Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

$Mg(ClO_4)_2$-Promoted [4 + 3] Cycloaddition of Oxindole Derivatives with Conjugated Dienes: Concise Synthesis of Spirocycloheptane Oxindole Derivatives

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1. General information

Chemicals were either purchased or purified by standard techniques without special instructions. CH_2Cl_2 was dried by distillation over CaH_2. THF was dried by distillation over Na/K. All moisture-sensitive reactions were performed under an atmosphere of Ar. The silica gel (200-300 meshes) was used for column chromatography and TLC inspections were on silica gel GF254 plates. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AM 400 MHz spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants *J* are given in Hz. IR spectra were recorded on a *Nicolet NEXUS* 670 FT-IR spectrometer. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker Apex II by means of the ESI technique. Melting points were measured on an XT-4 melting point apparatus and were uncorrected.

2. Optimization of the reaction condition.

Table 1. Optimization of the reaction condition.[a]

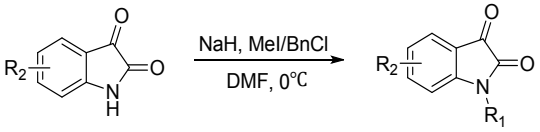
Entry	Conditions	Solvent	T(°C)	Yield(%)[c]
1	TFA	DCM	-78 to 0	trace[d]
2	TfOH	DCM	-78 to 0	trace[d]
3	TsOAg	DCM	-78 to rt	NR[e]
4	Tf_2O/2,6-Lutidine	DCM	-78 to rt	ND[e]
5	CSA	DCM	-78 to rt	NR[e]
6	$HClO_4$	DCM	-78	ND[e]
7	$SnCl_4$	DCM	-78 to rt	18
8	$ZnCl_2$	DCM	rt	30
9	$ZnCl_2$	THF	rt	NR[e]
10	$FeCl_3$	DCM	-78 to rt	NR[e]
11	$CuCl_2$	DCM	-78 to rt	NR[e]
12[b]	$AuCl_3$	DCM	-78	17
13[b]	$AuCl_3$	THF	-78	NR[e]
14[b]	$AuCl_3$	Et_2O	-78	13
15[b]	$InBr_3$	DCM	-20	12
16[b]	$InCl_3$	DCM	-20	15
17[b]	$In(OAc)_3$	DCM	-20	ND[e]
18	$TiCl_4$	DCM	-78	ND[e]
19	$Zn(ClO_4)_2$	DCM	rt	NR[e]
20	$Mg(ClO_4)_2$	DCM	0	<5
21	$Mg(ClO_4)_2$	DCM	rt	58
22	$Mg(ClO_4)_2$	DCM	reflux	ND[e]
23	$Mg(ClO_4)_2$	THF	rt	20
24	$Mg(ClO_4)_2$	Et_2O	rt	25
25	$Mg(ClO_4)_2$	Tol	rt	NR[e]
26	$Mg(ClO_4)_2$	CH_3CH_2OH	rt	NR[e]
27	$Mg(ClO_4)_2$	CH_3COCH_3	rt	NR[e]
28	$Mg(ClO_4)_2$	CH_3CN	rt	ND[e]

29	$Mg(ClO_4)_2$	DMF	rt	ND[e]
30	$Mg(ClO_4)_2$	CH_2ClCH_2Cl	rt	NR[e]

[a] Unless otherwise noted, all reactions were performed on **3** (0.1 mmol, 1.0 eq), **4** (1.0 mmol, 10.0 eq) and Lewis acids or Brønsted acids (0.15 mmol, 1.5 eq) in solvent (15 mL). [b] 0.01 mmol Lewis acids. [c] Yield of isolated product. [d] Determined by ^{1}H NMR (400 MHz) analysis (starting material was decomposed). [e] NR = no reaction (starting material was recovered); ND = not determined (starting material was decomposed).

3. Preparation of Substrates 3a-3k and Analytic Data

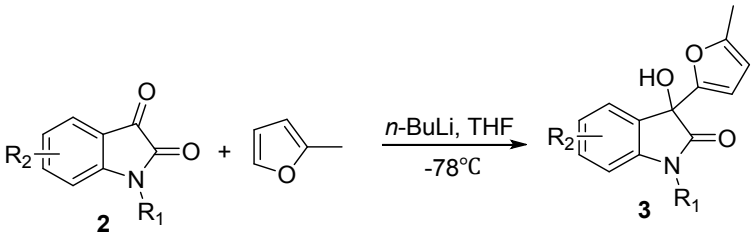
General procedure A: (the N of isatins were protected with Me/Bn)[1]



Scheme S1. General procedure A

To a solution of isatin (1.0 mmol, 1.0 eq) in 15 mL DMF was added NaH (1.2 mmol, 1.2 eq) at 0 °C. After stirring for 15 min, MeI (1.2 mmol, 1.2 eq) or BnCl (1.2 mmol, 1.2 eq) was added to the mixture at dropwise and the stirring was continued for 1 h at 0 °C. The reaction was then quenched by water and extracted with EtOAc. The organic layer was separated and washed with water and brine respectively. Then the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (Petroleum Ether/EtOAc = 2:1) to afford the products.

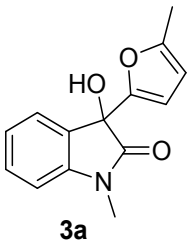
General procedure B:[2]



Scheme S2. General procedure B

To a solution of 2-methylfuran (1.1 mmol, 1.1 eq) in anhydrous THF (20 mL) at -78 °C was added *n*-BuLi (1.0 mmol, 1.0 eq). After the resulting light yellow coloured solution stirring for 2 h, the corresponding isatin (1.0 mmol, 1.0 eq) in anhydrous THF (20 mL) was added to the mixture at dropwise and the stirring was continued for 1 h at the same temperature. The reaction was then quenched by saturated aqueous NH_4Cl (2 mL) and was allowed to warm to room temperature. Then the mixture was extracted with EtOAc, and the organic layer was separated and washed with water and brine respectively. Then the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (Petroleum Ether/EtOAc = 4:1) to afford the products.

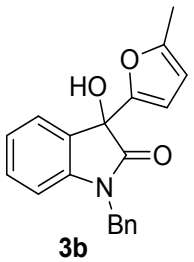
3a. 3-hydroxy-1-methyl-3-(5-methylfuran-2-yl)indolin-2-one



3a

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3a** (89%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 2.8 Hz, 1H), 5.87(d, *J* = 3.2 Hz, 1H), 3.98 (s, 1H), 3.19 (s, 3H), 2.27 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 175.1, 154.0, 149.2, 143.4, 130.1, 128.3, 125.4, 123.2, 110.0, 108.6, 106.3, 73.3, 26.4, 13.7; **HRMS-ESI** (m/z): calcd for $C_{14}H_{13}NO_3[M + Na]^+$: 266.0788; found: 266.0784.

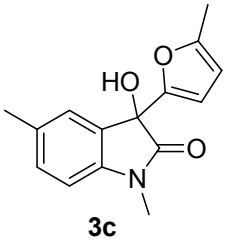
3b. 1-benzyl-3-hydroxy-3-(5-methylfuran-2-yl)indolin-2-one



3b

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3b** (84%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.32-7.21 (m, 6H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.21 (d, *J* = 2.8 Hz, 1H), 5.92 (d, *J* = 3.2 Hz, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.81 (d, *J* = 16.0 Hz, 1H), 3.58 (s, 1H), 2.30 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 175.3, 154.0, 149.3, 142.6, 135.2, 130.0, 128.8, 128.4, 127.7, 127.0, 125.4, 123.3, 109.8, 109.7, 106.4, 73.5, 43.8, 13.7; **HRMS-ESI** (m/z): calcd for $C_{20}H_{17}NO_3[M + Na]^+$: 342.1101; found: 342.1097.

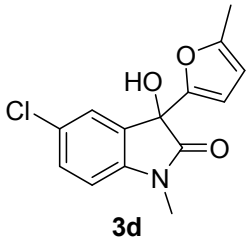
3c. 3-hydroxy-1,5-dimethyl-3-(5-methylfuran-2-yl)indolin-2-one



3c

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3c** (74%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.38 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 5.89 (d, *J* = 2.4 Hz, 1H), 3.37 (s, 1H), 3.20 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 175.2, 153.8, 149.5, 141.1, 132.9, 130.3, 128.4, 126.0, 109.8, 108.3, 106.3, 73.5, 26.4, 21.0, 13.7; **HRMS-ESI** (m/z): calcd for $C_{15}H_{15}NO_3[M + Na]^+$: 280.0944; found: 280.0939.

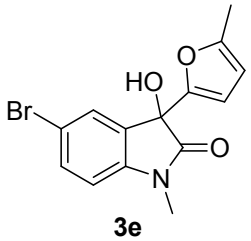
3d. 5-chloro-3-hydroxy-1-methyl-3-(5-methylfuran-2-yl)indolin-2-one



3d

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3d** (70%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.56 (d, *J* = 2.0 Hz, 1H), 7.34 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 5.91 (d, *J* = 2.4 Hz, 1H), 3.55 (s, 1H), 3.21 (s, 3H), 2.30 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.7, 154.3, 148.4, 142.0, 130.0, 129.7, 128.7, 125.9, 110.2, 109.6, 106.5, 73.2, 26.6, 13.8; **HRMS-ESI** (m/z): calcd for $C_{14}H_{12}ClNO_3[M + Na]^+$: 300.0398; found: 300.0394.

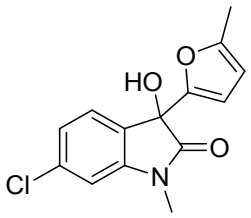
3e. 5-bromo-3-hydroxy-1-methyl-3-(5-methylfuran-2-yl)indolin-2-one



3e

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3e** (42%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 5.91 (d, *J* = 2.4 Hz, 1H), 3.32 (s, 1H), 3.21 (s, 3H), 2.30 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.5, 154.4, 148.5, 142.6, 133.0, 130.1, 128.7, 115.9, 110.3, 110.1, 106.5, 73.2, 26.6, 13.7; **HRMS-ESI** (m/z): calcd for $C_{14}H_{12}BrNO_3[M + Na]^+$: 343.9893; found: 343.9888.

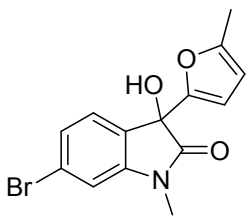
3f. 6-chloro-3-hydroxy-1-methyl-3-(5-methylfuran-2-yl)indolin-2-one



3f

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3f** (72%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.12 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 1.6 Hz, 1H), 6.15 (d, *J* = 2.8 Hz, 1H), 5.90 (d, *J* = 2.4 Hz, 1H), 3.47 (s, 1H), 3.21 (s, 3H), 2.29 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 175.0, 154.3, 148.6, 144.7, 136.0, 126.5, 126.4, 123.1, 110.1, 109.4, 106.5, 72.9, 26.6, 13.7; **HRMS-ESI** (m/z): calcd for $C_{14}H_{12}ClNO_3[M + Na]^+$: 300.0398; found: 300.0394.

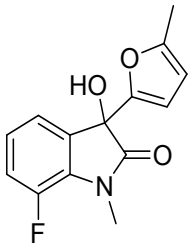
3g. 6-bromo-3-hydroxy-1-methyl-3-(5-methylfuran-2-yl)indolin-2-one



3g

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3g** (62%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.69 (d, *J* = 1.6 Hz, 1H), 7.49 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 3.41 (s, 1H), 3.21 (s, 3H), 2.30 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.5, 154.4, 148.4, 142.5, 132.9, 130.1, 128.6, 115.9, 110.3, 110.1, 106.5, 73.2, 26.6, 13.8; **HRMS-ESI** (m/z): calcd for $C_{14}H_{12}BrNO_3[M + H]^+$: 343.9893; found: 343.9891.

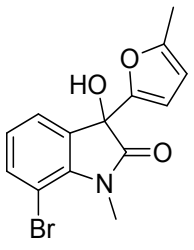
3h. 7-fluoro-3-hydroxy-1-methyl-3-(5-methylfuran-2-yl)indolin-2-one



3h

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3h** (85%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.37 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H), 7.08-7.04 (m, 2H), 6.16 (d, *J* = 3.2 Hz, 1H), 5.88 (d, *J* = 3.2 Hz, 1H), 3.96 (s, 1H), 3.41 (d, *J* = 2.8 Hz, 3H), 2.27 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 174.9, 154.1, 148.9, 148.8, 146.5, 131.1, 131.1, 130.0, 129.9, 123.9, 123.8, 121.3, 121.2, 118.1, 117.9, 110.1, 106.4, 73.3, 73.3, 29.0, 28.9, 13.6; **HRMS-ESI** (m/z): calcd for $C_{14}H_{12}FNO_3[M+Na]^+$: 284.0693; found: 284.0690.

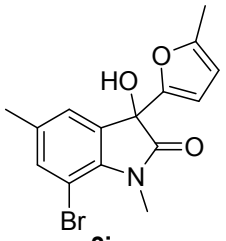
3i. 7-bromo-3-hydroxy-1-methyl-3-(5-methylfuran-2-yl)indolin-2-one



3i

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3i** (48%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.51 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.14 (d, *J* = 2.8 Hz, 1H), 5.89 (d, *J* = 2.0 Hz, 1H), 3.60 (s, 4H), 2.28 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 175.6, 154.2, 148.7, 140.8, 135.7, 131.3, 124.6, 124.4, 110.2, 106.4, 102.7, 72.7, 30.1, 13.7; **HRMS-ESI** (m/z): calcd for $C_{14}H_{12}BrNO_3[M + Na]^+$: 343.9893; found: 343.9891.

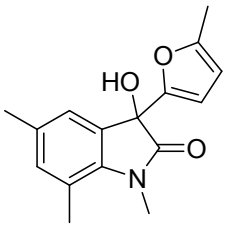
3j. 7-bromo-3-hydroxy-1,5-dimethyl-3-(5-methylfuran-2-yl)indolin-2-one



3j

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3j** (74%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.52 (d, *J* = 1.6 Hz, 1H), 7.23 (d, *J* = 1.2 Hz, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 5.89 (d, *J* = 2.4 Hz, 1H), 3.62 (s, 1H), 3.46 (s, 3H), 2.53 (s, 3H), 2.29 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 175.4, 154.2, 148.8, 140.2, 136.1, 130.8, 126.5, 122.2, 115.6, 110.1, 106.4, 72.7, 29.8, 18.7, 13.7; **HRMS-ESI** (m/z): calcd for $C_{15}H_{14}BrNO_3[M + Na]^+$: 358.0049; found: 358.0047.

3k. 3-hydroxy-1,5,7-trimethyl-3-(5-methylfuran-2-yl)indolin-2-one

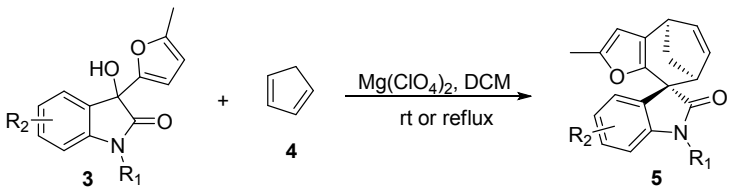


3k

Prepared according to general procedure A and B. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 4/1, v/v as eluent) to give the title compound **3k** (67%). And this is an unknown compound. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.21 (s, 1H), 6.90 (s, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 5.88 (dd, *J* = 3.2 Hz, *J* = 0.8 Hz, 1H), 3.47 (s, 3H), 3.28 (s, 1H), 2.52 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 175.8, 153.9, 149.7, 138.8, 134.3, 132.8, 128.9, 124.0, 119.9, 109.8, 106.3, 72.9, 29.8, 20.7, 18.8, 13.7; **HRMS-ESI** (m/z): calcd for $C_{16}H_{17}NO_3[M + Na]^+$: 294.1101; found: 294.1100.

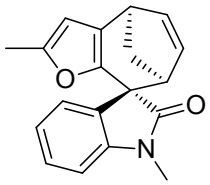
4. Synthesis of Products 5a-5k and Analytic Data

General procedure C: (The [4+3] cycloaddition reaction)



To a solution of **3** (0.1 mmol, 1.0 eq) and $Mg(ClO_4)_2$ (0.15 mmol, 1.5 eq) in anhydrous DCM (15 mL), **4** (1.0 mmol, 10.0 eq) in anhydrous DCM (1.0 mL) was added dropwise. The mixture was stirred at room temperature or at refluxing temperature. The reaction progress was monitored by TLC (Petroleum Ether/EtOAc = 16:1) until the reaction complete, then evaporated to afford the crude product. Purification via a column chromatography (Petroleum Ether/EtOAc = 16:1) provided the products.

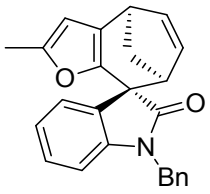
5a. 1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5a

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5a** (58%); **Mp:** 165-167 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.31 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.75 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 5.90 (s, 1H), 5.77 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 3.40 (t, *J* = 3.6 Hz, 1H), 3.28 (s, 3H), 2.99 (d, *J* = 10.0 Hz, 1H), 2.95 (t, *J* = 3.6 Hz, 1H), 2.09 (s, 3H), 2.07-2.04 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.8, 150.0, 146.4, 144.2, 143.4, 129.8, 128.7, 128.4, 127.7, 125.1, 121.9, 108.3, 105.0, 52.9, 49.2, 41.4, 37.9, 26.5, 13.6; **IR** (neat): 3400, 2954, 1710, 1610, 1492, 1345, 1125, 748 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{19}H_{17}NO_2[M + Na]^+$: 314.1151; found: 314.1148.

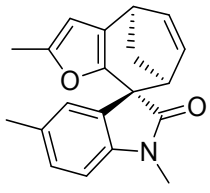
5b. 1'-benzyl-2-methyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5b

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5b** (74%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.34-7.32 (m, 4H), 7.28-7.25 (m, 2H), 7.18 -7.14 (m, 1H), 6.91 (d, *J* = 3.6 Hz, 2H), 6.77-6.75 (m, 2H), 5.92 (s, 1H), 5.79 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 3.42 (t, *J* = 3.6 Hz, 1H), 3.07-3.02 (m, 2H), 2.11 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.9, 150.1, 146.5, 144.3, 142.5, 136.0, 129.8, 128.8, 128.7, 128.3, 127.7, 127.5, 127.1, 125.3, 122.0, 109.3, 105.0, 52.9, 49.4, 43.8, 41.6, 37.9, 13.6; **IR** (neat): 3399, 3055, 2936, 1708, 1611, 1487, 1357, 1265, 738, 701 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{25}H_{21}NO_2[M + Na]^+$: 390.1465; found: 390.1459.

5c. 1',2,5'-trimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one

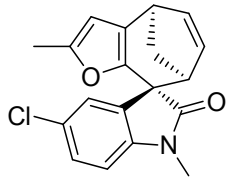


5c

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5c** (63%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.09 (d, *J* = 8.0 Hz, 1H), 6.80-6.75 (m, 2H), 6.72 (s, 1H), 5.91 (d, *J* = 0.8 Hz, 1H), 5.78 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 3.39 (t, *J* = 3.6 Hz, 1H), 3.25 (s, 3H), 3.00 (d, *J* = 10.0 Hz, 1H), 2.93 (t, *J* = 4.4 Hz, 1H), 2.27 (s, 3H), 2.10 (s, 3H), 2.08-2.03 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.7, 150.0, 146.4, 144.4, 141.1, 131.4, 130.0, 128.7, 127.6, 125.9, 108.0, 105.0, 52.9, 49.3, 41.4,

37.9, 26.6, 21.1, 13.6; **IR** (neat): 3392, 2925, 1707, 1618, 1500, 1265, 1090, 737, 703 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{20}H_{19}NO_2[M + Na]^+$: 328.1308; found: 328.1304.

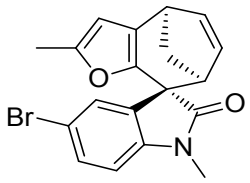
5d. 5'-chloro-1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5d

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5d** (39%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.29-7.27 (m, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.79-6.77 (m, 1H), 5.92 (d, *J* = 0.8 Hz, 1H), 5.77 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 1H), 3.41 (t, *J* = 3.6 Hz, 1H), 3.27 (s, 3H), 2.98-2.93 (m, 2H), 2.11 (s, 3H), 2.11-2.05 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.3, 150.3, 147.0, 143.5, 142.0, 130.5, 129.4, 128.0, 125.4, 125.2, 109.7, 109.2, 105.1, 53.0, 49.2, 41.5, 37.9, 25.9, 13.6; **IR** (neat): 3404, 2939, 1733, 1611, 1490, 1238, 1114, 1069 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{19}H_{16}ClNO_2[M+H]^+$: 326.0942; found: 326.0938.

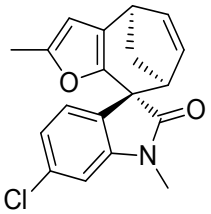
5e. 5'-bromo-1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5e

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5e** (50%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.43 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.78 (t, *J* = 4.4 Hz, 2H), 5.92 (d, *J* = 0.8 Hz, 1H), 5.77 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 3.41 (t, *J* = 4.0 Hz, 1H), 3.26 (s, 3H), 2.97-2.93 (m, 2H), 2.12 (s, 3H), 2.10-2.05 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.2, 150.3, 147.1, 143.4, 142.5, 131.2, 130.6, 129.4, 128.0, 128.0, 114.7, 109.7, 105.1, 52.9, 49.1, 41.4, 37.8, 26.7, 13.6; **IR** (neat): 2928, 1717, 1606, 1487, 1339, 1096, 731 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{19}H_{16}BrNO_2[M + Na]^+$: 392.0257; found: 392.0252.

5f. 6'-chloro-1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one

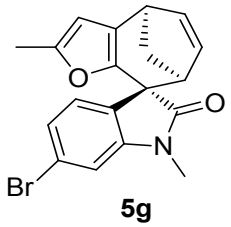


5f

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5f** (45%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.93-6.90 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.76-6.74 (m, 1H), 5.90 (s, 1H), 5.72 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 3.39 (t, *J* = 3.2 Hz, 1H),

3.26 (s, 3H), 2.98-2.91 (m, 2H), 2.10 (s, 3H), 2.07-2.03 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.7, 150.2, 146.9, 144.6, 143.6, 134.2, 129.5, 127.9, 126.9, 125.9, 121.8, 109.1, 105.0, 52.5, 49.1, 41.4, 37.8, 26.7, 13.6; **IR** (neat): 3417, 2938, 1719, 1607, 1493, 1364, 1076, 732 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{19}H_{16}ClNO_2[M + Na]^+$: 348.0762; found: 348.0758 .

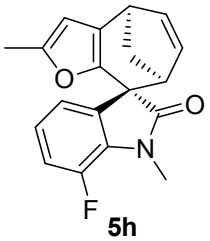
5g. 6'-bromo-1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5g

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5g** (56%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.08 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.04 (d, *J* = 1.6 Hz, 1H), 6.75 (dd, *J* = 5.2 Hz, *J* = 2.4 Hz, 2H), 5.89 (d, *J* = 0.8 Hz, 1H), 5.72 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 3.39 (t, *J* = 3.6 Hz, 1H), 3.25 (s, 3H), 2.96 (d, *J* = 10.0 Hz, 1H), 2.92 (dd, *J* = 4.4 Hz, *J* = 3.2 Hz, 1H), 2.09 (s 3H), 2.09-2.03 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.5, 150.2, 146.9, 144.8, 143.6, 129.4, 127.9, 127.6, 126.3, 124.7, 122.0, 111.8, 105.0, 52.6, 49.1, 41.4, 37.9, 26.7, 13.5; **IR** (neat): 2929, 1719, 1602, 1491, 1363, 1092, 731 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{19}H_{16}BrNO_2[M + Na]^+$: 392.0257; found: 392.0253.

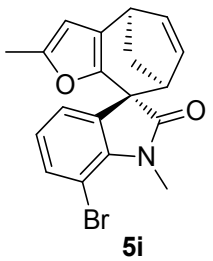
5h. 7'-fluoro-1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5h

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5h** (68%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.04-6.98 (m, 1H), 6.88-6.83 (m, 1H), 6.75-6.73 (m, 1H), 6.68-6.66 (m, 1H), 5.90 (d, *J* = 0.8 Hz, 1H), 5.72 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 3.49 (d, *J* = 2.8 Hz, 3H), 3.39 (t, *J* = 3.6 Hz, 1H), 3.00-2.94 (m, 2H), 2.10 (d, *J* = 0.8 Hz, 3H), 2.08-2.03 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 177.4, 150.2, 149.1, 146.6, 146.6, 143.7, 131.4, 131.4, 130.0, 129.9, 129.5, 127.7, 122.3, 122.3, 121.0, 120.9, 116.4, 116.2, 105.0, 53.0, 53.0, 49.3, 41.3, 37.8, 29.1, 29.0, 13.6; **IR** (neat): 3409, 2947, 1715, 1629, 1486, 1366, 1238, 1117, 909, 733 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{19}H_{16}FNO_2[M + Na]^+$: 332.1057; found: 332.1054.

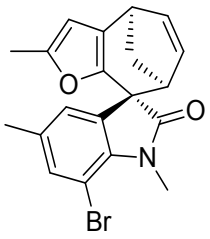
5i. 7'-bromo-1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5i

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5i** (35%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39 (t, *J* = 4.4 Hz, 1H), 6.78-6.77 (m, 2H), 6.75-6.72 (m, 1H), 5.90 (d, *J* = 0.8 Hz, 1H), 5.69 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 3.66 (s, 3H), 3.39 (t, *J* = 3.6 Hz, 1H), 2.99-2.92 (m, 2H), 2.11 (d, *J* = 0.8 Hz, 3H), 2.09-2.04 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 178.2, 150.3, 146.6, 143.7, 140.7, 134.1, 131.6, 129.5, 127.8, 124.1, 123.0, 105.1, 102.5, 52.7, 49.6, 41.5, 37.8, 29.7, 13.6; **IR** (neat): 3366, 2922, 1718, 1601, 1459, 1259, 1104 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{19}H_{16}BrNO_2[M + Na]^+$: 392.0257; found: 392.0253.

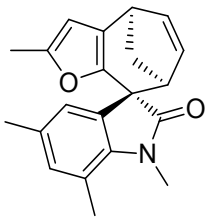
5j. 7'-bromo-1',2,5'-trimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



5j

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16/1, v/v as eluent) to give the title compound **5j** (52%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.17 (d, *J* = 1.6 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 6.75 (dd, *J* = 5.6 Hz, *J* = 2.8 Hz ,1H), 5.90 (d, *J* = 0.8 Hz, 1H), 5.72 (dd, *J* = 5.6 Hz, *J* = 2.8 Hz, 1H), 3.53 (s, 3H), 3.39 (t, *J* = 3.6 Hz, 1H), 2.97 (d, *J* = 10.4 Hz, 1H), 2.90 (dd, *J* = 4.4 Hz, *J* = 3.2 Hz, 1H), 2.58 (s, 3H), 2.12 (d, *J* = 0.4 Hz, 3H), 2.08-2.03 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 178.0, 150.3, 146.8, 143.8, 140.3, 134.6, 131.1, 129.4, 127.8, 125.9, 121.7, 114.4, 105.1, 52.5, 49.6, 41.5, 37.9, 29.9, 18.9, 13.6; **IR** (neat): 2931, 1711, 1600, 1461, 1331, 1115, 731 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{20}H_{18}BrNO_2[M + Na]^+$: 406.0413; found: 406.0410.

5k. 1',2,5',7'-tetramethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one



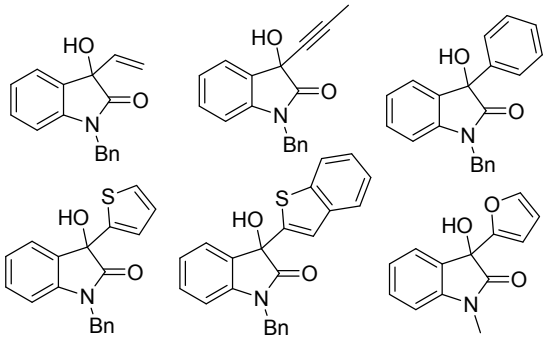
5k

Prepared according to general procedure C. The crude product was purified via flash column chromatography (silica gel, PE/EtOAc = 16:1, v/v as eluent) to give the title compound **5k** (69%). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.83 (s, 1H), 6.73 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 6.52 (s, 1H), 5.90 (s, 1H), 5.74 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 3.53 (s, 3H), 3.38 (t, *J* = 3.6 Hz, 1H), 3.01 (d, *J* = 10.0 Hz, 1H), 2.90 (t, *J* = 4.0 Hz, 1H), 2.57 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H), 2.06-2.01 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 178.5, 149.9, 146.1, 144.7, 138.7, 132.7, 131.2, 130.0, 129.2, 127.4, 123.8, 119.5, 105.0, 52.5, 49.6, 41.5, 37.9, 29.9, 20.7, 19.0, 13.7; **IR** (neat): 2930, 1706, 1601, 1475, 1344, 1104, 835, 732 cm^{-1}; **HRMS-ESI** (m/z): calcd for $C_{21}H_{21}NO_2[M + Na]^+$: 342.1465; found: 342.1463.

5. Additional Experiments

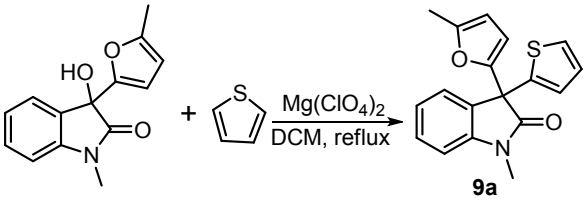
a) The scope of allylic alcohols:

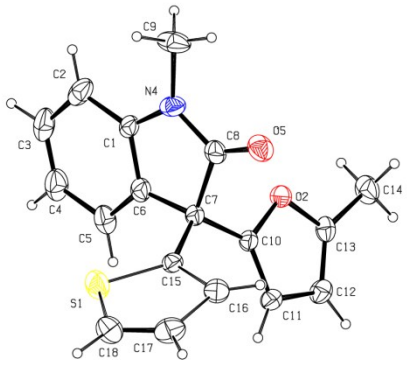
We have tried many types of allylic alcohols: such as ethenyl-, alkynyl-, phenyl-, thienyl-, furyl-, benzothiophenyl-group, etc. The unsubstituted furyl-oxindole derivatives could not exist stably for the C2 position of furan is the most reactive site towards electrophiles. And the others could not react with cyclopentadiene under the optimal reaction conditions to achieve the expected spirocycloheptane oxindole skeletons.



b) A control reaction of 2a with thiophenes:

In the experimental results, when we used thiophenes as dienes, only a Friedel–Crafts intermolecular alkylation reaction occurred, giving an ordinary electrophilic adducts **9a** (determined by the single X-ray crystallographic analysis). We expected that these results might support for a two-step pathway mechanism of the intermolecular [4 + 3] cycloaddition reactions.





6. Relative Configuration and X-Ray Analysis Data

5a. 1',2-dimethyl-4,7-dihydrospiro[4,7-methanocyclohepta[b]furan-8,3'-indolin]-2'-one

(The CCDC deposition number: CCDC(**5a**): 1434481)

Bond precision: C-C = 0.0024 A Wavelength=1.54180

Cell: a=16.9806(5) b=8.6168(2) c=20.4475(6)
alpha=90 beta=98.426(3) gamma=90

Temperature: 293 K

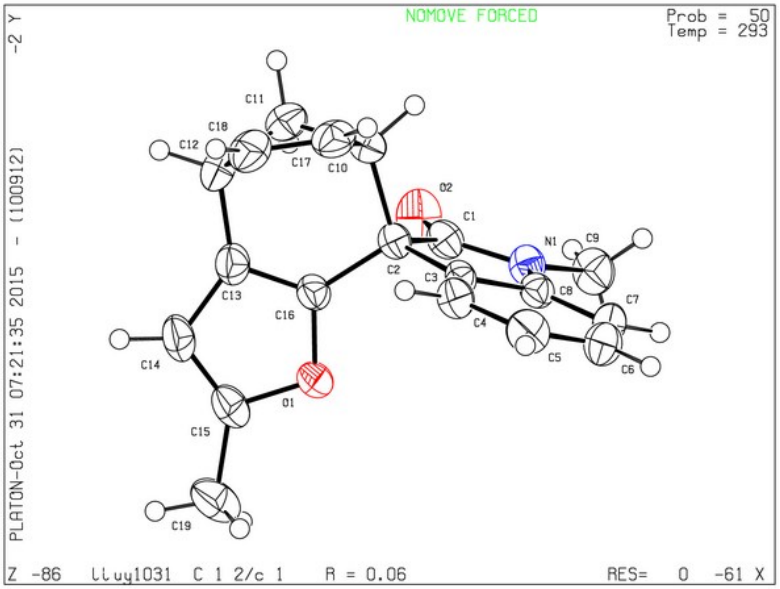
	Calculated	Reported
Volume	2959.55(14)	2959.57(14)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C19 H17 N O2	C19 H17 N O2
Sum formula	C19 H17 N O2	C19 H17 N O2
Mr	291.34	291.34
Dx,g cm-3	1.308	1.308
Z	8	8
Mu (mm-1)	0.676	0.676
F000	1232.0	1232.0
F000'	1235.61	
h,k,lmax	20,10,24	20,10,24
Nref	2817	2808
Tmin,Tmax	0.907,0.947	0.693,1.000
Tmin'	0.795	

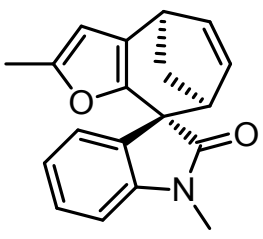
Correction method= # Reported T Limits: Tmin=0.693 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 70.050

R(reflections)= 0.0639(2526) wR2(reflections)= 0.1780(2808)

S = 1.070 Npar= 201





5a

9a. 1-methyl-3-(5-methylfuran-2-yl)-3-(thiophen-2-yl)indolin-2-one

(The CCDC deposition number: CCDC(**9a**): 1456972)

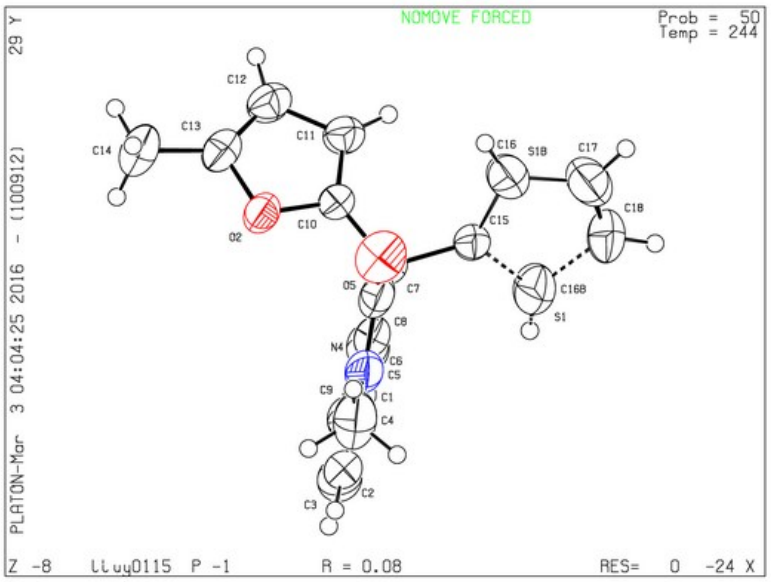
Bond precision:	C-C = 0.0070 A		Wavelength=0.71073
Cell:	a=8.282(2)	b=8.6821(17)	c=12.051(3)
	alpha=74.13(2)	beta=82.60(2)	gamma=68.31(2)
Temperature:	244 K		
	Calculated		Reported
Volume	774.1(3)		774.1(3)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	C18 H15 N O2 S		C18 H15 N O2 S
Sum formula	C18 H15 N O2 S		C18 H15 N O2 S
Mr	309.37		309.37
Dx,g cm-3	1.327		1.327
Z	2		2
Mu (mm-1)	0.215		0.215
F000	324.0		324.0
F000'	324.38		
h,k,lmax	10,10,14		10,10,14
Nref	3054		3046
Tmin,Tmax	0.920,0.934		0.627,1.000
Tmin'	0.920		

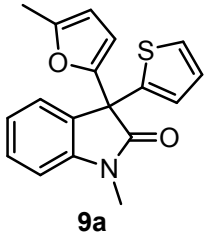
Correction method= # Reported T Limits: Tmin=0.627 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 26.021

R(reflections)= 0.0783(1594) wR2(reflections)= 0.2516(3046)

S = 1.040 Npar= 201



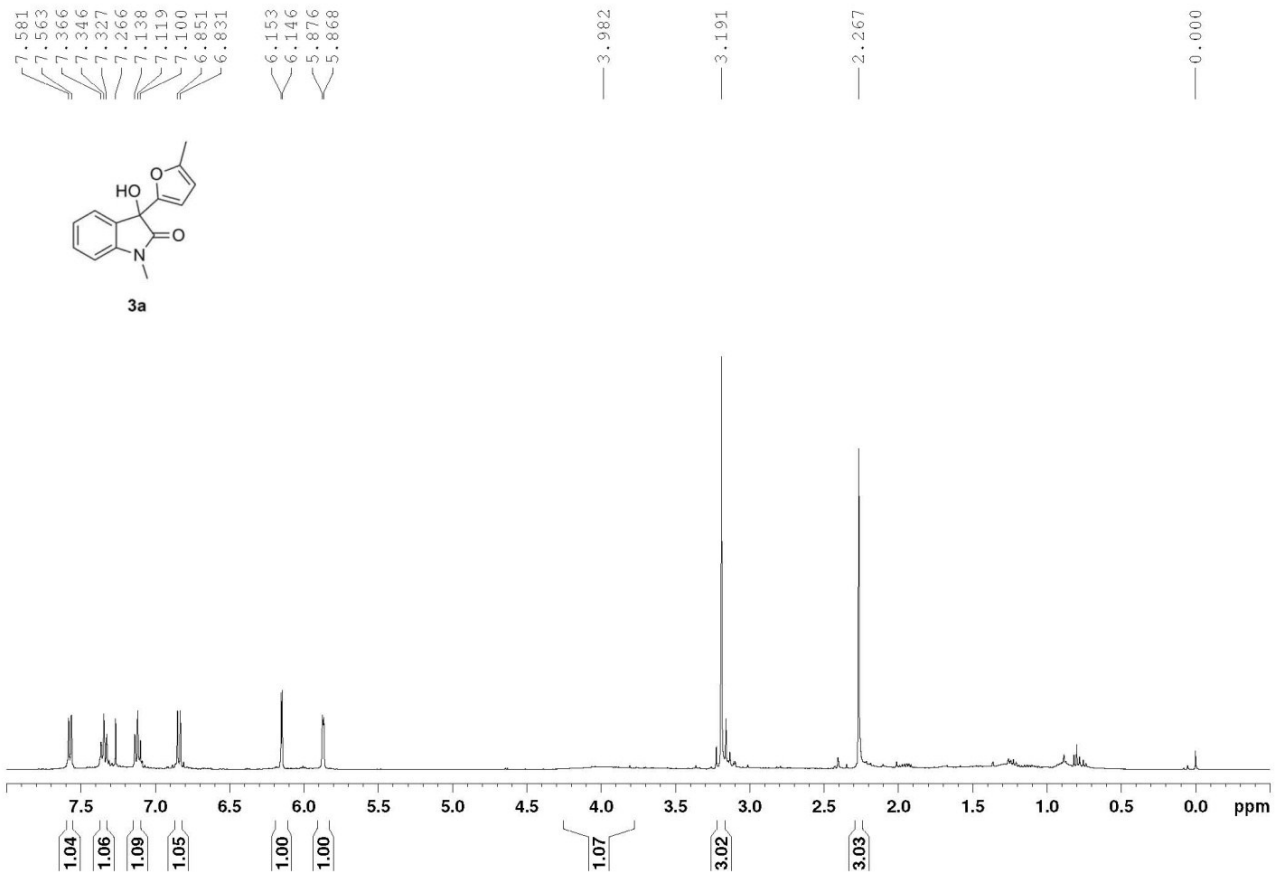


9a

7. References.

1. B. M. Trost, K. Hirano, *Angew. Chem. Int. Ed.* 2012, **51**, 6480-6483; *Angew. Chem*. 2012, **124**, 6586.

2. (a) S. Chowdhury, M. Chafeev, S. Liu, J. Sun, V. Raina, R. Chui, W. Young, R. Kwan, J. Fu and J. A. Cadieux, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 3676; (b) T. Teruhisa, U. Takashi, *PCT Int. Appl.* WO0010975.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7.266
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7.119
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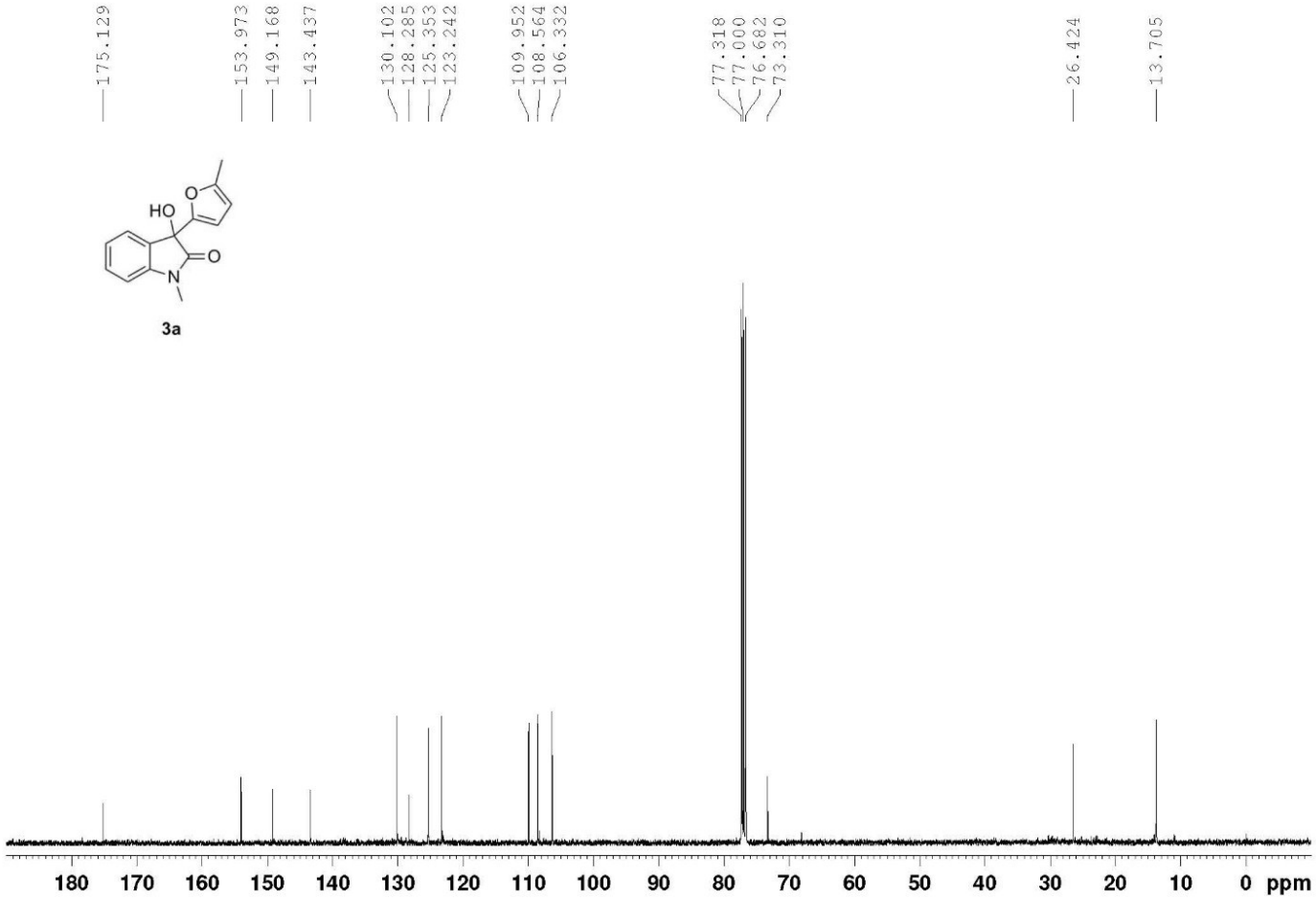
6.153
6.146
5.876
5.868
3.982
3.191
2.267
0.000
HO
O
O
N
3a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.04
1.06
1.09
1.05
1.00
1.00
1.07
3.02
3.03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149.168
143.437
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128.285
125.353
123.242
109.952
108.564
106.332
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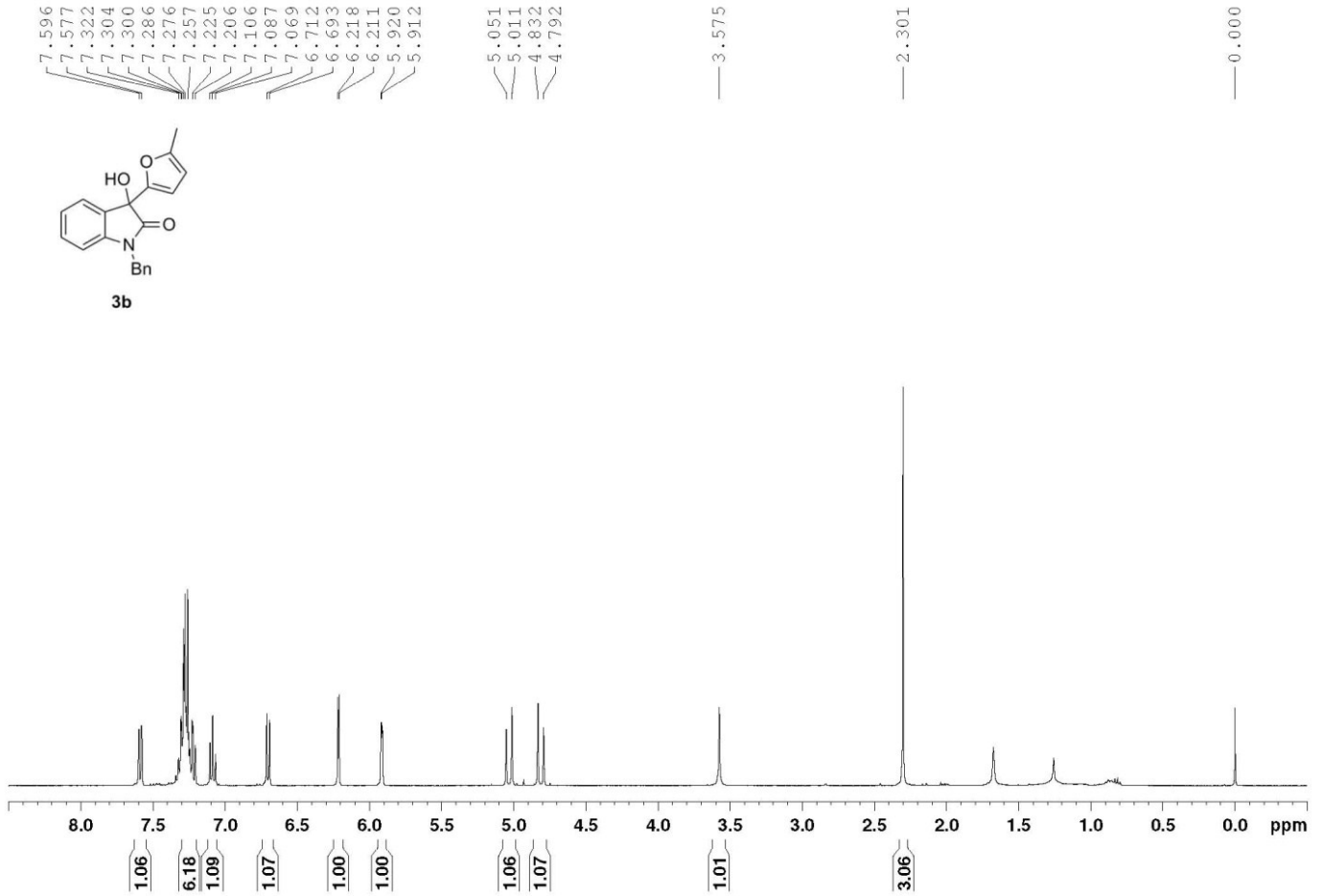
77.000
76.682
73.310
26.424
13.705
HO
O
O
N
3a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.257
7.225
7.206
7.106
7.087
7.069
6.712
6.693
6.218
6.211
5.920
5.912
5.051
5.011
4.832
4.792
3.575
2.301
0.000
HO
O
O
N
Bn
3b
8.0
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
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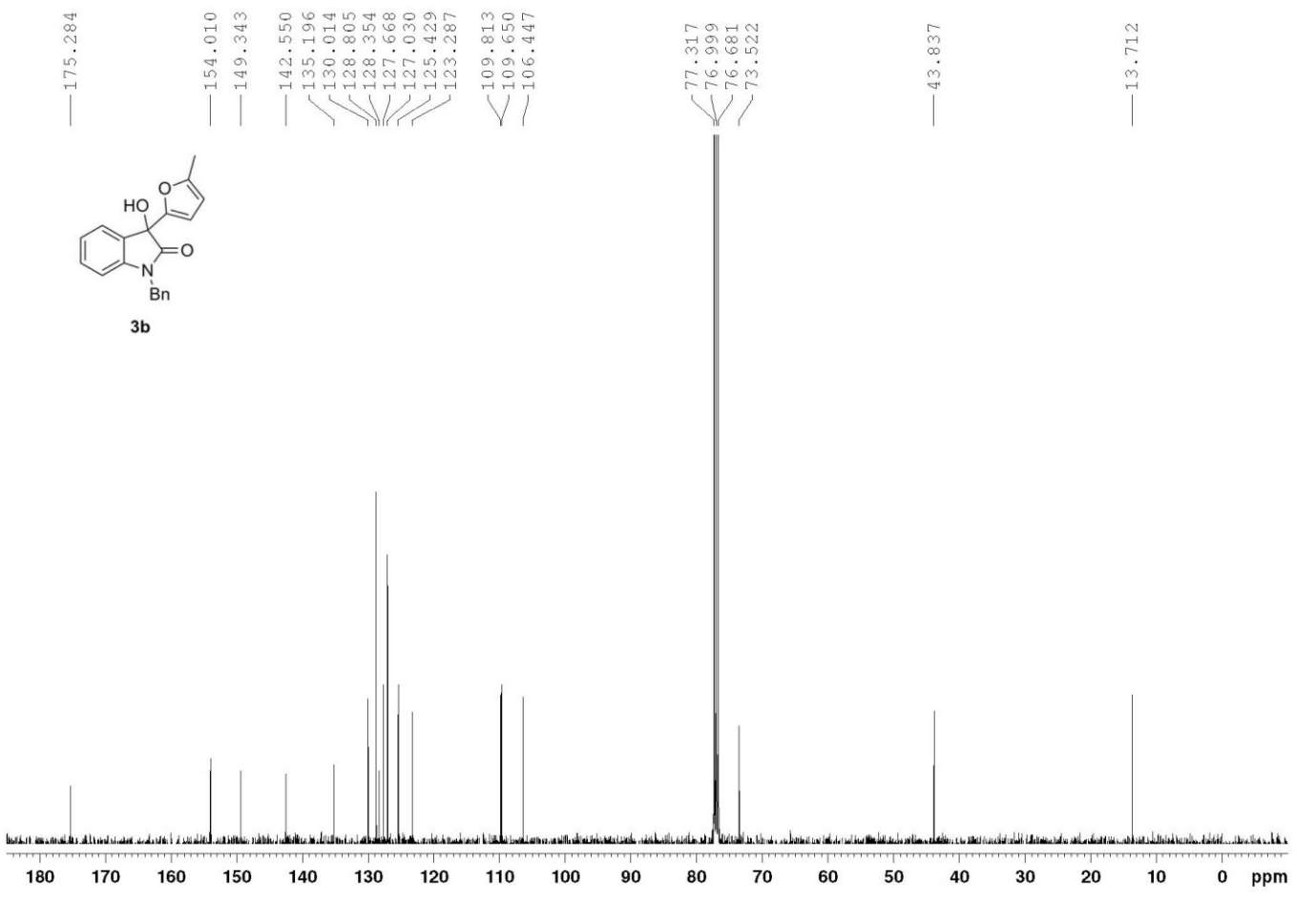
6.18
1.09
1.07
1.00
1.00
1.06
1.07
1.01
3.06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142.550
135.196
130.014
128.805
128.354
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125.429
123.287
109.813
109.650
106.447
77.317
76.999
76.681
73.522
43.837
13.712
HO
O
O
N
Bn
3b
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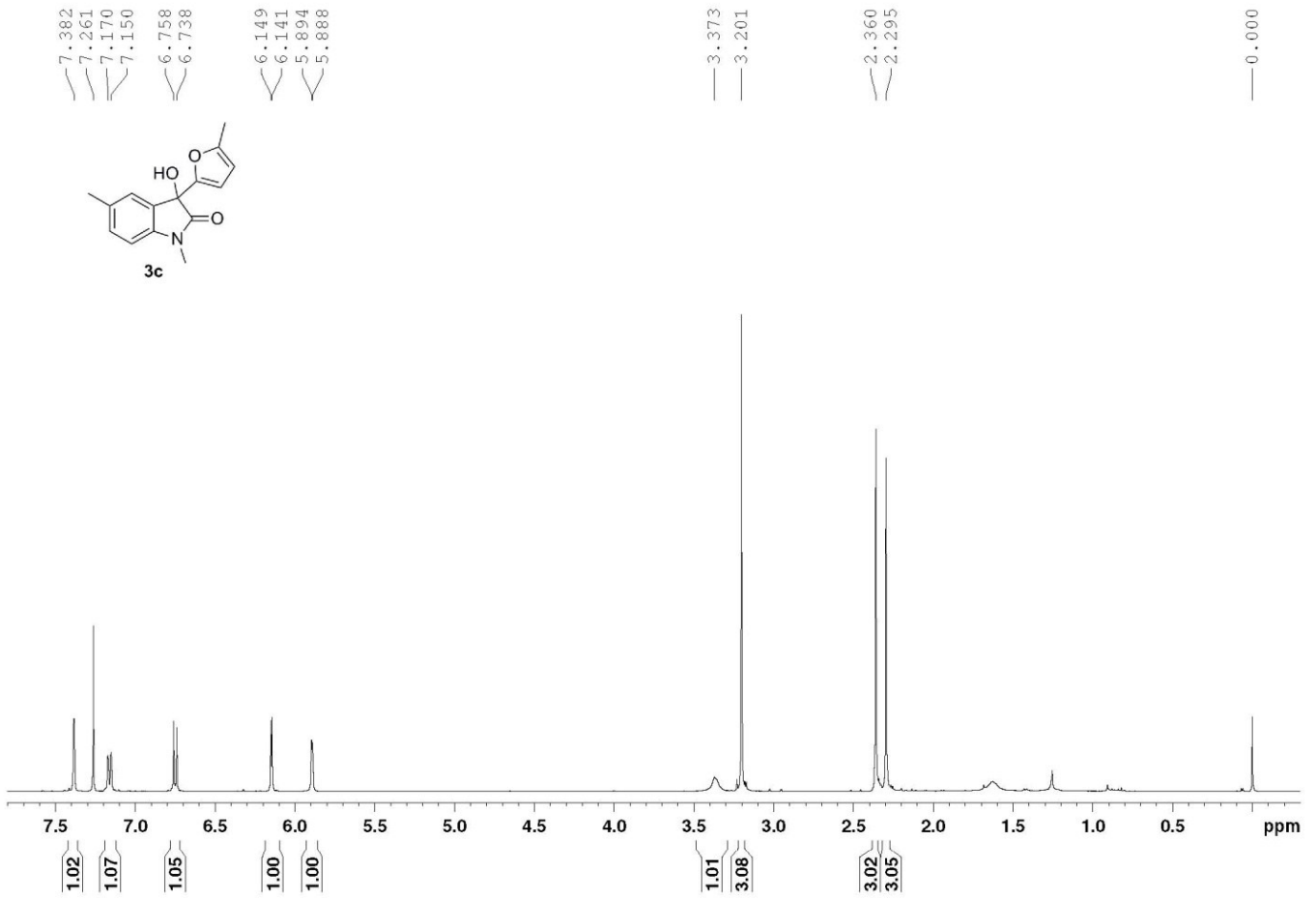
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.141
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2.360
2.295
0.000
HO
O
O
N
3c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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ppm
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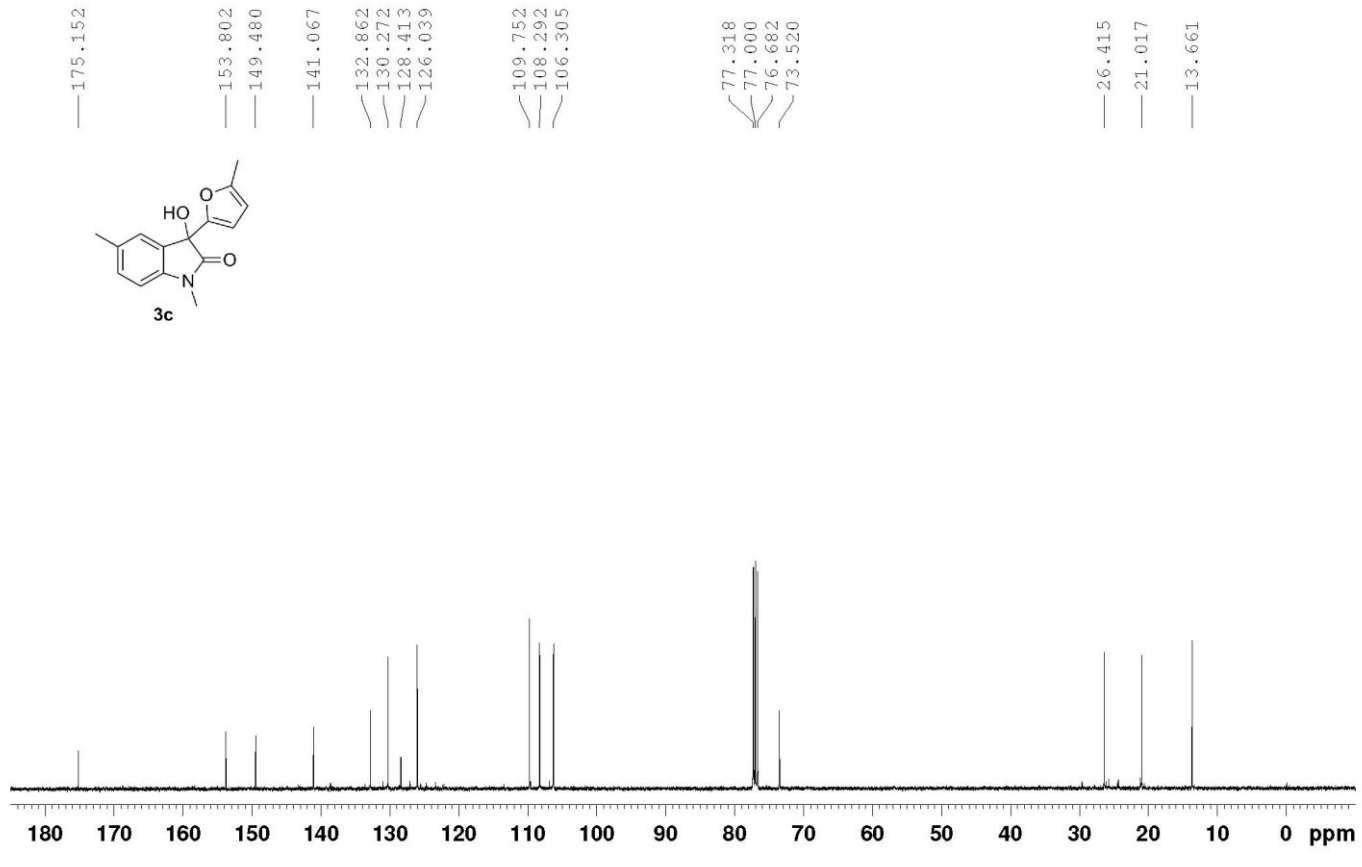
1.05
1.00
1.00
1.01
3.08
3.02
3.05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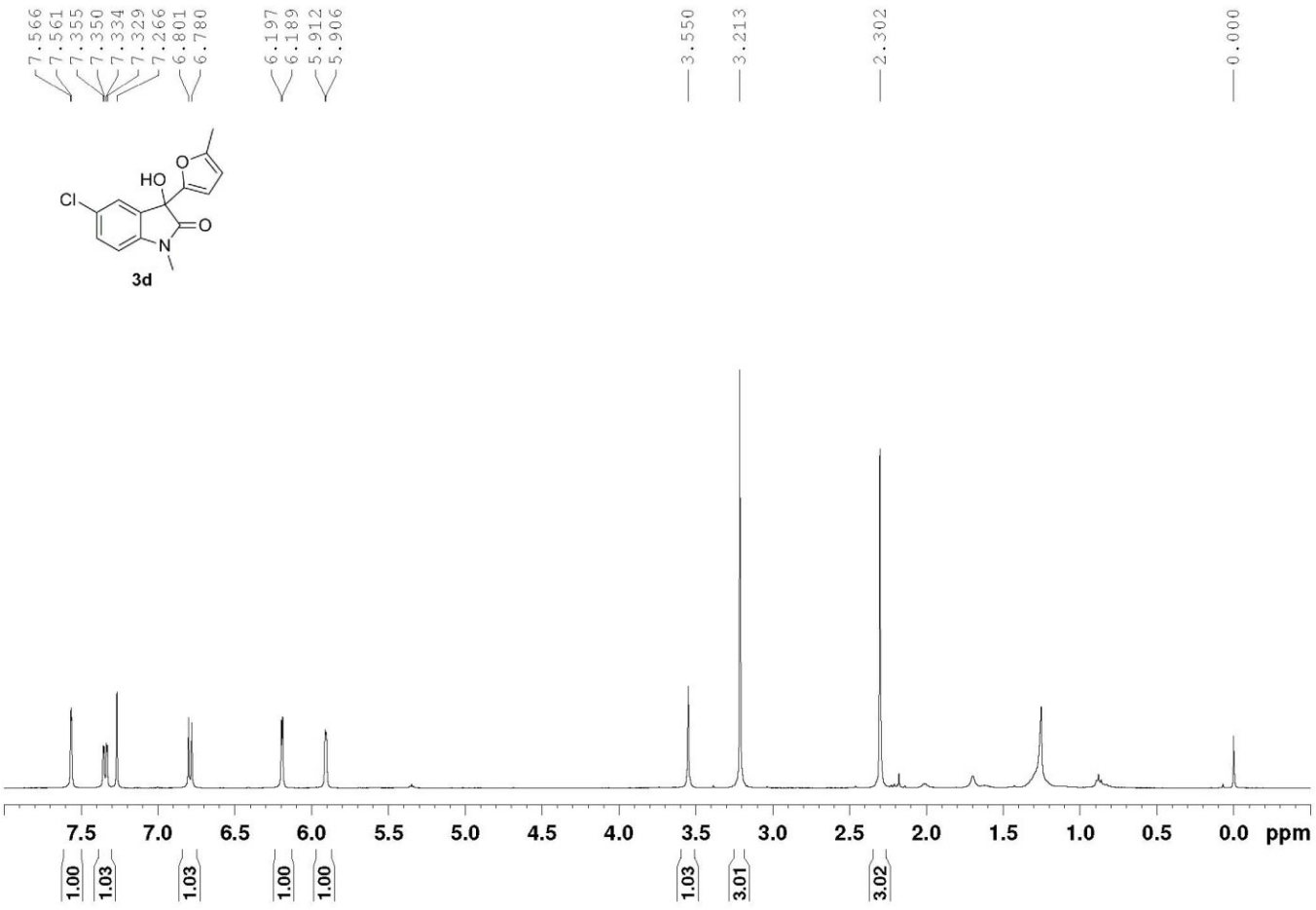
149.480
141.067
132.862
130.272
128.413
126.039
109.752
108.292
106.305
77.318
77.000
76.682
73.520
26.415
21.017
13.661
HO
O
O
N
3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.266
6.801
6.780
6.197
6.189
5.912
5.906
3.550
3.213
2.302
0.000
HO
O
Cl
O
N
3d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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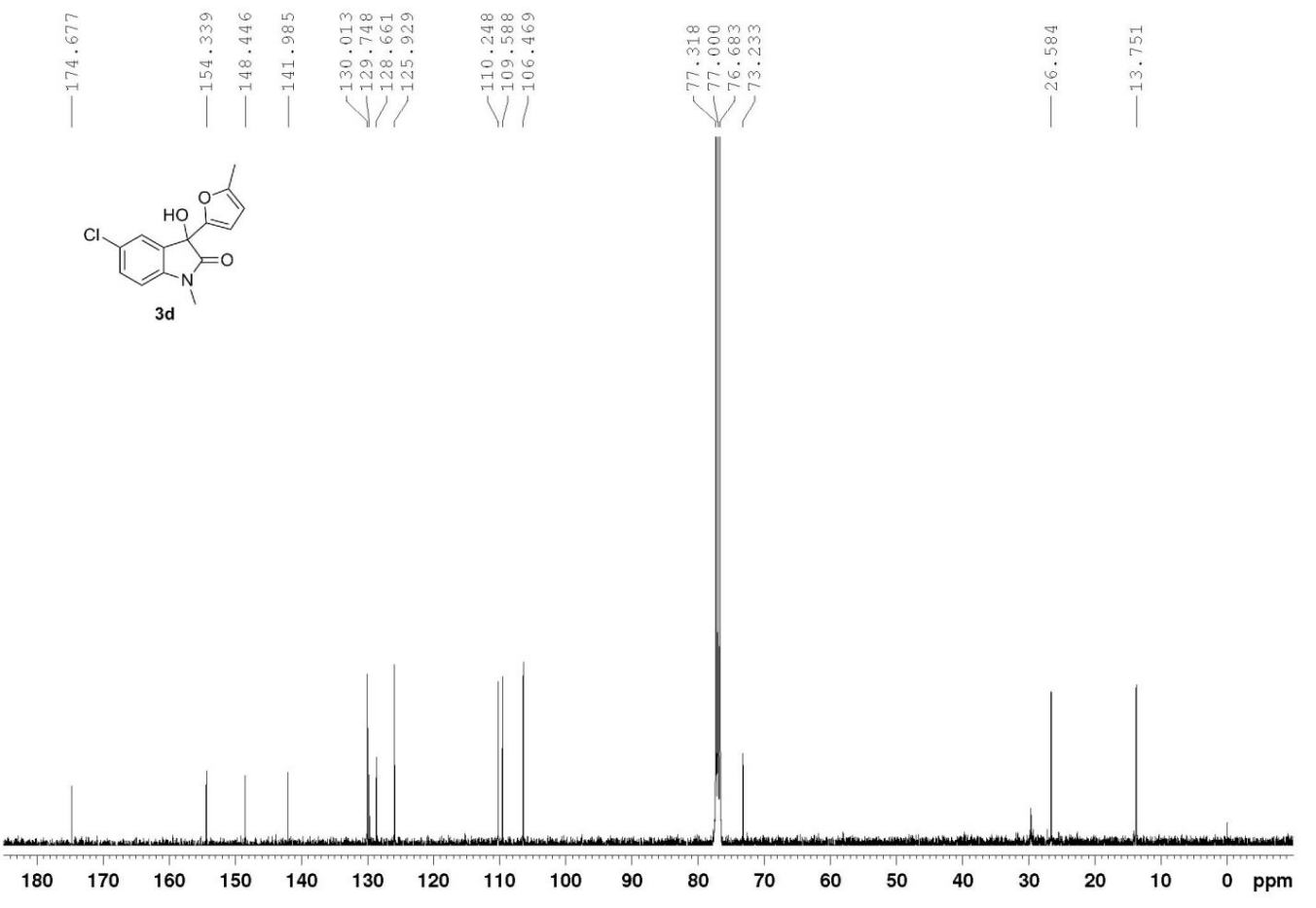
1.03
1.03
1.00
1.00
1.03
3.01
3.02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148.446
141.985
130.013
129.748
128.661
125.929
110.248
109.588
106.469
77.318
77.000
76.683
73.233
26.584
13.751
HO
O
Cl
O
N
3d
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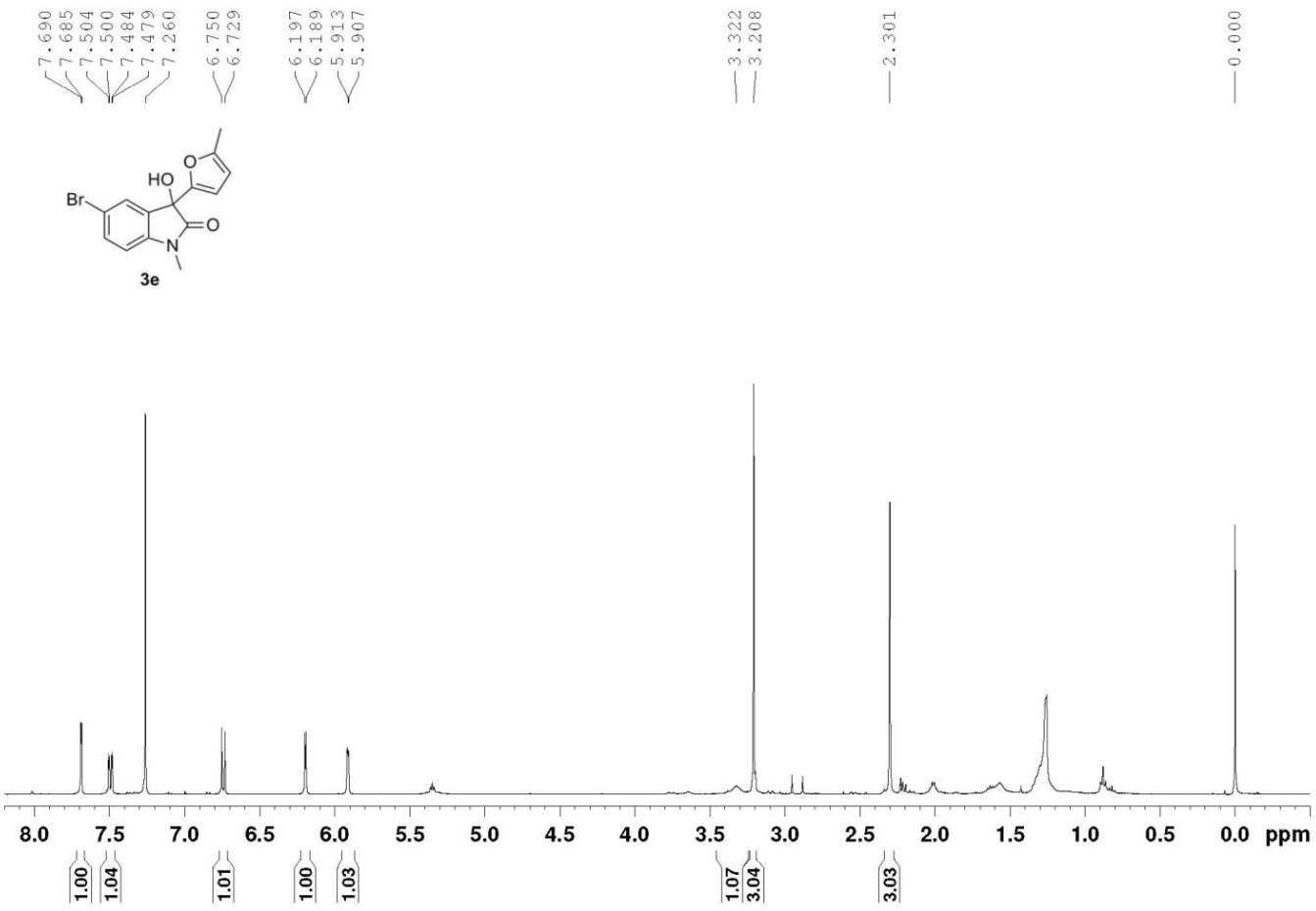
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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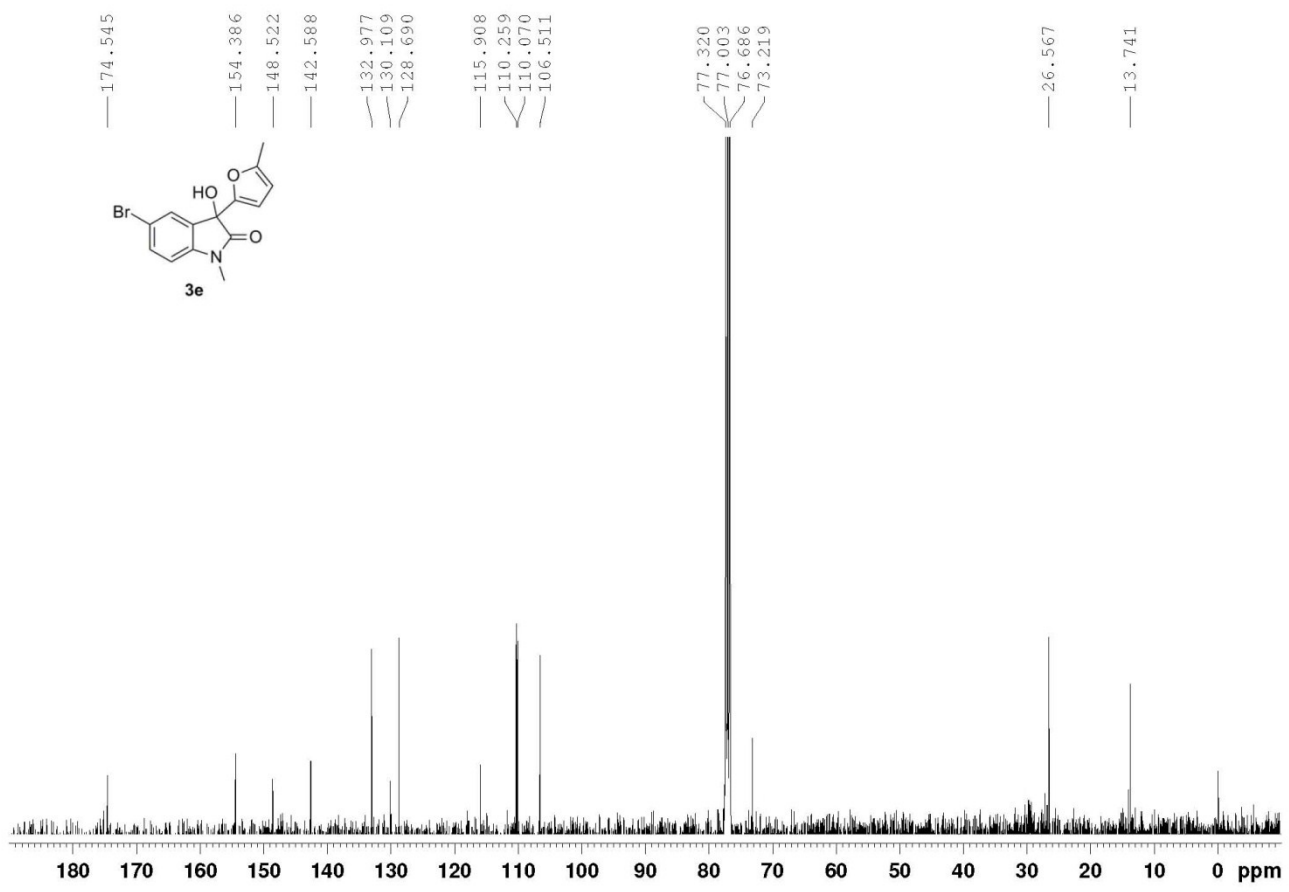
7.504
7.500
7.484
7.479
7.260
6.750
6.729
6.197
6.189
5.913
5.907
3.322
3.208
2.301
0.000
HO
Br
O
N
3e
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.04
1.01
1.00
1.03
1.07
3.04
3.03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130.109
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115.908
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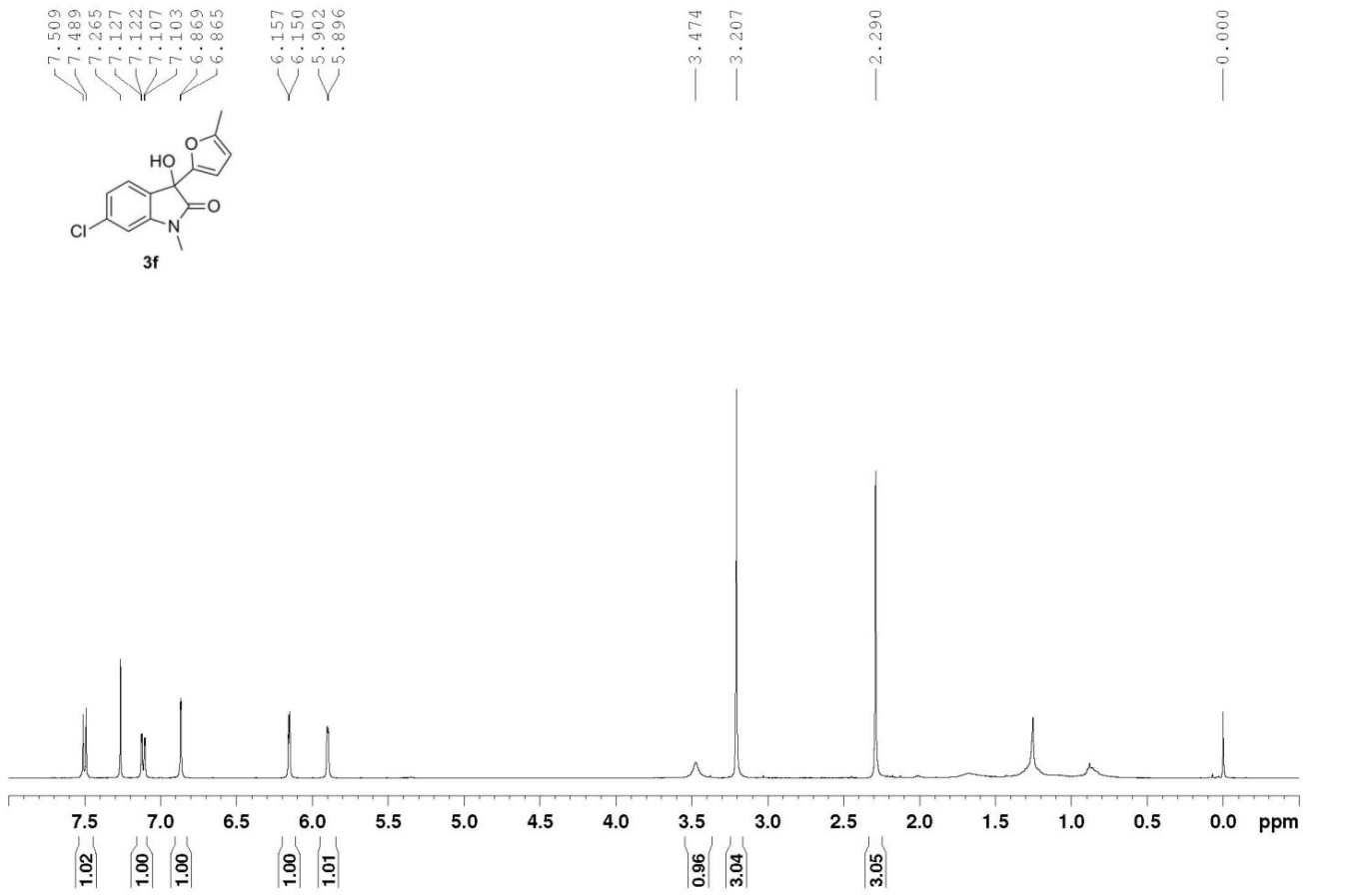
110.070
106.511
77.320
77.003
76.686
73.219
26.567
13.741
HO
Br
O
N
3e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.122
7.107
7.103
6.869
6.865
6.157
6.150
5.902
5.896
3.474
3.207
2.290
0.000
HO
O
O
N
Cl
3f
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
0.0
ppm
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1.00
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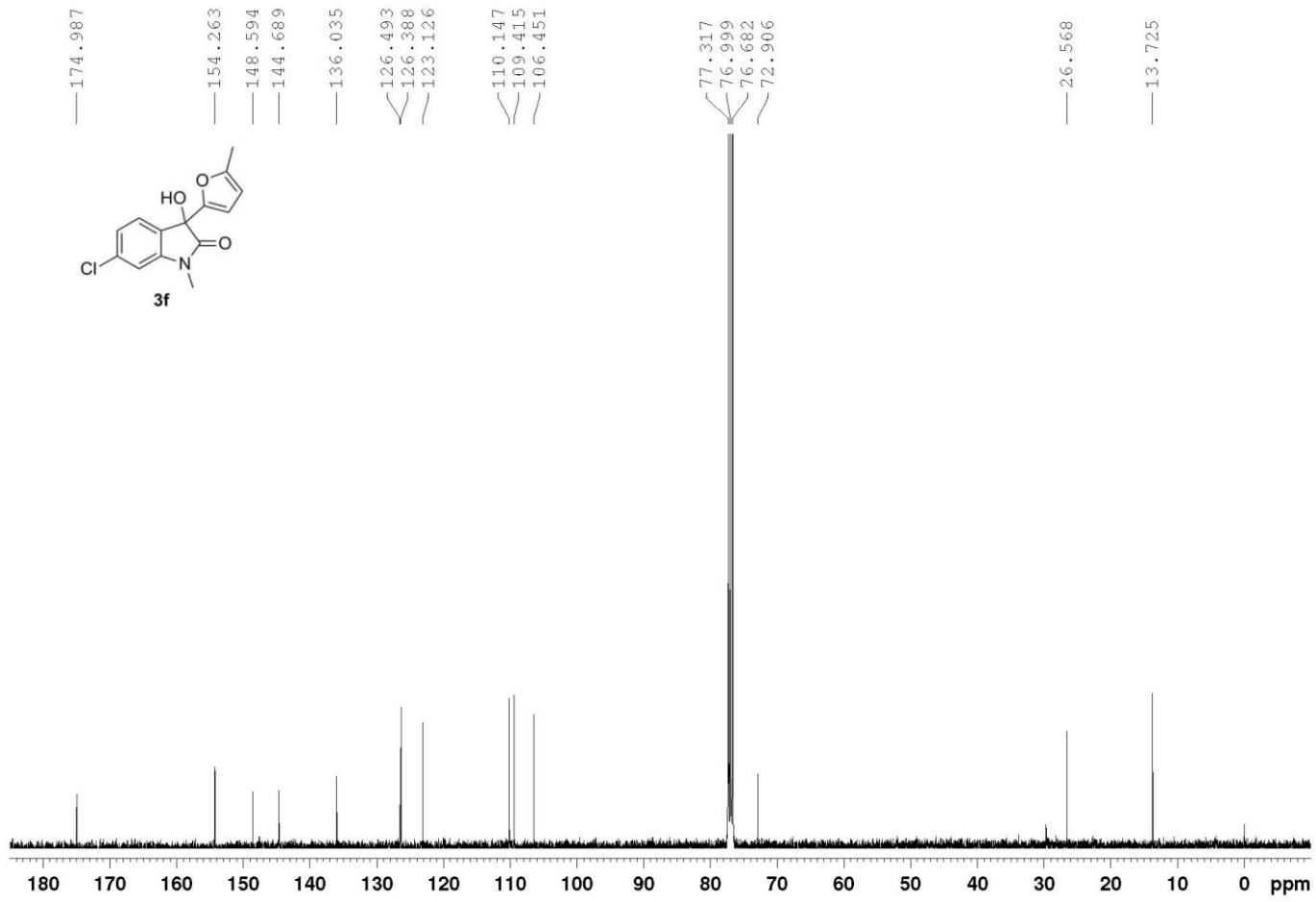
3.05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136.035
126.493
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123.126
110.147
109.415
106.451
77.317
76.999
76.682
72.906
26.568
13.725
HO
O
O
N
Cl
3f
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150
140
130
120
110
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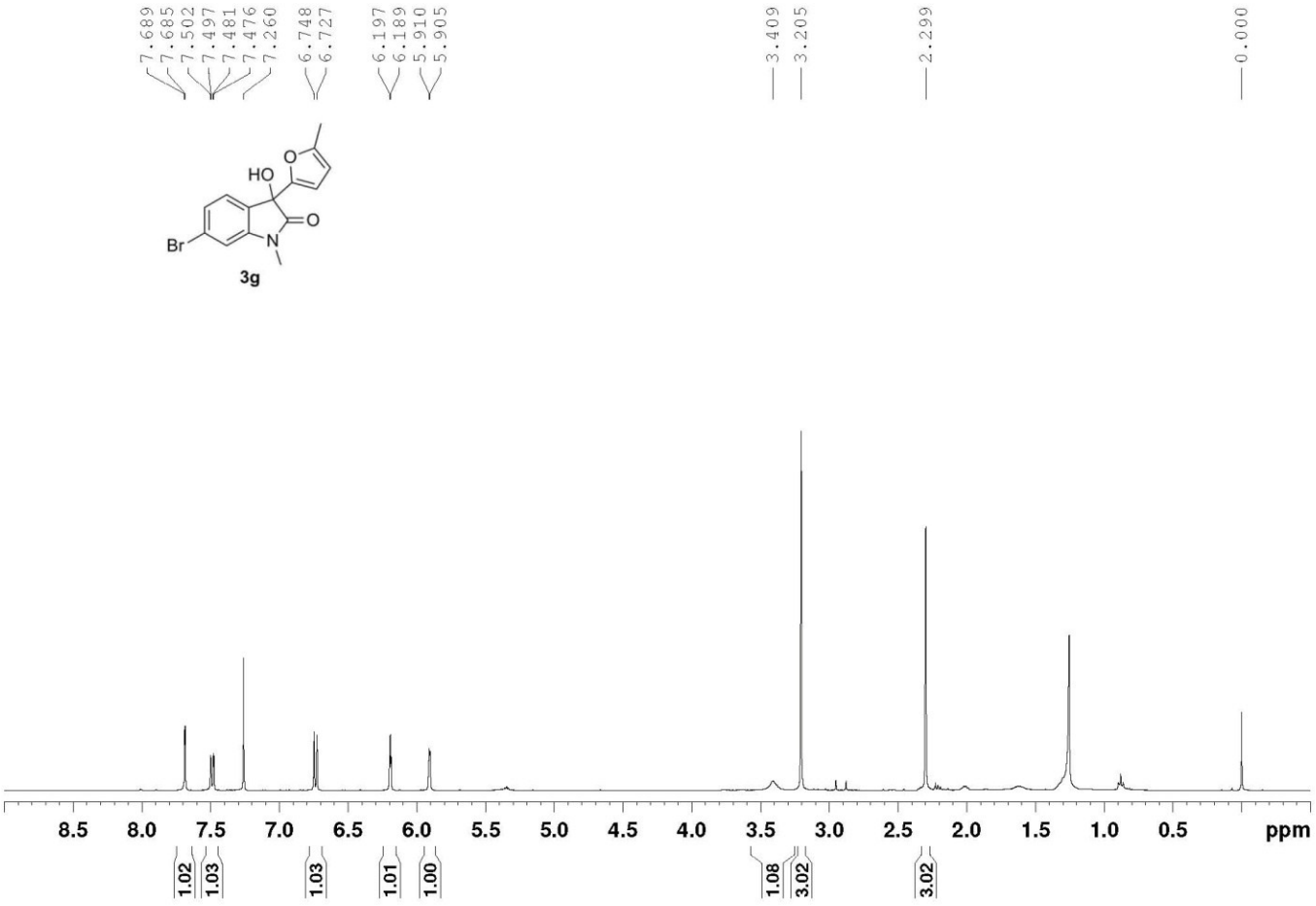
90
80
70
60
50
40
30
20
10
0
ppm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6.748
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6.197
6.189
5.910
5.905
3.409
3.205
2.299
0.000
HO
O
O
N
Br
3g
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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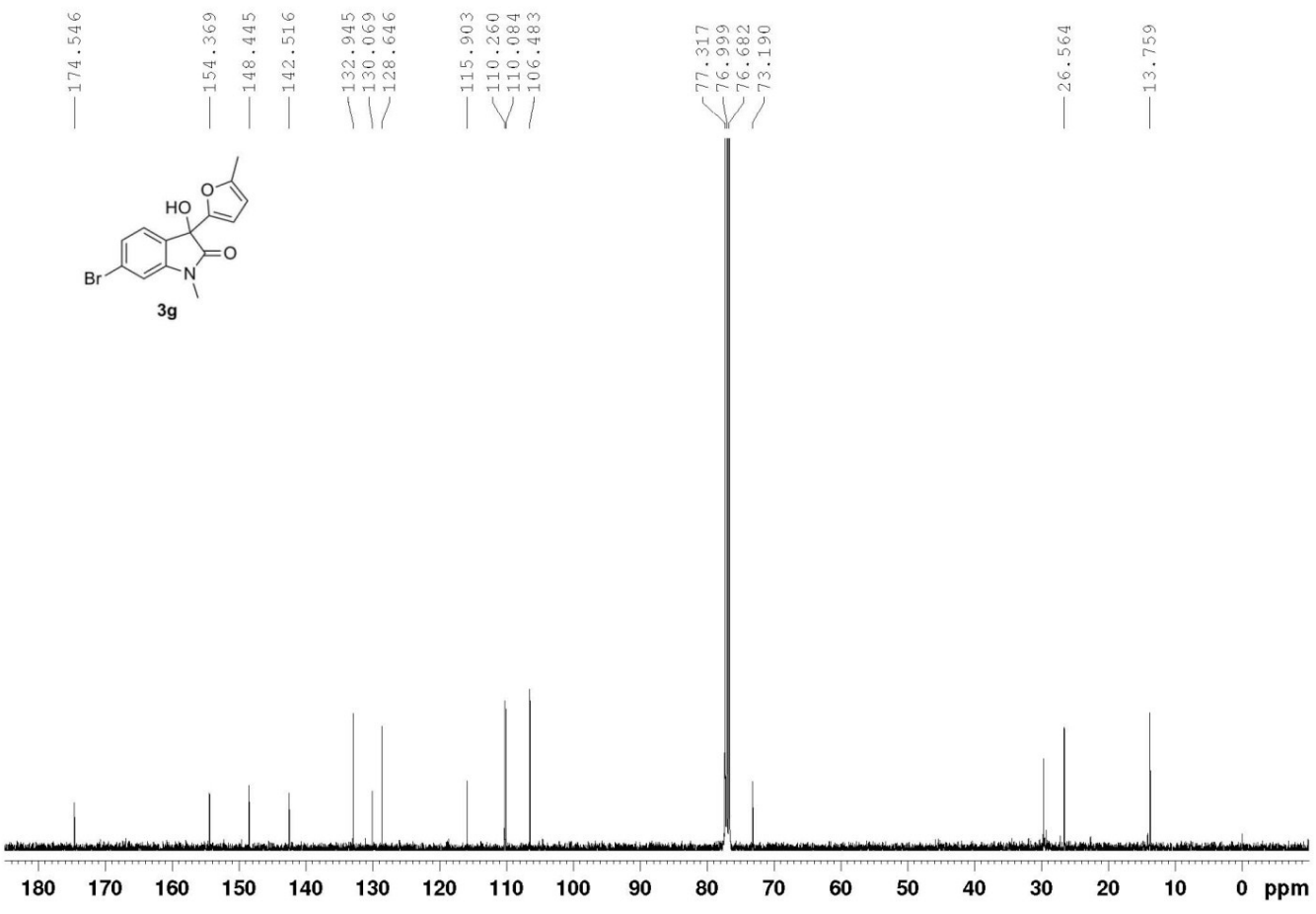
1.03
1.03
1.01
1.00
1.08
3.02
3.02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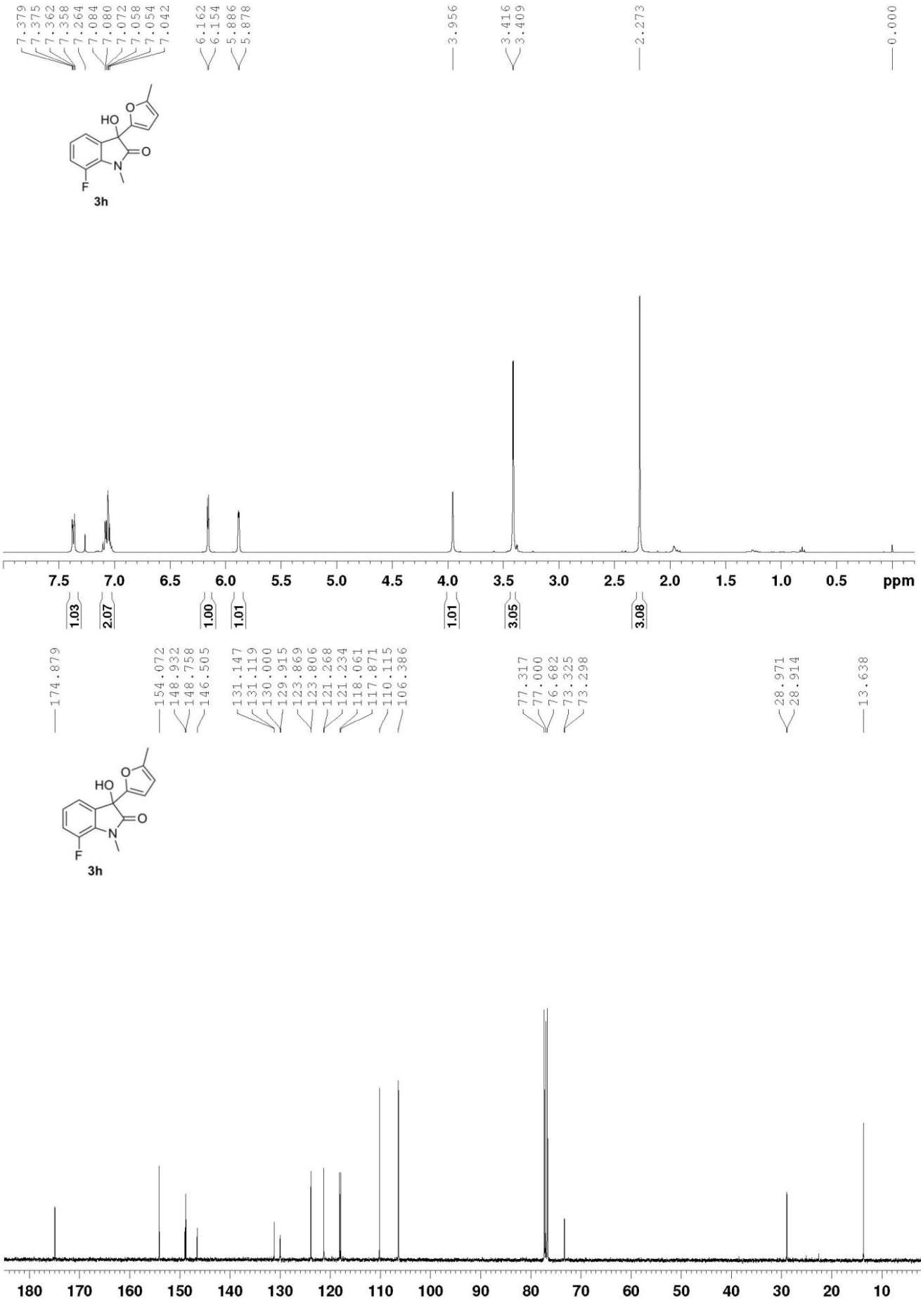
115.903
110.260
110.084
106.483
77.317
76.999
76.682
73.190
26.564
13.759
HO
O
O
N
Br
3g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.054
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6.154
5.886
5.878
3.956
3.416
3.409
2.273
0.000
HO
O
O
N
F
3h
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
1.03
2.07
1.00
1.01
1.01
3.05
3.08
174.879
154.072
148.932
148.758
146.505
131.147
131.119
130.000
129.915
123.869
123.806
121.268
121.234
118.061
117.871
110.115
106.386
77.317
77.000
76.682
73.325
73.298
28.971
28.914
13.638
HO
O
O
N
F
3h
180
170
160
150
140
130
120
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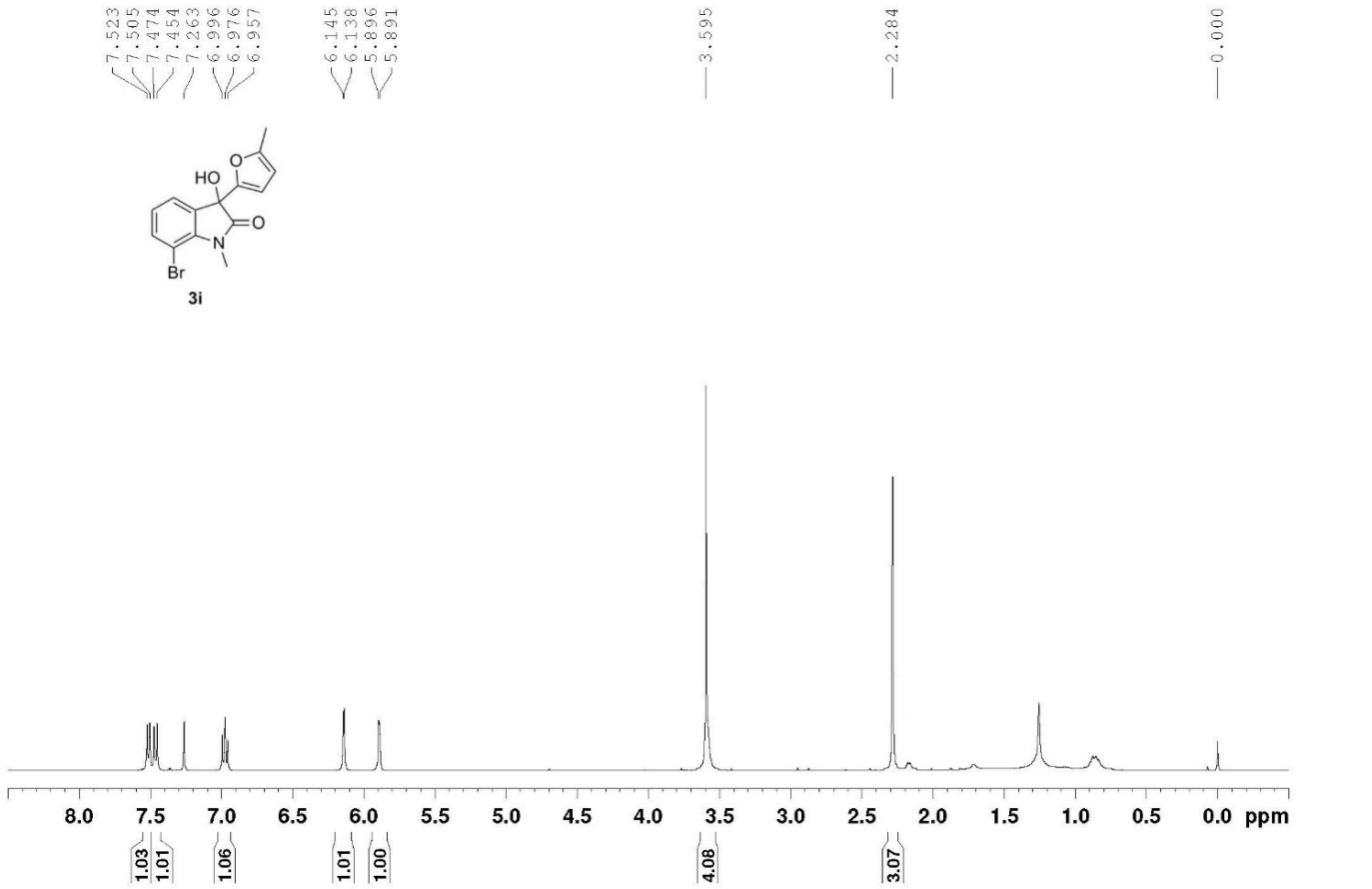
100
90
80
70
60
50
40
30
20
10
ppm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7.263
6.996
6.976
6.957
6.145
6.138
5.896
5.891
3.595
2.284
0.000
HO
O
O
N
Br
3i
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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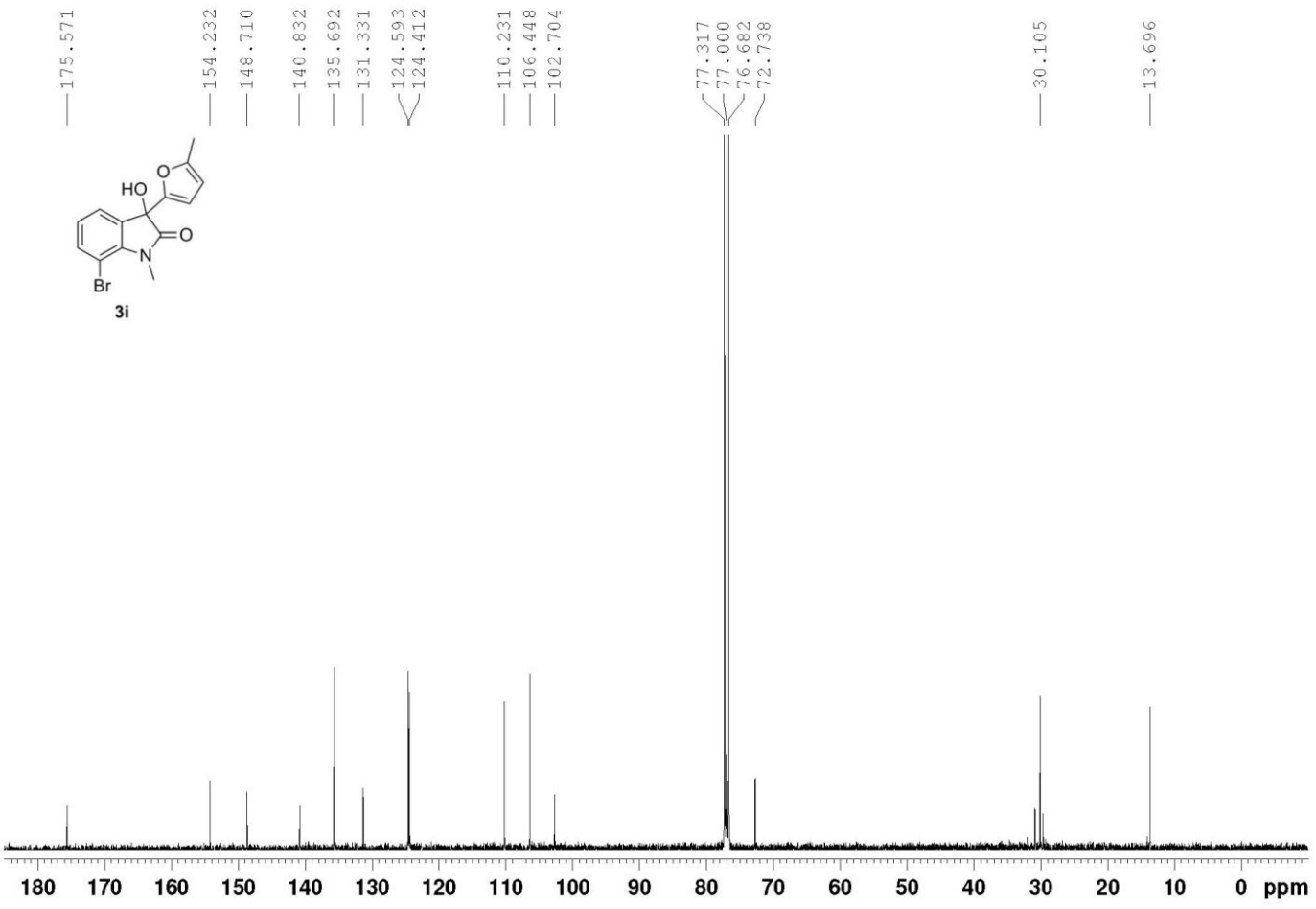
1.01
1.06
1.01
1.00
4.08
3.07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102.704
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77.000
76.682
72.738
30.105
13.696
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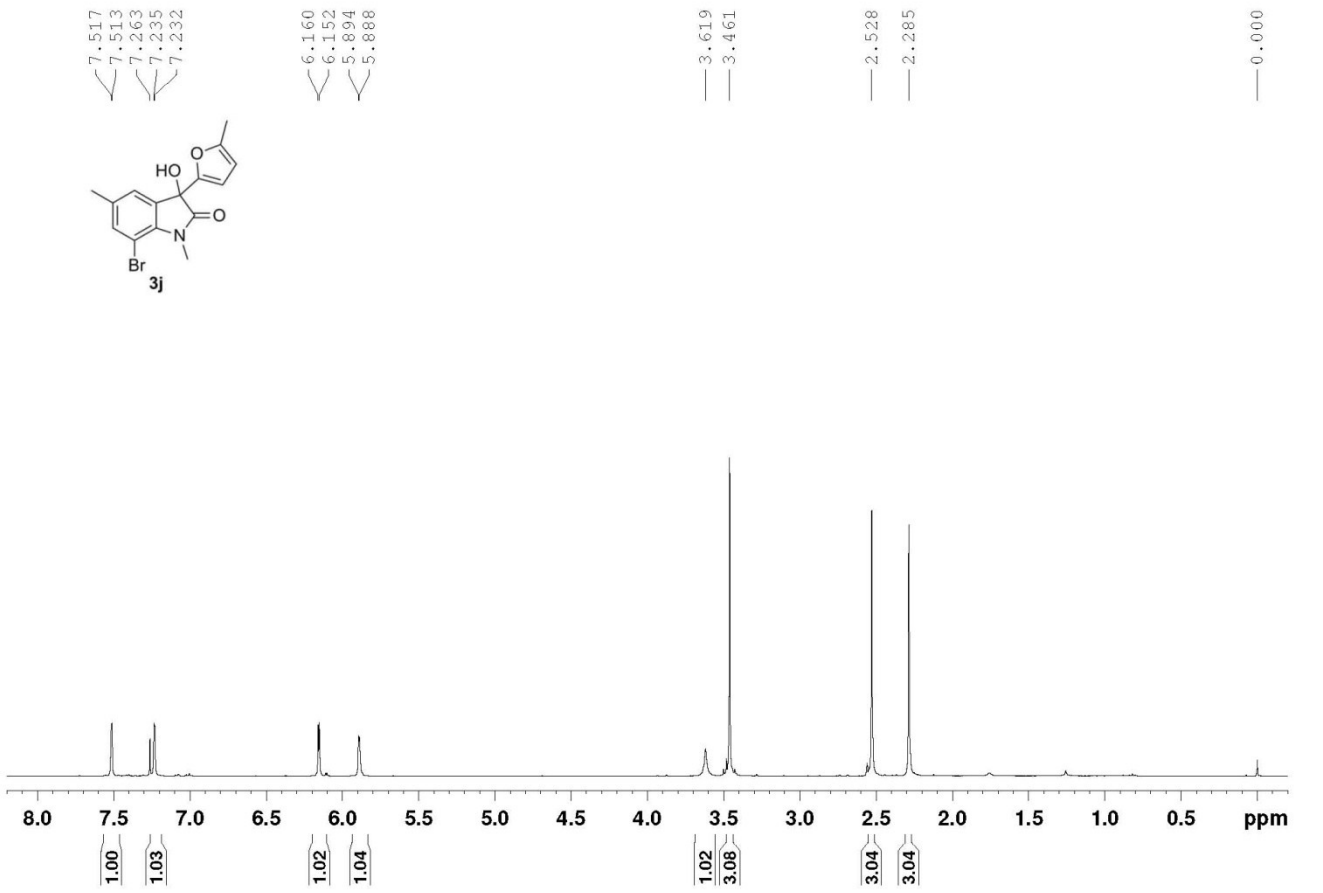
O
N
Br
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.513
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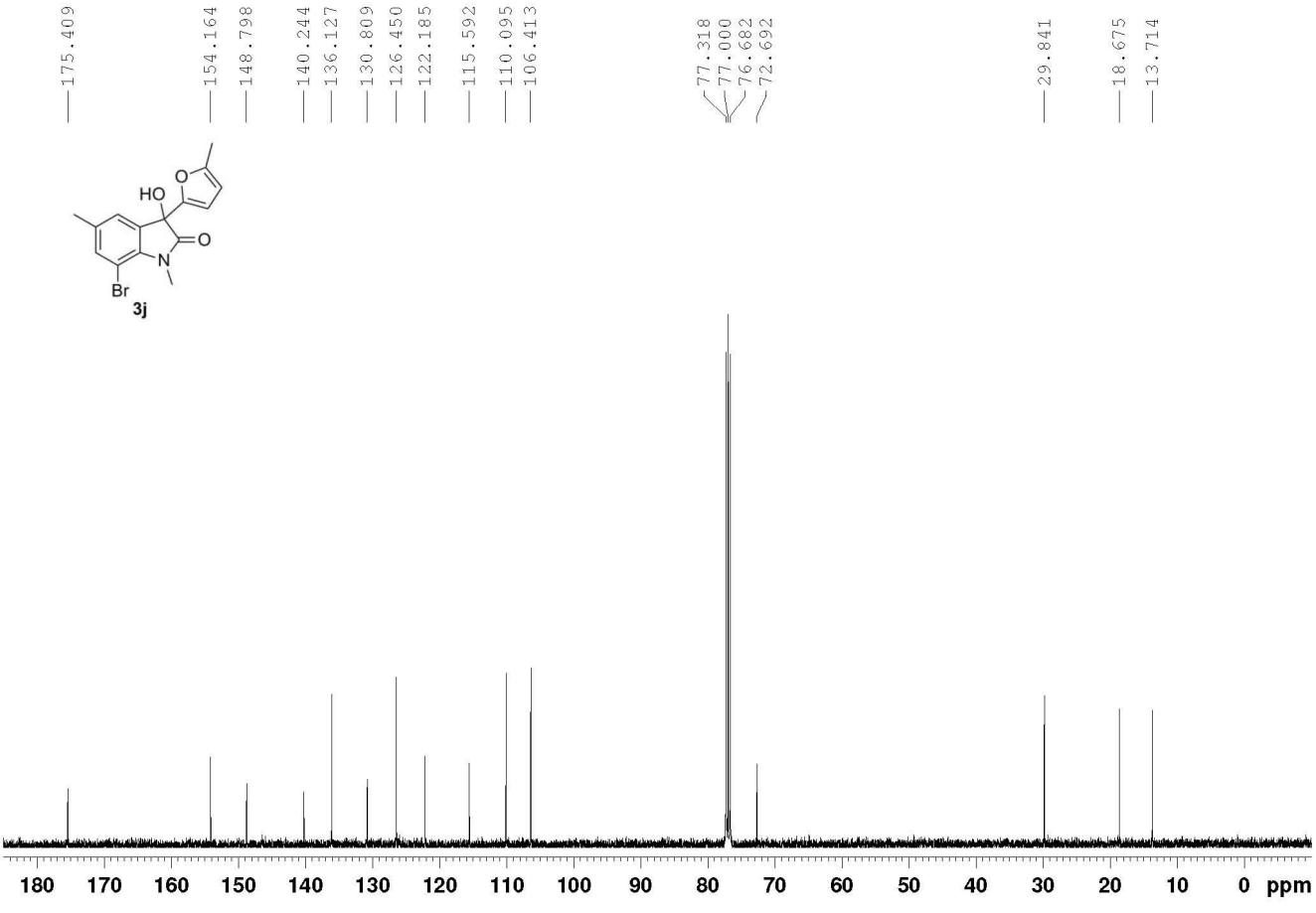
6.160
6.152
5.894
5.888
3.619
3.461
2.528
2.285
0.000
HO
O
O
N
Br
3j
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
1.02
1.04
1.02
3.08
3.04
3.04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130.809
126.450
122.185
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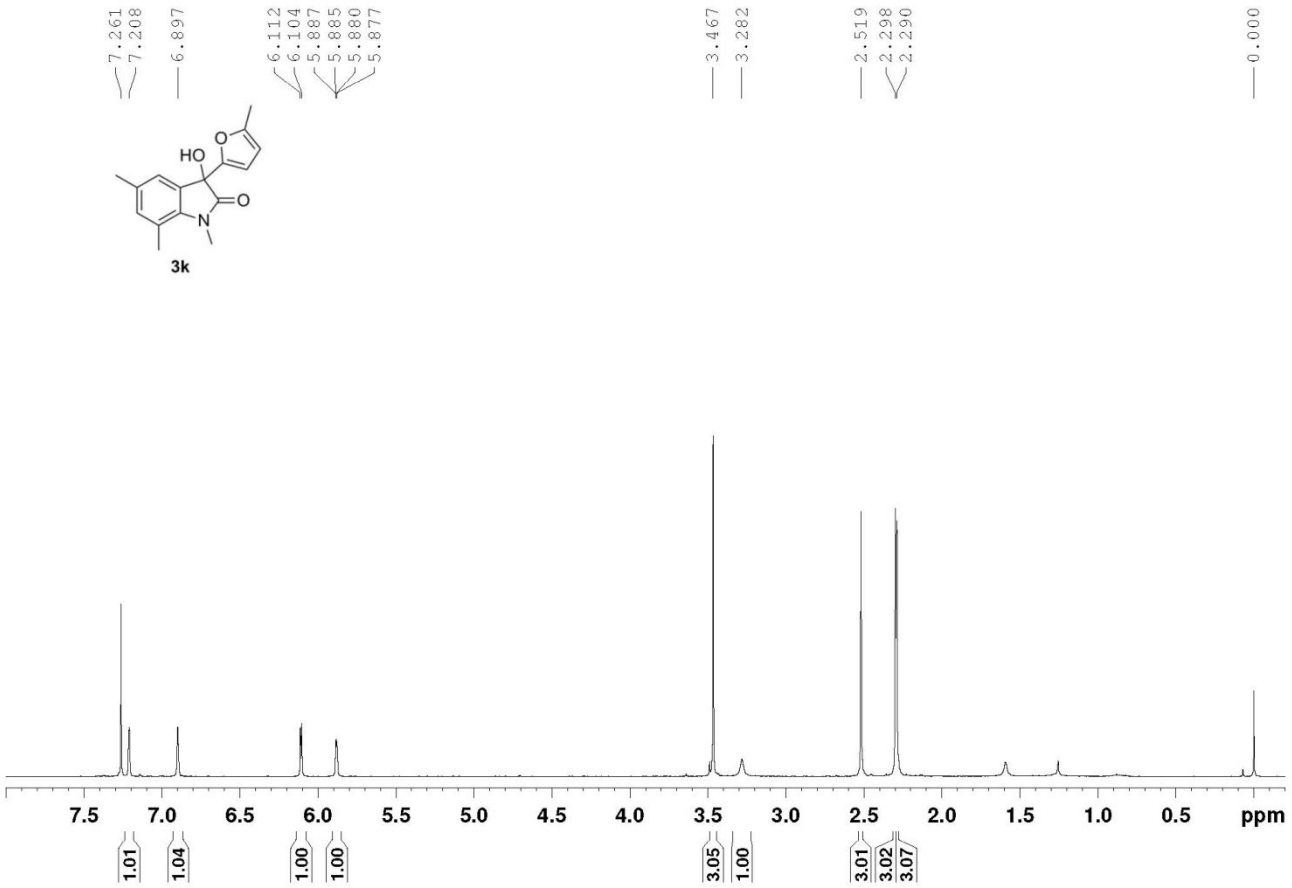
110.095
106.413
77.318
77.000
76.682
72.692
29.841
18.675
13.714
HO
O
O
N
Br
3j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.208
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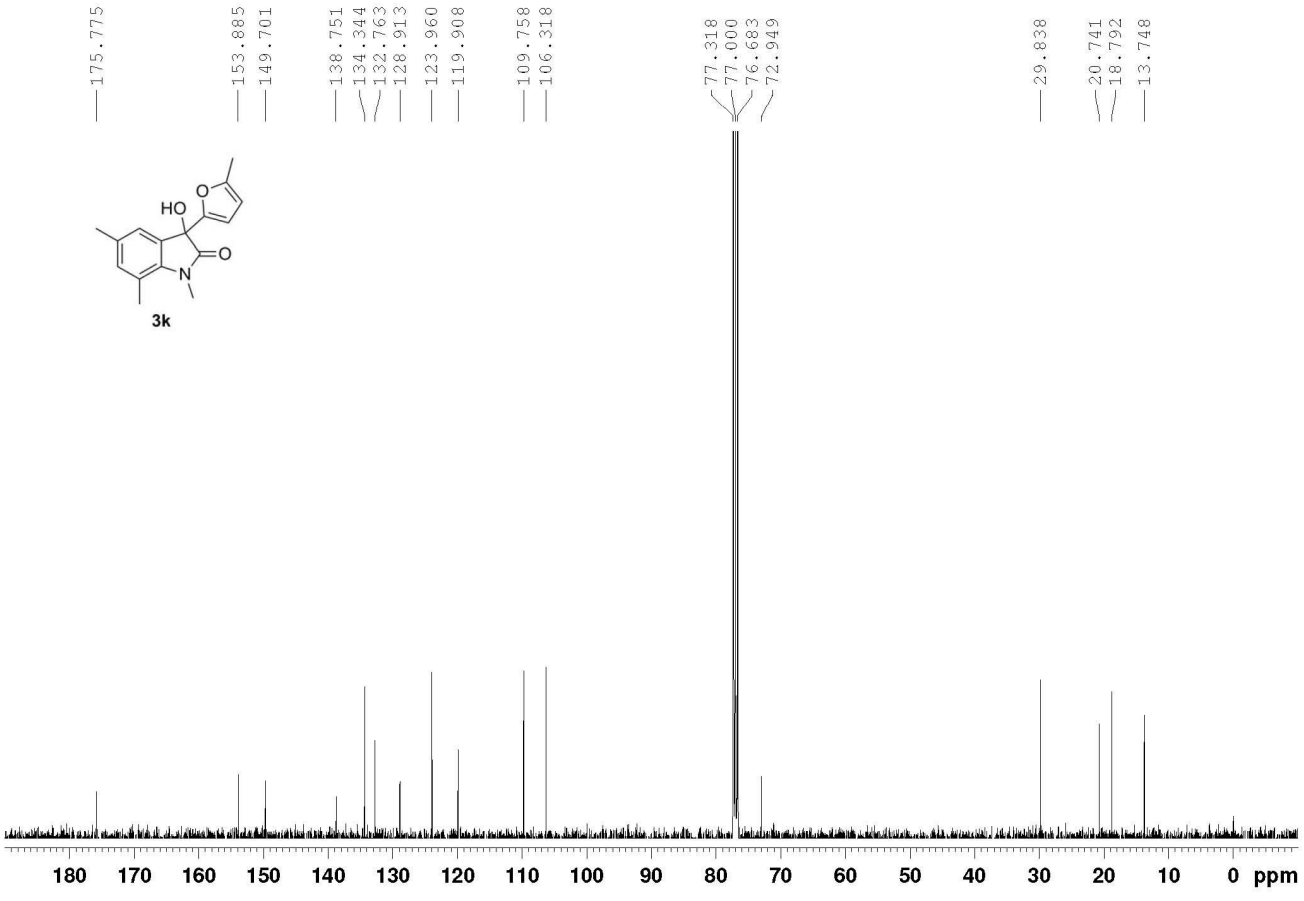
6.112
6.104
5.887
5.885
5.880
5.877
3.467
3.282
2.519
2.298
2.290
0.000
HO
O
N
O
3k
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
1.04
1.00
1.00
3.05
1.00
3.01
3.02
3.07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138.751
134.344
132.763
128.913
123.960
119.908
109.758
106.318
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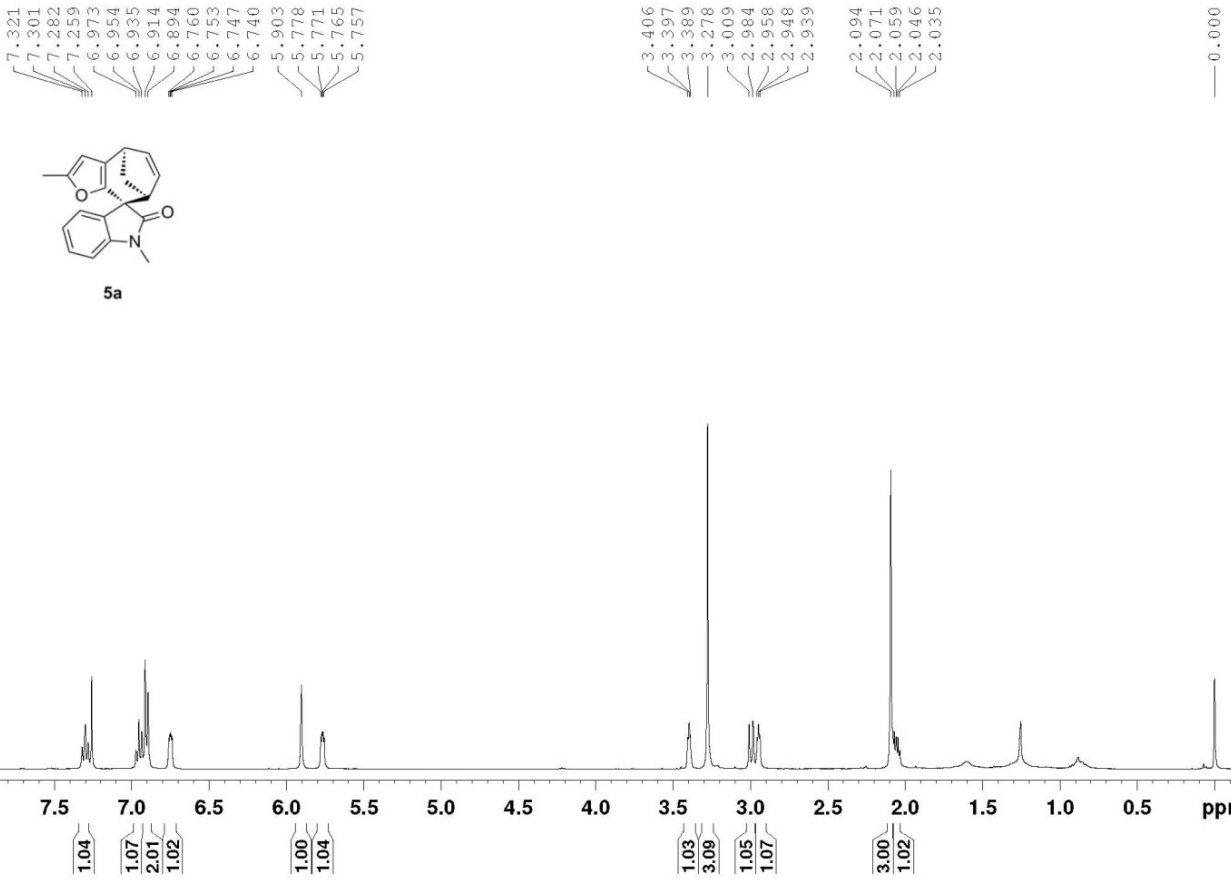
77.000
76.683
72.949
29.838
20.741
18.792
13.748
HO
O
N
O
3k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.321
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7.259
6.973
6.954
6.935
6.914
6.894
6.760
6.753
6.747
6.740
5.903
5.778
5.771
5.765
5.757
3.406
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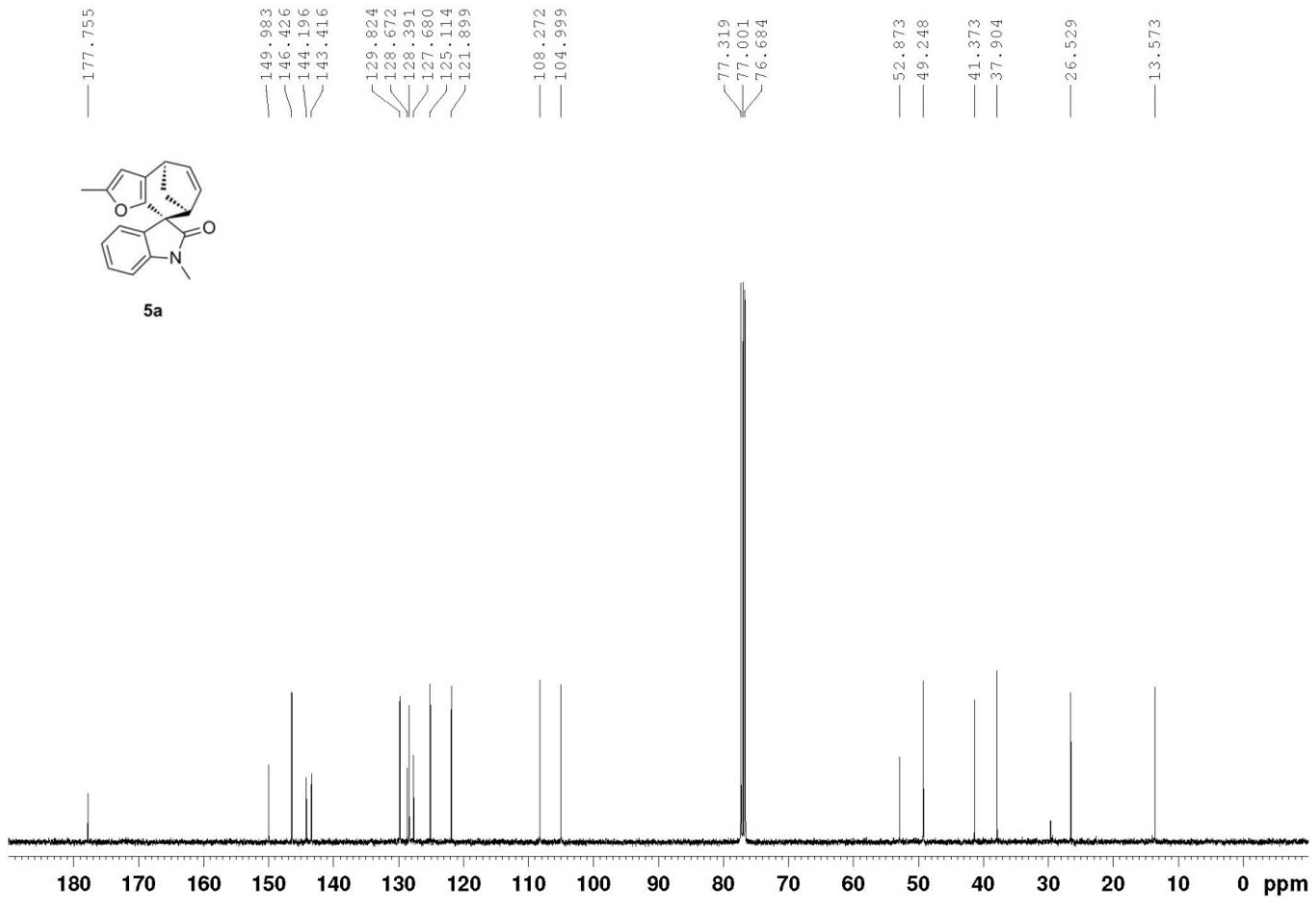
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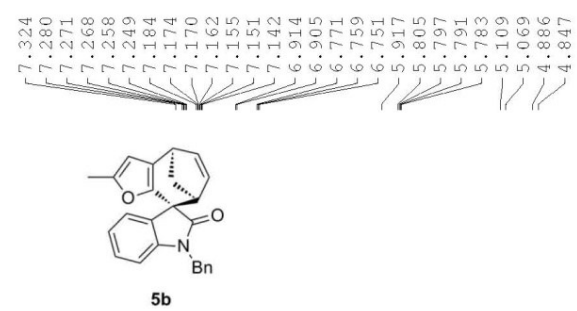
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6.751
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5.805
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5.069
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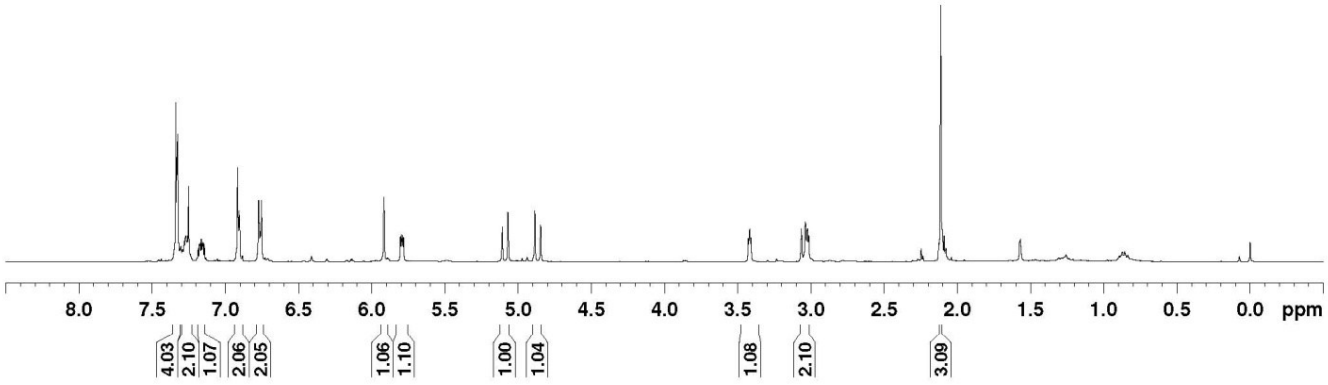
N
Bn

5b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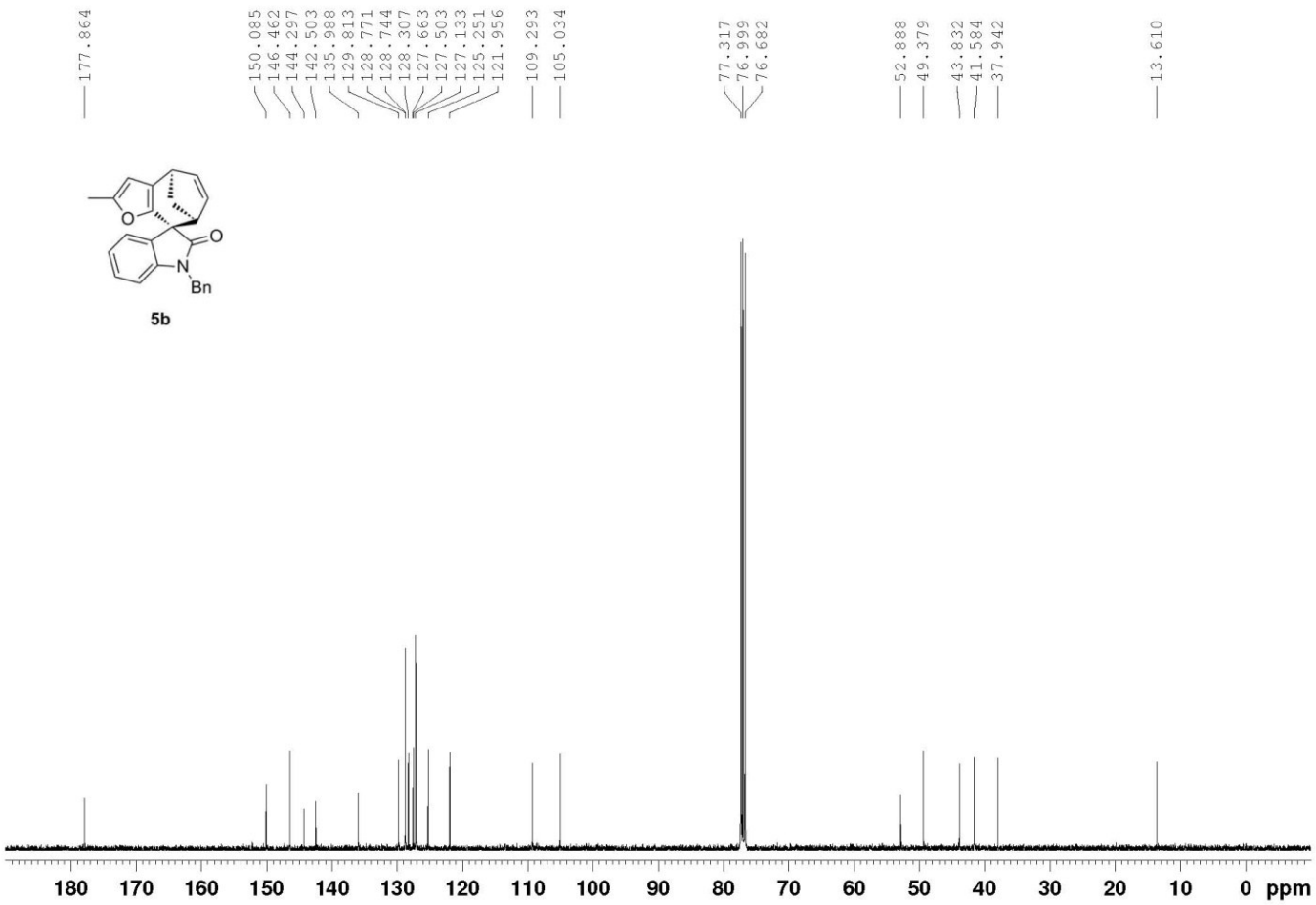
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43.832
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37.942
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160
150
140
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70
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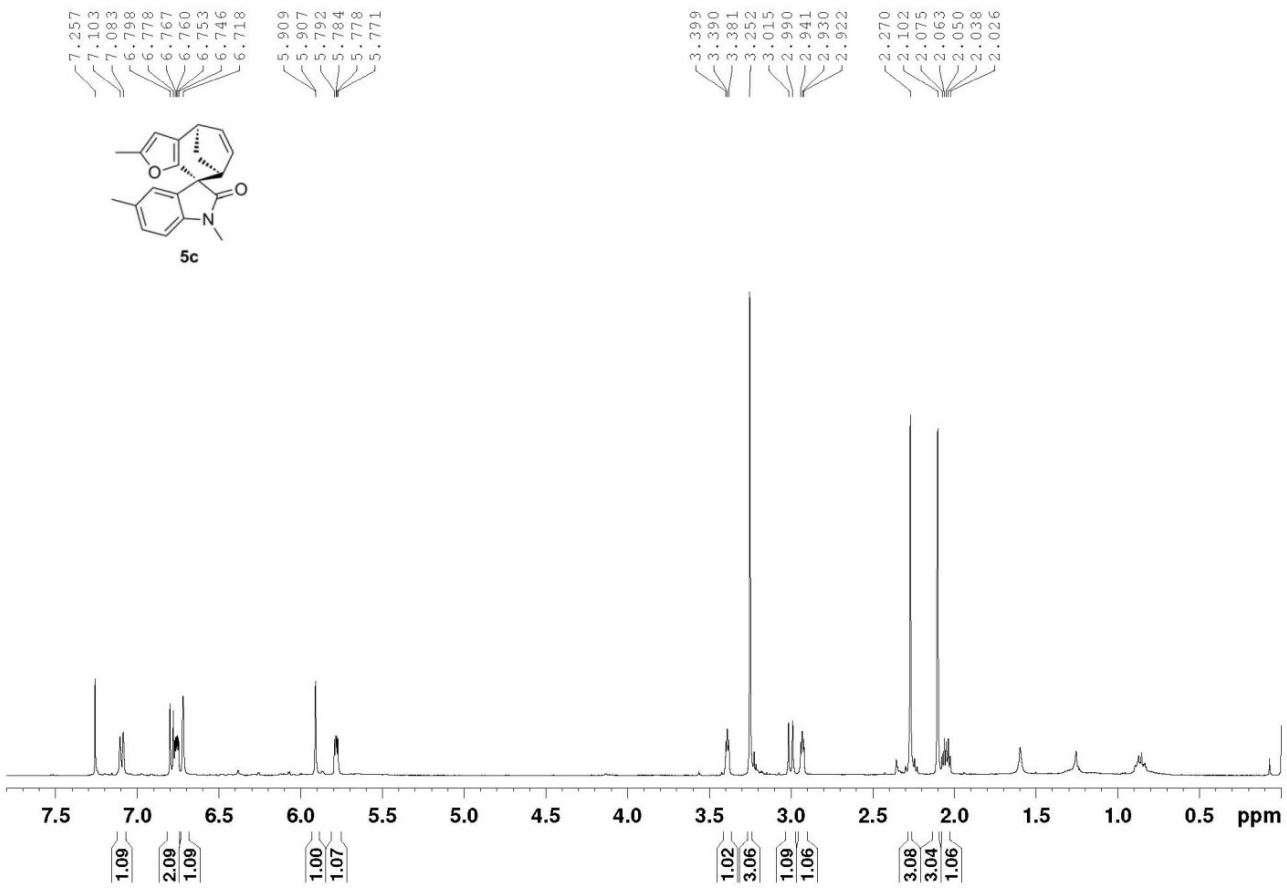
N
Bn

5b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2.038
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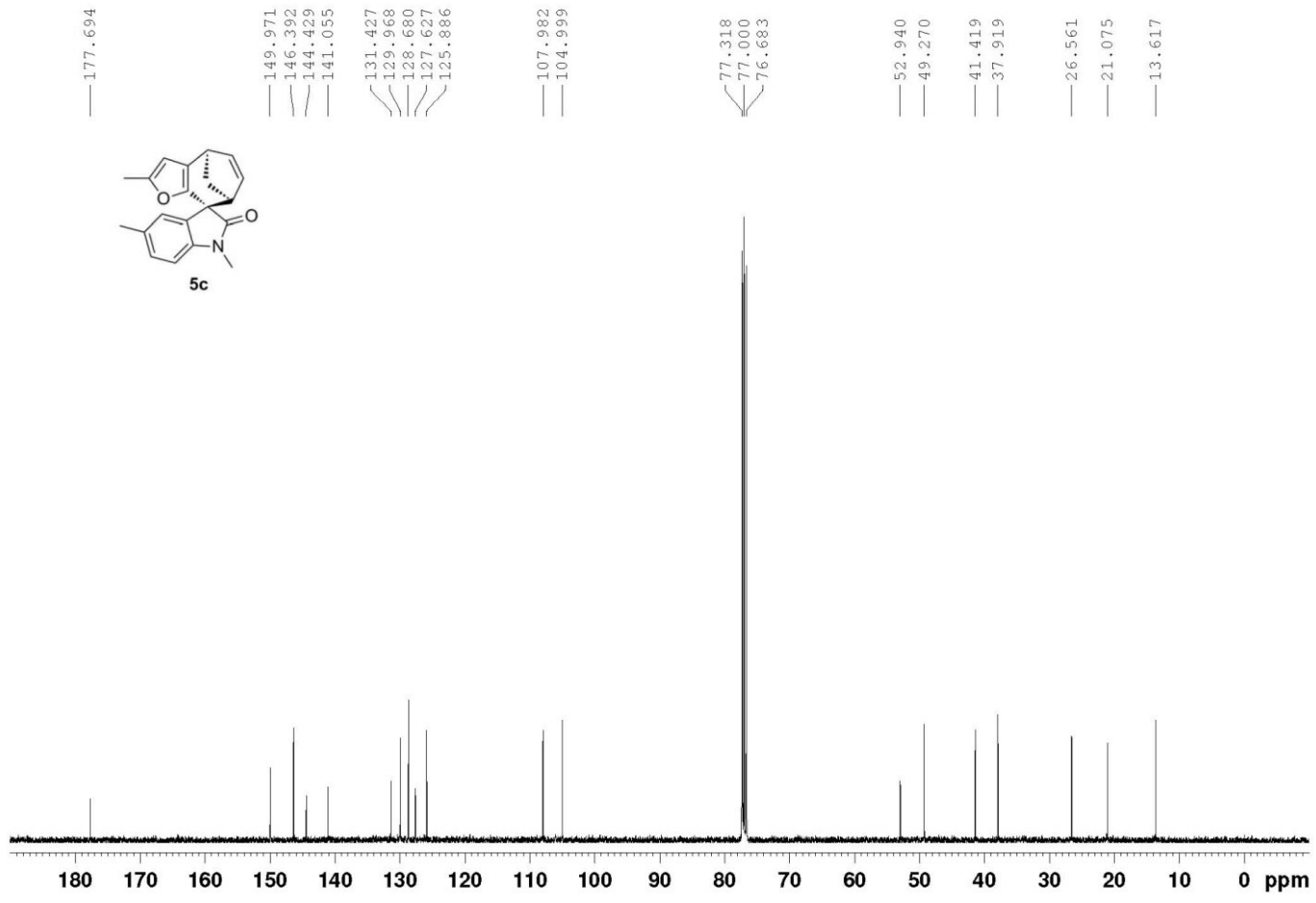
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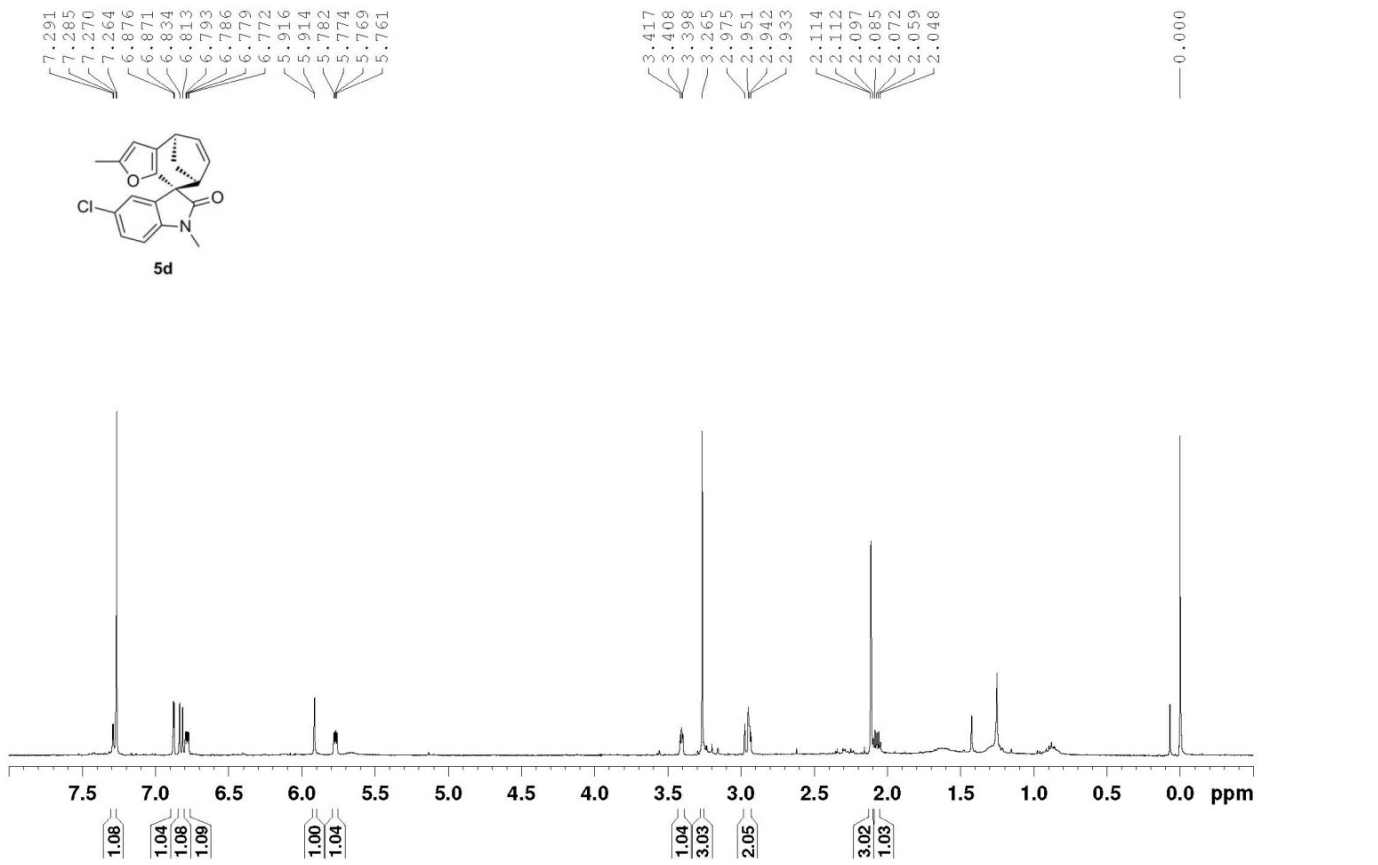
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6.772
5.916
5.914
5.782
5.774
5.769
5.761
3.417
3.408
3.398
3.265
2.975
2.951
2.942
2.933
2.114
2.112
2.097
2.085
2.072
2.059
2.048
0.000
Cl
O
N
5d
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6.5
6.0
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5.0
4.5
4.0
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3.0
2.5
2.0
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1.0
0.5
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1.08
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1.04
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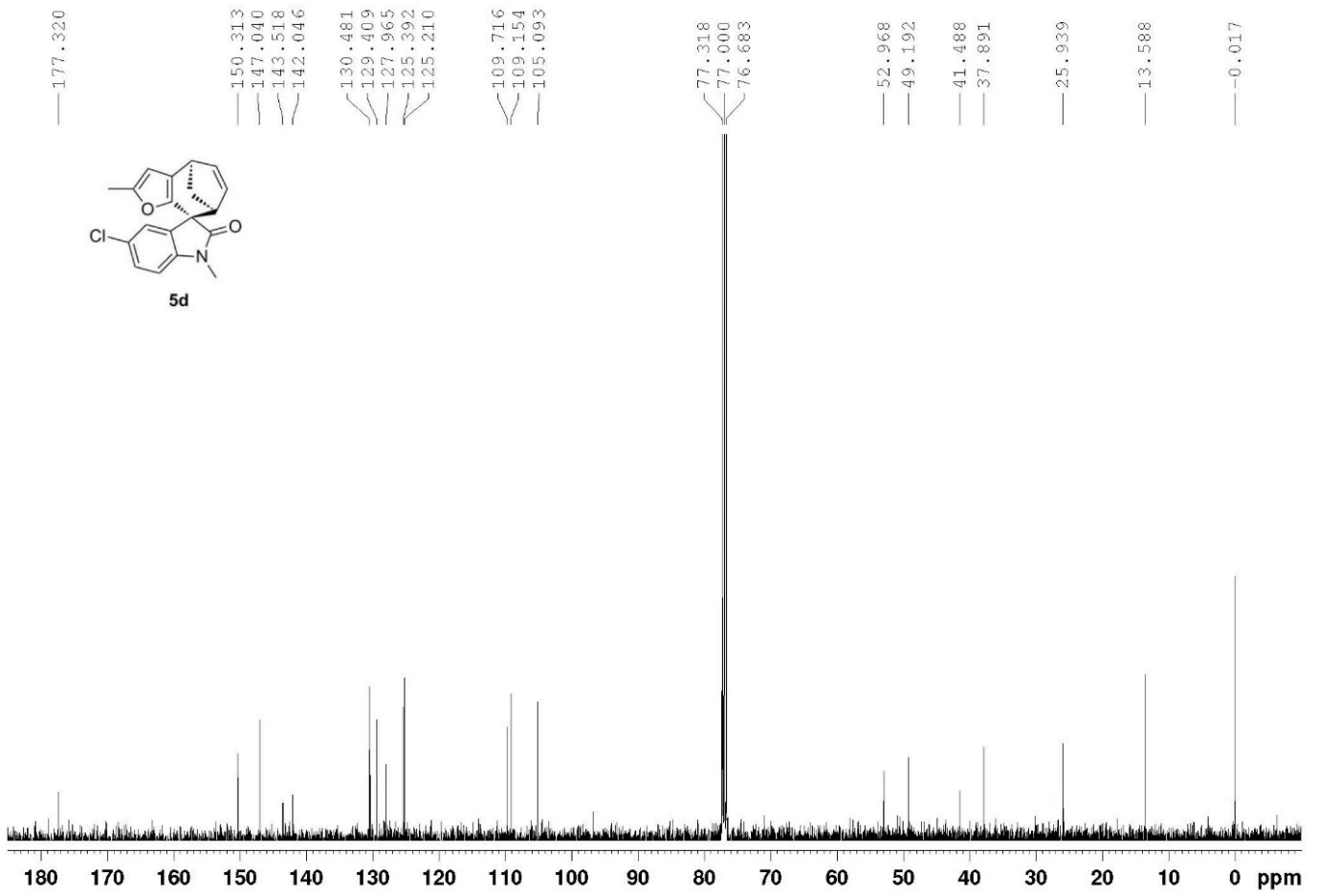
1.03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77.000
76.683
52.968
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37.891
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Cl
O
N
5d
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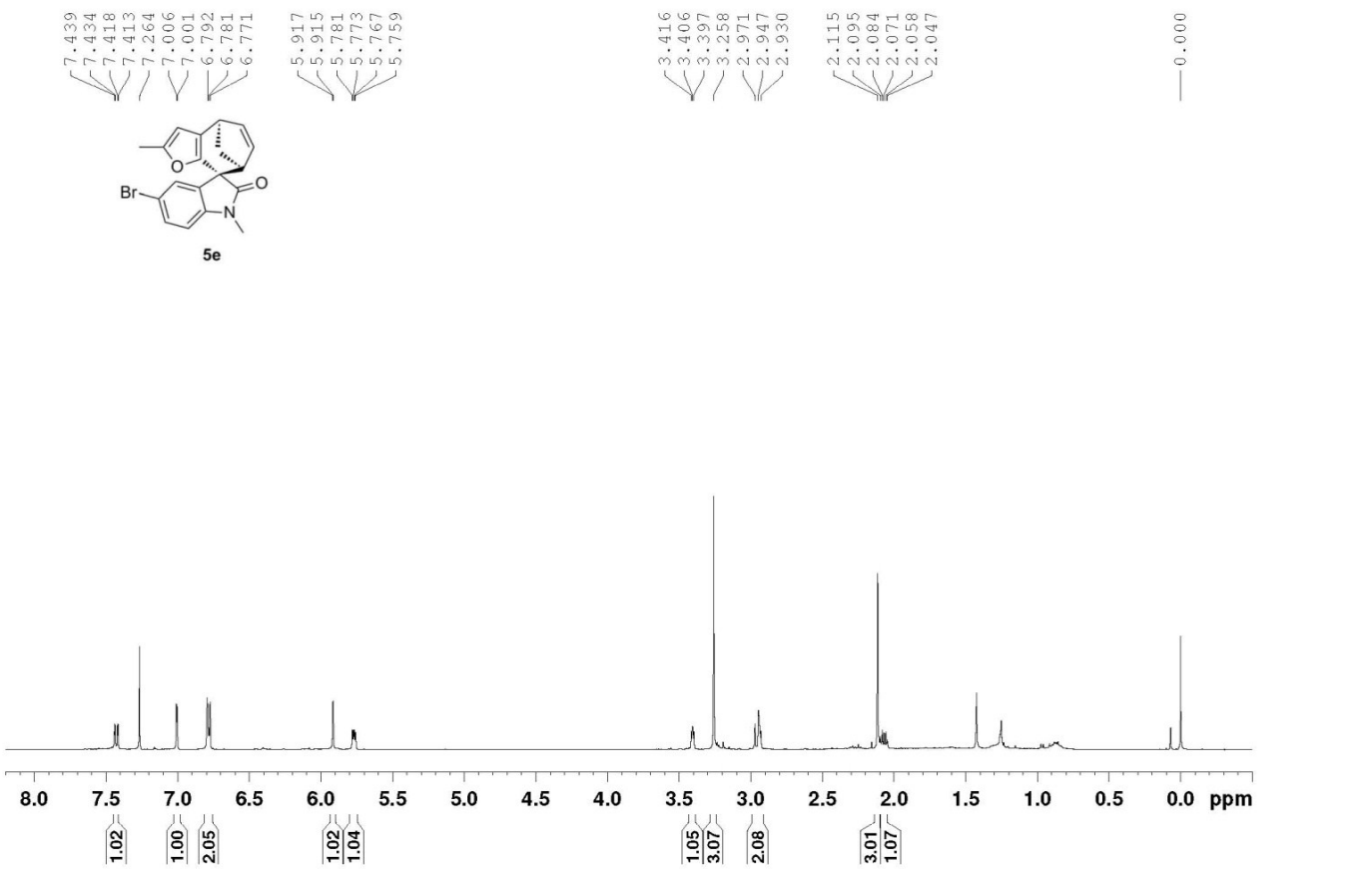
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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5.781
5.773
5.767
5.759
3.416
3.406
3.397
3.258
2.971
2.947
2.930
2.115
2.095
2.084
2.071
2.058
2.047
0.000
Br
O
N
O
5e
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7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
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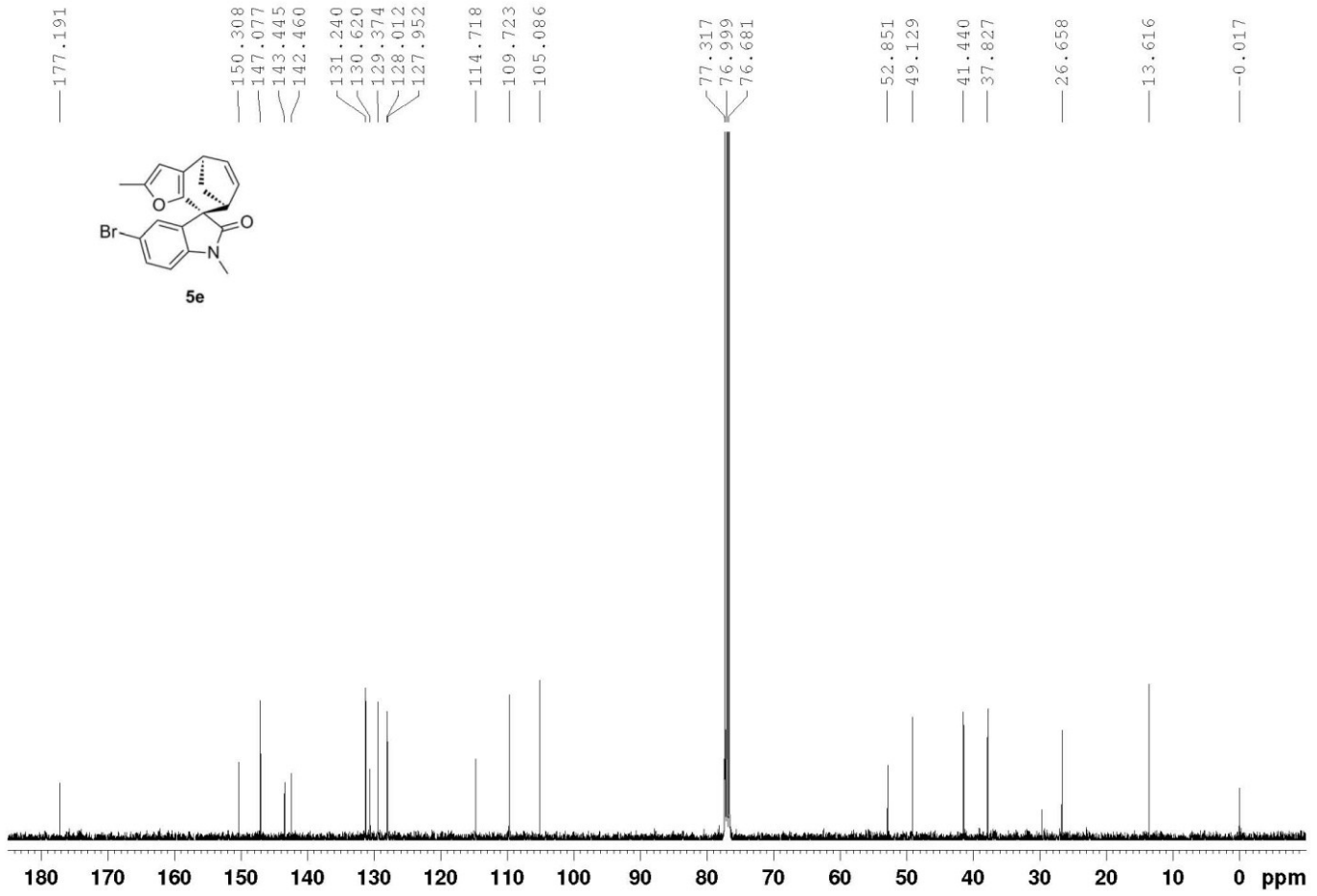
1.07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76.999
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41.440
37.827
26.658
13.616
-0.017
Br
O
N
O
5e
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150
140
130
120
110
100
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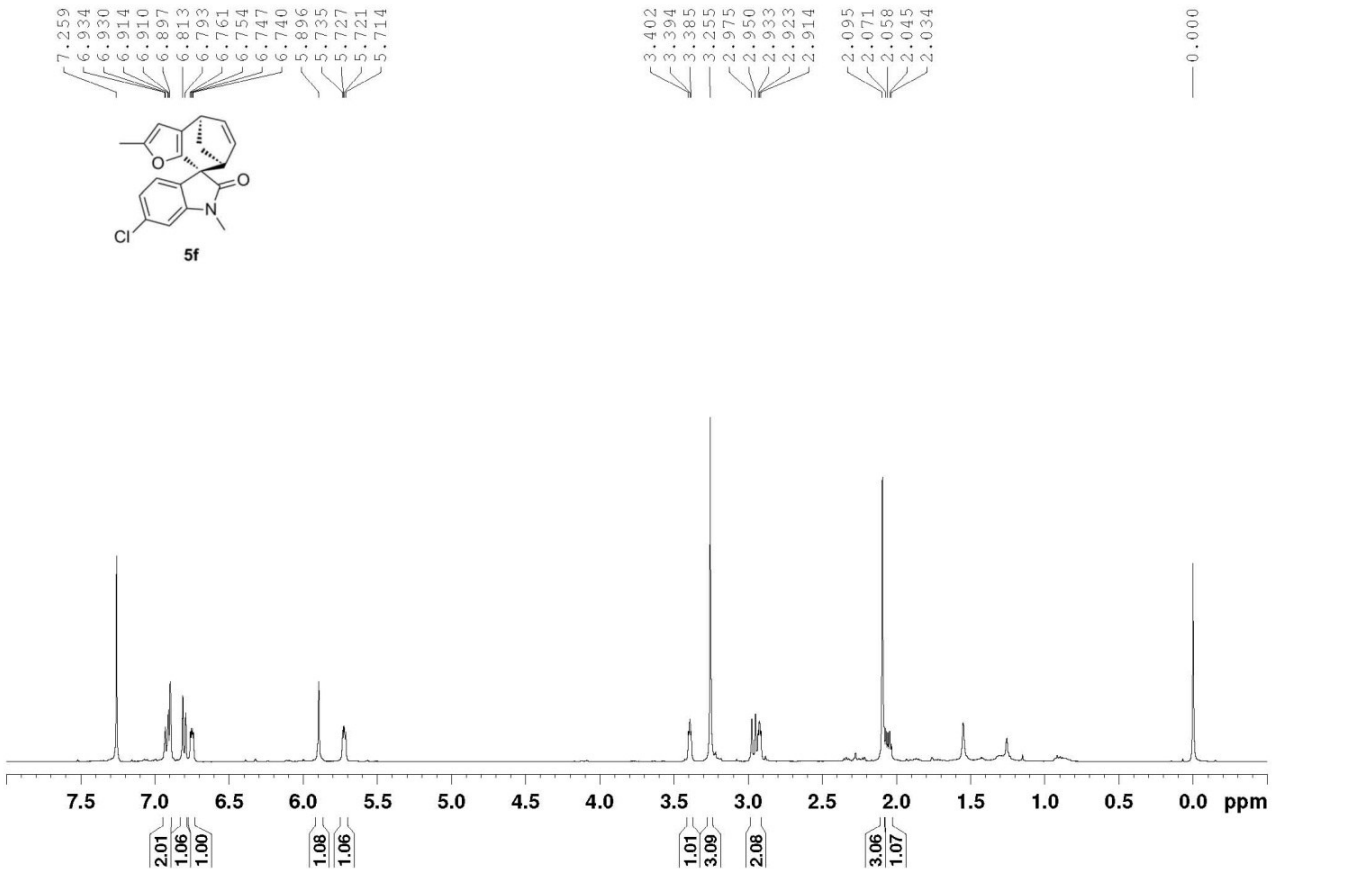
80
70
60
50
40
30
20
10
0
ppm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5.896
5.735
5.727
5.721
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3.394
3.385
3.255
2.975
2.950
2.933
2.923
2.914
2.095
2.071
2.058
2.045
2.034
0.000
5f
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.01
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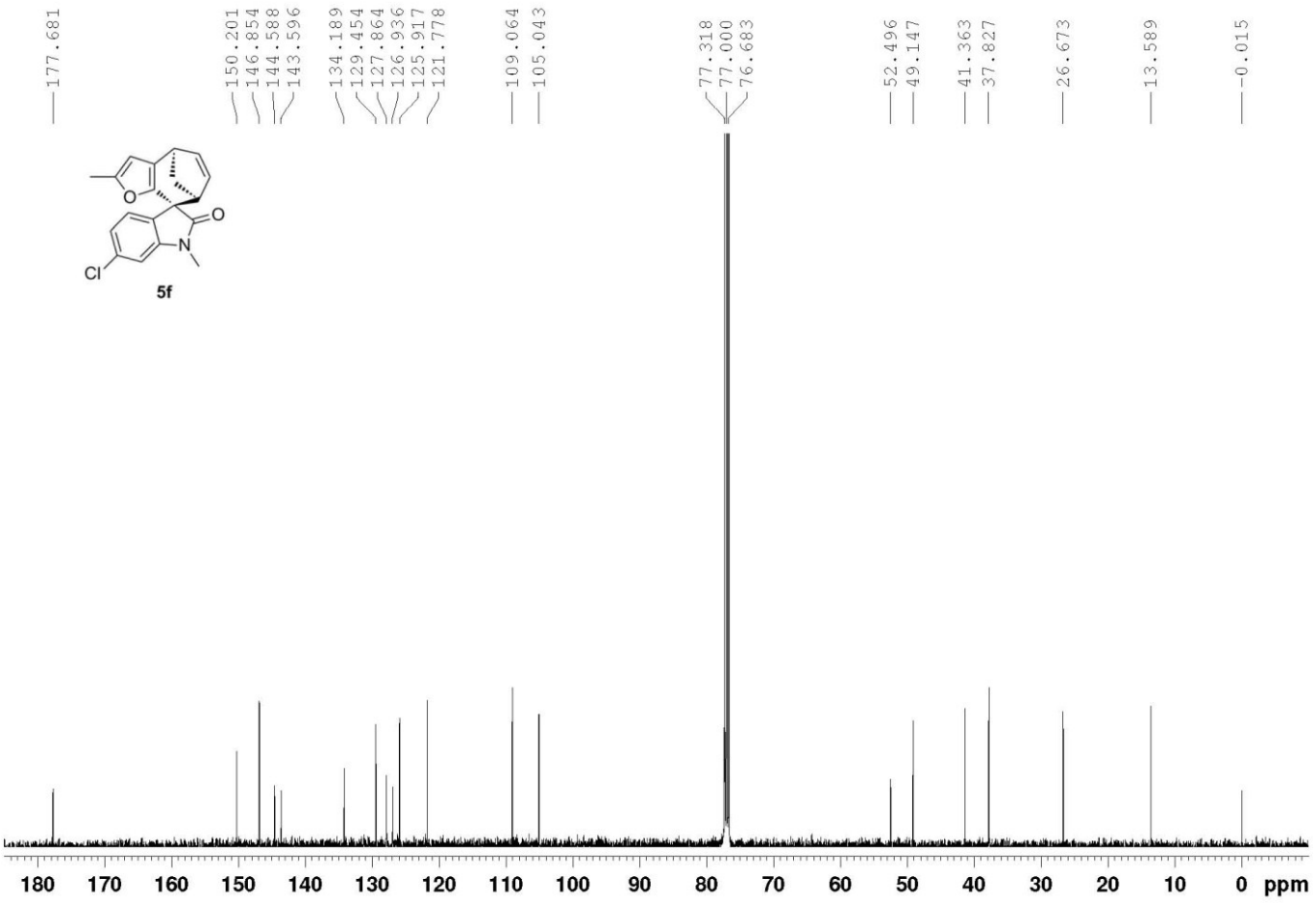
3.06
1.07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77.000
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52.496
49.147
41.363
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26.673
13.589
-0.015
5f
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140
130
120
110
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50
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30
20
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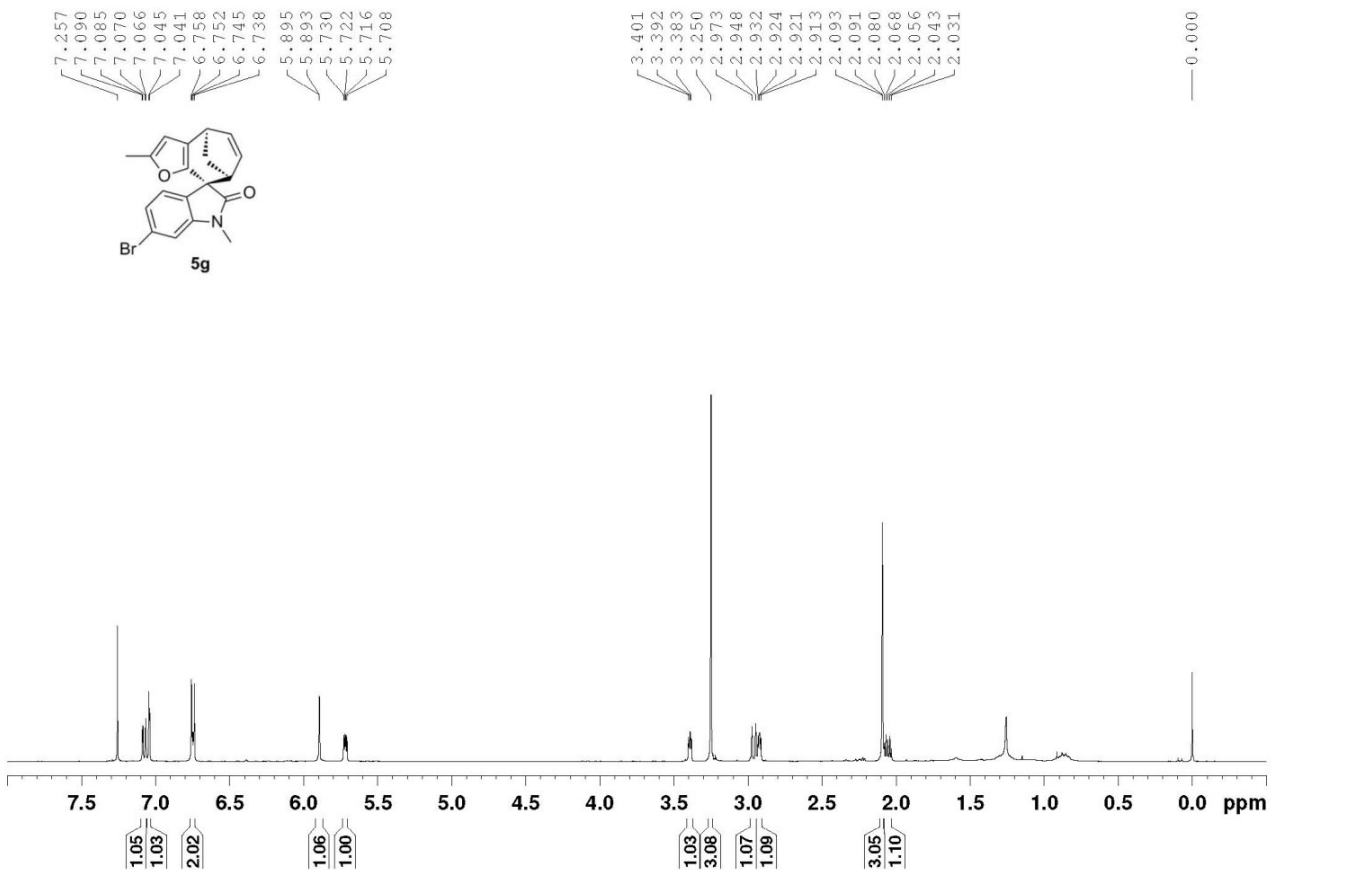
ppm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5.722
5.716
5.708
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3.392
3.383
3.250
2.973
2.948
2.932
2.924
2.921
2.913
2.093
2.091
2.080
2.068
2.056
2.043
2.031
0.000
O
O
N
Br
5g
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6.5
6.0
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5.0
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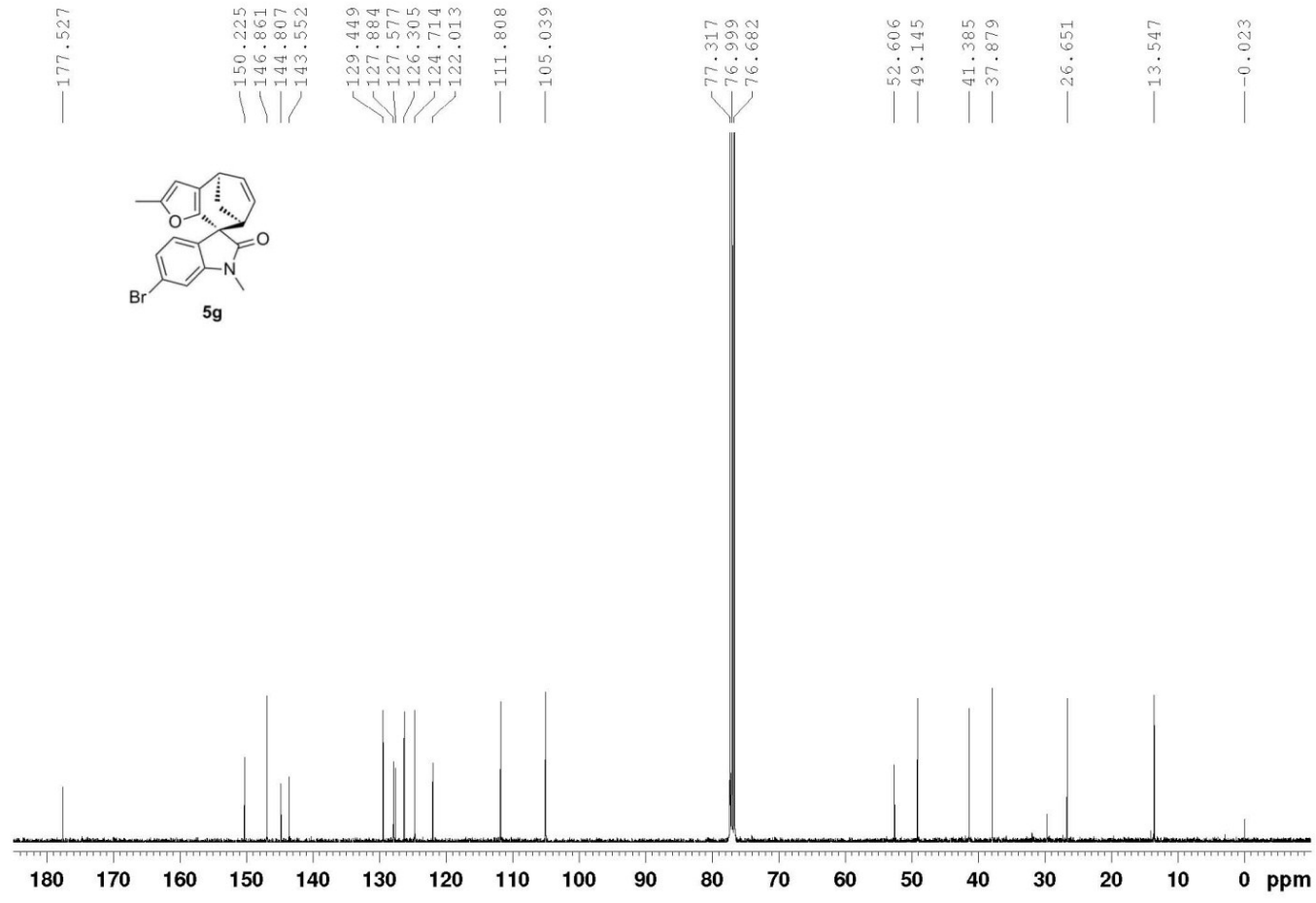
1.10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76.999
76.682
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41.385
37.879
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O
O
N
Br
5g
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50
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10
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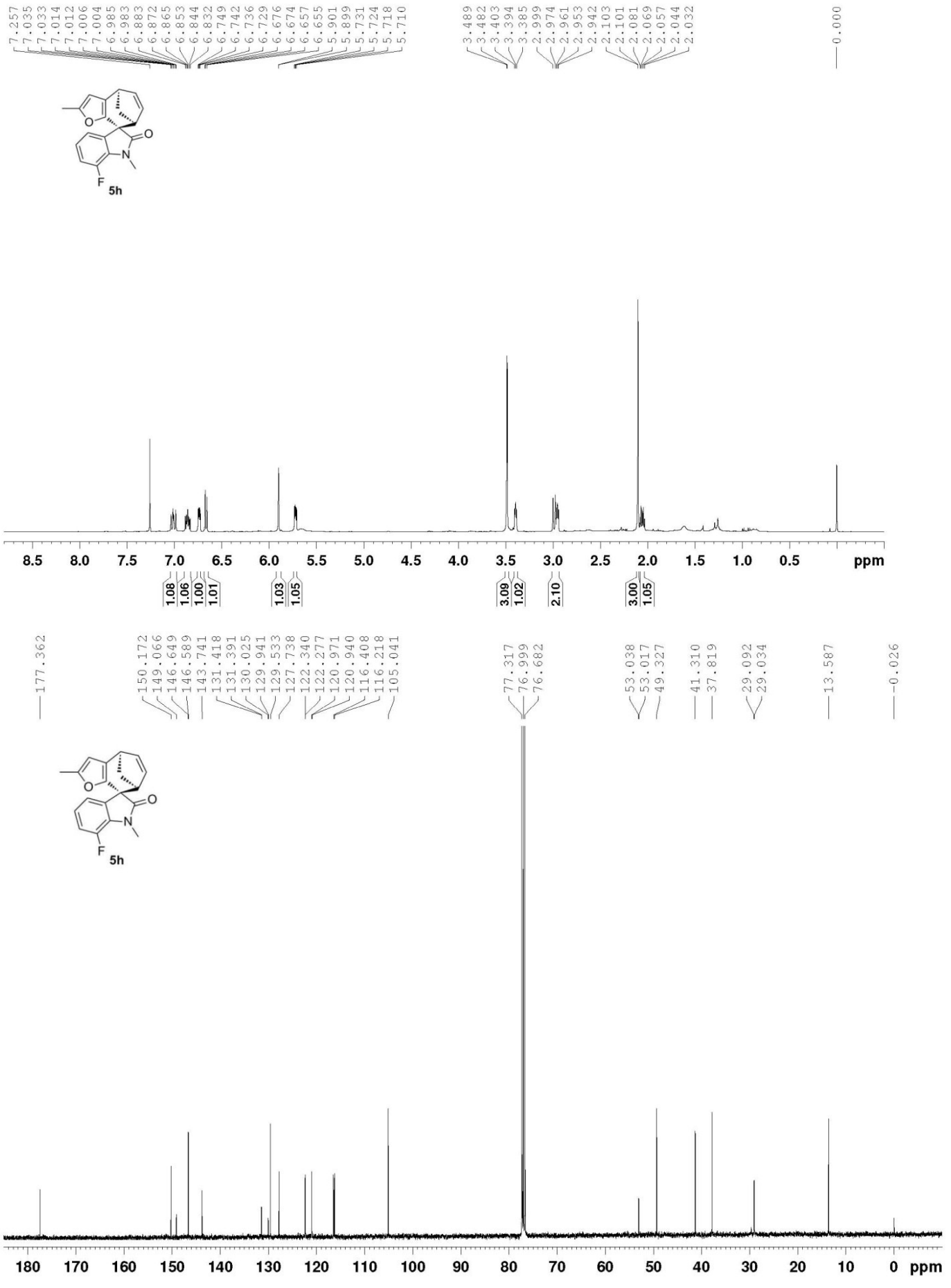
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6.832
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6.742
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6.674
6.657
6.655
5.901
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5.718
5.710
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3.482
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3.394
3.385
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2.953
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2.101
2.081
2.069
2.057
2.044
2.032
0.000
5h
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
1.08 1.06 1.00 1.01 1.03 1.05 3.09 1.02 2.10 3.00 1.05
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131.391
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122.340
122.277
120.971
120.940
116.408
116.218
105.041
77.317
76.999
76.682
53.038
53.017
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5h
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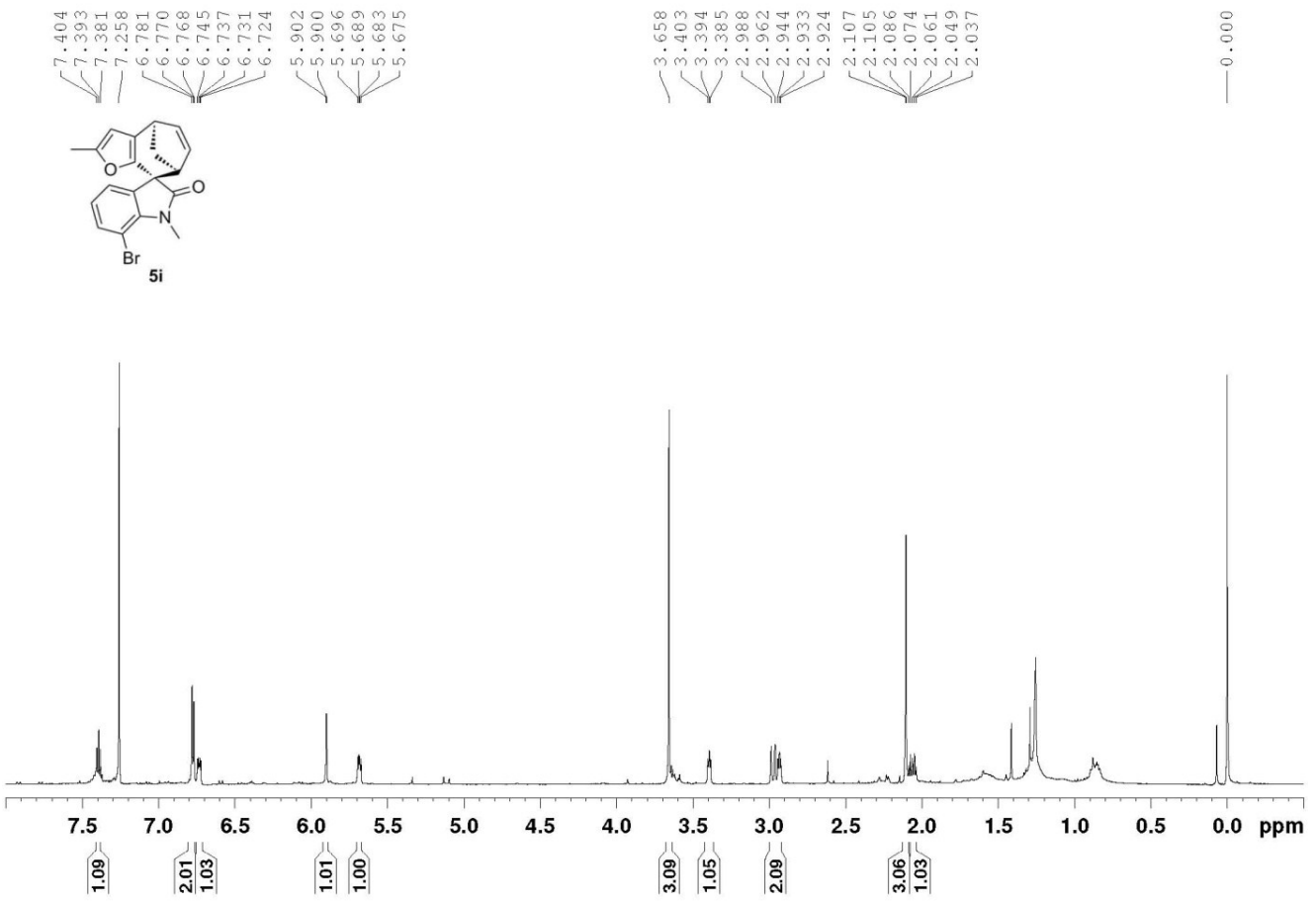
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5.900
5.696
5.689
5.683
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2.962
2.944
2.933
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2.105
2.086
2.074
2.061
2.049
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0.000
O
N
Br
5i
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7.0
6.5
6.0
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5.0
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4.0
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3.0
2.5
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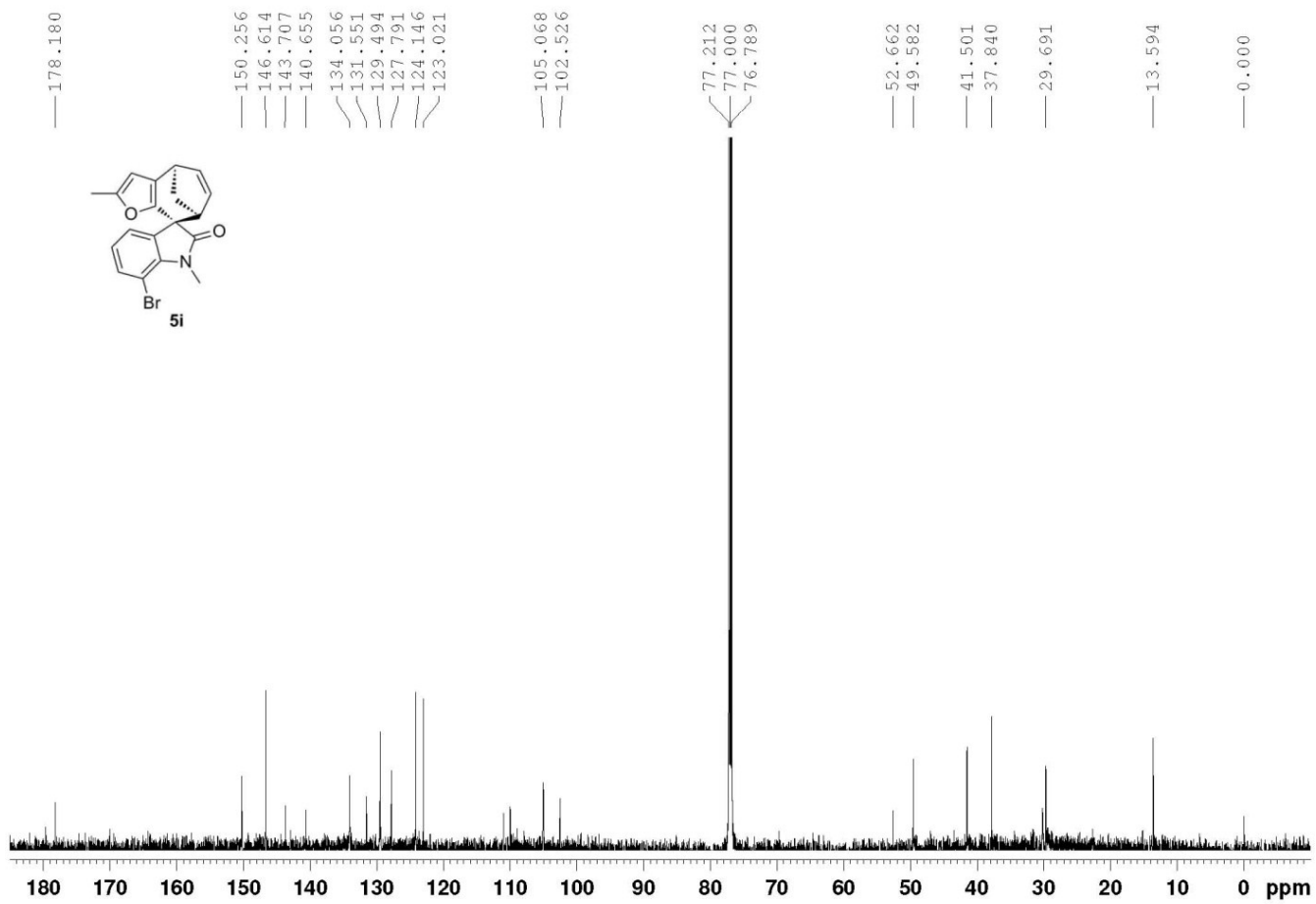
1.03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77.000
76.789
52.662
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41.501
37.840
29.691
13.594
0.000
O
N
Br
5i
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60
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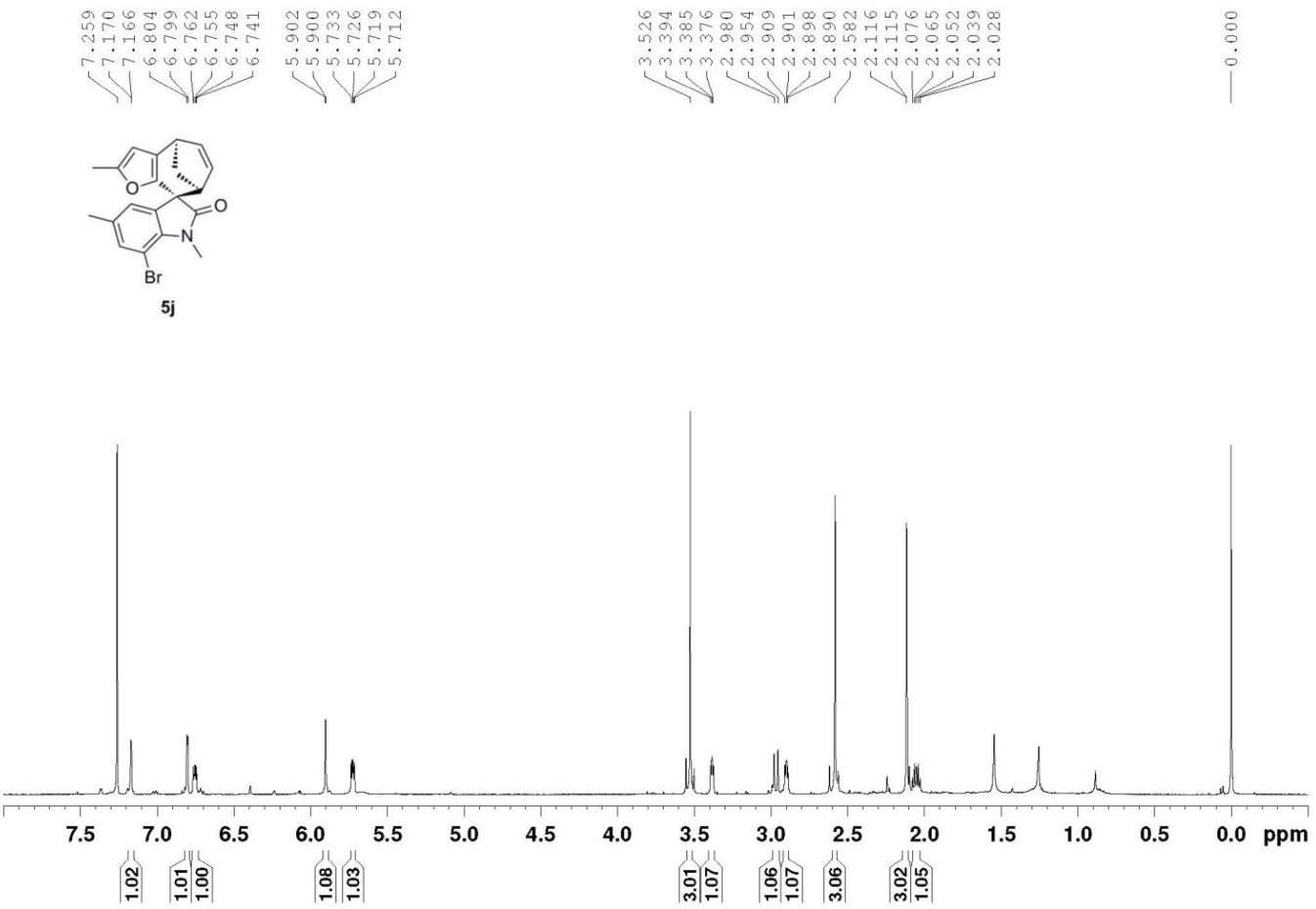
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5.719
5.712
3.526
3.394
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2.980
2.954
2.909
2.901
2.898
2.890
2.582
2.116
2.115
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2.065
2.052
2.039
2.028
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O
O
N
Br
5j
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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0.0
ppm
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1.06
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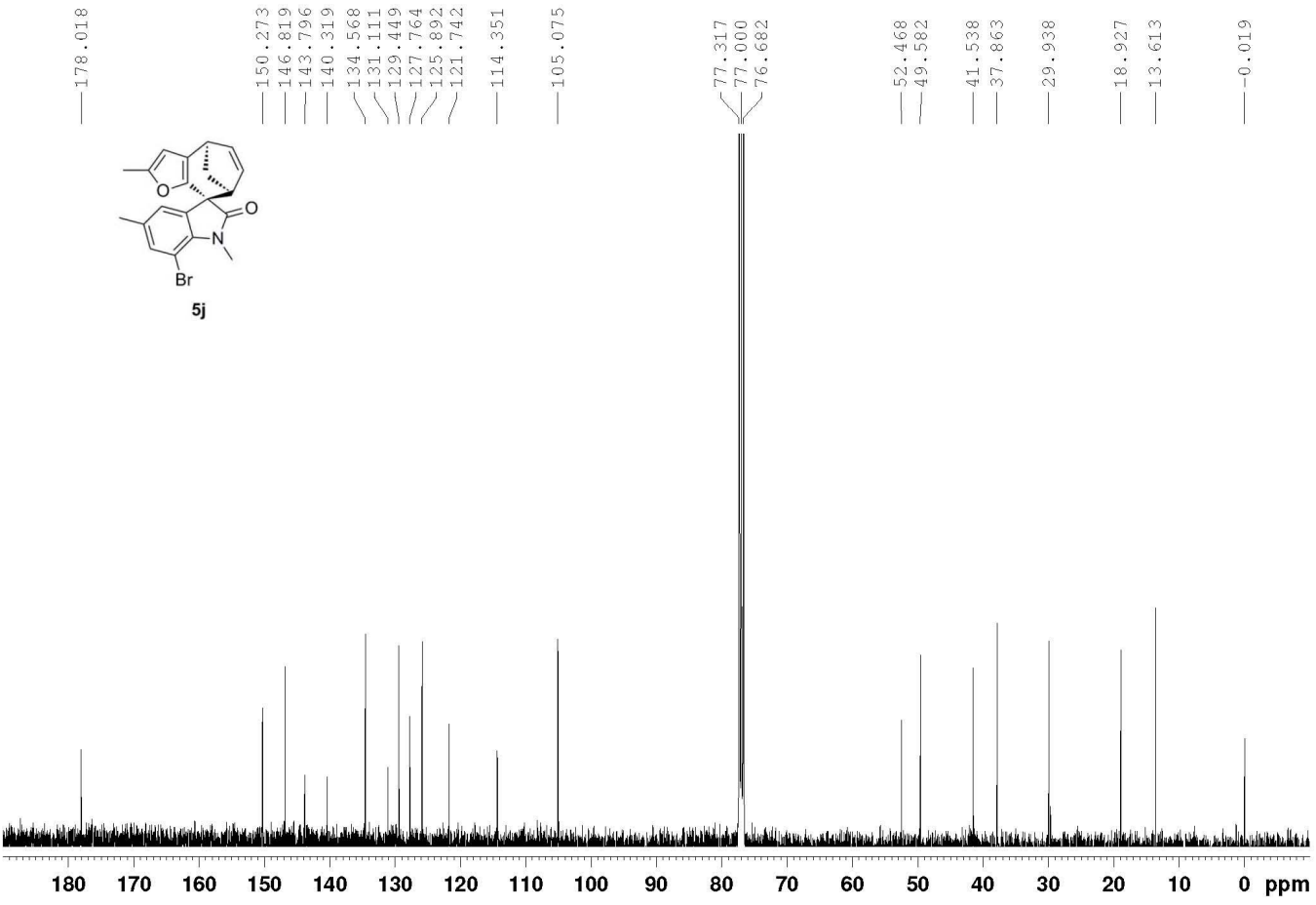
1.05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77.317
77.000
76.682
52.468
49.582
41.538
37.863
29.938
18.927
13.613
-0.019
O
O
N
Br
5j
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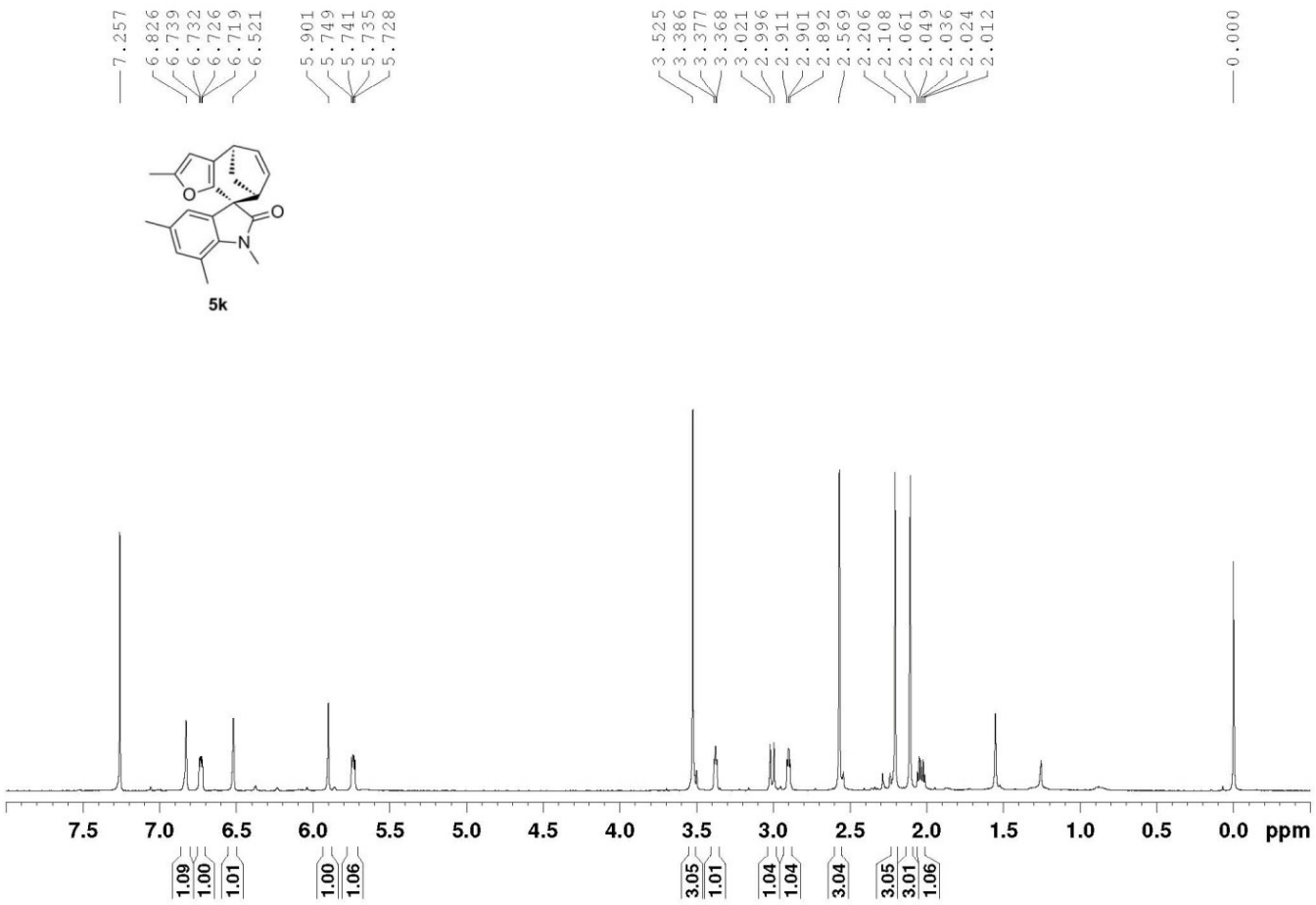
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3.021
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2.206
2.108
2.061
2.049
2.036
2.024
2.012
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6.0
5.5
5.0
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4.0
3.5
3.0
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2.0
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1.0
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ppm
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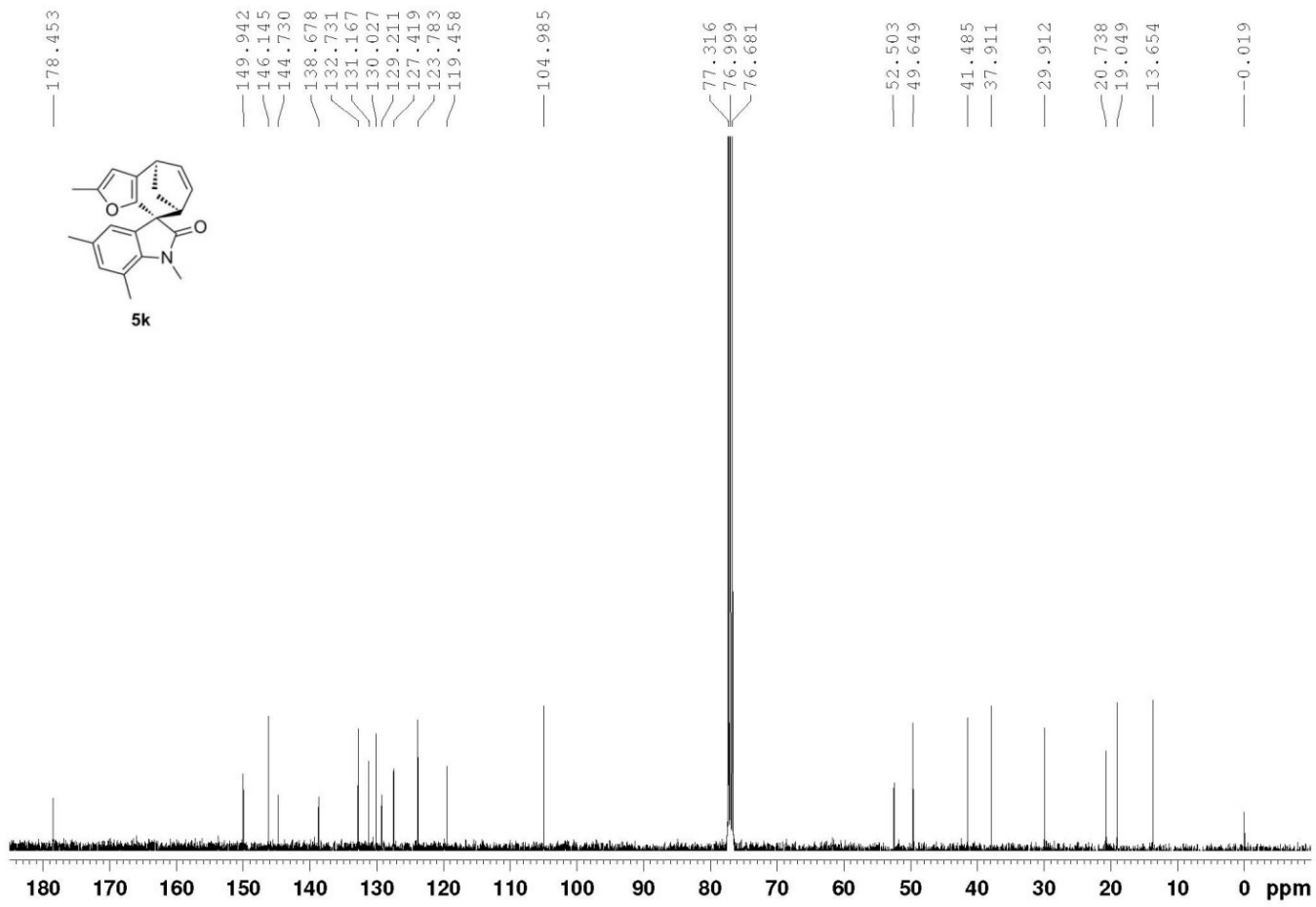
1.06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127.419
123.783
119.458
104.985
77.316
76.999
76.681
52.503
49.649
41.485
37.911
29.912
20.738
19.049
13.654
-0.019
5k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm