Cover Page for Supporting Information

Title:

Metal-free Synthesis of Cyclic Di-oxoguanidines via One-pot Sequential Transformation of Amines, Carbodiimides and Acid Dichlorides

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Contents:

1) **Experimental Details and Characterization Data** **S2-S10**

2) **X-ray Crystallographic Studies for 1e, 1i and 4c** **S11-S24**

3) **^{1}H NMR and ^{13}C NMR Spectra of All New Compounds** **S25-S59**

1) Experimental Details and Characterization Data

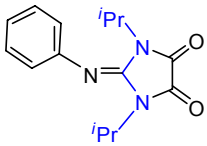
General Method

All the reactions were carried out under nitrogen atmosphere using standard Schlenk technique. All the starting materials were purchased from Acros, Aldrich, TCI and Alfa Aesar without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and stored under nitrogen. Column chromatography was performed on silica gel 200-300 mesh.

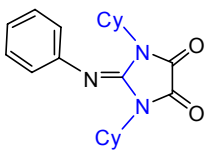
^{1}H NMR and ^{13}C NMR were recorded on a JEOL 300 MHz spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) or a Bruker AVANCE III 400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) at room temperature with $CDCl_3$ or C_6D_6 as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm, or C_6D_6 resonance in the ^{13}C spectrum as 128.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Infrared spectra (IR) were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization).

Typical Procedures for Metal-free One-pot Synthesis of Cyclic Di-oxoguanidines.

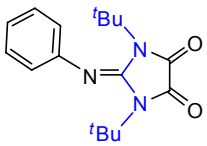
Preparation of 1a–x: To an Et_2O solution of *N,N'*-diisopropylcarbodiimide (126 mg, 1.0 mmol) was charged with oxalyl chloride (140 mg, 1.1 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and the 2,2-dichloro-imidazolidindione intermediate was precipitated from the solution. This precipitation was resolved by charging THF into the reaction. Then aniline (102 mg, 1.1 mmol) and Et_3N (202 mg, 2.0 mmol) were added with a syringe and the whole reaction mixture was allowed to stirred for another 12 h at room temperature. The reaction mixture was quenched by brine and extracted with ethyl acetate. The organic solution was dried over Na_2SO_4. After filtration, the solution was concentrated under vacuum and the product was purified by flash column chromatography on silica gel (treated with Et_3N before used). The product **1a** was obtained as yellow oil, and slowly turned to yellow solid at low temperature.



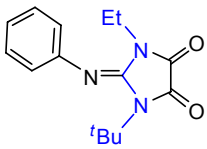
1a: Yellow solid, isolated yield 91% (248 mg); m.p. 42-43 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.37 (d, J = 6.8 Hz, 12H, CH_3), 4.10-4.32 (m, 2H, CH), 6.85-6.87 (m, 2H, CH), 7.09-7.12 (m, 1H, CH), 7.31-7.35 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 19.02 (4 CH_3), 46.44 (2 CH), 118.94 (2 CH), 123.72 (1 CH), 129.16 (2 CH), 136.06 (1 quat. C), 144.95 (1 quat. C), 157.27 (2 quat. C); IR (neat): ν 1776 (C=O), 1693 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{20}N_3O_2$ $[M+H]^+$: 274.1550; found 274.1550.



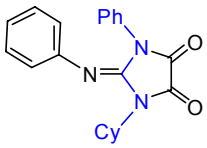
1b: Yellow solid, isolated yield 75% (265 mg); m.p. 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.94-2.20 (m, 20H, CH_2), 3.47-3.95 (m, 2H, CH), 6.84-6.86 (m, 2H, CH), 7.12-7.14 (m, 1H, CH), 7.31-7.35 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 24.54 (2 CH_2), 25.59 (4 CH_2), 28.55 (4 CH_2), 54.00 (2 CH), 118.76 (2 CH), 123.55 (1 CH), 129.02 (2 CH), 136.42 (1 quat. C), 145.20 (1 quat. C), 157.08 (2 quat. C); IR (neat): ν 1776 (C=O), 1685 (C=N) cm^{-1}; HRMS calcd for $C_{21}H_{28}N_3O_2$ $[M+H]^+$: 354.2176; found 354.2179.



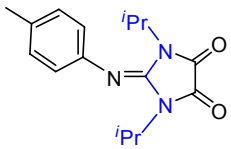
1c: Yellow solid, isolated yield 57% (172 mg); m.p. 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.49 (s, 18H, CH_3), 6.79-6.81 (m, 2H, CH), 7.06-7.10 (m, 1H, CH), 7.32-7.35 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 28.74 (6 CH_3), 60.47 (2 quat. C), 120.42 (2 CH), 123.46 (1 CH), 129.16 (2 CH), 137.41 (1 quat. C), 146.18 (1 quat. C), 158.44 (2 quat. C); IR (neat): ν 1774 (C=O), 1676 (C=N) cm^{-1}; HRMS calcd for $C_{17}H_{24}N_3O_2$ $[M+Na]^+$: 324.1682; found 324.1680.



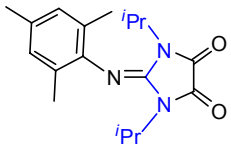
1d: Yellow solid, isolated yield 97% (265 mg); m.p. 147-148 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.88 (t, J = 7.2 Hz, 3H, CH_3), 1.76 (s, 9H, CH_3), 3.30 (q, J = 7.2 Hz, 2H, CH_2), 6.86-6.89 (m, 2H, CH), 7.07-7.12 (m, 1H, CH), 7.30-7.35 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 13.23 (1 CH_3), 29.21 (3 CH_3), 36.95 (1 CH_2), 60.59 (1 quat. C), 119.22 (2 CH), 123.53 (1 CH), 128.93 (2 CH), 136.79 (1 quat. C), 144.44 (1 quat. C), 156.49 (1 quat. C), 158.29 (1 quat. C); IR (neat): ν 1784 (C=O), 1684 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{20}N_3O_2$ $[M+H]^+$: 274.1550; found 274.1550.



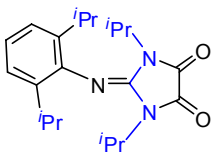
1e: Yellow solid, isolated yield 64% (222 mg); m.p. 124-125 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.26-2.31 (m, 10H, CH_2), 4.28-4.44 (m, 1H, CH), 6.49-7.08 (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 24.76 (1 CH_2), 25.69 (2 CH_2), 28.87 (2 CH_2), 53.31 (1 CH), 120.49 (1 CH), 123.17 (1 CH), 127.24 (2 CH), 128.05 (2 CH), 128.34 (2 CH), 128.58 (2 CH), 131.54 (1 quat. C), 135.79 (1 quat. C), 143.44 (1 quat. C), 155.52 (1 quat. C), 157.50 (1 quat. C); IR (neat): ν 1781 (C=O), 1681 (C=N) cm^{-1}; HRMS calcd for $C_{21}H_{22}N_3O_2$ $[M+H]^+$: 348.1706; found 348.1707.



1f: Yellow solid, isolated yield 99% (284 mg); m.p. 148-149 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.37 (d, J = 6.9 Hz, 12H, CH_3), 2.34 (s, 3H, CH_3), 4.03-4.43 (m, 2H, CH), 6.75 (d, J = 8.1 Hz, 2H, CH), 7.12 (d, J = 8.1 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.95 (4 CH_3), 20.69 (1 CH_3), 46.30 (2 CH), 118.70 (2 CH), 129.66 (2 CH), 133.15 (1 quat. C), 135.81 (1 quat. C), 142.16 (1 quat. C), 157.26 (2 quat. C); IR (neat): ν 1777 (C=O), 1685 (C=N) cm^{-1}; HRMS calcd for $C_{16}H_{22}N_3O_2$ $[M+H]^+$: 288.1706; found 288.1707.

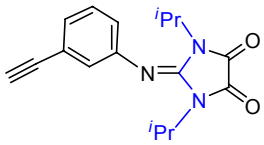


1g: Yellow solid, isolated yield 74% (233 mg); m.p. 111-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.39 (d, J = 6.9 Hz, 12H, CH_3), 2.09 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 4.18-4.33 (m, 2H, CH), 6.86 (s, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.01 (2 CH_3), 19.38 (4 CH_3), 20.44 (1 CH_3), 46.00 (2 CH), 125.52 (2 quat. C), 128.47 (2 CH), 132.39 (1 quat. C), 135.49 (1 quat. C), 139.54 (1 quat. C), 156.90 (2 quat. C); IR (neat): ν 1779 (C=O), 1690 (C=N) cm^{-1}; HRMS calcd for $C_{18}H_{26}N_3O_2$ $[M+H]^+$: 316.2020; found 316.2020.

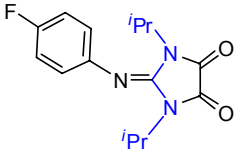


1h: Yellow solid, isolated yield 67% (239 mg); m.p. 84-85 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.21 (d, J = 6.9 Hz, 12H, CH_3), 1.37 (d, J = 6.6 Hz, 12H, CH_3), 2.70-2.84 (m, 2H, CH), 4.22-4.32 (m, 2H, CH), 7.04-7.14 (m, 3H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.45 (4 CH_3), 22.37 (4 CH_3), 28.98 (2 CH), 46.10 (2 CH), 122.86 (2 CH), 123.84 (1 CH), 134.49 (1 quat. C), 136.08 (2 quat. C),

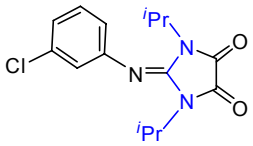
139.97 (1 quat. C), 157.20 (2 quat. C); IR (neat): ν 1779 (C=O), 1696 (C=N) cm^{-1}; HRMS calcd for $C_{21}H_{32}N_3O_2$ $[M+H]^+$: 358.2489; found 358.2492.



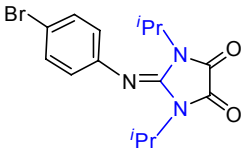
1i: Yellow solid, isolated yield 71% (211 mg); m.p. 176-177 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.38 (d, J = 6.9 Hz, 12H, CH_3), 3.10 (s, 1H, CH), 4.13-4.27 (m, 2H, CH), 6.83-6.87 (m, 1H, CH), 7.00-7.01 (m, 1H, CH), 7.22-7.32 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.10 (4 CH_3), 46.66 (2 CH), 77.92 (1 quat. C), 82.73 (1 CH), 119.73 (1 CH), 122.49 (1 CH), 123.17 (1 quat. C), 127.53 (1 CH), 129.31 (1 CH), 136.80 (1 quat. C), 145.03 (1 quat. C), 157.20 (2 quat. C); IR (neat): ν 1770 (C=O), 1679 (C=N) cm^{-1}; HRMS calcd for $C_{17}H_{20}N_3O_2$ $[M+H]^+$: 298.1550; found 298.1547.



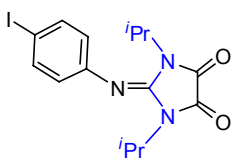
1j: Yellow solid, isolated yield 82% (239 mg); m.p. 71-72 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.38 (d, J = 6.6 Hz, 12H, CH_3), 4.08-4.33 (m, 2H, CH), 6.82-6.87 (m, 2H, CH), 7.02-7.07 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.93 (4 CH_3), 46.42 (2 CH), 115.91 (d, J = 22.3 Hz, 2 CH), 120.16 (d, J = 7.4 Hz, 2 CH), 136.67 (1 quat. C), 141.00 (d, J = 2.5 Hz, 1 quat. C), 157.14 (2 quat. C), 159.18 (d, J = 241.0 Hz, 1 quat. C); IR (neat): ν 1778 (C=O), 1684 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{19}FN_3O_2$ $[M+H]^+$: 292.1456; found 292.1456.



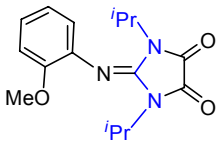
1k: Yellow solid, isolated yield 95% (293 mg); m.p. 121-122 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.39 (d, J = 6.9 Hz, 12H, CH_3), 4.13-4.30 (m, 2H, CH), 6.76-6.79 (m, 1H, CH), 6.90-6.92 (m, 1H, CH), 7.08-7.11 (m, 1H, CH), 7.25-7.30 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.00 (4 CH_3), 46.58 (2 CH), 117.35 (1 CH), 119.27 (1 CH), 123.76 (1 CH), 130.22 (1 CH), 134.82 (1 quat. C), 136.88 (1 quat. C), 146.10 (1 quat. C), 157.03 (2 quat. C); IR (neat): ν 1780 (C=O), 1685 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{19}ClN_3O_2$ $[M+H]^+$: 308.1160; found 308.1163.



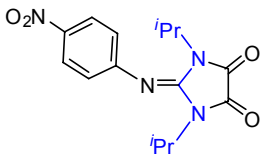
1l: Yellow solid, isolated yield 89% (313 mg); m.p. 122-123 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.38 (d, J = 6.9 Hz, 12H, CH_3), 4.14-4.30 (m, 2H, CH), 6.79 (d, J = 8.7 Hz, 2H, CH), 7.45 (d, J = 9.0 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.89 (4 CH_3), 46.38 (2 CH), 116.30 (1 quat. C), 120.67 (2 CH), 132.03 (2 CH), 136.44 (1 quat. C), 143.92 (1 quat. C), 156.95 (2 quat. C); IR (neat): ν 1778 (C=O), 1686 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{19}BrN_3O_2$ $[M+H]^+$: 352.0655; found 352.0659.



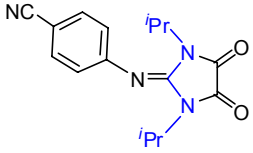
1m: Yellow solid, isolated yield 93% (371 mg); m.p. 135-136 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.38 (d, J = 6.9 Hz, 12H, CH_3), 4.14-4.32 (m, 2H, CH), 6.64 (d, J = 8.4 Hz, 2H, CH), 7.63 (d, J = 8.4 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.08 (4 CH_3), 46.59 (2 CH), 86.94 (1 quat. C), 121.19 (2 CH), 136.52 (1 quat. C), 138.14 (2 CH), 144.68 (1 quat. C), 157.12 (2 quat. C); IR (neat): ν 1778 (C=O), 1685 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{19}IN_3O_2$ $[M+H]^+$: 400.0516; found 400.0516.



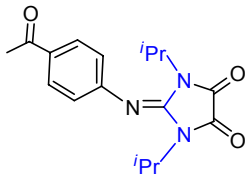
1n: Yellow solid, isolated yield 87% (264 mg); m.p. 51-52 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.37 (d, J = 6.9 Hz, 12H, CH_3), 3.80 (s, 3H, CH_3), 4.22-4.32 (m, 2H, CH), 6.85-6.97 (m, 3H, CH), 7.04-7.10 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.00 (4 CH_3), 46.07 (2 CH), 55.28 (1 CH_3), 110.85 (1 CH), 120.00 (1 CH), 120.92 (1 CH), 124.33 (1 CH), 133.67 (1 quat. C), 136.97 (1 quat. C), 148.41 (1 quat. C), 157.12 (2 quat. C); IR (neat): ν 1777 (C=O), 1686 (C=N) cm^{-1}; HRMS calcd for $C_{16}H_{22}N_3O_3$ $[M+H]^+$: 304.1656; found 304.1654.



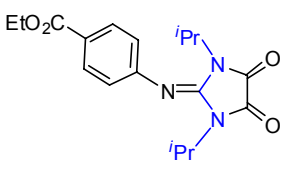
1o: Yellow solid, isolated yield 61% (194 mg); m.p. 161-162 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.41 (d, J = 6.6 Hz, 12H, CH_3), 4.13-4.22 (m, 2H, CH), 7.03 (d, J = 9.3 Hz, 2H, CH), 8.25 (d, J = 8.7 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.02 (4 CH_3), 46.79 (2 CH), 119.50 (2 CH), 125.24 (2 CH), 137.27 (1 quat. C), 143.58 (1 quat. C), 151.21 (1 quat. C), 156.74 (2 quat. C); IR (neat): ν 1784 (C=O), 1690 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{19}N_4O_4$ $[M+H]^+$: 319.1401; found 319.1401.



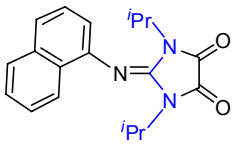
1p: Yellow solid, isolated yield 71% (282 mg); m.p. 134-135 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.40 (d, J = 6.6 Hz, 12H, CH_3), 4.12-4.22 (m, 2H, CH), 7.02 (d, J = 8.4 Hz, 2H, CH), 7.66 (d, J = 8.7 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.88 (4 CH_3), 46.56 (2 CH), 106.67 (1 quat. C), 118.64 (1 quat. C), 119.82 (2 CH), 133.26 (2 CH), 136.98 (1 quat. C), 149.12 (1 quat. C), 156.75 (2 quat. C); IR (neat): ν 2223 (C≡N), 1779 (C=O), 1674 (C=N) cm^{-1}; HRMS calcd for $C_{16}H_{19}N_4O_2$ $[M+H]^+$: 299.1502; found 299.1500.



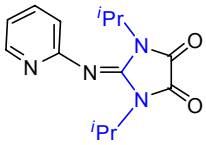
1q: Yellow solid, isolated yield 82% (258 mg); m.p. 126-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.39 (d, J = 6.9 Hz, 12H, CH_3), 2.62 (s, 3H, CH_3), 4.10-4.26 (m, 2H, CH), 6.94 (d, J = 8.4 Hz, 2H, CH), 7.97 (d, J = 8.4 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.08 (4 CH_3), 26.38 (1 CH_3), 46.67 (2 CH), 119.05 (2 CH), 129.90 (2 CH), 132.72 (1 quat. C), 136.58 (1 quat. C), 149.53 (1 quat. C), 156.99 (2 quat. C), 196.73 (1 quat. C); IR (neat): ν 1785 (C=O), 1686 (C=O), 1672 (C=N) cm^{-1}; HRMS calcd for $C_{17}H_{22}N_3O_3$ $[M+H]^+$: 316.1656; found 316.1655.



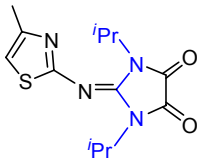
1r: Yellow solid, isolated yield 82% (283 mg); m.p. 125-126 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.37-1.44 (m, 15H, CH_3), 4.15-4.22 (m, 2H, CH), 4.39 (q, J = 7.2 Hz, 2H, CH_2), 6.92 (d, J = 8.4 Hz, 2H, CH), 8.04 (d, J = 8.7 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 14.26 (1 CH_3), 19.04 (4 CH_3), 46.61 (2 CH), 60.94 (1 CH_2), 118.84 (2 CH), 125.75 (1 quat. C), 130.89 (2 CH), 136.47 (1 quat. C), 149.21 (1 quat. C), 157.01 (2 quat. C), 166.02 (1 quat. C); IR (neat): ν 1778 (C=O), 1751 (C=O), 1692 (C=N) cm^{-1}; HRMS calcd for $C_{18}H_{24}N_3O_4$ $[M+H]^+$: 346.1761; found 346.1760.



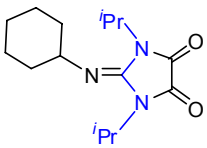
1s: Yellow solid, isolated yield 75% (242 mg); m.p. 119-120 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.28-1.39 (m, 12H, CH_3), 4.01-4.43 (m, 2H, CH), 6.89-6.92 (m, 1H, CH), 7.39-7.88 (m, 6H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.10 (4 CH_3), 46.52 (2 CH), 113.47 (1 CH), 122.91 (1 CH), 123.73 (1 CH), 125.50 (1 quat. C), 125.54 (1 CH), 126.06 (1 CH), 126.61 (1 CH), 128.11 (1 CH), 133.84 (1 quat. C), 137.02 (1 quat. C), 141.21 (1 quat. C), 157.18 (2 quat. C); IR (neat): ν 1781 (C=O), 1685 (C=N) cm^{-1}; HRMS calcd for $C_{19}H_{22}N_3O_2$ $[M+H]^+$: 324.1706; found 324.1705.



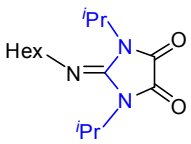
1t: Yellow solid, isolated yield 71% (194 mg); m.p. 117-118 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.41 (d, J = 6.9 Hz, 12H, CH_3), 3.93-4.19 (m, 2H, CH), 6.96-7.12 (m, 2H, CH), 7.72-7.77 (m, 1H, CH), 8.39-8.41 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.77 (4 CH_3), 46.55 (2 CH), 115.02 (1 CH), 119.17 (1 CH), 137.93 (1 CH), 138.26 (1 quat. C), 148.35 (1 quat. C), 156.67 (2 quat. C), 156.98 (1 CH); IR (neat): ν 1780 (C=O), 1685 (C=N) cm^{-1}; HRMS calcd for $C_{14}H_{19}N_4O_2$ $[M+H]^+$: 275.1502; found 275.1502.



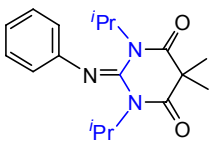
1u: Orange solid, isolated yield 54% (159 mg); m.p. 128-129 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.45 (d, J = 6.9 Hz, 12H, CH_3), 2.36 (s, 3H, CH_3), 4.17-4.27 (m, 2H, CH), 6.66 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 17.24 (1 CH_3), 19.12 (4 CH_3), 47.39 (2 CH), 110.50 (1 CH), 141.83 (1 quat. C), 149.85 (1 quat. C), 156.56 (2 quat. C), 164.72 (1 quat. C); IR (neat): ν 1773 (C=O), 1661 (C=N) cm^{-1}; HRMS calcd for $C_{13}H_{19}N_4O_2S$ $[M+H]^+$: 295.1223; found 295.1223.



1v: Colorless solid, isolated yield 93% (259 mg); m.p. 39-40 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.05-1.76 (m, 22H, CH_3 and CH_2), 3.59-3.68 (m, 1H, CH), 3.89-3.98 (m, 1H, CH), 4.36-4.50 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.87 (2 CH_3), 24.02 (2 CH_3), 24.32 (2 CH_2), 25.32 (1 CH_2), 32.88 (2 CH_2), 45.65 (1 CH), 46.84 (1 CH), 57.15 (1 CH), 138.97 (1 quat. C), 140.56 (1 quat. C), 156.70 (1 quat. C); IR (neat): ν 1728 (C=O), 1701 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{26}N_3O_2$ $[M+H]^+$: 280.2020; found 280.2018.



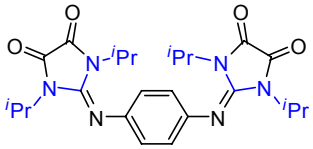
1w: Colorless liquid, isolated yield 87% (244 mg); ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.87 (t, J = 6.6 Hz, 3H, CH_3), 1.12-1.49 (m, 18H, CH_3 and CH_2), 1.65-1.75 (m, 2H, CH_2), 3.53 (t, J = 6.9 Hz, 2H, CH_2), 3.98-4.06 (m, 1H, CH), 4.46-4.56 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 13.97 (1 CH_3), 18.88 (2 CH_3), 22.47 (1 CH_2), 23.97 (2 CH_3), 26.96 (1 CH_2), 29.75 (1 CH_2), 31.39 (1 CH_2), 45.66 (1 CH), 46.89 (1 CH), 48.48 (1 CH_2), 138.83 (1 quat. C), 141.94 (1 quat. C), 156.47 (1 quat. C); IR (neat): ν 1774 (C=O), 1672 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{28}N_3O_2$ $[M+H]^+$: 282.2176; found 282.2175.



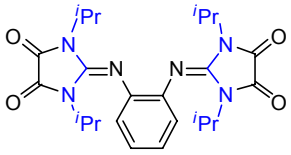
1x: Colorless solid, isolated yield 77% (243 mg); m.p. 73-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.29 (d, J = 6.8 Hz, 12H, CH_3), 1.50 (s, 6H, CH_3), 4.21-4.48 (m, 2H, CH), 6.88-6.90 (m, 2H, CH), 7.08-7.12 (m, 1H, CH), 7.34-7.38 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 19.55 (4

CH_3), 21.88 (2 CH_3), 48.62 (2 CH), 51.24 (1 quat. C), 120.13 (2 CH), 123.97 (1 CH), 129.35 (2 CH), 141.52 (1 quat. C), 145.73 (1 quat. C), 171.77 (2 quat. C); IR (neat): ν 1725 (C=O), 1641 (C=N) cm^{-1}; HRMS calcd for $C_{18}H_{26}N_3O_2$ $[M+H]^+$: 316.2020; found 316.2014. It is noted that Et_3N was added before aniline during the second step of preparation of **1x**.

Preparation of 2a and 2b: To an Et_2O solution of *N,N'*-diisopropylcarbodiimide (252 mg, 2.0 mmol) was charged with oxalyl chloride (280 mg, 2.2 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and the 2,2-dichloro-imidazolidindione intermediate was precipitated from the solution. This precipitation was resolved by charging THF into the reaction. Then 1,4- or 1,2-diaminobenzene (119 mg, 1.1 mmol) and Et_3N (404 mg, 4.0 mmol) were added with a syringe and the whole reaction mixture was allowed to stirred for another 12 h at room temperature. The products **2a** or **2b** was obtained as yellow solid in a manner analogous to that described for the synthesis of **1a**.

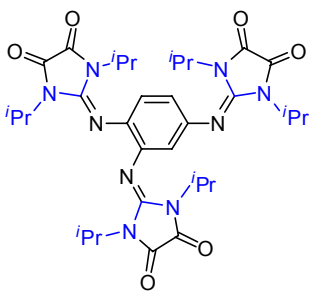


2a: Yellow solid, isolated yield 73% (342 mg); m.p. 97-98 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.41 (d, J = 6.9 Hz, 24H, CH_3), 4.22-4.38 (m, 4H, CH), 6.87 (s, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.10 (8 CH_3), 46.51 (4 CH), 119.97 (4 CH), 136.53 (2 quat. C), 140.95 (2 quat. C), 157.19 (4 quat. C); IR (neat): ν 1735 (C=O), 1680 (C=N) cm^{-1}; HRMS calcd for $C_{24}H_{33}N_6O_4$ $[M+H]^+$: 469.2558; found 469.2563.



2b: Yellow solid, isolated yield 74% (346 mg); m.p. 203-204 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.35 (d, J = 6.6 Hz, 24H, CH_3), 3.97-4.46 (m, 4H, CH), 6.87-6.90 (m, 2H, CH), 7.10-7.13 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 18.98 (8 CH_3), 46.24 (4 CH), 119.56 (2 CH), 124.50 (2 CH), 134.93 (2 quat. C), 136.74 (2 quat. C), 156.62 (4 quat. C); IR (neat): ν 1779 (C=N), 1672 (C=N) cm^{-1}; HRMS calcd for $C_{24}H_{33}N_6O_4$ $[M+H]^+$: 469.2558; found 469.2568.

Preparation of 2c: To an Et_2O solution of *N,N'*-diisopropylcarbodiimide (378 mg, 3.0 mmol) was charged with oxalyl chloride (419 mg, 3.3 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and the 2,2-dichloro-imidazolidindione intermediate was precipitated from the solution. This precipitation was resolved by charging THF into the reaction. Then 1,2,4-triaminobenzene (135 mg, 1.1 mmol) and Et_3N (606 mg, 6.0 mmol) were added with a syringe and the whole reaction mixture was allowed to stirred for another 12 h at room temperature. The product **2c** was obtained as yellow solid in a manner analogous to that described for the synthesis of **1a**.

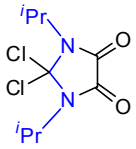


2c: Yellow solid, isolated yield 46% (305 mg); m.p. 135-136 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 1.37-1.44 (m, 36H, CH_3) 4.21-4.47 (m, 6H, CH), 6.58 (s, 1H, CH), 6.66 (d, J = 9.3 Hz, 1H, CH), 6.89 (d, J = 8.4 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.11 (8 CH_3), 19.14 (4 CH_3), 46.48 (6 CH), 110.94 (1 CH), 115.12 (1 CH), 120.33 (1 CH), 131.07 (1 quat. C), 136.32 (1

quat. C), 136.60 (1 quat. C), 137.34 (1 quat. C), 137.55 (1 quat. C), 141.80 (1 quat. C), 157.03 (6 quat. C); IR (neat): ν 1778 (C=O), 1676 (C=N) cm^{-1}; HRMS calcd for $C_{33}H_{46}N_9O_6$ $[M+H]^+$: 664.3566; found 664.3563.

Isolation of 2,2-Dichloro-imidazolidindione 3.

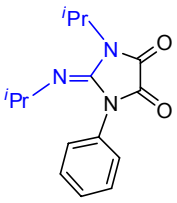
To a 40 mL Et_2O solution of *N,N'*-diisopropylcarbodiimide (1.6 mL, 10 mmol) was slowly charged with oxalyl chloride (0.94 mL, 11 mmol) at 0 °C. The reaction was highly exothermic and required keeping cool at 0 °C for several minutes. Then the reaction was allowed to stir at room temperature. After 2 days, the reaction was put into the glovebox. The solvent and excess acid dichloride were removed under vacuum. The residue was washed by hexane and dried under vacuum. 2,2-Dichloro-imidazolidindione **3** was obtained quantitatively as white powder.



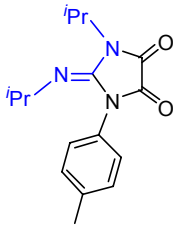
3: Colorless solid, isolated yield 99% (2.53 g); ^{1}H NMR (300 MHz, C_6D_6): δ 1.26 (d, J = 6.9 Hz, 12H, CH_3) 3.64-3.74 (m, 2H, CH); ^{13}C NMR (75 MHz, C_6D_6): δ 18.94 (4 CH_3), 49.25 (2 CH), 103.28 (1 quat. C), 154.29 (2 quat. C).

Typical Procedure for the $AlMe_3$-Catalyzed One-pot Synthesis of Cyclic Di-oxoguanidines 4.

General procedure for $AlMe_3$ catalyzed guanylation between anilines and carbodiimides were performed according to the literature.[1] In the glovebox, a solution of aniline (188 mg, 2.02 mmol) in benzene (3 mL) was added to a solution of $AlMe_3$ (40 μL, 0.04 mmol) in a Schlenk tube. *N,N'*-Diisopropylcarbodiimide (252 mg, 2.00 mmol) was then added to the above reaction mixture. The Schlenk tube was taken out of the glovebox, and the reaction was carried out at room temperature for 1 h. White solid was precipitated from the solution. This precipitation was resolved by charging 3 mL of THF into the reaction. Then oxalyl chloride (254 mg, 2.2 mmol) and Et_3N (202 mg, 2.0 mmol) were added and the reaction was allowed to stirred for another 12 h at room temperature. The reaction mixture was quenched by brine and extracted with ethyl acetate. The organic solution was dried over Na_2SO_4. After filtration, the solution was concentrated under vacuum and the product **4a** was purified by flash column chromatography on silica gel (treated with Et_3N before chromatography) as a colorless solid.

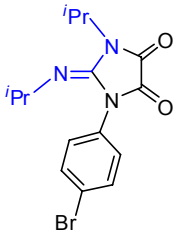


4a: Colorless solid, isolated yield 92% (251 mg); m.p. 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.90 (d, J = 6.0 Hz, 6H, CH_3), 1.51 (d, J = 7.2 Hz, 6H, CH_3), 3.32-3.41 (m, 1H, CH), 4.68-4.79 (m, 1H, CH), 7.30-7.33 (m, 2H, CH), 7.49-7.51 (m, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 19.26 (2 CH_3), 24.04 (2 CH_3), 44.72 (1 CH), 46.13 (1 CH), 127.56 (2 CH), 129.67 (2 CH), 129.69 (1 CH), 132.30 (1 quat. C), 133.72 (1 quat. C), 155.47 (1 quat. C), 158.31 (1 quat. C); IR (neat): ν 1777 (C=O), 1692 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{20}N_3O_2$ $[M+H]^+$: 274.1550; found 274.1546.

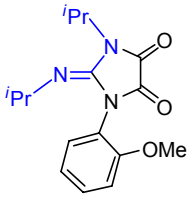


4b: Colorless solid, isolated yield 96% (276 mg); m.p. 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.91 (d, J = 6.0 Hz, 6H, CH_3), 1.50 (d, J = 6.8 Hz, 6H, CH_3), 2.41 (s, 3H, CH_3), 3.38-3.47 (m, 1H, CH), 4.67-4.78 (m, 1H, CH), 7.18 (d, J = 8.0 Hz, 2H, CH), 7.28 (d, J = 8.4 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 19.32 (2 CH_3), 21,13 (1 CH_3), 24.13 (2 CH_3), 44.72 (1 CH),

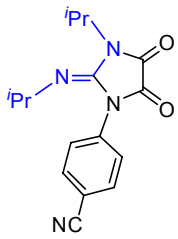
46.07 (1 CH), 127.32 (2 CH), 130.36 (2 CH), 131.06 (1 quat. C), 132.51 (1 quat. C), 139.94 (1 quat. C), 155.58 (1 quat. C), 158.54 (1 quat. C); IR (neat): ν 1785 (C=O), 1686 (C=N) cm^{-1}; HRMS calcd for $C_{16}H_{22}N_3O_2$ $[M+H]^+$: 288.1706; found 288.1707.



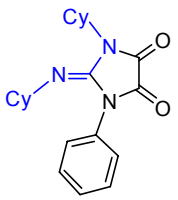
4c: Colorless solid, isolated yield 85% (299 mg); m.p. 115-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.93 (d, J = 6.3 Hz, 6H, CH_3), 1.48 (d, J = 6.9 Hz, 6H, CH_3), 3.37-3.45 (m, 1H, CH), 4.66-4.75 (m, 1H, CH), 7.24 (d, J = 8.4 Hz, 2H, CH), 7.62 (d, J = 8.4 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.14 (2 CH_3), 23.96 (2 CH_3), 44.73 (1 CH), 46.18 (1 CH), 123.64 (1 quat. C), 129.14 (2 CH), 131.80 (1 quat. C), 132.66 (1 quat. C), 132.81 (2 CH), 155.11 (1 quat. C), 158.05 (1 quat. C); IR (neat): ν 1777 (C=O), 1691 (C=N) cm^{-1}; HRMS calcd for $C_{15}H_{19}BrN_3O_2$ $[M+H]^+$: 352.0655; found 352.0654.



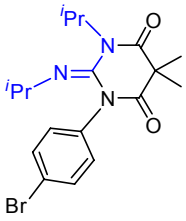
4d: Colorless liquid, isolated yield 75% (227 mg); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.85-0.89 (m, 6H, CH_3), 1.49-1.52 (m, 6H, CH_3), 3.39-3.45 (m, 1H, CH), 3.80 (s, 3H, CH_3), 4.70-4.76 (m, 1H, CH), 6.98-7.06 (m, 2H, CH), 7.27-7.29 (m, 1H, CH), 7.43-7.47 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 19.35 (1 CH_3), 19.41 (1 CH_3), 24.08 (1 CH_3), 24.36 (1 CH_3), 44.68 (1 CH), 45.90 (1 CH), 55.60 (1 CH_3), 111.79 (1 CH), 121.05 (1 CH), 122.53 (1 quat. C), 129.47 (1 CH), 131.40 (1 CH), 132.45 (1 quat. C), 155.01 (1 quat. C), 155.82 (1 quat. C), 158.62 (1 quat. C); IR (neat): ν 1776 (C=O), 1692 (C=N) cm^{-1}; HRMS calcd for $C_{16}H_{22}N_3O_3$ $[M+H]^+$: 304.1656; found 304.1656.



4e: Colorless solid, isolated yield 73% (218 mg); m.p. 114-115 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.95 (d, J = 6.0 Hz, 6H, CH_3), 1.50 (d, J = 6.9 Hz, 6H, CH_3), 3.29-3.37 (m, 1H, CH), 4.67-4.79 (m, 1H, CH), 7.53 (d, J = 8.4 Hz, 2H, CH), 7.83 (d, J = 8.4 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 19.38 (2 CH_3), 24.13 (2 CH_3), 45.33 (1 CH), 46.97 (1 CH), 113.69 (1 quat. C), 117.64 (1 quat. C), 128.69 (2 CH), 131.68 (1 quat. C), 133.67 (2 CH), 137.99 (1 quat. C), 155.20 (1 quat. C), 157.98 (1 quat. C); IR (neat): ν 2231 (C≡N), 1778 (C=O), 1693 (C=N) cm^{-1}; HRMS calcd for $C_{16}H_{19}N_4O_2$ $[M+H]^+$: 299.1502; found 299.1501.



4f: Colorless solid, isolated yield 66% (233 mg); m.p. 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.72-0.78 (m, 2H, CH_2), 1.07-1.85 (m, 16H, CH_2), 2.25-2.33 (m, 2H, CH_2), 2.92-2.94 (m, 1H, CH), 4.27-4.34 (m, 1H, CH), 7.32-7.47 (m, 5H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 23.38 (2 CH_2), 24.70 (1 CH_2), 24.86 (1 CH_2), 25.50 (2 CH_2), 28.56 (2 CH_2), 33.65 (2 CH_2), 52.22 (1 CH), 53.52 (1 CH), 127.44 (2 CH), 129.25 (2 CH), 129.32 (1 CH), 132.15 (1 quat. C), 132.56 (1 quat. C), 155.24 (1 quat. C), 157.94 (1 quat. C); IR (neat): ν 1776 (C=O), 1691 (C=N) cm^{-1}; HRMS calcd for $C_{21}H_{28}N_3O_2$ $[M+H]^+$: 354.2176; found 354.2178.



4g: Colorless solid, isolated yield 78% (307 mg); m.p. 175-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.87 (d, J = 6.0 Hz, 6H, CH_3), 1.48-1.49 (m, 12H, CH_3), 3.30-3.36 (m, 1H, CH), 4.89-4.96 (m, 1H, CH), 7.11 (d, J = 8.4 Hz, 2H,

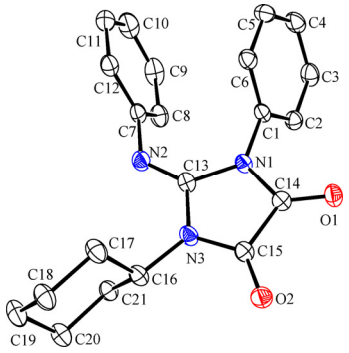
CH), 7.54 (d, J = 8.4 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 19.52 (2 CH_3), 21.70 (2 CH_3), 22.82 (2 CH_3), 48.34 (1 CH), 48.45 (1 CH), 48.65 (1 quat. C), 121.06 (1 quat. C), 127.79 (2 CH), 132.22 (2 CH), 136.33 (1 quat. C), 137.15 (1 quat. C), 170.35 (1 quat. C), 171.00 (1 quat. C); IR (neat): ν 1730 (C=O), 1654 (C=N) cm^{-1}; HRMS calcd for $C_{18}H_{25}BrN_3O_2$ $[M+H]^+$: 394.1125; found 394.1123.

Reference:

1. W.-X. Zhang, D. Li, Z. Wang, Z. Xi, *Organometallics,* 2009, **28**, 882.

2) X-ray Crystallographic Studies for 1e, 1i and 4c.

Single crystals of **1e** suitable for X-ray analysis were grown in CH_2Cl_2/hexane at room temperature for 1 days. Single crystals of **1i** suitable for X-ray analysis were grown in CH_2Cl_2/hexane at room temperature for 1 day. Single crystals of **4c** suitable for X-ray analysis were grown in CH_2Cl_2/hexane at room temperature for 1 days. Data collections for **1i** and **4c** were performed at 20 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collections for **1e** were performed at -100 °C on a RIGAKU CCD SATURN 724 diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by Rapid-AUTO (Rigaku 2000) program package for **1i** and **4c** or the CrystalClear (Rigaku Inc., 2007) for **1e**. The raw frame data was processed using Crystal Structure (Rigaku/MSC 2000) for **1i** and **4c** or Crystal Clear (Rigaku Inc., 2007) for **1e** to yield the reflection data file. The structures of **1e, 1i,** and **4c** were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-857963 (**1e**), CCDC-857966 (**1i**), and CCDC-857964 (**4c**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



SFigure 1. ORTEP drawing of **1e** with 30% thermal ellipsoids.

STable 1. Crystal data and structure refinement for **1e**.

Identification code	**1e**	
Empirical formula	$C_{21}H_{21}N_3O_2$	
Formula weight	347.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.086(2) Å	α = 73.23(3)°

	b = 12.727(3) Å	β = 84.08(3)°
	c = 13.649(3) Å	γ = 83.37(3)°
Volume	1826.4(6) $Å^3$	
Z	4	
Density (calculated)	1.263 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	736	
Crystal size	0.26 x 0.24 x 0.23 mm^3	
Theta range for data collection	2.50 to 25.00°	
Index ranges	-12<=h<=13, -15<=k<=15, -16<=l<=16	
Reflections collected	13045	
Independent reflections	6362 [R(int) = 0.0389]	
Completeness to theta = 25.00°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6891	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6362 / 0 / 469	
Goodness-of-fit on F^2	1.143	
Final R indices [I>2sigma(I)]	R1 = 0.0655, wR2 = 0.1300	
R indices (all data)	R1 = 0.0755, wR2 = 0.1364	
Largest diff. peak and hole	0.380 and -0.217 e. $Å^{-3}$	

STable 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10042(2)	5308(1)	1020(1)	40(1)
O(2)	12030(2)	3512(1)	1597(1)	41(1)
O(3)	12518(2)	6522(2)	1114(1)	42(1)
O(4)	10745(2)	7756(1)	-355(1)	41(1)
N(1)	8871(2)	3874(2)	1852(1)	30(1)
N(2)	8417(2)	2036(2)	2900(2)	37(1)
N(3)	10387(2)	2542(2)	2350(2)	35(1)
N(4)	10952(2)	6883(2)	2273(1)	32(1)
N(5)	9102(2)	7493(2)	2986(2)	35(1)
N(6)	9597(2)	7835(2)	1143(1)	31(1)
C(1)	7693(2)	4484(2)	1688(2)	30(1)
C(2)	7352(2)	4871(2)	693(2)	35(1)
C(3)	6216(2)	5441(2)	523(2)	45(1)
C(4)	5448(2)	5603(2)	1340(2)	49(1)
C(5)	5811(2)	5221(2)	2326(2)	45(1)
C(6)	6953(2)	4669(2)	2502(2)	37(1)
C(7)	7128(2)	2174(2)	2892(2)	33(1)

C(8)	6559(2)	2315(2)	1996(2)	41(1)
C(9)	5302(3)	2422(2)	2028(2)	53(1)
C(10)	4608(3)	2368(2)	2937(3)	58(1)
C(11)	5172(3)	2192(2)	3832(2)	51(1)
C(12)	6432(2)	2086(2)	3806(2)	39(1)
C(13)	9113(2)	2752(2)	2406(2)	32(1)
C(14)	9937(2)	4357(2)	1479(2)	32(1)
C(15)	10954(2)	3438(2)	1796(2)	33(1)
C(16)	11077(2)	1462(2)	2763(2)	36(1)
C(17)	11033(3)	1138(2)	3919(2)	44(1)
C(18)	11835(3)	65(2)	4328(2)	46(1)
C(19)	11487(3)	-845(2)	3908(2)	50(1)
C(20)	11533(2)	-493(2)	2754(2)	42(1)
C(21)	10711(2)	562(2)	2355(2)	35(1)
C(22)	8558(2)	8508(2)	670(2)	31(1)
C(23)	7823(2)	8045(2)	177(2)	42(1)
C(24)	6854(2)	8706(3)	-313(2)	54(1)
C(25)	6630(2)	9795(3)	-313(2)	53(1)
C(26)	7375(2)	10240(2)	177(2)	47(1)
C(27)	8358(2)	9598(2)	663(2)	36(1)
C(28)	7880(2)	7964(2)	2986(2)	33(1)
C(29)	6974(2)	7525(2)	2642(2)	39(1)
C(30)	5786(2)	7978(2)	2692(2)	49(1)
C(31)	5483(3)	8868(2)	3085(2)	52(1)
C(32)	6379(3)	9293(2)	3439(2)	50(1)
C(33)	7567(2)	8841(2)	3402(2)	41(1)
C(34)	9768(2)	7423(2)	2200(2)	30(1)
C(35)	10601(2)	7541(2)	567(2)	33(1)
C(36)	11512(2)	6898(2)	1331(2)	33(1)
C(37)	11420(2)	6274(2)	3277(2)	35(1)
C(38)	11314(3)	5040(2)	3502(2)	46(1)
C(39)	11749(3)	4426(3)	4564(2)	58(1)
C(40)	13037(3)	4662(2)	4659(2)	54(1)
C(41)	13142(3)	5892(2)	4407(2)	48(1)
C(42)	12730(2)	6493(2)	3336(2)	39(1)

STable 3. Bond lengths [Å] and angles [°] for **1e**.

O(1)-C(14)	1.205(3)	N(1)-C(13)	1.419(3)
O(2)-C(15)	1.204(3)	N(1)-C(1)	1.443(3)
O(3)-C(36)	1.205(3)	N(2)-C(13)	1.258(3)
O(4)-C(35)	1.206(3)	N(2)-C(7)	1.421(3)
N(1)-C(14)	1.378(3)	N(3)-C(15)	1.356(3)

N(3)-C(13)	1.405(3)	C(37)-C(38)	1.527(3)
N(3)-C(16)	1.480(3)	C(38)-C(39)	1.533(4)
N(4)-C(36)	1.364(3)	C(39)-C(40)	1.518(4)
N(4)-C(34)	1.409(3)	C(40)-C(41)	1.518(4)
N(4)-C(37)	1.480(3)	C(41)-C(42)	1.530(3)
N(5)-C(34)	1.256(3)		
N(5)-C(28)	1.417(3)	C(14)-N(1)-C(13)	110.96(18)
N(6)-C(35)	1.375(3)	C(14)-N(1)-C(1)	121.96(18)
N(6)-C(34)	1.411(3)	C(13)-N(1)-C(1)	127.07(19)
N(6)-C(22)	1.443(3)	C(13)-N(2)-C(7)	124.4(2)
C(1)-C(6)	1.372(3)	C(15)-N(3)-C(13)	112.39(19)
C(1)-C(2)	1.381(3)	C(15)-N(3)-C(16)	121.5(2)
C(2)-C(3)	1.384(3)	C(13)-N(3)-C(16)	125.9(2)
C(3)-C(4)	1.380(4)	C(36)-N(4)-C(34)	111.89(18)
C(3)-H(3)	0.9500	C(36)-N(4)-C(37)	126.28(19)
C(4)-C(5)	1.378(4)	C(34)-N(4)-C(37)	121.44(19)
C(5)-C(6)	1.383(3)	C(34)-N(5)-C(28)	125.1(2)
C(7)-C(12)	1.381(3)	C(35)-N(6)-C(34)	110.80(18)
C(7)-C(8)	1.390(3)	C(35)-N(6)-C(22)	121.61(19)
C(8)-C(9)	1.382(4)	C(34)-N(6)-C(22)	127.57(19)
C(9)-C(10)	1.379(4)	C(6)-C(1)-C(2)	121.9(2)
C(10)-C(11)	1.378(4)	C(6)-C(1)-N(1)	120.3(2)
C(11)-C(12)	1.386(4)	C(2)-C(1)-N(1)	117.7(2)
C(14)-C(15)	1.526(3)	C(1)-C(2)-C(3)	118.5(2)
C(16)-C(17)	1.509(3)	C(4)-C(3)-C(2)	120.1(2)
C(16)-C(21)	1.519(3)	C(5)-C(4)-C(3)	120.5(2)
C(17)-C(18)	1.532(3)	C(4)-C(5)-C(6)	119.9(2)
C(18)-C(19)	1.533(4)	C(1)-C(6)-C(5)	119.0(2)
C(19)-C(20)	1.506(3)	C(12)-C(7)-C(8)	119.6(2)
C(20)-C(21)	1.526(3)	C(12)-C(7)-N(2)	119.0(2)
C(22)-C(27)	1.377(3)	C(8)-C(7)-N(2)	121.2(2)
C(22)-C(23)	1.384(3)	C(9)-C(8)-C(7)	119.2(3)
C(23)-C(24)	1.387(4)	C(10)-C(9)-C(8)	121.0(3)
C(24)-C(25)	1.380(4)	C(11)-C(10)-C(9)	119.8(3)
C(25)-C(26)	1.374(4)	C(10)-C(11)-C(12)	119.6(3)
C(26)-C(27)	1.388(3)	C(7)-C(12)-C(11)	120.7(2)
C(28)-C(29)	1.385(3)	N(2)-C(13)-N(3)	122.5(2)
C(28)-C(33)	1.388(3)	N(2)-C(13)-N(1)	131.6(2)
C(29)-C(30)	1.379(3)	N(3)-C(13)-N(1)	105.80(19)
C(30)-C(31)	1.381(4)	O(1)-C(14)-N(1)	127.1(2)
C(31)-C(32)	1.374(4)	O(1)-C(14)-C(15)	127.5(2)
C(32)-C(33)	1.377(4)	N(1)-C(14)-C(15)	105.35(19)
C(35)-C(36)	1.520(3)	O(2)-C(15)-N(3)	128.1(2)
C(37)-C(42)	1.524(3)	O(2)-C(15)-C(14)	126.5(2)

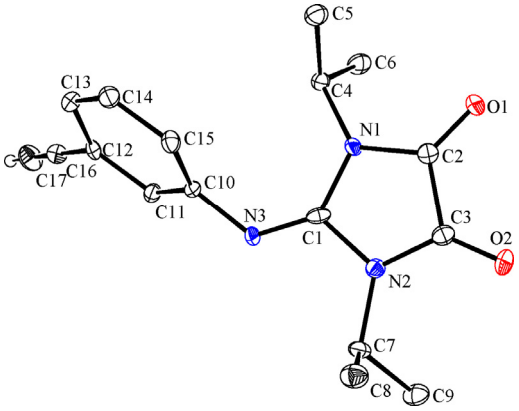
N(3)-C(15)-C(14)	105.4(2)	C(29)-C(30)-C(31)	120.8(3)
N(3)-C(16)-C(17)	111.5(2)	C(32)-C(31)-C(30)	119.3(3)
N(3)-C(16)-C(21)	113.09(18)	C(31)-C(32)-C(33)	120.5(3)
C(17)-C(16)-C(21)	112.5(2)	C(32)-C(33)-C(28)	120.4(2)
C(16)-C(17)-C(18)	110.8(2)	N(5)-C(34)-N(4)	121.5(2)
C(17)-C(18)-C(19)	110.5(2)	N(5)-C(34)-N(6)	132.3(2)
C(20)-C(19)-C(18)	111.6(2)	N(4)-C(34)-N(6)	106.17(18)
C(19)-C(20)-C(21)	111.4(2)	O(4)-C(35)-N(6)	127.4(2)
C(16)-C(21)-C(20)	109.37(19)	O(4)-C(35)-C(36)	126.6(2)
C(27)-C(22)-C(23)	121.6(2)	N(6)-C(35)-C(36)	105.91(19)
C(27)-C(22)-N(6)	120.1(2)	O(3)-C(36)-N(4)	129.3(2)
C(23)-C(22)-N(6)	118.2(2)	O(3)-C(36)-C(35)	125.4(2)
C(22)-C(23)-C(24)	118.1(3)	N(4)-C(36)-C(35)	105.18(19)
C(25)-C(24)-C(23)	121.0(3)	N(4)-C(37)-C(42)	111.8(2)
C(26)-C(25)-C(24)	119.9(3)	N(4)-C(37)-C(38)	110.8(2)
C(25)-C(26)-C(27)	120.1(3)	C(42)-C(37)-C(38)	110.6(2)
C(22)-C(27)-C(26)	119.2(2)	C(37)-C(38)-C(39)	110.2(2)
C(29)-C(28)-C(33)	119.1(2)	C(40)-C(39)-C(38)	111.3(2)
C(29)-C(28)-N(5)	121.6(2)	C(41)-C(40)-C(39)	111.2(2)
C(33)-C(28)-N(5)	119.2(2)	C(40)-C(41)-C(42)	111.2(2)
C(30)-C(29)-C(28)	119.9(2)	C(37)-C(42)-C(41)	109.4(2)

Symmetry transformations used to generate equivalent atoms:

STable 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	40(1)	29(1)	48(1)	-5(1)	-7(1)	-5(1)
O(2)	31(1)	40(1)	50(1)	-11(1)	-6(1)	-3(1)
O(3)	33(1)	53(1)	42(1)	-20(1)	0(1)	4(1)
O(4)	42(1)	47(1)	30(1)	-10(1)	2(1)	2(1)
N(1)	30(1)	26(1)	35(1)	-7(1)	-7(1)	-1(1)
N(2)	33(1)	32(1)	43(1)	-4(1)	-6(1)	-2(1)
N(3)	29(1)	29(1)	45(1)	-6(1)	-10(1)	1(1)
N(4)	29(1)	38(1)	30(1)	-11(1)	-3(1)	3(1)
N(5)	32(1)	40(1)	33(1)	-12(1)	1(1)	0(1)
N(6)	31(1)	30(1)	32(1)	-10(1)	-2(1)	1(1)
C(1)	29(1)	23(1)	39(1)	-8(1)	-6(1)	-1(1)
C(2)	34(1)	33(1)	37(1)	-8(1)	-4(1)	-4(1)
C(3)	38(2)	38(1)	53(2)	-1(1)	-15(1)	-3(1)
C(4)	28(1)	38(2)	78(2)	-11(1)	-6(1)	3(1)
C(5)	37(1)	38(1)	59(2)	-18(1)	8(1)	-1(1)

C(6)	42(1)	30(1)	39(1)	-12(1)	-2(1)	-5(1)
C(7)	35(1)	23(1)	39(1)	-5(1)	-6(1)	-4(1)
C(8)	50(2)	32(1)	42(1)	-10(1)	-11(1)	-7(1)
C(9)	58(2)	42(2)	61(2)	-5(1)	-29(2)	-14(1)
C(10)	38(2)	45(2)	87(2)	-5(2)	-16(2)	-6(1)
C(11)	46(2)	39(2)	58(2)	-4(1)	6(1)	-2(1)
C(12)	40(1)	32(1)	43(1)	-4(1)	-8(1)	-1(1)
C(13)	36(1)	27(1)	34(1)	-8(1)	-8(1)	-2(1)
C(14)	31(1)	33(1)	35(1)	-11(1)	-6(1)	-3(1)
C(15)	34(1)	31(1)	37(1)	-12(1)	-7(1)	-4(1)
C(16)	34(1)	31(1)	43(1)	-9(1)	-10(1)	3(1)
C(17)	59(2)	34(1)	40(1)	-14(1)	-10(1)	7(1)
C(18)	62(2)	37(1)	38(1)	-10(1)	-17(1)	7(1)
C(19)	73(2)	33(1)	43(2)	-9(1)	-14(1)	8(1)
C(20)	50(2)	33(1)	44(2)	-13(1)	-14(1)	3(1)
C(21)	35(1)	32(1)	37(1)	-9(1)	-9(1)	0(1)
C(22)	29(1)	35(1)	31(1)	-10(1)	0(1)	-4(1)
C(23)	41(2)	49(2)	42(1)	-19(1)	-1(1)	-12(1)
C(24)	37(2)	83(2)	48(2)	-23(2)	-10(1)	-14(2)
C(25)	33(2)	75(2)	43(2)	-6(2)	-7(1)	7(1)
C(26)	45(2)	42(2)	45(2)	-6(1)	-1(1)	9(1)
C(27)	34(1)	36(1)	40(1)	-13(1)	-4(1)	-2(1)
C(28)	32(1)	35(1)	30(1)	-7(1)	3(1)	-2(1)
C(29)	38(1)	35(1)	46(2)	-15(1)	2(1)	-6(1)
C(30)	34(2)	56(2)	57(2)	-16(1)	-1(1)	-9(1)
C(31)	37(2)	51(2)	62(2)	-13(2)	4(1)	7(1)
C(32)	50(2)	41(2)	59(2)	-21(1)	12(1)	2(1)
C(33)	40(2)	45(2)	43(1)	-20(1)	4(1)	-7(1)
C(34)	31(1)	30(1)	33(1)	-11(1)	-3(1)	-5(1)
C(35)	38(1)	31(1)	30(1)	-10(1)	2(1)	-5(1)
C(36)	32(1)	34(1)	35(1)	-14(1)	-2(1)	-2(1)
C(37)	36(1)	40(1)	29(1)	-12(1)	-4(1)	3(1)
C(38)	50(2)	44(2)	42(2)	-6(1)	-4(1)	-9(1)
C(39)	68(2)	53(2)	43(2)	3(1)	-7(2)	-7(2)
C(40)	59(2)	55(2)	41(2)	-5(1)	-12(1)	11(1)
C(41)	44(2)	58(2)	45(2)	-20(1)	-13(1)	8(1)
C(42)	39(1)	38(1)	41(1)	-15(1)	-8(1)	2(1)



SFigure 2. ORTEP drawing of **1i** with 30% thermal ellipsoids.

STable 5. Crystal data and structure refinement for **1i**.

Identification code	**1i**	
Empirical formula	$C_{17}H_{19}N_3O_2$	
Formula weight	297.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.082(2) Å	α = 90°
	b = 8.7000(17) Å	β = 100.67(3)°
	c = 16.612(3) Å	γ = 90°
Volume	1573.9(5) $Å^3$	
Z	4	
Density (calculated)	1.255 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	632	
Crystal size	0.40 x 0.40 x 0.20 mm^3	
Theta range for data collection	2.05 to 27.48°.	
Index ranges	-14<=h<=14, -11<=k<=11, -21<=l<=21	
Reflections collected	6400	
Independent reflections	3575 [R(int) = 0.0827]	
Completeness to theta = 27.48°	98.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9834 and 0.9671	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3575 / 0 / 204	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1324	

R indices (all data)	R1 = 0.1370, wR2 = 0.1391
Extinction coefficient	0.0113(11)
Largest diff. peak and hole	0.367 and -0.266 e. $Å^{-3}$

STable 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1i**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-445(3)	8605(4)	1995(2)	21(1)
C(2)	-2014(3)	7250(4)	2381(2)	26(1)
C(3)	-2370(3)	7602(4)	1458(2)	24(1)
C(4)	-116(3)	7577(4)	3481(2)	22(1)
C(5)	-650(3)	8373(4)	4149(2)	29(1)
C(6)	56(3)	5868(4)	3631(2)	30(1)
C(7)	-1223(3)	8892(4)	457(2)	23(1)
C(8)	-1971(3)	10364(4)	250(2)	34(1)
C(9)	-1569(3)	7666(4)	-202(2)	32(1)
C(10)	1317(3)	9971(4)	2628(2)	20(1)
C(11)	2541(3)	9570(4)	2724(2)	22(1)
C(12)	3376(3)	10171(4)	3373(2)	20(1)
C(13)	2981(3)	11198(4)	3907(2)	25(1)
C(14)	1755(3)	11628(4)	3789(2)	26(1)
C(15)	937(3)	11023(4)	3153(2)	24(1)
C(16)	4648(3)	9724(4)	3481(2)	28(1)
C(17)	5670(4)	9320(5)	3557(3)	39(1)
N(1)	-867(2)	7884(3)	2658(2)	20(1)
N(2)	-1348(2)	8307(3)	1280(2)	21(1)
N(3)	500(2)	9391(3)	1949(2)	20(1)
O(1)	-2644(2)	6523(3)	2776(2)	33(1)
O(2)	-3348(2)	7300(3)	1021(2)	34(1)
H(4)	699	8019	3487	26
H(5A)	-758	9447	4022	43
H(5B)	-100	8254	4664	43
H(5C)	-1430	7923	4183	43
H(6A)	-732	5383	3584	46
H(6B)	522	5700	4172	46
H(6C)	487	5438	3234	46
H(7)	-357	9152	478	28

H(8A)	-2823	10154	247	52
H(8B)	-1875	10727	-280	52
H(8C)	-1686	11135	654	52
H(9A)	-1084	6760	-52	48
H(9B)	-1416	8049	-716	48
H(9C)	-2424	7418	-254	48
H(11)	2804	8900	2356	26
H(13)	3537	11599	4345	30
H(14)	1491	12327	4143	31
H(15)	117	11321	3072	28
H(17)	6482	8999	3618	47

STable 7. Bond lengths [Å]and angles [°]for **1i**.

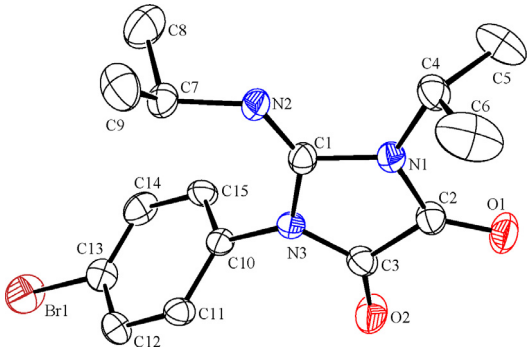
C(1)-N(3)	1.265(4)	N(3)-C(1)-N(1)	132.9(3)
C(1)-N(1)	1.419(4)	N(3)-C(1)-N(2)	120.6(3)
C(1)-N(2)	1.428(4)	N(1)-C(1)-N(2)	106.5(3)
C(2)-O(1)	1.220(4)	O(1)-C(2)-N(1)	127.6(3)
C(2)-N(1)	1.384(4)	O(1)-C(2)-C(3)	124.8(3)
C(2)-C(3)	1.541(5)	N(1)-C(2)-C(3)	107.6(3)
C(3)-O(2)	1.217(4)	O(2)-C(3)-N(2)	130.5(3)
C(3)-N(2)	1.368(4)	O(2)-C(3)-C(2)	126.0(3)
C(4)-N(1)	1.488(4)	N(2)-C(3)-C(2)	103.6(3)
C(4)-C(6)	1.514(4)	N(1)-C(4)-C(6)	111.1(3)
C(4)-C(5)	1.518(4)	N(1)-C(4)-C(5)	111.3(3)
C(7)-N(2)	1.489(4)	C(6)-C(4)-C(5)	112.5(3)
C(7)-C(9)	1.526(5)	N(2)-C(7)-C(9)	111.5(3)
C(7)-C(8)	1.530(4)	N(2)-C(7)-C(8)	110.7(3)
C(10)-C(11)	1.381(4)	C(9)-C(7)-C(8)	111.8(3)
C(10)-C(15)	1.383(4)	C(11)-C(10)-C(15)	120.1(3)
C(10)-N(3)	1.403(4)	C(11)-C(10)-N(3)	118.4(3)
C(11)-C(12)	1.386(5)	C(15)-C(10)-N(3)	121.2(3)
C(12)-C(13)	1.387(4)	C(10)-C(11)-C(12)	119.6(3)
C(12)-C(16)	1.441(5)	C(11)-C(12)-C(13)	119.8(3)
C(13)-C(14)	1.388(5)	C(11)-C(12)-C(16)	119.5(3)
C(14)-C(15)	1.363(5)	C(13)-C(12)-C(16)	120.8(3)
C(16)-C(17)	1.169(5)	C(12)-C(13)-C(14)	120.0(3)

C(15)-C(14)-C(13)	119.9(4)	C(1)-N(1)-C(4)	125.7(3)
C(14)-C(15)-C(10)	120.5(4)	C(3)-N(2)-C(1)	112.4(3)
C(17)-C(16)-C(12)	178.0(5)	C(3)-N(2)-C(7)	125.0(3)
C(2)-N(1)-C(1)	109.4(3)	C(1)-N(2)-C(7)	122.1(3)
C(2)-N(1)-C(4)	123.9(3)	C(1)-N(3)-C(10)	124.4(3)

Symmetry transformations used to generate equivalent atoms:

STable 8. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1i**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(2)	26(2)	14(2)	-1(2)	5(2)	10(2)
C(2)	27(2)	28(2)	23(2)	-2(2)	6(2)	-4(2)
C(3)	27(2)	25(2)	21(2)	-4(2)	5(2)	2(2)
C(4)	17(2)	30(2)	18(2)	0(2)	2(2)	-2(2)
C(5)	28(2)	35(2)	23(2)	0(2)	2(2)	1(2)
C(6)	29(2)	36(3)	24(2)	4(2)	-1(2)	5(2)
C(7)	24(2)	29(2)	17(2)	5(2)	7(2)	2(2)
C(8)	42(3)	30(2)	30(3)	3(2)	7(2)	3(2)
C(9)	42(3)	31(2)	24(2)	-6(2)	8(2)	2(2)
C(10)	21(2)	23(2)	16(2)	-5(2)	6(2)	-6(2)
C(11)	19(2)	25(2)	21(2)	-4(2)	3(2)	-4(2)
C(12)	15(2)	21(2)	25(2)	1(2)	6(2)	-5(2)
C(13)	26(2)	28(2)	21(2)	-3(2)	1(2)	-6(2)
C(14)	28(2)	24(2)	27(2)	-5(2)	9(2)	-2(2)
C(15)	19(2)	23(2)	29(2)	-2(2)	7(2)	-2(2)
C(16)	30(2)	30(2)	24(2)	1(2)	5(2)	-4(2)
C(17)	35(3)	35(3)	48(3)	7(2)	11(2)	2(2)
N(1)	14(2)	25(2)	19(2)	4(1)	3(1)	-3(1)
N(2)	19(2)	23(2)	20(2)	-2(2)	5(1)	1(1)
N(3)	16(2)	24(2)	21(2)	-2(2)	6(1)	-6(2)
O(1)	24(2)	51(2)	25(2)	3(1)	6(1)	-14(1)
O(2)	20(2)	46(2)	32(2)	0(1)	-5(1)	-9(1)



SFigure 3. ORTEP drawing of **4c** with 30% thermal ellipsoids.

STable 9. Crystal data and structure refinement for **4c**.

Identification code	**4c**	
Empirical formula	$C_{15}H_{18}BrN_3O_2$	
Formula weight	352.23	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.8707(18) Å	α = 90°
	b = 10.082(2) Å	β = 90°
	c = 18.499(4) Å	γ = 90°
Volume	1654.3(6) $Å^3$	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	2.492 mm^{-1}	
F(000)	720	
Crystal size	0.30 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.30 to 27.48°.	
Index ranges	-11<=h<=11, -13<=k<=13, -24<=l<=24	
Reflections collected	2200	
Independent reflections	2177 [R(int) = 0.0526]	
Completeness to theta = 27.48°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.6356 and 0.5218	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2177 / 0 / 195	
Goodness-of-fit on F^2	0.735	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0521	

R indices (all data)	R1 = 0.1173, wR2 = 0.0610
Absolute structure parameter	0.50(3)
Extinction coefficient	0.0128(6)
Largest diff. peak and hole	0.279 and -0.396 e. $Å^{-3}$

STable 10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	10619(1)	4132(1)	8426(1)	87(1)
C(1)	9114(6)	4829(6)	4712(3)	41(1)
C(2)	10889(6)	3803(6)	3975(3)	47(2)
C(3)	11425(7)	3776(6)	4766(3)	47(2)
C(4)	8552(6)	4711(6)	3375(2)	53(2)
C(5)	8162(8)	3500(6)	2959(3)	94(2)
C(6)	9282(7)	5770(6)	2919(3)	106(2)
C(7)	7352(6)	5979(6)	5496(2)	49(2)
C(8)	6039(6)	5130(6)	5758(3)	86(2)
C(9)	6860(7)	7379(5)	5342(3)	75(2)
C(10)	10379(6)	4392(6)	5936(2)	36(1)
C(11)	11362(6)	5206(5)	6296(2)	44(2)
C(12)	11448(6)	5154(5)	7055(2)	48(2)
C(13)	10538(7)	4253(6)	7397(2)	50(2)
C(14)	9541(7)	3426(6)	7047(3)	59(2)
C(15)	9529(7)	3479(5)	6288(2)	47(2)
N(1)	9522(5)	4410(4)	4004(2)	42(1)
N(2)	7905(5)	5428(4)	4810(2)	44(1)
N(3)	10346(4)	4428(4)	5155(2)	41(1)
O(1)	11529(4)	3348(4)	3459(2)	63(1)
O(2)	12581(4)	3279(4)	4978(2)	70(1)
H(4)	7607	5079	3563	63
H(5A)	7595	2906	3260	141
H(5B)	9070	3070	2801	141
H(5C)	7568	3741	2545	141
H(6A)	10281	5494	2786	160
H(6B)	9338	6582	3189	160
H(6C)	8694	5910	2490	160

H(7)	8161	5978	5857	59
H(8A)	6396	4255	5870	129
H(8B)	5288	5077	5386	129
H(8C)	5607	5522	6183	129
H(9A)	6198	7384	4931	112
H(9B)	7728	7916	5241	112
H(9C)	6339	7729	5755	112
H(11)	11971	5791	6039	53
H(12)	12093	5706	7313	58
H(14)	8906	2860	7301	71
H(15)	8938	2887	6027	56

STable 11. Bond lengths [Å] and angles [°] for **4c**.

Br(1)-C(13)	1.909(4)		
C(1)-N(2)	1.245(6)	N(2)-C(1)-N(1)	119.8(5)
C(1)-N(1)	1.423(5)	N(2)-C(1)-N(3)	135.7(5)
C(1)-N(3)	1.424(6)	N(1)-C(1)-N(3)	104.5(4)
C(2)-O(1)	1.202(5)	O(1)-C(2)-N(1)	128.7(5)
C(2)-N(1)	1.359(6)	O(1)-C(2)-C(3)	127.1(5)
C(2)-C(3)	1.539(7)	N(1)-C(2)-C(3)	104.2(4)
C(3)-O(2)	1.207(6)	O(2)-C(3)-N(3)	128.6(5)
C(3)-N(3)	1.366(6)	O(2)-C(3)-C(2)	125.4(5)
C(4)-N(1)	1.478(5)	N(3)-C(3)-C(2)	106.0(5)
C(4)-C(5)	1.485(6)	N(1)-C(4)-C(5)	112.1(4)
C(4)-C(6)	1.509(7)	N(1)-C(4)-C(6)	109.6(5)
C(7)-N(2)	1.470(5)	C(5)-C(4)-C(6)	113.0(4)
C(7)-C(9)	1.504(6)	N(2)-C(7)-C(9)	106.7(4)
C(7)-C(8)	1.525(7)	N(2)-C(7)-C(8)	108.5(5)
C(10)-C(15)	1.356(6)	C(9)-C(7)-C(8)	111.4(5)
C(10)-C(11)	1.370(6)	C(15)-C(10)-C(11)	121.8(4)
C(10)-N(3)	1.446(5)	C(15)-C(10)-N(3)	119.1(5)
C(11)-C(12)	1.408(5)	C(11)-C(10)-N(3)	118.9(5)
C(12)-C(13)	1.369(7)	C(10)-C(11)-C(12)	119.8(5)
C(13)-C(14)	1.377(7)	C(13)-C(12)-C(11)	117.0(5)
C(14)-C(15)	1.405(5)	C(12)-C(13)-C(14)	124.3(4)

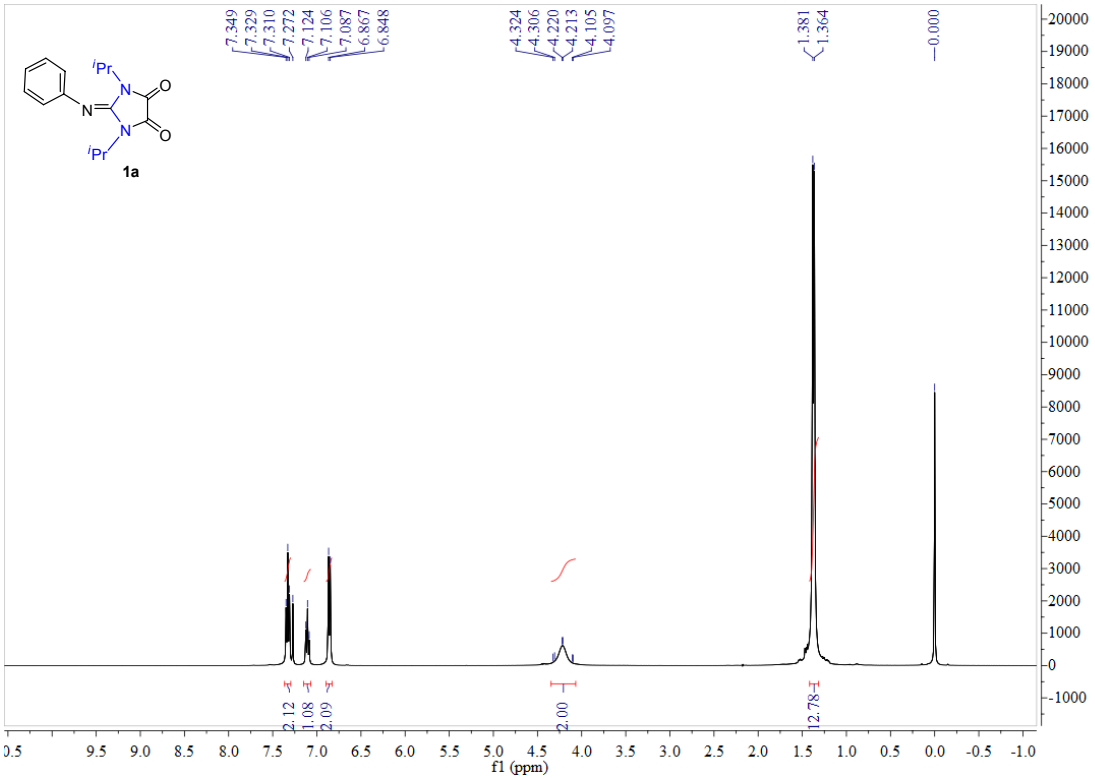
C(12)-C(13)-Br(1)	118.7(4)	C(1)-N(1)-C(4)	121.0(4)
C(14)-C(13)-Br(1)	117.0(4)	C(1)-N(2)-C(7)	126.6(5)
C(13)-C(14)-C(15)	116.8(6)	C(3)-N(3)-C(1)	111.8(4)
C(10)-C(15)-C(14)	120.1(6)	C(3)-N(3)-C(10)	120.0(5)
C(2)-N(1)-C(1)	113.4(4)	C(1)-N(3)-C(10)	126.7(4)
C(2)-N(1)-C(4)	125.5(4)		

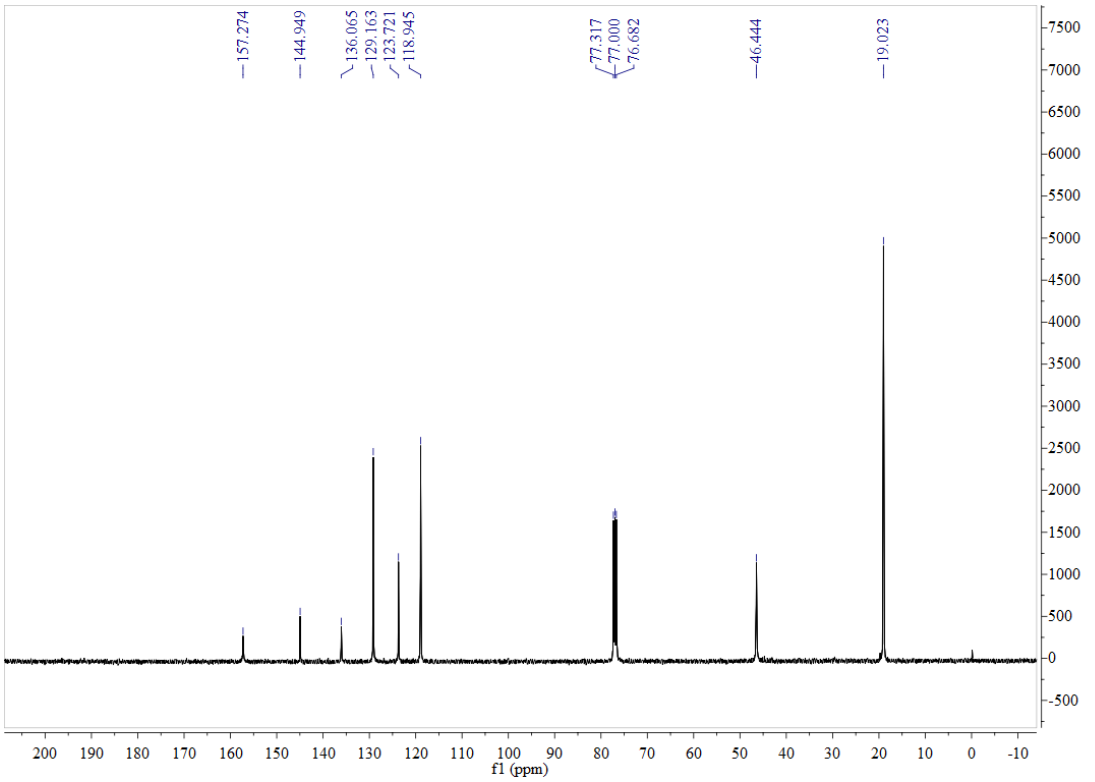
Symmetry transformations used to generate equivalent atoms:

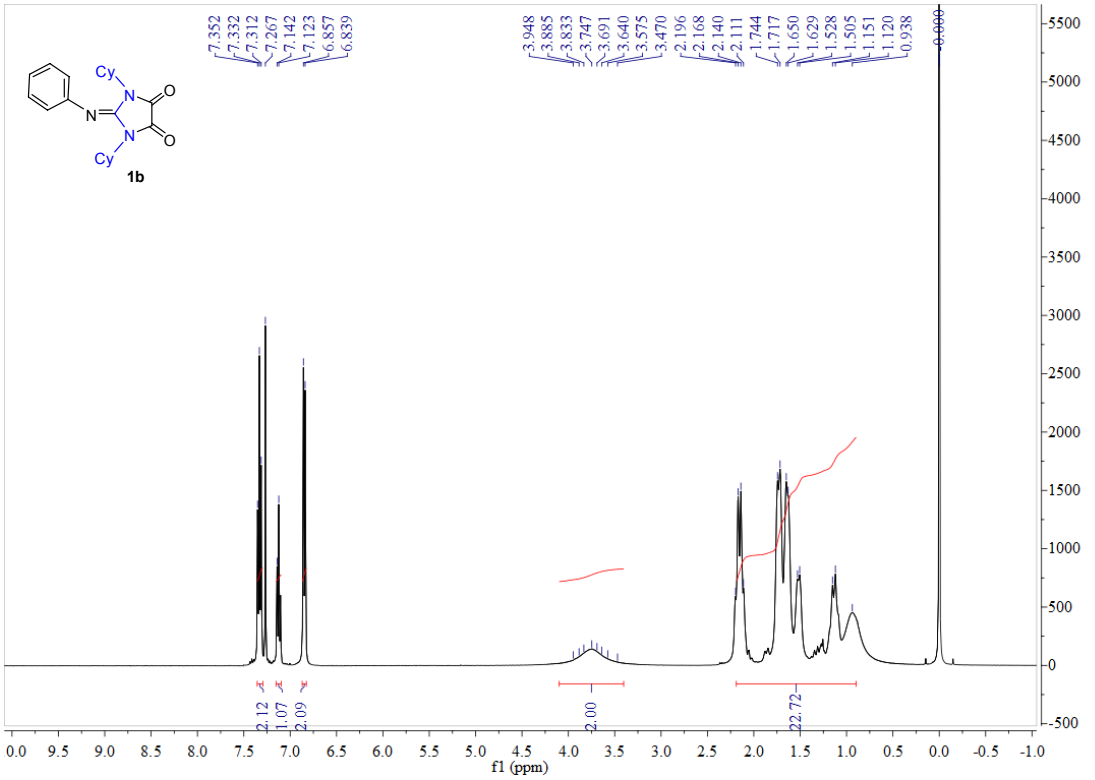
STable 12. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

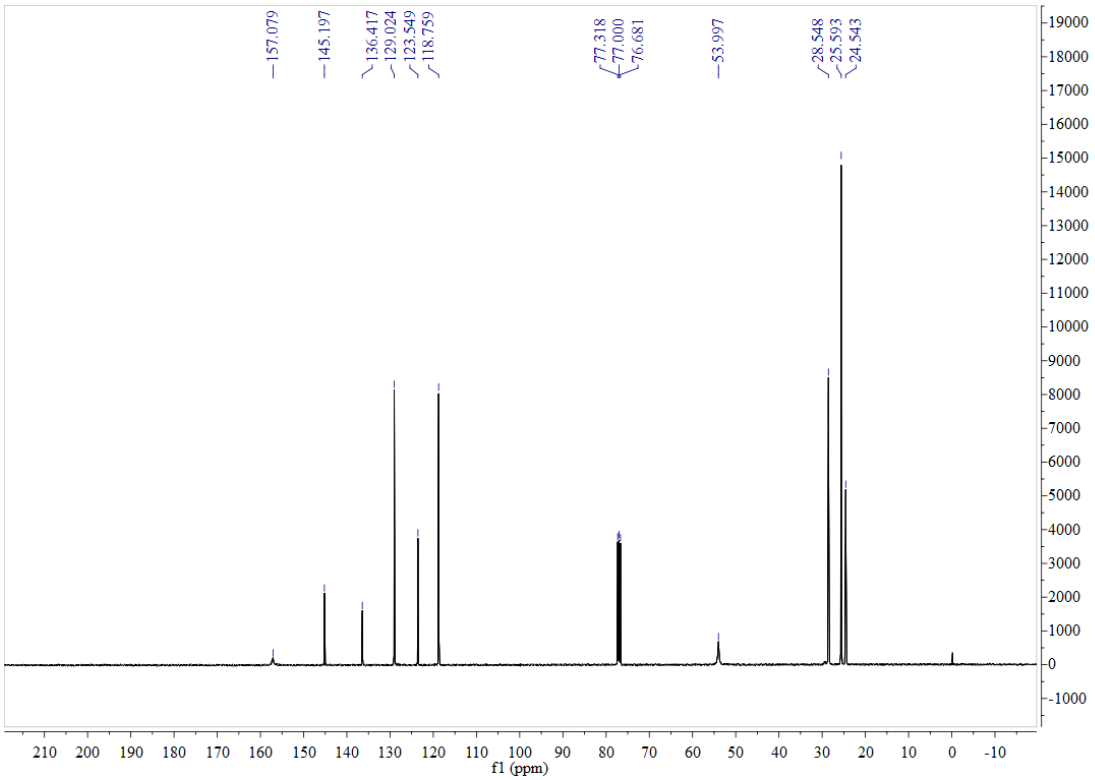
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	81(1)	138(1)	43(1)	14(1)	-3(1)	5(1)
C(1)	43(3)	41(4)	41(3)	-2(3)	6(3)	-3(4)
C(2)	49(4)	51(4)	41(3)	-2(3)	-4(3)	9(4)
C(3)	45(3)	52(5)	43(3)	1(3)	-6(3)	-4(4)
C(4)	59(3)	62(4)	36(2)	-2(3)	-6(3)	8(3)
C(5)	98(5)	95(5)	89(4)	-15(5)	-31(5)	-25(5)
C(6)	113(5)	98(5)	108(5)	58(5)	-48(5)	-26(6)
C(7)	47(3)	60(4)	41(3)	-3(4)	-1(3)	16(4)
C(8)	73(5)	102(6)	83(4)	5(4)	21(4)	2(5)
C(9)	96(5)	55(4)	75(4)	-11(4)	-20(5)	25(5)
C(10)	31(3)	44(4)	34(2)	1(3)	-4(3)	5(4)
C(11)	38(3)	55(4)	39(2)	7(3)	-4(3)	-3(4)
C(12)	59(4)	38(4)	47(3)	-3(3)	-7(3)	-2(4)
C(13)	54(4)	57(4)	40(3)	11(3)	-11(3)	4(5)
C(14)	56(4)	69(4)	51(3)	21(3)	11(4)	-2(5)
C(15)	41(3)	54(4)	45(3)	1(3)	-2(3)	-13(4)
N(1)	40(2)	52(3)	34(2)	-3(2)	0(2)	3(3)
N(2)	38(2)	55(3)	39(2)	-7(2)	0(2)	9(3)
N(3)	31(2)	53(3)	37(2)	-4(2)	-4(2)	4(3)
O(1)	64(2)	80(3)	47(2)	-10(3)	11(2)	19(2)
O(2)	57(3)	103(3)	49(2)	-6(3)	-9(2)	36(3)

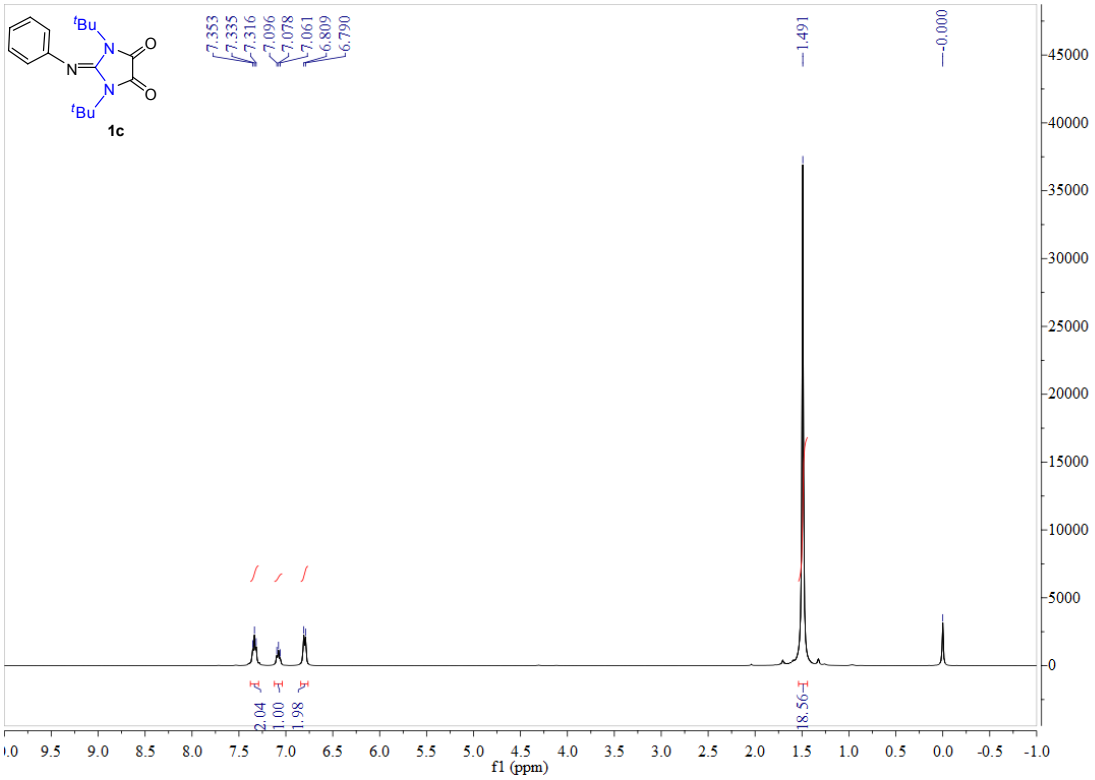
3) ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds

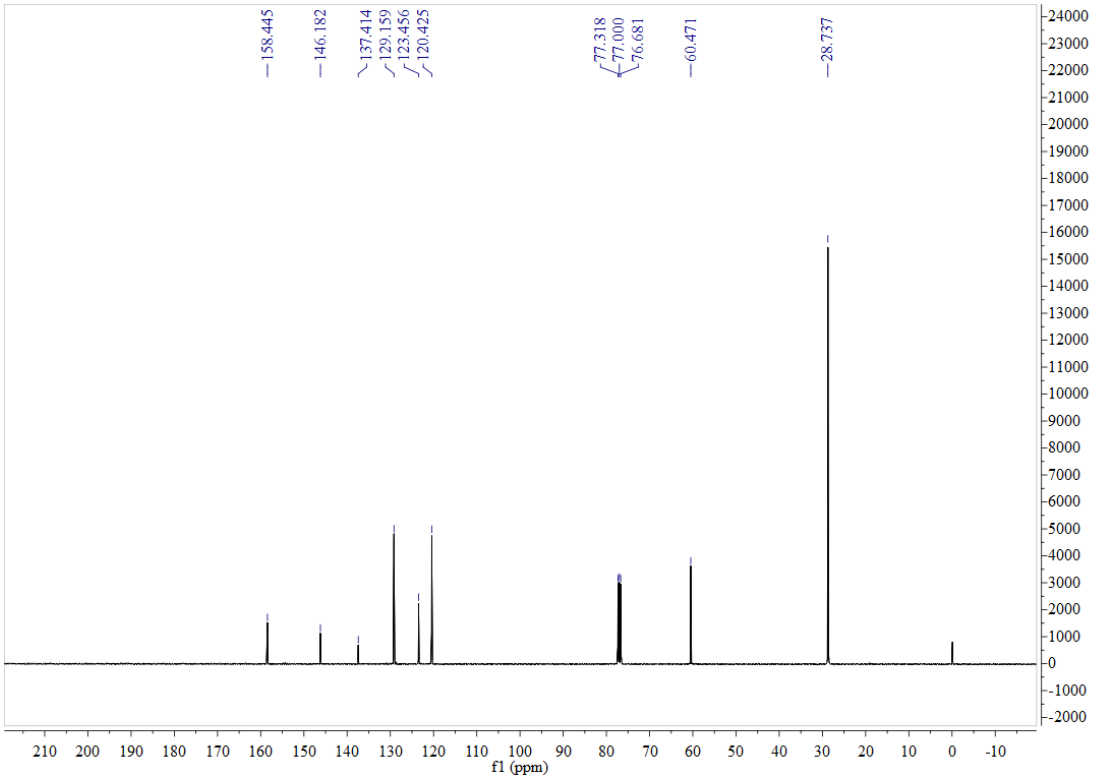


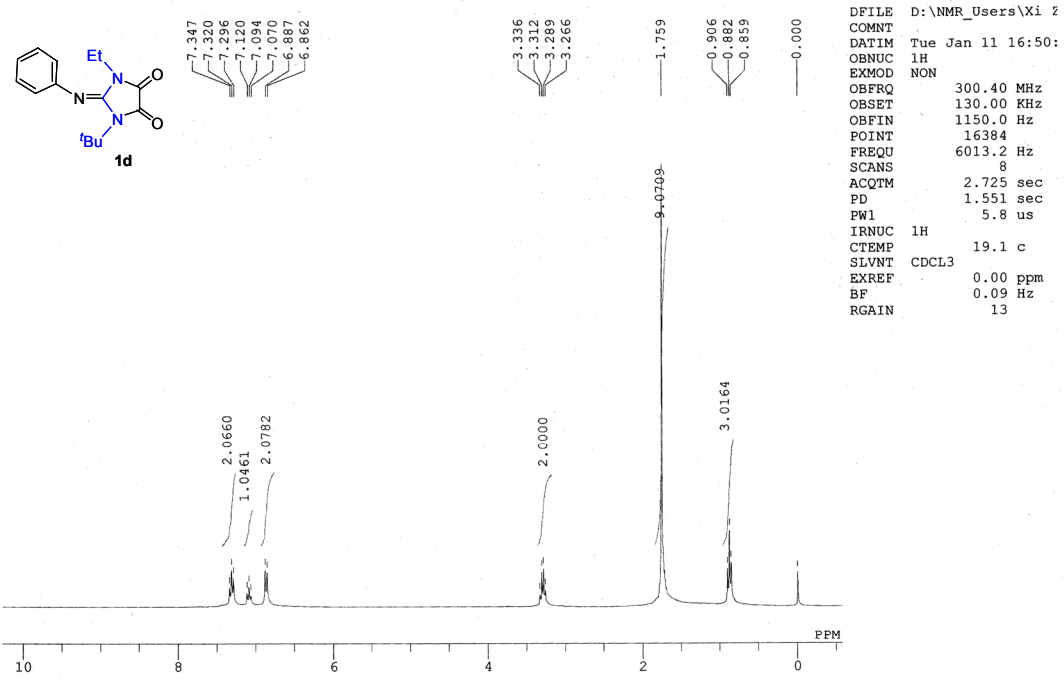


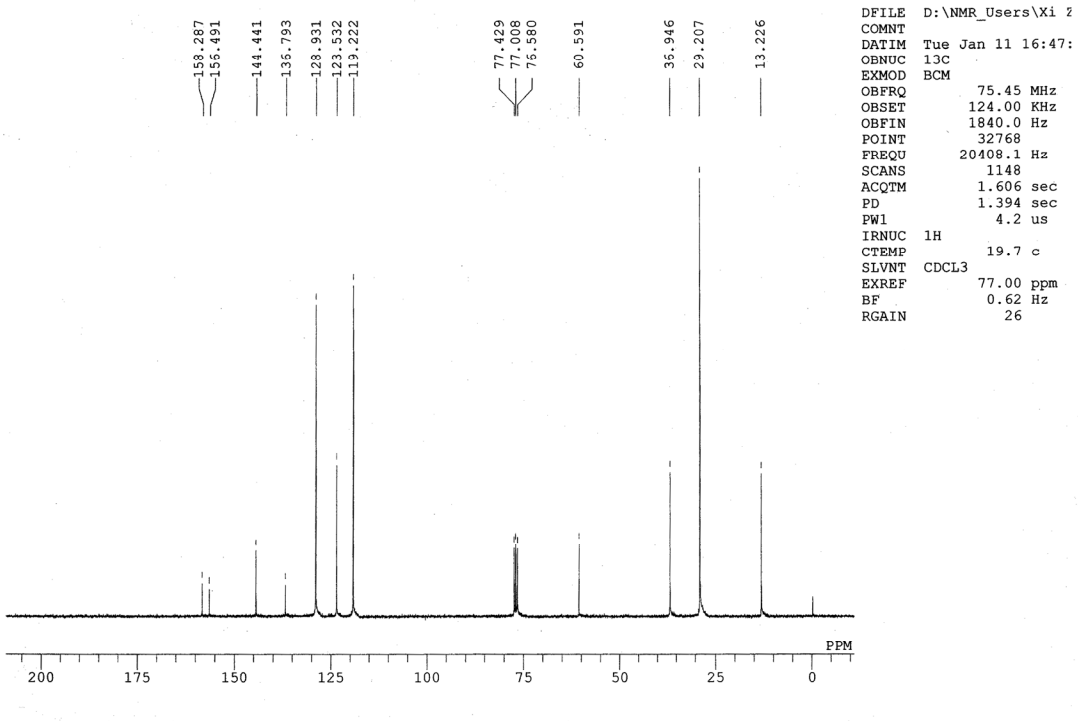


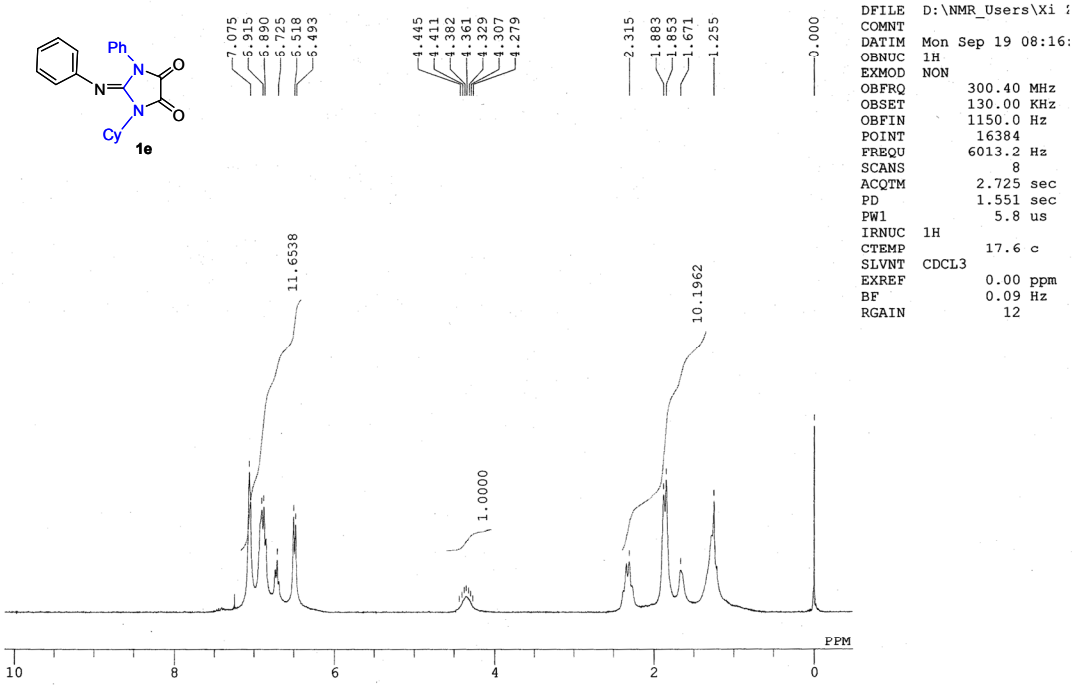


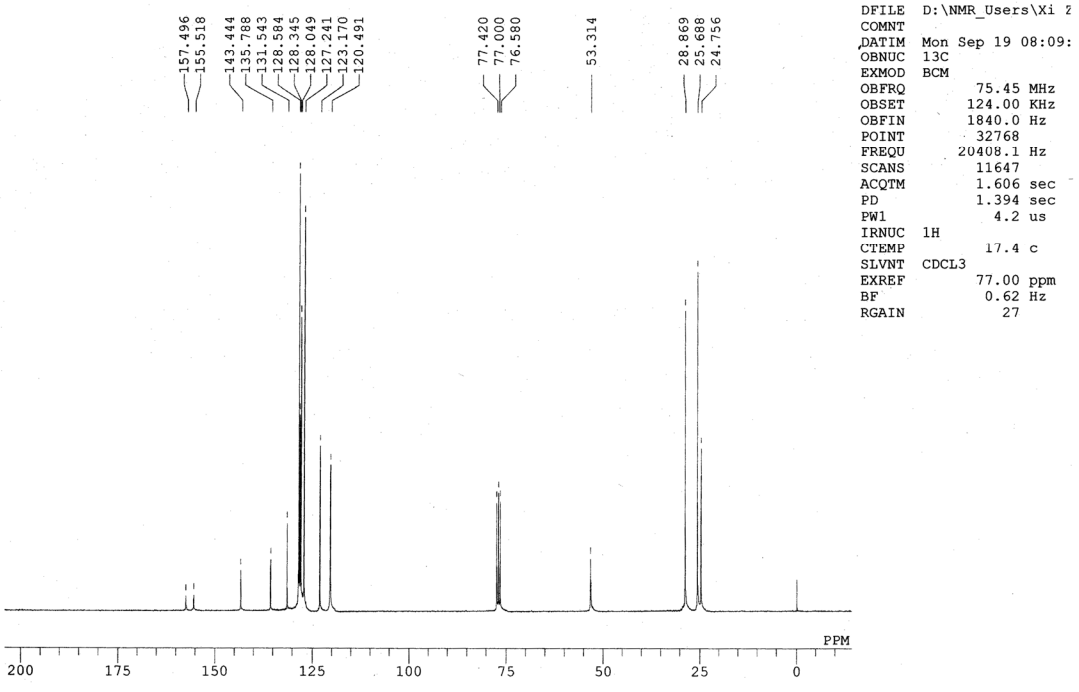

tBu
N
O
N
O
tBu
1c
7.353
7.335
7.316
7.096
7.078
7.061
6.809
6.790
1.491
0.000
2.04
1.00
1.98
18.56
f1 (ppm)

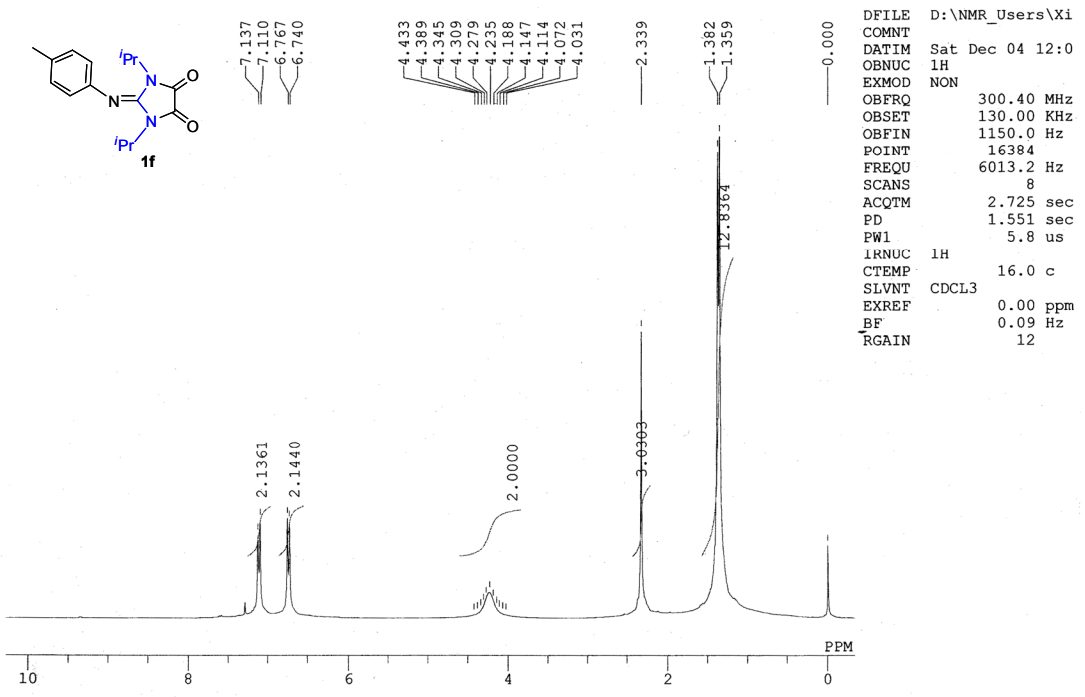

158.445
146.182
137.414
129.159
123.456
120.425
77.318
77.000
76.681
60.471
28.737
f1 (ppm)

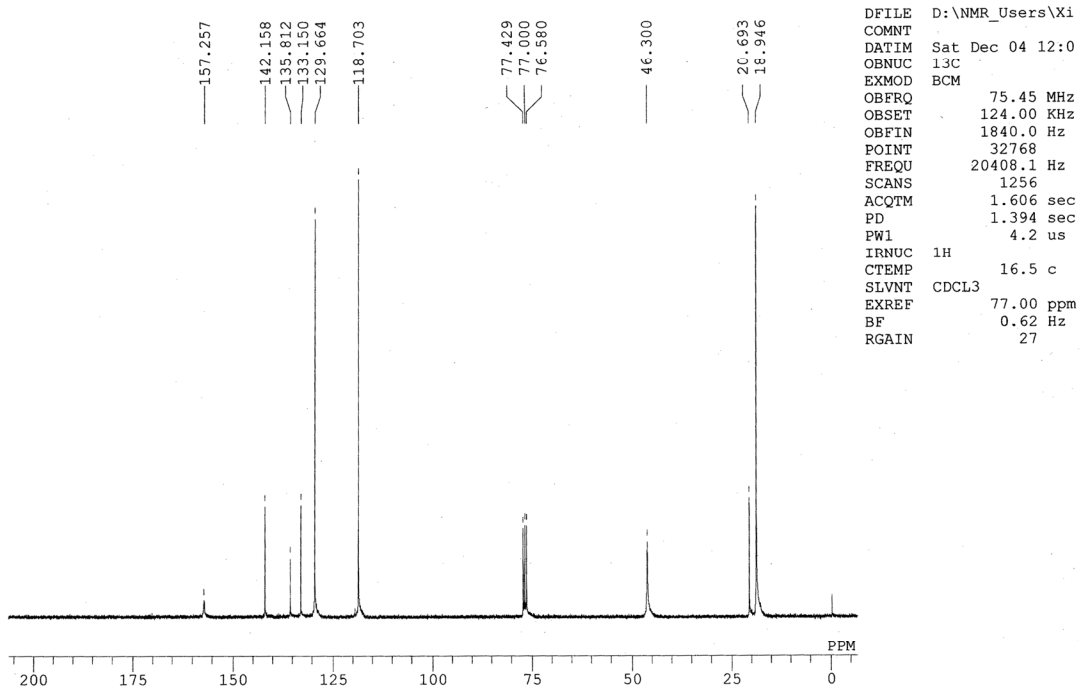


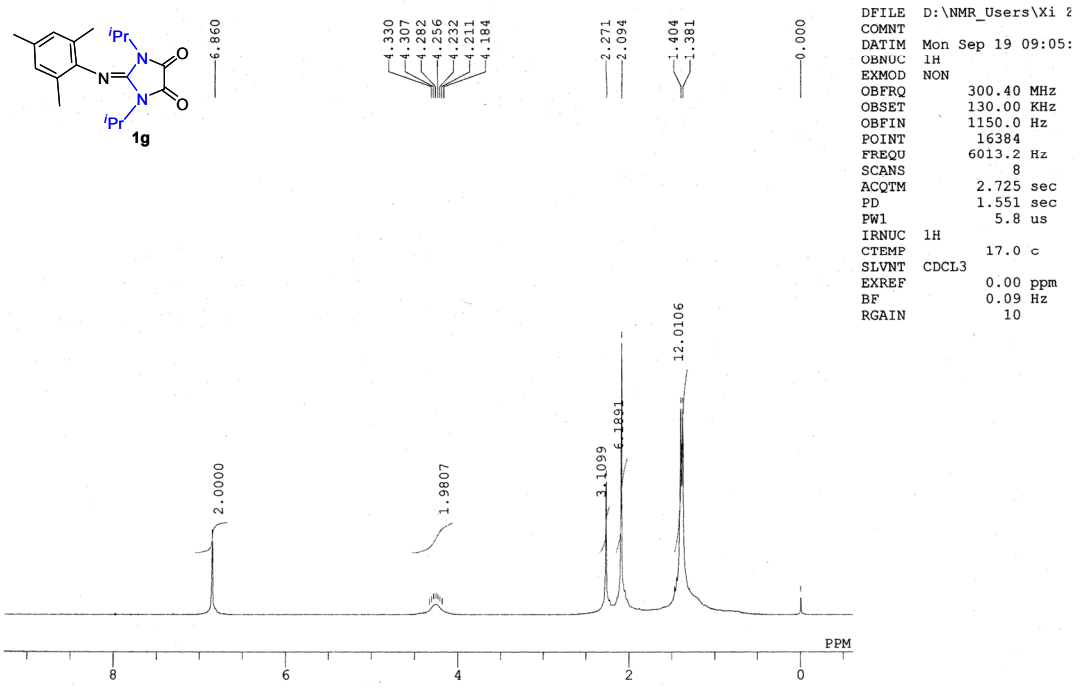


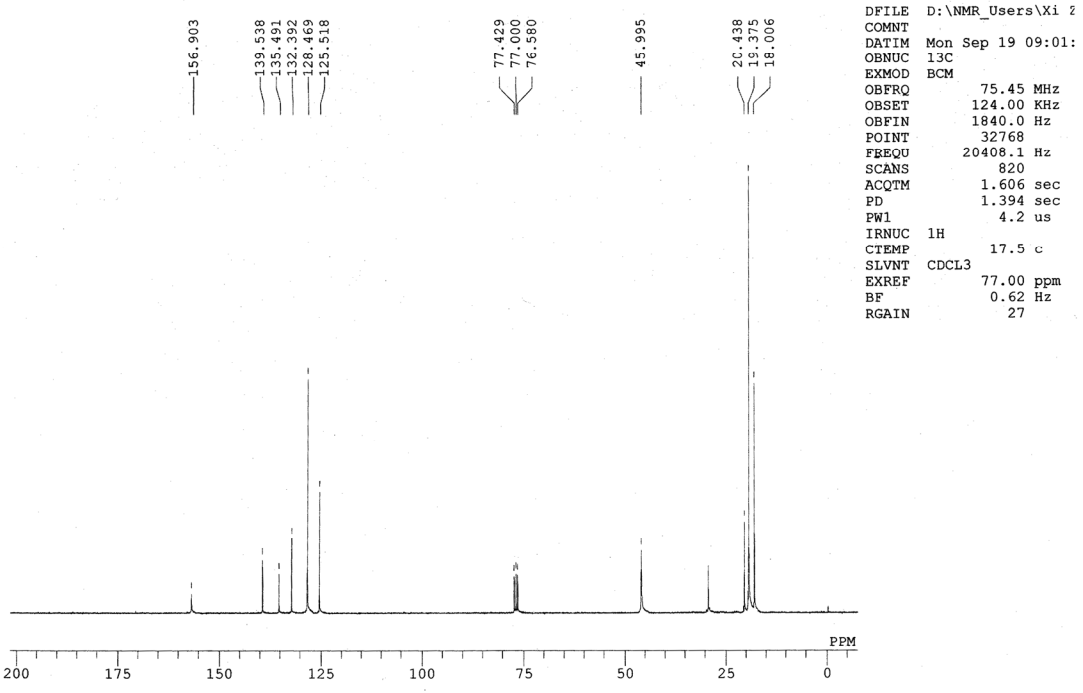


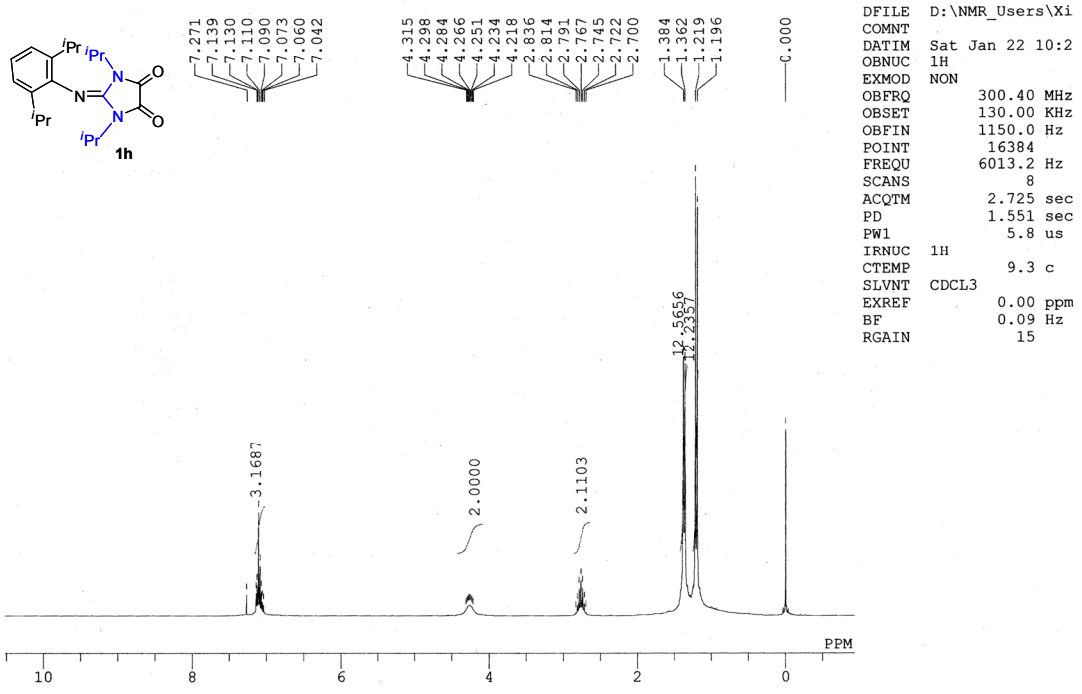


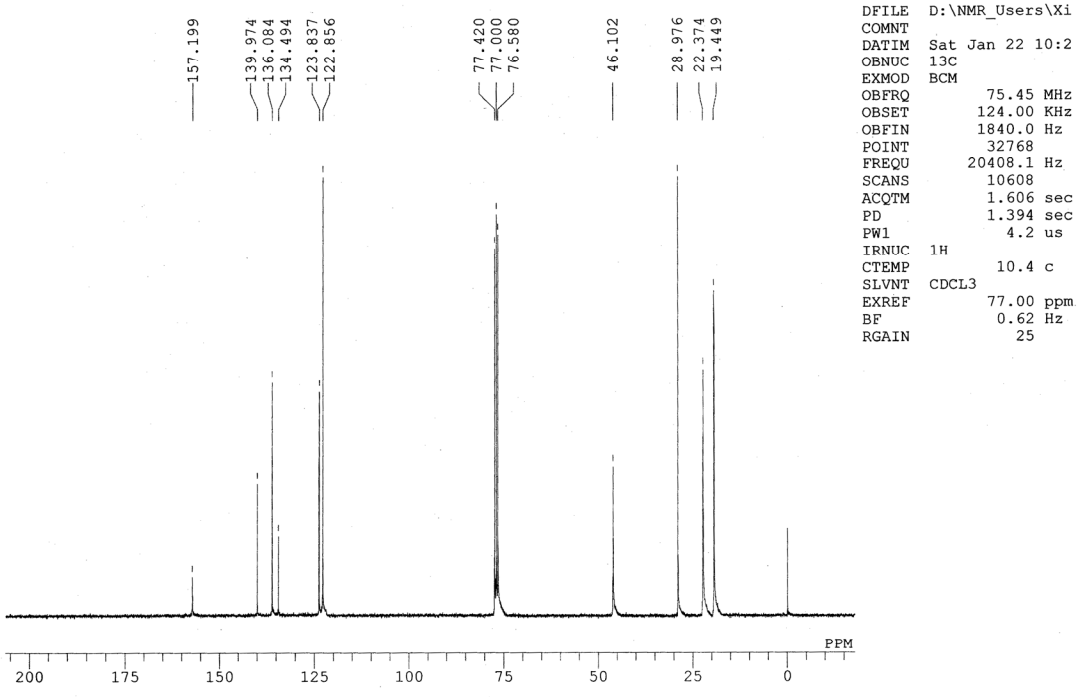


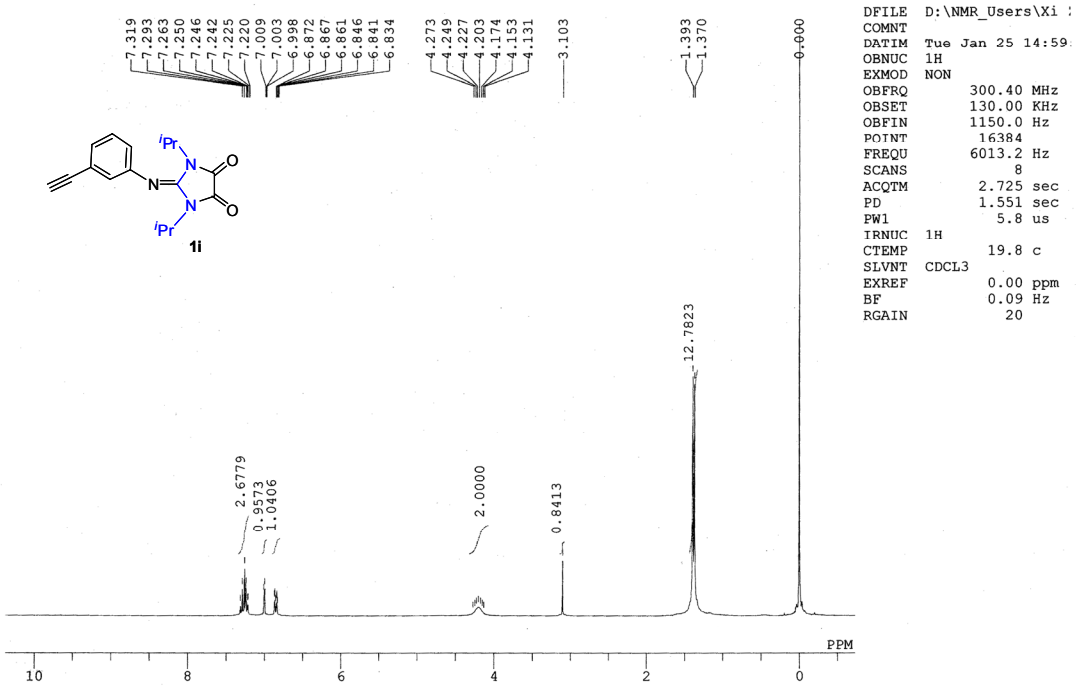




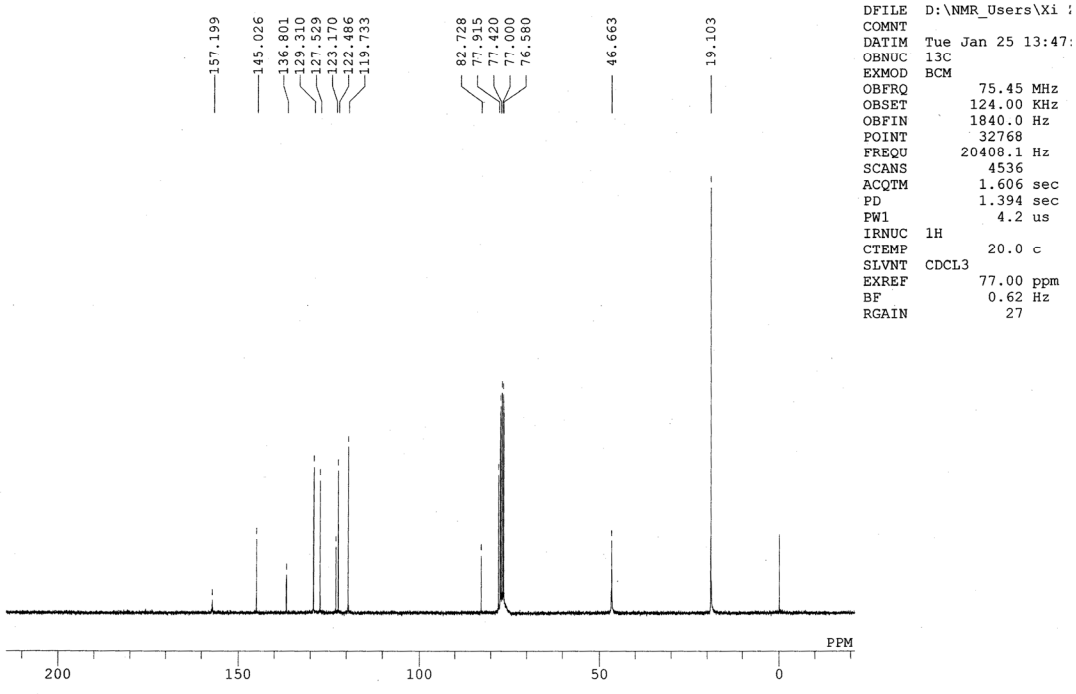


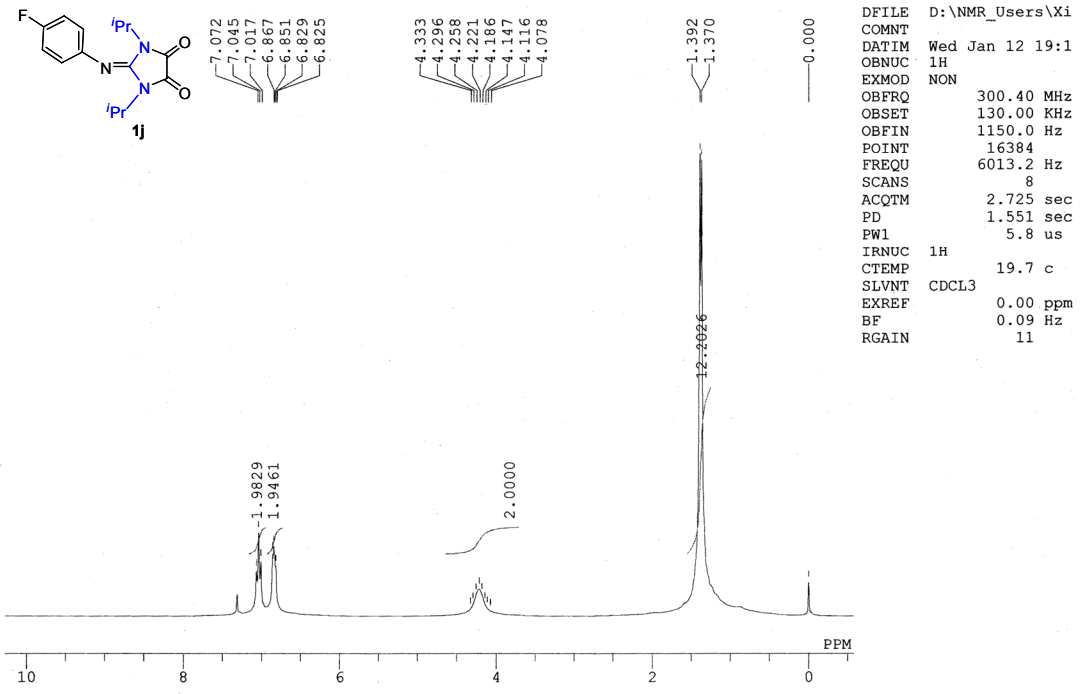

7.271
7.139
7.130
7.110
7.090
7.073
7.060
7.042
4.315
4.298
4.284
4.266
4.251
4.234
4.218
2.836
2.814
2.791
2.767
2.745
2.722
2.700
1.384
1.362
1.219
1.196
0.000
12.5656
12.2357
3.1687
2.0000
2.1103
PPM
10
8
6
4
2
0
1h
DFILE D:\NMR_Users\Xi
COMNT
DATIM Sat Jan 22 10:2
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 9.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 15

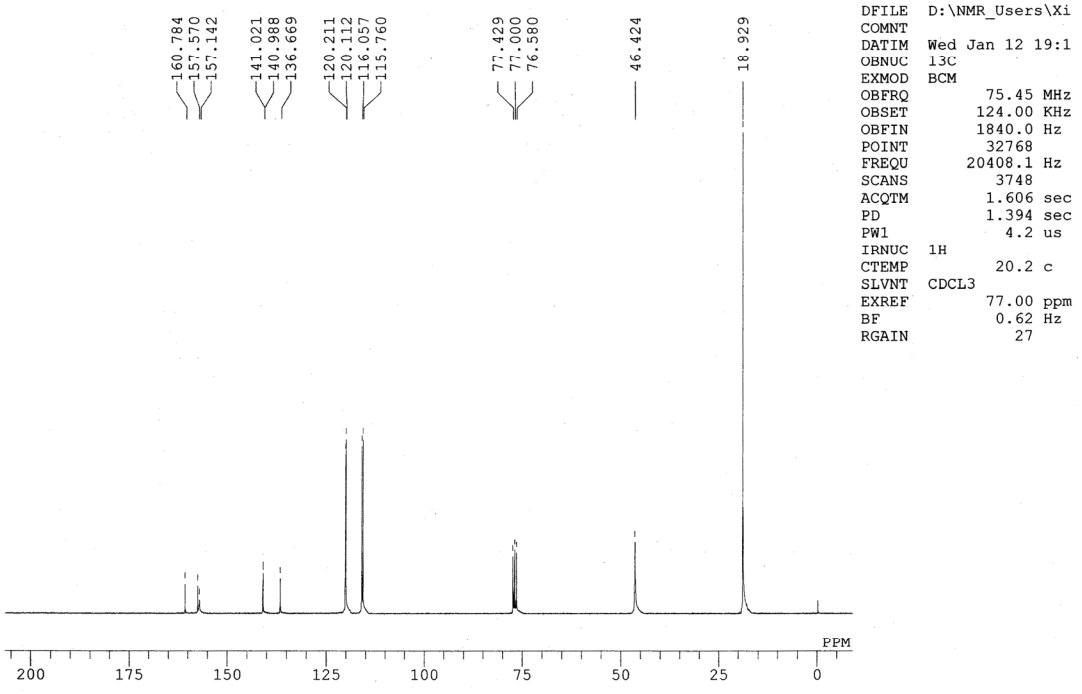

157.199
139.974
136.084
134.494
123.837
122.856
77.420
77.000
76.580
46.102
28.976
22.374
19.449
PPM
200
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Sat Jan 22 10:2
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 10608
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 10.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 25

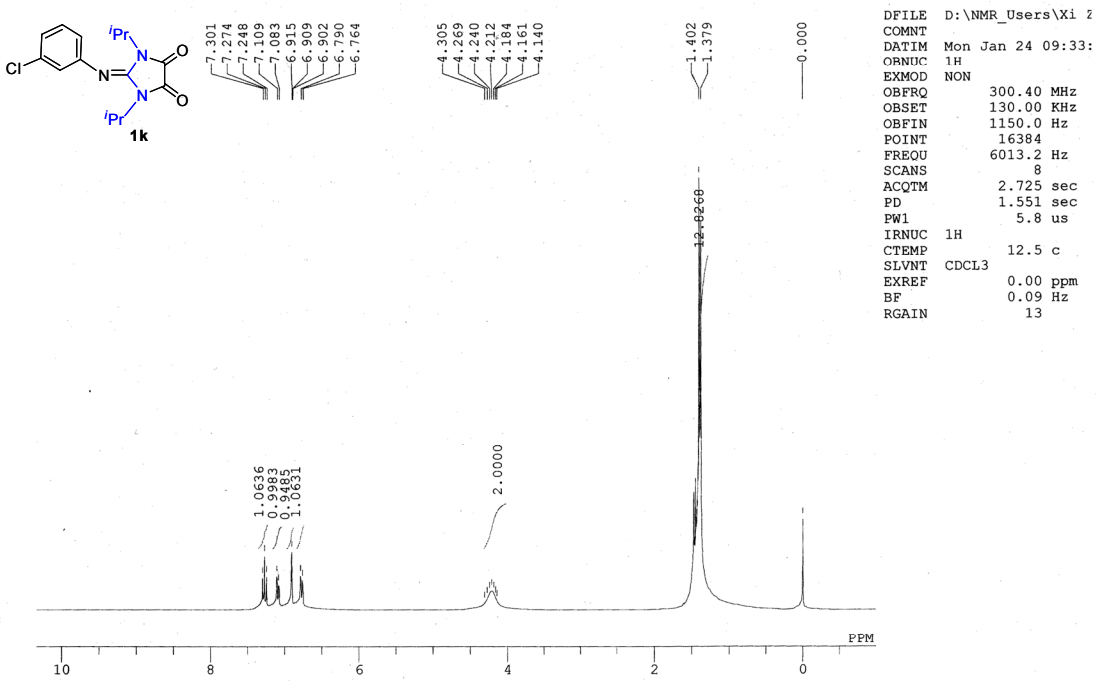


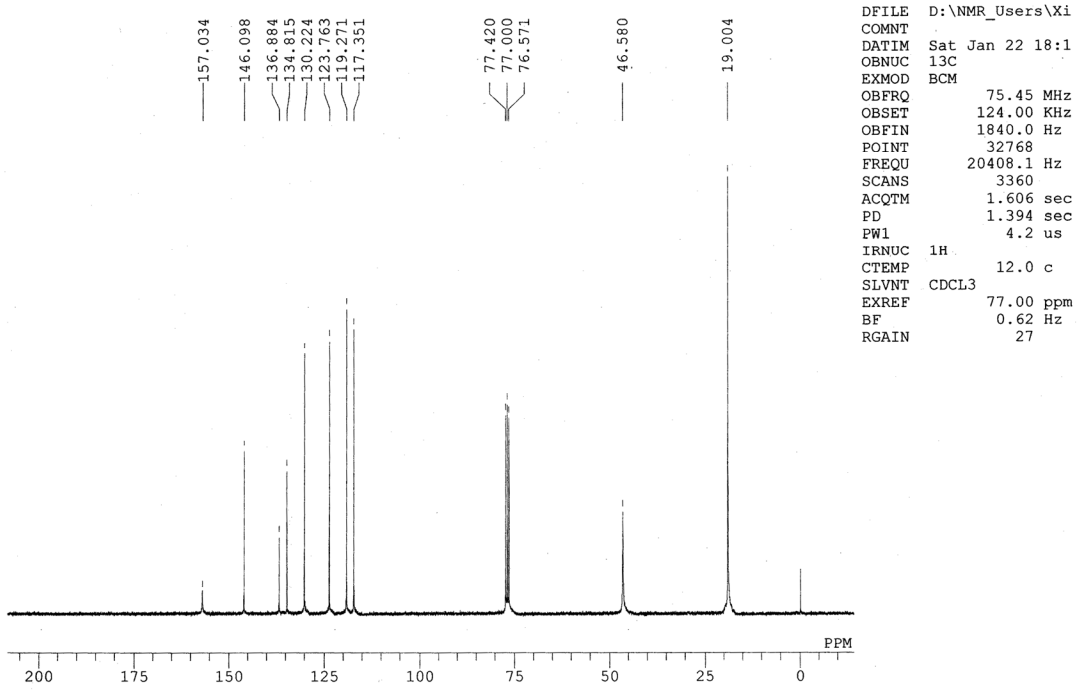
1i

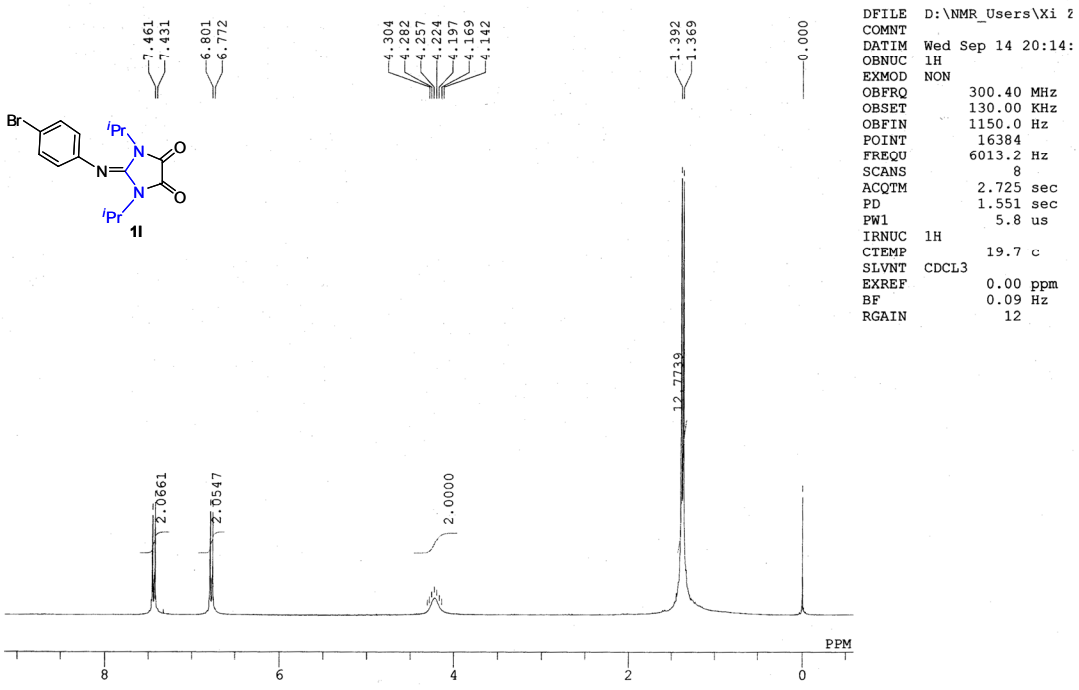


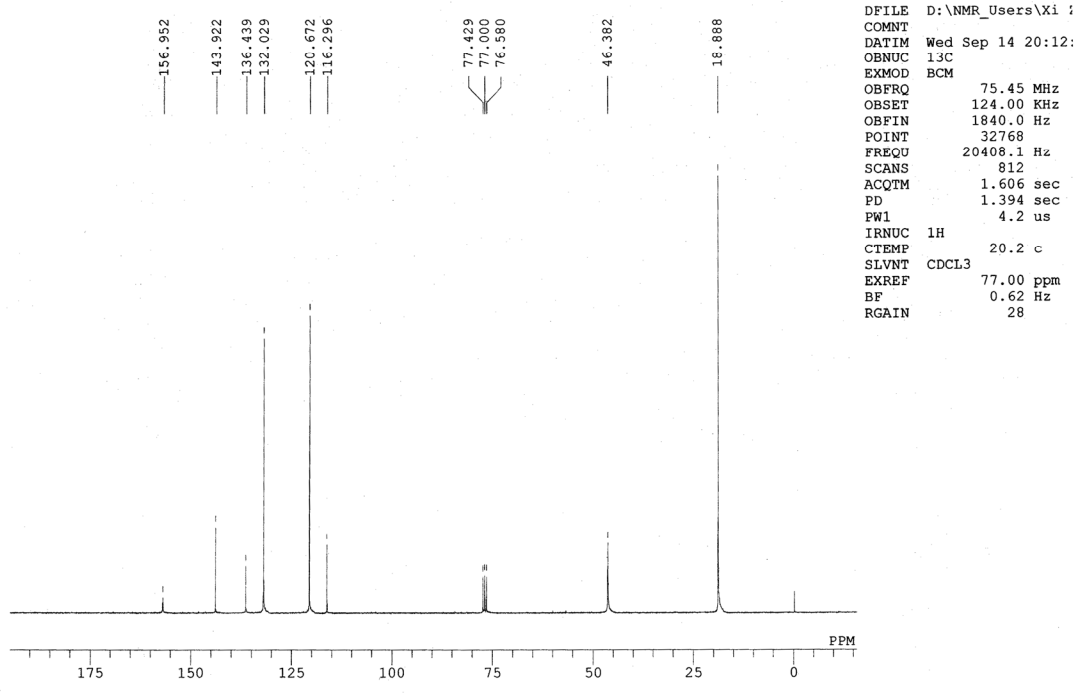

F
iPr
N
O
O
N
iPr
1j
7.072
7.045
7.017
6.867
6.851
6.829
6.825
4.333
4.296
4.258
4.221
4.186
4.147
4.116
4.078
1.392
1.370
0.000
1.9829
1.9461
2.0000
12.2026
PPM
10
8
6
4
2
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Wed Jan 12 19:1
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 11

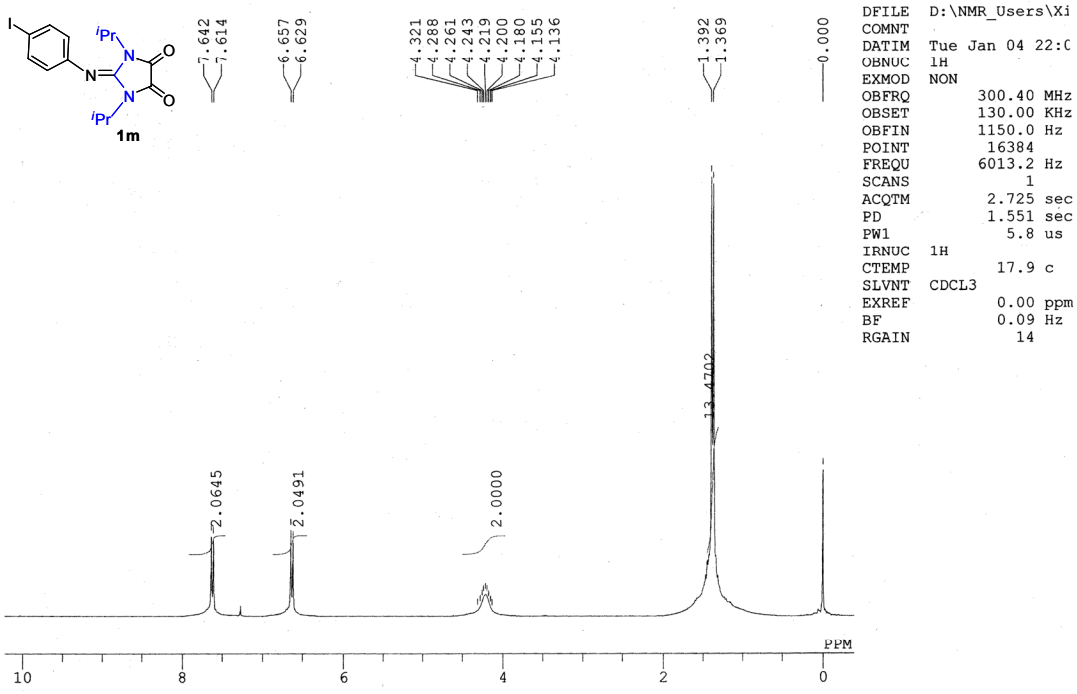

160.784
157.570
157.142
141.021
140.988
136.669
120.211
120.112
116.057
115.760
77.429
77.000
76.580
46.424
18.929
PPM
200
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Wed Jan 12 19:1
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 3748
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 27

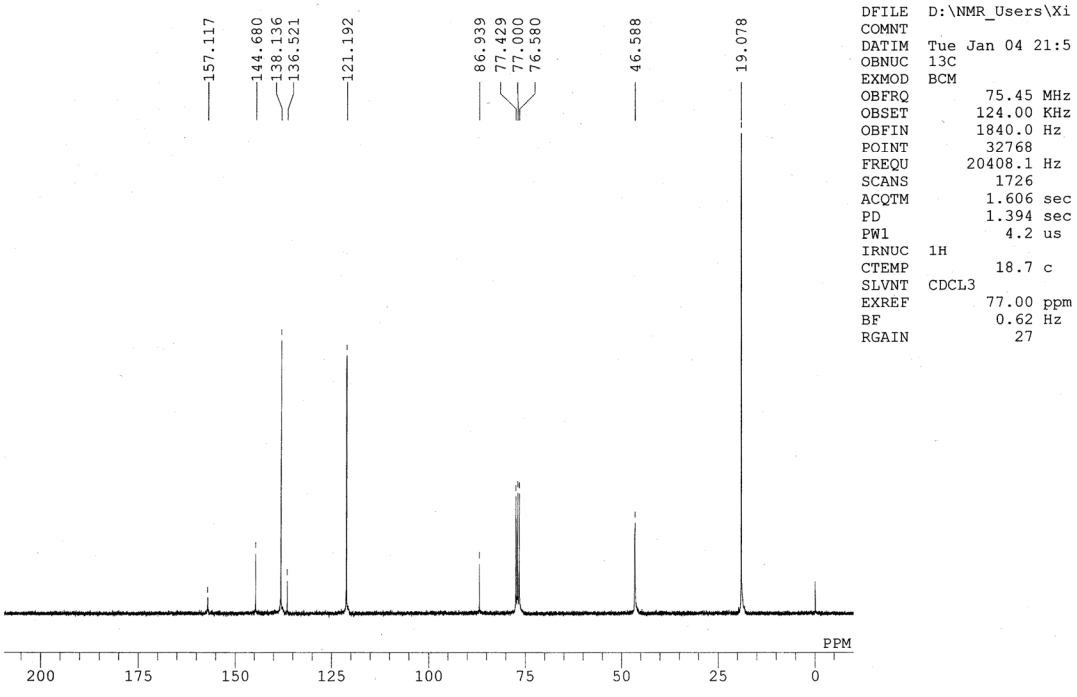

1k
7.301
7.274
7.248
7.109
7.083
6.915
6.909
6.902
6.790
6.764
4.305
4.269
4.240
4.212
4.184
4.161
4.140
1.402
1.379
0.000
12.0260
2.0000
1.0636
0.9983
0.9485
1.0631
PPM
10
8
6
4
2
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Mon Jan 24 09:33:
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 12.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 13

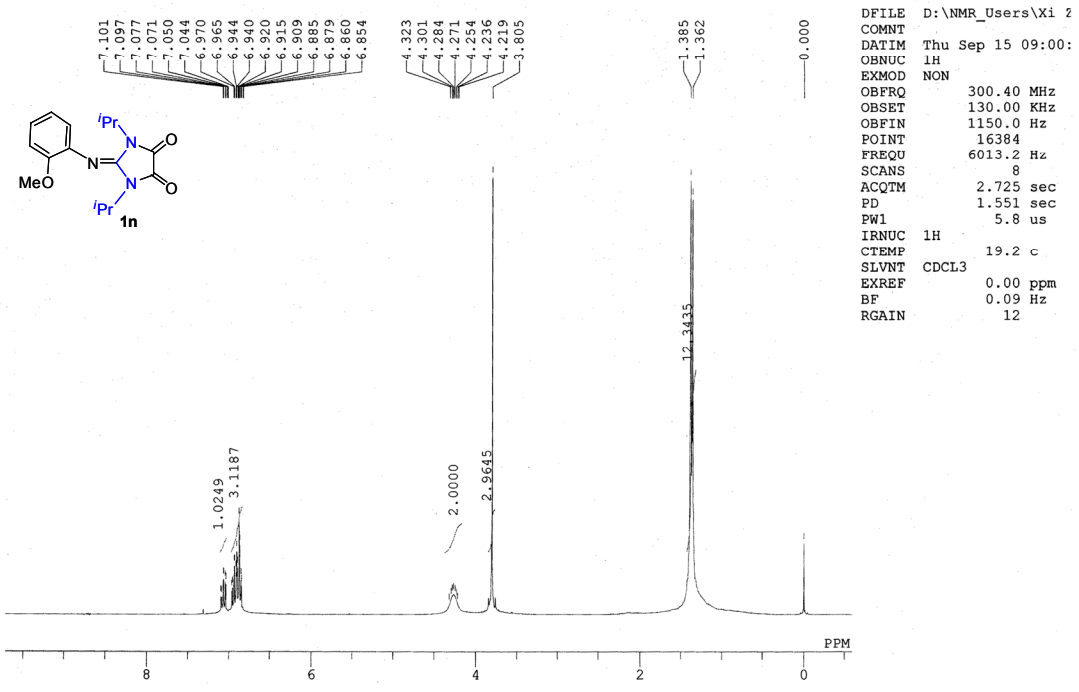

157.034
146.098
136.884
134.815
130.224
123.763
119.271
117.351
77.420
77.000
76.571
46.580
19.004
PPM
200
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Sat Jan 22 18:1
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 3360
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 12.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 27

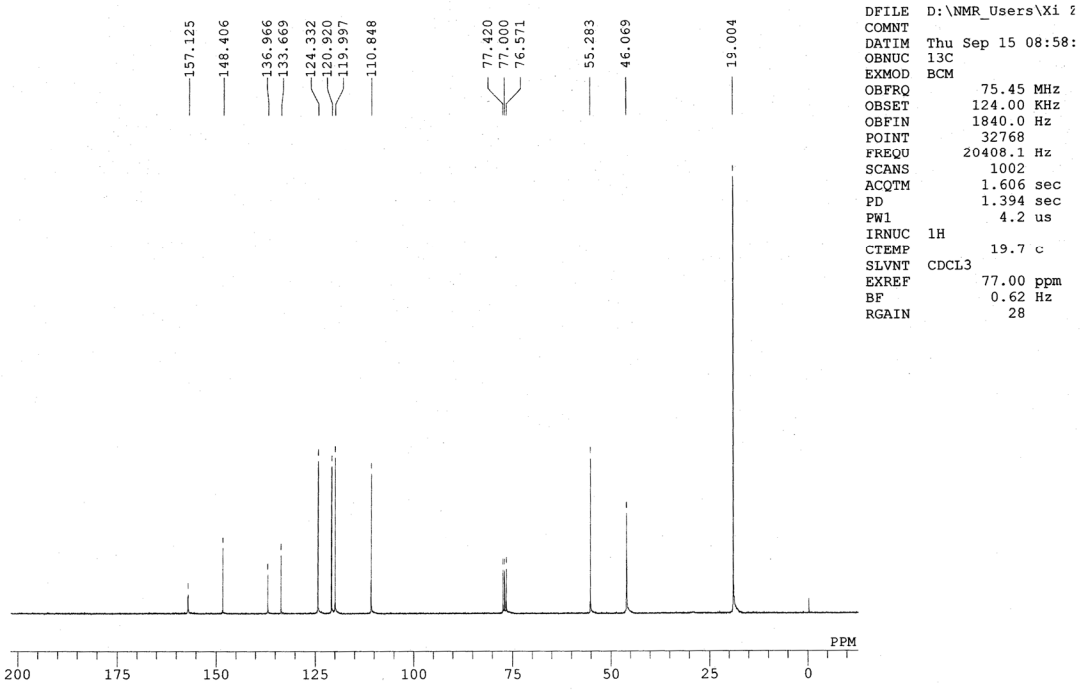

7.461
7.431
6.801
6.772
4.304
4.282
4.257
4.224
4.197
4.169
4.142
1.392
1.369
0.000
Br
iPr
N
O
N
O
iPr
1l
2.0661
2.0547
2.0000
12.7739
PPM
8
6
4
2
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Wed Sep 14 20:14:
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 12

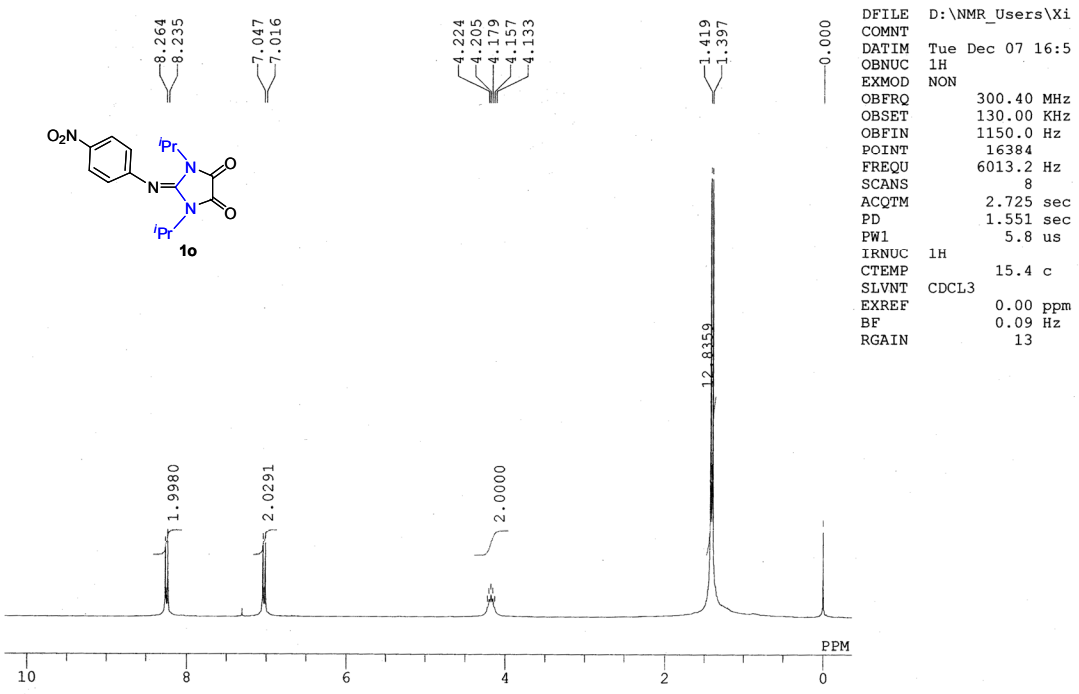

156.952
143.922
136.439
132.029
120.672
116.296
77.429
77.000
76.580
46.382
18.888
PPM
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Wed Sep 14 20:12:
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 812
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 28


1m
7.642
7.614
6.657
6.629
4.321
4.288
4.261
4.243
4.219
4.200
4.180
4.155
4.136
1.392
1.369
0.000
13.4702
2.0645
2.0491
2.0000
PPM
10
8
6
4
2
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Tue Jan 04 22:(
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 1
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 17.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 14

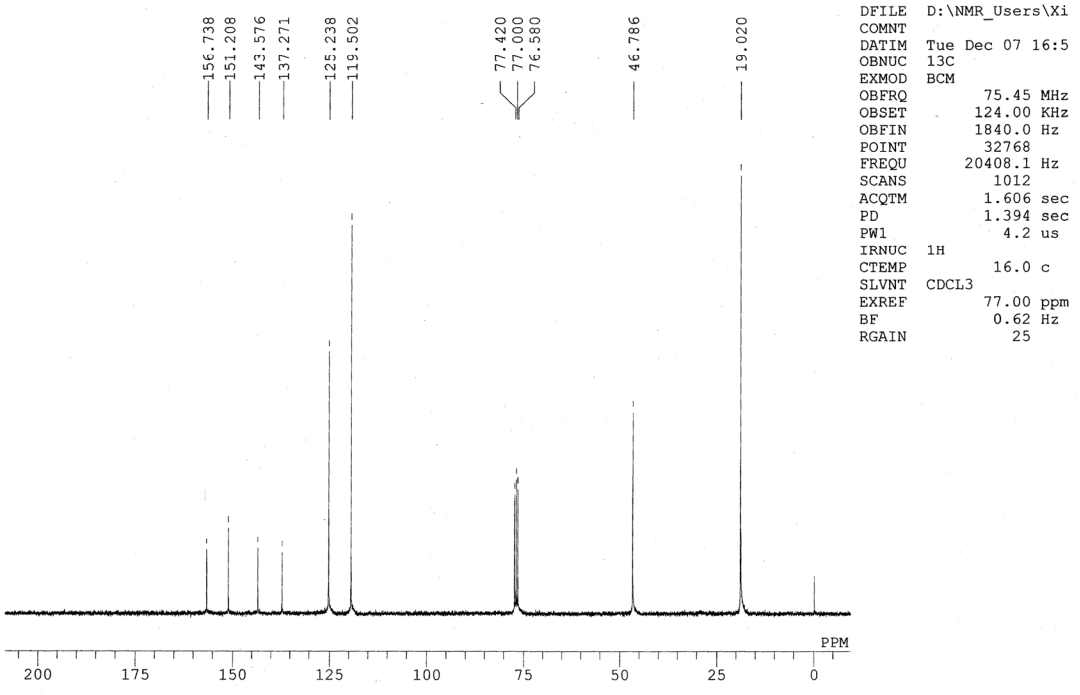

157.117
144.680
138.136
136.521
121.192
86.939
77.429
77.000
76.580
46.588
19.078
PPM
200
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Tue Jan 04 21:5
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 1726
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 18.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 27



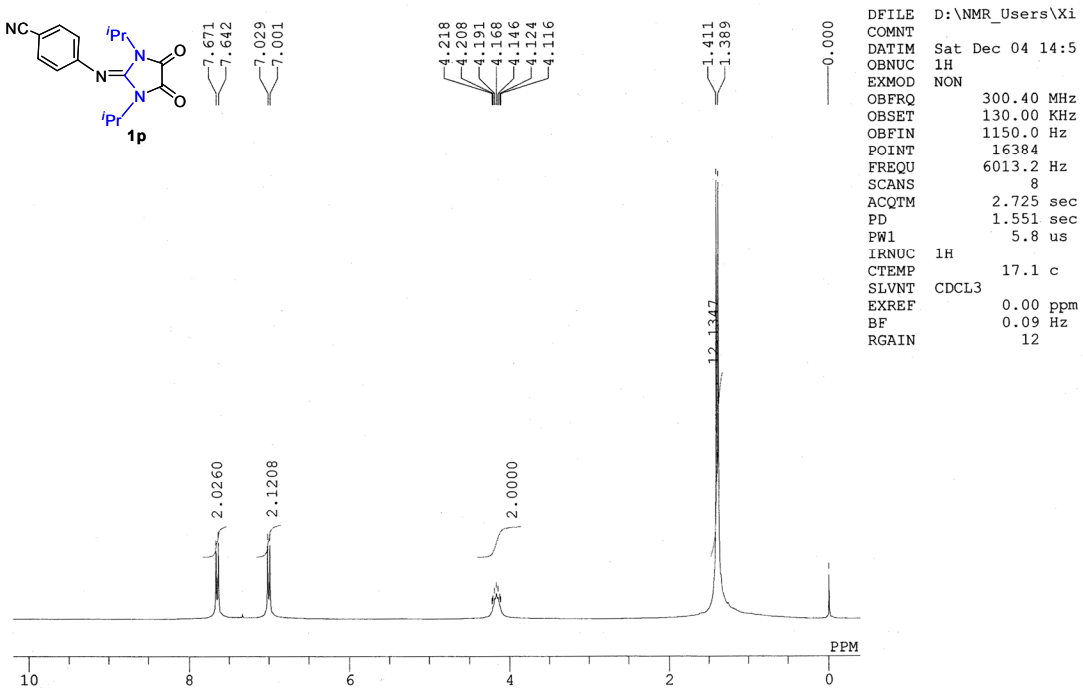


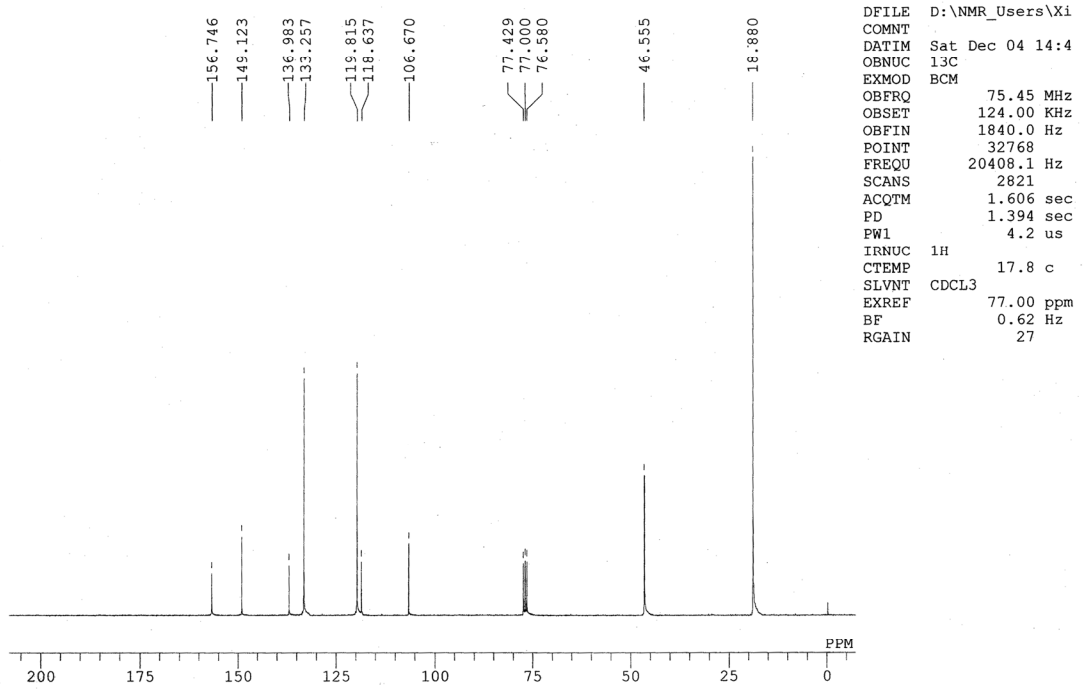


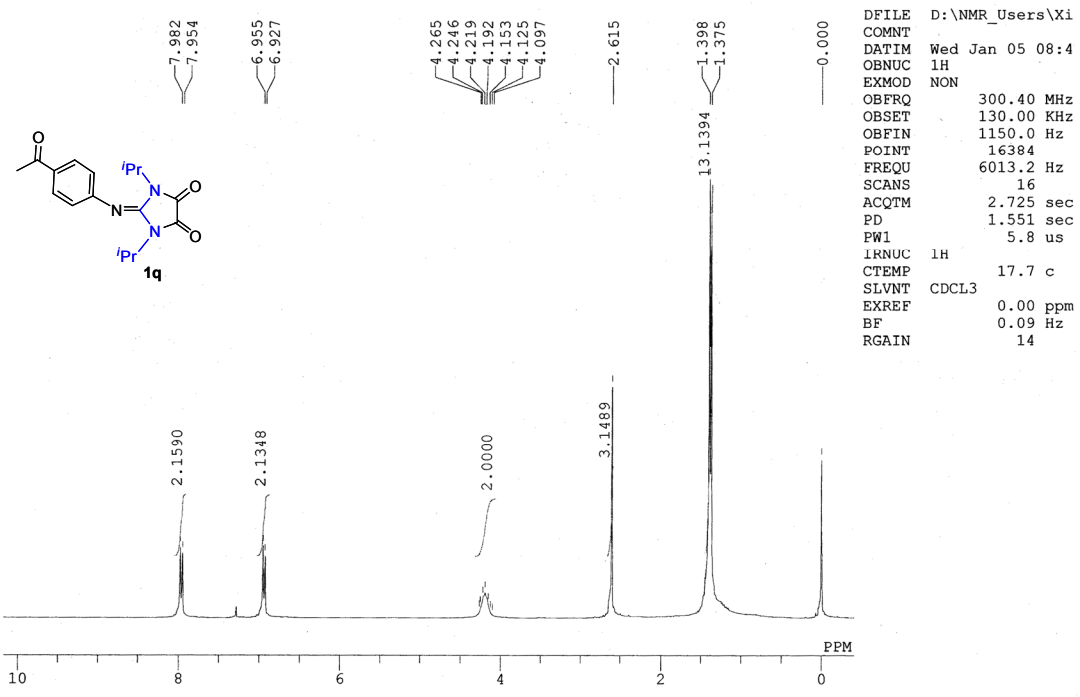

```
DFILE   D:\NMR_Users\Xi
COMNT
DATIM   Tue Dec 07 16:5
OBNUC   1H
EXMOD   NON
OBFRQ         300.40 MHz
OBSET         130.00 KHz
OBFIN         1150.0 Hz
POINT          16384
FREQU         6013.2 Hz
SCANS             8
ACQTM          2.725 sec
PD             1.551 sec
PW1              5.8 us
IRNUC   1H
CTEMP           15.4 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.09 Hz
RGAIN             13
```

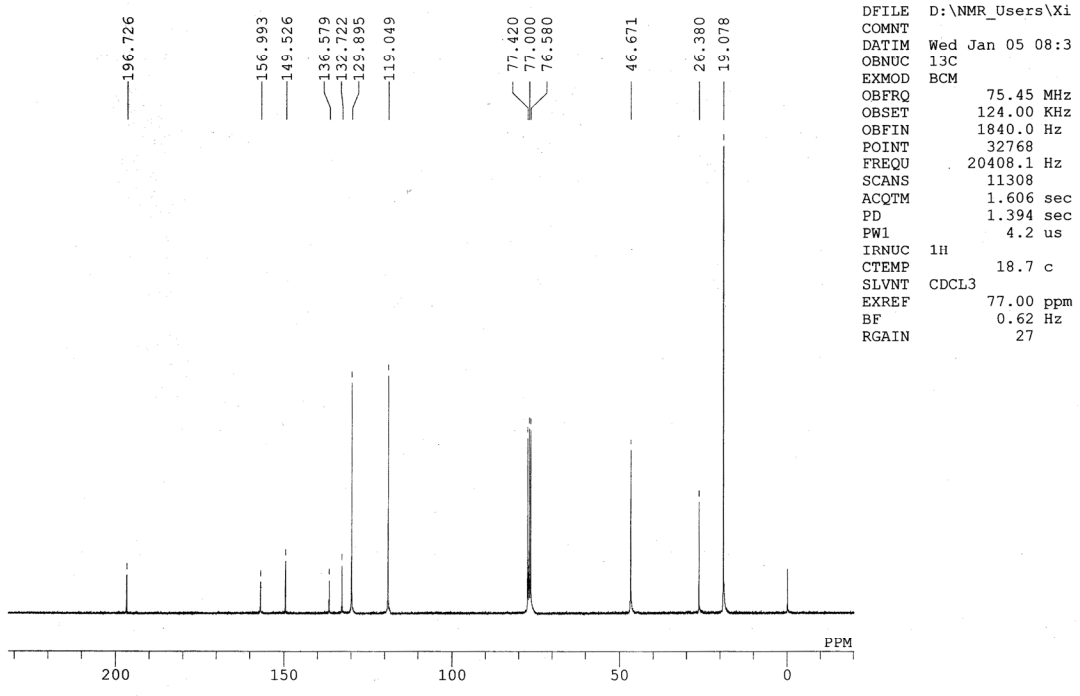


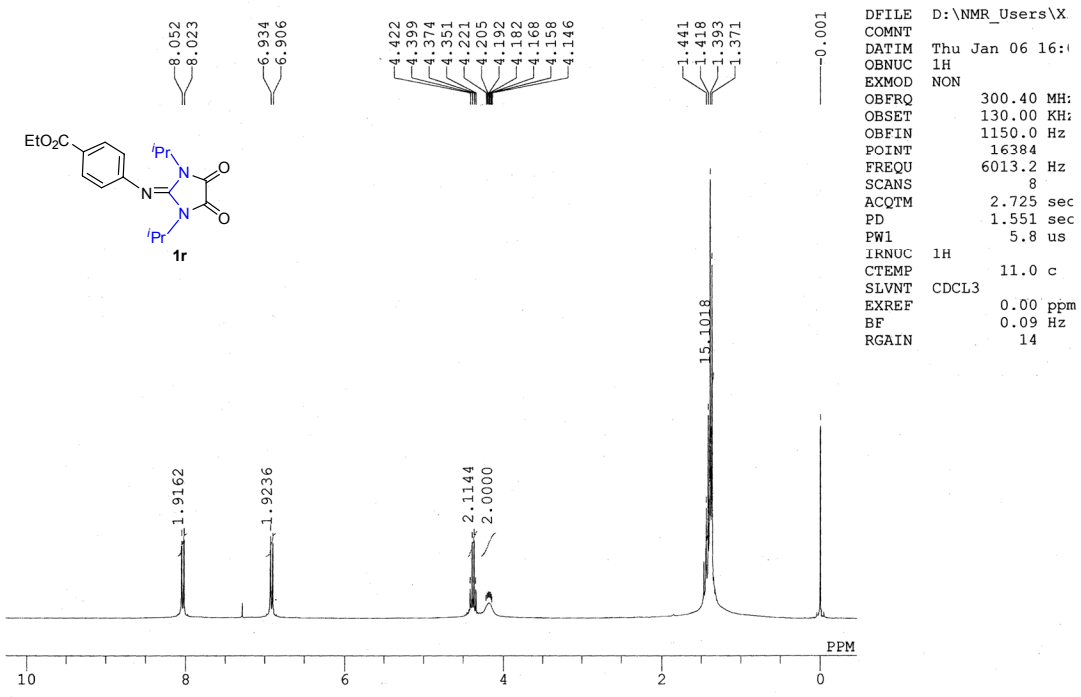

```
DFILE   D:\NMR_Users\Xi
COMNT
DATIM   Tue Dec 07 16:5
OBNUC   13C
EXMOD   BCM
OBFRQ          75.45 MHz
OBSET         124.00 KHz
OBFIN         1840.0 Hz
POINT          32768
FREQU        20408.1 Hz
SCANS           1012
ACQTM          1.606 sec
PD             1.394 sec
PW1              4.2 us
IRNUC   1H
CTEMP           16.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.62 Hz
RGAIN             25
```

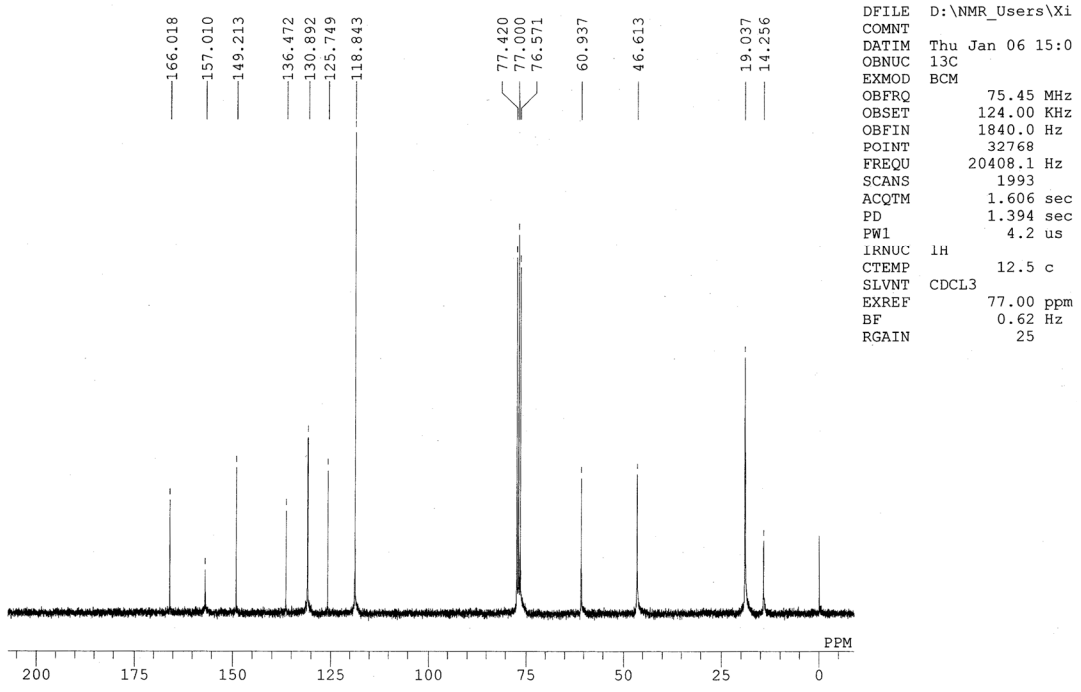

NC
iPr
N
O
N
O
iPr
1p
7.671
7.642
7.029
7.001
4.218
4.208
4.191
4.168
4.146
4.124
4.116
1.411
1.389
0.000
12.1347
2.0260
2.1208
2.0000
PPM
10
8
6
4
2
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Sat Dec 04 14:5
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 17.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 12

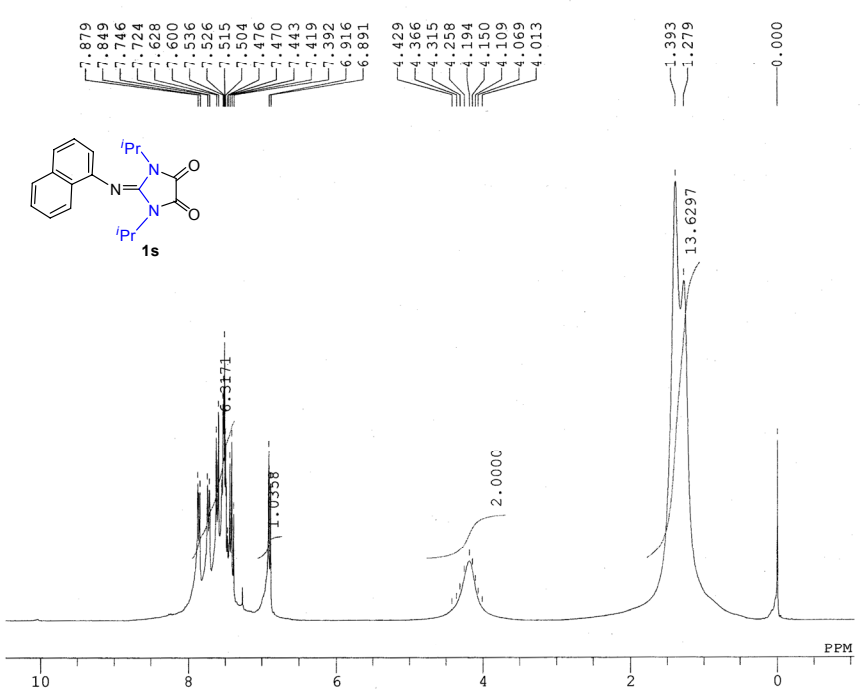

156.746
149.123
136.983
133.257
119.815
118.637
106.670
77.429
77.000
76.580
46.555
18.880
PPM
200
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Sat Dec 04 14:4
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 2821
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 17.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 27


7.982
7.954
6.955
6.927
4.265
4.246
4.219
4.192
4.153
4.125
4.097
2.615
1.398
1.375
0.000
13.1394
3.1489
2.1590
2.1348
2.0000
1q
PPM
10
8
6
4
2
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Wed Jan 05 08:4
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 16
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 17.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 14

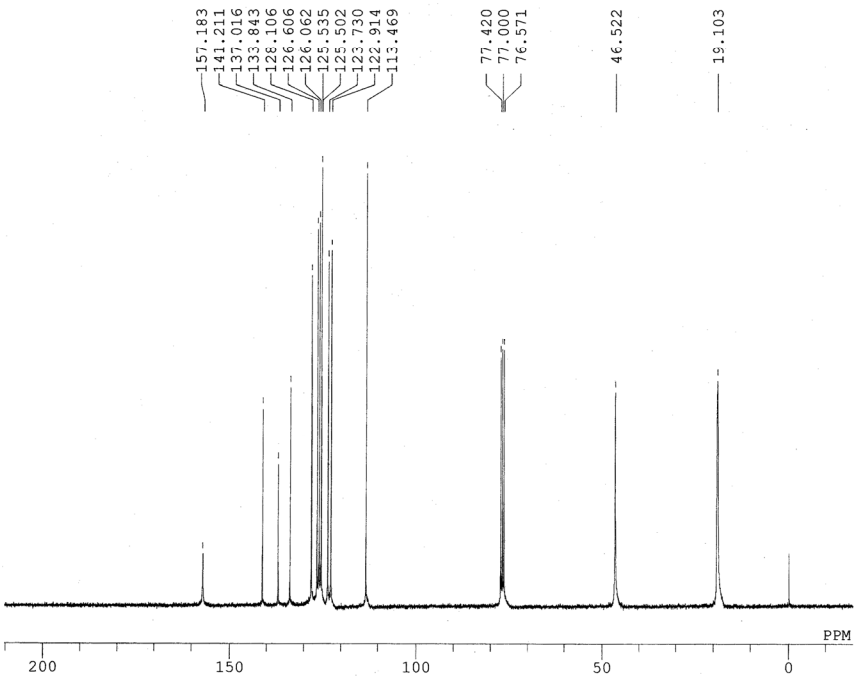

196.726
156.993
149.526
136.579
132.722
129.895
119.049
77.420
77.000
76.580
46.671
26.380
19.078
PPM
200
150
100
50
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Wed Jan 05 08:3
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 11308
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 18.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 27



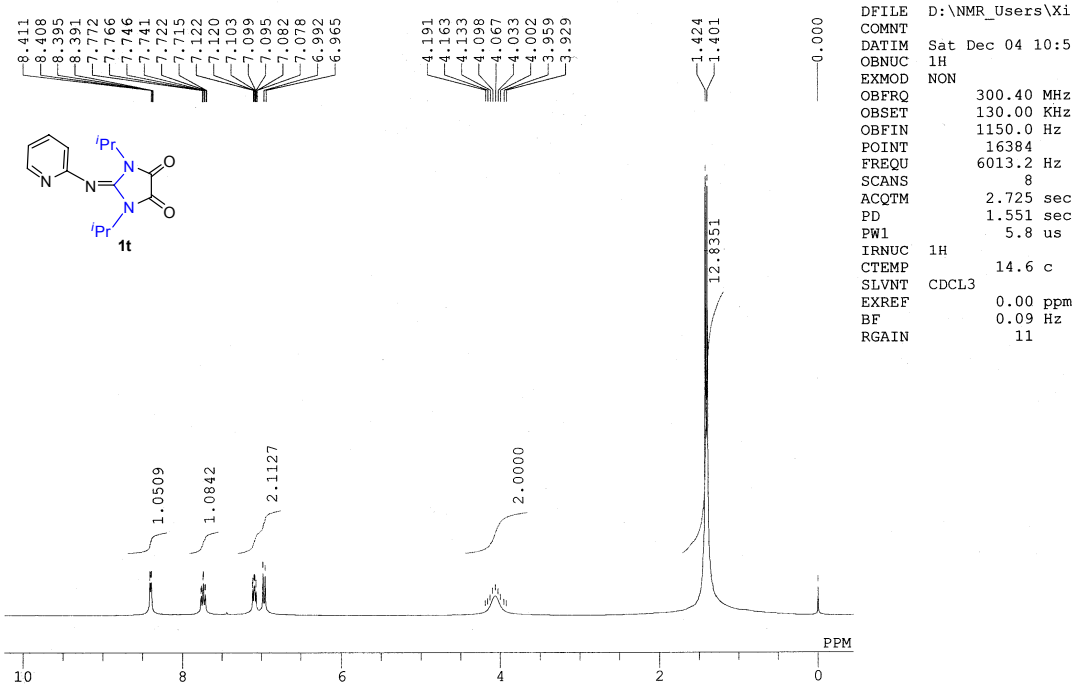


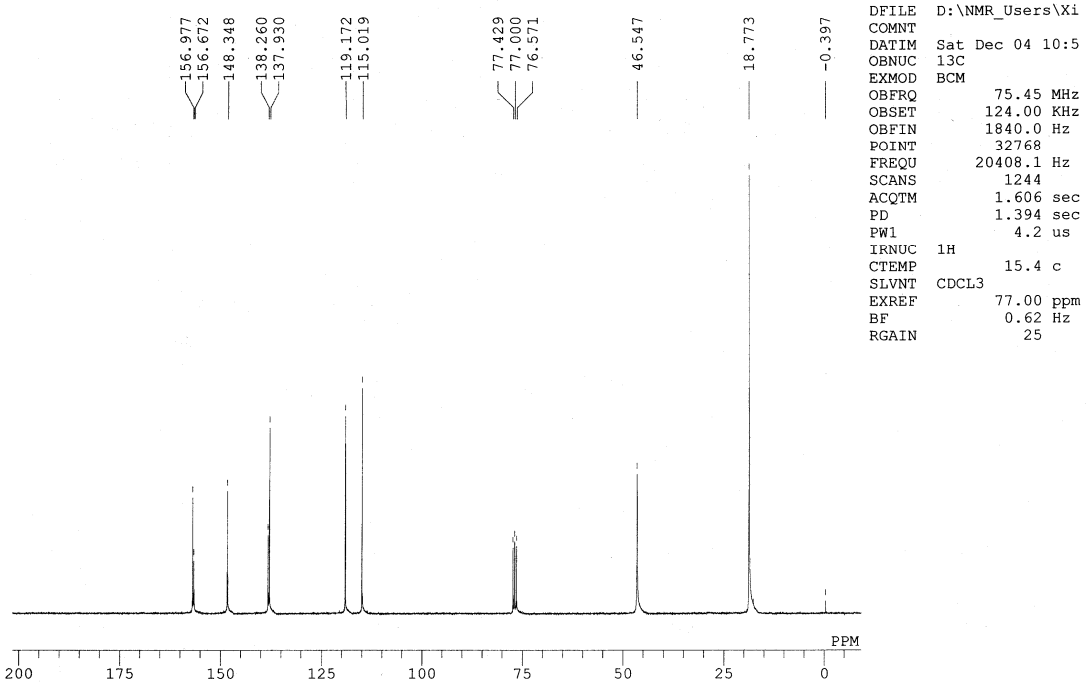


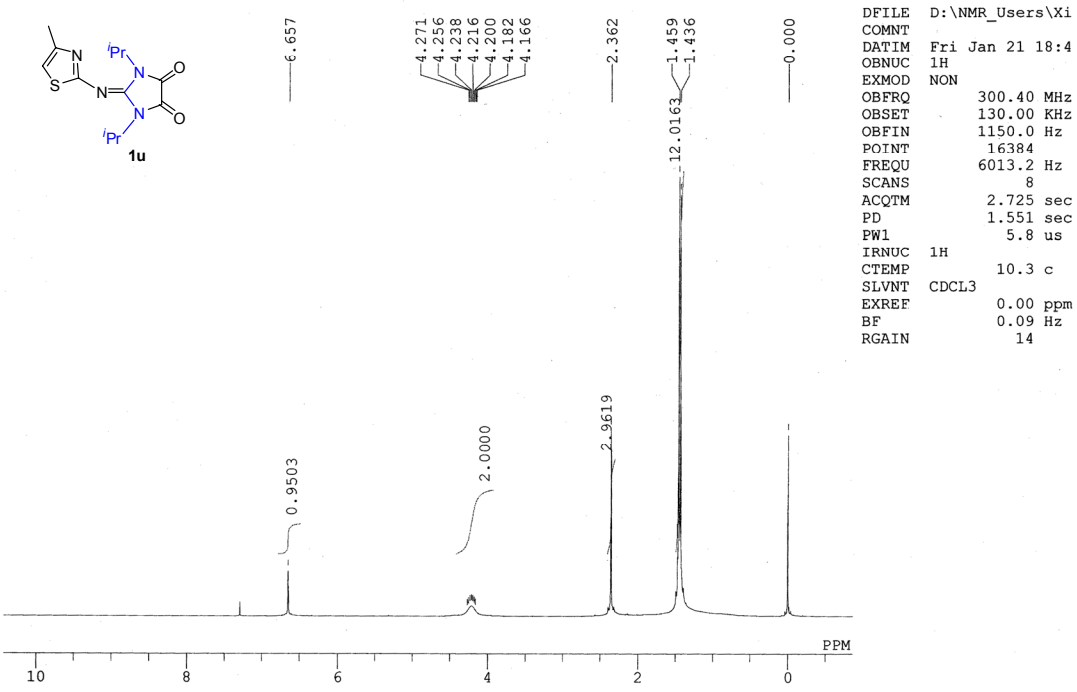

```
DFILE   D:\NMR_Users\Xi
COMNT
DATIM   Mon Jan 24 09:2
OBNUC   1H
EXMOD   NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN        1150.0 Hz
POINT         16384
FREQU        6013.2 Hz
SCANS            8
ACQTM         2.725 sec
PD            1.551 sec
PW1             5.8 us
IRNUC   1H
CTEMP          11.7 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.09 Hz
RGAIN            12
```

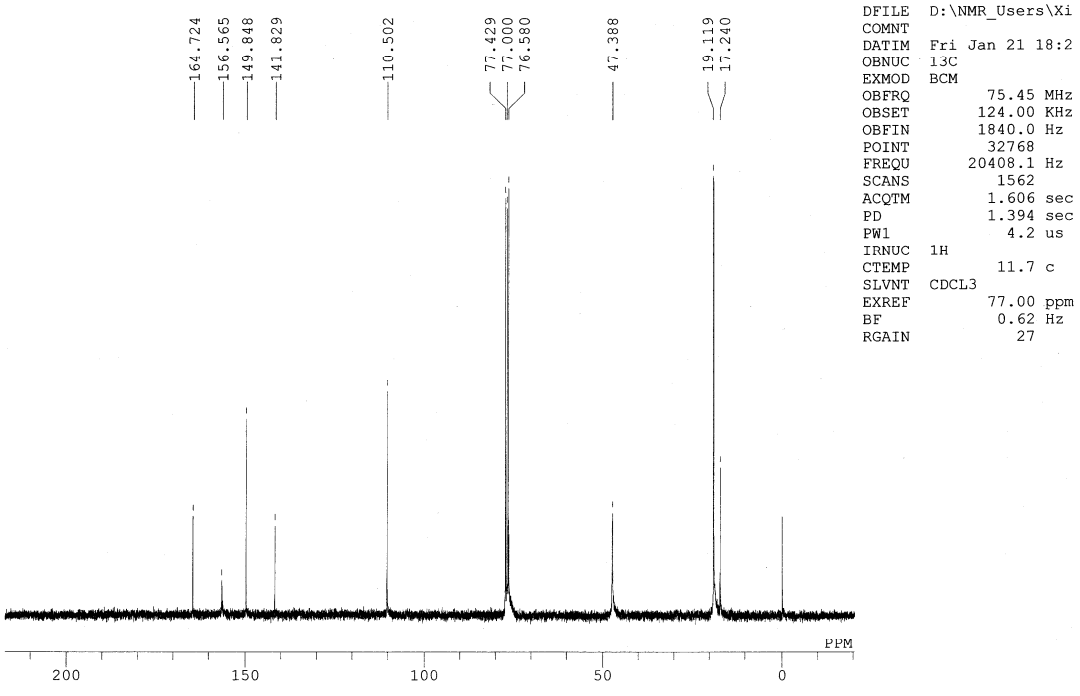


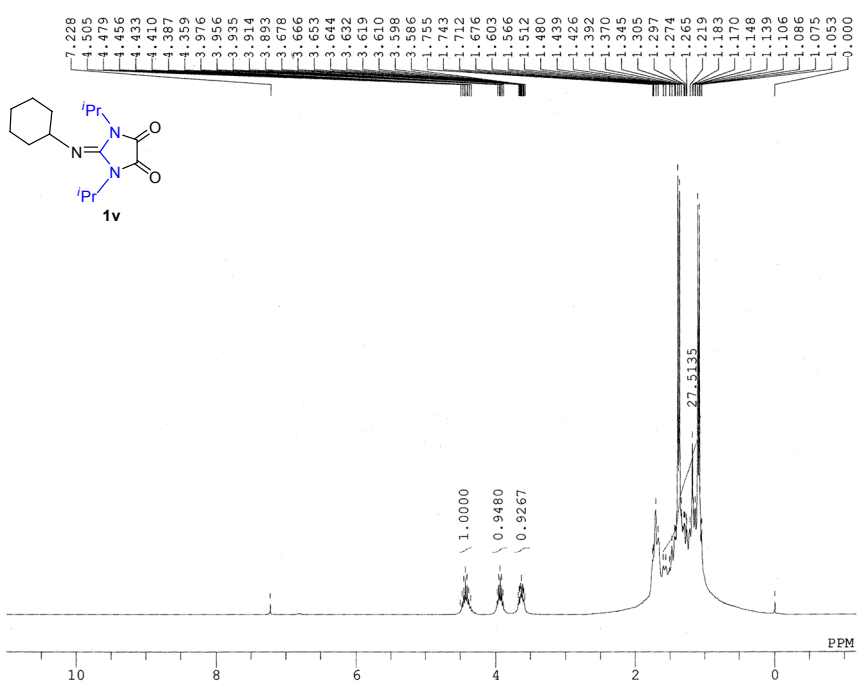

```
DFILE   D:\NMR_Users\Xi
COMNT
DATIM   Wed Jan 19 17:5
OBNUC   13C
EXMOD   BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN        1840.0 Hz
POINT         32768
FREQU       20408.1 Hz
SCANS          5458
ACQTM         1.606 sec
PD            1.394 sec
PW1             4.2 us
IRNUC   1H
CTEMP          10.9 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.62 Hz
RGAIN            27
```


8.411
8.408
8.395
8.391
7.772
7.766
7.746
7.741
7.722
7.715
7.122
7.120
7.103
7.099
7.095
7.082
7.078
6.992
6.965
4.191
4.163
4.133
4.098
4.067
4.033
4.002
3.959
3.929
1.424
1.401
0.000
12.8351
1.0509
1.0842
2.1127
2.0000
PPM
10
8
6
4
2
0
1t
DFILE D:\NMR_Users\Xi
COMNT
DATIM Sat Dec 04 10:5
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 14.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 11

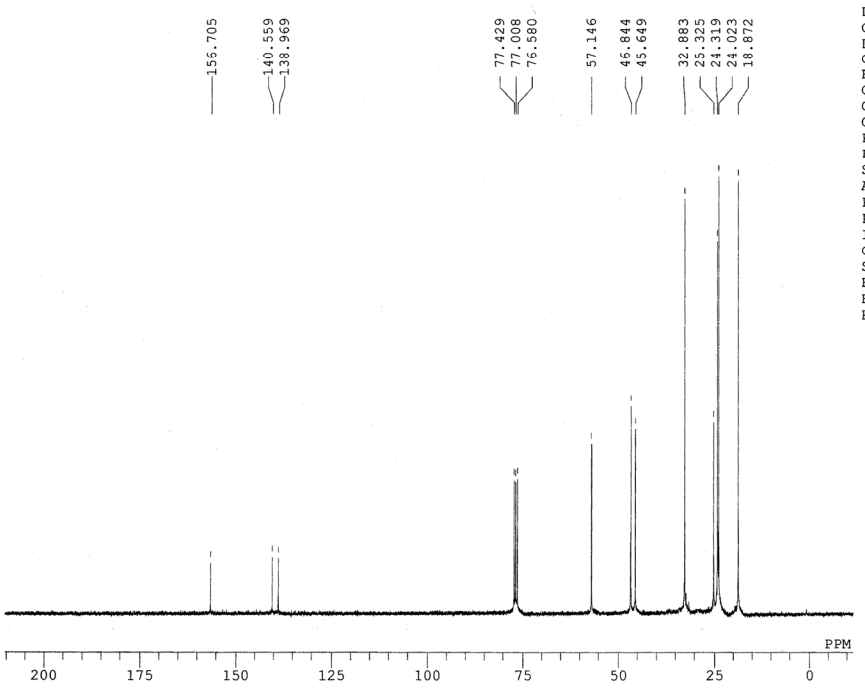

156.977
156.672
148.348
138.260
137.930
119.172
115.019
77.429
77.000
76.571
46.547
18.773
-0.397
PPM
200
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Sat Dec 04 10:5
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 1244
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 15.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 25



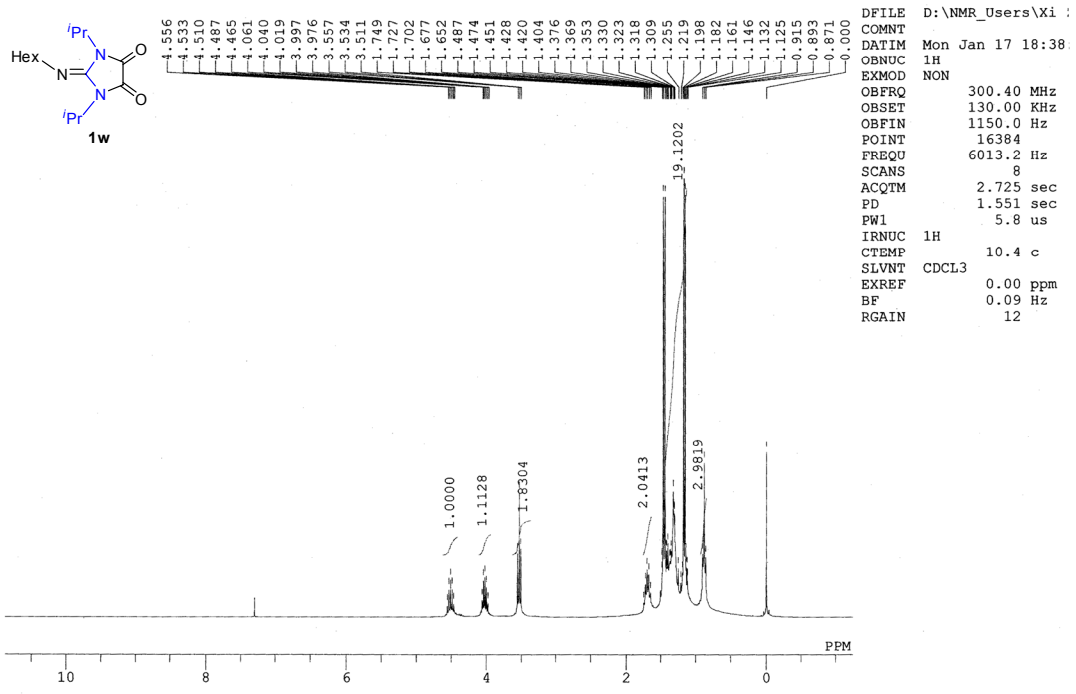


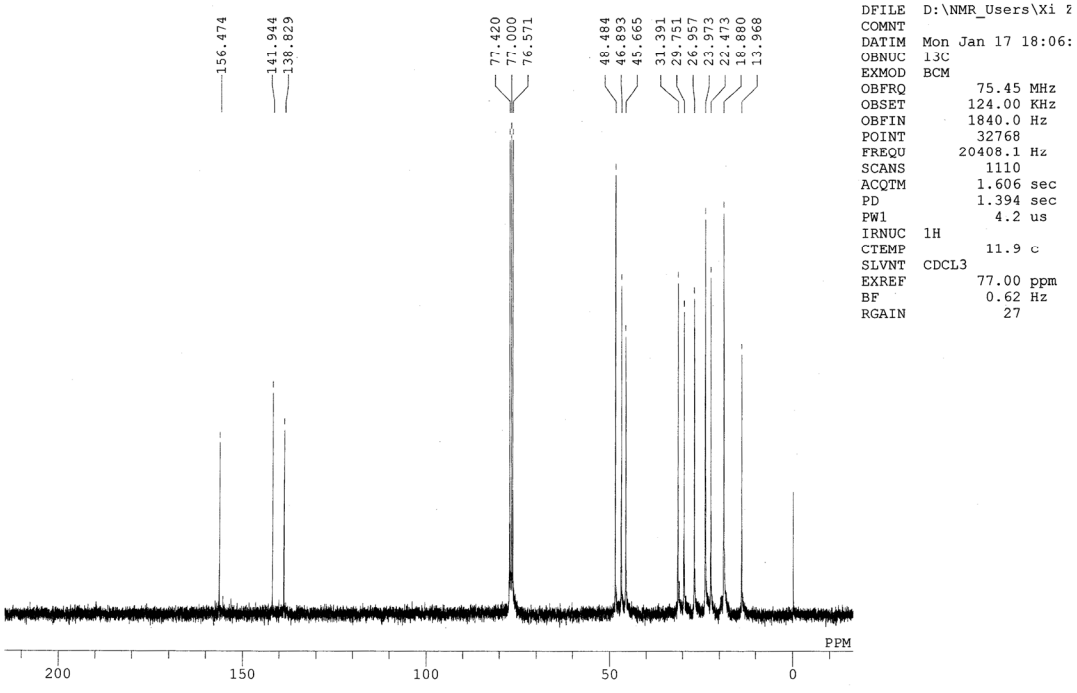


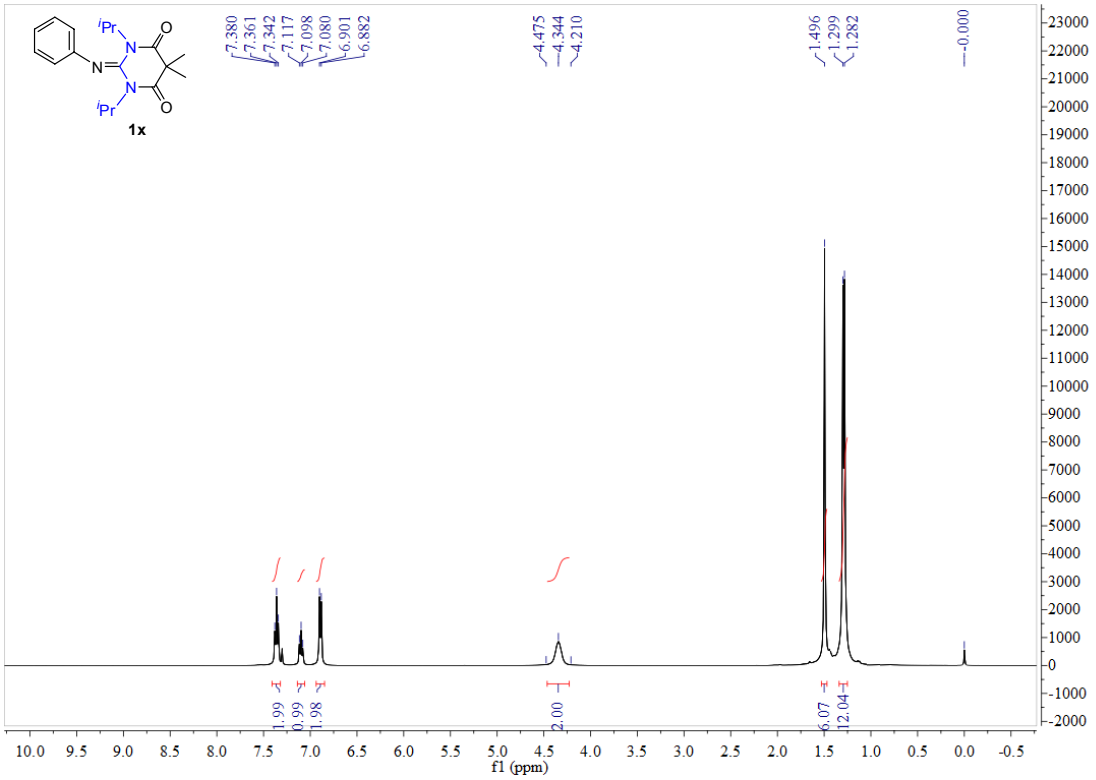

```
DFILE   D:\NMR_Users\Xi
COMNT
DATIM   Thu Nov 18 22:33
OBNUC   1H
EXMOD   NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN       1150.0 Hz
POINT        16384
FREQU       6013.2 Hz
SCANS            8
ACQTM        2.725 sec
PD           1.551 sec
PW1            5.8 us
IRNUC   1H
CTEMP        21.0 c
SLVNT   CDCL3
EXREF        0.00 ppm
BF           0.09 Hz
RGAIN          11
```

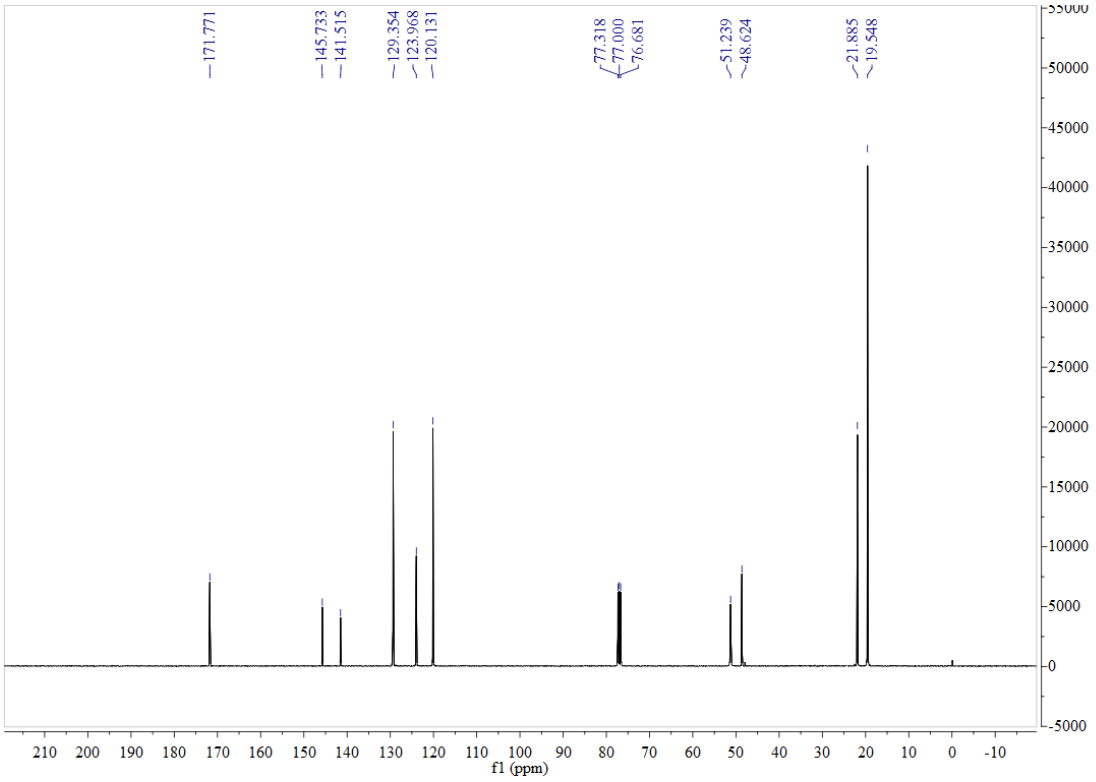


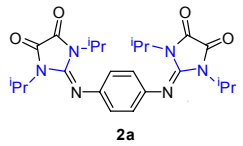

```
DFILE   D:\NMR_Users\Xi 2
COMNT
DATIM   Thu Nov 18 22:29:
OBNUC   13C
EXMOD   BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS         1764
ACQTM        1.606 sec
PD           1.394 sec
PW1            4.2 us
IRNUC   1H
CTEMP        21.4 c
SLVNT   CDCL3
EXREF        77.00 ppm
BF           0.62 Hz
RGAIN          26
```


Hex
iPr
iPr
1w
4.556 4.533 4.510 4.487 4.465 4.061 4.040 4.019 3.997 3.976 3.557 3.534 3.511 1.749 1.727 1.702 1.677 1.652 1.487 1.474 1.451 1.428 1.420 1.404 1.376 1.369 1.353 1.330 1.323 1.318 1.309 1.255 1.219 1.198 1.182 1.161 1.146 1.132 1.125 0.915 0.893 0.871 0.000
19.1202
1.0000
1.1128
1.8304
2.0413
2.9819
PPM
10
8
6
4
2
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Mon Jan 17 18:38
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 10.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 12


156.474
141.944
138.829
77.420
77.000
76.571
48.484
46.893
45.665
31.391
29.751
26.957
23.973
22.473
18.880
13.968
PPM
200
150
100
50
0
DFILE D:\NMR_Users\Xi
COMNT
DATIM Mon Jan 17 18:06:
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 1110
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 11.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 27

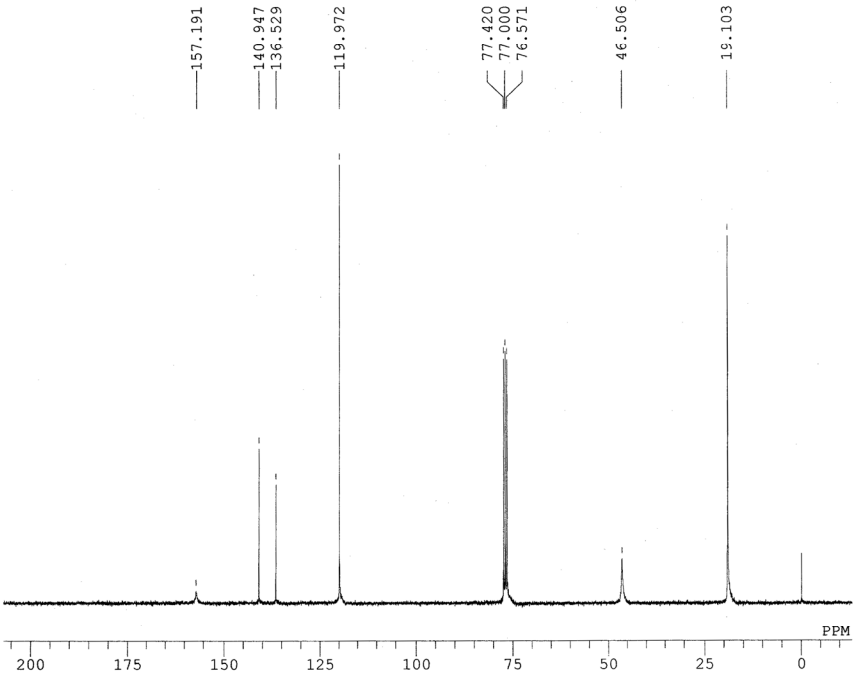

1x
7.380
7.361
7.342
7.117
7.098
7.080
6.901
6.882
4.475
4.344
4.210
1.496
1.299
1.282
0.000
1.99
0.99
1.98
2.00
6.07
12.04
f1 (ppm)


171.771
145.733
141.515
129.354
123.968
120.131
77.318
77.000
76.681
51.239
48.624
21.885
19.548
f1 (ppm)

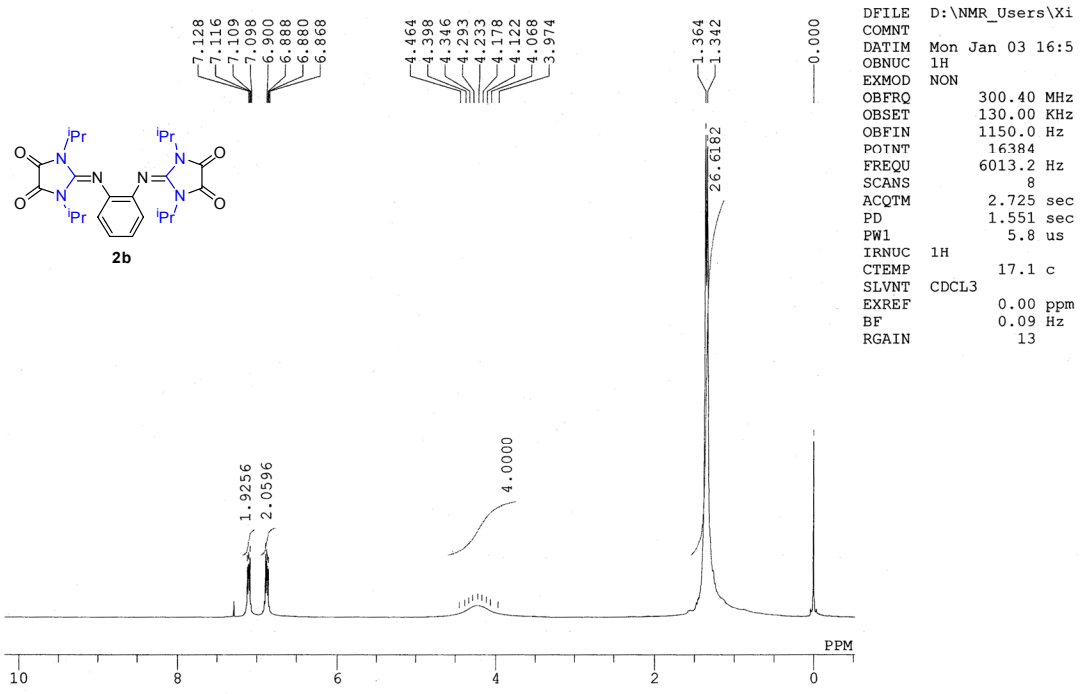


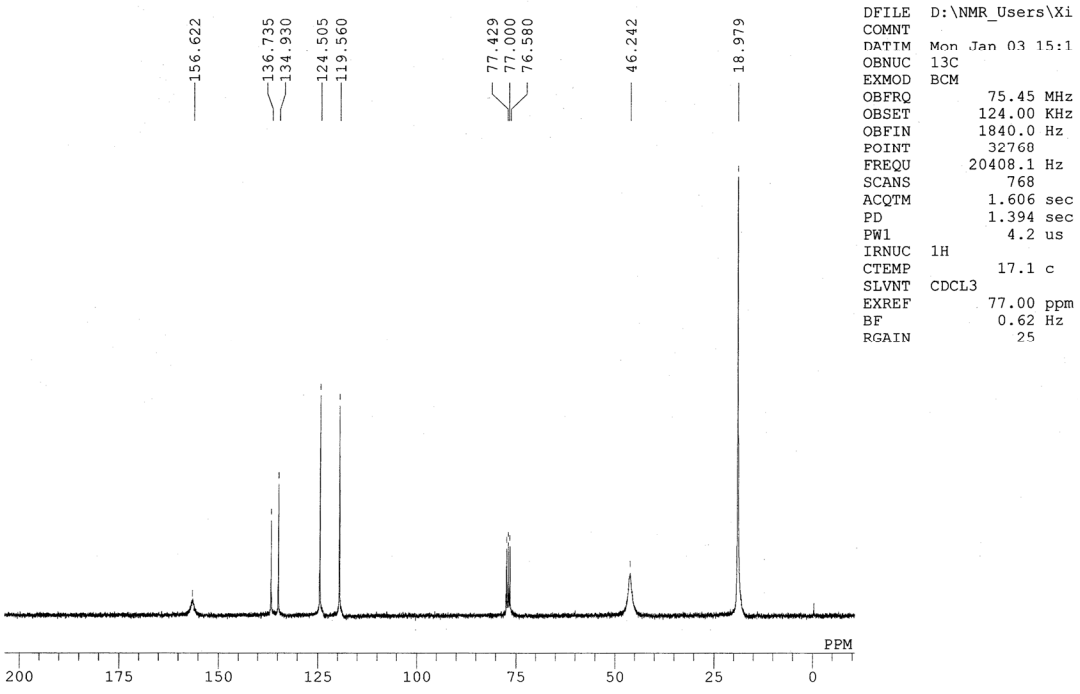
2a

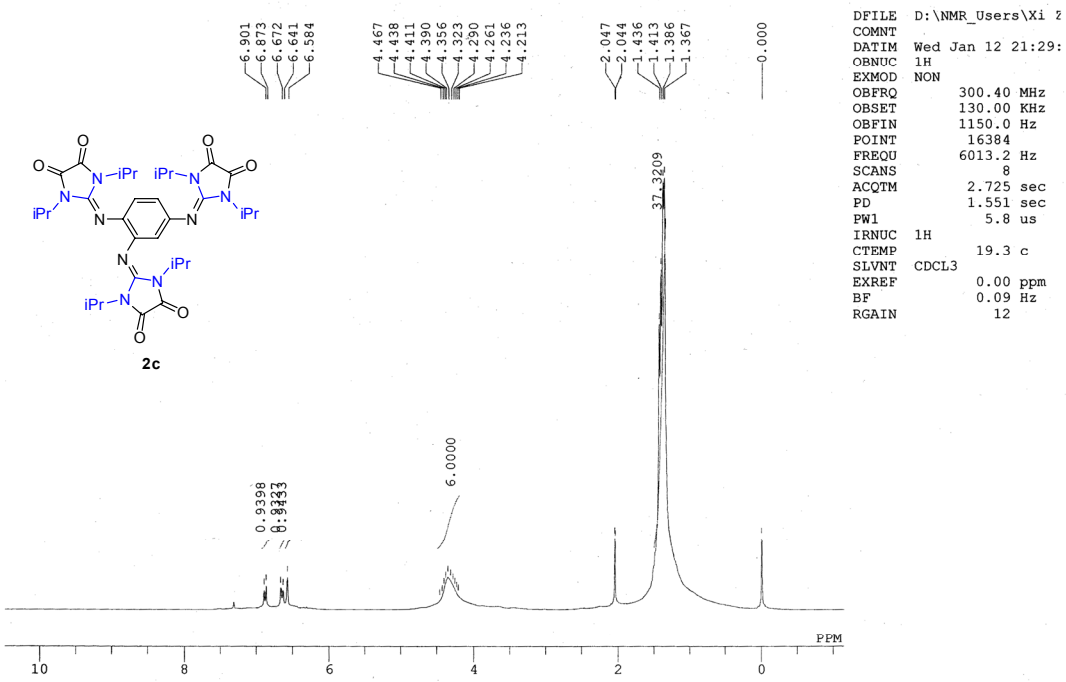

```
DFILE   D:\NMR_Users\Xi
COMNT
DATIM   Sat Jan 22 15:2
OBNUC   1H
EXMOD   NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN       1150.0 Hz
POINT        16384
FREQU       6013.2 Hz
SCANS            8
ACQTM        2.725 sec
PD           1.551 sec
PW1            5.8 us
IRNUC   1H
CTEMP         12.5 c
SLVNT   CDCL3
EXREF         0.00 ppm
BF            0.09 Hz
RGAIN           14
```




```
DFILE   D:\NMR_Users\Xi
COMNT
DATIM   Sat Jan 22 15:2
OBNUC   13C
EXMOD   BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS         4826
ACQTM        1.606 sec
PD           1.394 sec
PW1            4.2 us
IRNUC   1H
CTEMP         13.0 c
SLVNT   CDCL3
EXREF        77.00 ppm
BF            0.62 Hz
RGAIN           27
```

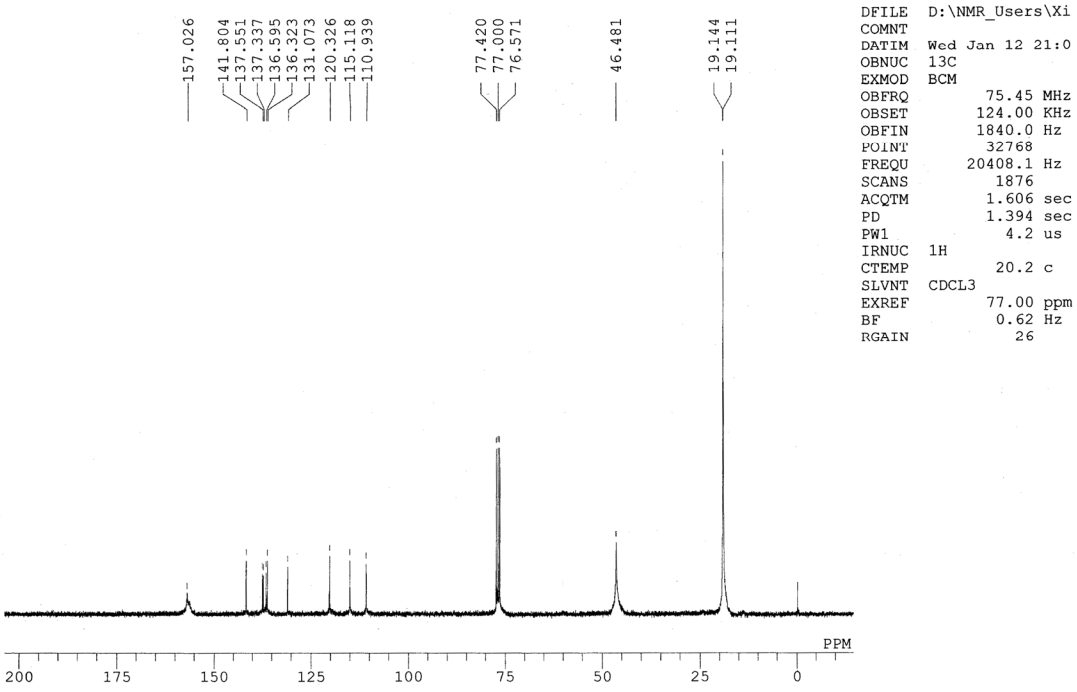




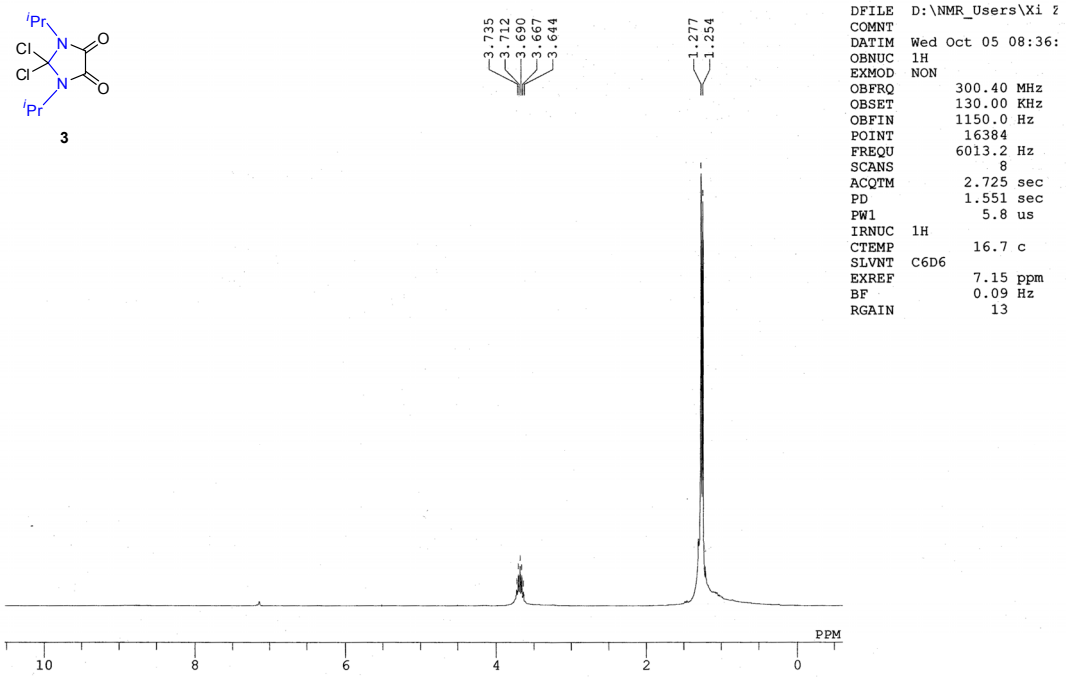


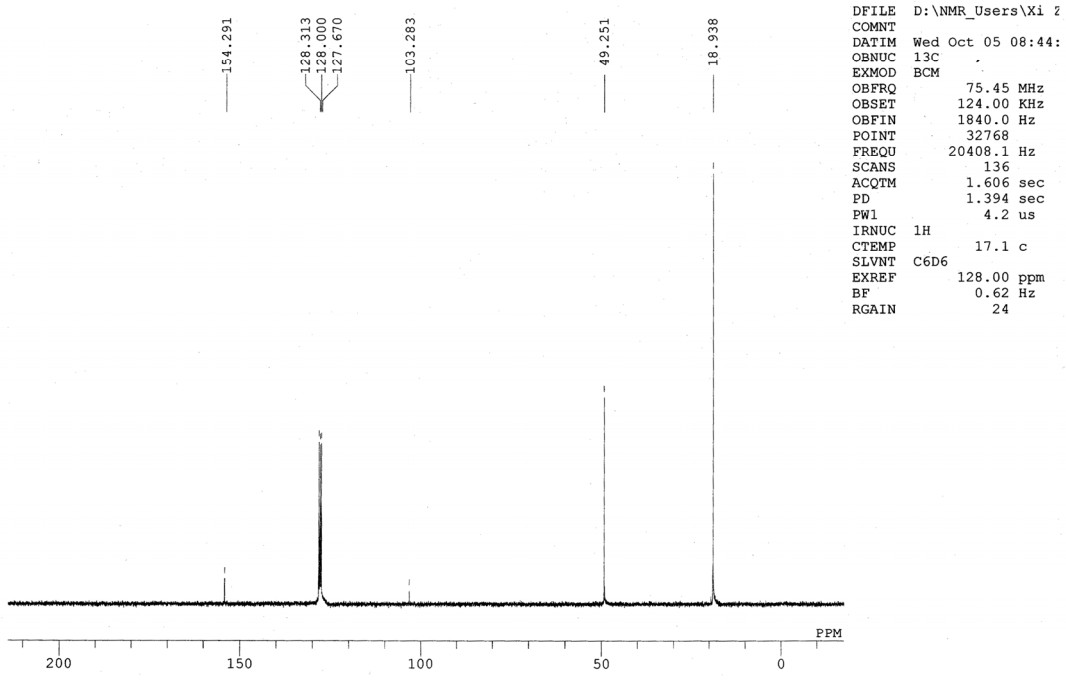
2c

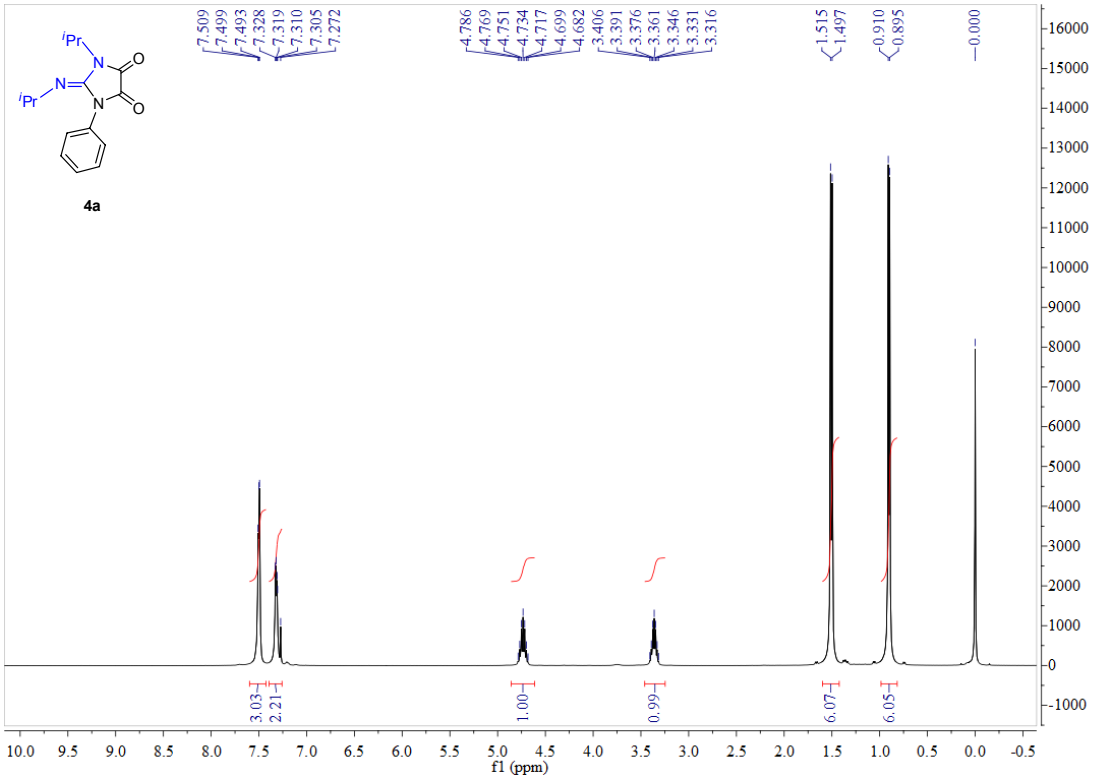
```
DFILE  D:\NMR_Users\Xi 2
COMNT
DATIM  Wed Jan 12 21:29:
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN       1150.0 Hz
POINT        16384
FREQU       6013.2 Hz
SCANS             8
ACQTM         2.725 sec
PD            1.551 sec
PW1             5.8 us
IRNUC  1H
CTEMP          19.3 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.09 Hz
RGAIN            12
```

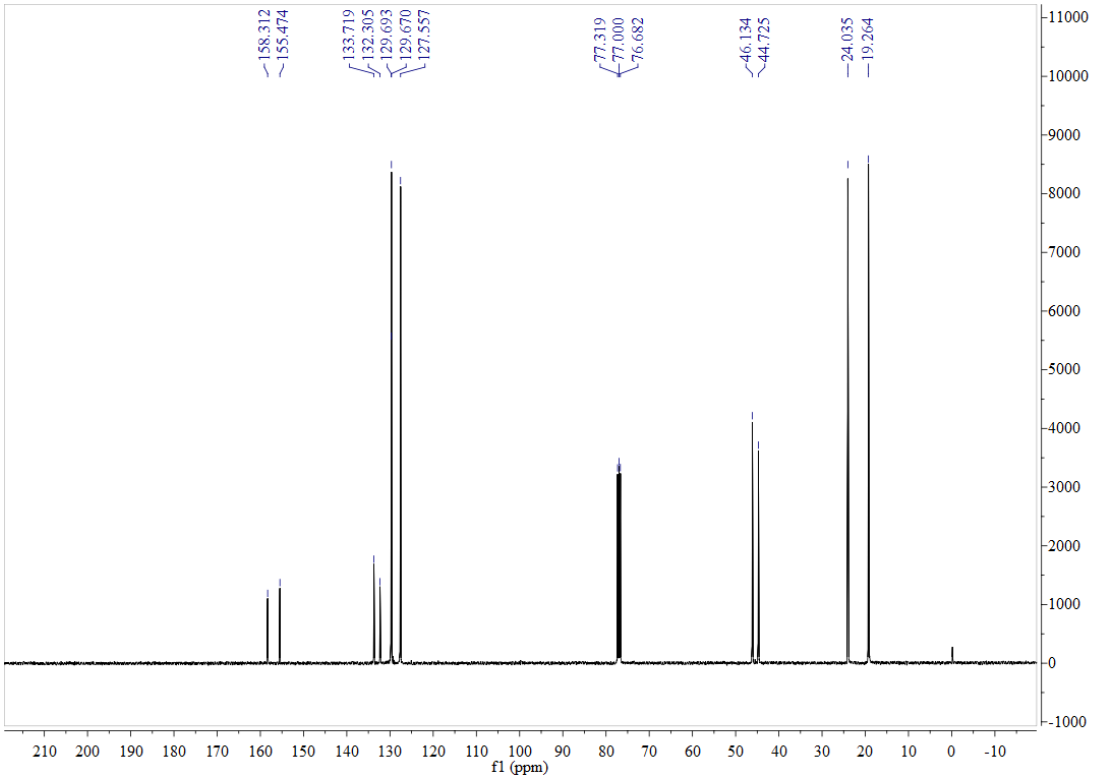


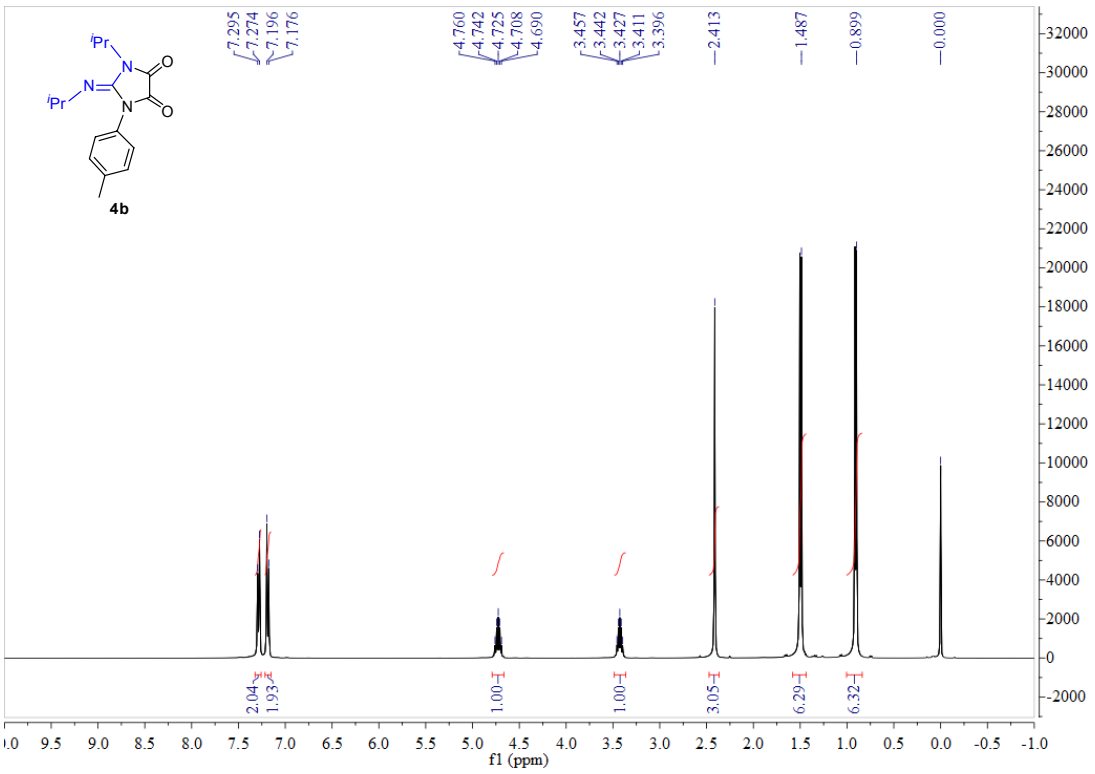

```
DFILE  D:\NMR_Users\Xi
COMNT
DATIM  Wed Jan 12 21:0
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS         1876
ACQTM         1.606 sec
PD            1.394 sec
PW1             4.2 us
IRNUC  1H
CTEMP         20.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.62 Hz
RGAIN            26
```


iPr
N
O
Cl
Cl
N
O
iPr
3
3.735
3.712
3.690
3.667
3.644
1.277
1.254
PPM
10
8
6
4
2
0
DFILE D:\NMR_Users\Xi 2
COMNT
DATIM Wed Oct 05 08:36:
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 16.7 c
SLVNT C6D6
EXREF 7.15 ppm
BF 0.09 Hz
RGAIN 13

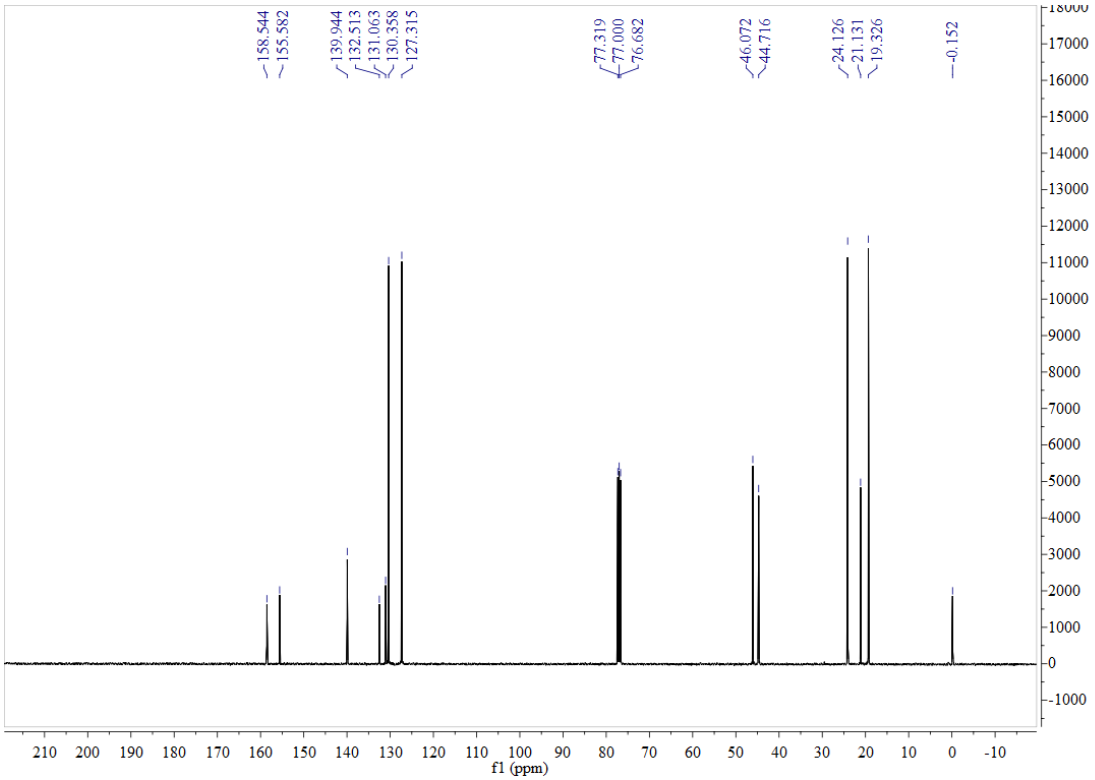

154.291
128.313
128.000
127.670
103.283
49.251
18.938
PPM
200
150
100
50
0
DFILE D:\NMR_Users\Xi 2
COMNT
DATIM Wed Oct 05 08:44:
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 136
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 17.1 c
SLVNT C6D6
EXREF 128.00 ppm
BF 0.62 Hz
RGAIN 24

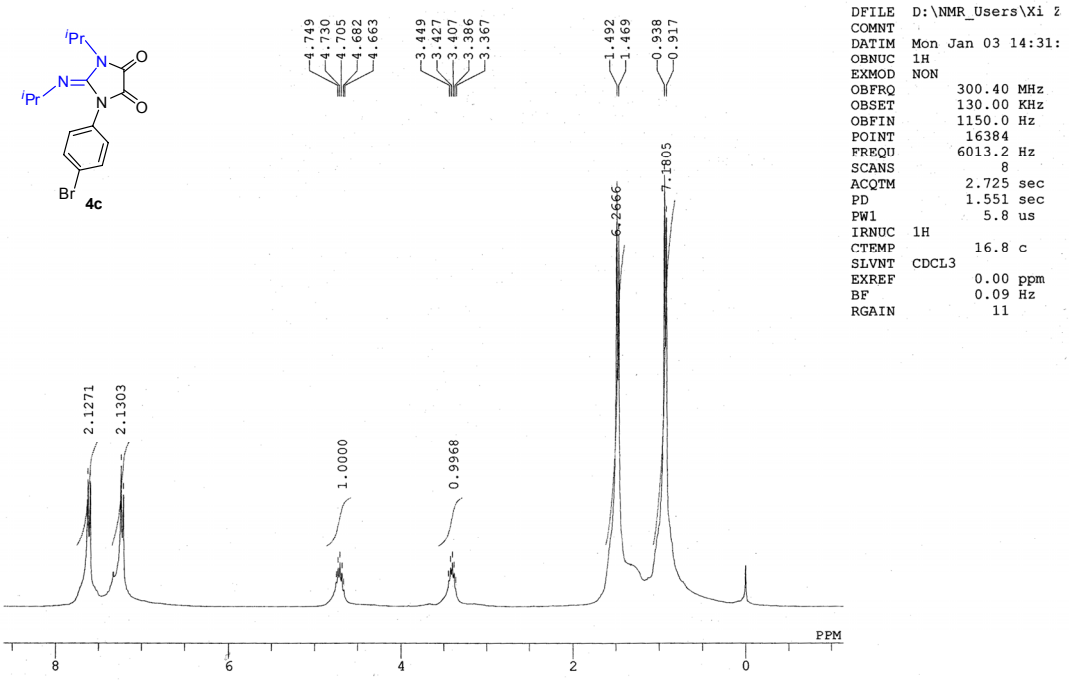

4a
7.509
7.499
7.493
7.328
7.319
7.310
7.305
7.272
4.786
4.769
4.751
4.734
4.717
4.699
4.682
3.406
3.391
3.376
3.361
3.346
3.331
3.316
1.515
1.497
0.910
0.895
0.000
3.03
2.21
1.00
0.99
6.07
6.05
f1 (ppm)


158.312
155.474
133.719
132.305
129.693
129.670
127.557
77.319
77.000
76.682
46.134
44.725
24.035
19.264
f1 (ppm)

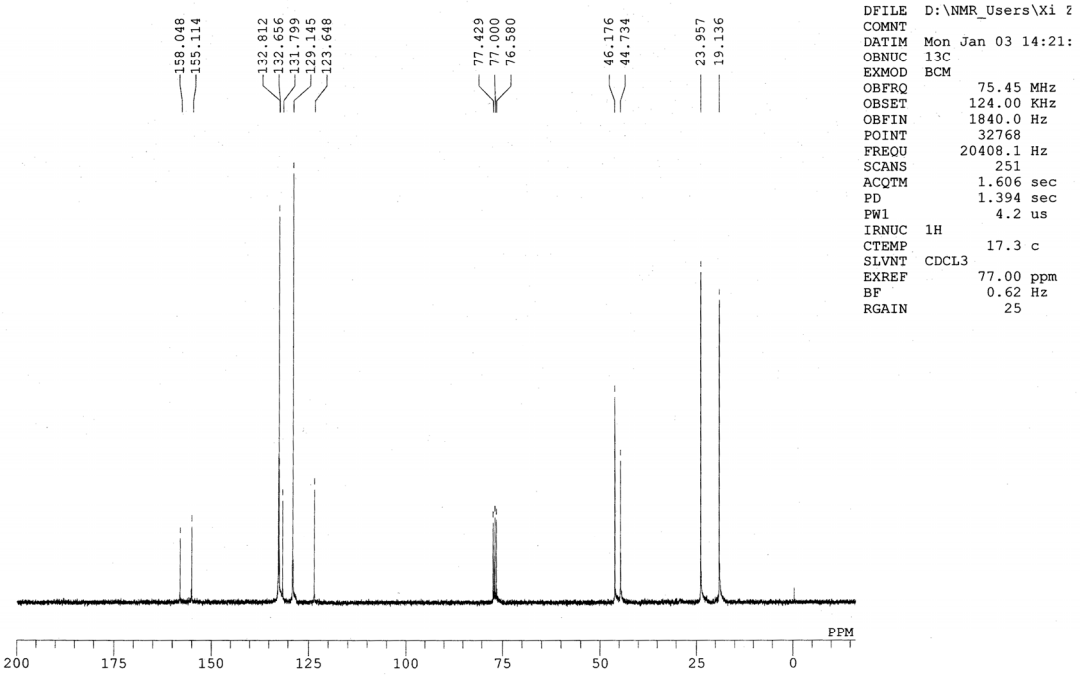

7.295
7.274
7.196
7.176
4.760
4.742
4.725
4.708
4.690
3.457
3.442
3.427
3.411
3.396
2.413
1.487
0.899
0.000
2.04
1.93
1.00
1.00
3.05
6.29
6.32
f1 (ppm)

4b

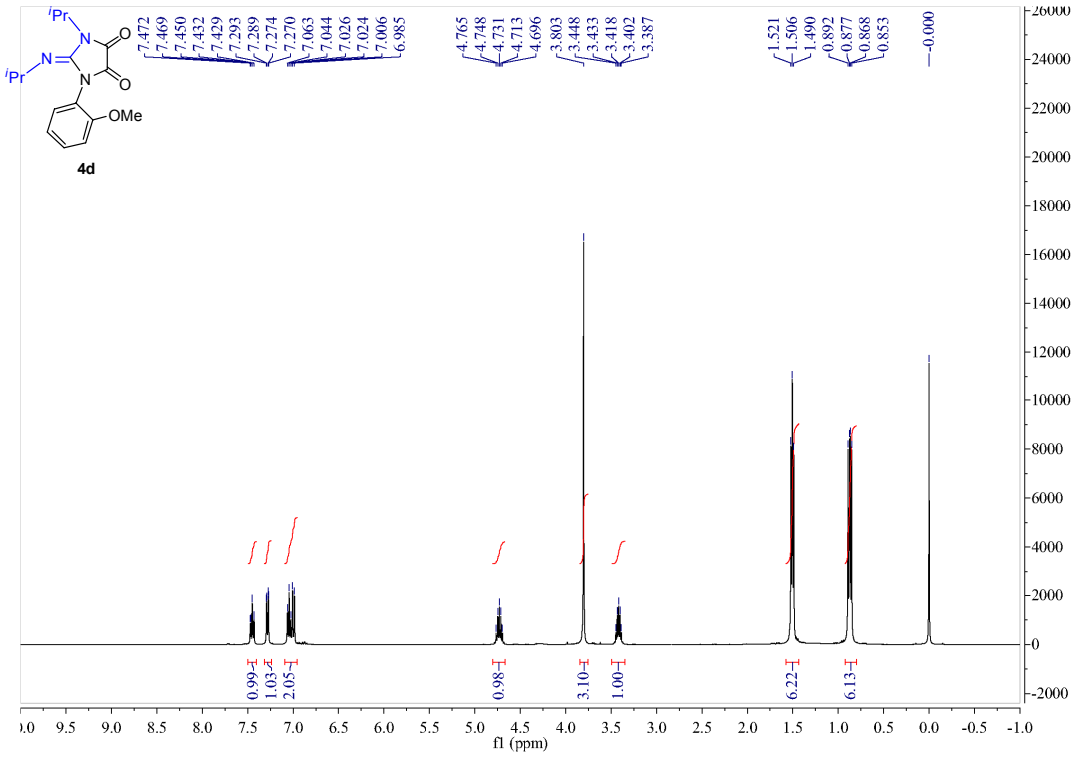

158.544
155.582
139.944
132.513
131.063
130.358
127.315
77.319
77.000
76.682
46.072
44.716
24.126
21.131
19.326
-0.152
f1 (ppm)

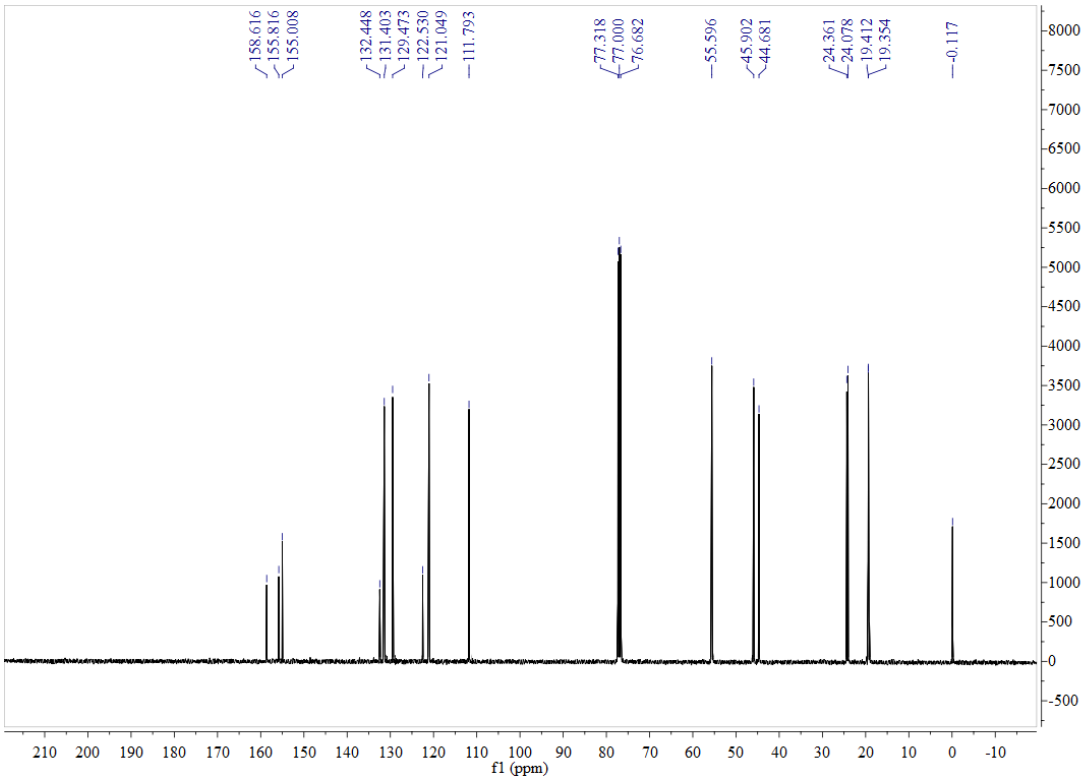


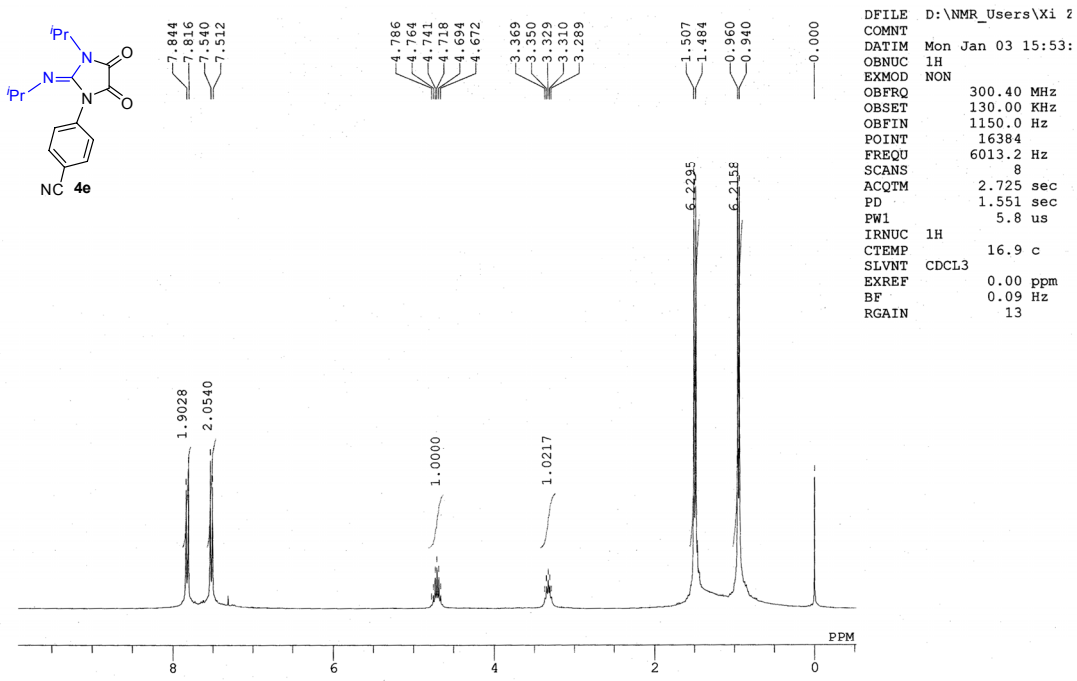

```
DFILE  D:\NMR_Users\Xi 2
COMNT
DATIM  Mon Jan 03 14:31:
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN        1150.0 Hz
POINT         16384
FREQU        6013.2 Hz
SCANS            8
ACQTM         2.725 sec
PD            1.551 sec
PW1             5.8 us
IRNUC  1H
CTEMP          16.8 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.09 Hz
RGAIN            11
```

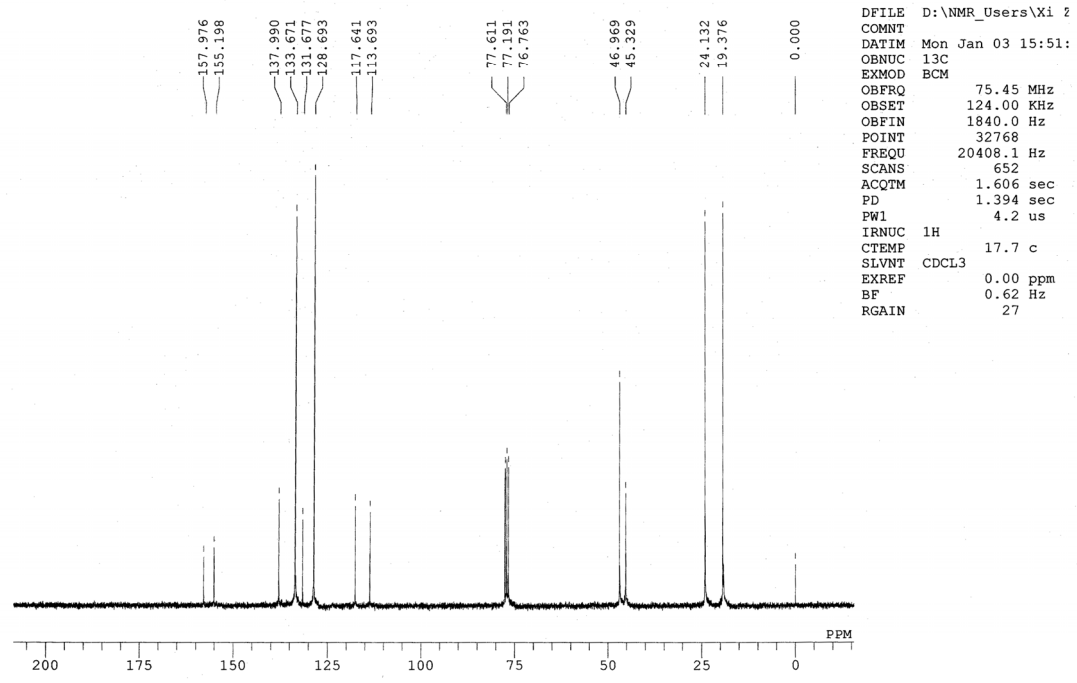


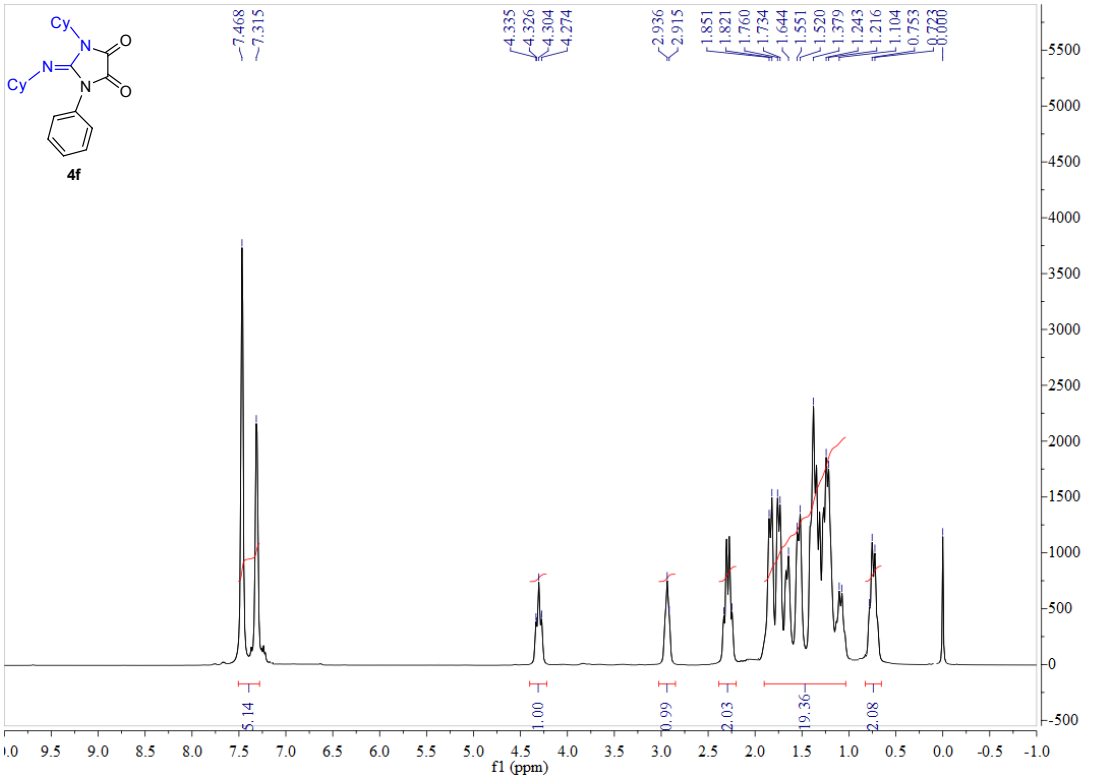

```
DFILE  D:\NMR_Users\Xi 2
COMNT
DATIM  Mon Jan 03 14:21:
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN        1840.0 Hz
POINT         32768
FREQU        20408.1 Hz
SCANS           251
ACQTM         1.606 sec
PD            1.394 sec
PW1             4.2 us
IRNUC  1H
CTEMP          17.3 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF             0.62 Hz
RGAIN            25
```

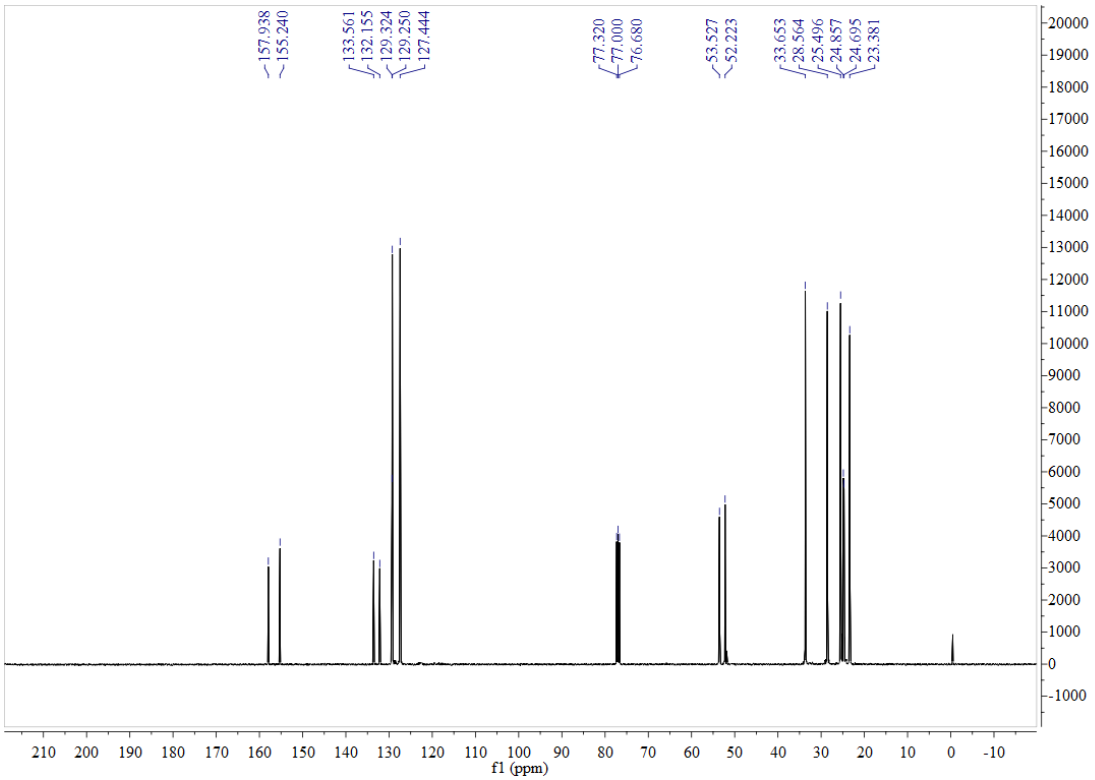

4d
7.472
7.469
7.450
7.432
7.429
7.293
7.289
7.274
7.270
7.063
7.044
7.026
7.024
7.006
6.985
4.765
4.748
4.731
4.713
4.696
3.803
3.448
3.433
3.418
3.402
3.387
1.521
1.506
1.490
0.892
0.877
0.868
0.853
-0.000
0.99
1.03
2.05
0.98
3.10
1.00
6.22
6.13
f1 (ppm)

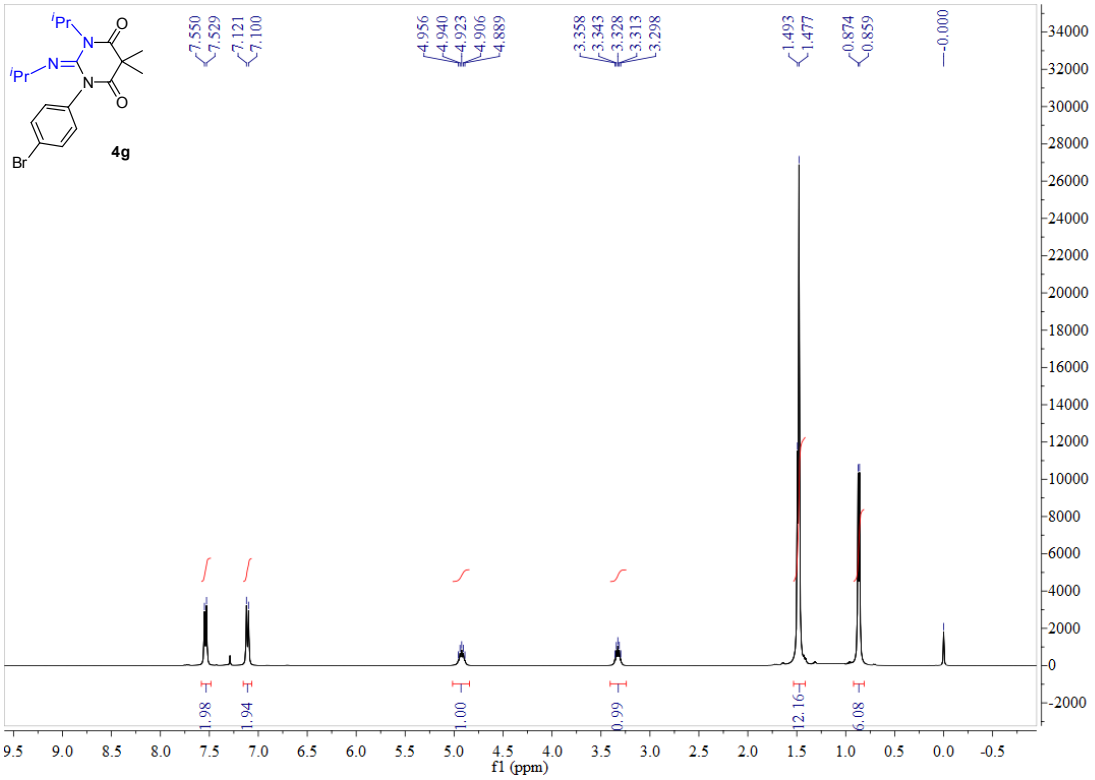

158.616
155.816
155.008
132.448
131.403
129.473
122.530
121.049
111.793
77.318
77.000
76.682
55.596
45.902
44.681
24.361
24.078
19.412
19.354
-0.117
f1 (ppm)

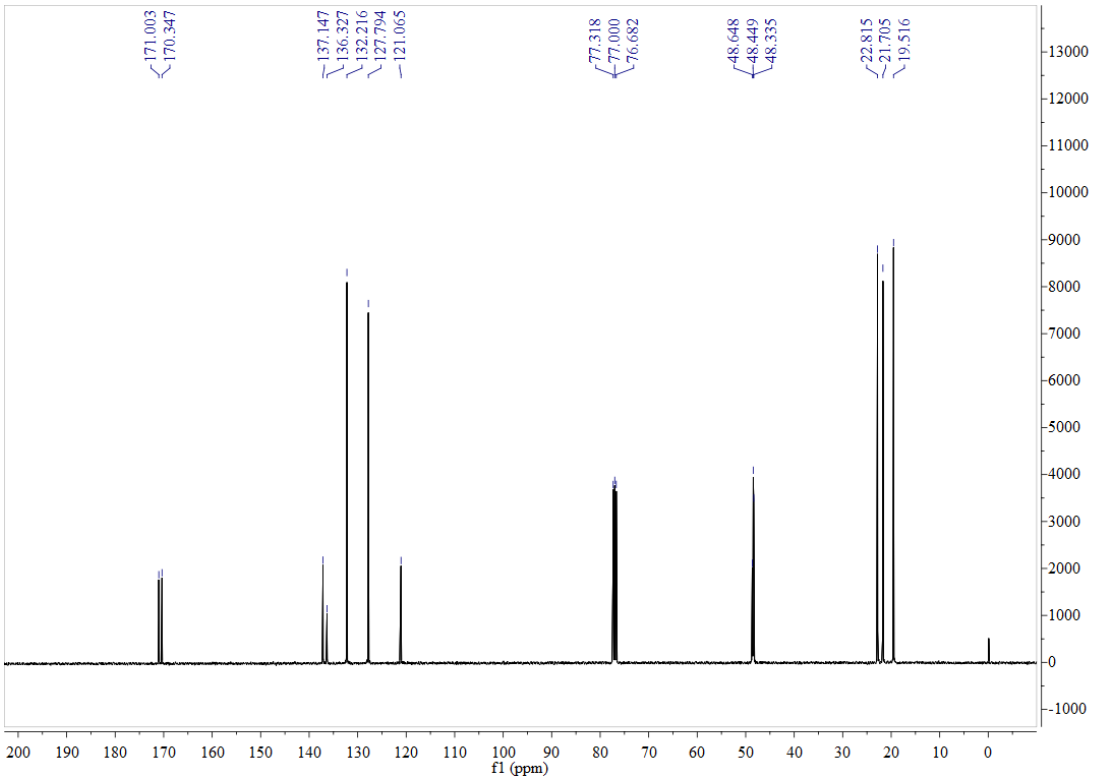

iPr
N
O
N
iPr
N
O
NC
4e
7.844
7.816
7.540
7.512
4.786
4.764
4.741
4.718
4.694
4.672
3.369
3.350
3.329
3.310
3.289
1.507
1.484
0.960
0.940
0.000
6.2295
6.2158
1.9028
2.0540
1.0000
1.0217
PPM
8
6
4
2
0
DFILE D:\NMR_Users\Xi 2
COMNT
DATIM Mon Jan 03 15:53:
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 16384
FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 16.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 13


157.976
155.198
137.990
133.671
131.677
128.693
117.641
113.693
77.611
77.191
76.763
46.969
45.329
24.132
19.376
0.000
PPM
200
175
150
125
100
75
50
25
0
DFILE D:\NMR_Users\Xi 2
COMNT
DATIM Mon Jan 03 15:51:
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 652
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 17.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 27


Cy
N
O
N
Cy
N
O
4f
7.468
7.315
4.335
4.326
4.304
4.274
2.936
2.915
1.851
1.821
1.760
1.734
1.644
1.551
1.520
1.379
1.243
1.216
1.104
0.753
0.723
0.000
5.14
1.00
0.99
2.03
19.36
2.08
f1 (ppm)


157.938
155.240
133.561
132.155
129.324
129.250
127.444
77.320
77.000
76.680
53.527
52.223
33.653
28.564
25.496
24.857
24.695
23.381
f1 (ppm)


4g
7.550
7.529
7.121
7.100
4.956
4.940
4.923
4.906
4.889
3.358
3.343
3.328
3.313
3.298
1.493
1.477
0.874
0.859
0.000
1.98
1.94
1.00
0.99
12.16
6.08
f1 (ppm)


171.003
170.347
137.147
136.327
132.216
127.794
121.065
77.318
77.000
76.682
48.648
48.449
48.335
22.815
21.705
19.516
f1 (ppm)