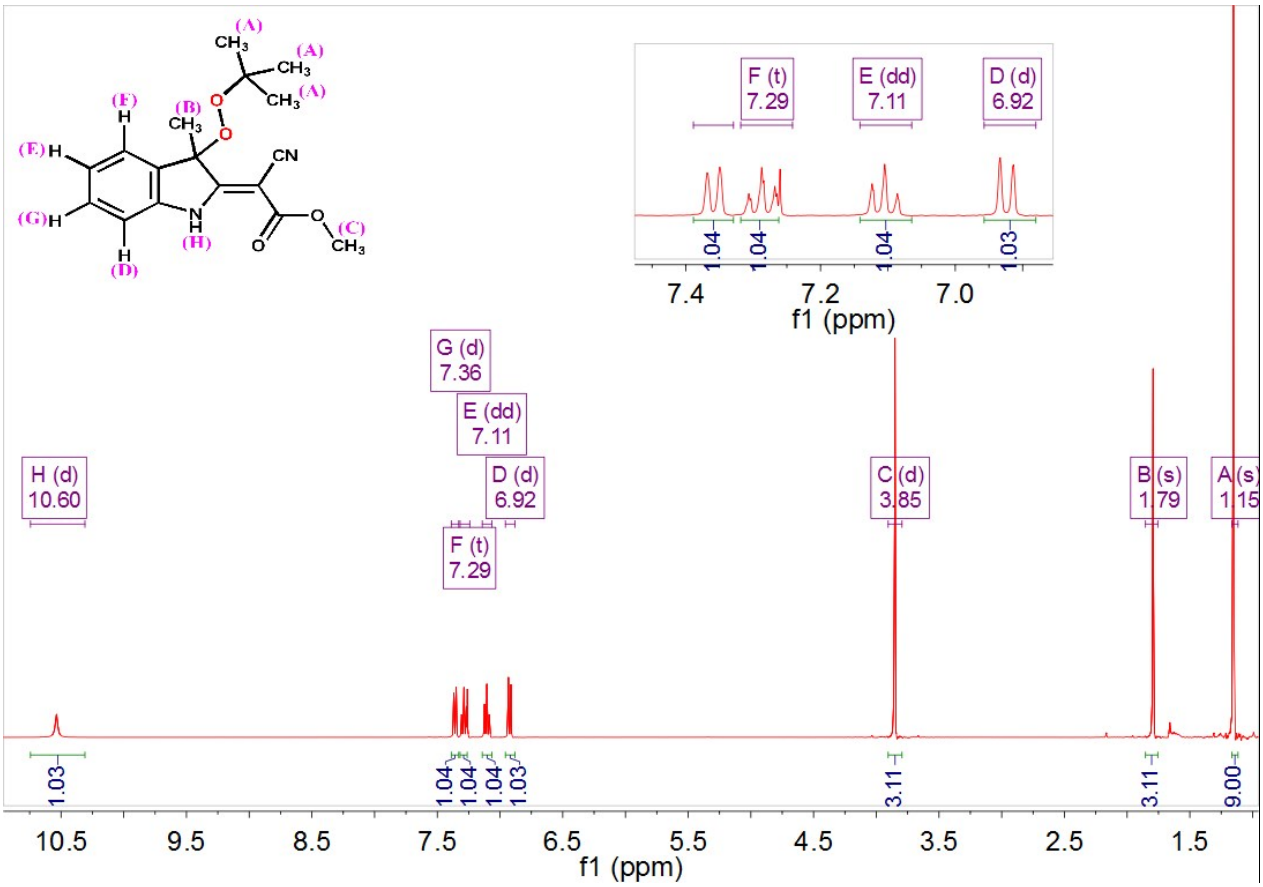

O (s) 167.62
N (d) 163.83
P (s) 172.80
M (d) 142.15
L (s) 127.38
J (s) 115.63
K (d) 124.72
I (d) 110.02
H (d) 99.23
G (s) 87.32
F (s) 80.69
E (s) 72.93
D (s) 61.47
B (s) 21.44
C (s) 26.42
A (s) 14.28
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

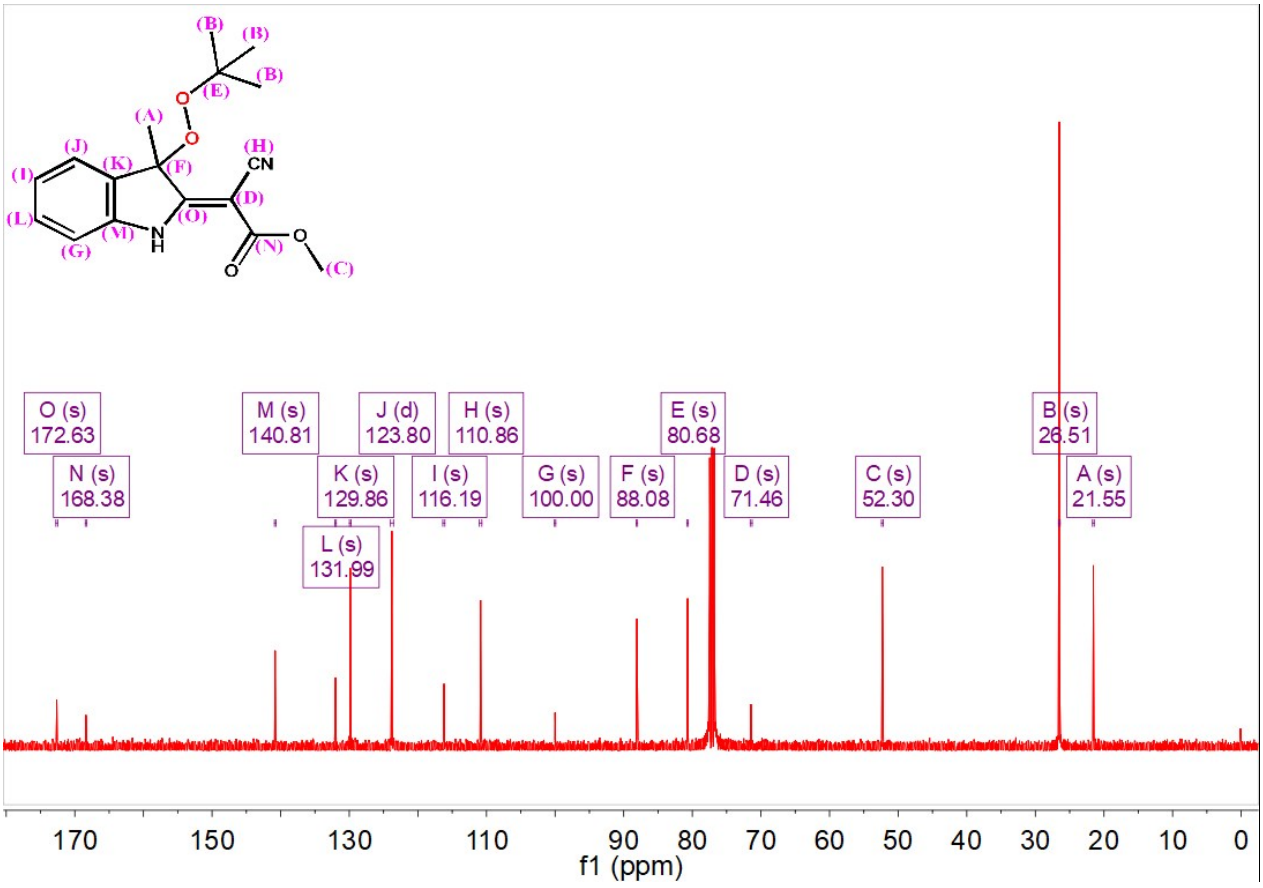

I (d) 7.29
F (d) 7.09
E (d) 6.94
0.92
1.22
0.94
7.35
7.10
f1 (ppm)
H (s) 10.56
E (d) 6.94
F (d) 7.09
I (d) 7.29
D (m) 4.33
B (t) 1.40
C (s) 1.81
A (s) 1.18
0.99
0.92
1.22
0.94
2.06
2.94
3.25
9.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)

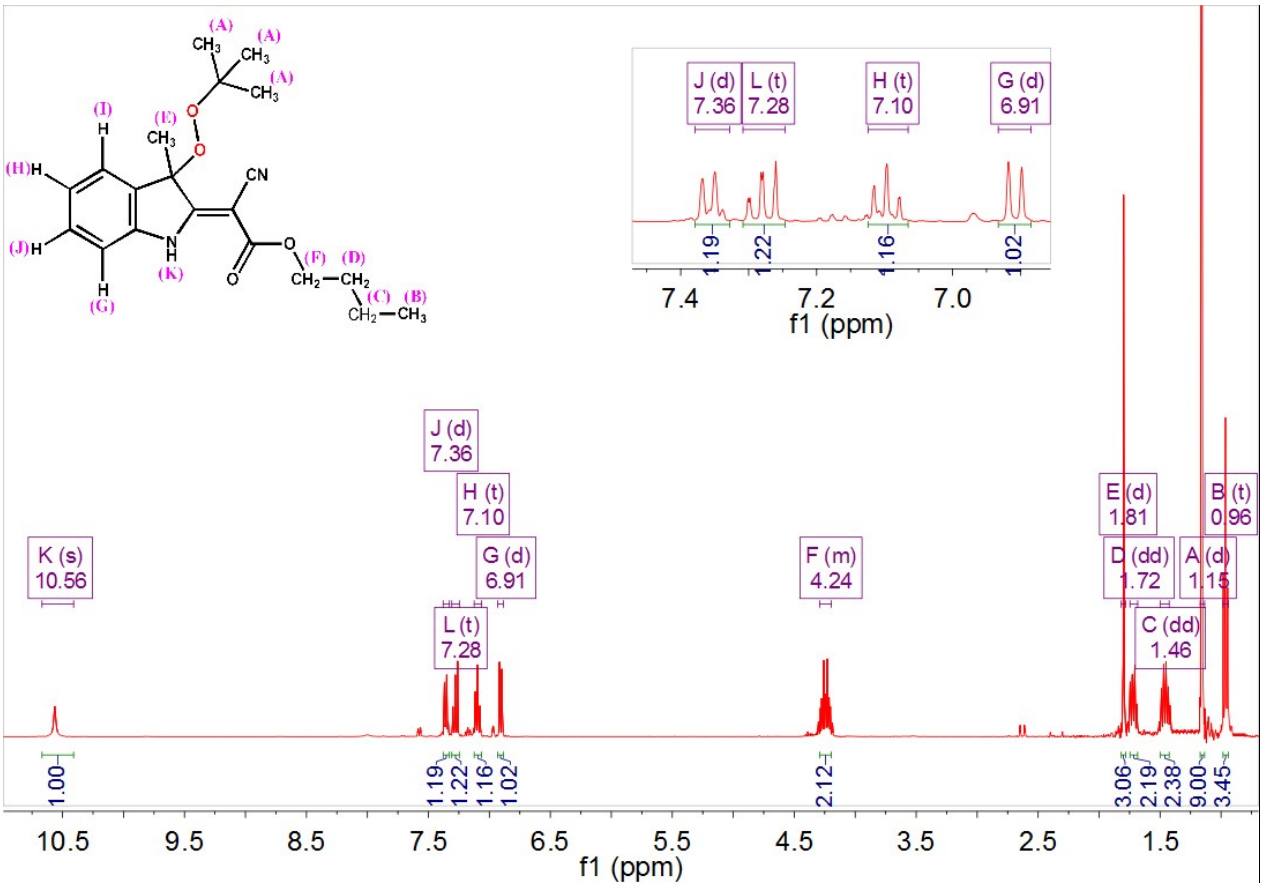

P (s) 172.39
O (s) 167.60
N (s) 141.91
L (s) 130.38
M (s) 135.41
J (s) 123.56
K (s) 124.51
I (s) 115.58
H (s) 111.31
F (s) 80.79
G (s) 87.44
E (s) 72.96
D (s) 61.49
B (s) 21.38
C (s) 26.40
A (s) 14.26
f1 (ppm)

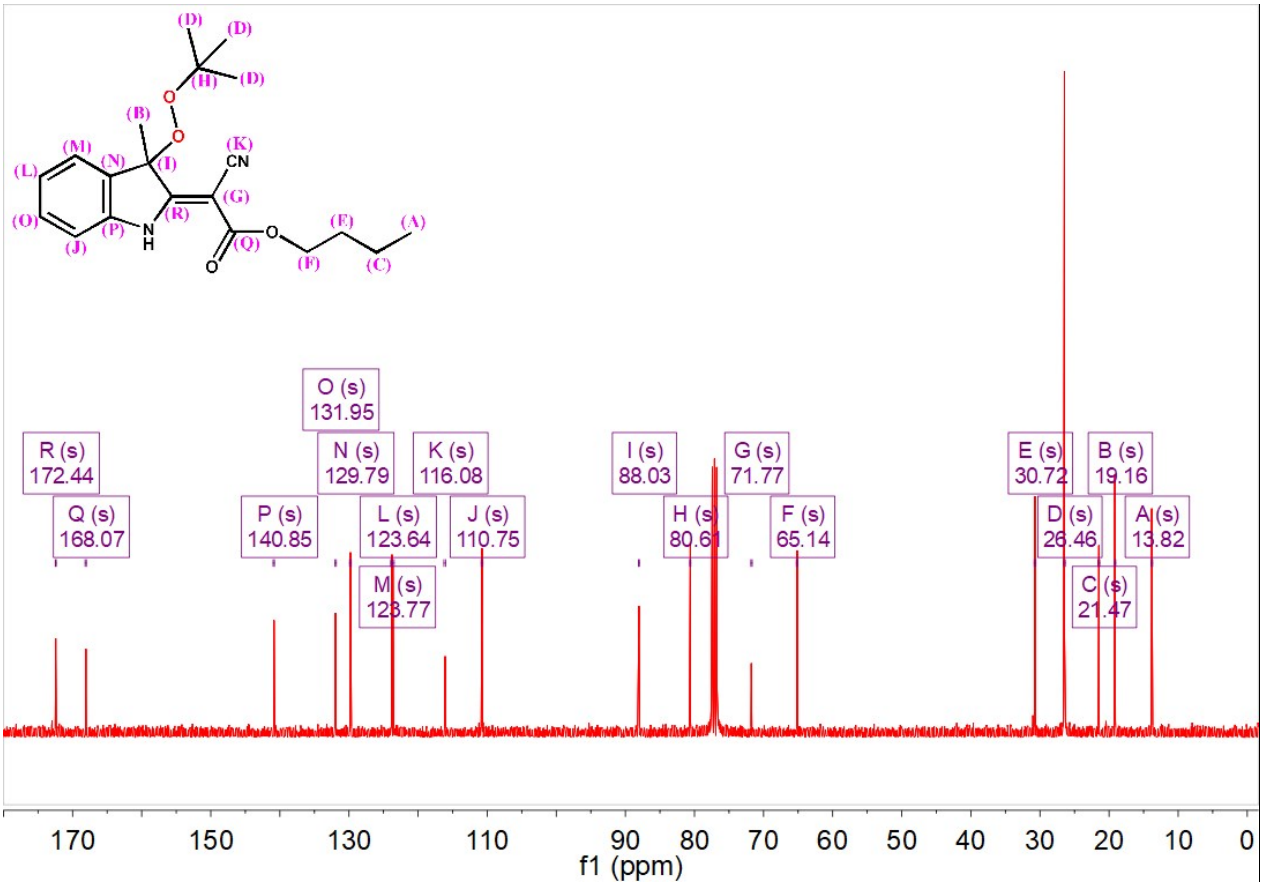

F (m) 7.22
E (d) 7.07
1.90
0.90
f1 (ppm)
G (s) 10.53
F (m) 7.22
E (d) 7.07
D (qq) 4.31
B (t) 1.37
C (s) 1.78
A (s) 1.16
0.83
1.90
0.90
1.97
2.89
2.99
9.00
f1 (ppm)

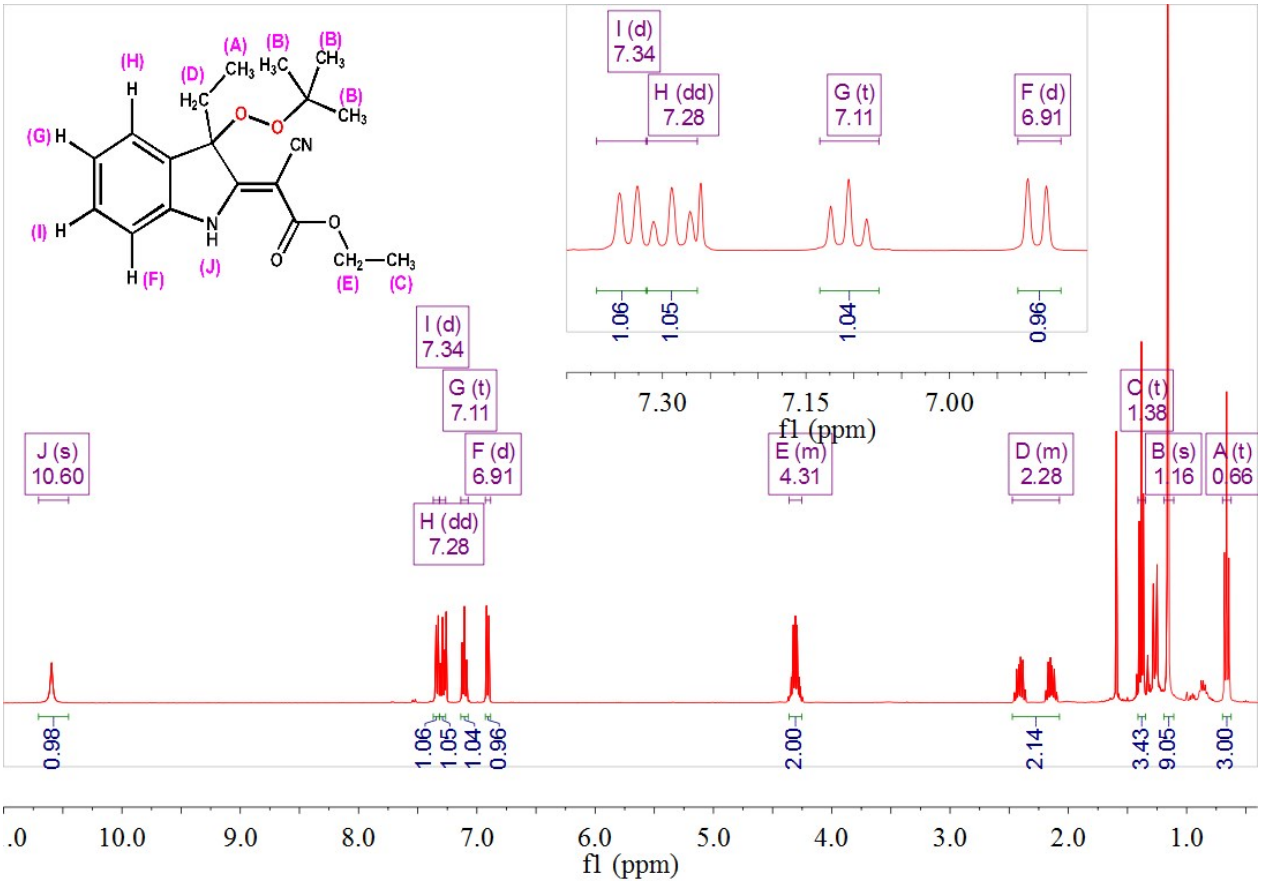

P (s) 172.24
O (s) 167.59
K (s) 124.88
M (s) 130.97
I (s) 115.55
N (s) 142.09
L (s) 126.48
H (s) 114.12
J (s) 123.18
F (s) 80.82
G (s) 87.53
E (s) 73.01
D (s) 61.50
B (s) 21.36
C (s) 26.42
A (s) 14.29
f1 (ppm)

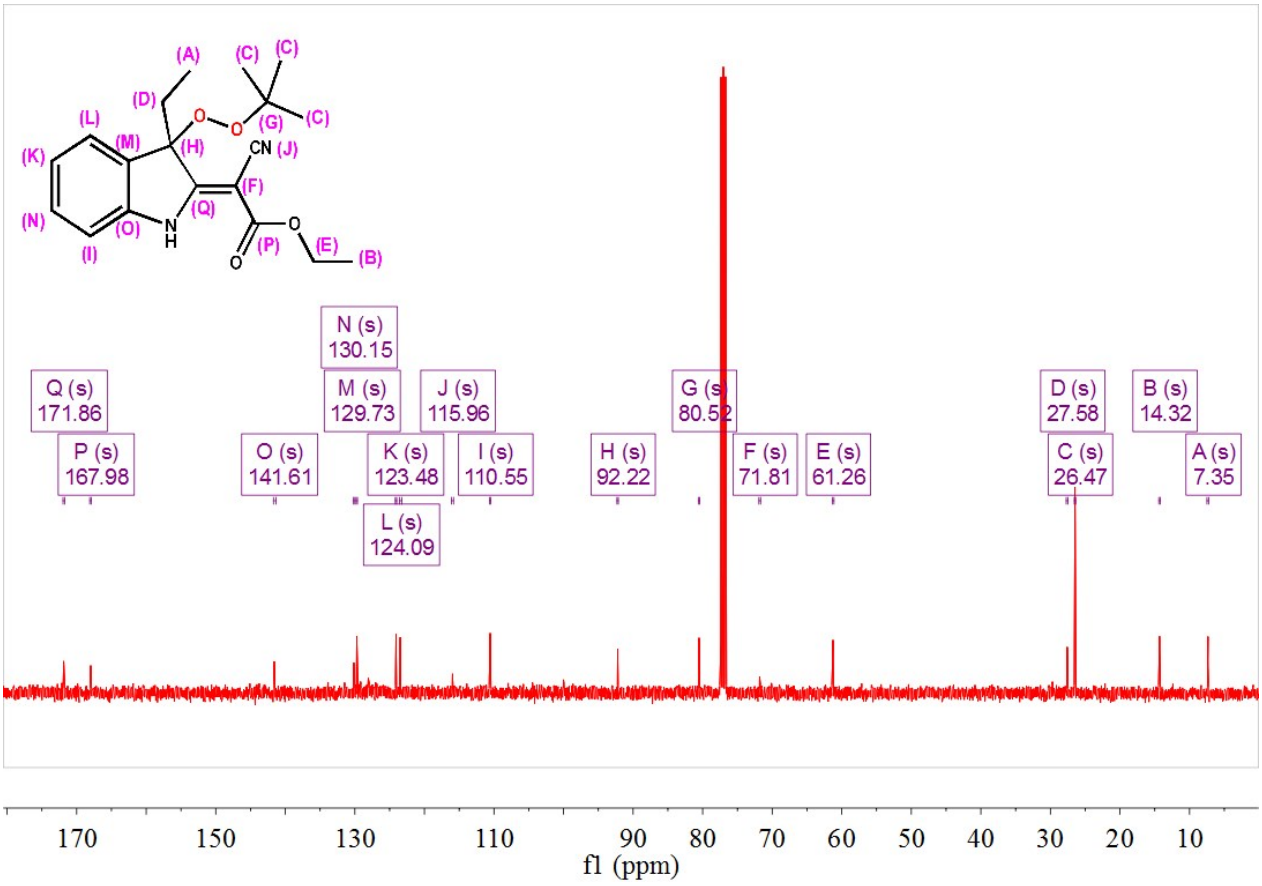

F (t) 7.29
E (dd) 7.11
D (d) 6.92
f1 (ppm)
H (d) 10.60
G (d) 7.36
E (dd) 7.11
D (d) 6.92
F (t) 7.29
C (d) 3.85
B (s) 1.79
A (s) 1.15
f1 (ppm)

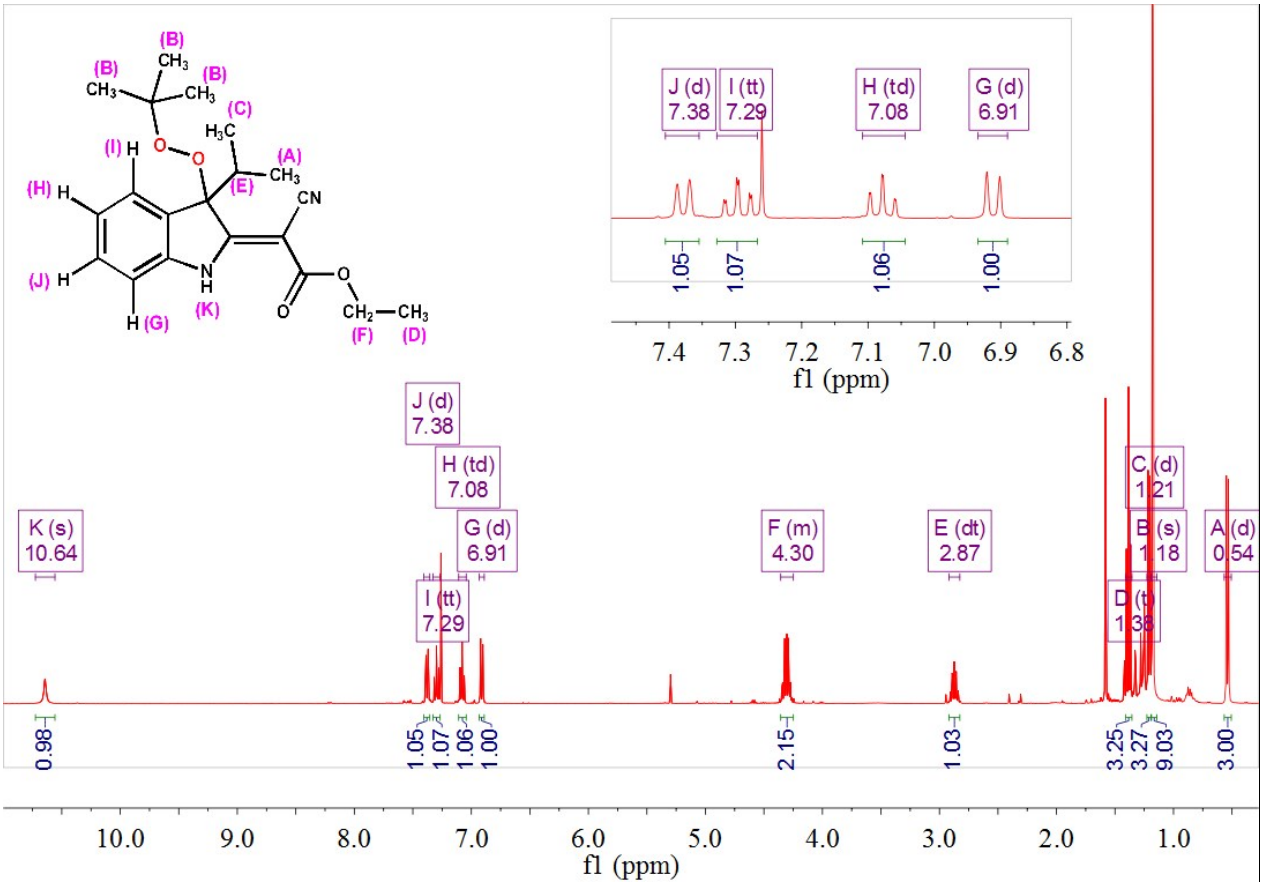

O (s) 172.63
N (s) 168.38
M (s) 140.81
K (s) 129.86
L (s) 131.99
J (d) 123.80
I (s) 116.19
H (s) 110.86
G (s) 100.00
F (s) 88.08
E (s) 80.68
D (s) 71.46
C (s) 52.30
B (s) 26.51
A (s) 21.55
f1 (ppm)

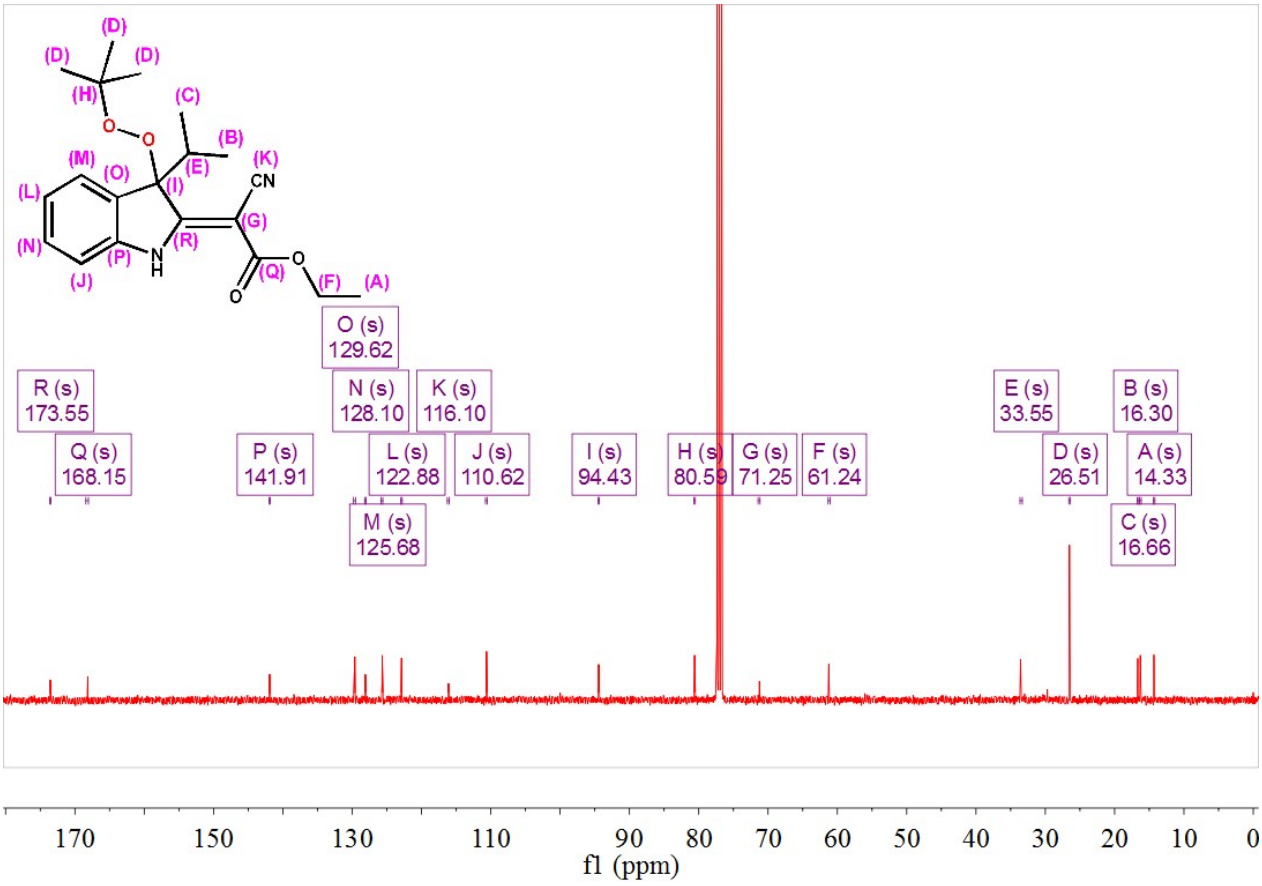

J (d) 7.36
L (t) 7.28
H (t) 7.10
G (d) 6.91
f1 (ppm)
K (s) 10.56
F (m) 4.24
E (d) 1.81
B (t) 0.96
D (dd) 1.72
A (d) 1.15
C (dd) 1.46
f1 (ppm)

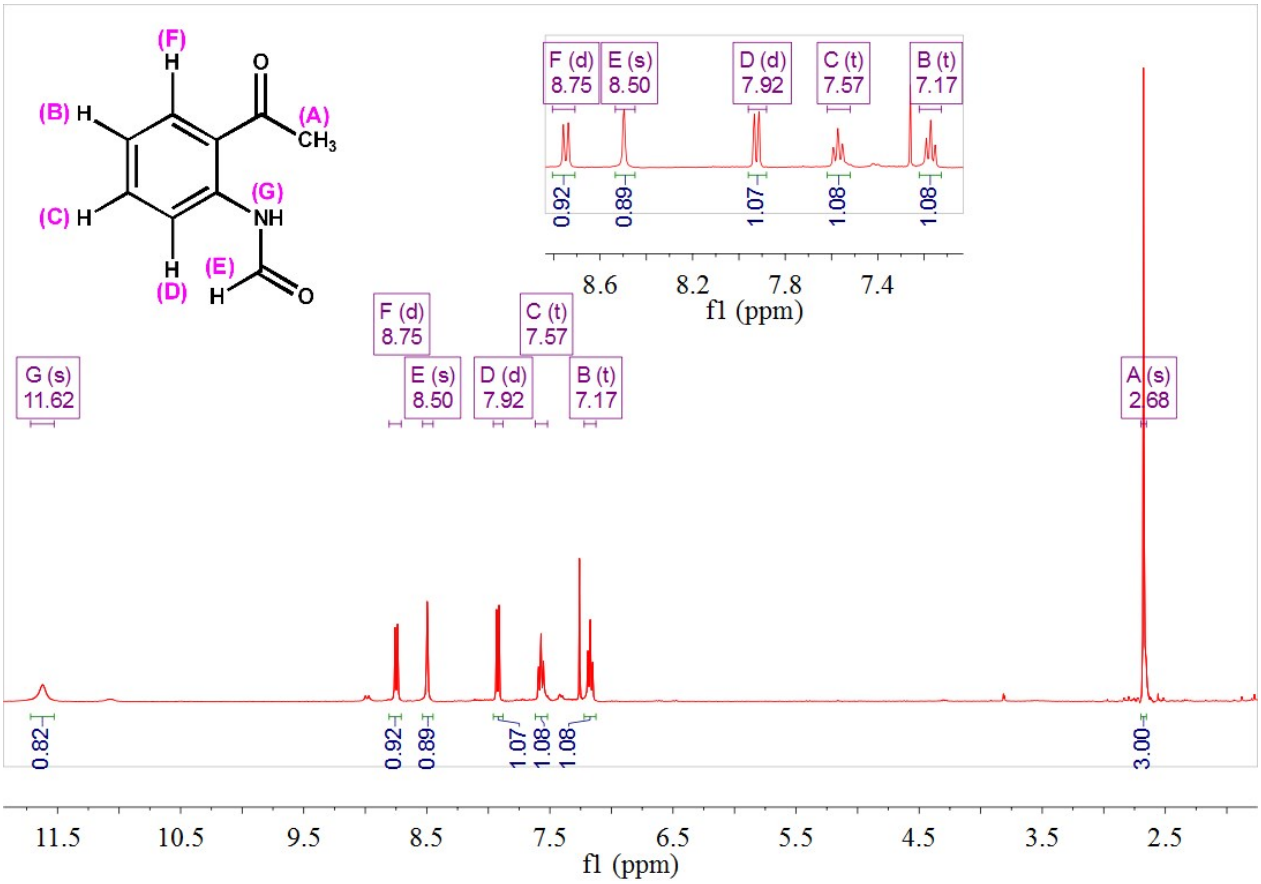

R (s) 172.44
Q (s) 168.07
O (s) 131.95
N (s) 129.79
P (s) 140.85
K (s) 116.08
L (s) 123.64
M (s) 128.77
J (s) 110.75
I (s) 88.03
H (s) 80.67
G (s) 71.77
F (s) 65.14
E (s) 30.72
D (s) 26.46
B (s) 19.16
C (s) 21.47
A (s) 13.82
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

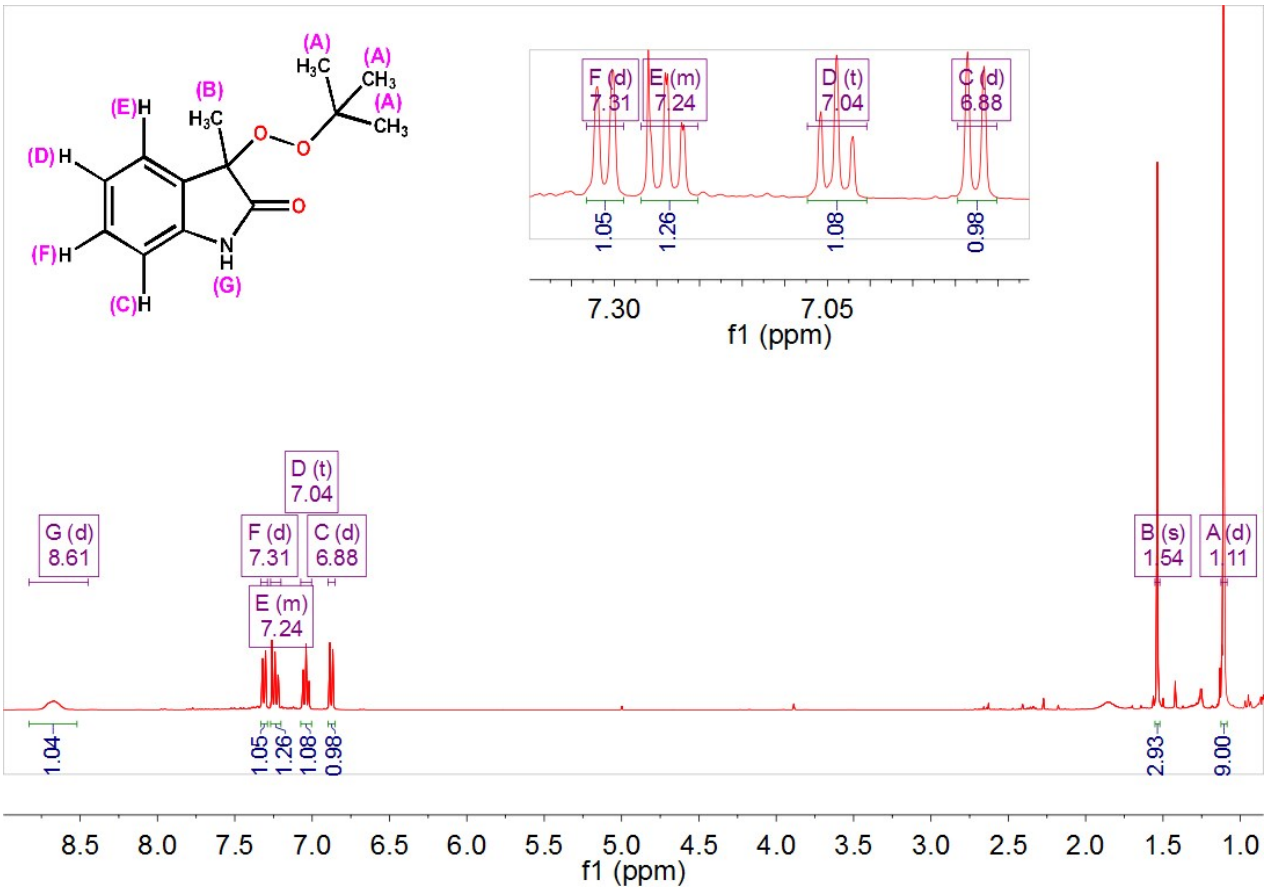

I (d) 7.34
H (dd) 7.28
G (t) 7.11
F (d) 6.91
1.06 1.05 1.04 0.96
7.30 7.15 7.00
f1 (ppm)
J (s) 10.60
I (d) 7.34
G (t) 7.11
F (d) 6.91
H (dd) 7.28
E (m) 4.31
D (m) 2.28
C (t) 1.38
B (s) 1.16
A (t) 0.66
0.98 1.06 1.05 1.04 0.96 2.00 2.14 3.43 9.05 3.00
.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
f1 (ppm)

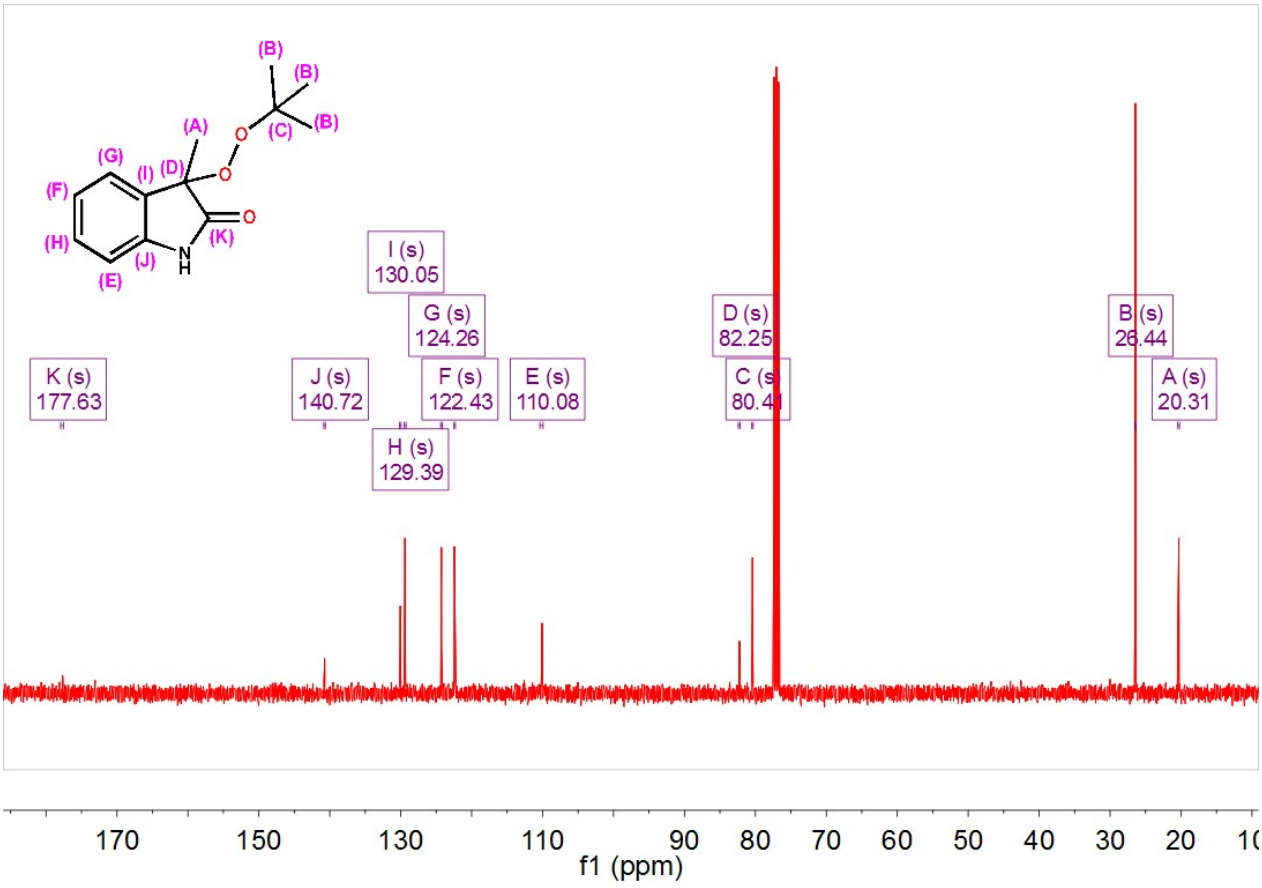

N (s) 130.15
Q (s) 171.86
M (s) 129.73
J (s) 115.96
G (s) 80.52
D (s) 27.58
B (s) 14.32
P (s) 167.98
O (s) 141.61
K (s) 123.48
I (s) 110.55
H (s) 92.22
F (s) 71.81
E (s) 61.26
C (s) 26.47
A (s) 7.35
L (s) 124.09
170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)

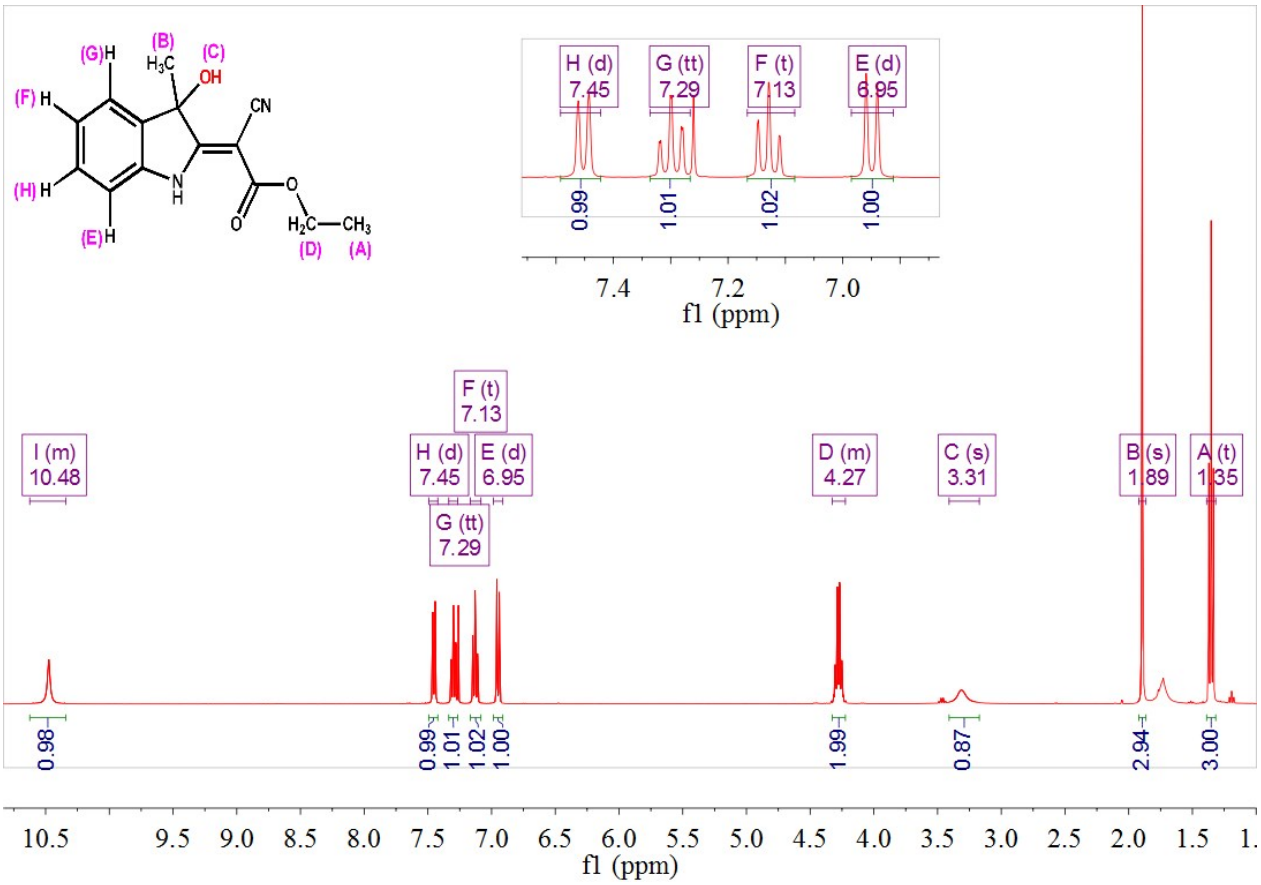

J (d) 7.38
I (tt) 7.29
H (td) 7.08
G (d) 6.91
1.05
1.07
1.06
1.00
7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
K (s) 10.64
F (m) 4.30
E (dt) 2.87
C (d) 1.21
B (s) 1.18
A (d) 0.54
0.98
2.15
1.03
3.25
3.27
9.03
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
f1 (ppm)

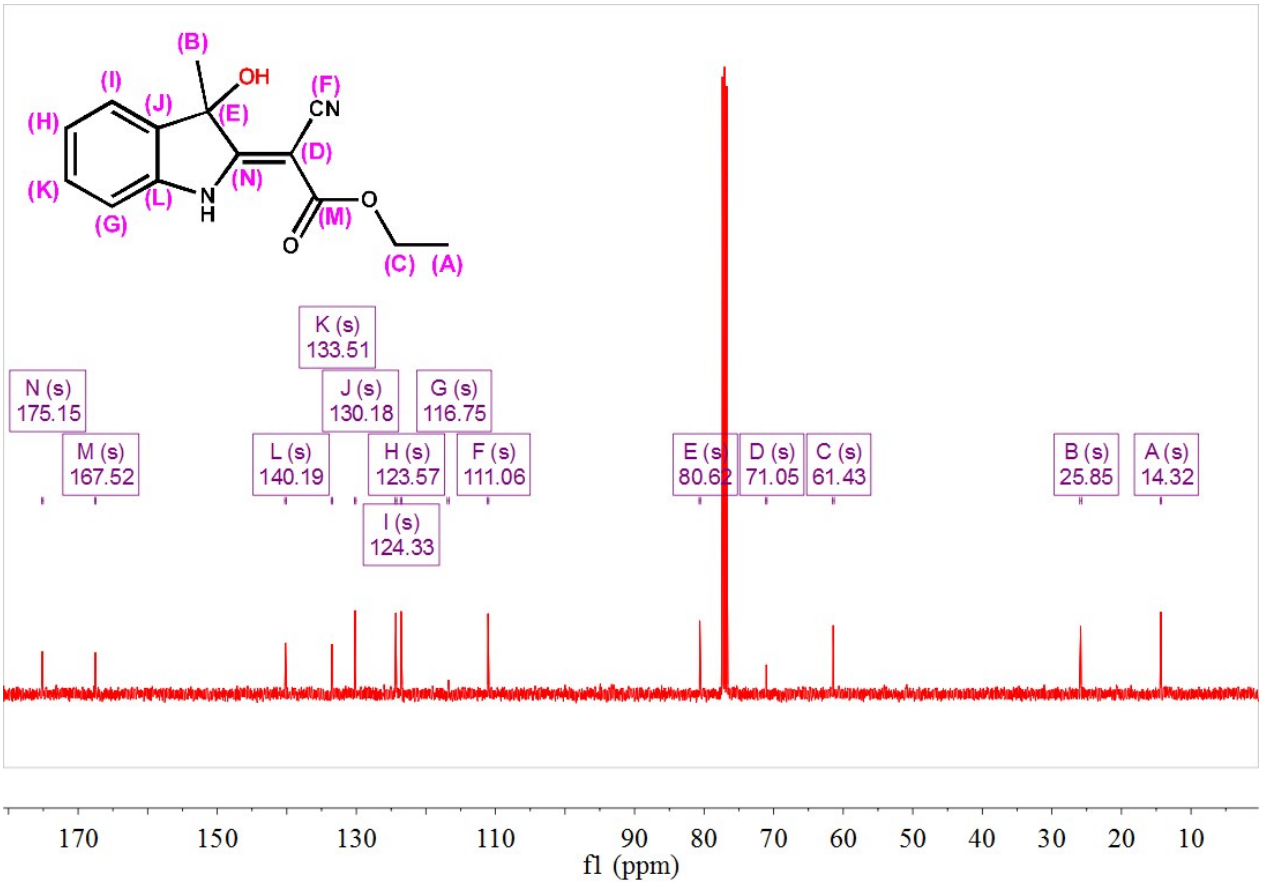

(D)
(D)
(D)
(H)
(C)
(B)
(K)
CN
(M)
(O)
(E)
(I)
(L)
(G)
(N)
(P)
(R)
(J)
(Q)
(F)
(A)
O (s) 129.62
R (s) 173.55
N (s) 128.10
K (s) 116.10
E (s) 33.55
B (s) 16.30
Q (s) 168.15
P (s) 141.91
L (s) 122.88
J (s) 110.62
I (s) 94.43
H (s) 80.59
G (s) 71.25
F (s) 61.24
D (s) 26.51
A (s) 14.33
M (s) 125.68
C (s) 16.66
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

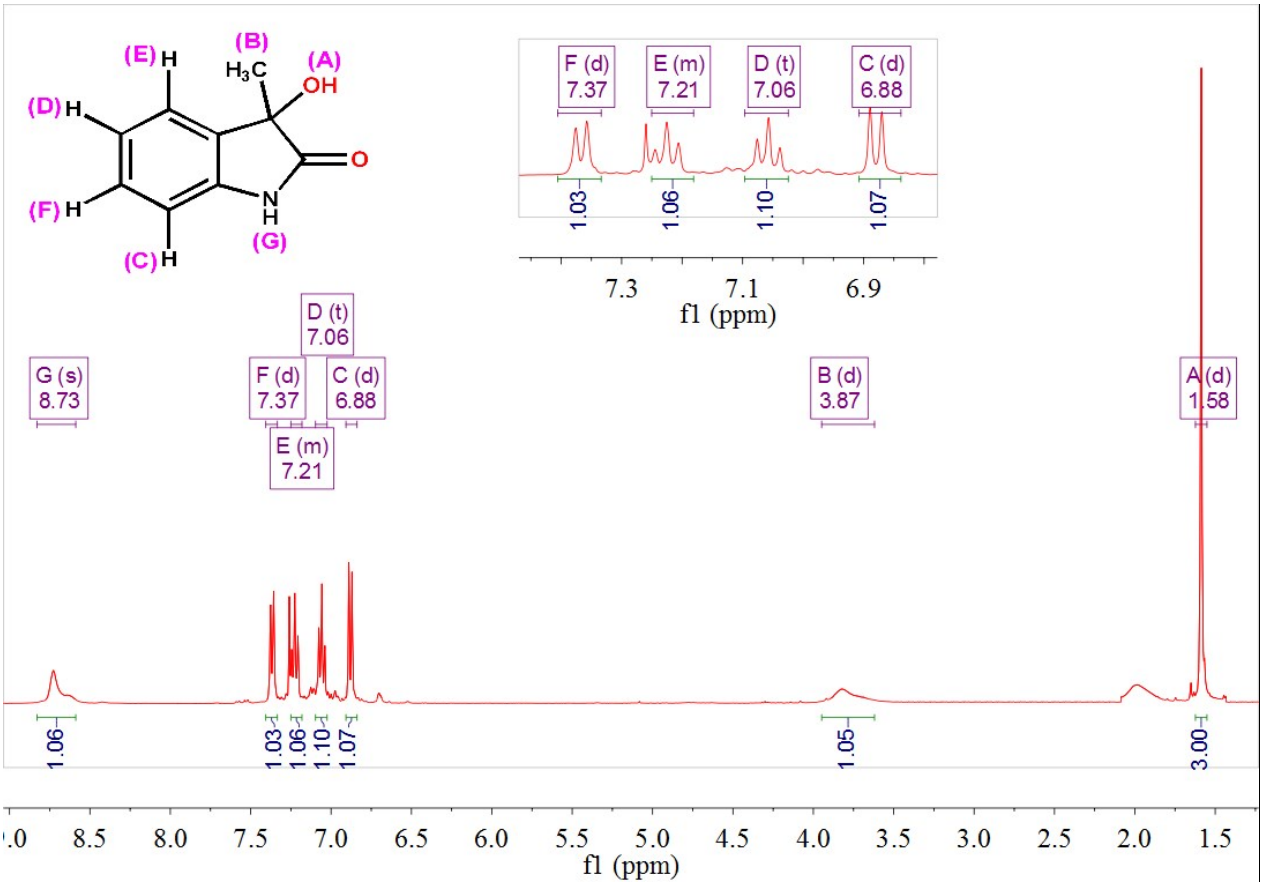

(F)
(B)
(A)
(C)
(G)
(E)
(D)
F (d) 8.75
E (s) 8.50
D (d) 7.92
C (t) 7.57
B (t) 7.17
0.92
0.89
1.07
1.08
1.08
8.6 8.2 7.8 7.4
f1 (ppm)
G (s) 11.62
A (s) 2.68
0.82
3.00
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5
f1 (ppm)

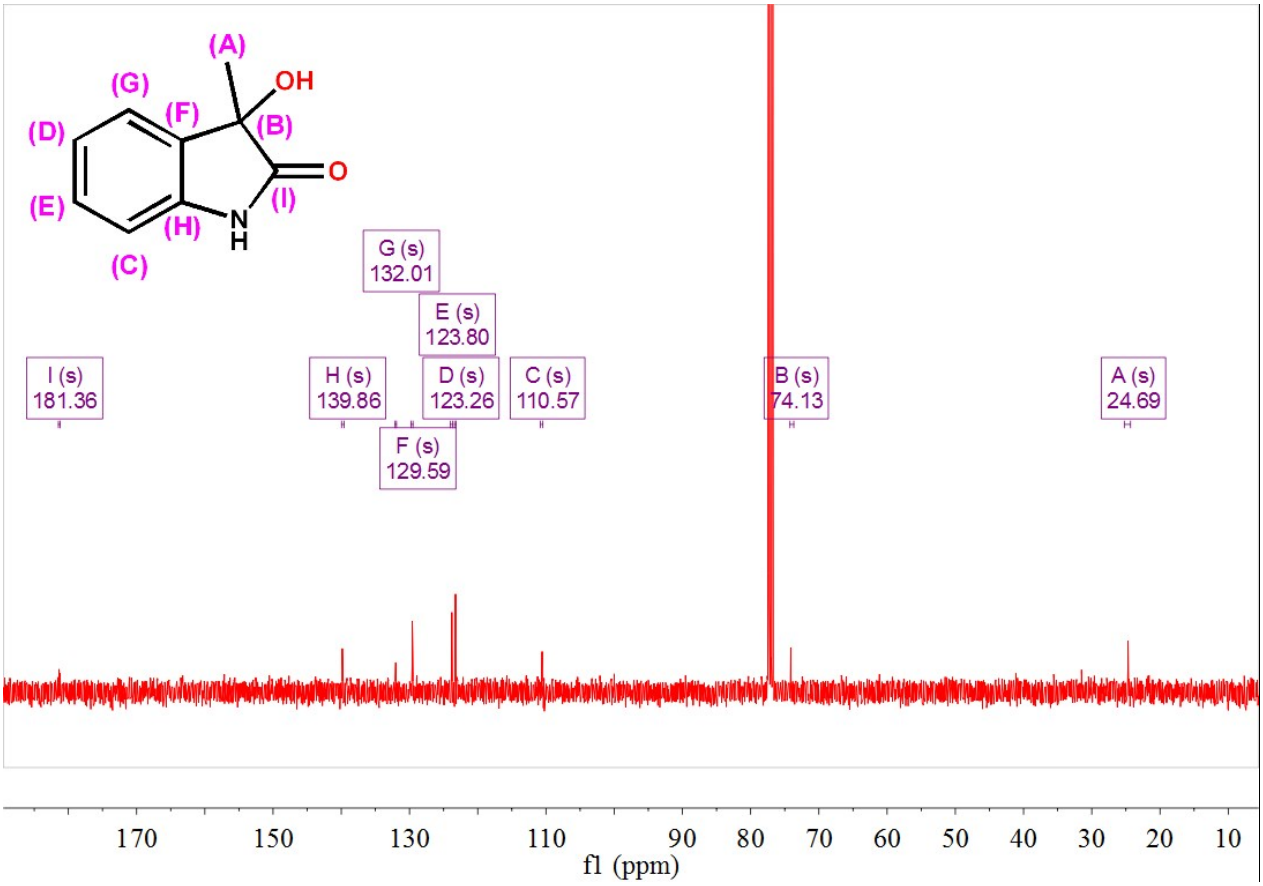

(A)
H3C
CH3
(A)
(A)
CH3
(B)
H3C
(E)H
(D)H
(F)H
(C)H
O
O
O
N
H
(G)
F (d) 7.31
E (m) 7.24
D (t) 7.04
C (d) 6.88
1.05
1.26
1.08
0.98
7.30
7.05
f1 (ppm)
G (d) 8.61
F (d) 7.31
C (d) 6.88
D (t) 7.04
E (m) 7.24
B (s) 1.54
A (d) 1.11
1.04
1.05
1.26
1.08
0.98
2.93
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


(B)
(B)
(A)
(C)
(B)
(G)
(I)
(D)
(F)
(H)
(J)
(K)
(E)
I (s)
130.05
G (s)
124.26
D (s)
82.25
B (s)
26.44
K (s)
177.63
J (s)
140.72
F (s)
122.43
E (s)
110.08
C (s)
80.41
A (s)
20.31
H (s)
129.39
170
150
130
110
90
80
70
60
50
40
30
20
f1 (ppm)


(G)H
(B)
(C)
(F) H
(H) H
(E)H
OH
CN
(D)
(A)
H (d)
7.45
G (tt)
7.29
F (t)
7.13
E (d)
6.95
0.99
1.01
1.02
1.00
7.4
7.2
7.0
f1 (ppm)
I (m)
10.48
D (m)
4.27
C (s)
3.31
B (s)
1.89
A (t)
1.35
0.98
1.99
0.87
2.94
3.00
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
f1 (ppm)


(B)
OH
(I)
(J)
(F)
CN
(H)
(E)
(D)
(K)
(N)
(L)
N
H
(G)
(M)
O
O
(C) (A)
K (s)
133.51
N (s)
175.15
J (s)
130.18
G (s)
116.75
M (s)
167.52
L (s)
140.19
H (s)
123.57
F (s)
111.06
E (s)
80.62
D (s)
71.05
C (s)
61.43
B (s)
25.85
A (s)
14.32
I (s)
124.33
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)


(E) H
(B)
H3C
(A)
OH
(D) H
O
(F) H
N
H
(G)
(C) H
F (d)
7.37
E (m)
7.21
D (t)
7.06
C (d)
6.88
1.03
1.06
1.10
1.07
7.3
7.1
6.9
f1 (ppm)
D (t)
7.06
G (s)
8.73
F (d)
7.37
C (d)
6.88
E (m)
7.21
B (d)
3.87
A (d)
1.58
1.06
1.03
1.06
1.10
1.07
1.05
3.00
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
f1 (ppm)


(A)
OH
(G)
(F)
(B)
(D)
O
(E)
(I)
(H)
N
H
(C)
G (s)
132.01
E (s)
123.80
I (s)
181.36
H (s)
139.86
D (s)
123.26
C (s)
110.57
B (s)
74.13
A (s)
24.69
F (s)
129.59
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

4. References

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