Supplementary Information

CuI/TEMPO Mediated Aerobic Oxidative sp^3 C-H Functionalization Leading to Pyrrol-2-one Derivatives

Aritra Mondal,[a] Sunanda Mandal,[a] Saikat Khamarui,[b] Souvik Mondal,[a,c] Bholanath Maity,[d] Tanmoy Dutta,[e] Ayan Hazra,[a] Paramita Das,*[f] Suman Ray*[a]

[a]*Department of Chemistry, Presidency University, 86/1 College Street, Kolkata 700073, India.*

[b]*Department of Chemistry, Government General Degree College, Kalna-1, Burdwan 713405, India.*

[c]*Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, SAMat, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India.*

[d]*KAUST Catalysis Centre (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.*

[e]*Department of Chemistry, JIS College of Engineering, Kalyani, Nadia WB-741235, India*

[f]*Department of Chemistry, Asutosh College, 92 S P Mukherjee Road, Kolkata-700026, India.*

**para.ita.das@gmail.com*, **sumanray48@gmail.com*

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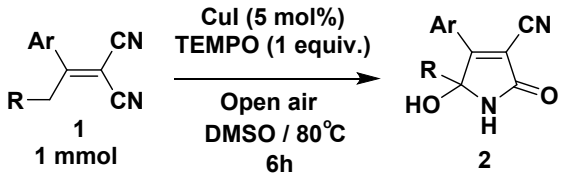
A. Materials and Methods.

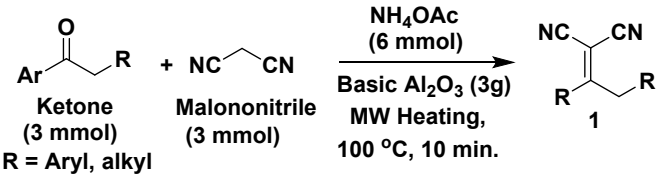
Reagents were purchased from Sigma-Aldrich, Spectrochem Pvt. Ltd., BLD Pharm etc. and used without further purification. Unless otherwise mentioned, all reactions were performed in oven-dried 50.0 mL standard joint round bottom flask with Teflon coated magnetic stirring bar. Reaction progress was monitored by thin layer chromatography (TLC) analysis on aluminium sheets pre-coated with silica gel 60 F254 and under short wave UV light. Column chromatography was done with Merck silica gel (60-120 and 100−200) with Hexane/ethylacetate (EtOAc) as eluent. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 (400 MHz) spectrometer in $CDCl_3$ and DMSO-d_6 with TMS as an internal reference. The chemical shifts were reported as δ values (ppm) relative to TMS. High resolution mass spectroscopic analyses were performed on Agilent UHD Accurate-Mass Q-TOF LC/MS instrument. X-Ray single crystal analysis was done on a Bruker-APEX II diffractometer.

B. General procedure for the synthesis of 5-Hydroxy-1*H*-pyrrol-2-ones (2) from the Knoevenagel condensation product (1)



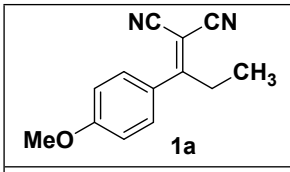
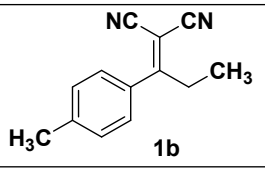
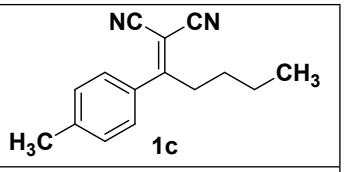
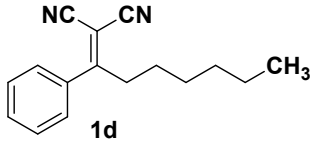
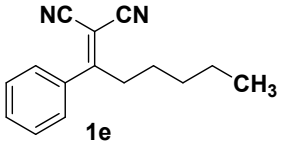
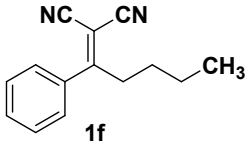
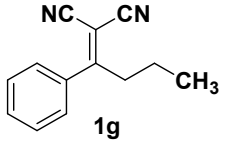
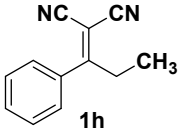
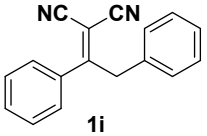
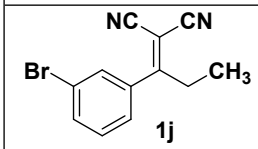
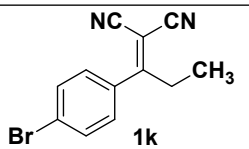
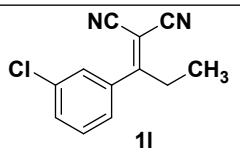
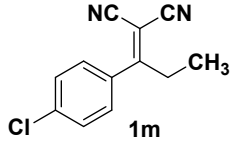
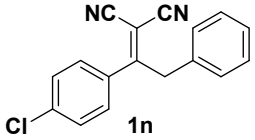
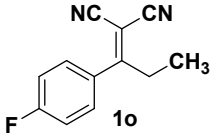
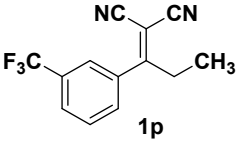
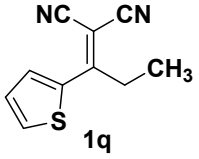
The Knoevenagel condensation product (**1**) (1 mmol), TEMPO (2 mmol), and CuI (0.1 mmol) in 5 mL DMSO were taken in a round bottomed flask under oxygen atmosphere and stirred at 80 °C for 6-8 hours (or until completion). The progress of the reaction was monitored by TLC of the crude reaction mixture. After completion of the reaction the resulting mixture was combined with 100 mL water and extracted with EtOAc (3 × 30 mL). The extracts were combined and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by silica gel column chromatography using EtOAc/hexane as eluent to afford the final product **2**.

C. Preparation of the starting material 1 by Knoevenagel condensation between aromatic ketones and malononitrile

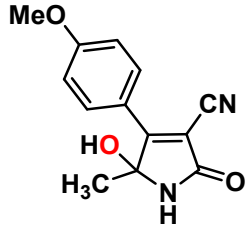


Malononitrile (3 mmol), different ketones (3 mmol), ammonium acetate (6 mmol), and basic alumina (6g) and were mixed thoroughly in a mortar and pestle. The reaction mixture was taken in a 100 ml conical flask and heated under microwave irradiation at 100 ˚C for 10 minutes. The progress of reaction was monitored by TLC using EtOAc/hexane eluent. The reaction mixture was extracted into dichloromethane then filtered to separate the alumina. The solvent was removed under reduced pressure by rotatory evaporator and purified by column chromatography on silica gel using different percentage of EtOAc in hexane as eluent.

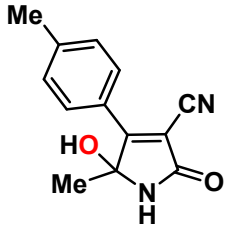
D. Structures of prepared starting substrates (1)

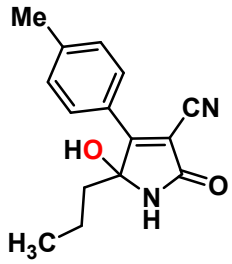
E. Spectroscopic Characterization for 2a-2p



5-hydroxy-4-(4-methoxyphenyl)-5-methyl-2-oxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (2a): Synthesized following the general procedure taking 2-(1-(4-methoxyphenyl)propylidene)malononitrile (**1a**) (1 mmol, 212 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 35% EtOAc in hexane as eluent to afford the final product **2a**; yield 81% (198 mg); brownish white solid; Mp: 222 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.16 (s, 1H), 8.10 (d, *J*= 8.0 Hz, 2H), 7.16 (d, *J*= 12.0 Hz, 2H), 6.85 (s, 1H), 3.86 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.4, 164.7, 162.8, 131.3, 121.9, 115.2, 102.0, 88.1, 56.1, 26.5; HRMS (ESI) m/z calcd. for $C_{13}H_{12}N_2O_3$ $[M+H]^+$: 245.0921, but found 245.0906.

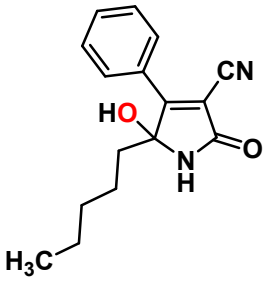


5-hydroxy-5-methyl-2-oxo-4-(p-tolyl)-2,5-dihydro-1H-pyrrole-3-carbonitrile (2b): Synthesized following the general procedure taking 2-(1-(p-tolyl)propylidene)malononitrile (**1b**) (1 mmol, 196 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 27% EtOAc in hexane as eluent to afford the final product **2b**; yield 78% (178 mg); yellowish white solid; Mp: 210 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.24 (s, 1H), 7.98 (d, *J*= 8.4 Hz, 2H), 7.42 (d, *J*= 8.0 Hz, 2H), 6.87 (s, 1H), 2.39 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.0, 164.5, 143.2, 130.2, 129.0, 126.9, 114.7, 104.0, 88.2, 26.1, 21.7; HRMS (ESI) m/z calcd. for $C_{13}H_{12}N_2O_2$ $[M+H]^+$: 229.0972, but found 229.0966.

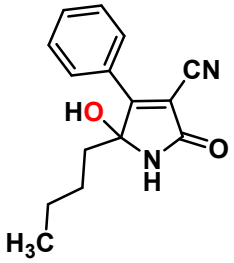


5-hydroxy-2-oxo-5-propyl-4-(p-tolyl)-2,5-dihydro-1H-pyrrole-3-carbonitrile (2c): Synthesized following the general procedure taking 2-(1-(p-tolyl)pentylidene)malononitrile (**1c**) (1 mmol, 224 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 23% EtOAc in hexane as

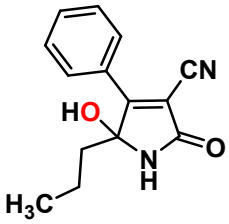
eluent to afford the final product **2c**; yield 77% (197 mg); yellowish white solid; Mp: 192 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.15 (s, 1H), 7.94(d, *J* =8.4 Hz, 2H), 7.40 (d, *J* =8.4 Hz, 2H), 6.89 (s, 1H), 2.39 (s, 3H), 1.79 (dt, *J* =12.6 Hz, *J* =3.2 Hz, 1H), 1.63 (dt, *J* =13.0 Hz, *J* =4.4 Hz, 1H), 1.20-1.11 (m, 1H), 0.98-0.89 (m,1H), 0.72 (t, *J* =7.6, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.9, 165.0, 143.2, 130.3, 128.8, 127.1, 114.6, 104.8, 90.6, 21.7, 16.6, 14.3; HRMS (ESI) m/z calcd. for $C_{15}H_{16}N_2O_2$ $[M+H]^+$: 257.1285, but found 257.1272.



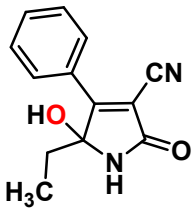
5-hydroxy-2-oxo-5-pentyl-4-phenyl-2,5-dihydro-1H-pyrrole-3-carbonitrile (2d): Synthesized following the general procedure taking 2-(1-phenylheptylidene)malononitrile (**1d**) (1 mmol, 238 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 20% EtOAc in hexane as eluent to afford the final product **2d**; yield 76% (205 mg); yellowish white solid; Mp: 118 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.09 (m, 3H), 7.56-7.53 (m, 1H), 7.51-7.47 (m, 2H), 5.56 (br, s, 1H), 2.02 (dt, *J* =12.6 Hz, *J* =3.6 Hz, 1H), 1.86-1.79 (m, 1H), 1.35-1.32 (m, 1H), 1.16-1.10 (m,4H), 0.98 (t, *J* =4.4 Hz, 1H) 0.76 (t, *J* =6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 166.6, 132.9, 129.3, 129.0, 128.9, 113.1, 104.8, 91.5, 37.6, 25.1, 22.4, 13.8; HRMS (ESI) m/z calcd. for $C_{16}H_{18}N_2O_2$ $[M+H]^+$: 271.1441, but found 271.1428.



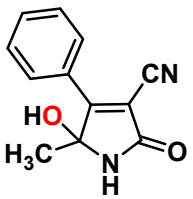
5-butyl-5-hydroxy-2-oxo-4-phenyl-2,5-dihydro-1H-pyrrole-3-carbonitrile (2e): Synthesized following the general procedure taking 2-(1-phenylhexylidene)malononitrile (**1e**) (1 mmol, 224 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 23% EtOAc in hexane as eluent to afford the final product **2e**; yield 77% (197 mg); white solid; Mp: 120 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* =7.2 Hz, 2H), 7.97(s, 1H), 7.57-7.48 (m, 3H), 5.43 (s, 1H), 2.03 (dt, *J* =12.8 Hz, *J* =3.6 Hz, 1H), 1.84 (dt, *J* =12.8 Hz, *J* =3.2 Hz, 1H), 1.36-1.10 (m, 3H), 1.00-0.93 (m,1H), 0.76 (t, *J* =7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 166.6, 132.9, 129.3, 129.0, 128.9, 113.1, 104.8, 91.5, 37.6, 25.1, 22.4, 13.8; HRMS (ESI) m/z calcd. for $C_{15}H_{16}N_2O_2$ $[M+H]^+$: 257.1285, but found 257.1280.



5-hydroxy-2-oxo-4-phenyl-5-propyl-2,5-dihydro-1H-pyrrole-3-carbonitrile (2f): Synthesized following the general procedure taking 2-(1-phenylpentylidene)malononitrile (**1f**) (1 mmol, 210 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 25% EtOAc in hexane as eluent to afford the final product **2f**; yield 79% (192 mg); white solid; Mp: 200 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.21 (s, 1H), 8.02-8.00 (m, 2H), 7.58 (dd, J =10.2 Hz,J =6.4 Hz,3H), 6.93 (s, 1H), 1.79 (dt, J =12.4 Hz, J =4.4 Hz, 1H), 1.63 (dt, J =12.6 Hz, J =3.6 Hz, 1H), 1.21-1.14 (m, 1H), 1.00-0.96 (m,1H), 0.72 (t, J =7.2, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.1, 164.8, 132.7, 129.9, 129.7, 128.8, 114.3, 106.0, 90.7, 16.6, 14.3; HRMS (ESI) m/z calcd. for $C_{14}H_{14}N_2O_2$ $[M+H]^+$: 243.1128, but found 243.1124.

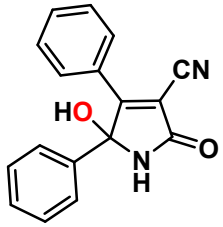


5-ethyl-5-hydroxy-2-oxo-4-phenyl-2,5-dihydro-1H-pyrrole-3-carbonitrile (2g): Synthesized following the general procedure taking 2-(1-phenylbutylidene)malononitrile (**1g**) (1 mmol, 196 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 27% EtOAc in hexane as eluent to afford the final product **2g**; yield 80% (183 mg); yellowish white solid; Mp: 220 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.18 (s, 1H), 8.02 (dd, J= 7.4 Hz, J =2.0 Hz, 2H), 7.61-7.56 (m, 3H), 6.95 (s, 1H), 1.88-1.81 (m, 1H), 1.69-1.65 (m, 1H), 0.63 (t, J =7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.9, 164.9, 132.7, 129.9, 129.7, 128.8, 114.3, 106.3, 91.3, 30.9, 7.8; HRMS (ESI) m/z calcd. for $C_{13}H_{12}N_2O_2$ $[M+H]^+$: 229.0972, but found 229.0970.

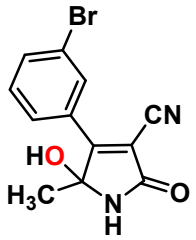


5-hydroxy-5-methyl-2-oxo-4-phenyl-2,5-dihydro-1H-pyrrole-3-carbonitrile (2h): Synthesized following the general procedure taking 2-(1-phenylpropylidene)malononitrile (**1h**) (1 mmol, 182 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 27% EtOAc in hexane as eluent to afford the final product **2h**; yield 77% (165 mg); white solid; Mp: 198 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.27 (br, s, 1H), 8.04-8.02 (m, 2H), 7.61-7.59 (m, 3H), 6.88 (br, s, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.3,

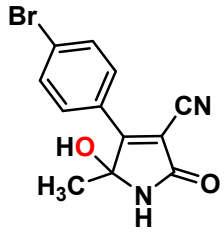
164.4, 132.6, 129.7, 129.6, 114.5, 105.3, 88.3, 25.8; HRMS (ESI) m/z calcd. for $C_{12}H_{10}N_2O_2$ $[M+H]^+$: 215.0815, but found 215.0821.



5-hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1H-pyrrole-3-carbonitrile (2i): Synthesized following the general procedure taking 2-(1,2-diphenylethylidene)malononitrile (**1i**) (1 mmol, 244 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 25% EtOAc in hexane as eluent to afford the final product **2i**; yield 76% (210 mg); yellowish white solid; Mp: 216 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.67 (s, 1H),7.84 (d, *J* =9.6 Hz, 2H), 7.68 (s, 1H), 7.55(d, *J* =7.2 Hz, 2H), 7.46 (d, *J*= 7.6 Hz, 2H), 7.34-7.28 (m, 3H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.3, 164.9, 139.3, 137.4, 130.9, 129.7, 129.1, 129.0, 128.2, 126.0, 106.3, 89.9, 25.3; HRMS (ESI) m/z calcd. for $C_{17}H_{12}N_2O_2$ $[M+H]^+$: 277.0972, but found 277.0970.

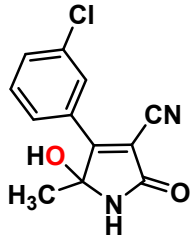


4-(3-bromophenyl)-5-hydroxy-5-methyl-2-oxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (2j): Synthesized following the general procedure taking 2-(1-(3-bromophenyl)propylidene)malononitrile (**1j**) (1 mmol, 261 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 30% EtOAc in hexane as eluent to afford the final product **2j**; yield 74% (217 mg); brown solid; Mp: 190 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.36 (s, 1H), 8.15(s, 1H), 7.98 (d, *J*= 8.0 Hz, 1H), 7.83 (d, *J*= 8.0 Hz, 1H), 7.58 (t, *J*= 8.0 Hz, 1H), 6.93 (s, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.5, 163.9, 135.1, 131.9, 131.0, 127.9, 122.6, 114.0, 106.9, 88.2, 25.4; HRMS (ESI) m/z calcd. for $C_{12}H_9BrN_2O_2$ $[M+H]^+$: 292.9920, but found 292.9922.

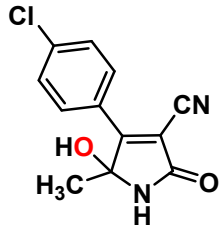


4-(4-bromophenyl)-5-hydroxy-5-methyl-2-oxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (2k): Synthesized following the general procedure taking 2-(1-(4-bromophenyl)propylidene)malononitrile (**1**) (1 mmol, 261 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography

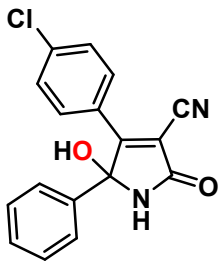
using 30% EtOAc in hexane as eluent to afford the final product **2k**; yield 71% (208 mg); brown solid; Mp: 180 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.33 (s, 1H), 7.96 (d, *J*= 8.8 Hz, 2H), 7.84 (d, *J*= 8.8 Hz, 2H), 6.92 (s, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.9, 164.2, 132.8, 130.9, 128.8, 126.5, 114.3, 105.9, 88.1, 25.6; HRMS (ESI) m/z calcd. for $C_{12}H_9BrN_2O_2$ $[M+H]^+$: 292.9920, but found 292.9894.



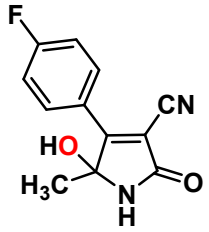
4-(3-chlorophenyl)-5-hydroxy-5-methyl-2-oxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (2l): Synthesized following the general procedure taking 2-(1-(3-chlorophenyl)propylidene)malononitrile (**1l**) (1 mmol, 217 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 30% EtOAc in hexane as eluent to afford the final product **2l**; yield 69% (172 mg); pink solid; Mp: 192 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.36 (s, 1H), 8.01(t, *J*= 2 Hz, 1H), 7.95-7.93 (m, 1H), 7.70 (d, *J*= 8.4 Hz, 1H), 7.65 (t, *J*= 8.0 Hz, 1H), 6.94 (s, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.5, 164.0, 134.2, 132.2, 131.7, 131.6, 128.2, 127.6, 114.0, 107.0, 88.2, 25.4; HRMS (ESI) m/z calcd. for $C_{12}H_9ClN_2O_2$ $[M+H]^+$: 249.0426, but found 249.0430.



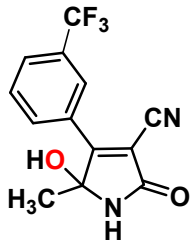
4-(4-chlorophenyl)-5-hydroxy-5-methyl-2-oxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (2m): Synthesized following the general procedure taking 2-(1-(4-chlorophenyl)propylidene)malononitrile (**1**) (1 mmol, 217 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 30% EtOAc in hexane as eluent to afford the final product **2m**; yield 65% (162 mg); yellowish white solid; Mp: 196 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.34 (s, 1H), 8.04 (d, *J*= 8.8 Hz, 2H), 7.69 (d, *J*= 8.8 Hz, 2H), 6.95 (s, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.9, 164.2, 137.5, 130.8, 129.8, 128.4, 114.4, 105.8, 88.2, 25.6; HRMS (ESI) m/z calcd. for $C_{12}H_9ClN_2O_2$ $[M+H]^+$: 249.0426, but found 249.0435.



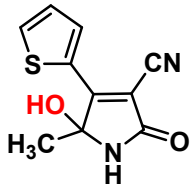
5-hydroxy-2-oxo-4-(4-chlorophenyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carbonitrile (2n): Synthesized following the general procedure taking 2-(1-(4-chlorophenyl)-2-phenylethylidene)malononitrile (**1n**) (1 mmol, 279 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 30% EtOAc in hexane as eluent to afford the final product **2n**; yield 65% (186 mg); yellowish white solid; Mp: 256 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.67 (s, 1H),7.84 (td, *J* =8.8 Hz, *J* =2.4 Hz, 2H), 7.66 (s, 1H), 7.55(td, *J* =8.8 Hz, *J* =2.0 Hz, 2H), 7.47-7.44 (m, 2H), 7.34-7.28 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.4, 164.9, 139.3, 137., 130.9, 129.7, 129.1, 129.0, 128.2, 126.0, 114.3, 106.3, 88.9, 80.8; HRMS (ESI) m/z calcd. for $C_{17}H_{11}N_2O_2Cl$ $[M+H]^+$: 311.0582, but found 311.0574.



4-(4-fluorophenyl)-5-hydroxy-5-methyl-2-oxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (2o): Synthesized following the general procedure taking 2-(1-(4-fluorophenyl)propylidene)malononitrile (**1o**) (1 mmol, 200 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 30% EtOAc in hexane as eluent to afford the final product **2o**; yield 71% (165 mg); yellowish white solid; Mp: 212 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.01 (s, 1H), 8.05 (d, *J*= 8.0 Hz, 2H), 7.09 (d, *J*= 8.8 Hz, 2H), 6.78 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.2, 165.3, 153.6, 131.1, 118.4, 115.9, 113.9, 98.6, 87.9, 66.3, 31.2, 27.1; HRMS (ESI) m/z calcd. for $C_{12}H_9FN_2O_2$ $[M+H]^+$: 233.0721, but found 249.0725.

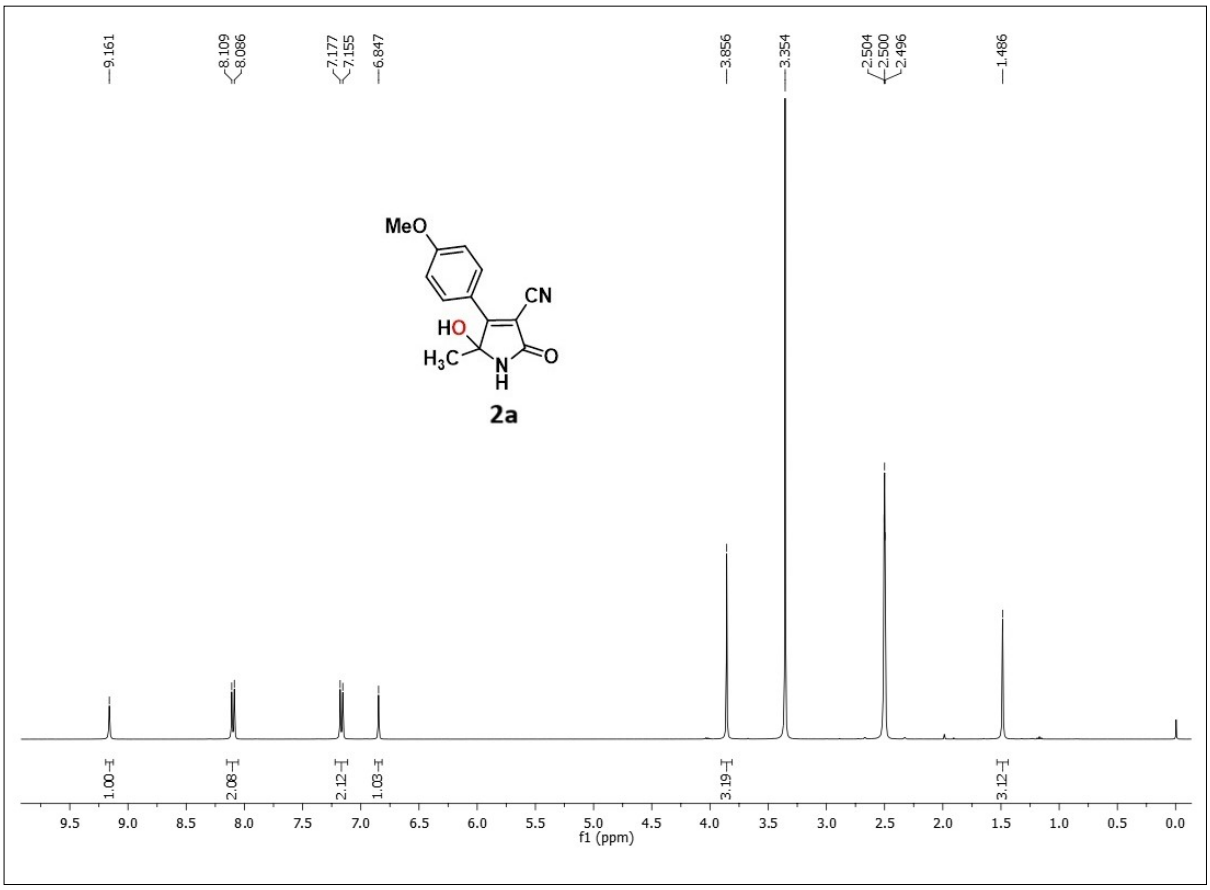


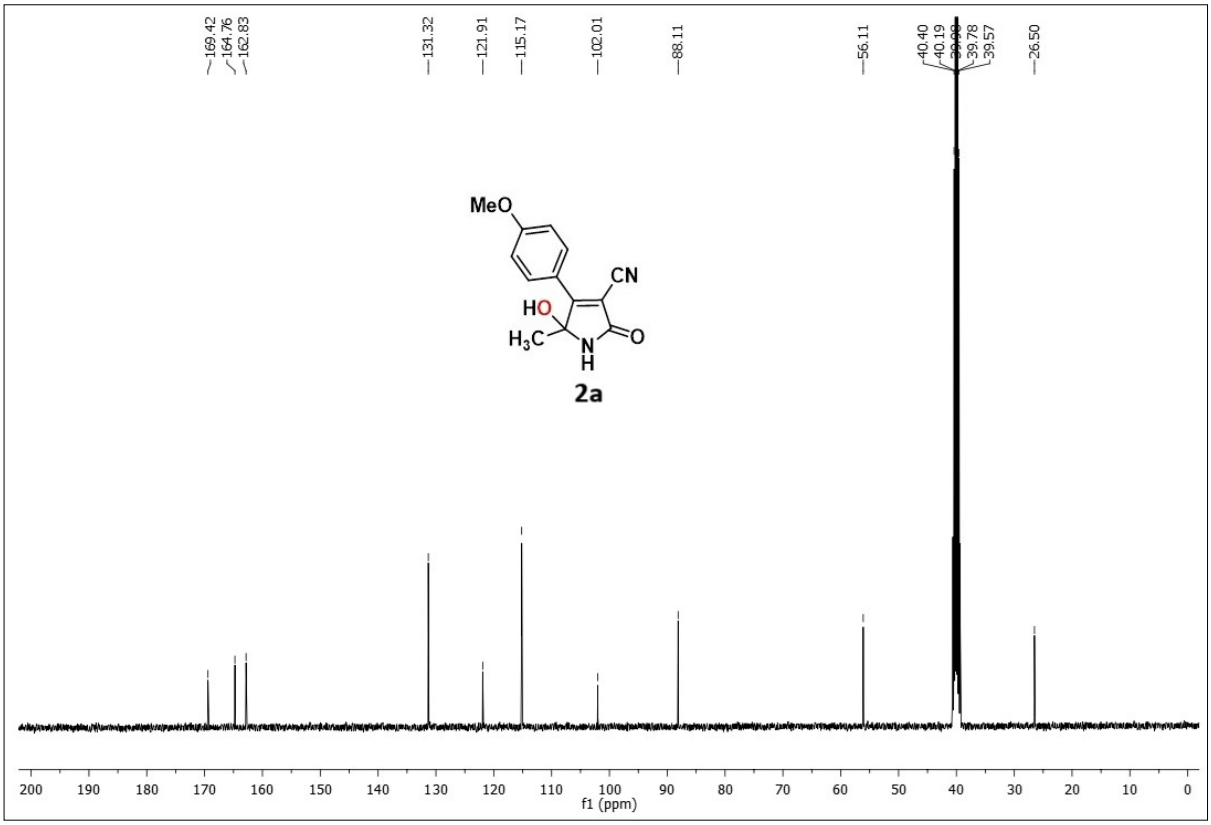
5-hydroxy-5-methyl-2-oxo-4-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1H-pyrrole-3-carbonitrile (2p): Synthesized following the general procedure taking 2-(1-(3-(trifluoromethyl)phenyl)propylidene)malononitrile (**1p**) (1 mmol, 250 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 30% EtOAc in hexane as eluent to afford the final product **2p**; yield 63% (178 mg); yellowish white solid; Mp: 148 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.39 (s, 1H), 8.32 (s, 1H), 8.26 (d, *J*= 8.0 Hz, 1H), 8.01 (d, *J*= 7.6 Hz, 1H), 7.89 (t, *J*= 8.0 Hz, 1H), 6.98 (s, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.4, 163.9, 132.9, 131.1, 130.6, 130.3, 130.0, 128.9, 125.6, 125.1, 125.0, 122.9, 113.9, 107.5, 88.2, 25.3; HRMS (ESI) m/z calcd. for $C_{13}H_9F_3N_2O_2$ $[M+H]^+$: 283.0689, but found 283.0695.

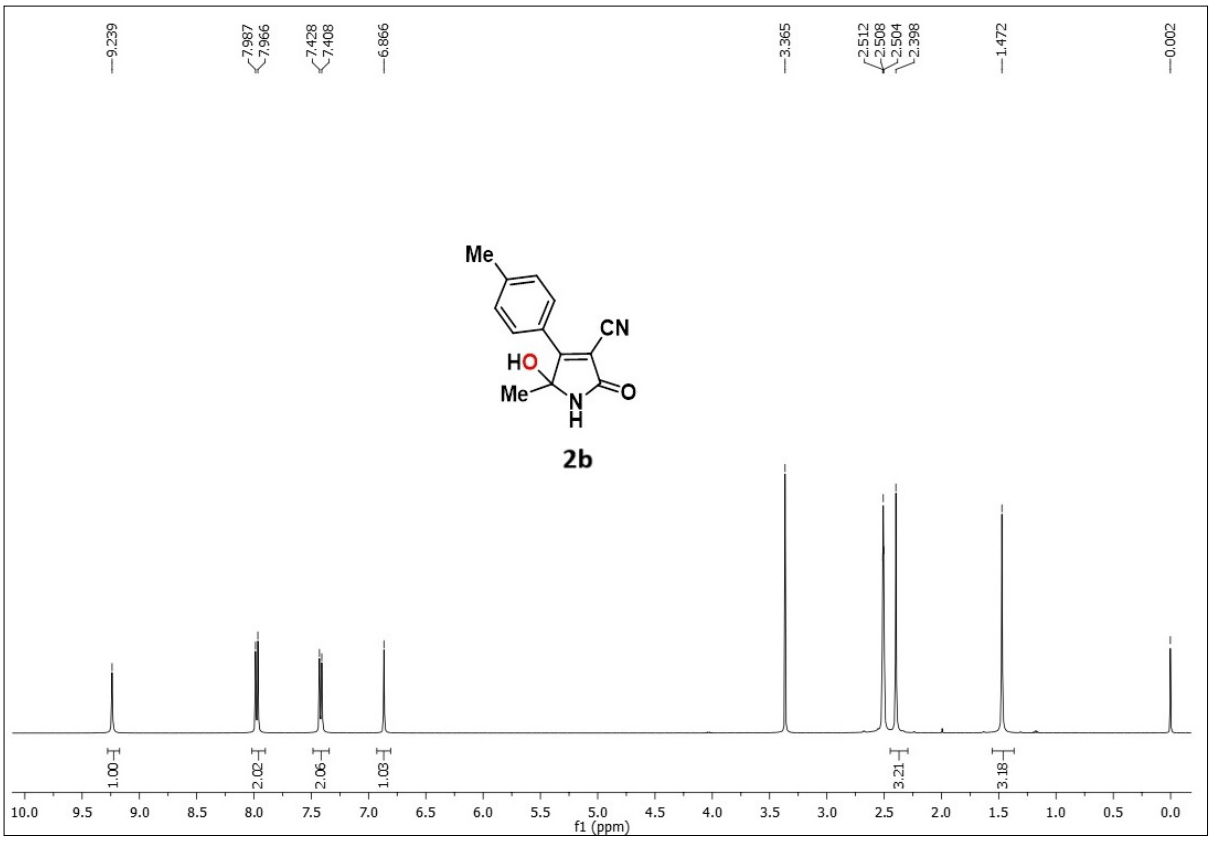


5-hydroxy-5-methyl-2-oxo-4-(thiophen-2-yl)-2,5-dihydro-1H-pyrrole-3-carbonitrile (2q): Synthesized following the general procedure taking 2-(1-(thiophen-2-yl)propylidene)malononitrile (**1q**) (1 mmol, 188 mg), TEMPO (2 mmol, 312 mg), and CuI (0.10 mmol, 19 mg). The compound was purified by silica gel column chromatography using 30% EtOAc in hexane as eluent to afford the final product **2q**; yield 73% (161 mg); white solid; Mp: 180 °C ($CHCl_3$/EtOAc 1:1 v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.21 (s, 1H), 8.16 (dd, *J*= 5.2 Hz and *J*= 1.2 Hz, 1H), 8.02 (dd, *J*= 3.6 Hz and *J*= 1.2 Hz, 1H), 7.39-7.37 (m, 1H), 6.89 (s, 1H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.5, 164.1, 135.5, 134.2, 131.2, 129.4, 114.8, 100.0, 87.7, 27.3; HRMS (ESI) m/z calcd. for $C_{10}H_8N_2O_2S$ [M+H]+: 221.0379, but found 221.0384.

G. Copy of ^{1}H NMR and ^{13}C NMR spectra for 2a-2q



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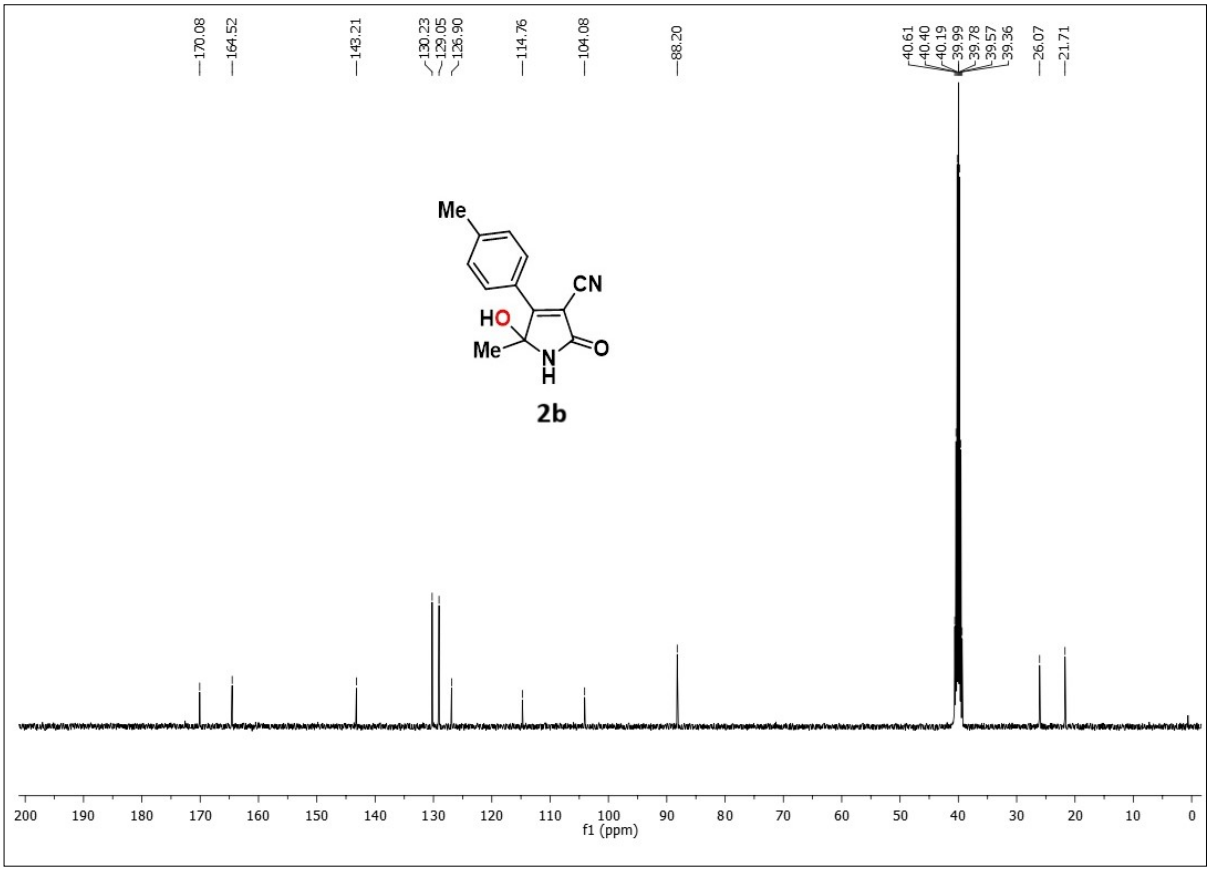
0.002
Me
CN
HO
Me
N
H
O
2b
1.00
2.02
2.06
1.03
3.21
3.18
f1 (ppm)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104.08
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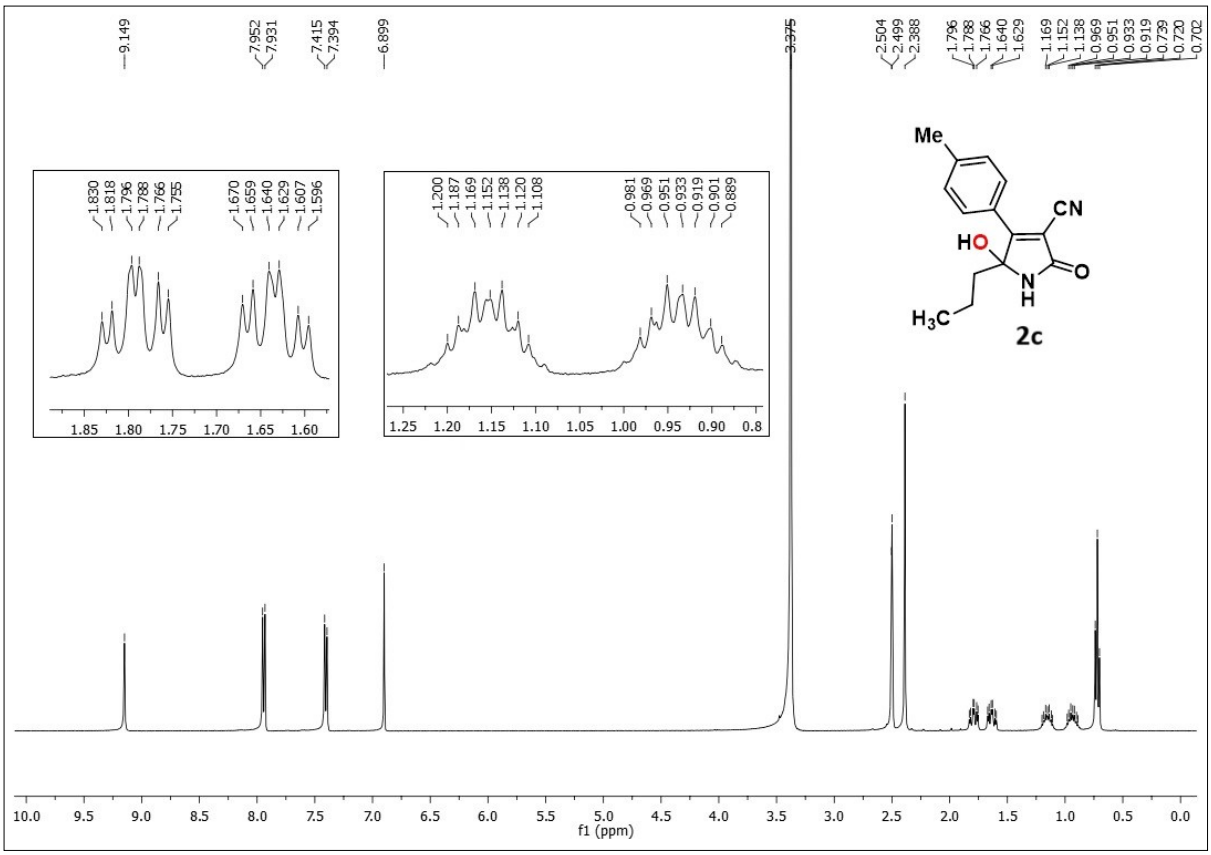
39.36
26.07
21.71
Me
CN
HO
Me
N
H
O
2b
f1 (ppm)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1.766
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0.951
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0.919
0.739
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0.702
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1.796
1.788
1.766
1.755
1.670
1.659
1.640
1.629
1.607
1.596
1.200
1.187
1.169
1.152
1.138
1.120
1.108
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0.969
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0.919
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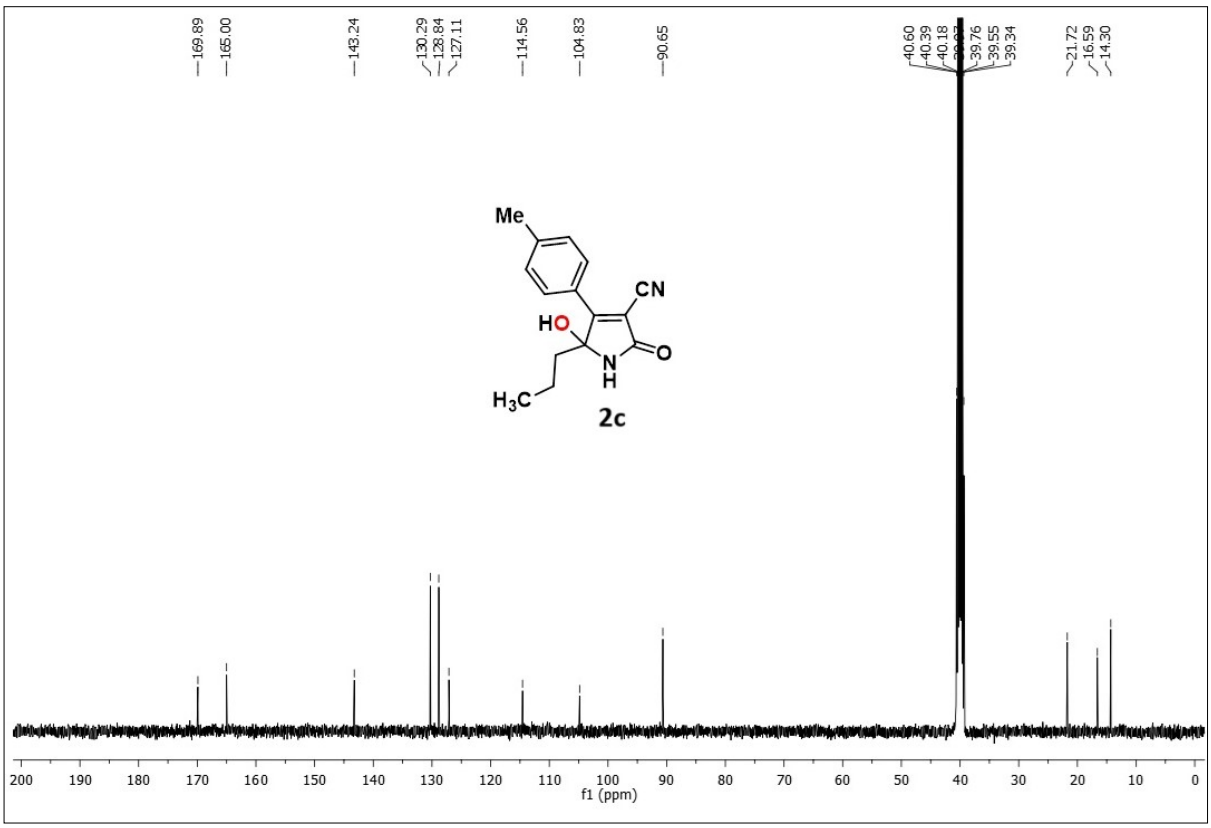
CN
HO
O
N
H
H3C
2c
f1 (ppm)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127.11
114.56
104.83
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40.60
40.39
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39.97
39.76
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CN
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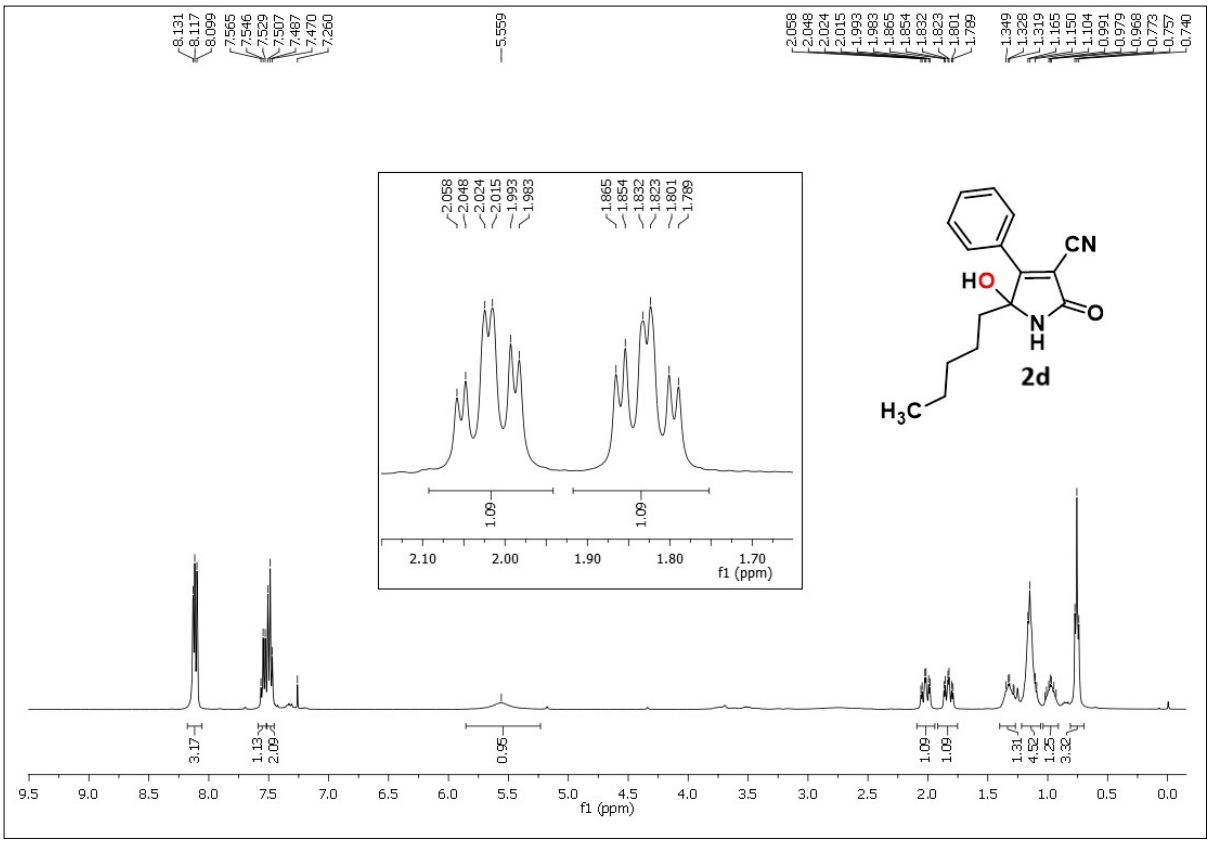
O
N
H
H3C
2c
f1 (ppm)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1.319
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HO
O
N
H
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H3C
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1.09
2.10
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f1 (ppm)
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0.95
1.09
1.09
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1.25
3.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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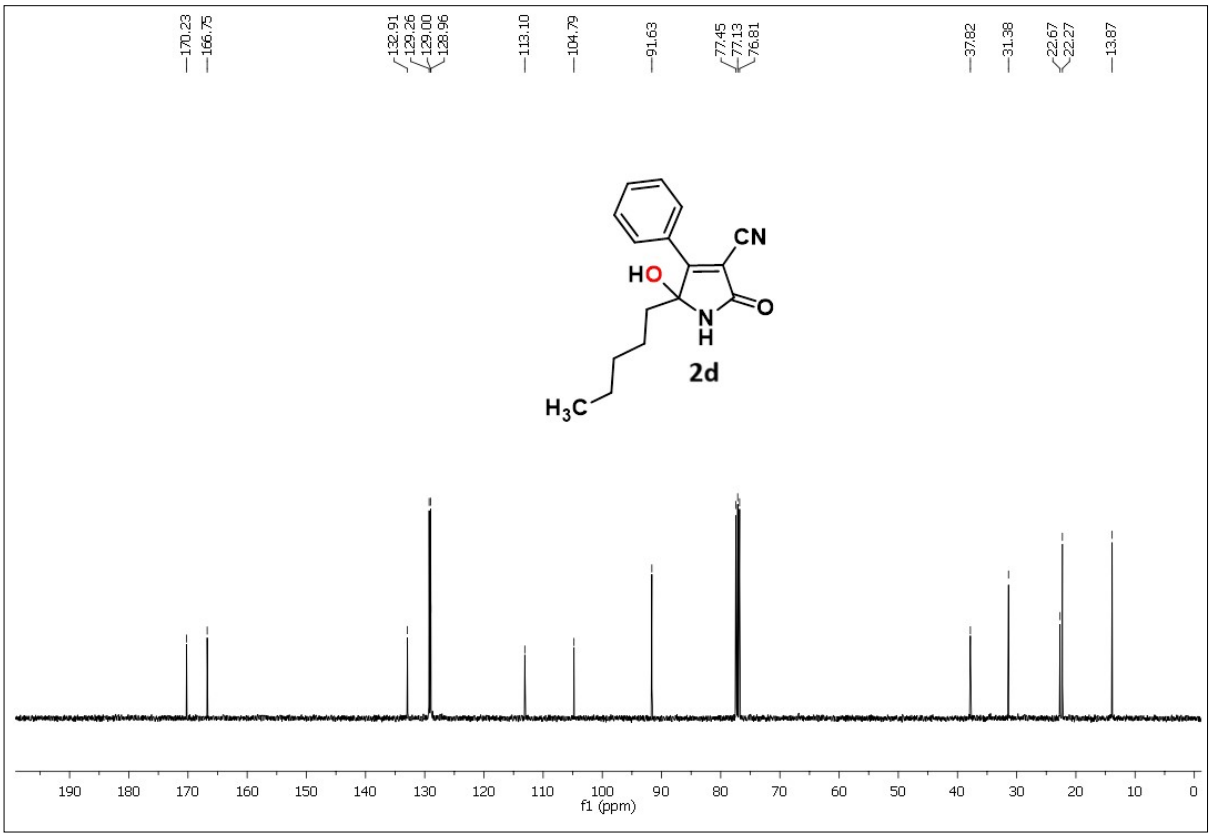
1.5
1.0
0.5
0.0
f1 (ppm)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22.67
22.27
13.87
CN
HO
O
N
H
2d
H3C
190
180
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120
110
100
90
80
70
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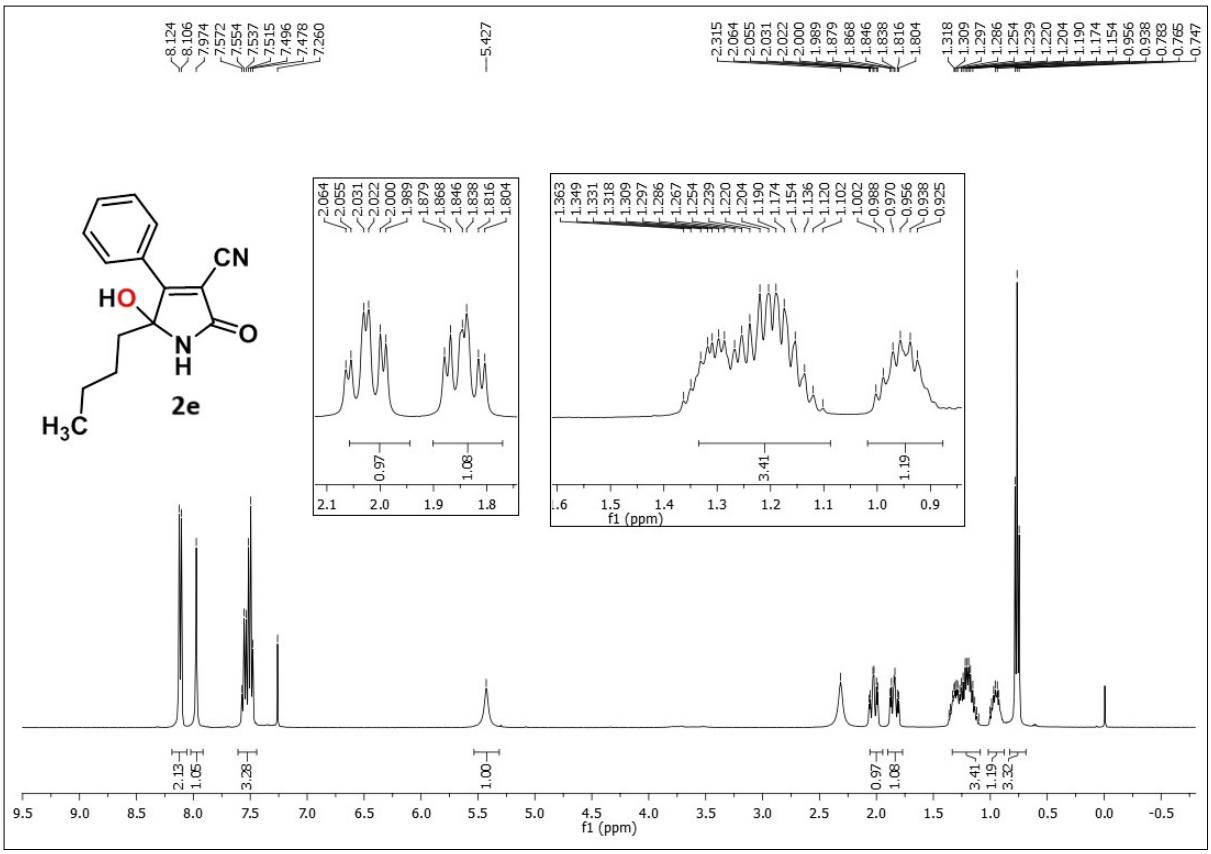
50
40
30
20
10
0
f1 (ppm)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1.297
1.286
1.254
1.239
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1.204
1.190
1.174
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0.765
0.747
CN
HO
N
H
O
2e
H3C
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1.19
f1 (ppm)
2.13
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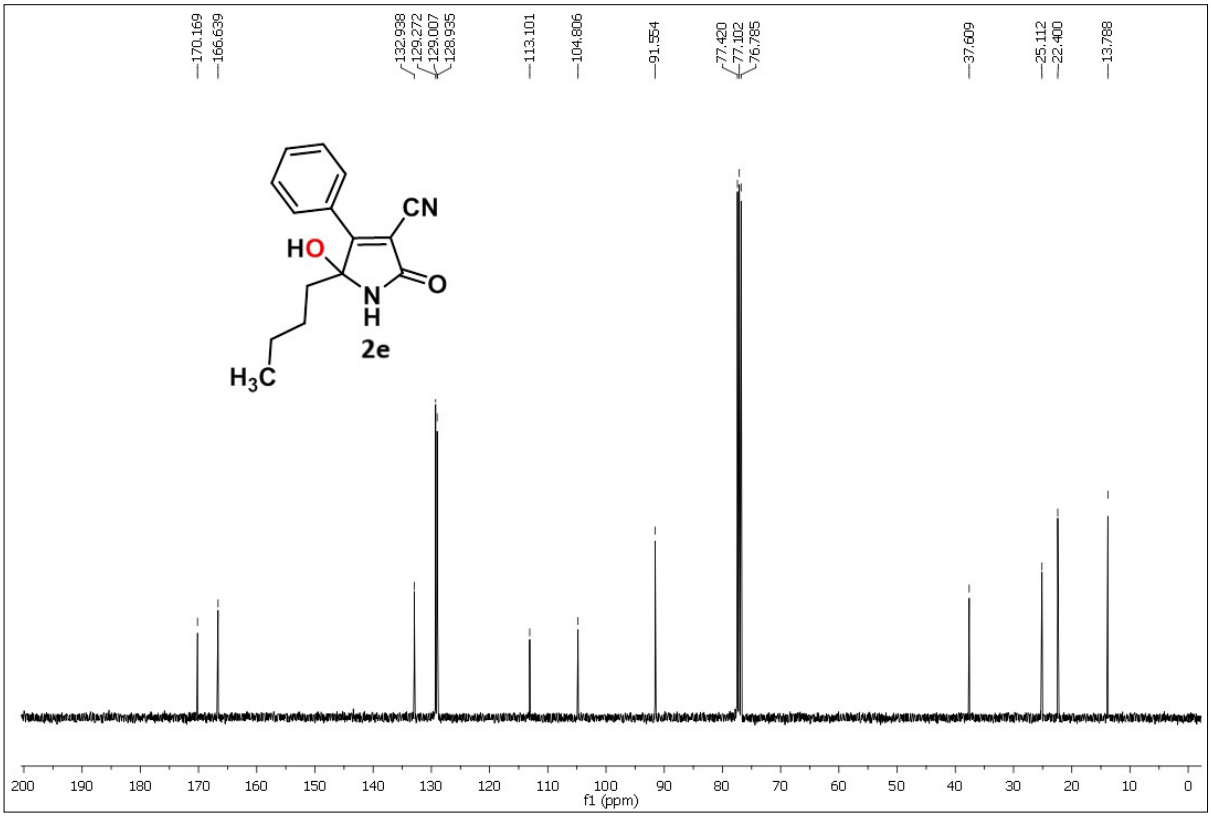
3.28
1.00
3.32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N
H
O
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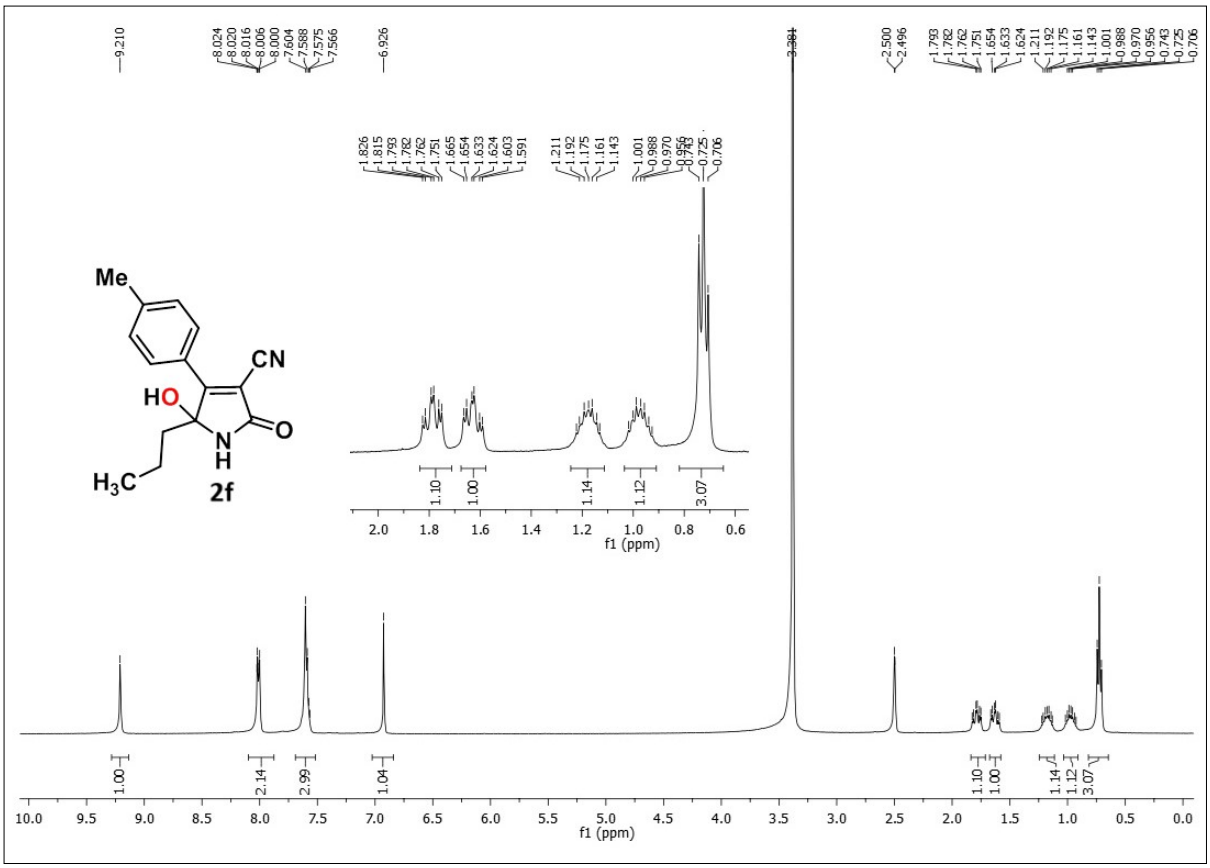
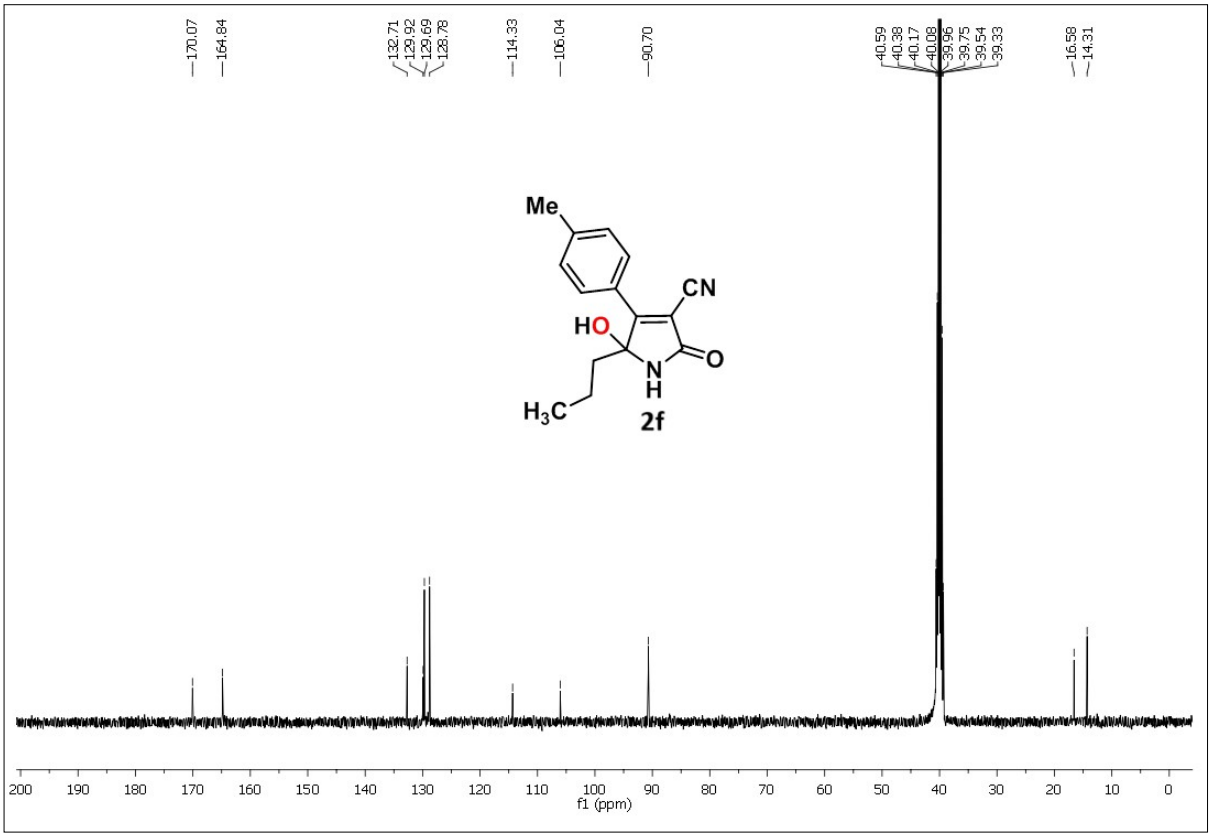
H3C
f1 (ppm)


Me
CN
HO
O
N
H
H3C
2f
f1 (ppm)


Me
CN
HO
O
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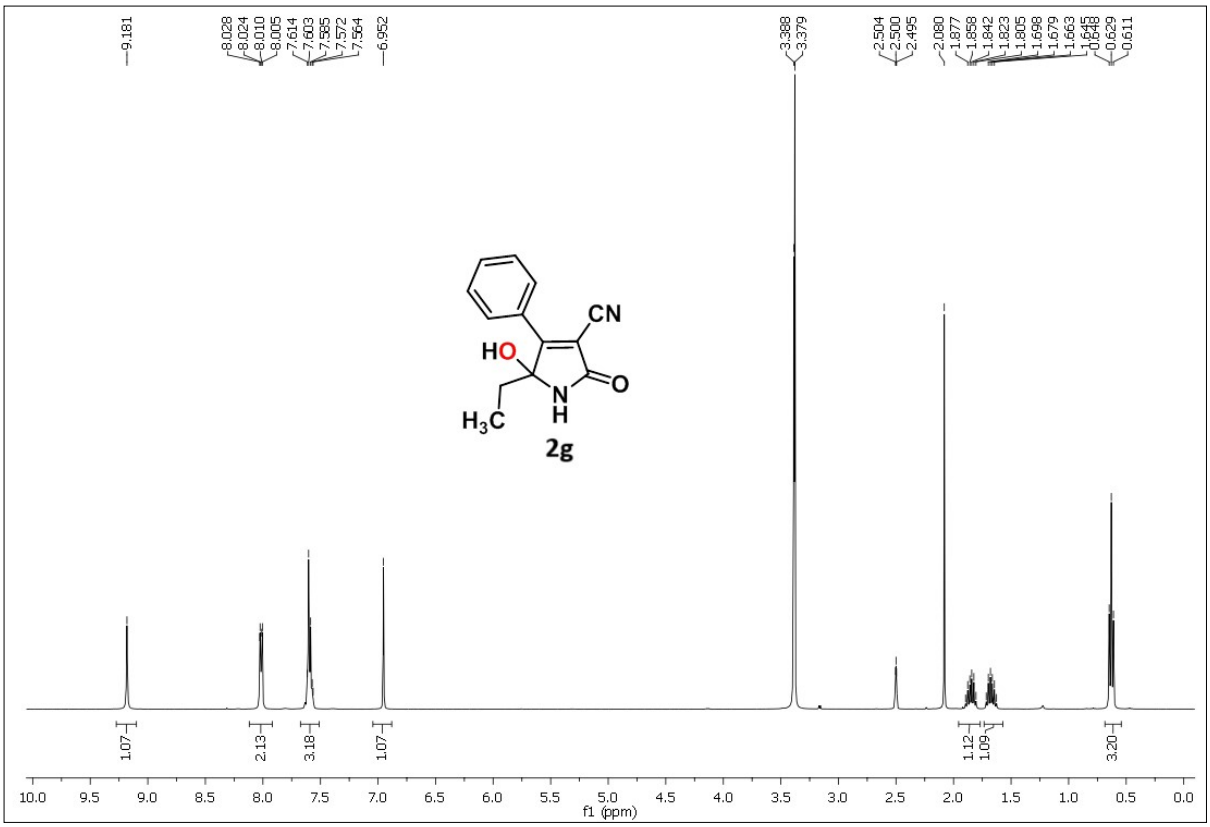
H
H3C
2f
f1 (ppm)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2.495
2.080
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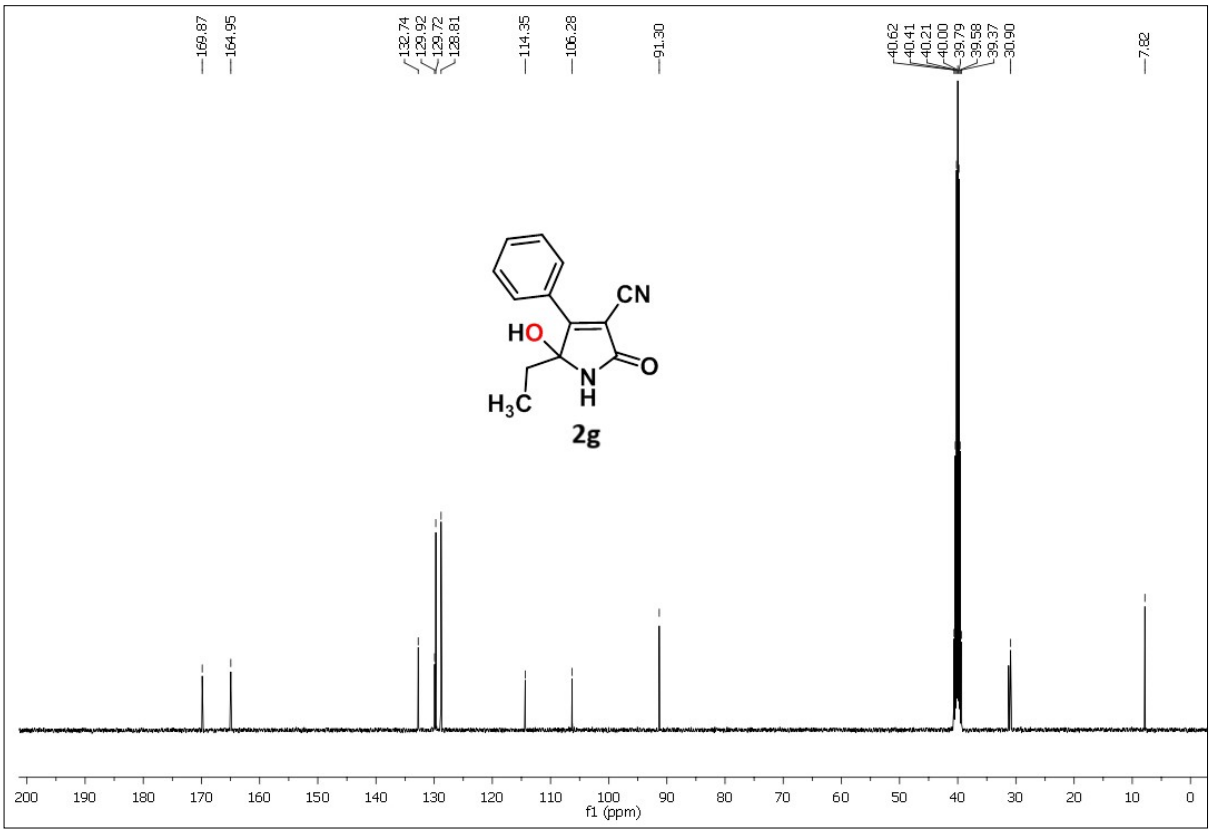
1.858
1.842
1.823
1.805
1.698
1.679
1.663
0.629
0.611
CN
HO
O
N
H
H3C
2g
1.07
2.13
3.18
1.07
1.12
1.09
3.20
f1 (ppm)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106.28
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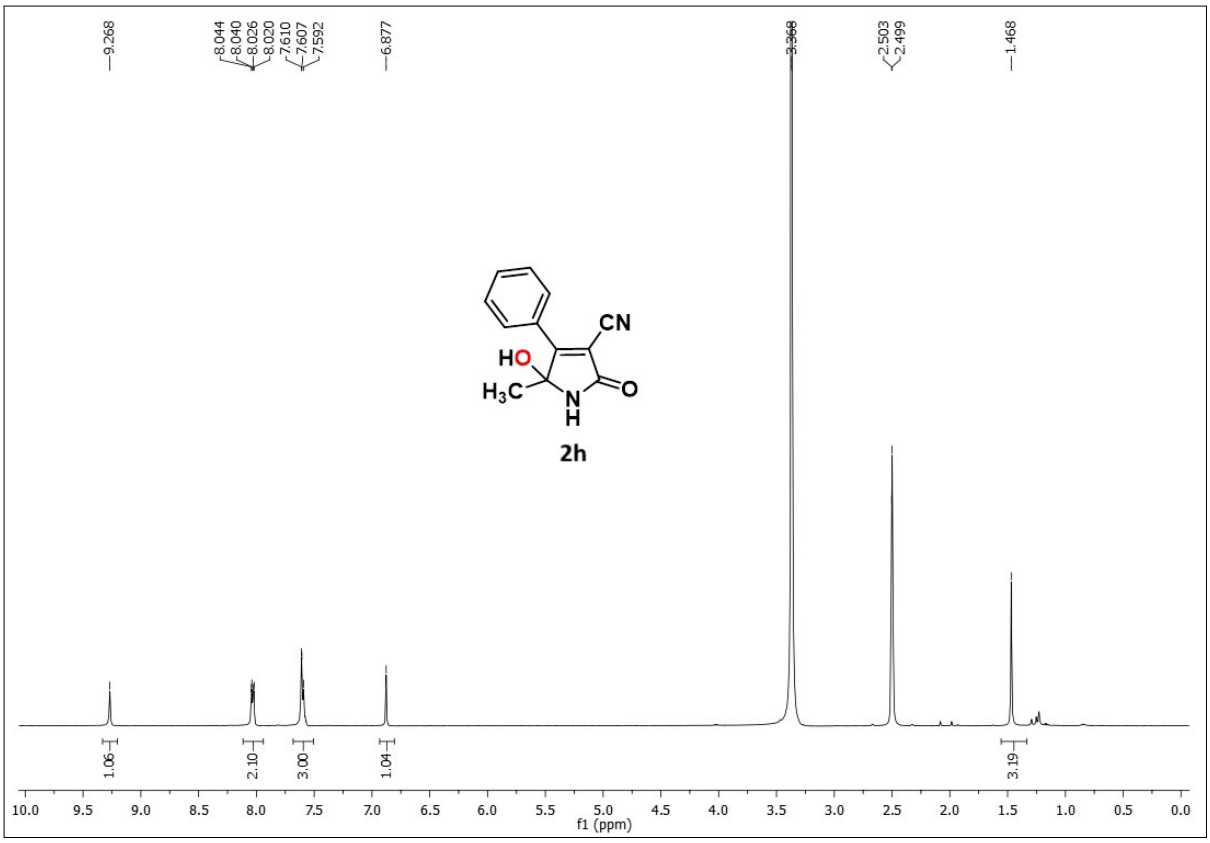
HO
O
N
H
H3C
2g
f1 (ppm)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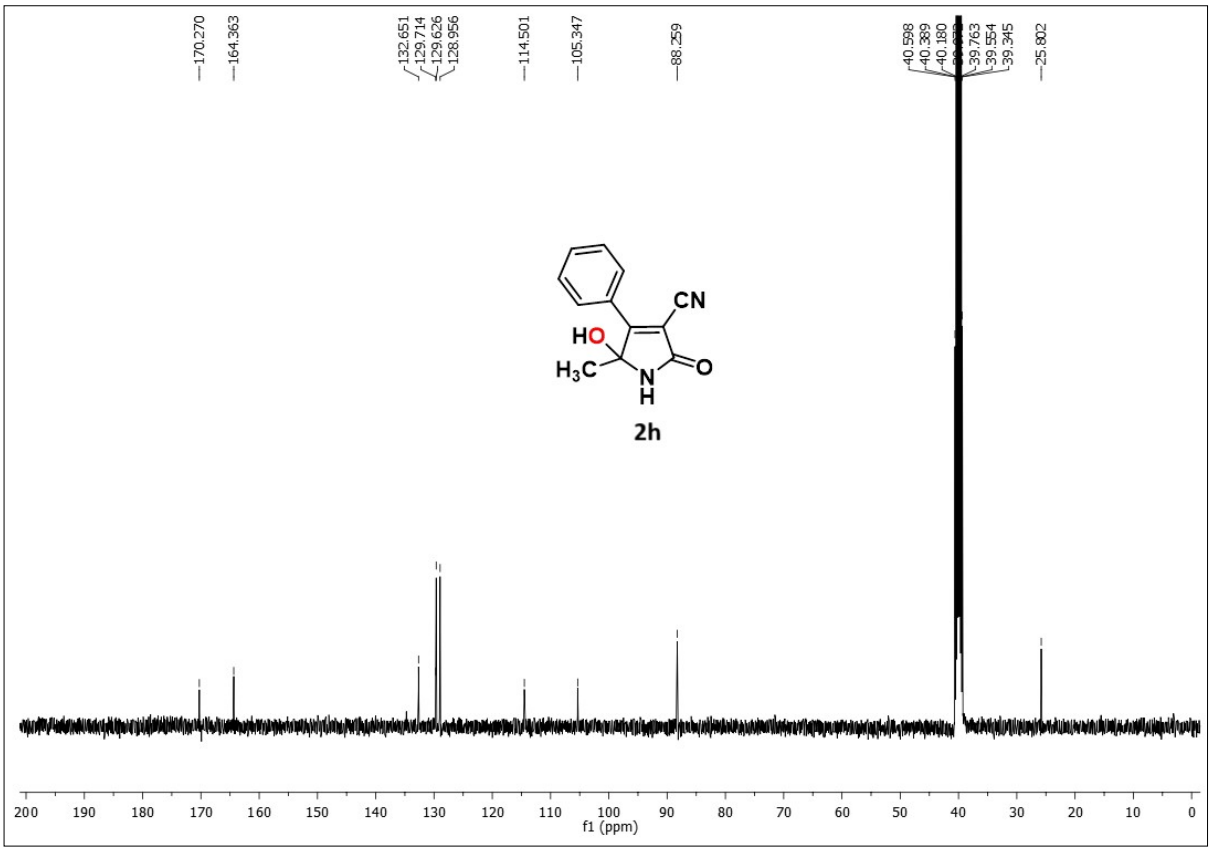
HO
H3C
N
H
O
2h
1.06
2.10
3.00
1.04
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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39.763
39.554
39.345
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H3C
N
H
O
2h
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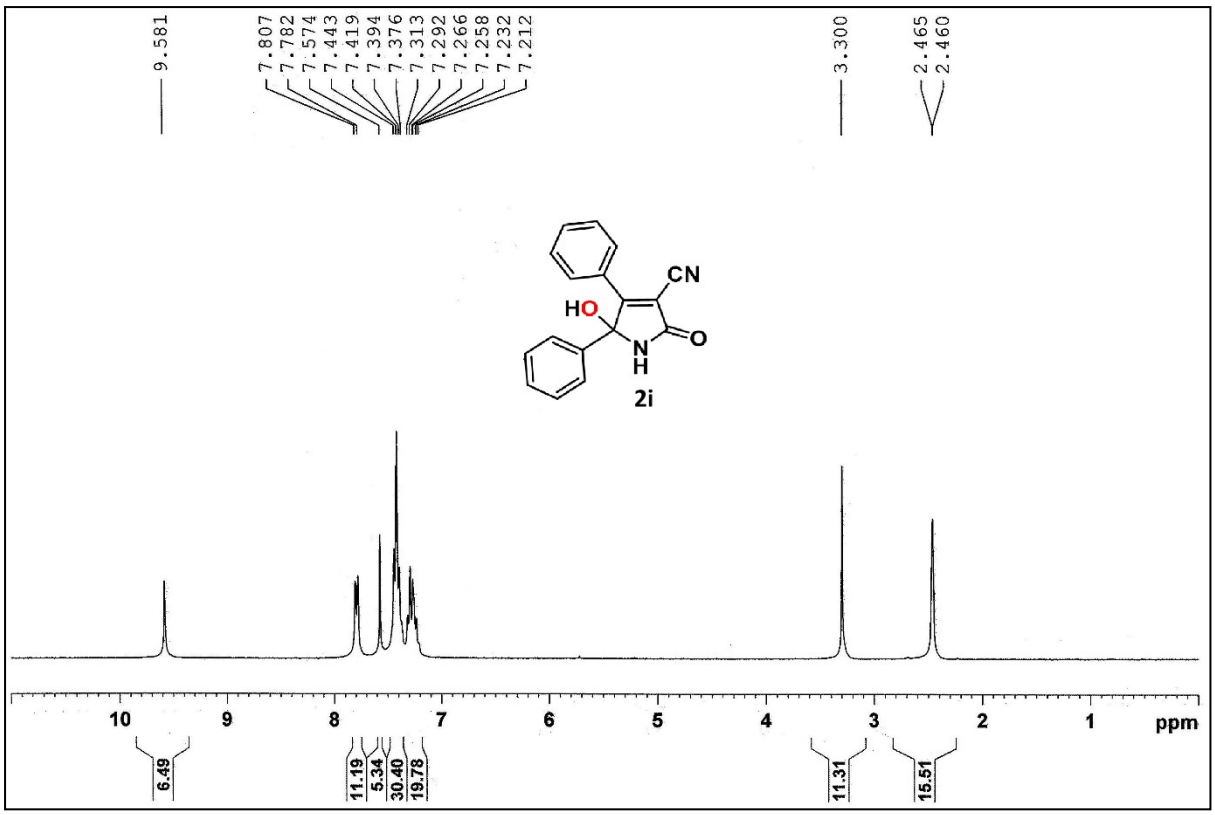
f1 (ppm)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7.376
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7.258
7.232
7.212
3.300
2.465
2.460
CN
HO
N
H
O
2i
10
9
8
7
6
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3
2
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ppm
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5.34
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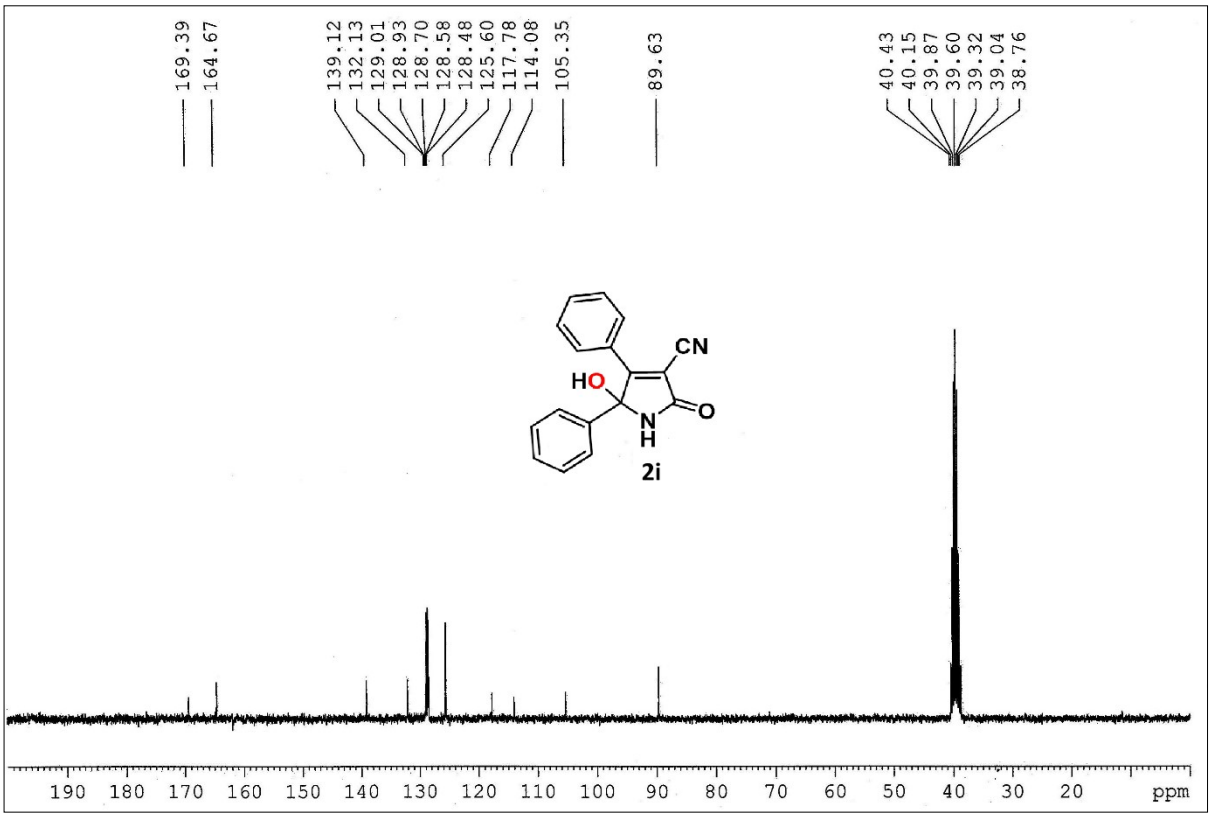
19.78
11.31
15.51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40.43
40.15
39.87
39.60
39.32
39.04
38.76
CN
HO
N
H
O
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150
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120
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80
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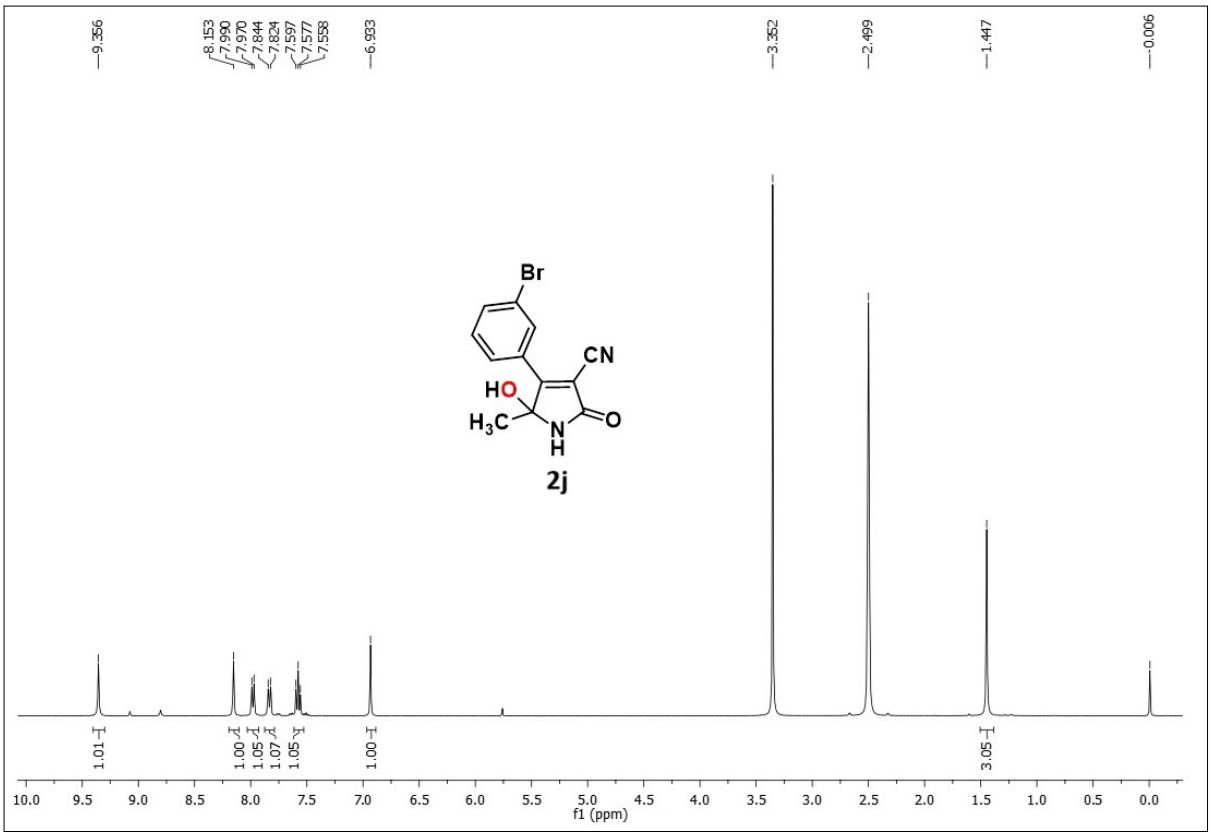
20
ppm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7.577
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2.499
1.447
0.006
Br
CN
HO
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O
2j
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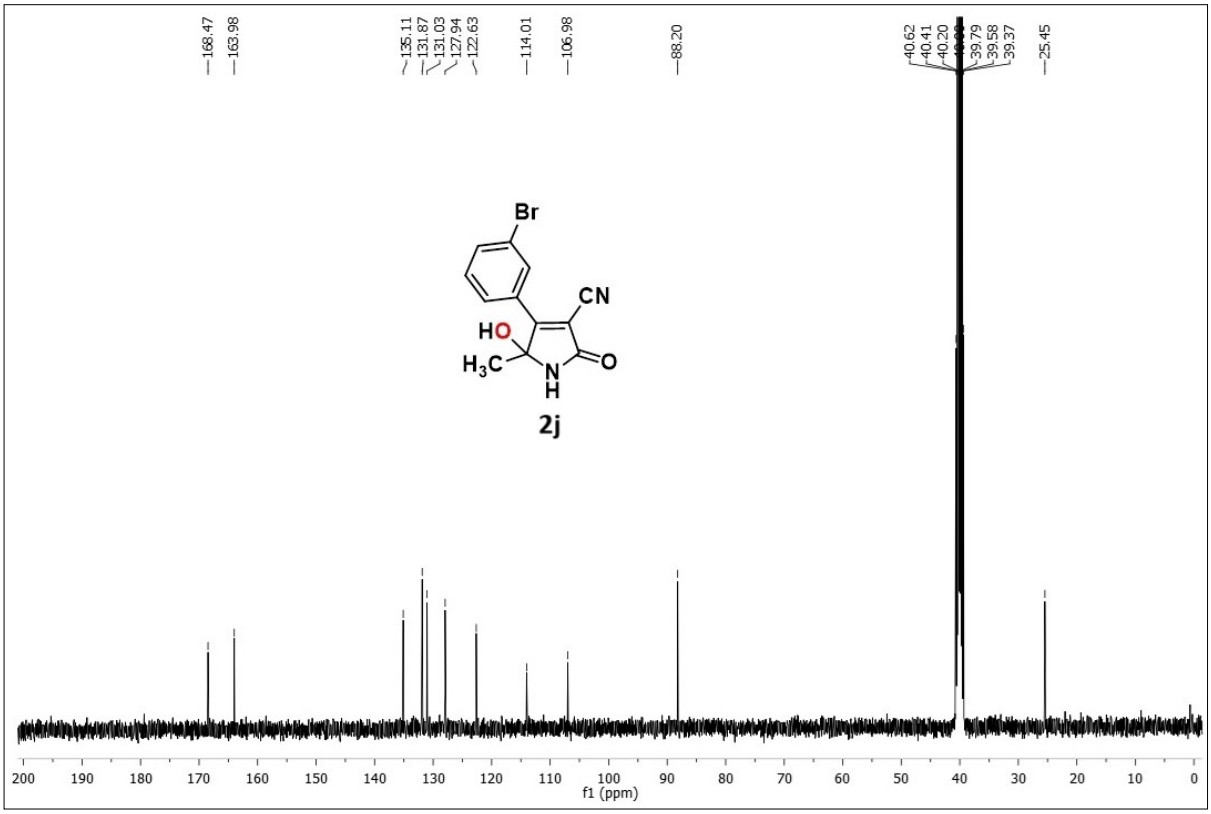
1.00
1.05
1.07
1.05
1.00
3.05
f1 (ppm)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HO
H3C
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H
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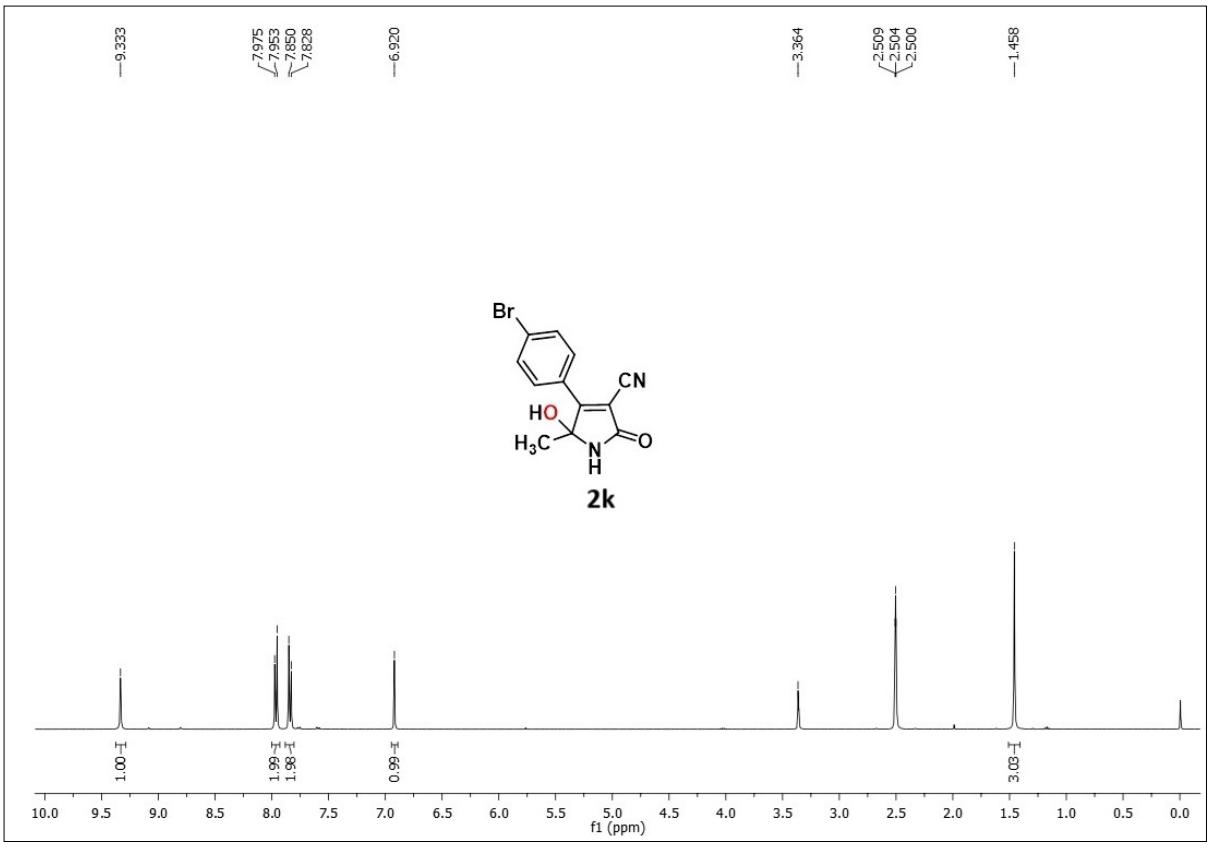
2j
f1 (ppm)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N
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O
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1.99
1.98
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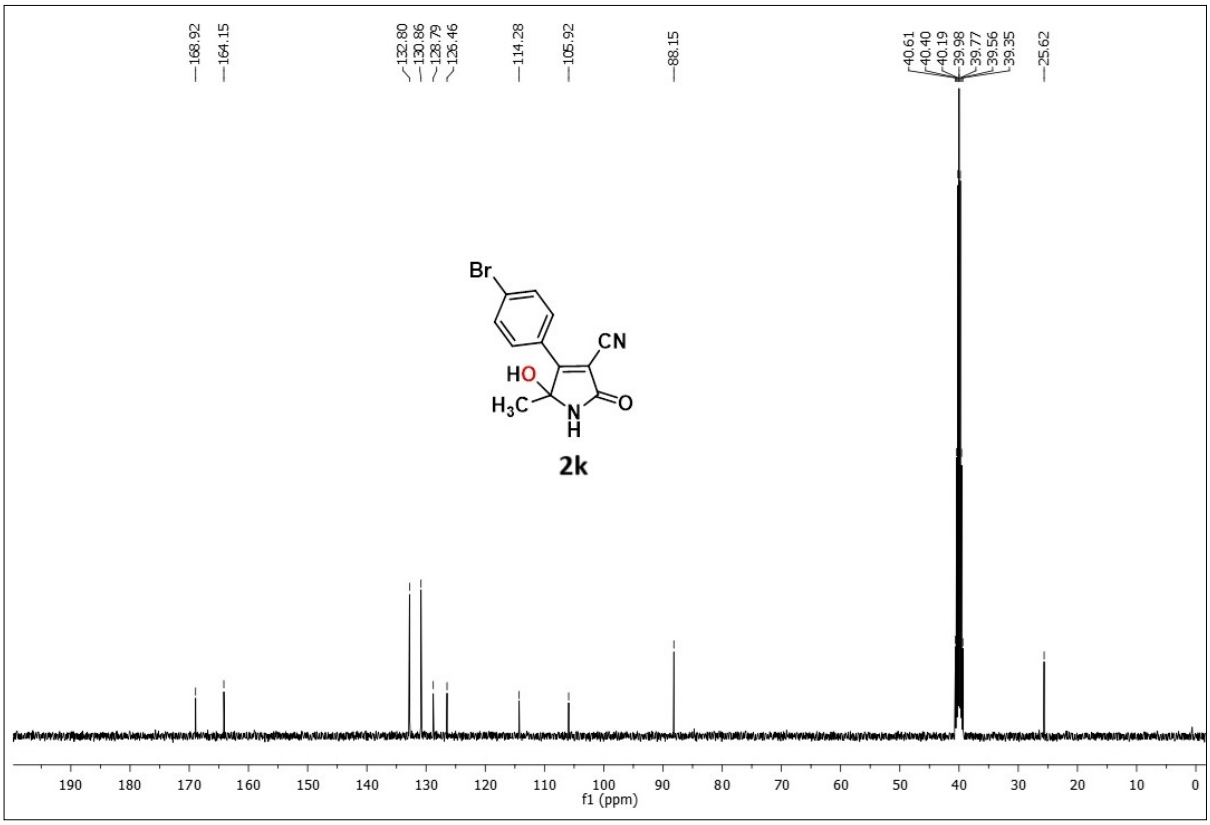
3.03
f1 (ppm)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40.40
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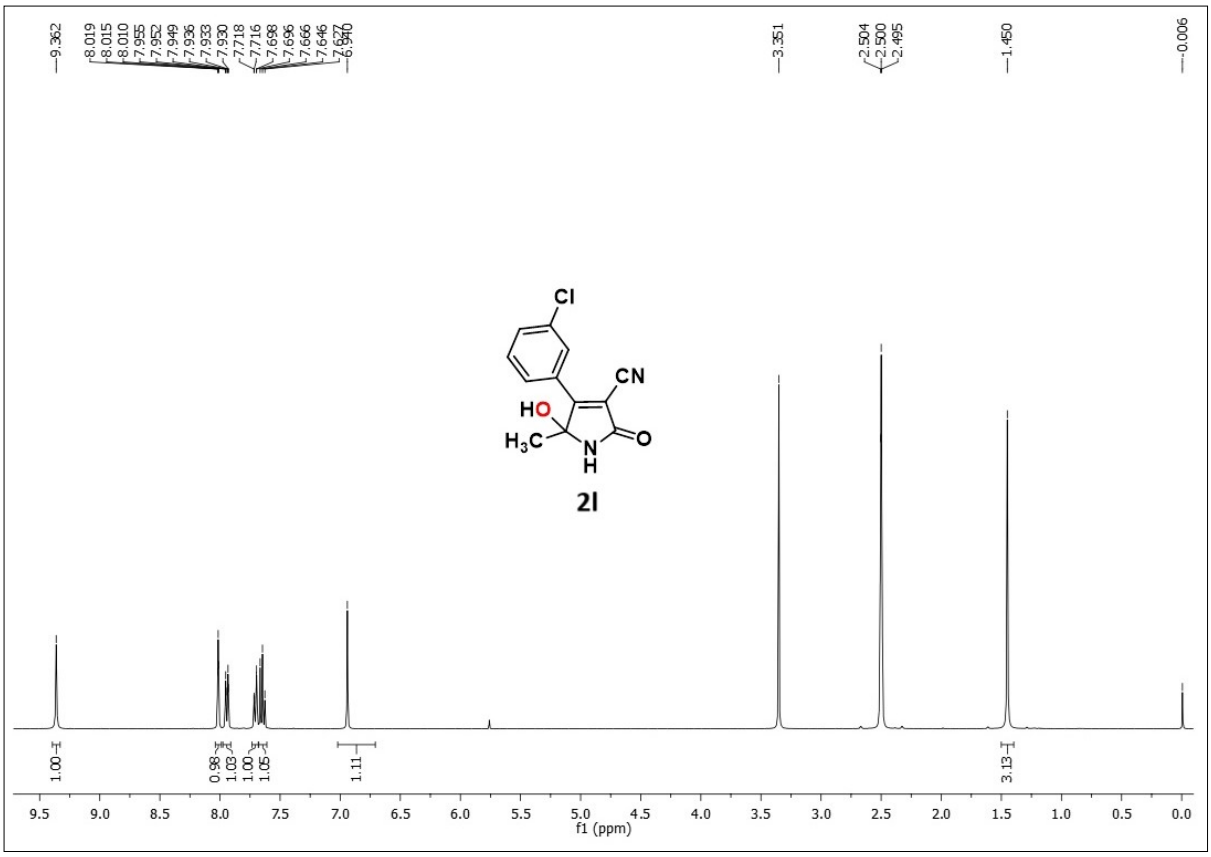
CN
HO
H3C
N
H
O
2k
f1 (ppm)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7.949
7.936
7.933
7.930
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7.716
7.698
7.696
7.666
7.646
7.627
6.940
3.351
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2.500
2.495
1.450
0.006
Cl
CN
HO
H3C
N
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O
2l
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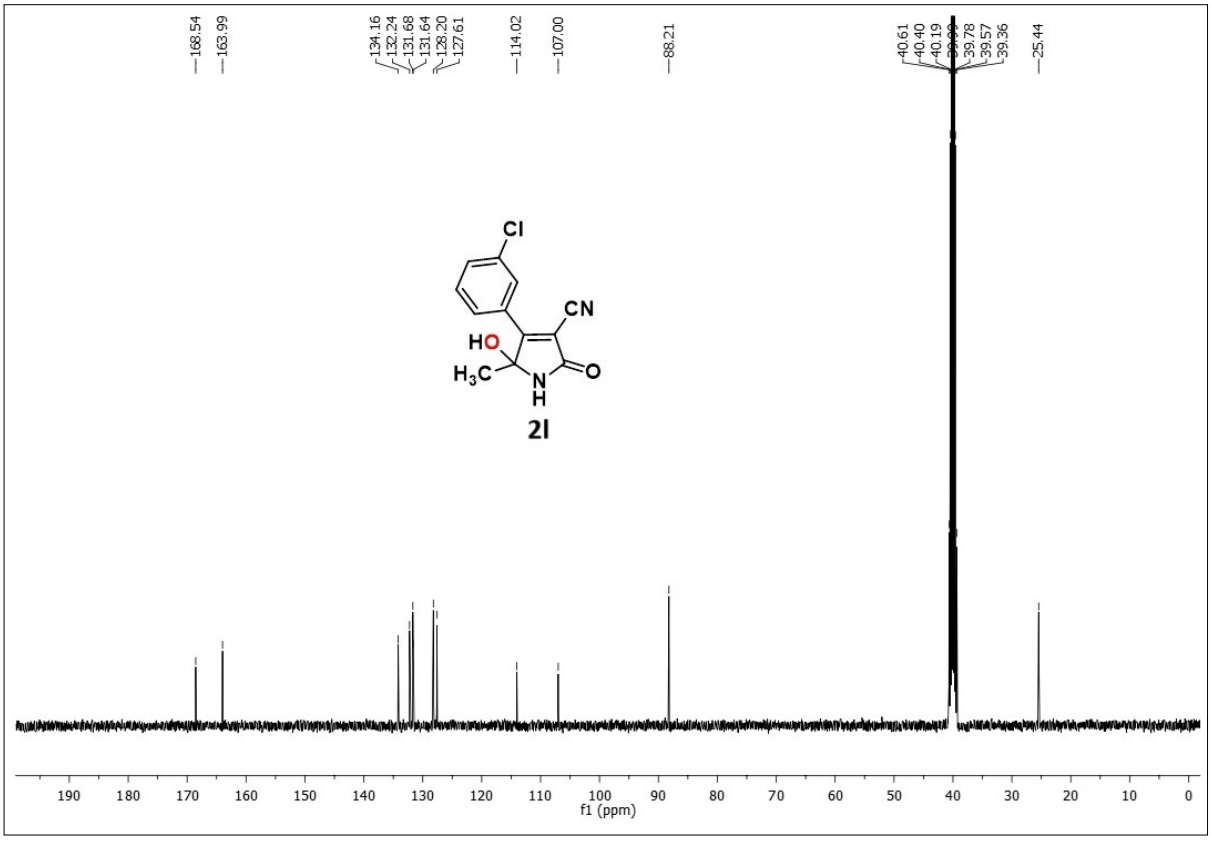
1.00
1.05
1.11
3.13
f1 (ppm)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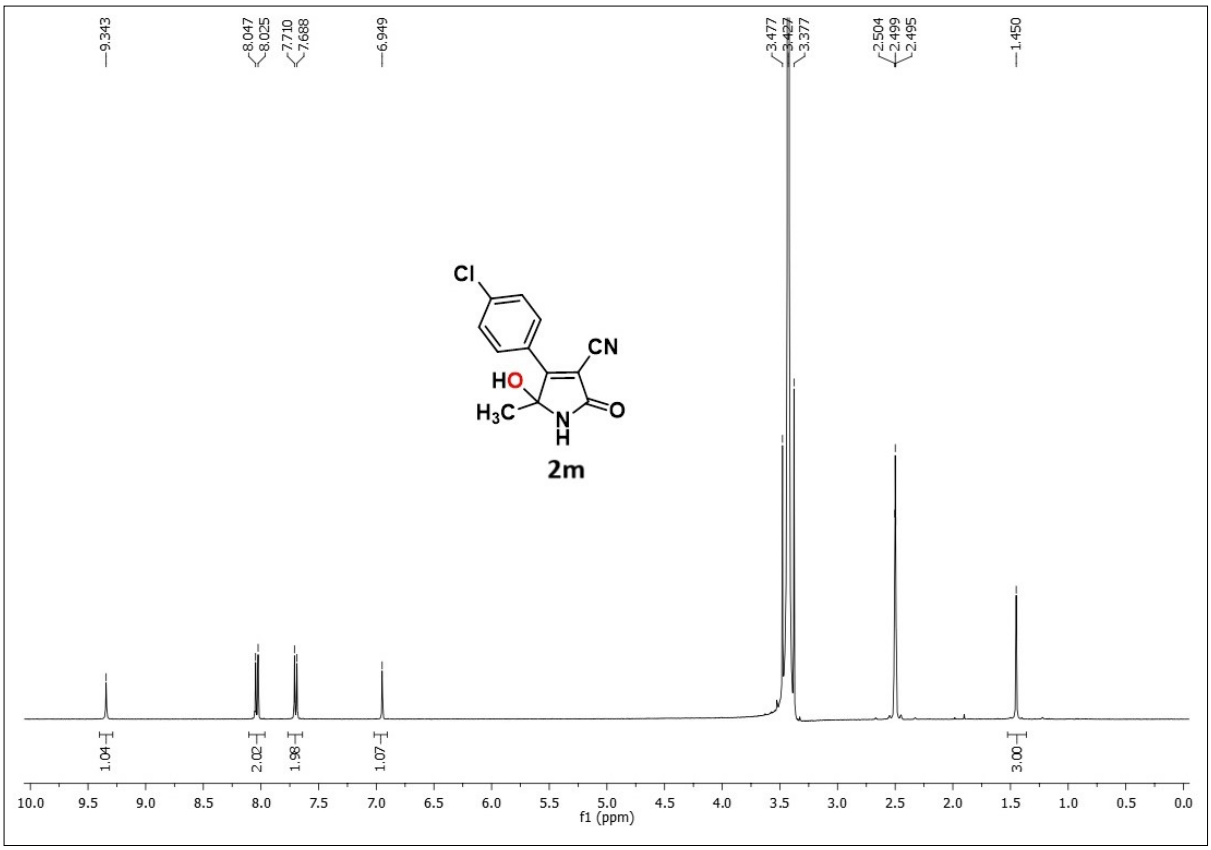
HO
H3C
N
H
O
2l
f1 (ppm)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N
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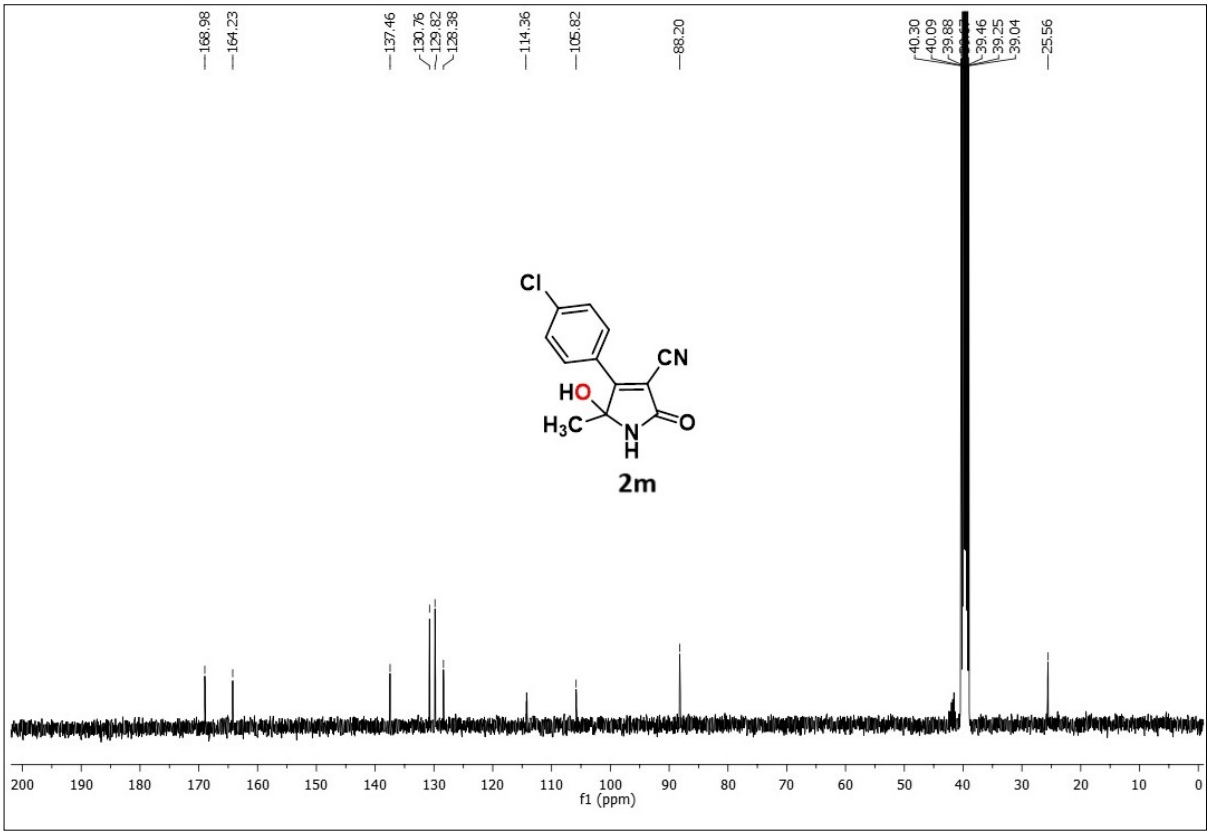
3.00
f1 (ppm)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105.82
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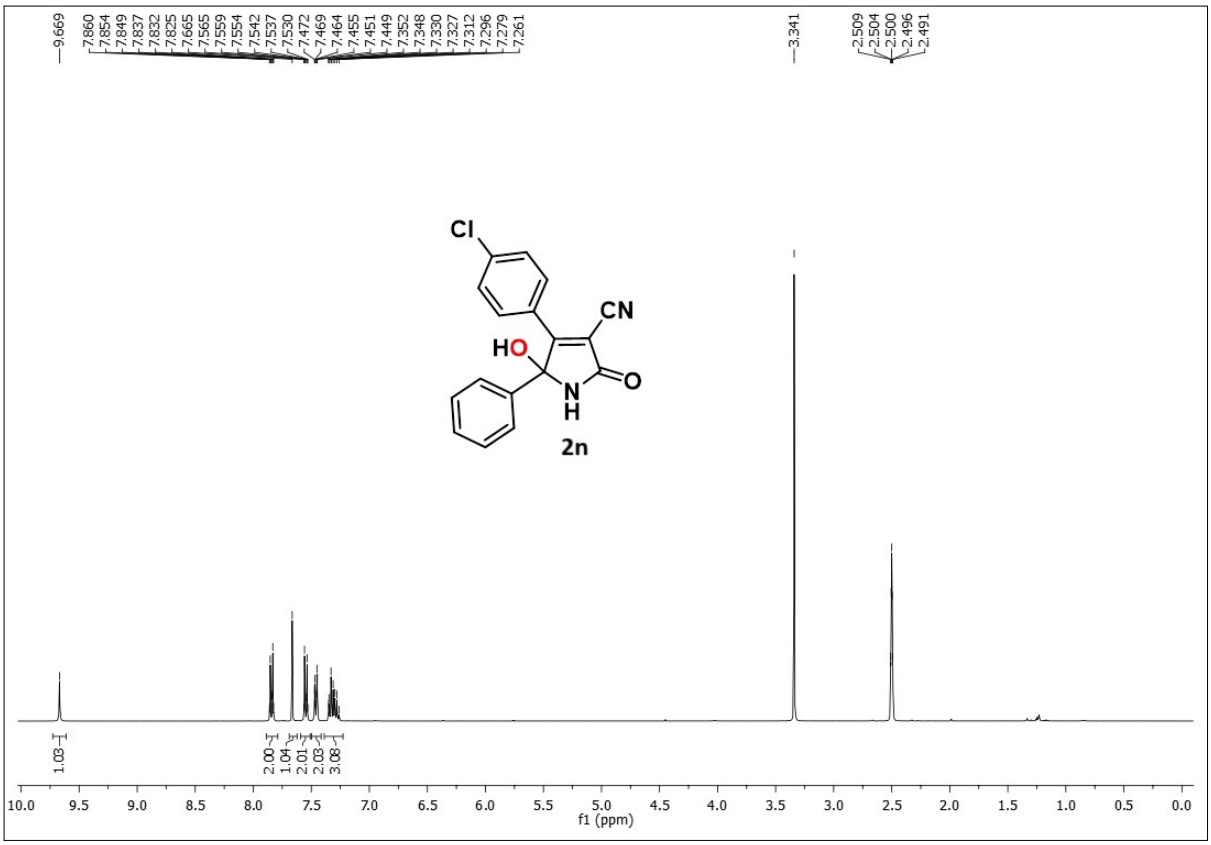
H3C
N
H
O
2m
f1 (ppm)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7.542
7.537
7.530
7.472
7.469
7.464
7.455
7.451
7.449
7.352
7.348
7.330
7.327
7.312
7.296
7.279
7.261
3.341
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2.504
2.500
2.496
2.491
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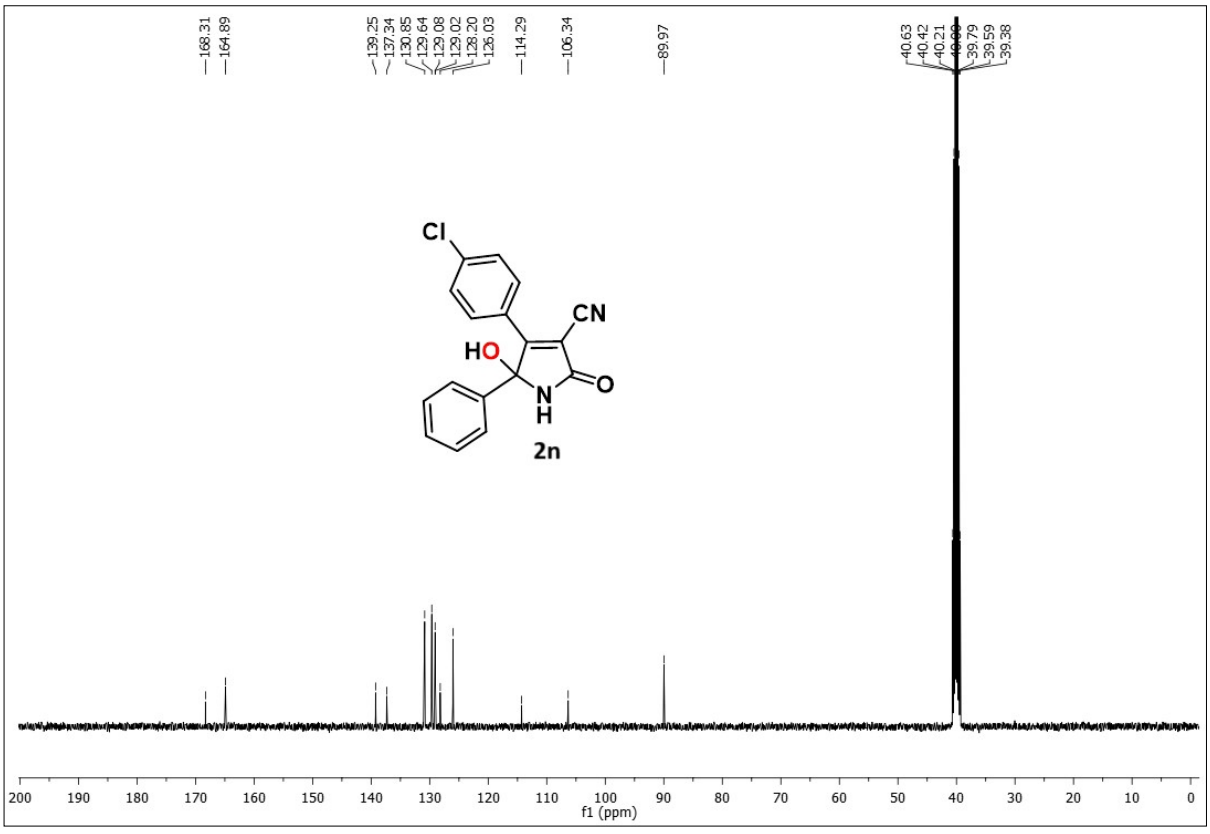
O
N
H
2n
1.03
2.00
1.04
2.01
2.03
3.08
f1 (ppm)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126.03
114.29
106.34
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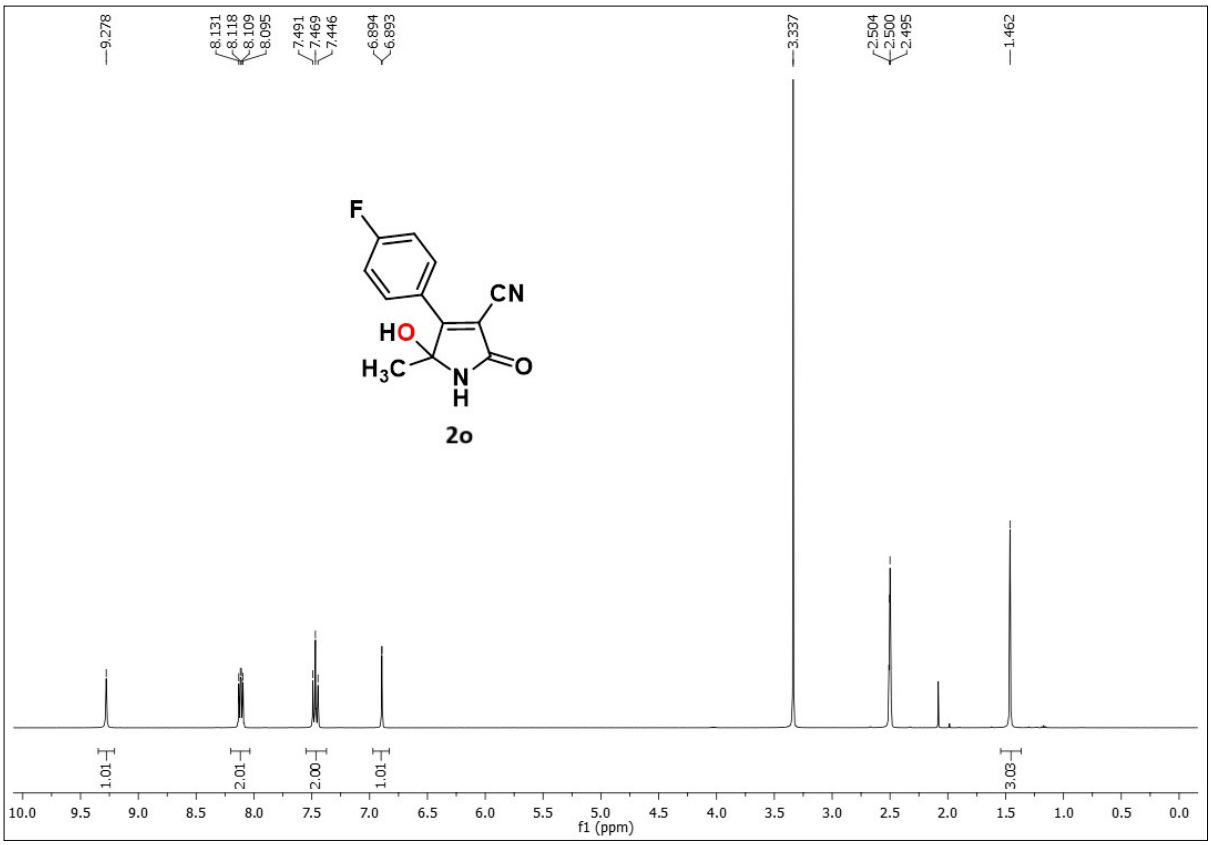
CN
HO
O
N
H
2n
f1 (ppm)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7.469
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6.893
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2.495
1.462
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HO
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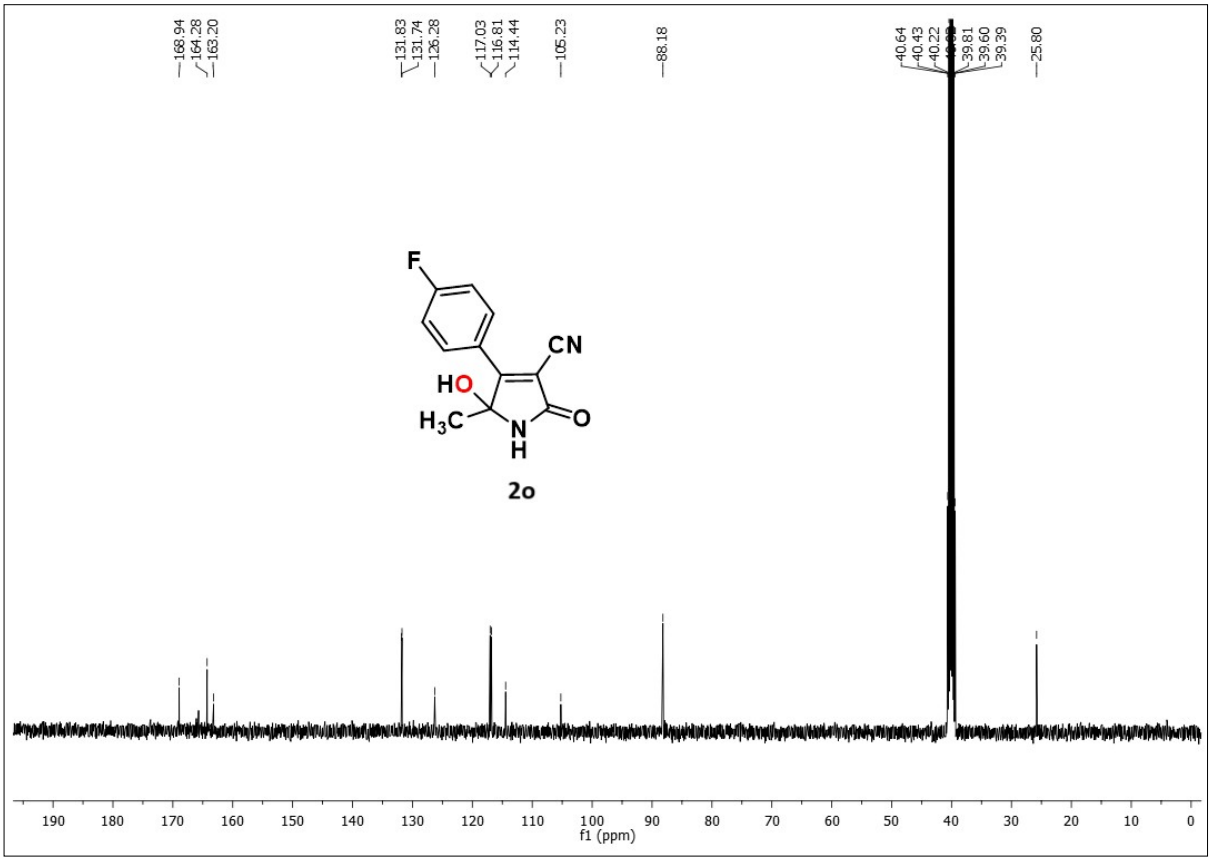
2.00
1.01
3.03
f1 (ppm)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H3C
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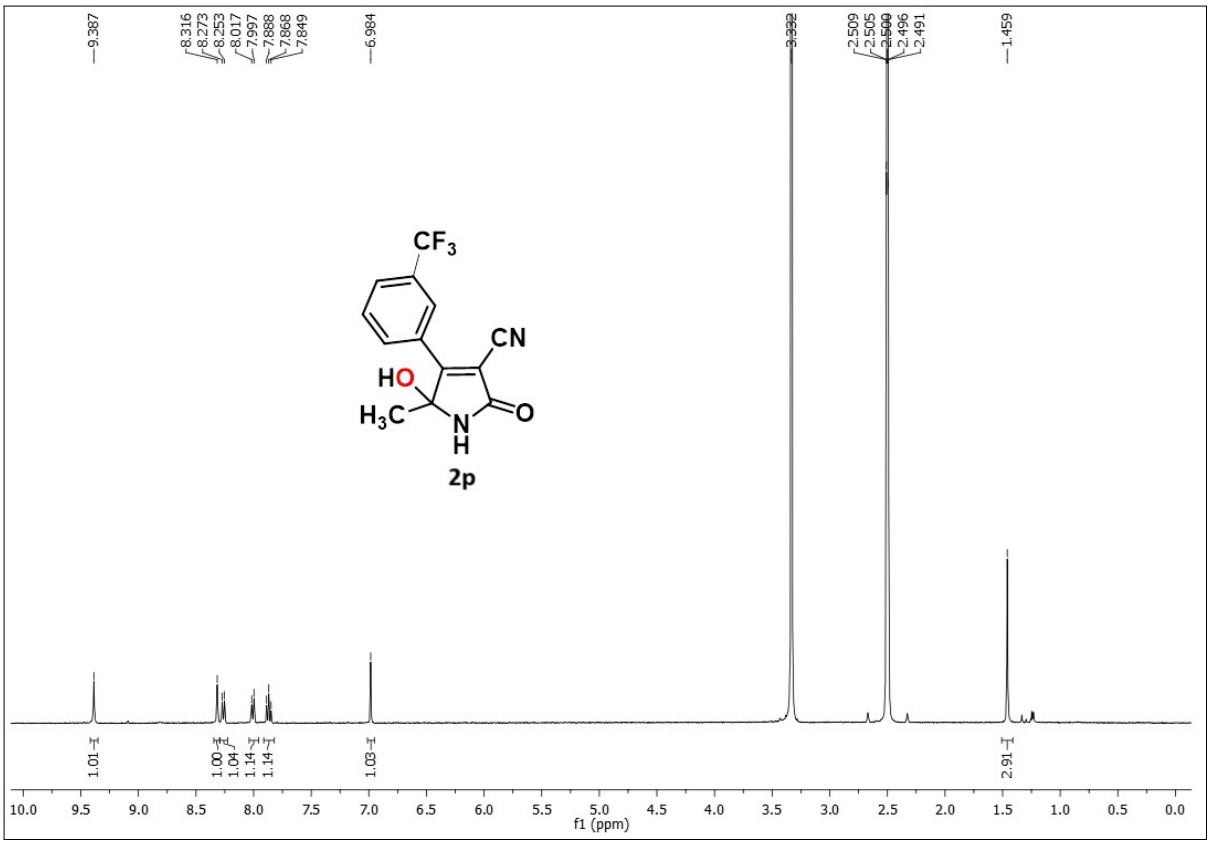
H
O
2o
f1 (ppm)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2.491
1.459
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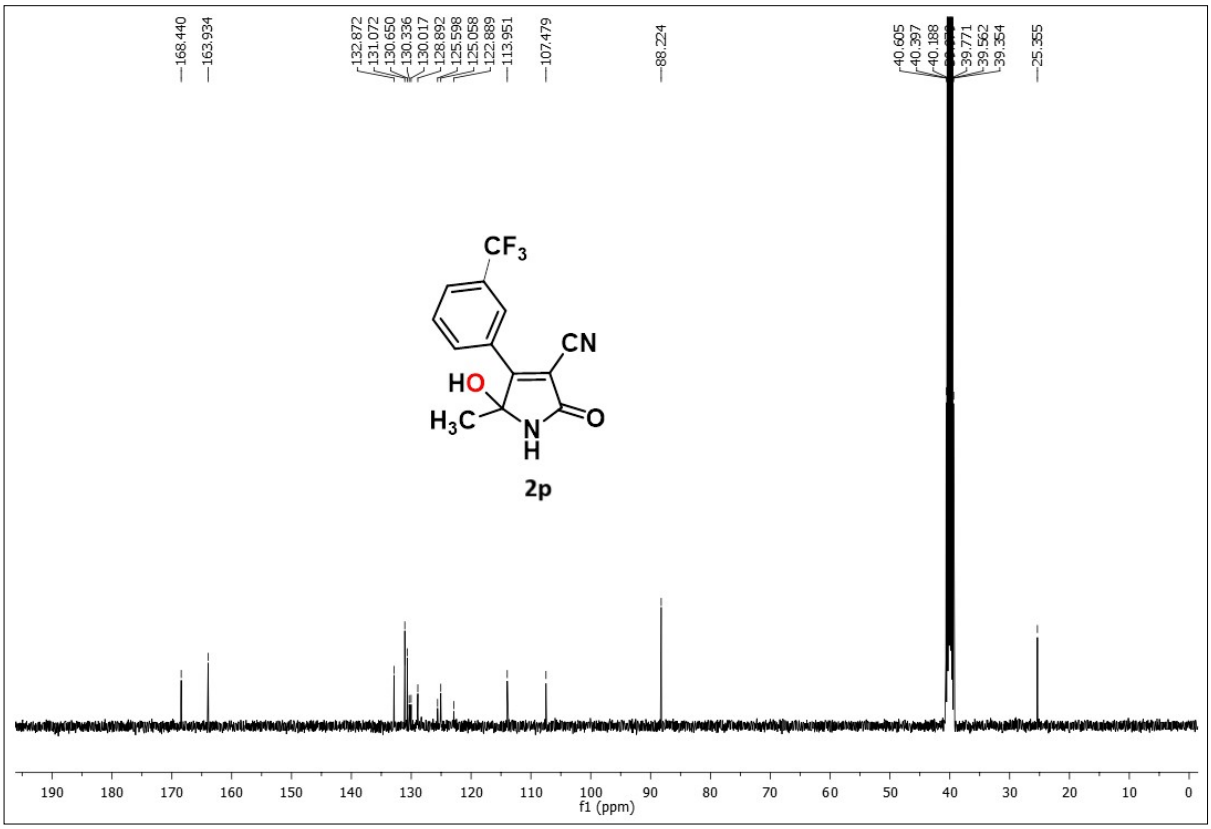
1.03
2.91
f1 (ppm)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H3C
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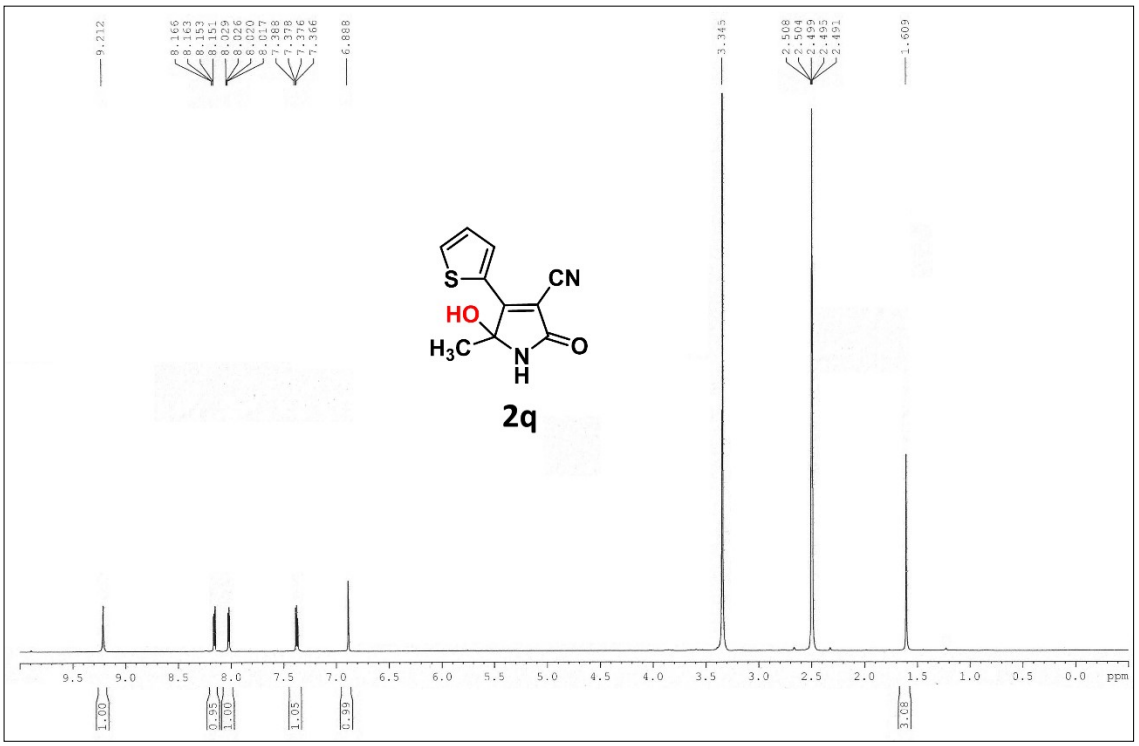
H
O
2p
f1 (ppm)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7.366
6.888
3.345
2.508
2.504
2.499
2.495
2.491
1.609
S
CN
HO
H3C
N
H
O
2q
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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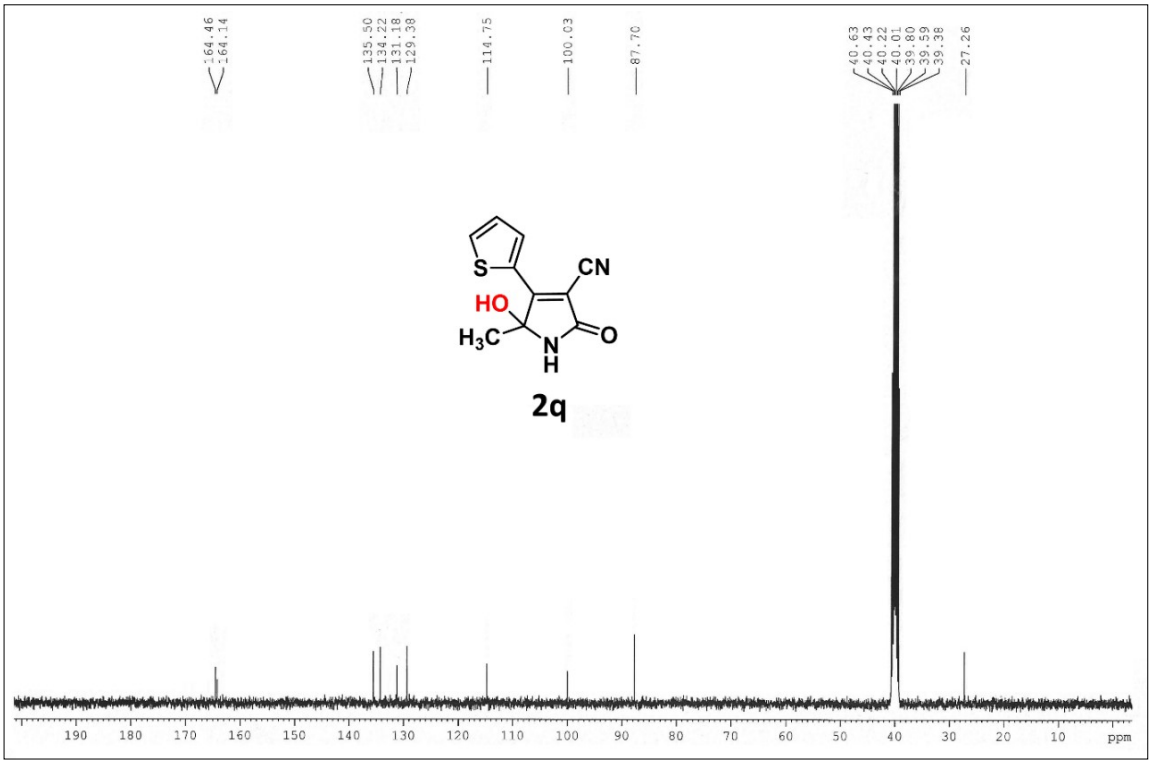
0.95
1.00
1.05
0.99
3.08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135.50
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131.18
129.38
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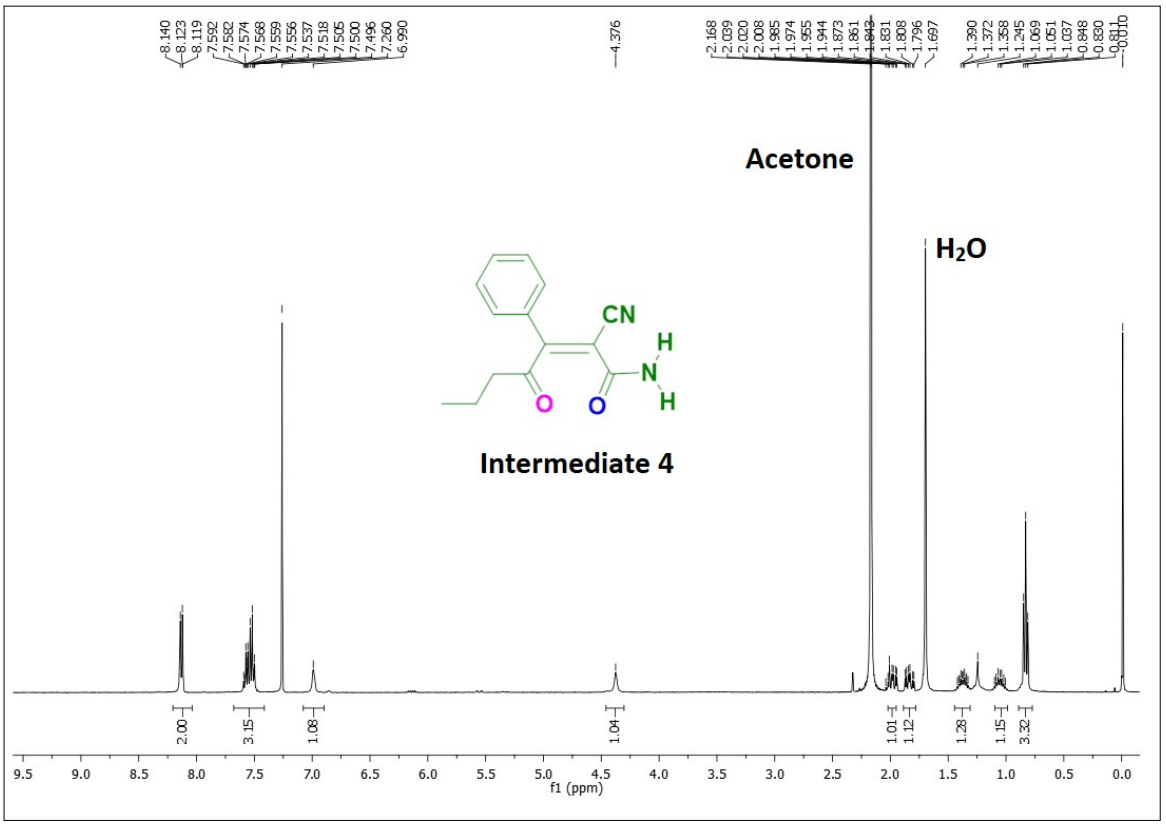
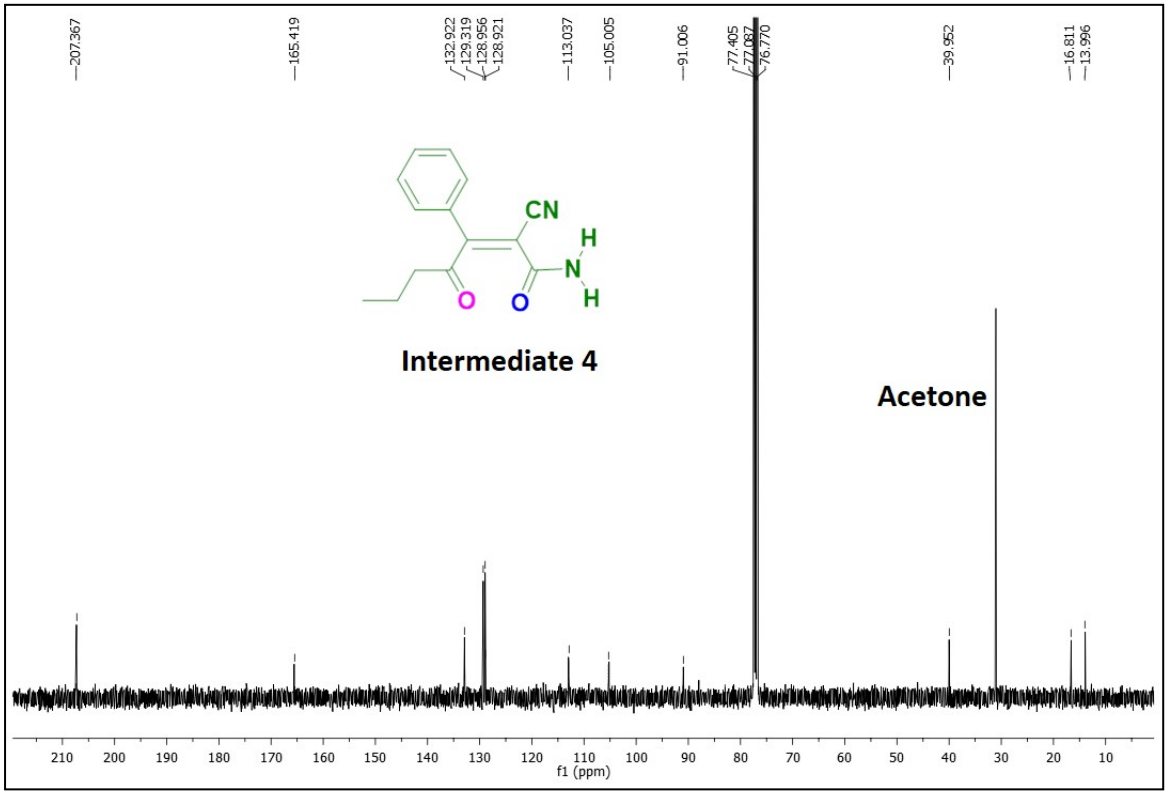
100.03
87.70
40.63
40.43
40.22
40.01
39.80
39.59
39.38
27.26
S
CN
HO
H3C
N
H
O
2q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

NMR Spectra of intermediate 4





G. Computational Results

Computational Methods: All computational calculations were carried out employing density functional theory (DFT) implemented in the Gaussian 16.[1] For geometry optimization we used hybrid density functional M06-2X[2] in conjunction with Ahlrichs' split valence polarization basis set (def2-SVP)[3,4] for all the atoms. No symmetry constraints were imposed during structural optimizations. The frequency analyses were executed on the optimized geometries at the same level to confirm the nature of stationary points on the potential energy surface either as minimal (intermediate) or the first-order saddle point (transition state) and to obtain thermochemistry. The minima were identified by having a full set of real frequencies, whereas the transition states possess only one imaginary frequency. The transition states were searched using the linear synchronous transit (LST) method,[5] and subsequent geometry optimizations were performed by utilizing the default Berny algorithm, implemented in the Gaussian 16 code. Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the transition state connects the corresponding real minima.[6,7] Furthermore, to improve the accuracy of the energies, single-point calculations were performed on the optimized geometries employing the def2-TZVPP basis set[3,4] for all atoms. To simulate the effect of the DMSO ($\varepsilon = 46.826$) solvent, the universal solvation model that is based on the full solute electron density (SMD) was used in single-point calculations.[8] Unless specified otherwise, the ΔG was used throughout the manuscript and supporting information. The ΔG value was obtained by augmenting the ΔE energy terms at M06-2X(SMD, DMSO)/def2-TZVPP with the respective free energy corrections at the M06-2X(SMD, DMSO)/def2-SVP level of theory. As it is known that translational and rotational entropies in solution for association/dissociation processes are overestimated/underestimated, and that the deviation in the free energies is approximately 1.89 kcal/mol from the standard state, we have reduced by 1.89 kcal/mol the free energy for addition steps and we have added 1.89 kcal/mol to the free energy of the dissociation steps.[9]

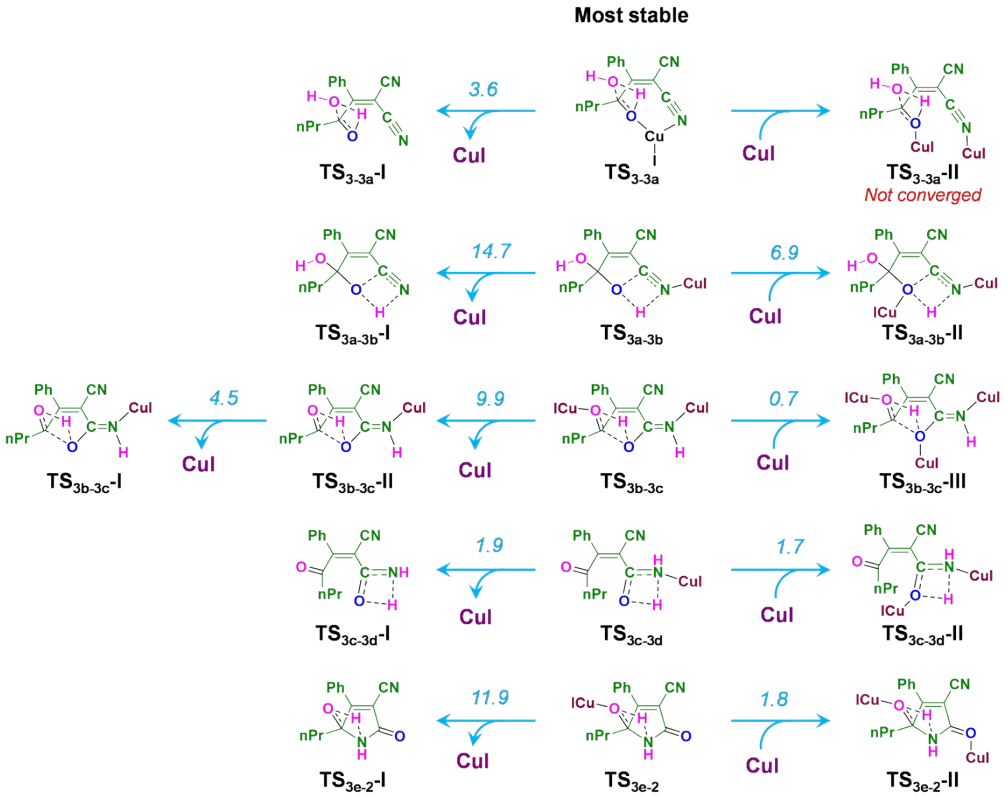


Figure S1. Relative free energies (in kcal mol^{-1}) of transition states varying the number of CuI coordination. Free energy values were calculated at the M06-2X(SMD, DMSO)/def2-TZVPP//M06-2X/def2-SVP level of theory.

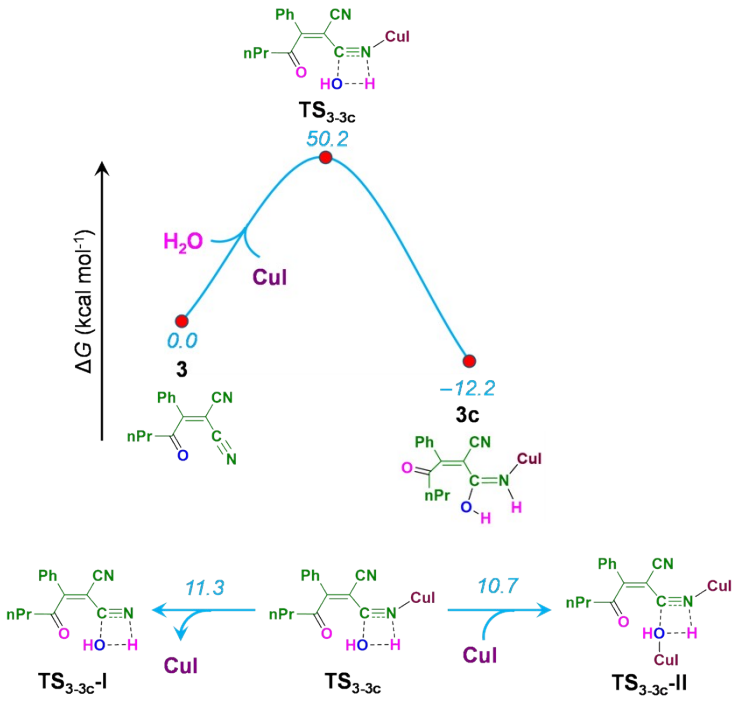


Figure S2. Energetics of nucleophilic addition of water to cyano group in intermediate **3**. Free energy values were calculated at the M06-2X(SMD, DMSO)/def2-TZVPP//M06-2X/def2-SVP level of theory.

References

(1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox,. Gaussian 16, Revision C.02, Gaussian, Inc., Wallingford CT, **2019**.

(2) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc*. **2008**, *120*, 215-241.

(3) F. Weigend, *Phys. Chem. Chem. Phys*. **2006**, *8*, 1057-1065.

(4) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297-3305.

(5) T. A. Halgren, W. N. Lipscomb, *Chem. Phys. Lett*. **1977**, *49*, 225-232.

(6) H. P. Hratchian, H. B. Schlegel, *Chem. Phys*. **2004**, *120*, 9918-9924.

(7) K. Fukui, *Acc. Chem. Res*. **1981**, *14*, 363–368.

(8) A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

(9) (a) C. P. Kelly, C. J. Cramer, D. G. Truhlar, *J. Chem. Theory Comput*. **2005**, *1*, 1133-1152; (b) C. P. Kelly, , C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2006**, *110*, 16066-16081.

H. Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states at M06-2X/def2-SVP level of theory. *E* represents the absolute electronic energy in Hartree at M06-2X(SMD, DMSO)/def2-TZVPP level of theory.

3
29
E: -725.380068094

C	1.978508	2.919477	-0.611595
C	0.989419	3.678314	-0.073724
C	-0.356623	3.024766	0.210509
C	1.739373	1.538467	-0.954281
N	1.519021	0.439638	-1.231668
O	-0.656607	2.761500	1.344699
C	-1.261939	2.811701	-0.976067
H	-1.438043	3.810609	-1.417422
H	-0.706453	2.246542	-1.743798
C	-2.567900	2.120980	-0.611258
H	-3.071605	2.704103	0.173910
H	-2.332657	1.146572	-0.157486
C	-3.480894	1.941356	-1.817570
H	-4.415954	1.439695	-1.534966
H	-3.742686	2.911145	-2.266713
H	-2.995666	1.333074	-2.595121
C	3.318642	3.400204	-0.835479
N	4.397771	3.763123	-1.025374
C	1.114895	5.107076	0.270595
C	0.518049	5.594376	1.445860
C	1.799702	5.994480	-0.575305
C	0.633697	6.940654	1.777604
H	-0.011277	4.905925	2.104873
C	1.896642	7.341713	-0.242658
H	2.241367	5.634531	-1.505085
C	1.320085	7.815668	0.935678
H	0.183397	7.308240	2.700300
H	2.424338	8.024403	-0.909369
H	1.402378	8.871792	1.196289

$TS_{3\text{-}3a}$
34
E: -2739.98490278

C	2.413715	2.798040	-0.073065
C	1.228959	3.368319	0.261117
C	-0.020917	2.501175	0.385248
C	2.598389	1.387972	-0.331611
N	2.760572	0.272736	-0.586522
H	-0.348028	1.689272	1.808649
O	0.178090	1.205526	0.624863
C	-1.089844	2.868160	-0.633964
H	-1.228297	3.960422	-0.657862
H	-0.669246	2.571241	-1.612290
C	-2.416585	2.135662	-0.438847
H	-2.904097	2.451480	0.504513
H	-2.219956	1.055614	-0.359656
C	-3.370585	2.396904	-1.598506
H	-4.331231	1.891438	-1.436020

H	-3.564009	3.472691	-1.723860
H	-2.938555	2.003348	-2.529722
O	-0.575947	2.782113	1.855893
H	-1.538349	2.930873	1.823079
C	3.608032	3.593520	-0.234111
N	4.575704	4.208738	-0.361064
C	1.092078	4.842901	0.360926
C	0.671383	5.462747	1.546268
C	1.380453	5.629016	-0.764333
C	0.547014	6.849048	1.598959
H	0.469237	4.861799	2.431928
C	1.239335	7.012579	-0.708138
H	1.707816	5.150092	-1.689380
C	0.823657	7.624454	0.473513
H	0.237471	7.326784	2.529279
H	1.460229	7.613424	-1.590849
H	0.720177	8.709304	0.519284
Cu	0.348513	-0.082193	-1.000475
I	-0.920911	-0.547464	-3.092849

3a

34

E: -2740.05055246

C	2.091285	2.975927	-0.284100
C	1.036945	3.608771	0.308296
C	-0.246391	2.813522	0.631793
C	2.023053	1.591164	-0.667467
N	1.898154	0.497395	-1.011310
H	0.370535	1.546322	1.955714
O	0.049343	1.510760	1.044237
C	-1.085535	2.705233	-0.649601
H	-1.213562	3.718547	-1.062544
H	-0.515949	2.116113	-1.386668
C	-2.440353	2.037000	-0.418357
H	-3.066674	2.671469	0.234083
H	-2.282438	1.074538	0.092688
C	-3.179177	1.796646	-1.729878
H	-4.158465	1.335414	-1.547132
H	-3.336459	2.736715	-2.279960
H	-2.608813	1.106401	-2.368173
O	-0.914448	3.494044	1.641056
H	-1.806696	3.126883	1.698735
C	3.329434	3.635968	-0.612804
N	4.340202	4.124064	-0.880980
C	1.075299	5.074040	0.499898
C	0.832346	5.660573	1.752410
C	1.378279	5.895321	-0.597540
C	0.915818	7.040962	1.899193
H	0.589014	5.031312	2.605776
C	1.433042	7.277782	-0.448355
H	1.556359	5.447142	-1.576884
C	1.208976	7.851450	0.801711
H	0.744410	7.488442	2.878789
H	1.656826	7.905724	-1.311153
H	1.261570	8.934375	0.922200

Cu	0.389199	-0.803546	-1.039094
I	-1.759304	-1.996489	-1.045733

TS_{3a-3b}

34

E: -2739.97402768

C	2.188902	2.788840	-0.199204
C	1.116588	3.572835	0.073247
C	-0.138675	2.718720	0.330537
C	1.826098	1.365310	-0.123583
N	2.144163	0.219549	0.165585
H	0.622883	0.389824	0.285122
O	0.320334	1.414994	-0.164612
C	-1.352137	3.112004	-0.494509
H	-1.617795	4.147448	-0.232070
H	-1.047609	3.112748	-1.551739
C	-2.547470	2.181176	-0.297732
H	-2.899139	2.223479	0.748512
H	-2.234230	1.142753	-0.488400
C	-3.709304	2.548532	-1.214654
H	-4.565251	1.879861	-1.057015
H	-4.045183	3.579542	-1.032642
H	-3.410885	2.473048	-2.269908
O	-0.355398	2.664203	1.684090
H	-1.245036	2.326619	1.856396
C	3.543548	3.208125	-0.379652
N	4.636185	3.543265	-0.540773
C	1.081249	5.035447	0.174249
C	0.254016	5.668529	1.118627
C	1.879645	5.818773	-0.675200
C	0.237120	7.056080	1.212333
H	-0.347147	5.064897	1.798508
C	1.850999	7.206394	-0.579754
H	2.512795	5.341503	-1.424126
C	1.032945	7.826847	0.363924
H	-0.395789	7.539198	1.957487
H	2.471006	7.805171	-1.247510
H	1.015752	8.914904	0.439438
Cu	3.713746	-0.919366	0.455414
I	5.605787	-2.436772	0.847075

3b

34

E: -2740.09344624

C	2.139592	2.867130	0.224297
C	1.093918	3.708046	0.398358
C	-0.148034	2.852353	0.641839
C	1.660281	1.479086	0.334889
N	2.351283	0.416927	0.228977
H	1.779662	-0.420321	0.354044
O	0.345510	1.495376	0.554805
C	-1.217685	3.022950	-0.432174
H	-1.512514	4.083589	-0.449129
H	-0.755089	2.797731	-1.405609
C	-2.438148	2.130275	-0.215387

H	-2.949757	2.415604	0.720241
H	-2.106683	1.087168	-0.097197
C	-3.432051	2.236128	-1.366953
H	-4.312109	1.603808	-1.191467
H	-3.778677	3.271801	-1.495380
H	-2.969971	1.917277	-2.312200
O	-0.604335	3.077995	1.921623
H	-1.421507	2.579026	2.053964
C	3.516751	3.167652	-0.000028
N	4.635046	3.389164	-0.186537
C	1.061954	5.169892	0.340537
C	0.077453	5.894135	1.037627
C	2.015691	5.868477	-0.421133
C	0.060343	7.283695	0.979990
H	-0.652146	5.360748	1.645337
C	1.986446	7.257294	-0.478684
H	2.773844	5.325857	-0.986222
C	1.012083	7.967421	0.223240
H	-0.698700	7.837069	1.533944
H	2.728156	7.786897	-1.077164
H	0.993942	9.057280	0.178980
Cu	4.291806	0.121734	-0.184089
I	6.571618	-0.612950	-0.732010

$TS_{3b\text{-}3c}$

36

E: -4678.23363742

C	2.064706	2.885243	-0.171188
C	1.060912	3.722854	0.204475
C	-0.208231	2.962187	0.570427
C	1.673909	1.475053	-0.120249
N	2.379065	0.460279	-0.386709
H	1.868009	-0.418529	-0.275702
O	0.355874	1.390295	0.268200
C	-1.409998	3.204547	-0.300897
H	-1.790139	4.194593	0.014891
H	-1.081311	3.316659	-1.345835
C	-2.515802	2.158082	-0.171482
H	-2.735401	1.978509	0.893695
H	-2.155676	1.204344	-0.586299
C	-3.789958	2.607165	-0.876526
H	-4.562892	1.830467	-0.816845
H	-4.190947	3.517532	-0.407730
H	-3.603193	2.818624	-1.939532
O	-0.374533	2.689240	1.856521
H	0.145065	1.509451	1.370239
C	3.409813	3.221363	-0.517427
N	4.504748	3.451705	-0.804515
C	1.066849	5.180138	0.291684
C	0.154030	5.838968	1.138844
C	1.971342	5.946630	-0.468323
C	0.155821	7.224783	1.234259
H	-0.553409	5.277123	1.751744
C	1.960484	7.332619	-0.374370
H	2.669638	5.464729	-1.152129

C	1.058381	7.973005	0.477581
H	-0.553558	7.714951	1.901625
H	2.658777	7.917056	-0.973778
H	1.055993	9.061598	0.548018
Cu	-1.943131	3.446828	2.836496
I	-3.843164	4.903783	3.344721
Cu	4.286786	0.286508	-1.035941
I	6.492367	-0.341842	-1.891808

3c

34

E: -2740.07378394

C	2.184225	2.732815	0.199340
C	0.994649	3.386620	0.212910
C	-0.337800	2.667163	0.383518
C	2.322999	1.257465	0.274327
N	3.455695	0.701914	0.463091
O	1.167724	0.613160	0.111139
C	-1.092785	2.364975	-0.885941
H	-1.361796	3.341147	-1.330306
H	-0.396664	1.894243	-1.599170
C	-2.328208	1.508765	-0.647807
H	-2.966831	2.008631	0.094835
H	-2.013695	0.562350	-0.180399
C	-3.103737	1.238760	-1.930929
H	-3.987808	0.616892	-1.737133
H	-3.448161	2.177021	-2.390539
H	-2.480499	0.715548	-2.671396
O	-0.765050	2.474706	1.490103
H	1.256328	-0.337608	0.264930
C	3.435051	3.444697	0.176561
N	4.464837	3.968887	0.162691
C	0.859136	4.854183	0.099346
C	-0.073479	5.523940	0.909585
C	1.620252	5.584978	-0.826529
C	-0.213148	6.904883	0.814669
H	-0.663996	4.960244	1.633378
C	1.461241	6.963339	-0.926974
H	2.326226	5.073246	-1.481567
C	0.551068	7.625583	-0.103314
H	-0.923162	7.420799	1.461840
H	2.053133	7.522062	-1.652487
H	0.434533	8.707482	-0.179566
H	3.415657	-0.318300	0.485742
Cu	5.366117	1.365695	0.729159
I	7.797827	1.326999	1.131384

$TS_{3c\text{-}3d}$

34

E: -2740.00409068

C	2.066783	2.721045	0.528420
C	0.932217	3.466226	0.428310
C	-0.438308	2.793961	0.441791
C	2.017777	1.257863	0.554382
N	3.035174	0.399688	0.313542

O	0.978432	0.559196	0.726448
C	-0.901215	2.259897	-0.887587
H	-1.172283	3.148047	-1.490242
H	-0.049786	1.804864	-1.422316
C	-2.075240	1.298844	-0.765105
H	-2.889339	1.798141	-0.219574
H	-1.759408	0.451935	-0.136584
C	-2.553011	0.808234	-2.126095
H	-3.386657	0.100764	-2.022003
H	-2.897824	1.645607	-2.750722
H	-1.742838	0.301979	-2.671281
O	-1.092761	2.815569	1.448933
H	1.914185	-0.302530	0.607131
C	3.396591	3.270683	0.549500
N	4.496017	3.623277	0.581626
C	0.915636	4.923143	0.236044
C	-0.059903	5.696737	0.889796
C	1.834646	5.542706	-0.627909
C	-0.080504	7.075765	0.713006
H	-0.776270	5.210492	1.553049
C	1.788300	6.919891	-0.816012
H	2.558204	4.942903	-1.182001
C	0.840093	7.687531	-0.139312
H	-0.823610	7.676112	1.238757
H	2.493353	7.393632	-1.499498
H	0.811734	8.768368	-0.284762
H	3.983020	0.623069	0.623941
Cu	3.011288	0.633764	-1.753010
I	2.338675	1.487201	-3.951783

3d

34

E: -2740.08509830

C	1.941935	2.598625	0.508613
C	0.848552	3.395292	0.402646
C	-0.556963	2.808793	0.453490
C	1.796587	1.111651	0.549912
N	2.984647	0.394062	0.224104
H	3.841615	0.774537	0.632580
O	0.756794	0.538463	0.721001
C	-1.080879	2.260610	-0.848740
H	-1.329848	3.144582	-1.466551
H	-0.267263	1.750651	-1.390609
C	-2.294484	1.360739	-0.661571
H	-3.057518	1.910948	-0.091996
H	-1.994052	0.510071	-0.030650
C	-2.858277	0.871442	-1.989506
H	-3.724524	0.214132	-1.834472
H	-3.183279	1.714118	-2.617710
H	-2.103721	0.307540	-2.557559
O	-1.200115	2.917843	1.462945
H	2.873039	-0.600050	0.424854
C	3.287825	3.105934	0.527375
N	4.409408	3.384293	0.564563
C	0.914310	4.848892	0.176927

C	0.036399	5.704521	0.863389
C	1.817992	5.375933	-0.760338
C	0.099254	7.076463	0.644133
H	-0.670719	5.285017	1.580122
C	1.855053	6.748221	-0.987831
H	2.457930	4.708239	-1.341703
C	1.005708	7.598643	-0.280166
H	-0.567448	7.741990	1.193530
H	2.546898	7.151523	-1.727753
H	1.042539	8.674524	-0.457321
Cu	3.070092	0.950312	-1.798053
I	2.603329	2.168726	-3.870632

3e

34

E: -2740.08733179

C	2.101119	2.714503	0.122917
C	1.009407	3.504140	0.235418
C	-0.333160	2.871254	0.537916
C	1.931447	1.218427	0.241869
N	3.059532	0.486541	0.225069
H	3.978810	0.905145	0.162755
O	0.814264	0.745033	0.338474
C	-1.201613	2.527738	-0.635141
H	-1.554090	3.497223	-1.037041
H	-0.556090	2.089687	-1.410786
C	-2.371253	1.609232	-0.305144
H	-3.074478	2.123882	0.370078
H	-1.982697	0.733051	0.239299
C	-3.116950	1.160356	-1.556298
H	-3.962114	0.511932	-1.292358
H	-3.512799	2.022292	-2.113430
H	-2.453885	0.597528	-2.229383
O	-0.692653	2.838756	1.702955
H	2.972745	-0.517713	0.321027
C	3.428008	3.225638	-0.077094
N	4.529620	3.538231	-0.233686
C	0.986316	4.973203	0.081153
C	0.155393	5.750702	0.905526
C	1.766073	5.603907	-0.901597
C	0.131937	7.134930	0.765300
H	-0.450456	5.271807	1.675613
C	1.726706	6.987083	-1.043619
H	2.389515	5.009736	-1.570531
C	0.915221	7.754745	-0.208073
H	-0.502856	7.731945	1.420764
H	2.331103	7.466888	-1.814008
H	0.889205	8.839519	-0.319762
Cu	-2.201448	1.967612	2.684360
I	-4.083311	1.001169	3.925448

TS_{3e-2}

34

E: -2740.03867015

C	2.164435	2.832844	-0.144241

C	1.153252	3.674781	0.207397
C	-0.105047	2.877545	0.585698
C	1.750873	1.420557	-0.073671
C	-1.311799	3.196372	-0.290578
H	-1.661708	4.192766	0.027897
H	-0.991076	3.299985	-1.340196
C	-2.457687	2.189844	-0.171480
H	-2.594432	1.904403	0.885528
H	-2.206587	1.266808	-0.724228
C	-3.766926	2.760391	-0.705148
H	-4.566555	2.009189	-0.673884
H	-4.084318	3.615746	-0.090431
H	-3.655727	3.099386	-1.745626
O	-0.326076	2.846378	1.949601
C	3.510334	3.151341	-0.504952
N	4.599429	3.386723	-0.806873
C	1.165508	5.134941	0.244384
C	0.288542	5.834617	1.094744
C	2.039885	5.864336	-0.583377
C	0.295396	7.224052	1.124290
H	-0.383743	5.291349	1.758636
C	2.033511	7.253847	-0.556507
H	2.711527	5.347483	-1.268500
C	1.165995	7.935542	0.298361
H	-0.385857	7.747913	1.795371
H	2.708172	7.807719	-1.209802
H	1.165889	9.026330	0.317659
N	0.388136	1.443895	0.464108
O	2.316011	0.419173	-0.367642
H	0.231358	1.592026	1.632163
H	-0.242454	0.752852	0.047202
Cu	-1.953090	3.606171	2.750178
I	-4.042997	4.801319	3.230861

2

32

E: -801.878404288

C	2.107658	2.806564	-0.146385
C	1.076876	3.618607	0.178094
C	-0.165340	2.751285	0.461249
C	1.661969	1.366793	-0.135456
C	-1.322347	3.096330	-0.477679
H	-1.612625	4.140708	-0.285168
H	-0.946177	3.047950	-1.511763
C	-2.533682	2.184611	-0.303768
H	-2.828777	2.187983	0.755702
H	-2.255526	1.147786	-0.555560
C	-3.703436	2.615879	-1.181143
H	-4.566100	1.948153	-1.053876
H	-4.027544	3.636456	-0.929649
H	-3.424506	2.607582	-2.245188
O	-0.636453	2.913027	1.775799
C	3.461515	3.144244	-0.448821
N	4.558551	3.404477	-0.699751
C	1.050741	5.086457	0.249805

C	0.139290	5.755880	1.086976
C	1.938104	5.847409	-0.531155
C	0.132621	7.146314	1.148702
H	-0.551649	5.177081	1.698401
C	1.921041	7.236817	-0.468286
H	2.636885	5.351939	-1.205127
C	1.021849	7.890326	0.374047
H	-0.573272	7.651796	1.808976
H	2.613225	7.811556	-1.084597
H	1.011680	8.980147	0.423440
N	0.347964	1.418267	0.249028
O	2.312103	0.394709	-0.407053
H	0.059266	2.626445	2.382443
H	-0.231492	0.589315	0.285555

$TS_{3\text{-}3a}$-I

32

E: -801.757180113

C	2.371743	2.734608	-0.116585
C	1.183332	3.337514	0.127140
C	-0.086246	2.499198	0.173134
C	2.593960	1.322241	-0.337264
N	2.940381	0.241146	-0.543541
H	-0.271257	1.500514	1.455620
O	0.037038	1.211352	0.223721
C	-1.241002	3.088806	-0.619866
H	-1.420997	4.132398	-0.320309
H	-0.879742	3.126430	-1.663174
C	-2.507658	2.243544	-0.554474
H	-2.885273	2.209646	0.483080
H	-2.244291	1.208854	-0.813367
C	-3.603179	2.775310	-1.470304
H	-4.507939	2.156090	-1.409398
H	-3.880613	3.806870	-1.207358
H	-3.268239	2.777407	-2.517880
O	-0.487356	2.583506	1.840591
H	-1.441568	2.716963	1.956806
C	3.588385	3.514370	-0.177531
N	4.570611	4.117662	-0.231703
C	1.077249	4.812977	0.254071
C	0.566394	5.402826	1.419317
C	1.475013	5.630150	-0.812600
C	0.461327	6.788544	1.509628
H	0.275258	4.769137	2.256643
C	1.356499	7.014615	-0.720249
H	1.875527	5.175233	-1.720716
C	0.849999	7.596017	0.440717
H	0.078492	7.241355	2.425226
H	1.666639	7.640011	-1.558109
H	0.762948	8.680807	0.515451

$TS_{3a\text{-}3b}$-I

32

E: -801.732765602

C	2.228490	2.797464	-0.170902

C	1.118559	3.534890	0.067712
C	-0.131717	2.642782	0.276074
C	2.014260	1.349725	-0.083980
N	2.238080	0.224667	0.255652
H	0.895577	0.429347	0.300800
O	0.243352	1.391632	-0.208652
C	-1.340388	3.138647	-0.517667
H	-1.584407	4.164452	-0.202947
H	-1.042530	3.179510	-1.576966
C	-2.554208	2.226974	-0.362334
H	-2.887939	2.223139	0.690451
H	-2.254019	1.197050	-0.608171
C	-3.719220	2.661397	-1.244461
H	-4.587511	2.001475	-1.115025
H	-4.035306	3.687765	-1.006428
H	-3.433177	2.638046	-2.306048
O	-0.356387	2.629065	1.657201
H	-1.160549	2.119353	1.820751
C	3.567497	3.290617	-0.291376
N	4.648677	3.679297	-0.405566
C	1.066742	4.999062	0.175763
C	0.259936	5.607927	1.152495
C	1.820691	5.804433	-0.691936
C	0.223133	6.994319	1.261034
H	-0.312644	4.979301	1.834631
C	1.769792	7.191091	-0.583814
H	2.436115	5.343648	-1.465784
C	0.974738	7.788028	0.393675
H	-0.394538	7.458899	2.030626
H	2.354564	7.807079	-1.267749
H	0.939767	8.875014	0.479657

$TS_{3a\text{-}3b}$-II

36

E: -4678.17885593

C	2.264458	2.834539	-0.293546
C	1.141649	3.548483	-0.014473
C	-0.081473	2.646309	0.263512
C	2.072379	1.395048	-0.189148
N	2.314291	0.271805	0.166569
H	0.948247	0.420301	0.248271
O	0.335741	1.369918	-0.296134
C	-1.355153	3.098800	-0.439170
H	-1.579815	4.123141	-0.107440
H	-1.152110	3.164065	-1.522316
C	-2.555520	2.186025	-0.180107
H	-2.860483	2.256683	0.879221
H	-2.280887	1.131148	-0.358760
C	-3.737452	2.552490	-1.071600
H	-4.609120	1.926005	-0.844252
H	-4.024648	3.604552	-0.930994
H	-3.477474	2.398984	-2.129453
O	-0.195568	2.533490	1.629283
H	-1.066138	2.171275	1.848226
C	3.592095	3.346536	-0.447597

N	4.664712	3.749839	-0.583354
C	1.064409	5.004884	0.098995
C	0.281504	5.597640	1.106539
C	1.780959	5.820438	-0.792702
C	0.229908	6.981860	1.220234
H	-0.252555	4.965405	1.816278
C	1.710288	7.204934	-0.680067
H	2.373431	5.371497	-1.591115
C	0.939858	7.786123	0.326737
H	-0.363740	7.436964	2.013540
H	2.259356	7.831631	-1.383088
H	0.891557	8.872145	0.416252
Cu	3.609447	-1.103751	0.772403
I	5.137029	-2.799816	1.640720
Cu	-0.428100	0.831443	-2.125454
I	-1.573482	0.527367	-4.255490

$TS_{3b\text{-}3c}$-I

32

E: -801.776352846

C	1.968683	2.785034	-0.060456
C	0.967529	3.654947	0.192092
C	-0.372213	2.996319	0.485263
C	1.568575	1.354996	0.007541
N	2.354497	0.392982	-0.186224
H	1.863581	-0.498820	-0.080780
O	0.238664	1.276518	0.300830
C	-1.456378	3.192587	-0.535577
H	-1.743284	4.257342	-0.450896
H	-1.029796	3.065333	-1.542626
C	-2.663026	2.291997	-0.303115
H	-3.021509	2.450325	0.723723
H	-2.328609	1.244658	-0.359152
C	-3.776220	2.549164	-1.310800
H	-4.634700	1.888750	-1.129529
H	-4.133671	3.588040	-1.251152
H	-3.430182	2.374392	-2.340325
O	-0.668329	2.749138	1.714291
H	-0.107856	1.649944	1.387773
C	3.336589	3.130225	-0.311874
N	4.433650	3.418242	-0.526655
C	1.021686	5.123984	0.256227
C	0.189737	5.800489	1.165390
C	1.879364	5.861692	-0.574035
C	0.228898	7.188800	1.247871
H	-0.463750	5.226594	1.825700
C	1.906169	7.250568	-0.490071
H	2.517643	5.349818	-1.294640
C	1.085161	7.915789	0.420400
H	-0.409984	7.705507	1.965031
H	2.572624	7.816253	-1.142069
H	1.111889	9.004493	0.484560

$TS_{3b\text{-}3c}$-II

34

E: -2740.00191525

C	2.062067	2.796552	-0.163437
C	1.073594	3.649920	0.199497
C	-0.200140	2.888159	0.555676
C	1.643099	1.387923	-0.113041
N	2.304117	0.361926	-0.362139
H	1.767678	-0.501290	-0.252024
O	0.278896	1.391711	0.281909
C	-1.398769	3.191295	-0.315714
H	-1.744039	4.192269	-0.000703
H	-1.067524	3.289242	-1.361720
C	-2.539135	2.182365	-0.193838
H	-2.755318	1.992978	0.870407
H	-2.217284	1.222366	-0.625821
C	-3.804518	2.683461	-0.879448
H	-4.603467	1.932669	-0.826244
H	-4.171059	3.598656	-0.391987
H	-3.620015	2.908136	-1.940402
O	-0.401227	2.675287	1.865037
H	0.085844	1.433183	1.371220
C	3.411737	3.115953	-0.512812
N	4.500044	3.366821	-0.803916
C	1.099007	5.112023	0.270744
C	0.240192	5.789819	1.155057
C	1.965957	5.858862	-0.546696
C	0.256335	7.177892	1.228254
H	-0.432465	5.235140	1.811415
C	1.972007	7.247227	-0.473526
H	2.623581	5.356936	-1.256298
C	1.121742	7.908518	0.413886
H	-0.413045	7.684016	1.924513
H	2.642664	7.816565	-1.117679
H	1.130669	8.998049	0.467585
Cu	-1.948425	3.468779	2.808037
I	-3.876904	4.825137	3.481615

$TS_{3b\text{-}3c}$-III

38

E: -6615.50685994

C	2.189789	2.782440	0.096759
C	1.024460	3.368213	0.449315
C	-0.085744	2.322717	0.396949
C	1.979207	1.340363	-0.072111
N	2.798506	0.444464	-0.411823
H	2.406415	-0.503106	-0.420811
O	0.662793	1.088672	0.248978
C	-1.035828	2.482653	-0.782323
H	-0.419326	2.642285	-1.681963
H	-1.544213	1.508589	-0.907847
C	-2.093362	3.580015	-0.657224
H	-1.643508	4.545282	-0.383328
H	-2.813023	3.306843	0.135296
C	-2.871991	3.725808	-1.963479
H	-3.456774	2.820021	-2.176960
H	-3.566291	4.573238	-1.903701

H	-2.194740	3.899476	-2.811869
O	-0.801075	2.192483	1.589964
H	-0.394831	1.439978	2.137146
C	3.468239	3.413269	0.003240
N	4.500391	3.925841	-0.059734
C	0.760177	4.789820	0.691459
C	0.159213	5.219945	1.885243
C	1.090133	5.723102	-0.303110
C	-0.168591	6.562105	2.053989
H	-0.006497	4.517687	2.706032
C	0.759666	7.063539	-0.125540
H	1.592172	5.394648	-1.215342
C	0.117446	7.479091	1.041859
H	-0.657212	6.883398	2.974780
H	1.000890	7.785732	-0.905990
H	-0.154460	8.527480	1.168968
Cu	-2.203431	3.529367	2.361590
I	-3.759985	5.019414	3.527524
Cu	4.550292	0.699391	-1.392243
I	6.467034	0.968436	-2.878156
Cu	-0.342053	-0.631499	-0.293061
I	-1.368773	-2.715450	-0.958313

$TS_{3c\text{-}3d}$-I

32

E: -801.784912662

C	2.068196	2.709903	0.133213
C	0.934574	3.450361	0.194122
C	-0.424372	2.777692	0.361935
C	2.035435	1.232615	0.158703
N	3.030921	0.400956	0.213905
H	4.014168	0.648986	0.255462
O	0.947147	0.550822	0.121307
C	-1.128365	2.358015	-0.902796
H	-1.467677	3.292088	-1.390325
H	-0.392212	1.899999	-1.579884
C	-2.295796	1.420448	-0.631444
H	-2.976319	1.899215	0.087565
H	-1.896552	0.525989	-0.129742
C	-3.038828	1.035891	-1.904367
H	-3.870744	0.352063	-1.687806
H	-3.455564	1.922263	-2.406349
H	-2.369061	0.533161	-2.617902
O	-0.911121	2.724600	1.460059
H	1.916665	-0.316773	0.183217
C	3.387585	3.284479	0.091484
N	4.473149	3.677804	0.056792
C	0.896106	4.926094	0.131914
C	0.007839	5.635100	0.958098
C	1.715166	5.631670	-0.763774
C	-0.033243	7.025023	0.905915
H	-0.627148	5.088982	1.656379
C	1.655616	7.020520	-0.821039
H	2.387136	5.091239	-1.431411
C	0.787046	7.719600	0.016918

H	-0.712437	7.568705	1.563570
H	2.290550	7.558454	-1.525796
H	0.746227	8.808904	-0.026446

$TS_{3c\text{-}3d}$-II

36

E: -4678.22014649

C	1.879583	2.353957	0.558826
C	0.782326	3.123758	0.343472
C	-0.583886	2.488118	0.181099
C	1.818023	0.890208	0.444688
N	2.842048	0.023578	0.377368
O	0.748202	0.233134	0.255814
C	-1.098460	2.372131	-1.212919
H	-1.247313	3.405796	-1.579140
H	-0.267112	1.981015	-1.830482
C	-2.361373	1.532132	-1.337230
H	-3.147905	1.965038	-0.701453
H	-2.152010	0.531140	-0.929975
C	-2.831170	1.432669	-2.783337
H	-3.733616	0.812482	-2.862287
H	-3.067530	2.425681	-3.193138
H	-2.054823	0.985500	-3.420849
O	-1.222837	2.164610	1.170999
H	1.651642	-0.654762	0.304785
C	3.194599	2.886037	0.795837
N	4.280522	3.231834	0.980292
C	0.794308	4.588611	0.218510
C	-0.256146	5.341632	0.771791
C	1.820932	5.232992	-0.490939
C	-0.252450	6.726667	0.654031
H	-1.059860	4.843024	1.317990
C	1.803776	6.618274	-0.619019
H	2.604049	4.646557	-0.975158
C	0.777153	7.364655	-0.040452
H	-1.055955	7.310963	1.103169
H	2.595443	7.115057	-1.180271
H	0.773123	8.451060	-0.138974
H	3.653910	0.164081	0.984442
Cu	3.304608	0.604839	-1.592850
I	2.634905	2.116653	-3.435735
Cu	-0.226945	1.519778	2.819496
I	1.728823	0.692266	4.078145

$TS_{3e\text{-}2}$-I

32

E: -801.801471000

C	2.113596	2.834851	-0.075320
C	1.064151	3.659797	0.188019
C	-0.226134	2.879306	0.510233
C	1.731433	1.413316	0.006520
C	-1.319780	3.085861	-0.537657
H	-1.561560	4.161036	-0.513983
H	-0.932466	2.871083	-1.548430
C	-2.576783	2.281050	-0.227429

H	-2.835040	2.464588	0.824964
H	-2.364838	1.199877	-0.310551
C	-3.738678	2.633482	-1.148193
H	-4.633471	2.044224	-0.906293
H	-4.001732	3.697376	-1.054262
H	-3.485873	2.445454	-2.202378
O	-0.576168	2.928582	1.787872
C	3.473291	3.189490	-0.342600
N	4.571000	3.464809	-0.572032
C	1.059126	5.121751	0.242412
C	0.158811	5.777676	1.103512
C	1.930022	5.879804	-0.558843
C	0.145831	7.167296	1.161467
H	-0.493710	5.171990	1.735041
C	1.898010	7.269145	-0.502060
H	2.620405	5.384468	-1.242138
C	1.010458	7.914033	0.359887
H	-0.542863	7.671705	1.840338
H	2.570219	7.850763	-1.133711
H	0.992697	9.004030	0.406463
N	0.354369	1.405155	0.477829
O	2.349902	0.426935	-0.241943
H	0.137750	1.633715	1.587133
H	-0.219561	0.650244	0.093923

$TS_{3e\text{-}2}$-II

36

E: -4678.25144419

C	2.196214	2.927139	0.050537
C	1.145366	3.765736	0.329675
C	-0.107480	2.945276	0.690832
C	1.811072	1.535102	0.177017
C	-1.276252	3.157073	-0.265787
H	-1.678328	4.158070	-0.037542
H	-0.904924	3.199146	-1.303031
C	-2.392958	2.120447	-0.127740
H	-2.582655	1.919778	0.940278
H	-2.081718	1.164578	-0.586758
C	-3.684533	2.597409	-0.783103
H	-4.461138	1.823915	-0.729580
H	-4.062547	3.492042	-0.266591
H	-3.522264	2.846775	-1.841827
O	-0.382808	2.960993	2.034058
C	3.557324	3.226006	-0.263820
N	4.669116	3.402979	-0.522685
C	1.129328	5.216206	0.321622
C	0.108409	5.923683	0.991461
C	2.124872	5.945090	-0.364887
C	0.090917	7.311666	0.985864
H	-0.664863	5.393888	1.546558
C	2.092980	7.332374	-0.376813
H	2.913079	5.430769	-0.913384
C	1.081075	8.017342	0.300709
H	-0.702067	7.837583	1.518204
H	2.860632	7.883646	-0.920049

H	1.063147	9.108183	0.290662
N	0.449688	1.511357	0.648488
O	2.426350	0.518686	-0.040765
H	0.252572	1.688483	1.789367
H	-0.137881	0.774746	0.243021
Cu	-2.041007	3.764420	2.734019
I	-4.091819	5.100374	2.900208
Cu	4.246860	0.111454	-0.840505
I	6.298141	-0.626788	-1.933420

$TS_{3\text{-}3c}$

34

E: -2739.97093902

C	2.146907	2.449961	0.686334
C	1.316493	3.019296	-0.218973
C	0.606926	2.117143	-1.210990
C	2.272508	0.972573	0.827130
N	1.792424	0.130867	1.596079
H	2.579273	-0.553333	0.534794
O	3.067225	0.249633	-0.168894
C	-0.836397	2.409186	-1.481167
H	-0.968243	3.460753	-1.776179
H	-1.169000	1.754449	-2.297625
C	-1.630968	2.139034	-0.187739
H	-1.260306	2.785601	0.624080
H	-1.441800	1.103334	0.140257
C	-3.125397	2.364326	-0.368886
H	-3.652113	2.174496	0.575578
H	-3.330788	3.402086	-0.669760
H	-3.540994	1.697290	-1.138261
O	1.167265	1.137873	-1.672368
H	2.569559	0.394190	-1.024742
C	2.872979	3.218712	1.662765
N	3.489905	3.796006	2.449652
C	0.997186	4.463755	-0.214778
C	0.551263	5.078731	0.962923
C	1.112677	5.212395	-1.394867
C	0.233800	6.435374	0.955788
H	0.422540	4.488097	1.874860
C	0.806410	6.569490	-1.390428
H	1.457953	4.732312	-2.314049
C	0.366151	7.180634	-0.214730
H	-0.122289	6.906601	1.872307
H	0.910836	7.152726	-2.306000
H	0.120196	8.243419	-0.214391
Cu	0.432628	0.847073	2.865788
I	-1.285969	2.331328	3.842657

$TS_{3\text{-}3c}$-I

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E: -801.732956985

C	2.049153	2.725970	1.001753
C	1.141067	3.191697	0.112032
C	0.210822	2.204162	-0.562110
C	2.152783	1.299322	1.407209

N	1.858026	0.554085	2.318918
H	2.529216	-0.201121	1.270073
O	2.913887	0.412083	0.331139
C	-1.223753	2.632236	-0.745637
H	-1.566852	3.048239	0.218839
H	-1.240006	3.491151	-1.437789
C	-2.127714	1.509705	-1.233326
H	-2.066425	0.669265	-0.525573
H	-1.733470	1.125962	-2.185995
C	-3.572319	1.965798	-1.395722
H	-4.210272	1.144390	-1.747986
H	-3.984954	2.325270	-0.441397
H	-3.650820	2.787813	-2.122873
O	0.596827	1.106234	-0.900452
H	2.286909	0.335113	-0.418341
C	2.967194	3.612355	1.671190
N	3.715161	4.300074	2.219718
C	0.977220	4.630359	-0.208583
C	0.831878	5.590634	0.800010
C	0.967464	5.037805	-1.550801
C	0.682688	6.935901	0.469640
H	0.829783	5.281238	1.846472
C	0.826402	6.383070	-1.877087
H	1.088938	4.294663	-2.343193
C	0.681839	7.334061	-0.865996
H	0.567817	7.675805	1.262484
H	0.832838	6.691238	-2.923256
H	0.568451	8.388506	-1.121256

$TS_{3\text{-}3c}$-II

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E: -4678.17278634

C	1.903417	2.207504	0.915803
C	1.278988	2.903538	-0.076018
C	0.520698	2.195748	-1.132235
C	1.920454	0.720021	1.044470
N	1.421052	-0.050717	1.885655
H	2.069965	-0.811608	0.800437
O	2.508845	-0.015582	0.005227
C	-0.651538	2.846963	-1.748226
H	-0.424524	3.891472	-1.992669
H	-0.925501	2.287400	-2.651554
C	-1.811263	2.799315	-0.706500
H	-2.664901	3.296730	-1.188072
H	-1.544470	3.406609	0.172403
C	-2.185565	1.389534	-0.272374
H	-3.057572	1.422526	0.393462
H	-2.421700	0.748454	-1.135047
H	-1.378743	0.909377	0.304966
O	0.712122	0.988257	-1.452738
H	1.479725	0.485201	-0.985337
C	2.560096	2.892302	1.997090
N	3.123169	3.383880	2.877291
C	1.195663	4.388812	-0.034951
C	0.589387	5.015572	1.061402

C	1.731280	5.152442	-1.081062
C	0.514567	6.406194	1.103420
H	0.160756	4.415630	1.870493
C	1.657964	6.541480	-1.023691
H	2.226863	4.656489	-1.919499
C	1.048261	7.167619	0.064849
H	0.036688	6.890764	1.955325
H	2.087319	7.136559	-1.830338
H	0.992360	8.256405	0.103935
Cu	0.045069	0.811027	3.040052
I	-1.669838	2.530648	3.535055
Cu	3.920539	0.803598	-1.234922
I	4.129337	2.496828	-3.012320