Supporting Information

Manganese-Catalysed C–H Activation: A Regioselective C–H Alkenylation of Indoles and other (hetero)aromatics with 4-Hydroxy-2-Alkynoates Leading to Concomitant Lactonization

Anil Kumar, Nachimuthu Muniraj, and Kandikere Ramaiah Prabhu*

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Manganese-Catalysed C-H Activation: A Regioselective C-H Alkenylation of Indoles and other (hetero)aromatics with 4-Hydroxy-2-Alkynoates with concomitant Lactonization

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Table of contents

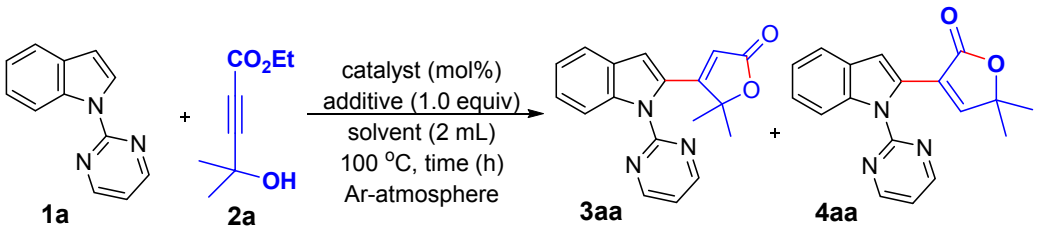
General experimental

All reactions were carried out using distilled solvents. Reactions were monitored by using precoated silica TLC plates. Mass spectra were recorded on EI, and ESI (TOF) modes. NMR spectra were recorded in at 400 MHz spectrometers in $CDCl_3$, tetramethylsilane (TMS; $\delta = 0.00$ ppm) served as an internal standard for ^1H NMR. The coupling constants were given in Hz. The corresponding residual non-deuterated solvent signal ($CDCl_3$; $\delta = 77.00$ ppm and was used as internal standard for ^{13}C NMR. Column chromatography was carried out on silica gel 230-400 mesh or 100-200 mesh (Merck) and thin-layer chromatography was carried out using SILICA GEL GF-254. Chemicals obtained from commercial suppliers were used without further purification.

All Indole derivatives[1], 4-Hydroxy-2-Alkynoates derivatives [2] were prepared according to reported literature procedure.

Detailed optimization studies:

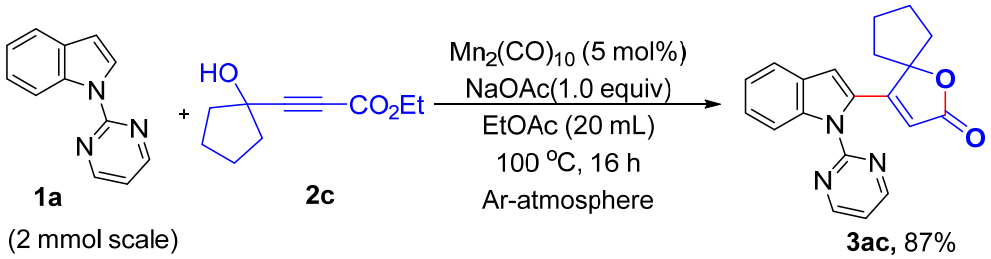
Table-S1. Survey of the reaction parameters[a]



entry	catalyst (mol %)	additive (1.0 equiv)	solvent (2 mL)	time (h)	NMR yield (%)[b]	ratio (**3aa:4aa**)
1	$Cp^*Co(CO)I_2$ (5)	NaOAc	DCE	16	nd	-
2[c]	$MnBr(CO)_5$ (10)	NaOAc/KF	DCE	16	42	80:20
3	$MnBr(CO)_5$ (10)	K_2CO_3	DCE	16	21	74:26
4	$MnBr(CO)_5$ (10)	CsOAc	DCE	16	21	67:33
5	$MnBr(CO)_5$ (10)	CsF	DCE	16	20	69:31
6	$MnBr(CO)_5$ (10)	NaOAc	H_2O	16	47	90:10
7[d]	$MnBr(CO)_5$ (10)	NaOAc	H_2O	16	57	73:27
8[e]	$MnBr(CO)_5$ (10)	NaOAc	H_2O	4	71	86:14
9	$Mn_2(CO)_{10}$ (5)	NaOAc	DME	16	nd	-
10	$Mn_2(CO)_{10}$-(5)	NaOAc	Et_2O	16	57	85:15
11[f]	$Mn_2(CO)_{10}$ (5)	NaOAc	EtOAc	16	81	89:11
12[g]	$Mn_2(CO)_{10}$ (5)	NaOAc	EtOAc	16	77	85:15
13[h]	$Mn_2(CO)_{10}$ (5)	NaOAc	EtOAc	16	79	86:14
14[i]	$Mn_2(CO)_{10}$ (5)	NaOAc	EtOAc	16	87	90:10

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), [Mn] catalyst (mol %), additive (1.0 equiv), solvent (2 mL) under argon atmosphere at 100 °C for 16 h. [b] ^{1}H NMR yield using terepthalaldehyde as an internal standard. [c] 2.0 equiv KF was used. [d,e] Reaction at 80 °C. [f] 50 mol % additive was used. [g] Under air. [h] Reaction time reduced to 12 h. [i] Reaction time increased to 24 h. nd = not detected.

Experimental procedure for scale-up reaction



1a
(2 mmol scale)

2c

3ac, 87%

In a 50-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with 1-(pyrimidin-2-yl)-1H-indole (390 mg, 2 mmol), ethyl 3-(1-hydroxycyclopentyl)propiolate (437 mg, 24 mmol), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (39 mg, 10 mol %), NaOAc (164 mg, 1.0 equiv) in ethyl acetate solvent (20 mL) were taken. The vial was sealed under argon atmosphere with a screw cap and placed in a pre-heated oil bath at 100 °C and the reaction mixture was stirred at same temperature for 16 h. After completion of the reaction the reaction mixture was cooled to room temperature and concentrated under vacuo. The crude product was purified on a silica gel (230-400 mess size) using flash column chromatography using EtOAc/petroleum ether as eluent to afford the desired product **3ac** in 87% yield.

Crystal structural data for compound 3aa

Cambridge Crystallographic Data Centre (CCDC 1577780)

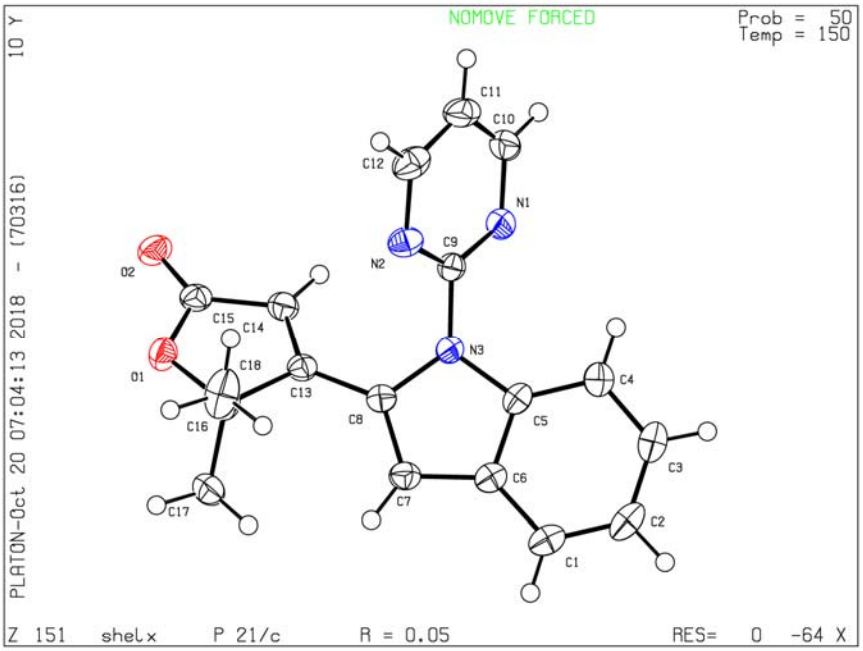
Bond precision: C-C = 0.0080 A Wavelength: 0.71073
Cell: a= 14.2573(13) b= 19.037 (2) c= 25.037(2)
alpha= 90 beta= 90 gamma= 90
Temperature: 293K

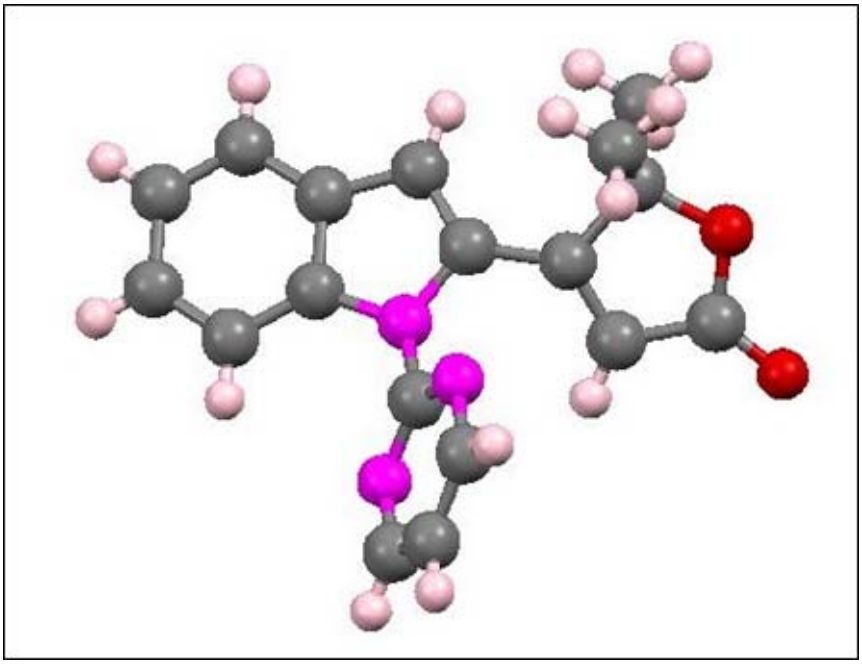
	Calculated	Reported
Volume	1533.09 (11)	1533.09 (11)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H15 N3 O2	?
Sum formula	C18 H15 N3 O2	C18 H15 N3 O2
Mr	305.33	305.33
Dx, g cm-3	1.323	1.323
Z	4	4
Mu (mm-1)	0.089	0.089
F000	640.0	640.0
F000’	640.27	
h, k, 1max	12, 16, 15	12, 16, 15
Nref	3509	3509
Time, Tmax		0.973, 1.000

Data completeness= 0.999 Theta (max)= 27.482
R (reflections) = 0.0473 (2662) wR2 (reflections) = 0.1171 (3505)
S = 1.042 Npar= 208

ORTEP diagram for compound 3aa (50% ellipsoid probability)

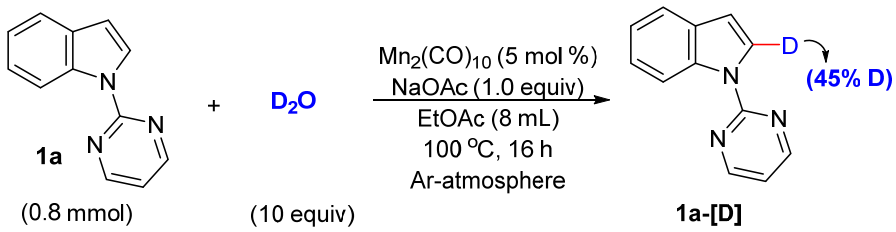
Cambridge Crystallographic Data Centre (CCDC 1577780).



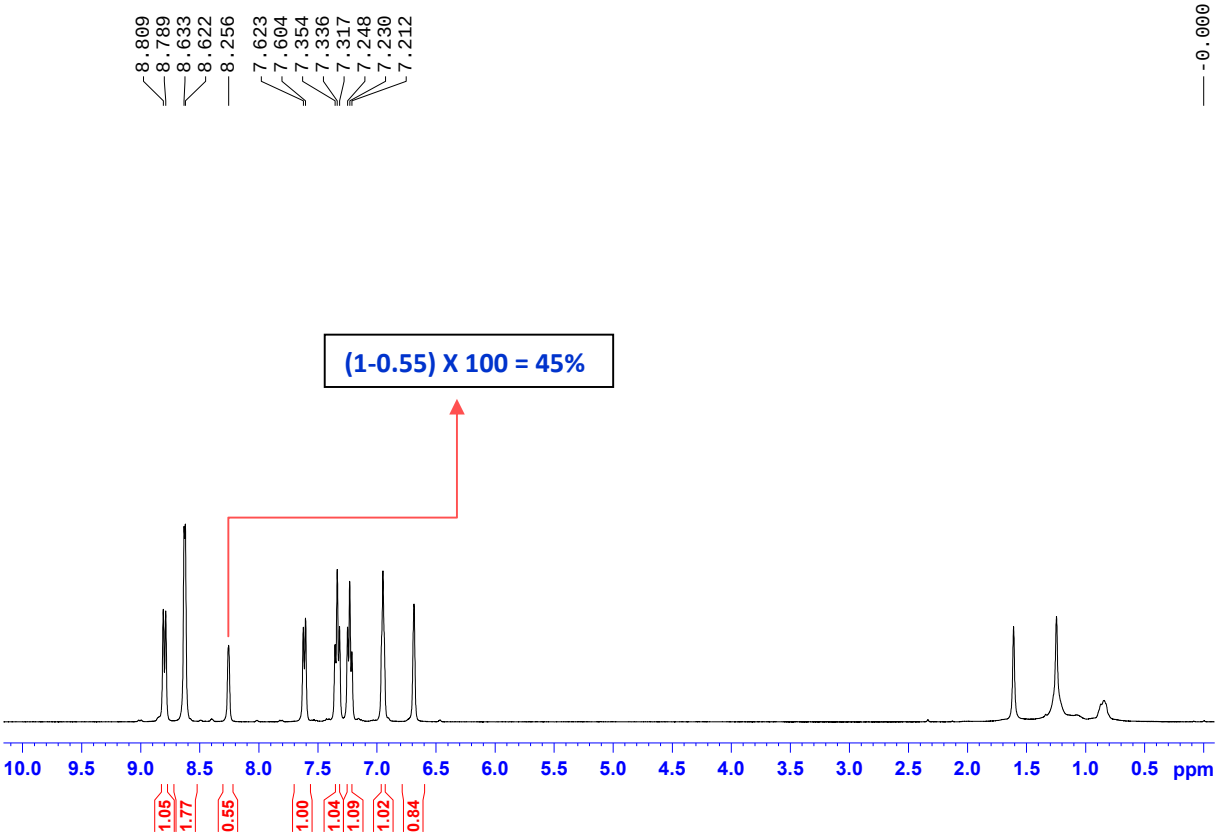


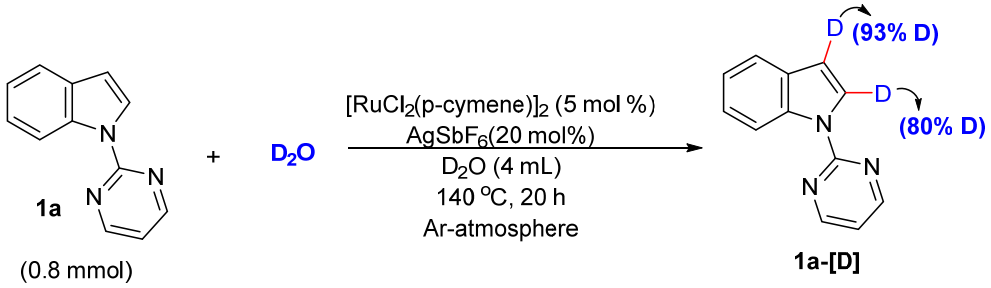
Mechanistic studies

i) H/D-Exchange experiment

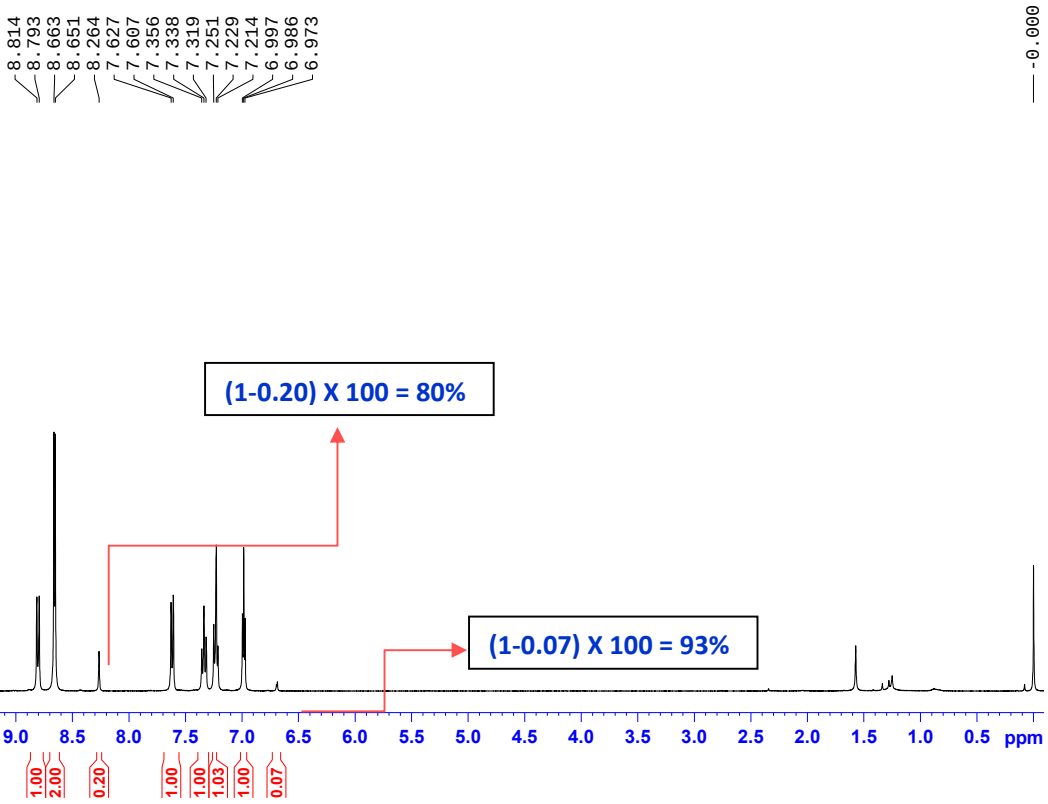


A 25-mL screw cap reaction vial, equipped with a magnetic stir bar was charged with 1-(pyrimidin-2-yl)-1H-indole **1a** (156 mg, 0.8 mmol), D_2O (10 equiv), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (15.6 mg, 10 mol %), and NaOAc (67.6 mg, 1.0 equiv), followed by addition of ethyl acetate (solvent, 8 mL). This vial was sealed under argon atmosphere with a screw cap, placed in an oil bath, and stirred for 16 h at 100 °C and filtered through anhydrous Na_2SO_4. Finally, the crude product was purified by flash column chromatography on silica gel (EtOAc/petroleum ether, 1:32) to yield 45% **1a-[D]** as a white solid (151 mg, 97%). Deuterium incorporation was estimated by ^{1}H-NMR analysis (see the following ^{1}H NMR spectra).

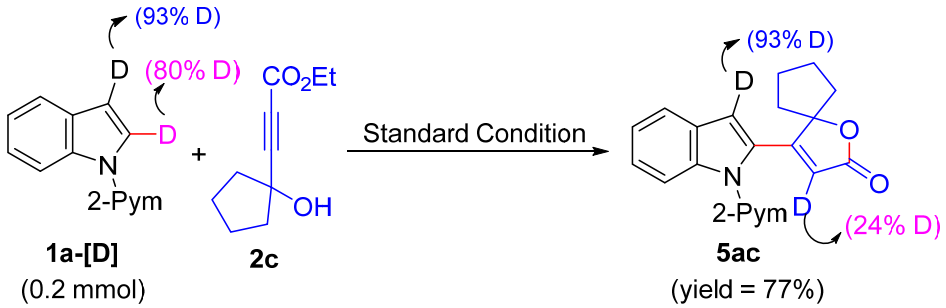




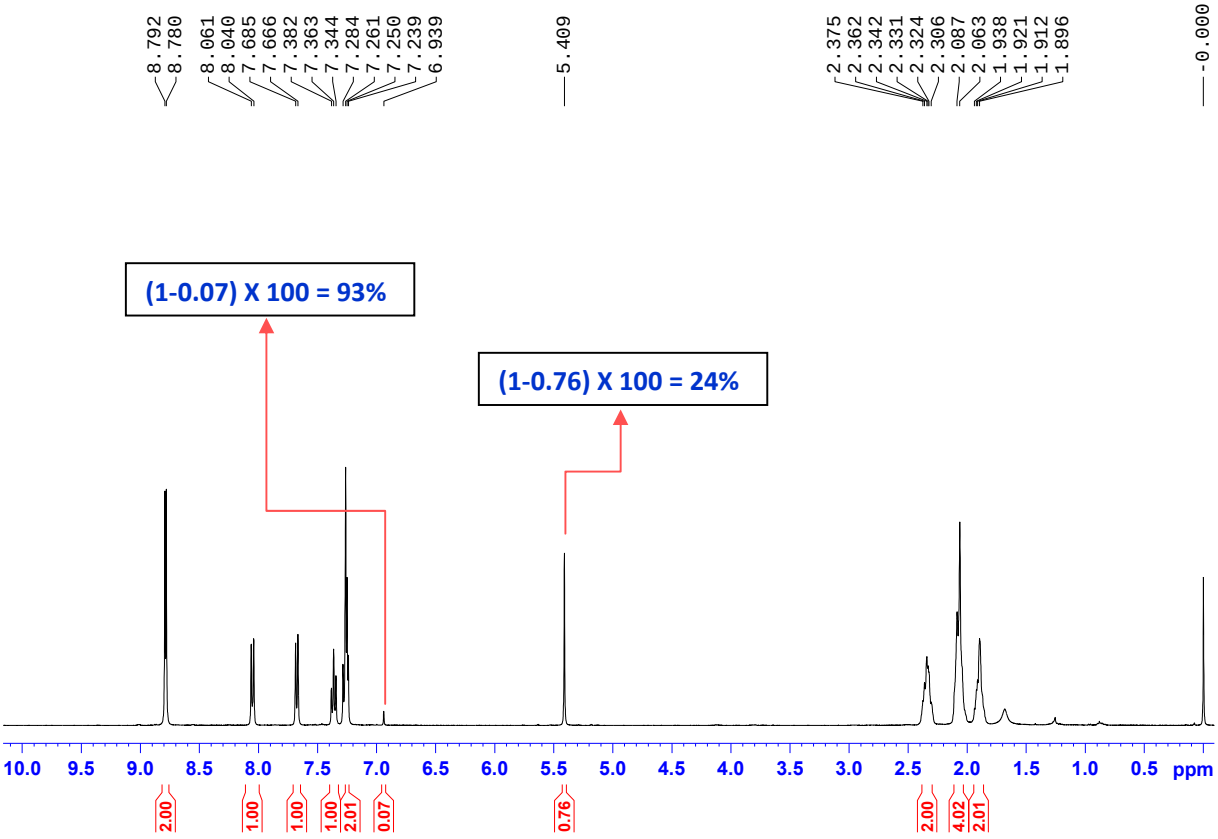
A 8-mL screw cap reaction vial, equipped with a magnetic stir bar was charged with 1-(pyrimidin-2-yl)-1H-indole **1a** (156 mg, 0.8 mmol), $[RuCl_2(p\text{-cymene})]_2$ (24.8 mg, 5 mol%), and $AgSbF_6$ (56.0 mg, 20 mol%). The reaction vessel was subjected to evacuation/backfilling under vacuum and refilled with argon followed by D_2O (4 mL) with vigorous stirring at room temperature. Afterwards, the reaction mixture was placed on a pre-heated metal block at 140 °C for 20 h and the reaction mixture was cooled down to the room temperature, diluted with EtOAc (100 mL), filtered through anhydrous Na_2SO_4. Finally, the crude product was purified by flash column chromatography on silica gel (EtOAc/petroleum ether, 1:32) to yield 80% **1a-[D]** as a white solid (149 mg, 96%). Deuterium incorporation was estimated by ^{1}H-NMR analysis (see the following ^{1}H NMR spectra).



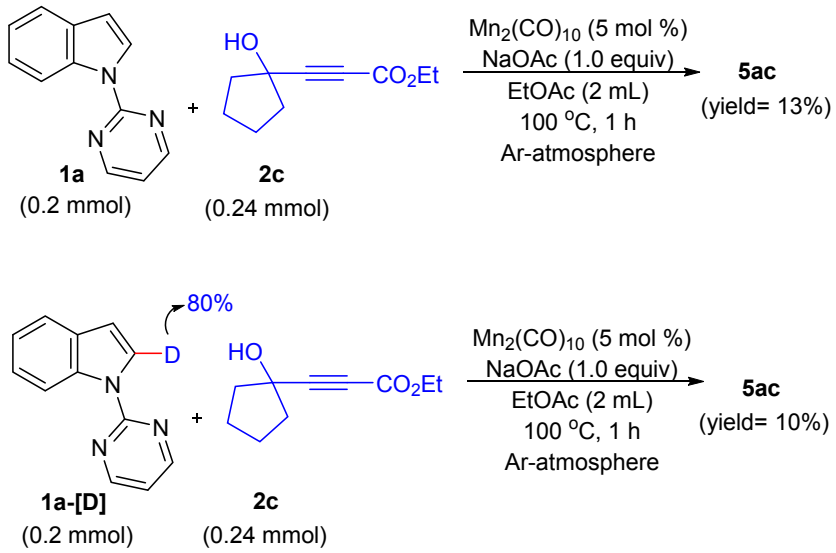
ii) Deuterium labeling experiment



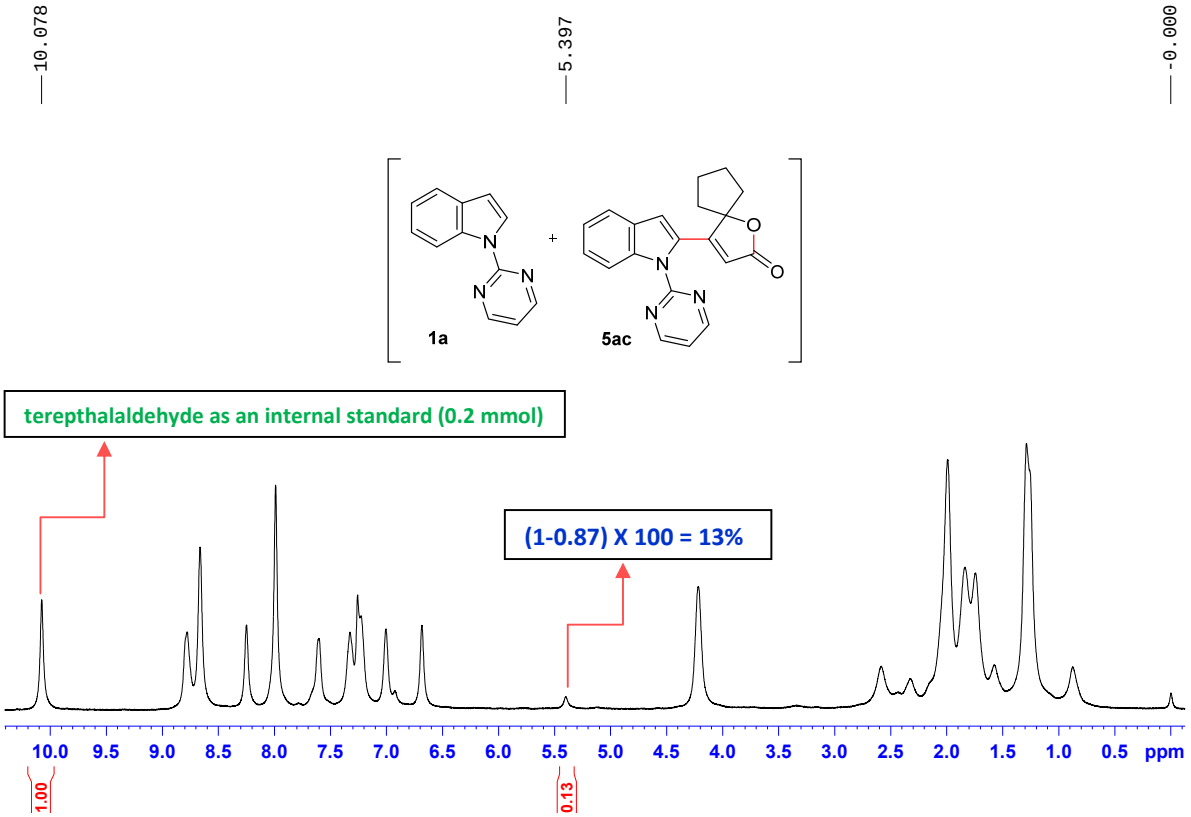
A 8-mL screw cap reaction vial, equipped with a magnetic stir bar was charged with **1a-[D]** (39.3 mg, 0.2 mmol), **2c** (43.7 mg, 0.24 mmol), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (3.9 mg, 10 mol %), abd NaOAc (16.4 mg, 1.0 equiv), and was added ethyl acetate (solvent, 2 mL). This vial was sealed under argon atmosphere with a screw cap, placed on a pre-heated metal block at 100 °C for 16 h. After completion of the reaction the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude product was purified on a silica gel (230-400 mess size) flash column chromatography using EtOAc/ petroleum ether mixture to obtain **5ac**. Deuterium incorporation was estimated by ^{1} H-NMR analysis (see the following ^{1}H NMR spectra).

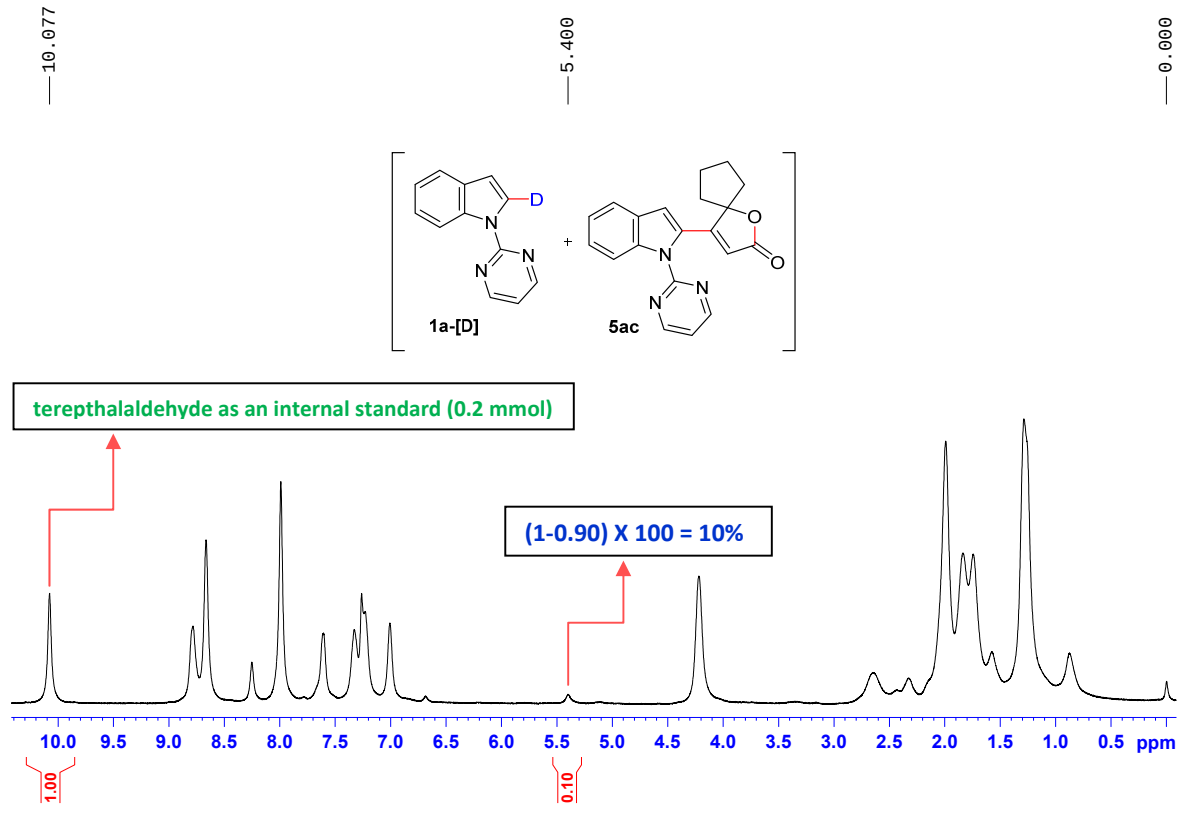


iii) KIE Experiment

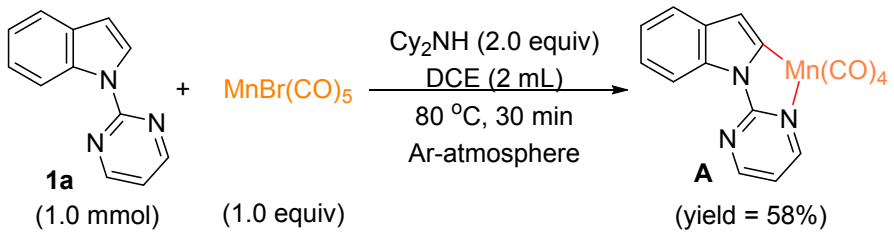


Two 8-mL screw cap reaction vials, one containing **1a** (39.0 mg, 0.2 mmol) and another one containing **1a-[D]** (39.25 mg, 0.2 mmol) were added with ethyl 3-(1-hydroxycyclopentyl)propiolate **2c** (43.7 mg, 0.24 mmol), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (3.9 mg, 10 mol %), NaOAc (16.4 mg,1.0 equiv), ethyl acetate (2 mL), respectively. Then these vials were sealed under argon atmosphere with screw caps, placed side-by-side on a pre-heated metal block at 100 °C for 1 h. After cooling to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (2:3, 250 mL), and concentrated under vacuum. The crude products were submitted directly for ^{1}H NMR analysis for calculating the NMR yields; terepthalaldehyde (0.2 mmol, 26.8 mg) has been used as an internal standard. Yield of **5ac** are 13% for **1a** and 10% for **1a-[D]** was observed (K_H/K_D = 1.3).

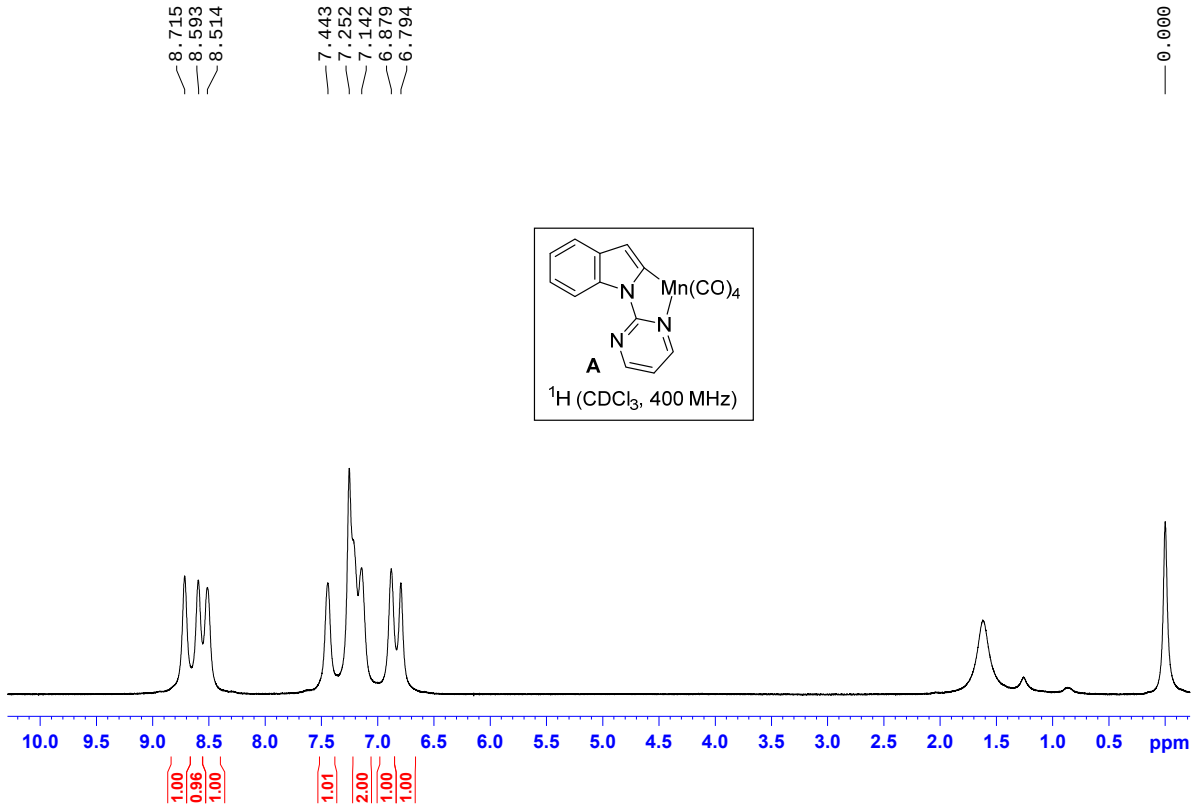

10.078
5.397
-0.000
1a
5ac
terepthalaldehyde as an internal standard (0.2 mmol)
(1-0.87) X 100 = 13%
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.13


10.077
5.400
0.000
1a-[D]
5ac
terepthalaldehyde as an internal standard (0.2 mmol)
(1-0.90) X 100 = 10%
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 ppm
1.00
0.10

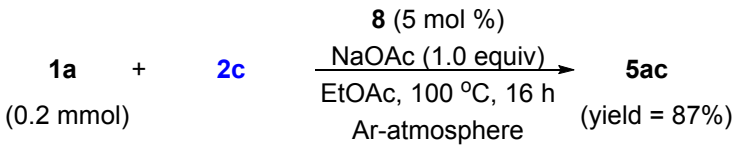
iv) Synthesis of metallacyclic complex



A 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with 1-(pyrimidin-2-yl)-1H-indole **1a** (1.0 mmol, 195 mg), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (100 mol %), Cy_2NH (2.0 equiv) and DCE (2 mL, solvent). The vial was sealed under argon atmosphere with a screw cap and placed in a pre-heated metal block at 80 °C stirred for 30 min. After completion of the reaction, the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude product was purified on a silica gel (230-400 mess size) flash column chromatography using EtOAc/ petroleum ether mixture to afford manganese complex **A**. NMR data is in accordance with the previous literature.[3]

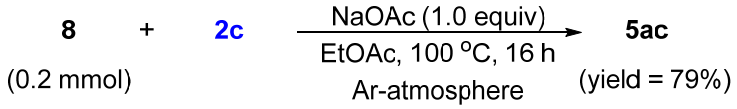


v) Complex A as a catalyst



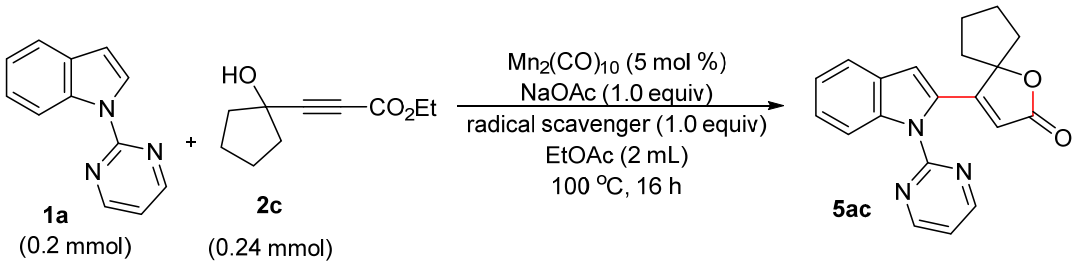
A 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with 1-(pyrimidin-2-yl)-1H-indole **1a** (0.2 mmol, 39 mg), ethyl 3-(1-hydroxycyclopentyl)propiolate **2c** (43.7 mg, 0.24 mmol), manganese complex **A** (10 mol %, 7.3 mg), NaOAc (1.0 equiv) and ethyl acetate (2 mL, solvent). The vial was sealed under argon atmosphere with a screw cap, and placed in a pre-heated metal block at 100 °C stirred for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude product was purified on a silica gel (230-400 mess size) flash column chromatography using EtOAc/ petroleum ether mixture to afford **5ac**.

vi) Stoichiometric reaction with complex A



A 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with manganese complex **A** (0.2 mmol, 72.3 mg), ethyl 3-(1-hydroxycyclopentyl)propiolate **2c** (43.7 mg, 0.24 mmol), NaOAc (1.0 equiv) and ethyl acetate (2 mL, Solvent). The vial was sealed under argon atmosphere with a screw cap and placed in a pre-heated metal block at 100 °C stirred for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude product was purified on a silica gel (230-400 mess size) flash column chromatography using EtOAc/ petroleum ether mixture to afford **5ac**.

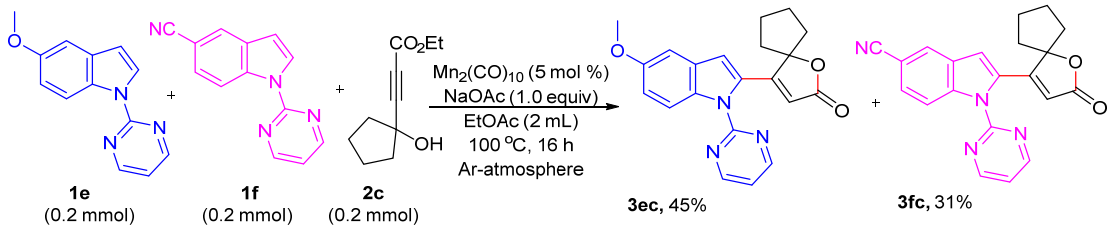
vii) Radical scavenger experiments



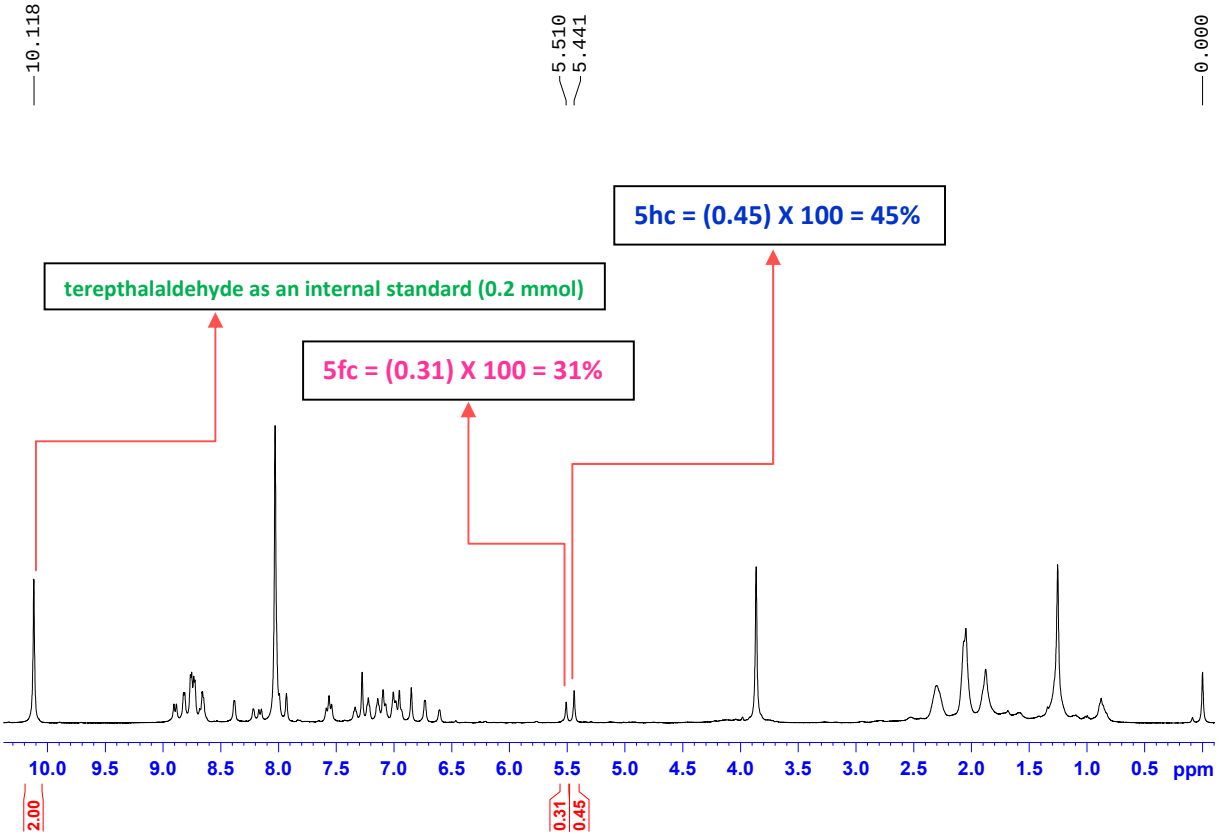
At standard conditions = 86 %
At air atmosphere = 77%
with TEMPO (1.0 equiv) = 70 %
with BHT (1.0 equiv) = 71 %

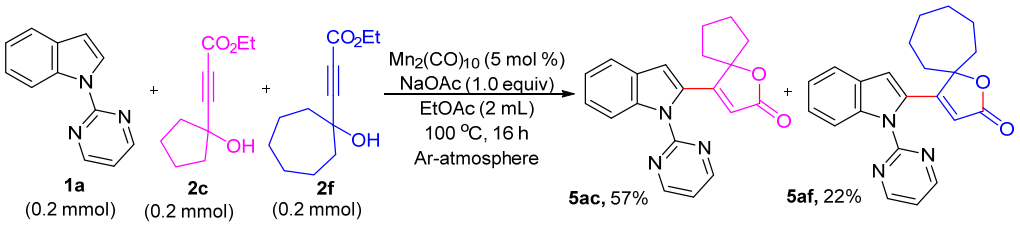
A 8-mL screw cap reaction vial, equipped with a magnetic stir bar was charged with **1a** (39 mg, 0.2 mmol), **2c** (43.7 mg, 0.24 mmol), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (3.9 mg, 10 mol %), NaOAc (16.4 mg,1.0 equiv),and radical scavenger (1.0 equiv), and ethyl acetate (2 mL, Solvent). This vial was sealed under argon or air atmosphere with a screw cap, placed on a pre-heated metal block at 100 °C for 16 h. After being cooled to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (2:3, 250 mL), and concentrated under vacuum. The crude products were submitted directly for ^{1}H NMR analysis for calculating the NMR yields; terepthalaldehyde (0.2 mmol, 26.8 mg) has been used as an internal standard.

viii) Competitive experiments

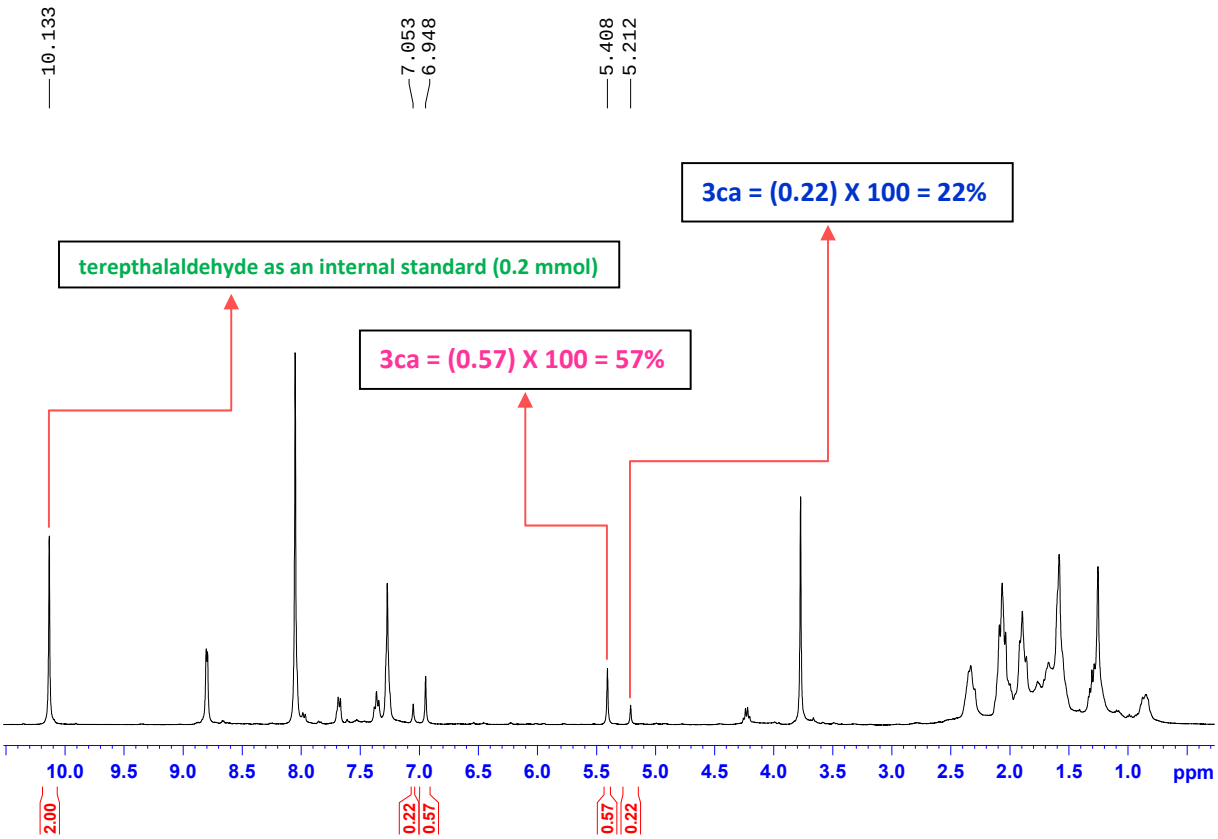


A 8-mL screw cap reaction vial, equipped with a magnetic stir bar was charged with 5-methoxy-1-(pyrimidin-2-yl)-1H-indole **1e** (44.1 mg, 0.2 mmol), 1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile **1f** (45.1 mg, 0.2 mmol), ethyl 3-(1-hydroxycyclopentyl)propiolate **2c** (43.7 mg, 0.24 mmol), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (3.9 mg, 10 mol %), NaOAc (16.4 mg,1.0 equiv), and ethyl acetate (2 mL, solvent)). This vial was sealed under argon atmosphere with a screw cap, placed on a pre-heated metal block at 100 °C for 16 h. After being cooled to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (2:3, 250 mL), and concentrated under vacuum. The crude products were submitted directly for ^{1}H NMR analysis for calculating the NMR yields (terepthalaldehyde (0.2 mmol, 26.8 mg) has been used as an internal standard; see the following ^{1}H NMR spectra. Aromatic protons were not assigned to individual products due to the intrinsic complexity of the spectrum.

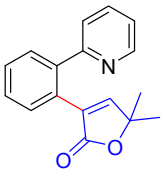




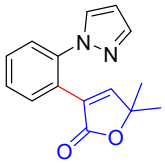
A 8-mL screw cap reaction vial, equipped with a magnetic stir bar was charged with **1a** (39 mg, 0.2 mmol), **2c** (43.7 mg, 0.24 mmol), **2f** (50.5 mg, 0.24 mmol), manganese decacarbonyl catalyst $Mn_2(CO)_{10}$ (3.9 mg, 10 mol %), NaOAc (16.4 mg, 1.0 equiv), and ethyl acetate (2 mL, solvent)). This vial was sealed under argon atmosphere with a screw cap, placed on a pre-heated metal block at 100 °C for 16 h. After being cooled to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (2:3, 250 mL), and concentrated under vacuum. The crude products were submitted directly for ^{1}H NMR analysis for calculating the NMR yields, terepthalaldehyde (0.2 mmol, 26.8 mg) has been used as an internal standard, see the following ^{1}H-NMR spectra. Aromatic protons were not assigned to individual products due to the intrinsic complexity of the spectrum.



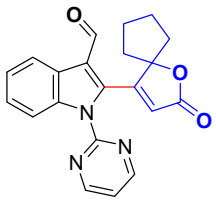
Unsuccessful substrates



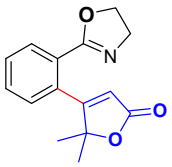
7%



21%



mixture of cyclize/uncycliz products



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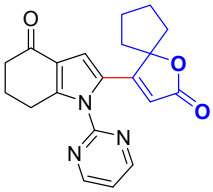

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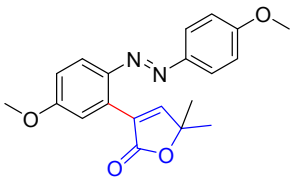
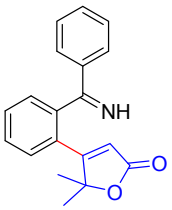


nd



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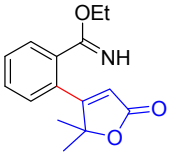

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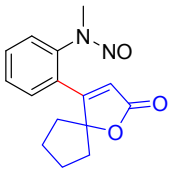
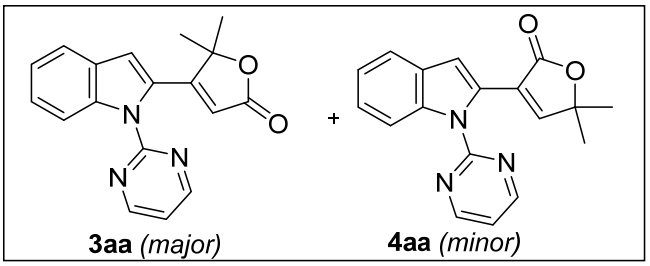


nd

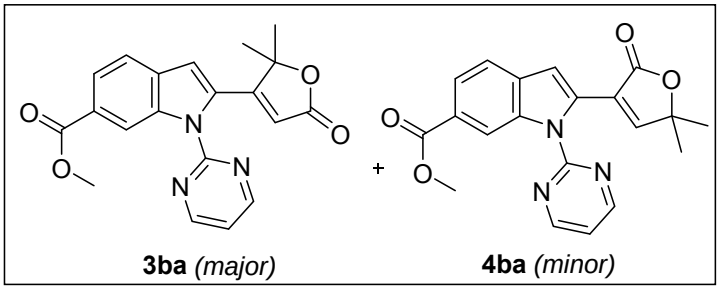
Characterization data for products

1. **Inseprable mixture (**Combined yield - 51.0 mg, 83%; **3aa:4aa** = 91:9); **Data for major isomer; 5,5-Dimethyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (3aa).** White solid; R_f (30% EtOAc/petroleum ether) 0.25;

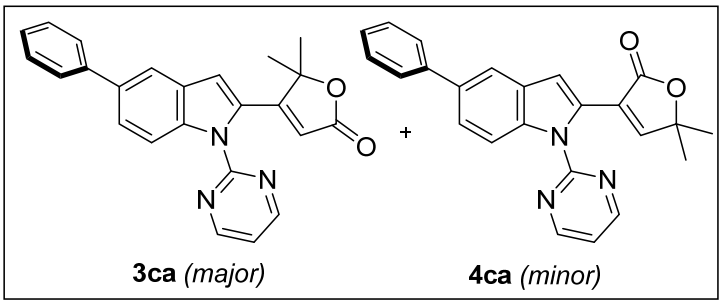


Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2924, 2853, 1744, 1610, 1565, 1421; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.79 (s, 6 H) 5.27 (s, 1 H) 7.03 (s, 1 H) 7.21 - 7.28 (m, 1 H) 7.36 (t, *J* = 7.52 Hz, 1 H) 7.68 (d, *J* = 7.93 Hz, 1 H) 7.99 (d, *J* = 8.55 Hz, 1 H) 8.79 (d, *J* = 4.58 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.5, 87.8,111.2, 112.8, 116.2, 118.8, 121.7, 122.8, 126.0, 128.3, 129.6, 139.2, 157.6, 158.7, 163.8, 171.3; **HRESI-MS** *(mz)*: Calculated for $C_{18}H_{15}N_3O_2$ (M + Na): 328.1062, found (M + Na): 320.1063.

2. **Inseprable mixture (**Combined yield - 56.0 mg, 77%; **3ba:4ba** = 94:6); **Data for major isomer; Methyl 2-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-1-(pyrimidin-2-yl)-1H-indole-6-carboxylate (3ba).** Brown solid; R_f (30% EtOAc/petroleum ether) 0.2; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2924, 2854, 1749, 1716, 1617, 1567, 1460, 1423; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78 (s, 6 H) 3.94 (s, 3 H) 5.36 (s, 1 H) 7.03 (s, 1 H) 7.34 (t, *J* = 4.88 Hz, 1 H) 7.72 (d, *J* = 8.24 Hz, 1 H) 7.96 (dd, *J* = 8.24, 1.22 Hz, 1 H) 8.67 (s, 1 H) 8.85 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.3, 52.2, 87.9, 110.2, 115.0, 117.5, 119.2, 121.3, 123.6, 127.3, 131.7, 132.3, 138.3, 157.1, 158.9, 163.4, 167.4, 170.9; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{17}N_3O_4$ (M + H): 364.1297, found (M + H): 364.1301.

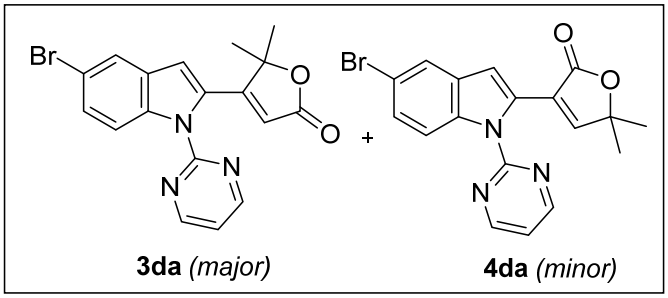


3. **Inseprable mixture (**Combined yield - 62.8 mg, 82%; **3ca:4ca** = 88:12); **Data for major isomer; 5,5-Dimethyl-4-(5-phenyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (3ca).** Yellow solid; R_f (30% EtOAc/petroleum ether) 0.3;



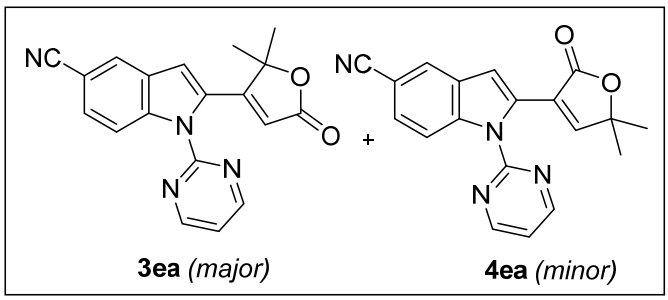
Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2924, 2852, 1745, 1618, 1567, 1451, 1421; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.80 (s, 6 H) 5.32 (s, 1 H) 7.07 (s, 1 H) 7.27 (t, *J* = 4.88 Hz, 1 H) 7.33 - 7.37 (m, 1 H) 7.44 - 7.48 (m, 2 H) 7.60 - 7.66 (m, 3 H) 7.88 (d, *J* = 1.22 Hz, 1 H) 8.07 (d, *J* = 8.85 Hz, 1 H) 8.81 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.4, 87.9, 111.4, 113.2, 116.4, 118.8, 120.0, 125.7, 127.0, 127.3, 128.8, 130.2, 136.3, 138.6, 141.3, 157.6, 158.7, 158.7, 163.8, 171.3; **HRESI-MS** *(mz)*: Calculated for $C_{24}H_{19}N_3O_2$ (M + H): 382.1556, found (M + H): 382.1558.

4. **Inseprable mixture (**Combined yield – 60.7 mg, 79%; **3da:4da** = 94:6); **Data for major isomer; 4-(5-Bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-5,5-dimethylfuran-2(5H)-one (3da).** Brown solid; R_f (30% EtOAc/petroleum ether) 0.3;



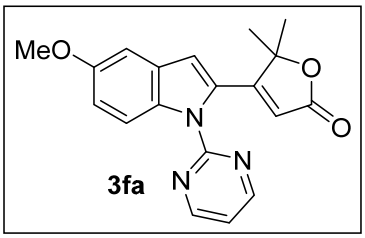
Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2924, 2854, 1745, 1619, 1567, 1420; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.77 (s, 6 H) 5.34 (s, 1 H) 6.93 (s, 1 H) 7.30 (t, *J* = 4.73 Hz, 1 H) 7.44 (dd, *J* = 9.00, 1.68 Hz, 1 H) 7.81 (d, *J* = 1.53 Hz, 1 H) 7.92 (d, *J* = 8.85 Hz, 1 H) 8.81 (d, *J* = 4.58 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.3, 87.9, 109.9, 114.5, 115.9, 117.1, 119.0, 124.1, 128.6, 129.9, 130.6, 137.6, 157.2, 158.7, 163.5, 171.0; **HRESI-MS** *(mz)*: Calculated for $C_{18}H_{14}N_3O_2Br$ (M + H): 384.0348, found (M + H): 384.0345.

5. **Inseprable mixture (**Combined yield - 57.5 mg, 87%; **3ea:4ea** = 90:10); **Data for major isomer; 2-(2,2-Dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (3ea).** Brown solid; R_f (50% EtOAc/petroleum ether) 0.4;

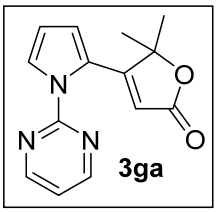


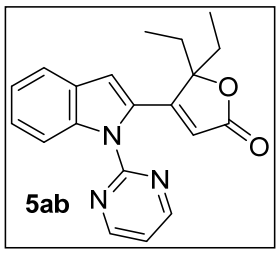
Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2925, 2854, 2223, 1747, 1614, 1568, 1460, 1419; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78 (s, 6 H) 5.36 (s, 1 H) 7.06 (s, 1 H) 7.38 (t, *J* = 4.88 Hz, 1 H) 7.59 (d, *J* = 8.54 Hz, 1 H) 8.05 (s, 1 H) 8.09 (d, *J* = 8.85 Hz, 1 H) 8.85 (d, *J* = 4.58 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.2, 87.9, 106.1, 110.0, 114.0, 117.9, 119.6, 126.8, 128.1, 128.3, 131.7, 140.2, 156.7, 158.1, 158.9, 163.0, 170.7; **HRESI-MS** *(mz)*: Calculated for $C_{18}H_{15}N_3O_2$ (M + H): 331.1195, found (M + H): 331.1194.

6. **4-(5-Methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-5,5-dimethylfuran-2(5H)-one (3fa).** Brown solid; Yield - (51.6 mg, 77%); ***mp***: 129-131 °C; R_f (30% EtOAc/petroleum ether) 0.2; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2925, 2853, 1745, 165, 1566, 1423; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78 (s, 6 H) 3.87 (s, 3 H) 5.30 (s, 1 H) 6.95 (s, 1 H) 7.01 (dd, *J* = 9.16, 2.44 Hz, 1 H) 7.11 (d, *J* = 2.44 Hz, 1 H) 7.24 (t, *J* = 4.88 Hz, 1 H) 7.94 (d, *J* = 9.16 Hz, 1 H) 8.78 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.4, 55.7, 87.8, 102.9, 111.0, 113.9, 116.0, 116.1, 118.5, 128.9, 130.0, 134.3, 156.0, 157.6, 158.6, 163.9, 171.4; **HRESI-MS** *(mz)*: Calculated for $C_{19}H_{17}N_3O_3$ (M + H): 336.1348, found (M + H): 336.1350.

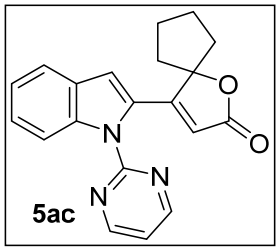


7. **5,5-Dimethyl-4-(1-(pyrimidin-2-yl)-1H-pyrrol-2-yl)furan-2(5H)-one (3ga).** Yellow solid; Yield - (31.7 mg, 62%); ***mp***: 127-129 °C; R_f (30% EtOAc/petroleum ether) 0.2; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2984, 2930, 1741, 1611, 1569, 1433, 1409; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.72 (s, 6 H) 5.27 (s, 1 H) 6.43 (t, *J* = 3.05 Hz, 1 H) 6.66 - 6.67 (m, 1 H) 7.24 (t, *J* = 4.82 Hz, 1 H) 7.63 (s, 1 H) 8.71 (d, *J* = 4.58 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.5, 87.7, 111.2, 114.2, 117.2, 119.1, 123.6, 128.1, 157.2, 158.7, 163.3, 171.9; **HRESI-MS** *(mz)*: Calculated for $C_{14}H_{13}N_3O_2$ (M + H): 256.1086, found (M + H): 256.1086.

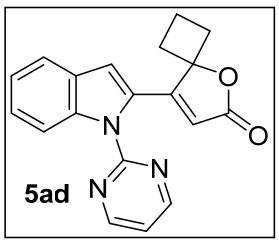


8. **5,5-Diethyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5ab).** 

Light yellow solid; Yield - (40.0 mg, 59%); ***mp***: 178-180 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2927, 2933, 1740, 1612, 1565, 1421; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.32 Hz, 6 H) 2.19 (dquin, *J* = 15.22, 7.41, 7.41, 7.41, 7.41 Hz, 4 H) 5.16 (s, 1 H) 7.06 (s, 1 H) 7.23 - 7.28 (m, 1 H) 7.31 - 7.38 (m, 2 H) 7.69 (d, *J* = 7.93 Hz, 1 H) 7.83 (d, *J* = 8.24 Hz, 1 H) 8.84 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 7.3, 31.2, 93.2, 111.5, 112.3, 117.5, 119.2, 121.9, 122.7, 126.3, 128.2, 129.8, 139.8, 157.8, 158.8, 158.9, 171.9; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{19}N_3O_2$ (M + H): 334.1556, found (M + H): 334.1558.

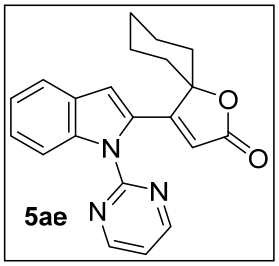
9. **4-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (5ac).** 

Light yellow solid; Yield - (55.0 mg, 83%); ***mp***: 186-188 °C; R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2958, 2854, 1743, 1610, 1568, 1423; **^{1}H NMR** (400 MHz, $CDCl_3$) 1.89 (br. s., 2 H) 2.06 - 2.08 (m, 4 H) 2.34 - 2.36 (m, 2 H) 5.41 (s, 1 H) 6.94 (s, 1 H) 7.24 - 7.28 (m, 2 H) 7.316 (t, *J* = 7.48 Hz, 1 H) 7.67 (d, *J* = 7.63 Hz, 1 H) 8.05 (d, *J* = 8.24 Hz, 1 H) 8.79 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.1, 38.2, 97.9, 110.9, 113.0, 117.4, 118.6, 121.6, 122.8, 125.8, 128.3, 129.6, 138.9, 157.6, 158.6, 161.7, 171.5; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{17}N_3O_2$ (M + H): 332.1399, found (M + H): 332.1399.

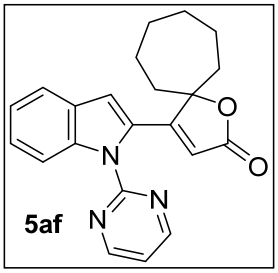
10. **8-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)-5-oxaspiro[3.4]oct-7-en-6-one (5ad).** 

Light yellow solid; Yield - (62.5 mg, 98%); ***mp***: 164-166 °C; R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (c). **IR** (KBr, cm^{-1}): 2966, 2927, 1742, 1679, 1612, 1565, 1420; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.82 - 1.93 (m, 1 H) 2.05 - 2.16 (m, 1 H) 2.69 - 2.83 (m, 4 H) 5.44 (s, 1 H) 7.11 (s, 1 H) 7.21 (t, *J* = 4.73 Hz, 1 H) 7.29 (t, *J* = 7.48 Hz, 1 H) 7.39 (t, *J* = 7.63 Hz, 1 H) 7.71 (d, *J* = 7.93 Hz, 1 H) 8.20 (d, *J* = 8.55 Hz, 1 H) 8.74 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.8, 32.6, 89.8, 110.3, 113.5, 116.9, 118.3, 121.6, 122.8, 125.6, 128.6, 129.4, 138.5, 157.4, 158.5, 161.7, 171.3; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{19}N_3O_2$ (M + H): 334.1556, found (M + H): 334.1556.

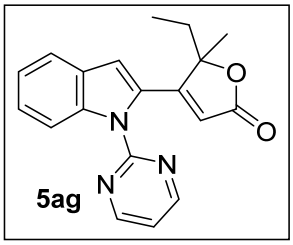
11. **4-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.5]dec-3-en-2-one (5ae).** Yellow solid; Yield - (45.2 mg, 67%); ***mp***: 197-199 °C; R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2935, 2859, 1744, 1566, 1445, 1422; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.75 - 1.92 (m, 8 H) 2.02 - 2.09 (m, 2 H) 5.37 (s, 1 H) 7.01 (s, 1 H) 7.24 (t, *J* = 4.88 Hz, 1 H) 7.26 - 7.28 (m, 1 H) 7.34 - 7.38 (m, 1 H) 7.68 (d, *J* = 7.63 Hz, 1 H) 8.04 (d, *J* = 8.24 Hz, 1 H) 8.78 (d, *J* = 4.58 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.3, 24.7, 35.0, 90.0, 111.0, 112.9, 117.2, 118.5, 121.6, 122.7, 125.7, 128.4, 129.8, 138.8, 157.6, 158.6, 164.7, 171.6; **HRESI-MS** *(mz)*: Calculated for $C_{21}H_{19}N_3O_2$ (M + H): 246.1556, found (M + H): 246.1554.

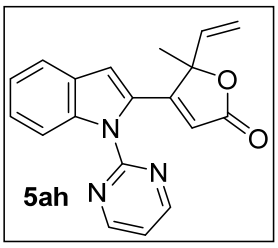


12. **4-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.6]undec-3-en-2-one (5af).** Yellow solid; Yield - (52.4 mg, 73%); ***mp***: 151-153 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (c). **IR** (KBr, cm^{-1}): 2927, 2856, 1744, 1615, 1566, 1423; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.60 - 1.66 (m, 2 H) 1.69 - 1.83 (m, 4 H) 1.90 - 1.98 (m, 2 H) 2.10 (dd, *J* = 14.65, 7.32 Hz, 2 H) 2.32 (ddd, *J* = 14.72, 10.60, 1.83 Hz, 2 H) 5.22 (s, 1 H) 7.04 (s, 1 H) 7.24 - 7.28 (m, 1 H) 7.34 - 7.38 (m, 1 H) 7.69 (d, *J* = 7.93 Hz, 1 H) 7.98 (d, *J* = 8.24 Hz, 1 H) 8.79 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 23.5, 28.4, 38.4, 92.9, 111.1, 112.7, 115.8, 118.7, 121.7, 122.7, 125.8, 128.3, 129.9, 139.0, 157.6, 158.6, 165.3, 171.8; **HRESI-MS** *(mz)*: Calculated for $C_{22}H_{21}N_3O_2$ (M + H): 360.1712, found (M + H): 360.1712.

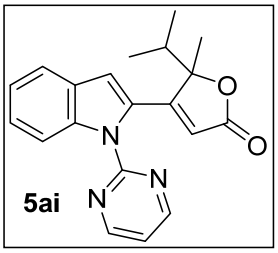


13. **5-Ethyl-5-methyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5ag).** Brown solid; Yield - (34 mg, 53%); ***mp***: 130-132 °C; R_f (30% EtOAc/petroleum ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3015, 2976, 2935, 2880,1743, 1614, 1567, 1416, 1212; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.33 Hz, 2 H) 1.79 (s, 3 H) 2.17 (q, *J* = 7.07 Hz, 3 H) 5.22 (s, 1 H) 7.04 (s, 1 H) 7.24 - 7.29 (m, 1 H) 7.36 (t, *J* = 7.58 Hz, 1 H) 7.69 (d, *J* = 7.83 Hz, 1 H) 7.91 (d, *J* = 8.34 Hz, 1 H) 8.81 - 8.83 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 7.6, 25.6, 31.8, 90.4, 111.4, 112.5, 116.8, 119.0, 121.9, 122.8, 126.2, 128.3, 129.7, 139.5, 157.7, 158.8, 161.5, 171.7; **HRESI-MS** *(mz)*: Calculated for $C_{19}H_{17}N_3O_2$ (M + H): 320.1399, found (M + H): 320.1399.

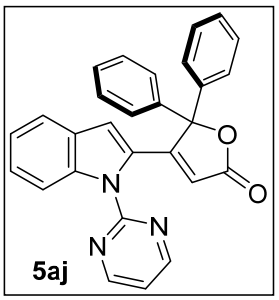


14. **5-Methyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)-5-vinylfuran-2(5H)-one (5ah).** 

Brown solid; Yield - (45 mg, 71%); ***mp***: 106-108 °C; R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2924, 2854, 1749, 1615, 1565, 1421, 1237; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.88 (s, 3 H) 5.28 (s, 1 H) 5.44 (d, *J* = 10.38 Hz, 1 H) 5.61 (d, *J* = 17.39 Hz, 1 H) 6.07 (dd, *J* = 17.40, 10.68 Hz, 1 H) 7.10 (s, 1 H) 7.23 - 7.26 (m, 1 H) 7.27 - 7.29 (m, 1 H) 7.36 (ddd, *J* = 8.39, 7.17, 1.22 Hz, 1 H) 7.66 (d, *J* = 7.93 Hz, 1 H) 7.95 - 7.97 (m, 1 H) 8.81 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 23.2, 88.4, 112.3, 112.7, 115.7, 118.8, 121.9, 122.8, 126.1, 128.2, 129.5, 137.2, 139.4, 157.6, 158.7, 161.7, 171.5; **HRESI-MS** *(mz)*: Calculated for $C_{19}H_{15}N_3O_2$ (M + H): 318.1243, found (M + H): 318.1242.

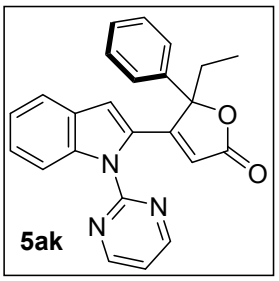
15. **5-Isopropyl-5-methyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5ai).** 

Light brown solid; Yield - (38.0 mg, 57%); ***mp***: 185-187 °C; R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (c). **IR** (KBr, cm^{-1}): 3001, 2952, 1750, 1613, 1568, 1424; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.71 Hz, 3 H) 1.24 (d, *J* = 6.71 Hz, 3 H) 1.80 (s, 3 H) 2.44 (spt, *J* = 6.76 Hz, 1 H) 5.13 (s, 1 H) 7.08 (s, 1 H) 7.24 - 7.27 (m, 1 H) 7.30 (t, *J* = 4.88 Hz, 1 H) 7.34 - 7.38 (m, 1 H) 7.69 (d, *J* = 7.93 Hz, 1 H) 7.86 (d, *J* = 8.55 Hz, 1 H) 8.83 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 16.6, 17.2, 24.1, 35.1, 92.1, 111.7, 112.4, 115.9, 119.1, 121.8, 122.7, 126.2, 128.2, 129.8, 139.6, 157.8, 158.9, 162.2, 171.9; **HRESI-MS** *(mz)*: Calculated for $C_{19}H_{15}N_3O_2$ (M + H): 318.1243, found (M + H): 318.1245.

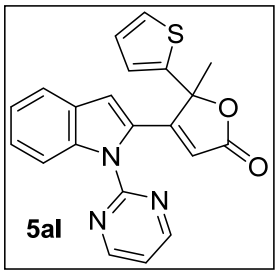
16. **5,5-Diphenyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5aj).** 

Light brown solid; Yield - (65 mg, 76%); ***mp***: 202-204 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3060, 3025, 2926, 1751, 1612, 1565, 1421, 1213; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.45 (s, 1 H) 6.28 (s, 1 H) 7.15 - 7.20 (m, 2 H) 7.32 (t, *J* = 7.78 Hz, 1 H) 7.35 - 7.40 (m, 6 H) 7.45 (d, *J* = 7.93 Hz, 1 H) 7.53 - 7.56 (m, 4 H) 7.95 (d, *J* = 8.54 Hz, 1 H) 8.68 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 93.6, 112.6, 113.6, 117.2, 118.7, 122.1, 122.7, 126.2, 128.1, 128.3, 128.6, 128.9, 130.9, 138.5, 139.3, 157.6, 158.7, 161.0, 171.4; **HRESI-MS** *(mz)*: Calculated for $C_{28}H_{19}N_3O_2$ (M + H): 430.1556, found (M + H): 430.1555.

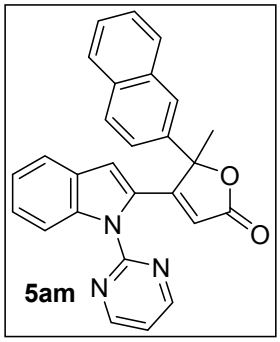
17. **5-Ethyl-5-phenyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5ak).** Brown solid; Yield - (70.0 mg, 92%); ***mp***: 160-162 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (c). **IR** (KBr, cm^{-1}): 3016, 2978, 2937, 1757, 1615, 1568, 1442, 1422, 1344, 1287, 1236, 1216, 1178; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.11 (t, *J* = 7.32 Hz, 3 H) 2.57 (dq, *J* = 14.38, 7.21 Hz, 1 H) 2.71 (dq, *J* = 14.38, 7.21 Hz, 1 H) 5.41 (s, 1 H) 6.42 (s, 1 H) 7.15 - 7.20 (m, 1 H) 7.23 (t, *J* = 4.88 Hz, 1 H) 7.29 - 7.33 (m, 1 H) 7.33 - 7.40 (m, 3 H) 7.47 - 7.51 (m, 3 H) 7.90 (d, *J* = 8.55 Hz, 1 H) 8.75 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 7.4, 29.2, 91.9, 112.6, 112.8, 116.6, 118.8, 121.9, 122.6, 126.2, 126.3, 128.0, 128.7, 128.8, 129.6, 138.6, 139.4, 157.5, 158.7, 160.9, 172.2; **HRESI-MS** *(mz)*: Calculated for $C_{24}H_{19}N_3O_2$ (M + H): 382.1556, found (M + H): 382.11555.

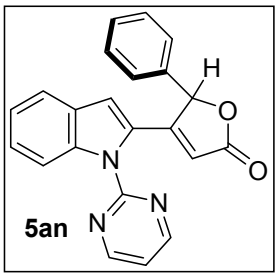


18. **5-Methyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)-5-(thiophen-2-yl)furan-2(5H)-one (5al).** Brown solid; Yield - (66 mg, 94%); ***mp***: 201-202 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3014, 2933, 1749, 1617, 1566, 1421, 1238; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.26 (s, 3 H) 5.36 (s, 1 H) 6.40 (s, 1 H) 7.03 - 7.06 (m, 1 H) 7.18 - 7.23 (m, 2 H) 7.28 (t, *J* = 4.88 Hz, 1 H) 7.33 (t, *J* = 7.78 Hz, 1 H) 7.41 (d, *J* = 4.88 Hz, 1 H) 7.53 (d, *J* = 7.93 Hz, 1 H) 7.95 (d, *J* = 8.24 Hz, 1 H) 8.82 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.5, 86.7, 112.6, 112.9, 115.3, 118.8, 122.0, 122.7, 126.3, 127.0, 127.1, 128.1, 129.3, 139.5, 142.9, 157.6, 158.8, 161.4, 170.9; **HRESI-MS** *(mz)*: Calculated for $C_{21}H_{15}N_3O_2S$ (M + H): 374.0963, found (M + H): 374.0961.

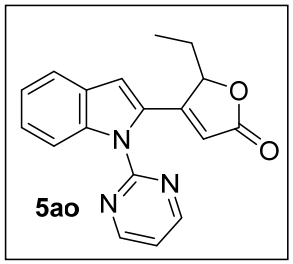


19. **5-Methyl-5-(naphthalen-2-yl)-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5am).** Light brown solid; Yield - (61 mg, 73%); ***mp***: 154-156 °C; R_f (30% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 3055, 3015, 2927, 2854, 1746, 1616, 1566, 1421, 1235; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.33 (s, 3 H) 5.50 (s, 1 H) 6.20 (s, 1 H) 7.14 - 7.23 (m, 2 H) 7.29 - 7.47 (m, 3 H) 7.57 (br. s., 2 H) 7.88 – 7.97 (m, 4 H) 8.07 (br. s., 1 H) 8.78 (br. s., 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.2, 89.4, 112.7, 115.9, 118.6, 121.9, 122.7, 123.7, 125.8, 126.1, 126.6,127.0, 127.7, 128.1, 128.5, 128.9, 129.6, 132.9, 133.4, 135.5, 139.4, 157.6, 158.7, 162.9, 172.0; **HRESI-MS** *(mz)*: Calculated for $C_{27}H_{19}N_3O_2$ (M + H): 418.1556, found (M + H): 418.1555.

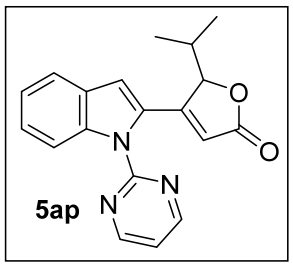


20. **5-Phenyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5an).** 

Brown solid; Yield - (40.0 mg, 54%); ***mp***: 123-125 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (b). **IR** (KBr, cm^{-1}): 2922, 2859, 1749, 1623, 1566, 1424; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.30 (s, 3 H) 5.72 (d, *J* = 1.22 Hz, 1 H) 6.27 - 6.28 (m, 1 H) 6.66 (s, 1 H) 7.12 - 7.17 (m, 2 H) 7.18 - 7.22 (m, 3 H) 7.28 - 7.33 (m, 2 H) 7.53 (d, *J* = 7.93 Hz, 1 H) 8.08 (d, *J* = 8.54 Hz, 1 H) 8.85 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.2, 84.9, 113.3, 113.5, 115.2, 118.5, 121.8, 122.8, 126.1, 127.7, 128.2, 129.6, 129.9, 132.0, 139.3, 139.5, 157.5, 158.7, 172.7; **HRESI-MS** *(mz)*: Calculated for $C_{23}H_{17}N_3O_2$ (M + H): 368.1399, found (M + H): 368.1401.

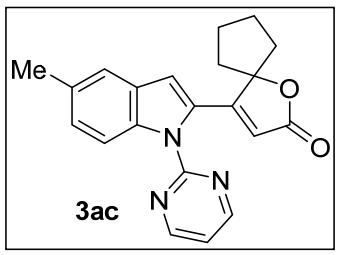
21. **5-Ethyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5ao).** 

Light yellow solid; Yield - (54.3 mg, 89%); ***mp***: 110-112 °C; R_f (30% EtOAc/petroleum ether) 0.40; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2973, 2930, 2852, 1747, 1626, 1567, 1422, 1344; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.32 Hz, 3 H) 1.75 (dquin, *J* = 14.34, 7.17, 7.17, 7.17, 7.17 Hz, 1 H) 2.04 (dqd, *J* = 14.65, 7.32, 7.32, 7.32, 3.97 Hz, 1 H) 5.34 - 5.37 (m, 1 H) 5.65 - 5.76 (m, 1 H) 6.94 (s, 1 H) 7.25 - 7.29 (m, 2 H) 7.38 (t, *J* = 7.32 Hz, 1 H) 7.67 (d, *J* = 7.63 Hz, 1 H) 8.20 (d, *J* = 8.54 Hz, 1 H) 8.81 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 8.2, 26.6, 83.9, 112.5, 113.6, 115.1, 118.5, 121.8, 123.0, 126.1, 128.3, 130.1, 139.3, 157.4, 158.7, 160.1, 173.1; **HRESI-MS** *(mz)*: Calculated for $C_{18}H_{15}N_3O_2$ (M + H): 306.1243, found (M + H): 306.1246.

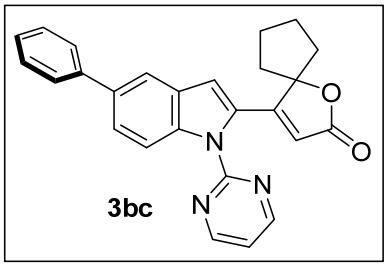
22. **5-Isopropyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)furan-2(5H)-one (5ap).** 

Light yellow solid; Yield - (84.3 mg, 88%); ***mp***: 163-165 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2964, 2923, 2852, 1744, 1626, 1566, 1422, 1016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.82 (d, *J* = 7.02 Hz, 3 H) 1.12 (d, *J* = 7.02 Hz, 3 H) 2.12 - 2.20 (m, 1 H) 5.25 - 5.26 (m, 1 H) 5.67 (d, *J* = 1.22 Hz, 1 H) 6.95 (s, 1 H) 7.26 - 7.30 (m, 2 H) 7.36 - 7.40 (m, 1 H) 7.67 (d, *J* = 7.93 Hz, 1 H) 8.20 (d, *J* = 8.54 Hz, 1 H) 8.81 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.0, 19.9, 31.6, 87.3, 122.5, 113.6, 115.4, 118.4, 121.8, 122.9, 126.1, 128.3, 130.3, 139.2, 157.4, 158.7, 159.6, 173.2; **HRESI-MS** *(mz)*: Calculated for $C_{19}H_{17}N_3O_2$ (M + H): 320.1399, found (M + H): 320.1399.

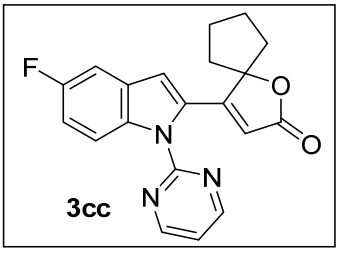
23. **4-(5-Methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3ac).** Light yellow solid; Yield - (58.7 mg, 85%); ***mp***: 136-138 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2963, 2922, 2869, 1746, 1610, 1565, 1422; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.91 - 1.96 (m, 2 H) 2.08 - 2.11 (m, 4 H) 2.32 - 2.39 (m, 2 H) 2.49 (s, 3 H) 5.45 (s, 1 H) 6.88 (s, 1 H) 7.21 (dd, *J* = 8.58, 1.34 Hz, 1 H) 7.26 (t, *J* = 4.73 Hz, 1 H) 7.48 (s, 1 H) 7.98 (d, *J* = 8.54 Hz, 1 H) 8.80 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.3, 25.1, 38.2, 97.9, 110.7, 112.8, 117.2, 118.4, 121.2, 127.4, 128.6, 29.6, 132.3, 137.3, 157.7, 158.5, 161.9, 171.6; **HRESI-MS** *(mz)*: Calculated for $C_{21}H_{19}N_3O_2$ (M + H): 346.1556, found (M + H): 346.1557.



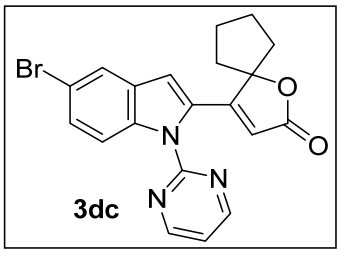
24. **4-(5-phenyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3bc).** Light brown solid; Yield - (73.4 mg, 90%); ***mp***: 195-197 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2964, 2924, 2872, 1744, 1628, 1608, 1566, 1420; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.89 - 1.90 (m, 2 H) 2.07 - 2.10 (m, 4 H) 2.34 – 2.37 (m, 2 H) 5.47 (s, 1 H) 6.98 (s, 1 H) 7.26 - 7.27 (m, 1 H) 7.34 - 7.37 (m, 1 H) 7.46 (t, *J* = 7.48 Hz, 2 H) 7.63 - 7.66 (m, 3 H) 7.88 (s, 1 H) 8.15 (d, *J* = 8.54 Hz, 1 H) 8.79 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.0, 38.1, 98.0, 111.1, 113.5, 117.6, 118.6, 119.8, 125.4, 127.0, 127.3, 128.8, 128.9, 130.2, 136.2, 138.2, 141.4, 157.5, 158.6, 161.8, 171.5; **HRESI-MS** *(mz)*: Calculated for $C_{26}H_{21}N_3O_2$ (M + H): 408.1712, found (M + H): 408.1715.



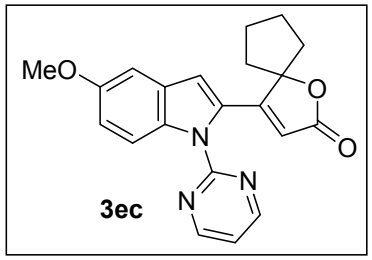
25. **4-(5-Fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3cc).** Light yellow solid; Yield - (64.3 mg, 92%); ***mp***: 155-157 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2925, 2853, 1745, 165, 1566, 1423; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.87 - 1.90 (m, 2 H) 2.05 - 2.07 (m, 4 H) 2.25 - 2.29 (m, 2 H) 5.49 (s, 1 H) 6.87 (s, 1 H) 7.10 (td, *J* = 9.00, 2.44 Hz, 1 H) 7.25 - 7.27 (m, 1 H) 7.31 (dd, *J* = 8.54, 2.44 Hz, 1 H) 8.08 (dd, *J* = 9.16, 4.58 Hz, 1 H) 8.78 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.9, 38.0, 98.0, 106.4 ($J_{C\text{-}F}$ = 23.63 Hz), 110.3 ($J_{C\text{-}F}$ = 4.5 Hz), 113.8 ($J_{C\text{-}F}$ = 25.23 Hz), 114.5 ($J_{C\text{-}F}$ = 9.34 Hz), 118.3 ($J_{C\text{-}F}$ = 55.44 Hz), 128.9 ($J_{C\text{-}F}$ = 10.61 Hz), 131.0, 135.1, 137.3, 158.6, 160.3, 161.8, 171.3; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{16}N_3O_2F$ (M + H): 350.1305, found (M + H): 350.1304.



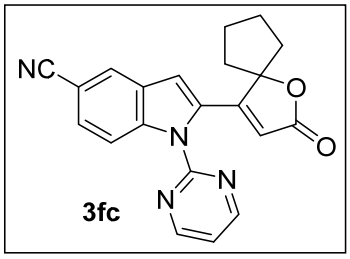
26. 4-(5-Bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3dc). Light brown solid; Yield - (69.2 mg, 84%); ***mp***: 168-170 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2971, 2874, 1752, 1613, 1567, 1418; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.86 (br. s., 2 H) 2.04 - 2.05 (m, 4 H) 2.27 (br. s., 2 H) 5.47 (s, 1 H) 6.83 (s, 1 H) 7.42 (d, *J* = 8.24 Hz, 1 H) 7.78 (s, 1 H) 7.98 (d, *J* = 8.54 Hz, 1 H) 8.77 (d, *J* = 3.97 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.9, 38.0, 98.0, 109.6, 114.9, 115.8, 118.3, 118.8, 123.9, 128.4, 130.0, 130.6, 137.2, 157.2, 158.6, 161.6, 171.3; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{16}N_3O_2Br$ (M + H): 410.0504, found (M + H): 410.0504.

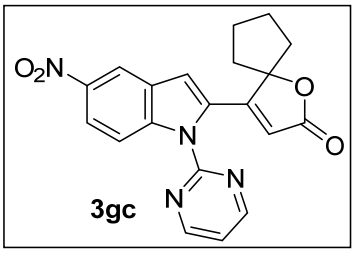


27. 4-(5-Methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3ec). Light yellow solid; Yield - (64.4 mg, 89%); ***mp***: 167-169 °C; R_f (30% EtOAc/petroleum ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2955, 2875, 1746, 1613, 1567, 1517, 1422, 1214; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.87 - 1.92 (m, 2 H) 2.05 - 2.07 (m, 4 H) 2.27 - 2.34 (m, 2 H) 3.86 (s, 3 H) 5.44 (s, 1 H) 6.85 (s, 1 H) 6.99 (dd, *J* = 9.16, 2.44 Hz, 1 H) 7.09 (d, *J* = 2.44 Hz, 1 H) 7.21 (t, *J* = 4.73 Hz, 1 H) 8.00 (d, *J* = 8.85 Hz, 1 H) 8.75 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.4, 55.7, 87.8, 102.9, 111.0, 113.9, 116.0, 116.1, 118.5, 128.9, 130.0, 134.3, 156.0, 157.6, 158.6, 163.9, 171.4; **HRESI-MS** *(mz)*: Calculated for $C_{21}H_{19}N_3O_3$ (M + H): 362.1505, found (M + H): 362.1503.

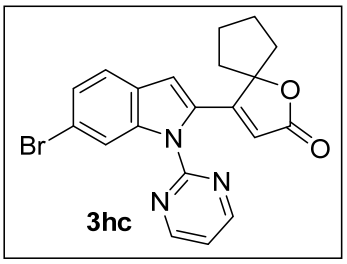


28. 2-(2-Oxo-1-oxaspiro[4.4]non-3-en-4-yl)-1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (3fc). Light yellow solid; Yield - (62.1 mg, 87%); ***mp***: 201-203 °C; R_f (50% EtOAc/petroleum ether) 0.25; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2925, 2853, 1745, 165, 1566, 1423; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.87 - 1.91 (m, 2 H) 2.02 - 2.06 (m, 4 H) 2.25 - 2.30 (m, 2 H) 5.50 (s, 1 H) 6.95 (s, 1 H) 7.34 (t, *J* = 4.73 Hz, 1 H) 7.57 (d, *J* = 8.85 Hz, 1 H) 8.01 (s, 1 H) 8.15 (d, *J* = 8.85 Hz, 1 H) 8.81 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.9, 37.9, 98.0, 106.1, 109.8, 114.3, 119.1, 119.4, 119.6, 126.6, 128.1, 128.2, 131.8, 139.8, 156.8, 158.8, 161.0, 171.0; **HRESI-MS** *(mz)*: Calculated for $C_{21}H_{16}N_4O_2$ (M + H): 357.1352, found (M + H): 357.1354.

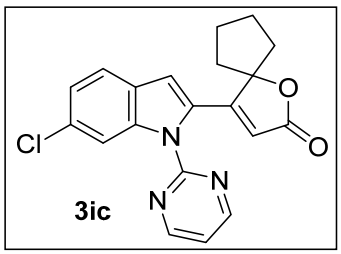


29. **4-(5-Nitro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3gc).** 

Yellow solid; Yield - (64.7 mg, 86%); ***mp***: 214-216 °C; R_f (30% EtOAc/petroleum ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2971, 2874, 1748, 1609, 1568, 1517, 1448, 1419, 1338; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.86 - 1.94 (m, 2 H) 2.03 - 2.09 (m, 4 H) 2.25 - 2.33 (m, 2 H) 5.53 (s, 1 H) 7.06 (s, 1 H) 7.38 (t, *J* = 4.88 Hz, 1 H) 8.16 (d, *J* = 9.46 Hz, 1 H) 8.23 (dd, *J* = 9.16, 2.14 Hz, 1 H) 8.62 (d, *J* = 2.14 Hz, 1 H) 8.85 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.9, 37.8, 97.9, 110.7, 113.6, 118.1, 119.2, 119.6, 120.4, 127.8, 132.6, 140.9, 143.6, 156.7, 158.9, 160.9, 170.9; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{16}N_4O_4$ (M + H): 377.1250, found (M + H): 377.1248.

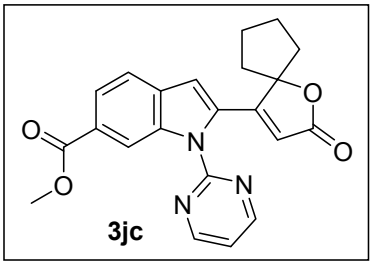
30. **4-(6-Bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3hc).** 

Pale yellow solid; Yield - (73.8 mg, 90%); ***mp***: 175-177 °C; R_f (30% EtOAc/petroleum ether) 0.35; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2969, 2873, 1746, 1606, 1568, 1421; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.80 (br. s., 2 H) 1.97 (br. s., 4 H) 2.21 (br. s., 2 H) 5.37 (s, 1 H) 6.81 (s, 1 H) 7.20 (d, *J* = 5.31 Hz, 1 H) 7.30 (d, *J* = 8.08 Hz, 1 H) 7.45 (d, *J* = 8.08 Hz, 1 H) 8.20 (s, 1 H) 8.72 - 8.72 (d, *J* = 2.36 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.0, 38.9, 97.9, 110.5, 116.3, 117.9, 118.9, 119.5, 122.7, 126.2, 127.2, 130.1, 139.3, 157.2, 158.8, 161.5, 171.4; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{16}N_3O_2Br$ (M + H): 410.0504, found (M + H): 410.0506.

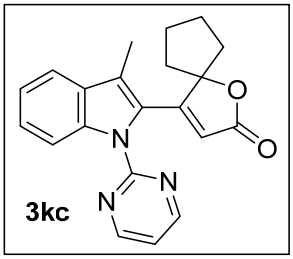
31. **4-(6-Chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3ic).** 

Light yellow solid; Yield - (64.3 mg, 93%); ***mp***: 190-192 °C; R_f (30% EtOAc/petroleum ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2970, 2873, 1747, 1607, 1567, 1420; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.88 - 1.91 (m, 2 H) 2.05 - 2.07 (m, 4 H) 2.28 - 2.30 (m, 2 H) 5.44 (s, 1 H) 6.89 (s, 1 H) 7.24 (dd, *J* = 8.39, 1.68 Hz, 1 H) 7.27 - 7.29 (m, 1 H) 7.58 (d, *J* = 8.54 Hz, 1 H) 8.12 (s, 1 H) 8.80 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.0, 38.1, 97.9, 110.5, 113.4, 117.9, 118.8, 122.3, 123.5, 126.8, 130.2, 131.6, 139.0, 157.2, 158.7, 161.4, 171.3; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{16}N_3O_2Cl$ (M + H): 366.1009, found (M + H): 366.1010.

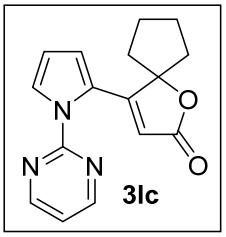
32. Methyl 2-(2-oxo-1-oxaspiro[4.4]non-3-en-4-yl)-1-(pyrimidin-2-yl)-1H-indole-6-carboxylate (3jc). Brown solid; Yield - (67.8 mg, 87%); ***mp***: 162-164 °C; R_f (30% EtOAc/petroleum ether) 0.20; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2953, 2846, 1750, 1711, 1613, 1567, 1423, 1224; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.86 (br. s., 2 H) 2.03 - 2.05 (m, 4 H) 2.28 (br. s., 2 H) 3.92 (s, 3 H) 5.48 (s, 1 H) 6.92 (s, 1 H) 7.29 (t, *J* = 4.74 Hz, 1 H) 7.68 (d, *J* = 8.28 Hz, 1 H); 7.93 (d, *J* = 8.32 Hz, 1 H) 8.72 (s,1 H) 8.80 (d, *J* = 4.56 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.9, 37.9, 52.2, 97.9, 110.0, 115.3, 118.6, 119.1, 121.2, 123.6, 127.1, 131.7, 132.3, 137.9, 157.1, 158.8, 161.4, 167.4, 171.1; **HRESI-MS** *(mz)*: Calculated for $C_{22}H_{19}N_3O_4$ (M + H): 390.1454, found (M + H): 390.1457.

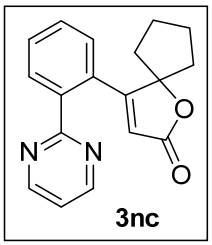


33. 4-(3-Methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3kc). Light yellow solid; Yield - (31.8 mg, 46%); ***mp***: 125-127 °C; R_f (30% EtOAc/petroleum ether) 0.40; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2971, 2923, 2851, 1752, 1637, 1425, 1337; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.26 (s, 1 H) 1.55 - 1.58 (m, 5 H) 1.85 (s, 2 H) 2.29 (s, 3 H) 6.21 (s, 1 H) 7.11 (s, 1 H) 7.31 (t, *J* = 7.17 Hz, 1 H) 7.39 (t, *J* = 7.48 Hz, 1 H) 7.62 (d, *J* = 7.32 Hz, 1 H) 8.54 (d, *J* = 8.24 Hz, 1 H) 8.68 (d, *J* = 3.97 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 9.4, 23.5, 36.9, 99.4, 114.8, 117.1, 118.6, 119.4, 120.8, 122.5, 125.2, 125.9, 130.1, 137.2, 157.9, 158.1, 164.8, 171.9; **HRESI-MS** *(mz)*: Calculated for $C_{21}H_{19}N_3O_2$ (M + H): 346.1556, found (M + H): 346.1558.

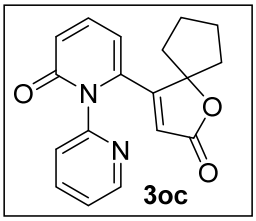


34. 4-(1-(Pyrimidin-2-yl)-1H-pyrrol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3lc). Light yellow solid; Yield - (35.5 mg, 42%); ***mp***: 115-117 °C; Rf (30% EtOAc/petroleum ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2962, 2872, 1746, 1607, 1569, 1437; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.81 - 1.89 (m, 2 H) 1.99 - 2.05 (m, 4 H) 2.20 - 2.27 (m, 2 H) 5.41 (s, 1 H) 6.40 (t, *J* = 3.36 Hz, 1 H) 6.55 - 6.56 (m, 1 H) 7.22 (t, *J* = 4.73 Hz, 1 H) 7.64 - 7.65 (m, 1 H) 8.69 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.1, 38.2, 97.9, 111.2, 115.6, 116.8, 118.9, 123.5, 127.3, 157.2, 158.6, 161.4; **HRESI-MS** *(mz)*: Calculated for $C_{16}H_{15}N_3O_2$ (M + H): 282.1243, found (M + H): 282.1243.

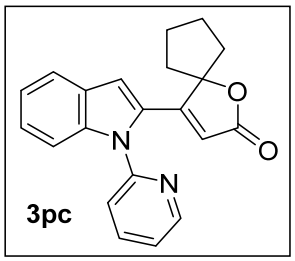


35. **4-(2-(Pyrimidin-2-yl)phenyl)-1-oxaspiro[4.4]non-3-en-2-one (3nc).** 

Brown solid; Yield - (27.2 mg, 31%); ***mp***: 121-123 °C; R_f (30% EtOAc/petroleum ether) 0.30; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2963, 2923, 2851, 1750, 1630, 1563, 1413; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.61 - 1.72 (m, 4 H) 1.77 - 1.84 (m, 2 H) 1.86 - 1.91 (m, 2 H) 5.86 (s, 1 H) 7.21 (t, *J* = 4.73 Hz, 1 H) 7.50 - 7.58 (m, 2 H) 8.10 (d, *J* = 7.63 Hz, 1 H) 8.75 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 23.7, 36.5, 99.1, 119.3, 119.5, 129.1, 129.3, 129.4, 130.8, 131.7, 137.4, 156.9, 165.5, 171.9, 172.0; **HRESI-MS** *(mz)*: Calculated for $C_{18}H_{16}N_2O_2$ (M + H): 293.1290, found (M + H): 293.1293.

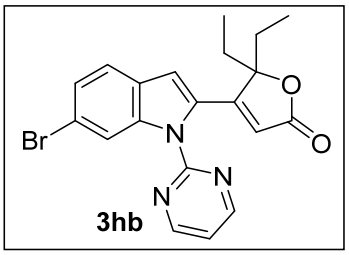
36. **6-(2-Oxo-1-oxaspiro[4.4]non-3-en-4-yl)-2H-[1,2'-bipyridin]-2-one (3oc).** 

Brown oil; Yield - (25.9 mg, 42%); R_f (50% EtOAc/petroleum ether) 0.15; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2970, 2875, 2011, 1756, 1672, 1629, 1586, 1537, 1434; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.71 (d, *J* = 6.41 Hz, 2 H) 1.84 (s, 2 H) 1.96 – 1.97 (m, 2 H) 2.18 (s, 2 H) 5.68 (s, 1 H) 6.25 (d, *J* = 5.49 Hz, 1 H) 6.73 (s, 1 H) 7.37-7.43 (m, 3 H) 7.84 (s, 1 H) 8.56 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 23.9, 37.1, 98.3, 107.2, 122.9, 123.7, 124.5, 124.6, 138.3, 138.7, 138.9, 149.5, 150.8, 161.8, 169.7; **HRESI-MS** *(mz)*: Calculated for $C_{18}H_{16}N_2O_3$ (M + H): 309.1239, found (M + H): 309.1236.

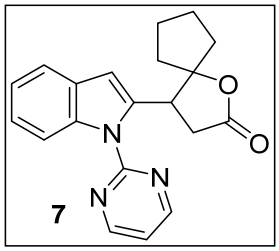
37. **4-(1-(Pyridin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]non-3-en-2-one (3pc).** 

Dark orange solid; Yield - (652.2 mg, 79%); ***mp***: 126-128 °C; R_f (30% EtOAc/petroleum ether) 0.40; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2962, 2924, 2854, 1744, 1602, 1469, 1439; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.01 - 2.11 (m, 6 H) 2.44 - 2.51 (m, 2 H) 4.96 (s, 1 H) 6.98 (s, 1 H) 7.22 (t, *J* = 7.93 Hz, 1 H) 7.26 - 7.28 (m, 1 H) 7.28 - 7.33 (m, 2 H) 7.45 (dd, *J* = 7.63, 4.88 Hz, 1 H) 7.70 (d, *J* = 7.93 Hz, 1 H) 7.93 (td, *J* = 7.71, 1.98 Hz, 1 H) 8.69 - 8.71 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.8, 39.3, 97.5, 109.6, 110.9, 114.5, 121.9, 122.8, 1244.0, 125.8, 127.3, 129.2, 139.1, 140.3, 150.4, 151.2, 158.7, 171.5; **HRESI-MS** *(mz)*: Calculated for $C_{21}H_{18}N_2O_2$ (M + H): 331.1147, found (M + H): 331.1147.

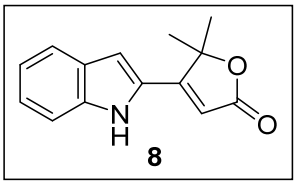
38. **4-(6-Bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)-5,5-diethylfuran-2(5H)-one (3hb).** Brown solid; Yield - (43.0 mg, 52%); ***mp***: 124-126 °C; R_f (30% EtOAc/petroleum ether) 0.45; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2974, 2934, 1742, 1611, 1461, 1419, 1336; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1. 0.93 (t, *J* = 7.32 Hz, 6 H) 2.09 - 2.26 (m, 4 H) 5.18 (s, 1 H) 7.01 (s, 1 H) 7.35 - 7.38 (m, 2 H) 7.55 (d, *J* = 8.54 Hz, 1 H) 8.02 - 8.03 (m, 1 H) 8.86 (d, *J* = 4.88 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 7.3, 31.1, 93.1, 111.0, 115.5, 118.0, 119.5, 120.1, 123.0, 126.1, 127.0, 130.3, 140.2, 157.4, 158.4, 159.0, 171.7; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{18}N_3O_2Br$ (M + H): 412.0661, found (M + H): 412.0663.



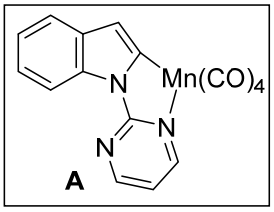
39. **4-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)-1-oxaspiro[4.4]nonan-2-one (7).** Colourless oil; Yield - (78.0 mg, 78%); R_f 30% EtOAc/petroleum ether) 0.3; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2963, 2924, 2853, 1772, 1565, 1455, 1422, 1345; **^{1}H NMR** (400 MHz, $CDCl_3$) 1.43 - 1.50 (m, 1 H) 1.55 - 1.80 (m, 6 H) 1.87 - 1.94 (m, 1 H) 2.96 (dd, *J* = 17.55, 5.34 Hz, 1 H) 3.13 (dd, *J* = 17.40, 8.85 Hz, 1 H) 4.94 (dd, *J* = 8.85, 5.49 Hz, 1 H) 6.64 (s, 1 H) 7.20 - 7.25 (m, 2 H) 7.29 (br. s., 1 H) 7.58 (d, *J* = 7.32 Hz, 1 H) 8.20 (d, *J* = 8.24 Hz, 1 H) 8.83 (d, *J* = 4.58 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 23.2, 23.6, 34.6, 37.3, 38.4, 40.4, 98.9, 106.1, 113.8, 117.7, 120.4, 122.4, 123.6, 128.7, 136.8, 139.3, 158.4, 176.1; **HRESI-MS** *(mz)*: Calculated for $C_{20}H_{19}N_3O_2$ (M + H): 334.1556, found (M + H): 334.1558.



40. **4-(1H-Indol-2-yl)-5,5-dimethylfuran-2(5H)-one (8).** Yellow solid; Yield - (30.5 mg, 67%); ***mp***: 126-128 °C; R_f (30% EtOAc/petroleum ether) 0.4; Prepared as shown in general experimental procedure (a). **IR** (KBr, cm^{-1}): 2961, 2851, 2363, 2330, 1723, 1608, 1608, 1459, 1261; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.70 (s, 6 H) 6.48 (s, 1 H) 7.06 - 7.11 (m, 2 H) 7.27 (t, *J* = 7.48 Hz, 1 H) 7.45 (d, *J* = 8.24 Hz, 1 H) 7.65 (d, *J* = 7.93 Hz, 1 H) 11.68 (br. s., 1 H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 27.3, 86.3, 107.6, 110.4, 112.1, 120.6, 122.1, 125.2, 127.9, 128.3, 138.3, 163.7, 171.3; **HRESI-MS** *(mz)*: Calculated for $C_{14}H_{13}NO_2$ (M + H): 228.1025, found (M + H): 228.1023.



41. Manganese complex (A). Brown solid; Yield - (209.0 mg, 58%); ***mp***: 209-212 °C; R_f(10% EtOAc/petroleum ether) 0.4; Prepared as shown in general experimental procedure (c). **IR** (KBr, cm^{-1}): 2077, 1998, 1943, 1591, 1496, 1379; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.79 (br. s., 1 H) 6.88 (br. s., 1 H) 7.14 - 7.25 (m, 2 H) 7.44 (br. s., 1 H) 8.51 (br. s., 1 H) 8.59 (br. s., 1 H) 8.72 (br. s., 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 113.7, 114.1, 17.6, 119.3, 120.7, 122.9, 136.1, 138.5, 160.1, 160.9, 16.4, 162.2, 210.7, 213.7, 218.5; **HRESI-MS** *(mz)*: Calculated for $C_{16}H_8N_3O_4Mn$ (M + H): 361.9974, found (M + H): 361.9971.



References

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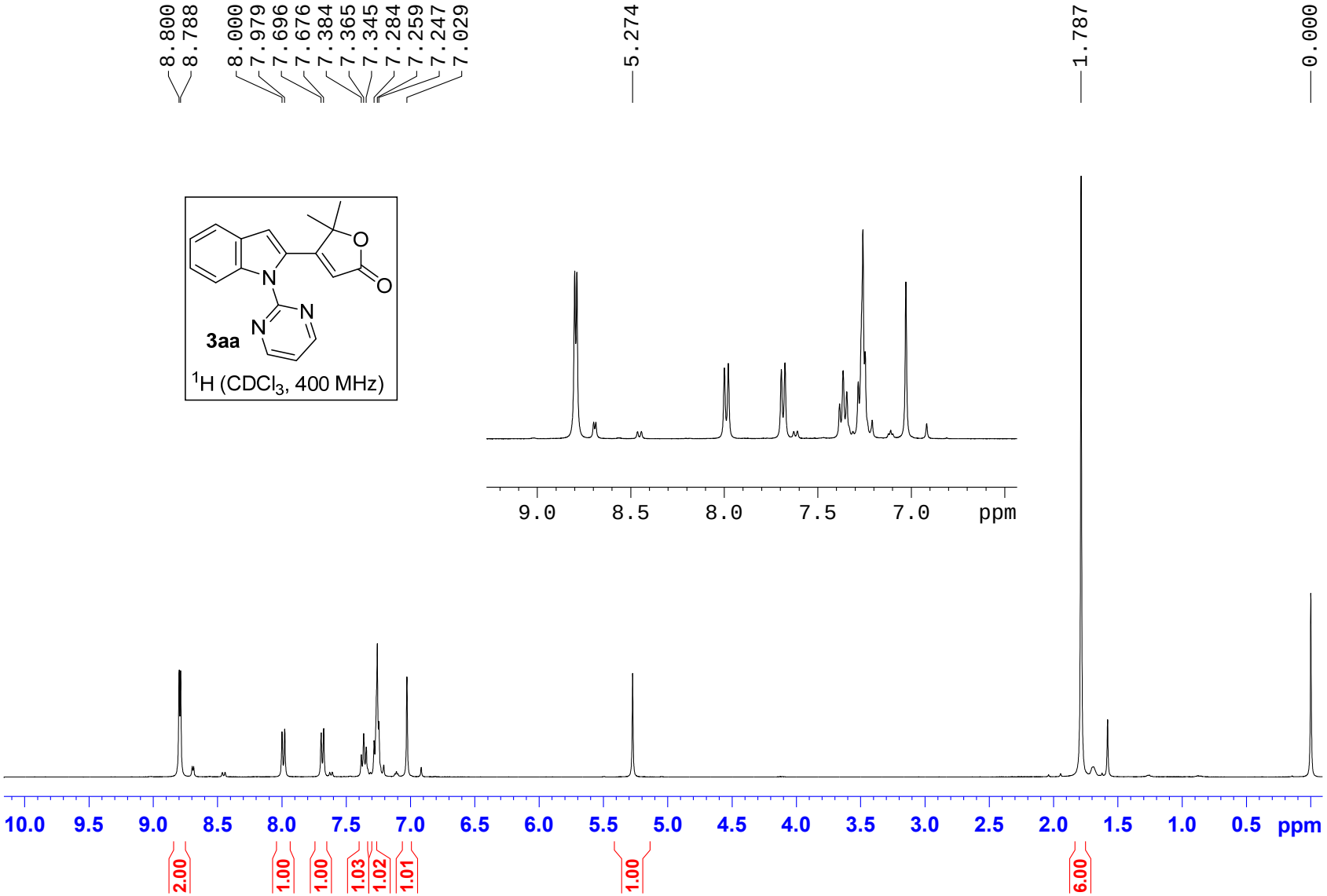
2. (a) G. Liao, H. Song, X. Yin and B. Shi, *Chem. Commun.* **2017**, 53, 7824-7827; (b) Y. Xu, B. Li, X. Zhang and X. Fan, *Adv. Synth. Catal.* **2018**, 360, 2613-2620.

3. Z. Ruan, N. Sauermann, E. Manoni, L. Ackermann, *Angew. Chem.* **2017**, 129, 3220-3224; *Angew. Chem. Int. Ed.* **2017**, 56, 3172-3176.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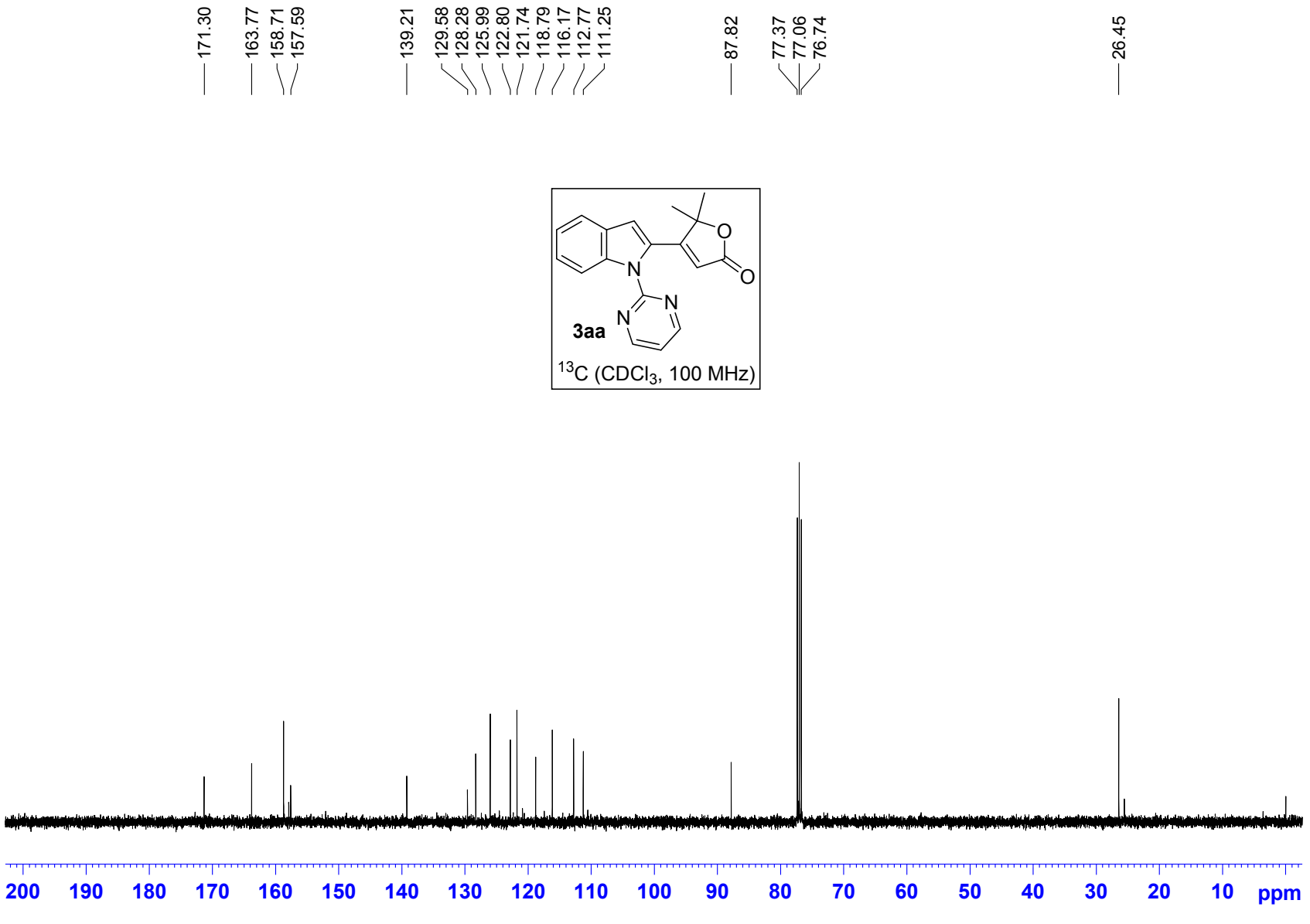
8.000
7.979
7.696
7.676
7.384
7.365
7.345
7.284
7.259
7.247
7.029
5.274
1.787
0.000
3aa
^{1}H (CDCl$_3$, 400 MHz)
9.0
8.5
8.0
7.5
7.0
ppm
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.00
1.00
1.03
1.02
1.01
1.00
6.00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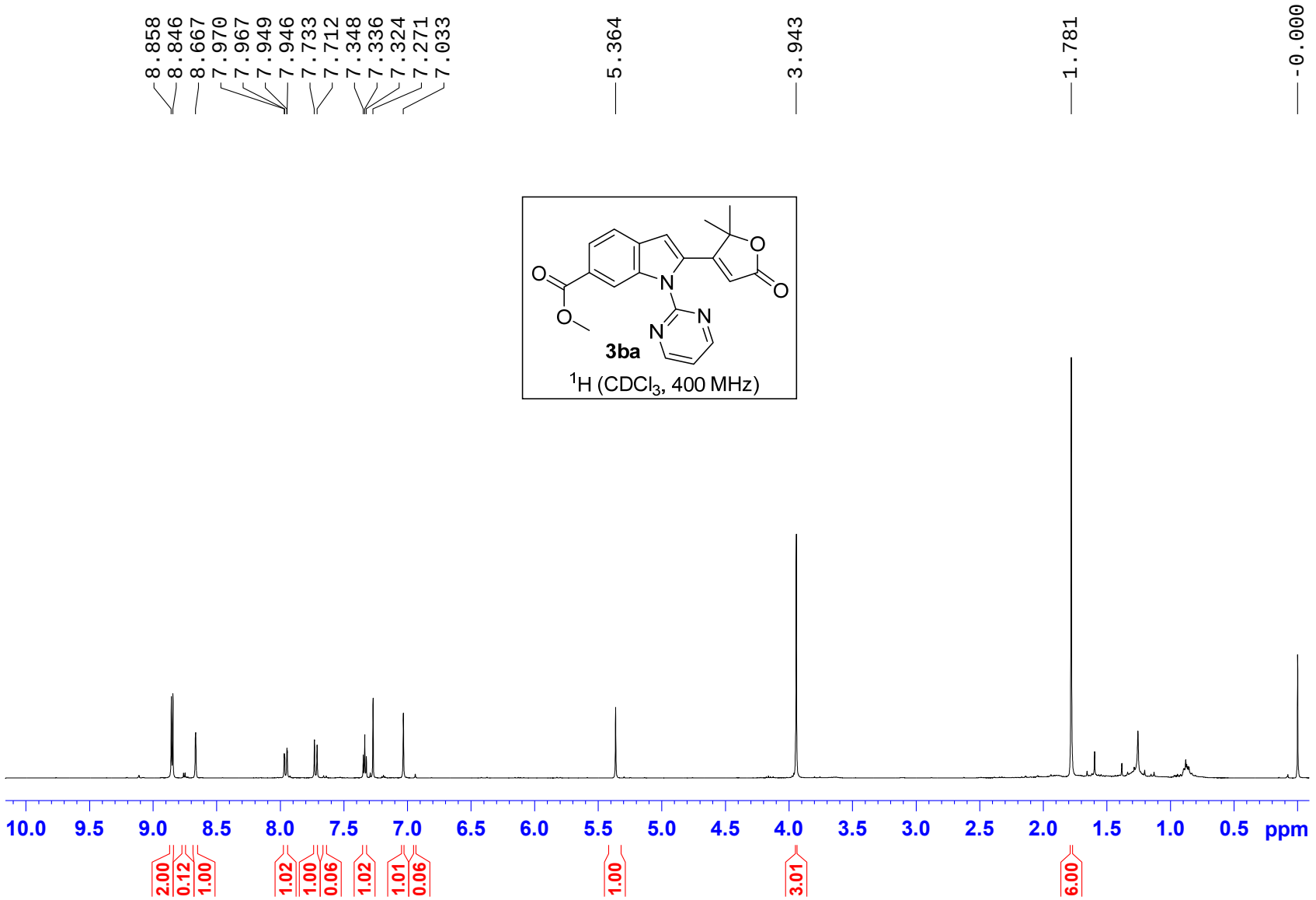
163.77
158.71
157.59
139.21
129.58
128.28
125.99
122.80
121.74
118.79
116.17
112.77
111.25
87.82
77.37
77.06
76.74
26.45
O
O
N
N
N
3aa
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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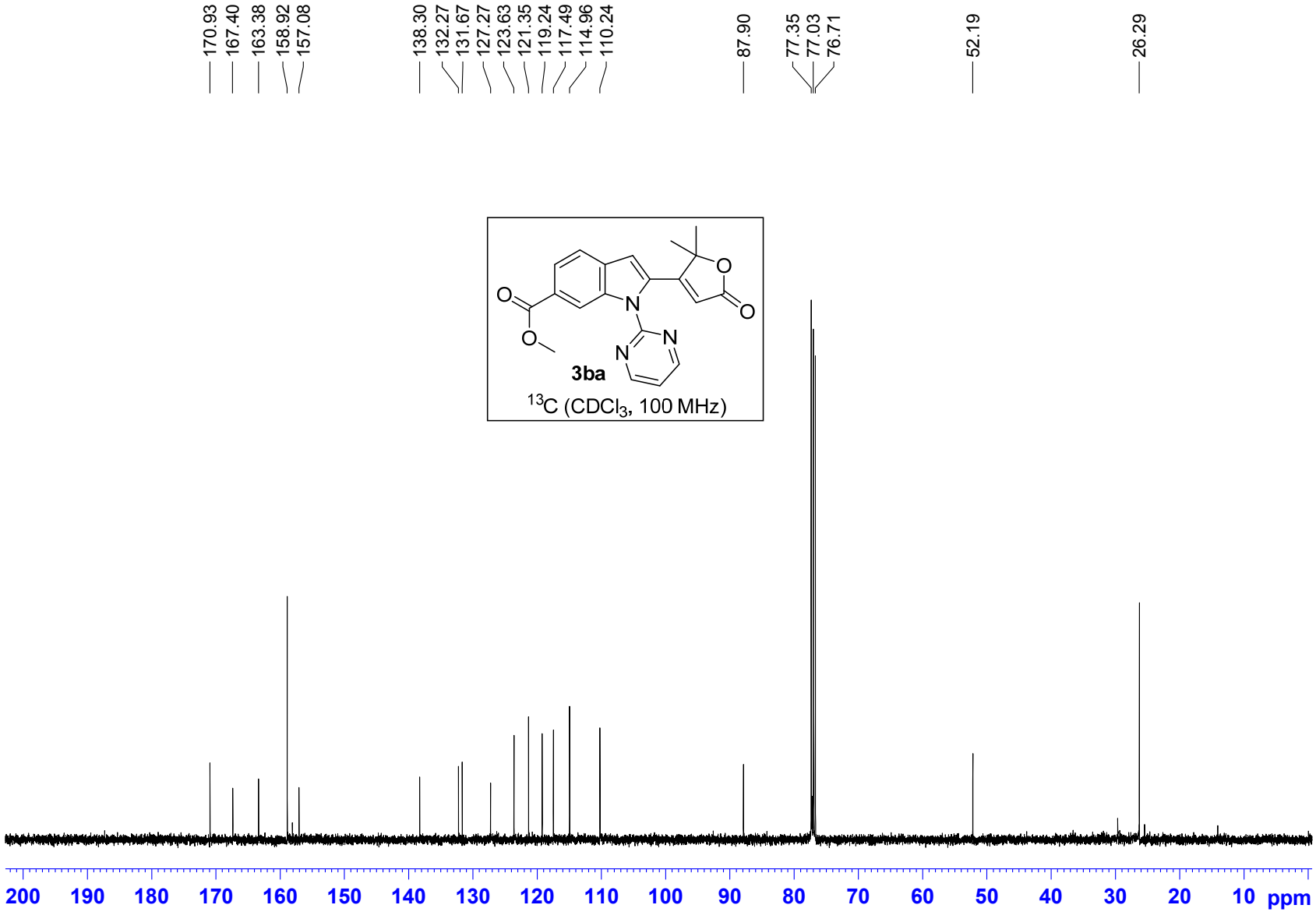
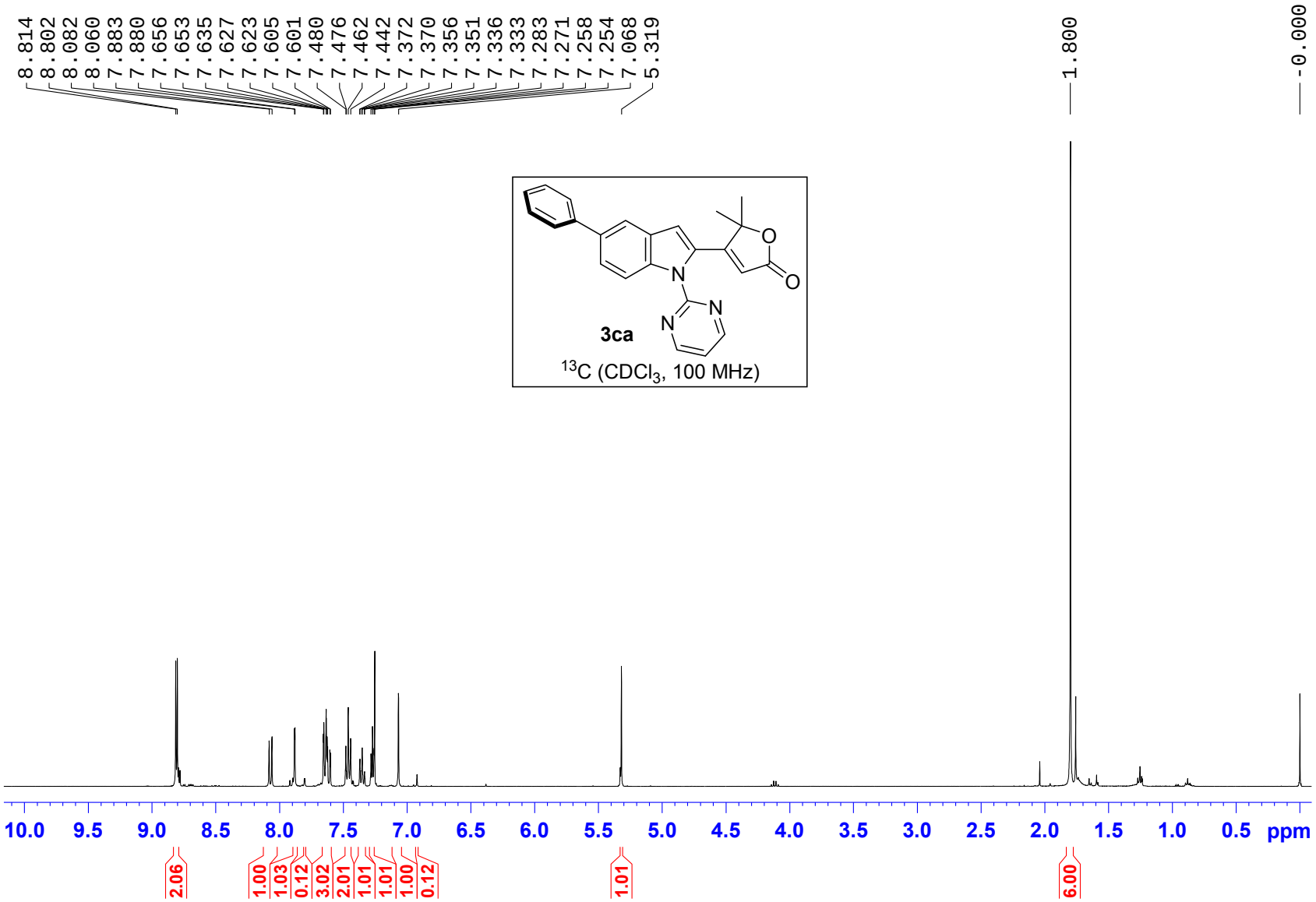
8.846
8.667
7.970
7.967
7.949
7.946
7.733
7.712
7.348
7.336
7.324
7.271
7.033
5.364
3.943
1.781
-0.000
3ba
1H (CDCl3, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 0.12 1.00 1.02 1.00 0.06 1.02 1.01 0.06 1.00 3.01 6.00


170.93
167.40
163.38
158.92
157.08
138.30
132.27
131.67
127.27
123.63
121.35
119.24
117.49
114.96
110.24
87.90
77.35
77.03
76.71
52.19
26.29
O
O
O
O
N
N
N
3ba
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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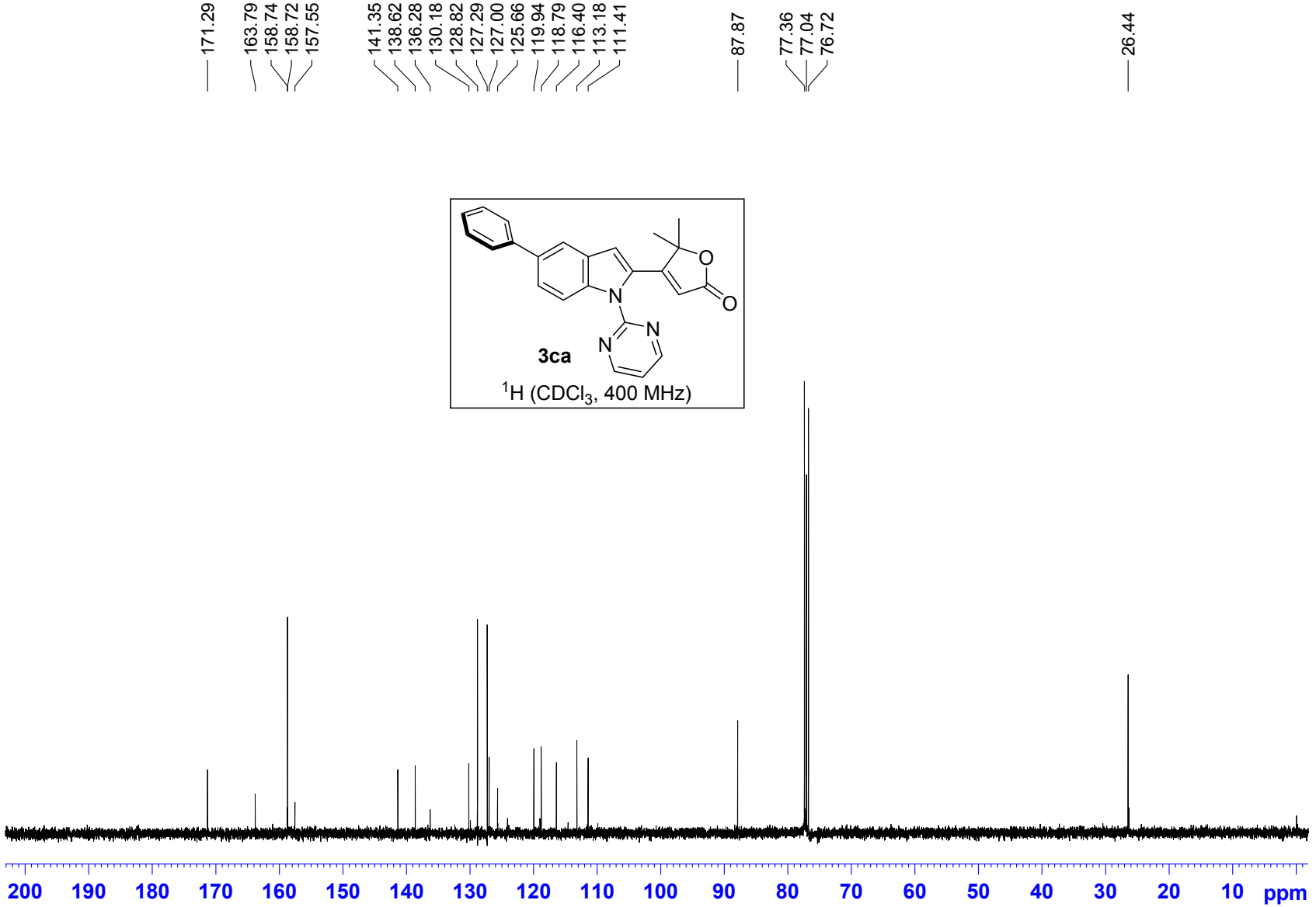
8.802
8.082
8.060
7.883
7.880
7.656
7.653
7.635
7.627
7.623
7.605
7.601
7.480
7.476
7.462
7.442
7.372
7.370
7.356
7.351
7.336
7.333
7.283
7.271
7.258
7.254
7.068
5.319
1.800
-0.000
O
O
N
N
N
3ca
13C (CDCl3, 100 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.06
1.00
1.03
0.12
3.02
2.01
1.01
1.01
1.00
0.12
1.01
6.00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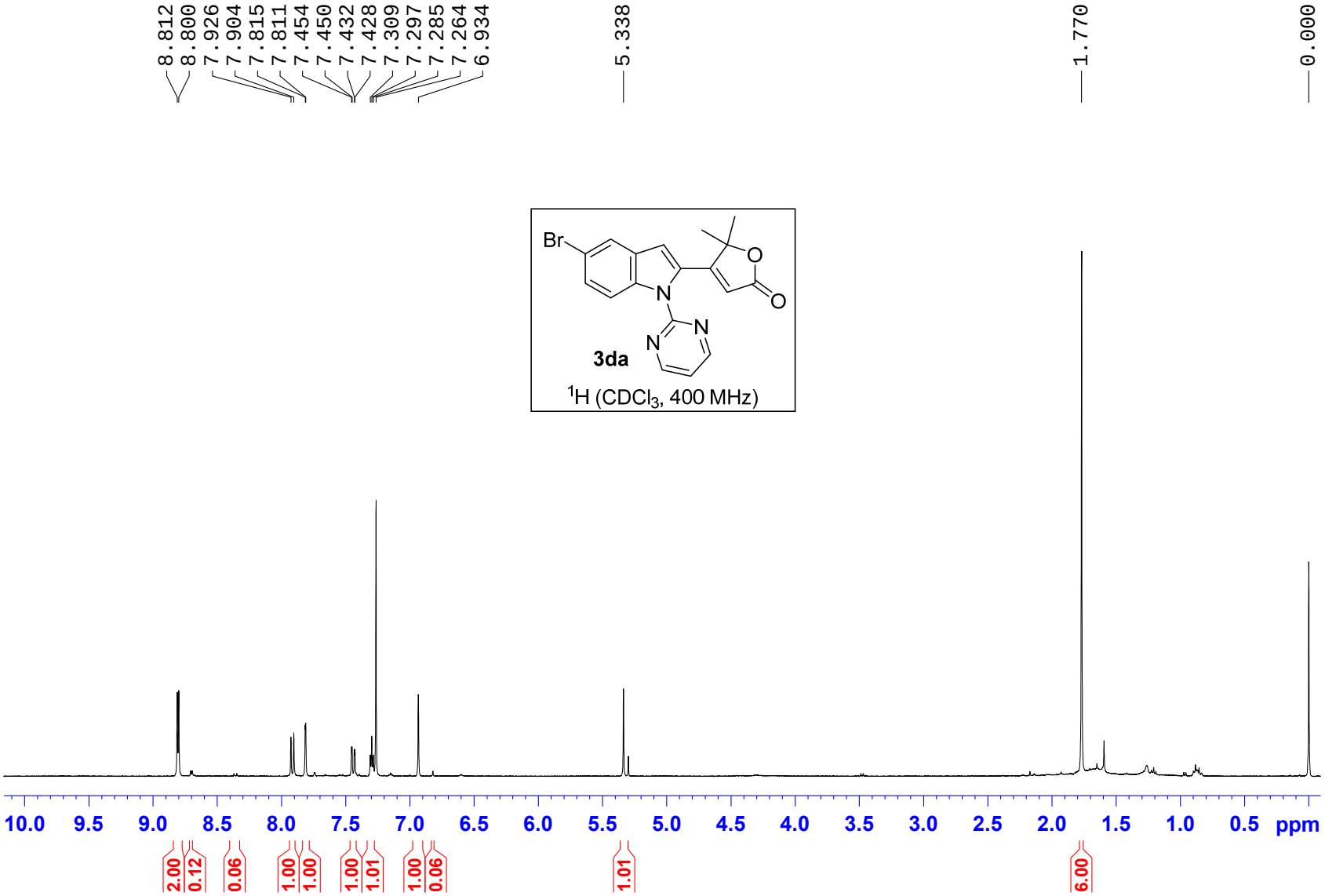
163.79
158.74
158.72
157.55
141.35
138.62
136.28
130.18
128.82
127.29
127.00
125.66
119.94
118.79
116.40
113.18
111.41
87.87
77.36
77.04
76.72
26.44
O
O
N
N
N
3ca
1H (CDCl3, 400 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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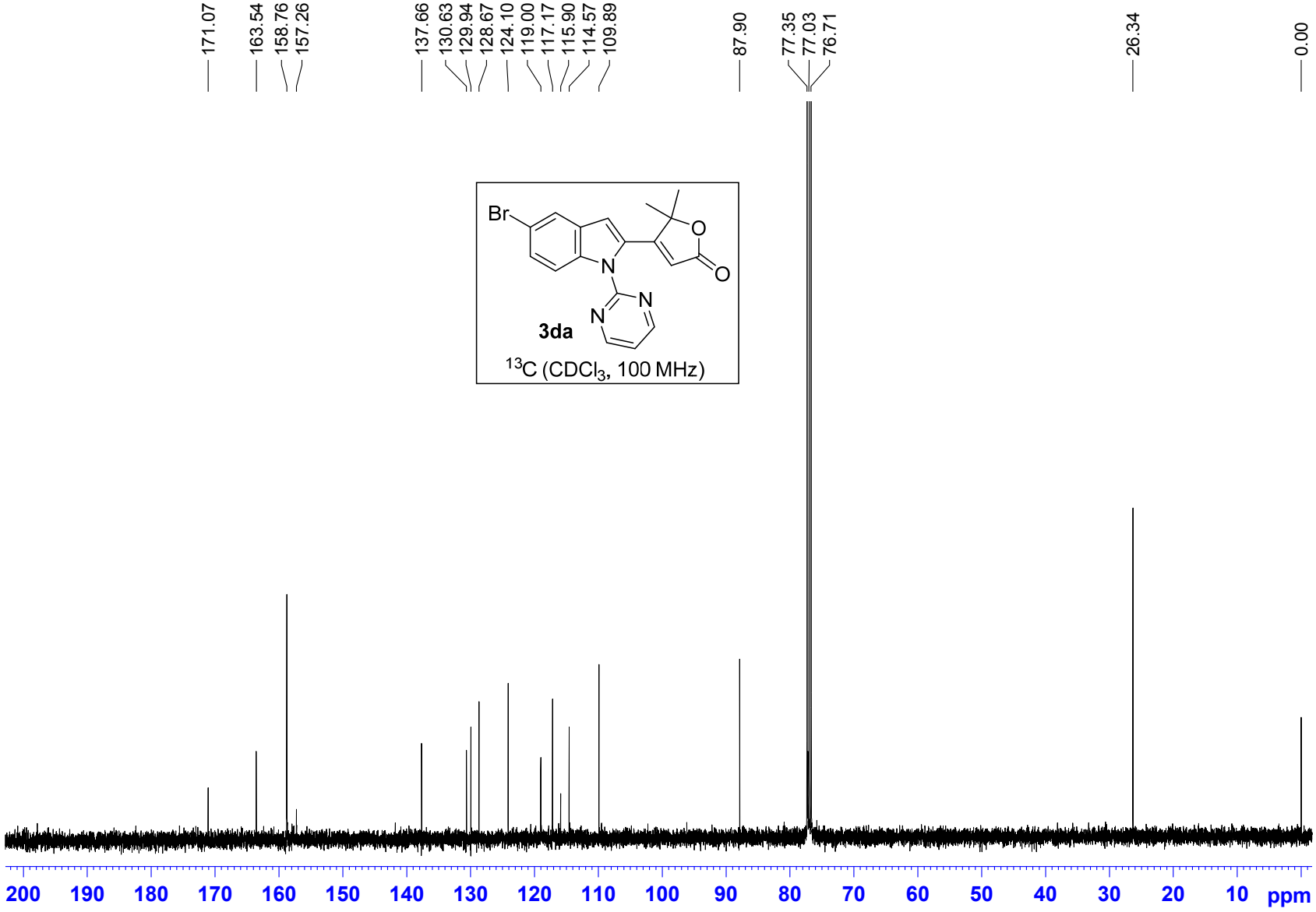
8.800
7.926
7.904
7.815
7.811
7.454
7.450
7.432
7.428
7.309
7.297
7.285
7.264
6.934
5.338
1.770
0.000
Br
O
O
N
N
N
3da
1H (CDCl3, 400 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
0.12
0.06
1.00
1.00
1.00
1.01
1.00
0.06
1.01
6.00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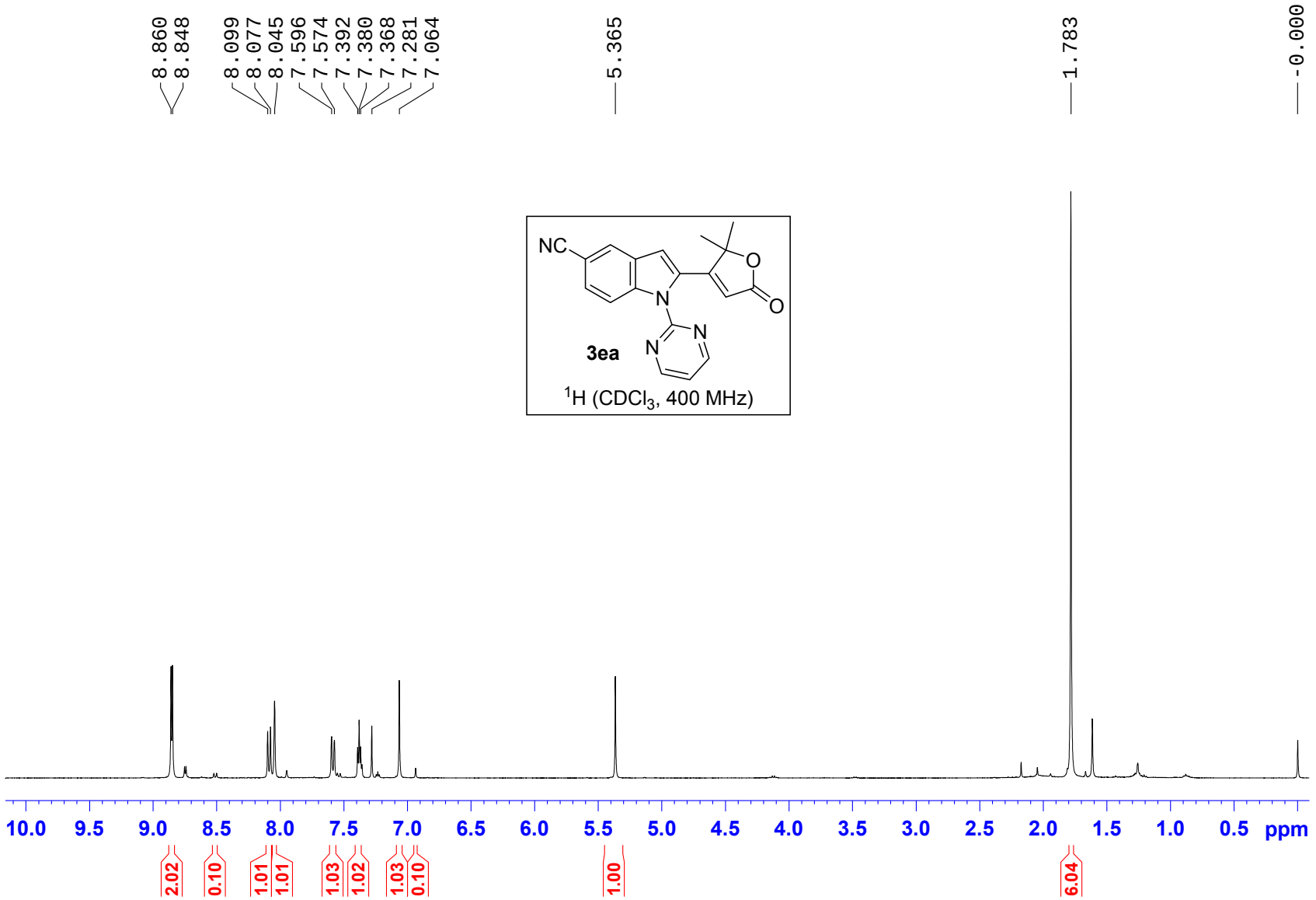
158.76
157.26
137.66
130.63
129.94
128.67
124.10
119.00
117.17
115.90
114.57
109.89
87.90
77.35
77.03
76.71
26.34
0.00
Br
O
O
N
N
N
3da
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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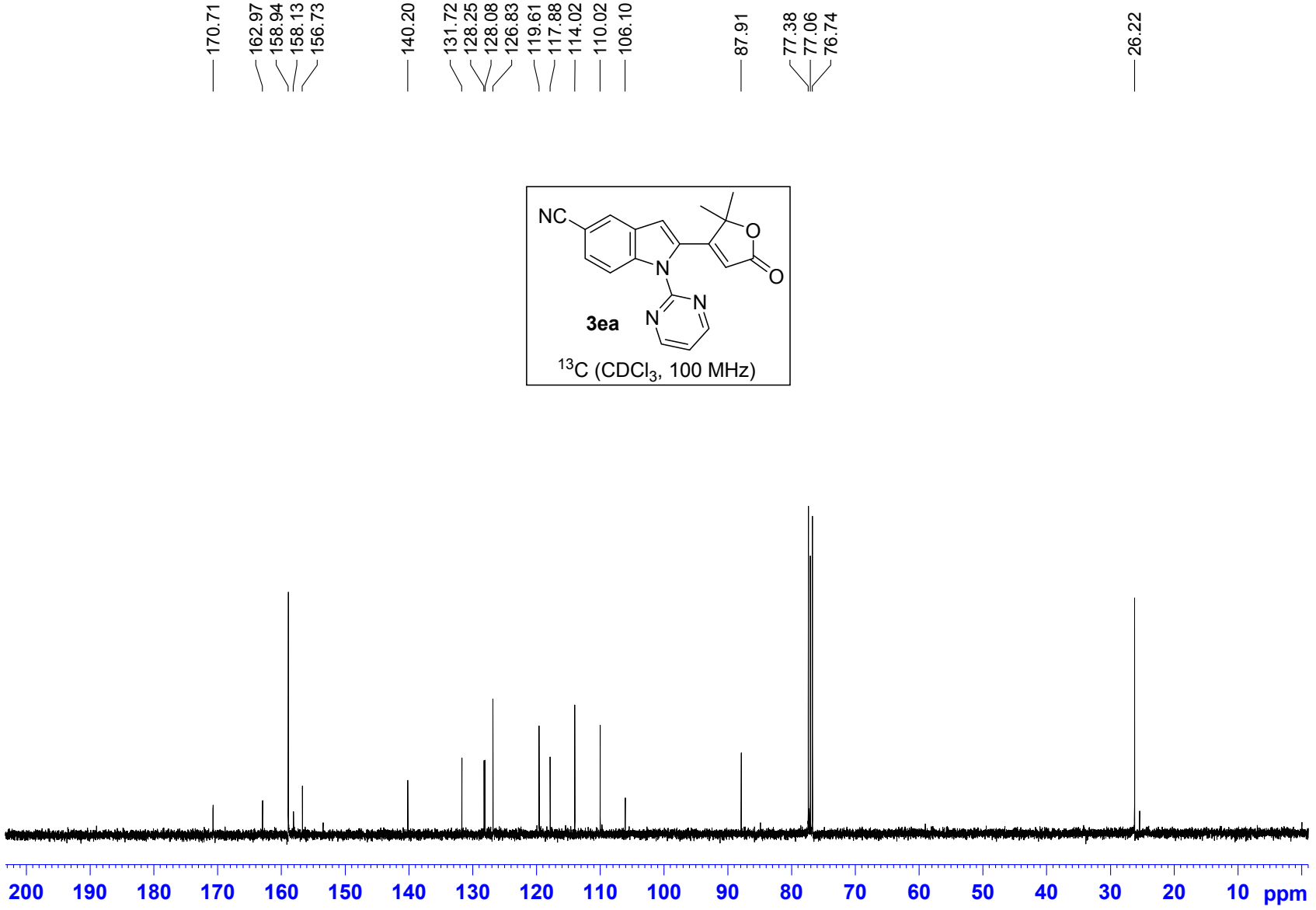
7.392
7.380
7.368
7.281
7.064
5.365
1.783
-0.000
NC
O
O
N
N
N
3ea
1H (CDCl3, 400 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
0.10
1.01
1.01
1.03
1.02
1.03
0.10
1.00
6.04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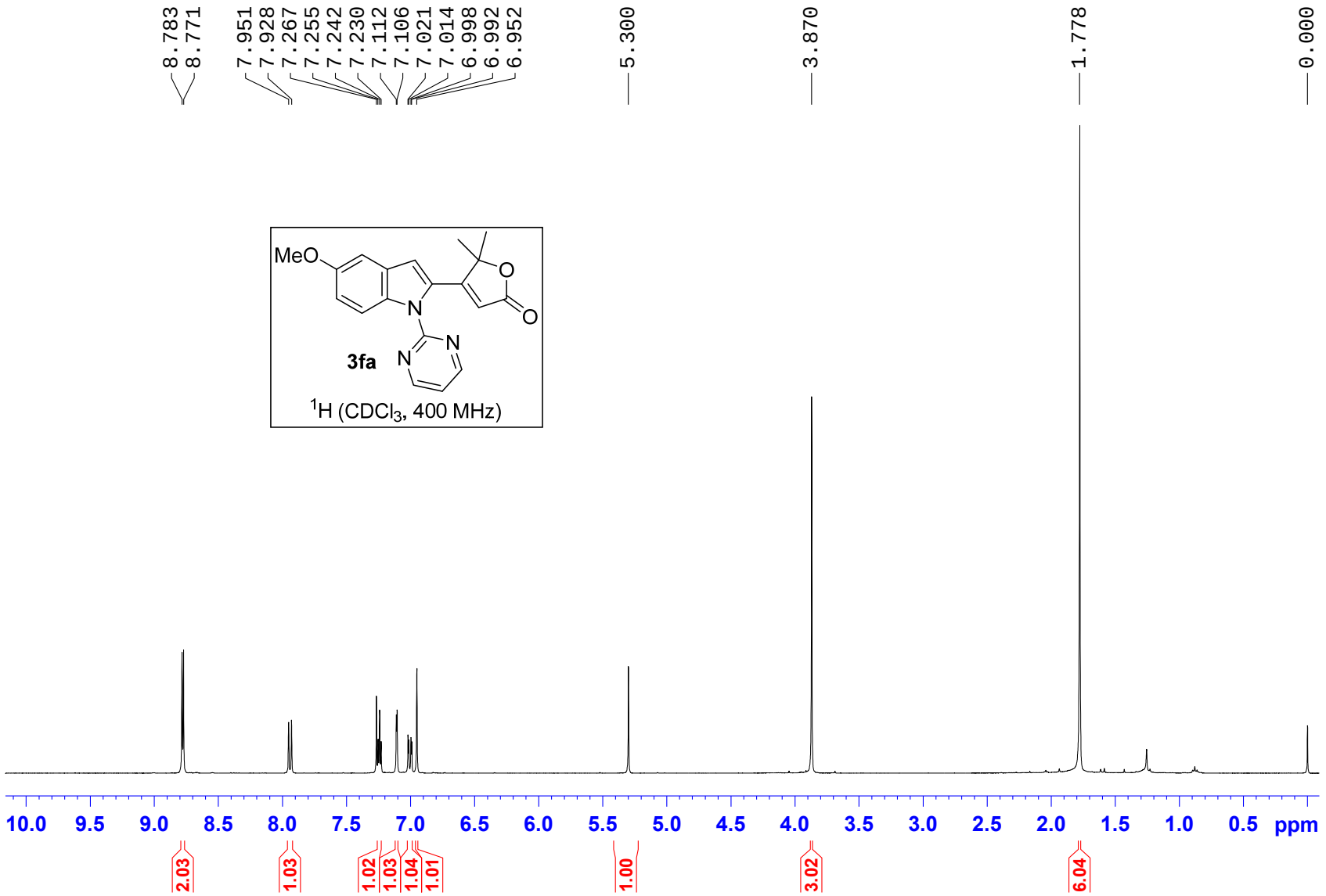
158.94
158.13
156.73
140.20
131.72
128.25
128.08
126.83
119.61
117.88
114.02
110.02
106.10
87.91
77.38
77.06
76.74
26.22
NC
O
O
N
N
N
3ea
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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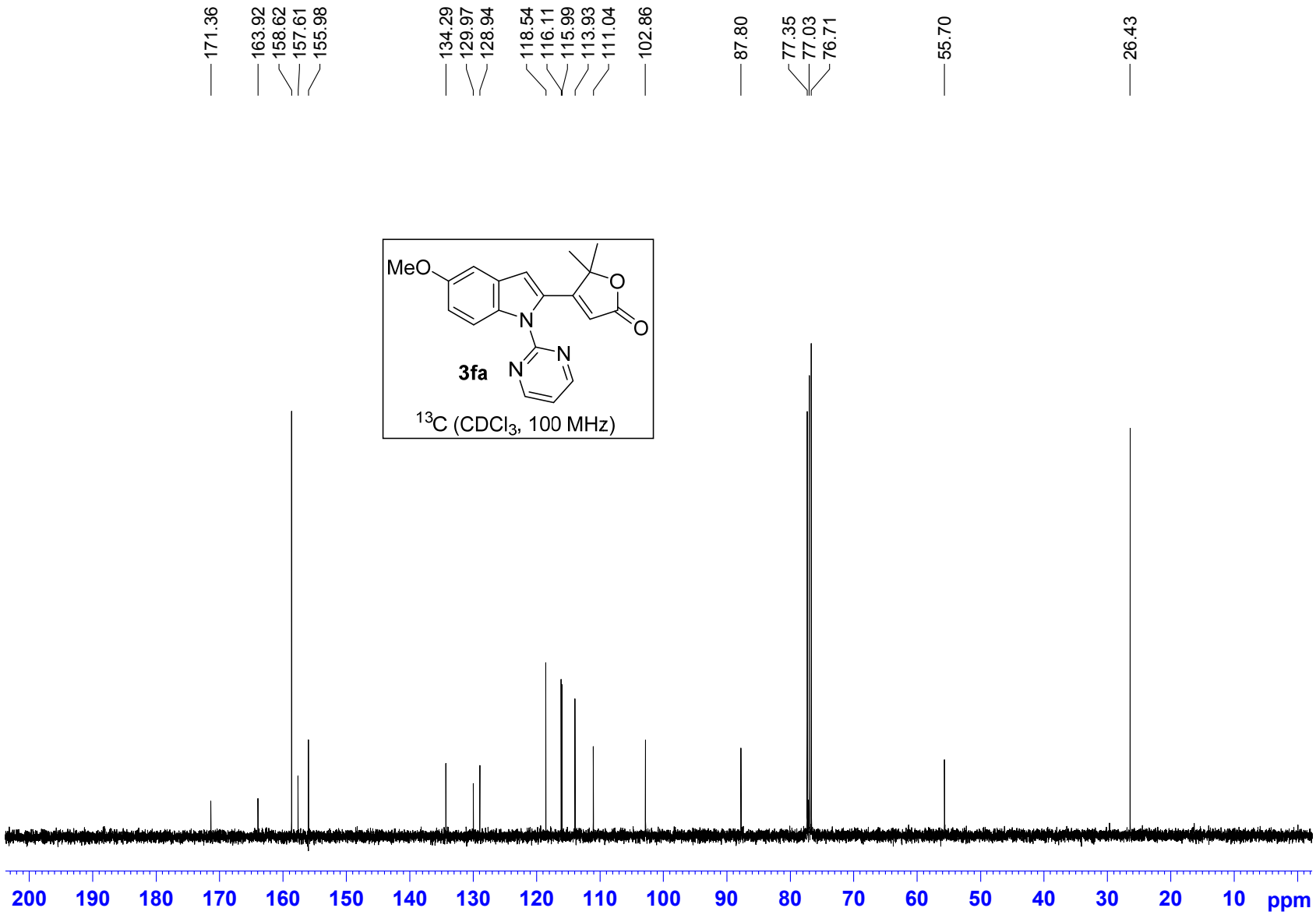
7.255
7.242
7.230
7.112
7.106
7.021
7.014
6.998
6.992
6.952
5.300
3.870
1.778
0.000
MeO
O
O
N
N
N
3fa
^{1}H (CDCl$_3$, 400 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
1.03
1.02
1.03
1.04
1.01
1.00
3.02
6.04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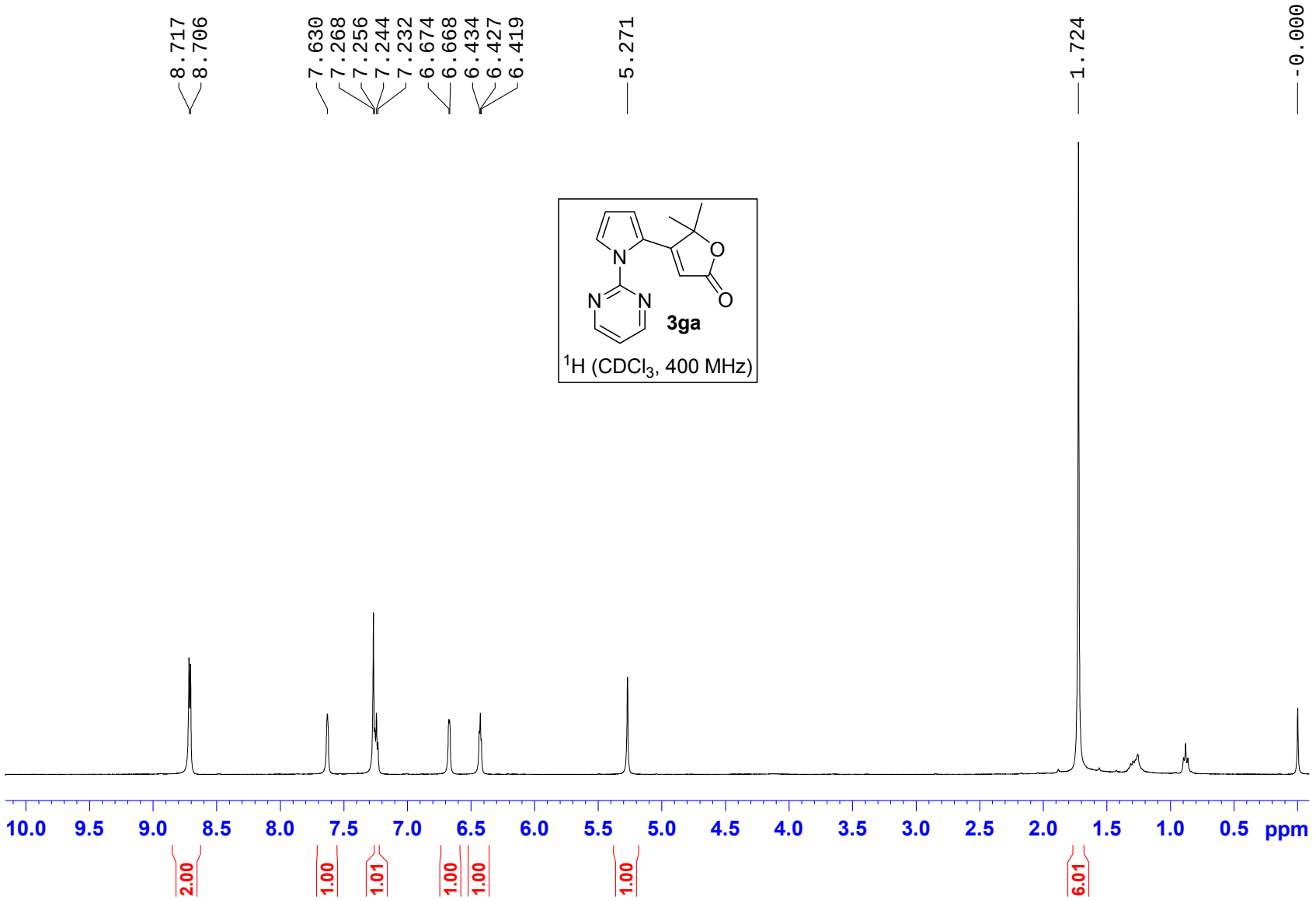
157.61
155.98
134.29
129.97
128.94
118.54
116.11
115.99
113.93
111.04
102.86
87.80
77.35
77.03
76.71
55.70
26.43
MeO
O
O
N
N
N
3fa
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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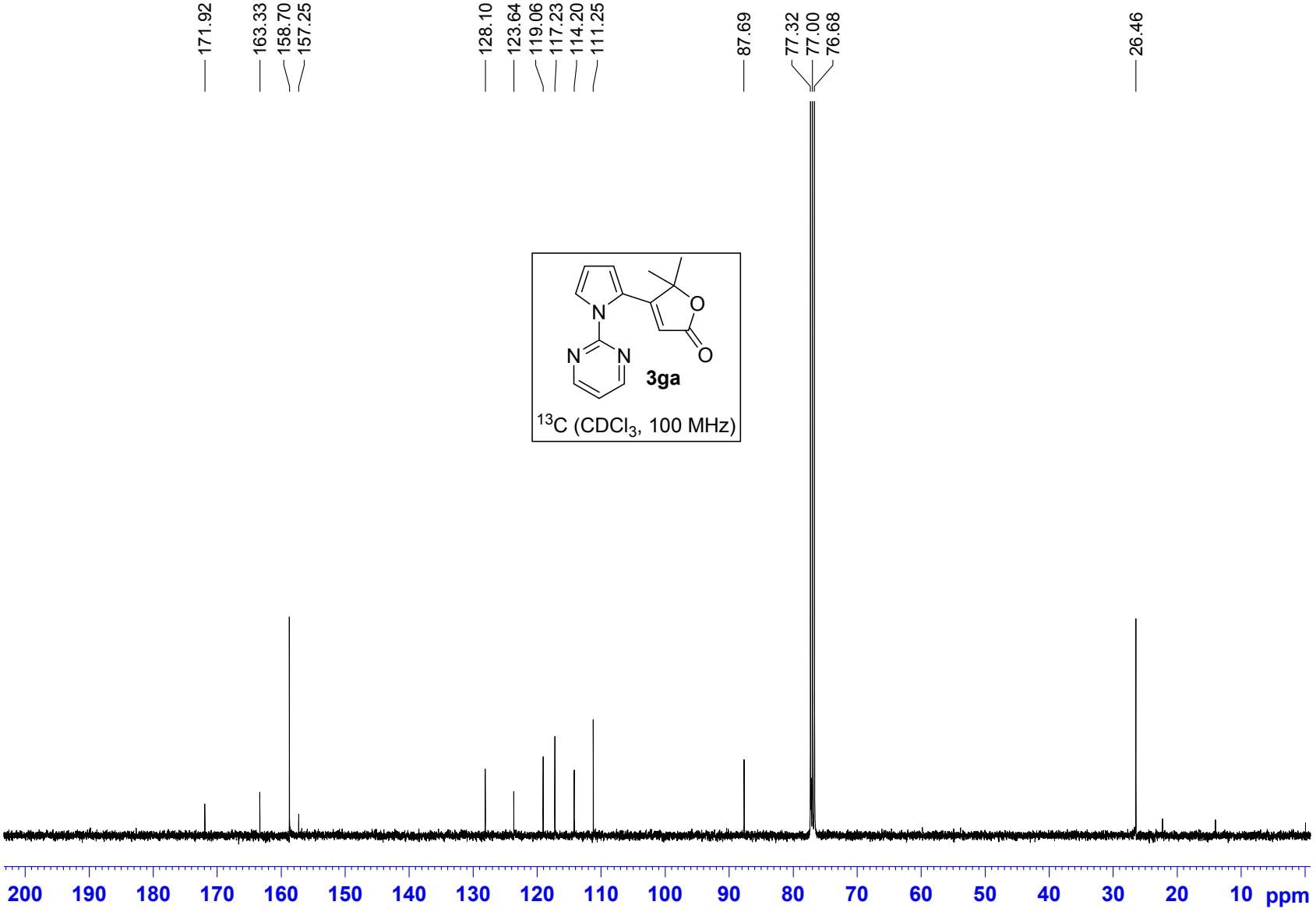
7.256
7.244
7.232
6.674
6.668
6.434
6.427
6.419
5.271
1.724
-0.000
3ga
1H (CDCl3, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.00
1.01
1.00
1.00
1.00
6.01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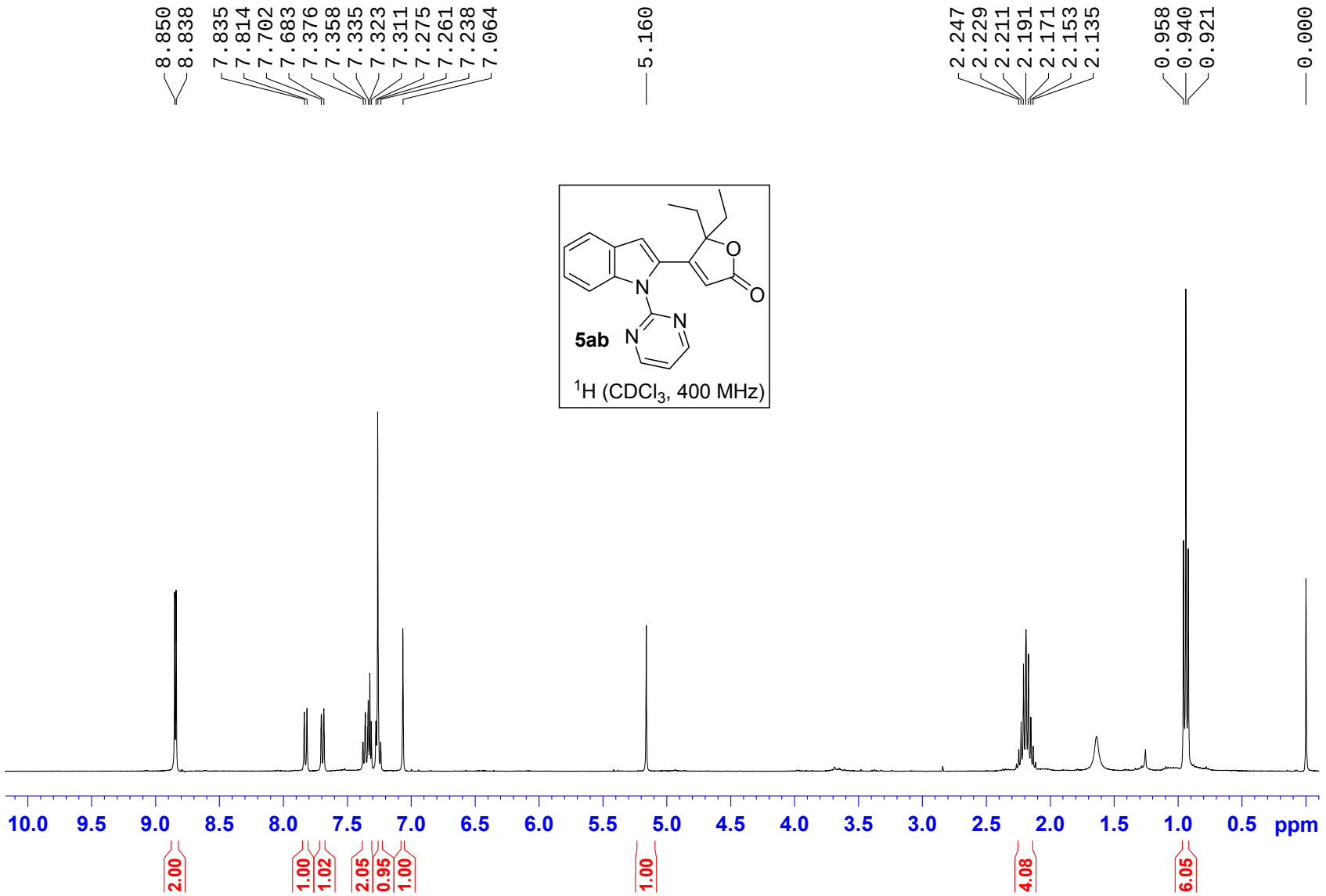
128.10
123.64
119.06
117.23
114.20
111.25
87.69
77.32
77.00
76.68
26.46
N
N
N
O
O
3ga
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.702
7.683
7.376
7.358
7.335
7.323
7.311
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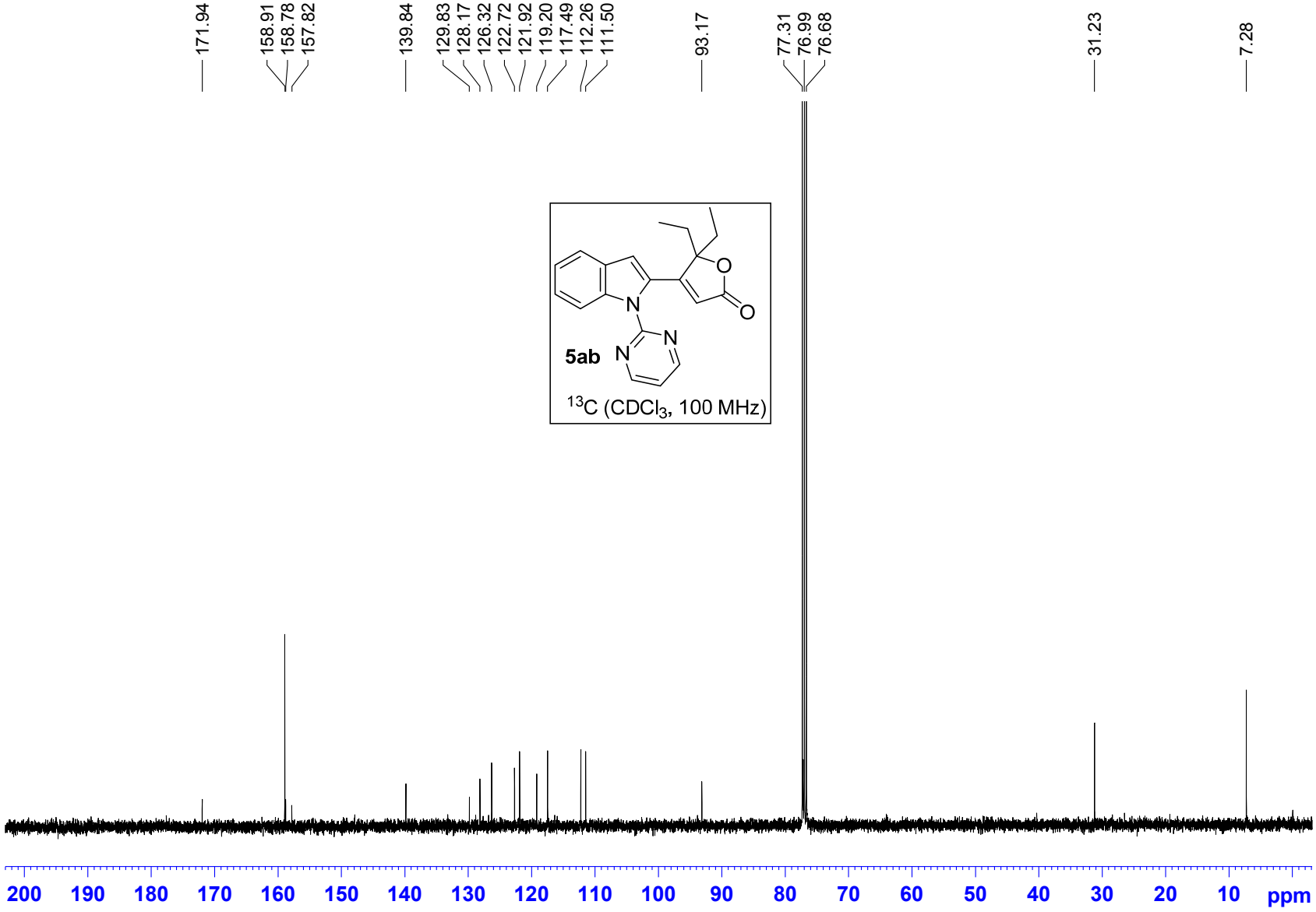
7.261
7.238
7.064
5.160
2.247
2.229
2.211
2.191
2.171
2.153
2.135
0.958
0.940
0.921
0.000
5ab
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.00
1.02
2.05
0.95
1.00
1.00
4.08
6.05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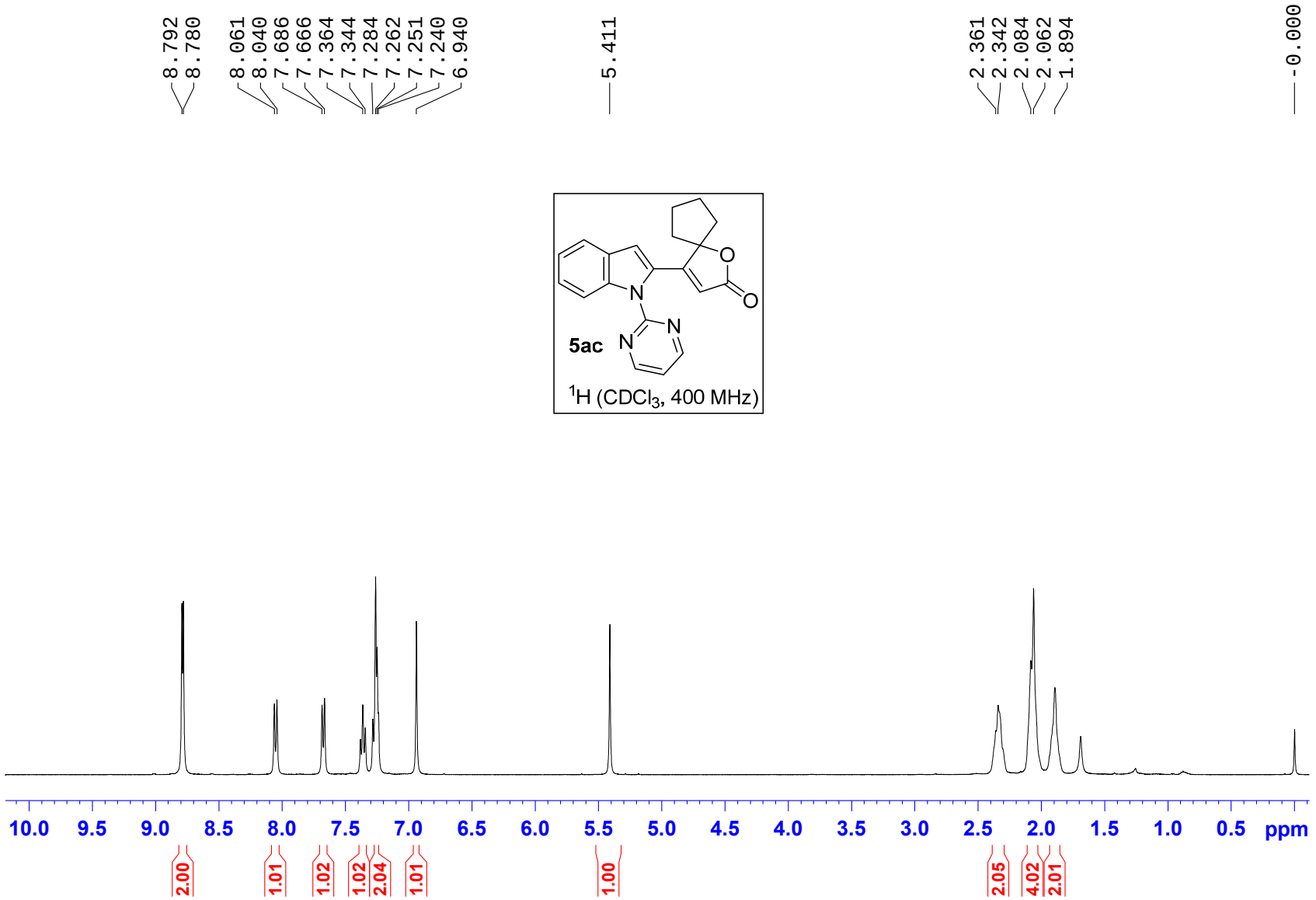
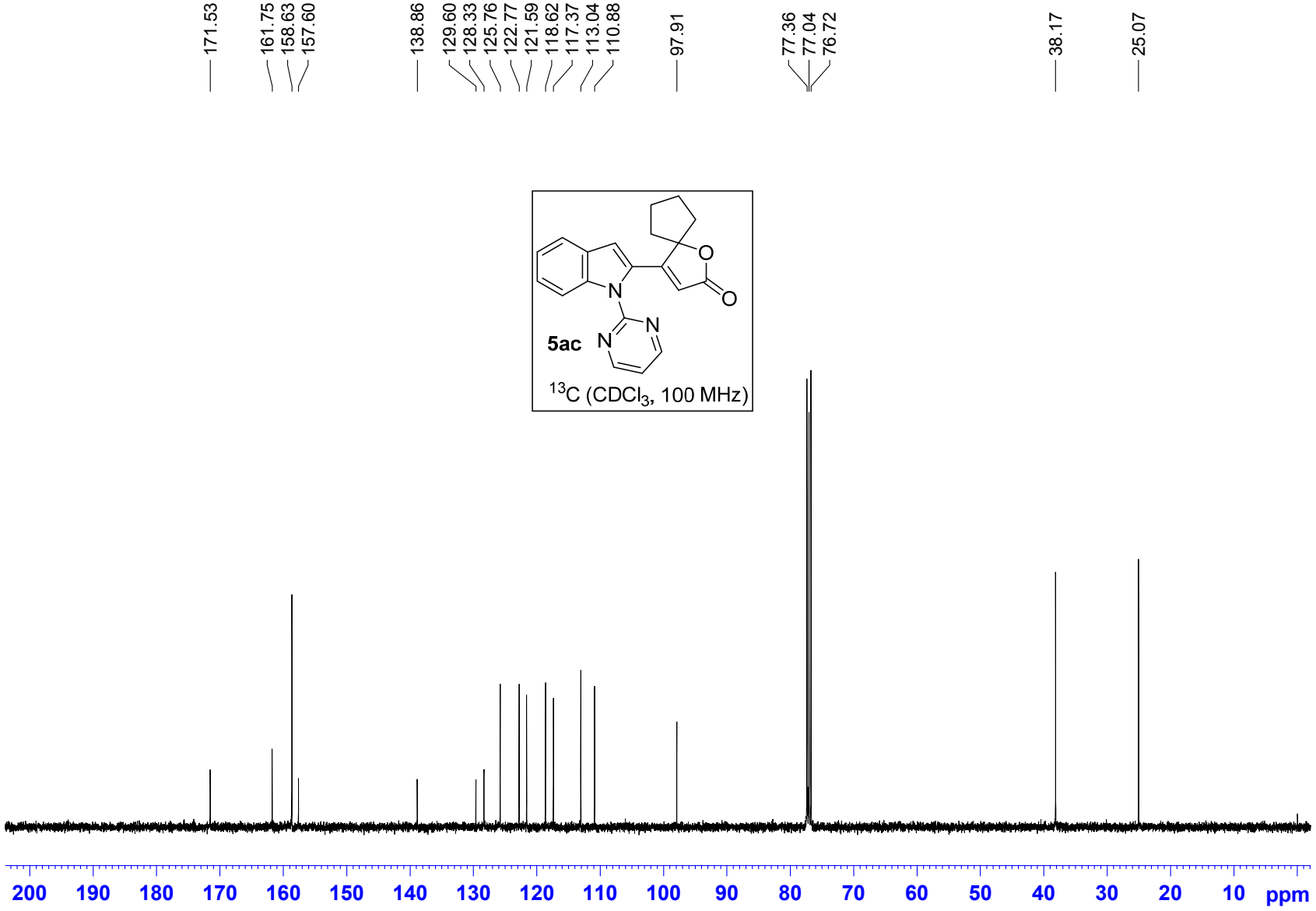
158.91
158.78
157.82
139.84
129.83
128.17
126.32
122.72
121.92
119.20
117.49
112.26
111.50
93.17
77.31
76.99
76.68
31.23
7.28
O
O
N
N
N
5ab
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.792
8.780
8.061
8.040
7.686
7.666
7.364
7.344
7.284
7.262
7.251
7.240
6.940
5.411
2.361
2.342
2.084
2.062
1.894
-0.000
O
O
N
N
N
5ac
^{1}H (CDCl$_3$, 400 MHz)
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
ppm
2.00
1.01
1.02
1.02
2.04
1.01
1.00
2.05
4.02
2.01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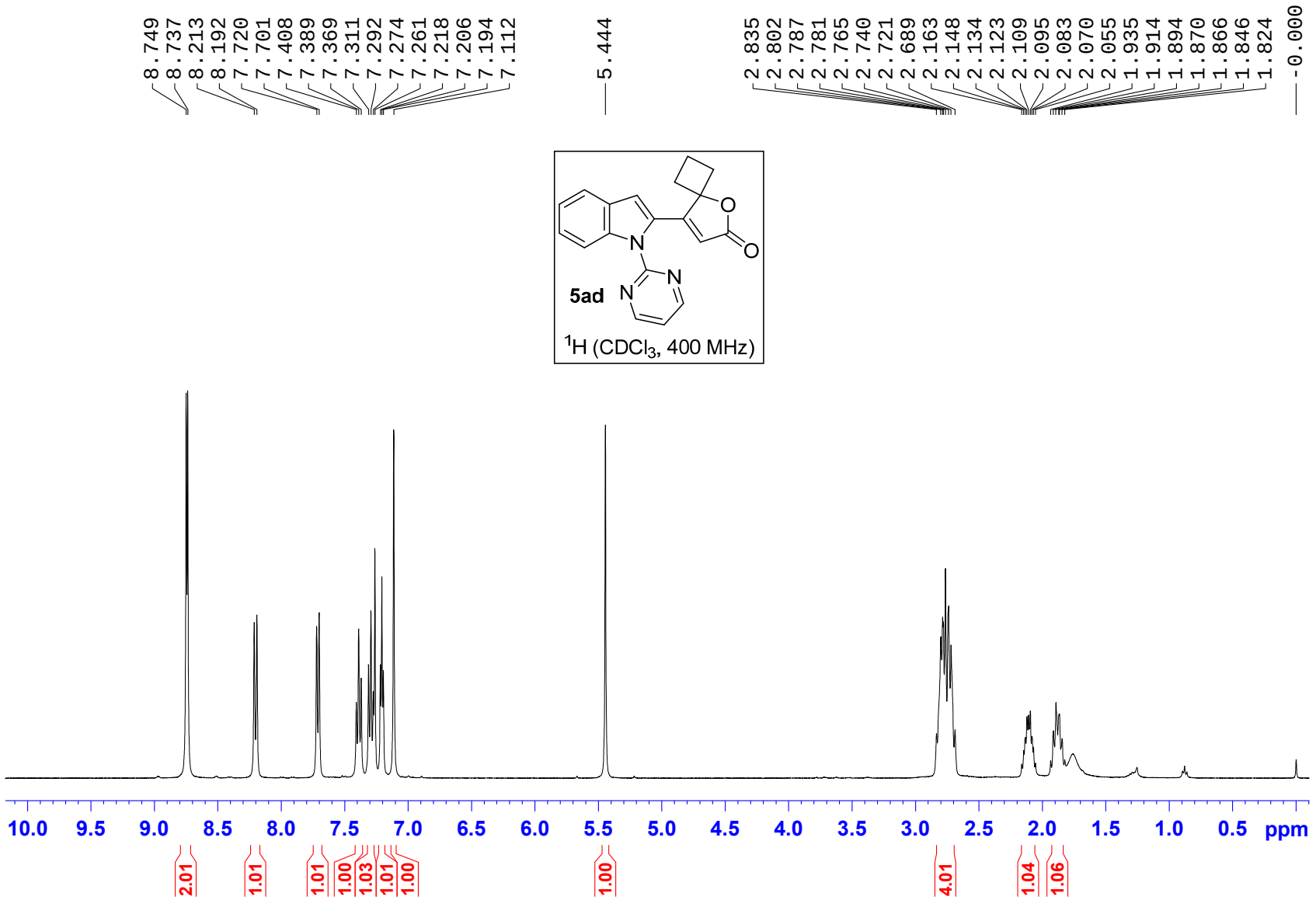
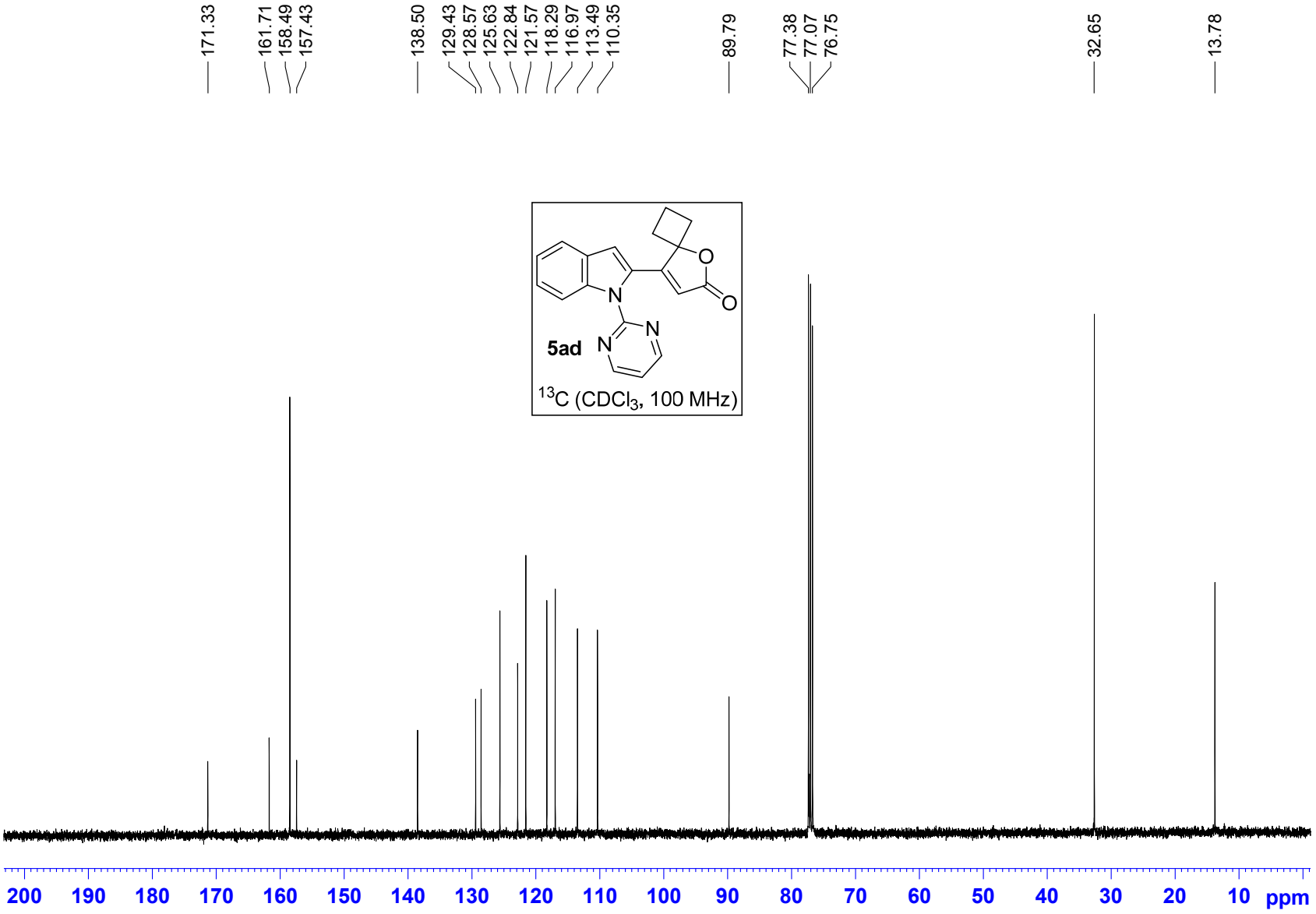
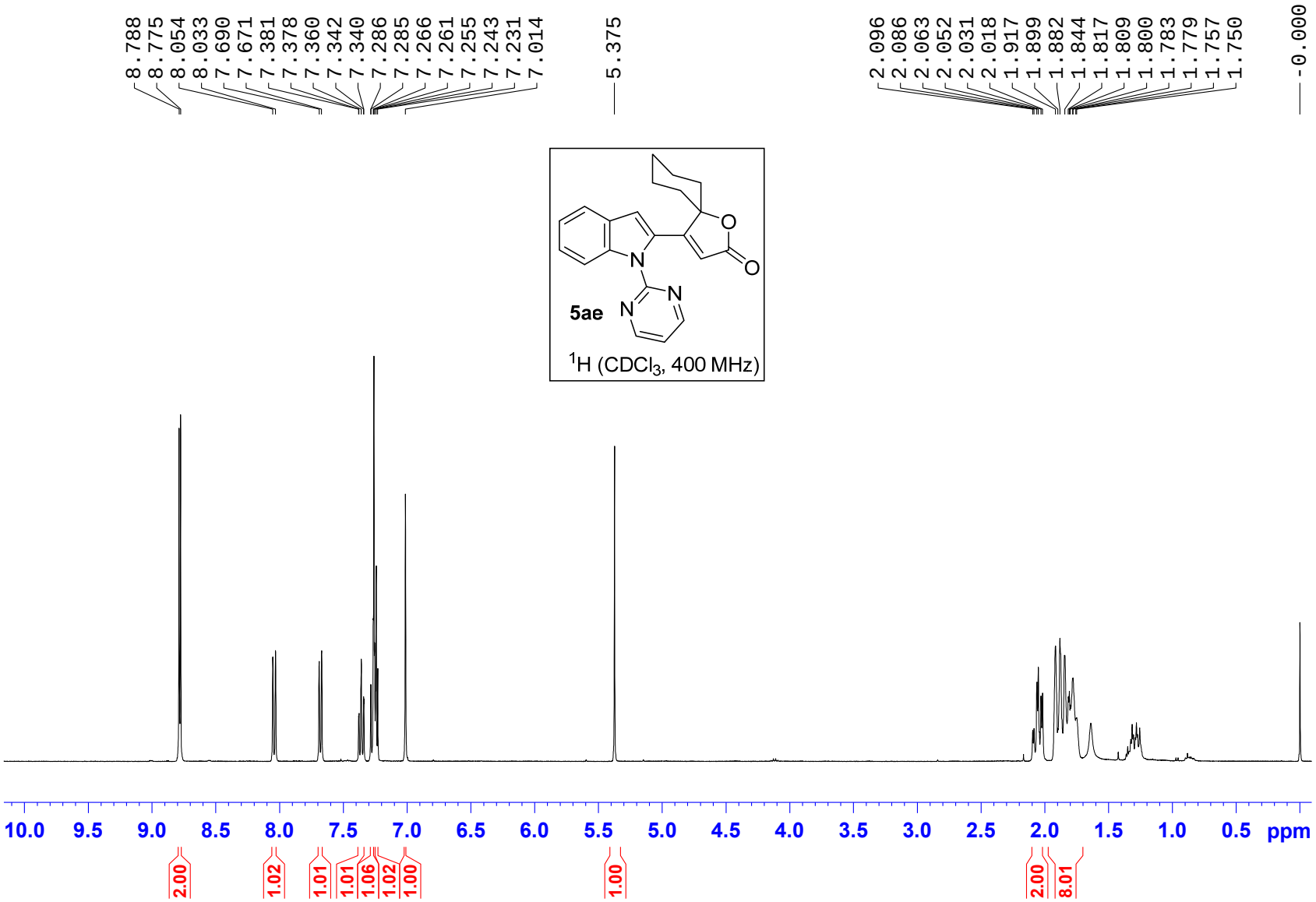
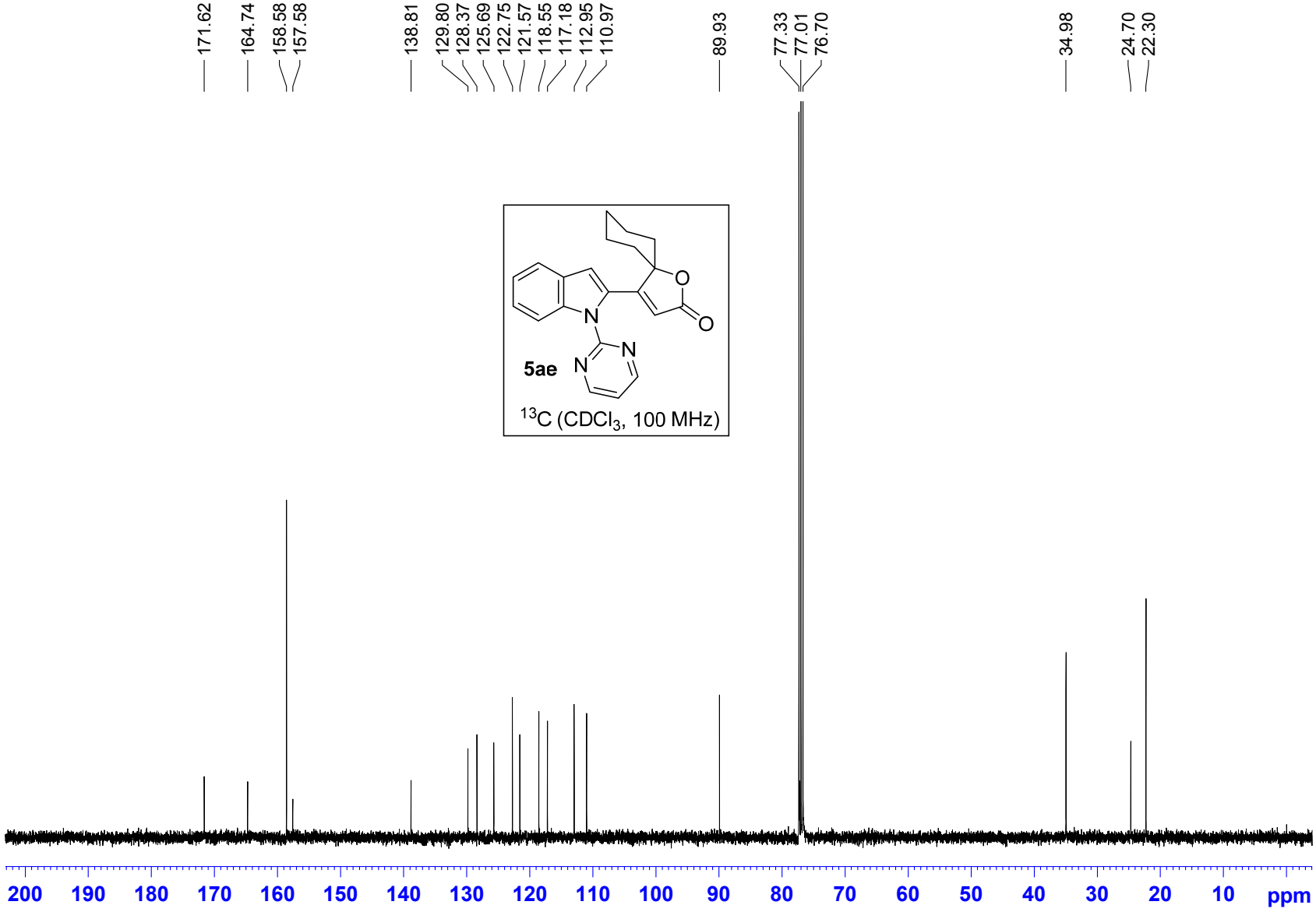
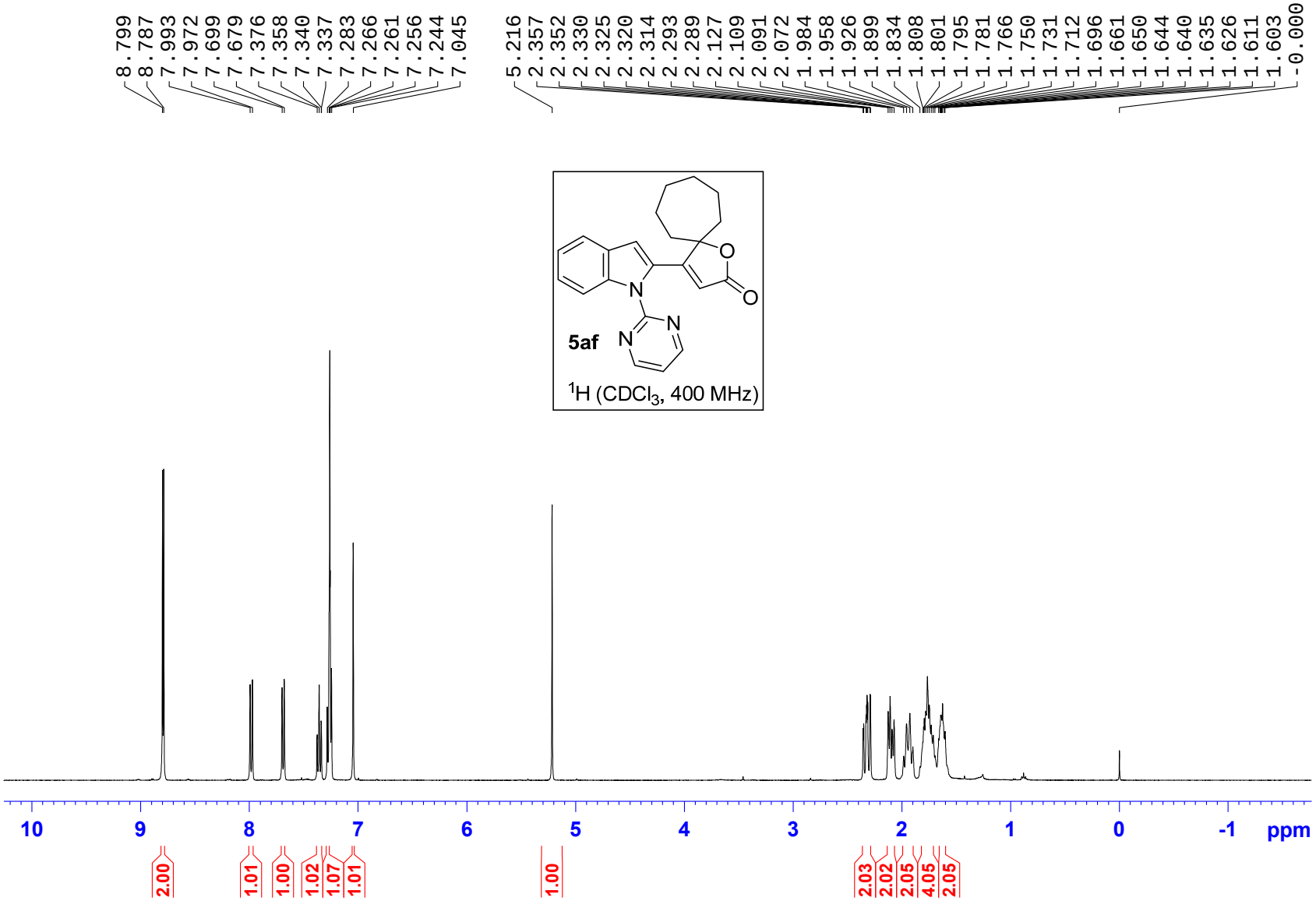
161.75
158.63
157.60
138.86
129.60
128.33
125.76
122.77
121.59
118.62
117.37
113.04
110.88
97.91
77.36
77.04
76.72
38.17
25.07
O
O
N
N
N
5ac
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

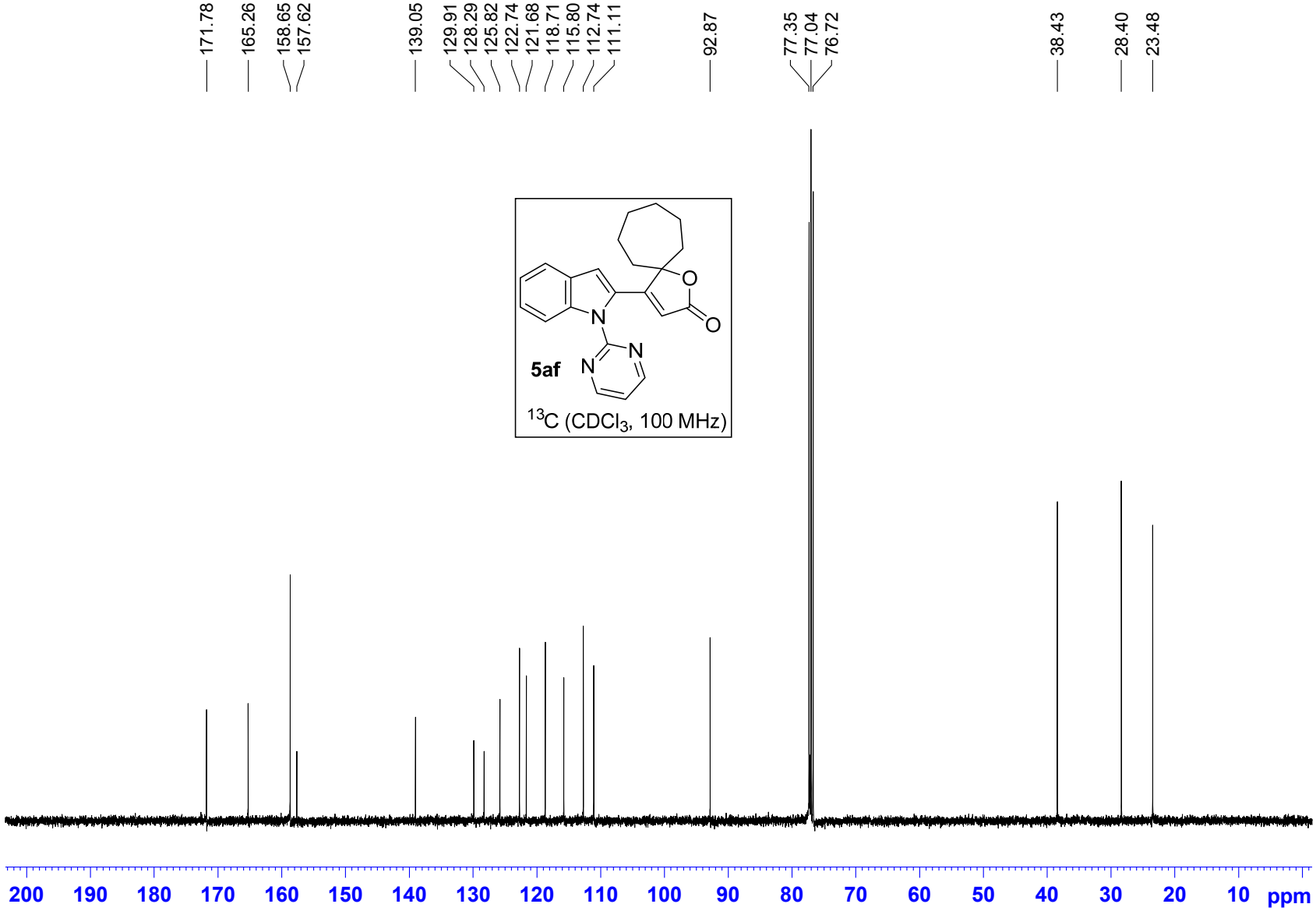

8.749
8.737
8.213
8.192
7.720
7.701
7.408
7.389
7.369
7.311
7.292
7.274
7.261
7.218
7.206
7.194
7.112
5.444
2.835
2.802
2.787
2.781
2.765
2.740
2.721
2.689
2.163
2.148
2.134
2.123
2.109
2.095
2.083
2.070
2.055
1.935
1.914
1.894
1.870
1.866
1.846
1.824
-0.000
O
O
N
N
N
5ad
^{1}H (CDCl$_3$, 400 MHz)
10.0
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
ppm
2.01
1.01
1.01
1.00
1.03
1.01
1.00
1.00
4.01
1.04
1.06

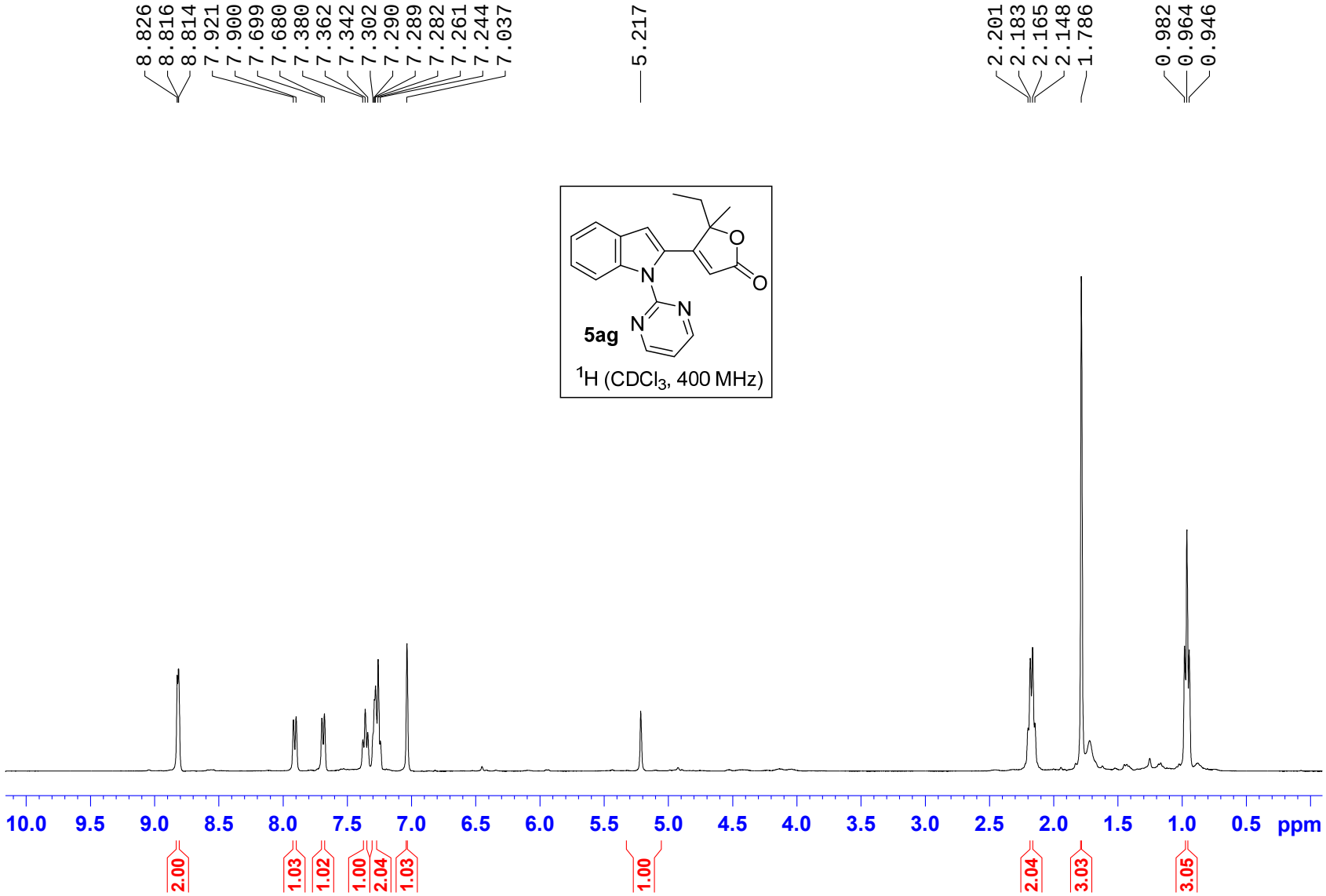

171.33
161.71
158.49
157.43
138.50
129.43
128.57
125.63
122.84
121.57
118.29
116.97
113.49
110.35
89.79
77.38
77.07
76.75
32.65
13.78
O
O
N
N
N
5ad
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

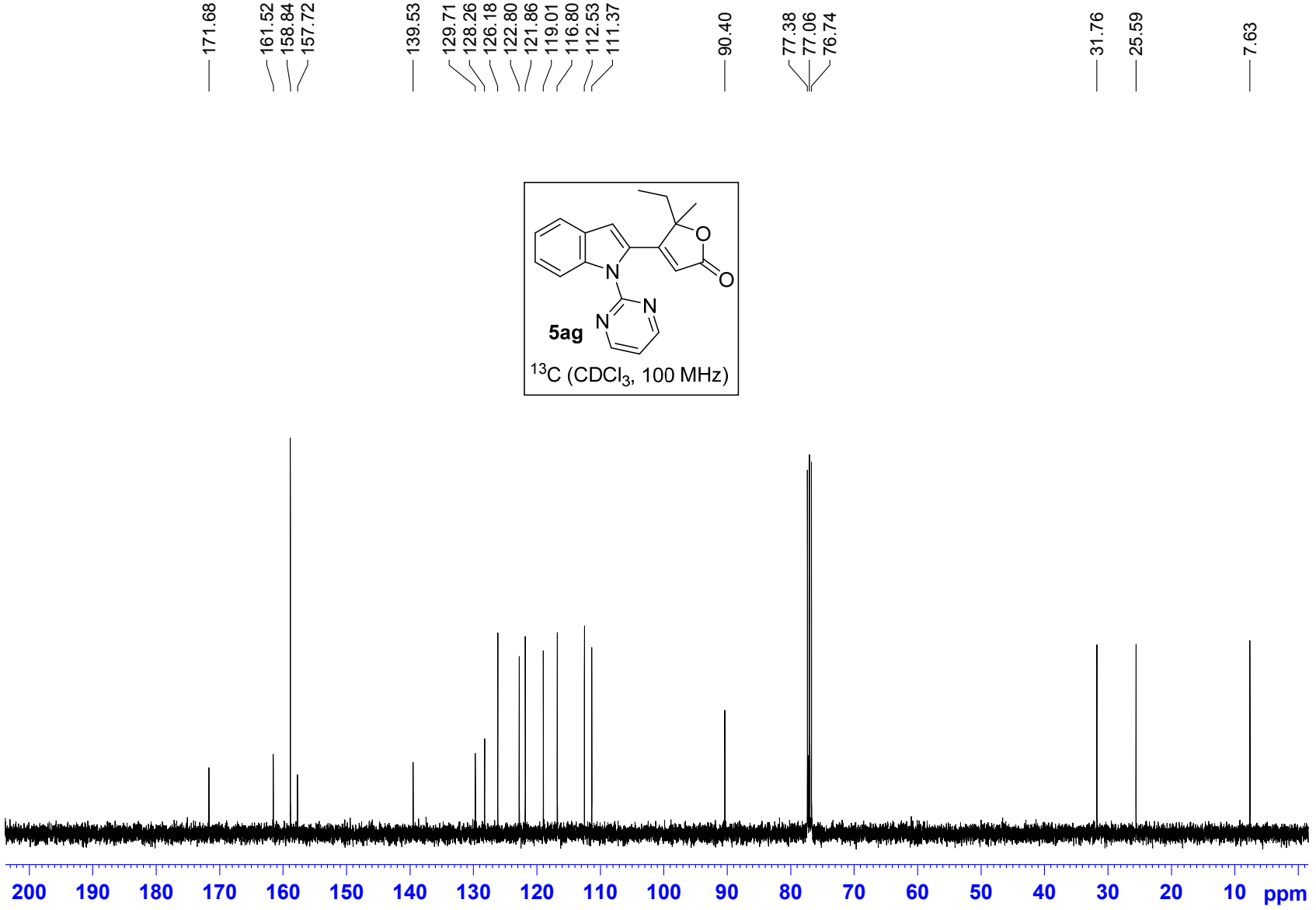

8.788
8.775
8.054
8.033
7.690
7.671
7.381
7.378
7.360
7.342
7.340
7.286
7.285
7.266
7.261
7.255
7.243
7.231
7.014
5.375
2.096
2.086
2.063
2.052
2.031
2.018
1.917
1.899
1.882
1.844
1.817
1.809
1.800
1.783
1.779
1.757
1.750
-0.000
5ae
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.02
1.01
1.01
1.06
1.02
1.00
1.00
2.00
8.01

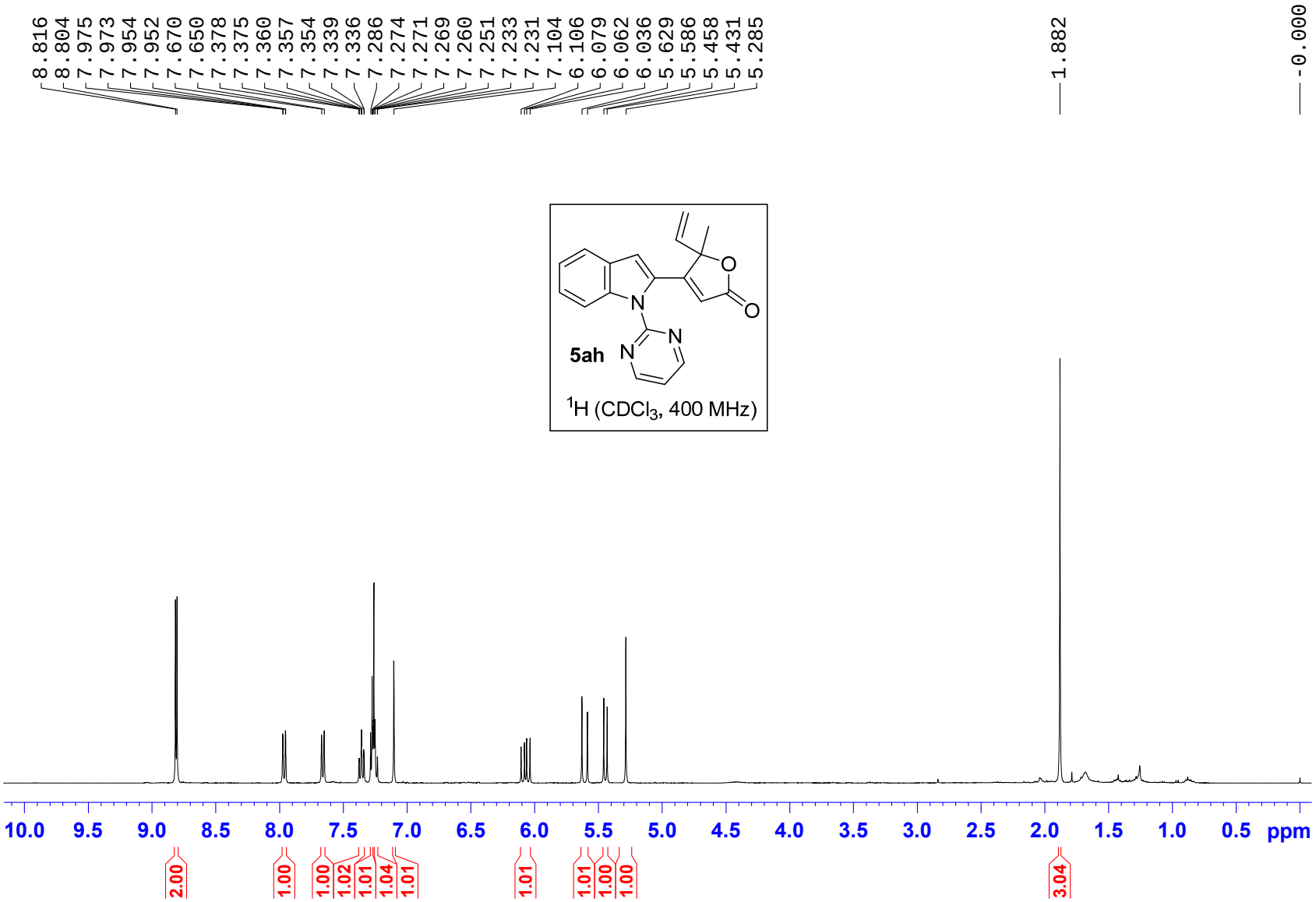

171.62
164.74
158.58
157.58
138.81
129.80
128.37
125.69
122.75
121.57
118.55
117.18
112.95
110.97
89.93
77.33
77.01
76.70
34.98
24.70
22.30
O
O
N
N
N
5ae
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

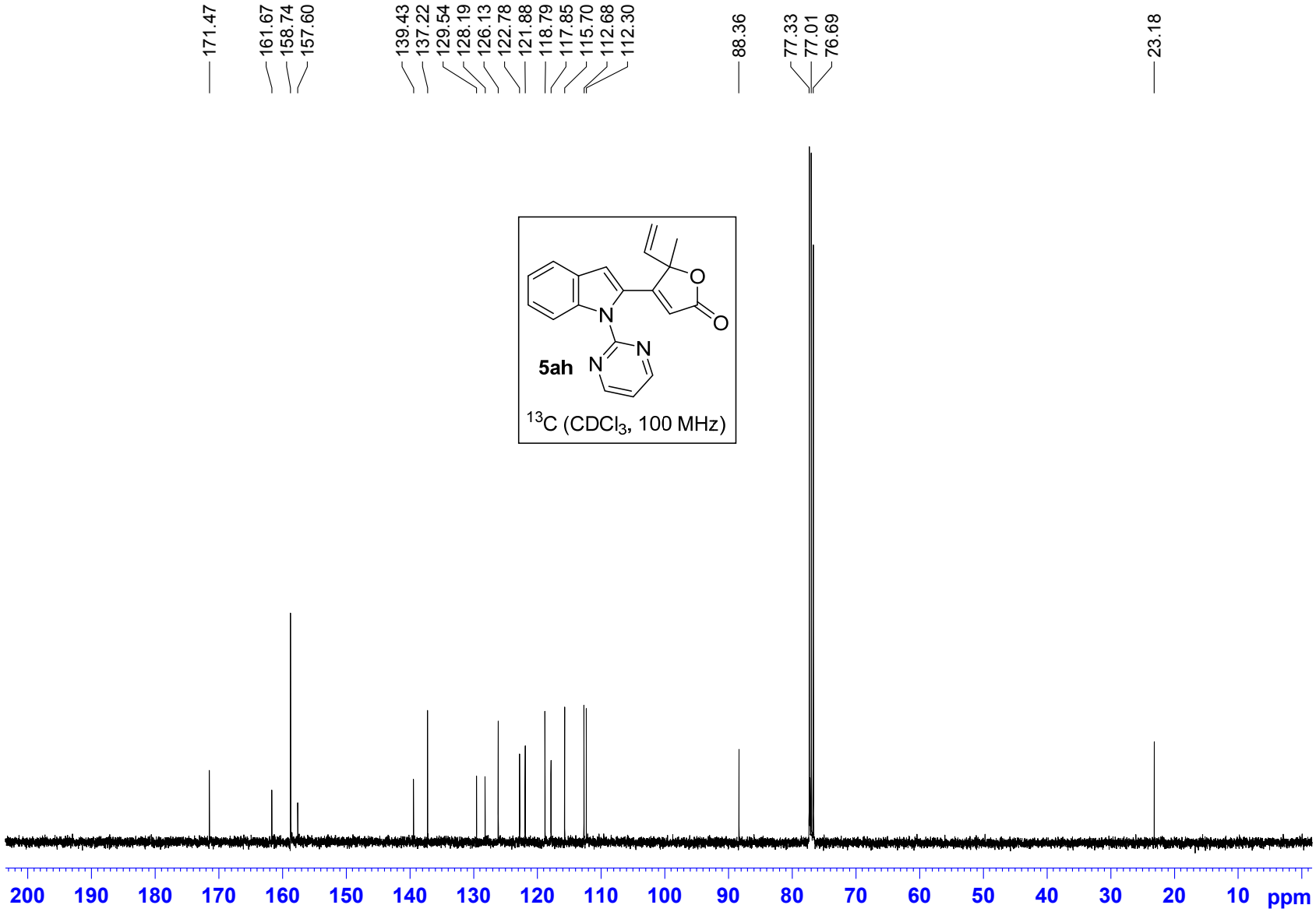

8.799
8.787
7.993
7.972
7.699
7.679
7.376
7.358
7.340
7.337
7.283
7.266
7.261
7.256
7.244
7.045
5.216
2.357
2.352
2.330
2.325
2.320
2.314
2.293
2.289
2.127
2.109
2.091
2.072
1.984
1.958
1.926
1.899
1.834
1.808
1.801
1.795
1.781
1.766
1.750
1.731
1.712
1.696
1.661
1.650
1.644
1.640
1.635
1.626
1.611
1.603
-0.000
O
O
N
N
N
5af
1H (CDCl3, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.00
1.01
1.00
1.02
1.07
1.01
1.00
2.03
2.02
2.05
4.05
2.05

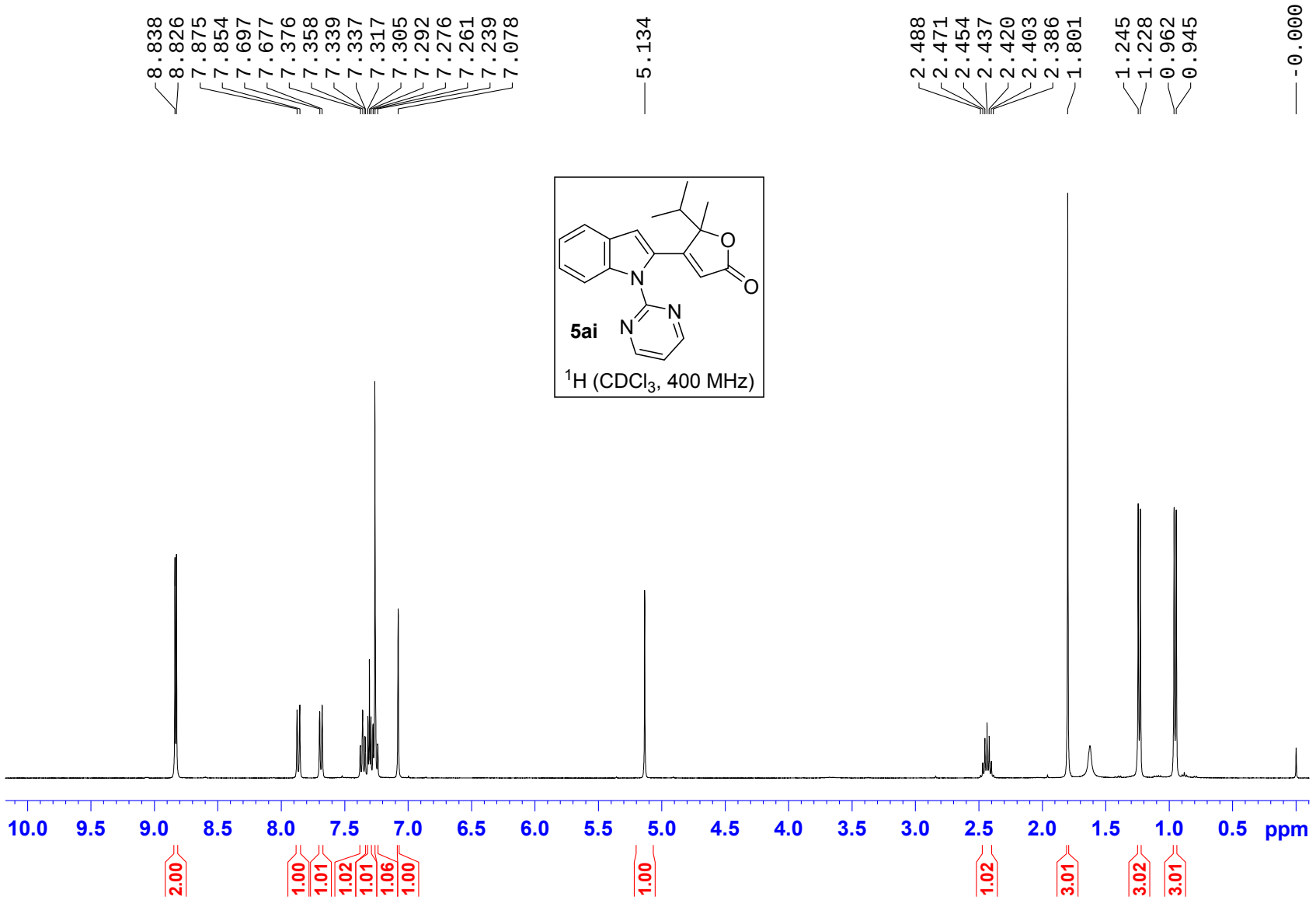

171.78
165.26
158.65
157.62
139.05
129.91
128.29
125.82
122.74
121.68
118.71
115.80
112.74
111.11
92.87
77.35
77.04
76.72
38.43
28.40
23.48
O
O
N
N
N
5af
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

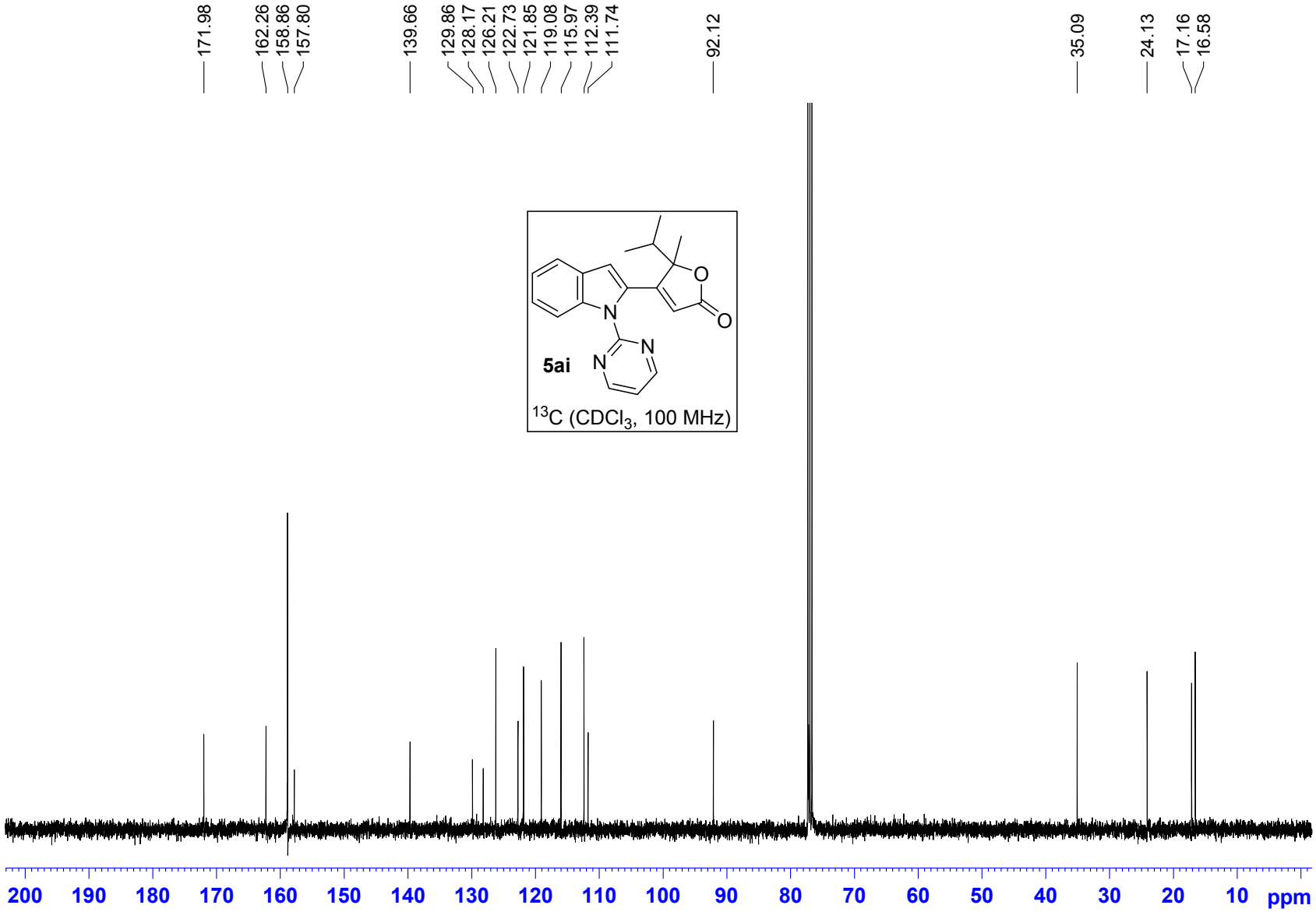

8.826
8.816
8.814
7.921
7.900
7.699
7.680
7.380
7.362
7.342
7.302
7.290
7.289
7.282
7.261
7.244
7.037
5.217
2.201
2.183
2.165
2.148
1.786
0.982
0.964
0.946
5ag
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.03
1.02
1.00
2.04
1.03
1.00
2.04
3.03
3.05

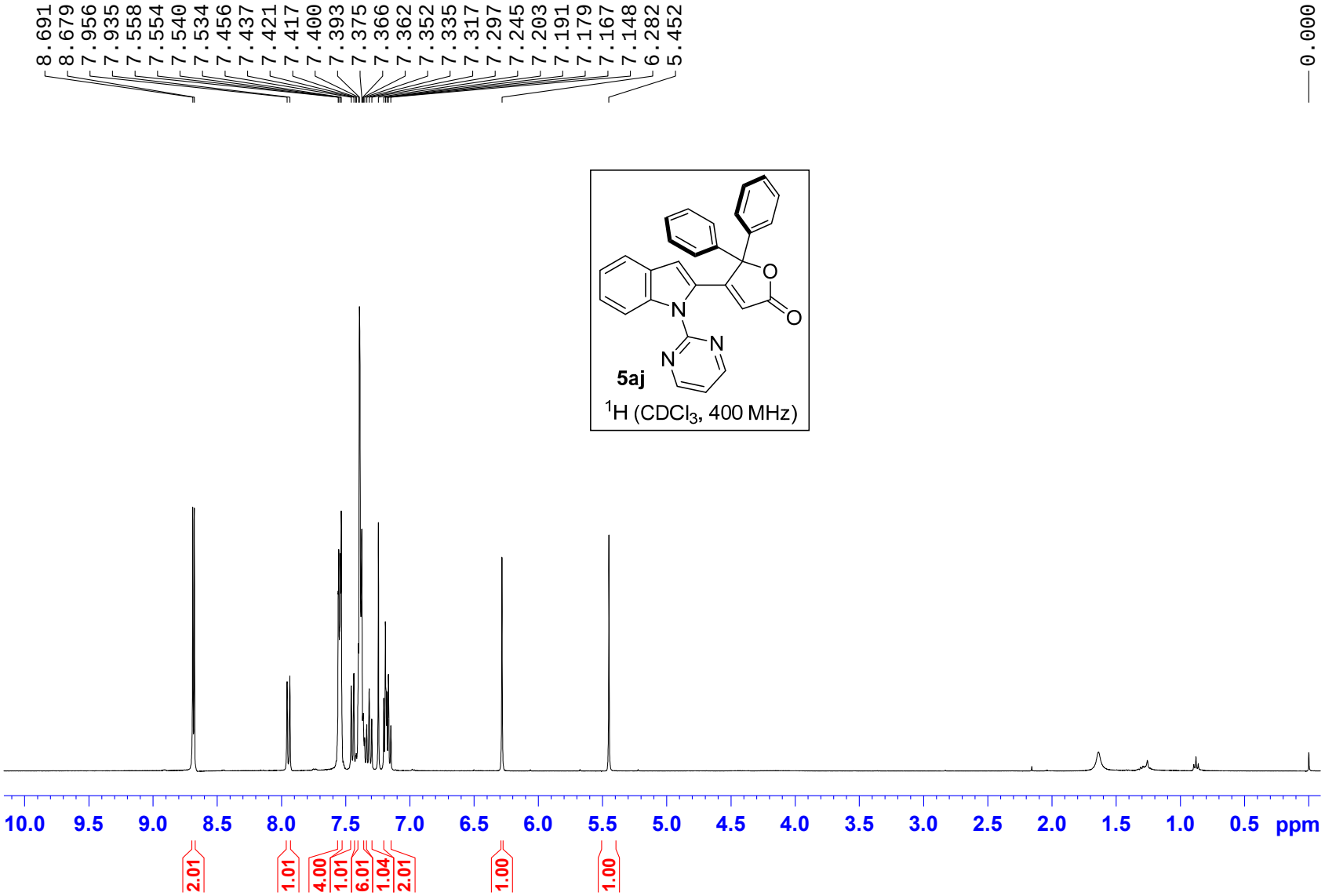

171.68
161.52
158.84
157.72
139.53
129.71
128.26
126.18
122.80
121.86
119.01
116.80
112.53
111.37
90.40
77.38
77.06
76.74
31.76
25.59
7.63
O
O
N
N
N
5ag
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

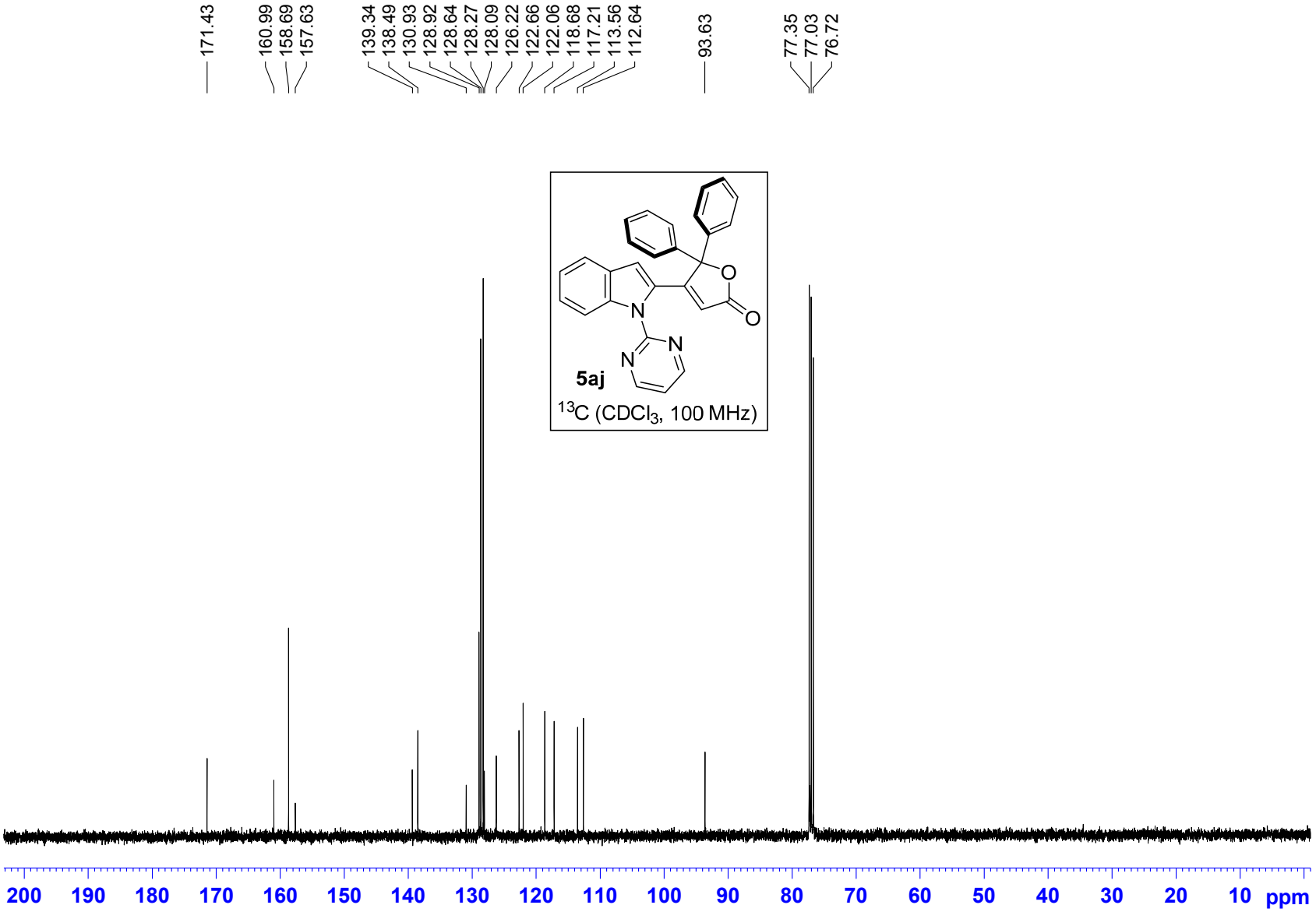

8.816
8.804
7.975
7.973
7.954
7.952
7.670
7.650
7.378
7.375
7.360
7.357
7.354
7.339
7.336
7.286
7.274
7.271
7.269
7.260
7.251
7.233
7.231
7.104
6.106
6.079
6.062
6.036
5.629
5.586
5.458
5.431
5.285
1.882
-0.000
5ah
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.00
1.00
1.02
1.01
1.04
1.01
1.01
1.01
1.00
1.00
3.04

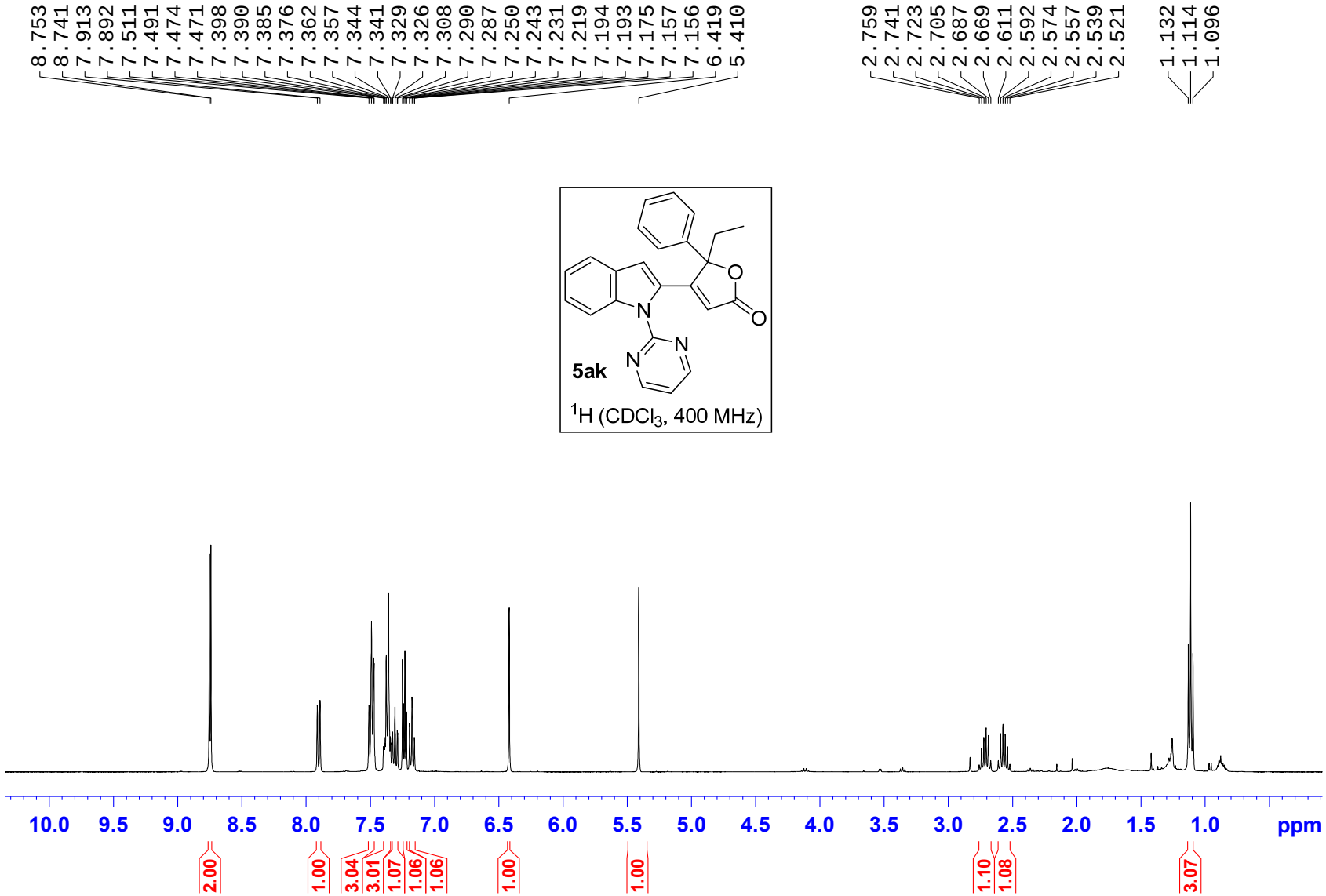

171.47
161.67
158.74
157.60
139.43
137.22
129.54
128.19
126.13
122.78
121.88
118.79
117.85
115.70
112.68
112.30
88.36
77.33
77.01
76.69
23.18
O
O
N
N
N
5ah
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

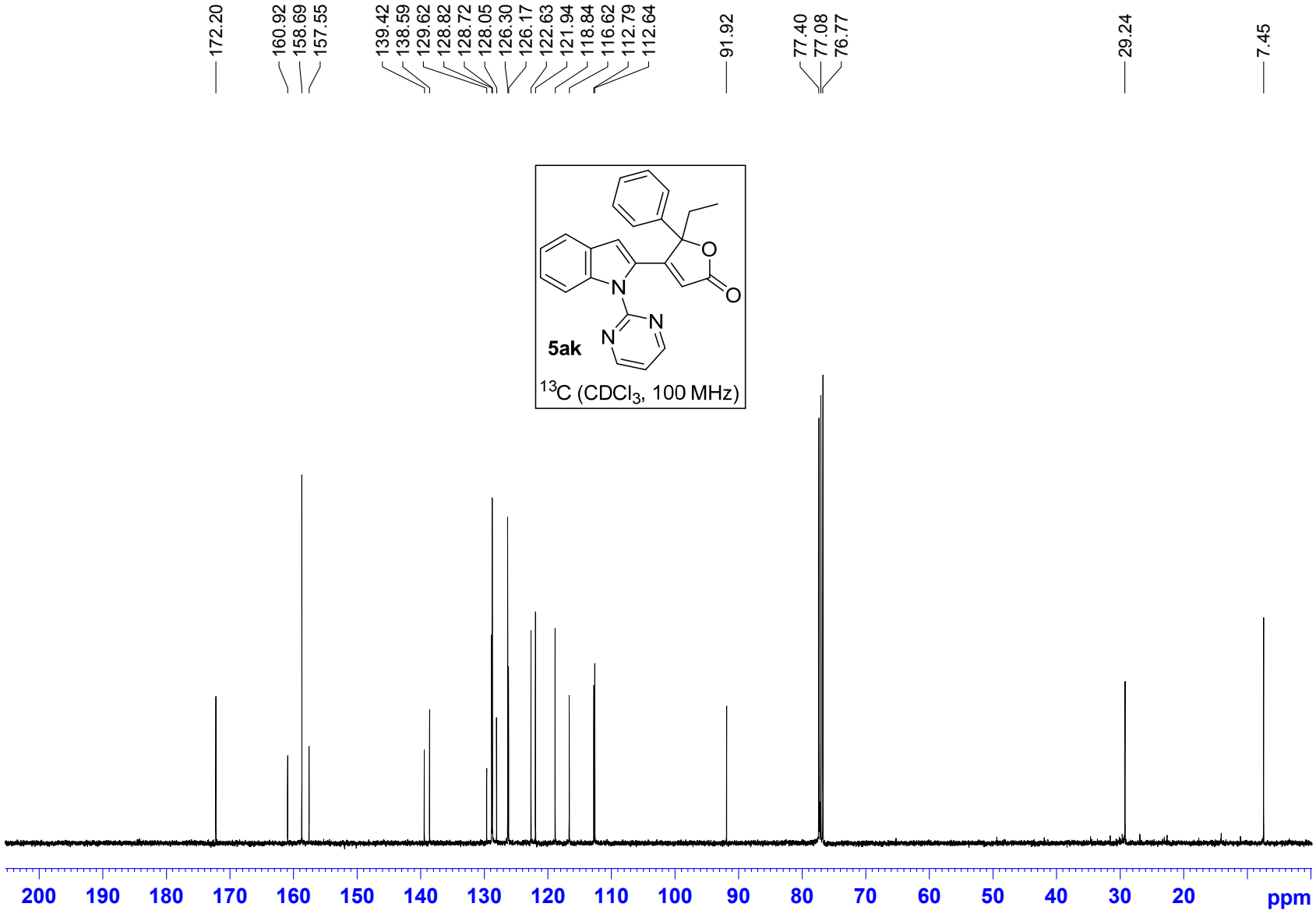

8.838
8.826
7.875
7.854
7.697
7.677
7.376
7.358
7.339
7.337
7.317
7.305
7.292
7.276
7.261
7.239
7.078
5.134
2.488
2.471
2.454
2.437
2.420
2.403
2.386
1.801
1.245
1.228
0.962
0.945
-0.000
5ai
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.00
1.01
1.02
1.01
1.06
1.00
1.00
1.02
3.01
3.02
3.01

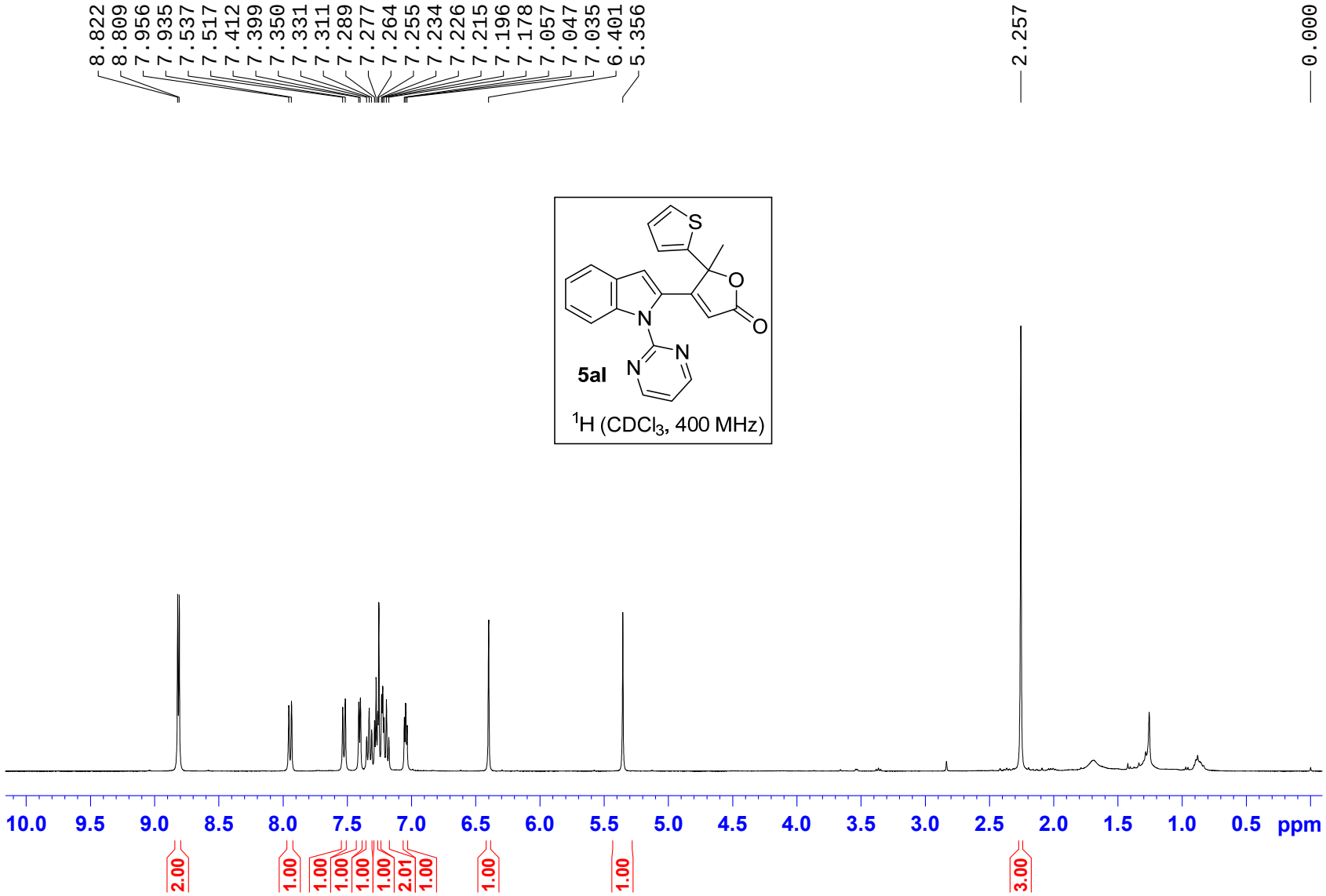

171.98
162.26
158.86
157.80
139.66
129.86
128.17
126.21
122.73
121.85
119.08
115.97
112.39
111.74
92.12
35.09
24.13
17.16
16.58
O
O
N
N
N
5ai
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

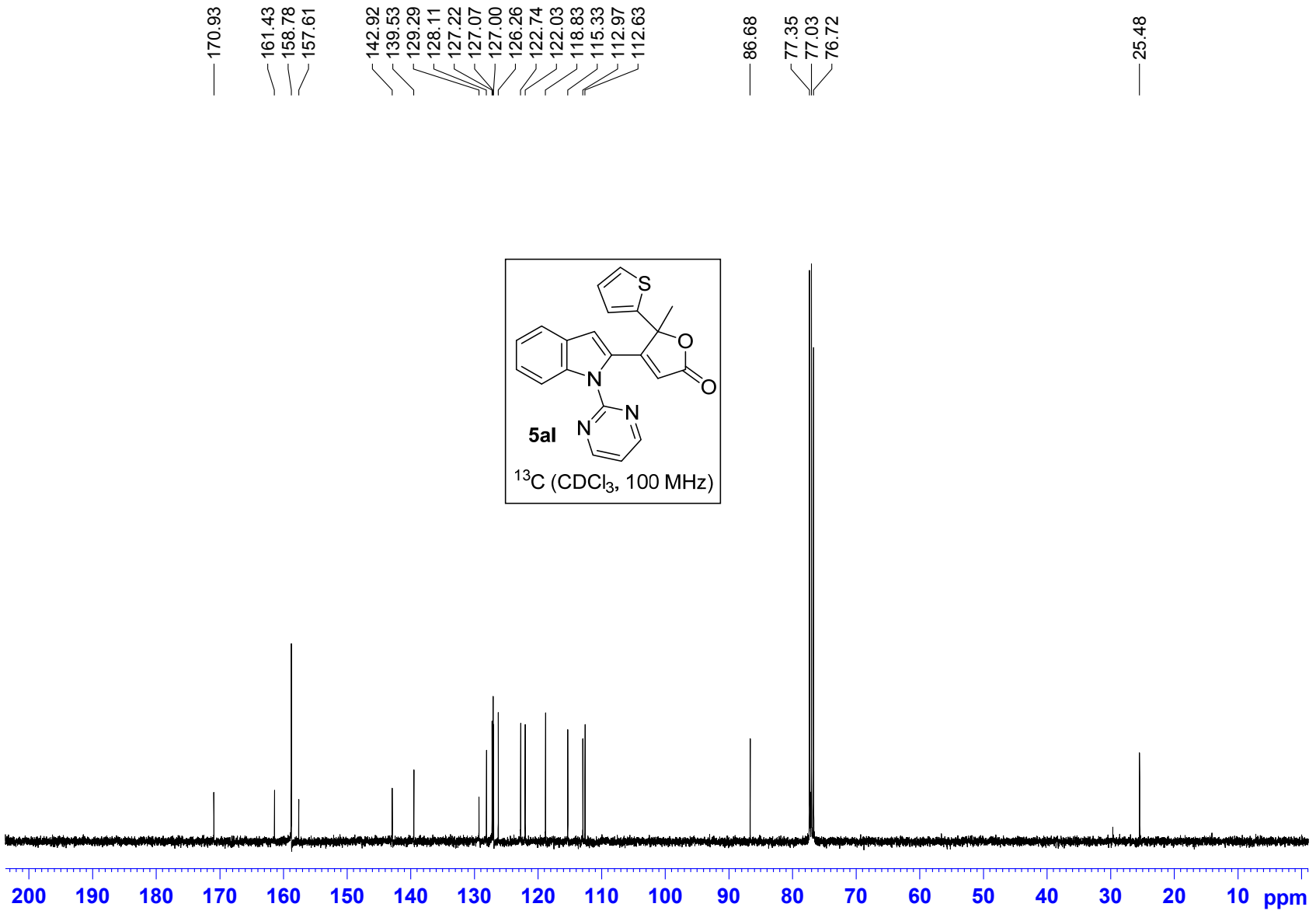

8.691
8.679
7.956
7.935
7.558
7.554
7.540
7.534
7.456
7.437
7.421
7.417
7.400
7.393
7.375
7.366
7.362
7.352
7.335
7.317
7.297
7.245
7.203
7.191
7.179
7.167
7.148
6.282
5.452
0.000
5aj
1H (CDCl3, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01
1.01
4.00
1.01
6.01
1.04
2.01
1.00
1.00

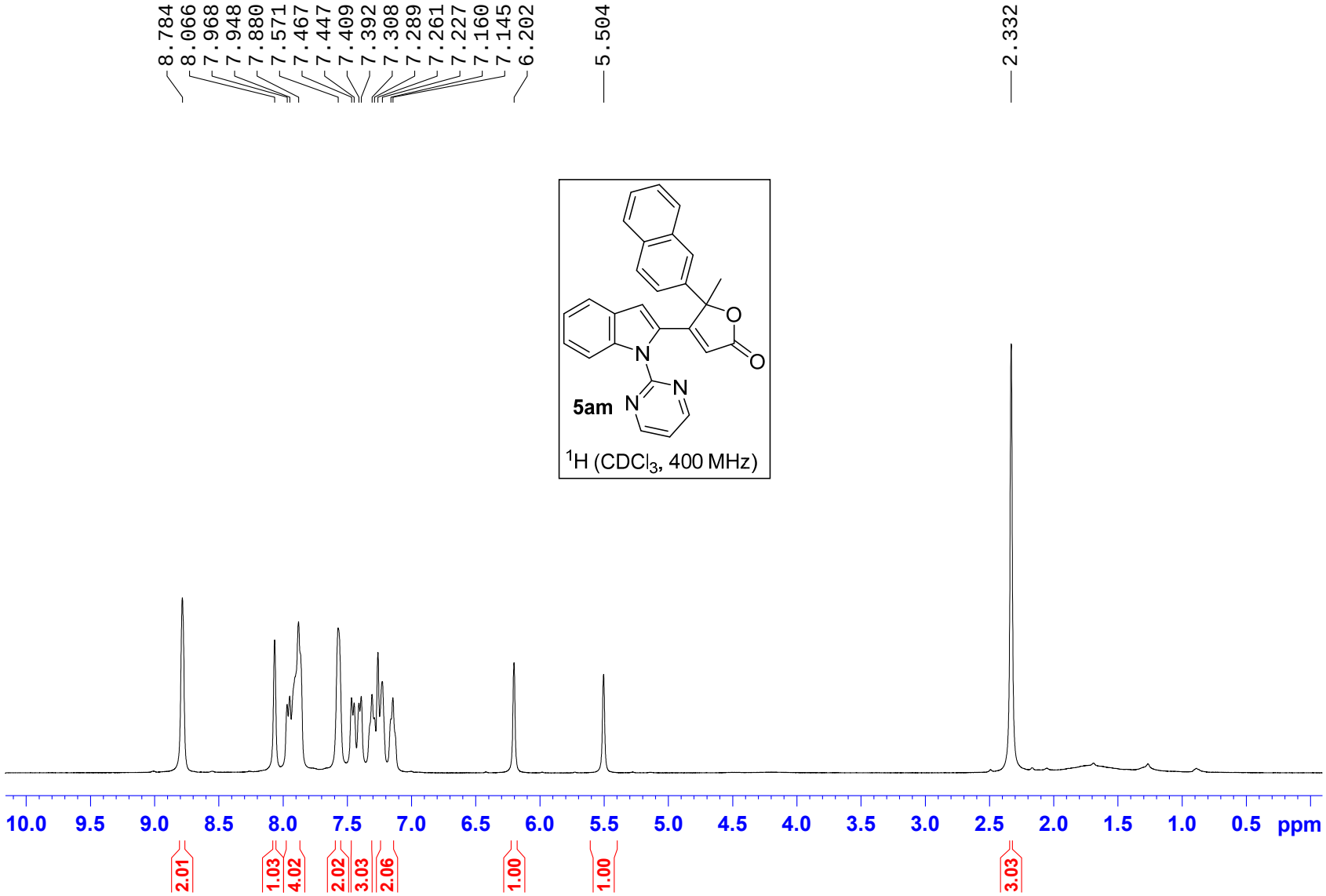

171.43
160.99
158.69
157.63
139.34
138.49
130.93
128.92
128.64
128.27
128.09
126.22
122.66
122.06
118.68
117.21
113.56
112.64
93.63
77.35
77.03
76.72
O
O
N
N
N
5aj
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

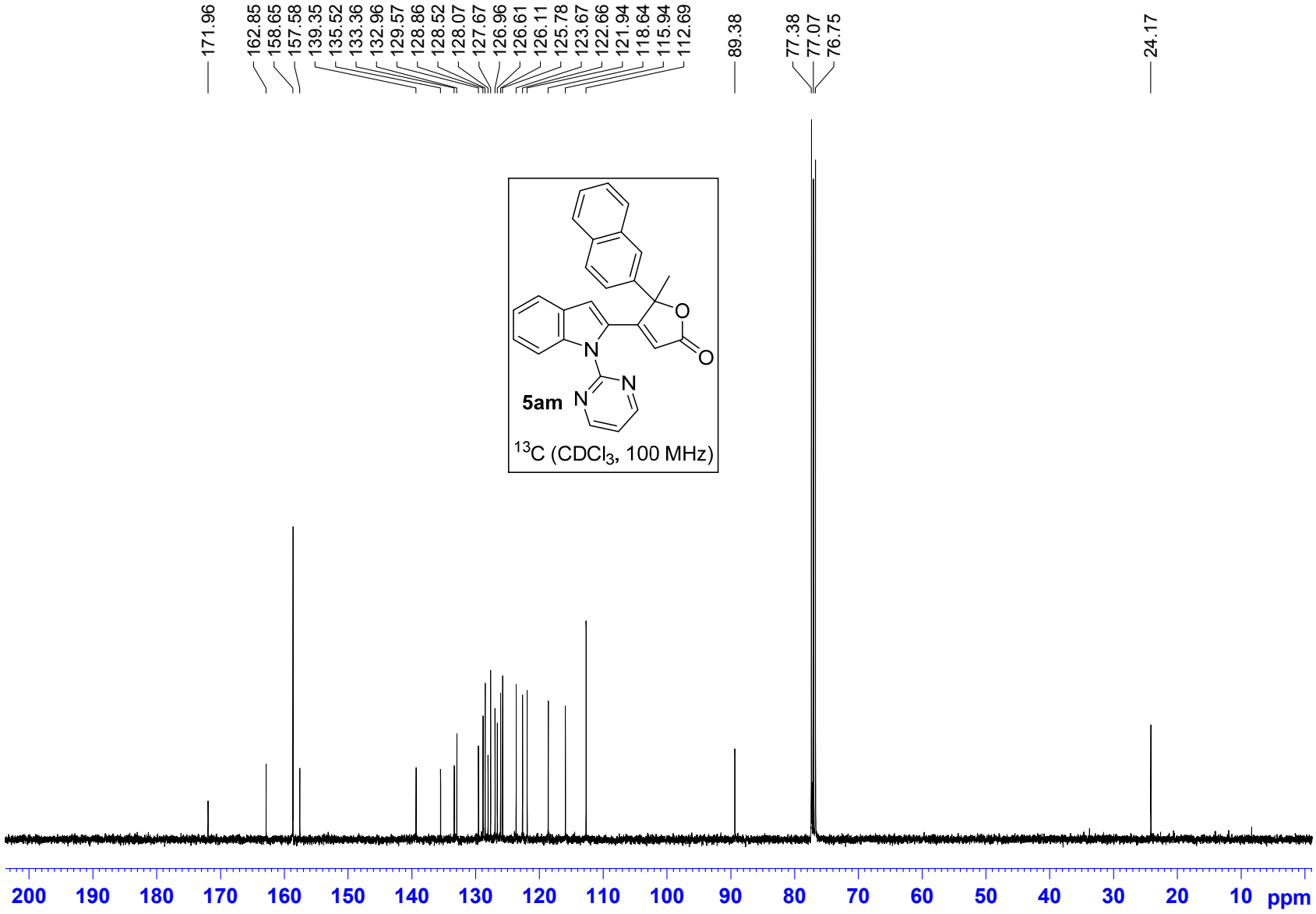

8.753
8.741
7.913
7.892
7.511
7.491
7.474
7.471
7.398
7.390
7.385
7.376
7.362
7.357
7.344
7.341
7.329
7.326
7.308
7.290
7.287
7.250
7.243
7.231
7.219
7.194
7.193
7.175
7.157
7.156
6.419
5.410
2.759
2.741
2.723
2.705
2.687
2.669
2.611
2.592
2.574
2.557
2.539
2.521
1.132
1.114
1.096
O
O
N
N
N
5ak
1H (CDCl3, 400 MHz)
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
ppm
2.00
1.00
3.04
3.01
1.07
1.06
1.06
1.00
1.00
1.10
1.08
3.07

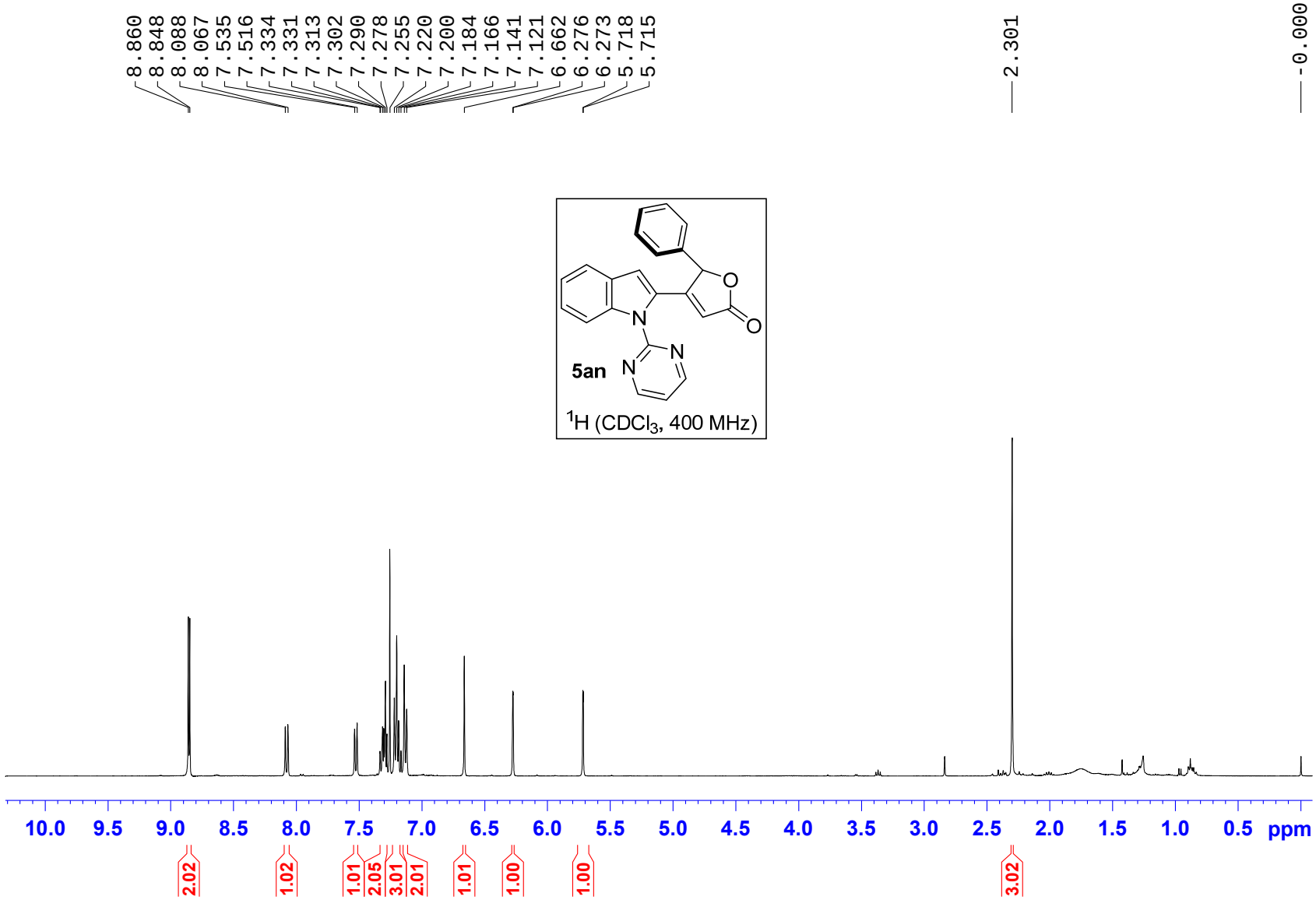

172.20
160.92
158.69
157.55
139.42
138.59
129.62
128.82
128.72
128.05
126.30
126.17
122.63
121.94
118.84
116.62
112.79
112.64
91.92
77.40
77.08
76.77
29.24
7.45
O
O
N
N
N
5ak
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

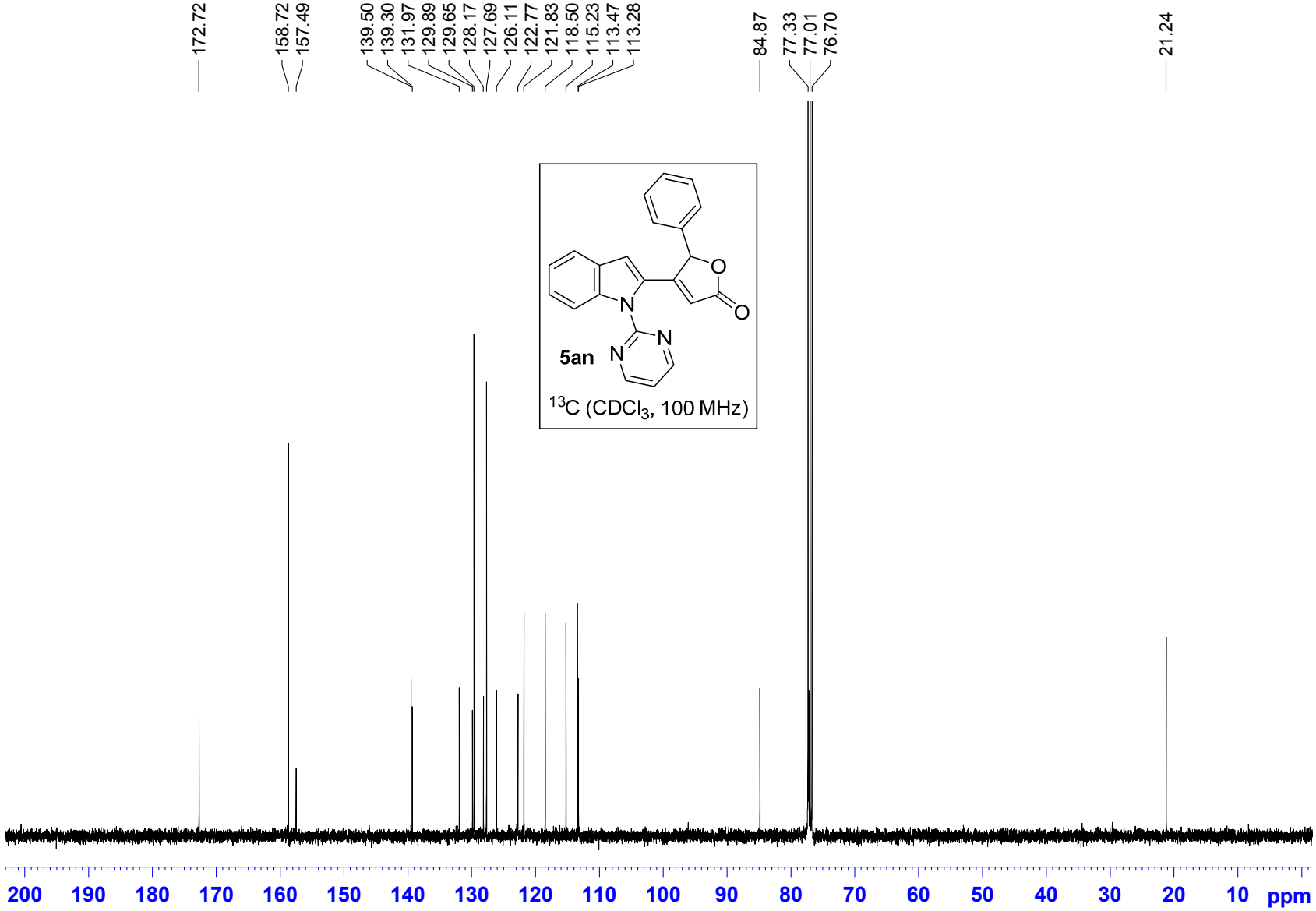

8.822
8.809
7.956
7.935
7.537
7.517
7.412
7.399
7.350
7.331
7.311
7.289
7.277
7.264
7.255
7.234
7.226
7.215
7.196
7.178
7.057
7.047
7.035
6.401
5.356
2.257
0.000
S
O
O
N
N
N
5al
1H (CDCl3, 400 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.00
1.00
1.00
1.00
1.00
2.01
1.00
1.00
1.00
3.00

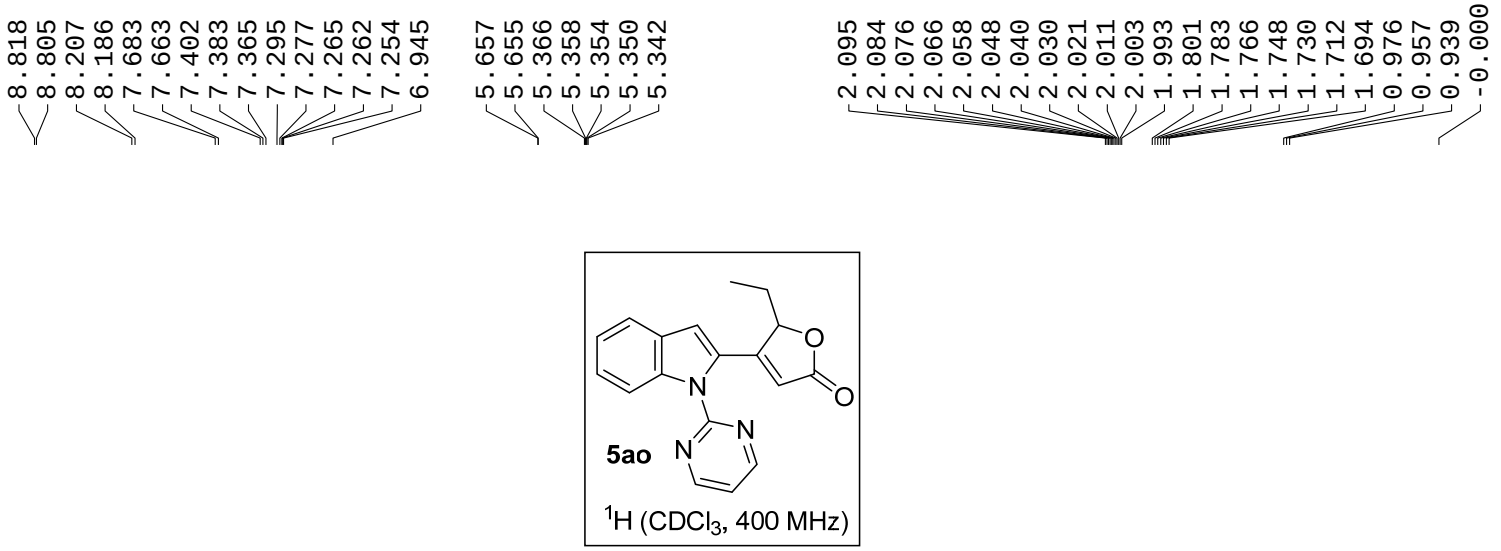

170.93
161.43
158.78
157.61
142.92
139.53
129.29
128.11
127.22
127.07
127.00
126.26
122.74
122.03
118.83
115.33
112.97
112.63
86.68
77.35
77.03
76.72
25.48
S
O
O
N
N
N
5al
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

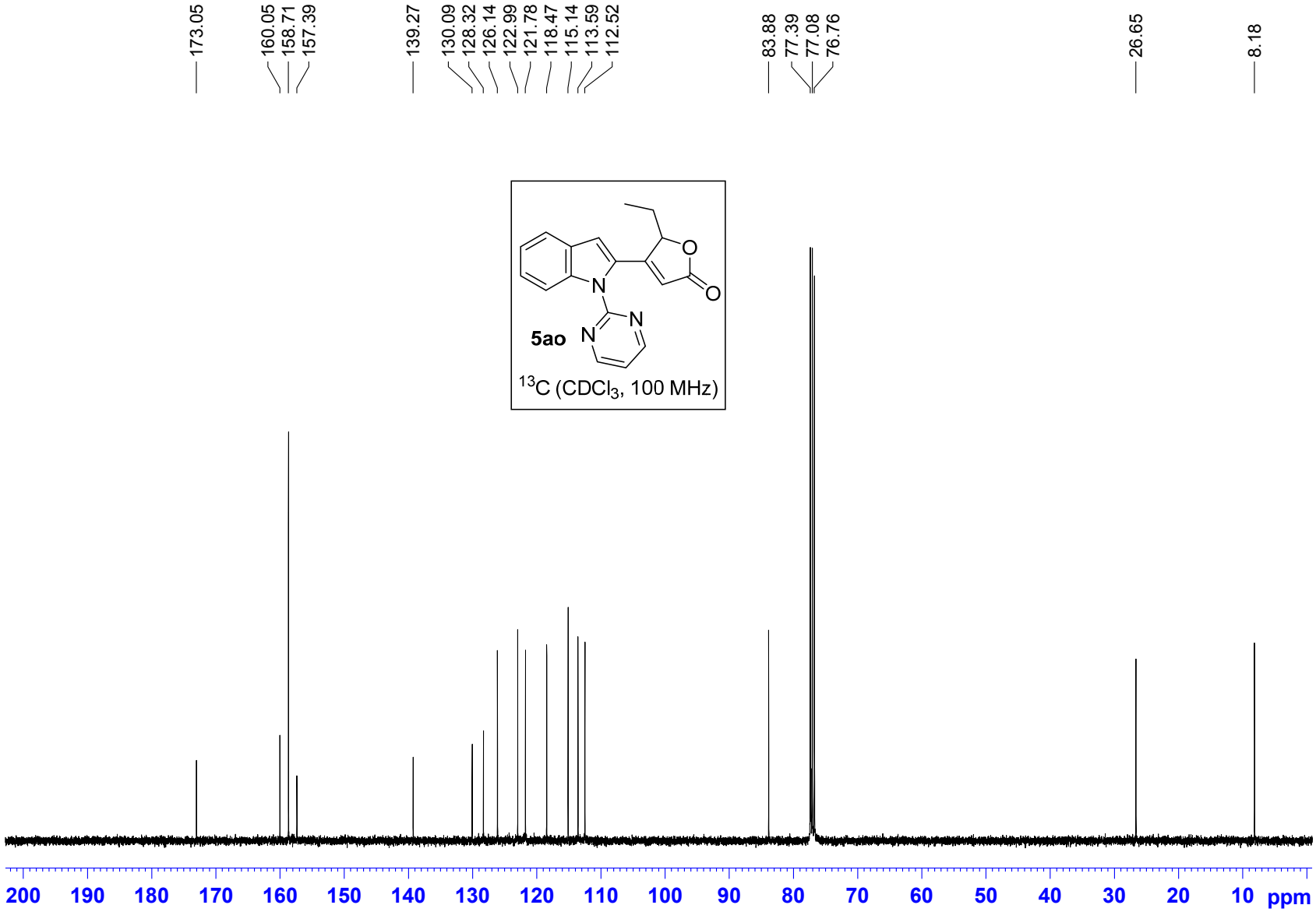

8.784
8.066
7.968
7.948
7.880
7.571
7.467
7.447
7.409
7.392
7.308
7.289
7.261
7.227
7.160
7.145
6.202
5.504
2.332
5am
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01
1.03
4.02
2.02
3.03
2.06
1.00
1.00
3.03

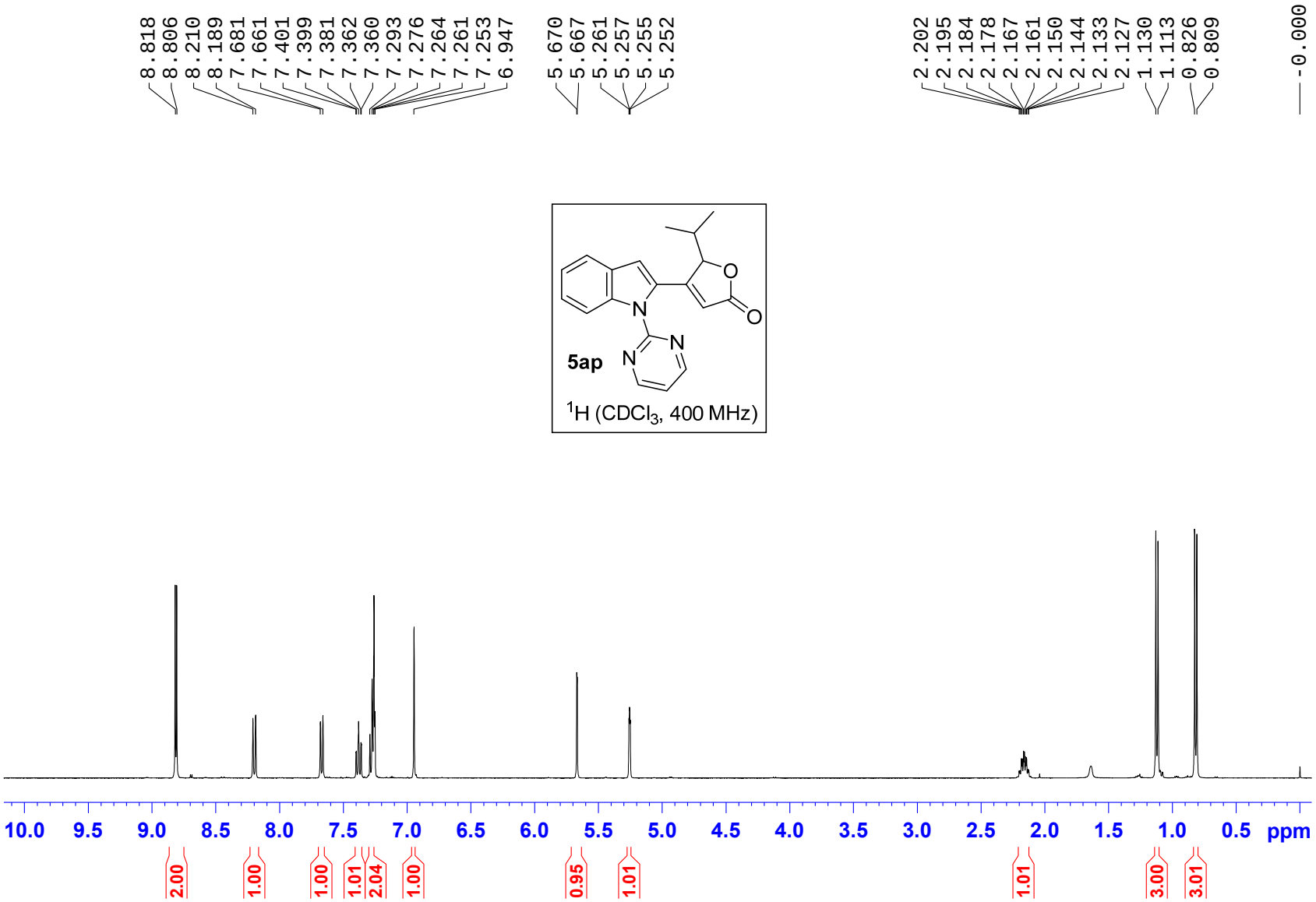

171.96
162.85
158.65
157.58
139.35
135.52
133.36
132.96
129.57
128.86
128.52
128.07
127.67
126.96
126.61
126.11
125.78
123.67
122.66
121.94
118.64
115.94
112.69
89.38
77.38
77.07
76.75
24.17
O
O
N
N
N
5am
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

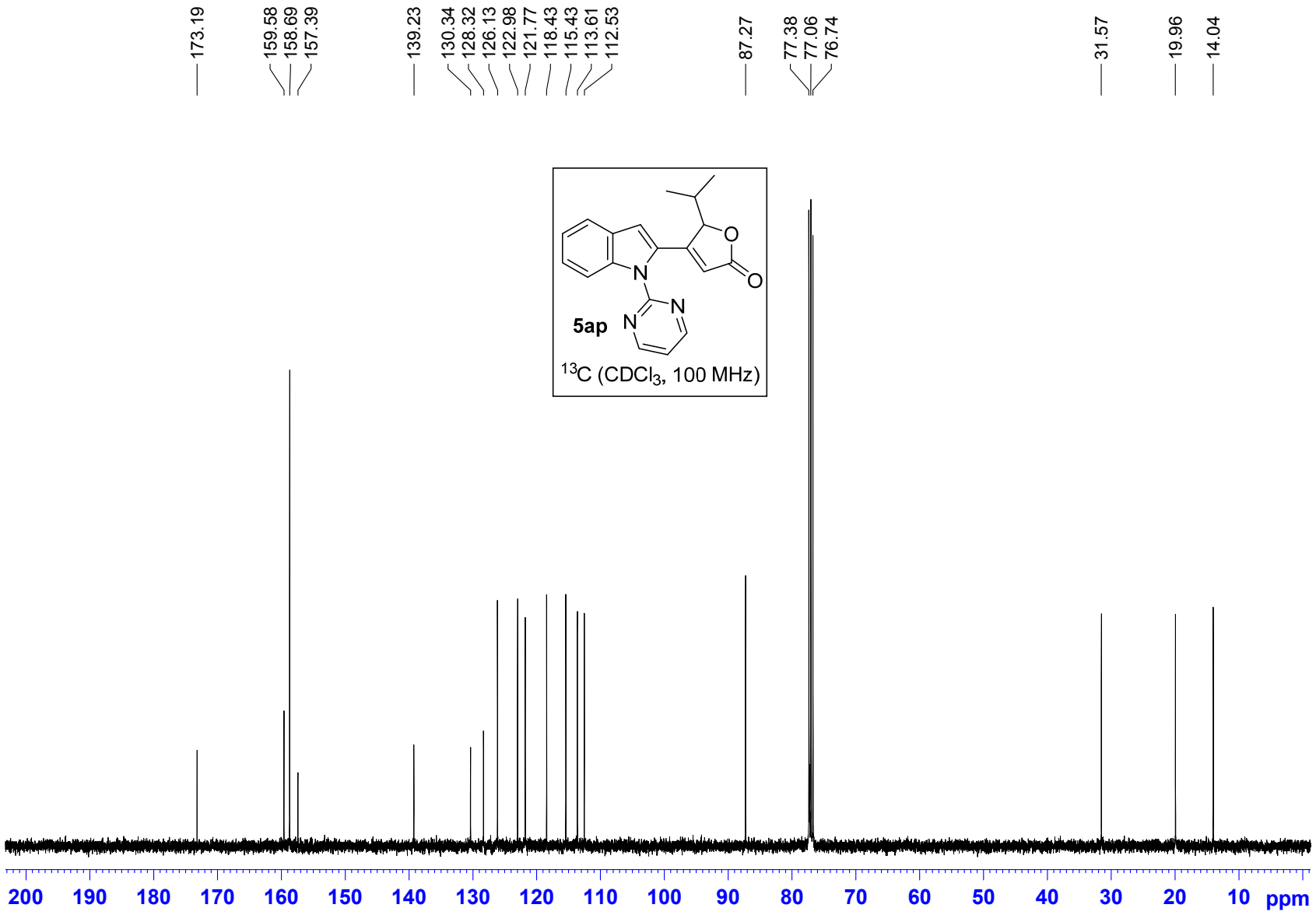

8.860
8.848
8.088
8.067
7.535
7.516
7.334
7.331
7.313
7.302
7.290
7.278
7.255
7.220
7.200
7.184
7.166
7.141
7.121
6.662
6.276
6.273
5.718
5.715
2.301
-0.000
5an
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
1.02
1.01
2.05
3.01
2.01
1.01
1.00
1.00
3.02

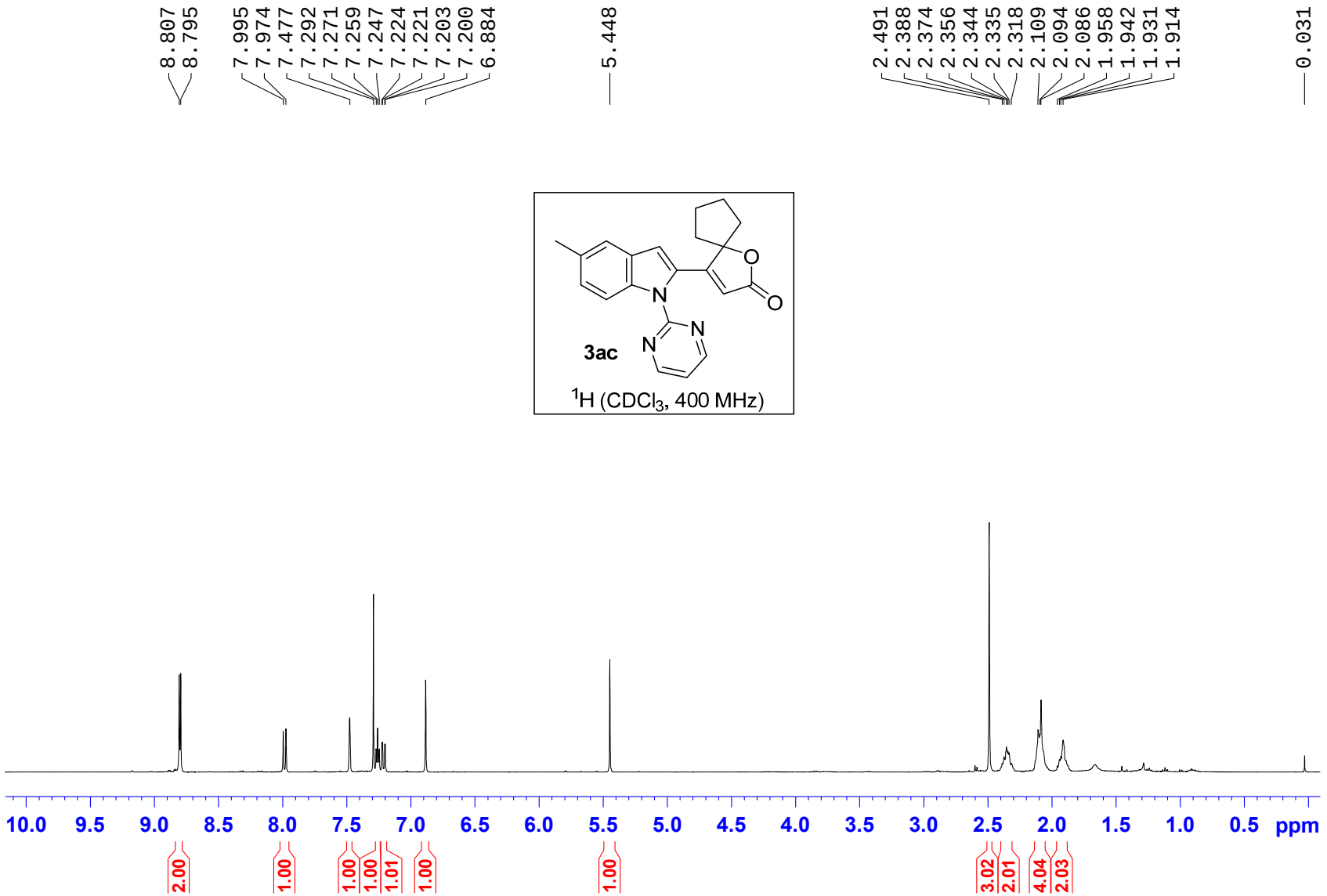

172.72
158.72
157.49
139.50
139.30
131.97
129.89
129.65
128.17
127.69
126.11
122.77
121.83
118.50
115.23
113.47
113.28
84.87
77.33
77.01
76.70
21.24
O
O
N
N
N
5an
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

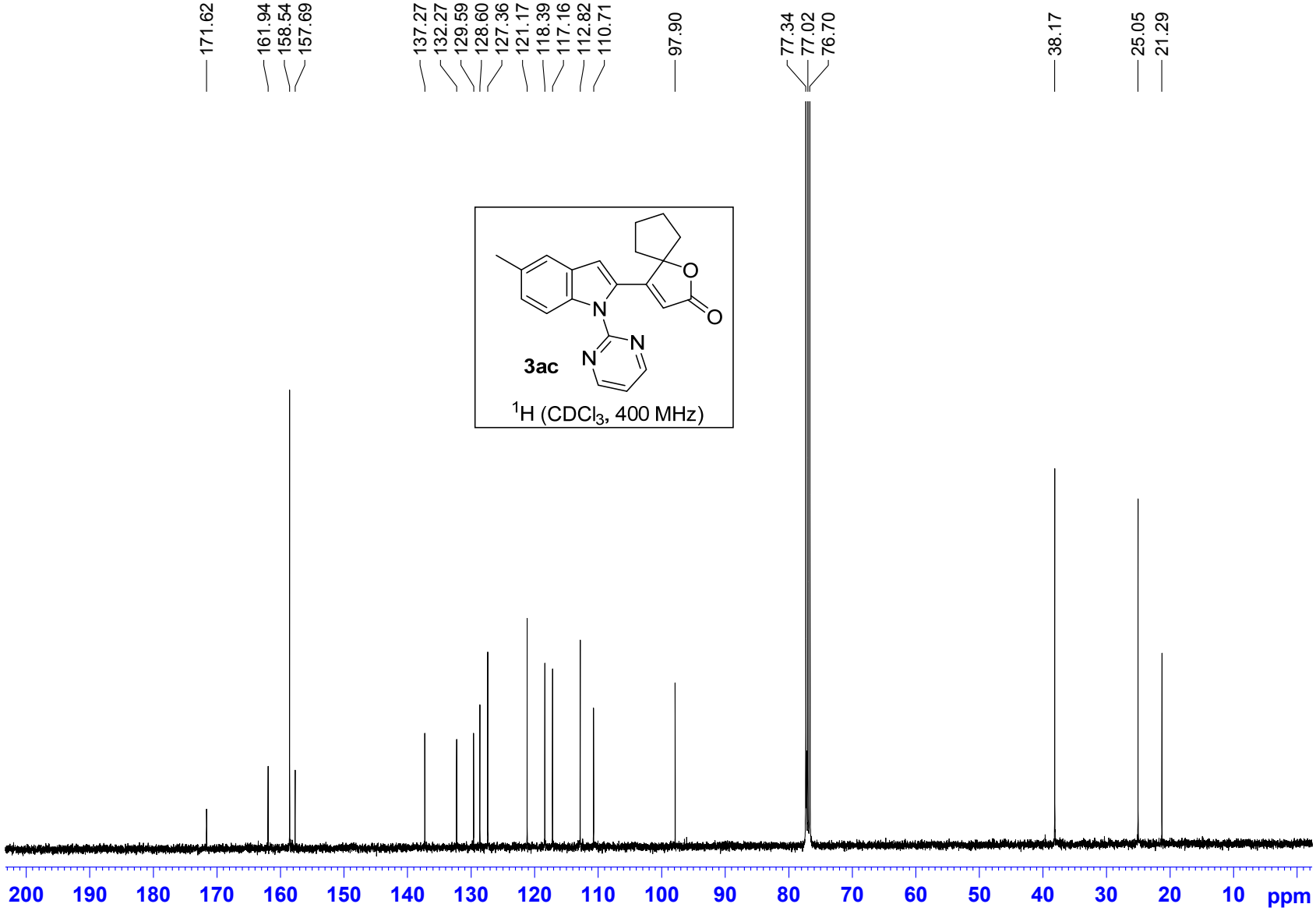

8.818
8.805
8.207
8.186
7.683
7.663
7.402
7.383
7.365
7.295
7.277
7.265
7.262
7.254
6.945
5.657
5.655
5.366
5.358
5.354
5.350
5.342
2.095
2.084
2.076
2.066
2.058
2.048
2.040
2.030
2.021
2.011
2.003
1.993
1.801
1.783
1.766
1.748
1.730
1.712
1.694
0.976
0.957
0.939
-0.000
O
O
N
N
N
5ao
1H (CDCl3, 400 MHz)
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
ppm
2.00
1.02
1.02
1.03
2.06
1.02
1.00
1.00
1.00
1.05
3.02


173.05
160.05
158.71
157.39
139.27
130.09
128.32
126.14
122.99
121.78
118.47
115.14
113.59
112.52
83.88
77.39
77.08
76.76
26.65
8.18
O
O
N
N
N
5ao
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

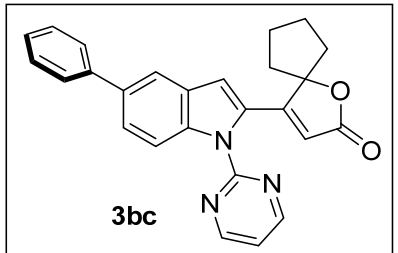

8.818
8.806
8.210
8.189
7.681
7.661
7.401
7.399
7.381
7.362
7.360
7.293
7.276
7.264
7.261
7.253
6.947
5.670
5.667
5.261
5.257
5.255
5.252
2.202
2.195
2.184
2.178
2.167
2.161
2.150
2.144
2.133
2.127
1.130
1.113
0.826
0.809
-0.000
5ap
1H (CDCl3, 400 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.00
1.00
1.01
2.04
1.00
0.95
1.01
1.01
3.00
3.01


173.19
159.58
158.69
157.39
139.23
130.34
128.32
126.13
122.98
121.77
118.43
115.43
113.61
112.53
87.27
77.38
77.06
76.74
31.57
19.96
14.04
O
O
N
N
N
5ap
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.807
8.795
7.995
7.974
7.477
7.292
7.271
7.259
7.247
7.224
7.221
7.203
7.200
6.884
5.448
2.491
2.388
2.374
2.356
2.344
2.335
2.318
2.109
2.094
2.086
1.958
1.942
1.931
1.914
0.031
O
O
N
N
N
3ac
1H (CDCl3, 400 MHz)
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
ppm
2.00
1.00
1.00
1.00
1.01
1.00
1.00
3.02
2.01
4.04
2.03

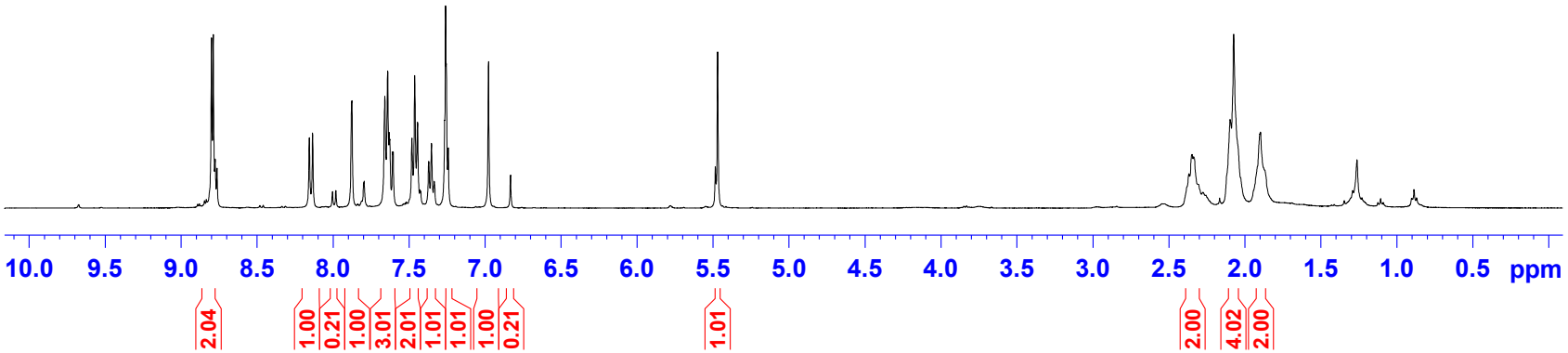

171.62
161.94
158.54
157.69
137.27
132.27
129.59
128.60
127.36
121.17
118.39
117.16
112.82
110.71
97.90
77.34
77.02
76.70
38.17
25.05
21.29
O
O
N
N
N
3ac
1H (CDCl3, 400 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

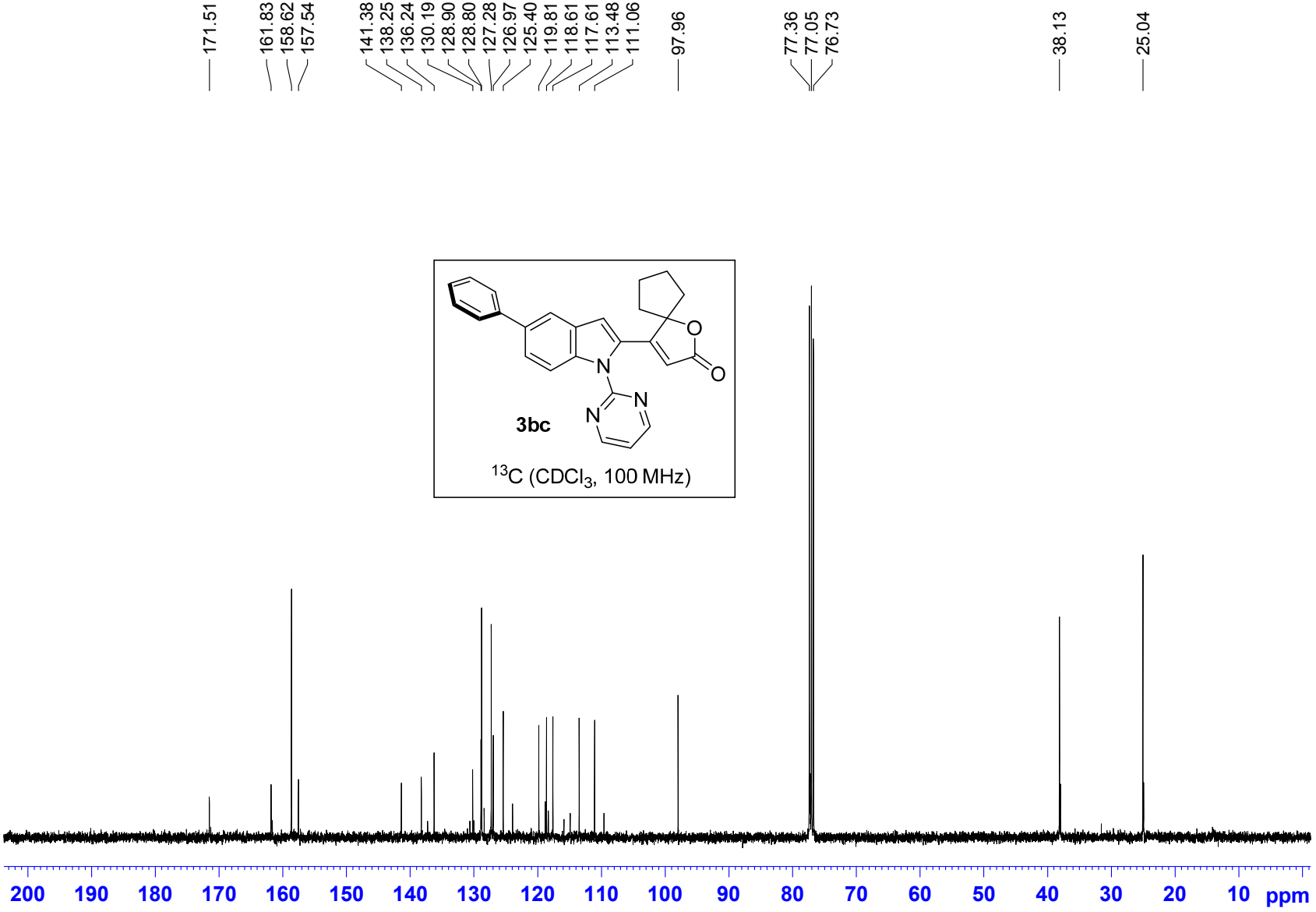
8.800
8.788
8.156
8.134
7.876
7.659
7.640
7.630
7.626
7.483
7.464
7.445
7.372
7.354
7.335
7.266
7.261
7.256
6.979
5.471
2.369
2.349
2.338
2.098
2.075
1.903
1.898

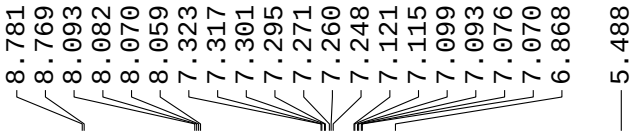


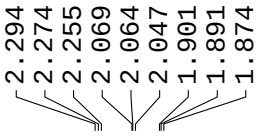
3bc

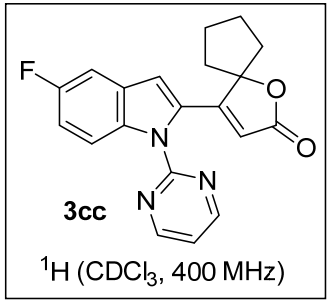
^{1}H ($CDCl_3$, 400 MHz)

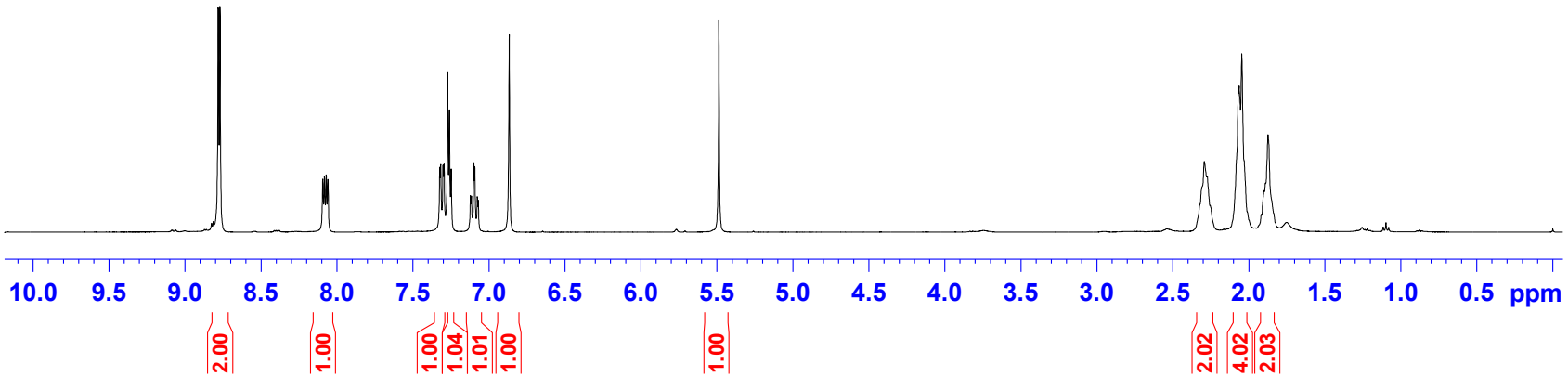


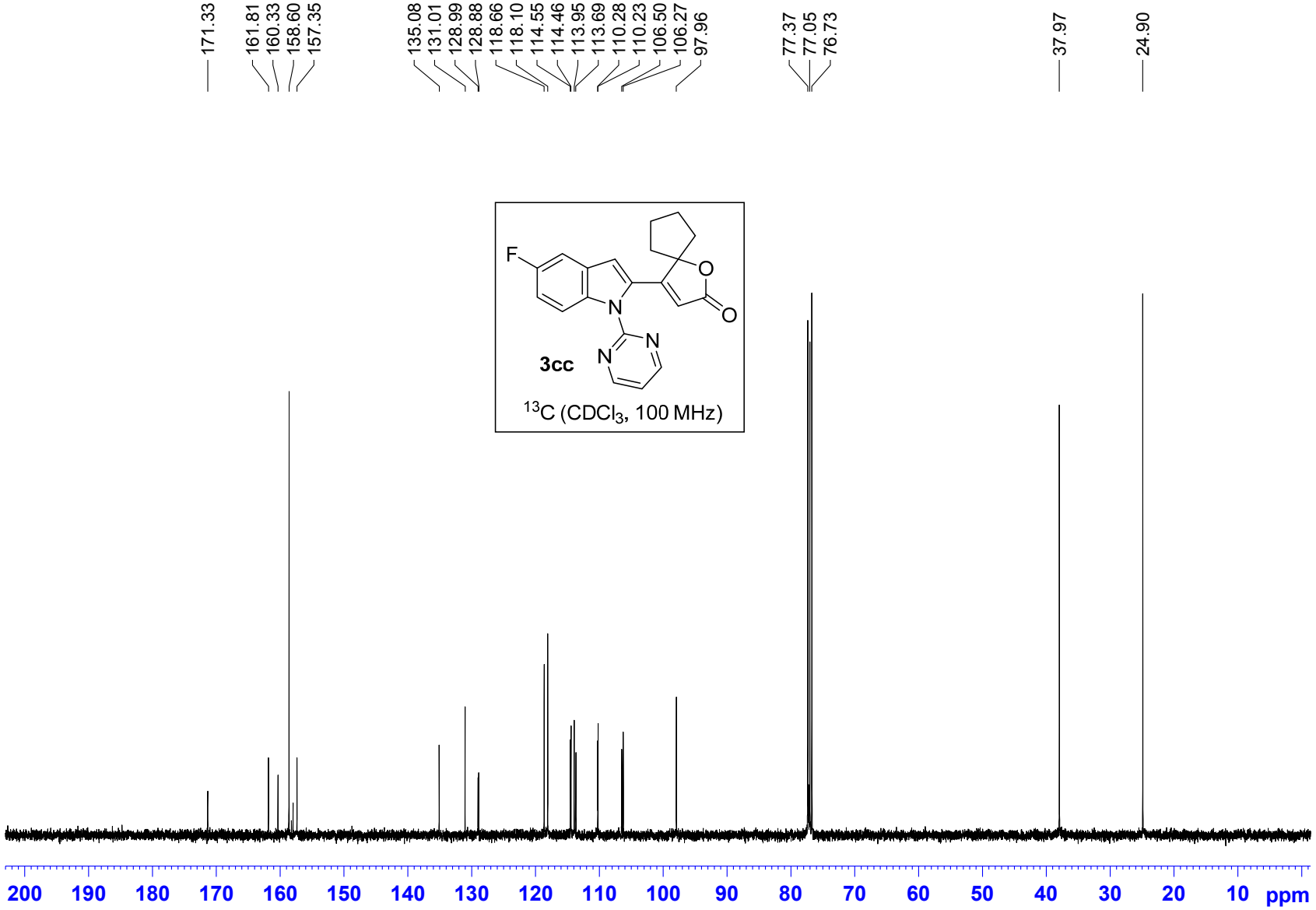

171.51
161.83
158.62
157.54
141.38
138.25
136.24
130.19
128.90
128.80
127.28
126.97
125.40
119.81
118.61
117.61
113.48
111.06
97.96
77.36
77.05
76.73
38.13
25.04
O
O
N
N
N
3bc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.781
8.769
8.093
8.082
8.070
8.059
7.323
7.317
7.301
7.295
7.271
7.260
7.248
7.121
7.115
7.099
7.093
7.076
7.070
6.868
5.488

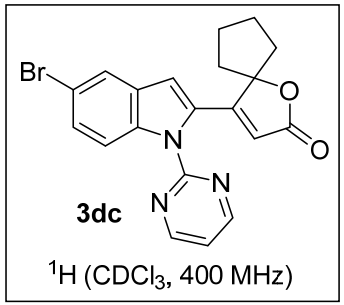

2.294
2.274
2.255
2.069
2.064
2.047
1.901
1.891
1.874


F
O
N
O
N
N
3cc
^{1}H (CDCl$_3$, 400 MHz)

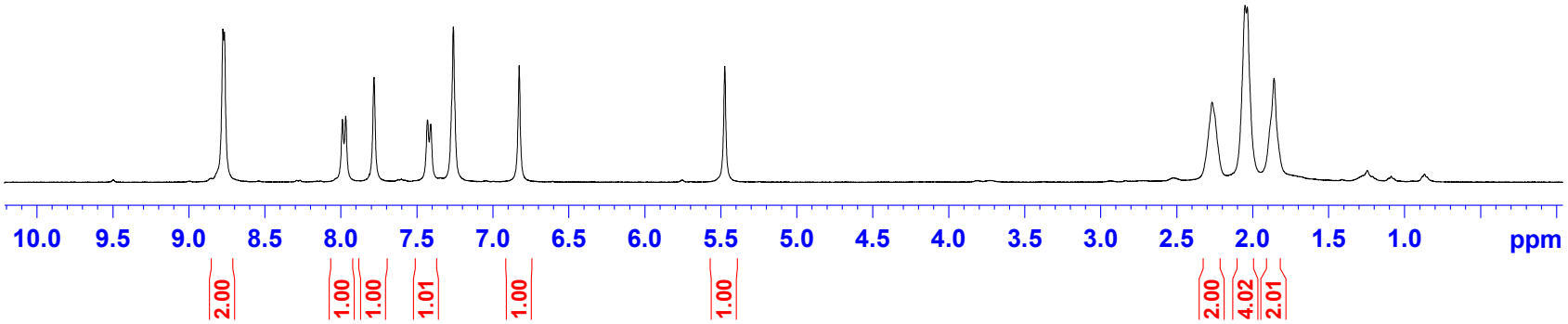

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.00
1.00
1.04
1.01
1.00
1.00
2.02
4.02
2.03

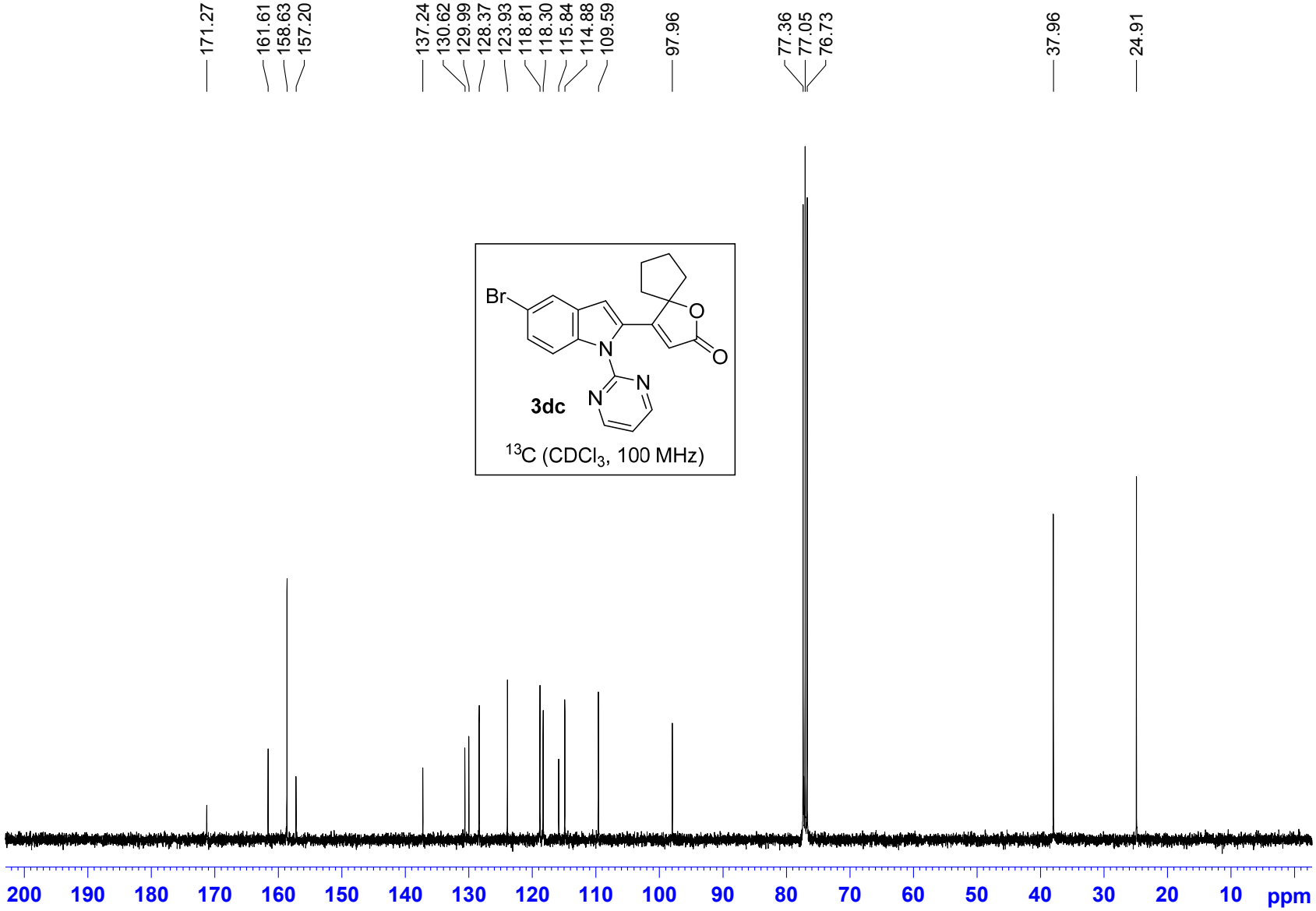

171.33
161.81
160.33
158.60
157.35
135.08
131.01
128.99
128.88
118.66
118.10
114.55
114.46
113.95
113.69
110.28
110.23
106.50
106.27
97.96
77.37
77.05
76.73
37.97
24.90
F
O
O
N
N
N
3cc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

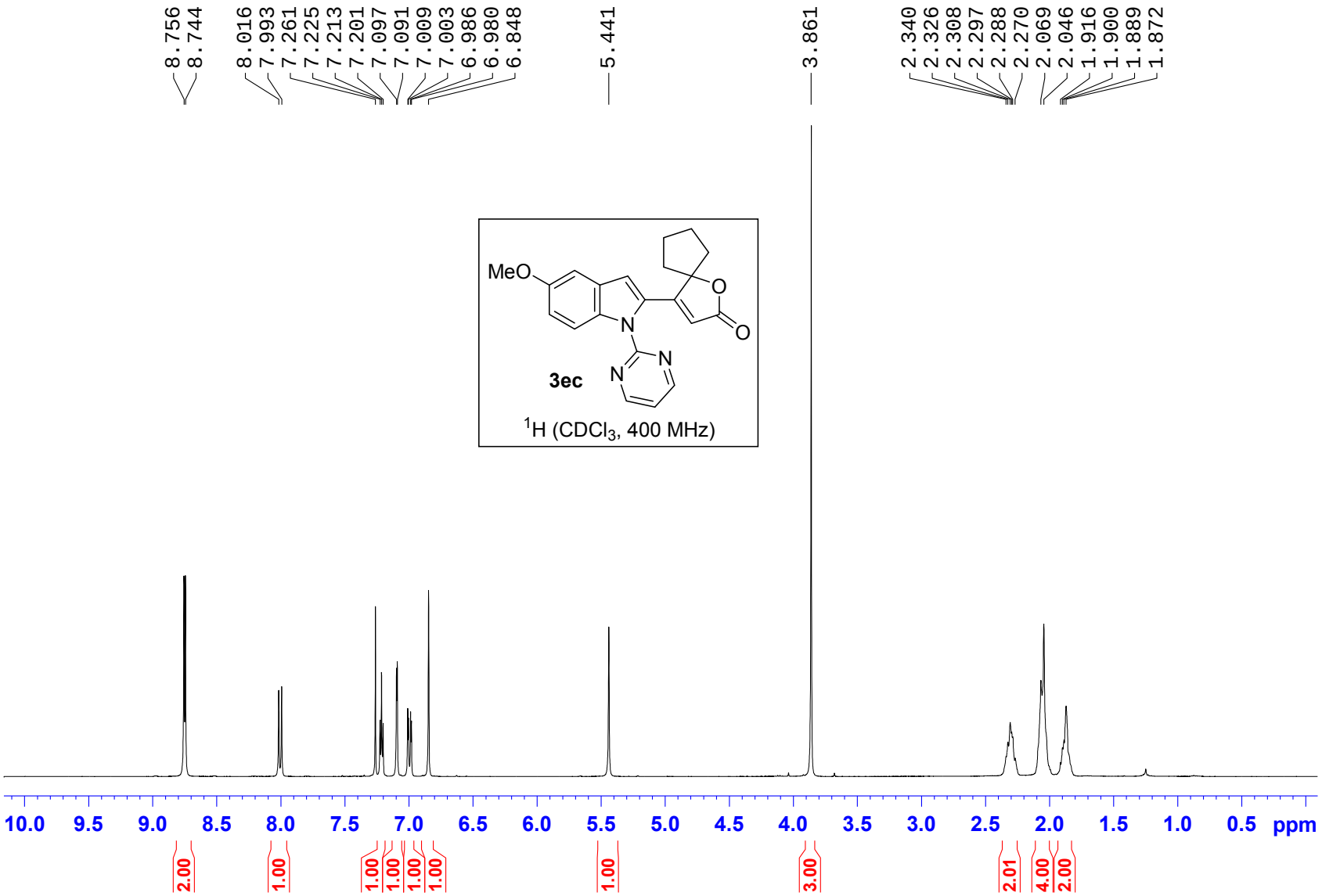
8.776
8.766
7.989
7.968
7.783
7.431
7.410
7.261
6.828
5.475
2.268
2.051
2.036
1.861

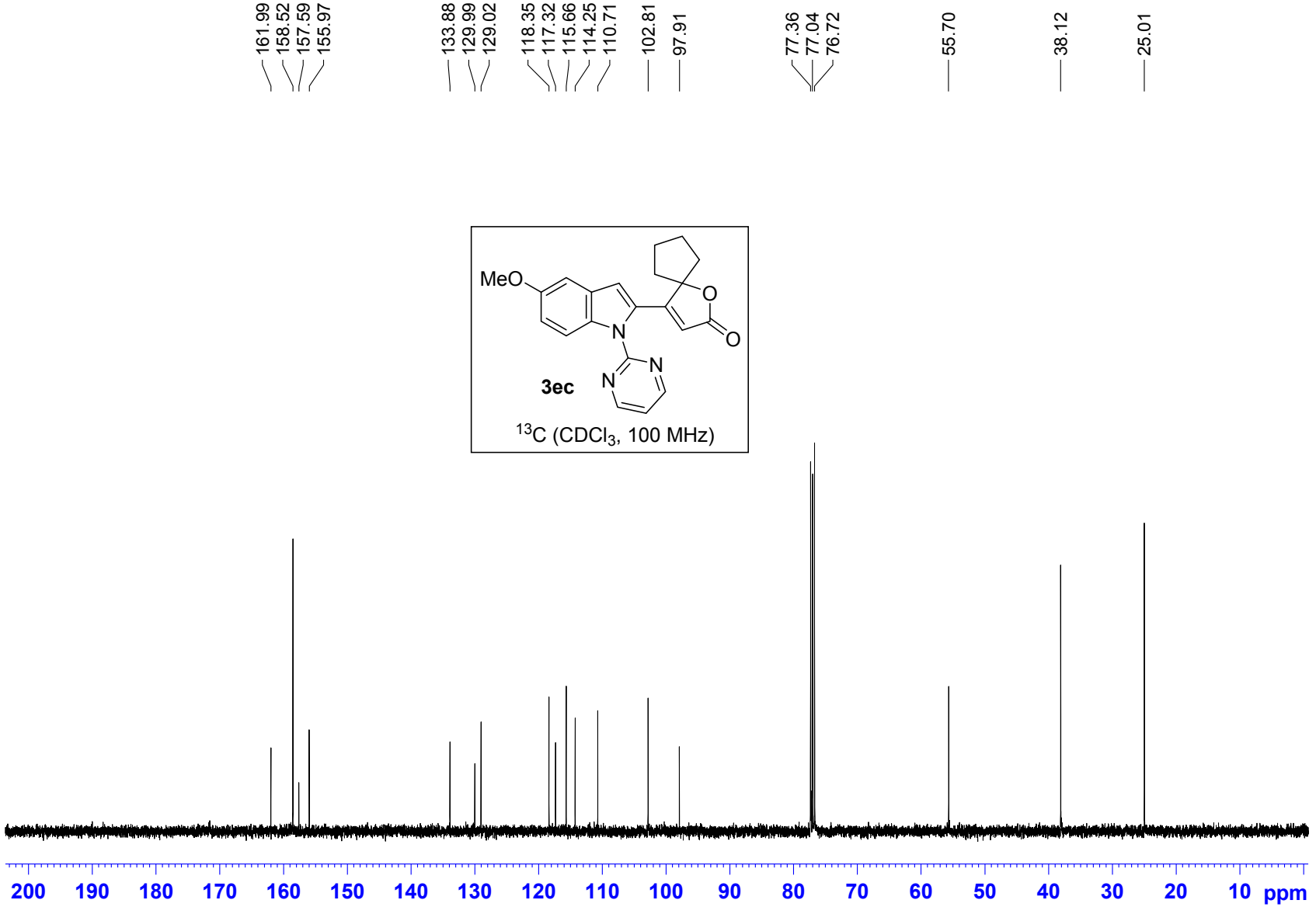


^{1}H ($CDCl_3$, 400 MHz)

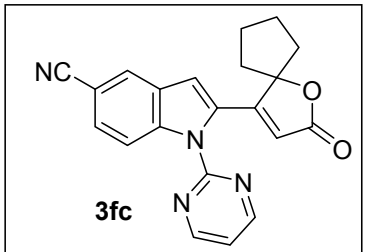



171.27
161.61
158.63
157.20
137.24
130.62
129.99
128.37
123.93
118.81
118.30
115.84
114.88
109.59
97.96
77.36
77.05
76.73
37.96
24.91
Br
O
O
N
N
N
3dc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.756
8.744
8.016
7.993
7.261
7.225
7.213
7.201
7.097
7.091
7.009
7.003
6.986
6.980
6.848
5.441
3.861
2.340
2.326
2.308
2.297
2.288
2.270
2.069
2.046
1.916
1.900
1.889
1.872
MeO
O
O
N
N
N
3ec
1H (CDCl3, 400 MHz)
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
ppm
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
2.01
4.00
2.00

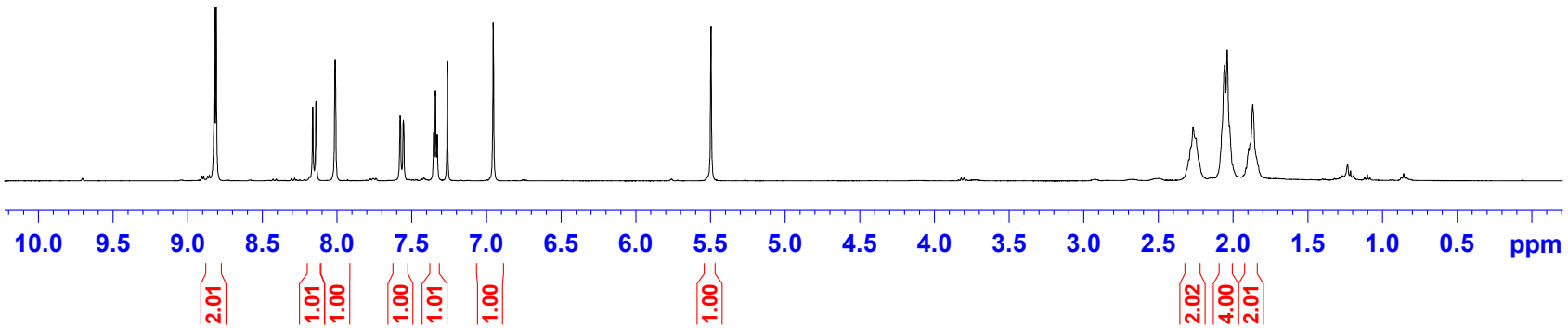

161.99
158.52
157.59
155.97
133.88
129.99
129.02
118.35
117.32
115.66
114.25
110.71
102.81
97.91
77.36
77.04
76.72
55.70
38.12
25.01
MeO
O
O
N
N
N
3ec
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

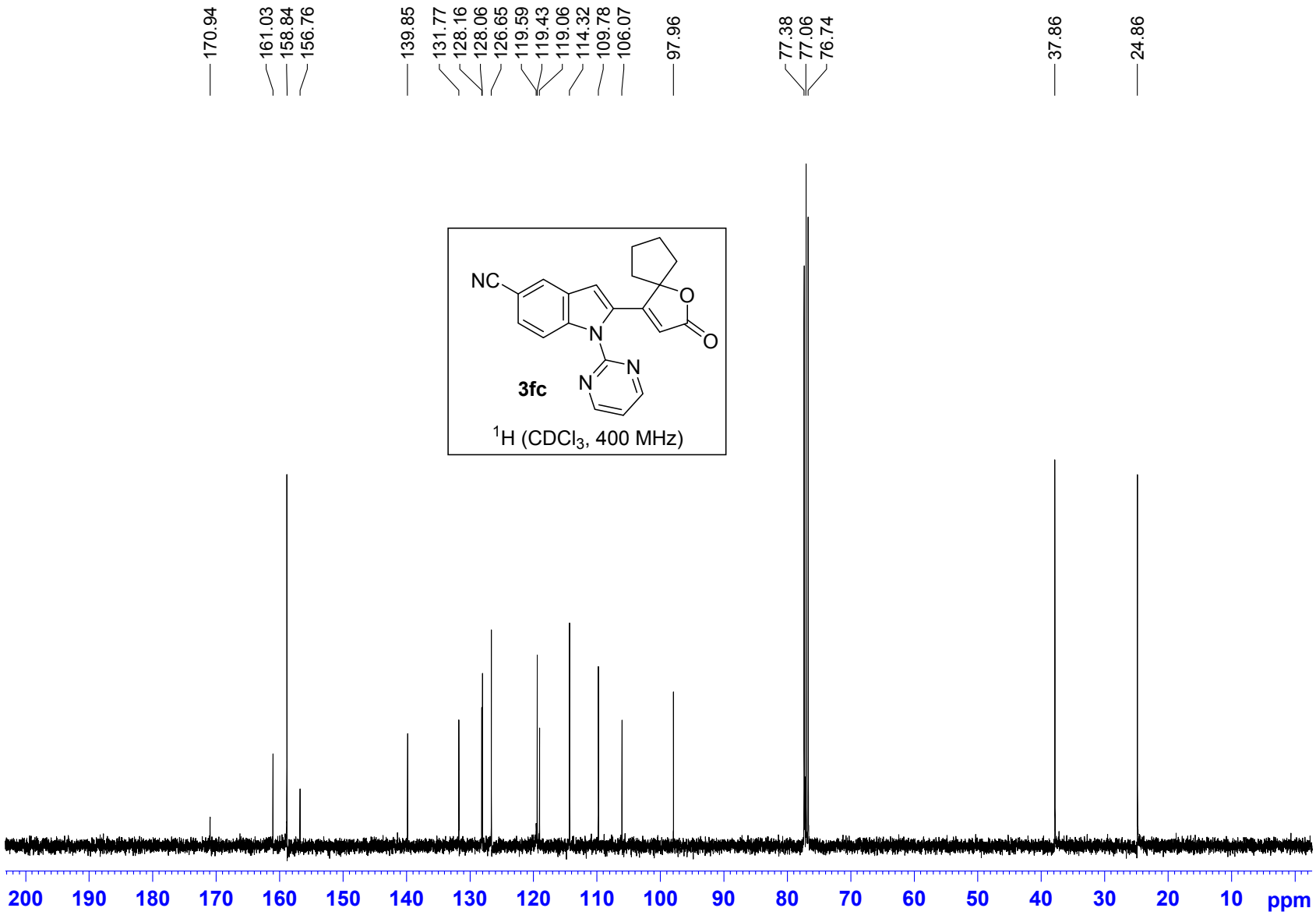
8.821
8.809
8.163
8.141
8.012
7.577
7.556
7.353
7.341
7.329
7.261
6.954
5.496
2.298
2.269
2.250
2.057
2.040
2.025
1.914
1.896
1.886
1.869



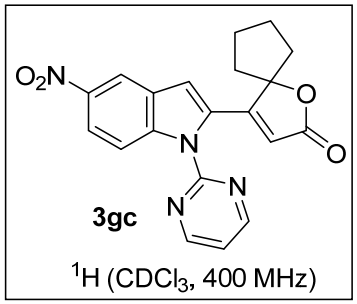
3fc

^{13}C ($CDCl_3$, 100 MHz)

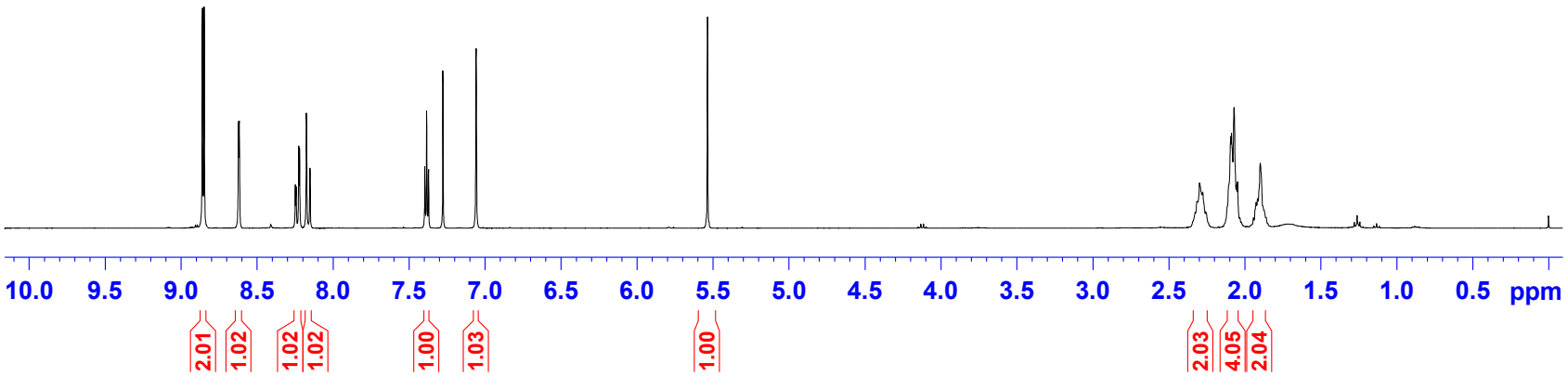


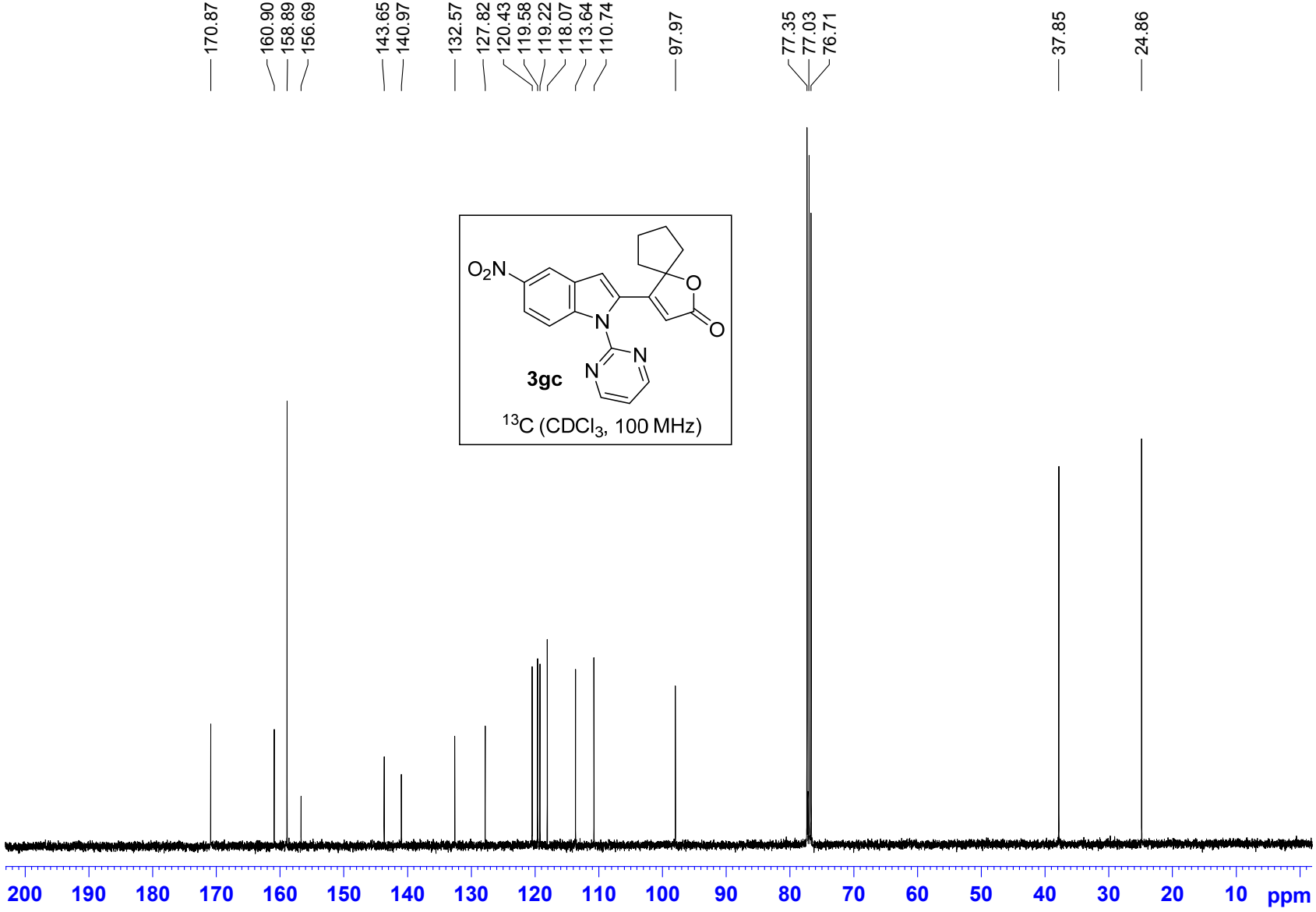

170.94
161.03
158.84
156.76
139.85
131.77
128.16
128.06
126.65
119.59
119.43
119.06
114.32
109.78
106.07
97.96
77.38
77.06
76.74
37.86
24.86
NC
O
O
N
N
N
3fc
^{1}H (CDCl$_3$, 400 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

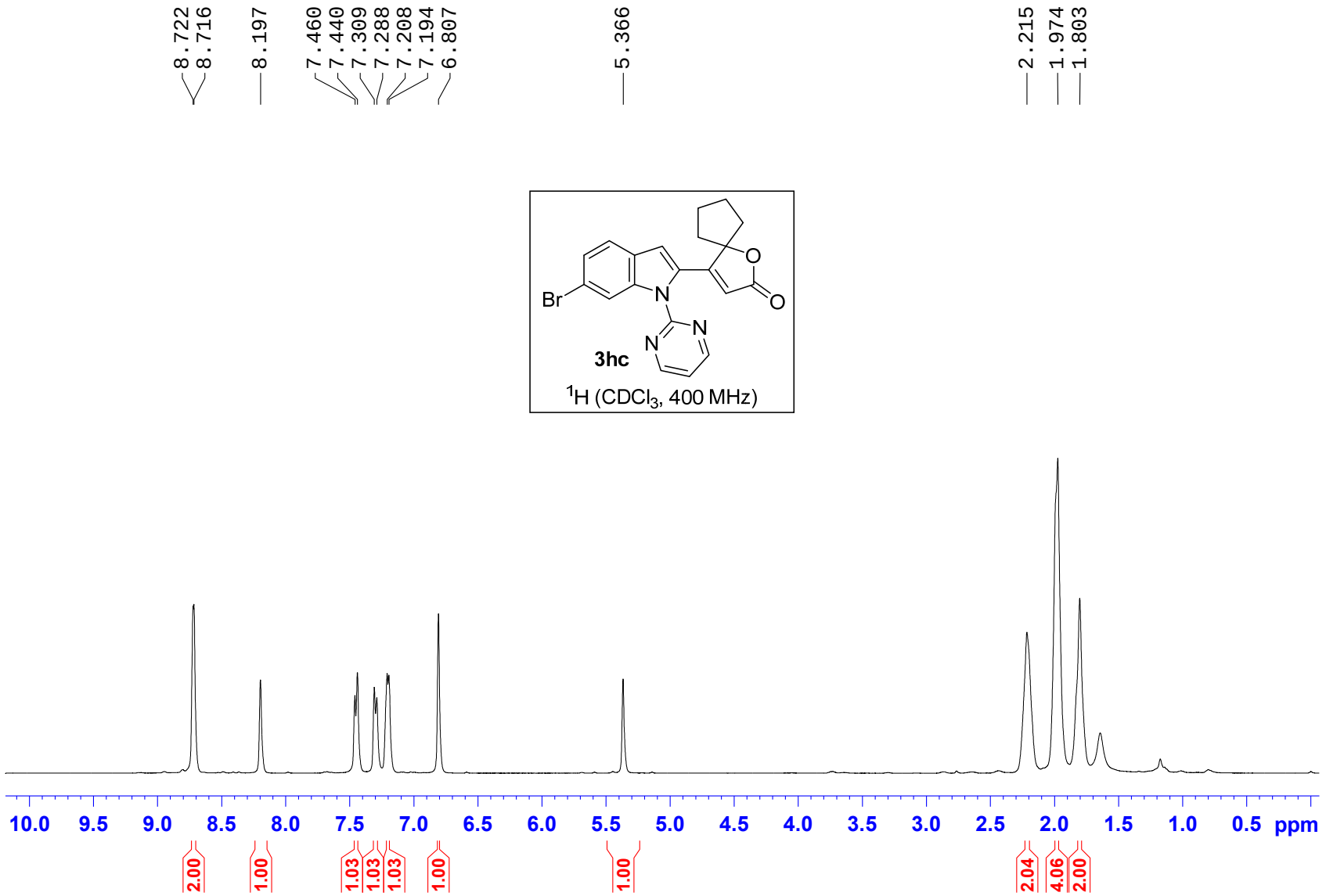
8.860
8.848
8.622
8.617
8.248
8.243
8.225
8.220
8.175
8.151
7.396
7.383
7.371
7.276
7.058
5.535
2.326
2.315
2.310
2.297
2.276
2.257
2.252
2.092
2.087
2.070
2.053
2.046
2.032
1.942
1.924
1.915
1.897
1.872
1.859
-0.000

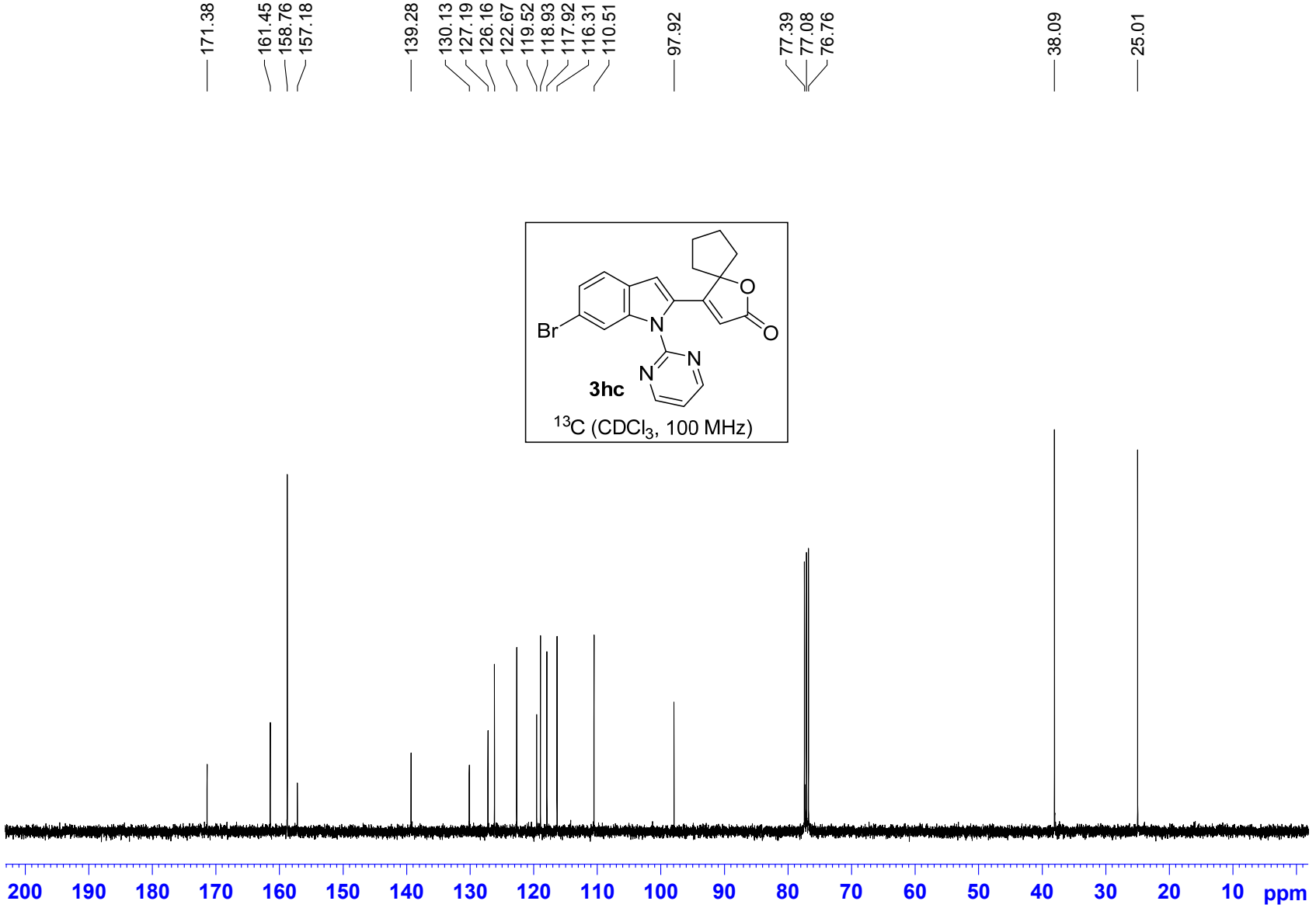


^{1}H ($CDCl_3$, 400 MHz)

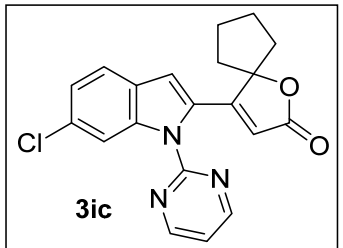



170.87
160.90
158.89
156.69
143.65
140.97
132.57
127.82
120.43
119.58
119.22
118.07
113.64
110.74
97.97
77.35
77.03
76.71
37.85
24.86
O2N
O
O
N
N
N
3gc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.722
8.716
8.197
7.460
7.440
7.309
7.288
7.208
7.194
6.807
5.366
2.215
1.974
1.803
Br
O
O
N
N
N
3hc
^{1}H (CDCl$_3$, 400 MHz)
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
ppm
2.00
1.00
1.03
1.03
1.03
1.00
1.00
2.04
4.06
2.00

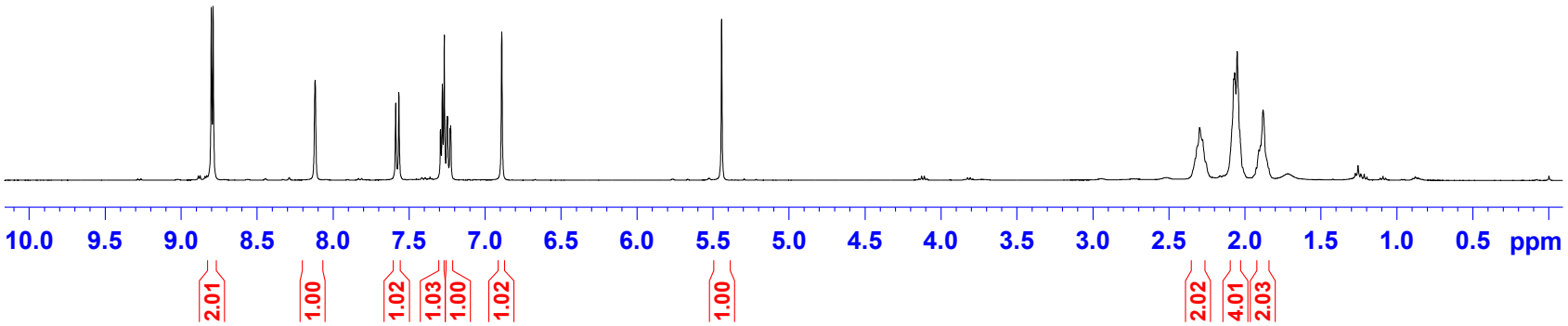

171.38
161.45
158.76
157.18
139.28
130.13
127.19
126.16
122.67
119.52
118.93
117.92
116.31
110.51
97.92
77.39
77.08
76.76
38.09
25.01
Br
N
O
O
N
N
3hc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

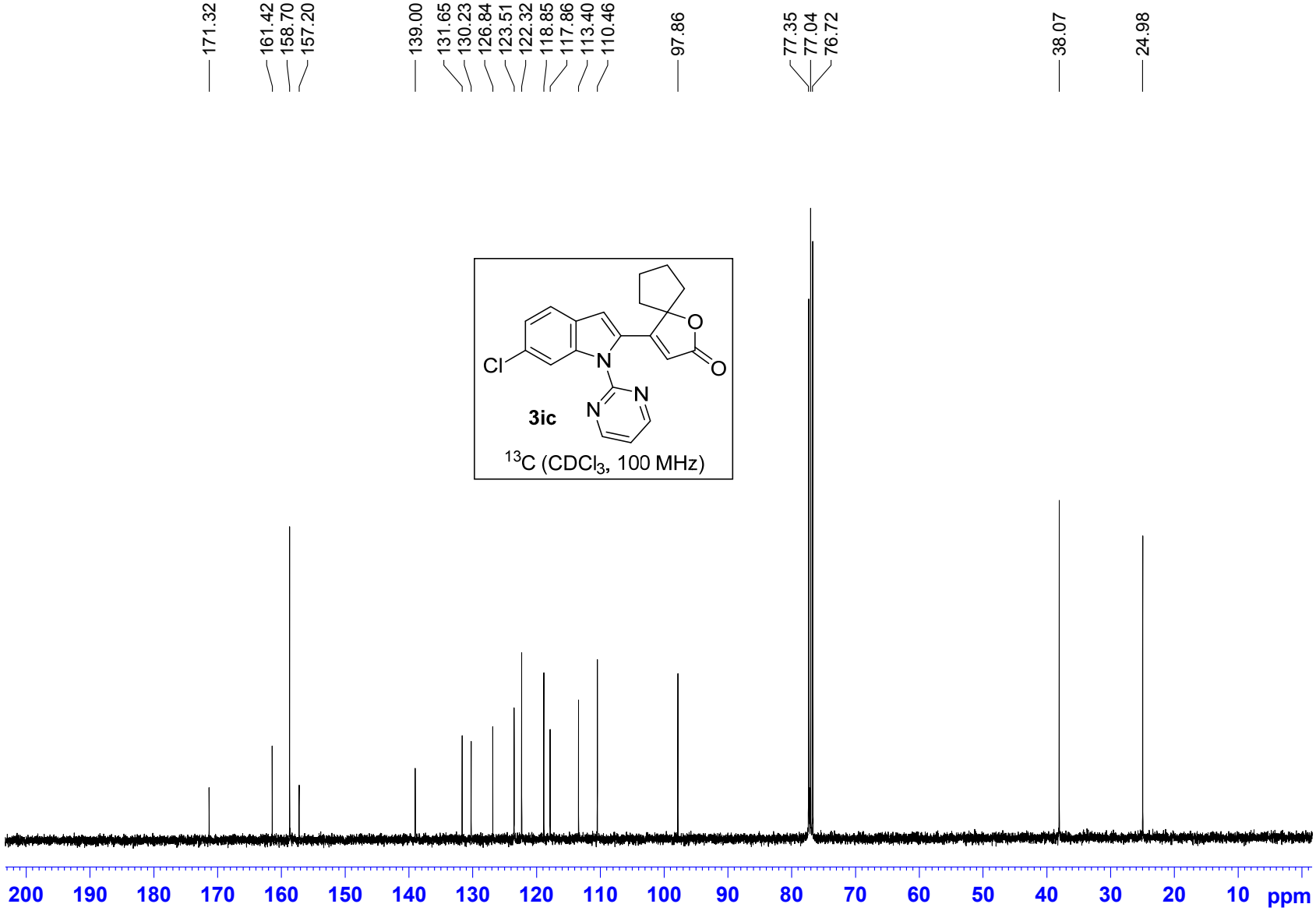
8.801
8.789
8.117
7.588
7.567
7.293
7.281
7.268
7.251
7.247
7.230
7.226
6.890
5.443
2.299
2.279
2.074
2.069
2.052
1.909
1.899
1.882
-0.000

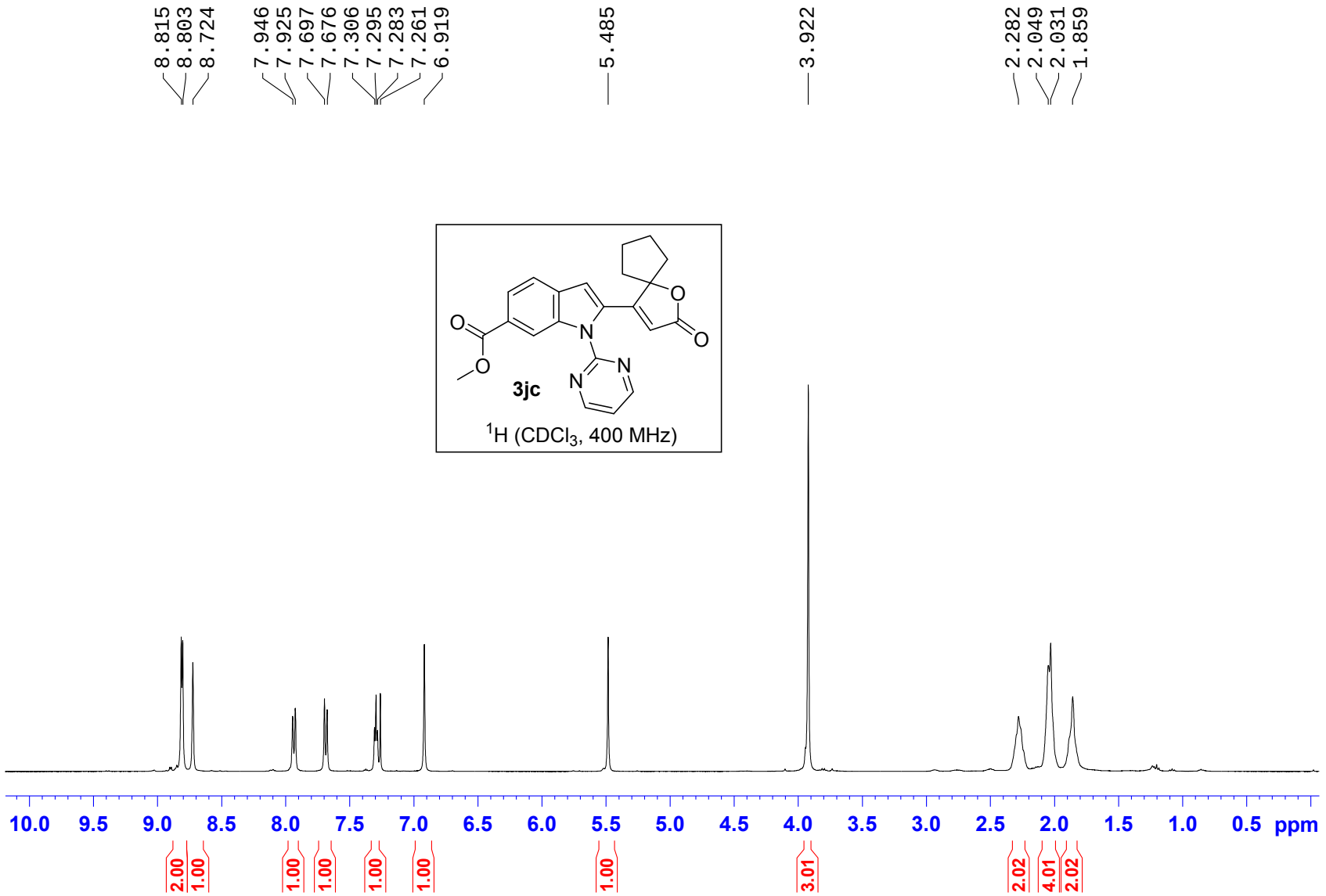


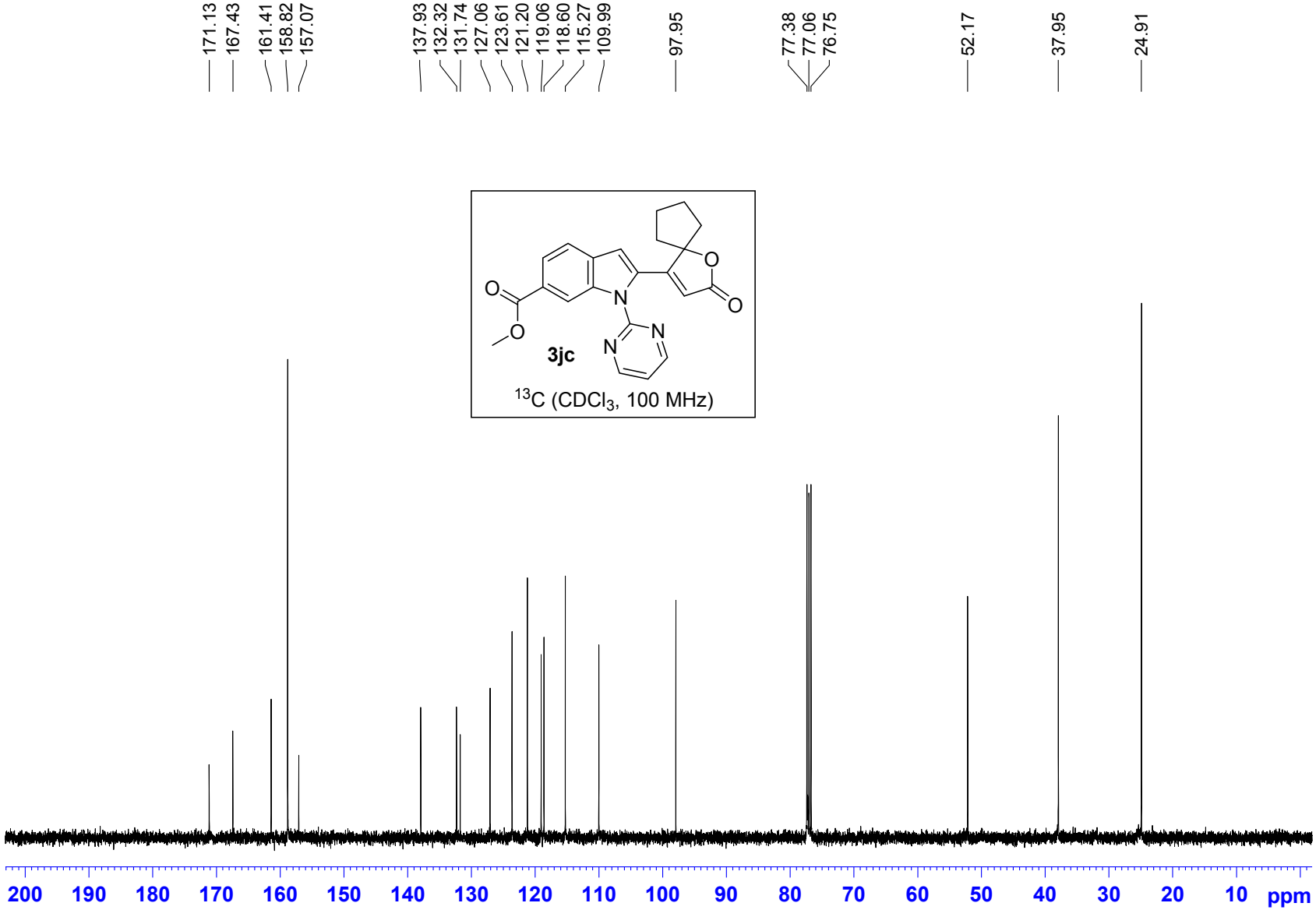
3ic

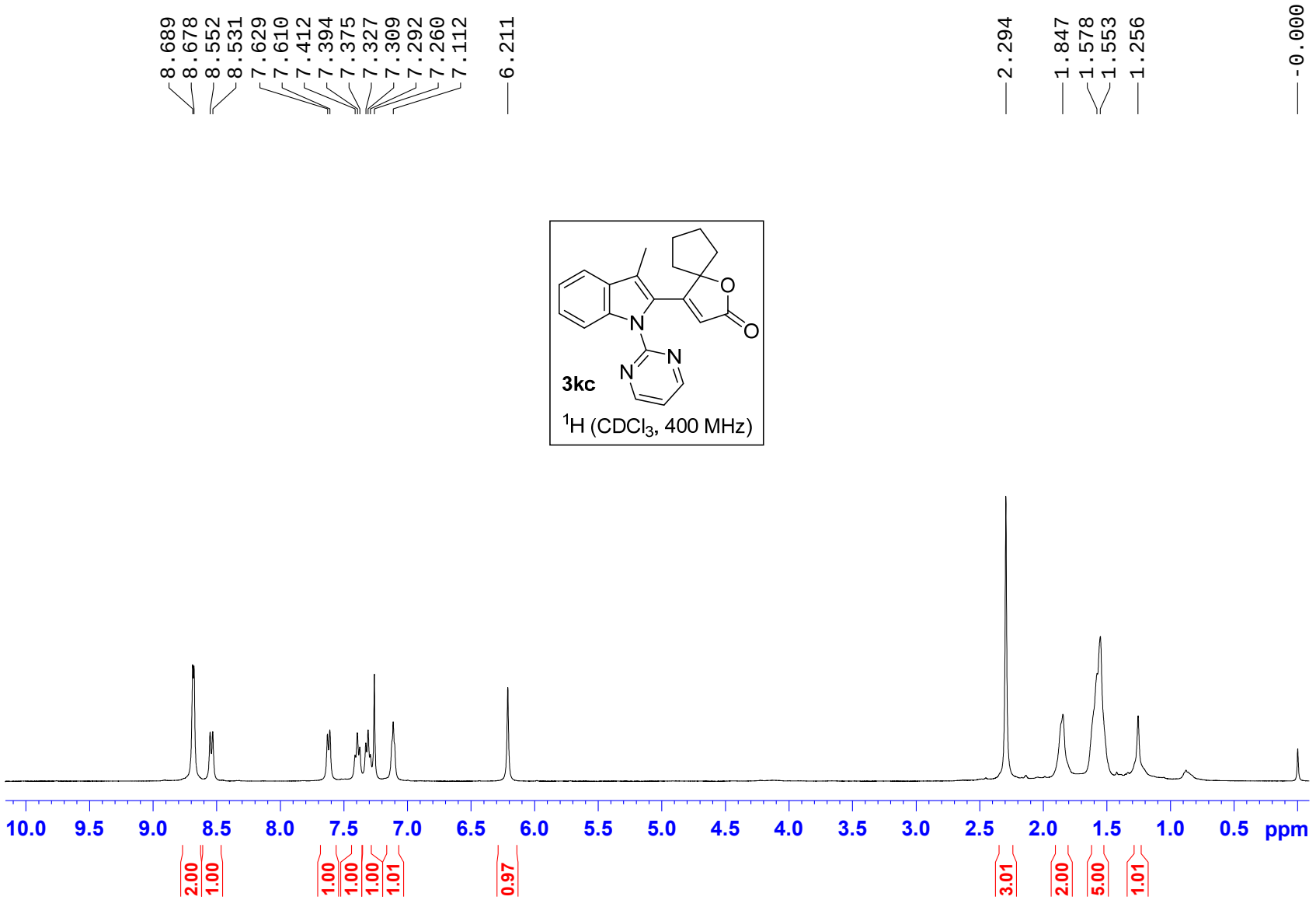
^{1}H ($CDCl_3$, 400 MHz)

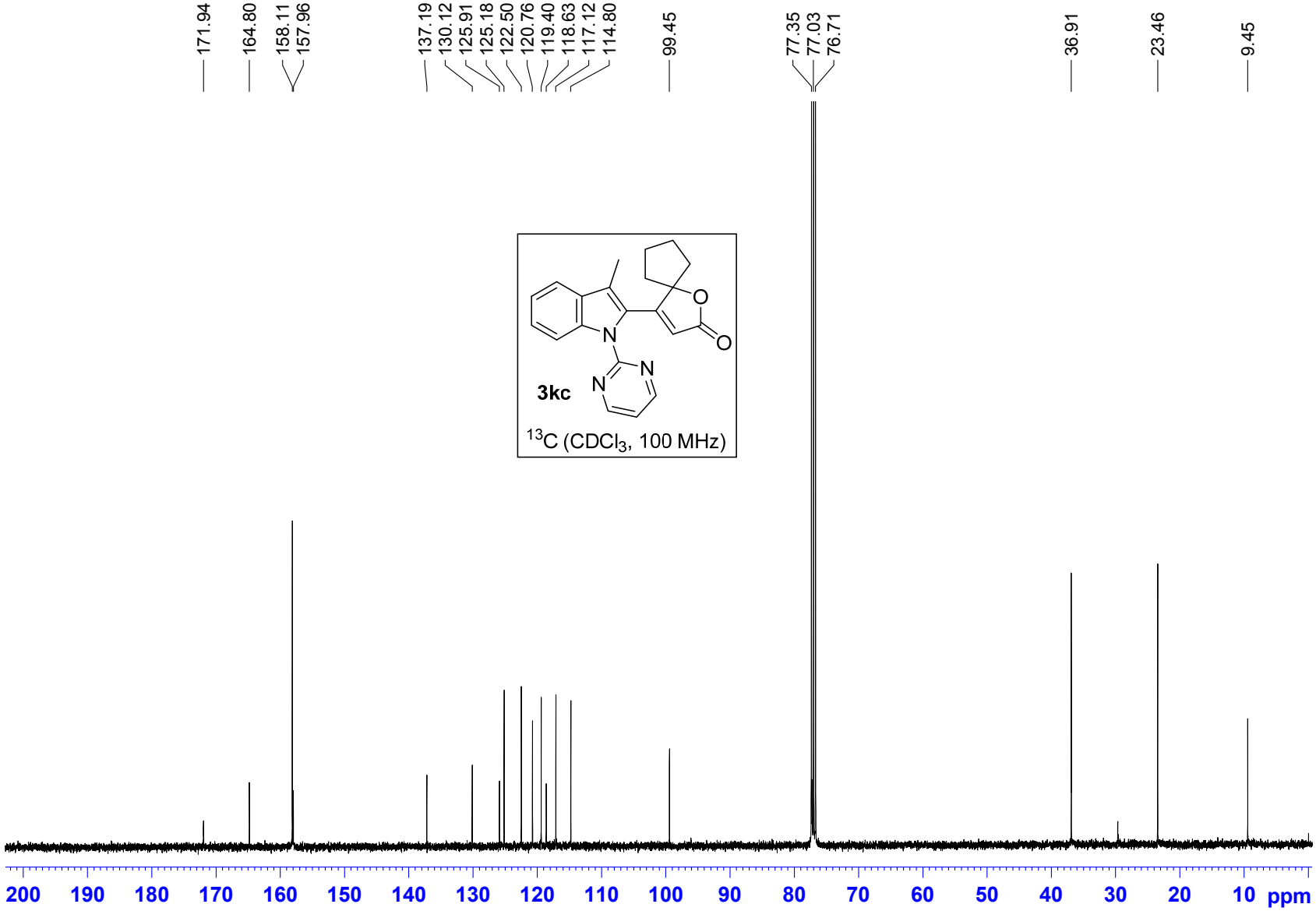


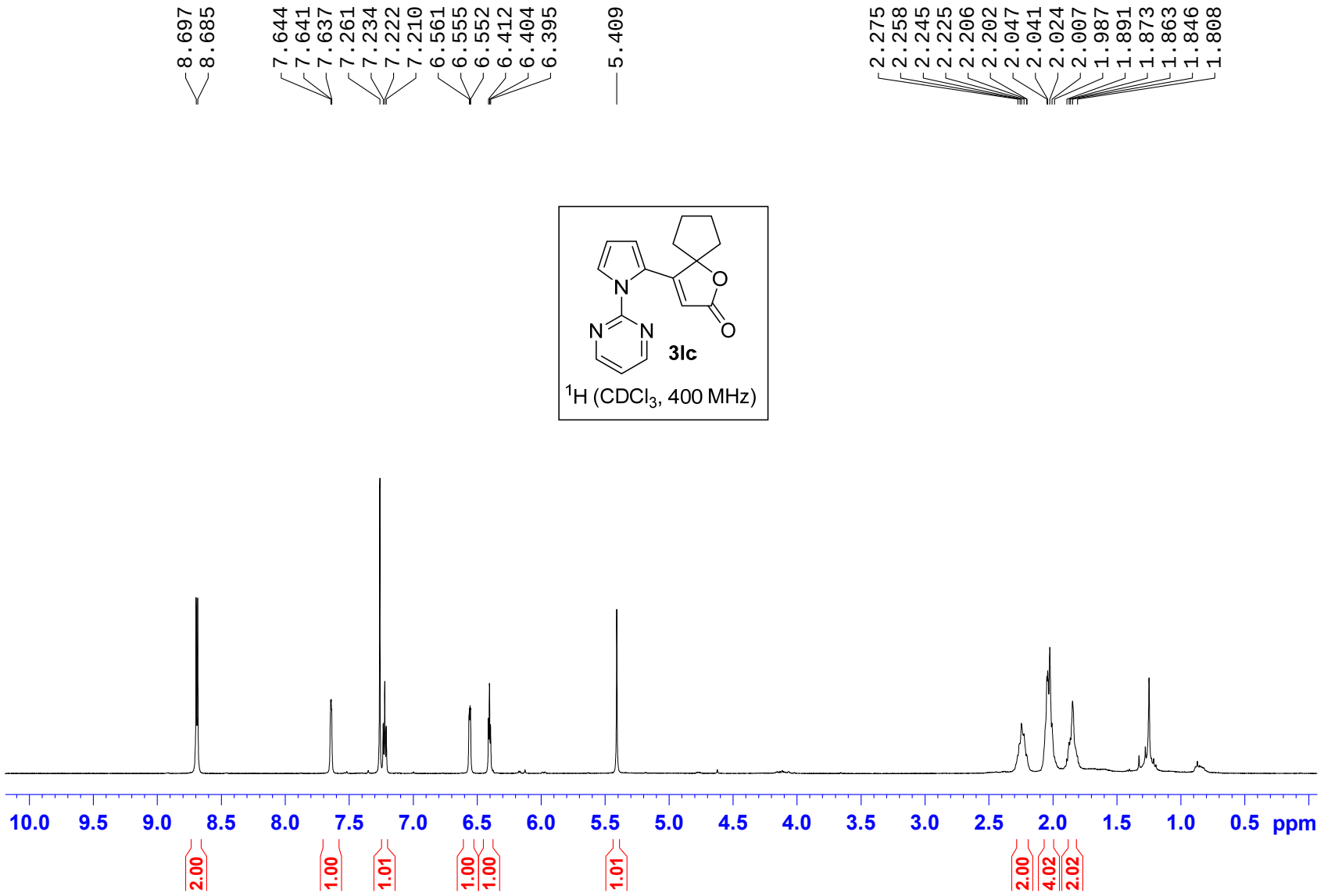

171.32
161.42
158.70
157.20
139.00
131.65
130.23
126.84
123.51
122.32
118.85
117.86
113.40
110.46
97.86
77.35
77.04
76.72
38.07
24.98
Cl
N
O
O
N
N
3ic
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

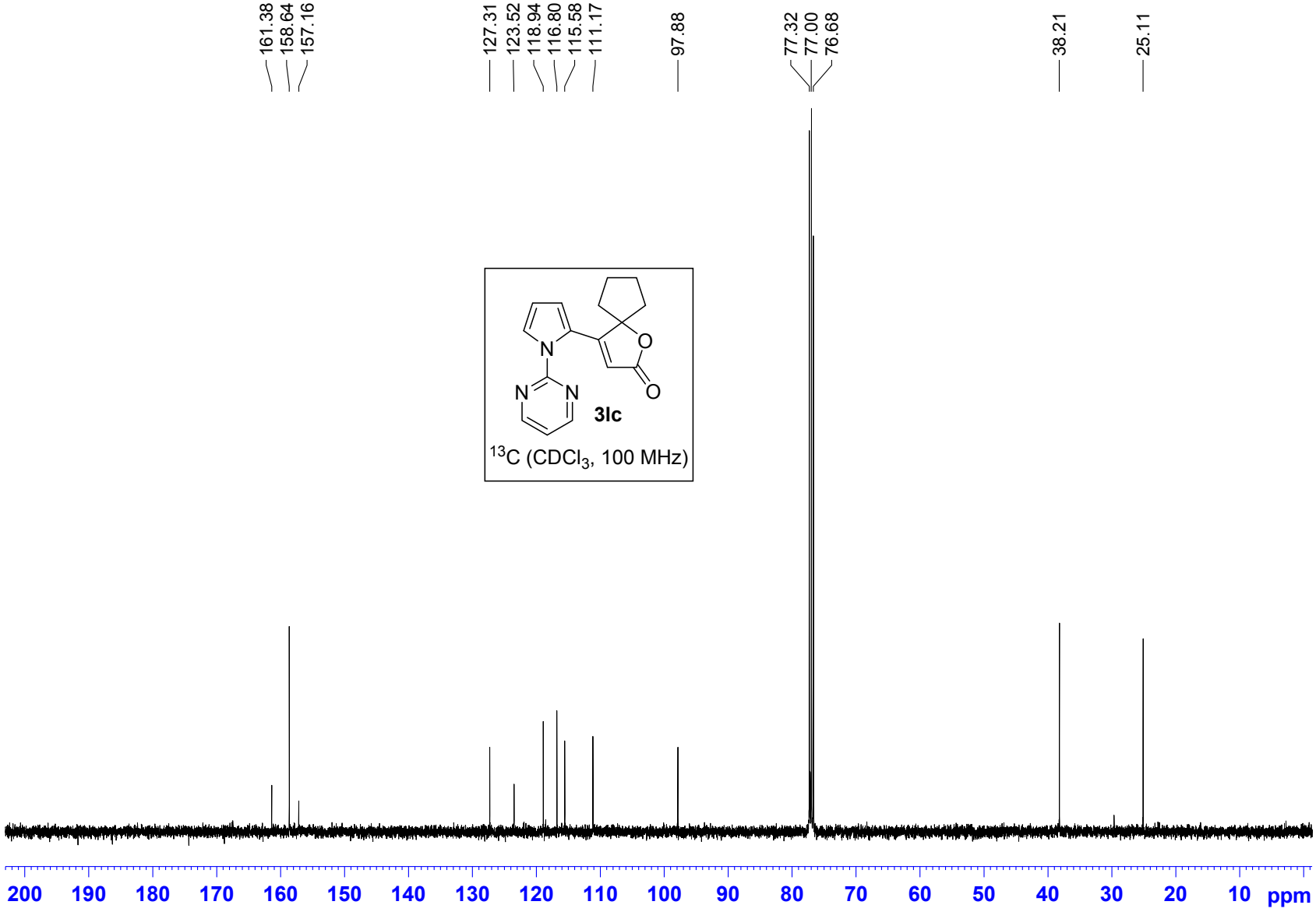

8.815
8.803
8.724
7.946
7.925
7.697
7.676
7.306
7.295
7.283
7.261
6.919
5.485
3.922
2.282
2.049
2.031
1.859
3jc
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.01
2.02
4.01
2.02

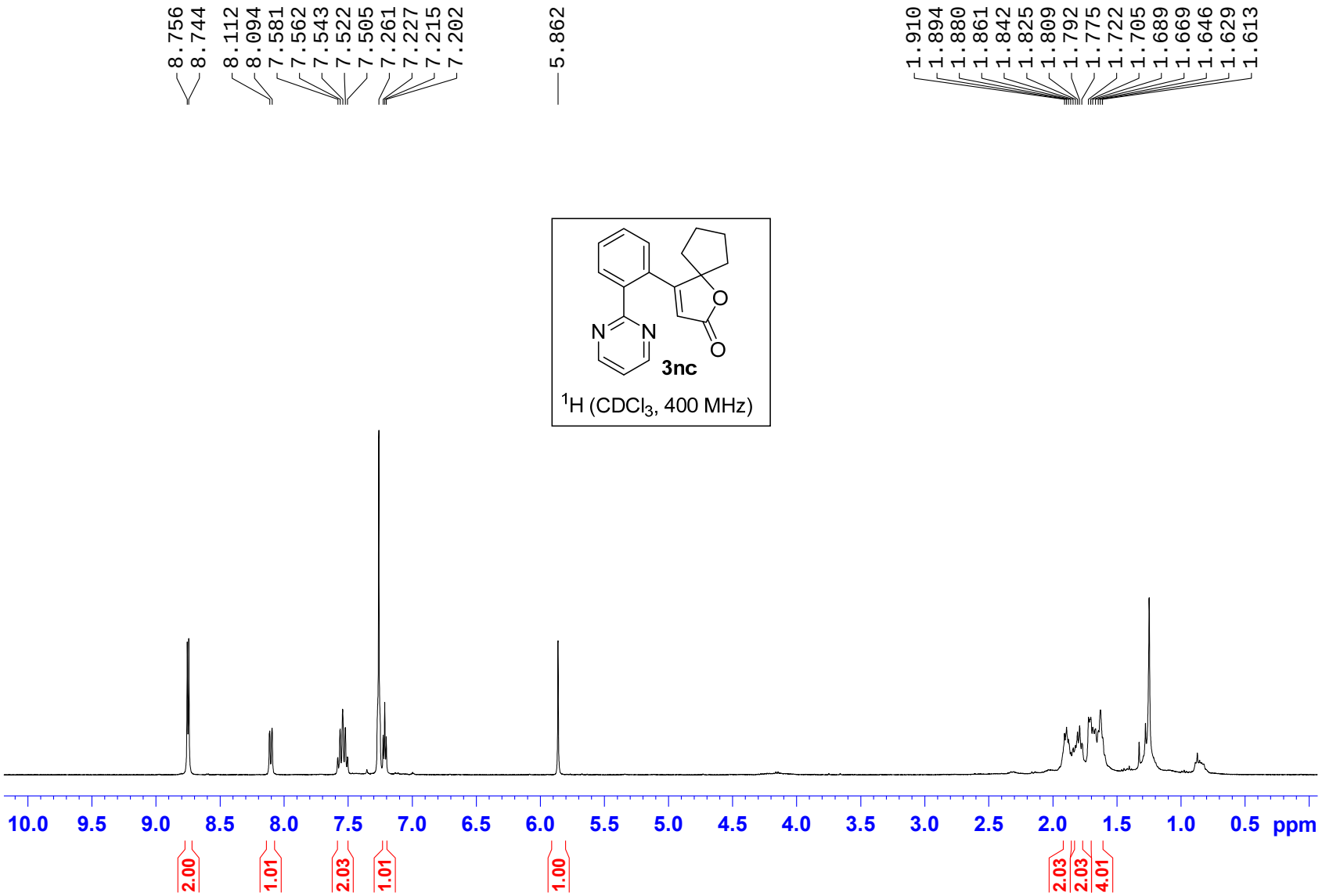

171.13
167.43
161.41
158.82
157.07
137.93
132.32
131.74
127.06
123.61
121.20
119.06
118.60
115.27
109.99
97.95
77.38
77.06
76.75
52.17
37.95
24.91
O
O
O
O
N
N
N
3jc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

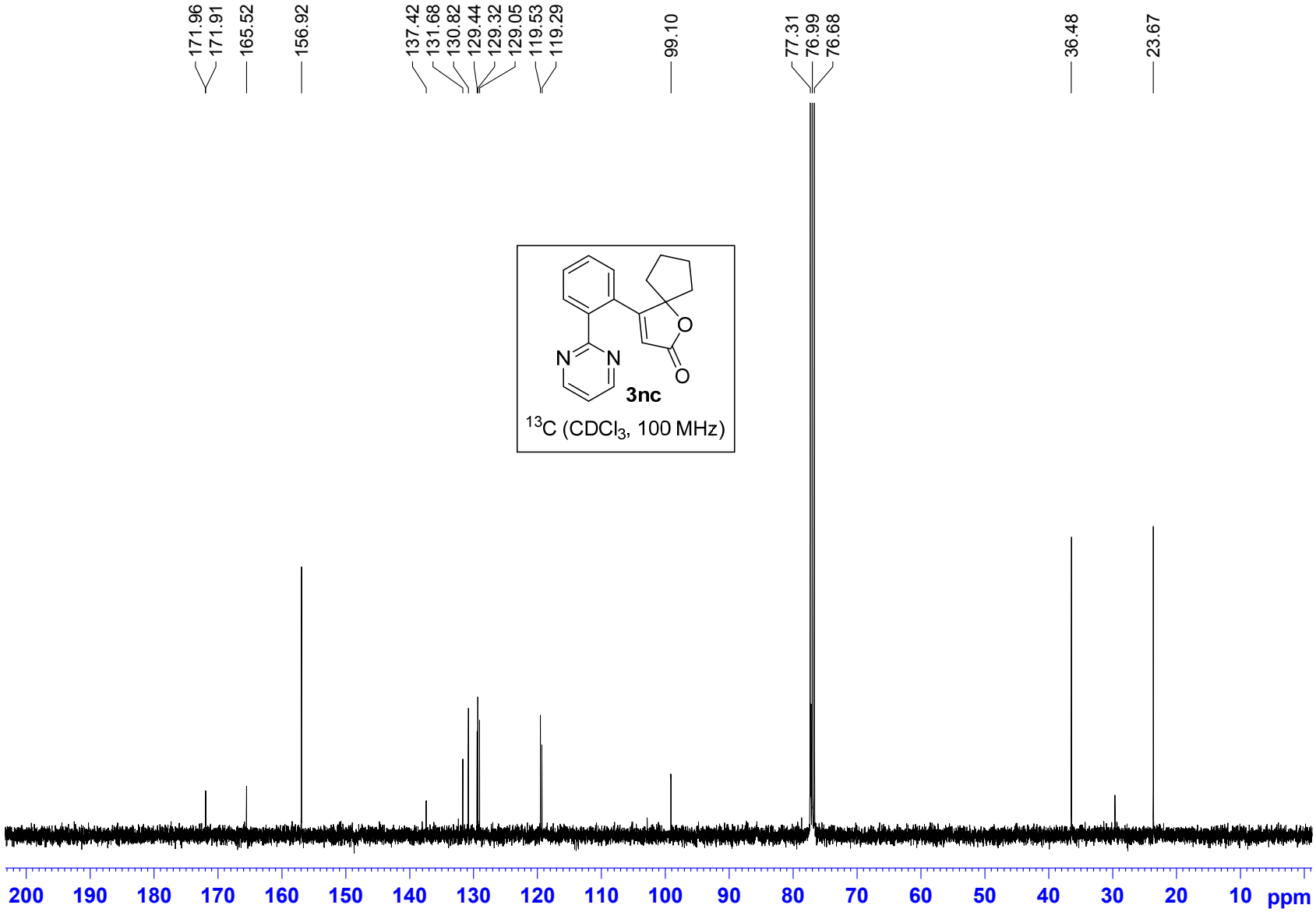

8.689
8.678
8.552
8.531
7.629
7.610
7.412
7.394
7.375
7.327
7.309
7.292
7.260
7.112
6.211
2.294
1.847
1.578
1.553
1.256
-0.000
3kc
^{1}H (CDCl$_3$, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.00
1.00
1.00
1.00
1.01
0.97
3.01
2.00
5.00
1.01

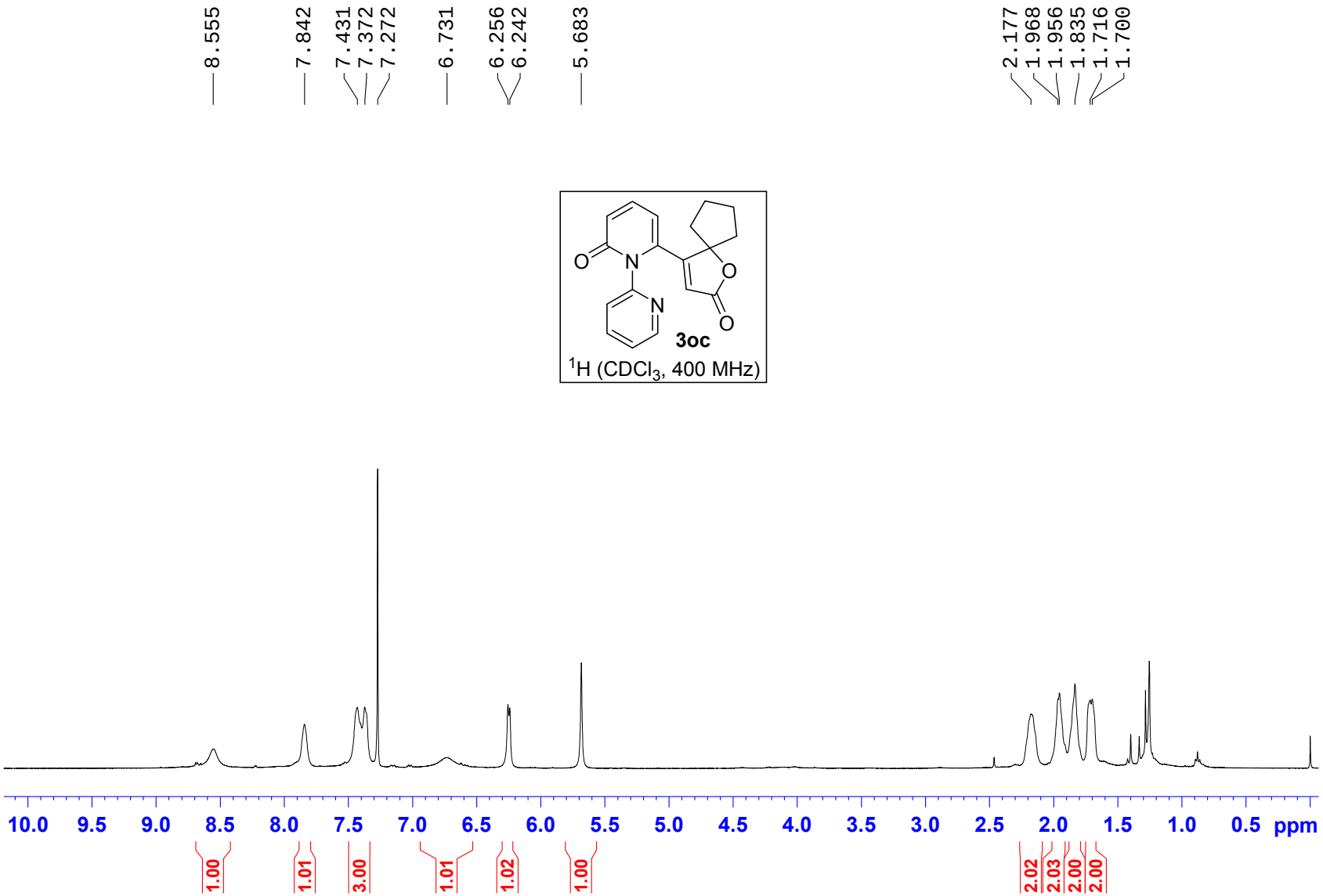

171.94
164.80
158.11
157.96
137.19
130.12
125.91
125.18
122.50
120.76
119.40
118.63
117.12
114.80
99.45
77.35
77.03
76.71
36.91
23.46
9.45
3kc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

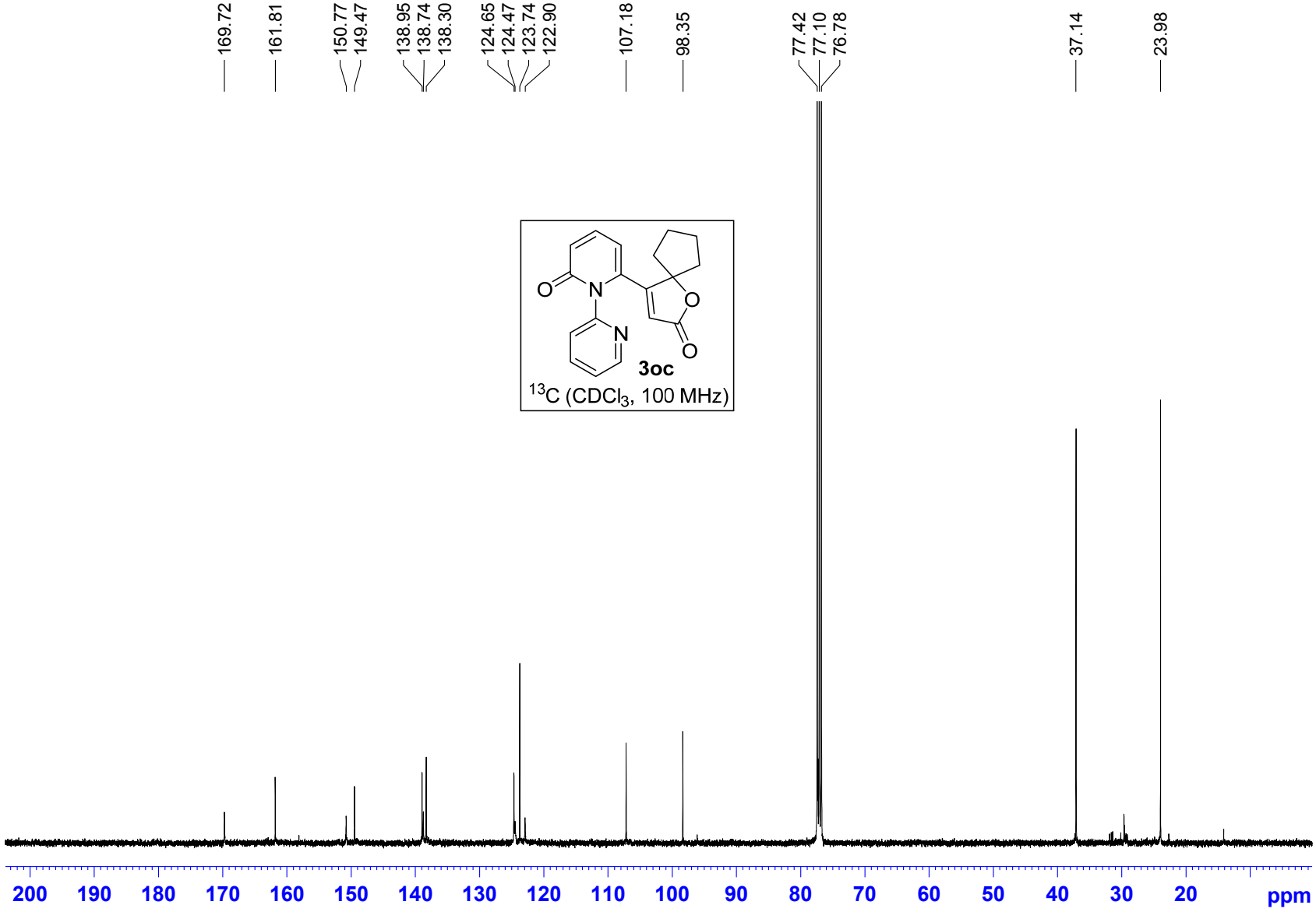

8.697
8.685
7.644
7.641
7.637
7.261
7.234
7.222
7.210
6.561
6.555
6.552
6.412
6.404
6.395
5.409
2.275
2.258
2.245
2.225
2.206
2.202
2.047
2.041
2.024
2.007
1.987
1.891
1.873
1.863
1.846
1.808
N
O
N
N
O
3Ic
1H (CDCl3, 400 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.00
1.01
1.00
1.00
1.01
2.00
4.02
2.02


161.38
158.64
157.16
127.31
123.52
118.94
116.80
115.58
111.17
97.88
77.32
77.00
76.68
38.21
25.11
N
N
N
O
O
3Ic
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.756
8.744
8.112
8.094
7.581
7.562
7.543
7.522
7.505
7.261
7.227
7.215
7.202
5.862
1.910
1.894
1.880
1.861
1.842
1.825
1.809
1.792
1.775
1.722
1.705
1.689
1.669
1.646
1.629
1.613
N
N
O
O
3nc
1H (CDCl3, 400 MHz)
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
ppm
2.00
1.01
2.03
1.01
1.00
2.03
2.03
4.01


171.96
171.91
165.52
156.92
137.42
131.68
130.82
129.44
129.32
129.05
119.53
119.29
99.10
77.31
76.99
76.68
36.48
23.67
N
N
O
O
3nc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

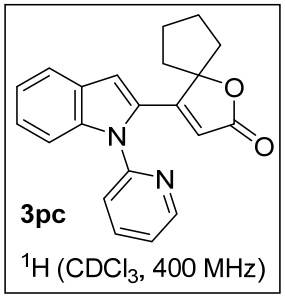

8.555
7.842
7.431
7.372
7.272
6.731
6.256
6.242
5.683
2.177
1.968
1.956
1.835
1.716
1.700
O
N
N
O
O
3oc
1H (CDCl3, 400 MHz)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.01
3.00
1.01
1.02
1.00
2.02
2.03
2.00
2.00


169.72
161.81
150.77
149.47
138.95
138.74
138.30
124.65
124.47
123.74
122.90
107.18
98.35
77.42
77.10
76.78
37.14
23.98
O
N
N
O
O
3oc
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

8.702 8.699 8.691 8.690 8.687 7.949 7.944 7.930 7.925 7.910 7.906 7.714 7.694 7.466 7.454 7.447 7.435 7.333 7.314 7.302 7.282 7.264 7.262 7.257 7.225 7.205 7.185 7.163 6.980 4.958

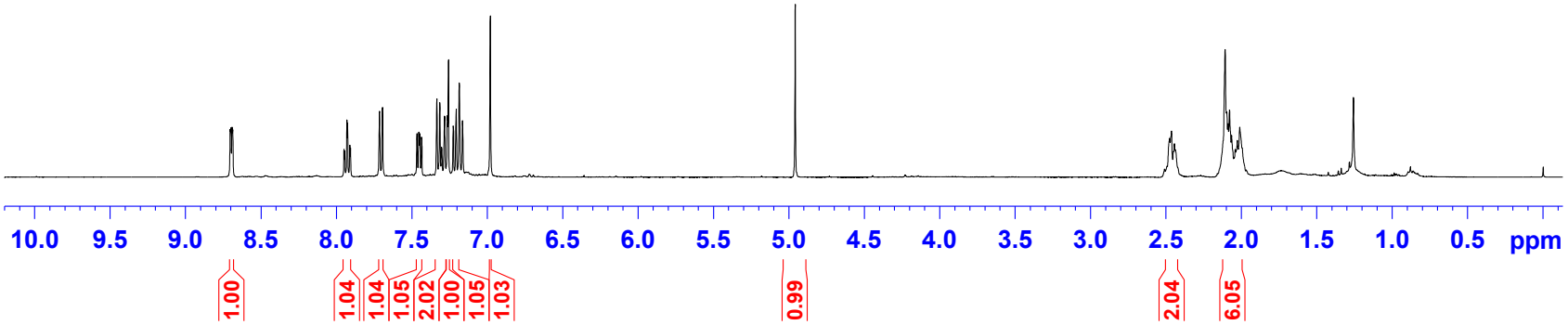
2.509 2.493 2.476 2.463 2.450 2.443 2.437 2.107 2.096 2.088 2.078 2.064 2.040 2.026 2.010

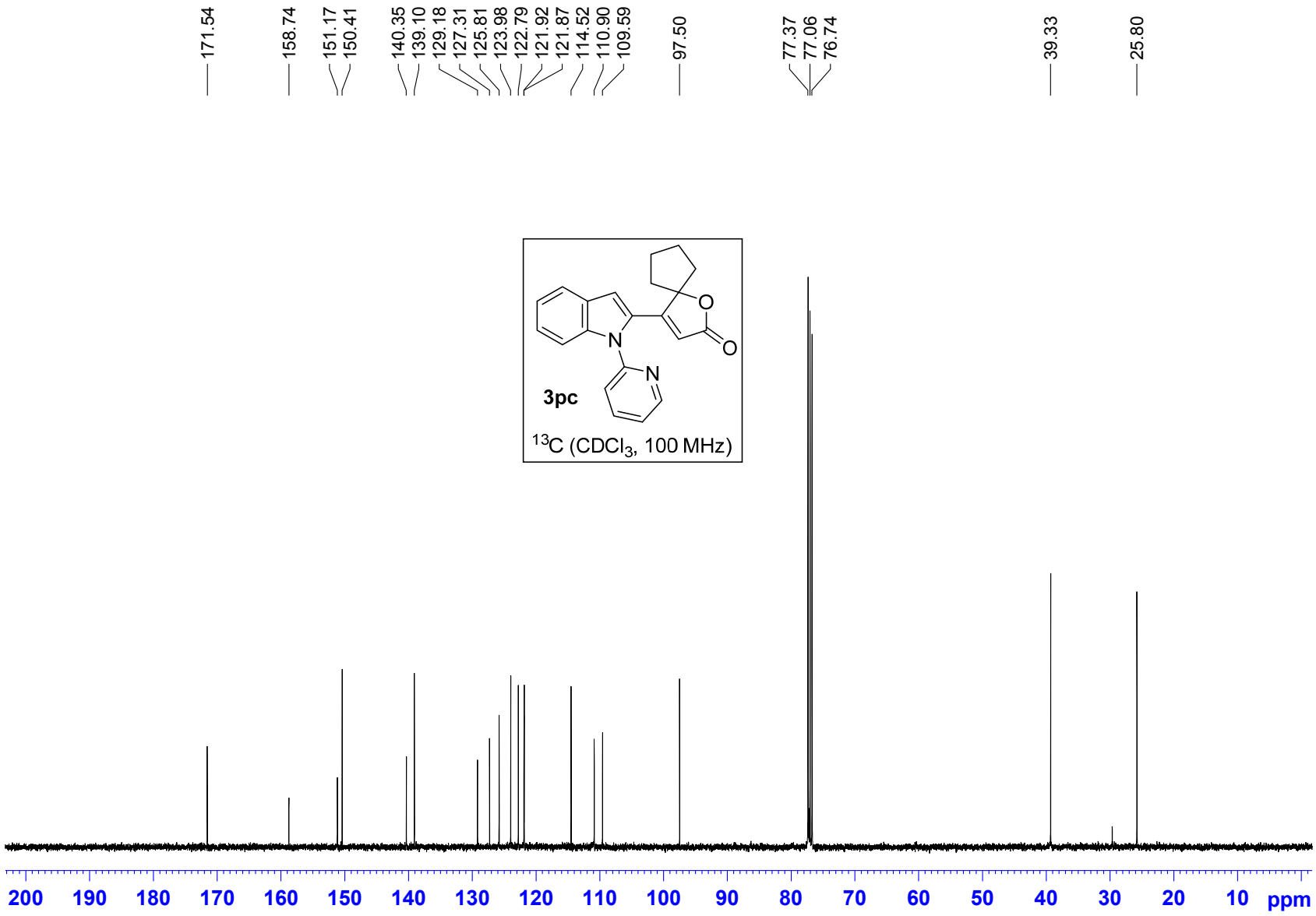
-0.000

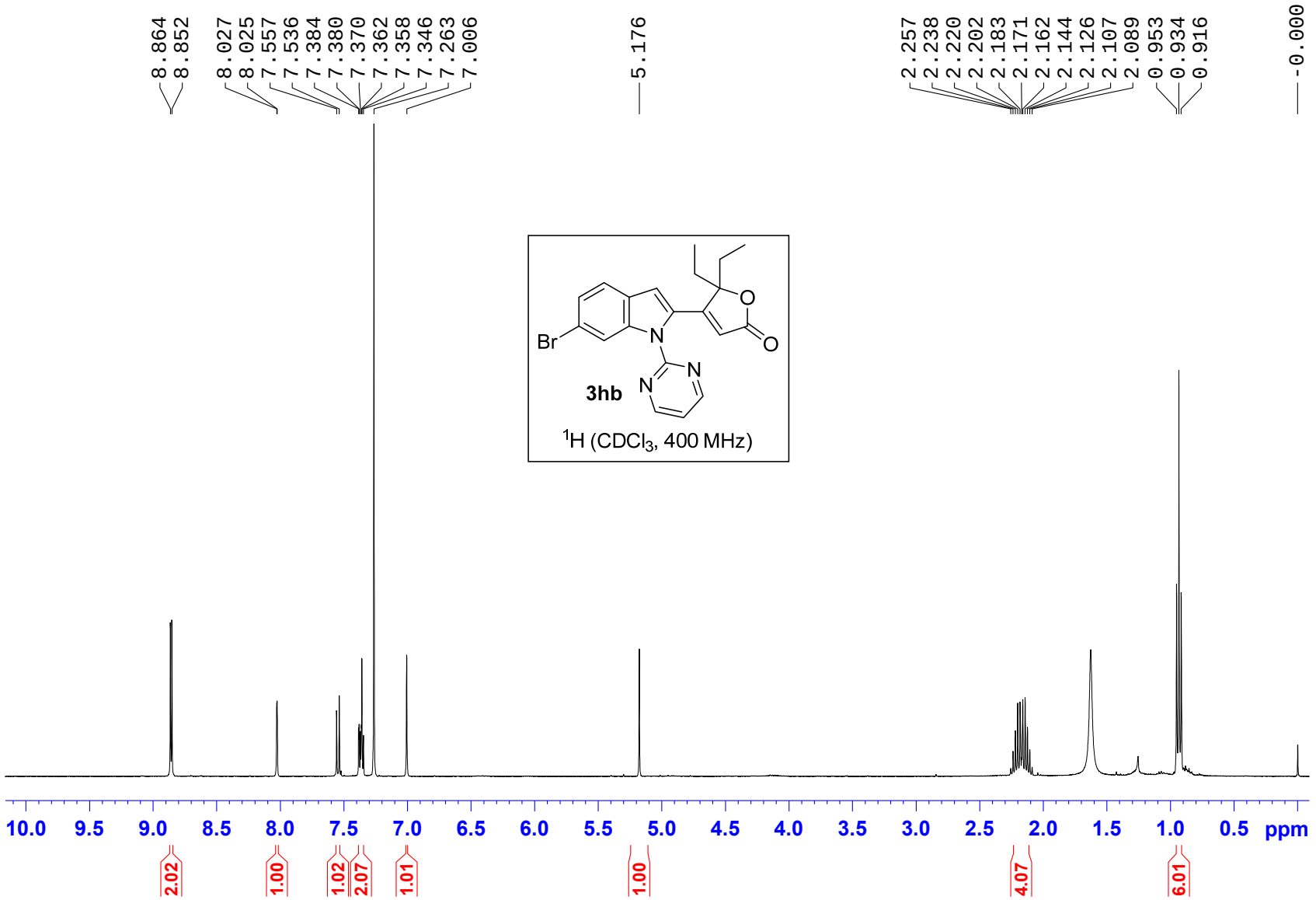


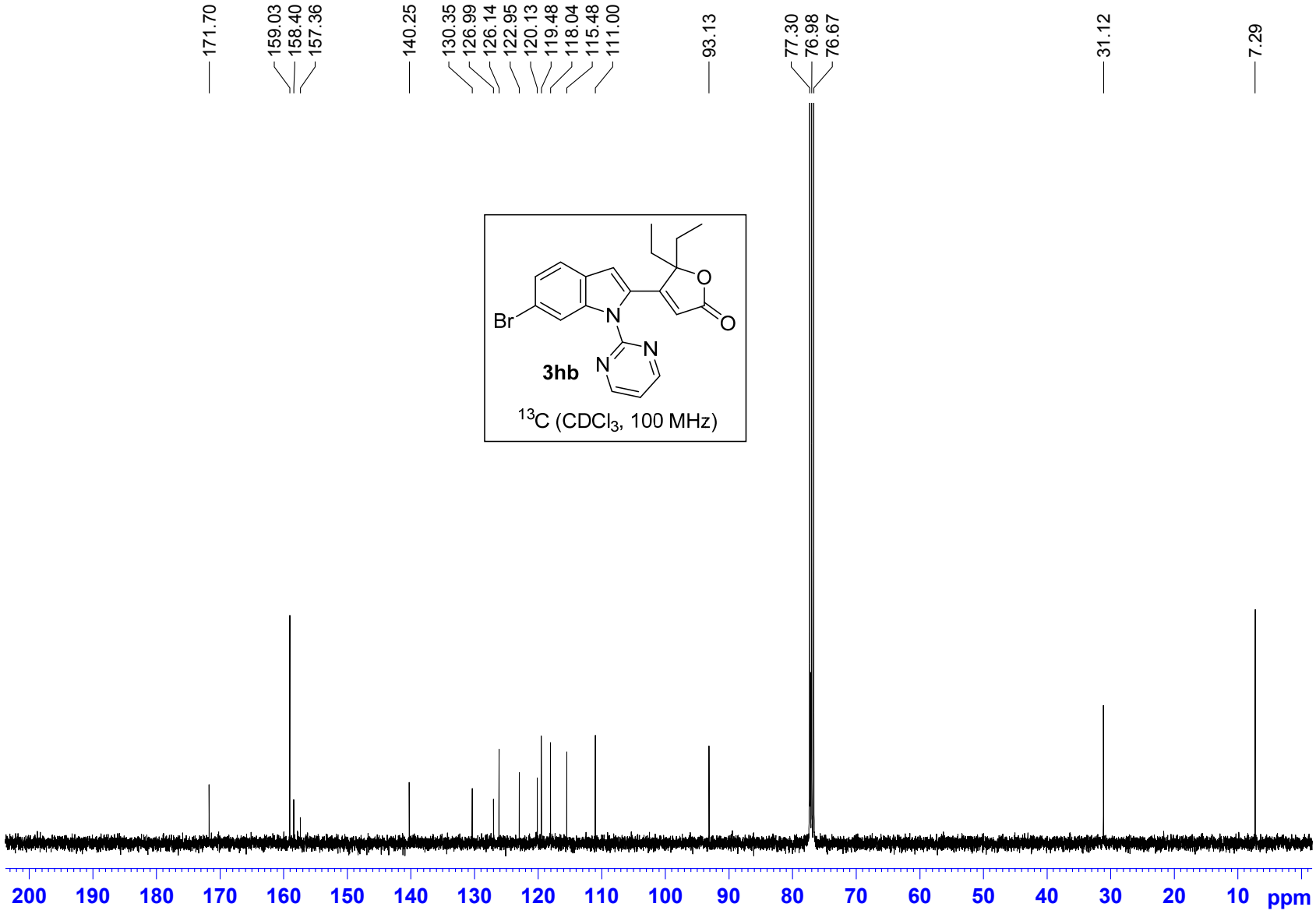
3pc

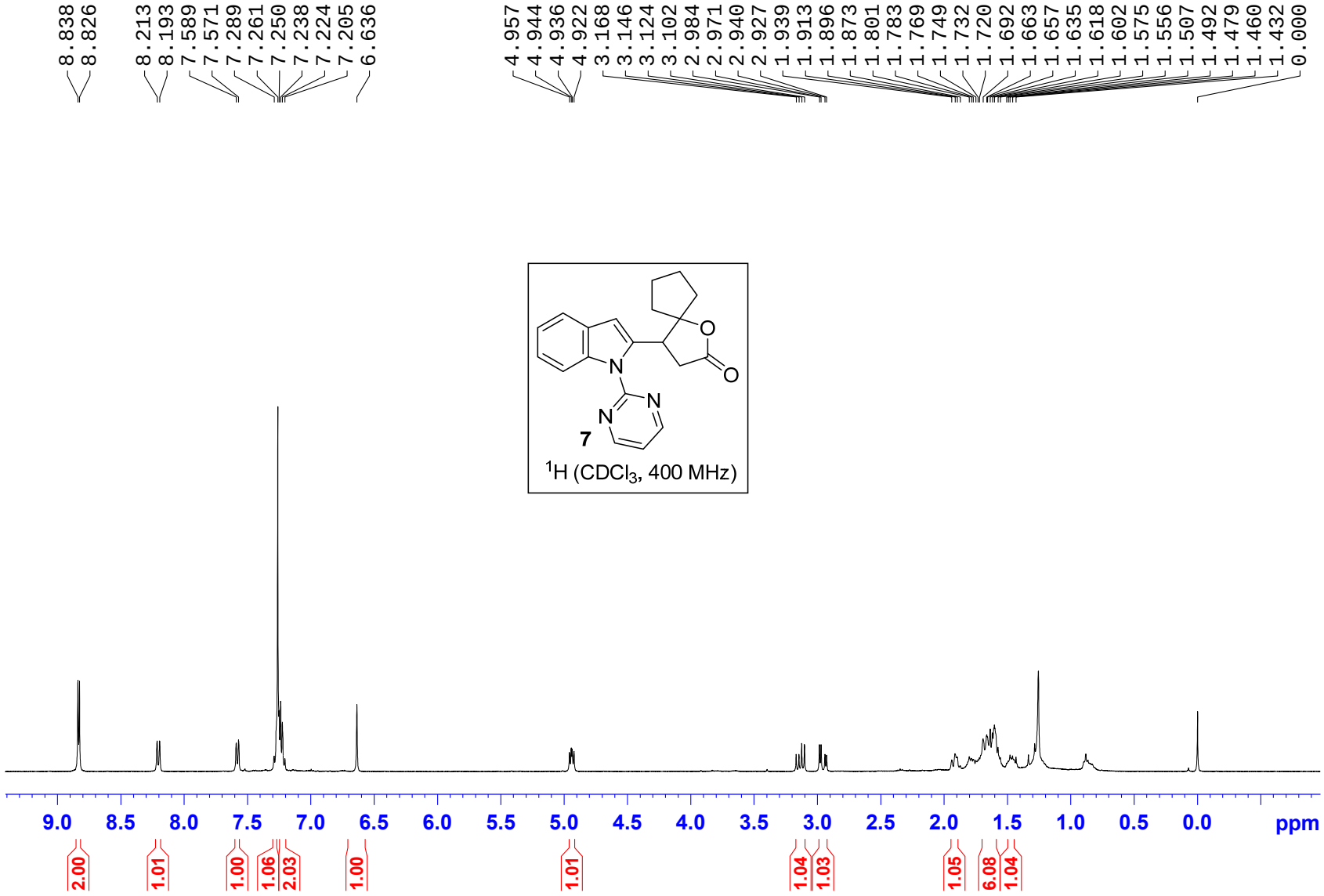
^{1}H ($CDCl_3$, 400 MHz)

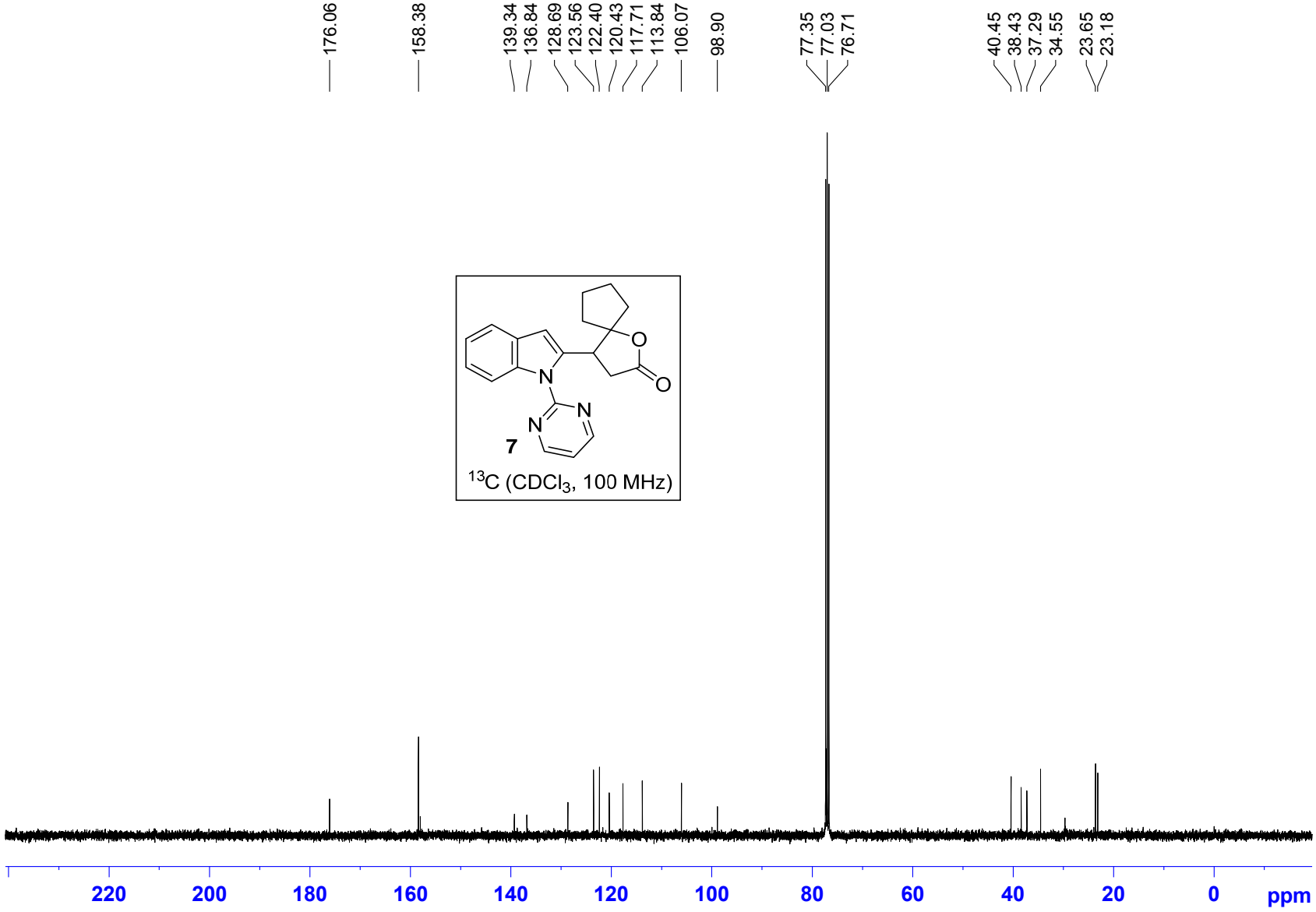


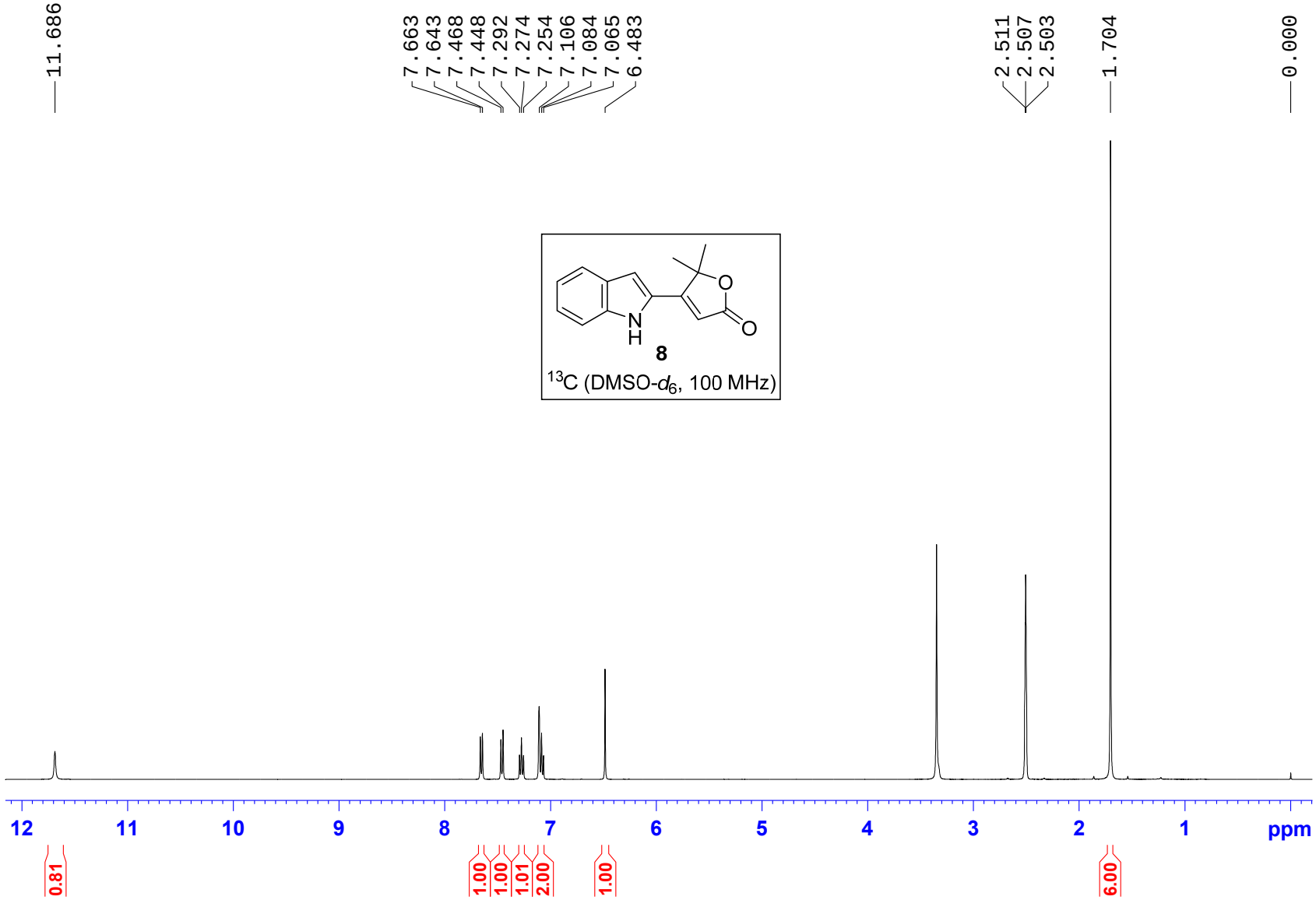

171.54
158.74
151.17
150.41
140.35
139.10
129.18
127.31
125.81
123.98
122.79
121.92
121.87
114.52
110.90
109.59
97.50
77.37
77.06
76.74
39.33
25.80
O
O
N
N
3pc
^{13}C (CDCl$_3$, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

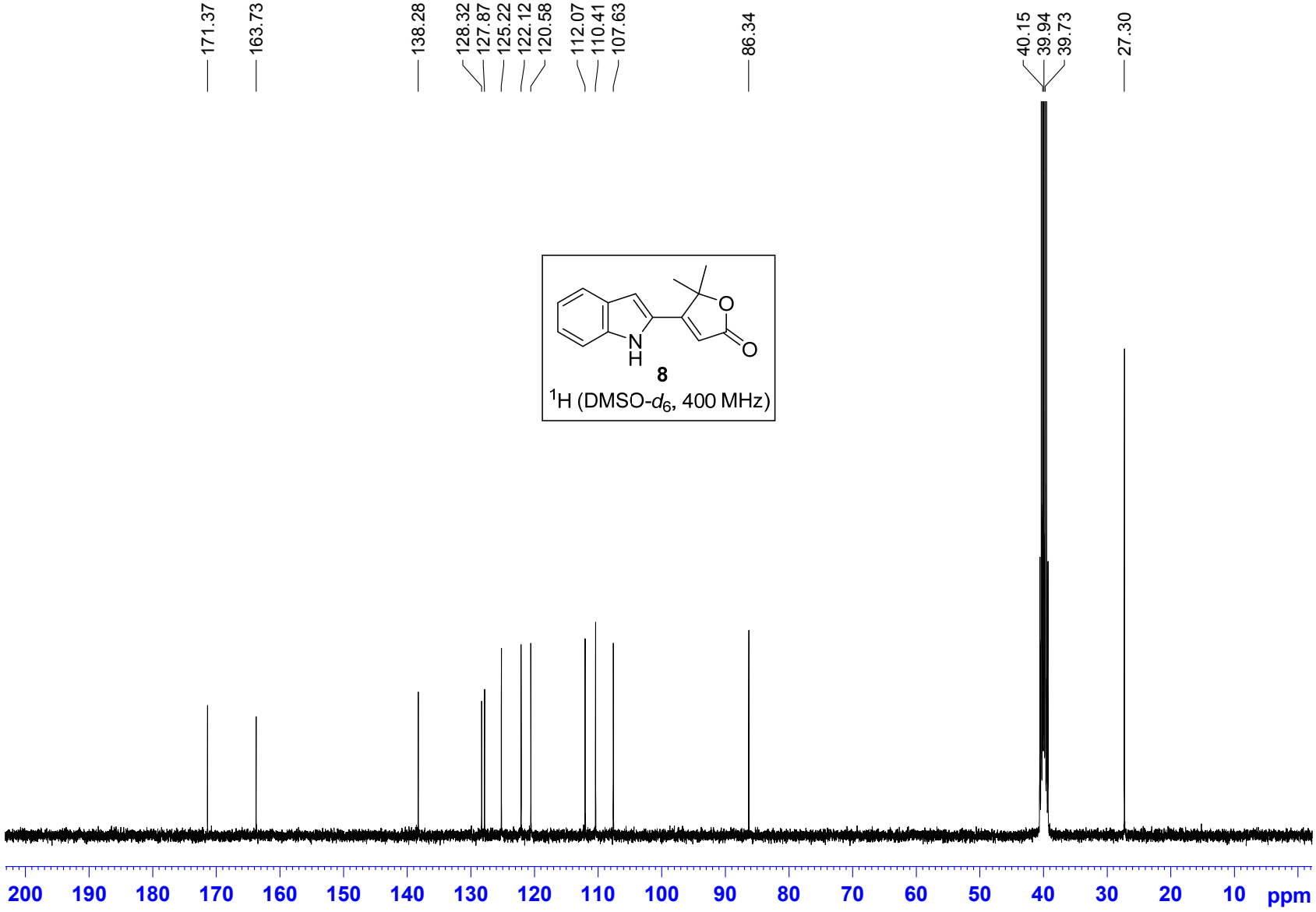

8.864
8.852
8.027
8.025
7.557
7.536
7.384
7.380
7.370
7.362
7.358
7.346
7.263
7.006
5.176
2.257
2.238
2.220
2.202
2.183
2.171
2.162
2.144
2.126
2.107
2.089
0.953
0.934
0.916
-0.000
Br
O
O
N
N
N
3hb
1H (CDCl3, 400 MHz)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
1.00
1.02
2.07
1.01
1.00
4.07
6.01

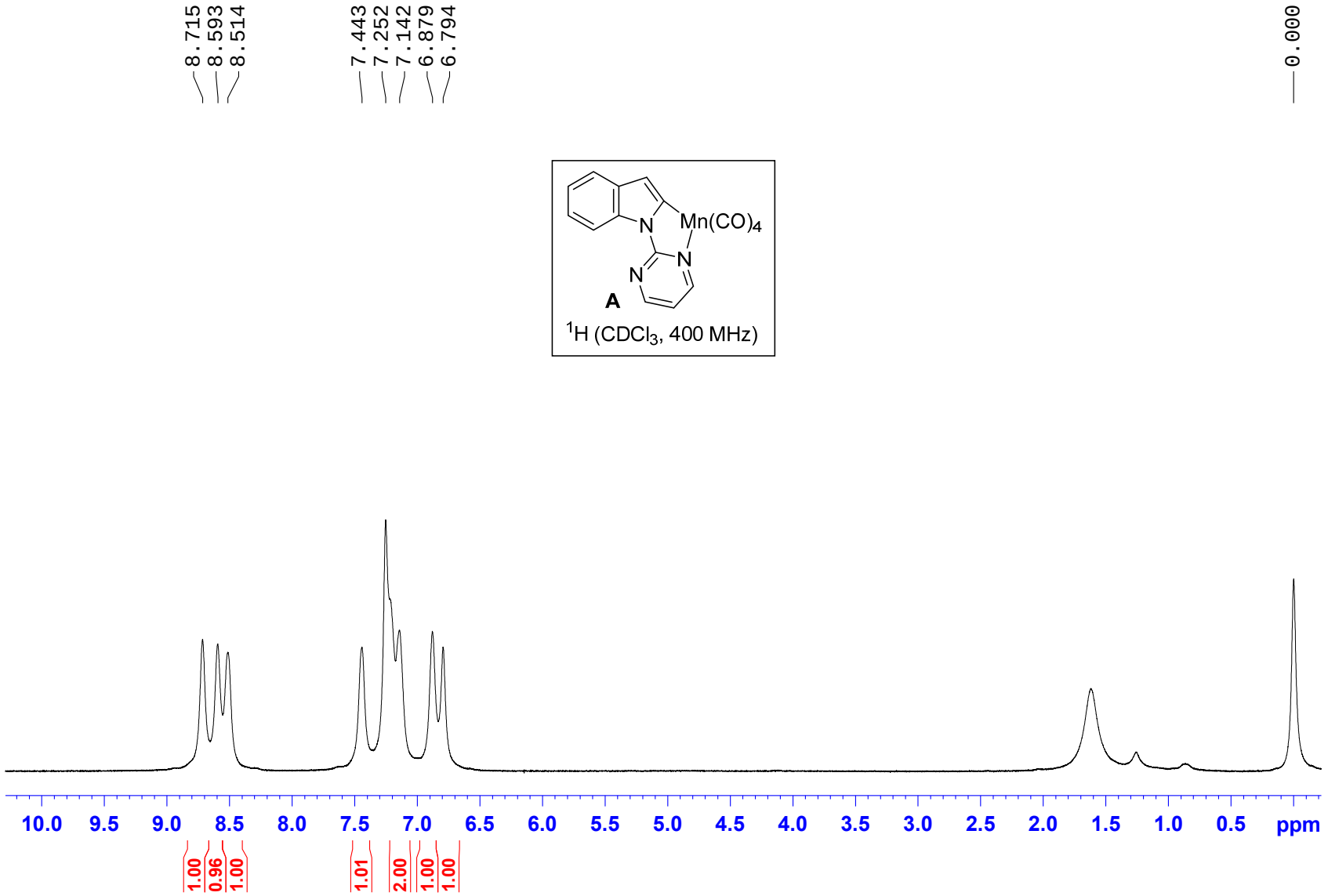

171.70
159.03
158.40
157.36
140.25
130.35
126.99
126.14
122.95
120.13
119.48
118.04
115.48
111.00
93.13
77.30
76.98
76.67
31.12
7.29
Br
N
O
O
N
N
3hb
13C (CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

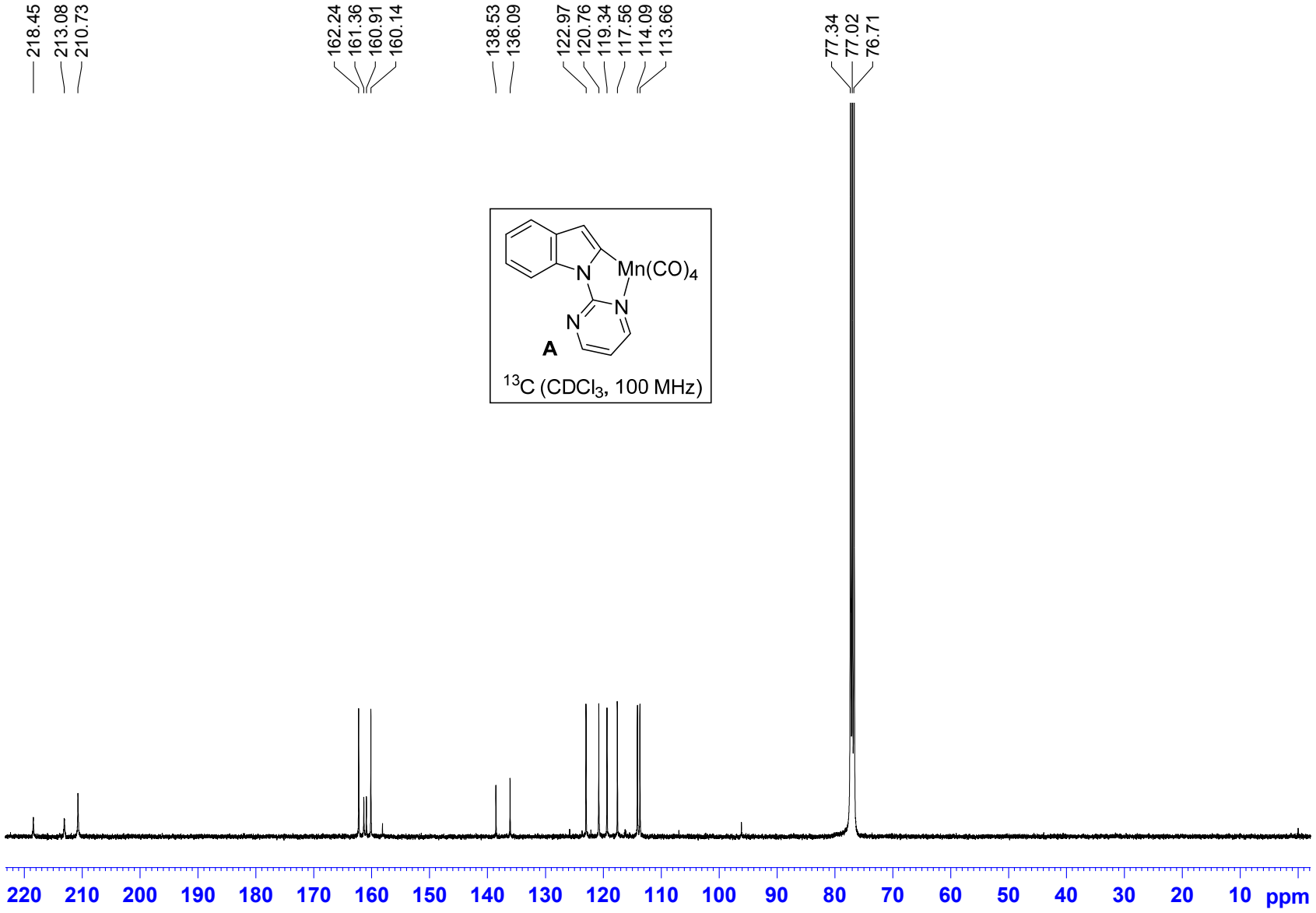

8.838
8.826
8.213
8.193
7.589
7.571
7.289
7.261
7.250
7.238
7.224
7.205
6.636
4.957
4.944
4.936
4.922
3.168
3.146
3.124
3.102
2.984
2.971
2.940
2.927
1.939
1.913
1.896
1.873
1.801
1.783
1.769
1.749
1.732
1.720
1.692
1.663
1.657
1.635
1.618
1.602
1.575
1.556
1.507
1.492
1.479
1.460
1.432
0.000
O
O
N
N
N
7
^{1}H ($CDCl_3$, 400 MHz)
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
2.00
1.01
1.00
1.06
2.03
1.00
1.01
1.04
1.03
1.05
6.08
1.04


176.06
158.38
139.34
136.84
128.69
123.56
122.40
120.43
117.71
113.84
106.07
98.90
77.35
77.03
76.71
40.45
38.43
37.29
34.55
23.65
23.18
O
O
N
N
N
7
^{13}C (CDCl$_3$, 100 MHz)
220
200
180
160
140
120
100
80
60
40
20
0
ppm


11.686
7.663
7.643
7.468
7.448
7.292
7.274
7.254
7.106
7.084
7.065
6.483
2.511
2.507
2.503
1.704
0.000
8
13C (DMSO-d6, 100 MHz)
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.81
1.00
1.00
1.01
2.00
1.00
6.00


171.37
163.73
138.28
128.32
127.87
125.22
122.12
120.58
112.07
110.41
107.63
86.34
40.15
39.94
39.73
27.30
O
N
H
O
8
1H (DMSO-d6, 400 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.715
8.593
8.514
7.443
7.252
7.142
6.879
6.794
0.000
Mn(CO)4
N
N
N
A
1H (CDCl3, 400 MHz)
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
ppm
1.00
0.96
1.00
1.01
2.00
1.00
1.00


218.45
213.08
210.73
162.24
161.36
160.91
160.14
138.53
136.09
122.97
120.76
119.34
117.56
114.09
113.66
77.34
77.02
76.71
N
Mn(CO)4
N
N
A
13C (CDCl3, 100 MHz)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm