Supporting Information

Iodine-catalyzed and solvent-controlled selective electrophilic cyclization and oxidative esterification of *ortho*-alkynyl aldehydes

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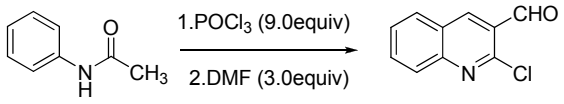
Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. Thin-layer chromatography was performed using commercially prepared 100-mesh silica gel plates, and visualization was effected with short wavelength UV light (254 nm) and a basic $KMnO_4$ solution [3 g of $KMnO_4$ + 20 g of K_2CO_3 + 5 mL of NaOH (5 %) + 300 mL of H_2O]. All melting points are uncorrected. Mass spectra were recorded on a Finnigan TSQ700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA). High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV.

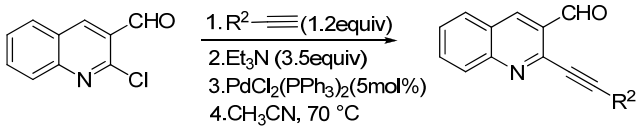
Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of ethyl ether, hexanes, ethyl acetate, and CH_2Cl_2 were purchased from Merk Chemical Co. 2-Bromobenzaldehyde, terminal alkynes, Et_3N and The palladium salts were purchased from Aldrich Chemical Co., Inc.

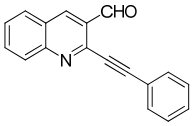
Preparation of starting materials:

(1). **2-chloroquinoline-3-carbaldehydes**[1]: They were prepared by the reported procedure.[1]

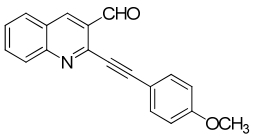


(2)**.2-(alkynyl)quinoline-3-carbaldehydes**[2]: They were prepared by the Sonogashira coupling reaction of 2-chloroquinoline-3-carbaldehyde with various terminal alkynes.[2] All commercially available compounds were used as received.

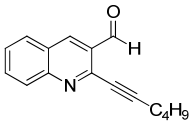




2-(phenylethynyl)quinoline-3-carbaldehyde (1a). The product was obtained as a white solid- mp 122-124 °C : ^{1}HNMR (300 MHz, $CDCl_3$): δ = 10.8 (s, 1H), 8.75 (s, 1H), 8.81 (d, *J* = 8.4Hz, 1H), 797 (d, *J* = 8.1Hz, 1H), 7.87 (td, *J* = 1.5Hz, 1H), 7.72-7.61 (m, 3H), 7.48-7.42 (m, 3H) ; ^{13}C NMR ($CDCl_3$): δ 190.81, 150.18, 143.91, 137.17, 133.07, 132.33, 129.88, 129.68, 129.34, 128.84, 128.62, 128.26, 126.44, 121.35, 95.55, 85.55. MS (ESI) :$[M]^+$ Calcd for $[C_{18}H_{11}NO]$: 257.0841, found 257.0852.

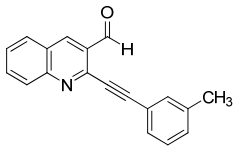


2-((4-methoxyphenyl)ethynyl)quinoline-3-carbaldehyde (1b). The product was obtained as a orange solid- mp 140-142 °C : ^{1}HNMR (300 MHz, [D]$CDCl_3$): δ = 10.80 (s, 1H), 8.73 (s, 1H), 8.16 (d, *J* = 8.4Hz, 1H), 7.96-7.83 (m, 2H), 7.66-7.59 (m, 3H), 6.95-6.83 (m, 2H), 3.86 (s, 3H); ^{13}C($CDCl_3$): 190.95, 160.86, 150.20, 144.24, 137.05, 133.99, 132.94, 129.63, 129.23, 128.69, 127.98, 126.27, 114.27, 113.28, 96.12, 84.22, 55.37. MS (ESI) :$[M]^+$ Calcd for $[C_{19}H_{13}NO_2]$: 287.0946, found 287.0951.

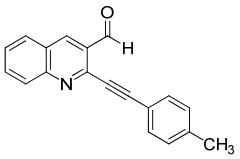


2-(hex-1-ynyl)quinoline-3-carbaldehyde (1c). The product was obtained as a yellow oil: ^{1}HNMR (300 MHz, [D]$CDCl_3$): δ = 10.68 (s, 1H), 8.68 (s, 1H), 8.11 (d, *J* =

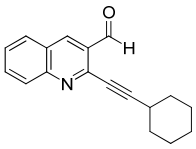
8.4Hz, 1H), 7.93-7.80 (m, 2H), 7.61-7.56 (m, 2H), 2.59 (t, *J* = 7.2Hz, 2H), 1.73-1.66 (m, 2H), 1.57-1.47 (m, 2H), 0.97 (t, *J* = 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$): 191, 150.07, 144.47, 136.76, 131.81, 129.57, 129.16, 128.74, 127.88, 126.24, 98.14, 87.79, 30.24, 22.19, 19.35, 13.58. MS (ESI) :$[M]^+$ Calcd for $[C_{16}H_{15}NO]$: 237.1154, found 237.1162.



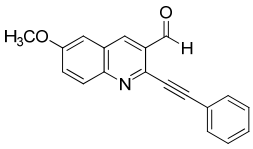
2-(m-tolylethynyl)quinoline-3-carbaldehyde (1d). The product was obtained as a orange solid - mp 126-128 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ :10.81 (s, 1H), 8.74 (s, 1H), 8.17 (d, *J* = 8.7Hz, 1H), 7.96 (d, *J* = 8.1Hz, 1H), 7.87 (t, *J* = 7.2Hz, 1H), 7.63 (t, *J* = 7.2Hz, 1H), 7.51 (d, *J* = 7.8Hz, 2H), 7.33-7.24 (m, 2H); ^{13}C NMR ($CDCl_3$): 190.90, 150.19, 144.01, 138.37, 137.09, 133.02, 132.86, 130.80, 129.67, 129.41, 129.32, 128.82, 128.50, 128.19, 126.40, 121.13, 95.88, 85.25, 21.25. MS (ESI) :$[M]^+$ Calcd for $[C_{19}H_{13}NO]$: 271.0997, found 271.0970.



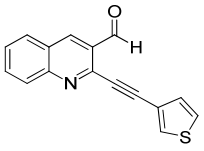
2-(p-tolylethynyl)quinoline-3-carbaldehyde (1e). The product was obtained as a white solid- mp 138-140 °C : ^{1}HNMR (300 MHz, [D]$CDCl_3$): δ = 10.78 (s, 1H), 8.71 (s, 1H), 8.15 (d, *J* = 8.7Hz, 1H), 7.91 (d, *J* = 8.1Hz, 1H), 7.85-7.79 (d, *J* = 8.4Hz, 1H), 7.60-7.53 (m, 3H), 7.19-7.15 (m, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$) : 190.94, 150.22, 144.14, 140.36, 137.07, 133.00, 132.26, 129.67, 129.39, 129.31, 128.80, 128.12, 126.38, 118.26, 96.03, 85.13, 21.70. MS (ESI) :$[M]^+$ Calcd for $[C_{19}H_{13}NO]$: 271.0997, found : 271.0979.



2-(cyclohexylethynyl)quinoline-3-carbaldehyde (1f). The product was obtained as a white solid- mp 130-132 °C : ^{1}HNMR (300 MHz, [D]$CDCl_3$): δ 8.6 (s, 1H), 8.12 (d, *J* = 8.7Hz, 1H), 7.93 (d, *J* = 8.1Hz, 1H), 7.86-7.80 (m, 1H), 7.58 (td, *J* = 0.9Hz, 7.9Hz, 1H), 2.02-1.97 (m, 2H), 1.82-1.55 (m, 5H), 1.47-1.36 (m, 3H). ^{13}C NMR ($CDCl_3$): 191.40, 150.10, 144.61, 136.76, 132.83, 129.61, 129.20, 128.77, 127.88, 126.25, 102.02, 77.47, 32.12, 29.90, 25.75, 24.94. MS (ESI) :$[M]^+$ Calcd for $[C_{18}H_{17}NO]$: 263.13, found : 263.11.

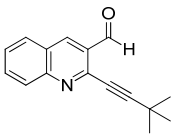


6-methoxy-2-(phenylethynyl)quinoline-3-carbaldehyde (1g). The product was obtained as a yellow solid- mp 164-166 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 10.78 (s, 1H), 8.61 (s, 1H), 8.06 (d, *J* = 9.3Hz, 1H), 7.70-7.67 (m, 2H), 7.52-7.41 (m, 4H), 7.17 (d, *J* = 2.7 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$): 191.04, 159.00, 146.59, 141.46, 135.33, 132.21, 130.77, 129.64, 129.07, 128.56, 127.75, 126.29, 121.58, 106.25, 94.73, 85.56, 55.77. MS (ESI) :$[M]^+$ Calcd for $[C_{19}H_{13}NO_2]$: 287.09, found : 287.13.



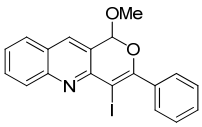
2-(thiophen-3-ylethynyl)quinoline-3-carbaldehyde (1h). The product was obtained as a white solid - mp 122-124 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 10.78 (s, 1H), 7.97 (d, *J* = 8.4Hz, 1H), 7.88 (td, *J* = 1.5Hz, 1H), 7.79-7.78 (m, 1H), 7.63 (td, *J* = 0.9 Hz, 1H), 7.39-7.33 (m, 2H); ^{13}C NMR ($CDCl_3$): 190.79, 150.21, 143.94, 137.17, 133.06, 131.60, 129.99,

129.68, 129.32, 128.76, 128.21, 126.41, 125.98, 120.52, 90.84, 85.38. MS (ESI) :$[M]^+$ Calcd for $[C_{16}H_9NOS]$: 263.0405, found : 263.0450.



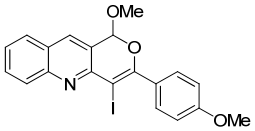
2-(3,3-dimethylbut-1-ynyl)quinoline-3-carbaldehyde (1i). The product was obtained as a dirty white solid- mp 118-120 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.7 (s, 1H), 8.14 (d, *J* = 8.4Hz, 1H), 7.91 (td, *J* = 0.6Hz, 7.5Hz, 1H), 7.86-7.81 (m, 1H), 7.60 (td, *J* = 0.6Hz, 7.5Hz, 1H) . 13C NMR ($CDCl_3$): 191.40, 150.06, 144.58, 136.77, 132.83, 129.63, 128.75, 127.88, 126.25, 105.82, 76.08, 30.57, 28.40. MS (ESI): $[M]^+$ Calcd for $[C_{16}H_{15}NO]$: 237.12, found: 237.20.

General procedure for the synthesis of 4-iodo-1H-pyrano[4,3-*b*]quinolines (2a-b). Into a solution of the 2-(alkynyl)quinoline-3-carbaldehyde (0.25 mmol), K_2CO_3 (2.5 equiv) and the nucleophile (1.2 equiv) in CH_2Cl_2 (2.0 mL), I_2 (2.5 equiv) was added and the solution was stirred at room temperature until the total disappearance of the starting material as determined by TLC analysis. The reaction mixture was then quenched with satd aq $Na_2S_2O_3$ (5.0 mL) and water (5.0 mL). The resulting solution was extracted using ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (neutral aluminum oxide, hexane/EtOAc) to afford pure compounds.



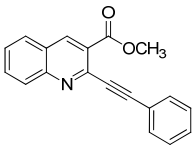
4-iodo-1-methoxy-3-phenyl-1H-pyrano[4,3-*b*]quinoline(2a). The product was obtained as a yellow solid- mp 116-118 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ : 8.20

(d, *J* = 8.7Hz, 1H), 7.97 (s, 1H), 7.82 (d, *J* = 8.1Hz, 1H), 7.75-7.70 (m, 3H), 7.53-7.45 (m, 4H), 6.22 (s, 1H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$) :157.69, 148.85, 147.82, 136.98, 133.12, 130.28, 129.92, 129.84, 129.53, 127.50, 126.39, 121.83, 100.45, 78.01, 77.23, 56.47. HRMS (ESI) :$[M]^+$ Calcd for $[C_{19}H_{14}INO_2]$: 415.0069, found : 415.0073.

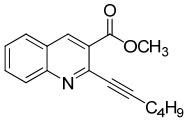


4-iodo-1-methoxy-3-(4-methoxyphenyl)-1H-pyrano[4,3-b]quinoline (2b). The product was obtained as yellow solid - mp 130-132 °C : ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.19 (d, *J* = 8.4Hz, 1H), 7.95 (s, 1H), 7.81 (d, *J* = 8.1Hz, 1H), 7.74-7.69 (m, 3H), 7.49 (td, *J* = 0.9, 6.9 Hz, 1H), 6.99-6.95 (m, 2H) 6.21 (s, 1H), 3.85 (s, 3H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$): 159.70, 156.35, 147.83, 147.19, 131.93, 130.69, 129.20, 128.44, 128.10, 126.47, 126.38, 125.24, 120.91, 112.21, 99.41, 76.21, 55.45, 54.35. HRMS (ESI): $[M]^+$ Calcd for $[C_{20}H_{16}INO_3]$: 445.0175, found : 445.034.

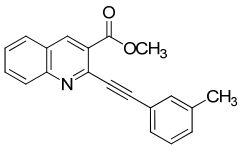
General procedure for the synthesis of alkyl 2-(alkynyl)quinoline-3-carboxylates (3a-i): To a solution of I_2 (2.5 equiv) in 30 equiv nucleophile were added 2-(alkynyl)quinoline-3-carbaldehyde (0.25 mmol), K_2CO_3 (2.5 equiv) . The resulting reaction mixture was heated under an Ar atmosphere at 70 ^{0}C until the total disappearance of the starting material as determined by TLC analysis. The reaction mixture was then quenched with satd aq $Na_2S_2O_3$ (5.0 mL) and water (5.0 mL). The resulting solution was extracted using ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (neutral aluminum oxide, hexane/EtOAc) to afford pure compounds.



Methyl 2-(phenylethynyl)quinoline-3-carboxylate (3a). The product was obtained as orange solid- mp 96-98 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.8 (s, 1H), 8.16 (d, *J* = 8.1Hz, 1H), 7.89 (d, *J* = 8.1Hz, 1H), 7.83 (td, *J* = 1.2, 7.2 Hz,,1H), 7.73-7.70 (m, 2H), 7.60 (t, *J* =7.8Hz, 1H), 7.4-7.38 (m, 3H), 4.04 (s, 3H); ^{13}C NMR ($CDCl_3$) : 165.65, 149.05, 141.62, 139.77, 132.40, 132.24, 129.30, 129.18, 128.55, 128.40, 127.93, 125.83, 125.56, 122.39, 93.46, 88.47, 52.64. HRMS (ESI): $[M]^+$ Calcd for $[C_{19}H_{13}NO_2]$: 287.0946, found : 287.0949.

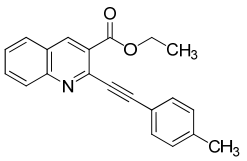


Methyl 2-(hex-1-ynyl)quinoline-3-carboxylate (3b). The product was obtained as orange oil: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.70 (s, 1H), 8.10 (d, *J* = 8.4Hz, 1H), 7.85-7.75 (m, 2H), 7.55 (t, *J* = 6.9Hz, 1H), 3.99 (s, 3H), 2.57 (t, *J* = 7.2Hz, 2H), 1.75-1.65 (m, 2H), 1.60-1.50 (m, 2H), 0.97 (t, *J* = 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 164.88, 147.86, 140.88, 138.39, 130.95, 127.96, 127.37, 126.55, 124.58, 124.53, 94.90, 78.90, 51.43, 29.35, 21.09, 18.54, 12.62. HRMS (ESI): $[M]^+$ Calcd for $[C_{17}H_{17}NO_2]$: 267.1259, found : 267.1261.

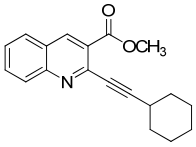


Methyl 2-(m-tolylethynyl)quinoline-3-carboxylate (3c). The product was obtained as orange solid- mp 104-106 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ : 8.79 (s, 1H), 8.16 (d, *J* = 8.7Hz, 1H), 7.89-7.79 (m, 2H), 7.62-7.51 (m, 3H), 7.30-7.19 (m, 2H), 4.04 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$): 165.66, 149.05, 141.69, 139.73, 138.07, 132.91, 132.20,

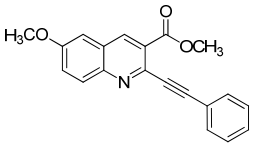
130.23, 129.51, 129.16, 128.53, 128.34, 127.87, 125.78, 125.52, 122.17, 93.73, 88.16, 52.63, 21.27. HRMS (ESI): $[M]^+$ Calcd for $[C_{20}H_{15}NO_2]$: 301.1103, found : 301.1110.



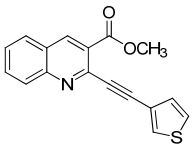
Ethyl 2-(p-tolylethynyl)quinoline-3-carboxylate (3d). The product was obtained as orange solid - mp 94-96 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.78 (s, 1H), 8.16 (d, *J* = 8.4Hz, 1H), 7.91-7.79 (m, 2H), 7.62-7.57 (m, 3H), 7.27-7.18 (m, 2H), 4.50 (q, *J* = 6.9Hz, 2H), 2.41 (s, 3H), 1.41 (t, *J* = 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 165.38, 149.00, 141.76, 139.55,132.95, 132.26, 132.10, 129.18, 129.14, 128.51, 127.79, 125.92, 125.81, 119.34, 93.76, 88.04, 61.74, 21.68, 14.40. HRMS (ESI): $[M]^+$ Calcd for $[C_{21}H_{17}NO_2]$: 315.1259, found : 315.1261.



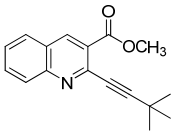
Methyl 2-(cyclohexylethynyl)quinoline-3-carboxylate (3e). The product was obtained as orange solid - mp 70-74 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.71 (s, 1H), 8.11 (d, *J* = 8.4Hz, 1H), 7.85 (d, *J* = 8.1Hz, 1H), 7.78 (td, *J* = 8.4Hz, 1.5Hz, 1H), 7.56 (t, *J* = 6.9Hz, 1H), 3.99 (s, 1H), 2.79-2.70 (m, 1H), 2.00-1.84 (m, 2H), 1.82-1.54 (m, 5H), 1.45-1.31 (m, 3H). ^{13}C NMR ($CDCl_3$): 166.11, 148.87, 141.93, 139.41, 131.95, 129.03, 128.40, 127.55, 125.87, 125.62, 99.65, 79.90, 52.48, 32.17, 30.03, 29.70, 25.88, 24.93. HRMS (ESI): $[M]^+$ Calcd for $[C_{19}H_{19}NO_2]$: 293.14, found: 293.22.



Methyl 6-methoxy-2-(phenylethynyl)quinoline-3-carboxylate (3f). The product was obtained as yellow solid - mp 152-154 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.68 (s, 1H), 8.05 (d, *J* = 9.3Hz, 1H), 7.71-7.69 (m, 2H), 7.469 (dd, *J* = 9.3Hz, 2.1Hz, 1H), 7.39-7.37 (m, 3H), 7.12 (d, *J* = 2.4Hz, 1H), 4.03 (s, 1H), 3.94 (m, 1H) . ^{13}C NMR ($CDCl_3$): 165.83, 158.82, 145.33, 139.00, 138.18, 132.25, 130.63, 129.04, 128.34, 127.07, 125.84, 125.23, 122.59, 105.50, 92.54, 88.49, 55.68, 52.55. HRMS (ESI): $[M]^+$ Calcd for $[C_{20}H_{15}NO_3]$: 317.11, found: 317.15.

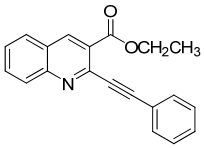


Methyl 2-(thiophen-3-ylethynyl)quinoline-3-carboxylate (3g). The product was obtained as orange solid- mp 86-88 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.79 (s, 1H), 8.14 (d, *J* = 8.4Hz, 1H), 7.89-7.76 (m, 3H), 7.59 (t, *J* = 7.2Hz, 1H), 7.36-7.31 (m, 2H), 4.03 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 165.48, 148.96, 141.56, 149.73, 132.19, 130.99, 130.12, 129.04, 128.49, 127.81, 125.68, 125.46, 125.25, 121.47, 88.72, 88.12, 52.53. HRMS (ESI): $[M]^+$ Calcd for $[C_{17}H_{11}NO_2S]$: 293.0510, found : 293.0570.



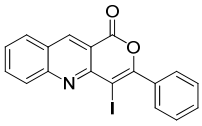
Methyl 2-(3,3-dimethylbut-1-ynyl)quinoline-3-carboxylate (3h). The product was obtained as yellow solid - mp 50-54 °C: ^{1}HNMR (300MHz, [D] $CHCl_3$) δ: 8.70 (s,1H), 8.125 (d, *J* = 8.4Hz, 1H), 7.86-7.76 (m, 2H), 7.56 (t, *J* = 7.2Hz, 1H), 3.05 (s, 1H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$): 166.23, 148.81, 141.84, 139.42, 131.91, 129.07, 128.40, 127.56,

126.13, 125.63, 103.28, 78.63, 52.46, 30.59, 28.30. HRMS (ESI): $[M]^+$ Calcd for $[C_{17}H_{17}NO_2]$: 267.13, found: 267.18.



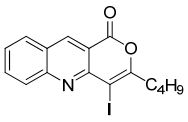
Ethyl 2-(phenylethynyl)quinoline-3-carboxylate (3i). The product was obtained as yellow solid- mp 90-92 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.80 (s, 1H), 8.17(d, *J* = 8.7Hz, 1H), 7.99-7.81 (m, 2H), 7.72-7.59 (m, 3H), 7.40-7.38 (m, 3H), 4.50 (q, *J* = 7.2Hz, 2H), 1.45 (t, *J* = 7.2Hz, 3H) ; ^{13}C NMR ($CDCl_3$): δ 165.29, 148.99, 139.60, 132.32, 132.15, 129.23, 129.17, 128.52, 128.38, 127.90, 125.91, 122.41, 93.46, 88.47, 61.76, 14.38. HRMS (ESI): $[M]^+$ Calcd for $[C_{20}H_{15}NO_2]$: 301.1103, found : 301.1119.

General procedure for the synthesis of 4-iodo-3-aryl-1H-pyrano[4,3-*b*]quinolin-1-one (4a-e): To a solution of I_2 (2.5 equiv) in CH_2Cl_2 (2.0 mL) were added 2-(alkynyl) quinoline-3-carbaldehyde (0.25 mmol). The resulting reaction mixture was stirred under an Ar atmosphere at room temperature until the total disappearance of the starting material as determined by TLC analysis. The reaction mixture was then quenched with satd aq $Na_2S_2O_3$ (5.0 mL) and water (5.0 mL). The resulting solution was extracted using ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by recrystallization.

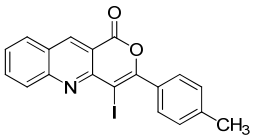


4-iodo-3-phenyl-1H-pyrano[4,3-b]quinolin-1-one (4a). The product was obtained as orange solid – mp 224-226 °C : ^{1}HNMR (300MHz, [D] $CHCl_3$) δ: 9.12 (s, 1H), 8.29

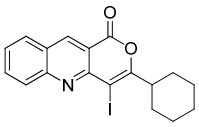
(d, *J* = 8.7Hz, 1H), 8.04 (d, *J* = 8.4Hz, 1H), 7.94 (t, *J* = 7.5Hz, 1H), 7.83-7.82 (m, 2H) , 7.67 (t, *J* = 7.5Hz, 1H), 7.52-7.50 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 161.64, 157.66, 151.64, 150.54, 140.73, 134.78, 133.64, 130.56, 130.03, 129.66, 129.09, 128.09, 127.79, 127.41, 114.23, 81.67. HRMS (ESI): $[M]^+$ Calcd for $[C_{18}H_{10}INO_2]$: 398.9756, found : 399.9750.



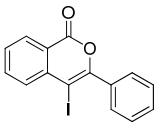
3-butyl-4-iodo-1H-pyrano[4,3-b]quinolin-1-one (4b). The product was obtained as yellow solid – mp 198-200 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 9.07 (s, 1H), 8.26 (d, *J* = 8.7Hz, 1H), 8.01 (d, *J* = 8.1Hz, 1H), 7.92 (td, *J* = 1.2, 6.9Hz, 1H), 7.637 (td, *J* = 0.9, 8.1Hz, 1H), 3.05 (t, *J* = 7.5Hz, 2H), 1.84-1.75 (m, 2H), 1.55-143 (m, 2H), 0.99 (t, *J* = 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 161.92, 161.80, 151.59, 150.24, 140.70, 133.53, 129.59, 1129.07, 127.48, 127.17, 114.03, 81.21, 37.45, 29.21, 22.29, 13.80. HRMS (ESI): $[M]^+$ Calcd for $[C_{16}H_{14}INO_2]$: 379.0069, found : 379.0062.



4-iodo-3-p-tolyl-1H-pyrano[4,3-b]quinolin-1-one (4c). The product was obtained as orange solid- mp 228-230 °C: ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 9.13 (s, 1H), 8.29 (d, *J* = 8.4Hz, 1H), 8.05 (d, *J* = 7.8Hz, 1H), 7.94 (td, *J* = 1.5, 6.9Hz, 1H), 7.75 (d, *J* = 8.1Hz, 2H), 7.68-7.64 (m, 1H), 7.31 (d, *J* = 7.8Hz, 2H), 2.45 (s, 3H) ; ^{13}C NMR ($CDCl_3$): δ 161.77, 157.82, 151.70, 150.71, 140.99, 140.71, 133.61, 131.90, 130.01, 129.68, 129.10, 128.78, 127.73, 127.41, 114.25, 81.23, 21.60. HRMS (ESI): $[M]^+$ Calcd for $[C_{19}H_{12}INO_2]$: 412.9913, found : 413.9925.



3-cyclohexyl-1H-pyrano[4,3-b]quinolin-1-one (4d). The product was obtained as orange solid – mp 180-182 °C : ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 9.05 (s, 1H), 8.25 (d, *J* = 8.4Hz, 1H), 8.00 (d, *J* = 8.1Hz, 1H), 7.93-7.88 (m, 1H), 7.62 (td, *J* = 0.9Hz, 8.1 Hz, 1H), 1.95-1.88 (m, 4H), 1.79-1.60 (m, 3H), 1.50-1.28 (m, 3H) . ^{13}C NMR ($CDCl_3$): 164.15, 162.00, 151.59, 150.41, 140.67, 133.50, 129.56, 129.06, 127.43, 127.19, 114.33, 80.42, 46.61, 29.39, 25.93, 25.58. HRMS (ESI): $[M]^+$ Calcd for $[C_{18}H_{17}NO_2]$: 279.13, found : 279.22.

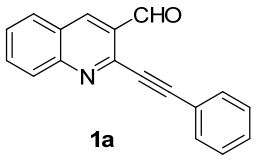


4-iodo-3-phenyl-1H-isochromen-1-one (4e). The product was obtained as white solid – mp 136-138 °C : ^{1}HNMR (300MHz, [D]$CHCl_3$) δ: 8.31 (dd, *J* = 8.1Hz, 1H), 7.91-7.80 (m, 1H), 7.83 (td, *J* = 1.2, 6.0Hz, 1H), 7.72-7.66 (m, 2H), 7.62-7.56 (m, 1H), 7.49-7.47 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 161.57, 154.82, 138.19, 135.73, 135.26, 131.51, 130.21, 130.00, 129.76, 129.27, 128.10, 120.29, 77.44. MS (ESI): $[M]^+$ Calcd for $[C_{15}H_9IO_2]$: 347.9647, found : 348.9649.

REFERENCES:

1. O. Meth-Cohn, B. Narine and B. Tarnowski, *Tetrahedron Lett.*, 1979, **33**, 3111.

2. A. Chandra, B. Singh, S. Upadhaya and R. M. Singh, *Tetrahedron,* 2008, **64**, 11680.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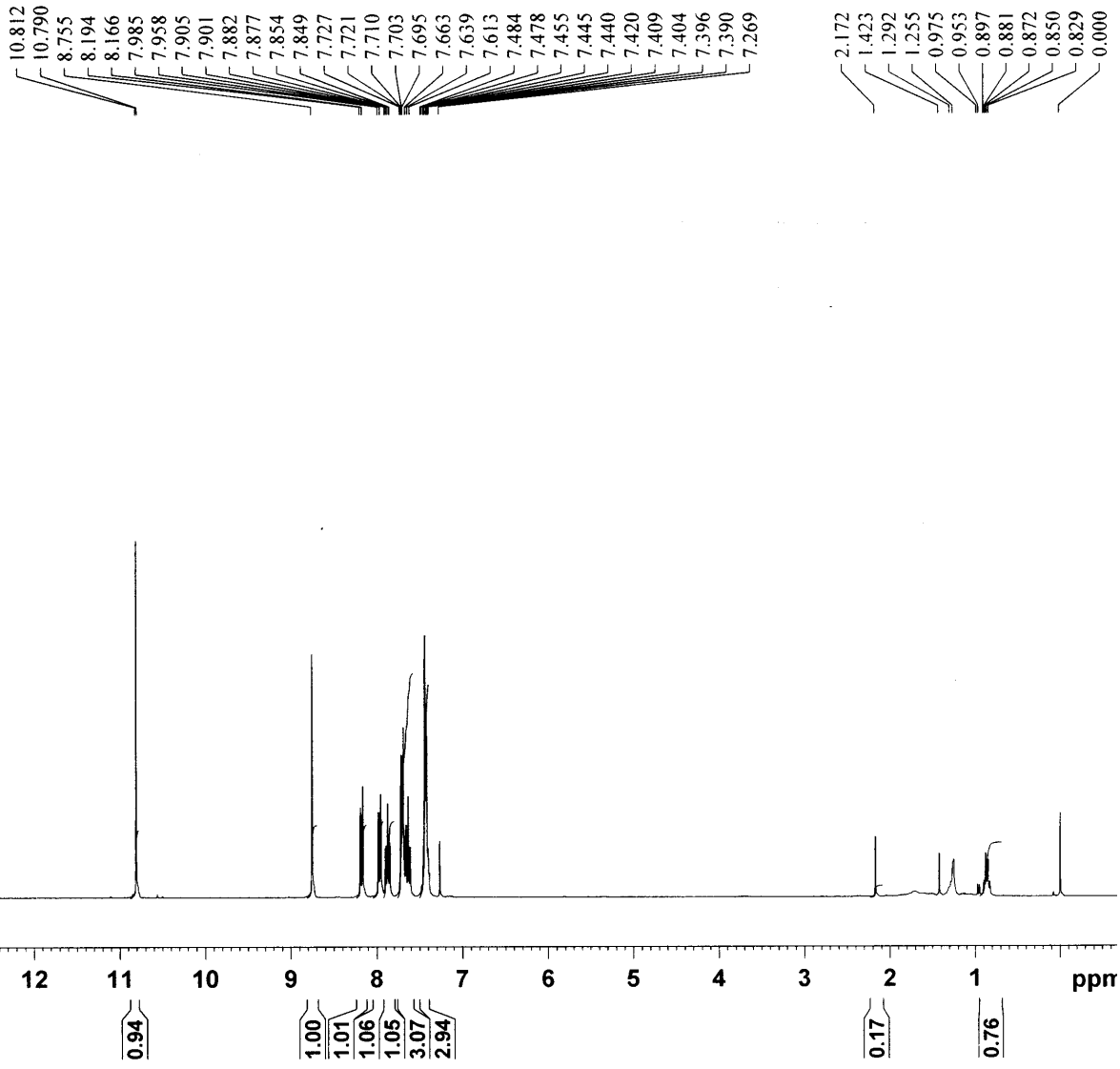
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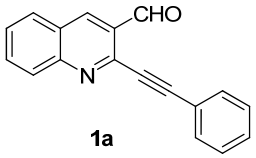
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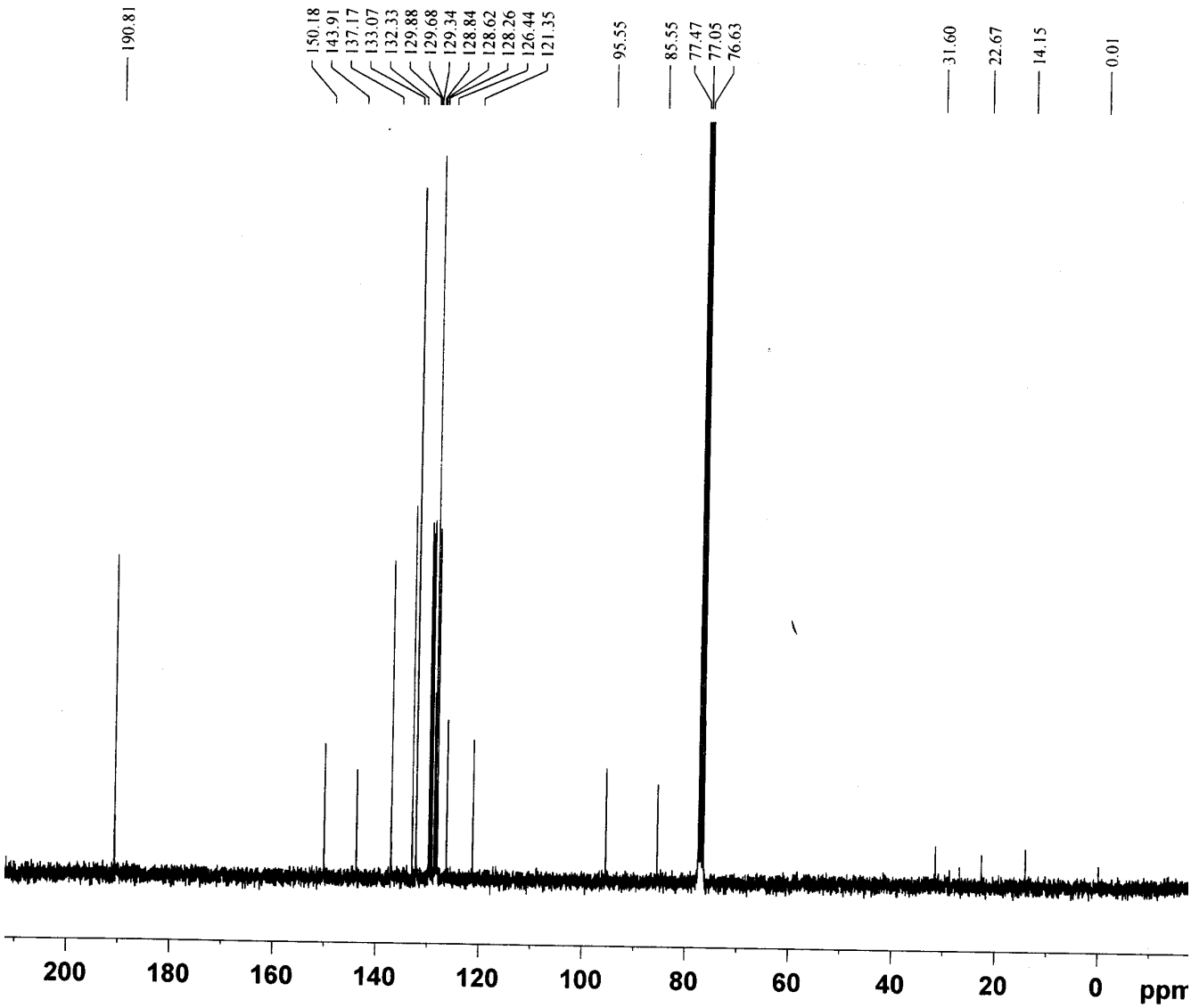
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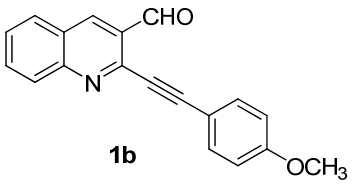
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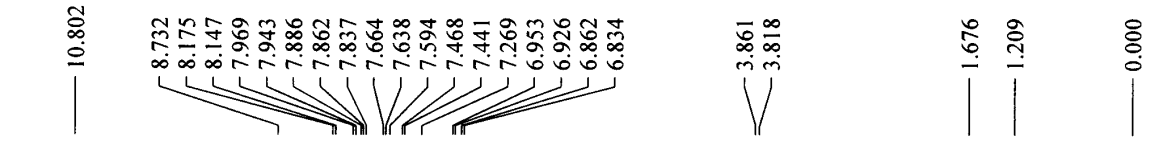
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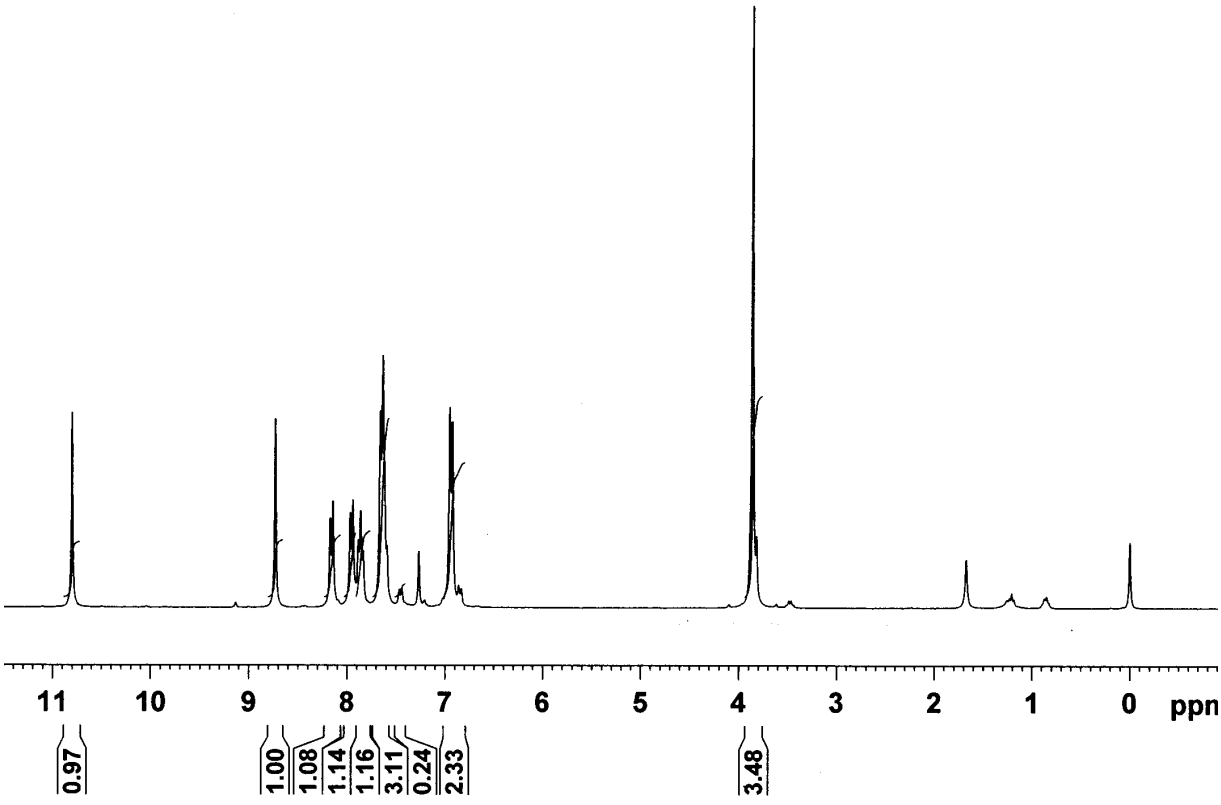
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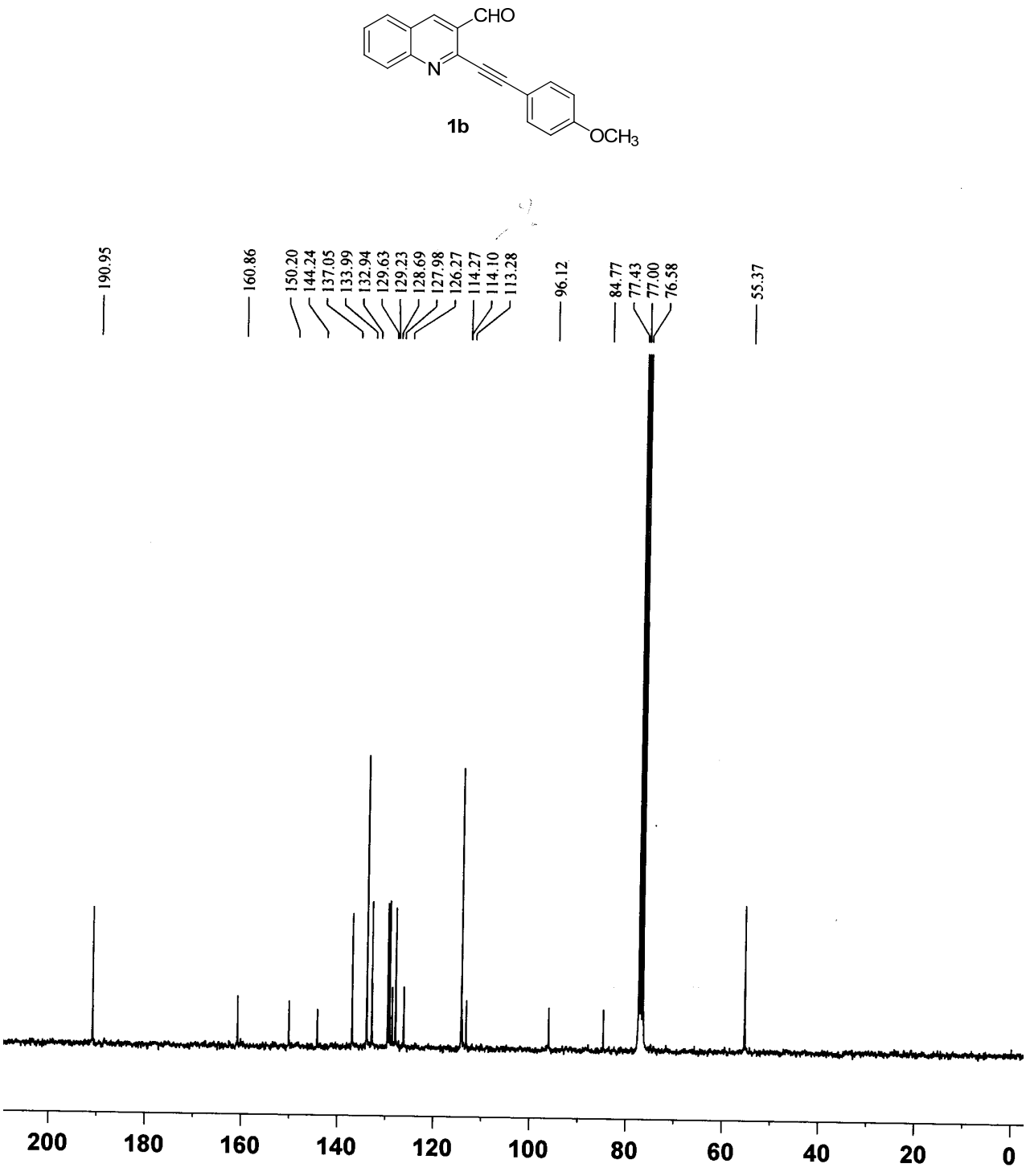
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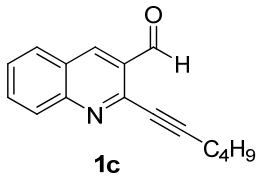
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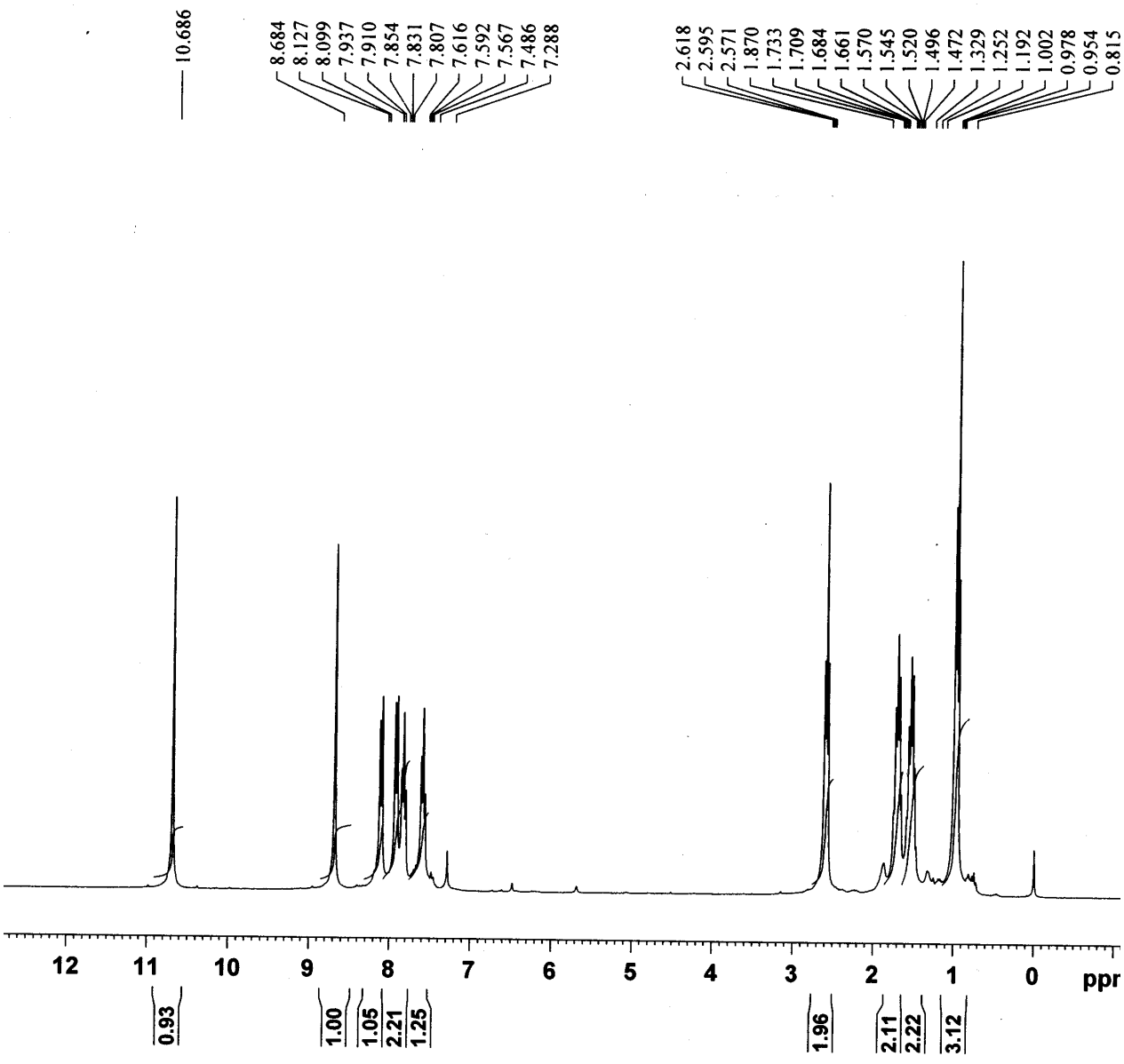
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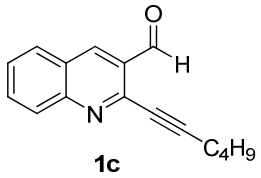
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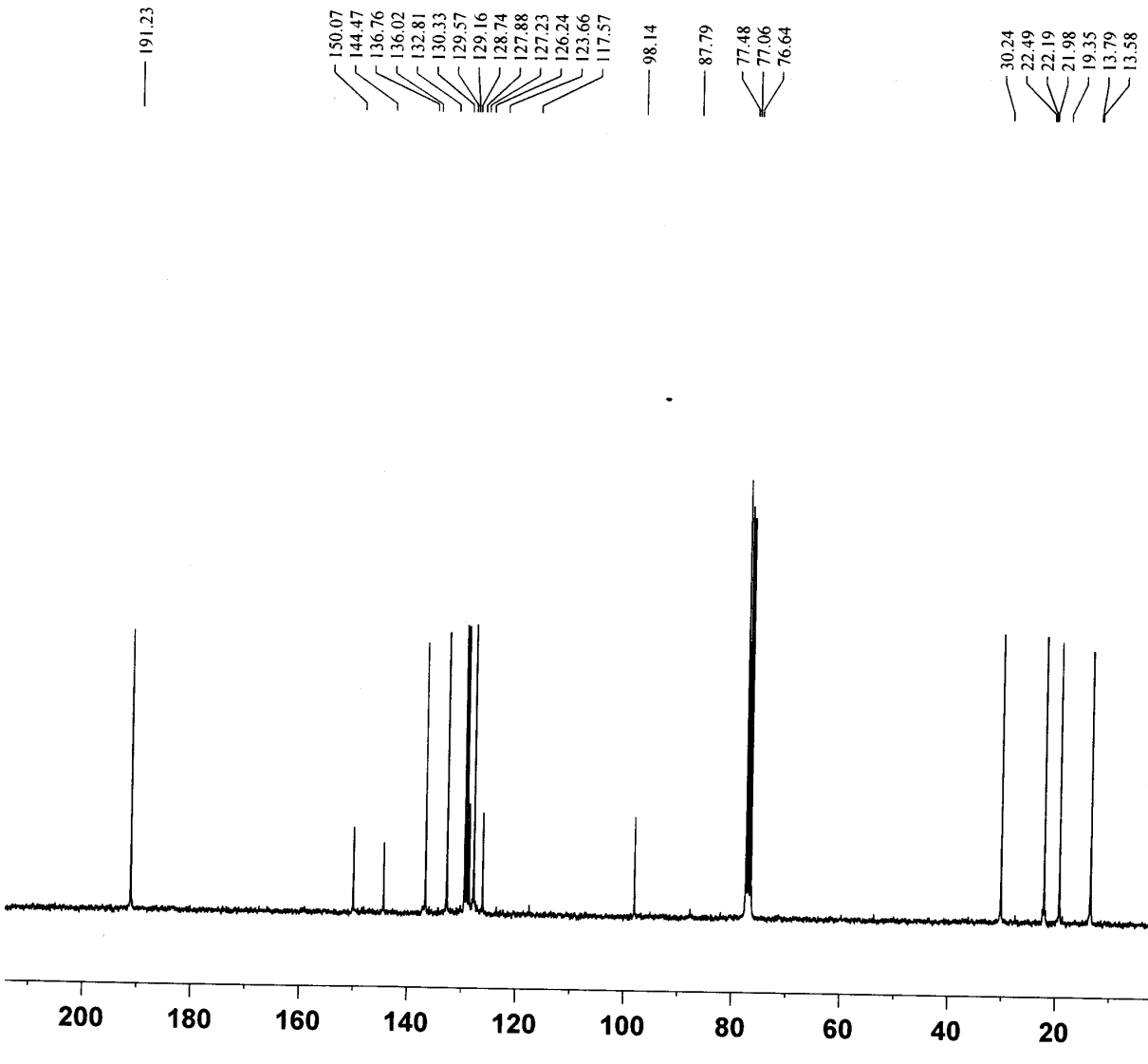
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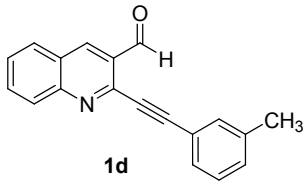
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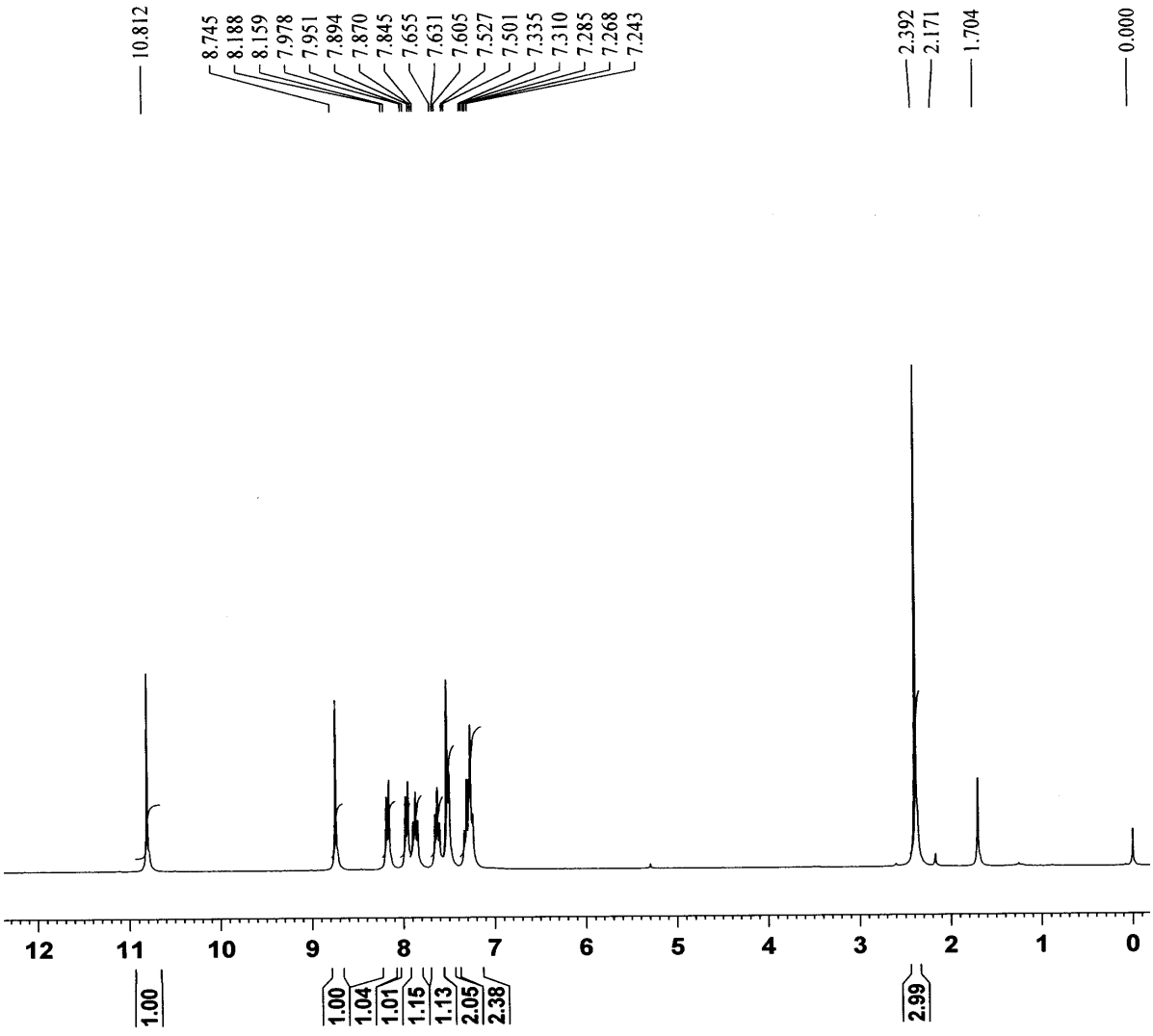
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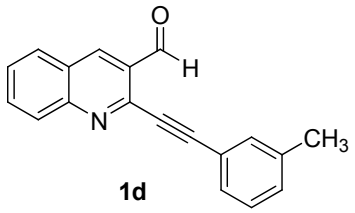
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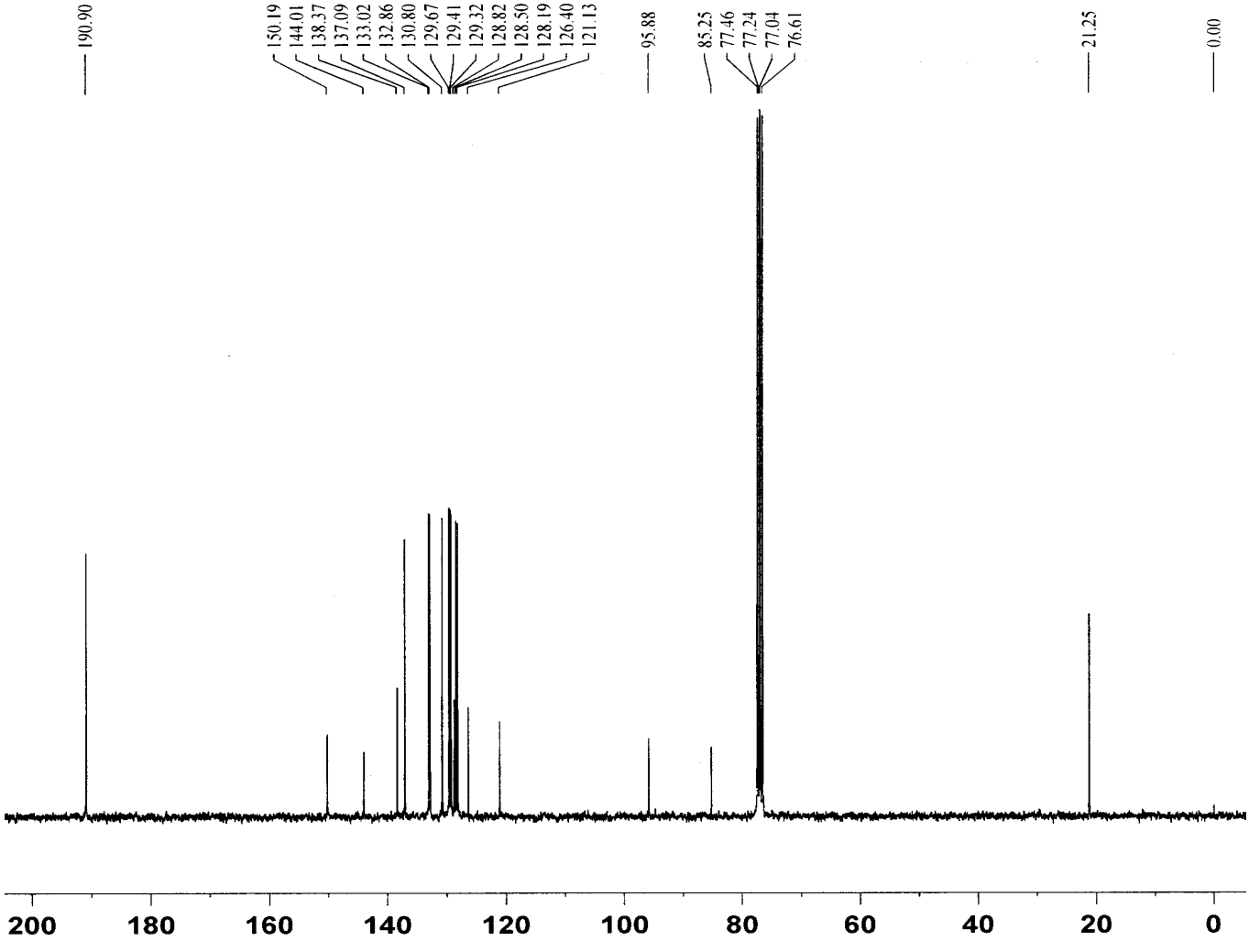
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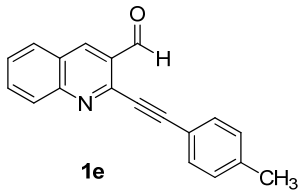
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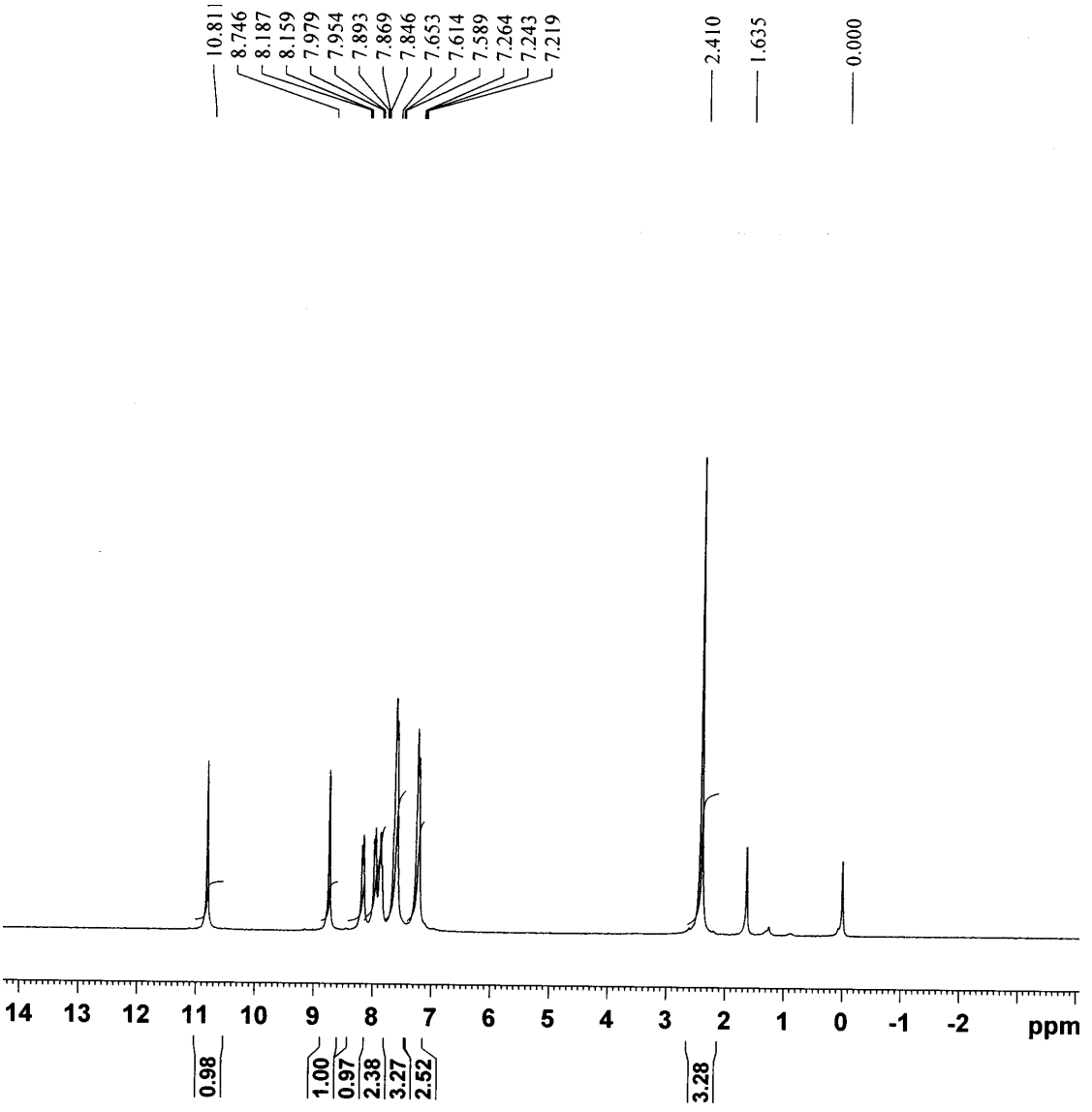
CH3

1e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7.589
7.264
7.243
7.219
2.410
1.635
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1.00
0.97
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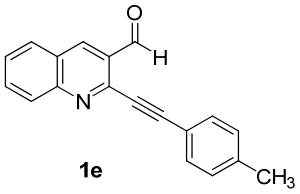
2.52
3.28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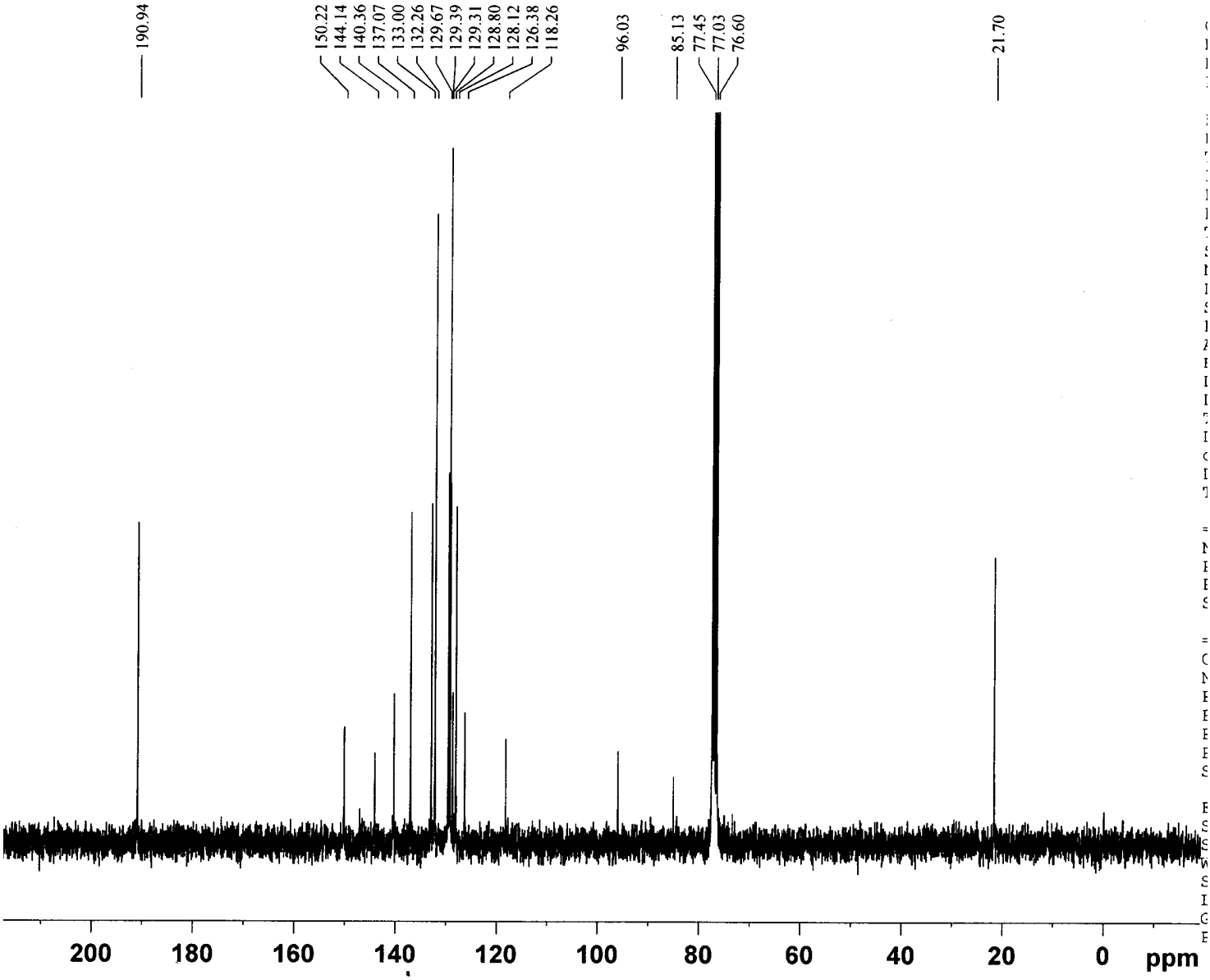
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128.12
126.38
118.26
96.03
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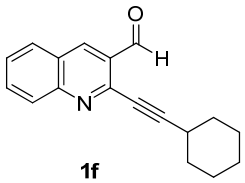
ppm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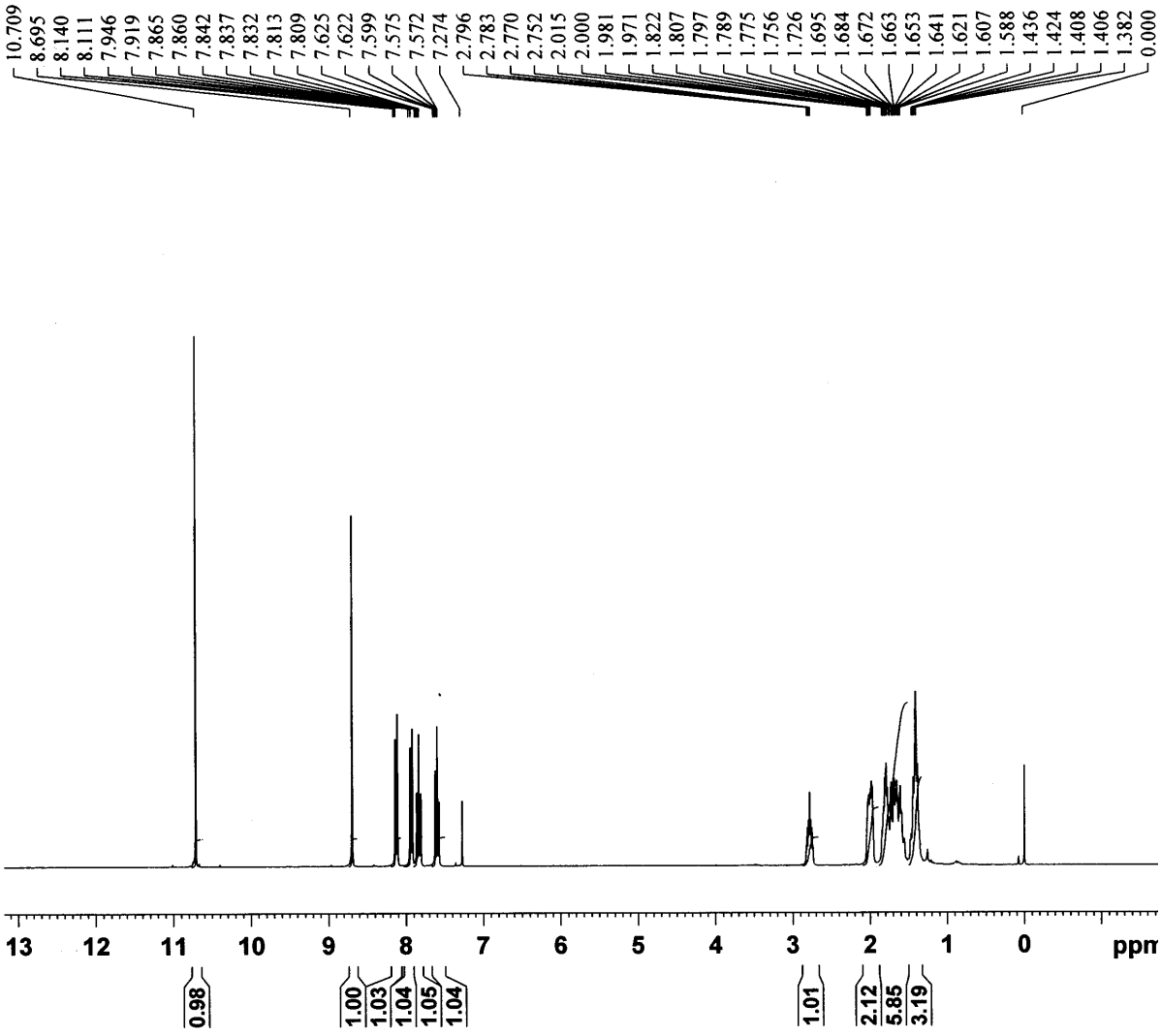
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2.770
2.752
2.015
2.000
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1.797
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1.726
1.695
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1.641
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1.406
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12
11
10
9
8
7
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3
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1.04
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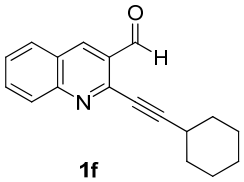
3.19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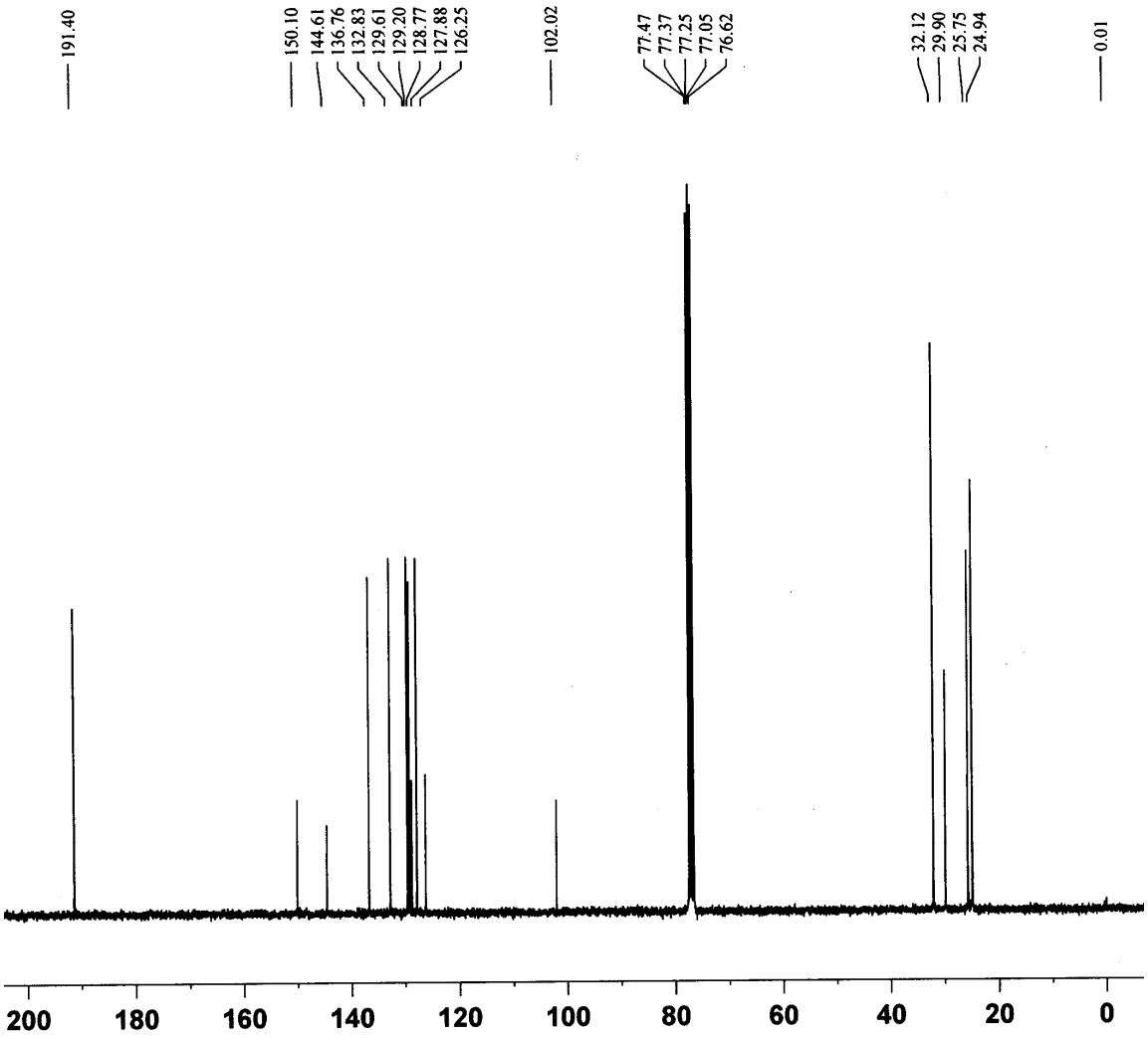
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80
60
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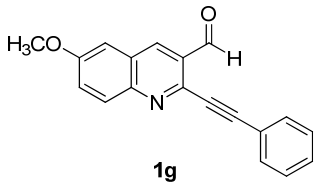
20
0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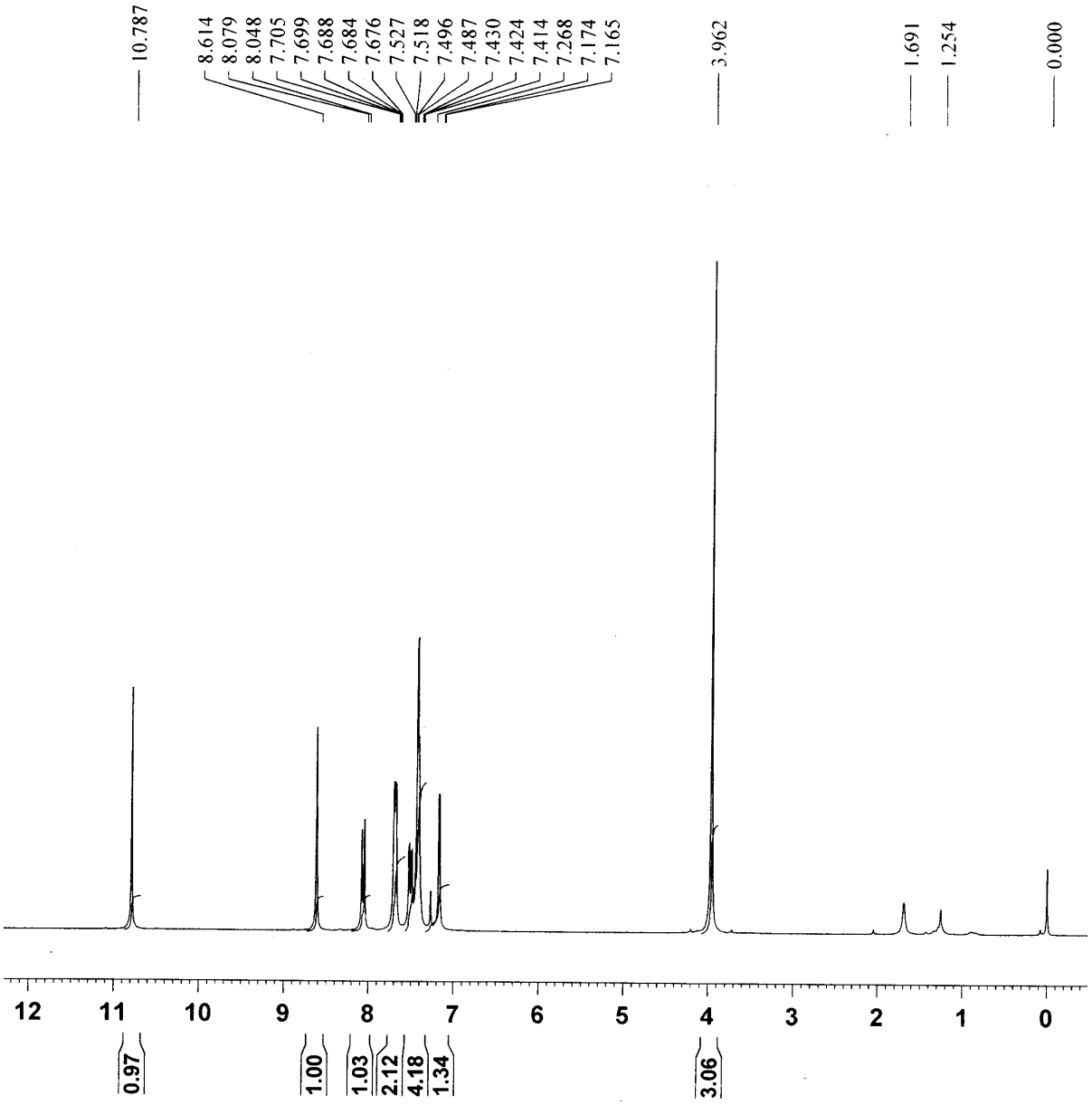
N

1g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7.518
7.496
7.487
7.430
7.424
7.414
7.268
7.174
7.165
3.962
1.691
1.254
0.000
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11
10
9
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6
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3
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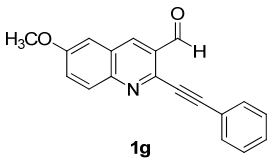
1.34
3.06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H
H3CO
N

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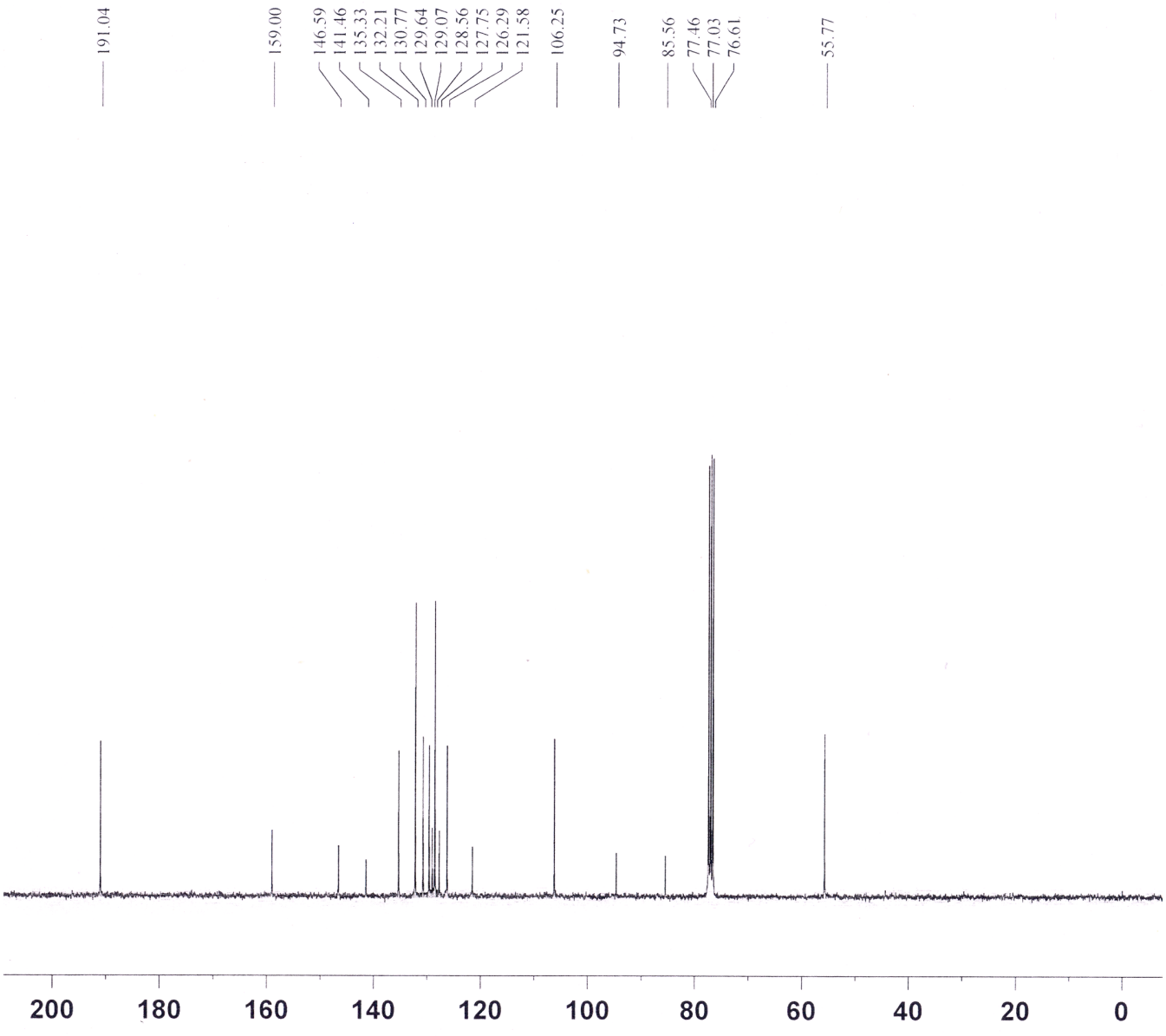
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129.64
129.07
128.56
127.75
126.29
121.58
106.25
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77.46
77.03
76.61
55.77
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140
120
100
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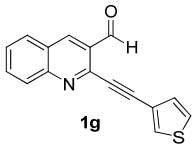
60
40
20
0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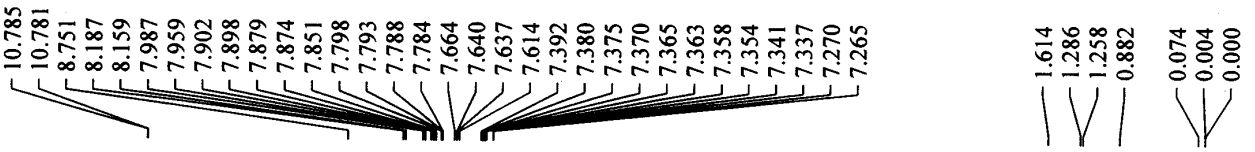
1g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7.798
7.793
7.788
7.784
7.664
7.640
7.637
7.614
7.392
7.380
7.375
7.370
7.365
7.363
7.358
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1.286
1.258
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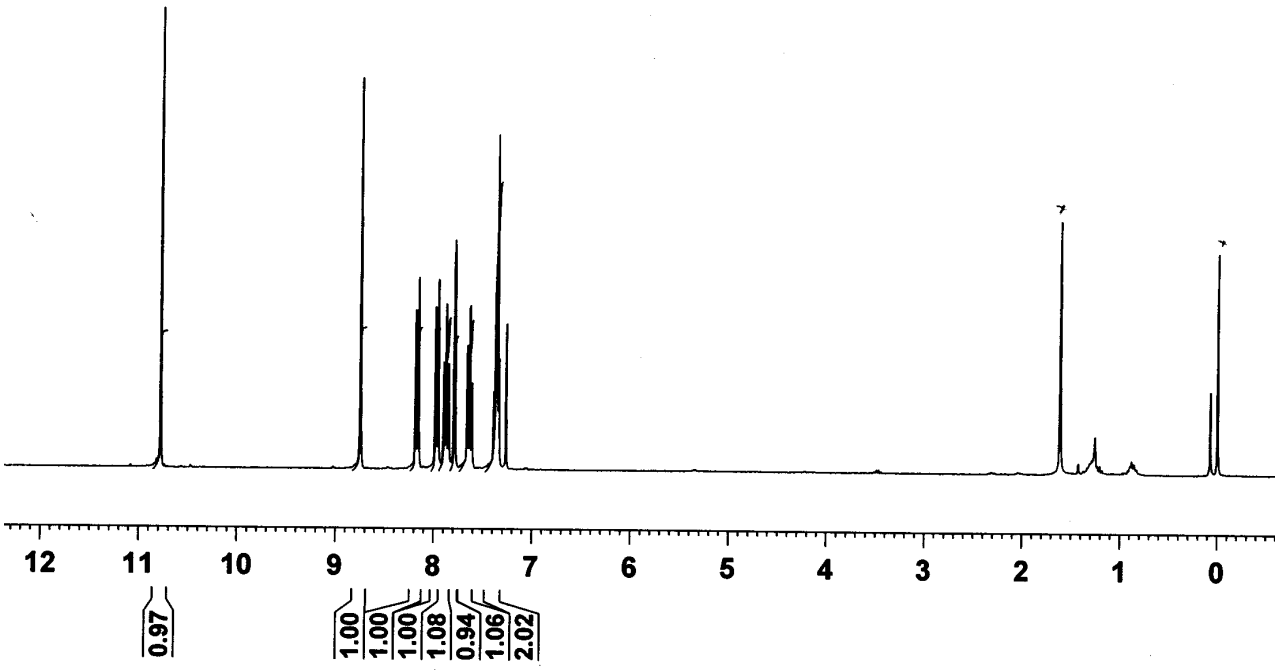
0.004
0.000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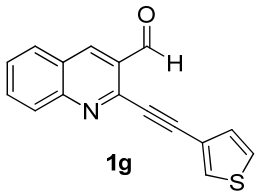
1.00
1.00
1.00
1.08
0.94
1.06
2.02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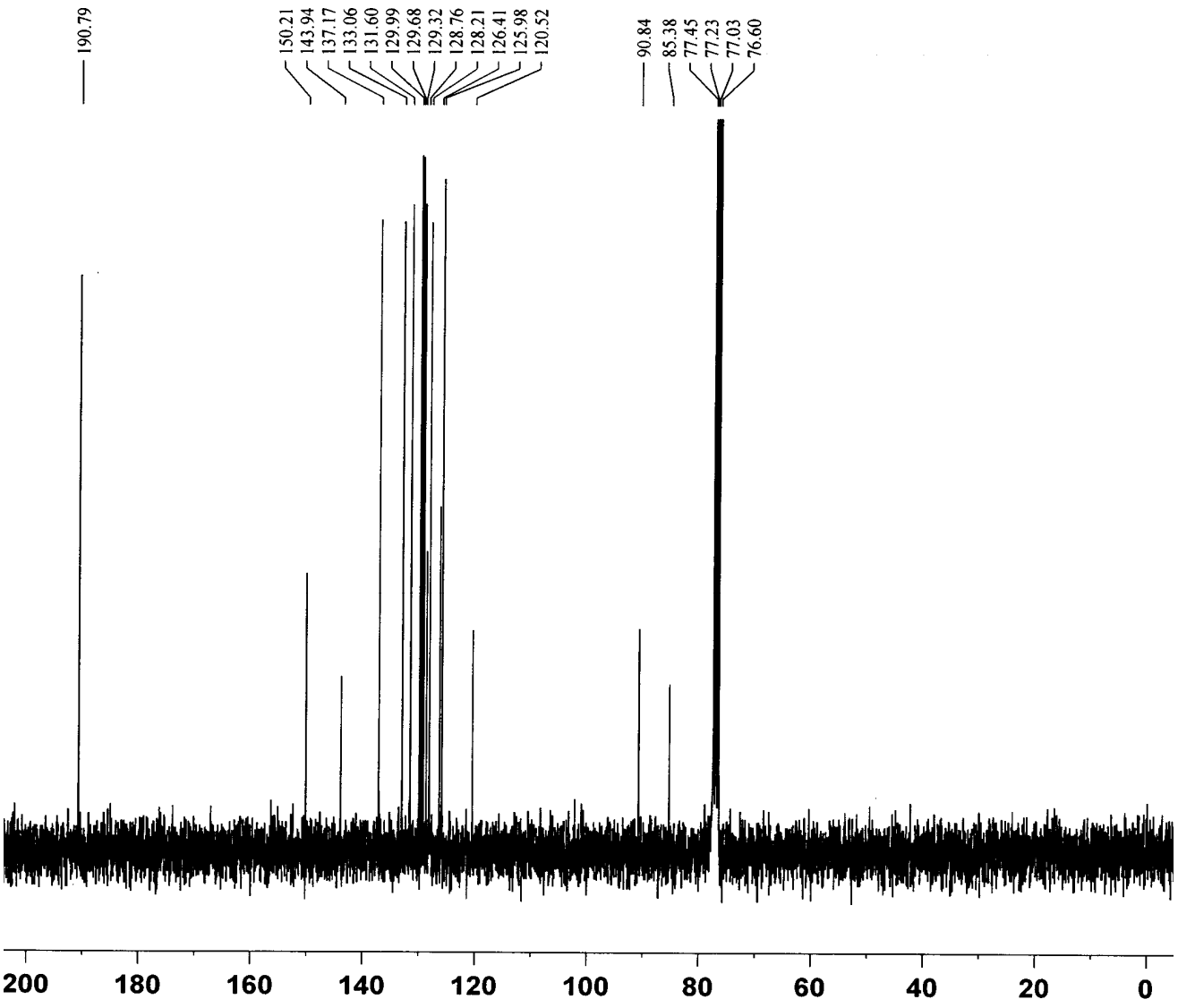
H
N
S

1g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128.76
128.21
126.41
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120.52
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77.23
77.03
76.60
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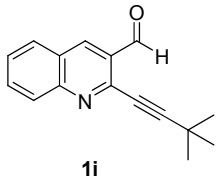
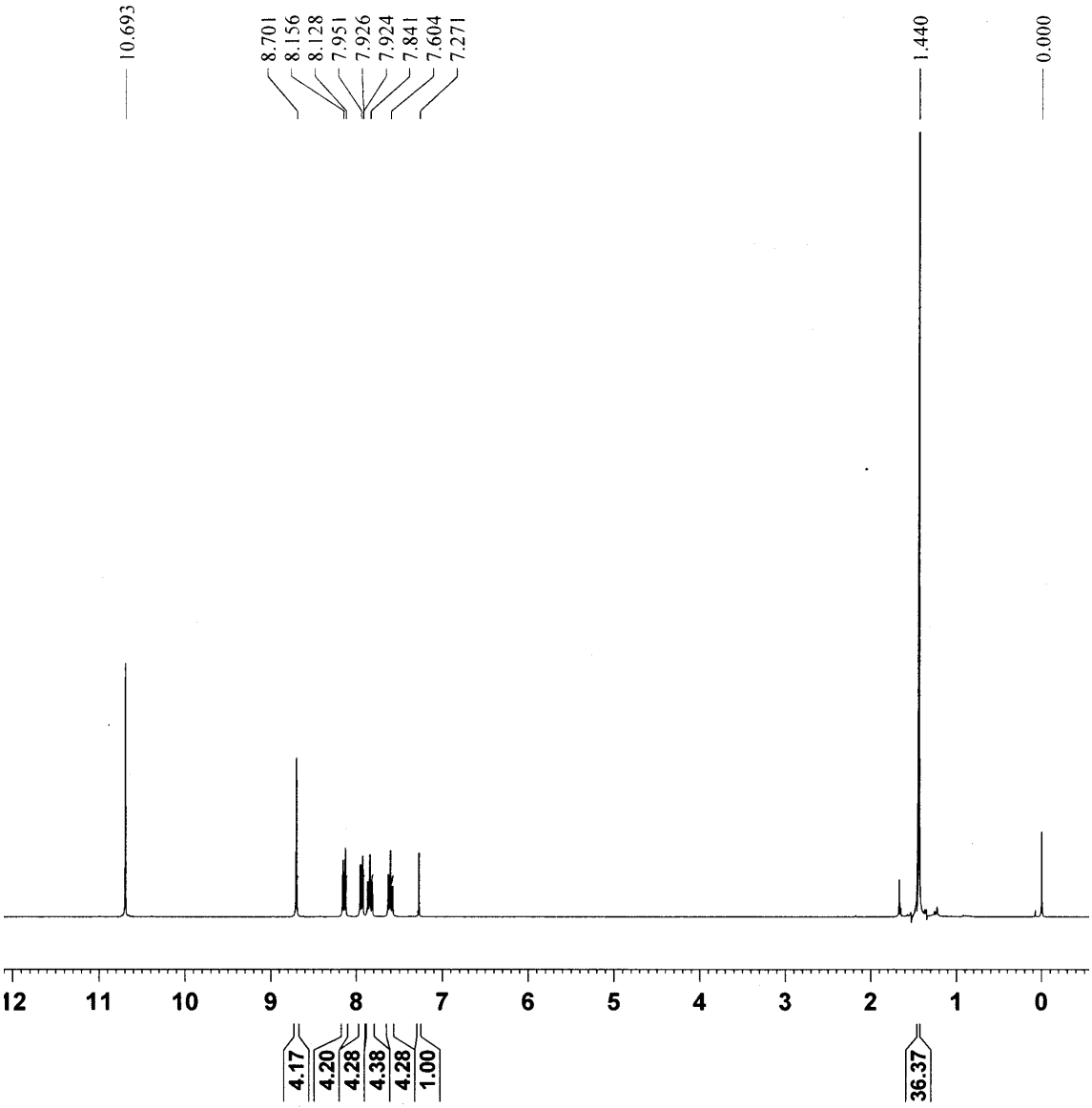
140
120
100
80
60
40
20
0


O
H
N

1i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7.841
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7.271
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0.000
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11
10
9
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2
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0
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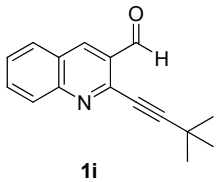
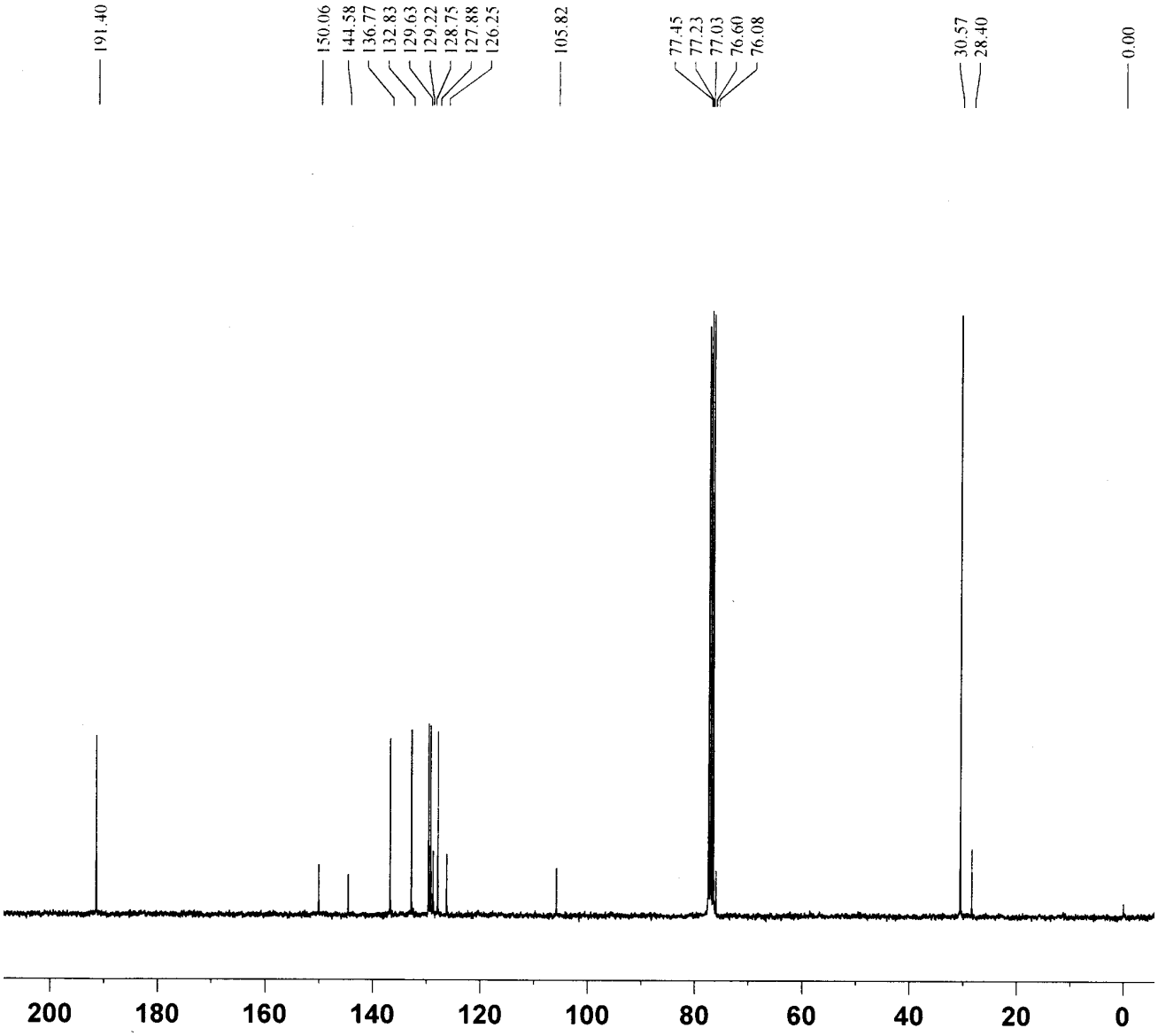
4.28
4.38
4.28
1.00
36.37


O
H
N

1i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127.88
126.25
105.82
77.45
77.23
77.03
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30.57
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0.00
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60
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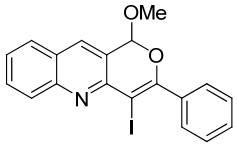
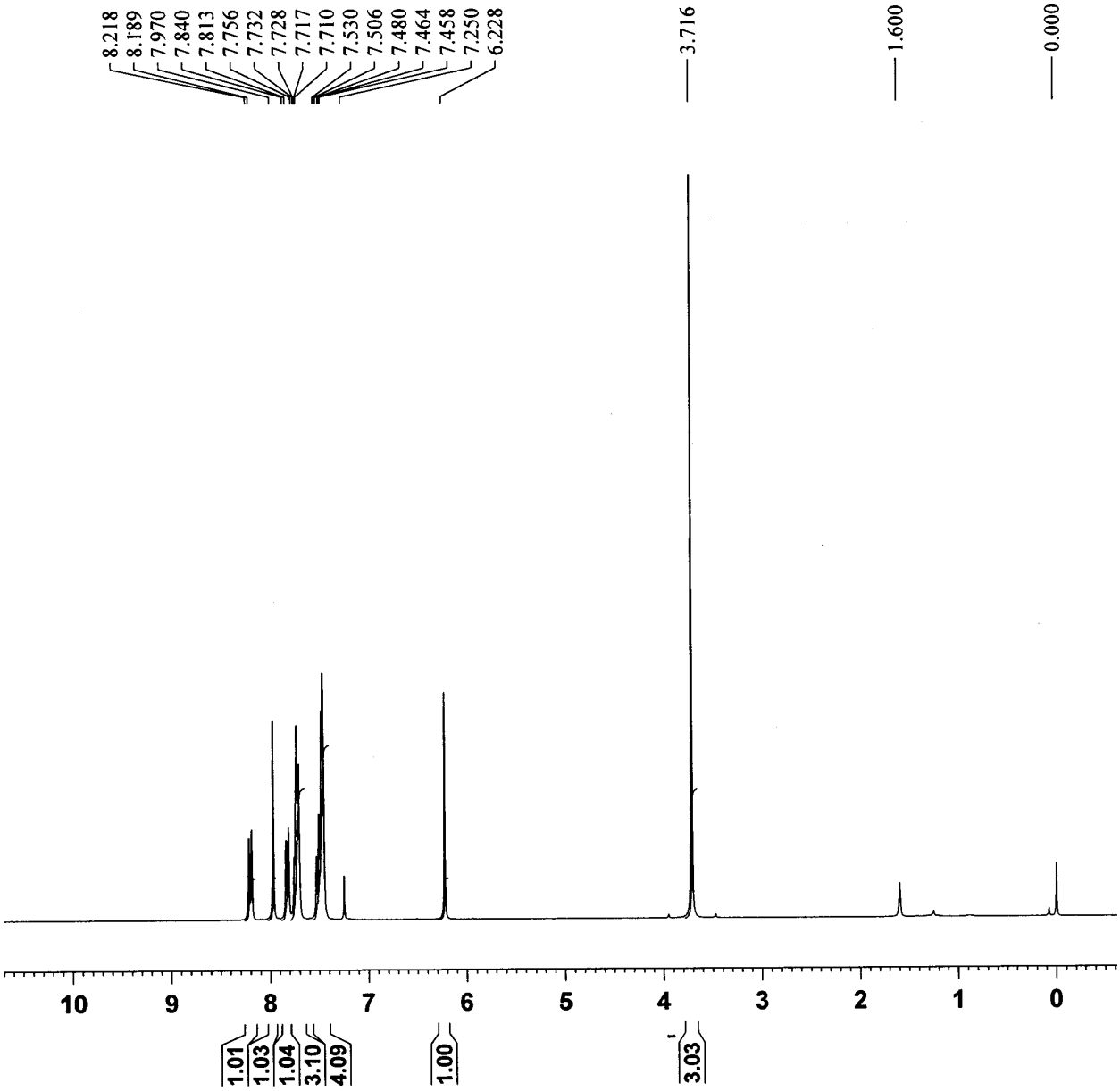
0


OMe
O
N
I

2a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7.464
7.458
7.250
6.228
3.716
1.600
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1.04
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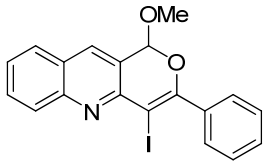
3.03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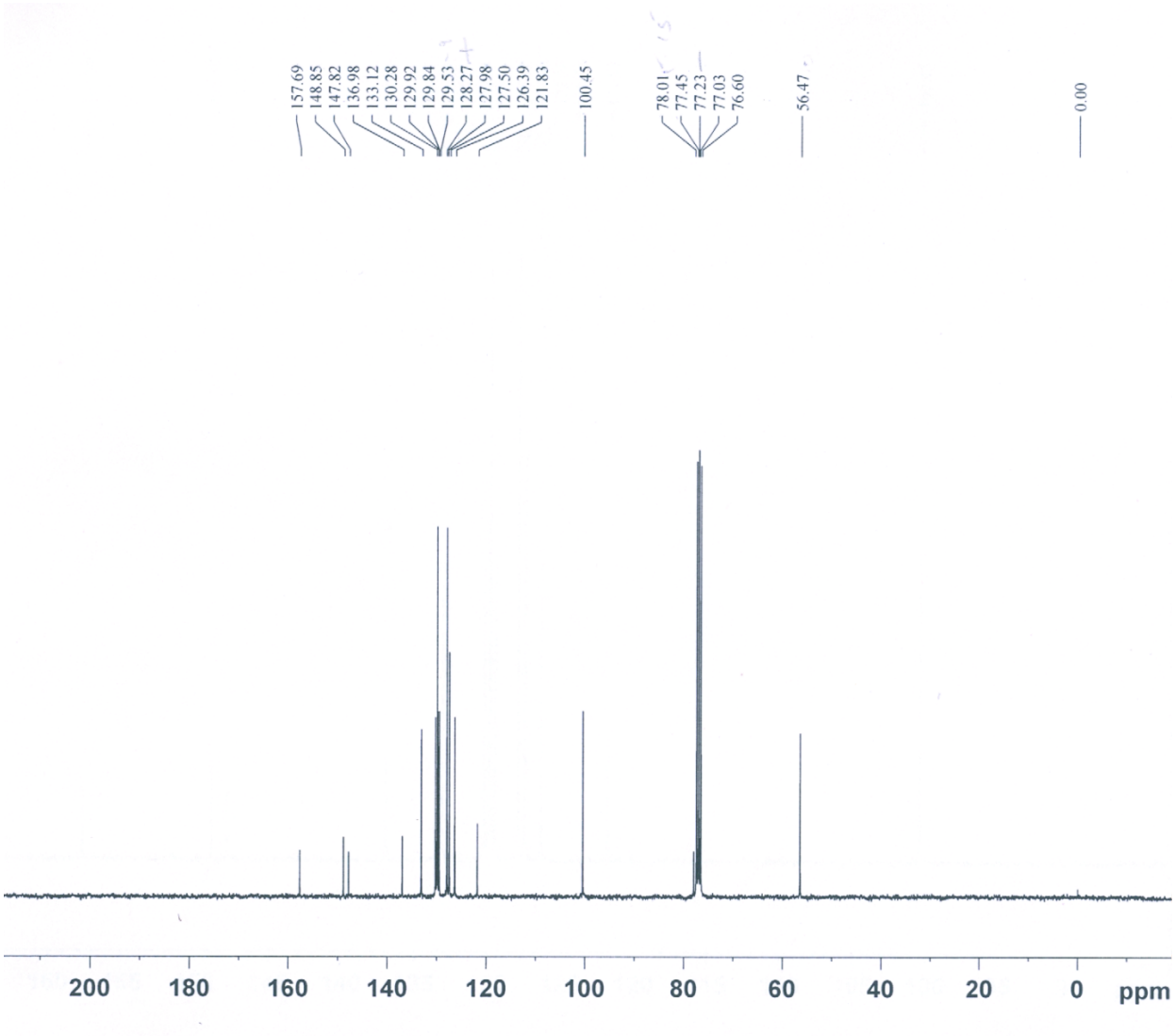
O
N
I

2a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127.50
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121.83
100.45
78.01
77.45
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77.03
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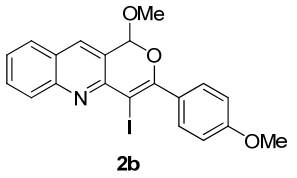
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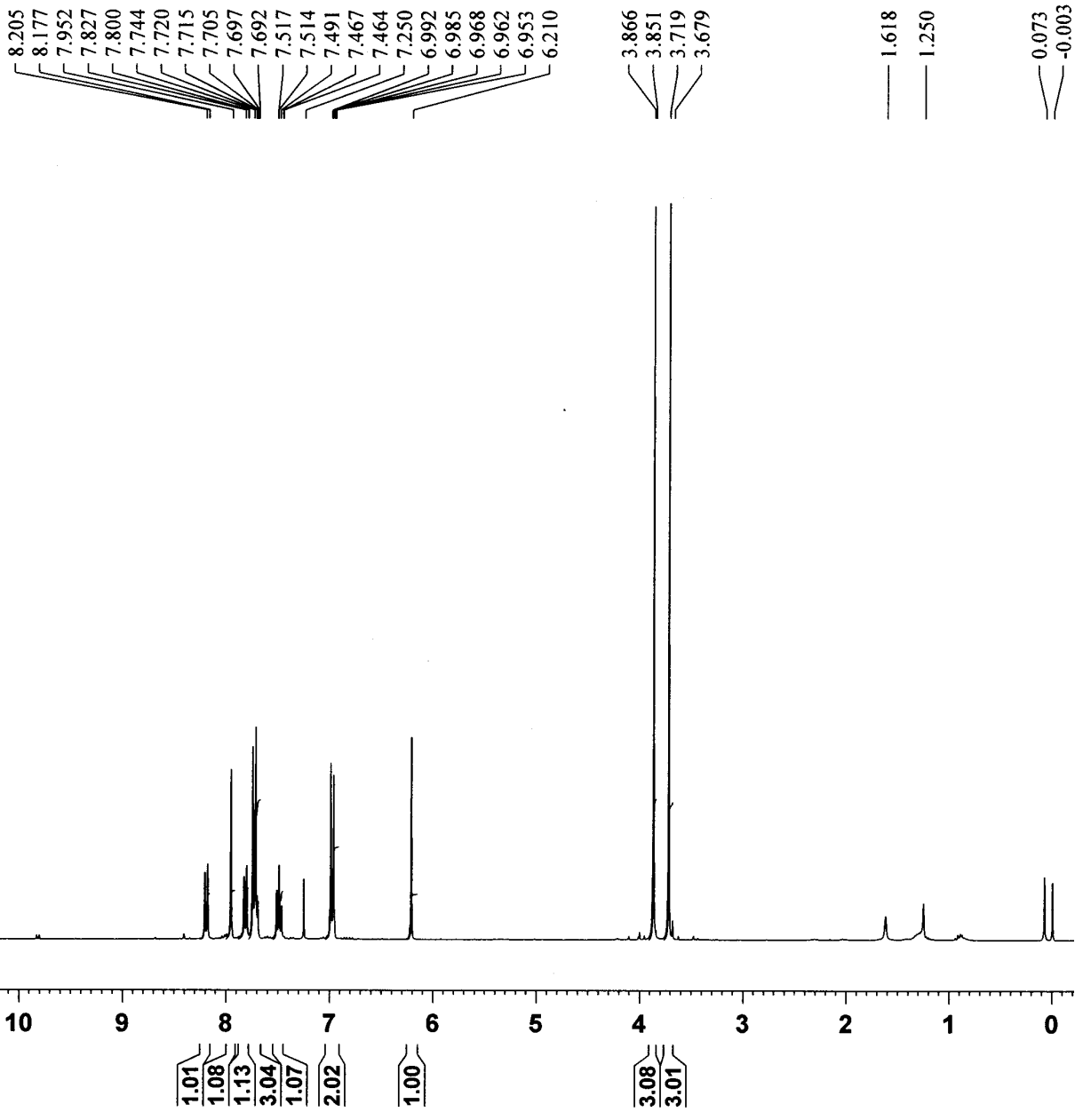
O
N
I
OMe

2b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7.514
7.491
7.467
7.464
7.250
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6.985
6.968
6.962
6.953
6.210
3.866
3.851
3.719
3.679
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1.250
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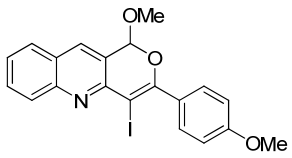
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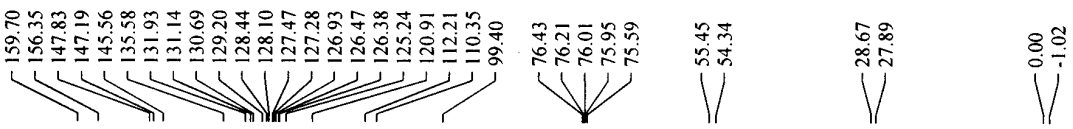
O
N
I
OMe

2b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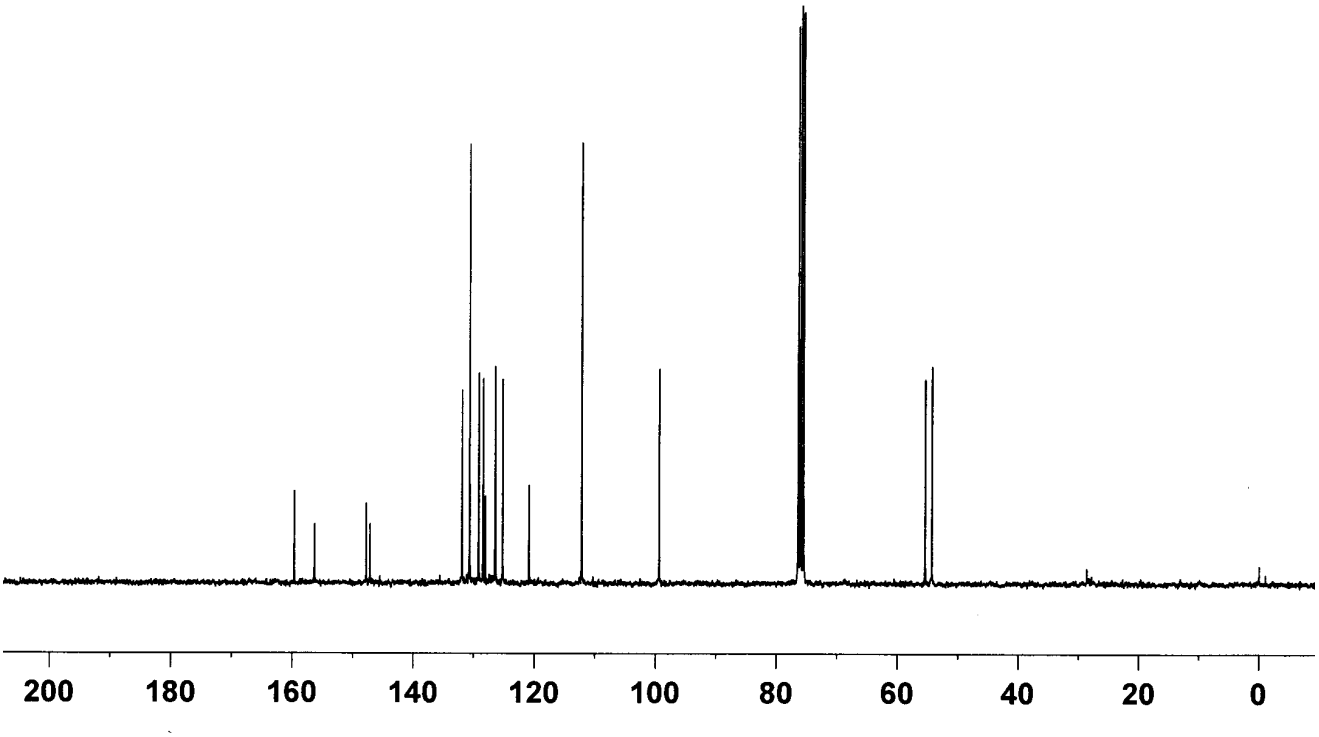
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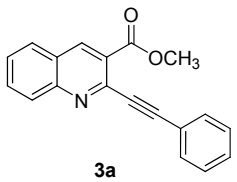
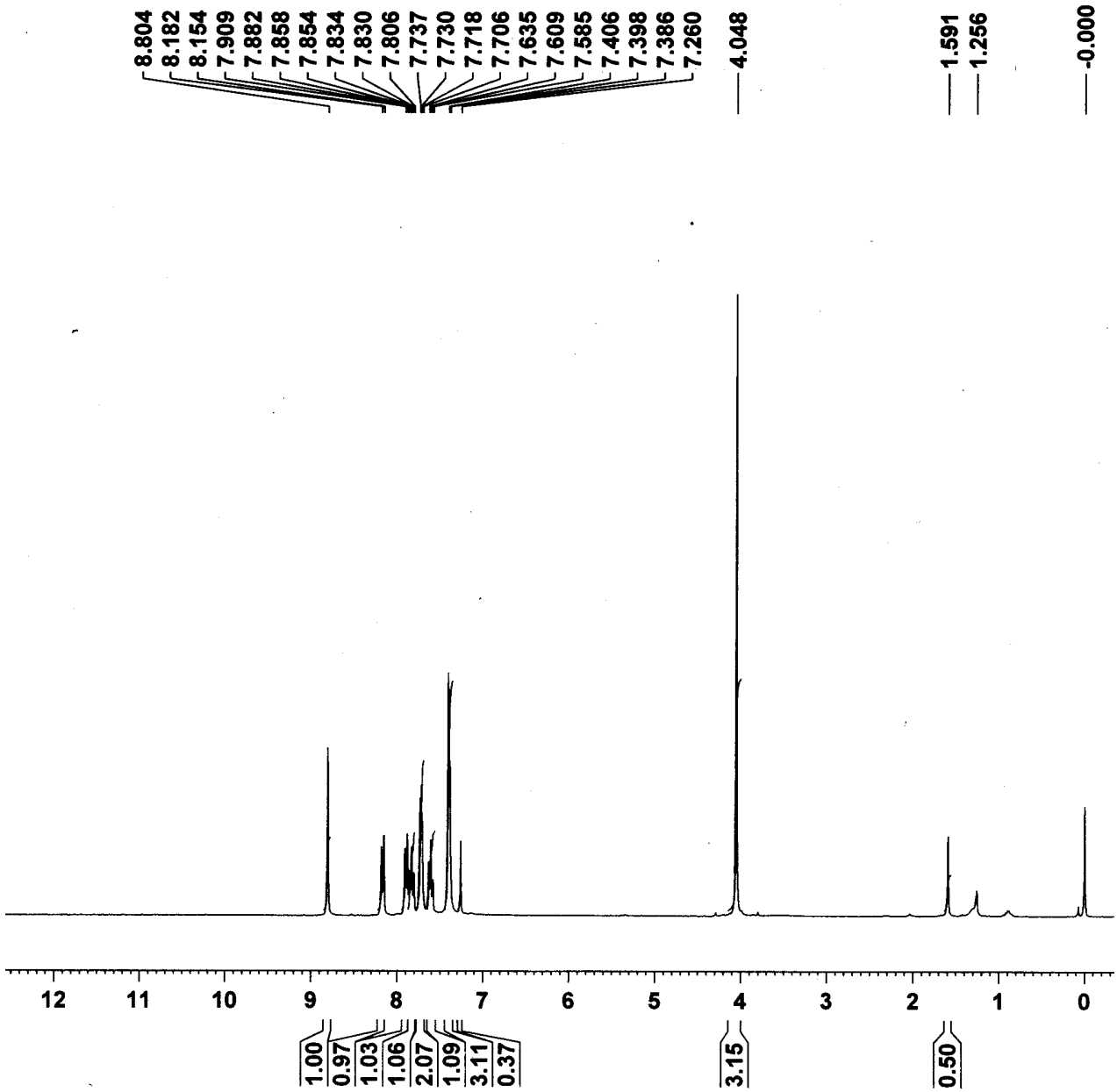

O
OCH3
N

3a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1.591
1.256
-0.000
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1.09
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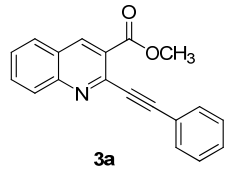
3.15
0.50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OCH3
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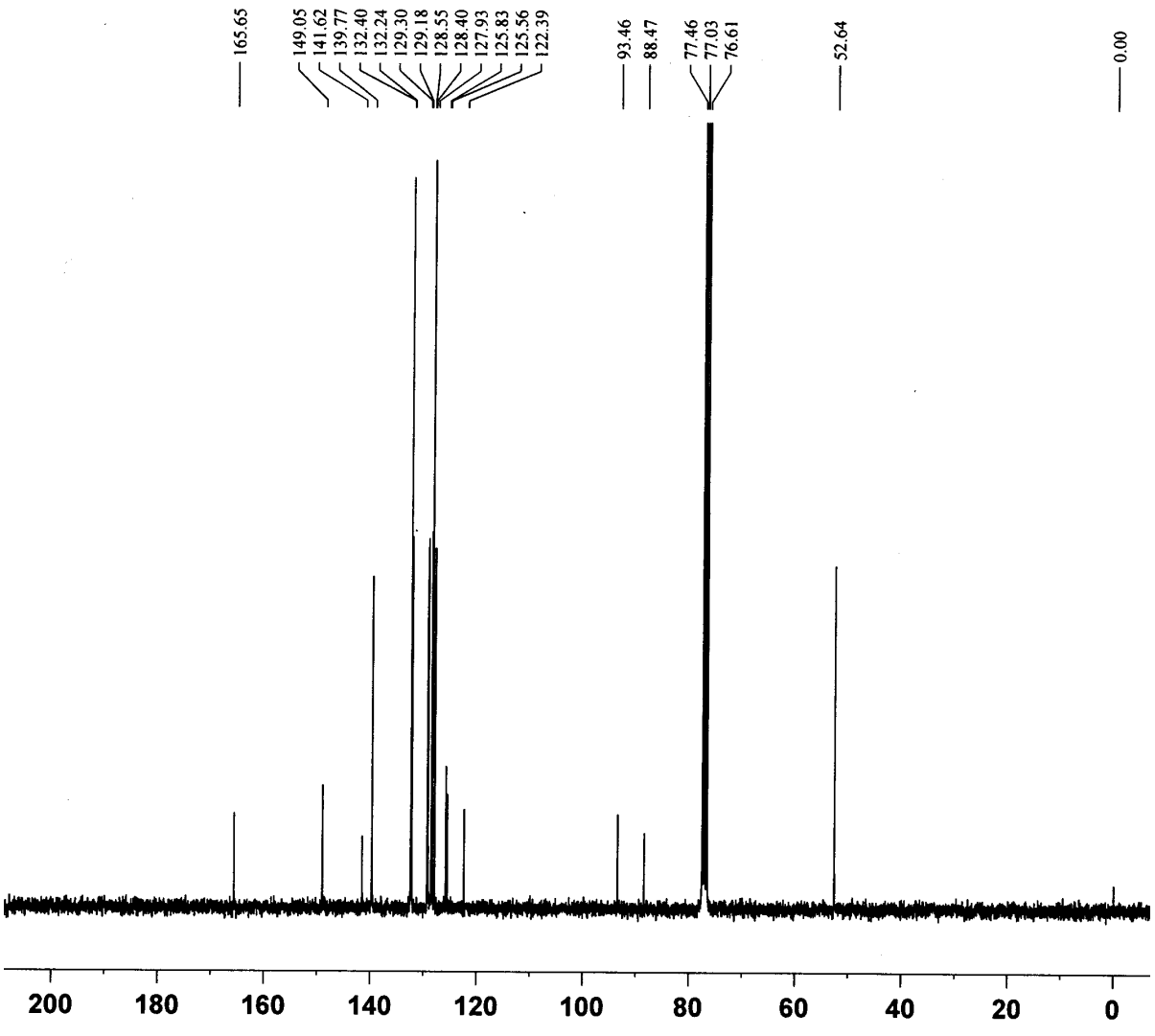
3a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122.39
93.46
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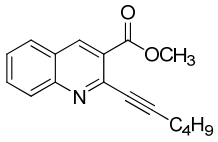
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C4H9

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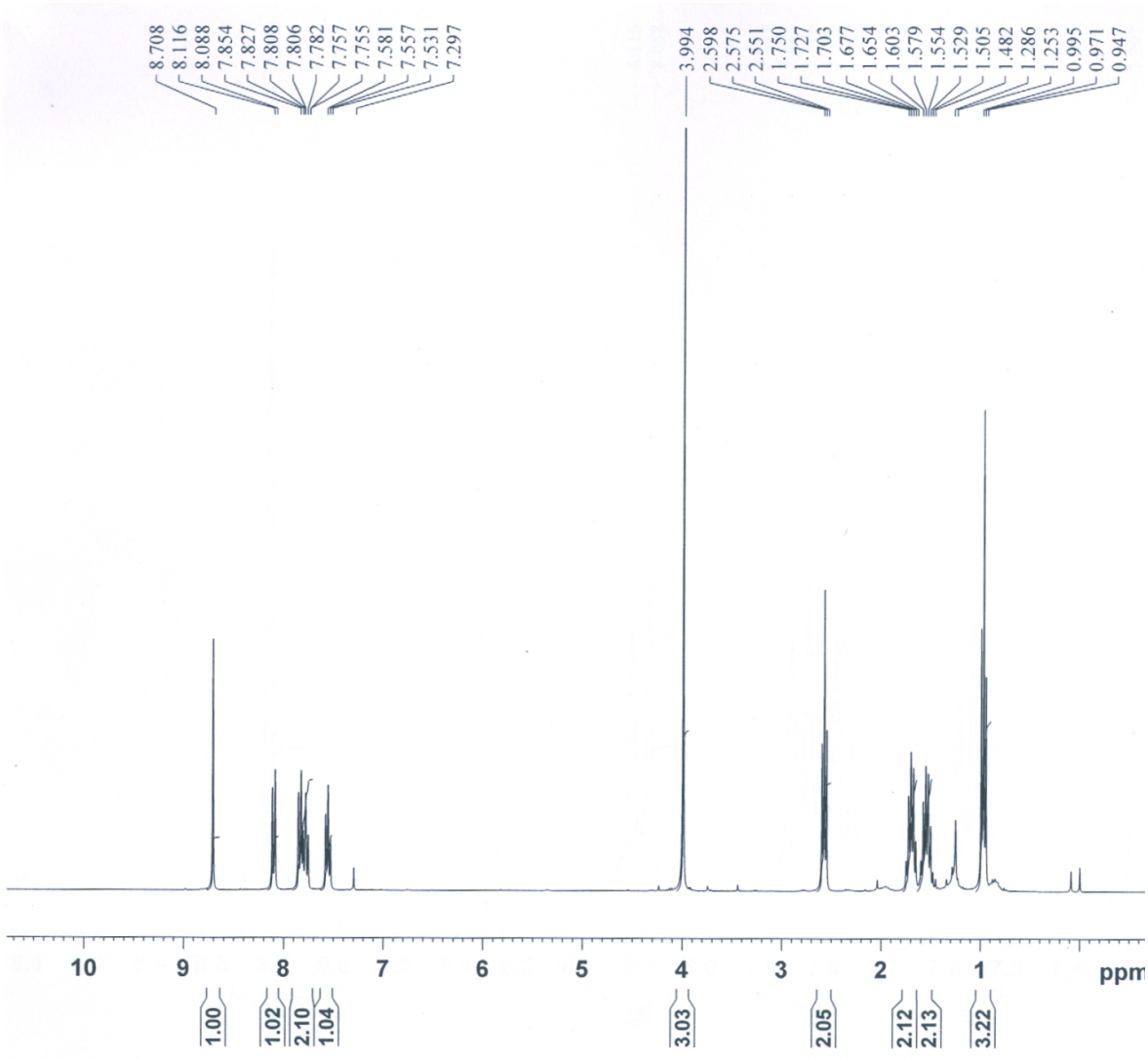
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7.531
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2.575
2.551
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0.947
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ppm
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3.03
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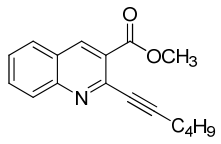
2.13
3.22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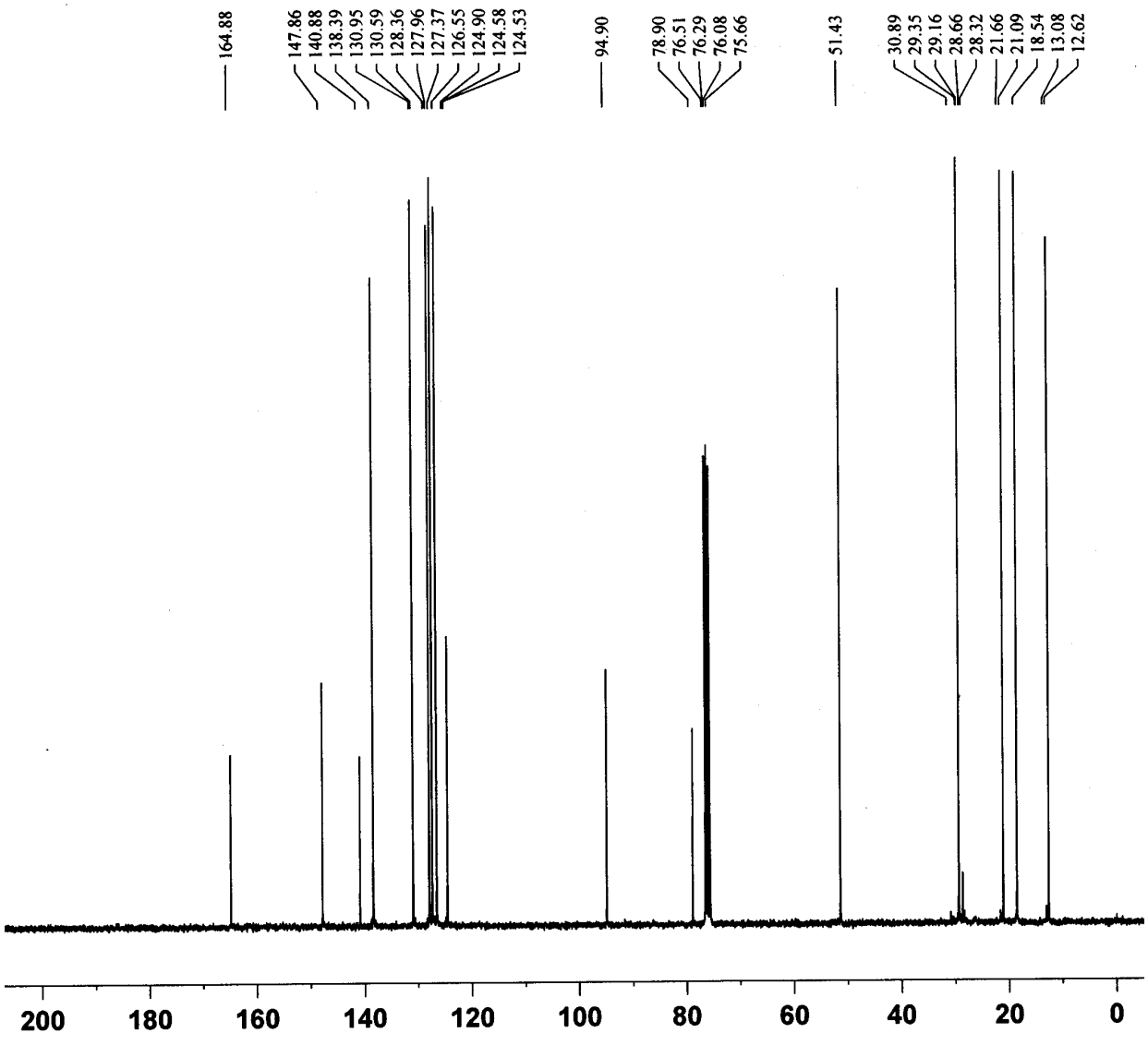
C4H9

3b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124.58
124.53
94.90
78.90
76.51
76.29
76.08
75.66
51.43
30.89
29.35
29.16
28.66
28.32
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12.62
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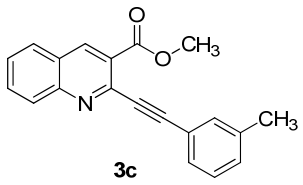
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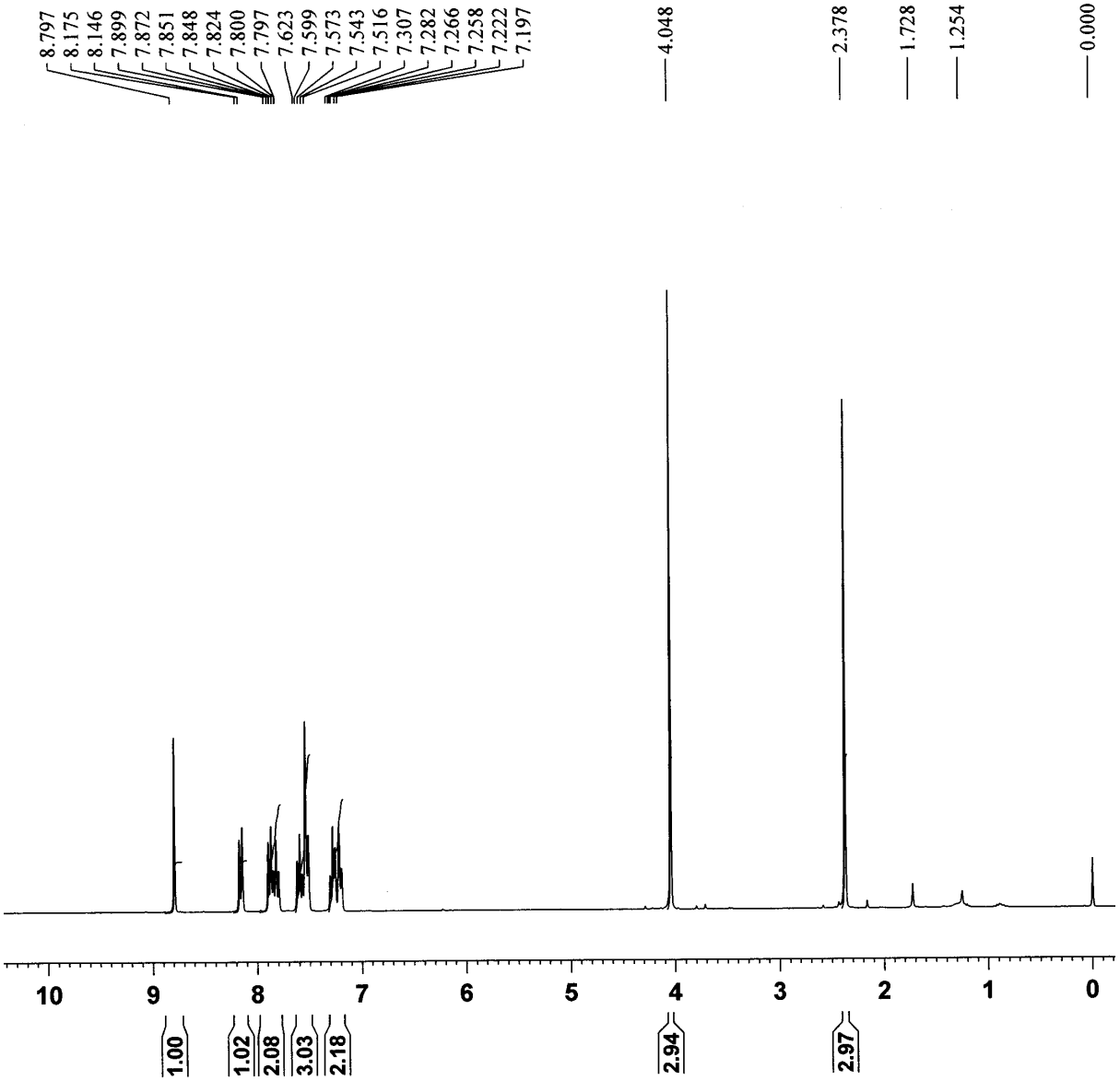
CH3
N
CH3

3c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7.848
7.824
7.800
7.797
7.623
7.599
7.573
7.543
7.516
7.307
7.282
7.266
7.258
7.222
7.197
4.048
2.378
1.728
1.254
0.000
10
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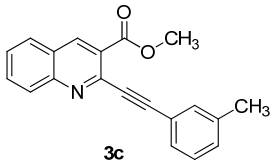
1.02
2.08
3.03
2.18
2.94
2.97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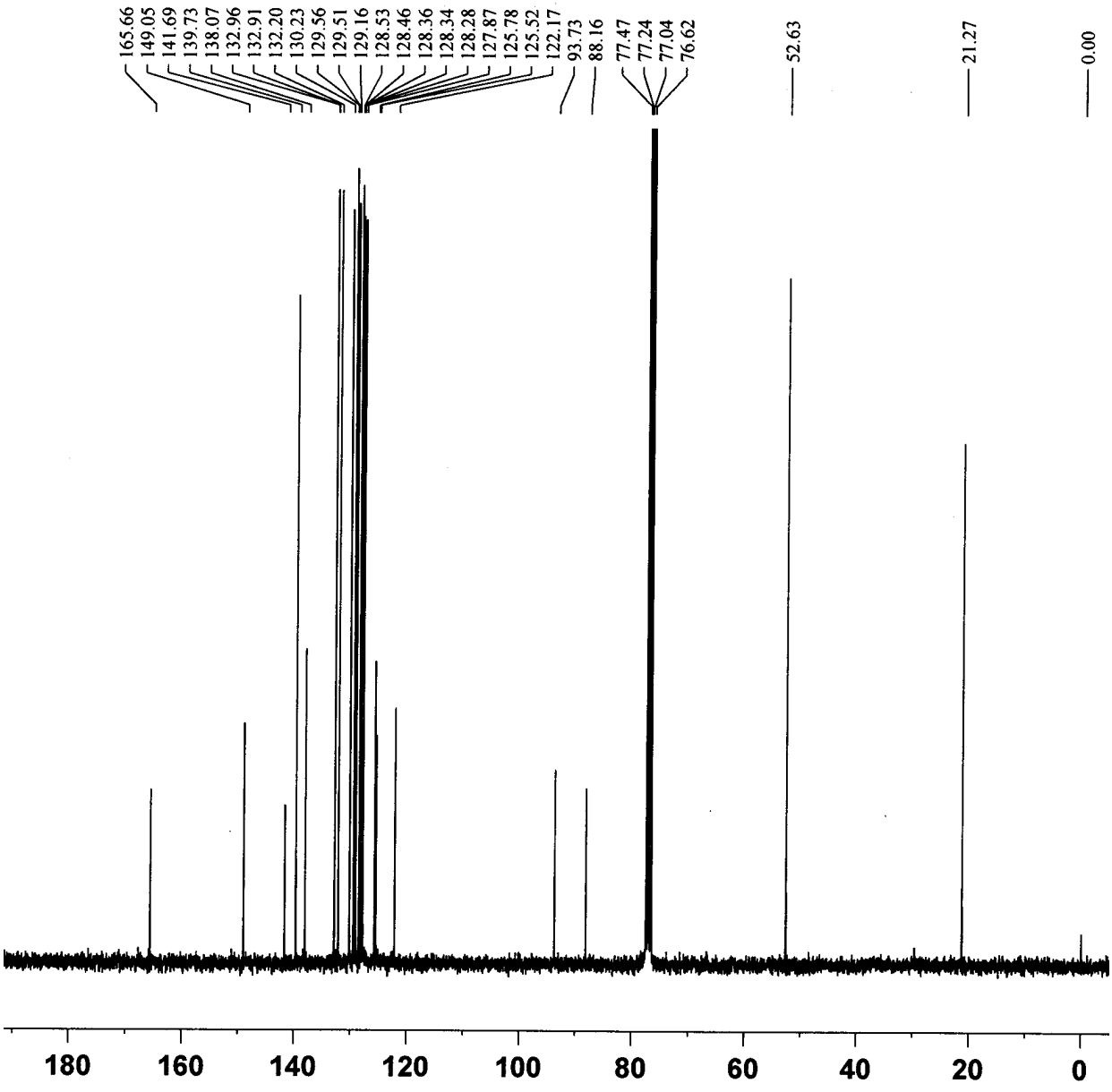
CH3
N
CH3

3c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132.20
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129.16
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128.46
128.36
128.34
128.28
127.87
125.78
125.52
122.17
93.73
88.16
77.47
77.24
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76.62
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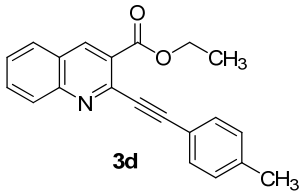
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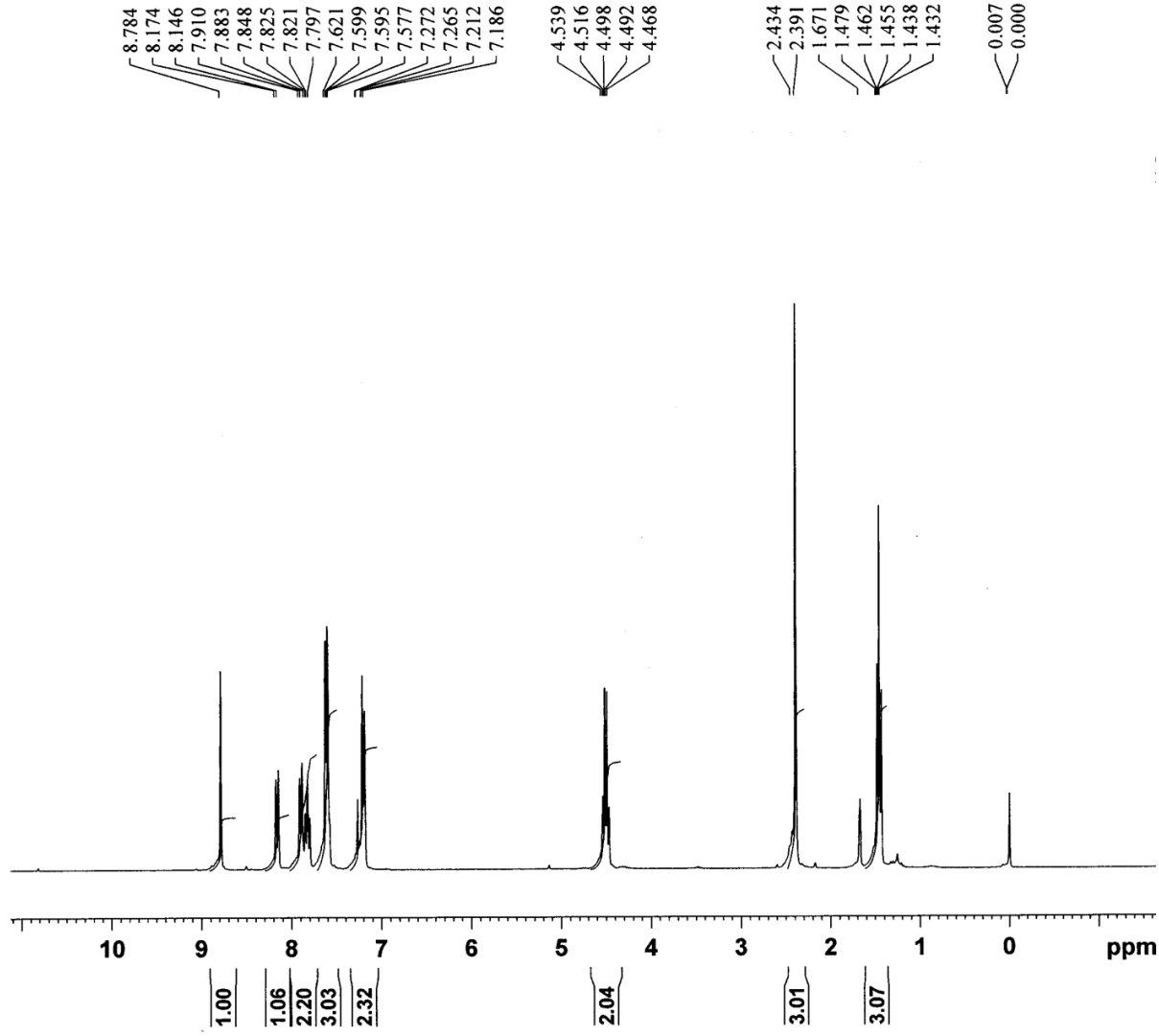
CH3
N
CH3

3d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7.797
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7.595
7.577
7.272
7.265
7.212
7.186
4.539
4.516
4.498
4.492
4.468
2.434
2.391
1.671
1.479
1.462
1.455
1.438
1.432
0.007
0.000
10
9
8
7
6
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1.06
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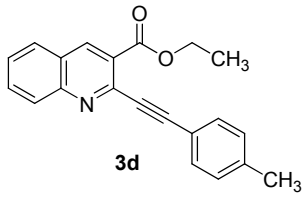
3.03
2.32
2.04
3.01
3.07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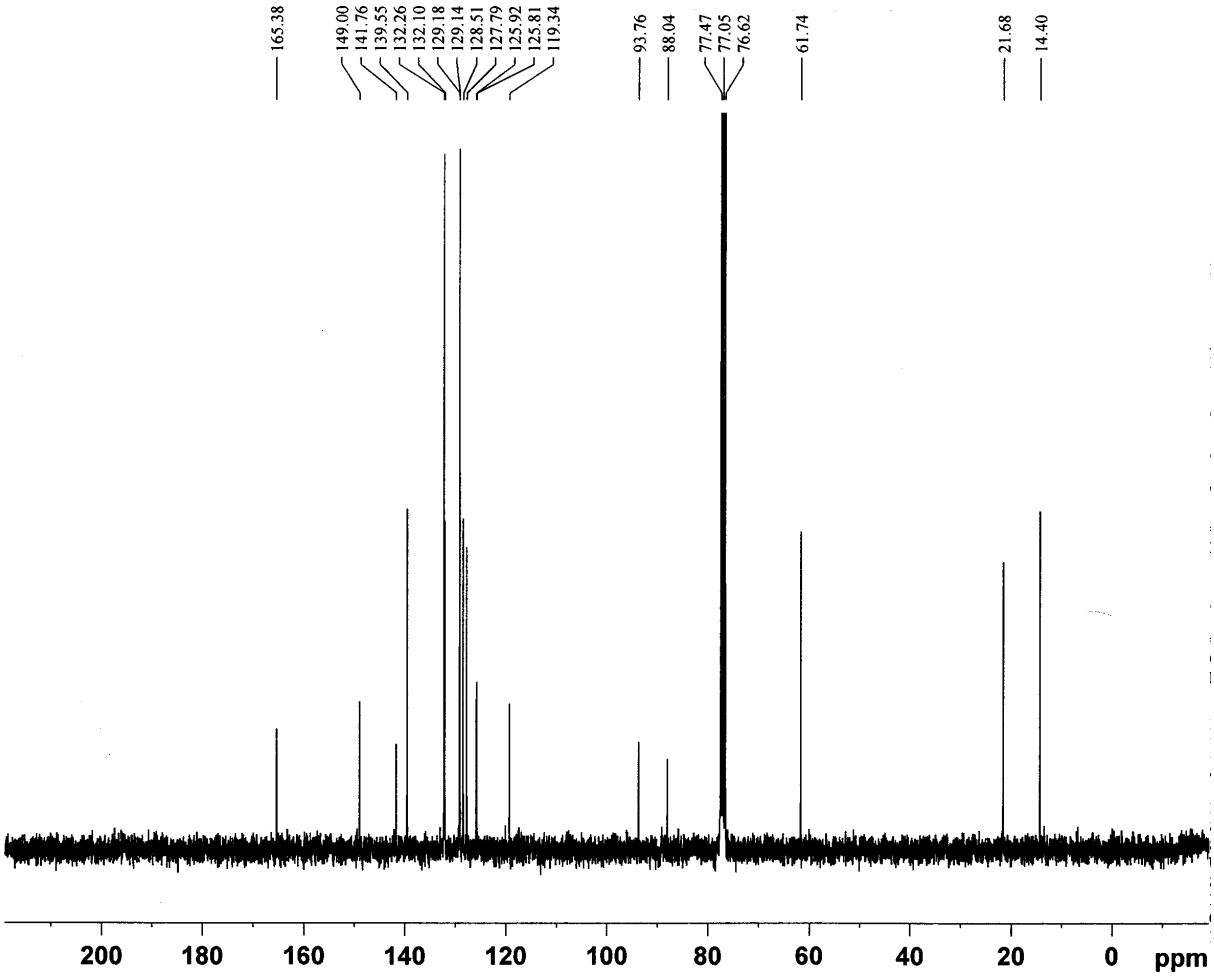
CH3
N
CH3

3d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128.51
127.79
125.92
125.81
119.34
93.76
88.04
77.47
77.05
76.62
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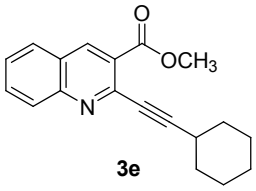
140
120
100
80
60
40
20
0
ppm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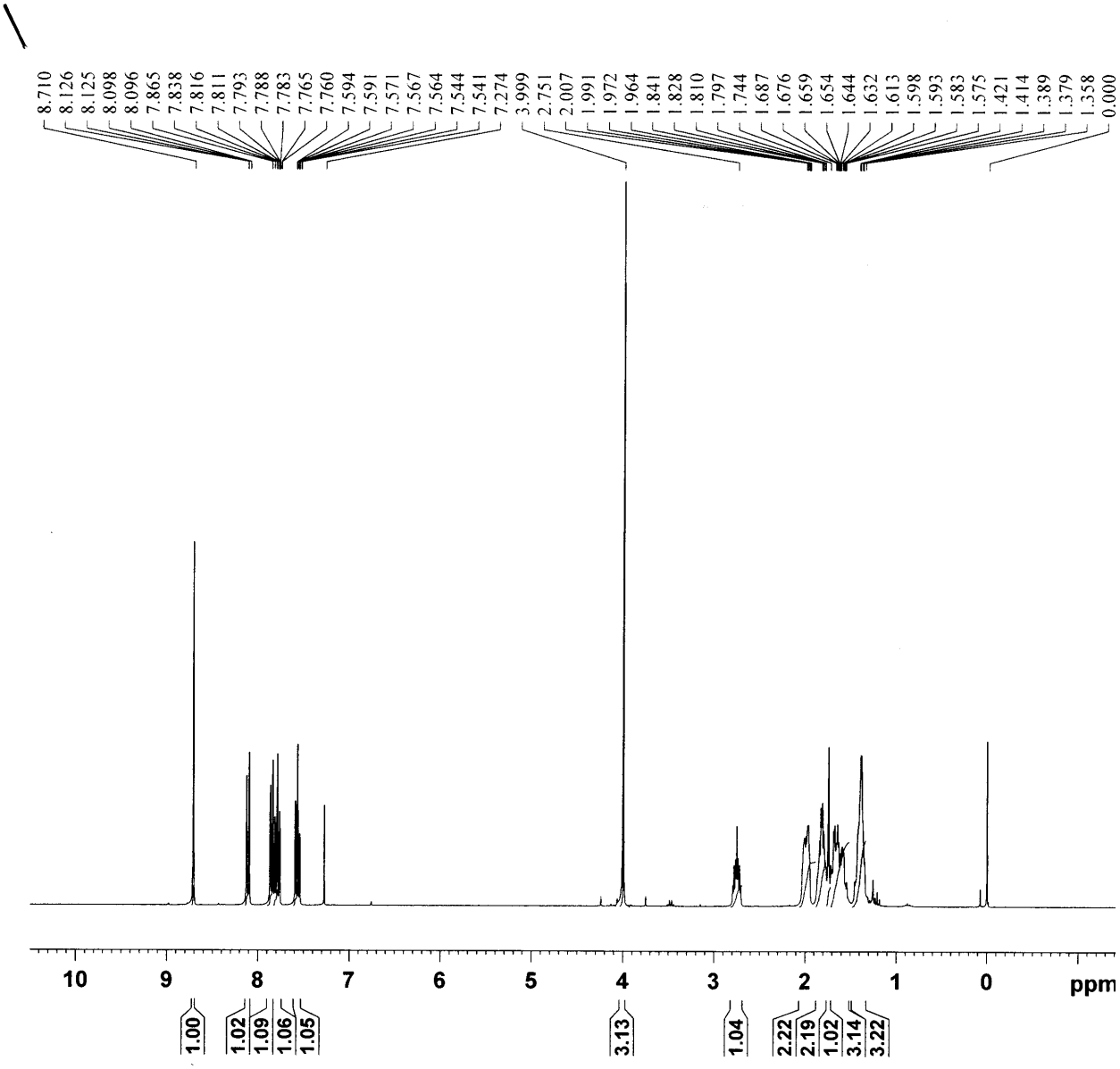
OCH3
N

3e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7.838
7.816
7.811
7.793
7.788
7.783
7.765
7.760
7.594
7.591
7.571
7.567
7.564
7.544
7.541
7.274
3.999
2.751
2.007
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1.972
1.964
1.841
1.828
1.810
1.797
1.744
1.687
1.676
1.659
1.654
1.644
1.632
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1.598
1.593
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1.06
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1.04
2.22
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1.02
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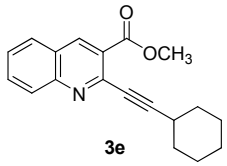
3.22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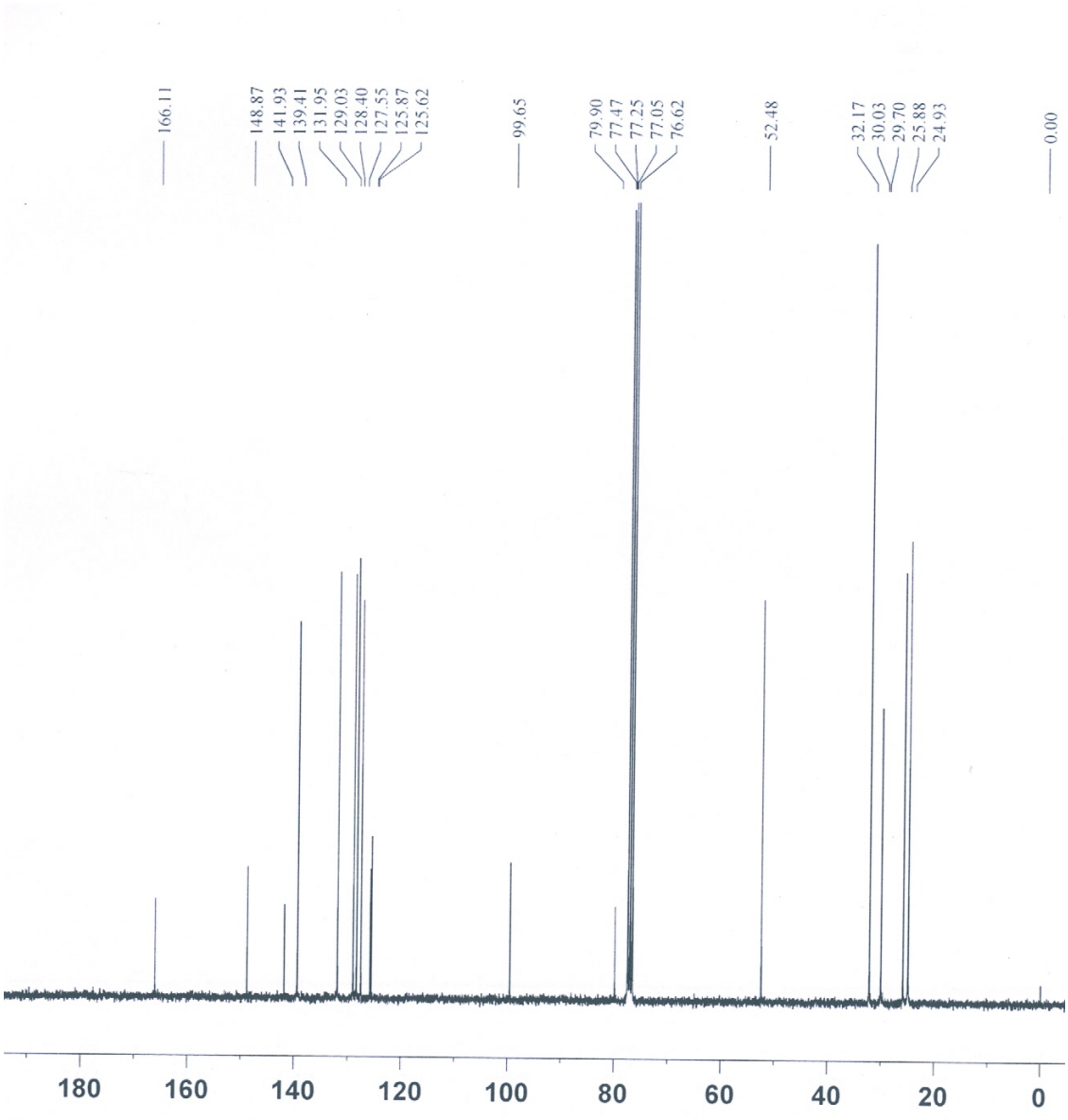
OCH3
N

3e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127.55
125.87
125.62
99.65
79.90
77.47
77.25
77.05
76.62
52.48
32.17
30.03
29.70
25.88
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140
120
100
80
60
40
20
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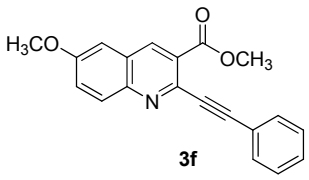
O
H3CO
OCH3
N

3f


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7.705
7.702
7.692
7.488
7.481
7.457
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7.113
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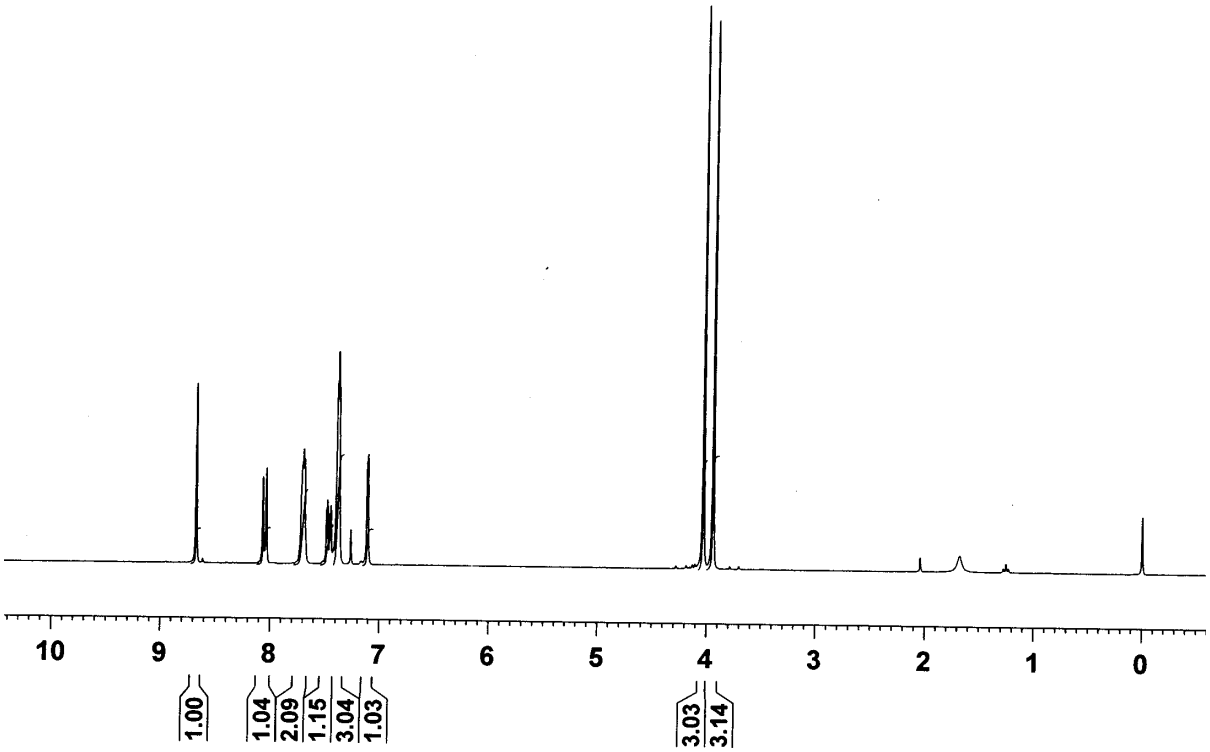
0.000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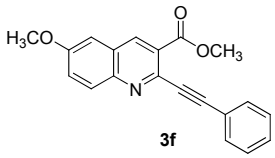
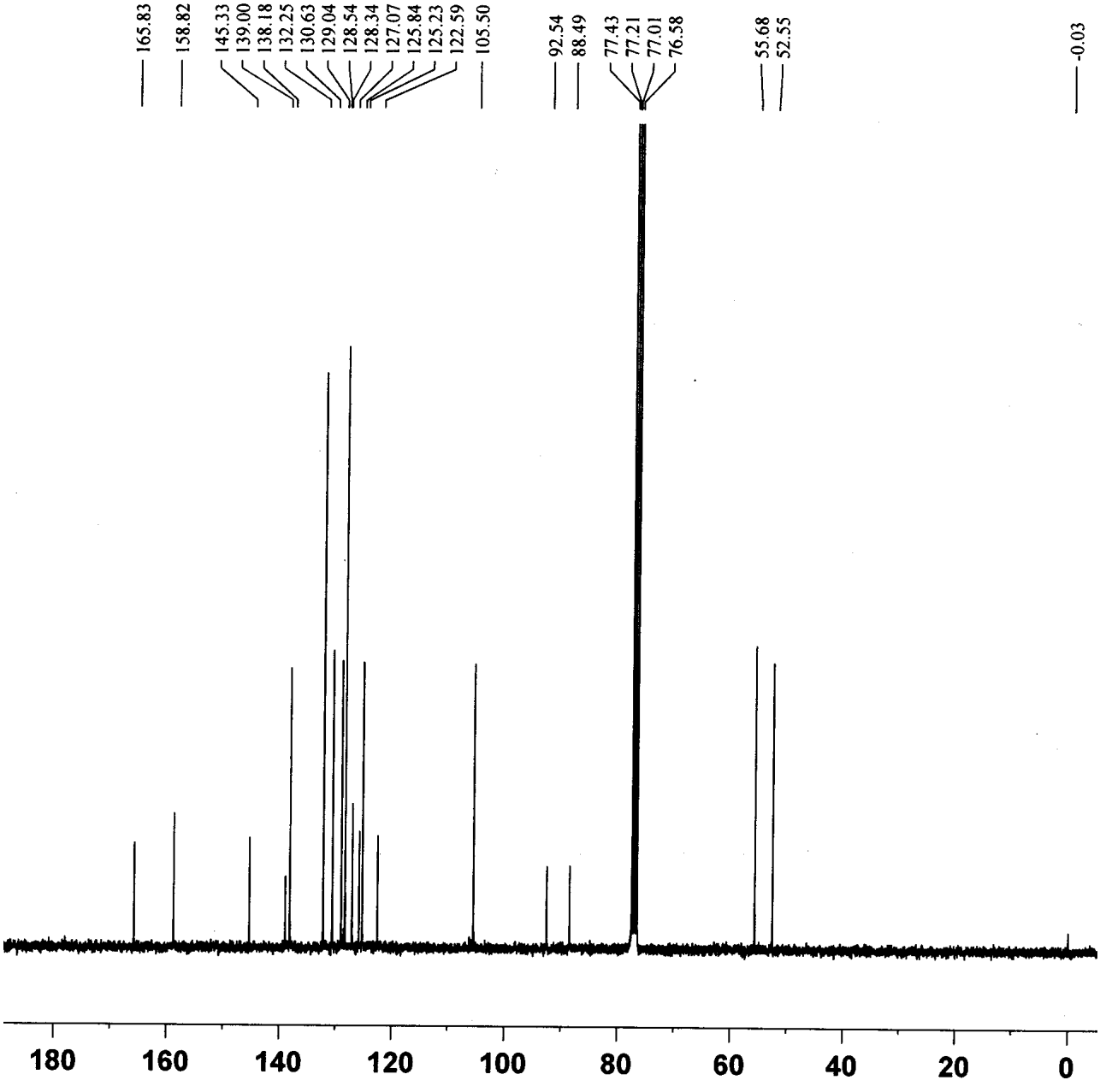
1.04
2.09
1.15
3.04
1.03
3.03
3.14


H3CO
O
OCH3
N

3f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129.04
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125.23
122.59
105.50
92.54
88.49
77.43
77.21
77.01
76.58
55.68
52.55
-0.03
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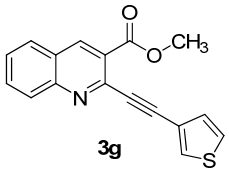
140
120
100
80
60
40
20
0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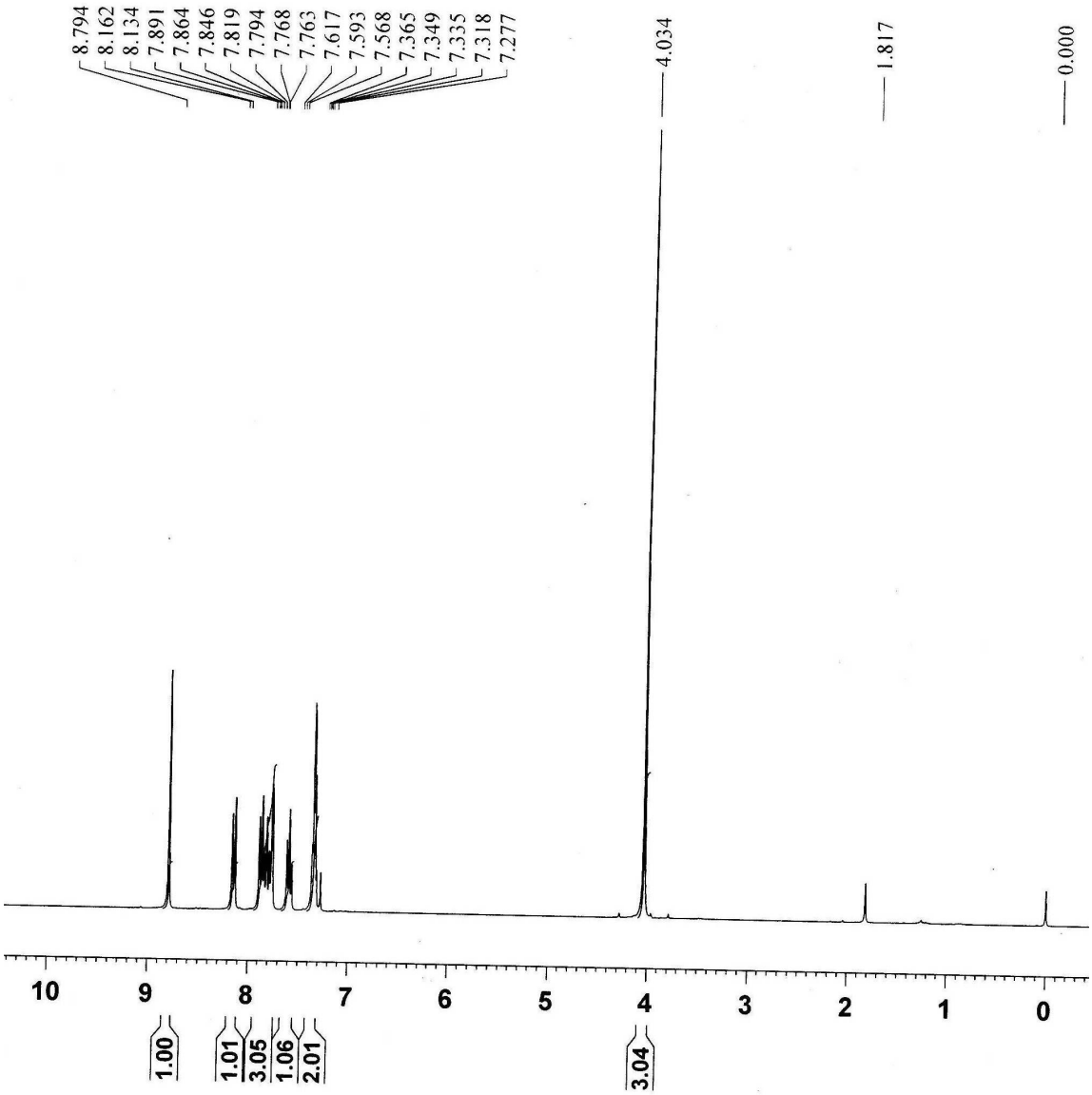
O
CH3
N
S

3g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7.593
7.568
7.365
7.349
7.335
7.318
7.277
4.034
1.817
0.000
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1.01
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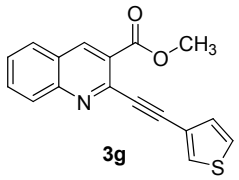
1.06
2.01
3.04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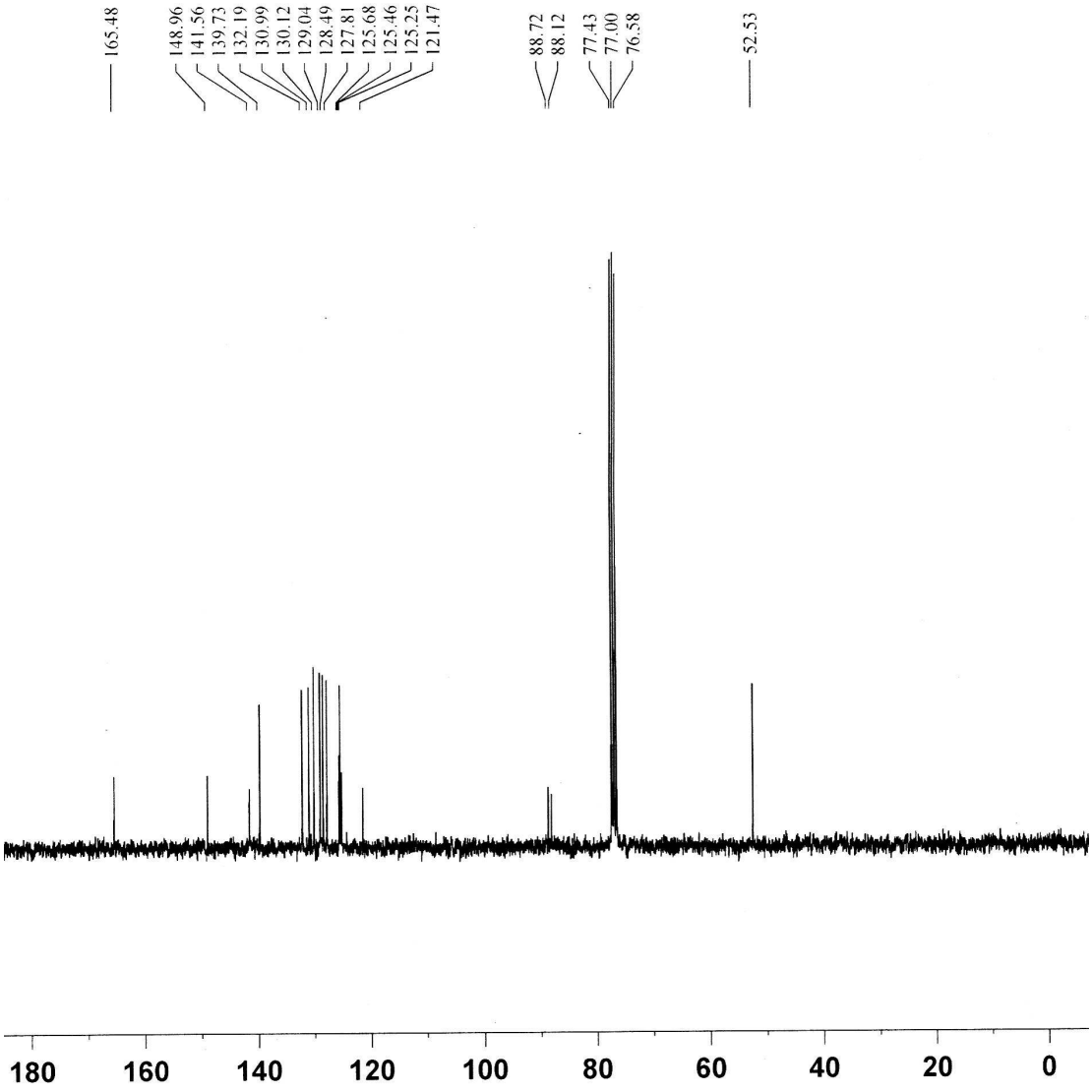
O
CH3
N
S

3g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125.46
125.25
121.47
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77.00
76.58
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140
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60
40
20
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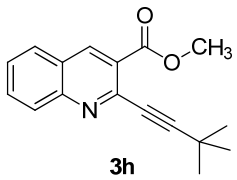
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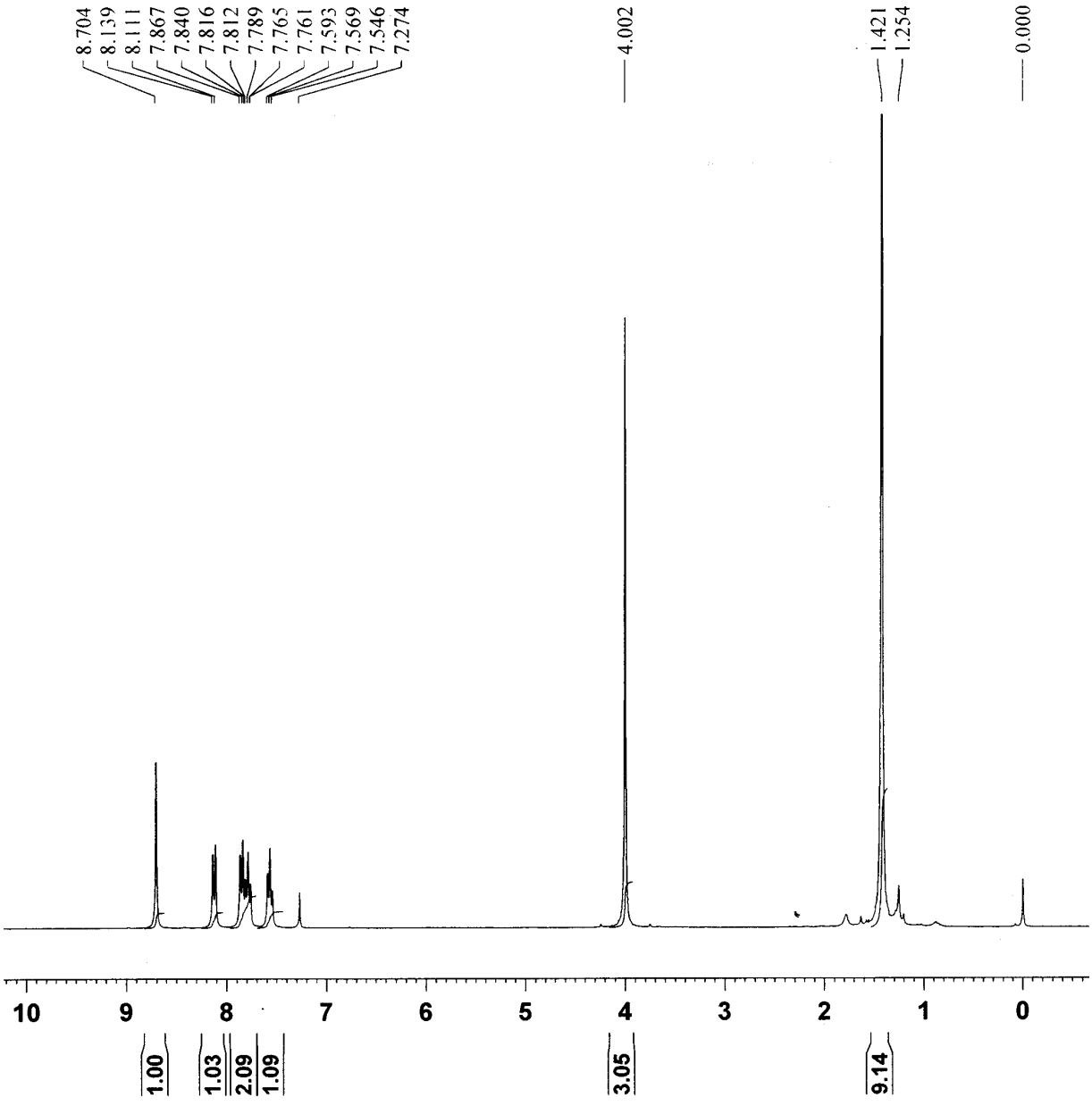
O
CH3
N

3h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7.274
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1.254
0.000
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1.03
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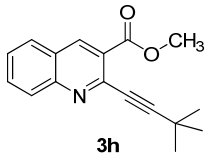
9.14


O
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CH3
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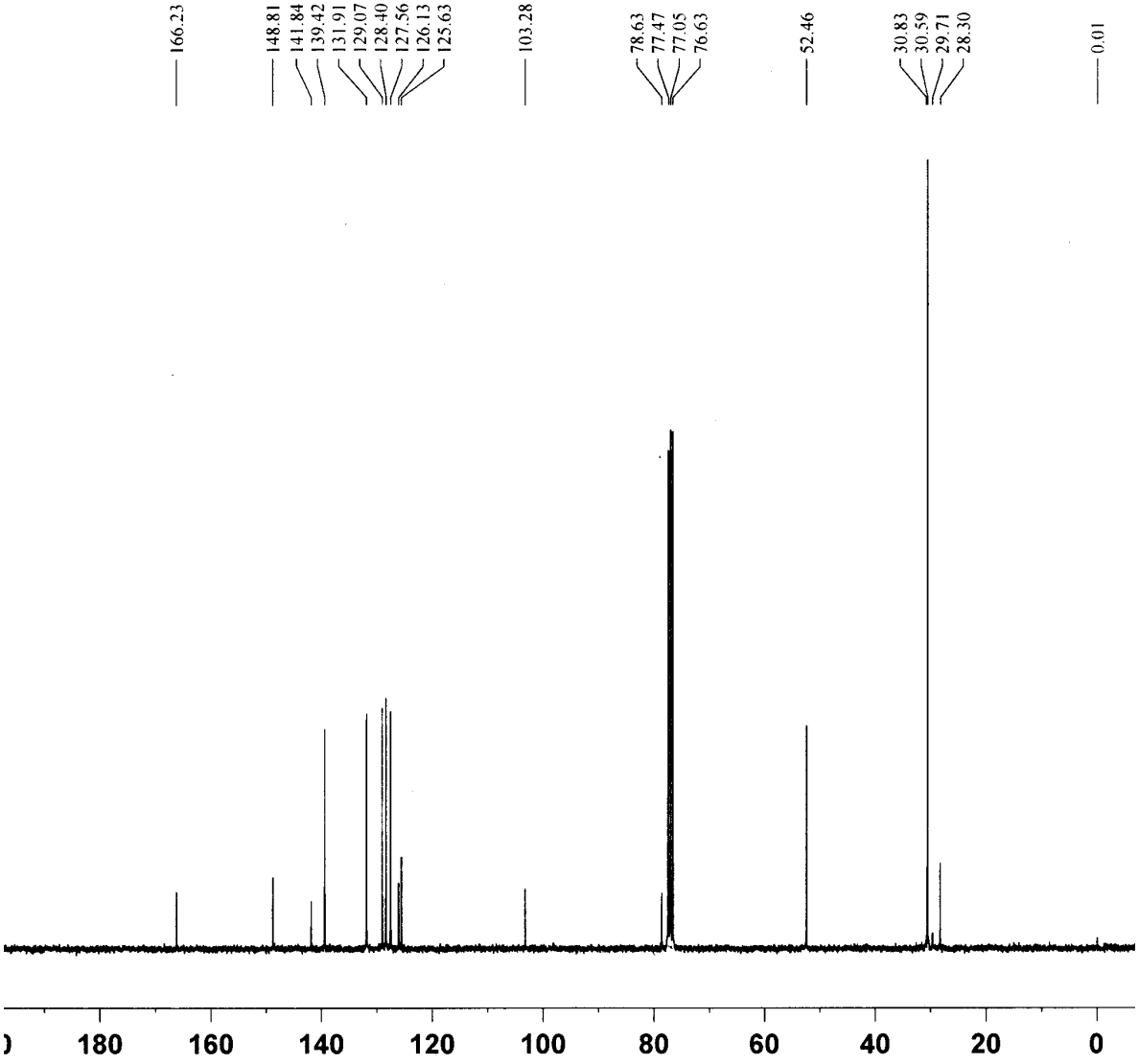
3h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125.63
103.28
78.63
77.47
77.05
76.63
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60
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20
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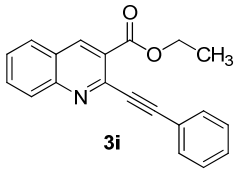
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O
CH3
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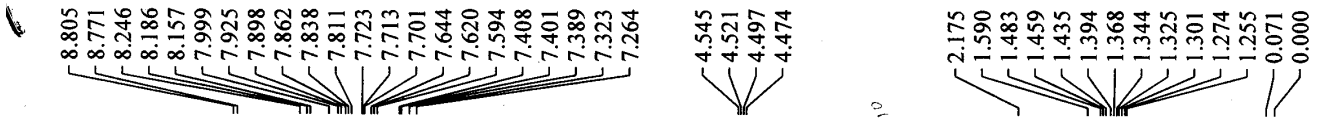
3i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7.713
7.701
7.644
7.620
7.594
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7.401
7.389
7.323
7.264
4.545
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4.497
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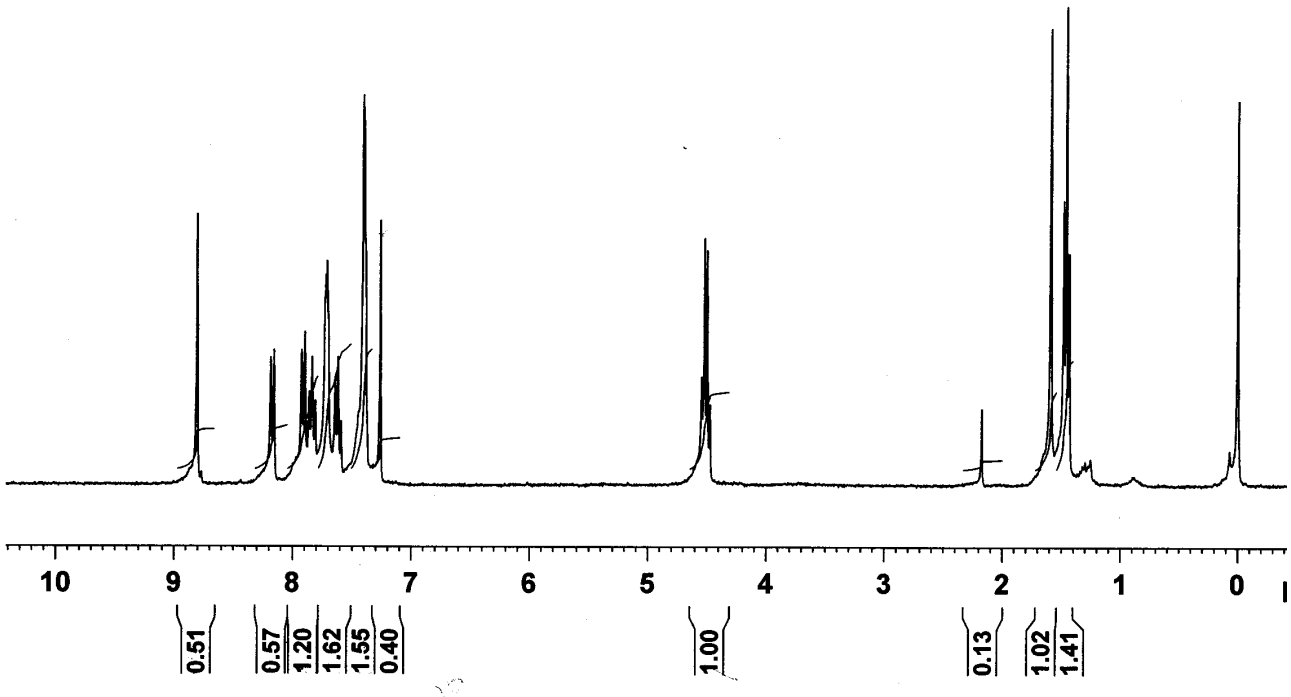
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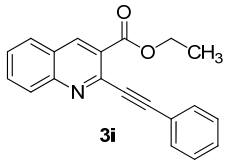
1.62
1.55
0.40
1.00
0.13
1.02
1.41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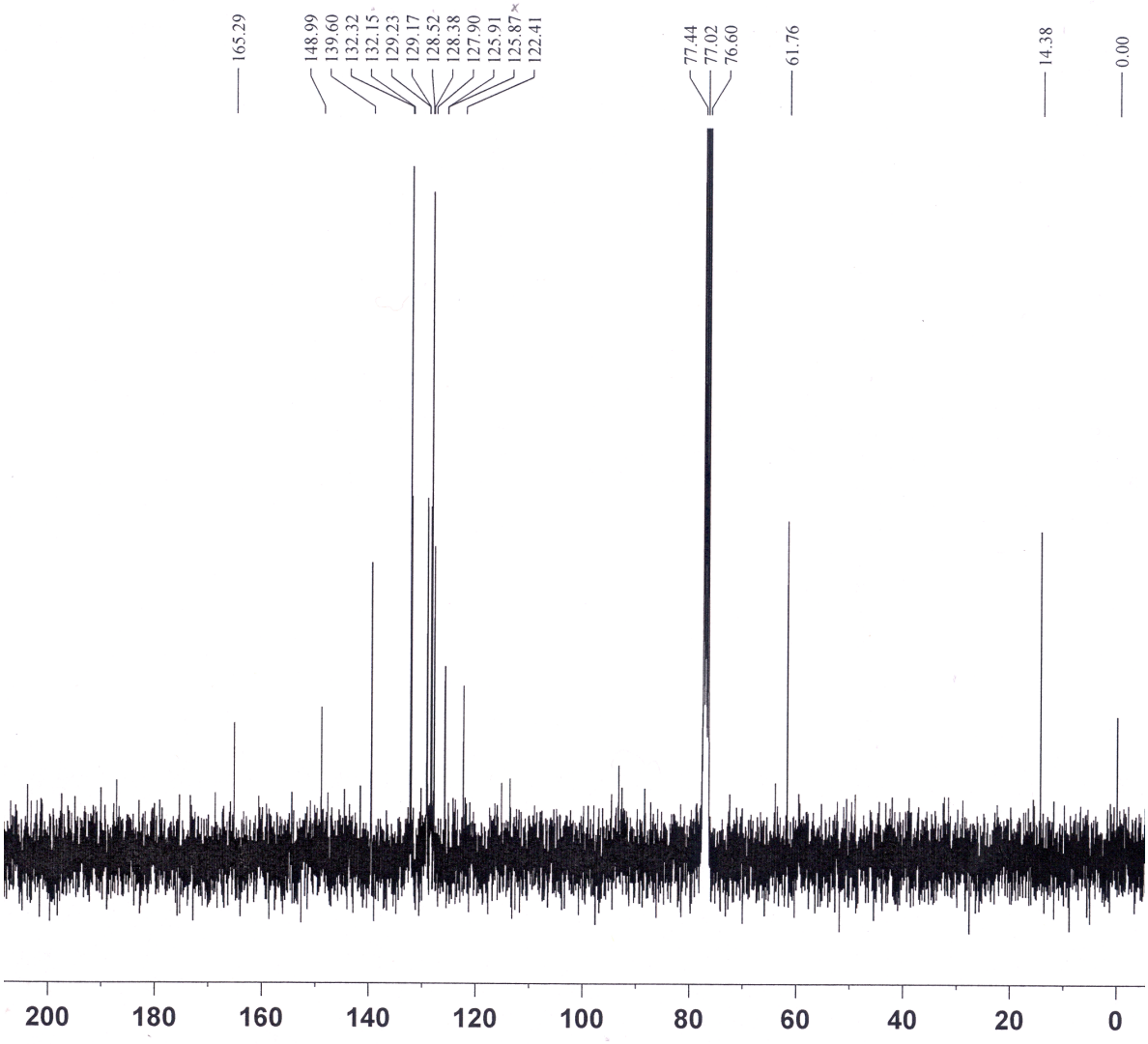
O
CH3
N

3i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129.17
128.52
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127.90
125.91
125.87
122.41
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77.02
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61.76
14.38
0.00
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140
120
100
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60
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20
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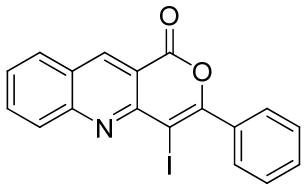
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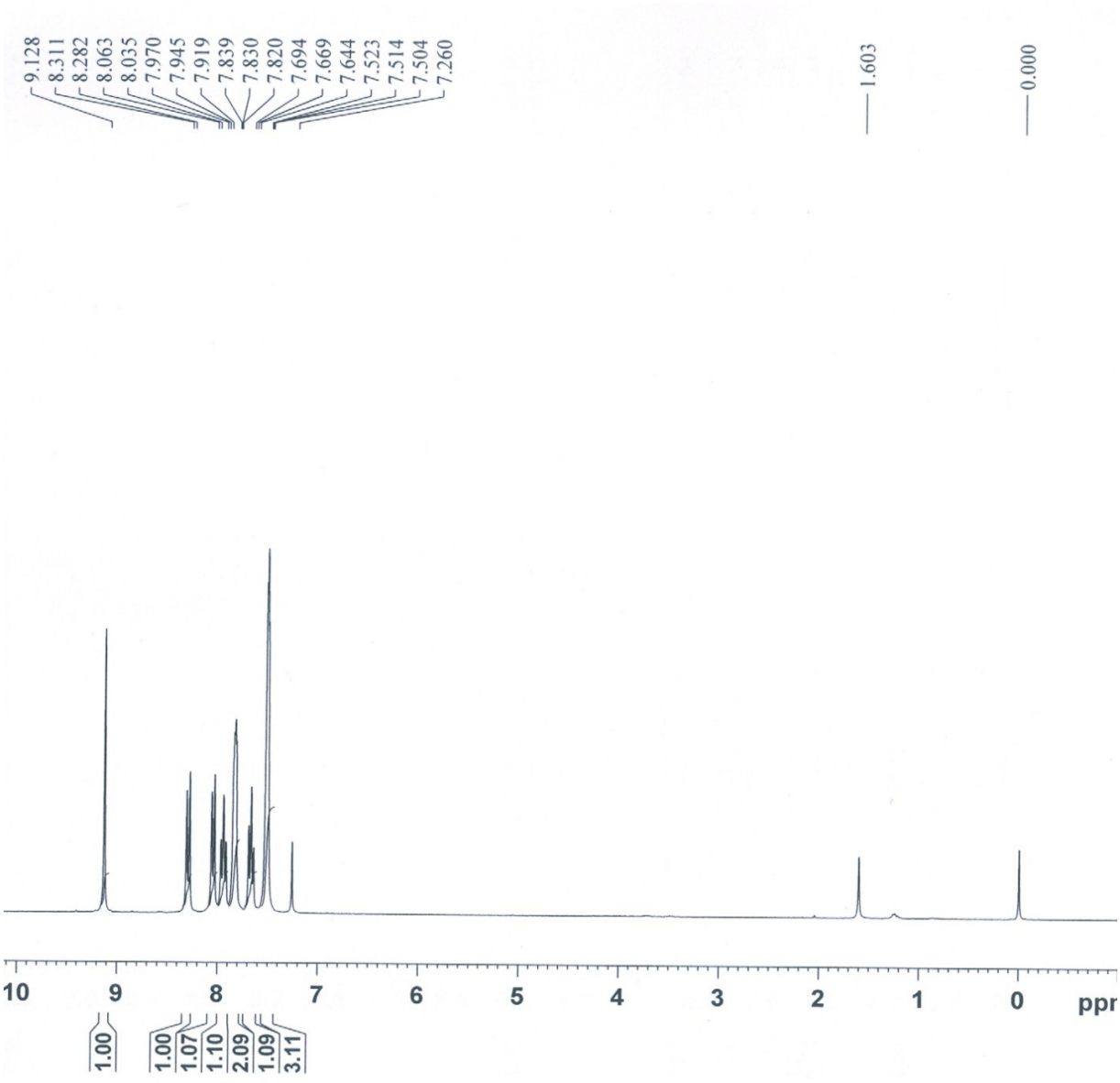
N
I

4a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7.644
7.523
7.514
7.504
7.260
1.603
0.000
10
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8
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5
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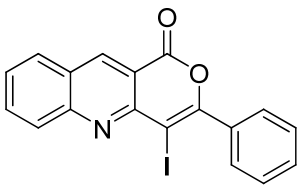
1.00
1.07
1.10
2.09
1.09
3.11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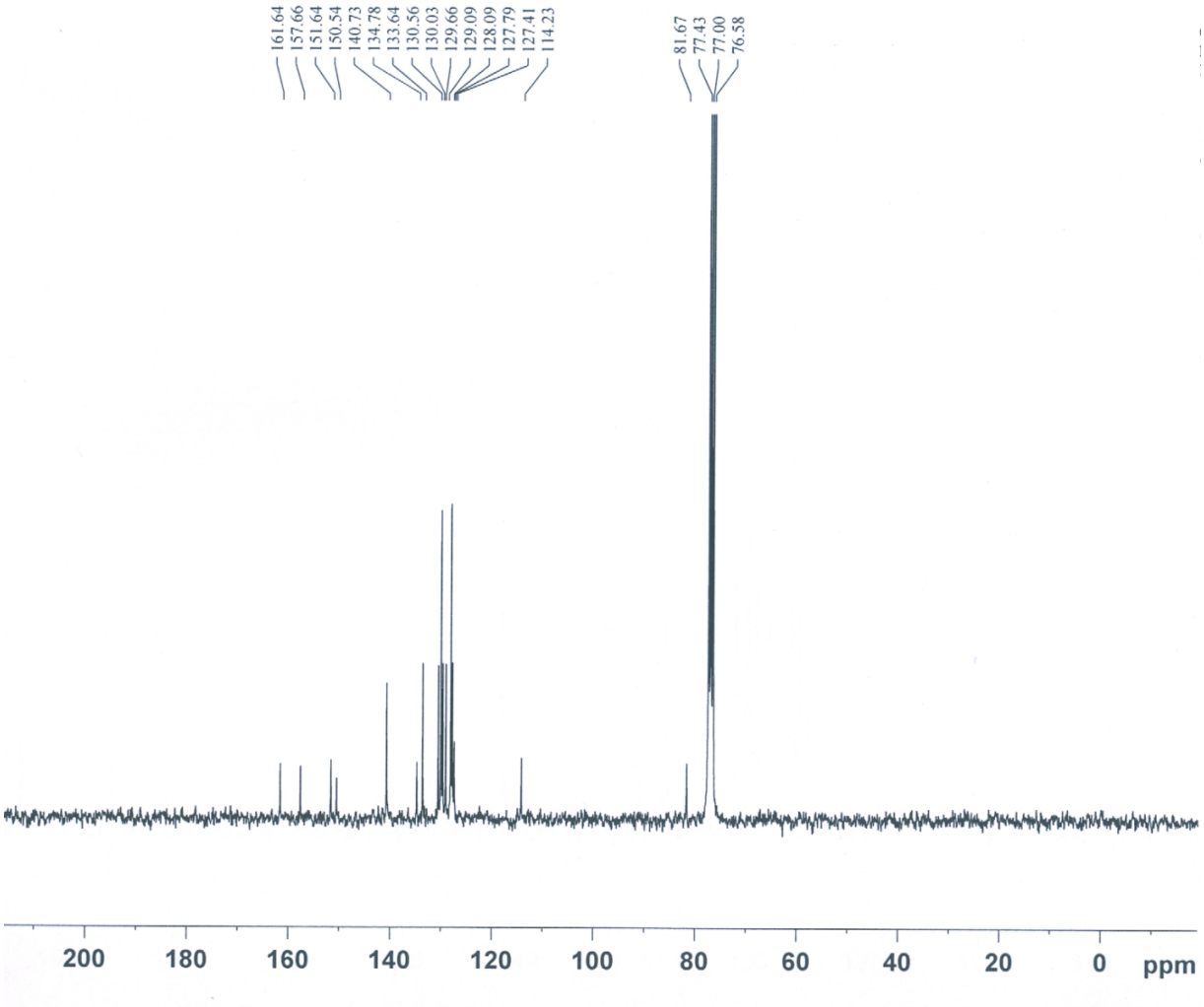
O
N
I

4a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133.64
130.56
130.03
129.66
129.09
128.09
127.79
127.41
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77.00
76.58
200
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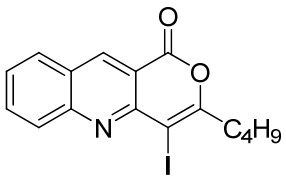
120
100
80
60
40
20
0
ppm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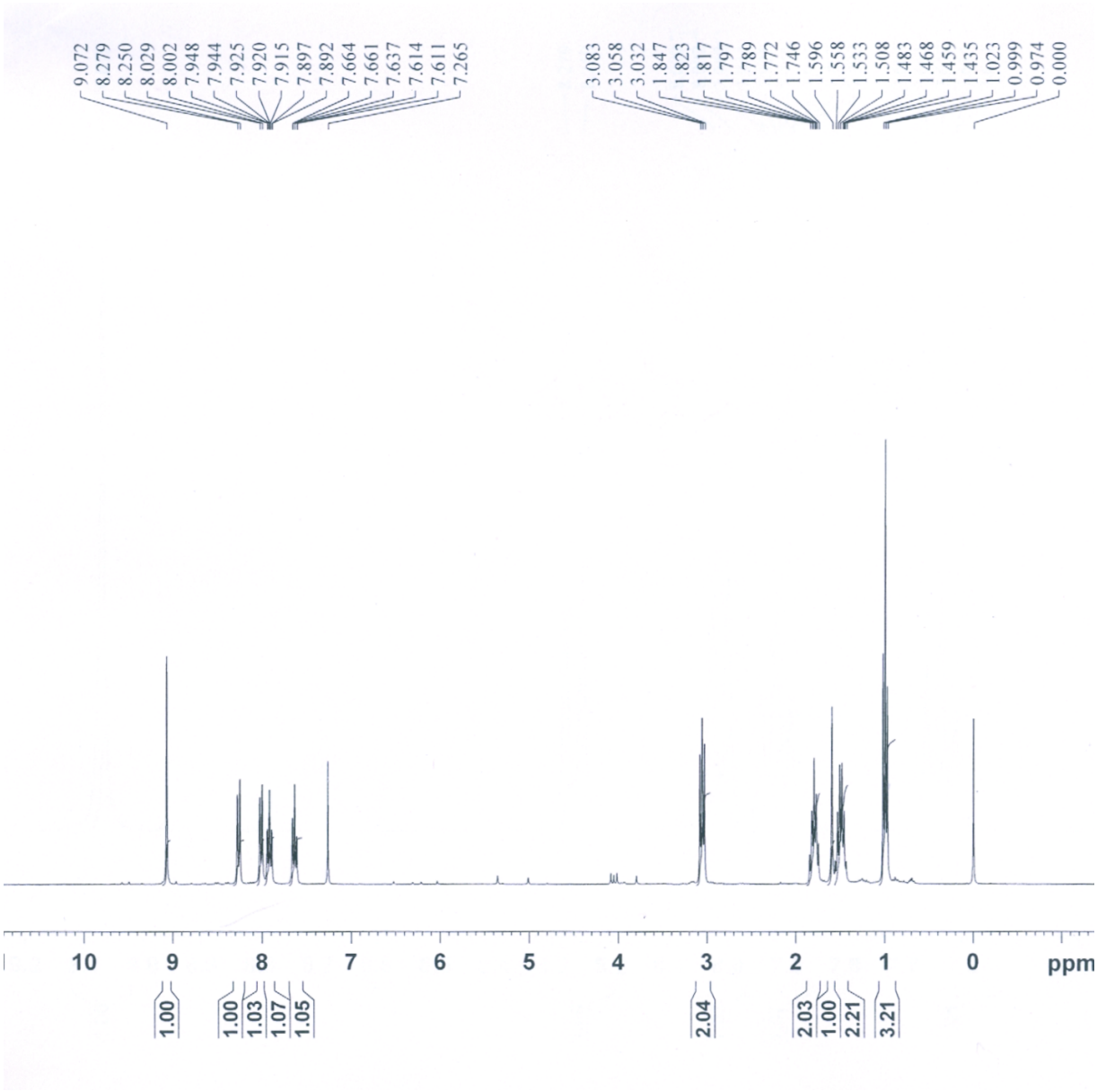
O
N
C_4H_9
I

4b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8.250
8.029
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7.925
7.920
7.915
7.897
7.892
7.664
7.661
7.637
7.614
7.611
7.265
3.083
3.058
3.032
1.847
1.823
1.817
1.797
1.789
1.772
1.746
1.596
1.558
1.533
1.508
1.483
1.468
1.459
1.435
1.023
0.999
0.974
0.000
10
9
8
7
6
5
4
3
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1.00
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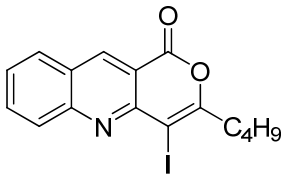
1.07
1.05
2.04
2.03
1.00
2.21
3.21


O
O
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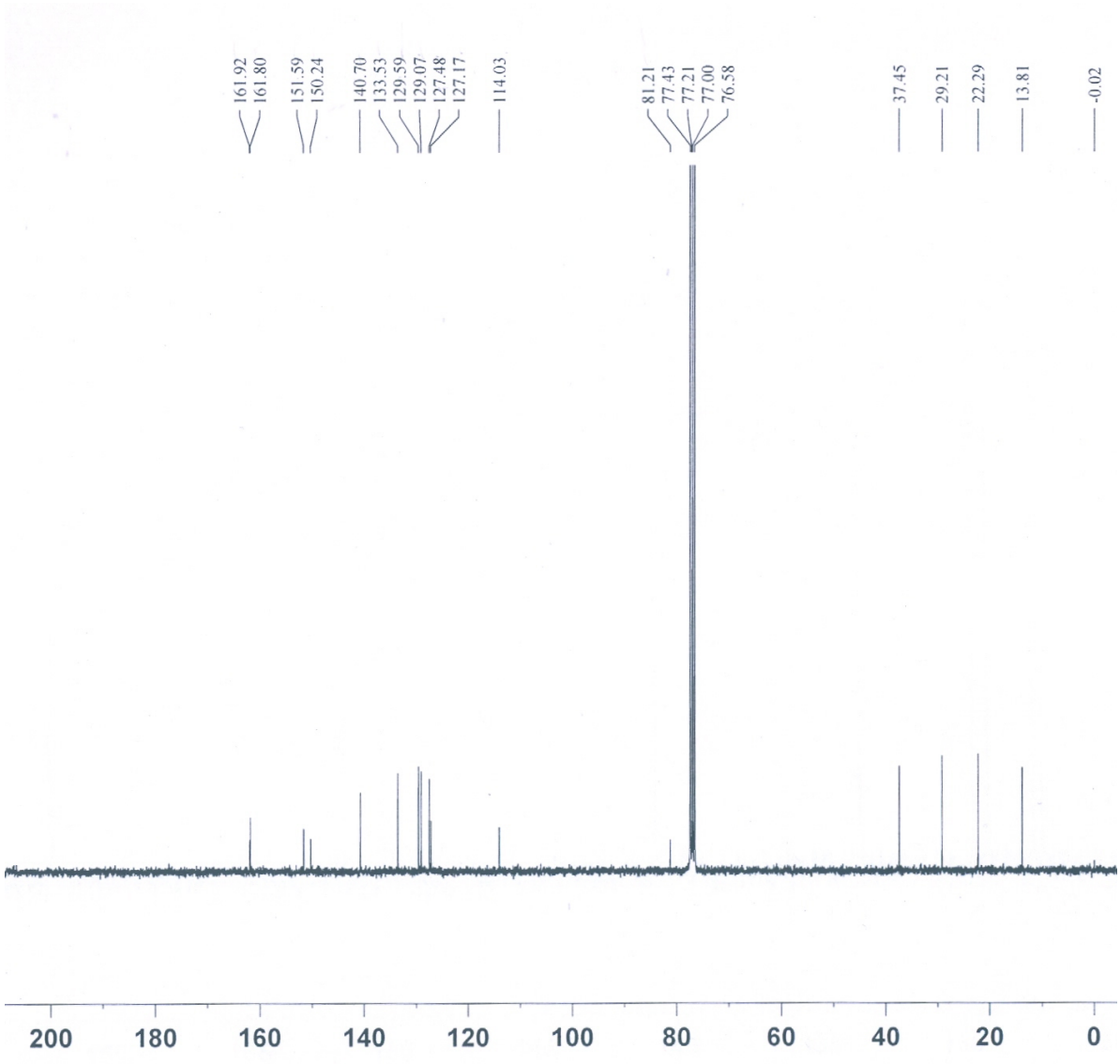
C_4H_9
I

4b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151.59
150.24
140.70
133.53
129.59
129.07
127.48
127.17
114.03
81.21
77.43
77.21
77.00
76.58
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22.29
13.81
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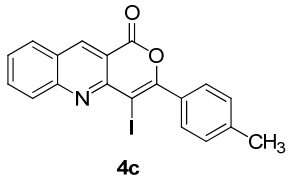
160
140
120
100
80
60
40
20
0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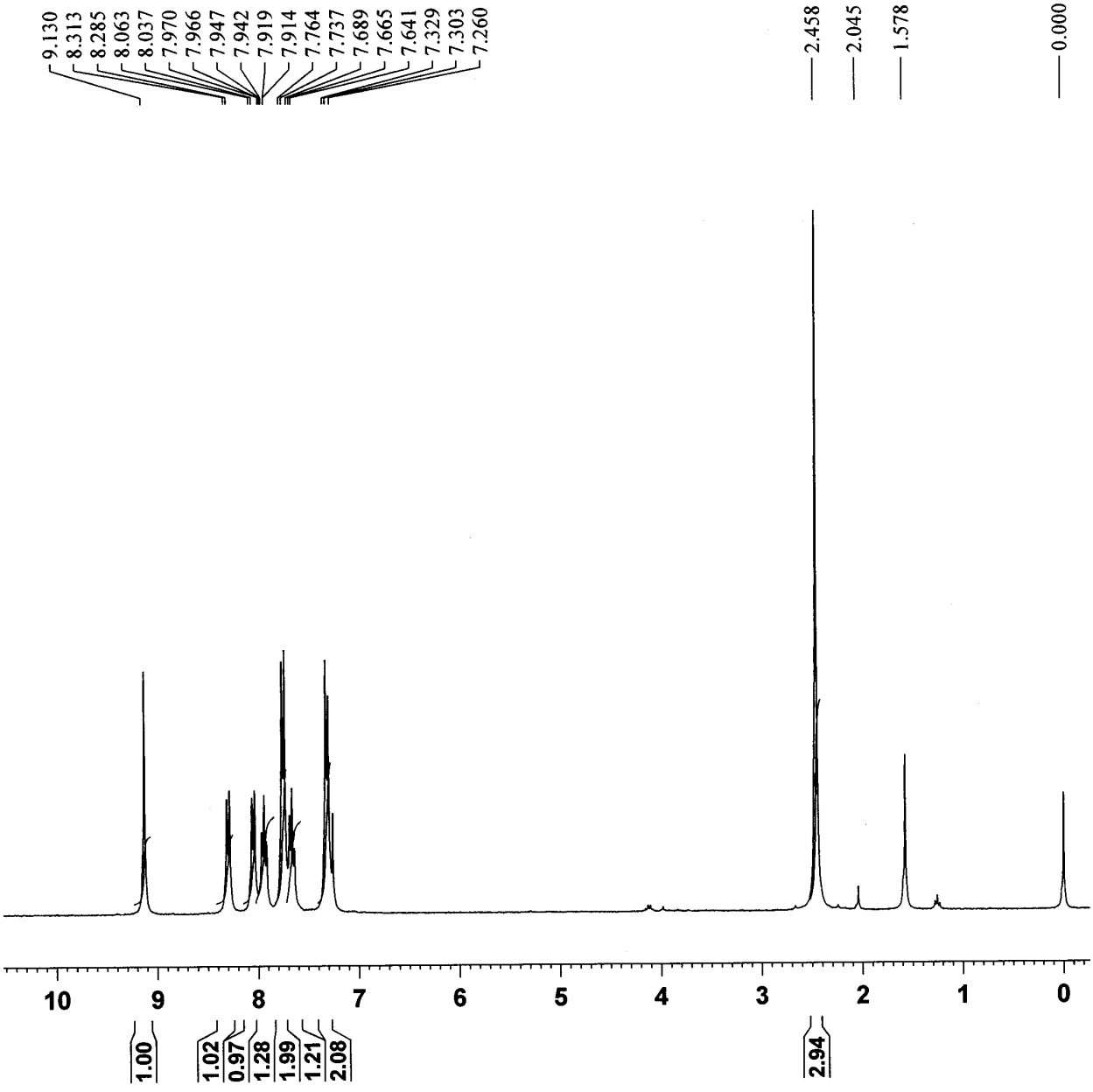
N
I
CH3

4c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7.966
7.947
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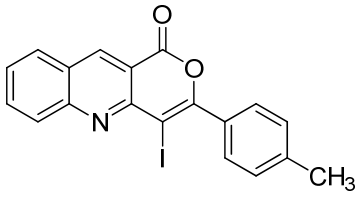
7.919
7.914
7.764
7.737
7.689
7.665
7.641
7.329
7.303
7.260
2.458
2.045
1.578
0.000
10
9
8
7
6
5
4
3
2
1
0
1.00
1.02
0.97
1.28
1.99
1.21
2.08
2.94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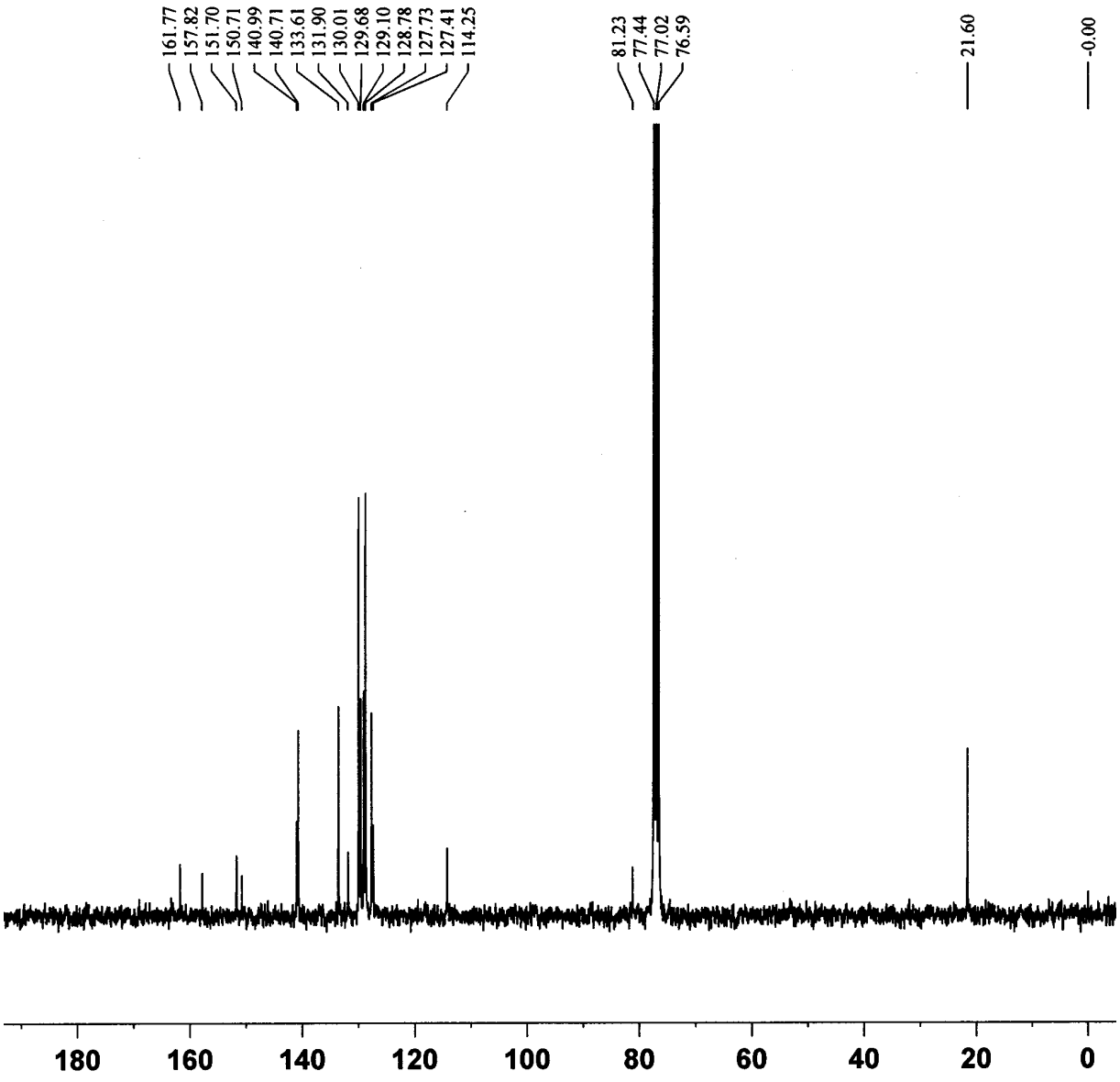
O
N
I
CH3

4c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127.41
114.25
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140
120
100
80
60
40
20
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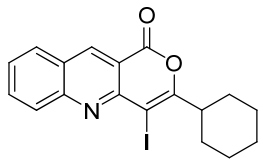
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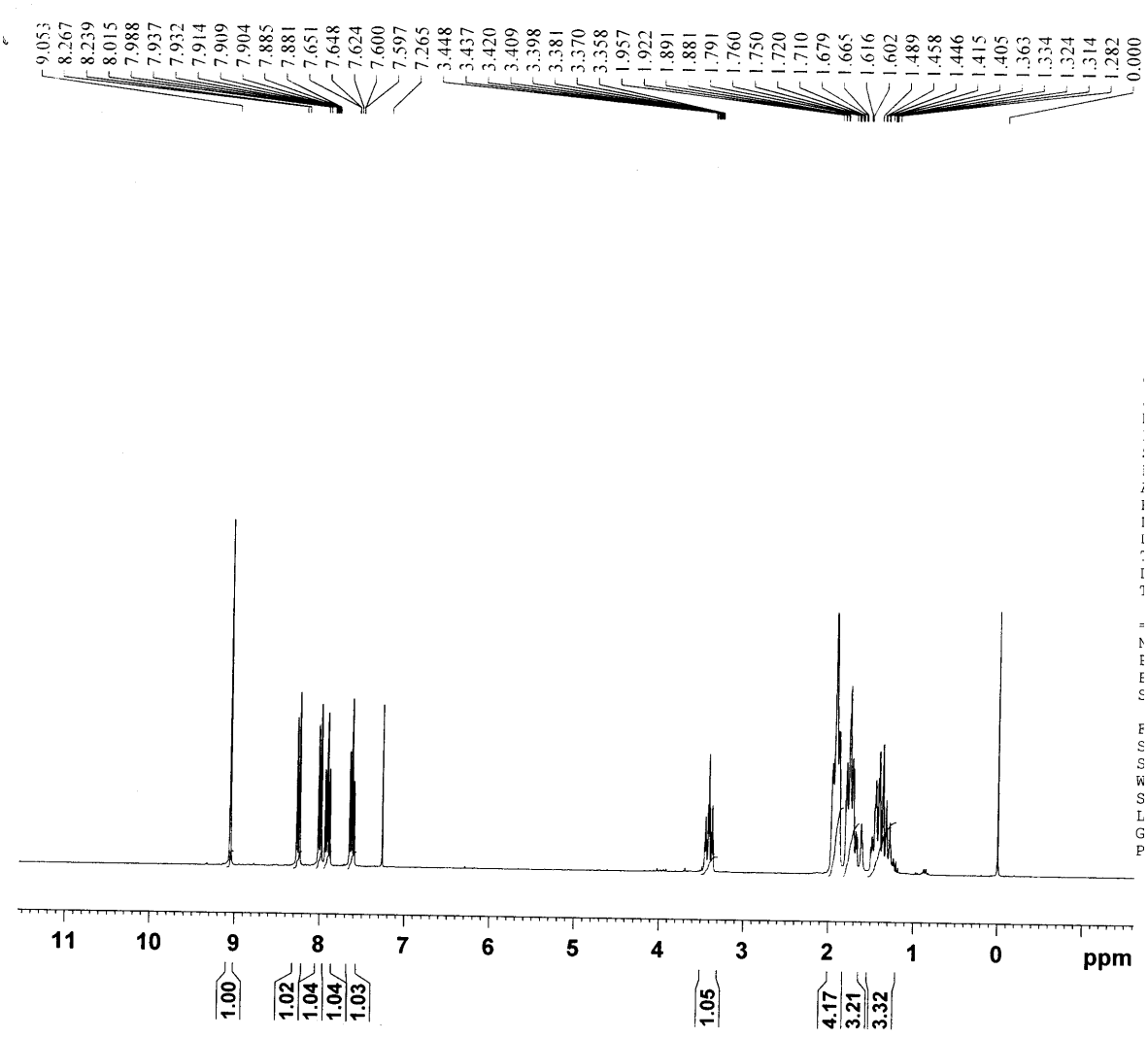
O
N
I

4d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7.932
7.914
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7.904
7.885
7.881
7.651
7.648
7.624
7.600
7.597
7.265
3.448
3.437
3.420
3.409
3.398
3.381
3.370
3.358
1.957
1.922
1.891
1.881
1.791
1.760
1.750
1.720
1.710
1.679
1.665
1.616
1.602
1.489
1.458
1.446
1.415
1.405
1.363
1.334
1.324
1.314
1.282
0.000
11
10
9
8
7
6
5
4
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ppm
1.00
1.02
1.04
1.04
1.03
1.05
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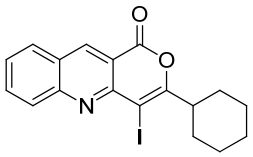
3.21
3.32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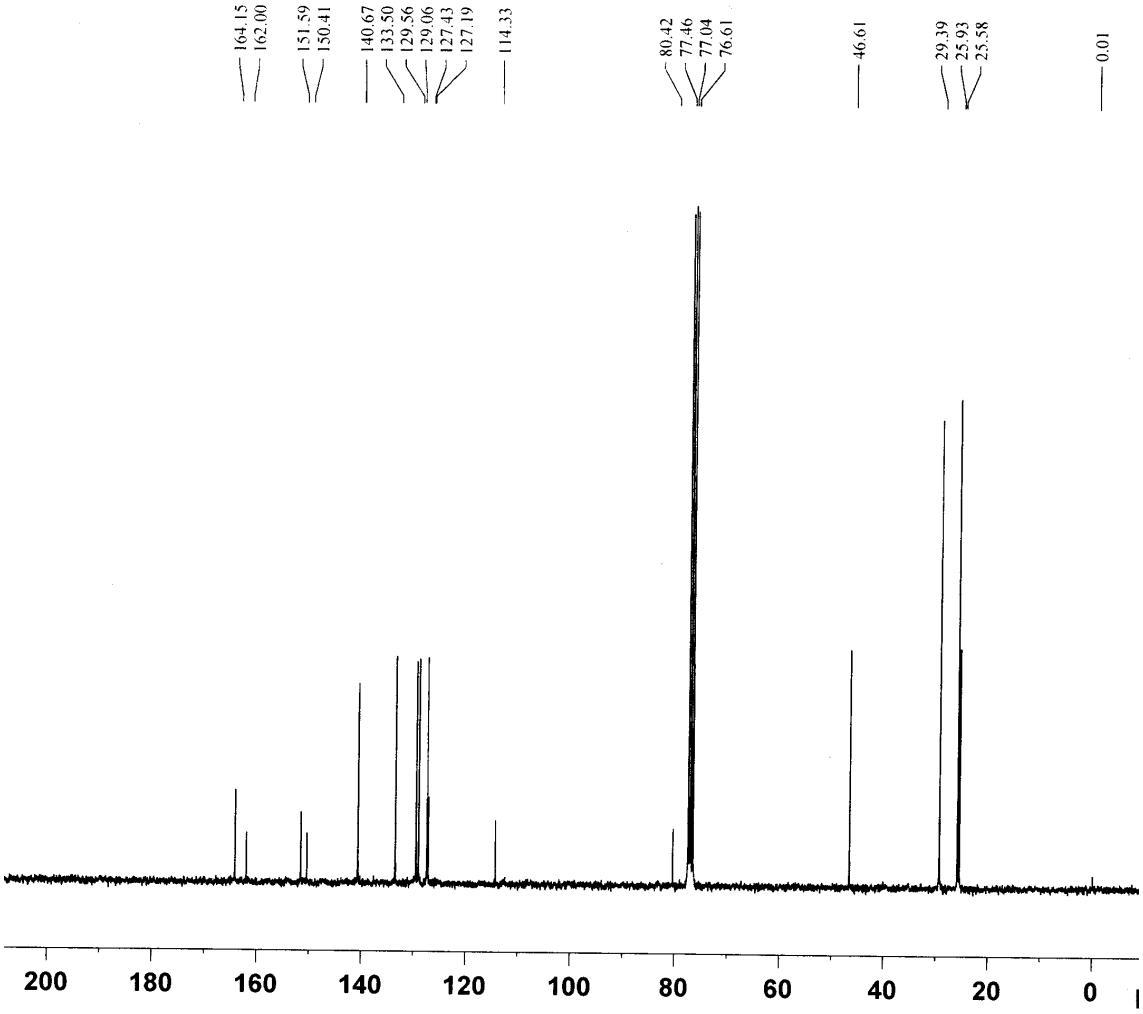
O
N
I

4d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151.59
150.41
140.67
133.50
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129.06
127.43
127.19
114.33
80.42
77.46
77.04
76.61
46.61
29.39
25.93
25.58
0.01
200
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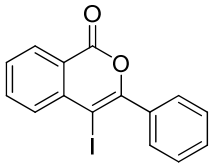
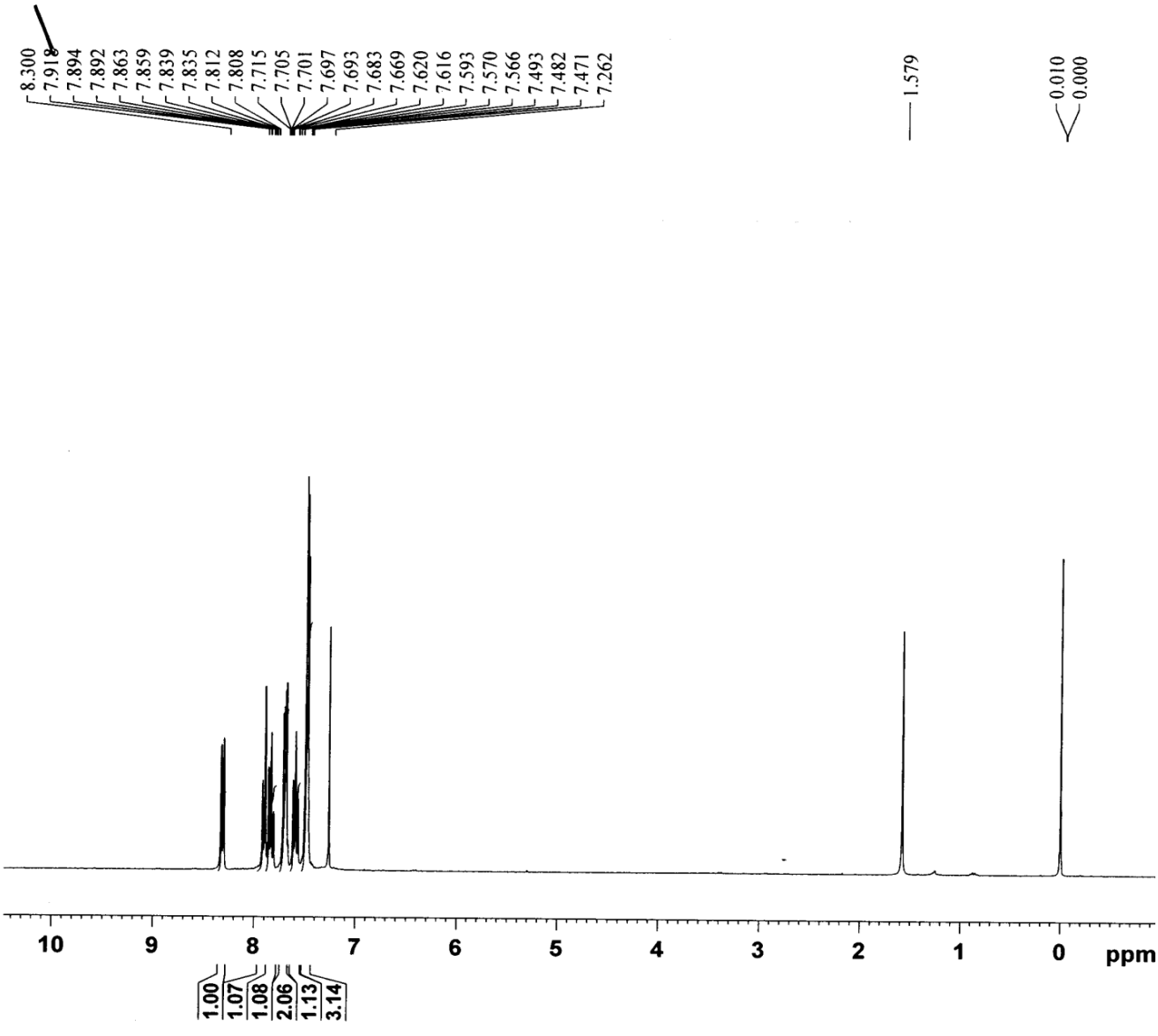
140
120
100
80
60
40
20
0



4e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7.835
7.812
7.808
7.715
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7.701
7.697
7.693
7.683
7.669
7.620
7.616
7.593
7.570
7.566
7.493
7.482
7.471
7.262
1.579
0.010
0.000
10
9
8
7
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4
3
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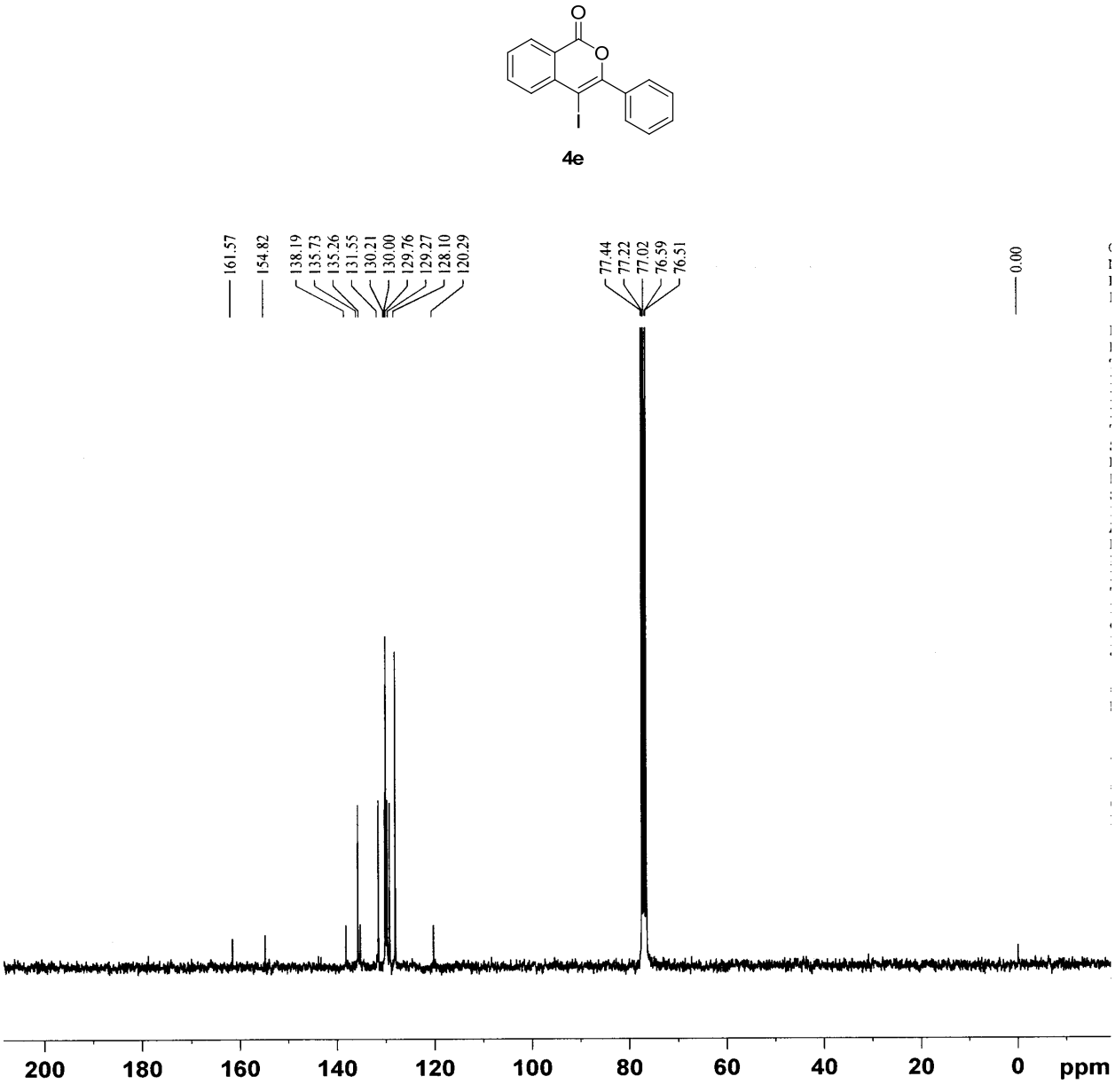
1
0
ppm
1.00
1.07
1.08
2.06
1.13
3.14


O
O
I
4e
161.57
154.82
138.19
135.73
135.26
131.55
130.21
130.00
129.76
129.27
128.10
120.29
77.44
77.22
77.02
76.59
76.51
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm