Nickel-Catalyzed Cyclization of 1,7-Enynes for the Selective Synthesis of Dihydrocyclobuta[*c*]quinolin-3-ones and Benzo[*b*]azocin-2-ones

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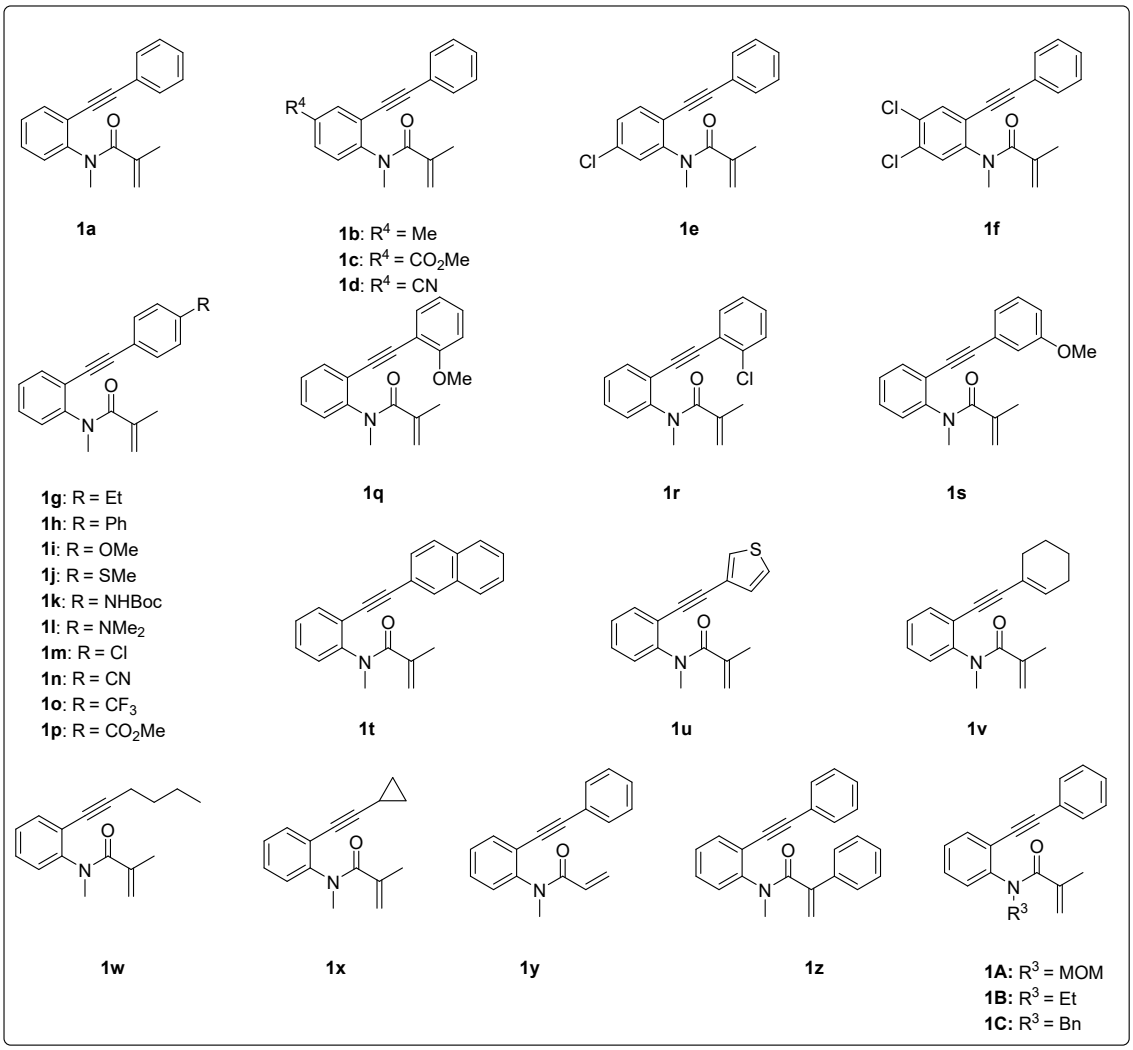
1. General Information

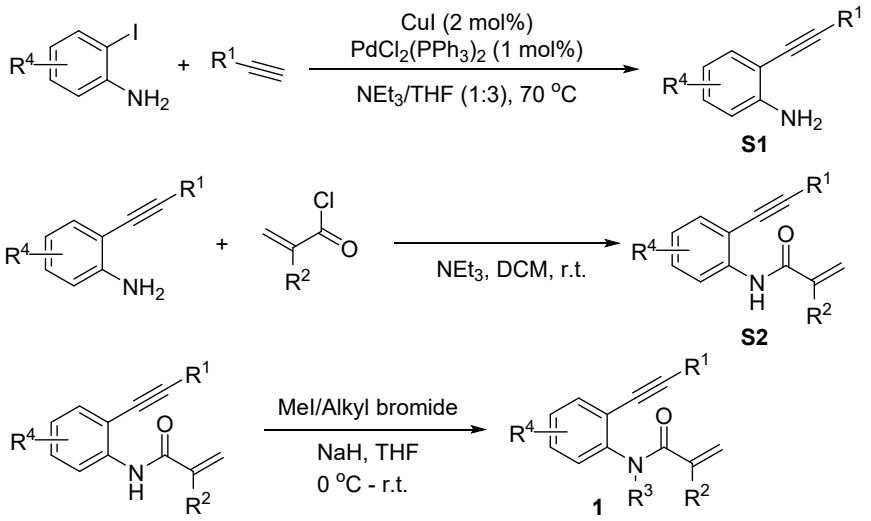
Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 500 AV spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. Coupling constant (*J*) was reported in hertz unit (Hz). The high resolution mass spectra (HRMS) were recorded on an Agilent 6210 LC/TOF spectrometer.

2 Preparation of 1,7-Enynes



1, 7-Enynes are prepared according to the reported procedures[1-4].



General procedure for synthesis of **S1**: To the suspension of $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 1 mol%) and CuI (0.2 mmol, 2 mol%) in a mixture of THF (20 mL) and Et_3N (20 mL), was added aryl iodide (10 mmol) and phenylacetylene (12 mmol). The mixture was allowed to react for 12 h at 70 °C. Then the crude mixture was filtered through a shot pad of celite and washed with CH_2Cl_2 (10 mL) for three times, and the combined organic layer was concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography using ethyl acetate and petroleum ether as eluent.

General procedure for synthesis of **S2**: To a stirred solution of **S1** (1.0 equiv.) in CH_2Cl_2 (5 mL) was added methacryloyl chloride (1.5 equiv.) and Et_3N (2.0 equiv.). The resulted mixture was stirred at room temperature for 12 h. Then the reaction was quenched by saturated $NaHCO_3$ solution and the reaction mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude mixture was purified by flash chromatography using ethyl acetate and petroleum as eluent.

General procedure for the synthesis of substrates **1**: To a solution of NaH (2.0 equiv.) in THF (5 mL) at 0 °C was added a solution of **S2** (1.0 equiv.) in THF dropwise and the reaction mixture was stirred for 30 min. Afterwards iodomethane or alkyl bromide (1.5 equiv.) was added and the reaction mixture was stirred at room temperature followed by TLC. The reaction was quenched by water and the reaction

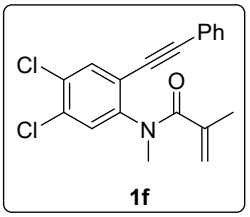
mixture was extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel using ethyl acetate and petroleum as eluent.

Characterization of new compounds:

N-(4, 5-dichloro-2-(phenylethynyl)phenyl)-N-methylmethacrylamide (1f)

white solid, mp: 117-118 °C.

^{1}H NMR (500 MHz, CDCl3) δ 7.64 (s, 1H), 7.54-7.51 (m, 2H), 7.40-7.37 (m, 3H), 7.31 (s, 1H), 5.08 (d, J = 34.5 Hz, 2H), 3.36 (s, 3H), 1.89 (s, 3H).

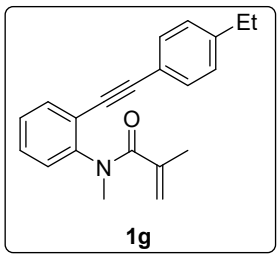


1f

^{13}C NMR (125 MHz, CDCl3) δ 172.03, 145.55, 140.02, 133.82, 132.87, 131.74, 131.66, 129.98, 129.32, 128.59, 122.31, 121.85, 119.76, 96.54, 83.74, 37.00, 20.05.

HRMS(ESI) Calculated for $C_{19}H_{16}Cl_2NO^+$ ($[M+H]^+$): 344.05307, found: 344.06035.

N-(2-((4-ethylphenyl)ethynyl)phenyl)-N-methylmethacrylamide (1g)



1g

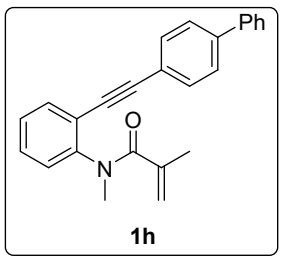
white solid, mp: 97-98 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, J_1 = 7.4, J_2 = 1.2 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.34-7.27 (m, 2H), 7.19 (t, J = 7.2 Hz, 3H), 5.02 (d, J = 16.6 Hz, 2H), 3.38 (s, 3H), 2.67 (q, J = 7.6 Hz, 2H), 1.85 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.31, 146.28, 145.32, 140.50, 132.84, 131.66, 129.01, 128.20, 128.06, 127.45, 122.54, 119.78, 118.90, 95.10, 85.13, 36.86, 28.87, 20.15, 15.32.

HRMS(ESI) Calculated for $C_{21}H_{21}NONa^+$ ($[M+Na]^+$): 326.16231, found: 326.1515

N-(2-([1,1'-biphenyl]-4-ylethynyl)phenyl)-N-methylmethacrylamide (1h)



1h

white solid, mp: 121-123 °C.

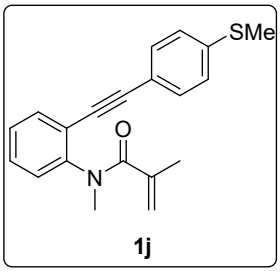
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.61 (m, 7H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.42-7.32 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.06 (d, *J* = 9.8 Hz, 2H), 3.42 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 172.42, 146.38, 141.53, 140.43, 140.23, 132.92, 132.12, 129.32, 128.93, 128.25, 127.79, 127.56, 127.20, 127.08, 122.31, 121.45, 119.19, 94.74, 86.45, 37.01, 20.24.

HRMS(ESI) Calculated for $C_{25}H_{22}NO^+$ ($[M+H]^+$): 352.16231, found: 352.16959.

N-methyl-N-(2-((4-(methylthio)phenyl)ethynyl)phenyl)methacrylamide (1j)

white solid, mp: 96-99 °C.



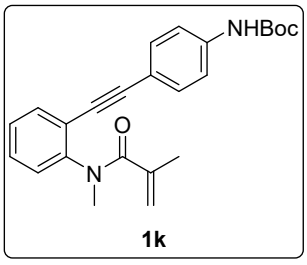
1j

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.36-7.29 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 3H), 5.02 (s, 2H), 3.38 (s, 3H), 2.51 (d, *J* = 0.9 Hz, 3H), 1.85 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 172.38, 146.24, 140.36, 140.16, 132.77, 131.90, 129.17, 128.19, 127.51, 125.77, 122.31, 119.16, 118.68, 94.64, 85.86, 36.97, 20.17, 15.26.

HRMS(ESI) Calculated for $C_{20}H_{20}NOS^+$ ($[M+H]^+$): 322.11873, found: 322.12601.

Tert-butyl(4-((2-(N-methylmethacrylamido)phenyl)ethynyl)phenyl)carbamate (1k)



1k

white solid, mp: 168-169 °C.

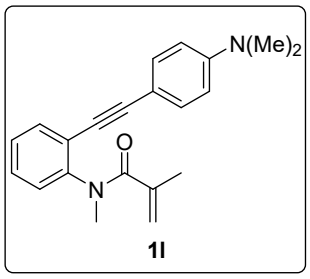
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.5 Hz, 1H), 7.43 (dd, J_1 = 18.2, J_2 = 8.6 Hz, 4H), 7.32-7.27 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 5.30 (s, 1H), 5.01 (d, *J* = 9.0 Hz, 2H), 3.37 (s, 3H), 1.84 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.43, 152.51, 140.39, 139.24, 132.74, 132.48, 128.93, 128.13, 127.48, 122.56, 119.07, 118.19, 116.60, 94.94, 84.95, 80.77, 53.43, 36.95, 28.31, 20.12.

HRMS(ESI) Calculated for $C_{24}H_{26}N_2O_3Na^+$ ($[M+Na]^+$): 413.19434, found:

413.18356.

N-(2-((4-(dimethylamino)phenyl)ethynyl)phenyl)-N-methylmethacrylamide (1l)



1l

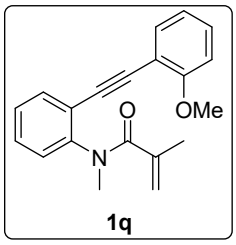
white solid, mp: 127-129 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.49 (m, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.28-7.25 (m, 2H), 7.19-7.13 (m, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.02 (d, *J* = 26.3 Hz, 2H), 3.38 (s, 3H), 3.00 (s, 6H), 1.86 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 172.38, 150.42, 145.78, 140.57, 132.86, 132.36, 128.19, 128.11, 127.37, 123.23, 118.72, 111.83, 109.27, 96.48, 83.98, 40.15, 36.78, 20.17.

HRMS(ESI) Calculated for $C_{21}H_{22}N_2ONa^+$ ([M+Na]$^+$): 341.17321, found: 341.16243.

N-(2-((2-methoxyphenyl)ethynyl)phenyl)-N-methylmethacrylamide (1q)



1q

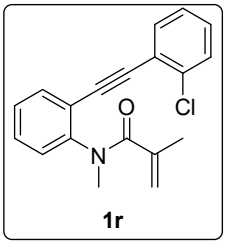
white solid, mp: 85-87 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J_1 = 7.3, J_2 = 1.7 Hz, 1H), 7.49 (dd, J_1 = 7.5, J_2 = 1.6 Hz, 1H), 7.34-7.28 (m, 3H), 7.15 (d, *J* = 7.1 Hz, 1H), 6.94 (dd, J_1 = 10.9, J_2 = 4.0 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 5.04 (d, *J* = 64.7 Hz, 2H), 3.91 (s, 3H), 3.40 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 172.15, 160.27, 146.20, 140.66, 133.34, 132.91, 130.25, 128.95, 128.24, 127.43, 122.67, 120.47, 118.36, 111.97, 110.66, 91.60, 89.72, 55.69, 36.60, 20.20.

HRMS(ESI) Calculated for $C_{20}H_{19}NO_2Na^+$ ([M+Na]$^+$): 328.14158, found: 328.13080.

N-(2-((2-chlorophenyl)ethynyl)phenyl)-N-methylmethacrylamide (1r)



1r

white solid, mp: 77-80 °C.

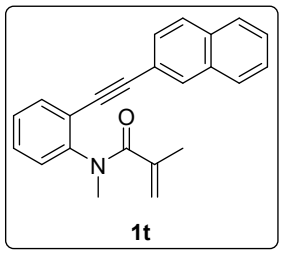
^{1}H NMR (500 MHz, CDCl3) δ 7.61 (dd, J_1 = 7.5, J_2 = 1.1 Hz, 1H), 7.57 (dd, J_1 = 7.3, J_2 = 1.9 Hz, 1H), 7.44-7.41 (m, 1H), 7.38-7.34 (m, 1H), 7.32-7.25 (m, 3H), 7.17 (d, J = 7.6 Hz, 1H), 5.04 (d, J = 40.4 Hz, 2H), 3.39 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 172.12, 146.37, 140.48, 135.93, 133.44, 133.32, 129.76, 129.66, 129.37, 128.32, 127.53, 126.60, 122.64, 121.91, 118.84, 91.44, 90.65, 36.92, 20.20.

HRMS(ESI) Calculated for $C_{19}H_{17}ClNO^+$ ([M+H]$^+$): 310.09204, found: 310.09932.

N-methyl-N-(2-(naphthalen-2-ylethynyl)phenyl)methacrylamide (1t)

white solid, mp: 102-104 °C.



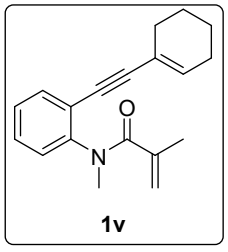
1t

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.88-7.83 (m, 3H), 7.64-7.58 (m, 2H), 7.55-7.51 (m, 2H), 7.39-7.31 (m, 2H), 7.23 (d, J = 7.5 Hz, 1H), 5.07 (d, J = 15.0 Hz, 2H), 3.45 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 172.44, 146.38, 140.43, 133.03, 132.95, 131.67, 129.34, 128.24, 128.23, 127.95, 127.82, 127.57, 126.98, 126.72, 122.29, 119.86, 119.21, 95.23, 86.08, 37.06, 20.24.

HRMS(ESI) Calculated for $C_{23}H_{20}NO^+$ ([M+H]$^+$): 326.14666, found: 326.15394.

N-(2-(cyclohex-1-en-1-ylethynyl)phenyl)-N-methylmethacrylamide (1v)



1v

white solid, mp: 57-60 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.0 Hz, 1H), 7.28-7.21 (m, 2H), 7.11 (d, J = 7.5 Hz, 1H), 6.23 (s, 1H), 4.98 (d, J = 9.9 Hz, 2H), 3.30 (s, 3H), 2.21-2.12 (m, 4H), 1.82 (s, 3H), 1.69-1.59 (m, 4H).

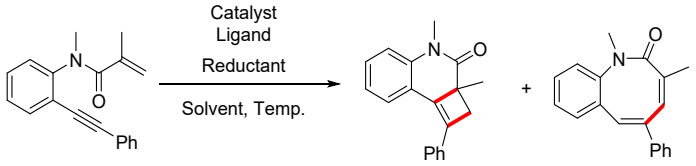
^{13}C NMR (125 MHz, CDCl3) δ 172.21, 145.94, 140.41, 136.36, 132.74, 128.63, 128.08, 127.41, 122.71, 120.36, 118.69, 96.84, 83.06, 36.66, 28.91, 25.78, 22.19, 21.40, 20.18.

HRMS(ESI) Calculated for $C_{19}H_{22}NO^+$ ([M+H]$^+$): 280.16231, found: 280.16959.

3 Nickel-Catalyzed Divergent Cyclization of 1,7-Enynes

3.1 Optimization of reaction conditions

Survey of the reaction parameters[a]

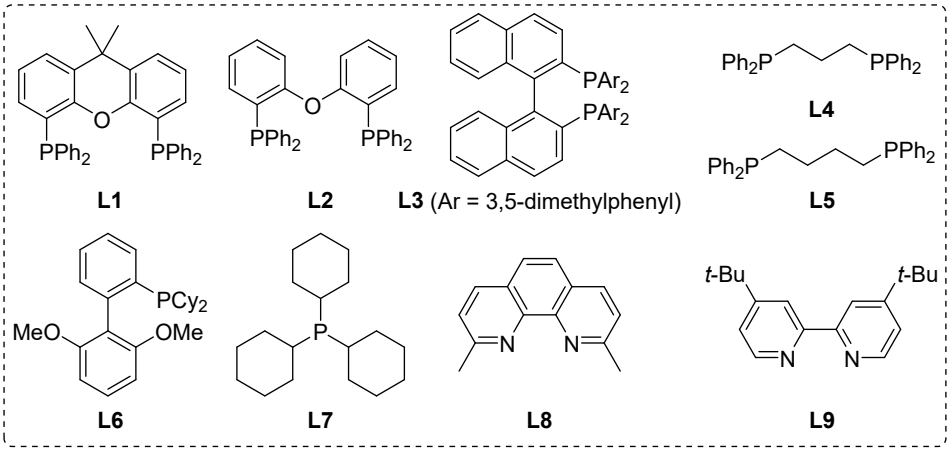


1a **2a** **3a**

Entry	Catalyst (mol%)	Ligand (mol%)	Reducant (equiv.)	Solvent	Temp. (°C)	Yield/**2a**/**3a** (%)
1	$NiBr_2$/10	**L1**/10	Zn/1	THF	60	99/0
2	$NiBr_2$/10	**L1**/10	Zn/0.5	THF	60	98/0
3	$NiBr_2$/10	**L1**/10	Zn/0.2	THF	60	98/0
4	$NiBr_2$/10	**L1**/10	-[b]	THF	60	0/0
5	$NiCl_2$/10	**L1**/10	Zn/0.2	THF	60	89/0
6	$Ni(acac)_2$/10	**L1**/10	Zn/0.2	THF	60	0/0
7	$Ni(PPh_3)_2Br_2$/10	**L1**/10	Zn/0.2	THF	60	0/0
8	$NiCl_2$·glyme/10	**L1**/10	Zn/0.2	THF	60	0/0
9	$Ni(dppe)Cl_2$/10	**L1**/10	Zn/0.2	THF	60	0/0
10	$Ni(OAc)_2$/10	**L1**/10	Zn/0.2	THF	60	0/0
11	$Ni(OTf)_2$/10	**L1**/10	Zn/0.2	THF	60	5/0
12	$Ni(cod)_2$/10	**L1**/10	-[b]	THF	60	98/0
13	$NiBr_2$/10	**L2**/10	Zn/0.2	THF	60	0/0
14	$NiBr_2$/10	**L3**/10	Zn/0.2	THF	60	0/0
15	$NiBr_2$/10	**L4**/10	Zn/0.2	THF	60	0/0
16	$NiBr_2$/10	**L5**/10	Zn/0.2	THF	60	0/0
17	$NiBr_2$/10	**L6**/20	Zn/0.2	THF	60	0/0
18	$NiBr_2$/10	**L7**/20	Zn/0.2	THF	60	0/0
19	$NiBr_2$/10	**L8**/10	Zn/0.2	THF	60	0/0
20	$NiBr_2$/10	**L9**/10	Zn/0.2	THF	60	0/0
21	$NiBr_2$/10	**L1**/10	Zn/0.2	Toluene	60	86/0
22	$NiBr_2$/10	**L1**/10	Zn/0.2	CH_3CN	60	0/0
23	$NiBr_2$/10	**L1**/10	Zn/0.2	DMF	60	35/0
24	$NiBr_2$/10	**L1**/10	Zn/0.2	Dioxane	60	94/0
25	$NiBr_2$/10	**L1**/10	Fe/0.2	THF	60	0/0
26	$NiBr_2$/10	**L1**/10	Mn/0.2	THF	60	95/0
27	*$NiBr_2$/5*	***L1*/5**	*Zn/0.2*	*THF*	*60*	*98/0*
28	-[c]	**L1**/5	Zn/0.2	THF	60	0/0
29	$NiBr_2$/5	-[d]	Zn/0.2	THF	60	0/0
30	$NiBr_2$/1[e]	**L1**/1	Zn/0.2	THF	60	63/0
31	$NiBr_2$/5	**L1**/5	Zn/0.2	THF	80	81/18
32	$NiBr_2$/5	**L1**/5	Zn/0.2	THF	100	50/47

33	$NiBr_2$/5	**L1**/5	Zn/0.2	THF	120	8/91
34	$NiBr_2$/5	**L1**/5	Zn/0.2	THF	140	0/98

[a]Reaction conditions unless otherwise noted: **1a** (0.1 mmol), catalyst, ligand, reducant, solvent (1 mL), 60-140 °C, 6 h under N_2 atmosphere. Isolated yields were given. [b]No reducant. [c]No catalyst. [d]No ligand. [e]For 24 h.

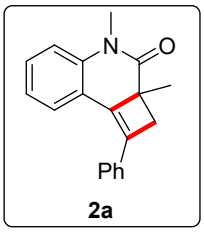


3.2 Experimental details and characterization of products

General procedure for the synthesis of dihydrocyclobuta[*c*]quinolin-3-ones **2**: In a 25 mL flame-dried Schlenk tube, 1, 7-Enynes (0.4 mmol), $NiBr_2$ (5 mol%, 0.02 mmol), **L1** (5 mol%, 0.02 mmol), Zn (0.2 equiv, 0.08 mmol), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 60 °C for 6 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 50 : 1) to provide the product **2**.

General procedure for the synthesis of benzo[*b*]azocin-2-ones **3**: In a 25 mL flame-dried Schlenk tube, 1, 7-Enynes (0.4 mmol), $NiBr_2$ (5 mol%, 0.02 mmol), **L1** (5 mol%, 0.02 mmol), Zn (0.2 equiv, 0.08 mmol), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 140 °C for 6 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 10 : 1) to provide the product **3**.

2a,4-dimethyl-1-phenyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2a)



2a

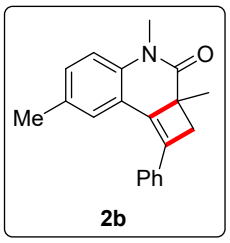
Yield: 98% (107.8 mg), white solid, mp: 78-79 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.42-7.28 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 3.38 (s, 3H), 3.35 (d, *J* = 13.7 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.06, 141.66, 138.47, 137.26, 134.55, 128.70, 128.53, 128.43, 125.83, 125.78, 122.70, 121.89, 115.70, 43.03, 39.59, 30.13, 21.79.

HRMS(ESI) Calculated for $C_{19}H_{18}NO^+$ ([M+H]$^+$): 276.13101, found: 276.13829.

2a,4,7-trimethyl-1-phenyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2b)



2b

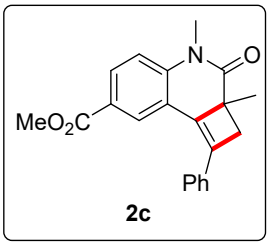
Yield: 90% (140.1 mg), white solid, mp: 136-137 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.6-7.53 (m, 2H), 7.50 (d, *J* = 1.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.16 (dd, J_1 = 8.3, J_2 = 1.4 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.36 (d, 4H, overlap), 2.90 (d, *J* = 13.4 Hz, 1H), 2.43 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.98, 139.40, 138.18, 137.52, 134.67, 132.26, 129.28, 128.55, 128.37, 126.25, 125.83, 121.85, 115.63, 43.07, 39.53, 30.12, 21.80, 20.83.

HRMS(ESI) Calculated for $C_{20}H_{20}NO^+$ ([M+H]$^+$): 290.14666, found: 290.15394.

Methyl 2a,4-dimethyl-3-oxo-1-phenyl-2,2a,3,4-tetrahydrocyclobuta[*c*]quinoline-6-carboxylate (2c)



2c

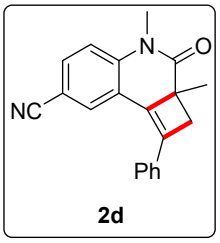
Yield: 80% (106.6 mg), white solid, mp: 155-156 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.9 Hz, 1H), 8.03 (dd, J_1 = 8.6, J_2 =1.9 Hz, 1H), 7.59-7.52 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H), 3.41 (s, 3H), 3.38 (d, *J* = 13.6 Hz, 1H), 2.93 (d, *J* = 13.6 Hz, 1H), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) 174.02, 166.41, 145.23, 139.85, 135.76, 134.22, 130.31, 128.80, 128.68, 127.04, 126.00, 124.37, 121.60, 115.35, 52.22, 42.94, 39.78, 30.35, 21.72.

HRMS(ESI) Calculated for $C_{21}H_{20}NO_3^+$ ([M+H]$^+$): 334.13649, found: 334.14377.

2a,4-dimethyl-3-oxo-1-phenyl-2,2a,3,4-tetrahydrocyclobuta[*c*]quinoline-7-carbonitrile (2d)



2d

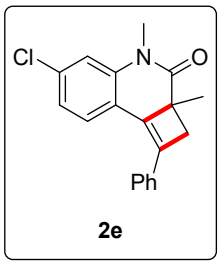
Yield: 87% (104.4 mg), white solid, mp: 164-167 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 1.9 Hz, 1H), 7.55 (dd, J_1 = 8.6, J_2 = 1.9 Hz, 1H), 7.43-7.39 (m, 2H), 7.36-7.31 (m, 2H), 7.30-7.24 (m, 1H), 7.07 (d, J = 8.6 Hz, 1H), 3.30 (d, 4H, overlap), 2.86 (d, J = 13.8 Hz, 1H), 1.28 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.66, 144.99, 141.56, 134.11, 133.82, 132.58, 129.30, 129.07, 128.83, 126.05, 122.47, 118.77, 116.13, 105.93, 42.86, 40.02, 30.35, 21.71.

HRMS(ESI) Calculated for $C_{20}H_{17}N_2O^+$ ([M+H]$^+$): 301.12626, found: 301.13354.

6-chloro-2a,4-dimethyl-1-phenyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2e)



2e

Yield: 75% (92.7 mg), white solid, mp: 111-112 °C.

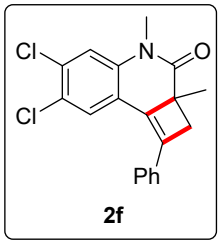
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 1H), 7.56-7.50 (m, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.34-7.29 (m, 1H), 7.16 (dd, J_1 = 8.1, J_2 = 1.9 Hz, 1H), 7.09 (d, J = 1.8 Hz, 1H), 3.37 (s, 3H), 3.37 (d, J = 13.5 Hz, 1H), 2.91 (d, J = 13.6 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.81, 142.80, 139.22, 135.93, 134.34, 134.20, 128.68, 128.63, 126.62, 125.88, 122.59, 120.23, 116.13, 42.93, 39.74, 30.21, 21.82.

HRMS(ESI) Calculated for $C_{19}H_{17}ClNO^+$ ([M+H]$^+$): 310.09204, found: 310.09932.

6,7-dichloro-2a,4-dimethyl-1-phenyl-2,4-dihydrocyclobuta[c]quinolin-3(*2aH*)-one (2f)

Yield: 82% (112.5 mg), white solid, mp: 182-184 °C.



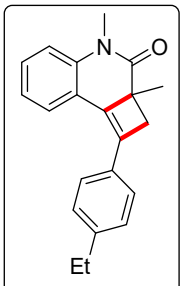
2f

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.51-7.47 (m, 2H), 7.42-7.36 (m, 2H), 7.36-7.31 (m, 1H), 7.16 (s, 1H), 3.35 (d, *J* = 13.7 Hz, 1H), 3.35 (s, 3H), 2.90 (d, *J* = 13.7 Hz, 1H), 1.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.45, 141.13, 140.59, 134.51, 134.02, 132.06, 129.04, 128.75, 126.74, 126.07, 126.00, 121.63, 117.57, 42.91, 39.87, 30.33, 21.77.

HRMS(ESI) Calculated for $C_{19}H_{16}Cl_2NO^+$ ([M+H]$^+$): 343.05307, found: 344.06035.

1-(4-ethylphenyl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2g)



2g

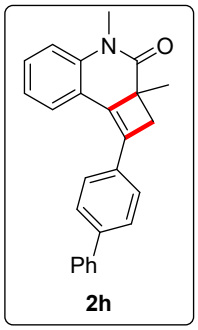
Yield: 91% (110.4 mg), white solid, mp: 52-53 °C.

^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.42-7.31 (m, 1H), 7.26-7.13 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 3.40 (s, 3H), 3.37 (d, *J* = 13.4 Hz, 1H), 2.91 (d, *J* = 13.4 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.38 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.16, 144.93, 141.63, 138.59, 136.08, 132.18, 128.52, 128.08, 125.93, 125.77, 122.68, 122.07, 115.69, 42.96, 39.64, 30.14, 28.83, 21.85, 15.55.

HRMS(ESI) Calculated for $C_{21}H_{22}NO^+$ ([M+H]$^+$): 304.16231, found: 304.16959

1-([1,1'-biphenyl]-4-yl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2h)



2h

Yield: 78% (109.6 mg), white solid, mp: 181-183 °C.

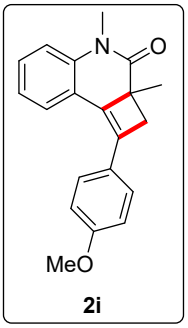
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 6H), 7.47 (t, *J* = 6.6 Hz, 2H), 7.38 (t, *J* = 6.2 Hz, 2H), 7.22 (t, *J* = 6.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 3.42 (s, 4H, overlap), 2.96 (d, *J* = 13.3 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.04, 141.72, 141.08, 140.50,

138.13, 137.48, 133.58, 128.89, 128.79, 127.57, 127.22, 126.97, 126.35, 125.82, 122.78, 121.95, 115.79, 43.20, 39.66, 30.18, 21.90.

HRMS(ESI) Calculated for $C_{25}H_{22}NO^+$ ([M+H]$^+$): 352.16231, found: 352.16959.

1-(4-methoxyphenyl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2i)



2i

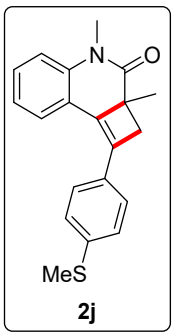
Yield: 97% (118.4 mg), white solid, mp: 127-129 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.45-7.37 (m, 2H), 7.27-7.19 (m, 1H), 7.08-7.01 (m, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.84-6.73 (m, 2H), 3.71 (s, 3H), 3.28 (s, 3H), 3.23 (d, J = 13.4 Hz, 1H), 2.77 (d, J = 13.4 Hz, 1H), 1.25 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.17, 159.84, 141.58, 138.20, 134.37, 128.36, 127.71, 127.33, 125.58, 122.66, 122.16, 115.69, 113.99, 55.31, 42.81, 39.65, 30.14, 21.82.

HRMS(ESI) Calculated for $C_{20}H_{20}NO_2^+$ ([M+H]$^+$): 306.14158, found: 306.14886.

2a,4-dimethyl-1-(4-(methylthio)phenyl)-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2j)



2j

Yield: 86% (110.5 mg), white solid, mp: 145-147 °C.

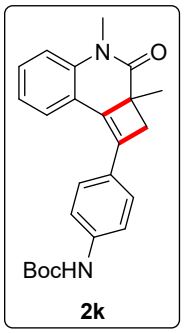
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.4, 1.2 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.38-7.32 (m, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 3.39 (s, 3H), 3.34 (d, J = 13.4 Hz, 1H), 2.88 (d, J = 13.4 Hz, 1H), 2.50 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.03, 141.62, 139.18, 137.92, 136.52, 131.41, 128.63, 126.20, 125.71, 122.70, 121.95, 115.73, 43.04, 39.54, 30.15, 21.81, 15.57.

HRMS(ESI) Calculated for $C_{20}H_{20}NOS^+$ ([M+H]$^+$): 322.11873, found: 322.12601.

Tert-butyl(4-(2a,4-dimethyl-3-oxo-2,2a,3,4-tetrahydrocyclobuta[*c*]quinolin-1-yl)

phenyl)carbamate (2k)



2k

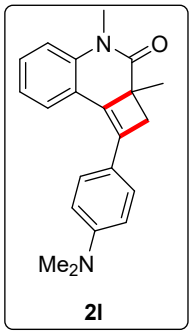
Yield: 83% (129.5 mg), white solid, mp: 175-177 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.52-7.45 (m, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.36-7.31 (m, 1H), 7.21-7.13 (m, 1H), 7.09 (d, J = 8.1 Hz, 1H), 6.79 (s, 1H), 3.39 (s, 3H), 3.33 (d, J = 13.4 Hz, 1H), 2.87 (d, J = 13.4 Hz, 1H), 1.52 (s, 9H), 1.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.17, 152.52, 141.57, 138.69, 138.10, 135.31, 129.51, 128.46, 126.68, 125.63, 122.70, 122.06, 118.22, 115.70, 80.72, 42.90, 39.58, 30.15, 28.34, 21.80.

HRMS(ESI) Calculated for $C_{24}H_{27}N_2O_3^+$ ($[M+H]^+$): 391.19434, found: 391.20162.

1-(4-(dimethylamino)phenyl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2l)



2l

yield: 87% (110.7 mg), white solid, mp: 130-131 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J_1 = 7.5, J_2 = 1.3 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.38-7.28 (m, 1H), 7.20-7.11 (m, 1H), 7.08 (d, J = 8.2 Hz, 1H), 6.71 (d, J = 7.4 Hz, 2H), 3.39 (s, 3H), 3.33 (d, J = 13.4 Hz, 1H), 3.00 (s, 6H), 2.87 (d, J = 13.4 Hz, 1H), 1.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.44, 150.41, 141.46, 138.96, 127.79, 127.15, 126.64, 125.54, 123.31, 122.68, 122.54, 115.58, 111.94, 42.61, 40.34, 39.59, 30.14, 21.93.

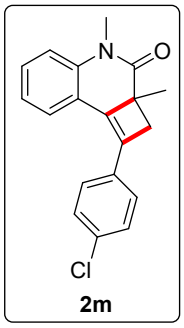
HRMS(ESI) Calculated for $C_{21}H_{23}N_2O^+$ ($[M+H]^+$): 319.17321, found: 319.18049.

1-(4-chlorophenyl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2m)

Yield: 68% (84.1 mg), white solid, mp: 100-102 °C.

^{1}HNMR (500 MHz, $CDCl_3$) δ 7.70 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.59-7.53 (m, 2H), 7.42-7.34 (m, 2H), 7.34-7.28 (m, 1H), 7.22-7.16 (m, 1H), 7.11 (d, J = 8.2 Hz, 1H),

3.40 (s, 3H), 3.37 (d, J = 13.5 Hz, 1H), 2.91 (d, J = 13.4 Hz, 1H), 1.38 (s, 3H).

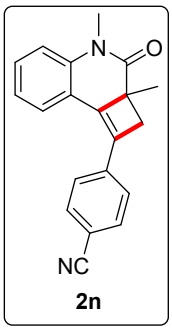


2m

^{13}C NMR (125 MHz, CDCl$_3$) δ 174.09, 141.67, 138.48, 137.27, 134.56, 128.71, 128.55, 128.45, 125.84, 125.80, 122.72, 121.91, 115.72, 43.04, 39.60, 30.15, 21.80.

HRMS(ESI) Calculated for $C_{19}H_{17}ClNO^+$ ([M+H]$^+$): 310.09204, found: 310.09932.

4-(2a,4-dimethyl-3-oxo-2,2a,3,4-tetrahydrocyclobuta[*c*]quinolin-1-yl)benzonitrile (2n)



2n

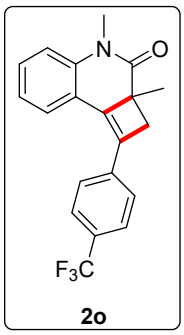
Yield: 90% (108.0 mg), white solid, mp: 155-156 °C.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68-7.57 (m, 5H), 7.46-7.36 (m, 1H), 7.23-7.18 (m, 1H), 7.13 (d, J = 8.2 Hz, 1H), 3.39 (s, 3H), 3.35 (d, J = 13.4 Hz, 1H), 2.91 (d, J = 13.4 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 173.47, 142.30, 141.80, 138.43, 136.21, 132.39, 129.69, 126.13, 125.73, 122.95, 121.08, 118.84, 115.99, 111.26, 43.70, 39.39, 30.19, 21.79.

HRMS(ESI) Calculated for $C_{20}H_{17}N_2O^+$ ([M+H]$^+$): 301.12626, found: 301.13354.

2a,4-dimethyl-1-(4-(trifluoromethyl)phenyl)-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2o)



2o

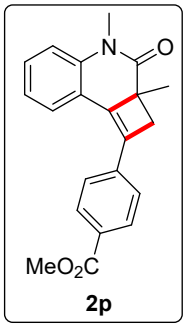
Yield: 95% (130.4 mg), white solid, mp: 98-100 °C.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (dd, J_1 = 7.5, J_2 =1.3 Hz, 1H), 7.66-7.60 (m, 4H), 7.45-7.37 (m, 1H), 7.24-7.18 (m, 1H), 7.13 (d, J = 8.2 Hz, 1H), 3.40 (s, 3H), 3.38 (d, J = 13.5 Hz, 1H), 2.93 (d, J = 13.4 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 173.70, 141.78, 140.53, 137.67, 136.75, 129.87 (d, $^2J_{C\text{-}F}$ = 32.5 Hz), 129.35, 125.92, 125.71, 125.53 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.04 (d, $^1J_{C\text{-}F}$ = 272.0 Hz), 122.86, 121.32, 115.90, 43.48, 39.53, 30.17, 21.78.

HRMS(ESI) Calculated for $C_{20}H_{17}F_3NO^+$ ([M+H]$^+$): 344.11840, found: 344.12568.

Methyl 4-(2a,4-dimethyl-3-oxo-2,2a,3,4-tetrahydrocyclobuta[*c*]quinolin-1-yl)benzoate (2p)



2p

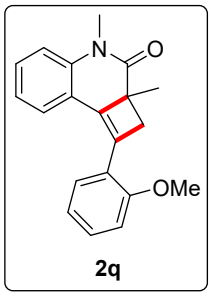
yield: 95% (126.6 mg), white solid, mp: 158-160 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.69 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.41-7.36 (m, 1H), 7.22-7.17 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 3.38 (d, *J* = 15.6 Hz, 4H), 2.92 (d, *J* = 13.4 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.70, 166.66, 141.78, 140.63, 138.56, 137.26, 129.88, 129.49, 129.28, 125.80, 125.62, 122.84, 121.46, 115.84, 52.14, 43.50, 39.55, 30.15, 21.79.

HRMS(ESI) Calculated for $C_{21}H_{20}NO_3^+$ ([M+H]$^+$): 334.13649, found: 334.14377.

1-(2-methoxyphenyl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2q)



2q

Yield: 93% (113.5 mg), light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.47 (m, 2H), 7.37-7.24 (m, 2H), 7.16-7.11 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.99-6.93 (m, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 3.77 (s, 3H), 3.42 (d, *J* = 13.7 Hz, 1H), 3.40 (s, 3H), 3.03 (d, *J* = 13.7 Hz, 1H), 1.35 (s, 3H).

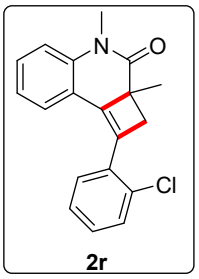
^{13}C NMR (125 MHz, $CDCl_3$) δ 174.39, 157.28, 141.72, 137.62, 135.23, 129.63, 128.33, 128.17, 127.40, 123.79, 122.94, 122.17, 120.35, 115.29, 110.79, 54.68, 43.69, 41.68, 30.15, 21.73.

HRMS(ESI) Calculated for $C_{20}H_{20}NO_2^+$ ([M+H]$^+$): 306.14158, found: 306.14886.

1-(2-chlorophenyl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2r)

Yield: 75% (92.7 mg), light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.64 (m, 1H), 7.59-7.48 (m, 1H), 7.43-7.32 (m,



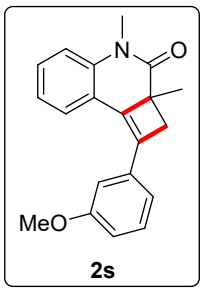
2r

2H), 7.24-7.15 (m, 2H), 7.15-7.05 (m, 2H), 3.58 (d, J = 13.9 Hz, 1H), 3.41 (s, 3H), 3.23 (d, J = 13.9 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.89, 141.75, 141.03, 136.84, 133.09, 132.68, 130.57, 129.16, 129.01, 128.77, 126.44, 125.76, 122.60, 121.42, 115.69, 44.48, 43.88, 30.12, 22.02.

HRMS(ESI) Calculated for $C_{19}H_{17}ClNO^+$ ([M+H]$^+$): 310.09204, found: 310.09932.

1-(3-methoxyphenyl)-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2s)



2s

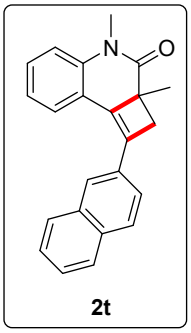
Yield: 92% (112.3 mg), light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.29-7.22 (m, 1H), 7.21-7.15 (m, 1H), 7.09-7.04 (m, 2H), 7.01-6.97 (m, 2H), 6.75 (dd, J = 8.2, 2.0 Hz, 1H), 3.72 (s, 3H), 3.29 (s, 3H), 3.25 (d, J = 13.4 Hz, 1H), 2.79 (d, J = 13.4 Hz, 1H), 1.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.00, 159.71, 141.71, 138.36, 137.66, 135.88, 129.61, 128.78, 125.76, 122.72, 121.83, 118.47, 115.76, 114.15, 111.20, 55.26, 43.03, 39.68, 30.14, 21.79.

HRMS(ESI) Calculated for $C_{20}H_{20}NO_2^+$ ([M+H]$^+$): 306.14158, found: 306.14886.

2a,4-dimethyl-1-(naphthalen-2-yl)-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2t)



2t

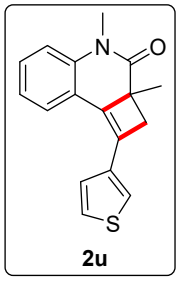
Yield: 94% (122.2 mg), white solid, mp: 128-130 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.85-7.77 (m, 4H), 7.56-7.45 (m, 2H), 7.44-7.34 (m, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H), 3.48 (d, J = 13.3 Hz, 1H), 3.42 (s, 3H), 3.04 (d, J = 13.3 Hz, 1H), 1.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.06, 141.76, 138.47, 137.80, 133.35, 133.22, 132.18, 128.80, 128.31, 128.18, 127.77, 126.50, 126.40, 125.80, 125.19, 123.60, 122.79, 122.02, 115.80, 43.17, 39.68, 30.19, 21.86.

HRMS(ESI) Calculated for $C_{23}H_{20}NO^+$ ([M+H]$^+$): 326.14666, found: 326.15394.

2a,4-dimethyl-1-(thiophen-3-yl)-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2u)



2u

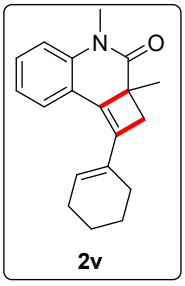
Yield : 95% (106.8 mg), white solid, mp: 103-104 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J_1 = 7.4, J_2 =1.2 Hz, 1H), 7.40-7.30 (m, 4H), 7.16 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 3.39 (s, 3H), 3.36 (d, J = 13.4 Hz, 1H), 2.88 (d, J = 13.4 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.94, 141.62, 136.88, 134.91, 133.52, 128.57, 126.28, 125.57, 125.35, 122.96, 122.75, 121.72, 115.68, 43.67, 40.31, 30.13, 21.94.

HRMS(ESI) Calculated for $C_{17}H_{16}NOS^+$ ([M+H]$^+$): 282.08743, found: 282.09471.

1-(cyclohex-1-en-1-yl)-2a,4-dimethyl-2,4-dihydrocyclobuta[c]quinolin-3(2aH)-one (2v)



2v

Yield: 97% (108.3 mg), white solid, mp: 109-110 °C.

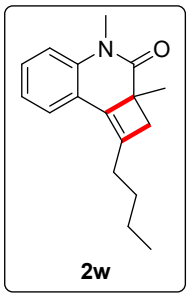
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.39 (m, 1H), 7.30-7.20 (m, 1H), 7.14-6.99 (m, 2H), 5.87 (t, J = 4.0 Hz, 1H), 3.35 (s, 3H), 3.09 (d, J = 13.3 Hz, 1H), 2.61 (d, J = 13.3 Hz, 1H), 2.49-2.38 (m, 1H), 2.31-2.23 (m, 1H), 2.17 (d, J = 1.7 Hz, 2H), 1.82-1.71 (m, 1H), 1.72-1.61 (m, 1H), 1.61-1.51 (m, 2H), 1.25 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.38, 141.54, 140.96, 133.99, 133.73, 128.87, 127.95, 126.24, 122.45, 122.26, 115.47, 42.16, 38.79, 30.11, 26.88, 25.71, 22.36, 21.88, 21.60.

HRMS(ESI) Calculated for $C_{19}H_{22}NO^+$ ([M+H]$^+$): 280.16231, found: 280.16959.

1-butyl-4-methyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2w)

yield: 92% (93.9 mg), light yellow oil.



2w

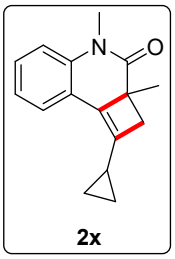
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.23 (m, 2H), 7.07-7.01 (m, 2H), 3.35 (s, 3H), 3.01 (d, J = 13.8 Hz, 1H), 2.53 (d, J = 13.8 Hz,

1H), 2.26 (t, J = 7.5 Hz, 2H), 1.50 (dt, J_1 = 12.5, J_2 = 7.0 Hz, 2H), 1.34 (dd, J_1 = 15.0, J_2 = 7.6 Hz, 2H), 1.26 (s, 3H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.54, 144.00, 141.33, 137.12, 127.80, 125.00, 122.48, 121.48, 115.34, 43.06, 41.97, 29.98, 29.49, 22.59, 21.97, 13.84.

HRMS(ESI) Calculated for $C_{17}H_{22}NO^+$ ($[M+H]^+$): 256.16231, found: 256.16959.

1-cyclopropyl-2a,4-dimethyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2x)



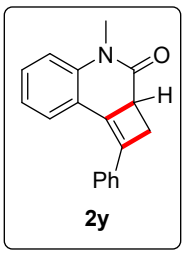
Yield: 91% (87.0 mg), white solid, mp: 55-56 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.28 (m, 1H), 7.31-7.23 (m, 1H), 7.15-6.95 (m, 2H), 3.36 (s, 3H), 2.81 (d, J = 13.5 Hz, 1H), 2.32 (d, J = 13.5 Hz, 1H), 1.79-1.60 (m, 1H), 1.25 (s, 3H), 0.89-0.80 (m, 1H), 0.80-0.69 (m, 2H), 0.65-0.54 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.34, 144.52, 141.07, 135.18, 127.64, 124.90, 122.58, 121.56, 115.42, 41.92, 38.77, 30.04, 21.91, 11.35, 6.78, 5.37.

HRMS(ESI) Calculated for $C_{16}H_{18}NO^+$ ($[M+H]^+$): 240.13101, found: 240.13829.

4-methyl-1-phenyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2y)



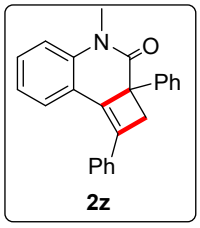
yield: 94% (98.2 mg), light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.51 (m, 1H), 7.45 (dd, J_1 = 8.0, J_2 = 1.3 Hz, 1H), 7.41-7.37 (m, 3H), 7.33-7.30 (m, 3H), 7.09-7.06 (m, 1H), 6.77 (s, 1H), 5.94 (d, J = 0.6 Hz, 1H), 5.45 (s, 1H), 3.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.17, 150.82, 145.52, 140.09, 138.77, 130.53, 128.69, 128.34, 127.92, 126.31, 121.95, 121.84, 120.26, 116.87, 114.35, 29.46.

HRMS(ESI) Calculated for $C_{18}H_{16}NO^+$ ($[M+H]^+$): 262.11536, found: 262.12264.

4-methyl-1,2a-diphenyl-2,4-dihydrocyclobuta[c]quinolin-3(*2aH*)-one (2z)



yield: 81% (109.2 mg), white solid, mp: 160-161 °C.

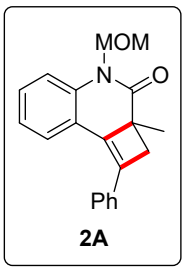
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.5, 1.3 Hz, 1H), 7.66-

7.62 (m, 2H), 7.43-7.38 (m, 4H), 7.36-7.31 (m, 2H), 7.27-7.18 (m, 4H), 7.03 (d, J = 8.2 Hz, 1H), 3.79 (d, J = 13.4 Hz, 1H), 3.41 (s, 3H), 3.14 (d, J = 13.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.51, 141.74, 141.08, 140.02, 134.66, 134.19, 128.84, 128.81, 128.63, 128.49, 127.21, 126.11, 126.04, 125.42, 123.03, 122.84, 115.97, 49.73, 42.70, 30.50.

HRMS(ESI) Calculated for $C_{24}H_{20}NO^+$ ([M+H]$^+$): 338.14666, found: 338.15394.

4-(methoxymethyl)-2a-methyl-1-phenyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2A)



2A

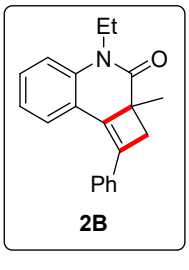
yield: 95% (116.0 mg), white solid, mp: 110-111 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.61-7.57 (m, 2H), 7.45 (d, J = 8.1 Hz, 1H), 7.42-7.35 (m, 3H), 7.35-7.29 (m, 1H), 7.26-7.17 (m, 1H), 5.84 (d, J = 10.7 Hz, 1H), 4.89 (d, J = 10.7 Hz, 1H), 3.43 (s, 3H), 3.39 (d, J = 13.5 Hz, 1H), 2.94 (d, J = 13.5 Hz, 1H), 1.45 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.89, 140.96, 138.49, 136.82, 134.49, 129.02, 128.60, 128.57, 125.90, 125.67, 123.42, 121.62, 116.72, 74.34, 56.00, 43.05, 39.45, 21.68.

HRMS(ESI) Calculated for $C_{20}H_{19}NO_2Na^+$ ([M+Na]$^+$): 328.14158, found: 328.13080.

4-ethyl-2a-methyl-1-phenyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2B)



2B

yield: 91% (105.2 mg), white solid, mp: 103-104 °C.

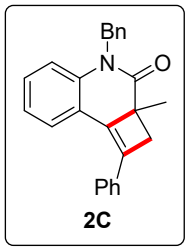
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 7.5, 1.5 Hz, 1H), 7.60-7.57 (m, 2H), 7.41-7.34 (m, 3H), 7.33-7.29 (m, 1H), 7.21-7.15 (m, 1H), 7.12 (d, J = 8.3 Hz, 1H), 4.19-4.11 (m, 1H), 3.94-3.86 (m, 1H), 3.39 (d, J = 13.5 Hz, 1H), 2.91 (d, J = 13.5 Hz, 1H), 1.37 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.57, 140.55, 138.34, 137.47, 134.65, 128.75, 128.55, 128.40, 126.08, 125.87, 122.49, 122.02, 115.46, 42.92, 39.45, 37.62, 21.65,

12.76.

HRMS(ESI) Calculated for $C_{20}H_{20}NO^+$ ([M+H]$^+$): 290.14666, found: 290.15394.

4-benzyl-2a-methyl-1-phenyl-2,4-dihydrocyclobuta[*c*]quinolin-3(*2aH*)-one (2C)



2C

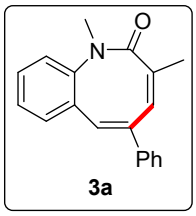
yield: 83% (116.6 mg), white solid, mp: 149-150 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J_1 = 7.4, J_2 = 1.5 Hz, 1H), 7.65-7.62 (m, 2H), 7.44-40 (m, 2H), 7.37-7.33 (m, 3H), 7.29-7.24 (m, 3H), 7.23-7.20 (m, 1H), 7.17-7.13 (m, 1H), 7.01-6.98 (m, 1H), 5.69 (d, J = 16.4 Hz, 1H), 4.75 (d, J = 16.4 Hz, 1H), 3.50 (d, J = 13.5 Hz, 1H), 3.00 (d, J = 13.5 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.23, 141.22, 138.62, 137.31, 137.19, 134.62, 128.84, 128.77, 128.63, 128.55, 127.07, 126.17, 125.96, 125.87, 122.86, 121.93, 116.52, 46.69, 43.13, 39.70, 22.01.

HRMS(ESI) Calculated for $C_{25}H_{22}NO^+$ ([M+H]$^+$): 352.16231, found: 352.16959.

(3*Z*,5*E*)-1,3-dimethyl-5-phenylbenzo[*b*]azocin-2(1*H*)-one (3a)



3a

Yield: 98% (107.9 mg), white solid, mp: 122-124 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.56 (m, 1H), 7.52-7.48 (m, 1H), 7.41-7.37 (m, 3H), 7.33-7.29 (m, 3H), 7.14-7.10 (m, 1H), 6.16 (s, 1H), 5.25 (s, 1H), 3.84 (s, 3H), 2.19 (s, 3H).

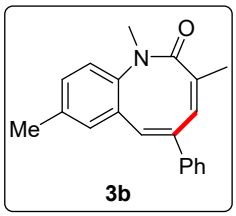
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.73, 146.28, 143.88, 138.76, 137.98, 129.38, 128.75, 128.31, 127.75, 127.40, 125.81, 122.01, 120.91, 115.88, 113.92, 29.92, 15.04.

HRMS(ESI) Calculated for $C_{19}H_{18}NO^+$ ([M+H]$^+$): 276.13101, found: 276.13829.

(3*Z*,5*E*)-1,3,8-trimethyl-5-phenylbenzo[*b*]azocin-2(1*H*)-one (3b)

Yield: 93% (107.6 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.35 (m, 3H), 7.34-7.28 (m, 5H), 6.15 (s, 1H), 5.23 (s, 1H), 3.82 (s, 3H), 2.31 (s, 3H), 2.16 (s, 3H).

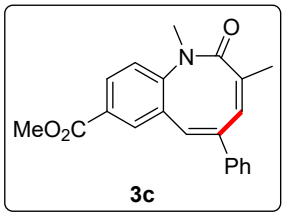


3b

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.59, 146.08, 143.91, 138.04, 136.80, 131.44, 130.62, 128.74, 128.25, 127.60, 127.09, 125.82, 120.87, 115.73, 113.85, 29.91, 20.79, 15.04.

HRMS(ESI) Calculated for $C_{20}H_{20}NO^+$ ([M+H]$^+$): 290.14666, found: 290.15394.

Methyl(3*Z*,5*E*)-1,3-dimethyl-2-oxo-5-phenyl-1,2-dihydrobenzo[*b*]azocine-8-carboxylate (3c)



3c

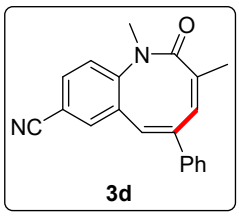
Yield: 84% (111.9 mg), white solid, mp: 120-122 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.9 Hz, 1H), 8.17-8.11 (m, 1H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.38-7.28 (m, 5H), 6.19 (s, 1H), 5.27 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.41, 162.76, 146.45, 143.31, 141.76, 137.90, 130.25, 129.43, 128.82, 128.55, 128.43, 125.84, 123.85, 120.53, 116.53, 113.96, 52.08, 30.20, 15.06.

HRMS(ESI) Calculated for $C_{21}H_{20}NO_3^+$ ([M+H]$^+$): 334.13649, found: 334.14377.

(3*Z*,5*E*)-1,3-dimethyl-2-oxo-5-phenyl-1,2-dihydrobenzo[*b*]azocine-8-carbonitrile (3d)



3d

Yield: 92% (110.4 mg), white solid, mp: 160-162 °C.

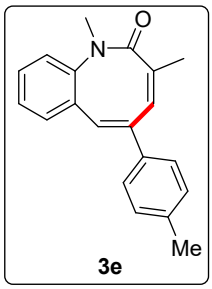
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.73-7.68 (m, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.34-7.30 (m, 5H), 6.20 (s, 1H), 5.26 (s, 1H), 3.82 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.42, 145.31, 142.77, 141.34, 137.12, 131.98, 131.97, 129.99, 129.00, 128.78, 125.67, 121.12, 118.69, 116.74, 114.92, 105.50, 30.21, 15.15.

HRMS(ESI) Calculated for $C_{20}H_{17}N_2O^+$ ([M+H]$^+$): 301.12626, found: 301.13354.

(3*Z*,5*E*)-1,3-dimethyl-5-(*p-tolyl*)benzo[*b*]azocin-2(1*H*)-one (3e)

Yield: 94% (108.7 mg), colorless oil.



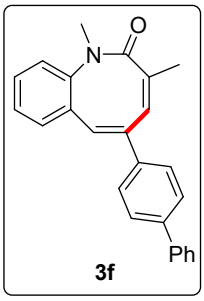
3e

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.11 (m, 3H), 6.11 (s, 1H), 5.19 (s, 1H), 3.84 (d, *J* = 0.5 Hz, 3H), 2.34 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (125MHz, $CDCl_3$) δ 162.77, 146.50, 143.67, 138.73, 138.27, 135.13, 129.46, 129.35, 127.63, 127.45, 125.71, 122.01, 120.96, 114.85, 113.90, 29.91, 21.13, 15.03.

HRMS(ESI) Calculated for $C_{20}H_{20}NO^+$ ($[M+H]^+$): 290.14666, found: 290.15394.

(3*Z*,5*E*)-5-([1,1'-biphenyl]-4-yl)-1,3-dimethylbenzo[*b*]azocin-2(1*H*)-one (3f)



3f

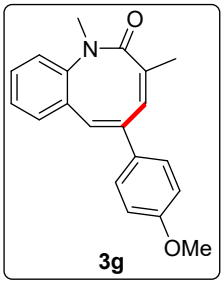
Yield: 97% (127.8 mg), white solid, mp: 133-135 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.57 (m, 3H), 7.56-7.50 (m, 3H), 7.47-7.40 (m, 5H), 7.38-7.33 (m, 1H), 7.17-7.12 (m, 1H), 6.22 (s, 1H), 5.28 (s, 1H), 3.86 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.74, 146.23, 143.45, 141.13, 140.38, 138.79, 136.84, 129.45, 128.82, 127.82, 127.51, 127.45, 127.42, 126.96, 126.25, 122.07, 120.92, 115.80, 113.98, 29.96, 15.12.

HRMS(ESI) Calculated for $C_{25}H_{22}NO^+$ ($[M+H]^+$): 352.16231, found: 352.16959.

(3*Z*,5*E*)-5-(4-methoxyphenyl)-1,3-dimethylbenzo[*b*]azocin-2(1*H*)-one (3g)



3g

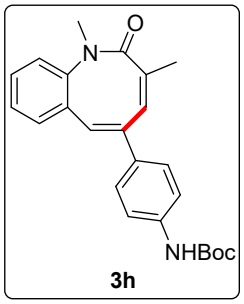
Yield: 96% (117.2 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.55 (m, 1H), 7.52-7.47 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.32-7.28 (m, 2H), 7.14-7.10 (m, 1H), 6.85-6.81 (m, 2H), 6.03 (s, 1H), 5.13 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.76, 159.73, 146.55, 143.21, 138.74, 130.57, 129.33, 127.58, 127.45, 127.09, 121.98, 120.92, 114.11, 113.88, 113.70, 55.25, 29.89, 14.98.

HRMS(ESI) Calculated for $C_{20}H_{20}NO_2^+$ ([M+H]$^+$): 306.14158, found: 306.14886.

Tert-butyl(4-((3*Z*,5E)-1,3-dimethyl-2-oxo-1,2-dihydrobenzo[*b*]azocin-5-yl)phenyl)carbamate (3h)



3h

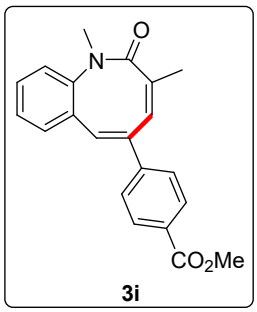
Yield: 89% (138.9 mg), white solid, mp: 204-206 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.52 (m, 1H), 7.50-7.45 (m, 1H), 7.39-7.32 (m, 3H), 7.29-7.26 (m, 2H), 7.11-7.08 (m, 1H), 7.02 (s, 1H), 6.06 (s, 1H), 5.14 (s, 1H), 3.82 (s, 3H), 2.17 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.77, 152.75, 146.46, 143.22, 138.79, 138.68, 132.48, 129.39, 127.58, 127.46, 126.46, 122.04, 120.89, 118.67, 114.34, 113.90, 80.53, 31.56, 29.94, 28.30, 22.62, 15.02, 14.09.

HRMS(ESI) Calculated for $C_{24}H_{25}N_2O_3^+$ ([M-H]$^+$): 389.19434, found: 389.18707.

Methyl 4-((3*Z*,5*E*)-1,3-dimethyl-2-oxo-1,2-dihydrobenzo[*b*]azocin-5-yl)benzoate (3i)



3i

Yield: 88% (117.2 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.53-7.48 (m, 2H), 7.44-7.39 (m, 3H), 7.13-7.09 (m, 1H), 6.26 (s, 1H), 5.37 (s, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.16 (s, 3H).

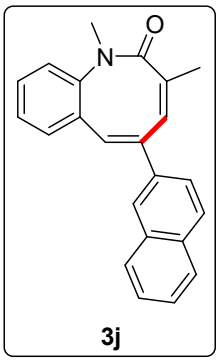
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.59, 162.58, 145.51, 143.16, 142.27, 138.79, 130.10, 129.87, 129.56, 127.97, 127.11, 125.76, 122.09, 120.64, 118.18, 114.05, 52.11, 29.95, 15.04.

HRMS(ESI) Calculated for $C_{21}H_{20}NO_3^+$ ([M+H]$^+$): 334.13649, found: 334.14377.

(3*Z*,5*E*)-1,3-dimethyl-5-(naphthalen-2-yl)benzo[b]azocin-2(1*H*)-one (3j)

Yield: 95% (123.56 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.76-7.73 (m, 1H), 7.70-7.67 (m, 1H), 7.62-7.58 (m, 2H), 7.51-7.41 (m, 4H), 7.13-7.09 (m, 1H), 6.30 (s, 1H), 5.35 (s, 1H), 3.88 (s, 3H), 2.25 (s, 3H).

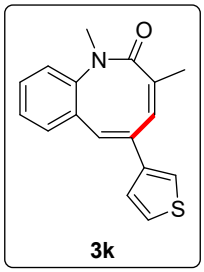


3j

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.83, 146.35, 143.84, 138.82, 135.12, 133.43, 133.18, 129.44, 128.57, 128.38, 127.89, 127.55, 127.46, 126.39, 125.54, 123.17, 122.09, 120.96, 116.33, 113.99, 29.99, 15.12.

HRMS(ESI) Calculated for $C_{23}H_{20}NO^+$ ([M+H]$^+$): 326.14666, found: 326.15394.

(3*Z*,5*E*)-1,3-dimethyl-5-(thiophen-3-yl)benzo[*b*]azocin-2(1*H*)-one (3k)



3k

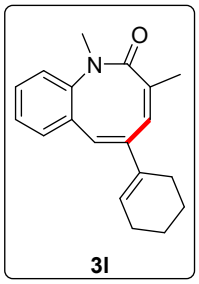
Yield: 96% (107.9 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.46 (m, 2H), 7.42-7.27 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.88-6.85 (m, 1H), 6.03 (s, 1H), 5.17 (s, 1H), 3.83 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.74, 146.20, 140.20, 139.13, 138.77, 129.42, 127.41, 127.32, 126.39, 124.87, 123.02, 122.00, 120.61, 114.67, 113.90, 29.91, 14.94.

HRMS(ESI) Calculated for $C_{17}H_{16}NOS^+$ ([M+H]$^+$): 282.08743, found: 282.09471.

(3*Z*,5*E*)-5-(cyclohex-1-en-1-yl)-1-methyl-3-phenylbenzo[*b*]azocin-2(1*H*)-one (3l)



3l

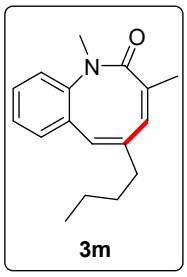
yield:80% (89.3 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17-7.13 (m, 1H), 5.53 (s, 1H), 5.41 (s, 1H), 4.88 (s, 1H), 3.77 (s, 3H), 2.41-2.37 (m, 2H), 2.10 (d, *J* = 3.4 Hz, 3H), 2.01-1.93 (m, 2H), 1.78-1.73 (m, 2H), 1.60-1.54 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.66, 147.19, 145.64, 138.40, 134.26, 129.20, 129.04, 127.46, 127.16, 121.74, 121.27, 113.68, 111.97, 29.75, 25.74, 24.76, 22.65, 21.96, 14.79.

HRMS(ESI) Calculated for $C_{19}H_{22}NO^+$ ([M+H]$^+$): 280.16231, found: 280.16959.

(3*Z*,5*Z*)-5-butyl-1,3-dimethylbenzo[*b*]azocin-2(1*H*)-one (3m)



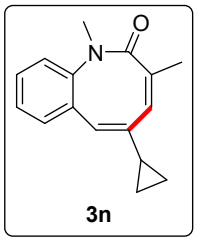
Yield: 95% (96,7 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.60 (m, 1H), 7.52-7.46 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22-7.16 (m, 1H), 5.46 (d, *J* = 1.5 Hz, 1H), 4.97 (d, *J* = 1.0 Hz, 1H), 3.77 (s, 3H), 2.36-2.25 (m, 2H), 2.21 (s, 3H), 1.53-1.45 (m, 2H), 1.40-1.31 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.74, 148.24, 145.49, 138.70, 129.18, 126.92, 125.91, 121.75, 120.34, 114.96, 113.95, 36.71, 29.78, 29.54, 22.65, 14.92, 13.91.

HRMS(ESI) Calculated for $C_{17}H_{22}NO^+$ ([M+H]$^+$): 256.16231, found: 256.16959.

(3*Z*,5*Z*)-5-cyclopropyl-1,3-dimethylbenzo[*b*]azocin-2(1*H*)-one (3n)



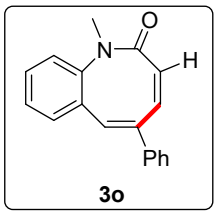
Yield: 94% (89.9 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (m, 1H), 7.49 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.23-7.18 (m, 1H), 5.42 (d, *J* = 1.0 Hz, 1H), 4.87 (d, *J* = 1.0 Hz, 1H), 3.76 (s, 3H), 2.21 (s, 3H), 1.69 (m, 1H), 0.77-0.67 (m, 2H), 0.49-0.43 (m, 1H), 0.35-0.30 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.62, 146.35, 145.92, 138.53, 129.23, 127.51, 126.91, 121.77, 120.88, 113.83, 112.90, 29.78, 17.31, 15.31, 7.11, 6.82.

HRMS(ESI) Calculated for $C_{16}H_{18}NO^+$ ([M+H]$^+$): 240.13101, found: 240.13829.

(3*Z*,5*E*)-1-methyl-5-phenylbenzo[*b*]azocin-2(1*H*)-one (3o)



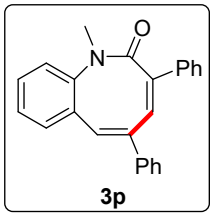
Yield: 96% (100.2 mg), white solid, mp: 89-91 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 1H), 7.46-7.35 (m, 4H), 7.35-7.28 (m, 3H), 7.09-7.05 (m, 1H), 6.77 (s, 1H), 5.94 (d, *J* = 0.5 Hz, 1H), 5.44 (d, *J* = 0.5 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.16, 150.82, 145.54, 140.12, 138.78, 130.52, 128.67, 128.33, 127.92, 126.31, 121.93, 121.82, 120.27, 116.83, 114.33, 29.44.

HRMS(ESI) Calculated for $C_{18}H_{16}NO^+$ ($[M+H]^+$): 262.11536, found: 262.12264.

(3*Z*,5*E*)-1-methyl-3,5-diphenylbenzo[*b*]azocin-2(1*H*)-one (3p)



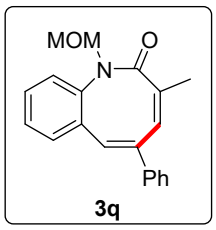
Yield: 80% (107.9 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.67 (m, 1H), 7.61-7.56 (m, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.27-7.20 (m, 8H), 7.19-7.14 (m, 3H), 5.92 (s, 1H), 5.18 (s, 1H), 3.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.96, 147.50, 143.30, 139.50, 139.16, 136.08, 132.12, 130.32, 129.69, 128.36, 128.32, 127.87, 127.50, 127.10, 125.96, 122.10, 120.79, 117.55, 114.06, 30.04.

HRMS(ESI) Calculated for $C_{24}H_{20}NO^+$ ($[M+H]^+$): 338.14666, found: 338.15394.

(3*Z*,5*E*)-1-(methoxymethyl)-3-methyl-5-phenylbenzo[*b*]azocin-2(1*H*)-one (3q)



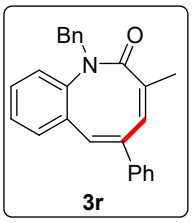
Yield: 97% (118.4 mg), colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.54 (m, 2H), 7.50-7.45 (m, 1H), 7.41-7.37 (m, 2H), 7.35-7.28 (m, 3H), 7.15-7.11 (m, 1H), 6.16 (s, 1H), 5.92-5.80 (m, 2H), 5.27 (s, 1H), 3.53 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.27, 147.59, 143.84, 137.90, 137.82, 129.55, 128.81, 128.39, 127.37, 127.31, 125.80, 122.62, 120.96, 115.87, 115.00, 73.90, 56.80, 14.88.

HRMS(ESI) Calculated for $C_{20}H_{20}NO_2^+$ ($[M+H]^+$): 306.14158, found: 306.14886.

(3*Z*,5*E*)-1-benzyl-3-methyl-5-phenylbenzo[*b*]azocin-2(1*H*)-one (3r)



3r

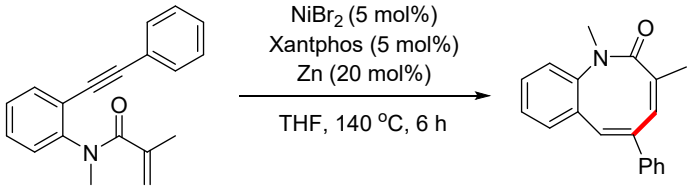
Yield: 91% (127.8 mg), white solid, mp: 122-124 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.56 (m, 1H), 7.43-7.39 (m, 2H), 7.39-7.27 (m, 10H), 7.10-7.06 (m, 1H), 6.19 (s, 1H), 5.75 (d. *J* = 15.5 Hz, 1H), 5.59 (d, *J* = 15.5 Hz, 1H), 5.30 (s, 1H), 2.25 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.87, 146.87, 143.92, 138.26, 137.96, 136.69, 129.38, 128.80, 128.36, 127.70, 127.49, 127.23, 126.76, 125.82, 122.09, 121.15, 115.97, 114.80, 46.60, 15.09.

HRMS(ESI) Calculated for $C_{25}H_{22}NO^+$ ([M+H]$^+$): 352.16231, found: 352.16959.

3.3 Gram-scale reaction



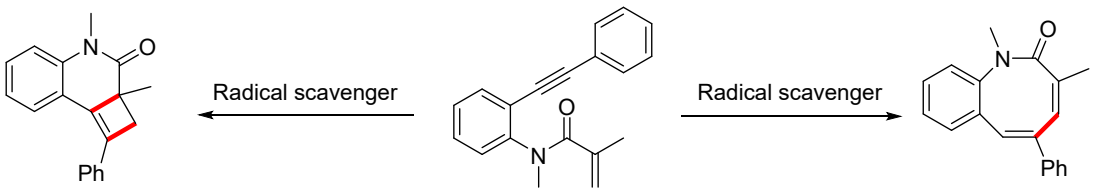
1a: 8 mmol

3a: 94% (2.07 g)

In a 250 mL flame-dried Schlenk tube, 1, 7-Enynes (8 mmol, 2.2 g), $NiBr_2$ (5 mol%,), **L1** (5 mol%), Zn (0.2 equiv), THF (25 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 140 °C for 6 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 10 : 1) to provide the product **3a** in 94% yield.

4 Mechanistic experiments

4.1 Radical inhibition reaction



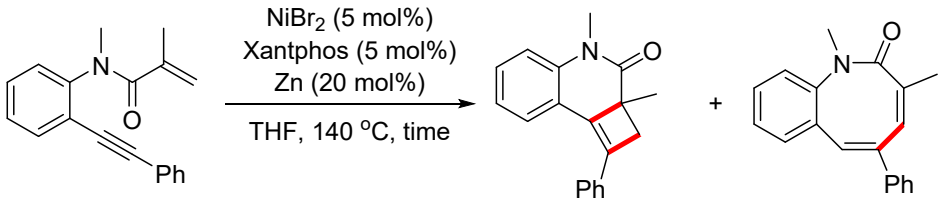
2a **1a** **3a**

Radical scavenger	Yield/**2a**	Yield/**3a**
TEMPO	0	0
BHT	90%	89%
1,1-diphenylethylene	93%	91%

(a) General procedure for the radical inhibition reaction: In a 25 mL flame-dried Schlenk tube, **1a** (0.4 mmol), $NiBr_2$ (5 mol%, 0.02 mmol), **L1** (5 mol%, 0.02 mmol), Zn (0.2 equiv, 0.08 mmol), radical scavenger (1 equiv, 0.4 mmol), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 60 °C for 6 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 50 : 1) to provide the product **2a**.

(b) General procedure for the radical inhibition reaction: In a 25 mL flame-dried Schlenk tube, **1a** (0.4 mmol), $NiBr_2$ (5 mol%, 0.02 mmol), **L1** (5 mol%, 0.02 mmol), Zn (0.2 equiv, 0.08 mmol), radical scavenger (1 equiv, 0.4 mmol), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 140 °C for 6 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 10 : 1) to provide the product **3a**.

4.2 Time evaluation for the model reaction

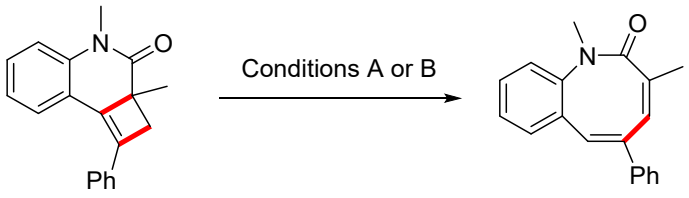


1a **2a** **3a**

time/h	yield/**2a**	yield/**3a**
0.5	78%	17%
1	55%	42%

In a 25 mL flame-dried Schlenk tube, **1a** (0.4 mmol), $NiBr_2$ (5 mol%, 0.02 mmol), **L1** (5 mol%, 0.02 mmol), Zn (0.2 equiv, 0.08 mmol), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 140 °C for 0.5 h or 1 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 10 : 1) to provide the product **2a** and **3a**.

4.3 Formation of 3a from 2a



2a **3a**

Conditions A: In a 25 mL flame-dried Schlenk tube, **2a** (0.4 mmol), $NiBr_2$ (5 mol%, 0.02 mmol), **L1** (5 mol%, 0.02 mmol), Zn (0.2 equiv, 0.08 mmol), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 140 °C for 0.5 h or 1 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 10 : 1) to provide the product **3a** in 17% and 44% yield, respectively.

Conditions B: In a 25 mL flame-dried Schlenk tube, **2a** (0.4 mmol) in THF (4 mL), under nitrogen. The tube was sealed and stirred at 140 °C for 0.5 h or 1 h. After

completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 10 : 1) to provide the product **3a** in 18% and 46% yield, respectively.

5. X-Ray Crystallography of 2i

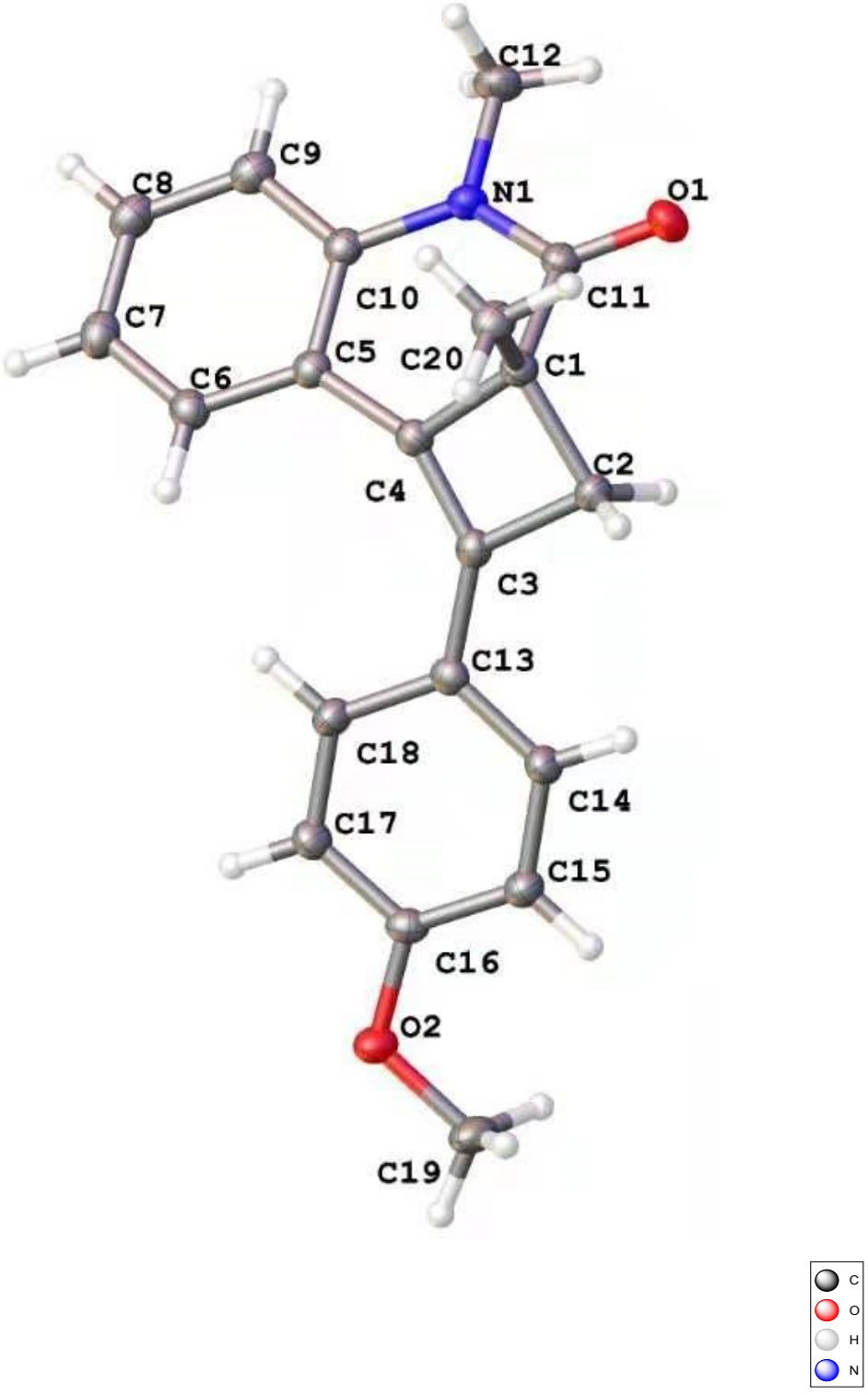


Figure S1. The X-Ray Crystallographic Structure of 2i

Table S1. Crystal data and structure refinement for 2i

Identification code	2103027077	
Empirical formula	C20 H19 N O2	
Formula weight	305.36	
Temperature	173.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 36.302(4) Å	a= 90°.
	b = 8.0420(10) Å	b= 90°.
	c = 5.3509(6) Å	g = 90°.
Volume	1562.1(3) $Å^3$	
Z	4	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.427 mm^{-1}	
F(000)	648	
Crystal size	0.07 x 0.06 x 0.05 mm^3	
Theta range for data collection	4.238 to 54.989°.	
Index ranges	-44<=h<=42, -6<=k<=9, -6<=l<=5	
Reflections collected	9828	
Independent reflections	2815 [R(int) = 0.0479]	
Completeness to theta = 53.594°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4755	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2815 / 1 / 211	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1024	
R indices (all data)	R1 = 0.0536, wR2 = 0.1113	
Absolute structure parameter	0.2(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.137 and -0.181 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement

parameters ($Å^2$ x 10^3) for 2-1l. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	2923(1)	8362(3)	677(4)	47(1)
O(2)	5509(1)	7045(3)	2423(4)	41(1)
N(1)	3001(1)	6458(3)	3795(5)	35(1)
C(1)	3424(1)	8795(4)	3526(6)	32(1)
C(2)	3742(1)	9340(4)	1744(6)	33(1)
C(3)	3985(1)	8177(3)	3284(6)	31(1)
C(4)	3699(1)	7634(4)	4691(6)	31(1)
C(5)	3571(1)	6303(4)	6320(6)	31(1)
C(6)	3765(1)	5569(4)	8275(6)	36(1)
C(7)	3611(1)	4303(4)	9685(7)	42(1)
C(8)	3259(1)	3758(4)	9140(7)	44(1)
C(9)	3056(1)	4479(4)	7226(6)	41(1)
C(10)	3207(1)	5761(4)	5802(6)	33(1)
C(11)	3101(1)	7859(4)	2463(6)	34(1)
C(12)	2649(1)	5682(4)	3125(8)	48(1)
C(13)	4377(1)	7857(3)	3022(6)	31(1)
C(14)	4577(1)	8618(4)	1109(6)	35(1)
C(15)	4953(1)	8392(4)	832(6)	36(1)
C(16)	5139(1)	7373(4)	2495(6)	33(1)
C(17)	4948(1)	6590(4)	4403(6)	37(1)
C(18)	4575(1)	6821(4)	4671(6)	36(1)
C(19)	5713(1)	7722(4)	379(7)	49(1)
C(20)	3277(1)	10172(4)	5225(7)	40(1)

Table S3. Bond lengths [Å] for 2i

Atom 1,2	d 1,2 [Å]	Atom 1,2	d 1,2 [Å]
O(1)-C(11)	1.224(4)	C(8)-C(9)	1.389(5)
O(2)-C(16)	1.370(3)	C(9)-H(9)	0.9500
O(2)-C(19)	1.428(4)	C(9)-C(10)	1.394(4)

N(1)-C(10)	1.424(4)	C(12)-H(12A)	0.9800
N(1)-C(11)	1.382(4)	C(12)-H(12B)	0.9800
N(1)-C(12)	1.467(4)	C(12)-H(12C)	0.9800
C(1)-C(2)	1.562(4)	C(13)-C(14)	1.396(4)
C(1)-C(4)	1.504(4)	C(13)-C(18)	1.410(4)
C(1)-C(11)	1.503(4)	C(14)-H(14)	0.9500
C(1)-C(20)	1.528(4)	C(14)-C(15)	1.384(4)
C(2)-H(2A)	0.9900	C(15)-H(15)	0.9500
C(2)-H(2B)	0.9900	C(15)-C(16)	1.386(4)
C(2)-C(3)	1.528(4)	C(16)-C(17)	1.387(4)
C(3)-C(4)	1.355(4)	C(17)-H(17)	0.9500
C(3)-C(13)	1.453(4)	C(17)-C(18)	1.374(4)
C(4)-C(5)	1.456(4)	C(18)-H(18)	0.9500
C(5)-C(6)	1.392(4)	C(19)-H(19A)	0.9800
C(5)-C(10)	1.419(4)	C(19)-H(19B)	0.9800
C(6)-H(6)	0.9500	C(19)-H(19C)	0.9800
C(6)-C(7)	1.384(4)	C(20)-H(20A)	0.9800
C(7)-H(7)	0.9500	C(20)-H(20B)	0.9800
C(8)-H(8)	0.9500		

Table S4. Bond angles[°] for 2i

Atom 1,2,3	Angle 1,2,3[°]	Atom 1,2,3	Angle 1,2,3[°]
C(16)-O(2)-C(19)	117.1(2)	O(1)-C(11)-N(1)	122.2(3)
C(10)-N(1)-C(12)	118.4(2)	O(1)-C(11)-C(1)	122.9(3)
C(11)-N(1)-C(10)	124.8(2)	N(1)-C(11)-C(1)	114.7(2)
C(11)-N(1)-C(12)	116.8(2)	N(1)-C(12)-H(12A)	109.5
C(4)-C(1)-C(2)	86.3(2)	N(1)-C(12)-H(12B)	109.5
C(4)-C(1)-C(20)	115.8(3)	N(1)-C(12)-H(12C)	109.5
C(11)-C(1)-C(2)	119.1(3)	H(12A)-C(12)-H(12B)	109.5
C(11)-C(1)-C(4)	111.3(2)	H(12A)-C(12)-H(12C)	109.5
C(11)-C(1)-C(20)	108.5(2)	H(12B)-C(12)-H(12C)	109.5
C(20)-C(1)-C(2)	114.7(2)	C(14)-C(13)-C(3)	120.2(3)
C(1)-C(2)-H(2A)	114.4	C(14)-C(13)-C(18)	117.0(2)
C(1)-C(2)-H(2B)	114.4	C(18)-C(13)-C(3)	122.8(3)

H(2A)-C(2)-H(2B)	111.5	C(13)-C(14)-H(14)	118.9
C(3)-C(2)-C(1)	85.8(2)	C(15)-C(14)-C(13)	122.2(3)
C(3)-C(2)-H(2A)	114.4	C(15)-C(14)-H(14)	118.9
C(3)-C(2)-H(2B)	114.4	C(14)-C(15)-H(15)	120.3
C(4)-C(3)-C(2)	93.1(2)	C(14)-C(15)-C(16)	119.3(3)
C(4)-C(3)-C(13)	138.3(3)	C(16)-C(15)-H(15)	120.3
C(13)-C(3)-C(2)	128.5(3)	O(2)-C(16)-C(15)	125.1(3)
C(3)-C(4)-C(1)	94.6(2)	O(2)-C(16)-C(17)	115.2(3)
C(3)-C(4)-C(5)	144.5(3)	C(15)-C(16)-C(17)	119.8(2)
C(5)-C(4)-C(1)	119.4(2)	C(16)-C(17)-H(17)	119.7
C(6)-C(5)-C(4)	126.9(2)	C(18)-C(17)-C(16)	120.6(3)
C(6)-C(5)-C(10)	119.1(3)	C(18)-C(17)-H(17)	119.7
C(10)-C(5)-C(4)	114.0(2)	C(13)-C(18)-H(18)	119.5
C(5)-C(6)-H(6)	119.4	C(17)-C(18)-C(13)	121.0(3)
C(7)-C(6)-C(5)	121.2(3)	C(17)-C(18)-H(18)	119.5
C(7)-C(6)-H(6)	119.4	O(2)-C(19)-H(19A)	109.5
C(6)-C(7)-H(7)	120.3	O(2)-C(19)-H(19B)	109.5
C(8)-C(7)-C(6)	119.4(3)	O(2)-C(19)-H(19C)	109.5
C(8)-C(7)-H(7)	120.3	H(19A)-C(19)-H(19B)	109.5
C(7)-C(8)-H(8)	119.5	H(19A)-C(19)-H(19C)	109.5
C(7)-C(8)-C(9)	120.9(3)	H(19B)-C(19)-H(19C)	109.5
C(9)-C(8)-H(8)	119.5	C(1)-C(20)-H(20A)	109.5
C(8)-C(9)-H(9)	119.9	C(1)-C(20)-H(20B)	109.5
C(8)-C(9)-C(10)	120.1(3)	C(1)-C(20)-H(20C)	109.5
C(10)-C(9)-H(9)	119.9	H(20A)-C(20)-H(20B)	109.5
C(5)-C(10)-N(1)	121.1(3)	H(20A)-C(20)-H(20C)	109.5
C(9)-C(10)-N(1)	119.7(2)	H(20B)-C(20)-H(20C)	109.5
C(9)-C(10)-C(5)	119.2(3)		

Table S5. Anisotropic displacement parameters ($Å^2$x 10^3) for 1-2l. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	35(1)	59(2)	47(2)	14(1)	-9(1)	1(1)
O(2)	30(1)	44(1)	48(1)	9(1)	6(1)	4(1)
N(1)	27(1)	40(2)	37(2)	4(1)	0(1)	-5(1)
C(1)	28(1)	33(2)	36(2)	4(1)	1(1)	3(1)
C(2)	31(1)	35(2)	33(2)	5(1)	1(1)	-1(1)
C(3)	33(1)	31(2)	28(2)	0(1)	-1(1)	0(1)
C(4)	29(1)	32(2)	32(2)	0(1)	-2(1)	0(1)
C(5)	32(1)	31(2)	30(2)	-1(1)	3(1)	1(1)
C(6)	36(1)	36(2)	35(2)	0(1)	0(1)	4(1)
C(7)	50(2)	39(2)	37(2)	6(2)	4(1)	7(1)
C(8)	50(2)	39(2)	44(2)	6(2)	9(2)	-2(2)
C(9)	40(2)	40(2)	43(2)	1(2)	6(1)	-3(1)
C(10)	33(1)	32(2)	32(2)	0(1)	4(1)	2(1)
C(11)	27(1)	39(2)	38(2)	4(1)	1(1)	2(1)
C(12)	31(2)	56(2)	58(2)	6(2)	0(2)	-8(1)
C(13)	30(1)	32(2)	30(2)	-3(1)	-2(1)	-1(1)
C(14)	31(1)	38(2)	36(2)	6(1)	-1(1)	3(1)
C(15)	32(1)	40(2)	35(2)	4(1)	3(1)	-1(1)
C(16)	27(1)	33(2)	39(2)	-3(1)	2(1)	1(1)
C(17)	33(1)	37(2)	39(2)	5(2)	-1(1)	5(1)
C(18)	33(1)	38(2)	35(2)	6(2)	4(1)	-2(1)
C(19)	33(2)	56(2)	57(2)	13(2)	13(2)	2(2)
C(20)	39(2)	37(2)	43(2)	1(2)	5(1)	6(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 2i.

Atom	x	y	z	U(eq)
H(2A)	3709	8995	-18	40
H(2B)	3809	10530	1870	40
H(6)	4007	5943	8649	43
H(7)	3746	3814	11015	50

H(8)	3155	2877	10088	53
H(9)	2813	4099	6885	49
H(12A)	2686	4487	2870	73
H(12B)	2555	6183	1581	73
H(12C)	2471	5857	4475	73
H(14)	4451	9314	-43	42
H(15)	5082	8930	-484	43
H(17)	5075	5886	5536	44
H(18)	4448	6274	5989	43
H(19A)	5602	7357	-1199	73
H(19B)	5968	7336	463	73
H(19C)	5707	8939	468	73
H(20A)	3132	9678	6579	60
H(20B)	3121	10927	4251	60
H(20C)	3484	10794	5936	60

6. References

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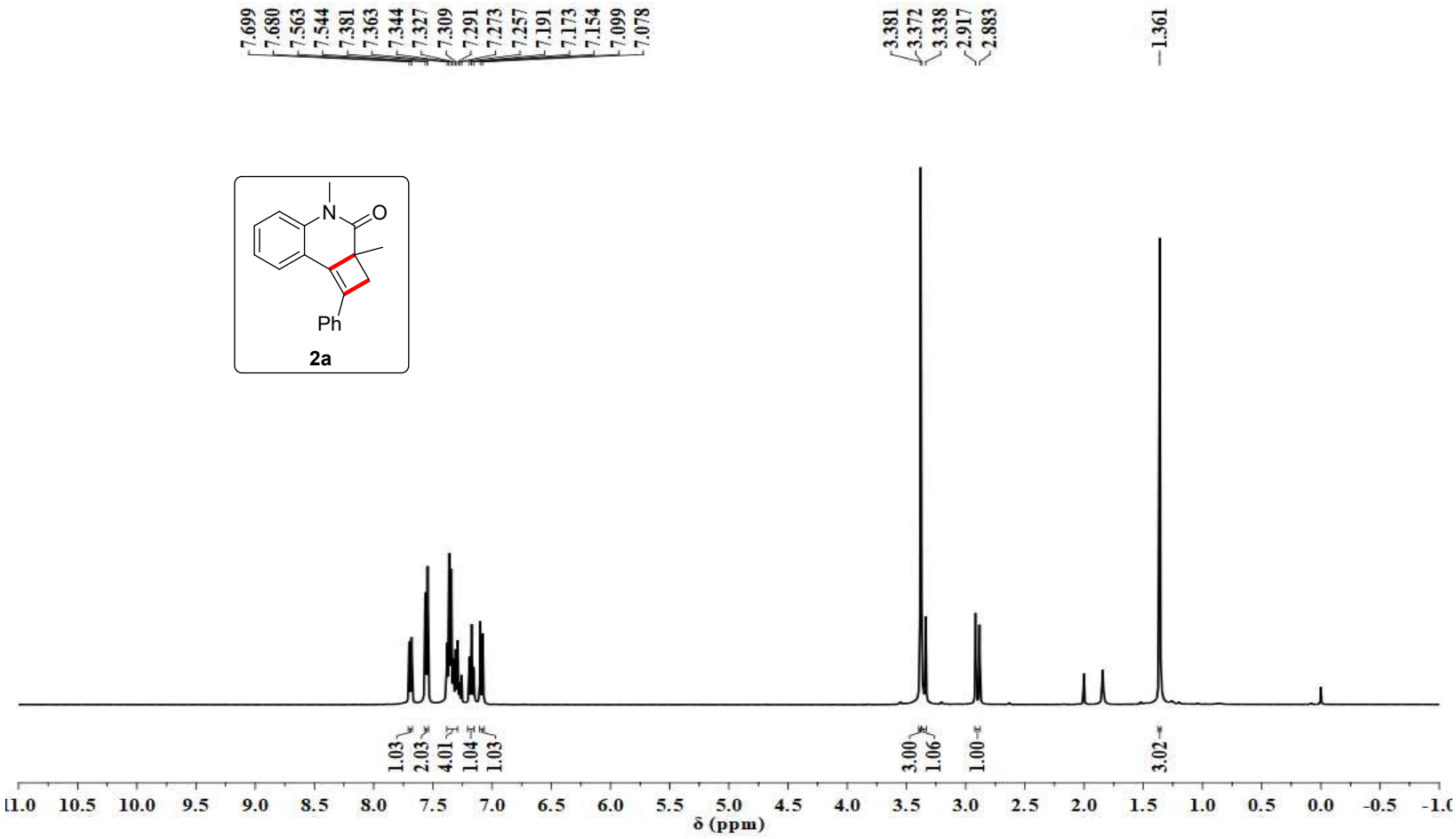
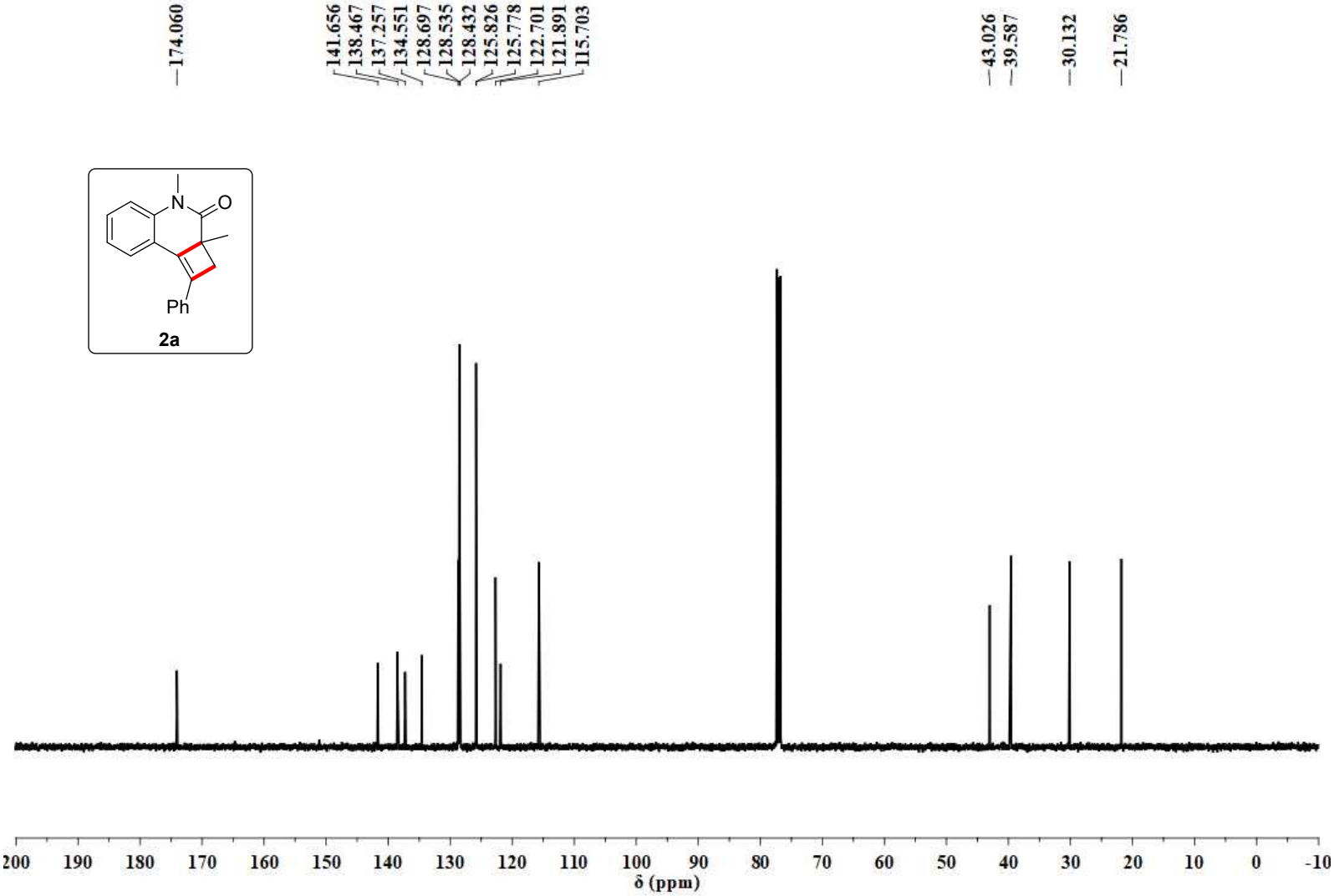
2. C. Wu, J. Liao and S. Ge, *Angew. Chem. Int. Ed.* 2019, **58**, 8882.

3. H.-Y. Liu, Y. Lu, Y. Li and J.-H. Li, *Organ. Lett.* 2020, **22**, 8819.

4. Y. Qu, W. Xu, J. Zhang, Y. Liu, Y. Li, H. Song and Q. Wang, *J. Org. Chem.* 2020, **85**, 5379.

7. ^{1}H-NMR and ^{13}C-NMR Spectra

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O
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180
170
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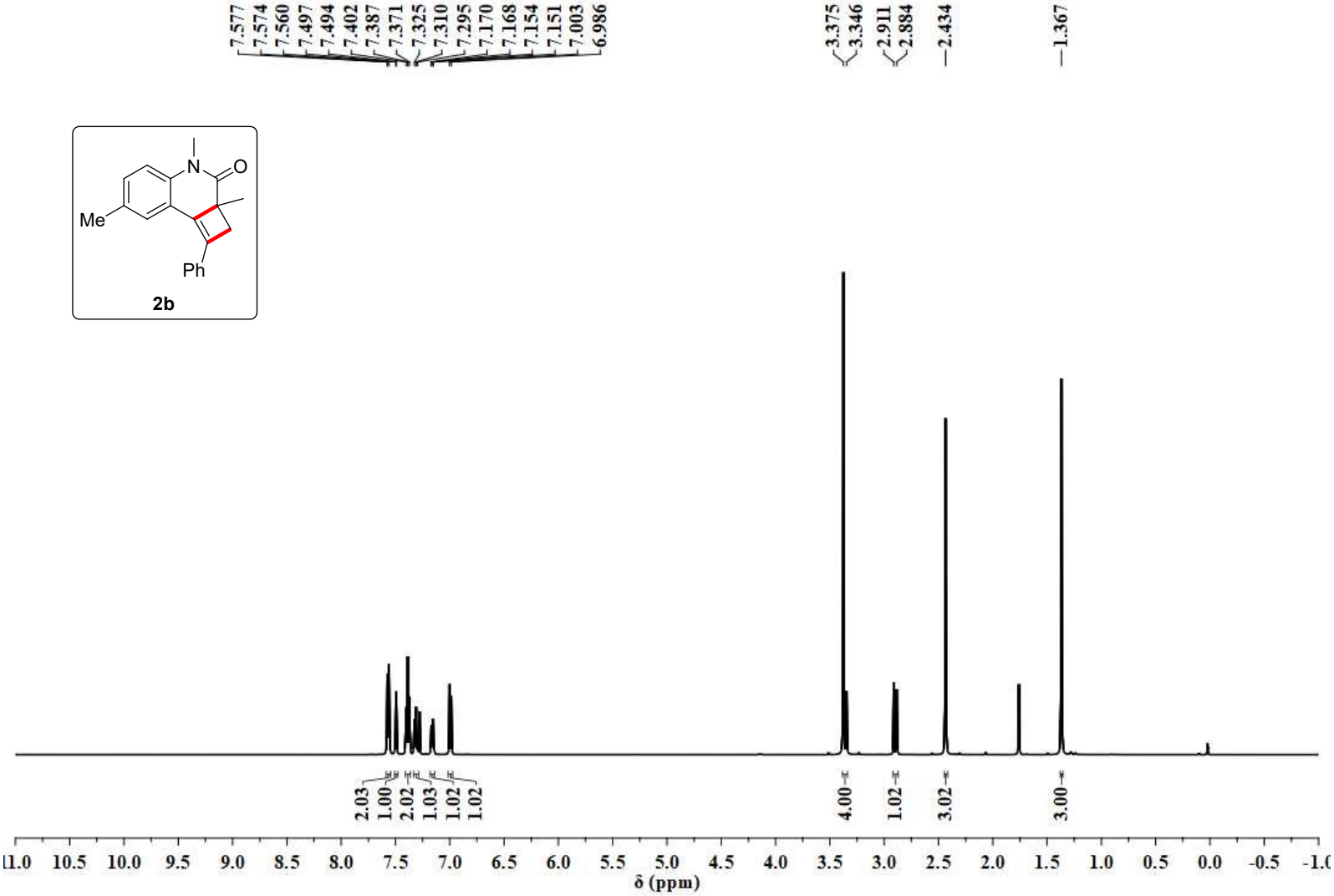
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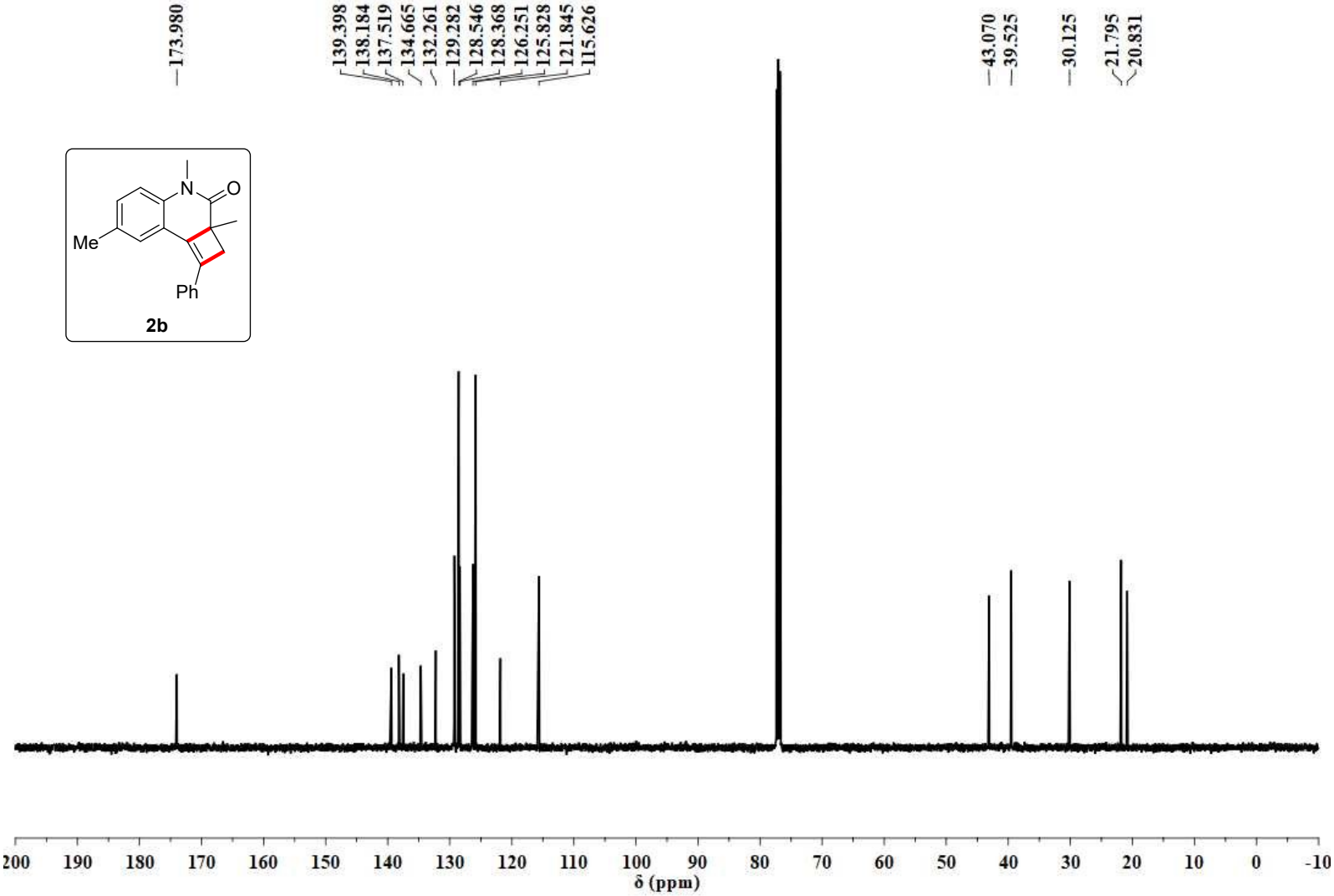
δ (ppm)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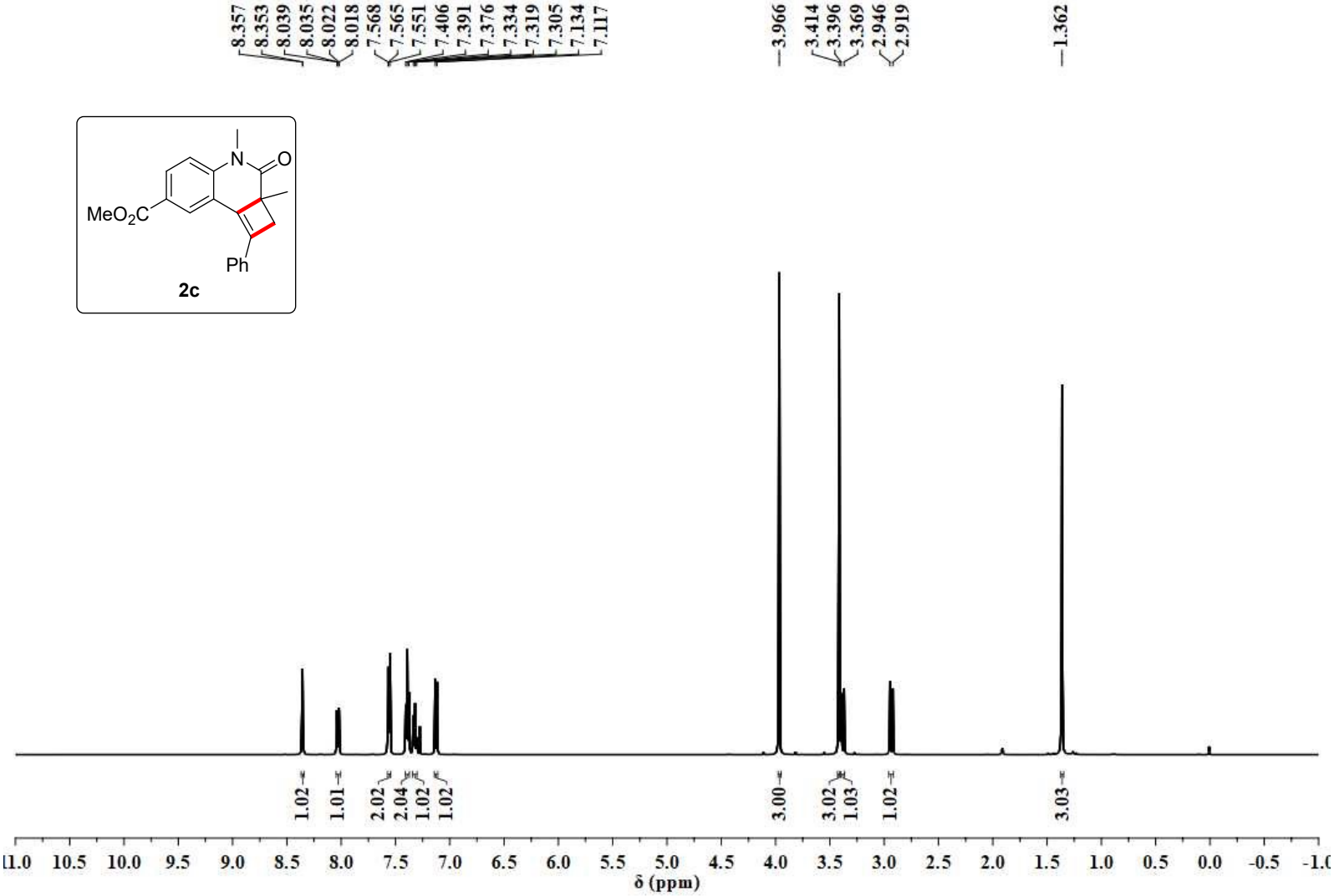
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MeO2C
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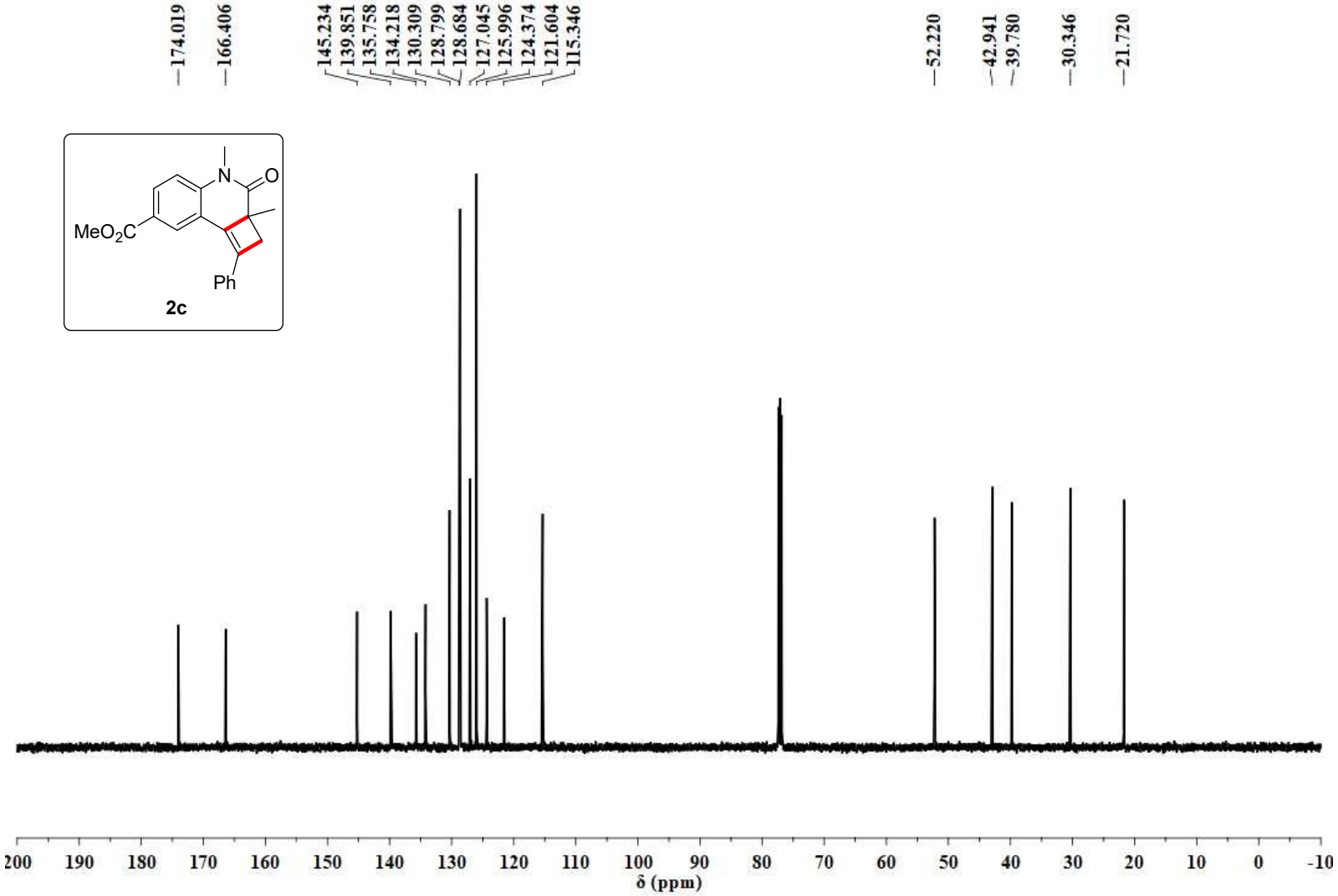
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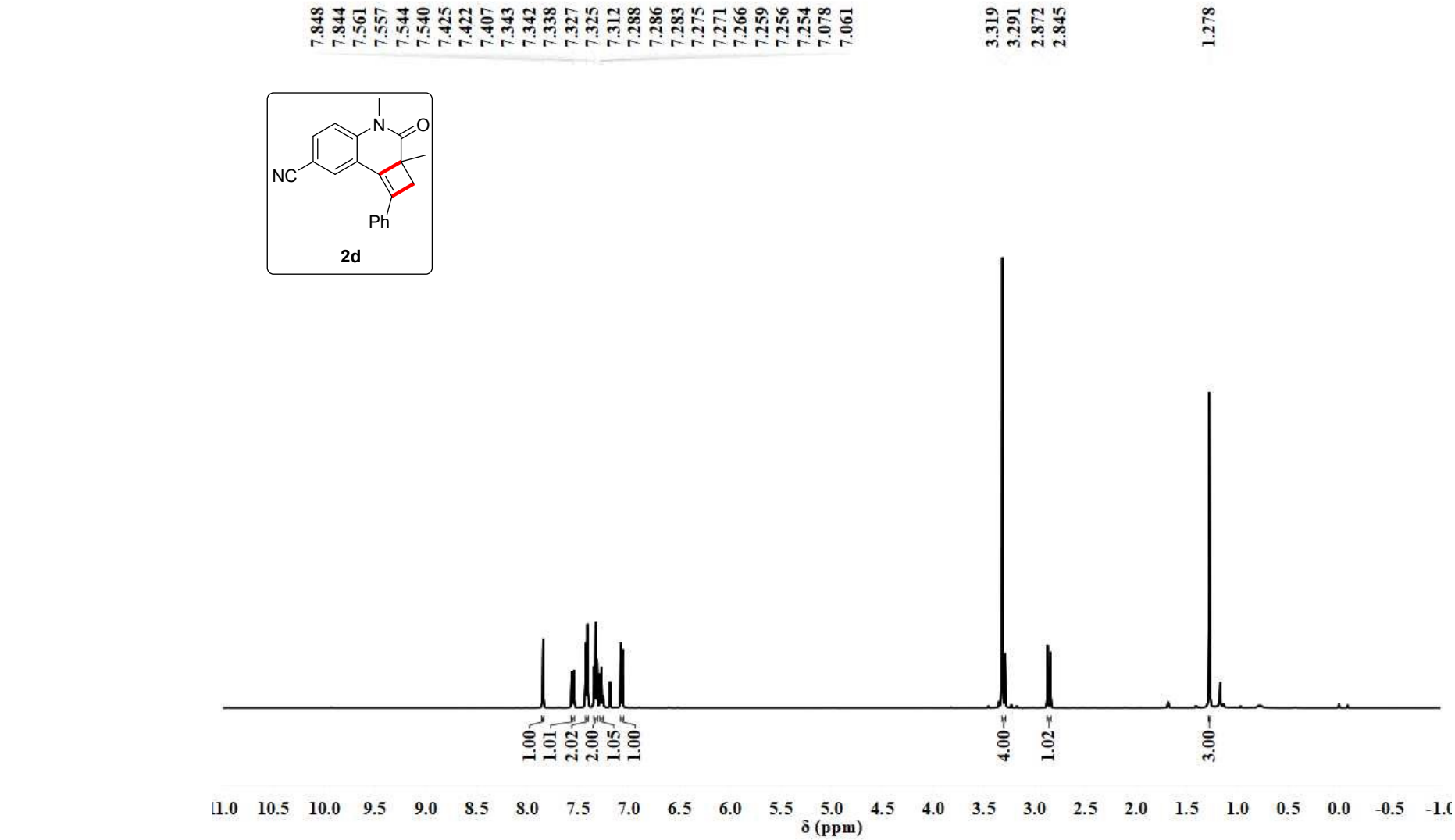
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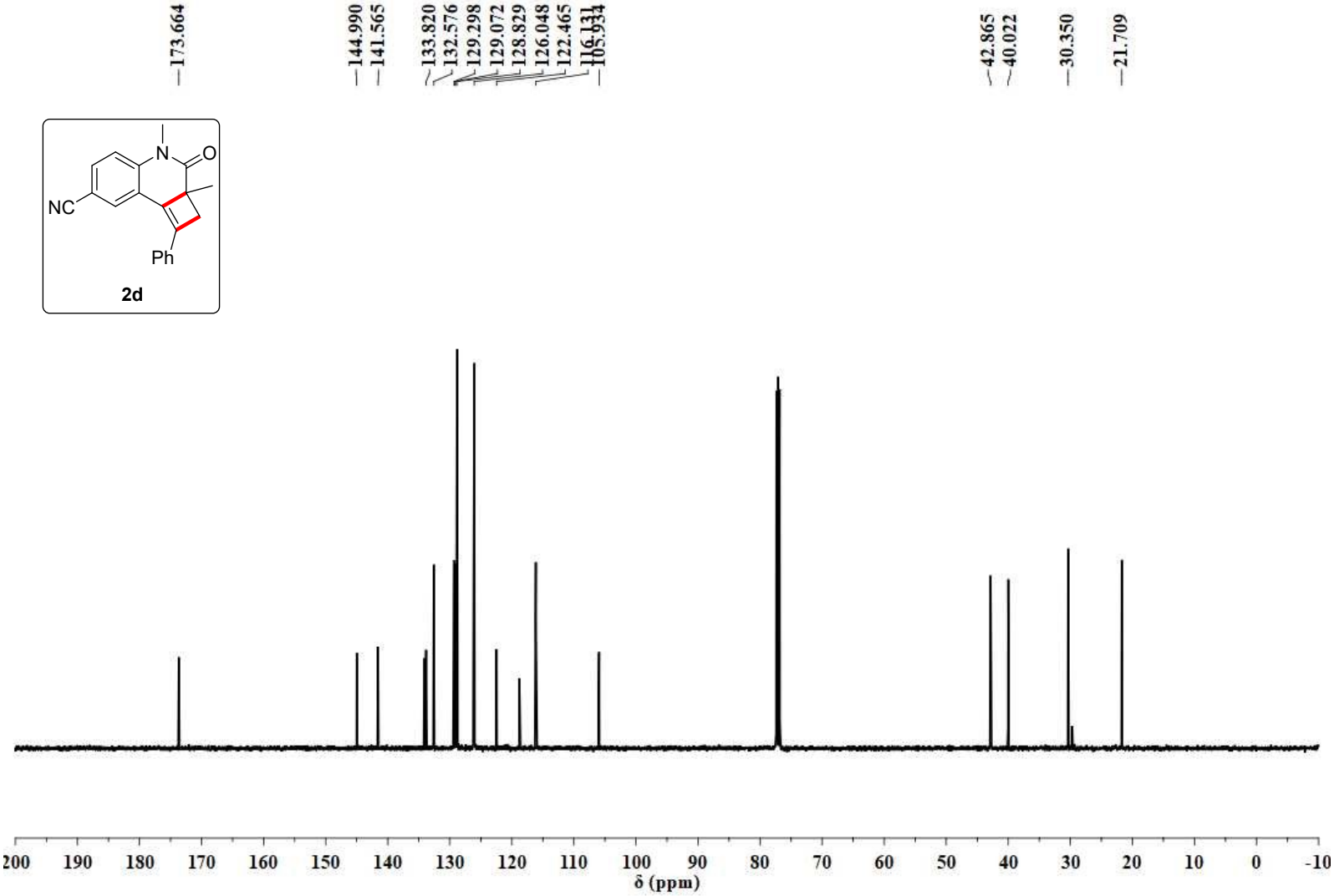
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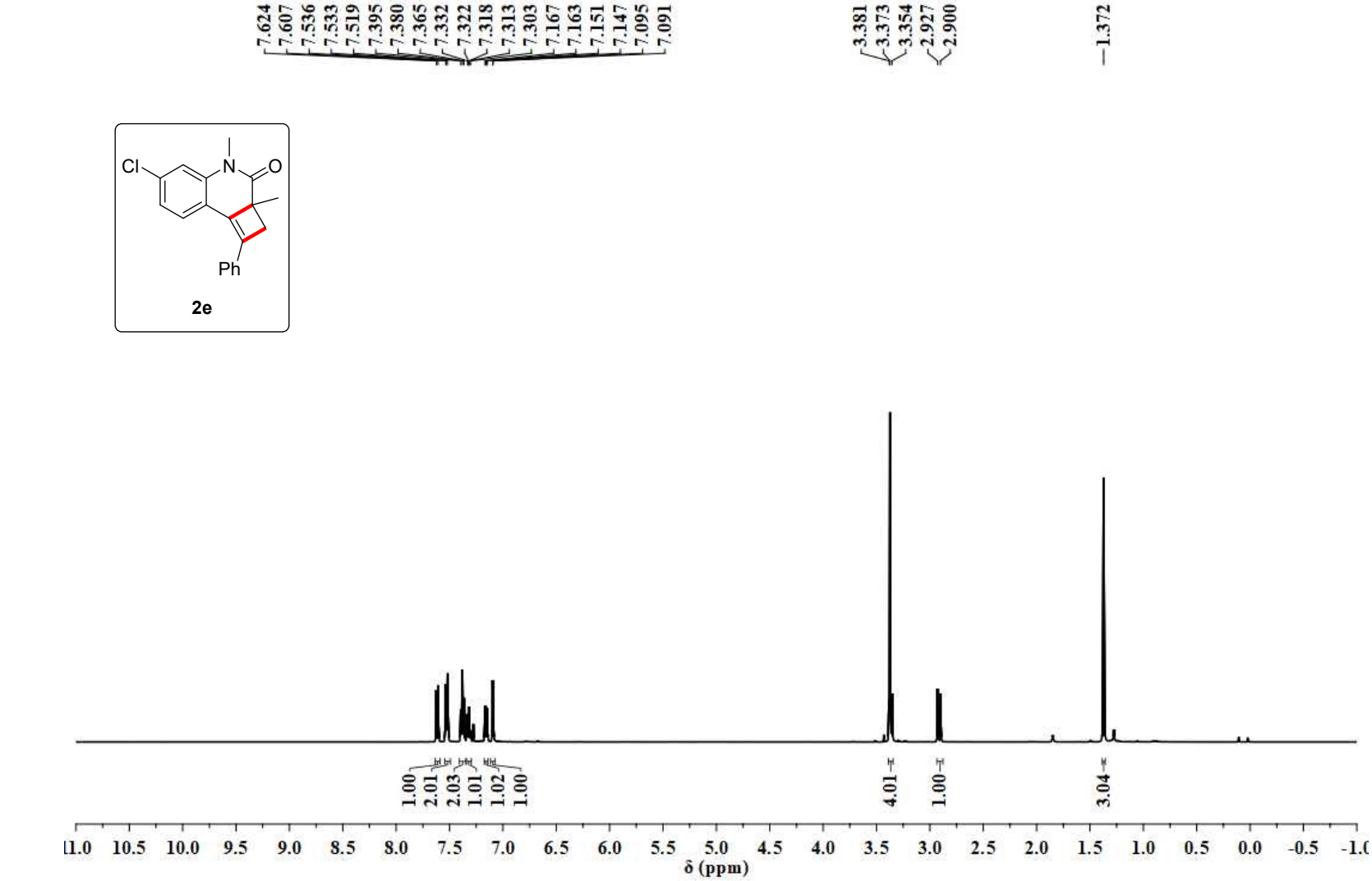
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3.373
3.354
2.927
2.900
1.372
Cl
N
O
Ph
2e
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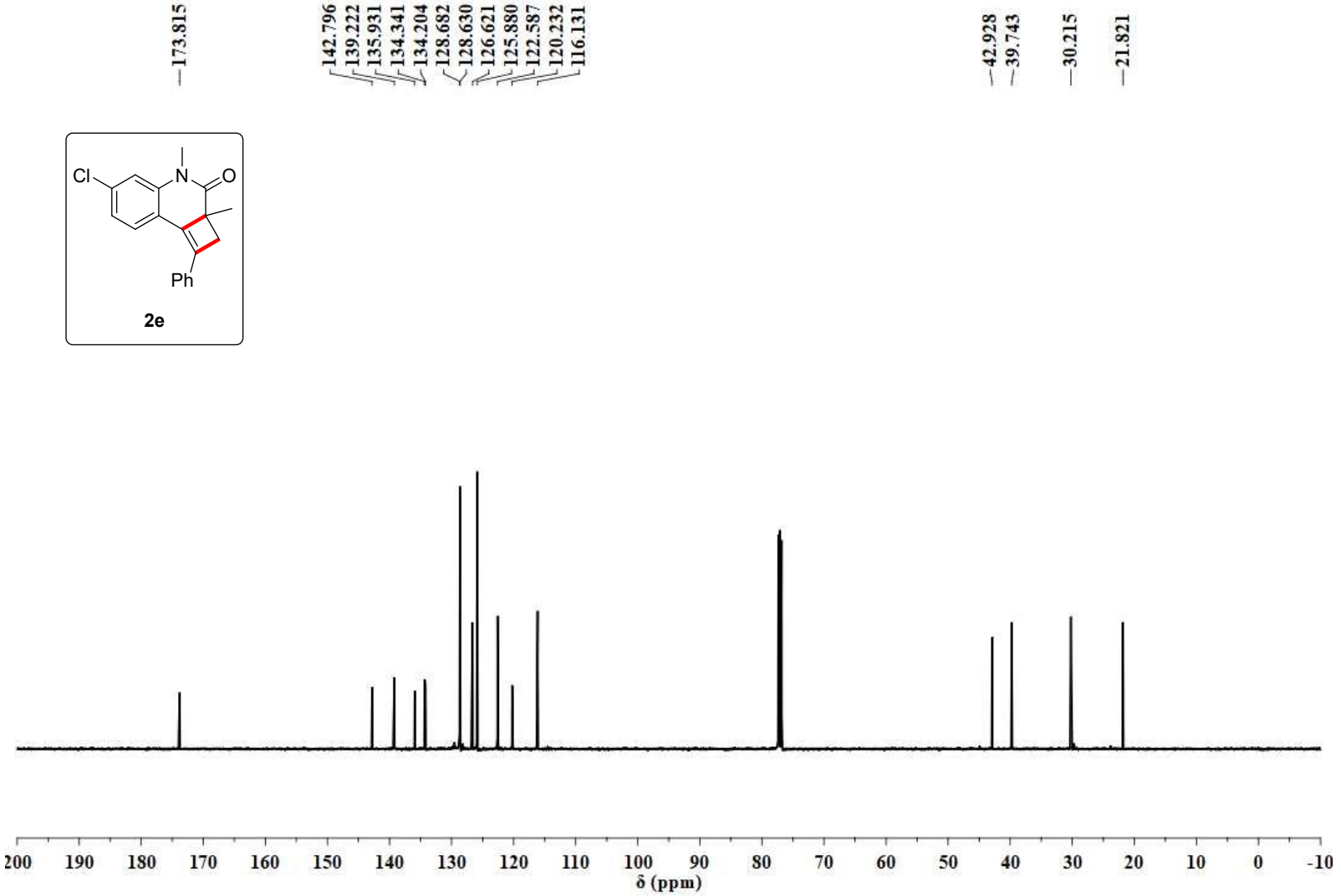
2.01
2.03
1.01
1.02
1.00
4.01
1.00
3.04
δ (ppm)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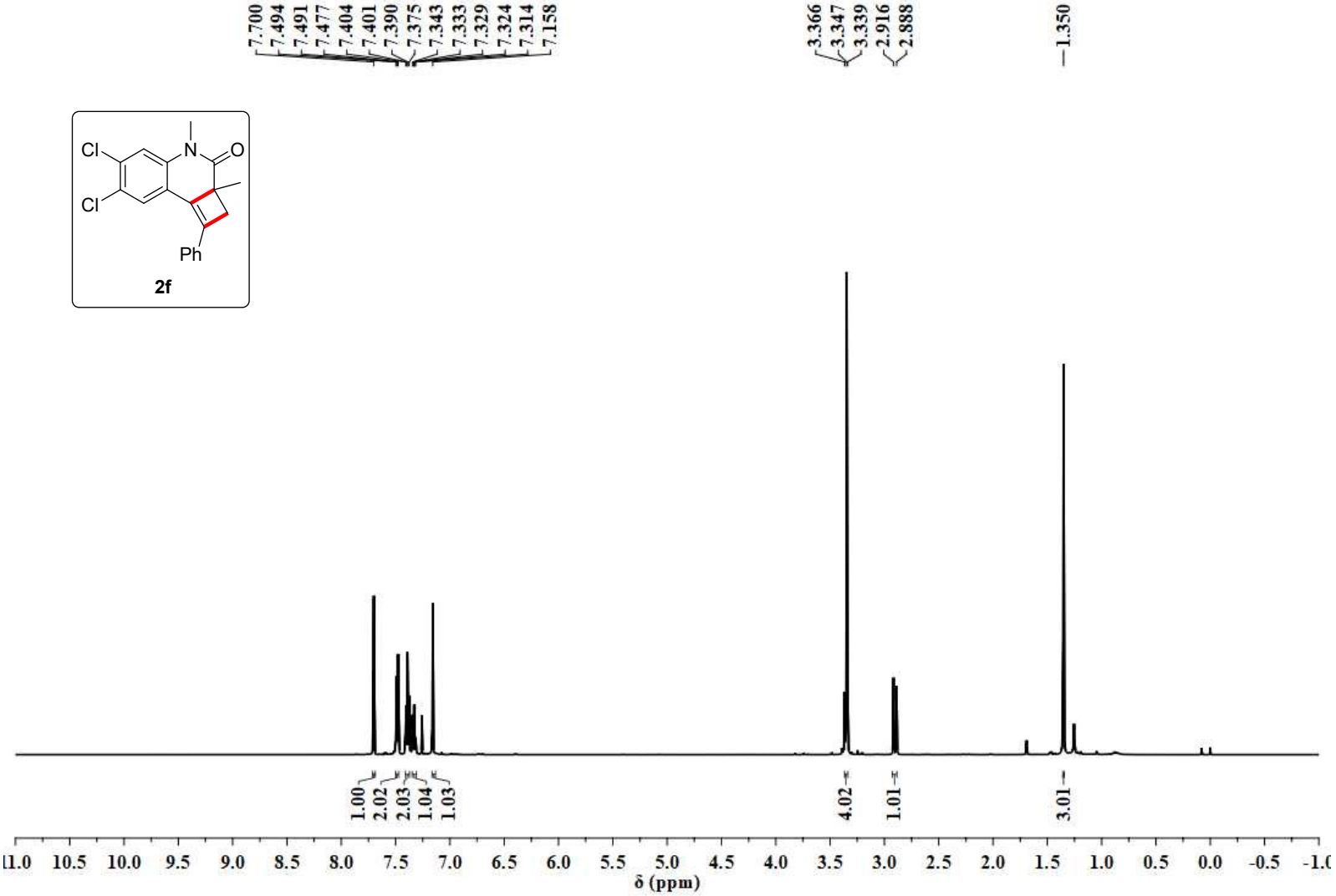
139.222
135.931
134.341
134.204
128.682
128.630
126.621
125.880
122.587
120.232
116.131
42.928
39.743
30.215
21.821
Cl
N
O
Ph
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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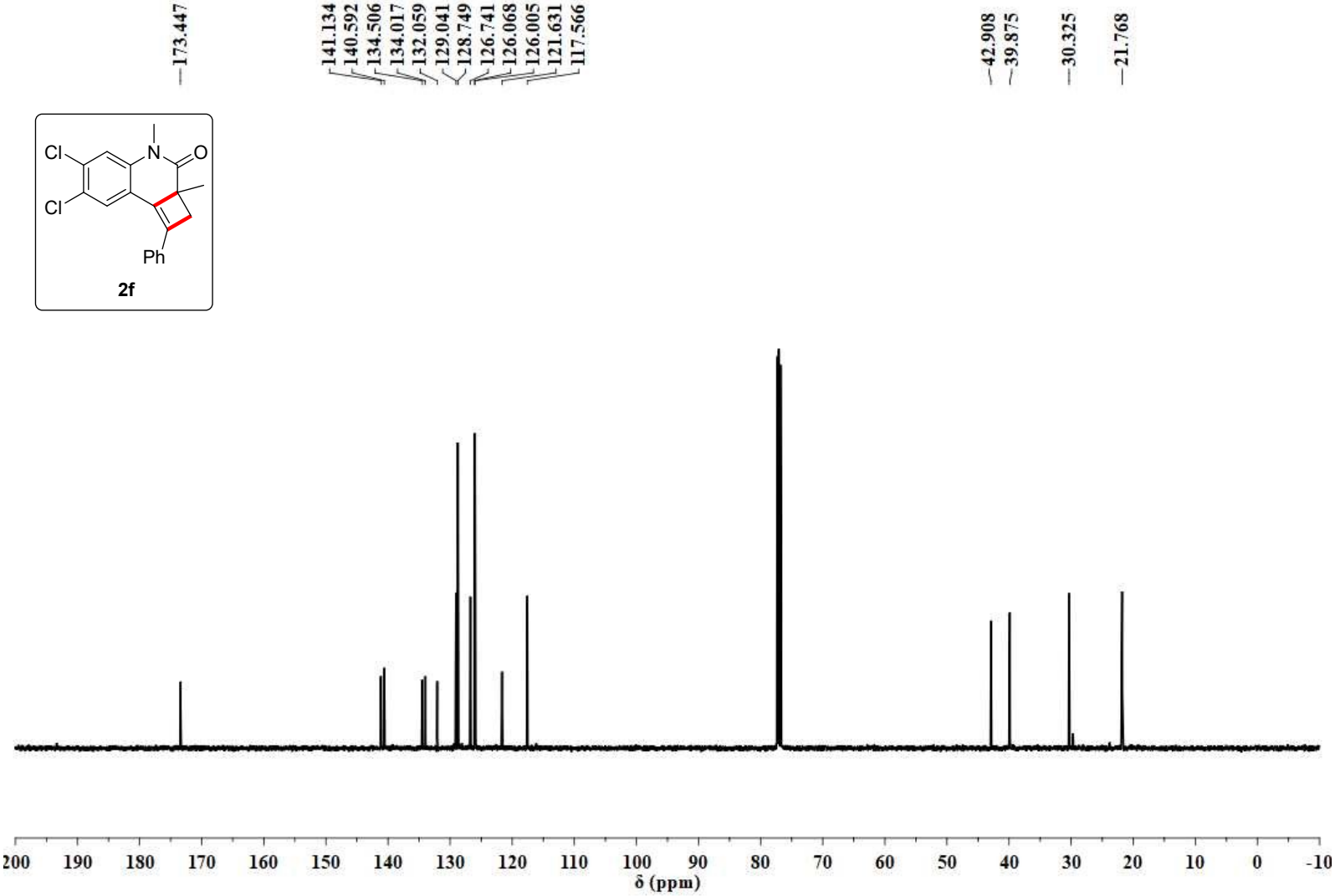
7.491
7.477
7.404
7.401
7.390
7.375
7.343
7.333
7.329
7.324
7.314
7.158
3.366
3.347
3.339
2.916
2.888
1.350
Cl
Cl
N
O
Ph
2f
1.00
2.02
2.03
1.04
1.03
4.02
1.01
3.01
δ (ppm)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140.592
134.506
134.017
132.059
129.041
128.749
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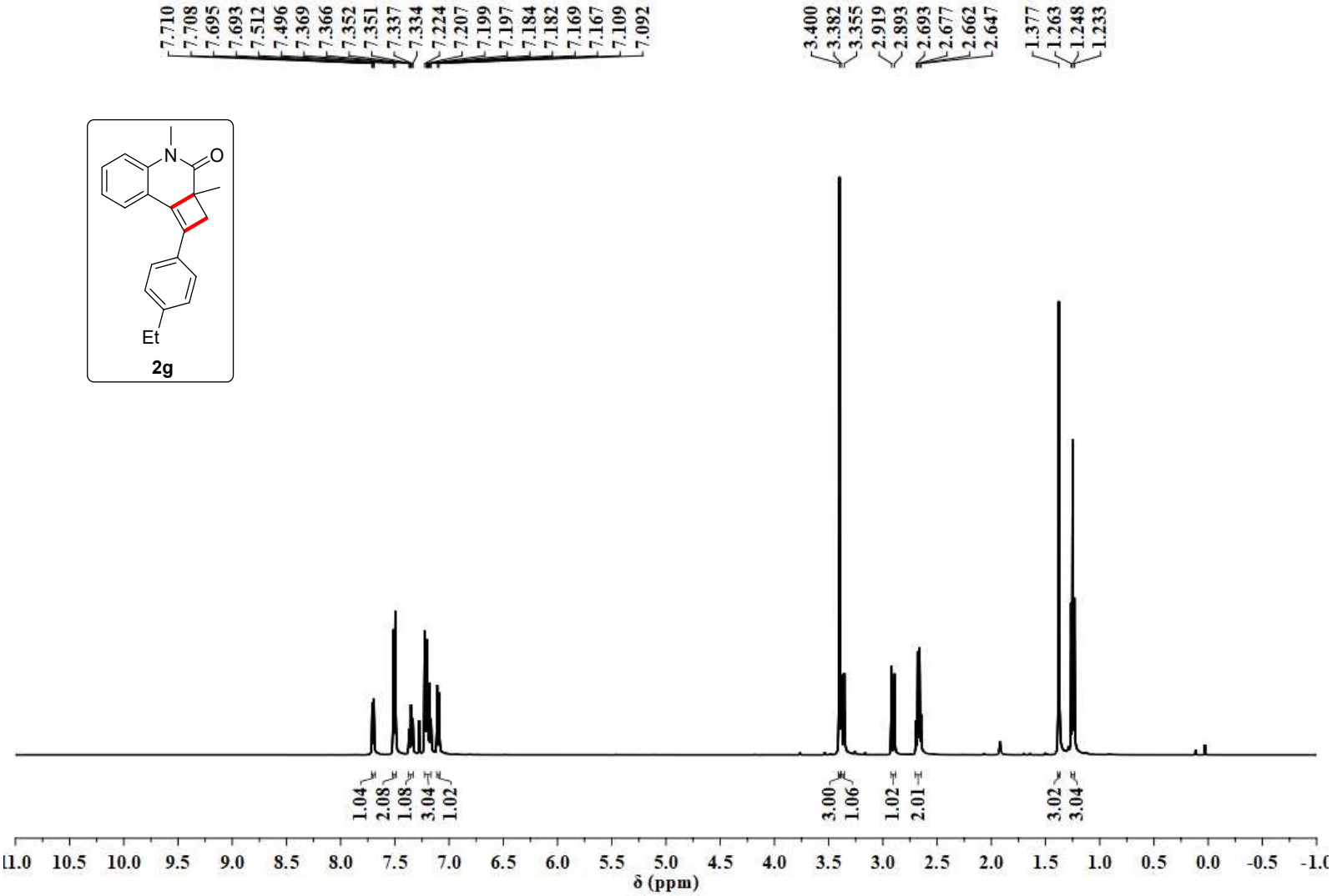
126.068
126.005
121.631
117.566
42.908
39.875
30.325
21.768
Cl
Cl
N
O
Ph
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.708
7.695
7.693
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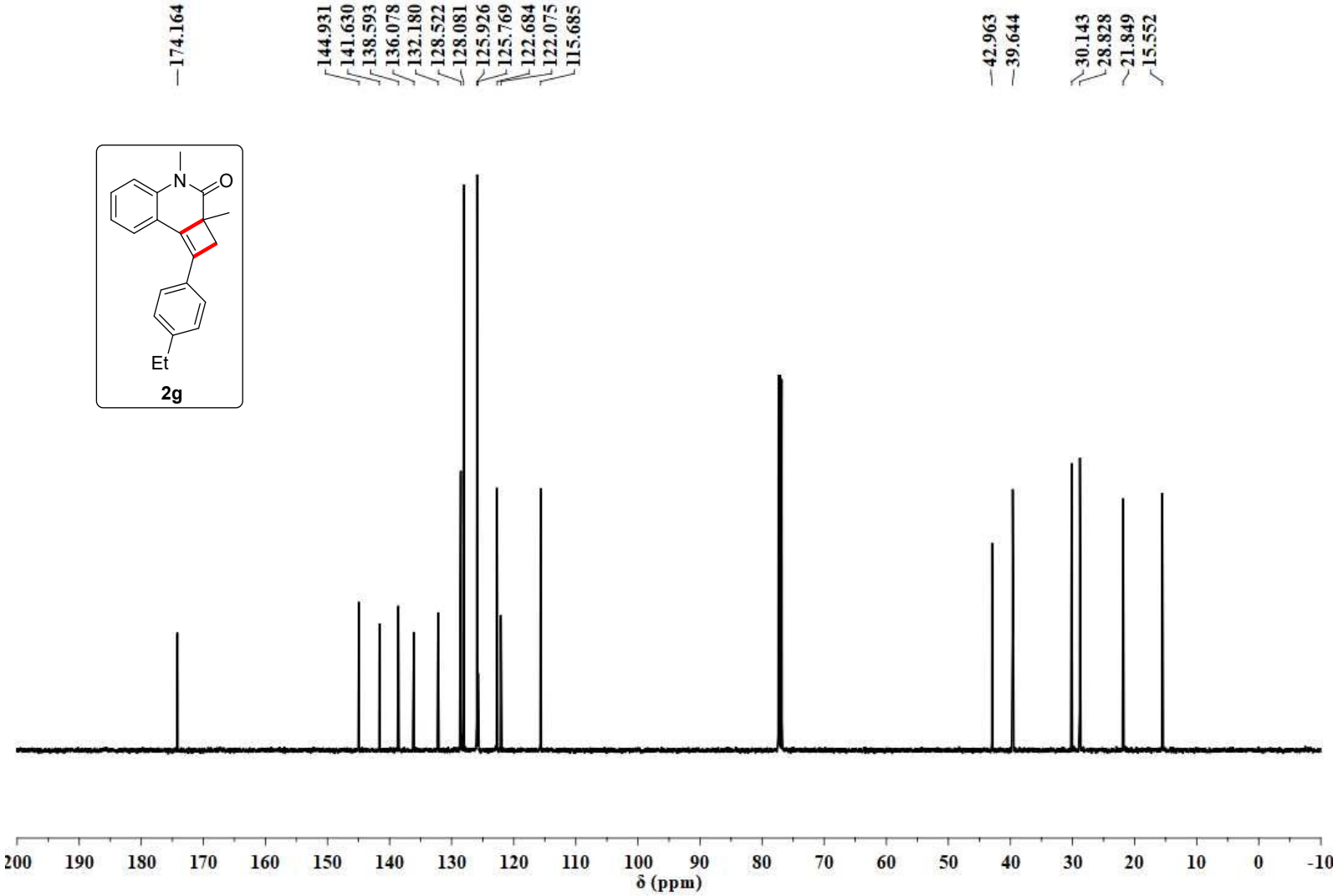
7.496
7.369
7.366
7.352
7.351
7.337
7.334
7.224
7.207
7.199
7.197
7.184
7.182
7.169
7.167
7.109
7.092
3.400
3.382
3.355
2.919
2.893
2.693
2.677
2.662
2.647
1.377
1.263
1.248
1.233
N
O
Et
2g
1.04
2.08
1.08
3.04
1.02
3.00
1.06
1.02
2.01
3.02
3.04
δ (ppm)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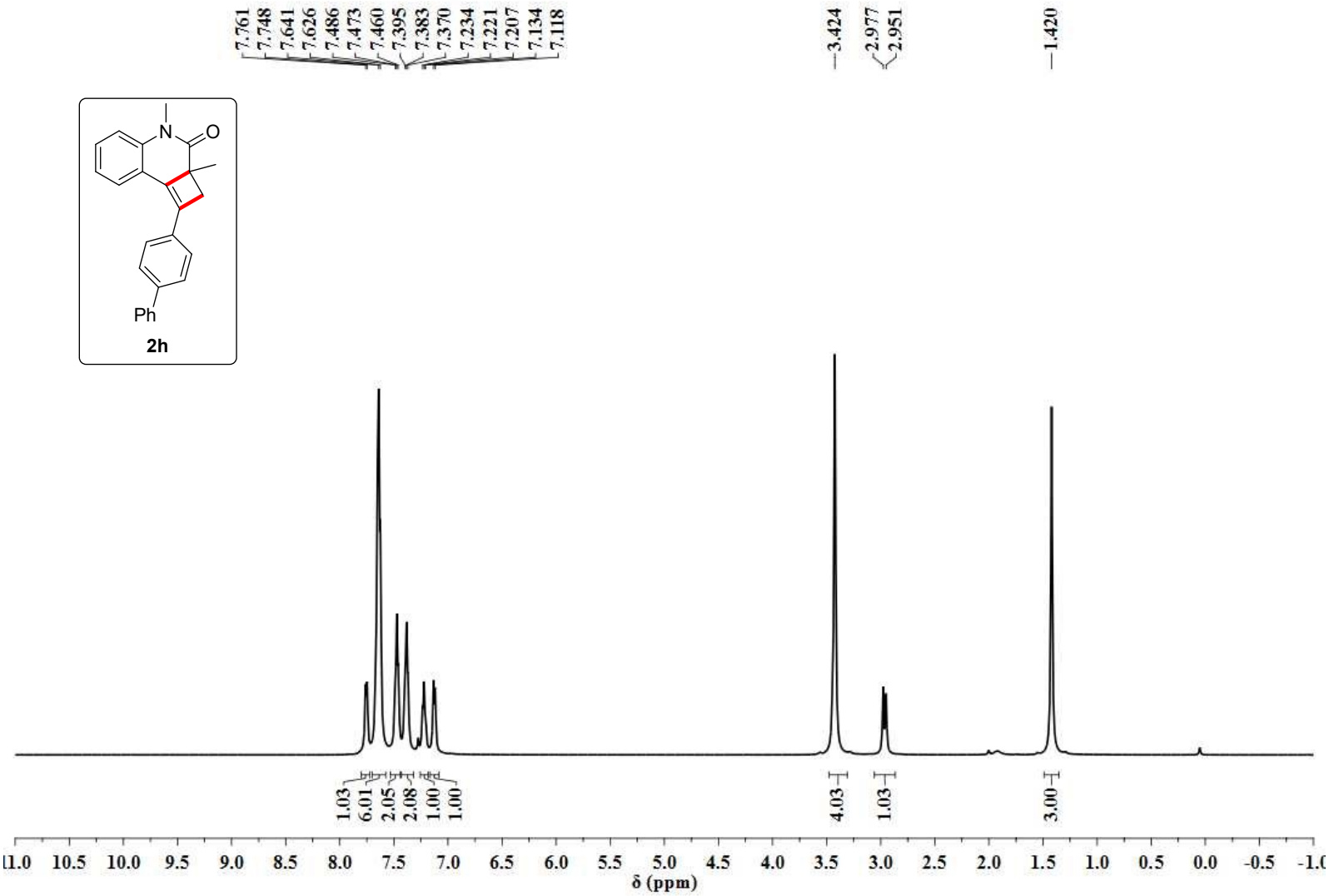
144.931
141.630
138.593
136.078
132.180
128.522
128.081
125.926
125.769
122.684
122.075
115.685
42.963
39.644
30.143
28.828
21.849
15.552
N
O
Et
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.626
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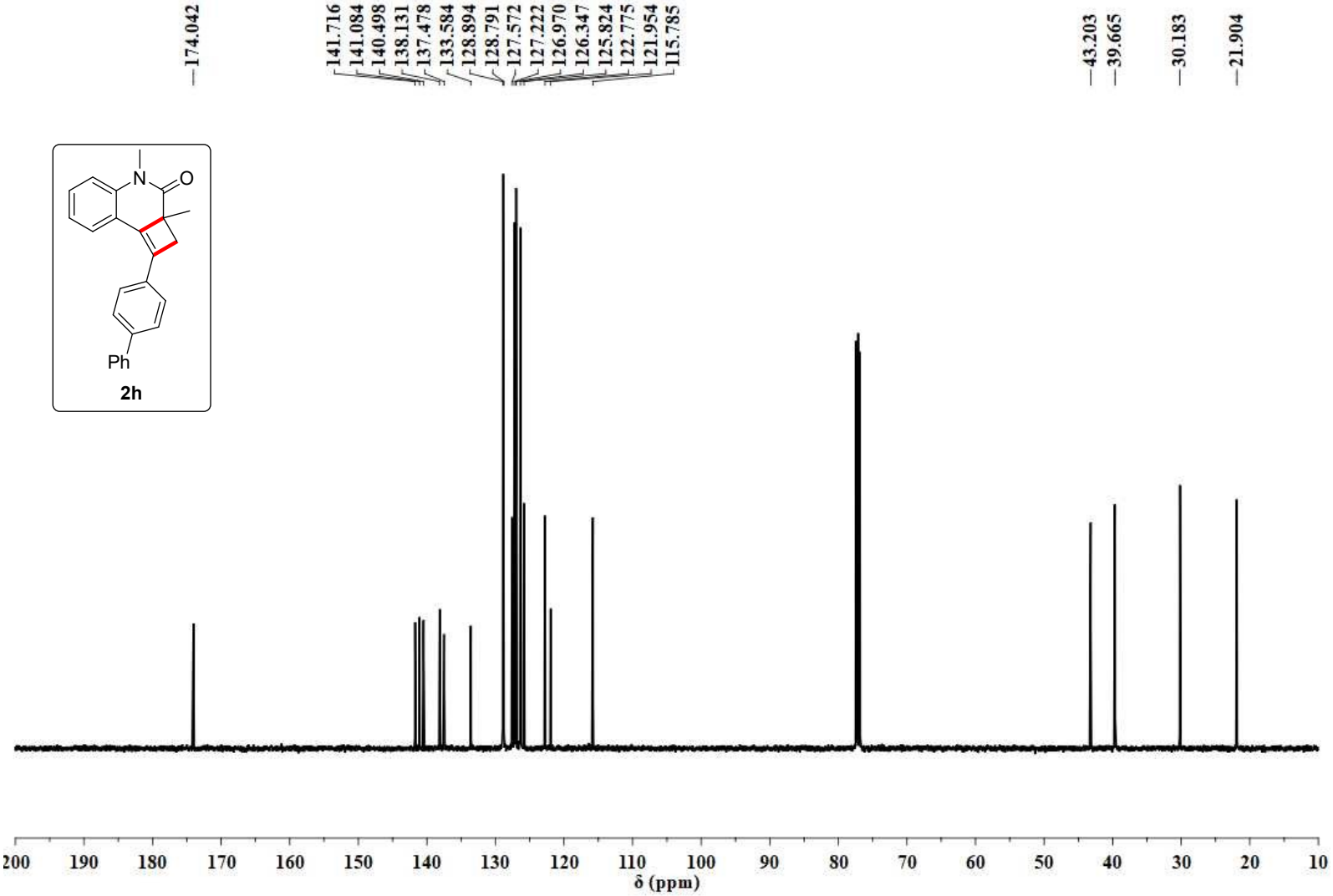
7.473
7.460
7.395
7.383
7.370
7.234
7.221
7.207
7.134
7.118
3.424
2.977
2.951
1.420
N
O
Ph
2h
1.03
6.01
2.05
2.08
1.00
1.00
4.03
1.03
3.00
δ (ppm)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141.084
140.498
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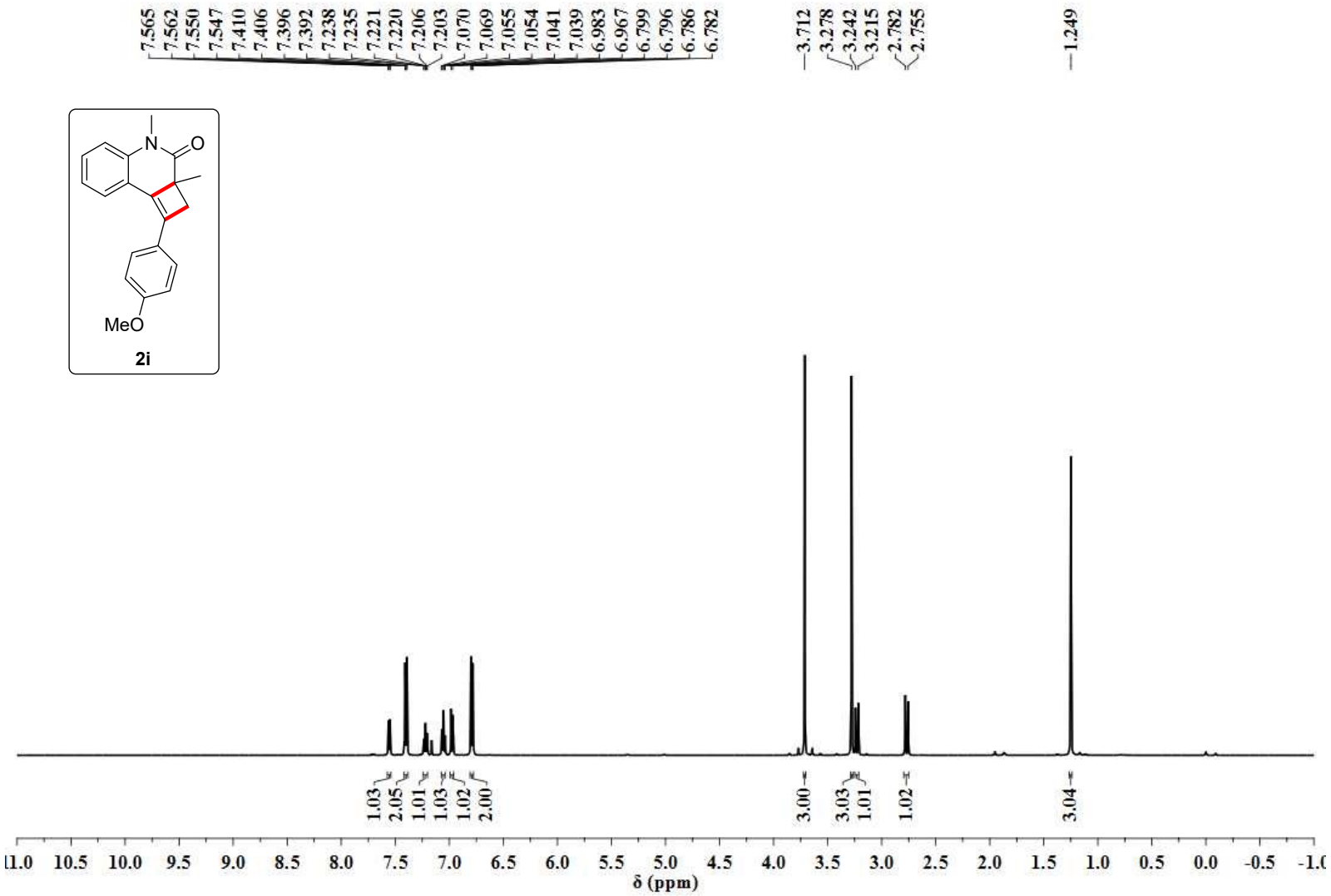
137.478
133.584
128.894
128.791
127.572
127.222
126.970
126.347
125.824
122.775
121.954
115.785
43.203
39.665
30.183
21.904
N
O
Ph
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ (ppm)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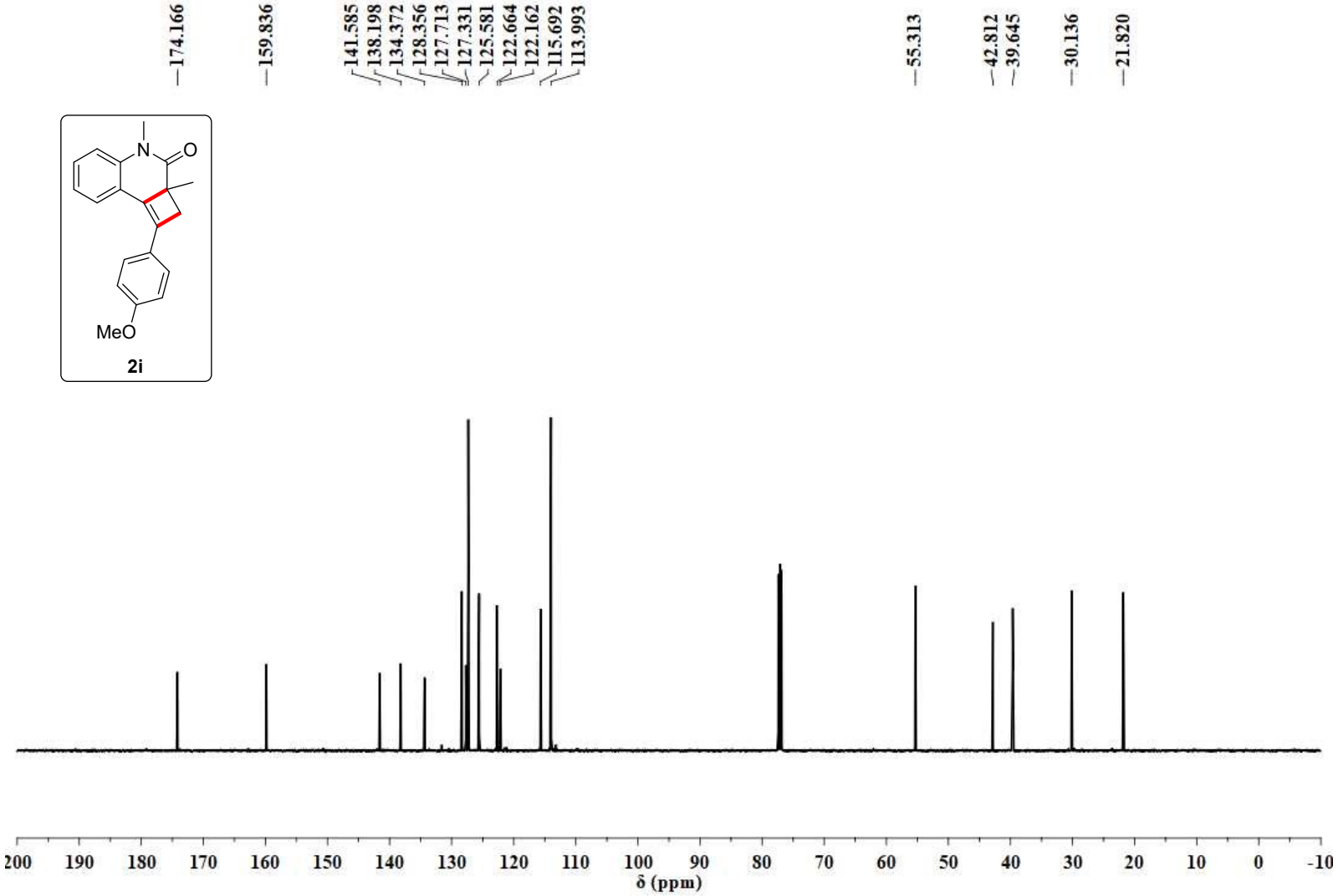
7.562
7.550
7.547
7.410
7.406
7.396
7.392
7.238
7.235
7.221
7.220
7.206
7.203
7.070
7.069
7.055
7.054
7.041
7.039
6.983
6.967
6.799
6.796
6.786
6.782
3.712
3.278
3.242
3.215
2.782
2.755
1.249
N
O
MeO
2i
1.03
2.05
1.01
1.03
1.02
2.00
3.00
3.03
1.01
1.02
3.04
δ (ppm)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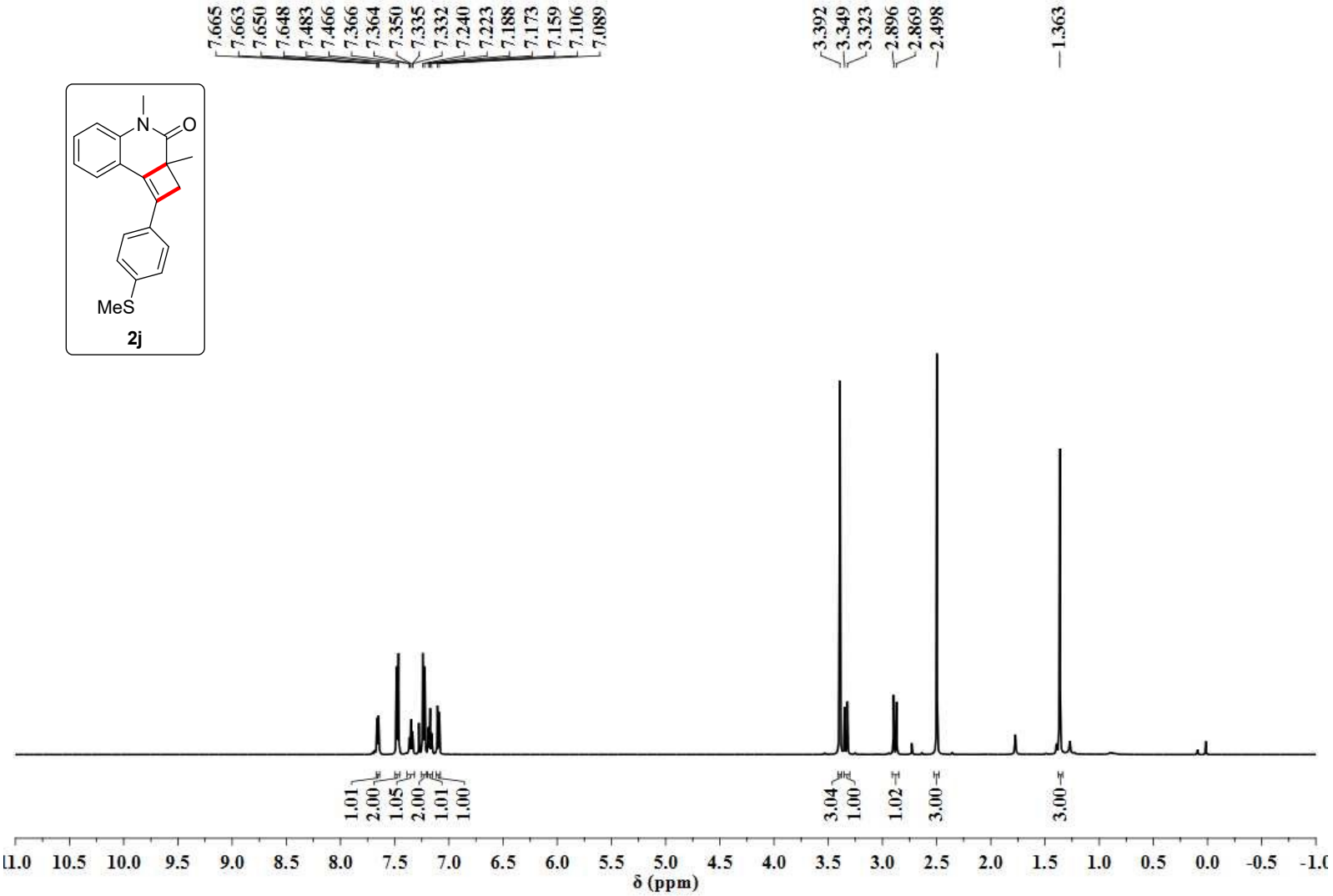
159.836
141.585
138.198
134.372
128.356
127.713
127.331
125.581
122.664
122.162
115.692
113.993
55.313
42.812
39.645
30.136
21.820
N
O
MeO
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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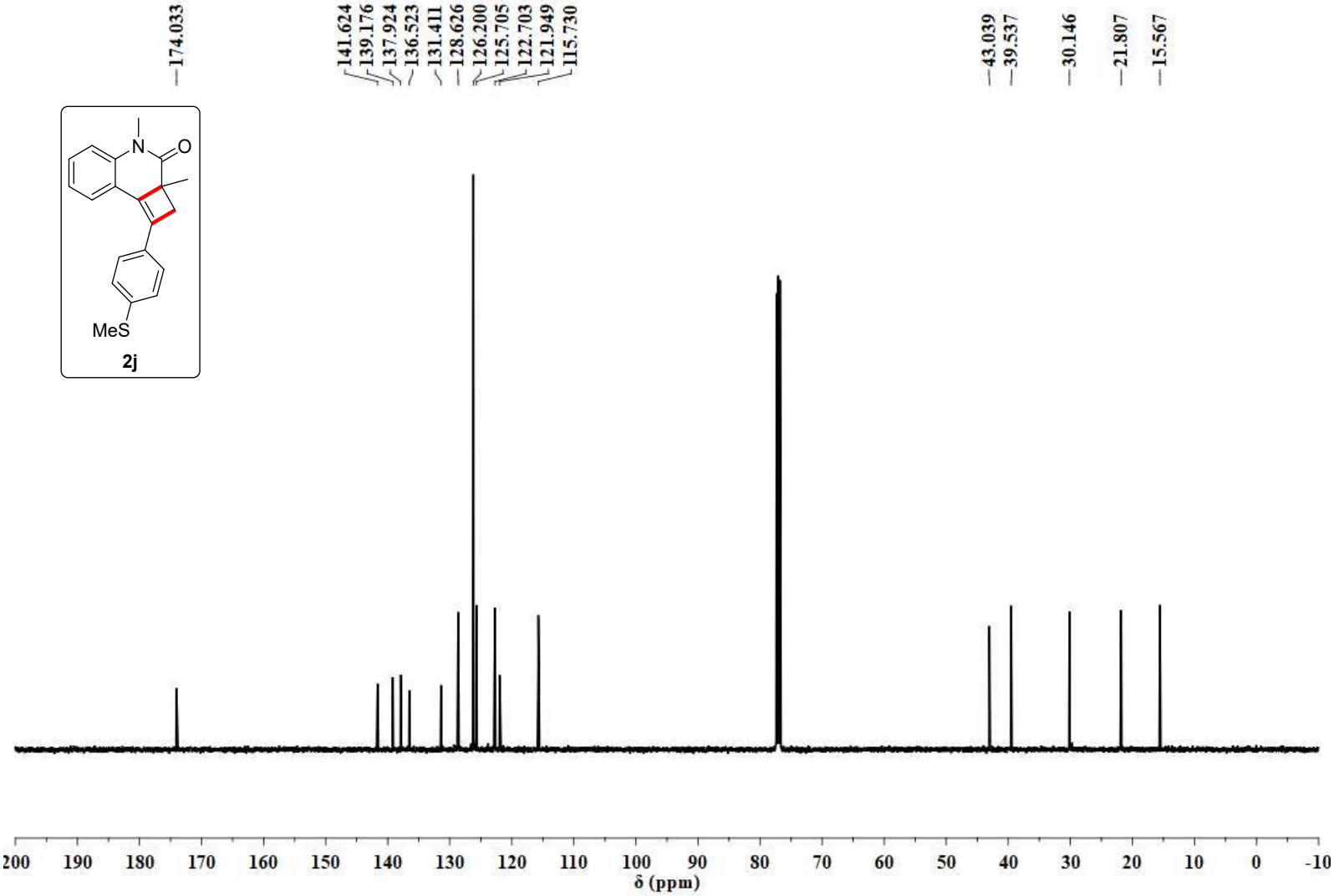
7.466
7.366
7.364
7.350
7.335
7.332
7.240
7.223
7.188
7.173
7.159
7.106
7.089
3.392
3.349
3.323
2.896
2.869
2.498
1.363
N
O
MeS
2j
1.01
2.00
1.05
2.00
1.01
1.00
3.04
1.00
1.02
3.00
3.00
δ (ppm)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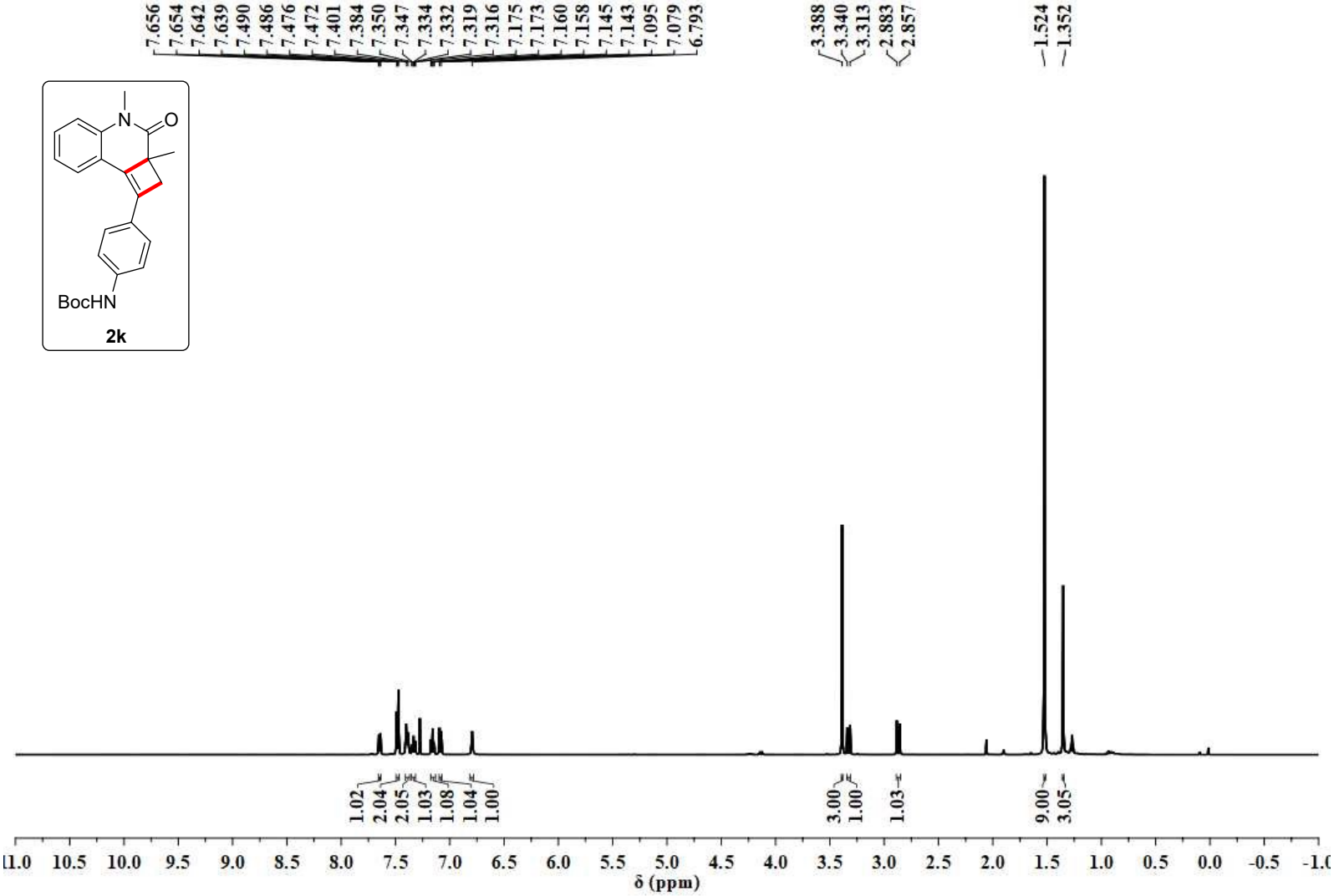
141.624
139.176
137.924
136.523
131.411
128.626
126.200
125.705
122.703
121.949
115.730
43.039
39.537
30.146
21.807
15.567
N
O
MeS
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.642
7.639
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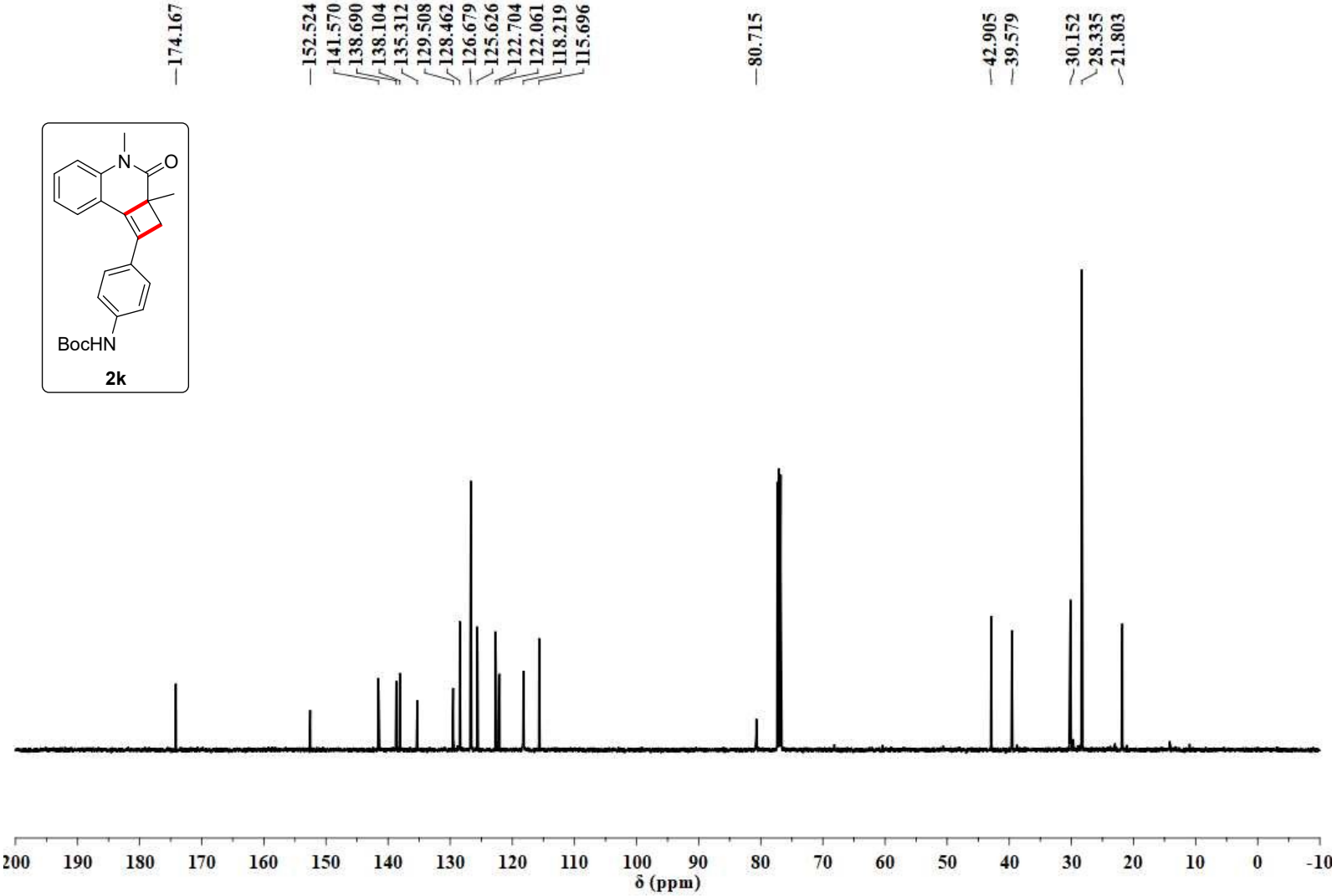
7.486
7.476
7.472
7.401
7.384
7.350
7.347
7.334
7.332
7.319
7.316
7.175
7.173
7.160
7.158
7.145
7.143
7.095
7.079
6.793
3.388
3.340
3.313
2.883
2.857
1.524
1.352
N
O
BocHN
2k
1.02
2.04
2.05
1.03
1.08
1.04
1.00
3.00
1.00
1.03
9.00
3.05
δ (ppm)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152.524
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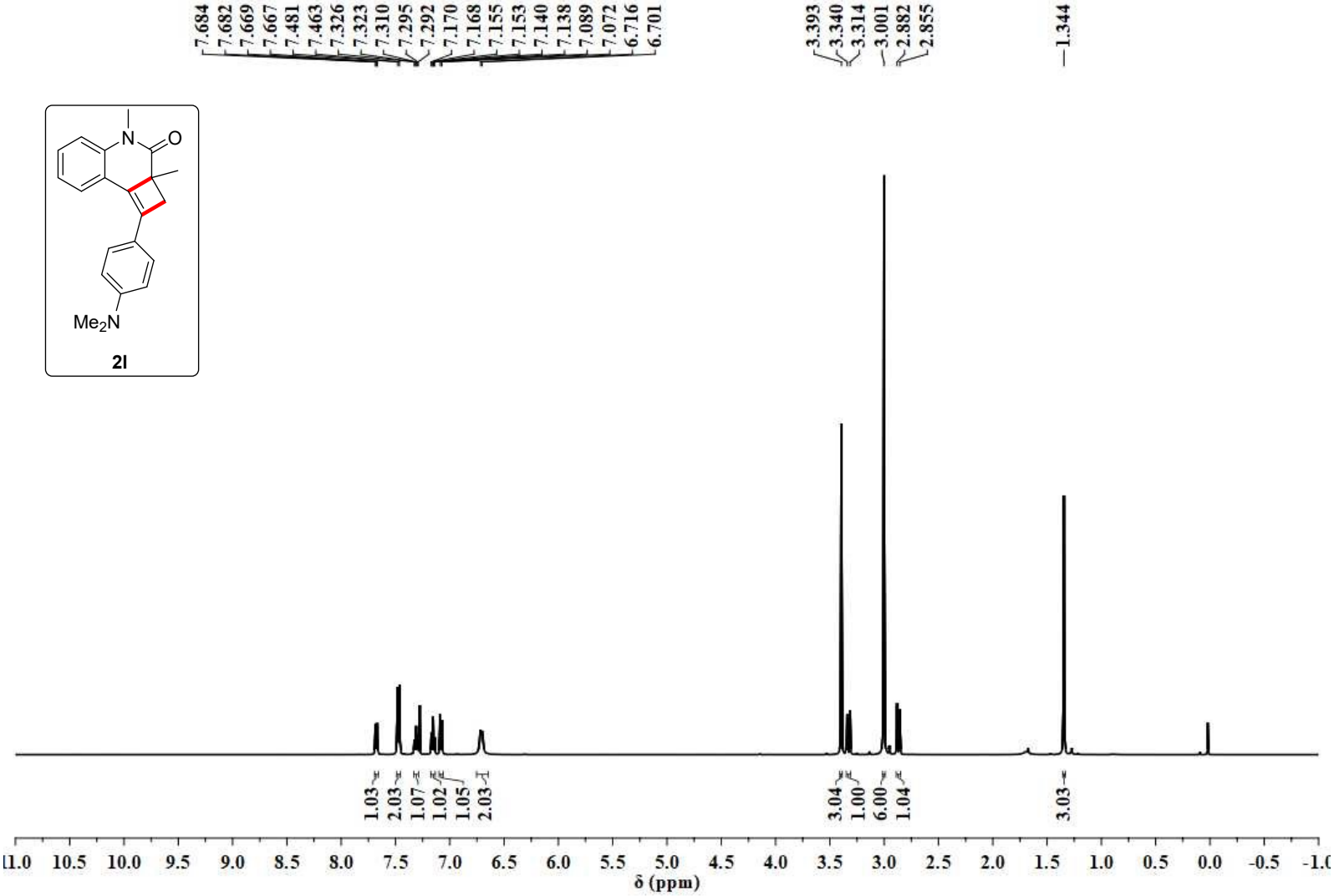
138.690
138.104
135.312
129.508
128.462
126.679
125.626
122.704
122.061
118.219
115.696
80.715
42.905
39.579
30.152
28.335
21.803
N
O
BocHN
2k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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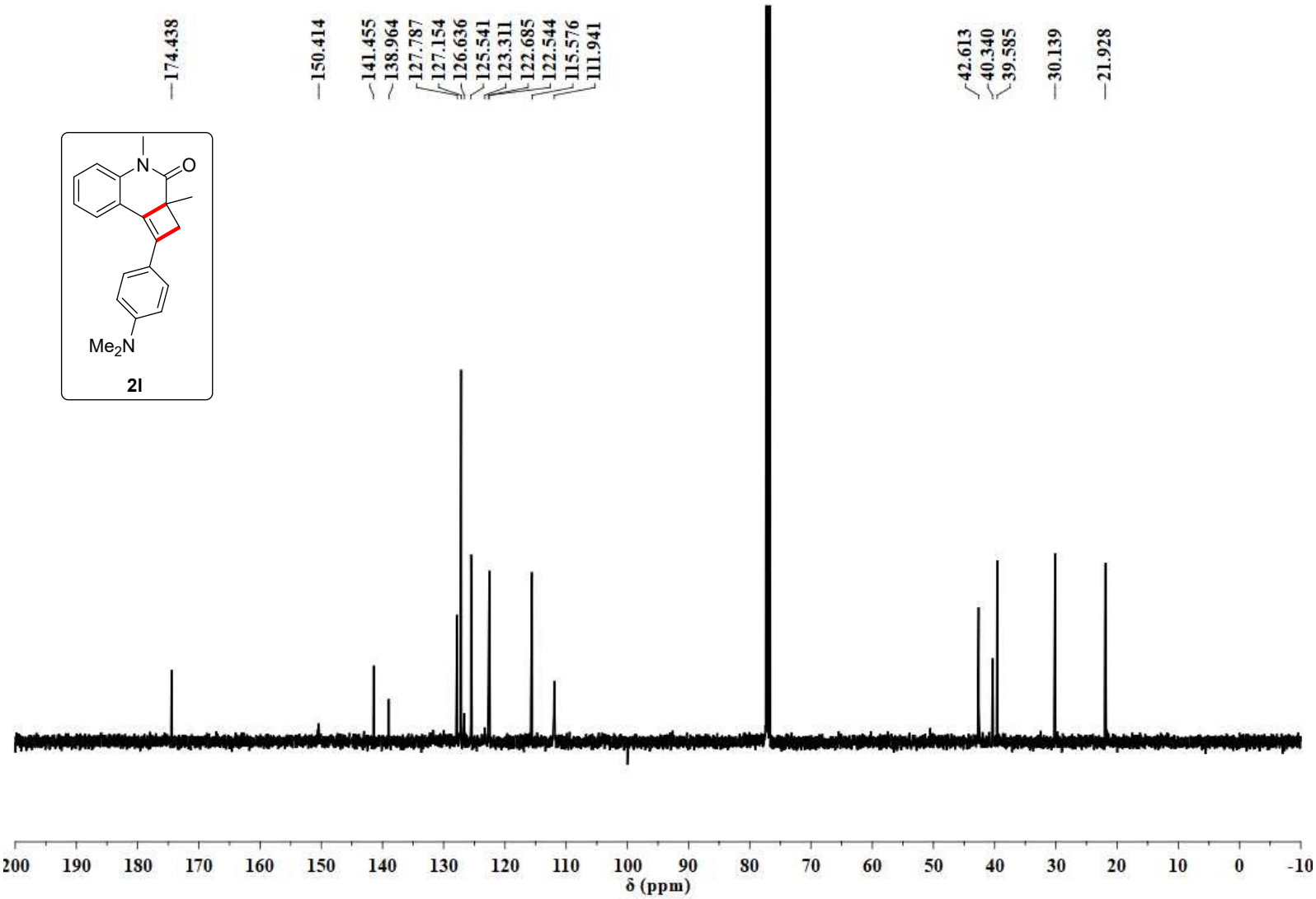
7.669
7.667
7.481
7.463
7.326
7.323
7.310
7.295
7.292
7.170
7.168
7.155
7.153
7.140
7.138
7.089
7.072
6.716
6.701
3.393
3.340
3.314
3.001
2.882
2.855
1.344
N
O
Me2N
2l
1.03
2.03
1.07
1.02
1.05
2.03
3.04
1.00
6.00
1.04
3.03
δ (ppm)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127.154
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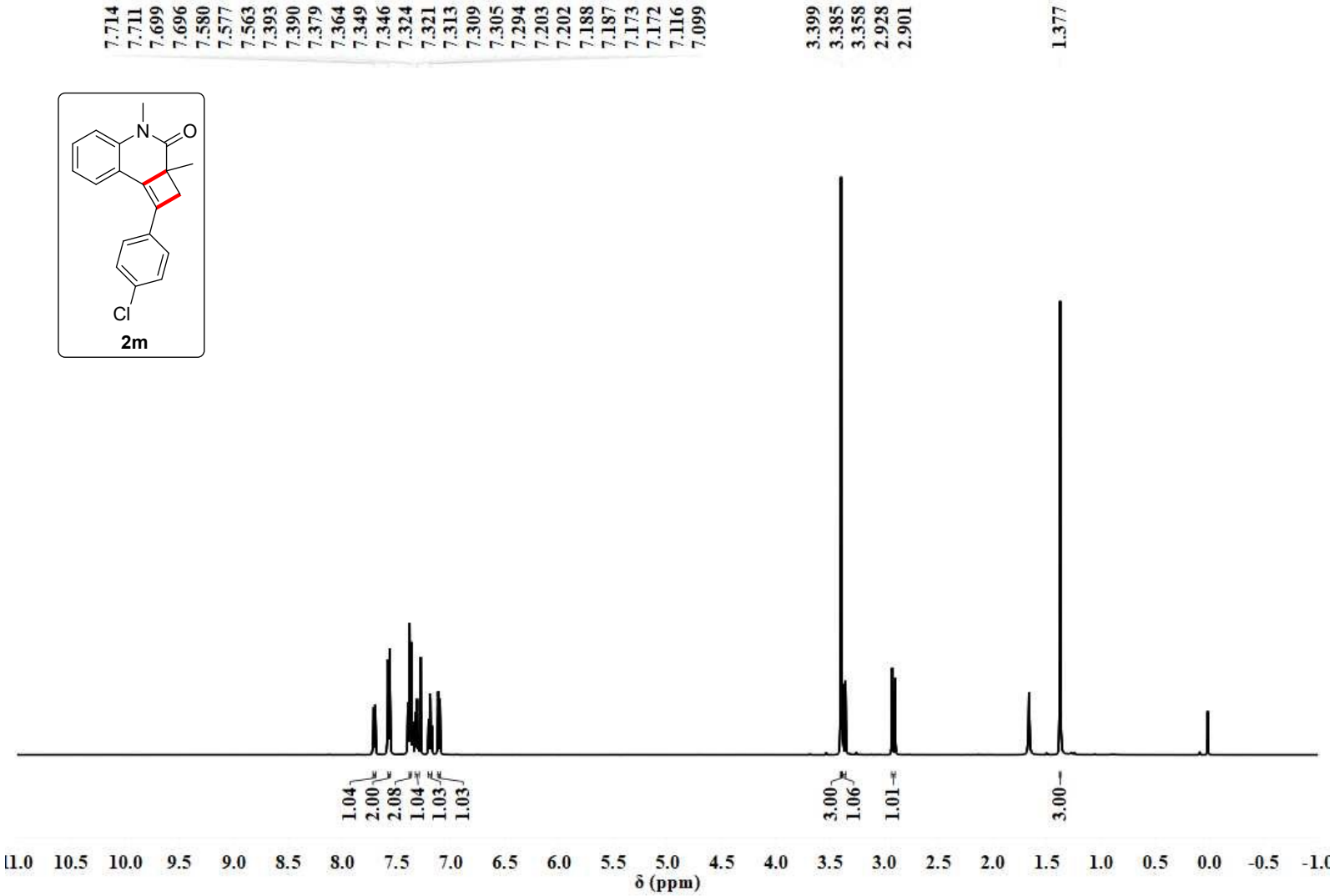
125.541
123.311
122.685
122.544
115.576
111.941
42.613
40.340
39.585
30.139
21.928
N
O
Me2N
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.580
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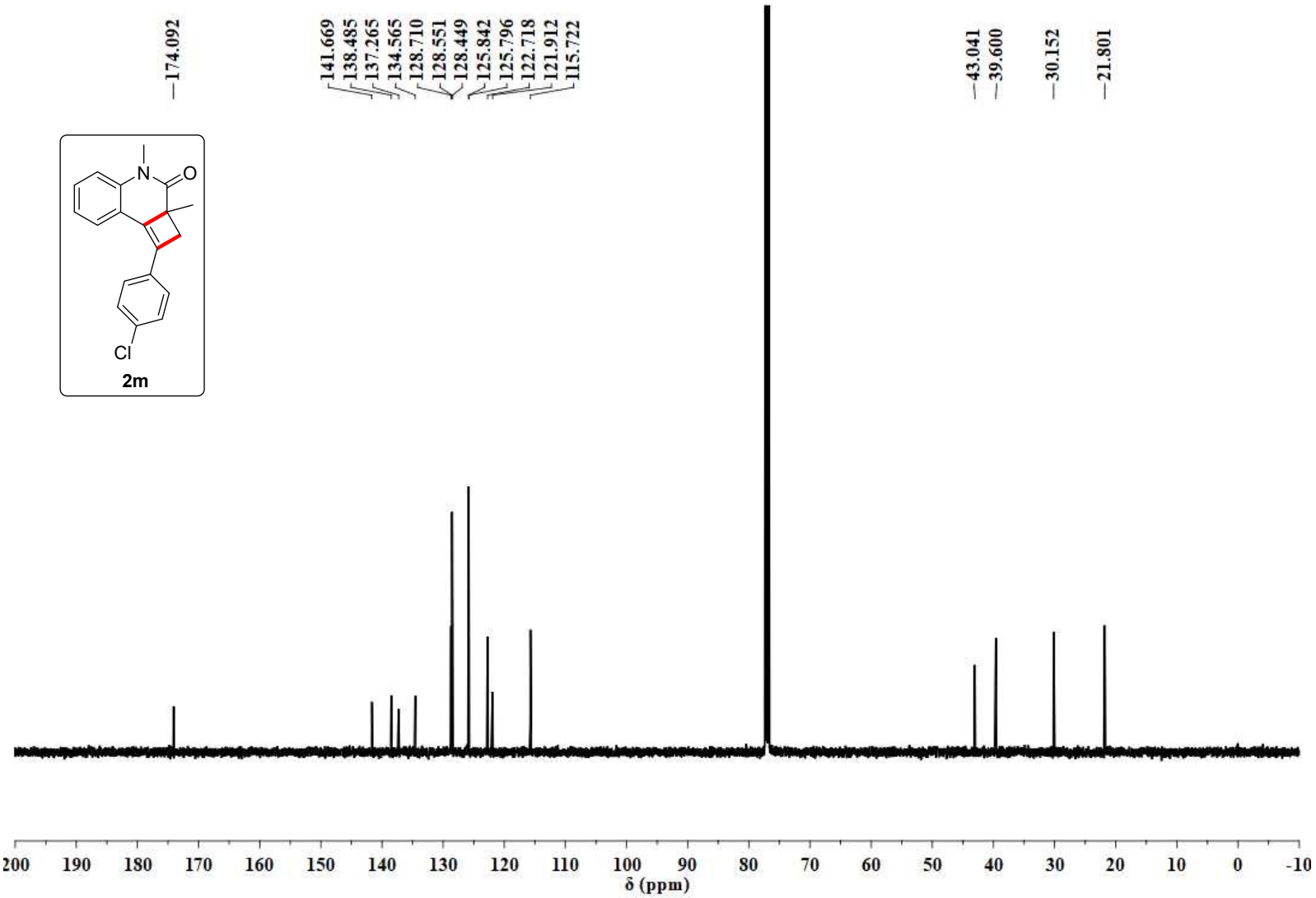
7.563
7.393
7.390
7.379
7.364
7.349
7.346
7.324
7.321
7.313
7.309
7.305
7.294
7.203
7.202
7.188
7.187
7.173
7.172
7.116
7.099
3.399
3.385
3.358
2.928
2.901
1.377
N
O
Cl
2m
1.04
2.00
2.08
1.04
1.03
1.03
3.00
1.06
1.01
3.00
δ (ppm)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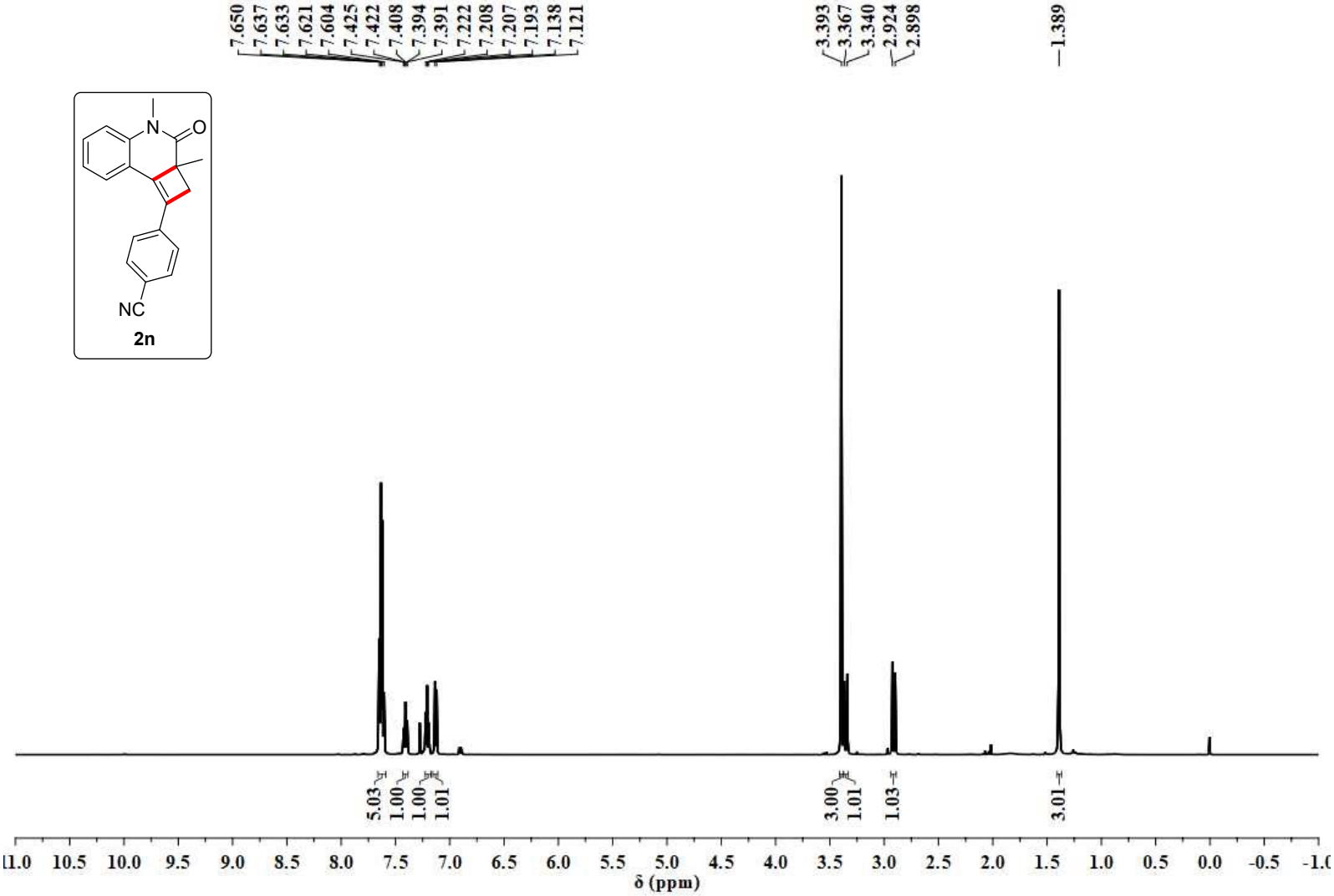
128.551
128.449
125.842
125.796
122.718
121.912
115.722
43.041
39.600
30.152
21.801
N
O
Cl
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.422
7.408
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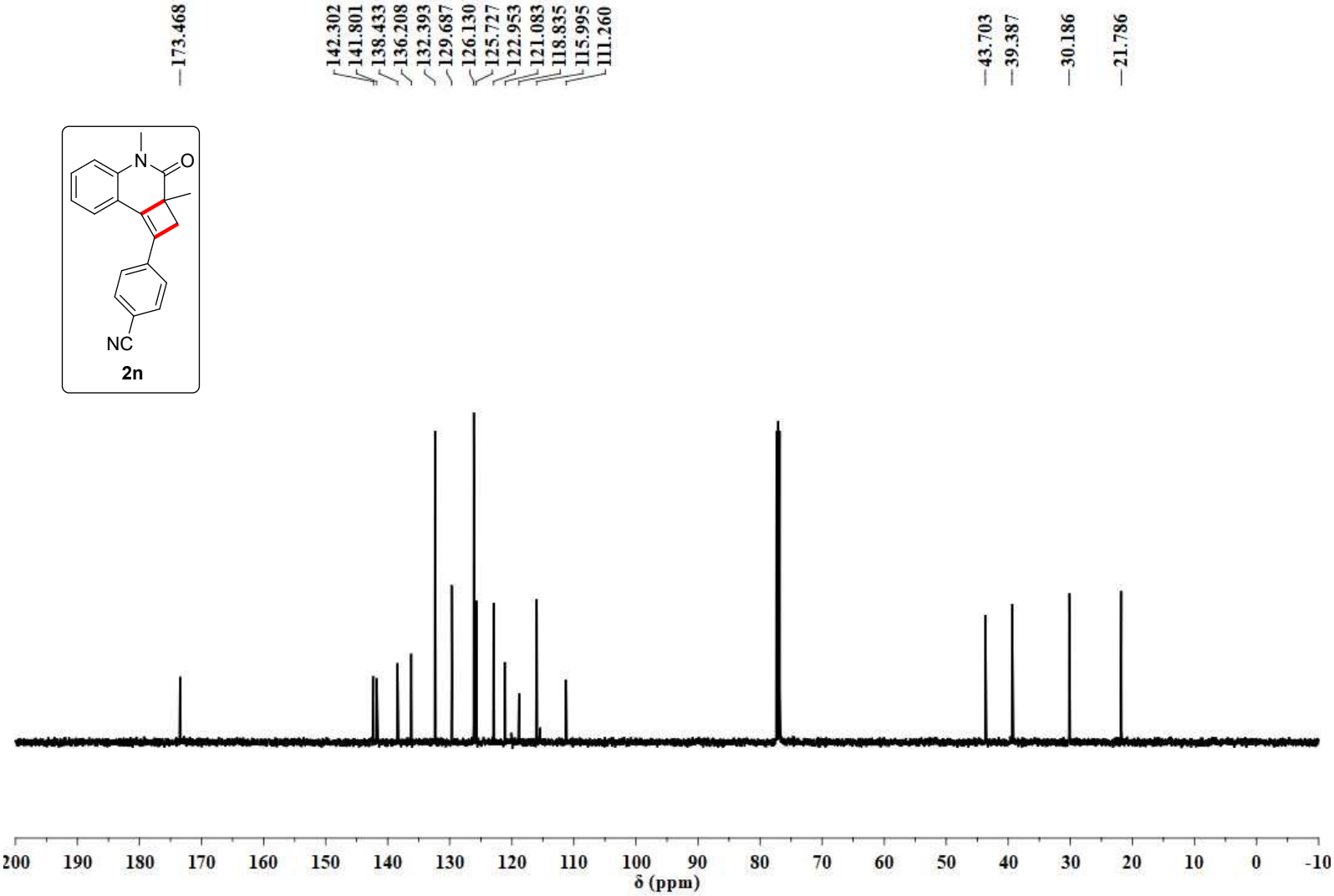
7.391
7.222
7.208
7.207
7.193
7.138
7.121
3.393
3.367
3.340
2.924
2.898
1.389
N
O
NC
2n
5.03
1.00
1.00
1.01
3.00
1.01
1.03
3.01
δ (ppm)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129.687
126.130
125.727
122.953
121.083
118.835
115.995
111.260
43.703
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30.186
21.786
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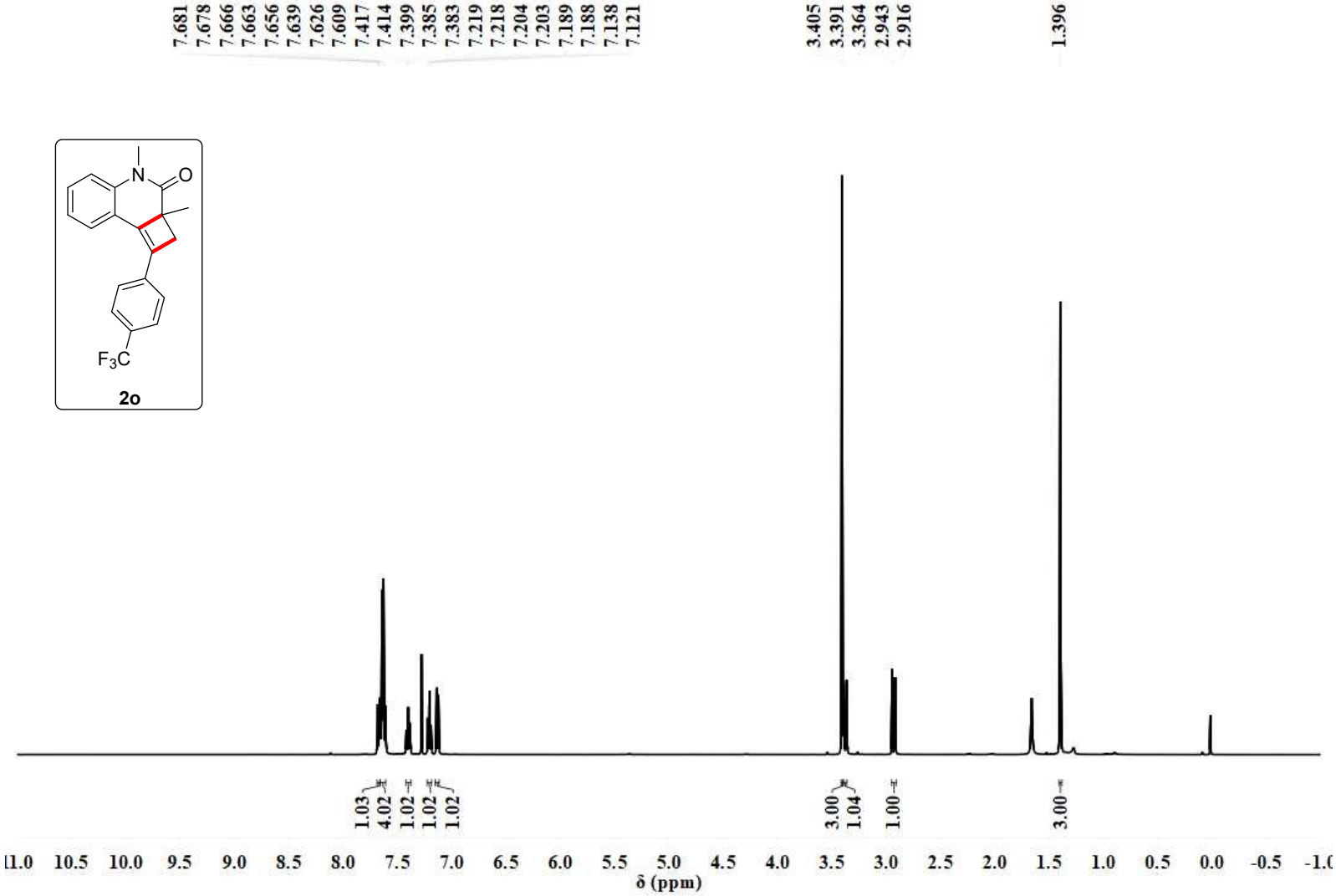
NC
2n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.609
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7.414
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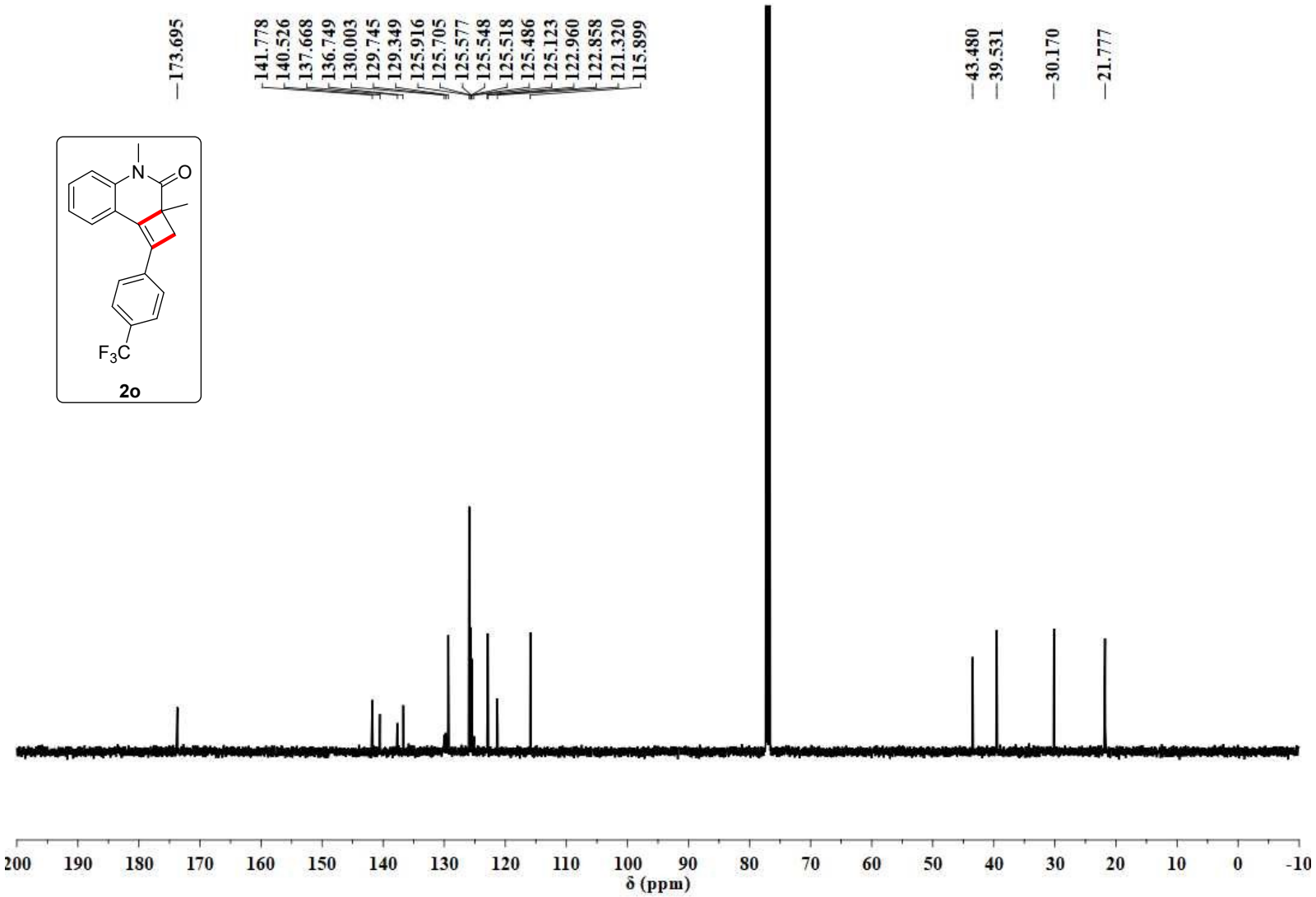
7.385
7.383
7.219
7.218
7.204
7.203
7.189
7.188
7.138
7.121
3.405
3.391
3.364
2.943
2.916
1.396
N
O
F3C
2o
1.03
4.02
1.02
1.02
1.02
3.00
1.04
1.00
3.00
δ (ppm)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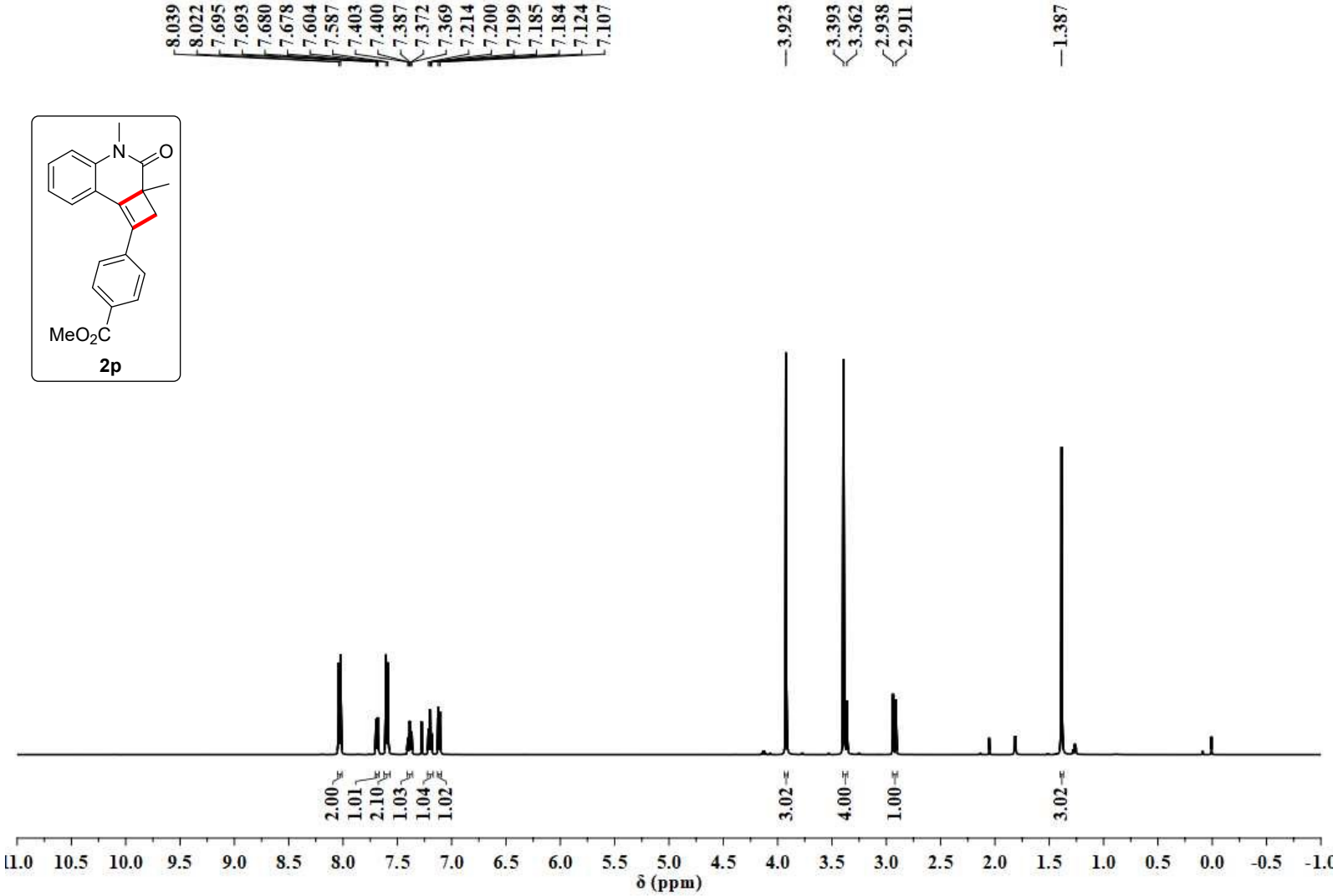
136.749
130.003
129.745
129.349
125.916
125.705
125.577
125.548
125.518
125.486
125.123
122.960
122.858
121.320
115.899
43.480
39.531
30.170
21.777
N
O
F3C
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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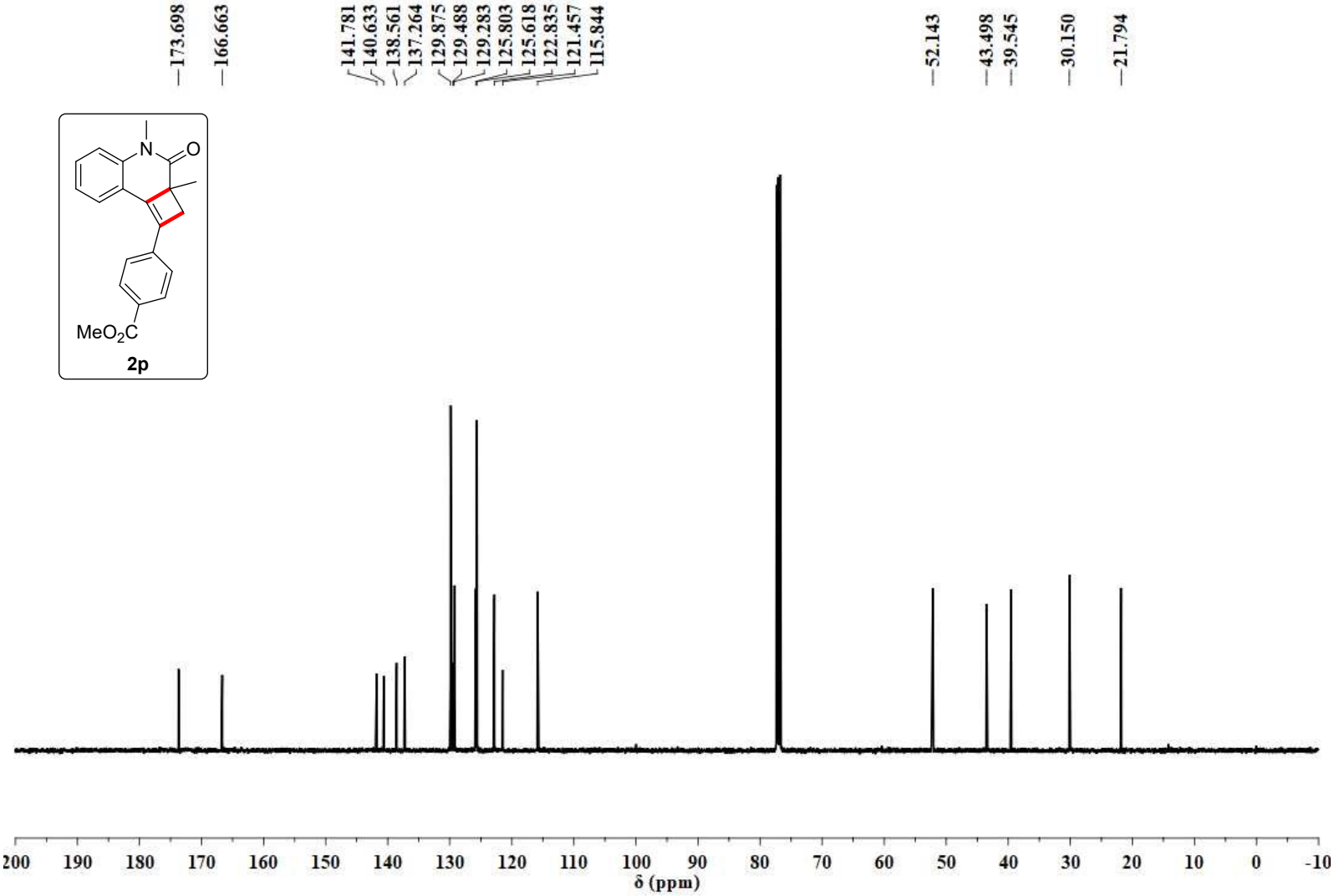
7.587
7.403
7.400
7.387
7.372
7.369
7.214
7.200
7.199
7.185
7.184
7.124
7.107
3.923
3.393
3.362
2.938
2.911
1.387
N
O
MeO2C
2p
2.00
1.01
2.10
1.03
1.04
1.02
3.02
4.00
1.00
3.02
δ (ppm)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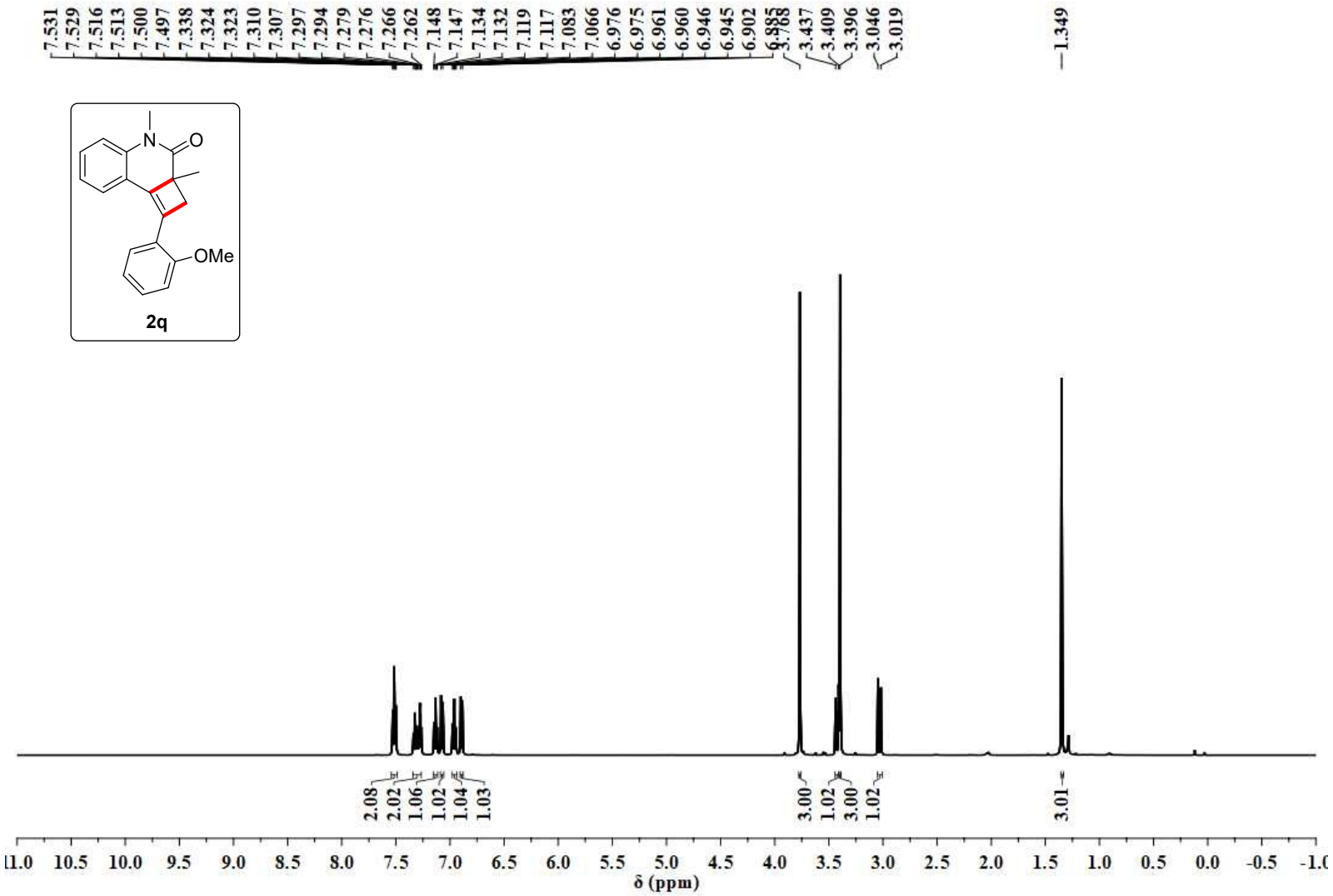
129.488
129.283
125.803
125.618
122.835
121.457
115.844
52.143
43.498
39.545
30.150
21.794
N
O
MeO2C
2p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.307
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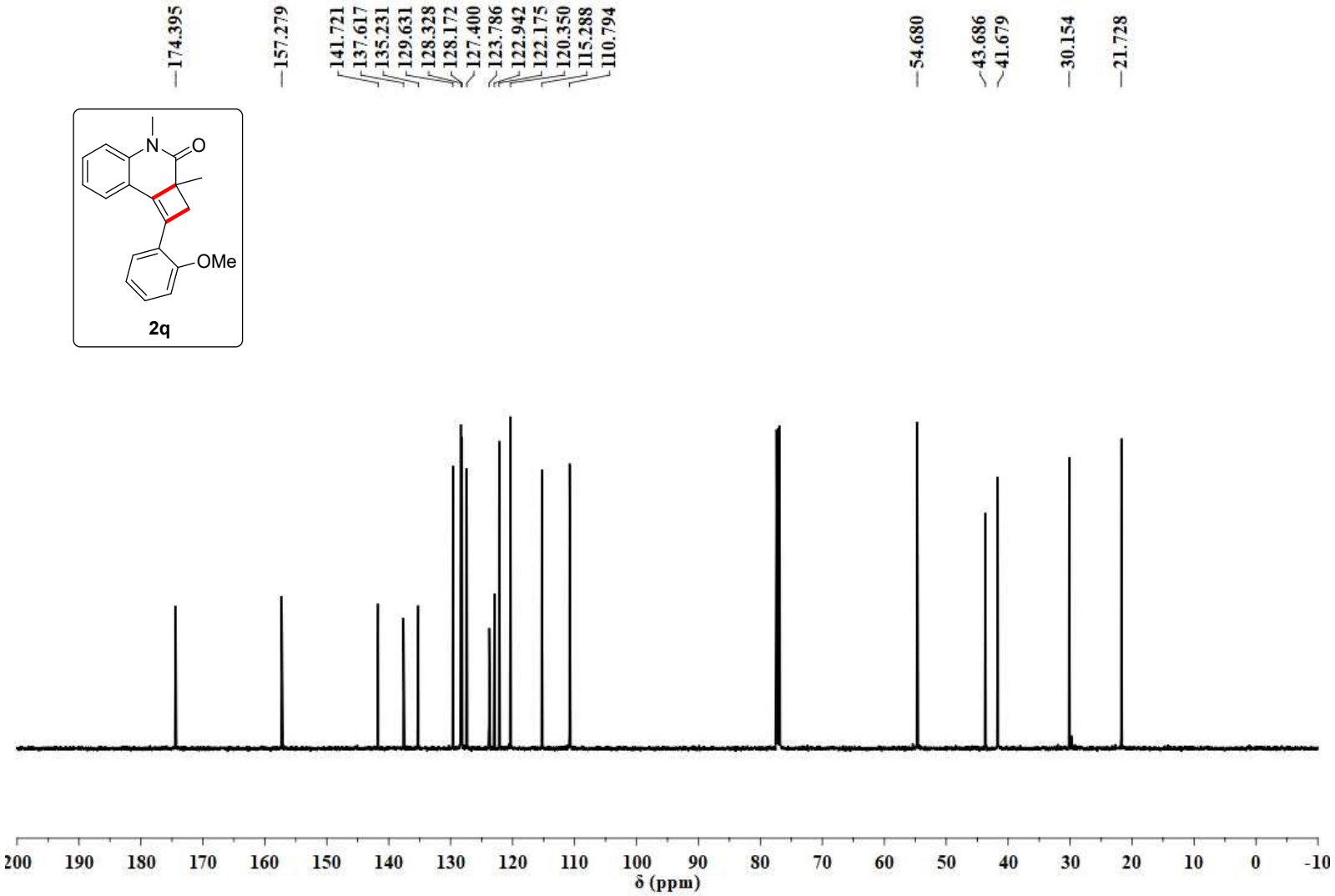
7.294
7.279
7.276
7.266
7.262
7.148
7.147
7.134
7.132
7.119
7.117
7.083
7.066
6.976
6.975
6.961
6.960
6.946
6.945
6.902
3.437
3.409
3.396
3.046
3.019
1.349
N
O
OMe
2q
2.08
2.02
1.06
1.02
1.04
1.03
3.00
1.02
3.00
1.02
3.01
δ (ppm)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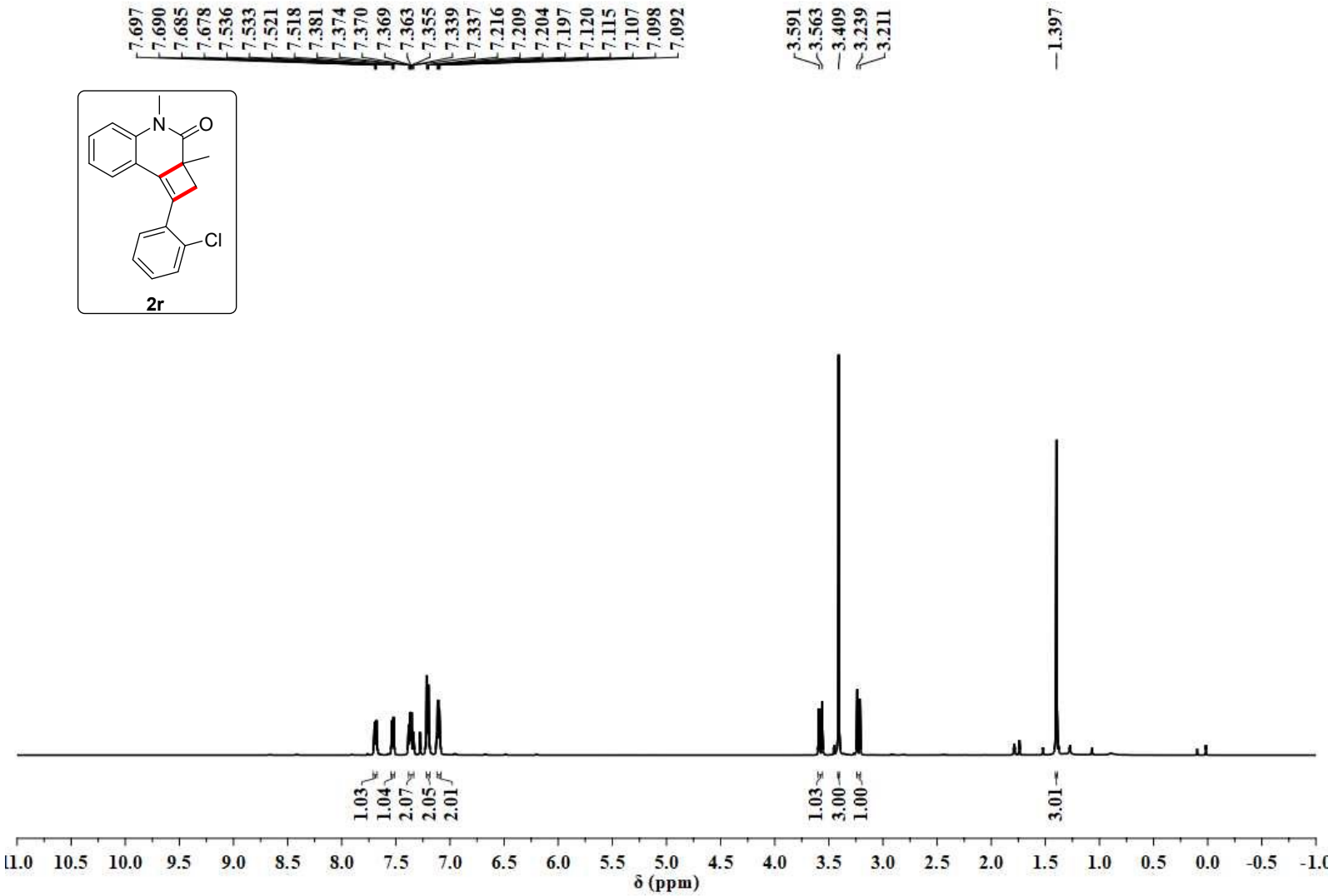
128.172
127.400
123.786
122.942
122.175
120.350
115.288
110.794
54.680
43.686
41.679
30.154
21.728
N
O
OMe
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.521
7.518
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7.374
7.370
7.369
7.363
7.355
7.339
7.337
7.216
7.209
7.204
7.197
7.120
7.115
7.107
7.098
7.092
3.591
3.563
3.409
3.239
3.211
1.397
N
O
Cl
2r
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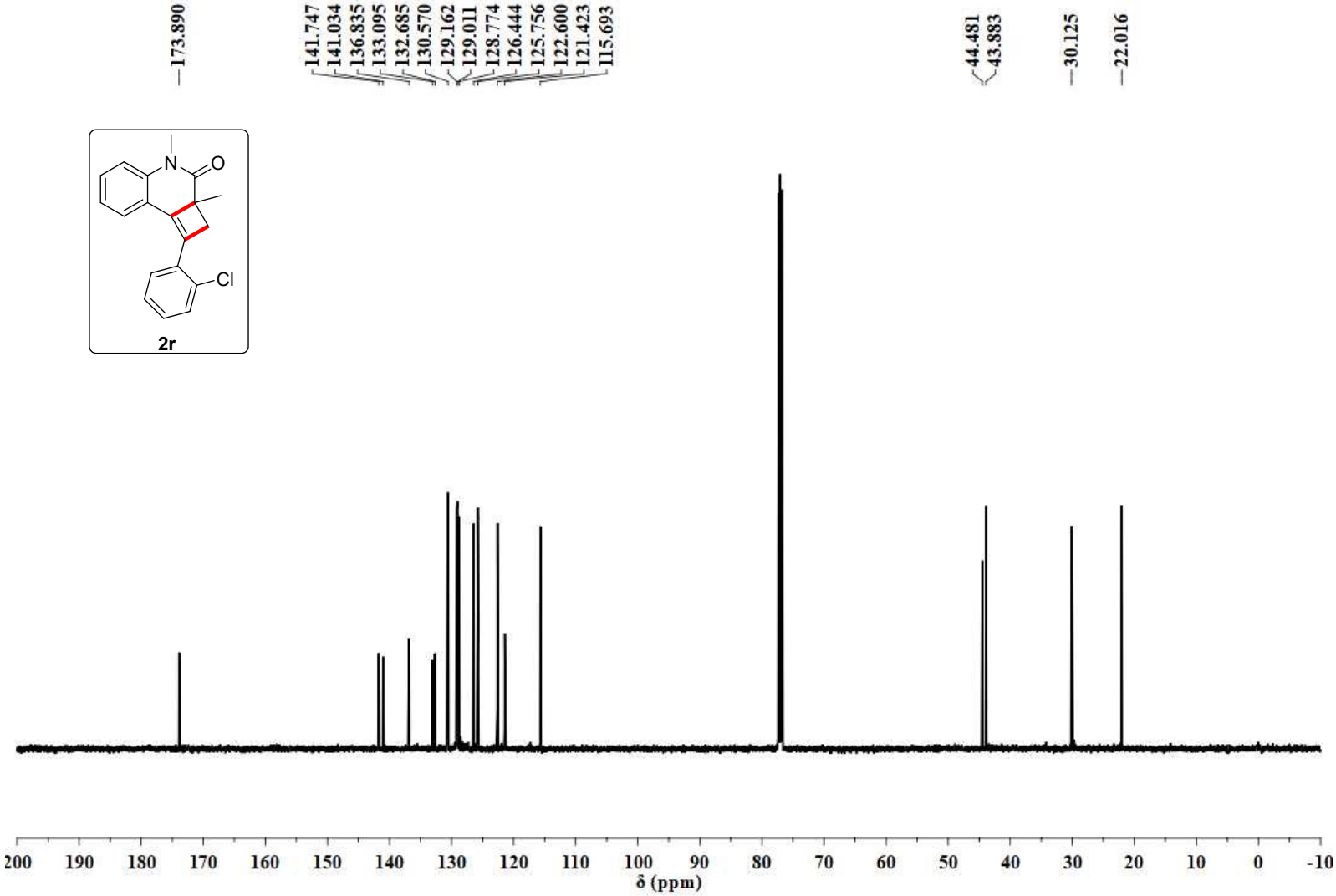
1.04
2.07
2.05
2.01
1.03
3.00
1.00
3.01
δ (ppm)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130.570
129.162
129.011
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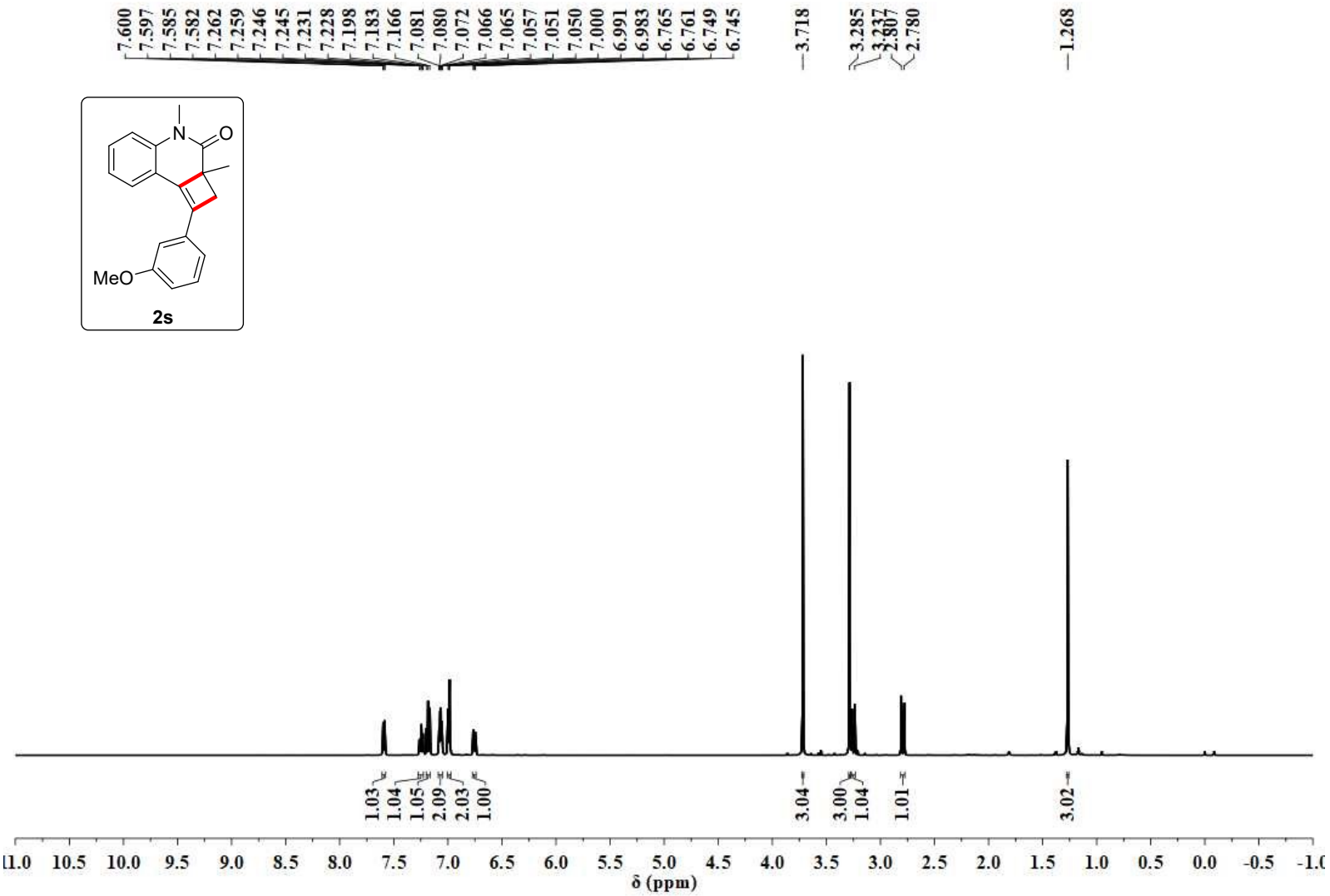
125.756
122.600
121.423
115.693
44.481
43.883
30.125
22.016
N
O
Cl
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.245
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7.228
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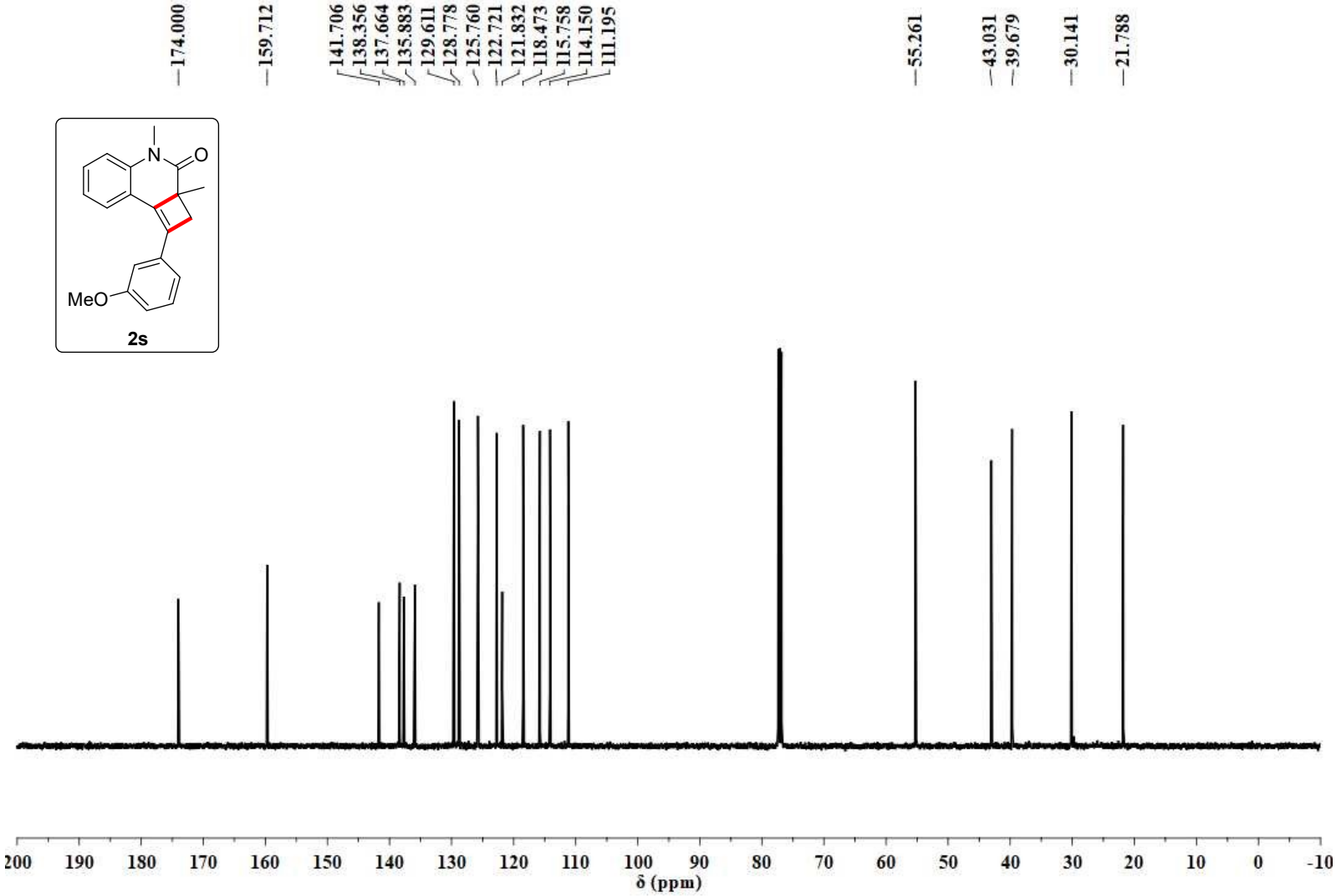
7.166
7.081
7.080
7.072
7.066
7.065
7.057
7.051
7.050
7.000
6.991
6.983
6.765
6.761
6.749
6.745
3.718
3.285
3.237
2.807
2.780
1.268
N
O
MeO
2s
1.03
1.04
1.05
2.09
2.03
1.00
3.04
3.00
1.04
1.01
3.02
δ (ppm)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128.778
125.760
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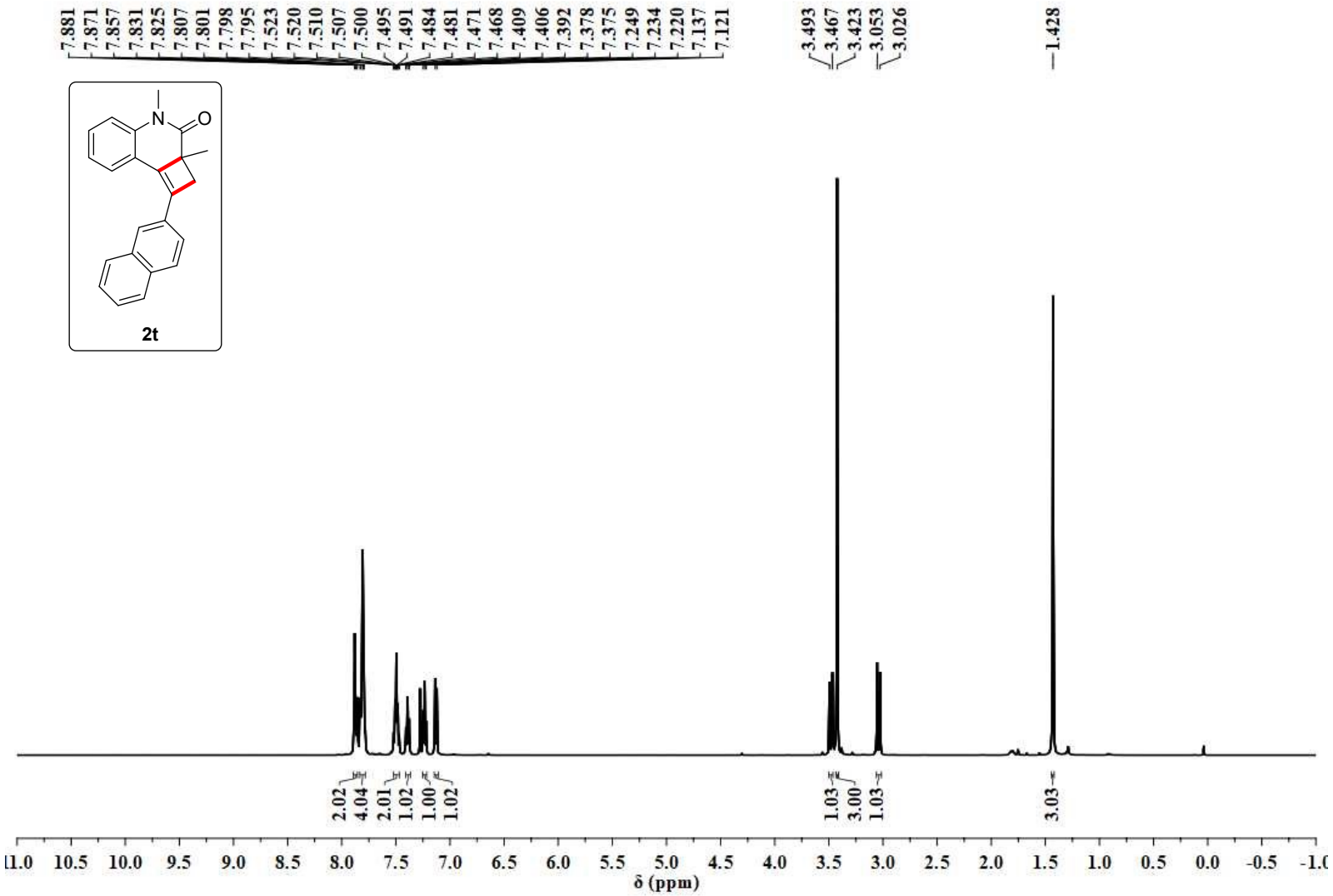
121.832
118.473
115.758
114.150
111.195
55.261
43.031
39.679
30.141
21.788
N
O
MeO
2s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.798
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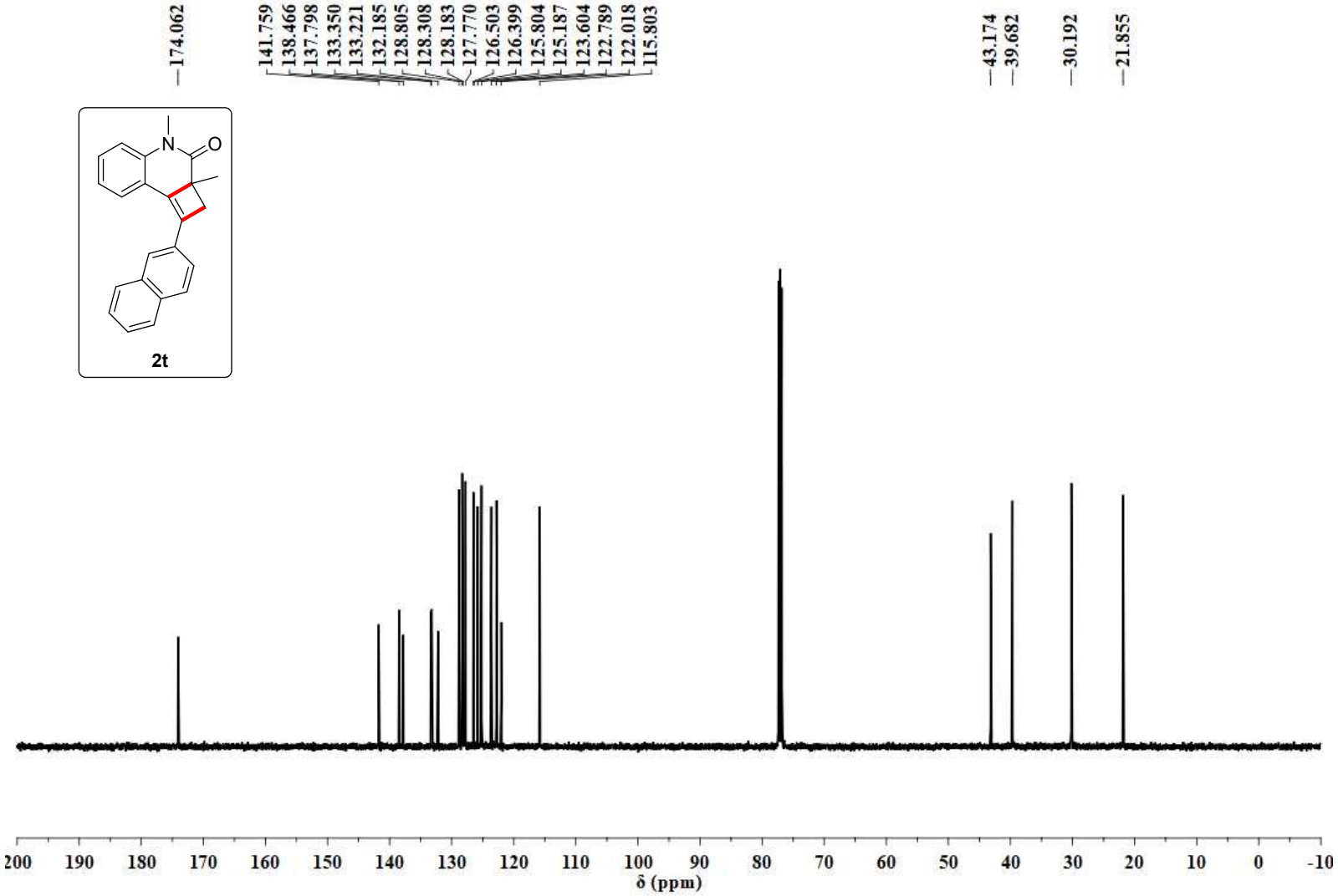
7.520
7.510
7.507
7.500
7.495
7.491
7.484
7.481
7.471
7.468
7.409
7.406
7.392
7.378
7.375
7.249
7.234
7.220
7.137
7.121
3.493
3.467
3.423
3.053
3.026
1.428
N
O
2t
2.02
4.04
2.01
1.02
1.00
1.02
1.03
3.00
1.03
3.03
δ (ppm)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138.466
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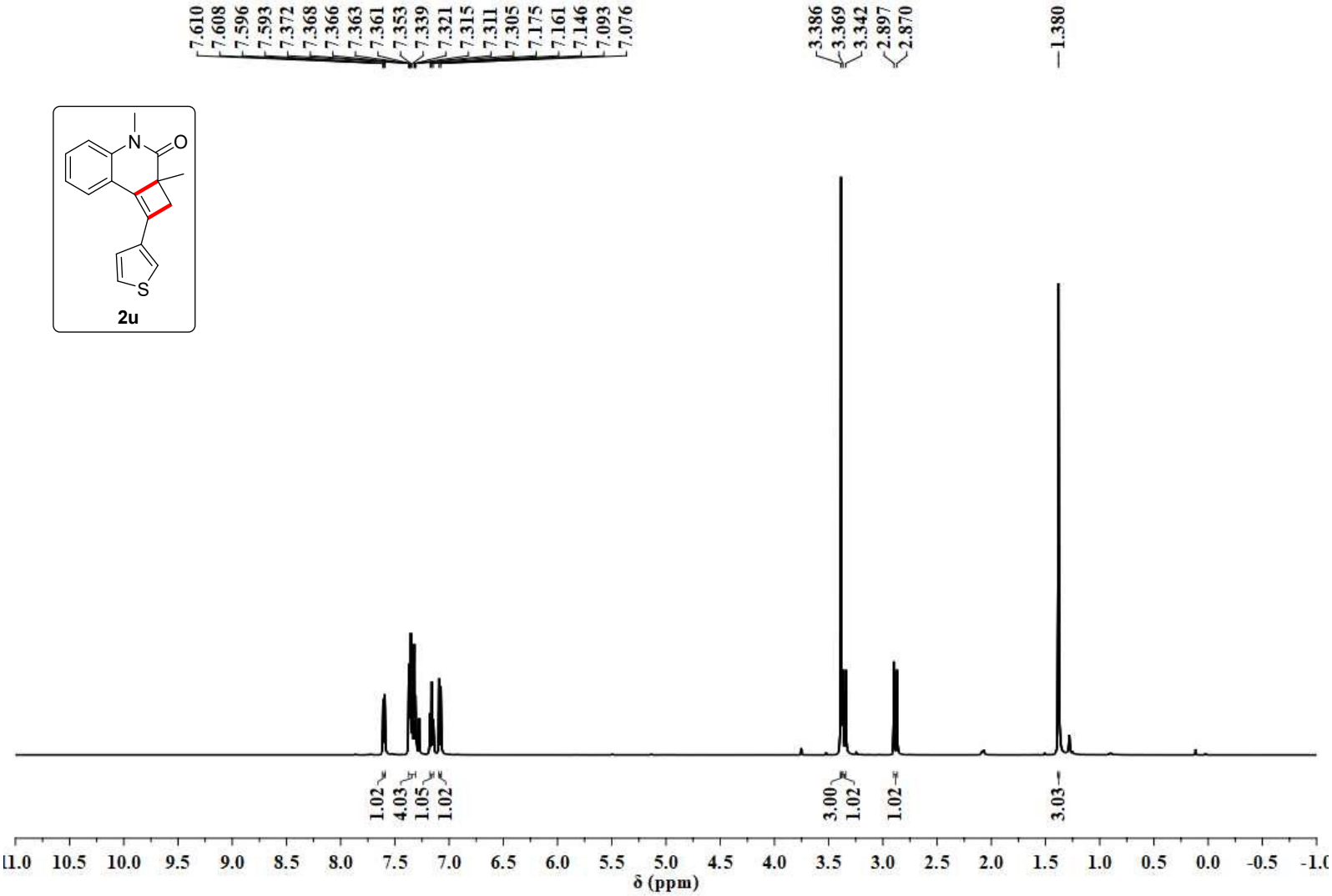
133.221
132.185
128.805
128.308
128.183
127.770
126.503
126.399
125.804
125.187
123.604
122.789
122.018
115.803
43.174
39.682
30.192
21.855
N
O
2t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.596
7.593
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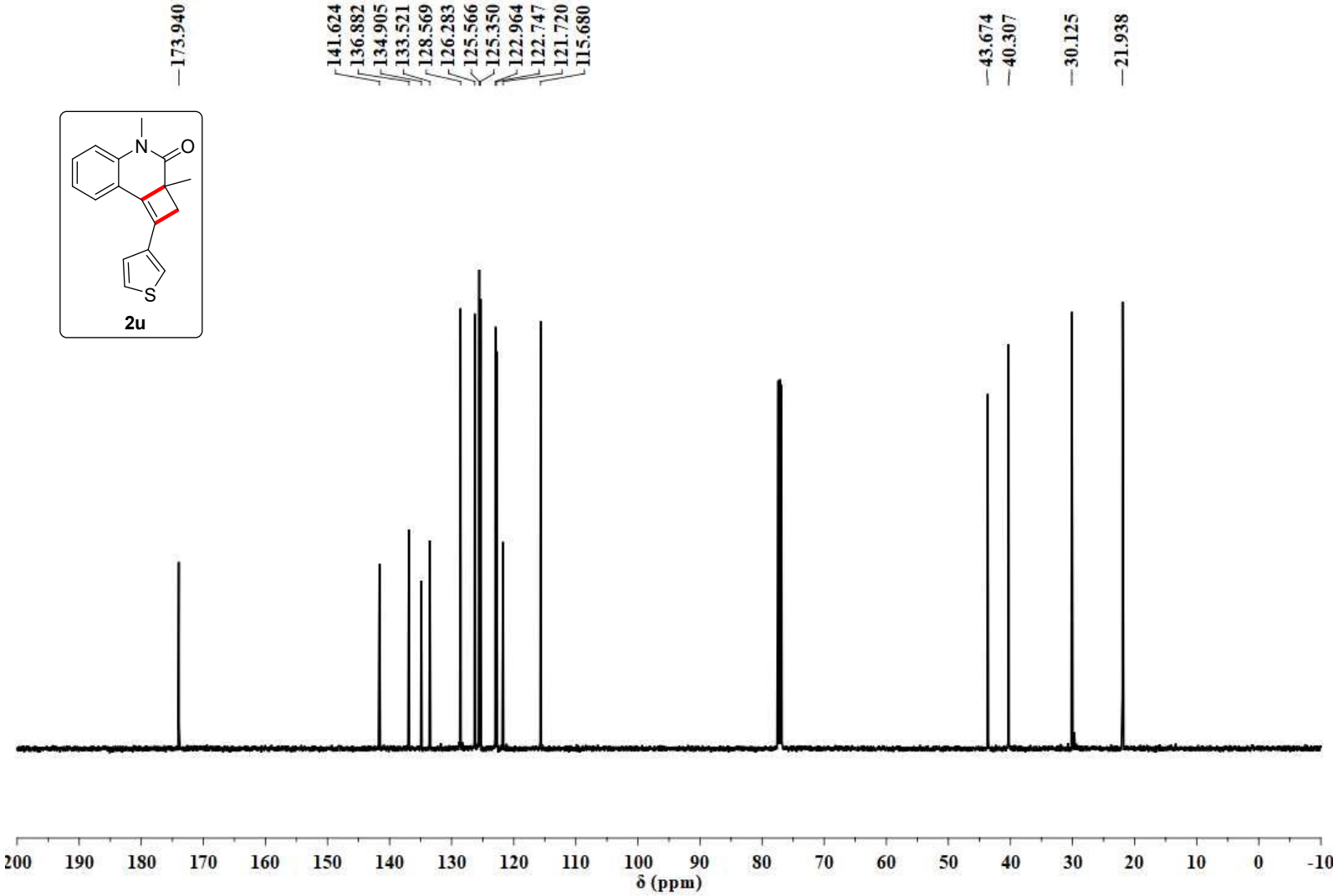
7.368
7.366
7.363
7.361
7.353
7.339
7.321
7.315
7.311
7.305
7.175
7.161
7.146
7.093
7.076
3.386
3.369
3.342
2.897
2.870
1.380
N
O
S
2u
1.02
4.03
1.05
1.02
3.00
1.02
1.02
3.03
δ (ppm)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136.882
134.905
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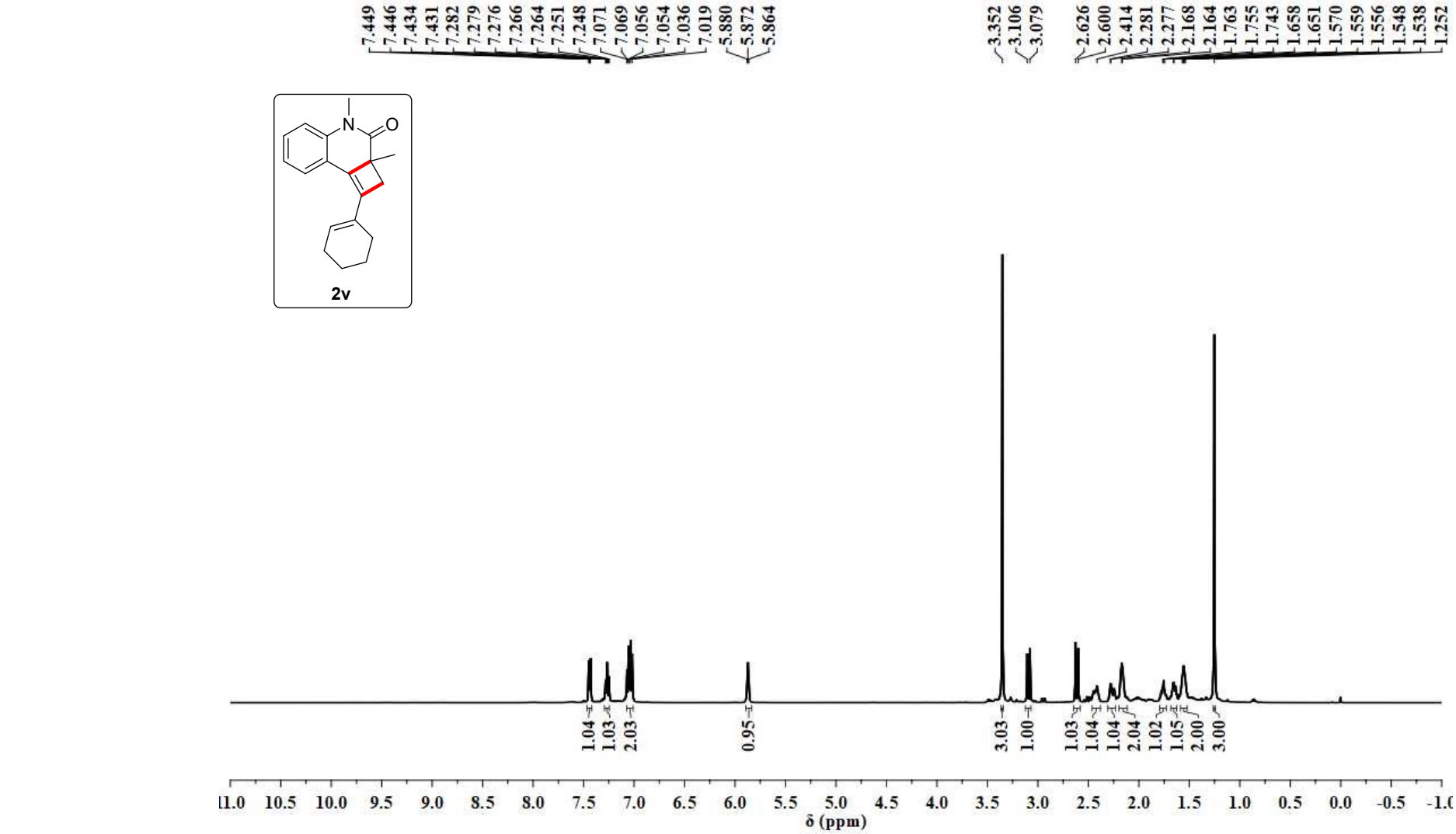
128.569
126.283
125.566
125.350
122.964
122.747
121.720
115.680
43.674
40.307
30.125
21.938
N
O
S
2u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.434
7.431
7.282
7.279
7.276
7.266
7.264
7.251
7.248
7.071
7.069
7.056
7.054
7.036
7.019
5.880
5.872
5.864
3.352
3.106
3.079
2.626
2.600
2.414
2.281
2.277
2.168
2.164
1.763
1.755
1.743
1.658
1.651
1.570
1.559
1.556
1.548
1.538
1.252
N
O
2v
1.04
1.03
2.03
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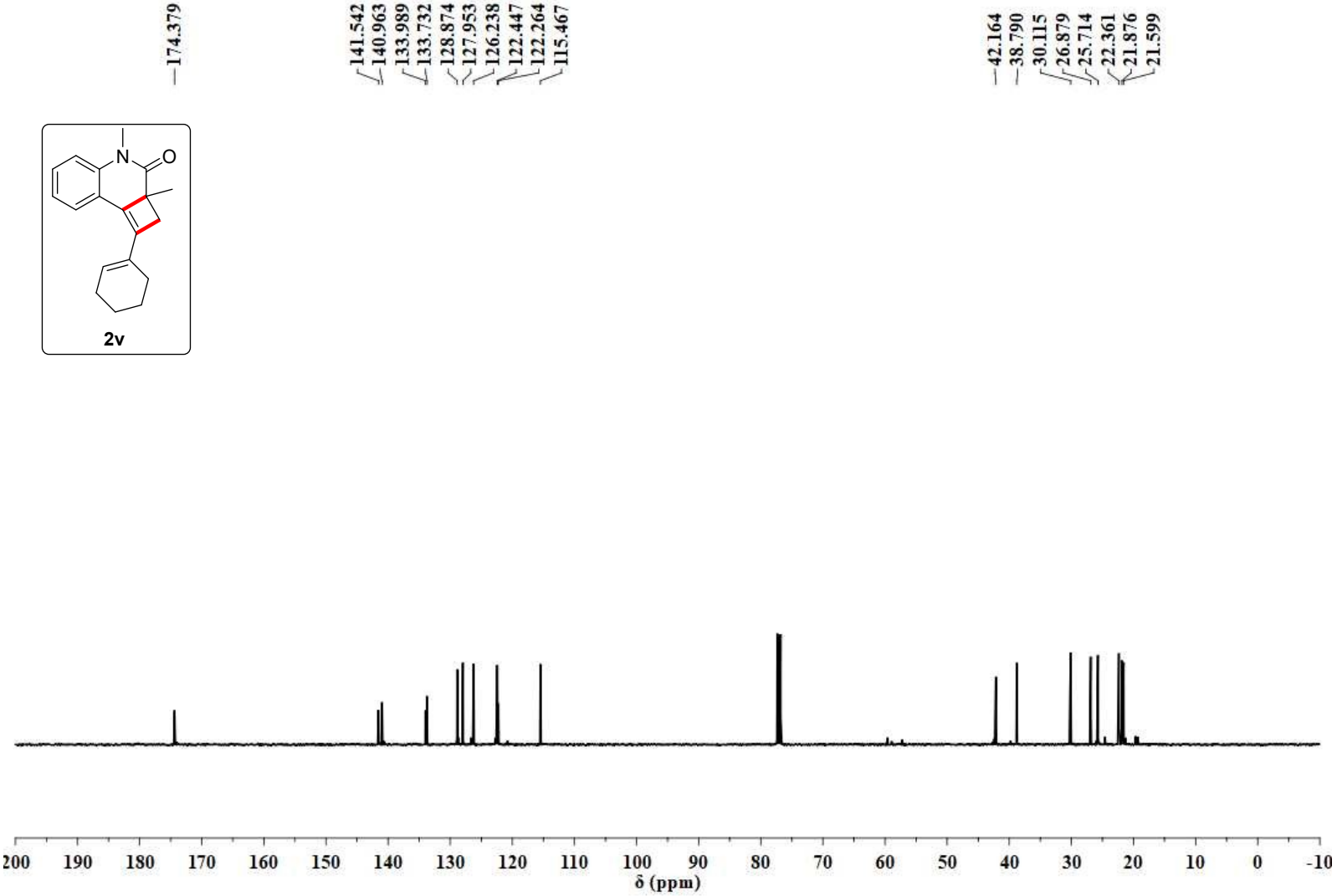
1.03
1.04
1.04
2.04
1.02
1.05
2.00
3.00
δ (ppm)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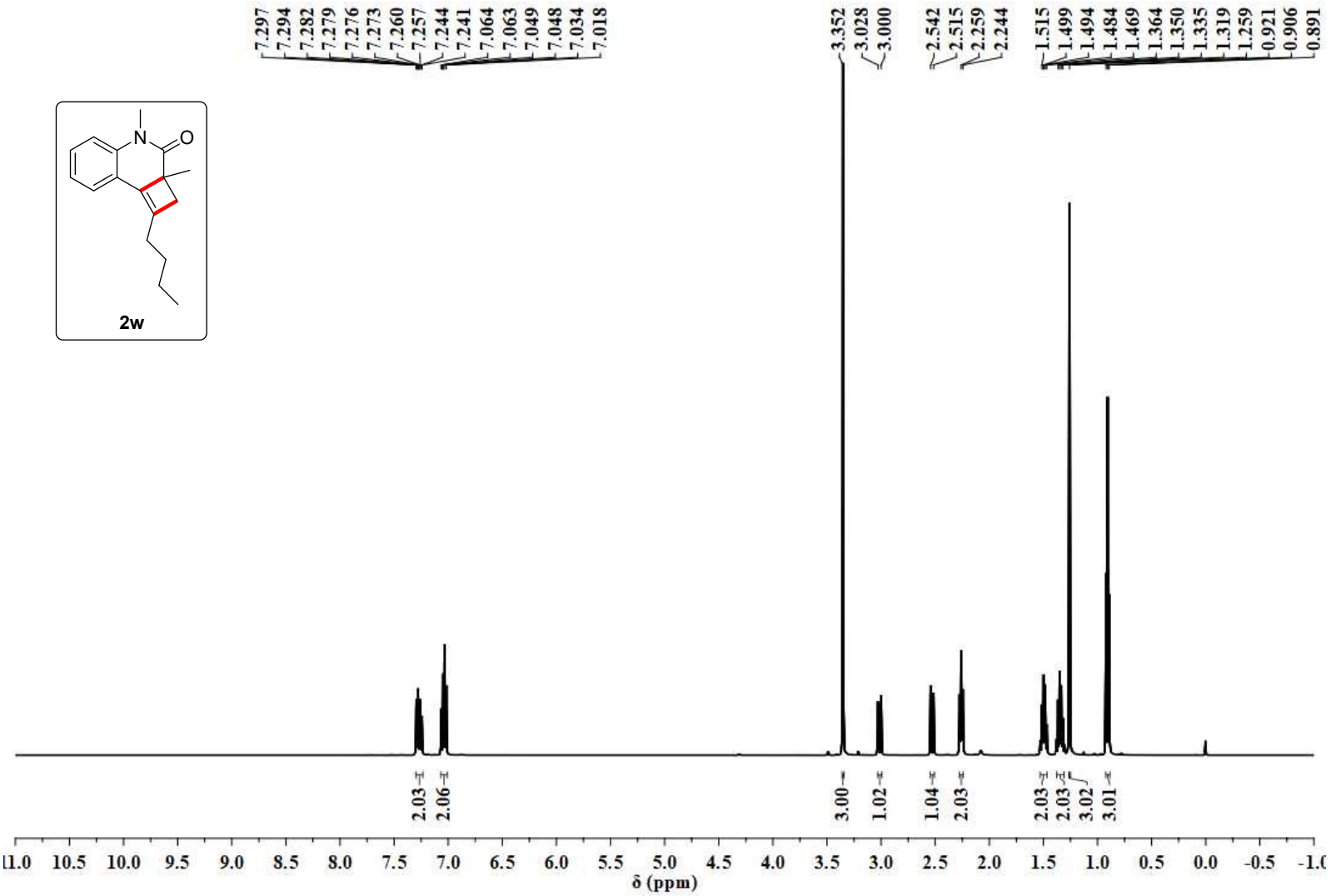
140.963
133.989
133.732
128.874
127.953
126.238
122.447
122.264
115.467
42.164
38.790
30.115
26.879
25.714
22.361
21.876
21.599
N
O
2v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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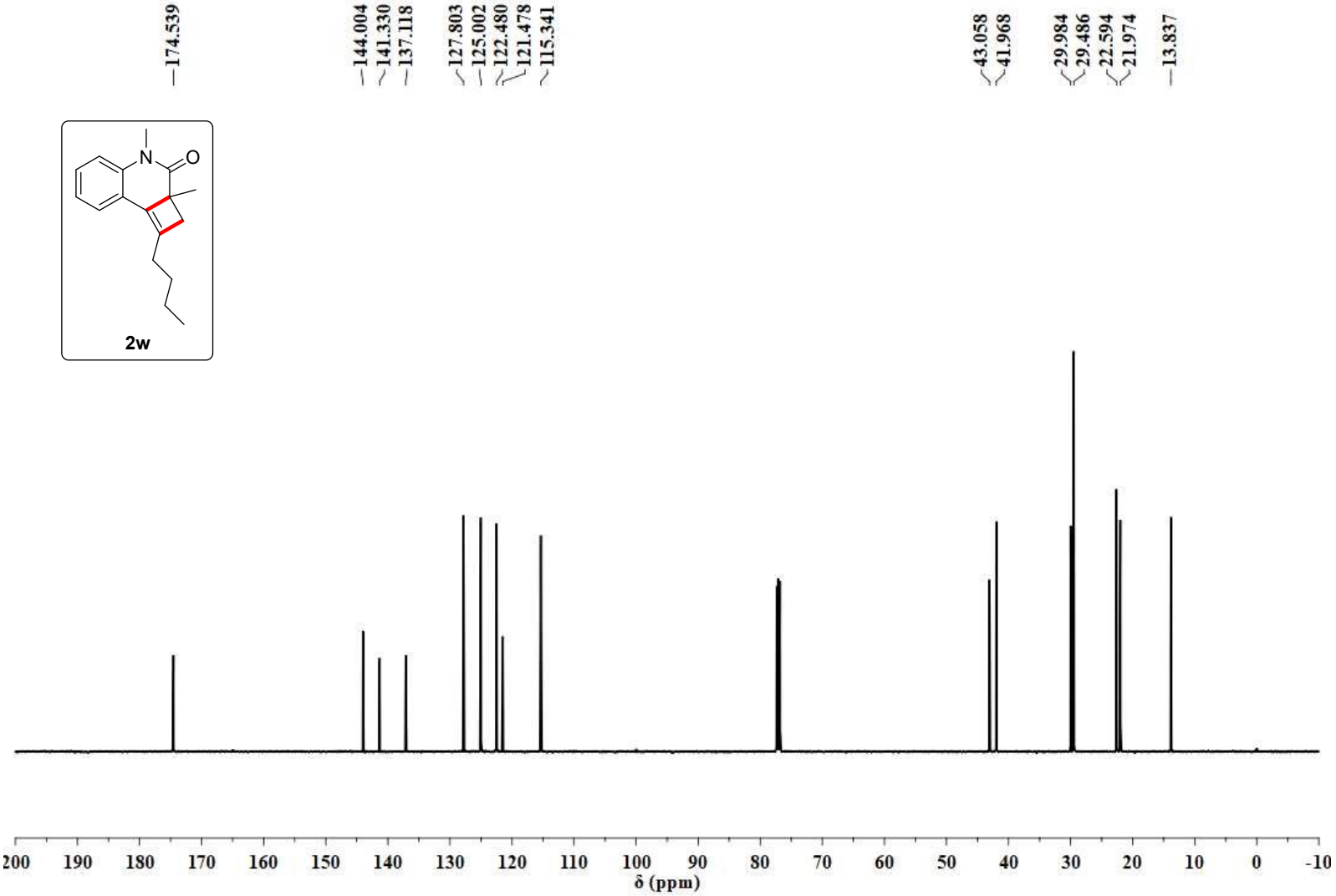
7.279
7.276
7.273
7.260
7.257
7.244
7.241
7.064
7.063
7.049
7.048
7.034
7.018
3.352
3.028
3.000
2.542
2.515
2.259
2.244
1.515
1.499
1.494
1.484
1.469
1.364
1.350
1.335
1.319
1.259
0.921
0.906
0.891
2w
2.03
2.06
3.00
1.02
1.04
2.03
2.03
2.03
3.02
3.01
δ (ppm)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141.330
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125.002
122.480
121.478
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41.968
29.984
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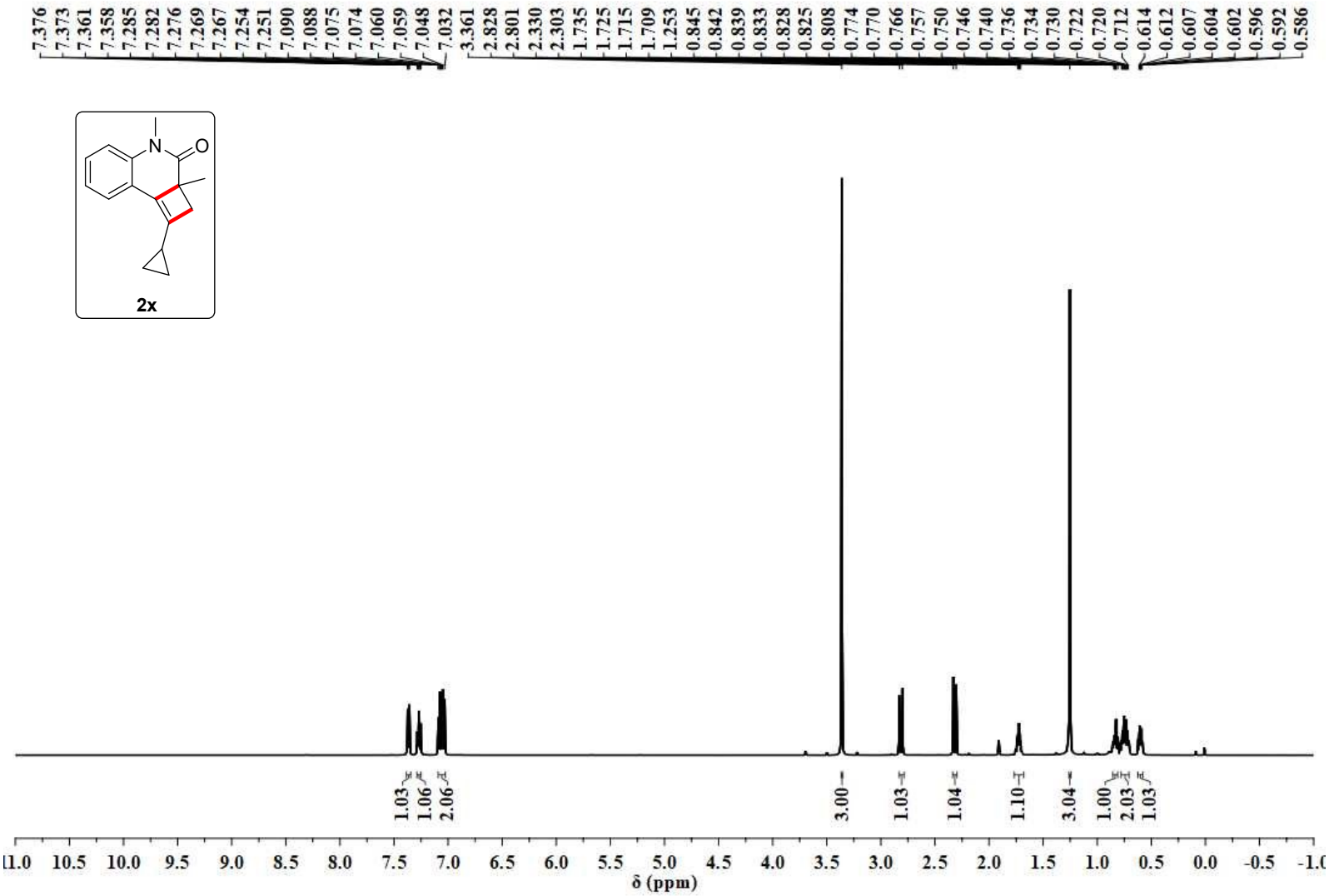
22.594
21.974
13.837
N
O
2w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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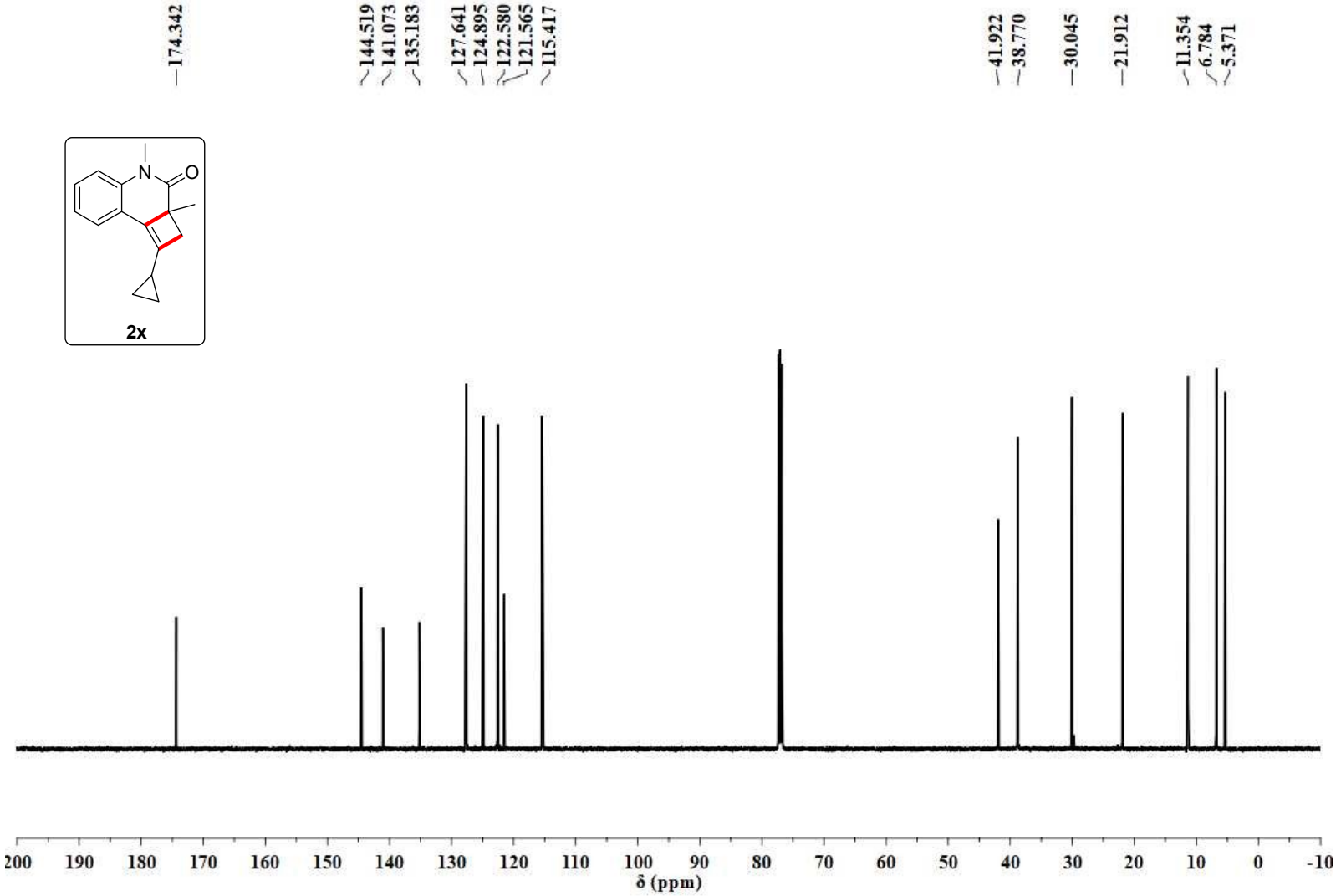
7.282
7.276
7.269
7.267
7.254
7.251
7.090
7.088
7.075
7.074
7.060
7.059
7.048
7.032
3.361
2.828
2.801
2.330
2.303
1.735
1.725
1.715
1.709
1.253
0.845
0.842
0.839
0.833
0.828
0.825
0.808
0.774
0.770
0.766
0.757
0.750
0.746
0.740
0.736
0.734
0.730
0.722
0.720
0.712
0.614
0.612
0.607
0.604
0.602
0.596
0.592
0.586
N
O
2x
1.03
1.06
2.06
3.00
1.03
1.04
1.10
3.04
1.00
2.03
1.03
δ (ppm)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121.565
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38.770
30.045
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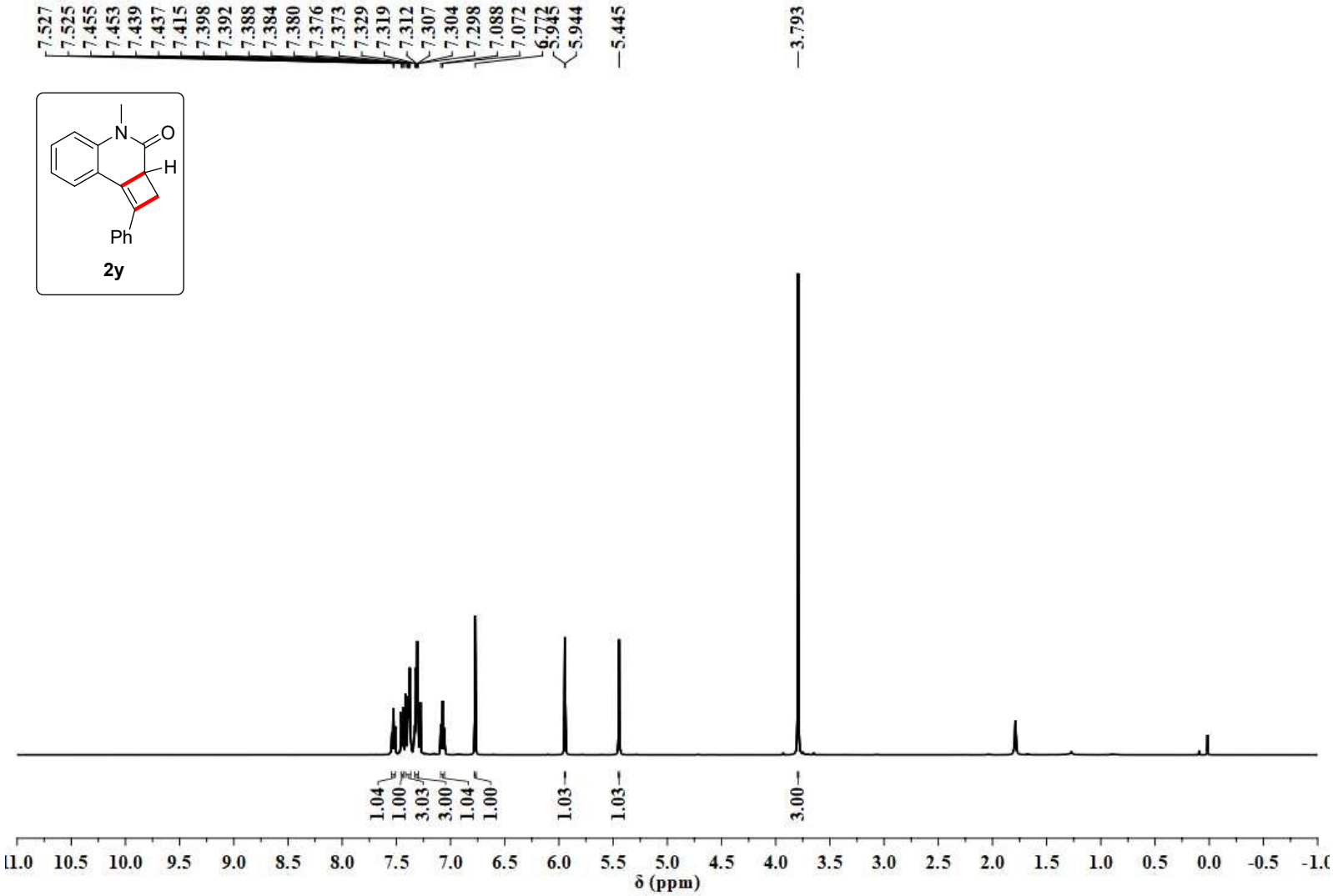
11.354
6.784
5.371
N
O
2x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.392
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7.384
7.380
7.376
7.373
7.329
7.319
7.312
7.307
7.304
7.298
7.088
7.072
6.772
5.945
5.944
5.445
3.793
N
O
H
Ph
2y
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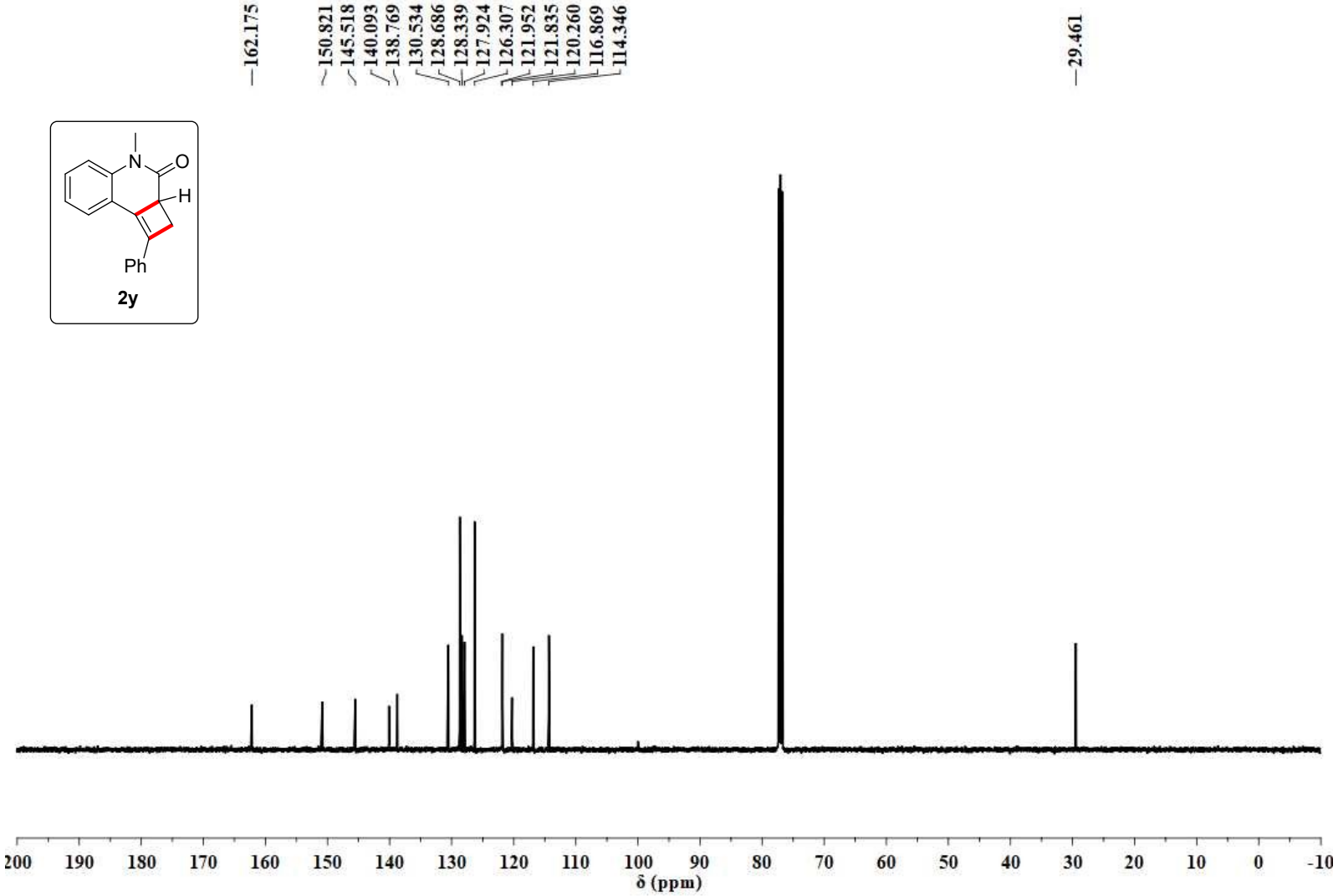
1.00
3.03
3.00
1.04
1.00
1.03
1.03
3.00
δ (ppm)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140.093
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121.952
121.835
120.260
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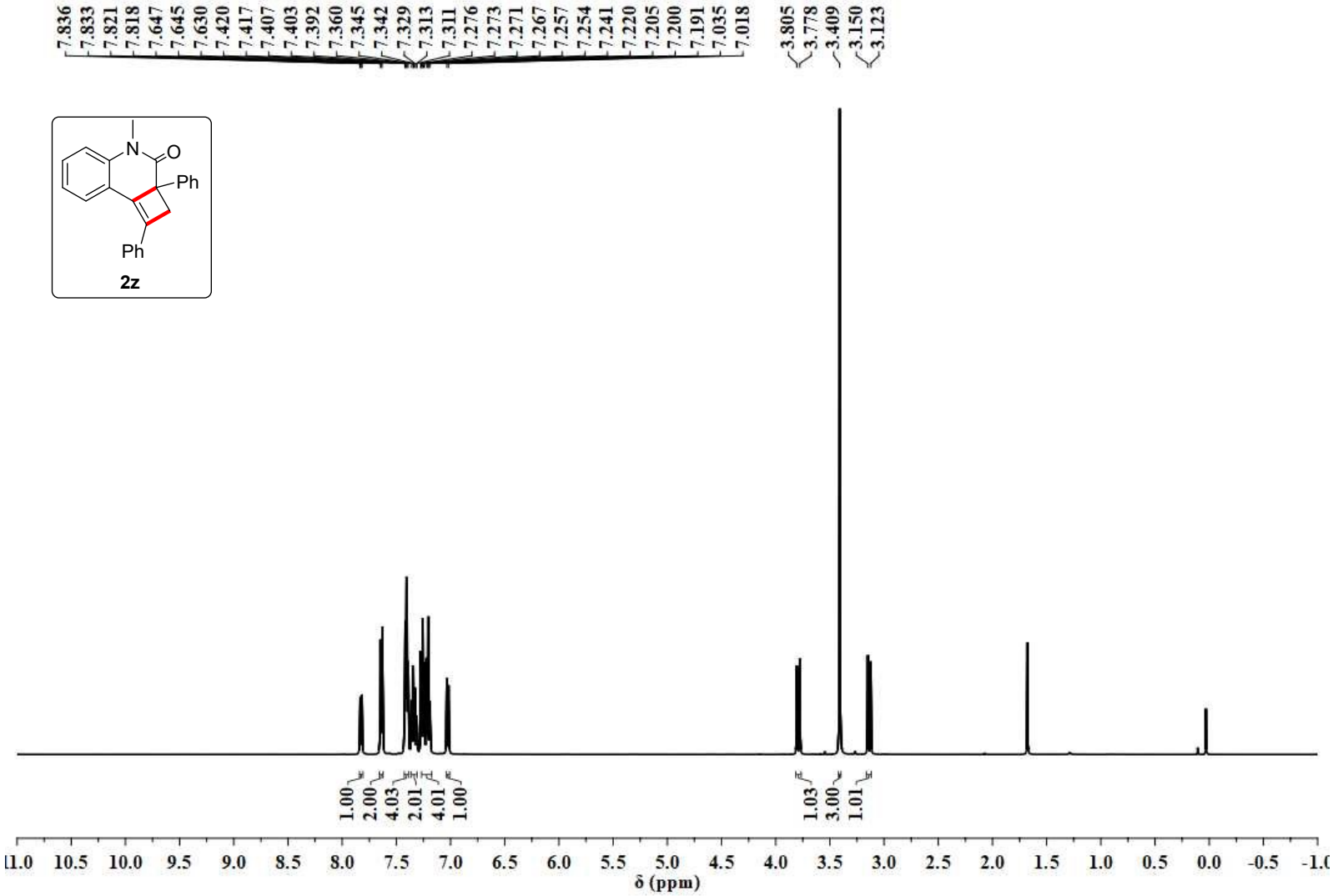
114.346
29.461
N
O
H
Ph
2y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.417
7.407
7.403
7.392
7.360
7.345
7.342
7.329
7.313
7.311
7.276
7.273
7.271
7.267
7.257
7.254
7.241
7.220
7.205
7.200
7.191
7.035
7.018
3.805
3.778
3.409
3.150
3.123
N
O
Ph
Ph
2z
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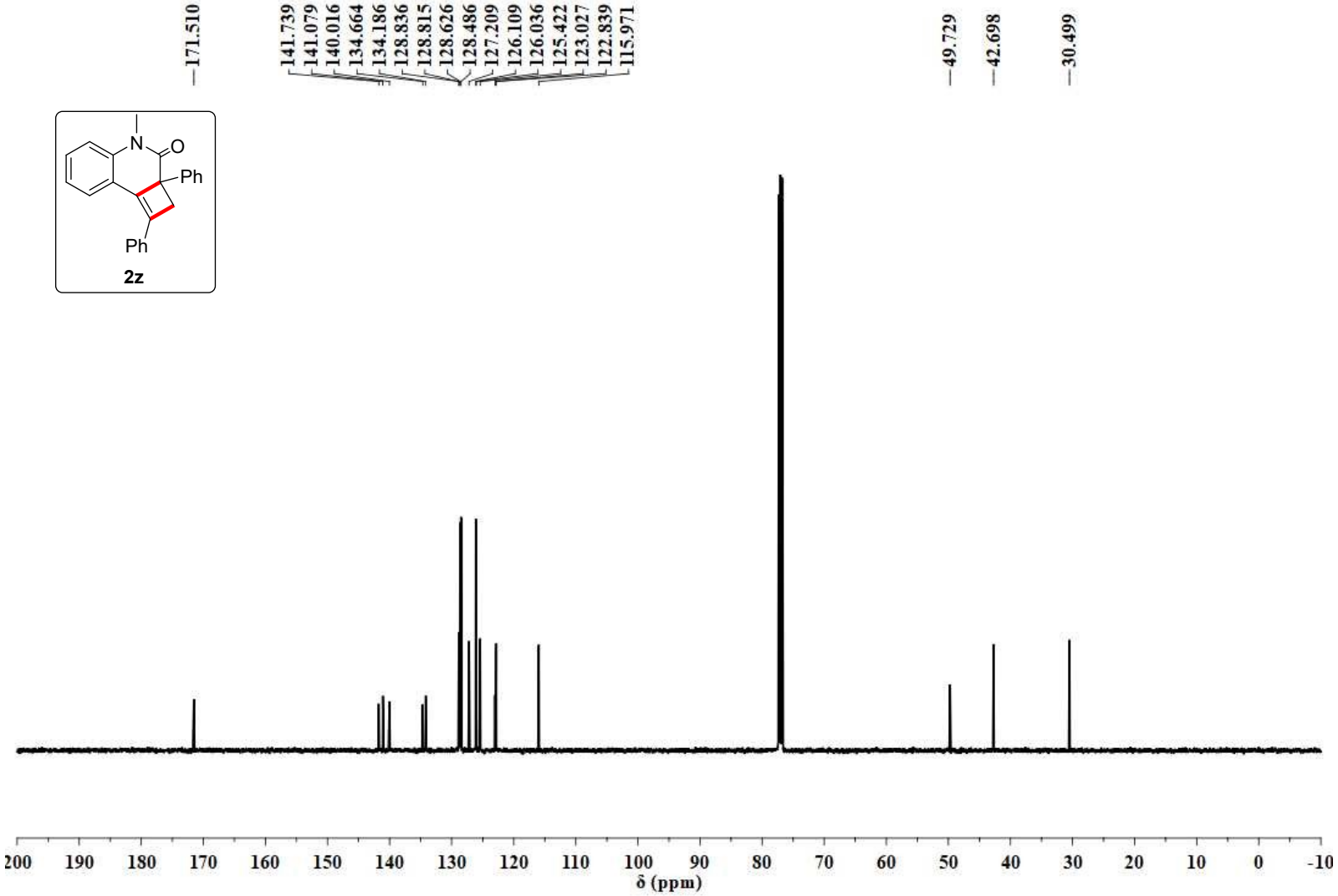
2.00
4.03
2.01
4.01
1.00
1.03
3.00
1.01
δ (ppm)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140.016
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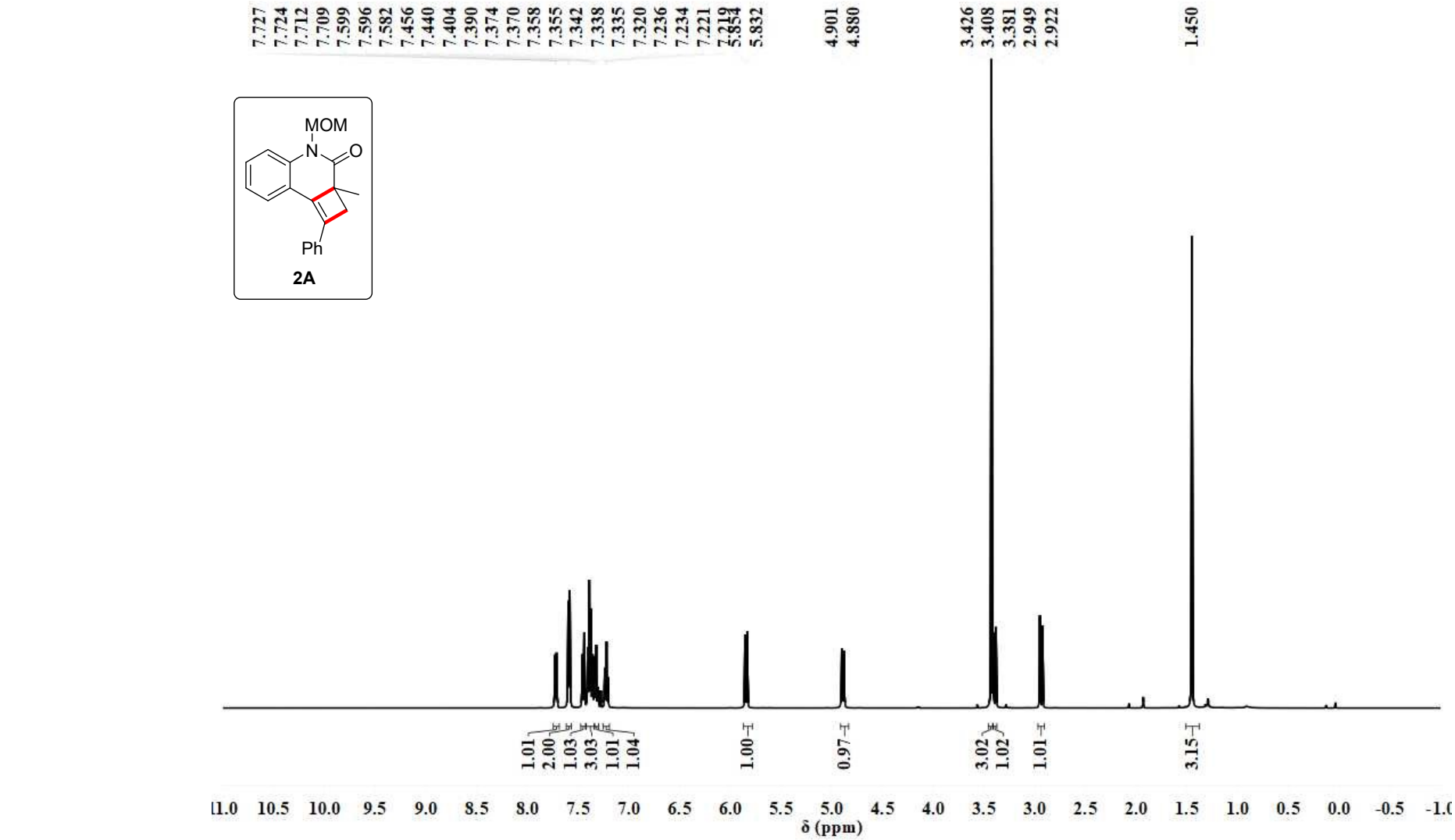
128.815
128.626
128.486
127.209
126.109
126.036
125.422
123.027
122.839
115.971
49.729
42.698
30.499
N
O
Ph
Ph
2z
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.404
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7.374
7.370
7.358
7.355
7.342
7.338
7.335
7.320
7.236
7.234
7.221
5.854
5.832
4.901
4.880
3.426
3.408
3.381
2.949
2.922
1.450
MOM
N
O
Ph
2A
1.01
2.00
1.03
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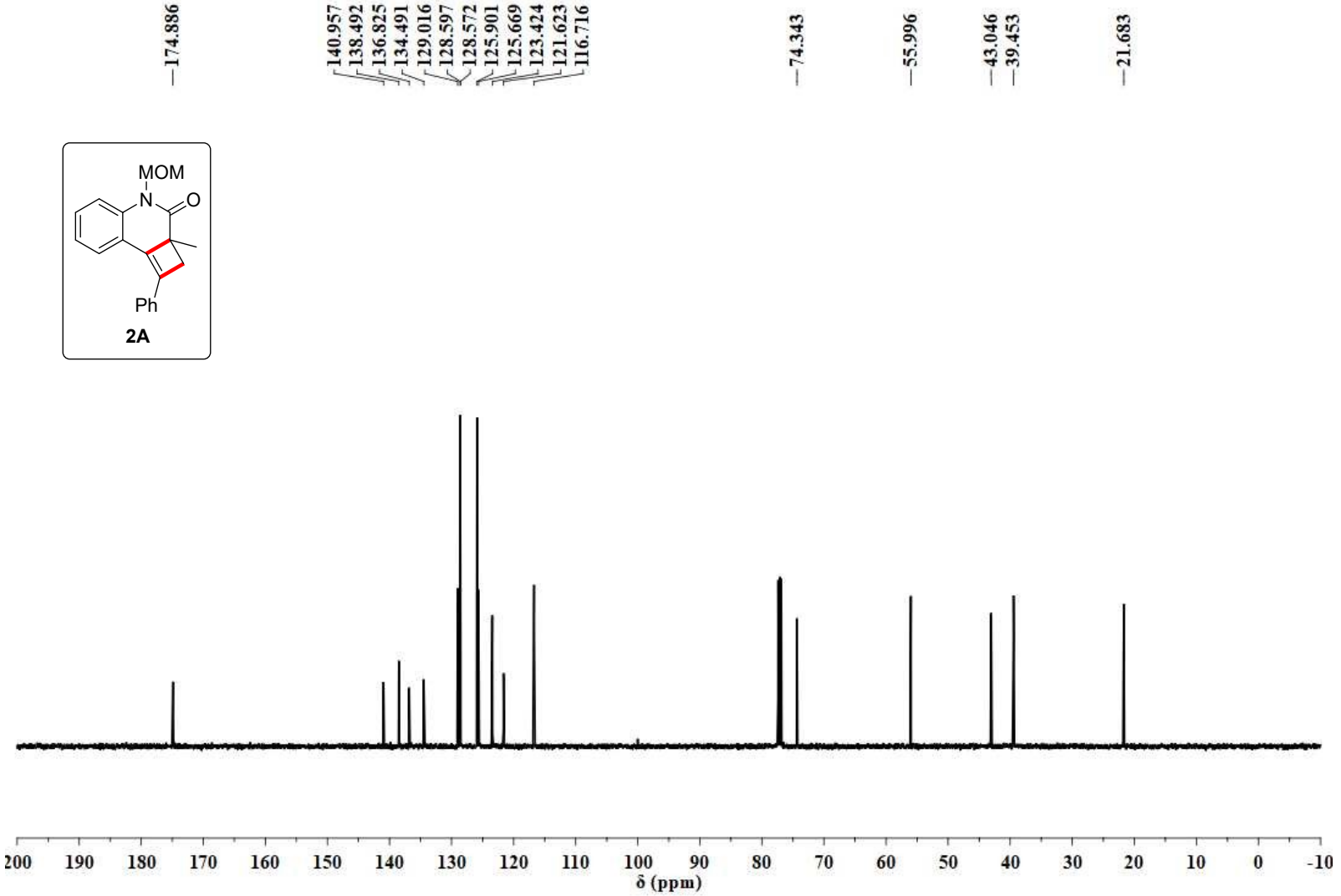
1.01
1.04
1.00
0.97
3.02
1.02
1.01
3.15
δ (ppm)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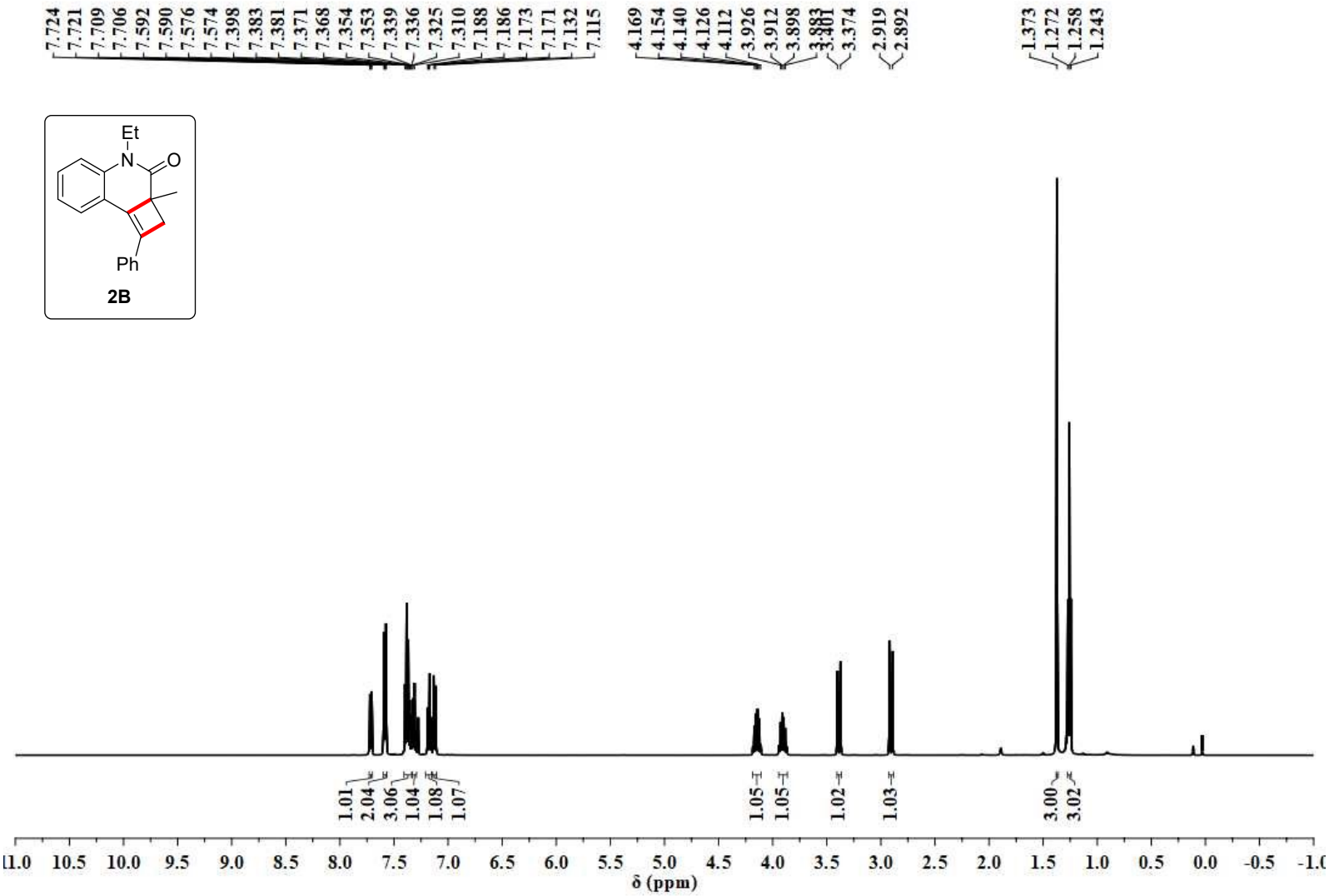
134.491
129.016
128.597
128.572
125.901
125.669
123.424
121.623
116.716
74.343
55.996
43.046
39.453
21.683
MOM
N
O
Ph
2A
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.590
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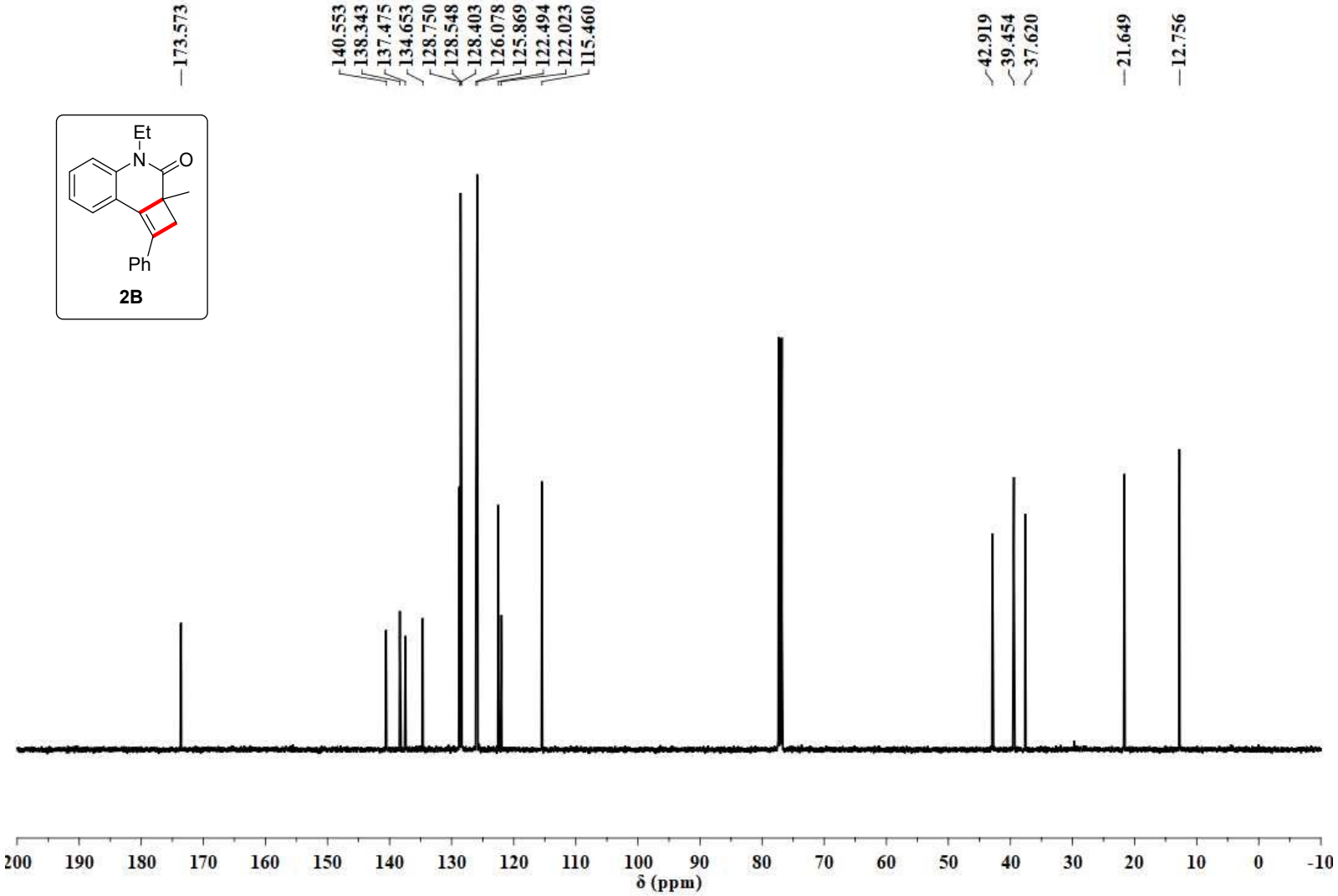
7.574
7.398
7.383
7.381
7.371
7.368
7.354
7.353
7.339
7.336
7.325
7.310
7.188
7.186
7.173
7.171
7.132
7.115
4.169
4.154
4.140
4.126
4.112
3.926
3.912
3.898
3.374
2.919
2.892
1.373
1.272
1.258
1.243
Et
N
O
Ph
2B
1.01
2.04
3.06
1.04
1.08
1.07
1.05
1.05
1.02
1.03
3.00
3.02
δ (ppm)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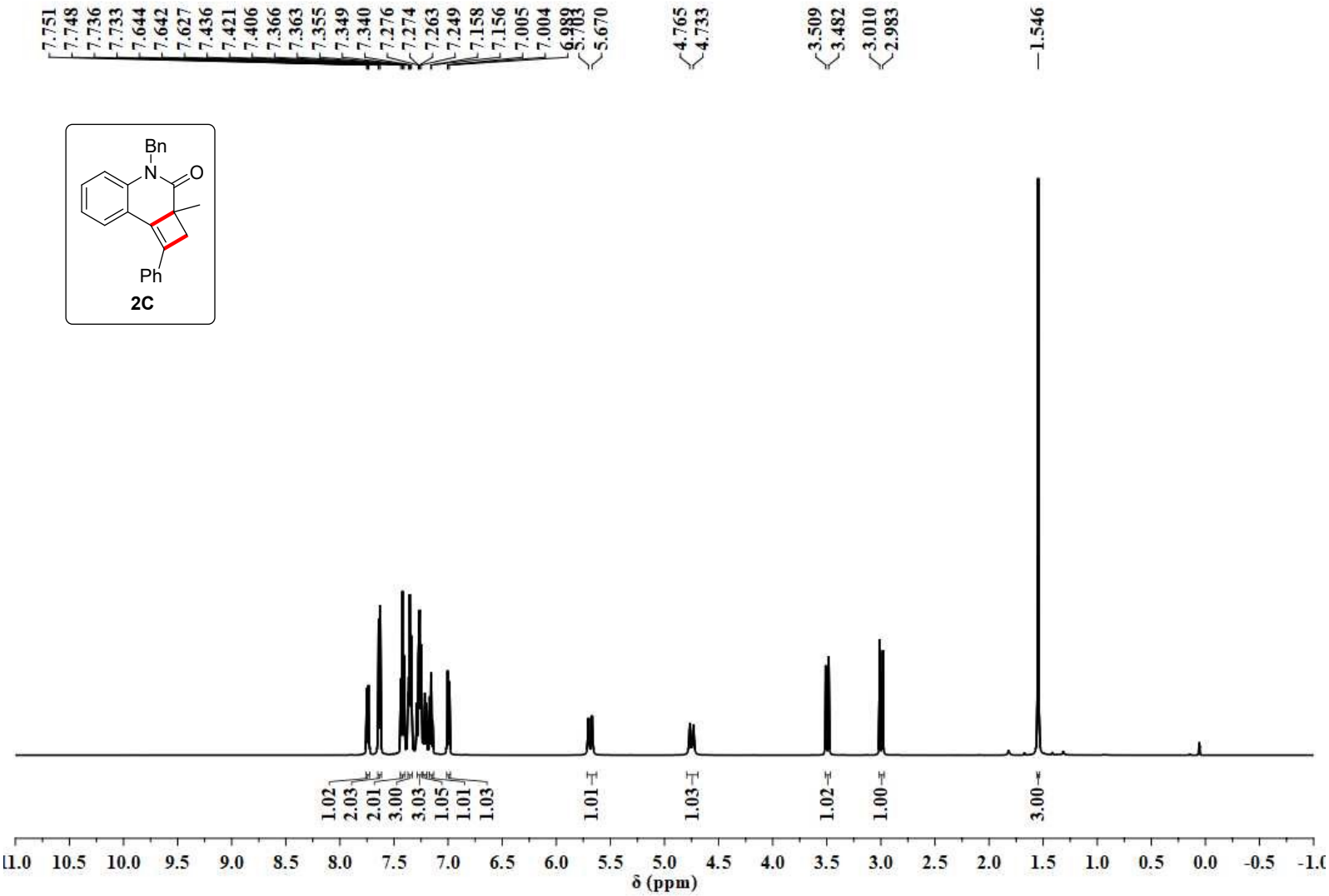
137.475
134.653
128.750
128.548
128.403
126.078
125.869
122.494
122.023
115.460
42.919
39.454
37.620
21.649
12.756
Et
N
O
Ph
2B
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.733
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7.436
7.421
7.406
7.366
7.363
7.355
7.349
7.340
7.276
7.274
7.263
7.249
7.158
7.156
7.005
7.004
6.989
5.703
5.670
4.765
4.733
3.509
3.482
3.010
2.983
1.546
Bn
N
O
Ph
2C
1.02
2.03
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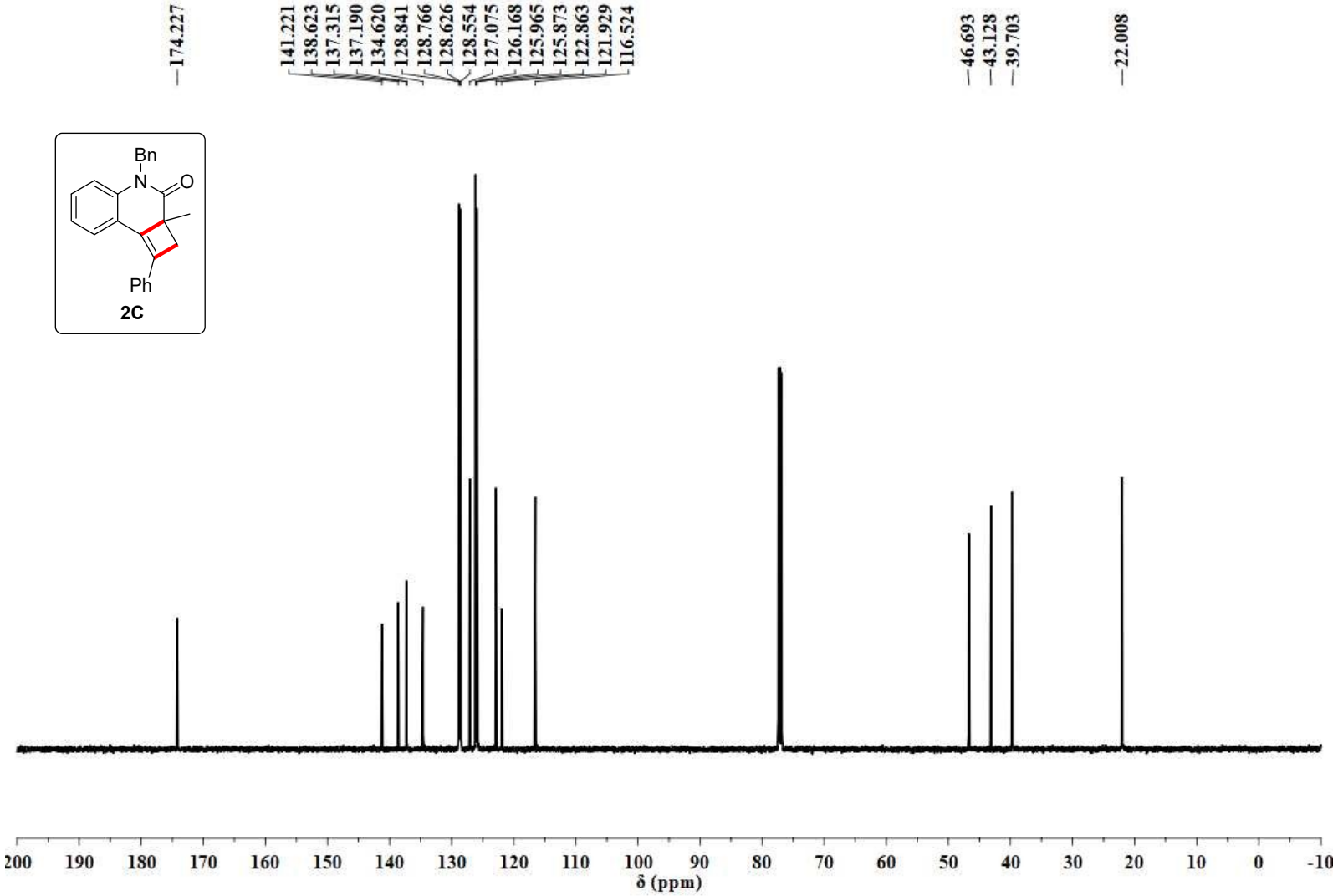
1.03
1.01
1.03
1.02
1.00
3.00
δ (ppm)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137.315
137.190
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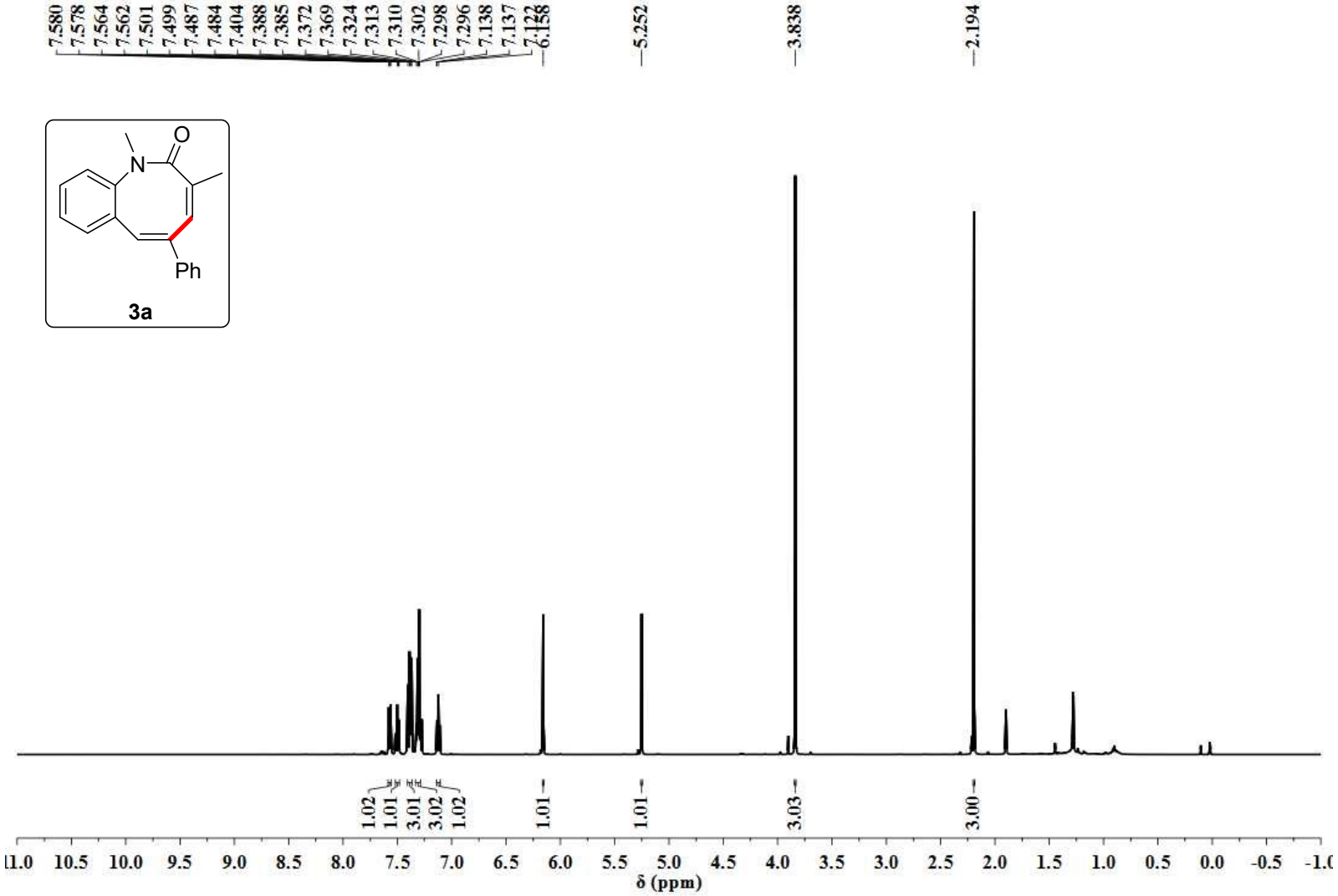
128.766
128.626
128.554
127.075
126.168
125.965
125.873
122.863
121.929
116.524
46.693
43.128
39.703
22.008
Bn
N
O
Ph
2C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.578
7.564
7.562
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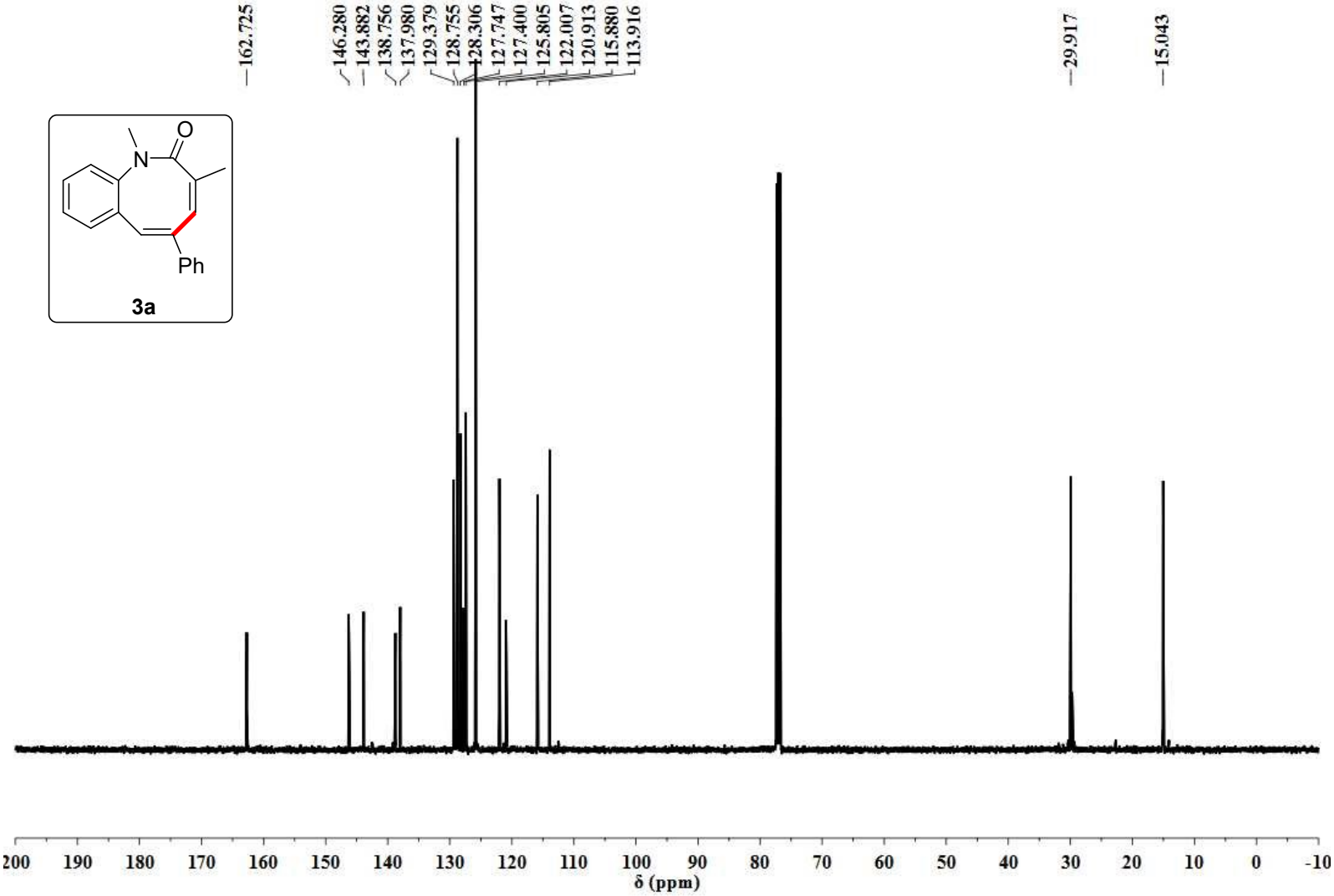
7.499
7.487
7.484
7.404
7.388
7.385
7.372
7.369
7.324
7.313
7.310
7.302
7.298
7.296
7.138
7.137
7.122
6.158
5.252
3.838
2.194
O
N
Ph
3a
1.02
1.01
3.01
3.02
1.02
1.01
1.01
3.03
3.00
δ (ppm)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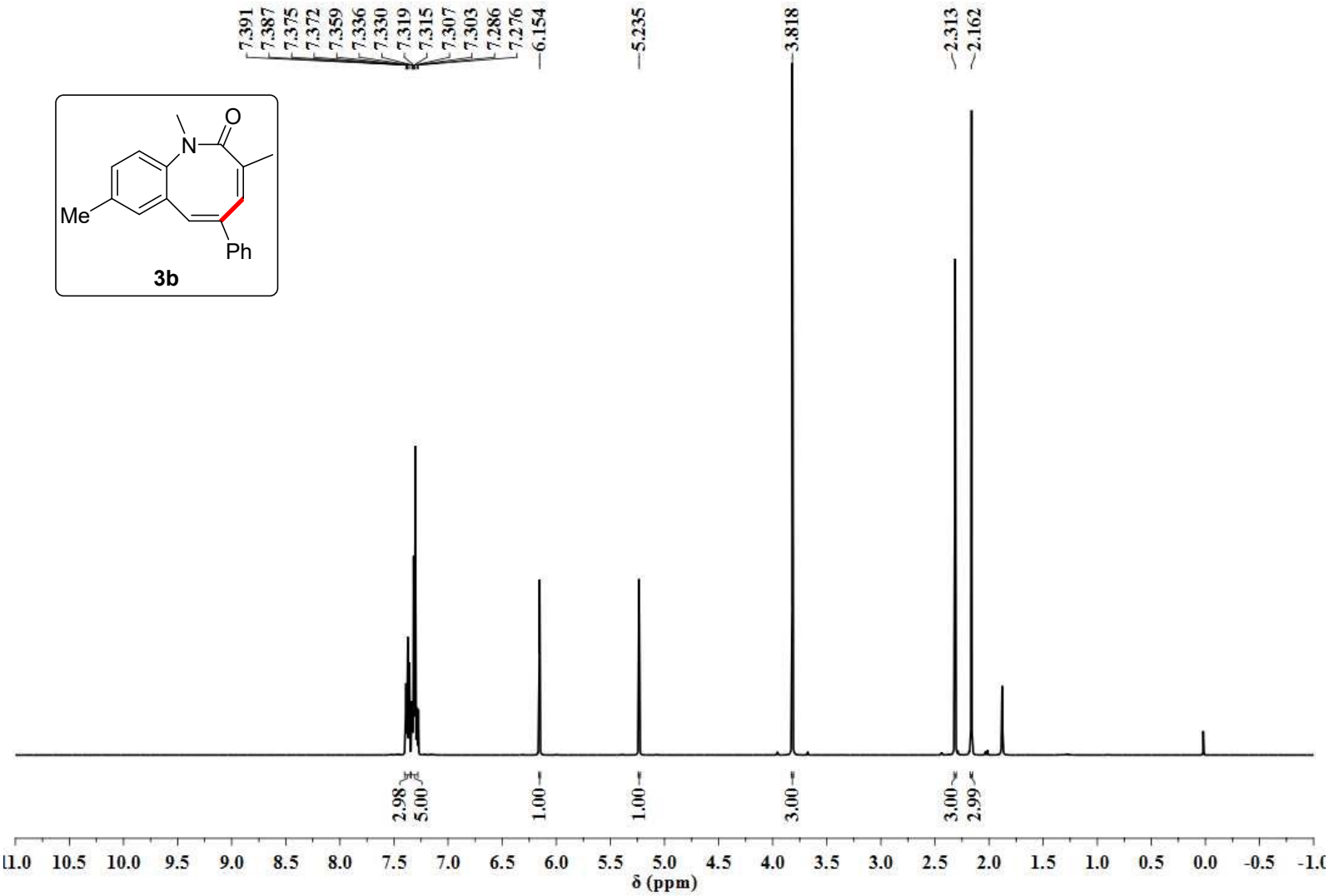
146.280
143.882
138.756
137.980
129.379
128.755
128.306
127.747
127.400
125.805
122.007
120.913
115.880
113.916
29.917
15.043
O
N
Ph
3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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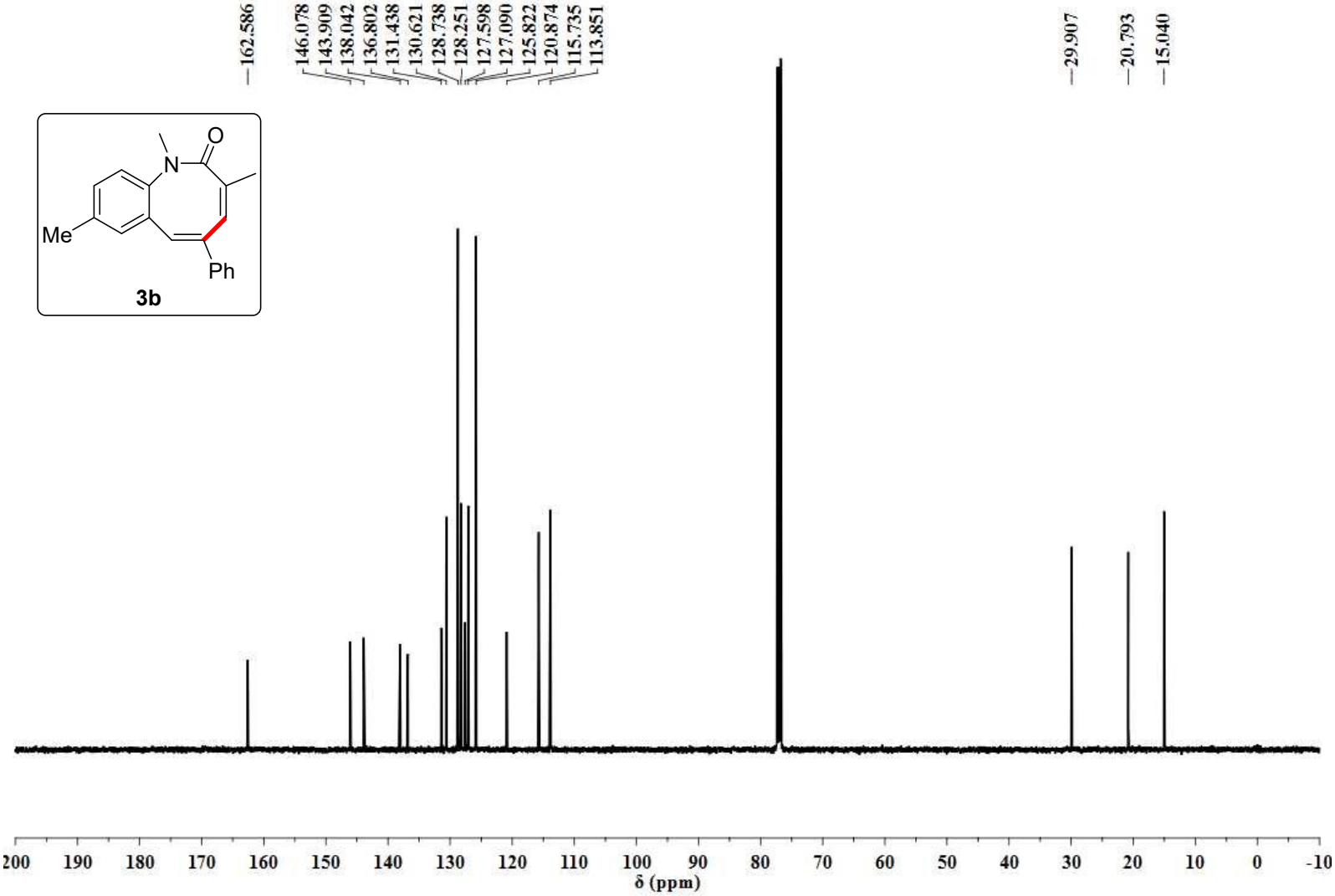
7.387
7.375
7.372
7.359
7.336
7.330
7.319
7.315
7.307
7.303
7.286
7.276
6.154
5.235
3.818
2.313
2.162
O
N
Me
Ph
3b
2.98
5.00
1.00
1.00
3.00
3.00
2.99
δ (ppm)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143.909
138.042
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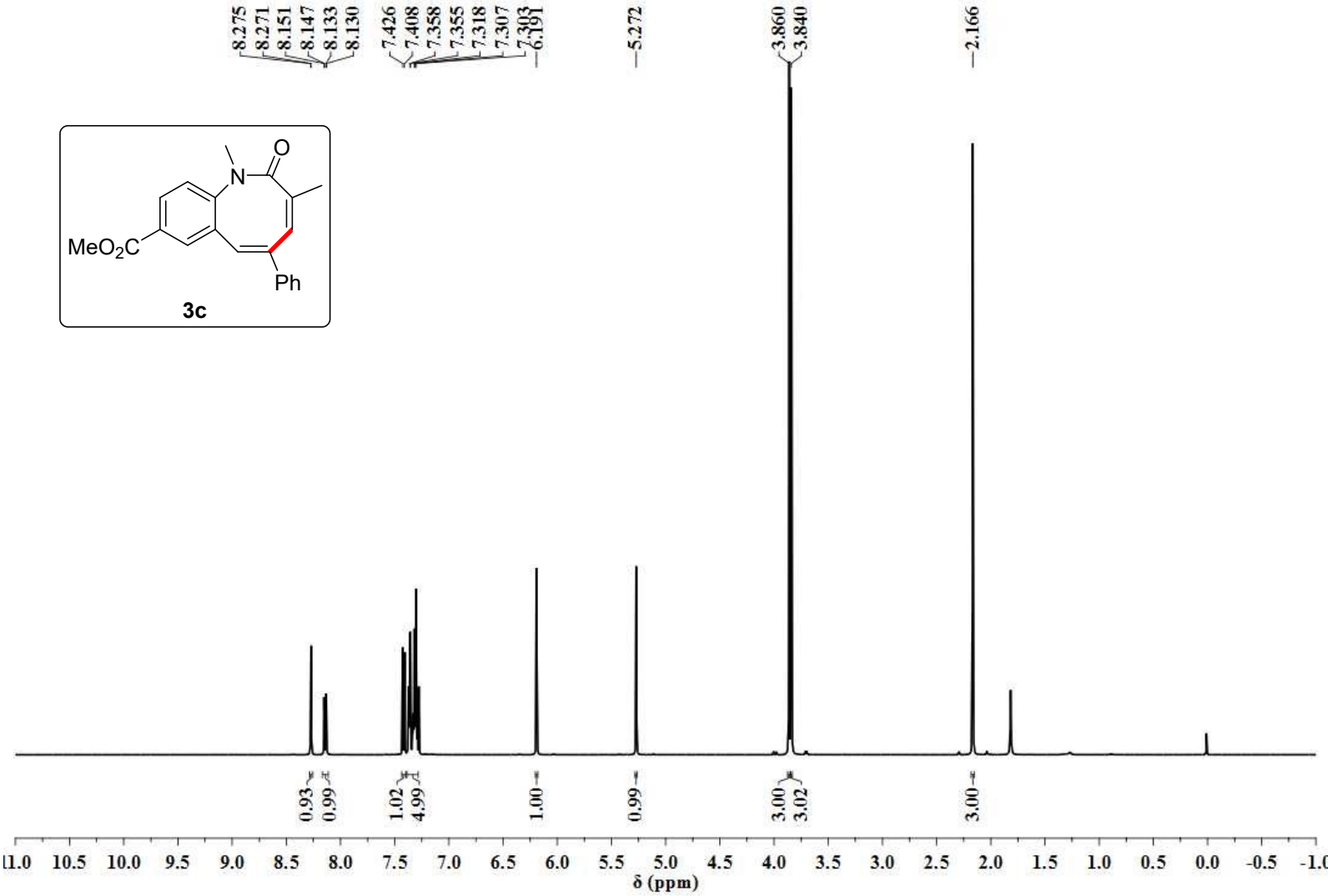
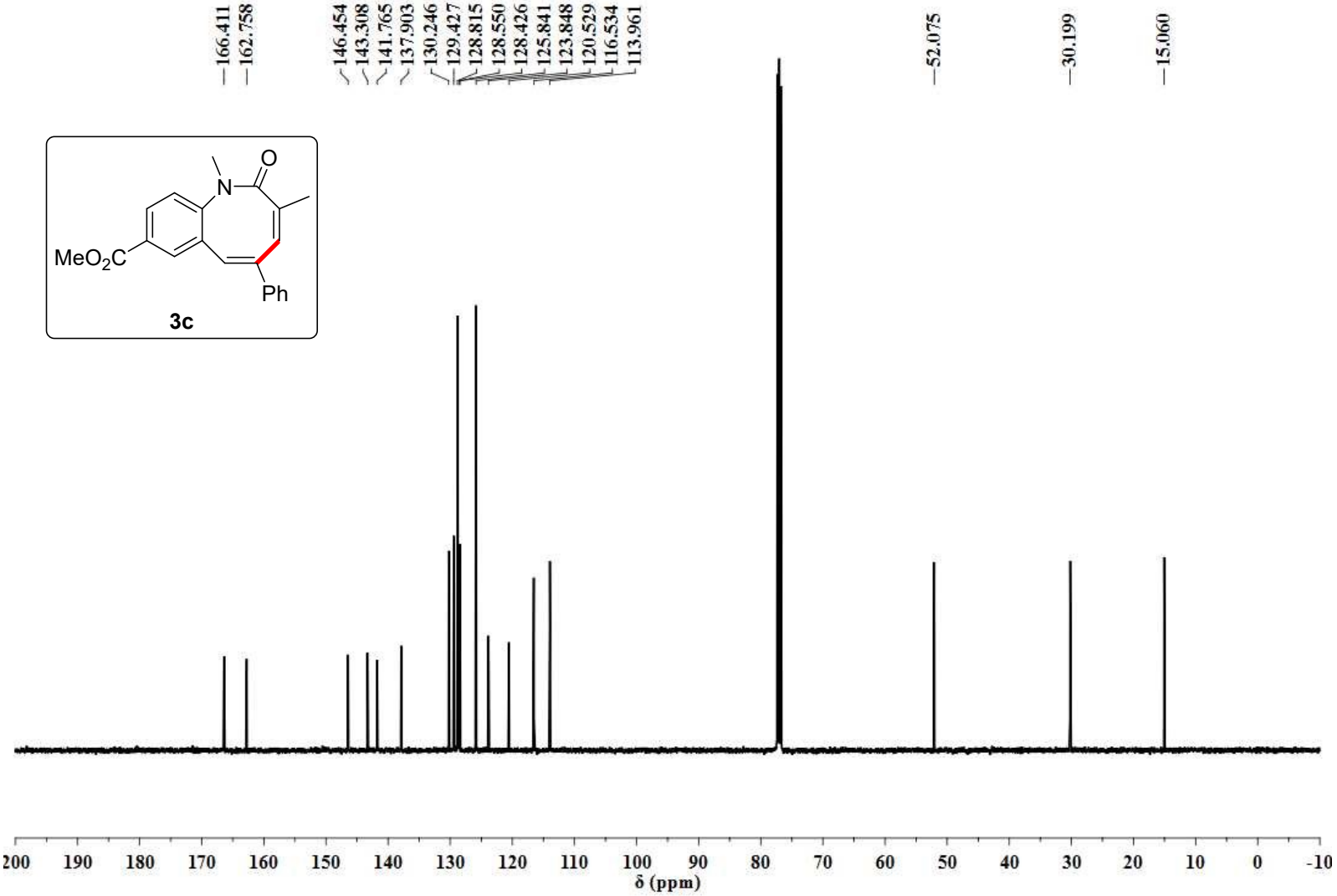
131.438
130.621
128.738
128.251
127.598
127.090
125.822
120.874
115.735
113.851
29.907
20.793
15.040
O
N
Me
Ph
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


8.275
8.271
8.151
8.147
8.133
8.130
7.426
7.408
7.358
7.355
7.318
7.307
7.303
6.191
5.272
3.860
3.840
2.166
MeO2C
Ph
3c
0.93
0.99
1.02
4.99
1.00
0.99
3.00
3.02
3.00
δ (ppm)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146.454
143.308
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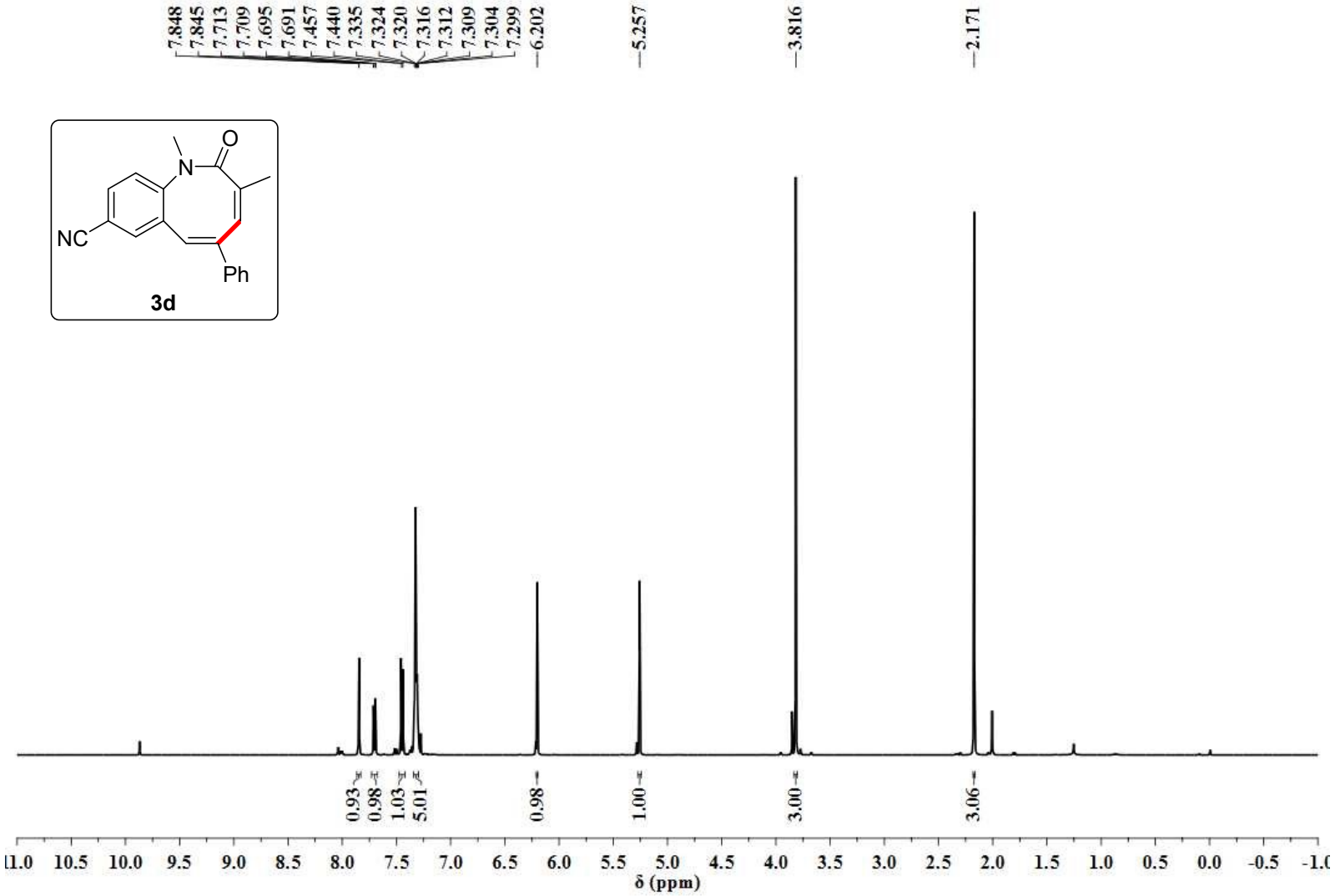
137.903
130.246
129.427
128.815
128.550
128.426
125.841
123.848
120.529
116.534
113.961
52.075
30.199
15.060
MeO2C
Ph
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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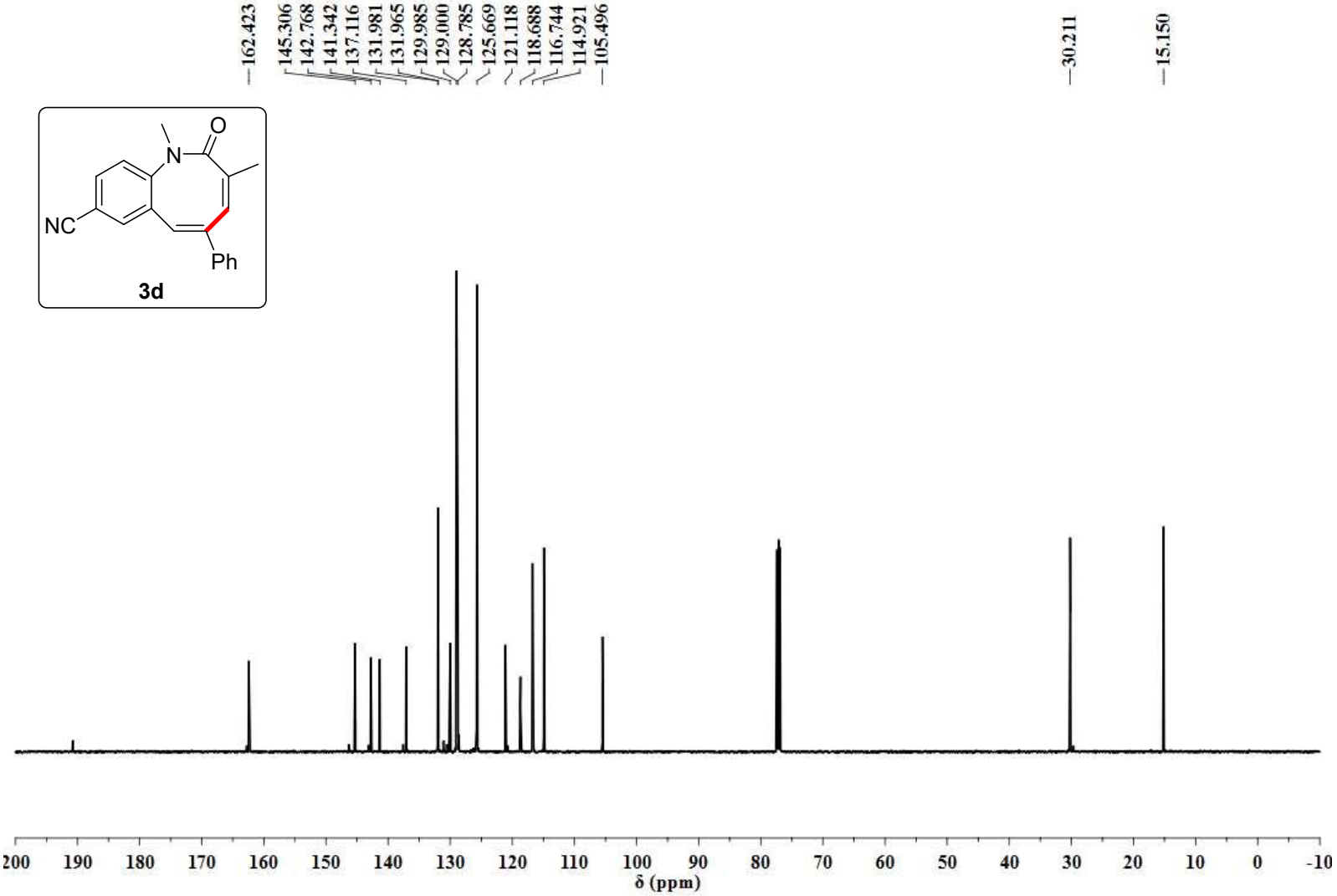
7.845
7.713
7.709
7.695
7.691
7.457
7.440
7.335
7.324
7.320
7.316
7.312
7.309
7.304
7.299
6.202
5.257
3.816
2.171
O
N
NC
Ph
3d
0.93
0.98
1.03
5.01
0.98
1.00
3.00
3.06
δ (ppm)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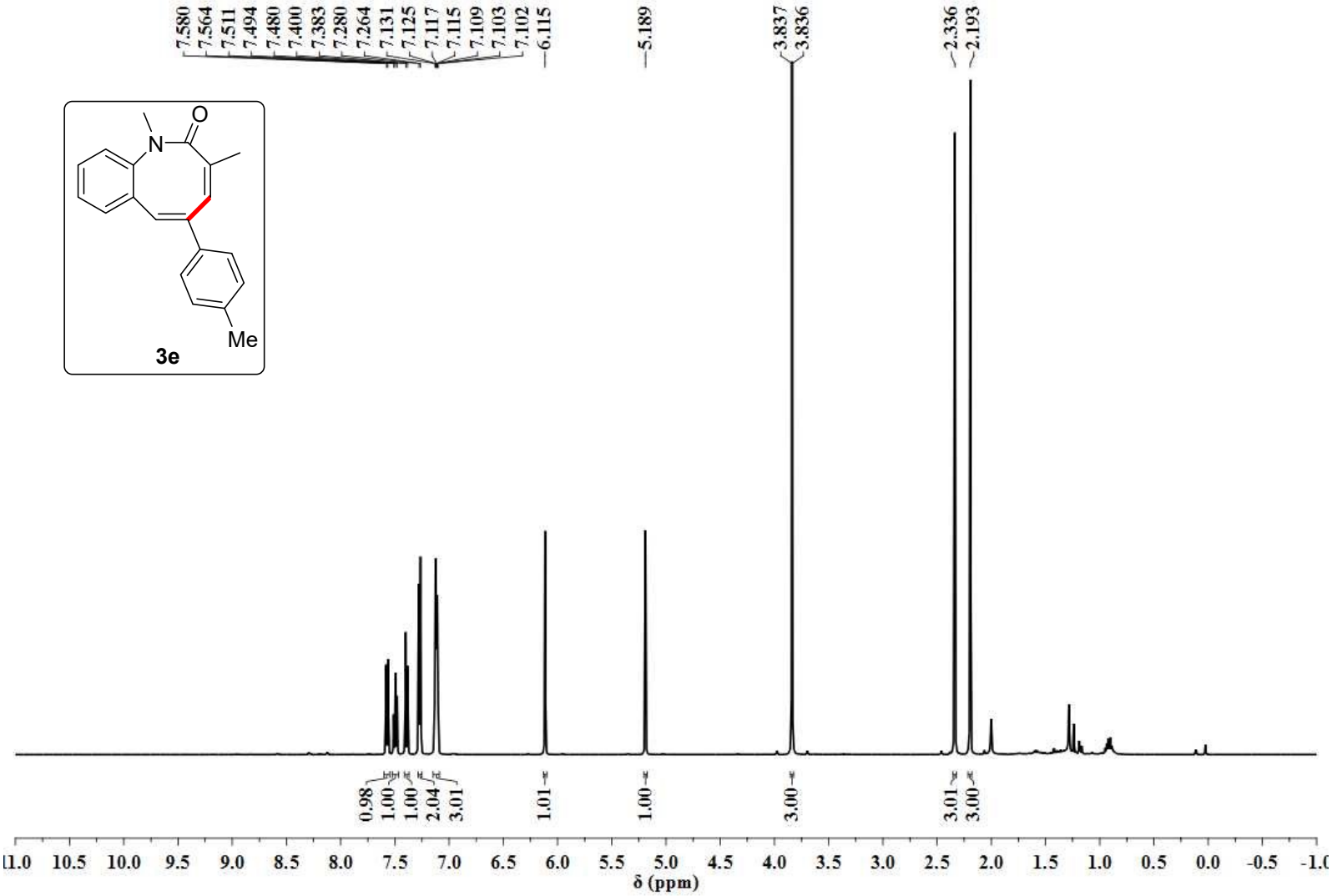
142.768
141.342
137.116
131.981
131.965
129.985
129.000
128.785
125.669
121.118
118.688
116.744
114.921
105.496
30.211
15.150
O
N
NC
Ph
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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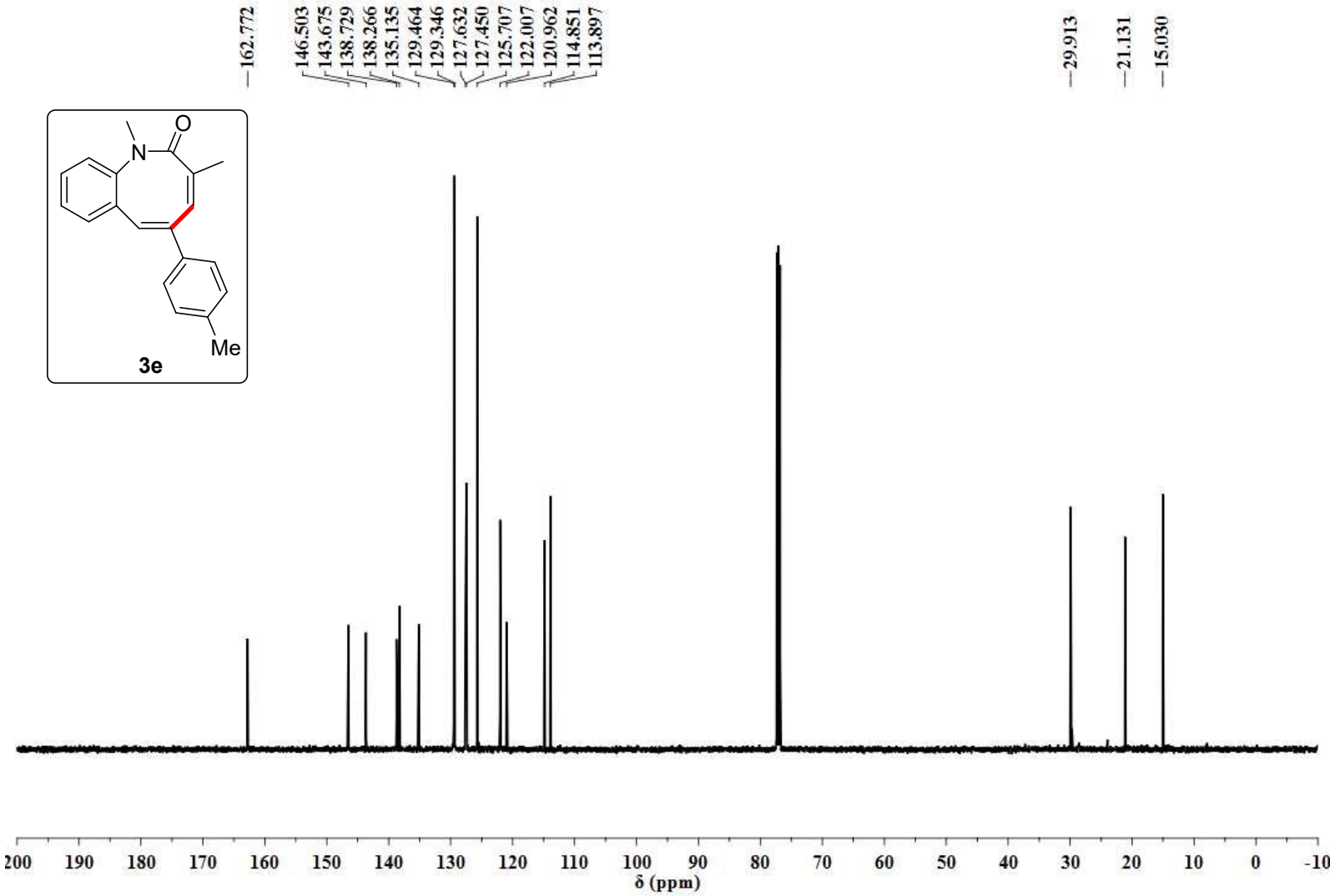
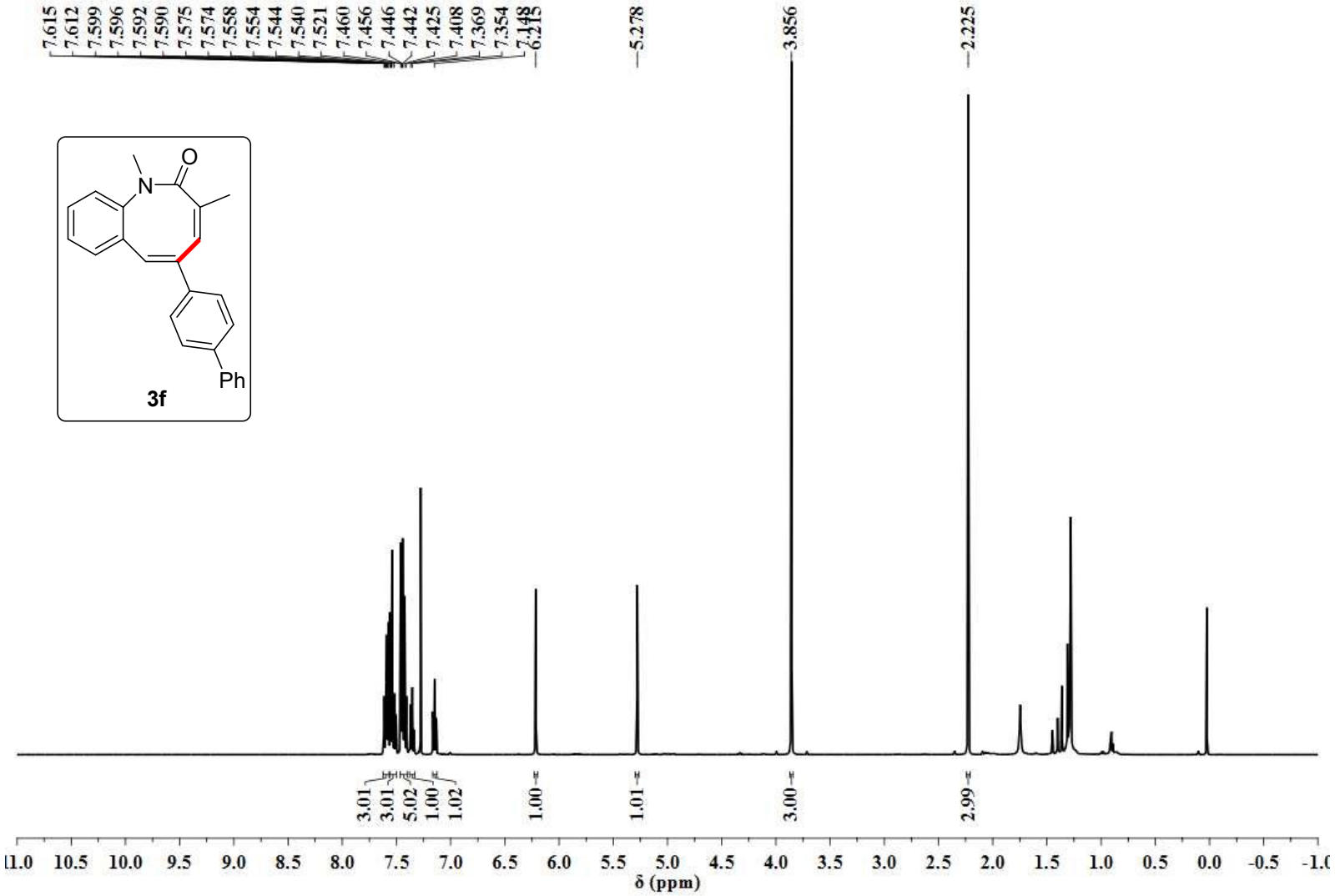
7.564
7.511
7.494
7.480
7.400
7.383
7.280
7.264
7.131
7.125
7.117
7.115
7.109
7.103
7.102
6.115
5.189
3.837
3.836
2.336
2.193
O
N
Me
3e
0.98
1.00
1.00
2.04
3.01
1.01
1.00
3.00
3.01
3.00
δ (ppm)


162.772
146.503
143.675
138.729
138.266
135.135
129.464
129.346
127.632
127.450
125.707
122.007
120.962
114.851
113.897
29.913
21.131
15.030
O
N
Me
3e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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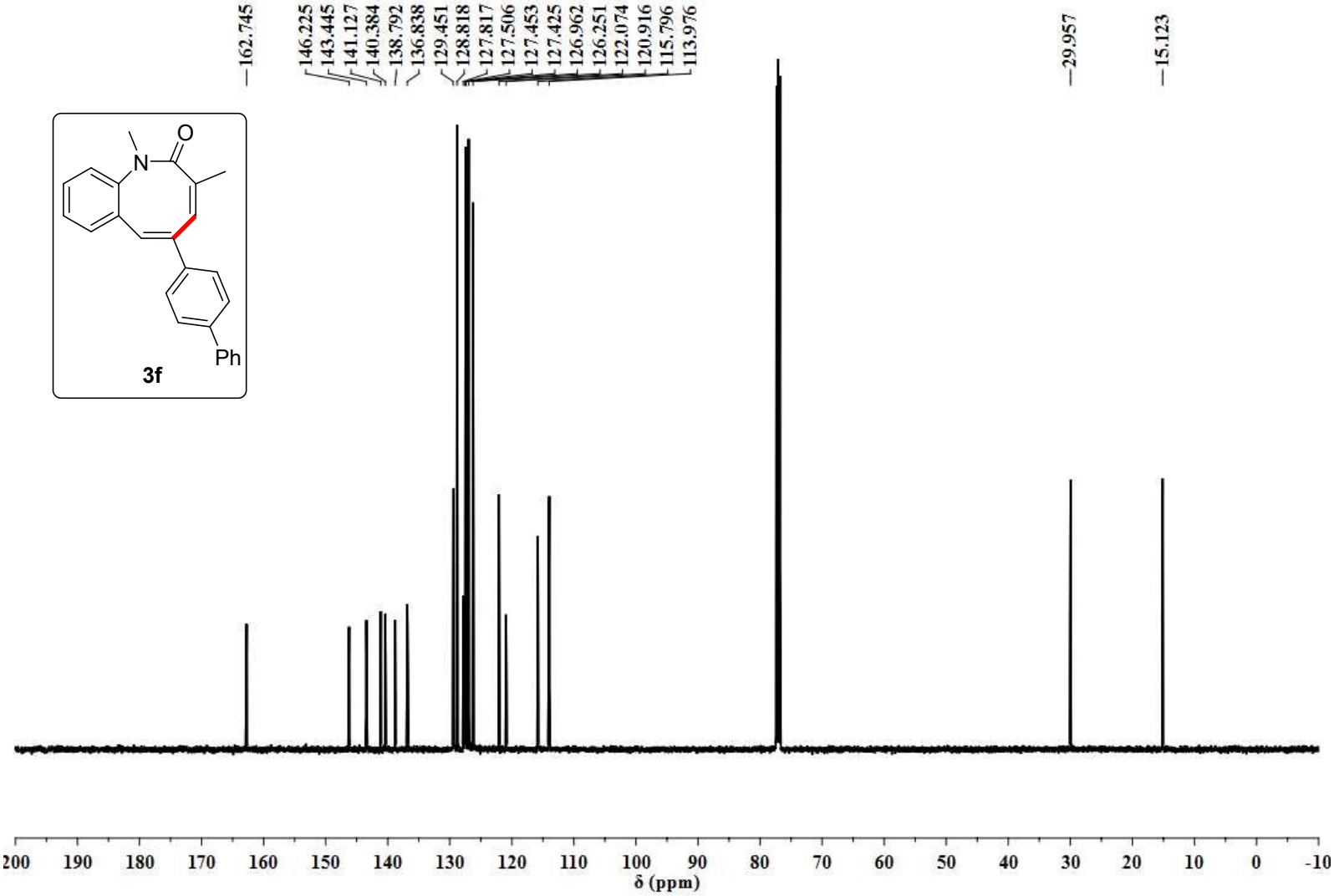
7.612
7.599
7.596
7.592
7.590
7.575
7.574
7.558
7.554
7.544
7.540
7.521
7.460
7.456
7.446
7.442
7.425
7.408
7.369
7.354
7.148
7.145
6.215
5.278
3.856
2.225
O
N
Ph
3f
3.01
3.01
5.02
1.00
1.02
1.00
1.01
3.00
2.99
δ (ppm)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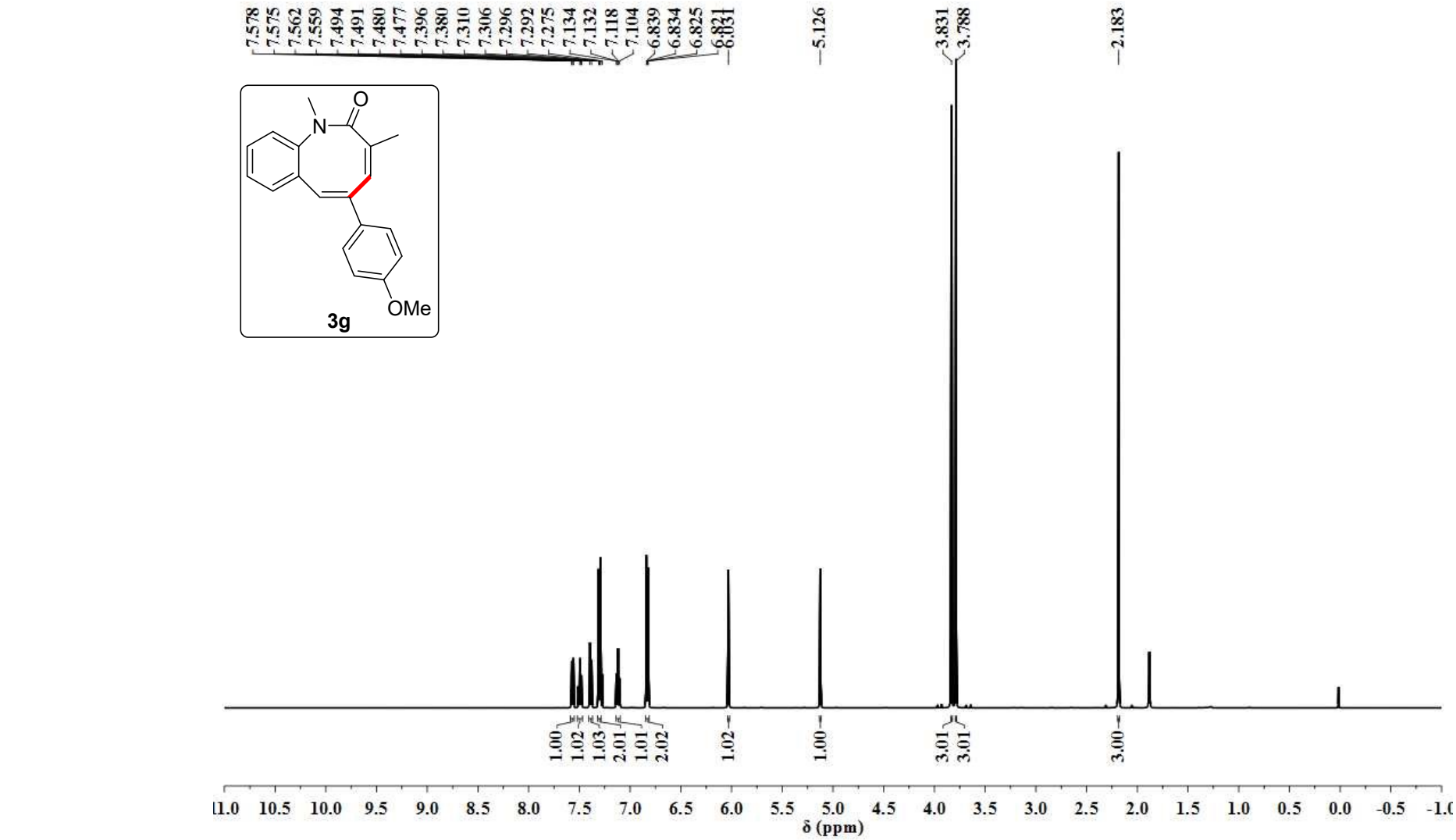
146.225
143.445
141.127
140.384
138.792
136.838
129.451
128.818
127.817
127.506
127.453
127.425
126.962
126.251
122.074
120.916
115.796
113.976
29.957
15.123
O
N
Ph
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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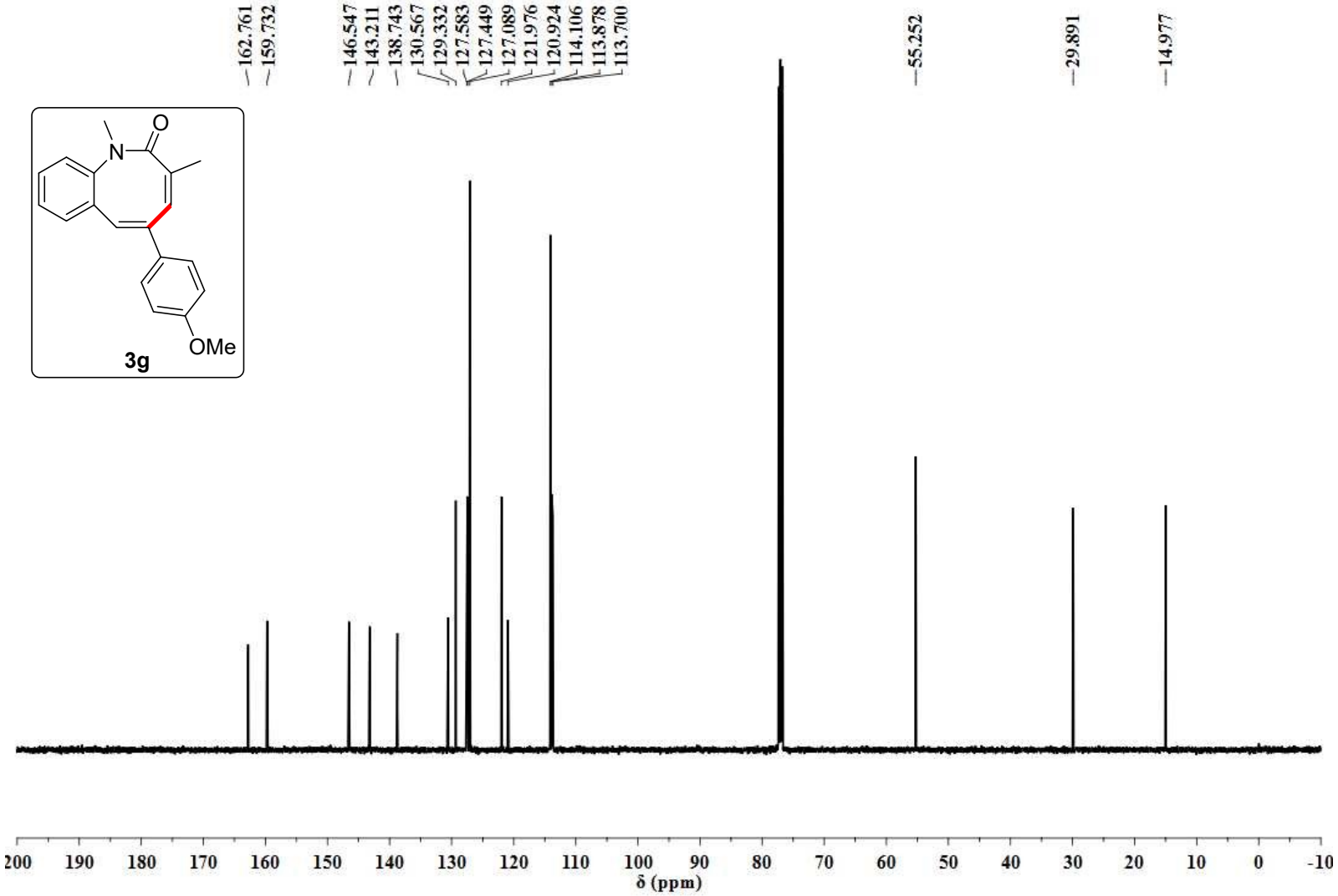
7.575
7.562
7.559
7.494
7.491
7.480
7.477
7.396
7.380
7.310
7.306
7.296
7.292
7.275
7.134
7.132
7.118
7.104
6.839
6.834
6.825
6.821
6.031
5.126
3.831
3.788
2.183
O
N
OMe
3g
1.00
1.02
1.03
2.01
1.01
2.02
1.02
1.00
3.01
3.01
3.00
δ (ppm)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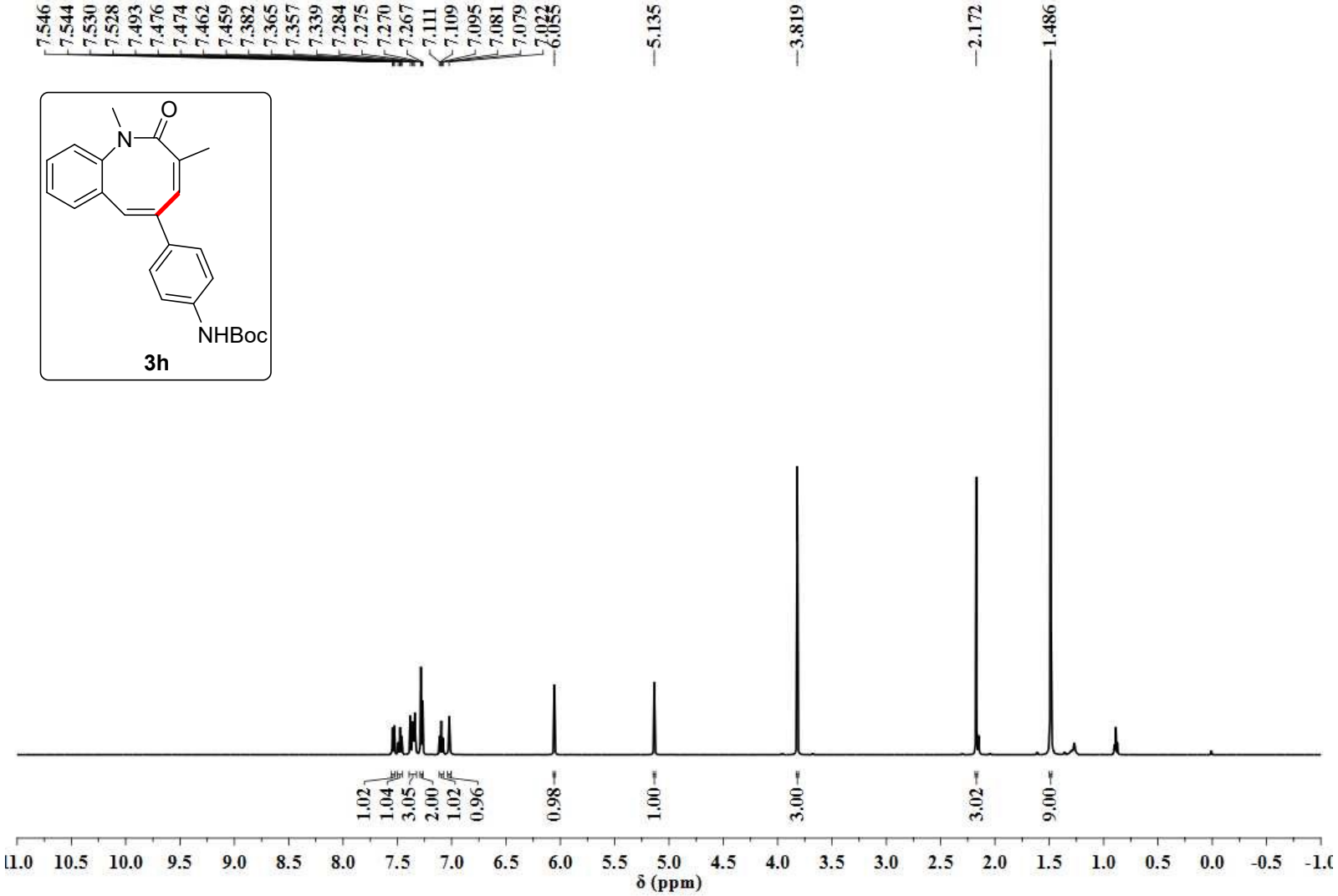
146.547
143.211
138.743
130.567
129.332
127.583
127.449
127.089
121.976
120.924
114.106
113.878
113.700
55.252
29.891
14.977
O
N
OMe
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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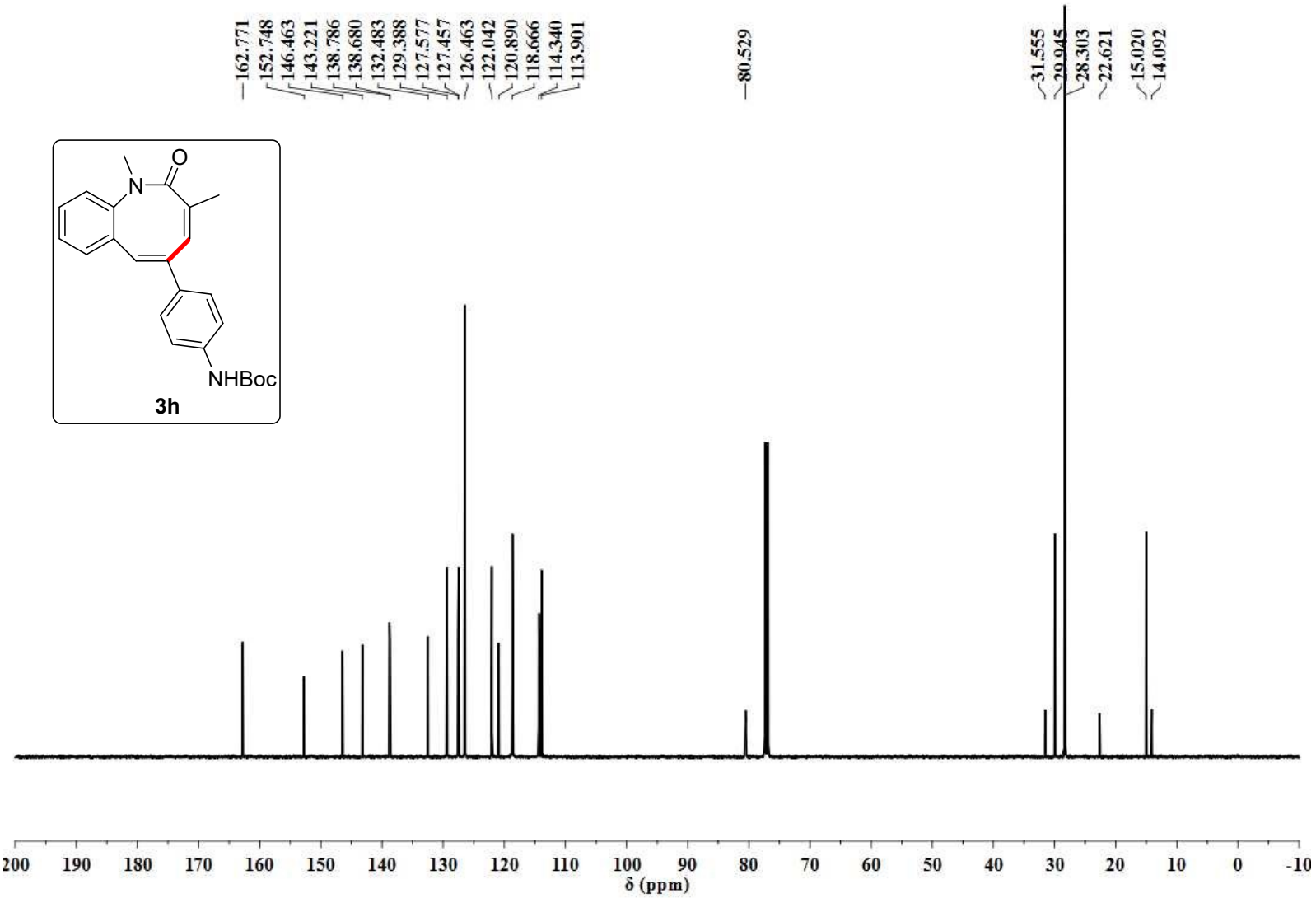
7.544
7.530
7.528
7.493
7.476
7.474
7.462
7.459
7.382
7.365
7.357
7.339
7.284
7.275
7.270
7.267
7.111
7.109
7.095
7.081
7.079
7.022
6.055
5.135
3.819
2.172
1.486
O
N
NHBoc
3h
1.02
1.04
3.05
2.00
1.02
0.96
0.98
1.00
3.00
3.02
9.00
δ (ppm)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143.221
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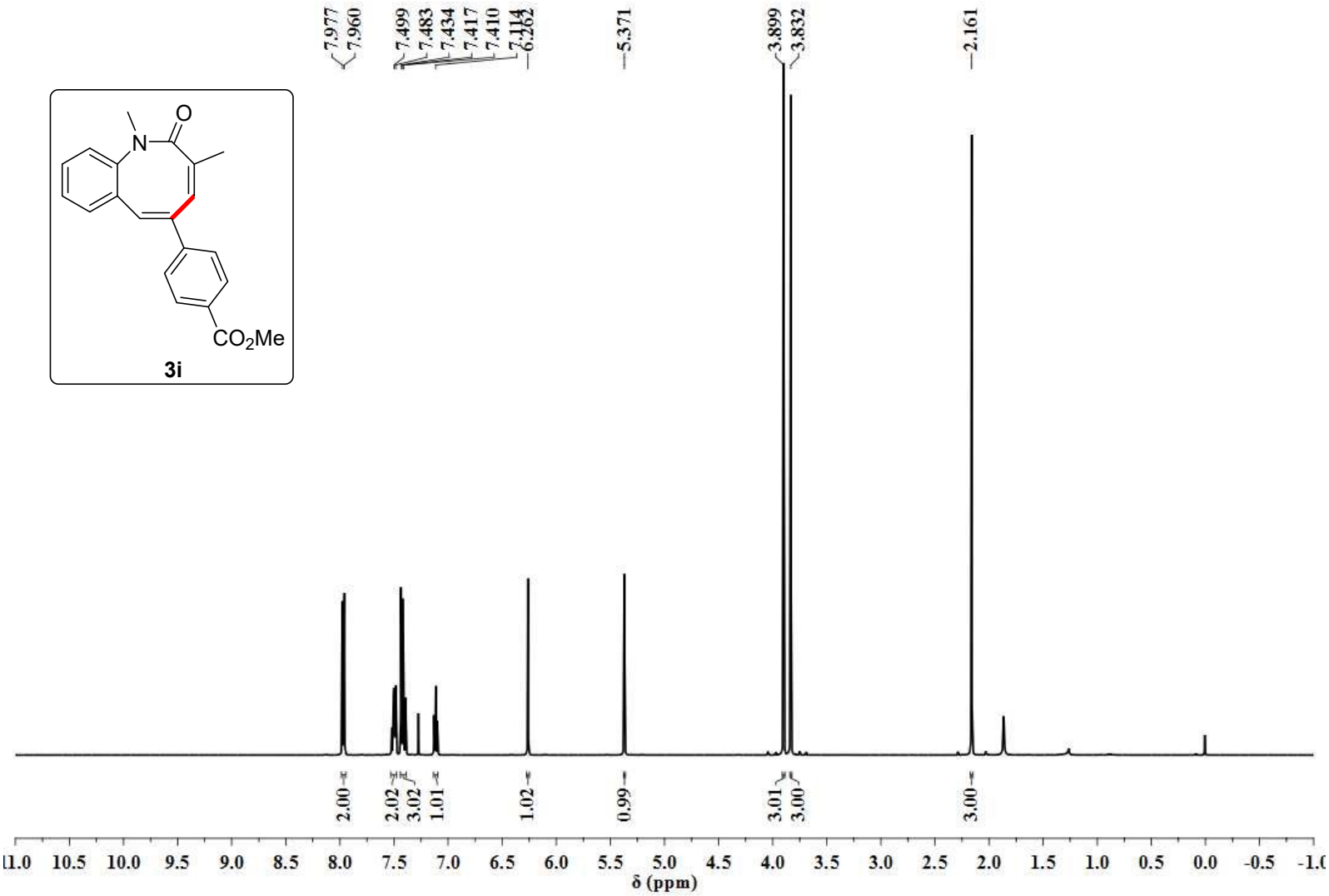
132.483
129.388
127.577
127.457
126.463
122.042
120.890
118.666
114.340
113.901
80.529
31.555
29.945
28.303
22.621
15.020
14.092
O
N
NHBoc
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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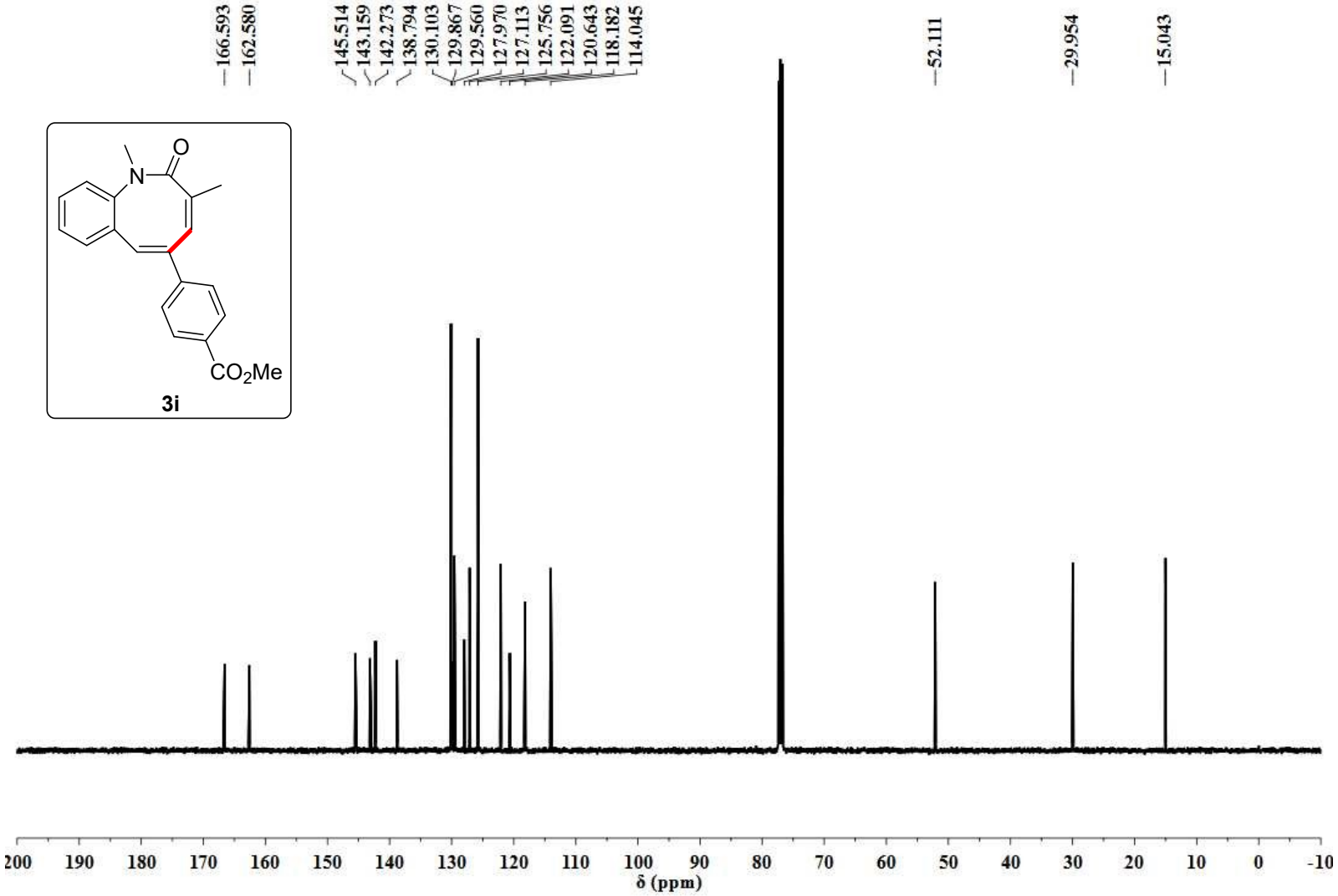
7.499
7.483
7.434
7.417
7.410
7.114
6.262
5.371
3.899
3.832
2.161
O
N
CO2Me
3i
2.00
2.02
3.02
1.01
1.02
0.99
3.01
3.00
3.00
δ (ppm)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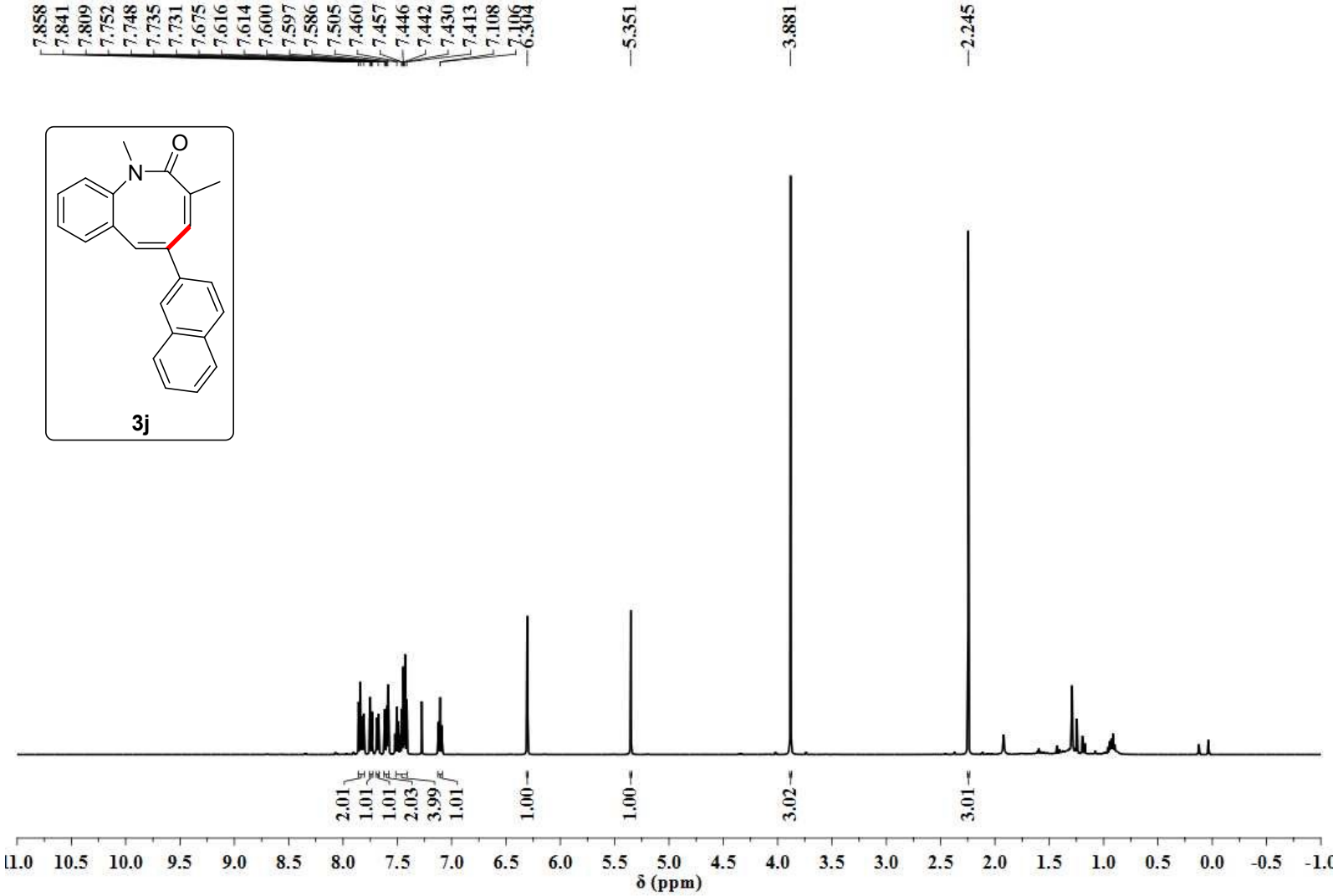
145.514
143.159
142.273
138.794
130.103
129.867
129.560
127.970
127.113
125.756
122.091
120.643
118.182
114.045
52.111
29.954
15.043
O
N
CO2Me
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.752
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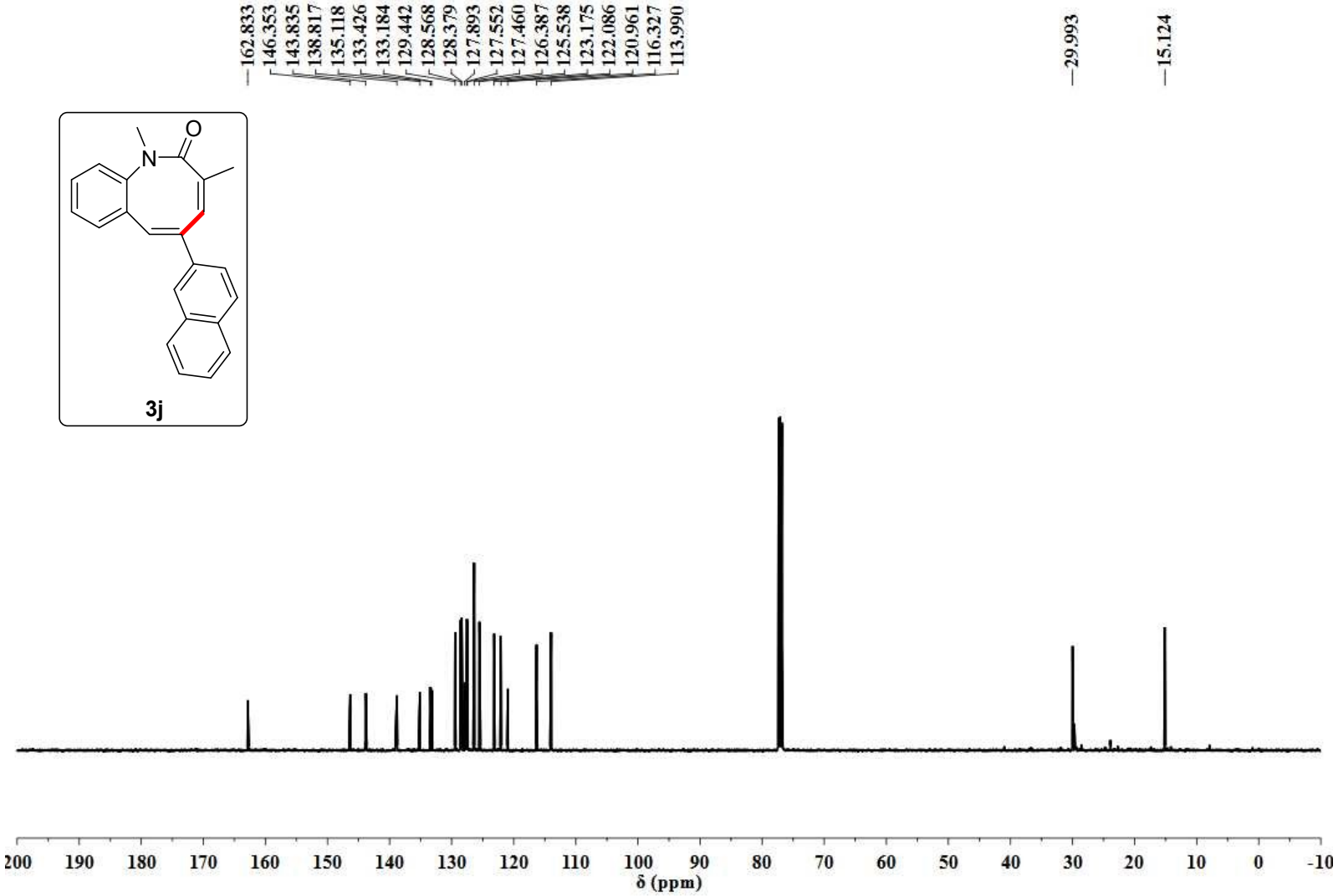
7.735
7.731
7.675
7.616
7.614
7.600
7.597
7.586
7.505
7.460
7.457
7.446
7.442
7.430
7.413
7.108
7.106
6.304
5.351
3.881
2.245
O
N
3j
2.01
1.01
1.01
2.03
3.99
1.01
1.00
1.00
3.02
3.01
δ (ppm)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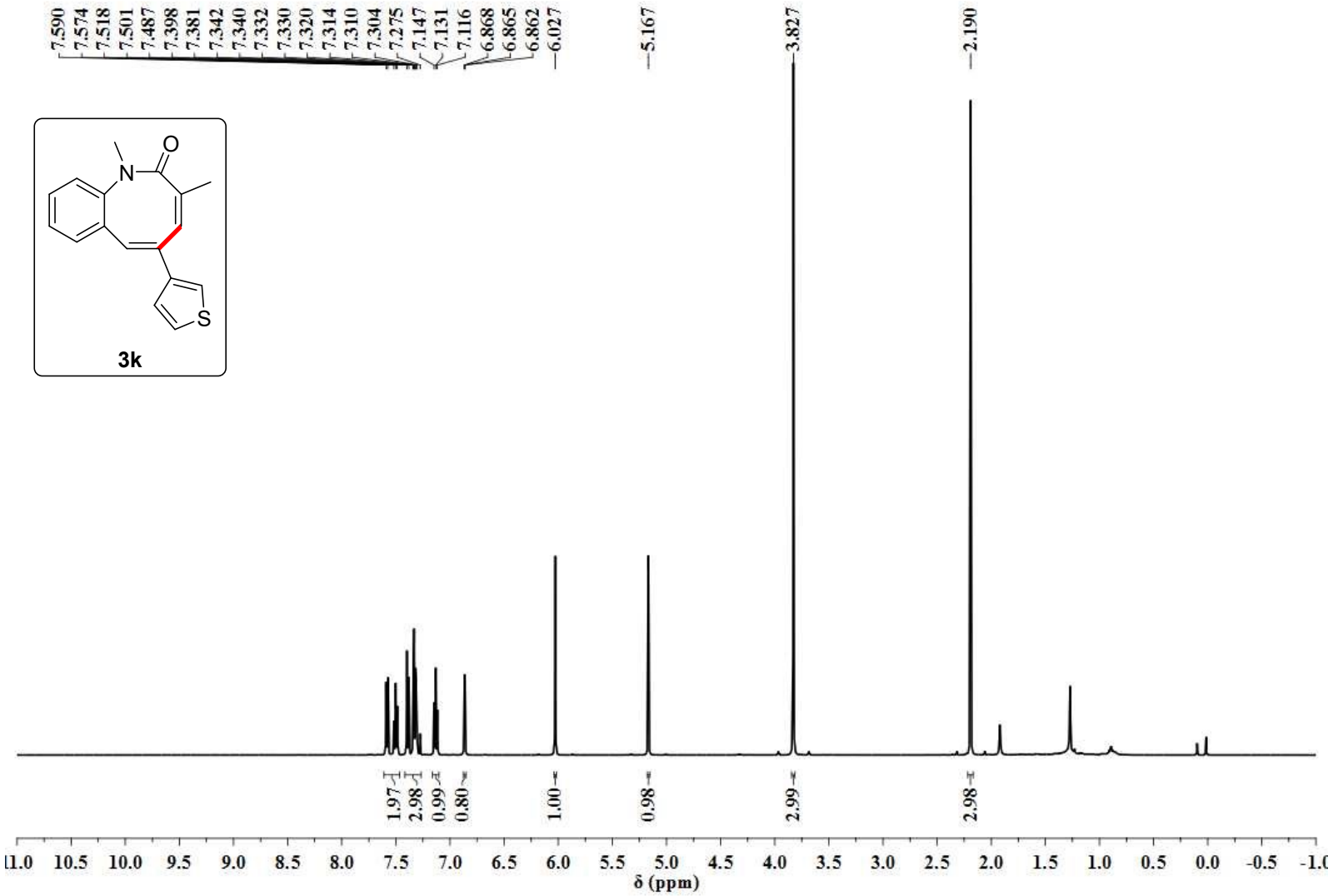
133.426
133.184
129.442
128.568
128.379
127.893
127.552
127.460
126.387
125.538
123.175
122.086
120.961
116.327
113.990
29.993
15.124
O
N
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.487
7.398
7.381
7.342
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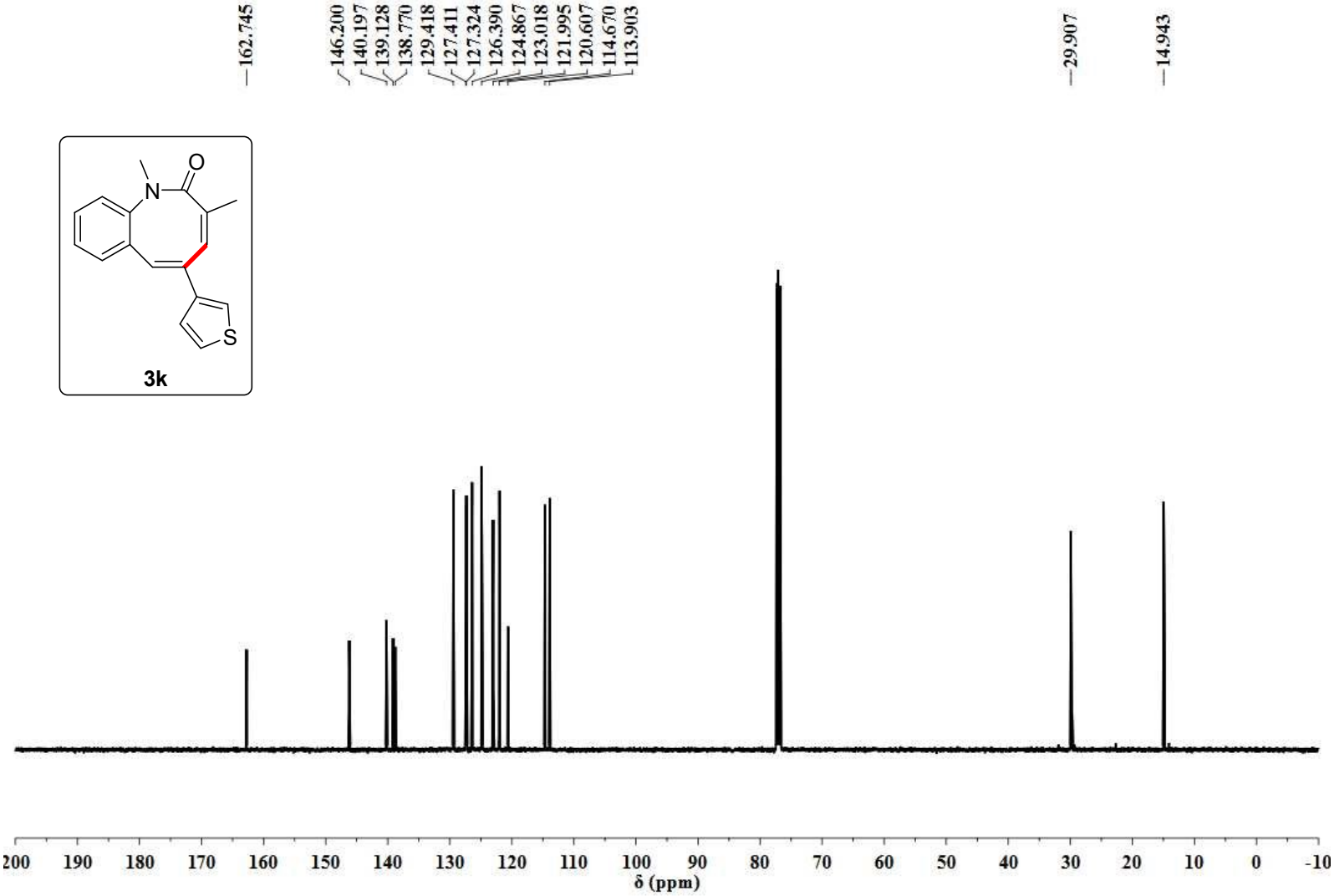
7.332
7.330
7.320
7.314
7.310
7.304
7.275
7.147
7.131
7.116
6.868
6.865
6.862
6.027
5.167
3.827
2.190
O
N
S
3k
1.97
2.98
0.99
0.80
1.00
0.98
2.99
2.98
δ (ppm)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139.128
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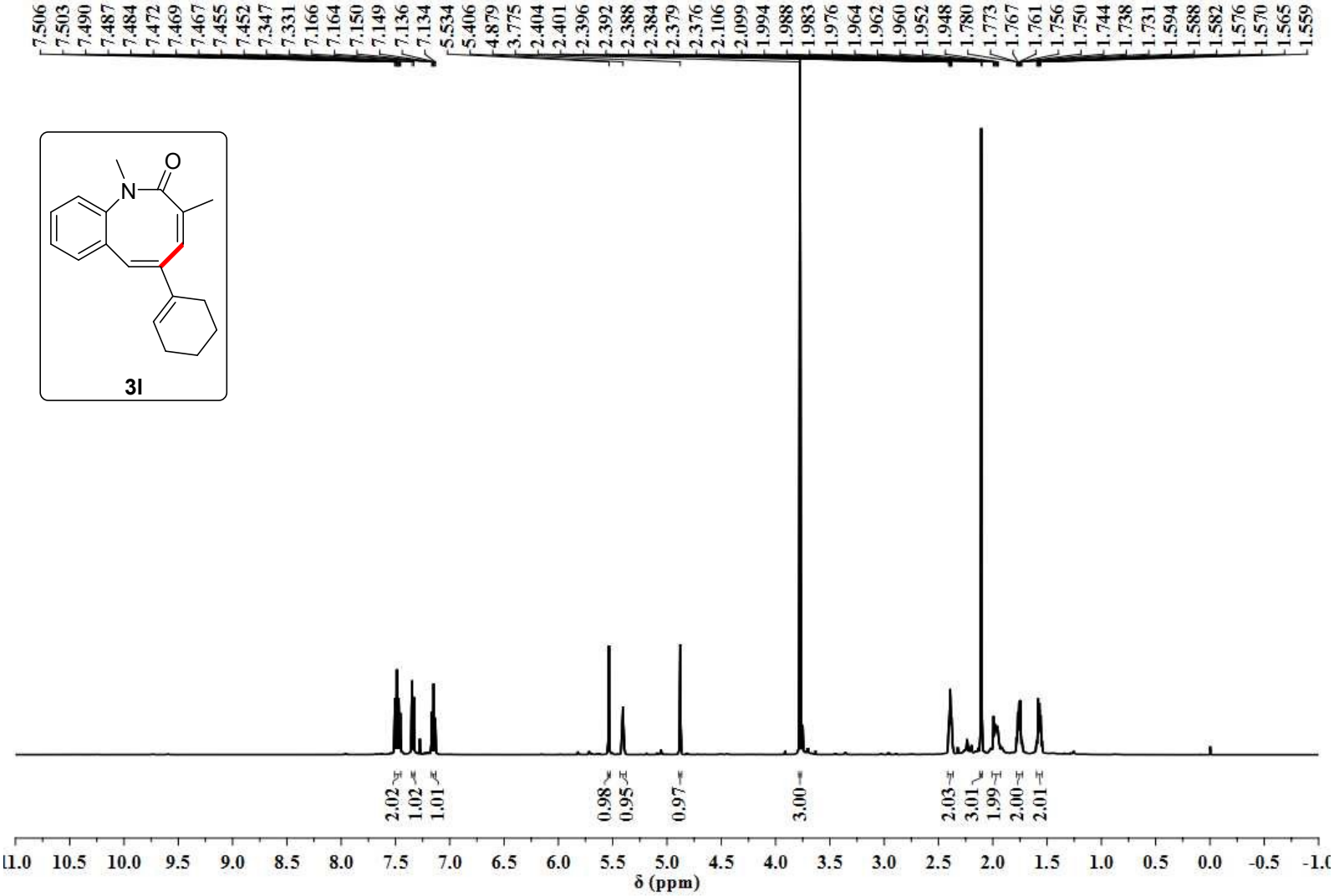
129.418
127.411
127.324
126.390
124.867
123.018
121.995
120.607
114.670
113.903
29.907
14.943
O
N
S
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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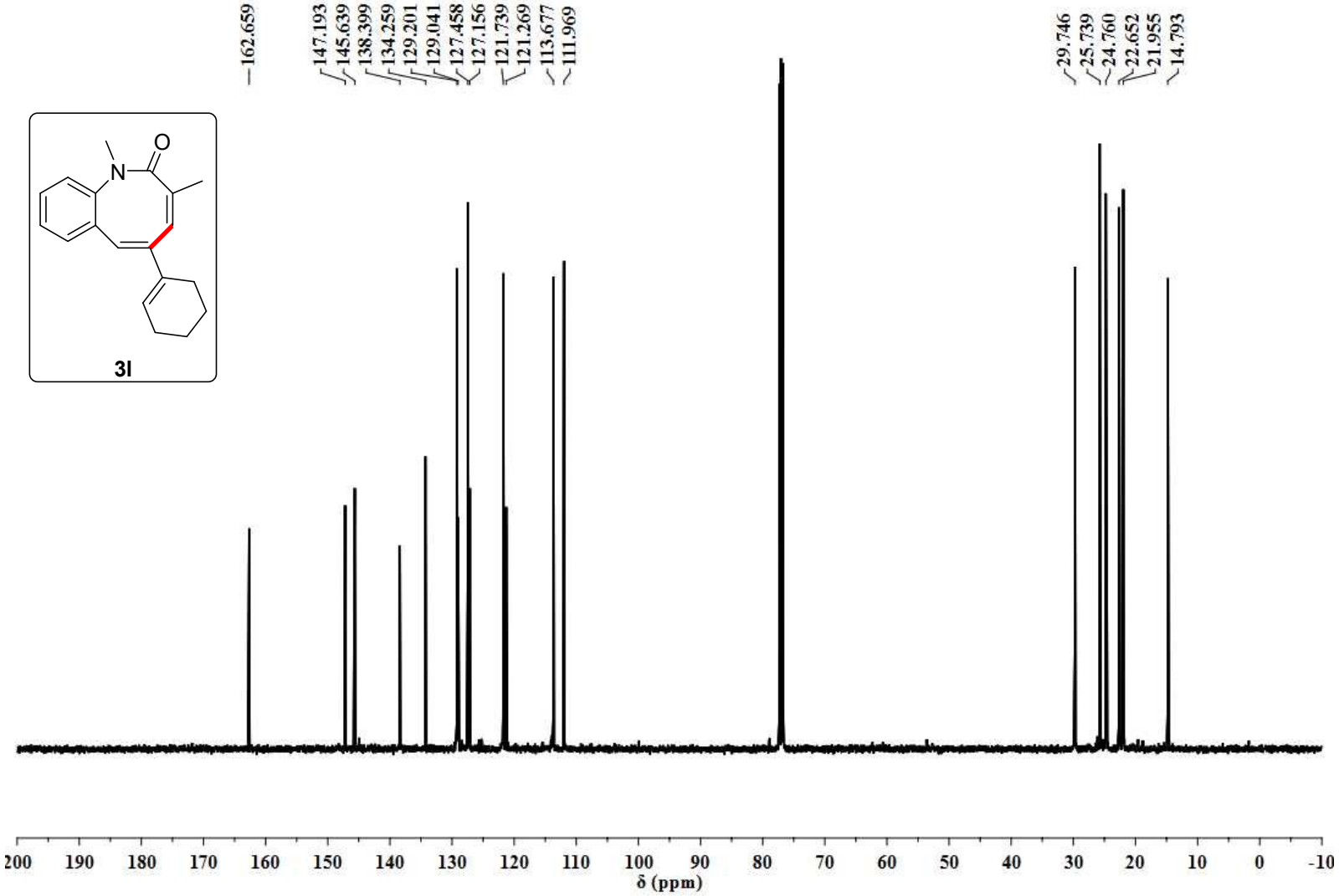
7.347
7.331
7.166
7.164
7.150
7.149
7.136
7.134
5.534
5.406
4.879
3.775
2.404
2.401
2.396
2.392
2.388
2.384
2.379
2.376
2.106
2.099
1.994
1.988
1.983
1.976
1.964
1.962
1.960
1.952
1.948
1.780
1.773
1.767
1.761
1.756
1.750
1.744
1.738
1.731
1.594
1.588
1.582
1.576
1.570
1.565
1.559
O
N
3l
2.02
1.02
1.01
0.98
0.95
0.97
3.00
2.03
3.01
1.99
2.00
2.01
δ (ppm)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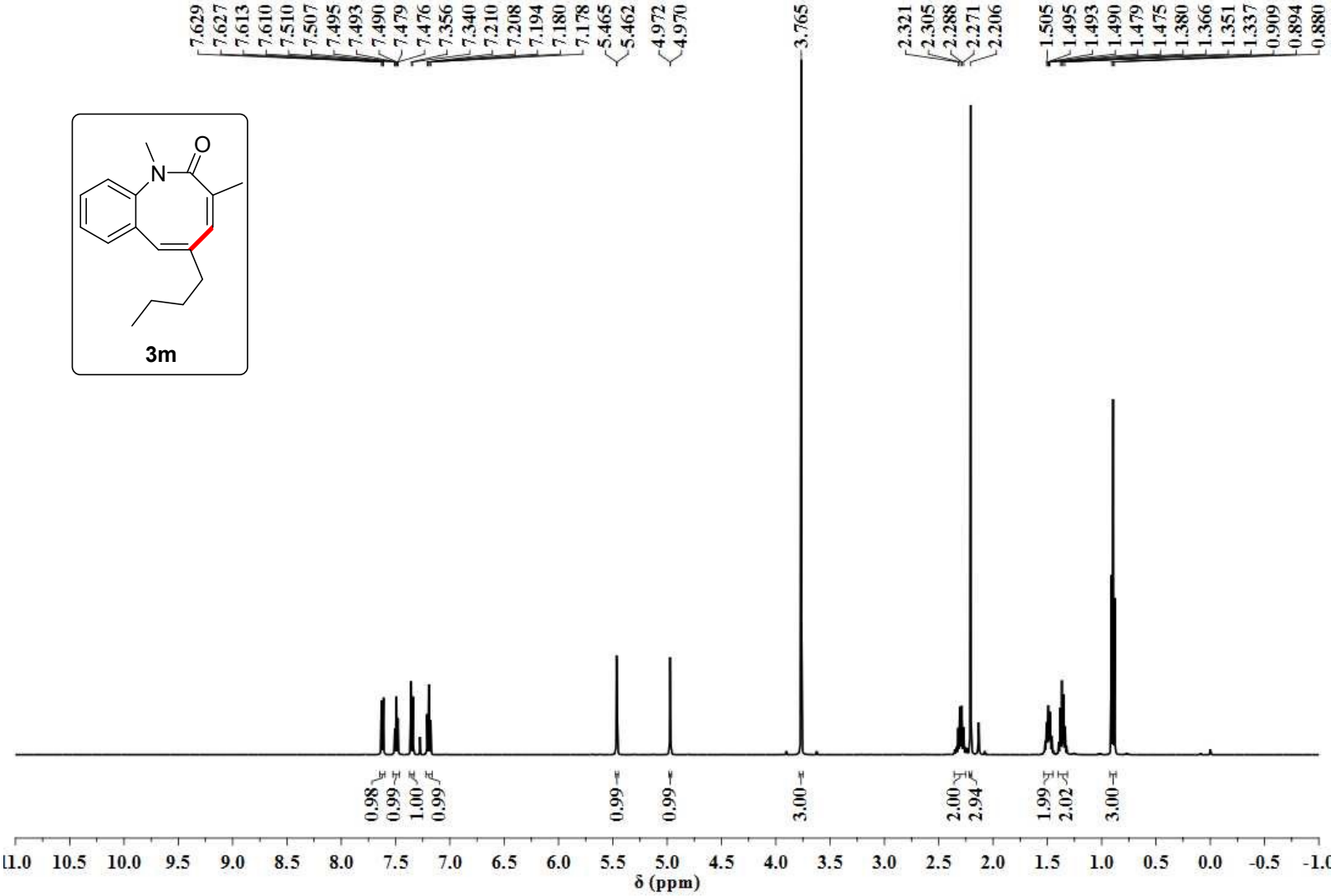
129.041
127.458
127.156
121.739
121.269
113.677
111.969
29.746
25.739
24.760
22.652
21.955
14.793
O
N
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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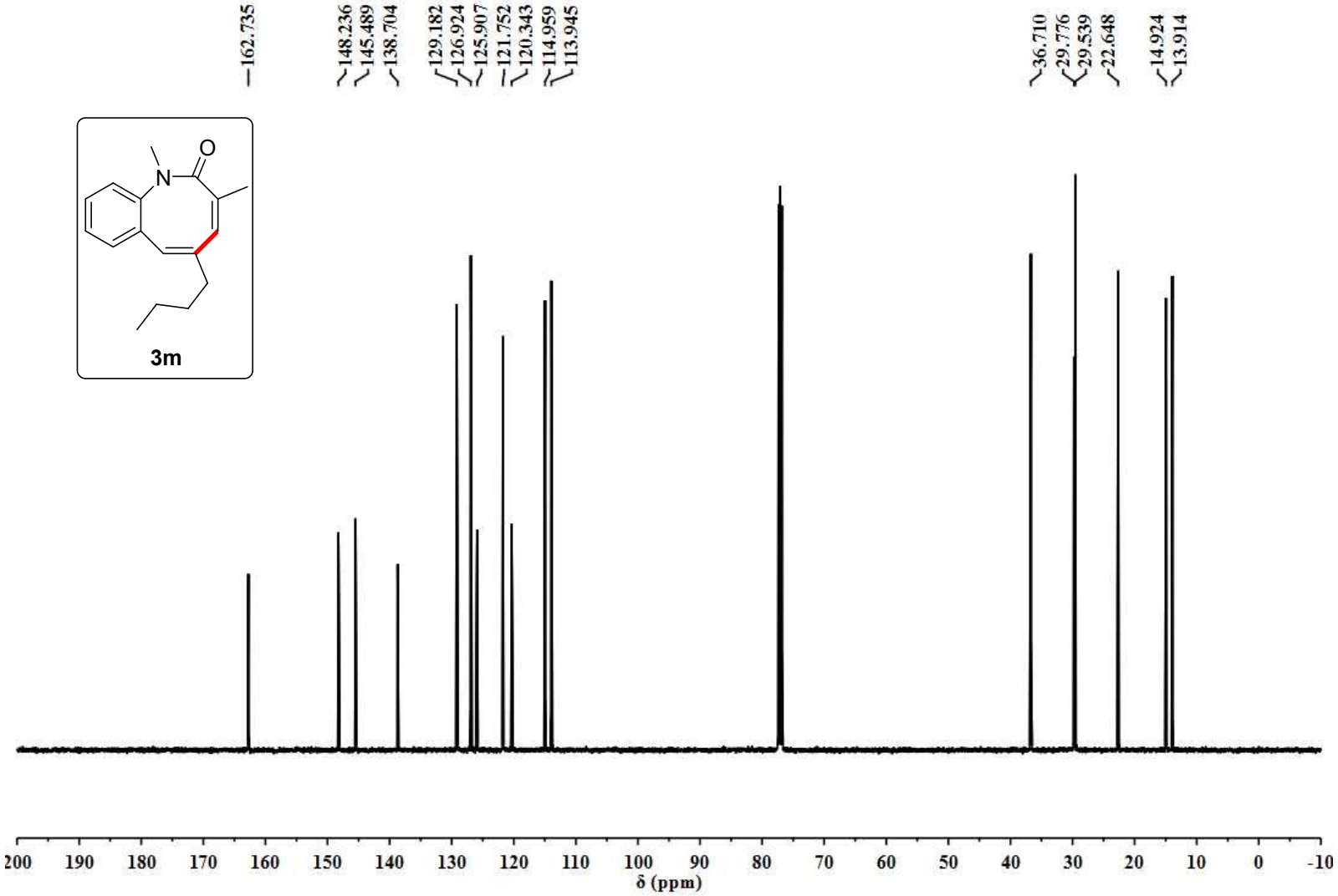
7.610
7.510
7.507
7.495
7.493
7.490
7.479
7.476
7.356
7.340
7.210
7.208
7.194
7.180
7.178
5.465
5.462
4.972
4.970
3.765
2.321
2.305
2.288
2.271
2.206
1.505
1.495
1.493
1.490
1.479
1.475
1.380
1.366
1.351
1.337
0.909
0.894
0.880
O
N
3m
0.98
0.99
1.00
0.99
0.99
0.99
3.00
2.00
2.94
1.99
2.02
3.00
δ (ppm)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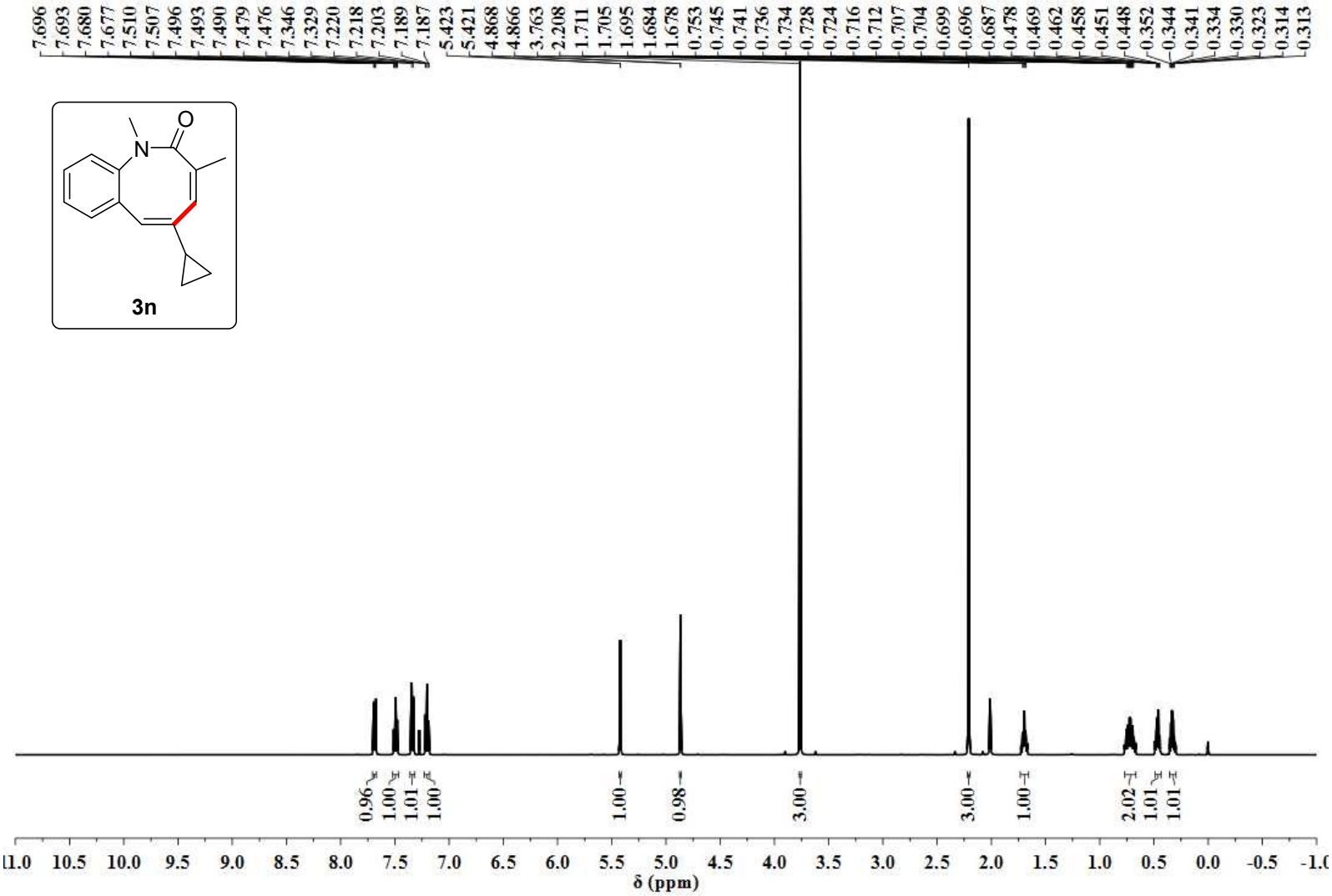
126.924
125.907
121.752
120.343
114.959
113.945
36.710
29.776
29.539
22.648
14.924
13.914
O
N
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.693
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7.507
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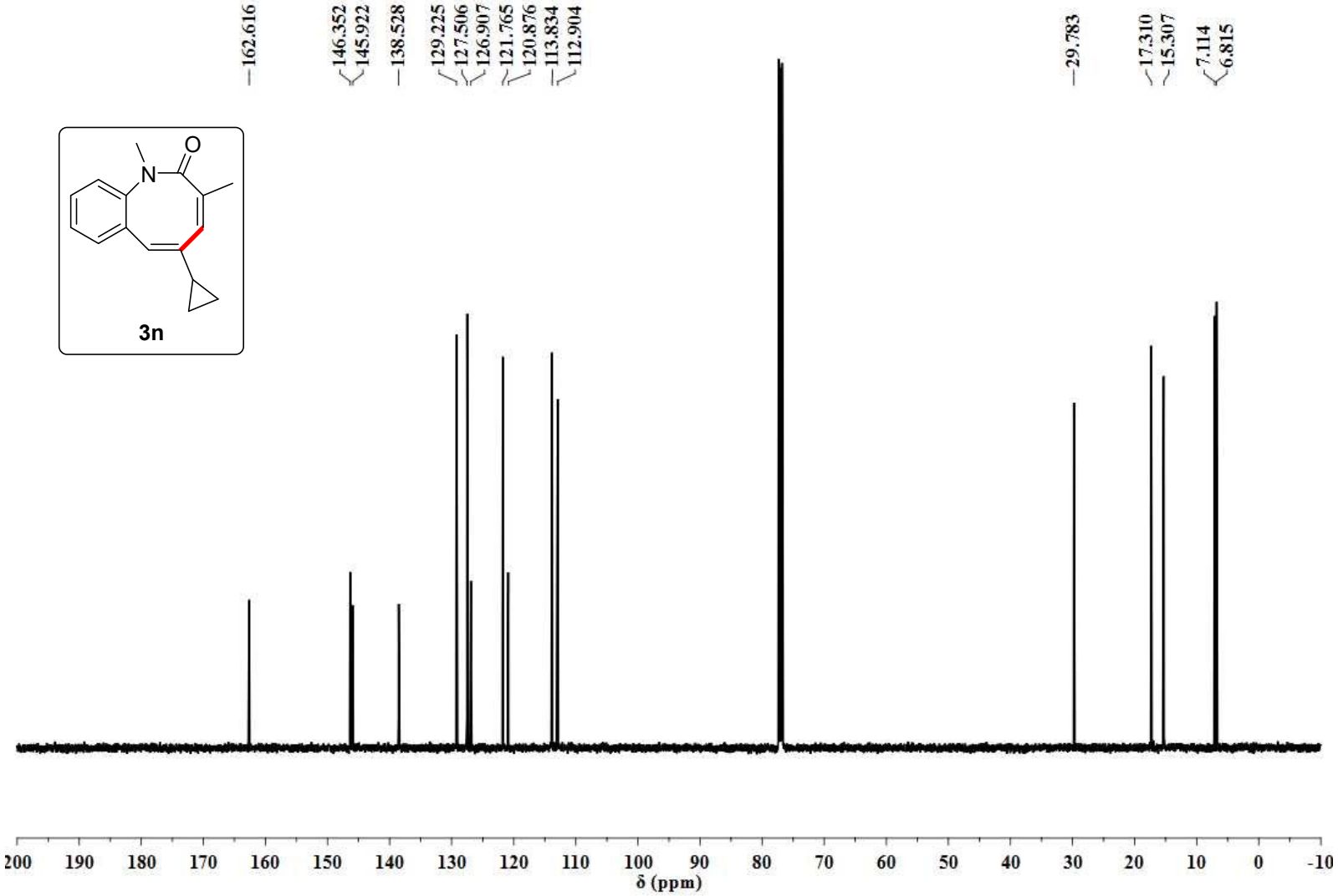
7.493
7.490
7.479
7.476
7.346
7.329
7.220
7.218
7.203
7.189
7.187
5.423
5.421
4.868
4.866
3.763
2.208
1.711
1.705
1.695
1.684
1.678
0.753
0.745
0.741
0.736
0.734
0.728
0.724
0.716
0.712
0.707
0.704
0.699
0.696
0.687
0.478
0.469
0.462
0.458
0.451
0.448
0.352
0.344
0.341
0.334
0.330
0.323
0.314
0.313
O
N
3n
0.96
1.00
1.01
1.00
1.00
0.98
3.00
3.00
1.00
2.02
1.01
1.01
δ (ppm)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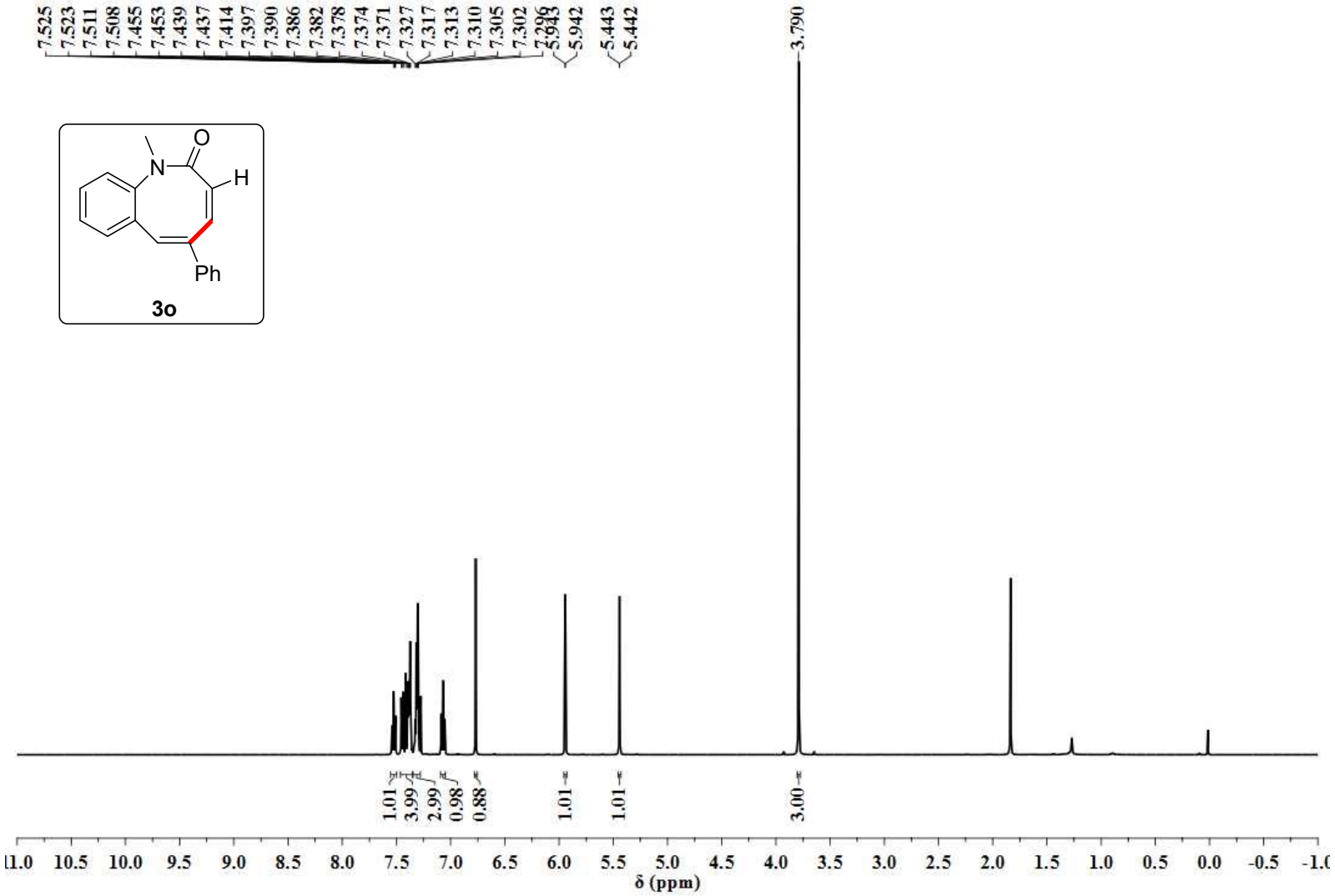
121.765
120.876
113.834
112.904
29.783
17.310
15.307
7.114
6.815
O
N
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.437
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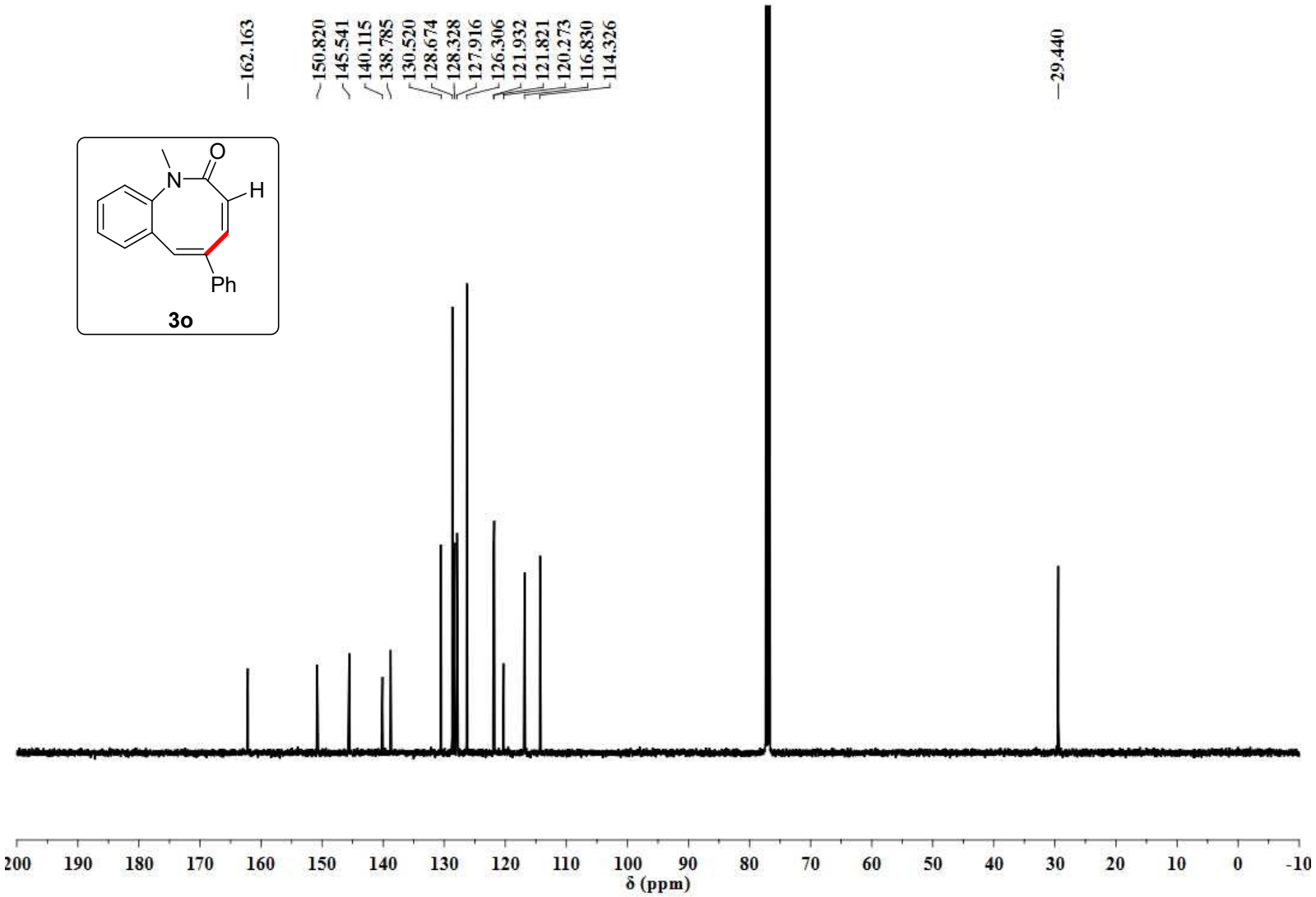
7.390
7.386
7.382
7.378
7.374
7.371
7.327
7.317
7.313
7.310
7.305
7.302
5.943
5.942
5.443
5.442
3.790
O
N
H
Ph
3o
1.01
3.99
2.99
0.98
0.88
1.01
1.01
3.00
δ (ppm)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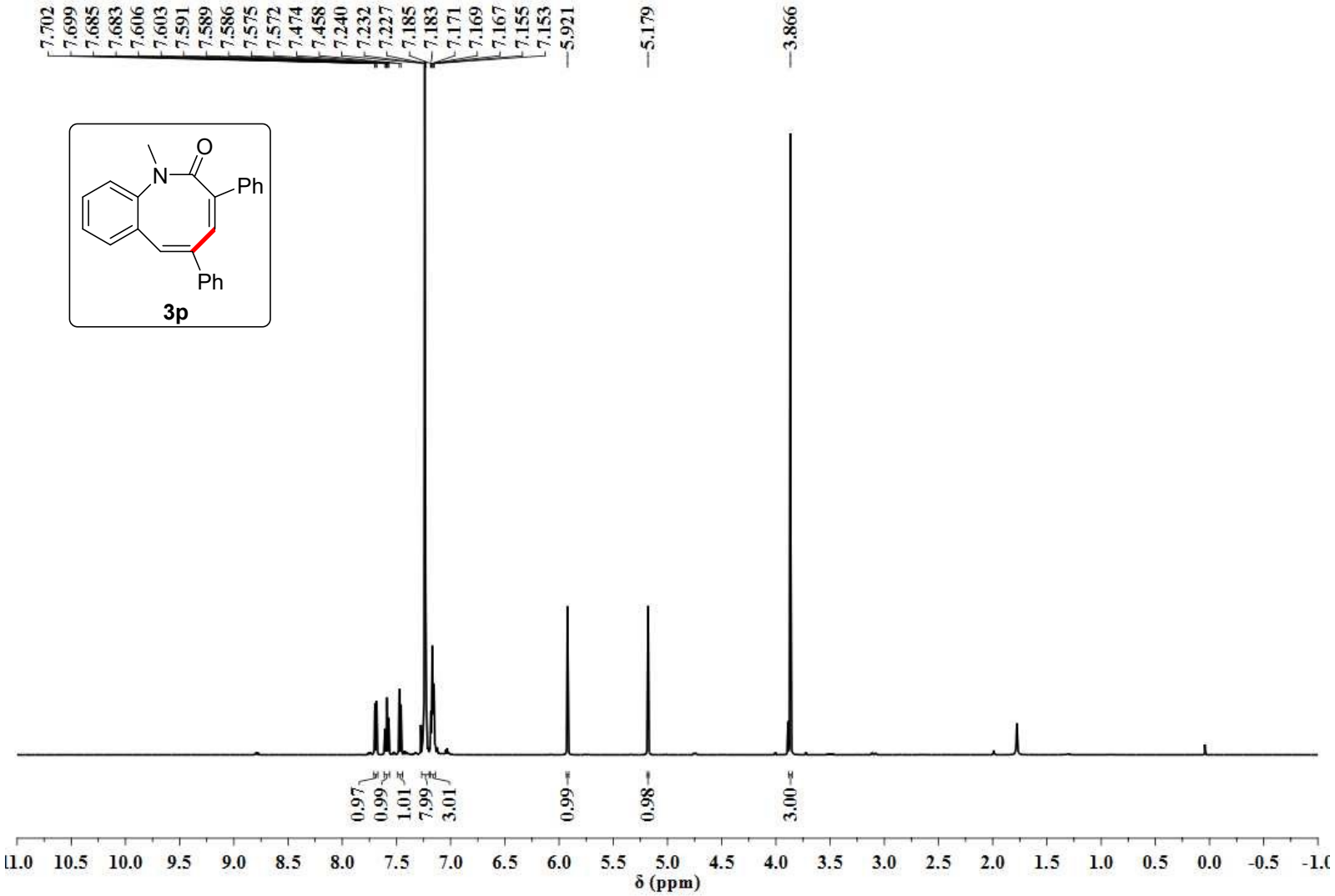
145.541
140.115
138.785
130.520
128.674
128.328
127.916
126.306
121.932
121.821
120.273
116.830
114.326
29.440
O
N
H
Ph
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.685
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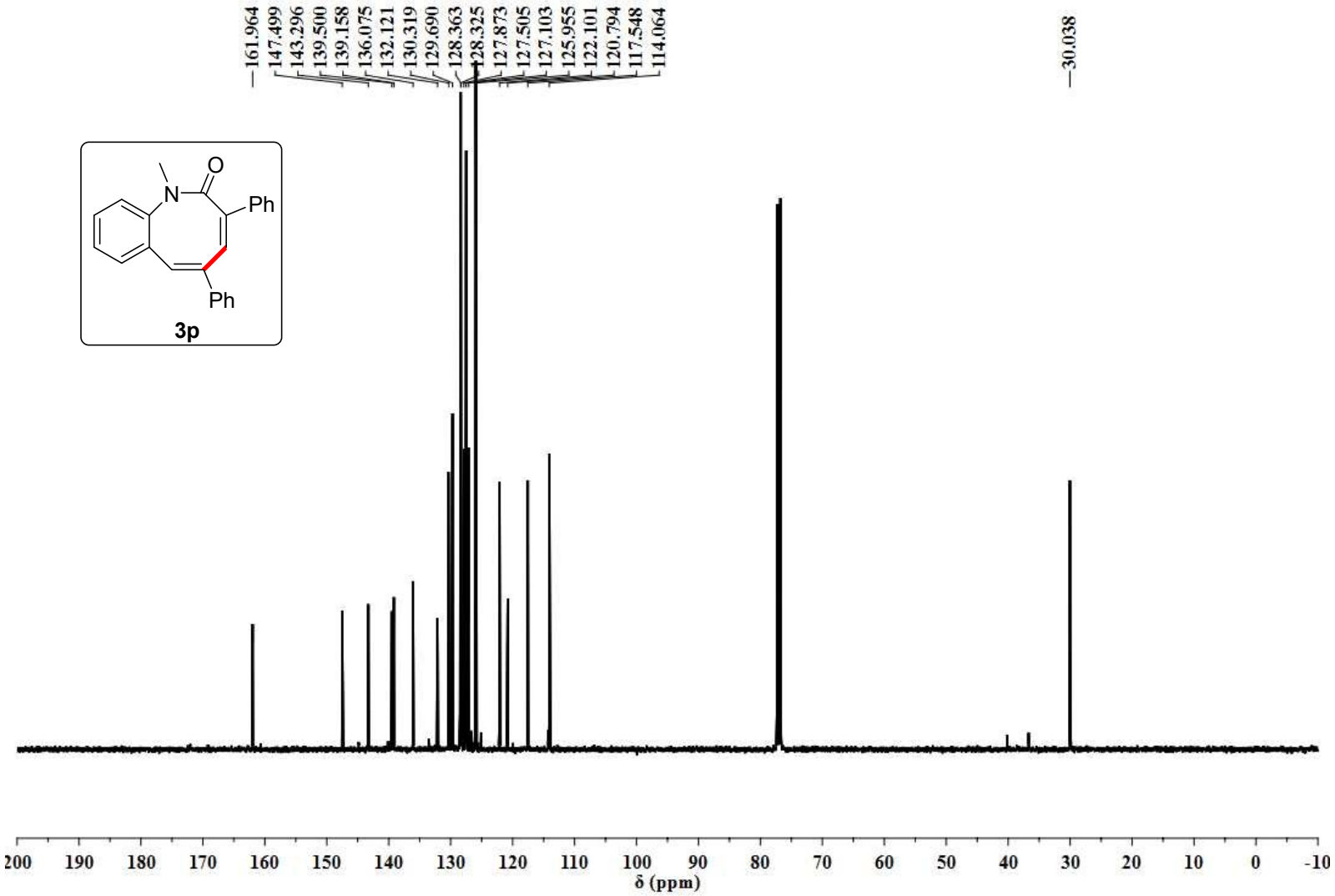
7.589
7.586
7.575
7.572
7.474
7.458
7.240
7.232
7.227
7.185
7.183
7.171
7.169
7.167
7.155
7.153
5.921
5.179
3.866
O
N
Ph
Ph
3p
0.97
0.99
1.01
7.99
3.01
0.99
0.98
3.00
δ (ppm)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143.296
139.500
139.158
136.075
132.121
130.319
129.690
128.363
128.325
127.873
127.505
127.103
125.955
122.101
120.794
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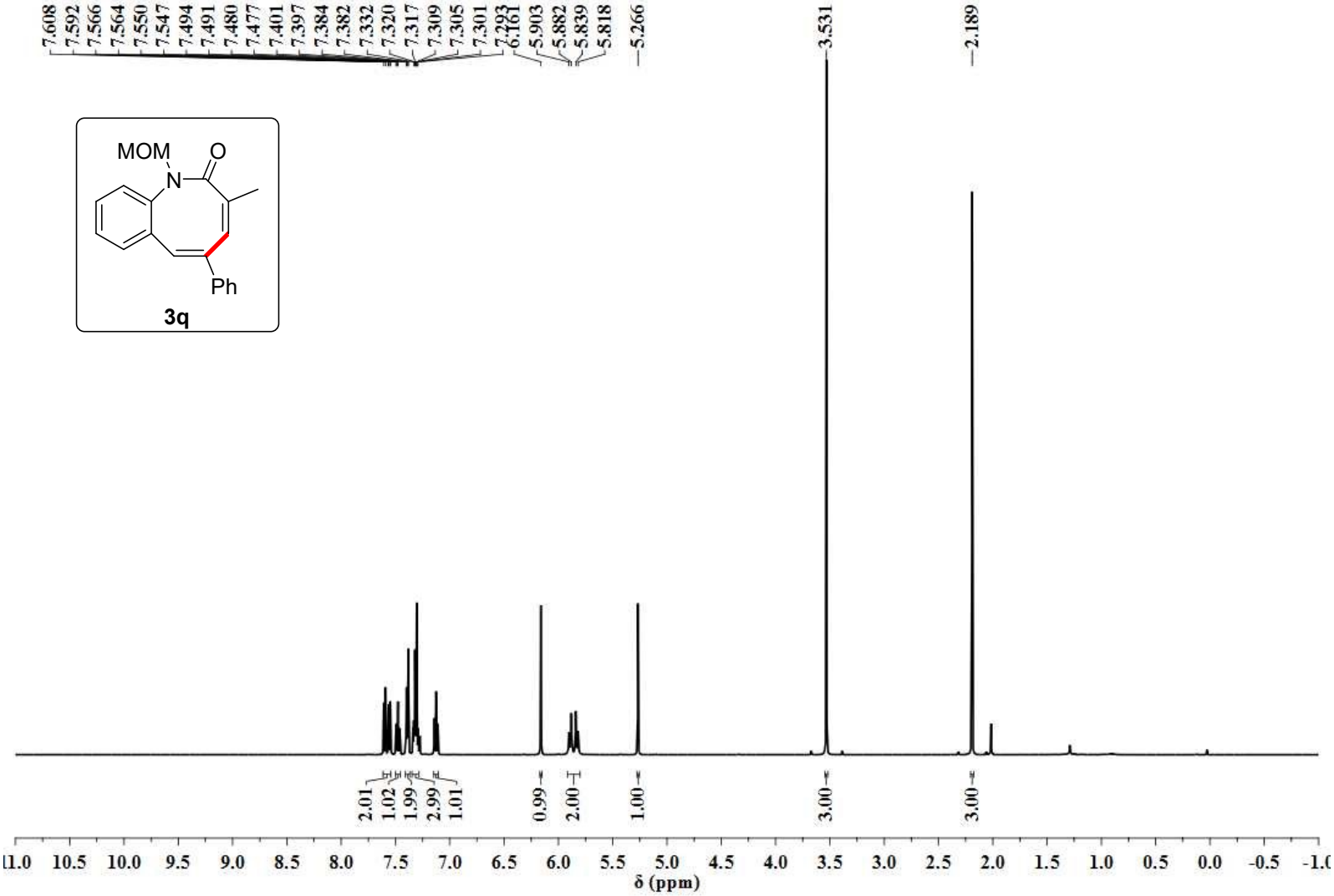
114.064
30.038
N
O
Ph
Ph
3p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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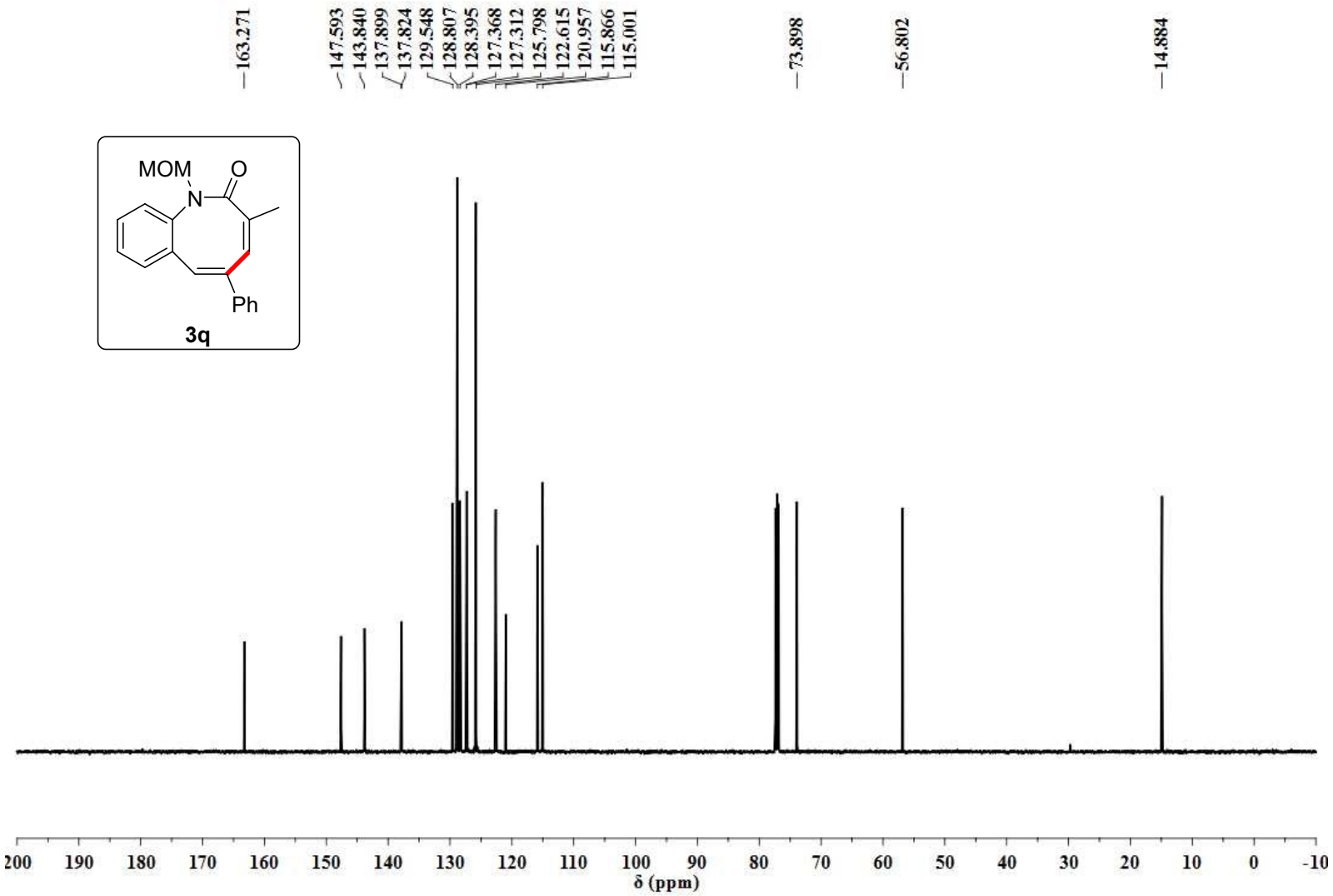
7.592
7.566
7.564
7.550
7.547
7.494
7.491
7.480
7.477
7.401
7.397
7.384
7.382
7.332
7.320
7.317
7.309
7.305
7.301
7.293
6.161
5.903
5.882
5.839
5.818
5.266
3.531
2.189
MOM
N
O
Ph
3q
2.01
1.02
1.99
2.99
1.01
0.99
2.00
1.00
3.00
3.00
δ (ppm)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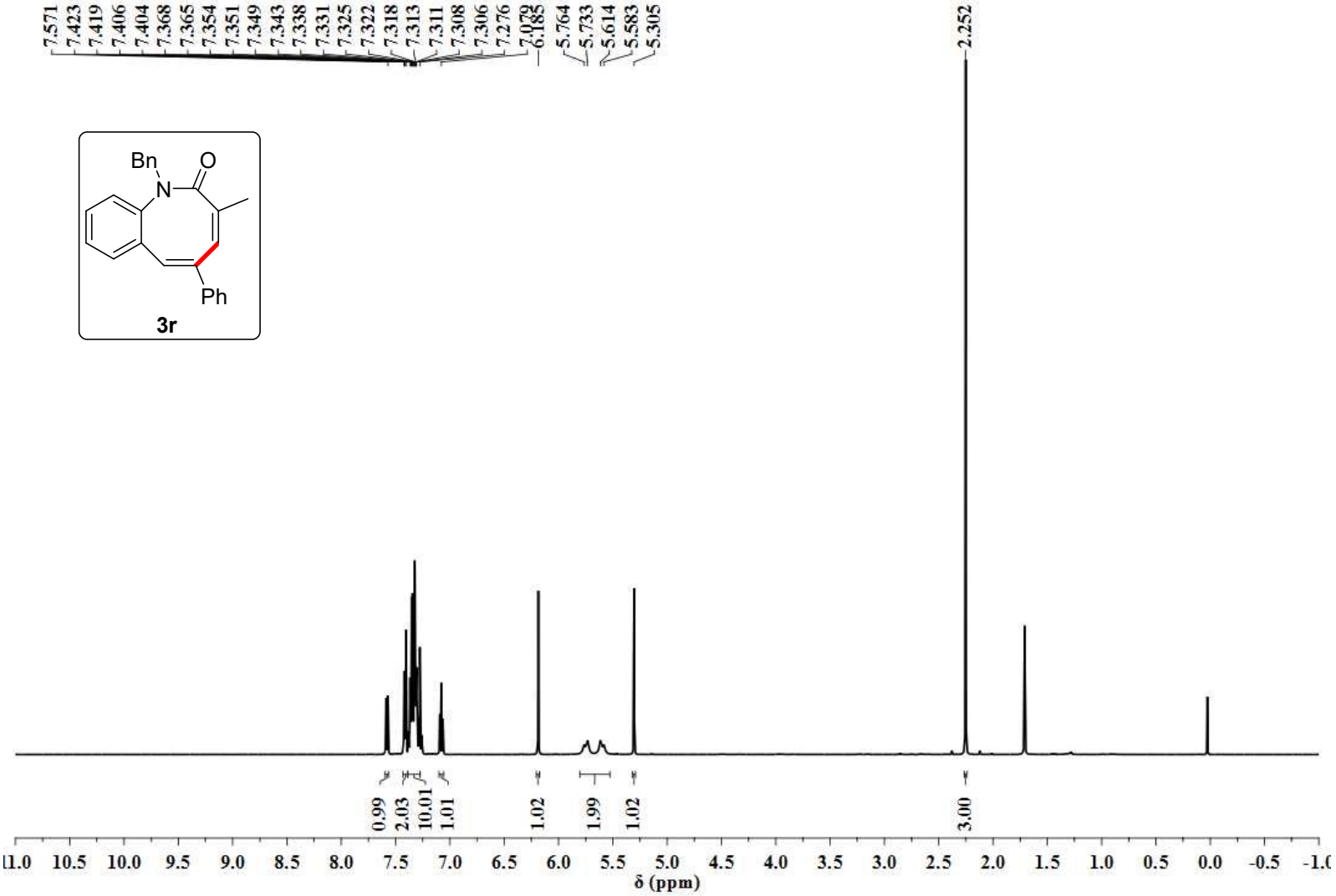
147.593
143.840
137.899
137.824
129.548
128.807
128.395
127.368
127.312
125.798
122.615
120.957
115.866
115.001
73.898
56.802
14.884
MOM
O
N
Ph
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.419
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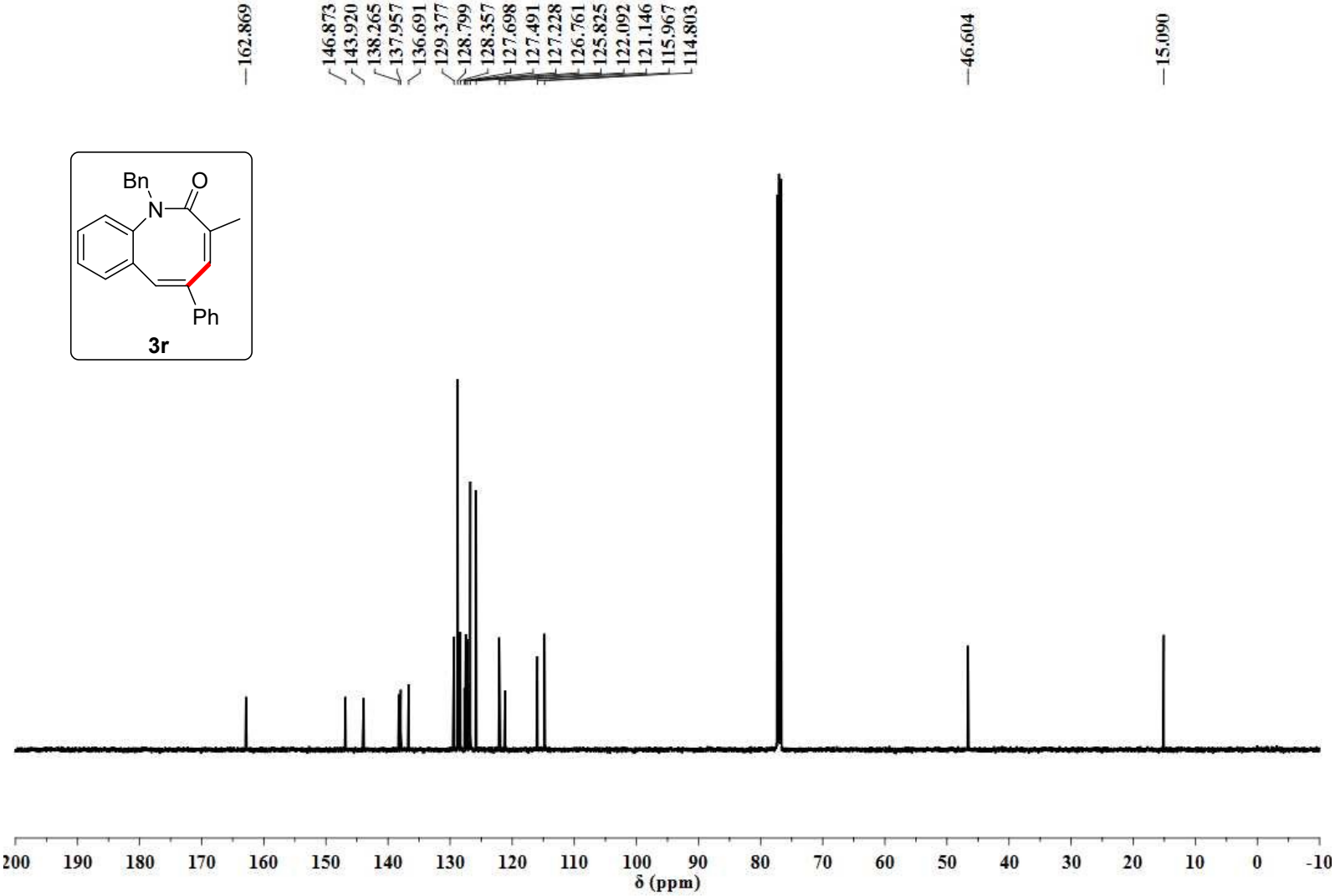
7.404
7.368
7.365
7.354
7.351
7.349
7.343
7.338
7.331
7.325
7.322
7.318
7.313
7.311
7.308
7.306
7.276
7.079
6.185
5.764
5.733
5.614
5.583
5.305
2.252
Bn
N
O
Ph
3r
0.99
2.03
10.01
1.01
1.02
1.99
1.02
3.00
δ (ppm)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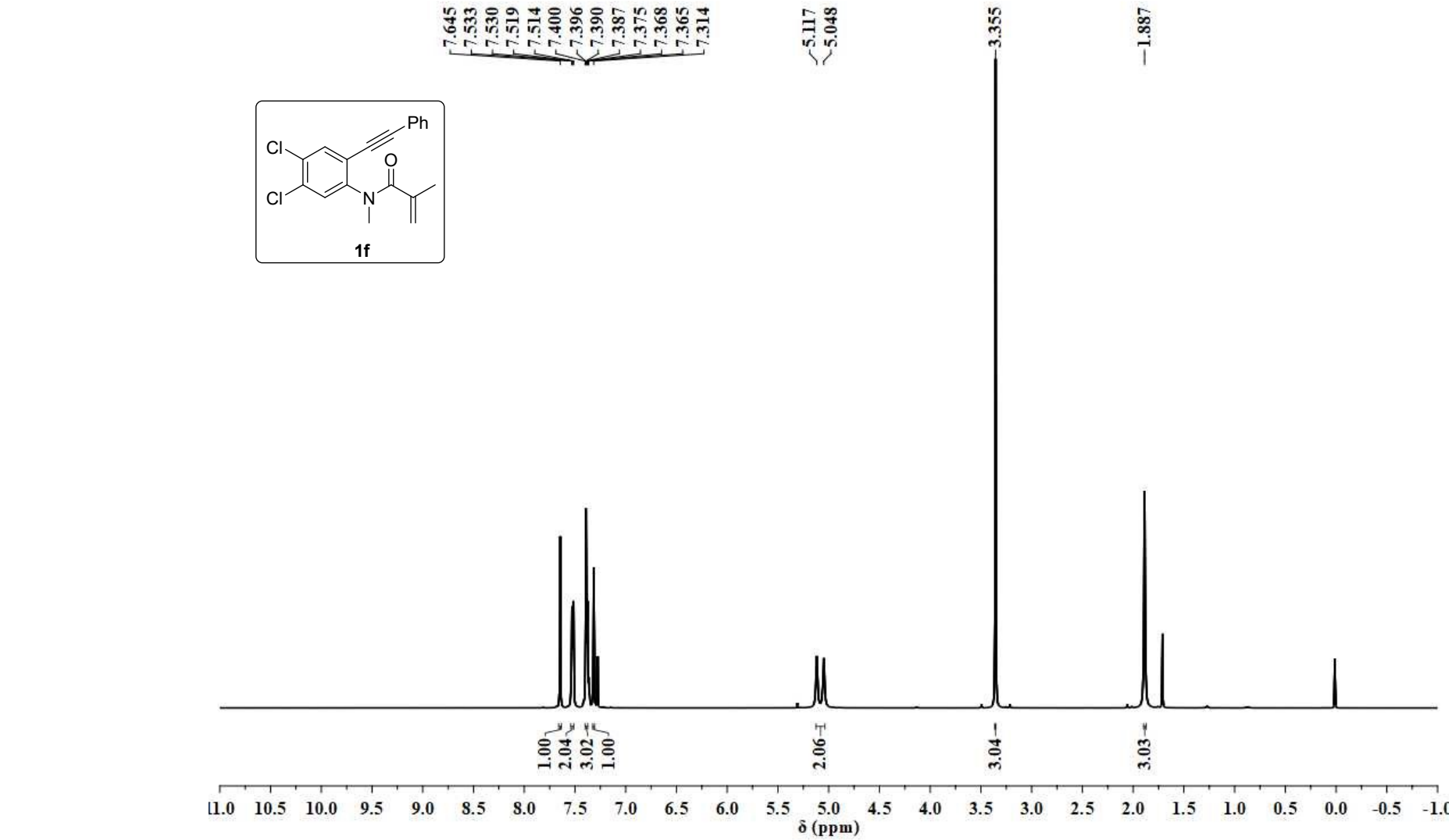
138.265
137.957
136.691
129.377
128.799
128.357
127.698
127.491
127.228
126.761
125.825
122.092
121.146
115.967
114.803
46.604
15.090
Bn
N
O
Ph
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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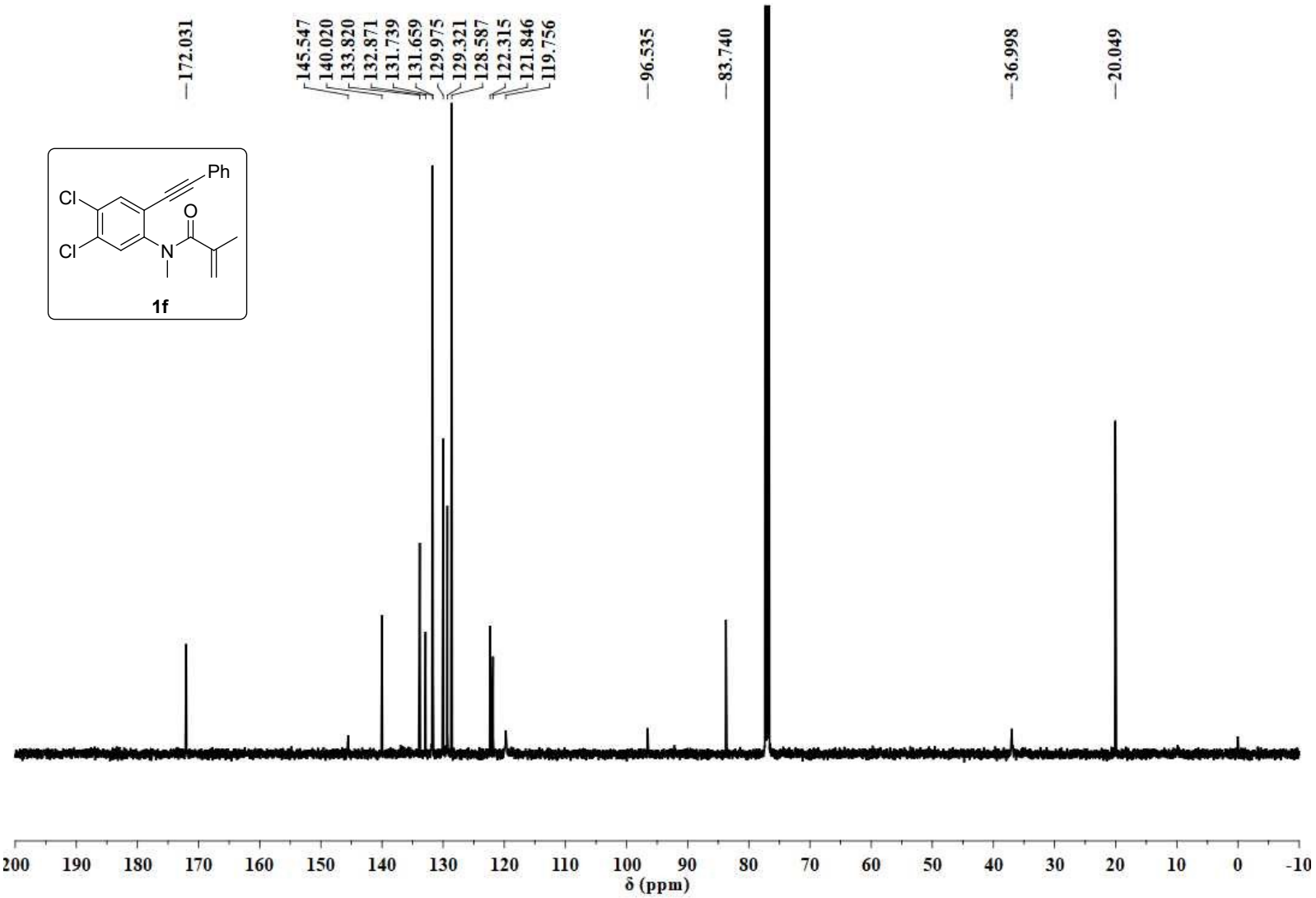
7.400
7.396
7.390
7.387
7.375
7.368
7.365
7.314
5.117
5.048
3.355
1.887
Ph
Cl
Cl
O
N
1f
1.00
2.04
3.02
1.00
2.06
3.04
3.03
δ (ppm)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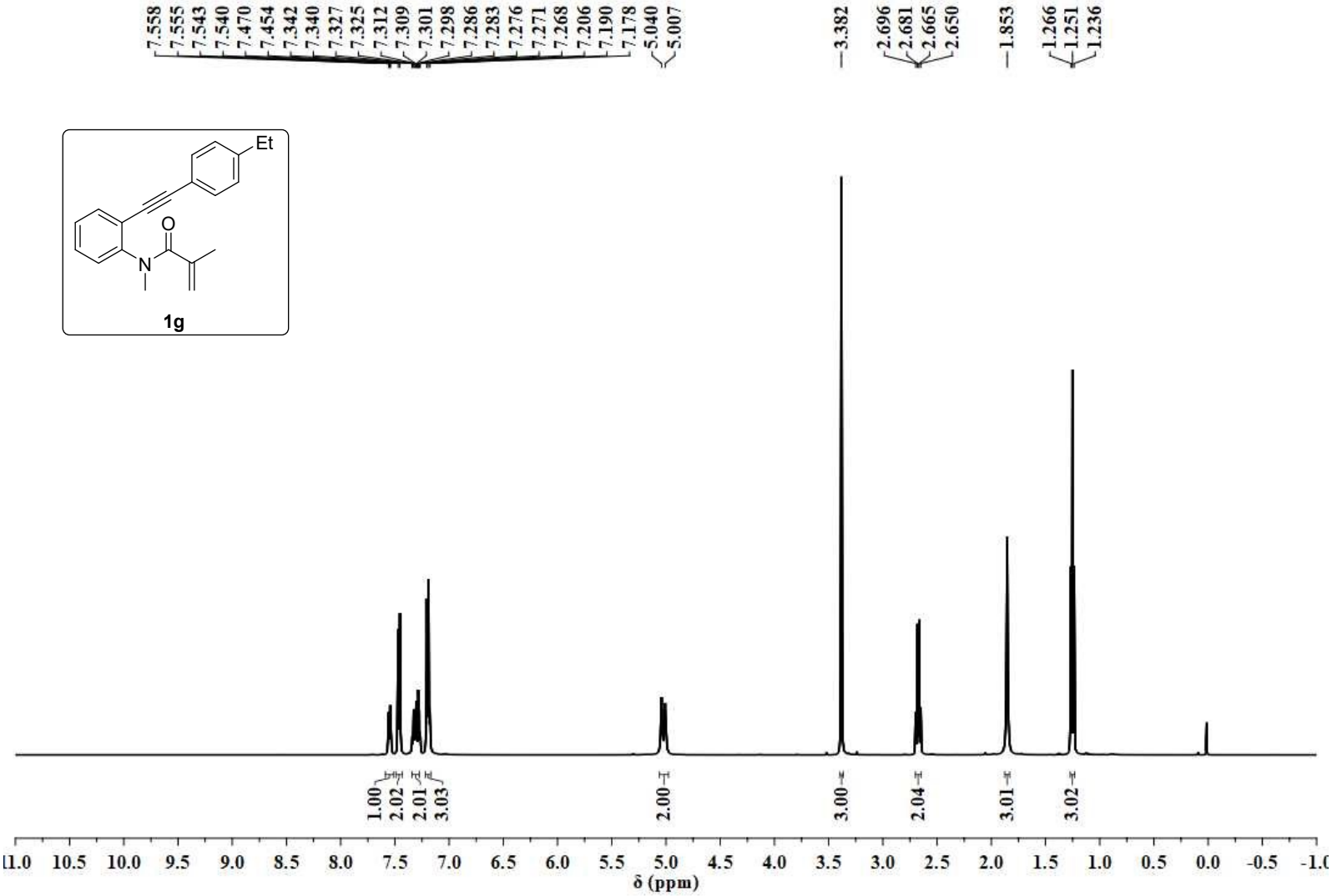
140.020
133.820
132.871
131.739
131.659
129.975
129.321
128.587
122.315
121.846
119.756
96.535
83.740
36.998
20.049
Ph
Cl
Cl
O
N
1f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.540
7.470
7.454
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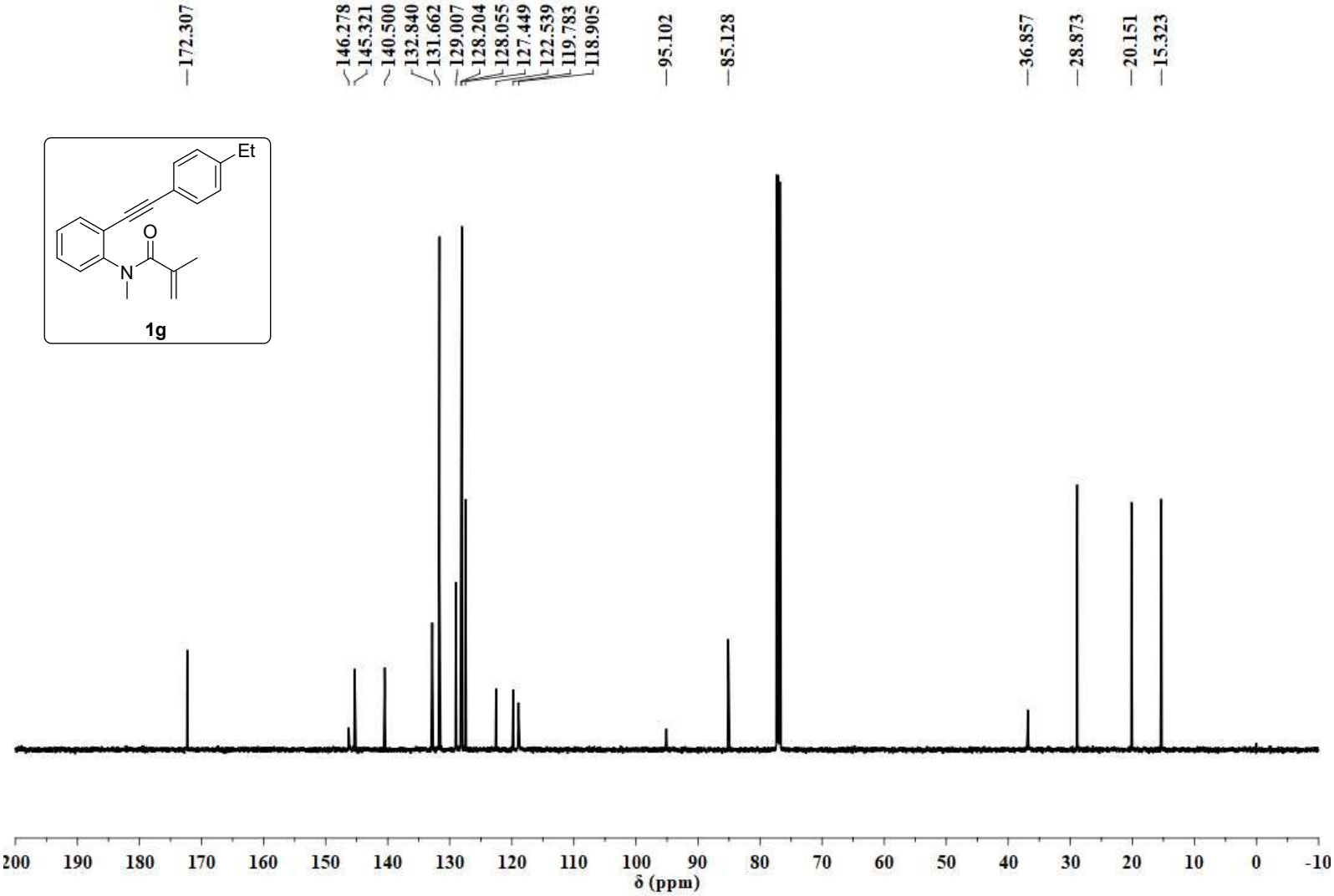
7.340
7.327
7.325
7.312
7.309
7.301
7.298
7.286
7.283
7.276
7.271
7.268
7.206
7.190
7.178
5.040
5.007
3.382
2.696
2.681
2.665
2.650
1.853
1.266
1.251
1.236
Et
O
N
1g
1.00
2.02
2.01
3.03
2.00
3.00
2.04
3.01
3.02
δ (ppm)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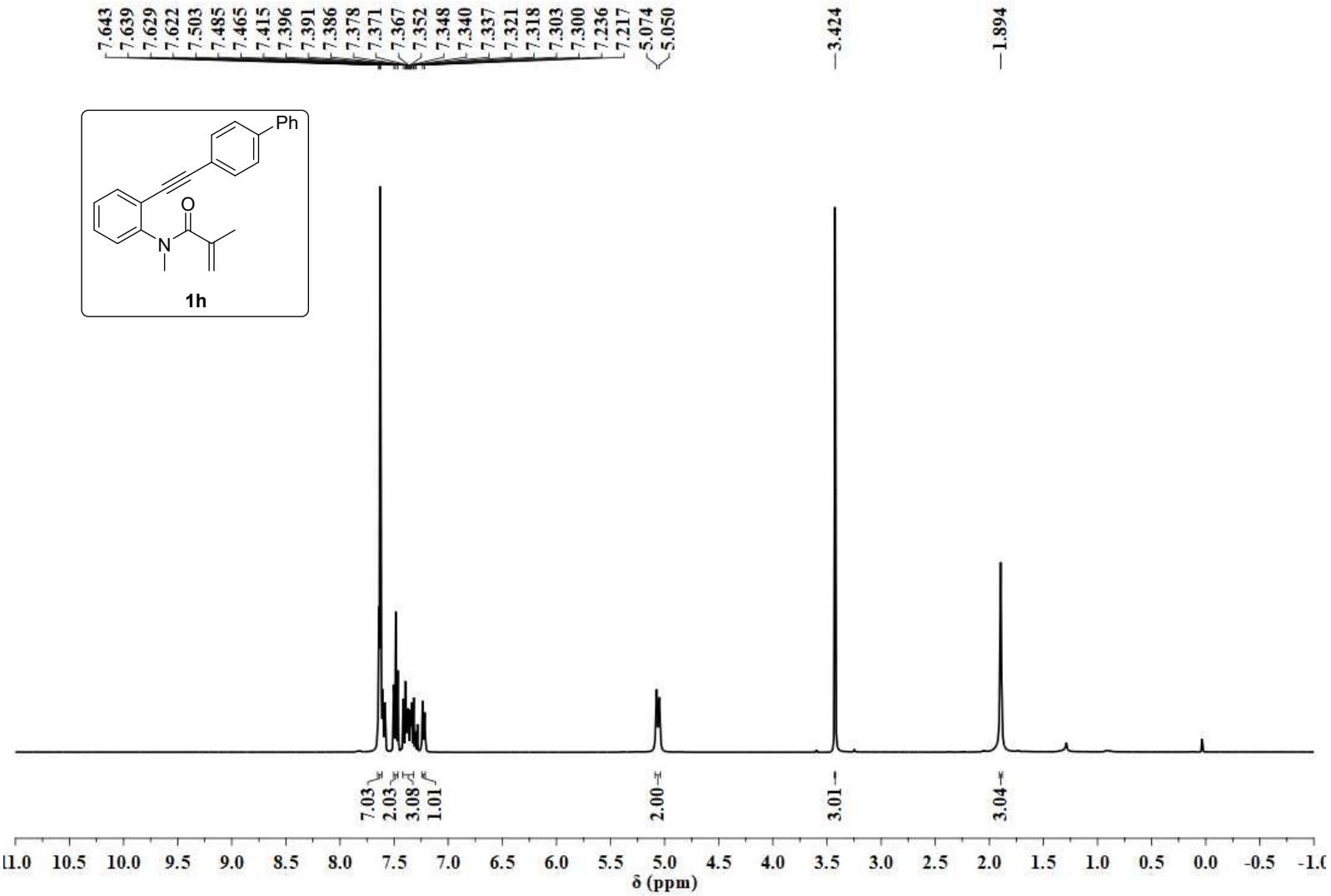
140.500
132.840
131.662
129.007
128.204
128.055
127.449
122.539
119.783
118.905
95.102
85.128
36.857
28.873
20.151
15.323
Et
O
N
1g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.629
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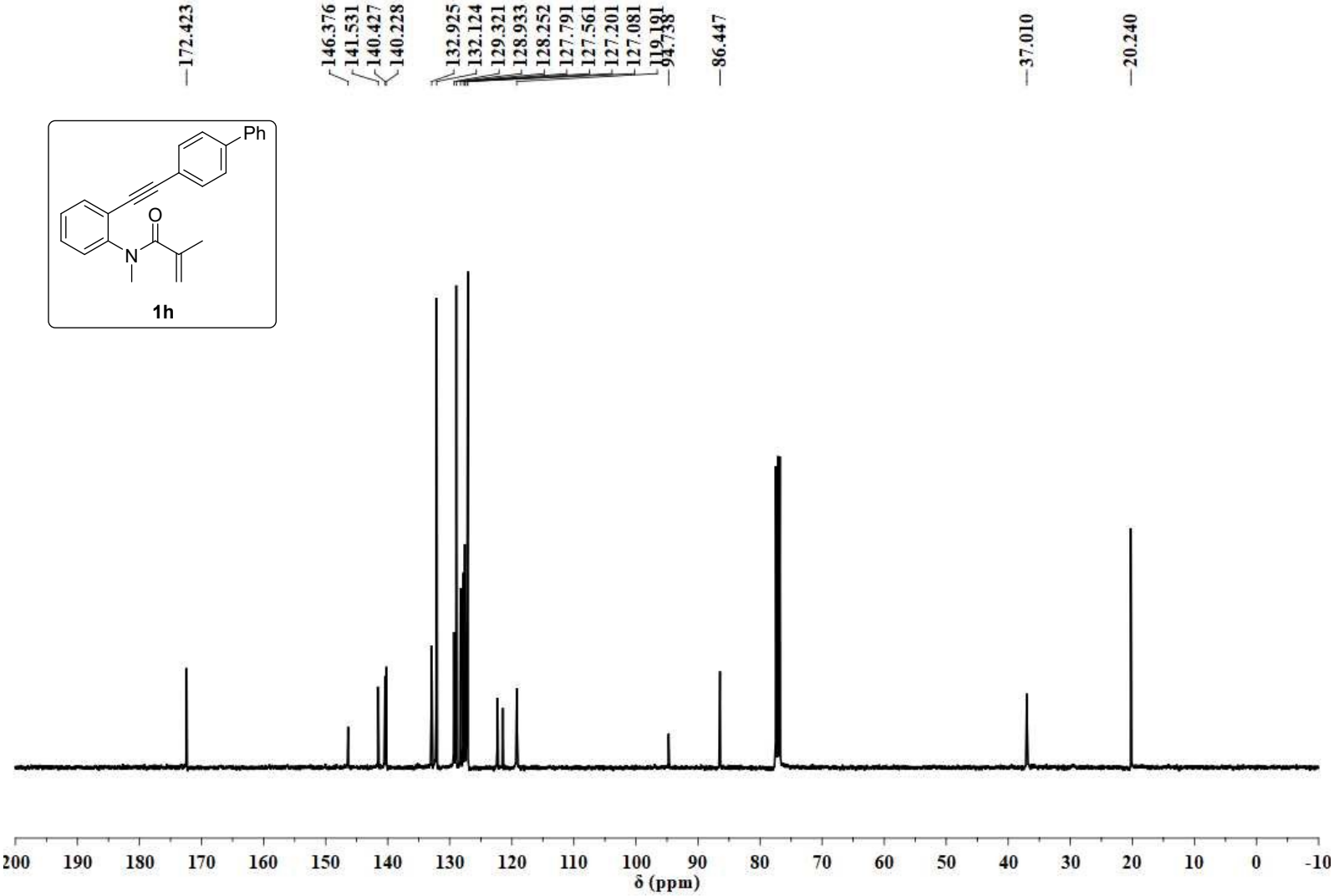
7.503
7.485
7.465
7.415
7.396
7.391
7.386
7.378
7.371
7.367
7.352
7.348
7.340
7.337
7.321
7.318
7.303
7.300
7.236
7.217
5.074
5.050
3.424
1.894
Ph
O
N
1h
7.03
2.03
3.08
1.01
2.00
3.01
3.04
δ (ppm)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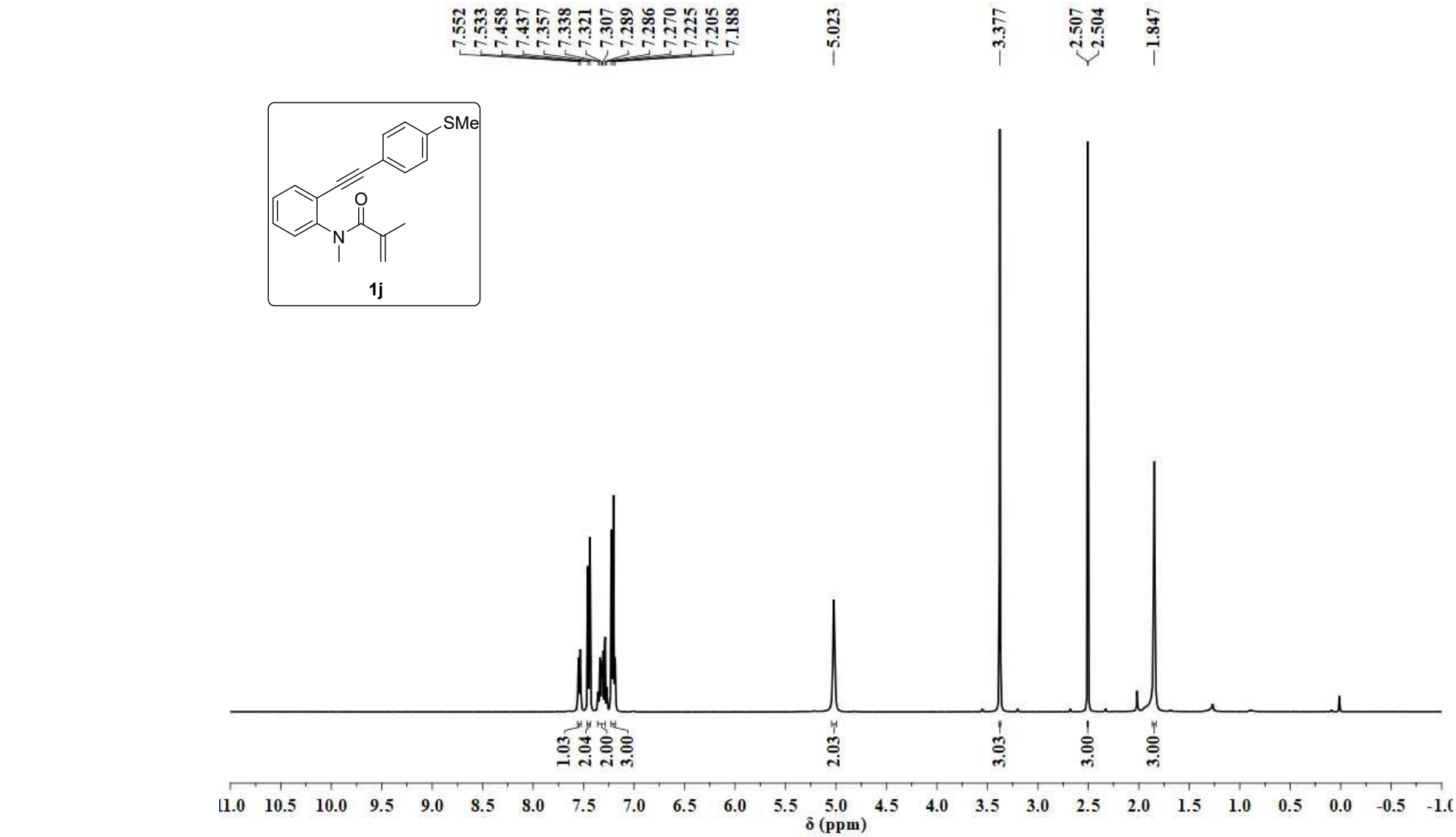
140.427
140.228
132.925
132.124
129.321
128.933
128.252
127.791
127.561
127.201
127.081
119.191
94.738
86.447
37.010
20.240
Ph
O
N
1h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.357
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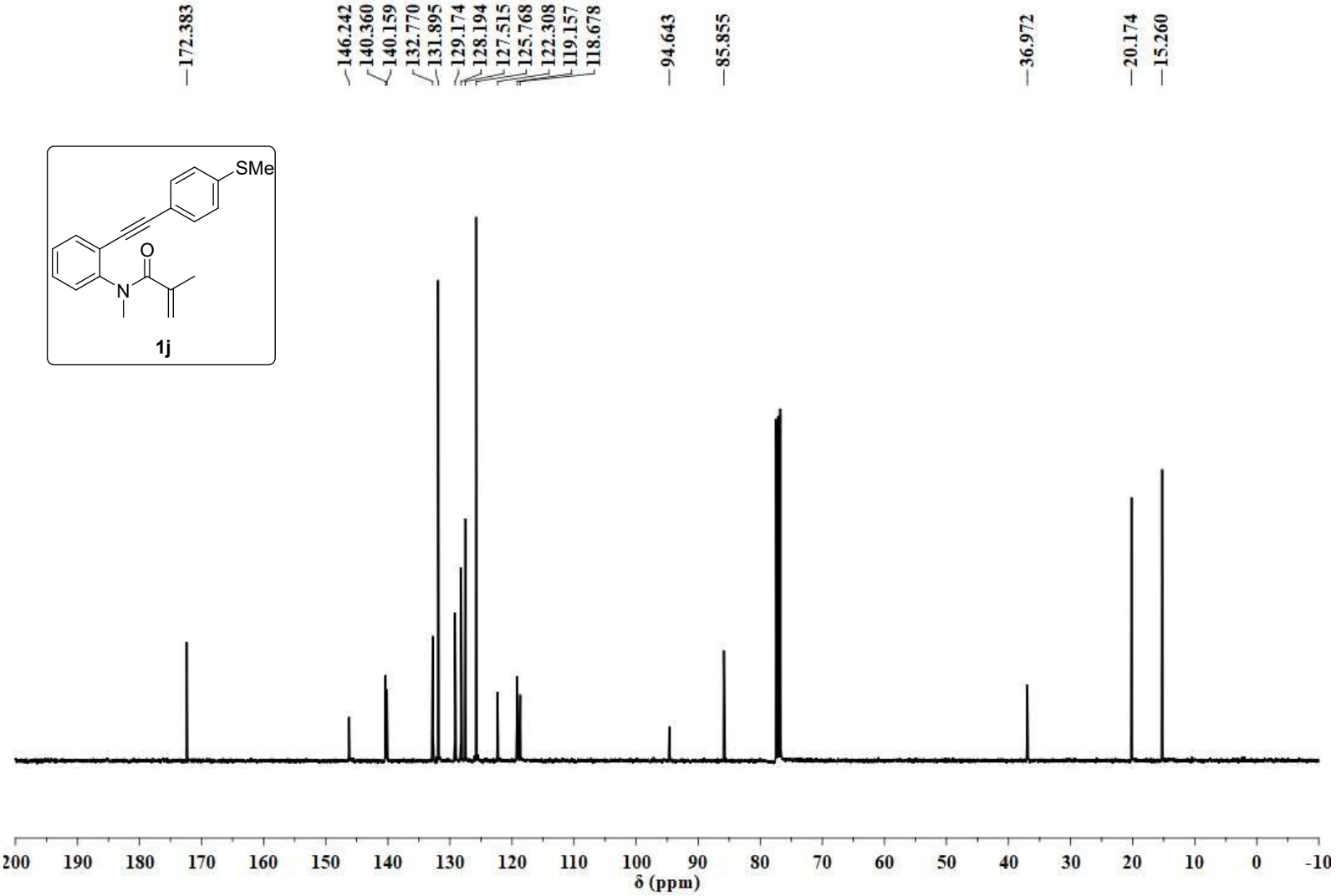
7.321
7.307
7.289
7.286
7.270
7.225
7.205
7.188
5.023
3.377
2.507
2.504
1.847
SMe
O
N
1j
1.03
2.04
2.00
3.00
2.03
3.03
3.00
3.00
δ (ppm)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128.194
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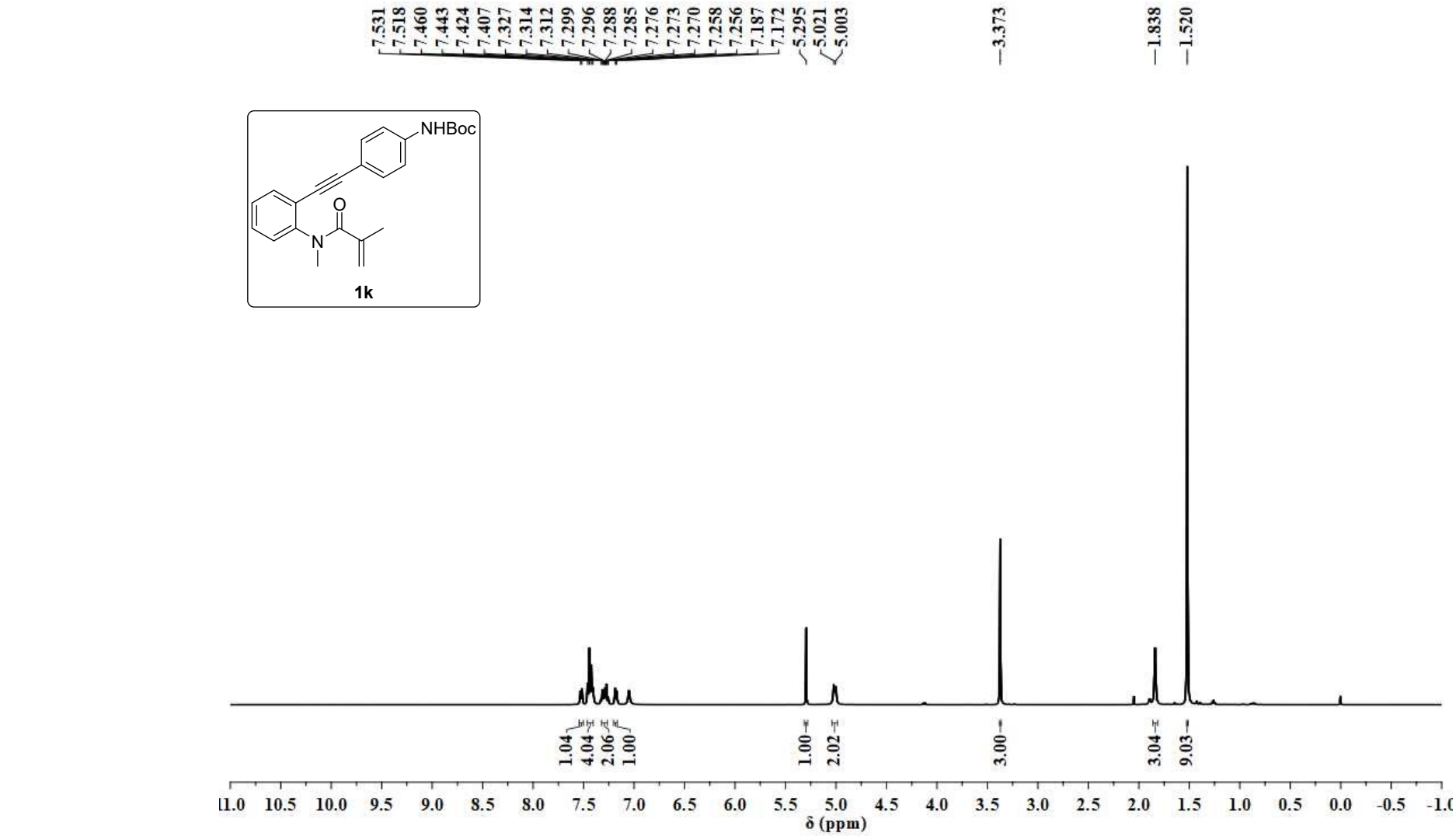
125.768
122.308
119.157
118.678
94.643
85.855
36.972
20.174
15.260
SMe
O
N
1j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.443
7.424
7.407
7.327
7.314
7.312
7.299
7.296
7.288
7.285
7.276
7.273
7.270
7.258
7.256
7.187
7.172
5.295
5.021
5.003
3.373
1.838
1.520
NHBoc
O
N
1k
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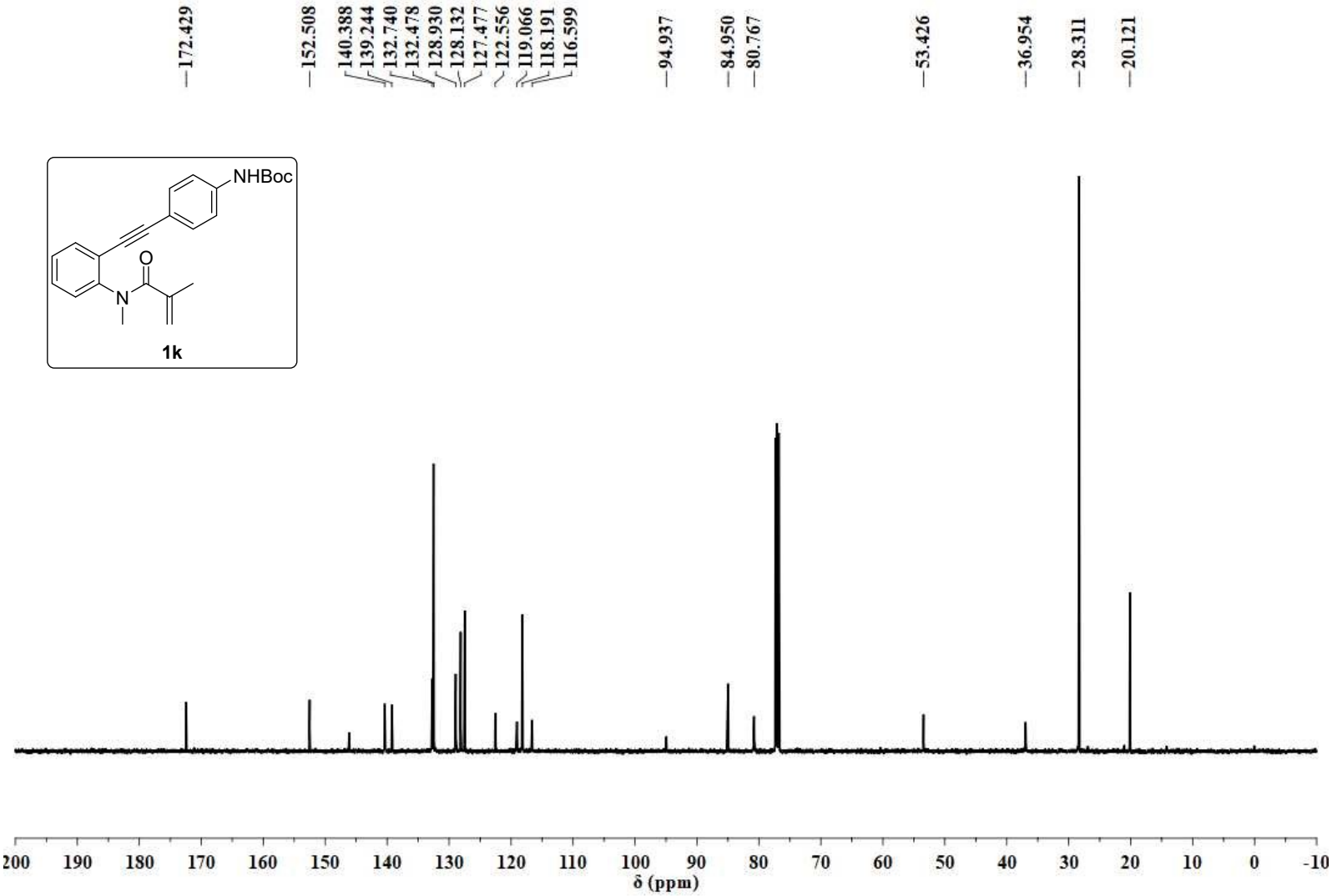
4.04
2.06
1.00
1.00
2.02
3.00
3.04
9.03
δ (ppm)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128.132
127.477
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119.066
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116.599
94.937
84.950
80.767
53.426
36.954
28.311
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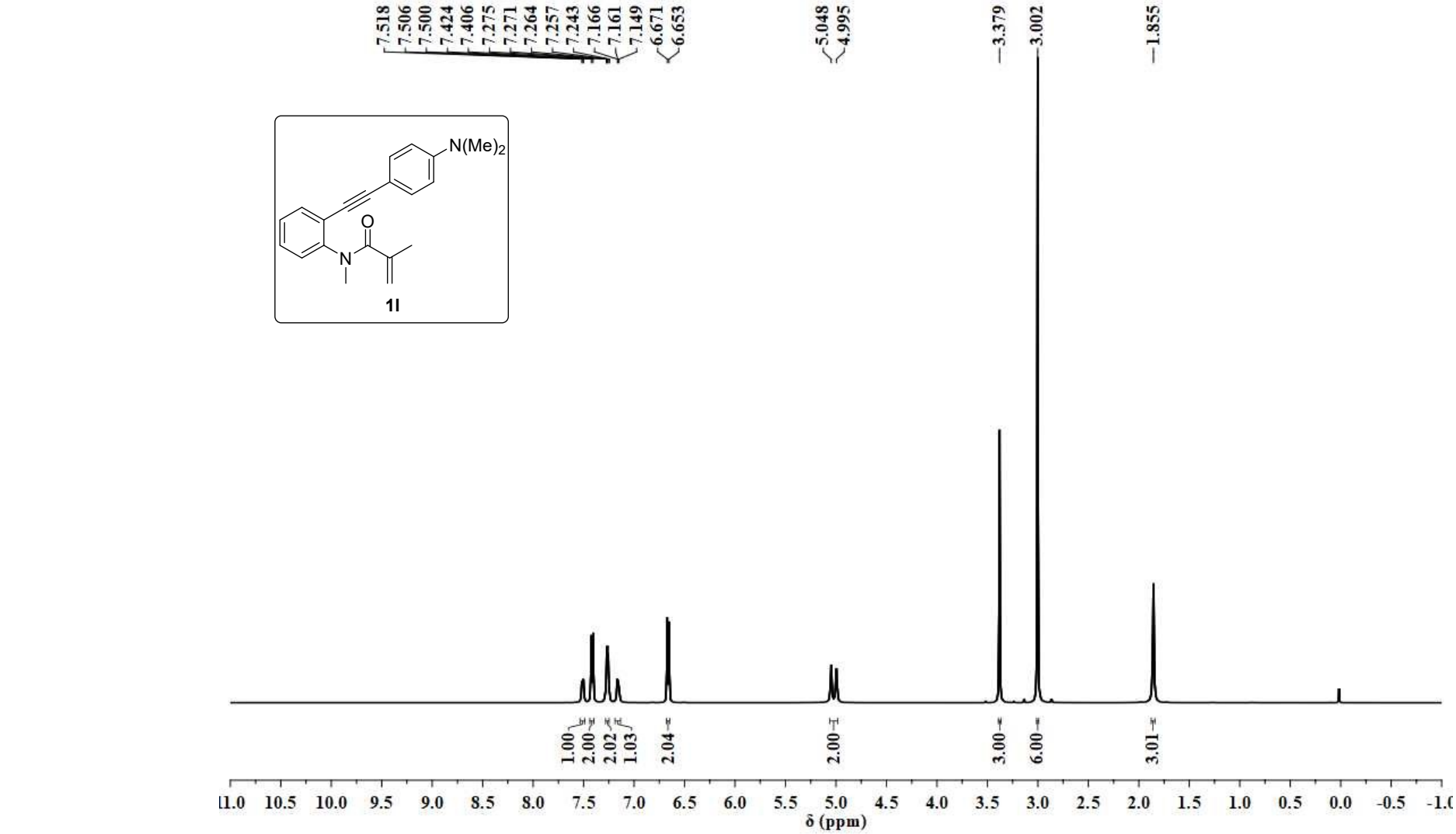
NHBoc
O
N
1k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.506
7.500
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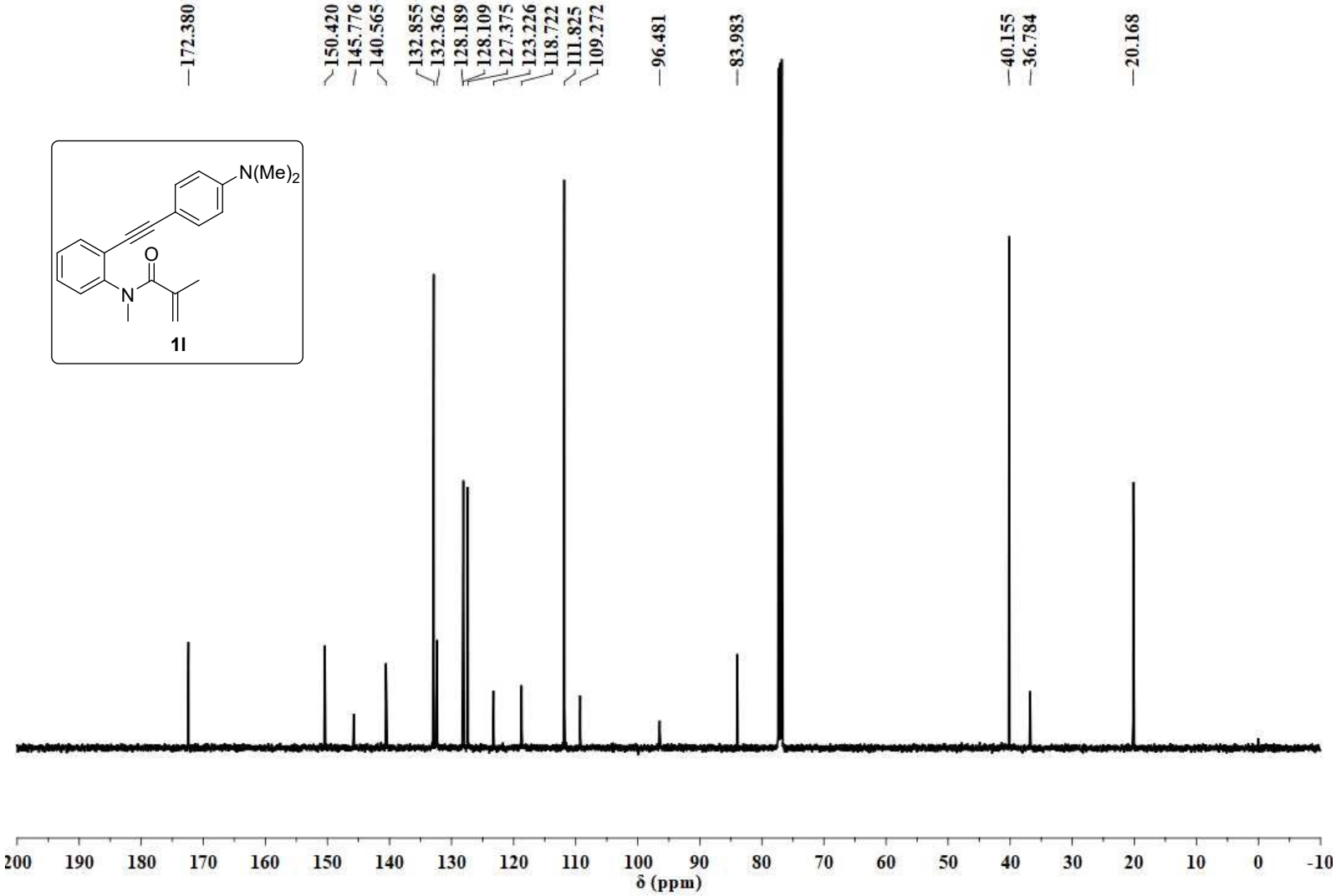
7.406
7.275
7.271
7.264
7.257
7.243
7.166
7.161
7.149
6.671
6.653
5.048
4.995
3.379
3.002
1.855
N(Me)2
O
N
1l
1.00
2.00
2.02
1.03
2.04
2.00
3.00
6.00
3.01
δ (ppm)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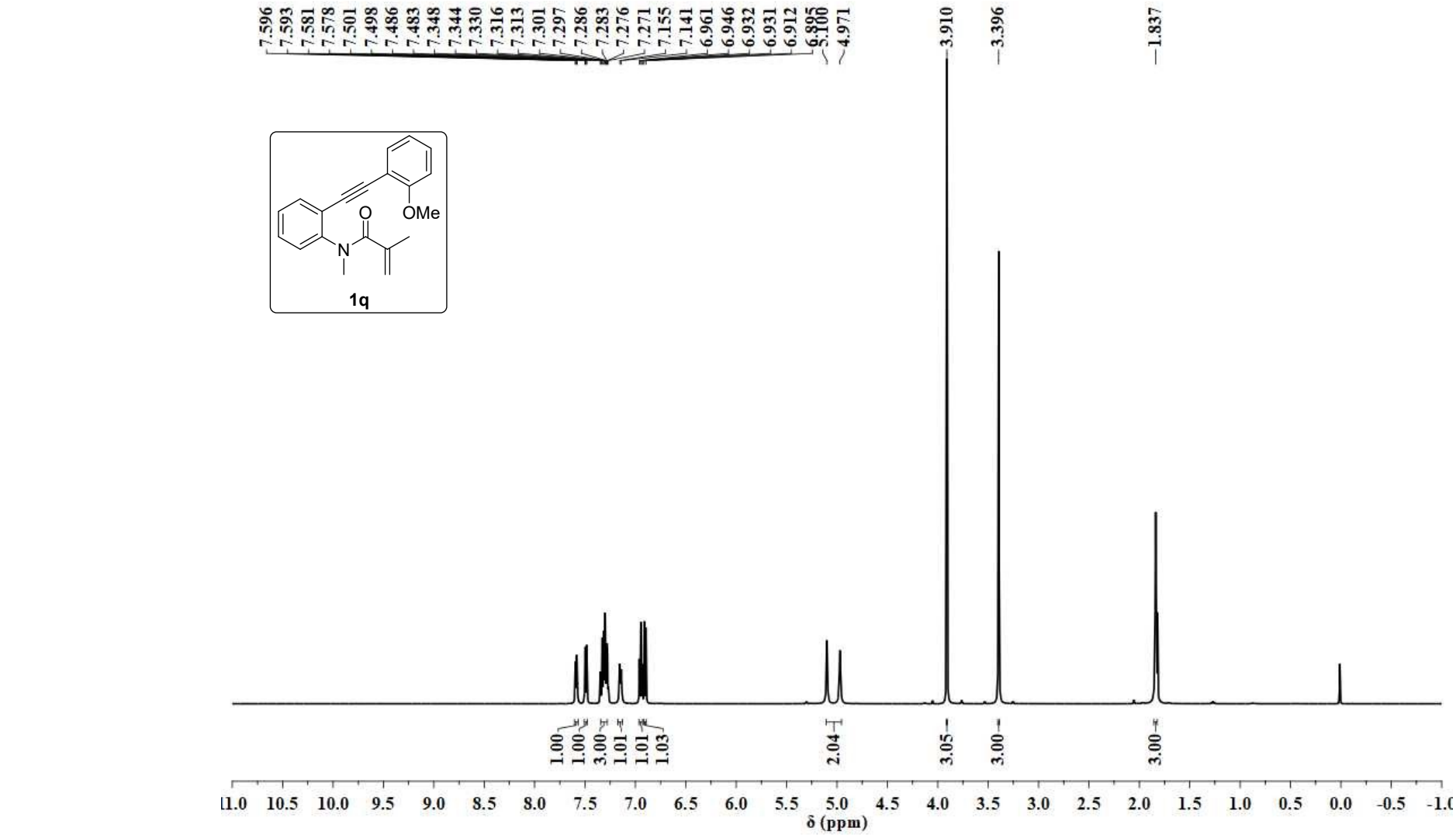
123.226
118.722
111.825
109.272
96.481
83.983
40.155
36.784
20.168
N(Me)2
O
N
1l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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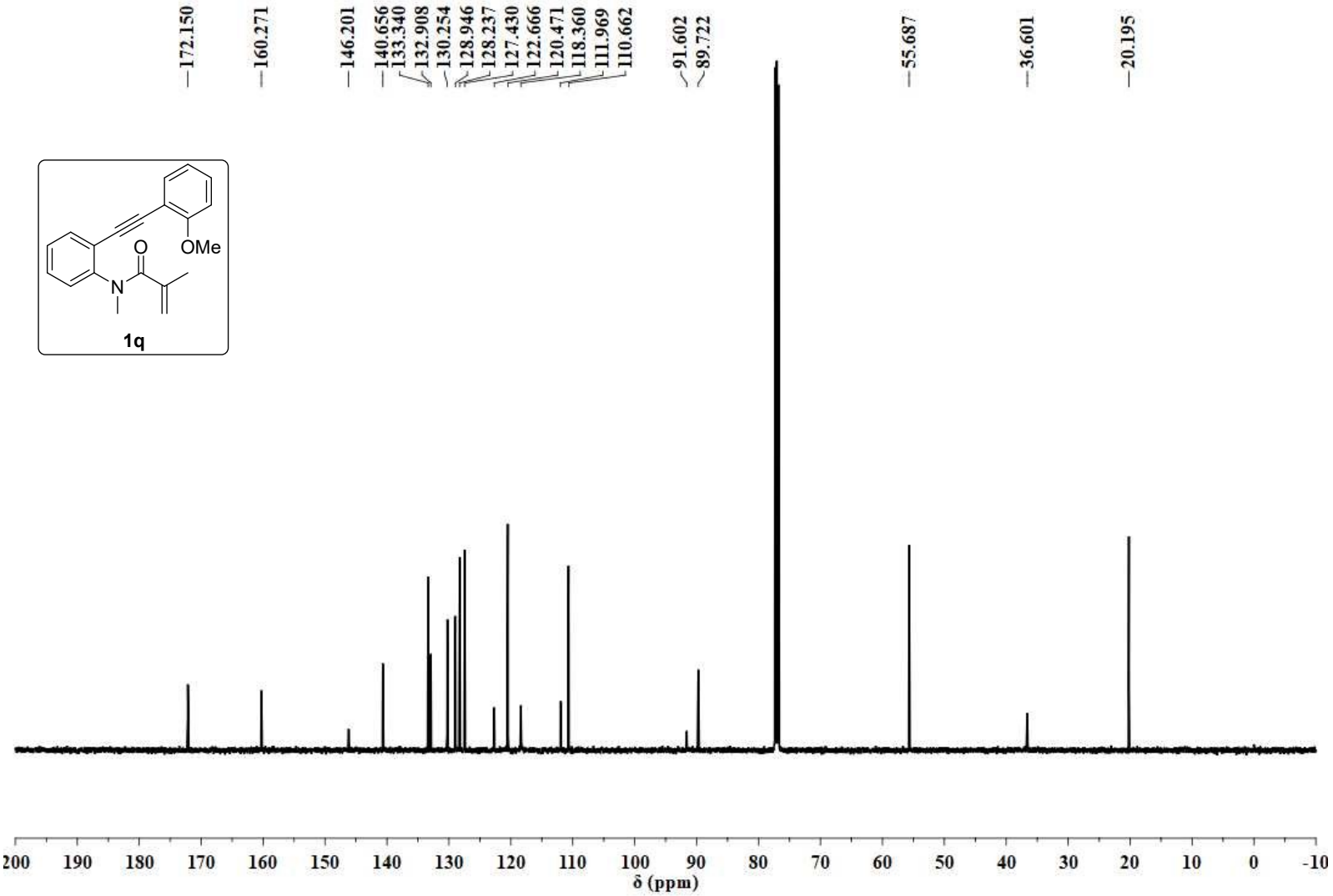
7.483
7.348
7.344
7.330
7.316
7.313
7.301
7.297
7.286
7.283
7.276
7.271
7.155
7.141
6.961
6.946
6.932
6.931
6.912
6.895
5.100
4.971
3.910
3.396
1.837
O
OMe
N
1q
1.00
1.00
3.00
1.01
1.01
1.03
2.04
3.05
3.00
3.00
δ (ppm)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130.254
128.946
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127.430
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120.471
118.360
111.969
110.662
91.602
89.722
55.687
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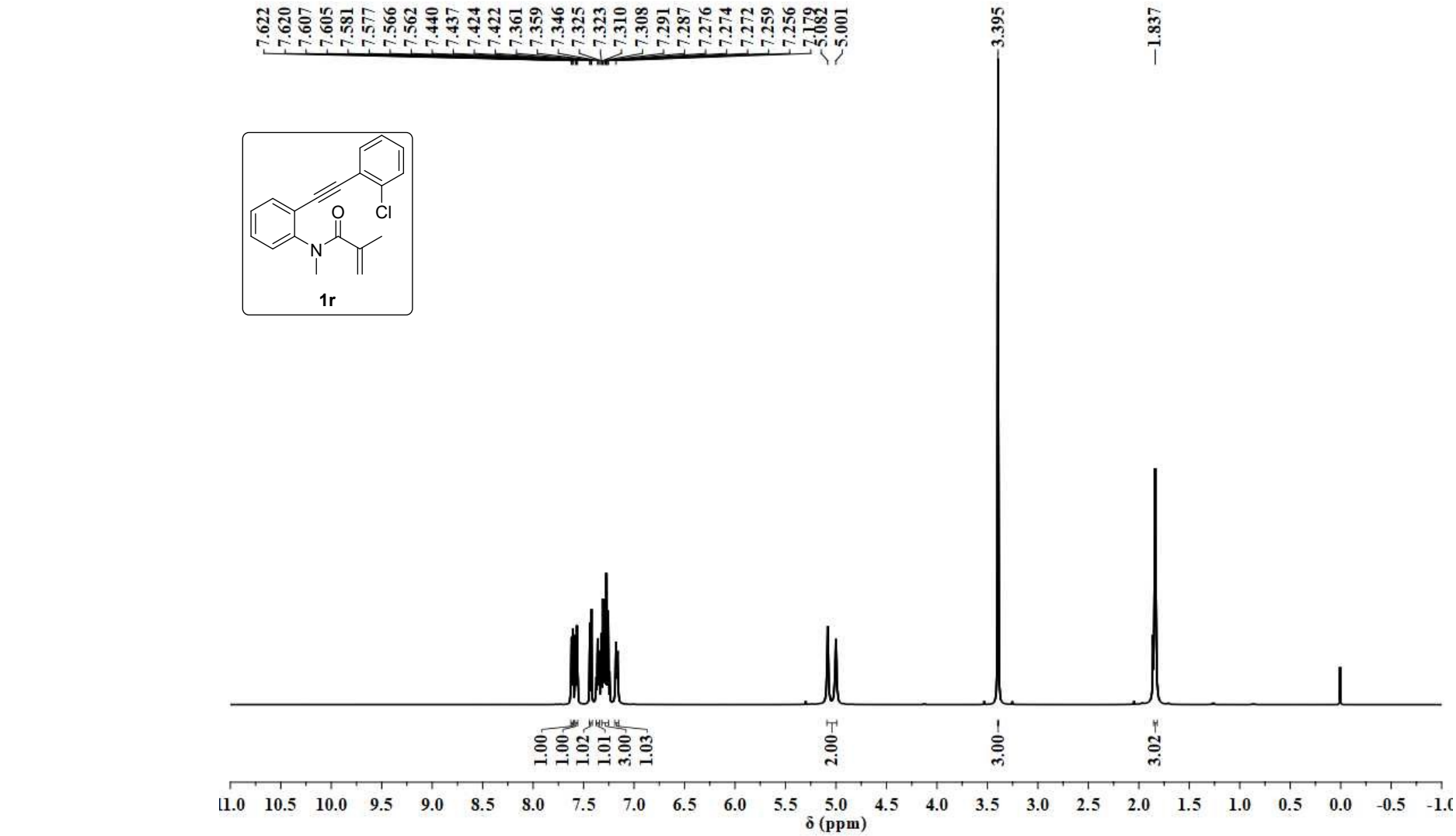
20.195
O
OMe
N
1q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.562
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7.424
7.422
7.361
7.359
7.346
7.325
7.323
7.310
7.308
7.291
7.287
7.276
7.274
7.272
7.259
7.256
7.179
5.082
5.001
3.395
1.837
O
Cl
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1r
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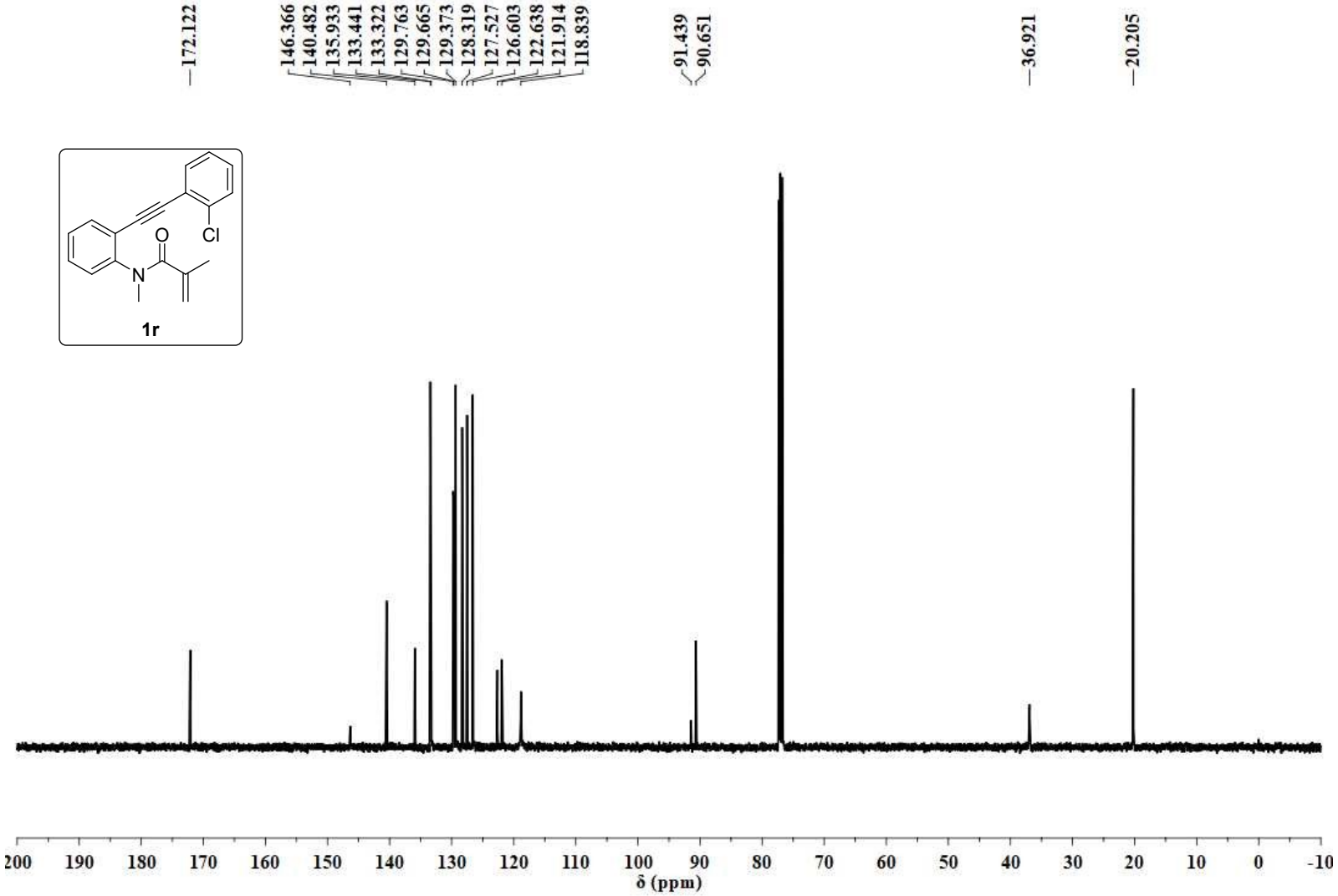
1.03
2.00
3.00
3.02
δ (ppm)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129.665
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128.319
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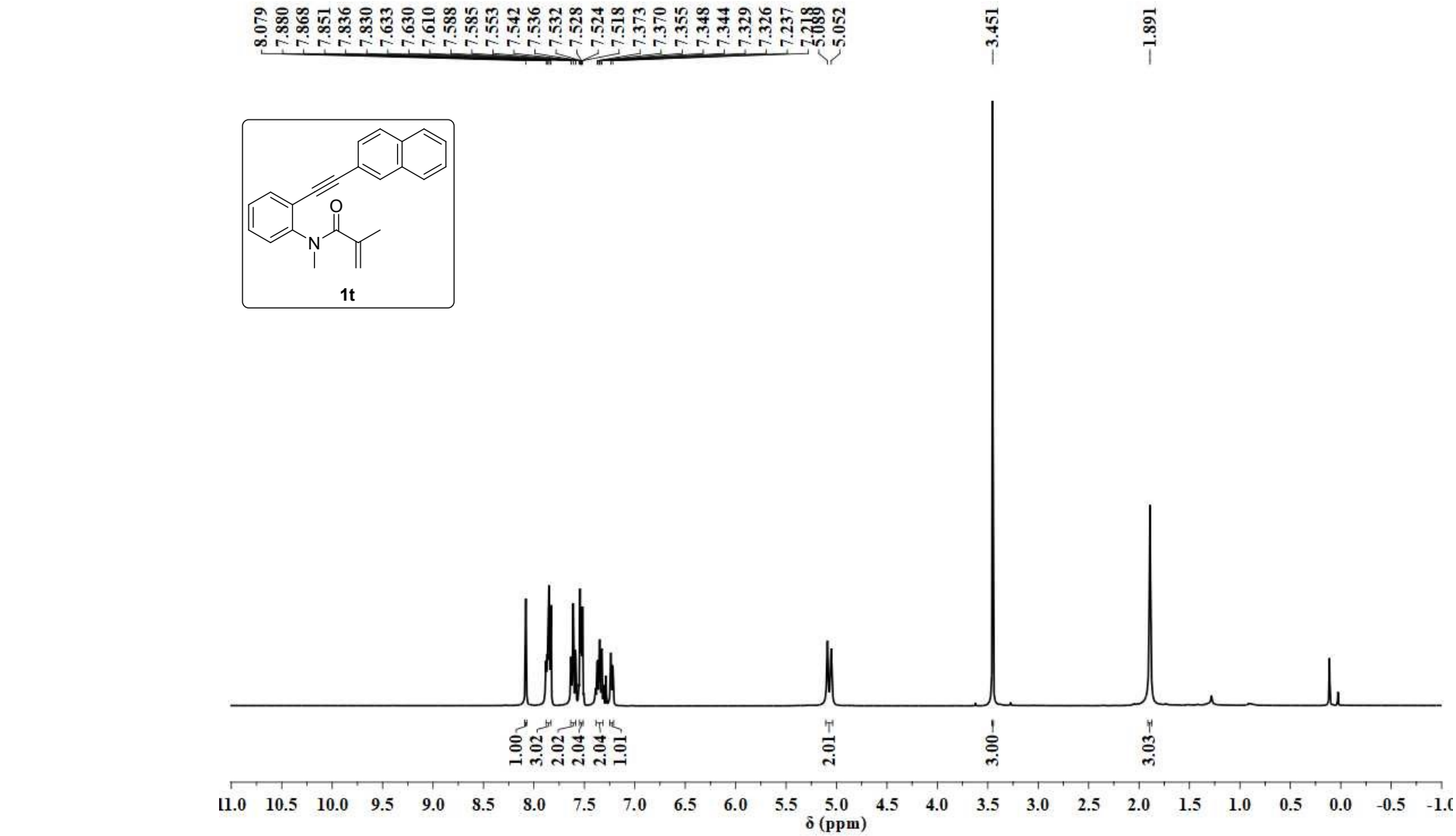
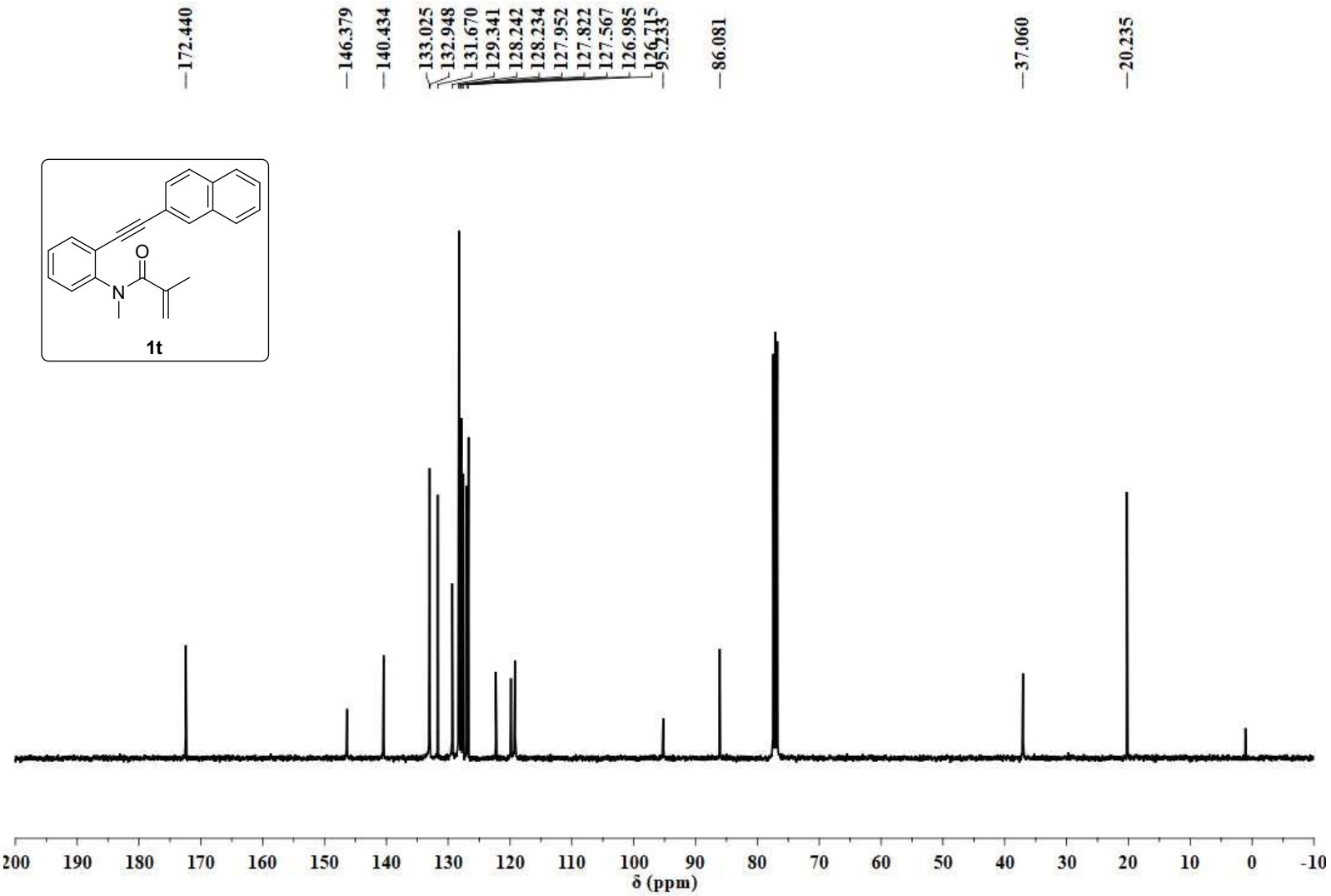
122.638
121.914
118.839
91.439
90.651
36.921
20.205
O
Cl
N
1r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


8.079
7.880
7.868
7.851
7.836
7.830
7.633
7.630
7.610
7.588
7.585
7.553
7.542
7.536
7.532
7.528
7.524
7.518
7.373
7.370
7.355
7.348
7.344
7.329
7.326
7.237
7.218
5.089
5.052
3.451
1.891
O
N
1t
1.00
3.02
2.02
2.04
2.04
1.01
2.01
3.00
3.03
δ (ppm)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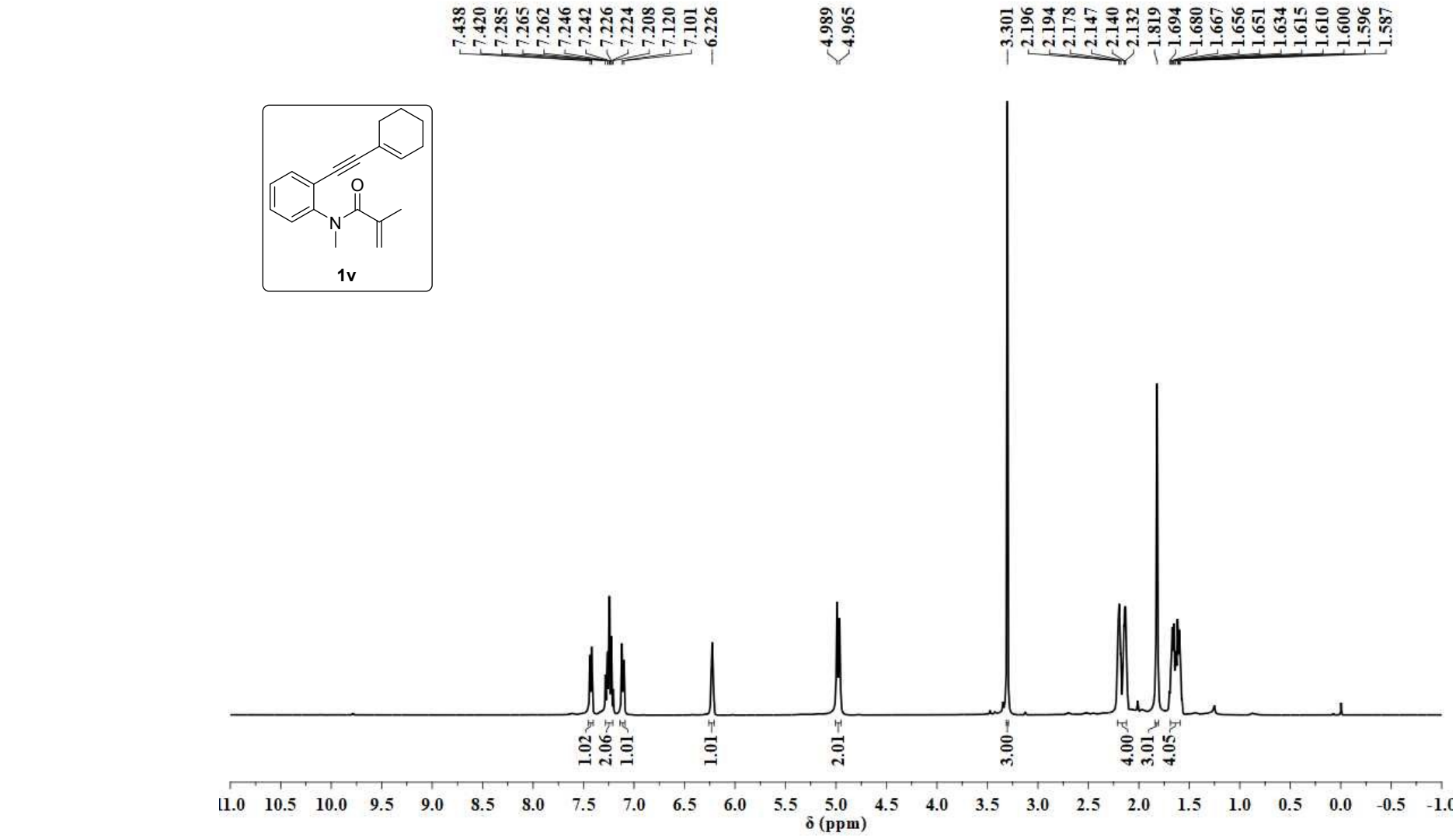
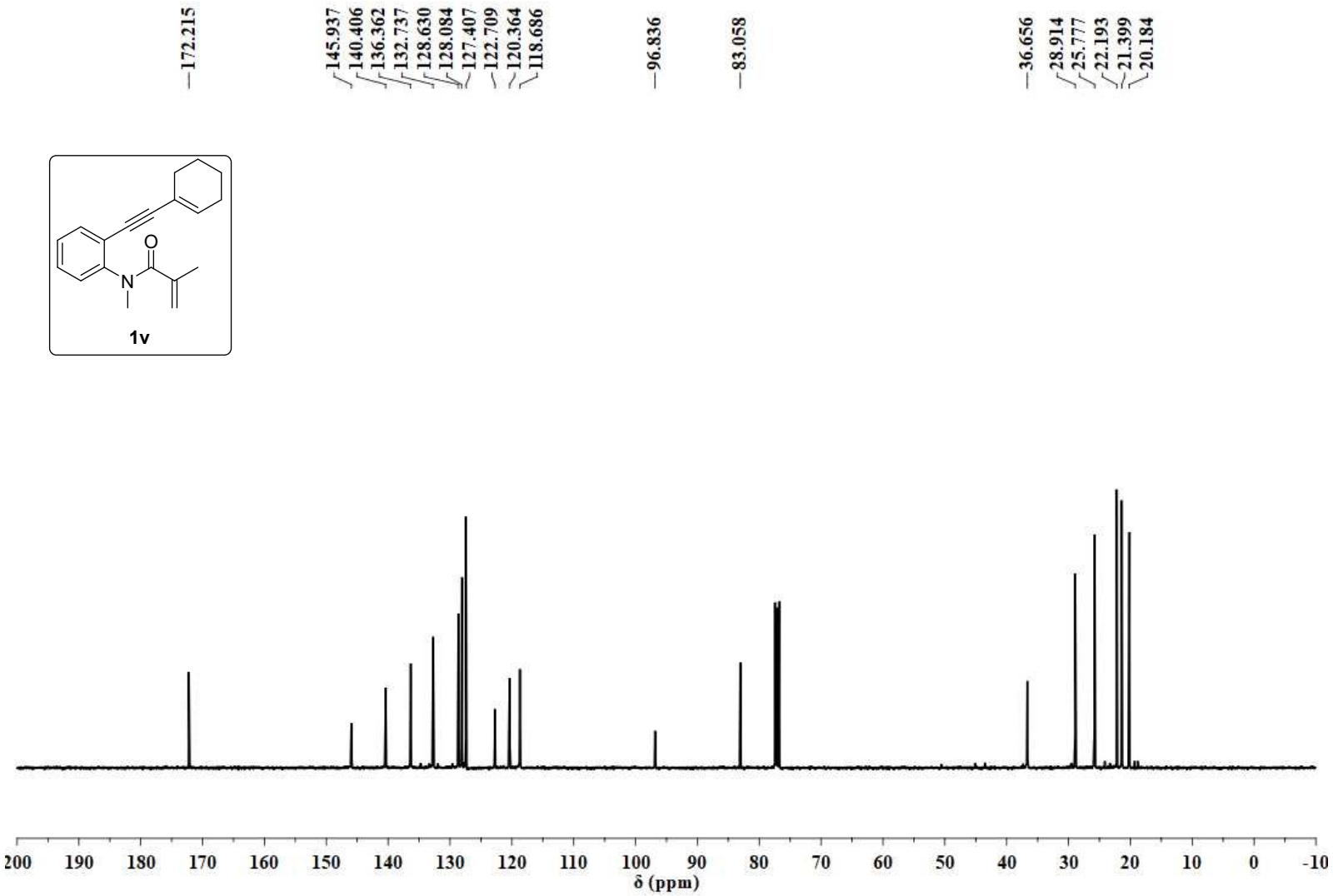
146.379
140.434
133.025
132.948
131.670
129.341
128.242
128.234
127.952
127.822
127.567
126.985
126.715
95.233
86.081
37.060
20.235
O
N
1t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.438
7.420
7.285
7.265
7.262
7.246
7.242
7.226
7.224
7.208
7.120
7.101
6.226
4.989
4.965
3.301
2.196
2.194
2.178
2.147
2.140
2.132
1.819
1.694
1.680
1.667
1.656
1.651
1.634
1.615
1.610
1.600
1.596
1.587
O
N
1v
1.02
2.06
1.01
1.01
2.01
3.00
4.00
3.01
4.05
δ (ppm)


172.215
145.937
140.406
136.362
132.737
128.630
128.084
127.407
122.709
120.364
118.686
96.836
83.058
36.656
28.914
25.777
22.193
21.399
20.184
O
N
1v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)