Discovery of Intermolecular Cascade Annulation for Dihydrobenzo[*b*][1,8]naphthyridines-Ylidene-Pyrrolidinetriones

Wenjun Luo,*[a] Xinghua Zheng,[a] Hehua Lin,[a] Li Fu,[b] Lipeng Long,[a] Daohong Yu,[a] Zhengwang Chen,[a] Min Yang,*[b] Zhong-Xia Wang*[a]

[a.] Jiangxi Provincial Key Laboratory of Synthetic Pharmaceutical Chemistry, Gannan Normal University, Ganzhou 341000, P.R. China.

[b.]School of Pharmacy, Jiangxi Provincial Key Laboratory of Tissue Engineering, Gannan Medical University, Ganzhou 341000, China.

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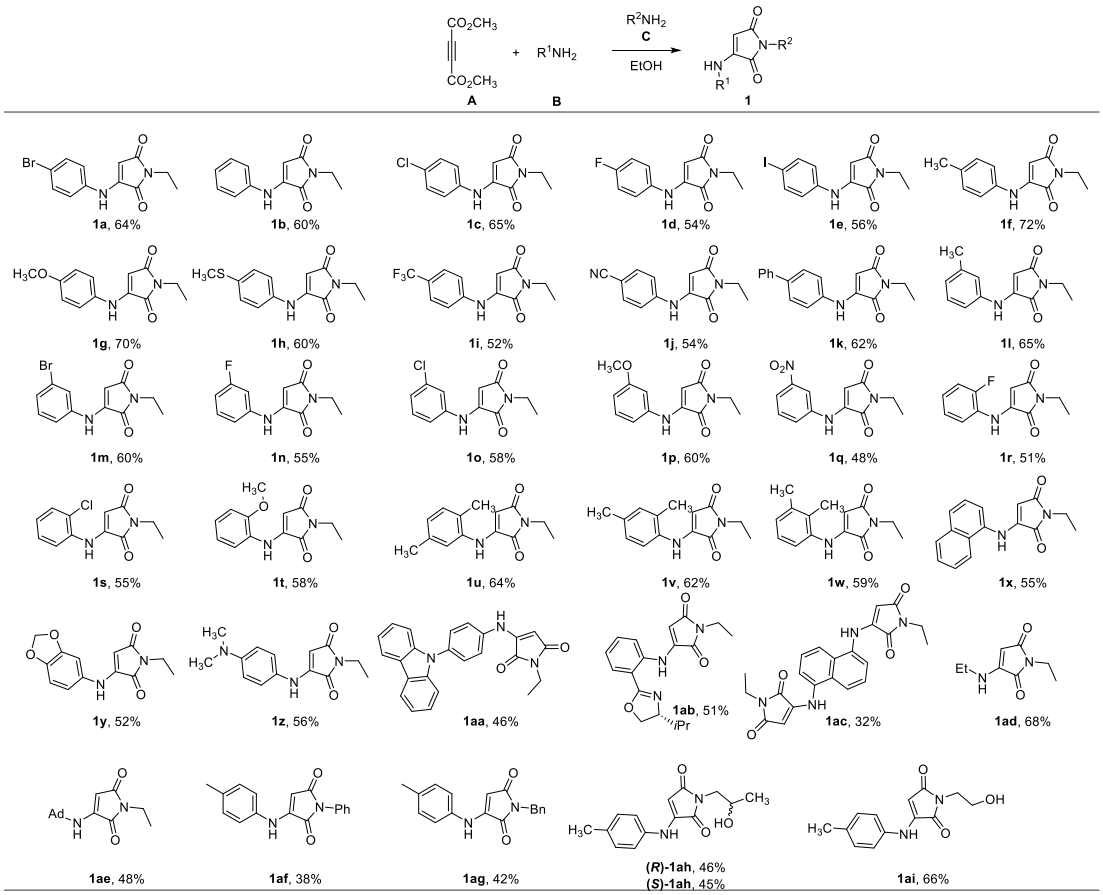
1. General experimental methods

All commercially available starting materials including reagents and solvents were purchased and used without further purification. Detailed information regarding conventional reagents is presented as follows: Potassium carbonate (Energy Chemical, AR, ≥99.0%), Sodium carbonate (Energy Chemical, AR, ≥99.8%), Cesium carbonate (Adamas-beta, 99.9%), Triethylamine (Energy Chemical, AR, ≥99.5%), 1,8-Diazabicyclo[5.4.0]undec-7-ene (Energy Chemical, AR, ≥98.0%), Triethylenediamine (Energy Chemical, AR, ≥99.0%), Piperidine (Aladdin, AR, ≥99.5%), Triphenylphosphine (Energy Chemical, AR, ≥98.0%), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (Energy Chemical, AR, ≥98.0%), Potassium persulfate (Energy Chemical, AR, ≥99.5%), Benzoyl peroxide (Energy Chemical, ≥74%), 2-Iodoxybenzoic acid (Energy Chemical, AR, ≥97%), EtOH (Energy Chemical, AR, ≥99.7), MeOH (Energy Chemical, AR, ≥99.5), EA (Energy Chemical, AR, ≥99.5), Toluene (XILONG SCIENTIFIC, AR, ≥99.5), THF (Energy Chemical, AR, ≥99.0), DMSO (Energy Chemical, AR, ≥99.8), CH_3CN (Energy Chemical, AR, ≥99.9), DMF (GENERAL-REAGENT, AR, ≥99.5), anhydrous DMF (Energy Chemical, 99.8%, with molecular sieves, Moisture, 39.5 ppm (by K. F.)). The dry DMF was obtained through treatment with calcium hydride following the procedures outlined in the 'Purification of Laboratory Chemicals' edited by W. L. F. Armarego and D. D. Perrin, 4th Edition. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin-layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25-35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker spectrometer operating at 400 MHz, 500 MHz, or 600 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants are quoted in Hz. High-resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument. The infrared spectrums were recorded on ThermoFisher Nicolet iS50. The fluorescence spectra were recorded on ThermoFisher Varioskan LUX. The live-cell imaging was recorded on Leica STELLARIS 5. The FTIR spectra were recorded as KBr disks in the range 3500–500 cm^{-1} using a Nicolet is 50 spectrometer at r.t.

2. General procedures for the synthesis of Aminomaleimides

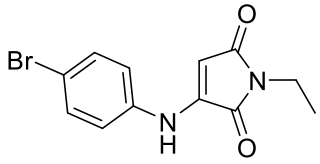


Scheme S1. Scope of aminomaleimides

In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5.0 mmol) and either an aromatic amine or an aliphatic amine **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) or the corresponding amine (15 mmol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with yields ranging from 32% to 72%. **1b**, **1g**, **1ad**, **1af**, **1ag**, **1ai**, which we have synthesized, have been reported in previous literatures[1-6]. The following are unreported in the literature.

2.1. Characterization of 1a, 1c-1ac, 1ae, (*R*) or (*S*) 1ah

3-((4-bromophenyl)amino)-1-ethyl-*1H*-pyrrole-2,5-dione (1a)

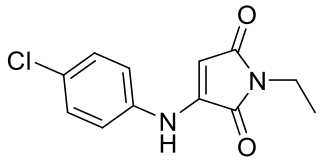


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate

A (5 mmol) and *p*-bromoaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 64% yield.

64% yield, yellow solid, m.p.:192-193°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.44 (s, 1H), 7.08 – 6.99 (m, 2H), 5.46 (s, 1H), 3.58 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 167.9, 142.1, 137.6, 132.7, 120.2, 117.1, 89.6, 32.8, 14.0. IR(KBr):ν_{max}: 3307, 3126, 2936, 1689, 1639, 1561, 1541, 1492, 1450, 1402, 819, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}BrN_2O_2$ $[M+H]^+$ = 295.0076, found = 295.0097.

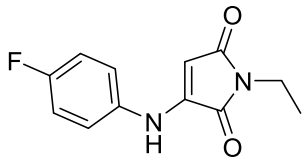
3-((4-chlorophenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1c)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-chloroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 65% yield.

65% yield, yellow solid, m.p.:196-197°C, 1H NMR (400 MHz, CDCl3) δ 7.44 – 7.32 (m, 3H), 7.14 – 7.06 (m, 2H), 5.46 (s, 1H), 3.59 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 172.3, 167.9, 142.2, 137.1, 129.8, 129.6, 119.90, 89.5, 32.8, 14.0. IR(KBr): ν_{max}: 3308, 3128, 2940, 1690, 1638, 1561, 1542, 1494, 1420, 1406, 821, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}ClN_2O_2$ $[M+H]^+$ = 251.0581, found = 251.0581.

1-ethyl-3-((4-fluorophenyl)amino)-1*H*-pyrrole-2,5-dione (1d)

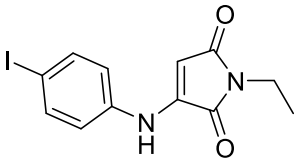


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-fluoroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the

mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 54% yield.

54% yield, brown yellow solid, m.p.:192-193°C, 1H NMR (400 MHz, CDCl3) δ 7.34 (s, 1H), 7.11 (dd, J = 7.1, 5.4 Hz, 4H), 5.41 (s, 1H), 3.58 (dd, J = 13.7, 6.7 Hz, 2H), 1.20 (dd, J = 9.3, 4.3 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 172. 5, 167.9, 160.6, 158.2, 142.8, 134.6, 120.6, 120.516, 116.7, 116.4, 88.4, 32.8, 14.0. IR(KBr): ν_{max}: 3303, 3141, 2946, 1691, 1640, 1552, 1511, 1446, 1411, 1331, 826, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}FN_2O_2$ $[M+H]^+$ = 235.0873, found = 235.0893.

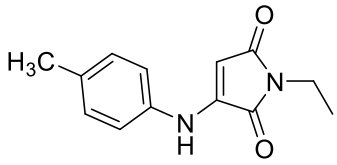
1-ethyl-3-((4-iodophenyl)amino)-1*H*-pyrrole-2,5-dione (1e)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-fluoroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 56% yield.

56% yield, yellow solid, m.p.:192-193°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.47 (s, 1H), 3.59 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.9, 141.9, 138.6, 138.3, 120.5, 89.9, 87.5, 32.8, 140. IR(KBr): ν_{max}: 3305, 3119, 2937, 1686, 1639, 1590, 1538, 1487, 1455, 1400, 824, 705 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}IN_2O_2$ $[M+H]^+$ = 342.9938, found = 342.9956.

1-ethyl-3-(*p*-tolylamino)-1*H*-pyrrole-2,5-dione (1f)

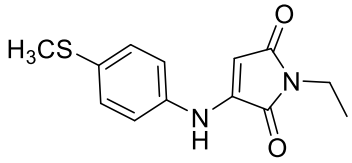


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-methylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced

into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 72% yield.

72% yield, yellow solid, m.p.:154-155°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.43 (s, 1H), 3.58 (d, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 168.1, 142.7, 135.9, 134.2, 130.2, 118.8, 88.2, 32.7, 20.8, 14.0. IR(KBr): ν_{max}: 3304, 3127, 2976, 1692, 1642, 1586, 1543, 1513, 1444, 1422, 814, 683 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{14}N_2O_2$ $[M+H]^+$ = 231.1128, found = 231.1141.

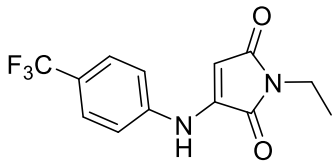
1-ethyl-3-((4-(methylthio)phenyl)amino)-1*H*-pyrrole-2,5-dione (1h)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-thiomethylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 60% yield.

60% yield, brown solid, m.p.:145-146°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.31 – 7.26 (m, 2H), 7.12 – 7.07 (m, 2H), 5.44 (s, 1H), 3.58 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 168.0, 142.4, 135.9, 134.3, 128.2, 119.3, 88.8, 32.7, 16.3, 13.9. IR(KBr): ν_{max}: 3308, 3118, 2921, 1688, 1636, 1538, 1495, 1448, 1422, 1407, 814, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{14}N_2O_2S$ $[M+H]^+$ = 263.0848, found = 263.0856.

1-ethyl-3-((4-(trifluoromethyl)phenyl)amino)-1*H*-pyrrole-2,5-dione (1i)

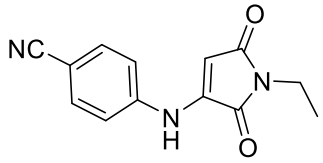


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *P*-trifluoromethyl aniline **B** (5.0 mmol). The resulting mixture was stirred at room

temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 52% yield.

52% yield, orange solid, m.p.:205-206°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.44 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.59 (s, 1H), 3.61 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 172.5, 167.9, 143.6, 143.2, 126.9, 119.8, 91.6, 32.5, 14.2. IR(KBr):v v_{max}: 3307, 3122, 2949, 1688, 1638, 1552, 1451, 1419, 1337, 1116, 837, 705 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}F_3N_2O_2$ $[M+H]^+$ = 285.0845, found = 285.0847.

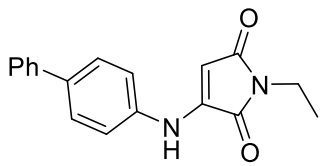
4-((1-ethyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)amino)benzonitrile (1j)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-cyananiline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 54% yield.

54% yield, yellow solid, m.p.:262-263°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.45 (s, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 5.62 (s, 1H), 3.61 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 172.4, 167.9, 144.3, 142.7, 134.0, 119.8, 119.4, 105.4, 92.8, 32.6 14.2. IR(KBr): v_{max}: 3300, 3125, 2997, 2223, 1687, 1639, 1605, 1561, 1541, 1448, 1414, 834, 710 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}N_3O_2$ $[M+H]^+$ = 242.0924, found = 242.0935.

3-([1,1'-biphenyl]-4-ylamino)-1-ethyl-1*H*-pyrrole-2,5-dione (1k)

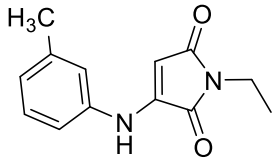


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-phenylaniline **B** (5.0 mmol). The resulting mixture was stirred at room

temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 62% yield.

62% yield, yellow solid, m.p.:222-223°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.45 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.25 – 7.19 (m, 2H), 5.54 (s, 1H), 3.61 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 168.1, 142.2, 139.9, 137.6, 137.4, 128.9, 128.3, 127.4, 126.8, 119.0, 89.2, 32.8, 14.0. IR(KBr): ν_{max}: 3285, 3132, 2952, 1686 1628, 1607, 1534, 1511, 1448, 1405, 760, 696 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{16}N_2O_2$ $[M+H]^+$ = 293.1284, found = 293.1303.

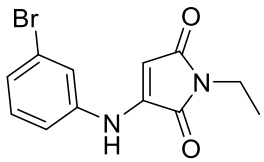
1-ethyl-3-(m-tolylamino)-1*H*-pyrrole-2,5-dione (1l)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and m-methylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 65% yield.

65% yield, yellow solid, m.p.:126-127°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.27 (dd, *J* = 11.6, 3.8 Hz, 1H), 7.03 – 6.94 (m, 3H), 5.50 (s, 1H), 3.60 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 168.1, 142.5, 139.6, 138.4, 129.4, 125.2, 119.4, 115.8, 88.8, 32.7, 21.4, 13.9. IR(KBr): ν_{max}: 3296 3125, 2974, 1695, 1628, 1594, 1552, 1492, 1444, 1418, 797, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{14}N_2O_2$ $[M+H]^+$ = 231.1128, found = 231.1147.

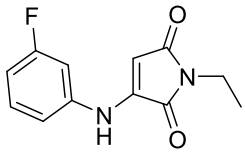
3-((3-bromophenyl)amino)-1-ethyl-1H-pyrrole-2,5-dione (1m)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and m-bromoaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 60% yield.

60% yield, orange yellow solid, m.p.:180-181°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.34 (d, *J* = 1.5 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.13 – 7.05 (m, 1H), 5.53 (s, 1H), 3.60 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.9, 141.9, 139.8, 130.9, 127.3, 123.3, 121.7, 117.1, 90.2, 32.9, 14.0. IR(KBr): ν_{max}: 3307, 3136, 2976, 1692, 1637, 1593, 1561, 1544, 1445, 1414, 779, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}BrN_2O_2$ $[M+H]^+$ = 295.0076, found = 295.0091.

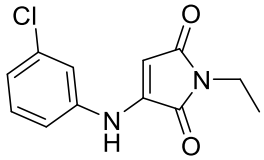
1-ethyl-3-((3-fluorophenyl)amino)-1*H*-pyrrole-2,5-dione (1n)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and m-fluoroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 55% yield.

55% yield, brown yellow solid, m.p.:130-131°C , **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.33 (dd, *J* = 14.6, 8.1 Hz, 1H), 7.01 – 6.88 (m, 2H), 6.83 (td, *J* = 8.3, 2.0 Hz, 1H), 5.53 (s, 1H), 3.59 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 168.0, 164.5, 162.0, 142.1, 140.2, 140.1, 131.0, 130.9, 114.3, 114.3, 111.2, 111.0, 106.2, 106.0, 90.1, 32.8, 13.9. IR(KBr): ν_{max}: 3309, 3115, 2985, 1692, 1640, 1581, 1495, 1448, 1434, 1421, 766, 683 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}FN_2O_2$ $[M+H]^+$ = 235.0873, found = 235.0893.

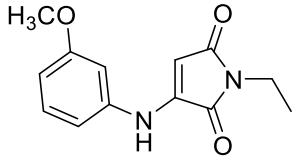
3-((3-chlorophenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1o)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and m-chloroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 58% yield.

58% yield, yellow green solid, m.p.:178-179°C , **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 1.9 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.4 Hz, 1H), 5.53 (s, 1H), 3.60 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 168.0 141.9, 139.7, 135.5, 130.7, 124.4, 118.8, 116.7, 90.2, 32.9, 14.0. IR(KBr): ν_{max}: 3305, 3125, 2920, 1697, 1632, 1595, 1439, 14410, 1350, 1331, 776, 689 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}ClN_2O_2$ $[M+H]^+$ = 251.0581, found = 251.0586.

1-ethyl-3-((3-methoxyphenyl)amino)-1*H*-pyrrole-2,5-dione (1p)

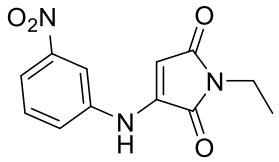


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and m-methoxyaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 60% yield.

60% yield, brown solid, m.p.:106-107°C , **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.31 – 7.25 (m, 1H), 6.80 – 6.64 (m, 3H), 5.49 (s, 1H), 3.80 (s, 3H), 3.58 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 168.0, 160.6, 142.3, 139.6, 130.4, 111.1, 109.7, 104.8, 89.3, 55.3, 32.7, 14.0. IR(KBr): ν_{max}: 3289, 3162, 2936, 1697, 1628, 1604, 1500, 1461, 1448, 1423, 782, 685 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{14}N_2O_3$ $[M+H]^+$ = 247.1072, found =

247.1096.

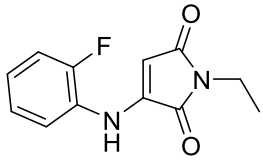
1-ethyl-3-((3-nitrophenyl)amino)-1*H*-pyrrole-2,5-dione (1q)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and m-nitroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 48% yield.

48% yield, Yellow solid, m.p.:230-231°C. **^{1}H NMR** (400 MHz, DMSO) δ 10.03 (s, 1H), 8.21 (d, *J* = 1.4 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 8.2 Hz, 1H), 5.80 (d, *J* = 1.7 Hz, 1H), 3.46 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 172.4, 167.7, 148.8, 143.4, 141.3, 131.2, 125.3, 118.1, 114.6, 91.3, 32.5, 14.2. IR(KBr): ν_{max}: 3298, 3125, 2922, 1674, 1629,1578, 1525, 1442, 1410, 1325, 779, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}N_3O_4$ $[M+H]^+$ = 262.0822, found = 262.0827.

1-ethyl-3-((2-fluorophenyl)amino)-1*H*-pyrrole-2,5-dione (1r)

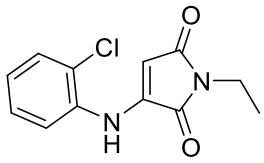


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and o-fluoroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 51% yield.

51% yield, orange yellow solid, m.p.:146-147°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.28 (dd, *J* = 12.7, 4.8 Hz, 1H), 7.17 (dt, *J* = 11.0, 4.2 Hz, 2H), 7.14 – 7.07 (m, 1H), 5.52 (s, 1H), 3.60 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.6, 154.3,

151.9, 141.8, 127.1, 126.9, 124.9, 124.8, 124.8, 124.7, 118.6, 115.9, 115.7, 90.2, 32.8, 13.9. IR(KBr): ν_{max}: 3310, 3120, 2945, 1702, 1652, 1618, 1489, 1447, 1423, 1335, 788, 685 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}FN_2O_2$ $[M+H]^+$ = 235.0873, found = 235.0898.

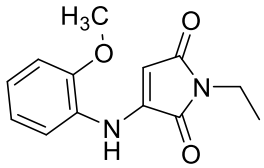
3-((2-chlorophenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1s)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and o-chloroaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 55% yield.

55% yield, brown yellow solid, m.p.:111-112°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.43 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.31 (ddd, *J* = 14.7, 8.2, 3.8 Hz, 2H), 7.07 (td, *J* = 8.0, 1.7 Hz, 1H), 5.53 (s, 1H), 3.60 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.7, 141.4, 135.2, 130.1, 128. 0, 124.7, 124.0, 118.1, 90.4, 32.8, 14.0. IR(KBr): ν_{max}: 3342, 3136, 2980, 1708, 1639, 1592, 1538, 1462, 1443, 1412, 775, 747 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}ClN_2O_2$ $[M+H]^+$ = 251.0581, found = 251.0601.

1-ethyl-3-((2-methoxyphenyl)amino)-1*H*-pyrrole-2,5-dione (1t)

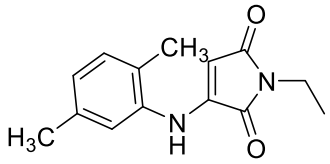


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and o-methoxyaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 58% yield.

58% yield, yellow green solid, m.p.:106-107°C , **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.16

(dd, *J* = 7.8, 1.3 Hz, 1H), 7.06 (td, *J* = 7.8, 1.4 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.92 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.48 (s, 1H), 3.89 (d, *J* = 8.2 Hz, 3H), 3.58 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 167.9, 149.0, 141.6, 127.9, 124.1, 121.0, 116.6, 110.5, 88.8, 55.7, 32.6, 13.9. IR(KBr): ν_{max}: 3360, 3131, 2948, 1707, 1644, 1599, 1533, 1488, 1462, 1413, 775, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{14}N_2O_3$ $[M+H]^+$ = 247.1072, found = 247.1098.

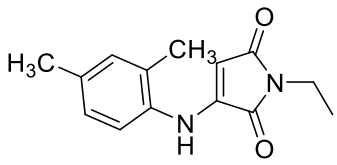
3-((2,5-dimethylphenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1u)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and 2, 5-dimethylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 64% yield.

64% yield, yellow solid, m.p.:144-145°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 9.5 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 5.37 (s, 1H), 3.59 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.28 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 168.1, 143.1, 137.1, 136.3, 131.0, 125.6, 125.5, 119.6, 88.3, 32.71, 21.2, 16.9, 14.0. IR(KBr): ν_{max}: 3379, 3119, 2974, 1705, 1642, 1583, 1542, 1447, 1415, 1414, 797, 691 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{16}N_2O_2$ $[M+H]^+$ = 245.1284, found = 245.1273.

3-((2,4-dimethylphenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1v)

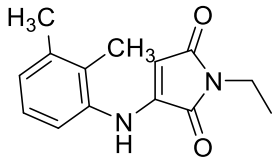


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and 2, 4-dimethylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then

recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 62% yield.

62% yield, yellow solid, m.p.:115-116°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 1H), 7.05 (d, *J* = 5.3 Hz, 2H), 7.00 (s, 1H), 5.26 (s, 1H), 3.58 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 2.28 (d, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 168.0, 143.6, 134.8, 133.9, 131.9, 128.8, 127.6, 119.3, 87.7, 32.6, 20.8, 17.3, 14.0. IR(KBr): ν_{max}: 3371, 3128, 2940, 1703, 1638, 1614, 1535, 1444, 1413, 1380, 776, 680 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{16}N_2O_2$ $[M+H]^+$ = 245.1284, found = 245.1292.

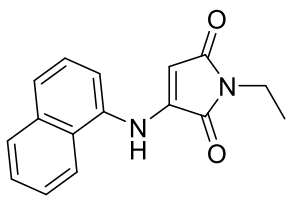
3-((2,3-dimethylphenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1w)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and 2, 3-dimethylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 59% yield.

59% yield, yellow solid, m.p.:84-85°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.06 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 3.57 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 2.20 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 167.9, 144.0, 138.2, 136.2, 128.0, 127.0, 126.2, 117.9, 87.7, 32.5, 20.4, 13.9, 13.2. IR(KBr): ν_{max}: 3379, 3976, 2938, 1703, 1641, 1586, 1474, 1448, 1414, 1379, 775, 708 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{16}N_2O_2$ $[M+H]^+$ = 245.1284, found = 245.1274.

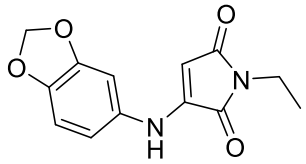
1-ethyl-3-(naphthalen-1-ylamino)-1*H*-pyrrole-2,5-dione (1x)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and naphthalen-1-amine **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 55% yield.

55% yield, brown solid, m.p.:101-102°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, 2H), 7.74 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 5.35 (s, 1H), 3.61 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 167.9, 143.9, 134.1, 133.5, 128.7, 126.6, 126.2, 125.6, 125.4, 120.4, 116.8, 109.5, 88.9, 32.6, 14.0. IR(KBr): ν_{max}: 3374, 3057, 2977, 1701, 1638, 1577, 1501, 1446, 1414, 1379, 770, 680 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{14}N_2O_2$ $[M+H]^+$ = 267.1128, found = 267.1142.

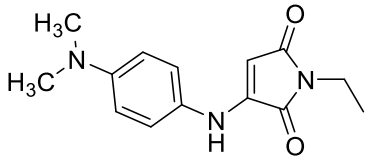
3-(benzo[d][1,3]dioxol-5-ylamino)-1-ethyl-1*H*-pyrrole-2,5-dione (1y)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and benzo[d][1,3]dioxol-5-amine **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 52% yield.

52% yield, brown black solid, m.p.:166-167°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.60 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.99 (s, 2H), 5.35 (s, 1H), 3.58 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 168.0, 148.5, 144.6, 143.1, 132.8, 112.3, 108.7, 101.6, 101.1, 87.8, 32.7, 13.9. IR(KBr): ν_{max}: 3302, 3137, 2940, 1697, 1642, 1621, 1556, 1499, 1447, 1418, 774, 689 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{12}N_2O_4$ $[M+H]^+$ = 261.0869, found = 261.0868.

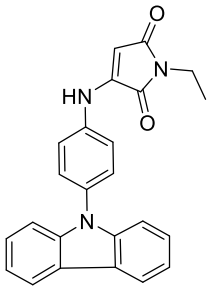
3-((4-(dimethylamino)phenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1z)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *N*,*N*-dimethylbenzene-1,4-diamine **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 56% yield.

56% yield, orange yellow solid, m.p.:159-160°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 5.30 (s, 1H), 3.57 (q, *J* = 7.2 Hz, 2H), 2.95 (s, 6H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ 172.8, 168.1, 147.9, 143.3, 127.8, 120.5, 113.1, 86.1, 40.6, 32.6, 14.0. IR(KBr): ν_{max}: 3295, 3101, 2936, 1692, 1633, 1534, 1518, 1444, 1418, 1347, 815, 672 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{17}N_3O_2$ $[M+H]^+$ = 260.1393, found = 260.1410.

3-((4-(9*H*-carbazol-9-yl)phenyl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1aa)

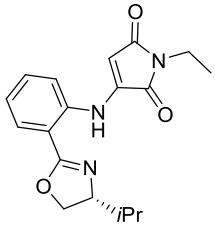


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and 4-(9*H*-carbazol-9-yl)aniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 46% yield.

46% yield, yellow solid, m.p.:222-223°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 9.3 Hz, 3H), 7.46 – 7.34 (m, 6H), 7.34 – 7.28 (m, 2H), 5.61 (s, 1H), 3.65 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 168.0, 142.1, 140.6, 137.5,

133.7, 128.4, 126.0, 123.4, 120.4, 120.1, 119.8, 109.5, 89.69, 32.9, 14.0. IR(KBr): ν_{max}: 3308, 3128, 2949, 1700, 1639, 1604, 1535, 1513, 1450, 1411, 749, 624 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{19}N_3O_2$ $[M+H]^+$ = 382.1550, found = 382.1559.

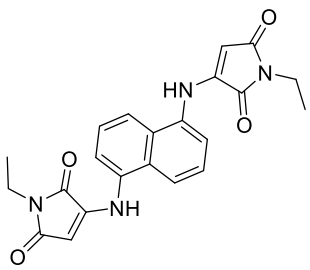
(*R*)-1-ethyl-3-((2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl)amino)-1*H*-pyrrole-2,5-dione (1ab)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and (*S*)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 51% yield.

51% yield, yellow solid, m.p.:156-157°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.34 (s, 1H), 7.91 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.34 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.14 – 7.07 (m, 1H), 5.64 (s, 1H), 4.44 (dd, *J* = 9.6, 8.2 Hz, 1H), 4.32 – 4.19 (m, 1H), 4.08 (t, *J* = 8.3 Hz, 1H), 3.61 (q, *J* = 7.2 Hz, 2H), 1.85 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 168.3, 162.7, 142.3, 140.4, 132.3, 130.1, 122.1, 116.7, 114.8, 91.5, 73.0, 69.6, 33.3, 32.6, 18.9, 18.7, 14.0. IR(KBr): ν_{max}: 3300, 3134, 2959, 1702, 1652, 1631, 1541, 1441, 1411, 1354 , 775, 704 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{21}N_3O_3$ $[M+H]^+$ = 328.1655, found = 328.1675.

3,3'-(naphthalene-1,5-diylbis(azanediyl))bis(1-ethyl-1*H*-pyrrole-2,5-dione) (1ac)

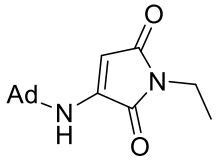


In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate

A (12 mmol) and naphthalene-1,5-diamine **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (30 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 32% yield.

32% yield, orange yellow solid, m.p.:155-156°C, **^{1}H NMR** (400 MHz, DMSO) δ 9.81 (s, 2H), 7.96 – 7.85 (m, 2H), 7.59 (d, *J* = 7.8 Hz, 3H), 7.43 – 7.23 (m, 1H), 4.94 (s, 2H), 3.47 (dd, *J* = 14.1, 7.0 Hz, 4H), 1.13 (dd, *J* = 9.8, 4.5 Hz, 6H). **^{13}C NMR** (100 MHz, DMSO) δ 172.4, 167.5, 148.5, 135.7, 129.2, 126.6, 122.4, 122.0, 87.5, 32.4, 14.5. IR(KBr): v_{max}: 3451, 3137, 2922, 1698, 1632, 1558, 1495, 1411, 1345, 1414, 764, 704 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{20}N_4O_4$ $[M+H]^+$ = 405.1557, found =405.1575.

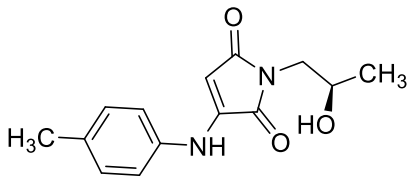
3-(((3s,5s,7s)-adamantan-1-yl)amino)-1-ethyl-1*H*-pyrrole-2,5-dione (1ae)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and adamantine **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, ethylamine (15 mmol, 30% in ethanol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 48% yield.

48% yield, yellow green solid, m.p.:171-172°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 4.88 (s, 1H), 3.51 (d, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 1.89 (d, *J* = 2.6 Hz, 6H), 1.73 – 1.61 (m, 7H), 1.16 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 168.2, 145.0, 84.9, 52.5, 40.9, 36.0, 32.4, 29.1, 14.0. IR(KBr): v_{max}: 3317, 3116, 2908, 1696, 1625, 1561, 1520, 1444, 1418, 1343, 788, 684 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{22}N_2O_2$ $[M+H]^+$ = 275.1754, found =275.1760.

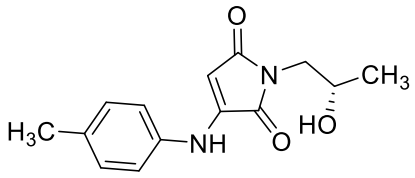
(*R*)-3-([1,1'-biphenyl]-4-ylamino)-1-(2-hydroxypropyl)-1*H*-pyrrole-2,5-dione ((*R*)-1ah)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-methylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, (*R*)-1-aminopropan-2-ol (30 mmol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 46% yield.

46% yield, yellow solid, m.p.:173-174°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 5.33 (s, 1H), 3.71 (d, *J* = 16.6 Hz, 6H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 168.6, 142.9, 135.6, 134.6, 130.3, 119.0, 88.1, 66.8, 45.5, 20.8. IR(KBr): ν_{max}: 3483, 3312, 3131, 2964, 1685, 1639, 1561, 1544, 1447, 1412, 1325, 769, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{18}N_2O_3$ $[M+H]^+$ = 261.1233, found =261.1241.

(*S*)-1-(2-hydroxypropyl)-3-(*p*-tolylamino)-1*H*-pyrrole-2,5-dione ((*S*)-1ah)



In a 50-mL flame-dried flask, 10 mL ethanol was added to the mixture of dimethyl but-2-ynedioate **A** (5 mmol) and *p*-methylaniline **B** (5.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Subsequently, (*S*)-1-aminopropan-2-ol (30 mmol) was introduced into the mixture. After 4 hrs, the solvent was removed under reduced pressure. The residue was then recrystallized using a mixture of petroleum ether (15 mL) and ethanol (5 mL). The resulting mixture was filtered, washed, and precipitated with cold ethanol. The products were obtained without further purification, with 45% yield.

45% yield, yellow solid, m.p.:173-174°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 5.33 (s, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 168.6, 142.9, 135.7, 134.6, 130.2, 118.9, 88.1, 66.7, 45.5, 20.8. IR(KBr):

ν_{max}: 3492, 3315, 3133, 2971, 1686, 1636, 1557, 1509, 1439, 1412, 1376, 768, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{18}N_2O_3$ $[M+H]^+$ = 261.1233, found =261.1233.

References

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3. Z. Wang, S. Huang, L. Yin, J. Wan, C. Liu, T. Liu and C. Huang, *J. Org. Chem.,* 2024, **89**, 5498-5510.
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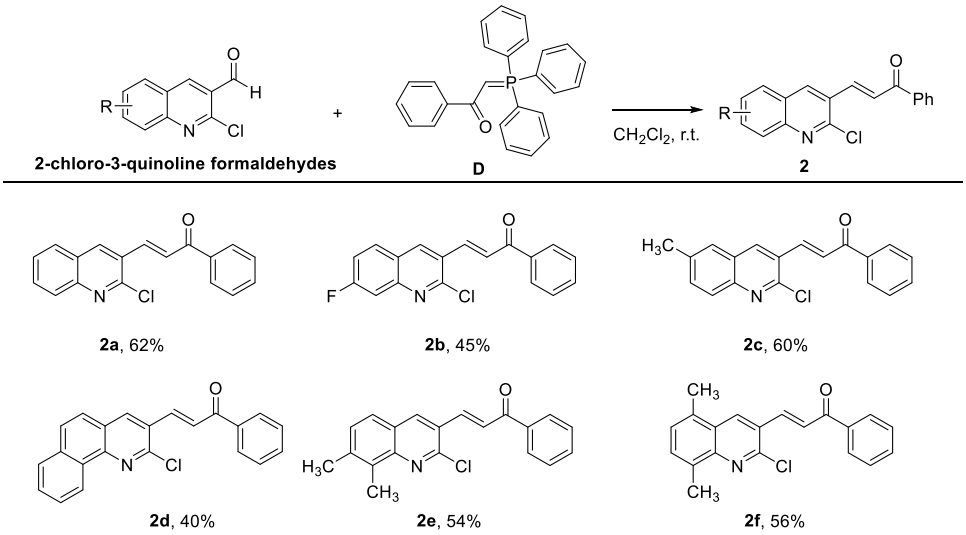
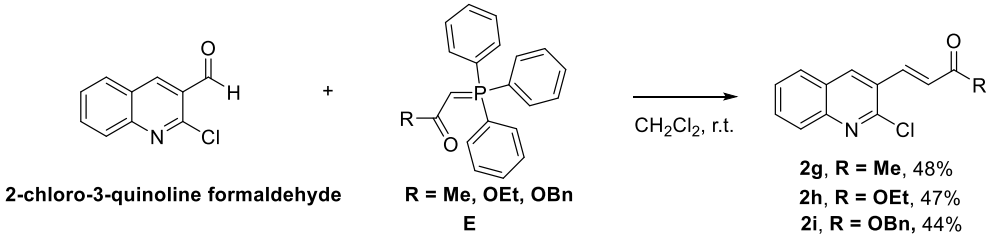
3. General procedures for the synthesis of 2, 6a, 6b.



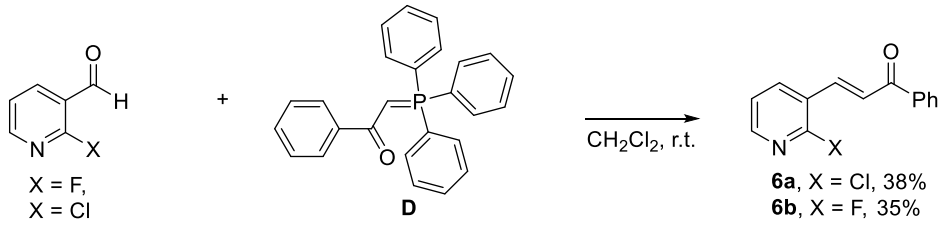
Scheme S2. Scope of 2a-2f

In a 50-mL flame-dried flask, 20 mL dichloromethane to the mixture of 2-(triphenylphosphoranylidene)acetophenone **D** (6.0 mmol, 1.2 equiv.) and corresponding substituted 2-chloro-3-quinoline formaldehyde (5 mmol, 1.0 equiv.) was stirred at room temperature for 24 h. After the starting material was consumed, the mixture was concentrated and simply purified by flash column (PE:EA = 20:1) to give the corresponding product (**2a**-**2f**).



Scheme S3. Scope of 2g-2i

In a 50-mL flame-dried flask, 20 mL dichloromethane to the mixture of corresponding Wittig reagent **E** (6 mmol, 1.2 equiv.) and 2-chloro-3-quinoline formaldehyde (5 mmol, 1.0 equiv.) was stirred at room temperature for 24 h. After the starting material was consumed, the mixture was concentrated and simply purified by flash column (PE:EA = 10:1) to give the product (**2g-2i**).



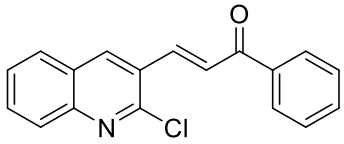
Scheme S4. Scope of 6a and 6b

In a 50-mL flame-dried flask, 20 mL dichloromethane to the mixture of 2-(triphenylphosphoranylidene)acetophenone (6 mmol, 1.2 equiv.) with 2-chloronicotinaldehyde or 2-fluoronicotinaldehyde formaldehyde (5 mmol, 1.0 equiv.) was stirred at room temperature for 24

h. After the starting material was consumed, the mixture was concentrated and simply purified by flash column (PE:EA = 20:1) to give the corresponding product (**6a** and **6b**).

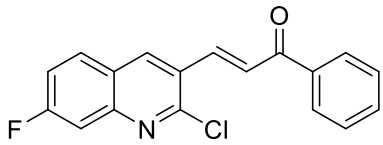
Characterization of *ortho*-halogenatedquinolin/pyridine chalcones

(*E*)-3-(2-chloroquinolin-3-yl)-1-phenylprop-2-en-1-one (2a)



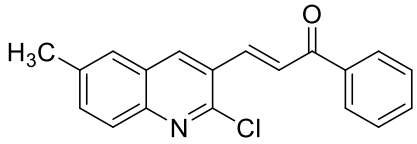
62% yield, yellowish solid, m.p.:139-140°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.16 (d, J = 15.7 Hz, 1H), 8.01 (dd, J = 20.6, 8.1 Hz, 3H), 7.86 (d, J = 8.1 Hz, 1H), 7.74 (t, J = 7.7 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.7, 150.3, 147.8, 139.21, 137.5, 136.1, 133.2, 131.6, 128.7, 128.6, 128.3, 128.0, 127.9, 127.7, 126.9, 126.2. IR(KBr): ν_{max}: 3060, 2924, 1663, 1604, 1486, 1446, 1403, 1373, 1049, 1013, 782, 708 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{12}ClNO$ $[M+H]^+$ = 294.0680, found =294.0680.

(*E*)-3-(2-chloro-7-fluoroquinolin-3-yl)-1-phenylprop-2-en-1-one (2b)



45% yield, yellowish solid, m.p.:150-151°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.16 (d, J = 15.7 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.89 (dd, J = 9.0, 5.9 Hz, 1H), 7.67 – 7.57 (m, 3H), 7.53 (t, J = 7.6 Hz, 2H), 7.39 (td, J = 8.7, 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.7, 165.5, 163.0, 151.7, 139.0, 137.5, 135.9, 133.2, 128.8, 128.6, 126.3, 118.5, 118.2, 112.7, 112.5. IR(KBr): ν_{max}: 3039, 2921, 1653, 1639, 1561, 1493, 1438, 1368, 1049, 1013, 782, 708 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{11}ClFNO$ $[M+H]^+$ = 312.0586, found =312.0586.

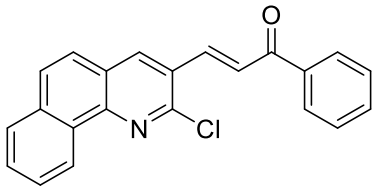
(*E*)-3-(2-chloro-6-methylquinolin-3-yl)-1-phenylprop-2-en-1-one (2c)



60% yield, yellowish solid, m.p.:145-146°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.14 (d, J = 15.8 Hz, 1H), 8.06 – 8.01 (m, 2H), 7.86 (d, J = 8.6 Hz, 1H), 7.58 (ddd, J = 7.2, 4.2, 2.0 Hz, 3H), 7.55 – 7.49 (m, 3H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8, 149.4, 146.4, 139.4, 137.8, 137.5, 135.5, 133.9, 133.1, 128.7, 128.6, 127.9, 127.7, 126.9, 126.8, 126.0, 21.55. IR(KBr): ν_{max}:

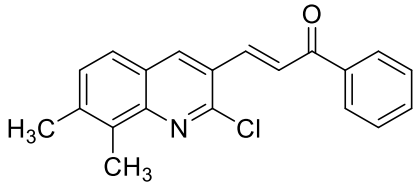
3059, 2922, 1654, 1639, 1561, 1494, 1446, 1400, 1055, 1013, 822, 706 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{14}ClNO$ $[M+H]^+$ = 308.0836, found =308.0857.

(*E*)-3-(2-chlorobenzo[h]quinolin-3-yl)-1-phenylprop-2-en-1-one (2d)



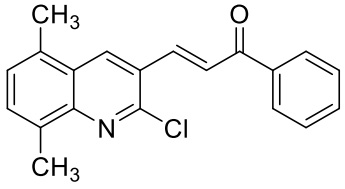
40% yield, yellowish solid, m.p.:195-196°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.22 (d, J = 15.8 Hz, 1H), 8.10 – 8.04 (m, 2H), 7.88 (dt, J = 6.3, 2.6 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.65 (tt, J = 7.3, 3.5 Hz, 3H), 7.55 (dd, J = 15.7, 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8, 149.7, 146.9, 139.4, 137.6, 135.6, 134.1, 133.1, 130.1, 129.3, 128.9, 128.74, 128.66, 128.0, 127.9, 127.6, 125.9, 125.2, 124.9, 124.4. IR(KBr): ν_{max}: 3053, 2923, 1664, 1640, 1578, 1561, 1437, 1401, 1055, 1015, 817, 693 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{14}ClNO$ $[M+H]^+$ = 344.0836, found =344.0836.

(*E*)-3-(2-chloro-7,8-dimethylquinolin-3-yl)-1-phenylprop-2-en-1-one (2e)



54% yield, yellowish solid, m.p.:198-199°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.20 (d, J = 15.7 Hz, 1H), 8.10 – 8.00 (m, 2H), 7.64 – 7.50 (m, 5H), 7.40 (d, J = 8.3 Hz, 1H), 2.69 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9, 149.2, 147.1, 140.0, 139.8, 137.7, 136.3, 134.1, 133.1, 130.5, 128.7, 128.6, 126.3, 125.5, 125.3, 124.9, 20.9, 13.3. IR(KBr): ν_{max}: 3012, 2922, 1662, 1639, 1576 1561, 1438, 1401, 1076, 1039, 809, 706 cm^{-1}. HRMS (ESI) m/z calculated for $C_{20}H_{16}ClNO$ $[M+H]^+$ = 322.0993, found =322.1011.

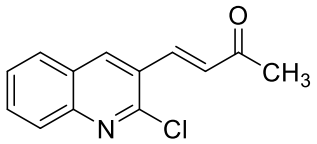
(*E*)-3-(2-chloro-5,8-dimethylquinolin-3-yl)-1-phenylprop-2-en-1-one (2f)



56% yield, yellowish solid, m.p.:192-193°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.18 (d, J = 15.8 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.65 – 7.51 (m, 4H), 7.46 (d, J = 7.2 Hz, 1H), 7.30 – 7.27 (m, 1H), 2.70 (s, 3H), 2.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2, 148.8, 147.5, 140.1, 137.6,

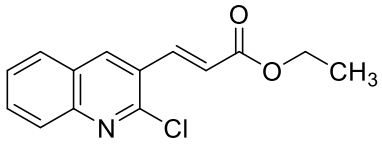
134.5, 133.15, 133.07, 132.8, 131.5, 128.70, 128.66, 127.8, 126.8, 126.4, 126.1, 18.6, 17.7. IR(KBr): ν_{max}: 3056, 2922, 1654, 1602, 1494 1464, 1446, 1385, 1092, 1014, 828, 710 cm^{-1}. HRMS (ESI) m/z calculated for $C_{20}H_{16}ClNO$ $[M+H]^+$ = 322.0993, found =322.1013.

(*E*)-4-(2-chloroquinolin-3-yl)but-3-en-2-one (2g)



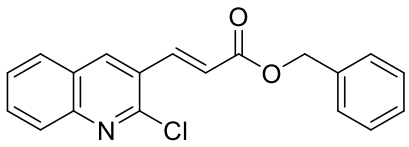
48% yield, yellowish solid, m.p.:134-135°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.94 (dd, J = 22.7, 12.3 Hz, 2H), 7.85 – 7.71 (m, 2H), 7.57 (t, J = 7.1 Hz, 1H), 6.76 (d, J = 16.3 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 150.0, 147.8, 137.9, 136.0, 131.6, 130.9, 128.3, 128.0, 127.7, 127.3, 126.9, 27.4. IR(KBr): ν_{max}: 3053, 2922, 1673, 1642, 1615 1583, 1485, 1397, 1132, 1047, 777, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{10}ClNO$ $[M+H]^+$ = 232.0523, found =232.0541.

Ethyl (*E*)-3-(2-chloroquinolin-3-yl)acrylate (2h)



47% yield, yellowish solid, m.p.:155-156°C, **^{1}H NMR** (400 MHz, CDCl3) δ 8.38 (s, 1H), 8.21 – 7.96 (m, 2H), 7.81 (d, J = 29.1 Hz, 2H), 7.60 (s, 1H), 6.82 – 6.34 (m, 1H), 4.33 (d, J = 6.6 Hz, 2H), 1.37 (d, J = 5.9 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl3) δ 165.9, 150.0, 147.8, 139.2, 136.1, 131.5, 128.4, 128.0, 127.6, 127.5, 127.0, 122.7, 60.9, 14.3. IR(KBr): ν_{max}: 2987, 2922, 1711, 1653, 1616 1579, 1561, 1448, 1393, 1039, 816, 746 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{12}ClNO_2$ $[M+H]^+$ = 261.0556, found =261.0551.

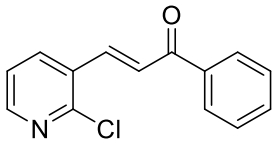
Benzyl (*E*)-3-(2-chloroquinolin-3-yl)acrylate (2i)



44% yield, yellowish solid, m.p.:185-186°C, **^{1}H NMR** (400 MHz, CDCl3) δ 8.31 (s, 1H), 8.14 (d, J = 15.9 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 – 7.32 (m, 5H), 6.59 (d, J = 15.9 Hz, 1H), 5.29 (s, 2H). **^{13}C NMR** (100 MHz, CDCl3) δ 165.6, 149.9, 147.8, 139.7, 136.0, 135.7, 131.5, 128.6, 128.3, 128.2, 127.9, 127.6, 127.2,

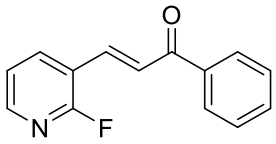
126.8, 122.2, 66.6. IR(KBr): ν_{max}: 3057, 2920, 1710, 1654, 1614, 1584, 1561, 1452, 1378, 1043, 774, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{14}ClNO_2$ $[M+H]^+$ = 323.0713, found =323.0721.

(*E*)-3-(2-chloropyridin-3-yl)-1-phenylprop-2-en-1-one (6a)



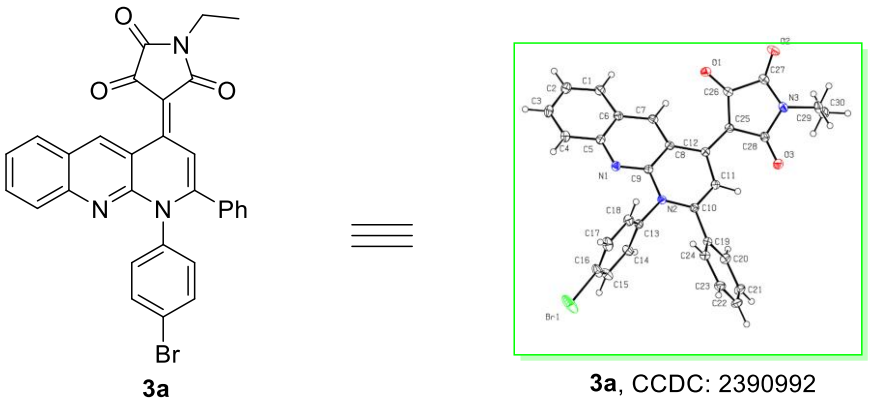
38% yield, yellowish solid, m.p.:115-116°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 4.7, 1.8 Hz, 1H), 8.01 (ddd, J = 13.9, 8.4, 1.7 Hz, 4H), 7.58 (dd, J = 10.5, 4.2 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.30 (dd, J = 7.7, 4.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6, 151.6, 150.4, 138.7, 137.3, 136.1, 133.2, 123.0, 128.7, 128.5, 126.4, 122.8. IR(KBr): ν_{max}: 3060, 2923, 1656, 1605, 1577, 1560, 1495, 1447, 1064, 1013, 807, 691 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{10}ClNO$ $[M+H]^+$ = 244.0523, found =244.0540.

(*E*)-3-(2-fluoropyridin-3-yl)-1-phenylprop-2-en-1-one (6b)



35% yield, yellowish solid, m.p.:87-88°C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, J = 4.7 Hz, 1H), 8.02 (ddd, J = 8.8, 5.5, 1.6 Hz, 3H), 7.73 (q, J = 15.9 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.49 (dd, J = 10.4, 4.6 Hz, 2H), 7.28 – 7.23 (dd, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.7, 162.6, 160.2, 148.5, 148.4, 140.2, 140.2, 137.5, 135.7, 135.6, 133.2, 128.7, 128.5, 126.3, 126.3, 121.9, 121.9, 118.2, 118.0. IR(KBr): ν_{max}: 3059, 2922, 1665, 1606, 1576 1495, 1448, 1426, 1099, 1013, 806, 685 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{10}FNO$ $[M+H]^+$ = 228.0819, found =228.0834.

4. X-ray of 3a



Scheme S5. X-ray of 3a

Table S1. Crystal data and structure refinement for 3a.

Empirical formula	$C_{30}H_{20}BrN_3O_3$
Formula weight	550.40
Temperature/K	170.00
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.7313(6)
b/Å	13.6060(5)
c/Å	24.1199(10)
α/°	90
β/°	108.5050(10)
γ/°	90
Volume/Å^3	4895.7(3)
Z	8
ρ_{calc}g/cm^3	1.493
μ/mm^{-1}	1.712
F(000)	2240.0
Crystal size/mm^3	0.09 × 0.06 × 0.04
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.576 to 121.278
Index ranges	-20 ≤ h ≤ 20, -16 ≤ k ≤ 17, -31 ≤ l ≤ 31
Reflections collected	62961
Independent reflections	11216 [R_{int} = 0.0362, R_{sigma} = 0.0289]
Data/restraints/parameters	11216/0/669
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0896
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.0943
Largest diff. peak/hole / e Å^{-3}	0.43/-1.01

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	-1714.2(2)	10404.4(2)	2104.1(2)	70.52(11)
O1	4737.2(7)	6573.0(9)	4769.8(5)	27.1(2)
N1	2064.6(9)	8184.1(10)	3072.1(6)	23.3(3)
C1	4079.6(11)	7027.5(14)	2875.9(7)	31.0(4)
O2	5413.7(8)	5515.6(10)	5855.0(6)	36.0(3)
N2	1235.1(8)	7847.7(10)	3676.2(6)	21.9(3)
C2	4083.2(13)	7484.3(14)	2375.0(8)	33.7(4)
O3	2383.1(8)	5318.3(10)	5386.7(6)	36.9(3)
N3	3914.1(9)	5252.3(10)	5719.3(6)	26.1(3)
C3	3433.7(13)	8207.4(14)	2114.1(7)	31.1(4)
C4	2783.6(12)	8452.8(13)	2352.8(7)	27.5(3)
C5	2754.3(10)	7978.4(11)	2871.3(7)	22.6(3)
C6	3419.2(10)	7270.0(12)	3144.6(7)	23.5(3)
C7	3387.0(10)	6828.0(12)	3662.4(7)	22.8(3)
C8	2704.6(10)	7062.4(11)	3891.2(6)	19.9(3)
C9	2030.6(10)	7716.4(11)	3544.3(7)	20.5(3)
C10	1073.1(10)	7307.7(11)	4109.6(7)	21.8(3)
C11	1725.9(10)	6706.7(12)	4461.9(7)	23.2(3)
C12	2591.4(10)	6608.4(11)	4409.8(6)	19.9(3)
C13	546.9(10)	8459.2(12)	3284.7(7)	23.3(3)
C14	-168.5(12)	8017.7(13)	2874.2(8)	30.0(4)
C15	-845.3(13)	8598.9(15)	2513.1(8)	38.8(4)
C16	-773.7(14)	9605.6(15)	2576.6(8)	38.4(4)
C17	-49.3(14)	10052.1(14)	2977.2(8)	37.1(4)
C18	624.1(12)	9469.0(13)	3337.8(8)	30.1(4)
C19	190.4(10)	7370.8(12)	4210.8(7)	24.1(3)
C20	-235.6(12)	6493.9(14)	4264.1(8)	30.9(4)
C21	-1041.7(12)	6507.8(16)	4386.6(8)	37.2(4)
C22	-1415.0(12)	7393.8(16)	4467.0(8)	37.1(4)
C23	-989.0(11)	8265.0(15)	4427.8(8)	33.2(4)
C24	-192.9(11)	8262.6(13)	4293.8(7)	28.0(3)
C25	3272.6(10)	6102.6(11)	4842.5(7)	20.9(3)
C26	4237.3(10)	6162.3(11)	4993.5(7)	21.6(3)
C27	4627.5(11)	5608.9(12)	5576.4(7)	25.0(3)
C28	3091.0(11)	5543.4(12)	5314.4(7)	25.0(3)
C29	3963.9(13)	4638.9(13)	6222.2(7)	31.2(4)
C30	3843.6(13)	3559.9(13)	6058.7(8)	34.6(4)

Br1A	10226.2(2)	6269.0(2)	6151.0(2)	58.20(9)
O1A	2954.7(8)	9674.3(8)	4349.8(5)	27.1(2)
N1A	6525.4(9)	8640.4(10)	4609.1(6)	22.1(3)
C1A	4747.5(12)	9636.3(13)	3321.4(7)	27.5(3)
O2A	1515.3(8)	9541.4(9)	4824.2(6)	33.3(3)
N2A	6545.6(8)	8177.4(10)	5529.8(5)	21.0(3)
C2A	5250.4(12)	9862.5(14)	2971.7(7)	31.3(4)
O3A	3686.5(8)	7582.5(9)	5996.1(5)	29.1(3)
N3A	2463.2(9)	8498.2(10)	5492.1(6)	25.3(3)
C3A	6179.1(13)	9665.5(14)	3160.3(8)	33.0(4)
C4A	6594.6(12)	9245.1(13)	3693.5(7)	29.4(4)
C5A	6091.6(11)	9019.4(11)	4073.5(7)	21.9(3)
C6A	5160.0(11)	9219.6(11)	3884.2(6)	21.6(3)
C7A	4683.4(10)	9039.2(11)	4274.2(7)	21.8(3)
C8A	5119.8(10)	8716.8(10)	4838.6(6)	18.7(3)
C9A	6059.8(10)	8518.0(11)	4973.7(6)	19.5(3)
C10A	6159.5(10)	8170.5(11)	5961.6(6)	21.3(3)
C11A	5257.1(10)	8325.9(12)	5838.9(7)	22.0(3)
C12A	4679.6(10)	8556.5(11)	5277.4(6)	19.1(3)
C13A	7426.7(10)	7738.1(12)	5643.9(6)	21.6(3)
C14A	8178.1(11)	8313.1(12)	5709.0(7)	24.8(3)
C15A	9013.2(11)	7871.1(13)	5861.9(7)	28.2(3)
C16A	9073.5(11)	6862.0(13)	5938.2(8)	31.5(4)
C17A	8325.7(12)	6281.3(13)	5856.8(9)	33.8(4)
C18A	7488.3(12)	6728.3(12)	5710.1(8)	28.5(3)
C19A	6733.4(11)	8100.1(12)	6581.5(7)	24.5(3)
C20A	7407.6(11)	8796.3(13)	6804.0(7)	28.0(3)
C21A	7871.3(13)	8824.3(15)	7398.3(8)	36.5(4)
C22A	7669.5(15)	8164.4(19)	7770.3(8)	48.2(5)
C23A	7003.1(16)	7478(2)	7554.1(9)	53.1(6)
C24A	6529.7(13)	7438.4(16)	6958.5(8)	38.2(4)
C25A	3746.6(10)	8658.2(11)	5198.9(6)	20.4(3)
C26A	3035.7(10)	9197.2(11)	4798.5(7)	21.3(3)
C27A	2227.0(11)	9124.8(12)	5026.8(7)	24.5(3)
C28A	3359.8(10)	8186.0(12)	5615.0(7)	22.4(3)
C29A	1845.8(11)	8097.3(14)	5779.6(8)	29.5(4)
C30A	1815.4(15)	8700.4(16)	6298.4(10)	43.1(5)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	80.9(2)	59.32(17)	49.12(15)	6.61(12)	-10.82(13)	45.30(15)
O1	22.9(5)	28.1(6)	30.1(6)	-1.5(5)	8.0(5)	-4.0(5)
N1	24.9(6)	21.9(6)	23.8(6)	1.7(5)	8.5(5)	0.5(5)
C1	26.8(8)	40.7(10)	26.3(8)	-1.9(7)	9.6(7)	6.2(7)
O2	24.6(6)	37.0(7)	37.5(7)	3.0(6)	-2.8(5)	4.5(5)
N2	19.5(6)	21.5(6)	24.0(6)	4.0(5)	6.0(5)	2.0(5)
C2	34.9(9)	42.7(10)	27.9(8)	-4.2(8)	16.4(7)	2.1(8)
O3	27.7(6)	42.8(7)	41.1(7)	19.1(6)	12.1(5)	2.6(5)
N3	27.2(7)	24.5(7)	23.2(7)	4.5(5)	3.2(5)	2.9(5)
C3	41.4(10)	32.8(9)	22.0(8)	-2.5(7)	14.3(7)	-3.7(7)
C4	33.8(9)	25.3(8)	23.7(8)	-0.1(6)	9.4(7)	-0.6(7)
C5	24.3(7)	22.0(7)	21.4(7)	-2.8(6)	7.1(6)	-3.1(6)
C6	21.9(7)	26.5(8)	21.2(7)	-4.8(6)	5.6(6)	-1.1(6)
C7	20.8(7)	24.1(8)	21.3(7)	-2.6(6)	3.7(6)	1.2(6)
C8	19.7(7)	17.7(7)	20.3(7)	-1.5(6)	3.6(6)	-1.5(5)
C9	19.5(7)	19.3(7)	22.0(7)	-2.0(6)	5.7(6)	-0.8(6)
C10	21.1(7)	20.9(7)	23.4(7)	0.8(6)	7.1(6)	-1.2(6)
C11	21.9(7)	24.1(8)	23.4(7)	3.4(6)	6.9(6)	0.2(6)
C12	21.0(7)	17.0(7)	20.5(7)	-1.8(6)	5.1(6)	-1.0(5)
C13	22.8(7)	23.8(8)	24.0(7)	6.2(6)	8.5(6)	5.6(6)
C14	29.7(8)	25.9(8)	30.3(8)	2.6(7)	3.9(7)	4.1(7)
C15	32.7(9)	40.9(11)	33.6(9)	3.4(8)	-2.4(8)	7.9(8)
C16	43.5(11)	37.7(10)	30.1(9)	9.6(8)	6.1(8)	20.3(8)
C17	52.3(11)	24.1(9)	34.5(9)	5.3(7)	13.1(9)	11.3(8)
C18	33.8(9)	25.3(8)	30.5(9)	3.2(7)	9.0(7)	1.6(7)
C19	18.7(7)	30.6(8)	22.0(7)	3.7(6)	5.2(6)	-0.5(6)
C20	29.2(8)	32.1(9)	32.1(9)	2.2(7)	10.8(7)	-3.7(7)
C21	30.7(9)	48.8(11)	33.6(9)	1.1(8)	12.4(8)	-14.8(8)
C22	21.9(8)	61.7(13)	30.1(9)	-4.4(9)	11.6(7)	-6.8(8)
C23	22.7(8)	46.6(11)	30.5(9)	-2.5(8)	8.8(7)	4.4(7)
C24	22.0(8)	32.1(9)	29.5(8)	1.9(7)	7.6(6)	1.2(6)
C25	20.9(7)	19.1(7)	21.9(7)	0.5(6)	5.5(6)	0.6(6)
C26	21.9(7)	18.0(7)	22.7(7)	-2.9(6)	3.9(6)	1.0(6)
C27	26.0(8)	19.6(7)	25.6(8)	-1.6(6)	2.7(6)	2.4(6)
C28	25.2(8)	23.5(8)	25.2(8)	3.8(6)	6.3(6)	2.2(6)
C29	39.9(10)	29.2(9)	22.9(8)	6.7(7)	7.8(7)	7.3(7)
C30	33.9(9)	31.1(9)	36.4(9)	6.8(8)	7.7(8)	-2.9(7)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1A	29.18(11)	39.54(13)	98.8(2)	4.99(12)	10.22(12)	12.03(9)
O1A	29.7(6)	26.5(6)	25.7(6)	6.0(5)	9.7(5)	3.8(5)
N1A	24.7(6)	23.2(7)	19.7(6)	-0.2(5)	8.6(5)	-0.2(5)
C1A	30.8(8)	29.8(8)	19.6(7)	-0.3(6)	4.9(6)	-1.9(7)
O2A	22.8(6)	34.1(7)	42.4(7)	6.2(6)	9.5(5)	1.7(5)
N2A	21.9(6)	22.7(6)	18.7(6)	1.0(5)	7.0(5)	0.6(5)
C2A	39.9(10)	34.7(9)	18.3(7)	1.6(7)	8.0(7)	-4.1(8)
O3A	29.7(6)	33.0(6)	26.0(6)	8.1(5)	10.8(5)	0.3(5)
N3A	22.1(6)	29.8(7)	25.8(7)	2.5(6)	9.8(5)	-2.3(5)
C3A	41.6(10)	38.3(10)	23.9(8)	1.2(7)	17.1(7)	-6.4(8)
C4A	30.0(8)	34.9(9)	26.1(8)	-0.4(7)	13.2(7)	-2.2(7)
C5A	28.3(8)	19.8(7)	19.1(7)	-2.0(6)	9.5(6)	-2.1(6)
C6A	26.9(8)	19.6(7)	17.6(7)	-3.6(6)	6.1(6)	-3.5(6)
C7A	23.6(7)	21.6(7)	19.4(7)	-3.7(6)	5.8(6)	-2.6(6)
C8A	22.0(7)	15.8(7)	18.8(7)	-2.8(5)	6.9(6)	-1.9(5)
C9A	22.8(7)	17.2(7)	18.2(7)	-2.1(6)	5.9(6)	-1.2(6)
C10A	25.3(7)	20.0(7)	18.7(7)	0.7(6)	7.1(6)	-1.3(6)
C11A	24.9(7)	23.9(8)	18.2(7)	-1.0(6)	8.2(6)	-2.0(6)
C12A	23.5(7)	15.9(7)	18.7(7)	-2.8(5)	7.6(6)	-2.2(5)
C13A	22.1(7)	23.7(8)	18.9(7)	1.0(6)	6.3(6)	2.8(6)
C14A	26.1(8)	21.8(8)	27.4(8)	0.1(6)	9.4(6)	0.5(6)
C15A	24.8(8)	27.9(8)	31.5(8)	-1.2(7)	8.4(7)	-1.3(6)
C16A	25.4(8)	31.1(9)	36.2(9)	1.1(7)	7.3(7)	7.4(7)
C17A	32.8(9)	22.8(8)	44.7(10)	3.3(7)	10.7(8)	3.7(7)
C18A	28.3(8)	23.4(8)	33.2(9)	1.4(7)	8.7(7)	-0.9(6)
C19A	24.3(7)	29.6(8)	19.1(7)	1.6(6)	6.0(6)	2.4(6)
C20A	28.9(8)	30.0(9)	24.1(8)	-0.5(7)	7.3(7)	0.5(7)
C21A	33.3(9)	44.8(11)	26.6(9)	-7.0(8)	2.7(7)	1.2(8)
C22A	47.3(12)	71.3(15)	19.4(8)	3.5(9)	0.9(8)	2.8(11)
C23A	58.4(14)	70.0(16)	27.2(10)	18.4(10)	8.5(9)	-8.1(12)
C24A	38.3(10)	46.2(11)	28.0(9)	8.8(8)	7.3(8)	-8.5(8)
C25A	24.5(7)	19.7(7)	17.7(7)	-1.3(6)	7.8(6)	-2.5(6)
C26A	22.7(7)	18.9(7)	22.0(7)	-3.1(6)	7.0(6)	-3.3(6)
C27A	22.9(7)	23.9(8)	26.5(8)	-1.8(6)	7.5(6)	-3.2(6)
C28A	23.4(7)	24.5(8)	19.9(7)	-2.6(6)	7.6(6)	-2.6(6)
C29A	24.6(8)	35.8(9)	31.4(9)	2.8(7)	13.3(7)	-4.9(7)
C30A	47.5(12)	45.3(11)	47.6(12)	-3.9(9)	31.0(10)	-6.5(9)

Table S4. Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C16	1.8971(18)	Br1A	C16A	1.9004(17)
O1	C26	1.2211(19)	O1A	C26A	1.2335(19)
N1	C5	1.351(2)	N1A	C5A	1.357(2)
N1	C9	1.320(2)	N1A	C9A	1.322(2)
C1	C2	1.360(3)	C1A	C2A	1.362(2)
C1	C6	1.427(2)	C1A	C6A	1.423(2)
O2	C27	1.212(2)	O2A	C27A	1.211(2)
N2	C9	1.3972(19)	N2A	C9A	1.3954(19)
N2	C10	1.366(2)	N2A	C10A	1.3620(19)
N2	C13	1.4516(19)	N2A	C13A	1.4534(19)
C2	C3	1.414(3)	C2A	C3A	1.411(3)
O3	C28	1.220(2)	O3A	C28A	1.218(2)
N3	C27	1.364(2)	N3A	C27A	1.364(2)
N3	C28	1.409(2)	N3A	C28A	1.412(2)
N3	C29	1.454(2)	N3A	C29A	1.466(2)
C3	C4	1.365(2)	C3A	C4A	1.369(3)
C4	C5	1.421(2)	C4A	C5A	1.422(2)
C5	C6	1.421(2)	C5A	C6A	1.416(2)
C6	C7	1.402(2)	C6A	C7A	1.398(2)
C7	C8	1.391(2)	C7A	C8A	1.387(2)
C8	C9	1.433(2)	C8A	C9A	1.435(2)
C8	C12	1.456(2)	C8A	C12A	1.453(2)
C10	C11	1.375(2)	C10A	C11A	1.371(2)
C10	C19	1.487(2)	C10A	C19A	1.484(2)
C11	C12	1.413(2)	C11A	C12A	1.406(2)
C12	C25	1.415(2)	C12A	C25A	1.426(2)
C13	C14	1.379(2)	C13A	C14A	1.384(2)
C13	C18	1.382(2)	C13A	C18A	1.383(2)
C14	C15	1.389(2)	C14A	C15A	1.384(2)
C15	C16	1.379(3)	C15A	C16A	1.385(3)
C16	C17	1.379(3)	C16A	C17A	1.378(3)
C17	C18	1.387(3)	C17A	C18A	1.391(2)
C19	C20	1.394(2)	C19A	C20A	1.396(2)
C19	C24	1.397(2)	C19A	C24A	1.387(2)
C20	C21	1.391(2)	C20A	C21A	1.387(2)
C21	C22	1.381(3)	C21A	C22A	1.376(3)
C22	C23	1.380(3)	C22A	C23A	1.377(3)

Table S4. Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C23	C24	1.389(2)	C23A	C24A	1.394(3)
C25	C26	1.446(2)	C25A	C26A	1.427(2)
C25	C28	1.470(2)	C25A	C28A	1.476(2)
C26	C27	1.540(2)	C26A	C27A	1.541(2)
C29	C30	1.516(3)	C29A	C30A	1.510(3)

Table S5. Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	N1	C5	117.80(14)	C9A	N1A	C5A	117.64(13)
C2	C1	C6	120.44(16)	C2A	C1A	C6A	120.12(16)
C9	N2	C13	117.53(12)	C9A	N2A	C13A	121.13(12)
C10	N2	C9	120.24(13)	C10A	N2A	C9A	119.75(13)
C10	N2	C13	121.62(13)	C10A	N2A	C13A	118.84(12)
C1	C2	C3	120.46(16)	C1A	C2A	C3A	120.19(16)
C27	N3	C28	111.95(13)	C27A	N3A	C28A	110.73(13)
C27	N3	C29	125.76(14)	C27A	N3A	C29A	125.00(14)
C28	N3	C29	122.28(14)	C28A	N3A	C29A	123.82(14)
C4	C3	C2	120.99(16)	C4A	C3A	C2A	121.27(16)
C3	C4	C5	119.87(16)	C3A	C4A	C5A	119.89(16)
N1	C5	C4	118.40(15)	N1A	C5A	C4A	118.77(15)
N1	C5	C6	122.08(14)	N1A	C5A	C6A	122.43(14)
C4	C5	C6	119.44(14)	C6A	C5A	C4A	118.78(14)
C5	C6	C1	118.75(15)	C5A	C6A	C1A	119.73(14)
C7	C6	C1	122.89(15)	C7A	C6A	C1A	122.14(15)
C7	C6	C5	118.35(14)	C7A	C6A	C5A	118.06(14)
C8	C7	C6	120.39(14)	C8A	C7A	C6A	120.79(14)
C7	C8	C9	115.59(14)	C7A	C8A	C9A	115.83(13)
C7	C8	C12	124.33(14)	C7A	C8A	C12A	124.08(14)
C9	C8	C12	119.71(13)	C9A	C8A	C12A	120.08(13)
N1	C9	N2	114.78(13)	N1A	C9A	N2A	115.55(13)
N1	C9	C8	125.31(14)	N1A	C9A	C8A	125.02(14)
N2	C9	C8	119.78(13)	N2A	C9A	C8A	119.42(13)
N2	C10	C11	120.56(14)	N2A	C10A	C11A	121.08(14)
N2	C10	C19	120.35(13)	N2A	C10A	C19A	119.63(14)
C11	C10	C19	119.08(14)	C11A	C10A	C19A	118.97(14)
C10	C11	C12	123.57(14)	C10A	C11A	C12A	123.39(14)
C11	C12	C8	114.86(13)	C11A	C12A	C8A	115.04(13)

Table S5. Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	C12	C25	120.41(14)	C11A	C12A	C25A	118.21(13)
C25	C12	C8	124.72(14)	C25A	C12A	C8A	126.66(13)
C14	C13	N2	119.19(14)	C14A	C13A	N2A	121.19(14)
C14	C13	C18	121.84(15)	C18A	C13A	N2A	117.26(14)
C18	C13	N2	118.96(15)	C18A	C13A	C14A	121.49(15)
C13	C14	C15	119.39(17)	C15A	C14A	C13A	119.27(15)
C16	C15	C14	118.47(18)	C14A	C15A	C16A	119.03(16)
C15	C16	Br1	118.80(15)	C15A	C16A	Br1A	118.43(13)
C15	C16	C17	122.38(17)	C17A	C16A	Br1A	119.55(13)
C17	C16	Br1	118.81(14)	C17A	C16A	C15A	122.02(16)
C16	C17	C18	118.96(17)	C16A	C17A	C18A	118.83(16)
C13	C18	C17	118.92(17)	C13A	C18A	C17A	119.32(16)
C20	C19	C10	117.84(15)	C20A	C19A	C10A	119.24(14)
C20	C19	C24	119.21(15)	C24A	C19A	C10A	120.59(15)
C24	C19	C10	122.80(15)	C24A	C19A	C20A	119.58(15)
C21	C20	C19	120.36(17)	C21A	C20A	C19A	120.14(17)
C22	C21	C20	119.91(18)	C22A	C21A	C20A	120.09(19)
C23	C22	C21	120.19(16)	C21A	C22A	C23A	120.08(18)
C22	C23	C24	120.48(18)	C22A	C23A	C24A	120.68(19)
C23	C24	C19	119.82(17)	C19A	C24A	C23A	119.43(19)
C12	C25	C26	130.33(14)	C12A	C25A	C26A	133.82(14)
C12	C25	C28	122.34(14)	C12A	C25A	C28A	119.79(13)
C26	C25	C28	106.27(13)	C26A	C25A	C28A	106.28(13)
O1	C26	C25	133.30(15)	O1A	C26A	C25A	134.82(15)
O1	C26	C27	120.07(14)	O1A	C26A	C27A	118.68(14)
C25	C26	C27	106.54(13)	C25A	C26A	C27A	106.49(13)
O2	C27	N3	126.82(16)	O2A	C27A	N3A	126.88(15)
O2	C27	C26	126.73(16)	O2A	C27A	C26A	126.03(15)
N3	C27	C26	106.45(13)	N3A	C27A	C26A	107.08(13)
O3	C28	N3	120.68(15)	O3A	C28A	N3A	121.03(14)
O3	C28	C25	130.62(15)	O3A	C28A	C25A	129.82(15)
N3	C28	C25	108.69(13)	N3A	C28A	C25A	109.06(13)
N3	C29	C30	111.68(14)	N3A	C29A	C30A	112.94(15)

Table S6. Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C16	C17	C18	177.72(14)	Br1A	C16A	C17A	C18A	179.01(14)
O1	C26	C27	O2	-0.8(3)	O1A	C26A	C27A	O2A	-4.3(2)
O1	C26	C27	N3	178.70(14)	O1A	C26A	C27A	N3A	175.01(14)
N1	C5	C6	C1	174.26(15)	N1A	C5A	C6A	C1A	178.71(15)
N1	C5	C6	C7	-4.7(2)	N1A	C5A	C6A	C7A	1.6(2)
C1	C2	C3	C4	-0.9(3)	C1A	C2A	C3A	C4A	0.1(3)
C1	C6	C7	C8	-177.20(15)	C1A	C6A	C7A	C8A	-174.07(15)
N2	C10	C11	C12	0.6(2)	N2A	C10A	C11A	C12A	-3.8(2)
N2	C10	C19	C20	131.61(16)	N2A	C10A	C19A	C20A	56.3(2)
N2	C10	C19	C24	-52.9(2)	N2A	C10A	C19A	C24A	-132.53(18)
N2	C13	C14	C15	177.64(16)	N2A	C13A	C14A	C15A	175.04(14)
N2	C13	C18	C17	-177.79(15)	N2A	C13A	C18A	C17A	-175.92(15)
C2	C1	C6	C5	1.5(3)	C2A	C1A	C6A	C5A	-1.5(2)
C2	C1	C6	C7	-179.57(17)	C2A	C1A	C6A	C7A	175.44(16)
C2	C3	C4	C5	0.0(3)	C2A	C3A	C4A	C5A	-1.4(3)
C3	C4	C5	N1	-175.14(16)	C3A	C4A	C5A	N1A	-177.33(16)
C3	C4	C5	C6	1.7(2)	C3A	C4A	C5A	C6A	1.2(2)
C4	C5	C6	C1	-2.4(2)	C4A	C5A	C6A	C1A	0.2(2)
C4	C5	C6	C7	178.64(15)	C4A	C5A	C6A	C7A	-176.87(15)
C5	N1	C9	N2	-170.62(13)	C5A	N1A	C9A	N2A	-176.61(13)
C5	N1	C9	C8	5.3(2)	C5A	N1A	C9A	C8A	2.8(2)
C5	C6	C7	C8	1.7(2)	C5A	C6A	C7A	C8A	2.9(2)
C6	C1	C2	C3	0.1(3)	C6A	C1A	C2A	C3A	1.4(3)
C6	C7	C8	C9	4.0(2)	C6A	C7A	C8A	C9A	-4.4(2)
C6	C7	C8	C12	176.96(14)	C6A	C7A	C8A	C12A	177.05(14)
C7	C8	C9	N1	-7.9(2)	C7A	C8A	C9A	N1A	1.6(2)
C7	C8	C9	N2	167.77(14)	C7A	C8A	C9A	N2A	-179.10(13)
C7	C8	C12	C11	-160.62(15)	C7A	C8A	C12A	C11A	-173.80(14)
C7	C8	C12	C25	19.6(2)	C7A	C8A	C12A	C25A	2.9(2)
C8	C12	C25	C26	22.0(3)	C8A	C12A	C25A	C26A	-23.4(3)
C8	C12	C25	C28	-171.44(14)	C8A	C12A	C25A	C28A	161.06(14)
C9	N1	C5	C4	178.00(14)	C9A	N1A	C5A	C4A	174.14(15)
C9	N1	C5	C6	1.3(2)	C9A	N1A	C5A	C6A	-4.4(2)
C9	N2	C10	C11	6.9(2)	C9A	N2A	C10A	C11A	11.6(2)
C9	N2	C10	C19	-173.75(14)	C9A	N2A	C10A	C19A	-161.79(14)
C9	N2	C13	C14	100.51(18)	C9A	N2A	C13A	C14A	77.47(19)
C9	N2	C13	C18	-80.04(19)	C9A	N2A	C13A	C18A	-105.32(17)
C9	C8	C12	C11	12.1(2)	C9A	C8A	C12A	C11A	7.7(2)

Table S6. Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C9	C8	C12	C25	-167.72(14)	C9A	C8A	C12A	C25A	-175.66(14)
C10	N2	C9	N1	171.84(14)	C10A	N2A	C9A	N1A	170.05(14)
C10	N2	C9	C8	-4.3(2)	C10A	N2A	C9A	C8A	-9.3(2)
C10	N2	C13	C14	-70.5(2)	C10A	N2A	C13A	C14A	-108.62(17)
C10	N2	C13	C18	108.98(18)	C10A	N2A	C13A	C18A	68.59(19)
C10	C11	C12	C8	-9.9(2)	C10A	C11A	C12A	C8A	-5.8(2)
C10	C11	C12	C25	169.90(15)	C10A	C11A	C12A	C25A	177.23(15)
C10	C19	C20	C21	176.95(16)	C10A	C19A	C20A	C21A	171.38(16)
C10	C19	C24	C23	-175.40(15)	C10A	C19A	C24A	C23A	-171.28(19)
C11	C10	C19	C20	-49.1(2)	C11A	C10A	C19A	C20A	-117.28(18)
C11	C10	C19	C24	126.41(17)	C11A	C10A	C19A	C24A	53.9(2)
C11	C12	C25	C26	-157.76(16)	C11A	C12A	C25A	C26A	153.18(17)
C11	C12	C25	C28	8.8(2)	C11A	C12A	C25A	C28A	-22.4(2)
C12	C8	C9	N1	178.77(14)	C12A	C8A	C9A	N1A	-179.80(14)
C12	C8	C9	N2	-5.5(2)	C12A	C8A	C9A	N2A	-0.5(2)
C12	C25	C26	O1	-8.2(3)	C12A	C25A	C26A	O1A	9.1(3)
C12	C25	C26	C27	168.45(15)	C12A	C25A	C26A	C27A	-170.04(16)
C12	C25	C28	O3	9.3(3)	C12A	C25A	C28A	O3A	-11.2(3)
C12	C25	C28	N3	-171.32(14)	C12A	C25A	C28A	N3A	172.26(13)
C13	N2	C9	N1	0.7(2)	C13A	N2A	C9A	N1A	-16.1(2)
C13	N2	C9	C8	-175.40(14)	C13A	N2A	C9A	C8A	164.50(13)
C13	N2	C10	C11	177.68(15)	C13A	N2A	C10A	C11A	-162.36(15)
C13	N2	C10	C19	-3.0(2)	C13A	N2A	C10A	C19A	24.2(2)
C13	C14	C15	C16	0.4(3)	C13A	C14A	C15A	C16A	0.8(2)
C14	C13	C18	C17	1.6(3)	C14A	C13A	C18A	C17A	1.3(3)
C14	C15	C16	Br1	-177.87(15)	C14A	C15A	C16A	Br1A	-179.76(13)
C14	C15	C16	C17	1.2(3)	C14A	C15A	C16A	C17A	1.1(3)
C15	C16	C17	C18	-1.3(3)	C15A	C16A	C17A	C18A	-1.9(3)
C16	C17	C18	C13	-0.1(3)	C16A	C17A	C18A	C13A	0.7(3)
C18	C13	C14	C15	-1.8(3)	C18A	C13A	C14A	C15A	-2.0(2)
C19	C10	C11	C12	-178.76(15)	C19A	C10A	C11A	C12A	169.67(15)
C19	C20	C21	C22	-1.2(3)	C19A	C20A	C21A	C22A	0.1(3)
C20	C19	C24	C23	0.0(2)	C20A	C19A	C24A	C23A	-0.1(3)
C20	C21	C22	C23	-0.2(3)	C20A	C21A	C22A	C23A	-0.4(3)
C21	C22	C23	C24	1.5(3)	C21A	C22A	C23A	C24A	0.4(4)
C22	C23	C24	C19	-1.4(3)	C22A	C23A	C24A	C19A	-0.1(4)
C24	C19	C20	C21	1.3(3)	C24A	C19A	C20A	C21A	0.1(3)
C25	C26	C27	O2	-177.94(16)	C25A	C26A	C27A	O2A	174.99(16)

Table S6. Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C25	C26	C27	N3	1.55(17)	C25A	C26A	C27A	N3A	-5.68(17)
C26	C25	C28	O3	178.62(18)	C26A	C25A	C28A	O3A	172.09(16)
C26	C25	C28	N3	-1.98(17)	C26A	C25A	C28A	N3A	-4.40(17)
C27	N3	C28	O3	-177.37(16)	C27A	N3A	C28A	O3A	-176.11(15)
C27	N3	C28	C25	3.15(19)	C27A	N3A	C28A	C25A	0.74(18)
C27	N3	C29	C30	-98.2(2)	C27A	N3A	C29A	C30A	-93.6(2)
C28	N3	C27	O2	176.60(16)	C28A	N3A	C27A	O2A	-177.71(16)
C28	N3	C27	C26	-2.88(18)	C28A	N3A	C27A	C26A	2.97(17)
C28	N3	C29	C30	81.5(2)	C28A	N3A	C29A	C30A	94.9(2)
C28	C25	C26	O1	-176.34(17)	C28A	C25A	C26A	O1A	-174.92(17)
C28	C25	C26	C27	0.28(16)	C28A	C25A	C26A	C27A	5.94(16)
C29	N3	C27	O2	-3.7(3)	C29A	N3A	C27A	O2A	9.8(3)
C29	N3	C27	C26	176.80(14)	C29A	N3A	C27A	C26A	-169.54(14)
C29	N3	C28	O3	2.9(3)	C29A	N3A	C28A	O3A	-3.5(2)
C29	N3	C28	C25	-176.54(14)	C29A	N3A	C28A	C25A	173.36(14)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

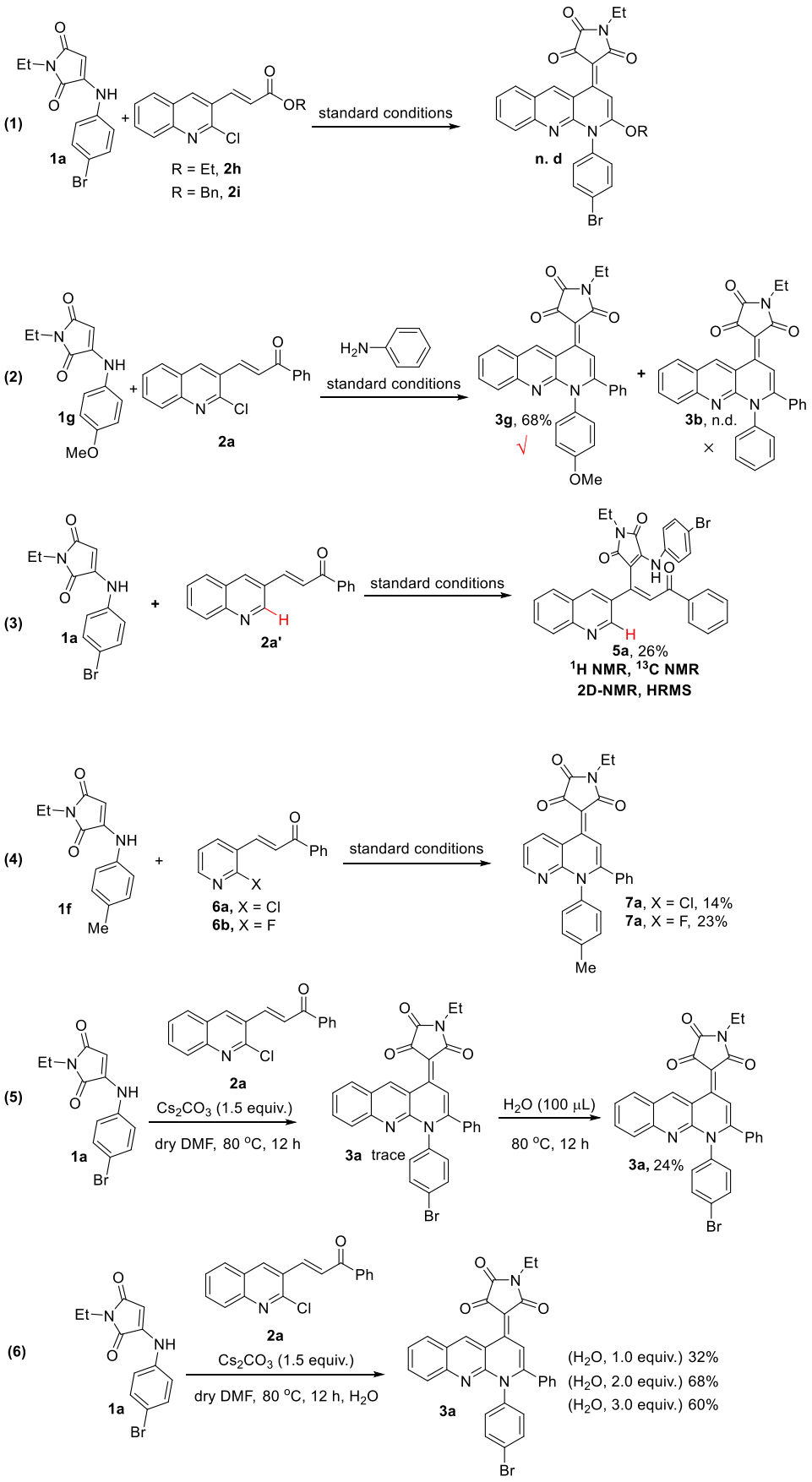
Atom	*x*	*y*	*z*	U(eq)
H1	4519.72	6543.65	3047.97	37
H2	4525.18	7316.43	2199.18	40
H3	3450.09	8527.05	1767.51	37
H4	2351.55	8939.84	2172.65	33
H7	3833.91	6365.62	3858.33	27
H11	1587.3	6337.59	4756.4	28
H14	-198.29	7322.15	2838.6	36
H15	-1345.98	8309.64	2228.93	47
H17	-12.2	10748.16	3005.68	45
H18	1130.17	9759.13	3616.8	36
H20	26.31	5883.57	4216.54	37
H21	-1335.35	5908.68	4414.95	45
H22	-1966.6	7403.23	4549.59	45
H23	-1241.91	8871.03	4492.96	40
H24	90.18	8865.56	4258.66	34
H29A	3492.69	4843.18	6389.73	37
H29B	4552.92	4734.97	6525.33	37
H30A	3265.05	3464.04	5754.25	52

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H30B	3860.43	3171.54	6404.18	52
H30C	4327.7	3346.8	5911.9	52
H1A	4120.25	9756.93	3189.34	33
H2A	4975.22	10153.78	2599.82	38
H3A	6522.55	9827.66	2912.6	40
H4A	7218	9104.37	3809.22	35
H7A	4053.22	9138.62	4151.08	26
H11A	5009.38	8274.97	6149.29	26
H14A	8121.28	9003.32	5649.52	30
H15A	9537.42	8254.64	5913.67	34
H17A	8381.29	5588.05	5900.16	41
H18A	6963.99	6343.89	5655.96	34
H20A	7549.16	9251.78	6547.96	34
H21A	8328.85	9299.88	7548.68	44
H22A	7990.22	8182.33	8176.79	58
H23A	6864.69	7026.88	7813.57	64
H24A	6071.33	6962.43	6811.89	46
H29C	2032.02	7418.57	5911.03	35
H29D	1236.13	8065.15	5492.29	35
H30D	1587.59	9359.24	6166.82	65
H30E	2420.1	8752.07	6579.55	65
H30F	1418.59	8381.44	6485.47	65

5. Control experiments

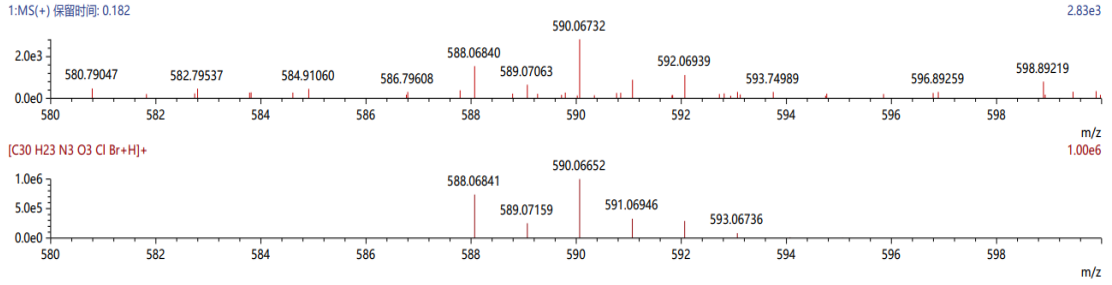
Other control experiments were also tested as follows: When an *ortho*-chloroquinolin-*α*,*β*-unsaturated ester (**2h** and **2i**) was used, the expected product could not be obtained. This can likely be ascribed to the fact that the ester group is less reactive compared to the ketone (Scheme S6 (1)). Subsequently, aniline was added to the reaction mixture of **1g** and **2a**. The experimental results revealed that the sole product formed was **3g** (Scheme S6 (2)). These experiments clearly demonstrate that the reformation of the aniline fragment in this reaction occurs strictly via an intramolecular mechanism. Furthermore, under the same standard conditions, chloro-free quinoline chalcones **2a'** were reacted with **1a**. The results indicated that the formation of **5a** was feasible by using ^{1}H-NMR, ^{13}C-NMR, and HRMS (Scheme S6 (3)), indicating that the step S_NAr reaction might serve as the driving force for the formation of this reaction. 2-chloropyridine chalcone and 2-fluoropyridine chalcone were also examined within our reaction. Fortunately, the target products were obtained with yields of 14% and 23% respectively (Scheme S6 (4)). The purer and dry DMF was employed for the reaction. Nevertheless, no [3+3] product was observed, and only trace amounts of **3a** were detected. Subsequently, 0.1 mL of H_2O was added to the reaction system, leading to a 24% yield of **3a** (Scheme S6 (5)). To further validate the vital effect of H_2O, different equivalents of H_2O were introduced into the reaction, and it was determined that 2.0 equivalents of H_2O were the most appropriate for the best yield (Scheme S6 (6)).



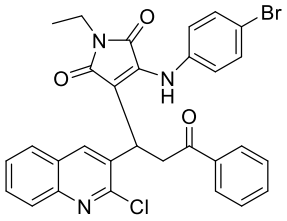
Scheme S6. Control experiments

6. Characterization of 4a

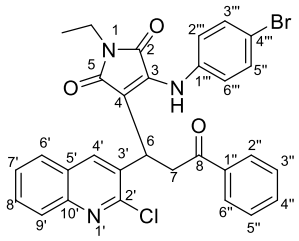
Table S8. HR-ESI-MS of 4a

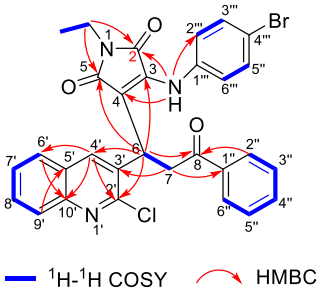


Score	Pred. (M)	Pred m/z	Meas. m/z	Diff. mDa)	Formulae (M)	Ion	Diff. (ppm)	Iso Score	DBE
13.71	587.06113	588.06841	588.06840	-0.01	$C_{30}H_{20}N_3O_3ClBr$	$[M+H]^+$	-0.017	26.34	20.0



Chemical Formula: $C_{30}H_{23}BrClN_3O_3$
Exact Mass: 587.06





Scheme S7. Structure of 4a

^{1}H NMR (600 MHz, Chloroform-d): δ 8.07 (s, 1H, H-4'), 7.98 (s, 1H, H-7'), 7.96 (d, *J* = 7.9 Hz, 2H, H-2", 6"), 7.76 (d, *J* = 8.2 Hz, 1H, H-6'), 7.69 (t, *J* = 7.7 Hz, 1H, H-8'), 7.56 (d, *J* = 8.1 Hz, 1H, H-4"), 7.53 (d, *J* = 8.0 Hz, 1H, H-9'), 7.45 (t, *J* = 7.6 Hz, 2H, H-3", 5"), 7.35 (d, *J* = 8.1 Hz, 2H, H-3"', 5"'), 7.18 (s, 1H, -NH-), 6.94 (d, *J* = 8.1 Hz, 2H, H-2"', 6"'), 4.70 (dd, *J* = 10.1, 4.1 Hz, 1H, H-6), 4.37 (dd, *J* = 18.0, 10.1 Hz, 1H, H-7a), 3.51 (q, *J* = 7.2 Hz, 2H, NC<u>H</u>$_2$-), 3.42 (dd, *J* = 18.1, 4.1 Hz, 1H, H-7b), 1.15 (t, *J* = 7.2 Hz, 3H, NCH$_2$C<u>H</u>$_3$).

^{13}C NMR (150MHz, Chloroform-*d*): δ 197.93 (s, 8), 173.02 (s, 5), 167.29 (s, 3), 150.39 (s, 2'), 146.52 (s, 10'), 140.43 (s, 3), 137.93 (d, 4'), 136.64 (s, 1"'), 136.52 (s, 1"), 133.51 (s, 3'), 133.46 (d, 4"), 132.51 (d, 3"', 5"'), 130.38 (d, 8'), 128.79 (d, 3", 5"), 128.19 (d, 2", 6"), 128.19 (d, 7'), 127.62 (d, 6'), 127.35 (s, 5'), 127.25 (d, 9'), 125.29 (d, 2"', 6"'), 119.66 (s, 4"'), 101.68 (s, 4), 41.15 (t, 7), 33.82 (d, 6), 32.99 (t, N-<u>C</u>H$_2$), 14.05 (q, N-CH$_2$<u>C</u>H$_3$).

IR(KBr): ν_{max}: 3295, 2925, 2851, 1761, 1698, 1641, 1587, 1520, 1486, 1447, 1413, 1070, 1010, 817, 689 cm^{-1}.

Table S9. Hydrogen and carbon spectra data of compound 4a in deuterated $CDCl_3$

No.	Compound **4a**				
	δ_H (J in Hz)	δ_C	COSY(H)	HMBC(H→C)	NOESY
2	−	167.3 (s)	−	−	−
3	−	140.4 (s)	−	−	−
4	−	101.7 (s)	−	−	−
5	−	173.0 (s)	−	−	−
6	4.70 (dd, J = 10.1, 4.1 Hz, 1H)	33.5 (d)	7	3, 4, 5, 7, 8, 2', 4'	−
7	4.37 (dd, J = 18.0, 10.1 Hz, 1H) 3.42 (dd, J = 18.1, 4.1 Hz, 1H)	33.8 (t)	6	4, 6, 3', 1"	−
8	−	197.9 (s)	−	−	−
2'	−	150.4 (s)	−	−	−
3'	−	133.5 (s)	−	−	−
4'	8.07 (s, 1H)	137.9 (d)		6, 2', 6', 10'	−
5'	−	127.4 (s)	−	−	−
6'	7.76 (d, J = 8.2 Hz, 1H)	127.6 (d)	−	4', 8', 10'	−
7'	7.98 (s, 1H)	128.2 (d)	8'	9'	−
8'	7.69 (t, J = 7.7 Hz, 1H)	130.4 (d)	7', 9'	6', 10'	−
9'	7.53 (d, J = 8.0 Hz, 1H)	127.3 (d)	8'	5'	−
10'	−	146.5 (s)	−	−	−
1"	−	136.5 (s)	−	−	−
2", 6"	7.96 (d, J = 9.2 Hz, 2H)	128.2 (d)	3", 5"	3", 4", 5", 8	−
3", 5"	7.45 (t, J = 7.6 Hz, 2H)	128.8 (d)	2", 4", 6"	1", 2", 6"	−
4"	7.56 (d, J = 8.1 Hz, 1H)	133.4 (d)	3", 5"	−	−
1"'	−	136.6 (s)	−	−	−
2"', 6"'	6.94 (d, J = 8.1 Hz, 2H)	125.3 (d)	3"', 5"'	1"', 4"'	−
3"', 5"'	7.35 (d, J = 8.1 Hz, 2H)	132.5 (d)	2"', 6"'	1"', 4"'	−
4"'	−	119.7 (s)	−	−	−
NH	7.18 (s, 1H)	−	−	2, 4, 2"'	−
NCH_2-	3.51 (q, J = 7.2 Hz, 2H)	33.0 (t)	$CH_2\underline{CH_3}$	2, 5, CH_3	−
$CH_2\underline{CH_3}$	1.15 (t, J = 7.2 Hz, 3H)	12.1 (q)	NCH_2-	NCH_2-	−
Measured in $CDCl_3$ at 600 MHz.					

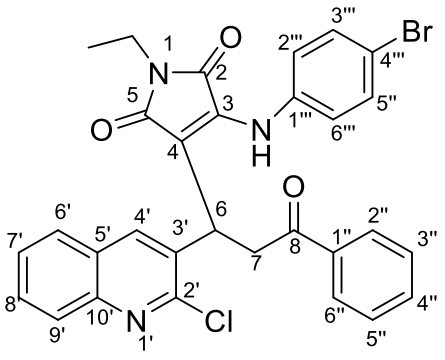


Figure S1. Structure of New Compound 4a

Analysis process:

The ^{1}H-NMR spectrum of the compound shows 23 proton signals, including 14 aromatic ring proton signals with a δ 8.07 (s, 1H, H-4'), 7.98 (s, 1H, H-7'), 7.96 (d, J = 7.9 Hz, 2H, H-2'', 6''), 7.76 (d, J = 8.2 Hz, 1H, H-6'), 7.69 (t, J = 7.7 Hz, 1H, H-8'), 7.56 (d, J = 8.1 Hz, 1H, H-4''), 7.53 (d, J = 8.0 Hz, 1H, H-9'), 7.45 (t, J = 7.6 Hz, 2H, H-3'', 5''), 7.35 (d, J = 8.1 Hz, 2H, H-3''', 5'''), 6.94 (d, J = 8.1 Hz, 2H, H-2''', 6'''); One secondary amine bond hydrogen proton signal δ H7.18 (s, 1H, - NH -); 1 NCH_2CH_3 signal δ H 3.51 (q, J = 7.2 Hz, 2H, NCH_2-), 1.15 (t, J = 7.2 Hz, 3H, NCH_2CH_3).

The ^{13}C-NMR spectrum combined with DEPT spectrum of the compound shows 30 carbon signals, including 3 carbonyl carbon signals δ C197.93 (s, 8), 173.02 (s, 5), 167.29 (s, 3); 21 aromatic ring carbon signals: δ C 150.39 (s, 2 '), 146.52 (s, 10'), 137.93 (d, 4 '), 136.64 (s, 1' '), 136.52 (s, 1' '), 133.51 (s, 3'), 133.46 (d, 4 ''), 132.51 (d, 3 '' ', 5' ''), 130.38 (d, 8 '), 128.79 (d, 3' ', 5'), 128.19 (d, 2 '', 6 ''), 128.19 (d, 7 '), 127.62 (d, 6'), 127.19 (d, 7 ') 35 (s, 5'), 127.25 (d, 9 '), 125.29 (d, 2' ', 6' '), 119.66 (s, 4' ').

According to HR-ESI-MS (positive), the molecular weight of $C_{30}H_{23}BrClN_3O_3$ was determined to be 587 based on m/z: 588.0684 $[M+H]^+$, indicating the presence of binding ^{1}H-NMR, ^{13}C-NMR, and DEPT spectra. The molecular formula was determined to be $C_{30}H_{23}BrClN_3O_3$ with an unsaturation of 20.

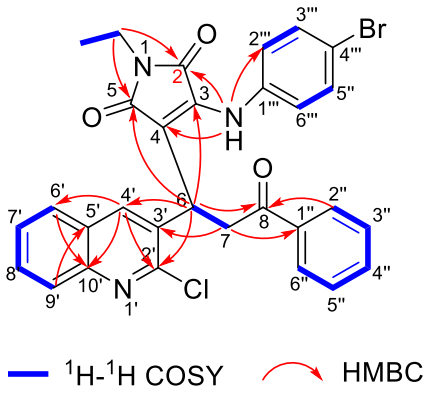
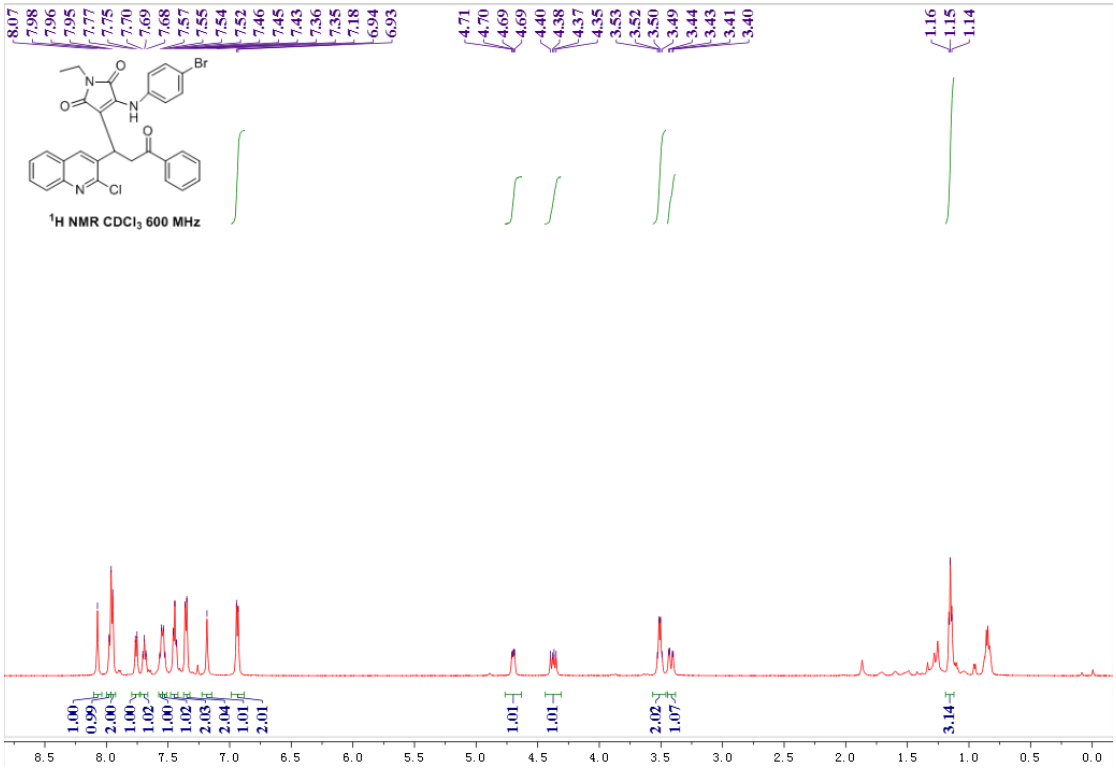


Figure S2. ^{1}H-^{1}H COSY and HMBC related signal diagrams of compound

Based on the ^{1}H-^{1}H COSY spectrum, six structural fragments were obtained as shown by the thick blue solid line in Figure S2, combined with the relevant signals from H-6 to C-3, C-4, C-5, C-8, C-2 ', C-4' in the HMBC spectrum; Related signals from H-7 to C-4, C-3 ', C-1' '; Related signals from H-4 'to C-6, C-2', C-6 ', C-10; Related signals from H-6 'to C-8', C-10 '; Related signals from H-N to C-2, C-4, C-2 " '. It is speculated that the planar structure of the compound is shown in Figure S1.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N
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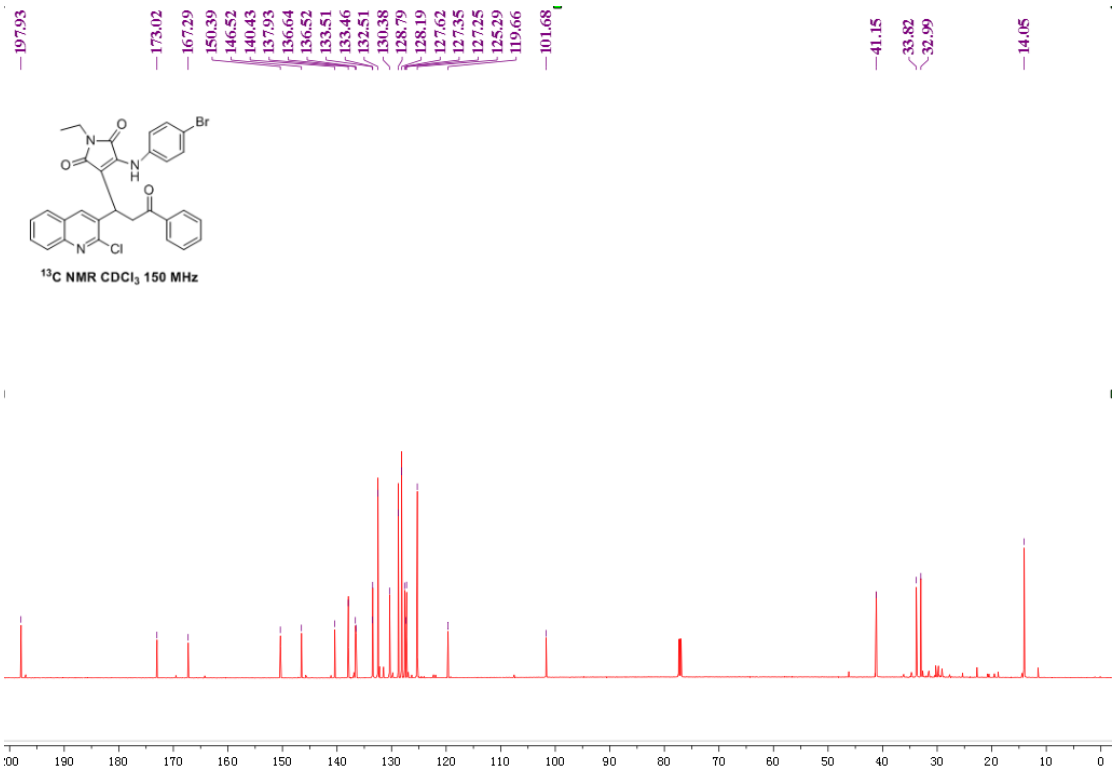
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H
N
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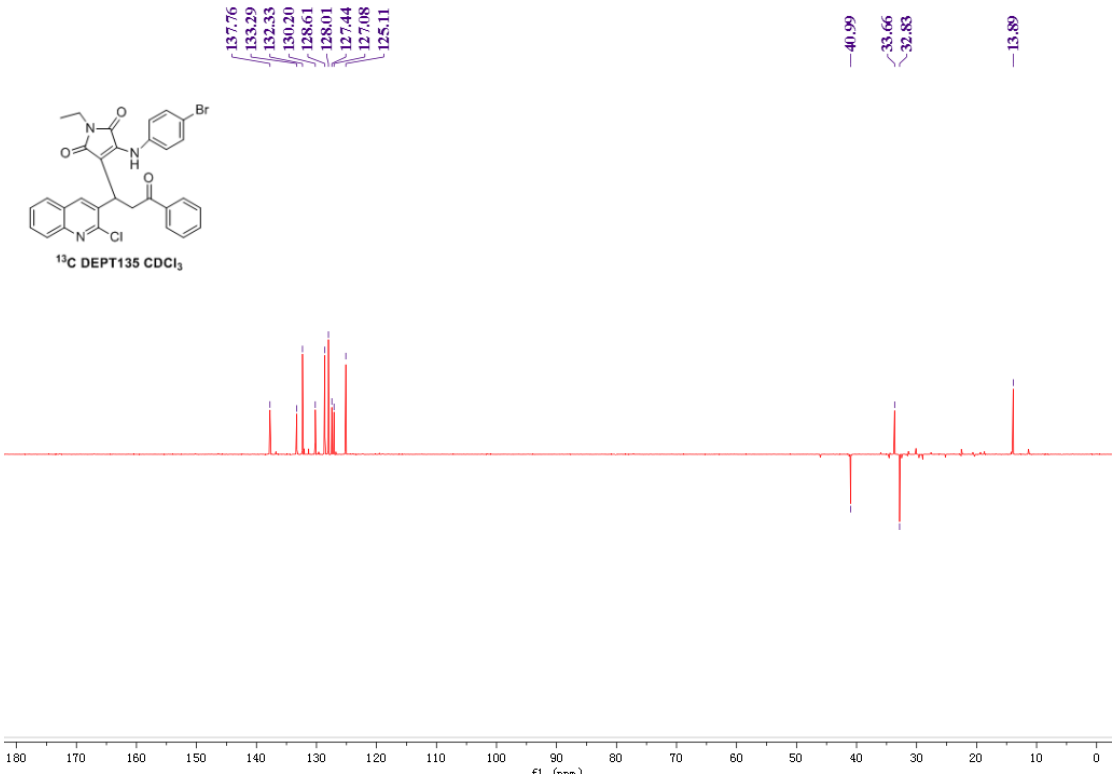
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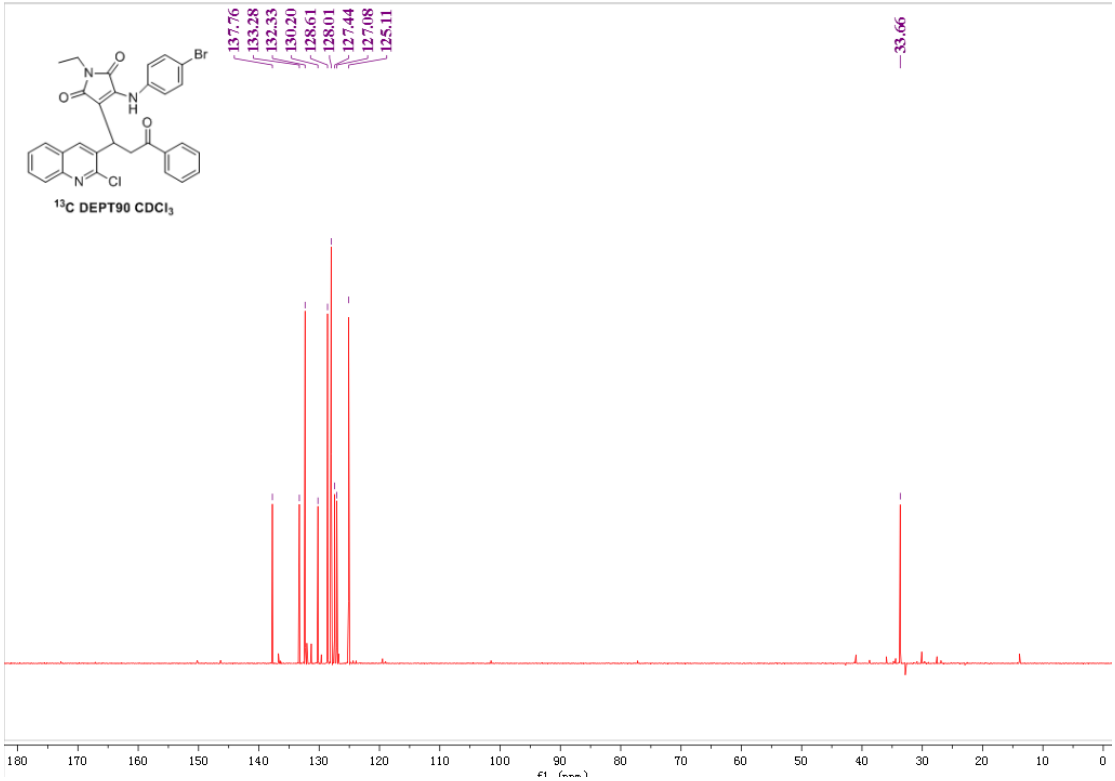
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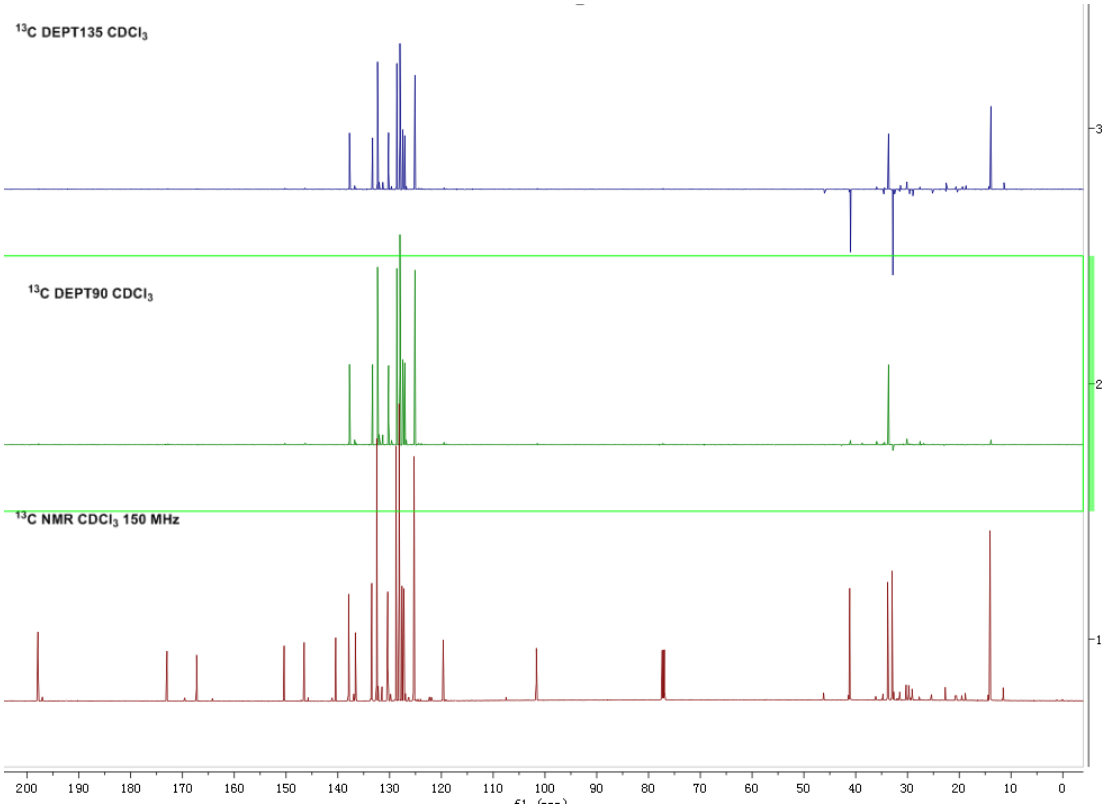
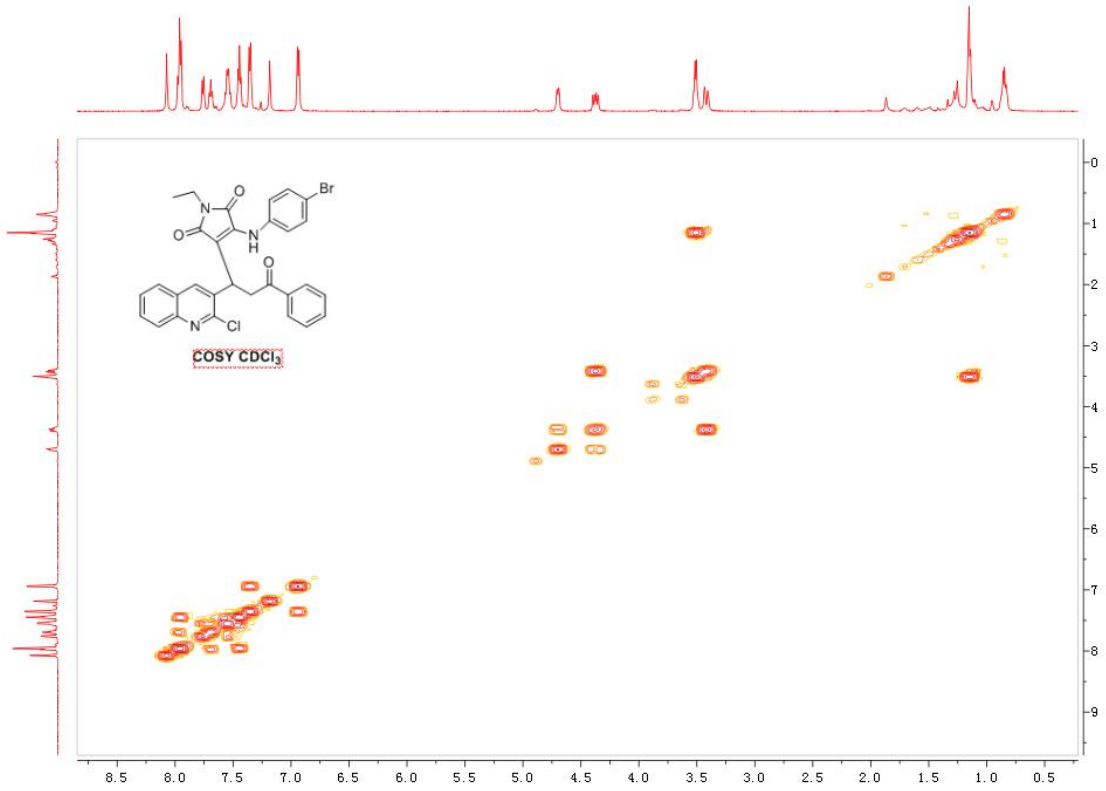
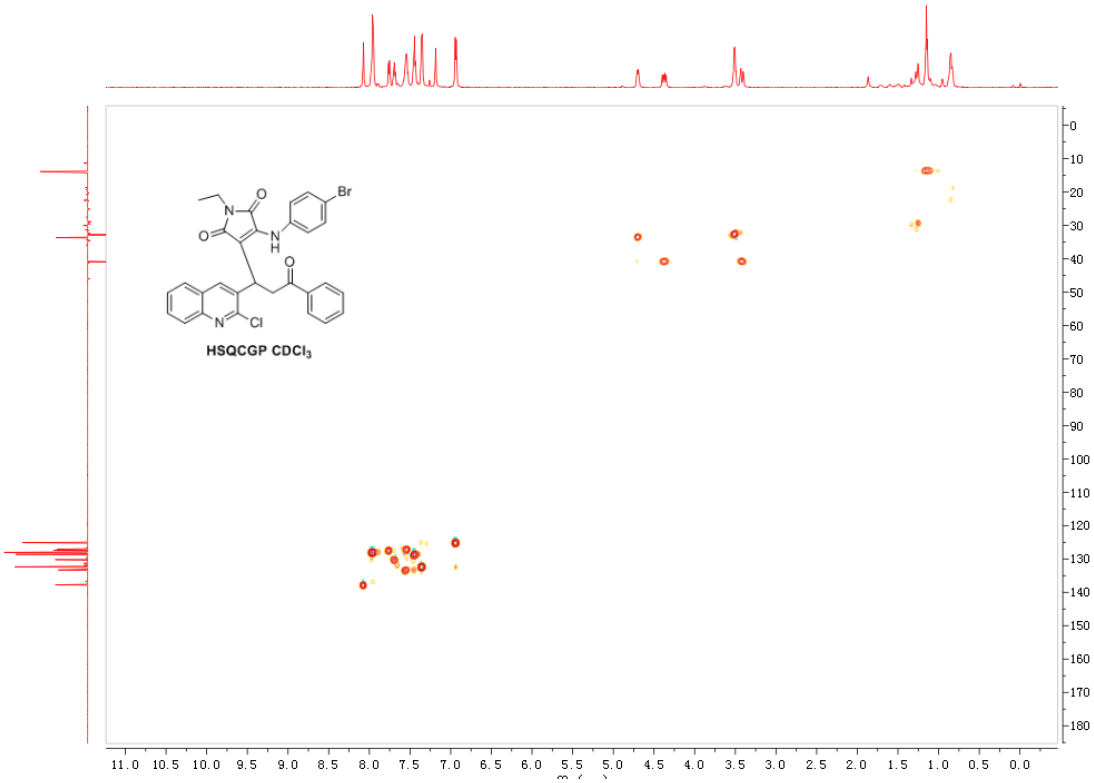
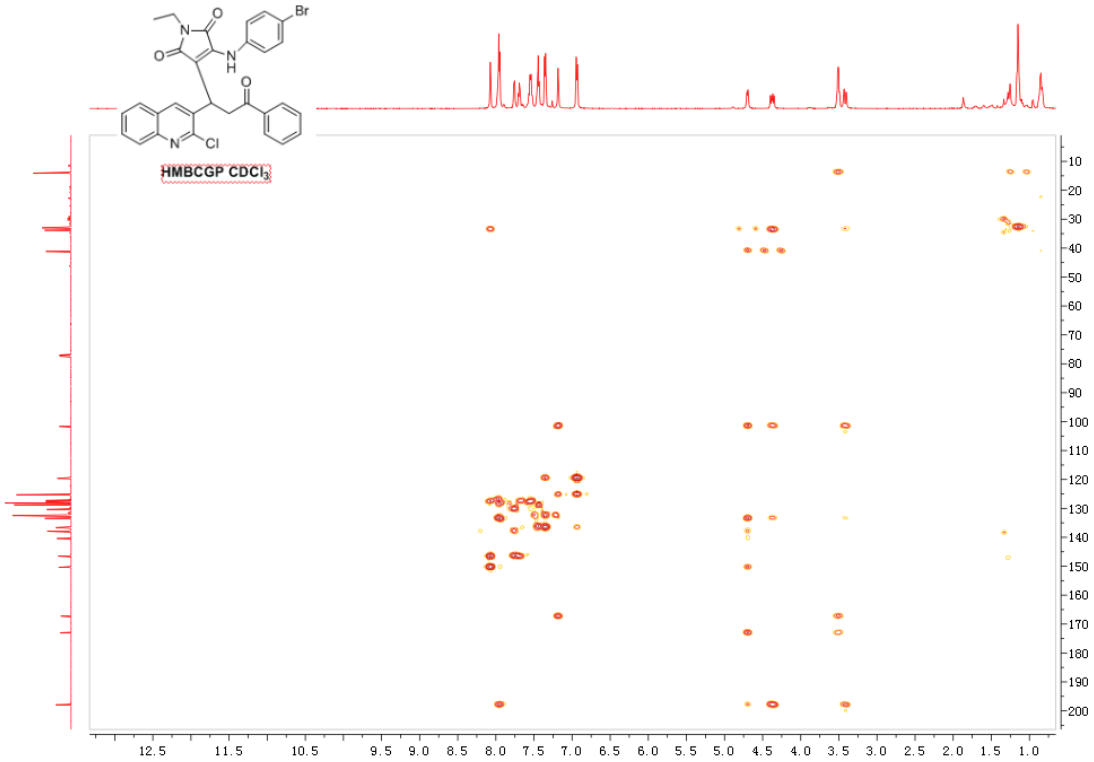
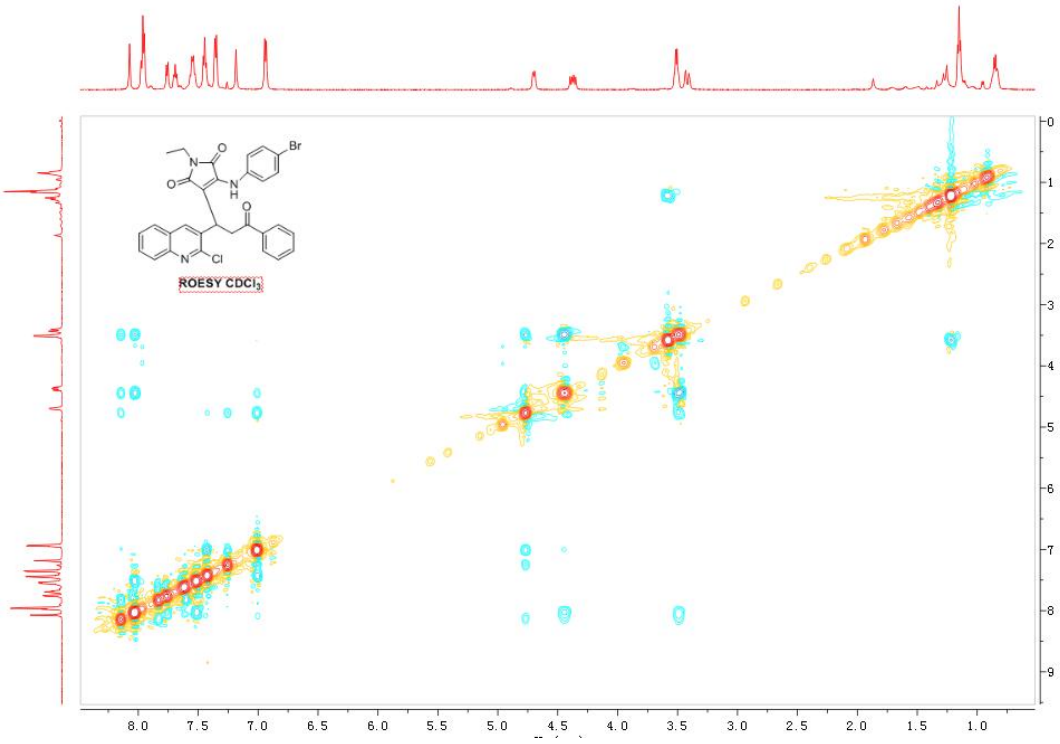
^{13}C DEPT90 CDCl$_3$
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


^{13}C DEPT135 CDCl$_3$
^{13}C DEPT90 CDCl$_3$
^{13}C NMR CDCl$_3$ 150 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3
2
1


Br
O
N
H
O
N
Cl
COSY CDCl$_3$
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 0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8 9

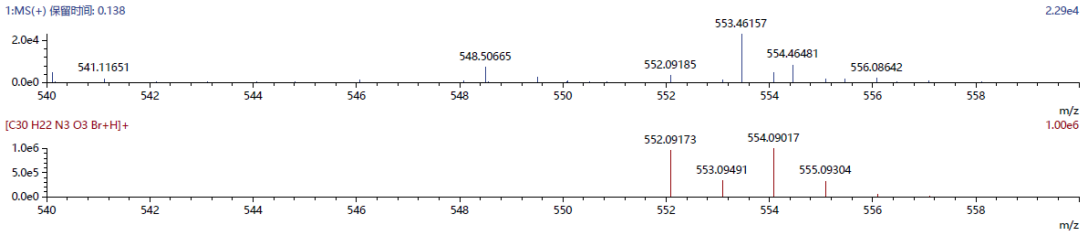

HSQCGP CDCl3


HMBCGP CDCl3

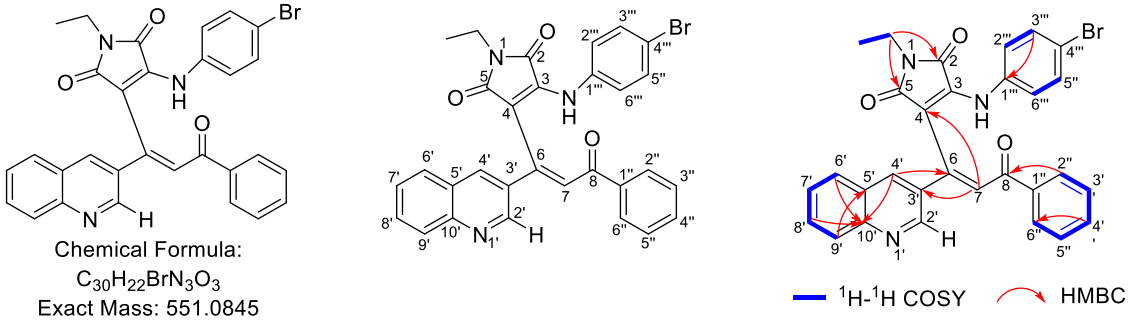

ROESY CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
1
2
3
4
5
6
7
8
9

7. Characterization of 5a

Table S10. HR-ESI-MS of 5a



Score	Pred. (M)	Pred m/z	Meas. m/z	Diff. mDa)	Formulae (M)	Ion	Diff. (ppm)	Iso Score	DBE
24.14	551.08445	552.09173	552.09185	0.12	$C_{30}H_{22}N_3O_3Br$	$[M+H]^+$	0.217	26.91	21.0



Scheme S8. Structure of 5a

^{1}H NMR (500 MHz, Chloroform-d): δ 8.61 (d, *J* = 2.3 Hz, 1H, H-2'), 8.06 (d, *J* = 9.0 Hz, 1H, H-7'), 7.89 (m, 2H, H-2'', 6''), 7.74 (m, overlap, 1H, H-6'), 7.74 (m, overlap, 1H, H-8'), 7.70 (d, *J* = 2.0 Hz, 1H, H-4'), 7.58 (m, 1H, H-4''), 7.57 (m, 1H, H-9'), 7.48 (d, *J* = 8.1 Hz, 2H, H-3'', 5''), 7.26 (s, 1H, H-7), 7.14 (s, 1H, NH), 6.95 (d, *J* = 8.7 Hz, 2H, H-3''', 5'''), 6.55 (d, *J* = 8.7 Hz, 2H, H-2''', 6'''), 3.65 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 190.1 (s, 8), 169.8 (s, 5), 167.3 (s, 2), 149.3 (d, 2'), 147.9 (s, 10'), 140.8 (s, 3), 140.0 (s, 6), 138.2 (s, 1''), 136.0 (s, 1'''), 134.7 (d, 4'), 133.0 (d, 4''), 131.8 (s, 3'), 131.6 (d, 3''', 5'''), 130.5 (d, 8'), 129.1 (d, 7'), 128.7 (d, 3'', 5''), 128.5 (d, 2'', 6''), 128.3 (d, 6'), 127.6 (s, 5'), 127.3 (d, 9'), 126.4 (d, 7), 125.0 (d, 2''', 6'''), 119.2 (s, 4'''), 100.3 (s, 4), 33.7 (t, N-$\underline{C}H_2$), 14.2 (q, N-$CH_2\underline{C}H_3$).

IR(KBr): ν_{max}: 3356, 2922, 2854, 1735, 1700, 1654, 1631, 1493, 1458, 1401, 1082, 1009, 830, 703 cm^{-1}.

Table S11. Hydrogen and carbon spectra data of compound 5a in deuterated $CDCl_3$

No.	Compound **5a**				
	δ_H (J in Hz)	δ_C	COSY(H)	HMBC(H→C)	ROESY
2	—	167.3 (s)	—	—	—
3	—	140.8 (s)	—	—	—
4	—	100.3 (s)	—	—	—
5	—	169.8 (s)	—	—	—
6	—	140.0 (s)	—	—	—
7	7.26 (s, 1H)	126.4 (d)	—	4, 3'	2', 2", 4'
8	—	190.1 (s)	—	—	—
2'	8.61 (d, J = 2.3 Hz, 1H)	149.3 (d)	—	4', 6	—
3'	—	131.8 (s)	—	—	—
4'	7.70 (d, J = 2.0 Hz, 1H)	134.7 (d)	—	6, 2', 6', 10'	—
5'	—	127.6 (s)	—	—	—
6'	7.74 (m, overlap, 1H)	128.3 (d)	—	4', 8', 10'	—
7'	8.06 (d, J = 9.0 Hz, 1H)	129.1 (d)	8'	9'	—
8'	7.74 (m, overlap, 1H)	130.5 (d)	7', 9'	6', 10'	—
9'	7.57 (m, 1H)	127.3 (d)	8'	5'	—
10'	—	147.9 (s)	—	—	—
1"	—	138.2 (s)	—	—	—
2", 6"	7.89 (m, 2H)	128.5 (d)	3", 5"	4", 8	3", 5"
3", 5"	7.48 (d, J = 8.1 Hz, 2H)	128.7 (d)	2", 4", 6"	1", 2", 6"	2", 6"
4"	7.58 (m, 1H)	133.0 (d)	3", 5"	—	—
1'"	—	136.0 (s)	—	—	—
2'", 6'"	6.55 (d, J = 8.7 Hz, 2H)	125.0 (d)	3'", 5'"	1'", 4'"	—
3'", 5'"	6.95 (d, J = 8.7 Hz, 2H)	131.6 (d)	2'", 6'"	1'", 4'"	—
4'"	—	119.2 (s)	—	—	—
NH	7.14 (s, 1H)	—	—	2, 4, 2'", 6'"	—
NCH_2-	3.65 (q, J = 7.1 Hz, 2H)	33.7 (t)	$CH_2\underline{CH_3}$	2, 5, CH_3	—
$CH_2\underline{CH_3}$	1.27 (t, J = 7.1 Hz, 3H)	14.2 (q)	NCH_2-	NCH_2-	—
Measured in $CDCl_3$ at 500 MHz.					

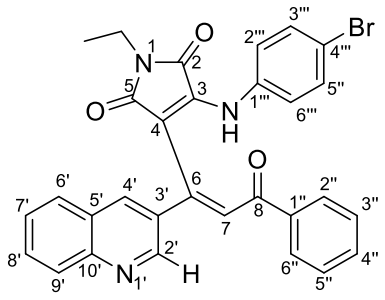


Figure S3. Structure of New Compound 5a

Analysis process:

The ^{1}H-NMR spectrum of the compound shows 22 proton signals, including 15 aromatic ring proton signals with a δ 8.61 (d, *J* = 2.3 Hz, 1H, H-2'), 8.06 (d, *J* = 9.0 Hz, 1H, H-7'), 7.89 (m, 2H, H-2'', 6''), 7.74 (m, overlap, 1H, H-6'), 7.74 (m, overlap, 1H, H-8'), 7.70 (d, *J* = 2.0 Hz, 1H, H-4'), 7.58 (m, 1H, H-4''), 7.57 (m, 1H, H-9'), 7.48 (d, *J* = 8.1 Hz, 2H, H-3'', 5''), 6.95 (d, *J* = 8.7 Hz, 2H, H-3''', 5'''), 6.55 (d, *J* = 8.7 Hz, 2H, H-2''', 6'''); One secondary amine bond hydrogen proton signal δ_H7.14 (s, 1H, -NH-); A proton signal of a trisubstituted vinyl group 7.26 (s, 1H, H-7); A set of ethyl proton signals 3.65 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H).

The ^{13}C-NMR spectrum combined with DEPT spectrum of the compound shows 30 carbon signals, including 3 carbonyl carbon signals δ_C190.1 (s, 8), 169.8 (s, 5), 167.3 (s, 2); 21 aromatic ring carbon signals: δ_C 149.3 (d, 2'), 147.9 (s, 10'), 140.8 (s, 3), 138.2 (s, 1''), 136.0 (s, 1'''), 134.7 (d, 4'), 133.0 (d, 4''), 131.8 (s, 3'), 131.6 (d, 3''', 5'''), 130.5 (d, 8'), 129.1 (d, 7'), 128.7 (d, 3'', 5''), 128.5 (d, 2'', 6''), 128.3 (d, 6'), 127.6 (s, 5'), 127.3 (d, 9'), 126.4 (d, 7), 125.0 (d, 2''', 6'''), 119.2 (s, 4'''), 100.3 (s, 4).

According to HR-ESI-MS (positive), the molecular weight of $C_{30}H_{22}BrN_3O_3$ was determined to be 551 based on m/z: 552.0918 $[M+H]^+$, indicating the presence of binding ^{1}H-NMR, ^{13}C-NMR, and DEPT spectra. The molecular formula was determined to be $C_{30}H_{22}BrN_3O_3$ with an unsaturation of 21.

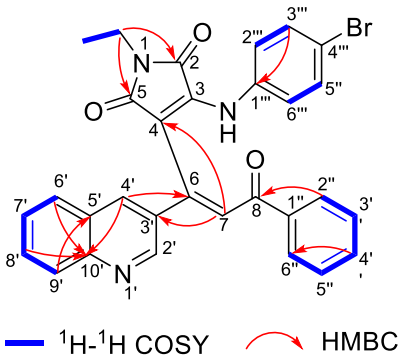
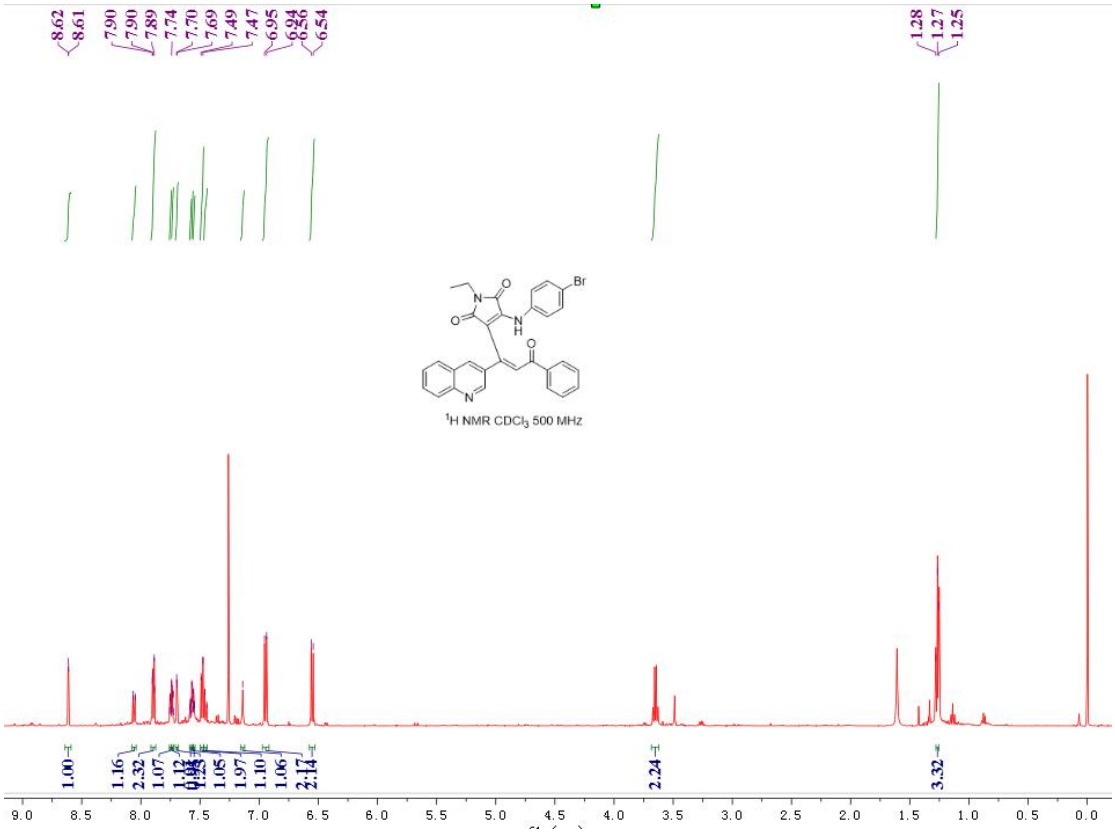
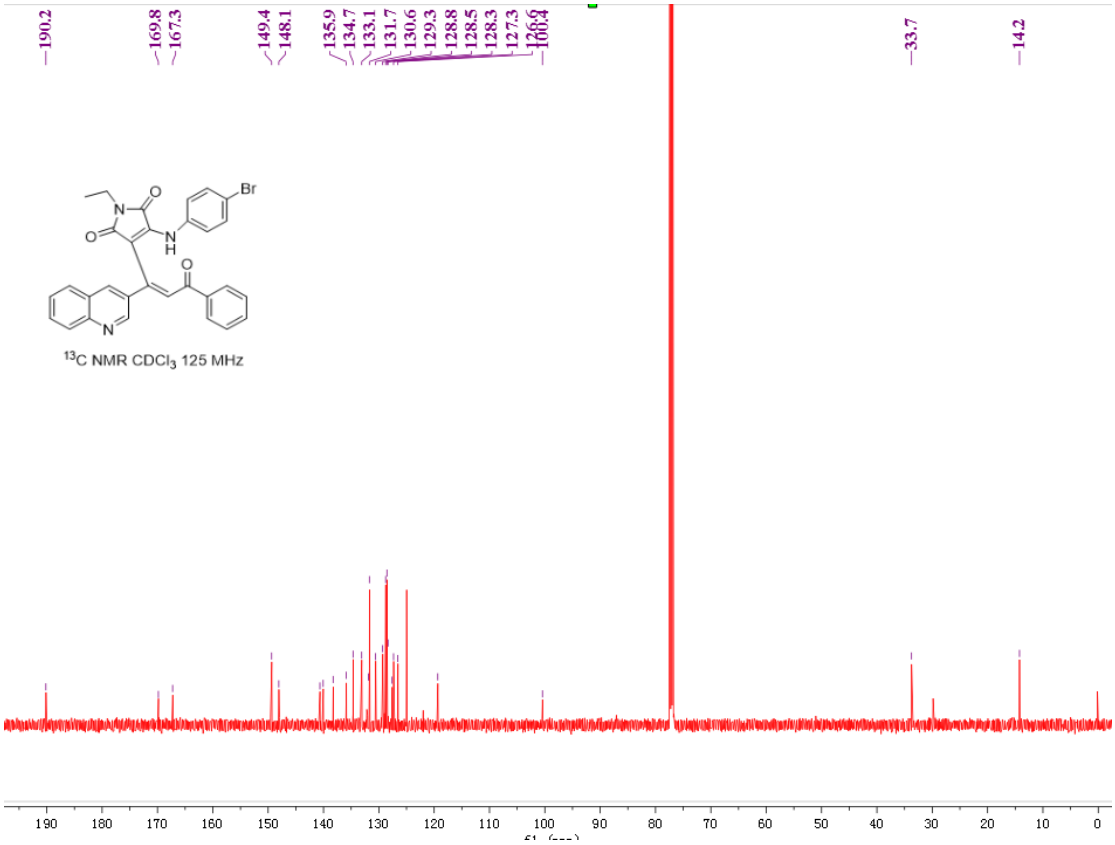


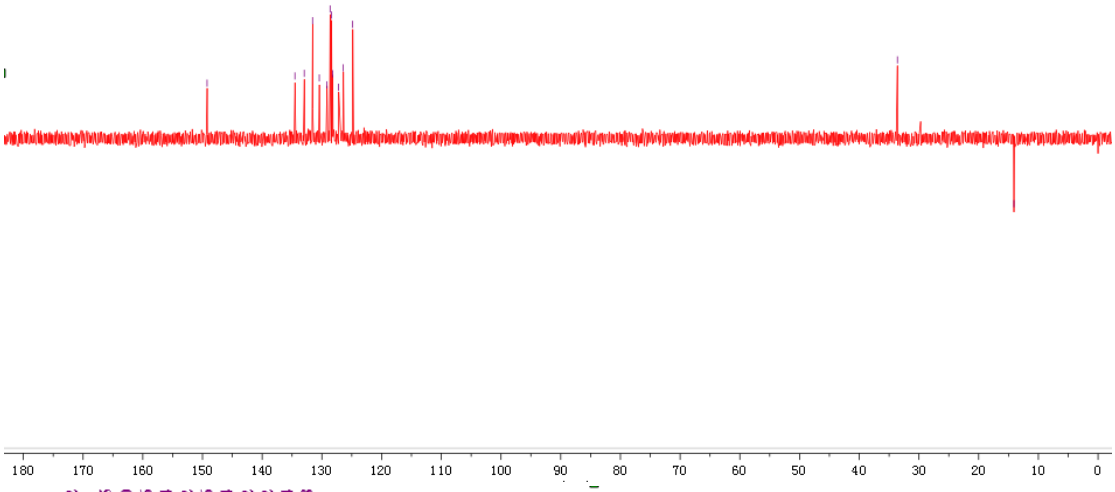
Figure S4. ^{1}H-^{1}H COSY and HMBC related signal diagrams of compound

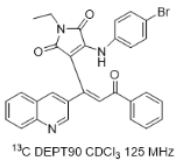
Based on the ^{1}H-^{1}H COSY spectrum, five structural fragments were obtained as shown by the thick blue solid line in Figure S4, combined with the relevant signals from H-7 to C-4, C-3'; Related signals from H-2' to C-4', C-6; Related signals from H-4' to C-6, C-2'; C-6', C-10; Related signals from H-6' to C-4', C-8'; C-10'; Related signals from H-7' to C-9'; Related signals from H-N to C-2, C-4; C-2'''. Based on the ROESY correlation signals between H-7 and H-2', it is inferred that the configuration at position 7 is *E*. Therefore, the proposed planar structure of the compound is shown in Figure S3.


8.62
8.61
7.90
7.90
7.89
7.74
7.70
7.69
7.49
7.47
6.95
6.94
6.56
6.54
1.28
1.27
1.25
Br
O
N
O
H
N
O
N
^{1}H NMR CDCl$_3$ 500 MHz
1.00
1.16
2.32
1.07
1.12
1.05
1.97
1.10
1.06
2.17
2.14
2.24
3.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

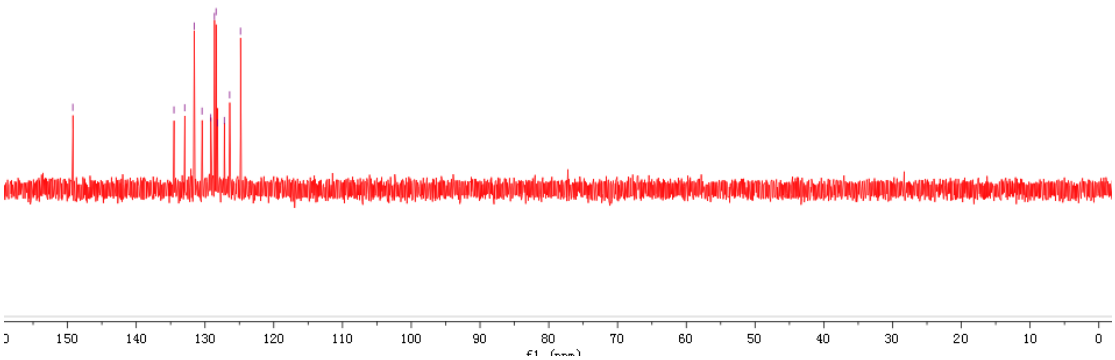

190.2
169.8
167.3
149.4
148.1
135.9
134.7
133.1
131.7
130.6
129.3
128.8
128.5
128.3
127.3
126.6
100.4
33.7
14.2
Br
O
N
O
H
N
O
N
^{13}C NMR CDCl$_3$ 125 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

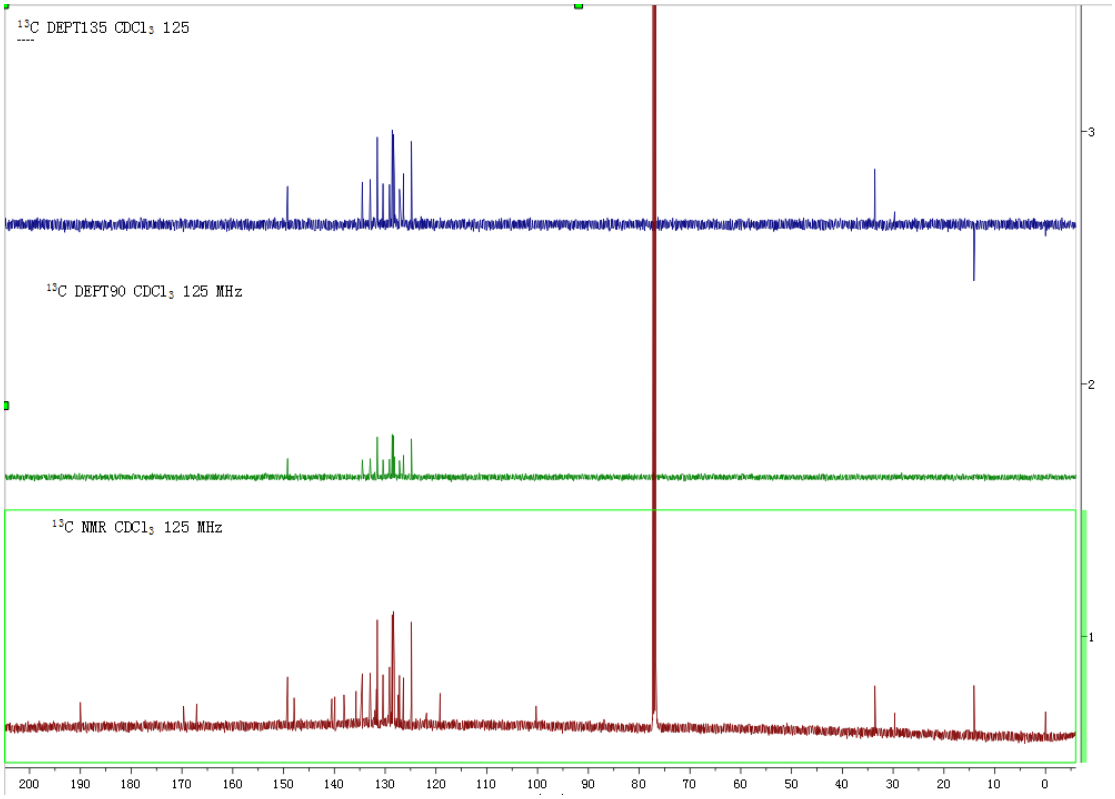
^{13}C DEPT135 $CDCl_3$ 125 MHz

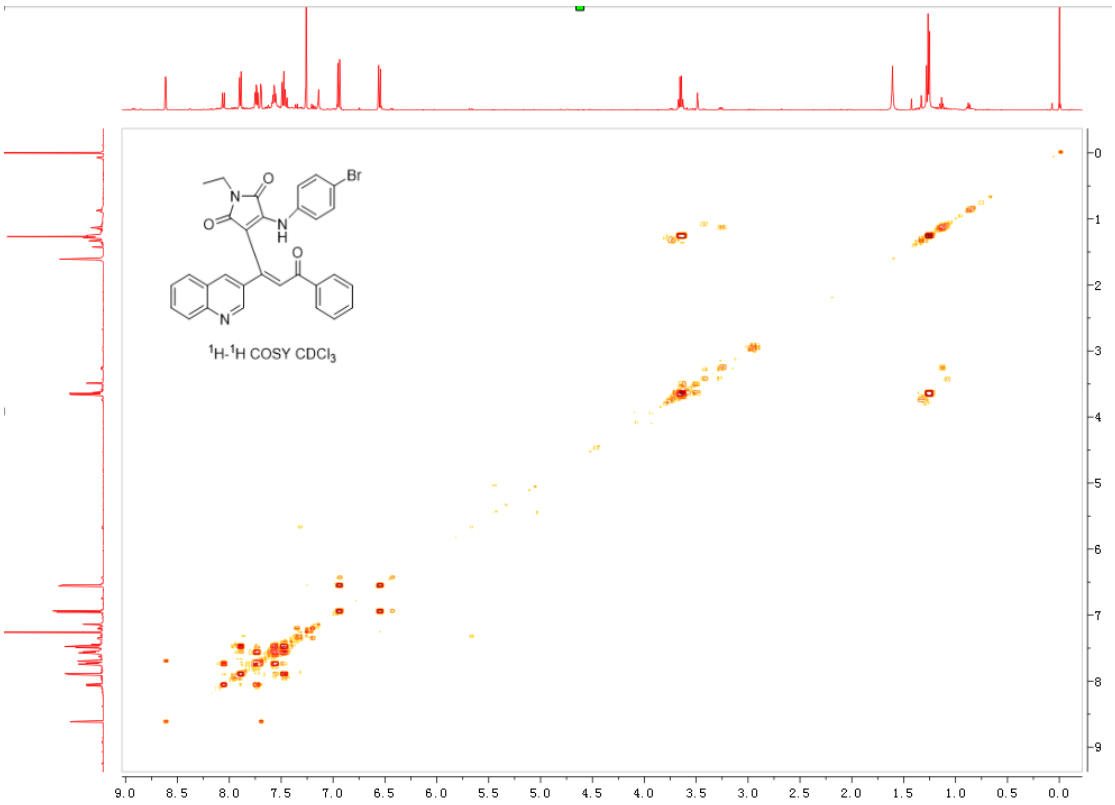


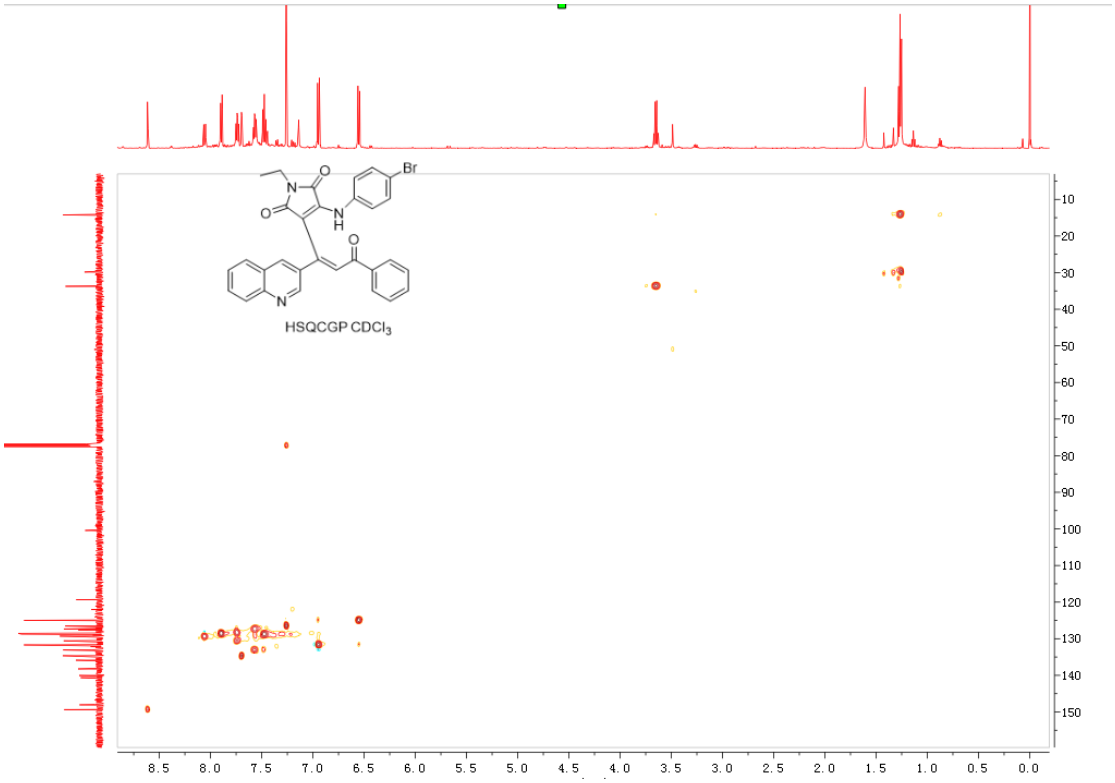


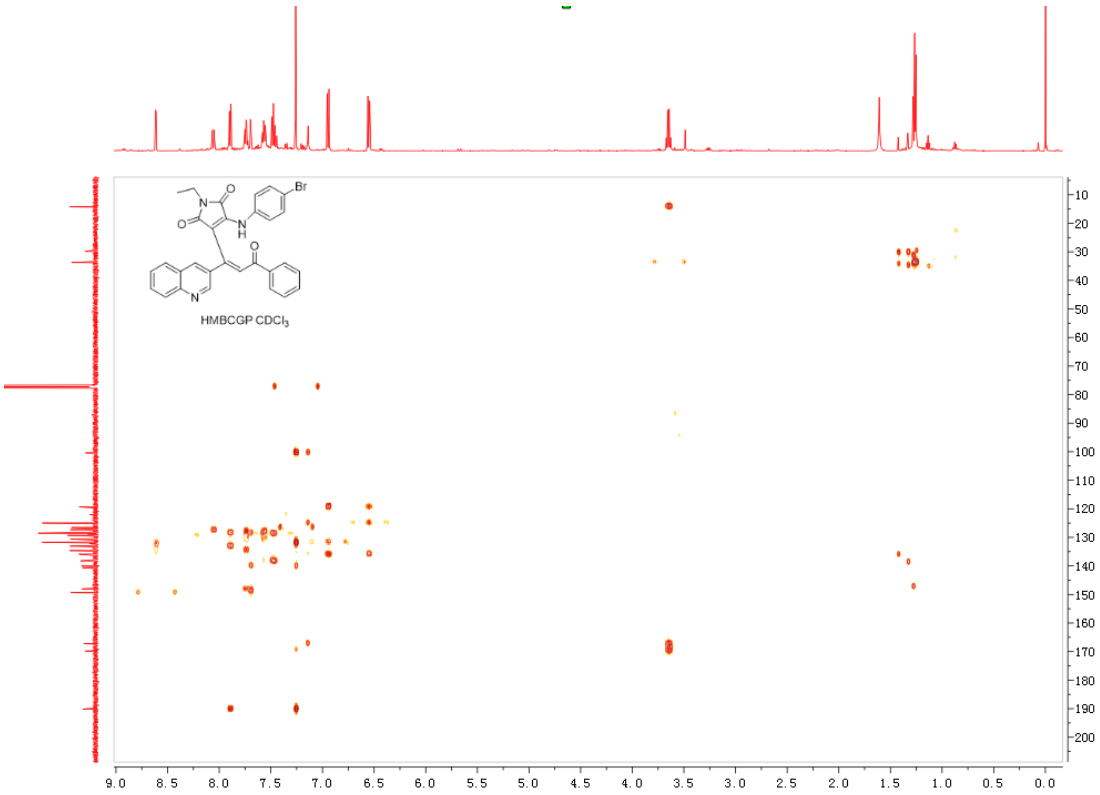
^{13}C DEPT90 $CDCl_3$ 125 MHz

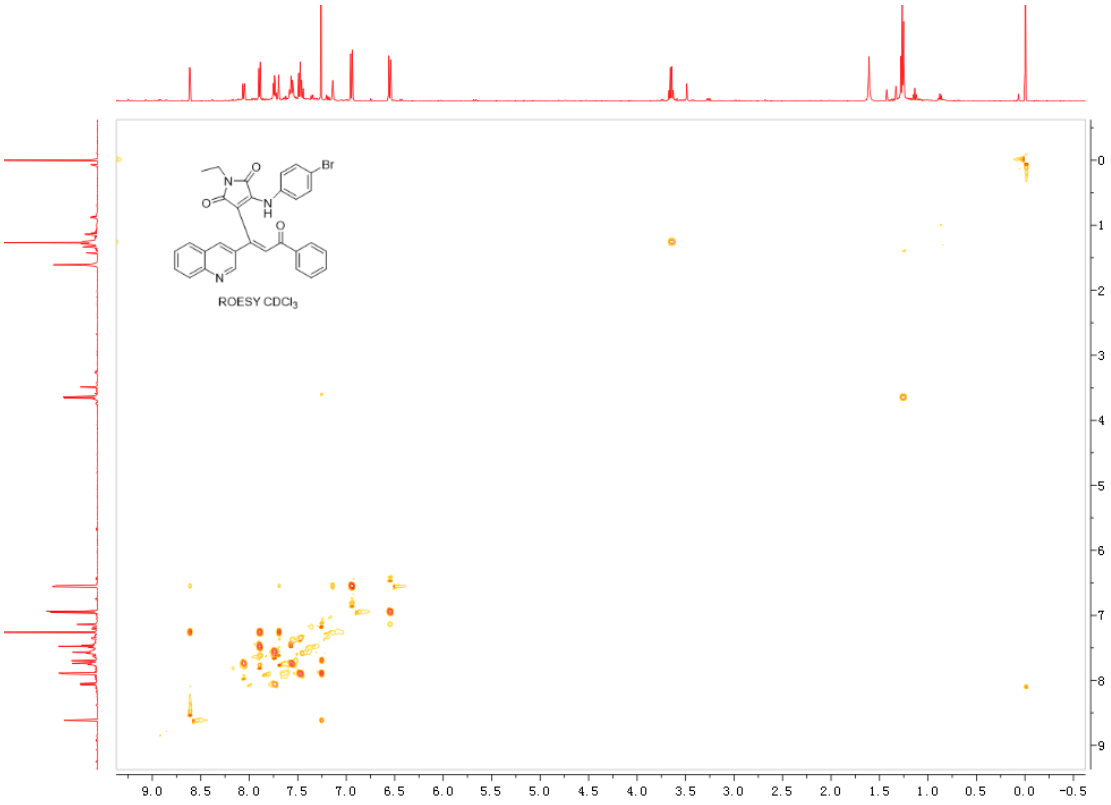



^{13}C DEPT135 $CDCl_3$ 125
^{13}C DEPT90 $CDCl_3$ 125 MHz
^{13}C NMR $CDCl_3$ 125 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Br
^{1}H-^{1}H COSY $CDCl_3$
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

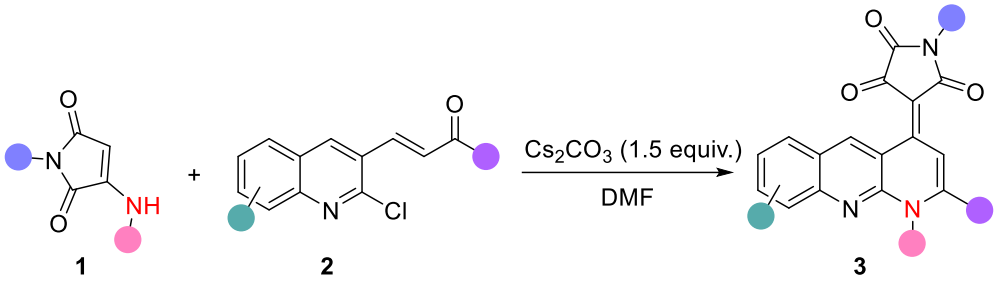

HSQCGP CDCl3


HMBCGP CDCl3


ROESY CDCl3
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
7
8
9

8. General procedure for the synthesis of 3 and 7a

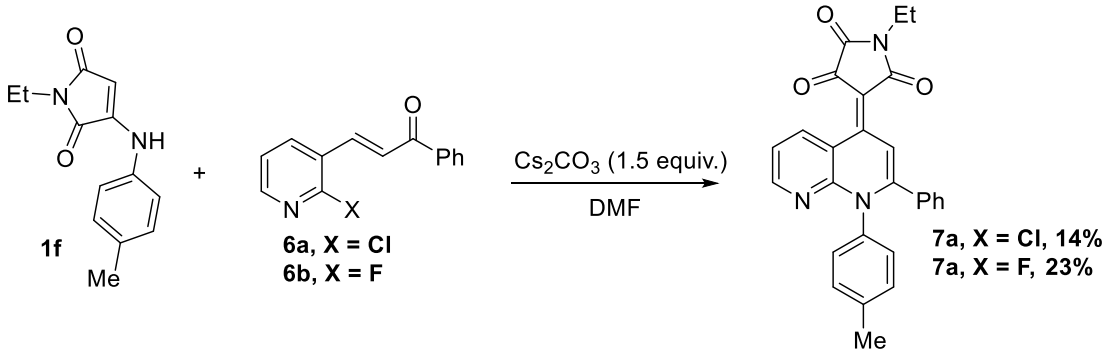
General procedure for the synthesis of 3



Scheme S9. Synthesis of 3

To a mixture of aminomaleimides **1** (0.1 mmol, 1 equiv) and *ortho*-chloroquinolin chalcone **2** (0.2 mmol, 2.0 equiv) in DMF (2 mL) was added Cs_2CO_3 (0.15 mmol, 1.5 equiv). Then the reaction solution was vigorously stirred at 80 °C for 12 h in air and monitored by TLC. After the reaction was complete, the mixture was concentrated in vacuo and purified by column chromatography on silica gel with petroleum ether/EtOAc (5:1) as the eluent to furnish the corresponding product **3**.

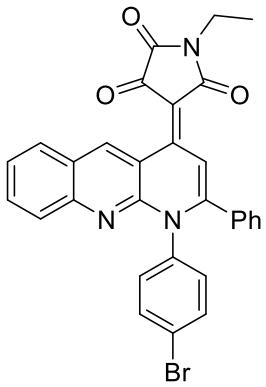
General procedure for the synthesis of 7a



Scheme S10. Synthesis of 7a

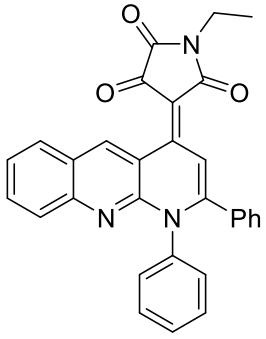
To a mixture of 1-ethyl-3-(*p*-tolylamino)-1*H*-pyrrole-2,5-dione **1f** (0.1 mmol, 1 equiv) and 2-chloropyridine chalcone **6a** or 2-fluoropyridine chalcone **6b** (0.2 mmol, 2.0 equiv) in DMF (2 mL) was added Cs_2CO_3 (0.15 mmol, 1.5 equiv). Then the reaction solution was vigorously stirred at 80 °C for 12 h in air and monitored by TLC. After the reaction was complete, the mixture was concentrated in vacuo and purified by column chromatography on silica gel with petroleum ether/EtOAc (5:1) as the eluent to furnish the corresponding product **7a**.

(*E*)-4-(1-(4-bromophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3a)



70% yield, red solid, m.p.: 145-146 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.51 (s, 1H), 8.09 (t, *J* = 8.2 Hz, 1H), 7.81 (q, *J* = 8.8 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.28 (m, 5H), 7.11 (d, *J* = 8.6 Hz, 2H), 3.72 (q, *J* = 6.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100MHz, $CDCl_3$): δ 177.1, 171.2, 163.6, 156.5, 153.4, 149.7, 147.3, 143.3, 137.7, 134.6, 133.9, 132.0, 131.3, 130.0, 129.7, 129.3, 128.5, 128.1, 126.8, 125.5, 122.8, 116.3, 114.1, 101.4, 32.6, 13.8. IR(KBr): ν_{max}: 2923, 2852, 1735, 1685, 1634, 1569, 1537, 1493, 1482, 1468, 1444, 1399, 1070, 1013, 831, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}BrN_3O_3$ $[M+H]^+$ = 550.0760, found = 550.0756.

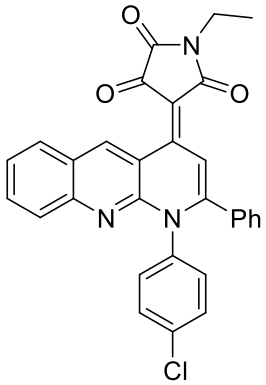
(*E*)-4-(1,2-diphenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3b)



68% yield, red solid, m.p.: 132-133 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.52 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.60 (ddd, *J* = 8.1, 6.0, 1.8 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.34 – 7.27 (m, 5H), 7.24 – 7.20 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 171.6, 163.9, 157.1, 153.6, 149.9, 147.5, 143.3, 138.7, 134.9, 133.8, 129.8, 129.7, 129.6, 129.3, 128.8, 128.35, 128.33, 126.8, 125.6, 116.5, 114.4, 101.0, 32.7, 13.9. IR(KBr): ν_{max}: 2922, 2850, 1734, 1685, 1652, 1561, 1537, 1493 1467, 1437, 1400, 1070, 1008, 831, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{21}N_3O_3$ $[M+H]^+$ = 472.1655, found =472.1650.

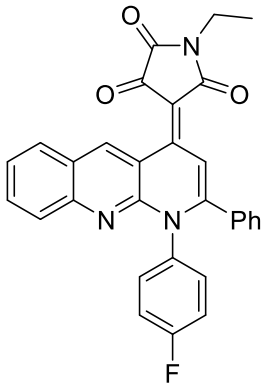
(*E*)-4-(1-(4-chlorophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-

ethylpyrrolidine-2,3,5-trione (3c)



66% yield, red solid, m.p.: 152-153 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.53 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.78 (m, 2H), 7.61 (ddd, *J* = 8.0, 6.2, 1.5 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.37 – 7.33 (m, 2H), 7.33 – 7.27 (m, 4H), 7.20 – 7.13 (m, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.2, 171.3, 163.7, 156.7, 153.6, 149.8, 147.4, 143.4, 137.2, 134.8, 134.6, 134.0, 131.0, 130.0, 129.7, 129.3, 129.1, 128.6, 128.2, 126.9, 125.6, 116.3, 114.2, 101.4, 32.7, 13.8. IR(KBr): ν_{max}: 2923, 2854, 1756, 1688, 1652, 1561, 1538, 1494, 1467, 1437, 1401, 1089, 1015, 837, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}ClN_3O_3$ $[M+H]^+$ = 506.1266, found = 506.1270.

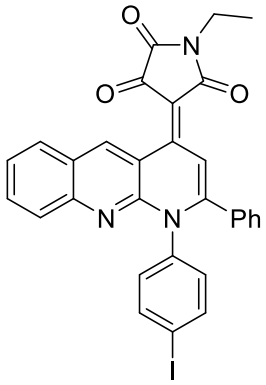
(*E*)-1-ethyl-4-(1-(4-fluorophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3d)



63% yield, red solid, m.p.: 119-120 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.53 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.65 – 7.57 (m, 1H), 7.35 – 7.28 (m, 5H), 7.23 – 7.17 (m, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.4, 163.7, 160.9, 156.9, 153.6, 149.8, 147.5, 143.4, 134.8, 134.0, 131.4, 131.3, 129.9, 129.7, 129.2, 128.5, 128.2, 126.9, 125.6, 116.4, 116.1, 115.8, 114.2, 101.3, 32.7, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -110.22 – -113.73 (m). IR(KBr): ν_{max}: 2923, 2851, 1735, 1697, 1653, 1577, 1561, 1494, 1436, 1401, 1072, 1008, 831, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}FN_3O_3$ $[M+H]^+$ = 490.1561, found = 490.1570.

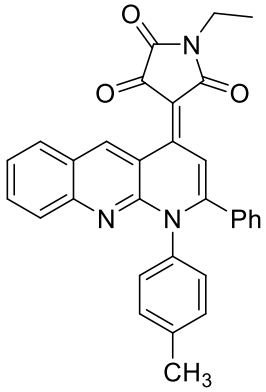
(*E*)-1-ethyl-4-(1-(4-iodophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-

ylidene)pyrrolidine-2,3,5-trione (3e)



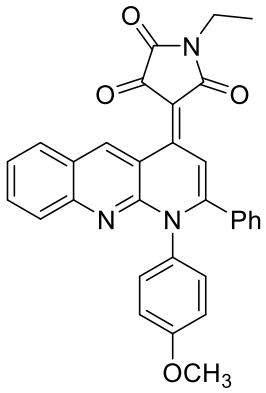
68% yield, red solid, m.p.: 155-156 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.50 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.64 – 7.55 (m, 1H), 7.39 – 7.27 (m, 5H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.74 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.1, 171.2, 163.6, 156.5, 153.4, 149.7, 147.2, 143.3, 138.4, 138.0, 134.6, 133.9, 131.4, 130.0, 129.7, 129.3, 128.5, 128.2, 126.8, 125.5, 116.3, 114.2, 101.3, 94.4, 32.6, 13.8. IR(KBr): ν_{max}: 2922, 2850, 1734, 1697, 1652, 1631, 1561, 1537, 1493, 1467 1437, 1072, 1008 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}IN_3O_3$ $[M+H]^+$ = 598.0622, found =598.0615.

(*E*)-1-ethyl-4-(2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3f)



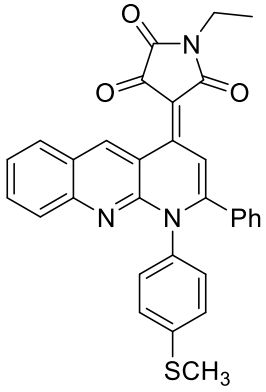
72% yield, red solid, m.p.: 108-109 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.51 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.62 – 7.56 (m, 1H), 7.30 (qd, *J* = 7.2, 3.4 Hz, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.9, 171.6, 163.9, 157.3, 153.5, 149.9, 147.6, 143.2, 138.8, 136.1, 135.0, 133.7, 129.7, 129.7, 129.4, 129.3, 129.3, 128.4, 128.3, 126.7, 125.6, 116.6, 114.5, 100.8, 32.6, 21.2, 13.9. IR(KBr): ν_{max}: 2924, 2851, 1734, 1696, 1652, 1631, 1577, 1561, 1542, 1494, 1436, 1073, 831, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_3O_3$ $[M+H]^+$ = 486.1812, found =486.1816.

(*E*)-1-ethyl-4-(1-(4-methoxyphenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3g)



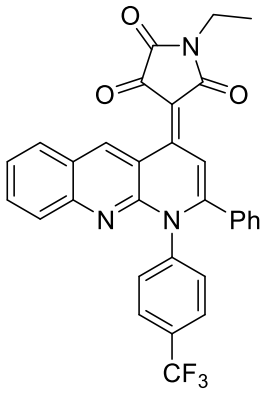
74% yield, red solid, m.p.: 137-138 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.50 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 3.4 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.37 – 7.27 (m, 5H), 7.14 – 7.08 (m, 2H), 6.92 – 6.83 (m, 2H), 3.83 (s, 3H), 3.76 (d, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.9, 171.5, 163.9, 159.4, 157.5, 153.5, 149.9, 147.7, 143.2, 135.1, 133.7, 131.3, 130.6, 129.70, 129.66, 129.3, 128.4, 128.3, 126.7, 125.5, 116.6, 114.5, 113.9, 100.7, 55.4, 32.6, 13.9. IR(KBr): ν_{max}: 2923, 2851, 1754, 1694, 1652, 1631, 1567, 1538, 1509, 1494, 1467, 1442, 1071,1029, 833, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_3O_4$ $[M+H]^+$ =502.1761, found =502.1755.

(*E*)-1-ethyl-4-(1-(4-(methylthio)phenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3h)



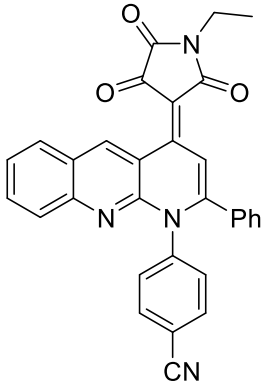
70% yield, red solid, m.p.:149-150 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.52 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 3.4 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.36 – 7.29 (m, 5H), 7.24 – 7.20 (m, 2H), 7.16 – 7.08 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.5, 163.9, 161.2, 157.1, 153.5, 149.8, 147.5, 143.3, 140.1, 135.3, 134.9, 133.8, 129.9, 129.8, 129.7, 129.3, 128.5, 128.3, 126.8, 125.8, 125.6, 116.5, 114.5, 101.0, 32.7, 15.3, 13.9. IR(KBr): ν_{max}: 2922, 2854, 1753, 1703, 1652, 1578, 1561, 1537, 1493, 1467, 1437, 1401, 1090,1010, 831, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_3O_3S$ $[M+H]^+$ = 518.1532, found = 518.1539.

(*E*)-1-ethyl-4-(2-phenyl-1-(4-(trifluoromethyl)phenyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3i)



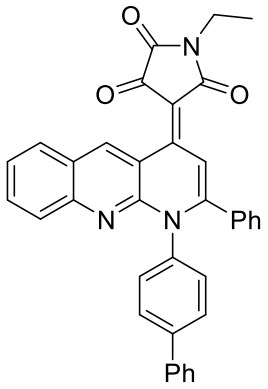
42% yield, red solid, m.p.: 252-253 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.55 (s, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.76 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.27 (m, 5H), 3.76 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 163.5, 156.3, 153.5, 149.7, 147.2, 143.5, 141.8, 134.4, 134.1, 130.4, 130.1, 129.7, 129.3, 128.6, 128.1, 126.9, 126.0, 125.9, 125.6, 116.2, 114.1, 101.7, 32.7, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.60. IR(KBr): ν_{max}: 2922, 2851 1754, 1697, 1653, 1578, 1540, 1494, 1467, 1437, 1400, 1067, 1021, 831, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{20}F_3N_3O_3$ $[M+H]^+$ = 506.1266, found = 506.1270.

(*E*)-4-(4-(1-ethyl-2,4,5-trioxopyrrolidin-3-ylidene)-2-phenylbenzo[*b*][1,8]naphthyridin-1(4*H*)-yl)benzonitrile (3j)



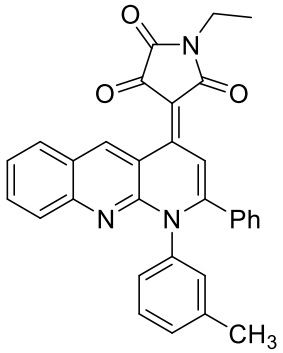
44% yield, red solid, m.p.:169-170 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.55 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 3H), 7.29 (dd, *J* = 8.1, 4.1 Hz, 4H), 3.74 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.4, 171.0, 163.4, 155.8, 153.4, 149.6, 147.1, 143.6, 142.7, 134.3, 134.2, 132.6, 130.9, 130.3, 129.8, 129.2, 128.7, 128.0, 127.0, 125.5, 117.7, 116.1, 113.9, 112.8, 102.1, 32.8, 13.8. IR(KBr): ν_{max}: 2924, 2851 1755, 1697, 1654, 1569, 1538, 1493, 1468, 1435, 1400, 1071, 1021, 837, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{20}N_4O_3$ $[M+H]^+$ = 497.1608, found = 497.1612.

(*E*)-4-(1-([1,1'-biphenyl]-4-yl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3k)



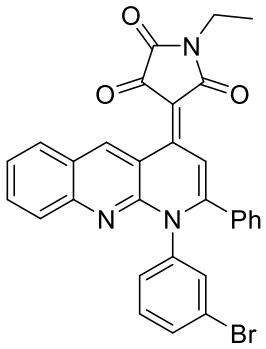
56% yield, red solid, m.p.:145-146 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.54 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 8.0, 5.5 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 5H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.30 (t, *J* = 8.4 Hz, 5H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 171.5, 163.8, 157.1, 153.5, 149.8, 147.5, 143.3, 141.5, 139.5, 137.7, 134.9, 133.8, 129.9, 129.8, 129.7, 129.3, 128.9, 128.4, 128.3, 128.0, 127.3, 127.1, 126.8, 125.6, 116.5, 114.5, 101.0, 32.7, 13.9. IR(KBr): v_{max}: 2922, 2851 1753, 1697, 1652, 1578, 1562, 1494, 1468, 1444, 1400, 1071, 1009, 789, 698 cm^{-1}. HRMS (ESI) m/z calculated for $C_{36}H_{25}N_3O_3$ $[M+H]^+$ = 548.1968, found = 548.1972.

(*E*)-1-ethyl-4-(2-phenyl-1-(m-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3l)



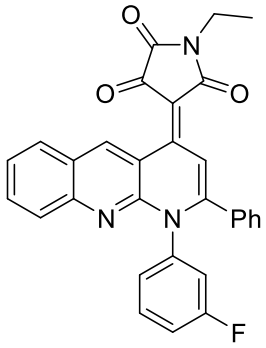
48% yield, red solid, m.p.: 239-240 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.51 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 3.4 Hz, 2H), 7.59 (dt, *J* = 8.1, 3.9 Hz, 1H), 7.29 (ddd, *J* = 13.6, 8.3, 4.4 Hz, 6H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.06 – 6.96 (m, 2H), 3.77 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.9, 171.6, 163.9, 157.2, 153.9, 153.5, 149.9, 147.5, 143.2, 138.9, 138.5, 135.0, 133.7, 130.0, 129.7, 129.7, 129.5, 129.2, 128.5, 128.4, 128.3, 126.8, 125.6, 116.6, 114.5, 100.8, 77.3, 77.0, 76.7, 32.6, 21.2, 13.9. IR(KBr): v_{max}: 2923, 2848 1753, 1694, 1652, 1566, 1538, 1497, 1468, 1437, 1400, 1075, 1003, 792, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_3O_3$ $[M+H]^+$ = 486.1812, found = 486.1814.

(*E*)-4-(1-(3-bromophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3m)



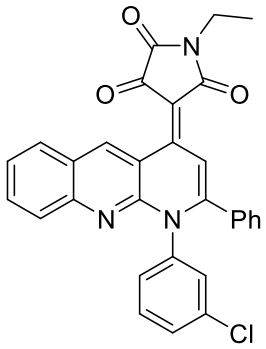
45% yield, red solid, m.p.:262-263 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.53 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.61 (ddd, *J* = 8.1, 5.8, 2.1 Hz, 1H), 7.52 (ddd, *J* = 8.0, 1.7, 1.0 Hz, 1H), 7.44 (t, *J* = 1.9 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.15 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H), 3.77 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 168.5, 163.6, 156.5, 153.5, 149.7, 147.3, 143.4, 139.7, 134.5, 134.0, 132.9, 132.0, 130.0, 129.9, 129.7, 129.2, 128.5, 128.5, 128.2, 126.9, 125.6, 122.0, 116.3, 114.0, 101.6, 32.7, 13.8. IR(KBr): ν_{max}: 2923, 2851, 1753, 1697,1685, 1653, 1577, 1562, 1538 1494, 1467, 1437, 1400, 1071, 1008, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}BrN_3O_3$ $[M+H]^+$ = 550.0760, found = 550.0777.

(*E*)-1-ethyl-4-(1-(3-fluorophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3n)



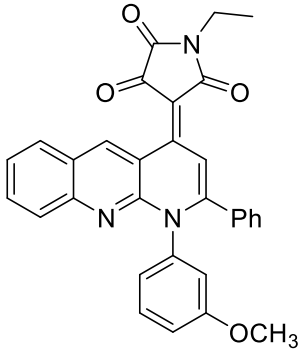
41% yield, red solid, m.p.: 256-257 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.53 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.61 (ddd, *J* = 8.1, 6.1, 1.7 Hz, 1H), 7.38 – 7.29 (m, 6H), 7.11 (td, *J* = 8.3, 1.8 Hz, 1H), 7.03 (ddd, *J* = 17.3, 9.7, 5.0 Hz, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 163.6, 161.2, 156.6, 153.6, 149.8, 147.3, 143.4, 139.8, 134.6, 134.0, 130.0, 129.9, 129.7, 129.2, 128.5, 128.2, 126.9, 125.6, 117.8, 117.5, 116.3, 116.2, 116.0, 114.1, 101.5, 32.7, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -111.20 (dd, *J* = 15.1, 8.3 Hz). IR(KBr): ν_{max}: 2922, 2851, 1753, 1698,1685, 1653, 1577, 1561, 1537 1494, 1467, 1436, 1401, 1069, 1007, 830, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}FN_3O_3$ $[M+H]^+$ = 490.1561, found = 490.1567.

(*E*)-4-(1-(3-chlorophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3o)



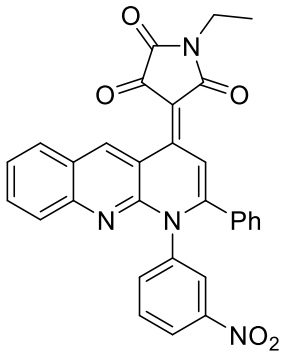
43% yield, red solid, m.p.: 271-272 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.53 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.79 (m, 2H), 7.61 (ddd, *J* = 8.0, 6.0, 1.7 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.32 – 7.28 (m, 5H), 7.13 – 7.08 (m, 1H), 3.77 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.6, 171.3, 163.6, 156.5, 153.6, 149.7, 147.3, 143.4, 139.6, 134.5, 134.4, 134.0, 130.1, 130.0, 129.73, 129.72, 129.2, 129.1, 128.5, 128.2, 128.0, 126.9, 125.6, 116.3, 114.1, 101.5, 32.7, 13.8. IR(KBr): ν_{max}: 2924, 2853, 1756, 1697,1653, 1625, 1567, 1538, 1494, 1468, 1444, 1399, 1072, 1009, 791, 697 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}ClN_3O_3$ $[M+H]^+$ = 506.1266, found = 506.1273.

(*E*)-1-ethyl-4-(1-(3-methoxyphenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3p)



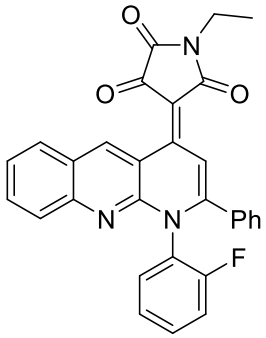
48% yield, red solid, m.p.: 232-233 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.50 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 7.9, 4.5 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.36 – 7.26 (m, 6H), 6.94 – 6.89 (m, 1H), 6.82 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.76 (t, *J* = 2.1 Hz, 1H), 3.76 (dd, *J* = 14.2, 7.1 Hz, 2H), 3.73 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 171.5, 163.9, 159.8, 157.0, 153.5, 149.9, 147.4, 143.2, 139.5, 134.9, 133.8, 129.8, 129.7, 129.4, 129.1, 128.35, 128.33, 126.8, 125.6, 122.1, 116.5, 115.6, 114.5, 114.4, 100.9, 55.5, 32.6, 13.9. IR(KBr): ν_{max}: 2923, 2848, 1754, 1698, 1653, 1625, 1568, 1537, 1493, 1467, 1436, 1400, 1071, 1009, 830, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_3O_4$ $[M+H]^+$ = 502.1761, found = 502.1770.

(*E*)-1-ethyl-4-(1-(3-nitrophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3q)



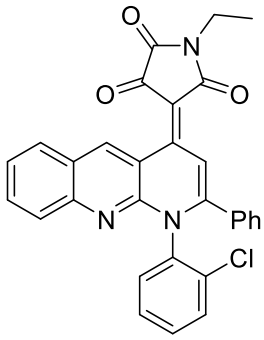
38% yield, red solid, m.p.: 284-285 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.59 (s, 1H), 8.28 – 8.23 (m, 1H), 8.18 – 8.13 (m, 2H), 7.88 – 7.82 (m, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.63 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.35 – 7.28 (m, 5H), 3.77 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.4, 171.0, 163.3, 155.9, 153.5, 149.6, 148.2, 147.2, 143.7, 139.7, 135.9, 134.2, 130.2, 129.8, 129.6, 129.3, 128.8, 128.0, 127.0, 125.6, 125.3, 123.7, 119.6, 116.1, 113.8, 102.3, 32.8, 13.8. IR(KBr): ν_{max}: 2922, 2851, 1754, 1694, 1653, 1575, 1562, 1532, 1494, 1467, 1436, 1400, 1071, 1009, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}N_4O_5$ $[M+H]^+$ = 517.1506, found = 517.1514.

(*E*)-1-ethyl-4-(1-(2-fluorophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3r)



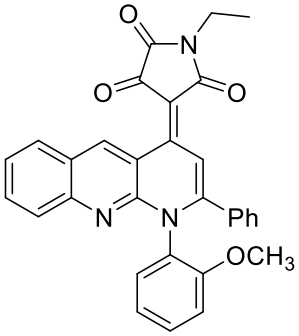
40% yield, red solid, m.p.: 239-240 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.54 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.82 (ddd, *J* = 13.4, 10.5, 4.5 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.44 – 7.38 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 3H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.20 – 7.13 (m, 3H), 3.79 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.1, 171.3, 163.6, 157.0, 153.9, 149.9, 146.9, 143.4, 134.4, 133.9, 131.2, 131.1, 130.7, 130.1, 129.8, 128.6, 128.4, 128.2, 126.7, 125.7, 124.4, 124.4, 116.2, 116.0, 113.8, 101.7, 32.7, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.51 (dd, *J* = 8.8, 6.1 Hz). IR(KBr): ν_{max}: 2924, 2851, 1755 1697, 1654, 1572, 1540, 1493, 1468, 1436, 1400, 1071, 1008, 830, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}FN_3O_3$ $[M+H]^+$ = 490.1561, found = 490.1556.

(*E*)-4-(1-(2-chlorophenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3s)



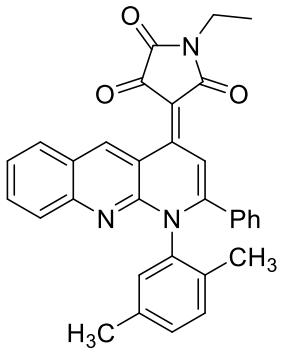
44% yield, red solid, m.p.: 257-258°C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.54 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.75 (m, 2H), 7.60 (ddd, *J* = 8.0, 5.0, 1.3 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.38 (ddd, *J* = 9.1, 5.1, 1.4 Hz, 3H), 7.35 – 7.32 (m, 1H), 7.29 (ddd, *J* = 8.5, 4.2, 2.6 Hz, 3H), 7.24 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.2, 171.4, 163.7, 156.9, 153.9, 150.0, 146.8, 143.4, 136.8, 134.2, 133.9, 133.2, 131.3, 130.4, 130.1, 130.0, 129.8, 128.8, 128.3, 128.2, 127.3, 126.8, 125.7, 116.3, 114.0, 101.6, 32.7, 13.8. IR(KBr): v_{max}: 2922, 2850, 1755 1697, 1653, 1562, 1539, 1494, 1468, 1438, 1399, 1074, 1006, 831, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{20}ClN_3O_3$ $[M+H]^+$ = 506.1266, found = 506.1273.

(*E*)-1-ethyl-4-(1-(2-methoxyphenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3t)



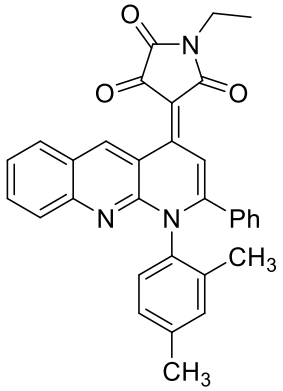
60% yield, red solid, m.p.: 232-233°C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.47 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 2.5 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.40 – 7.30 (m, 4H), 7.29 – 7.26 (m, 2H), 7.17 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.98 (td, *J* = 7.7, 1.1 Hz, 1H), 6.91 – 6.86 (m, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 3.59 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.8, 171.7, 164.1, 158.2, 154. 6, 153.9, 150.0, 147.1, 143.1, 134.8, 133.6, 130.7, 130.5, 129.9, 129.7, 128.7, 128.3, 128.0, 127.7, 126. 6, 125.7, 120.4, 116.7, 114.4, 111.8, 100.6, 55.5, 32.6, 13.9. IR(KBr): v_{max}: 2923, 2851, 1753 1697, 1652, 1561, 1537, 1494, 1467, 1438, 1400, 1070, 1006, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_3O_4$ $[M+H]^+$ = 502.1761, found = 502.1770.

(*E*)-4-(1-(2,5-dimethylphenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3u)



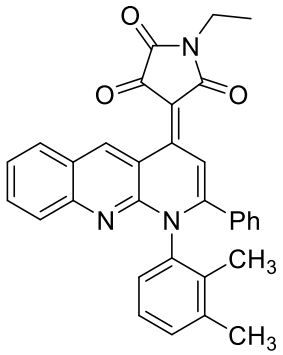
56% yield, red solid, m.p.: 231-232 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.52 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 3.6 Hz, 2H), 7.60 (ddd, *J* = 8.1, 4.7, 3.1 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.12 (q, *J* = 8.2 Hz, 2H), 6.83 (s, 1H), 3.79 (q, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.93 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.9, 171.7, 164.0, 157.3, 153.6, 150.1, 146.9, 143.3, 137.8, 136.3, 134.6, 133.8, 132.8, 130.5, 130.0, 130.0, 129.8, 129.7, 128.9, 128.4, 128.2, 126.8, 125.6, 116.6, 114.6, 100.7, 32.6, 20.7, 17.7, 13.9. IR(KBr): ν_{max}: 2923, 2850, 1755 1697, 1652, 1569, 1536, 1494, 1468, 1444, 1400, 1070, 1009, 831, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{25}N_3O_3$ $[M+H]^+$ = 500.1968, found = 500.1978.

(*E*)-4-(1-(2,4-dimethylphenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3v)



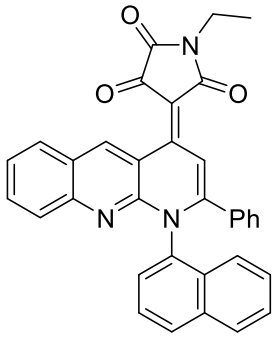
58% yield, red solid, m.p.: 221-222 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.51 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 3.5 Hz, 2H), 7.60 (ddd, *J* = 8.1, 4.5, 3.3 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.06 (s, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.79 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.93 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.9, 171.7, 164.0, 157.5, 153.6, 150.2, 147.0, 143.3, 139.2, 135.5, 135.4, 134.7, 133.7, 131.4, 129.9, 129.7, 129.2, 129.0, 128.4, 128.3, 127.2, 126.8, 125.6, 116.6, 114.7, 100.7, 32.6, 21.2, 18.1, 13.9. IR(KBr): ν_{max}: 2924, 2850, 1755 1697, 1652, 1568, 1537, 1493, 1468, 1444, 1401, 1069, 855, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{25}N_3O_3$ $[M+H]^+$ = 500.1968, found = 500.1976.

(*E*)-4-(1-(2,3-dimethylphenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3w)



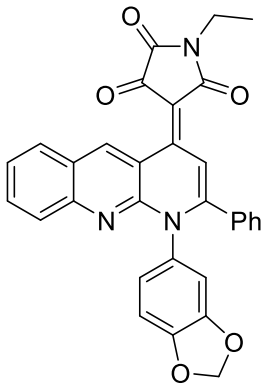
60% yield, red solid, m.p.: 254-255 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.51 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 5.6, 1.2 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.35 – 7.26 (m, 5H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 3.79 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.83 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.9, 171.7, 164.0, 157.5, 153.6, 150.1, 147.0, 143.3, 138.1, 138.0, 134.6, 134.4, 133.7, 130.6, 129.9, 129.7, 128.9, 128.4, 128.2, 127.2, 126.8, 125.7, 125.6, 116.6, 114. 6, 100.7, 32.6, 20.3, 15.0, 13.9. IR(KBr): ν_{max}: 2924, 2853, 1756 1697, 1653, 1565, 1537, 1494, 1468, 1444, 1400, 1076, 1006, 791, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{25}N_3O_3$ $[M+H]^+$ = 500.1968, found = 500.1971.

(*E*)-1-ethyl-4-(1-(naphthalen-1-yl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3x)



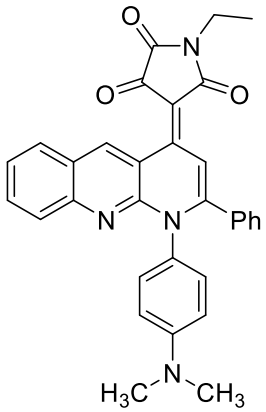
70% yield, red solid, m.p.: 283-284 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.59 (s, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.58 – 7.48 (m, 3H), 7.48 – 7.35 (m, 3H), 7.30 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.21 – 7.15 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 1.32 (dd, *J* = 9.5, 4.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.1, 171.6, 163.9, 158.1, 153.8, 150.0, 147.7, 143.3, 135.7, 134.6, 133.7, 130.9, 129.8, 129.7, 129.6, 128.5, 128.4, 128.3, 128.0, 127.7, 127.6, 126.8, 126.6, 125.7, 124.9, 122.5, 116.4, 114.4, 101.1, 32.7, 13.9. IR(KBr): ν_{max}: 2924, 2851, 1754 1696, 1653, 1563, 1540, 1497, 1471, 1438, 1400, 1067, 1008, 831, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{34}H_{23}N_3O_3$ $[M+H]^+$ = 522.1812, found = 522.1812.

(*E*)-4-(1-(benzo[*d*][1,3]dioxol-4-yl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3y)



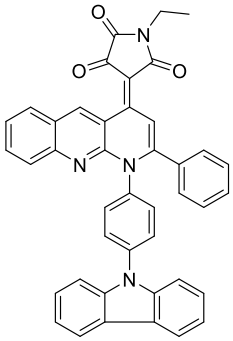
47% yield, red solid, m.p.:258-259 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.48 (s, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.60 (ddd, *J* = 8.1, 6.2, 1.6 Hz, 1H), 7.40 – 7.30 (m, 5H), 6.76 (dd, *J* = 14.8, 5.1 Hz, 2H), 6.58 (d, *J* = 2.1 Hz, 1H), 6.06 (d, *J* = 17.8 Hz, 2H), 3.76 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 171.5, 163.8, 157.3, 153.5, 149.9, 147.9, 147.8, 147. 7, 143.3, 135.0, 133.8, 132.2, 129.8, 129.7, 129.1, 128.4, 128.3, 126.8, 125.6, 123.2, 116.5, 114.4, 110.7, 107.9, 102.0, 101.0, 32.6, 13.9. IR(KBr): ν_{max}: 2923, 2851, 1754, 1703, 1652, 1569, 1537, 1482, 1468, 1444, 1400, 1069, 1036, 811, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{21}N_3O_5$ $[M+H]^+$ = 516.1554, found = 516.1564.

(*E*)-4-(1-(4-(dimethylamino)phenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3*z*)



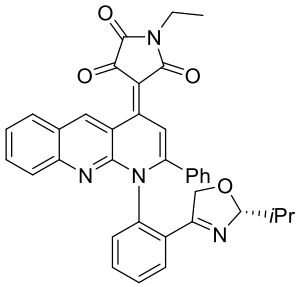
46% yield, red solid, m.p.: 186-187 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.48 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.76 (m, 2H), 7.56 (t, *J* = 7.1 Hz, 1H), 7.31 (td, *J* = 7.6, 3.4 Hz, 5H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 3.76 (q, *J* = 7.1 Hz, 2H), 2.98 (s, 6H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.6, 171. 7, 164.1, 157.9, 153.2, 149.9, 149.9, 147.9, 143.1, 135.4, 133.5, 129.9, 129.6, 129.5, 129.2, 128.5, 128.3, 127.0, 126.6, 125.5, 116.8, 114.8, 111.3, 100.2, 40.2, 32.5, 13.9. IR(KBr): ν_{max}: 2927, 2854, 1753, 1697, 1652, 1561, 1520, 1493, 1467, 1438, 1400, 1070, 1008, 830, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{26}N_4O_3$ $[M+H]^+$ = 515.2077, found = 515.2081.

(*E*)-4-(1-(4-(9*H*-carbazol-9-yl)phenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3aa)



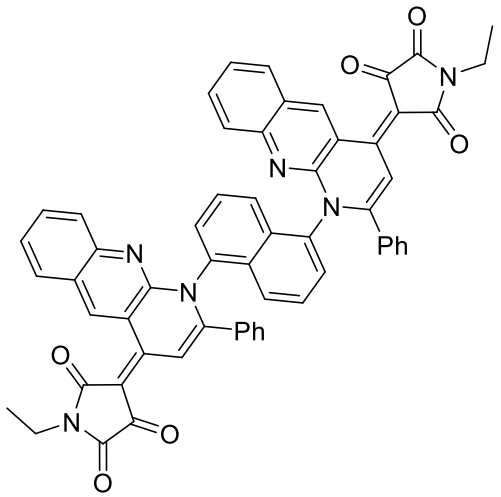
45% yield, red solid, m.p.: 277-278 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.60 (s, 1H), 8.16 (t, *J* = 6.8 Hz, 3H), 7.91 (dt, *J* = 6.5, 4.7 Hz, 2H), 7.61 (ddt, *J* = 9.5, 4.7, 2.0 Hz, 4H), 7.47 – 7.43 (m, 4H), 7.39 – 7.32 (m, 8H), 3.79 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.1, 171.4, 165.5, 156.8, 153. 6, 149.8, 147.4, 143.4, 140.4, 138.0, 137.3, 134.8, 134.0, 131.3, 130.0, 129.8, 129.4, 128.5, 128.2, 127.1, 126.9, 126.1, 125.6, 123.5, 120.5, 120.4, 116.4, 114.2, 109.4, 32.7, 13.9. IR(KBr): ν_{max}: 2925, 2854, 1755, 1697, 1653, 1574, 1539, 1512, 1493, 1467, 1446, 1400, 1070, 1009, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{42}H_{28}N_4O_3$ $[M+H]^+$ = 637.2234, found = 637.2229.

(*E*)-1-ethyl-4-(1-(2-(2-isopropyl-2,5-dihydrooxazol-4-yl)-4-methylphenyl)-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3ab)



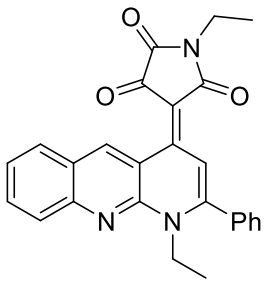
38% yield(d.r.=1:1), red solid, m.p.: 255-256 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.07 (d, *J* = 6.0 Hz, 1H), 8.52 (d, *J* = 3.6 Hz, 1H), 8.12 (dd, *J* = 8.2, 2.9 Hz, 1H), 8.02 – 7.95 (m, 1H), 7.75 (ddd, *J* = 21.5, 12.1, 7.6 Hz, 2H), 7.56 (dd, *J* = 9.6, 5.2 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 (dd, *J* = 11.8, 4.2 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.18 – 7.14 (m, 1H), 4.01 (dd, *J* = 8.8, 7.7 Hz, 1H), 3.78 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.63 (m, 1H), 3.55 – 3.47 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.92 – 0.86 (m, 1H), 0.59 (dd, *J* = 40.1, 6.7 Hz, 3H), 0.26 (dd, *J* = 13.6, 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.7, 164.1, 160.3, 159.8, 157.7, 157.3, 153.8, 153.7, 149.7, 149.6, 147.6, 147.6, 143.1, 137.9, 137.7, 134.9, 134.8, 133.5, 131.1, 130.6, 130.5, 130.2, 129.0, 129.85, 129.78, 129.7, 129.6, 129.1, 129.0, 128.3, 128.2, 128.1, 127.3, 127.1, 126.5, 126.4, 125.4, 114.6, 114.5, 100.5, 72.9, 72.8, 70.2, 69.6, 32.7, 32,6, 32.4, 18.8, 18.2, 18.0, 17.8, 13.9. IR(KBr): ν_{max}: 2925, 2853, 1756, 1698, 1652, 1566, 1538, 1493, 1468, 1444, 1400, 1059, 855, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{36}H_{30}N_4O_4$ $[M+H]^+$ =583.2339, found =583.2344.

(4*Z*,4'*E*)-4,4'-(naphthalene-1,5-diylbis(2-phenylbenzo[*b*][1,8]naphthyridine-1(1*H*)-yl-4(1*H*)-ylidene))bis(1-ethylpyrrolidine-2,3,5-trione) (3ac)



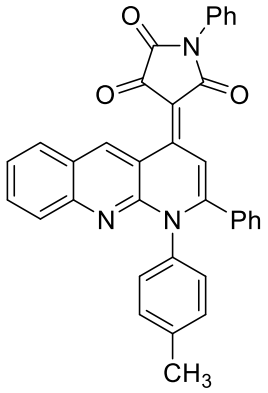
30% yield, red solid, m.p.: 219-220 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.13 (s, 2H), 8.62 (d, *J* = 20.4 Hz, 2H), 8.17 (d, *J* = 8.2 Hz, 2H), 7.91 – 7.79 (m, 3H), 7.63 (dd, *J* = 12.5, 6.2 Hz, 4H), 7.41 (d, *J* = 1.4 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.32 (d, *J* = 6.4 Hz, 3H), 7.20 – 7.15 (m, 4H), 7.15 – 7.09 (m, 4H), 3.81 (q, *J* = 7.0 Hz, 4H), 1.33 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.4, 168.7, 163.7, 157.6, 157.4, 153.7, 147.7, 143.5, 136.4, 134.5, 134.1, 131.6, 130.0, 128.5, 128.4, 128.2, 128.1, 127.0, 126.8, 125.7, 124.4, 116.3, 114.2, 109.0, 101.7, 32.8, 13.9. IR(KBr): ν_{max}: 2925, 2857, 1753, 1698, 1653, 1572, 1537, 1494, 1467, 1435, 1400, 1076, 1008, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{58}H_{38}N_6O_6$ $[M+H]^+$ =915.2925, found = 915.2918.

(*E*)-1-ethyl-4-(1-ethyl-2-phenylbenzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3ad)



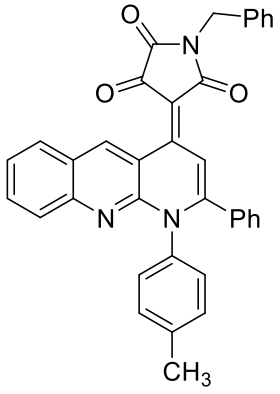
52% yield, red solid, m.p.: 109-110 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.18 (s, 1H), 8.15 – 8.10 (m, 2H), 7.91 (dd, *J* = 8.0, 3.7 Hz, 2H), 7.74 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.50 (tdd, *J* = 6.9, 4.2, 2.5 Hz, 4H), 4.97 (q, *J* = 7.0 Hz, 2H), 3.69 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.6, 167.4, 163.4, 147. 9, 147.0, 141.4, 141.2, 140.6, 138.5, 132.1, 129.1, 128.5, 128.3, 127.6, 126.1, 125.4, 118.5, 112.2, 107.5, 39.6, 33.0, 14.6, 13.9. IR(KBr): ν_{max}: 2931, 2851, 1752, 1700, 1652, 1640, 1604, 1561, 1494, 1439, 1402, 1085, 1008, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{21}N_3O_3$ $[M+H]^+$ = 423.1582, found = 423.1581.

(*E*)-1-phenyl-4-(2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3af)



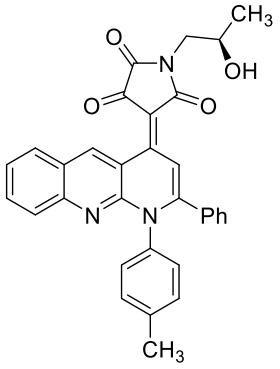
48% yield, red solid, m.p.: 142-143 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.56 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 3.5 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.51 (t, *J* = 7.3 Hz, 4H), 7.37 (d, *J* = 6.9 Hz, 1H), 7.33 – 7.27 (m, 5H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.7, 170.8, 163.1, 157.9, 154.1, 150.0, 147.4, 143.3, 139.0, 135.9, 134.8, 134.0, 131.9, 129.9, 129.8 129.5, 129.3, 129.2, 128.9, 128.4, 128.4, 127.7, 127.0, 126.4, 125.7, 116.9, 115.7, 99.9, 21.3. IR(KBr): ν_{max}: 2924, 2851, 1753, 1734, 1653, 1562, 1538, 1494, 1438, 1401, 1093, 1008, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{35}H_{23}N_3O_3$ $[M+H]^+$ = 534.1812, found = 534.1805.

(*E*)-1-benzyl-4-(2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3ag)



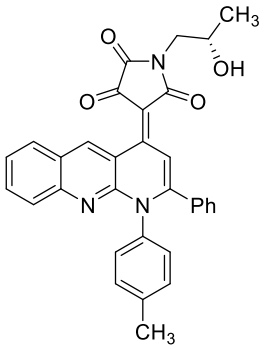
62% yield, red solid, m.p.: 144-145 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.47 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.80 (t, *J* = 6.4 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.29 (dd, *J* = 11.2, 7.6 Hz, 7H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 4.86 (s, 2H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.5, 171.1, 163.7, 157.4, 153.5, 149.8, 147.4, 143.1, 138.8, 136.7, 135.9, 134.9, 133.7, 129.7, 129.6, 129.4, 129.20, 129.16, 128.54, 128.47, 128.2, 127.7, 127.5, 126.7, 125.5, 116.5, 114.6, 100.6, 41.2, 21.2. IR(KBr): ν_{max}: 2925, 2854, 1754, 1734, 1697, 1653, 1567, 1537, 1493, 1467, 1444, 1073, 1022, 831, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{36}H_{25}N_3O_3$ $[M+H]^+$ = 548.1968, found = 548.1971.

(*R*,*E*)-1-(2-hydroxypropyl)-4-(2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione ((*R*)-3ah)



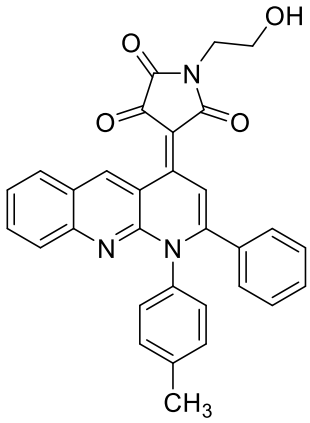
46% yield, red solid, m.p.: 139-140°C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 8.46 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 3.4 Hz, 2H), 7.60 (dt, *J* = 8.1, 3.9 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.13 (td, *J* = 6.9, 3.0 Hz, 1H), 3.80 (ddd, *J* = 21.5, 14.1, 5.2 Hz, 2H), 3.10 (s, 1H), 2.39 (s, 3H), 1.27 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100MHz, $CDCl_3$): δ 176.2, 172. 7, 164.6, 157.7, 153.7, 149.9, 147.4, 143.2, 138.9, 135.9, 134.8, 133.9, 129.8, 129.7, 129. 5, 129.3, 129.2, 128.4, 126.9, 125.6, 116.6, 115.1, 100.1, 67.1, 45.5, 21.3, 21.0. IR(KBr): ν_{max}: 3448, 2924, 2853, 1753, 1734, 1697, 1652, 1562, 1538, 1510, 1494, 1468, 1436, 1070, 1024, 831, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{25}N_3O_4$ $[M+H]^+$ = 516.1917, found = 516.1911.

(*S*,*E*)-1-(2-hydroxypropyl)-4-(2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione ((*S*)-3ah)



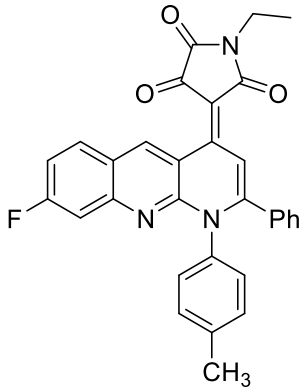
43% yield, red solid, m.p.: 139-140 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 8.46 (s, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 3.5 Hz, 2H), 7.60 (dd, *J* = 8.2, 4.0 Hz, 1H), 7.32 (dt, *J* = 10.8, 4.3 Hz, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 4.19 – 4.08 (m, 1H), 3.80 (ddd, *J* = 21.5, 14.1, 5.0 Hz, 2H), 3.10 (s, 1H), 2.39 (s, 3H), 1.27 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.2, 172.7, 164.6, 157.7, 153.7, 149.9, 147.4, 143.2, 138.9, 135.9, 134.8, 133. 9, 129.9, 129.7, 129.5, 129.30, 129.2, 128.4, 126.9, 125.6, 116.6, 115.1, 100.1, 67.1, 45.5, 21.3, 21.0. IR(KBr): ν_{max}: 3445, 2923, 2854, 1754, 1734, 1698, 1653, 1571, 1540, 1512, 1493, 1467, 1438, 1069, 1013, 831, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{25}N_3O_4$$[M+H]^+$ = 516.1917, found = 516.1913.

(*E*)-1-(2-hydroxyethyl)-4-(2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3ai)



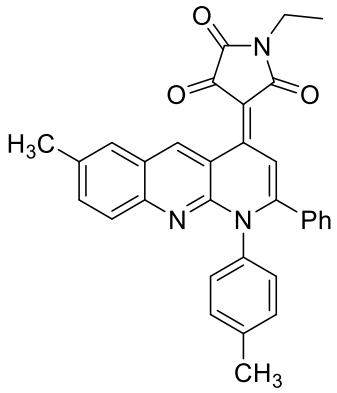
48% yield, red solid, m.p.: 205-206 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.47 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 3.4 Hz, 2H), 7.60 (dt, *J* = 8.1, 3.9 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 3.92 (dt, *J* = 9.3, 4.2 Hz, 4H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.2, 172.5, 164.6, 157.7, 153.7, 150.0, 147.4, 143.2, 139.0, 135.9, 134.8, 133.9, 129.9, 129.7, 129.5, 129.3, 129.2, 128.4, 126.9, 125.7, 116.6, 115.0, 100.2, 61.7, 41.0, 21.3. IR(KBr): ν_{max}: 3449, 2924, 2854, 1753, 1734, 1652, 1571, 1539, 1497, 1467, 1432, 1400, 1066, 1008, 831, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_3O_4$ $[M+H]^+$ = 502.1761, found = 502.1757.

(*E*)-1-ethyl-4-(8-fluoro-2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3aj)



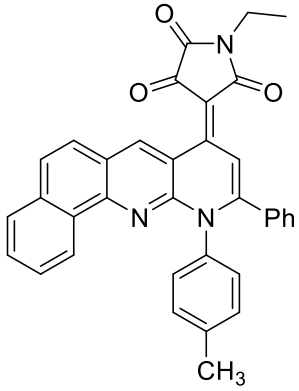
51% yield, red solid, m.p.: 243-244 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.51 (s, 1H), 8.14 (dd, *J* = 9.1, 6.1 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.33 – 7.27 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 171.5, 163.9, 157.3, 153.4, 151.0, 148.3, 143.3, 138.9, 135. 9, 134.9, 132.3, 129. 8, 129.5, 129.3, 129.2, 128.4, 122.8, 118.6, 118.3, 114.6, 111.6, 111.4, 100. 9, 32.7, 21.2, 13.9. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -98.61 – -103.02 (m). IR(KBr): ν_{max}: 2922, 2851, 1754, 1735, 1698, 1653, 1576, 1543, 1494, 1467, 1439, 1402, 1073, 1010, 830, 702 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{22}FN_3O_3$ $[M+H]^+$ = 504.1718, found = 504.1728.

(*E*)-1-ethyl-4-(7-methyl-2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3ak)



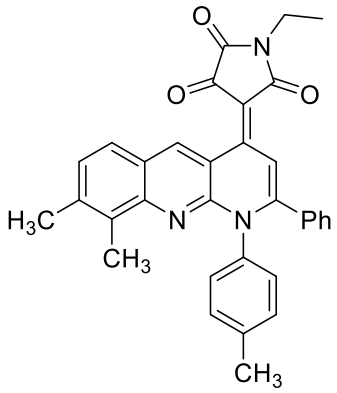
60% yield, red solid, m.p.: 280-281 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.46 (s, 1H), 7.86 (s, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.30 (ddt, *J* = 11.3, 8.1, 3.9 Hz, 5H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 3.74 (q, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 2.37 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.7, 171.5, 163.9, 157.0, 153.4, 148.6, 147.0, 141.9, 138.7, 136.8, 136.5, 136.0, 135.0, 129.6, 129.3, 129.23, 129.19, 128.2, 127.9, 127.8, 125.6, 116.5, 114.6, 100.3, 32.5, 21.6, 21.2, 13.8. IR(KBr): ν_{max}: 2923, 2854, 1754, 1719, 1698, 1653, 1561, 1537, 1493, 1483, 1448, 1401, 1072, 1022, 824, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{25}N_3O_3$ $[M+H]^+$ = 500.1968, found = 500.1962.

(*E*)-1-ethyl-4-(10-phenyl-11-(*p*-tolyl)naphtho[1,2-*b*][1,8]naphthyridin-8(11*H*)-ylidene)pyrrolidine-2,3,5-trione (3al)



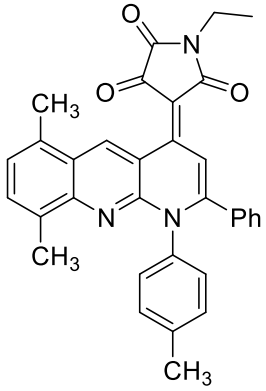
64% yield, red solid, m.p.: 164-165 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.57 (s, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 8.4, 3.8 Hz, 2H), 7.77 – 7.71 (m, 2H), 7.57 (dd, *J* = 9.5, 2.3 Hz, 1H), 7.36 – 7.29 (m, 5H), 7.24 (s, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.7, 171.8, 164.1, 156.0, 152.8, 149.6, 147.0, 141.2, 138.9, 136.2, 135.2, 134.8, 130.5, 130.0, 129.7, 129.45, 129.41, 129.2, 128.6, 128.4, 128.1, 127.4, 125.7, 125.5, 124.2, 117.0, 115.6,100.0, 32.6, 21.3, 13.9. IR(KBr): ν_{max}: 2924, 2853, 1754, 1694, 1651, 1570, 1544, 1493, 1460, 1443, 1419, 1082, 1022, 830, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{35}H_{25}N_3O_3$ $[M+H]^+$ = 536.1968, found = 536.1971.

(*E*)-4-(8,9-dimethyl-2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3am)



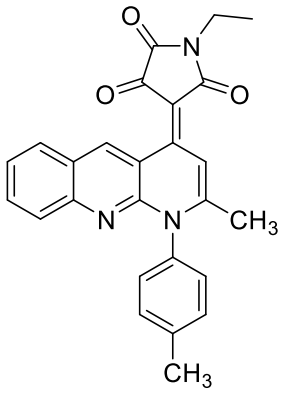
62% yield, red solid, m.p.: 269-270 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.48 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.32 (ddd, *J* = 9.2, 6.6, 2.1 Hz, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.78 (q, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 2.39 (s, 3H), 2.29 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.8, 171.8, 164.2, 156.8, 153.5, 149.0, 146.8, 142.9, 142.3, 138.6, 136.4, 135.0, 133.2, 130.4, 129.7, 129.4, 129.3, 129.2, 128.3, 126.5, 124.3, 115.8, 114.6, 100.3, 32.6, 21.2, 21.1, 13.9, 12.6. IR(KBr): ν_{max}: 2922, 2851, 1753, 1697, 1652, 1561, 1542, 1493, 1466, 1440, 1402, 1082, 1007, 831, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{33}H_{27}N_3O_3$ $[M+H]^+$ = 514.2125, found = 514.2118.

(*E*)-4-(8,9-dimethyl-2-phenyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)-1-ethylpyrrolidine-2,3,5-trione (3an)



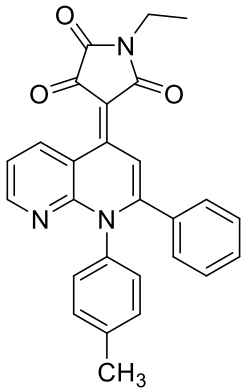
63% yield, red solid, m.p.: 230-231 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.37 (s, 1H), 8.57 (s, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.78 (q, *J* = 7.2 Hz, 2H), 2.86 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.7, 171.9, 164.0, 156.8, 153.6, 149.6, 146.3, 140.2, 138.6, 136.2, 135.1, 135.0, 134.0, 133.2, 129.7, 129.4, 129.23, 129.15, 128.3, 126.5, 125.6, 116.0, 114.6, 100.3, 32.6, 21.2, 18.9, 17.0, 13.9. IR(KBr): vmax: 2924, 2857, 1753, 1698, 1652, 1560, 1545, 1493, 1477, 1440, 1402, 1074, 1007, 830, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{33}H_{27}N_3O_3$ $[M+H]^+$ = 514.2125, found = 514.2121.

(*E*)-1-ethyl-4-(2-methyl-1-(*p*-tolyl)benzo[*b*][1,8]naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (3ao)



45% yield, red solid, m.p.: 121-122 °C, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.37 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.59 – 7.54 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 3H), 2.44 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.8, 171.8, 164.2, 156.6, 153.6, 149.7, 147.9, 143.1, 139.8, 135.9, 133.7, 130.6, 129.7, 128.3, 127.6, 126.6, 125.4, 116.4, 113.4, 99.6, 32.6, 23.7, 21.4, 14.0. IR(KBr): vmax: 2924, 2853, 1753, 1697, 1653, 1576, 1561, 1543, 1494, 1438, 1401, 1078, 1008, 830, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{21}N_3O_3$ $[M+H]^+$ = 424.1655, found = 424.1650.

(*E*)-1-ethyl-4-(2-phenyl-1-(*p*-tolyl)-1,8-naphthyridin-4(1*H*)-ylidene)pyrrolidine-2,3,5-trione (7a)



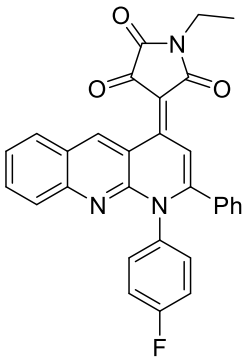
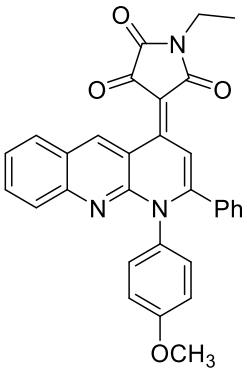
23% yield, red solid, m.p.: 132-133 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.41 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 2H), 8.08 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 3H), 7.19 (dd, *J* = 8.1, 4.7 Hz, 3H), 3.57 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.7, 167.3, 162.1, 151.2, 139.4, 138.2, 133.6, 132.2, 130.1, 128.4, 128.2, 128.2, 127.7, 125.0, 119.8, 119.2, 117.8, 110.6, 109.6, 96.3, 32.92 21.4, 13.7. IR(KBr): vmax: 2922, 2853, 1766, 1713, 1642, 1615, 1561, 1525, 1510, 1439, 1400, 1067, 1003, 830, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{27}H_{21}N_3O_3$ $[M+H]^+$ = 436.1655, found = 436.1661.

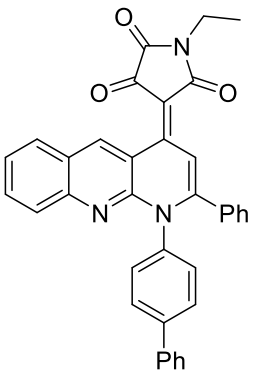
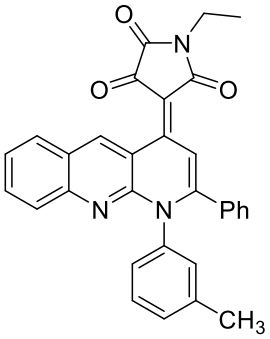
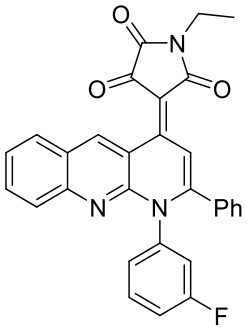
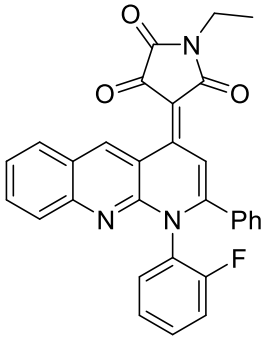
9. Properties of Fluorescent Dyes of 3

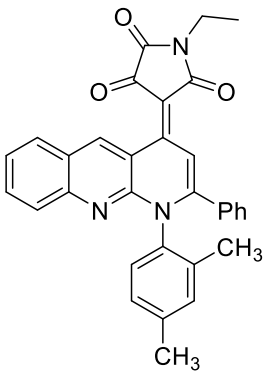
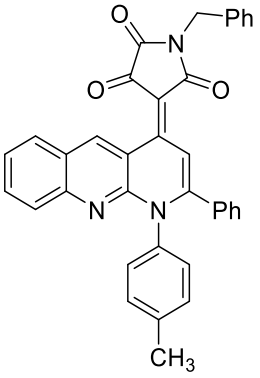
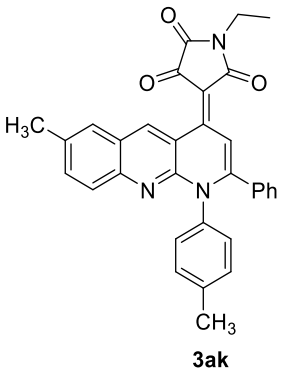
9.1. Fluorescence spectra analysis of 3d, 3g, 3k, 3l, 3n, 3r, 3v, 3ag, 3ak

Experiments were set up using 96 well plates with black flat bottoms. Solutions of 5 mM in DMSO, EtOH, toluene, 1,4-dioxane, DCM, and PBS were separately placed in well plates and excited at wavelengths ranging from 320 nm to 520 nm. The best results were selected for presentation below.

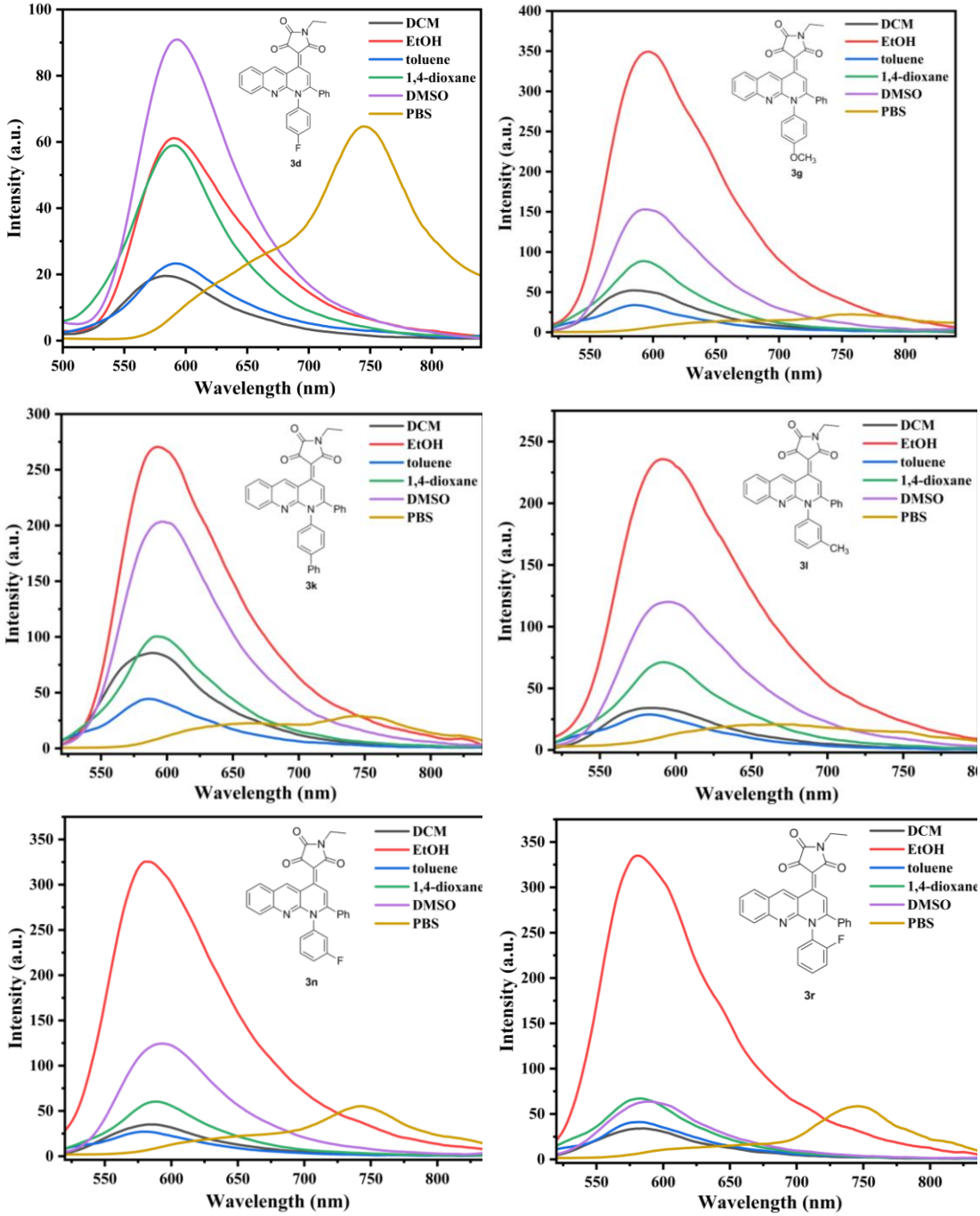
9.2. Table S12. Maximum intensity (I) and their emission wavelength (λem) of dihydrobenzo[*b*][1,8]naphthyridine-ylidene-pyrrolidinetriones (3d, 3g, 3k, 3l, 3n, 3r, 3v, 3ag, 3ak) in organic solvents were obtained at the corresponding excitation wavelength (λex = 420 nm).

Solvent / λ_{em} / I / Compound	DCM	EtOH	toluene	1,4-dioxane	DMSO	PBS
 **3d**	584 nm 20	590 nm 61	592 nm 24	590 nm 61	590 nm 91	742 nm 69
 **3g**	582 nm 52	594 nm 350	584 nm 34	590 nm 91	594 nm 153	766 nm 24

 **3k**	584 nm 86	594 nm 271	590 nm 45	590 nm 101	598 nm 204	740 nm 31
 **3l**	584 nm 34	592 nm 237	586 nm 29	588 nm 71	594 nm 121	668 nm 22
 **3n**	590 nm 36	586 nm 327	576 nm 27	584 nm 61	590 nm 125	744 nm 59
 **3r**	578 nm 34	582 nm 336	588 nm 41	582 nm 67	584 nm 64	744 nm 59

 **3v**	586 nm 37	588 nm 184	586 nm 31	590 nm 57	594 nm 110	676 nm 24
 **3ag**	600 nm 6	596 nm 17	594 nm 5	594 nm 9	604 nm 23	744 nm 128
 **3ak**	588 nm 63	602 nm 317	596 nm 35	596 nm 73	592 nm 153	674 nm 28

9.3. Photophysical properties in six selected organic solvents.



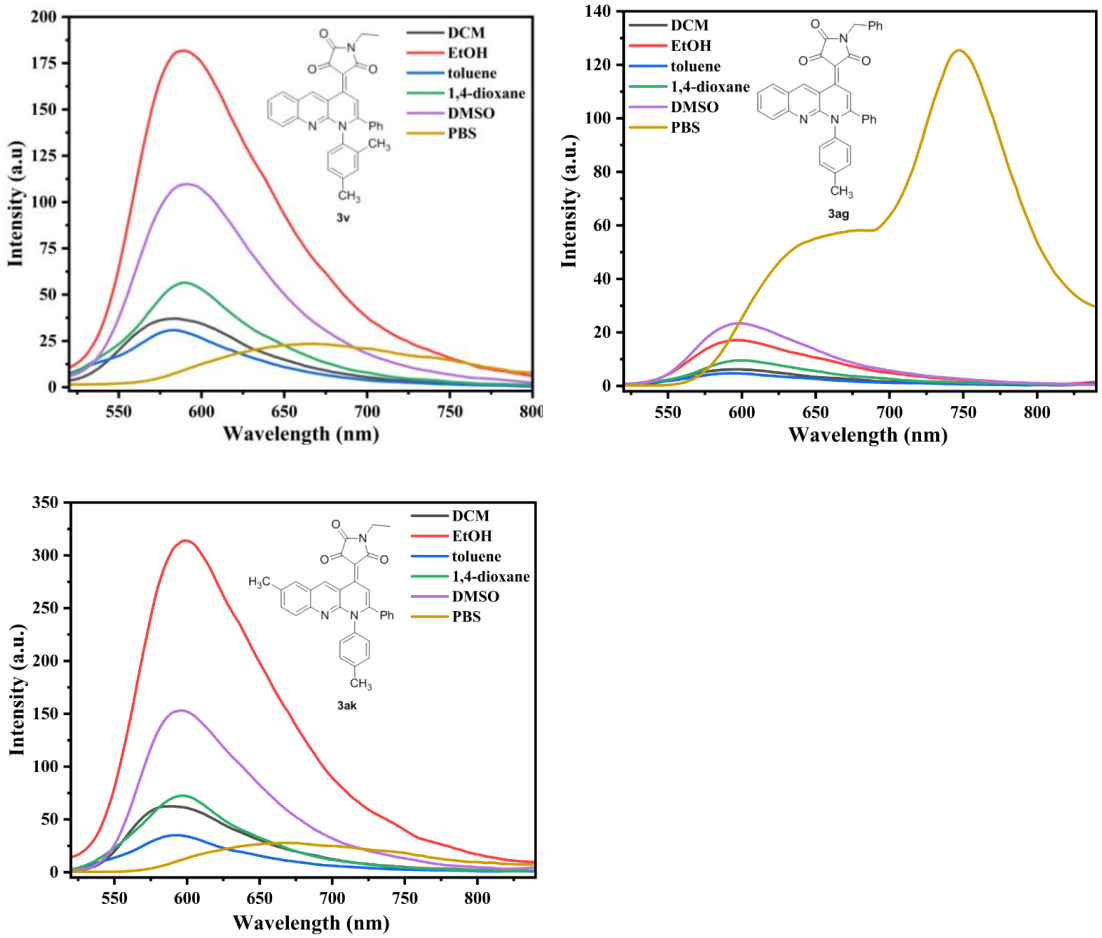
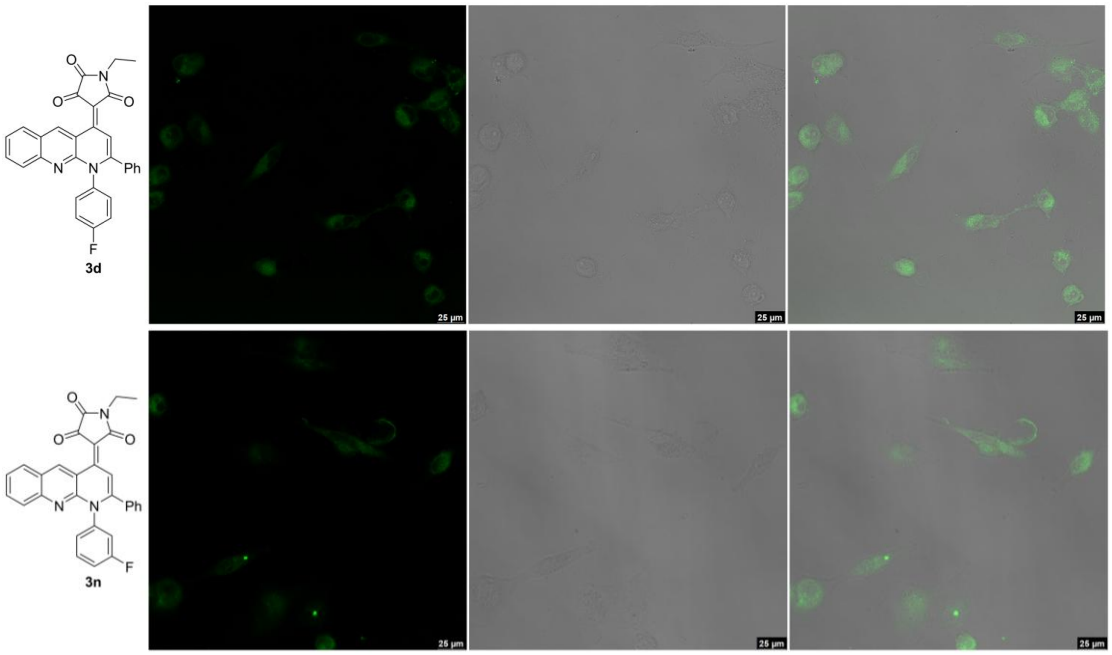
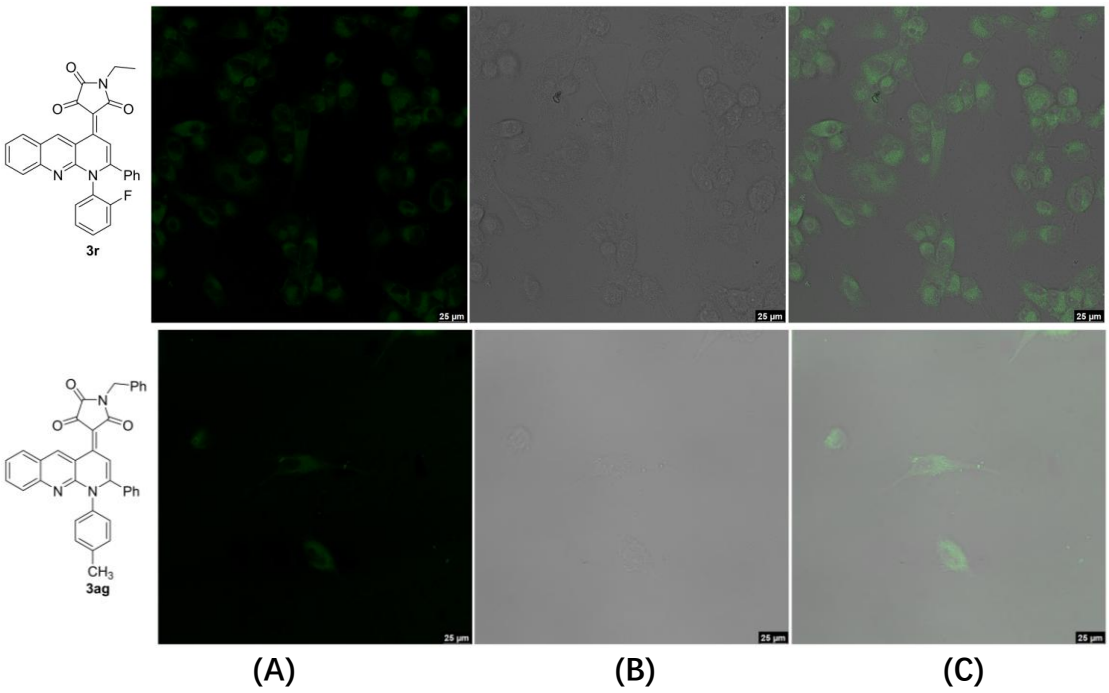


Figure S5. Photophysical properties in six selected organic solvents

9.4. Live human glioma U251 cell imaging of 3d, 3n, 3r, 3ag.



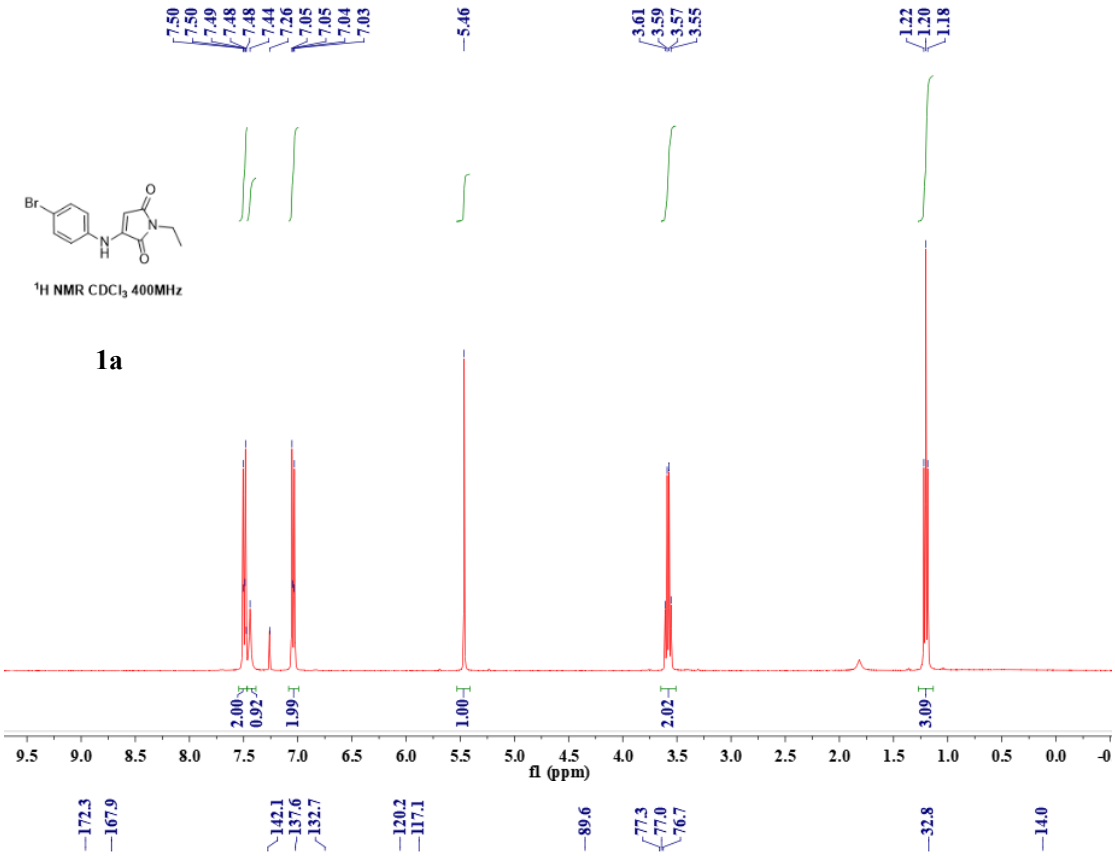


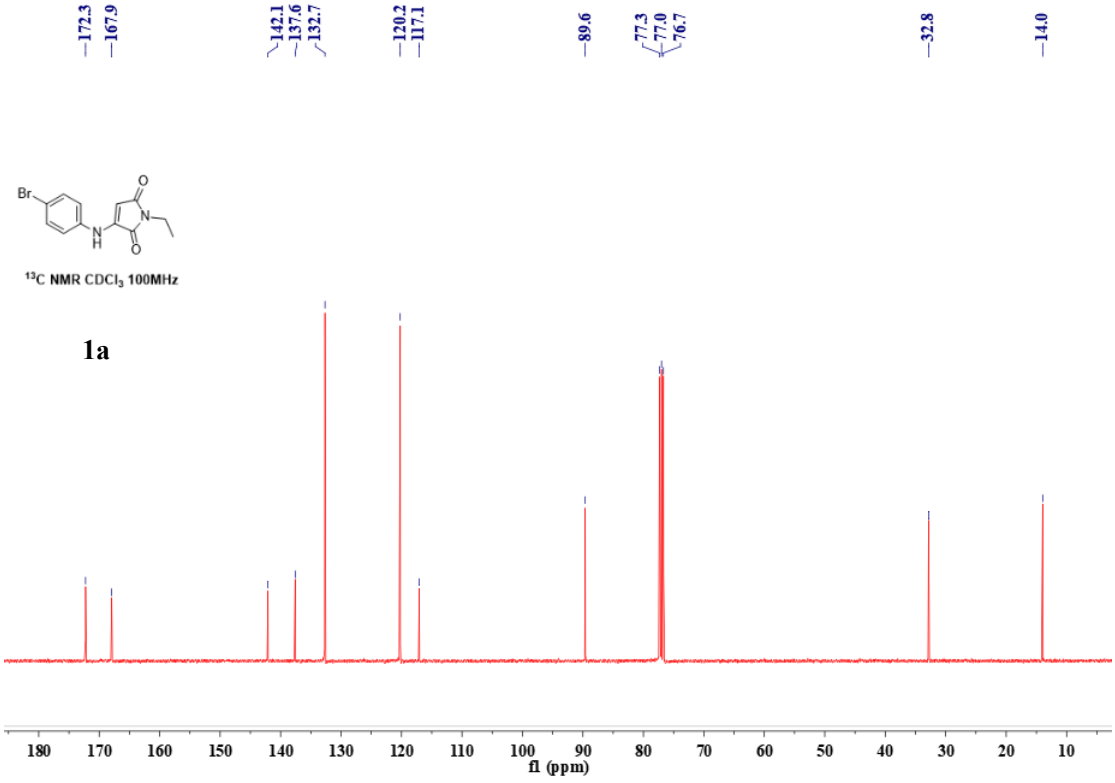
Live human glioma U251 cell imaging after 4 h incubation.

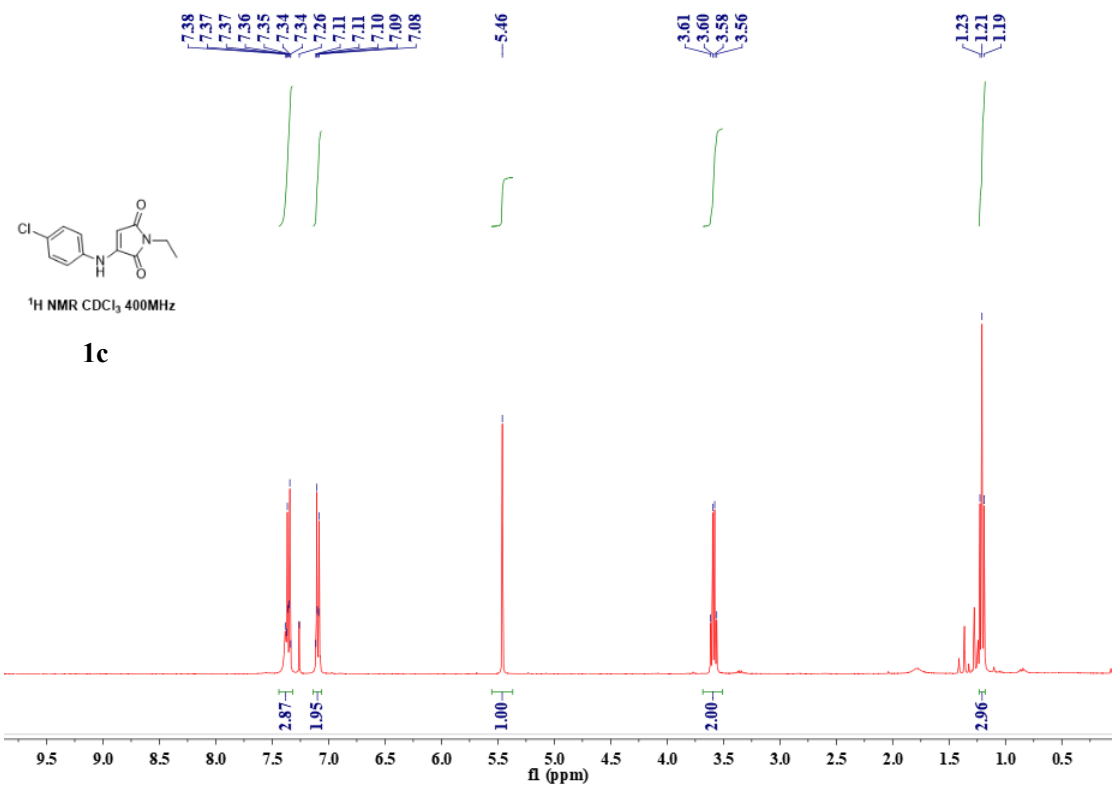
(A) FITC channel: λ_{ex}= 488 nm; (B) Bright field; (C) Merged image.

Figure S6. Live human glioma U251 cell imaging of 3d, 3n, 3r, 3ag

10. NMR Spectra of Aminomaleimides

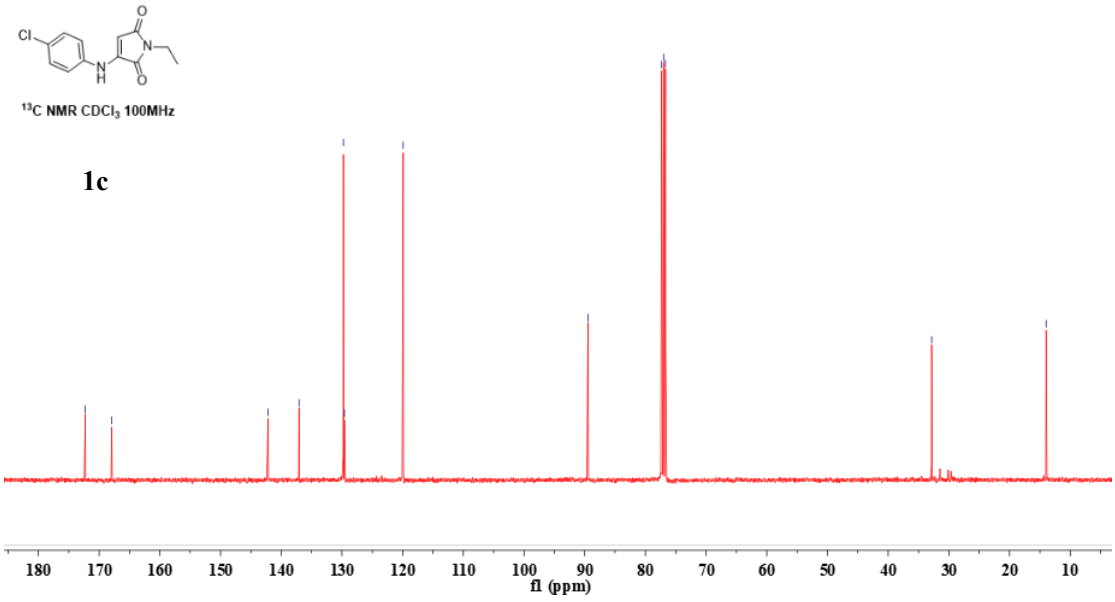






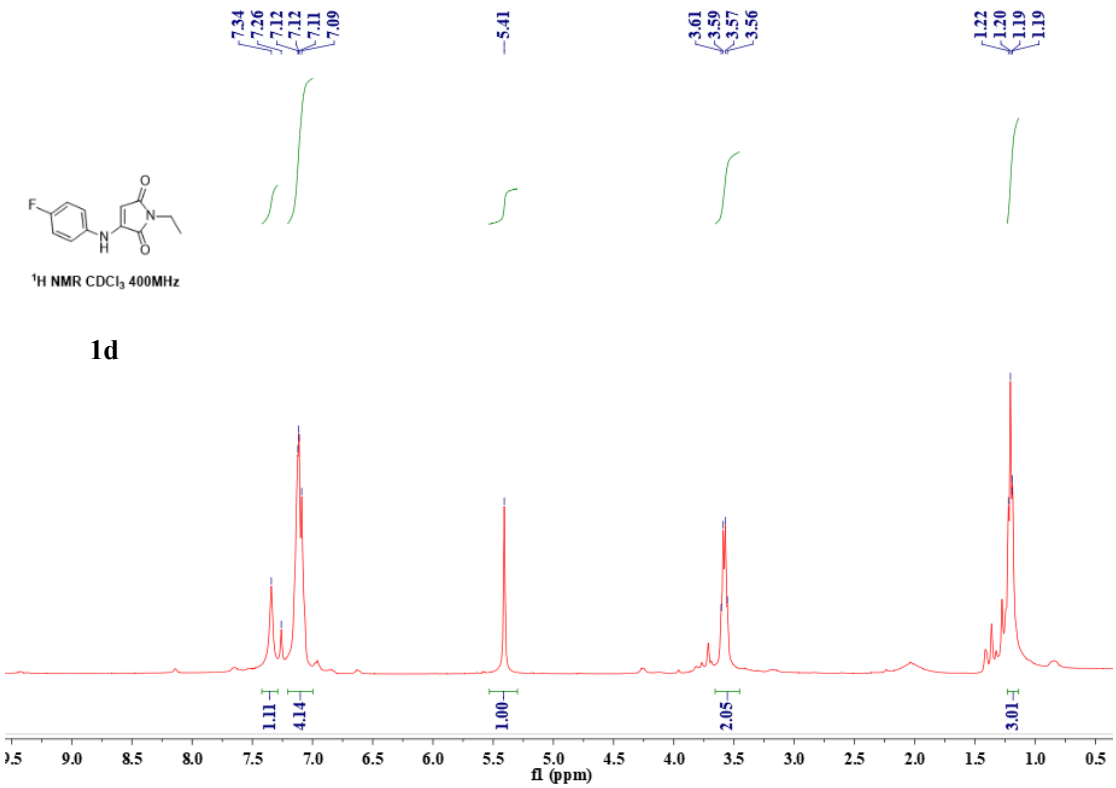
^{1}H NMR $CDCl_3$ 400MHz

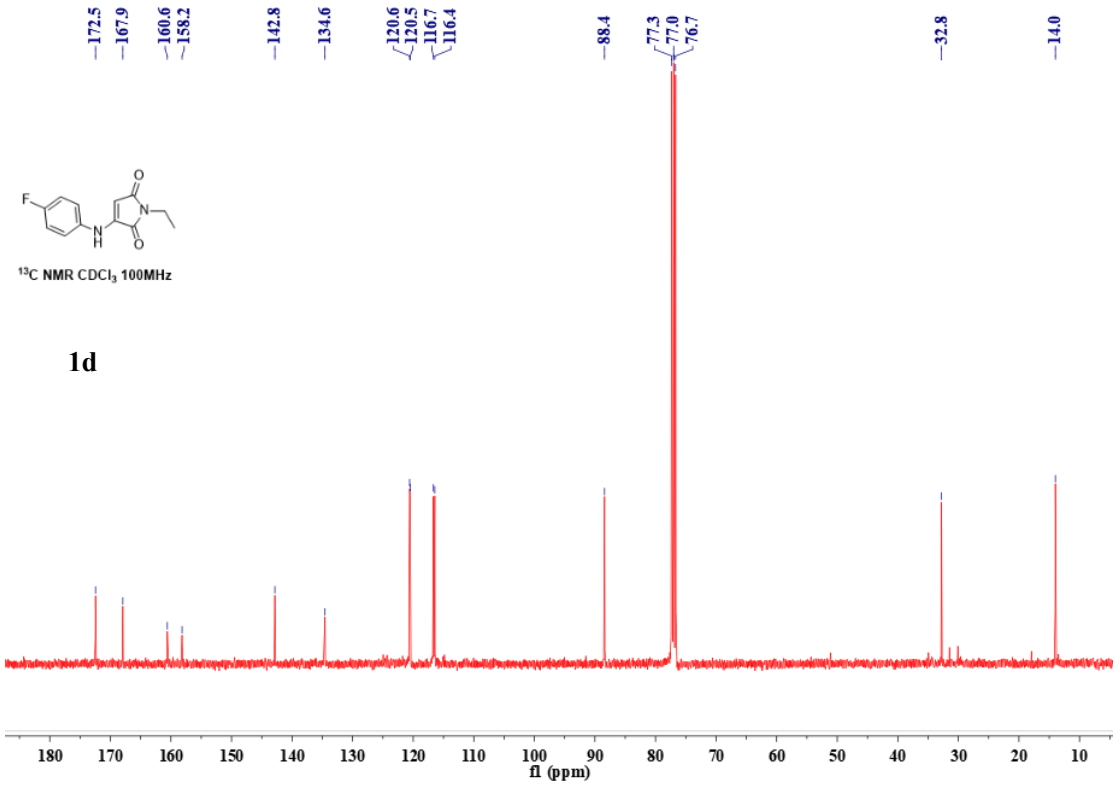
1c

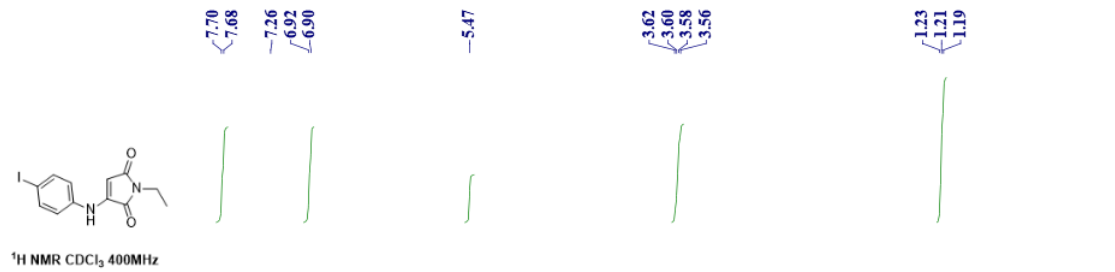


^{13}C NMR $CDCl_3$ 100MHz

1c

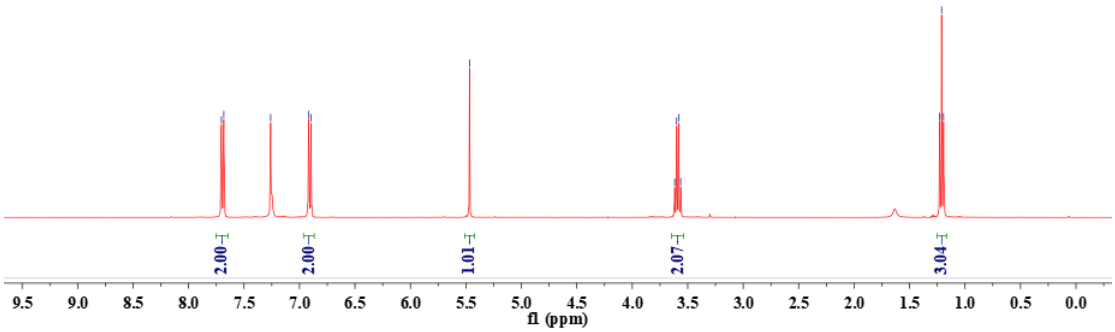

7.34
7.26
7.12
7.12
7.11
7.09
5.41
3.61
3.59
3.57
3.56
1.22
1.20
1.19
1.19
F
O
N
H
O
O
1H NMR CDCl3 400MHz
1d
1.11
4.14
1.00
2.05
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

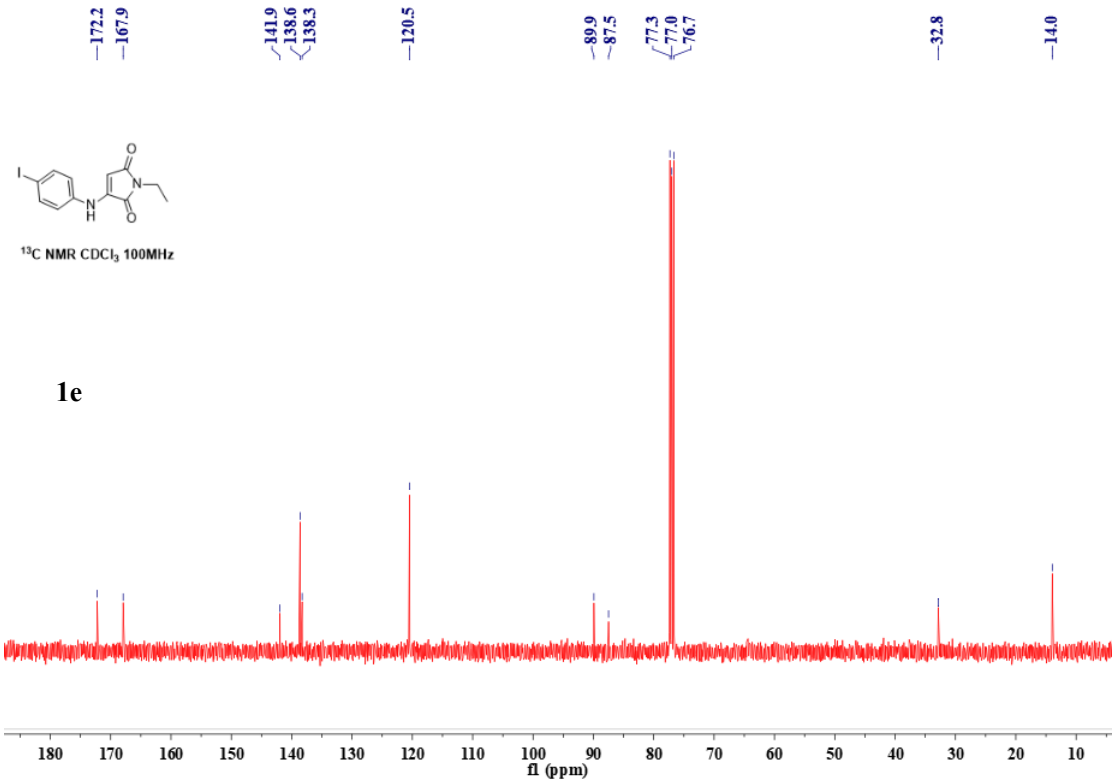

172.5
167.9
160.6
158.2
142.8
134.6
120.6
120.5
116.7
116.4
88.4
77.3
77.0
76.7
32.8
14.0
F
O
N
H
O
13C NMR CDCl3 100MHz
1d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



^{1}H NMR $CDCl_3$ 400MHz

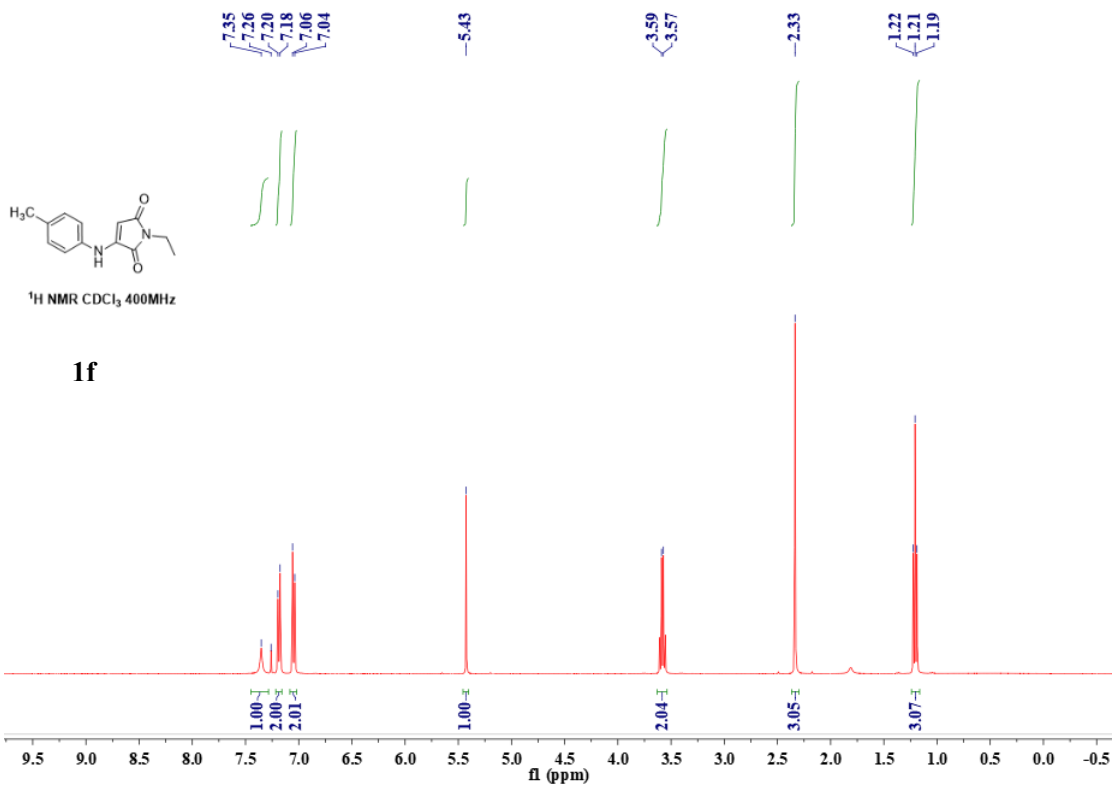
1e





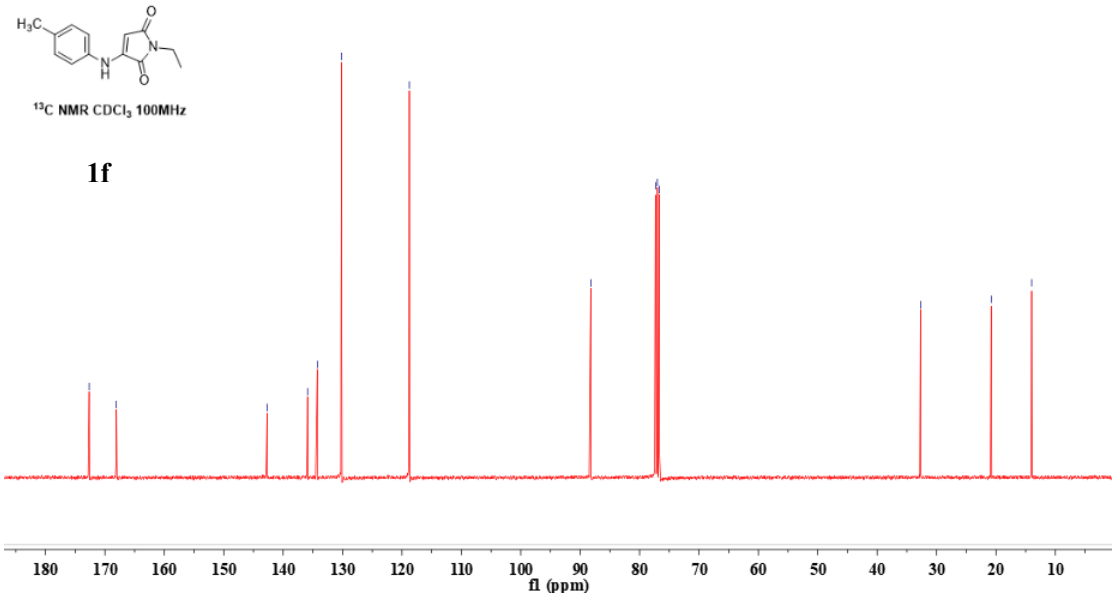
^{13}C NMR $CDCl_3$ 100MHz

1e



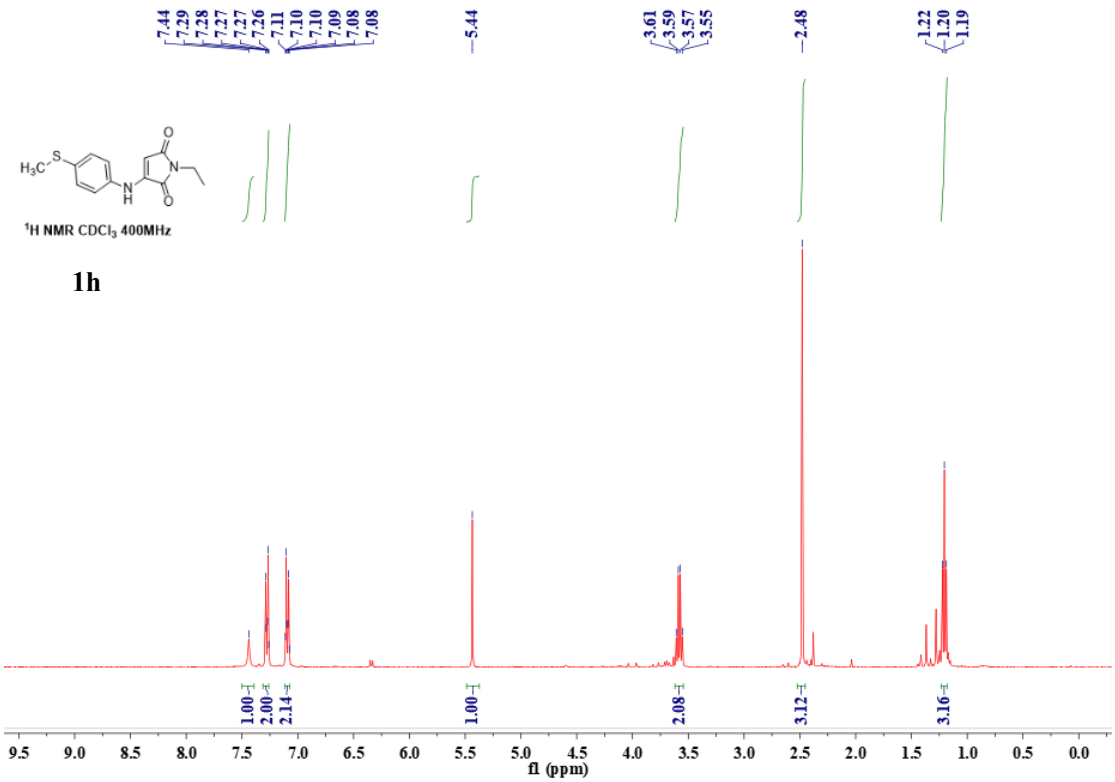
^{1}H NMR $CDCl_3$ 400MHz

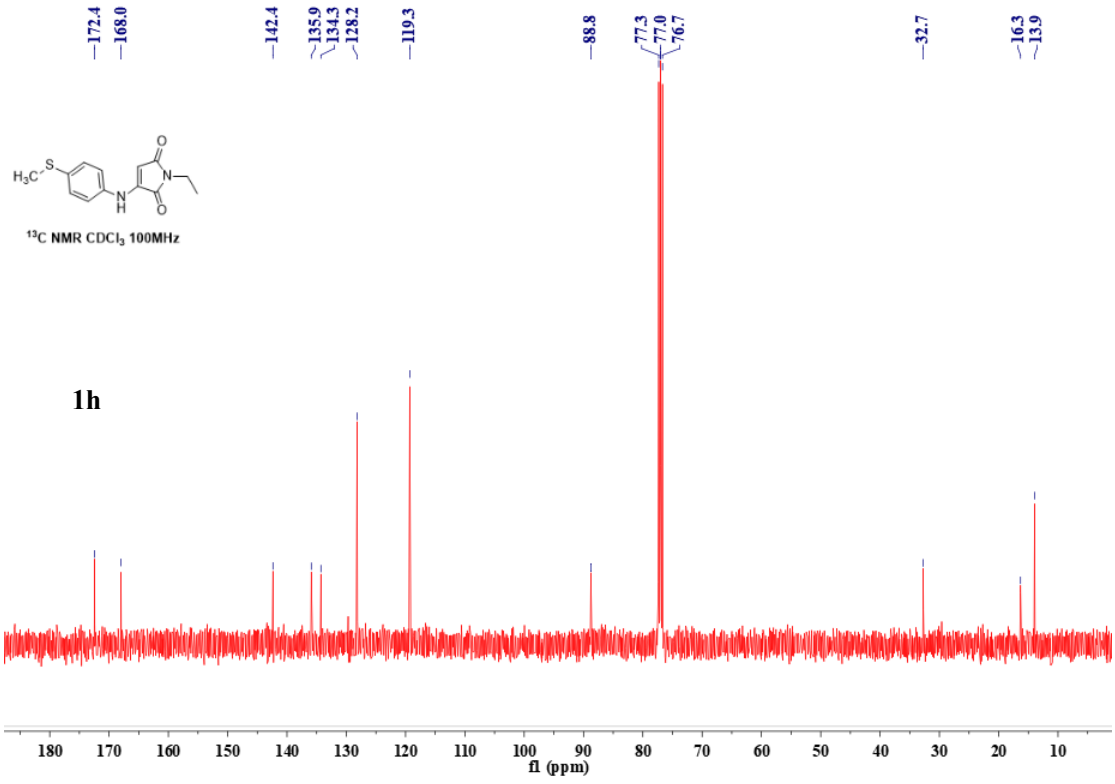
1f

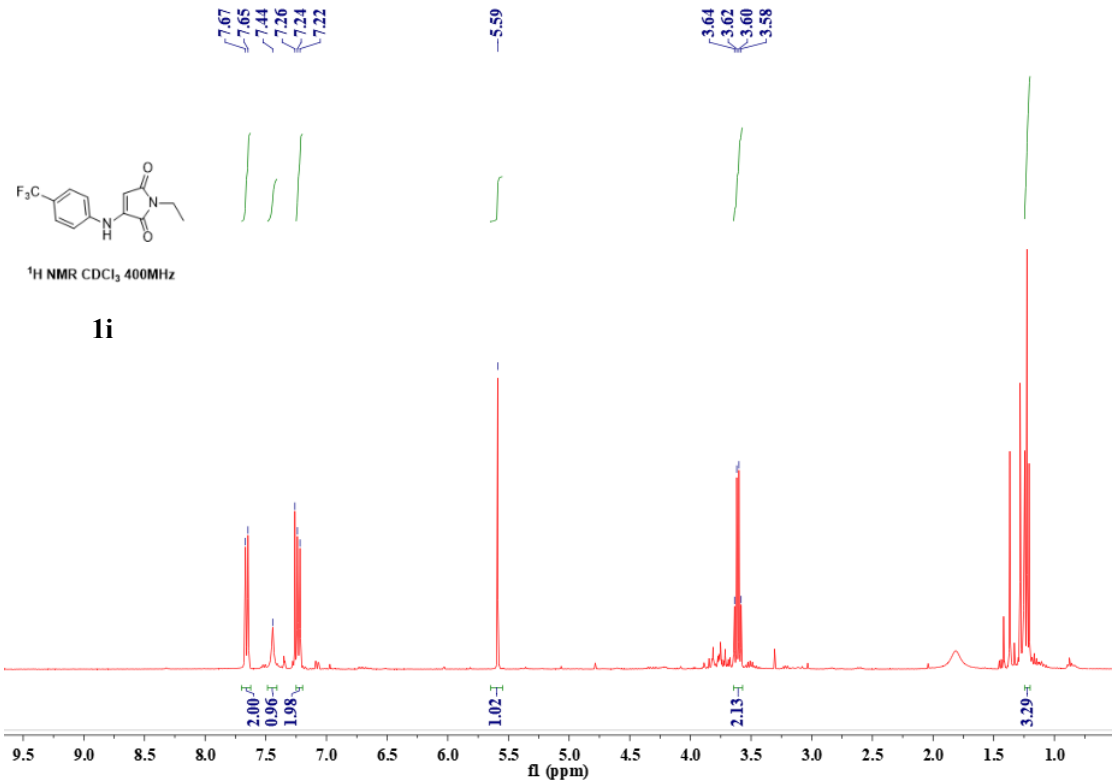


^{13}C NMR $CDCl_3$ 100MHz

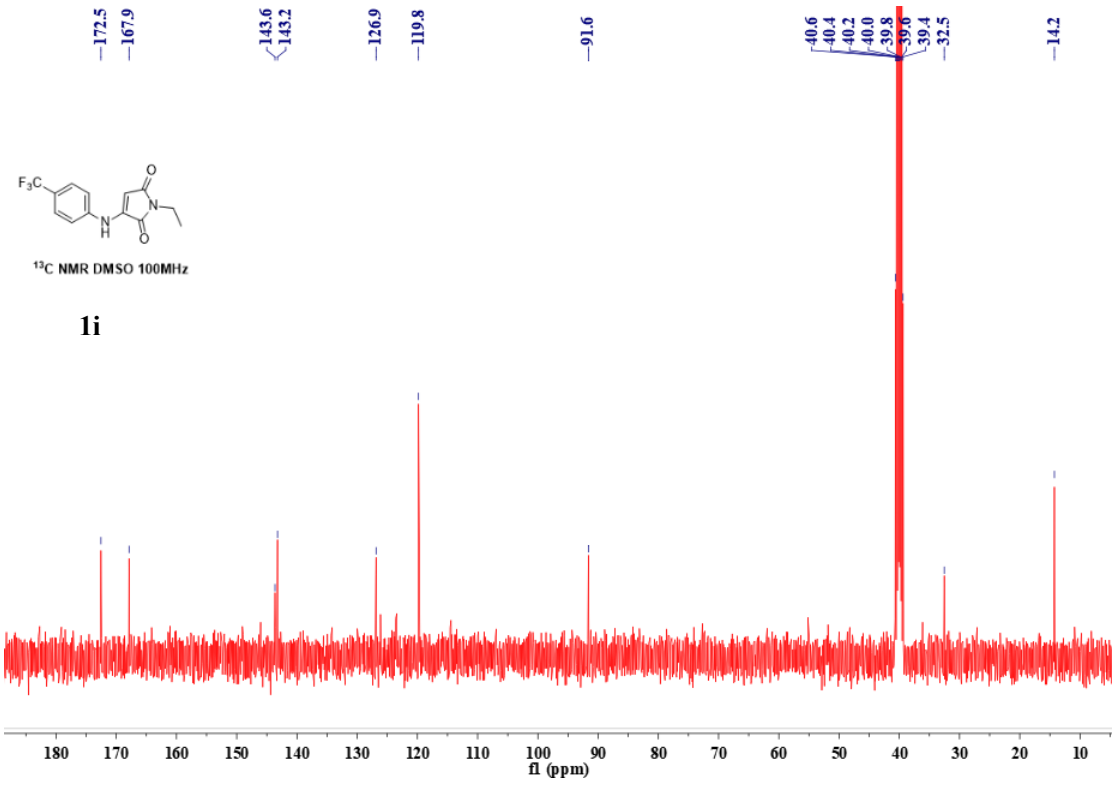
1f


7.44
7.29
7.28
7.27
7.27
7.26
7.11
7.10
7.10
7.09
7.08
7.08
5.44
3.61
3.59
3.57
3.55
2.48
1.22
1.20
1.19
^{1}H NMR CDCl$_3$ 400MHz
1h
1.00
2.00
2.14
1.00
2.08
3.12
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

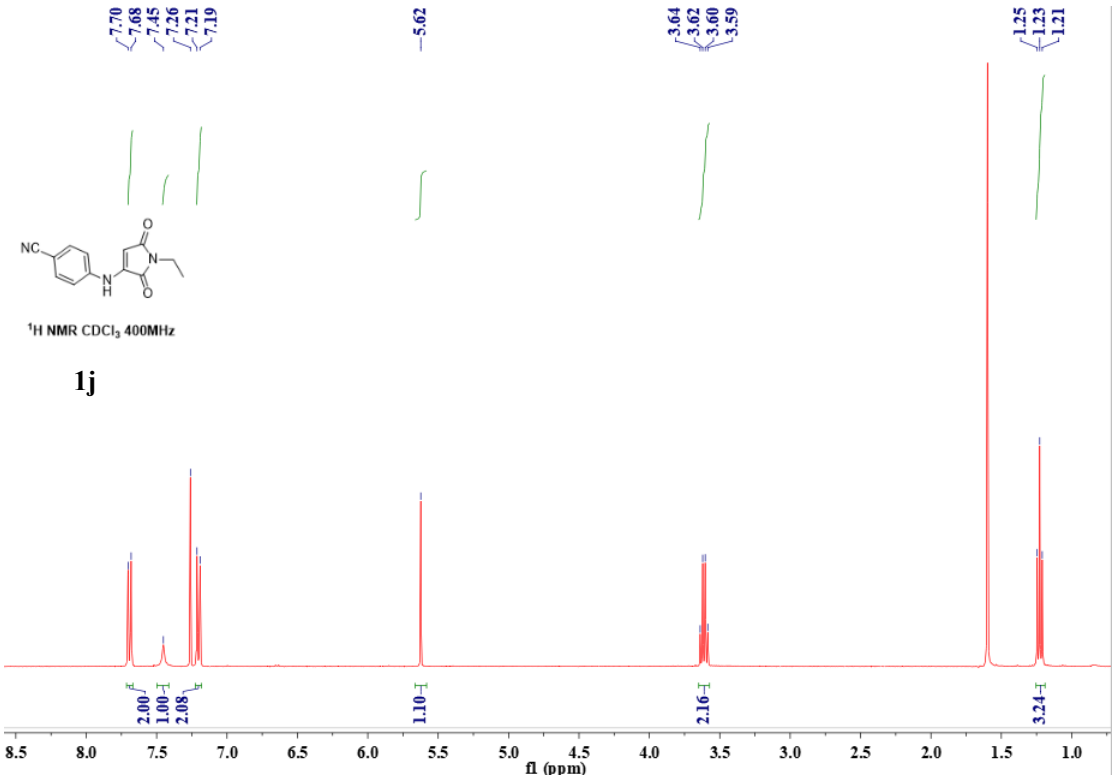

172.4
168.0
142.4
135.9
134.3
128.2
119.3
88.8
77.3
77.0
76.7
32.7
16.3
13.9
^{13}C NMR CDCl$_3$ 100MHz
1h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.67
7.65
7.44
7.26
7.24
7.22
5.59
3.64
3.62
3.60
3.58
F3C
N
H
O
O
N
1H NMR CDCl3 400MHz
2.00
0.96
1.98
1.02
2.13
3.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

1i

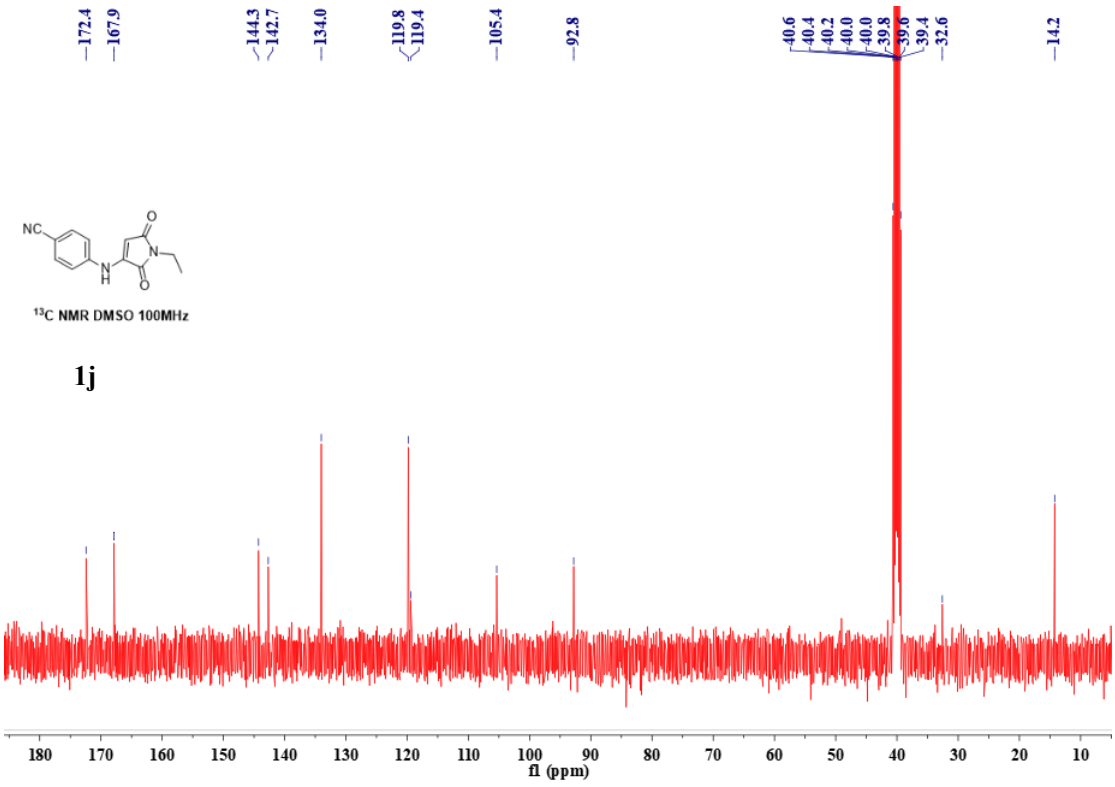

172.5
167.9
143.6
143.2
126.9
119.8
91.6
40.6
40.4
40.2
40.0
39.8
39.6
39.4
32.5
14.2
F3C
N
H
O
O
N
13C NMR DMSO 100MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1i



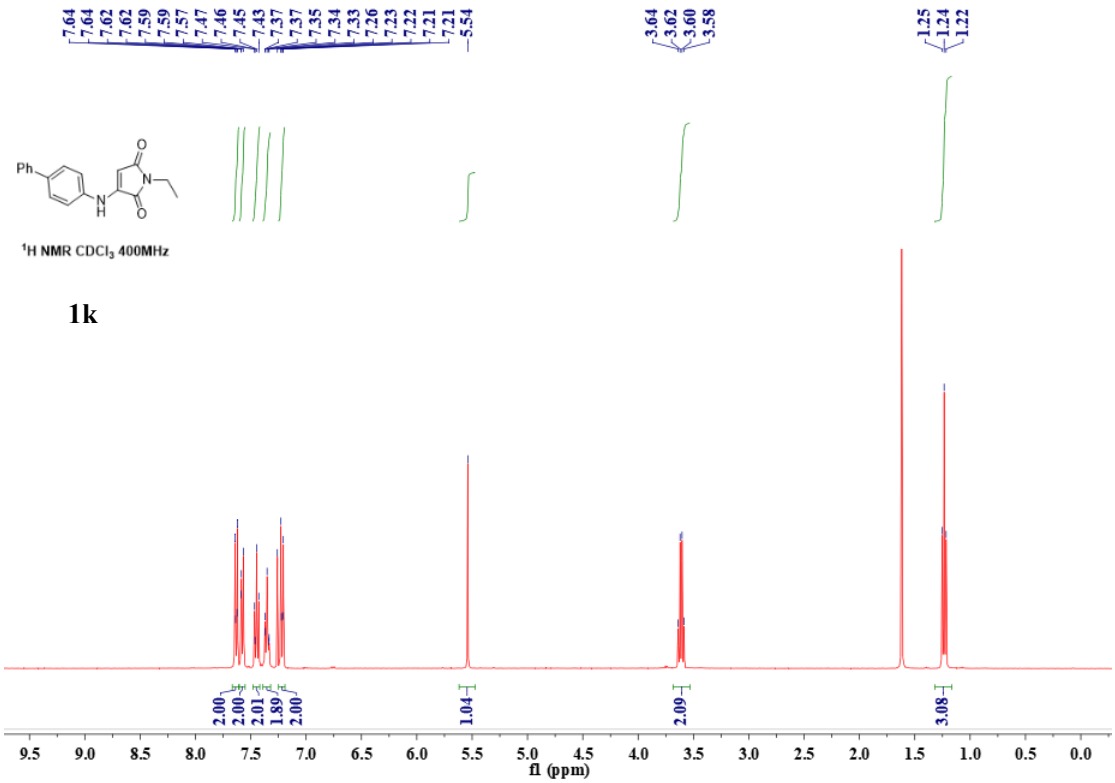
^{1}H NMR $CDCl_3$ 400MHz

1j



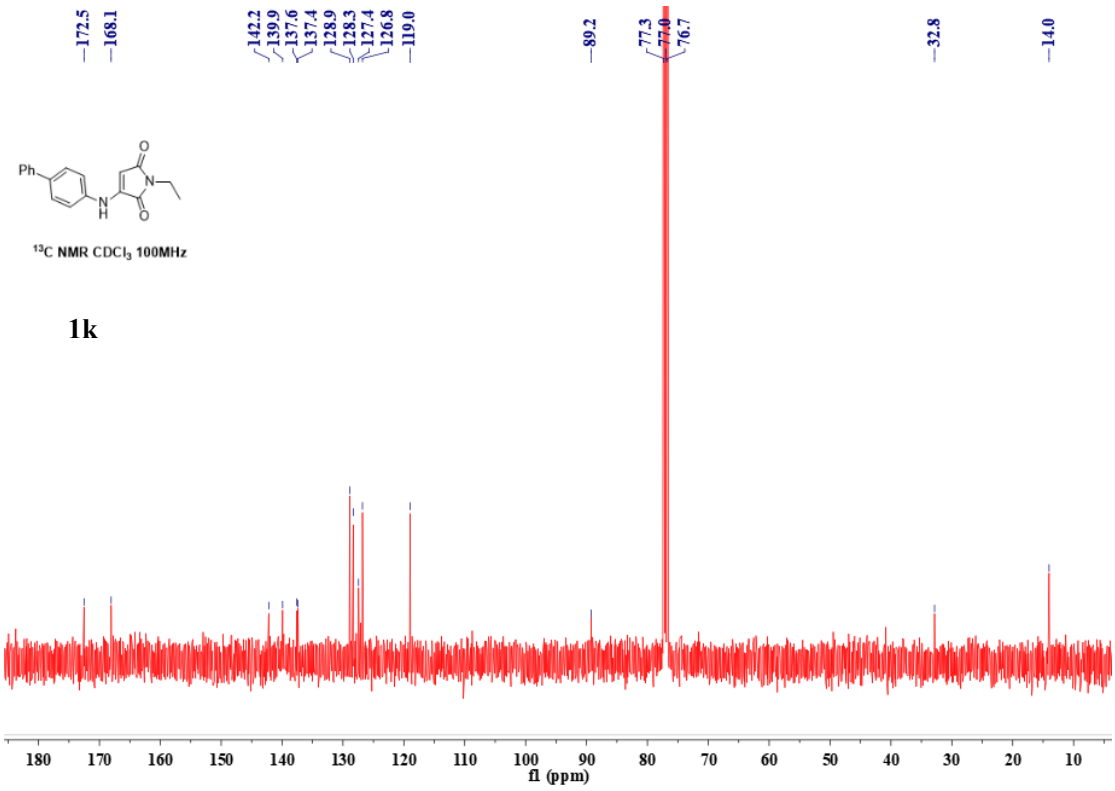
^{13}C NMR DMSO 100MHz

1j



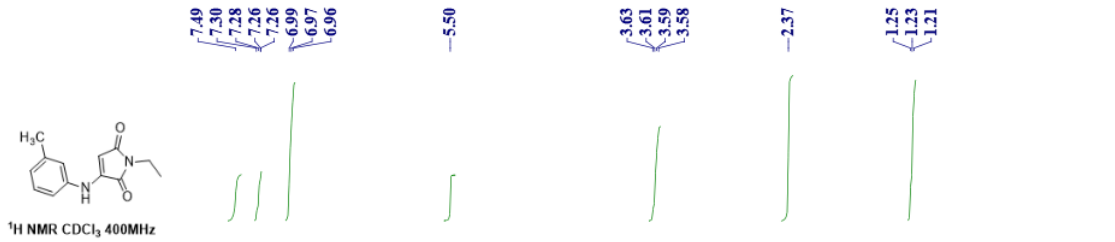
^{1}H NMR $CDCl_3$ 400MHz

1k



^{13}C NMR $CDCl_3$ 100MHz

1k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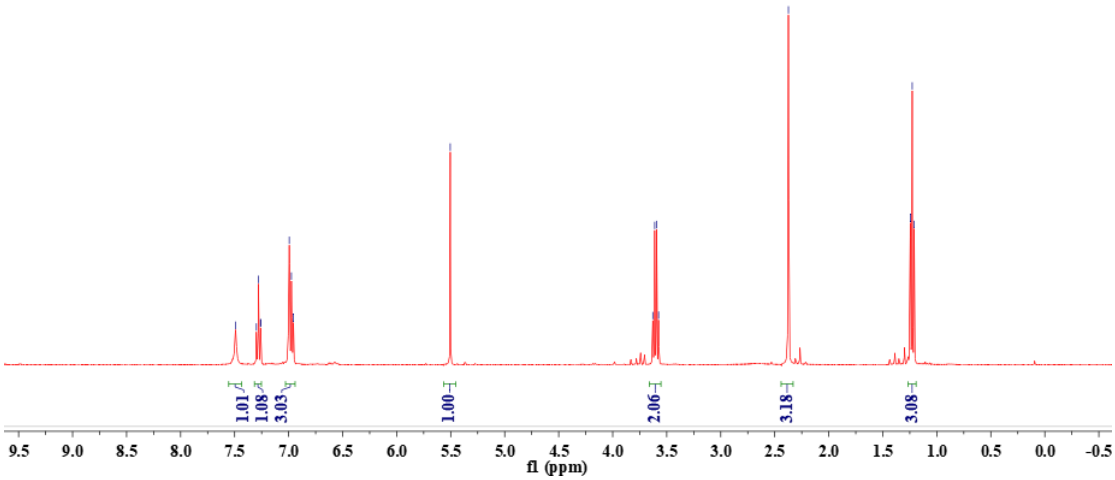
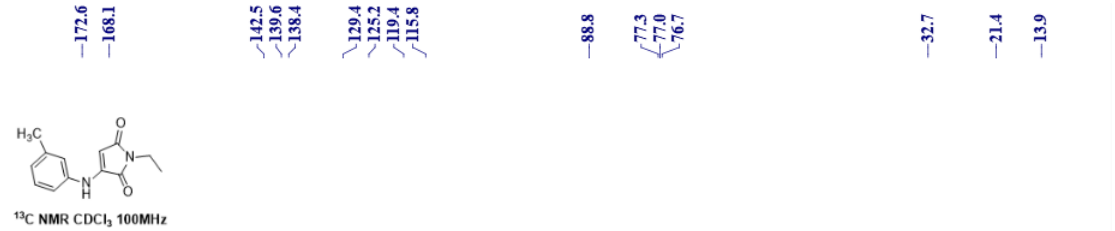
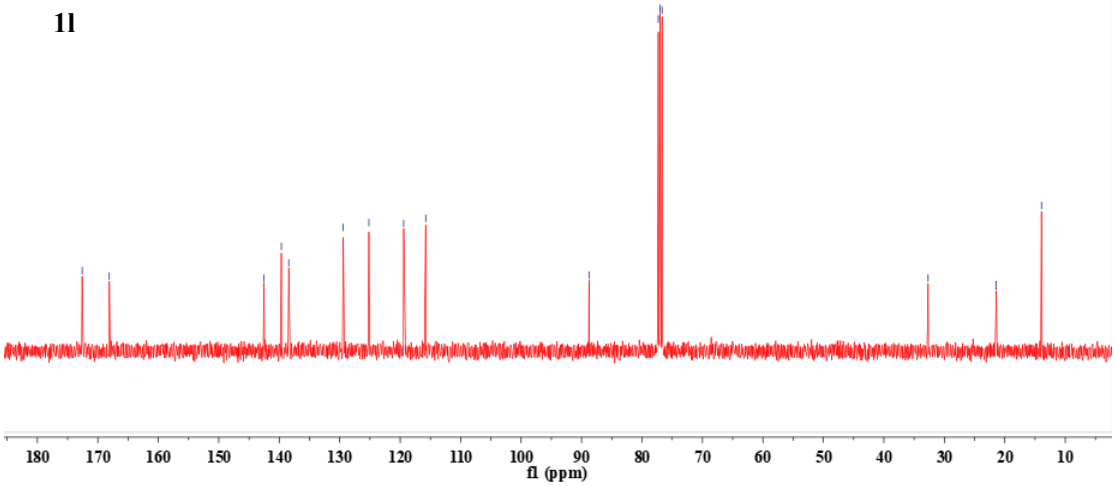
7.30
7.28
7.26
7.26
6.99
6.97
6.96
5.50
3.63
3.61
3.59
3.58
2.37
1.25
1.23
1.21
H3C
O
N
H
O
1H NMR CDCl3 400MHz

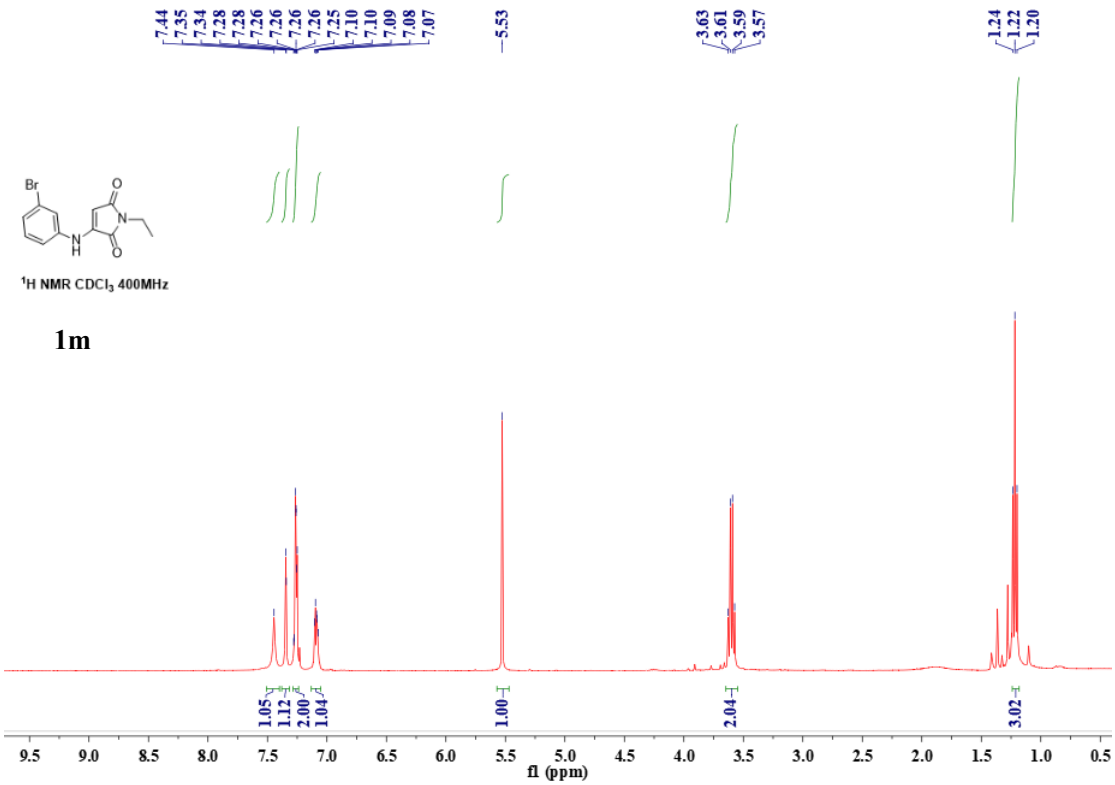
1l


1.01
1.08
3.03
1.00
2.06
3.18
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


172.6
168.1
142.5
139.6
138.4
129.4
125.2
119.4
115.8
88.8
77.3
77.0
76.7
32.7
21.4
13.9
H3C
O
N
H
O
13C NMR CDCl3 100MHz

1l


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.44
7.35
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7.28
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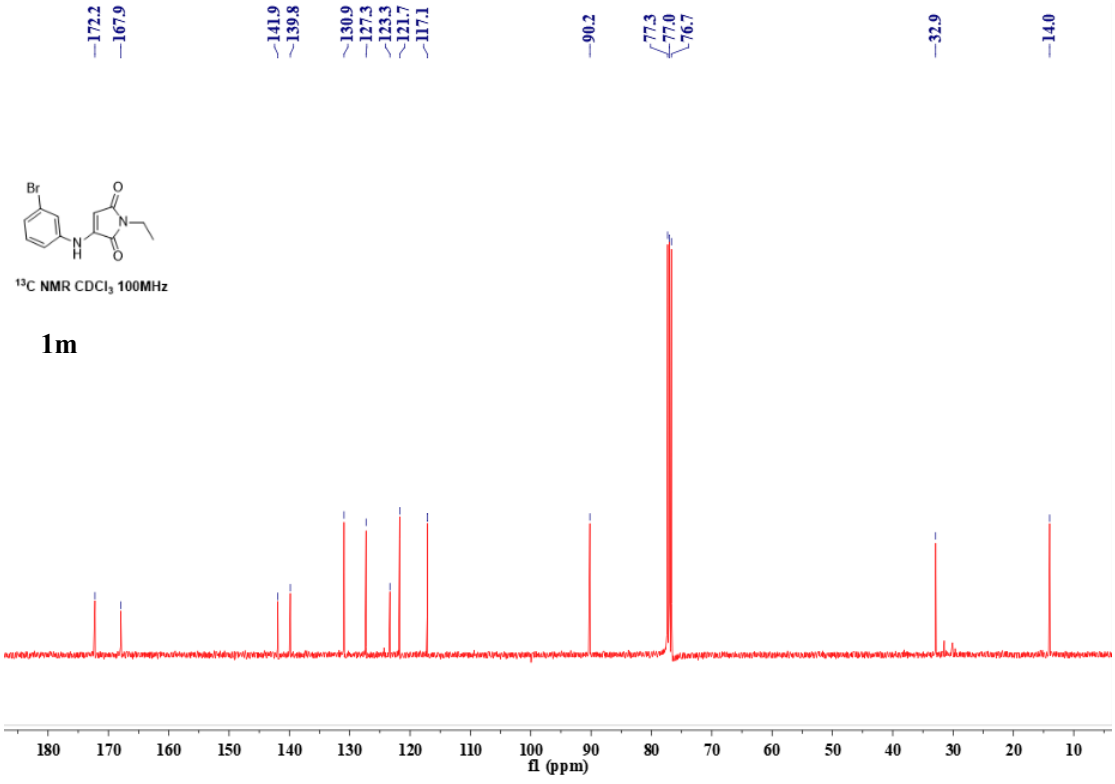
7.26
7.26
7.26
7.25
7.10
7.10
7.09
7.08
7.07
5.53
3.63
3.61
3.59
3.57
1.24
1.22
1.20
Br
O
N
H
O
1H NMR CDCl3 400MHz
1m
1.05
1.12
2.00
1.04
1.00
2.04
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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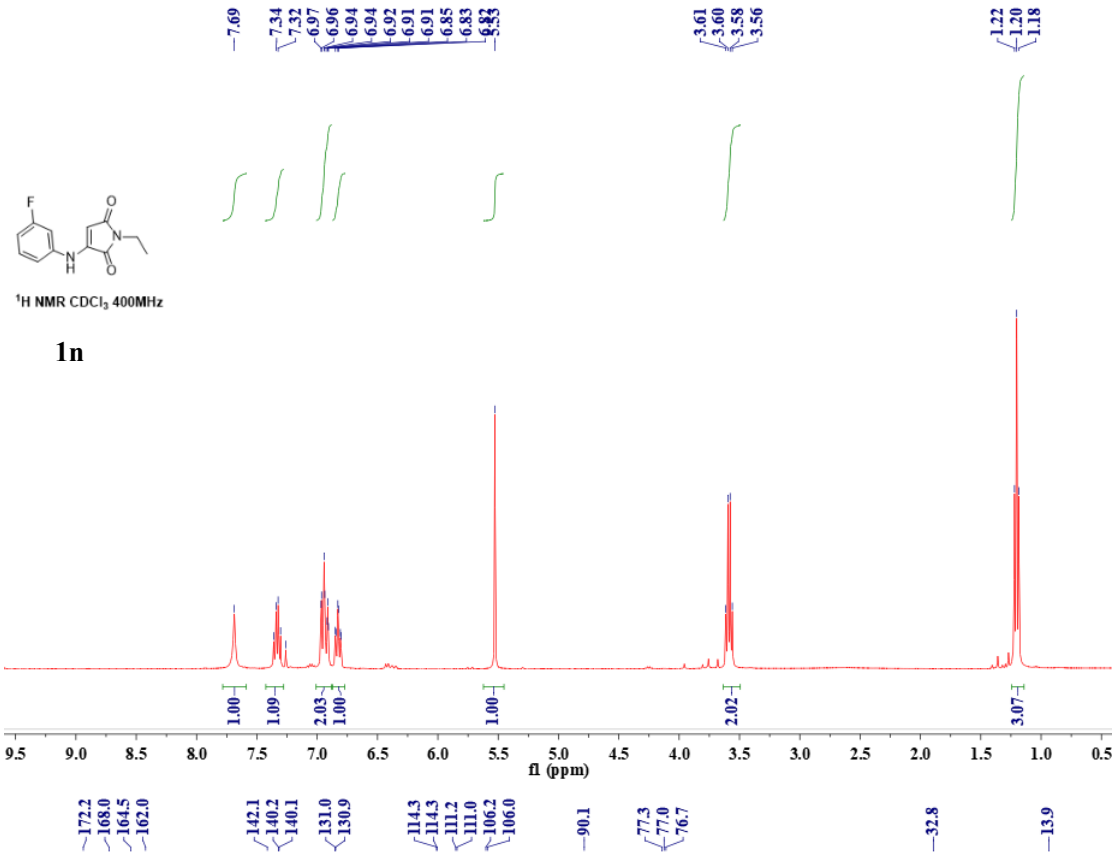
167.9
141.9
139.8
130.9
127.3
123.3
121.7
117.1
90.2
77.3
77.0
76.7
32.9
14.0
Br
O
N
H
O
13C NMR CDCl3 100MHz
1m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.34
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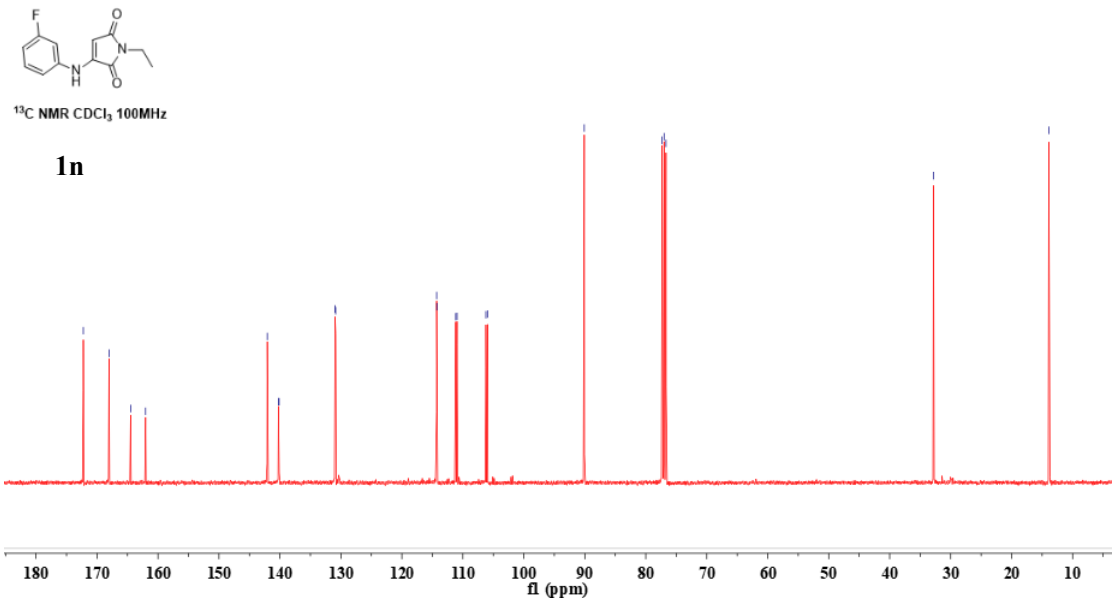
6.97
6.96
6.94
6.94
6.92
6.91
6.91
6.85
6.83
5.53
3.61
3.60
3.58
3.56
1.22
1.20
1.18
F
O
N
H
O
1H NMR CDCl3 400MHz
1n
1.00
1.09
2.03
1.00
1.00
2.02
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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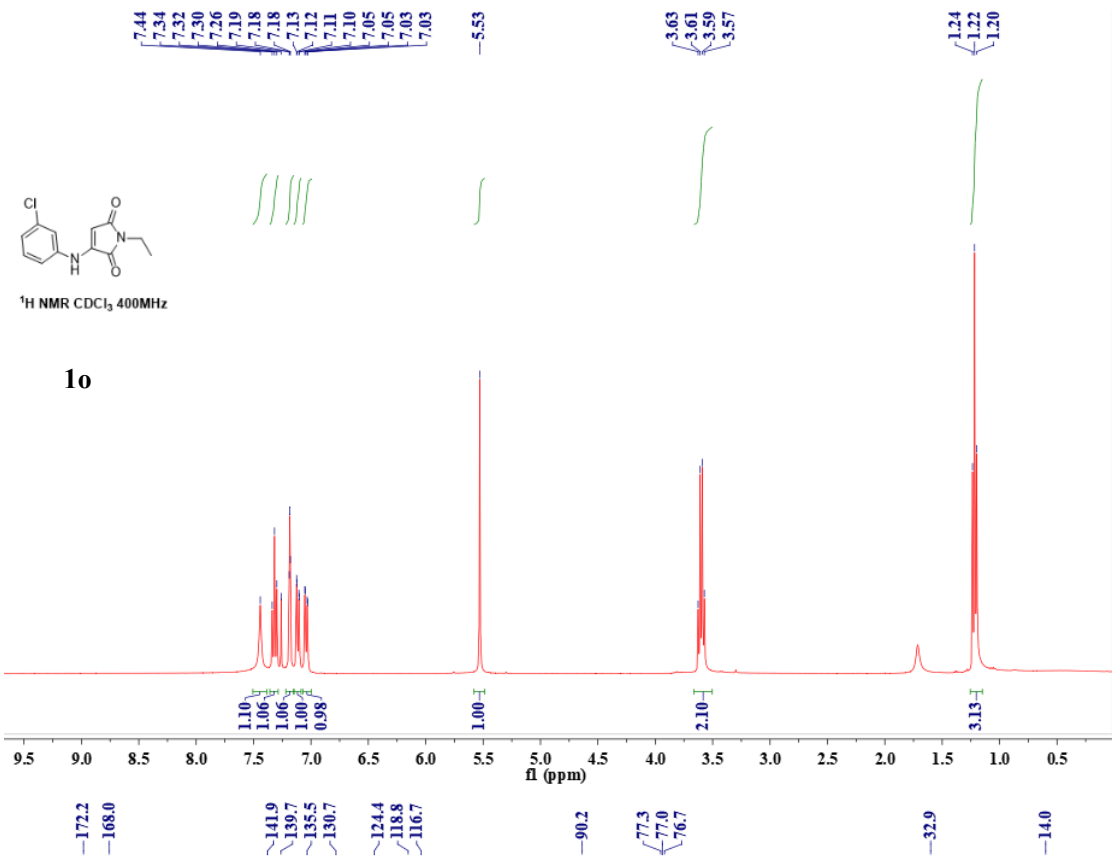
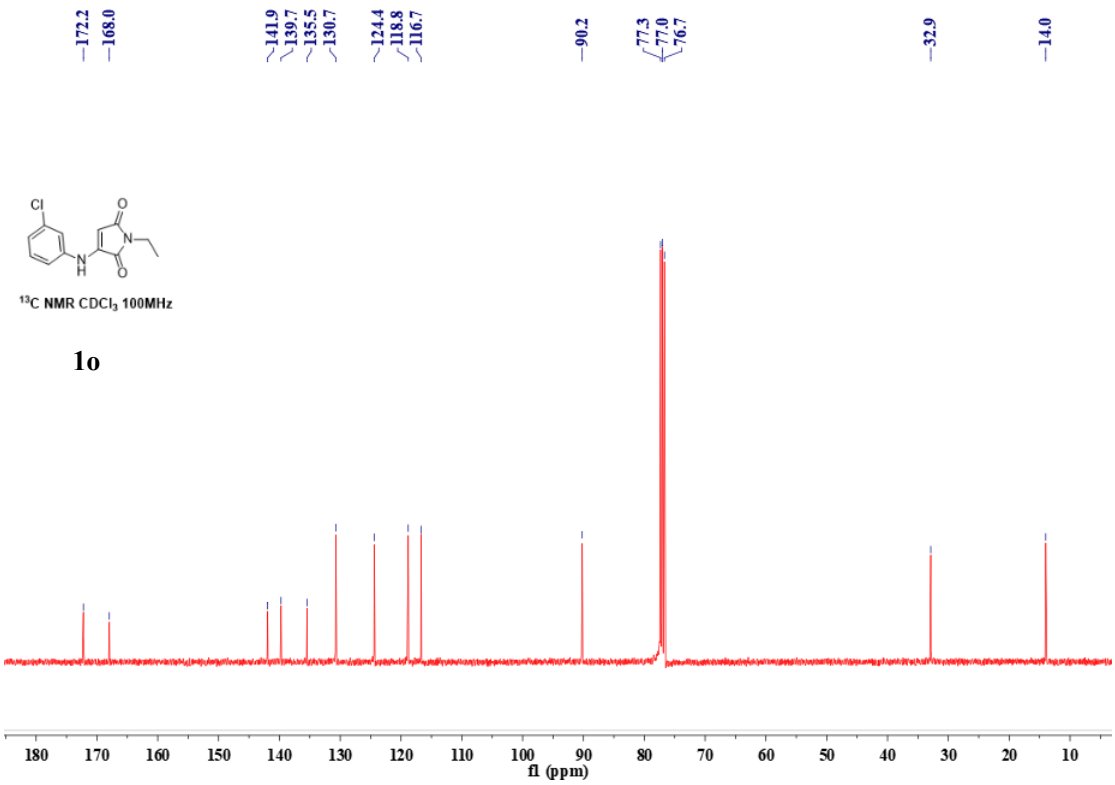
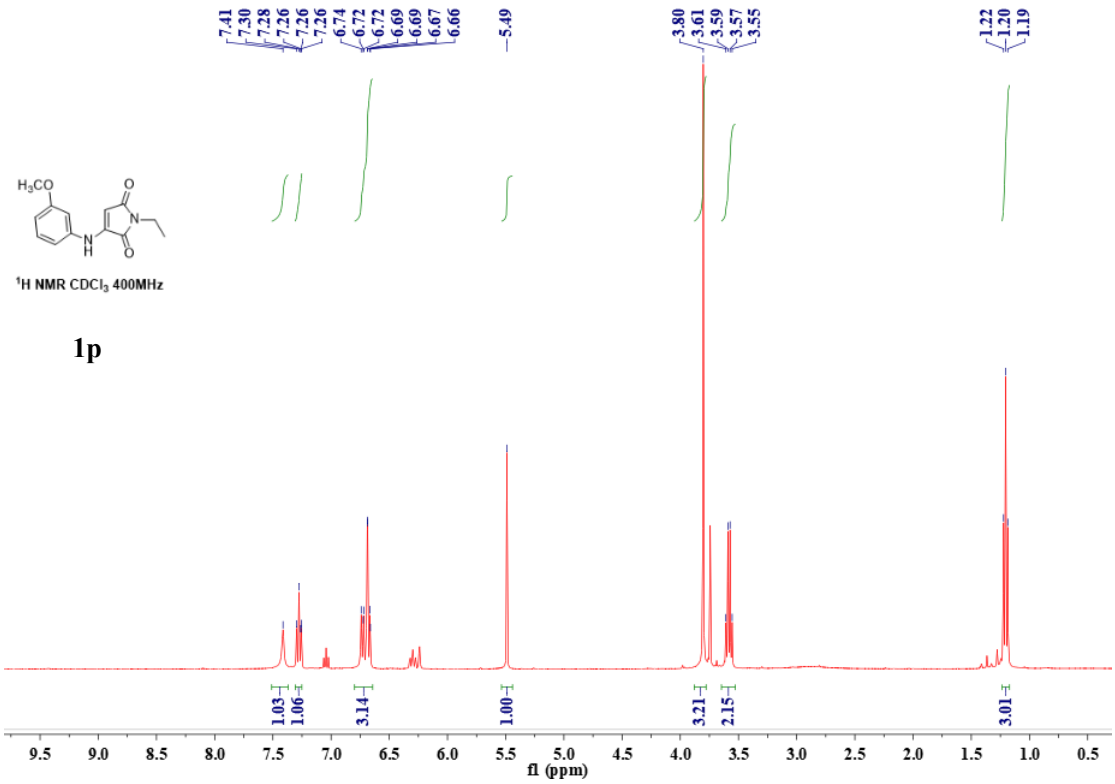
164.5
162.0
142.1
140.2
140.1
131.0
130.9
114.3
114.3
111.2
111.0
106.2
106.0
90.1
77.3
77.0
76.7
32.8
13.9
F
O
N
H
O
13C NMR CDCl3 100MHz
1n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

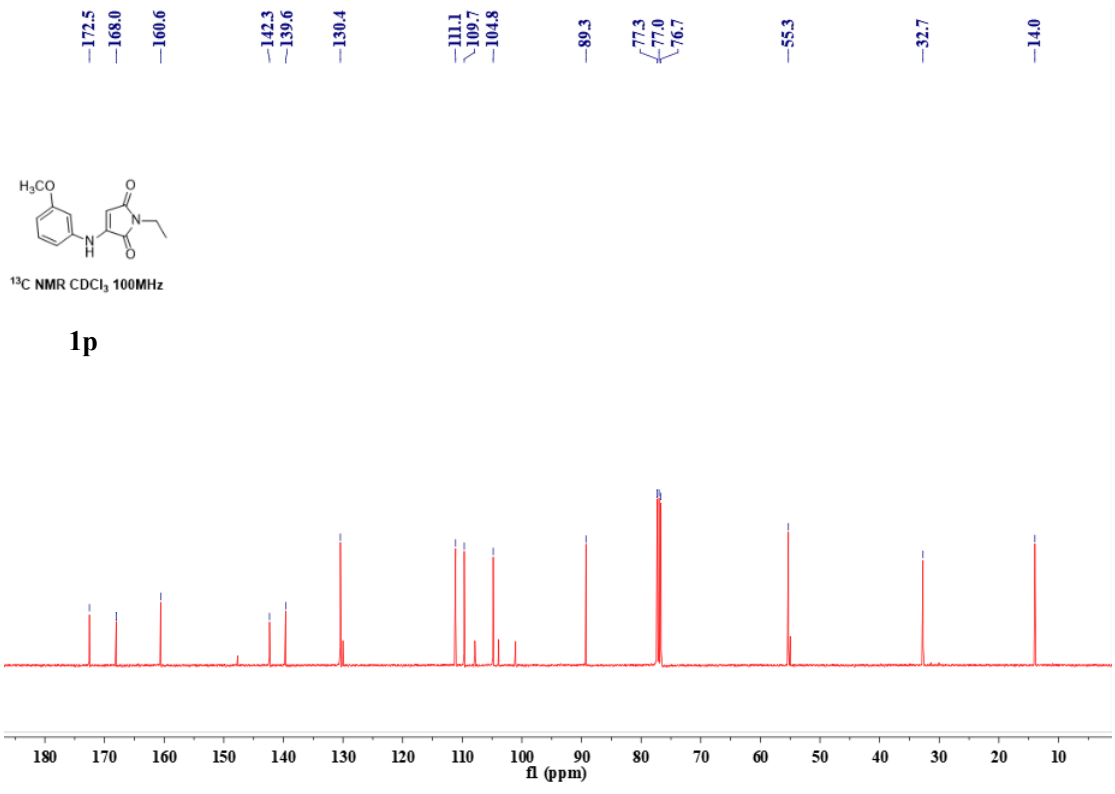

7.44
7.34
7.32
7.30
7.26
7.19
7.18
7.18
7.13
7.12
7.11
7.10
7.05
7.05
7.03
7.03
5.53
3.63
3.61
3.59
3.57
1.24
1.22
1.20
Cl
O
N
H
O
O
1H NMR CDCl3 400MHz
1o
1.10
1.06
1.06
1.00
0.98
1.00
2.10
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


172.2
168.0
141.9
139.7
135.5
130.7
124.4
118.8
116.7
90.2
77.3
77.0
76.7
32.9
14.0
Cl
O
N
H
O
13C NMR CDCl3 100MHz
1o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



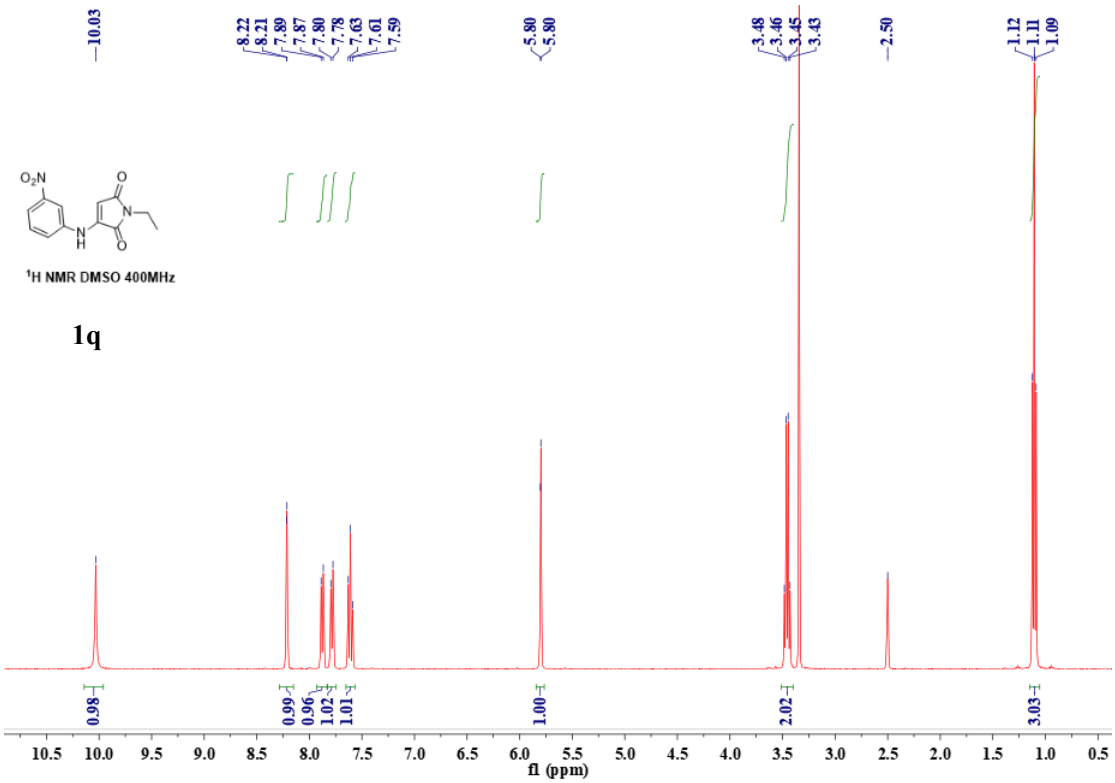
^{1}H NMR $CDCl_3$ 400MHz

1p



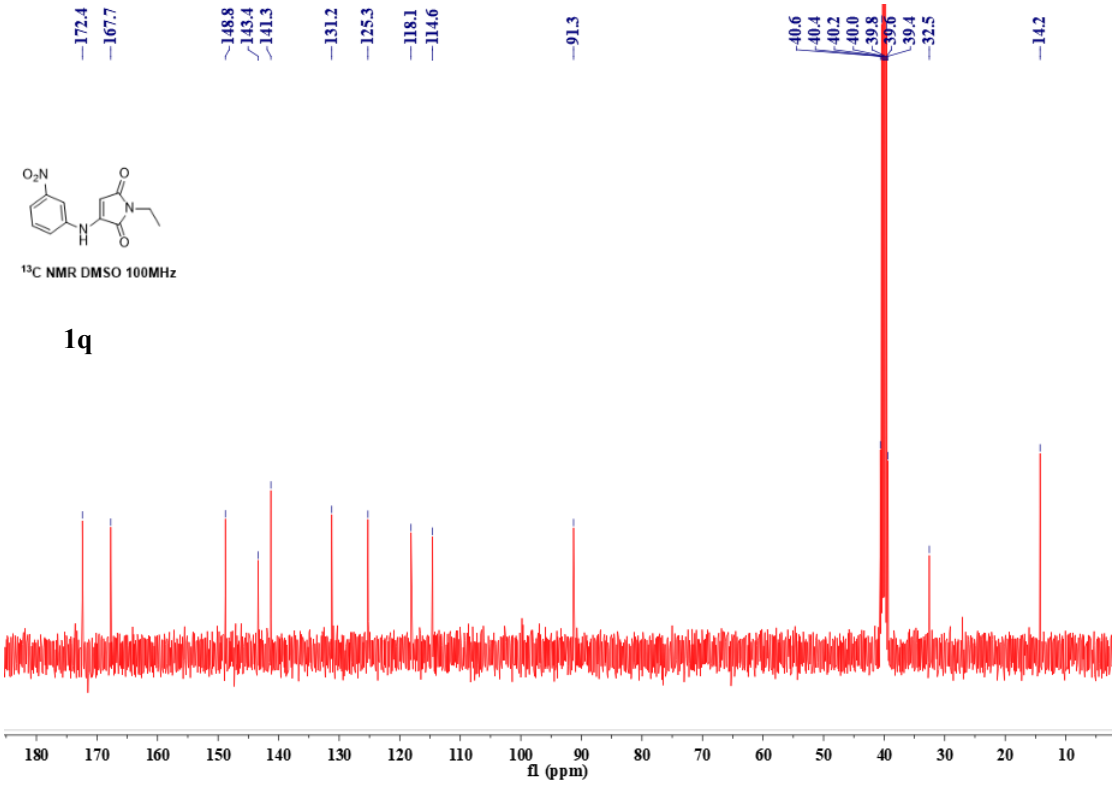
^{13}C NMR $CDCl_3$ 100MHz

1p



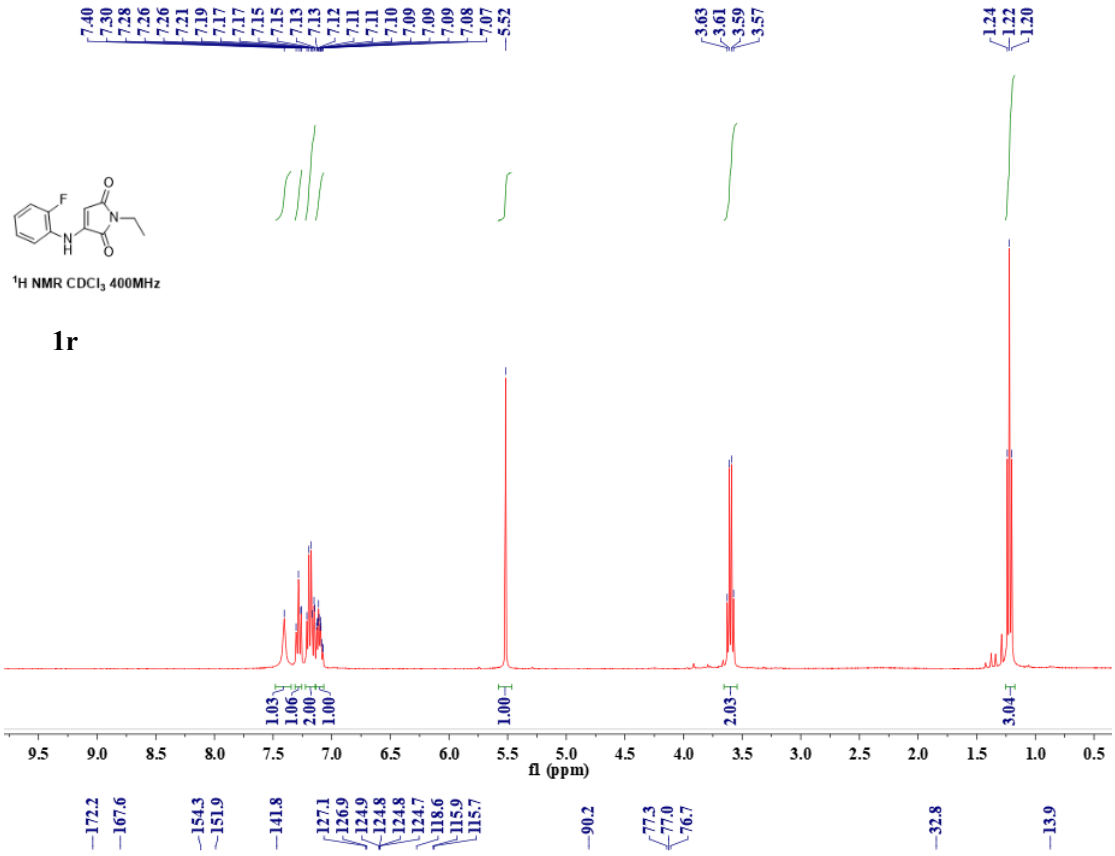
^{1}H NMR DMSO 400MHz

1q



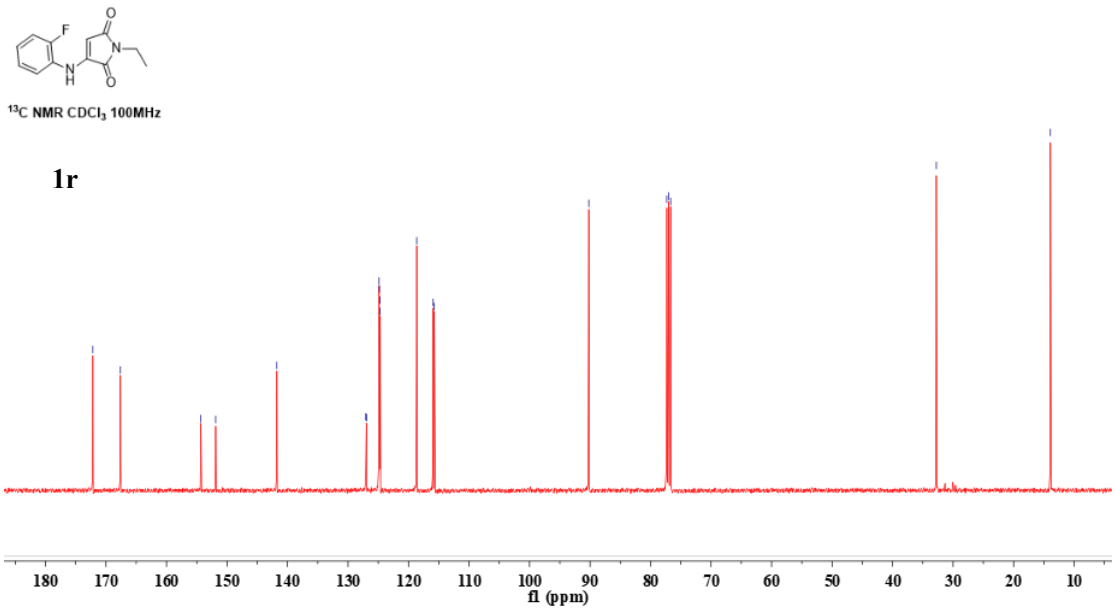
^{13}C NMR DMSO 100MHz

1q



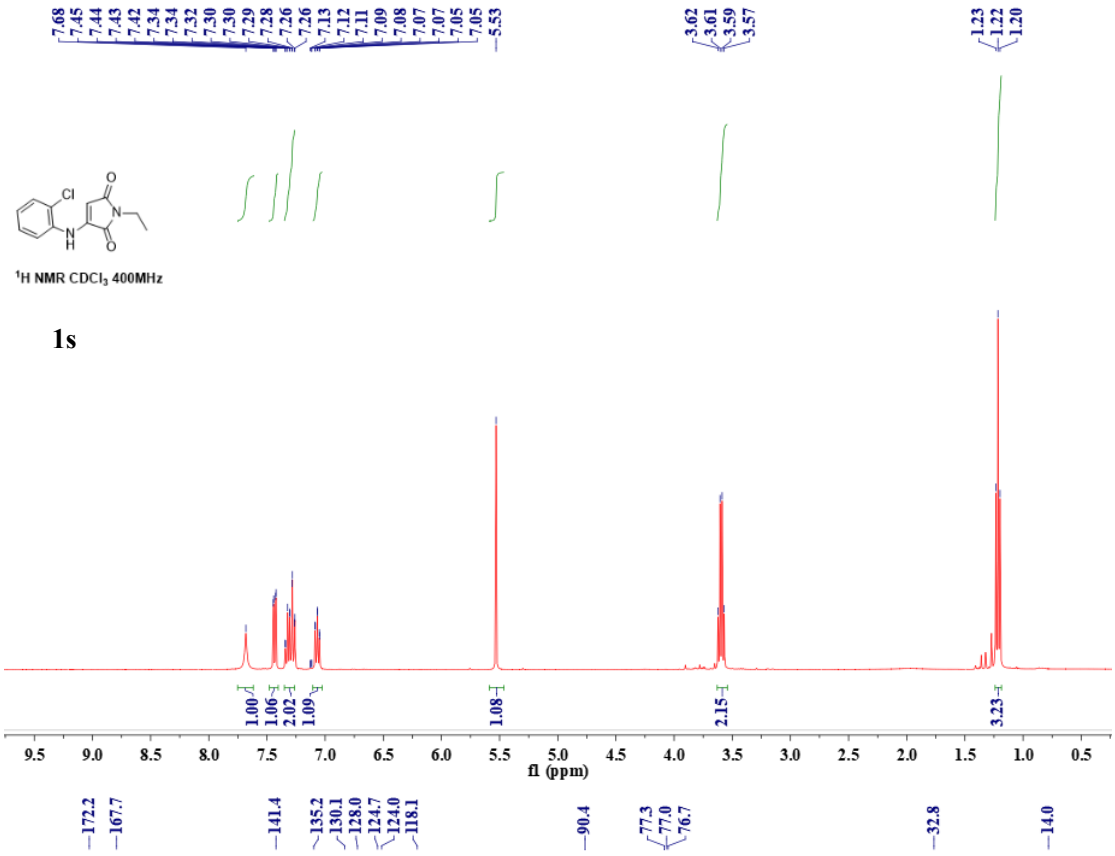
^{1}H NMR $CDCl_3$ 400MHz

1r



^{13}C NMR $CDCl_3$ 100MHz

1r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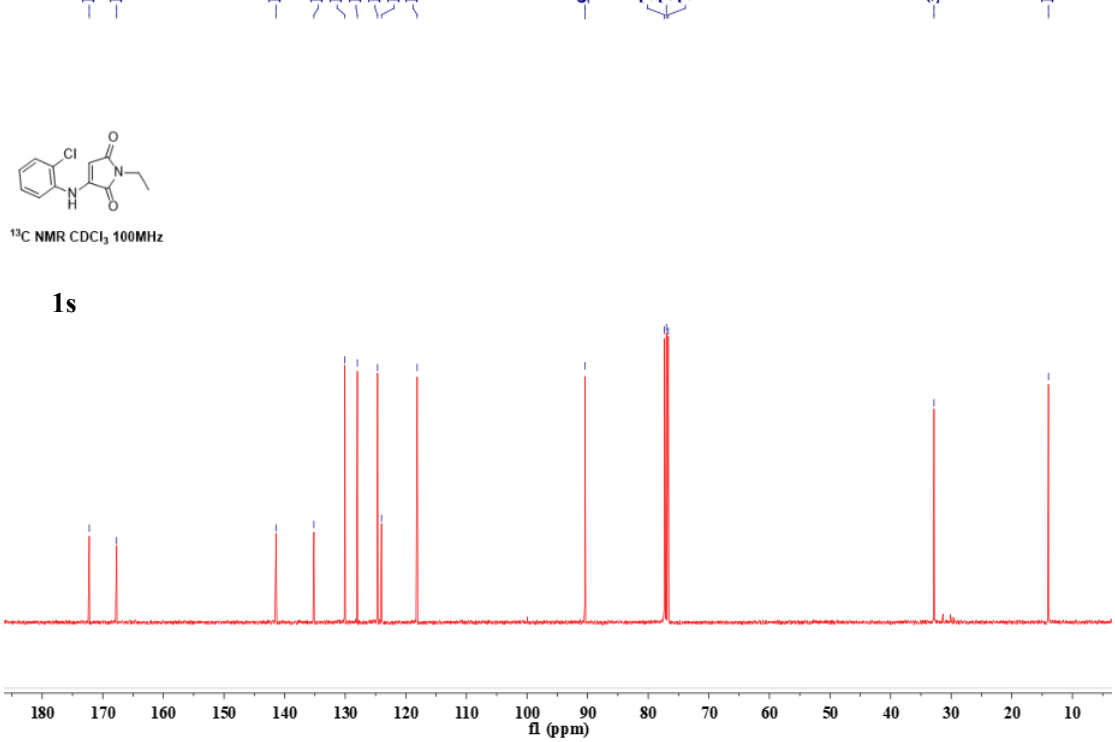
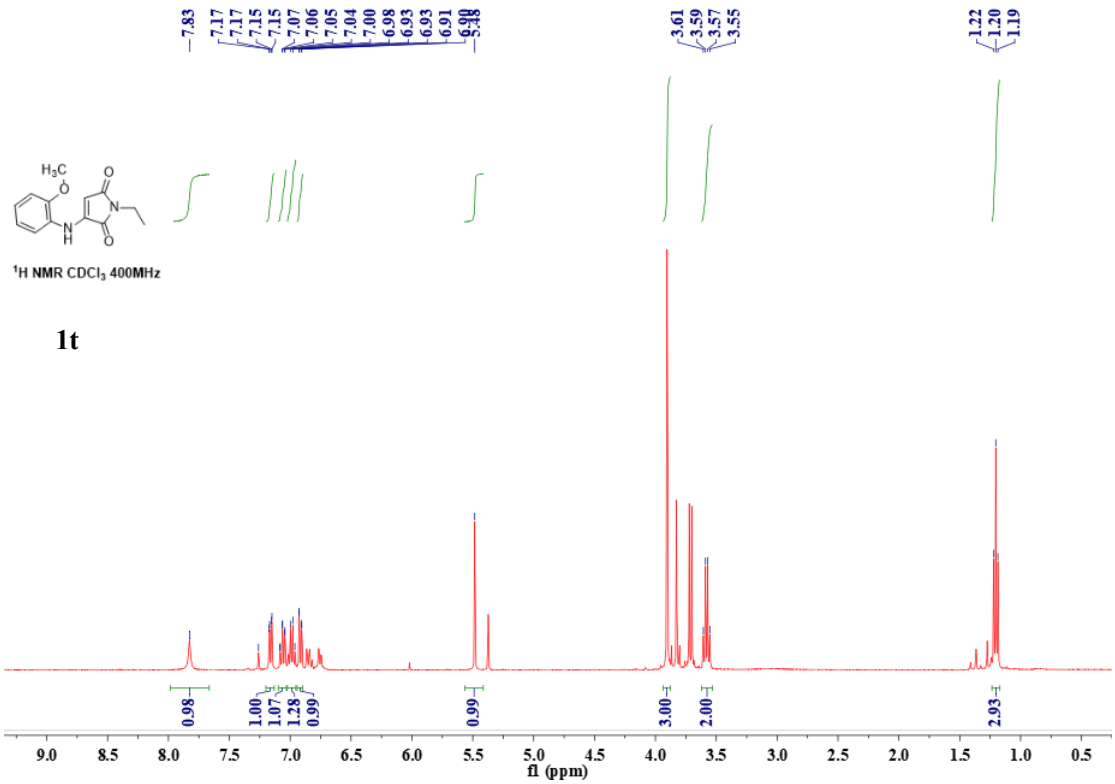
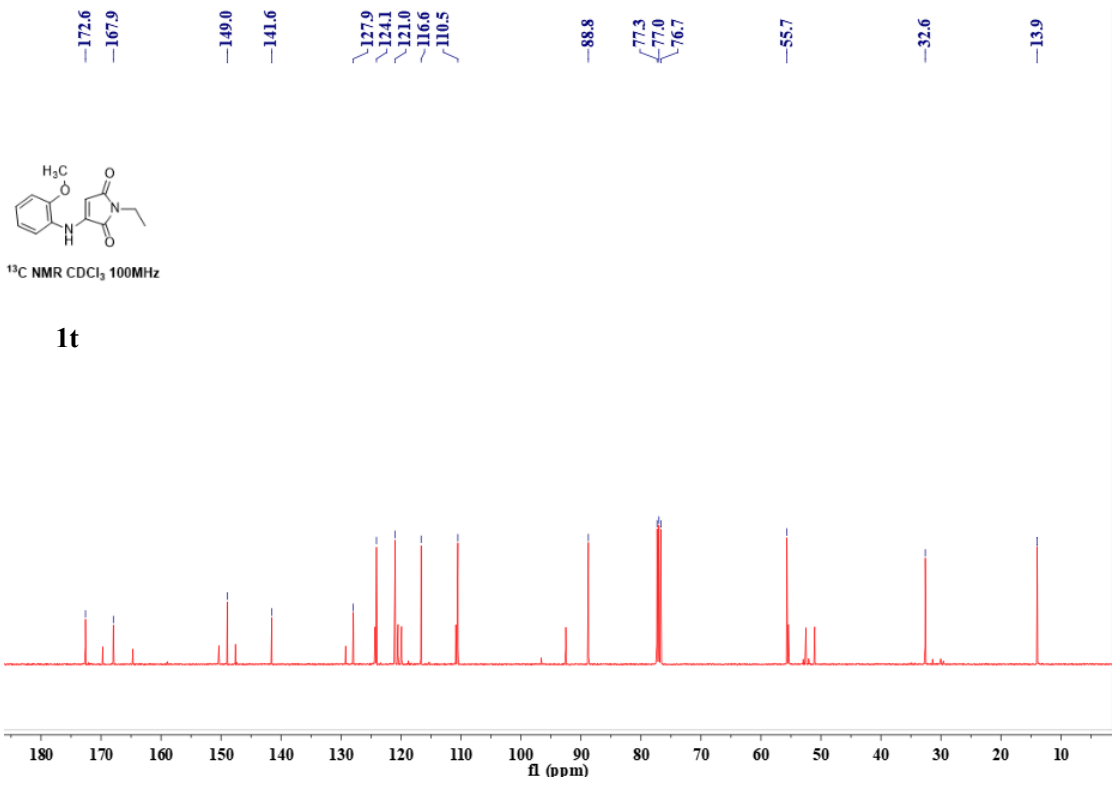
7.43
7.42
7.34
7.34
7.32
7.30
7.30
7.29
7.28
7.26
7.26
7.13
7.12
7.11
7.09
7.08
7.07
7.07
7.05
7.05
5.53
3.62
3.61
3.59
3.57
1.23
1.22
1.20
Cl
O
N
H
O
O
1H NMR CDCl3 400MHz
1s
1.00
1.06
2.02
1.09
1.08
2.15
3.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


172.2
167.7
141.4
135.2
130.1
128.0
124.7
124.0
118.1
90.4
77.3
77.0
76.7
32.8
14.0
Cl
O
N
H
O
13C NMR CDCl3 100MHz
1s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



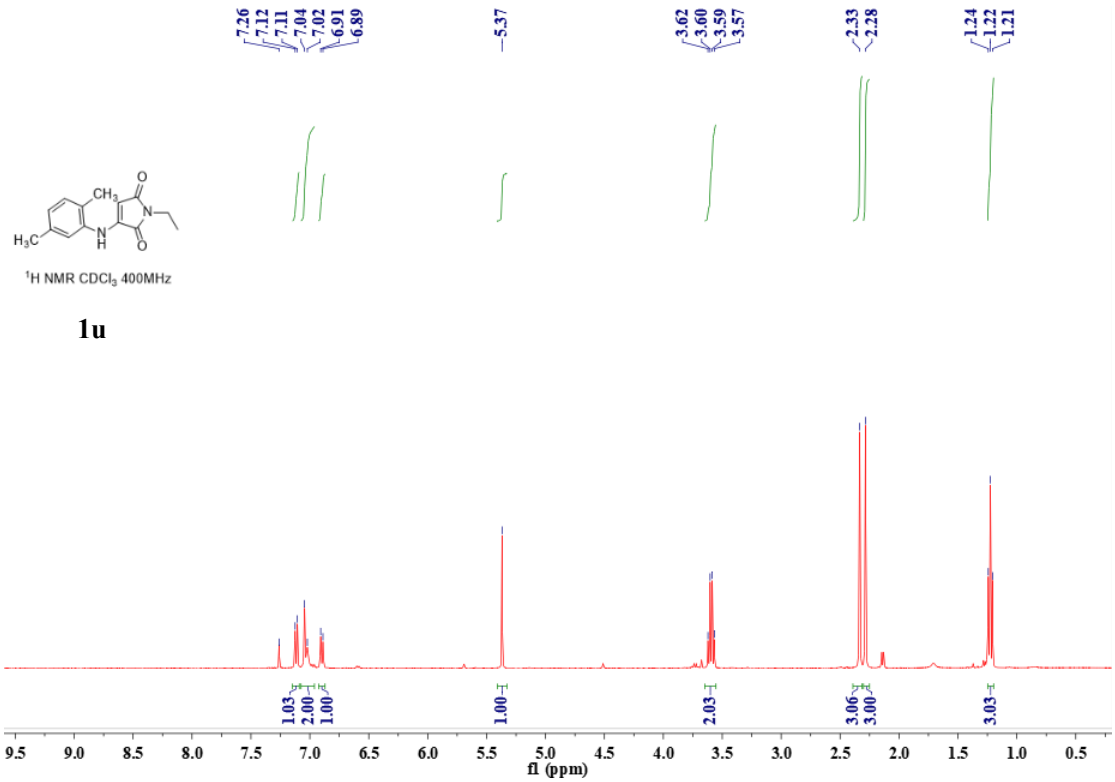
^{1}H NMR $CDCl_3$ 400MHz

1t



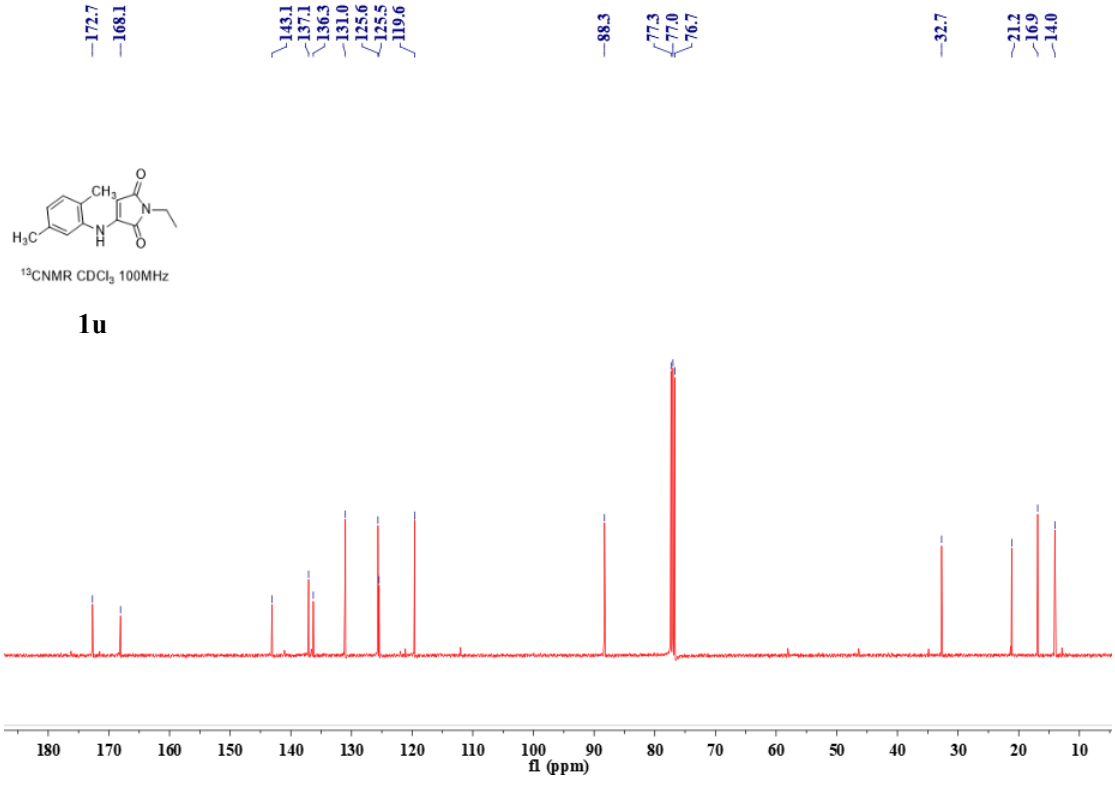
^{13}C NMR $CDCl_3$ 100MHz

1t



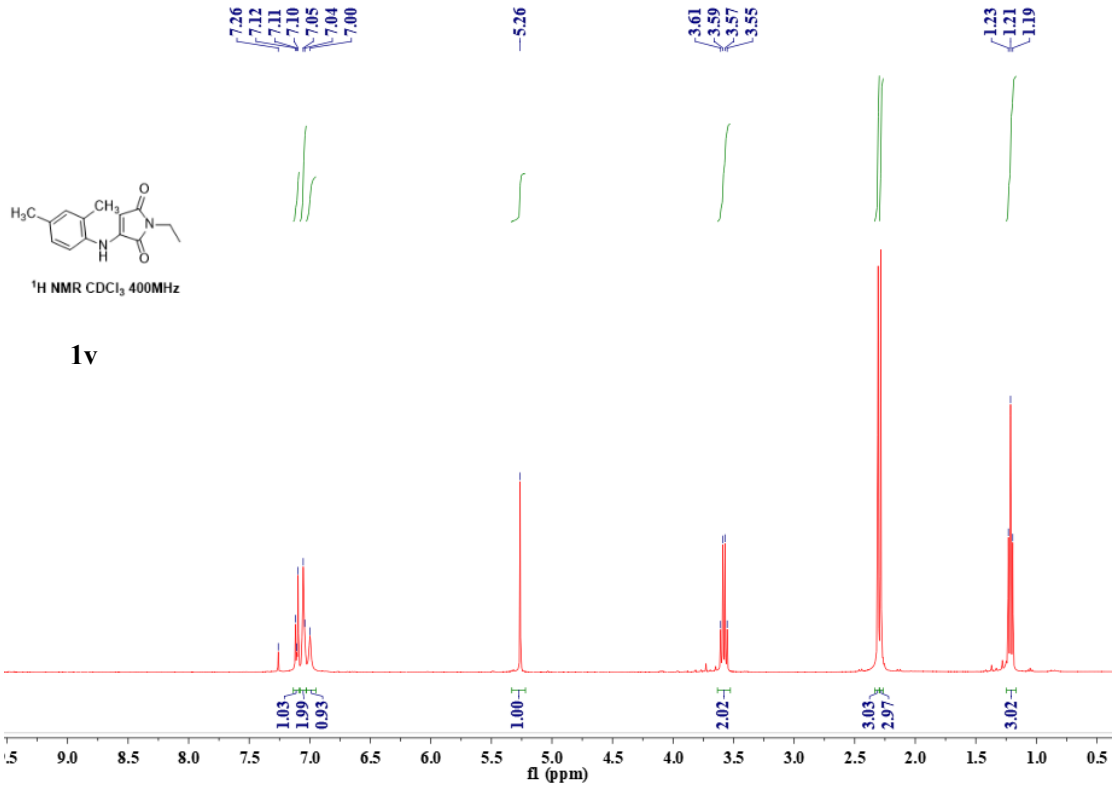
^{1}H NMR $CDCl_3$ 400MHz

1u



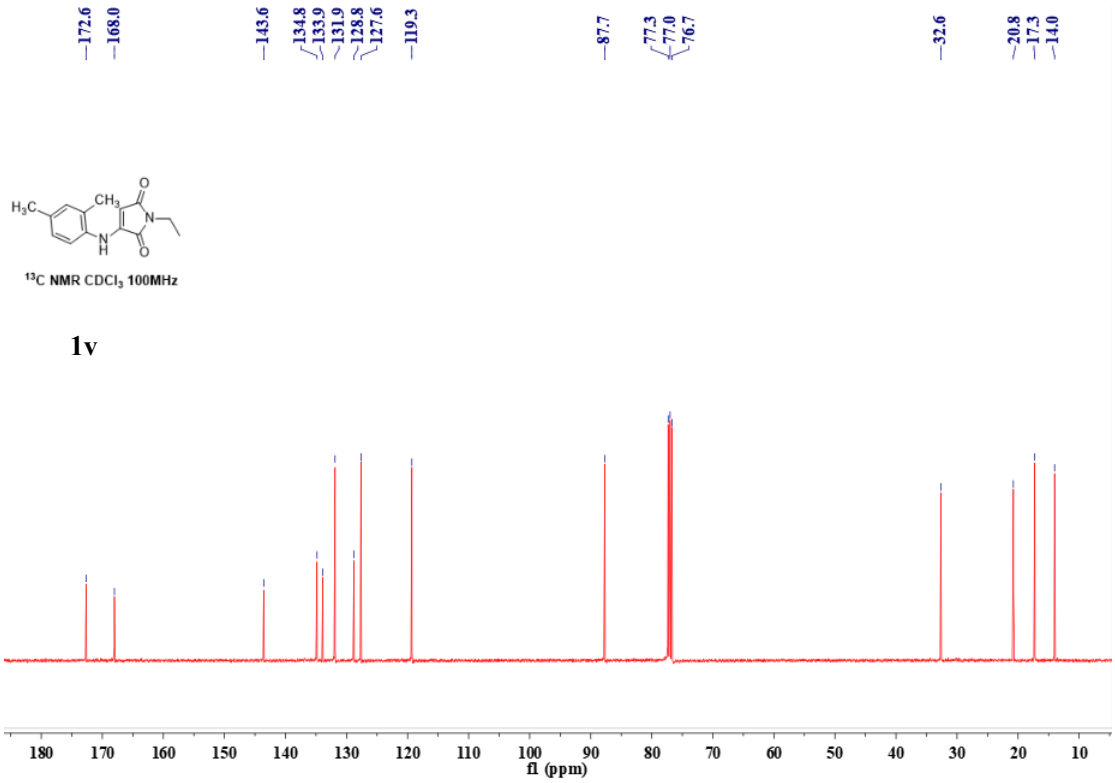
^{13}CNMR $CDCl_3$ 100MHz

1u



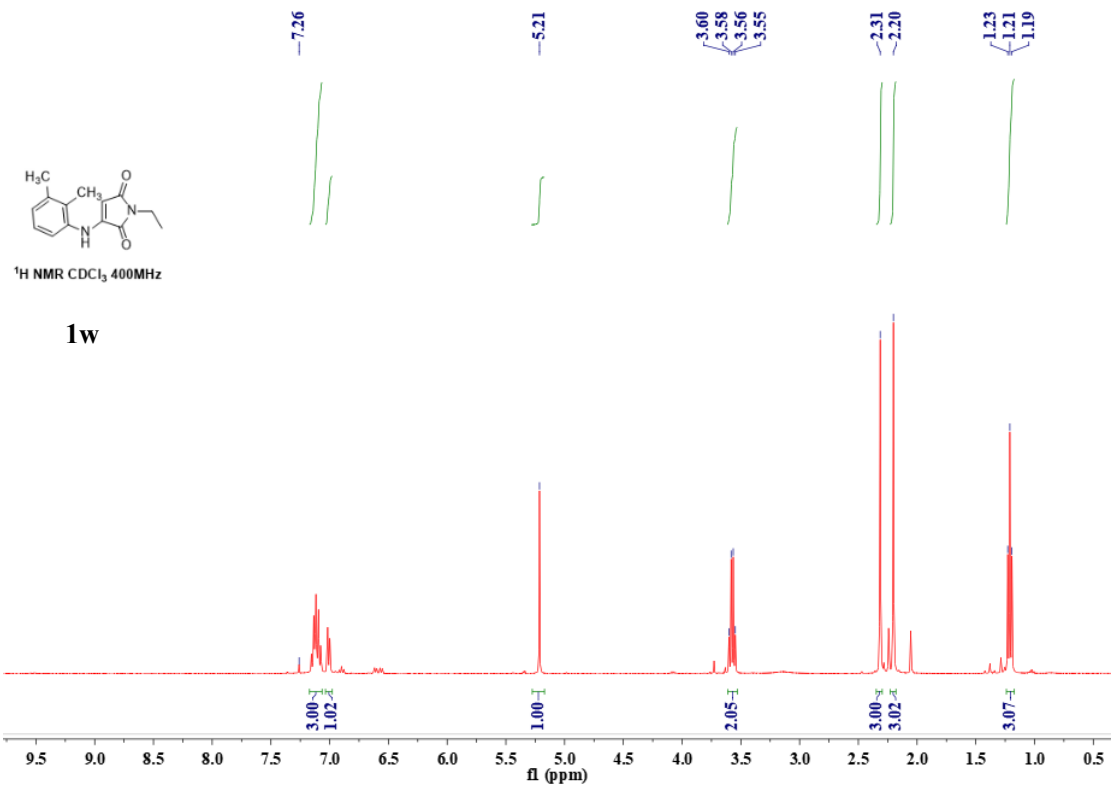
^{1}H NMR $CDCl_3$ 400MHz

1v



^{13}C NMR $CDCl_3$ 100MHz

1v

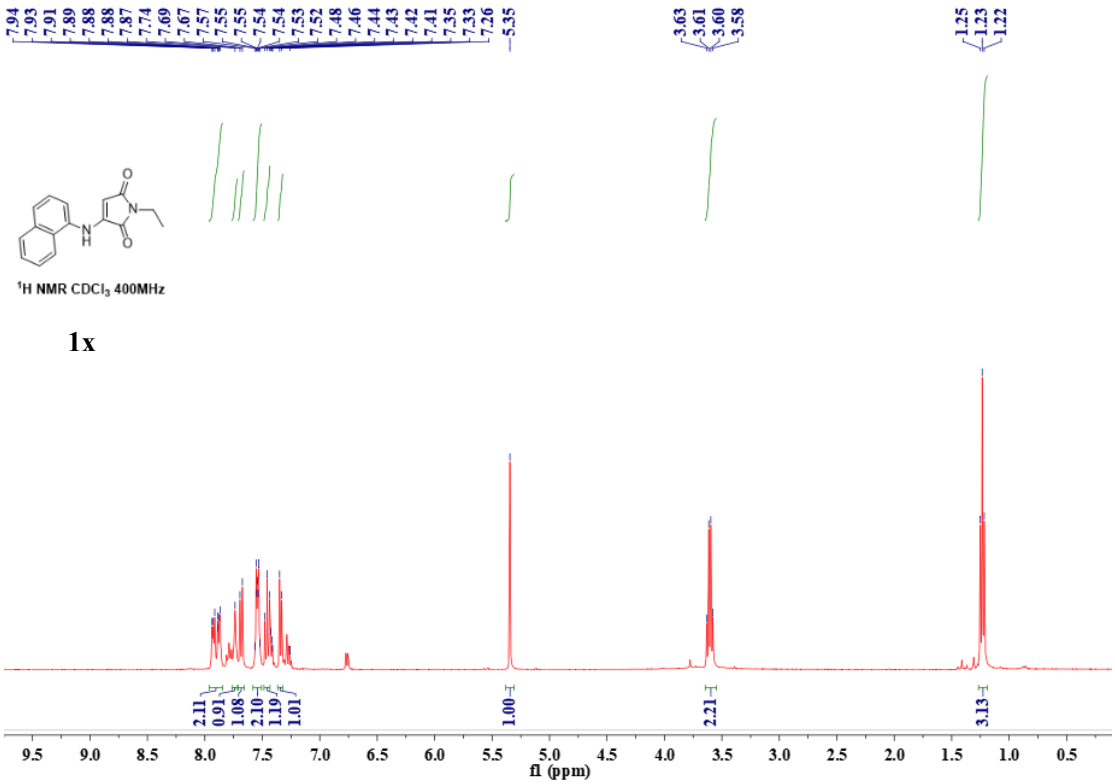


^{1}H NMR $CDCl_3$ 400MHz

1w

^{13}C NMR $CDCl_3$ 100MHz

1w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7.74
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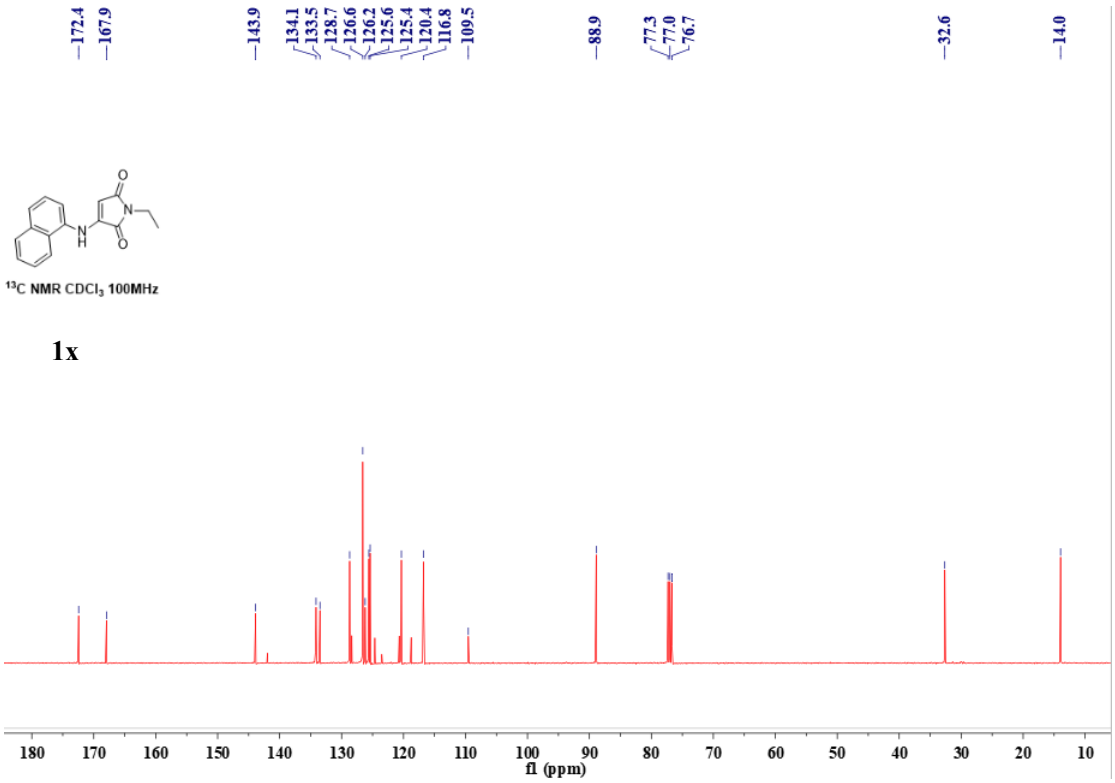
7.54
7.54
7.53
7.52
7.48
7.46
7.44
7.43
7.42
7.41
7.35
7.33
7.26
5.35
3.63
3.61
3.60
3.58
1.25
1.23
1.22
O
N
H
O
^{1}H NMR CDCl$_3$ 400MHz
2.11
0.91
1.08
2.10
1.19
1.01
1.00
2.21
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

1x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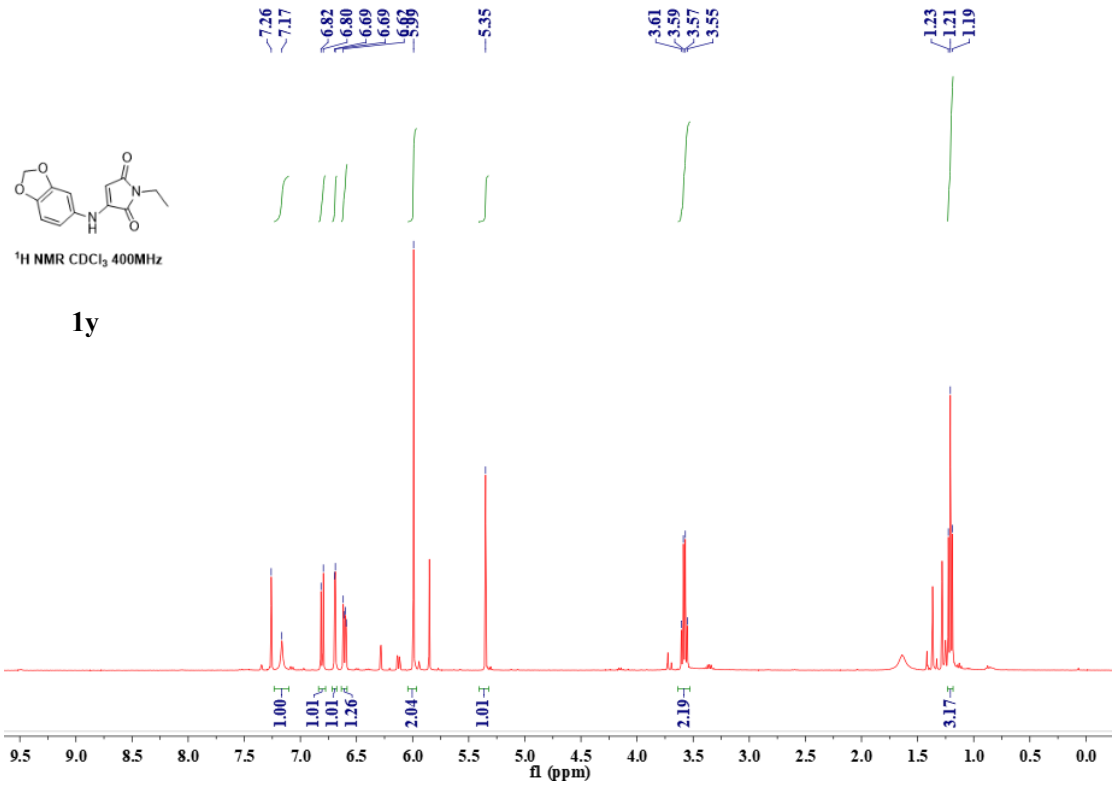
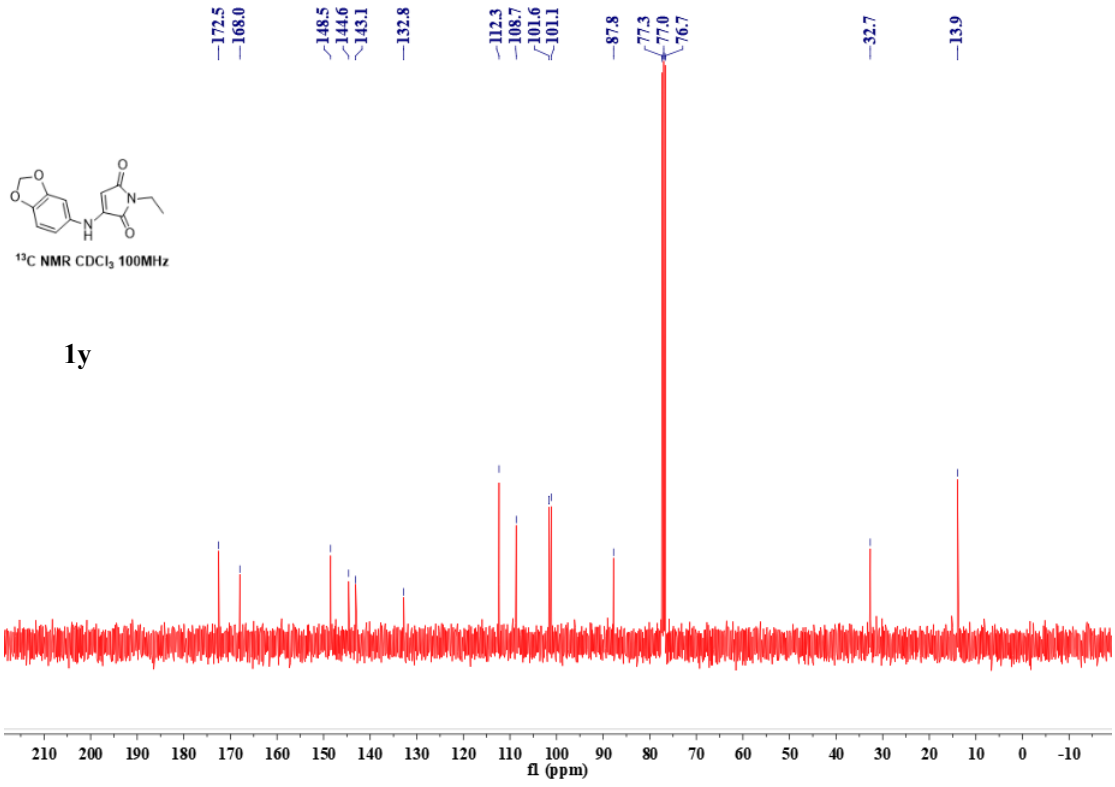
167.9
143.9
134.1
133.5
128.7
126.6
126.2
125.6
125.4
120.4
116.8
109.5
88.9
77.3
77.0
76.7
32.6
14.0
O
N
H
O
^{13}C NMR CDCl$_3$ 100MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1x



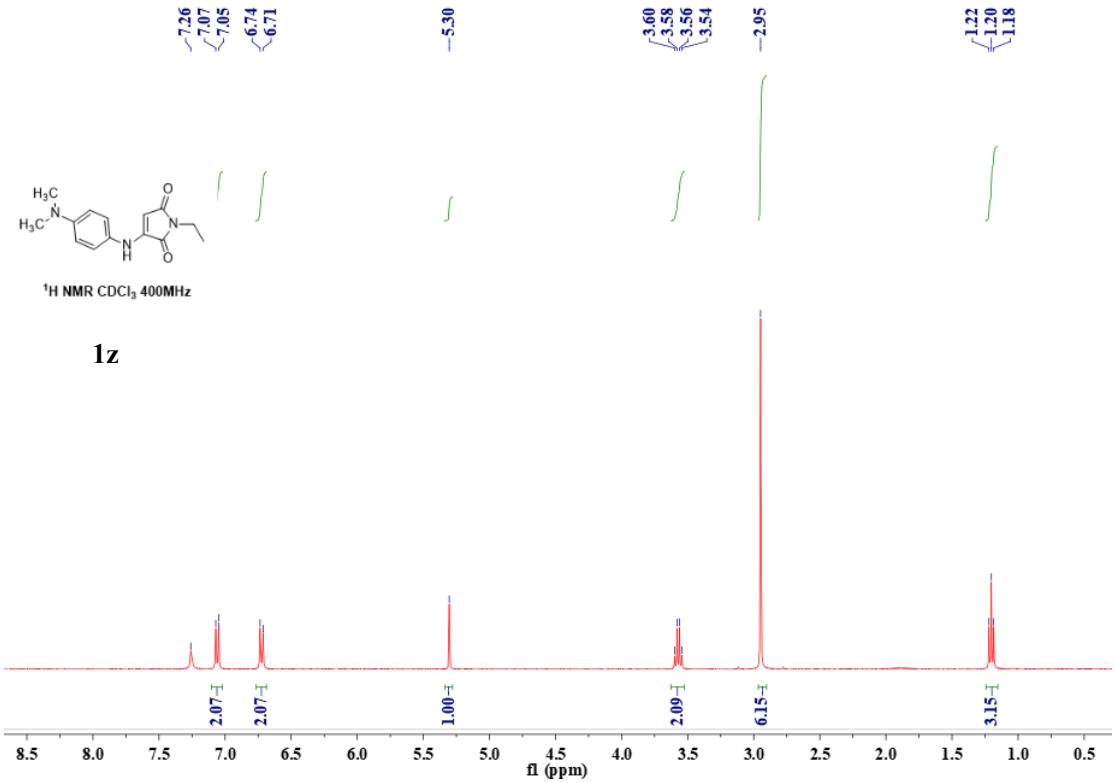
^{1}H NMR $CDCl_3$ 400MHz

1y



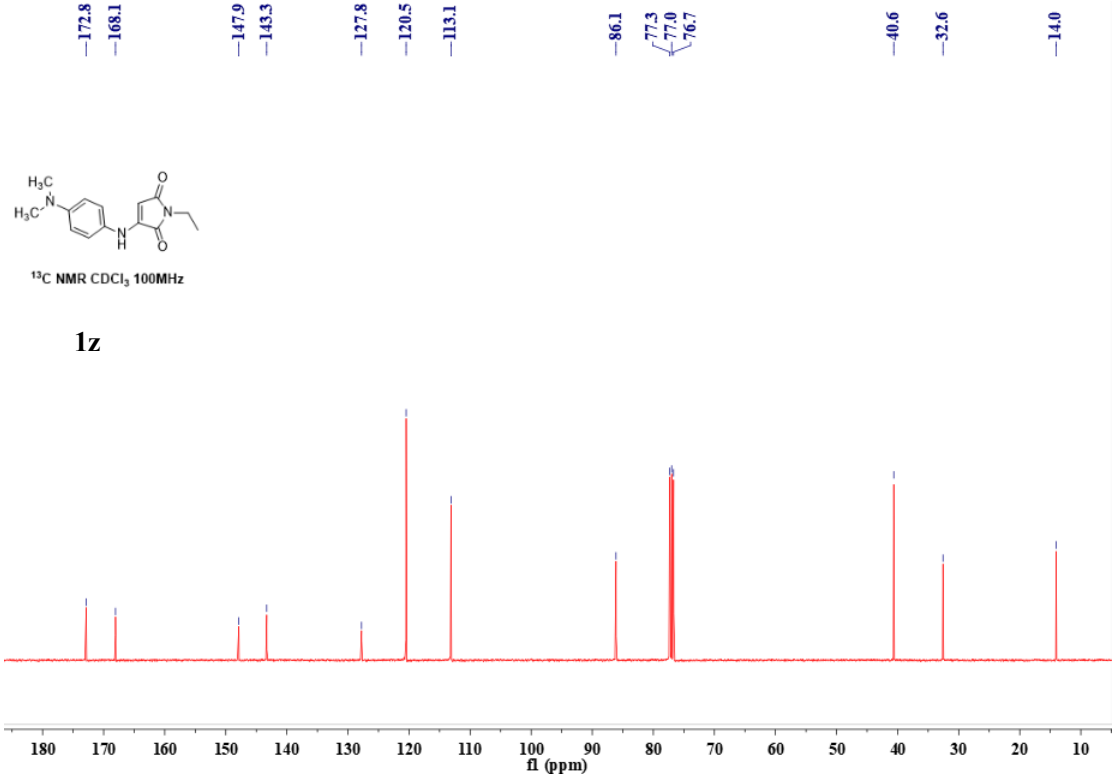
^{13}C NMR $CDCl_3$ 100MHz

1y



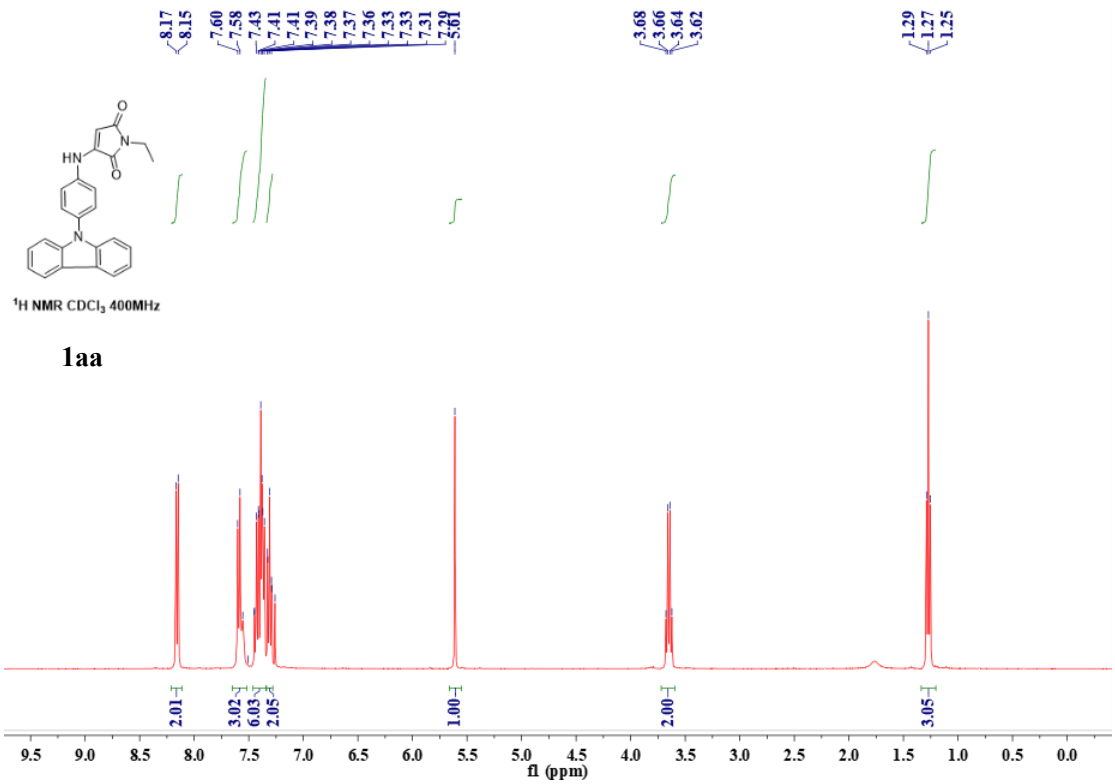
^{1}H NMR $CDCl_3$ 400MHz

1z



^{13}C NMR $CDCl_3$ 100MHz

1z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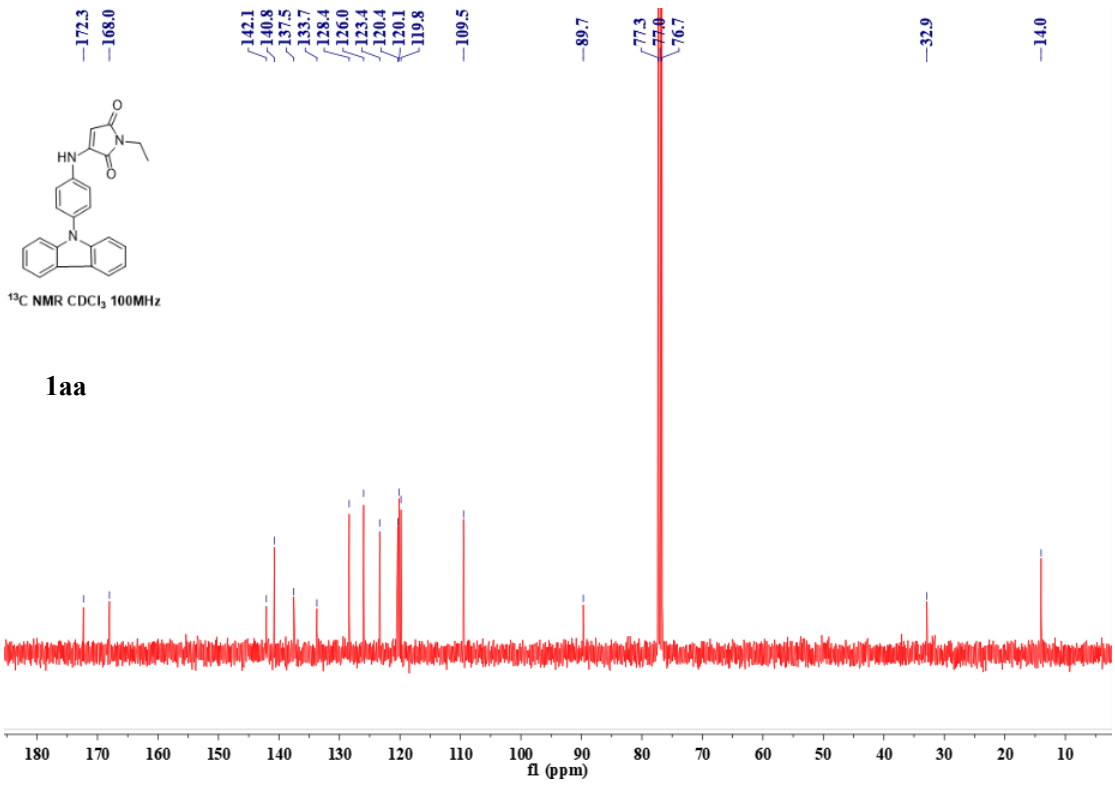
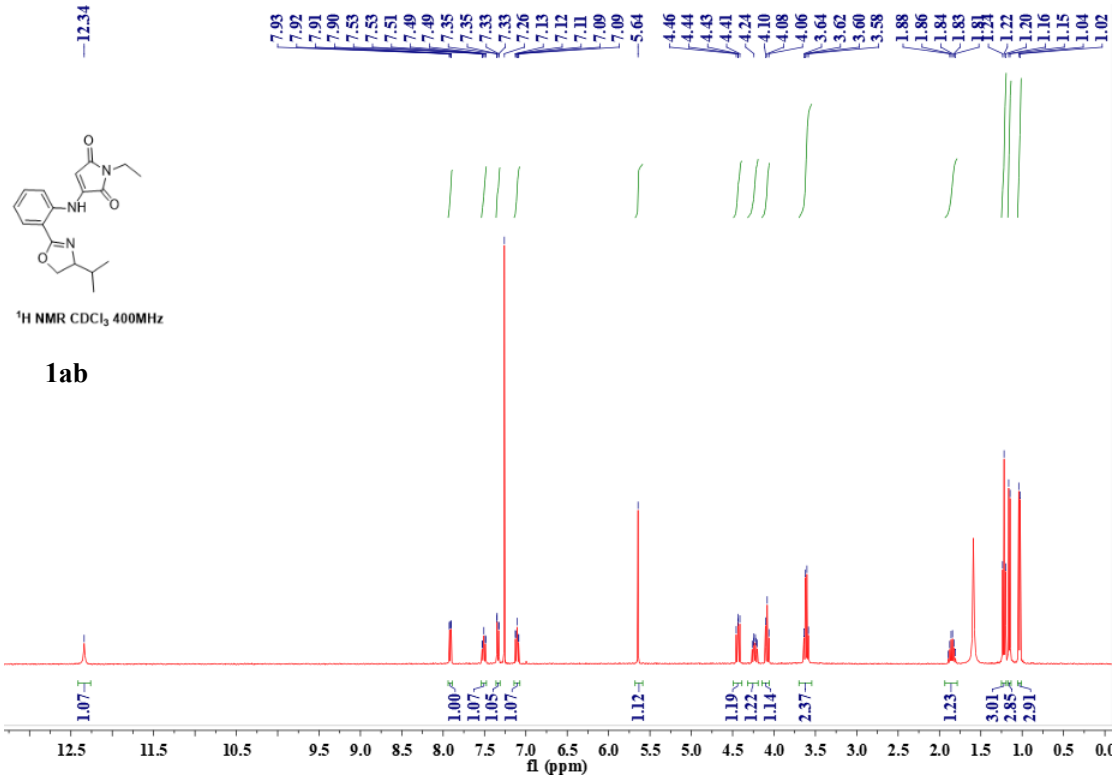
7.31
7.29
5.61
3.68
3.66
3.64
3.62
1.29
1.27
1.25
HN
O
N
O
N
^{1}H NMR CDCl$_3$ 400MHz
2.01
3.02
6.03
2.05
1.00
2.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

1aa

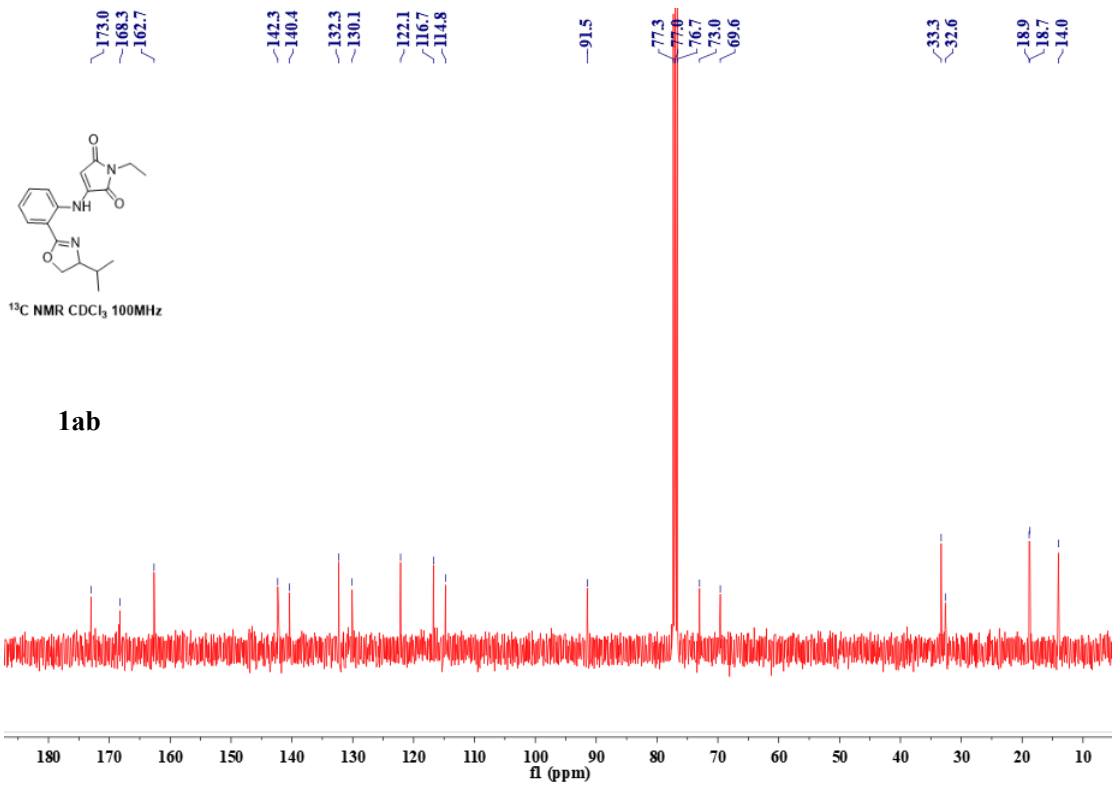

172.3
168.0
142.1
140.8
137.5
133.7
128.4
126.0
123.4
120.4
120.1
119.8
109.5
89.7
77.3
77.0
76.7
32.9
14.0
HN
O
N
O
N
^{13}C NMR CDCl$_3$ 100MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1aa



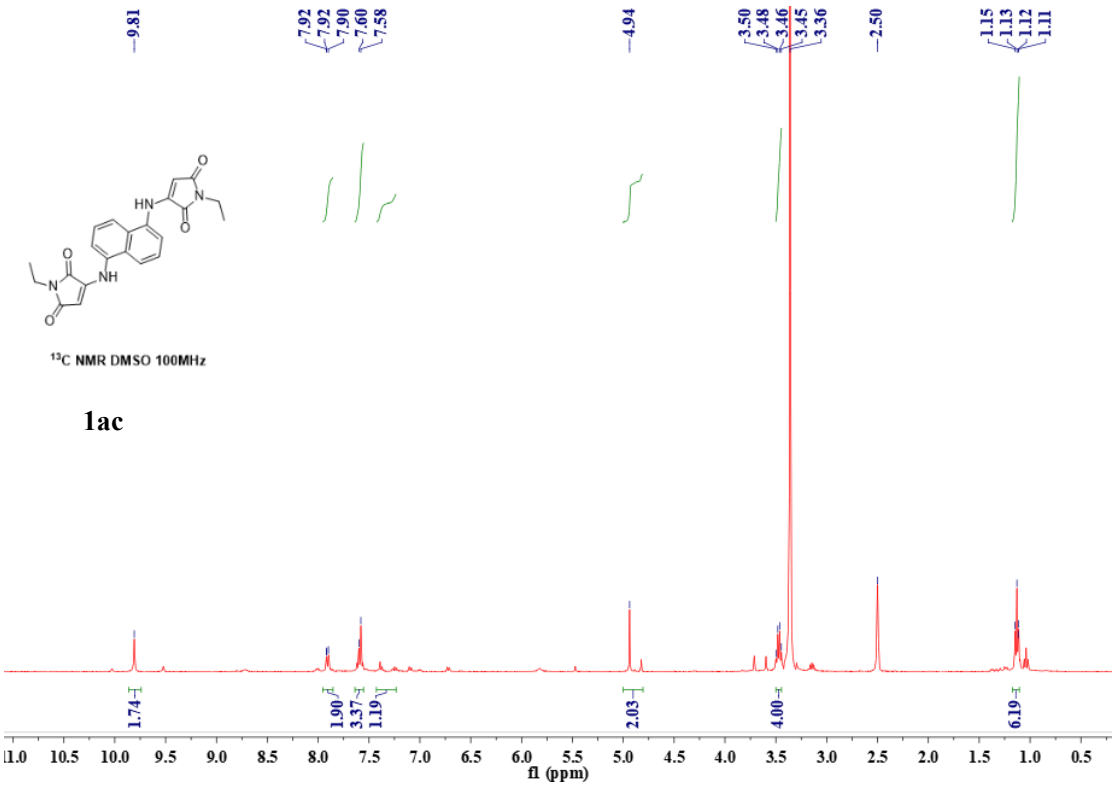
^{1}H NMR $CDCl_3$ 400MHz

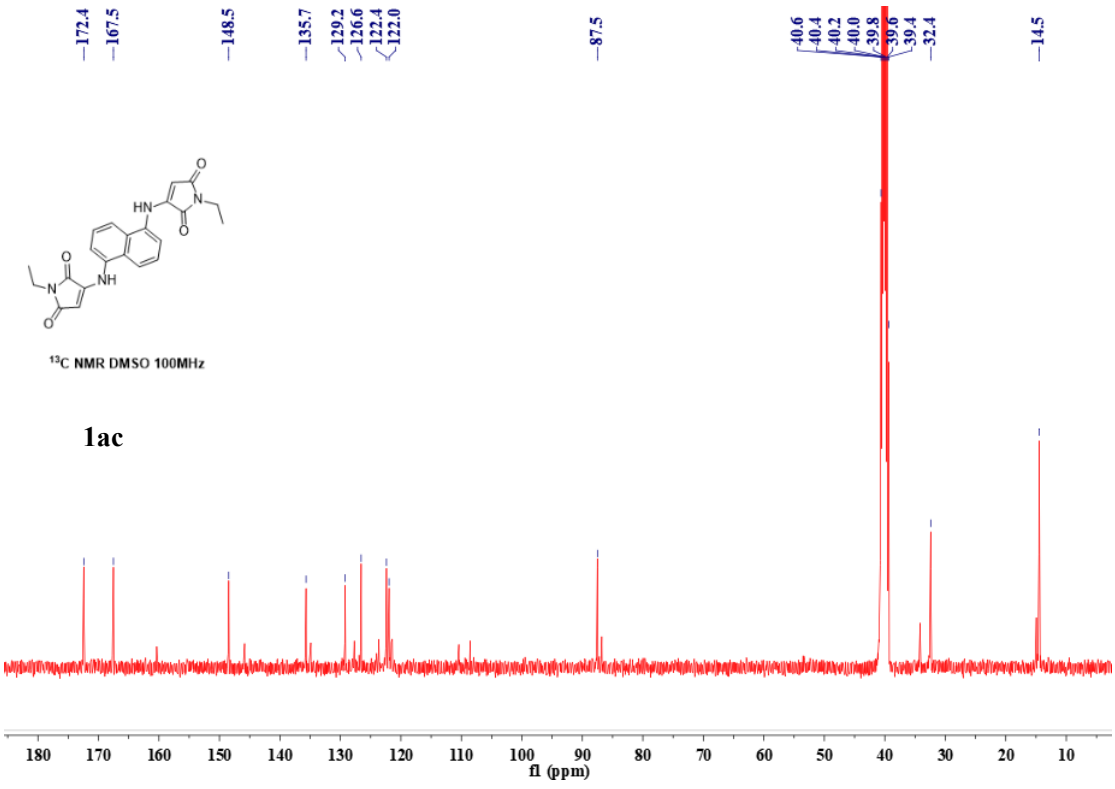
1ab

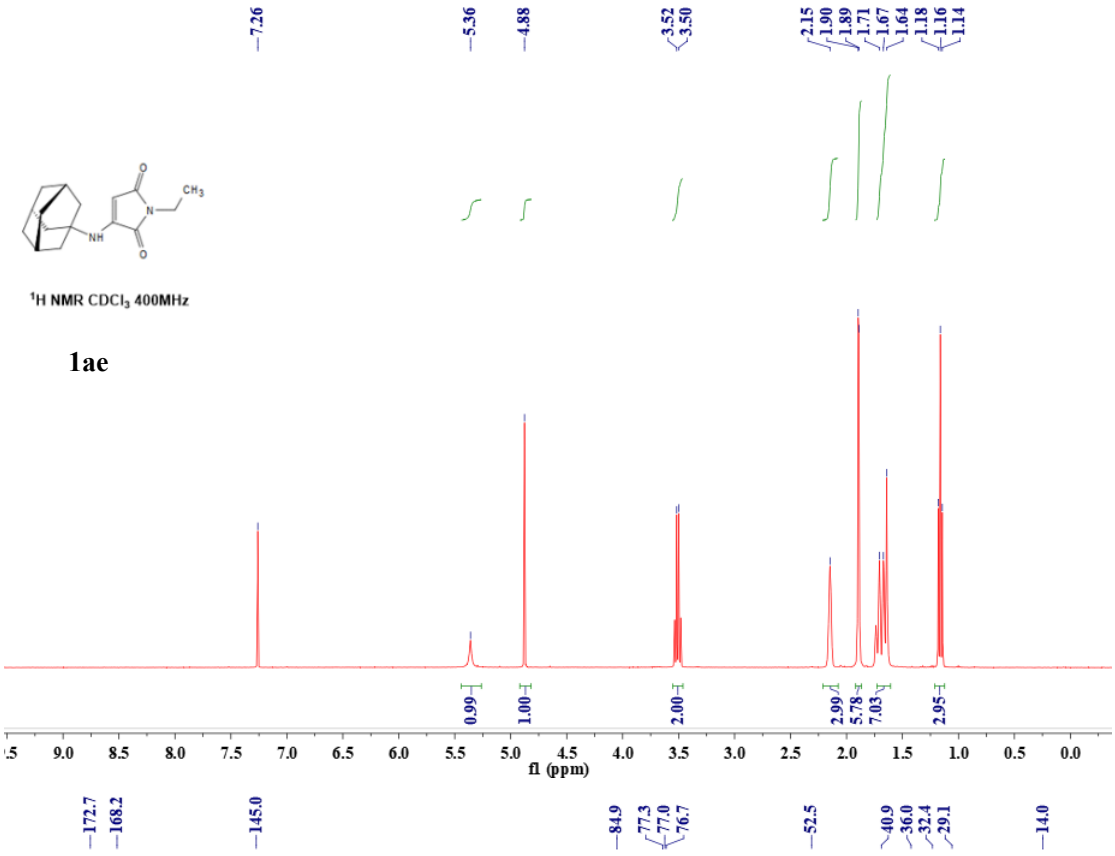


^{13}C NMR $CDCl_3$ 100MHz

1ab

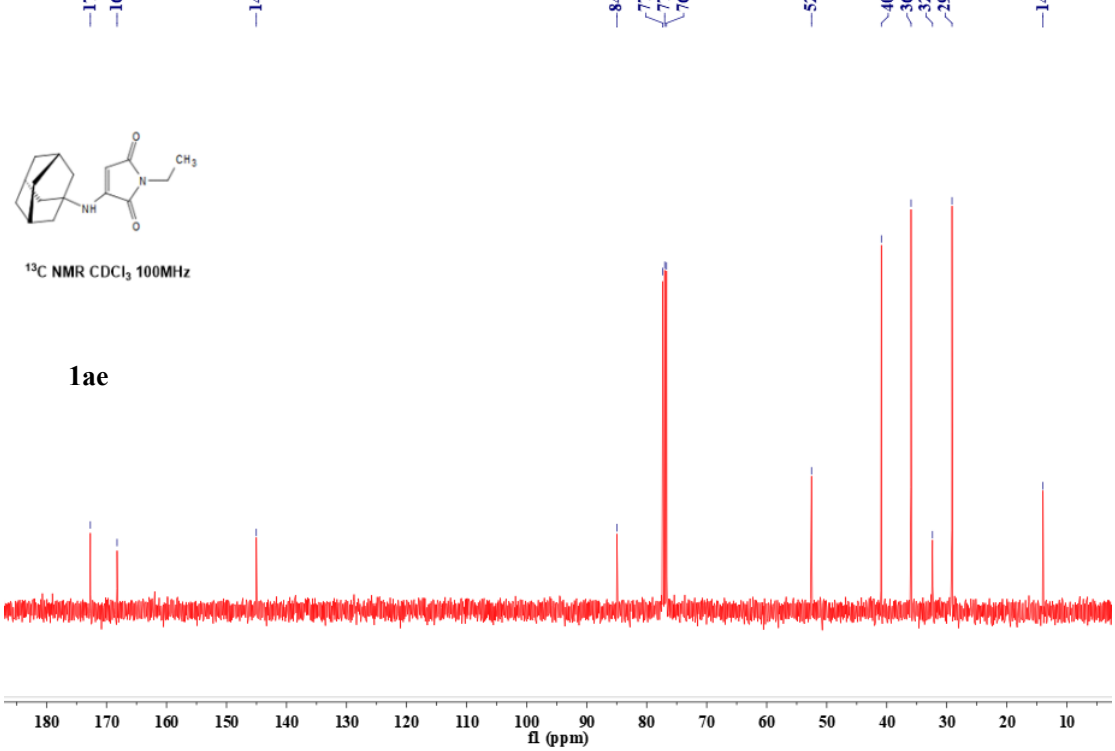

9.81
7.92
7.92
7.90
7.60
7.58
4.94
3.50
3.48
3.46
3.45
3.36
2.50
1.15
1.13
1.12
1.11
HN
NH
O
N
O
13C NMR DMSO 100MHz
1ac
1.74
1.90
3.37
1.19
2.03
4.00
6.19
f1 (ppm)


172.4
167.5
148.5
135.7
129.2
126.6
122.4
122.0
87.5
40.6
40.4
40.2
40.0
39.8
39.6
39.4
32.4
14.5
HN
NH
O
N
O
13C NMR DMSO 100MHz
1ac
f1 (ppm)



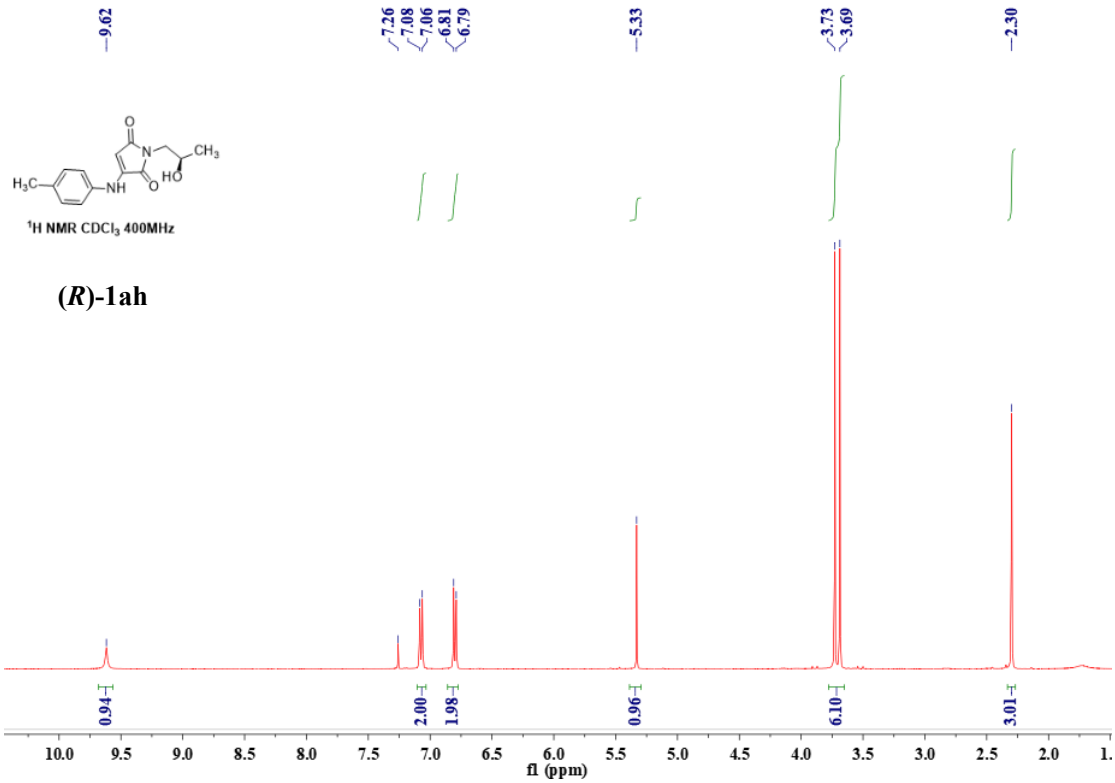
^{1}H NMR $CDCl_3$ 400MHz

1ae



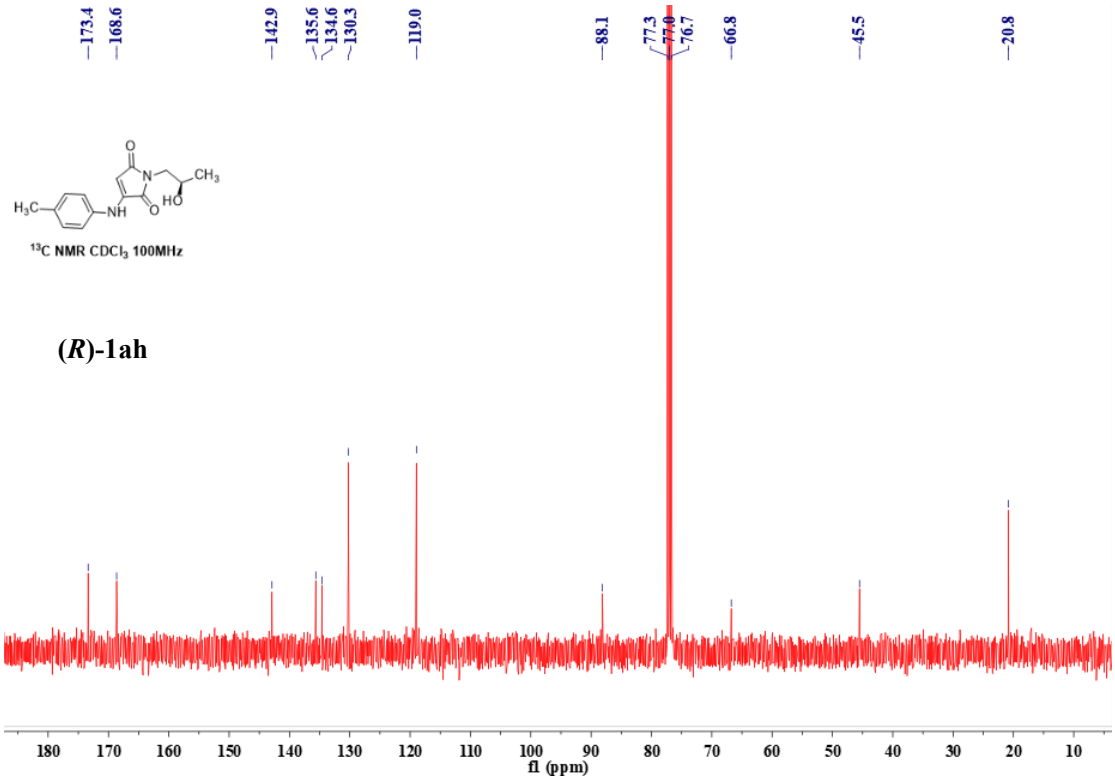
^{13}C NMR $CDCl_3$ 100MHz

1ae



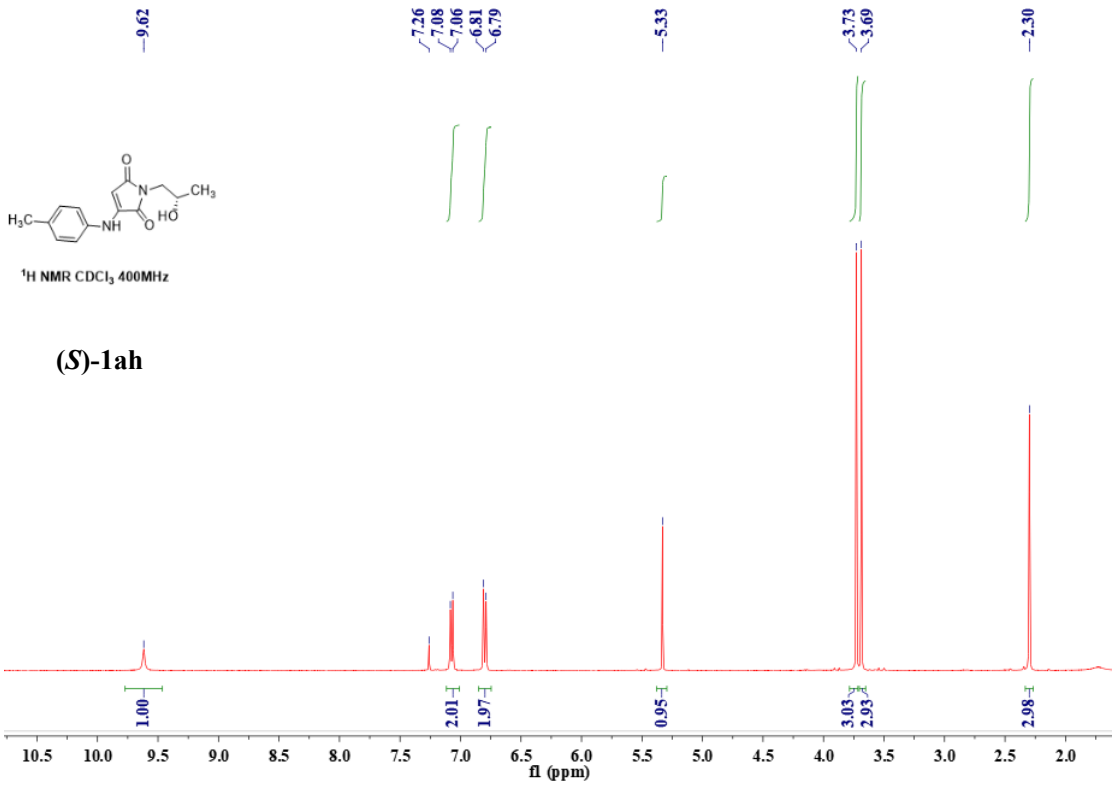
^{1}H NMR $CDCl_3$ 400MHz

(*R*)-1ah

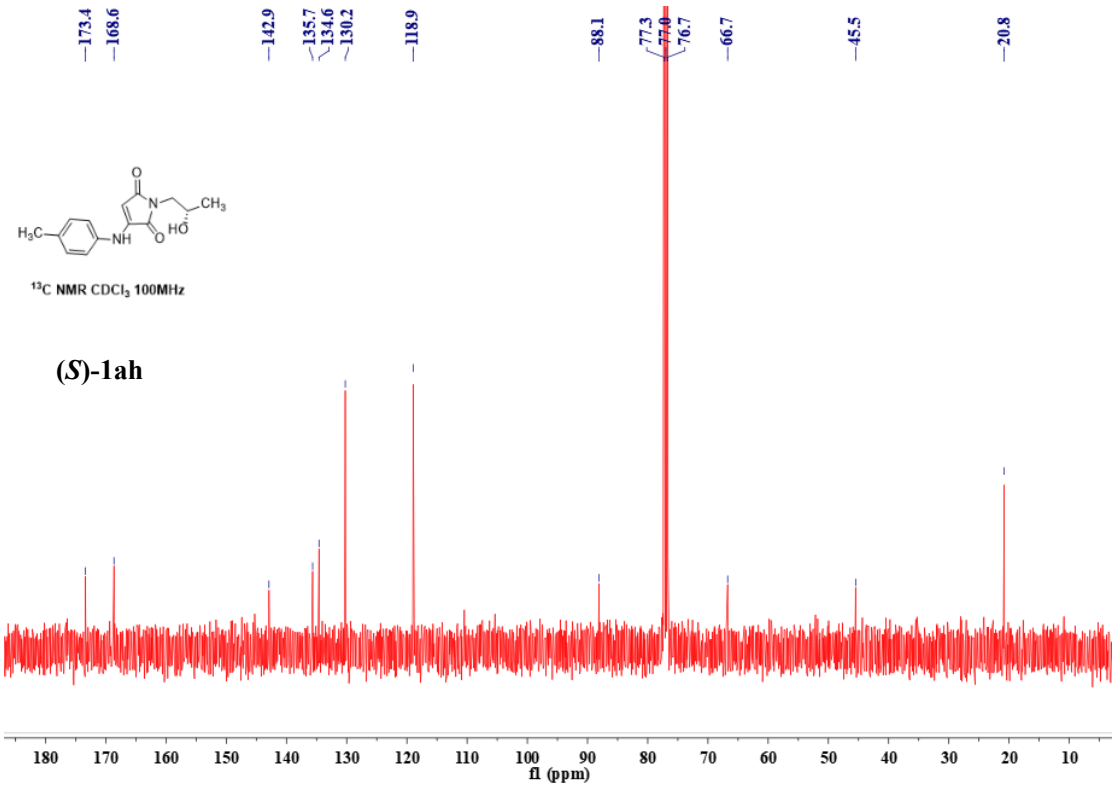


^{13}C NMR $CDCl_3$ 100MHz

(*R*)-1ah

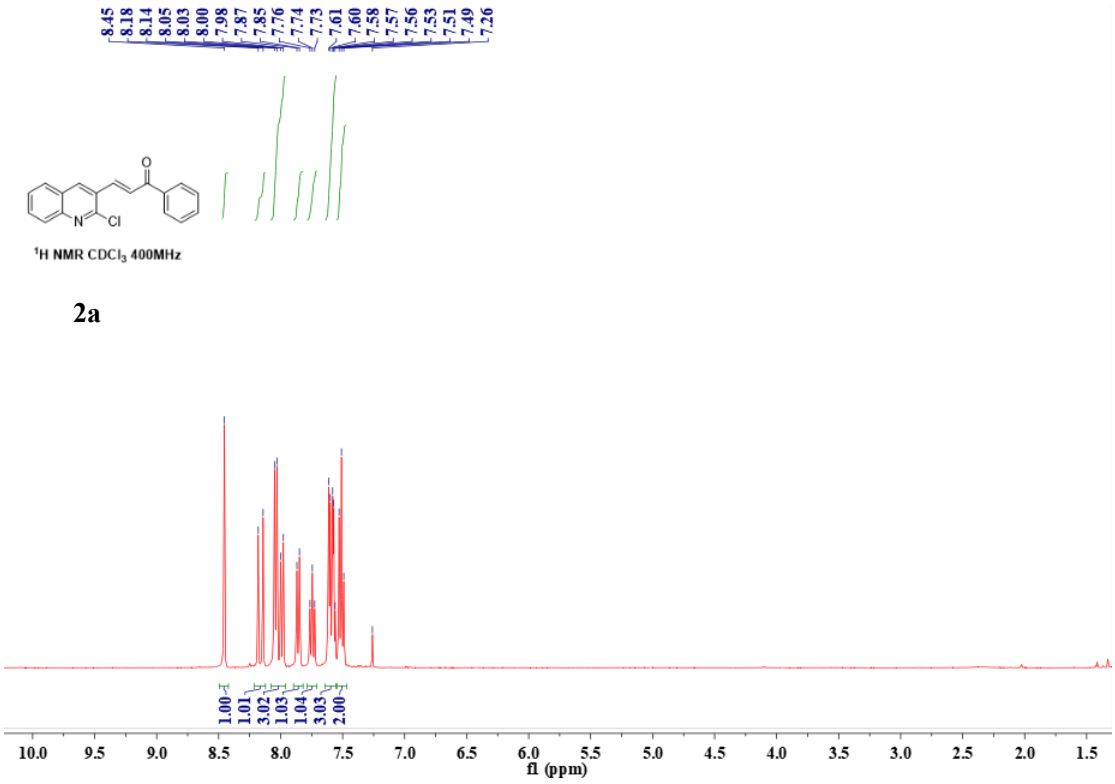

9.62
7.26
7.08
7.06
6.81
6.79
5.33
3.73
3.69
2.30
1H NMR CDCl3 400MHz
1.00
2.01
1.97
0.95
3.03
2.93
2.98
f1 (ppm)

(*S*)-1ah


173.4
168.6
142.9
135.7
134.6
130.2
118.9
88.1
77.3
77.0
76.7
66.7
45.5
20.8
13C NMR CDCl3 100MHz
f1 (ppm)

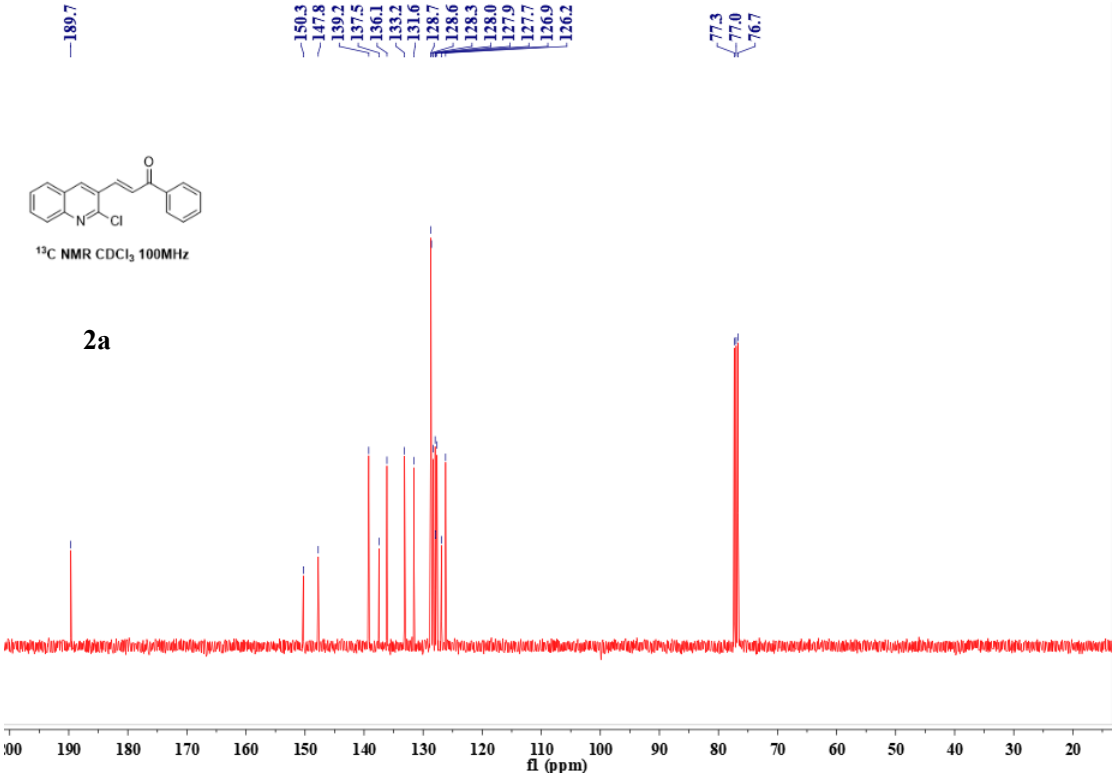
(*S*)-1ah

11. NMR Spectra of *ortho*-halogenatedquinolin/pyridine chalcones



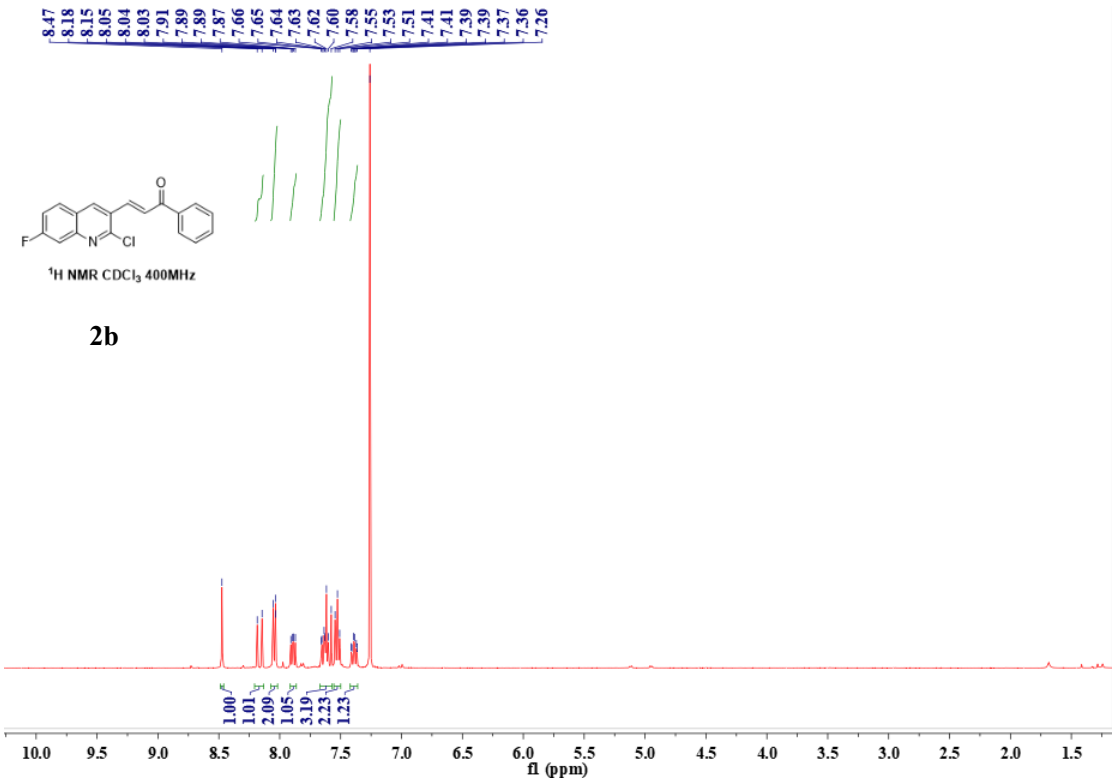
^{1}H NMR $CDCl_3$ 400MHz

2a

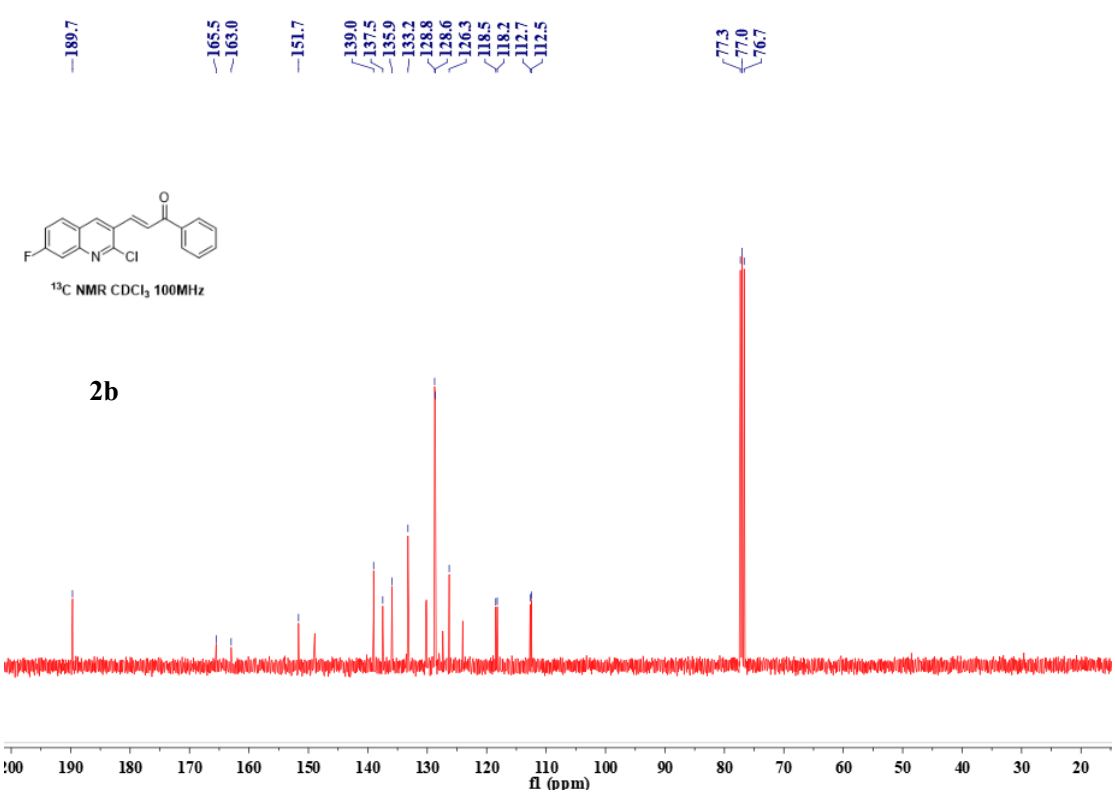


^{13}C NMR $CDCl_3$ 100MHz

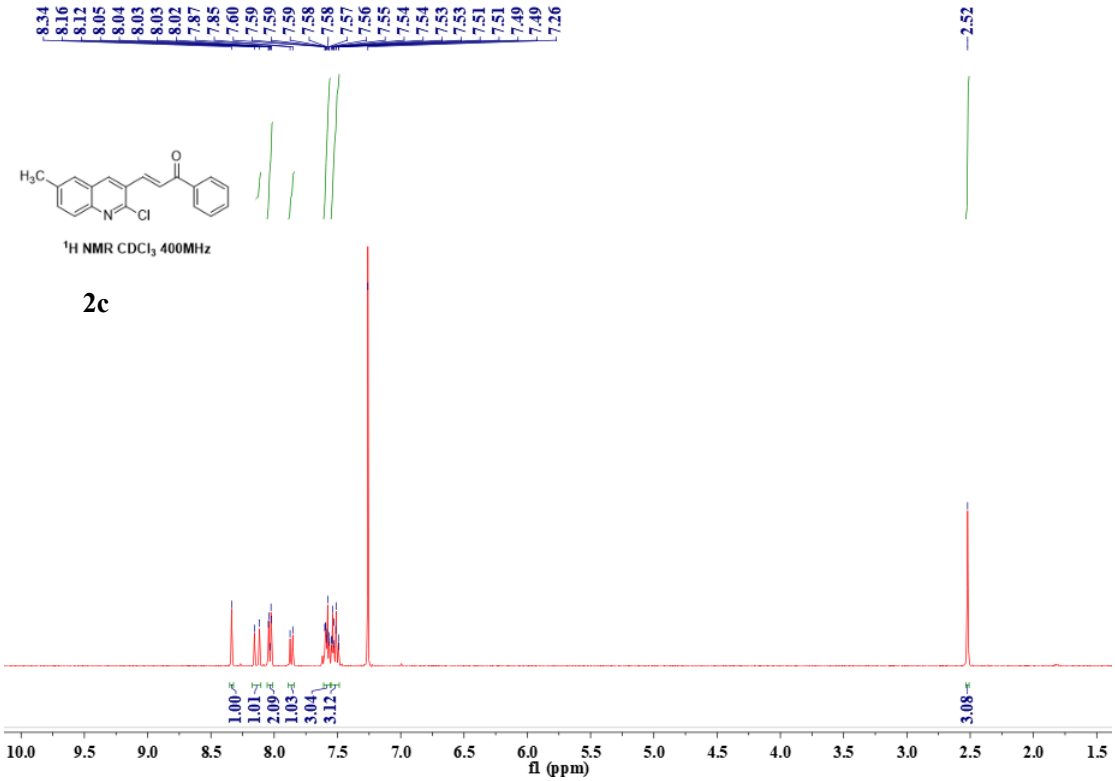
2a

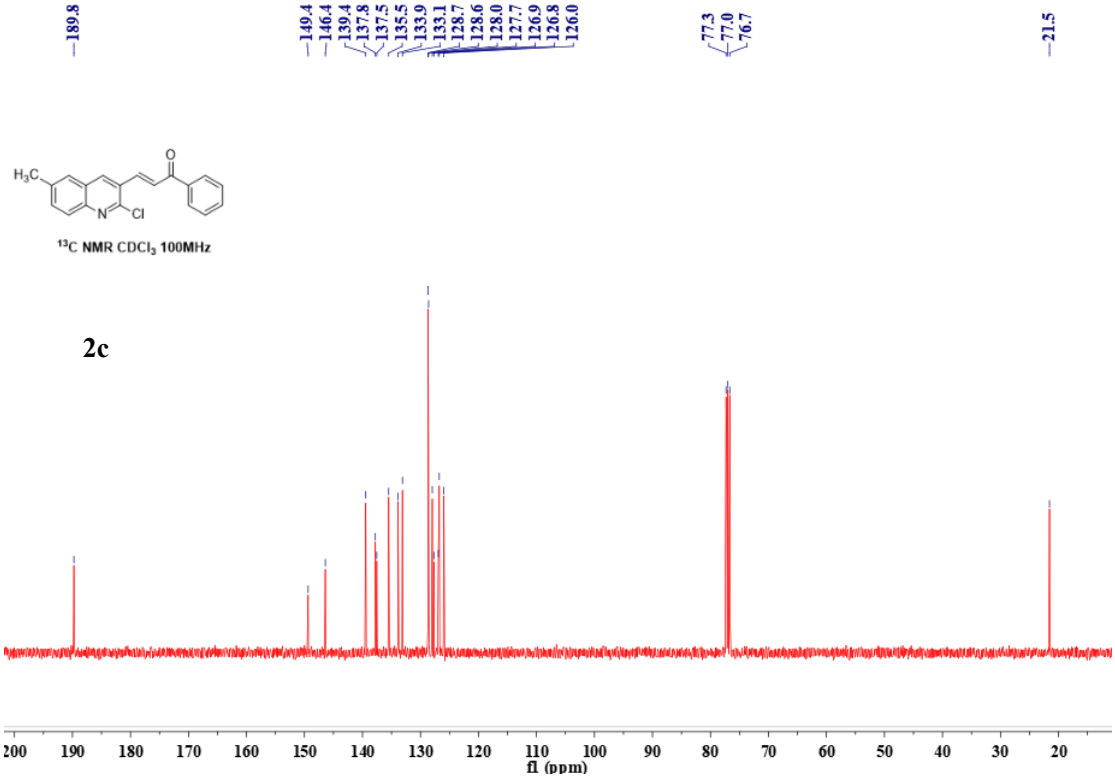

8.47
8.18
8.15
8.05
8.04
8.03
7.91
7.89
7.89
7.87
7.66
7.65
7.64
7.63
7.62
7.60
7.58
7.55
7.53
7.51
7.41
7.41
7.39
7.39
7.37
7.36
7.26
O
F
N
Cl
1H NMR CDCl3 400MHz
1.00
1.01
2.09
1.05
3.19
2.23
1.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

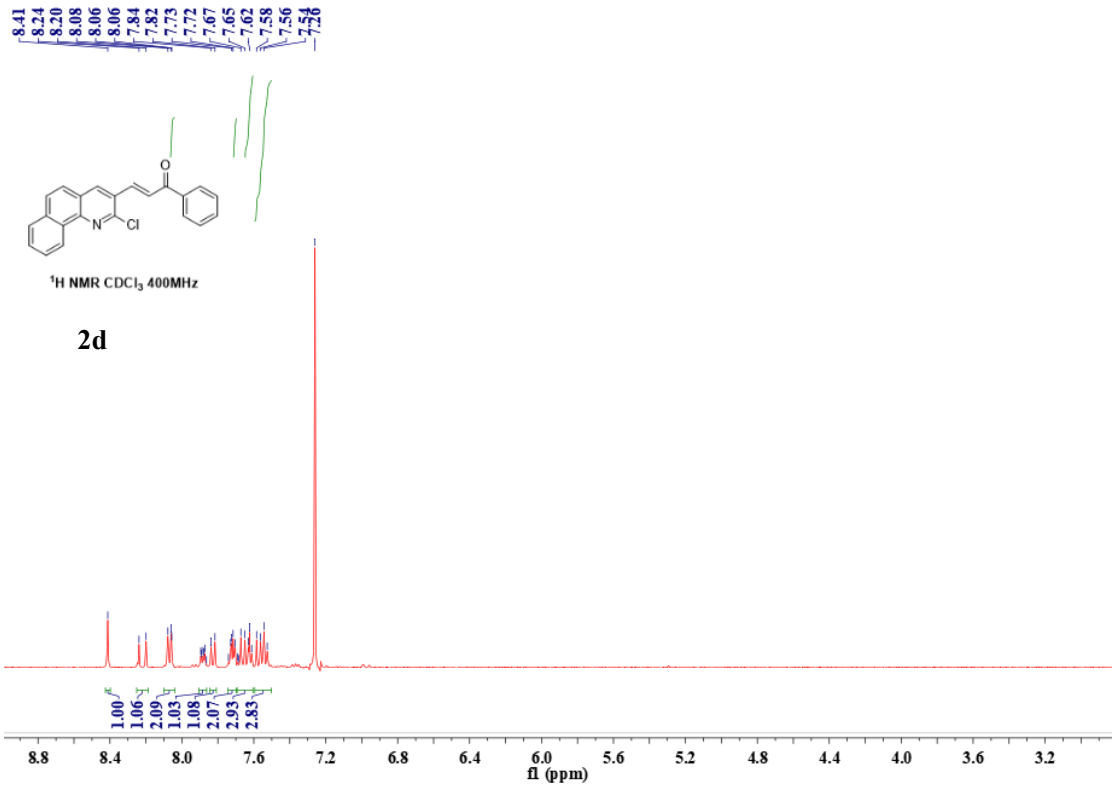
2b

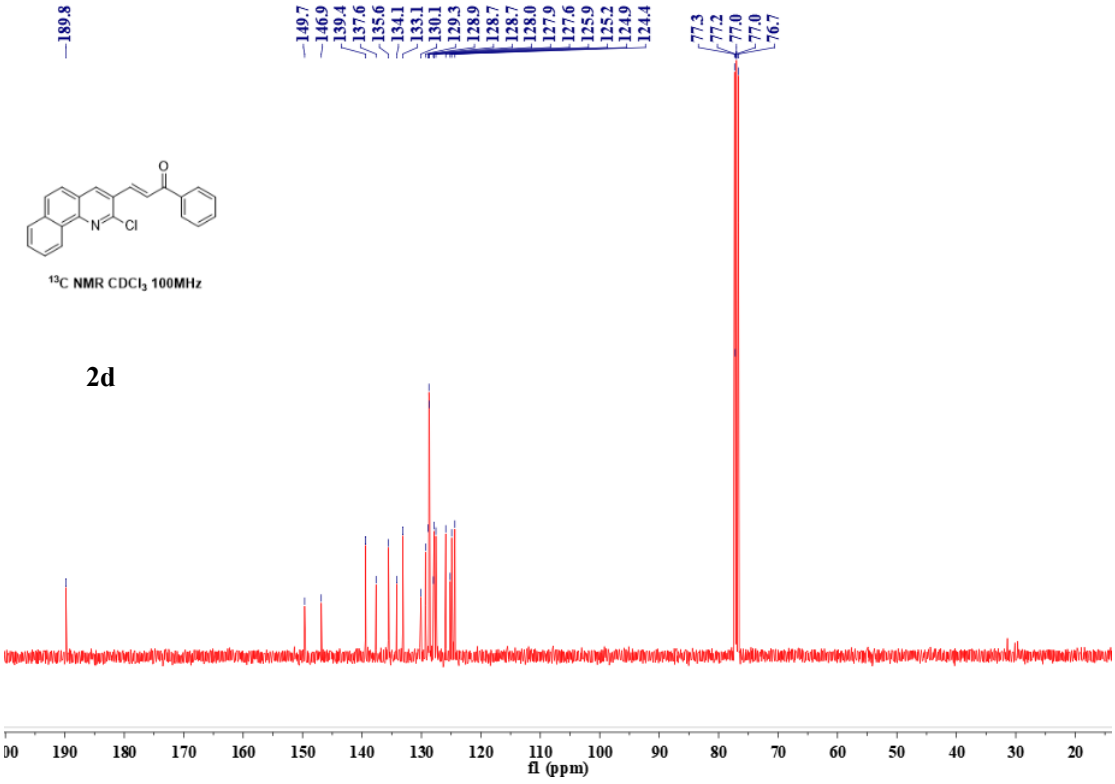

189.7
165.5
163.0
151.7
139.0
137.5
135.9
133.2
128.8
128.6
126.3
118.5
118.2
112.7
112.5
77.3
77.0
76.7
O
F
N
Cl
13C NMR CDCl3 100MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

2b


8.34
8.16
8.12
8.05
8.04
8.03
8.03
8.02
7.87
7.85
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.56
7.55
7.54
7.54
7.53
7.53
7.51
7.51
7.49
7.49
7.26
2.52
H3C
O
N
Cl
1H NMR CDCl3 400MHz
2c
1.00
1.01
2.09
1.03
3.04
3.12
3.08
10.0
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)

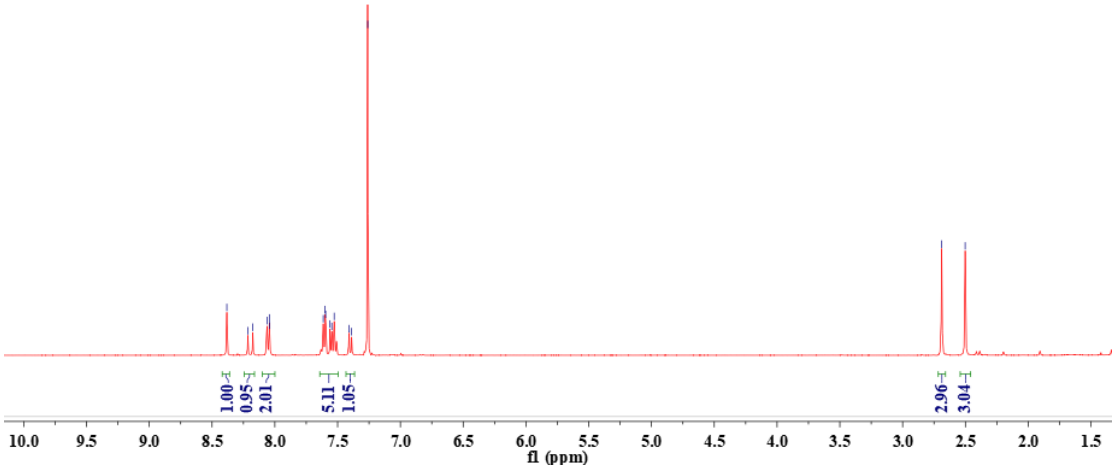

189.8
149.4
146.4
139.4
137.8
137.5
135.5
133.9
133.1
128.7
128.6
128.0
127.7
126.9
126.8
126.0
77.3
77.0
76.7
21.5
H3C
O
N
Cl
13C NMR CDCl3 100MHz
2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

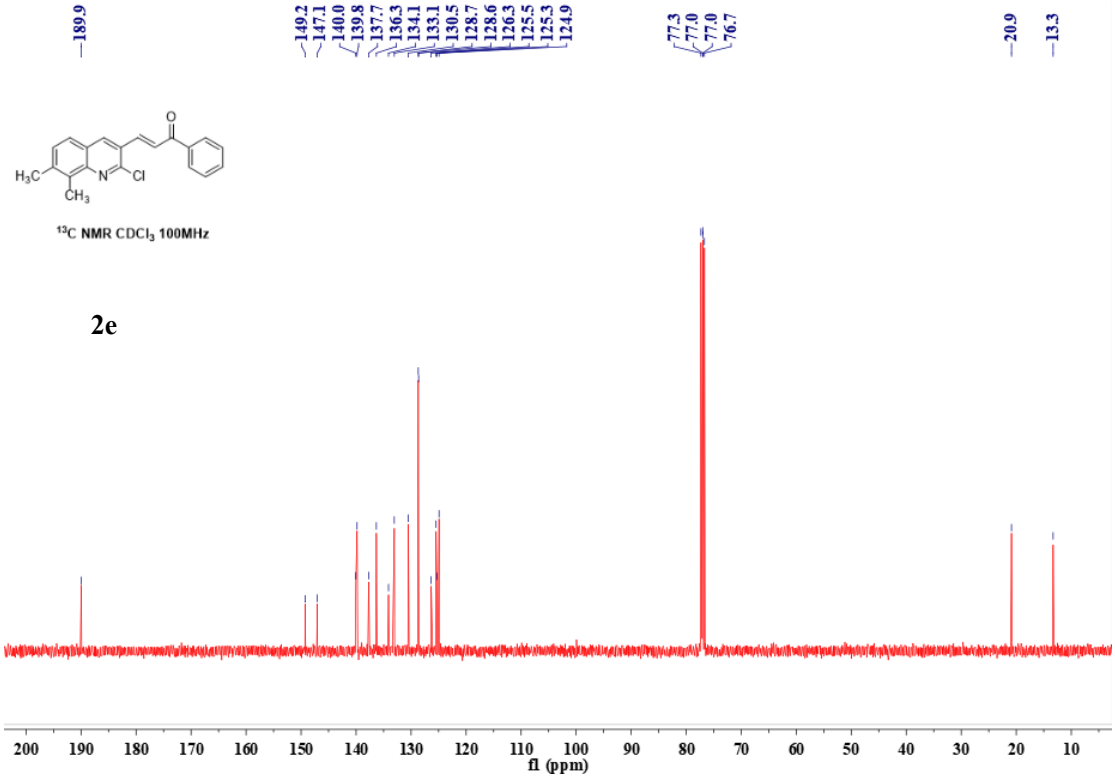

8.41
8.24
8.20
8.08
8.06
8.06
7.84
7.82
7.73
7.72
7.67
7.65
7.62
7.58
7.56
7.54
7.26
O
N
Cl
1H NMR CDCl3 400MHz
2d
1.00
1.06
2.09
1.03
1.08
2.07
2.93
2.83
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
f1 (ppm)


189.8
149.7
146.9
139.4
137.6
135.6
134.1
133.1
130.1
129.3
128.9
128.7
128.7
128.0
127.9
127.6
125.9
125.2
124.9
124.4
77.3
77.2
77.0
77.0
76.7
O
N
Cl
13C NMR CDCl3 100MHz
2d
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

^{1}H NMR $CDCl_3$ 400MHz

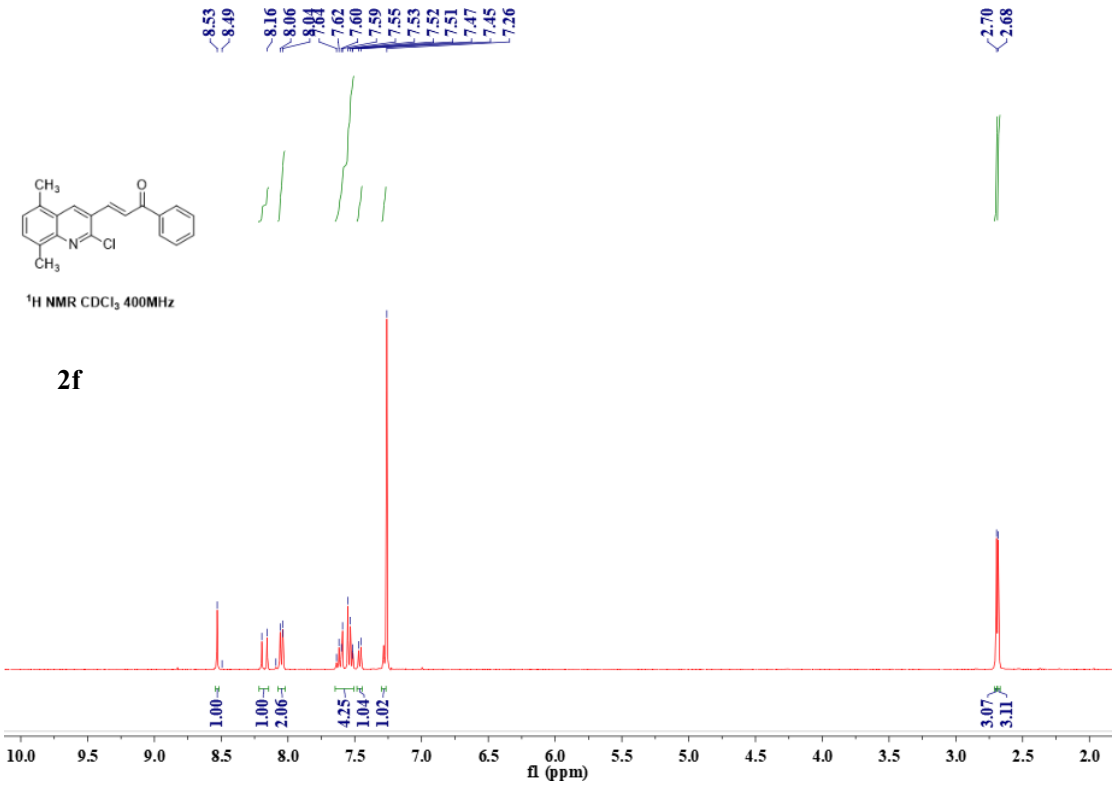
2e

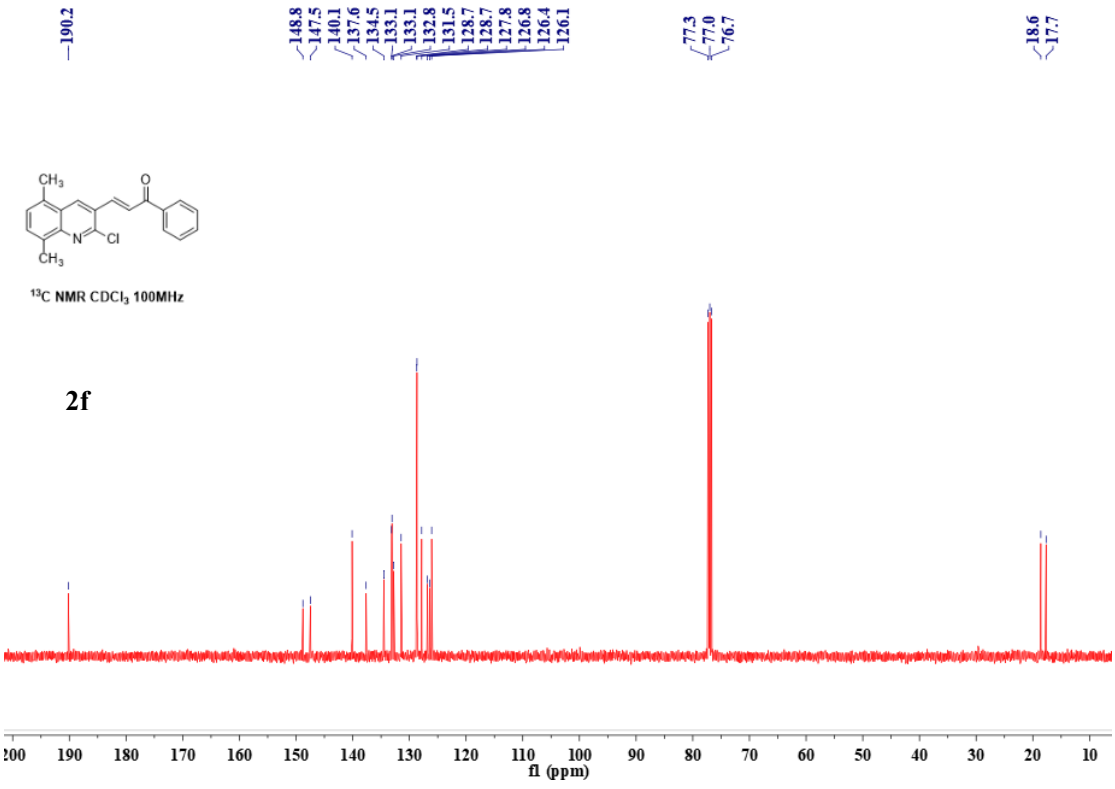




^{13}C NMR $CDCl_3$ 100MHz

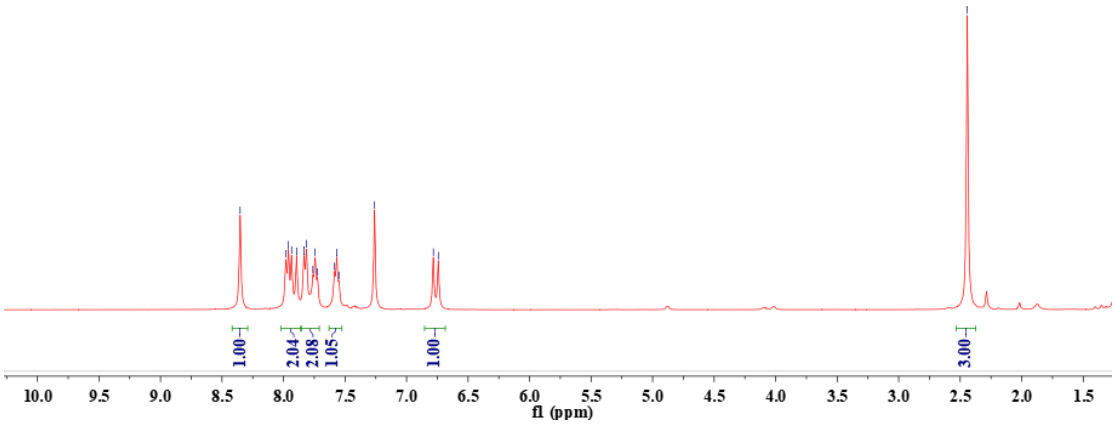
2e

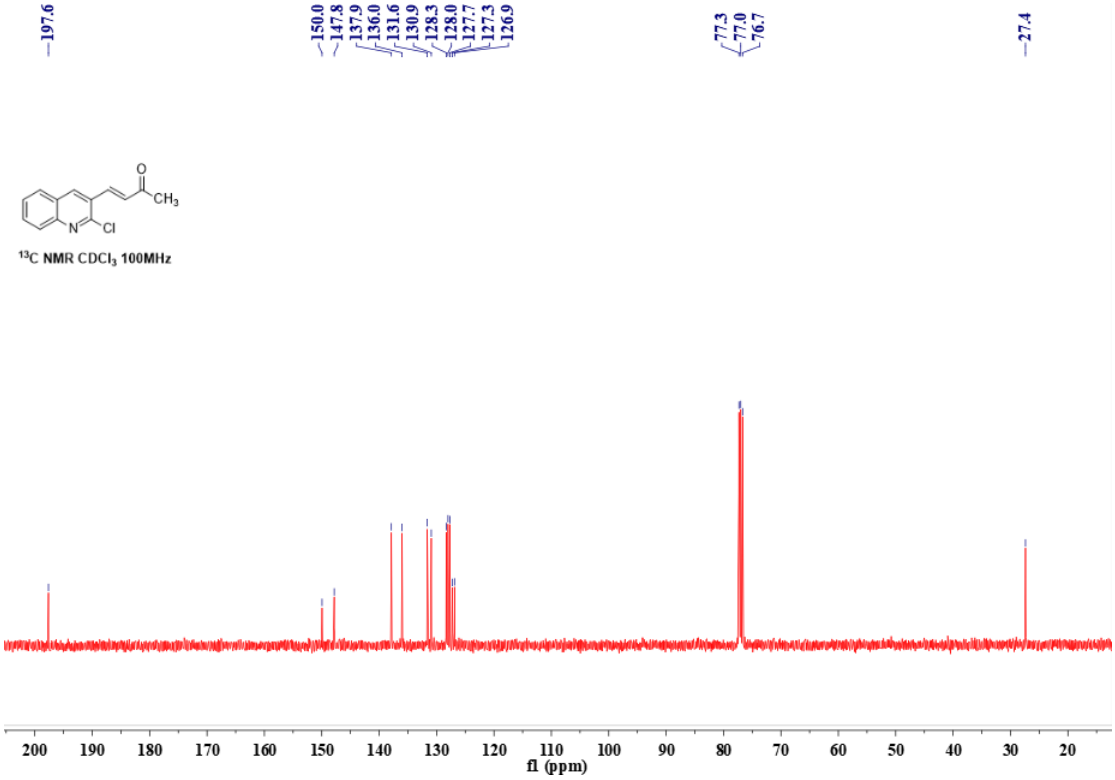

8.53
8.49
8.16
8.06
8.04
8.01
7.62
7.60
7.59
7.55
7.53
7.52
7.51
7.47
7.45
7.26
2.70
2.68
CH3
O
N
Cl
CH3
1H NMR CDCl3 400MHz
2f
1.00
1.00
2.06
4.25
1.04
1.02
3.07
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


190.2
148.8
147.5
140.1
137.6
134.5
133.1
133.1
132.8
131.5
128.7
128.7
127.8
126.8
126.4
126.1
77.3
77.0
76.7
18.6
17.7
CH3
O
N
Cl
CH3
13C NMR CDCl3 100MHz
2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

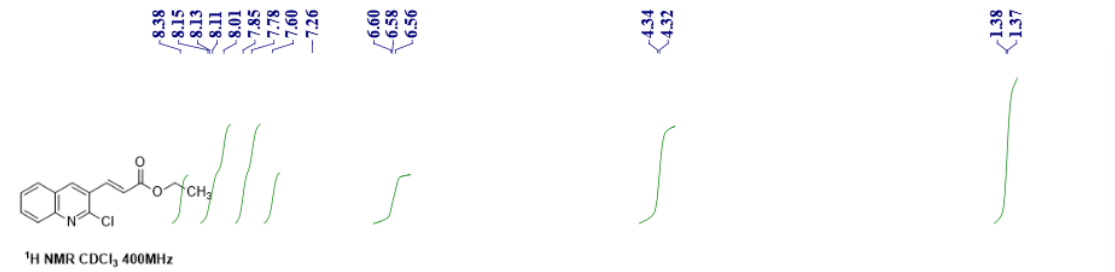
^{1}H NMR $CDCl_3$ 400MHz

2g



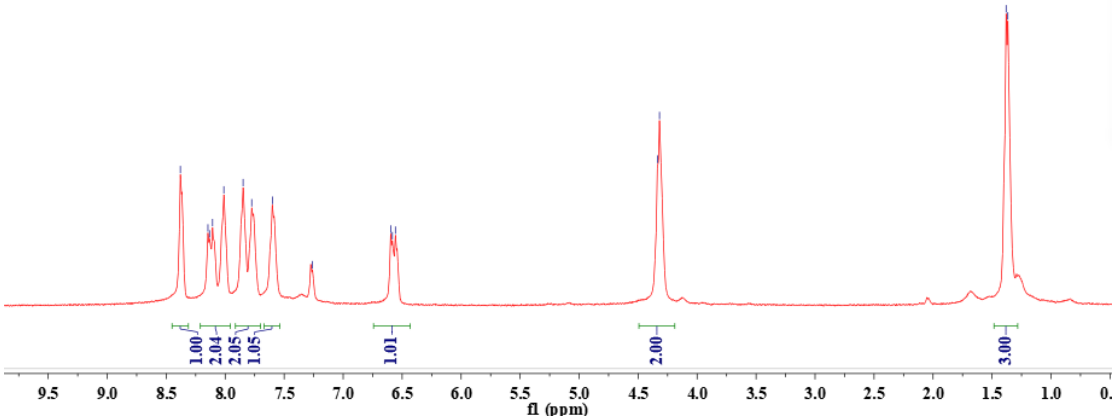


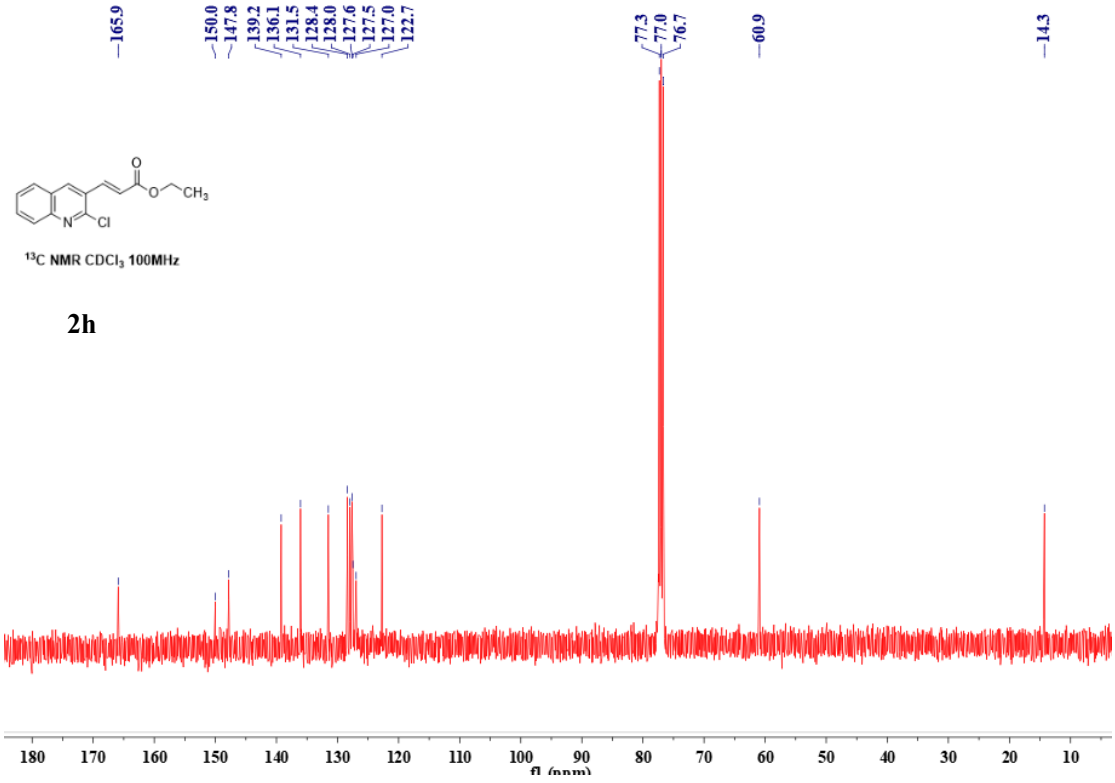
^{13}C NMR $CDCl_3$ 100MHz



^{1}H NMR $CDCl_3$ 400MHz

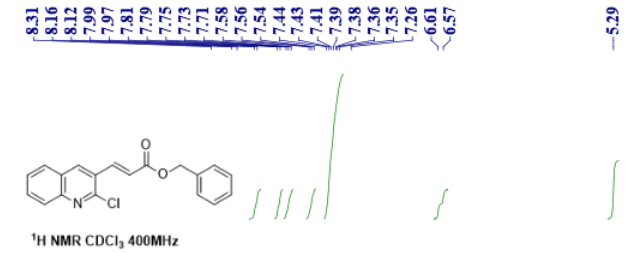
2h





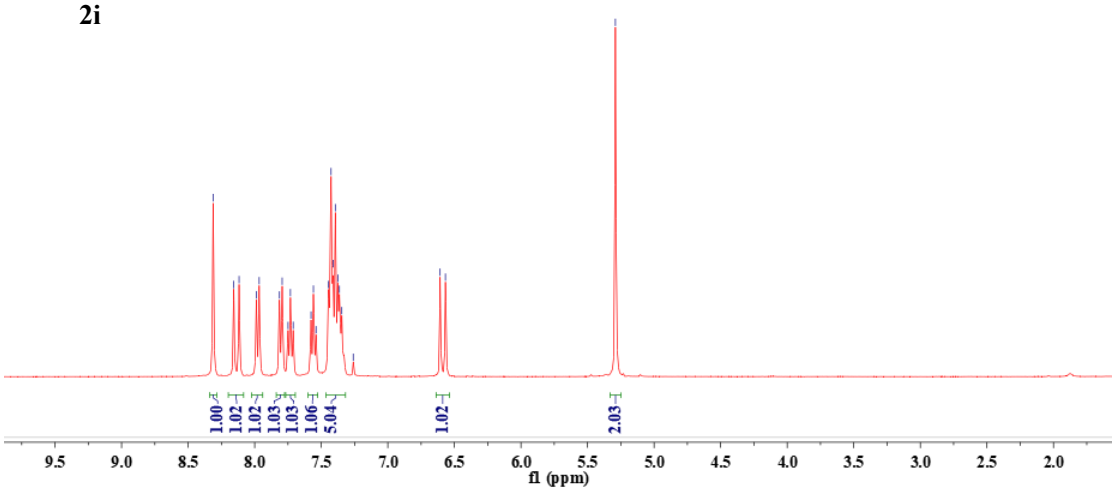
^{13}C NMR $CDCl_3$ 100MHz

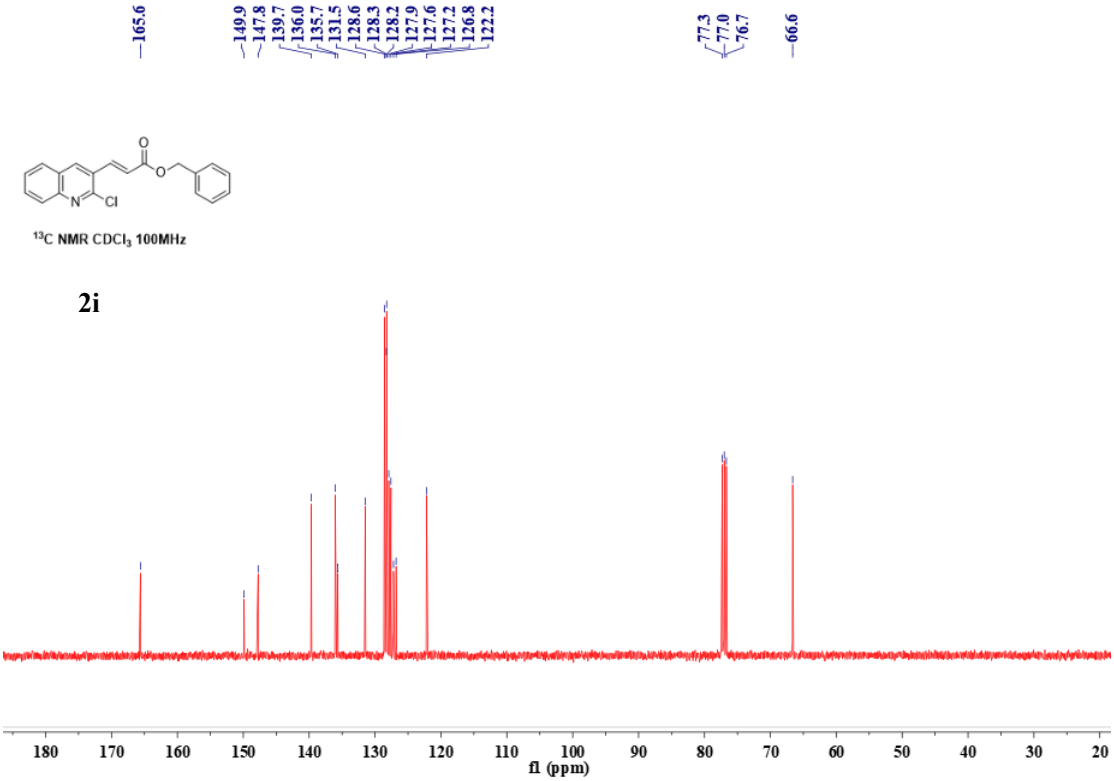
2h



^{1}H NMR $CDCl_3$ 400MHz

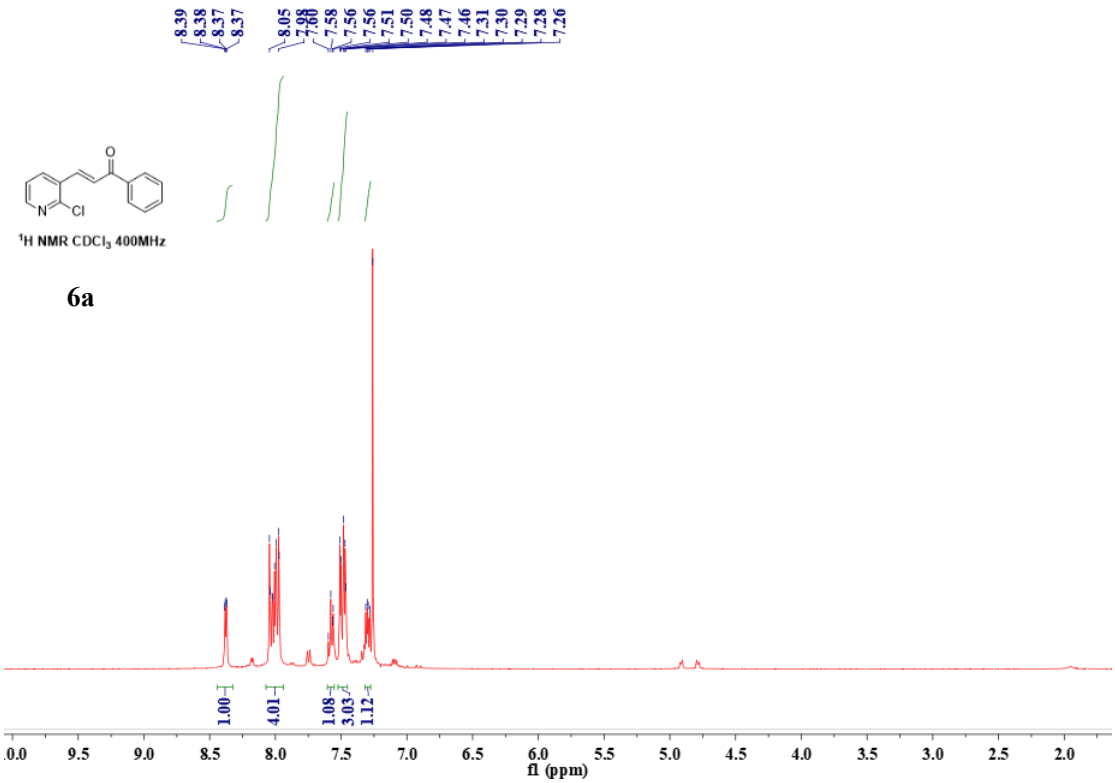
2i





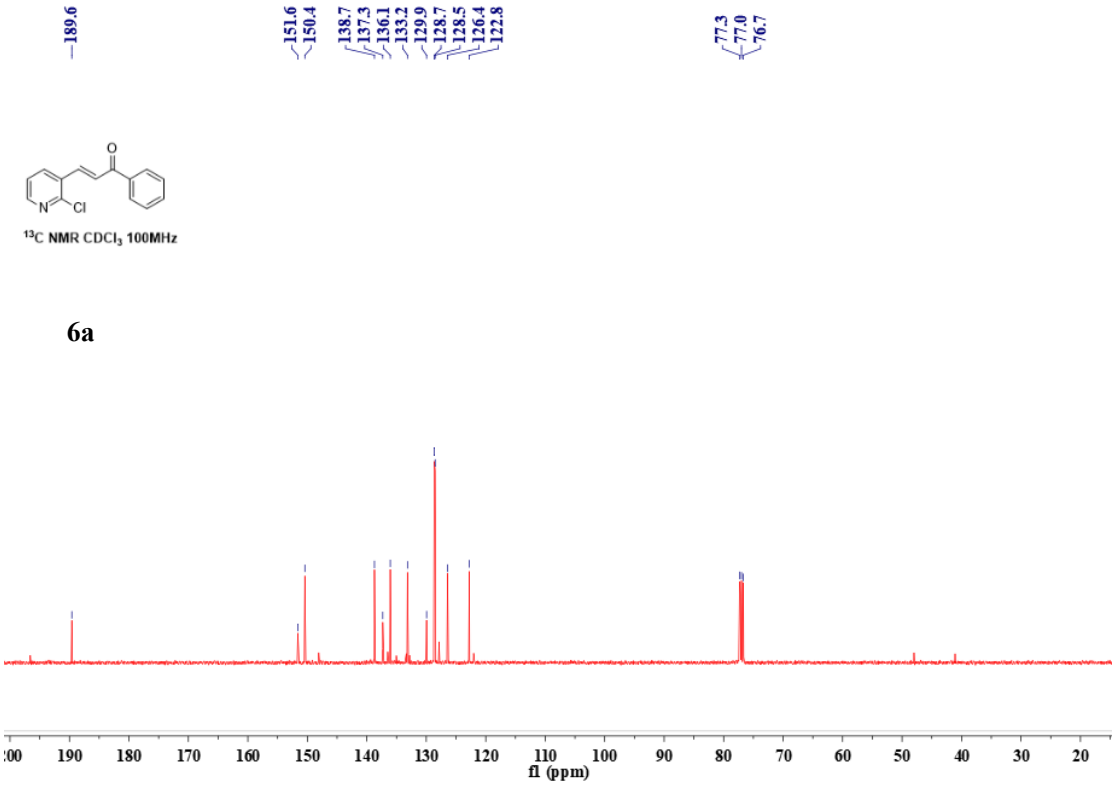
^{13}C NMR $CDCl_3$ 100MHz

2i



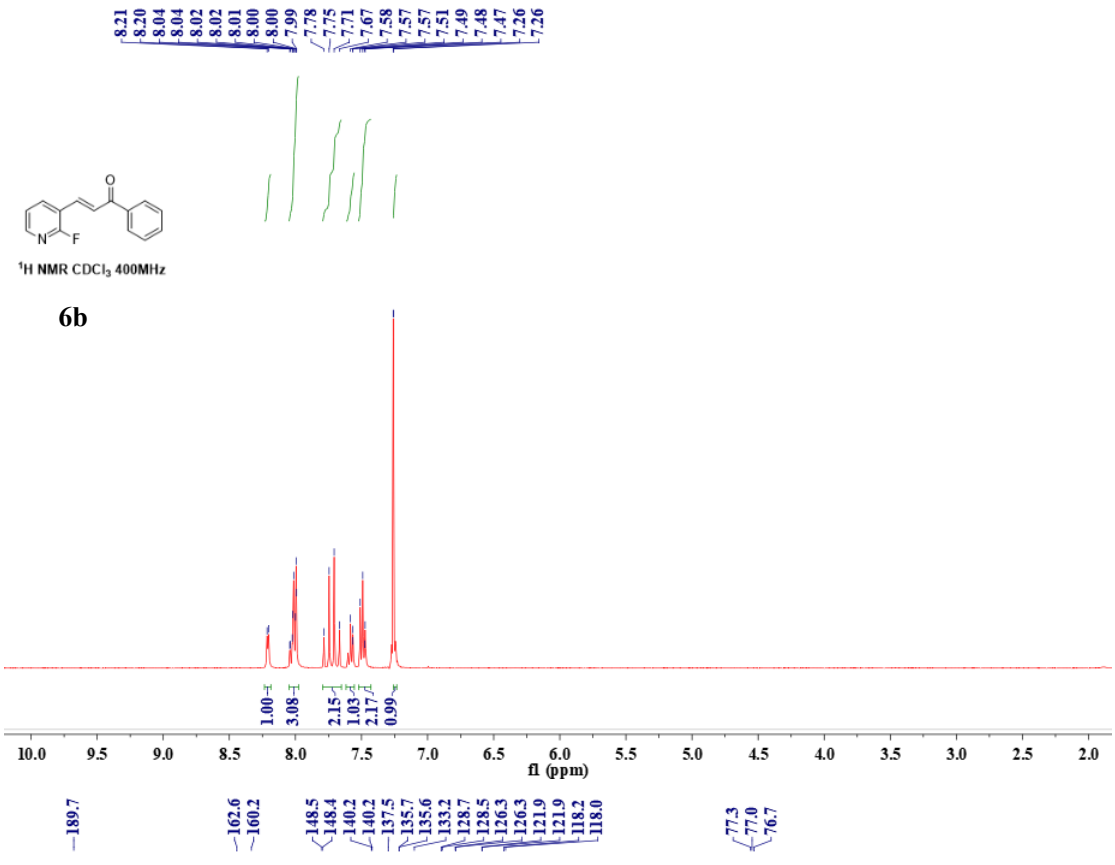
^{1}H NMR $CDCl_3$ 400MHz

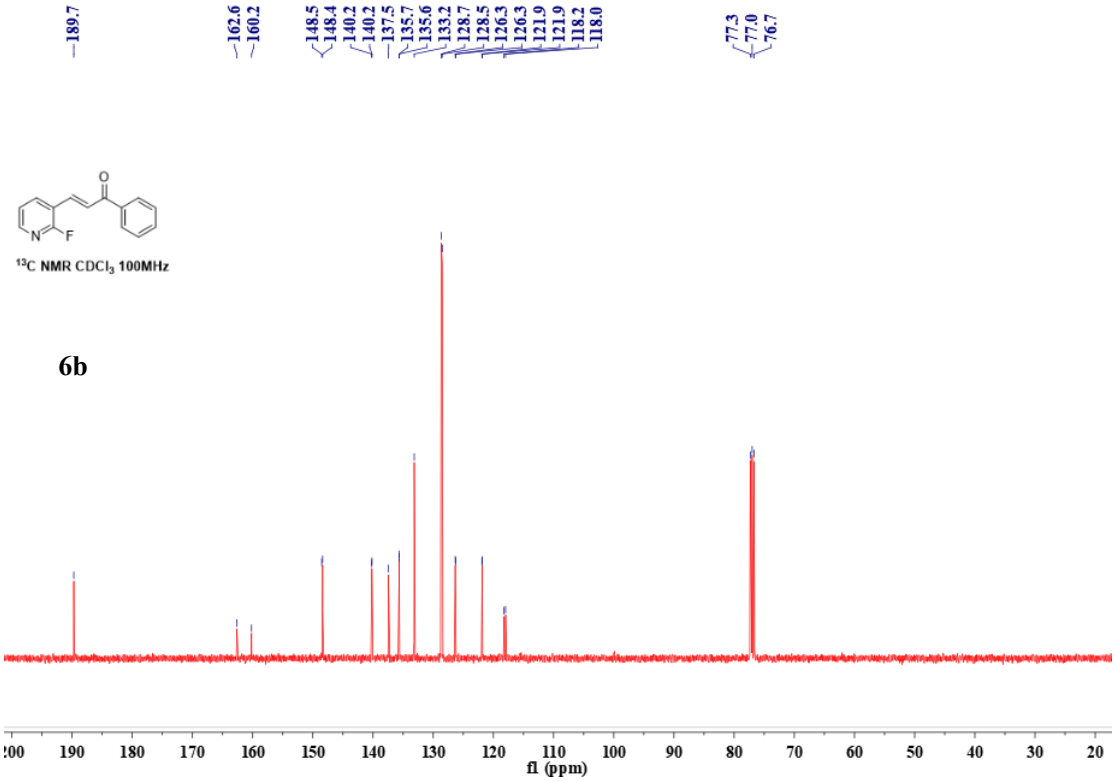
6a



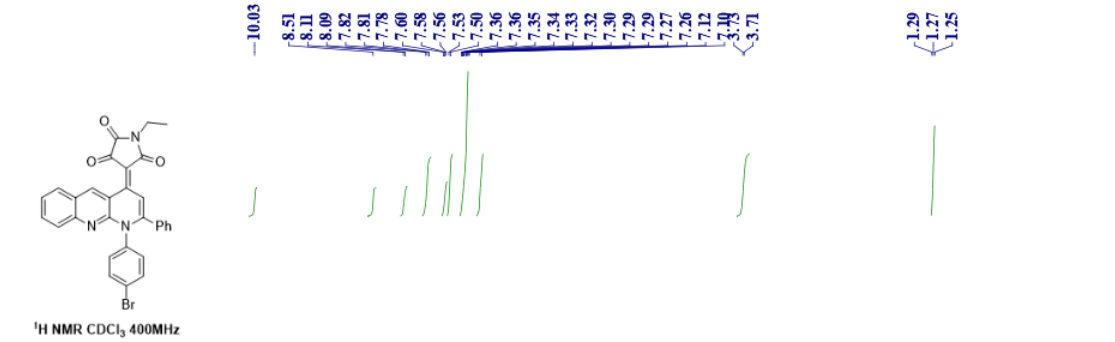
^{13}C NMR $CDCl_3$ 100MHz

6a

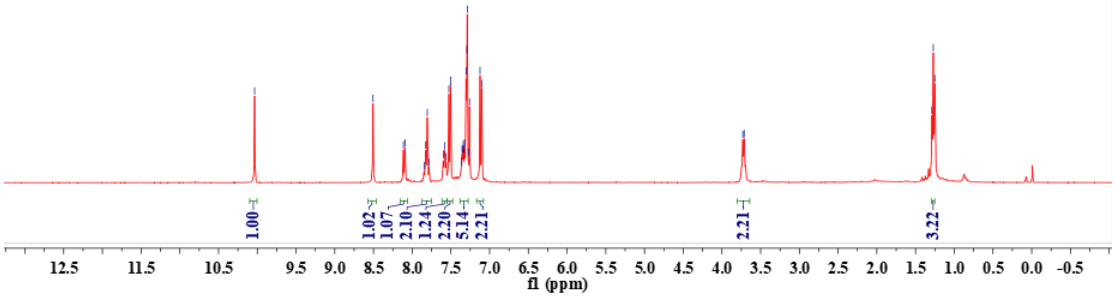

8.21
8.20
8.04
8.04
8.02
8.02
8.01
8.00
8.00
7.99
7.78
7.75
7.71
7.67
7.58
7.57
7.57
7.51
7.49
7.48
7.47
7.26
7.26
O
N
F
1H NMR CDCl3 400MHz
6b
1.00
3.08
2.15
1.03
2.17
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

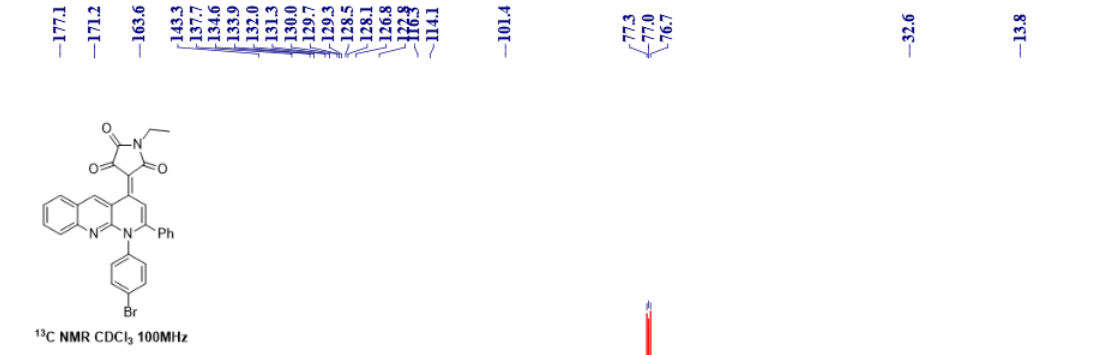

189.7
162.6
160.2
148.5
148.4
140.2
140.2
137.5
135.7
135.6
133.2
128.7
128.5
126.3
121.9
121.9
118.2
118.0
77.3
77.0
76.7
O
N
F
13C NMR CDCl3 100MHz
6b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

12. NMR Spectra of 3, 7a

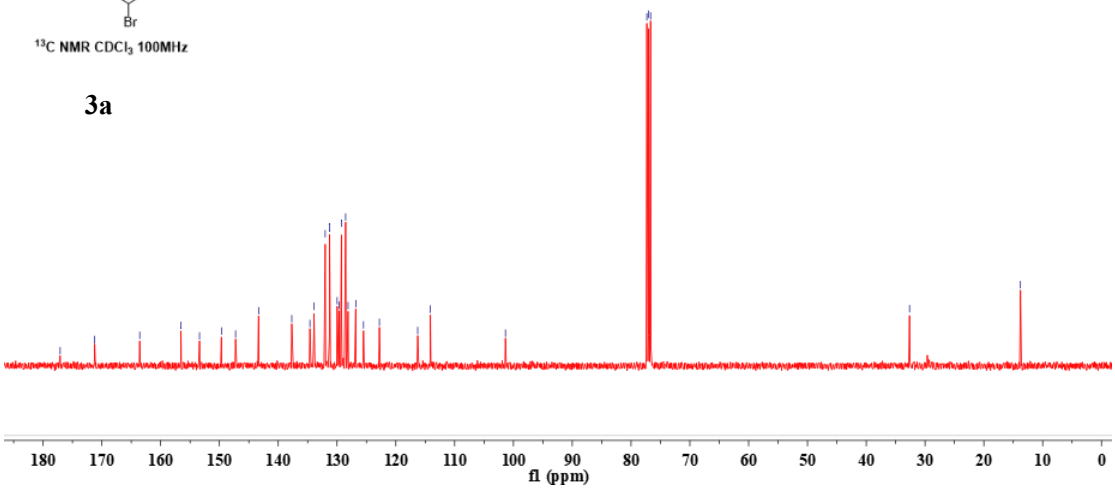


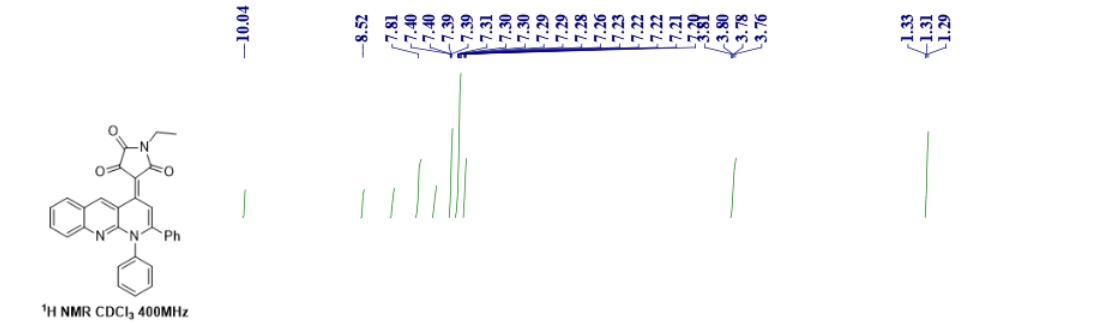
3a





3a

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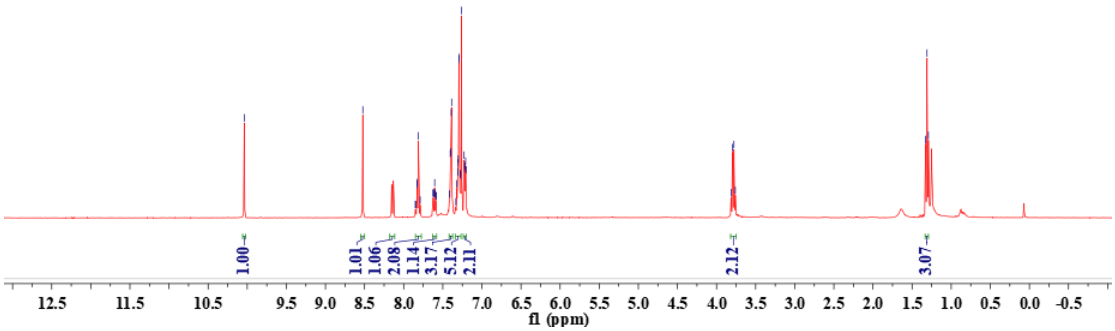
8.52
7.81
7.40
7.40
7.39
7.39
7.31
7.30
7.30
7.29
7.29
7.28
7.26
7.23
7.22
7.22
7.21
7.20
3.81
3.80
3.78
3.76
1.33
1.31
1.29
Ph
^{1}H NMR CDCl$_3$ 400MHz

3b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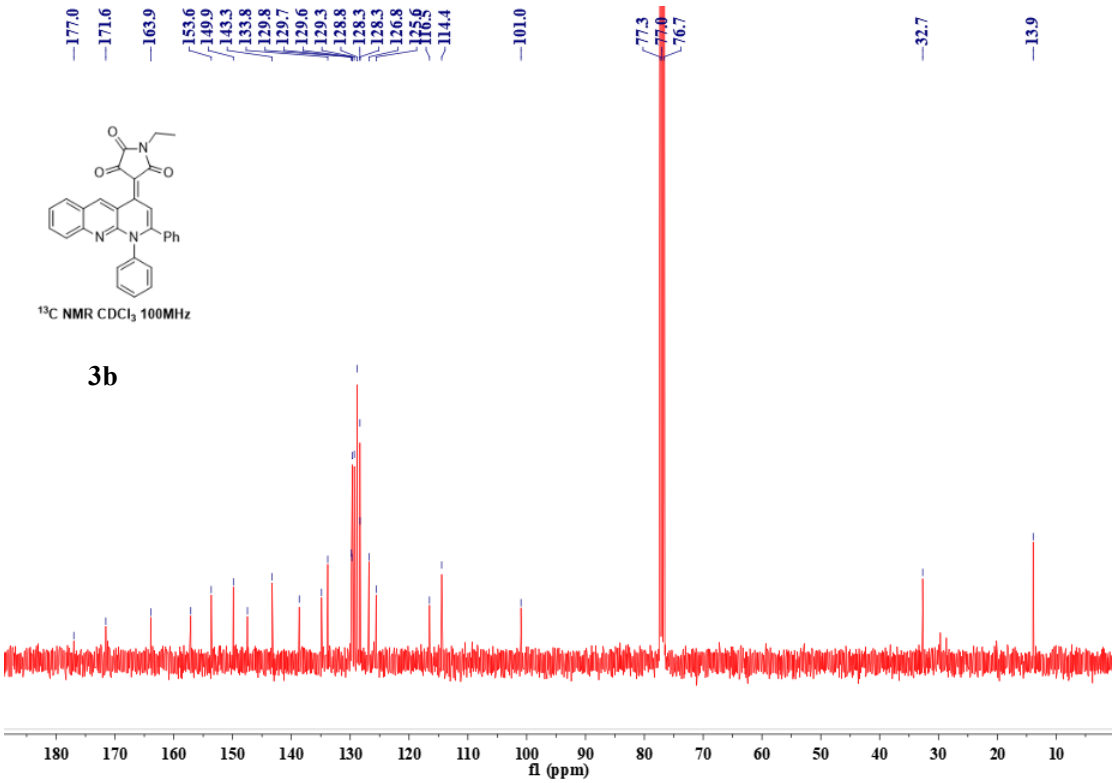
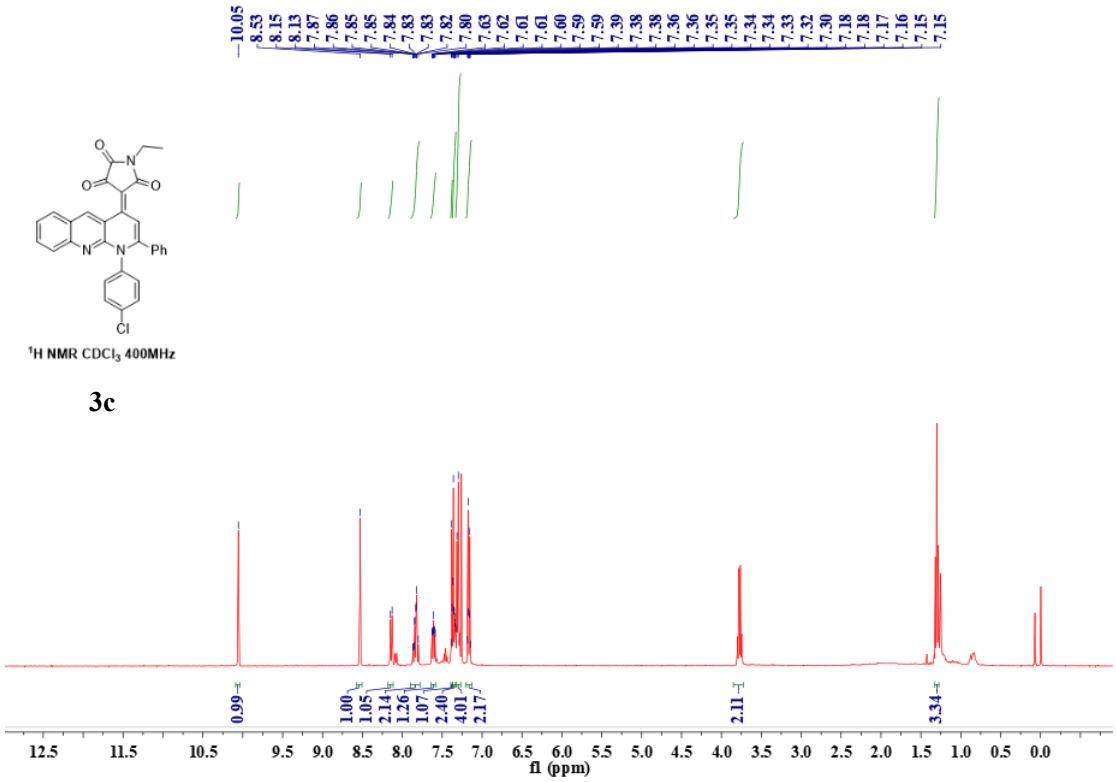
1.01
1.06
2.08
1.14
3.17
5.12
2.11
2.12
3.07
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

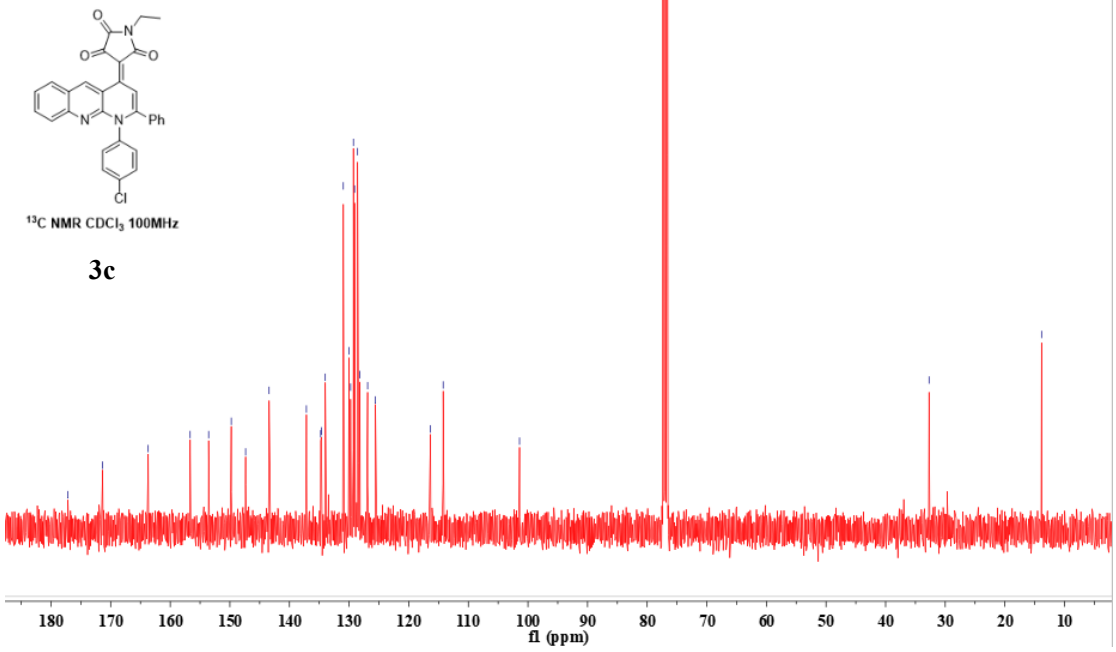

177.0
171.6
163.9
153.6
149.9
143.3
133.8
129.8
129.7
129.6
129.3
128.8
128.3
128.3
126.8
125.6
116.5
114.4
101.0
77.3
77.0
76.7
32.7
13.9
Ph
^{13}C NMR CDCl$_3$ 100MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3b



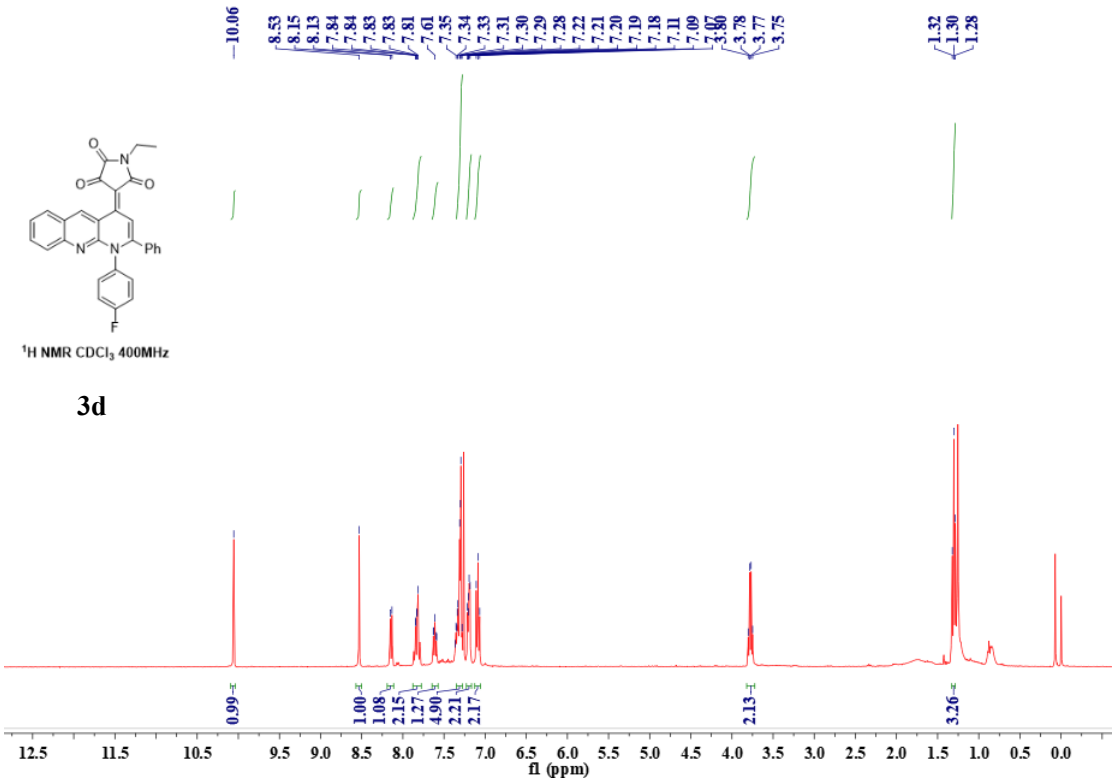
^{1}H NMR $CDCl_3$ 400MHz

3c



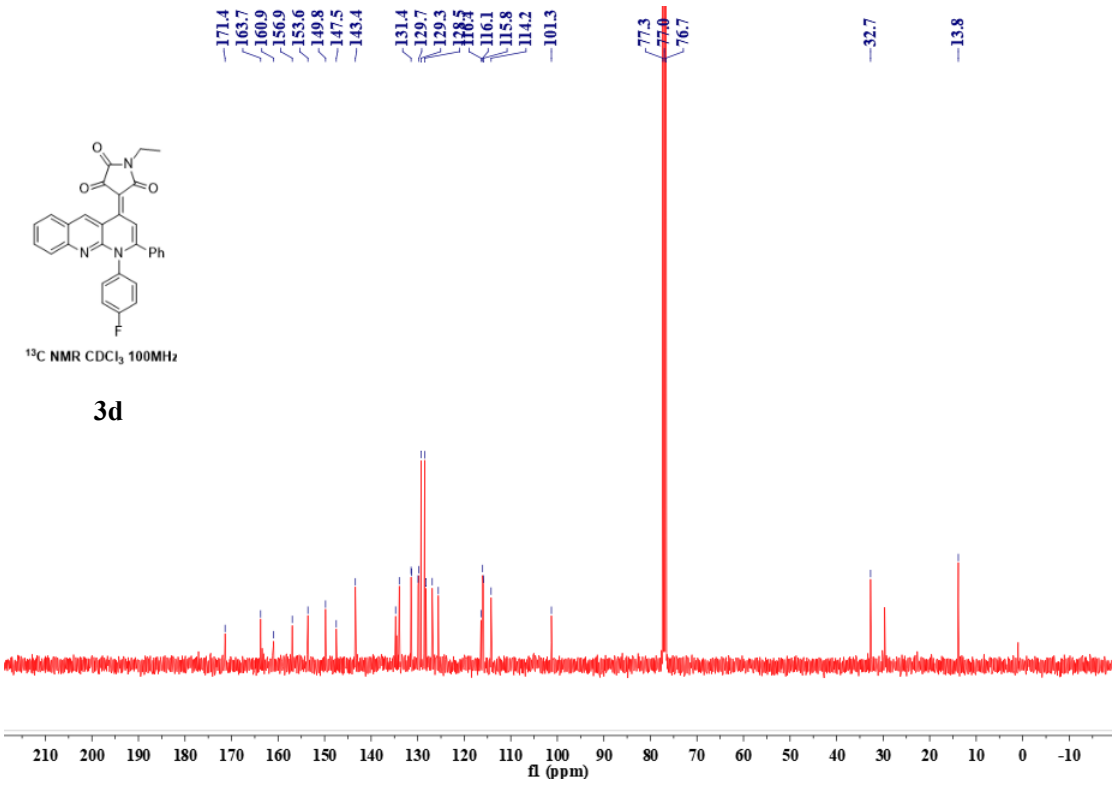
^{13}C NMR $CDCl_3$ 100MHz

3c



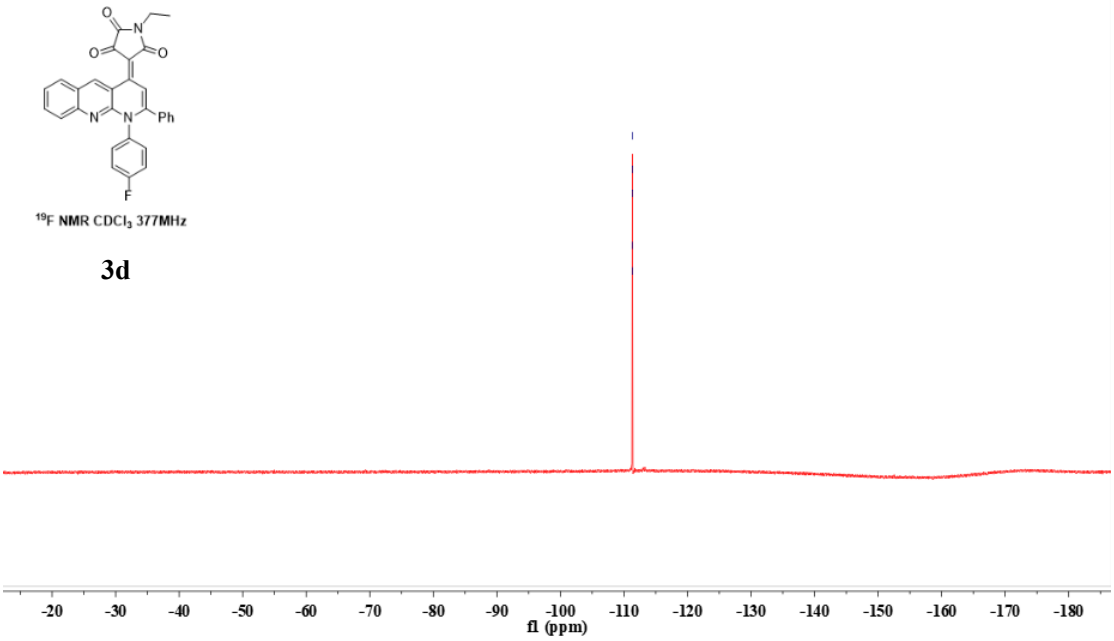
^{1}H NMR $CDCl_3$ 400MHz

3d



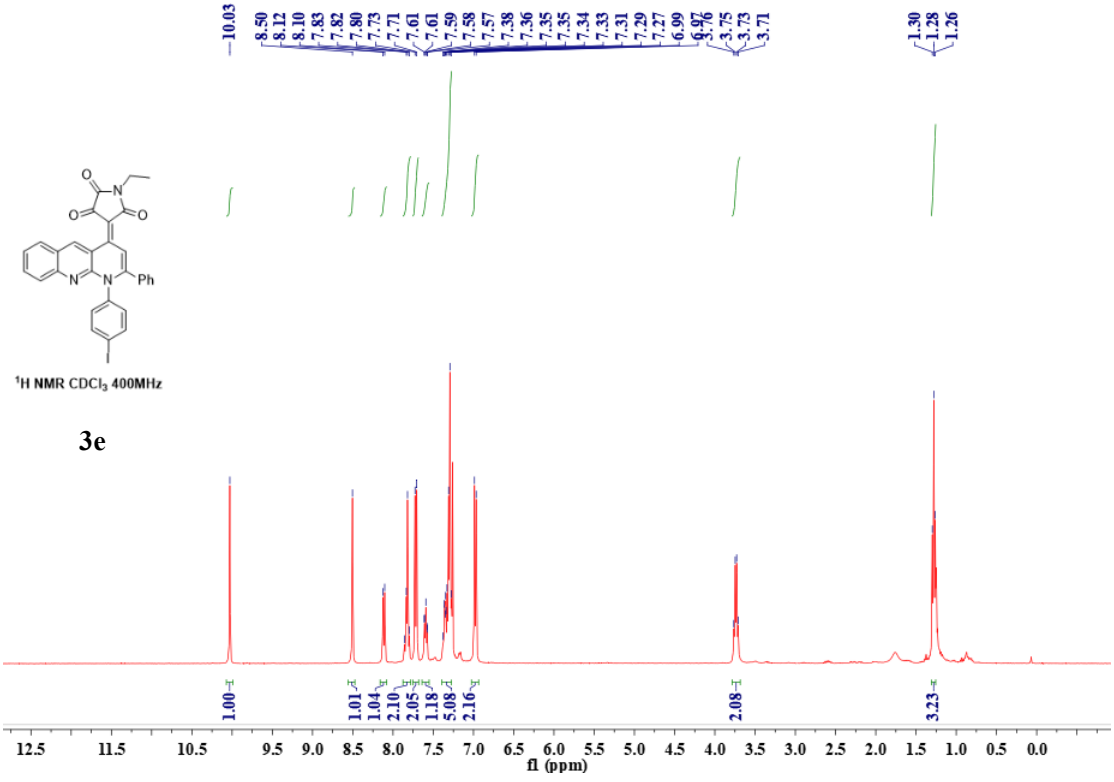
^{13}C NMR $CDCl_3$ 100MHz

3d



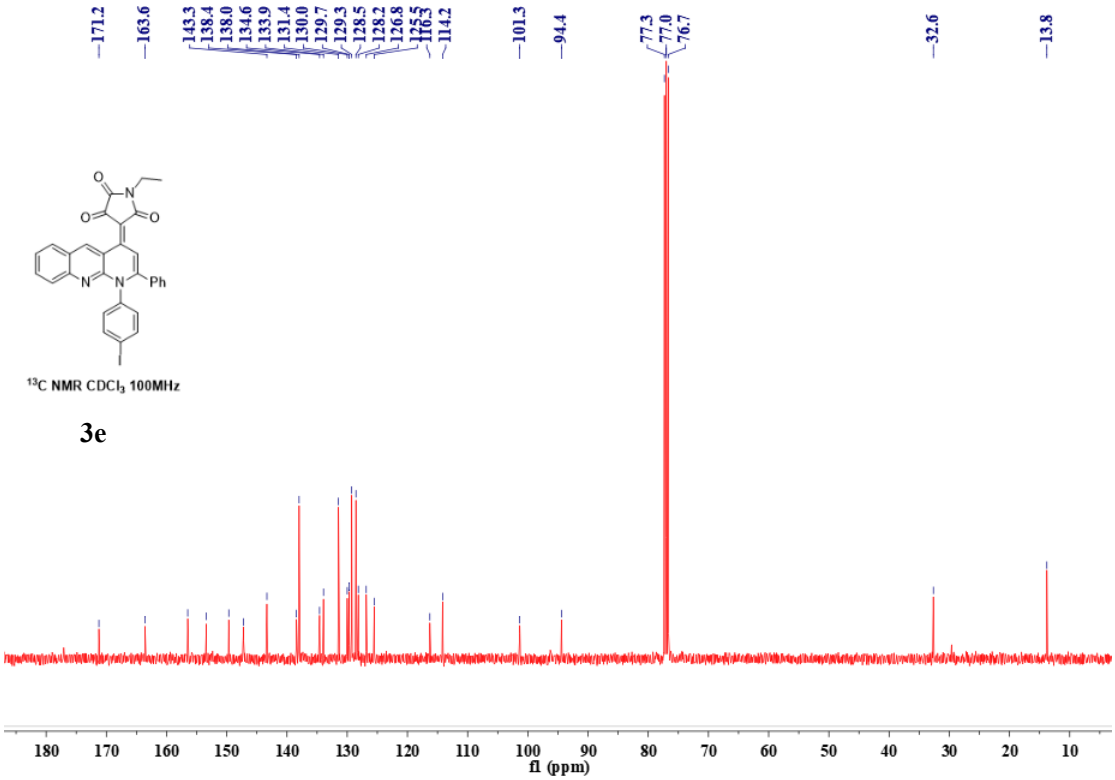
^{19}F NMR $CDCl_3$ 377MHz

3d



^{1}H NMR $CDCl_3$ 400MHz

3e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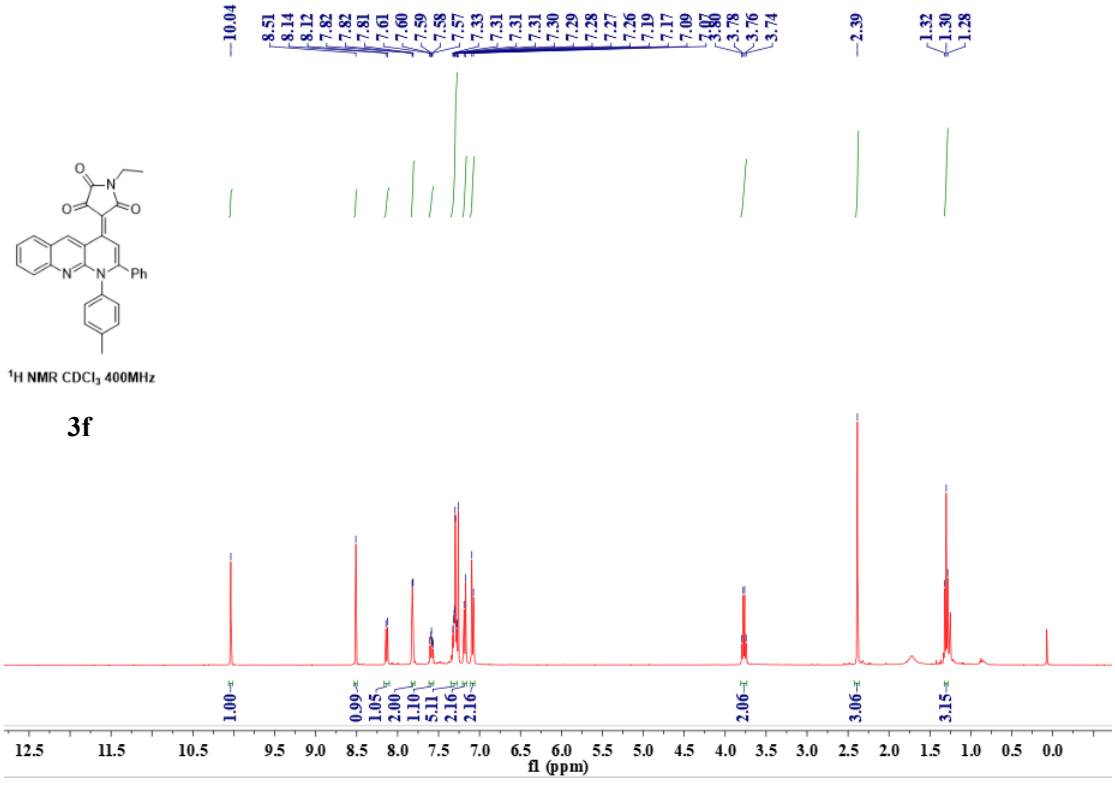
163.6
143.3
138.4
138.0
134.6
133.9
131.4
130.0
129.7
129.3
128.5
128.2
126.8
125.5
116.3
114.2
101.3
94.4
77.3
77.0
76.7
32.6
13.8
Ph
13C NMR CDCl3 100MHz
f1 (ppm)

3e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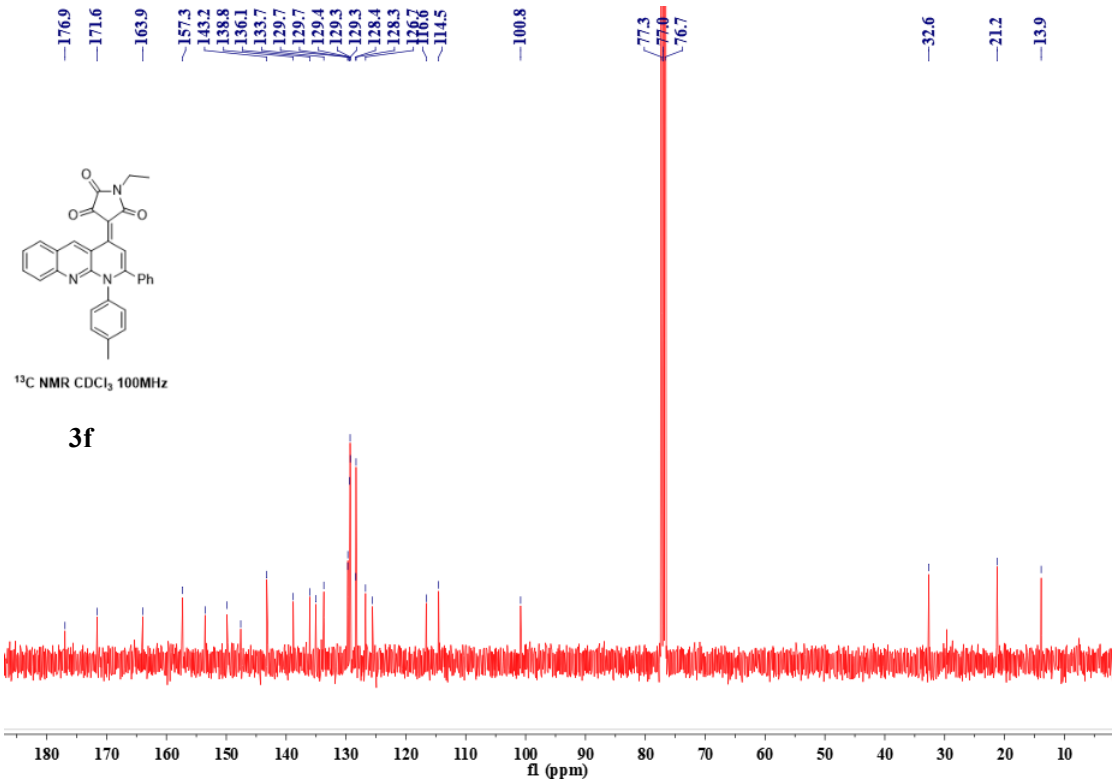
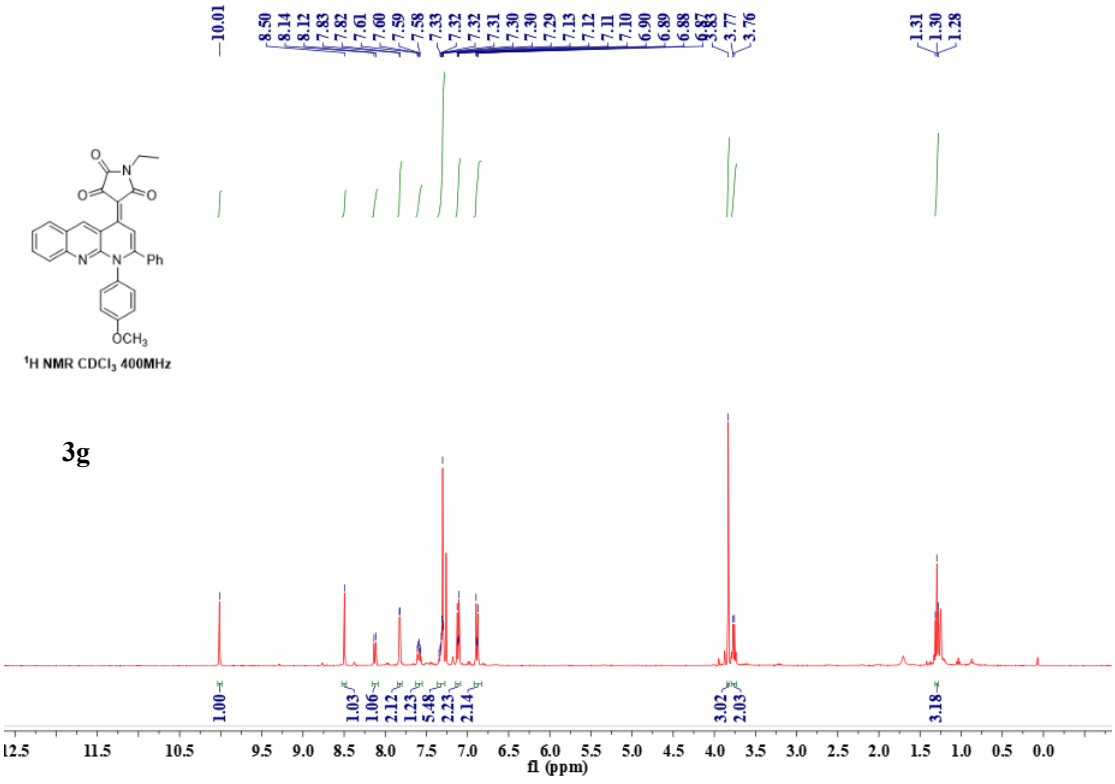
8.51
8.14
8.12
7.82
7.82
7.81
7.61
7.60
7.59
7.58
7.57
7.33
7.31
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.19
7.17
7.09
3.78
3.76
3.74
2.39
1.32
1.30
1.28
Ph
1H NMR CDCl3 400MHz
1.00
0.99
1.05
2.00
1.10
5.11
2.16
2.16
2.06
3.06
3.15
f1 (ppm)

3f


176.9
171.6
163.9
157.3
143.2
138.8
136.1
133.7
129.7
129.7
129.4
129.3
129.3
128.4
128.3
126.7
116.6
114.5
100.8
77.3
77.0
76.7
32.6
21.2
13.9
Ph
13C NMR CDCl3 100MHz
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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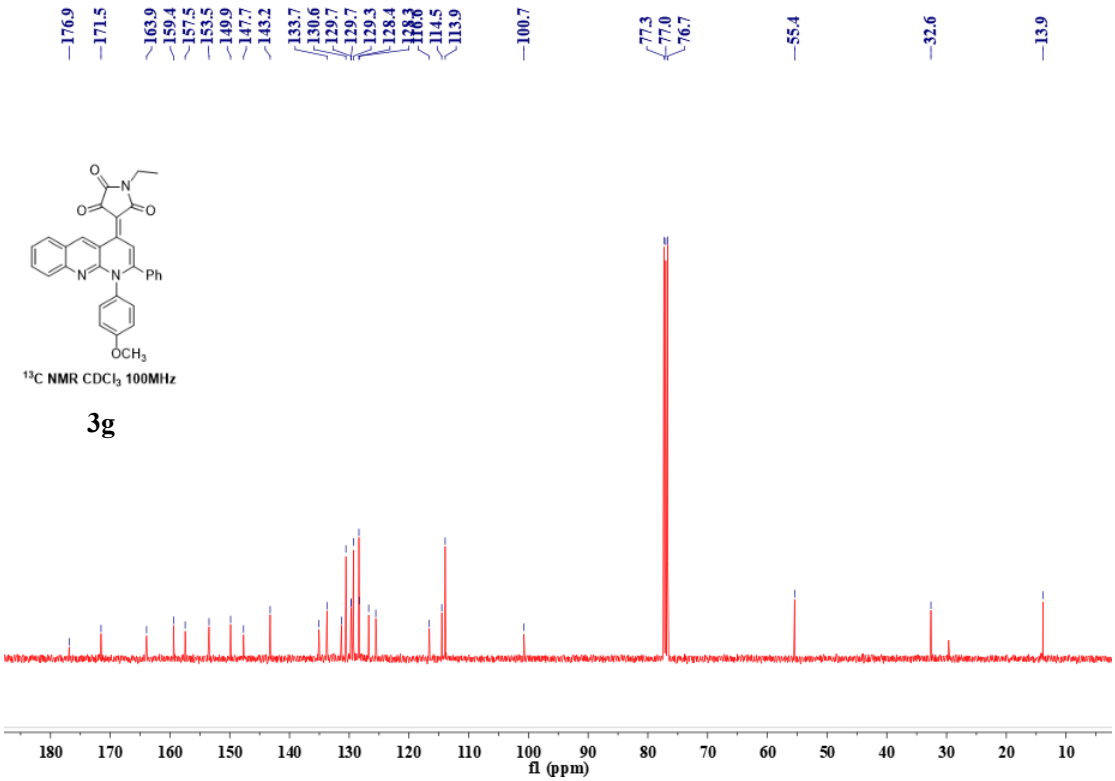
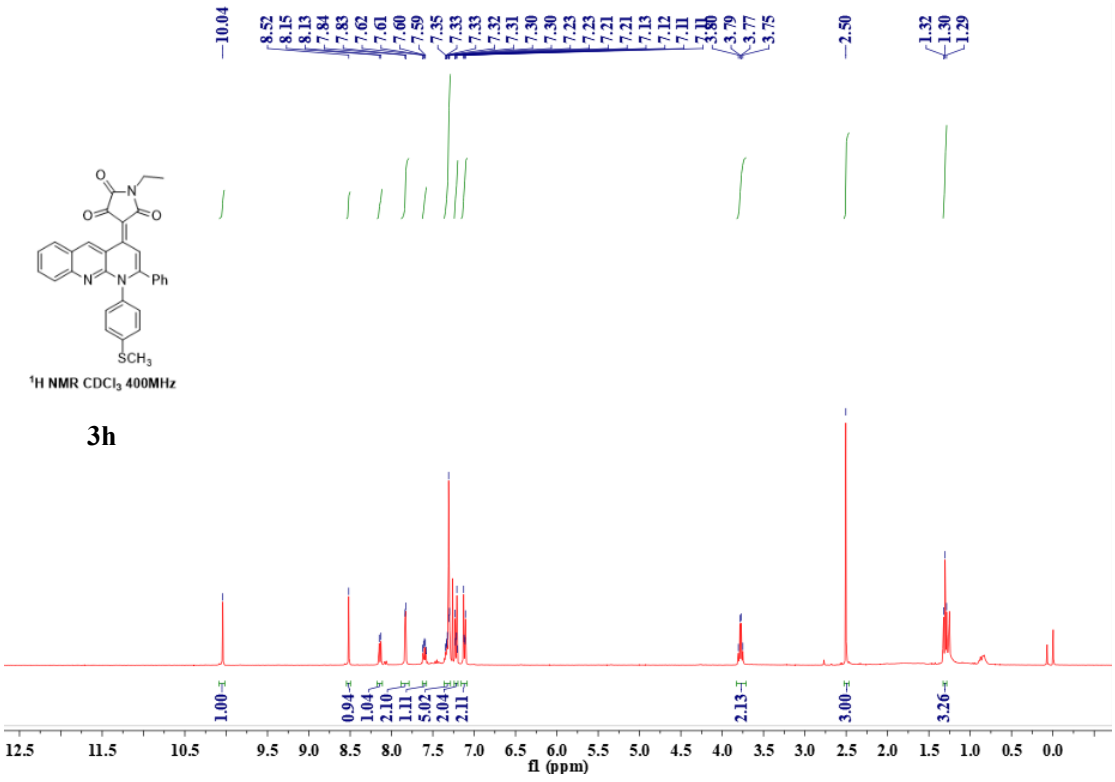
8.50
8.14
8.12
7.83
7.82
7.61
7.60
7.59
7.58
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.13
7.12
7.11
7.10
6.90
6.89
6.88
3.77
3.76
1.31
1.30
1.28
Ph
OCH3
1H NMR CDCl3 400MHz
3g
1.00
1.03
1.06
2.12
1.23
5.48
2.23
2.14
3.02
2.03
3.18
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



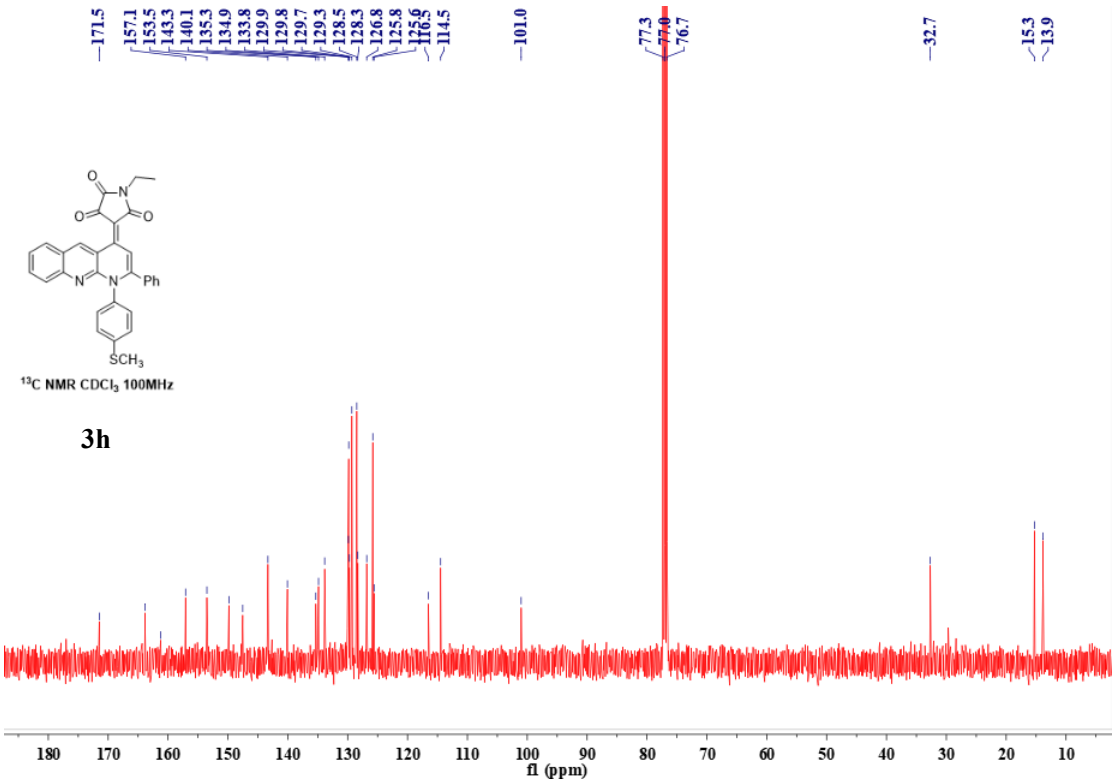
^{13}C NMR $CDCl_3$ 100MHz

3g



^{1}H NMR $CDCl_3$ 400MHz

3h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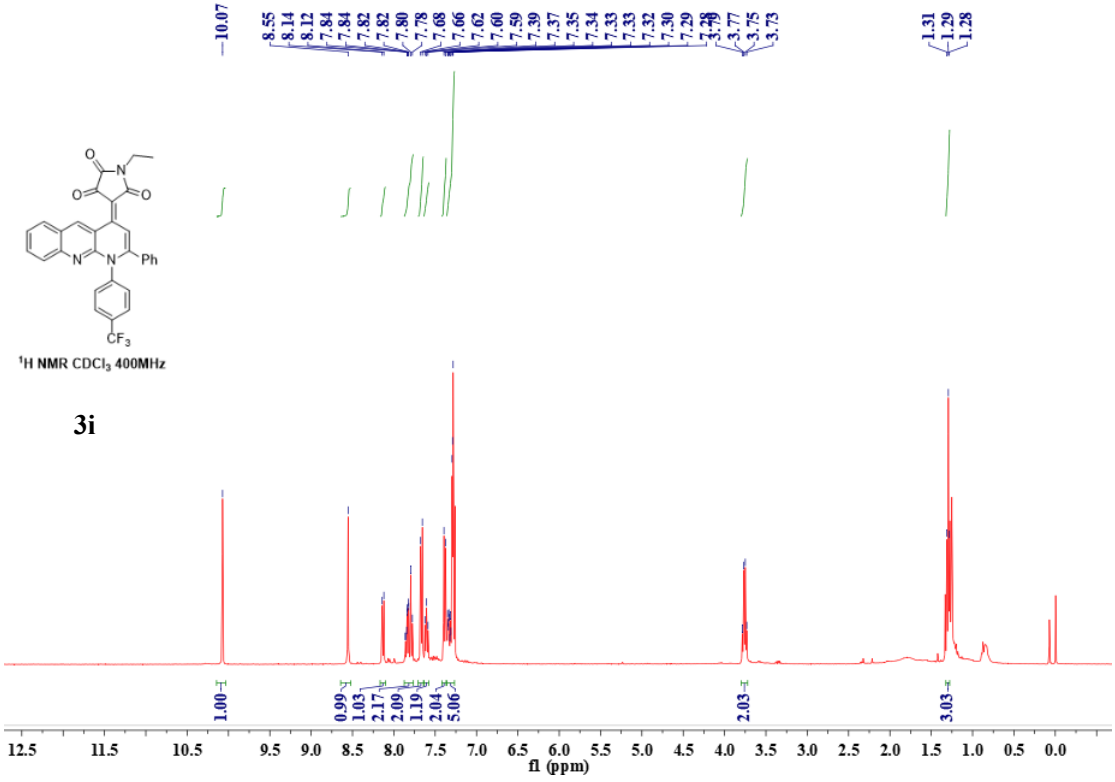
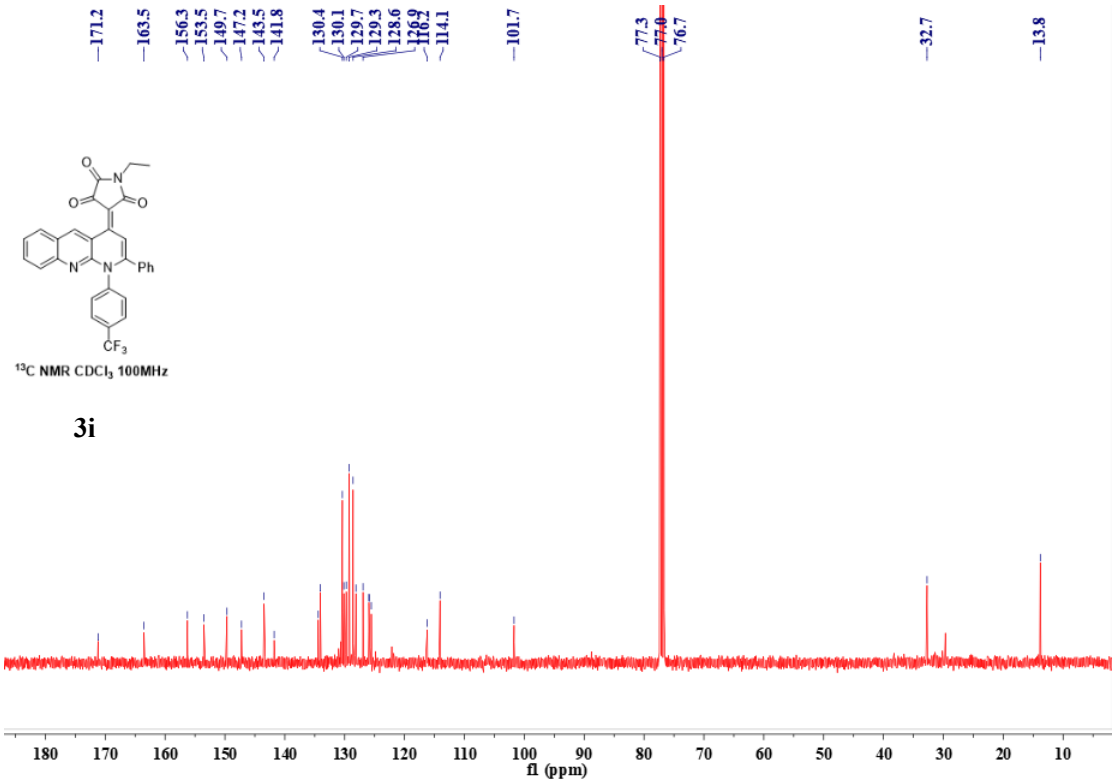
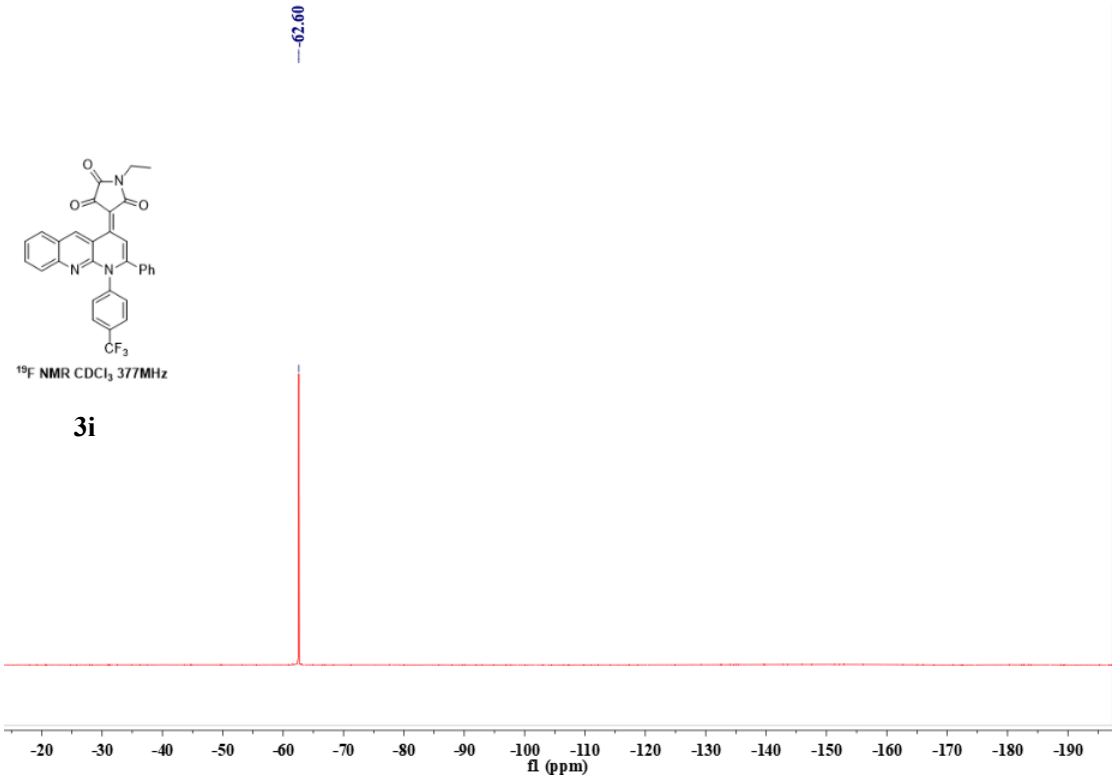
157.1
153.5
143.3
140.1
135.3
134.9
133.8
129.9
129.8
129.7
129.3
128.5
128.3
126.8
125.8
125.6
116.5
114.5
101.0
77.3
77.0
76.7
32.7
15.3
13.9
Ph
SCH3
13C NMR CDCl3 100MHz
3h
f1 (ppm)


10.07
8.55
8.14
8.12
7.84
7.84
7.82
7.82
7.80
7.78
7.68
7.66
7.62
7.60
7.59
7.39
7.37
7.35
7.34
7.33
7.33
7.32
7.30
7.29
3.77
3.75
3.73
1.31
1.29
1.28
Ph
CF3
1H NMR CDCl3 400MHz
3i
1.00
0.99
1.03
2.17
2.09
1.19
2.04
5.06
2.03
3.03
f1 (ppm)



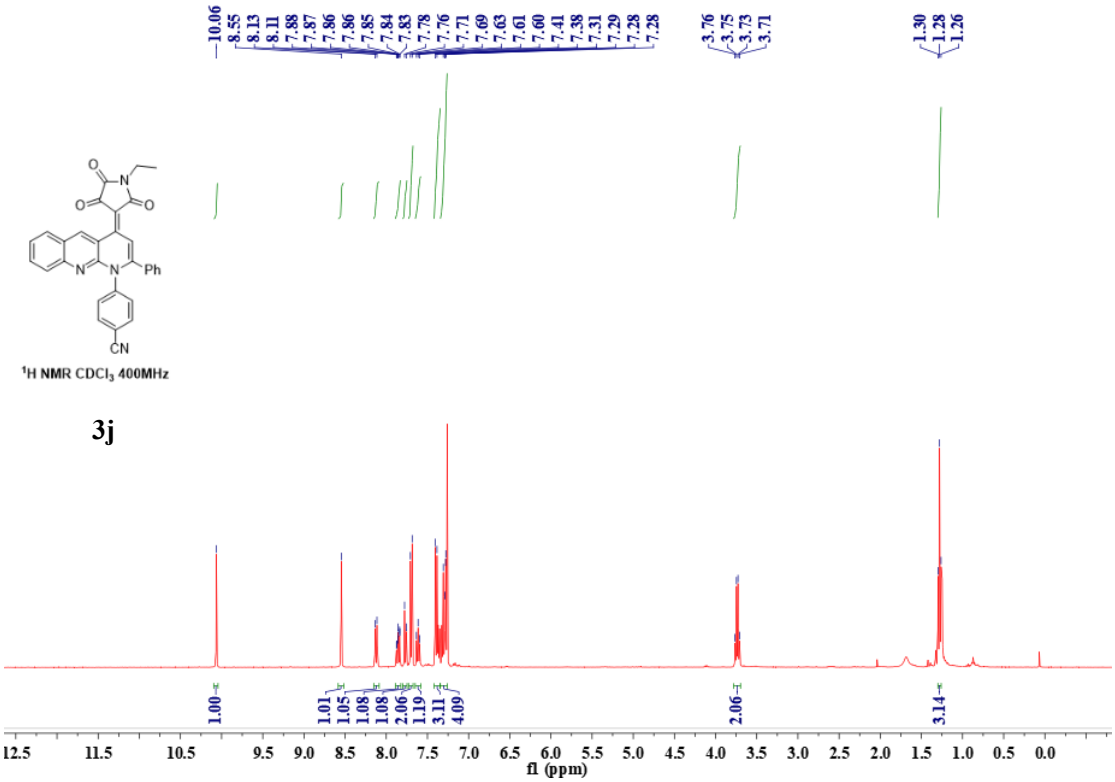
^{13}C NMR $CDCl_3$ 100MHz

3i



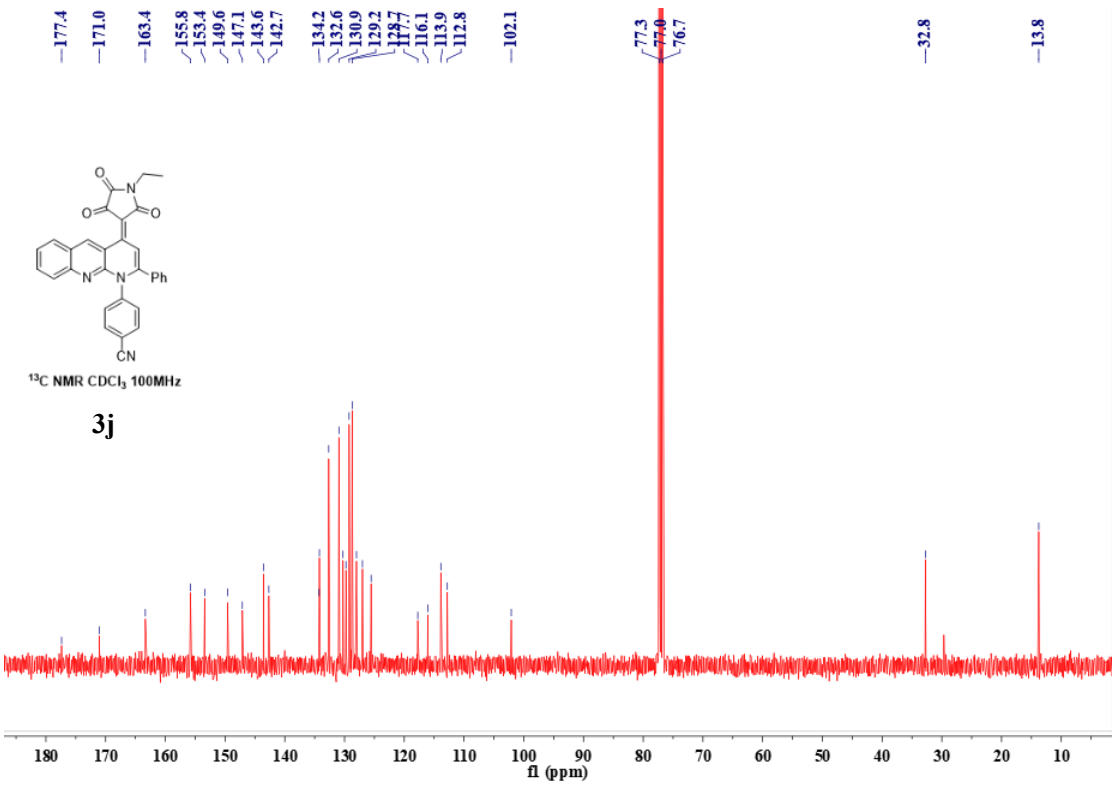
^{19}F NMR $CDCl_3$ 377MHz

3i



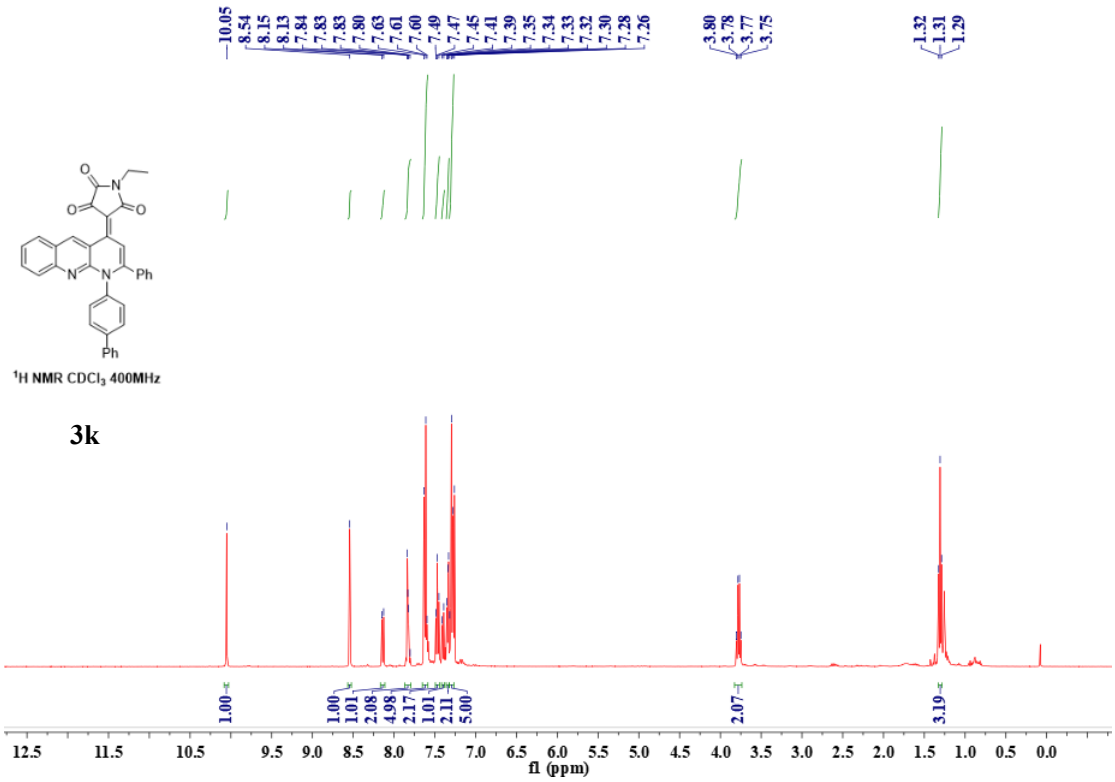
^{1}H NMR $CDCl_3$ 400MHz

3j



^{13}C NMR $CDCl_3$ 100MHz

3j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8.15
8.13
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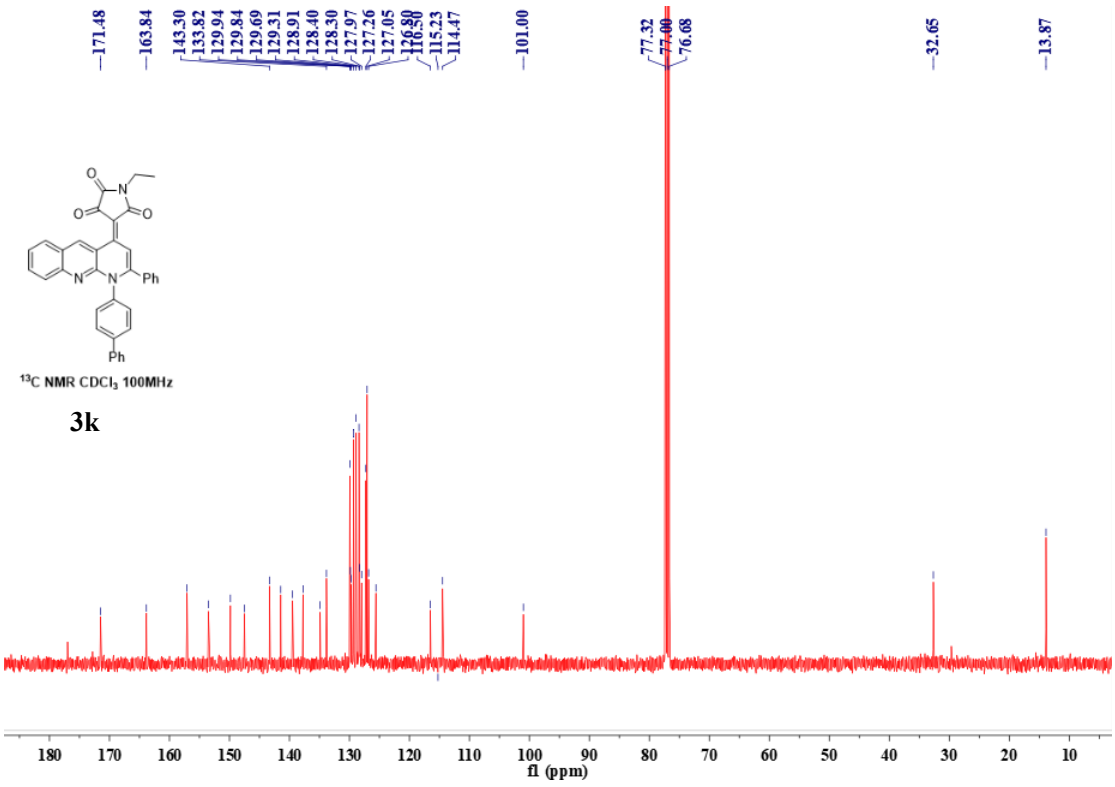
7.83
7.83
7.80
7.63
7.61
7.60
7.49
7.47
7.45
7.41
7.39
7.35
7.34
7.33
7.32
7.30
7.28
7.26
3.80
3.78
3.77
3.75
1.32
1.31
1.29
Ph
Ph
1H NMR CDCl3 400MHz
3k
1.00
1.00
1.01
2.08
4.98
2.17
1.01
2.11
5.00
2.07
3.19
fl (ppm)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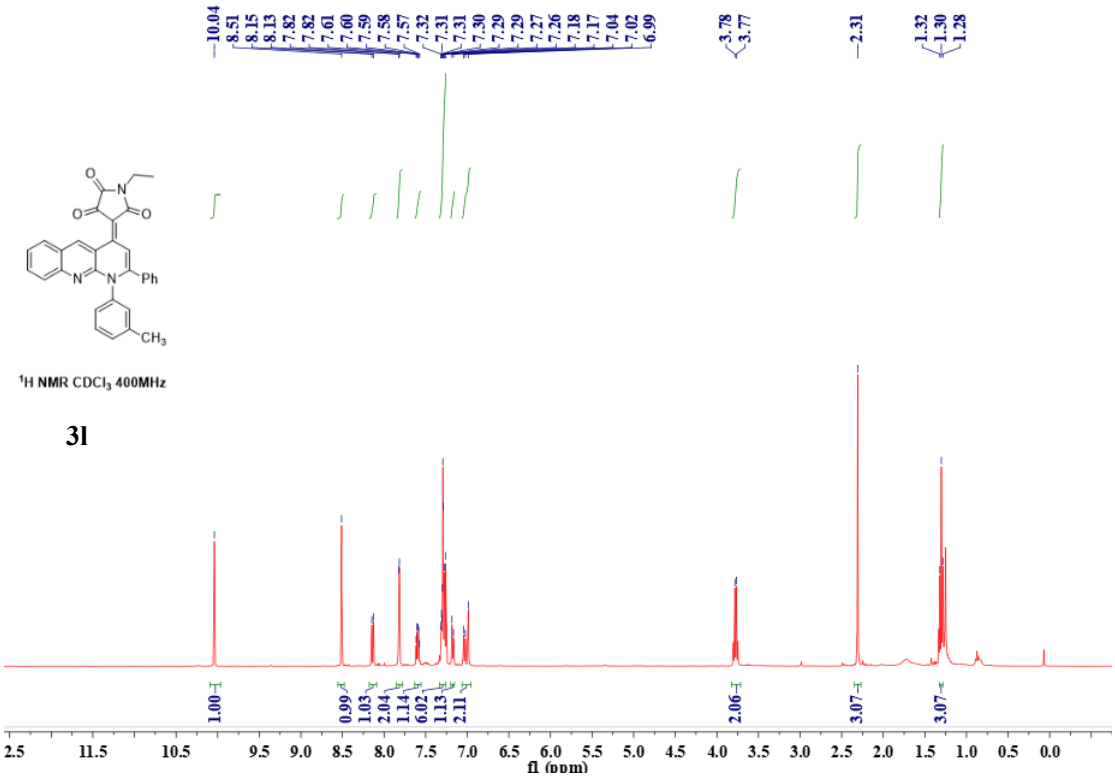
143.30
133.82
129.94
129.84
129.69
129.31
128.91
128.40
128.30
127.97
127.26
127.05
115.23
114.47
101.00
77.32
77.00
76.68
32.65
13.87
Ph
Ph
13C NMR CDCl3 100MHz
3k
fl (ppm)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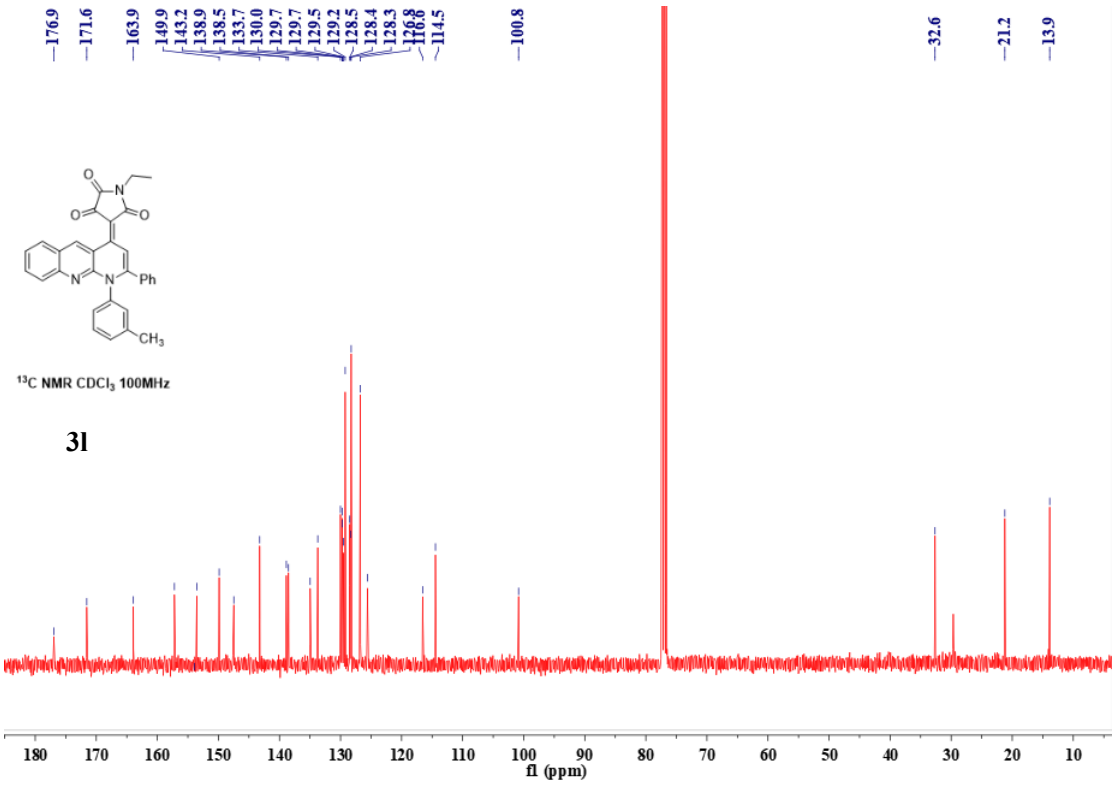
8.51
8.15
8.13
7.82
7.82
7.61
7.60
7.59
7.58
7.57
7.32
7.31
7.31
7.30
7.29
7.29
7.27
7.26
7.18
7.17
7.04
7.02
6.99
3.78
3.77
2.31
1.32
1.30
1.28
Ph
CH3
1H NMR CDCl3 400MHz
3l
1.00
0.99
1.03
2.04
1.14
6.02
1.13
2.11
2.06
3.07
3.07
f1 (ppm)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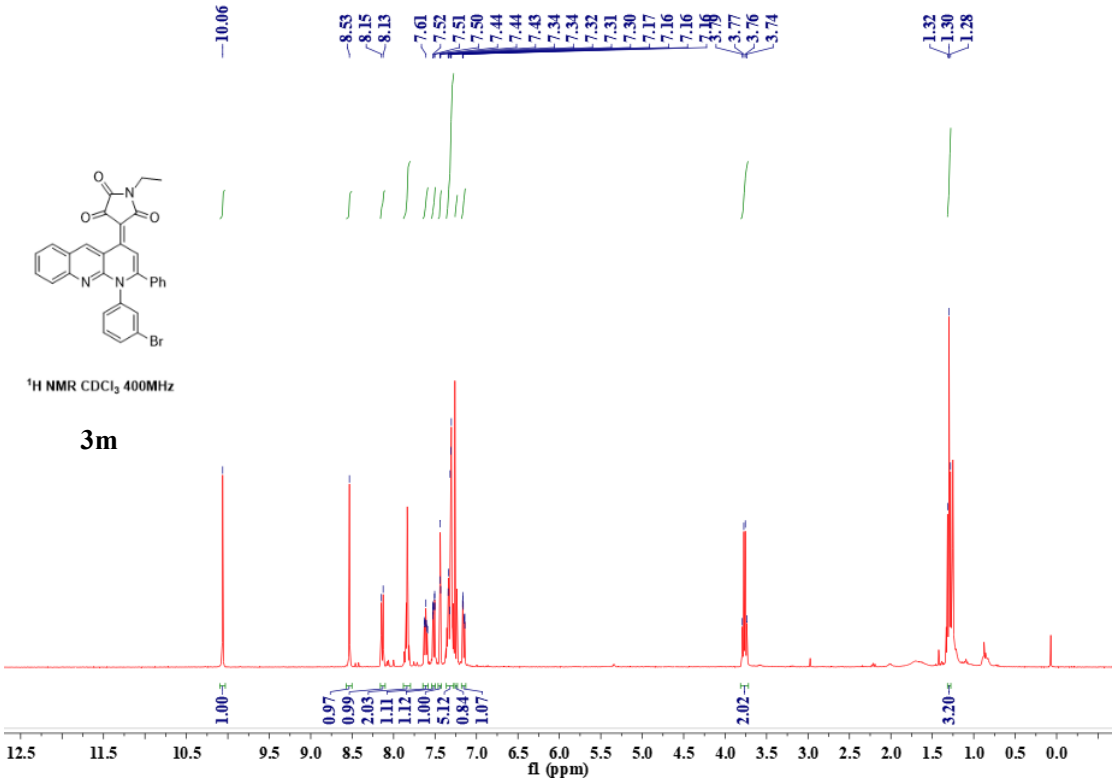
149.9
143.2
138.9
138.5
133.7
130.0
129.7
129.7
129.5
129.2
128.5
128.4
128.3
126.8
116.6
114.5
100.8
32.6
21.2
13.9
Ph
CH3
13C NMR CDCl3 100MHz
3l
f1 (ppm)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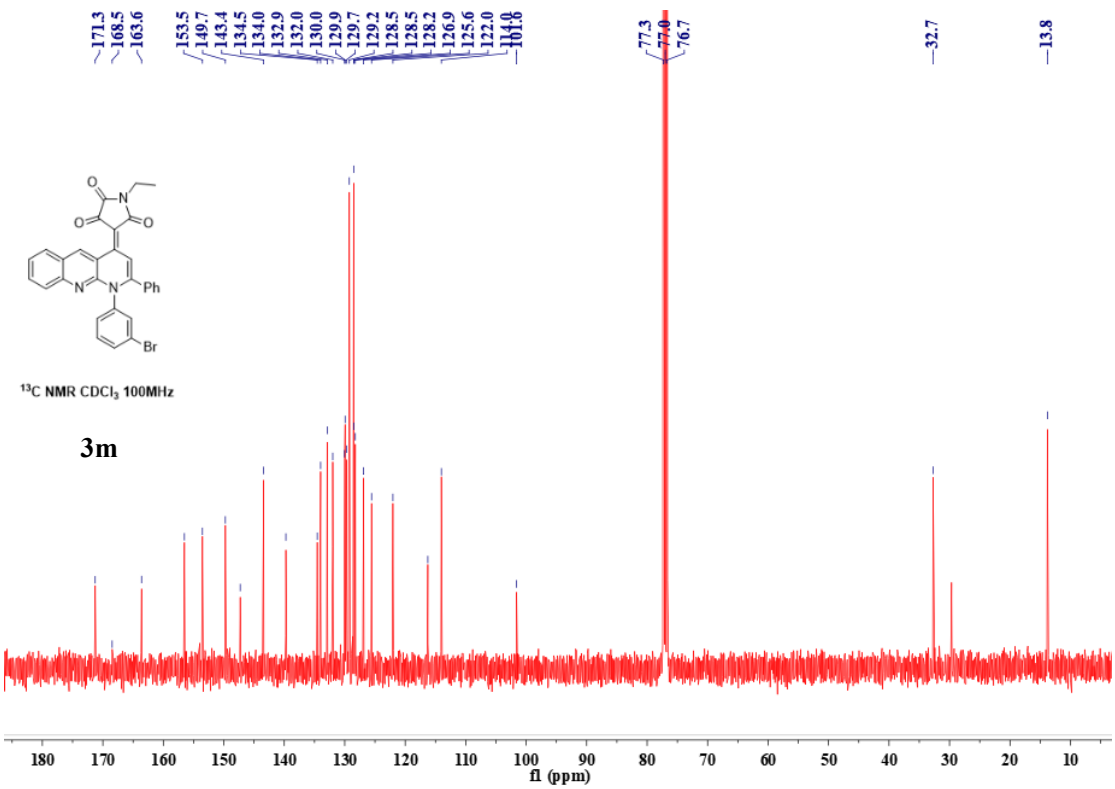
8.15
8.13
7.61
7.52
7.51
7.50
7.44
7.44
7.43
7.34
7.34
7.32
7.31
7.30
7.17
7.16
7.16
3.77
3.76
3.74
1.32
1.30
1.28
Ph
Br
1H NMR CDCl3 400MHz
3m
1.00
0.97
0.99
2.03
1.11
1.12
1.00
5.12
0.84
1.07
2.02
3.20
f1 (ppm)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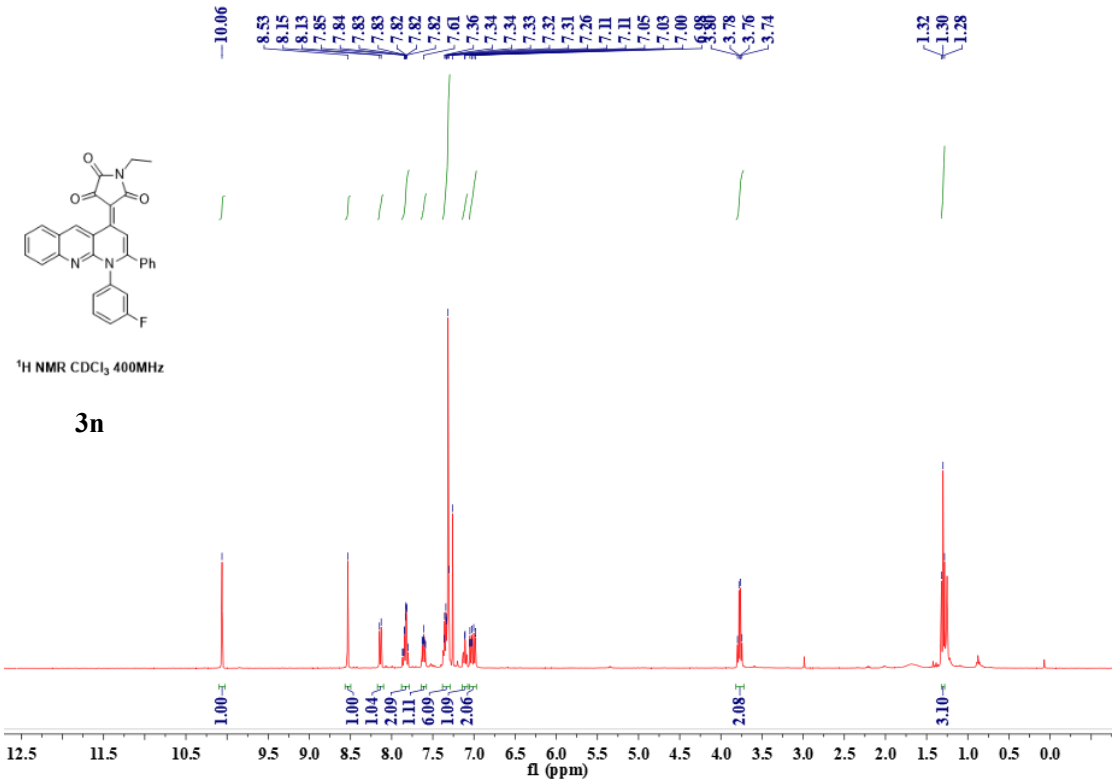
153.5
149.7
143.4
134.5
134.0
132.9
132.0
130.0
129.9
129.7
129.2
128.5
128.5
128.2
126.9
125.6
122.0
77.3
77.0
76.7
32.7
13.8
Ph
Br
13C NMR CDCl3 100MHz
3m
f1 (ppm)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8.13
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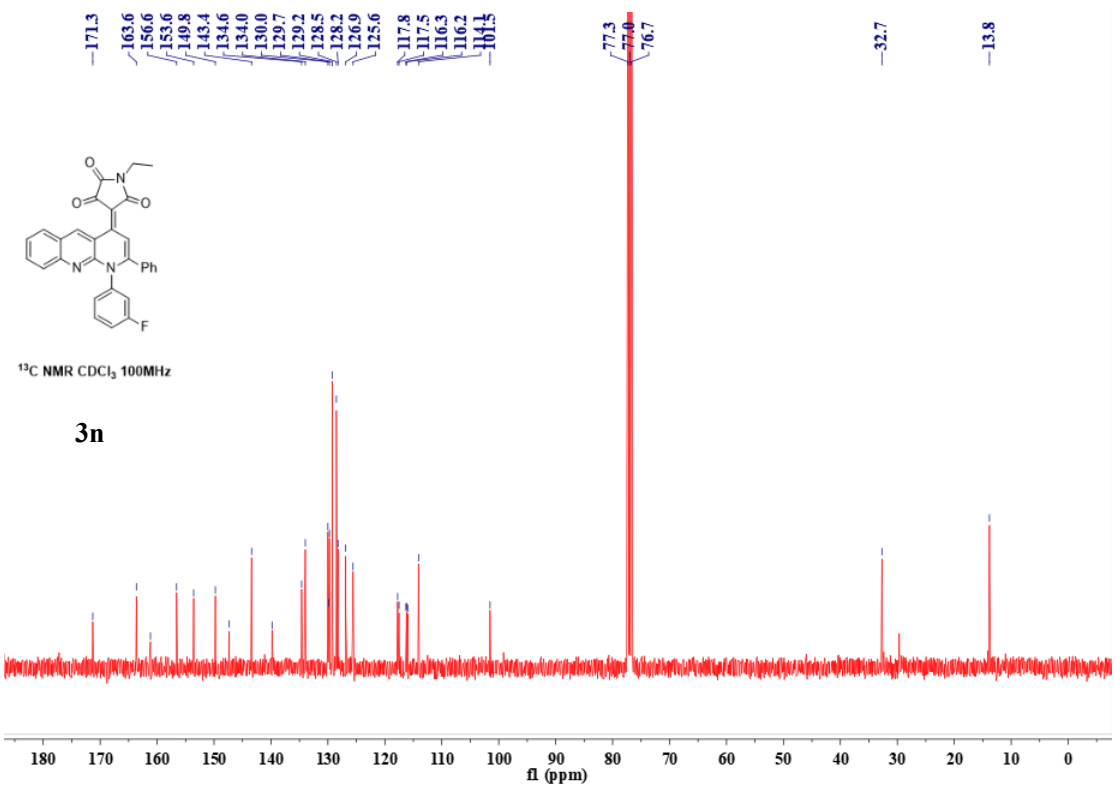
7.84
7.83
7.83
7.82
7.82
7.82
7.61
7.36
7.34
7.34
7.33
7.32
7.31
7.26
7.11
7.11
7.05
7.03
7.00
3.78
3.76
3.74
1.32
1.30
1.28
Ph
F
1H NMR CDCl3 400MHz
3n
1.00
1.00
1.04
2.09
1.11
6.09
1.09
2.06
2.08
3.10
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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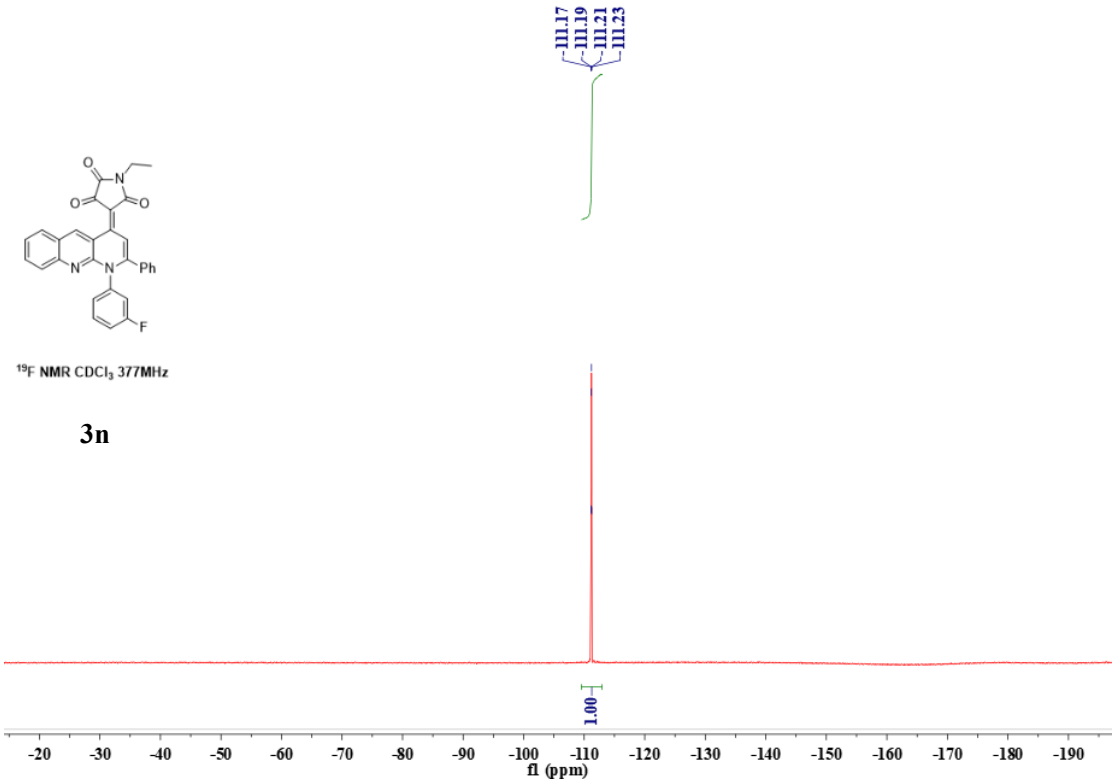
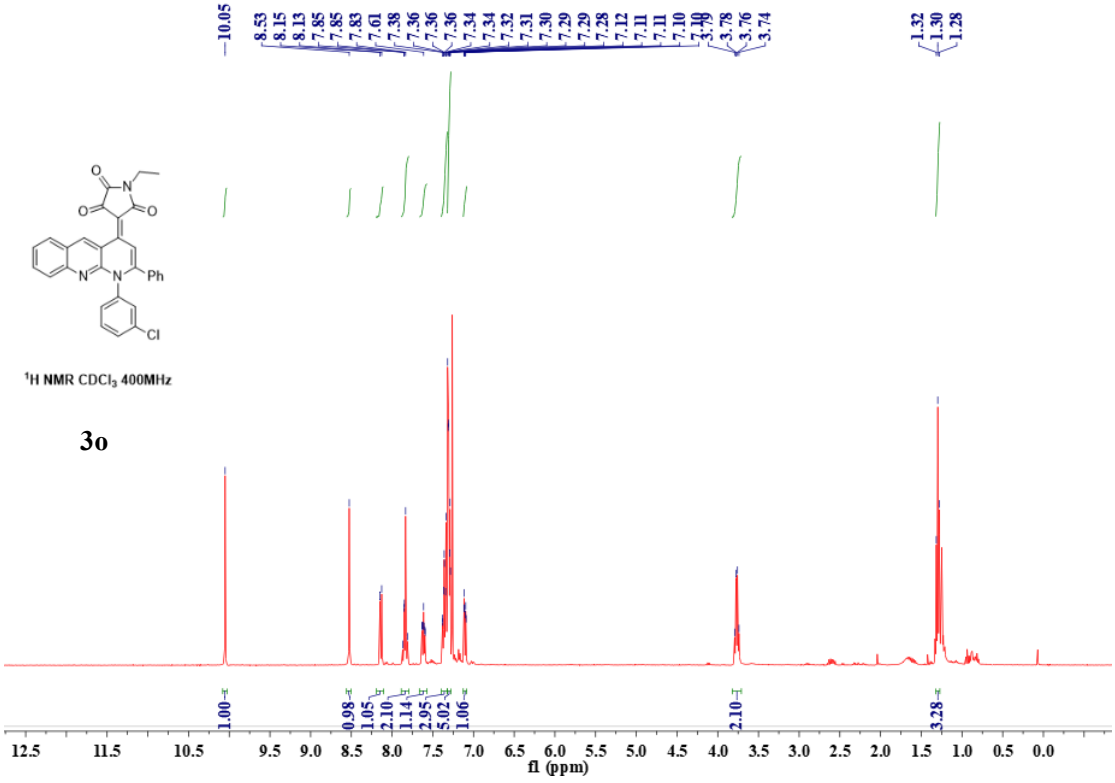
163.6
156.6
153.6
149.8
143.4
134.6
134.0
130.0
129.7
129.2
128.5
128.2
126.9
125.6
117.8
117.5
116.3
116.2
101.5
77.3
77.0
76.7
32.7
13.8
Ph
F
13C NMR CDCl3 100MHz
3n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{19}F NMR $CDCl_3$ 377MHz

3n



^{1}H NMR $CDCl_3$ 400MHz

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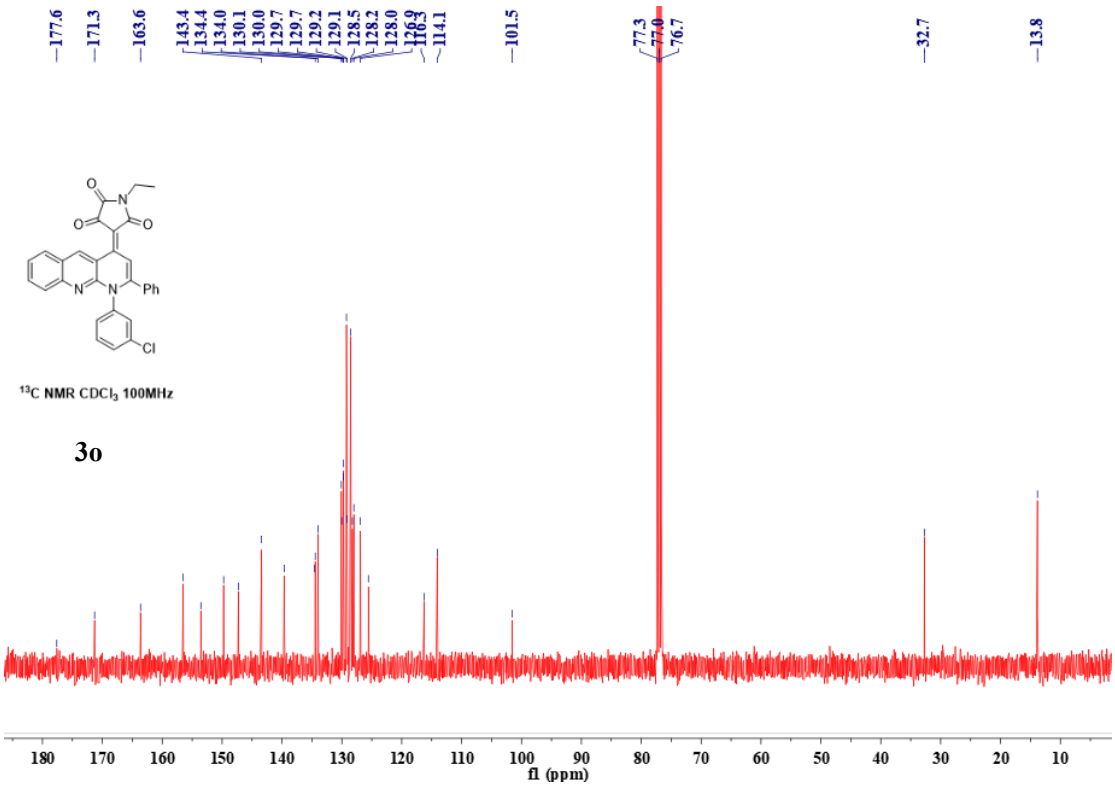

^{13}C NMR $CDCl_3$ 100MHz

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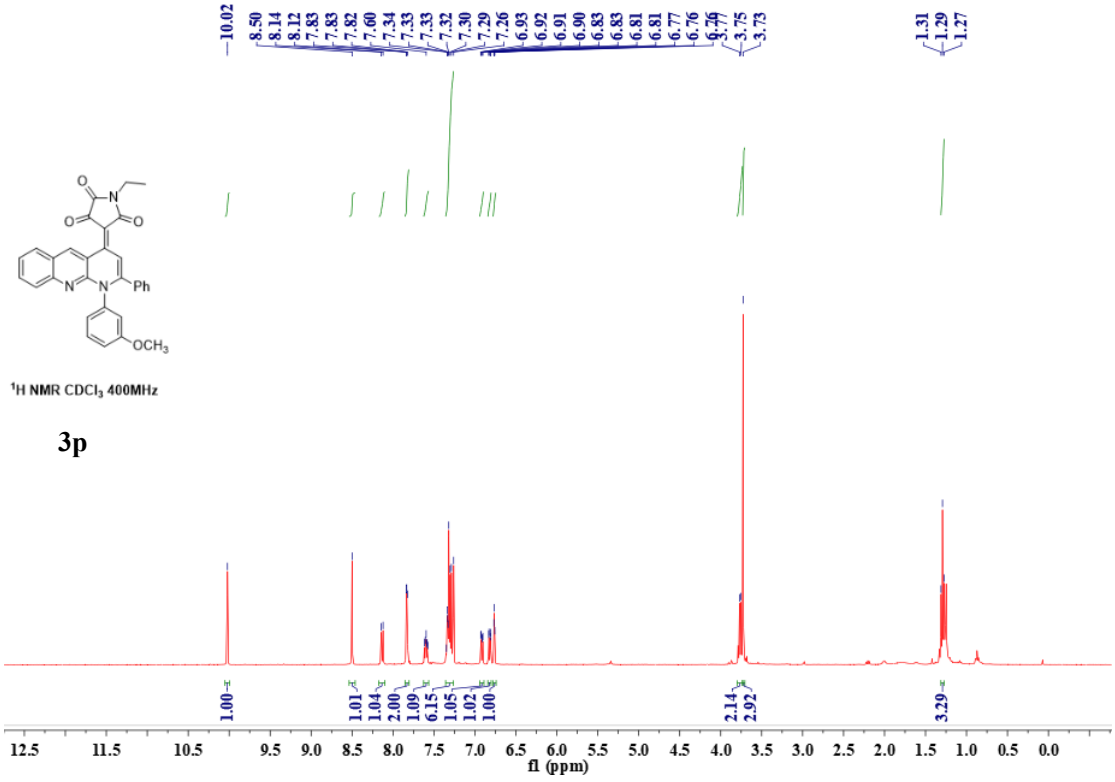
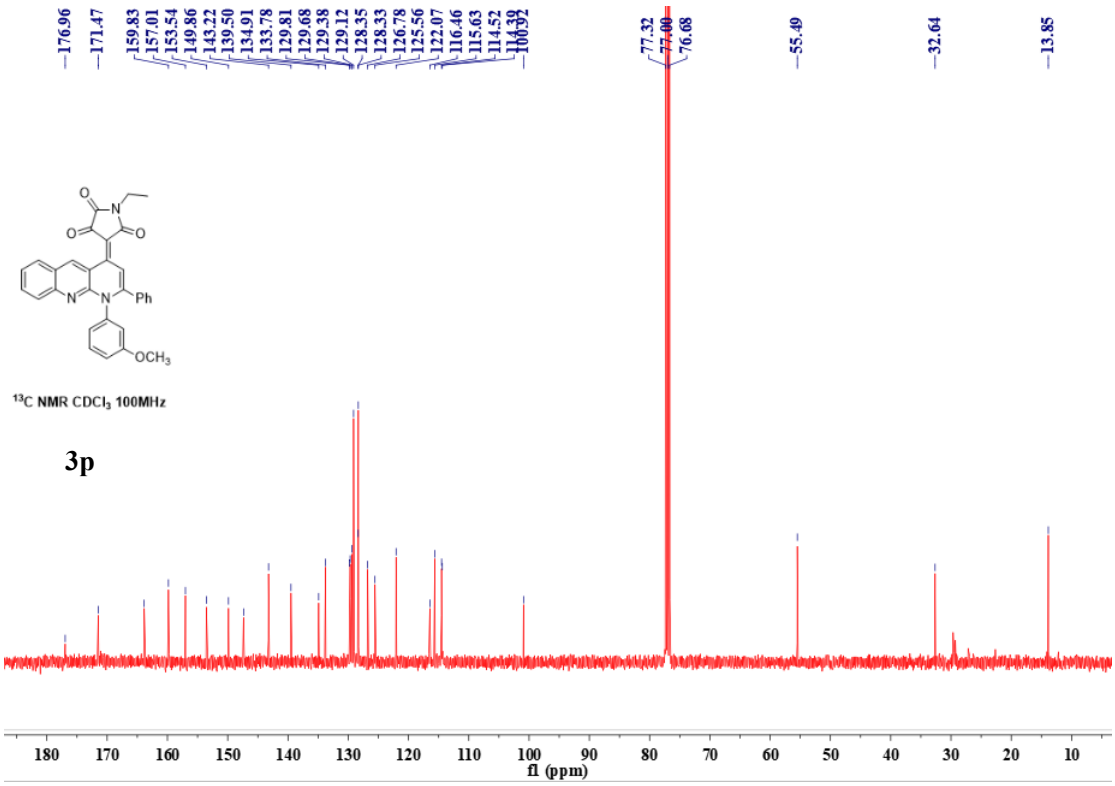


^{1}H NMR $CDCl_3$ 400MHz

3p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128.35
128.33
126.78
125.56
122.07
116.46
115.63
114.52
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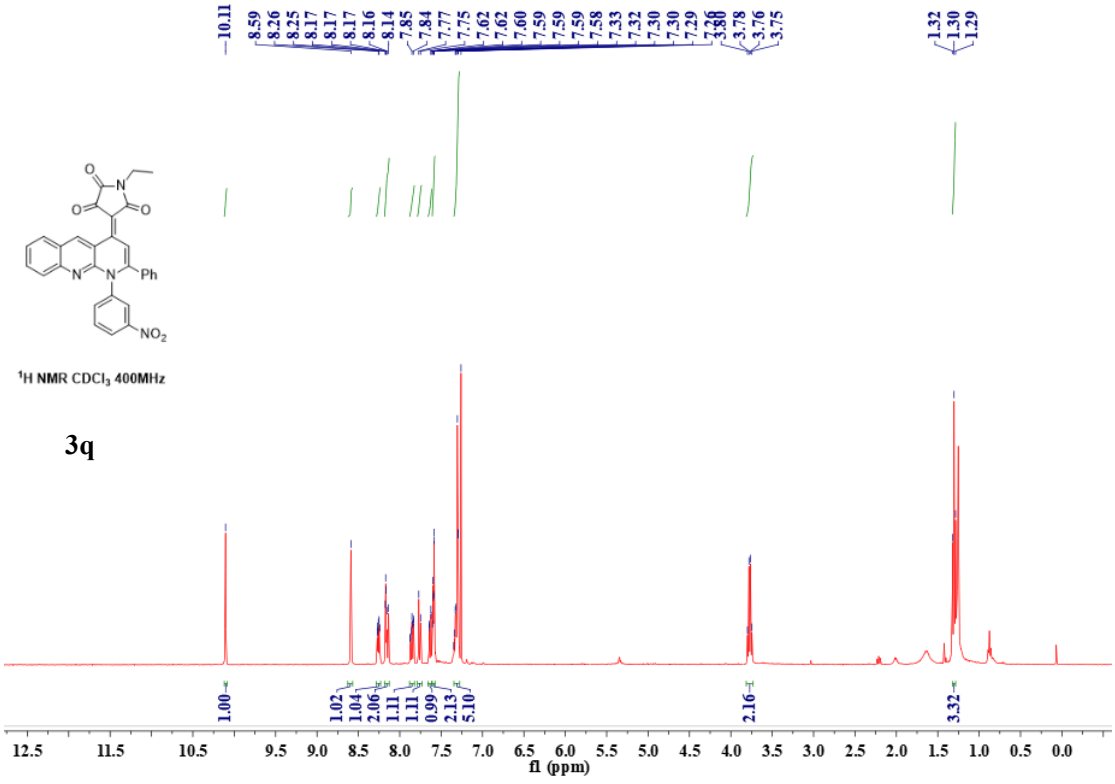
76.68
55.49
32.64
13.85
Ph
OCH3
13C NMR CDCl3 100MHz
3p
f1 (ppm)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8.16
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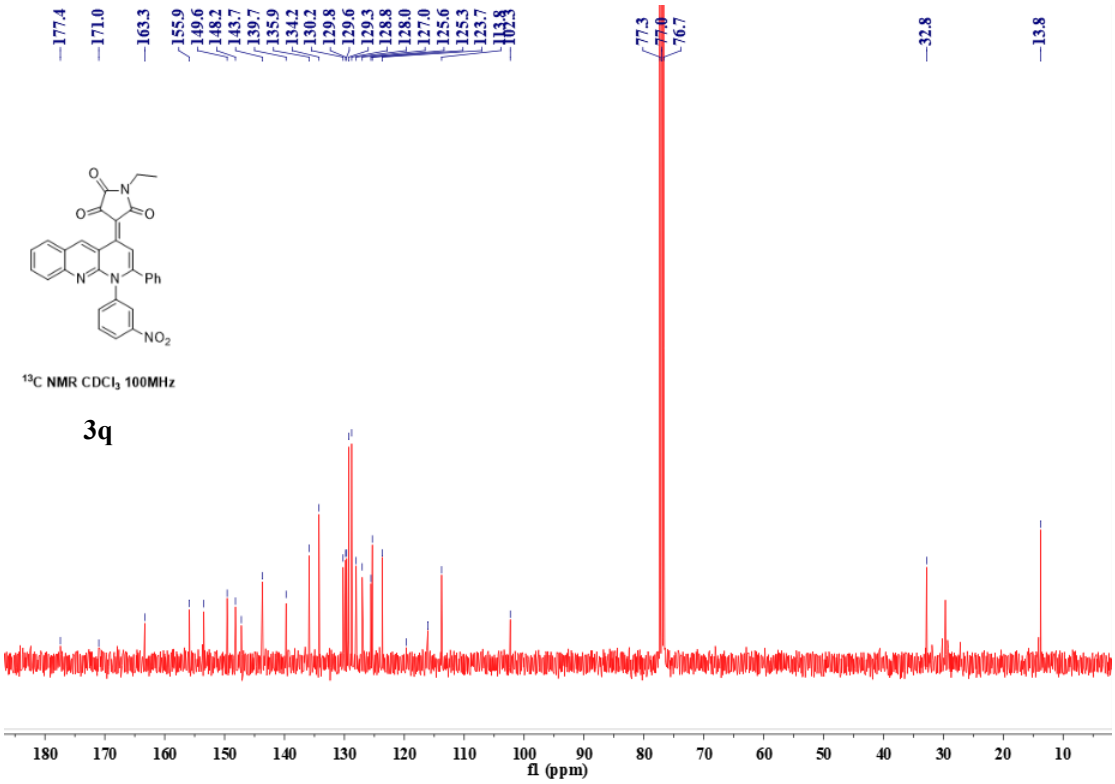
7.75
7.62
7.62
7.60
7.59
7.59
7.59
7.58
7.33
7.32
7.30
7.30
7.29
3.78
3.76
3.75
1.32
1.30
1.29
Ph
NO2
1H NMR CDCl3 400MHz
3q
1.00
1.02
1.04
2.06
1.11
1.11
0.99
2.13
5.10
2.16
3.32
f1 (ppm)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128.0
127.0
125.6
125.3
123.7
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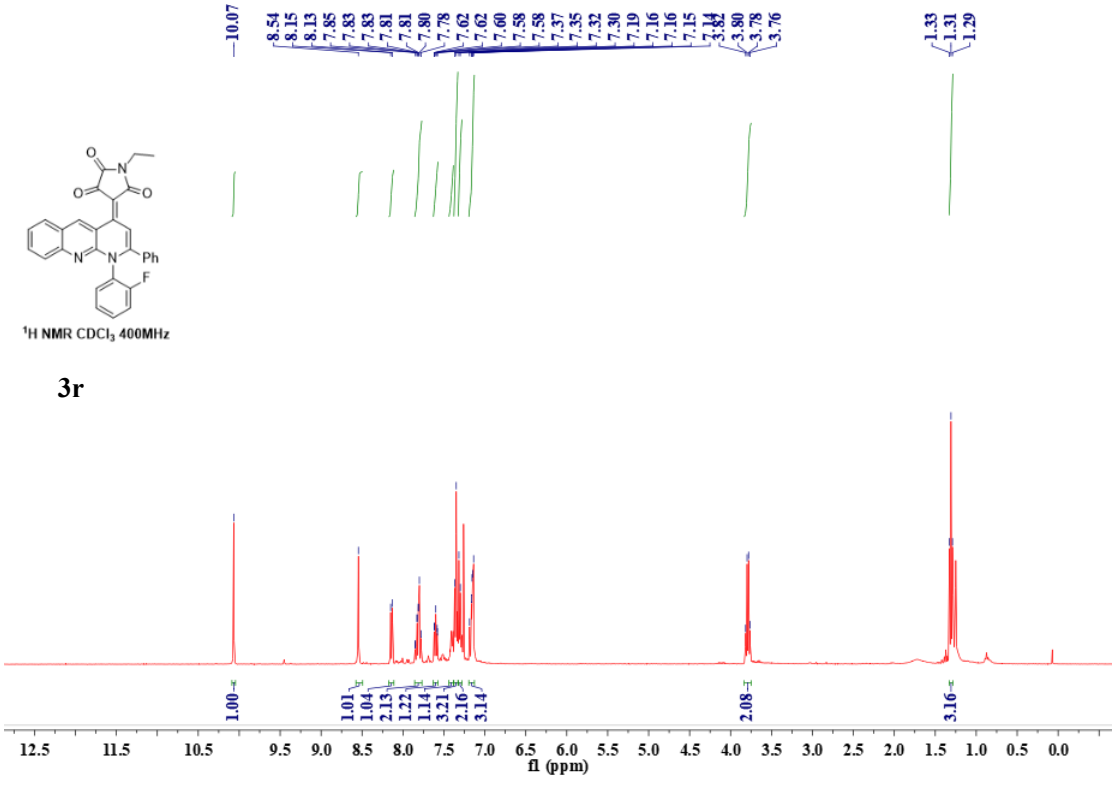
77.0
76.7
32.8
13.8
Ph
NO2
13C NMR CDCl3 100MHz
f1 (ppm)

3q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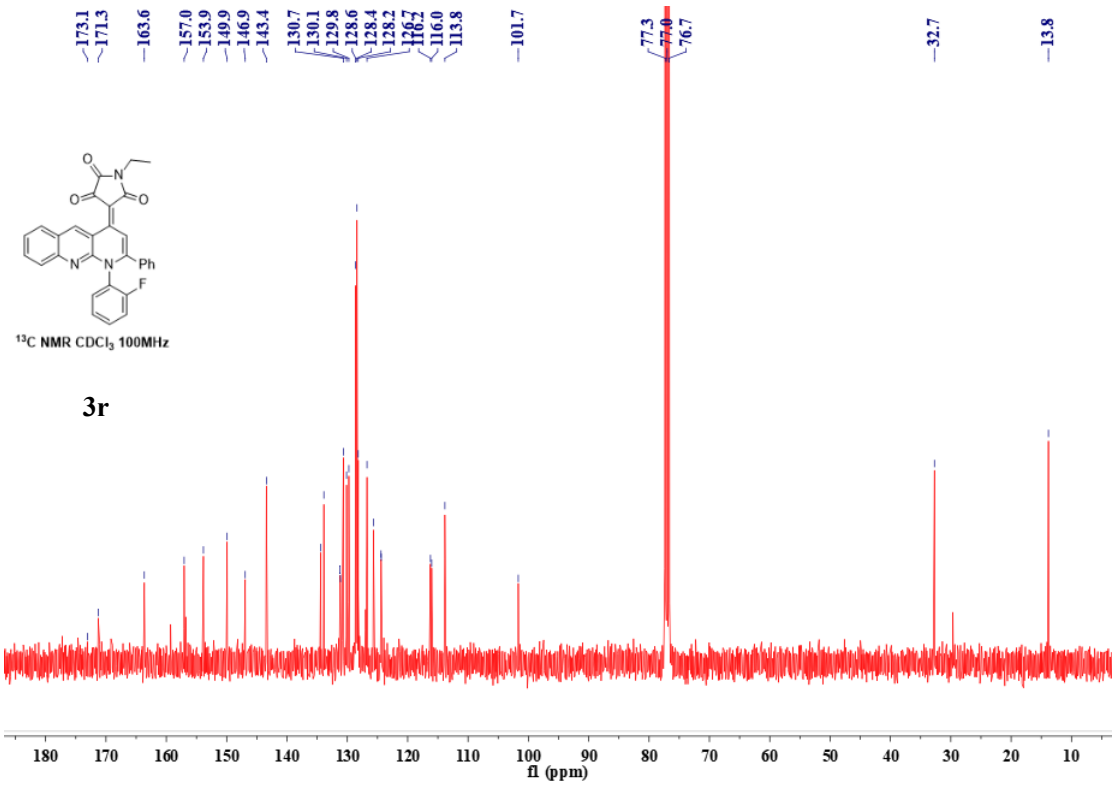
7.62
7.60
7.58
7.58
7.37
7.35
7.32
7.30
7.19
7.16
7.16
7.15
7.14
3.82
3.80
3.78
3.76
1.33
1.31
1.29
Ph
F
1H NMR CDCl3 400MHz
1.00
1.01
1.04
2.13
1.22
1.14
3.21
2.16
3.14
2.08
3.16
f1 (ppm)

3r



^{13}C NMR $CDCl_3$ 100MHz

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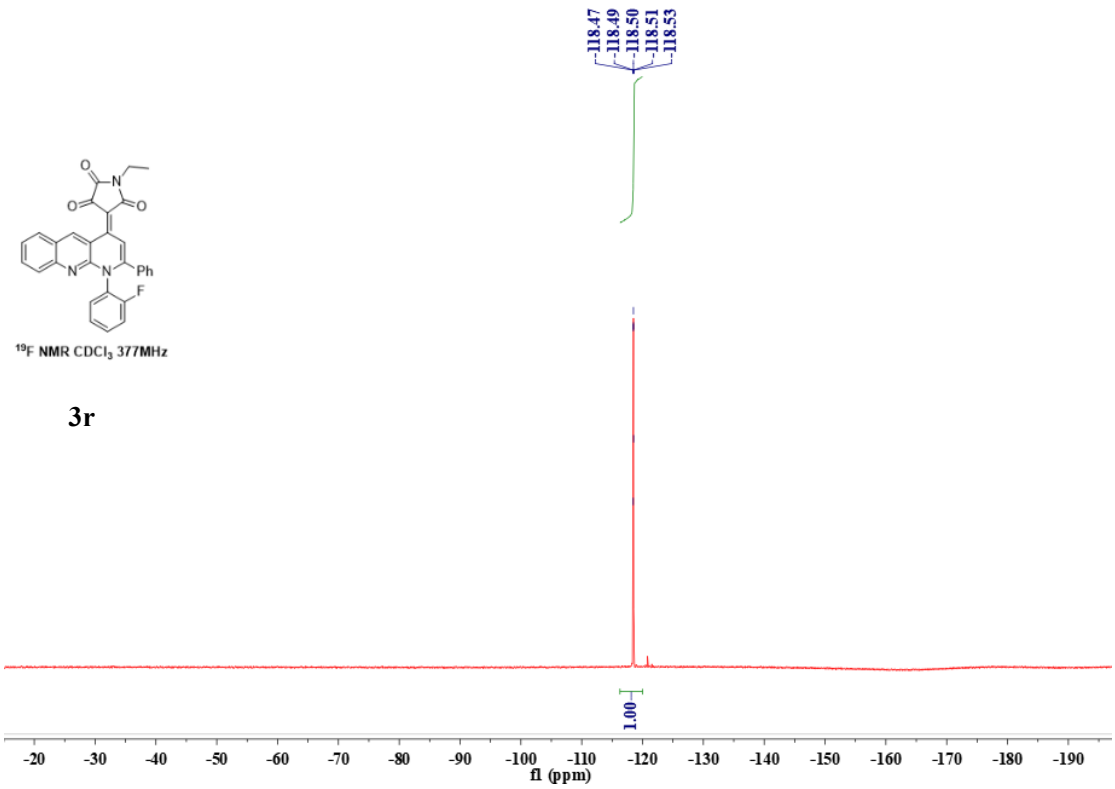
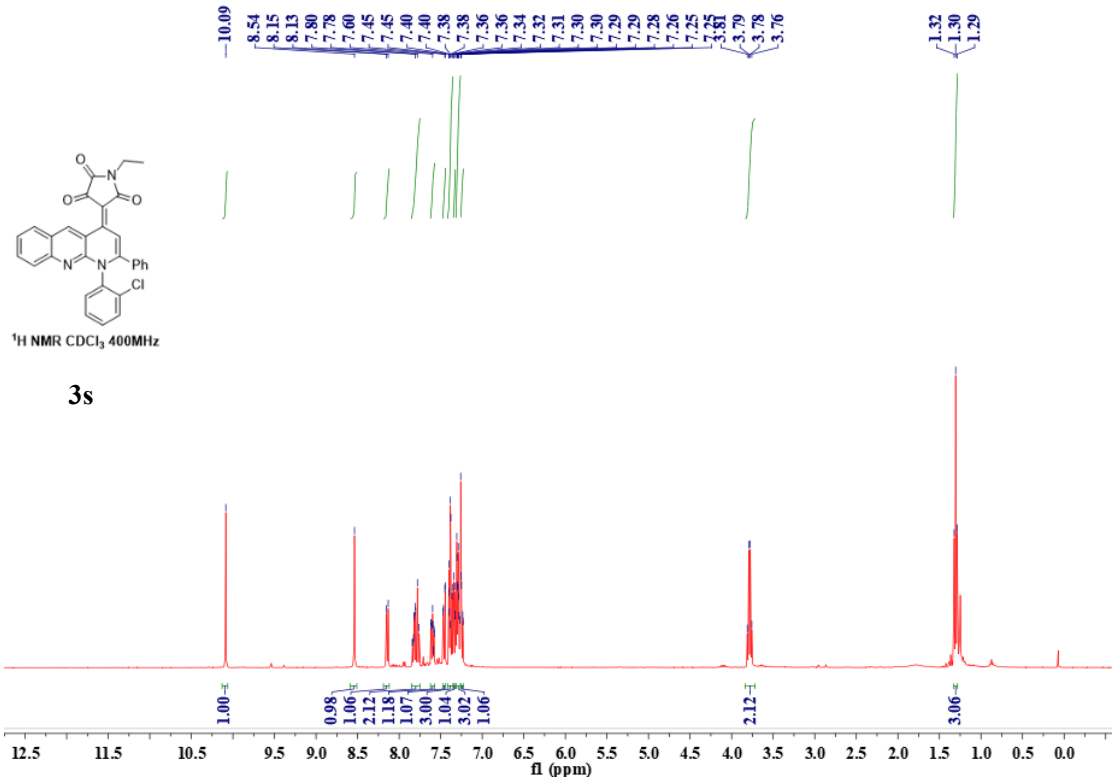


^{19}F NMR $CDCl_3$ 377MHz

3r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7.32
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7.30
7.30
7.29
7.29
7.28
7.26
7.25
3.81
3.79
3.78
3.76
1.32
1.30
1.29
Ph
Cl
1H NMR CDCl3 400MHz
3s
1.00
0.98
1.06
2.12
1.18
1.07
3.00
1.04
3.02
1.06
2.12
3.06
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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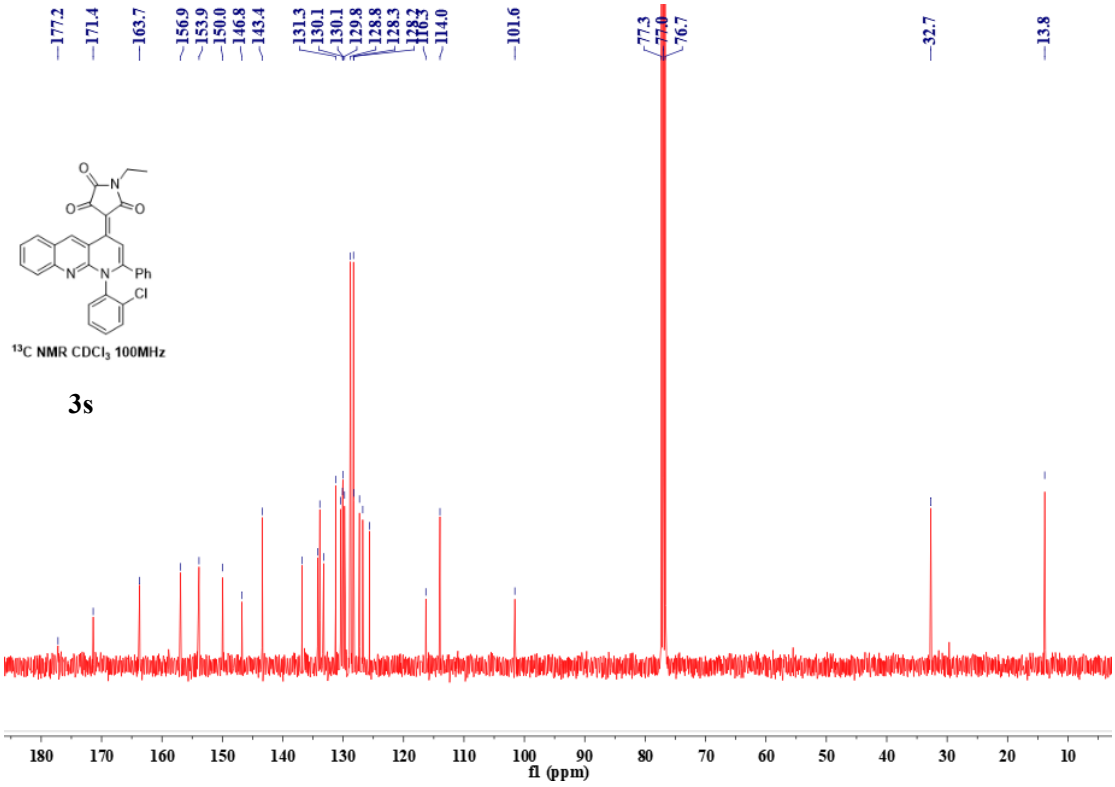
1.0
0.5
0.0
f1 (ppm)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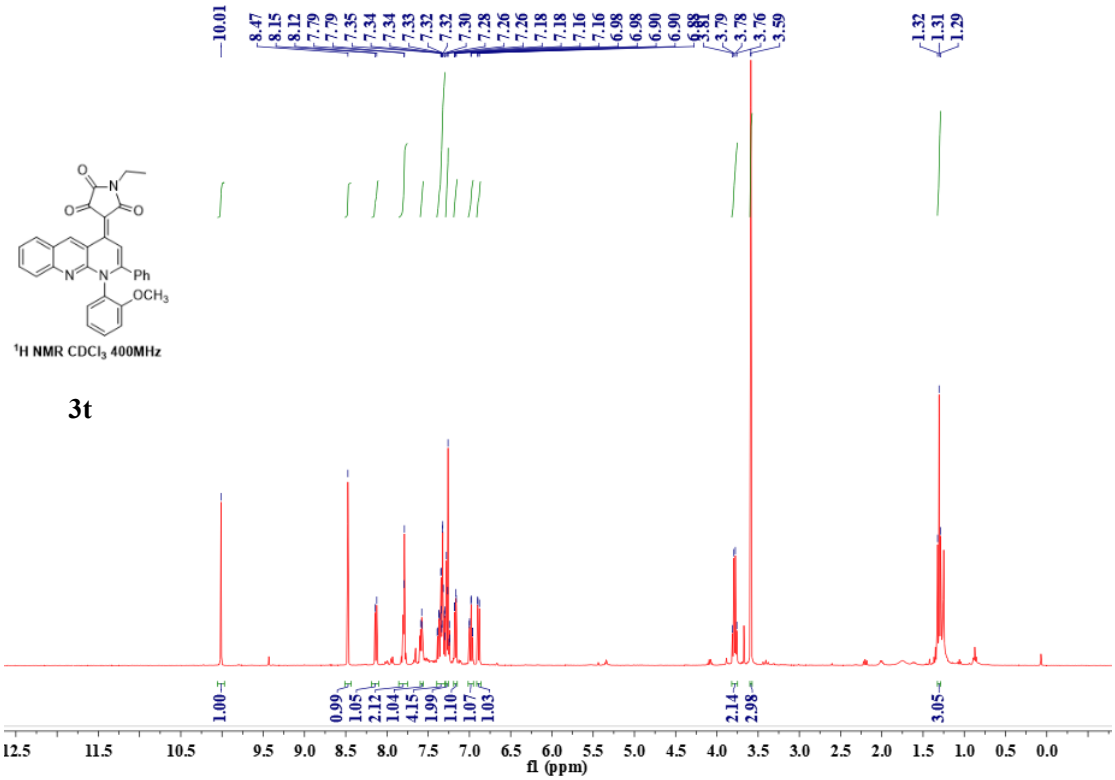
130.1
129.8
128.8
128.3
118.2
116.3
114.0
101.6
77.3
77.0
76.7
32.7
13.8
Ph
Cl
13C NMR CDCl3 100MHz
3s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.26
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7.18
7.16
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6.90
3.79
3.78
3.76
3.59
1.32
1.31
1.29
Ph
OCH3
1H NMR CDCl3 400MHz
3t
1.00
0.99
1.05
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4.15
1.99
1.10
1.07
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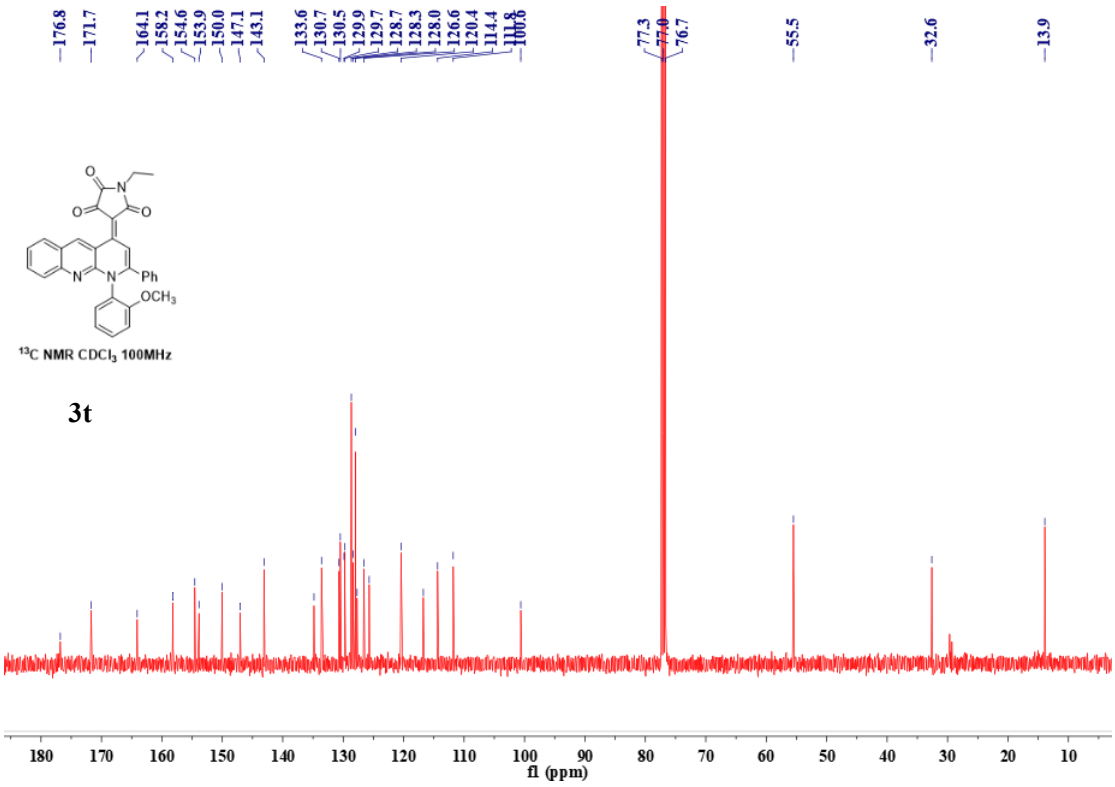
2.98
3.05
f1 (ppm)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129.7
128.7
128.3
128.0
126.6
120.4
114.4
111.8
100.6
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76.7
55.5
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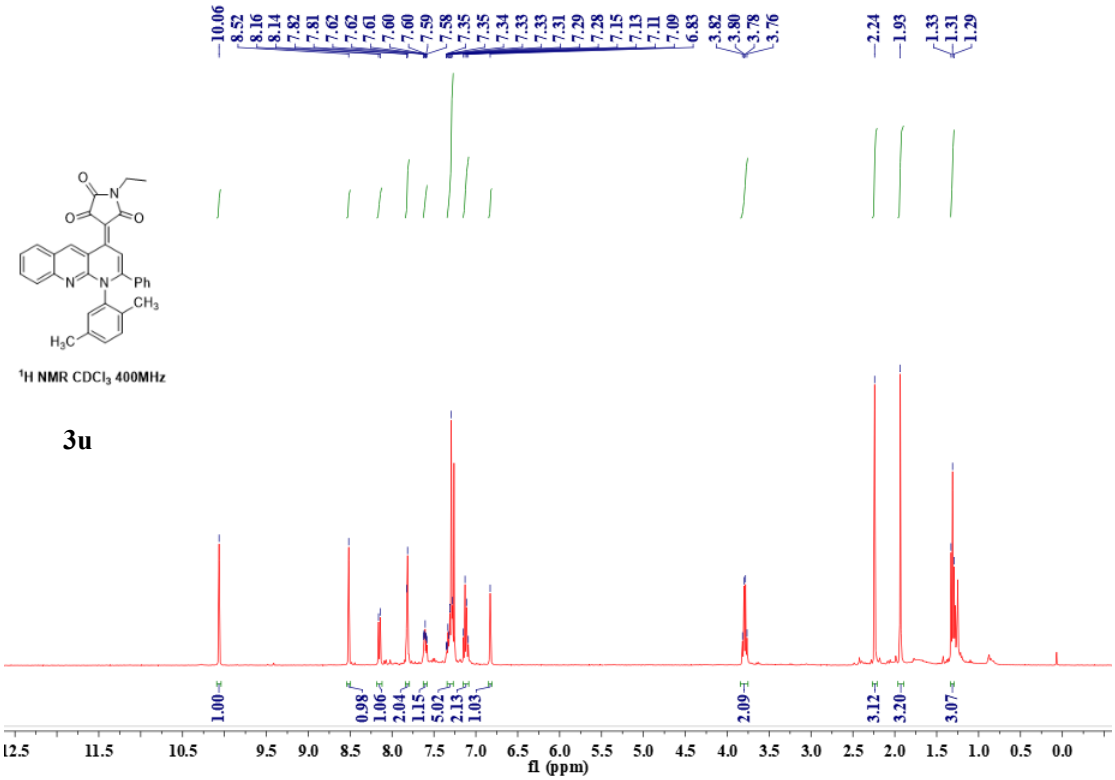
13.9
Ph
OCH3
13C NMR CDCl3 100MHz
3t
f1 (ppm)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7.15
7.13
7.11
7.09
6.83
3.82
3.80
3.78
3.76
2.24
1.93
1.33
1.31
1.29
Ph
CH3
H3C
1H NMR CDCl3 400MHz
3u
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1.15
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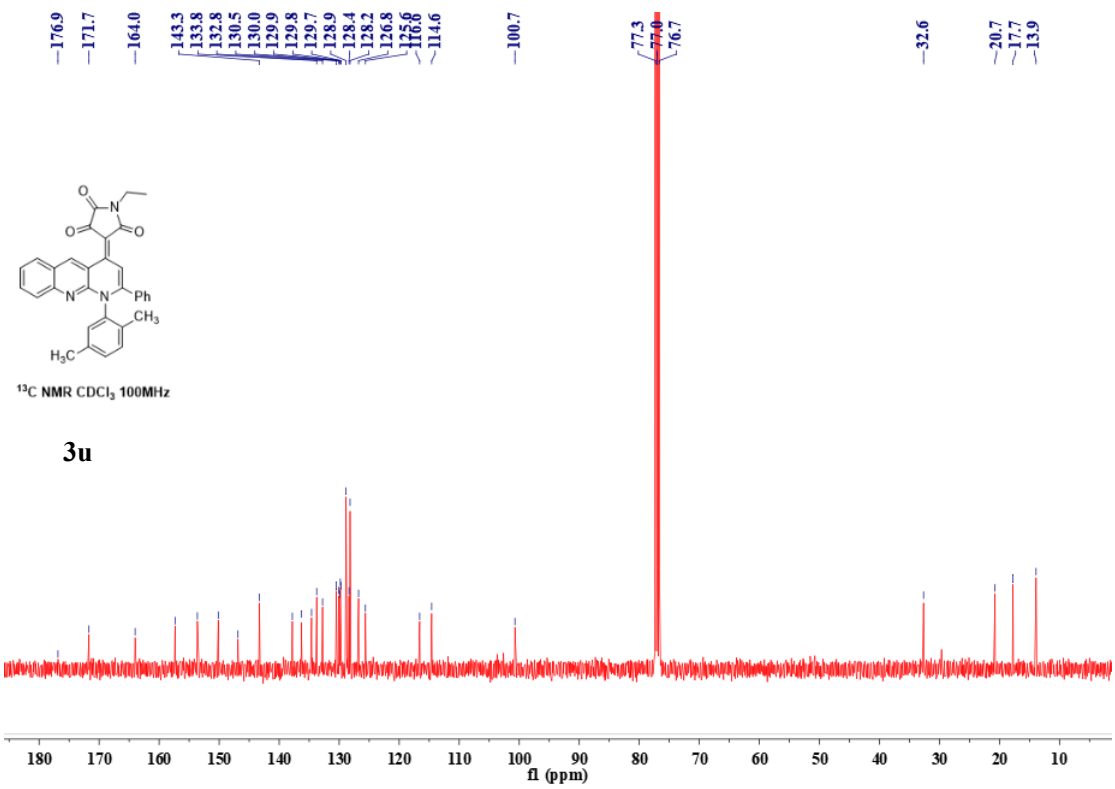
2.13
1.03
2.09
3.12
3.20
3.07
f1 (ppm)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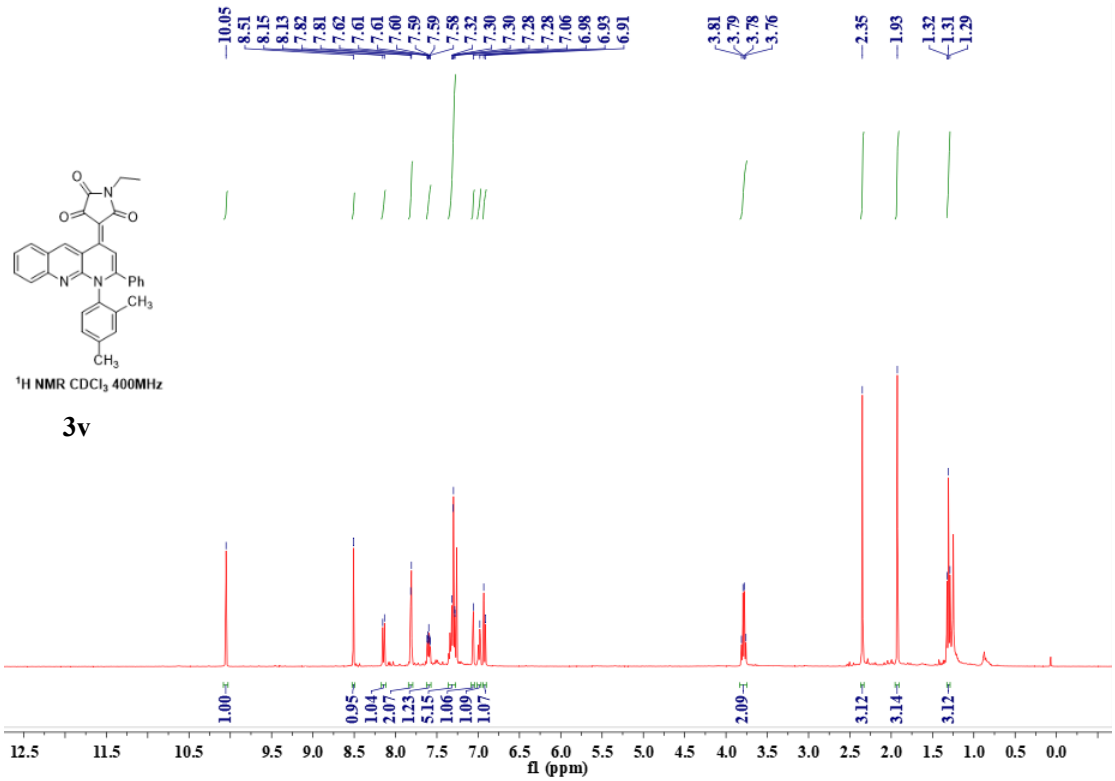
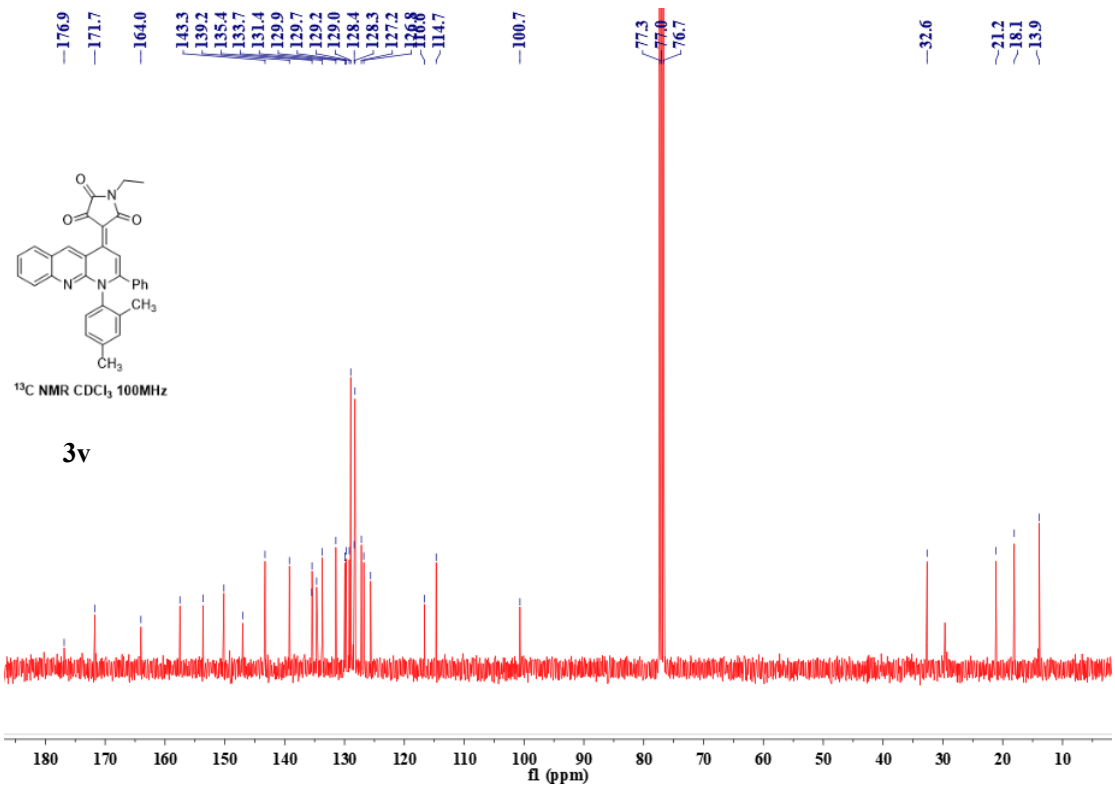
126.8
125.6
116.6
114.6
100.7
77.3
77.0
76.7
32.6
20.7
17.7
13.9
Ph
CH3
H3C
13C NMR CDCl3 100MHz
3u
f1 (ppm)



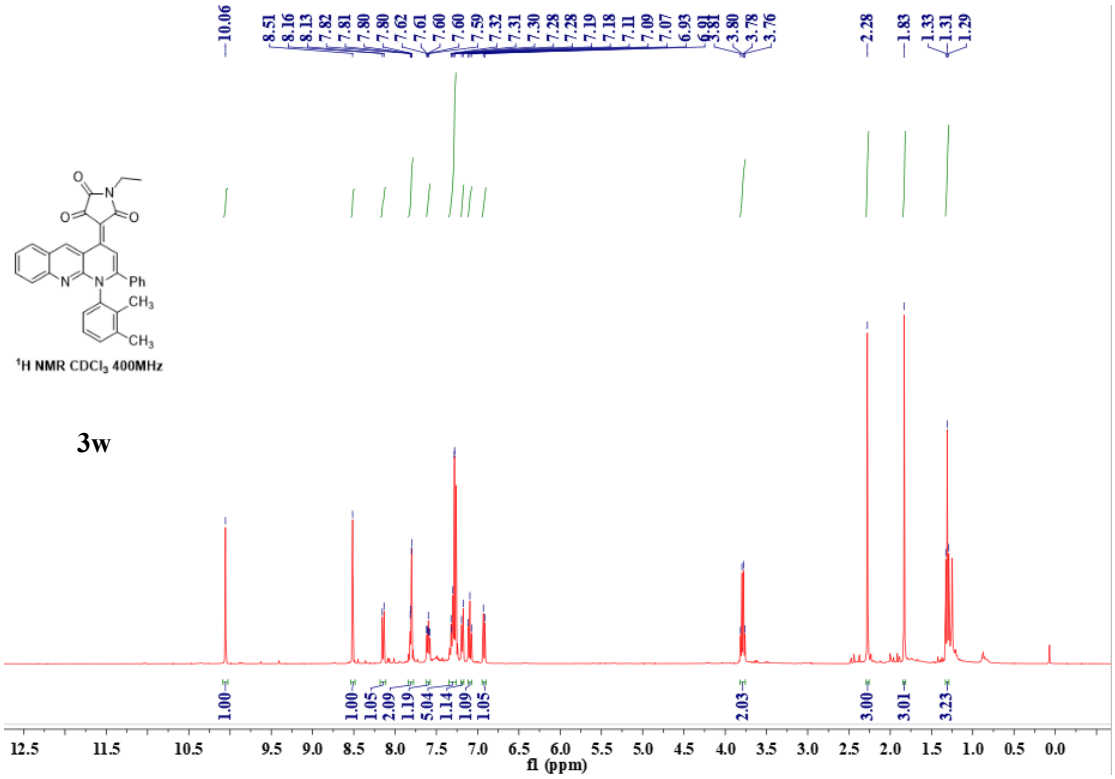
^{1}H NMR $CDCl_3$ 400MHz

3v



^{13}C NMR $CDCl_3$ 100MHz

3v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7.18
7.11
7.09
7.07
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6.91
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3.76
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1.33
1.31
1.29
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1.00
1.05
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1.19
5.04
1.14
1.09
1.05
2.03
3.00
3.01
3.23
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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0.0
f1 (ppm)
Ph
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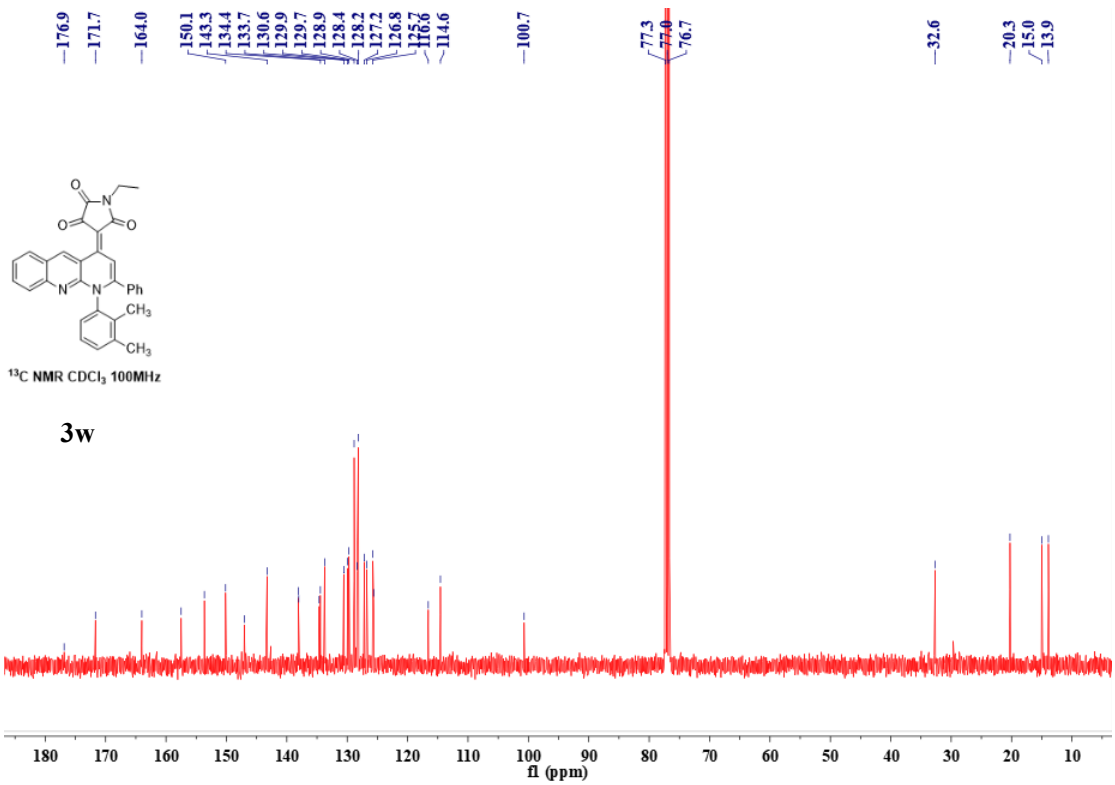
CH3
1H NMR CDCl3 400MHz

3w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128.2
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126.8
125.7
116.6
114.6
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77.3
77.0
76.7
32.6
20.3
15.0
13.9
180
170
160
150
140
130
120
110
100
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50
40
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20
10
f1 (ppm)
Ph
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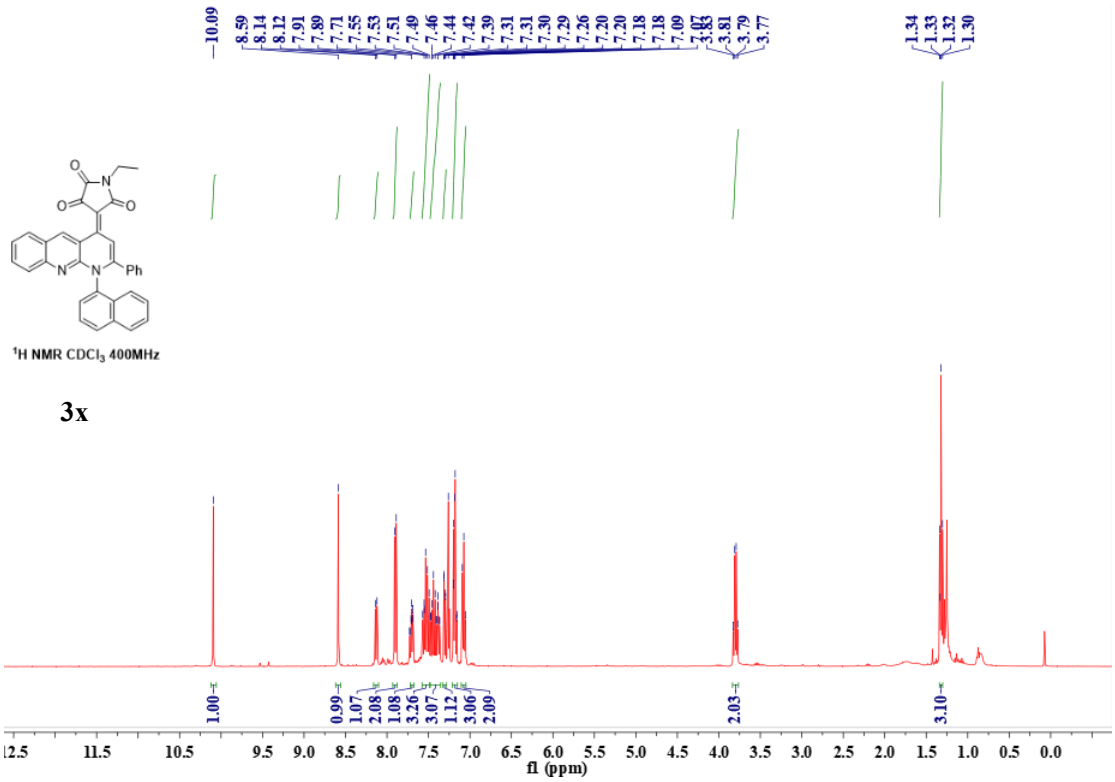
CH3
13C NMR CDCl3 100MHz

3w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7.39
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7.31
7.30
7.29
7.26
7.20
7.20
7.18
7.18
7.09
7.07
3.83
3.81
3.79
3.77
1.34
1.33
1.32
1.30
Ph
1H NMR CDCl3 400MHz
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0.99
1.07
2.08
1.08
3.26
3.07
1.12
3.06
2.09
2.03
3.10
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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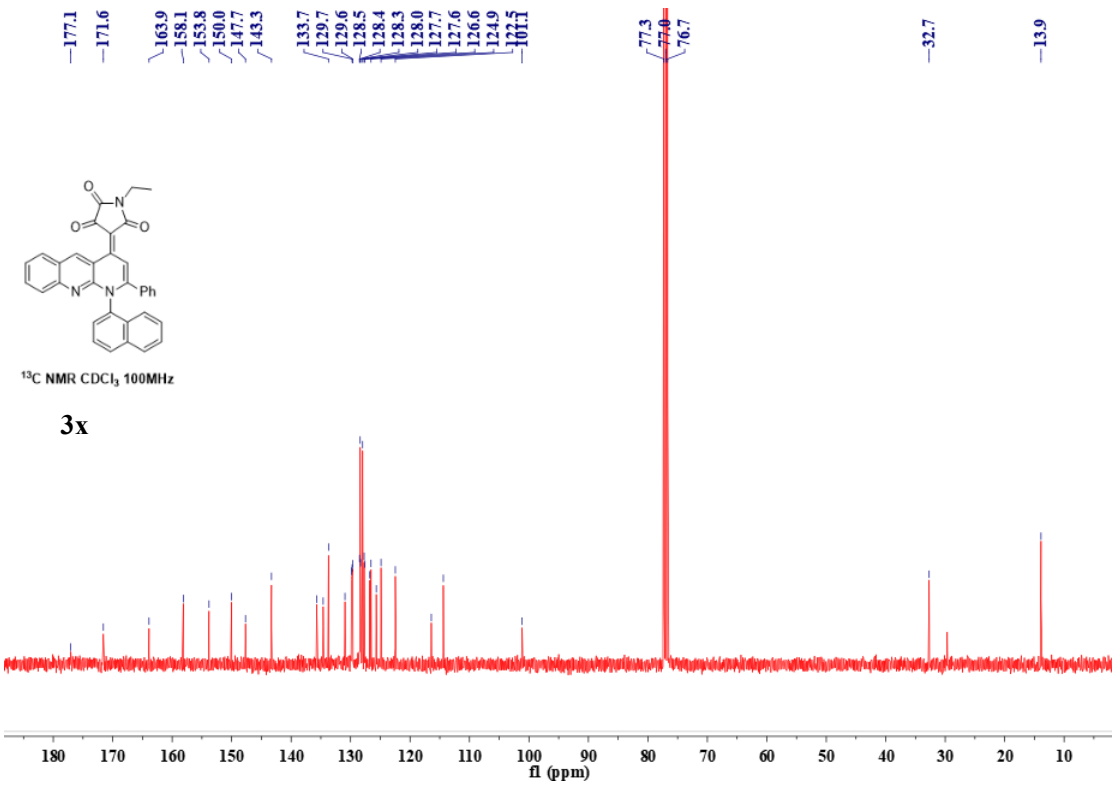
f1 (ppm)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128.4
128.3
128.0
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127.6
126.6
124.9
77.3
77.0
76.7
32.7
13.9
Ph
13C NMR CDCl3 100MHz
3x
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50
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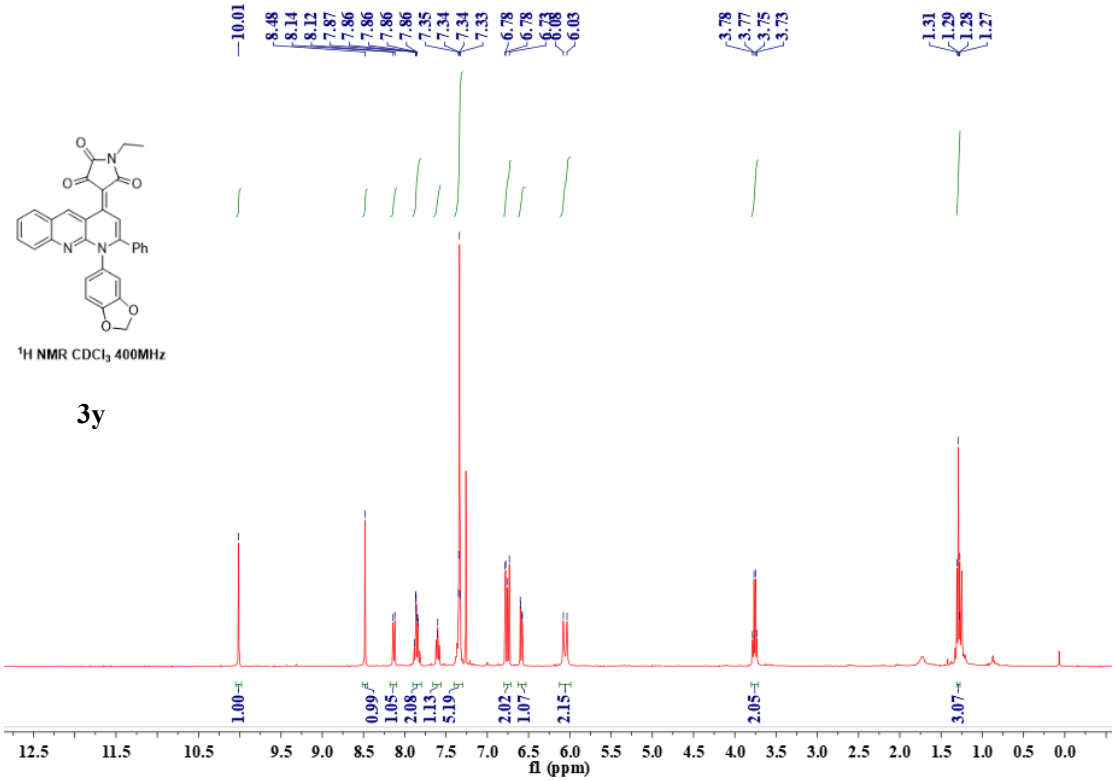
20
10
f1 (ppm)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6.78
6.73
6.08
6.03
3.78
3.77
3.75
3.73
1.31
1.29
1.28
1.27
Ph
1H NMR CDCl3 400MHz
3y
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5.19
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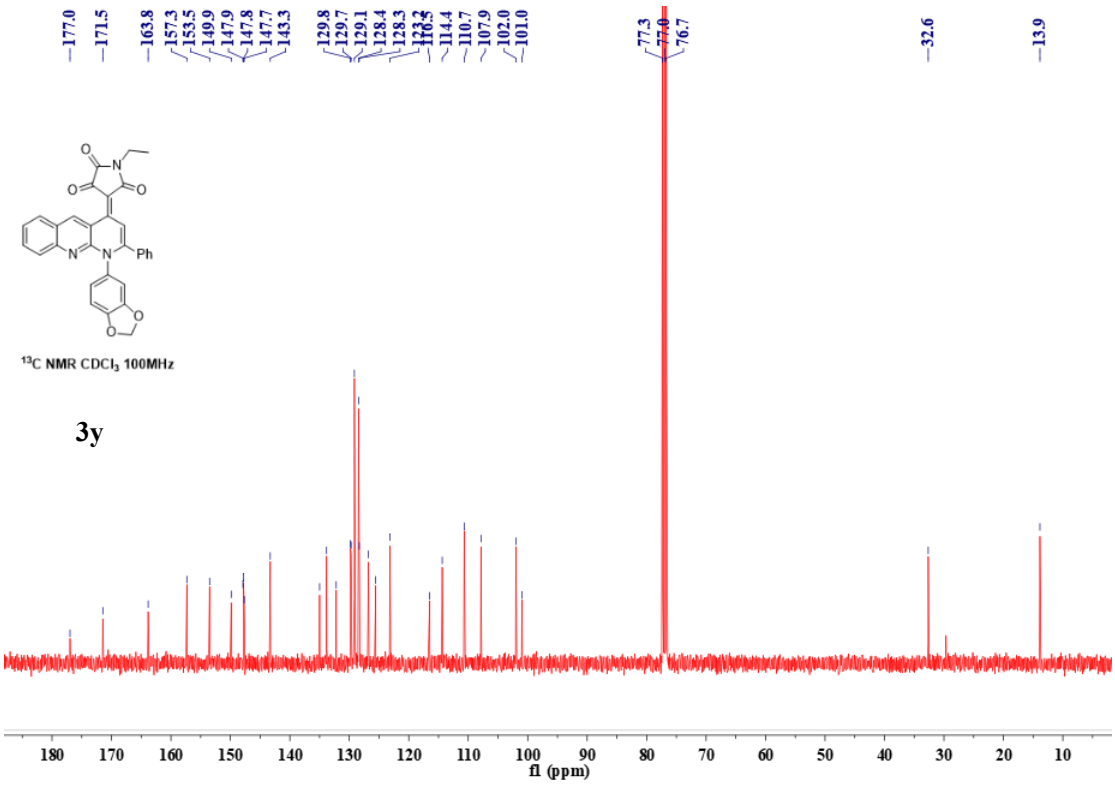
1.07
2.15
2.05
3.07
f1 (ppm)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128.4
128.3
123.2
116.5
114.4
110.7
107.9
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77.3
77.0
76.7
32.6
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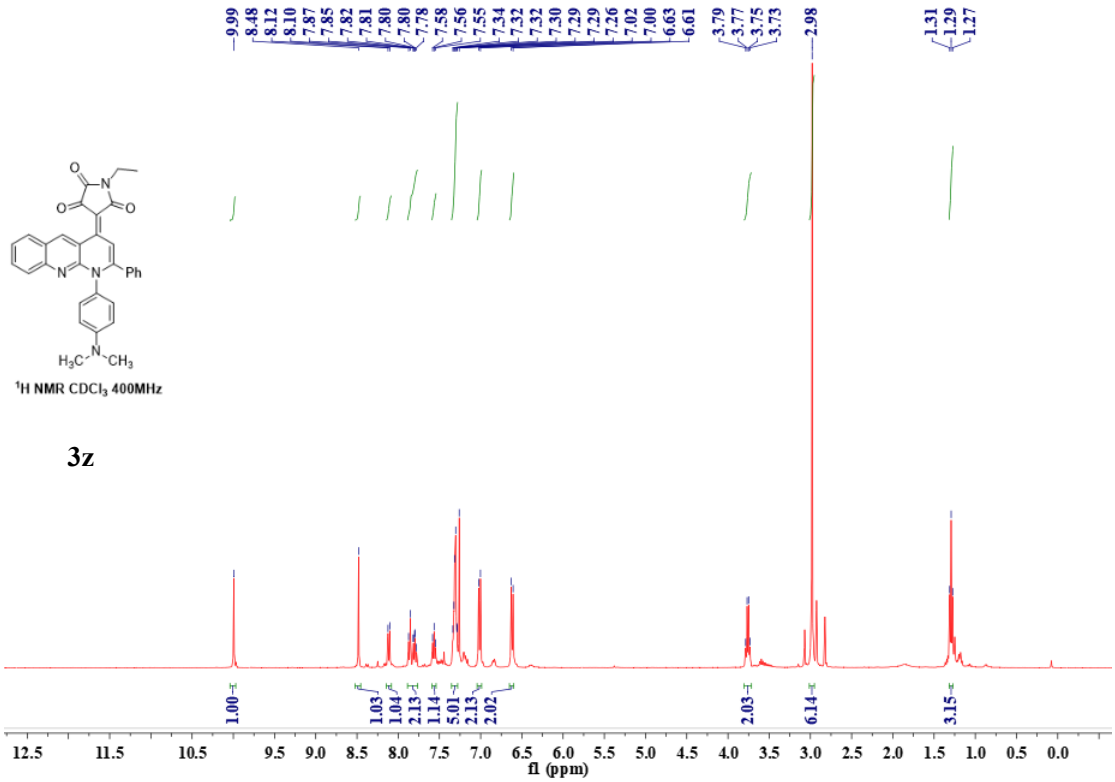
Ph
13C NMR CDCl3 100MHz
3y
f1 (ppm)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7.32
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7.29
7.26
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7.00
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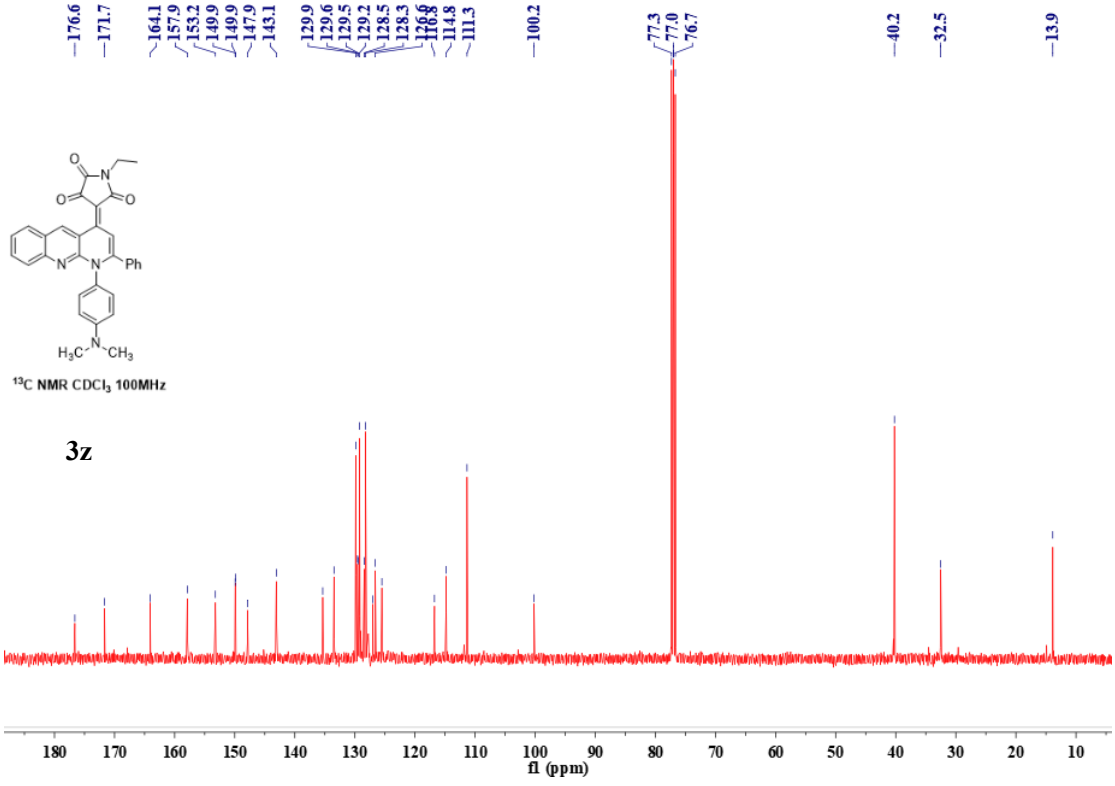
6.61
3.79
3.77
3.75
3.73
2.98
1.31
1.29
1.27
Ph
H3C
CH3
1H NMR CDCl3 400MHz
3z
1.00
1.03
1.04
2.13
1.14
5.01
2.13
2.02
2.03
6.14
3.15
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.5
128.3
126.6
114.8
111.3
100.2
77.3
77.0
76.7
40.2
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CH3
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3z
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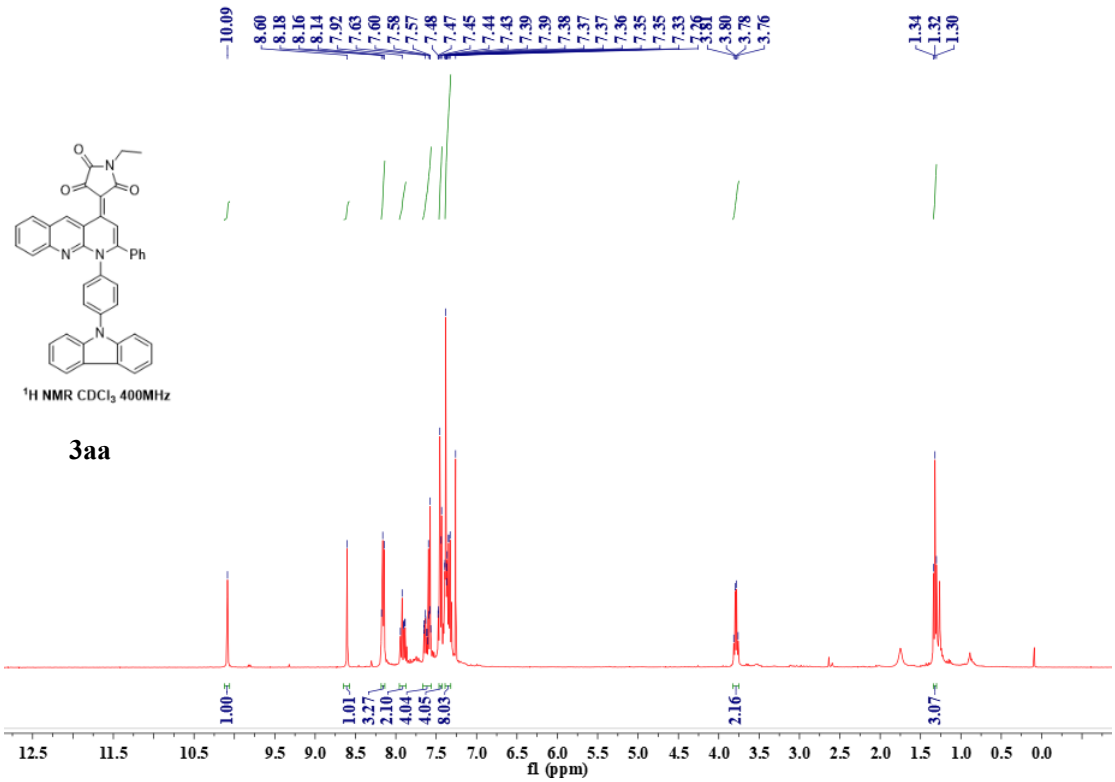
f1 (ppm)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7.26
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3.80
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3.76
1.34
1.32
1.30
Ph
1H NMR CDCl3 400MHz
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1.01
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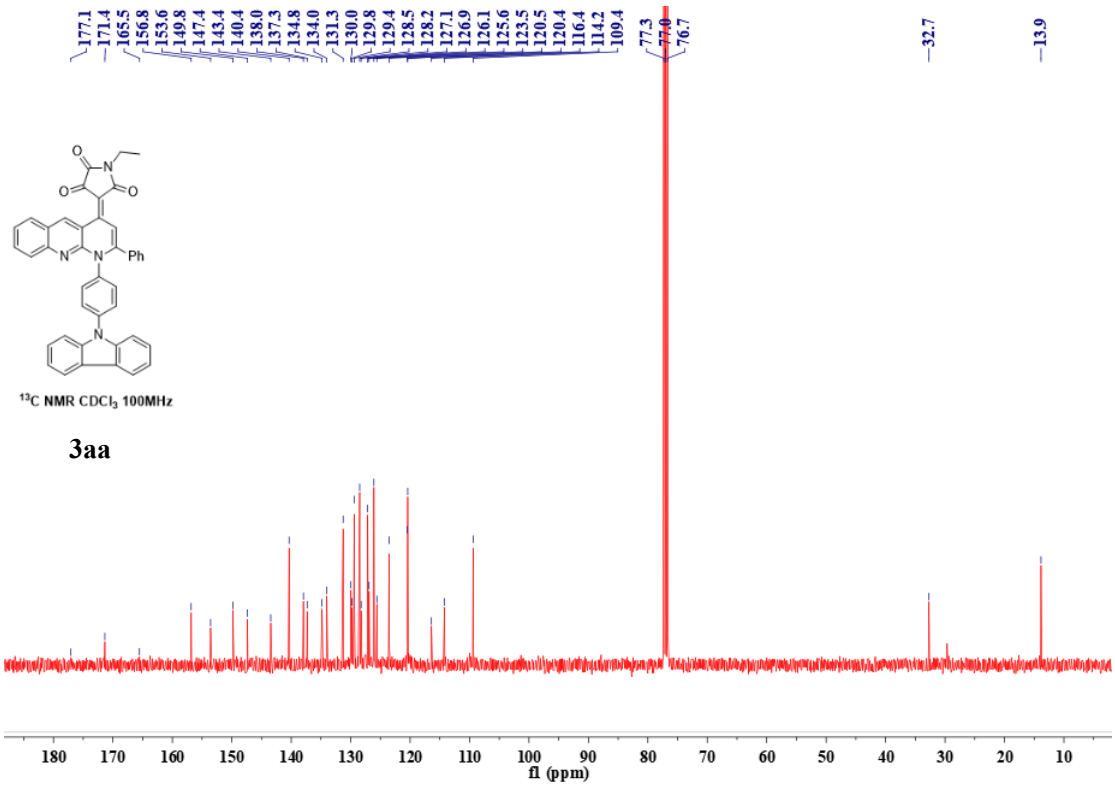
4.04
4.05
8.03
2.16
3.07
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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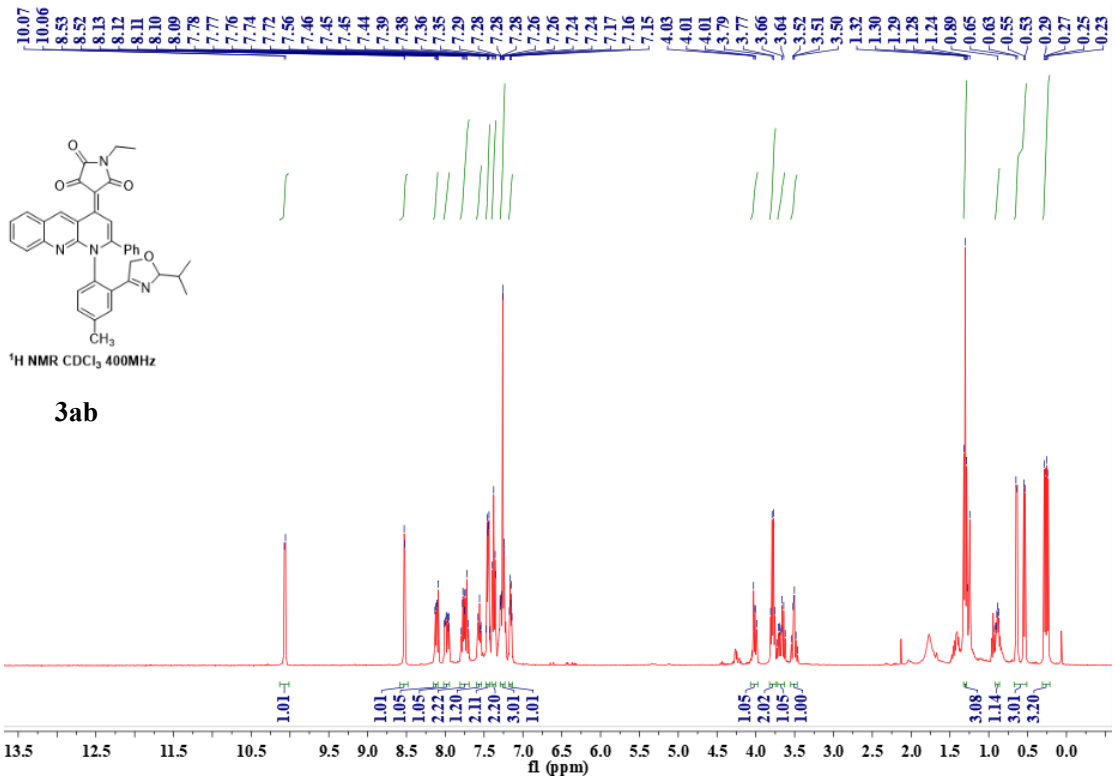
171.4
165.5
156.8
153.6
149.8
147.4
143.4
140.4
138.0
137.3
134.8
134.0
131.3
130.0
129.8
129.4
128.5
128.2
127.1
126.9
126.1
125.6
123.5
120.5
120.4
116.4
114.2
109.4
77.3
77.0
76.7
32.7
13.9
Ph
13C NMR CDCl3 100MHz
3aa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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10.06
8.53
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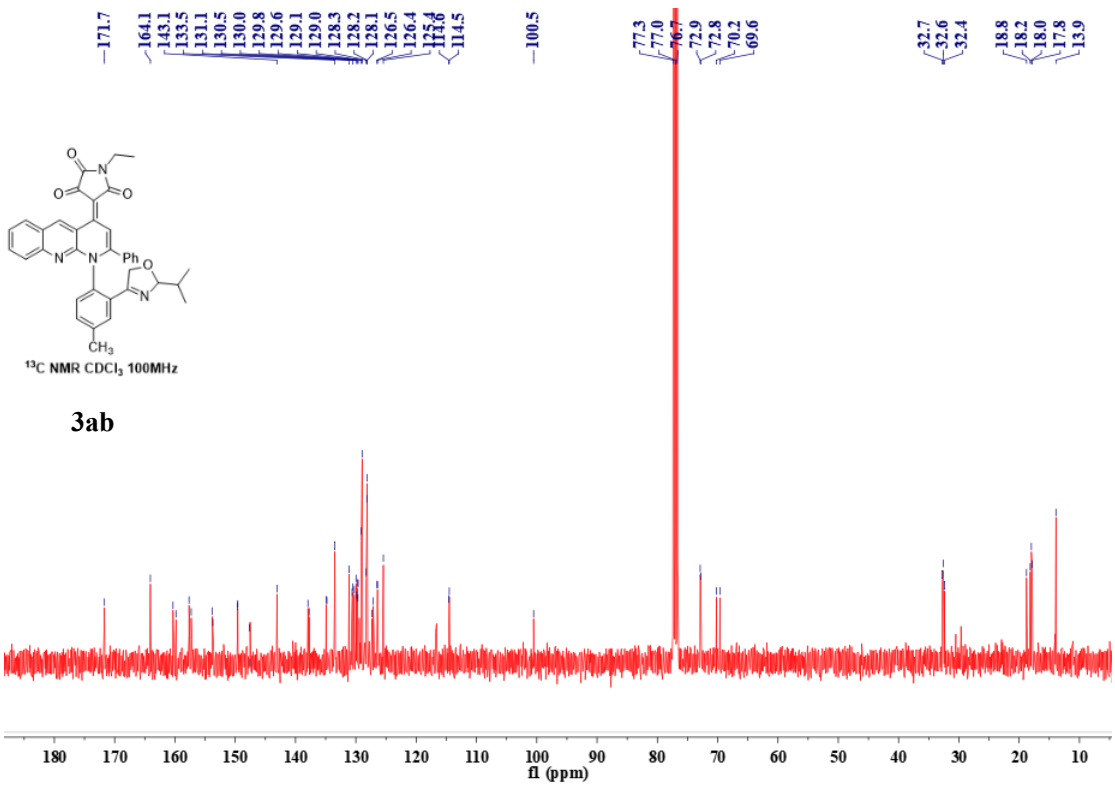
8.12
8.11
8.10
8.09
7.78
7.77
7.76
7.74
7.72
7.56
7.46
7.45
7.45
7.44
7.39
7.38
7.36
7.35
7.29
7.28
7.28
7.28
7.26
7.26
7.24
7.24
7.17
7.16
7.15
4.03
4.01
4.01
3.79
3.77
3.66
3.64
3.52
3.51
3.50
1.32
1.30
1.29
1.28
1.24
0.89
0.65
0.63
0.55
0.53
0.29
0.27
0.25
0.23
Ph
CH3
1H NMR CDCl3 400MHz
3ab
1.01
1.01
1.05
1.05
2.22
1.20
2.11
2.20
3.01
1.01
1.05
2.02
1.05
1.00
3.08
1.14
3.01
3.20
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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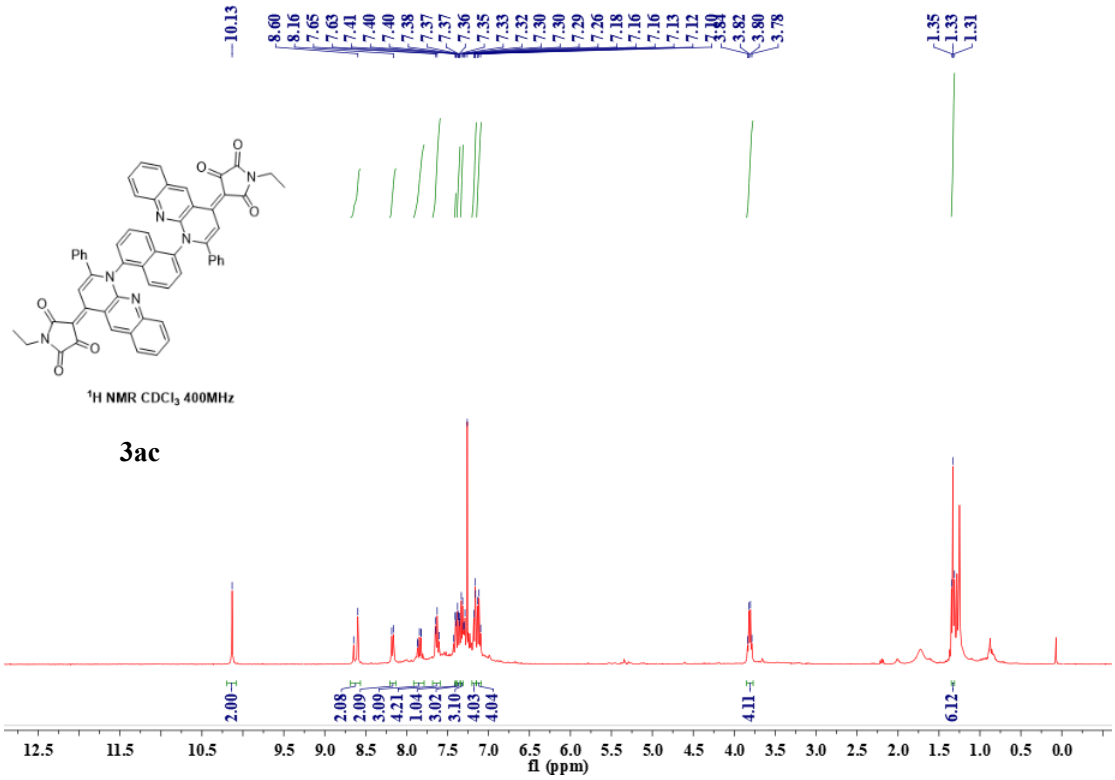
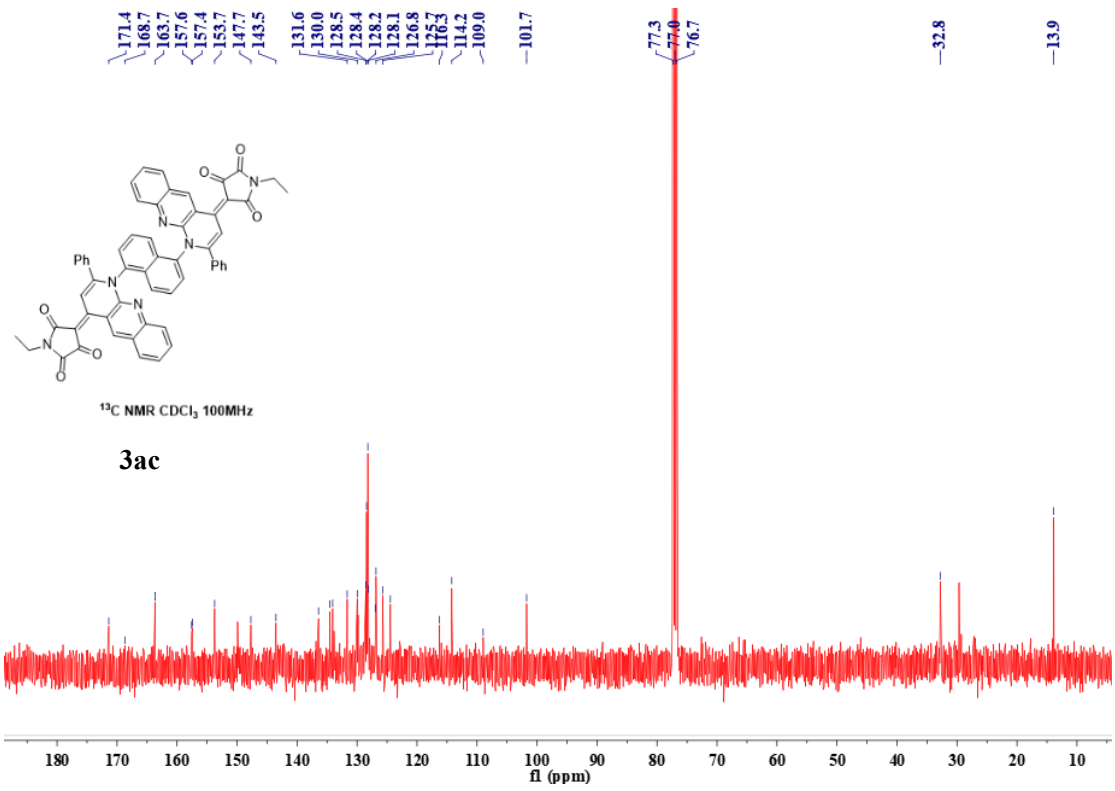
164.1
143.1
133.5
131.1
130.5
130.0
129.8
129.6
129.1
129.0
128.3
128.2
128.1
126.5
126.4
125.4
114.6
114.5
100.5
77.3
77.0
76.7
72.9
72.8
70.2
69.6
32.7
32.6
32.4
18.8
18.2
18.0
17.8
13.9
Ph
CH3
13C NMR CDCl3 100MHz
3ab
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



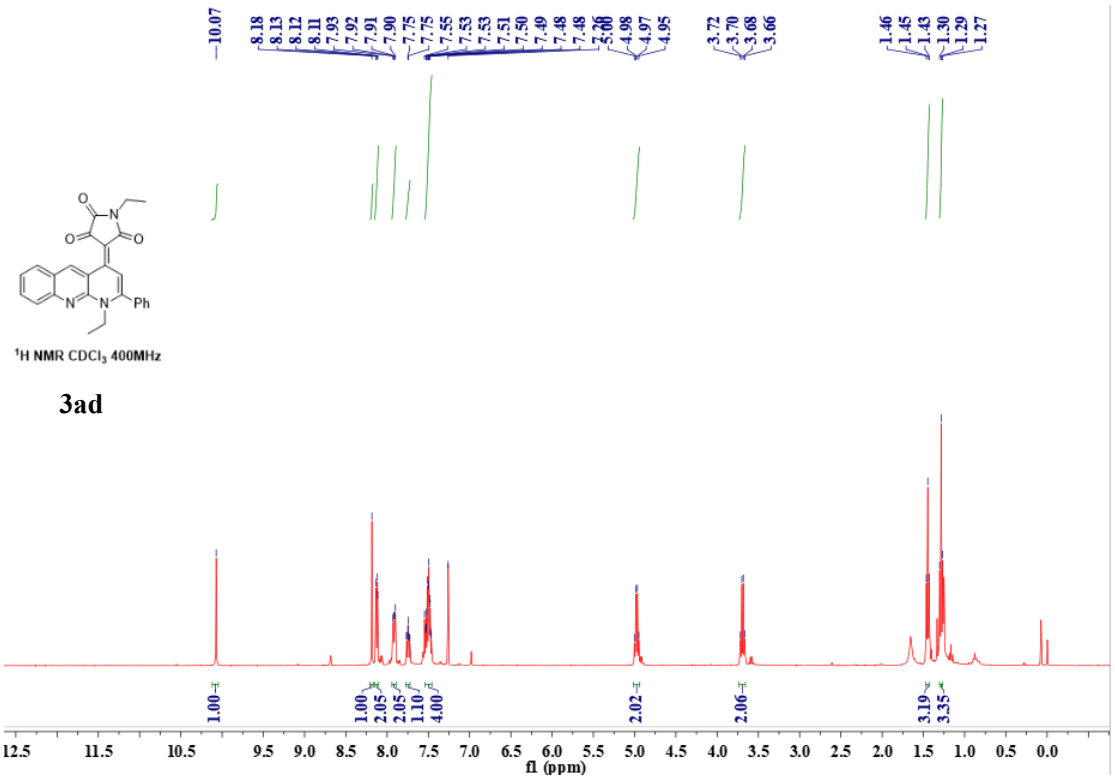
^{1}H NMR $CDCl_3$ 400MHz

3ac



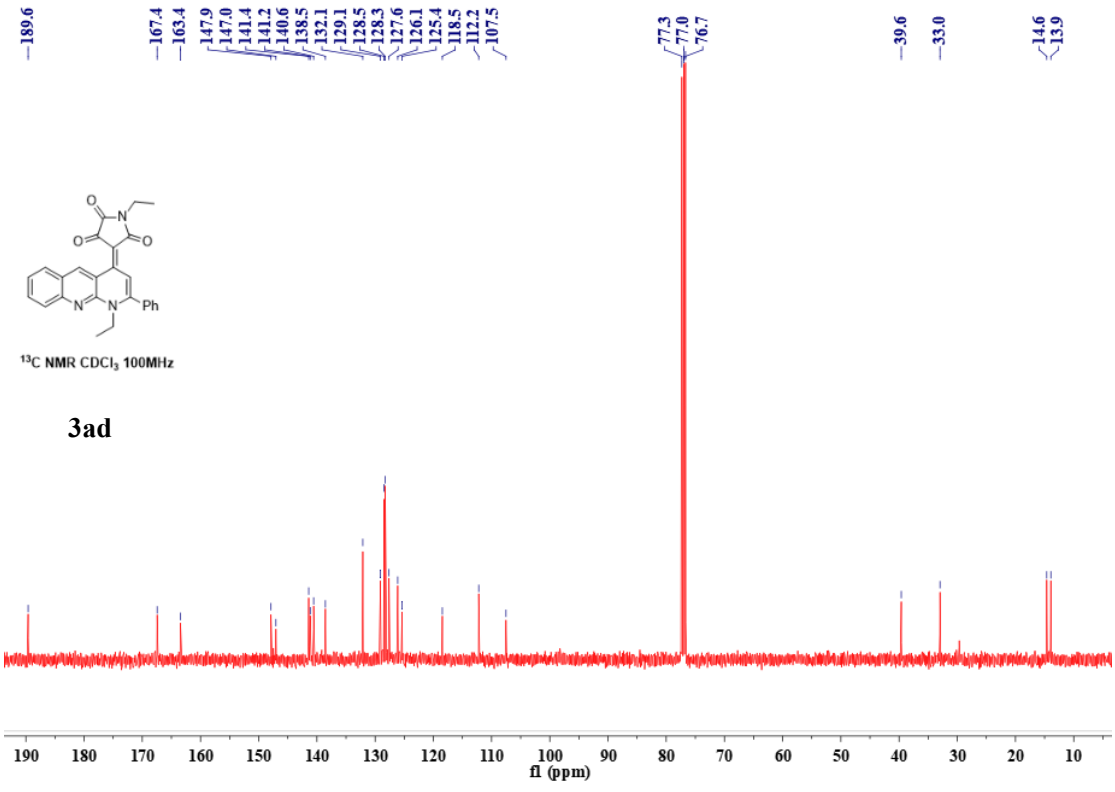
^{13}C NMR $CDCl_3$ 100MHz

3ac



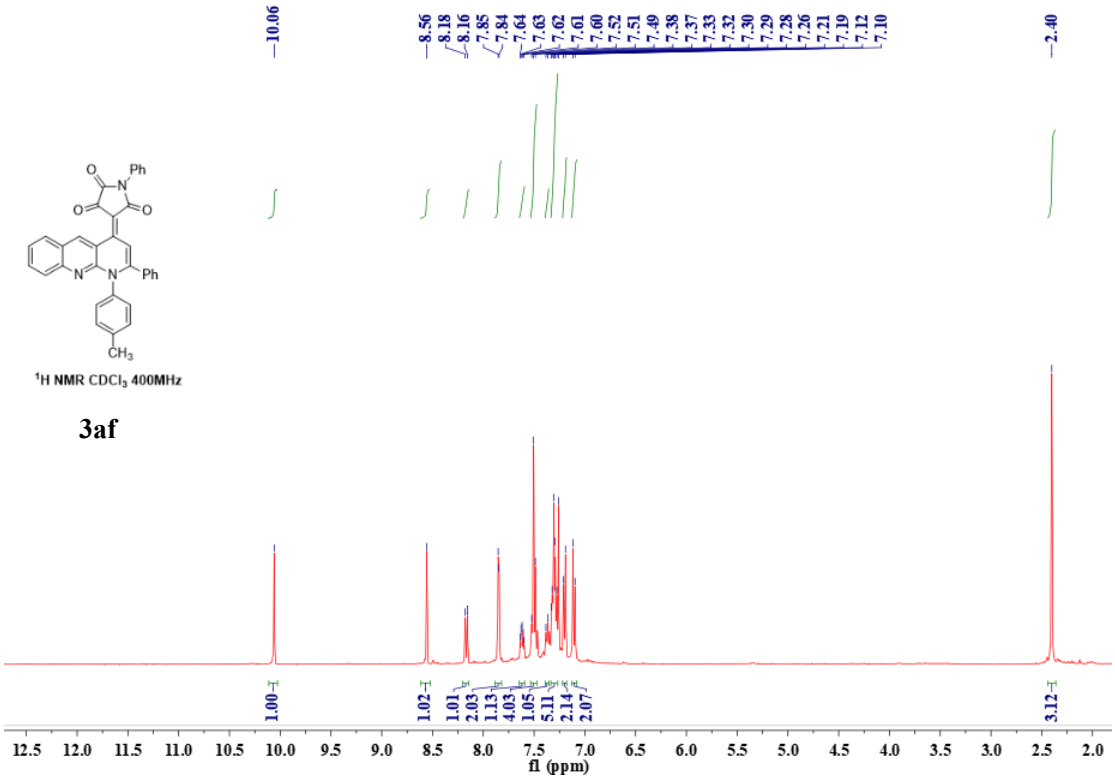
^{1}H NMR $CDCl_3$ 400MHz

3ad



^{13}C NMR $CDCl_3$ 100MHz

3ad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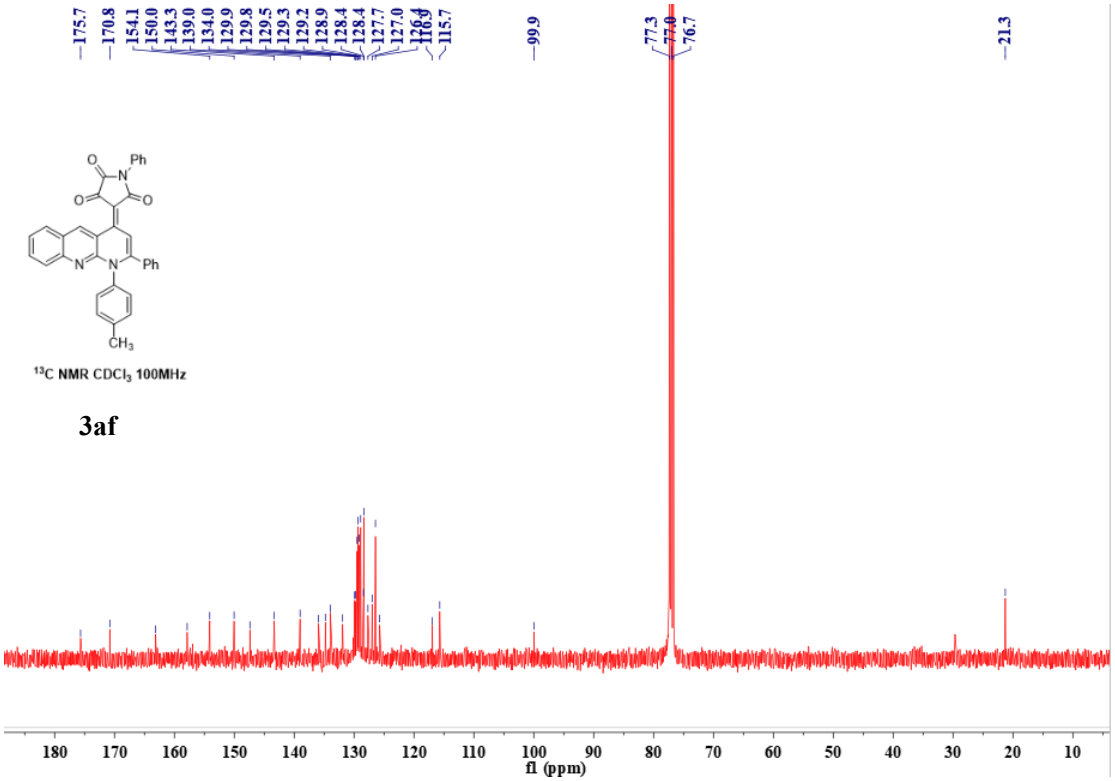
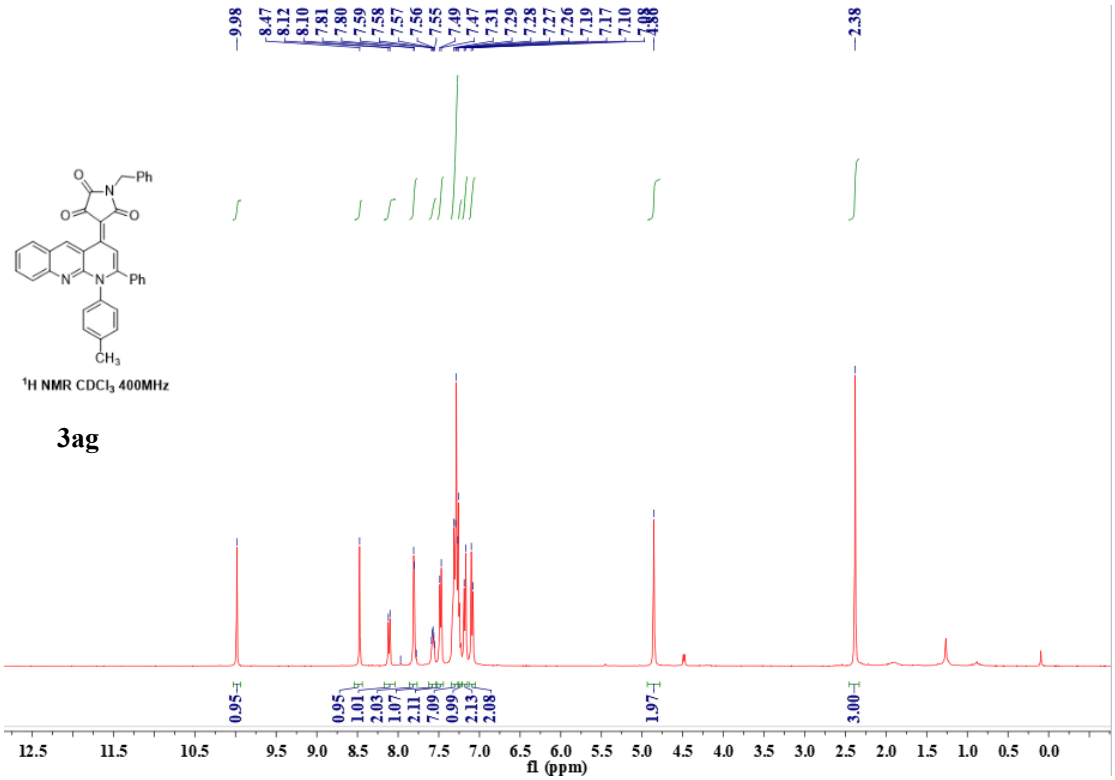
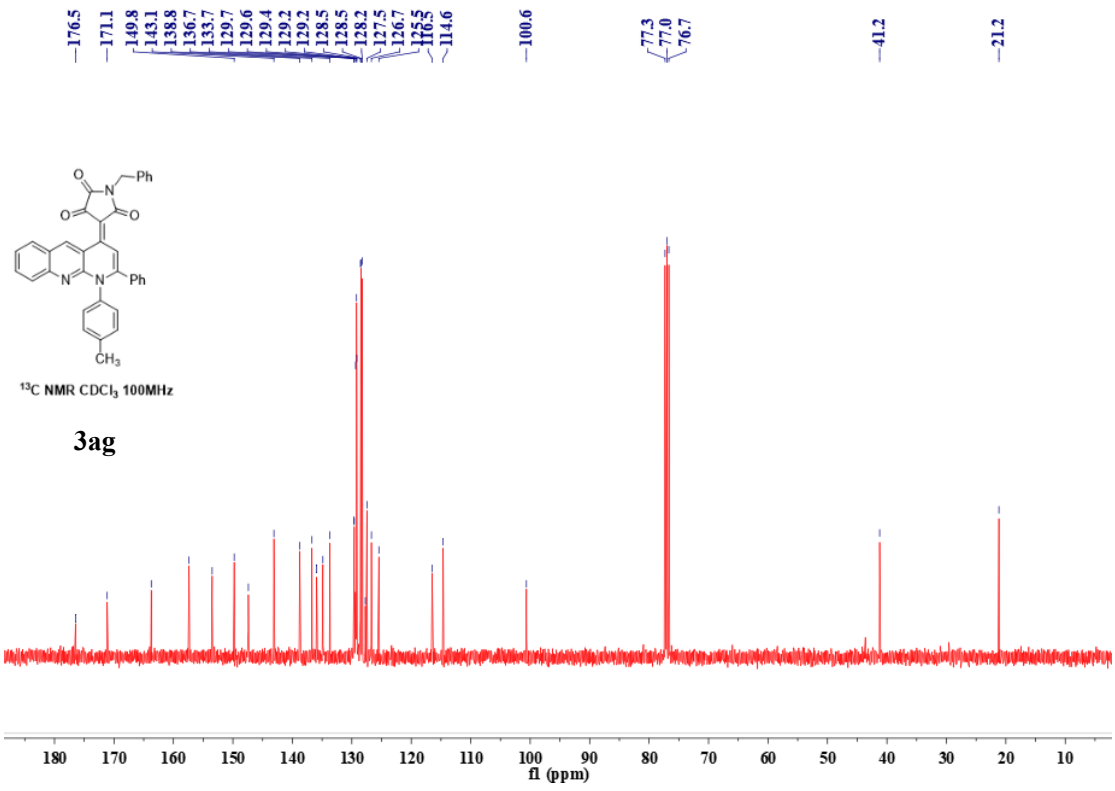
8.18
8.16
7.85
7.84
7.64
7.63
7.62
7.61
7.60
7.52
7.51
7.49
7.38
7.37
7.33
7.32
7.30
7.29
7.28
7.26
7.21
7.19
7.12
7.10
2.40
Ph
Ph
CH3
1H NMR CDCl3 400MHz
3af
1.00
1.02
1.01
2.03
1.13
4.03
1.05
5.11
2.14
2.07
3.12
f1 (ppm)


175.7
170.8
154.1
150.0
143.3
139.0
134.0
129.9
129.8
129.5
129.3
129.2
128.9
128.4
128.4
127.7
127.0
126.4
116.9
115.7
99.9
77.3
77.0
76.7
21.3
Ph
Ph
CH3
13C NMR CDCl3 100MHz
3af
f1 (ppm)



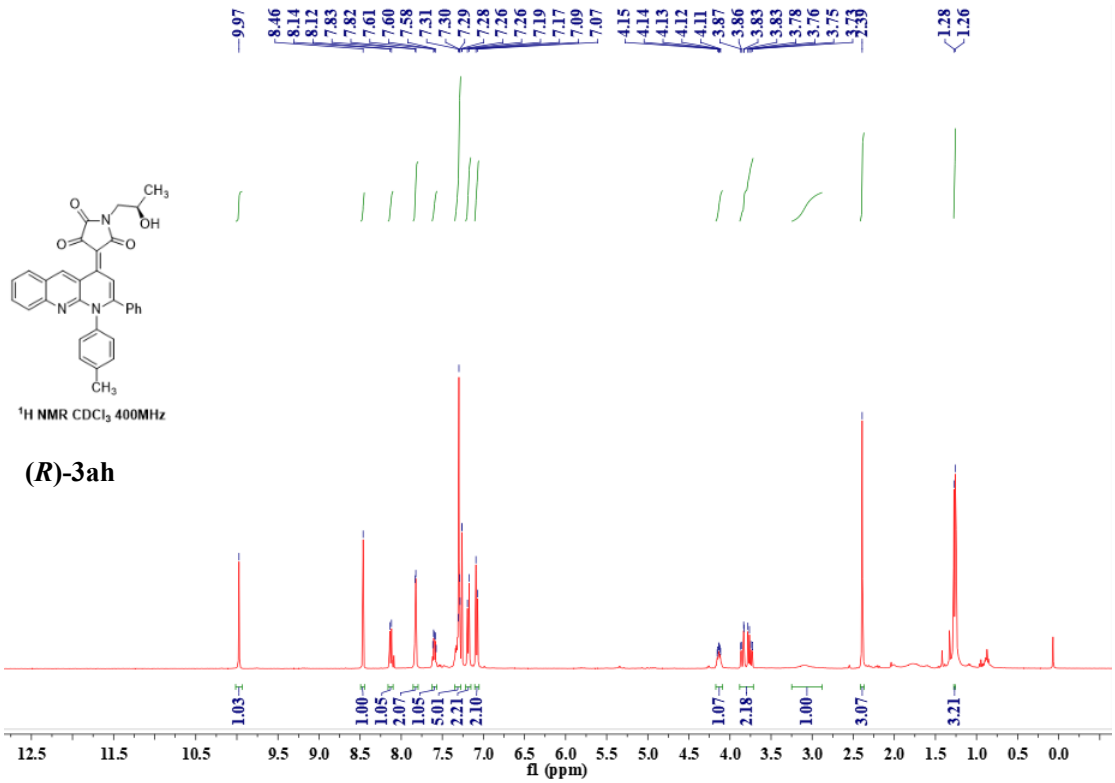
^{1}H NMR $CDCl_3$ 400MHz

3ag



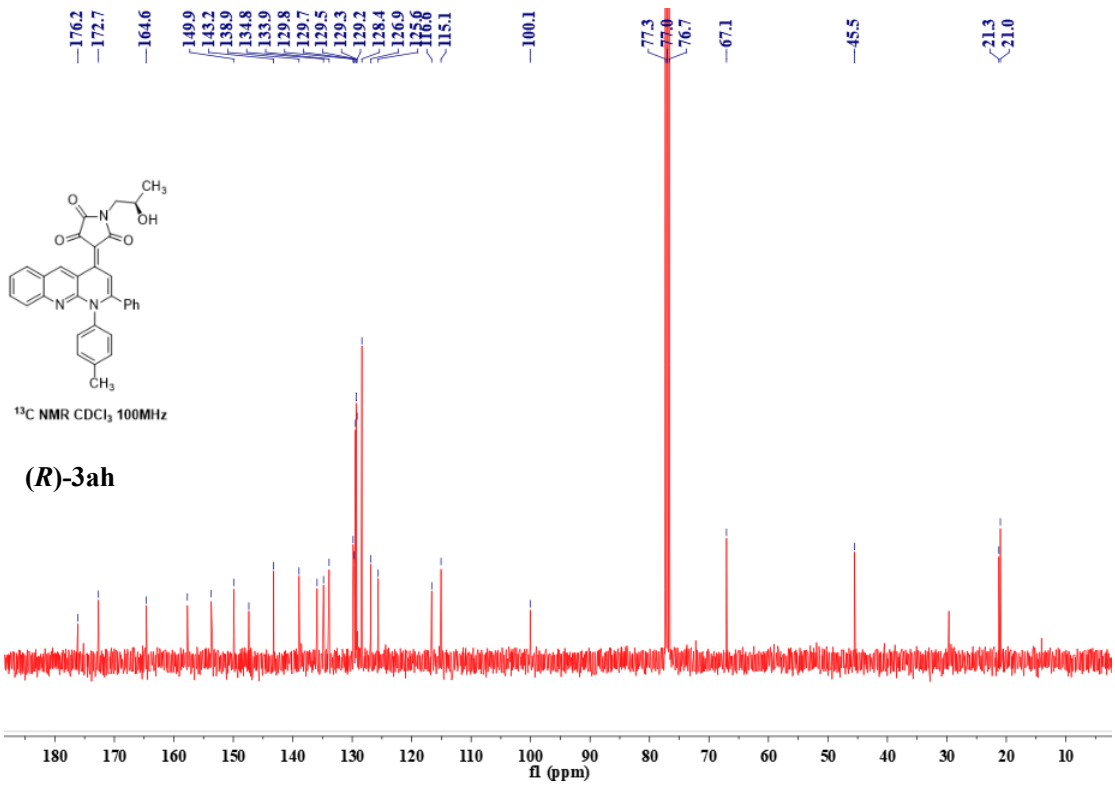
^{13}C NMR $CDCl_3$ 100MHz

3ag



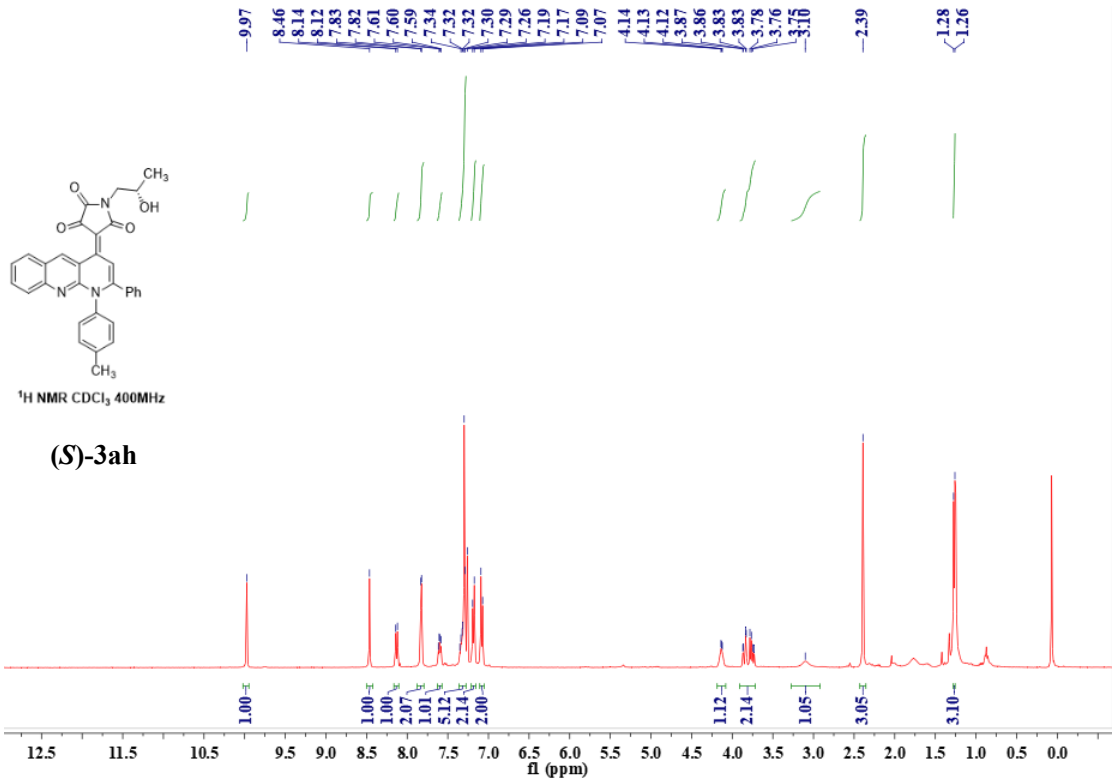
^{1}H NMR $CDCl_3$ 400MHz

(*R*)-3ah



^{13}C NMR $CDCl_3$ 100MHz

(*R*)-3ah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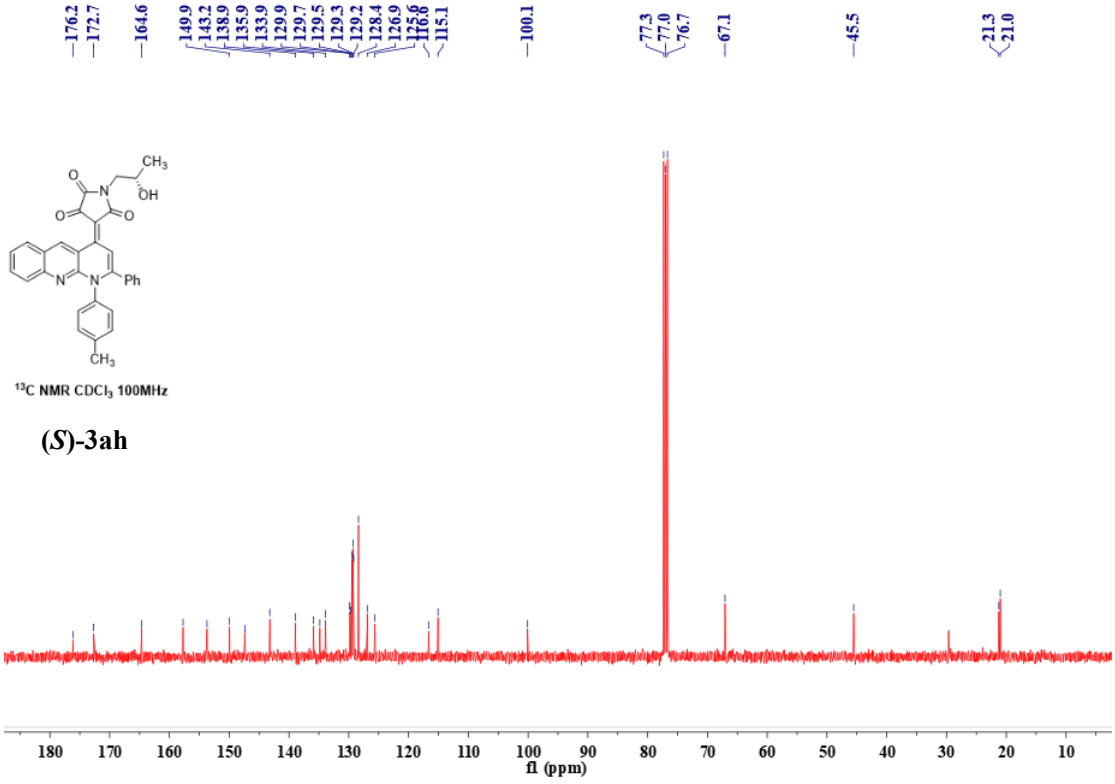
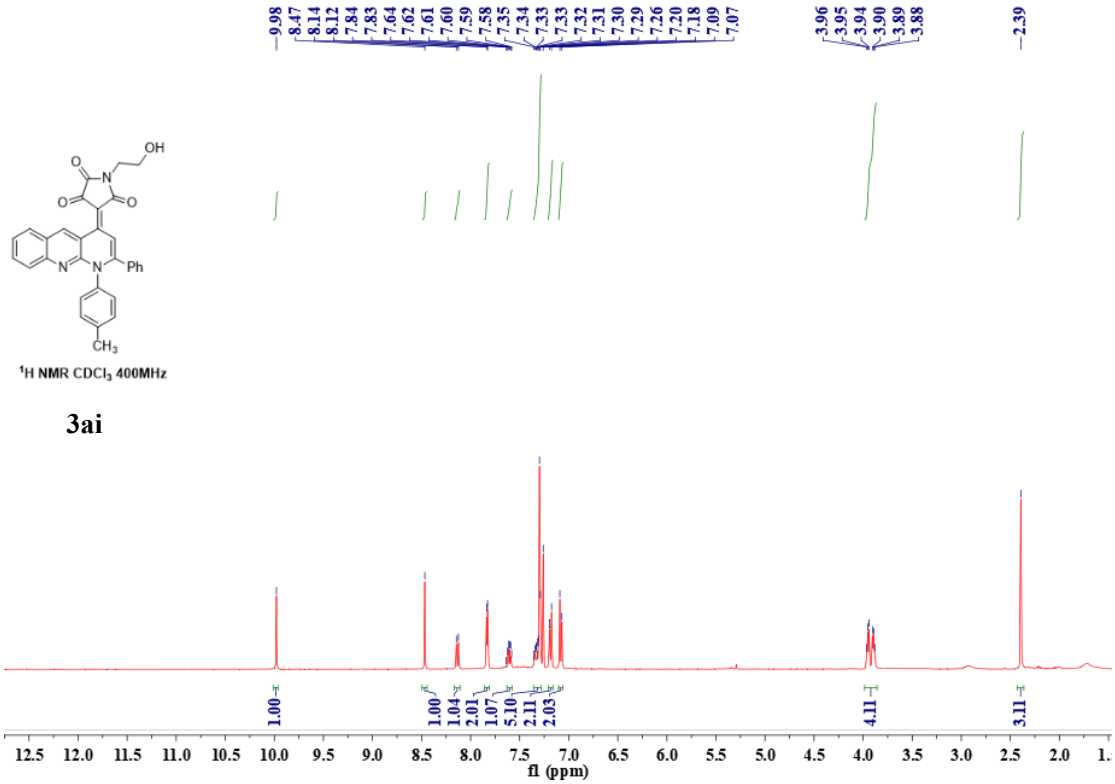
8.46
8.14
8.12
7.83
7.82
7.61
7.60
7.59
7.34
7.32
7.32
7.30
7.29
7.26
7.19
7.17
7.09
7.07
4.14
4.13
4.12
3.87
3.86
3.83
3.83
3.78
3.76
3.75
3.10
2.39
1.28
1.26
CH3
O
N
OH
O
O
N
Ph
CH3
1H NMR CDCl3 400MHz
1.00
1.00
1.00
2.07
1.01
5.12
2.14
2.00
1.12
2.14
1.05
3.05
3.10
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(*S*)-3ah


176.2
172.7
164.6
149.9
143.2
138.9
135.9
133.9
129.9
129.7
129.5
129.3
129.2
128.4
126.9
125.6
116.8
115.1
100.1
77.3
77.0
76.7
67.1
45.5
21.3
21.0
CH3
O
N
OH
O
O
N
Ph
CH3
13C NMR CDCl3 100MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

(*S*)-3ah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7.83
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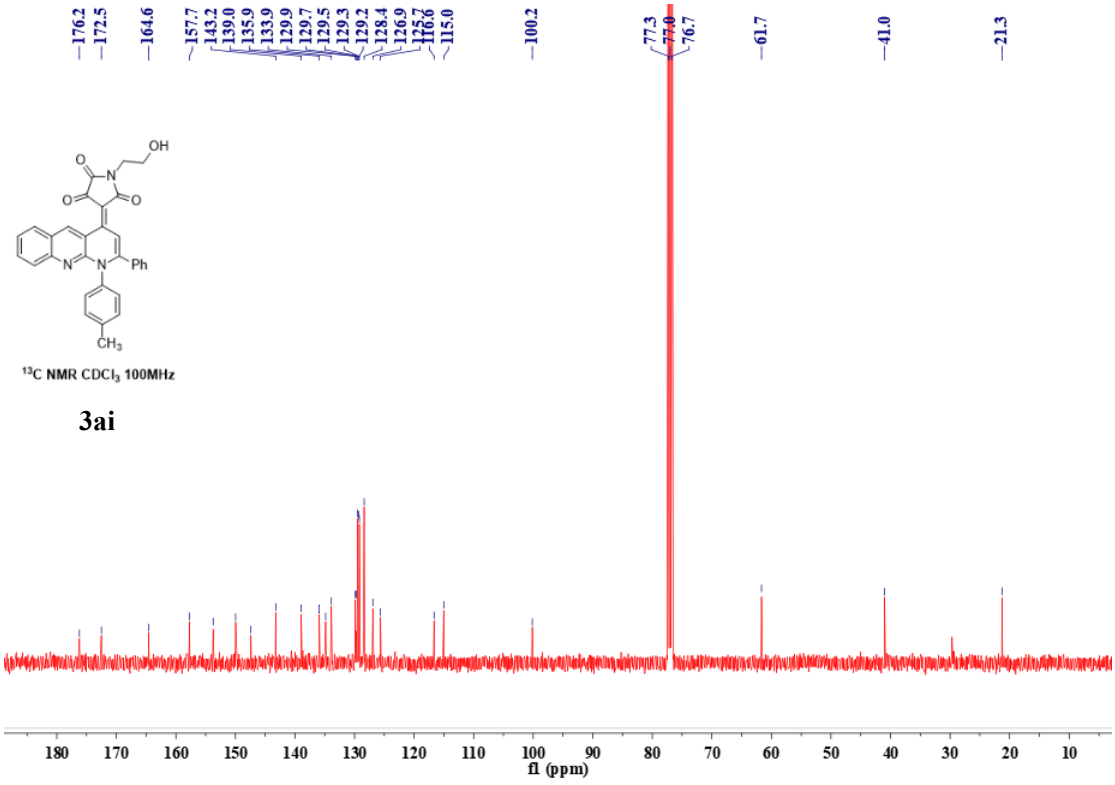
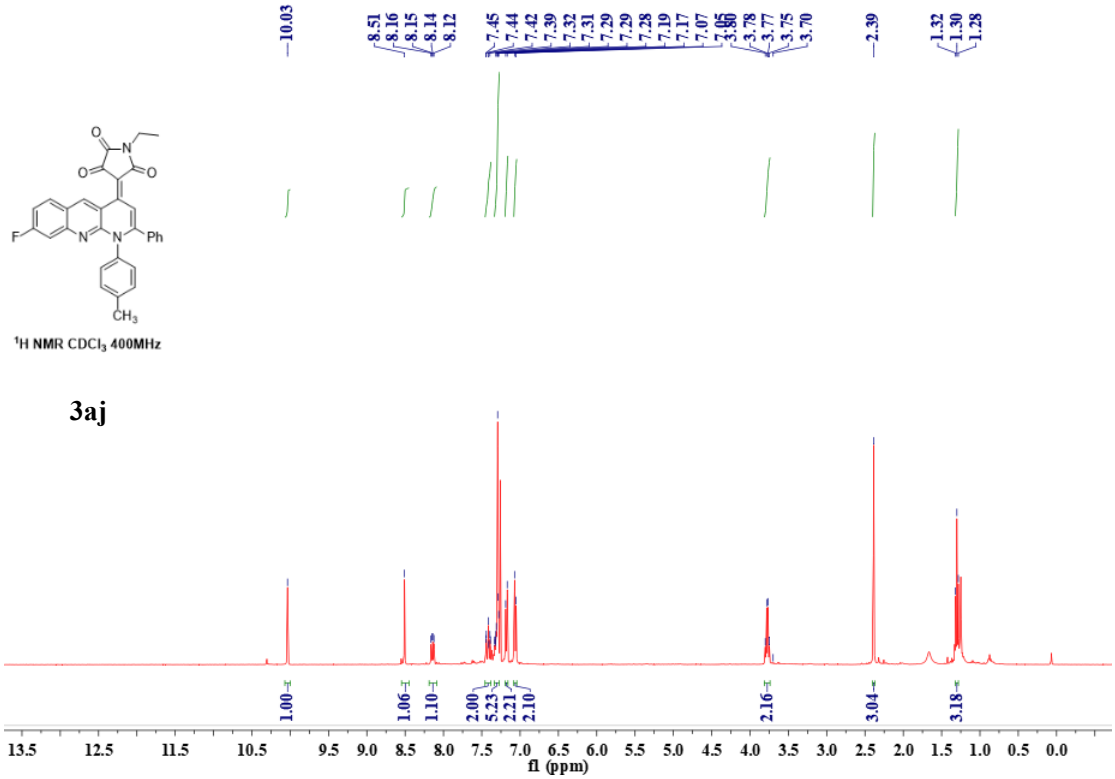
7.62
7.61
7.60
7.59
7.58
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.26
7.20
7.18
7.09
7.07
3.96
3.95
3.94
3.90
3.89
3.88
2.39
OH
O
N
O
O
N
N
Ph
CH3
1H NMR CDCl3 400MHz
1.00
1.00
1.04
2.01
1.07
5.10
2.11
2.03
4.11
3.11
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)

3ai


176.2
172.5
164.6
157.7
143.2
139.0
135.9
133.9
129.9
129.7
129.5
129.3
129.2
128.4
126.9
125.7
116.6
115.0
100.2
77.3
77.0
76.7
61.7
41.0
21.3
OH
O
N
O
O
N
N
Ph
CH3
13C NMR CDCl3 100MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3ai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8.15
8.14
8.12
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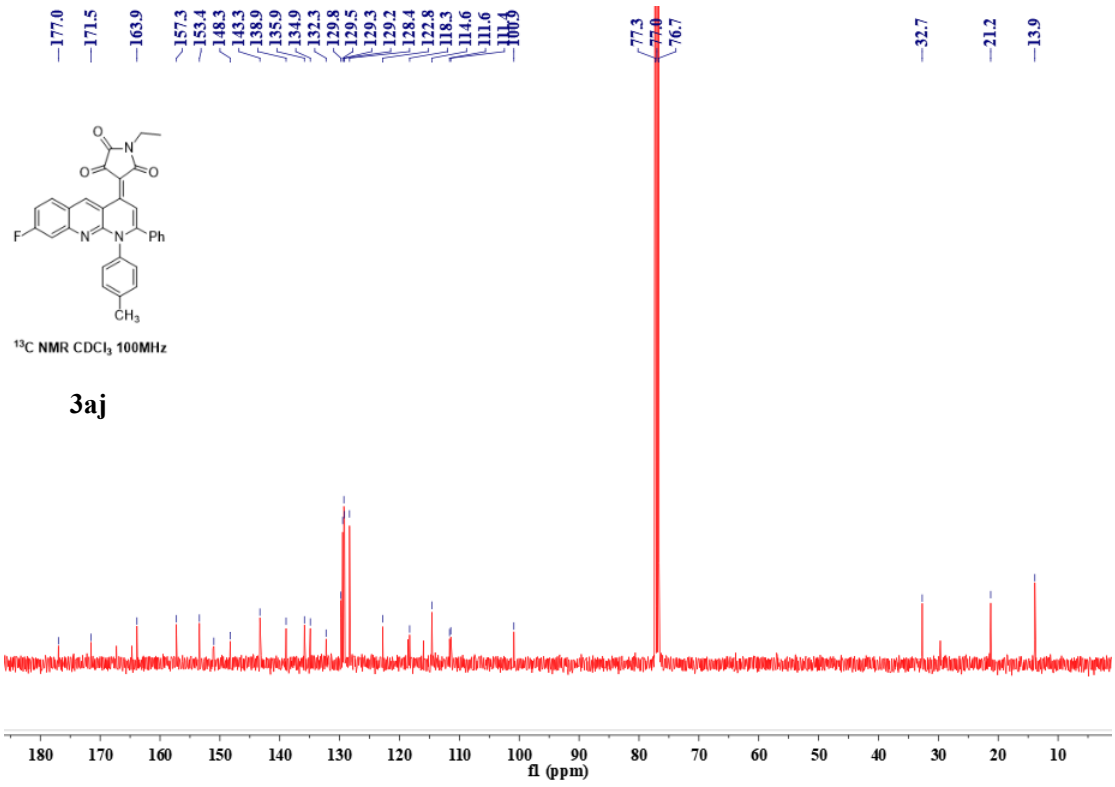
7.44
7.42
7.39
7.32
7.31
7.29
7.29
7.28
7.19
7.17
7.07
3.80
3.78
3.77
3.75
3.70
2.39
1.32
1.30
1.28
F
N
N
Ph
CH3
1H NMR CDCl3 400MHz
1.00
1.06
1.10
2.00
5.23
2.21
2.10
2.16
3.04
3.18
f1 (ppm)

3aj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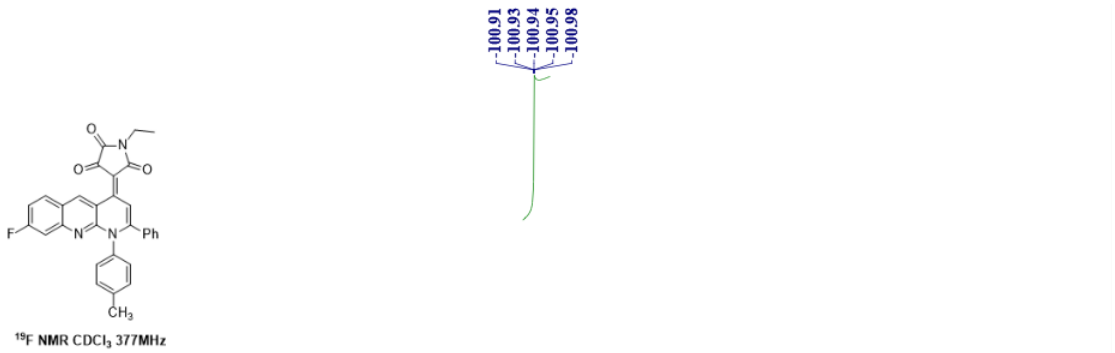
163.9
157.3
153.4
148.3
143.3
138.9
135.9
134.9
132.3
129.8
129.5
129.3
129.2
128.4
122.8
118.3
114.6
111.6
111.4
100.9
77.3
77.0
76.7
32.7
21.2
13.9
F
N
N
Ph
CH3
13C NMR CDCl3 100MHz
f1 (ppm)

3aj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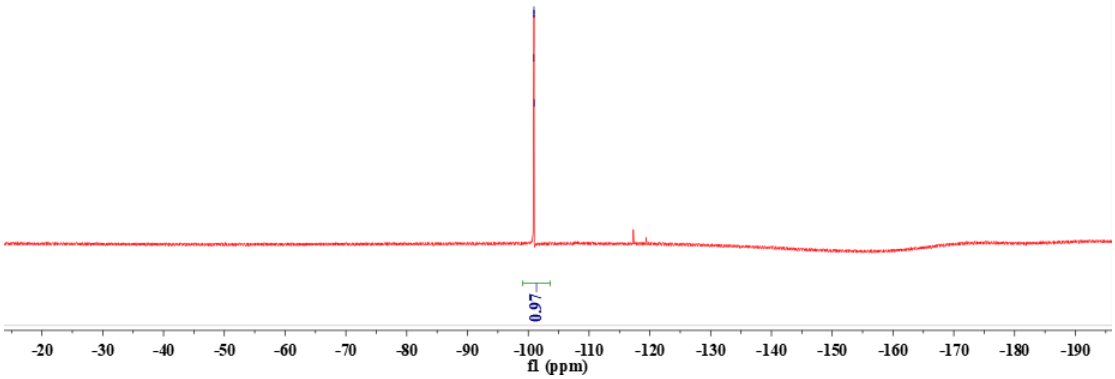
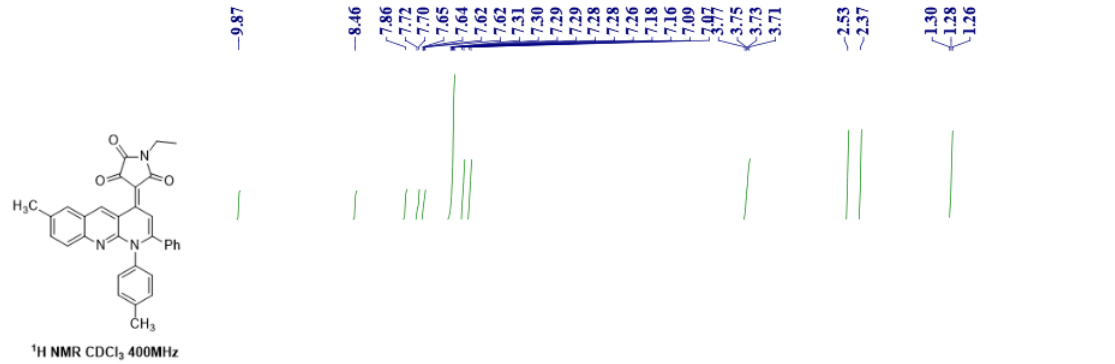
100.93
100.94
100.95
100.98
F
Ph
CH3
19F NMR CDCl3 377MHz

3aj


0.97
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)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7.62
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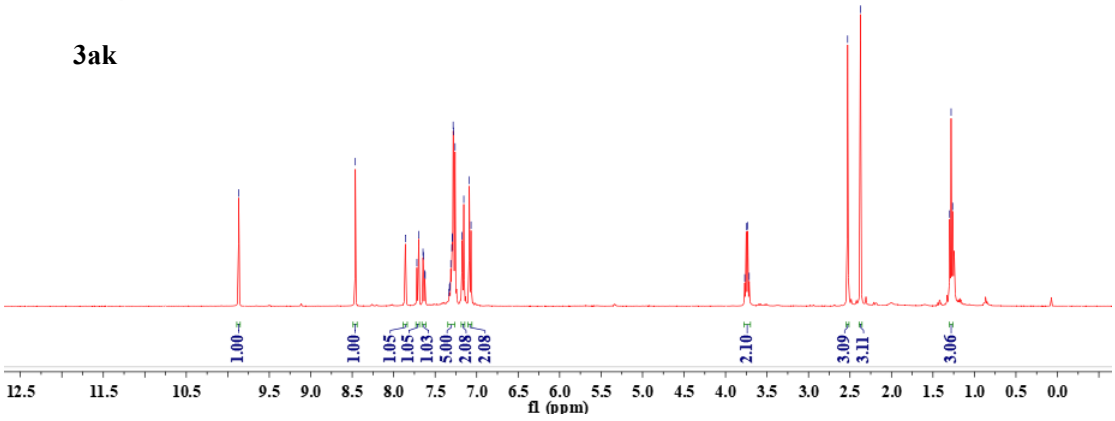
7.30
7.29
7.29
7.28
7.28
7.26
7.18
7.16
7.09
3.77
3.75
3.73
3.71
2.53
2.37
1.30
1.28
1.26
H3C
Ph
CH3
1H NMR CDCl3 400MHz

3ak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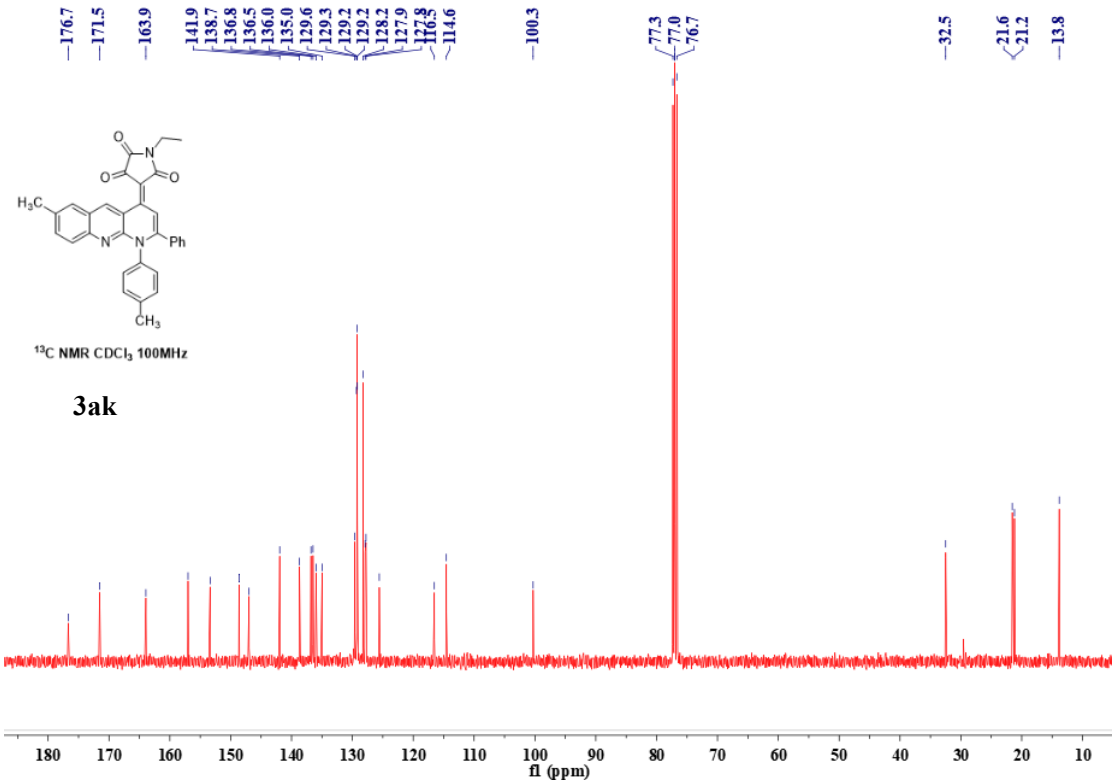
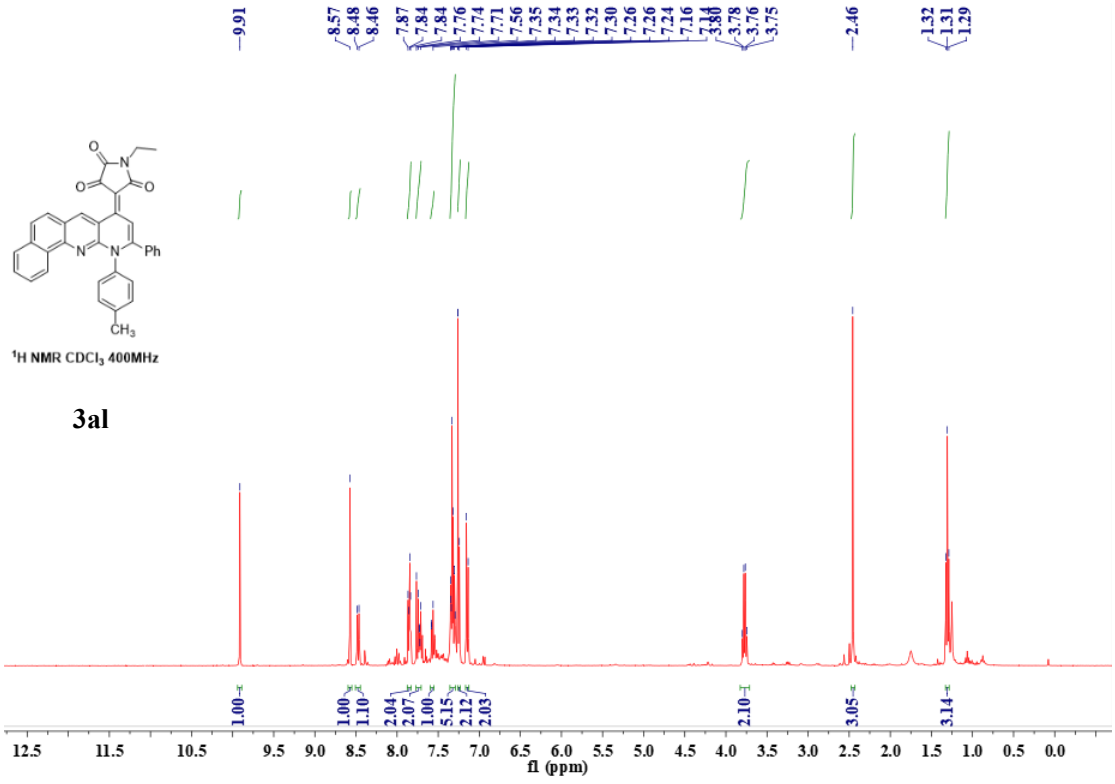
1.00
1.05
1.05
1.03
5.00
2.08
2.08
2.10
3.09
3.11
3.06
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.7
171.5
163.9
141.9
138.7
136.8
136.5
136.0
135.0
129.6
129.3
129.2
129.2
128.2
127.9
127.8
116.5
114.6
100.3
77.3
77.0
76.7
32.5
21.6
21.2
13.8
Ph
CH3
13C NMR CDCl3 100MHz
3ak
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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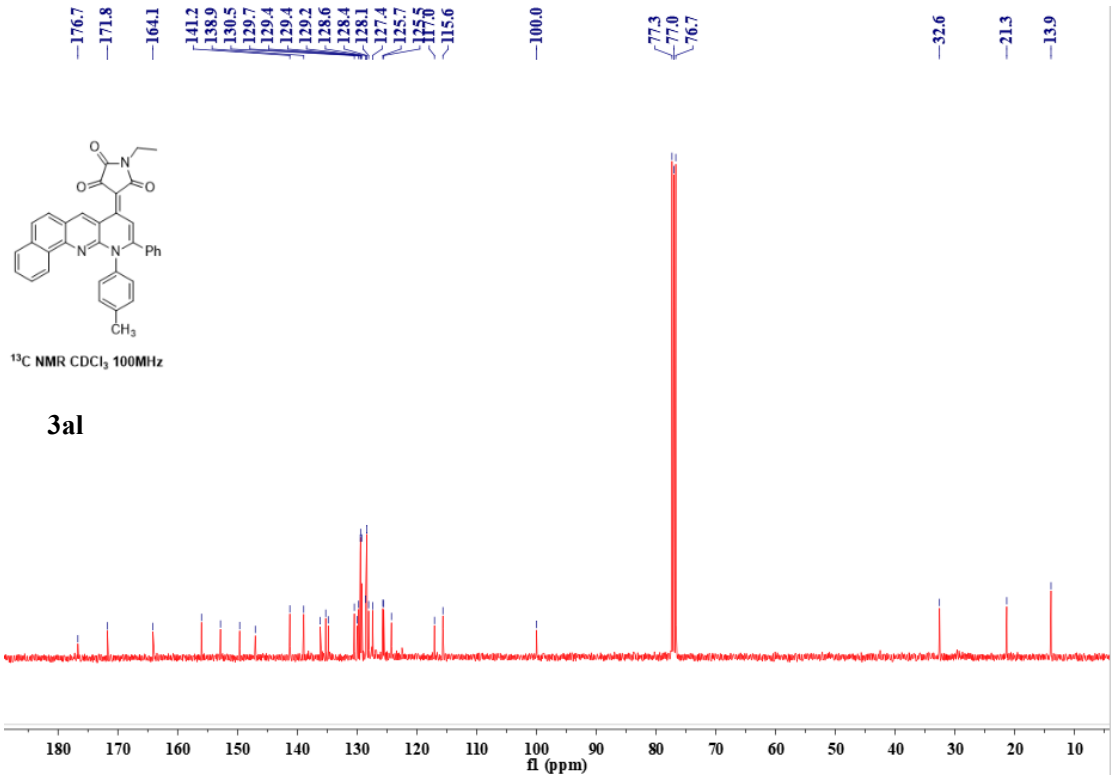
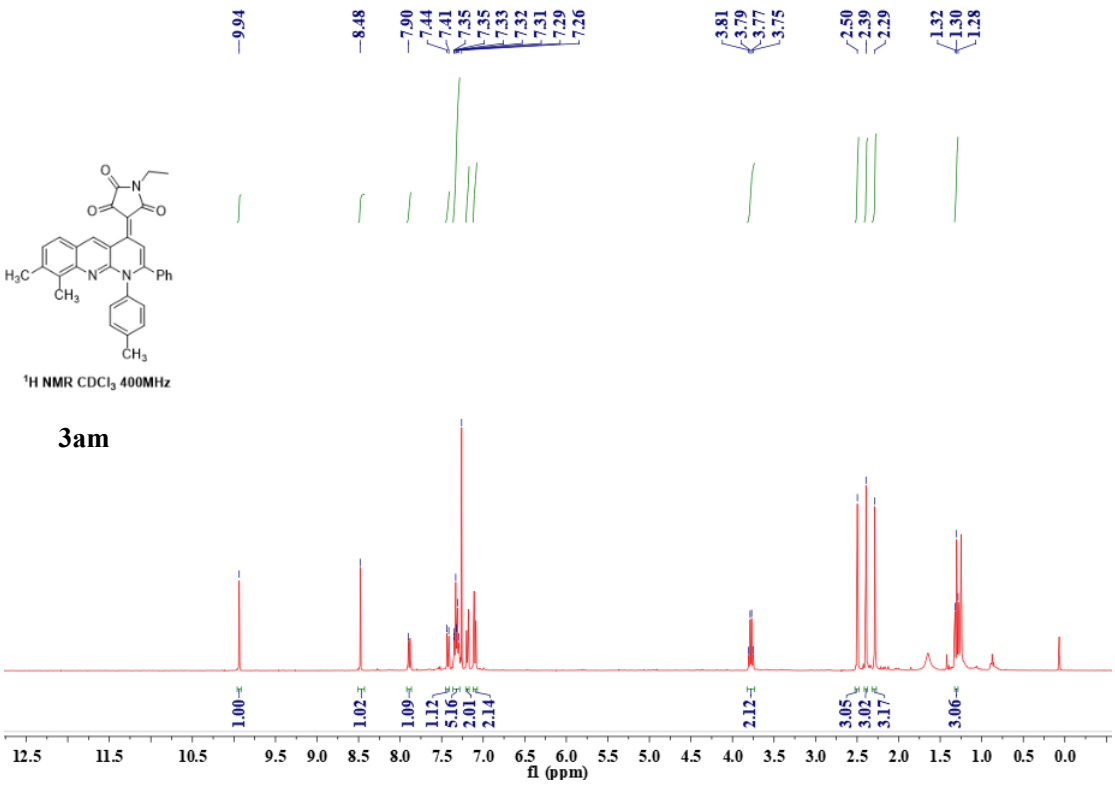
7.84
7.76
7.74
7.71
7.56
7.35
7.34
7.33
7.32
7.30
7.26
7.26
7.24
7.16
3.80
3.78
3.76
3.75
2.46
1.32
1.31
1.29
Ph
CH3
1H NMR CDCl3 400MHz
3al
1.00
1.00
1.10
2.04
2.07
1.00
5.15
2.12
2.03
2.10
3.05
3.14
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.7
171.8
164.1
141.2
138.9
130.5
129.7
129.4
129.4
129.2
128.6
128.4
128.1
127.4
125.7
125.5
117.0
115.6
100.0
77.3
77.0
76.7
32.6
21.3
13.9
Ph
CH3
13C NMR CDCl3 100MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3al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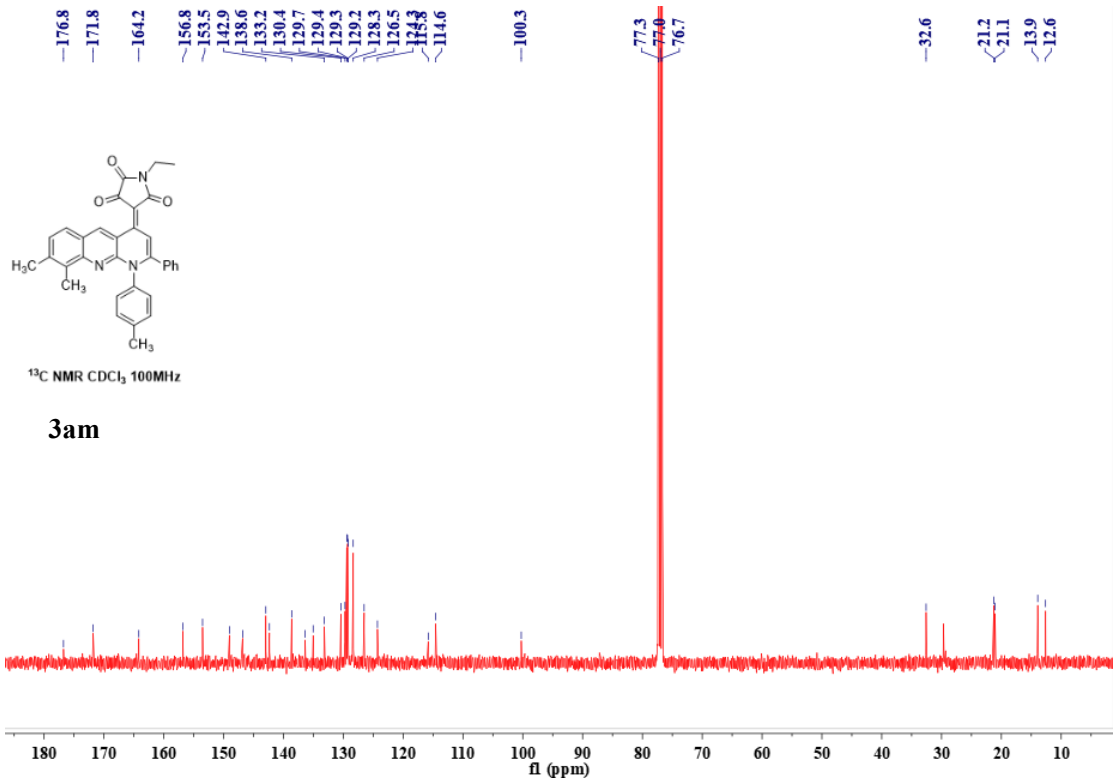
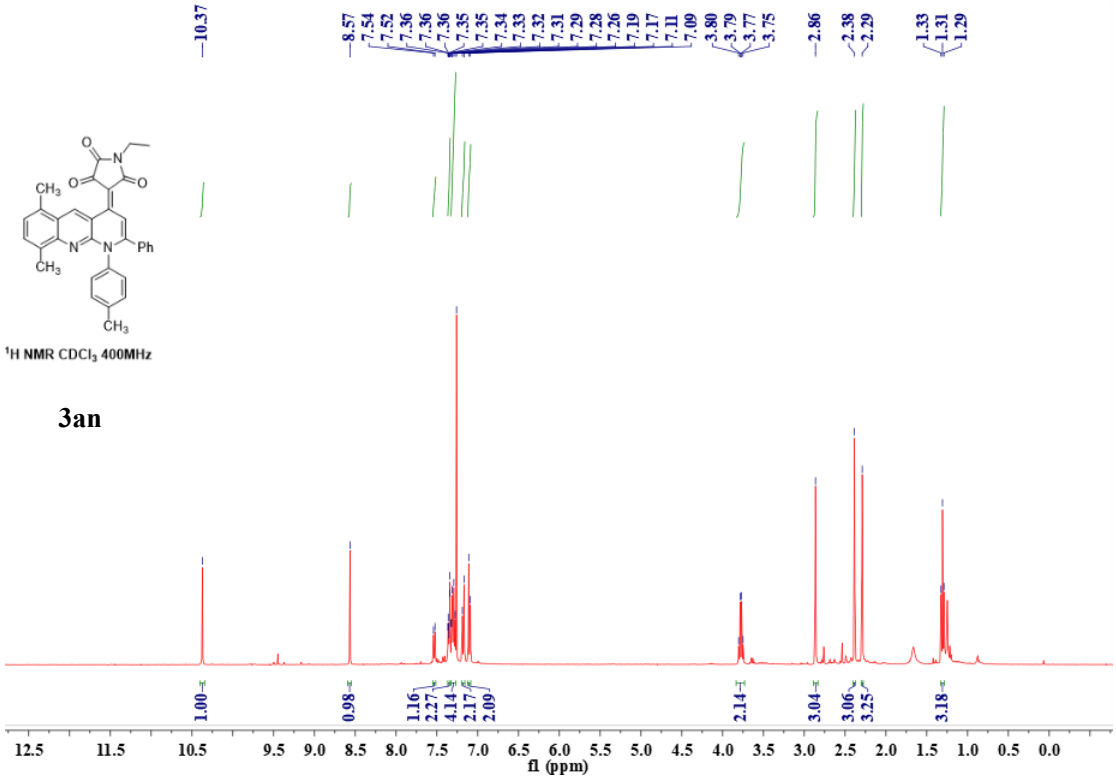
7.41
7.35
7.35
7.33
7.32
7.31
7.29
7.26
3.81
3.79
3.77
3.75
2.50
2.39
2.29
1.32
1.30
1.28
H3C
CH3
Ph
CH3
1H NMR CDCl3 400MHz
1.00
1.02
1.09
1.12
5.16
2.01
2.14
2.12
3.05
3.02
3.17
3.06
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

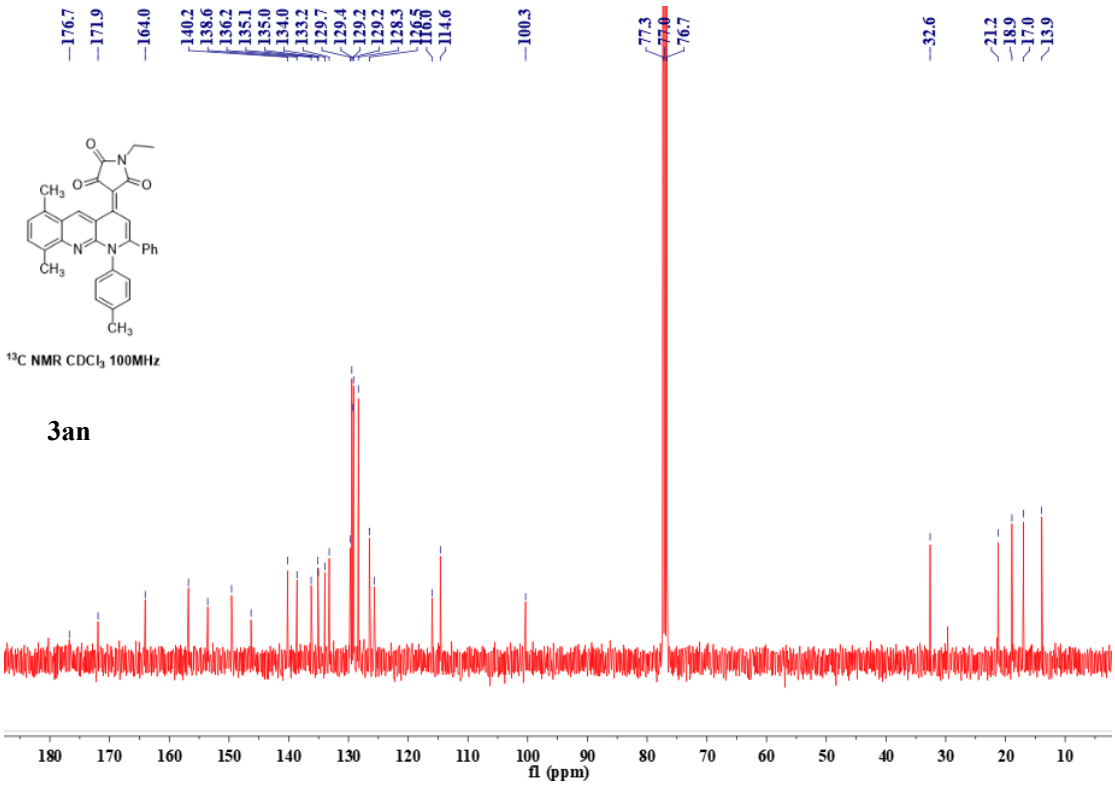
3am

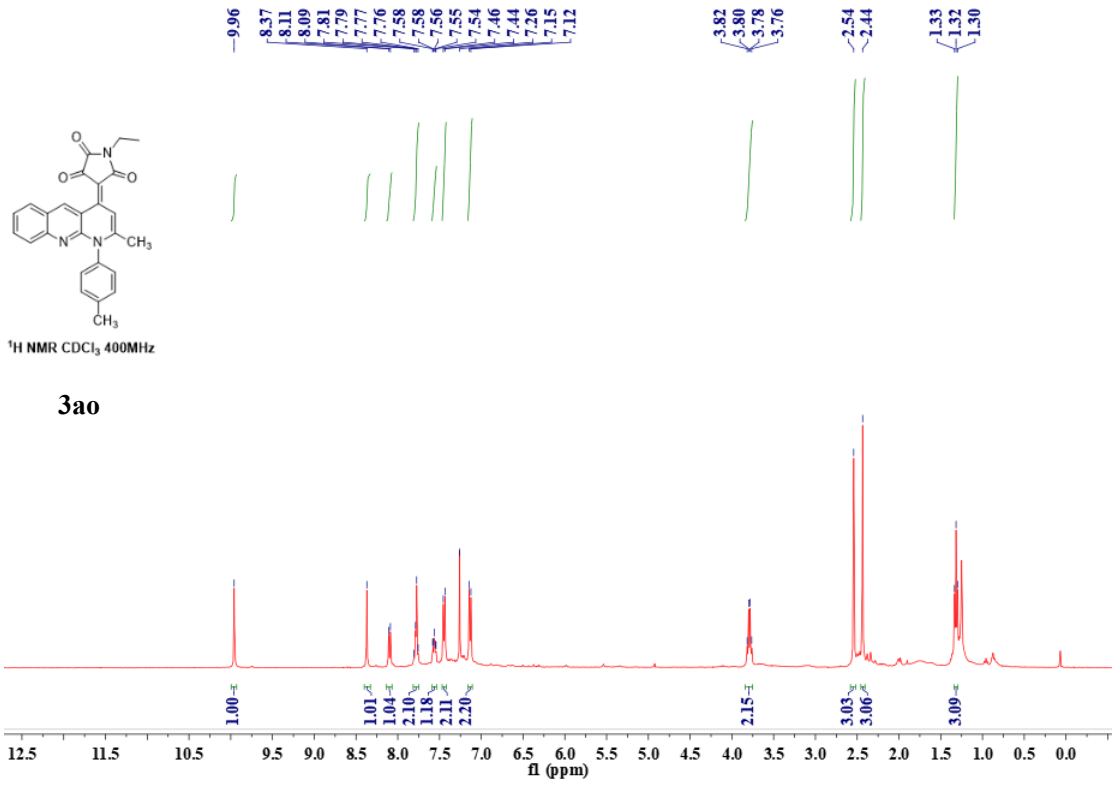

176.8
171.8
164.2
156.8
153.5
142.9
138.6
133.2
130.4
129.7
129.4
129.3
129.2
128.3
126.5
114.6
100.3
77.3
77.0
76.7
32.6
21.2
21.1
13.9
12.6
H3C
CH3
N
N
Ph
CH3
O
O
O
N
13C NMR CDCl3 100MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

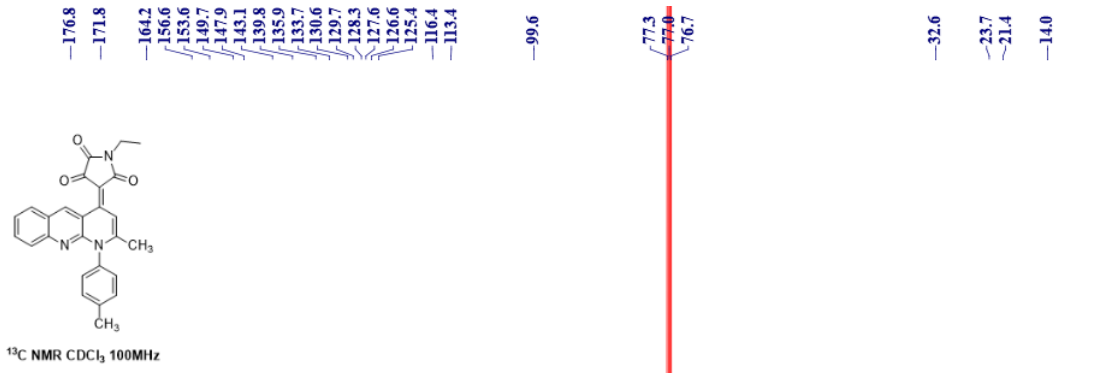
3am


10.37
8.57
7.54
7.52
7.36
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.29
7.28
7.26
7.19
7.17
7.11
7.09
3.80
3.79
3.77
3.75
2.86
2.38
2.29
1.33
1.31
1.29
CH3
CH3
N
N
Ph
CH3
O
O
O
N
1H NMR CDCl3 400MHz
1.00
0.98
1.16
2.27
4.14
2.17
2.09
2.14
3.04
3.06
3.25
3.18
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3an

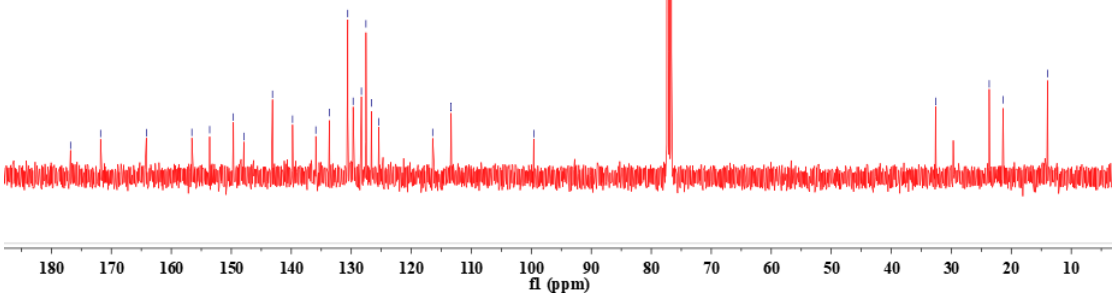

176.7
171.9
164.0
140.2
138.6
136.2
135.1
135.0
134.0
133.2
129.7
129.4
129.2
129.2
128.3
116.5
116.0
114.6
100.3
77.3
77.0
76.7
32.6
21.2
18.9
17.0
13.9
Ph
CH3
CH3
CH3
13C NMR CDCl3 100MHz
3an
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9.96
8.37
8.11
8.09
7.81
7.79
7.77
7.76
7.58
7.58
7.56
7.55
7.54
7.46
7.44
7.26
7.15
7.12
3.82
3.80
3.78
3.76
2.54
2.44
1.33
1.32
1.30
CH3
CH3
1H NMR CDCl3 400MHz
3ao
1.00
1.01
1.04
2.10
1.18
2.11
2.20
2.15
3.03
3.06
3.09
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



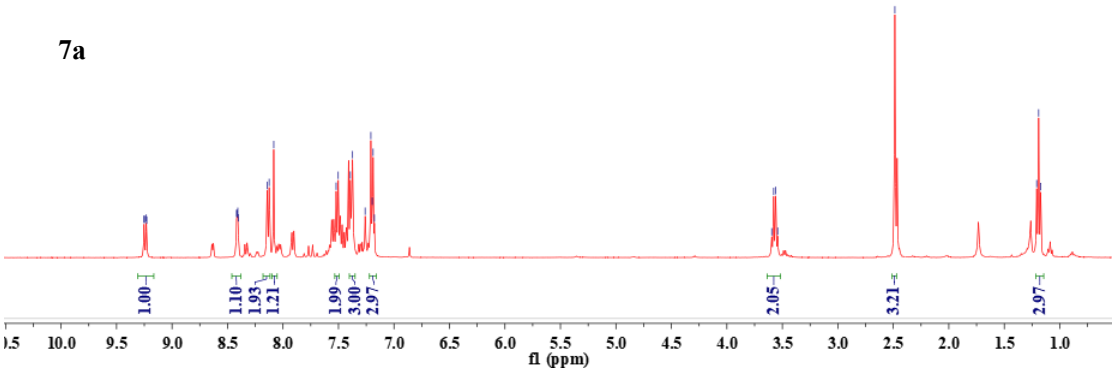
^{13}C NMR $CDCl_3$ 100MHz

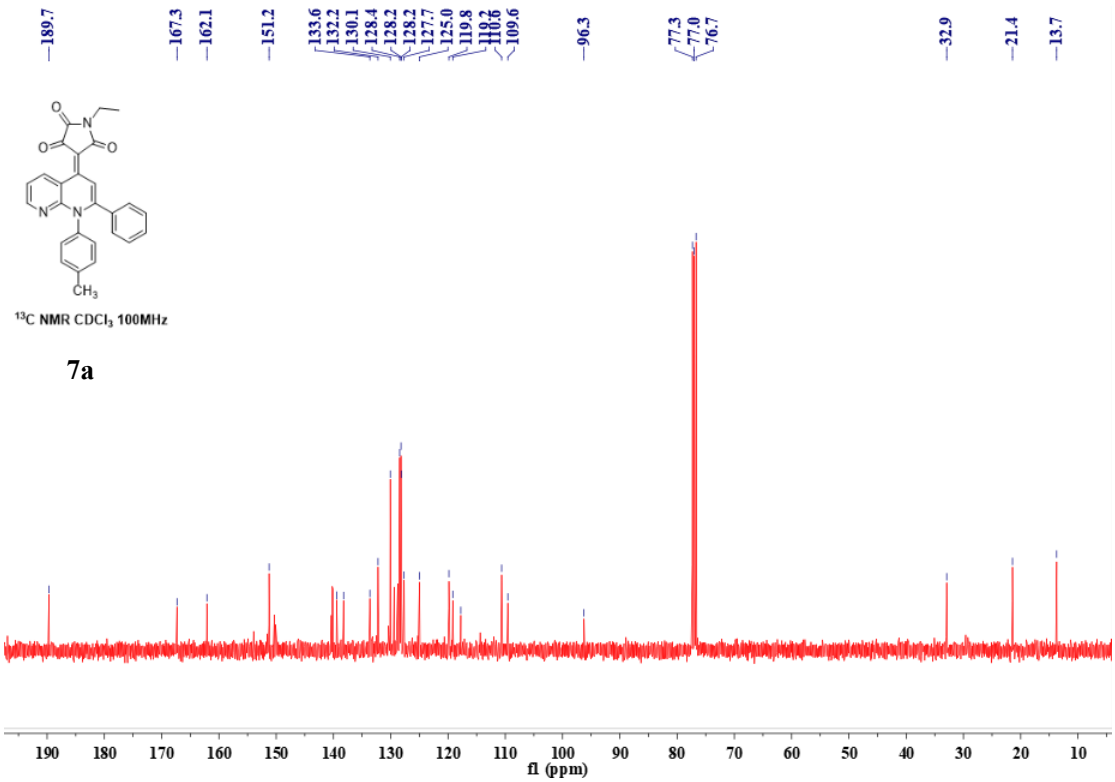
3ao



^{1}H NMR $CDCl_3$ 400MHz

7a




189.7
167.3
162.1
151.2
133.6
132.2
130.1
128.4
128.2
128.2
127.7
125.0
119.8
110.2
110.6
109.6
96.3
77.3
77.0
76.7
32.9
21.4
13.7
O
N
O
O
N
N
CH3
13C NMR CDCl3 100MHz
7a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)