Supporting Information

Rhodium(III)-catalyzed intramolecular amidoarylation and hydroarylation of alkyne via C–H activation: Switchable synthesis of 3,4-fused tricyclic indoles and chromans

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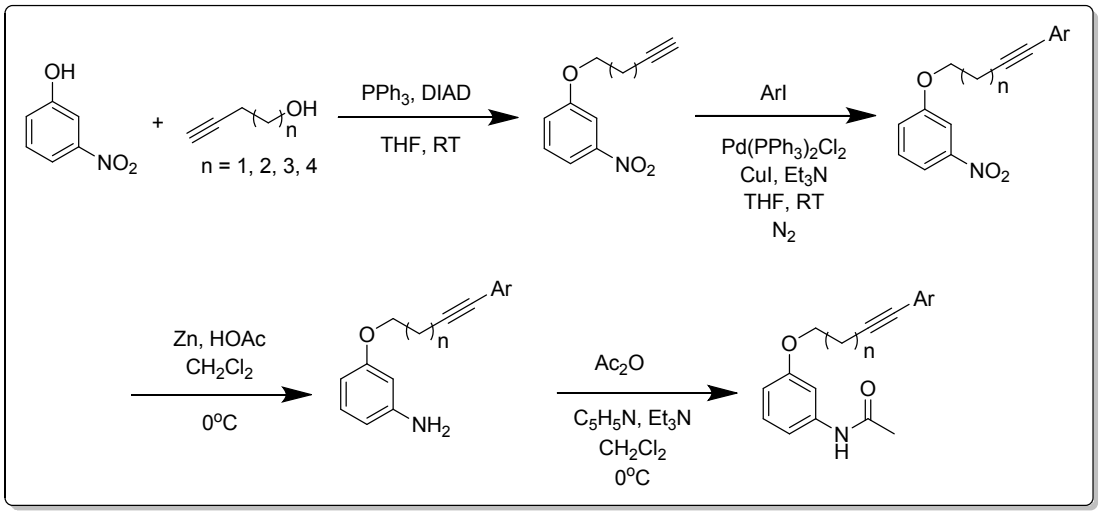
I. General Information

All Rhodium-catalyzed reactions were carried out without any particular precautions to extrude moisture or oxygen.

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300−400 mesh). Melting points were uncorrected. NMR spectra were obtained on a Varian Inova 500 spectrometer (500 MHz for ^{1}H NMR; 125 MHz for ^{13}C NMR), with TMS as the internal standard. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

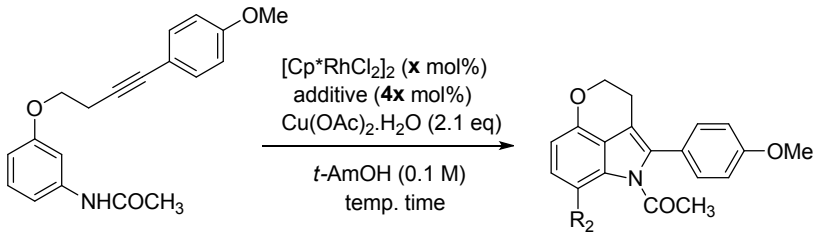
The starting materials **1** were prepared according to the literature procedures[1].



1. Dong Shan, Yan Gao, and Yanxing Jia, *Angew. Chem. Int. Ed*., **2013**, *52*, 4902.

II. Optimization of Reaction Conditions

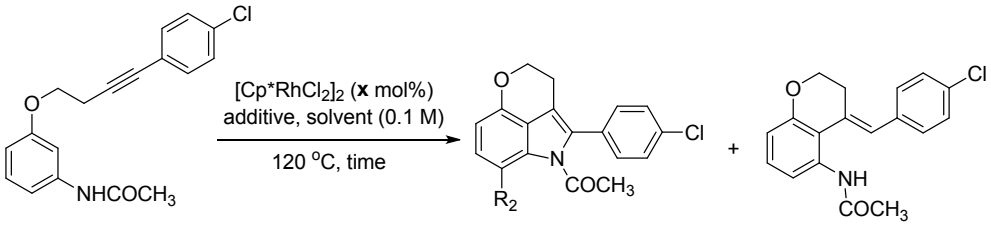
Table 1 Optimization of Reaction Conditions



1a **2a**

entry	x	additive	temp	Time (h)	yield of **2a** (%)
1	2.5	$AgSbF_6$	120℃	0.3	70
2	***1.0***	***$AgSbF_6$***	***120℃***	***0.3***	***87***
3	1.0	$AgSbF_6$	100℃	1.0	65
4	2.5	AgOAc	100℃	2.0	Trace

Table 2 Optimization of Reaction Conditions for **2d** and **3d**

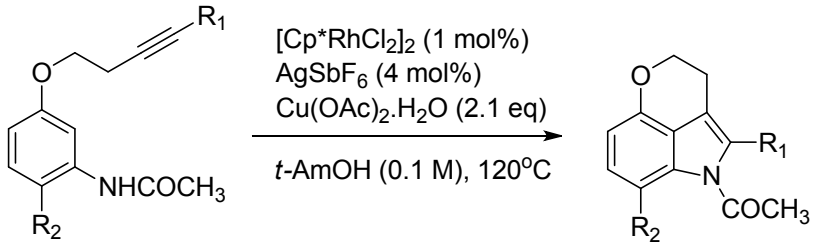


1d **2d** **3d**

entry	x	additive (equiv)	solvent (0.1 M)	time (h)	yield (%)	
					2d	**3d**
1	1.0	$Cu(OAc)_2.H_2O$ (2.1)	*t*-AmOH	0.3	26	51
2	1.0	$Cu(OAc)_2.H_2O$ (2.1)	acetone	0.3	53	40
3	1.0	$Cu(OAc)_2.H_2O$ (2.1)	DCE	0.3	32	55
4	1.0	$Cu(OAc)_2.H_2O$ (2.1)	CH_3CN	48	5	---
5	2.5	$Cu(OAc)_2.H_2O$ (2.1)	CH_3CN	8.0	32	---
6	***5.0***	***$Cu(OAc)_2.H_2O$ (2.1)***	***CH_3CN***	***3.0***	***85***	***---***
7	1.0	PivOH (1.0)	*t*-AmOH	3.5	20	56
8	2.5	PivOH (1.0)	*t*-AmOH	0.4	0	94
9	***2.5***	***PivOH (5.0)***	***t-AmOH***	***0.3***	***0***	***98***

III. Synthetic procedures and analytical data of compounds 2, 3

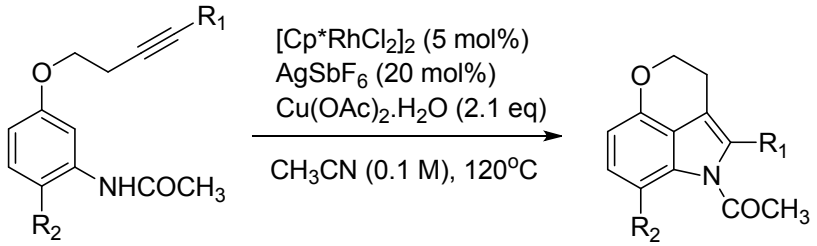
Synthesis of 3, 4-fused tricyclic indole 2 by conditions A



1 **2**

General procedure for the synthesis of 2 (taking 2a as an example): To a 1 dram screw-cap vial mixture of **1a** (R^1 = 4-CH_3OPh, R^2 = H, 62.0 mg, 0.200 mmol, 1.0 eq), $[Cp^*RhCl_2]_2$ (1.2 mg, 0.002 mmol, 1.0 mol%) and $Cu(OAc)_2.H_2O$ (84.0 mg, 0.420 mmol, 2.1 eq) in *t*-AmOH (2 mL, 0.1 M), then the reaction mixture was added $AgSbF_6$ (2.8 mg, 0.008 mmol, 4.0 mol%) in glove-box. The reaction mixture was sealed and placed in a pre-heated (120 °C) block until the substrate **1a** was consumed as indicated by TLC. Then the reaction is cooled to room temperature, the solvent was removed and the residue was purified by flash chromatography on silica gel (petroleum ether /EtOAc = 10:1) to give **2a** (53.0 mg, 87%) as a white solid.

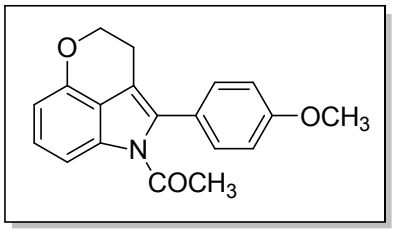
Synthesis of 3, 4-fused tricyclic indole 2 by conditions B



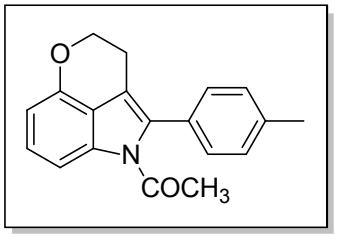
1 **2**

General procedure for the synthesis of 2 (taking 2d as an example): To a 1 dram screw-cap vial mixture of **1d** (R^1 = 4-ClPh, R^2 = H, 63.0 mg, 0.200 mmol, 1.0 eq), $[Cp^*RhCl_2]_2$ (6.0 mg, 0.010 mmol, 5.0 mol%) and $Cu(OAc)_2.H_2O$ (84.0 mg, 0.420 mmol, 2.1 eq) in CH_3CN (2 mL, 0.1 M) , then the reaction mixture was added $AgSbF_6$ (14.0 mg, 0.040 mmol, 20.0 mol%) in glove-box. The reaction mixture was sealed and placed in a pre-heated (120 °C) block until the substrate **1d** was consumed as indicated by TLC. Then the reaction is cooled to room temperature, the solvent was removed and the residue was purified by flash chromatography on silica gel (petroleum ether /EtOAc = 10:1) to give **2d** (53.0 mg, 85%) as a white solid.

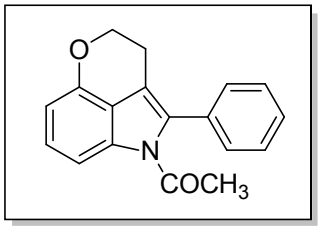
Analytical data of compounds 2



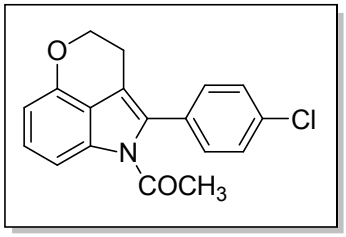
2a, 1-(4-(4-Methoxyphenyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 164–166 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.11(s, 3H), 2.89 (t, *J* = 5.5 Hz, 2H), 3.86 (s, 3H), 4.34 (t, *J* = 5.5 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.0, 27.2, 55.3, 67.7, 107.8, 109.4, 114.2, 114.3, 118.5, 125.1, 126.6, 130.6, 130.7, 136.5, 150.4, 159.6, 171.1. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 308.1281. Found 308.1285.



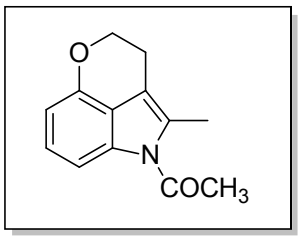
2b, 1-(4-(*p*-Tolyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 153–155 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12 (s, 3H), 2.42, (s, 3H), 2.91 (t, *J* = 5.5 Hz, 2H). 4.35 (t, *J* = 5.5 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.5 Hz, 1H), 7.26−7.28 (m, 4H), 7.74 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 23.0, 27.4, 67.7, 107.8, 109.3, 114.6, 118.5, 126.8, 129.1, 129.5, 129.9, 130.9, 136.6, 138.2, 150.5, 171.2. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 292.1332. Found 292.1331.



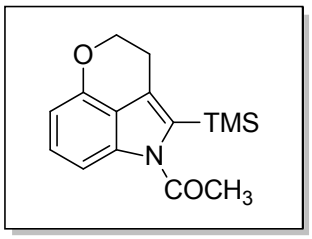
2c, 1-(4-(4-Methoxyphenyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 142–144 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12 (s, 3H), 2.93 (t, *J* = 6.0 Hz, 2H), 4.35 (t, *J* = 6.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 7.23−7.26 (m, 1H), 7.39−7.42 (m, 3H), 7.46−7.49 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.0, 27.3, 67.7, 107.8, 109.3, 115.0, 118.5, 126.9, 128.2, 128.7, 129.2, 130.8, 133.0, 136.6, 150.6, 171.0. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 300.0995. Found 300.0993.



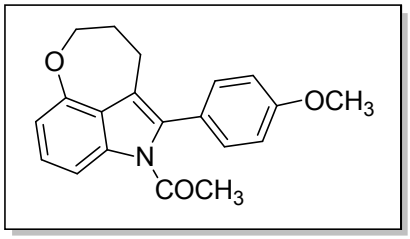
2d, 1-(4-(4-Chlorophenyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 153–155 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.21 (s, 3H), 2.91 (t, *J* = 6.0 Hz, 2H), 4.35 (t, *J* = 6.0 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.0, 27.4, 67.6, 107.9, 109.1, 115.6, 118.4, 127.2, 129.0, 129.7, 130.4, 131.5 134.2, 136.6, 150.7, 170.6. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 312.0786. Found 312.0785.



2e, 1-(4-Methyl-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 123–125 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.55 (s, 3H), 2.73 (s, 3H), 2.91 (t, *J* = 5.5 Hz, 2H), 4.36 (t, *J* = 5.5 Hz, 2H), 6.69 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.0, 22.3, 27.1, 67.6, 107.3, 108.0, 111.8, 119.1, 125.0, 129.5, 135.2, 150.1, 170.5.

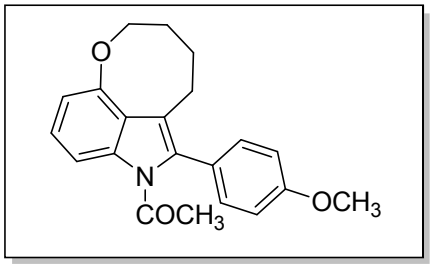


2f, 1-(4-(Trimethylsilyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. Yellow oli. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 3.13 (t, *J* = 5.5 Hz, 2H), 4.35 (t, *J* = 5.5 Hz, 2H), 6.67 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 1.93, 25.6, 25.9, 67.7, 106.8, 107.0, 121.5, 125.3, 126.6, 133.1, 136.7, 151.4, 169.3. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 274.1258. Found 274.1238.

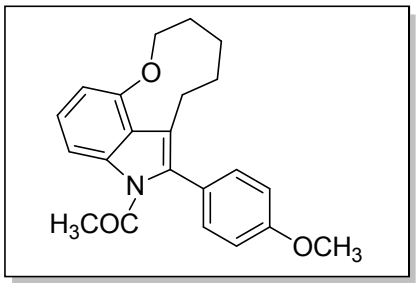


2g, 1-(5-(4-Methoxyphenyl)-3,4-dihydrooxepino[4,3,2-*cd*]indol-6(2*H*)-yl)ethanone. White solid. m.p. 166–168 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.97 (s, 3H), 2.09−2.14 (m, 2H), 2.71 (t, *J* = 6.0

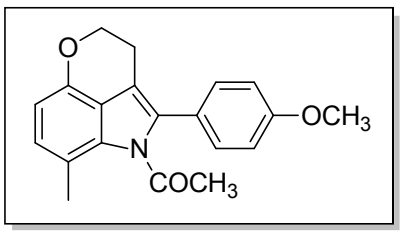
Hz, 2H), 3.88 (s, 3H), 4.34 (dd, *J* = 6.5, 4.5 Hz, 2H), 6.83 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.00–7.02 (m, 2H), 7.21–7.26 (m, 1H), 7.28–7.30 (m, 2H), 8.08 (dd, *J* = 8.0, 0.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.3, 27.8, 29.5, 55.3, 72.6, 108.9, 111.7, 114.3, 118.2, 120.1, 125.8, 125.9, 131.4, 132.6, 138.8, 152.4, 159.7, 171.1. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 322.1438. Found 322.1427.



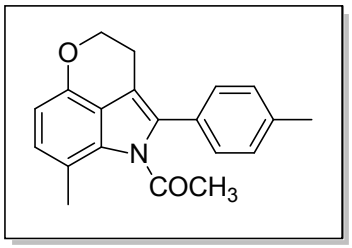
2h, 1-(6-(4-Methoxyphenyl)-4,5-dihydro-2H-oxocino[4,3,2-*cd*]indol-7(3*H*)-yl)ethanone. White solid. m.p. 120–122 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.69 (d, *J* = 5.5 Hz, 2H), 1.79 (d, *J* = 6.0 Hz, 2H), 1.97 (s, 3H), 2.82 (t, *J* = 6.5 Hz, 2H), 3.88 (s, 3H), 4.23 (s, 2H), 6.93 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.00 (d, *J* = 3.5 Hz, 2H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 2.5 Hz, 1H), 8.18 (dd, *J* = 8.0, 0.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.2, 27.6, 27.7, 29.7, 55.3, 75.5, 112.6, 114.1, 116.4, 121.1, 125.2, 126.0, 126.2, 131.6, 133.8, 137.5, 150.9, 159.8, 171.2. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 336.1594. Found 336.1593.



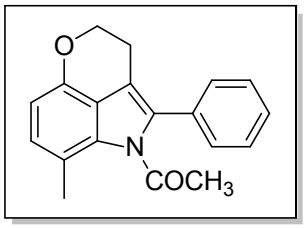
2i, 1-(7-(4-Methoxyphenyl)-3,4,5,6-tetrahydrooxonino[4,3,2-*cd*]indol-8(2*H*)-yl)ethanone. White solid. m.p. 104–106 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.58 (d, *J* = 5.5 Hz, 4H), 1.78 (s, 2H), 1.94 (s, 3H), 2.85 (s, 2H), 3.88 (s, 3H), 4.24 (t, *J* = 5.5 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 7.25–7.30 (m, 4H), 8.16 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.3, 24.7, 27.7, 33.3, 55.3, 79.1, 111.9, 114.1, 116.1, 122.4, 124.8, 125.6, 125.9, 131.6, 134.4, 137.5, 155.6, 159.7, 171.3. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 350.1751. Found 350.1755.



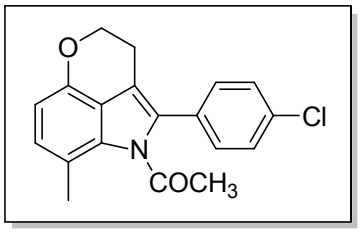
2j, 1-(4-(4-Methoxyphenyl)-6-methyl-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 128–130 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.43 (s, 3H), 2.90 (t, *J* = 5.0 Hz, 2H), 3.86 (s, 3H), 4.31 (t, *J* = 5.0 Hz, 2H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 23.0, 28.4, 55.3, 67.5, 107.1, 112.7, 114.2, 117.8, 119.2, 125.0, 128.7, 130.4, 130.7, 135.0, 148.7, 159.5, 172.2. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 322.1438. Found 322.1430.



2k, 1-(6-Methyl-4-(p-tolyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 132–134 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.41 (s, 3H), 2.44 (s, 3H), 2.90 (t, *J* = 5.5 Hz, 2H), 4.30 (t, *J* = 5.5 Hz, 2H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 7.23−7.27 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 21.3, 23.1, 28.5, 67.5, 107.1, 113.0, 117.8, 119.2, 128.8, 128.9, 129.5, 129.8, 130.9, 135.1, 138.1, 148.8, 172.2. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 306.1489. Found 306.1495.

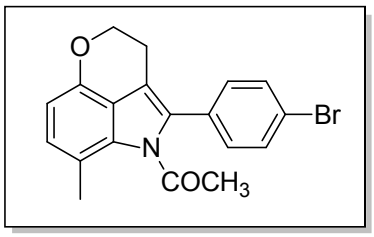


2l, 1-(6-Methyl-4-phenyl-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 118–120 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.08 (s, 3H), 2.45 (s, 3H), 2.92 (s, 2H), 4.31 (s, 2H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 6.5 Hz, 3H), 7.45 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 23.1, 28.5, 67.5, 107.1, 113.4, 117.8, 119.1, 128.1, 128.8, 128.9, 129.0, 130.8, 132.8, 135.2, 148.9, 172.1. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 292.1332. Found 292.1323.

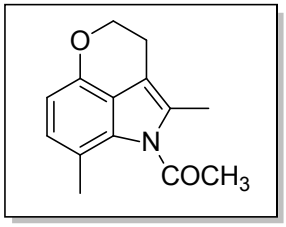


2m, 1-(4-(4-Chlorophenyl)-6-methyl-2*H*-pyrano[4,3,2-*cd*]indol-5(3H)-yl)ethanone. White solid. m.p. 173–175 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12 (s, 3H), 2.44 (s, 3H), 2.91 (s, 2H), 4.32 (s, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 23.1, 28.6, 67.4, 107.3, 114.0, 117.9, 119.1, 129.1,

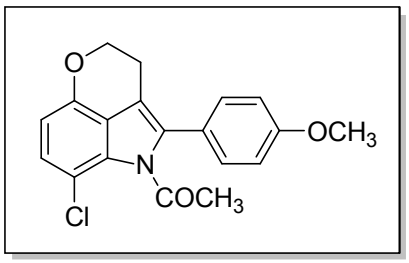
129.3, 129.5, 130.2, 131.2, 134.2, 135.3, 148.9, 171.8. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 326.0942. Found 326.0939.



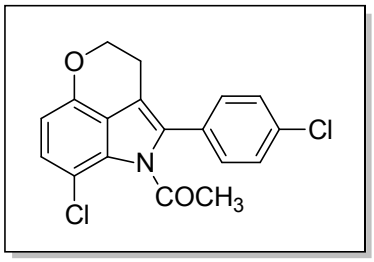
2n, 1-(4-(4-Bromophenyl)-6-methyl-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 127–129 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ2.12 (s, 3H), 2.44 (s, 3H), 2.90 (t, J = 5.5 Hz, 2H), 4.31 (t, J = 6.0 Hz, 2H), 6.64 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 23.1, 28.6, 67.4, 107.3, 114.1, 117.9, 119.1, 122.3, 129.4, 129.6, 130.1, 131.7, 132.0, 135.4, 148.9, 171.8. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 370.0437. Found 370.0424.



2o, 1-(4,6-Dimethyl-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 94–96 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.36 (s, 3H), 2.45 (s. 3H), 2.61 (s, 3H), 2.89 (t, J = 5.0 Hz, 2H), 4.33 (t, J = 5.5 Hz, 2H), 6.61 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.8, 20.7, 22.6, 27.4, 67.6, 107.2, 110.8, 117.3, 119.7, 127.4, 127.8, 135.1, 148.2, 171.3. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 230.1176. Found 230.1187.

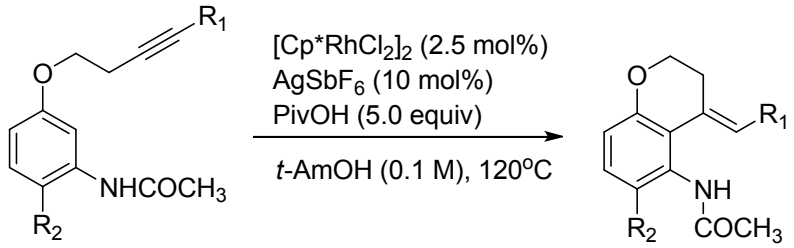


2p, 1-(6-Chloro-4-(4-methoxyphenyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 137–139 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.25 (s, 3H), 2.92 (t, J = 5.5 Hz, 2H), 3.86 (s, 3H), 4.34 (t, J = 5.5 Hz, 2H), 6.63 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.8, 28.8, 55.3, 67.9, 107.7, 110.8, 111.2, 114.1, 121.0, 123.6, 126.9, 130.7, 131.8, 131.9, 149.4, 159.7, 172.1. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 342.0891. Found 342.0887.



2q, 1-(6-Chloro-4-(4-chlorophenyl)-2*H*-pyrano[4,3,2-*cd*]indol-5(3*H*)-yl)ethanone. White solid. m.p. 136–138 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (s, 3H), 2.93 (t, *J* = 6.0 Hz, 2H), 4.35 (t, *J* = 6.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.8, 29.0, 67.8, 108.0, 110.8, 112.2, 120.9, 127.4, 128.9, 129.8, 130.6, 130.9, 132.0, 134.6, 149.7, 171.8. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 368.0216. Found 368.0210.

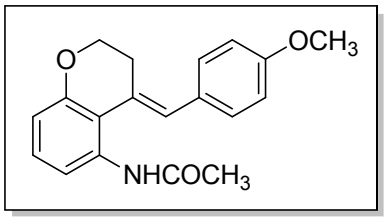
Synthesis of chromans 3 by condition C



1 **3**

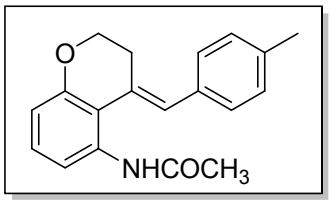
General procedure for the synthesis of 3 (taking 3d as an example): To a 1 dram screw-cap vial mixture of **1d** (R_1 = 4-ClPh, R_2 = H, 63.0 mg, 0.200 mmol, 1.0 eq), $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol, 2.5 mol%) and PivOH (102.0 mg, 1.000 mmol, 5.0 eq) in *t*-AmOH (2 mL, 0.1 M), then the reaction mixture was added $AgSbF_6$ (6.9 mg, 0.020 mmol, 10.0 mol%) in glove-box. The reaction mixture was sealed and placed in a pre-heated (120 ºC) block until the substrate **1d** was consumed as indicated by TLC. Then the reaction is cooled to room temperature , the solvent was removed and the residue was purified by flash chromatography on silica gel (petroleum ether /EtOAc = 10:1) to give **3d** (61.0 mg, 98%) as a white solid.

Analytical data of compounds 3

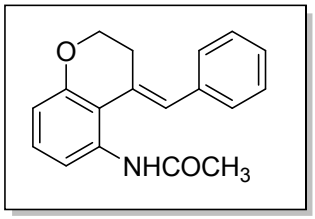


3a, (*E*)-N-(4-(4-methoxybenzylidene)chroman-5-yl)acetamide. White solid. m.p. 142–144 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.11 (s, 3H), 2.90 (t, *J* = 5.5 Hz, 2H), 3.84 (s, 3H), 4.19 (t, *J* = 6.0 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 3H), 7.14 (t, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 10.5

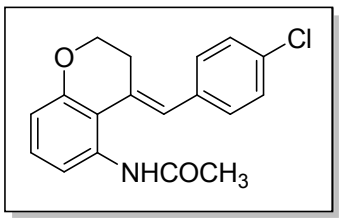
Hz, 2H), 7.61 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.8, 27.1, 55.3, 66.8, 113.1, 113.9, 115.1, 115.3, 127.4, 128.7, 128.8, 129.1, 130.3, 134.3, 155.0, 158.8, 168.2. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 310.1438. Found 310.1464.



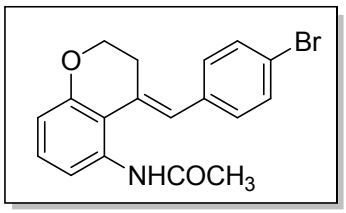
3b, (*E*)-N-(4-(4-methylbenzylidene)chroman-5-yl)acetamide. White solid. m.p. 96–98 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.37 (s, 3H), 2.89 (s, 2H), 4.17 (t, J = 5.0 Hz, 2H), 6.63 (d, J = 7.5 Hz, 1H), 6.95 (s, 1H), 7.12 (t, J = 8.0 Hz, 1H), 7.20 (s, 4H), 7.67 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 24.6, 27.0, 66.8, 113.2, 115.3, 127.6, 128.8, 128.9, 129.1, 129.9, 133.3, 137.1, 155.0, 168.2. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 294.1489. Found 294.1493.



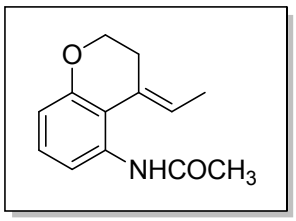
3c, (*E*)-N-(4-benzylidenechroman-5-yl)acetamide. White solid. m.p. 99–101 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.11 (s, 3H), 2.90 (t, J = 5.5 Hz, 2H), 4.20 (t, J = 6.0 Hz, 2H), 6.65 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 7.0 Hz, 3H), 7.40 (t, J = 8.0 Hz, 2H), 7.60 (s, 1H), 7.71 (d, J = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.6, 26.9, 66.8, 113.4, 115.6, 127.2, 127.6, 128.1, 128.4, 128.9, 130.6, 131.6, 134.2, 136.3, 155.1, 168.4. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 280.1332. Found 280.1335.



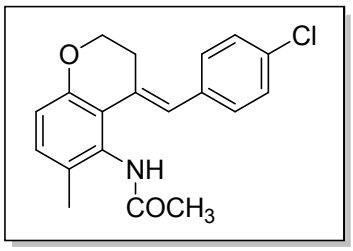
3d, (*E*)-N-(4-(4-chlorobenzylidene)chroman-5-yl)acetamide. White solid. m.p. 172–174 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.10 (s, 3H), 2.86 (t, J = 5.5 Hz, 2H), 4.19 (t, J = 6.0 Hz, 2H), 6.65 (d, J = 7.0 Hz, 1H), 6.93 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.53 (s, 1H), 7.65 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.6, 27.0, 66.7, 113.5, 115.2, 115.6, 126.3, 128.7, 129.2, 130.2, 131.4, 133.0, 134.3, 134.7, 155.2, 168.2. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 314.0942. Found 314.0951.



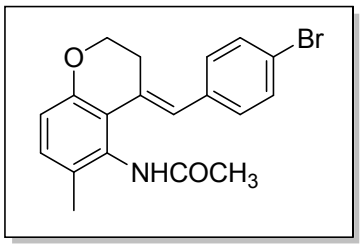
3e, (*E*)-N-(4-(4-bromobenzylidene)chroman-5-yl)acetamide. White solid. m.p. 167–169 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.84 (s, 2H), 4.17 (t, *J* = 5.0 Hz, 2H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.90 (s, 1H), 7.11–7.16 (m, 3H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.65 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.5, 27.0, 66.6, 113.5, 115.4, 115.9, 121.1, 126.3, 129.1, 130.5, 131.4, 131.5, 134.2, 135.1, 155.2, 168.3. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H] $^+$) 358.0437. Found 358.0443.



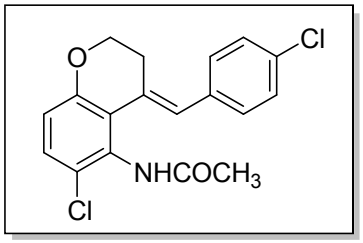
3f, (*E*)-N-(4-ethylidenechroman-5-yl)acetamide. White solid. m.p. 188–190 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.85 (d, *J* = 7.0 Hz, 3H), 2.15 (s, 3H), 2.64 (t, *J* = 6.0 Hz, 2H), 4.24 (t, *J* = 6.0 Hz, 2H), 6.01 (d, *J* = 6.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H, 7.52 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.6, 24.7, 26.3, 67.0, 113.0, 114.6, 115.4, 122.2, 128.1, 129.3, 134.1, 154.8, 168.0. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H] $^+$) 218.1176. Found 218.1203.



3g, (*E*)-N-(4-(4-chlorobenzylidene)-6-methylchroman-5-yl)acetamide. White solid. m.p. 135–137 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.92 (s, 3H), 2.07 (s, 3H), 2.73 (s, 2H), 4.13 (s, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.98 (s, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 9.42 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.3, 23.2, 27.2, 66.8, 115.5, 122.1, 125.4, 128.9, 129.0, 130.4, 131.0, 131.2, 131.8, 133.8, 136.4, 153.8, 168.8. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H] $^+$) 328.1099. Found 328.1106.

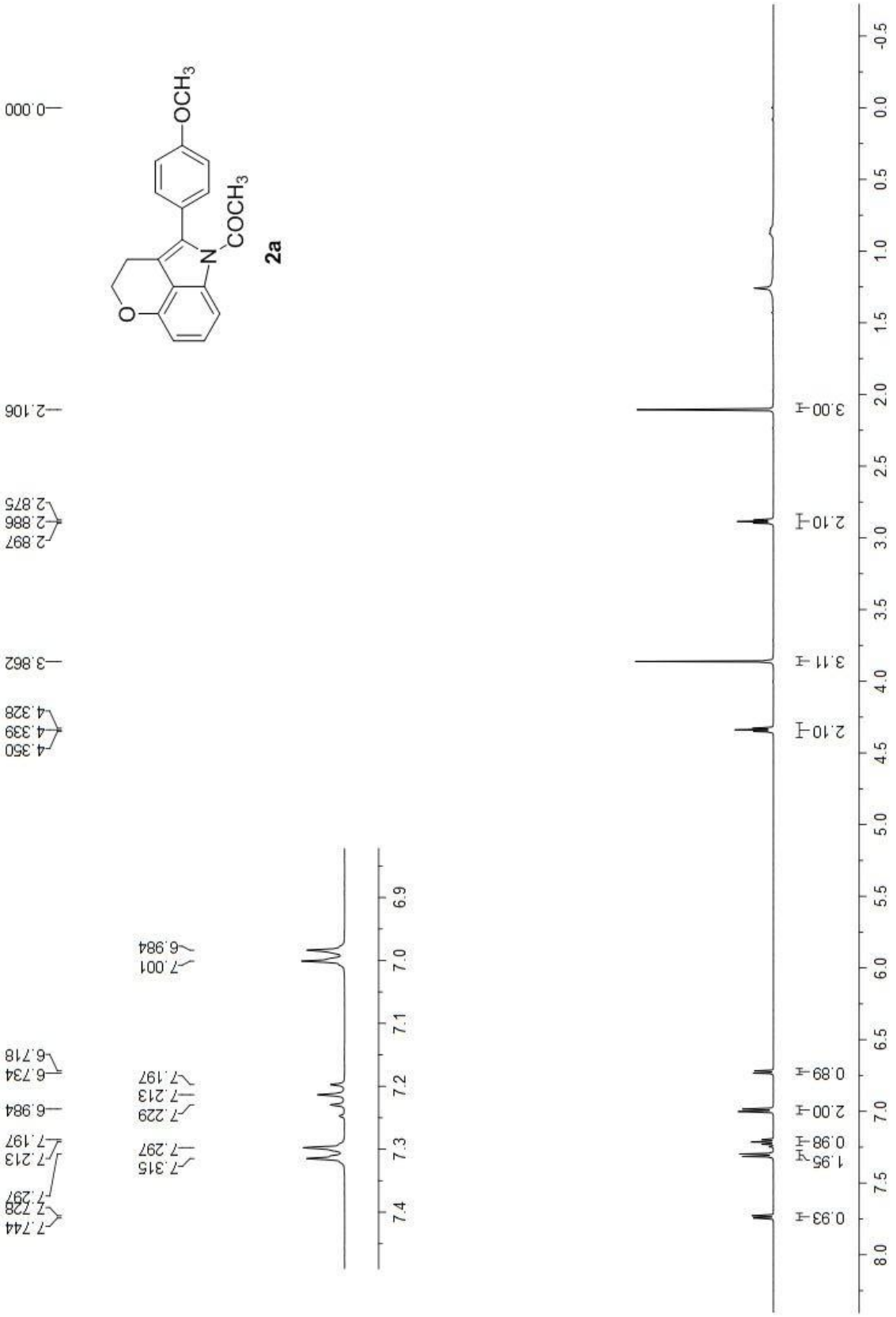


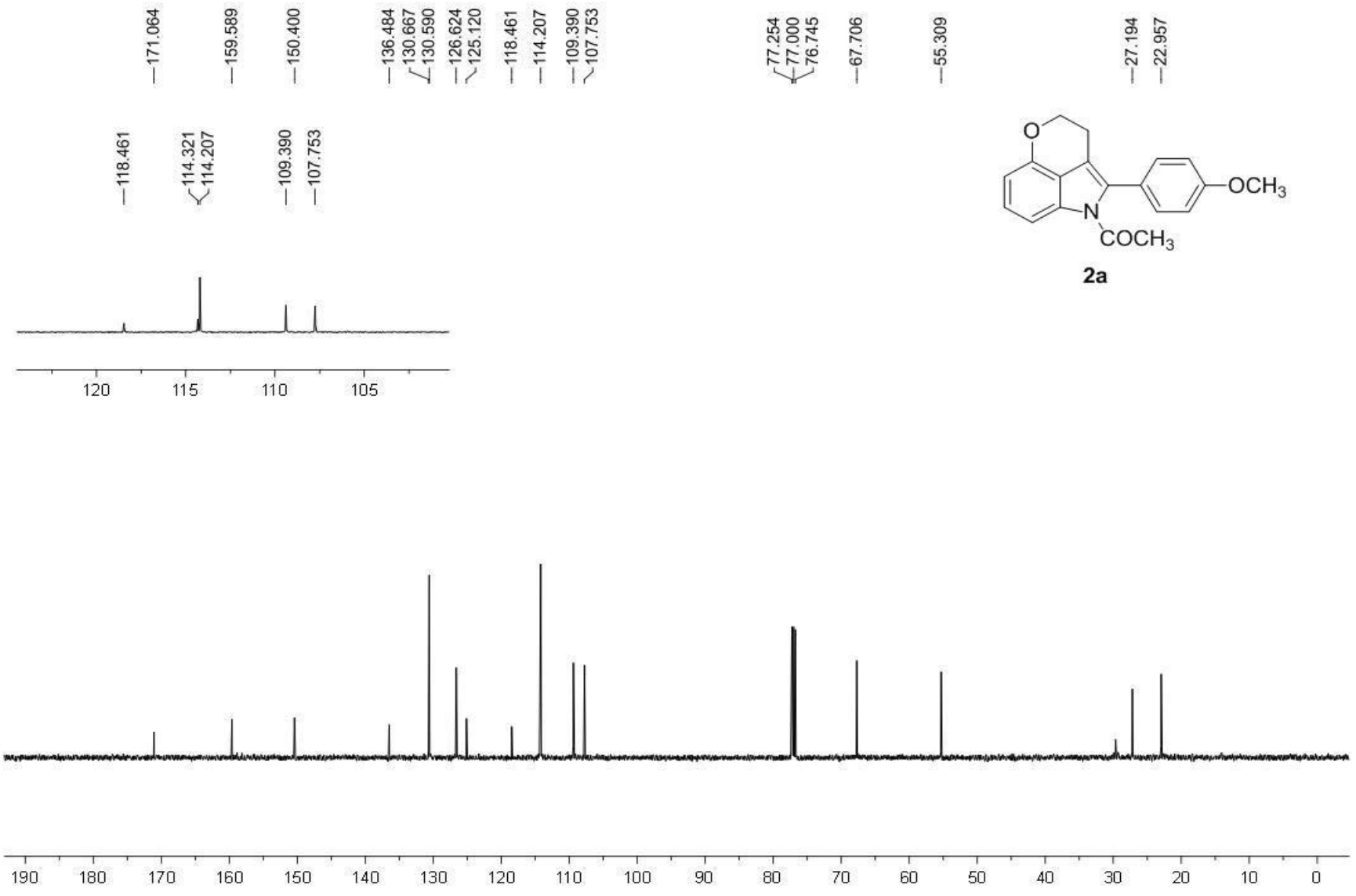
3h, (*E*)-N-(4-(4-bromobenzylidene)-6-methylchroman-5-yl)acetamide. White solid. m.p. 166–168 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.92 (s, 3H), 2.07 (s, 3H), 2.72 (t, *J* = 6.0 Hz, 2H), 4.12 (t, *J* = 5.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.91 (s, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 9.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.2, 23.2, 27.2, 66.8, 115.5, 120.4, 122.1, 125.4, 128.9, 130.4, 131.1, 131.5, 131.9, 133.8, 136.8, 153.7, 168.8. HRMS (ESI-TOF) Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 372.0594. Found 372.0603.



3i, (*E*)-N-(6-chloro-4-(4-chlorobenzylidene)chroman-5-yl)acetamide. White solid. m.p. 214–216 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.25 (s, 1H), 3.33 (s, 1H), 4.00 (s, 3H), 4.68 (d, *J* = 6.0 Hz, 1H), 4.77 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H), 7.86 (t, *J* = 8.5 Hz, 3H), 8.01 (d, *J* = 8.5 Hz, 2H), 10.27 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.1, 26.6, 67.1, 117.3, 124.2, 125.3, 126.5, 129.1, 129.3, 130.2, 131.2, 132.2, 132.6, 136.0, 154.4, 169.1. Calcd for $C_{26}H_{23}O_2S_4^+$ ([M+H]$^+$) 348.0553. Found 348.0556.

V. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 2, 3

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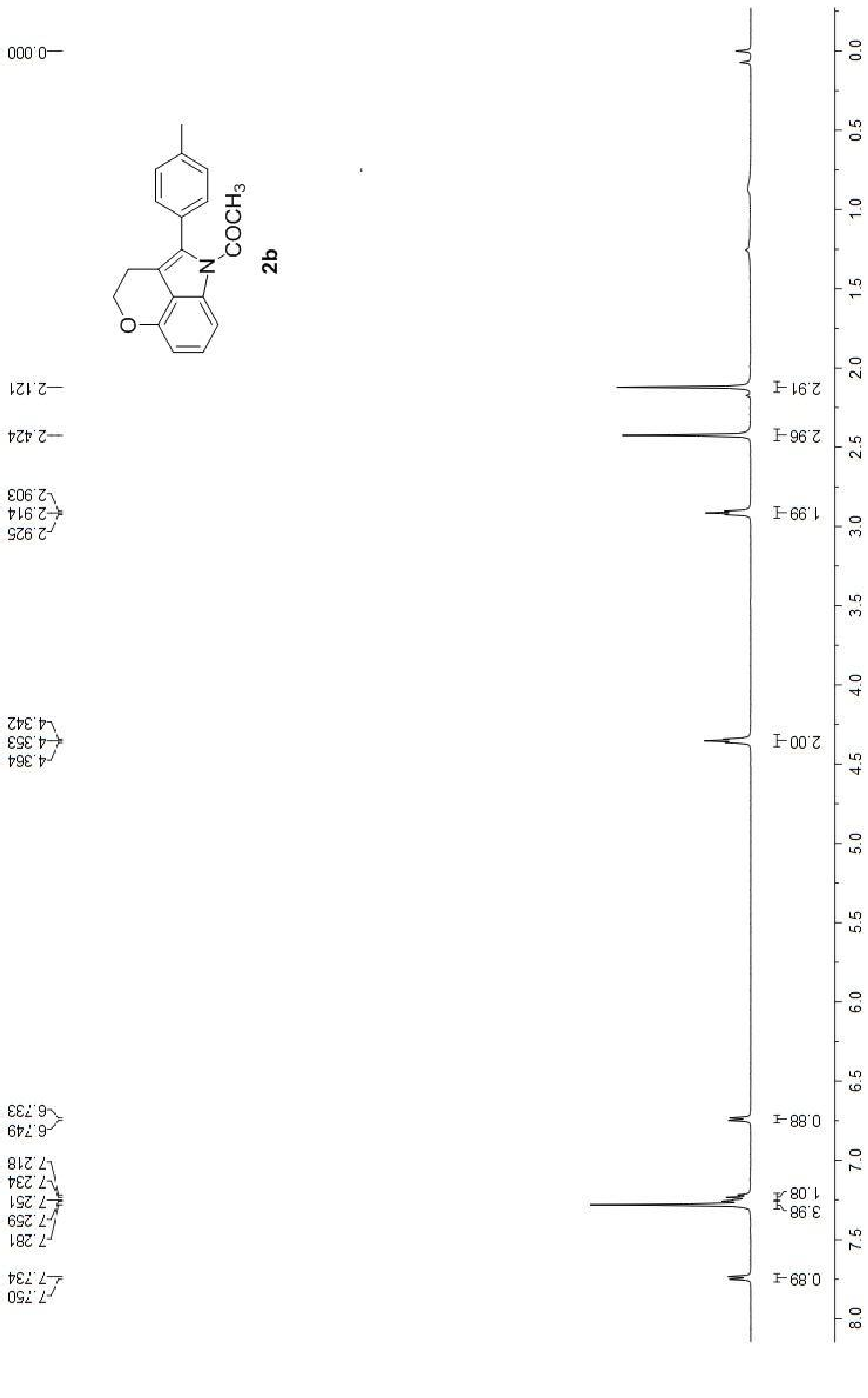

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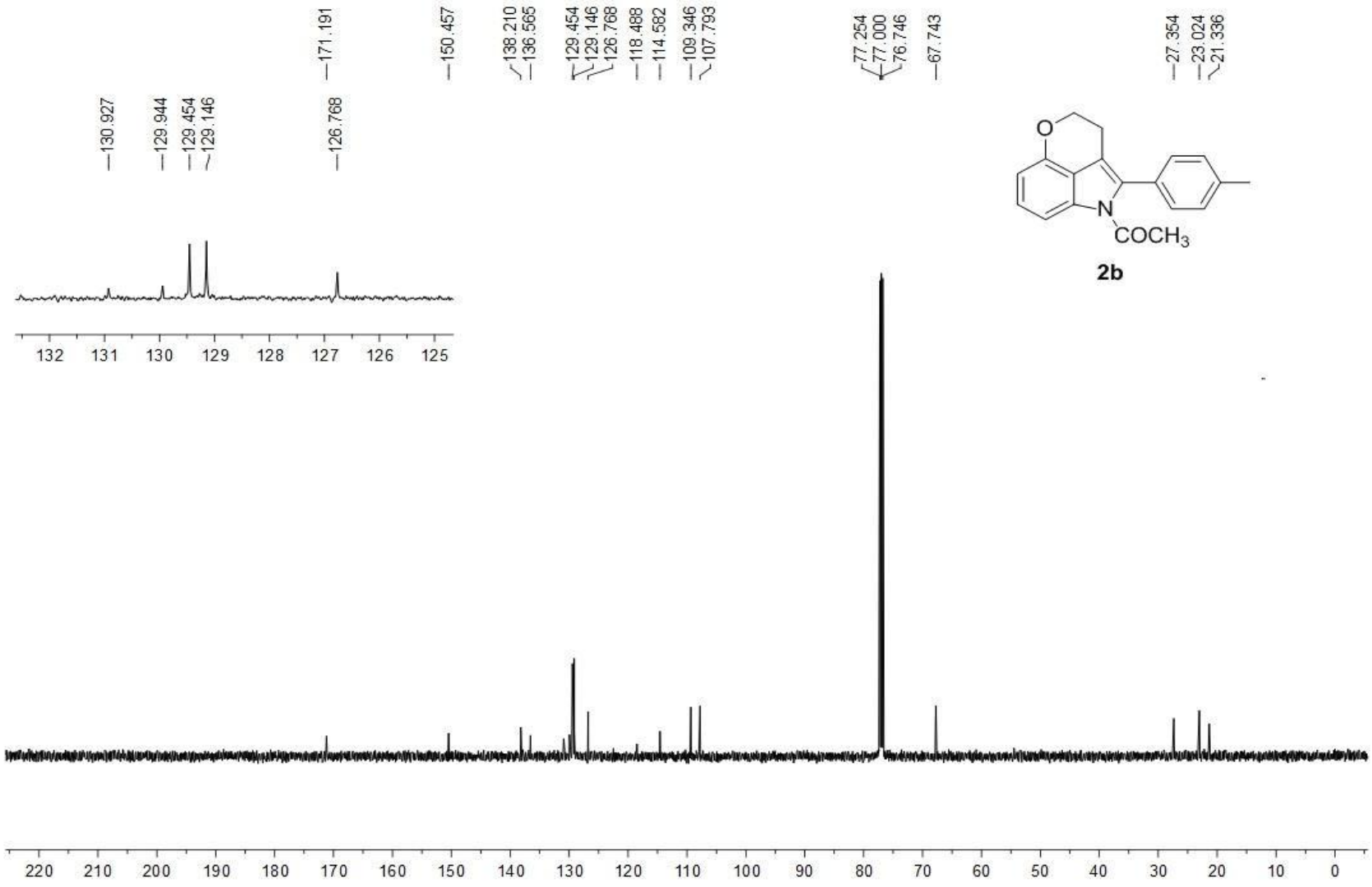
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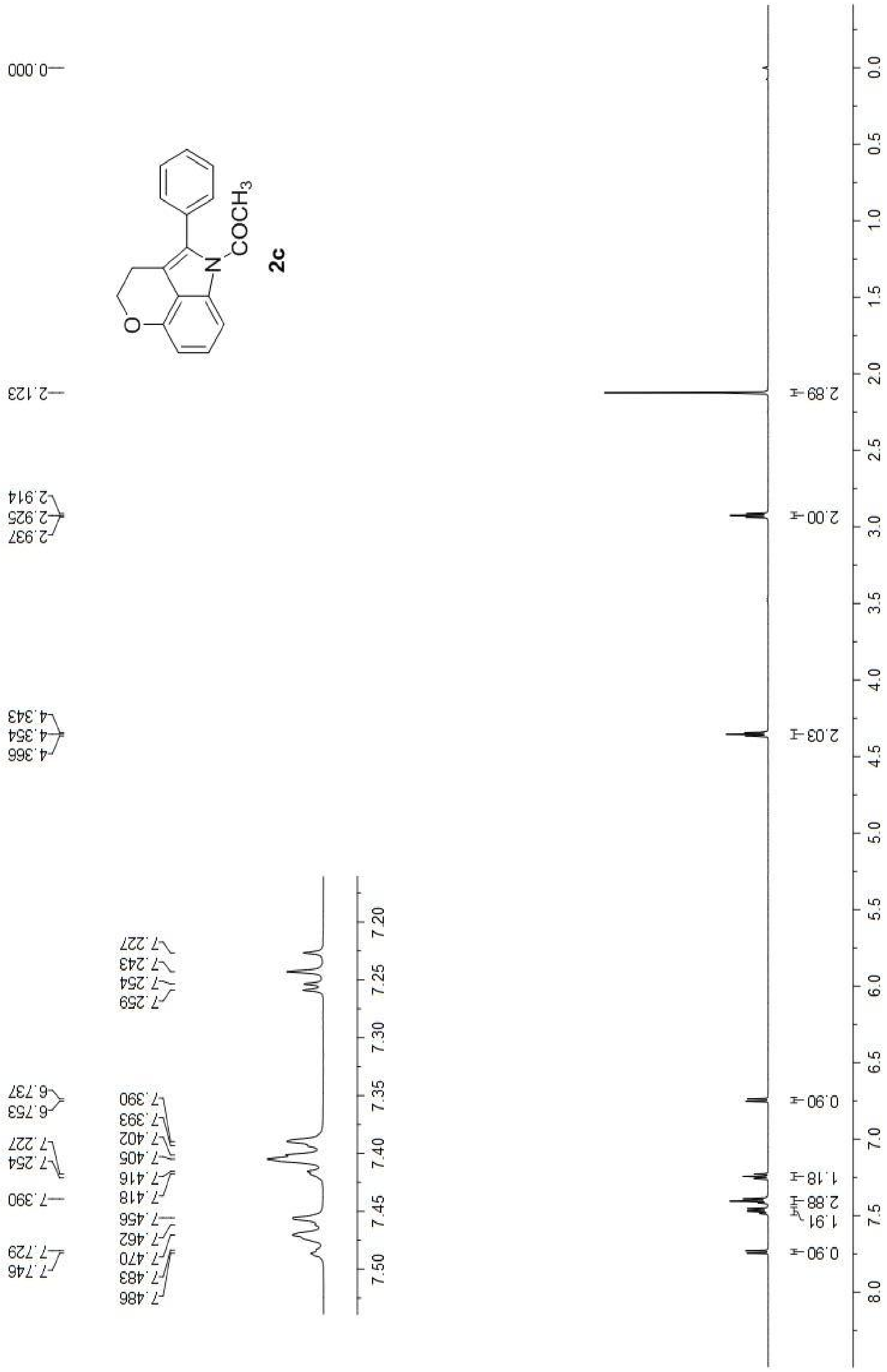
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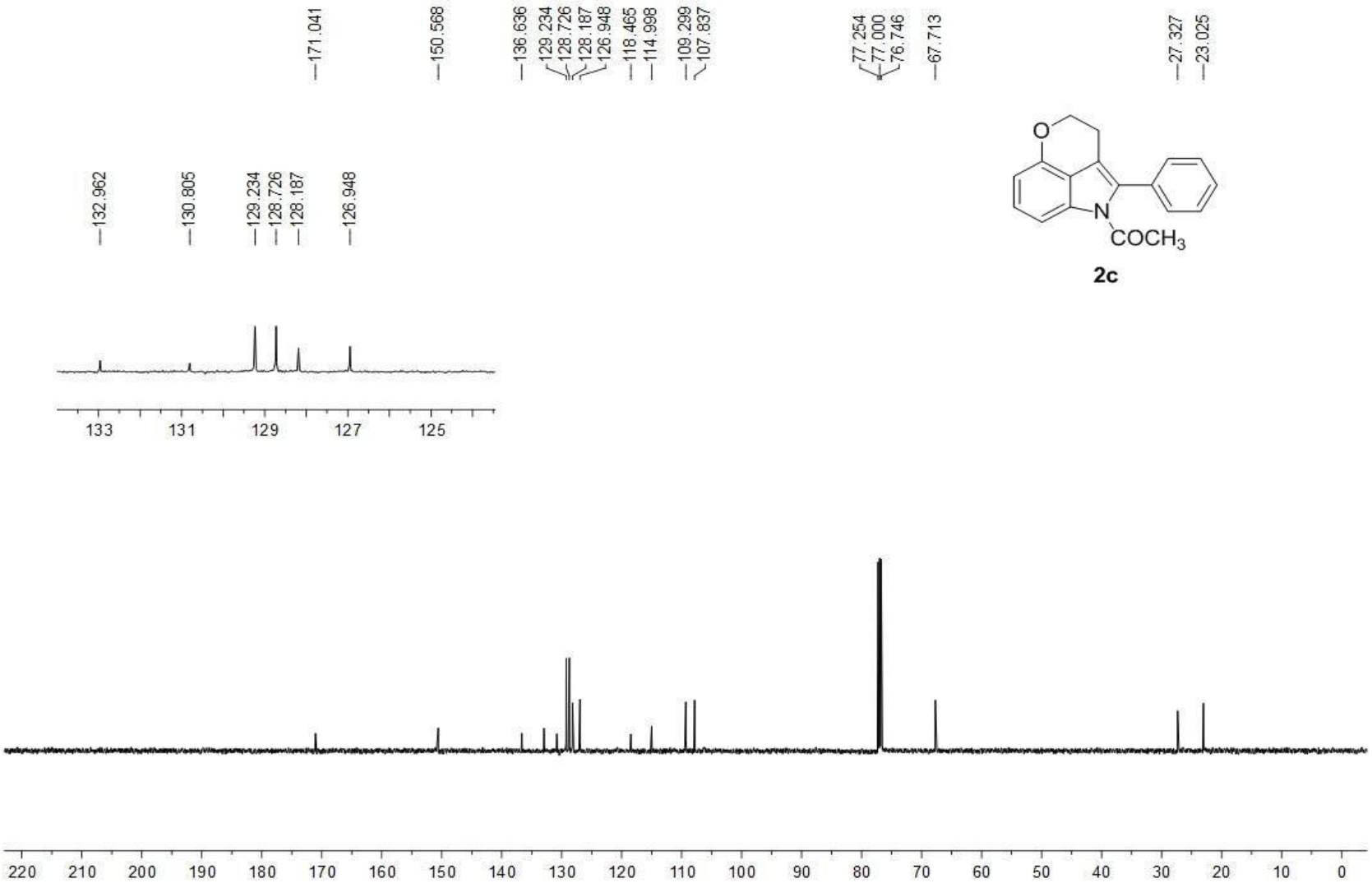
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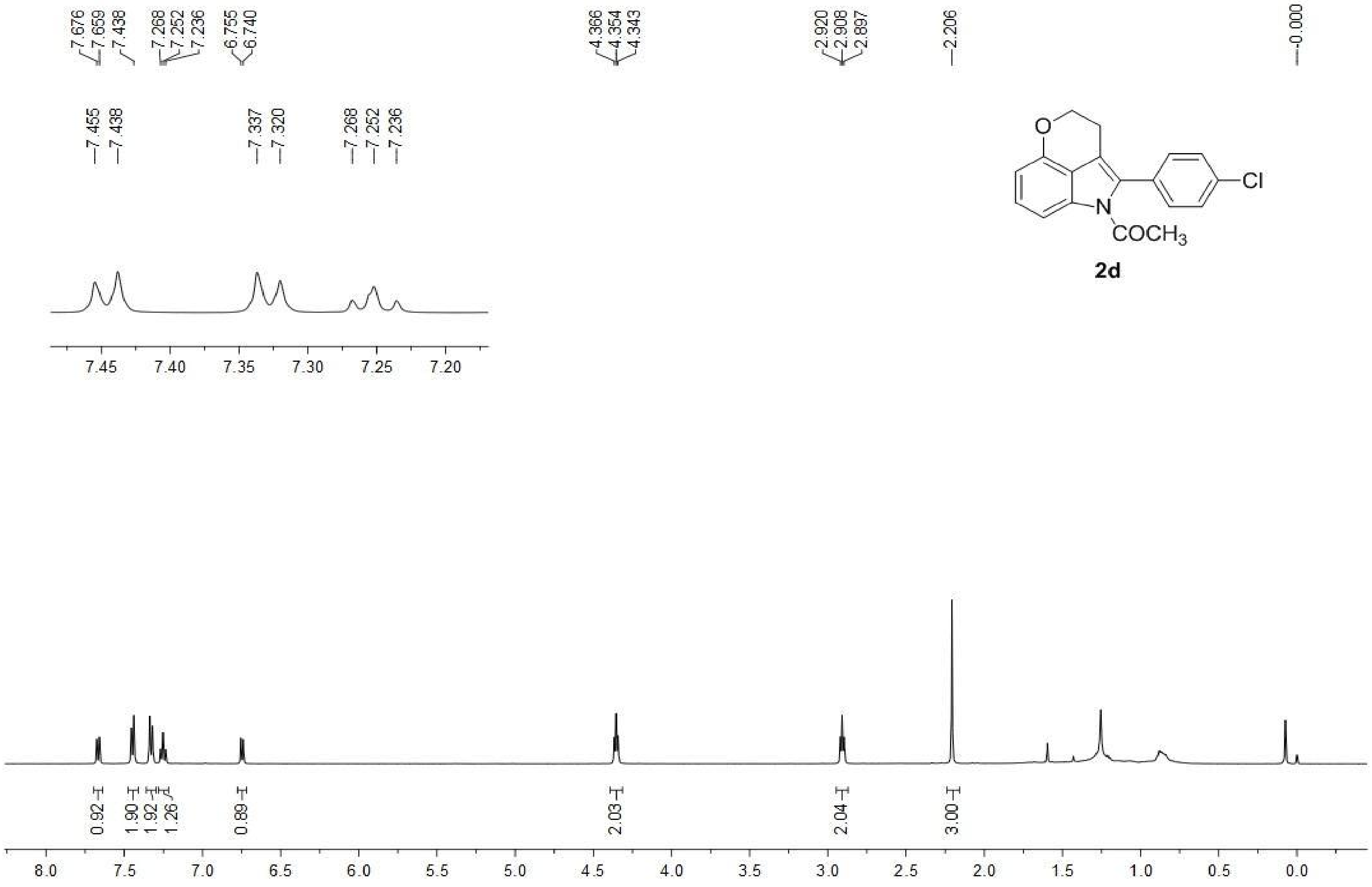
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7.236
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O
N
Cl
COCH3
2d
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1.92
1.26
0.89
2.03
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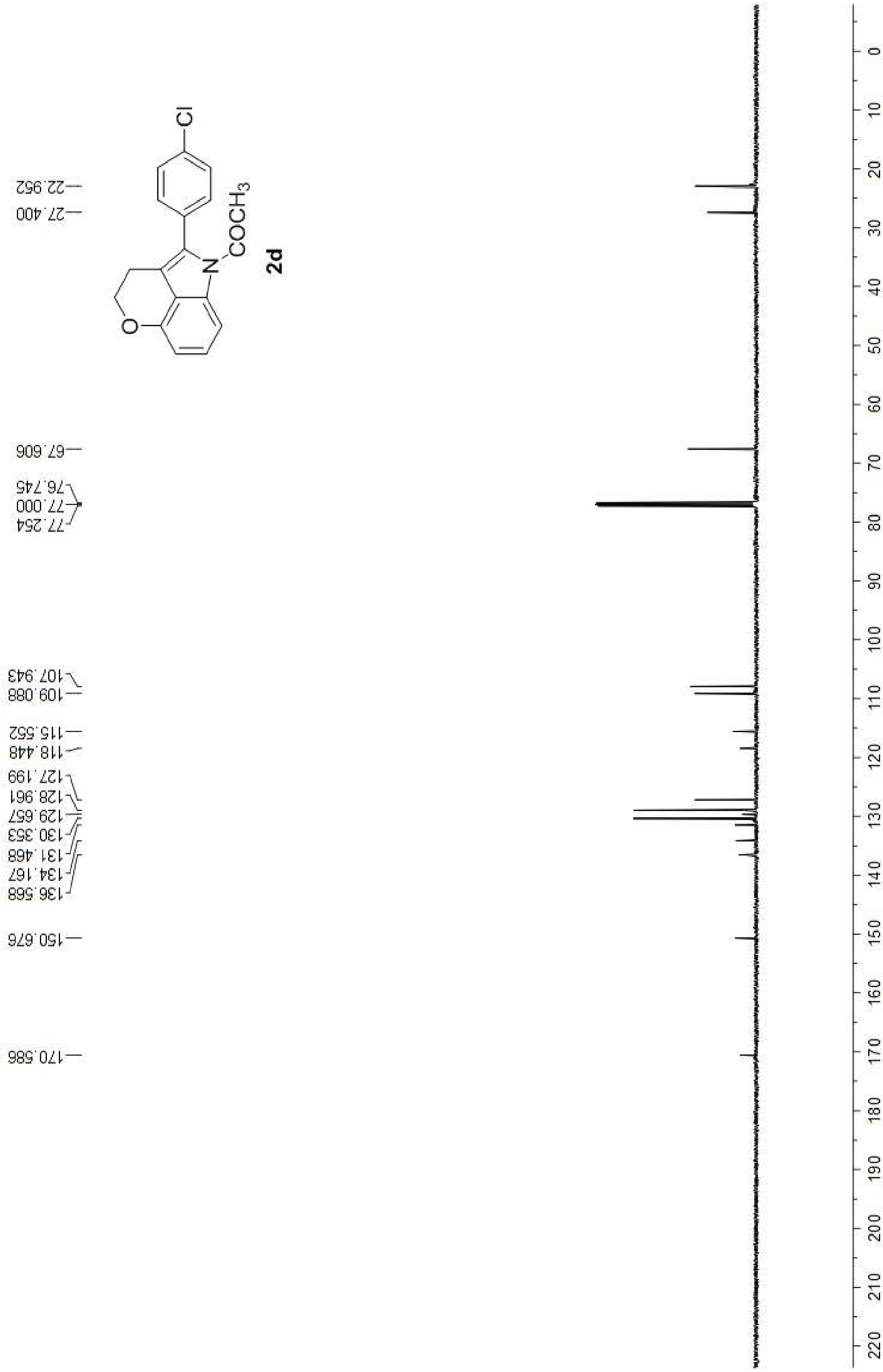
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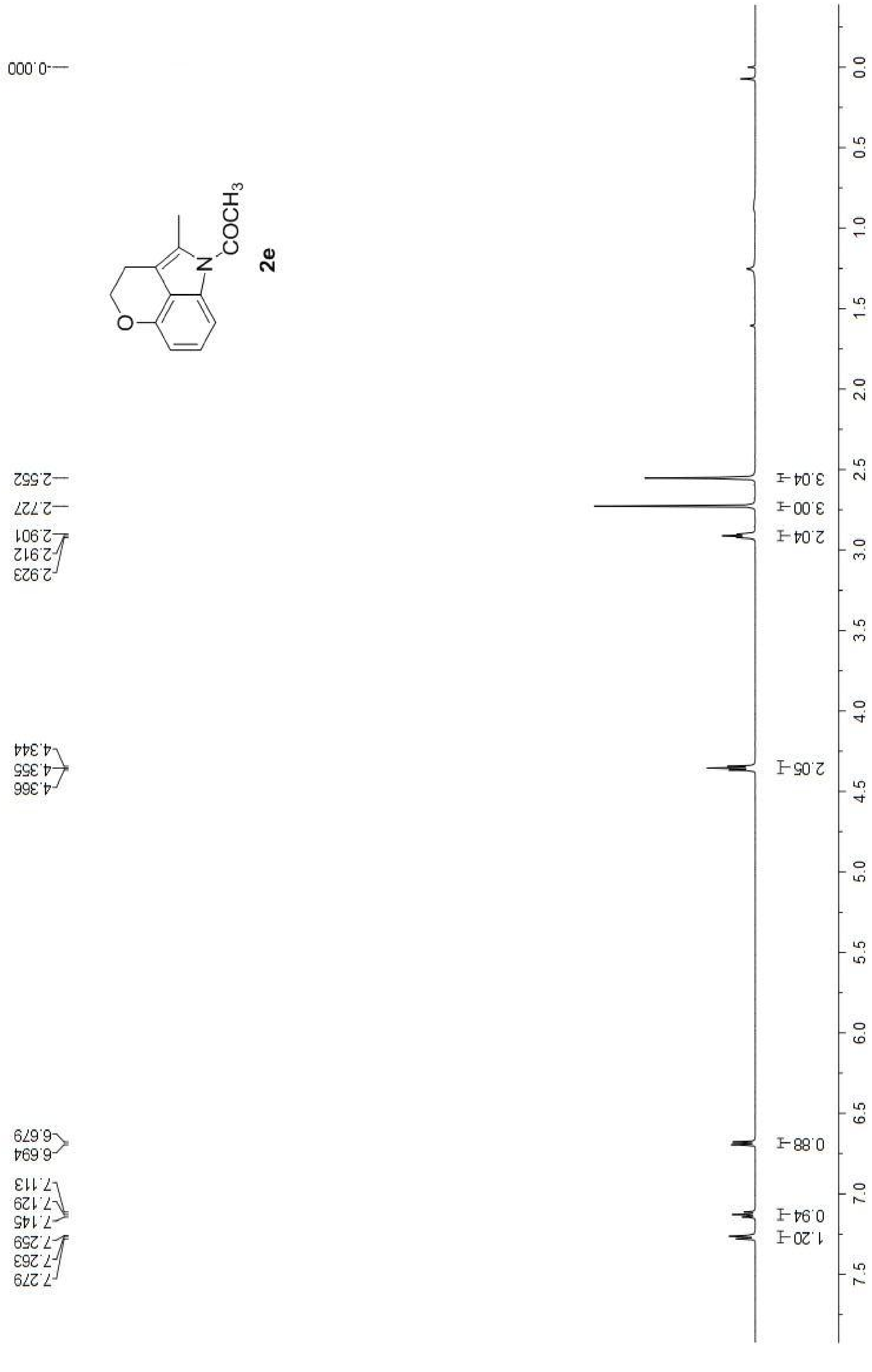

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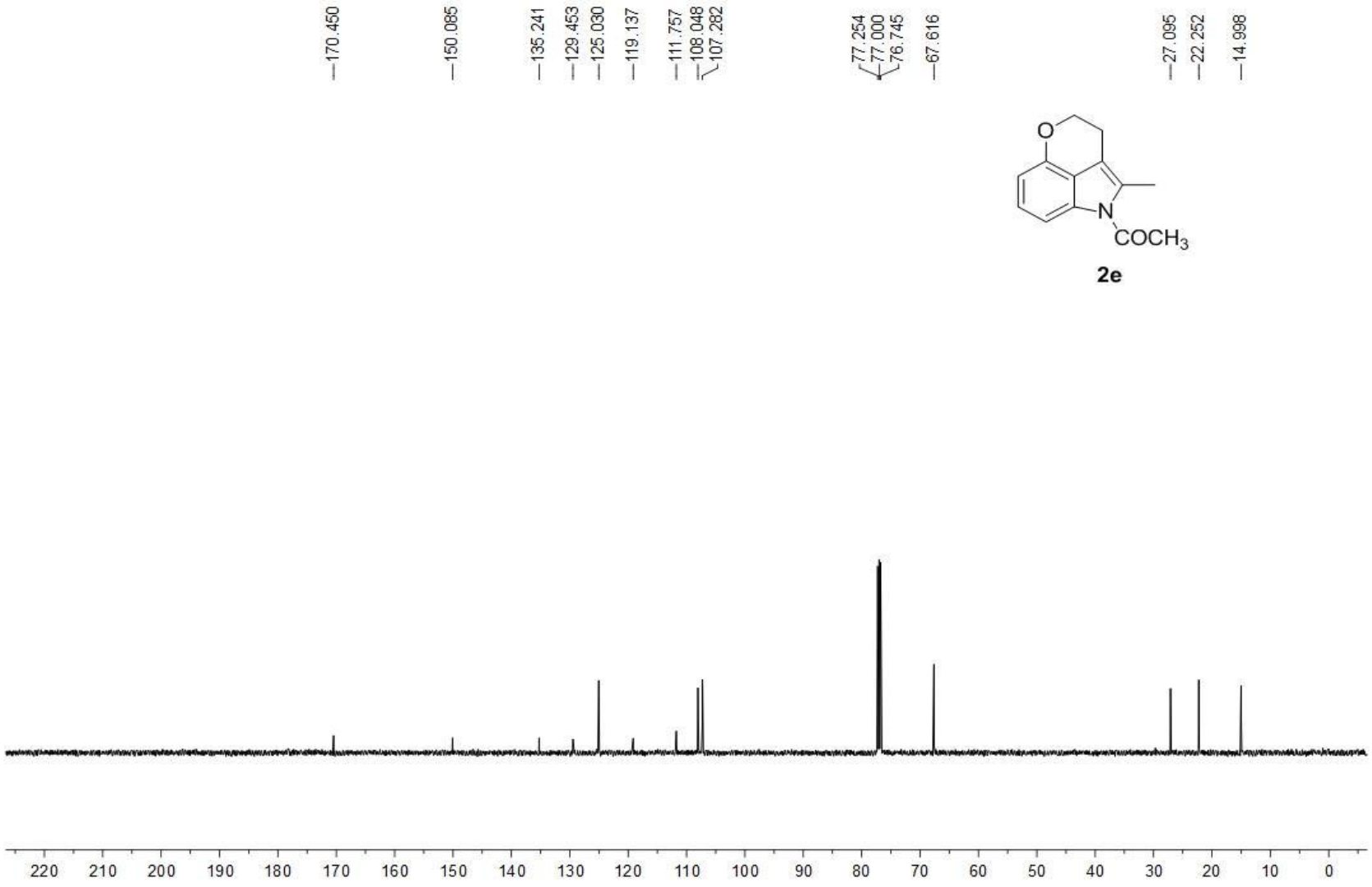
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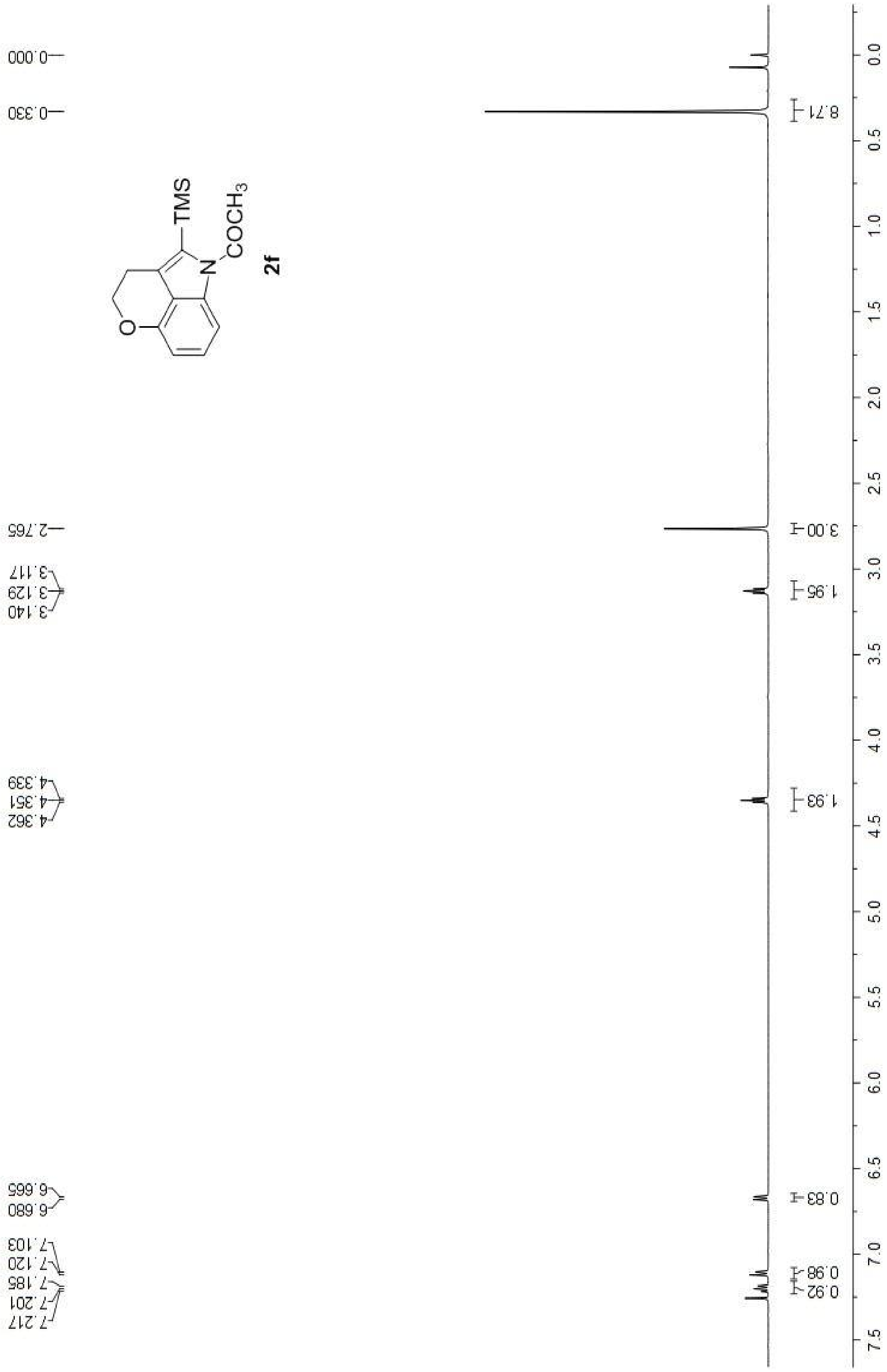

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0.98
0.92
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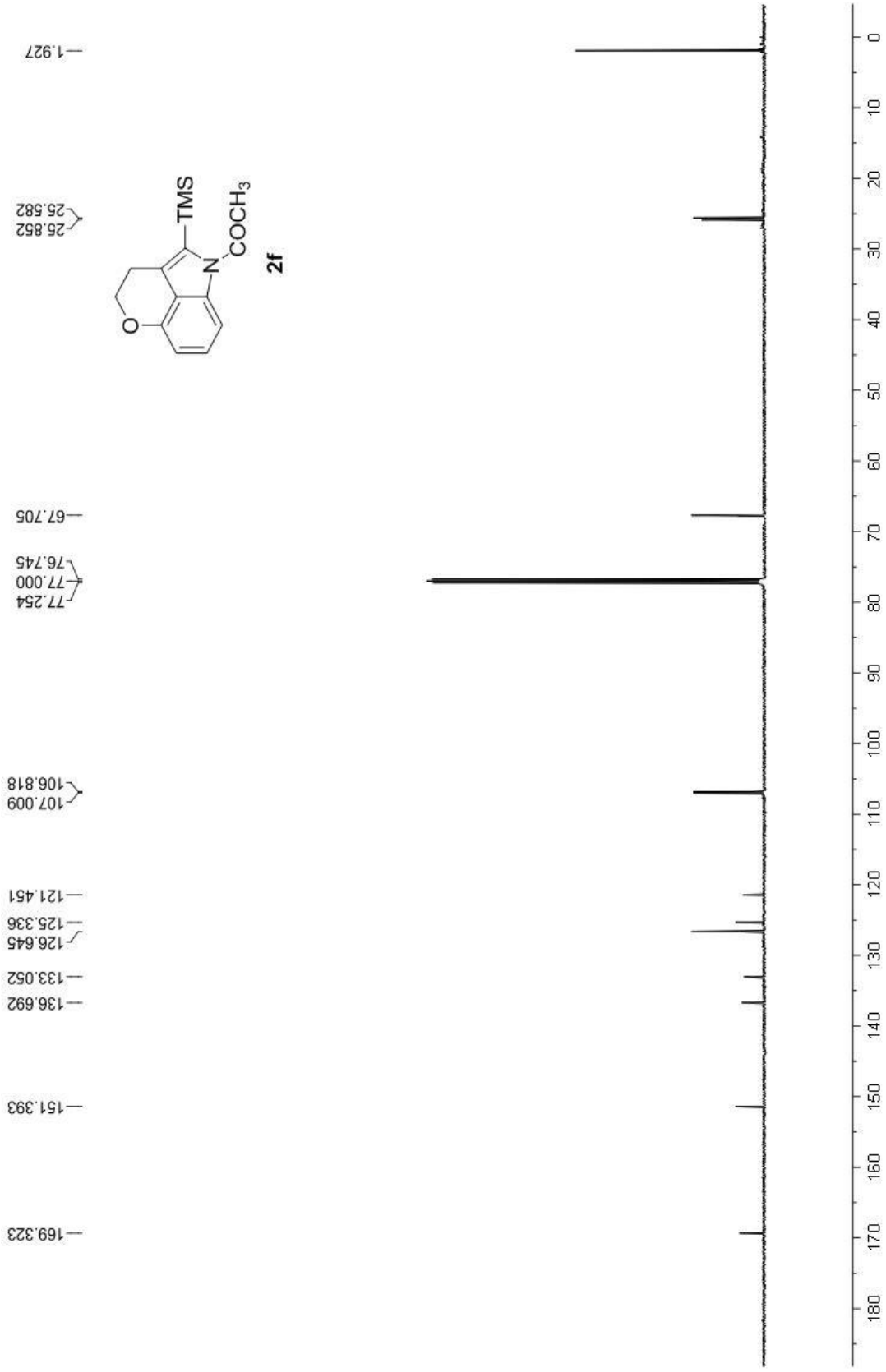
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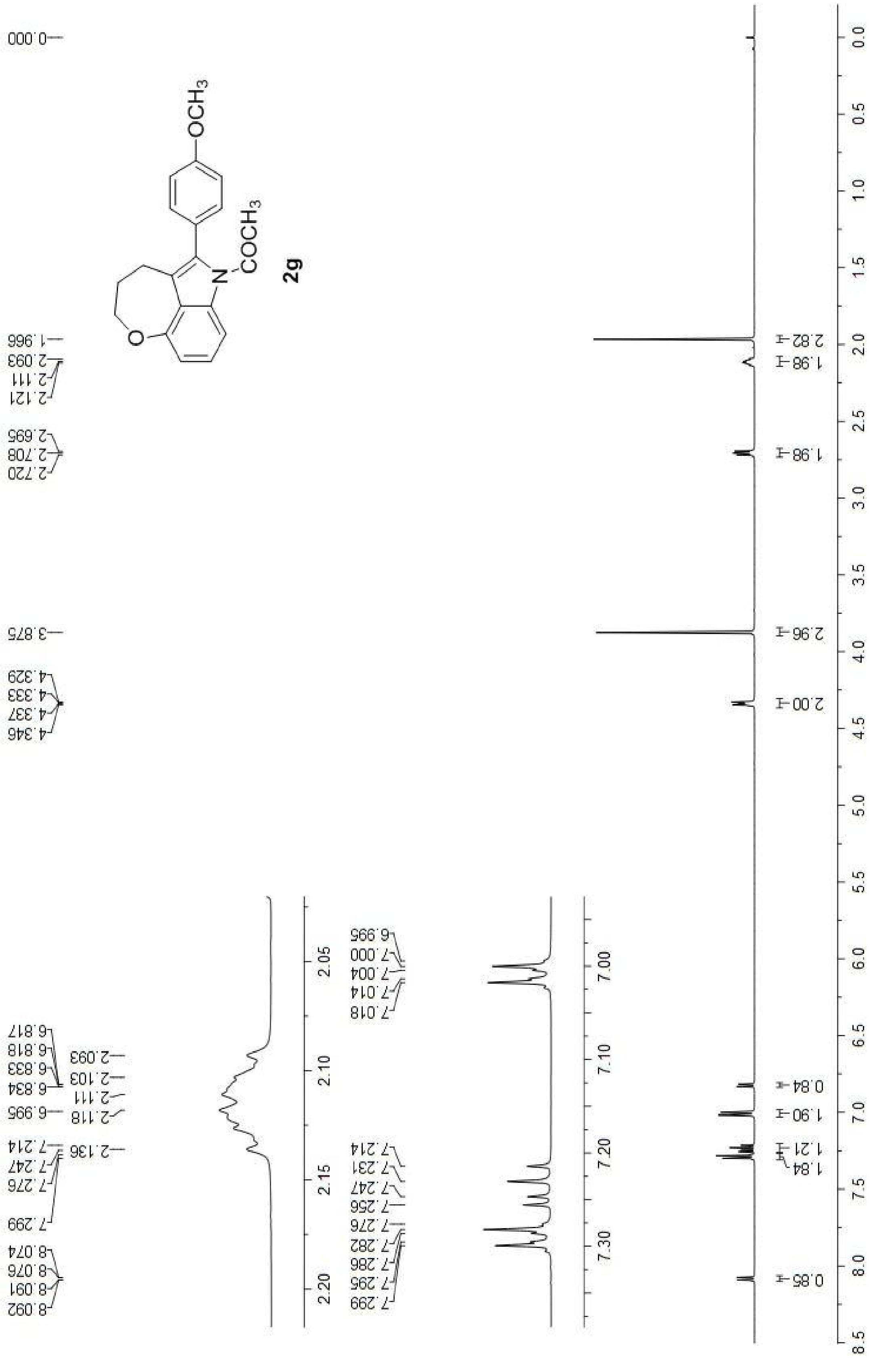
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6.818
6.833
6.834
6.995
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7.247
7.276
7.299
8.074
8.076
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8.092
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2.111
2.118
2.136
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7.004
7.014
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7.276
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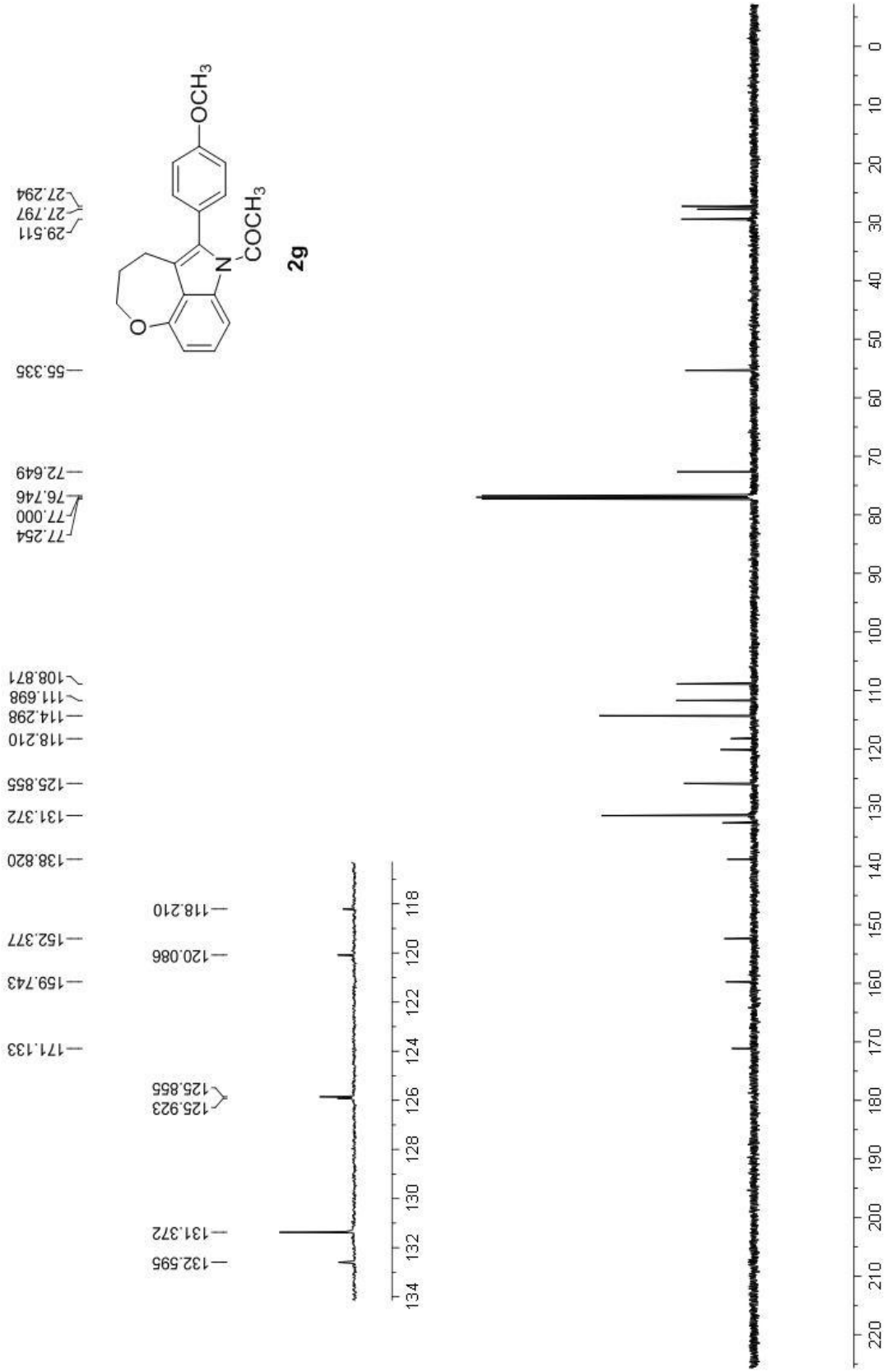
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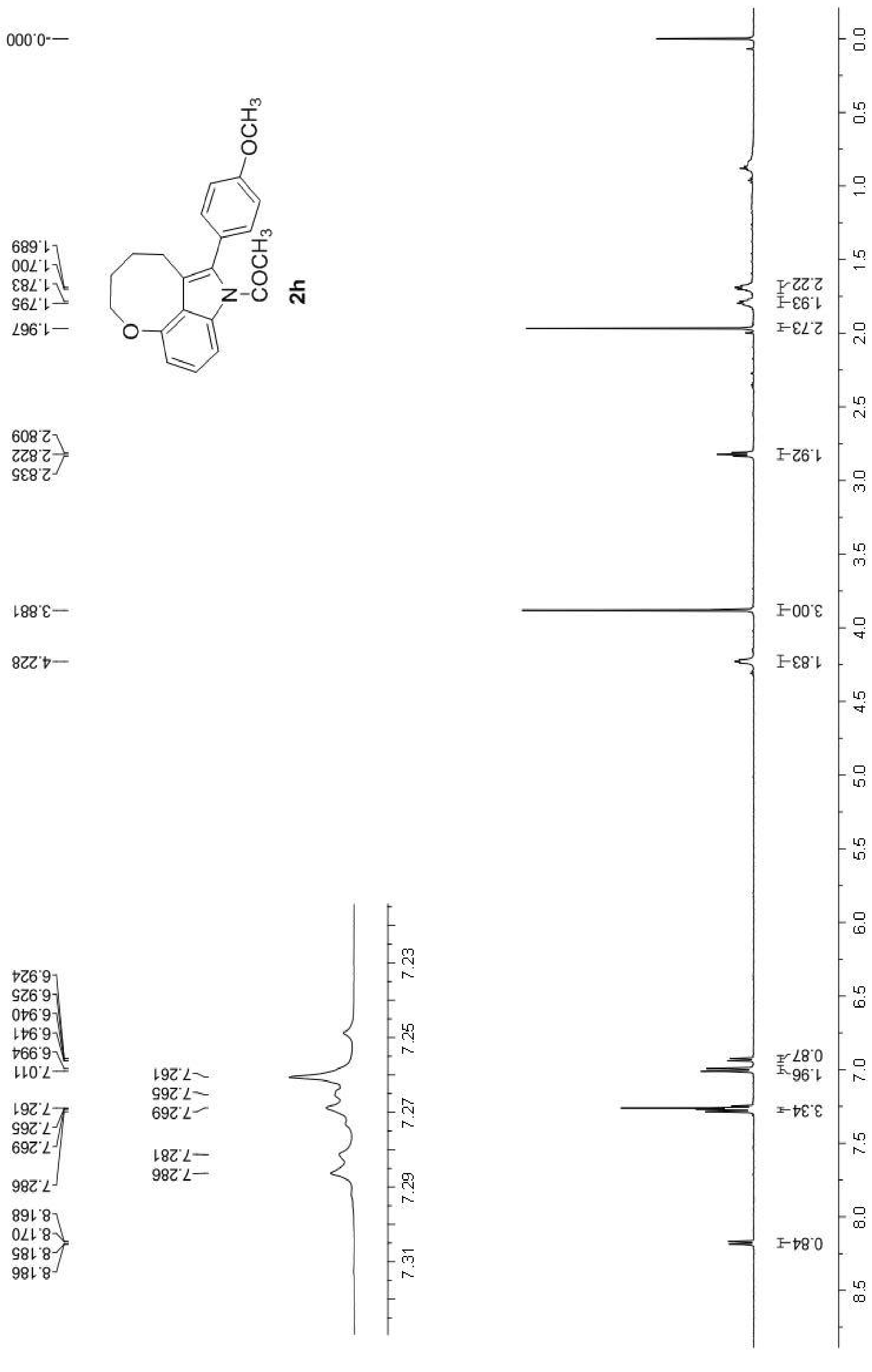
132.595



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6.925
6.940
6.941
6.994
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7.269
7.286
8.168
8.170
8.185
8.186
7.261
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7.269
7.281
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7.23
7.25
7.27
7.29
7.31
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COCH3
N
O
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1.92
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0.87
1.96
3.34
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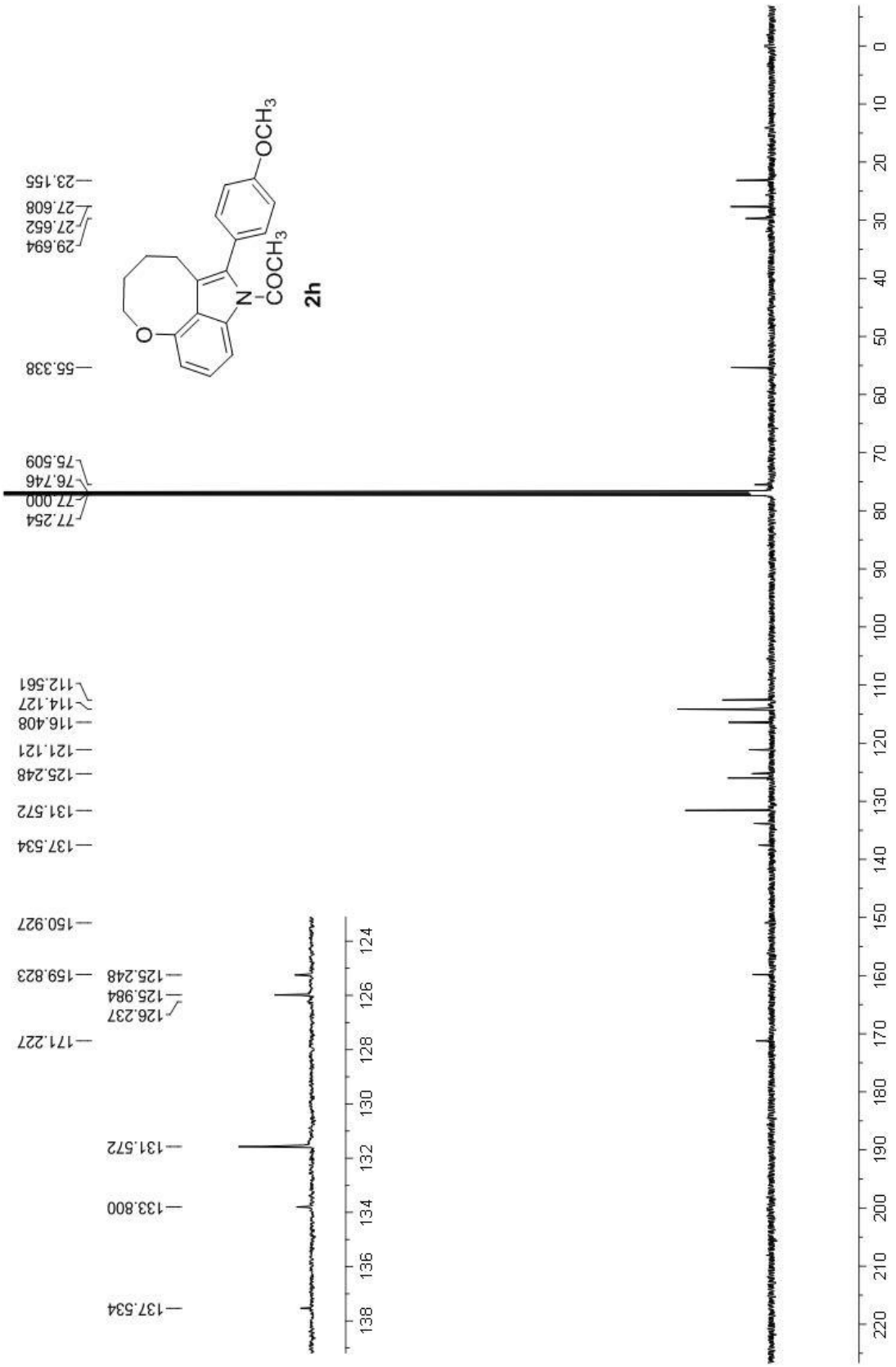
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77.254
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116.408
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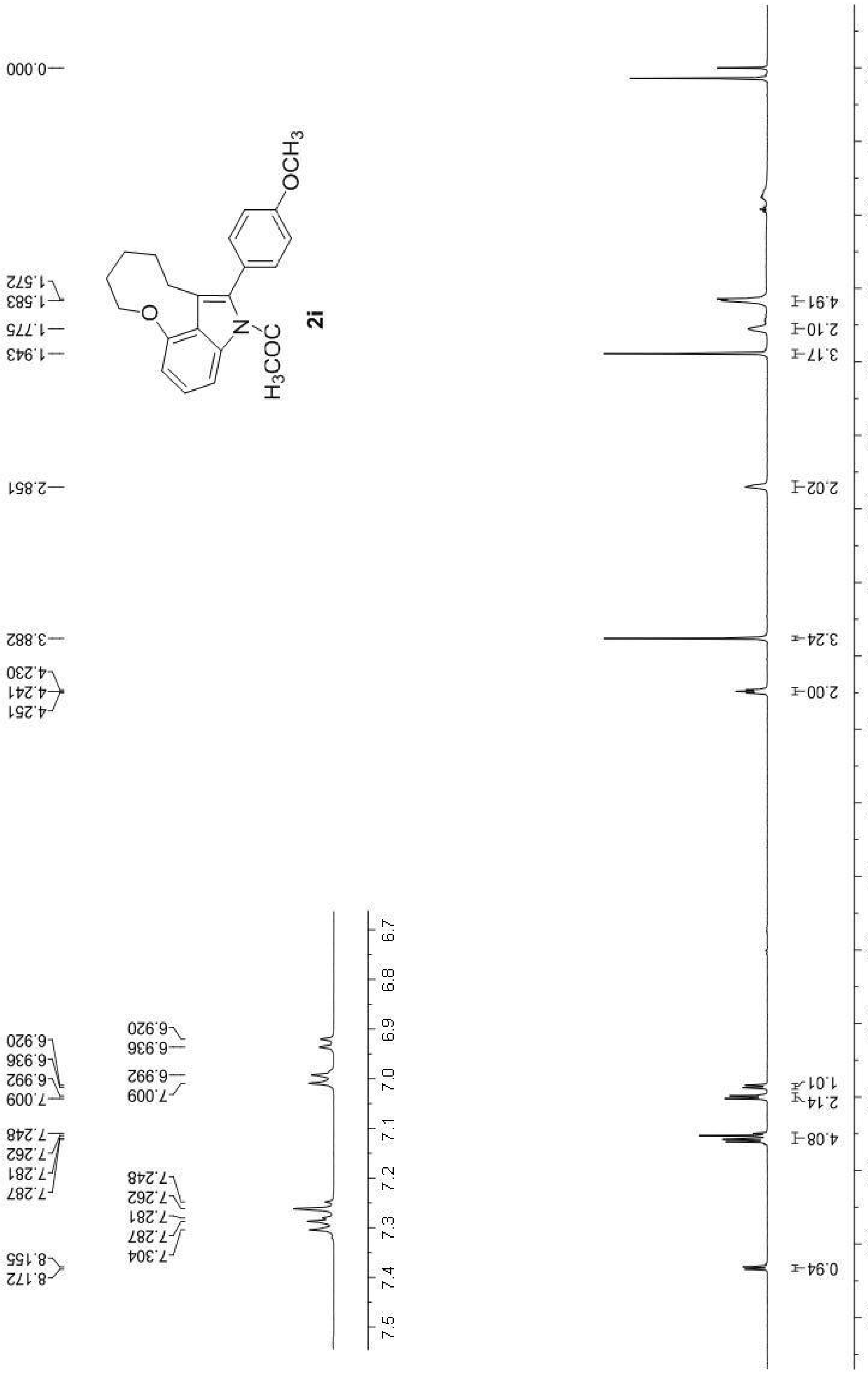

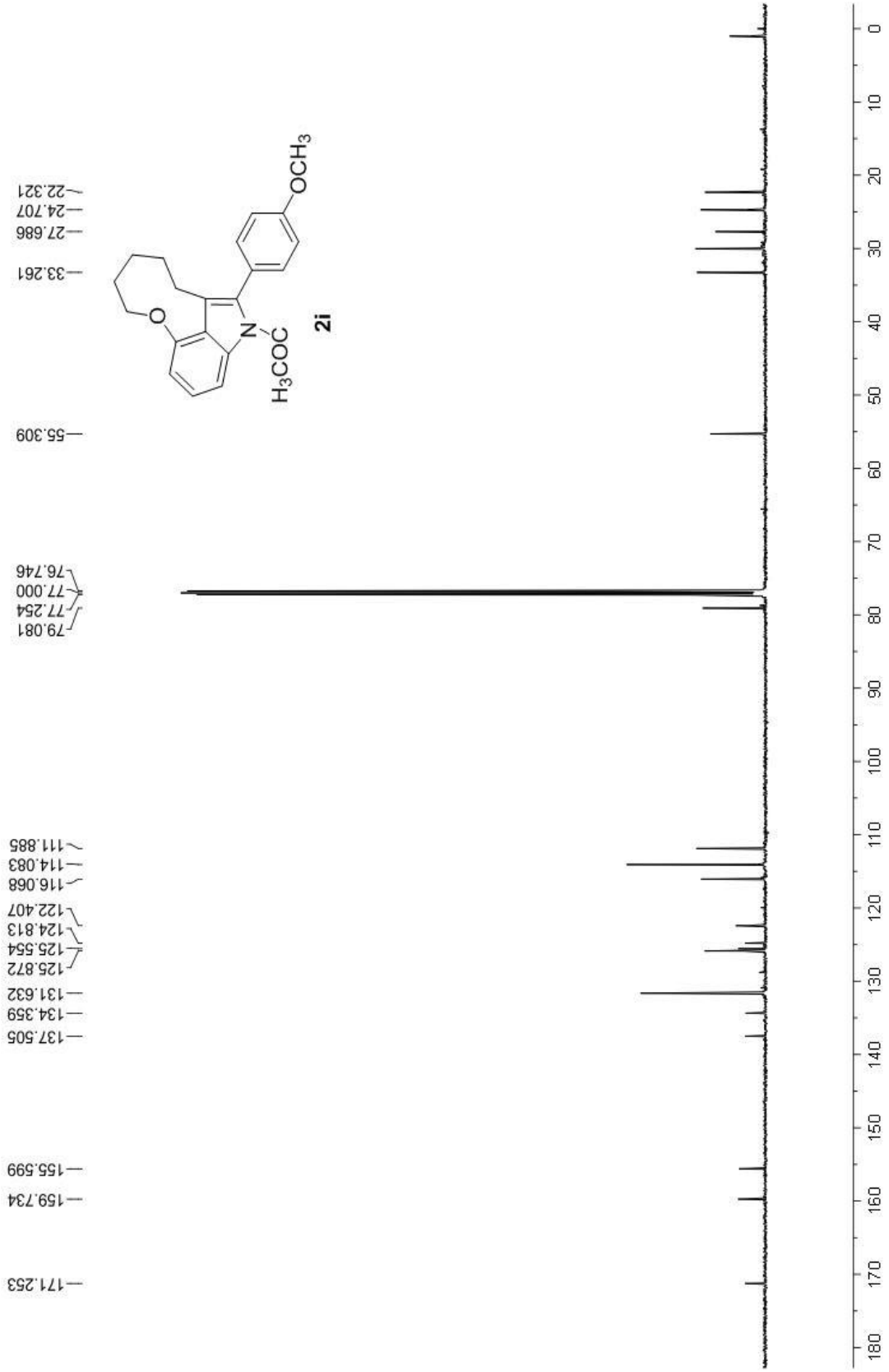
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O
N
H3COC
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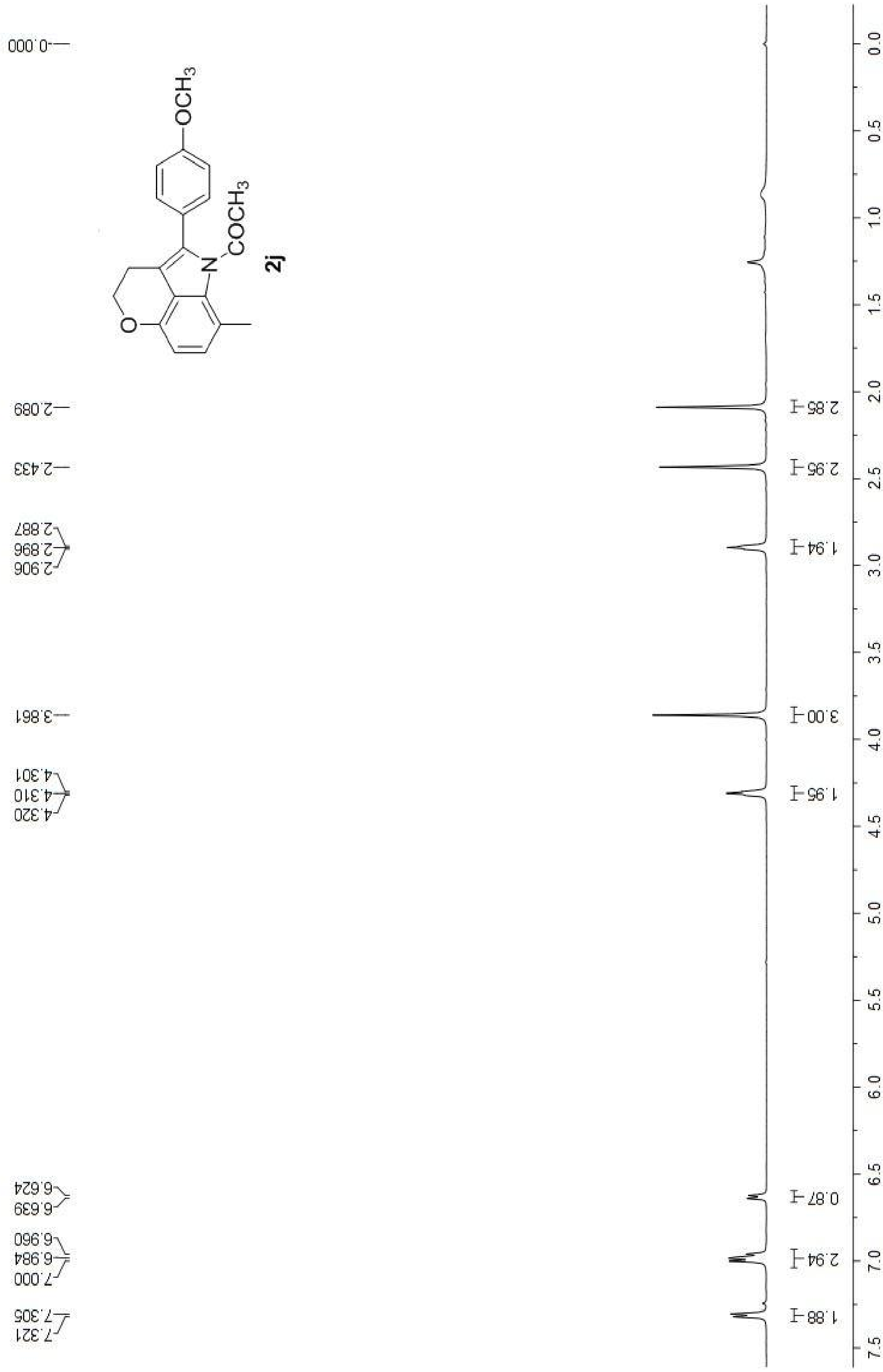

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6.639
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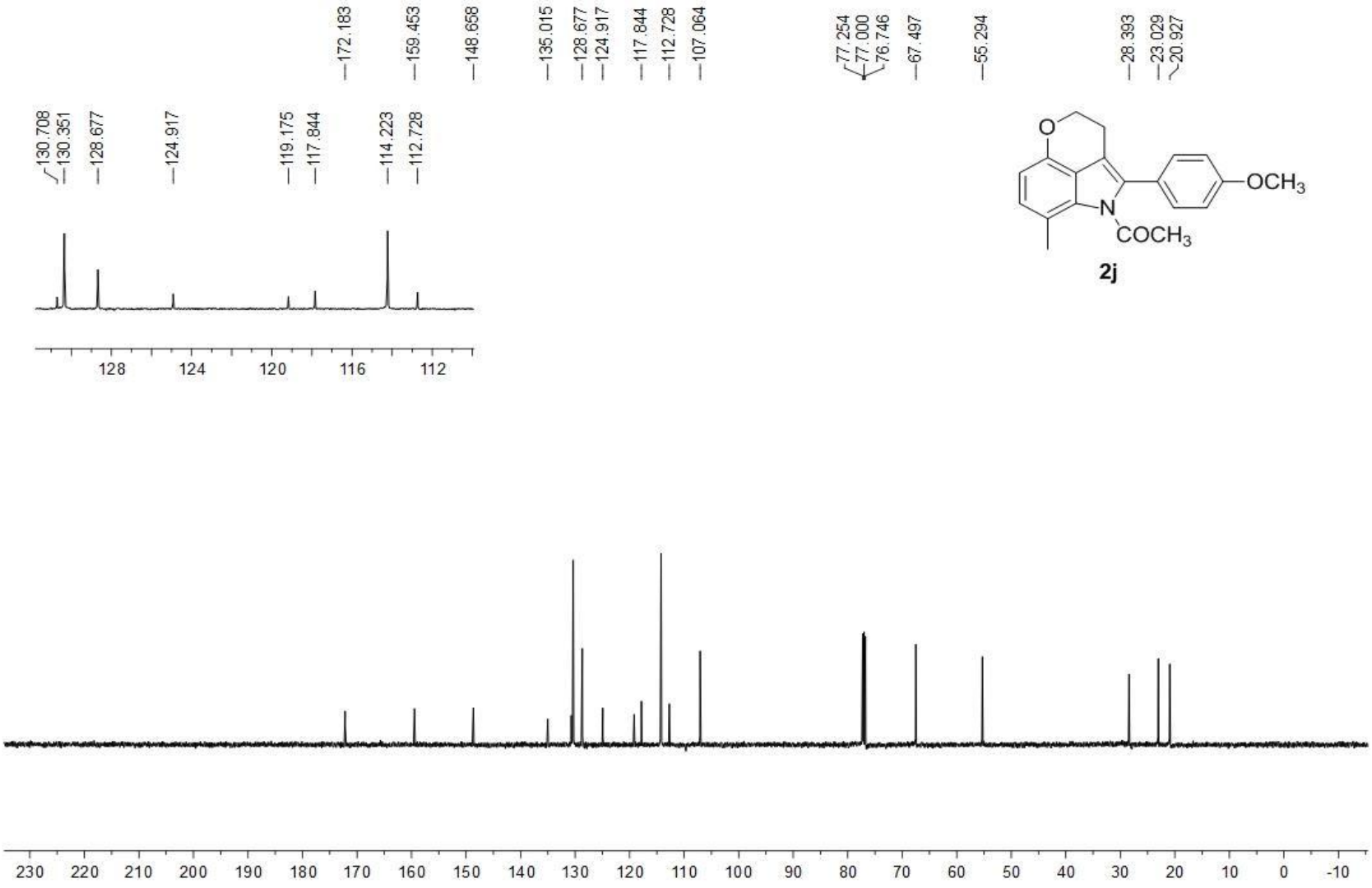
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23.029
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119.175
117.844
114.223
112.728
128
124
120
116
112
O
N
COCH3
OCH3
2j
230
220
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200
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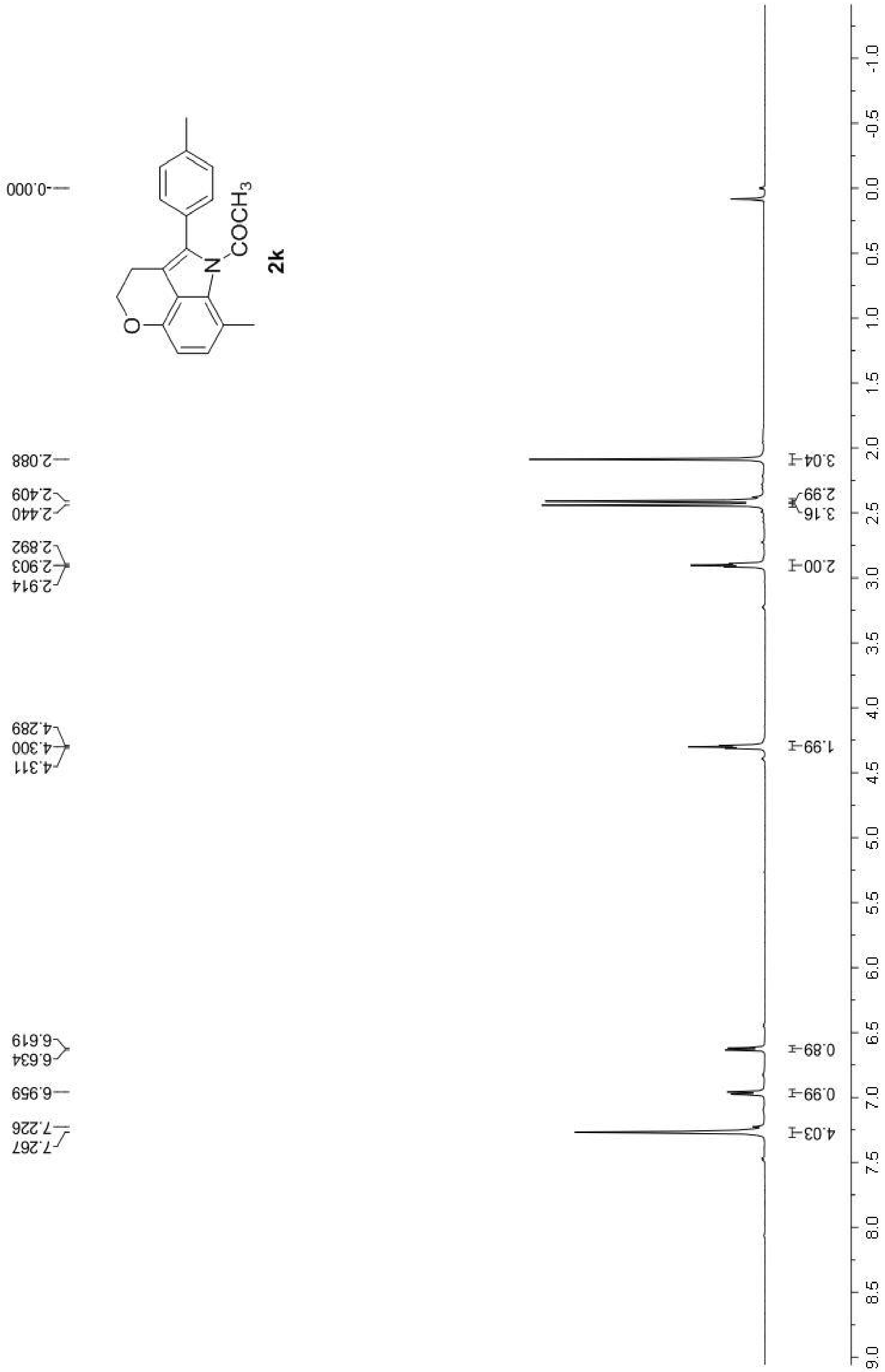

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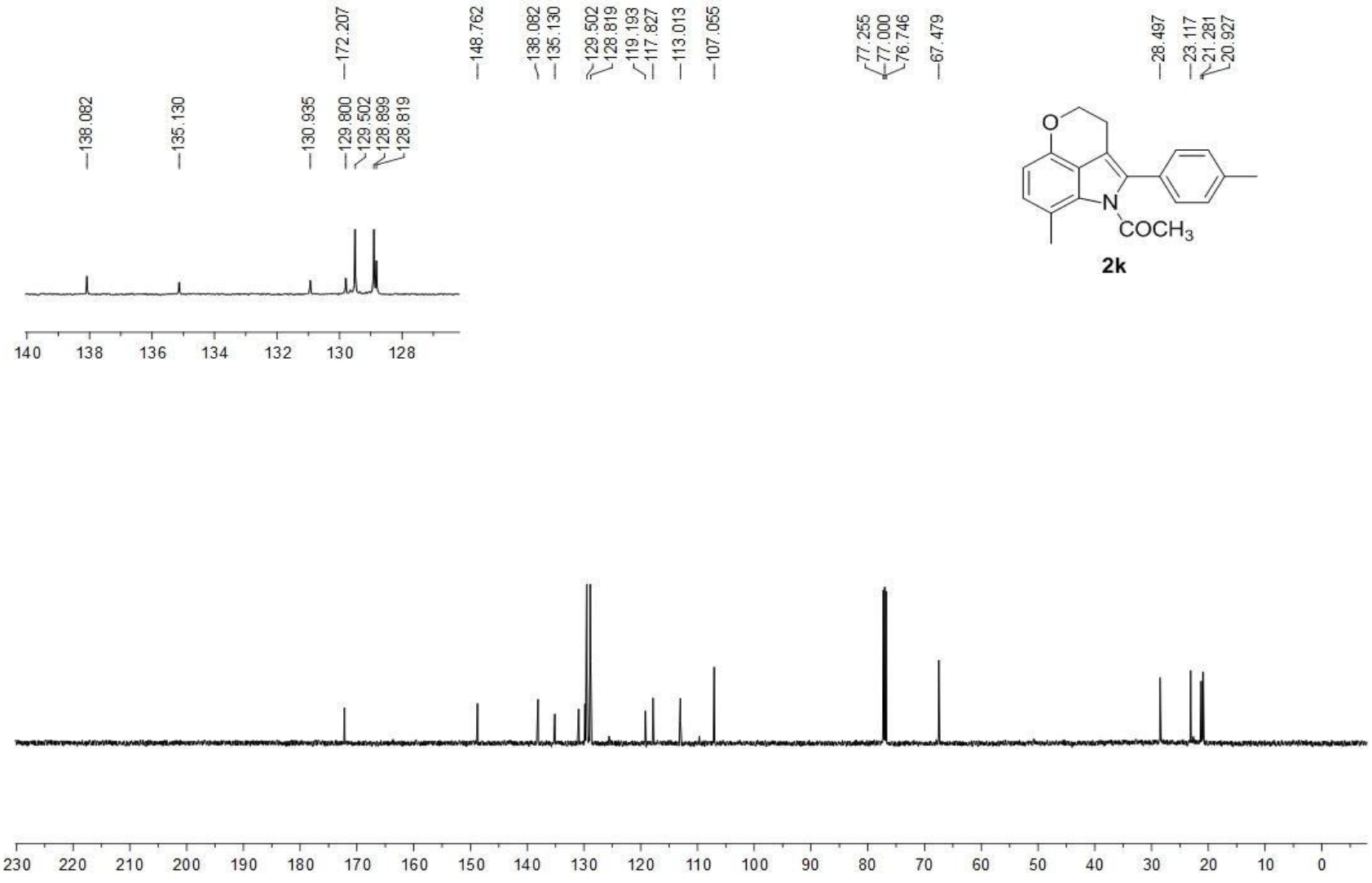
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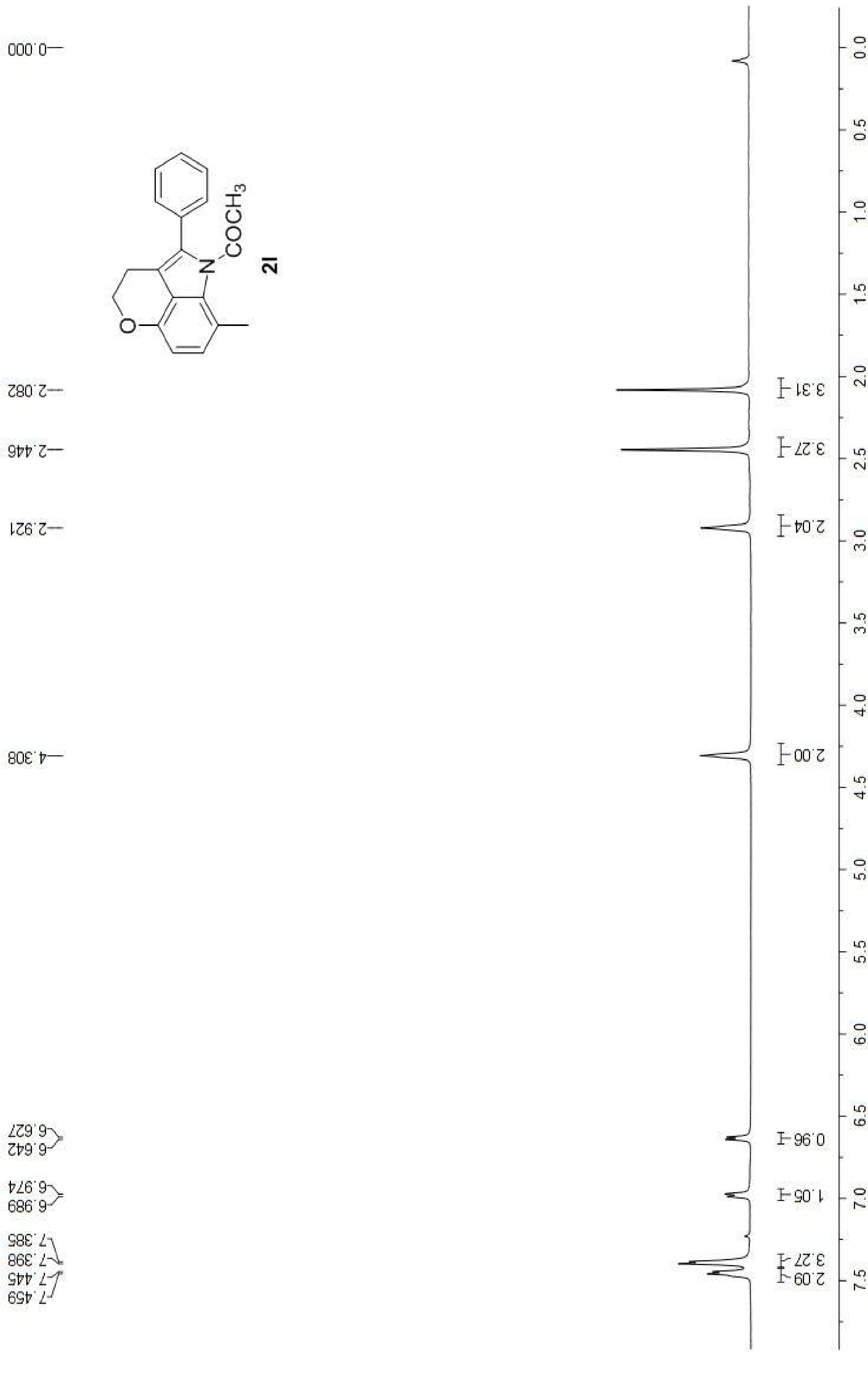

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O
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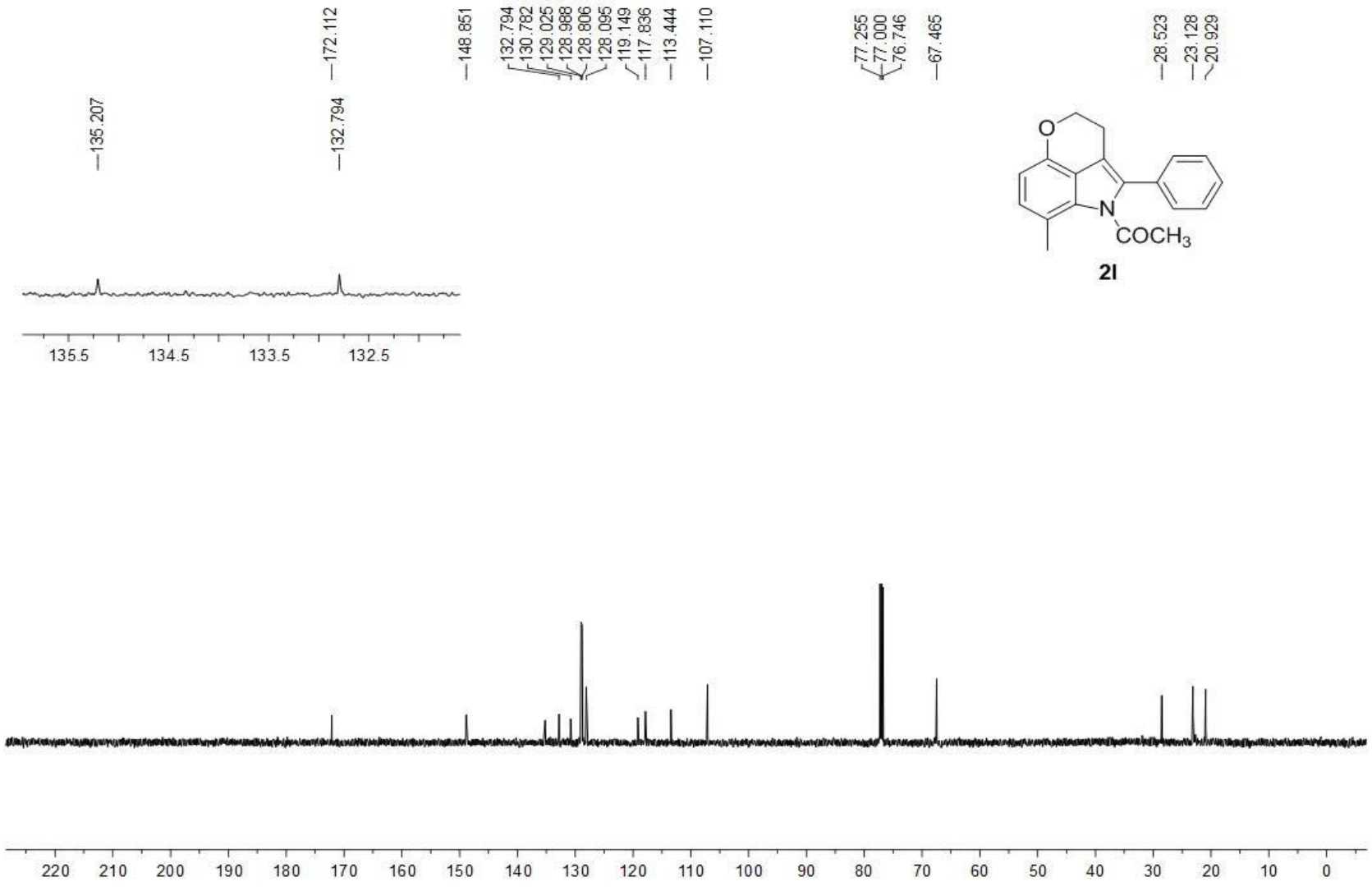
7.5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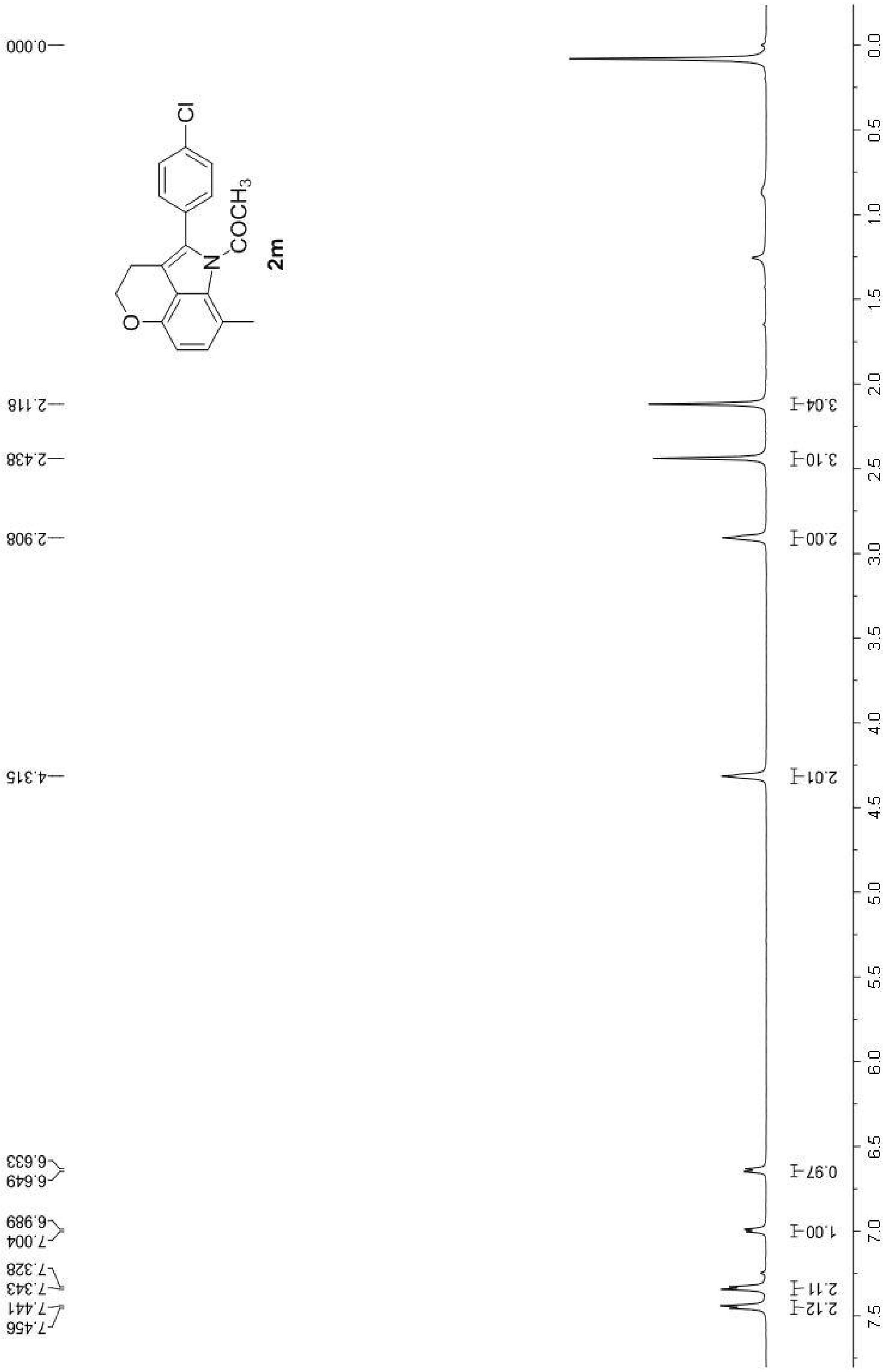
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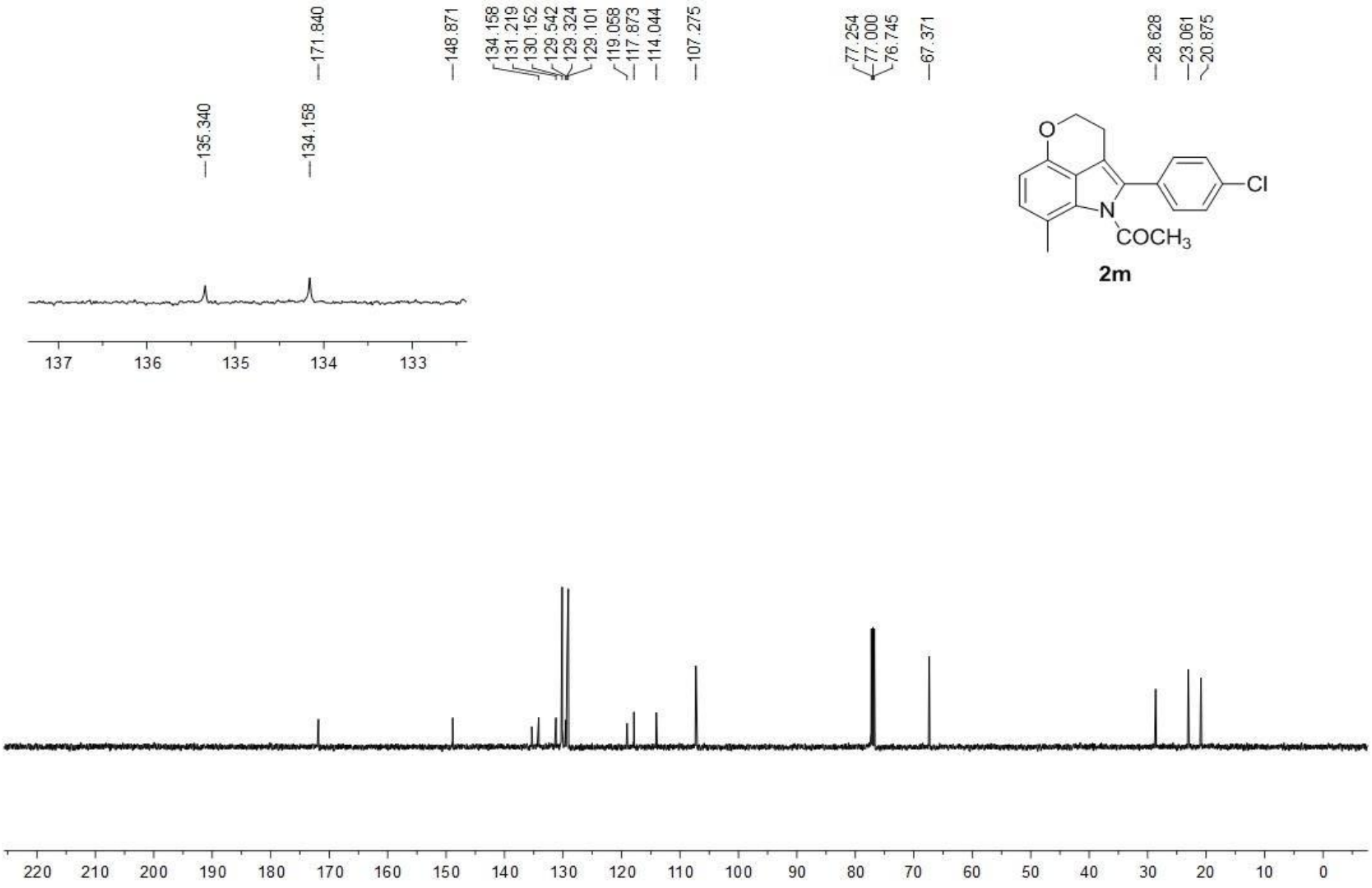
COCH3
2m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134
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O
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COCH3
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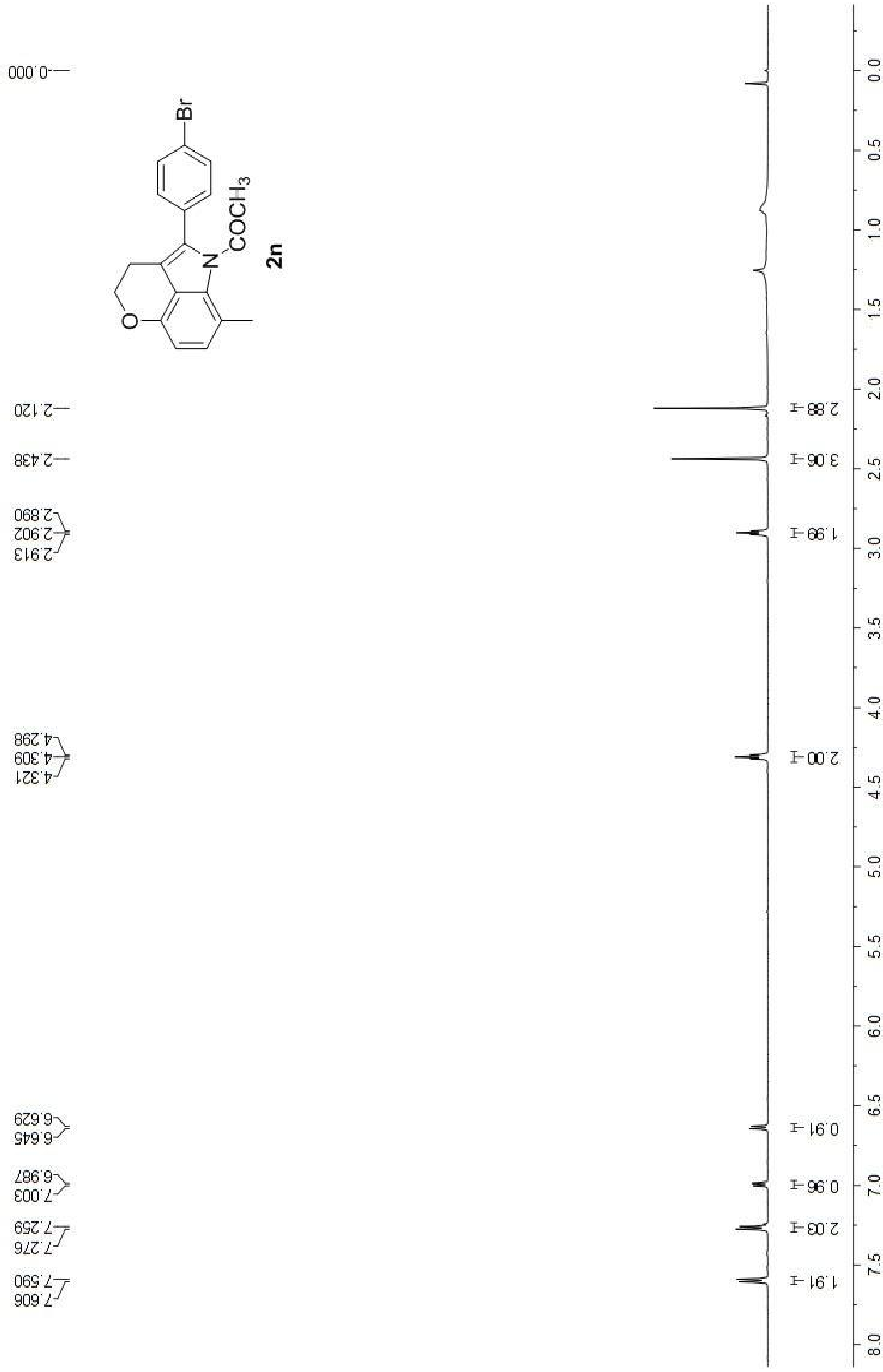
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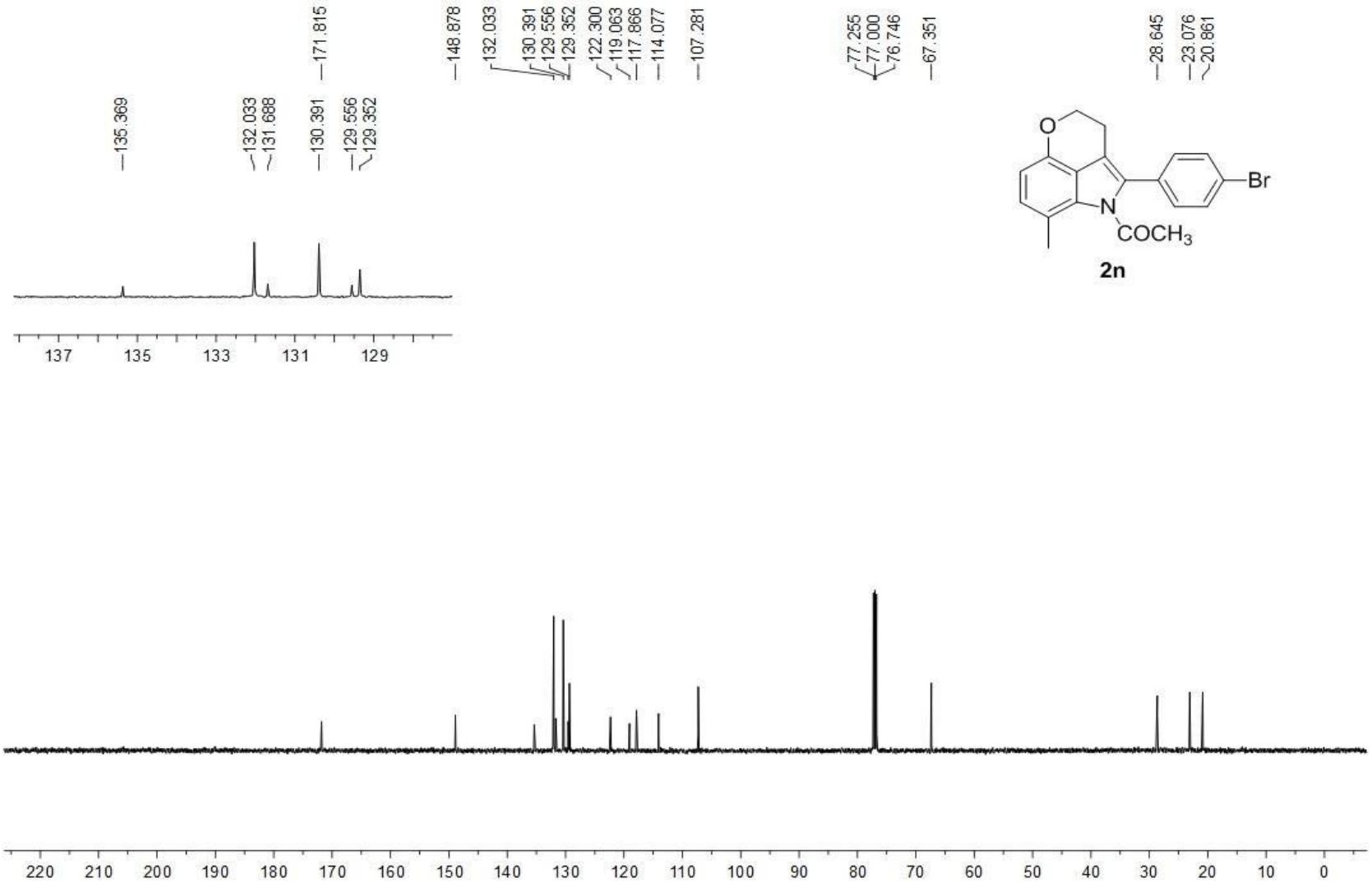
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Br
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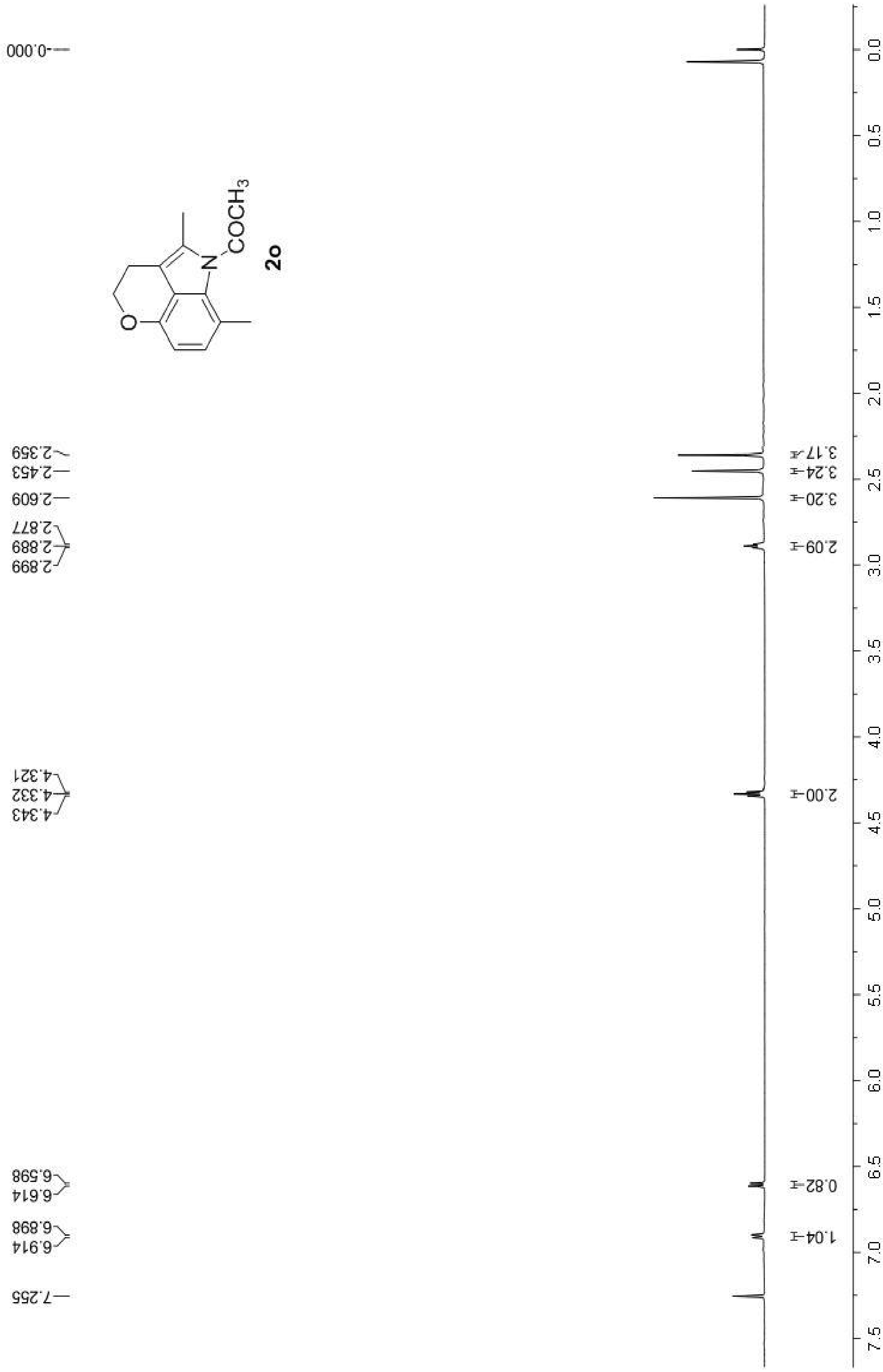

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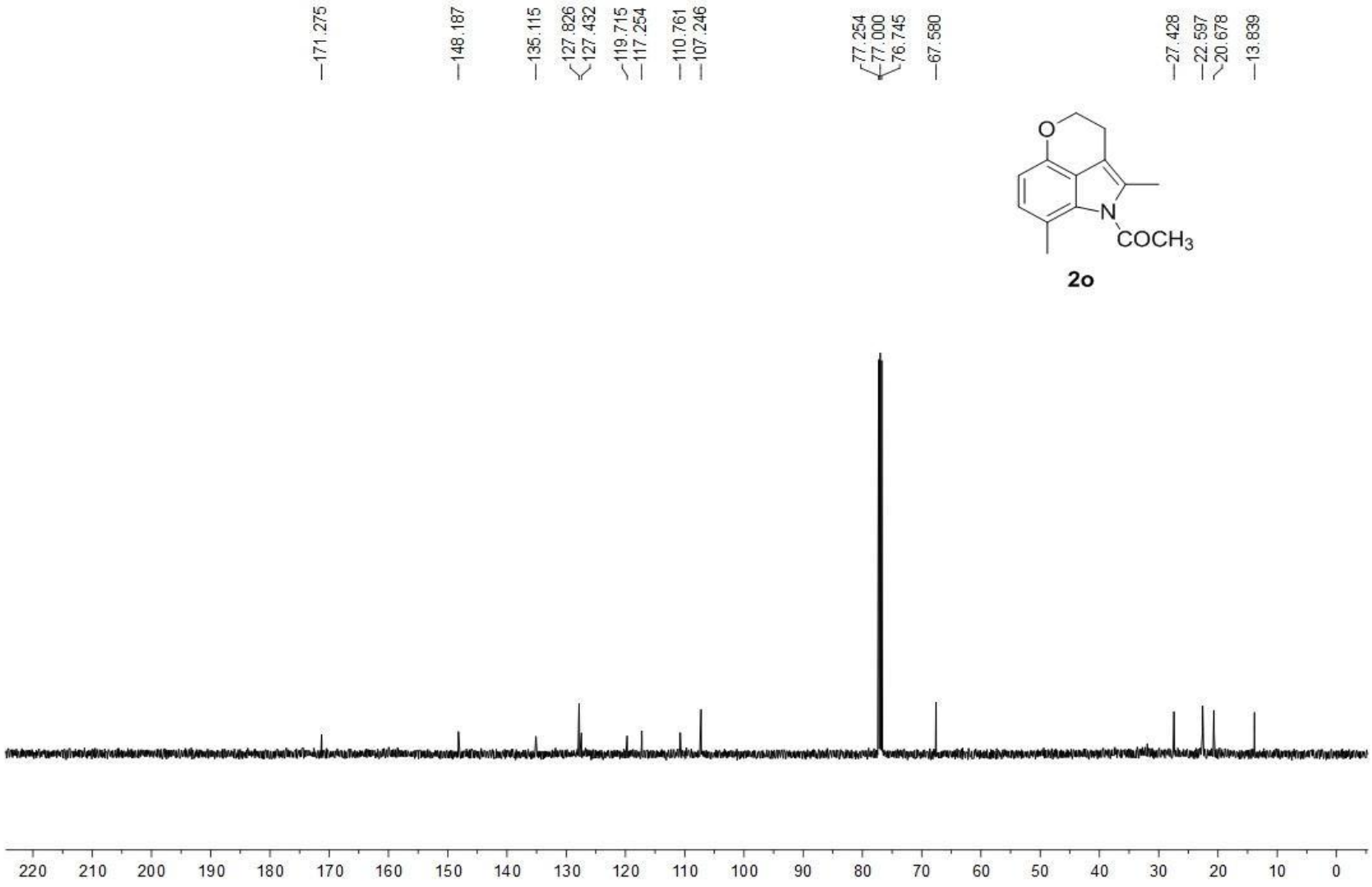
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COCH3
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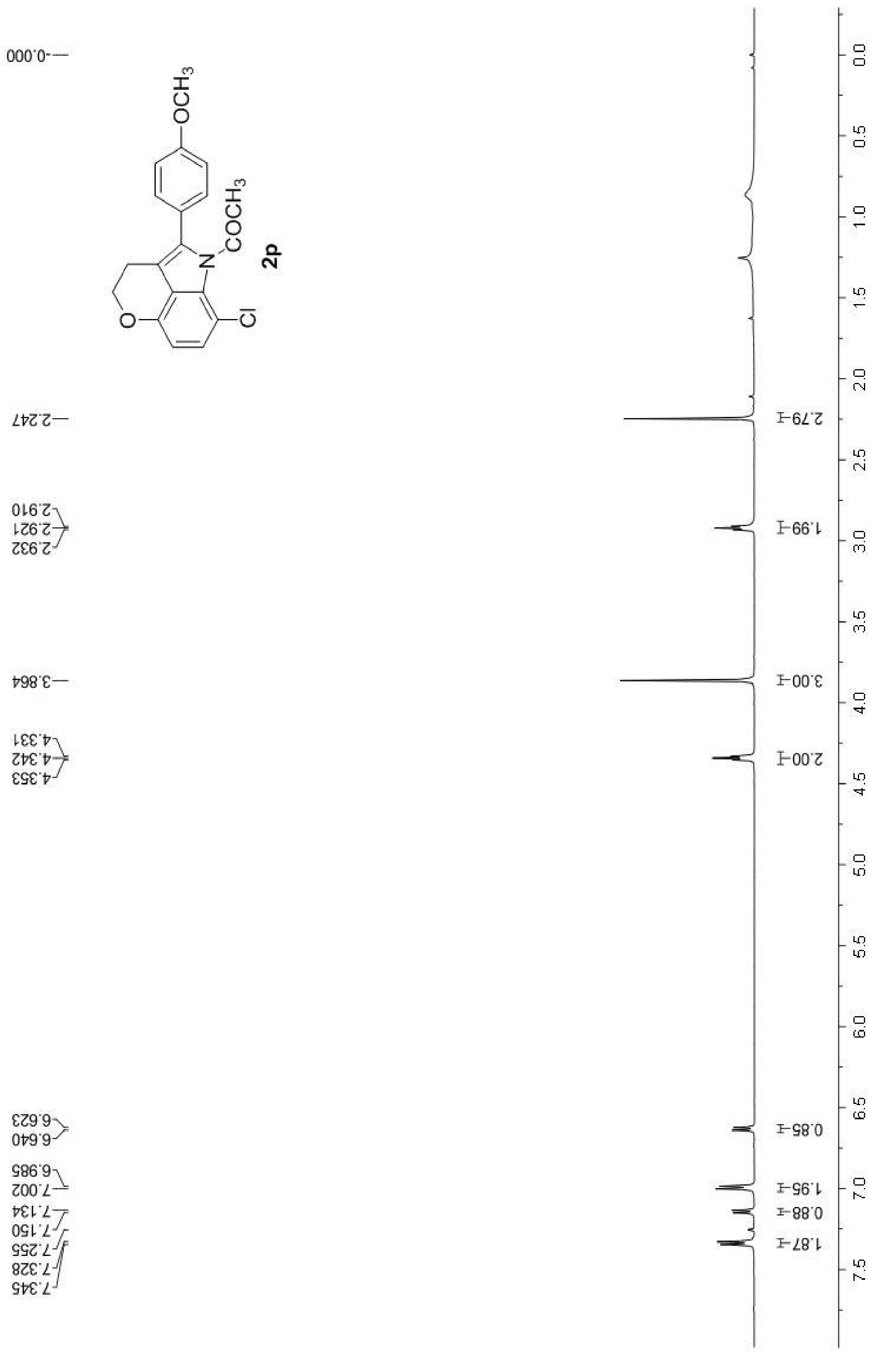

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COCH3
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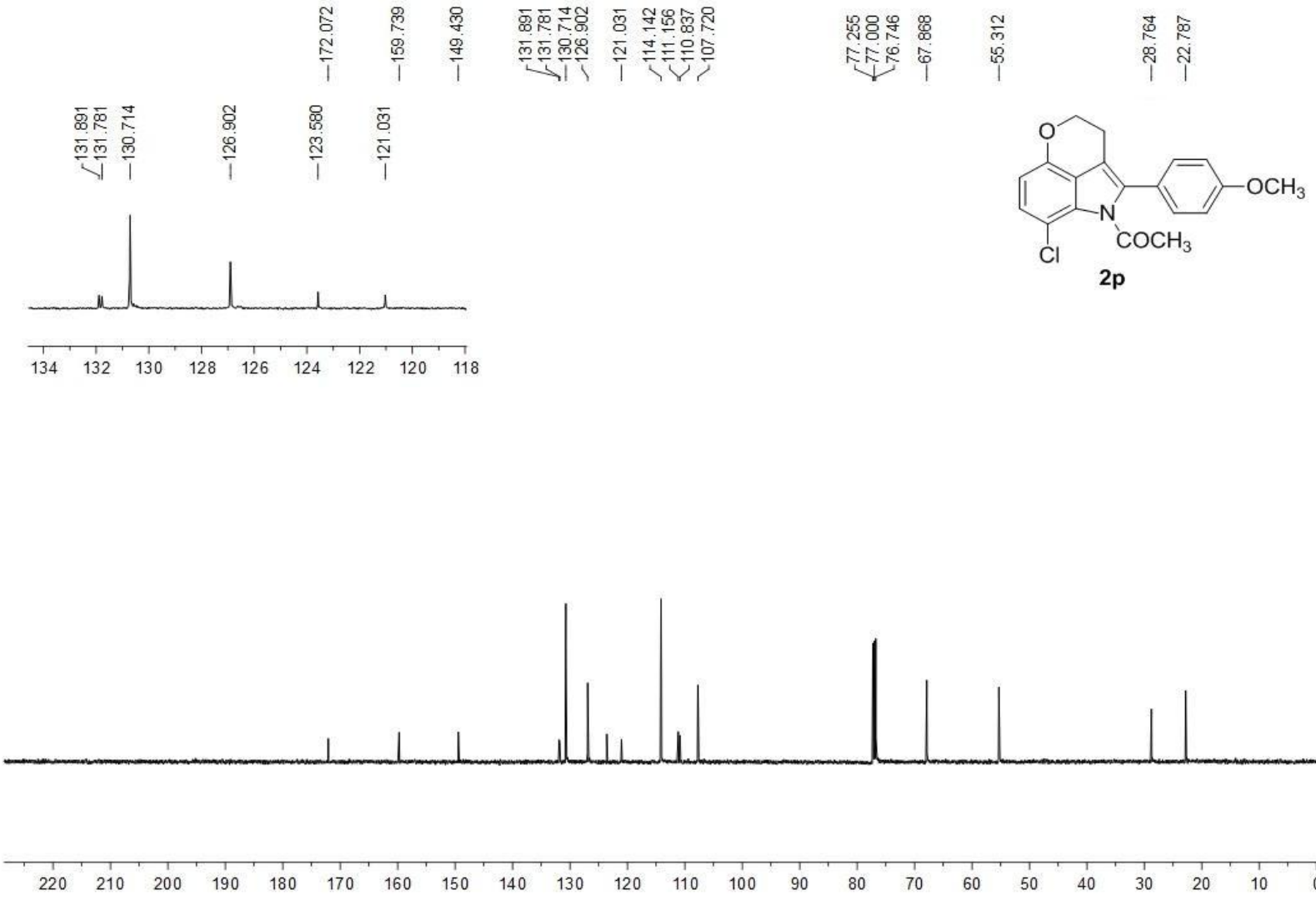
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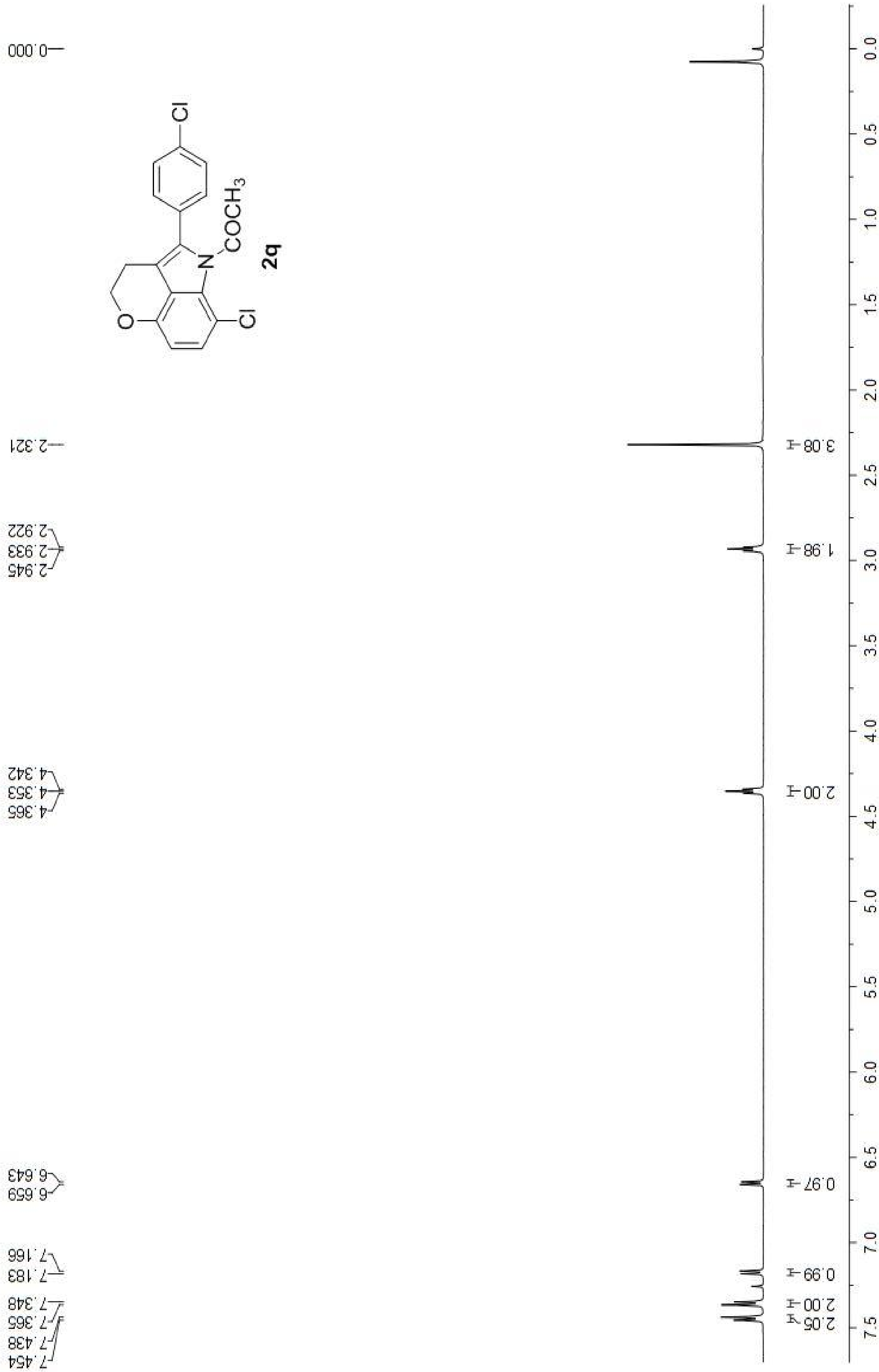
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0.0
0.5
1.0
1.5
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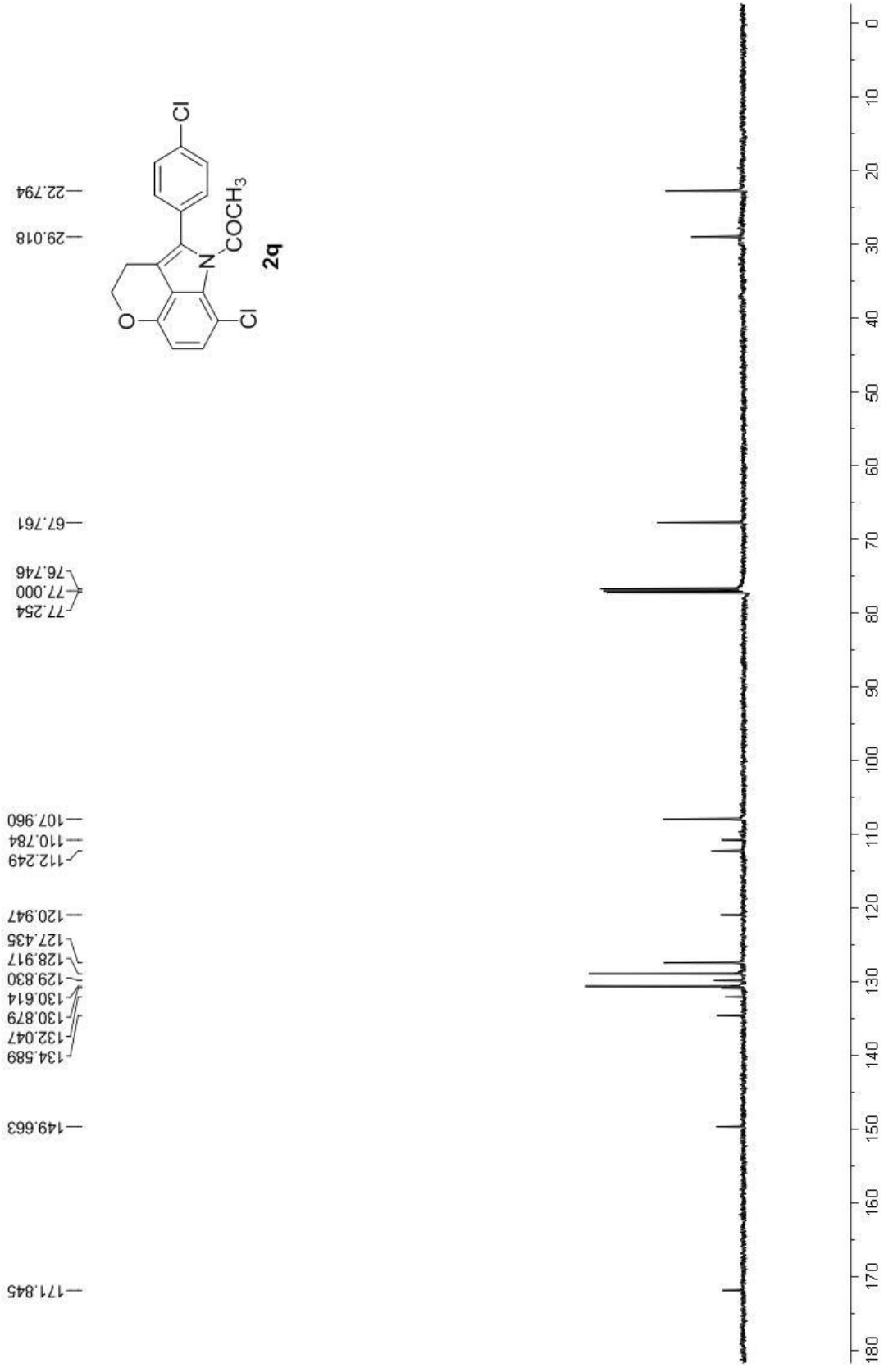
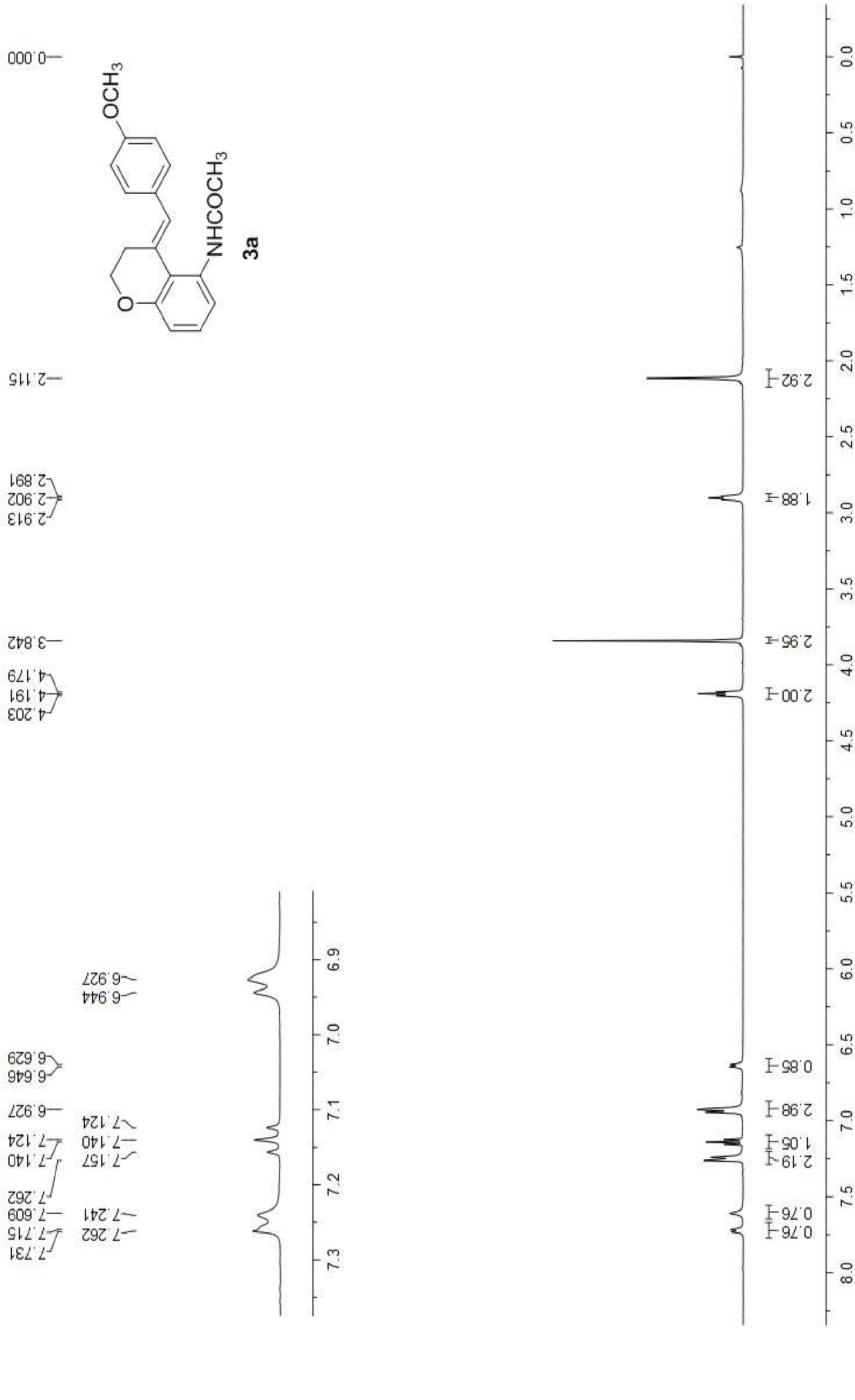
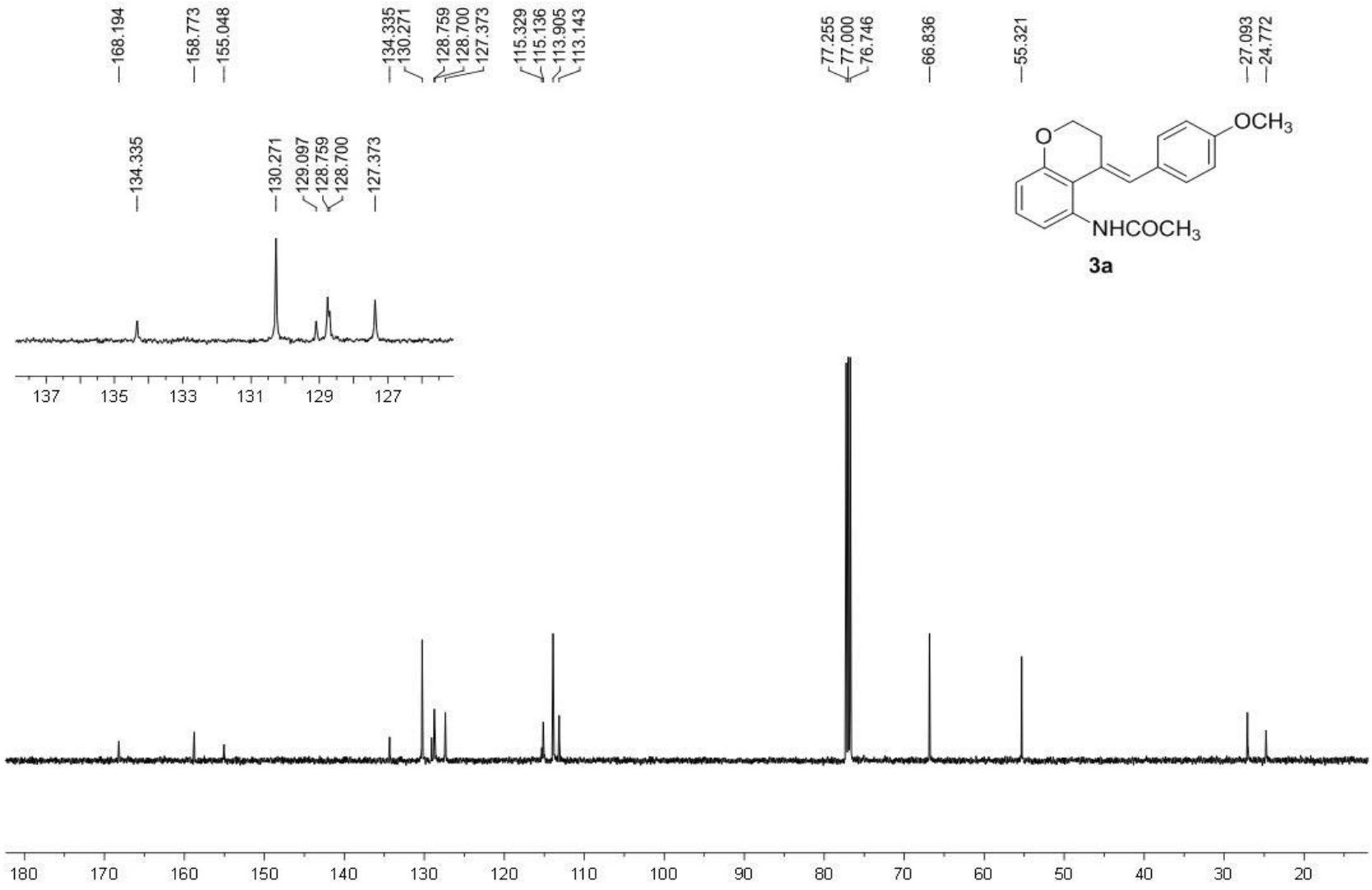
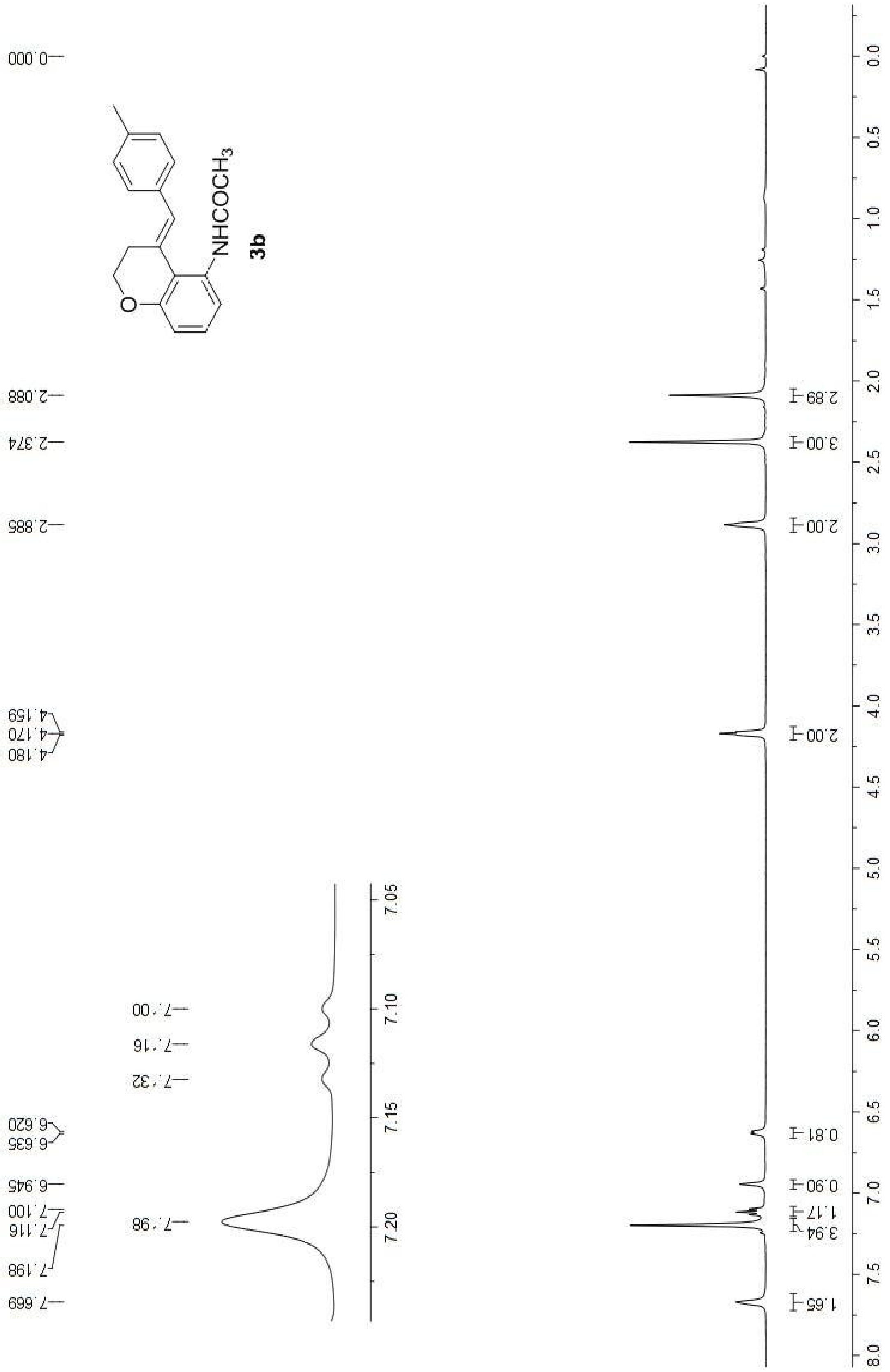
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

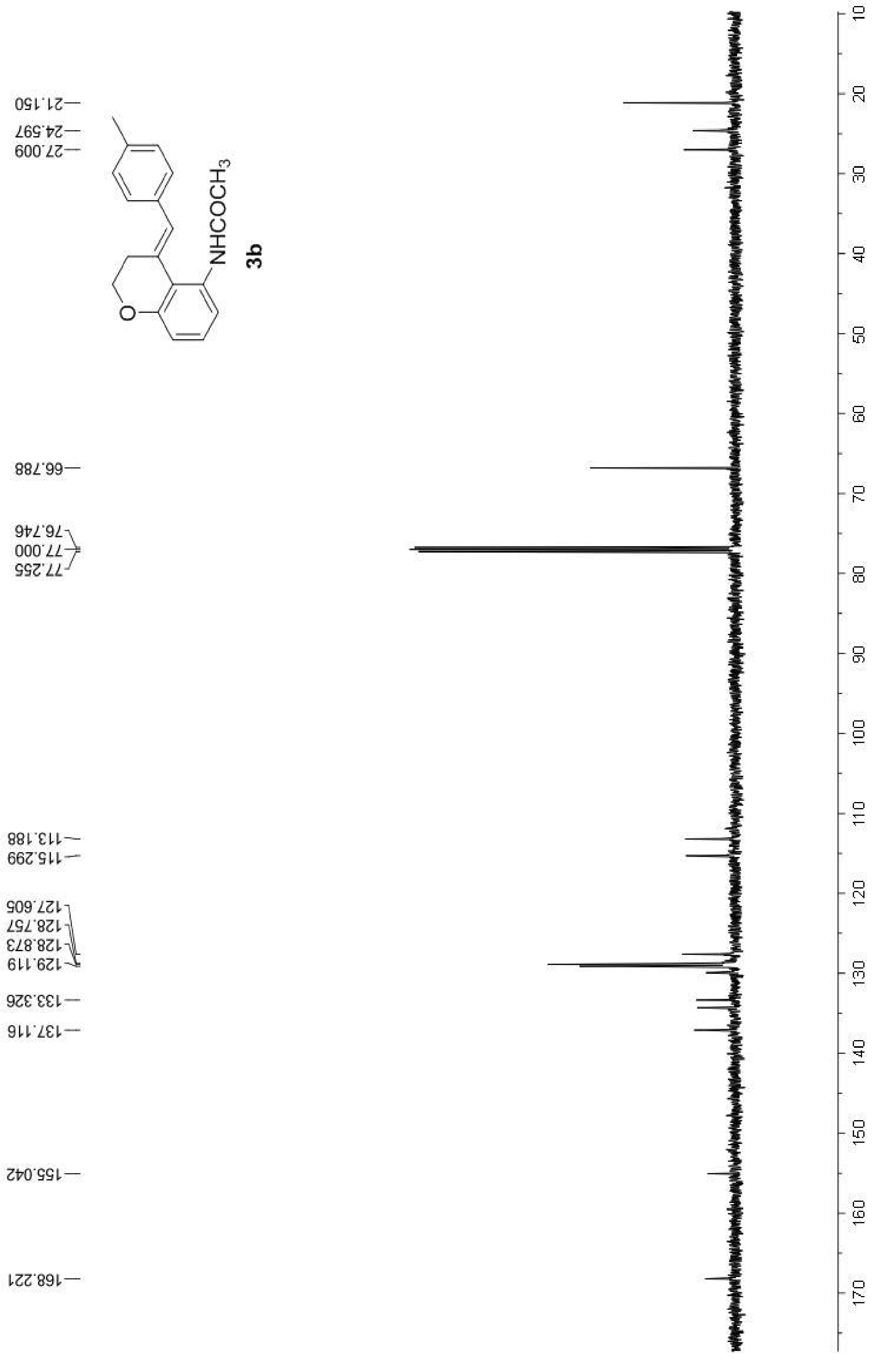

22.794
29.018
67.761
76.746
77.000
77.254
107.960
110.784
112.249
120.947
127.435
128.917
129.830
130.614
130.879
132.047
134.589
149.663
171.845
Cl
COCH3
N
O
Cl
2q
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

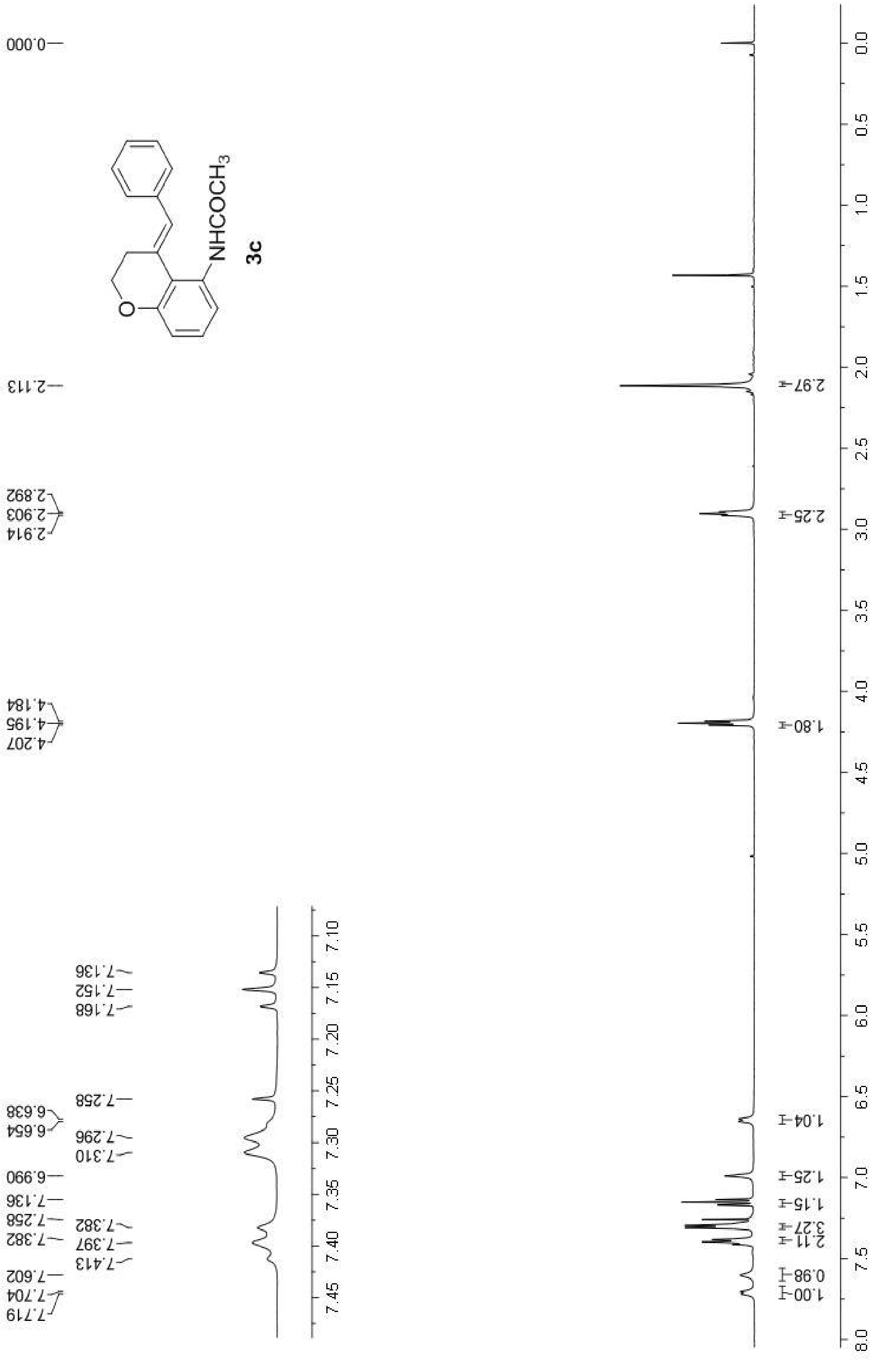


OCH$_3$
NHCOCH$_3$
3a

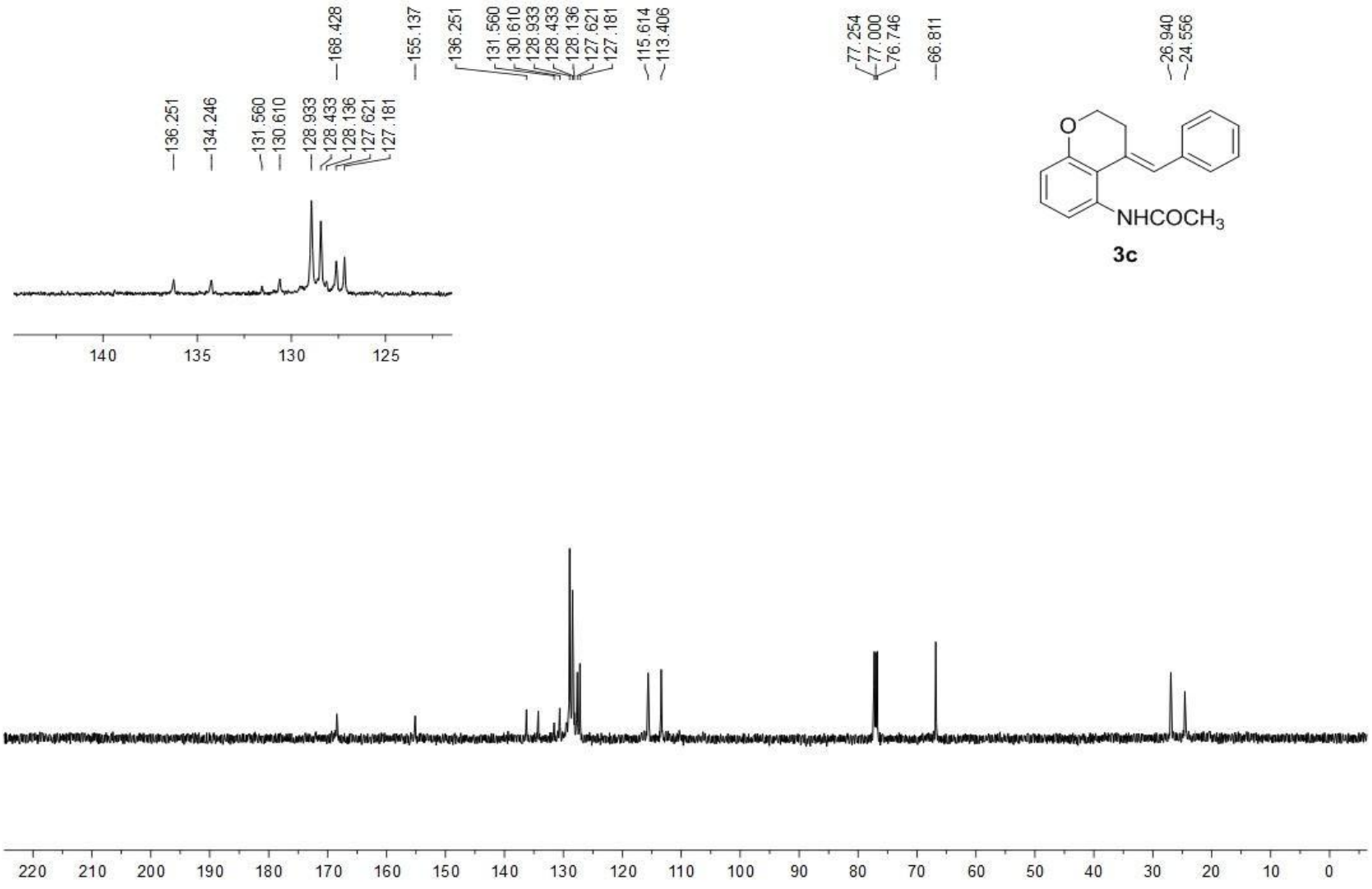

168.194
158.773
155.048
134.335
130.271
128.759
128.700
127.373
115.329
115.136
113.905
113.143
77.255
77.000
76.746
66.836
55.321
27.093
24.772
OCH3
O
NHCOCH3
3a
134.335
130.271
129.097
128.759
128.700
127.373
137
135
133
131
129
127
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

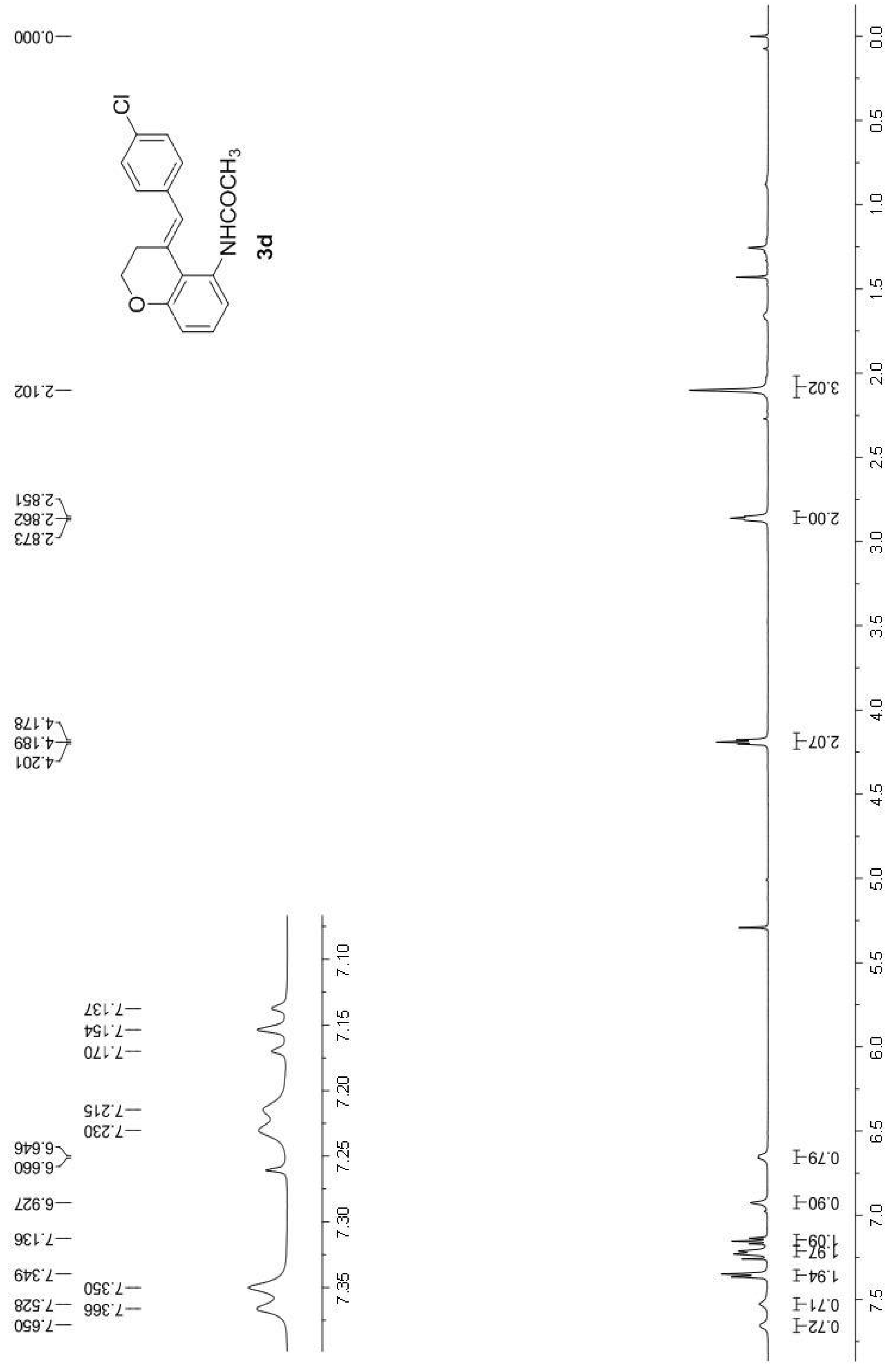

NHCOCH3
3b
0.000
2.088
2.374
2.885
4.159
4.170
4.180
6.620
6.635
6.945
7.100
7.116
7.132
7.198
7.669
2.89
3.00
2.00
2.00
0.81
0.90
1.17
3.94
1.65

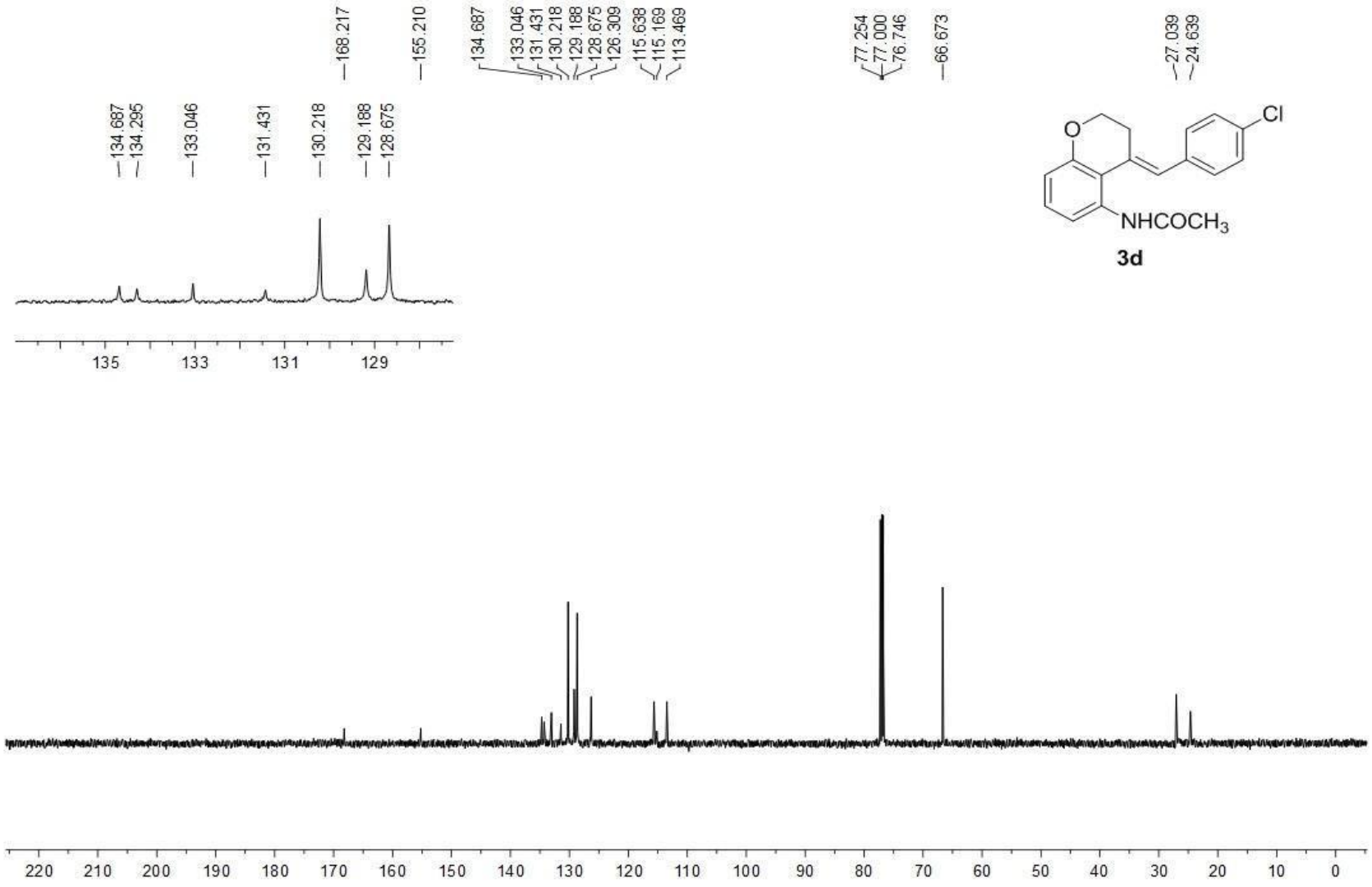

21.150
24.597
27.009
66.788
76.746
77.000
77.255
113.188
115.299
127.605
128.757
128.873
129.119
133.326
137.116
155.042
168.221
NHCOCH3
3b

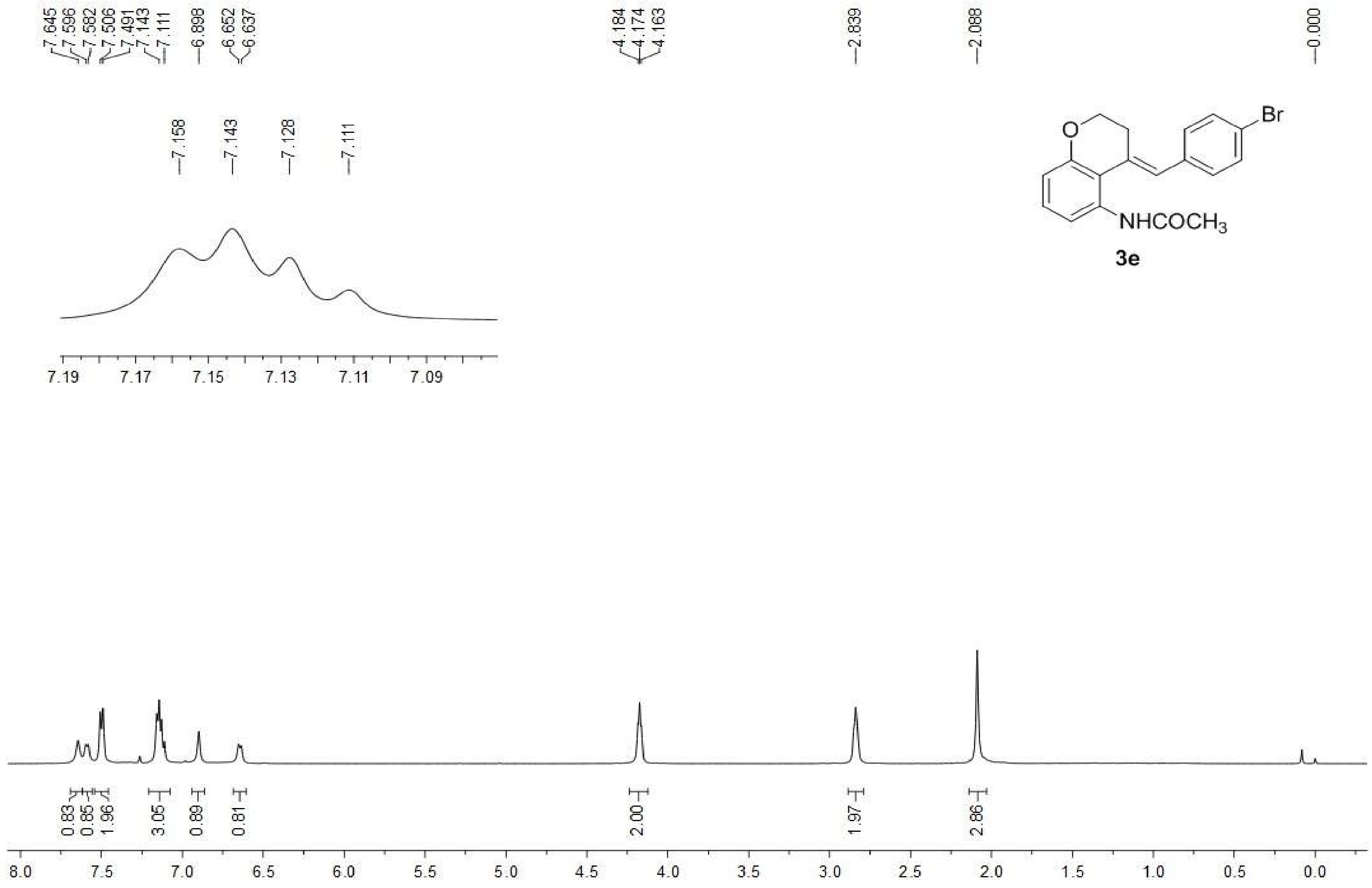


NHCOCH3
3c
0.000
2.113
2.892
2.903
2.914
4.184
4.195
4.207
6.638
6.654
6.990
7.136
7.258
7.382
7.602
7.704
7.719
7.136
7.152
7.168
7.258
7.296
7.310
7.382
7.397
7.413
2.97
2.25
1.80
1.04
1.25
1.15
3.27
2.11
0.98
1.00

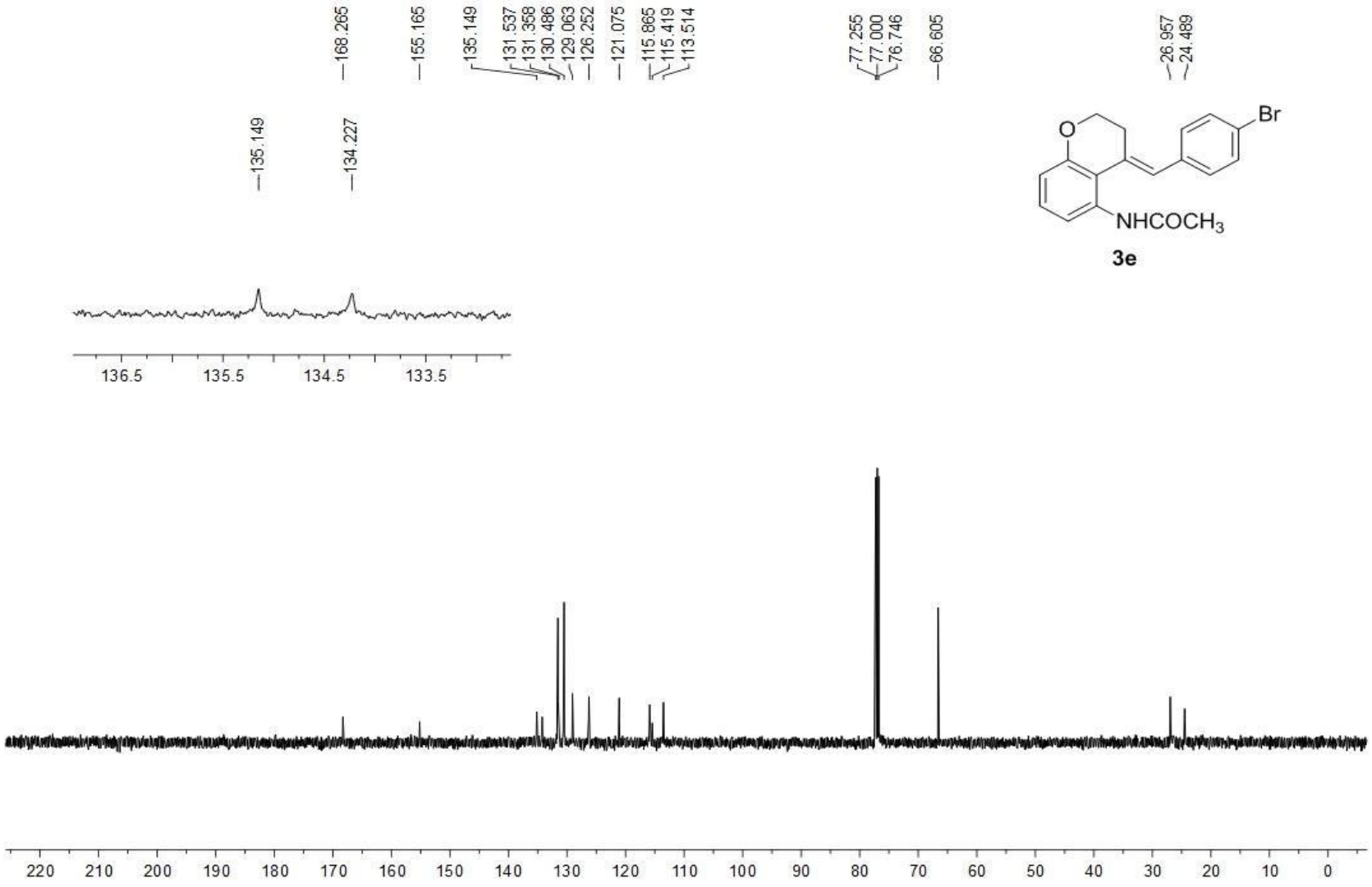

168.428
155.137
136.251
131.560
130.610
128.933
128.433
128.136
127.621
127.181
115.614
113.406
77.254
77.000
76.746
66.811
26.940
24.556
136.251
134.246
131.560
130.610
128.933
128.433
128.136
127.621
127.181
140
135
130
125
O
NHCOCH3
3c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

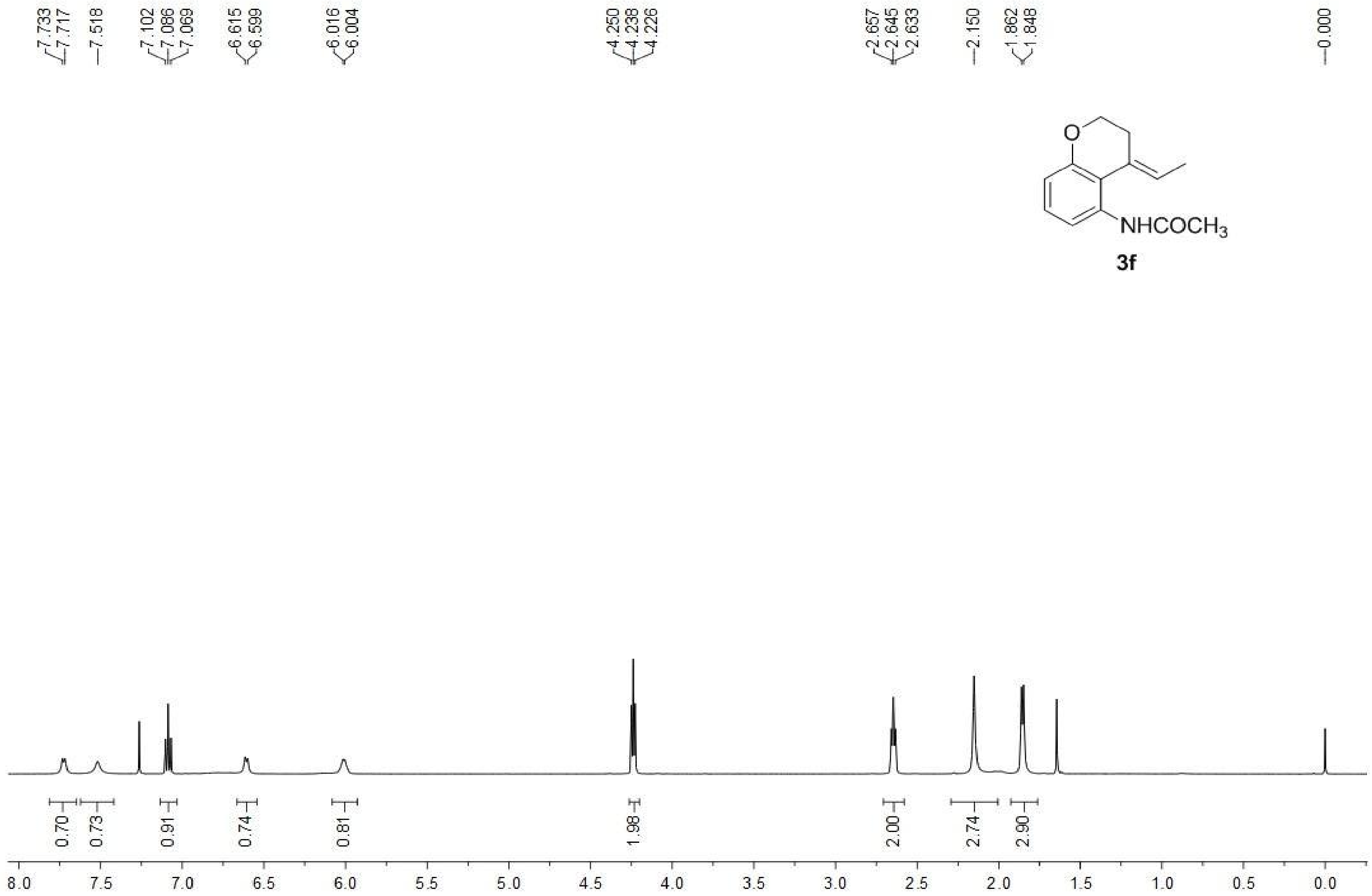

Cl
O
NHCOCH3
3d

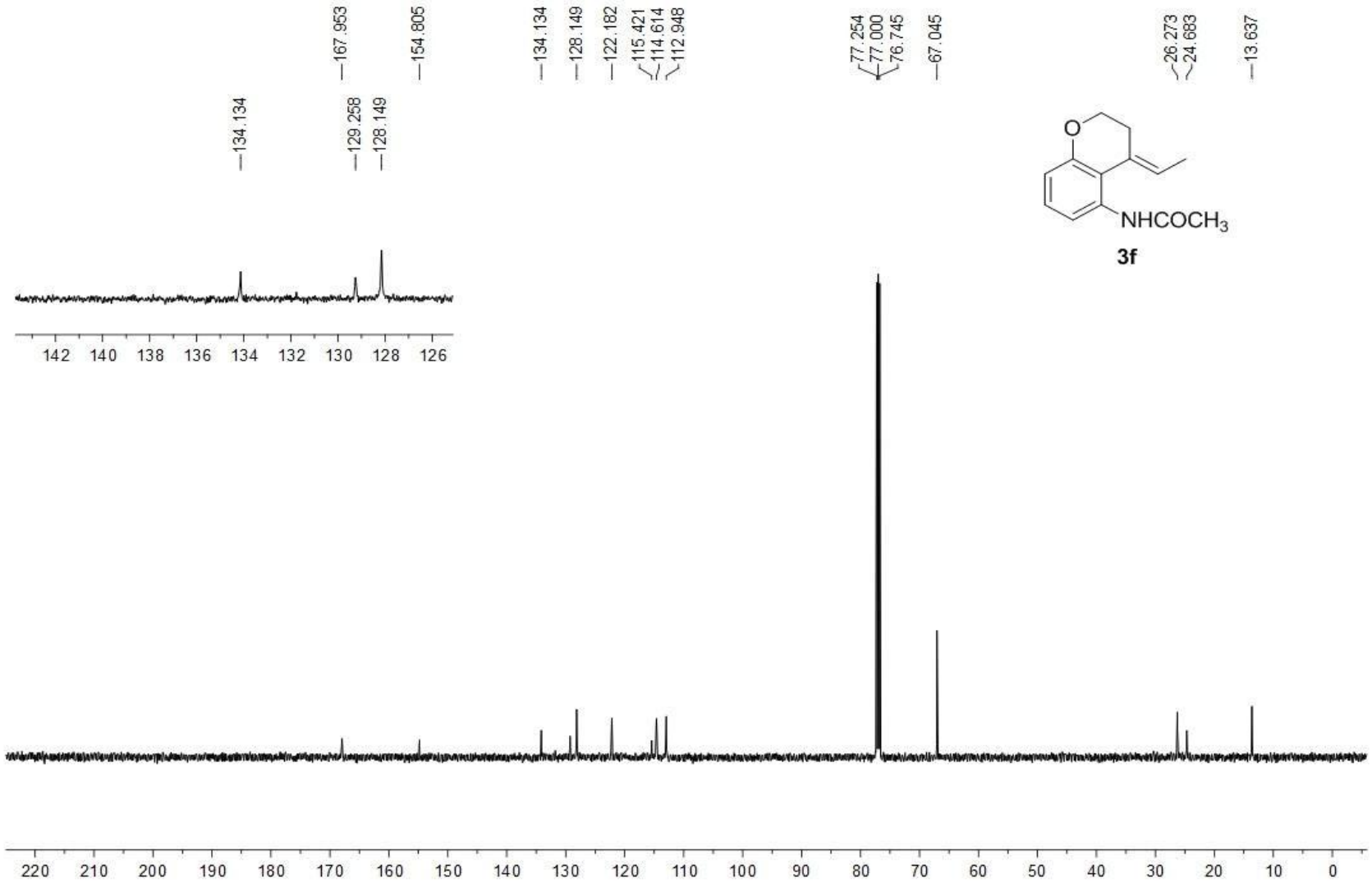

168.217
155.210
134.687
133.046
131.431
130.218
129.188
128.675
126.309
115.638
115.169
113.469
77.254
77.000
76.746
66.673
27.039
24.639
134.687
134.295
133.046
131.431
130.218
129.188
128.675
135
133
131
129
O
Cl
NHCOCH3
3d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

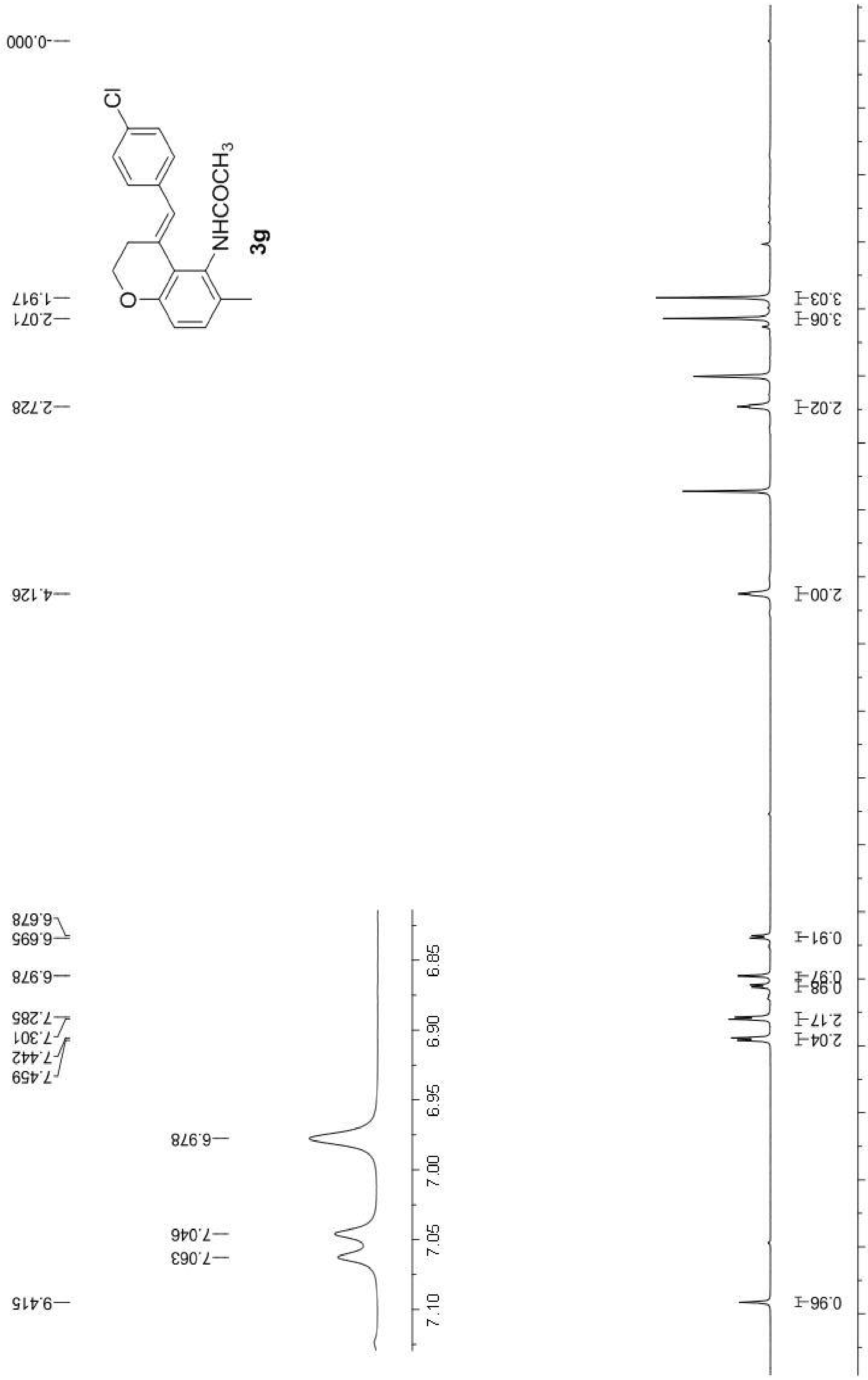

7.645
7.596
7.582
7.506
7.491
7.143
7.111
6.898
6.652
6.637
4.184
4.174
4.163
2.839
2.088
0.000
7.158
7.143
7.128
7.111
7.19
7.17
7.15
7.13
7.11
7.09
0.83
0.85
1.96
3.05
0.89
0.81
2.00
1.97
2.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
O
Br
NHCOCH3

3e

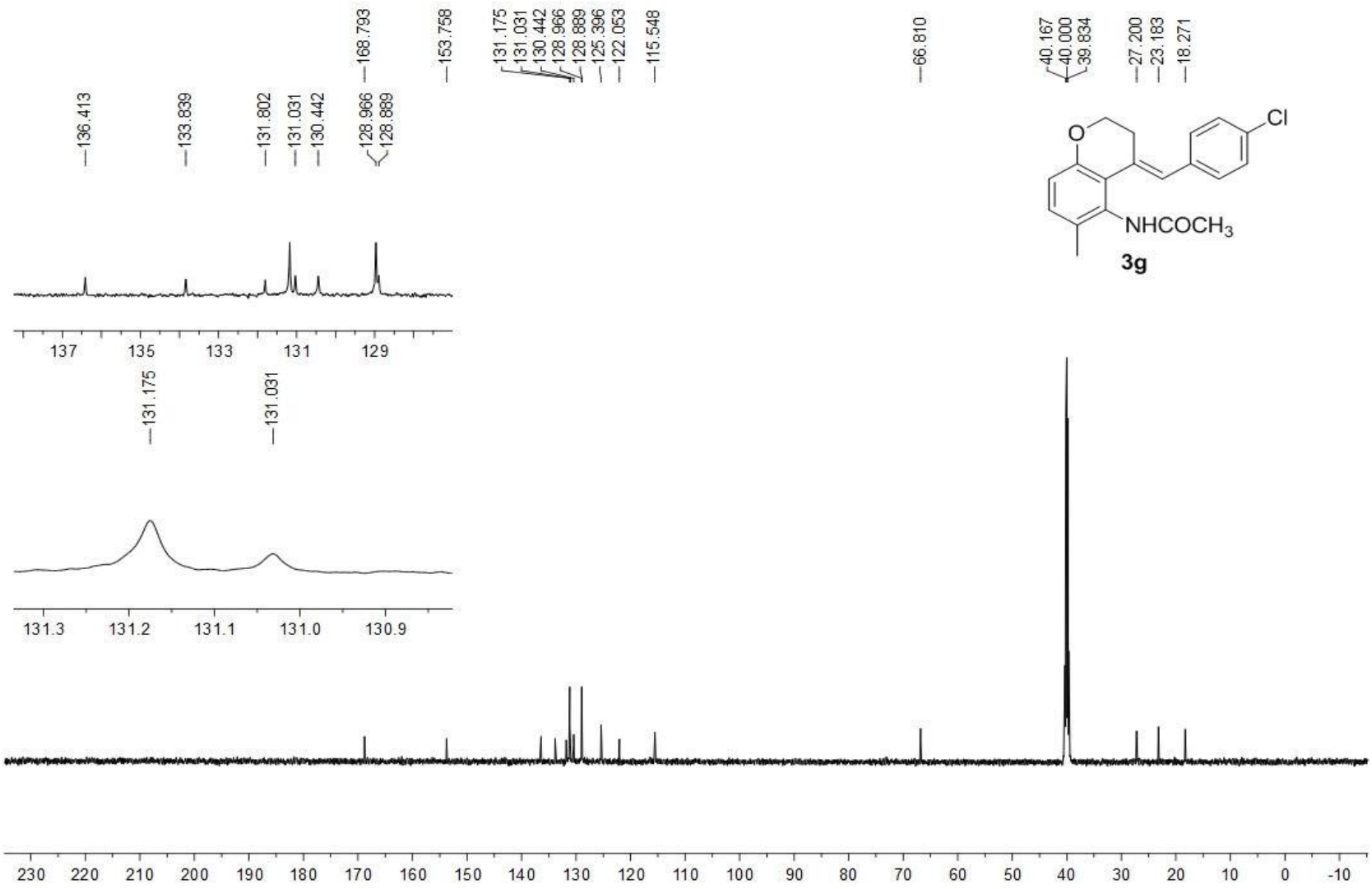

168.265
155.165
135.149
131.537
131.358
130.486
129.063
126.252
121.075
115.865
115.419
113.514
77.255
77.000
76.746
66.605
26.957
24.489
135.149
134.227
136.5
135.5
134.5
133.5
O
Br
NHCOCH3
3e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

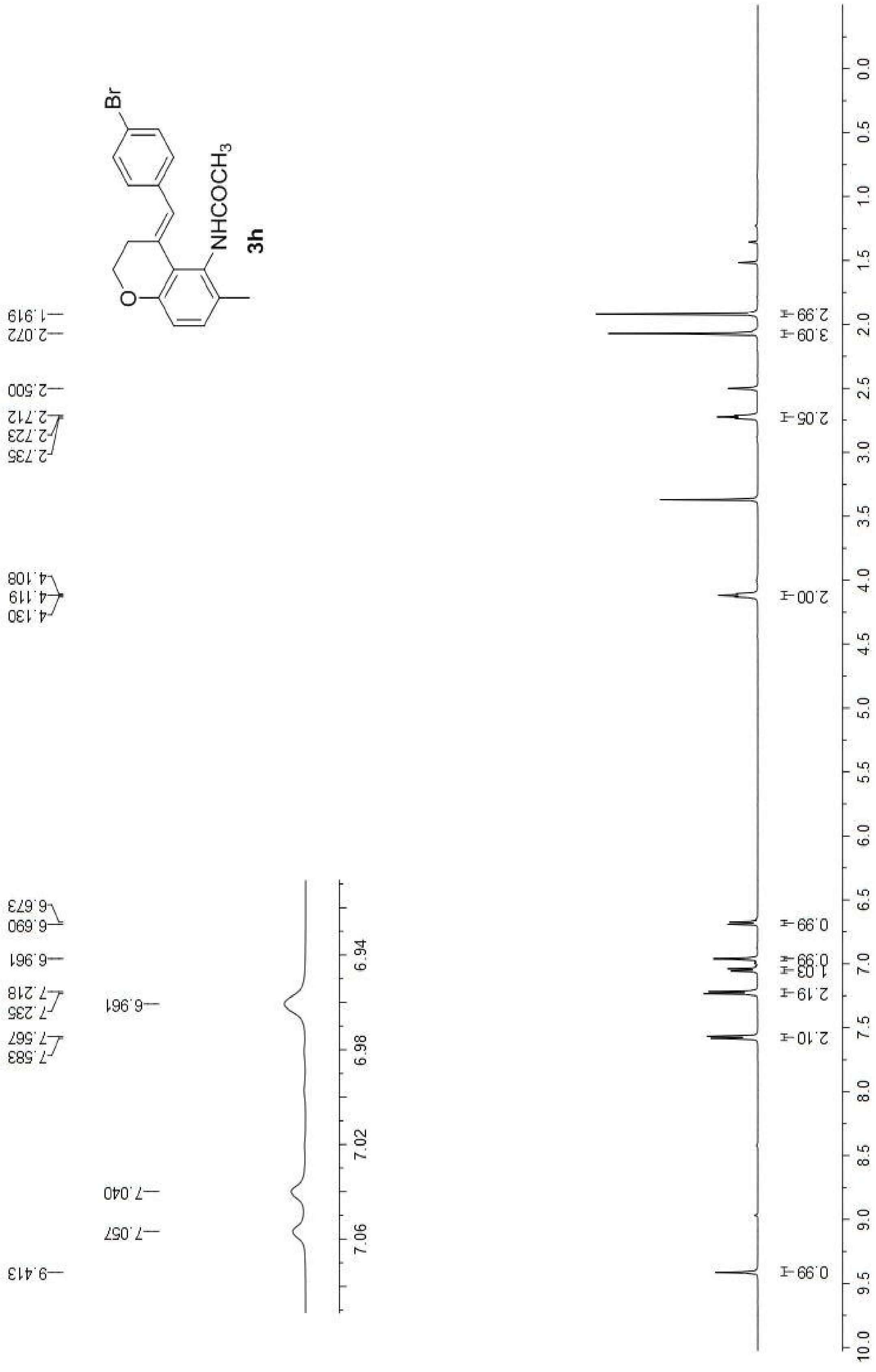

7.733
7.717
7.518
7.102
7.086
7.069
6.615
6.599
6.016
6.004
4.250
4.238
4.226
2.657
2.645
2.633
2.150
1.862
1.848
0.000
NHCOCH3
3f
0.70
0.73
0.91
0.74
0.81
1.98
2.00
2.74
2.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

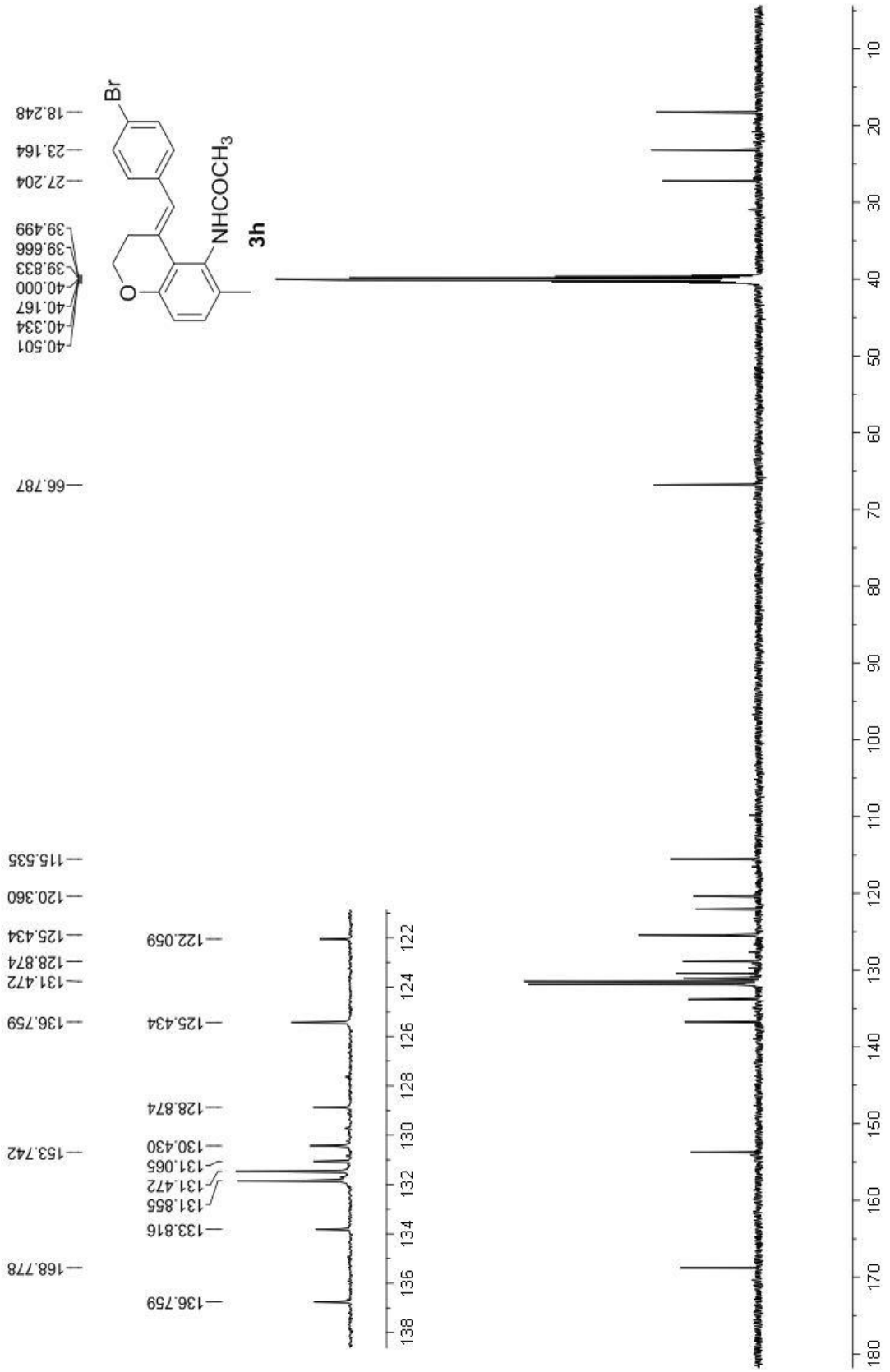

167.953
154.805
134.134
128.149
122.182
115.421
114.614
112.948
77.254
77.000
76.745
67.045
26.273
24.683
13.637
134.134
129.258
128.149
NHCOCH3
3f

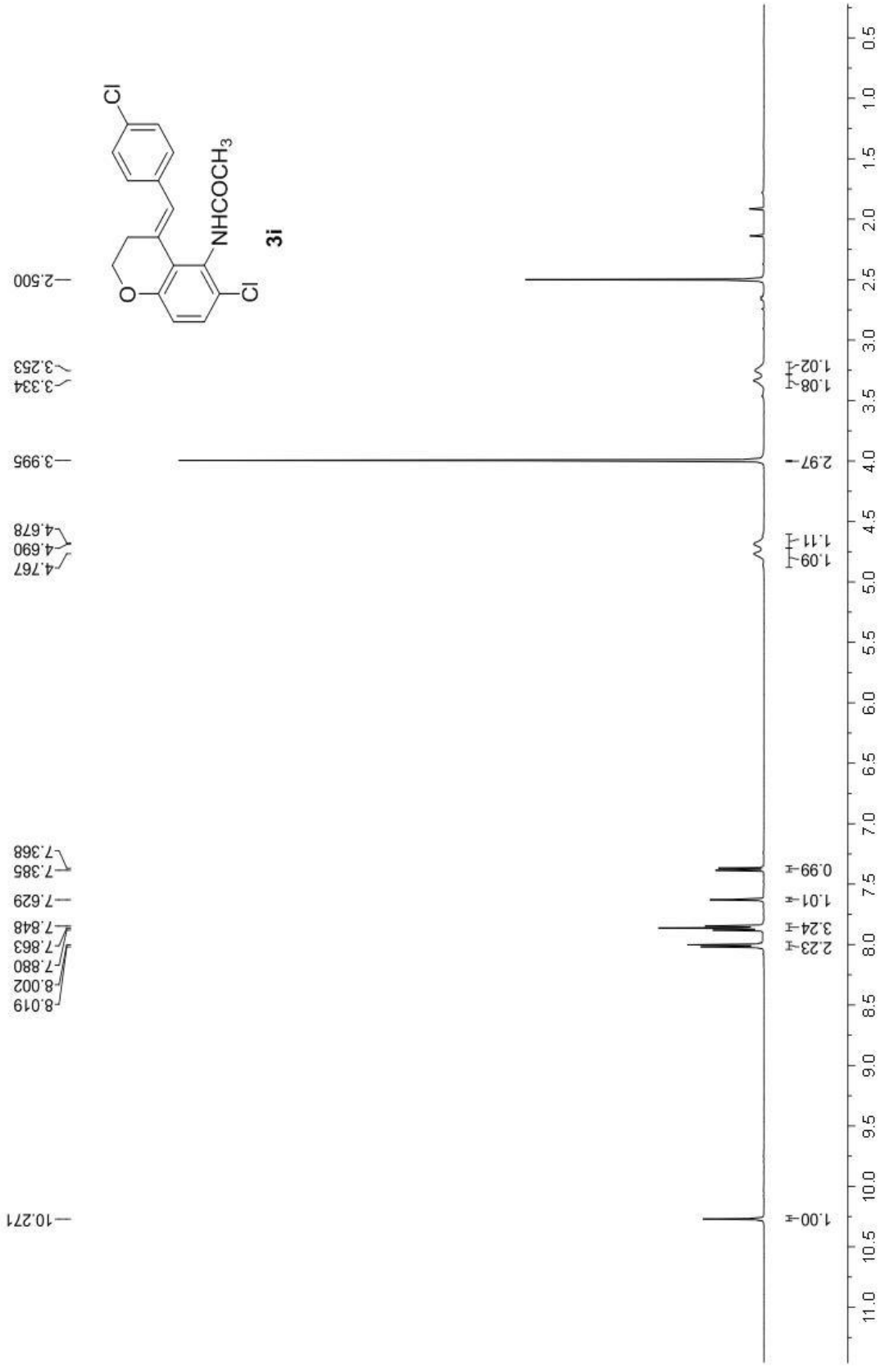


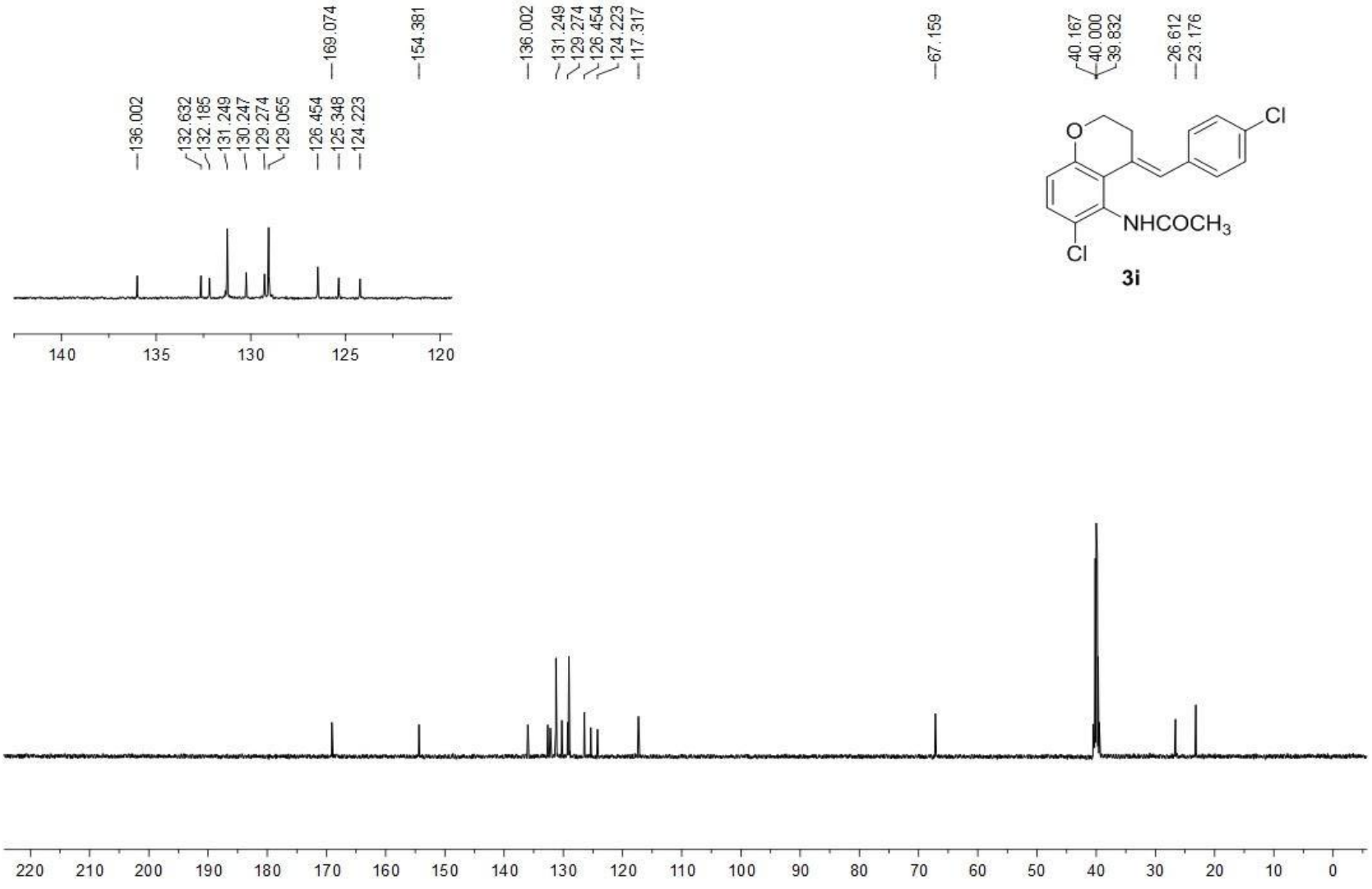
0.000
1.917
2.071
2.728
4.126
6.678
6.695
6.978
7.285
7.301
7.442
7.459
9.415
6.978
7.046
7.063
Cl
O
NHCOCH3
3g
3.03
3.06
2.02
2.00
0.91
0.97
0.98
2.17
2.04
0.96

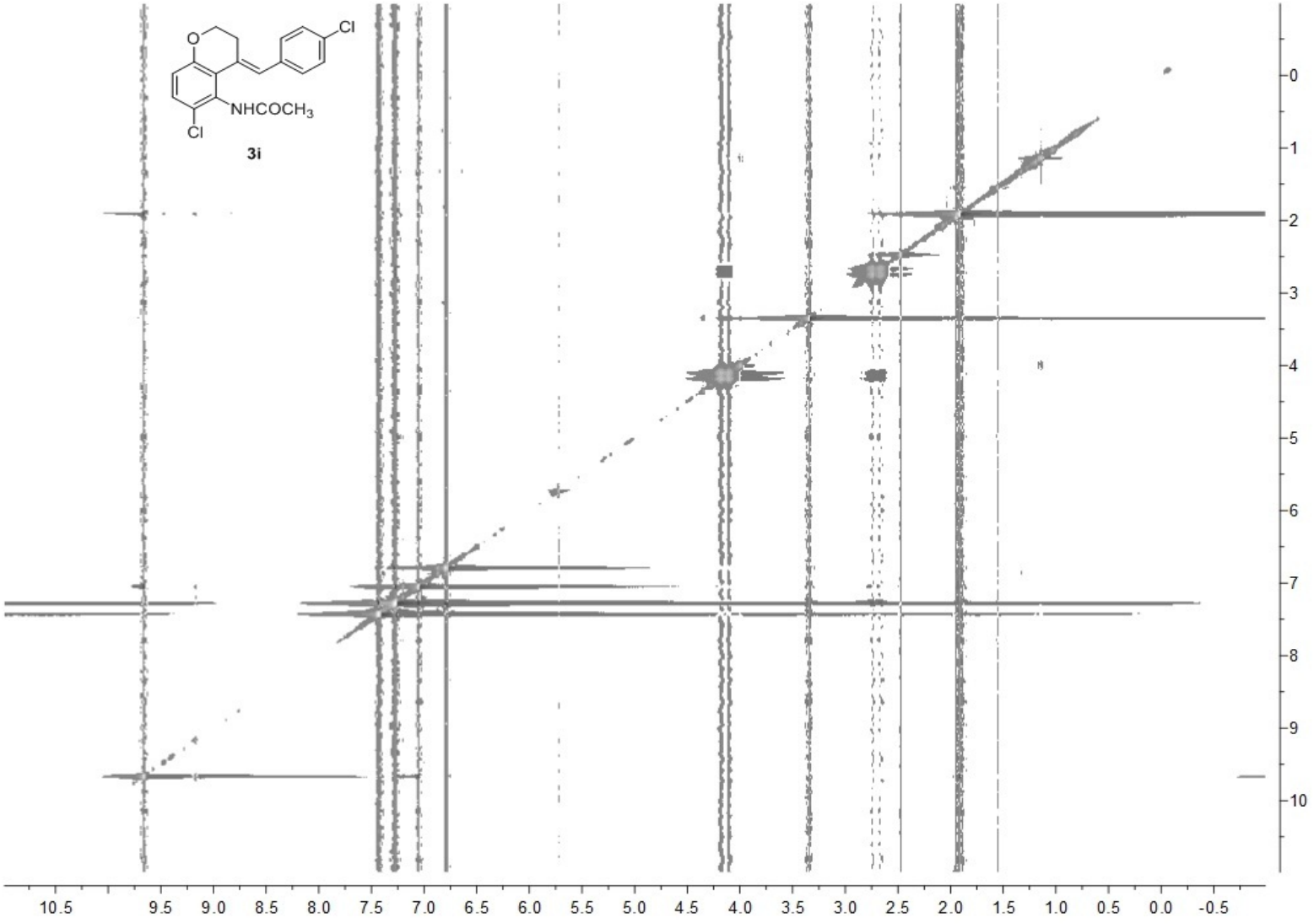

136.413
133.839
131.802
131.031
130.442
128.966
128.889
168.793
153.758
131.175
131.031
130.442
128.966
128.889
125.396
122.053
115.548
66.810
40.167
40.000
39.834
27.200
23.183
18.271
137
135
133
131
129
131.175
131.031
131.3
131.2
131.1
131.0
130.9
O
Cl
NHCOCH3
3g
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Br
NHCOCH3
3h
1.919
2.072
2.500
2.712
2.723
2.735
4.108
4.119
4.130
6.673
6.690
6.961
7.218
7.235
7.567
7.583
9.413
6.961
7.040
7.057
2.99
3.09
2.05
2.00
0.99
0.99
1.03
2.19
2.10
0.99

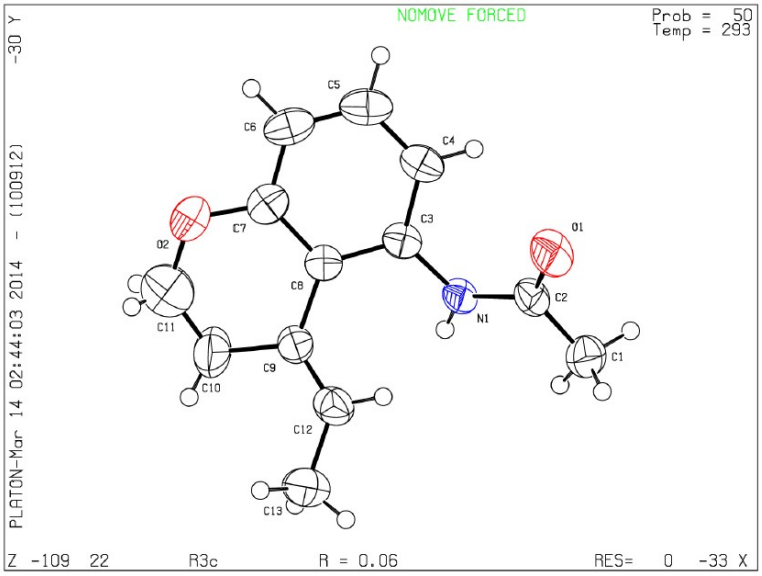

Br
NHCOCH3
O
3h
18.248
23.164
27.204
39.499
39.666
39.833
40.000
40.167
40.334
40.501
66.787
115.535
120.360
125.434
128.874
131.472
136.759
153.742
168.778
122.059
125.434
128.874
130.430
131.065
131.472
131.855
133.816
136.759

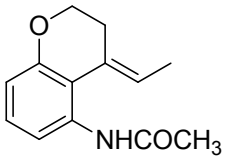

Cl
NHCOCH3
Cl
O
3i
2.500
3.253
3.334
3.995
4.678
4.690
4.767
7.368
7.385
7.629
7.848
7.863
7.880
8.002
8.019
10.271
1.00
2.23
3.24
1.01
0.99
2.97
1.09
1.11
1.08
1.02


169.074
154.381
136.002
131.249
129.274
126.454
124.223
117.317
67.159
40.167
40.000
39.832
26.612
23.176
136.002
132.632
132.185
131.249
130.247
129.274
129.055
126.454
125.348
124.223
140
135
130
125
120
O
Cl
NHCOCH3
Cl
3i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
Cl
NHCOCH3
Cl
3i
f1 (ppm)
0
1
2
3
4
5
6
7
8
9
10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

VI. Crystal structure of 3f





3f