Supporting Information for:

Intramolecular Oxycyanation of Alkenes by Cooperative Pd/BPh_3 Catalysis

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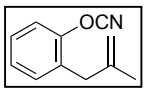
General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon or nitrogen atmosphere. Medium pressure chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

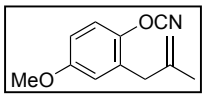
Apparatus. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer or a Varian Mercury 300 (^{1}H NMR, 300 MHz; ^{13}C NMR, 75.4 MHz) spectrometer with Me_4Si or solvent resonance as the internal standard (^{1}H NMR, Me_4Si at 0 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.16 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a Thermo Scientific Exactive (APCI, ESI). Elemental analyses were performed by Elemental Analysis Center of Kyoto University. Medium pressure liquid chromatography (MPLC) was performed with a SHOKO Scientific Purif-espoir 2 chromatograph using hexane–ethyl acetate with gradient as an eluent. GC analysis was performed on a Shimadzu GC 2014 equipped with an ENV-1 column (Kanto Chemical, 0.25 mm x 30 m, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier.

Chemicals. Unless otherwise noted, commercially available chemicals were used without further purification. Anhydrous hexane, diethyl ether, and THF were purchased from Kanto Chemical and degassed by purging vigorously with argon for 30 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[1] $Pd[P(o\text{-tol})_3]_2$ was prepared according to the literature procedure.[2]

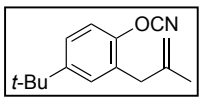
Preparation of 1. *Caution! All operations must be carried out in a well-ventilated fume food because cyanogen bromide is highly toxic and can generate hydrogen cyanide upon hydrolysis. A general procedure*. The respective phenol derivative (1.00 equiv) prepared according to the literature procedures[3] was dissolved in a mixture of anhydrous hexane and diethyl ether (5:2) under an argon atmosphere. The solution was cooled to 0 °C, and cyanogen bromide (1.20 equiv.) was added in one portion. Subsequently, triethylamine (1.20 equiv) was added dropwise to the resulting reaction mixture. The reaction mixture was maintained at 0 °C for 3 h. The precipitate was filtered through a pad of Celite and washed with hexane for several times. The solvent was removed by rotary evaporation and the crude product was pure enough to be used for the catalytic reaction without further purification.



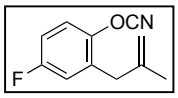
1-Cyanato-2-(2-methylallyl)benzene (1a). The procedure on a 10 mmol-scale gave **1a** (1.73 g, quant.) as a pale yellow oil, R_f 0.63 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (s, 3H), 3.34 (s, 2H), 4.60 (s, 1H), 4.84 (s, 1H), 7.24–7.27 (m, 2H), 7.33 (dd, J = 6.2, 3.3 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 37.4, 109.0, 112.6, 114.5, 126.8, 128.0, 128.3, 131.9, 142.6, 151.3; HRMS (APCI) Calcd for $C_{11}H_{12}NO$: $[M+H]^+$, 174.0913. Found: *m/z* 174.0906.



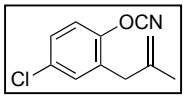
1-Cyanato-4-methoxy-2-(2-methylallyl)benzene (1b). The procedure on a 20 mmol-scale gave **1b** (2.5 g, 61%) as a colorless oil, R_f 0.54 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72 (s, 3H), 3.31 (s, 2H), 3.80 (s, 3H), 4.65 (s, 1H), 4.86 (s, 1H), 6.72–6.82 (m, 2H), 7.35 (d, J = 9.3 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2, 37.6, 55.6, 109.6, 112.5, 112.8, 115.8, 116.9, 129.3, 142.4, 145.4, 157.8; HRMS (APCI) Calcd for $C_{12}H_{14}NO_2$: $[M+H]^+$, 204.1019. Found: *m/z* 204.1009.



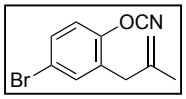
4-(*tert*-Butyl)-1-cyanato-2-(2-methylallyl)benzene (1c). The procedure on a 51 mmol-scale gave **1c** (10.4 g, 89%) as a colorless oil, R_f 0.62 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.73 (s, 3H), 3.33 (s, 2H), 4.60 (s, 1H), 4.84 (s, 1H), 7.24–7.25 (m, 1H), 7.31–7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 31.2, 34.4, 37.6, 109.2, 112.4, 114.0, 125.0, 127.1, 128.9, 142.7, 149.2, 149.9; HRMS (APCI) Calcd for $C_{15}H_{20}NO$: $[M+H]^+$, 230.1539. Found: *m/z* 230.1528.



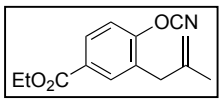
1-Cyanato-4-fluoro-2-(2-methylallyl)benzene (1d). The procedure on a 5.0 mmol-scale gave **1d** (0.94 g, 98%) as a pale yellow oil, R_f 0.59 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (s, 3H), 3.33 (s, 2H), 4.66 (s, 1H), 4.90 (s, 1H), 6.97–7.06 (m, 2H), 7.43 (dd, J = 8.9, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 37.5, 109.0, 113.4, 114.9 (d, J = 25 Hz), 116.3 (d, J = 10 Hz), 118.2 (d, J = 25 Hz), 130.6 (d, J = 10 Hz), 141.8, 147.2, 160.6 (d, J = 250 Hz); HRMS (APCI) Calcd for $C_{11}H_{11}FNO$: $[M+H]^+$, 192.0819. Found: *m/z* 192.0817.



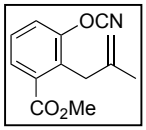
4-Chloro-1-cyanato-2-(2-methylallyl)benzene (1e). The procedure on a 5.0 mmol-scale gave **1e** (1.02 g, 99%) as a yellowish oil, R_f 0.63 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72 (s, 3H), 3.31 (s, 2H), 4.64 (s, 1H), 4.89 (s, 1H), 7.25–7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 37.3, 108.6, 113.4, 116.0, 128.2, 130.0, 131.6, 132.3, 141.8, 149.8; HRMS (APCI) Calcd for $C_{11}H_{11}ClNO$: $[M+H]^+$, 208.0524. Found: *m/z* 208.0522.



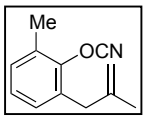
4-Bromo-1-cyanato-2-(2-methylallyl)benzene (1f). The procedure on a 5.0 mmol-scale gave **1f** (1.25 g, 99%) as a pale yellow oil, R_f 0.64 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72 (s, 3H), 3.31 (s, 2H), 4.64 (s, 1H), 4.89 (s, 1H), 7.33–7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 37.2, 108.5, 113.4, 116.3, 119.9, 130.3, 131.2, 134.6, 141.8, 150.4; HRMS (APCI) Calcd for $C_{11}H_{11}BrNO$: $[M+H]^+$, 252.0019. Found: *m/z* 252.0015.



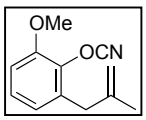
Ethyl 4-cyanato-3-(2-methylallyl)benzoate (1g). The procedure on a 25 mmol-scale gave **1g** (5.7 g, 93%) as a colorless oil, R_f 0.34 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (t, *J* = 6.9 Hz, 3H), 1.73 (s, 3H), 3.38 (s, 2H), 4.39 (q, *J* = 6.9 Hz, 2H), 4.60 (s, 1H), 4.87 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 2.5 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.4, 37.4, 61.5, 108.2, 113.1, 114.4, 128.3, 129.2, 130.0, 133.5, 142.0, 154.1, 165.1; HRMS (APCI) Calcd for $C_{14}H_{14}NO_3$: $[M–H]^–$, 244.0979. Found: *m/z* 244.0975.



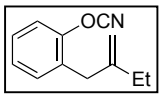
Methyl 3-cyanato-2-(2-methylallyl)benzoate (1h). The procedure on a 3.9 mmol-scale gave **1h** (0.71 g, 78%) as a colorless solid, R_f 0.39 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 3.73 (s, 2H), 3.88 (s, 3H), 4.22 (s, 1H), 4.75 (s, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 33.3, 52.5, 108.7, 110.8, 117.8, 127.8, 128.9, 129.7, 133.3, 143.1, 151.9, 166.5; HRMS (APCI) Calcd for $C_{13}H_{12}NO_3$: $[M–H]^–$, 230.0823. Found: *m/z* 230.0819.



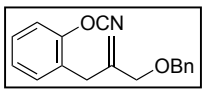
2-Cyanato-1-methyl-3-(2-methylallyl)benzene (1i). The procedure on a 3.0 mmol-scale gave **1i** (0.55 g, 97%) as a yellowish oil, R_f 0.55 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, 3H), 2.45 (s, 3H), 3.44 (s, 2H), 4.68 (s, 1H), 4.90 (s, 1H), 7.10–7.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 22.3, 38.1, 110.4, 113.0, 127.8, 129.0, 129.5, 130.4, 130.7, 142.6, 151.2; HRMS (APCI) Calcd for $C_{12}H_{14}NO$: $[M+H]^+$, 188.1070. Found: *m/z* 188.1067.



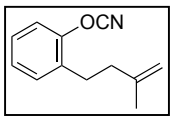
2-Cyanato-1-methoxy-3-(2-methylallyl)benzene (1j). The procedure on a 4.0 mmol-scale gave **1j** (0.82 g, quant.) as a colorless oil, R_f 0.38 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (s, 3H), 3.39 (s, 2H), 3.96 (s, 3H), 4.67 (s, 1H), 4.88 (s, 1H), 6.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.18–7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 37.9, 56.3, 110.4, 111.2, 112.8, 122.5, 127.8, 131.6, 141.0, 142.6, 150.1; HRMS (APCI) Calcd for $C_{12}H_{14}NO_2$: $[M+H]^+$, 204.1019. Found: *m/z* 204.1010.



1-Cyanato-2-(2-methylenbutyl)benzene (1k). The procedure on a 3.0 mmol-scale gave **1k** (0.49 g, 86%) as a colorless oil, R_f 0.52 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.4 Hz, 3H), 1.99–2.06 (m, 2H), 3.37 (s, 2H), 4.59 (s, 1H), 4.86 (s, 1H), 7.22–7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 28.6, 36.1, 109.0, 110.4, 114.6, 126.8, 128.2, 128.3, 132.0, 148.3, 151.4; HRMS (APCI) Calcd for $C_{12}H_{12}NO$: $[M–H]^–$, 186.0924. Found: *m/z* 186.0922.



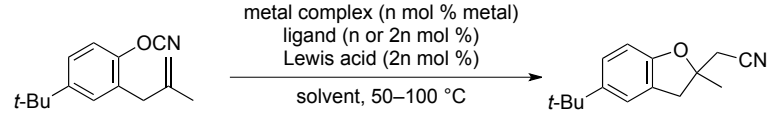
1-{2-[(Benzyloxy)methyl]allyl}-2-cyanatobenzene (1l). The procedure on a 1.16 mmol-scale gave **1l** (0.31 g, 96%) as a pale yellow oil, R_f 0.12 (hexane–ethyl acetate =4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.45 (s, 2H), 3.95 (s, 2H), 4.49 (s, 2H), 4.81 (s, 1H), 5.17 (s, 1H), 7.24–7.48 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.1, 72.0, 72.6, 108.9, 114.5, 114.6, 126.9, 127.5, 127.67, 127.72, 128.4, 128.5, 132.2, 138.0, 143.2, 151.4; HRMS (APCI) Calcd for $C_{18}H_{18}NO_2$: $[M+H]^+$, 280.1332. Found: *m/z* 280.1318.



1-Cyanato-2-(3-methylenbut-3-en-1-yl)benzene (1m). The procedure on a 9.3 mmol-scale gave **1m** (1.69 g, 90%) as a colorless oil, R_f 0.65 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 3H), 2.28 (d, J = 9.2 Hz, 2H), 2.77–2.81 (m, 2H), 4.67 (s, 1H), 4.76 (s, 1H), 7.21–7.33 (m, 3H), 7.44 (dd, J = 8.3, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 27.8, 37.9, 109.0, 110.9, 114.4, 126.8, 127.9, 130.2, 131.2, 144.2, 151.2; HRMS (APCI) Calcd for $C_{12}H_{14}NO$: $[M+H]^+$, 188.1070. Found: *m/z* 188.1061.

Intramolecular oxycyanation of alkenes catalyzed by Pd/BPh_3. *A general procedure*. The respective cyanate (1.0 equiv) was measured in a 3 mL-vial and transferred into a dry box. It was dissolved in THF (4 mL per 1.00 mmol), and dodecane (0.11–0.66 equiv) was added to the mixture as an internal GC-standard. Xantphos (10 mol % unless otherwise stated), a palladium complex (10 mol % unless otherwise stated), and then BPh_3 (20 mol % unless otherwise stated) were added sequentially to the vial. The reaction mixture was sealed with a screw-cap, taken outside the dry box, and heated with a heating block at the temperature for the time both specified in Table 1. The reaction mixture was flushed through a pad of silica gel, and the residue was purified by MPLC on silica gel to give the products in yields listed in Table 1.

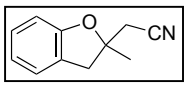
Table S1. Optimization of Reaction Conditions for the Reaction of **1c**



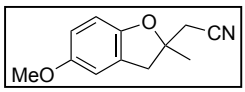
1c (0.20 or 0.50 mmol) **2c**

entry	scale	n	metal complex	ligand[a]	Lewis acid	solvent	temp (°C)	time (h)	conv. of **1c** (%)[b]	yield of **2c** (%)[c]
1	0.20	10	$Ni(cod)_2$	Xantphos	BPh_3	toluene	100	24	75	<5
2	0.20	10	CpPd(allyl)	none	BPh_3	toluene	100	18	>95	<5
3	0.20	10	CpPd(allyl)	P(4-CF_3–C_6H_4)$_3$	BPh_3	toluene	100	18	>95	<5
4	0.20	10	CpPd(allyl)	P(4-MeO–C_6H_4)$_3$	BPh_3	toluene	100	18	>95	<5
5	0.20	10	CpPd(allyl)	PMe_3	BPh_3	toluene	100	18	>95	<5
6	0.20	10	CpPd(allyl)	PCy_3	BPh_3	toluene	100	18	>95	<5
7	0.20	10	CpPd(allyl)	P*t*-Bu_3	BPh_3	toluene	100	18	>95	<5
8	0.20	10	CpPd(allyl)	Dppp	BPh_3	toluene	100	18	>95	<5
9	0.50	5	CpPd(allyl)	Xantphos	BPh_3	toluene	80	9	>95	67
10	0.50	5	$Pd(OAc)_2$	Xantphos	BPh_3	toluene	80	3	>95	46
11	0.50	5	$Pd_2[P(o\text{-tol})_3]_2$	Xantphos	BPh_3	toluene	80	3	>95	73
12	0.50	5	$Pd_2(dba)_3$	Xantphos	BPh_3	toluene	80	3	>95	91
13	0.50	5	$Pd_2(dba)_3$	Xantphos	BPh_3	toluene	50	3	>95	77
14	0.50	5	$Pd_2(dba)_3$	DPEphos	BPh_3	toluene	50	3	12	<5
15	0.50	5	$Pd_2(dba)_3$	Dpph	BPh_3	toluene	50	3	<5	<5
16	0.50	5	$Pd_2(dba)_3$	Dppf	BPh_3	toluene	50	3	<5	<5
17	0.50	5	$Pd_2(dba)_3$	Binap	BPh_3	toluene	50	3	25	<5
18	0.50	5	CpPd(allyl)	Xantphos	$B(C_6F_5)_3$	toluene	80	9	>95	3
19	0.50	5	CpPd(allyl)	Xantphos	BEt_3	toluene	80	9	62	5
20	0.50	5	CpPd(allyl)	Xantphos	$AlPh_3$	toluene	80	9	>95	<5
21	0.50	5	CpPd(allyl)	Xantphos	$AlEt_3$	toluene	80	9	>95	38
22	0.50	5	$Pd_2(dba)_3$	Xantphos	BPh_3	THF	80	8	>95	>95
23	0.50	5	$Pd_2(dba)_3$	Xantphos	BPh_3	THF	50	8	>95	>95
24	0.50	5	$Pd_2(dba)_3$	Xantphos	none	THF	50	8	13	<5
25	0.50	5	$Pd_2(dba)_3$	Xantphos	BPh_3	NMP	80	8	25	<5

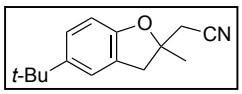
[a] n mol % for bidentate phosphines and 2n mol % for monodentate phosphines. [b] Estimated by GC. [c] Estimated by ^{1}H NMR.



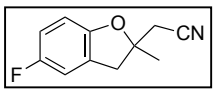
2-(2-Methyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2a). The procedure on a 1.00 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 90:10) gave **2a** (147 mg, 85%) as a yellow solid, R_f 0.36 (hexane–ethyl acetate =4:1). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.67 (s, 3H), 2.71 (d, J = 16.5 Hz, 1H), 2.77 (d, J = 16.5 Hz, 1H), 3.14 (d, J = 16.4 Hz, 1H), 3.23 (d, J = 16.4 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 6.89 (td, J = 7.5, 1.0 Hz, 1H), 7.13–7.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.9, 29.7, 41.2, 84.6, 110.0, 116.8, 121.1, 125.2, 128.6, 157.9; HRMS (APCI) Calcd for $C_{11}H_{12}NO$: $[M+H]^+$, 174.0913. Found: *m/z* 174.0907.



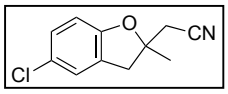
2-(5-Methoxy-2-methyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2b). The procedure on a 1.00 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 75:25) gave **2b** (177 mg, 88%) as a reddish solid, R_f 0.24 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3H), 2.72 (s, 2H), 3.11 (d, J = 16.0 Hz, 1H), 3.20 (d, J = 16.0 Hz, 1H), 3.75 (s, 3H), 6.68–6.75 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0, 29.6, 41.4, 56.9, 85.5, 111.3, 116.7, 117.2, 121.8, 126.3, 144.6, 146.2; HRMS (APCI) Calcd for $C_{12}H_{12}NO_2$: $[M+H]^+$, 204.1019. Found: *m/z* 204.1009.



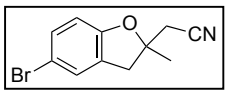
2-(5-*tert*-Butyl-2-methyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2c). The procedure on a 1.00 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 95:5) gave **2c** (162 mg, 71%) as a colorless solid, R_f 0.44 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 1.66 (s, 3H), 2.71 (d, J = 16.4 Hz, 1H), 2.76 (d, J = 16.4 Hz, 1H), 3.12 (d, J = 15.8 Hz, 1H), 3.20 (d, J = 15.8 Hz, 1H), 6.71 (d, J = 9.0 Hz, 1H), 7.16–7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 29.7, 31.7, 34.3, 41.4, 84.7, 109.2, 116.9, 122.2, 124.8, 125.4, 144.3, 155.7; HRMS (APCI) Calcd for $C_{15}H_{20}NO$: $[M+H]^+$, 230.1539. Found: *m/z* 230.1529; Anal. Calcd for $C_{15}H_{19}NO$; C, 78.56; H, 8.35; N, 6.11. Found: C, 78.73; H, 8.45; N, 5.93.



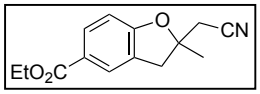
2-(5-Fluoro-2-methyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2d). The procedure on a 1.00 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 87:13) gave **2d** (151 mg, 79%) as a yellowish solid, R_f 0.31 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3H), 2.74 (s, 2H), 3.12 (d, J = 16.2 Hz, 1H), 3.22 (d, J = 16.2 Hz, 1H), 6.67–6.71 (m, 1H), 6.80–6.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 29.6, 41.3, 85.3, 110.2 (d, J = 10 Hz), 112.3 (d, J = 25 Hz), 114.8 (d, J = 25 Hz), 116.6, 126.6 (d, J = 10 Hz), 153.9 (d, J = 5 Hz), 157.7 (d, J = 250 Hz); HRMS (APCI) Calcd for $C_{11}H_9FNO$: $[M–H]^–$, 190.0674. Found: *m/z* 190.0672.



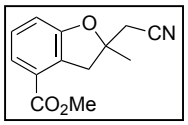
2-(5-Chloro-2-methyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2e). The procedure on a 0.50 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 88:12) gave **2e** (53 mg, 51%) as a yellowish solid, R_f 0.28 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3H), 2.74 (s, 2H), 3.12 (d, J = 16.2 Hz, 1H), 3.23 (d, J = 16.2 Hz, 1H), 6.65–6.68 (m, 1H), 7.23–7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 29.7, 41.0, 85.4, 111.6, 112.9, 116.4, 127.7, 128.2, 131.4, 157.1; HRMS (APCI) Calcd for $C_{11}H_9ClNO$: $[M–H]^–$, 206.0378. Found: *m/z* 206.0374.



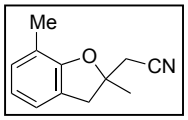
2-(5-Bromo-2-methyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2f). The procedure on a 0.50 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 88:12) gave **2f** (54 mg, 43%) as a reddish oil, R_f 0.25 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3H), 2.74 (s, 2H), 3.13 (d, *J* = 16.6 Hz, 1H), 3.22 (d, *J* = 16.6 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 7.09–7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 29.7, 41.0, 85.5, 110.9, 116.5, 125.3, 125.9, 127.1, 128.5, 156.6; HRMS (APCI) Calcd for $C_{11}H_9BrNO$: $[M–H]^–$, 249.9873. Found: *m/z* 249.9872.



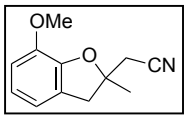
Ethyl 2-(cyanomethyl)-2-methyl-2,3-dihydrobenzofuran-5-carboxylate (2g). The procedure on a 0.50 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 50:50) gave **2g** (54 mg, 44%) as a reddish solid, R_f 0.16 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.1 Hz, 3H), 1.68 (s, 3H), 2.74 (d, *J* = 16.7 Hz, 1H), 2.79 (d, *J* = 16.7 Hz, 1H), 3.16 (d, *J* = 16.2 Hz, 1H), 3.26 (d, *J* = 16.2 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 7.85–7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 26.0, 29.8, 40.6, 60.7, 86.1, 109.6, 116.3, 123.8, 125.6, 127.0, 131.5, 161.7, 166.2; HRMS (APCI) Calcd for $C_{14}H_{14}NO_3$: $[M–H]^–$: 244.0979. Found: *m/z* 244.0976.



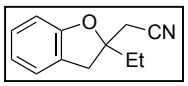
Methyl 2-(cyanomethyl)-2-methyl-2,3-dihydrobenzofuran-4-carboxylate (2h). The procedure on a 1.00 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 85:15) followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 90:10) gave **2h** (181 mg, 78%) as a colorless solid, R_f 0.21 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (s, 3H), 2.72 (d, *J* = 16.3 Hz, 1H), 2.78 (d, *J* = 16.3 Hz, 1H), 3.44 (d, *J* = 17.6 Hz, 1H), 3.57 (d, *J* = 17.6 Hz, 1H), 3.90 (s, 3H), 6.96–6.99 (m, 1H), 7.21–7.23 (m, 1H), 7.56 (dd, *J* = 7.9, 1.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1, 29.9, 42.6, 52.0, 85.0, 114.1, 116.5, 122.6, 127.3, 127.9, 128.7, 158.7, 166.5; HRMS (APCI) Calcd for $C_{13}H_{12}NO_3$: $[M–H]^–$, 230.0823. Found: *m/z* 230.0819.



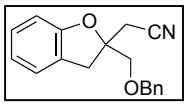
2-(2,7-Dimethyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2i). The procedure on a 0.50 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 87:13) gave **2i** (84 mg, 90%) as a yellow oil, R_f 0.35 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 3H), 2.19 (s, 3H), 2.71 (d, *J* = 16.6 Hz, 1H), 2.76 (d, *J* = 16.6 Hz, 1H), 3.13 (d, *J* = 16.3 Hz, 1H), 3.21 (d, *J* = 16.3 Hz, 1H), 6.78–6.81 (m, 1H), 6.96–7.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 26.0, 29.7, 41.5, 84.1, 116.9, 120.2, 120.9, 122.5, 124.5, 129.7, 156.4; HRMS (APCI) Calcd for $C_{12}H_{14}NO$: $[M+H]^+$, 188.1070. Found: *m/z* 188.1061.



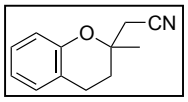
2-(7-Methoxy-2-methyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2j). The procedure on a 0.50 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 85:15) gave **2j** (65 mg, 64%) as a pale red solid, R_f 0.22 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 3H), 2.60 (s, 2H), 3.16 (d, *J* = 16.2 Hz, 1H), 3.31 (d, *J* = 16.2 Hz, 1H), 3.87 (s, 3H), 6.76–6.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 29.6, 41.4, 55.9, 85.5, 111.3, 116.7, 117.2, 121.8, 126.3, 144.6, 146.1; HRMS (APCI) Calcd for $C_{12}H_{14}NO_2$: $[M+H]^+$, 204.1019. Found: *m/z* 204.1010.



2-(2-Ethyl-2,3-dihydrobenzofuran-2-yl)acetonitrile (2k). The procedure on a 0.50 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 87:13) gave **2k** (66 mg, 71%) as a colorless oil, R_f 0.44 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, *J* = 7.4 Hz, 3H), 1.98 (qd, *J* = 7.4, 2.1 Hz, 2H), 2.71 (d, *J* = 16.7 Hz, 1H), 2.76 (d, *J* = 16.7 Hz, 1H), 3.12 (d, *J* = 16.6 Hz, 1H), 3.21 (d, *J* = 16.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.88 (td, *J* = 7.5, 0.8 Hz, 1H), 7.09–7.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.9, 27.8, 31.4, 38.8, 87.1, 109.8, 116.7, 121.0, 125.1, 125.2, 128.5, 158.2; HRMS (APCI) Calcd for $C_{12}H_{13}NO$: $[M+H]^+$, 188.1070. Found: *m/z* 188.1063.



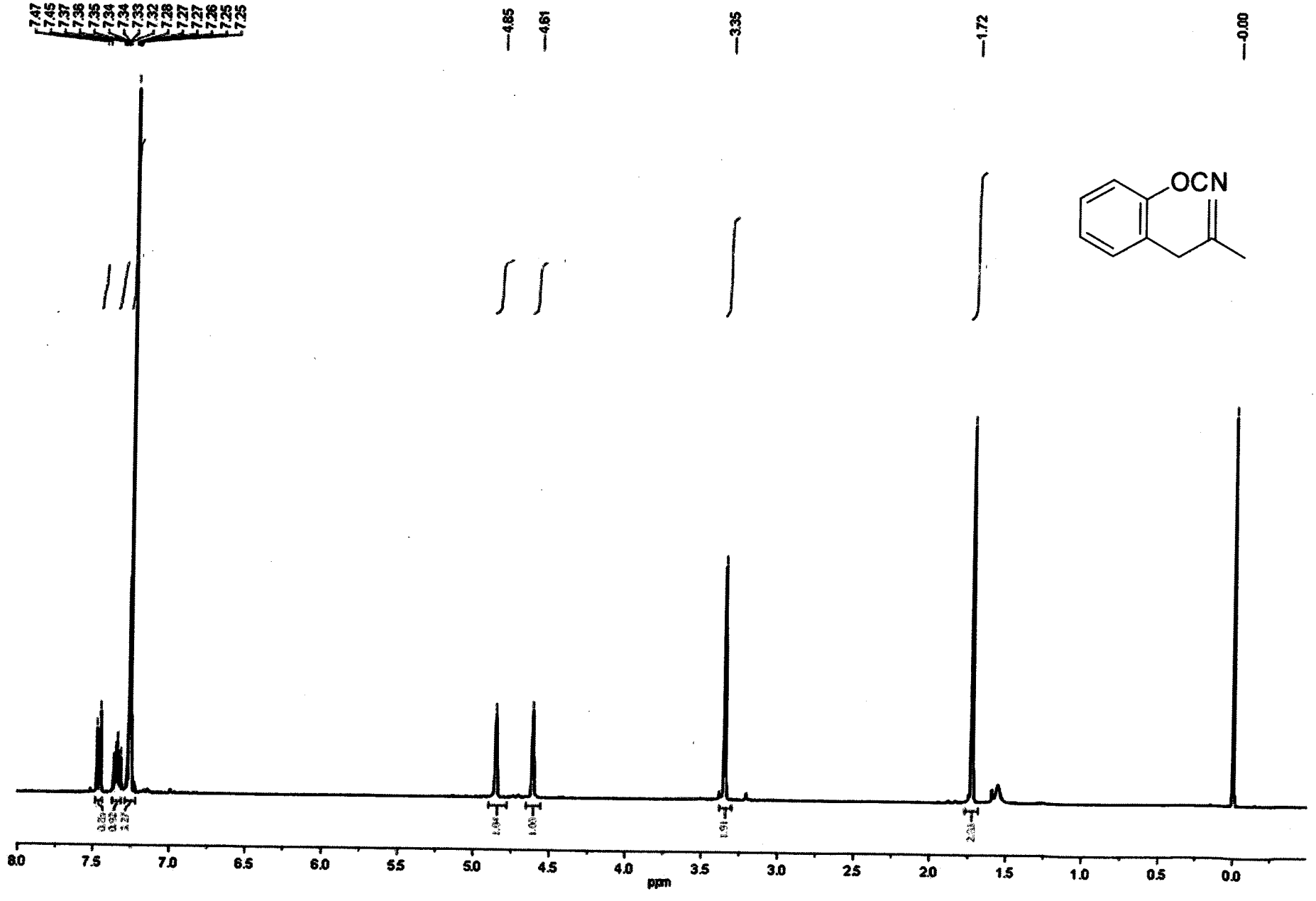
2-(2-((Benzoxy)methyl)-2,3-dihydrobenzofuran-2-yl)acetonitrile (2l). The procedure on a 0.20 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 87:13) gave **2l** (34 mg, 60%) as a yellowish oil, R_f 0.30 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (d, *J* = 16.0 Hz, 1H), 2.96 (d, *J* = 16.0 Hz, 1H), 3.16 (d, *J* = 17.0 Hz, 1H), 3.25 (d, *J* = 17.0 Hz, 1H), 3.64 (d, *J* = 10.0 Hz, 1H), 3.73 (d, *J* = 10.3 Hz, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 7.12–7.20 (m, 2H), 7.29–7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 37.6, 72.5, 73.8, 85.9, 110.0, 116.5, 121.3, 124.7, 125.2, 127.8, 128.0, 128.5, 128.6, 137.3, 158.0; HRMS (APCI) Calcd for $C_{18}H_{16}NO_2$: $[M–H]^–$, 278.1187. Found: *m/z* 278.1182.



2-(2-Methyl-chroman-2-yl)acetonitrile (2m). The procedure on a 0.50 mmol-scale followed by purification by MPLC (hexane–ethyl acetate = 100:0 to 87:13) gave **2m** (56 mg, 60%) as a pale yellow oil, R_f 0.37 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 3H), 1.91–2.09 (m, 2H) 2.67 (s, 2H), 2.75–2.88 (m, 2H), 6.83 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.89 (td, *J* = 7.4, 1.0 Hz, 1H), 7.05–7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.6, 28.8, 30.5, 73.5, 116.8, 117.4, 120.0, 120.8, 127.7, 129.5, 152.5; HRMS (ESI) Calcd for $C_{12}H_{14}NO$: $[M+H]^+$, 188.1070. Found: *m/z* 188.1071.

References

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
2. Ogata, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 13848.
3. (a) Nicolai, S.; Erard, S.; González, D. F.; Waser, J. *Org. Lett.* **2010**, *12*, 384. (b) Hoang, G. T.; Reddy, V. J.; Nguyen, H. H. K.; Douglas, C. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1882.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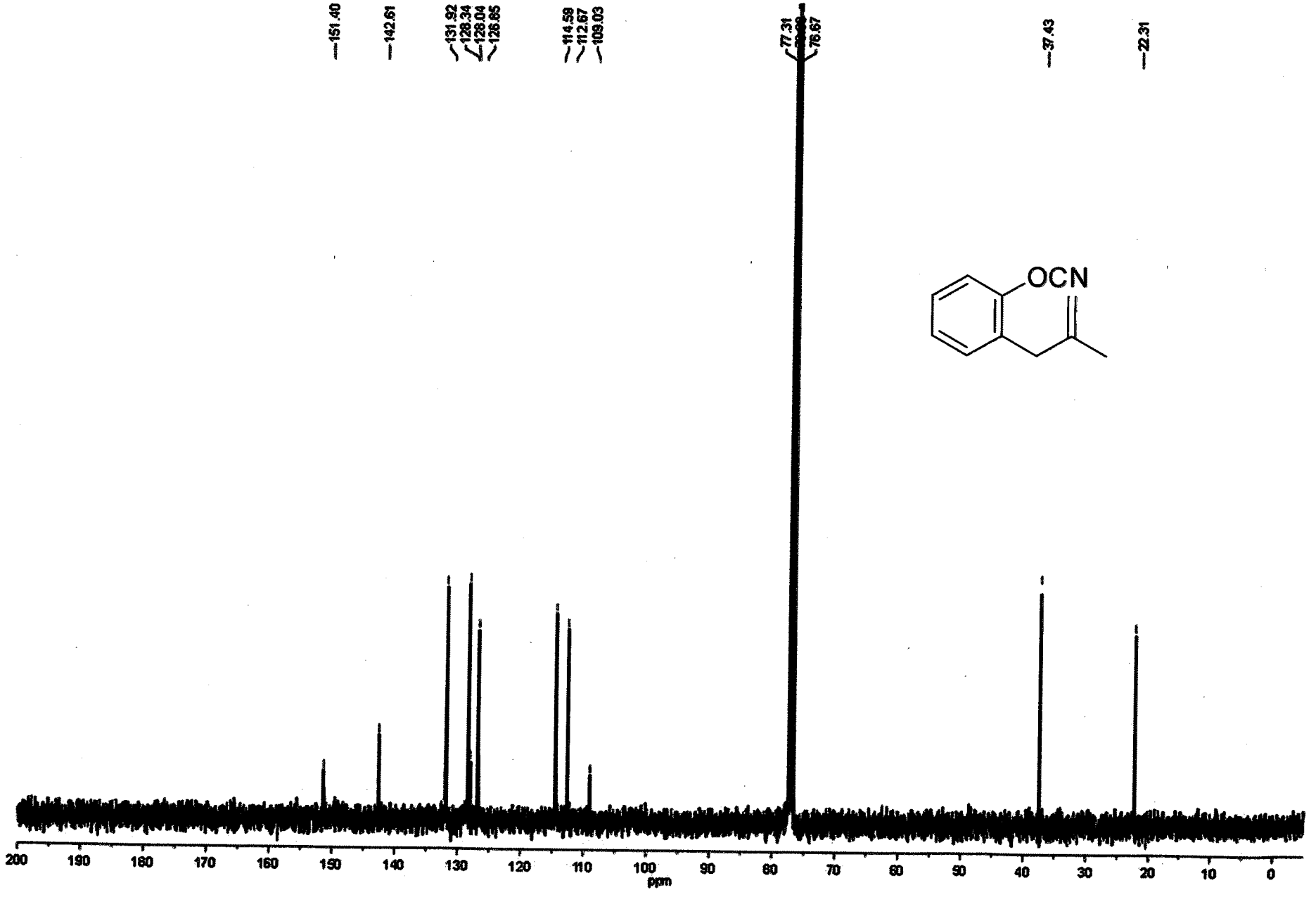
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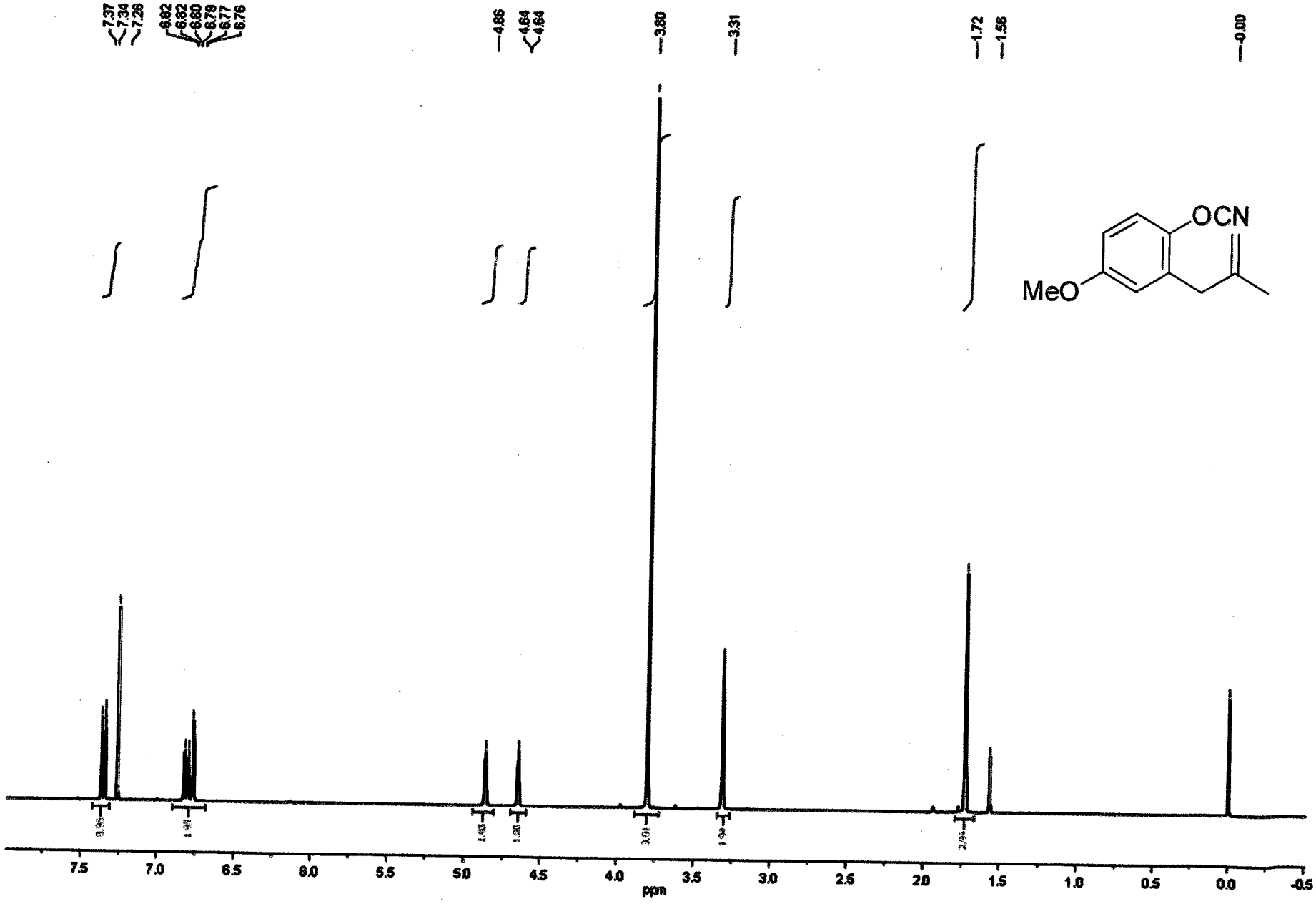
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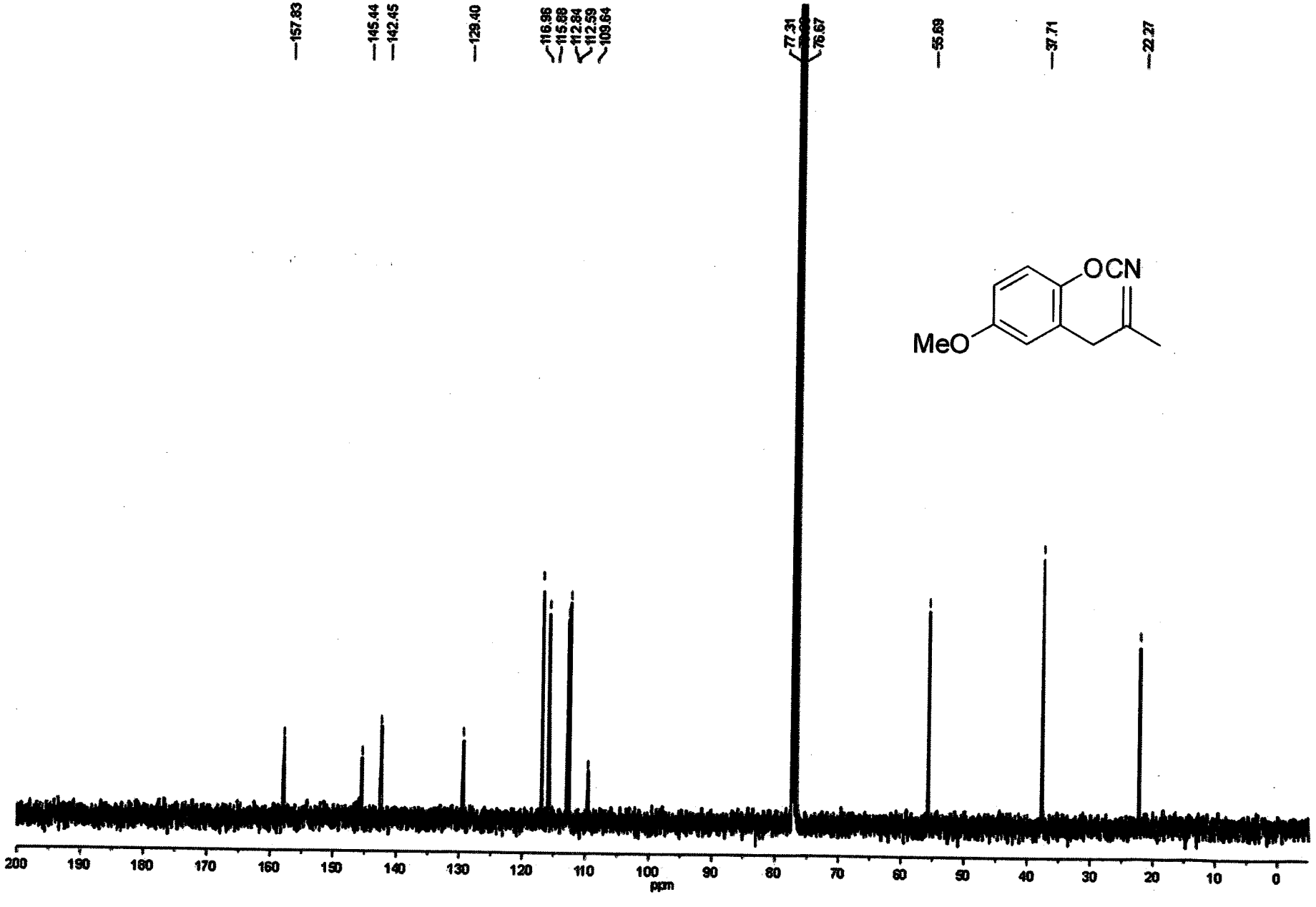
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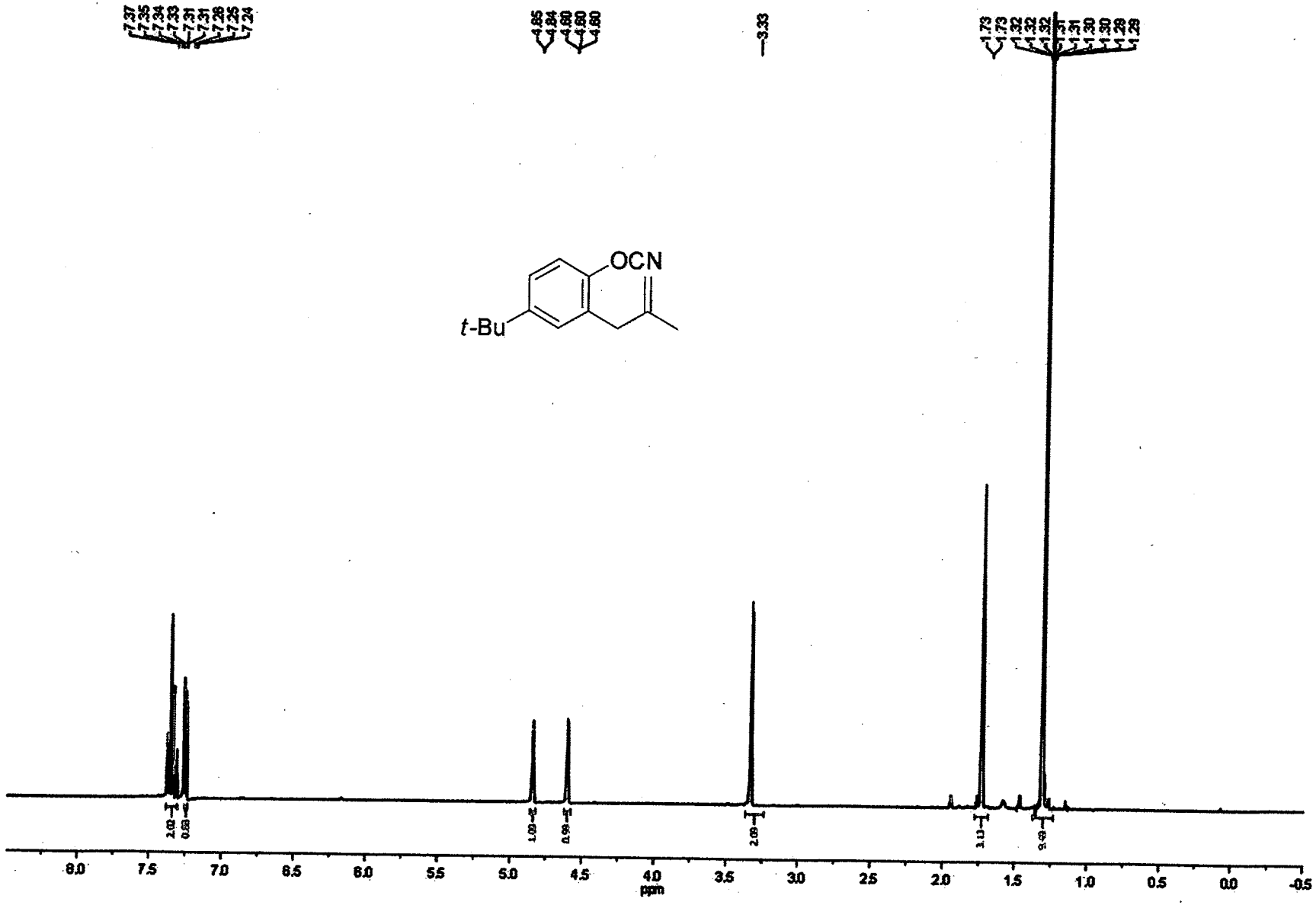
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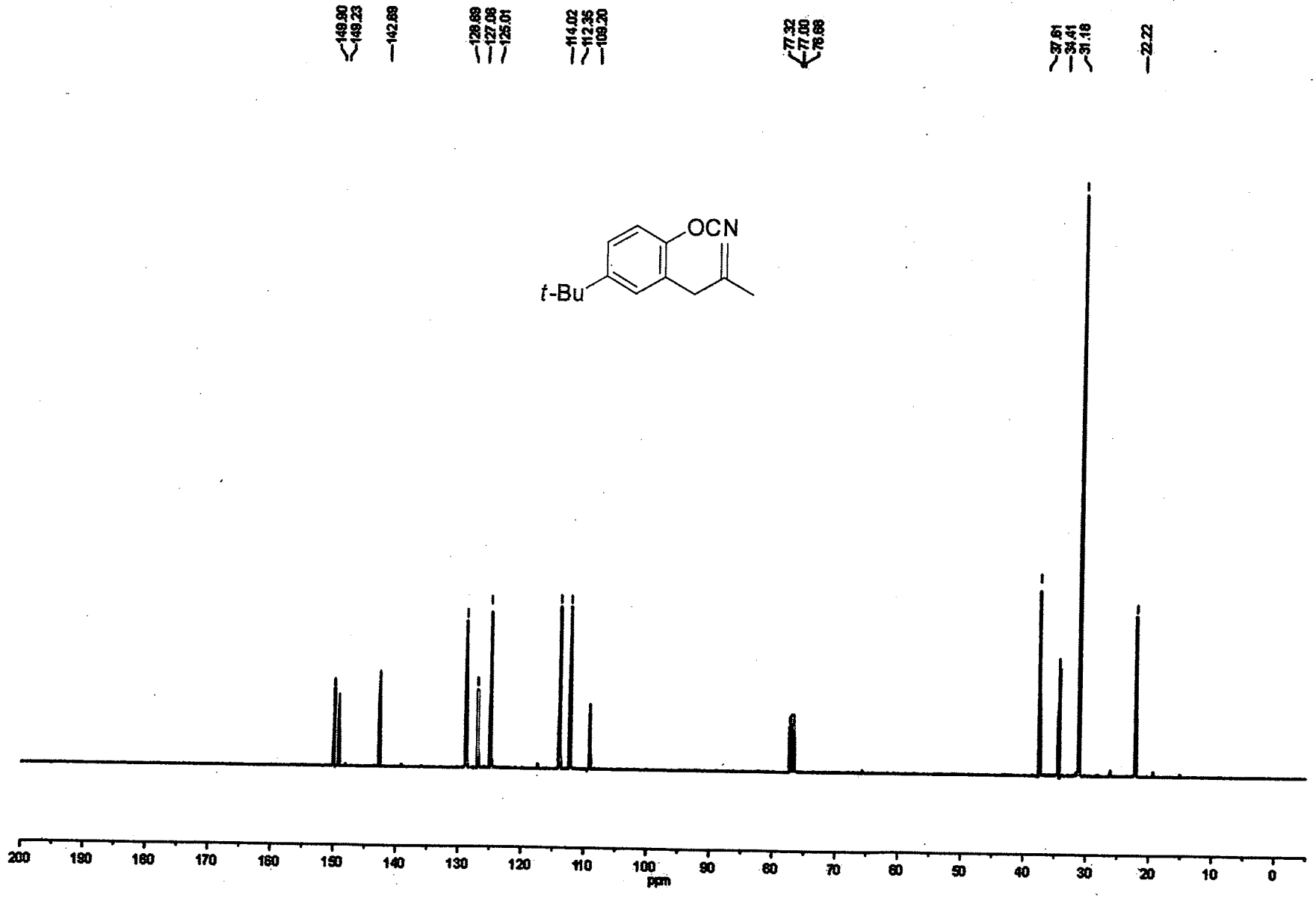
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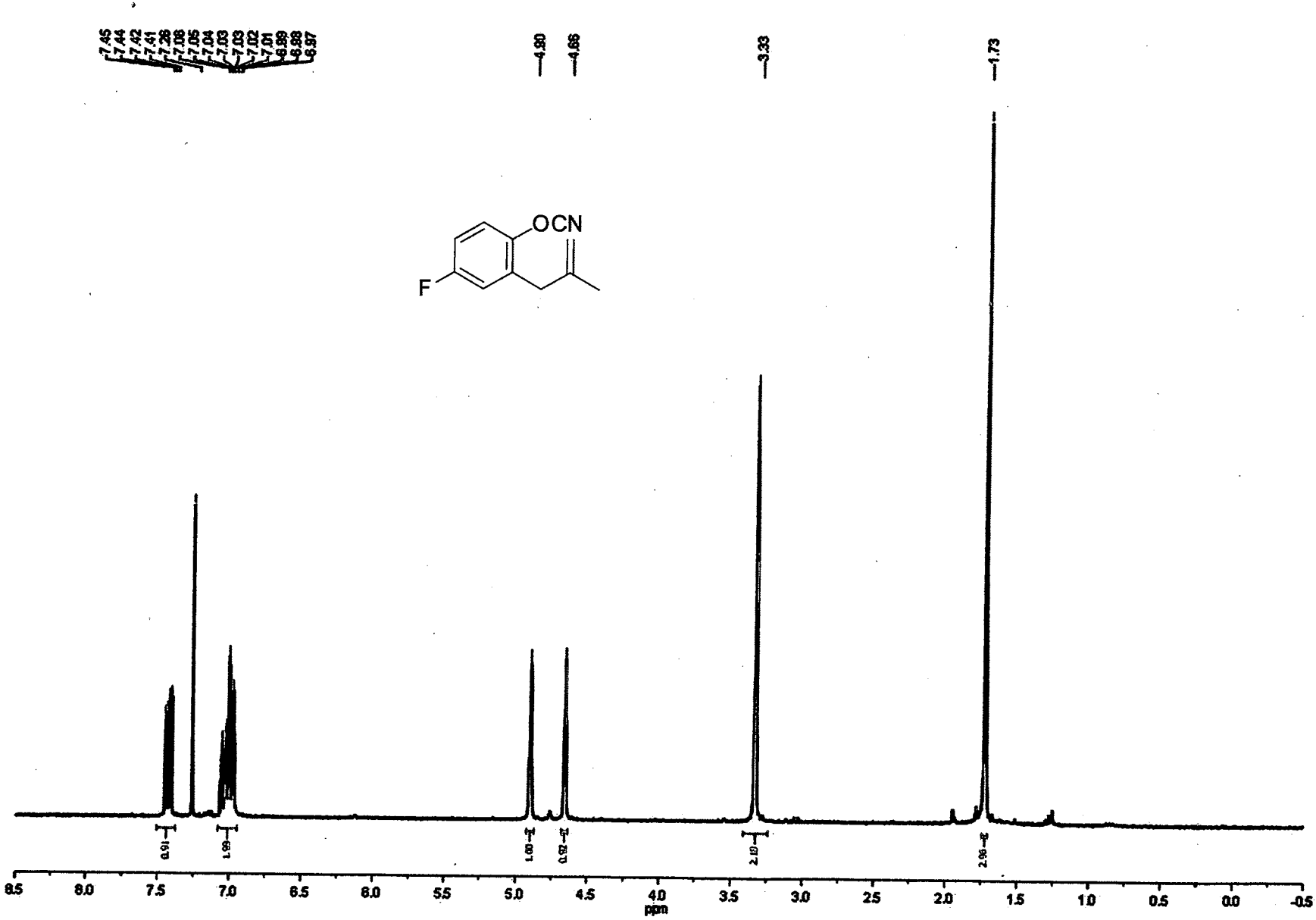
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0.92
2.10
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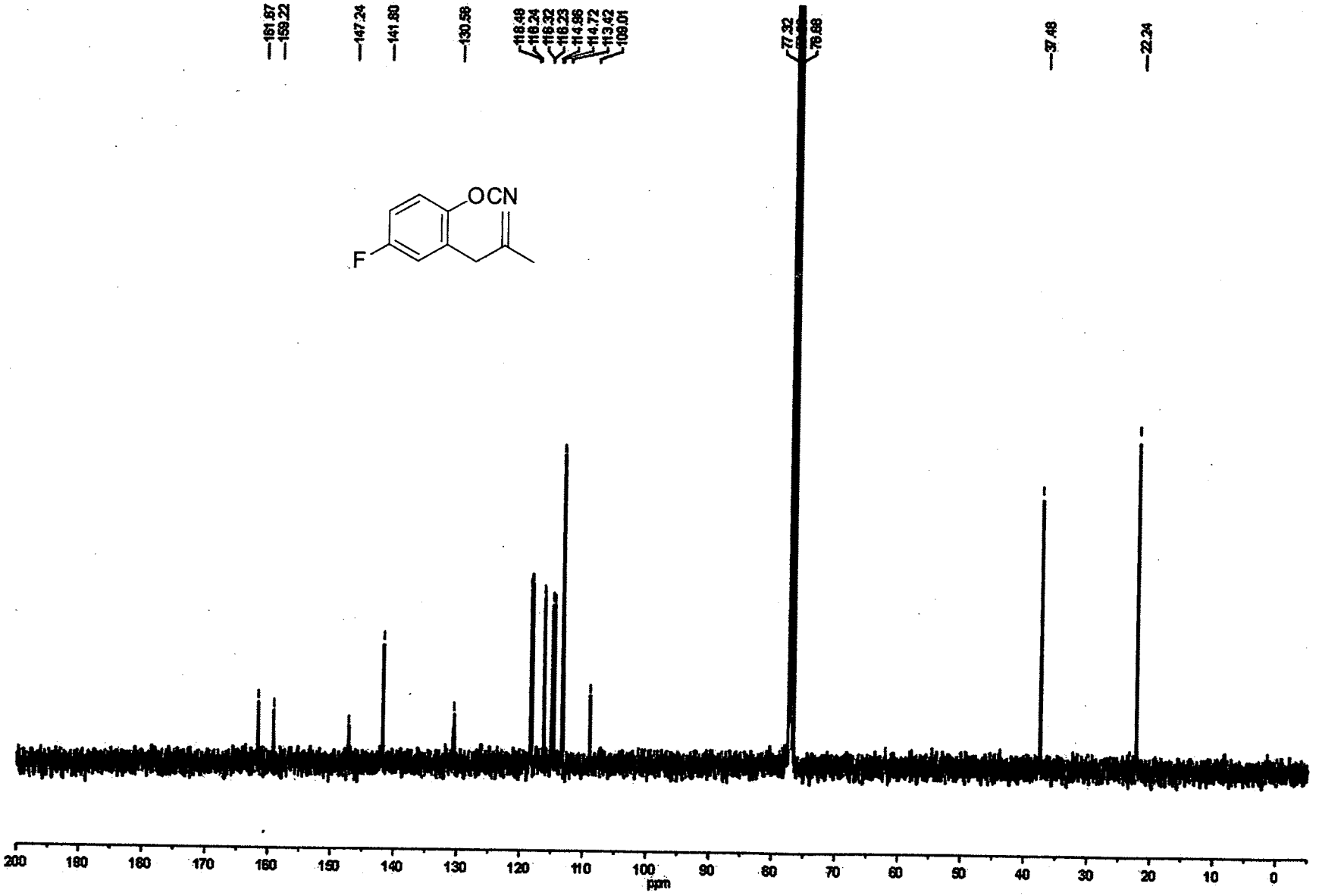
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F
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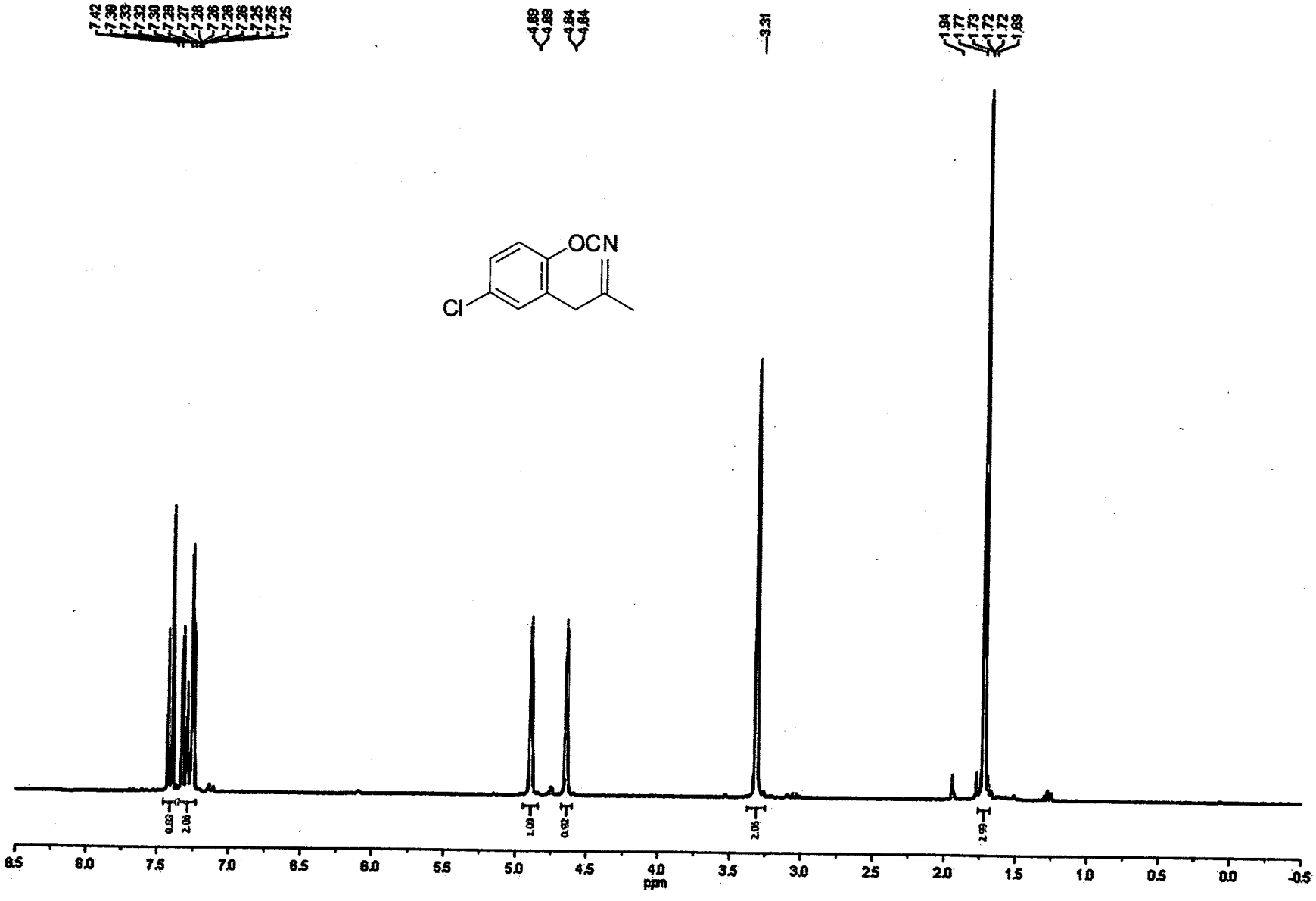
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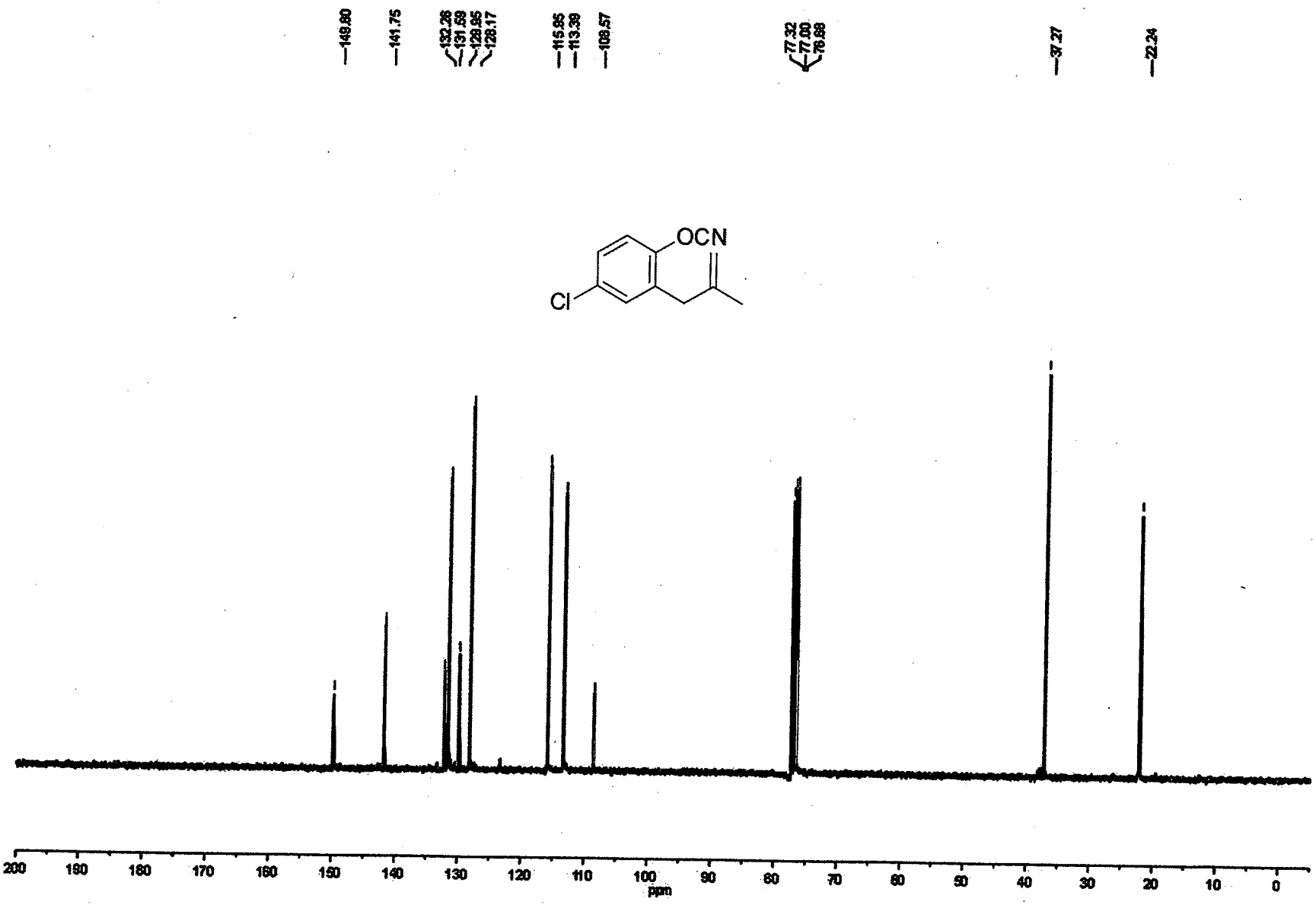
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Cl
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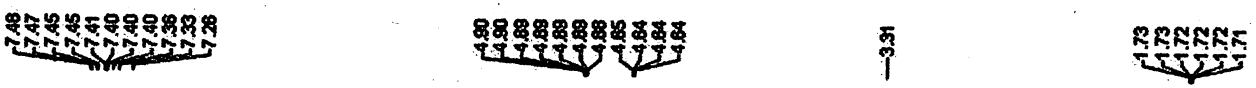
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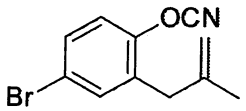
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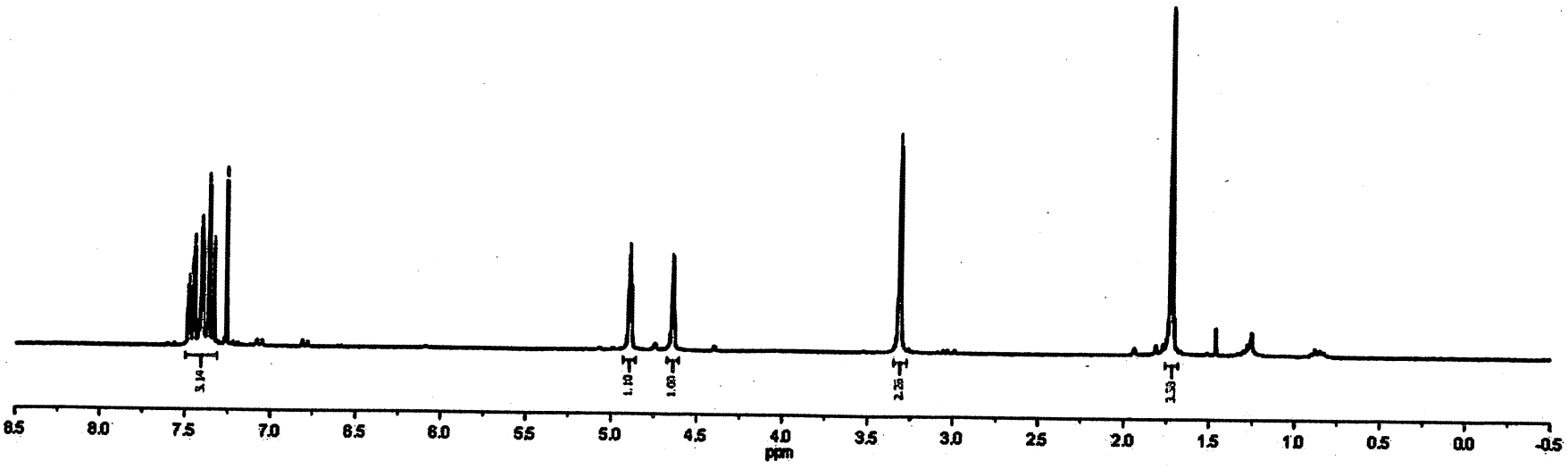
Br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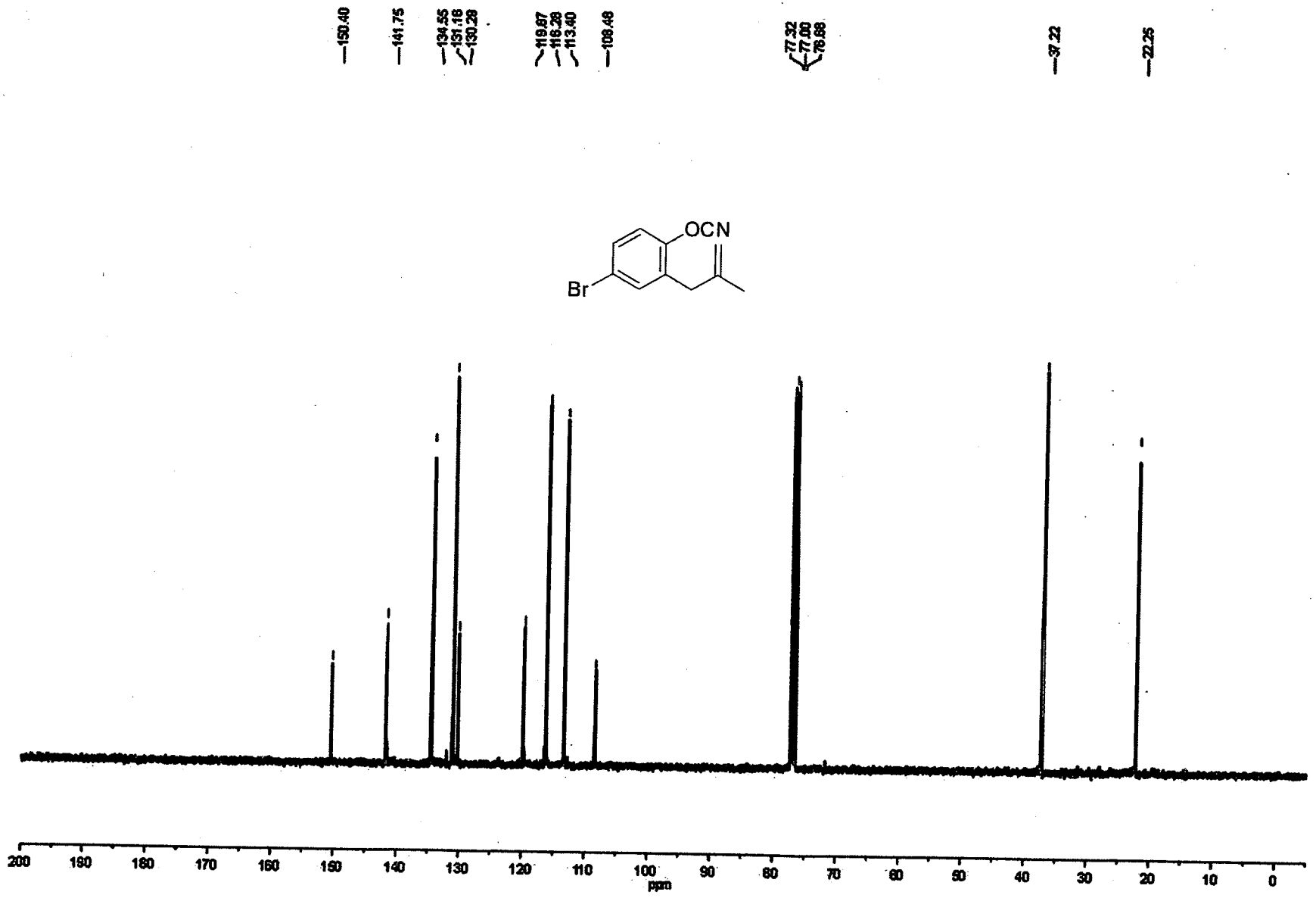
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OCN
Br
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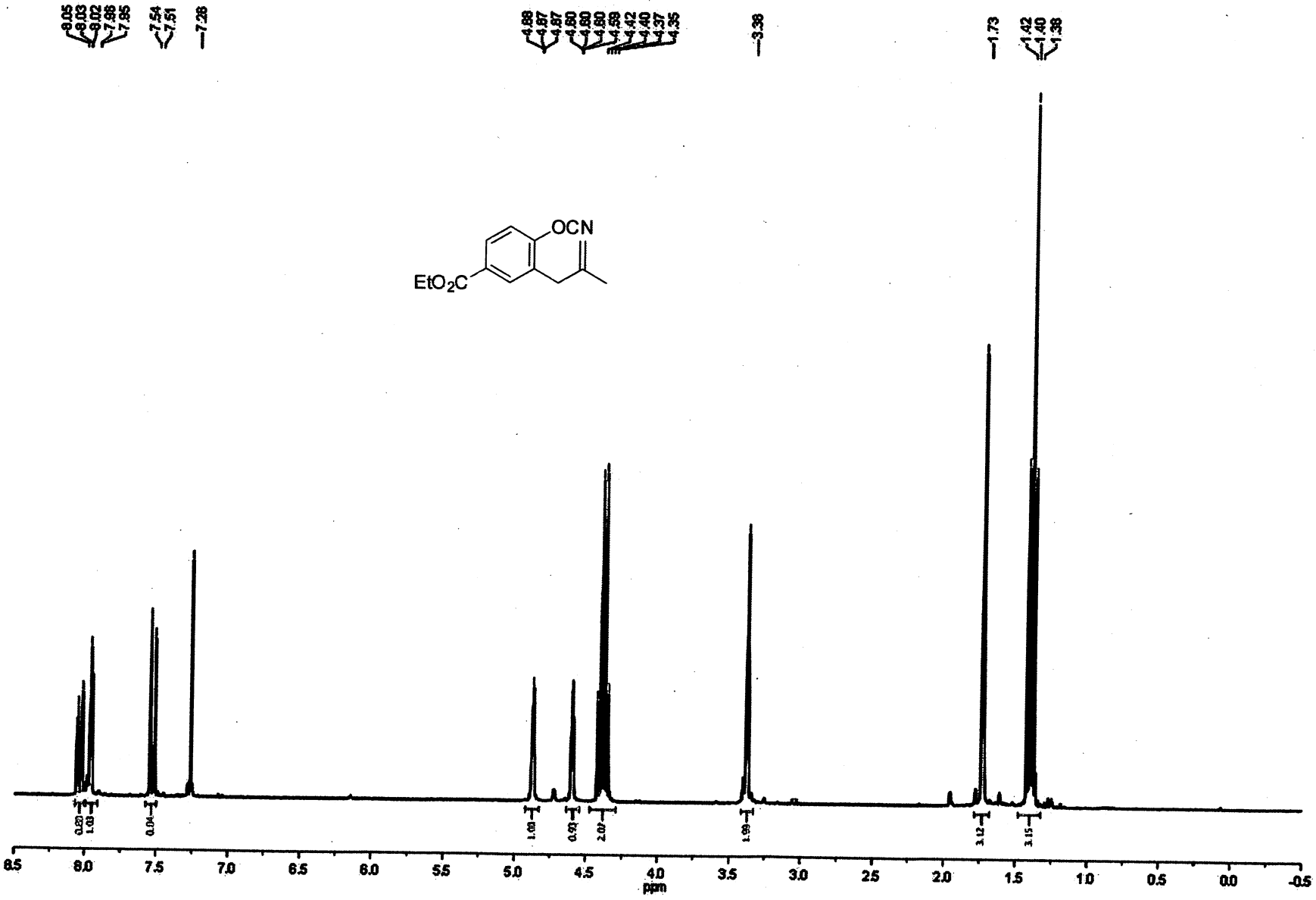
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4.80
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4.59
4.42
4.40
4.37
4.35
3.38
1.73
1.42
1.40
1.38
OCN
EtO2C
0.93
1.03
0.94
1.00
0.93
2.07
1.99
3.12
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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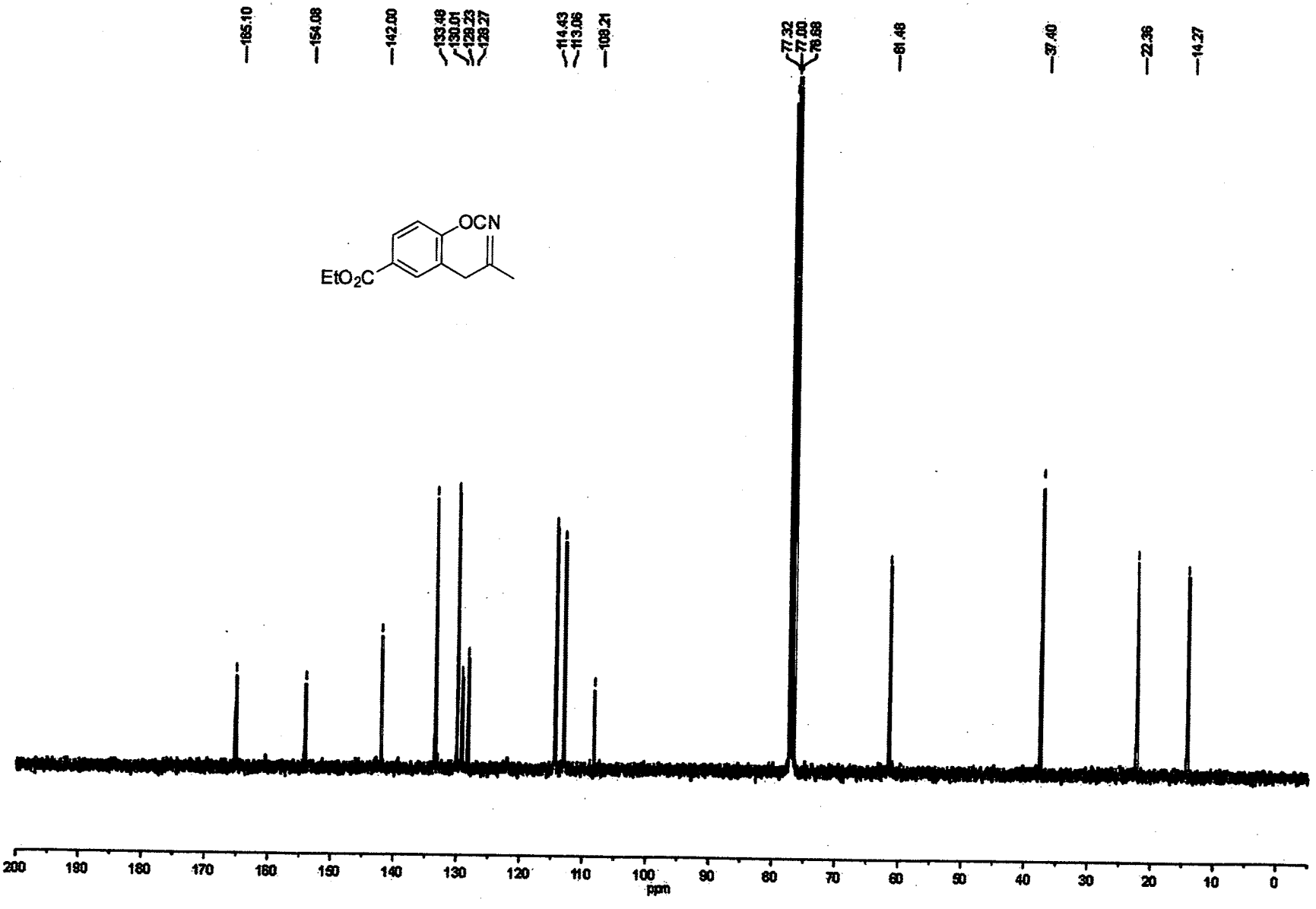
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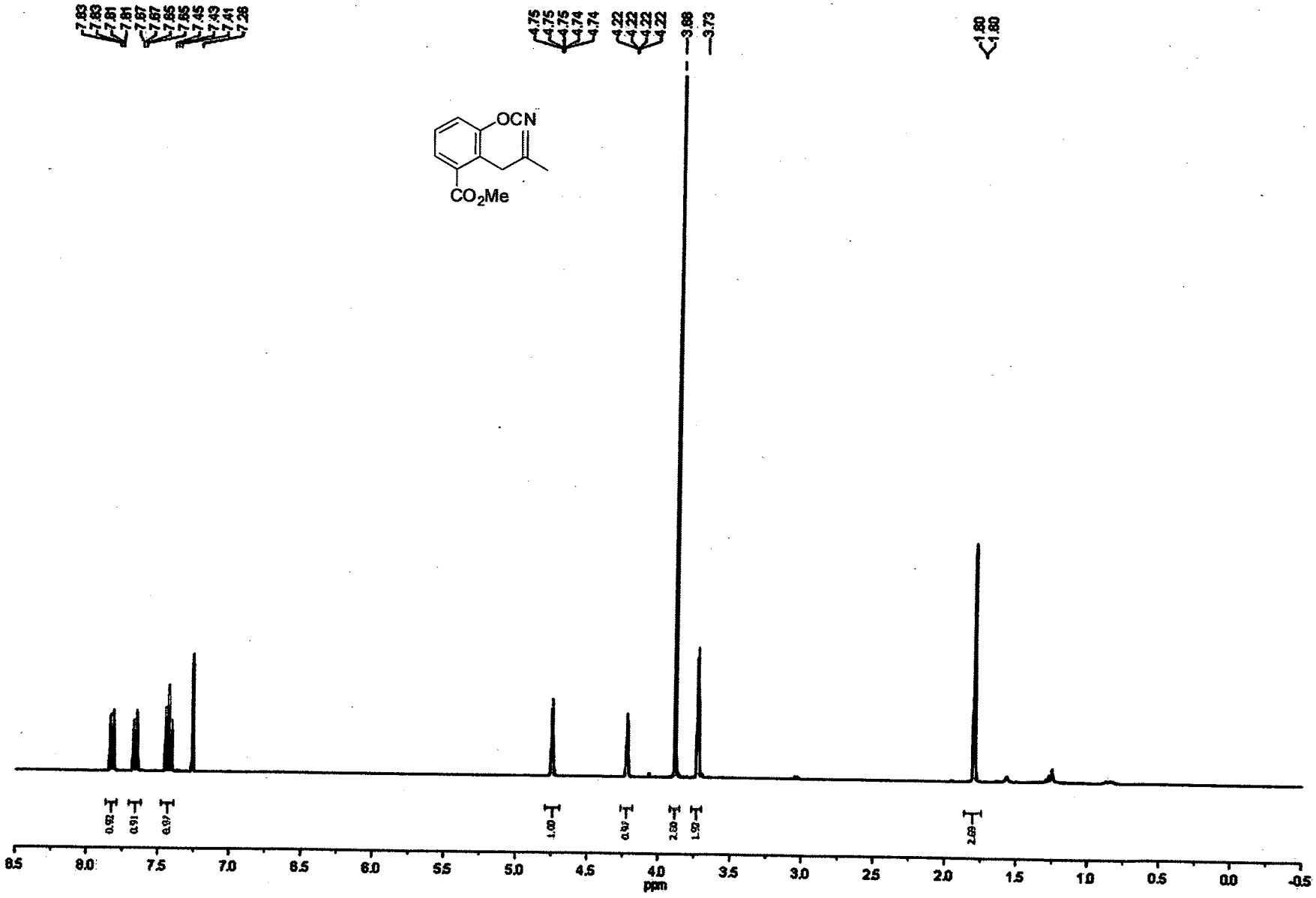
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4.22
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2.93
1.92
2.69
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6.5
6.0
5.5
5.0
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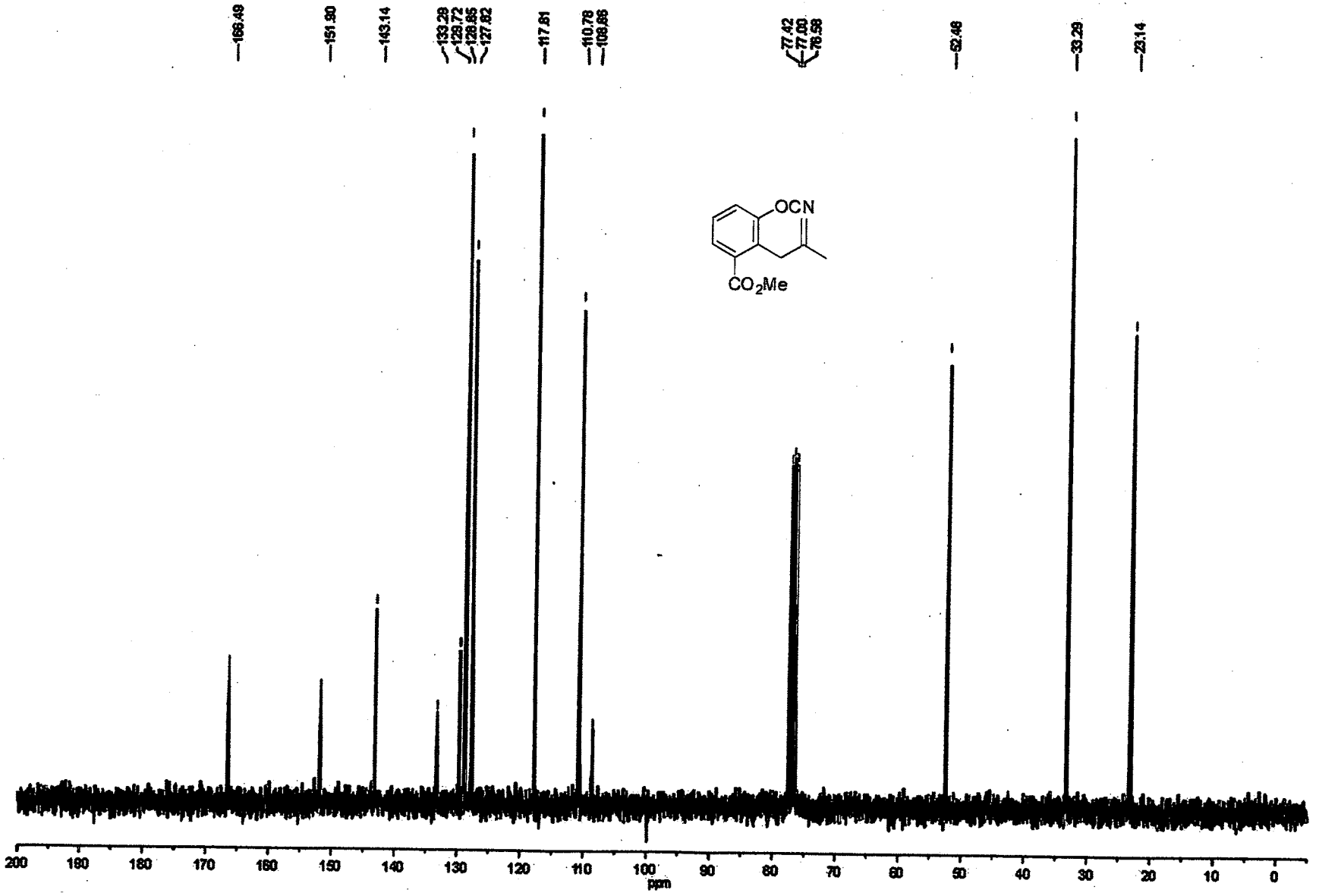
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CO2Me
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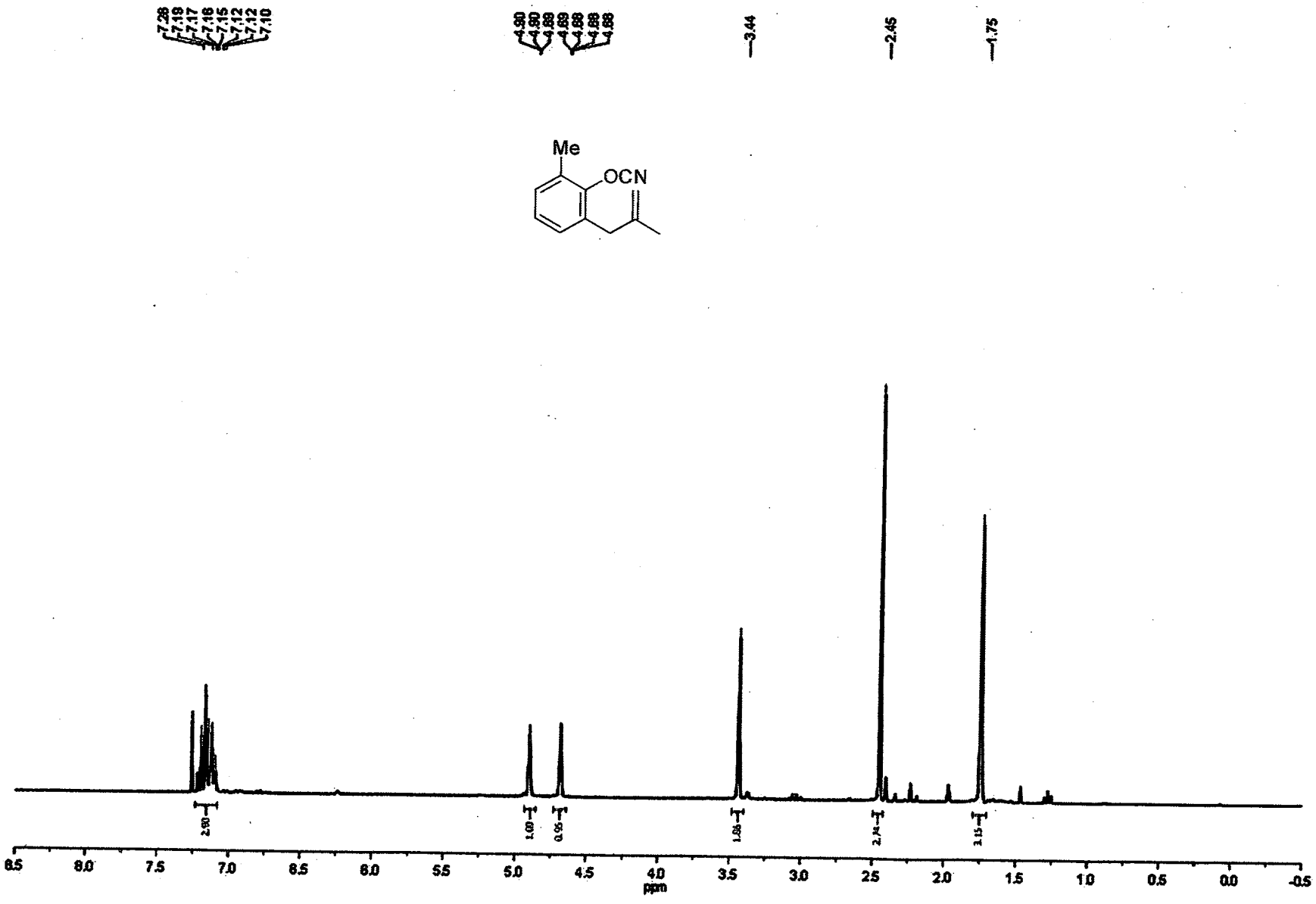
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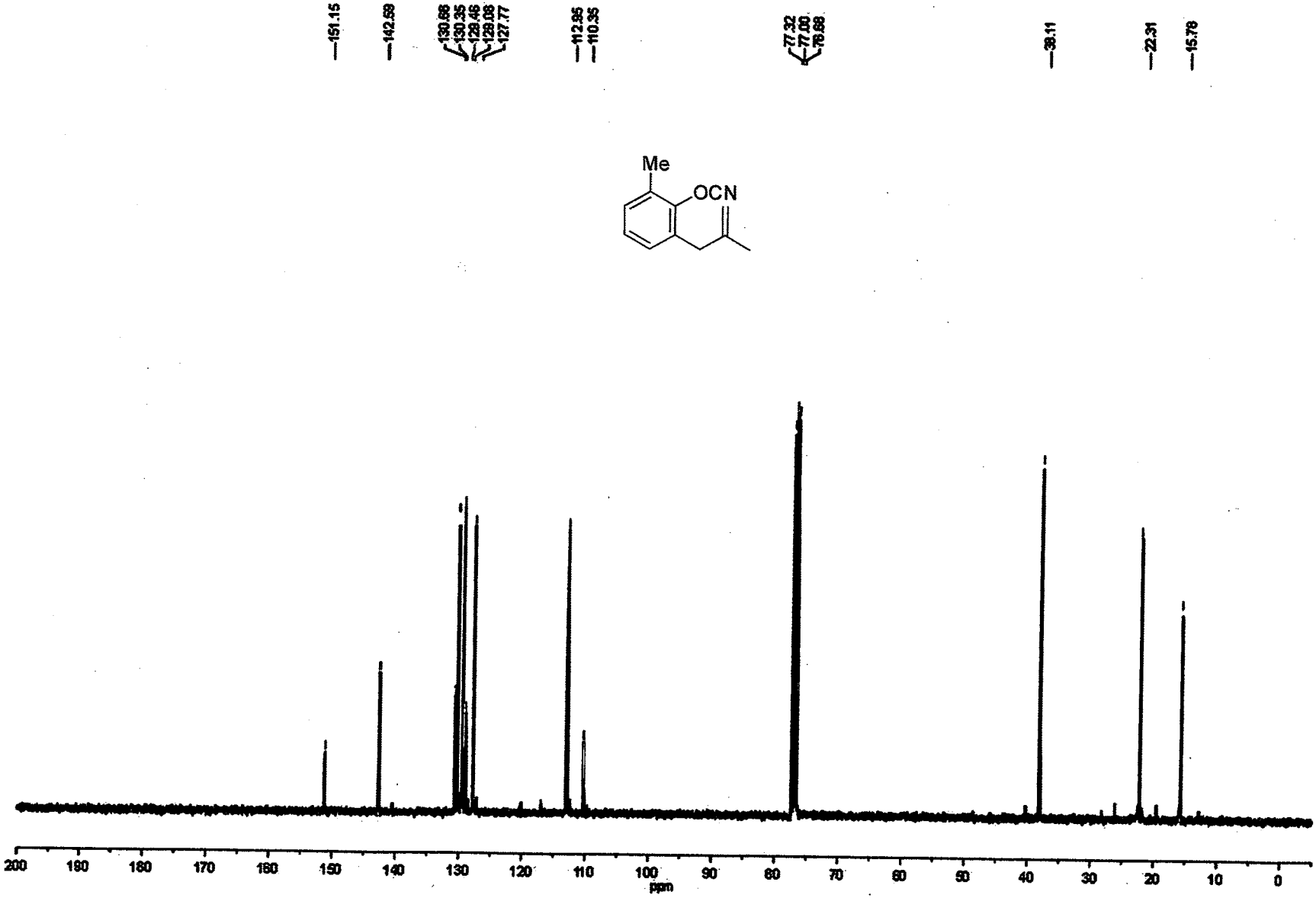
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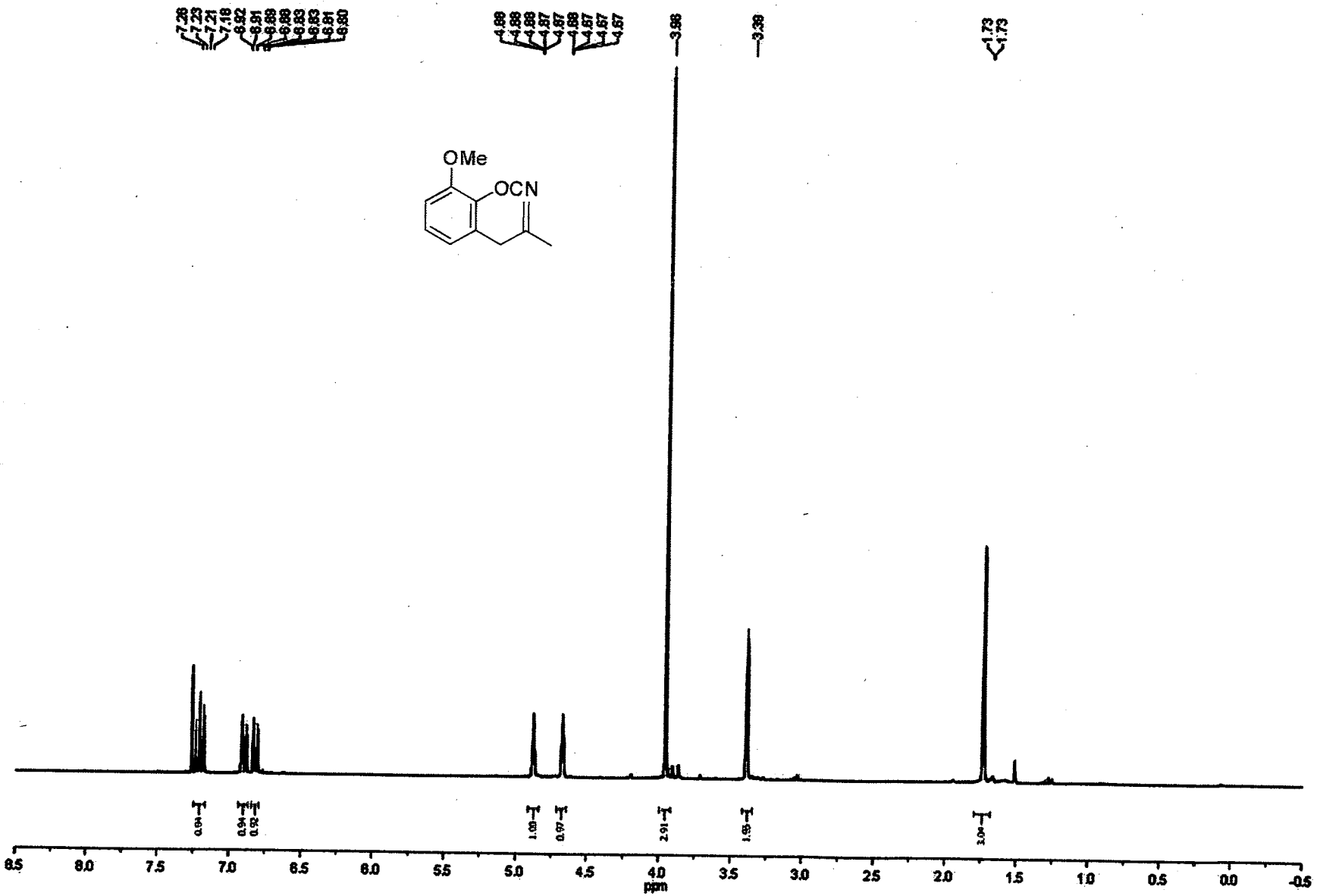
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OCN
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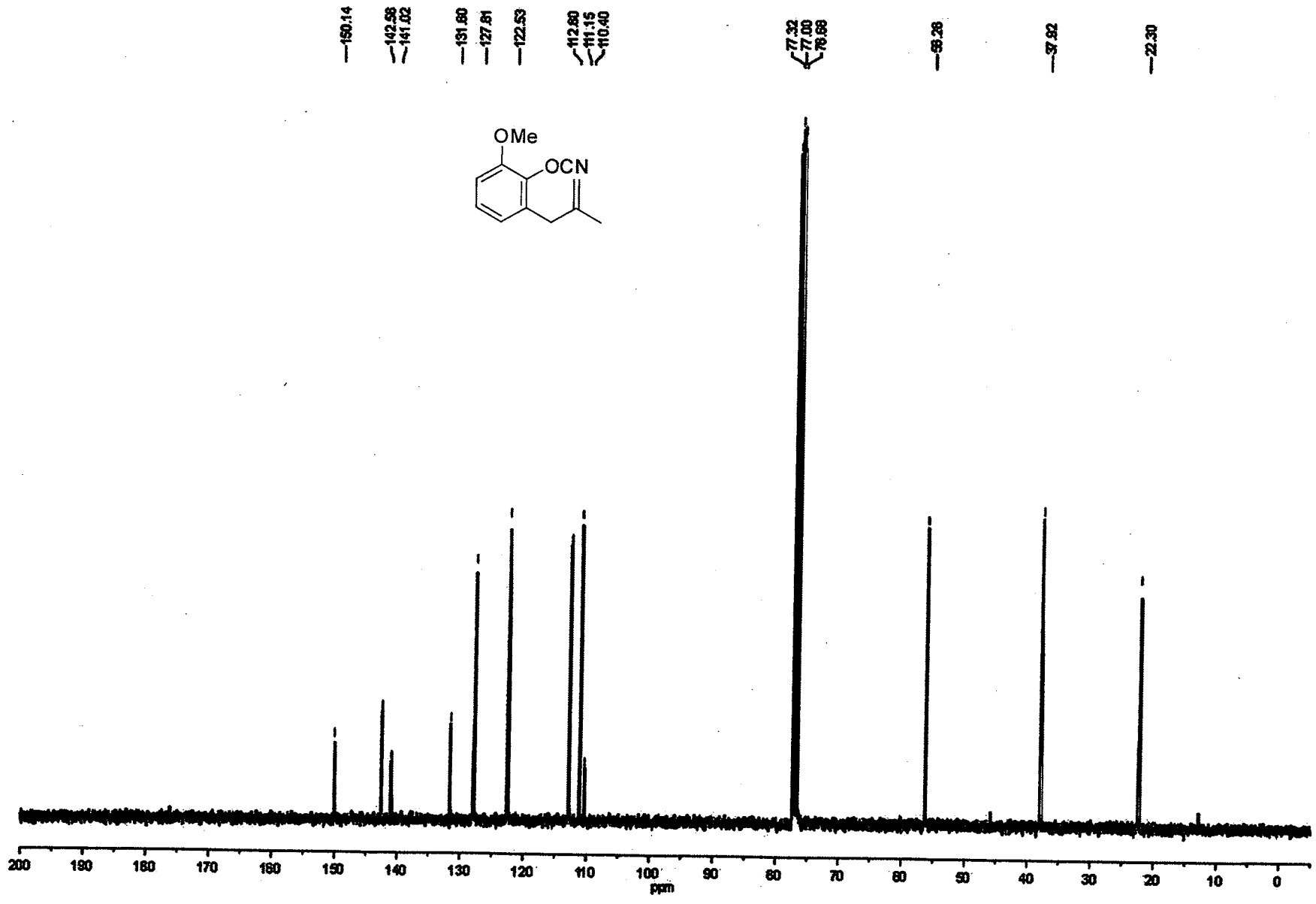
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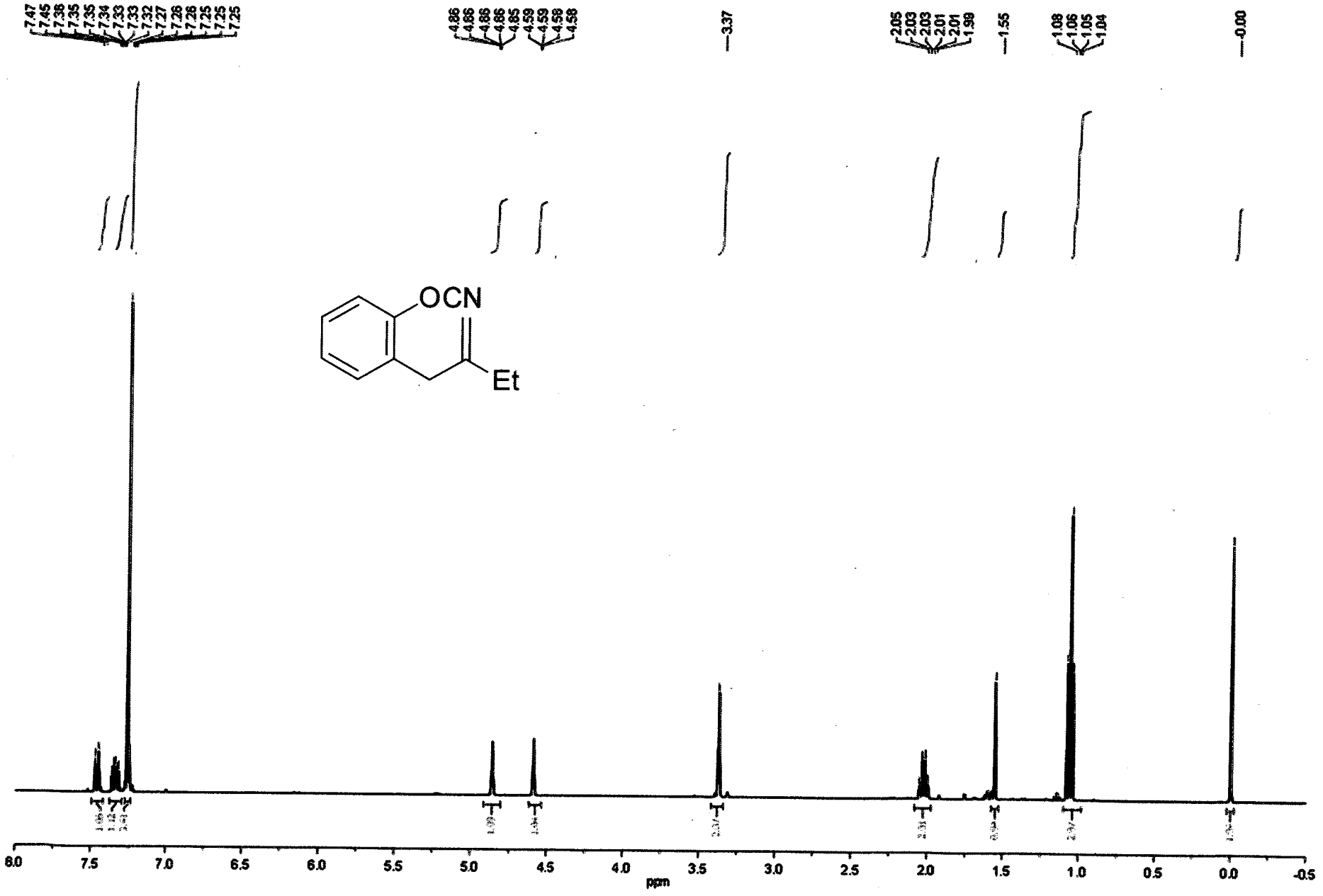
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Et
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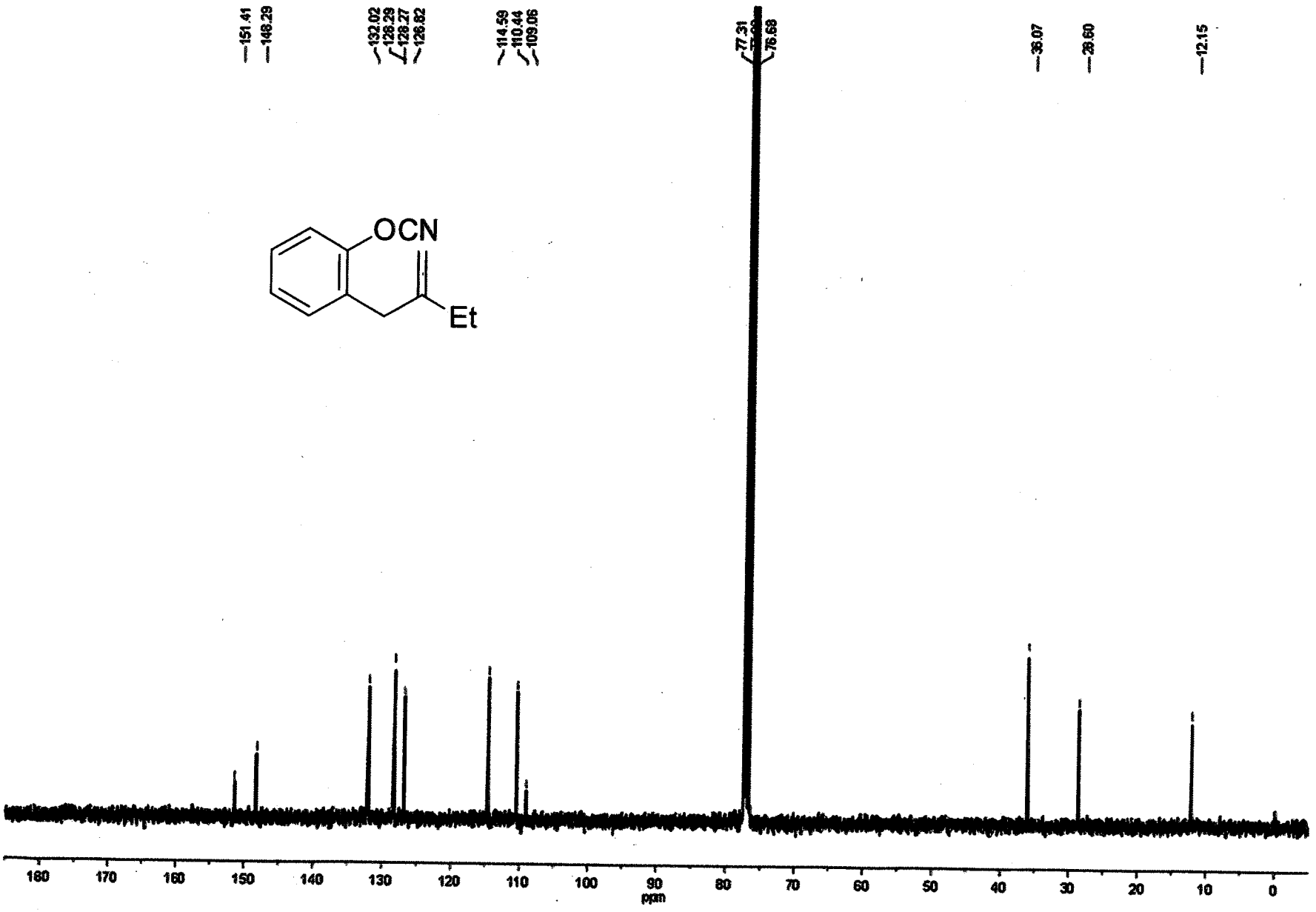
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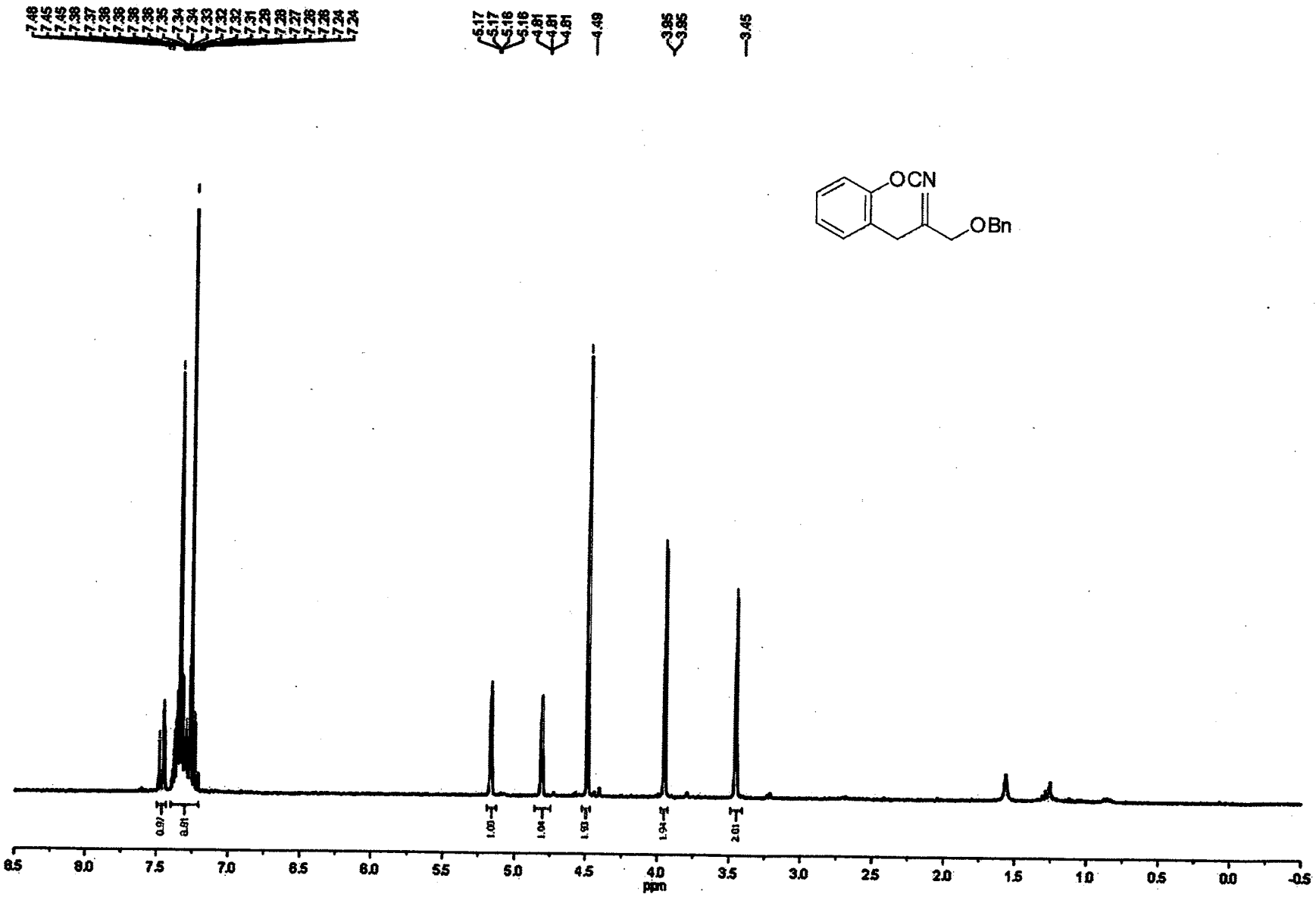
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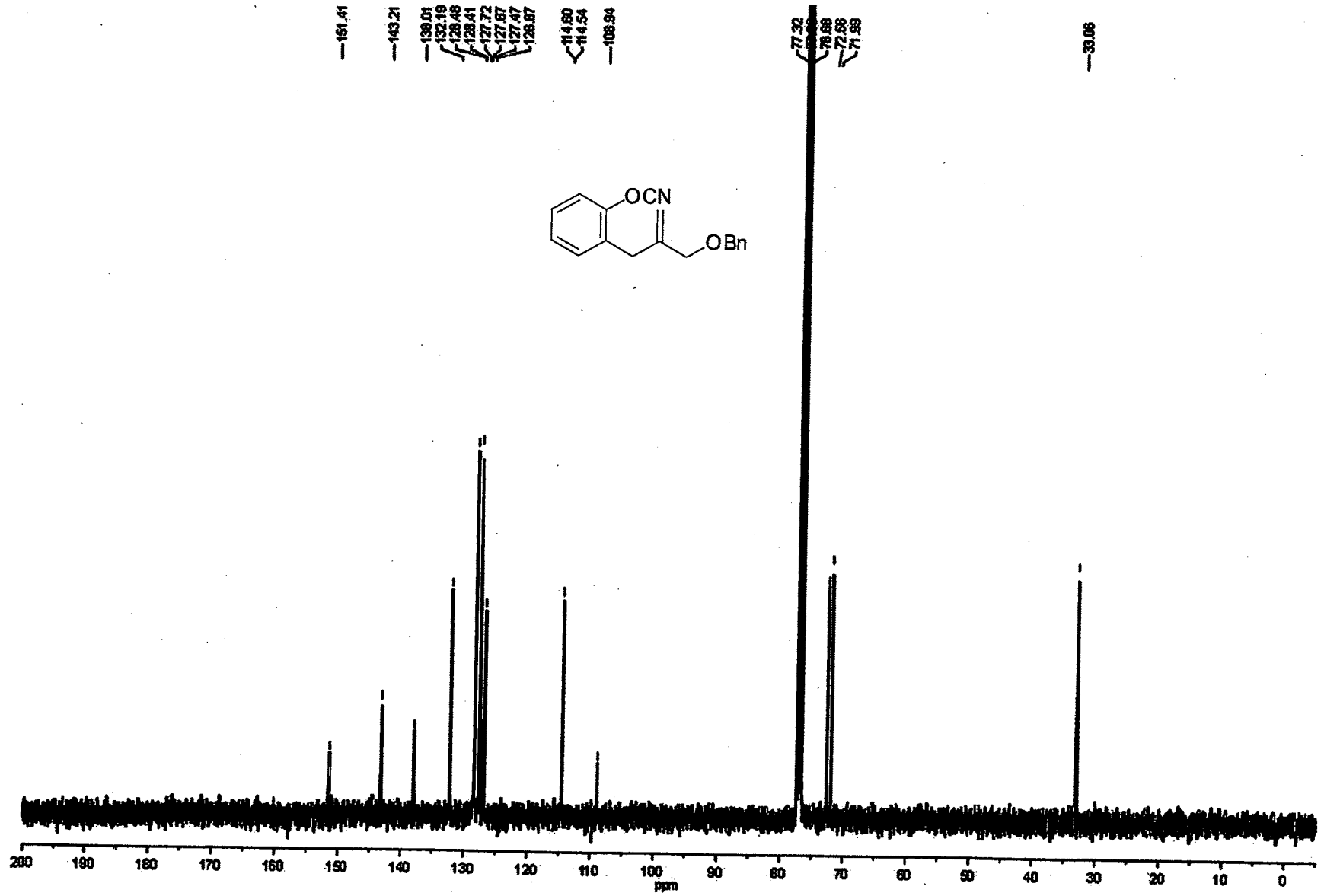
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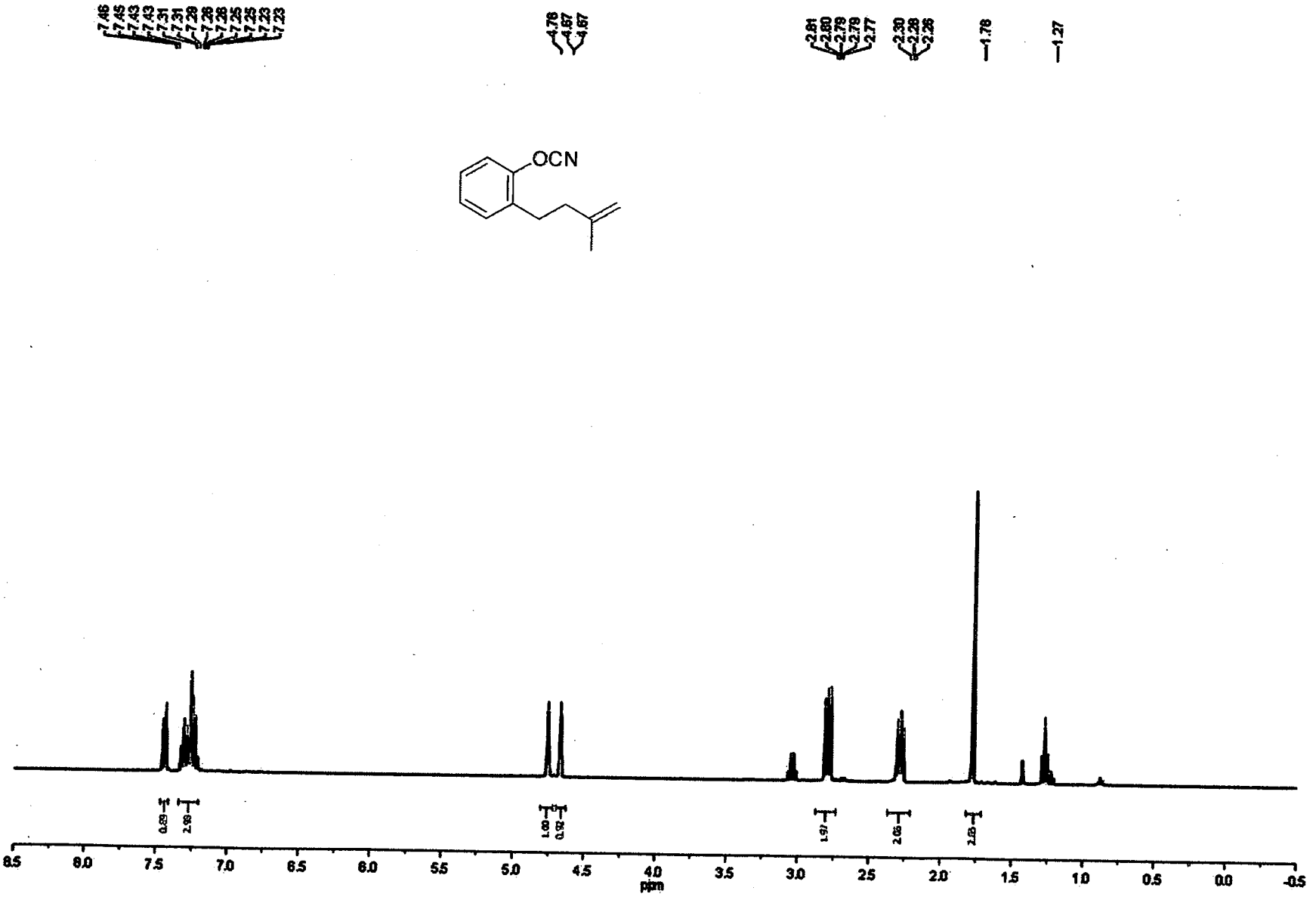
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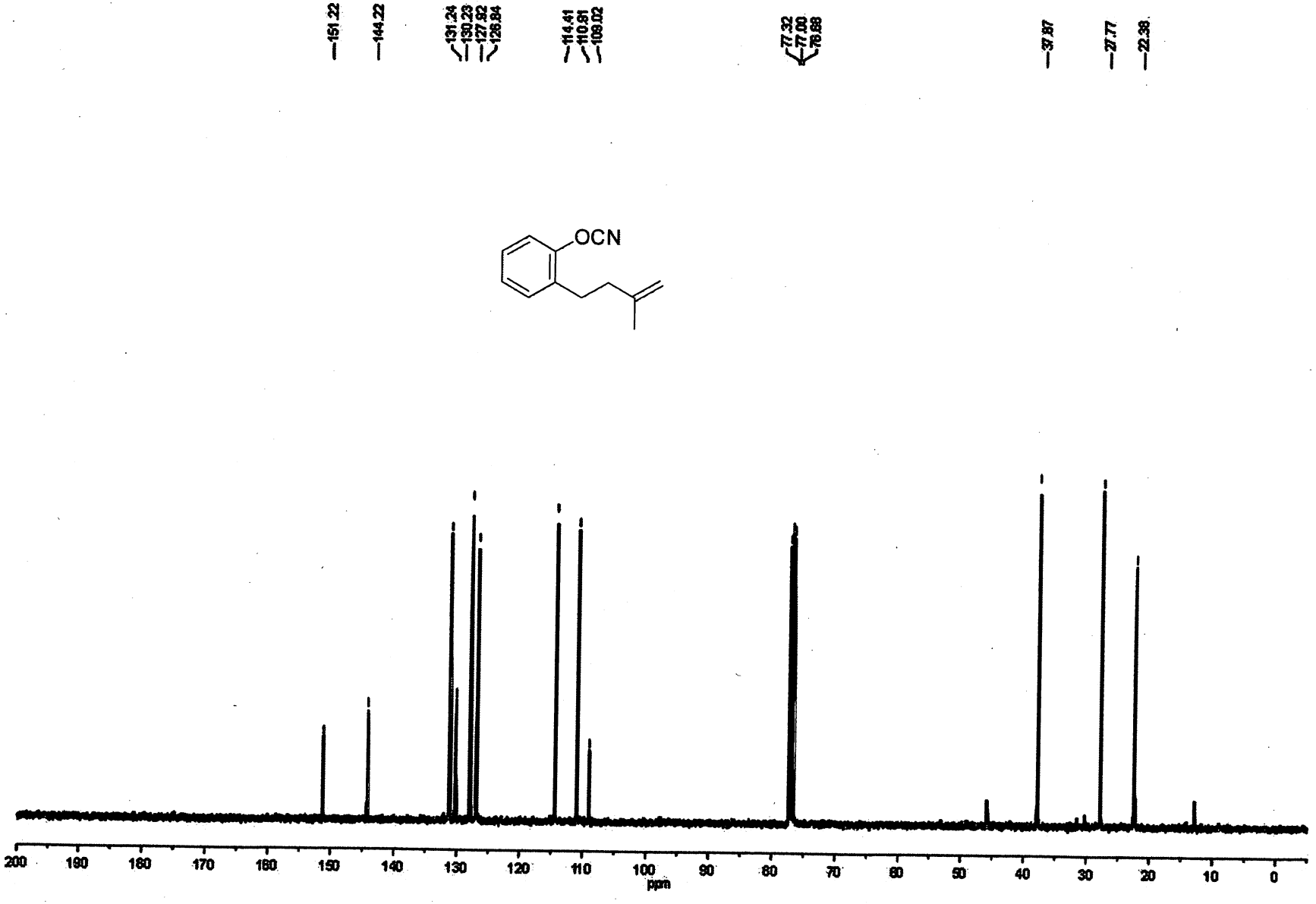
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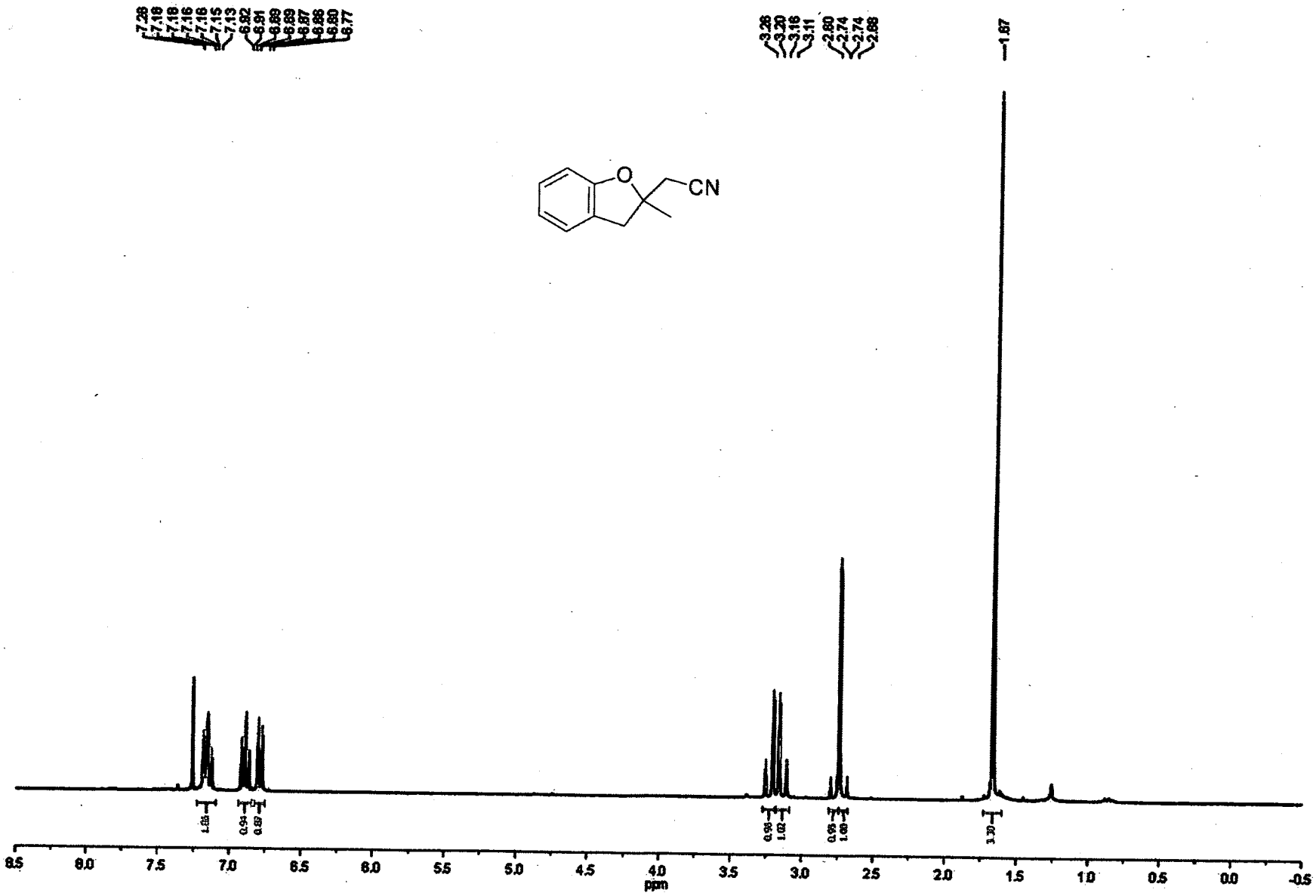
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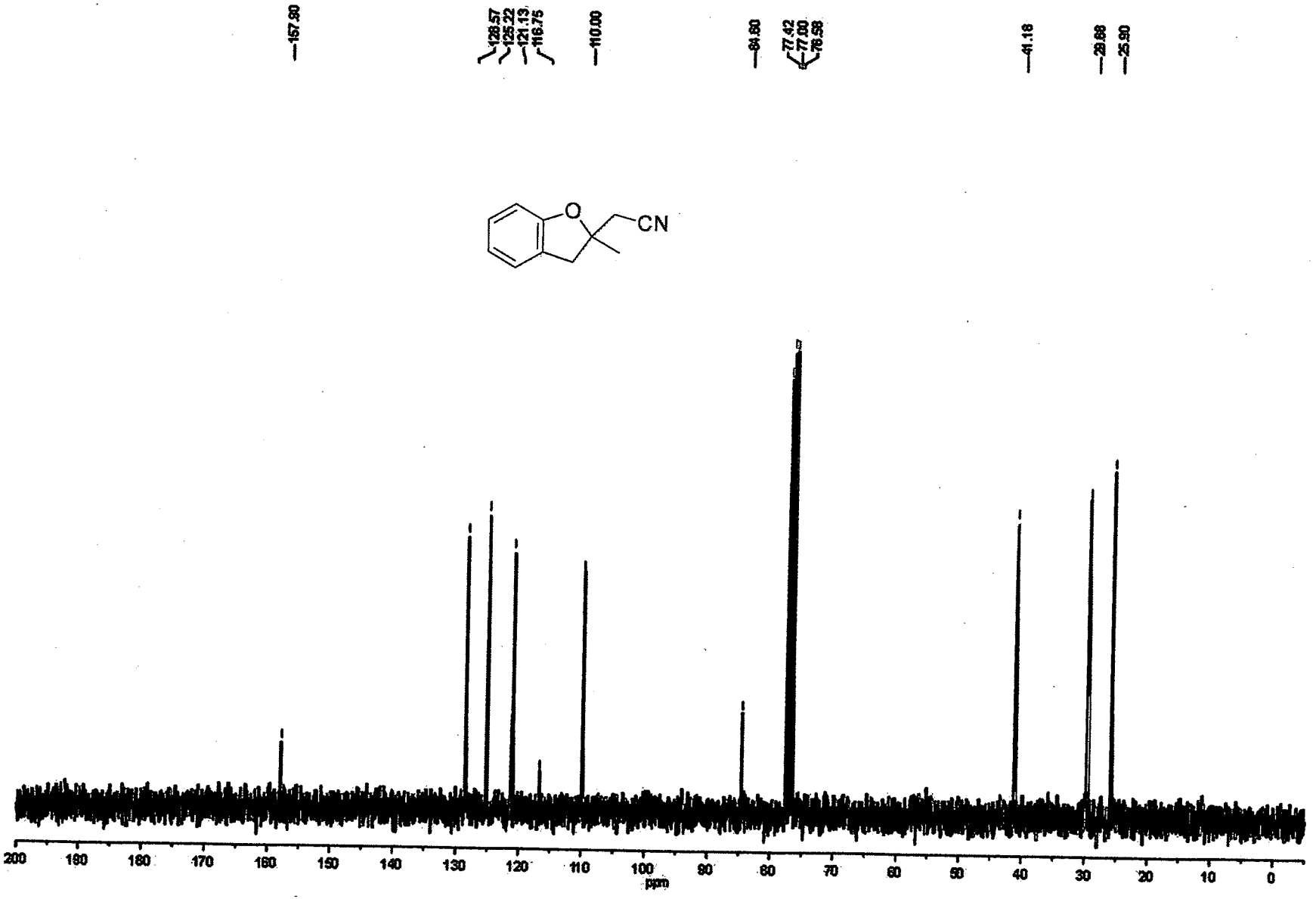
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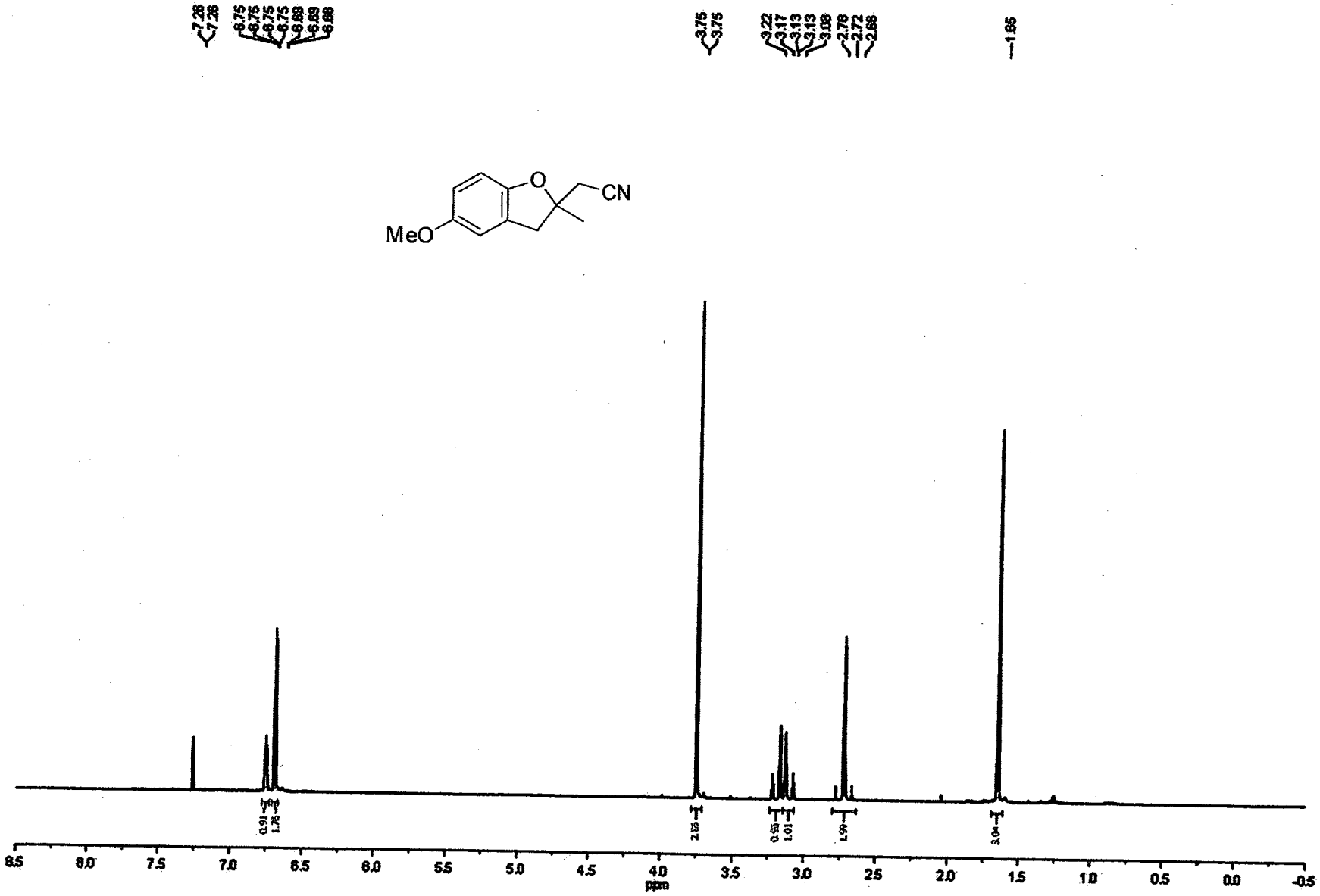
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3.13
3.08
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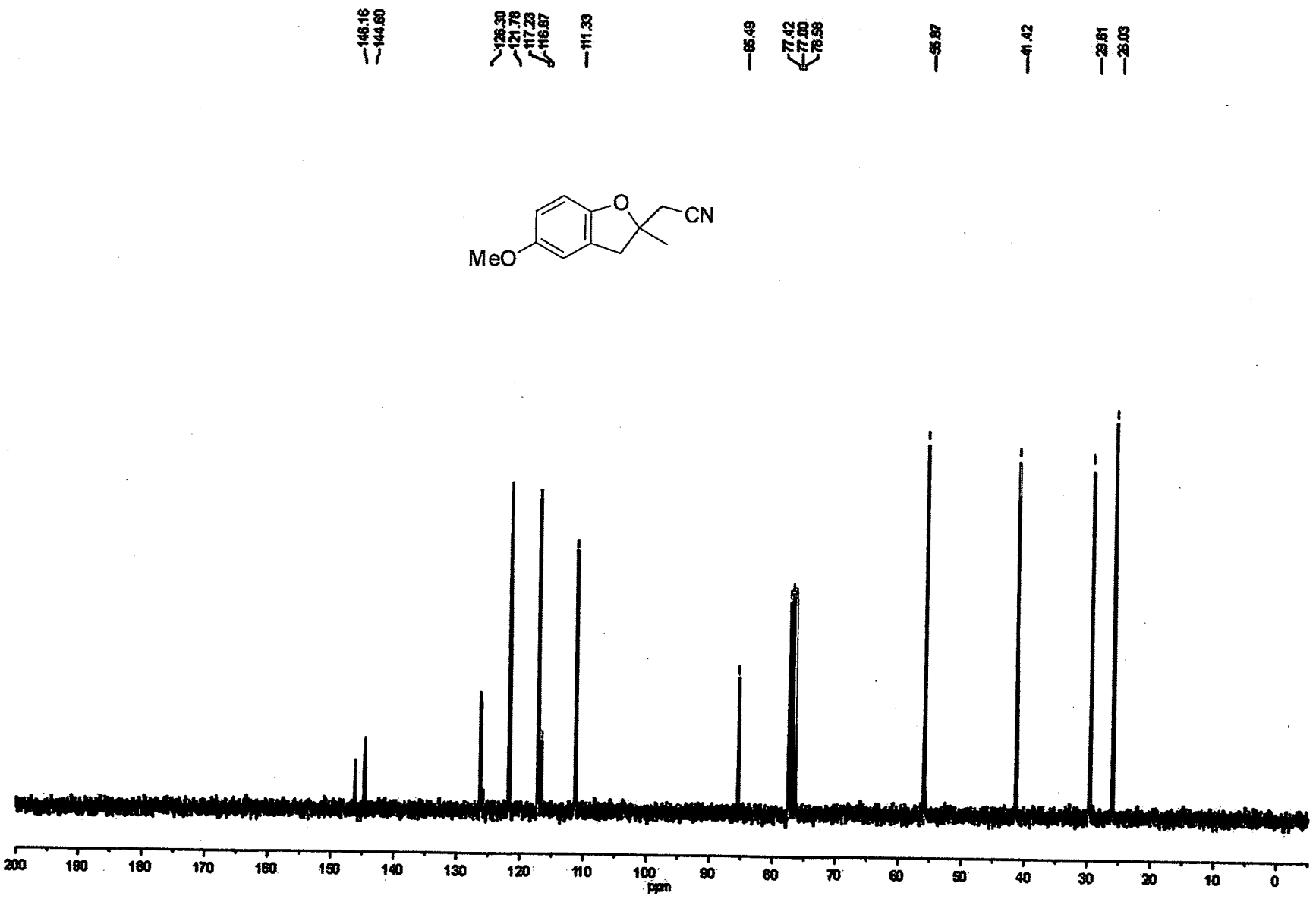
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28.03
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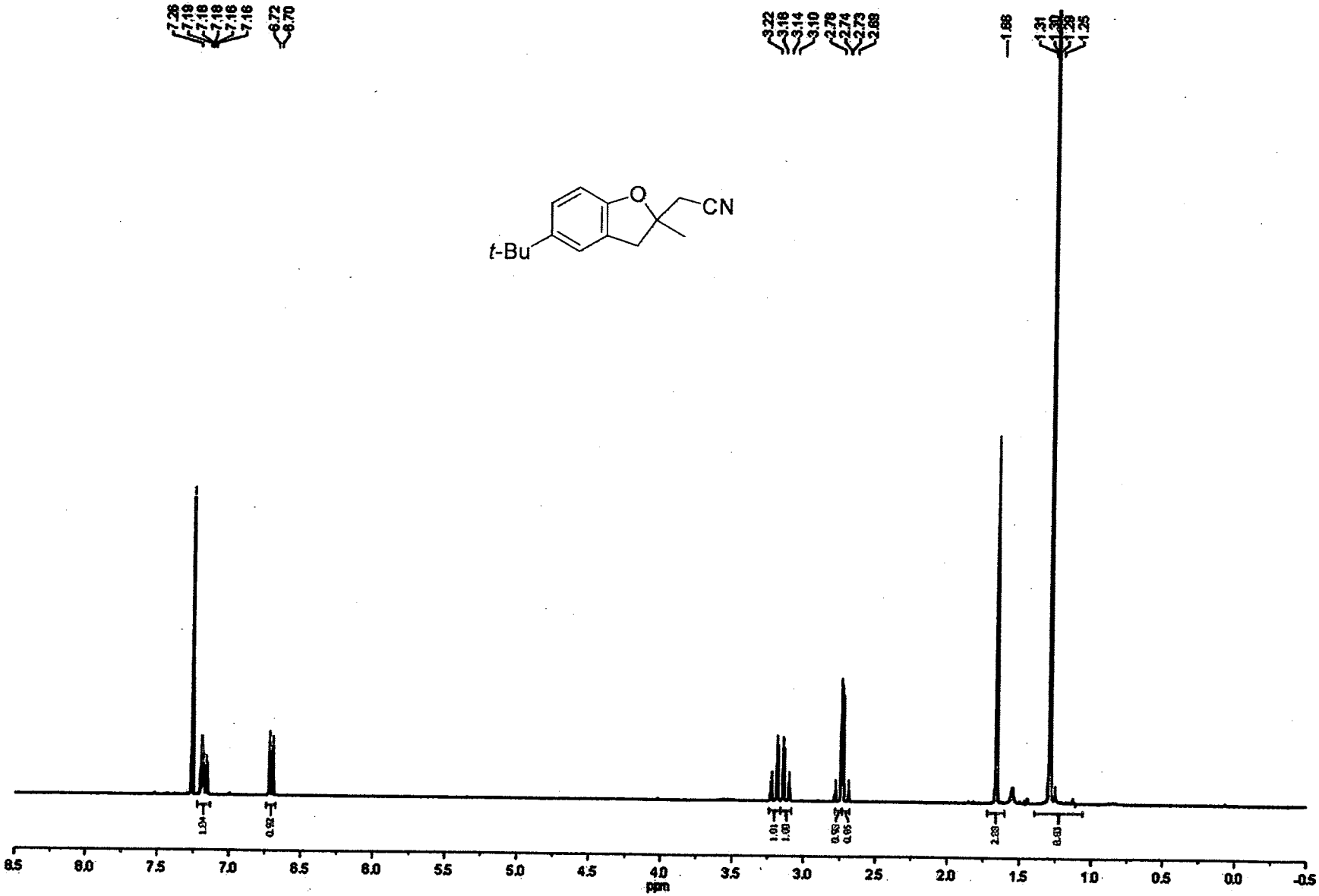
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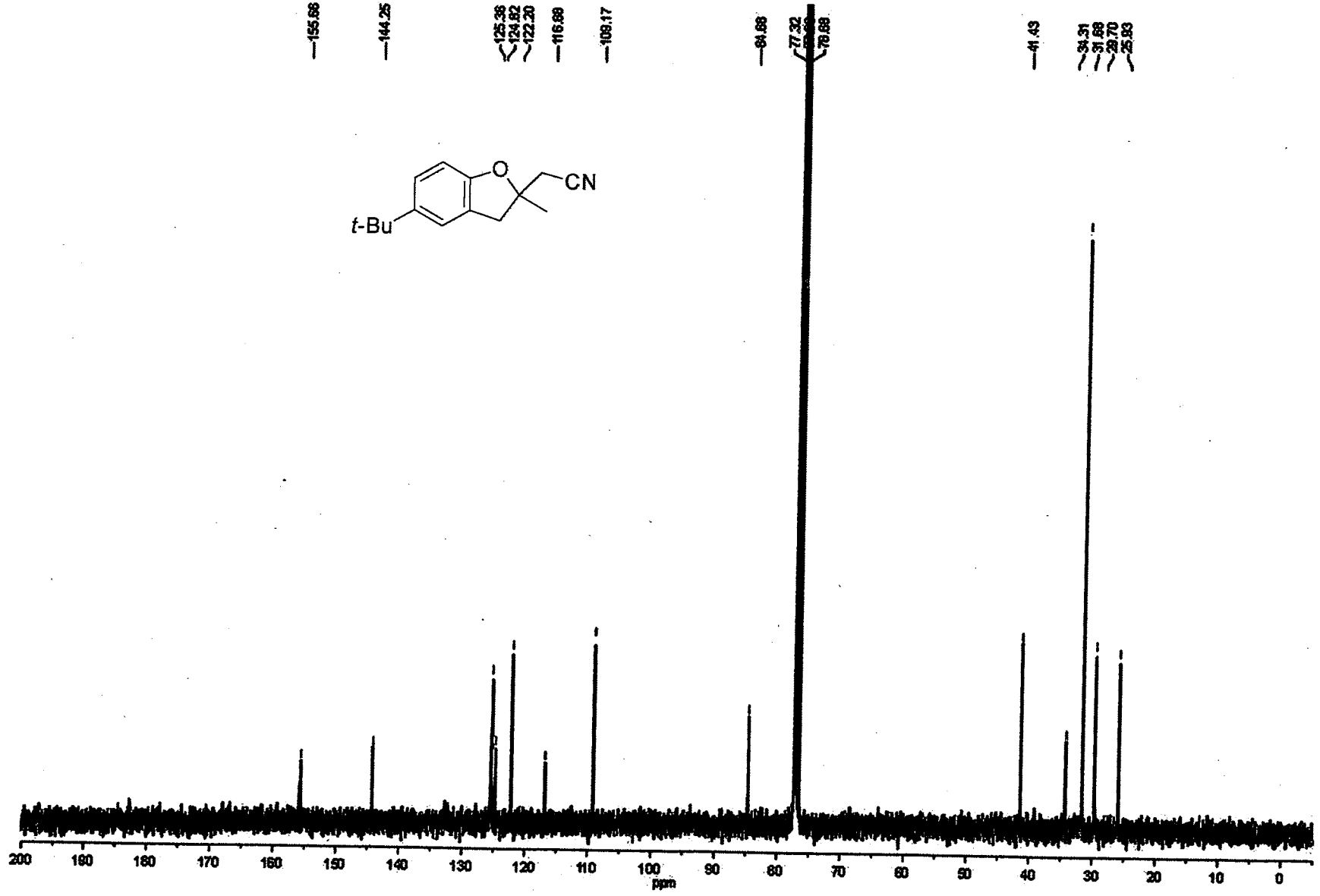
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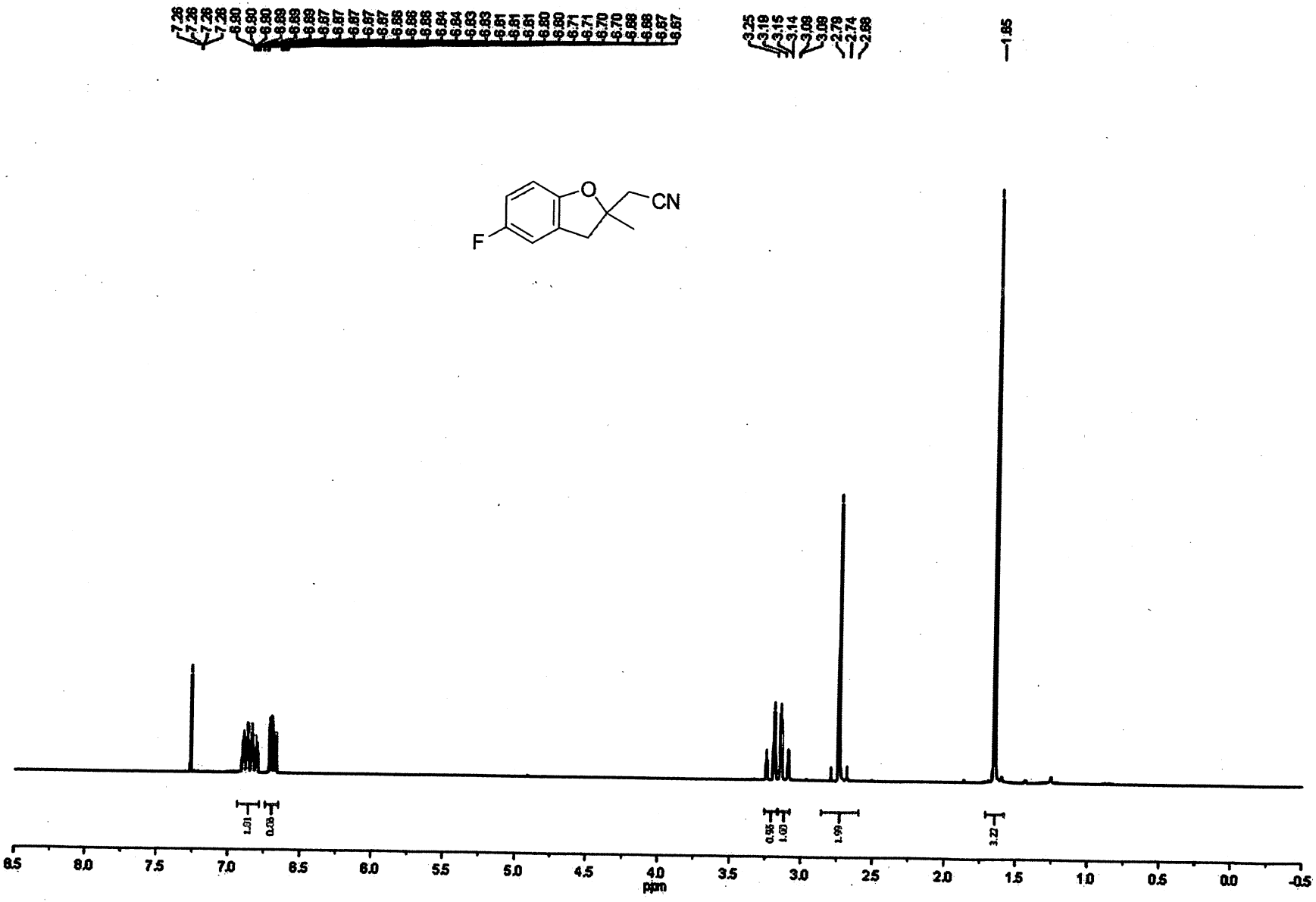
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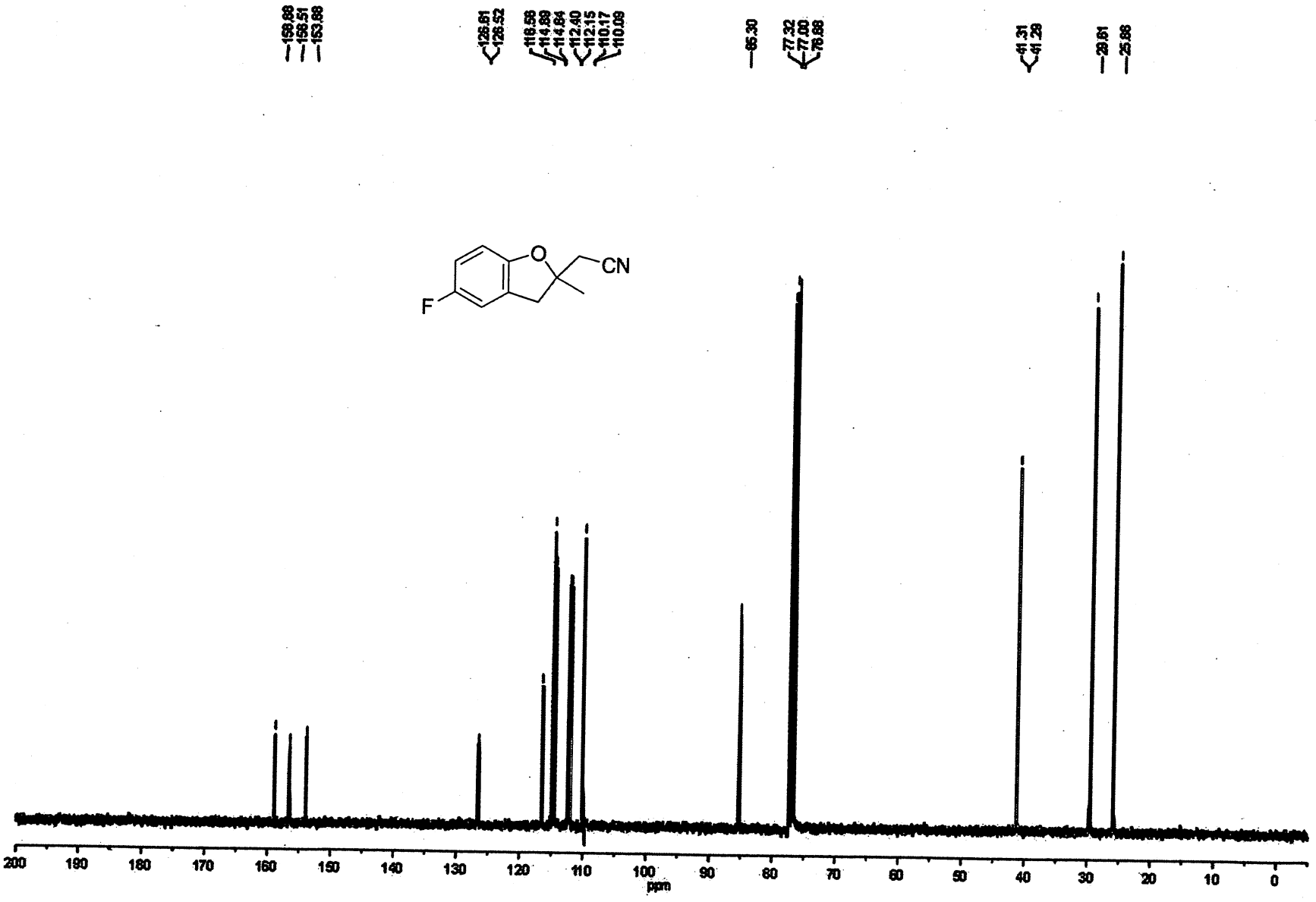
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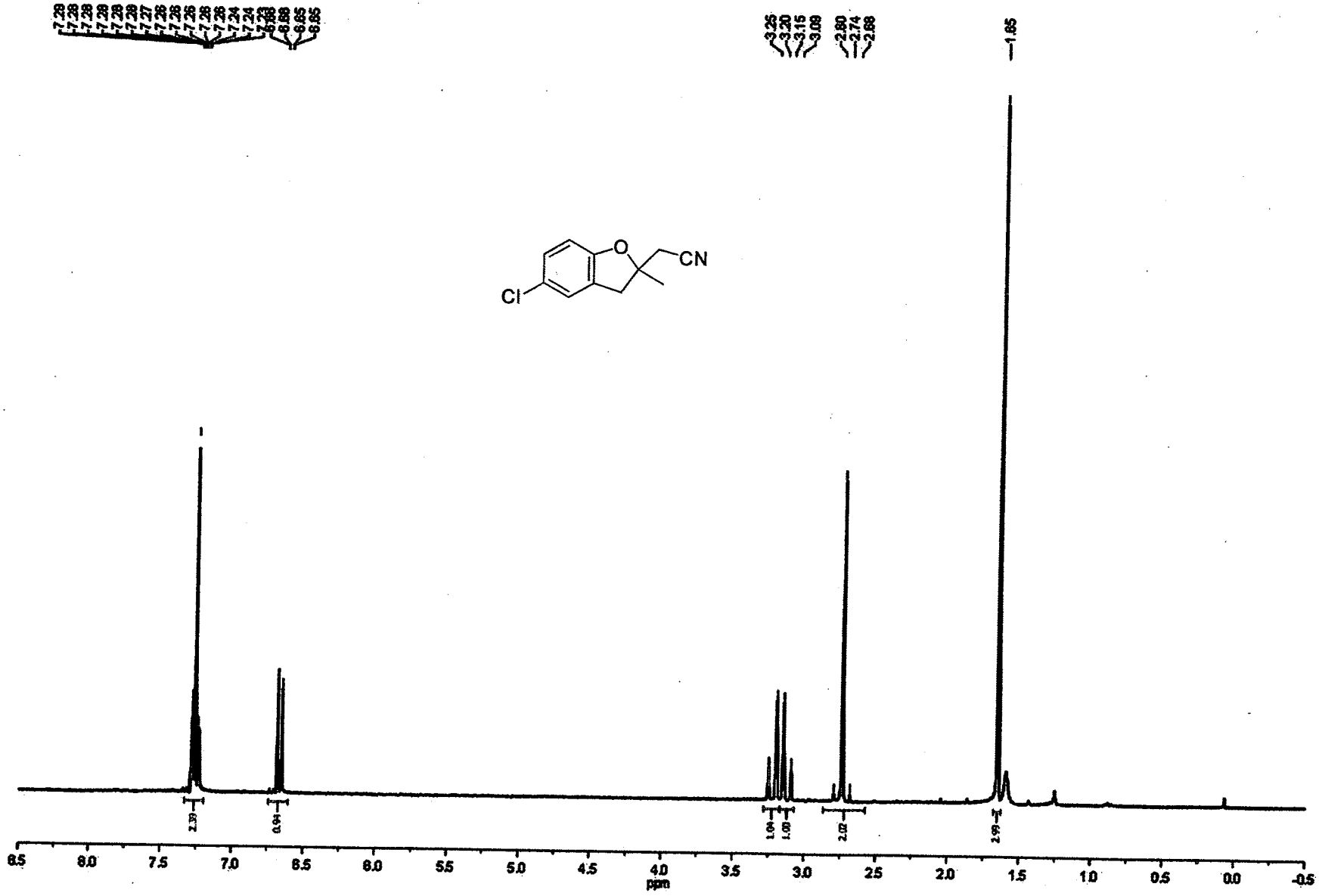
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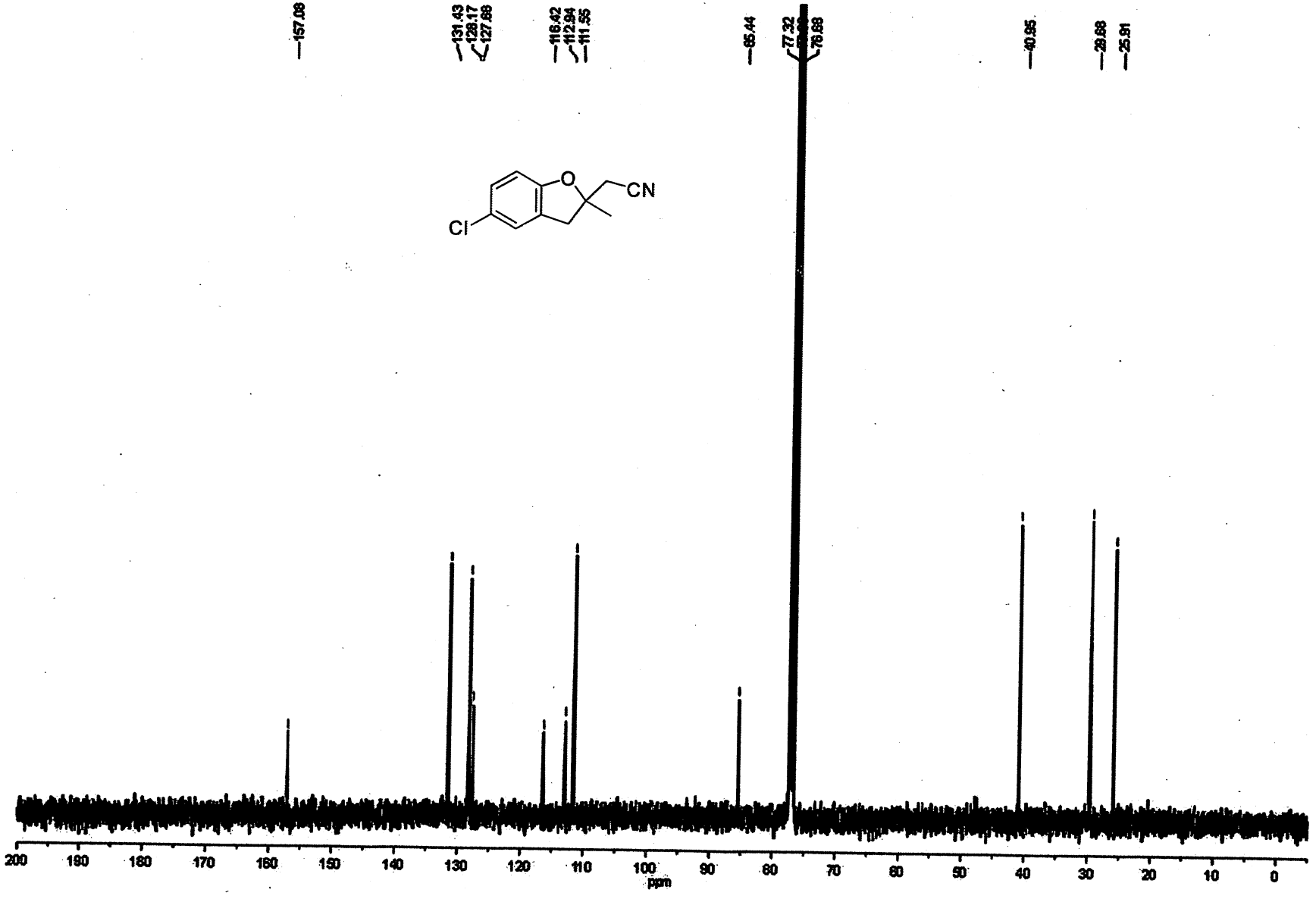
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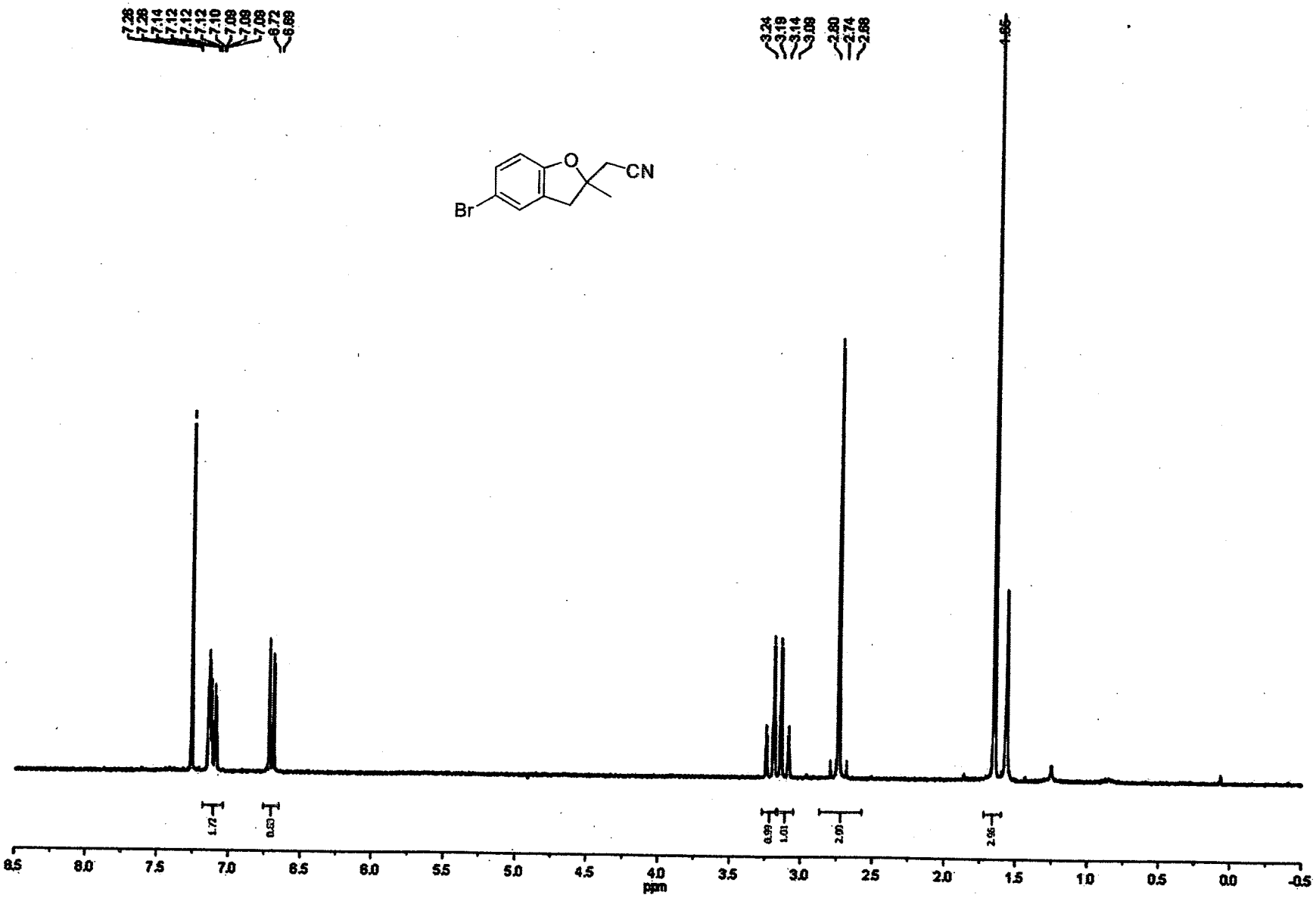
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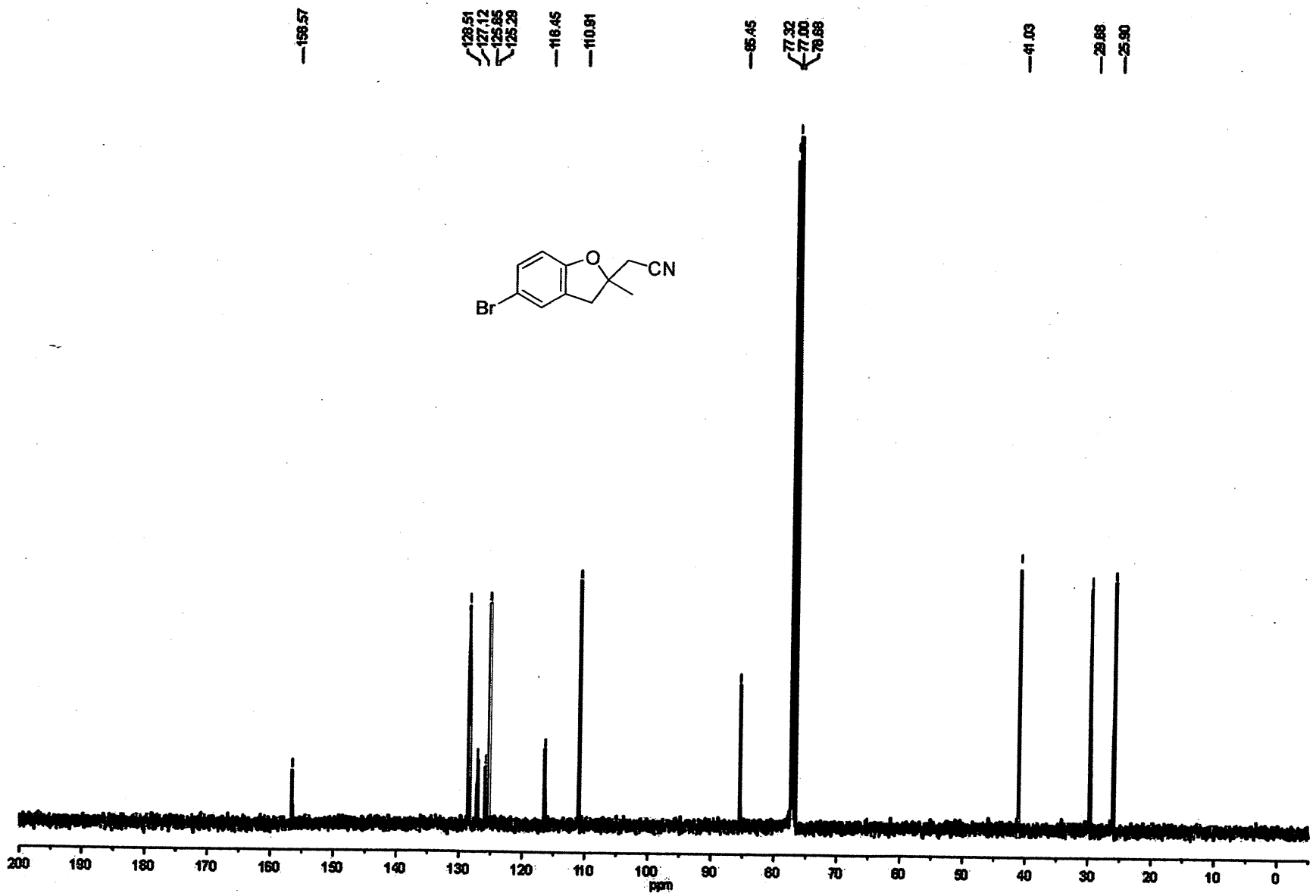
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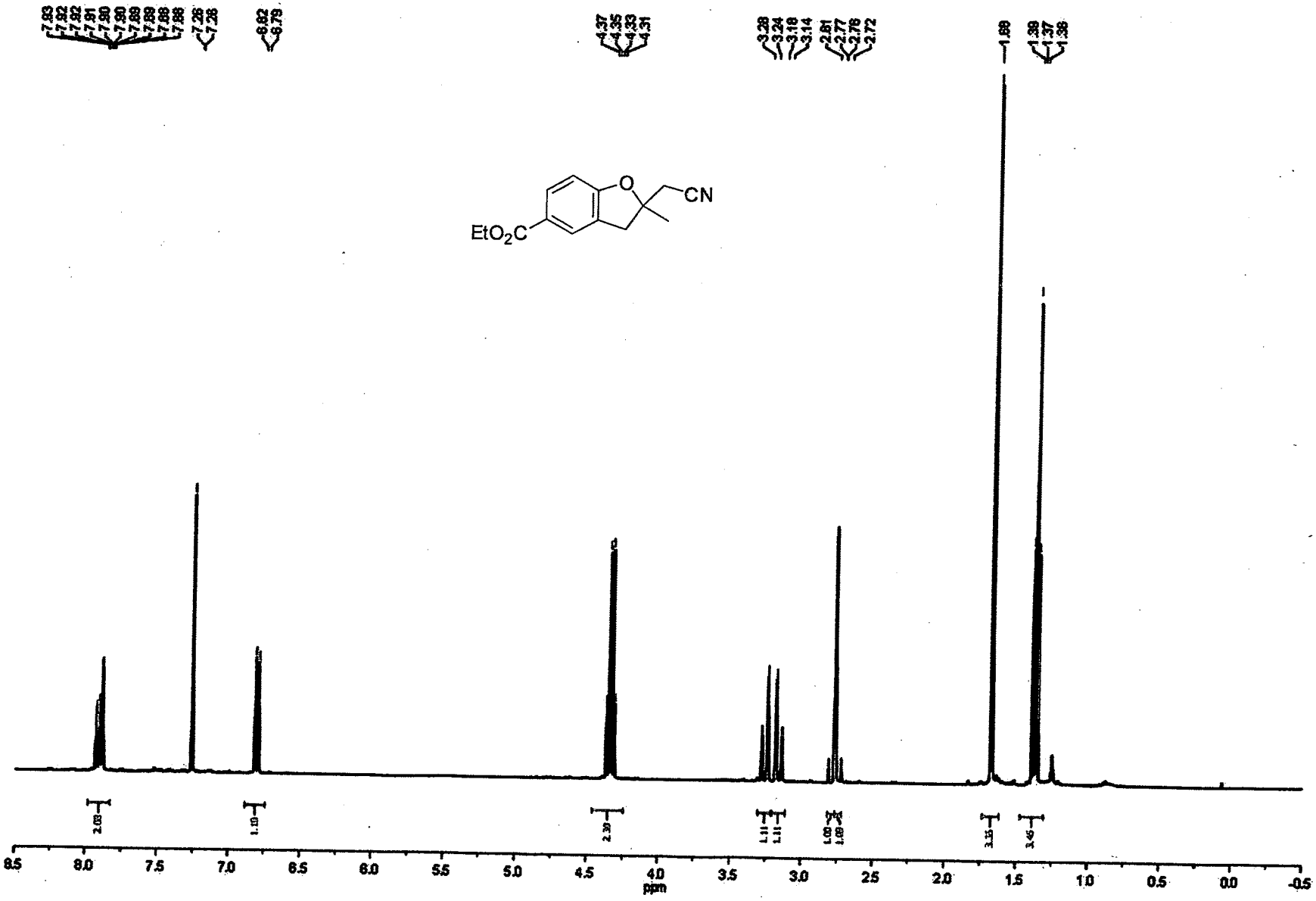
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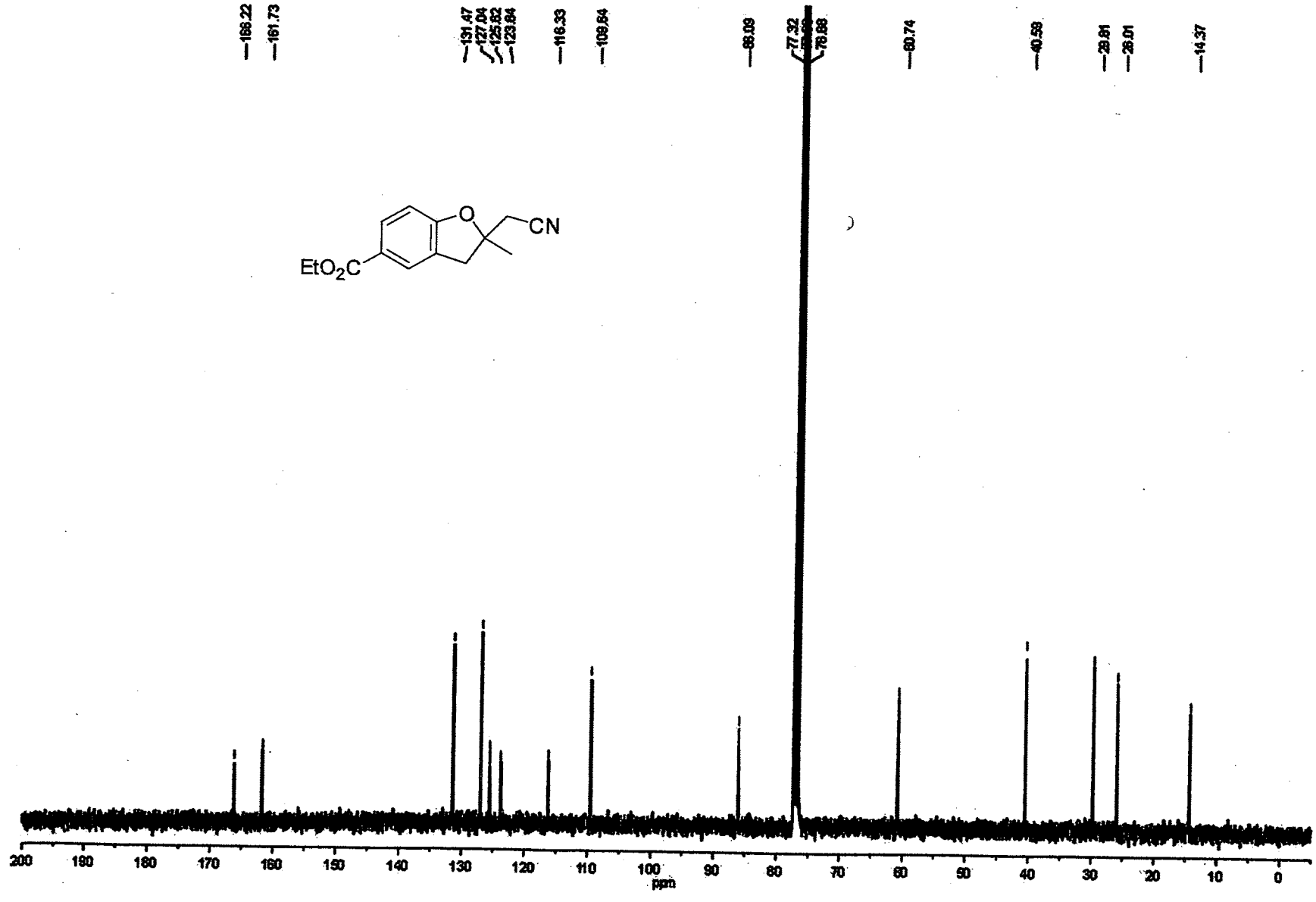
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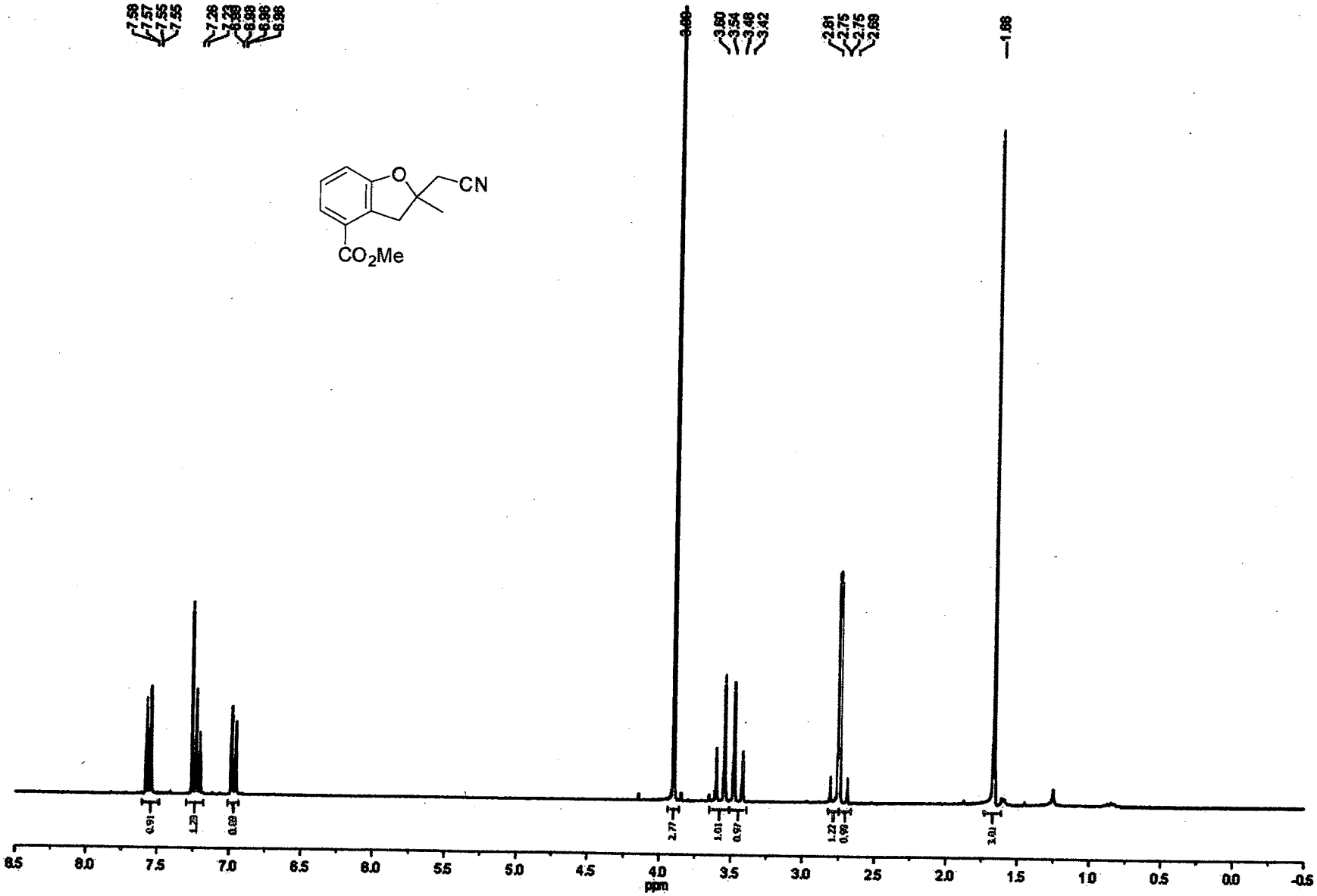
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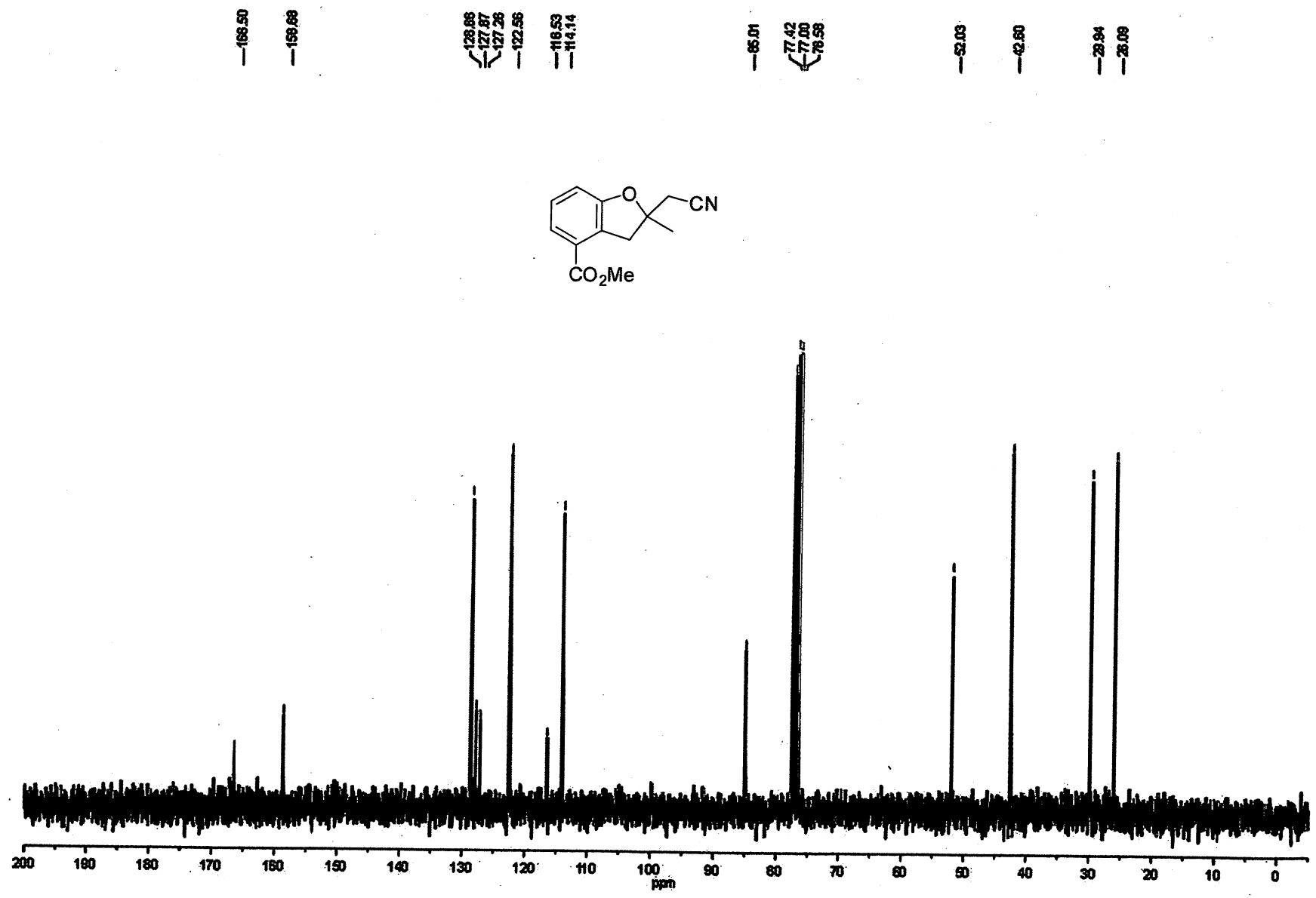
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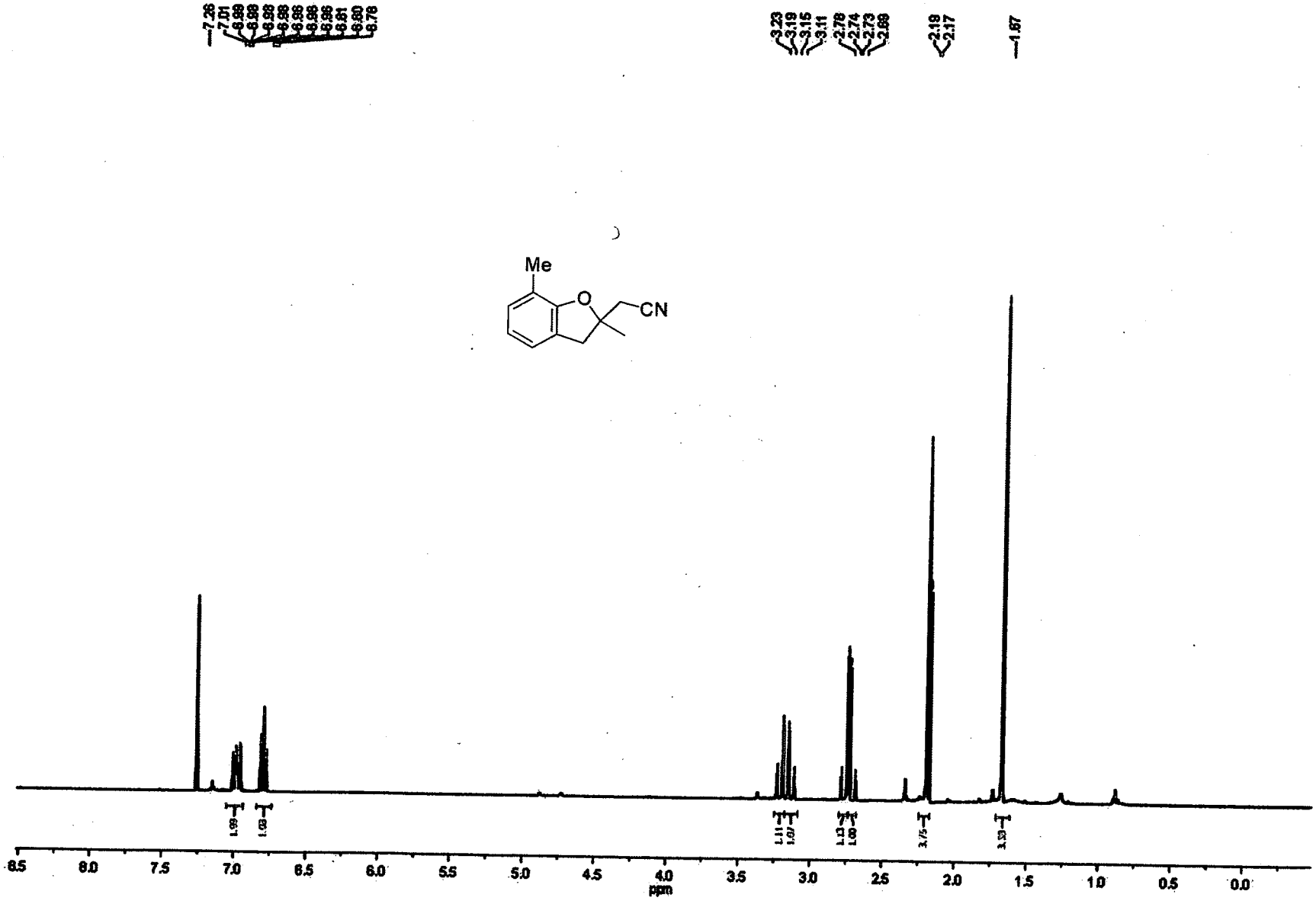
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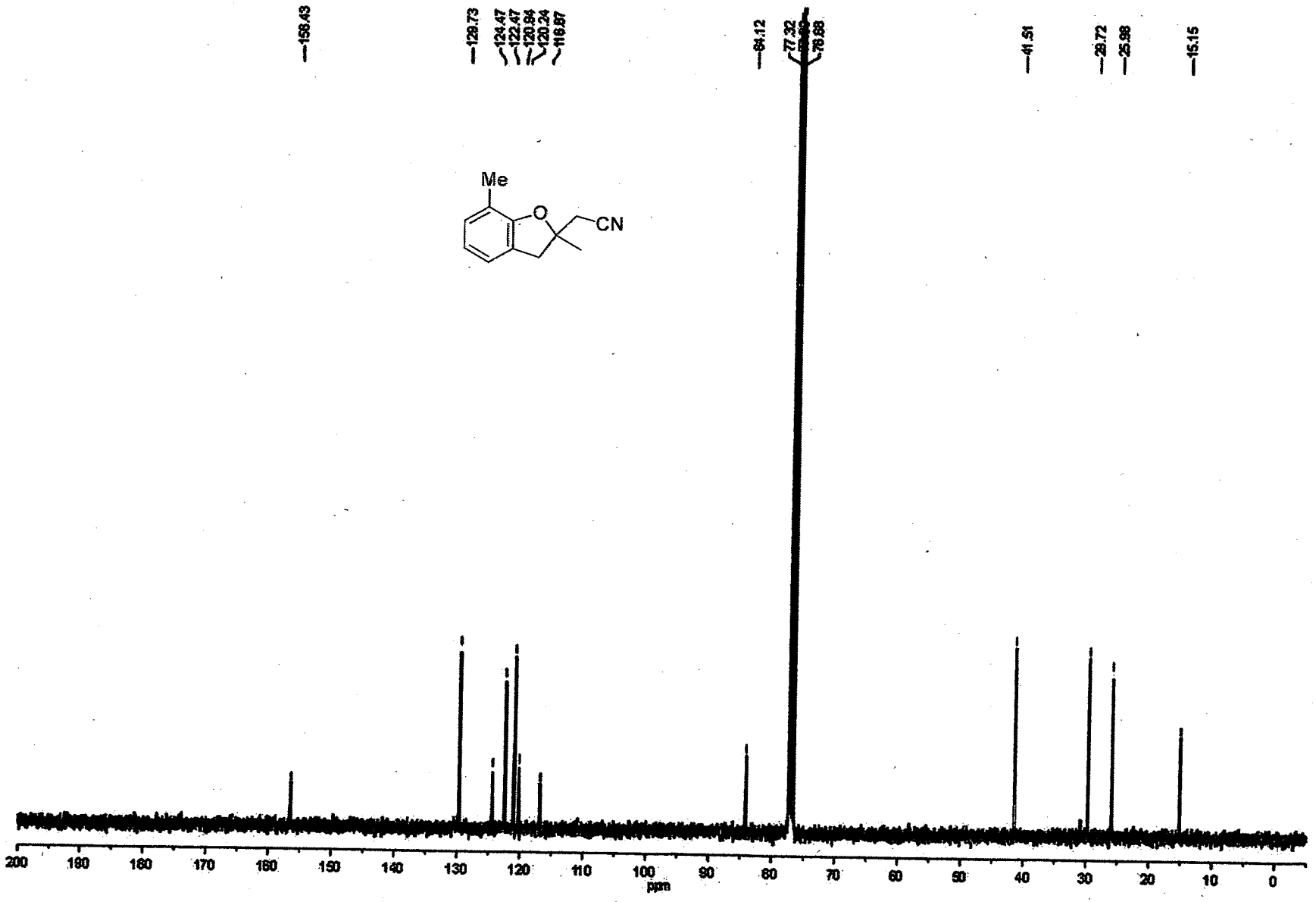
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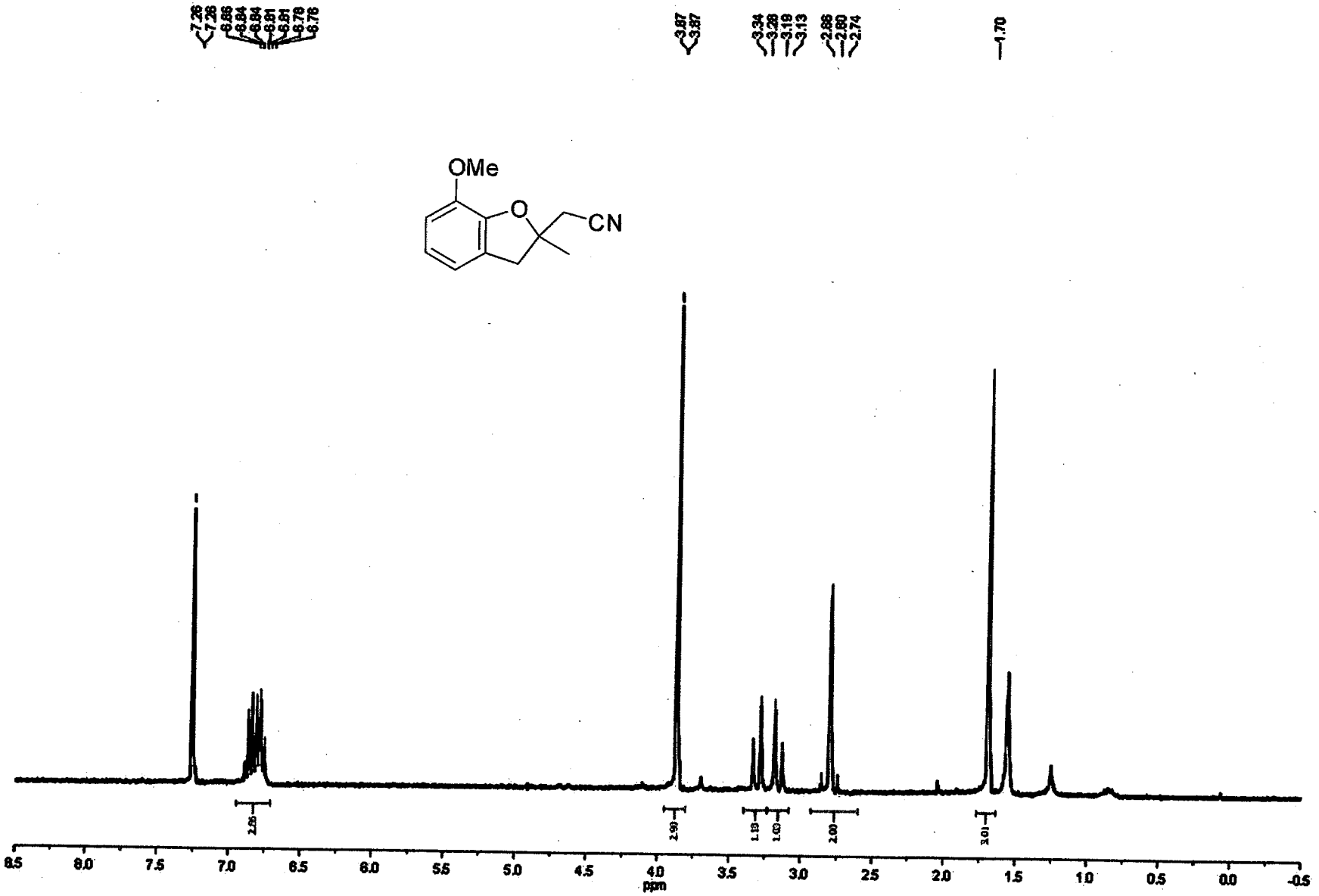
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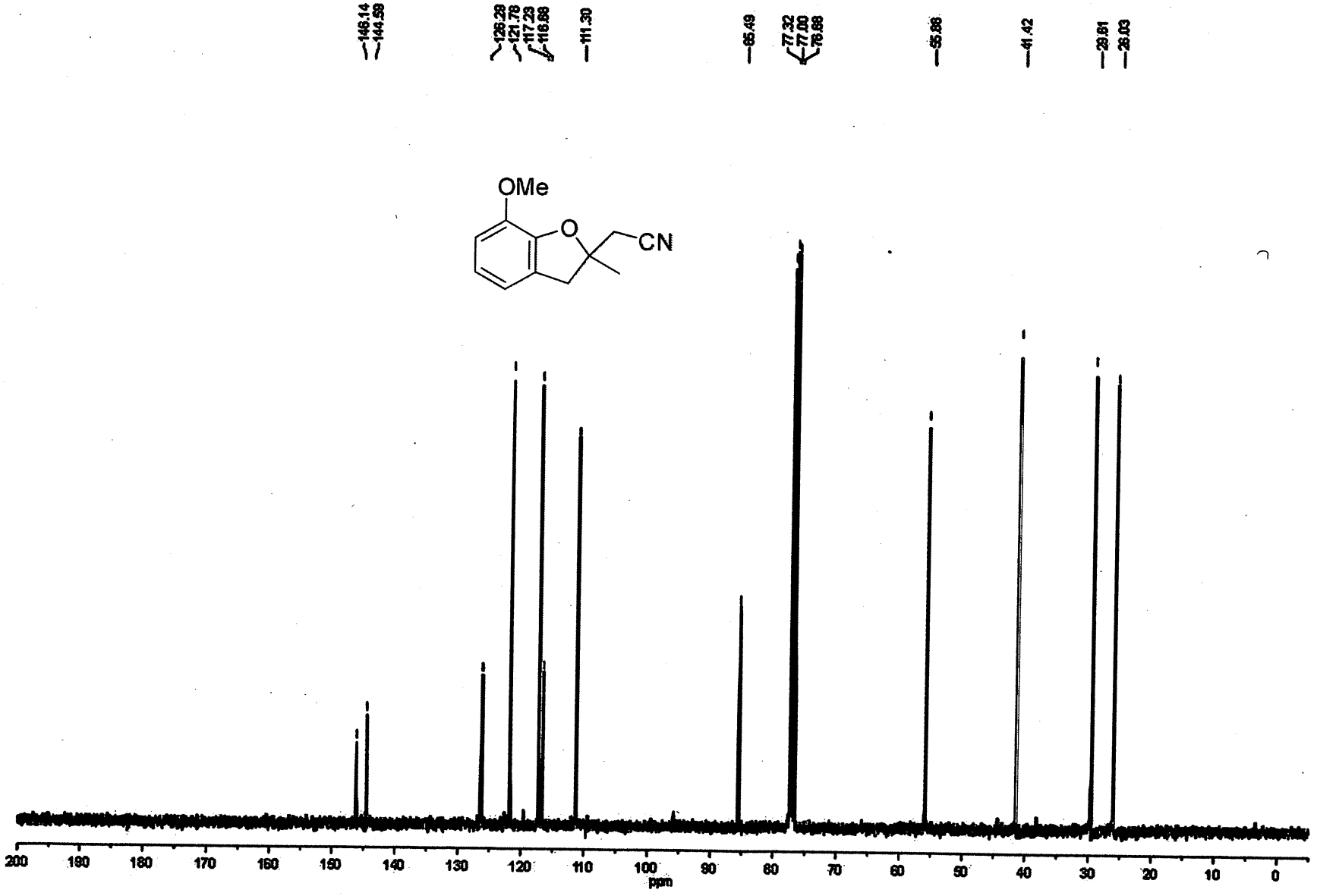
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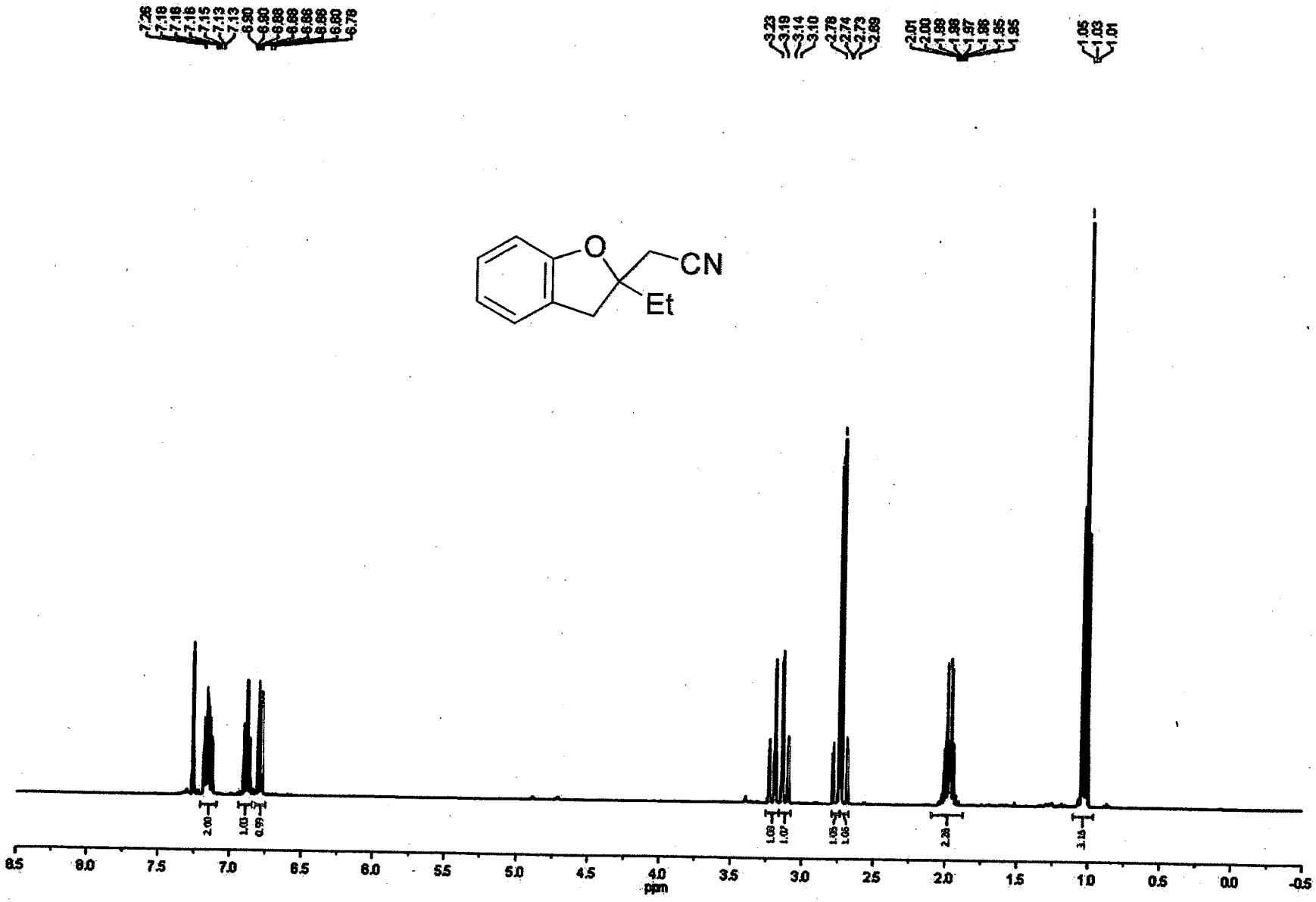
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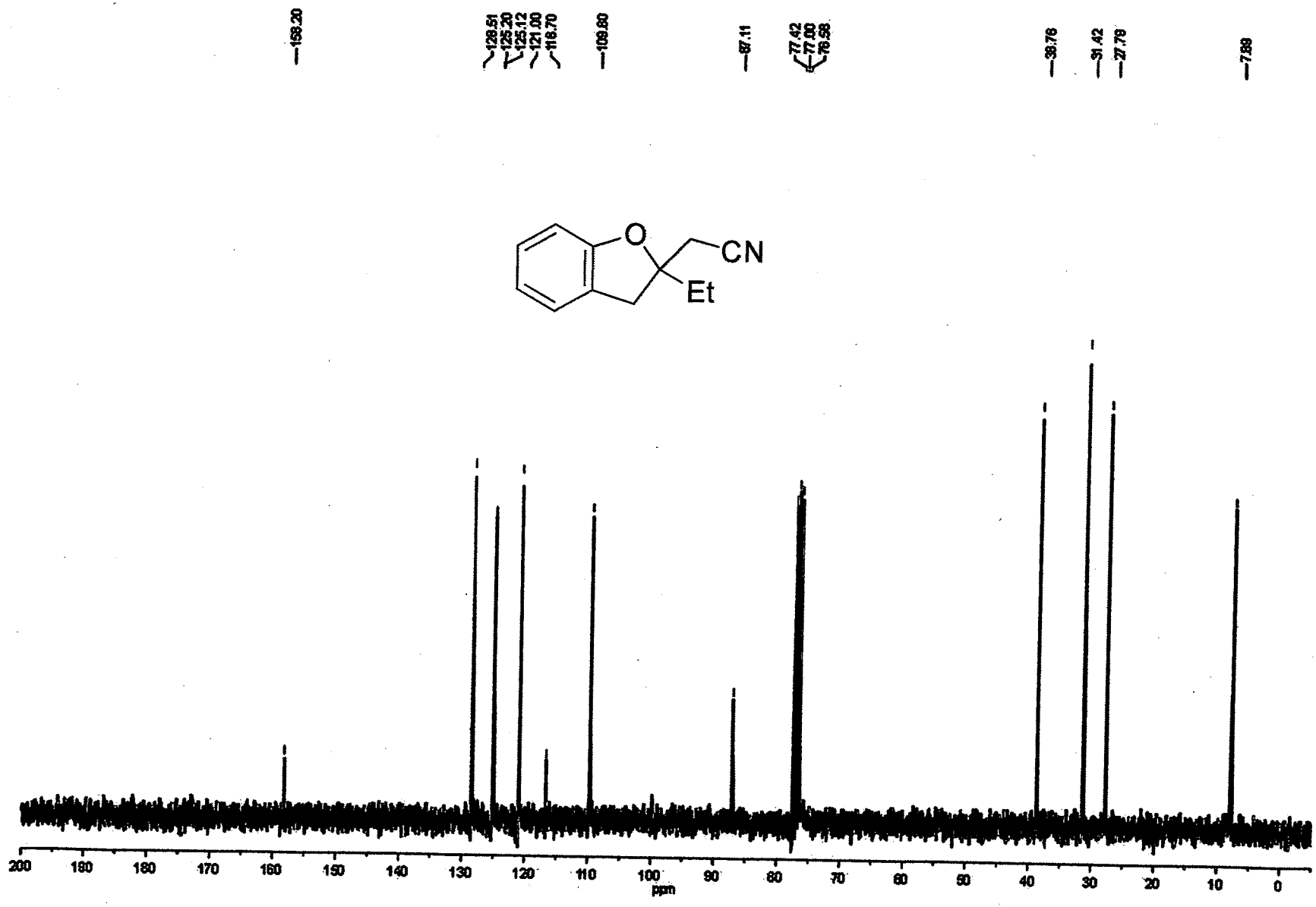
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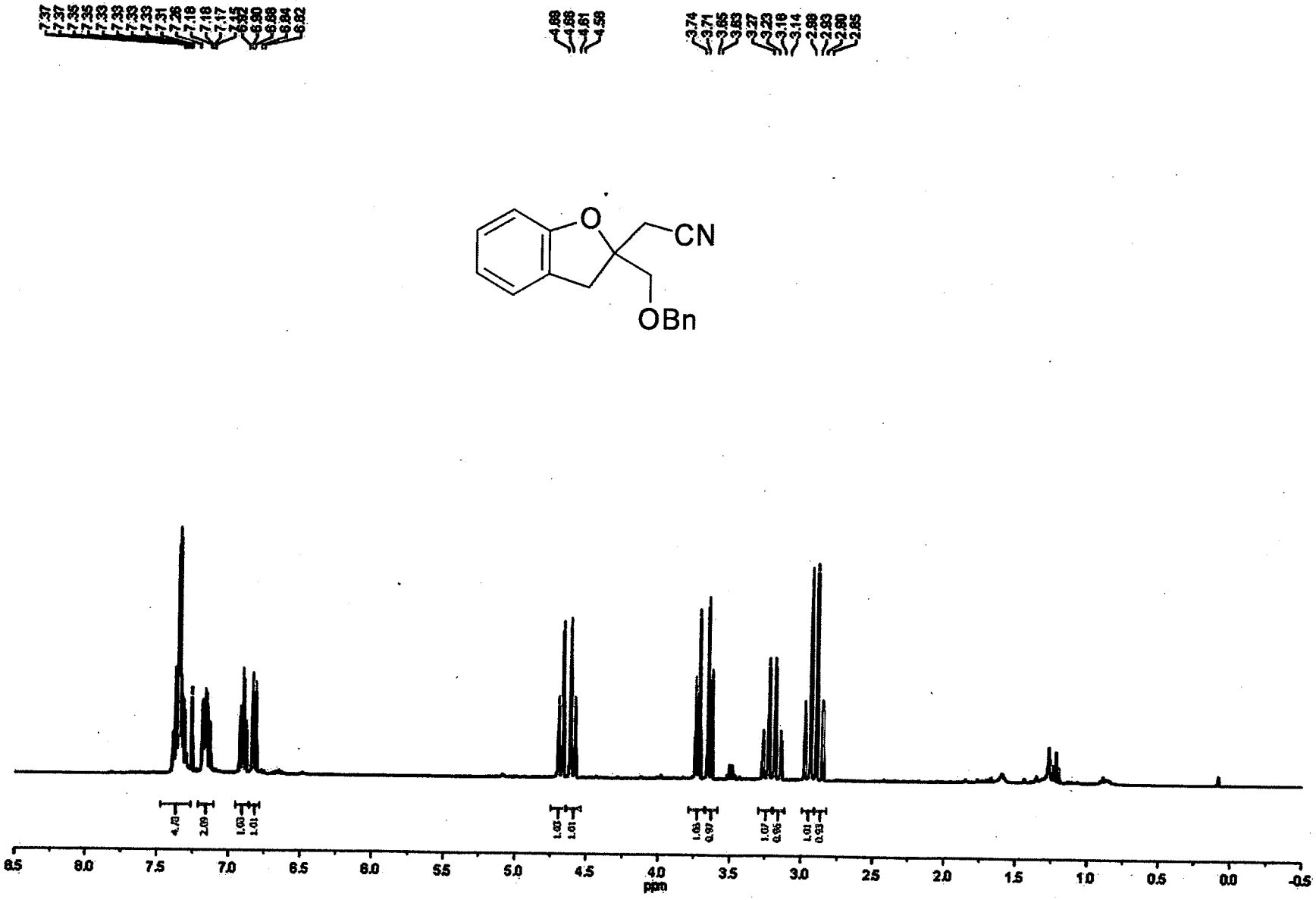
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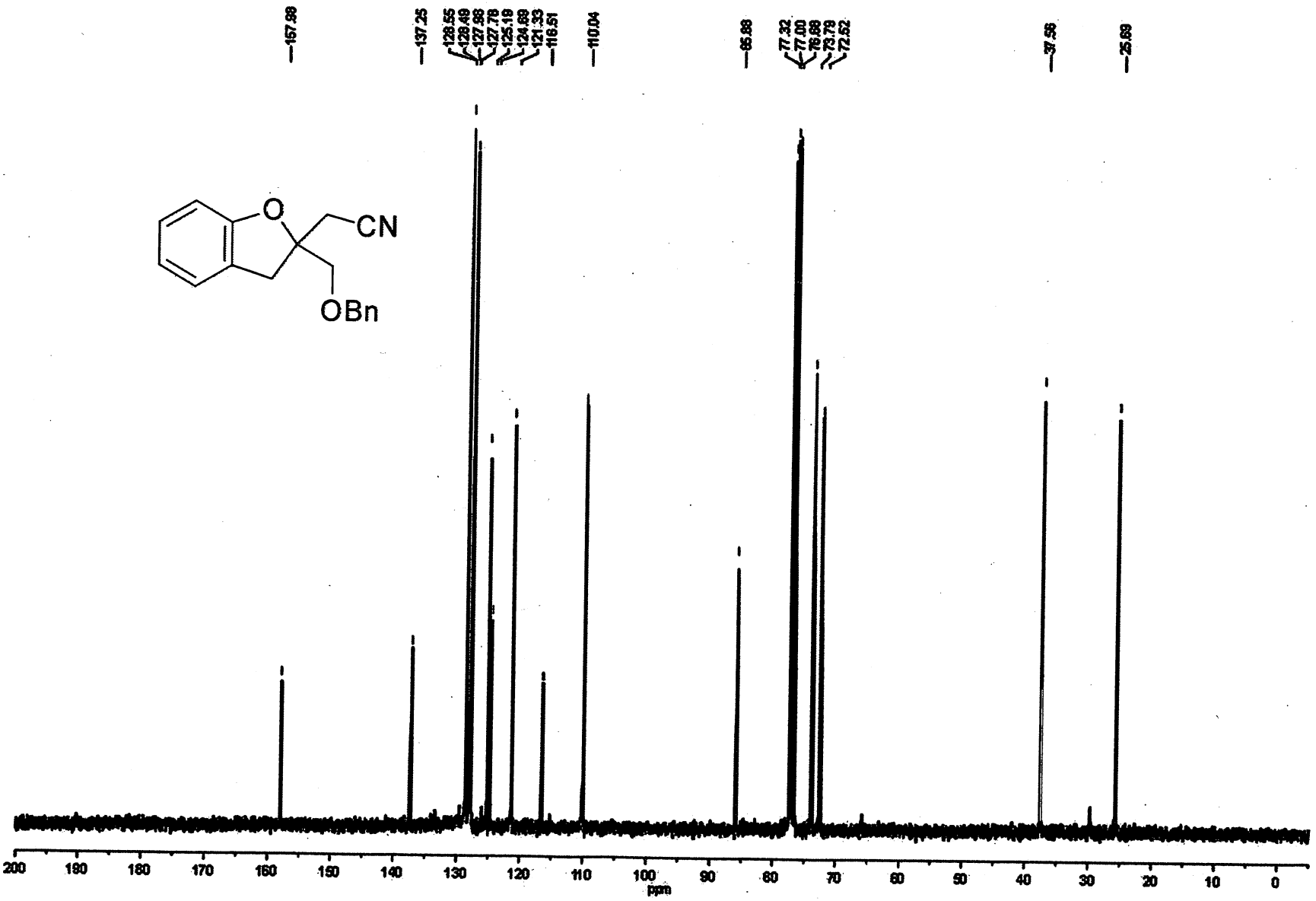
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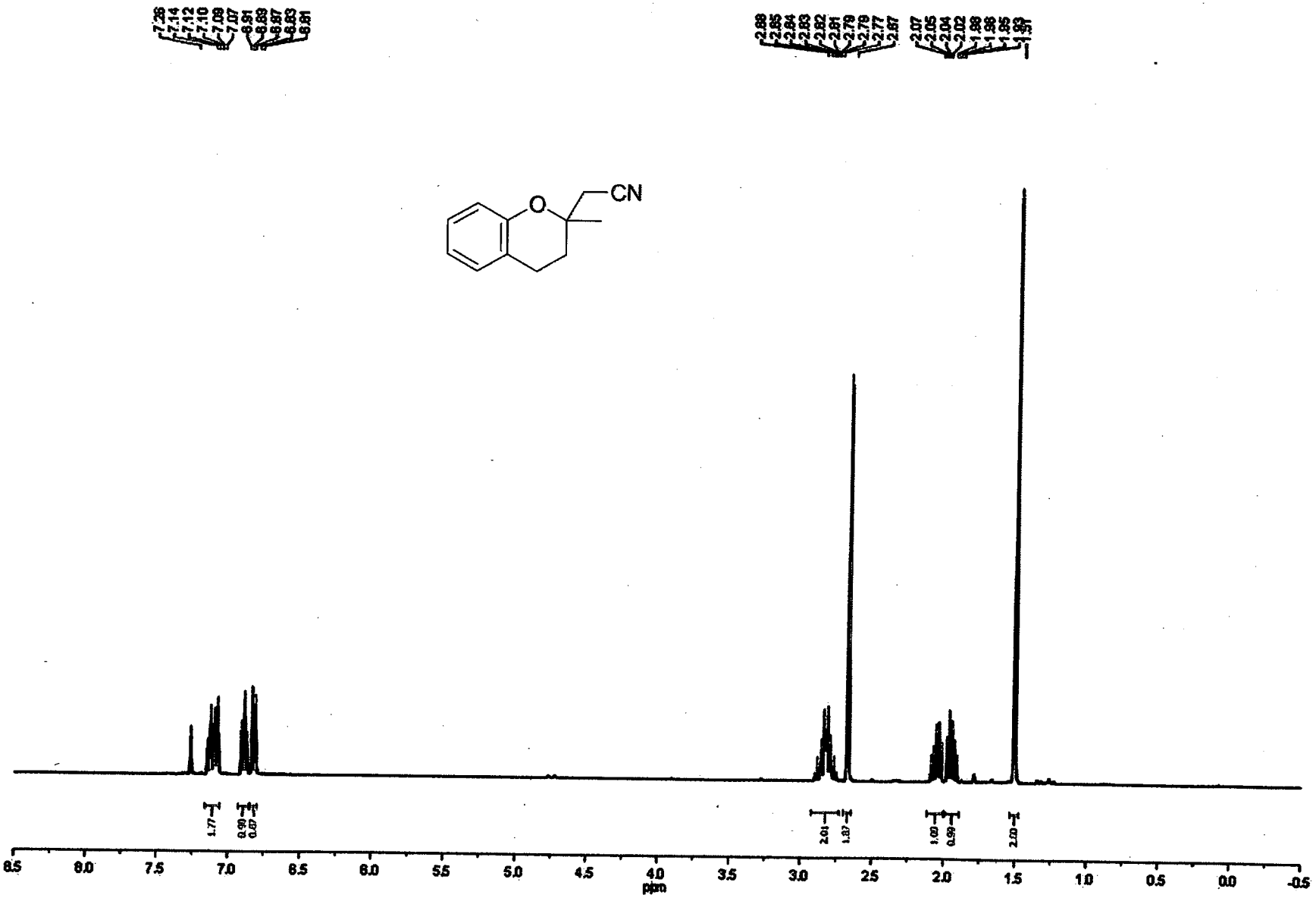
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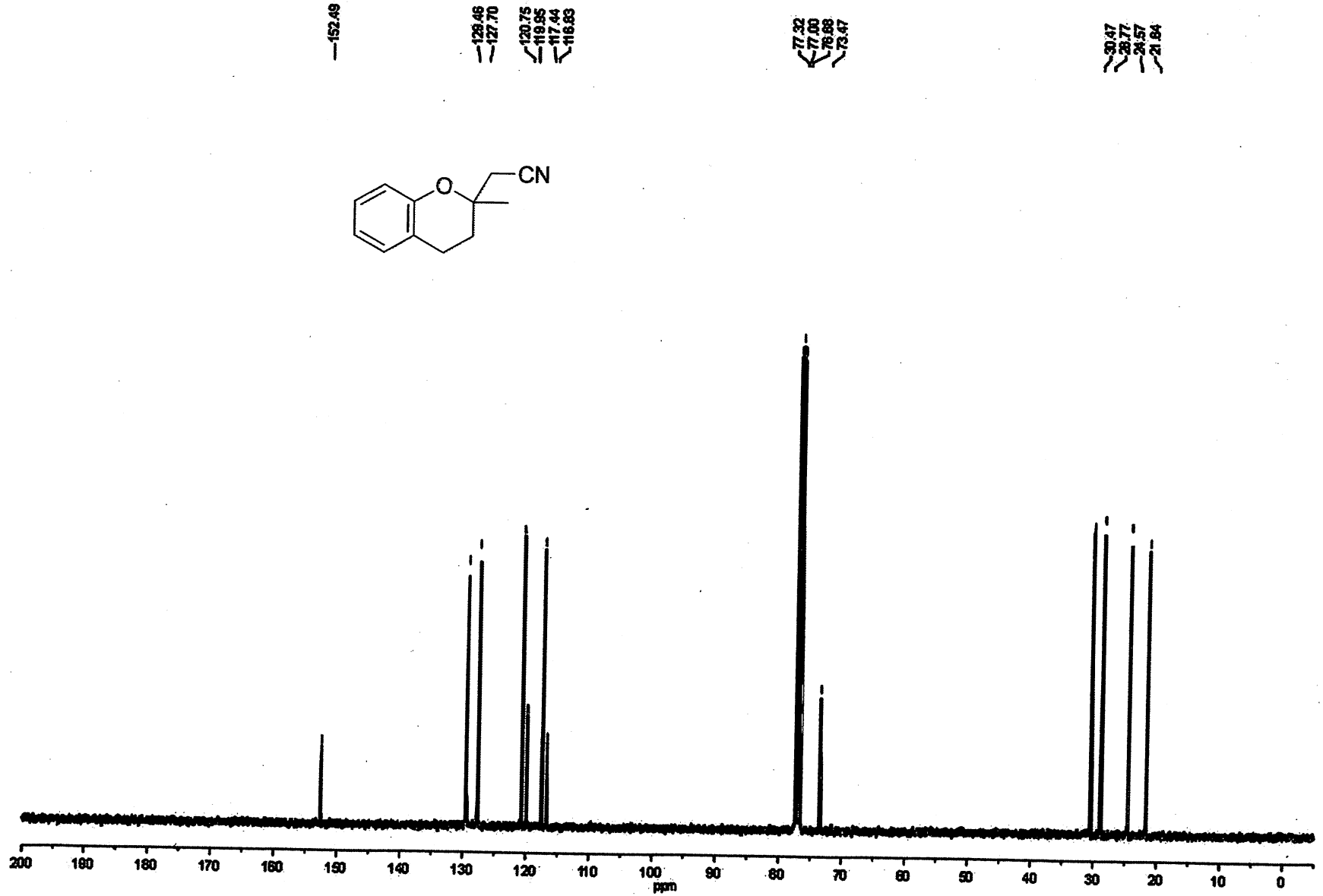
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