Electronic Supplementary Material (ESI) for RSC Advances.


# Cascade Annulation Reaction (CAR): Highly Diastereoselective Synthesis of Pyranopyrazole Scaffolds

**Supporting Information**

## Contents

**General Consideration**

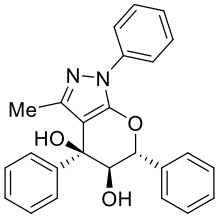
Commercial reagents were used without further purification. IR spectra were recorded on a Perkin Elmer-FTIR spectrometer using solid samples as KBr plates. For compounds $^{1}H$ NMR (400 MHz, $CDCl_3$) and $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra were recorded in deuterochloroform ($CDCl_3$) on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectra were recorded on Agilent 1200 LC/MS-6110 mass spectrometer. Aldehydes, acetophenone, $KOBu^t$ and $H_2O_2$ (30%) were purchased from Sigma Aldrich. Reactions were monitored by thin layer chromatography (TLC) on Silica gel 60 F254 aluminium plates. TLC plates were visualized using ultraviolet (UV) light at 254 nm. Column chromatography was performed with silica gel 60 Å (100 – 200 mesh) from Aldrich, using the stated mixture of solvents. Compounds spectral data and copy of $^{1}H$ and $^{13}C$ NMR spectra of all compounds **3a-w, 4a-h**, **5a-b and 3aa** are listed below (pages 2-52). Based on literature procedure, racemic chalcone epoxide were synthesized from substituted benzaldehyde and substituted acetophenone as starting materials which were comercially obtained and used without further purification.

**Typical experimental procedure for the synthesis of compounds (3a-w)**

A mixture of chalcone epoxide (**1**, 1mmol), pyrazolone (**2**, 1 mmol), and $KOBu^t$ (1 equiv.) in absolute ethanol (5 mL) was placed in a single neck round bottom flask and stirred at room temperature for 12 h. The reaction was monitored contineously by TLC. After completion of the reaction, the reaction mixture was washed with ethylacetate and water for three times. Then the combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated. The purification was carried out by 12% (ethylacetate / hexane) mixture to afford the product **3** as a white colour solid in very good yield.

## Analytical Data of the Products

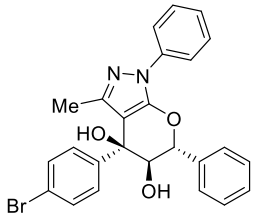
**3-Methyl-1,4,6-triphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3a)**




Yield : 79%; white solid; M.P. = 154 - 159 °C; Reaction time: 12 h; $^{1}H$ NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.18 (m, 15H), 5.28 (d, *J* = 9.9 Hz, 1H), 4.12 (d, *J* = 9.9 Hz, 1H), 3.47(s, 1H), 2.17(s, 1H), 1.67(s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 151.20, 147.41, 142.39, 138.35,

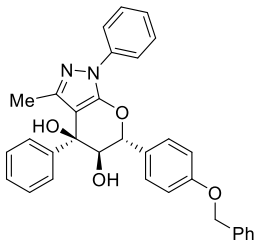
136.69, 129.23, 129.18, 128.77, 128.43, 128.01, 127.59, 126.22, 125.94, 120.45, 102.42, 81.70, 71.57, 13.47. IR (KBr) : 3504, 3366, 3036, 1599, 1517, 1447, 1070; HRMS (ESI-TOF) calcd for $C_{25}H_{22}N_2O_3$ ([M+H]$^+$): 399.1709, found: 399.1705.

**4-(4-Bromophenyl)-3-methyl-1,6-triphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3b)**



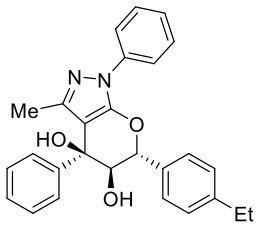

Yield : 61%; white solid; M.P. = 135-138 °C; Reaction time: 12 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, 2H), 7.47 – 7.21 (m, 12H), 5.24 (d, *J* = 9.9 Hz, 1H), 4.04 (d, *J* = 3.9 Hz, 1H), 3.54 (s, 1H), 2.40 (s, 1H), 1.68 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.15, 147.17, 141.72, 138.16, 136.41, 131.48, 129.33, 129.21, 128.81, 128.14, 127.97, 126.09, 121.61, 120.45, 101.95, 81.75, 71.31, 13.58. IR (KBr) : 3504, 3394, 3039, 1594, 1522, 1493, 1081; HRMS (ESI-TOF) calcd for $C_{25}H_{21}BrN_2O_3$ ([M+H] $^+$): 477.0814, found: 477.0815.

**6-(4-Benzyloxy)phenyl)-3-methyl-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3c)**



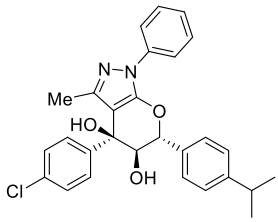

Yield : 64%; white solid; M.P. = 122-128 °C; Reaction time: 12 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.69 (m, 2H), 7.48 – 7.01 (m, 17H), 5.26 (d, *J* = 9.9 Hz, 1H), 5.07 (s, 2H), 4.11 (d, *J* = 9.7 Hz, 1H), 3.46 (s, 1H), 2.29 (s, 1H), 1.67 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.08, 151.09, 147.38, 142.40, 138.33, 138.17, 136.78, 129.89, 129.18, 128.75, 128.42, 128.22, 127.69, 127.58, 126.21, 125.92, 120.61, 120.44, 115.53, 114.64, 102.41, 81.61, 71.57, 70.28, 13.47. IR (KBr) : 3505, 3371, 3038, 1600, 1518, 1461, 1069; HRMS (ESI-TOF) calcd for $C_{32}H_{28}N_2O_4$ ([M+H] $^+$): 505.2128, found: 505.2133.

**6-(4-Ethylphenyl)-3-methyl-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3d)**



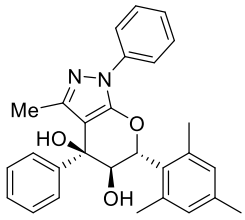

Yield : 62%; white solid; M.P. = 149-154 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.68 (m, 2H), 7.55 – 7.13 (m, 12H), 5.28 (d, *J* = 9.8 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.43 (s, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.22 (s, 1H), 1.67 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.28, 147.39, 145.49, 142.50, 138.40, 133.81, 129.15, 128.41, 128.32, 128.01, 127.55, 126.22, 125.86, 120.44, 102.43, 81.62, 71.61, 28.76, 15.54, 13.48. IR (KBr) : 3504, 3348, 3059, 1596, 1520, 1497, 1096; HRMS (ESI-TOF) calcd for $C_{27}H_{26}N_2O_3$ ([M+H]$^+$): 427.2021, found: 427.2009.

**4-(4-Chlorophenyl)-6-(4-isopropylphenyl)-3-methyl-1-phenyl-1,4,5,6 tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3e)**




Yield : 65%; white solid; M.P. = 154-160 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.20 (m, 12H), 5.23 (d, *J* = 9.8 Hz, 1H), 4.03 (d, *J* = 9.8 Hz, 1H), 2.92 (m, 1H), 2.47 (s, 1H), 1.66 (s, 3H), 1.36 (s, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.20, 147.18, 141.27, 138.17, 133.67, 129.19, 129.03, 128.78, 128.47, 127.90, 127.77, 126.92, 126.80, 126.03, 120.48, 102.01, 81.65, 71.25, 34.04, 24.06, 24.01, 23.85, 13.53. IR (KBr) : 3504, 3388, 3059, 1594, 1519, 1496, 1183; HRMS (ESI-TOF) calcd for $C_{28}H_{27}ClN_2O_3$ ([M+H]$^+$): 475.1789, found: 475.1791.

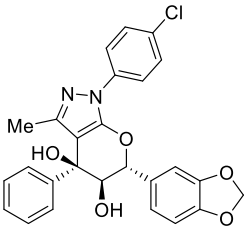
**6-Mesityl-3-methyl-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3f)**




Yield : 78%; white solid; M.P. = 139-143 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.40 – 6.87 (m, 8H), 5.89 (d, *J* = 10.4 Hz, 1H), 4.56 (d, *J* = 9.8 Hz, 1H), 3.54 (s, 1H), 2.49 (s, 3H), 2.40 (s, 3H), 2.28 (s, 3H), 2.27 (s, 1H), 1.64 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.09, 147.47, 142.87,

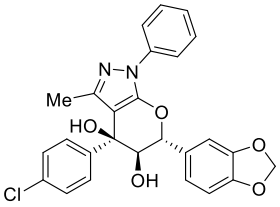
138.72, 138.58, 137.50, 131.43, 129.49, 129.12, 128.86, 128.45, 127.51, 126.13, 125.81, 120.38, 102.26, 78.10, 74.86, 71.74, 21.34, 21.11, 21.02, 13.41. IR (KBr) : 3457, 3252, 3025, 1598, 1519, 1446, 1070; HRMS (ESI-TOF) calcd for $C_{28}H_{28}N_2O_3$ ([M+H]$^+$): 441.2179, found: 441.2163.

**6-(Benzo[d][1,3]dioxol-5-yl)-1-(4-chlorophenyl)-3-methyl-4-phenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3g)**



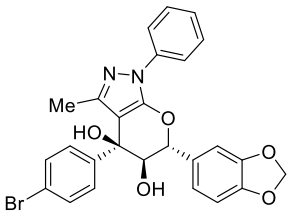

Yield : 60%; white solid; M.P. = 134-138 °C; Reaction time: 12 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.9 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.37 (d, *J* = 6.7 Hz, 2H), 7.33 (d, *J* = 5.6 Hz, 2H), 7.31 (d, *J* = 2.2 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 2H), 5.18 (d, *J* = 9.9 Hz, 1H), 4.07 (d, *J* = 9.9 Hz, 1H), 3.50 (s, 1H), 2.36 (s, 1H), 1.63 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.09, 148.49, 148.17, 147.74, 142.20, 136.81, 131.22, 130.00, 129.26, 128.46, 127.65, 126.13, 122.25, 121.40, 108.48, 107.91, 102.57, 101.53, 81.76, 71.47, 13.43. IR (KBr) : 3504, 3280, 2916, 1599, 1497, 1445, 1094; HRMS (ESI-TOF) calcd for $C_{26}H_{21}ClN_2O_5$ ([M+H]$^+$): 477.1218, found: 477.1211.

**6-(Benzo[d][1,3]dioxol-5-yl)-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3h)**



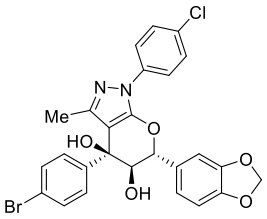

Yield : 80%; white solid; M.P. = 140-141 °C; Reaction time: 12 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 2H), 7.42 – 7.34 (m, 4H), 7.30 – 7.17 (m, 3H), 6.94 – 6.82 (m, 3H), 5.97 (s, 2H), 5.12 (d, 1H), 3.99 (d, *J* = 9.9 Hz, 1H), 3.64 (s, 1H), 2.51 (s, 1H), 1.64 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.08, 148.47, 148.15, 147.18, 141.19, 138.13, 133.42, 130.04, 129.22, 128.52, 127.76, 126.10, 122.21, 120.46, 108.44, 107.97, 102.02, 101.51, 81.75, 71.22, 13.52. IR (KBr) : 3504, 3371, 3039, 1601, 1557, 1451, 1069; HRMS (ESI-TOF) calcd for $C_{26}H_{21}ClN_2O_5$ ([M+H]$^+$): 477.1218, found: 477.1220.

**6-(Benzo[d][1,3]dioxol-5-yl)-4-(4-bromophenyl)-3-methyl-1-phenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3i)**



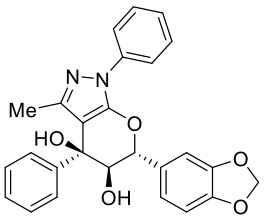
Yield : 81%; white solid; M.P. = 138-142 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.28 – 6.81 (m, 8H), 5.98 (s, 2H), 5.11 (d, *J* = 9.9 Hz, 1H), 3.97 (d, *J* = 9.9 Hz, 1H), 3.74 (s, 1H), 2.61 (s, 1H), 1.63 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.06, 148.43, 148.10, 147.18, 141.75, 138.05, 131.44, 130.03, 129.22, 128.11, 126.12, 122.20, 121.55, 120.46, 108.42, 107.95, 101.92, 101.50, 81.72, 71.21, 13.51. IR (KBr) : 3504, 3431, 3072, 1596, 1496, 1446, 1095; HRMS (ESI-TOF) calcd for $C_{26}H_{21}BrN_2O_5$ ($[M+H]^+$): 521.0712, found: 521.0695.

**6-(Benzo[d][1,3]dioxol-5-yl)-4-(4-bromophenyl)-1-(4-chlorophenyl)-3-methyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3j)**



Yield : 60%; white solid; M.P. = 140-145 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.33 – 6.84 (m, 7H), 5.99 (s, 2H), 5.17 (d, *J* = 10.0 Hz, 1H), 4.02 (d, *J* = 9.9 Hz, 1H), 3.51 (s, 1H), 2.36 (s, 1H), 1.67 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.09, 148.65, 148.29, 147.49, 141.57, 136.73, 131.56, 131.41, 129.69, 129.32, 128.08, 122.26, 121.75, 121.45, 108.57, 107.87, 102.15, 101.61, 81.84, 71.34, 13.58. IR (KBr) : 3504, 3432, 3075, 1598, 1496, 1446, 1093; HRMS (ESI-TOF) calcd for $C_{26}H_{20}BrClN_2O_5$ ($[M+H]^+$): 555.0322, found: 555.0291.

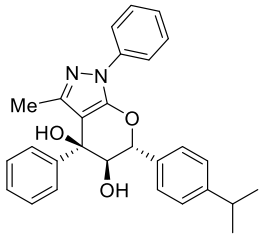
**6-(Benzo[d][1,3]dioxol-5-yl)-3-methyl-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3k)**



Yield : 78%; white solid; M.P. = 121-125 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.68 (m, 2H), 7.49 – 7.44 (m, 2H), 7.36 – 6.82 (m, 9H), 5.97 (s, 2H), 5.18 (d, *J* = 9.8 Hz, 1H), 4.07 (d, *J* = 9.9 Hz, 1H), 3.48 (s, 1H), 2.32 (s, 1H), 1.64 (s, 3H); $^{13}$C

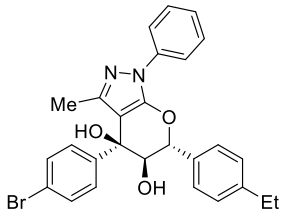
NMR (101 MHz, $CDCl_3$) δ 151.10, 148.41, 148.12, 147.39, 142.35, 138.26, 130.23, 129.19, 128.43, 127.59, 126.18, 125.95, 122.23, 120.43, 108.42, 108.00, 102.38, 101.48, 81.65, 71.51, 13.45; IR (KBr) : 3504, 3361, 3047, 1597, 1501, 1471, 1090; HRMS (ESI-TOF) calcd for $C_{26}H_{22}N_2O_5$ ($[M+H]^+$): 442.1569, found: 442.1768.

**6-(4-Isopropylphenyl)-3-methyl-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3l)**



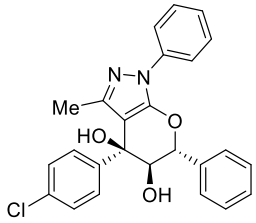

Yield : 64%; white solid; M.P. = 153-154 °C; Reaction time: 12 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.20 (m, 10H), 5.25 (d, *J* = 9.8 Hz, 1H), 4.09 (d, *J* = 9.8 Hz, 1H), 3.61 (s, 1H), 2.92 (q, *J* = 7.1 Hz, 1H), 2.32 (s, 1H), 1.65 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.15, 149.87, 149.43, 147.33, 143.87, 142.39, 141.29, 138.22, 134.71, 133.86, 129.06, 128.27, 127.83, 126.74, 126.09, 125.79, 120.36, 118.64, 102.27, 81.47, 71.38, 33.94, 23.99, 13.38; IR (KBr) : 3504, 3368, 3061, 1596, 1520, 1452, 1092; HRMS (ESI-TOF) calcd for $C_{28}H_{28}N_2O_3$ ($[M+H]^+$): 441.2179, found: 441.2176.

**4-(4-Bromophenyl)-6-(4-ethylphenyl)-3-methyl-1-phenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3m)**



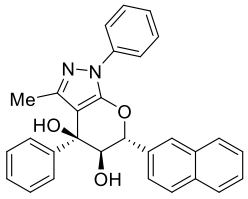

Yield : 66%; white solid; M.P. = 141-143 °C; Reaction time: 12 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.30 (m, 6H), 7.27 – 7.25 (m, 2H), 7.20 (t, 1H), 5.23 (d, *J* = 9.9 Hz, 1H), 4.05 (d, *J* = 9.9 Hz, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.18 (s, 1H), 1.68 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.11, 147.05, 145.49, 141.71, 138.08, 133.41, 131.34, 129.08, 128.26, 128.02, 127.85, 125.92, 121.45, 120.33, 101.84, 81.56, 71.21, 28.65, 15.45, 13.46; IR (KBr) : 3499, 3359, 3039, 1598, 1521, 1455, 1039; HRMS (ESI-TOF) calcd for $C_{27}H_{25}BrN_2O_3$ ($[M+H]^+$): 505.1128, found: 505.1134.

**4-(4-Chlorophenyl)-3-methyl-1,6-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3n)**



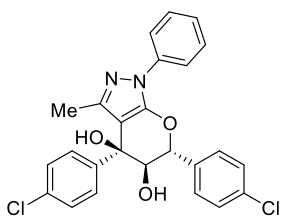

Yield : 62%; white solid; M.P. = 142-145 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.49 (m, 4H), 7.46 – 7.39 (m, 5H), 7.39 – 7.30 (m, 4H), 7.25 – 7.16 (m, 1H), 5.26 (d, *J* = 9.9 Hz, 1H), 4.07 (d, *J* = 2.9 Hz, 1H), 3.45 (s, 1H), 2.30 (s, 1H), 1.69 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.17, 147.16, 141.16, 138.24, 136.42, 133.50, 129.37, 129.22, 128.86, 128.57, 127.98, 127.79, 126.08, 120.47, 102.05, 81.79,71.34, 13.58. IR (KBr) : 3501, 3369, 3045, 1602, 1535, 1470, 1055; HRMS (ESI-TOF) calcd for $C_{25}H_{21}ClN_2O_3$ ([M+H]$^{+}$): 433.1316, found: 433.1320.

**3-Methyl-6-(naphthalen-2-yl)-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3o)**



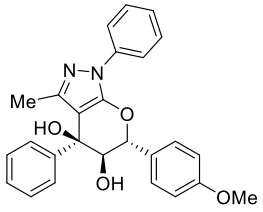

Yield : 60%; white solid; M.P. = 151-153 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.86 (m, 2H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.57 – 7.50 (m, 5H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.18 (d, *J* = 9.6 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 3.51 (s, 1H), 2.17 (s, 1H), 1.72 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.29, 147.42, 142.45, 138.37, 133.98, 129.92, 129.15, 128.48, 127.63, 126.75, 126.23, 126.11, 125.87, 125.44, 120.36, 102.59, 71.98, 13.51. IR (KBr) : 3501, 3366, 3061, 1597, 1514, 1454, 1096; HRMS (ESI-TOF) calcd for $C_{29}H_{24}N_2O_3$ ([M+H] $^{+}$): 449.1866, found: 449.1876.

**4,6-Bis(4-chlorophenyl)-3-methyl-1-phenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3p)**



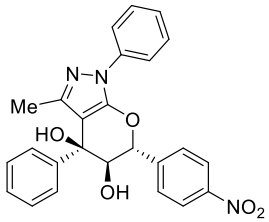
Yield : 71%; white solid; M.P. = 143-146 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.39 (m, 3H), 7.36 (d, *J* = 3.8 Hz, 6H), 7.33 – 7.27 (m, 2H), 7.26 – 7.19 (m, 1H), 5.15 (d, *J* = 9.9 Hz, 1H), 3.96 (d, *J* = 9.6 Hz, 1H), 3.72 (s, 1H), 2.68 (s, 1H), 1.64 (s, 3H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 150.93, 147.24, 140.89, 138.01, 135.10, 135.03, 133.51, 129.28, 129.27, 128.88, 128.56, 127.73, 126.23, 120.42, 102.02, 81.11, 71.09, 13.53. IR (KBr) : 3504, 3317, 3083, 1597, 1519, 1451, 1091; HRMS (ESI-TOF) calcd for $C_{25}H_{20}Cl_2N_2O_3$ ([M+H] $^{+}$): 467.0930, found: 467.0916.

**6-(4-Methoxyphenyl)-3-methyl-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3q)**



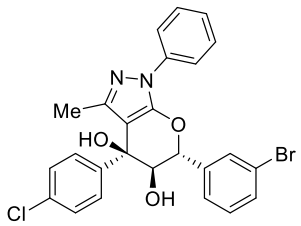

Yield : 72%; white solid; M.P. = 119-121 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.66 (m, 2H), 7.50 – 7.40 (m, 4H), 7.36 – 6.94 (m, 8H), 5.25 (d, *J* = 9.9 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.82 (s, 3H), 3.44 (s, 1H), 2.28 (s, 1H), 1.66 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 160.32, 151.29, 147.38, 142.51, 138.38, 129.39, 129.15, 128.58, 128.42, 128.22, 127.56, 126.21, 125.86, 120.59, 120.40, 114.24, 113.99, 102.44, 81.44, 71.61, 55.48, 13.48. IR (KBr) : 3504, 3423, 3076, 1598, 1517, 1450, 1075; HRMS (ESI-TOF) calcd for $C_{26}H_{24}N_2O_4$ ([M+H] $^{+}$): 429.1814, found: 429.1822.

**3-Methyl-6-(4-nitrophenyl)-3-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3r)**



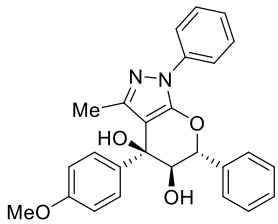

Yield : 60%; white solid; M.P. = 106-108 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.73 – 7.63 (m, 4H), 7.49 – 7.44 (m, 2H), 7.41 – 7.22 (m, 6H), 5.31 (d, *J* = 9.8 Hz, 1H), 4.03 (d, *J* = 9.9 Hz, 1H), 3.66 (s, 1H), 2.83 (s, 1H), 1.65 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 150.55, 148.21, 147.48, 144.07, 141.64, 138.05, 129.30, 128.80, 128.58, 127.87, 126.31, 126.18, 123.64, 120.47, 102.44, 80.69, 71.37, 13.49. IR (KBr) : 3504, 3432, 3072, 1598, 1520, 1450, 1109; HRMS (ESI-TOF) calcd for $C_{25}H_{21}N_3O_5$ ([M+H] $^{+}$): 444.1560, found: 444.1563.

**6-(3-Bromophenyl)-4-(4-chlorophenyl-3-methyl-1-phenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3s)**



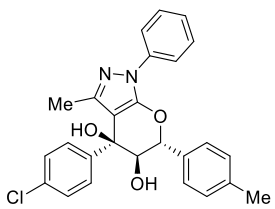

Yield : 66%; white solid; M.P. = 151-157 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.26 (m, 10H), 7.23 (d, *J* = 7.4 Hz, 1H), 5.10 (d, *J* = 9.9 Hz, 1H), 3.96 (d, *J* = 9.9 Hz, 1H), 3.74 (s, 1H), 2.67 (s, 1H), 1.64 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 150.86, 147.26, 140.81, 138.83, 137.99, 133.54, 132.28, 130.99, 130.21, 129.31, 128.58, 127.74, 126.65, 126.32, 122.71, 120.49, 102.01, 81.08, 71.06, 13.56. IR (KBr) : 3504, 3388, 3060, 1596, 1519, 1493, 1123; HRMS (ESI-TOF) calcd for $C_{25}H_{20}BrClN_2O_3$ ([M+H] $^{+}$): 511.0498, found: 511.0415.

**4-(4-Methoxyphenyl)-3-methyl-1,6-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3t)**



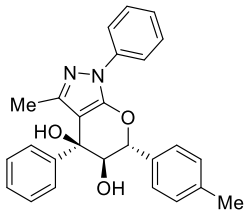

Yield : 70%; white solid; M.P. = 113-117 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.48 (m, 4H), 7.45 – 7.13 (m, 8H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.26 (d, *J* = 10.0 Hz, 1H), 4.06 (d, *J* = 9.9 Hz, 1H), 3.79 (s, 3H), 3.43 (s, 1H), 2.42 (s, 1H), 1.69 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.97, 151.10, 147.45, 138.31, 136.74, 134.27, 129.19, 129.16, 128.74, 127.98, 127.38, 125.90, 120.41, 113.74, 102.45, 81.73, 71.24, 55.40, 13.54. IR (KBr) : 3504, 3400, 3036, 1600, 1519, 1453, 1087; HRMS (ESI-TOF) calcd for $C_{26}H_{24}N_2O_4$ ([M+H] $^{+}$): 429.1814, found: 429.1809.

**4-(4-Chlorophenyl)-3-methyl-1-phenyl-6-(p-tolyl)-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3u)**



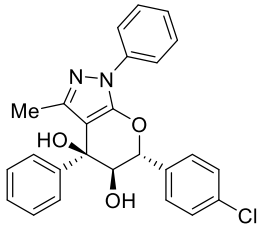
Yield : 67%; white solid; M.P. = 159-166 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.21 (m, 11H), 5.22 (d, *J* = 9.8 Hz, 1H), 4.05 (d, *J* = 10.0 Hz, 1H), 3.56 (s, 1H), 2.38 (s, 3H), 2.31 (s, 1H), 1.67 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.14, 147.06, 141.17, 139.24, 138.13, 133.31, 133.24, 129.08, 128.42, 120.31, 101.97, 81.59, 71.19, 21.29. IR (KBr) : 3504, 3360, 3001, 1617, 1519, 1450, 1067; HRMS (ESI-TOF) calcd for $C_{26}H_{23}ClN_2O_3$ ([M+H] $^{+}$): 447.1476, found: 447.1453.

**3-Methyl-1,4-diphenyl-6-(p-tolyl)-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3v)**




Yield : 75%; white solid; M.P. = 159-166 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.45 (m, 4H), 7.40 – 7.33 (m, 6H), 7.30 – 7.17 (m, 4H), 5.25 (d, *J* = 9.9 Hz, 1H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.46 (s, 1H), 2.38 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.16, 147.29, 142.37, 139.10, 138.26, 133.48, 129.39, 129.04, 128.29, 127.87, 127.43, 126.10, 125.75, 120.28, 102.32, 81.50, 71.45, 21.29, 13.35. IR (KBr) : 3504, 3401, 3081, 1597, 1520, 1496, 1096; HRMS (ESI-TOF) calcd for $C_{26}H_{24}N_2O_3$ ([M+H]$^{+}$): 413.1866, found: 413.1834.

**6-(4-Chlorophenyl)-3-methyl-1,4-diphenyl-1,4,5,6-tetrahydropyrano[2,3-c] pyrazole-4,5-diol (3w)**




Yield : 74%; white solid; M.P. = 159-166 °C; Reaction time: 12 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.64 (m, 2H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.33 – 7.22 (m, 7H), 5.10 (d, *J* = 9.9 Hz, 1H), 3.98 (d, *J* = 9.9 Hz, 1H), 3.80 (s, 1H), 2.82 (s, 1H), 1.58 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.89, 147.51, 142.14, 138.05, 135.35, 134.76, 129.26, 129.19, 128.72, 128.37, 127.56, 126.15, 126.07, 120.38, 102.35, 81.00, 71.21, 13.37; IR (KBr) : 3503, 3399, 3079, 1596, 1521, 1499, 1097; HRMS (ESI-TOF) calcd for $C_{25}H_{21}ClN_2O_3$ ([M+H] $^{+}$): 433.1319, found: 433.1336.

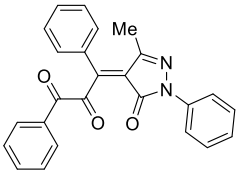
**(*4S,5R,6R*)-3-Methyl-1,4,6-triphenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (3aa)**

Yield : 75%;  white solid; M.P. = 154-159 °C; Reaction time: 12 h; HPLC (Daicel Chiralpak AD-H, hexane/2-propanol = 90:10, flow rate 0.5 mL/min) $t_{minor}$ = 14.0 min, $t_{major}$ = 20.4 min, 56% de; $[\alpha]_D^{25}$ = 35.023 (c =1.0, $CHCl_3$); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 4H), 7.36 – 7.25 (m, 7H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.20 (dd, *J* = 10.0, 7.4 Hz, 1H), 4.04 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.38 (d, *J* = 4.4 Hz, 1H), 2.17 (d, *J* = 6.3 Hz, 1H), 1.59 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.18, 147.40, 142.35, 138.34, 136.65, 129.24, 129.18, 128.77, 128.43, 127.99, 127.59, 126.20, 125.92, 120.42, 102.39, 81.68, 71.55, 13.51.

**Typical experimental procedure for the synthesis of compounds (4a-h)**

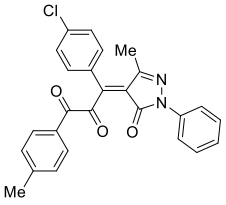
A mixture of 3-methyl-1,4,6-triphenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (**3**, 1mmol), aq. HBr 47% (0.2 eq.) and $H_2O_2$ 30% (3 eq.) in acetonitrile (5 mL) was placed in a round bottom flask and stirred at reflux for 2 h. After completion of the reaction, the crude reaction mixture was cooled to room temperature and washed with ethylacetate and water for three times. Then the combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated. The purification was carried out by 5% (ethylacetate / hexane) mixture to afford the product **4** as a reddish semi solid in  good yield.

**(*Z*)-3-(3-Methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)-1,3-diphenylpropane-1,2-dione (4a)**



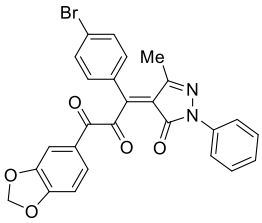

Yield : 71%;  Reddish semi solid; Reaction time: 2 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.49 (m, 8H), 7.34 – 7.16 (m, 3H), 1.90 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.07, 186.51, 163.15, 158.04, 148.21, 137.51, 134.32, 132.57, 132.30, 131.36, 130.74, 129.39, 128.99, 128.87, 128.65, 128.57, 125.48, 118.84, 16.58; IR (KBr) : 3060, 1710, 1676, 1622, 1496; HRMS (ESI-TOF) calcd for $C_{25}H_{18}N_2O_3$ ($[M+H]^+$): 395.1396, found: 395.1385.

**(*Z*)-3-(4-Chlorophenyl)-3-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)-1-(p-tolyl) propane-1,2-dione (4b)**



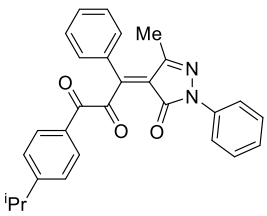
Yield : 78%;  Reddish semi solid; Reaction time: 2 h; ; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.71 (m, 2H), 7.56 – 7.50 (m, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.19 – 7.09 (m, 1H), 2.45 (s, 3H), 1.91 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.01, 186.16, 162.92, 156.81, 147.80, 145.69, 137.41, 137.16, 131.46, 131.34, 130.75, 130.19, 130.04, 129.94, 129.84, 129.52, 129.50, 129.40, 129.22, 128.98, 125.52, 118.80, 22.10, 16.72. IR (KBr) : 3059, 1725, 1656, 1642, 1486; HRMS (ESI-TOF) calcd for $C_{26}H_{19}ClN_2O_3$ ($[M+H]^+$) : 443.1162, found: 443.1190.

**(*Z*)-1-(Benzo[d][1,3] dioxol-5-yl)-3-(4-bromophenyl)-3-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)-propane-1,2-dione (4c)**



Yield : 82%;  Reddish semi solid; Reaction time: 2 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.72 (m, 3H), 7.70 – 7.59 (m, 3H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.19 – 7.11 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.08 (s, 2H), 1.90 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.94, 184.61, 162.92, 157.03, 153.28, 148.06, 147.84, 137.42, 132.19, 131.25, 130.20, 129.37, 129.02, 128.92, 126.81, 125.57, 125.50, 118.87, 110.49, 108.49, 102.14, 16.72. IR (KBr) : 3069, 1700, 1680, 1600, 1499; HRMS (ESI-TOF) calcd for $C_{26}H_{17}BrN_2O_5$ ($[M+H]^+$): 517.0400, found: 517.0397.

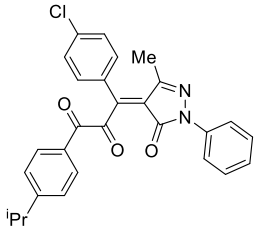
**(*Z*)-1-(4-Isopropylphenyl)-3-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)-3-phenylpropane-1,2-dione (4d)**



Yield : 80%;  Orange semi solid; Reaction time: 2 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.72 (m, 2H), 7.58 – 7.49 (m, 5H), 7.42 – 7.30 (m, 4H), 7.20 – 7.10 (m, 1H), 3.13 – 2.80 (m, 1H), 1.89 (s, 3H), 1.30 (d, *J* = 7.0 Hz, 6H); $^{13}$C NMR (101 MHz,

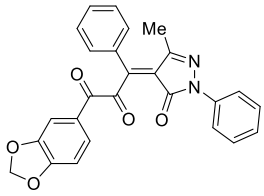
$CDCl_3$) δ 193.27, 186.20, 163.15, 158.44, 156.08, 148.21, 137.56, 132.41, 130.69, 130.38, 129.26, 128.98, 128.84, 128.65, 126.77, 118.93, 34.62, 23.71, 16.56. IR (KBr) : 3065, 1684, 1660, 1598, 1497; HRMS (ESI-TOF) calcd for $C_{28}H_{24}N_2O_3$ ([M+H] $^+$): 437.1866, found: 437.1853.

**(*Z*)-3-(4-Chlorophenyl)-1-(4-isopropylphenyl)-3-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)-1,3-diphenylpropane-1,2-dione (4e)**



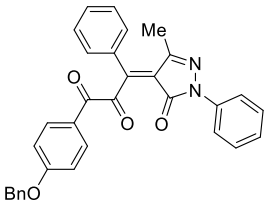

Yield : 75%; Reddish semi solid; Reaction time: 2 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.3 Hz, 2H), 7.80 – 7.73 (m, 2H), 7.57 – 7.44 (m, 4H), 7.41 – 7.31 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.00 (m, *J* = 7.0 Hz, 1H), 1.91 (s, 3H), 1.30 (d, *J* = 7.0 Hz, 6H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 193.04, 186.20, 162.95, 156.88, 156.24, 147.80, 137.42, 137.17, 131.62, 130.74, 130.15, 130.04, 129.50, 129.22, 129.00, 126.85, 125.54, 118.87, 34.61, 23.70, 16.70; IR (KBr) : 3041, 1681, 1633, 1598, 1495; HRMS (ESI-TOF) calcd for $C_{28}H_{23}ClN_2O_3$ ([M+H] $^+$): 471.1476, found: 471.1474.

**(*Z*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)-3-phenylpropane-1,2-dione (4f)**



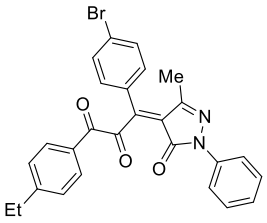

Yield : 72%; Brown semi solid; Reaction time: 2 h; $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.80 – 7.69 (m, 3H), 7.61 – 7.54 (m, 2H), 7.49 – 7.34 (m, 5H), 7.19 – 7.10 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.07 (s, 2H), 1.87 (s, 3H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 193.25, 84.61, 163.10, 158.57, 153.14, 148.23, 148.01, 137.51, 132.39, 130.69, 129.14, 128.99, 128.88, 128.85, 128.63, 127.00, 125.47, 118.89, 110.54, 108.45, 102.09, 16.58; IR (KBr) : 3063, 1705, 1686, 1633, 1498; HRMS (ESI-TOF) calcd for $C_{26}H_{18}N_2O_5$ ([M+H] $^+$): 439.1294, found: 439.1297.

**(*Z*)-1-(4-(Benzyloxy)phenyl)-3-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)-3-phenylpropane-1,2-dione (4g)**




Yield : 68%; Brown semi solid; Reaction time: 2 h; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 2H), 7.82 – 7.77 (m, 2H), 7.61 – 7.55 (m, 2H), 7.52 – 7.43 (m, 6H), 7.42 – 7.28 (m, 6H), 7.21 – 7.12 (m, 1H), 5.14 (s, 2H), 1.90 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.88, 186.01, 163.00, 158.67, 157.89, 148.11, 137.41, 136.55, 133.63, 132.16, 130.65, 129.61, 129.28, 128.90, 128.77, 128.66, 128.54, 128.14, 127.68, 125.38, 124.54, 121.94, 118.73, 115.81, 70.21, 16.49; IR (KBr) : 3058, 1707, 1679, 1578, 1497; HRMS (ESI-TOF) calcd for $C_{32}H_{24}N_2O_4$ ($[M+H]^+$): 501.1814, found: 501.1782.

**(*Z*)-3-(4-Bromophenyl)-1-(4-ethylphenyl)-3-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)propane-1,2-dione (4h)**

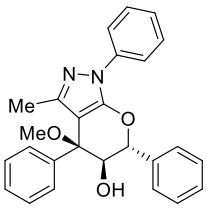



Yield : 81%; Brown semi solid; Reaction time: 2 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.56 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.28 (m, 4H), 7.15 (t, *J* = 7.3 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.91 (s, 3H), 1.28 (t, *J* = 7.7 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.83, 186.07, 162.80, 156.76, 151.67, 147.71, 137.27, 132.06, 131.47, 131.09, 130.08, 129.88, 129.34, 128.88, 128.13, 125.44, 118.74, 29.25, 16.64, 15.12; IR (KBr) : 3050, 1715, 1667, 1625, 1486; HRMS (ESI-TOF) calcd for $C_{27}H_{21}BrN_2O_3$ ($[M+H]^+$): 501.0814, found: 501.0811.

**Typical experimental procedure for the synthesis of compounds (5a-b)**

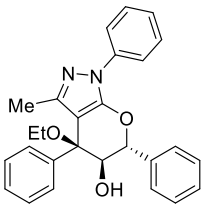
A mixture of 3-methyl-1,4,6-triphenyl-1,4,5,6-tetrahydropyrano[2,3-c]pyrazole-4,5-diol (**3**, 1mmol) and *p*-TsOH.$H_2$0 (1.0 eq.) in respective alcohols (5 mL) was placed in a round bottom flask and stirred at room temperature until the completion of the reaction. After completion of the reaction as indicated by TLC, the reaction mixture was washed with ethylacetate and water for three times. Then the combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated. The purification was carried out by 8% (ethylacetate / hexane) mixture to afford the product **5a** as a white solid in very good yield.

**4-Methoxy-3-methyl-1,4,6-triphenyl-1,4,5,6-tetrahydropyrano[2,3-*c*] pyrazol-5-ol (5a)**



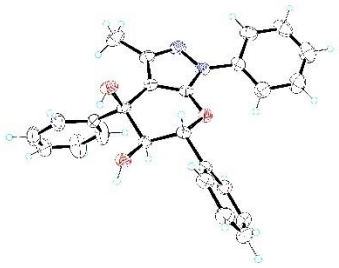

Yield : 90%;  White solid; Reaction time: 5 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 12H), 7.20 (d, *J* = 6.0 Hz, 1H), 5.40 (d, *J* = 9.8 Hz, 1H), 3.93 (d, *J* = 10.1 Hz, 1H), 3.46 (s, 3H), 2.36 (s, 1H), 1.86 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.17, 146.04, 137.28, 135.96, 129.18, 128.98, 128.92, 128.57, 128.34, 128.08, 127.99, 127.15, 127.05, 125.95, 122.72, 120.43, 113.60, 97.31, 81.53, 78.15, 52.28, 14.91; HRMS (ESI-TOF) calcd for $C_{26}H_{24}N_2O_3$ ([M+H] $^{+}$): 413.1866, found: 413.1857.

**4-Ethoxy-3-methyl-1,4,6-triphenyl-1,4,5,6-tetrahydropyrano[2,3-*c*] pyrazol-5-ol (5b)**



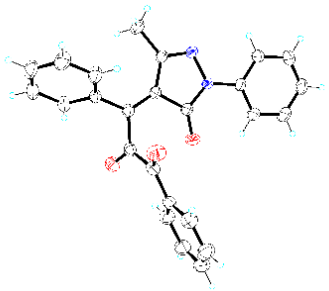

Yield : 85%;  White solid; Reaction time: 5 h; $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.78 (m, 2H), 7.52 – 7.35 (m, 11H), 7.32 (d, *J* = 6.6 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 5.39 (d, *J* = 9.9 Hz, 1H), 3.92 (d, *J* = 8.8 Hz, 1H), 3.65 (dd, *J* = 13.5, 6.8 Hz, 2H), 2.60 (s, 1H), 1.85 (s, 3H), 1.38 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 151.80, 148.04, 139.27, 138.42, 137.36, 129.16, 128.91, 128.58, 128.51, 128.14, 127.82, 126.99, 125.90, 120.39, 98.00, 81.63, 78.00, 59.78, 15.55, 14.87; HRMS (ESI-TOF) calcd for $C_{27}H_{26}N_2O_3$ ([M+H] $^{+}$): 427.2021, found: 427.2017.

**Crystal data and structure refinement for compound 3a**



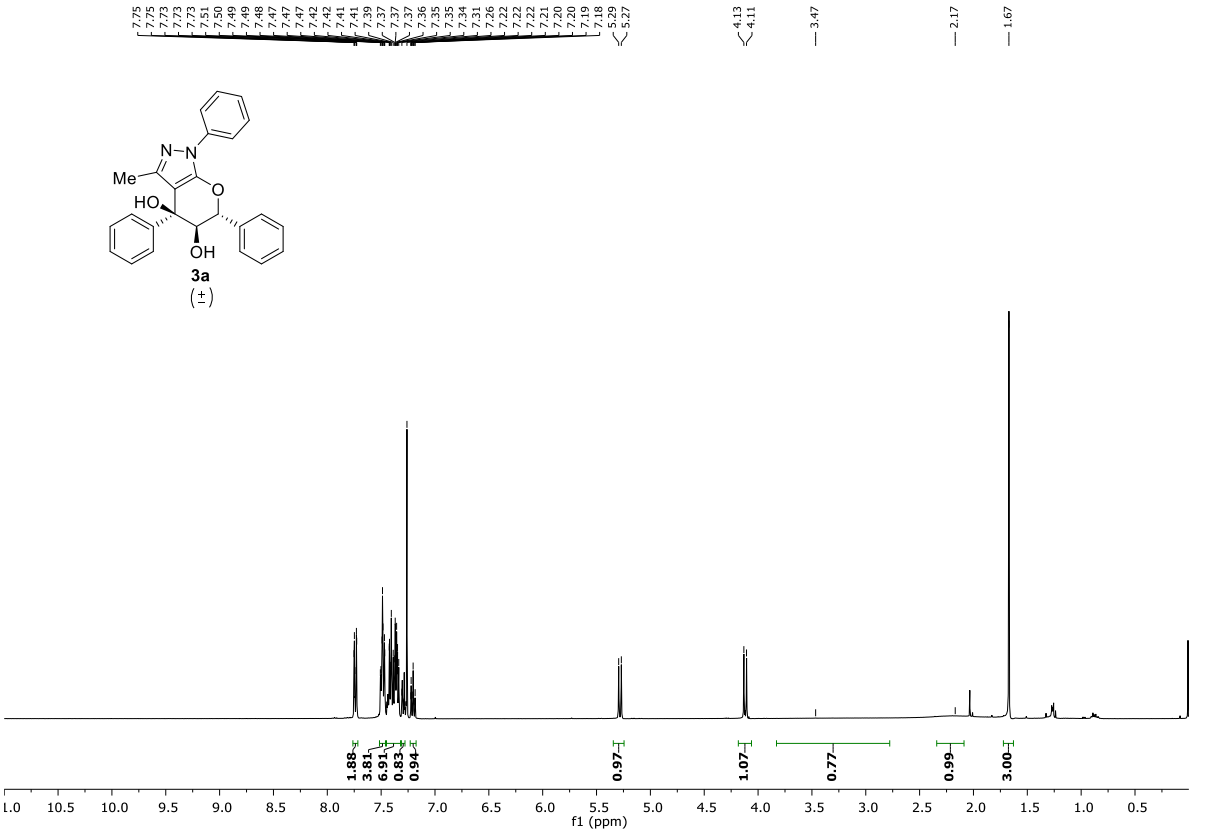
| | |
|---|---|
| Identification code | MB-MSP-AA-SS |
| Empirical formula | $C_{25}H_{22}N_2O_3$ |
| Formula weight | 398.44 |
| Temperature/K | 298 (2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 11.2883(4) |
| b/Å | 9.8313(4) |
| c/Å | 18.7276(7) |
| α/° | 90 |
| β/° | 101.498(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 2036.66(14) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 2.599 |
| μ/mm$^{-1}$ | 0.172 |
| F(000) | 1680.0 |
| Crystal size/mm$^3$ | 0.7 × 0.52 × 0.42 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 7.846 to 58.342 |
| Index ranges | $-13 \leq h \leq 15$, $-13 \leq k \leq 13$, $-23 \leq l \leq 25$ |
| Reflections collected | 15572 |
| Independent reflections | 4848 [$R_{int}$ = 0.0306, $R_{sigma}$ = 0.0329] |
| Data/restraints/parameters | 4848/0/275 |
| Goodness-of-fit on $F^2$ | 1.029 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0473, $wR_2$ = 0.1070 |
| Final R indexes [all data] | $R_1$ = 0.0784, $wR_2$ = 0.1235 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.19/-0.15 |

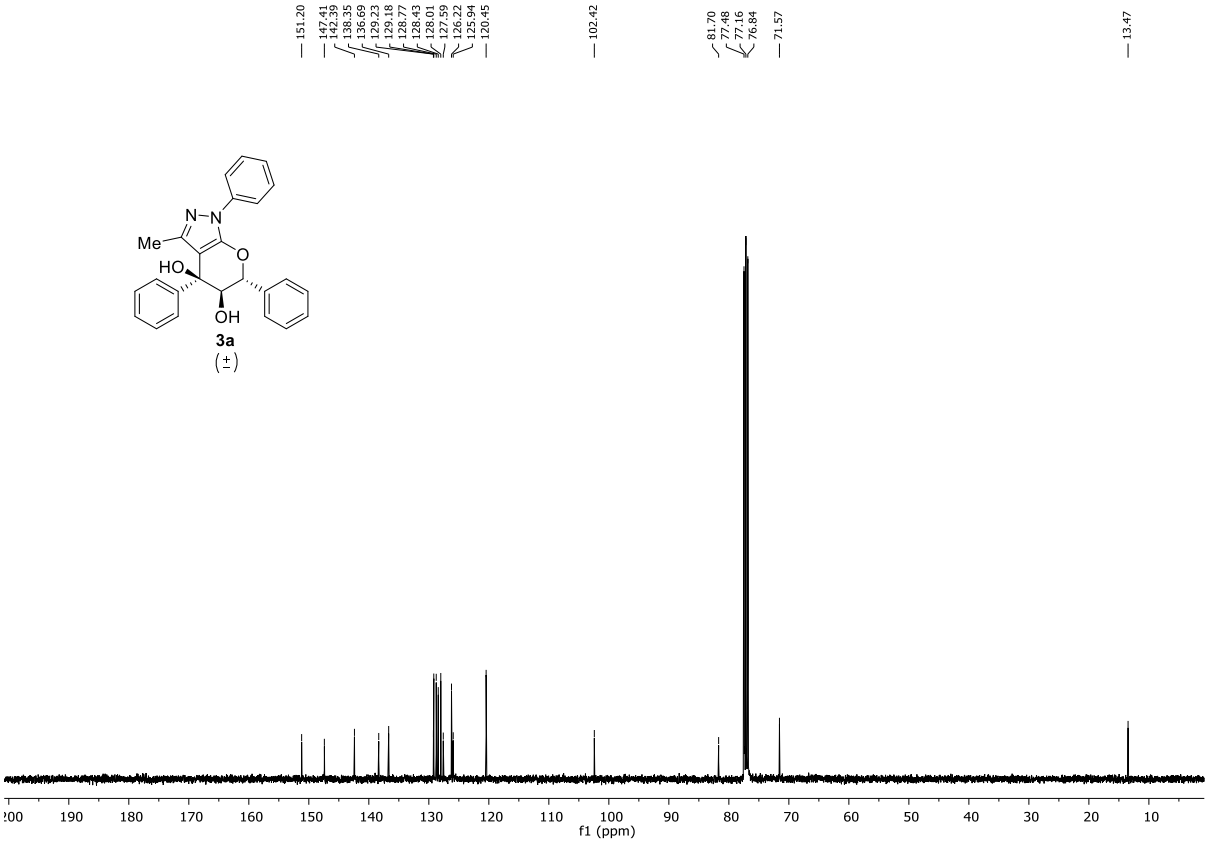
**Crystal data and structure refinement for compound 4a**

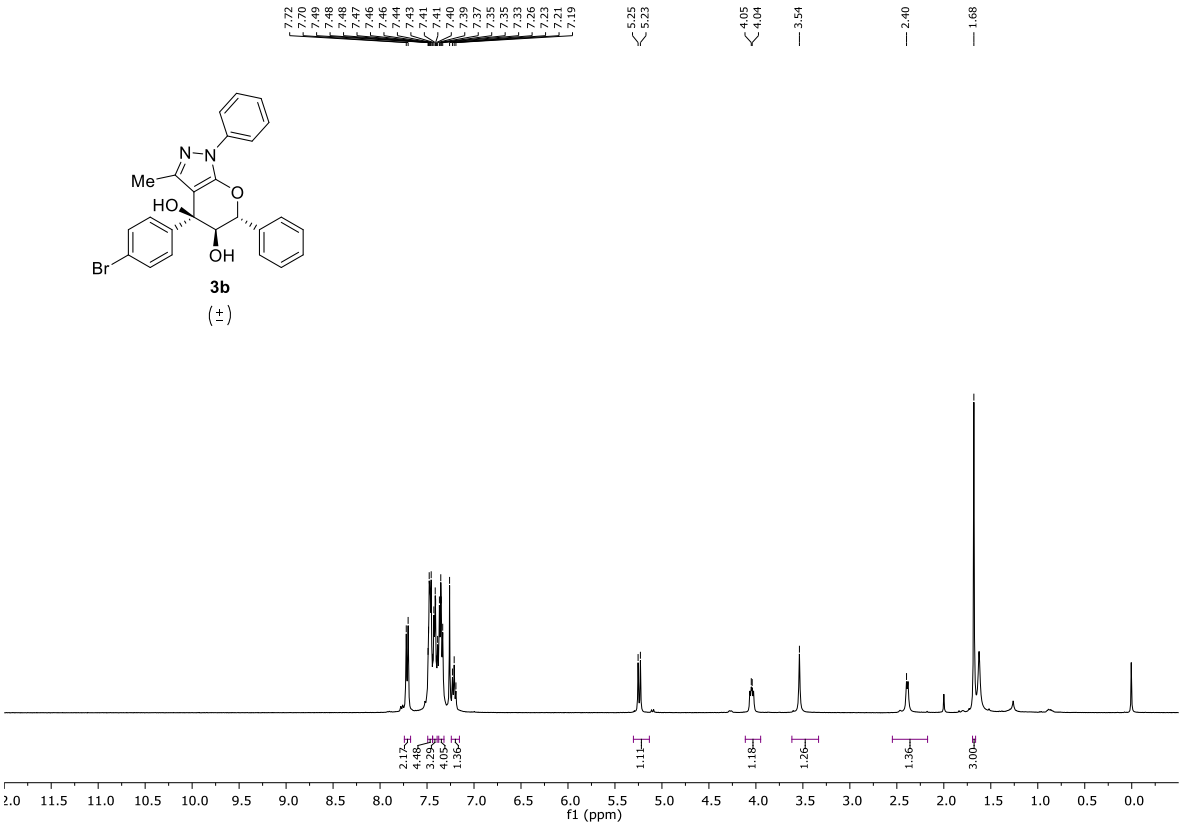


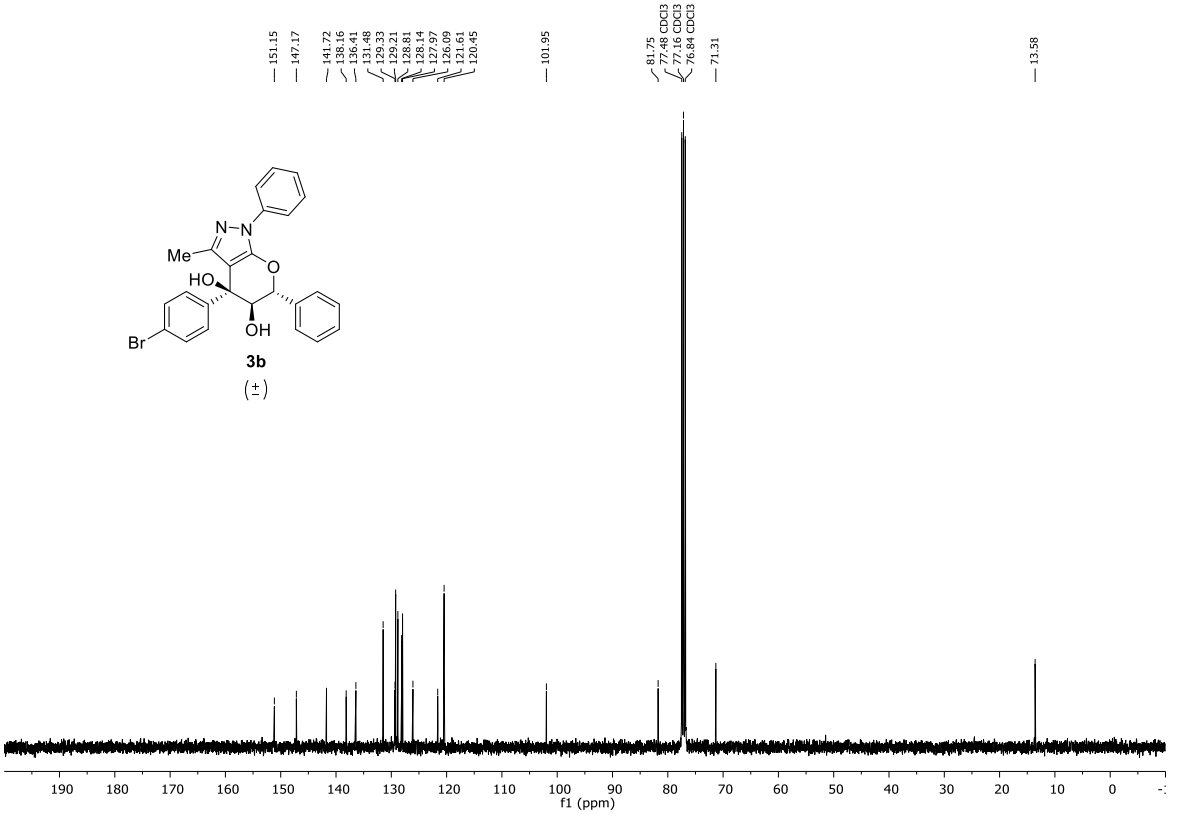
| | |
|---|---|
| Identification code | MB-MSP-609-S |
| Empirical formula | $C_{25}H_{18}N_2O_3$ |
| Formula weight | 394.41 |
| Temperature/K | 298(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.6663(14) |
| b/Å | 10.7447(16) |
| c/Å | 10.7533(10) |
| α/° | 66.900(12) |
| β/° | 85.830(10) |
| γ/° | 80.391(12) |
| Volume/Å$^3$ | 1012.9(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.293 |
| μ/mm$^{-1}$ | 0.086 |
| F(000) | 412.0 |
| Crystal size/mm$^3$ | 0.82 × 0.72 × 0.42 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.406 to 58.254 |
| Index ranges | -13 ≤ h ≤ 12, -14 ≤ k ≤ 13, -14 ≤ l ≤ 14 |
| Reflections collected | 10884 |
| Independent reflections | 4715 [$R_{int}$ = 0.0165, $R_{sigma}$ = 0.0197] |
| Data/restraints/parameters | 4715/0/272 |
| Goodness-of-fit on F$^2$ | 1.029 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0455, $wR_2$ = 0.1134 |
| Final R indexes [all data] | $R_1$ = 0.0583, $wR_2$ = 0.1231 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.15/-0.20 |

**1H, & 13C NMR Spectra for** the Compound**s 3a-w, 3aa, 4a-h & 5a-b**




7.72
7.70
7.49
7.48
7.48
7.47
7.46
7.46
7.44
7.43
7.41
7.41
7.40
7.39
7.37
7.35
7.35
7.33
7.26
7.23
7.21
7.19
5.25
5.23
4.05
4.04
3.54
2.40
1.68
Me
HO
OH
Br
3b
(±)
2.17
4.49
3.29
4.05
1.36
1.11
1.18
1.26
1.36
3.00
f1 (ppm)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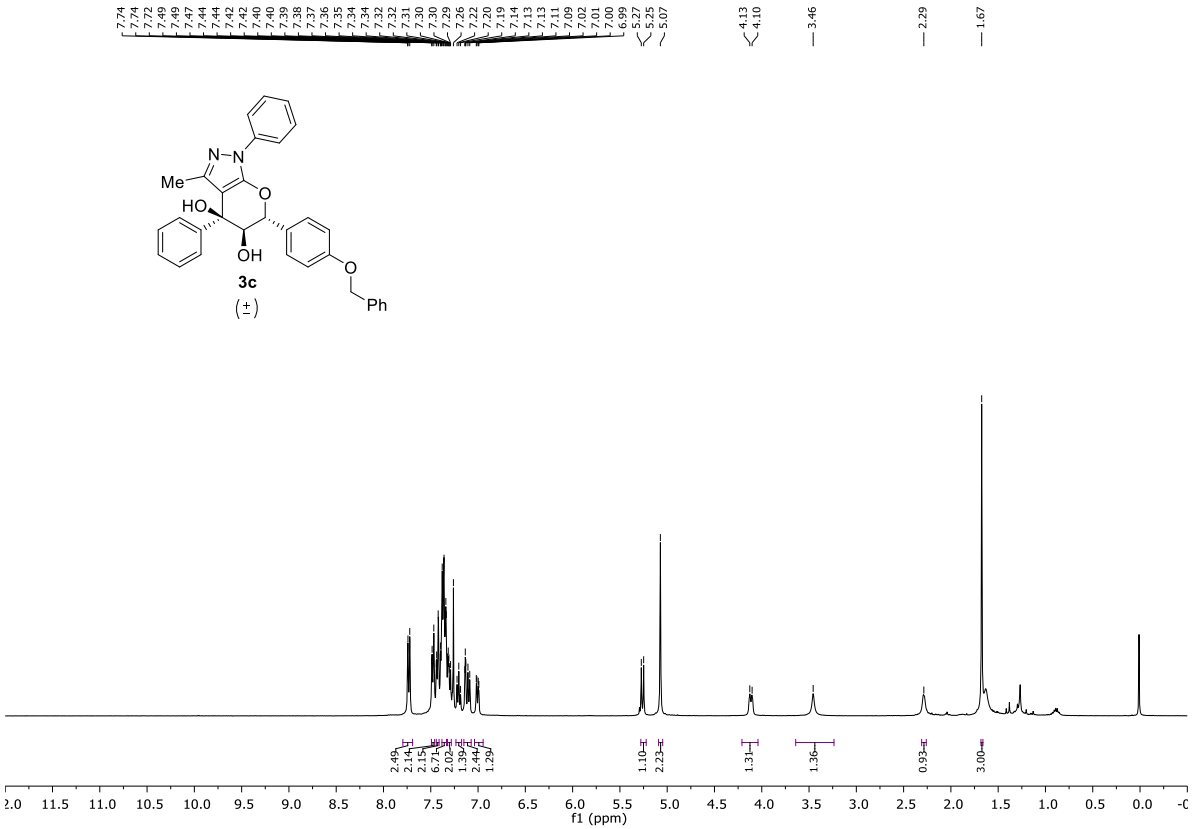
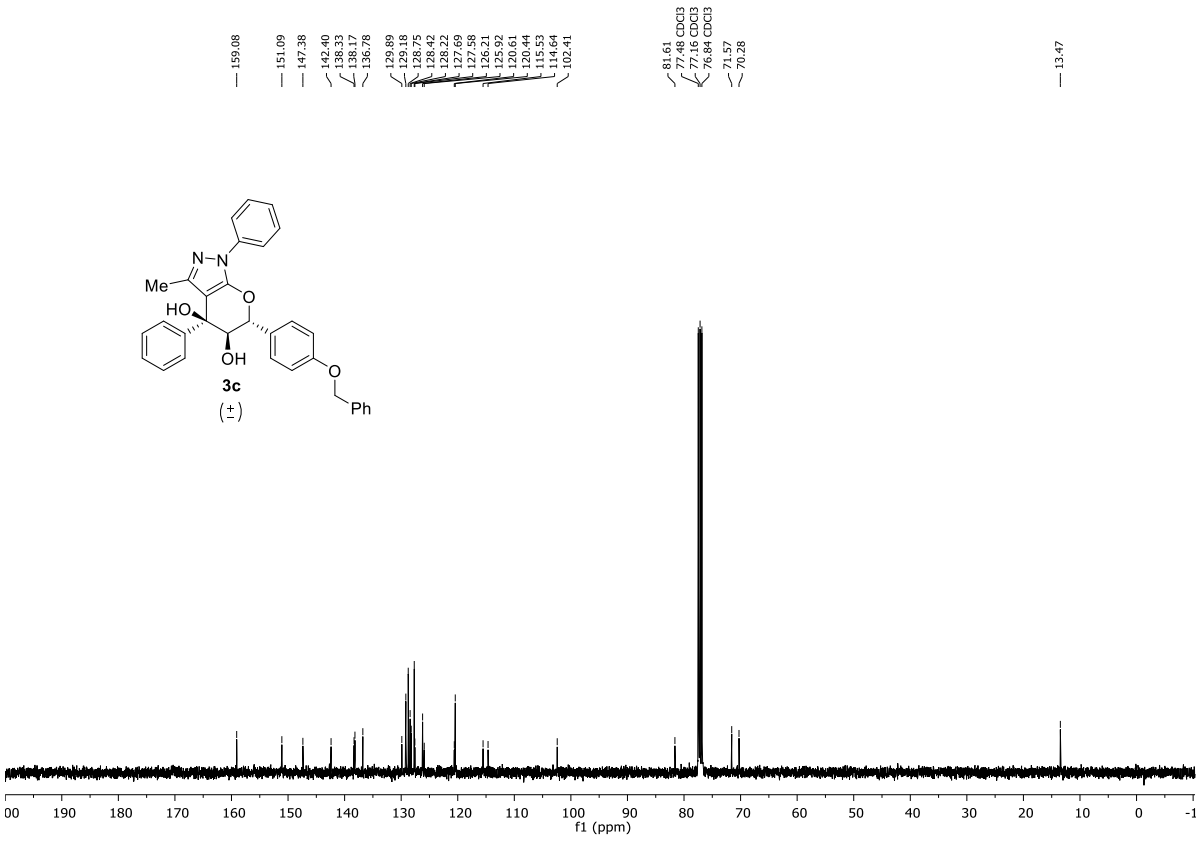
147.17
141.72
138.16
136.41
131.48
129.33
129.21
128.81
128.14
127.97
126.09
121.61
120.45
101.95
81.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.31
13.58
Me
HO
OH
Br
3b
(±)
f1 (ppm)


7.74 7.74 7.72 7.49 7.49 7.47 7.44 7.44 7.42 7.42 7.40 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.34 7.32 7.32 7.31 7.30 7.30 7.29 7.26 7.22 7.20 7.19 7.14 7.13 7.13 7.11 7.09 7.02 7.01 7.00 6.99 5.27 5.25 5.07 4.13 4.10 3.46 2.29 1.67
N
N
Me
O
HO
OH
O
Ph
3c
(±)
2.49 2.14 2.15 6.71 2.02 1.39 2.44 1.29 1.10 2.23 1.31 1.36 0.93 3.00
f1 (ppm)


159.08 151.09 147.38 142.40 138.33 138.17 136.78 129.89 129.18 128.75 128.42 128.22 127.69 127.58 125.21 125.02 120.61 120.44 115.53 114.64 102.41 81.61 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 71.57 70.28 13.47
N
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Me
O
HO
OH
O
Ph
3c
(±)
f1 (ppm)


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7.75
7.75
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7.73
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7.49
7.47
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5.27
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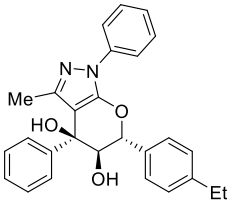
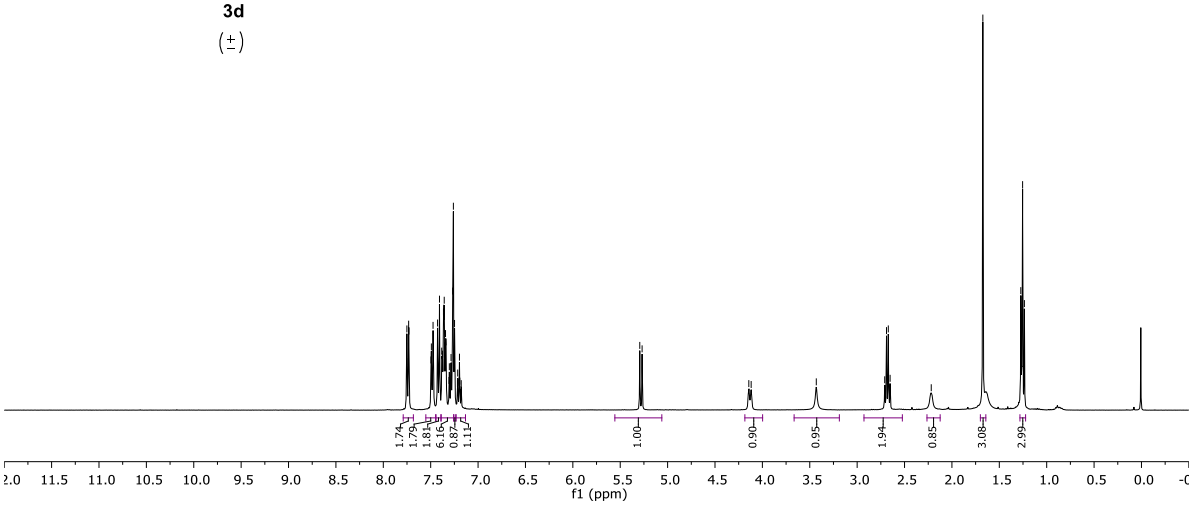
1.25
1.24


N
N
Me
HO
O
OH
Et

**3d**

(±)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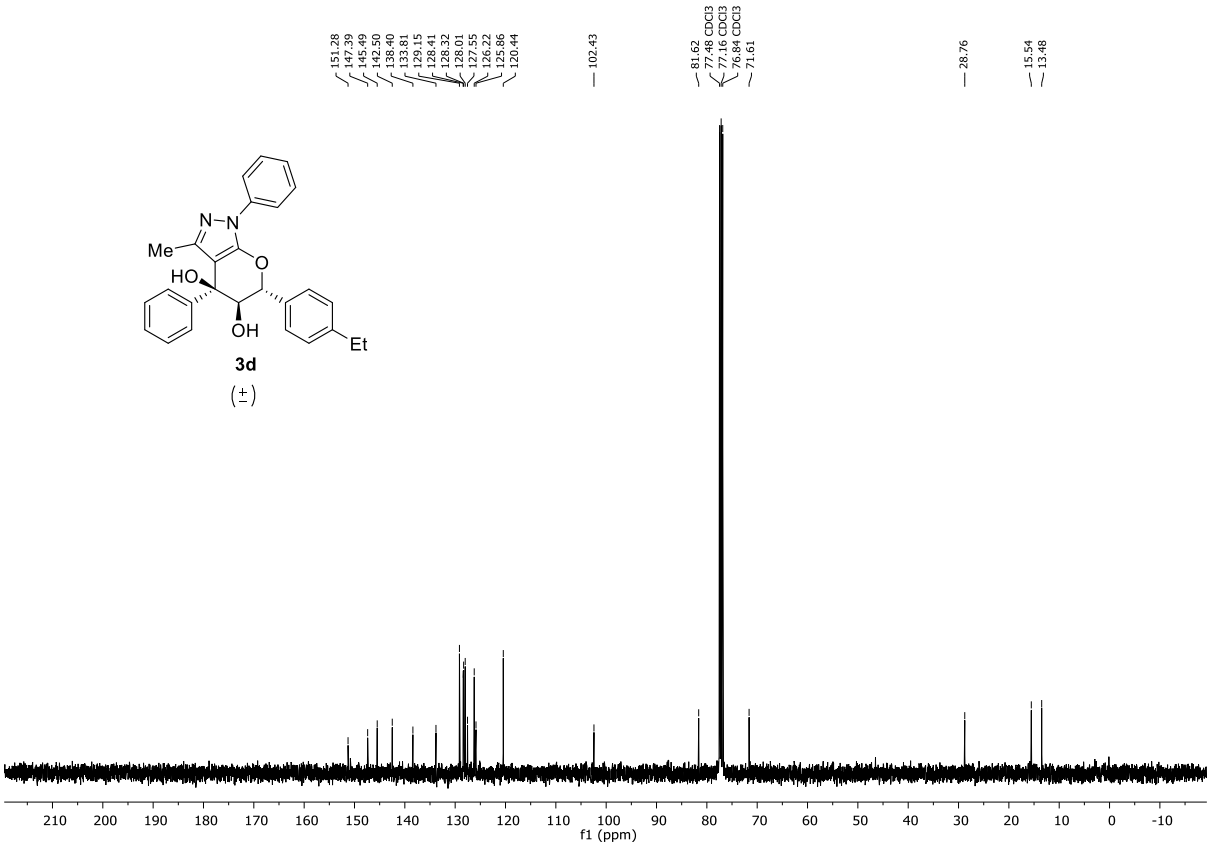
2.99
f1 (ppm)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147.39
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133.81
129.15
128.41
128.32
128.01
127.55
126.22
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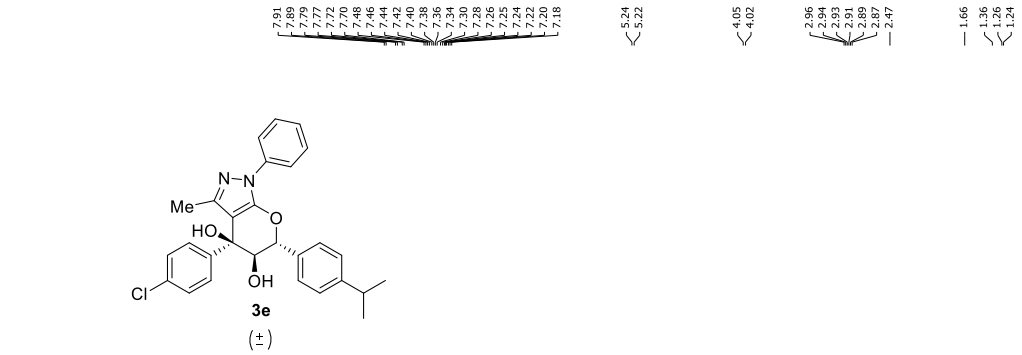
120.44
102.43
81.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.61
28.76
15.54
13.48
f1 (ppm)


N
N
Me
HO
O
OH
Et

**3d**

(±)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7.36
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7.28
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7.25
7.24
7.22
7.20
7.18
5.24
5.22
4.05
4.02
2.96
2.94
2.93
2.91
2.89
2.87
2.47
1.66
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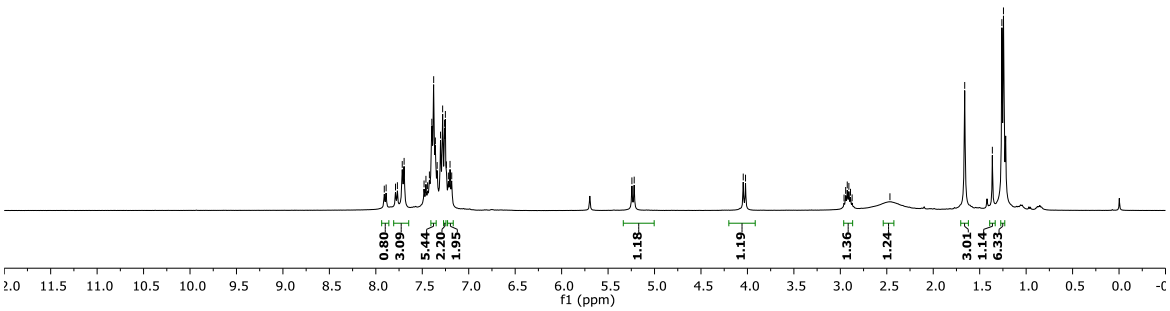
N
N
Me
O
HO
OH
Cl
3e
(±)


0.80
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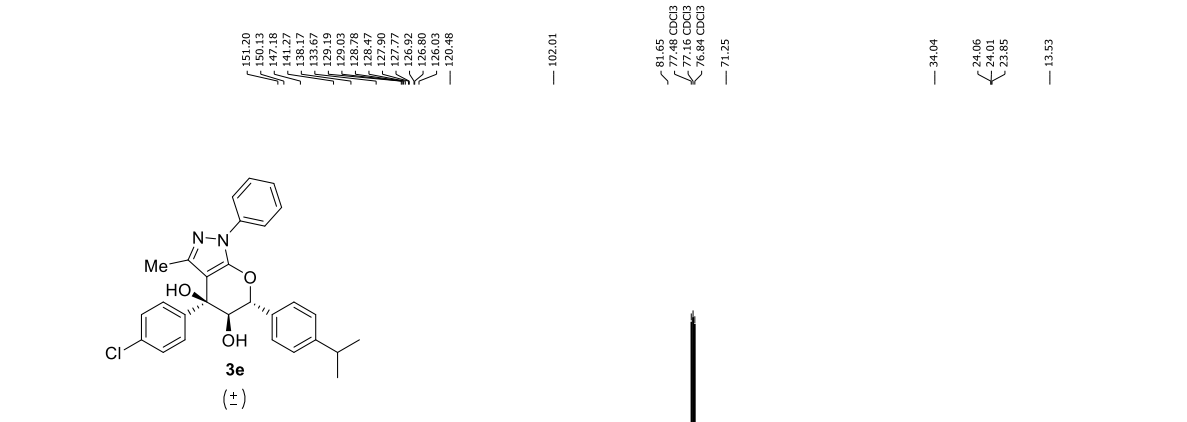
2.20
1.95
1.18
1.19
1.36
1.24
3.01
1.14
6.33
f1 (ppm)


151.20
150.13
147.18
141.27
138.17
133.67
129.19
129.03
128.78
128.47
127.90
127.77
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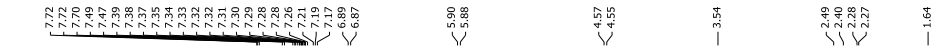
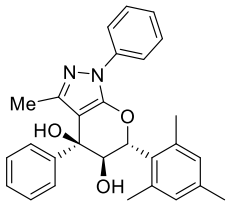
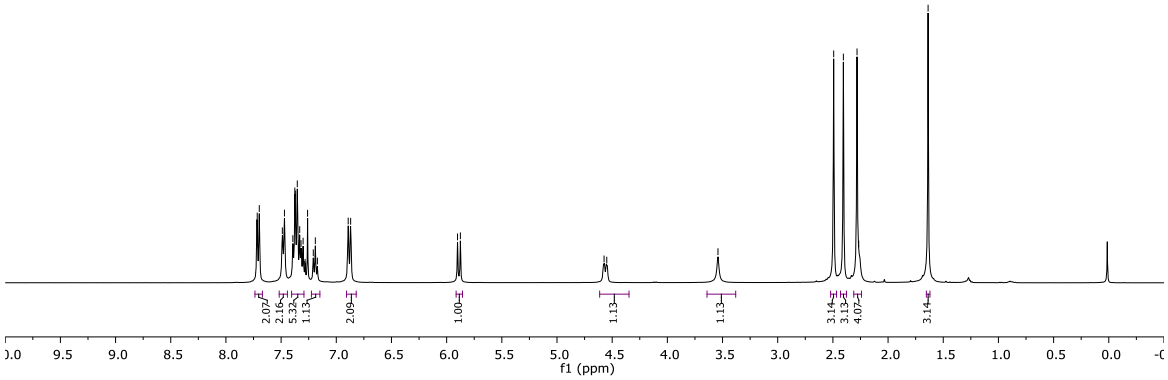
126.80
126.03
120.48
102.01
81.65
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.25
34.04
24.06
24.01
23.85
13.53
N
N
Me
O
HO
OH
Cl
3e
(±)
f1 (ppm)

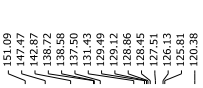

7.72
7.72
7.70
7.49
7.47
7.39
7.38
7.37
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.28
7.28
7.26
7.21
7.19
7.17
6.89
6.87
5.90
5.88
4.57
4.55
3.54
2.49
2.40
2.28
2.27
1.64

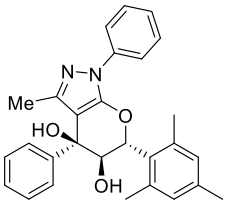

N
N
Me
O
HO
OH

**3f**

(±)

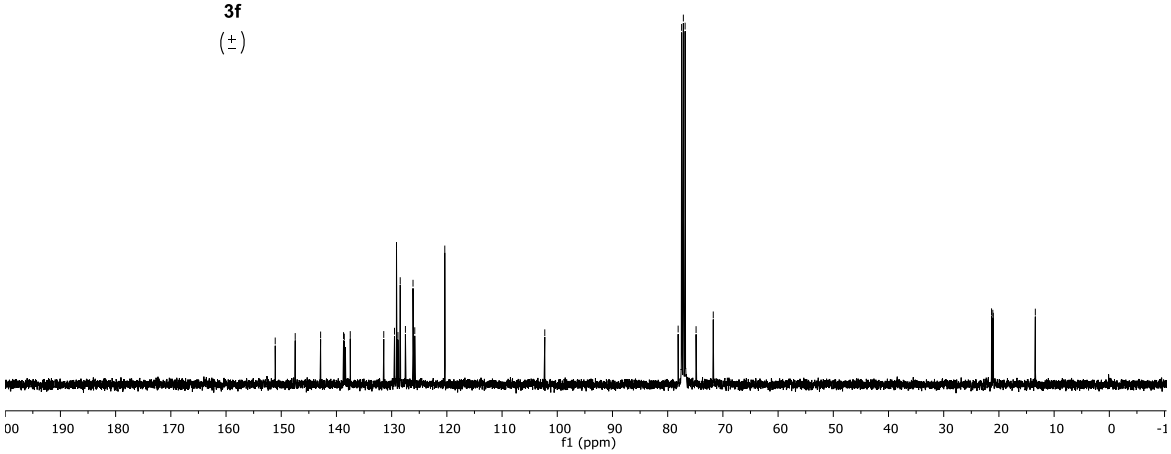

2.07
2.16
5.32
1.13
2.09
1.00
1.13
1.13
3.14
3.13
4.07
3.14
f1 (ppm)

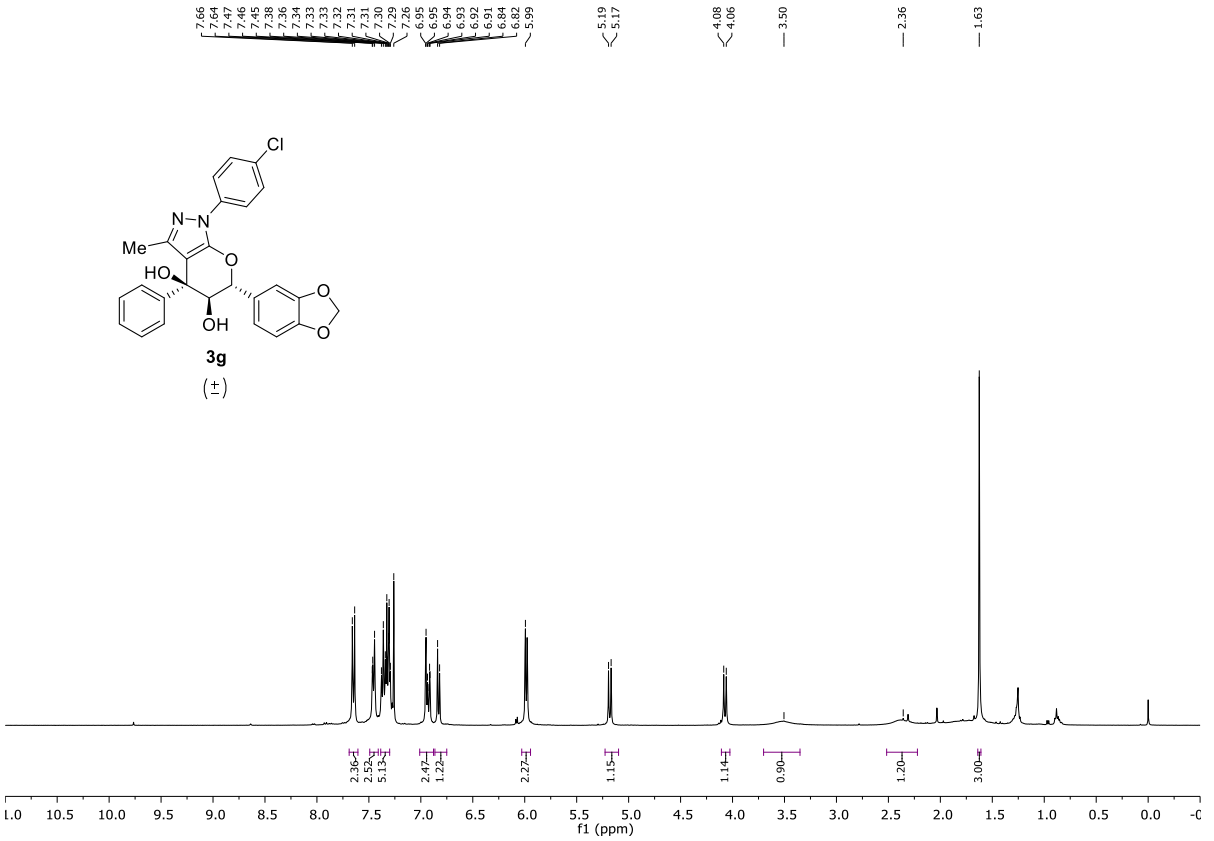

151.09
147.47
142.87
138.72
138.58
137.50
131.43
129.49
129.12
128.86
128.45
127.51
126.13
125.81
120.38
102.26
78.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.86
71.74
21.34
21.11
21.02
13.41

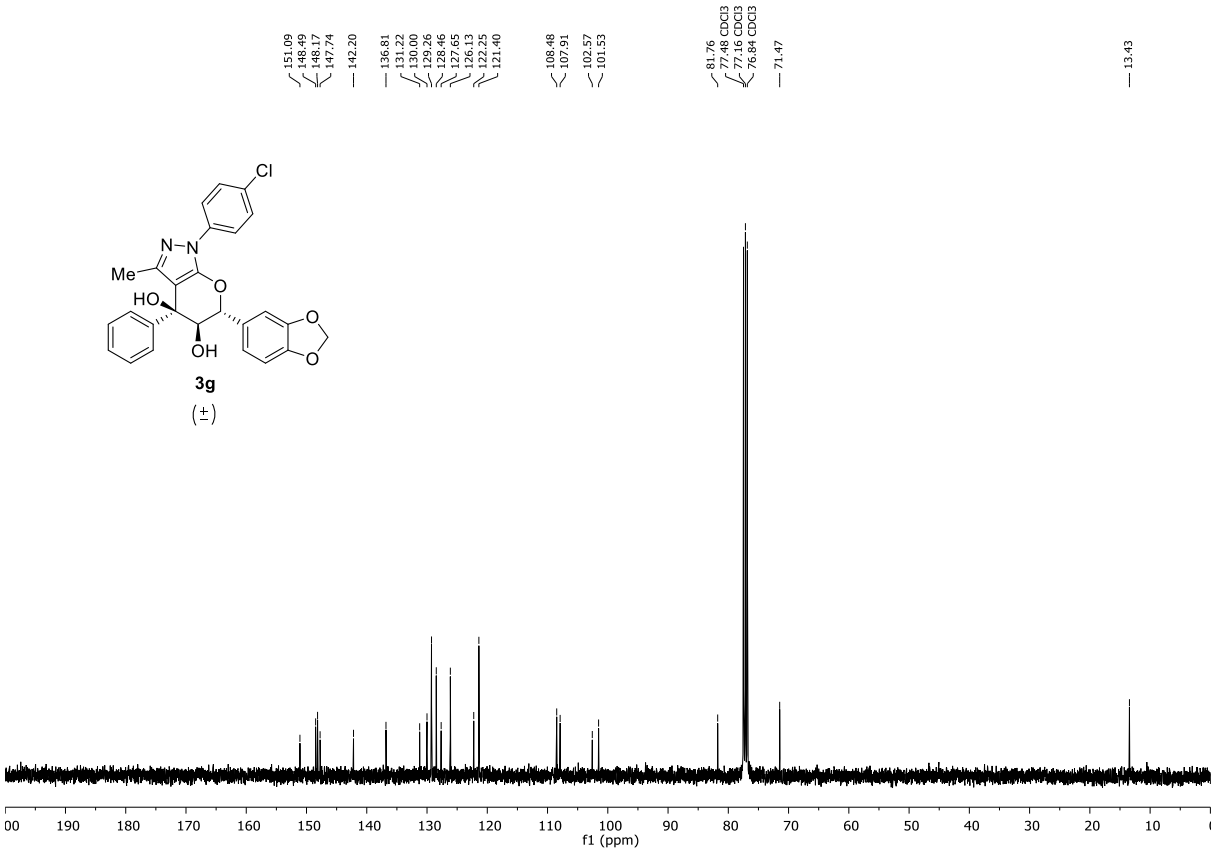

N
N
Me
O
HO
OH

**3f**

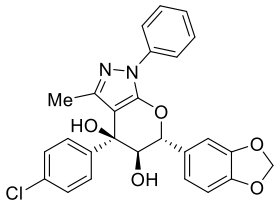
(±)


f1 (ppm)


7.66
7.64
7.47
7.46
7.45
7.38
7.36
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.26
6.95
6.95
6.94
6.93
6.92
6.91
6.84
6.82
5.99
5.19
5.17
4.08
4.06
3.50
2.36
1.63
Cl
N–N
Me
HO
O
OH
O
O
3g
(±)
2.36
2.53
5.13
2.47
1.22
2.27
1.15
1.14
0.90
1.20
3.00
f1 (ppm)

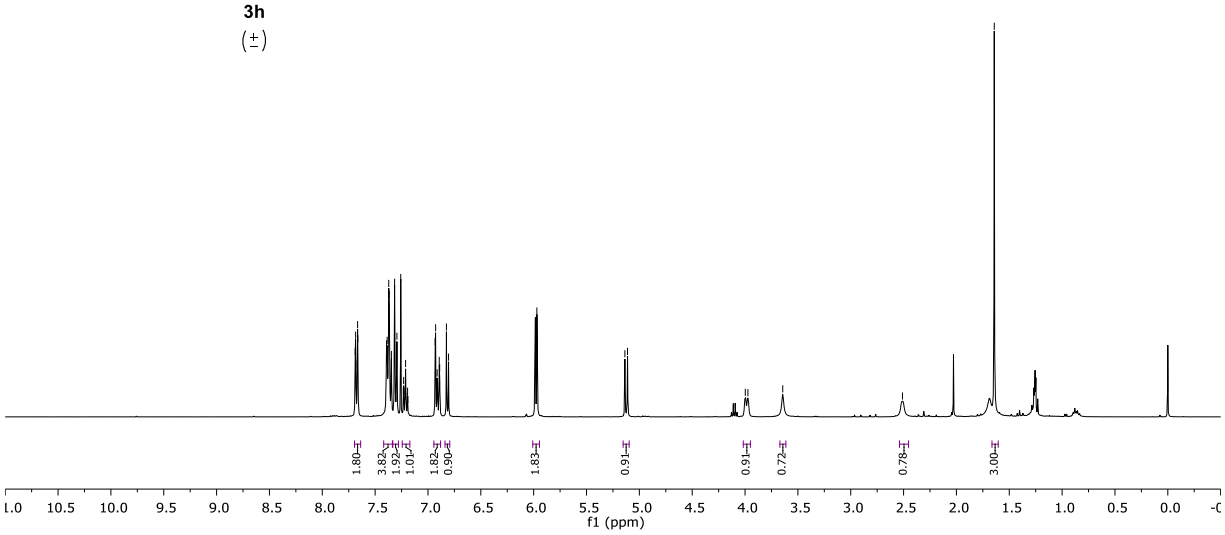

151.09
148.49
148.17
147.74
142.20
136.81
131.22
130.00
129.26
128.46
127.65
126.13
122.25
121.40
108.48
107.91
102.57
101.53
81.76
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.47
13.43
Cl
N–N
Me
HO
O
OH
O
O
3g
(±)
f1 (ppm)

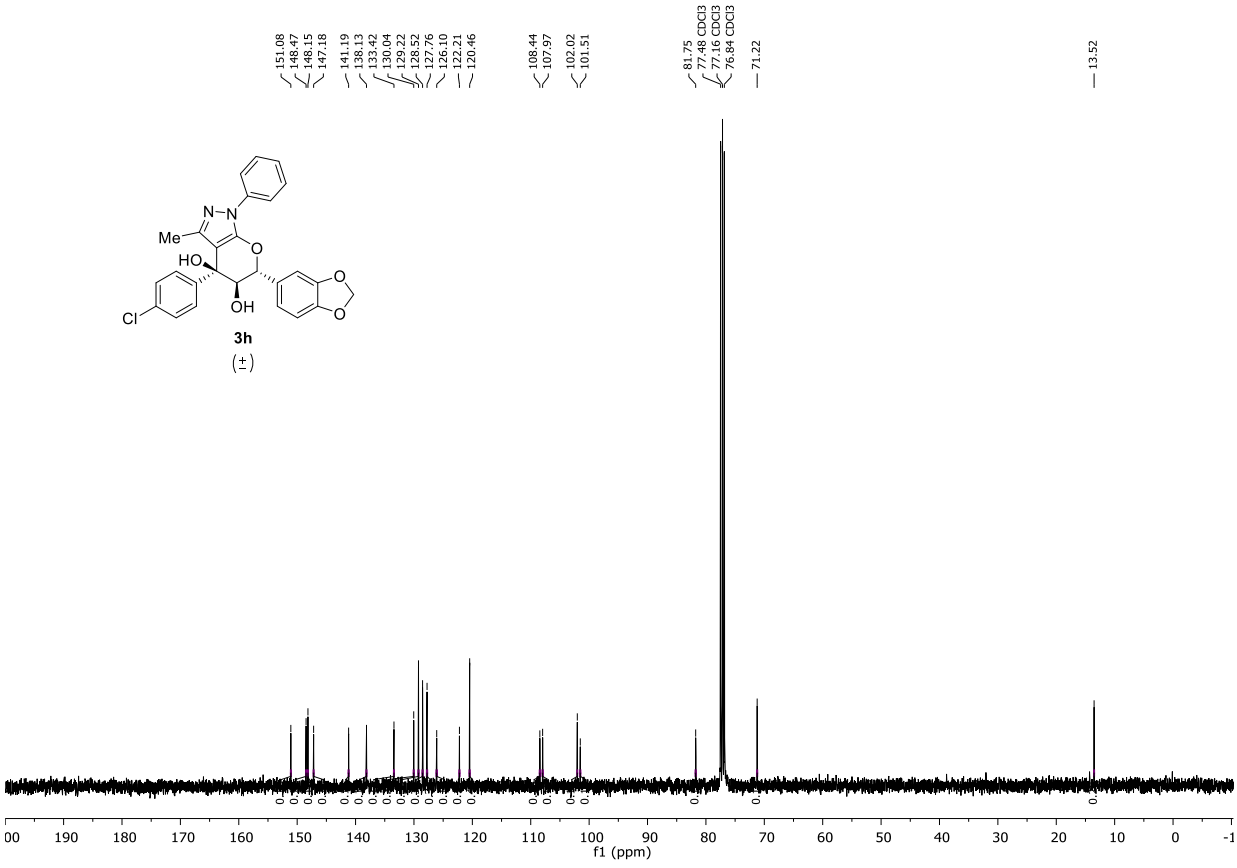

7.69
7.68
7.67
7.67
7.66
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.32
7.29
7.26
7.23
7.23
7.23
7.22
7.21
7.20
7.19
7.19
6.93
6.93
6.91
6.91
6.89
6.89
6.83
6.81
5.97
5.14
5.11
4.00
3.97
3.64
2.51
1.64


N
N
Me
O
HO
OH
Cl
O
O

**3h**

(±)

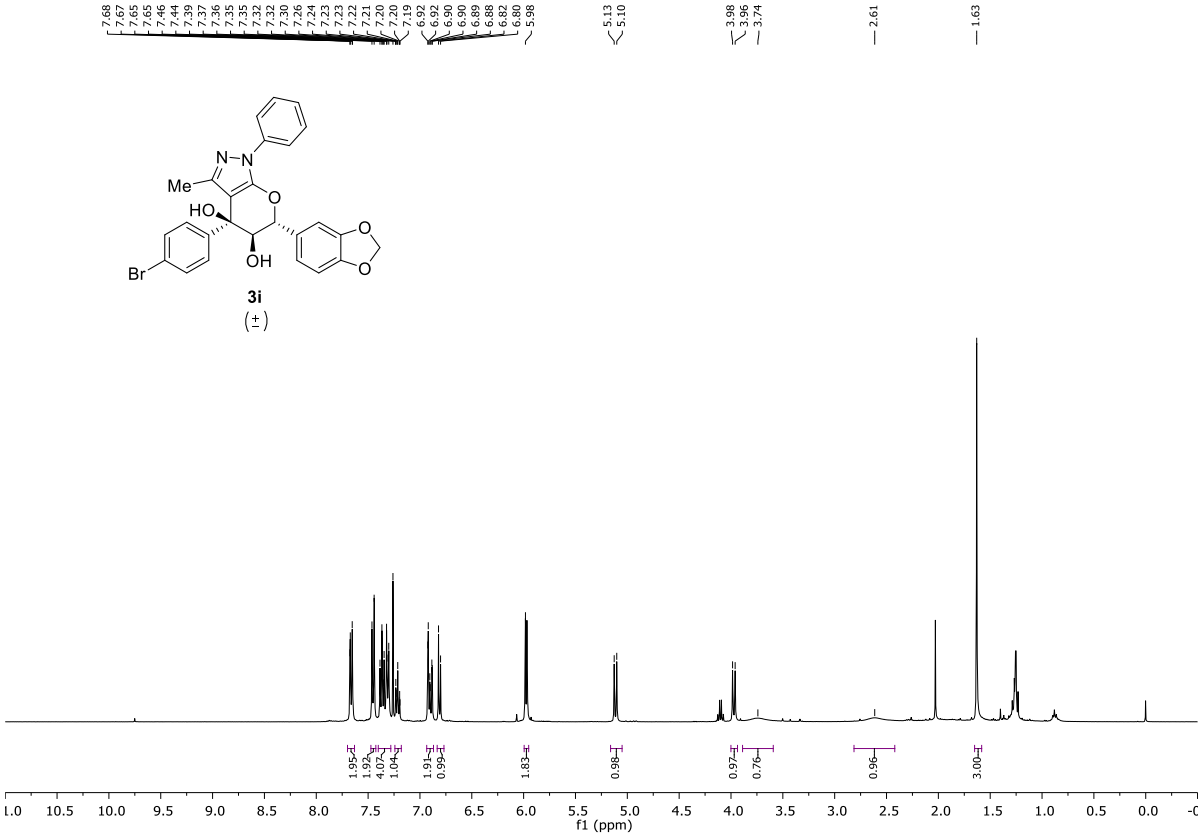

1.80
3.82
1.92
1.01
1.82
0.90
1.83
0.91
0.91
0.72
0.78
3.00
f1 (ppm)


151.08
148.47
148.15
147.18
141.19
136.13
133.42
130.04
129.22
128.52
127.76
126.10
122.21
120.46
108.44
107.97
102.02
101.51
81.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.22
13.52
f1 (ppm)


N
N
Me
O
HO
OH
Cl
O
O

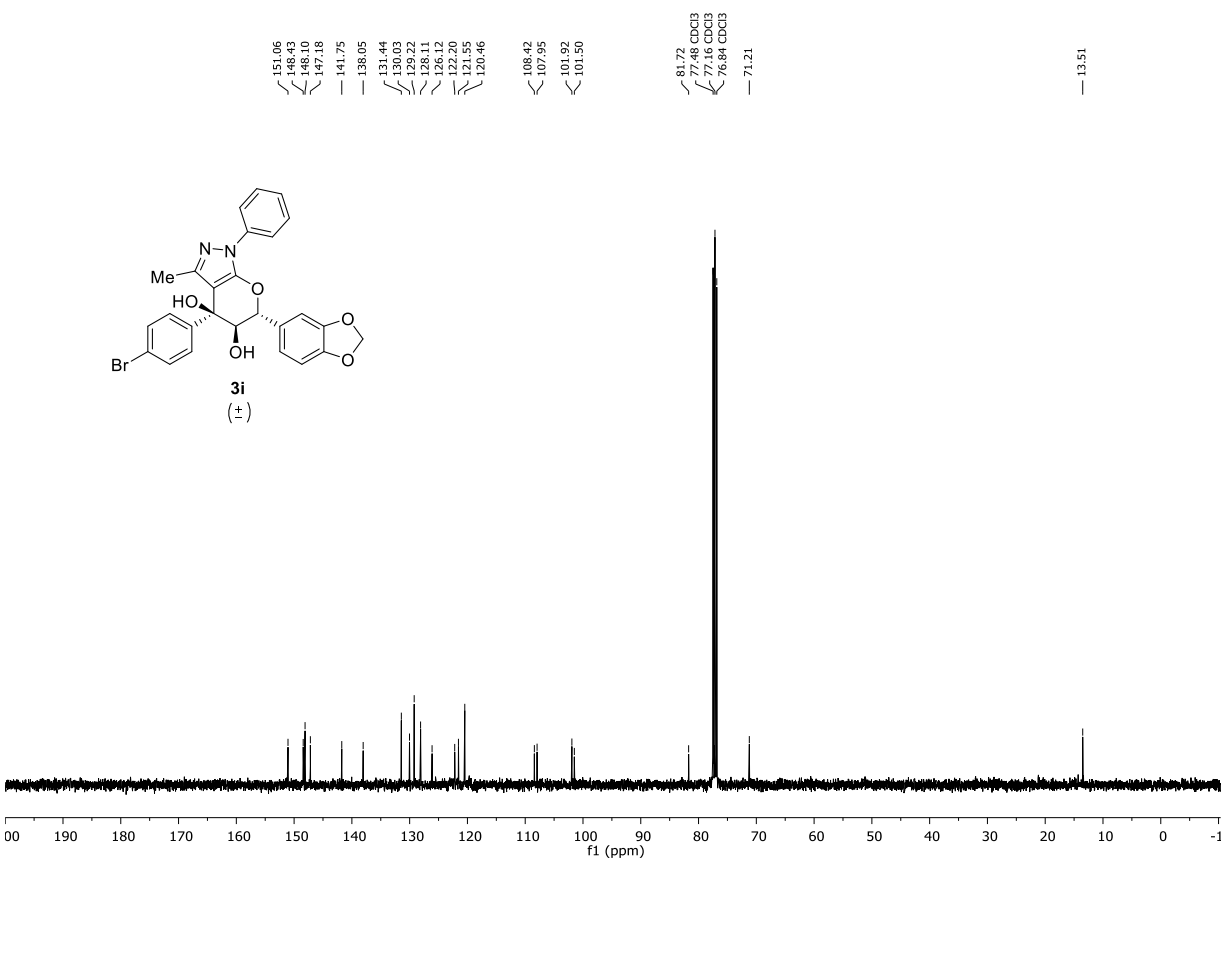
**3h**

(±)


7.68
7.67
7.65
7.65
7.46
7.44
7.39
7.37
7.36
7.35
7.35
7.32
7.32
7.30
7.26
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.19
6.92
6.92
6.90
6.90
6.89
6.88
6.82
6.80
5.98
5.13
5.10
3.98
3.96
3.74
2.61
1.63
N–N
Me
HO
O
OH
Br
O
O
1.95
1.92
4.07
1.04
1.91
0.99
1.83
0.98
0.97
0.76
0.96
3.00
f1 (ppm)

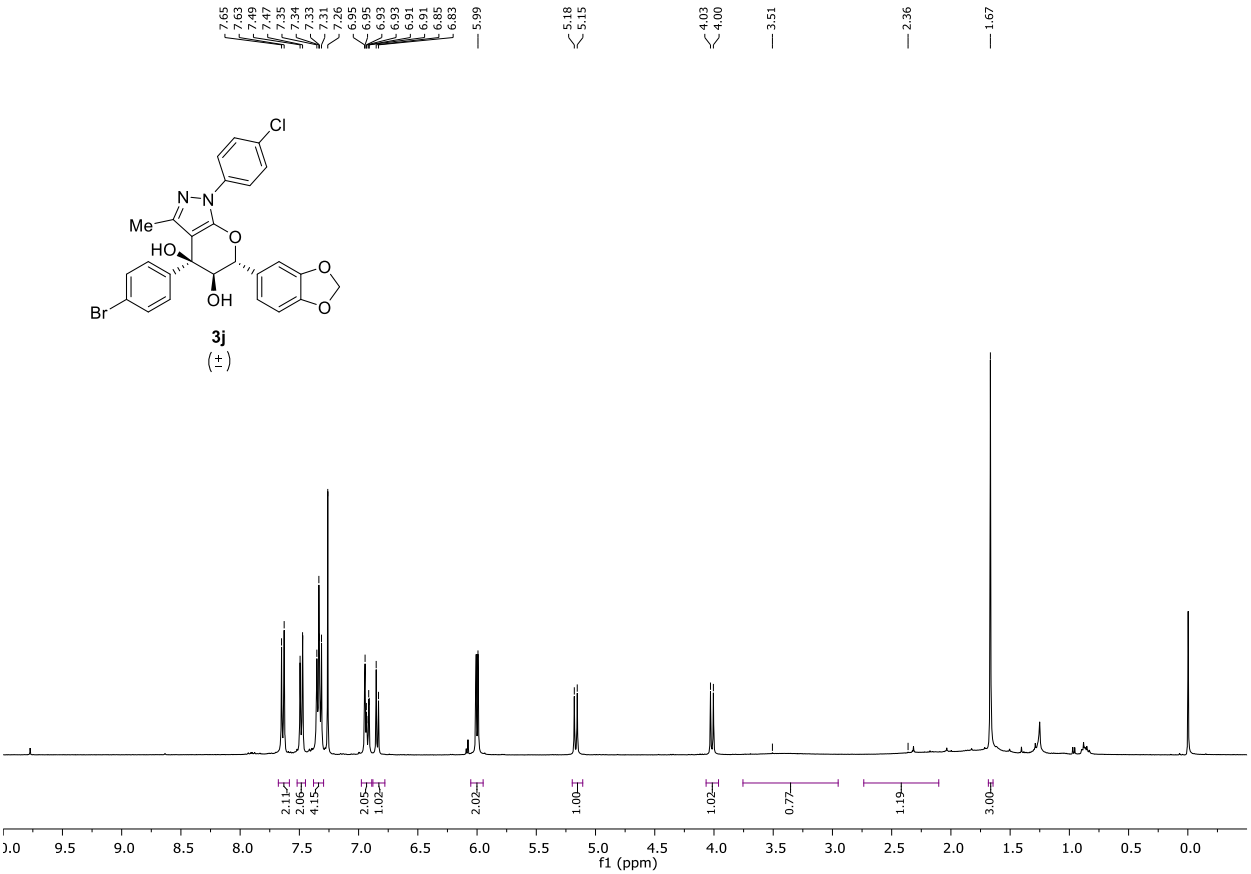
**3i**

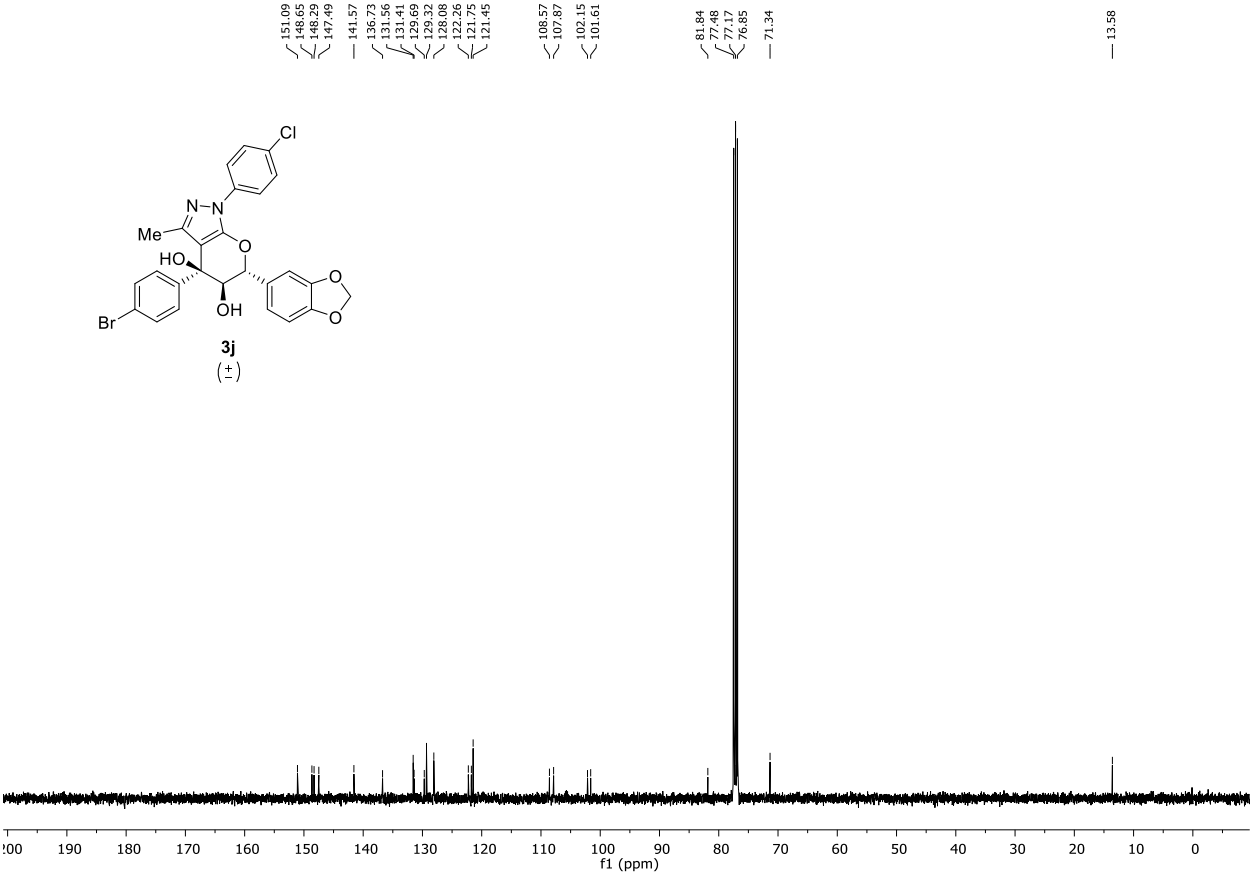
(±)

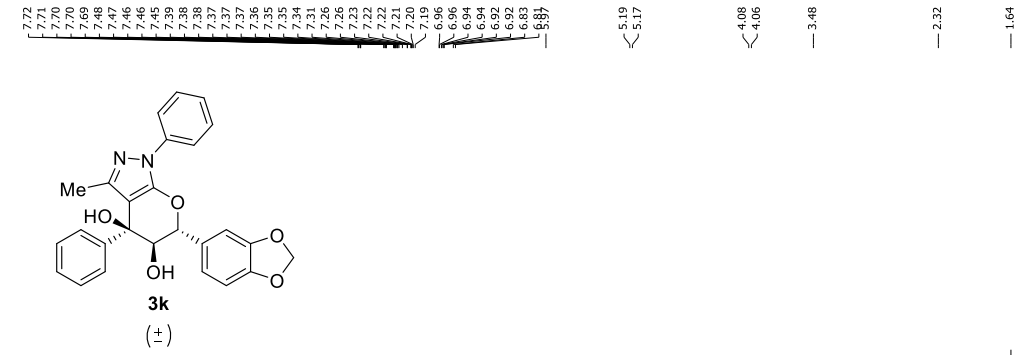

151.06
148.43
148.10
147.18
141.75
138.05
131.44
130.03
129.22
128.11
126.12
122.20
121.55
120.46
108.42
107.95
101.92
101.50
81.72
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.21
13.51
N–N
Me
HO
O
OH
Br
O
O
f1 (ppm)

**3i**

(±)


7.65
7.63
7.49
7.47
7.35
7.34
7.33
7.31
7.26
6.95
6.95
6.93
6.93
6.91
6.91
6.85
6.83
5.99
5.18
5.15
4.03
4.00
3.51
2.36
1.67
Cl
N
N
Me
HO
O
OH
Br
O
O
3j
(±)
2.11
2.06
4.15
2.05
1.02
2.02
1.00
1.02
0.77
1.19
3.00
f1 (ppm)

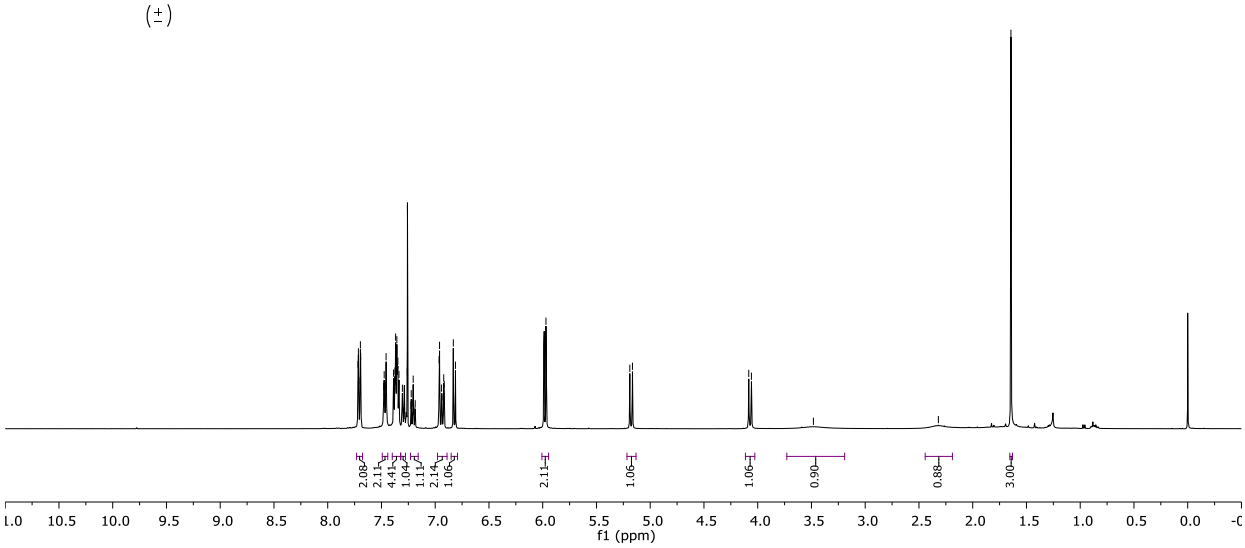

151.09
148.65
148.29
147.49
141.57
136.73
131.56
131.41
129.69
129.32
128.08
122.26
121.75
121.45
108.57
107.87
102.15
101.61
81.84
77.48
77.17
76.85
71.34
13.58
Cl
N
N
Me
HO
O
OH
Br
O
O
3j
(±)
f1 (ppm)

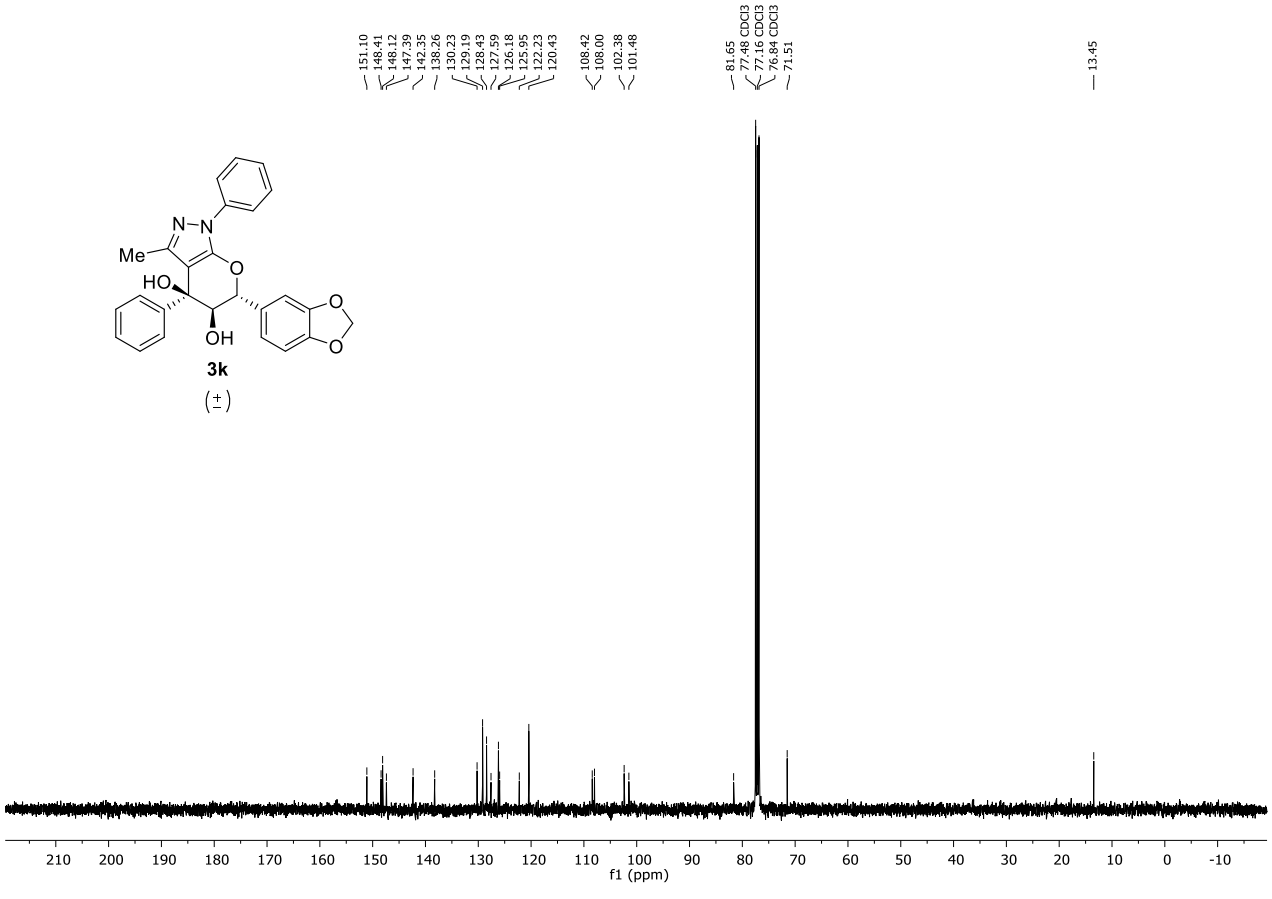




**3k**

(±)

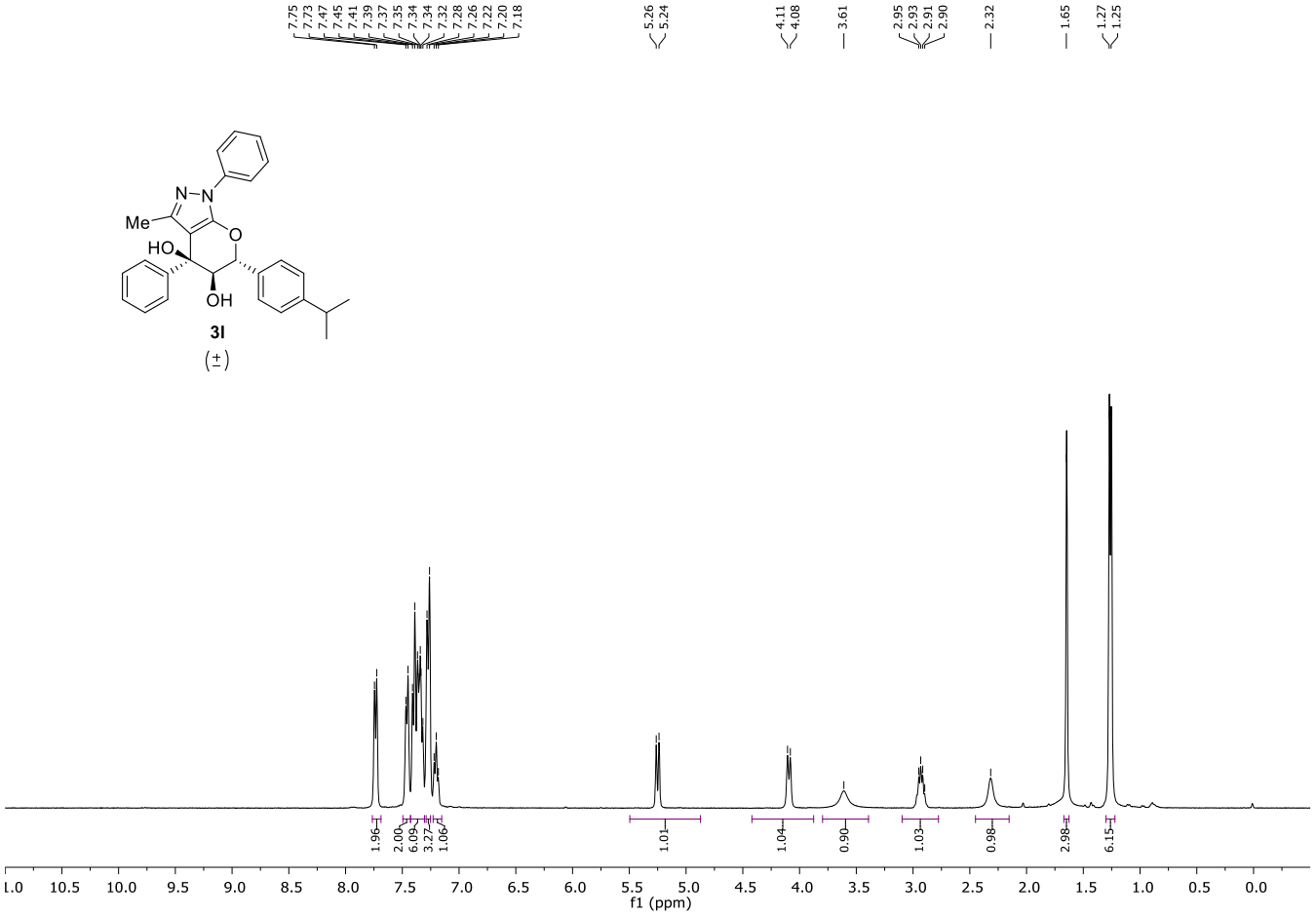


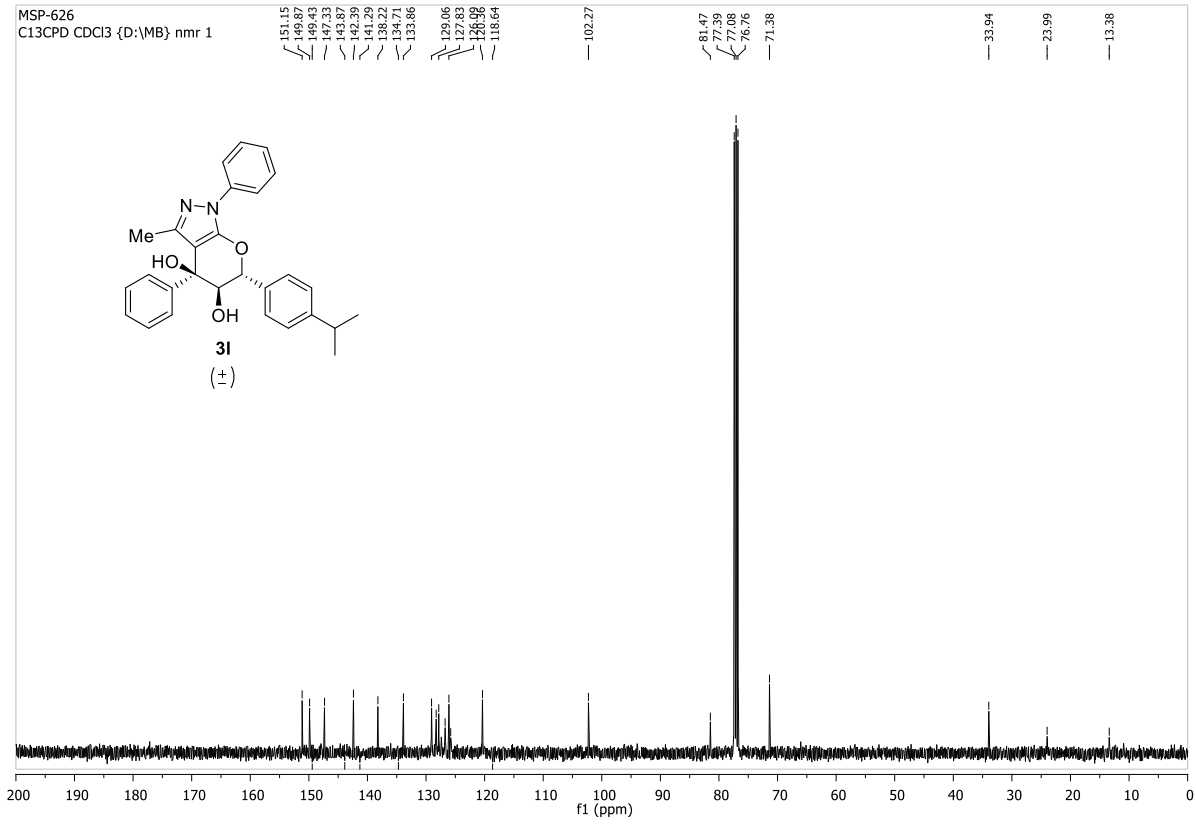


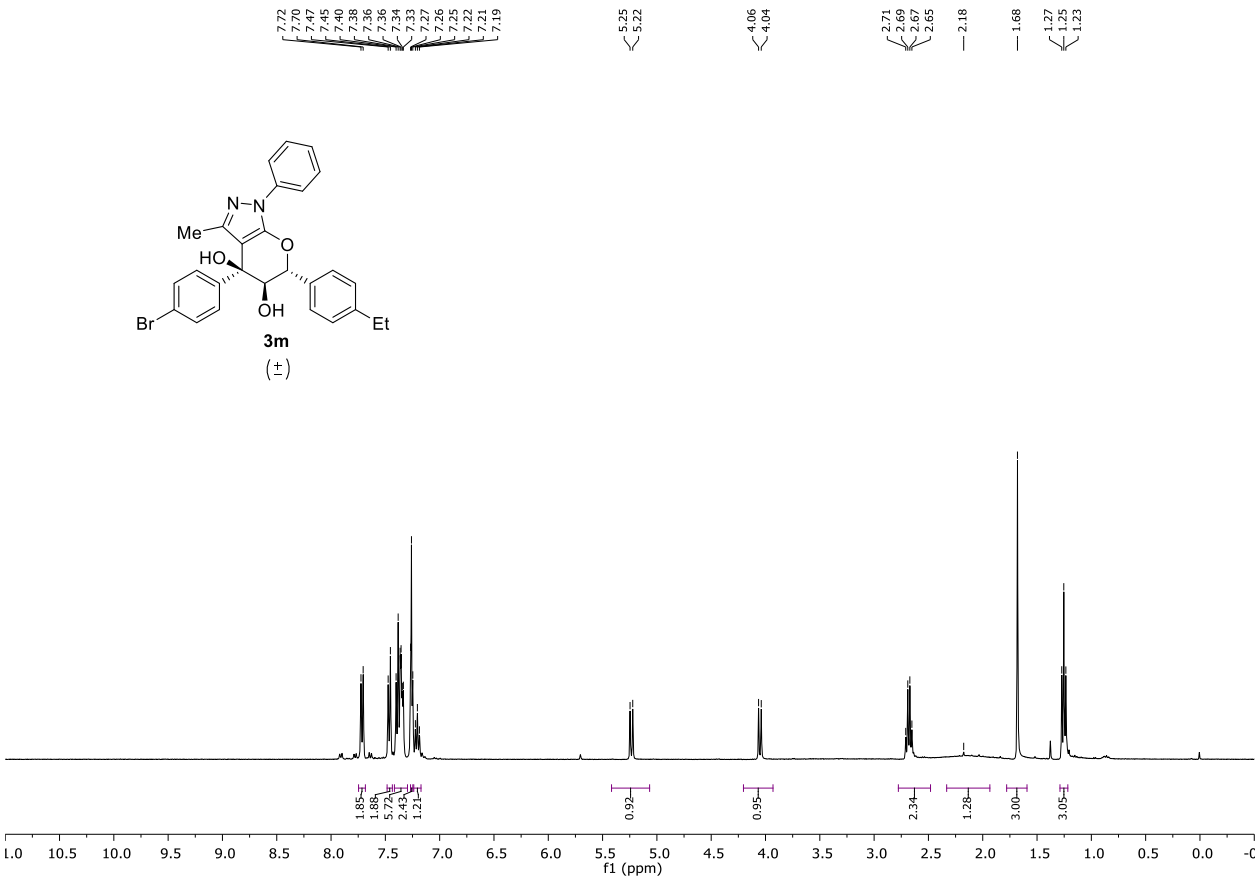


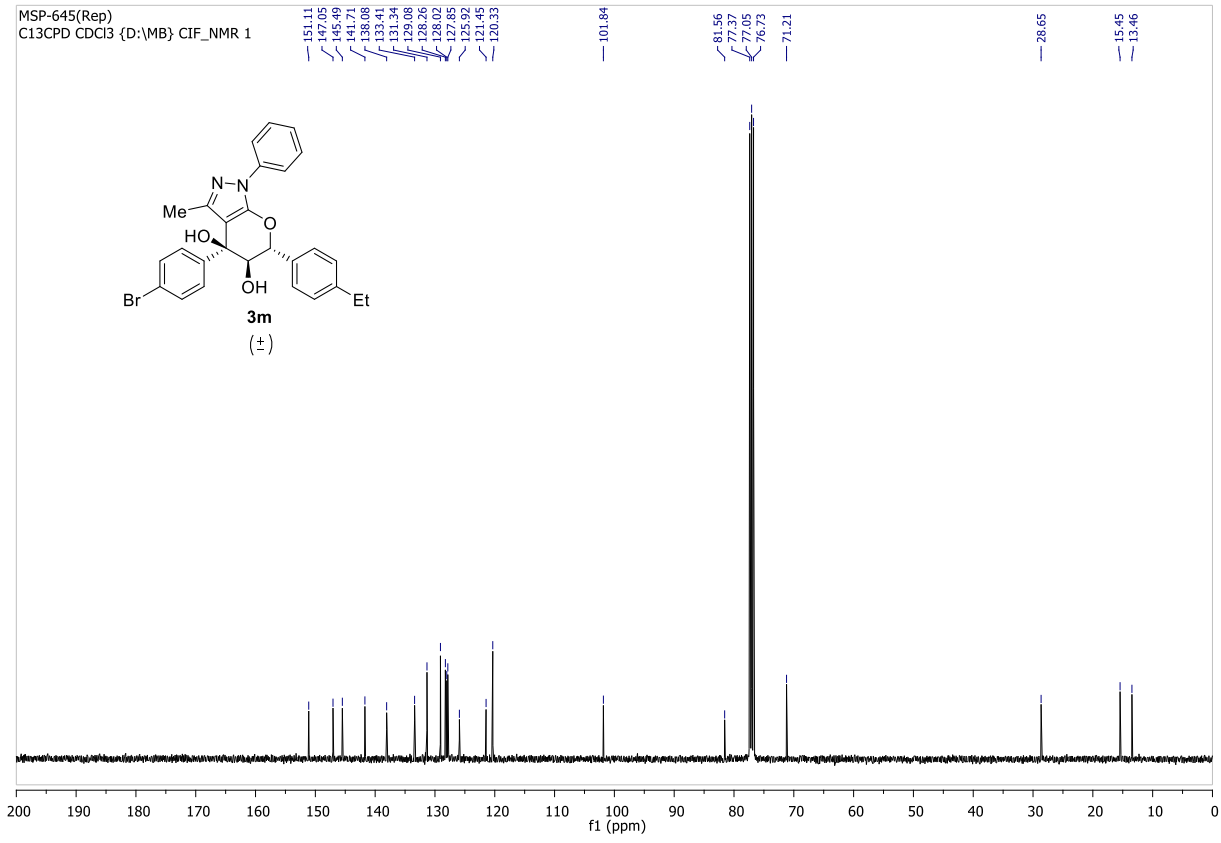
**3k**

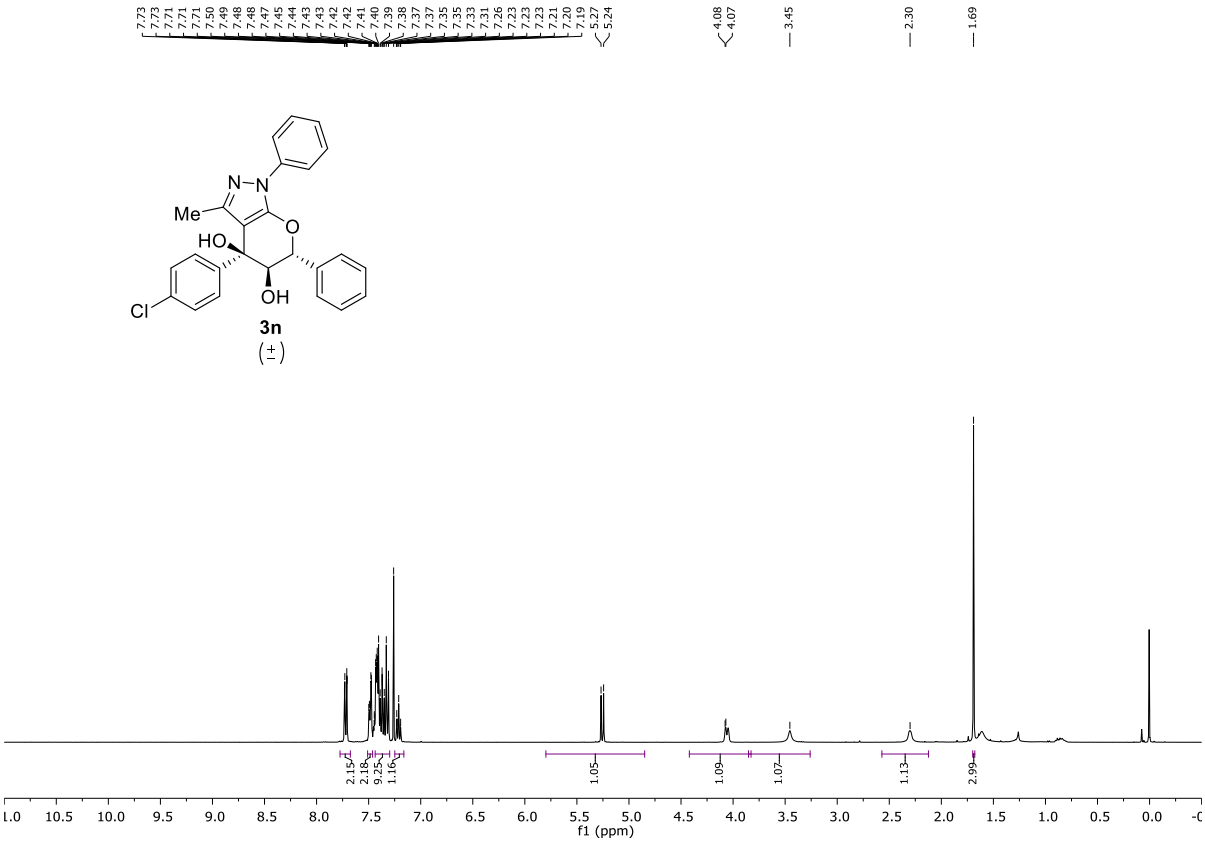
(±)

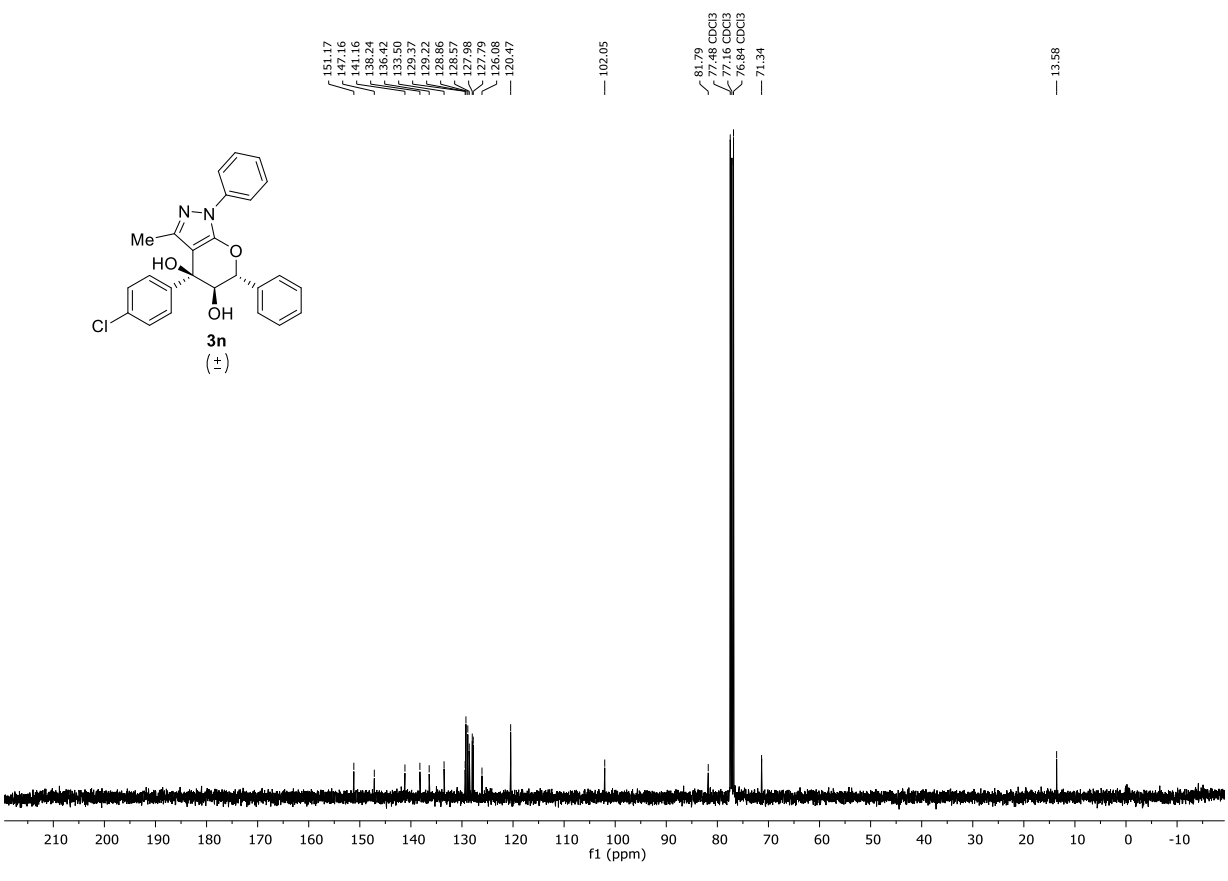

7.75
7.73
7.47
7.45
7.41
7.39
7.37
7.35
7.34
7.34
7.32
7.28
7.26
7.22
7.20
7.18
5.26
5.24
4.11
4.08
3.61
2.95
2.93
2.91
2.90
2.32
1.65
1.27
1.25
Me
HO
OH
3l
(±)
1.96
2.00
6.09
3.27
1.06
1.01
1.04
0.90
1.03
0.98
2.98
6.15
f1 (ppm)

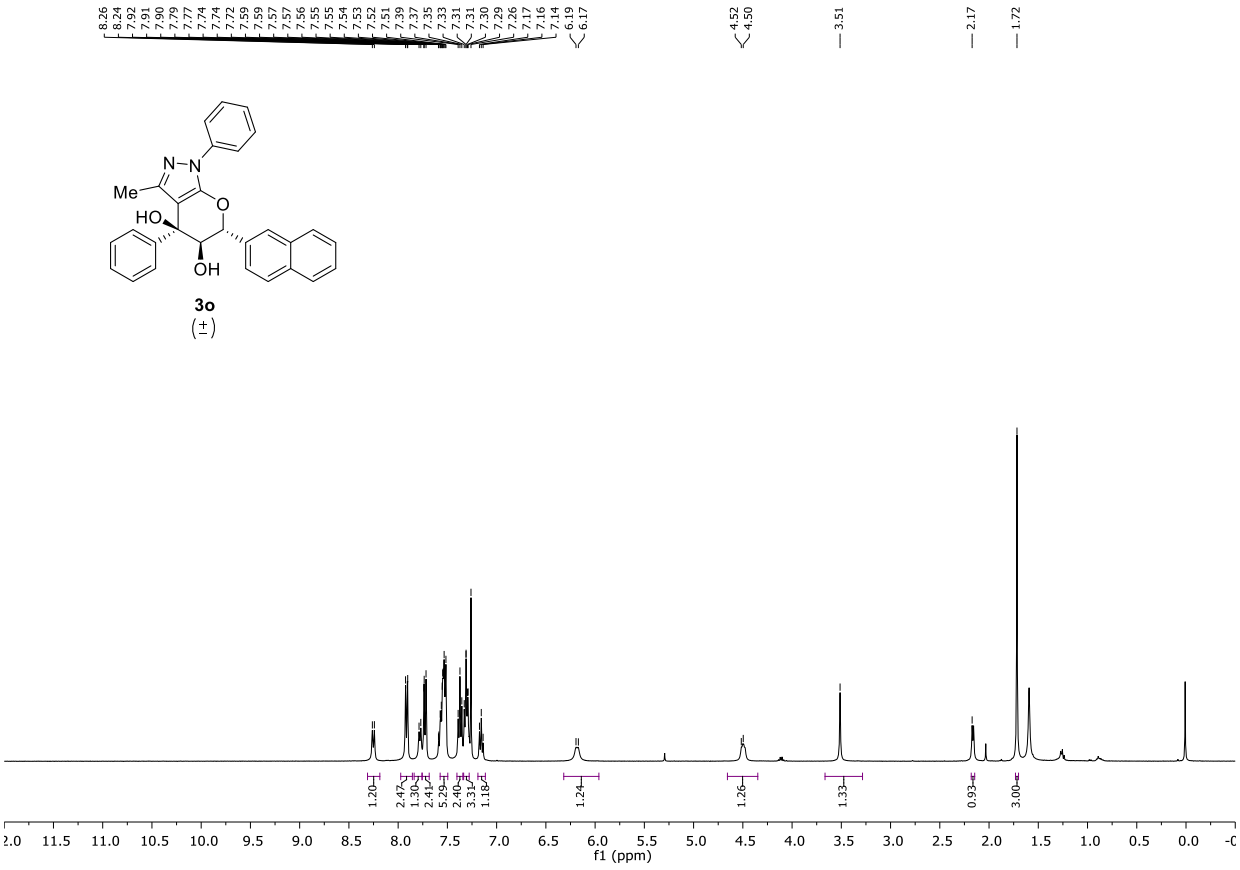

MSP-626
C13CPD CDCl3 {D:\MB} nmr 1
151.15
149.87
149.43
147.33
143.87
142.39
141.29
138.22
134.71
133.86
129.06
127.83
118.64
102.27
81.47
77.39
77.08
76.76
71.38
33.94
23.99
13.38
Me
HO
OH
3l
(±)
f1 (ppm)

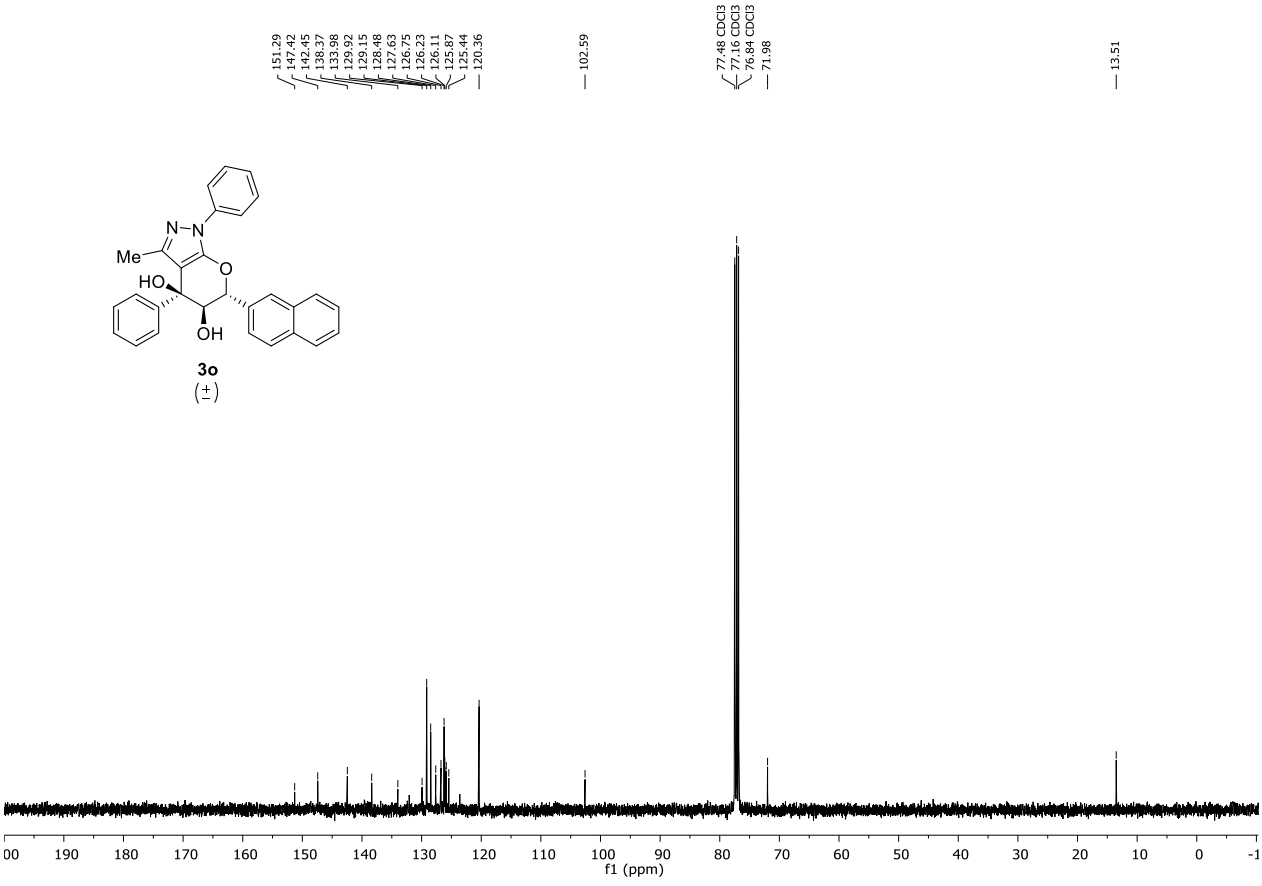

7.72
7.70
7.47
7.45
7.40
7.38
7.36
7.36
7.34
7.33
7.27
7.26
7.25
7.22
7.21
7.19
5.25
5.22
4.06
4.04
2.71
2.69
2.67
2.65
2.18
1.68
1.27
1.25
1.23
N–N
Me
HO
O
OH
Br
Et
3m
(±)
1.85
1.88
5.72
2.43
1.21
0.92
0.95
2.34
1.28
3.00
3.05
f1 (ppm)

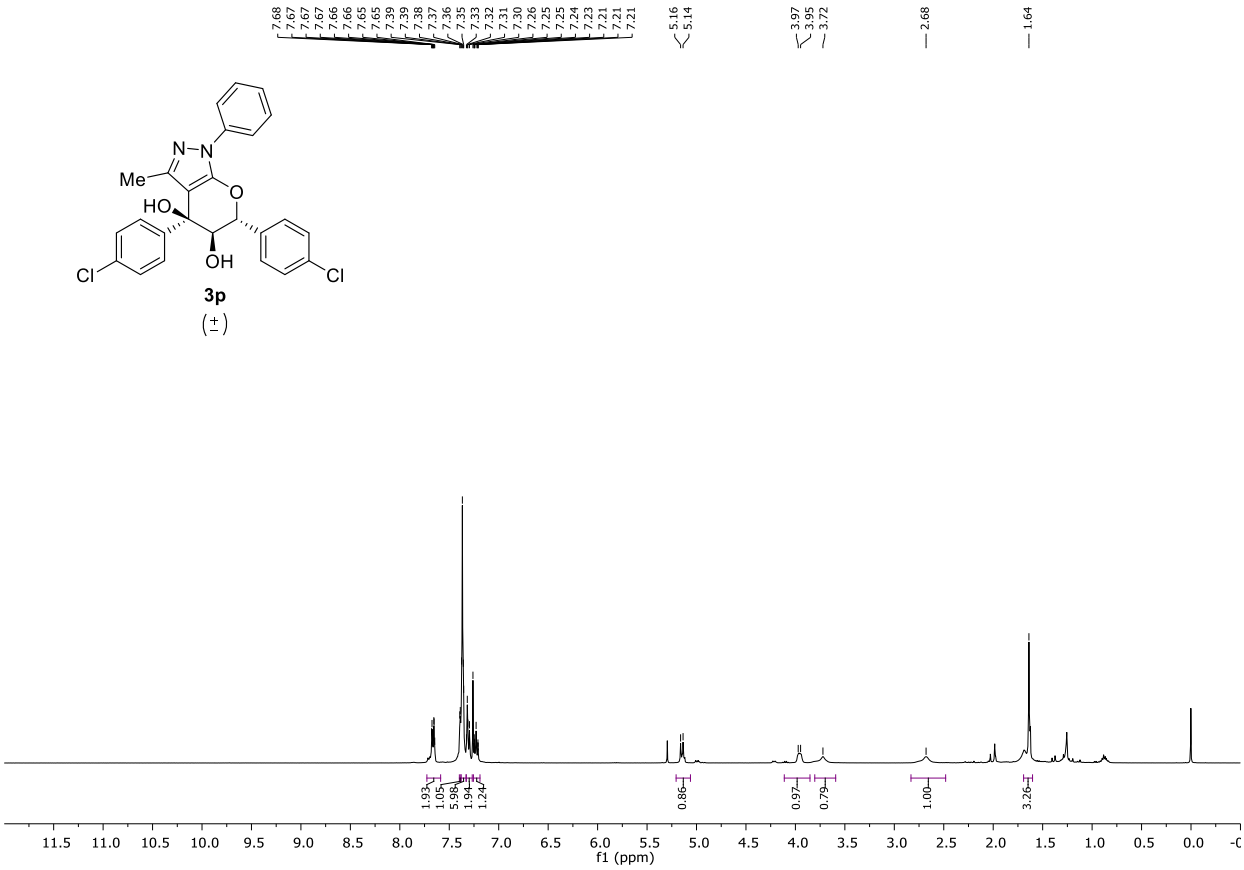

MSP-645(Rep)
C13CPD CDCl3 {D:\MB} CIF_NMR 1
151.11
147.05
145.49
141.71
138.08
133.41
131.34
129.08
128.26
128.02
127.85
125.92
121.45
120.33
101.84
81.56
77.37
77.05
76.73
71.21
28.65
15.45
13.46
N–N
Me
HO
O
OH
Br
Et
3m
(±)
f1 (ppm)


7.73
7.73
7.71
7.71
7.71
7.50
7.49
7.48
7.48
7.47
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.39
7.38
7.37
7.37
7.35
7.35
7.33
7.31
7.26
7.23
7.23
7.21
7.20
7.19
5.27
5.24
4.08
4.07
3.45
2.30
1.69
N
N
Me
O
HO
OH
Cl
3n
(±)
2.15
2.18
9.25
1.16
1.05
1.09
1.07
1.13
2.99
f1 (ppm)


151.17
147.16
141.16
138.24
136.42
133.50
129.37
129.22
128.86
128.57
127.98
127.79
126.08
120.47
102.05
81.79
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.34
13.58
N
N
Me
O
HO
OH
Cl
3n
(±)
f1 (ppm)

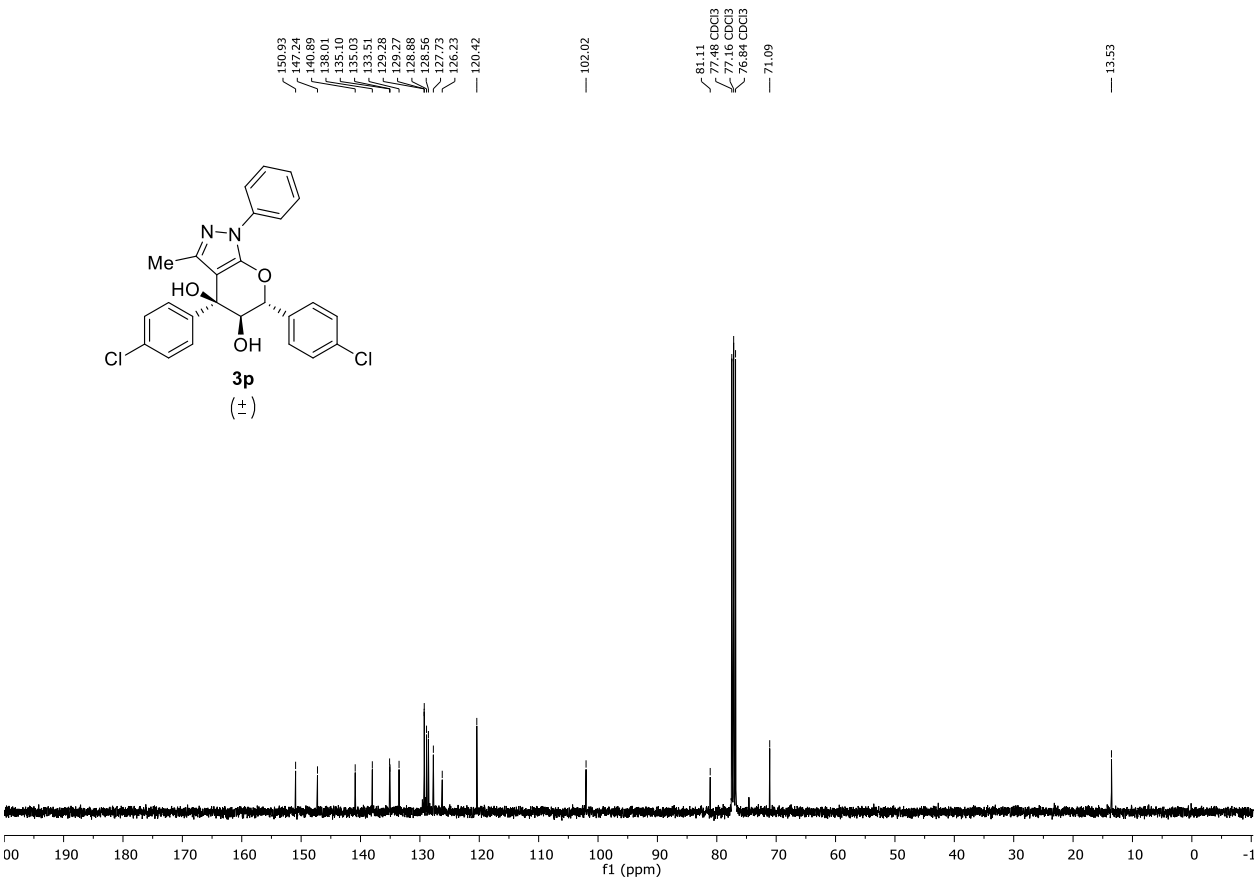

8.26
8.24
7.92
7.91
7.90
7.79
7.77
7.74
7.74
7.72
7.59
7.59
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.52
7.51
7.39
7.37
7.35
7.33
7.31
7.31
7.30
7.29
7.26
7.17
7.16
7.14
6.19
6.17
4.52
4.50
3.51
2.17
1.72
Me
HO
OH
3o
(±)
1.20
2.47
1.30
2.41
5.29
2.40
3.31
1.18
1.24
1.26
1.33
0.93
3.00
f1 (ppm)


151.29
147.42
142.45
138.37
133.98
129.92
129.15
128.48
127.63
126.75
126.23
126.11
125.87
125.44
120.36
102.59
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.98
13.51
Me
HO
OH
3o
(±)
f1 (ppm)


7.68
7.67
7.67
7.67
7.66
7.66
7.65
7.65
7.39
7.38
7.37
7.36
7.35
7.33
7.32
7.31
7.30
7.26
7.25
7.25
7.24
7.23
7.21
7.21
7.21
5.16
5.14
3.97
3.95
3.72
2.68
1.64
N
N
Me
O
HO
OH
Cl
Cl
1.93
1.05
5.98
1.94
1.24
0.86
0.97
0.79
1.00
3.26
f1 (ppm)

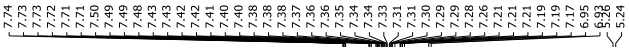
**3p**

(±)


150.93
147.24
140.89
138.01
135.10
135.03
133.51
129.28
129.27
128.88
128.56
127.73
126.23
120.42
102.02
81.11
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.09
13.53
N
N
Me
O
HO
OH
Cl
Cl
f1 (ppm)

**3p**

(±)


7.74
7.73
7.73
7.72
7.71
7.71
7.50
7.49
7.49
7.48
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.31
7.31
7.30
7.29
7.29
7.28
7.26
7.21
7.21
7.21
7.19
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7.17
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6.93
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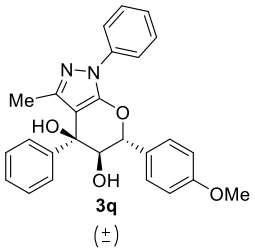
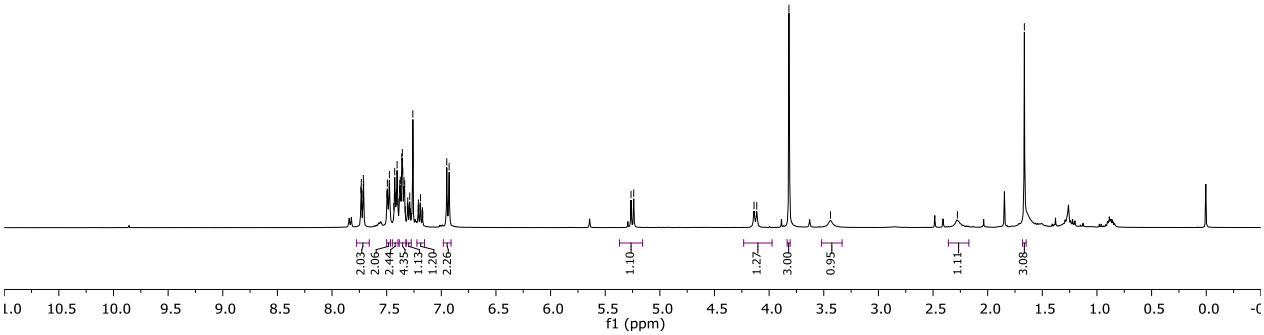
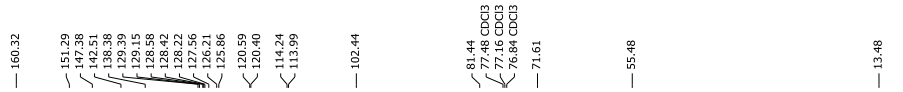
5.24
4.14
4.11
3.82
3.44
2.28
1.66

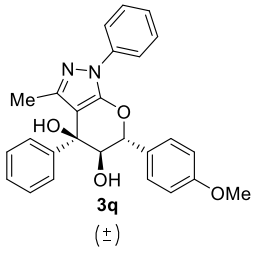

N
N
Me
O
HO
OH
OMe

**3q**

(±)

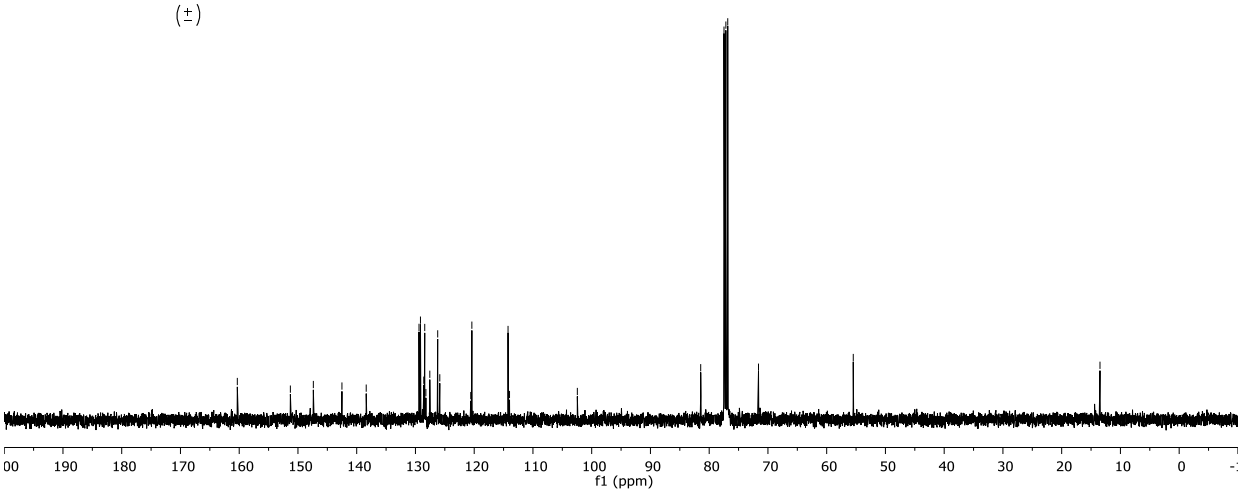

2.03
2.06
2.44
4.35
1.13
1.20
2.26
1.10
1.27
3.00
0.95
1.11
3.08
f1 (ppm)

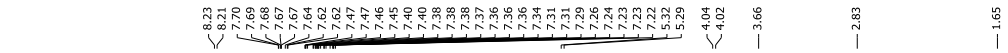

160.32
151.29
147.38
142.51
138.38
129.39
129.15
128.58
128.42
128.22
127.56
126.21
125.86
120.59
120.40
114.24
113.99
102.44
81.44
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.61
55.48
13.48

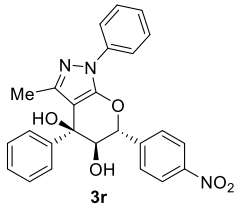

N
N
Me
O
HO
OH
OMe

**3q**

(±)

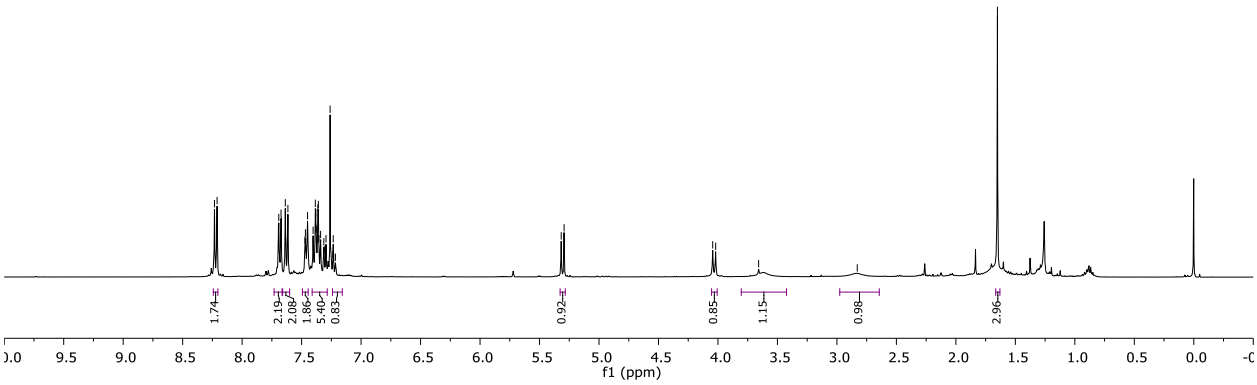

f1 (ppm)

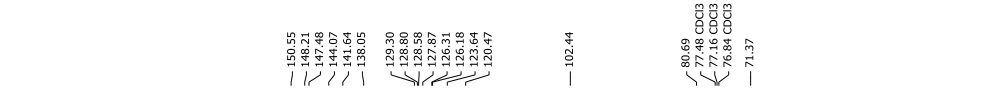

8.23
8.21
7.70
7.69
7.68
7.67
7.67
7.64
7.62
7.62
7.47
7.47
7.46
7.45
7.40
7.40
7.38
7.38
7.37
7.36
7.36
7.34
7.31
7.31
7.29
7.26
7.24
7.23
7.23
7.22
5.32
5.29
4.04
4.02
3.66
2.83
1.65

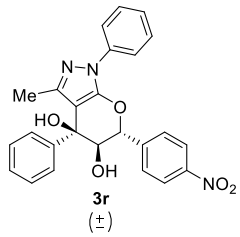

N
N
Me
HO
O
OH
NO2

**3r**

(±)


1.74
2.19
2.08
1.86
5.40
0.83
0.92
0.85
1.15
0.98
2.96
f1 (ppm)

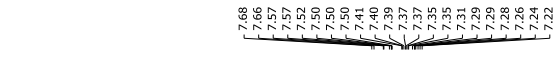

150.55
148.21
147.48
144.07
141.64
138.05
129.30
128.80
128.58
127.87
126.31
126.18
123.64
120.47
102.44
80.69
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.37
13.49

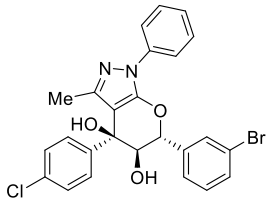

N
N
Me
HO
O
OH
NO2

**3r**

(±)

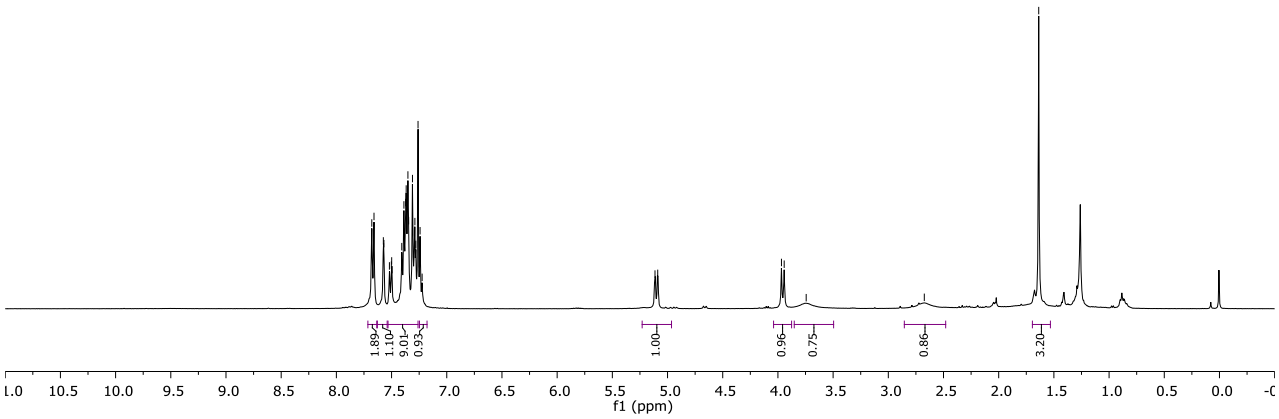

f1 (ppm)


7.68
7.66
7.57
7.57
7.57
7.52
7.50
7.50
7.50
7.41
7.40
7.39
7.37
7.37
7.35
7.35
7.31
7.29
7.29
7.28
7.26
7.24
7.22
5.11
5.09
3.97
3.94
3.74
2.67
1.64

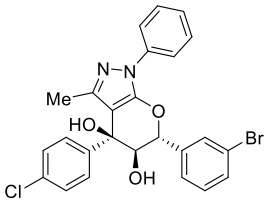

N
N
Me
O
HO
Br
OH
Cl

**3s**

(±)

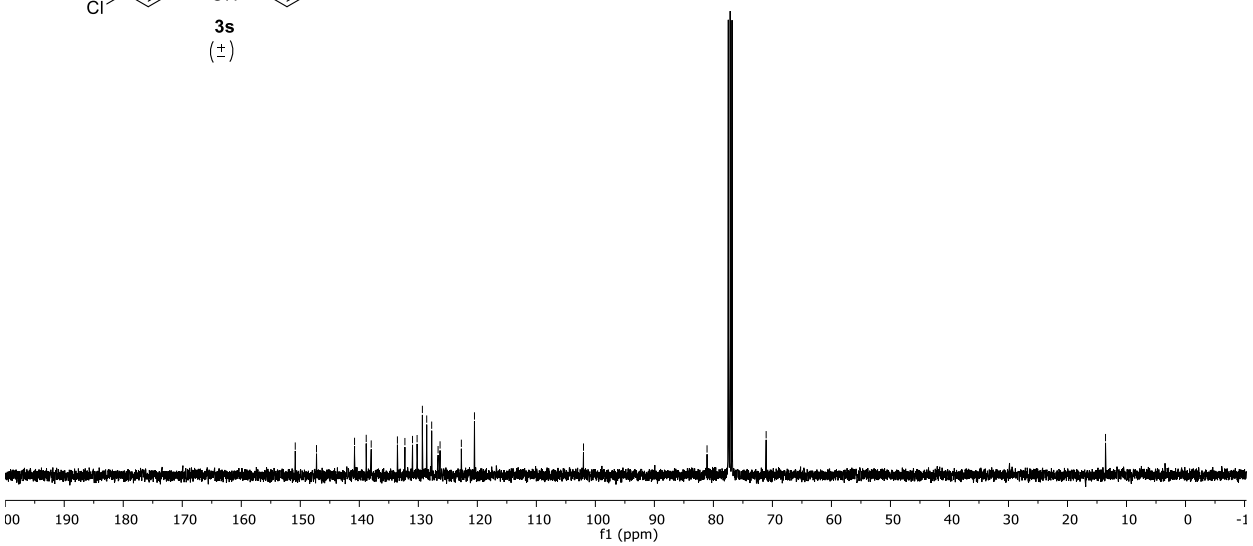

1.89
1.10
9.01
0.93
1.00
0.96
0.75
0.86
3.20
f1 (ppm)

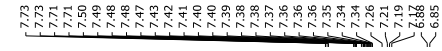

150.85
147.25
140.81
138.83
137.98
133.54
132.27
130.98
130.21
129.31
128.58
127.74
126.65
126.32
122.71
120.48
102.01
81.08
71.06
13.56

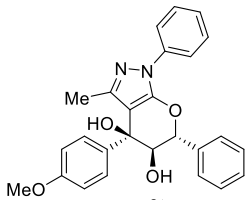

N
N
Me
O
HO
Br
OH
Cl

**3s**

(±)

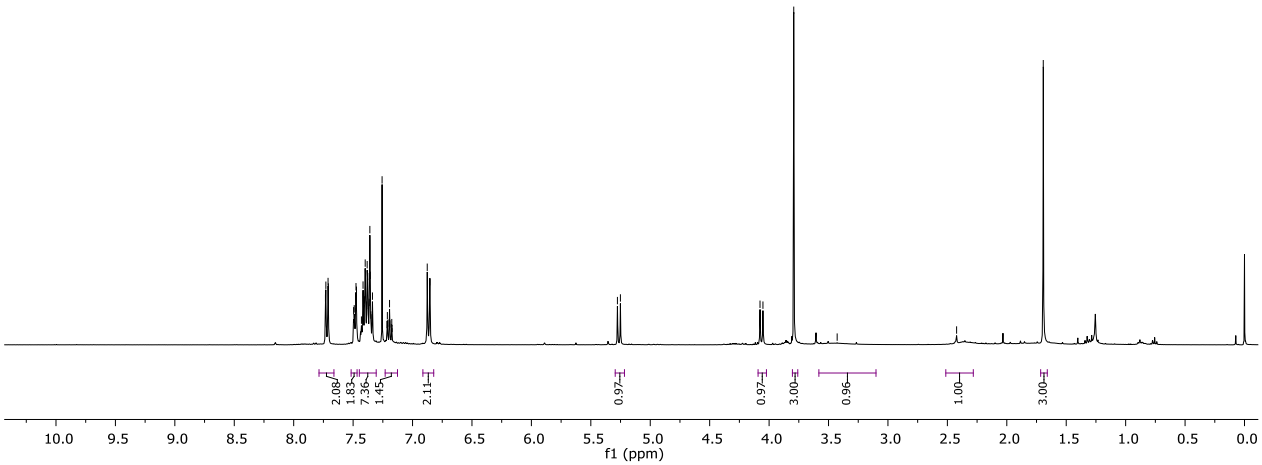

f1 (ppm)

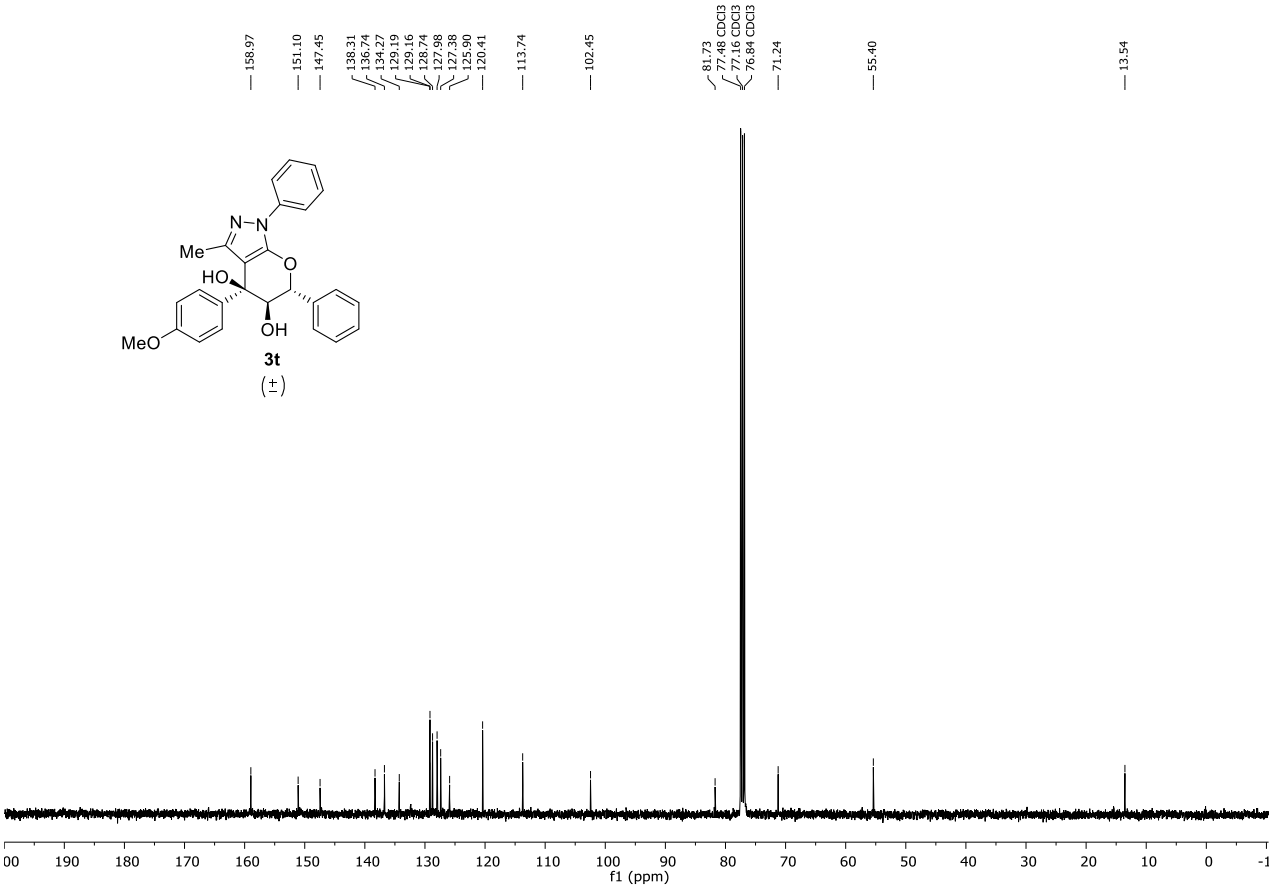

7.73
7.73
7.71
7.71
7.50
7.49
7.48
7.48
7.47
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.26
7.21
7.19
6.88
6.85
5.28
5.25
4.08
4.05
3.79
3.43
2.42
1.69


N
N
Me
O
HO
OH
MeO

**3t**

(±)

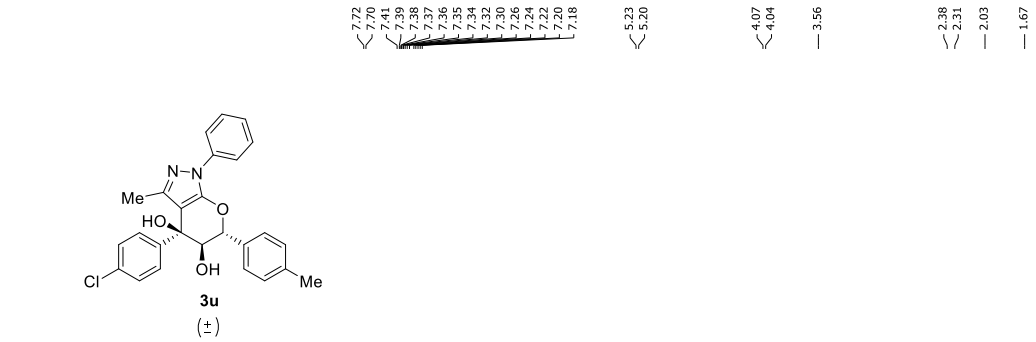

2.08
1.83
7.36
1.45
2.11
0.97
0.97
3.00
0.96
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.97
151.10
147.45
138.31
136.74
134.27
129.19
129.16
128.74
127.98
127.38
125.90
120.41
113.74
102.45
81.73
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.24
55.40
13.54
f1 (ppm)


N
N
Me
O
HO
OH
MeO

**3t**

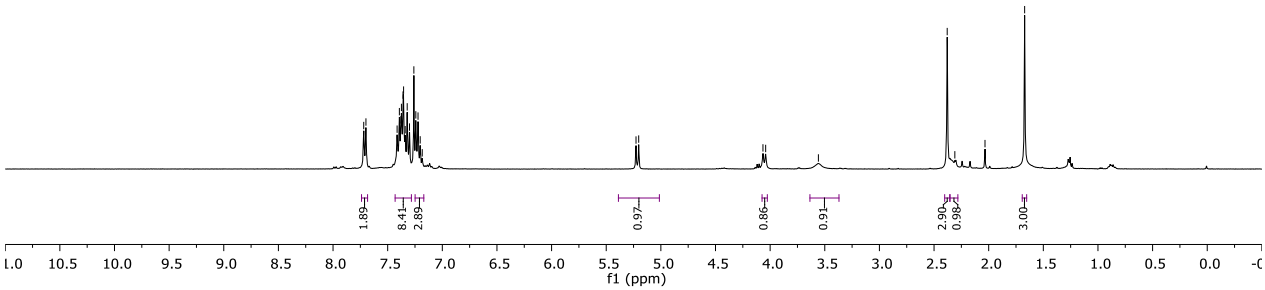
(±)

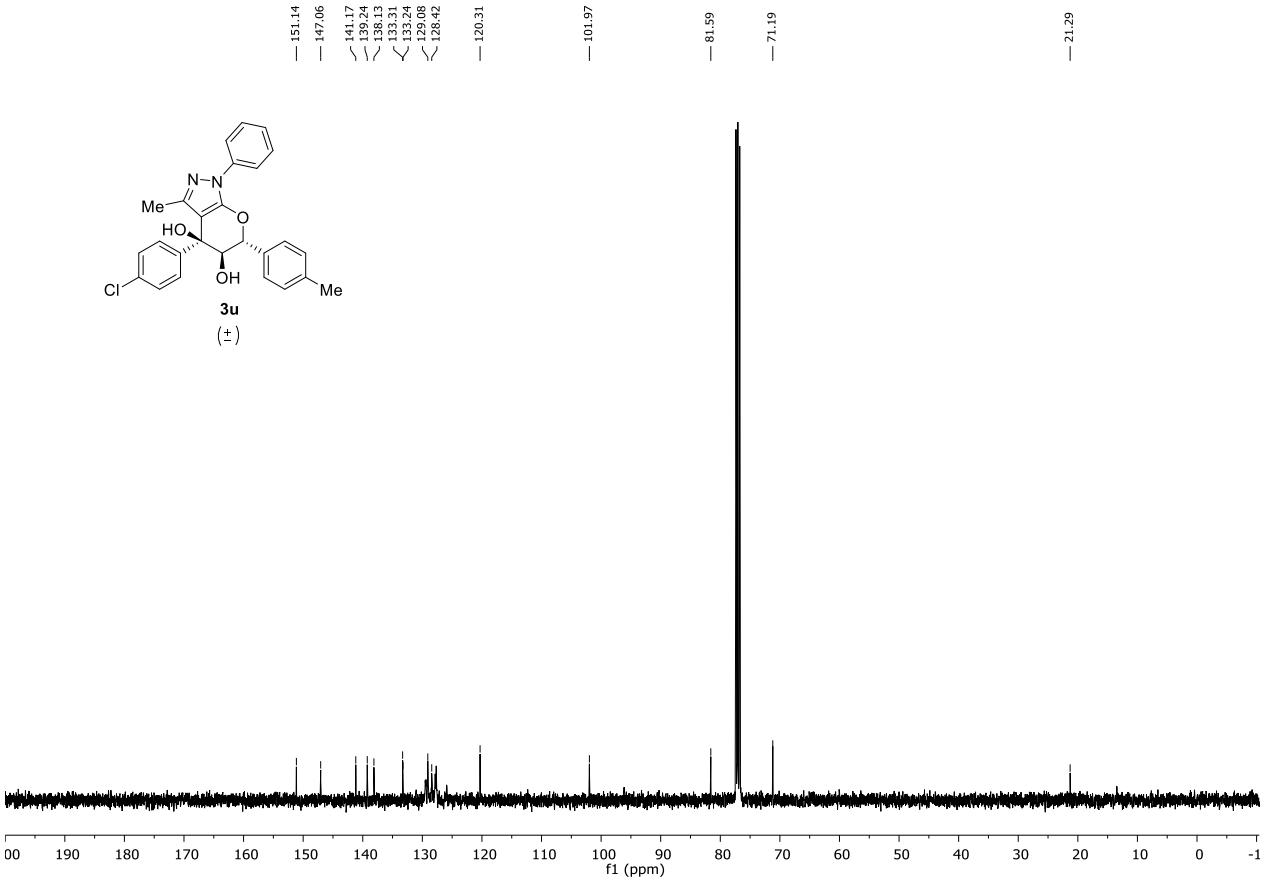

7.72
7.70
7.41
7.39
7.38
7.37
7.36
7.35
7.34
7.32
7.30
7.26
7.24
7.22
7.20
7.18
5.23
5.20
4.07
4.04
3.56
2.38
2.31
2.03
1.67


N
N
Me
HO
O
OH
Cl
Me

**3u**

(±)

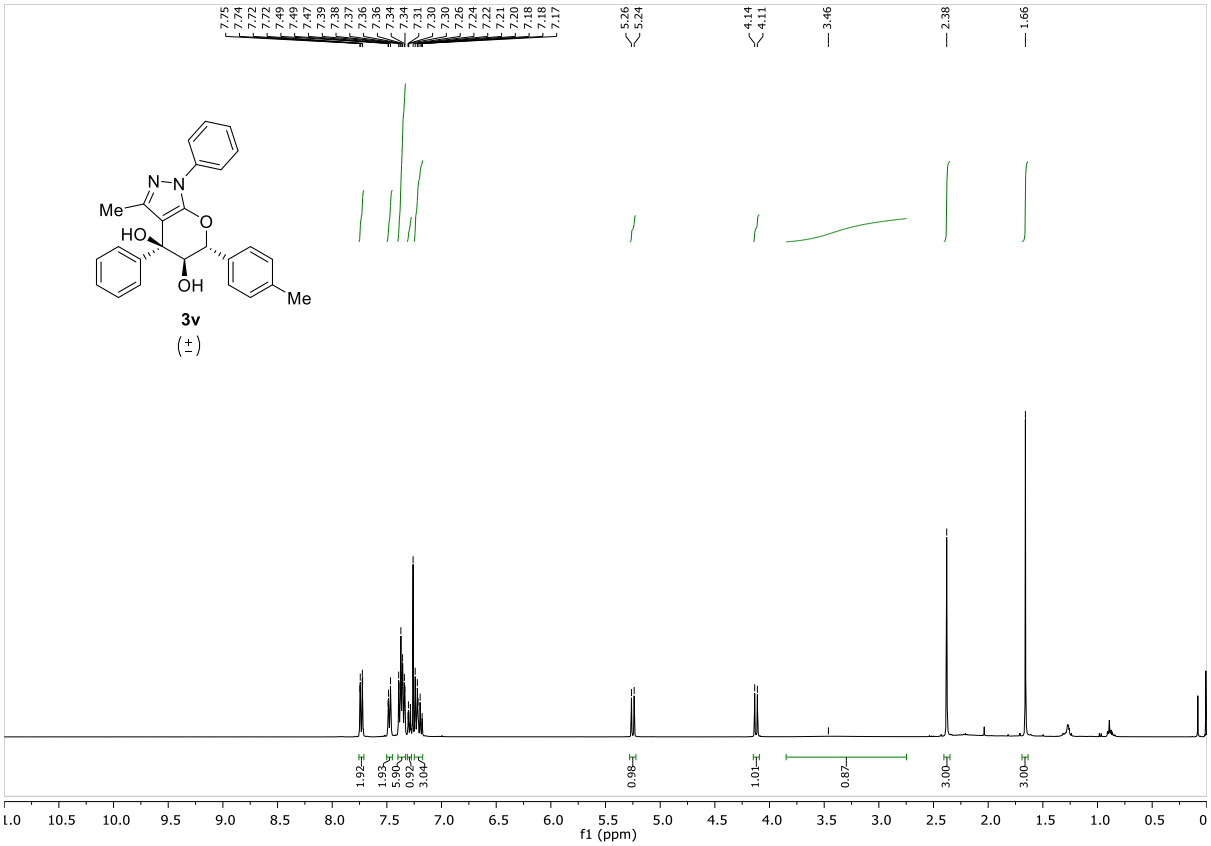

1.89
8.41
2.89
0.97
0.86
0.91
2.90
0.98
3.00
f1 (ppm)

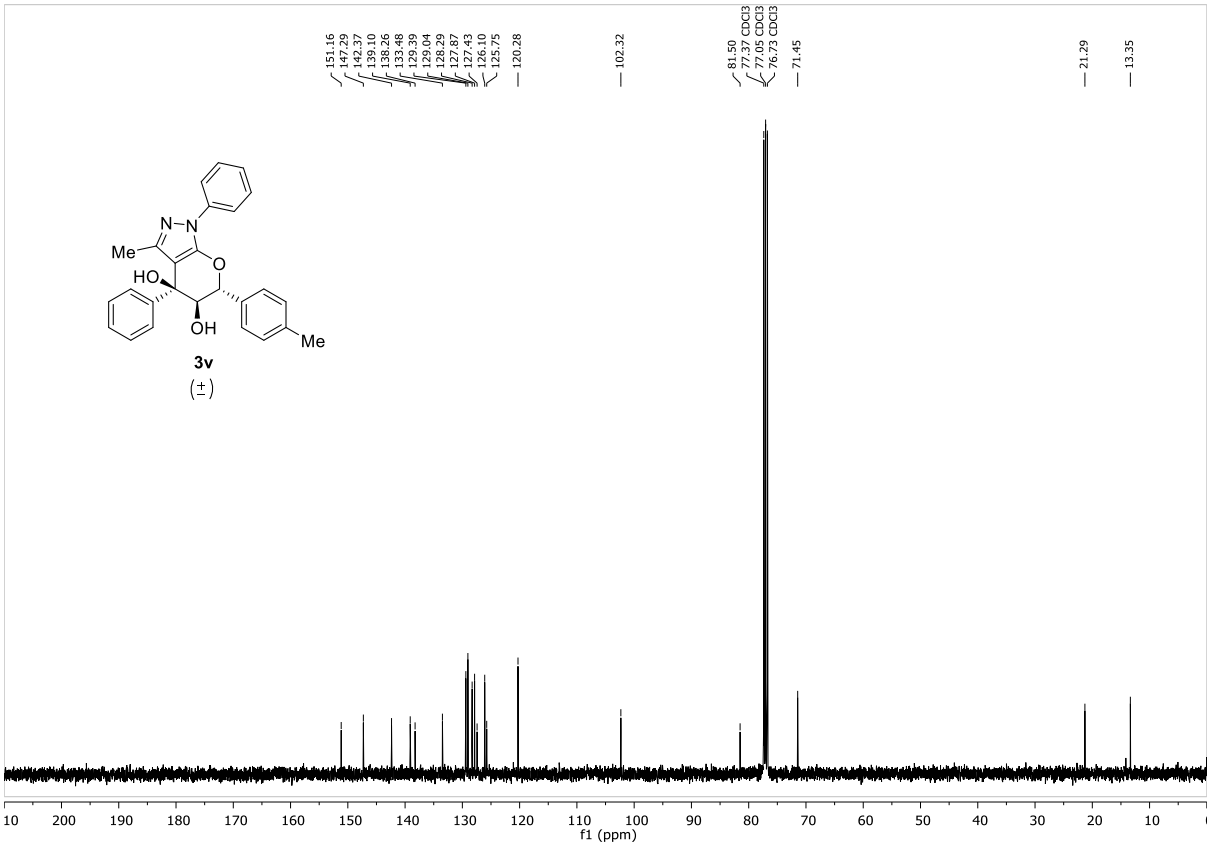

151.14
147.06
141.17
139.24
138.13
133.31
133.24
129.08
128.42
120.31
101.97
81.59
71.19
21.29
f1 (ppm)

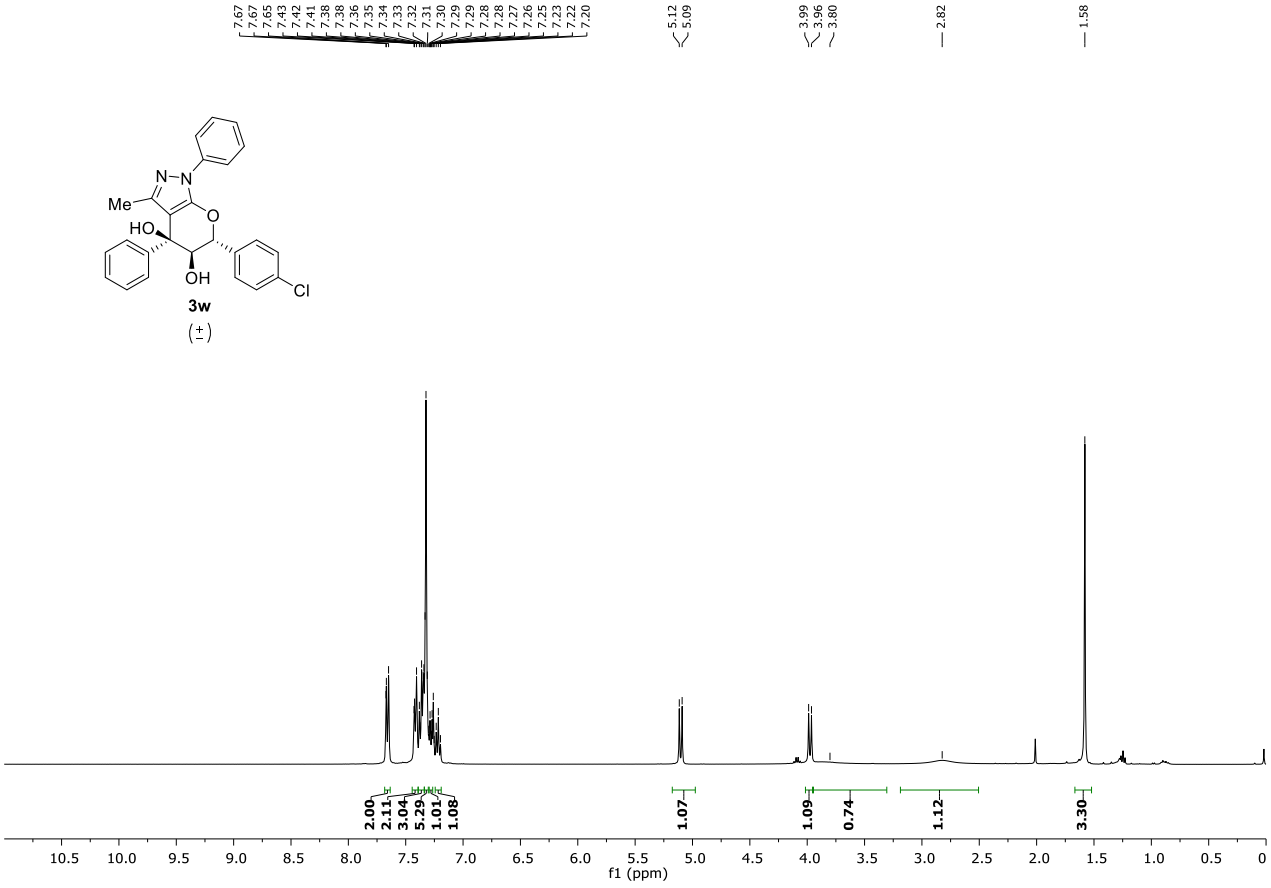

N
N
Me
HO
O
OH
Cl
Me

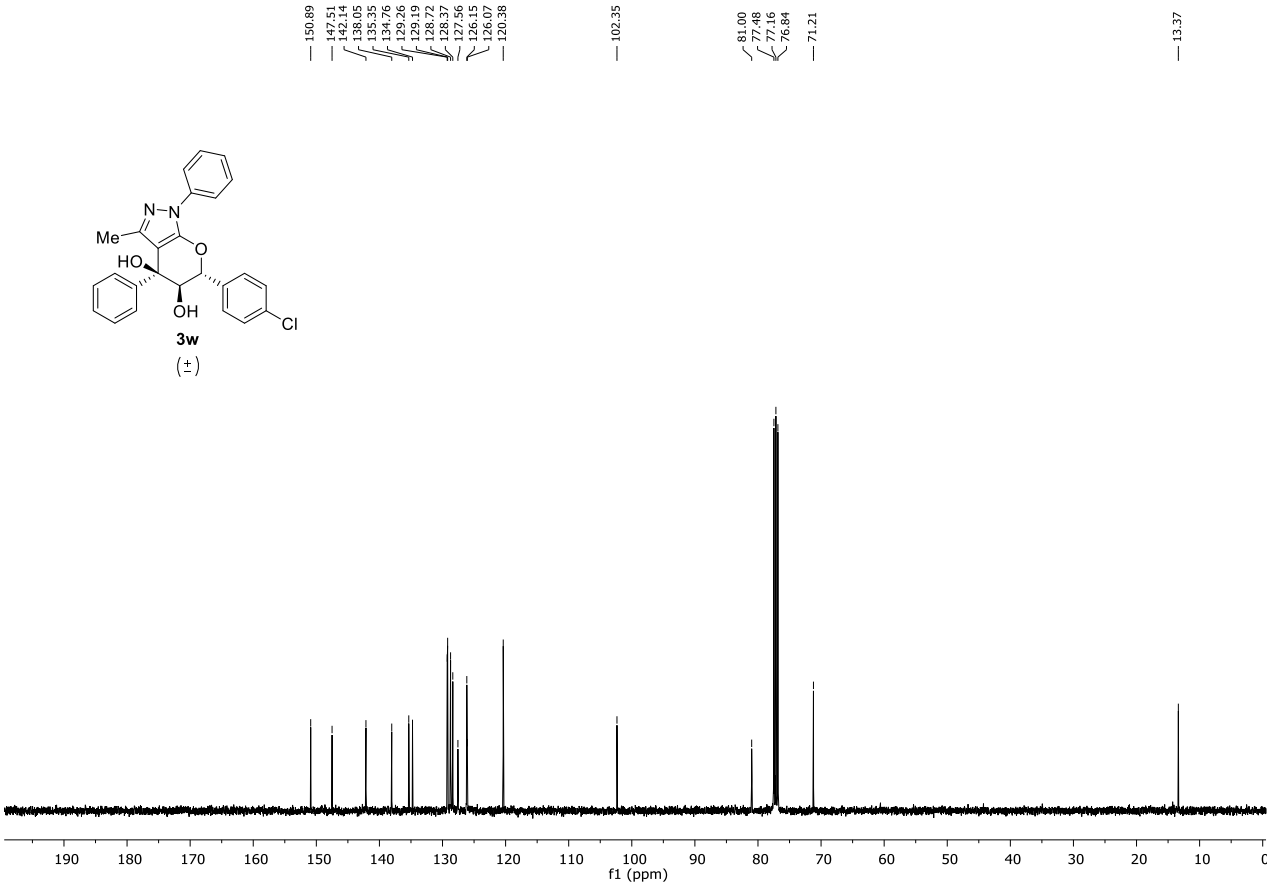
**3u**

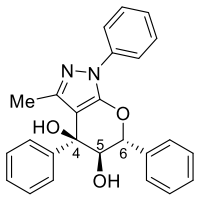
(±)


7.75
7.74
7.72
7.72
7.49
7.49
7.47
7.39
7.38
7.37
7.36
7.36
7.34
7.34
7.31
7.30
7.30
7.26
7.24
7.22
7.21
7.20
7.18
7.18
7.17
5.26
5.24
4.14
4.11
3.46
2.38
1.66
Me
HO
OH
Me
3v
(±)
1.92
1.93
5.90
0.92
3.04
0.98
1.01
0.87
3.00
3.00
f1 (ppm)


151.16
147.29
142.27
139.10
138.26
133.48
129.39
129.04
128.29
127.87
127.43
126.10
125.75
120.28
102.32
81.50
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
71.45
21.29
13.35
Me
HO
OH
Me
3v
(±)
f1 (ppm)

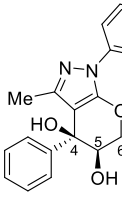

7.67
7.67
7.65
7.43
7.42
7.41
7.38
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.23
7.22
7.20
5.12
5.09
3.99
3.96
3.80
2.82
1.58
Me
HO
OH
Cl
3w
(±)
2.00
2.11
3.04
5.29
1.01
1.08
1.07
1.09
0.74
1.12
3.30
f1 (ppm)


150.89
147.51
142.14
136.05
135.35
134.76
129.26
129.19
128.72
128.37
127.56
126.15
126.07
120.38
102.35
81.00
77.48
77.16
76.84
71.21
13.37
Me
HO
OH
Cl
3w
(±)
f1 (ppm)

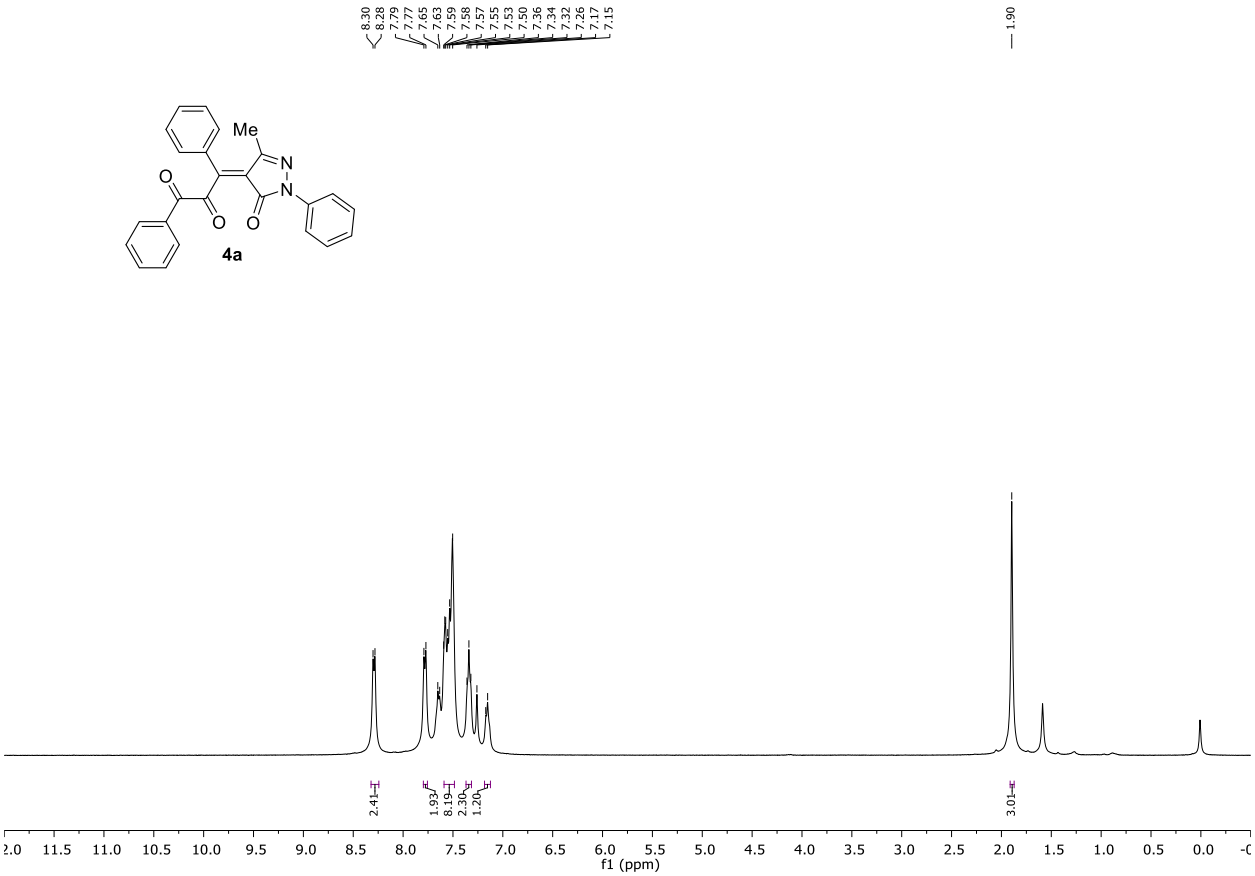


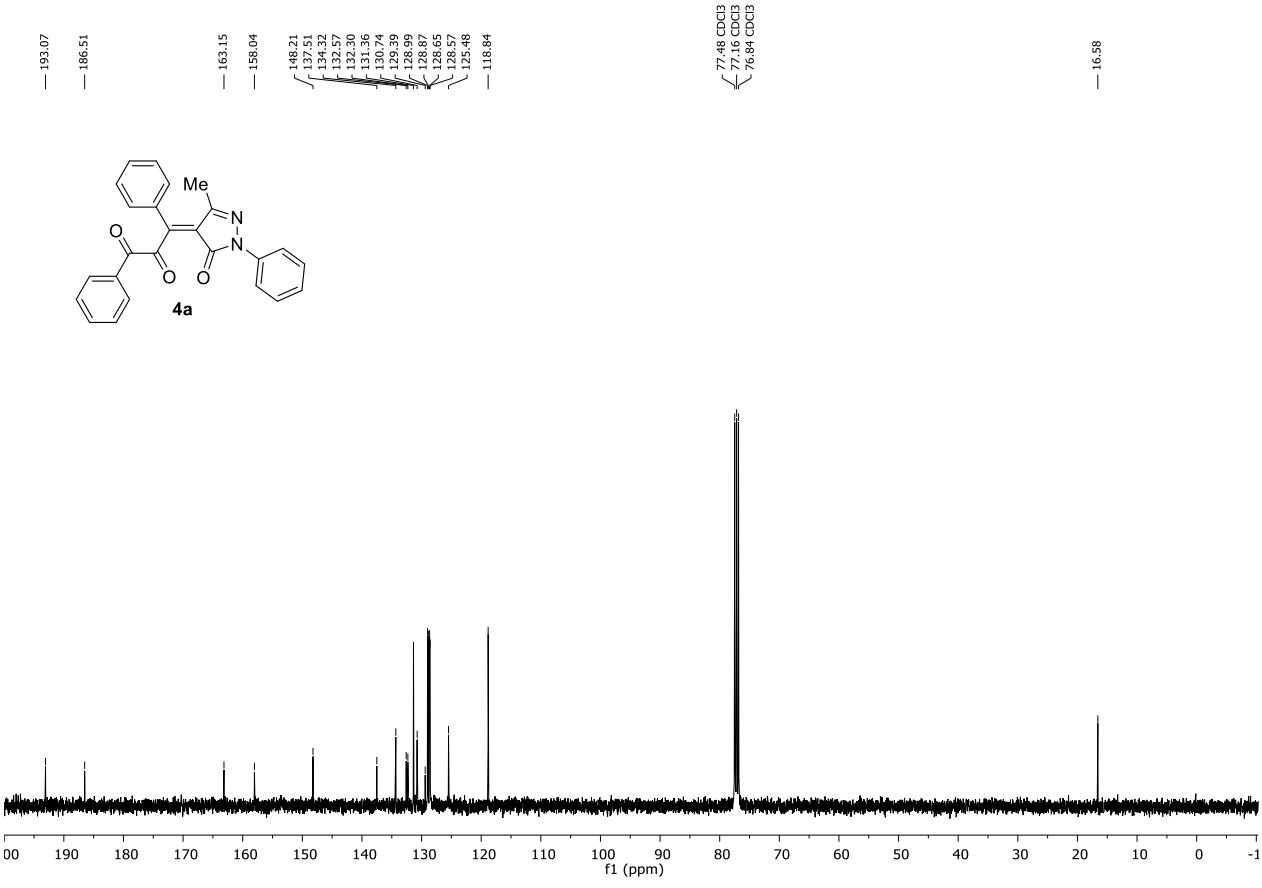

**(4S, 5R, 6R)**
**3aa**

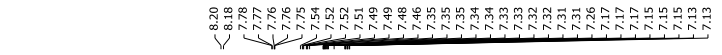


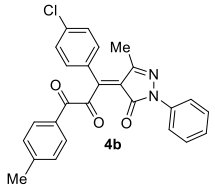




**(4S, 5R, 6R)**
**3aa**

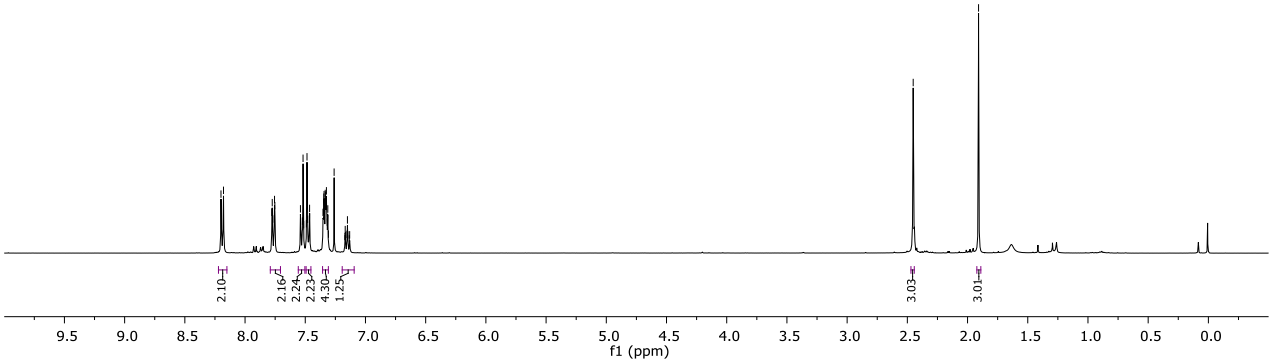

8.30
8.28
7.79
7.77
7.65
7.63
7.59
7.58
7.57
7.55
7.53
7.50
7.36
7.34
7.32
7.26
7.17
7.15
1.90
Me
N
N
O
O
O
4a
2.41
1.93
8.19
2.30
1.20
3.01
f1 (ppm)


193.07
186.51
163.15
158.04
148.21
137.51
134.32
132.57
132.30
131.36
130.74
129.39
128.99
128.87
128.65
128.57
125.48
118.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
16.58
Me
N
N
O
O
O
4a
f1 (ppm)

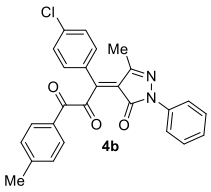

8.20
8.18
7.78
7.77
7.76
7.76
7.75
7.54
7.52
7.52
7.51
7.49
7.49
7.48
7.46
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.26
7.17
7.17
7.15
7.15
7.15
7.13
7.13
2.45
1.91


Cl
Me
O
O
N
N
O
Me

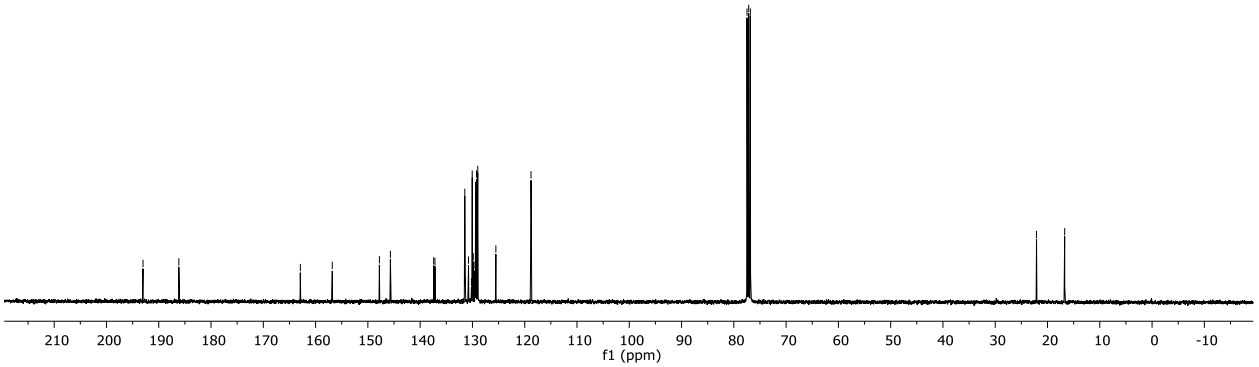
**4b**

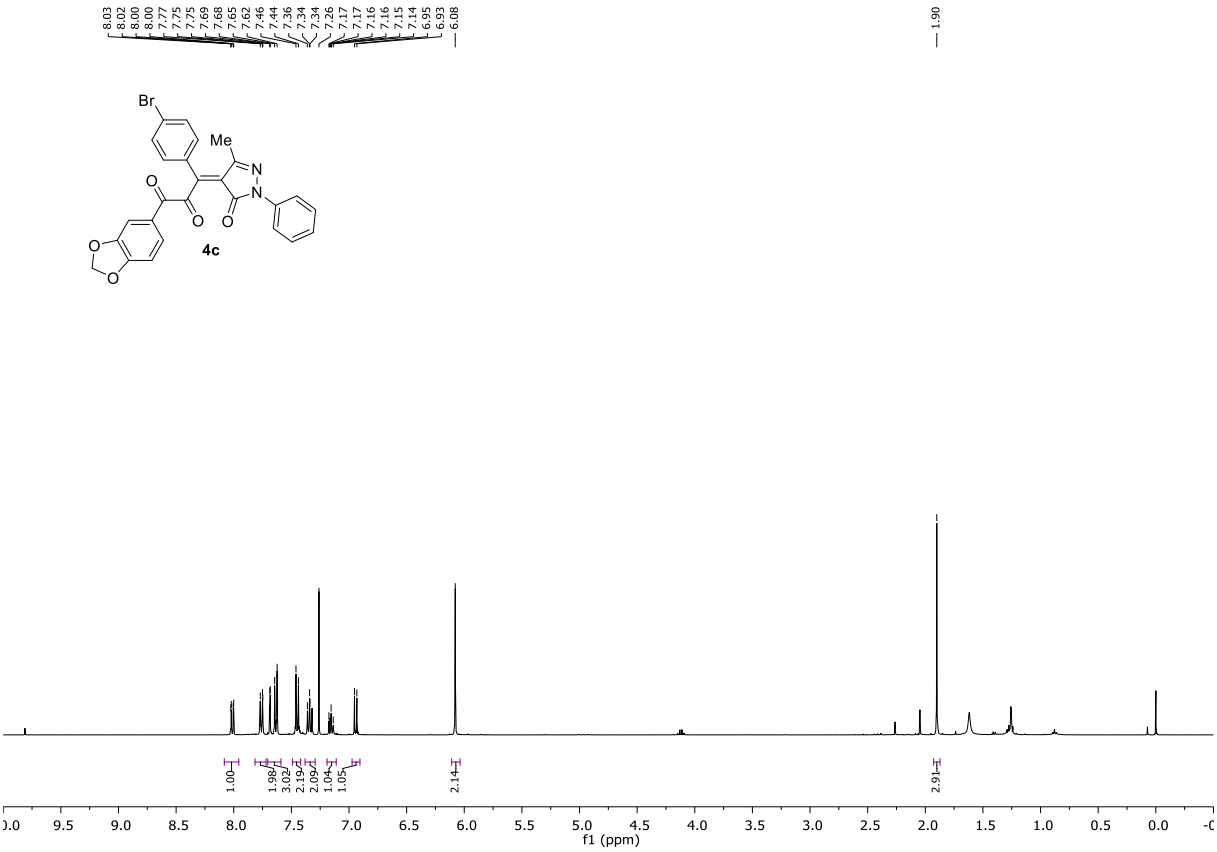

2.10
2.16
2.24
2.23
4.30
1.25
3.03
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

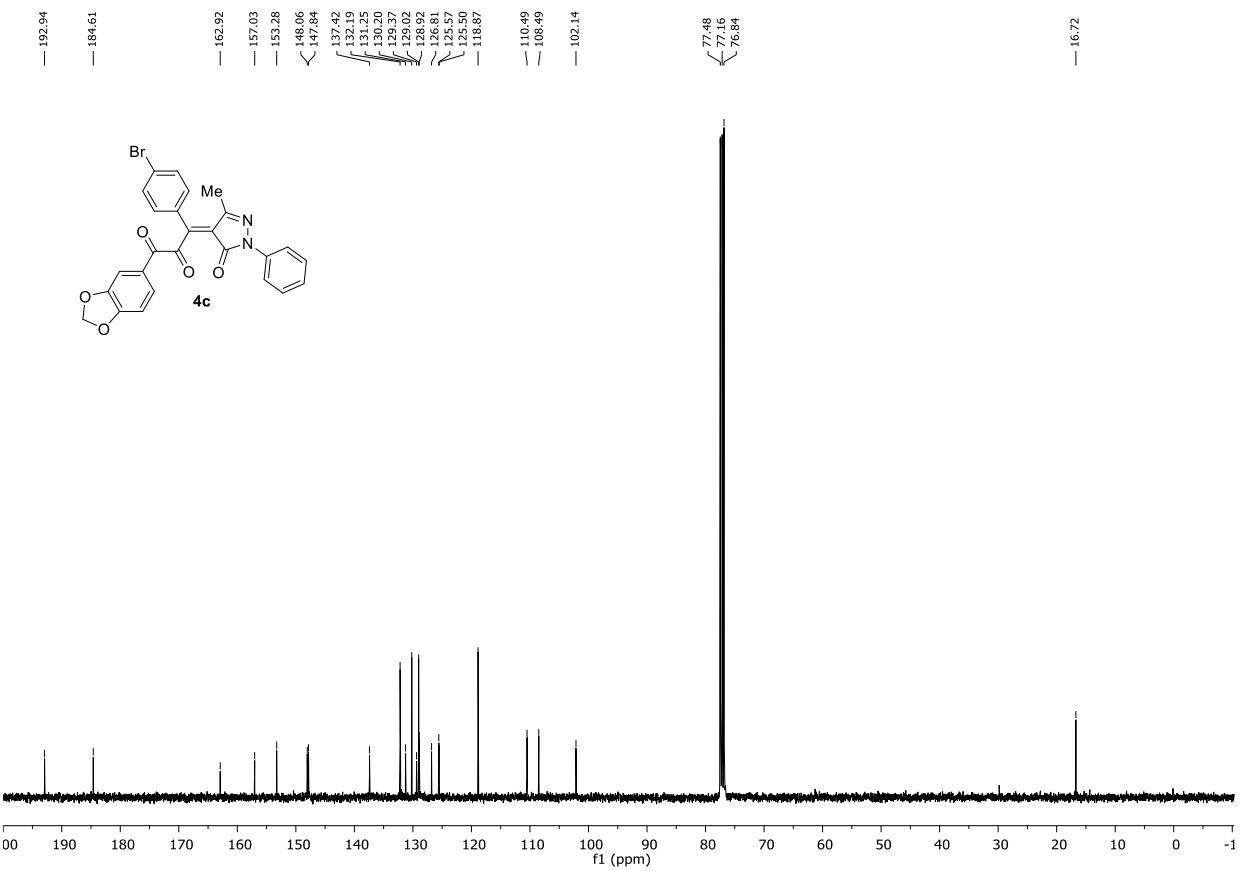

193.01
186.16
162.92
156.81
147.80
145.69
137.41
137.16
131.46
131.34
130.75
130.19
130.04
129.94
129.84
129.52
129.50
129.40
129.22
128.98
125.52
118.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
22.10
16.72

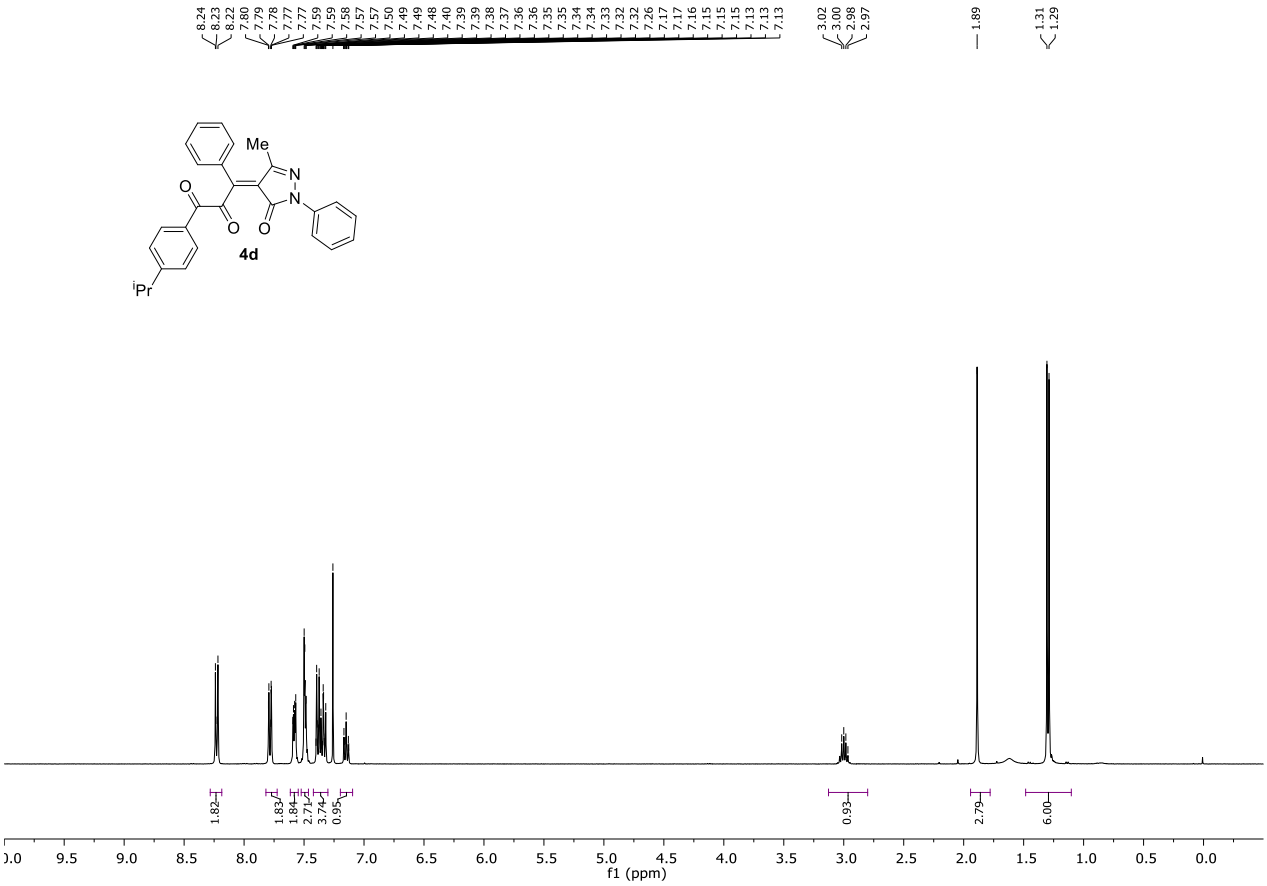

Cl
Me
O
O
N
N
O
Me

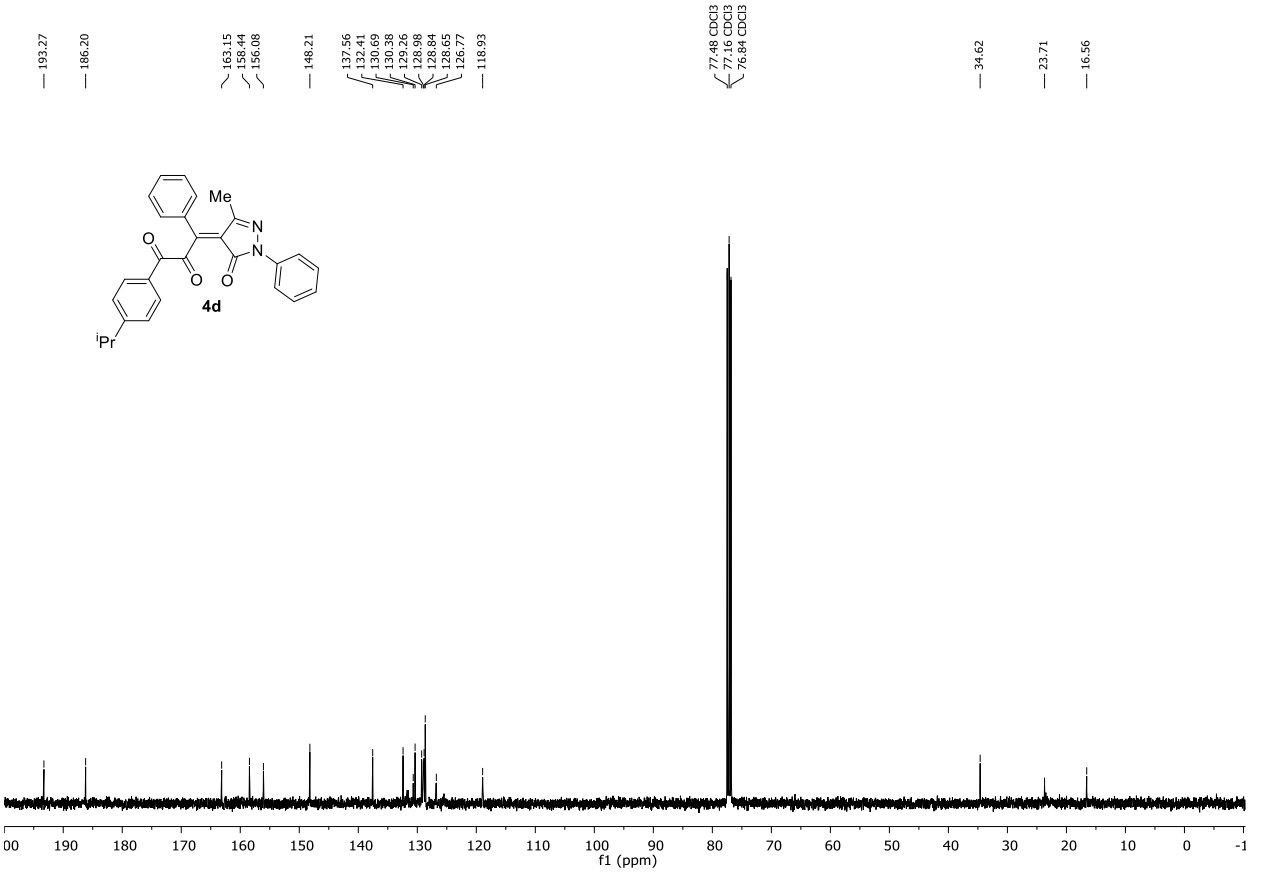
**4b**

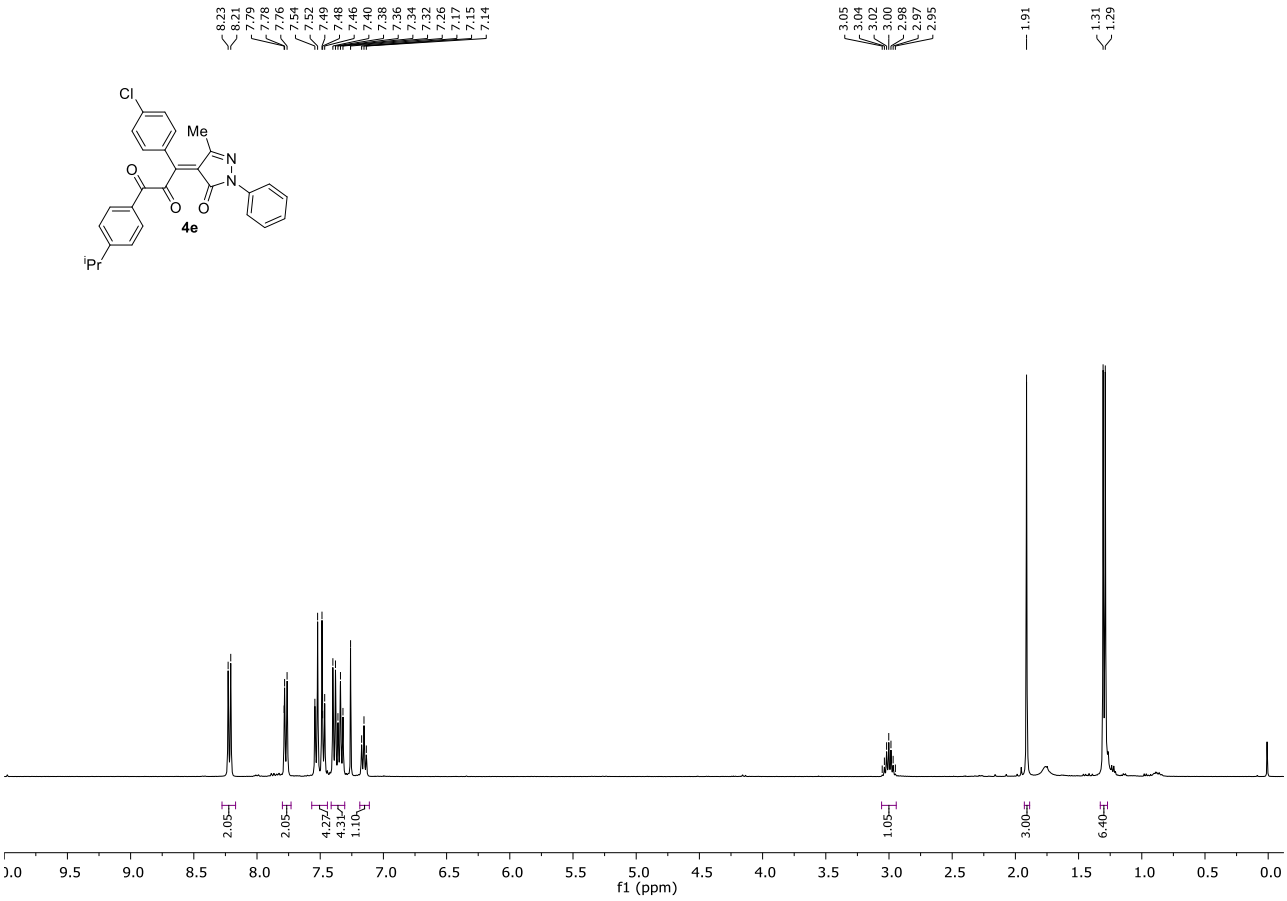

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

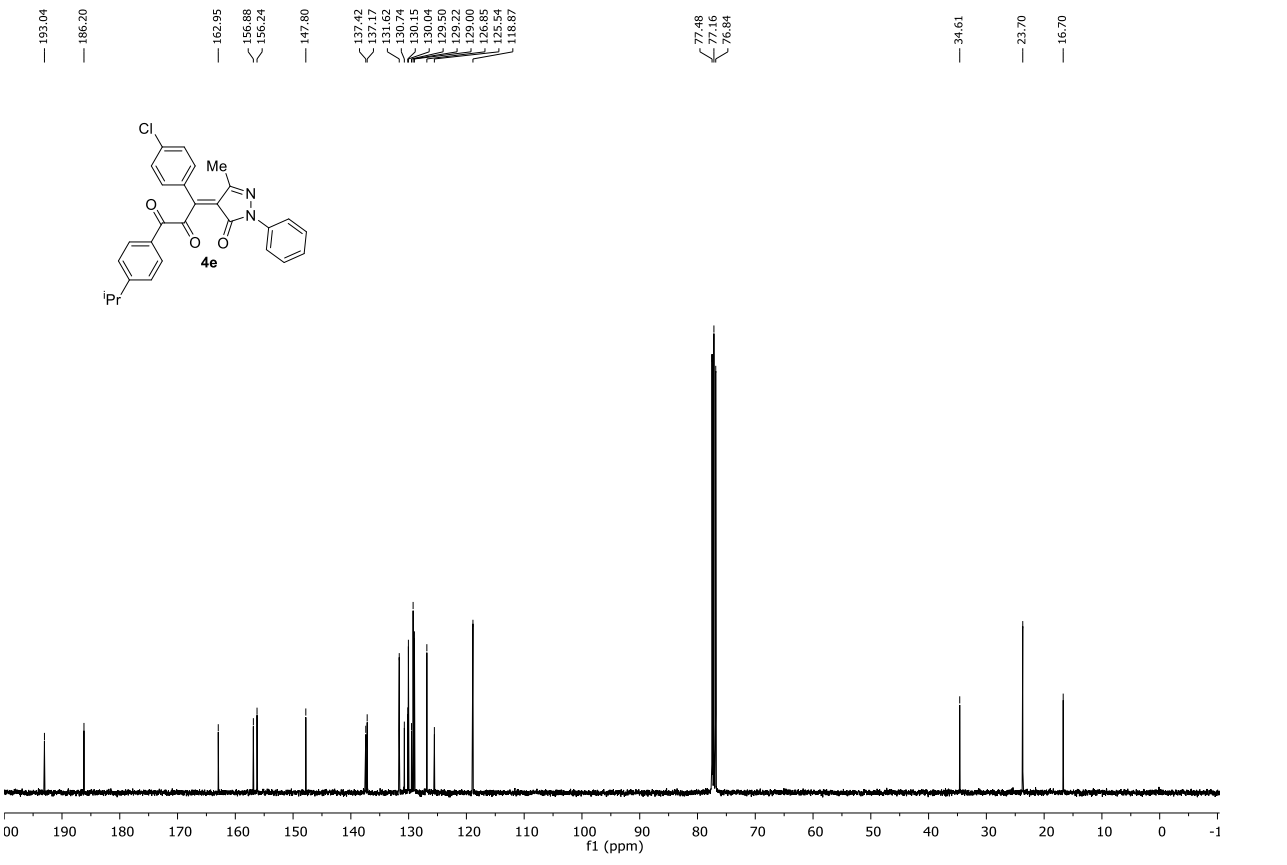

8.03
8.02
8.00
8.00
7.77
7.75
7.75
7.69
7.68
7.65
7.62
7.46
7.44
7.36
7.34
7.34
7.26
7.17
7.17
7.16
7.16
7.15
7.14
6.95
6.93
6.08
1.90
Br
Me
N
N
O
O
O
O
O
O
4c
1.00
1.98
3.02
2.19
2.09
1.04
1.05
2.14
2.91
f1 (ppm)


192.94
184.61
162.92
157.03
153.28
148.06
147.84
137.42
132.19
131.25
130.20
129.37
129.02
128.92
126.81
125.57
125.50
118.87
110.49
108.49
102.14
77.48
77.16
76.84
16.72
Br
Me
N
N
O
O
O
O
O
O
4c
f1 (ppm)

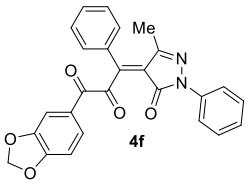

8.24
8.23
8.22
7.80
7.79
7.78
7.77
7.77
7.59
7.59
7.58
7.57
7.57
7.50
7.49
7.49
7.48
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.26
7.17
7.17
7.16
7.15
7.15
7.13
7.13
7.13
3.02
3.00
2.98
2.97
1.89
1.31
1.29
Me
N
N
O
O
O
O
4d
iPr
1.82
1.83
1.84
2.71
3.74
0.95
0.93
2.79
6.00
f1 (ppm)


193.27
186.20
163.15
158.44
156.08
148.21
137.56
132.41
130.69
130.38
129.26
128.98
128.84
128.65
126.77
118.93
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
34.62
23.71
16.56
Me
N
N
O
O
O
O
4d
iPr
f1 (ppm)

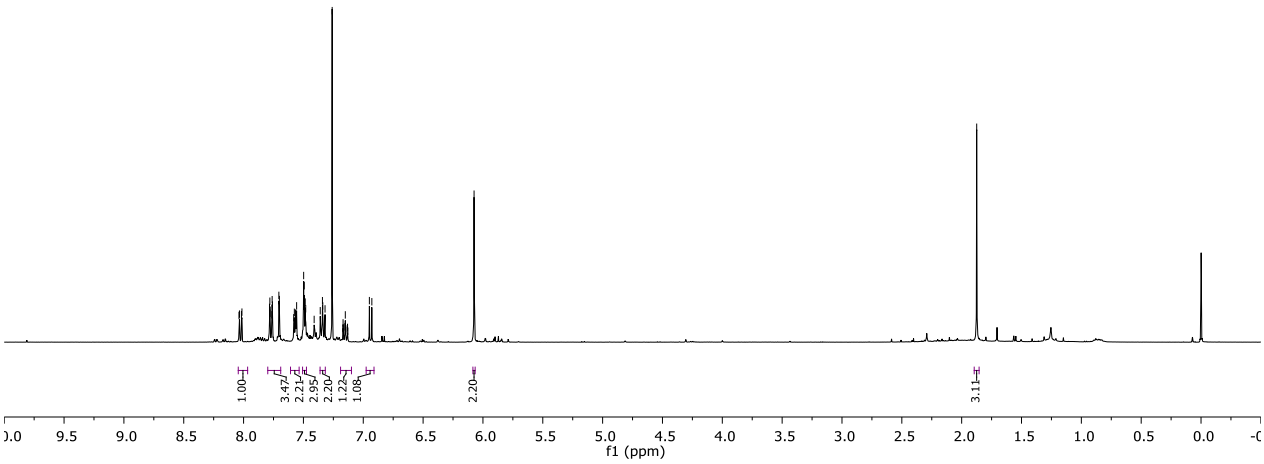

8.23
8.21
7.79
7.78
7.76
7.54
7.52
7.49
7.48
7.46
7.40
7.38
7.36
7.34
7.32
7.26
7.17
7.15
7.14
3.05
3.04
3.02
3.00
2.98
2.97
2.95
1.91
1.31
1.29
Cl
Me
N
N
O
O
O
O
4e
iPr
2.05
2.05
4.27
4.31
1.10
1.05
3.00
6.40
f1 (ppm)


193.04
186.20
162.95
156.88
156.24
147.80
137.42
137.17
131.62
130.74
130.15
130.04
129.50
129.22
124.00
125.85
125.54
118.87
77.48
77.16
76.84
34.61
23.70
16.70
Cl
Me
N
N
O
O
O
O
4e
iPr
f1 (ppm)

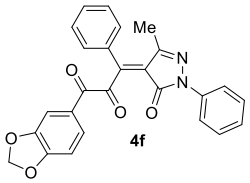

8.04
8.03
8.02
8.01
7.78
7.78
7.76
7.76
7.76
7.71
7.70
7.58
7.58
7.57
7.57
7.56
7.56
7.56
7.50
7.49
7.48
7.48
7.41
7.36
7.34
7.34
7.32
7.26
7.15
6.95
6.93
6.07
1.87


Me
N
N
O
O
O
O
O
O

4f

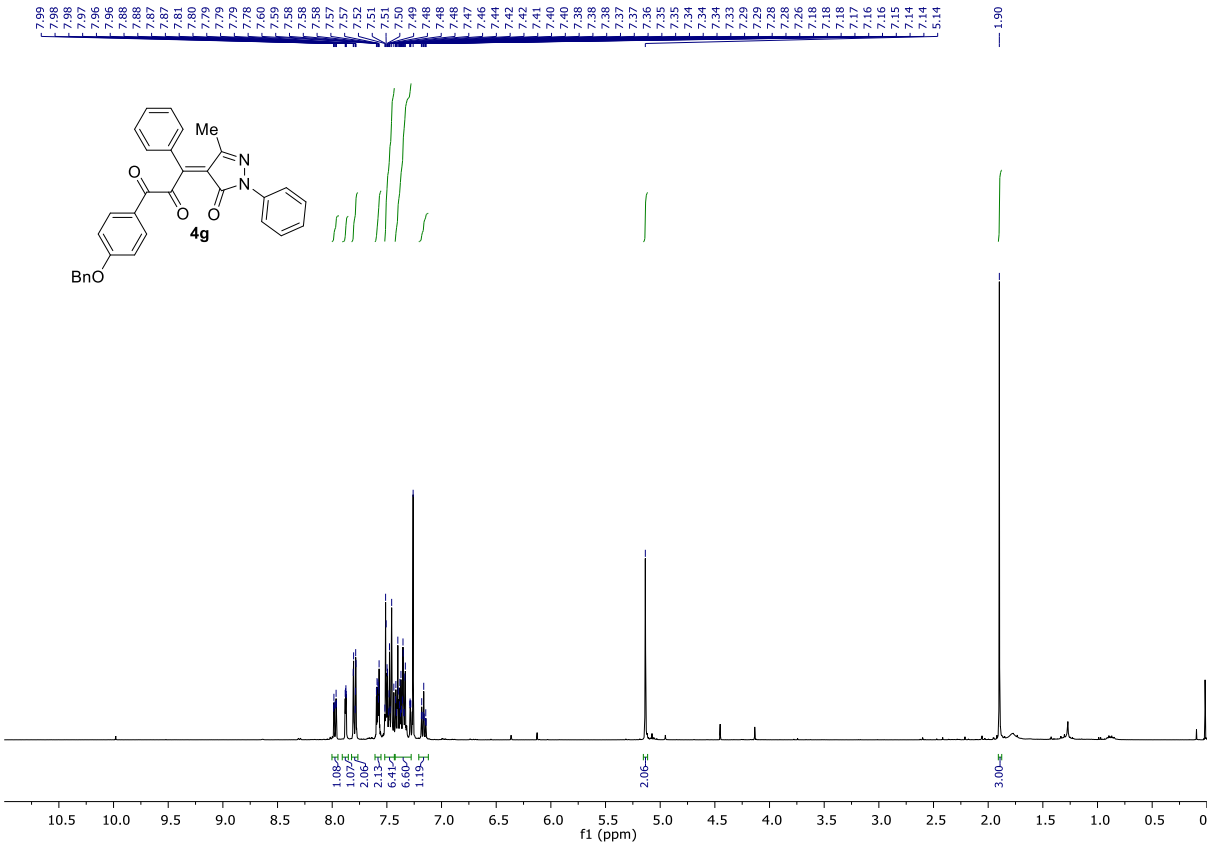

1.00
3.47
2.21
2.95
2.20
1.22
1.08
2.20
3.11
f1 (ppm)

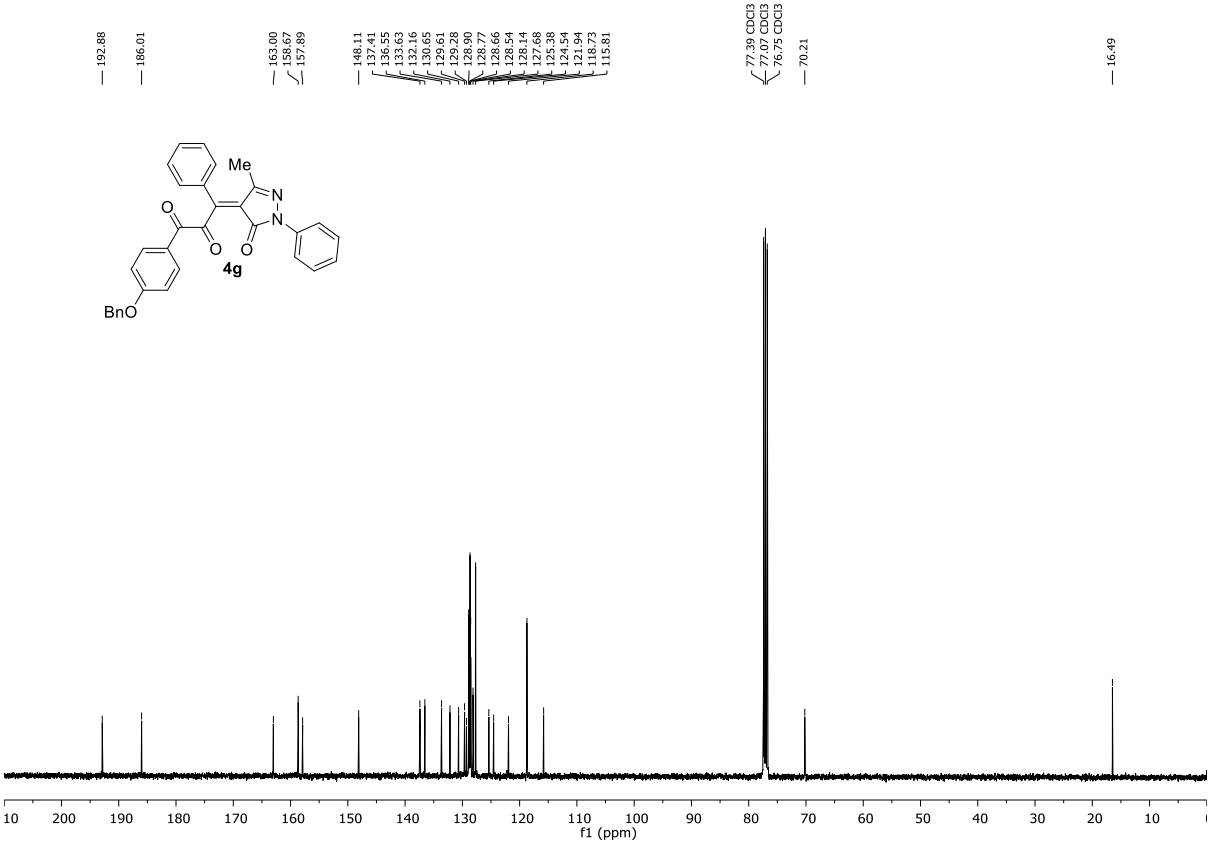

193.25
184.61
163.10
158.57
153.14
148.23
148.01
137.51
132.39
130.69
129.14
128.99
128.88
128.85
128.63
127.00
125.47
118.89
110.54
108.45
102.09
77.48
77.16
76.84
16.58

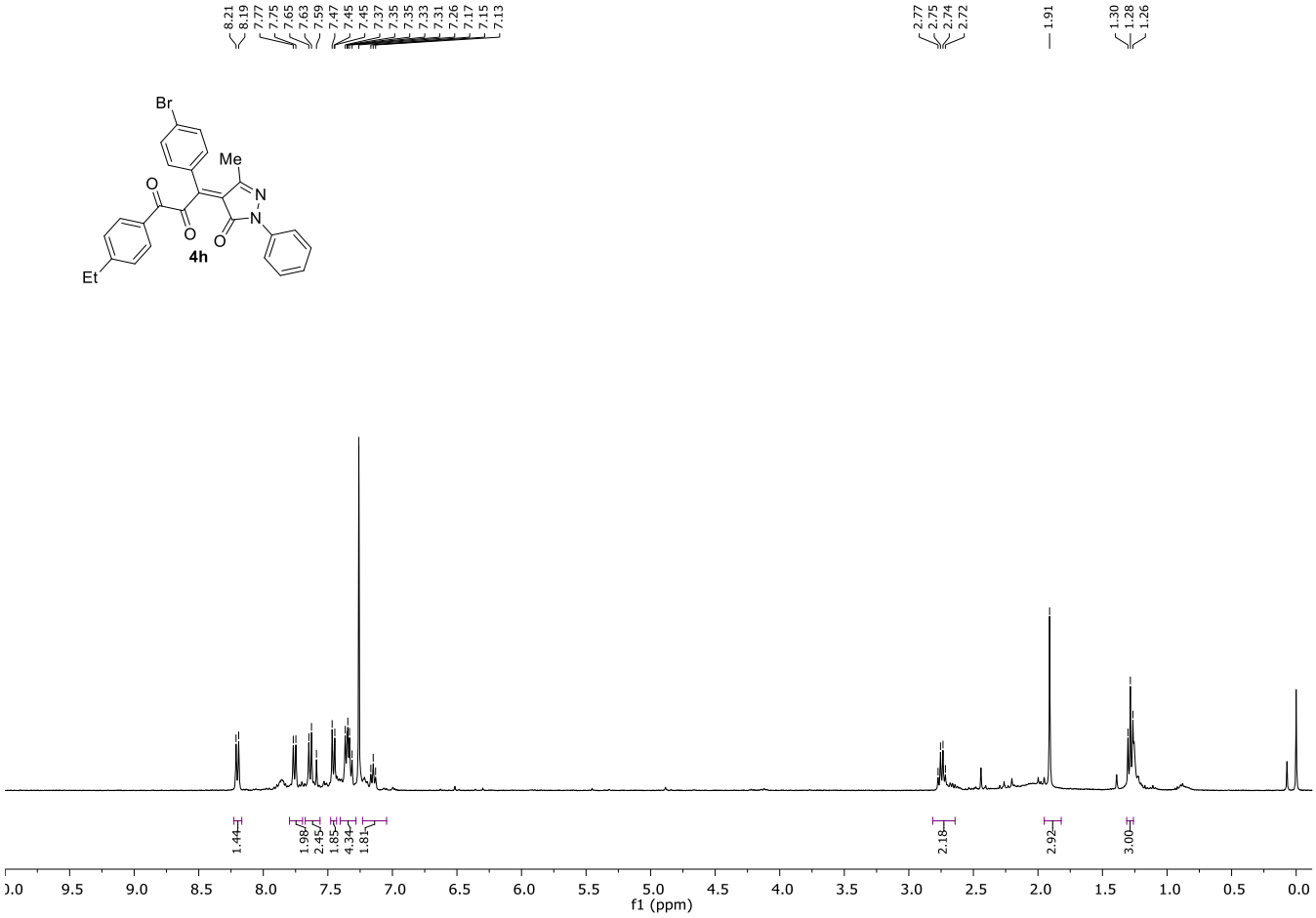

Me
N
N
O
O
O
O
O
O

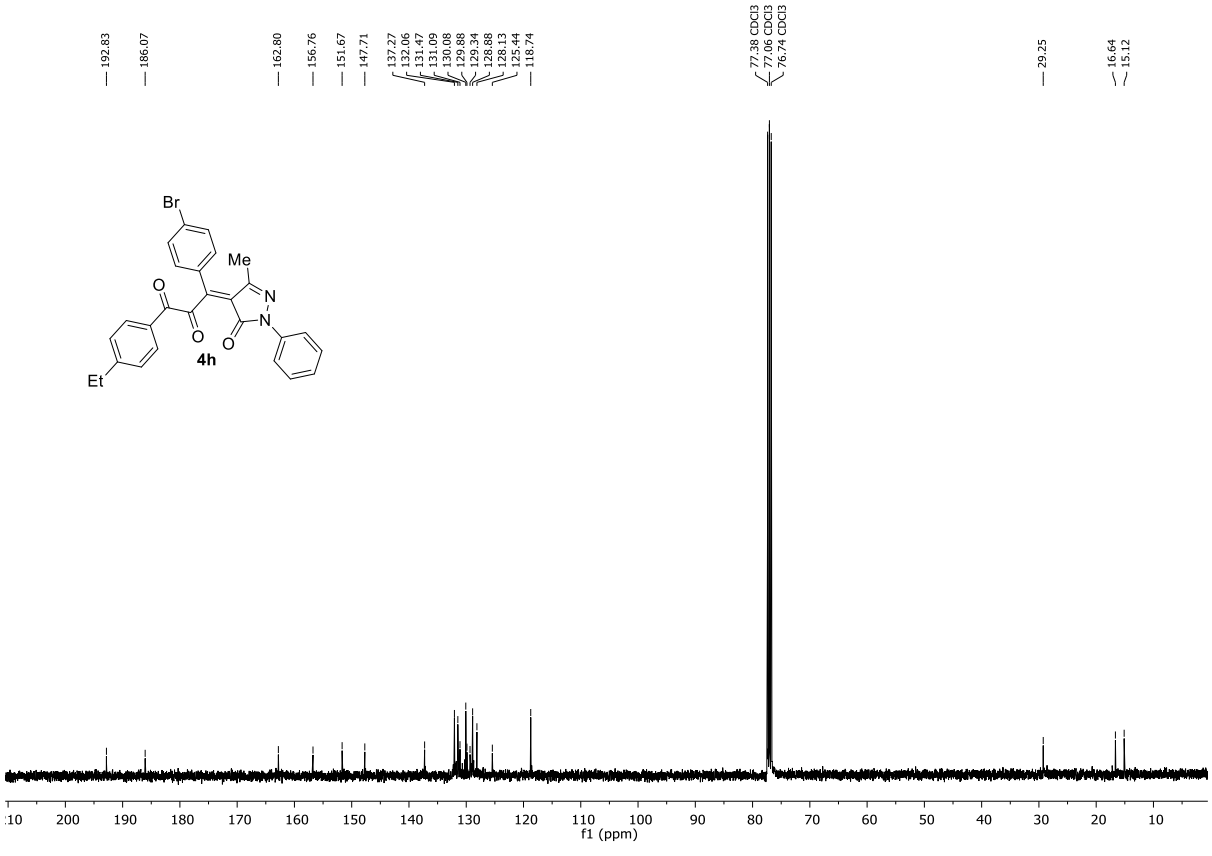
4f

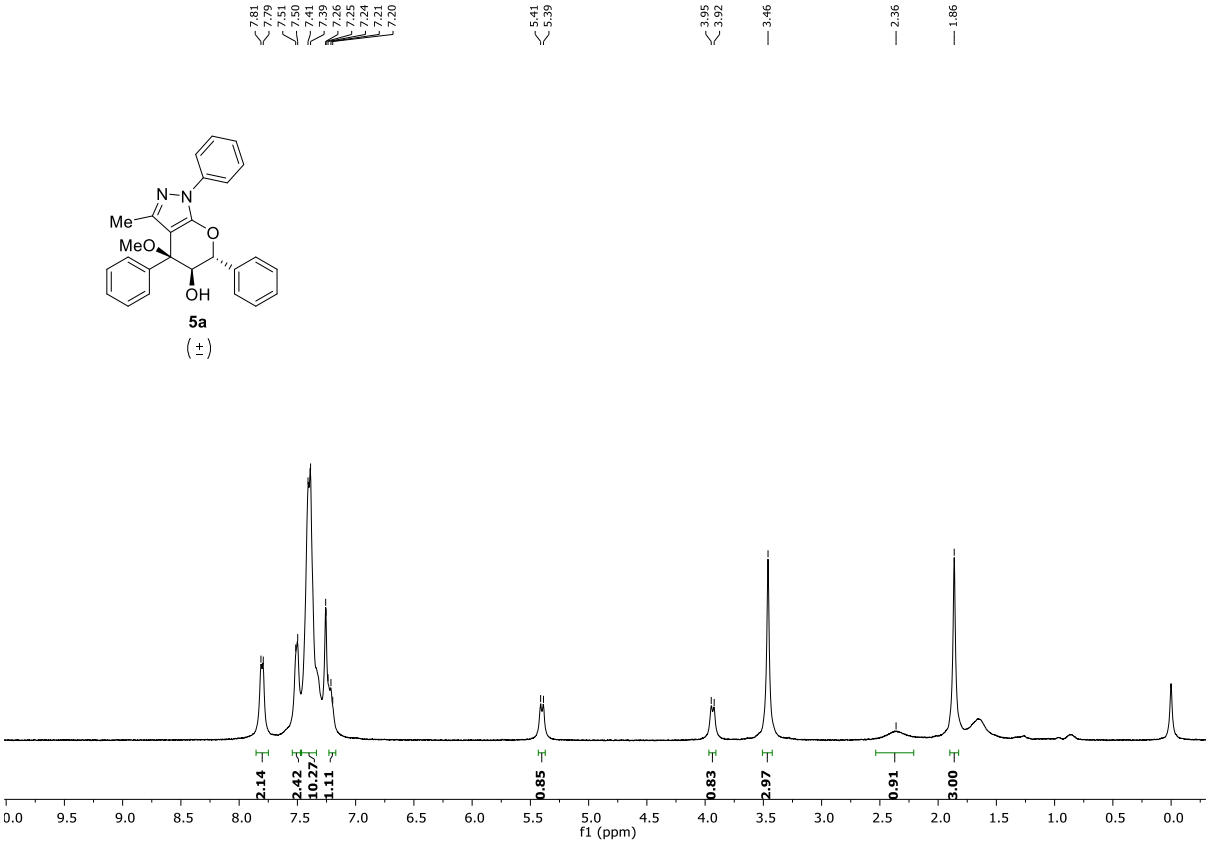

f1 (ppm)

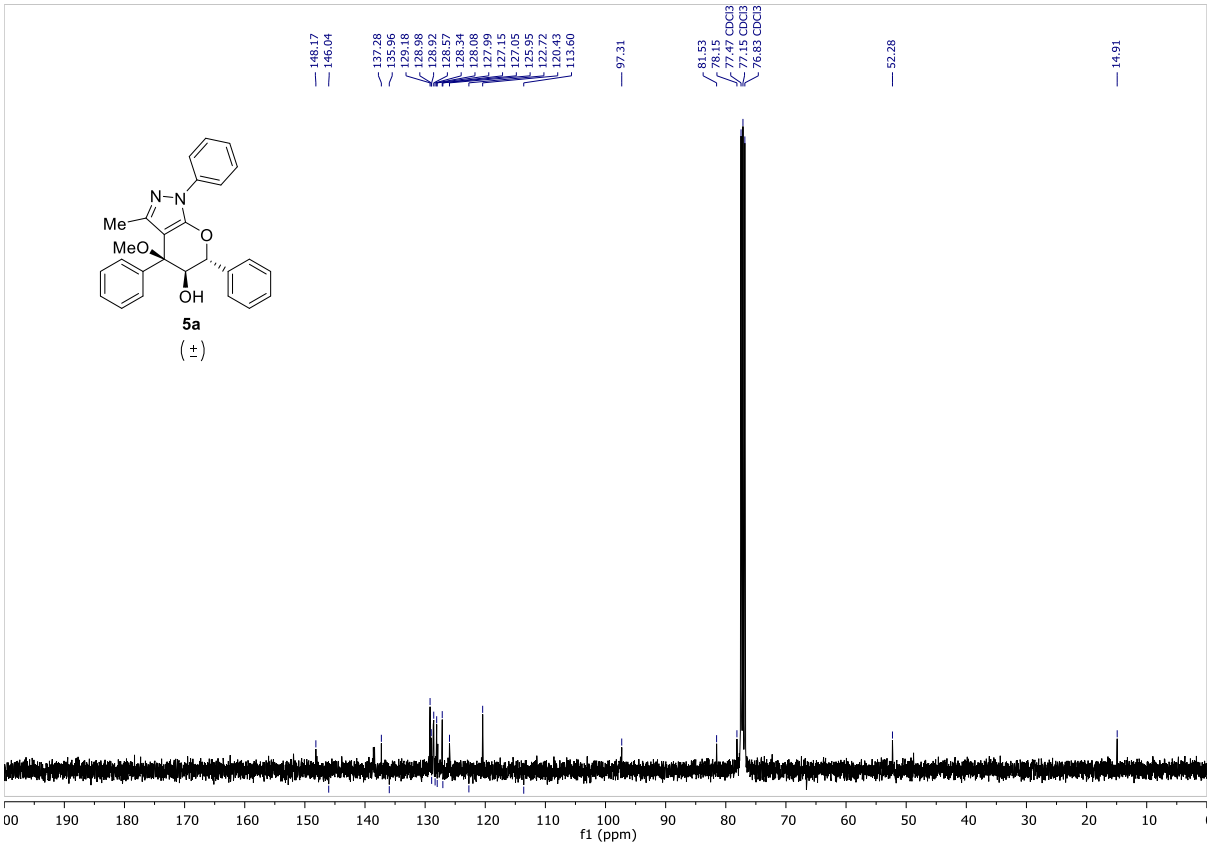

Me
N
N
O
O
O
O
4g
BnO
f1 (ppm)

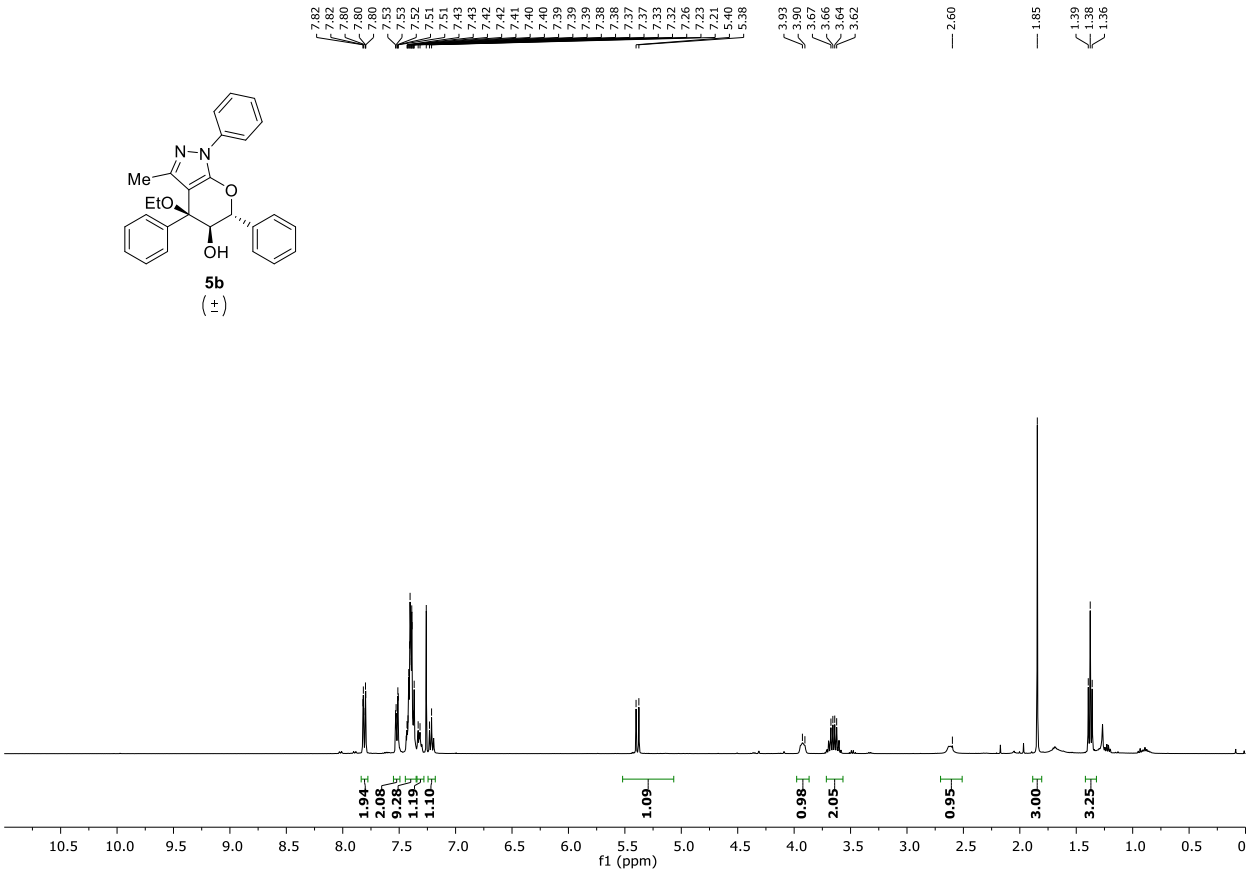

Me
N
N
O
O
O
O
4g
BnO
f1 (ppm)

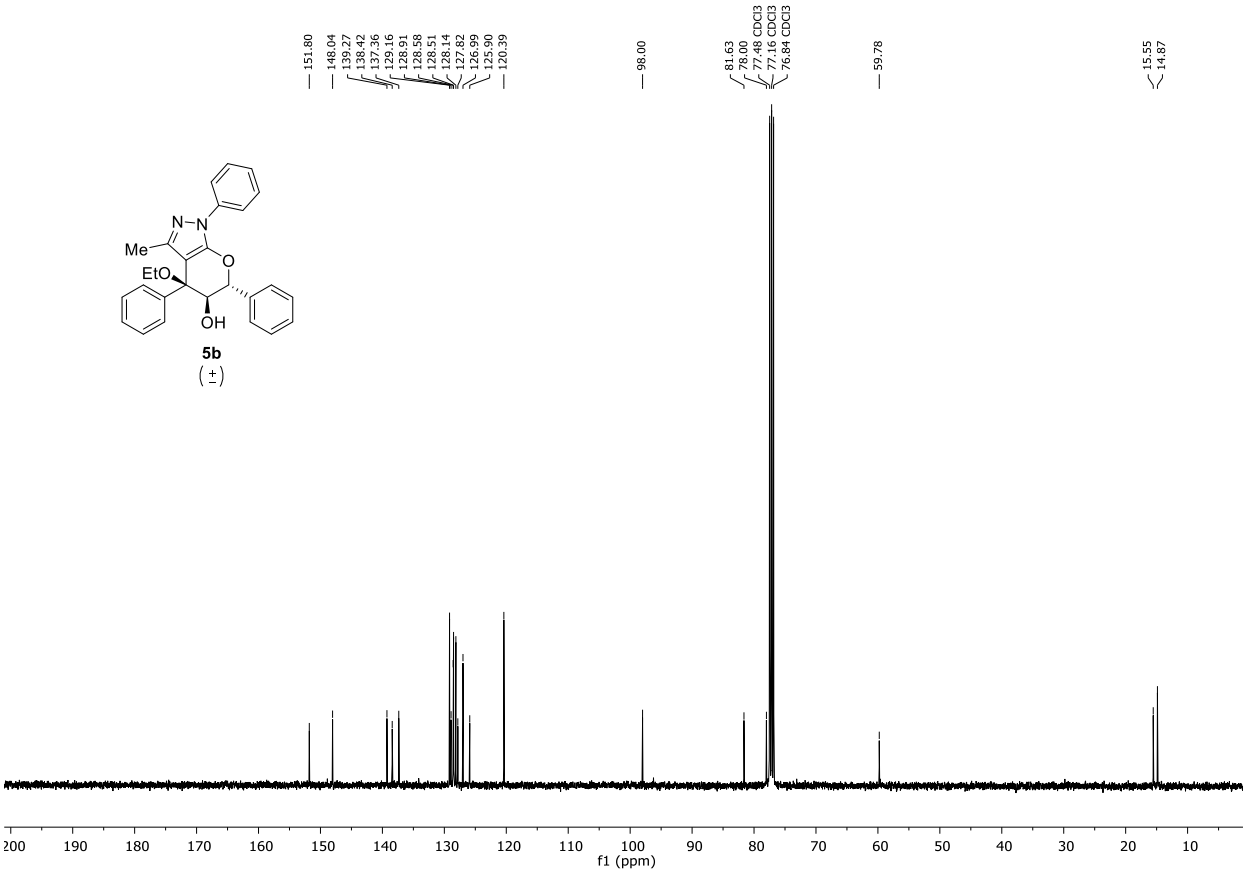

8.21
8.19
7.77
7.75
7.65
7.63
7.59
7.47
7.45
7.45
7.37
7.35
7.35
7.33
7.31
7.26
7.17
7.15
7.13
2.77
2.75
2.74
2.72
1.91
1.30
1.28
1.26
Br
Me
N
N
O
O
O
Et
4h
1.44
1.98
2.45
1.85
4.34
1.81
2.18
2.92
3.00
f1 (ppm)


192.83
186.07
162.80
156.76
151.67
147.71
137.27
132.06
131.47
131.09
130.08
129.88
129.34
128.88
128.13
125.44
118.74
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
29.25
16.64
15.12
Br
Me
N
N
O
O
O
Et
4h
f1 (ppm)

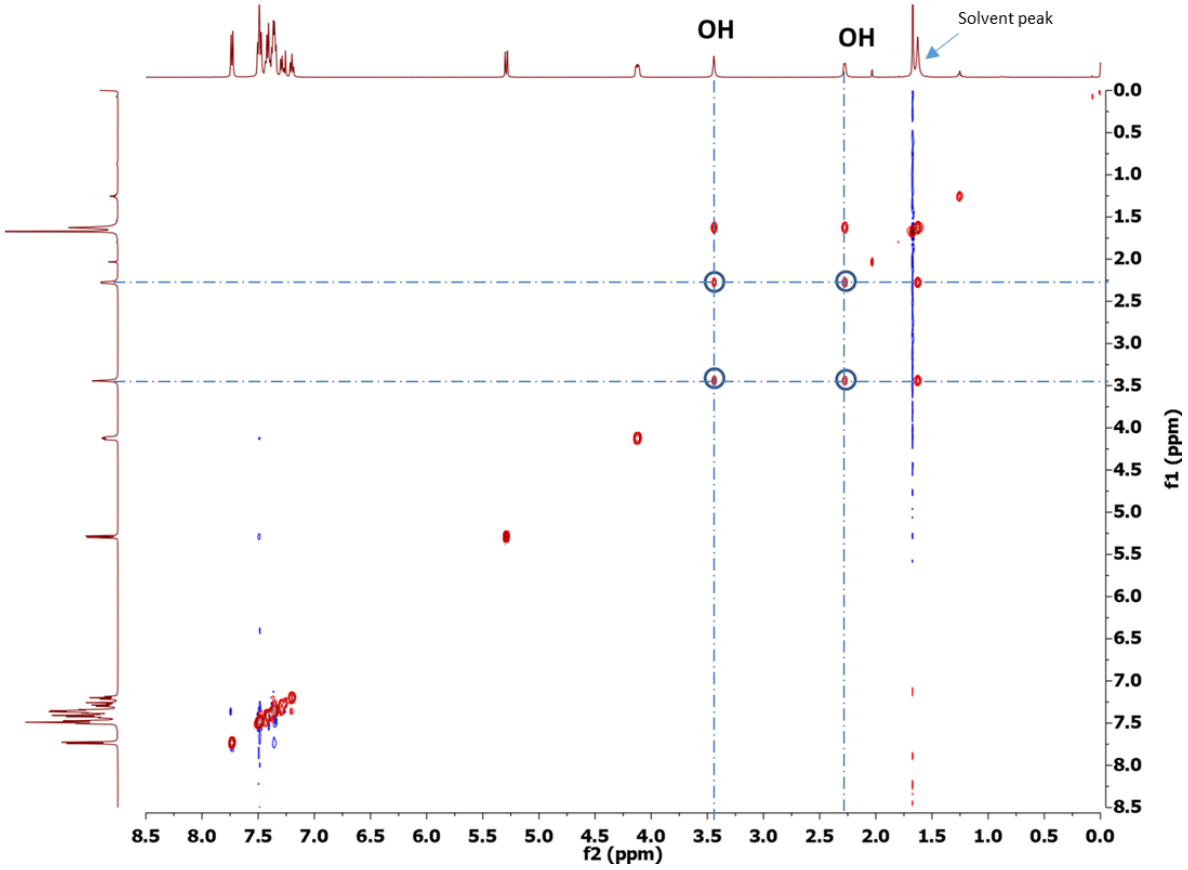

7.81
7.79
7.51
7.50
7.41
7.39
7.26
7.25
7.24
7.21
7.20
5.41
5.39
3.95
3.92
3.46
2.36
1.86
Me
MeO
N
N
O
OH
5a
(±)
2.14
2.42
10.27
1.11
0.85
0.83
2.97
0.91
3.00
f1 (ppm)


148.17
146.04
137.28
135.96
129.18
128.98
128.92
128.57
128.34
128.08
127.99
127.15
127.05
125.95
122.72
120.43
113.60
97.31
81.53
78.15
77.47 CDCl3
77.15 CDCl3
76.83 CDCl3
52.28
14.91
Me
MeO
N
N
O
OH
5a
(±)
f1 (ppm)

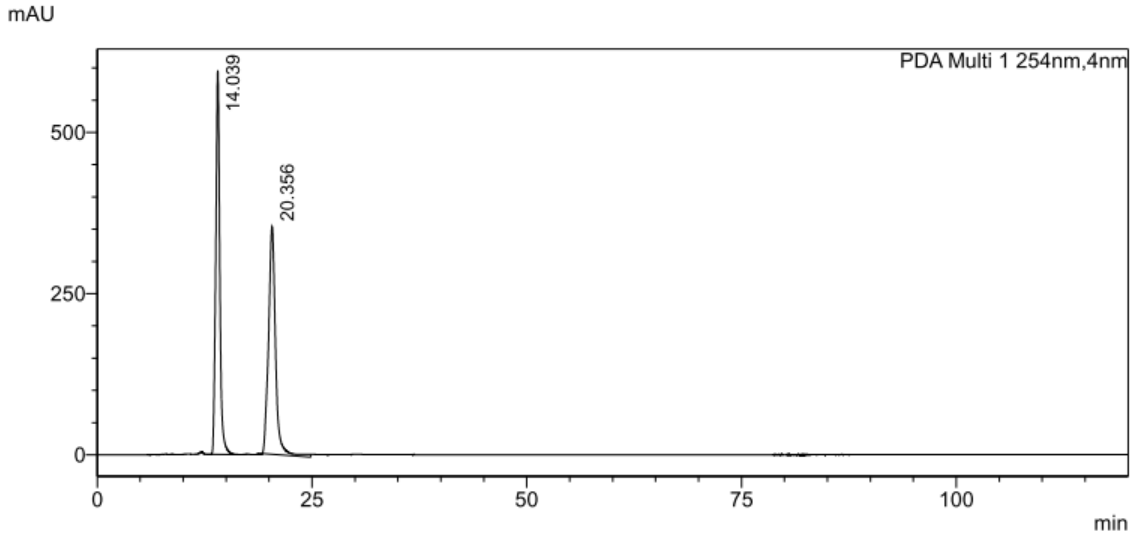

7.82
7.82
7.80
7.80
7.80
7.80
7.53
7.53
7.52
7.51
7.51
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.33
7.32
7.26
7.23
7.21
5.40
5.38
3.93
3.90
3.67
3.66
3.64
3.62
2.60
1.85
1.39
1.38
1.36
N–N
Me
EtO
O
OH
5b
(±)
1.94
2.08
9.28
1.19
1.10
1.09
0.98
2.05
0.95
3.00
3.25
f1 (ppm)


151.80
148.04
139.27
138.42
137.36
129.16
128.91
128.58
128.51
128.14
127.82
126.99
125.90
120.39
98.00
81.63
78.00
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
59.78
15.55
14.87
N–N
Me
EtO
O
OH
5b
(±)
f1 (ppm)

## NOESY Spectrum of Racemic Compound 3a



## HPLC of Racemic Compound 3a

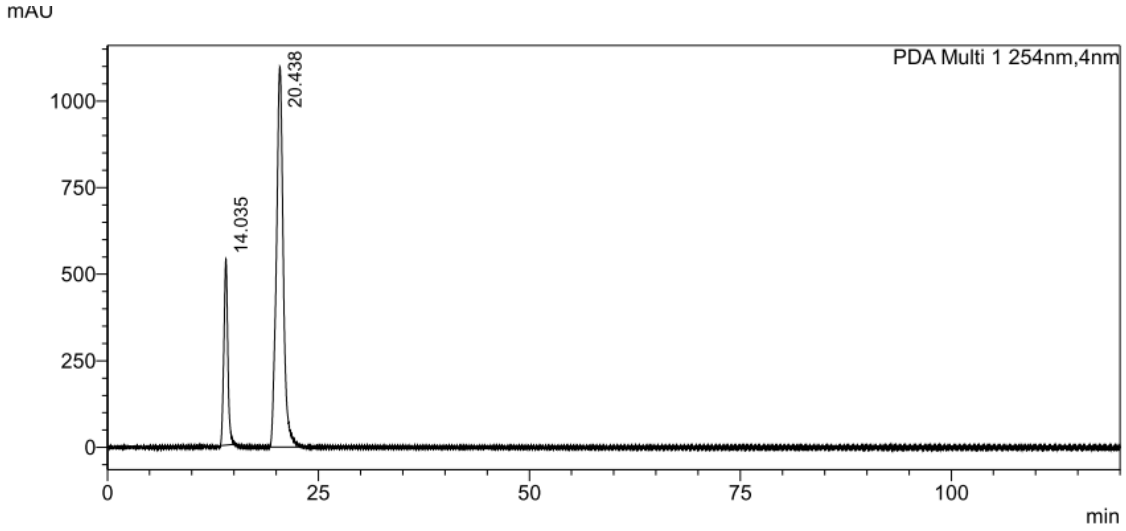



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 14.039 | 19552608 | 595245 | 49.518 | 62.766 |
| 2 | 20.356 | 19933003 | 353106 | 50.482 | 37.234 |
| Total | | 39485612 | 948350 | 100.000 | 100.000 |

## HPLC of Chiral Compound 3aa




**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Height% | Area% |
|---|---|---|---|---|---|
| 1 | 14.035 | 17272171 | 537249 | 32.853 | 21.756 |
| 2 | 20.438 | 62119112 | 1098053 | 67.147 | 78.244 |
| Total | | 79391282 | 1635302 | 100.000 | 100.000 |