Supporting Information

Tandem Reactions of 1,2-Allenic Ketones Leading to Substituted Benzenes and α,β-Unsaturated Nitriles

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I. General Experimental Information

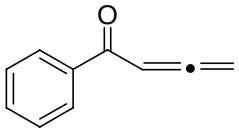
1,2-Allenic ketones and 2-substituted cyanoacetates were synthesized from commercially available reagents. Other reagents and solvents were purchased from commercial suppliers. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz or 100 MHz, respectively. Chemical shifts were reported in ppm from tetramethylsilane (TMS) as internal standard in $CDCl_3$ or DMSO-d_6 solutions. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), etc. and coupling constants were given in Hz. The conversion of starting materials were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental Procedures and Spectroscopic Data

1-Aryl substituted allenic ketones were prepared through oxidation of the corresponding homopropargyl alcohols,[1] which were prepared through zinc promoted propargylation of the corresponding aldehydes.[2] 1,4-Disubsituted allenic ketones were prepared through reactions of 1-(triphenylphosphoranylidene)-2-propanone or 2-(triphenylphosphoranylidene)acetophenone with phenylacetyl chloride based on a literature procedure.[3] 2-Substituted cyanoacetates were prepared through alkylation of ethyl cyanoacetate.[4]

1. Typical procedure for the preparation of 1-phenylbuta-2,3-dien-1-one

A solution of 1-phenylbut-3-yn-1-ol (1 mmol) in acetone (10 mL) was cooled to 0 °C. Jones reagent (0.42 mL, 3.0 M solution, 1.26 mmol) was added dropwise *via* syringe with stirring. Upon complete consumption of the starting material as monitored by TLC, the reaction was quenched by addition of isopropanol (0.2 mL). The mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:10) to give 1-phenylbuta-2,3-dien-1-one. Other 1-aryl substituted allenic ketones were obtained in a similar manner.

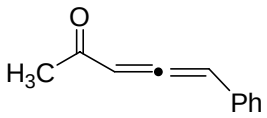


1-Phenylbuta-2,3-dien-1-one

Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.27 (d, J = 6.4 Hz, 2H), 6.46 (t, J = 6.4 Hz, 1H), 7.44-7.48 (m, 2H), 7.55-7.59 (m, 1H), 7.90-7.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 79.2, 93.2, 128.3, 128.7, 132.8, 137.4, 191.0, 217.1. MS: m/z 145 $[MH]^+$.

2. Typical procedure for the preparation of 5-phenylpenta-3,4-dien-2-one

To an ice-cooled solution of 1-(triphenylphosphoranylidene)-2-propanone (0.637 g, 2 mmol) and Et_3N (0.202 g, 2 mmol) in CH_2Cl_2 (10 mL) being stirred under nitrogen was added dropwise a solution of phenylacetyl chloride (0.309 g, 2 mmol) in CH_2Cl_2 (2 mL). Upon completion, approximately half of the solvent were removed, and diethyl ether was added to precipitate Ph_3PO. After filtration, silica gel was added to adsorb the reaction products and the solvent was evaporated in vacuo. Purification by column chromatography eluting with ethyl acetate/hexane (1:10) yielded 5-phenylpenta-3,4-dien-2-one as light yellow syrup. Other 1,4-disubstituted allenic ketones were obtained in a similar manner.

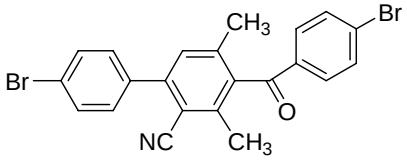


5-Phenylpenta-3,4-dien-2-one

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.26 (s, 3H), 6.14 (d, *J* = 6.0 Hz, 1H), 6.64 (d, *J* = 6.0 Hz, 1H), 7.27-7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.8, 98.6, 101.1, 127.3, 128.3, 129.1, 130.9, 198.0, 215.9. MS: m/z 159 $[MH]^+$.

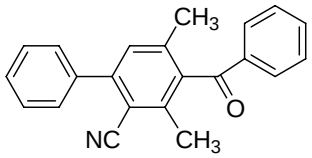
3. Typical procedure for the preparation of 1-(4-bromobenzoyl)-4-(4-bromophenyl)-3-cyano-2,6-dimethylbenzene (6a)

A mixture of 1-(4-bromophenyl)buta-2,3-dien-1-one (1 mmol), cyanoacetate (0.5 mmol) and K_2CO_3 (0.5 mmol) in acetone (5 mL) was refluxed for 15 min. Upon completion, the reaction mixture was cooled to room temperature, added with water (10 mL) and extracted with ethyl acetate. The combined organic phases were washed with brine, dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:20) to give **6a**. Other polysubsituted benzenes (**6b-6v**) were obtained in a similar manner.



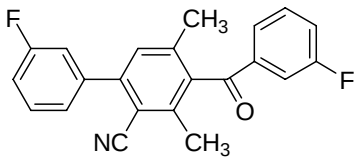
1-(4-Bromobenzoyl)-4-(4-bromophenyl)-3-cyano-2,6-dimethylbenzene (6a)

Colorless solid, m.p. 218-220 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.13 (s, 3H,), 2.25 (s, 3H), 7.45 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 18.7, 19.7, 110.0, 117.4, 123.0, 129.7, 130.0, 131.3, 131.5, 132.1, 133.1, 135.0, 137.4, 139.0, 139.2, 139.9, 144.7, 197.0. IR (KBr) ν = 2951, 2215, 1665, 1580 cm^{-1}; MS: *m/z* 468 $(MH)^+$. HRMS (FAB) calcd for $C_{22}H_{16}Br_2NO$: 467.9599 [M+H], found: 467.9593.



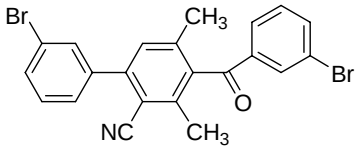
1-Benzoyl-3-cyano-2,6-dimethyl-4-phenylbenzene (6b)

Colorless solid, m.p. 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.40 (s, 3H), 7.25 (s, 1H), 7.46-7.54 (m, 5H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.6, 19.9, 110.3, 117.4, 128.68, 128.75, 128.82, 129.2, 129.4, 129.5, 134.5, 136.2, 138.1, 139.27 139.35, 139.5, 146.3, 198.2. IR (KBr) ν = 2949, 2217, 1665, 1594 cm^{-1}; MS: *m/z* 312 $(MH)^+$. HRMS (FAB) calcd for $C_{22}H_{18}NO$: 312.1389 [M+H], found: 312.1391.



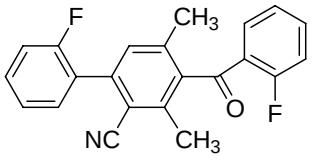
3-Cyano-2,6-dimethyl-1-(3-fluorobenzoyl)-4-(3-fluorophenyl)benzene (6c)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.40 (s, 3H), 7.17 (td, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.24-7.28 (m, 2H), 7.35-7.38 (m, 2H), 7.45-7.53 (m, 2H), 7.56 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.6, 19.9, 110.5, 115.5, 115.7, 116.0, 116.8, 121.6, 121.7, 124.6, 125.3, 129.5, 130.3, 130.4, 131.0, 131.0, 138.2, 138.3, 139.3, 139.5, 139.6, 140.0, 140.1, 145.1, 161.4, 161.9, 163.9, 164.4, 196.6. IR (KBr) ν = 3072, 2216, 1676, 1587 cm^{-1}; MS: *m/z* 348 $(MH)^+$. HRMS (FAB) calcd for $C_{22}H_{16}F_2NO$: 348.1201 [M+H], found: 348.1203.



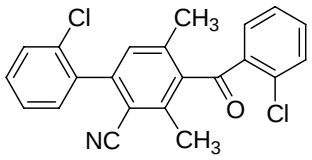
1-(3-Bromobenzoyl)-4-(3-bromophenyl)-3-cyano-2,6-dimethylbenzene (6d)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22 (s, 3H), 2.38 (s, 3H), 7.23 (s, 1H), 7.36-7.41 (m, 2H), 7.52-7.55 (m, 1H), 7.59-7.61 (m, 1H), 7.68-7.71 (m, 2H), 7.77-7.79 (m, 1H), 7.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.7, 20.0, 110.5, 116.8, 122.7, 123.7, 127.5, 128.0, 129.6, 130.2, 130.8, 131.7, 131.9, 137.4, 137.8, 139.1, 139.5, 139.7, 139.9, 144.9, 196.5. IR (KBr) ν = 2962, 2220, 1673, 1590 cm^{-1}; MS: *m/z* 468 $(MH)^+$. HRMS (FAB) calcd for $C_{22}H_{16}Br_2NO$: 467.9599 [M+H], found: 467.9594.



3-Cyano-2,6-dimethyl-1-(2-fluorobenzoyl)-4-(2-fluorophenyl)benzene (6e)

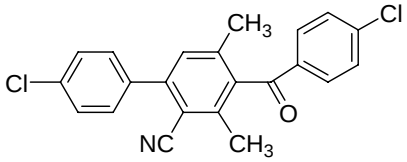
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.41 (s, 3H), 7.10-7.29 (m, 5H), 7.38-7.42 (m, 2H), 7.58-7.61 (m, 1H), 7.84 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.4, 19.7, 111.8, 116.0, 116.2, 116.8, 117.2, 124.36, 124.39, 124.9, 125.0, 125.1, 125.8, 125.9, 130.4, 130.9, 131.22, 131.24, 131.4, 136.3, 136.4, 138.3, 138.7, 140.2, 141.7, 158.1, 160.6, 160.8, 163.4, 194.7. IR (KBr) ν = 2926, 2223, 1670, 1607 cm^{-1}; MS: *m/z* 348 $(MH)^+$. HRMS (FAB) calcd for $C_{22}H_{16}F_2NO$: 348.1201 [M+H], found: 348.1202.



1-(2-Chlorobenzoyl)-4-(2-chlorophenyl)-3-cyano-2,6-dimethylbenzene (6f)

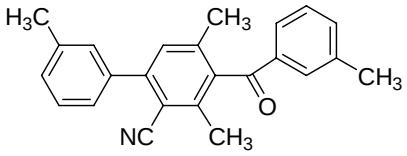
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.25 (s, 3H), 2.42 (s, 3H), 7.15 (s, 1H), 7.36-7.40 (m, 4H), 7.51-7.53 (m, 3H), 7.64 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.6, 20.2, 112.2, 116.6, 126.9, 127.3, 129.9, 130.2, 130.3, 130.9, 132.0, 132.1, 132.8, 133.8, 134.0, 135.6, 136.9, 139.1, 139.5, 140.6, 144.1, 196.5. IR (KBr) ν = 2924, 2223, 1683, 1586 cm^{-1};

MS: *m/z* 380 $(MH)^+$. HRMS (FAB) calcd for $C_{22}H_{16}Cl_2NO$: 380.061 [M+H], found: 380.0615.



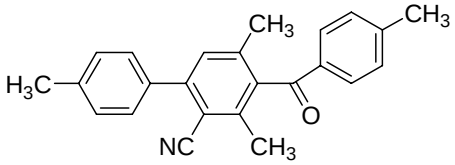
1-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-3-cyano-2,6-dimethylbenzene (6g)

Colorless solid, m.p. 189-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22 (s, 3H), 2.38 (s, 3H), 7.22 (s, 1H), 7.47-7.52 (m, 6H), 7.77 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.6, 19.9, 110.5, 117.0, 129.0, 129.4, 129.6, 130.0, 130.7, 134.5, 135.2, 136.4, 139.2, 139.4, 139.6, 141.2, 145.2, 196.6. IR (KBr) ν = 2919, 2216, 1667, 1585 cm^{-1}; MS: *m/z* 380 $(MH)^+$. HRMS (FAB) calcd for $C_{22}H_{16}Cl_2NO$: 380.061 [M+H], found: 380.0619.



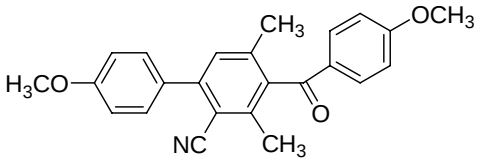
3-Cyano-2,6-dimethyl-1-(3-methylbenzoyl)-4-(3-methylphenyl)benzene (6h)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.41-2.44 (m, 9H), 7.25 (s, 2H), 7.36-7.40 (m, 4H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.6, 19.9, 21.3, 21.5, 110.3, 117.4, 125.9, 126.9, 128.5, 129.1, 129.46, 129.54, 135.3, 136.3, 138.2, 138.3, 139.1, 139.2, 139.4, 139.5, 146.4, 198.3. IR (KBr) ν = 2923, 2220, 1669, 1585 cm^{-1}; MS: *m/z* 340 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{22}NO$: 340.1702 [M+H], found: 340.1703.



3-Cyano-2,6-dimethyl-1-(4-methylbenzoyl)-4-(4-methylphenyl)benzene (6i)

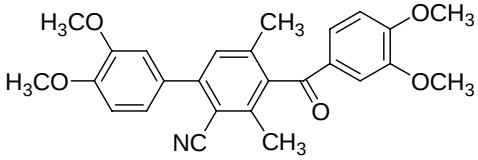
Colorless solid; m.p. 198-200 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.12 (s, 3H), 2.24 (s, 3H), 2.38 (s, 3H), 2.39 (s, 3H), 7.33-7.39 (m, 5H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 18.7, 19.7, 21.2, 21.8, 109.8, 117.7, 129.1, 129.7, 129.9, 130.5, 133.8, 135.4, 138.7, 138.8, 139.5, 139.7, 145.7, 146.0, 197.5. IR (KBr) ν = 2919, 2215, 1656, 1602 cm^{-1}; MS: *m/z* 340 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{22}NO$: 340.1702 [M+H], found: 340.1705**.**



3-Cyano-2,6-dimethyl-1-(4-methoxybenzoyl)-4-(4-methoxyphenyl)benzene (6j)

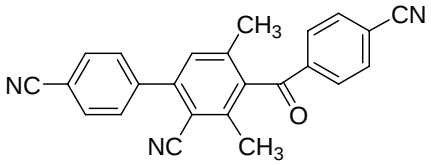
Colorless solid, m.p. 147-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.39 (s, 3H), 3.87 (s, 3H), 3.89 (s, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H),

7.20 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.6, 19.9, 55.4, 55.6, 110.0, 114.1, 114.4, 117.8, 129.3, 129.4, 130.0, 130.5, 131.9, 139.2, 139.4, 145.8, 160.0, 164.5, 196.7. IR (KBr) ν = 2956, 2838, 2216, 1652, 1598 cm^{-1}; MS: *m/z* 372 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{22}NO_3$: 372.16 [M+H], found: 372.1608.



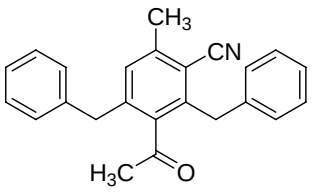
3-Cyano-1-(3,4-dimethoxybenzoyl)-4-(3,4-dimethoxyphenyl)-2, 6-dimethylbenzene (6k)

White solid, m.p. 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.40 (s, 3H), 3.94-3.98 (m, 12H), 6.84 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 7.11-7.23 (m, 4H), 7.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.6, 19.9, 55.9, 56.0, 56.1, 56.2, 110.0, 110.2, 111.1, 111.9, 117.7, 121.4, 125.6, 129.2, 129.6, 130.7, 139.2, 139.3, 139.5, 145.8, 148.8, 149.6, 149.7, 154.5, 196.7. IR (KBr) ν = 2932, 2215, 1649, 1592 cm^{-1}; MS: *m/z* 432 $(MH)^+$. HRMS (FAB) calcd for $C_{26}H_{26}NO_5$: 432.1812 [M+H], found: 432.1818.



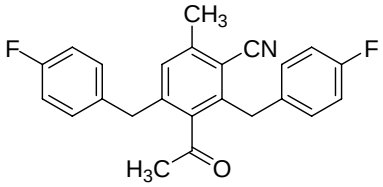
3-Cyano-1-(4-cyanobenzoyl)-4-(4-cyanophenyl)-2,6-dimethylbenze ne (6l)

White solid, m.p. 190-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 2.39 (s, 3H), 7.26 (s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.81-7.85 (m, 4H), 7.93 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.7, 20.0, 110.6, 112.8, 116.5, 117.6, 117.7, 118.3, 129.60, 129.64, 132.5, 133.2, 138.7, 139.2, 139.7, 140.0, 142.3, 144.6, 196.3. IR (KBr) ν = 2962, 2231, 1673, 1596 cm^{-1}; MS: *m/z* 362 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{16}N_3O$: 362.1294 [M+H], found: 362.1286.



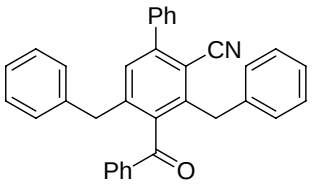
1-Acetyl-3-cyano-2,6-dibenzyl-4-methylbenzene (6m)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.96 (s, 3H), 2.51 (s, 3H), 3.91 (s, 2H, CH_2), 4.18 (s, 2H), 7.01 (s, 1H), 7.09-7.12 (m, 4H), 7.20-7.33 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.9, 32.7, 37.5, 38.9, 113.1, 116.8, 126.7, 126.8, 128.6, 128.77, 128.79, 129.1, 130.4, 137.9, 138.4, 139.8, 140.9, 141.3, 143.1, 206.2. IR (KBr) ν = 2926, 2220, 1701, 1593 cm^{-1}; MS: *m/z* 340 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{22}NO$: 340.1702 [M+H], found: 340.1709.



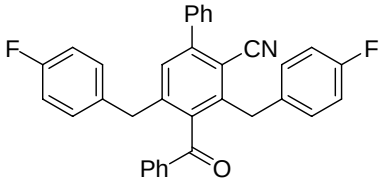
1-Acetyl-3-cyano-2,6-di-(4-fluorobenzyl)-4-methylbenzene (6n)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.04 (s, 3H), 2.50 (s, 3H), 3.87 (s, 2H), 4.12 (s, 2H), 6.94-7.10 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.8, 32.8, 36.7, 38.1, 113.1, 115.3, 115.6, 115.8, 116.6, 130.2, 130.3, 130.4, 130.5, 130.6, 133.5, 134.1, 139.6, 140.8, 141.2, 143.4, 160.5, 162.9, 205.9. IR (KBr) ν = 2926, 2220, 1701, 1601 cm^{-1}; MS: *m/z* 376 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{20}F_2NO$: 376.1514 [M+H], found: 376.1518.



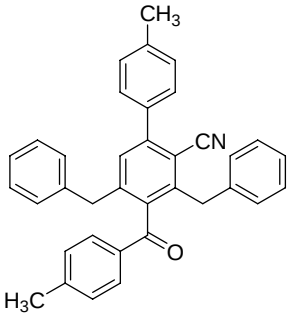
1-Benzoyl-2,6-dibenzyl-3-cyano-4-phenylbenzene (6o)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.88 (d, *J* = 7.2 Hz, 2H), 4.19 (d, *J* = 12.8 Hz, 2H), 7.04 (d, *J* = 6.8 Hz, 2H), 7.10-7.22 (m, 8H), 7.26 (s, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.46-7.58 (m, 6H), 7.65-7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 38.1, 39.3, 111.3, 117.5, 126.5, 126.7, 128.3, 128.62, 128.68, 128.7, 128.9, 129.0, 129.2, 129.4, 129.9, 134.1, 136.7, 137.6, 138.0, 138.1, 139.6, 142.6, 143.4, 146.9, 197.6. IR (KBr) ν = 3027, 2221, 1667, 1580 cm^{-1}; MS: *m/z* 464 $(MH)^+$. HRMS (FAB) calcd for $C_{34}H_{26}NO$: 464.2015 [M+H], found: 464.2018.



1-Benzoyl-3-cyano-2,6-di-(4-fluorobenzyl)-4-phenylbenzene (6p)

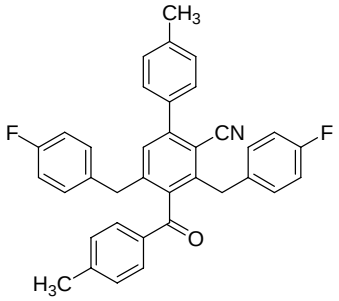
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.85 (s, 2H), 4.14 (d, *J* = 20.0 Hz, 2H), 6.80-6.89 (m, 4H), 6.97-7.00 (m, 2H), 7.06-7.09 (m, 2H), 7.26 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.46-7.52 (m, 3H), 7.55-7.64 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 37.2, 38.5, 111.3, 115.0, 115.2, 115.3, 115.6, 117.3, 128.7, 128.8, 128.9, 129.0, 129.4, 129.9, 130.5, 130.60, 130.6, 130.7, 133.3, 133.7, 134.3, 136.6, 137.8, 139.5, 142.5, 143.2, 147.1, 160.4, 162.8, 197.6. IR (KBr) ν = 3061, 2931, 2223, 1667, 1597 cm^{-1}; MS: *m/z* 500 $(MH)^+$. HRMS (FAB) calcd for $C_{34}H_{24}F_2NO$: 500.1827 [M+H], found: 500.1822.



3-Cyano-2,6-dibenzyl-1-(4-methylbenzoyl)-4-(4-methylphenyl)benzene (6q)

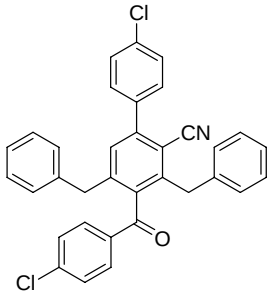
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 2.41 (s, 3H), 3.86 (d, *J* = 13.6 Hz, 2H), 4.16 (d, *J* = 17.6 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.09-7.22 (m, 11H), 7.26-7.29 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2, 21.8, 38.0, 39.2, 111.1, 117.6, 126.4, 126.6, 128.2, 128.6,

128.8, 129.0, 129.2, 129.3, 129.5, 129.7, 134.5, 135.2, 137.8, 138.2, 138.9, 139.6, 142.4, 143.3, 145.2, 146.8, 197.2. IR (KBr) ν = 3028, 2922, 2222, 1663, 1603 cm^{-1}; MS: *m/z* 492 $(MH)^+$. HRMS (FAB) calcd for $C_{36}H_{30}NO$: 492.2328 [M+H], found: 492.2321.



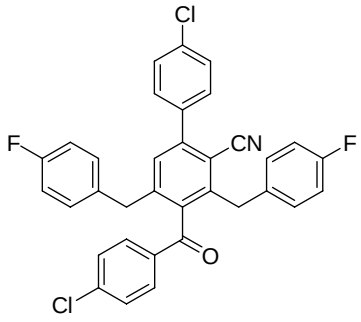
3-Cyano-2,6-di-(4-fluorobenzyl)-1-(4-methylbenzoyl)-4-(4-methylphenyl) benzene (6r)

Syrup. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 6H), 3.82 (d, *J* = 6.8 Hz, 2H), 4.10 (d, *J* = 23.2 Hz, 2H), 6.80-6.89 (m, 4H), 6.96-7.00 (m, 2H), 7.05-7.08 (m, 2H), 7.15-7.18 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2, 21.8, 37.2, 38.5, 111.1, 114.9, 115.2, 115.3, 115.5, 117.5, 128.7, 129.4, 129.5, 129.7, 130.46, 130.54, 130.6, 130.7, 133.4, 133.9, 134.3, 135.0, 139.1, 139.4, 142.4, 143.1, 145.5, 147.0, 160.4, 162.9, 197.2. IR (KBr) ν = 3032, 2923, 2223, 1662, 1604 cm^{-1}; MS: *m/z* 528 $(MH)^+$. HRMS (FAB) calcd for $C_{36}H_{28}F_2NO$: 528.214 [M+H], found: 528.2135.



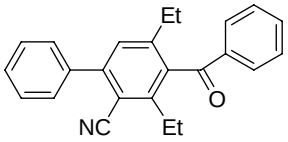
1-(4-Chlorobenzoyl)-3-cyano-2,6-dibenzyl-4-(4-chlorophenyl)benzene (6s)

Syrup. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.83 (d, *J* = 8.4 Hz, 2H), 4.14 (s, 2H), 6.98 (d, *J* = 6.4 Hz, 2H), 7.01-7.03 (m, 3H), 7.08-7.24 (m, 8H), 7.44-7.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 38.0, 39.3, 111.3, 117.2, 126.6, 126.8, 128.4, 128.6, 128.9, 129.0, 129.1, 129.8, 130.2, 130.6, 134.9, 135.3, 136.2, 137.2, 137.7, 139.4, 140.6, 142.9, 143.5, 145.8, 196.2. IR (KBr) ν = 2927, 2223, 1670, 1587 cm^{-1}; MS: *m/z* 532 $(MH)^+$. HRMS (FAB) calcd for $C_{34}H_{24}Cl_2NO$: 532.1236 [M+H], found: 532.1237.



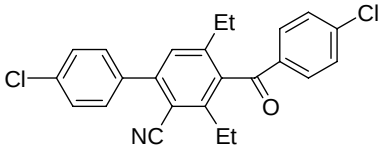
1-(4-Chlorobenzoyl)-3-cyano-2,6-di-(4-fluorobenzyl)-4-(4-chlorophenyl) benzene (6t)

Syrup. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.81 (s, 2H), 4.09 (d, *J* = 18.0 Hz, 2H), 6.80-7.03 (m, 8H), 7.19 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.46-7.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 37.2, 38.5, 111.3, 115.1, 115.3, 115.4, 115.7, 117.0, 129.0, 129.1, 129.8, 130.1, 130.4, 130.53, 130.57, 130.6, 132.9, 133.4, 134.8, 135.5, 136.0, 139.2, 141.0, 142.7, 143.3, 146.0, 160.1, 162.8, 196.1. IR (KBr) ν = 2962, 2929, 2223, 1669, 1587 cm^{-1}; MS: *m/z* 568 $(MH)^+$. HRMS (FAB) calcd for $C_{34}H_{22}Cl_2F_2NO$: 568.1047 [M+H], found: 568.1051.



1-Benzoyl-3-cyano-2,6-diethyl-4-phenylbenzene (6u)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.21 (m, 6H), 2.49-2.86 (m, 4H), 7.26 (s, 1H), 7.48-7.52 (m, 5H), 7.59-7.62 (m, 3H), 7.85 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.8, 15.3, 26.3, 26.6, 109.6, 117.2, 127.9, 128.6, 128.7, 128.8, 129.0, 129.5, 134.3, 136.9, 138.4, 145.6, 145.7, 146.9, 197.8. IR (KBr) ν = 2943, 2219, 1665, 1594 cm^{-1}; MS: *m/z* 340 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{22}NO$: 340.1702 [M+H], found: 340.1685.

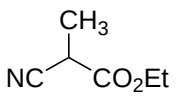


1-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-3-cyano-2,6-diethylbenzene (6v)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14-1.18 (m, 6H), 2.48-2.84 (m, 4H), 7.33 (s, 1H), 7.49-7.52 (m, 6H), 7.76-7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.8, 15.3, 26.3, 26.6, 109.7, 116.9, 127.8, 128.8, 128.9, 129.4, 130.1, 130.8, 132.4, 135.2, 136.6, 138.2, 141.1, 145.8, 145.9, 196.3. IR (KBr) ν = 2971, 2935, 2222, 1673, 1587 cm^{-1}; MS: *m/z* 408 $(MH)^+$. HRMS (FAB) calcd for $C_{24}H_{20}Cl_2NO$: 408.0923 [M+H], found: 408.0911.

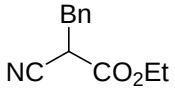
4. Typical procedure for the preparation of ethyl 2-cyanopropanoate (7a)

To an oven dried round bottom flask containing sodium hydride (60% dispersion in mineral oil, 19.9 mmol) was added THF (20 mL) under N_2, and the suspension was then cooled to 0 °C. To the suspension was slowly added ethyl cyanoacetate (6.8 g, 60 mmol) in THF (10 mL). After 15 min, iodomethane (2.838 g, 20 mmol) were added dropwise via syringe to the solution. The resulting reaction mixture was allowed to stir at 0 °C for 3 h. The mixture was then quenched with H_2O (30 mL) and diluted with Et_2O. The aqueous layer was removed and the organic layer was washed twice with brine. The combined aqueous layers were then extracted three times with Et_2O. The combined organic extracts were then dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:15) to give **7a**. Other 2-substituted cyanoacetates were obtained in a similar manner.



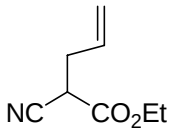
Ethyl 2-cyanopropanoate (7a)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.32 (t, *J* = 7.2 Hz, 3H), 1.58 (d, *J* = 7.2 Hz, 3H), 3.54 (q, *J* = 7.2 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H).



Ethyl 2-cyano-3-phenylpropanoate (7b)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, *J* = 7.2 Hz, 3H), 3.16-3.22 (m, 1H), 3.25-3.30 (m, 1H), 3.70-3.74 (m, 1H), 4.20-4.26 (m, 2H), 7.26-7.37 (m, 5H).

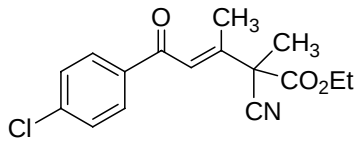


Ethyl 2-cyanopent-4-enoate (7c)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.32 (t, *J* = 7.2 Hz, 3H), 2.67-2.71 (m, 2H), 3.56 (t, *J* = 7.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 5.23-5.29 (m, 2H), 5.79-5.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 33.8, 37.5, 62.9, 116.0, 120.0, 131.3, 165.5

5. Precedure for the preparation of ethyl 5-(4-chlorophenyl)-2-cyano-2,3-dimethyl-5-oxopent-3-enoate (8)

A mixture of 1-(4-chlorophenyl)buta-2,3-dien-1-one (1 mmol), ethyl 2-cyanopropanoate (**7a**, 1 mmol) and K_2CO_3 (1 mmol) in acetone (5 mL) was stirred under reflux for 1 h. Upon completion, the reaction mixture was cooled to room temperature, added with water (10 mL) and extracted with ethyl acetate. The combined organic phases were washed with brine, dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:15) to give **8**.



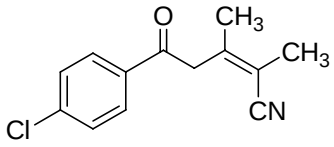
5-(4-Chlorophenyl)-2-cyano-2,3-dimethyl-5-oxopent-3-enoate (8)

Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.34 (t, *J* = 7.2 Hz, 3H), 1.83 (s, 3H), 2.14 (s, 3H), 4.32 (q, *J* = 7.2 Hz, 2H), 7.19 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 15.6, 21.8, 51.1, 63.6, 118.1, 123.5, 128.9, 129.8, 136.2, 139.5, 148.2, 166.3, 189.6. IR (KBr) ν = 2963, 2240, 1749, 1670 cm^{-1}; MS: *m/z* 306 $(MH)^+$. HRMS (FAB) calcd for $C_{16}H_{17}ClNO_3$: 306.0898 [M+H], found: 306.0891.

6. Typical procedure for the preparation of 5-(4-chlorophenyl)-2,3-dimethyl-5-oxopent-2- enenitrile (9a)

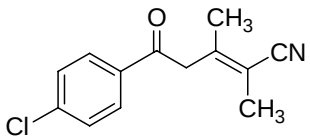
A mixture of 1-(4-chlorophenyl)buta-2,3-dien-1-one (1 mmol), ethyl 2-cyanopropanoate (**7a**, 1 mmol) and K_2CO_3 (1 mmol) in DMF (5 mL) was stirred at 80 °C for 20 min. Upon completion, the reaction

mixture was cooled to room temperature, added with water (10 mL) and extracted with ethyl acetate. The combined organic phases were washed with brine, dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:25) to give **(*Z*)-9a** and **(*E*)-9a**. Other α,β-unsaturated nitriles (**9b**-**9m**) were obtained in a similar manner.



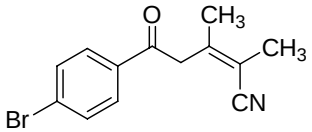
(*Z*)-5-(4-Chlorophenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*Z*-9a)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.86 (s, 3H), 1.93 (s, 3H), 4.05 (s, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.3, 19.1, 47.3, 107.9, 119.3, 129.1, 129.6, 134.5, 140.1, 149.0, 194.4. IR (KBr) ν = 2975, 2215, 1685, 1587 cm^{-1}; MS: *m/z* 234 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{13}ClNO$: 234.0686 [M+H], found: 234.0681.



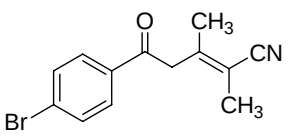
(*E*)-5-(4-Chlorophenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*E*-9a)

Colorless solid, m.p. 107-108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.87 (s, 3H), 2.10 (s, 3H), 3.85 (s, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.4, 23.6, 43.0, 107.7, 119.2, 129.2, 129.5, 134.6, 140.3, 148.3, 193.5. IR (KBr) ν = 2962, 2214, 1680, 1586 cm^{-1}; MS: *m/z* 234 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{13}ClNO$: 234.0686 [M+H], found: 234.0685.



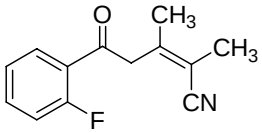
(*Z*)-5-(4-Bromophenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*Z*-9b)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.89 (s, 3H), 1.96 (s, 3H), 4.07 (s, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.3, 19.1, 47.3, 108.0, 119.4, 128.9, 129.7, 132.1, 134.9, 149.0, 194.7. IR (KBr) ν = 2982, 2213, 1683, 1585 cm^{-1}; MS: *m/z* 278 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{13}BrNO$: 278.0181 [M+H], found: 278.0188.



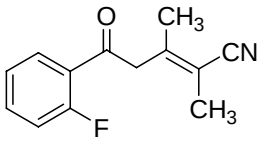
(*E*)-5-(4-Bromophenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*E*-9b)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.87 (s, 3H), 2.11 (s, 3H), 3.84 (s, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.5, 23.7, 43.0, 107.7, 119.2, 129.1, 129.6, 132.2, 134.9, 148.3, 193.7. IR (KBr) ν = 2959, 2213, 1678, 1585 cm^{-1}; MS: *m/z* 278 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{13}BrNO$: 278.0181 [M+H], found: 278.0186.



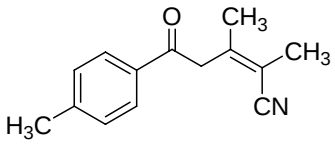
(*Z*)-5-(2-Fluorophenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*Z*-9c)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 1.96 (s, 3H), 4.11 (s, 2H), 7.13-7.26 (m, 2H), 7.54-7.58 (m, 1H), 7.88 (td, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.3, 19.4, 51.86, 51.95, 107.9, 116.7, 116.9, 119.3, 124.6, 124.8, 130.6, 135.2, 135.3, 149.1, 160.8, 193.8. IR (KBr) ν = 2925, 2213, 1707, 1610 cm^{-1}; MS: *m/z* 218 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{13}FNO$: 218.0982 [M+H], found: 218.0972.



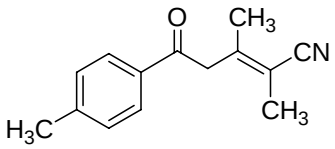
(*E*)-5-(2-Fluorophenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*E*-9c)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.83 (s, 3H), 2.09 (s, 3H), 3.86 (s, 2H), 7.12-7.26 (m, 2H), 7.52-7.57 (m, 1H), 7.81-7.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.4, 23.6, 47.7, 47.8, 107.6, 116.7, 116.9, 119.3, 124.75, 124.78, 124.85, 124.98, 130.6, 135.3, 135.4, 148.5, 160.7, 193.0. IR (KBr) ν = 2929, 2213, 1686, 1610 cm^{-1}; MS: *m/z* 218 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{13}FNO$: 218.0982 [M+H], found: 218.0986.



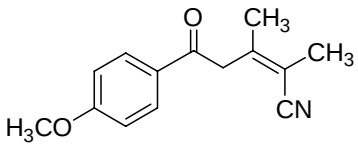
(*Z*)-2,3-Dimethyl-5-oxo-5-p-tolylpent-2-enenitrile (*Z*-9d)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.87 (s, 3H), 1.93 (s, 3H), 2.39 (s, 3H), 4.07 (s, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.3, 19.1, 21.7, 47.3, 107.5, 119.5, 128.3, 129.4, 133.8, 144.6, 149.7, 195.3. IR (KBr) ν = 2926, 2212, 1685, 1607 cm^{-1}; MS: *m/z* 214 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{16}NO$: 214.1233 [M+H], found: 214.1235.



(*E*)-2,3-Dimethyl-5-oxo-5-p-tolylpent-2-enenitrile (*E*-9d)

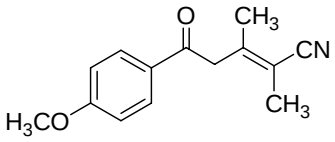
Colorless solid, m.p. 114-116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.88 (s, 3H), 2.11 (s, 3H), 2.43 (s, 3H), 3.85 (s, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.4, 21.7, 23.7, 43.0, 107.3, 119.4, 128.2, 129.5, 133.8,144.8, 149.1, 194.4. IR (KBr) ν = 2919, 2209, 1679, 1605 cm^{-1}; MS: *m/z* 214 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{16}NO$: 214.1233 [M+H], found: 214.1236.



(*Z*)-5-(4-Methoxyphenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*Z*-9e)

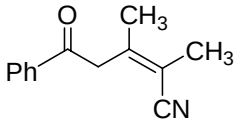
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.83 (s, 3H), 1.89 (s, 3H), 3.80 (s, 3H), 4.01 (s, 2H), 6.88 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.90 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.3, 19.1, 47.0, 55.5, 107.3, 113.9, 119.5, 129.2, 130.5, 149.9, 163.8, 194.1. IR (KBr) ν = 2931, 2214, 1679, 1601 cm^{-1}; MS: *m/z* 230 $(MH)^+$. HRMS (FAB)

calcd for $C_{14}H_{16}NO_2$: 230.1182 [M+H], found: 230.1188.



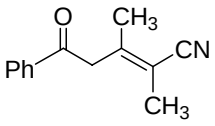
(*E*)-5-(4-Methoxyphenyl)-2,3-dimethyl-5-oxopent-2-enenitrile (*E*-9e)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.83 (s, 3H), 2.06 (s, 3H), 3.80 (s, 2H), 3.84 (s, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.4, 23.6, 42.7, 55.5, 107.1, 113.9, 119.4, 129.2, 130.4, 149.4, 163.9, 193.3. IR (KBr) ν = 2936, 2213, 1681, 1593 cm^{-1}; MS: *m/z* 230 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{16}NO_2$: 230.1182 [M+H], found: 230.1184.



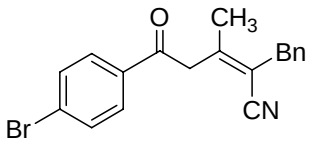
(*Z*)-2,3-Dimethyl-5-oxo-5-phenylpent-2-enenitrile (*Z*-9f)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 1.97 (s, 3H), 4.12 (s, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.4, 19.1, 47.4, 107.8, 119.4, 128.2, 128.8, 133.7, 136.2, 149.4, 195.7. IR (KBr) ν = 2962, 2212, 1688, 1597 cm^{-1}; MS: *m/z* 200 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{14}NO$: 200.1076 [M+H], found: 200.1082.



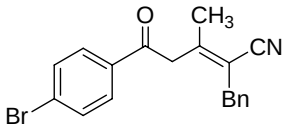
(*E*)-2,3-Dimethyl-5-oxo-5-phenylpent-2-enenitrile (*E*-9f)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.89 (s, 3H), 2.12 (s, 3H), 3.89 (s, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.4, 23.7, 43.1, 107.5, 119.3, 128.1, 128.9, 133.8, 136.2, 148.8, 194.7. IR (KBr) ν = 2964, 2211, 1689, 1592 cm^{-1}; MS: *m/z* 200 $(MH)^+$. HRMS (FAB) calcd for $C_{13}H_{14}NO$: 200.1076 [M+H], found: 200.1077.



(*Z*)-2-Benzyl-5-(4-bromophenyl)-3-methyl-5-oxopent-2-enenitrile (*Z*-9g)

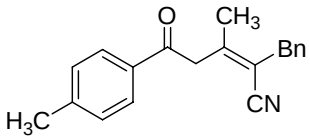
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.01 (s, 3H), 3.65 (s, 2H), 4.13 (s, 2H), 7.24-7.34 (m, 5H), 7.61-7.63 (m, 2H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.5, 36.0, 47.6, 112.8, 118.7, 127.1, 128.3, 128.8, 129.0, 129.7, 132.1, 134.9, 136.7, 149.8, 194.5. IR (KBr) ν = 2963, 2214, 1685, 1585 cm^{-1}; MS: *m/z* 354 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{17}BrNO$: 354.0494 [M+H], found: 354.0486.



(*E*)-2-Benzyl-5-(4-bromophenyl)-3-methyl-5-oxopent-2-enenitrile (*E*-9g)

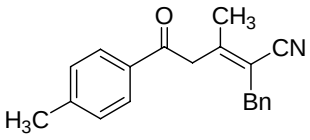
Colorless solid, m.p. 116-118 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.18 (s, 3H), 3.54 (s, 2H), 3.93 (s, 2H), 7.19-7.33 (m, 5H), 7.60-7.63 (m, 2H), 7.73-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 36.1, 43.0, 112.4, 118.6, 127.1, 128.3, 128.8, 129.1, 129.6,

132.2, 134.8, 136.5, 149.3, 193.8. IR (KBr) ν = 2963, 2211, 1677, 1584 cm^{-1}; MS: *m/z* 354 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{17}BrNO$: 354.0494 [M+H], found: 354.0482.



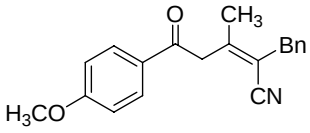
(*Z*)-2-Benzyl-3-methyl-5-oxo-5-p-tolylpent-2-enenitrile (*Z*-9h)

Syrup. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.01 (s, 3H), 2.42 (s, 3H), 3.66 (s, 2H), 4.16 (s, 2H), 7.27-7.35 (m, 7H), 7.34 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.5, 21.7, 36.0, 47.6, 112.3, 118.8, 127.0, 128.3, 128.8, 129.5, 133.8, 136.8, 144.6, 150.6, 195.1. IR (KBr) ν = 2921, 2212, 1684, 1606 cm^{-1}; MS: *m/z* 290 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{20}NO$: 290.1546 [M+H], found: 290.1541.



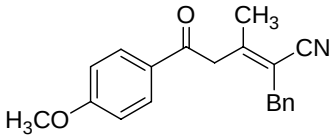
(*E*)-2-Benzyl-3-methyl-5-oxo-5-p-tolylpent-2-enenitrile (*E*-9h)

Syrup. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.19 (s, 3H), 2.43 (s, 3H), 3.55 (s, 2H), 3.96 (s, 2H), 7.21-7.34 (m, 7H), 7.82 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.7, 24.0, 36.1, 43.0, 112.1, 118.7, 127.0, 128.2, 128.4, 128.8, 129.5, 133.7, 136.7, 144.8, 149.9, 194.4. IR (KBr) ν = 2922, 2213, 1674, 1606 cm^{-1}; MS: *m/z* 290 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{20}NO$: 290.1546 [M+H], found: 290.1538.



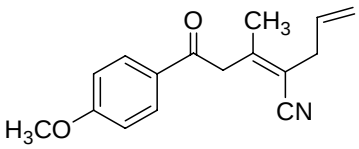
(*Z*)-2-Benzyl-5-(4-methoxyphenyl)-3-methyl-5-oxopent-2-enenitrile (*Z*-9i)

Syrup. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.01 (s, 3H), 3.65 (s, 2H), 3.85 (s, 3H), 4.13 (s, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.24-7.35 (m, 5H), 7.97 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.4, 36.0, 47.4, 55.5, 112.2, 113.9, 118.9, 127.0, 128.3, 128.8, 129.3, 130.6, 136.9, 150.7, 163.9, 193.9. IR (KBr) ν = 2935, 2212, 1676, 1600 cm^{-1}; MS: *m/z* 306 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{20}NO_2$: 306.1495 [M+H], found: 306.1501.



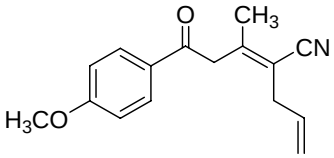
(*E*)-2-Benzyl-5-(4-methoxyphenyl)-3-methyl-5-oxopent-2-enenitrile (*E*-9i)

Syrup. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.19 (s, 3H), 3.56 (s, 2H), 3.88 (s, 3H), 3.93 (s, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.21-7.33 (m, 5H), 7.89 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 36.1, 42.8, 55.5, 112.0, 114.0, 118.7, 127.0, 128.4, 128.8, 129.3, 130.5, 136.8, 150.0, 164.0, 193.3. IR (KBr) ν = 2928, 2214, 1686, 1598 cm^{-1}; MS: *m/z* 306 $(MH)^+$. HRMS (FAB) calcd for $C_{20}H_{20}NO_2$: 306.1495 [M+H], found: 306.1502



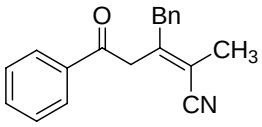
(*Z*)-2-Allyl-5-(4-methoxyphenyl)-3-methyl-5-oxopent-2-enenitrile (*Z*-9j)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 3.02-3.04 (m, 2H), 3.86 (s, 3H), 4.08 (s, 2H), 5.14-5.22 (m, 2H), 5.76-5.83 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.0, 34.1, 47.3, 55.5, 110.8, 113.9, 117.5, 118.7, 129.3, 130.5, 132.3, 150.8, 163.9, 193.9. IR (KBr) ν = 2925, 2214, 1681, 1583 cm^{-1}; MS: *m/z* 256 $(MH)^+$. HRMS (FAB) calcd for $C_{16}H_{18}NO_2$: 256.1338 [M+H], found: 256.1341.



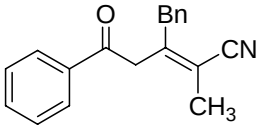
(*E*)-2-Allyl-5-(4-methoxyphenyl)-3-methyl-5-oxopent-2-enenitrile (*E*-9j)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.94-2.96 (m, 1H), 3.84 (s, 3H), 3.88 (s, 2H), 5.12-5.15 (m, 2H), 5.75-5.82 (m, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 34.4, 42.6, 55.5, 110.6, 114.0, 117.6, 118.5, 129.3, 130.4, 132.7, 150.1, 164.0, 193.2. IR (KBr) ν = 2934, 2212, 1682, 1585 cm^{-1}; MS: *m/z* 256 $(MH)^+$. HRMS (FAB) calcd for $C_{16}H_{18}NO_2$: 256.1338 [M+H], found: 256.1346.



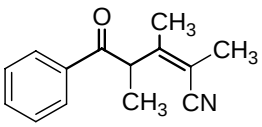
(*Z*)-3-Benzyl-2-methyl-5-oxo-5-phenylpent-2-enenitrile (*Z*-9k)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 3.69 (s, 2H), 4.01 (s, 2H), 7.07 (d, *J* = 6.8 Hz, 2H), 7.23-7.30 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 2H,), 7.57 (t, *J* = 7.2 Hz, 1H,), 7.88 (d, *J* = 7.2Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.6, 37.6, 44.3, 109.3, 119.3, 127.0, 128.1, 128.68, 128.72, 128.9, 133.6, 136.3, 136.6, 151.5, 195.7. IR (KBr) ν = 2926, 2212, 1724, 1686 cm^{-1}; MS: *m/z* 276 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}NO$: 276.1389 [M+H], found: 276.1387.



(*E*)-3-Benzyl-2-methyl-5-oxo-5-phenylpent-2-enenitrile (*E*-9k)

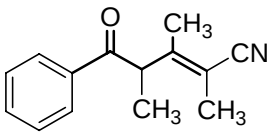
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 3.75 (s, 2H), 3.86 (s, 2H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.22-7.29 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H,), 7.58 (t, *J* = 7.2 Hz, 1H,), 7.82 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.8, 40.0, 43.0, 108.7, 119.3, 127.0, 128.0, 128.7, 128.8, 129.0, 133.6, 136.3, 136.9, 151.2, 194.6. IR (KBr) ν = 2930, 2211, 1713, 1692 cm^{-1}; MS: *m/z* 276 $(MH)^+$. HRMS (FAB) calcd for $C_{19}H_{18}NO$: 276.1389 [M+H], found: 276.1395.



(*Z*)-2,3,4-trimethyl-5-oxo-5-phenylpent-2-enenitrile (*Z*-9l)

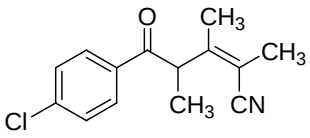
Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.29 (d, *J* = 6.8 Hz, 3H), 1.59 (s, 3H), 1.80 (s, 3H), 4.82 (q, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.47-7.51 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 15.3, 16.4, 48.9, 106.3, 119.3, 128.2, 128.7, 133.4, 136.0, 154.8, 198.9. IR (KBr) ν = 2936, 2213, 1696, 1589 cm^{-1}; MS: *m/z* 214 $(MH)^+$. HRMS (FAB)

calcd for $C_{14}H_{16}NO$: 214.1233 [M+H], found: 214.1245.



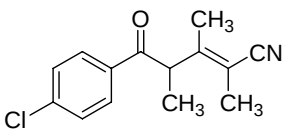
(*E*)-2,3,4-trimethyl-5-oxo-5-phenylpent-2-enenitrile (*E*-9l)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (d, *J* = 6.0 Hz, 3H), 1.86 (s, 3H), 2.06 (s, 3H), 4.41 (q, *J* = 6.0 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.54-7.58 (m, 1H), 7.79 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 16.1, 18.7, 45.0, 105.7, 119.3, 127.8, 128.8, 133.5, 136.1, 154.7, 198.8. IR (KBr) ν = 2938, 2214, 1698, 1601 cm^{-1}; MS: *m/z* 214 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{16}NO$: 214.1233 [M+H], found: 214.1249.



(*Z*)-5-(4-Chlorophenyl)-2,3,4-trimethyl-5-oxopent-2-enenitrile (*Z*-9m)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.34 (s, 3H), 1.63 (s, 3H), 1.87 (s, 3H), 4.81-4.83 (m, 1H), 7.42-7.43 (m, 2H), 7.90-7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 15.3, 16.4, 49.0, 106.6, 119.3, 129.1, 129.7, 134.3, 140.0, 154.5, 197.9. IR (KBr) ν = 2929, 2213, 1686, 1583 cm^{-1}; MS: *m/z* 248 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{15}ClNO$: 248.0843 [M+H], found: 248.0832.

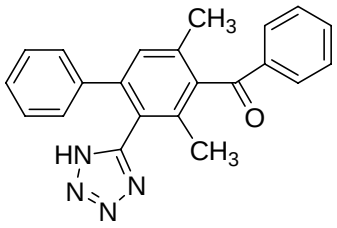


(*E*)-5-(4-Chlorophenyl)-2,3,4-trimethyl-5-oxopent-2-enenitrile (*E*-9m)

Syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (d, *J* = 6.4 Hz, 3H), 1.87 (s, 3H), 2.07 (s, 3H), 4.35-4.37 (m, 1H), 7.74-7.75 (m, 2H), 7.90-7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 16.1, 18.7, 45.1, 105.9, 119.1, 129.2, 129.9, 134.4, 140.1, 154.3, 197.6. IR (KBr) ν = 2938, 2212, 1688, 1589 cm^{-1}; MS: *m/z* 248 $(MH)^+$. HRMS (FAB) calcd for $C_{14}H_{15}ClNO$: 248.0843 [M+H], found: 248.0835.

7. Procedure for the preparation of 1-benzoyl-2,6-dimethyl-4-phenyl-3-(1*H*-tetrazol-5-yl)benzene (10)[5]

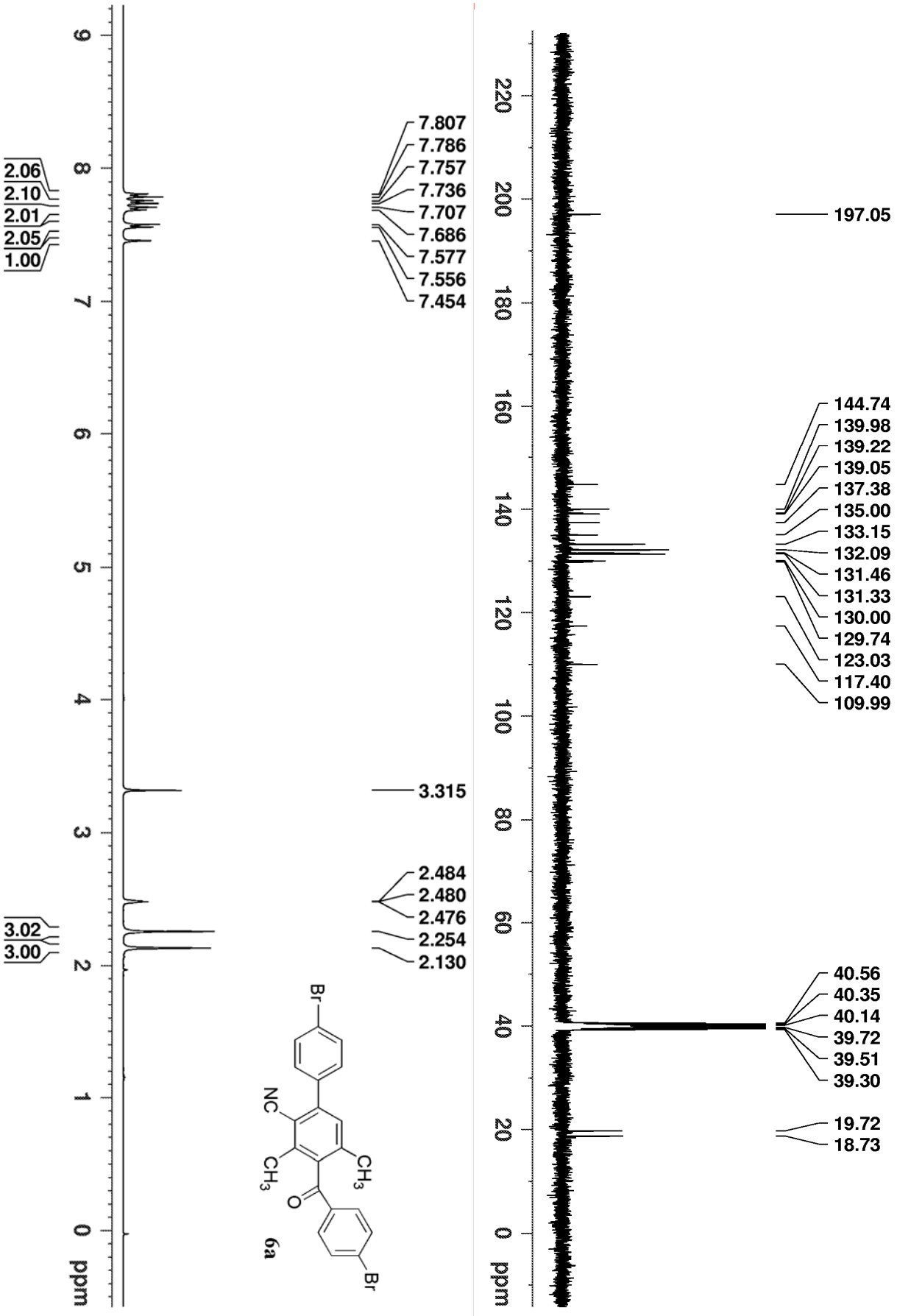
Under a nitrogen atmosphere, a mixture of 1-benzoyl-3-cyano-2,6-dimethyl-4-phenylbenzene (**6b**, 1 mmol), *n*-Bu_2SnO (0.5 mmol) and trimethylsilyl azide (5 mmol) in *o*-xylene (5 mL) was stirred at 90 °C for 50 h. Upon completion, the reaction mixture was cooled to room temperature, added with water (10 mL) and extracted with ethyl acetate. The combined organic phases were washed with brine, dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (2:1) to give **10**.

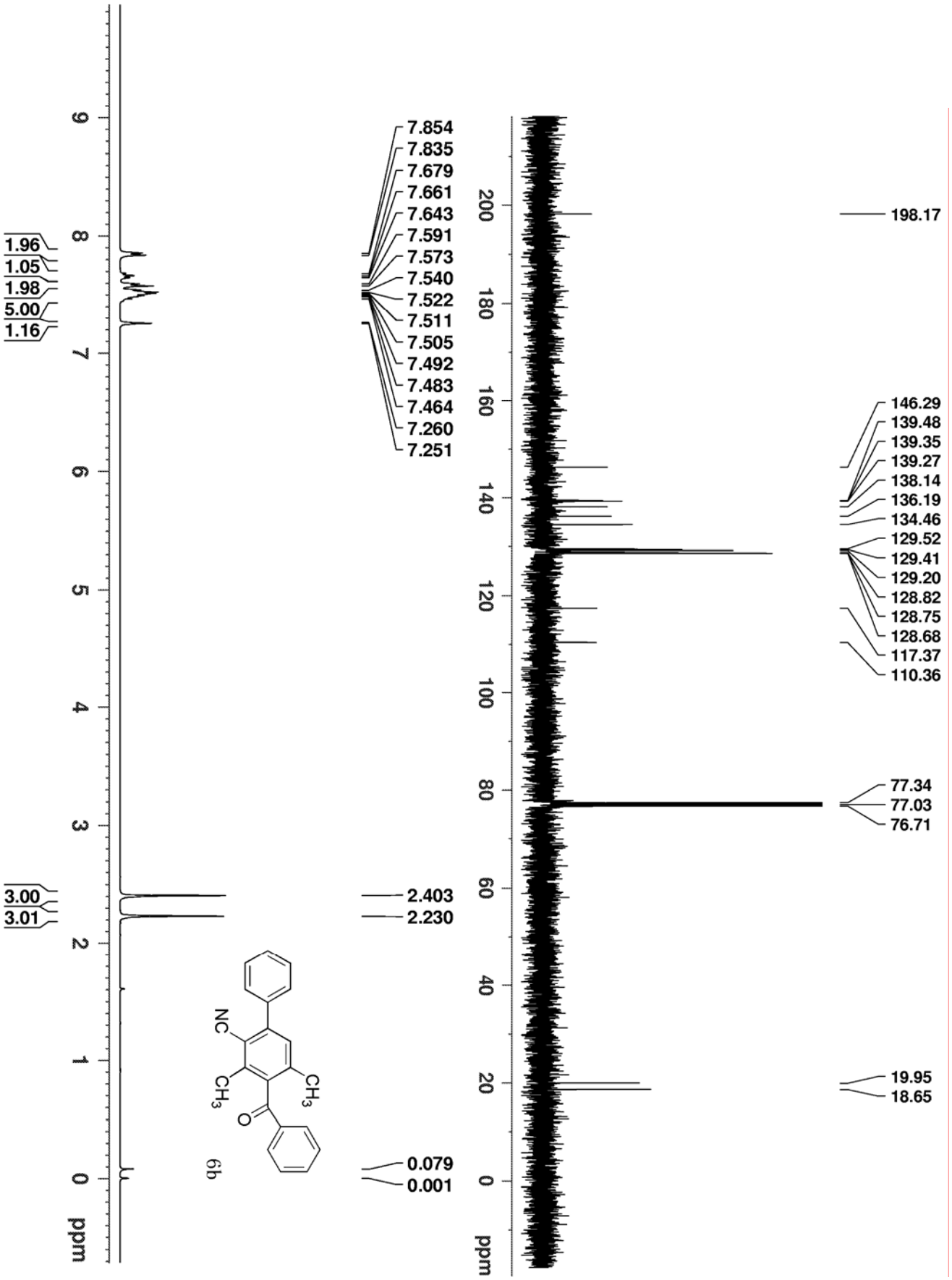


1-Benzoyl-2,6-dimethyl-4-phenyl-3-(1*H*-tetrazol-5-yl)benzene (10)

Colorless solid, m.p. 205-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.88 (s, 3H), 2.17 (s, 3H), 7.03 (d, *J* = 6.8 Hz, 2H), 7.20-7.23 (m, 4H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.5, 19.5, 120.9, 127.7, 128.3, 128.6, 129.2, 129.7, 129.8, 134.6, 134.8, 136.1, 137.3, 138.9, 139.3, 143.7, 153.4, 200.3. IR (KBr) ν = 3061, 2919, 1647, 1596 cm^{-1}; MS: *m/z* 355 $(MH)^{+}$. HRMS (FAB) calcd for $C_{22}H_{19}N_4O$: 355.156 [M+H], found: 355.1569.

III. Copies of ^{1}H and ^{13}C NMR spectra of 6a-6v, 8, 9a-9m, 10

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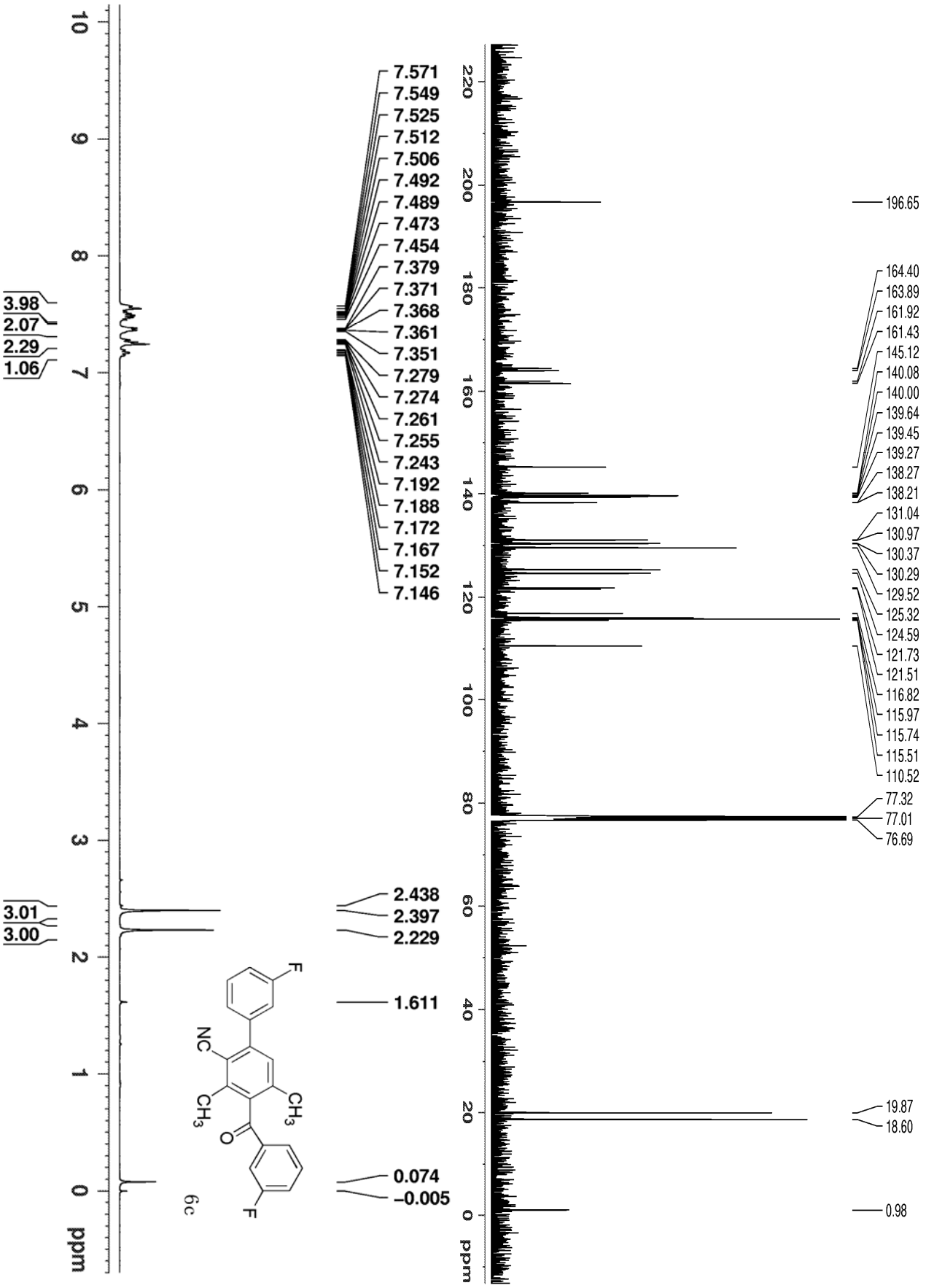
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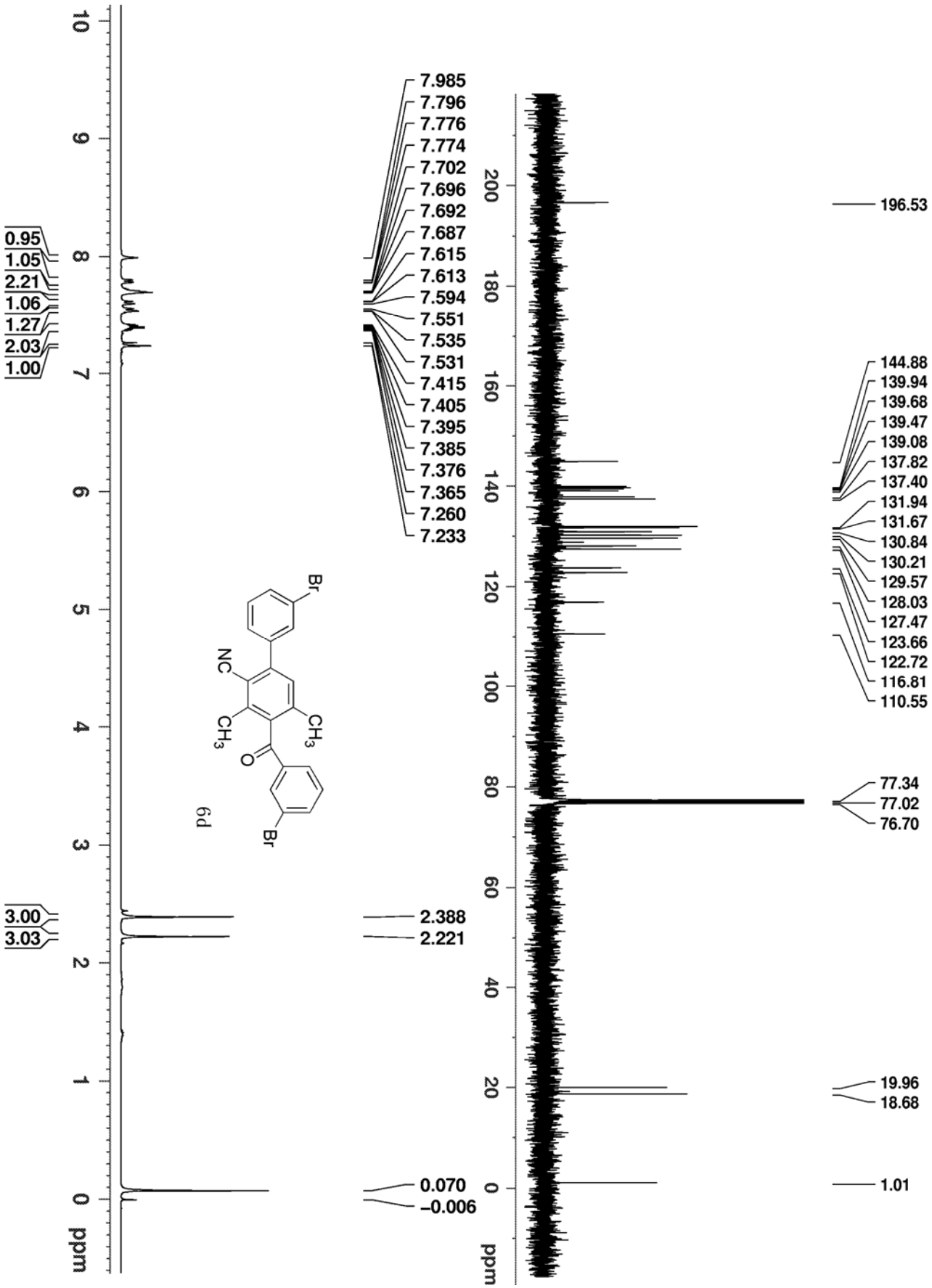
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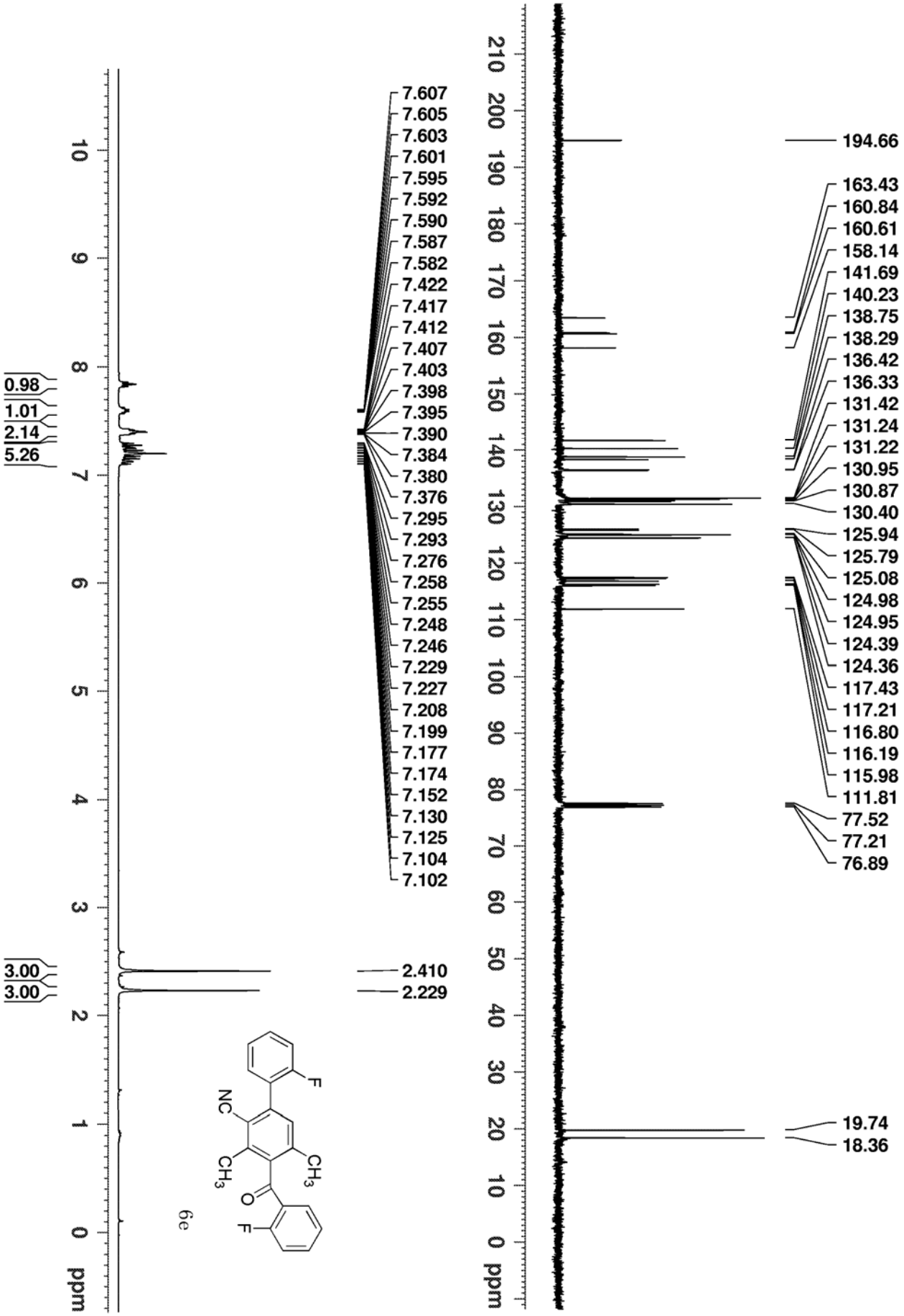
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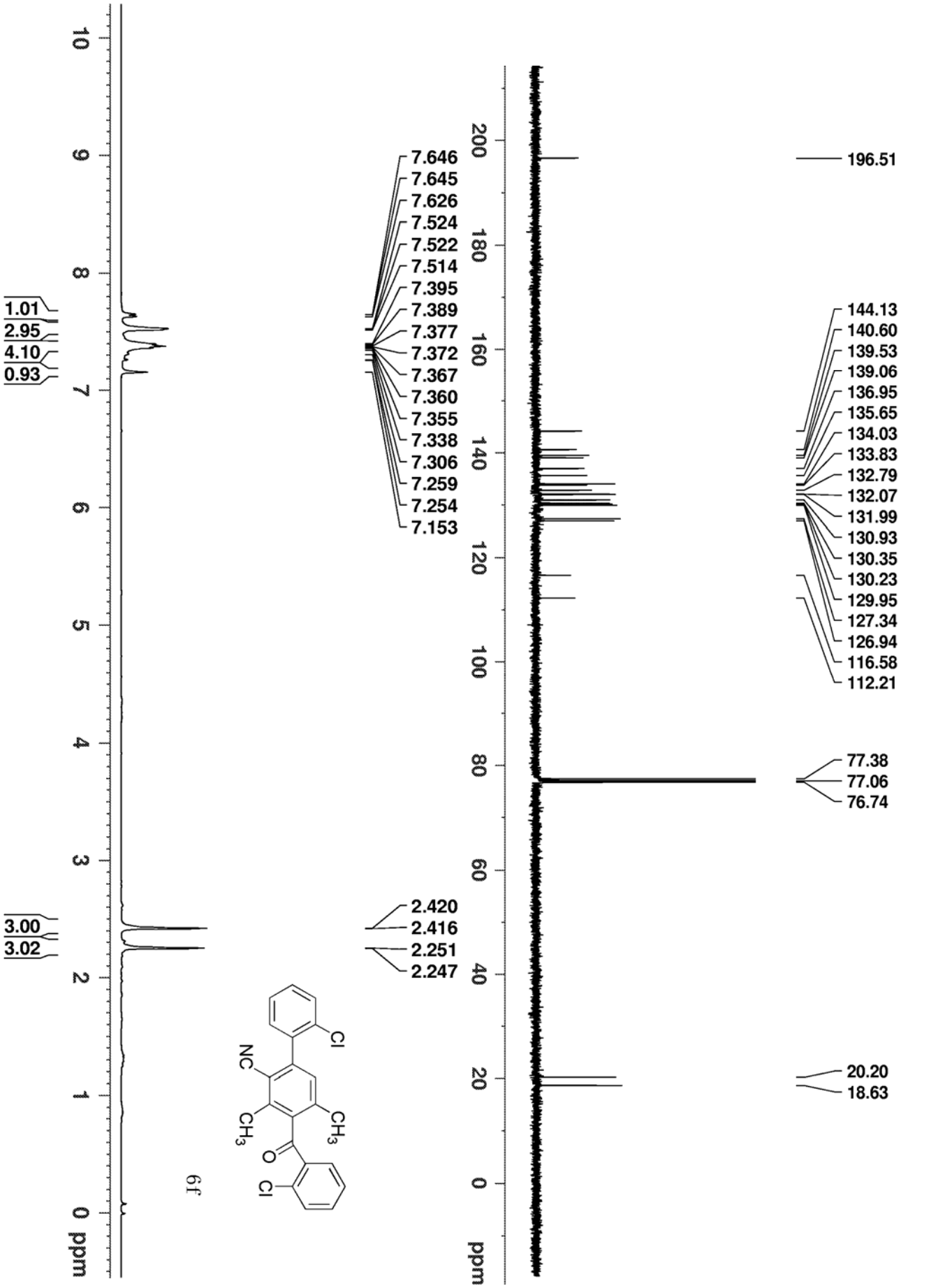
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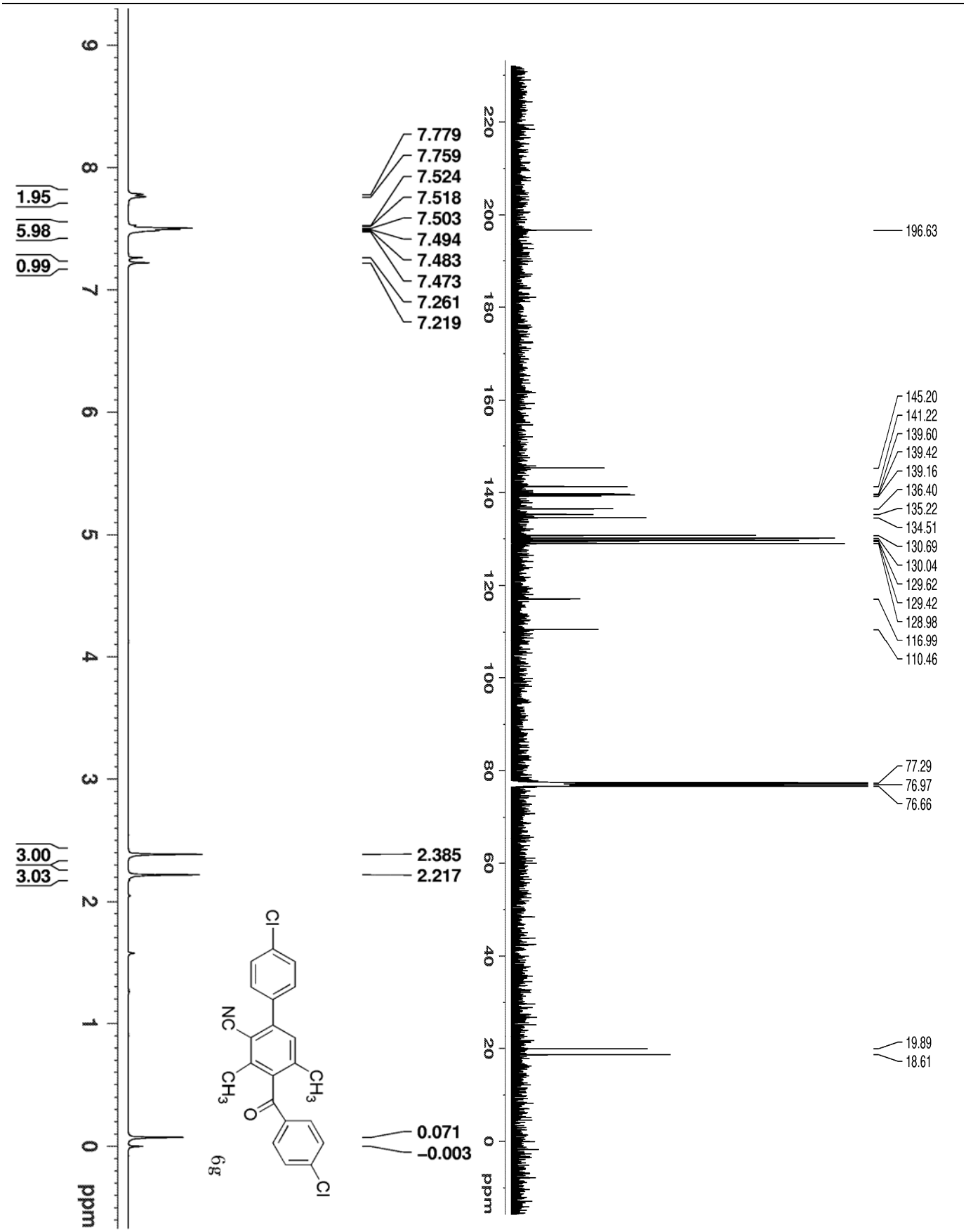
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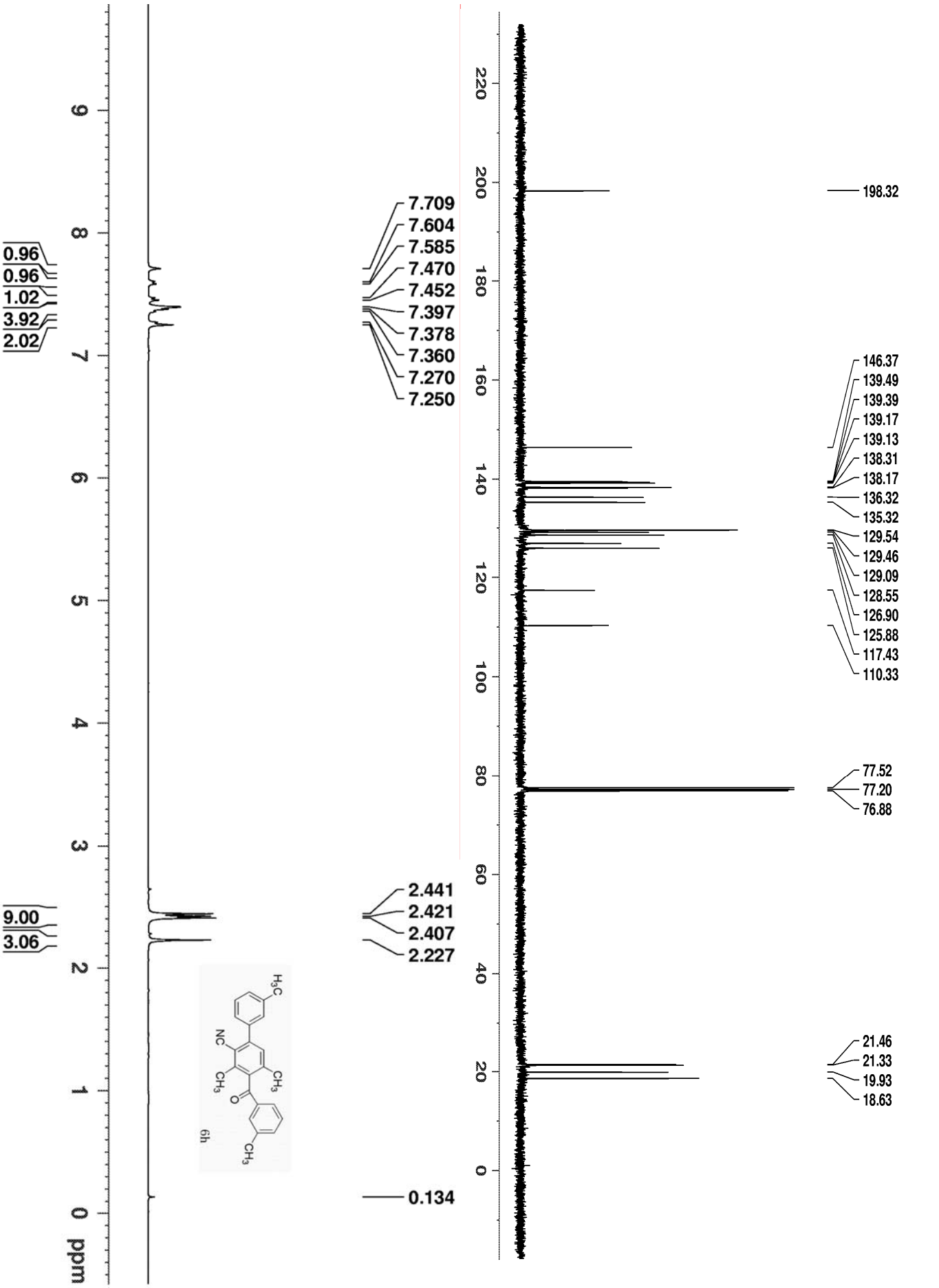
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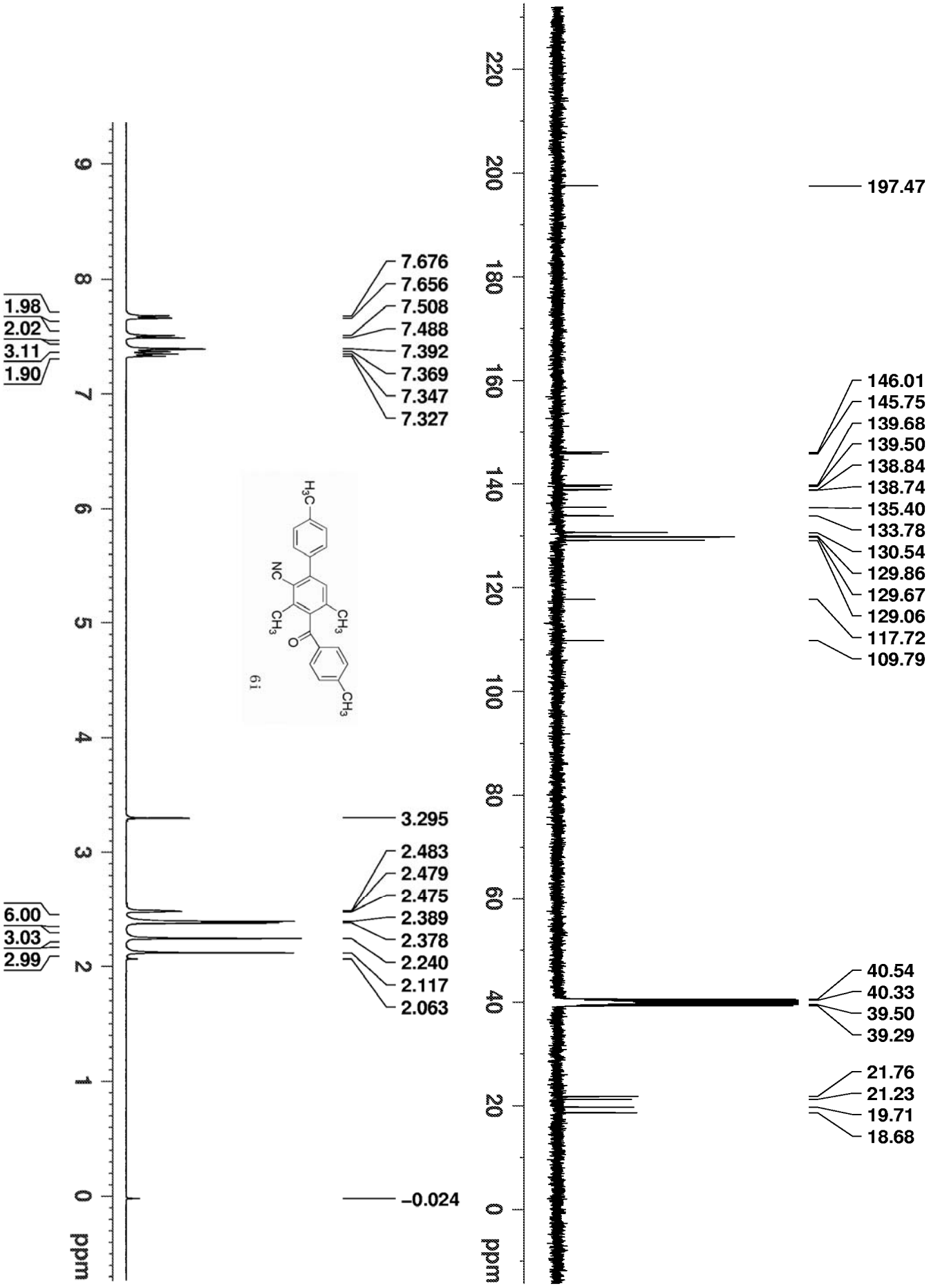
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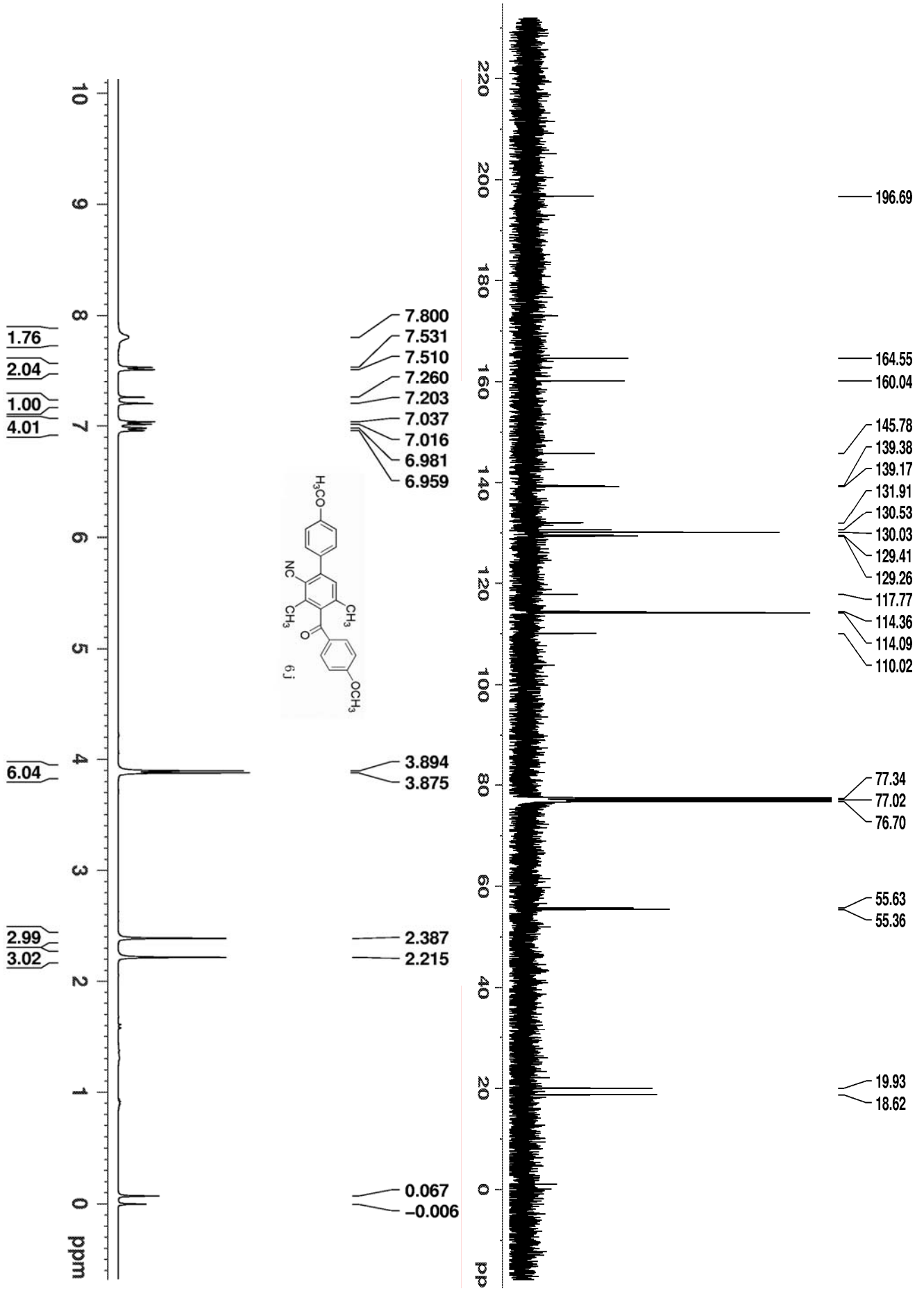
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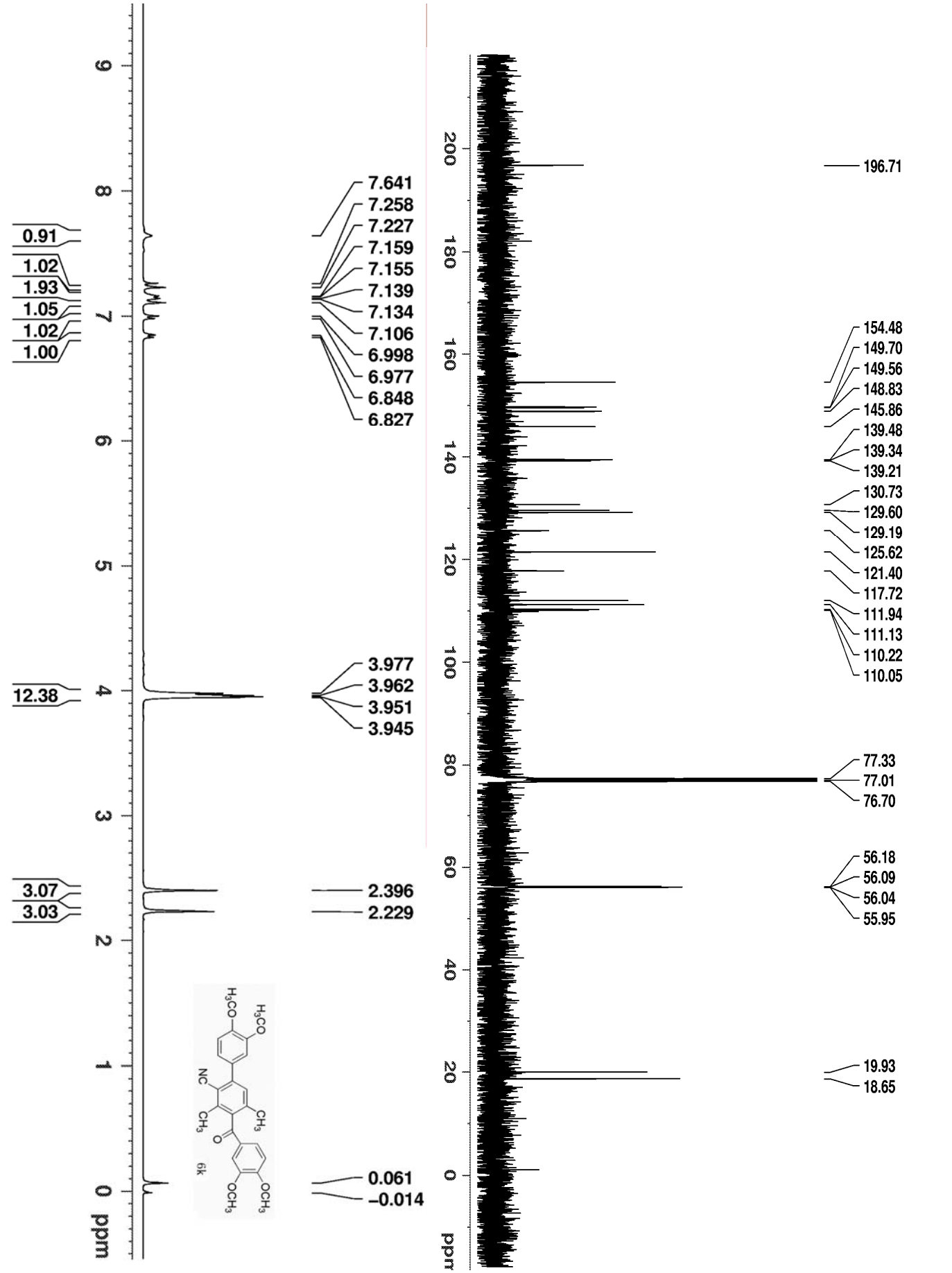
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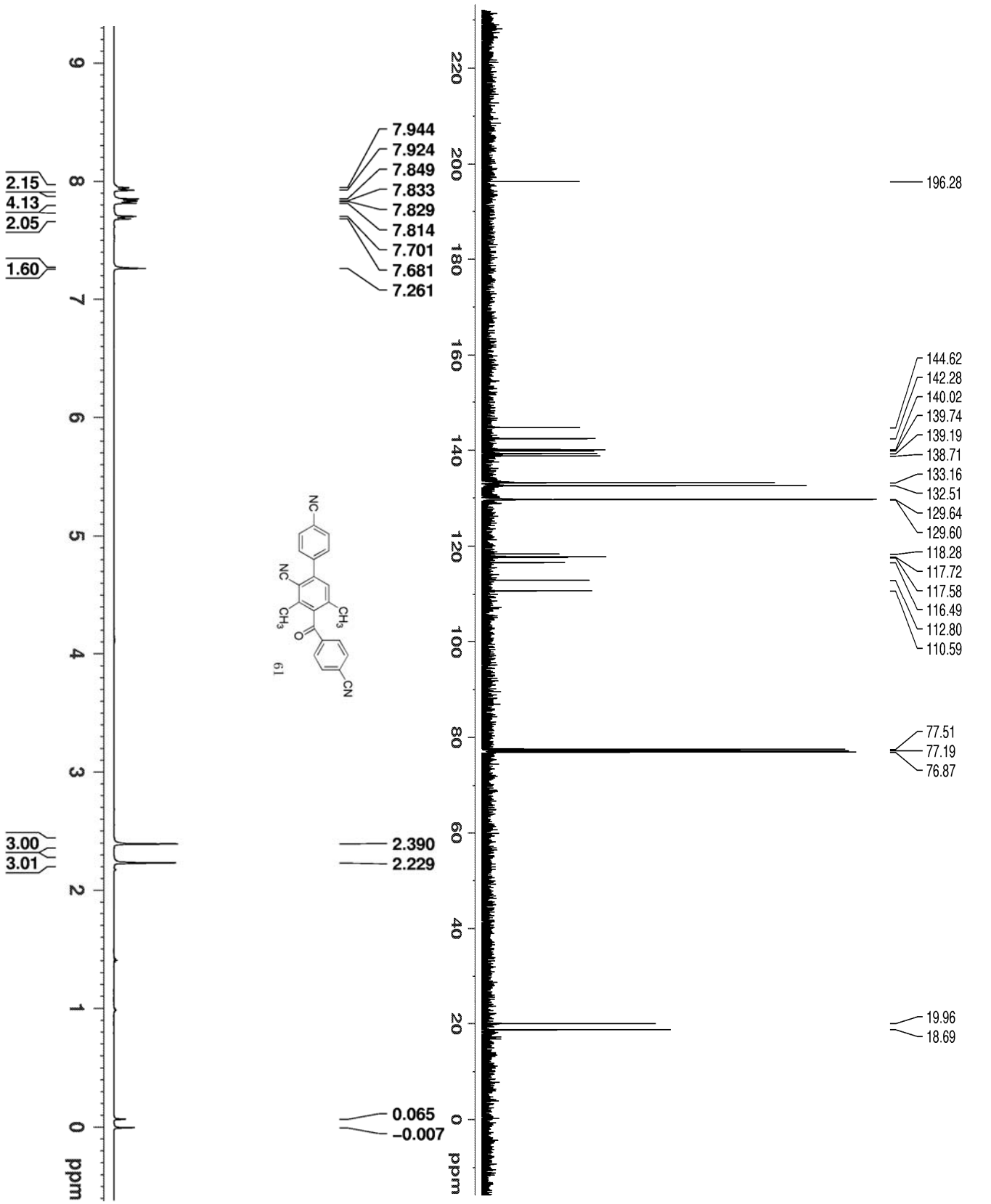
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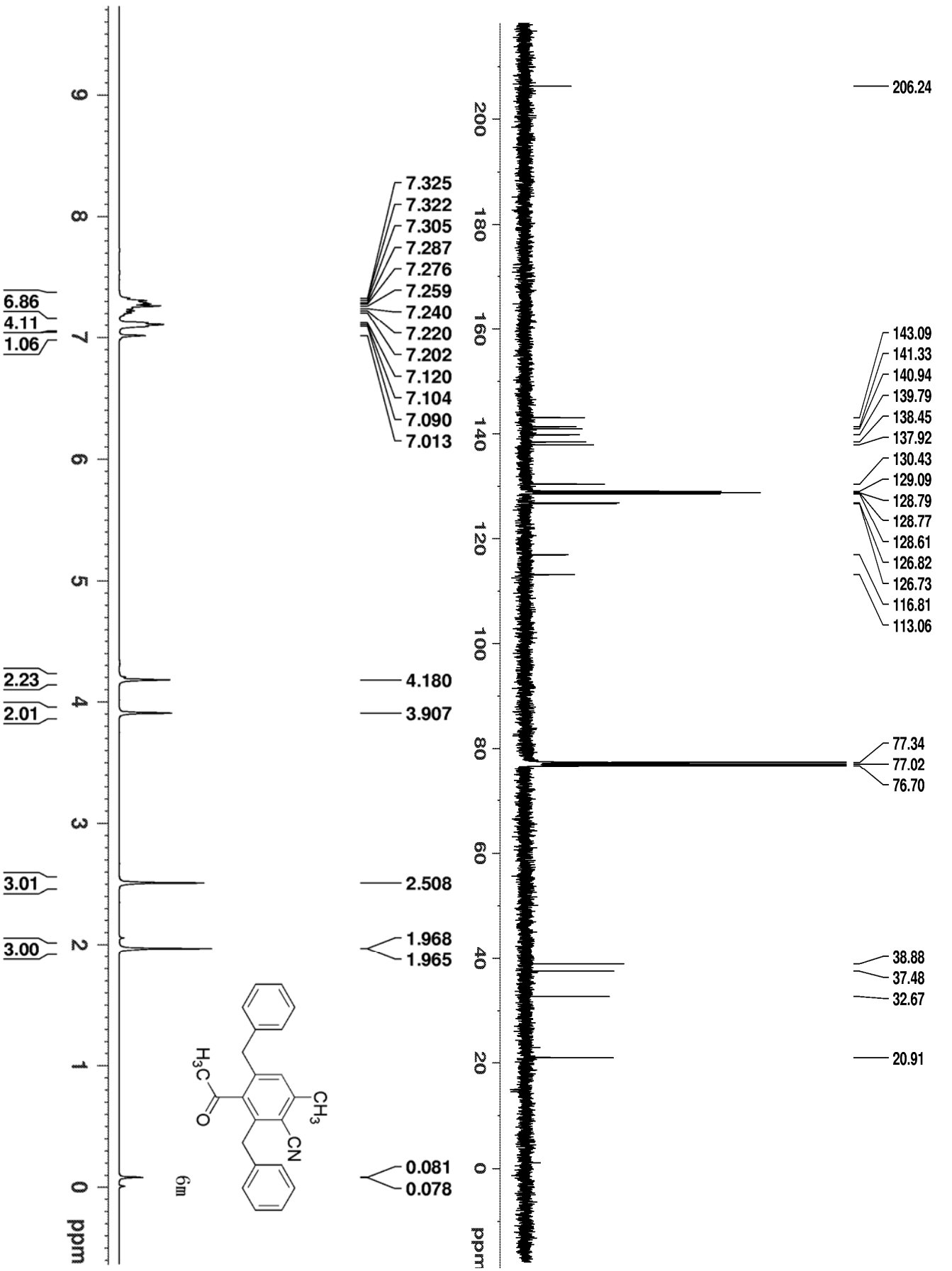
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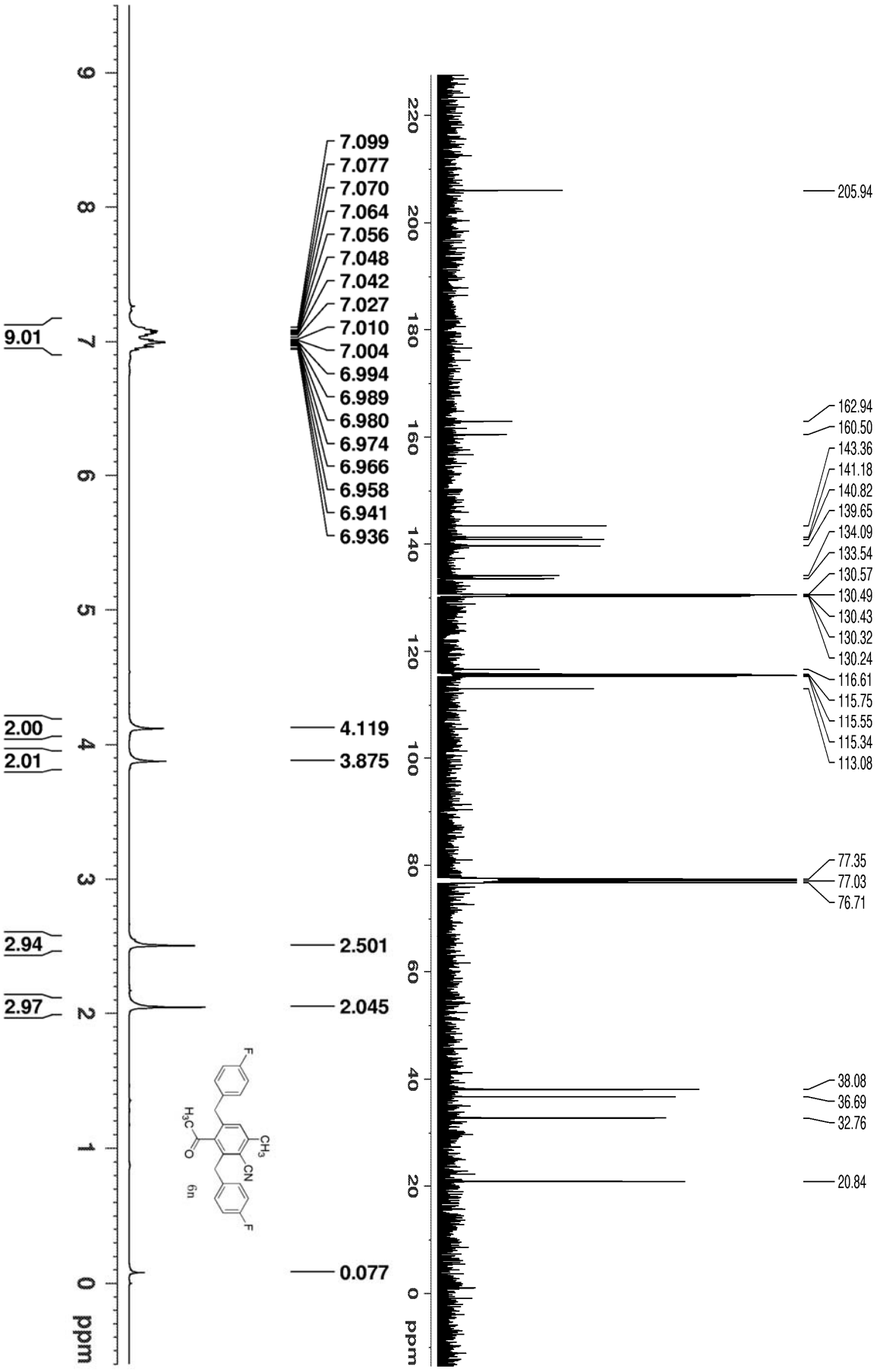
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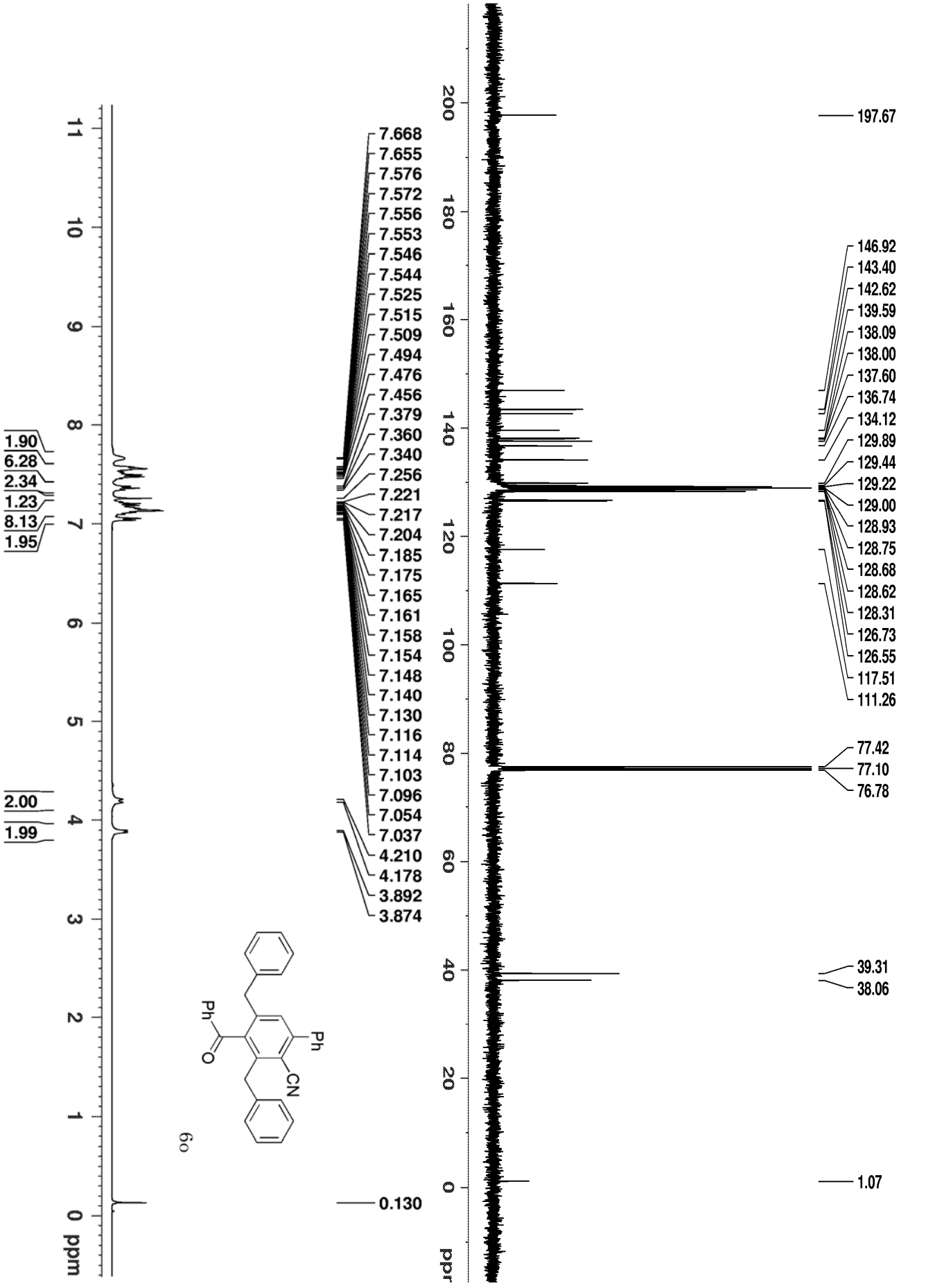
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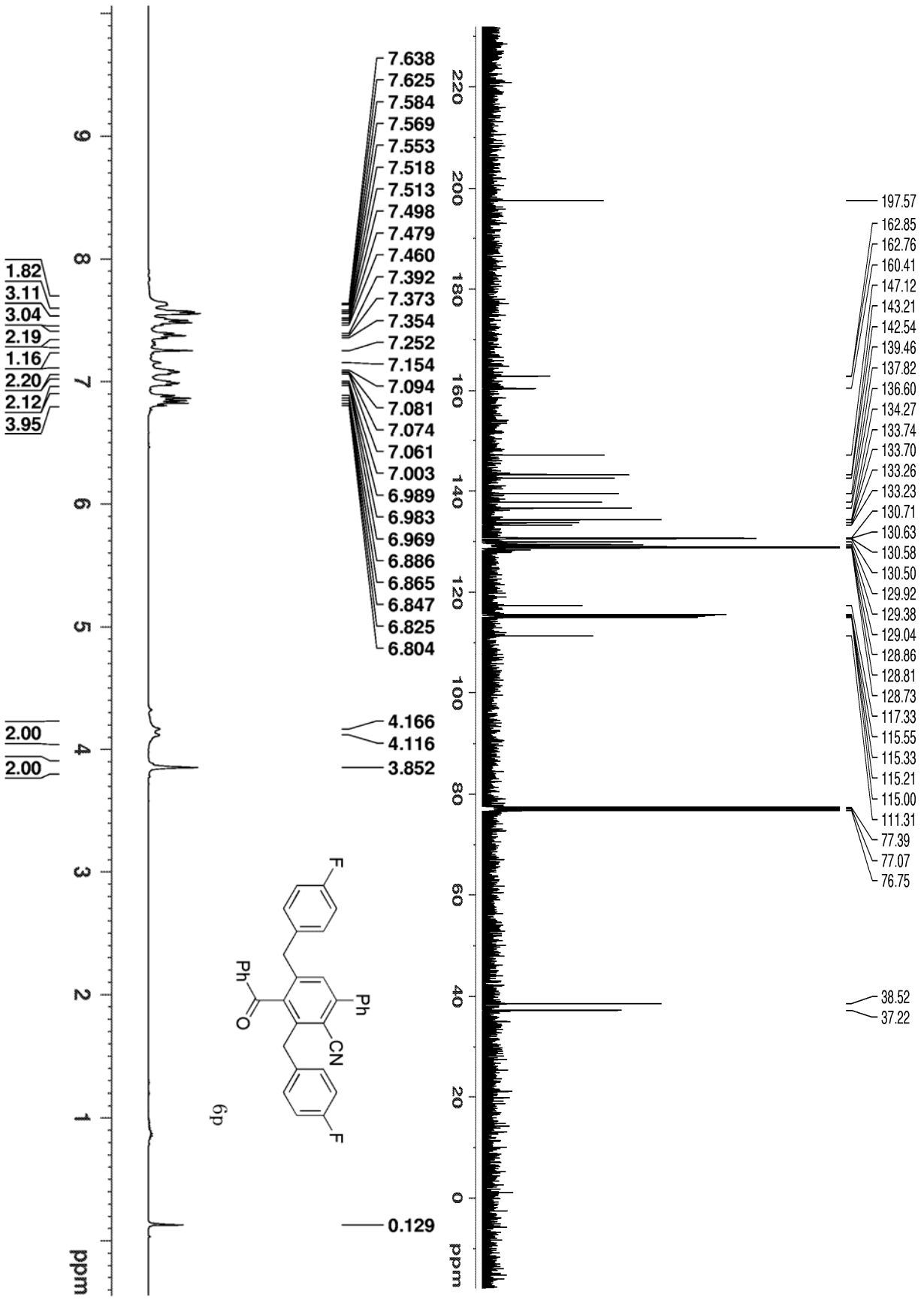
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7.081
7.074
7.061
7.003
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6.969
6.886
6.865
6.847
6.825
6.804
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4.116
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3.11
3.04
2.19
1.16
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2.12
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2.00
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162.76
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115.55
115.33
115.21
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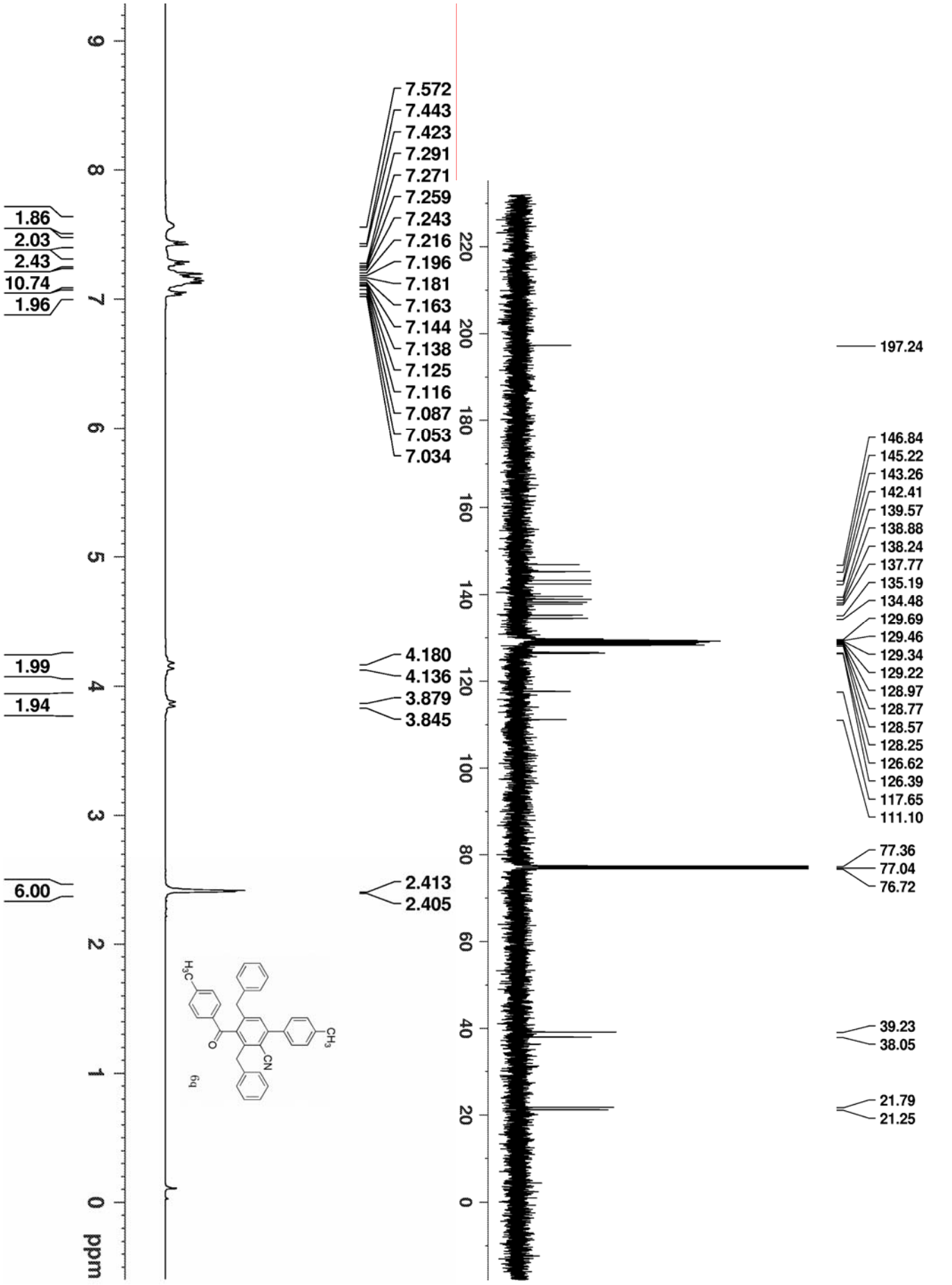
O
Ph
CN
F
6p
ppm
ppm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7.243
7.216
7.196
7.181
7.163
7.144
7.138
7.125
7.116
7.087
7.053
7.034
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2.405
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145.22
143.26
142.41
139.57
138.88
138.24
137.77
135.19
134.48
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129.46
129.34
129.22
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ppm
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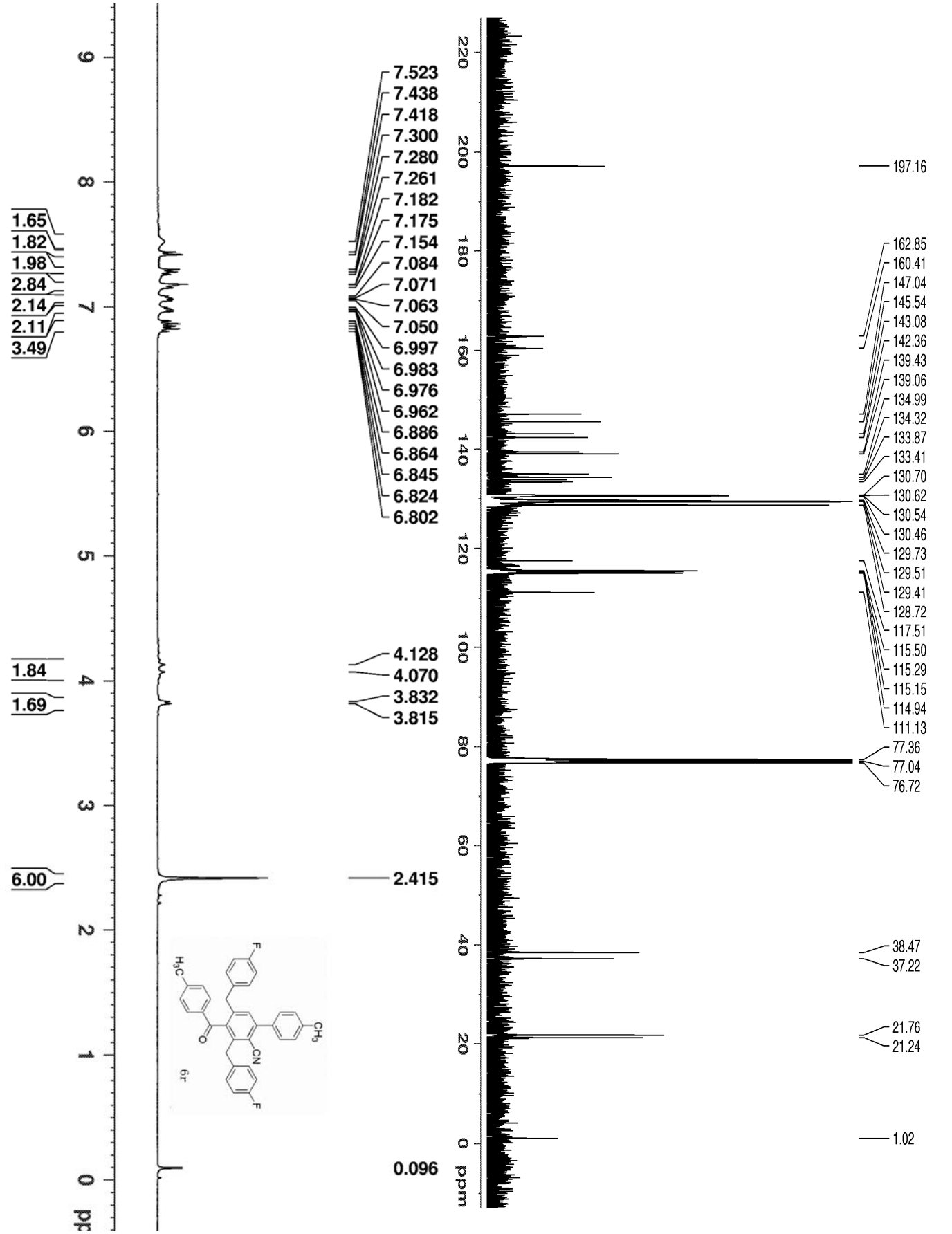
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7.300
7.280
7.261
7.182
7.175
7.154
7.084
7.071
7.063
7.050
6.997
6.983
6.976
6.962
6.886
6.864
6.845
6.824
6.802
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4.070
3.832
3.815
2.415
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197.16
162.85
160.41
147.04
145.54
143.08
142.36
139.43
139.06
134.99
134.32
133.87
133.41
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130.46
129.73
129.51
129.41
128.72
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115.50
115.29
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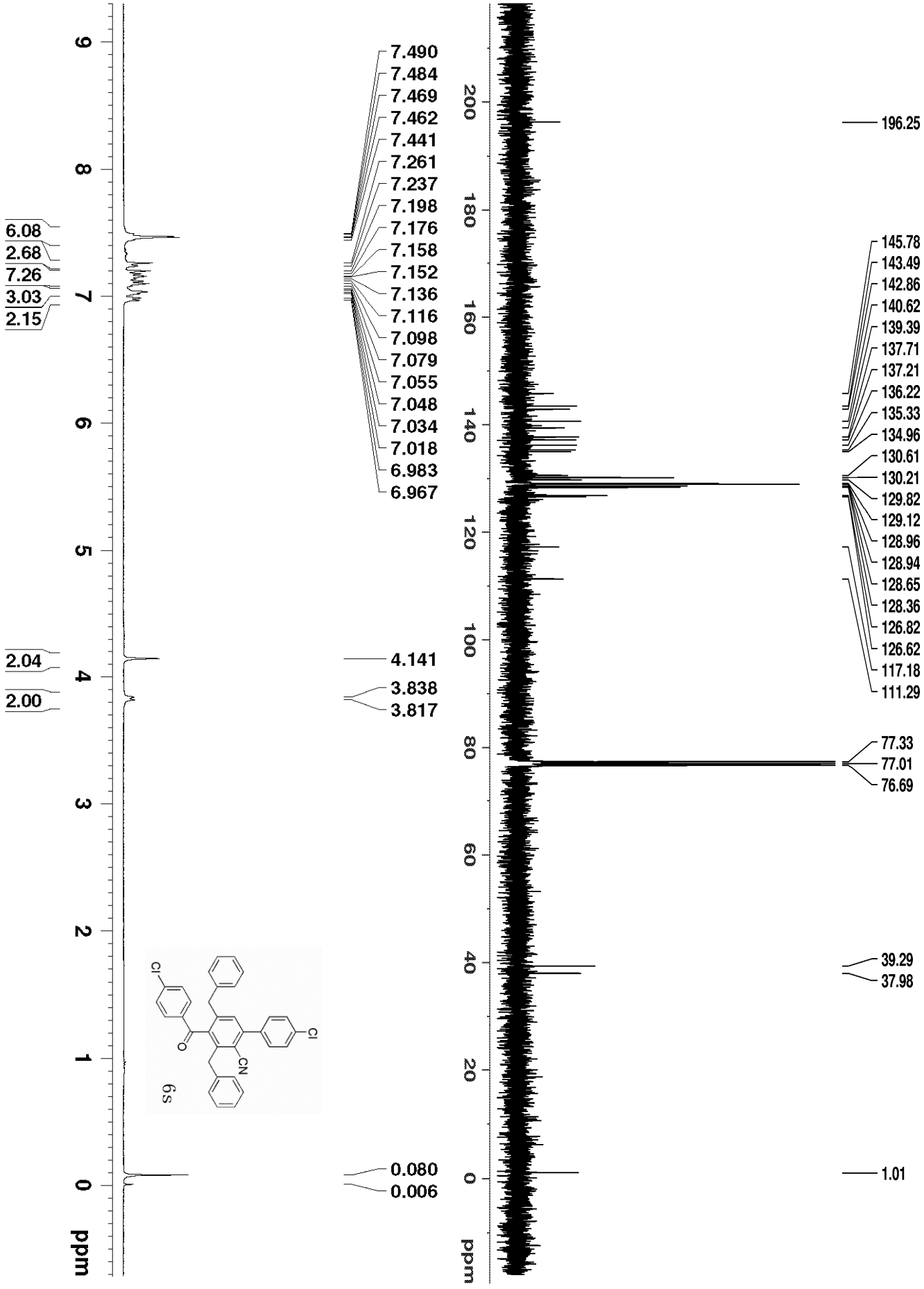
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7.237
7.198
7.176
7.158
7.152
7.136
7.116
7.098
7.079
7.055
7.048
7.034
7.018
6.983
6.967
4.141
3.838
3.817
0.080
0.006
196.25
145.78
143.49
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137.71
137.21
136.22
135.33
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130.61
130.21
129.82
129.12
128.96
128.94
128.65
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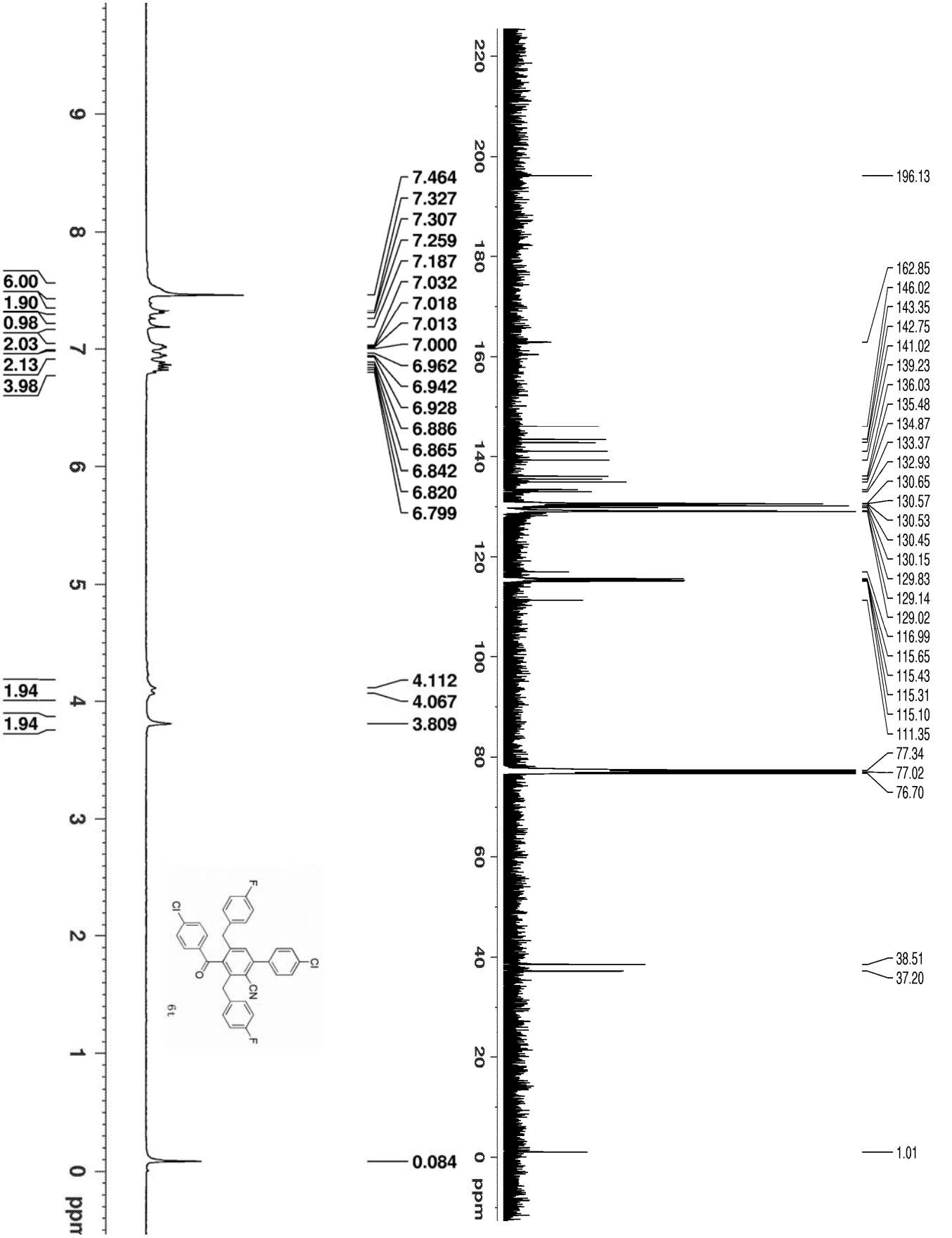
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1.94
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7.307
7.259
7.187
7.032
7.018
7.013
7.000
6.962
6.942
6.928
6.886
6.865
6.842
6.820
6.799
4.112
4.067
3.809
0.084
196.13
162.85
146.02
143.35
142.75
141.02
139.23
136.03
135.48
134.87
133.37
132.93
130.65
130.57
130.53
130.45
130.15
129.83
129.14
129.02
116.99
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115.10
111.35
77.34
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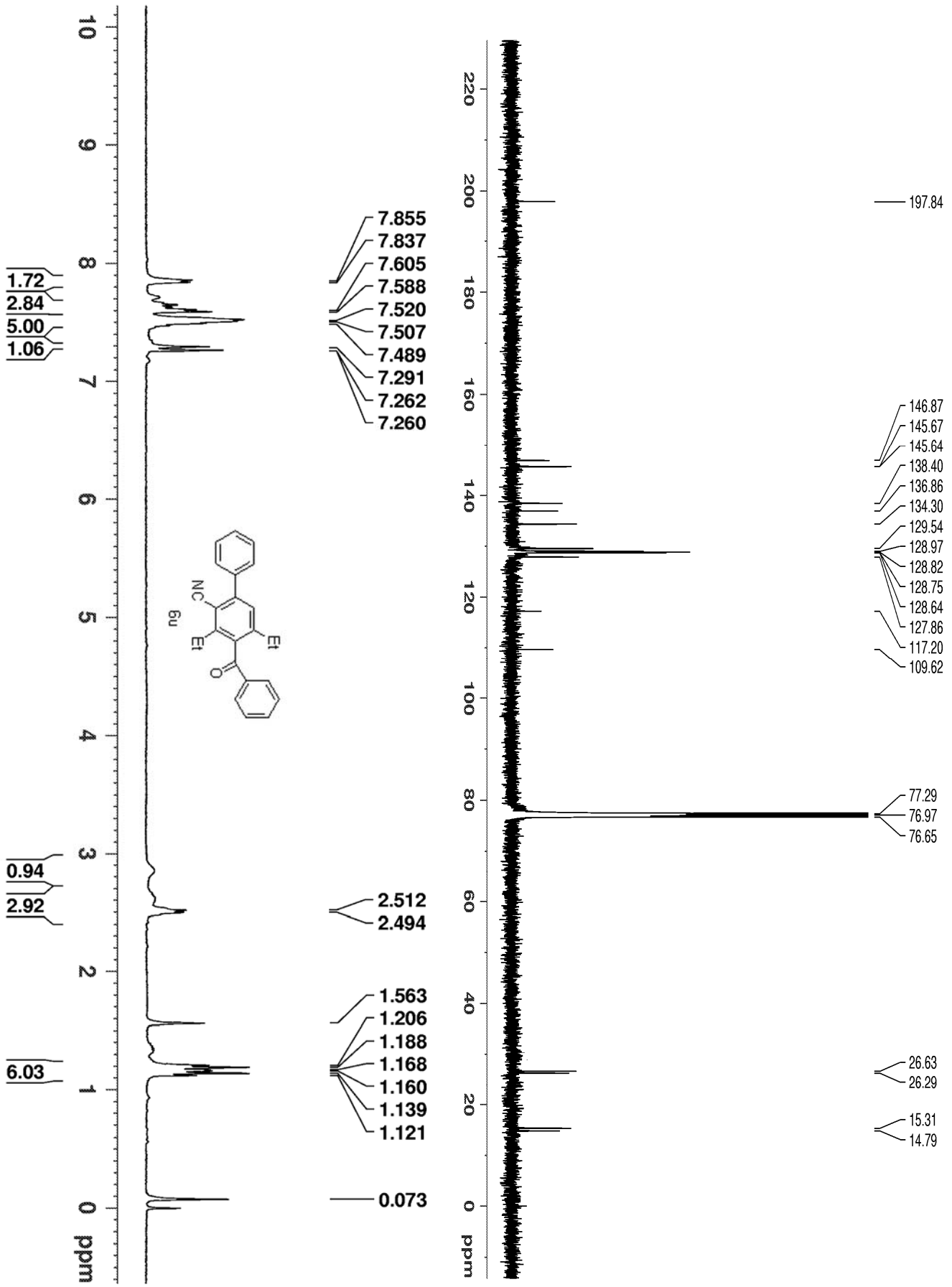
76.70
38.51
37.20
1.01
ppm
6t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1.06
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2.92
6.03
7.855
7.837
7.605
7.588
7.520
7.507
7.489
7.291
7.262
7.260
2.512
2.494
1.563
1.206
1.188
1.168
1.160
1.139
1.121
0.073
197.84
146.87
145.67
145.64
138.40
136.86
134.30
129.54
128.97
128.82
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117.20
109.62
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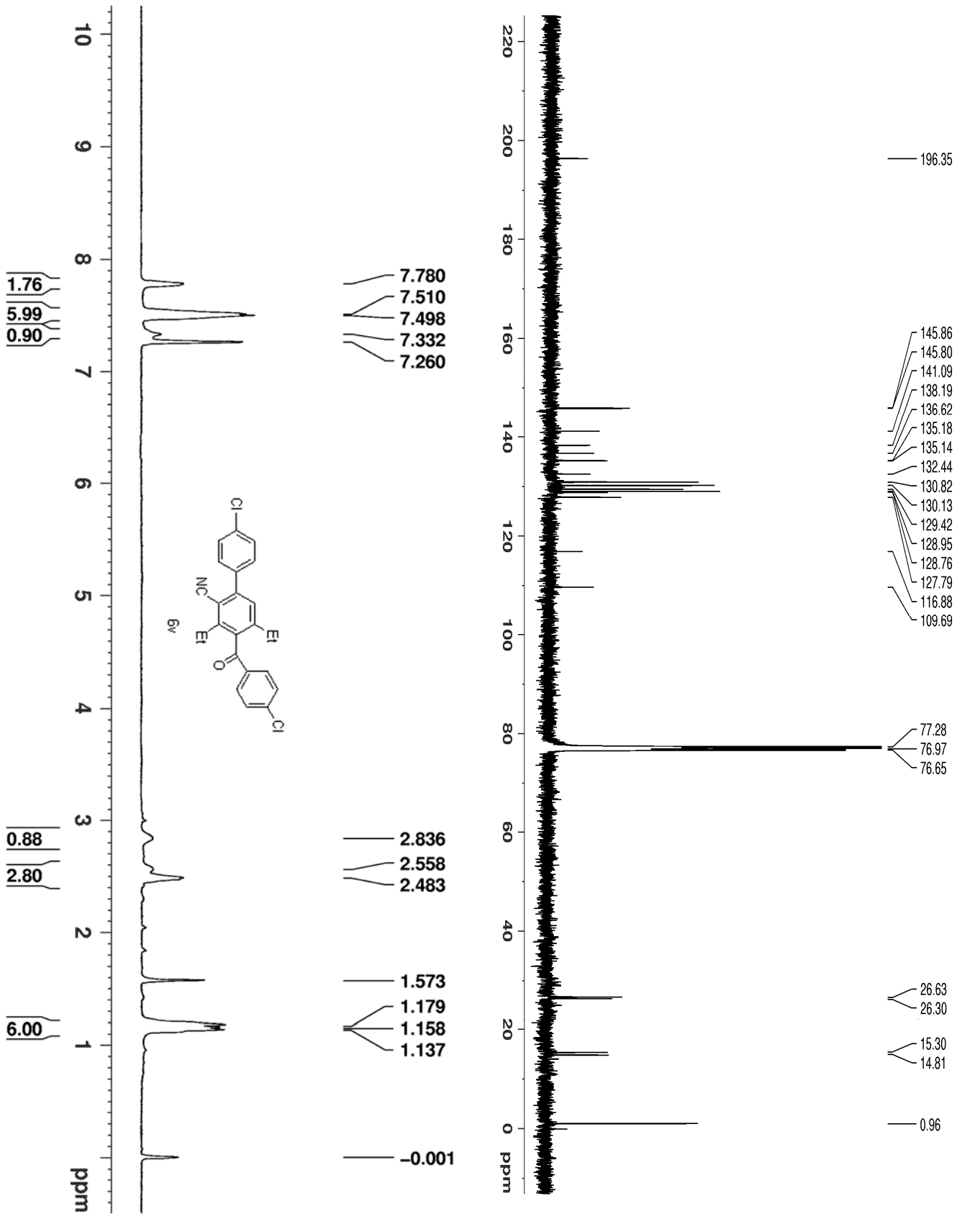
26.63
26.29
15.31
14.79
ppm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7.332
7.260
2.836
2.558
2.483
1.573
1.179
1.158
1.137
−0.001
Cl
NC
Et
Et
O
Cl
6v
196.35
145.86
145.80
141.09
138.19
136.62
135.18
135.14
132.44
130.82
130.13
129.42
128.95
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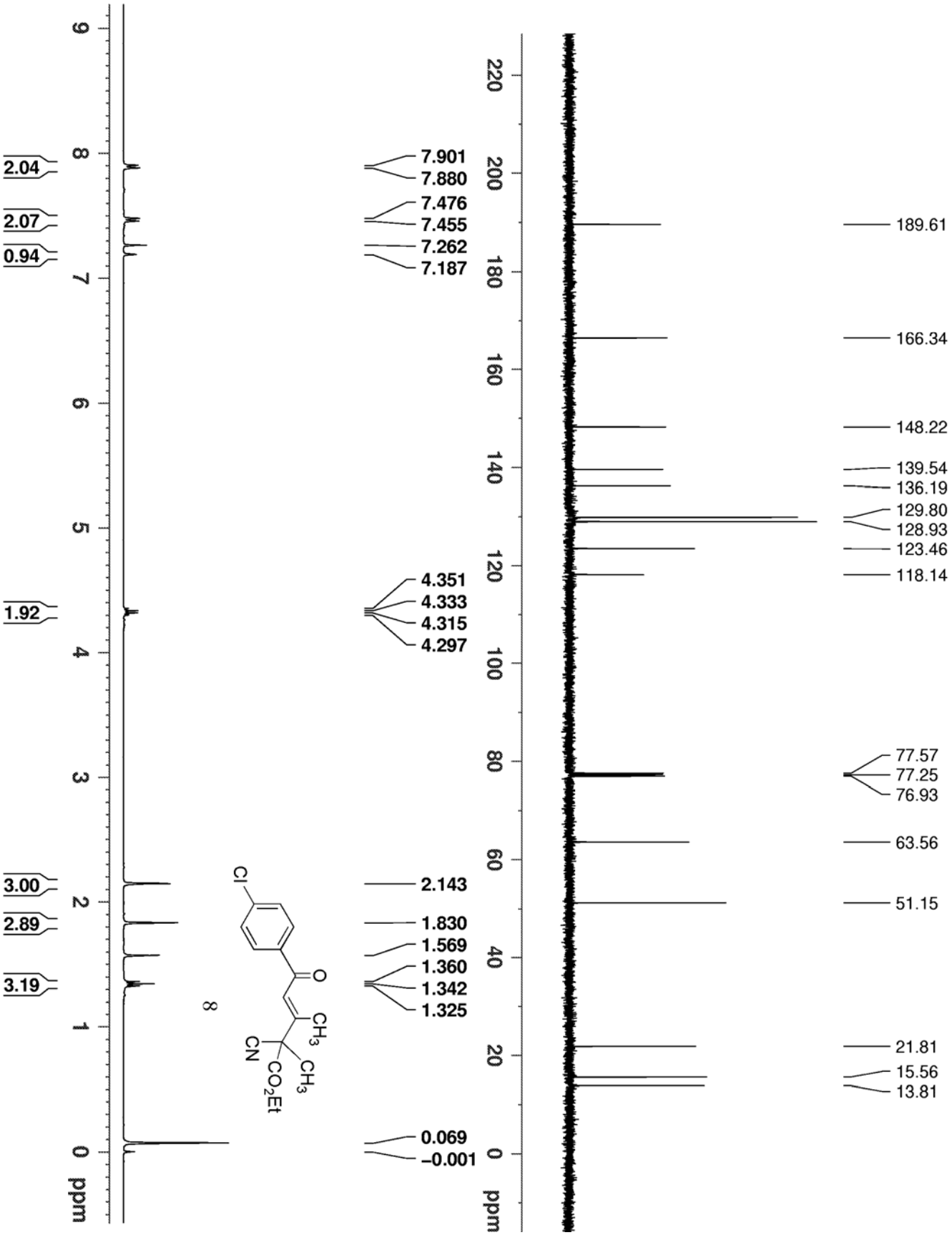
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7.455
7.262
7.187
4.351
4.333
4.315
4.297
2.143
1.830
1.569
1.360
1.342
1.325
0.069
−0.001
189.61
166.34
148.22
139.54
136.19
129.80
128.93
123.46
118.14
77.57
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76.93
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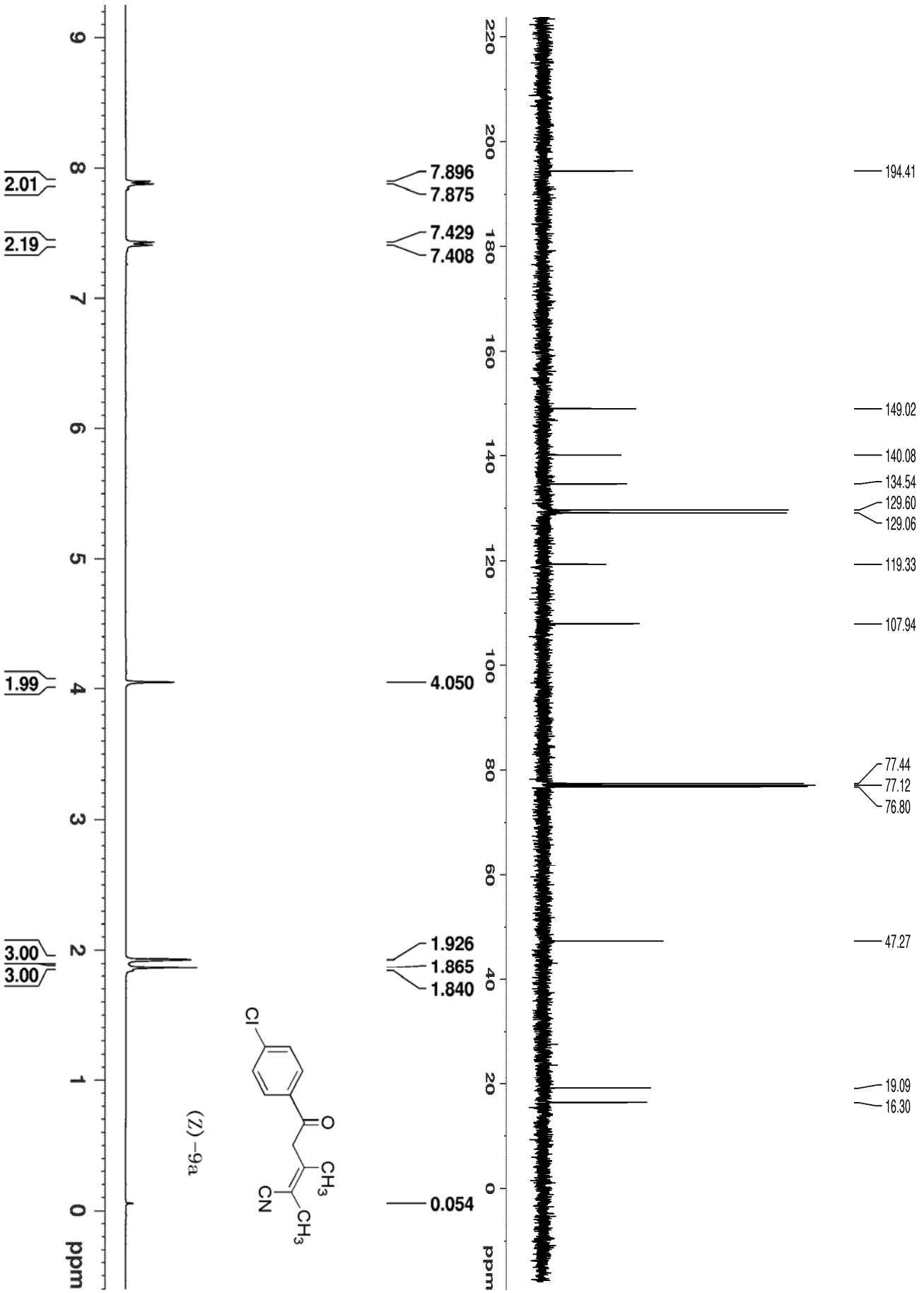
ppm
Cl
O
CH3
CH3
CN
CO2Et
8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2.19
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3.00
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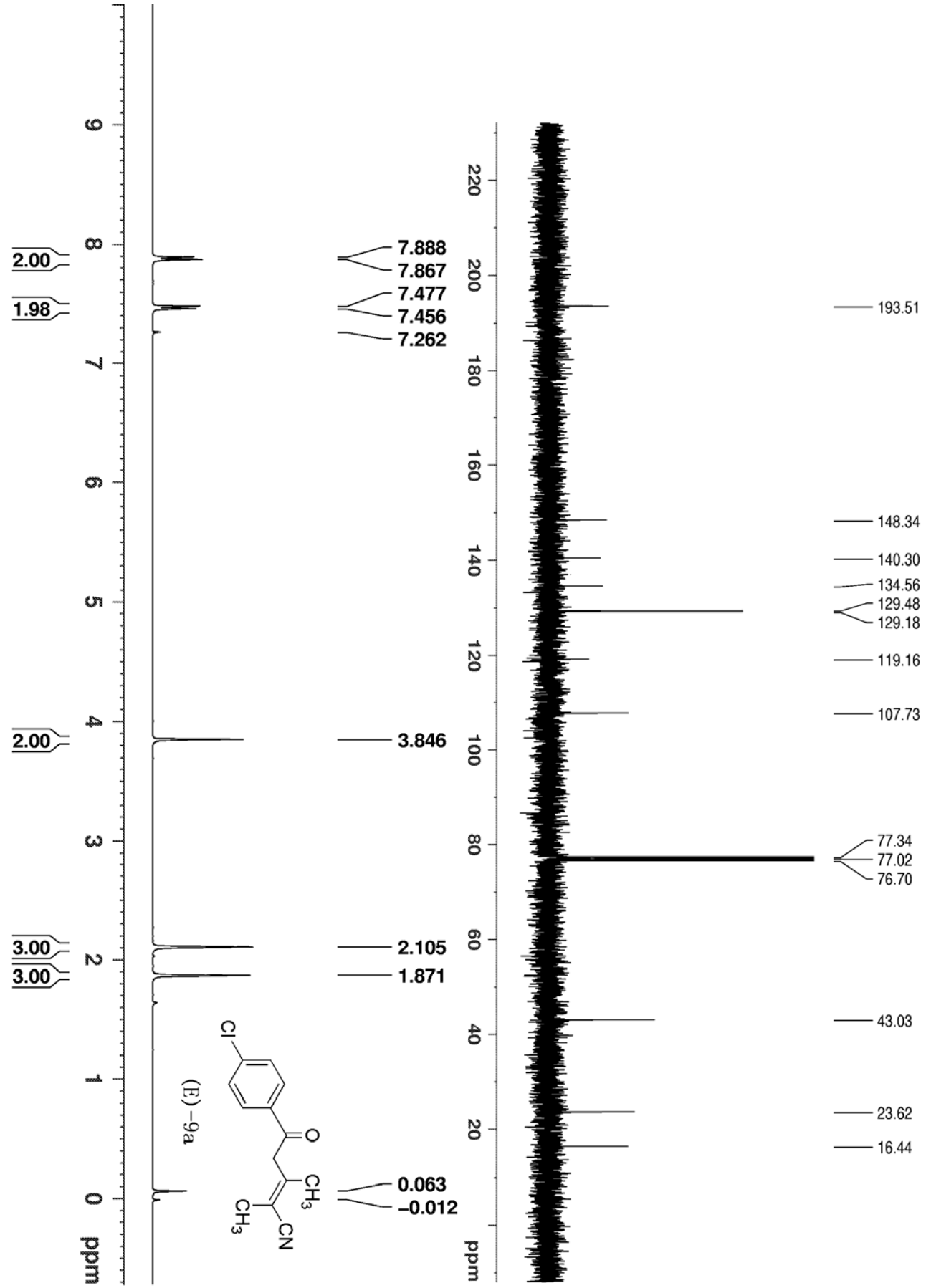
7.429
7.408
4.050
1.926
1.865
1.840
0.054
194.41
149.02
140.08
134.54
129.60
129.06
119.33
107.94
77.44
77.12
76.80
47.27
19.09
16.30
ppm
ppm
Cl
O
CH3
CN
CH3
(Z)−9a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2.00
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7.867
7.477
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3.846
2.105
1.871
0.063
−0.012
193.51
148.34
140.30
134.56
129.48
129.18
119.16
107.73
77.34
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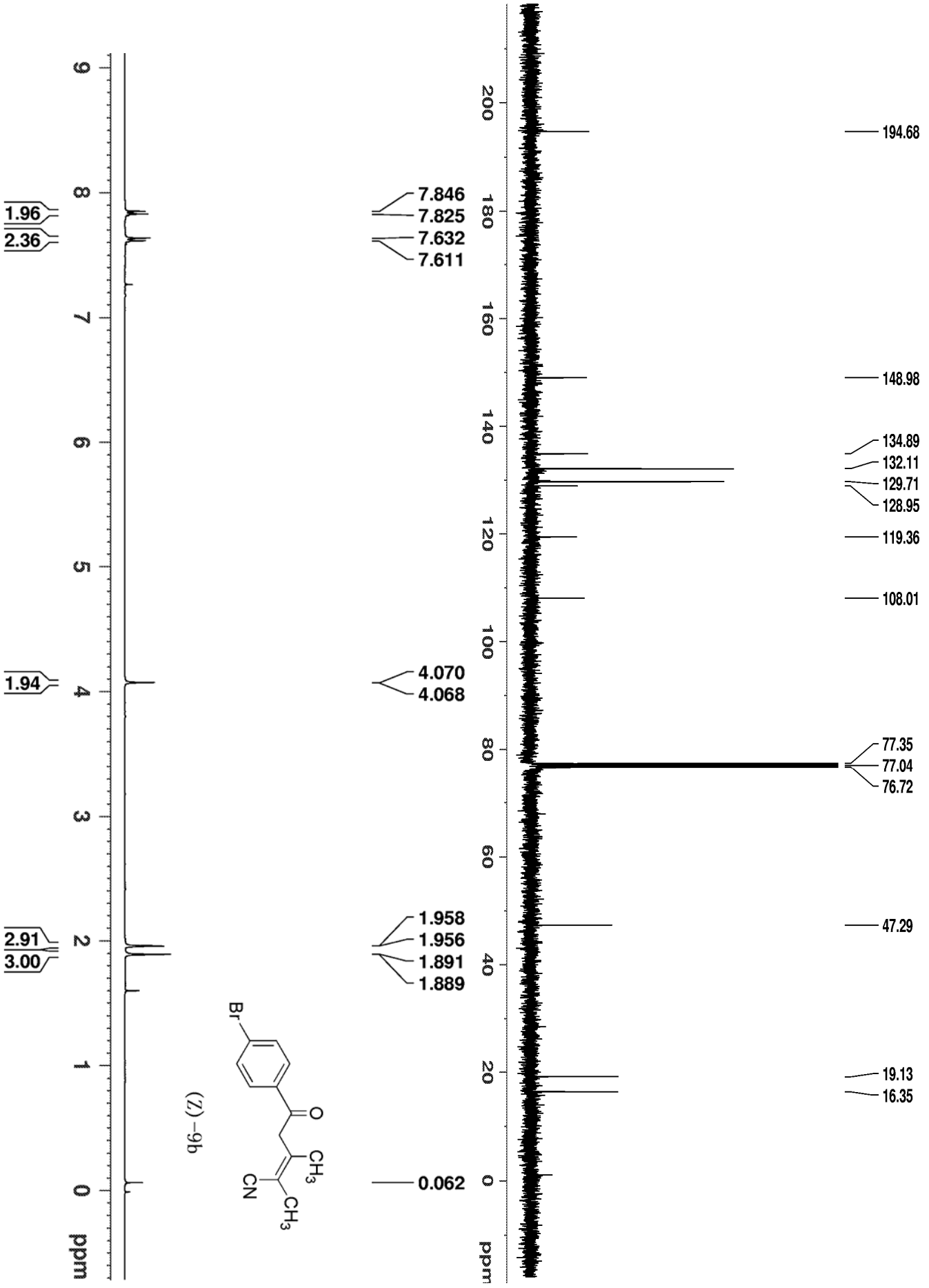
76.70
43.03
23.62
16.44
ppm
ppm
(E)−9a
Cl
O
CH3
CH3
CN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7.825
7.632
7.611
4.070
4.068
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1.956
1.891
1.889
0.062
194.68
148.98
134.89
132.11
129.71
128.95
119.36
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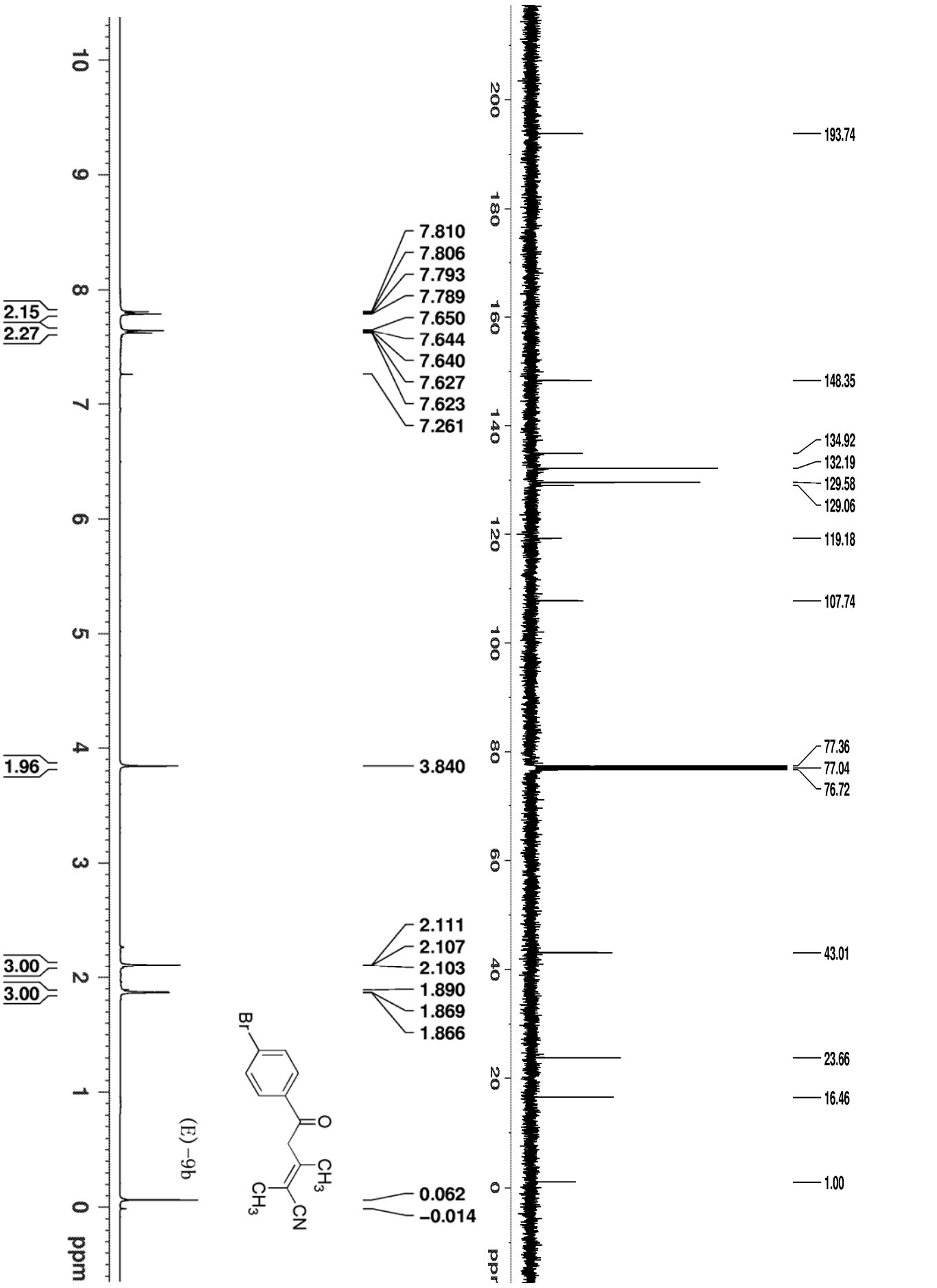
77.04
76.72
47.29
19.13
16.35
ppm
Br
O
CH3
CN
CH3
(Z)-9b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3.00
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7.806
7.793
7.789
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7.644
7.640
7.627
7.623
7.261
3.840
2.111
2.107
2.103
1.890
1.869
1.866
0.062
−0.014
193.74
148.35
134.92
132.19
129.58
129.06
119.18
107.74
77.36
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43.01
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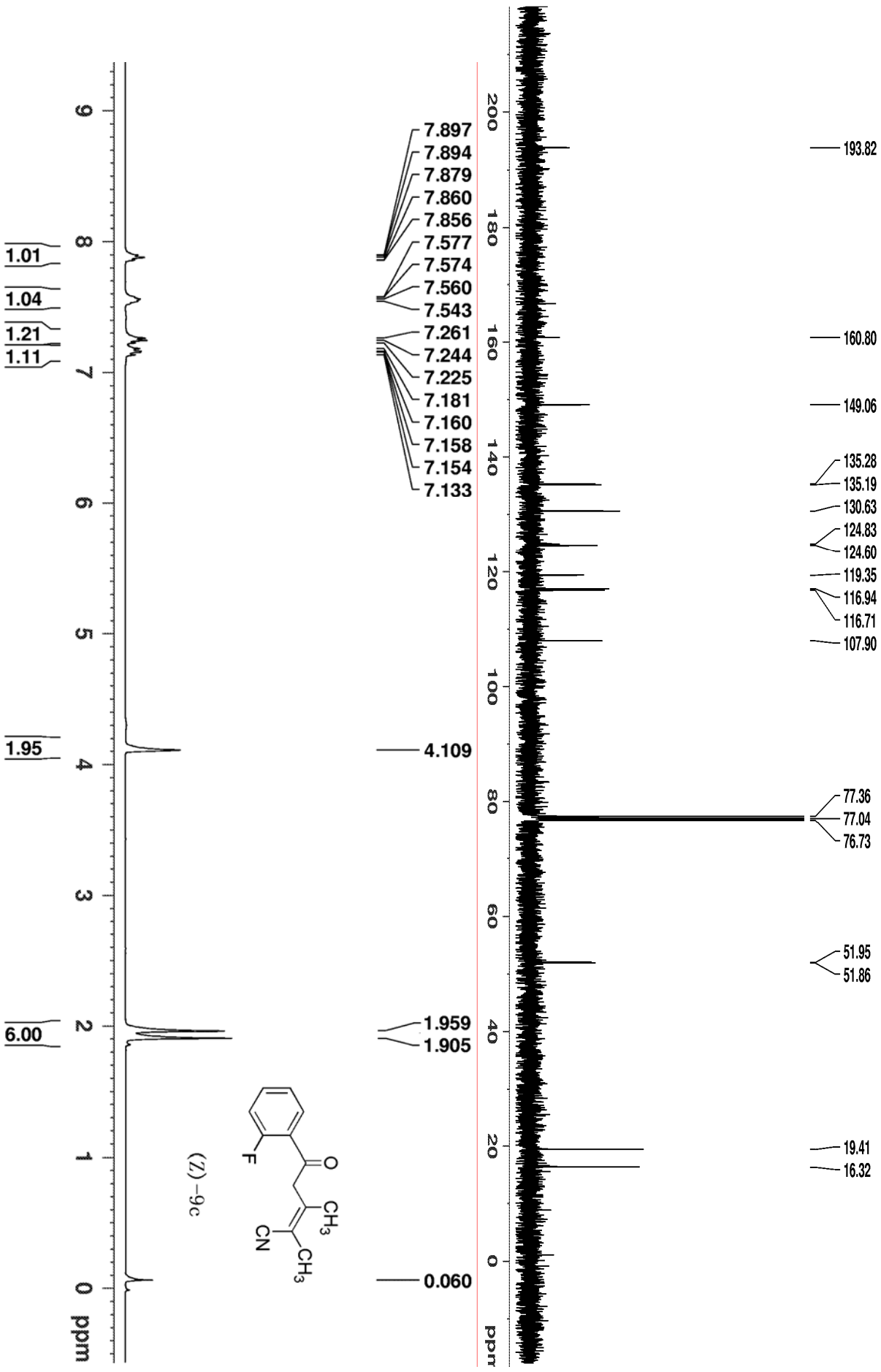
Br
O
CH3
CH3
CN
(E)−9b
ppm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7.560
7.543
7.261
7.244
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7.181
7.160
7.158
7.154
7.133
4.109
1.959
1.905
0.060
1.01
1.04
1.21
1.11
1.95
6.00
ppm
193.82
160.80
149.06
135.28
135.19
130.63
124.83
124.60
119.35
116.94
116.71
107.90
77.36
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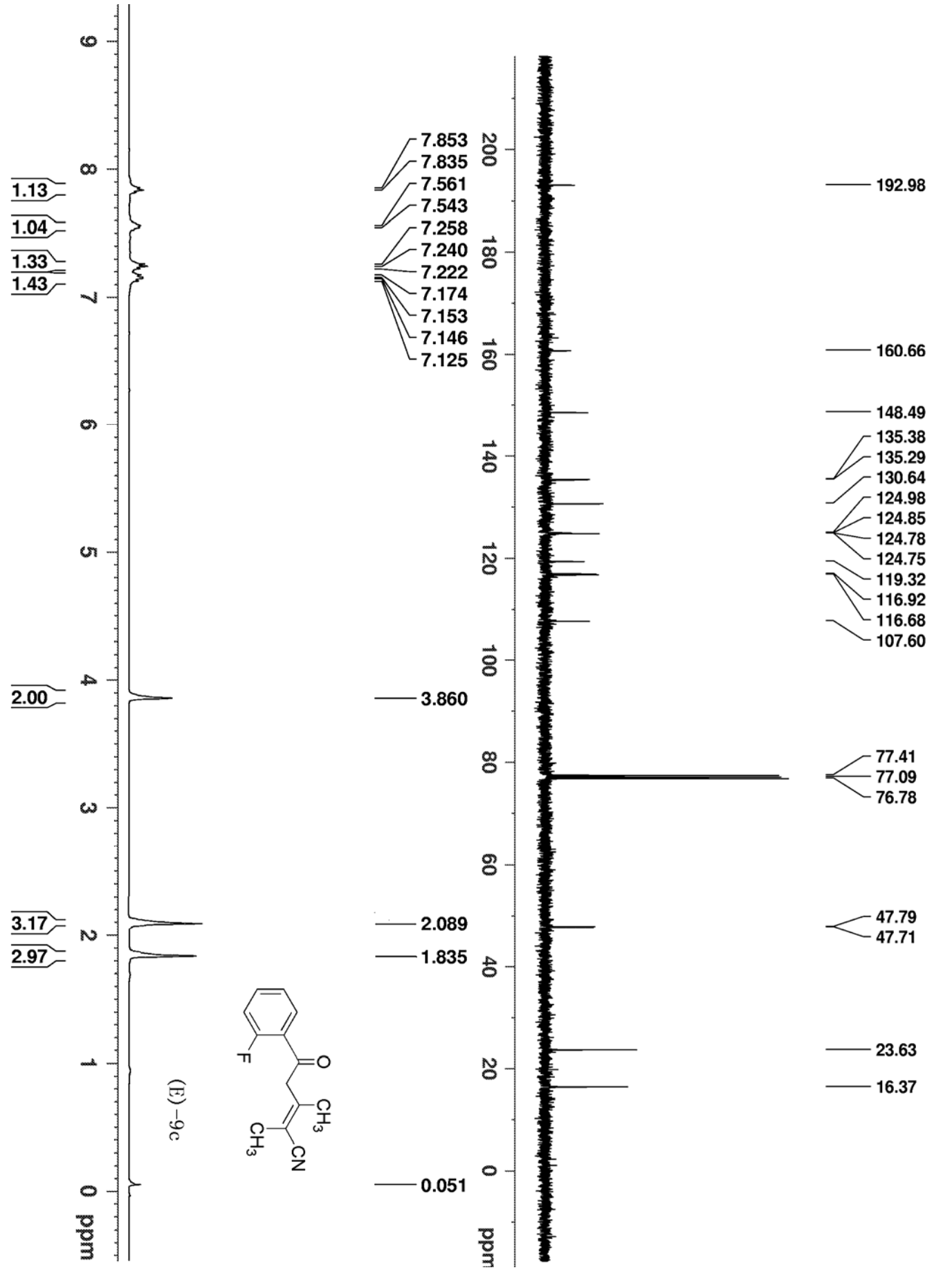
76.73
51.95
51.86
19.41
16.32
F
O
CH3
CN
CH3
(Z)−9c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1.33
1.43
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3.17
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9 8 7 6 5 4 3 2 1 0 ppm
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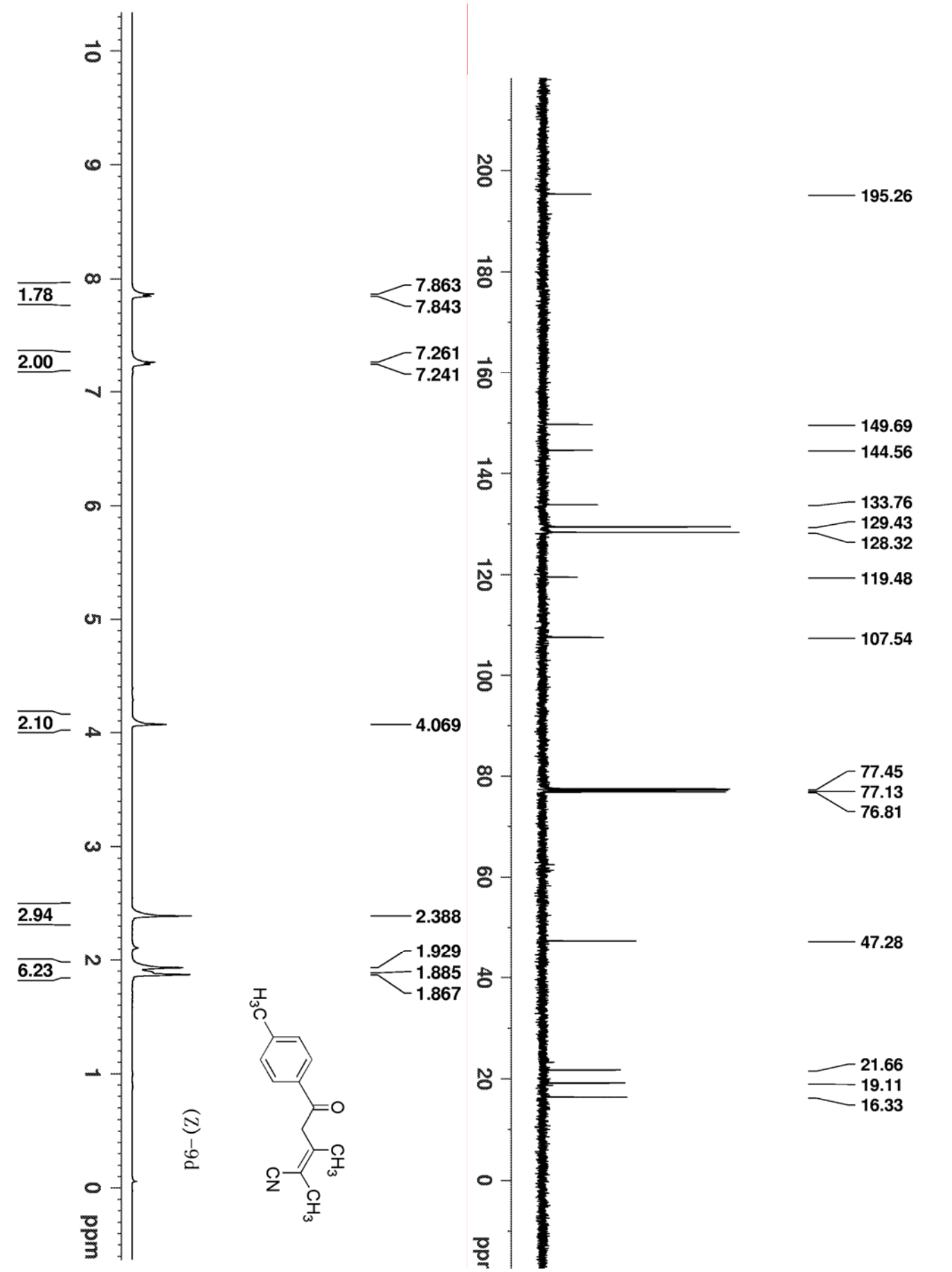
7.561
7.543
7.258
7.240
7.222
7.174
7.153
7.146
7.125
3.860
2.089
1.835
0.051
200 180 160 140 120 100 80 60 40 20 0 ppm
192.98
160.66
148.49
135.38
135.29
130.64
124.98
124.85
124.78
124.75
119.32
116.92
116.68
107.60
77.41
77.09
76.78
47.79
47.71
23.63
16.37
F
O
CH3
CH3
CN
(E)-9c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7.261
7.241
4.069
2.388
1.929
1.885
1.867
195.26
149.69
144.56
133.76
129.43
128.32
119.48
107.54
77.45
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47.28
21.66
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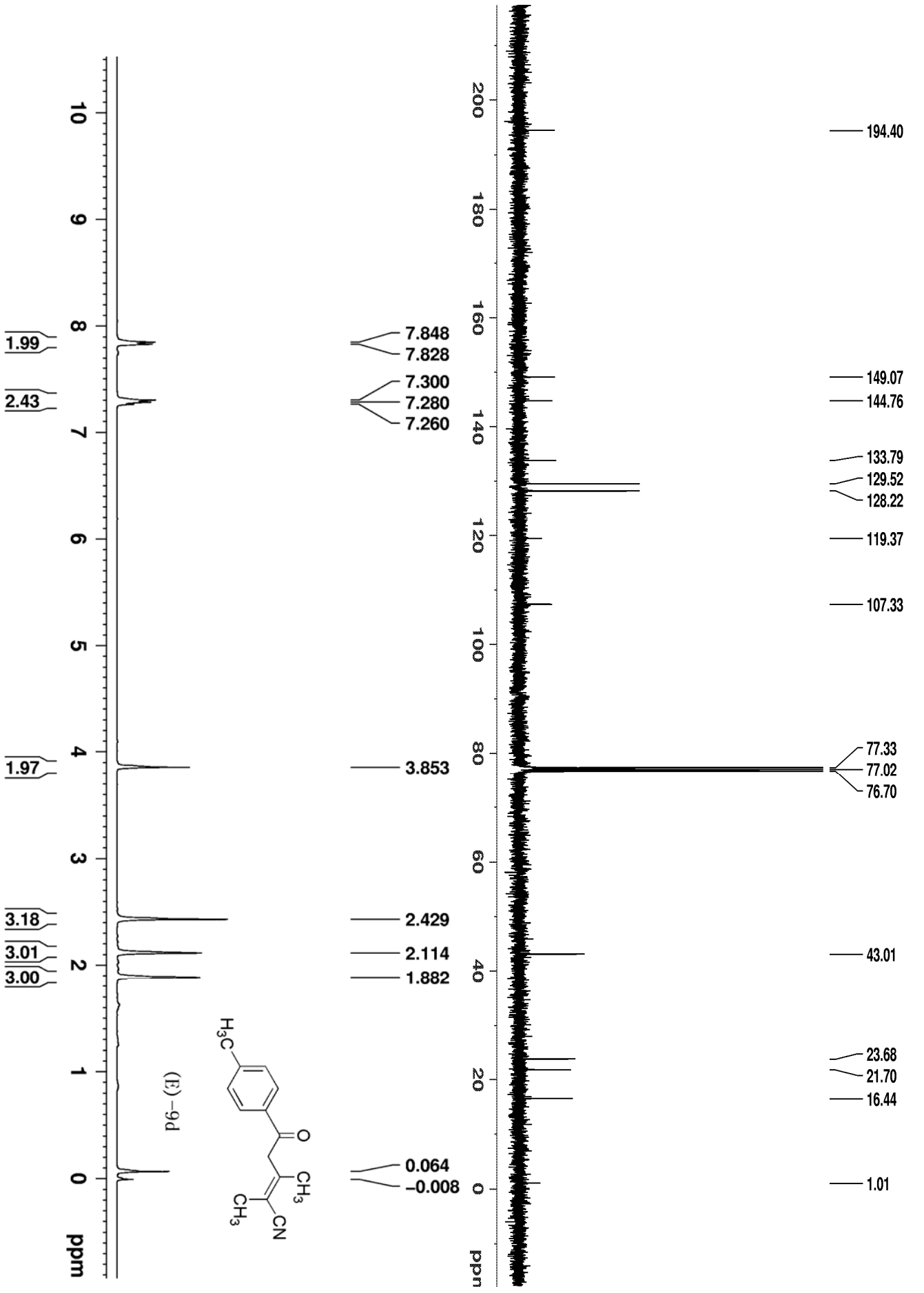
16.33
ppm
(Z)-9d
H3C
O
CH3
CN
CH3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3.01
3.00
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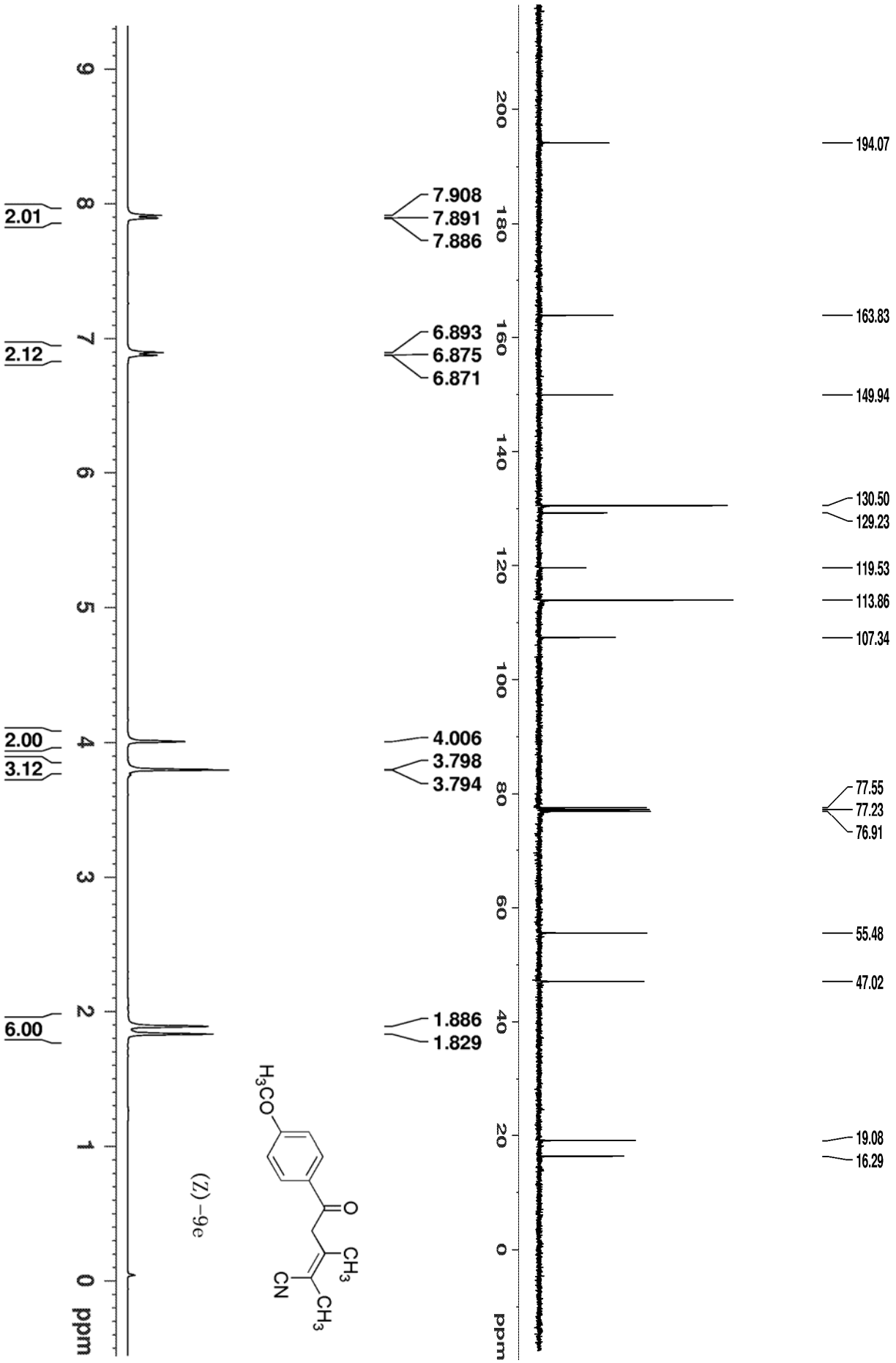
7.828
7.300
7.280
7.260
3.853
2.429
2.114
1.882
0.064
−0.008
194.40
149.07
144.76
133.79
129.52
128.22
119.37
107.33
77.33
77.02
76.70
43.01
23.68
21.70
16.44
1.01
ppm
ppm
p6–9d (E)
H3C
O
CH3
CH3
CN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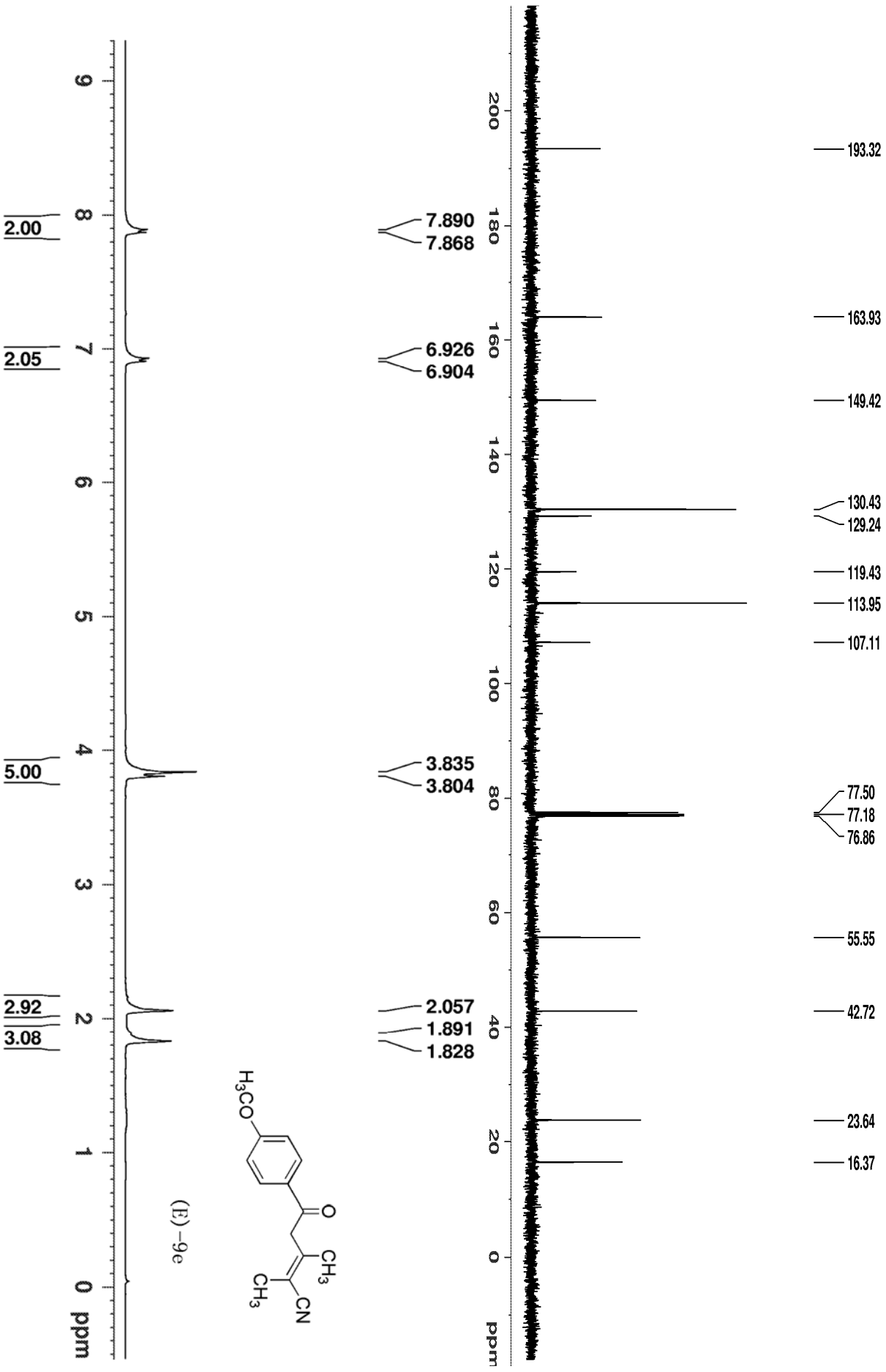
3.12
6.00
7.908
7.891
7.886
6.893
6.875
6.871
4.006
3.798
3.794
1.886
1.829
194.07
163.83
149.94
130.50
129.23
119.53
113.86
107.34
77.55
77.23
76.91
55.48
47.02
19.08
16.29
ppm
(Z)−9e
H3CO
O
CH3
CN
CH3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5.00
2.92
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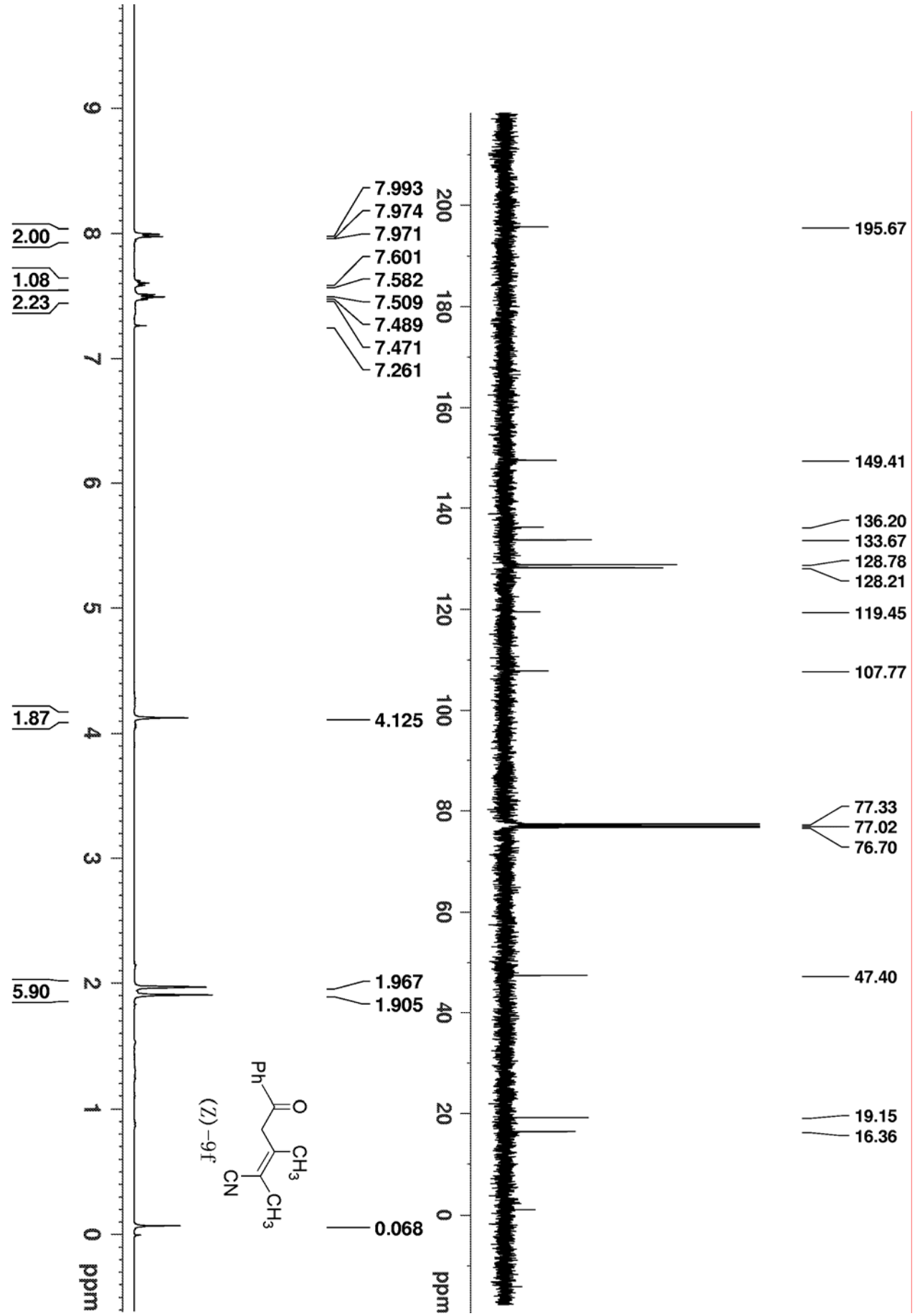
6.926
6.904
3.835
3.804
2.057
1.891
1.828
193.32
163.93
149.42
130.43
129.24
119.43
113.95
107.11
77.50
77.18
76.86
55.55
42.72
23.64
16.37
ppm
H3CO
O
CH3
CH3
CN
(E)−9e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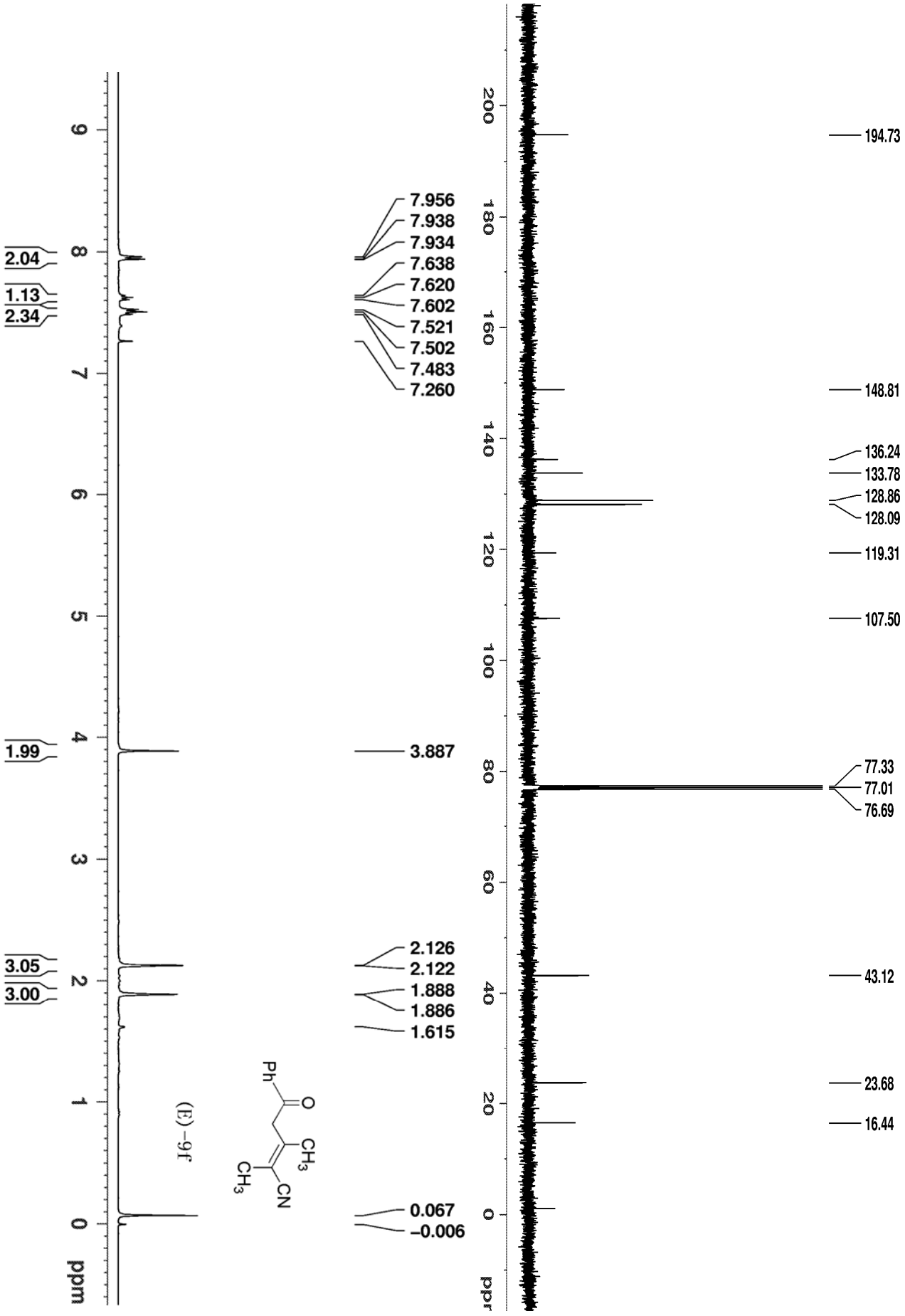
4.125
1.967
1.905
7.993
7.974
7.971
7.601
7.582
7.509
7.489
7.471
7.261
195.67
149.41
136.20
133.67
128.78
128.21
119.45
107.77
77.33
77.02
76.70
47.40
19.15
16.36
ppm
Ph
O
CH3
CN
CH3
(Z)−9f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1.99
3.05
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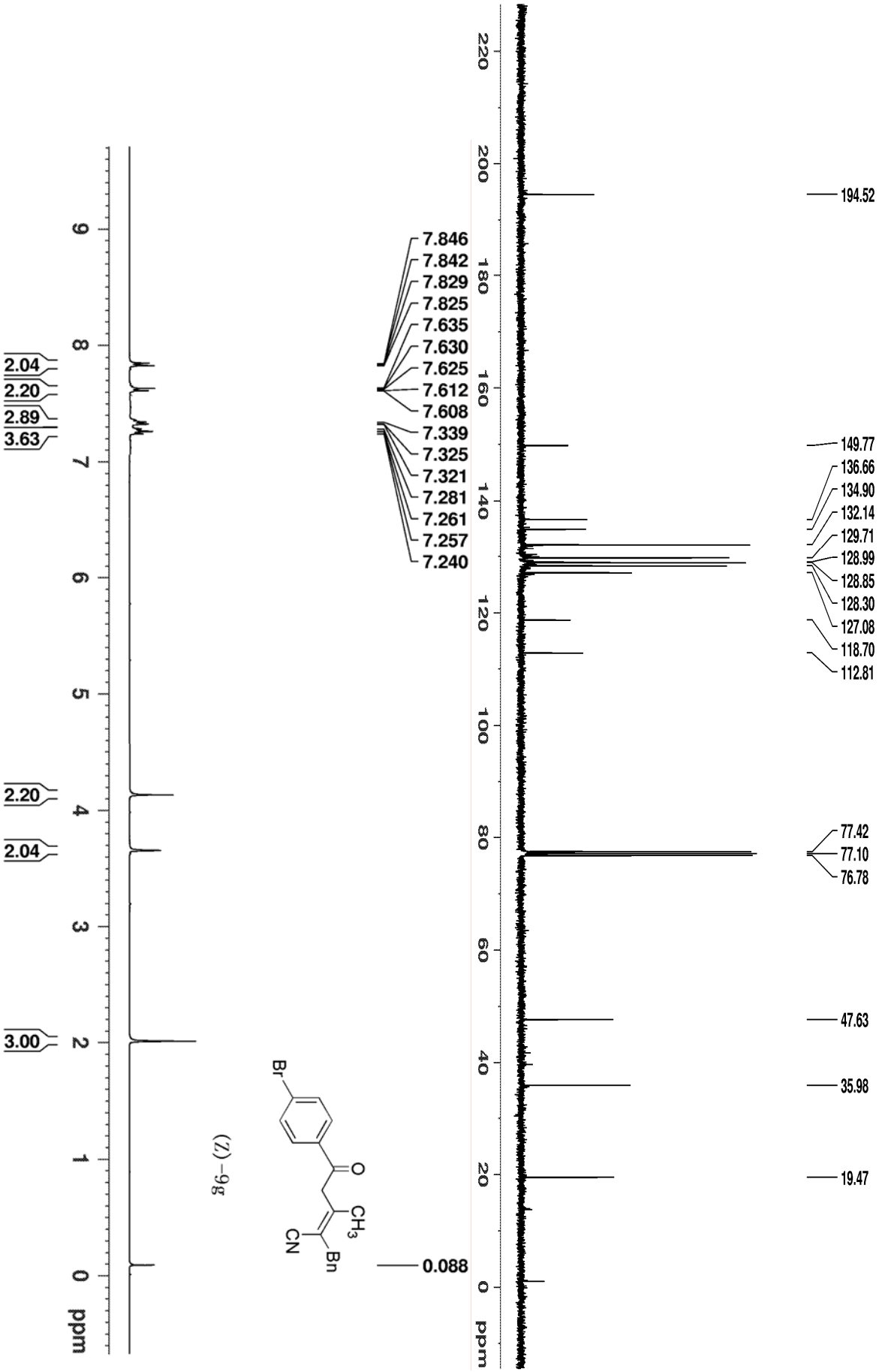
7.934
7.638
7.620
7.602
7.521
7.502
7.483
7.260
3.887
2.126
2.122
1.888
1.886
1.615
0.067
−0.006
194.73
148.81
136.24
133.78
128.86
128.09
119.31
107.50
77.33
77.01
76.69
43.12
23.68
16.44
ppm
(E)−9f
Ph
O
CH3
CH3
CN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2.20
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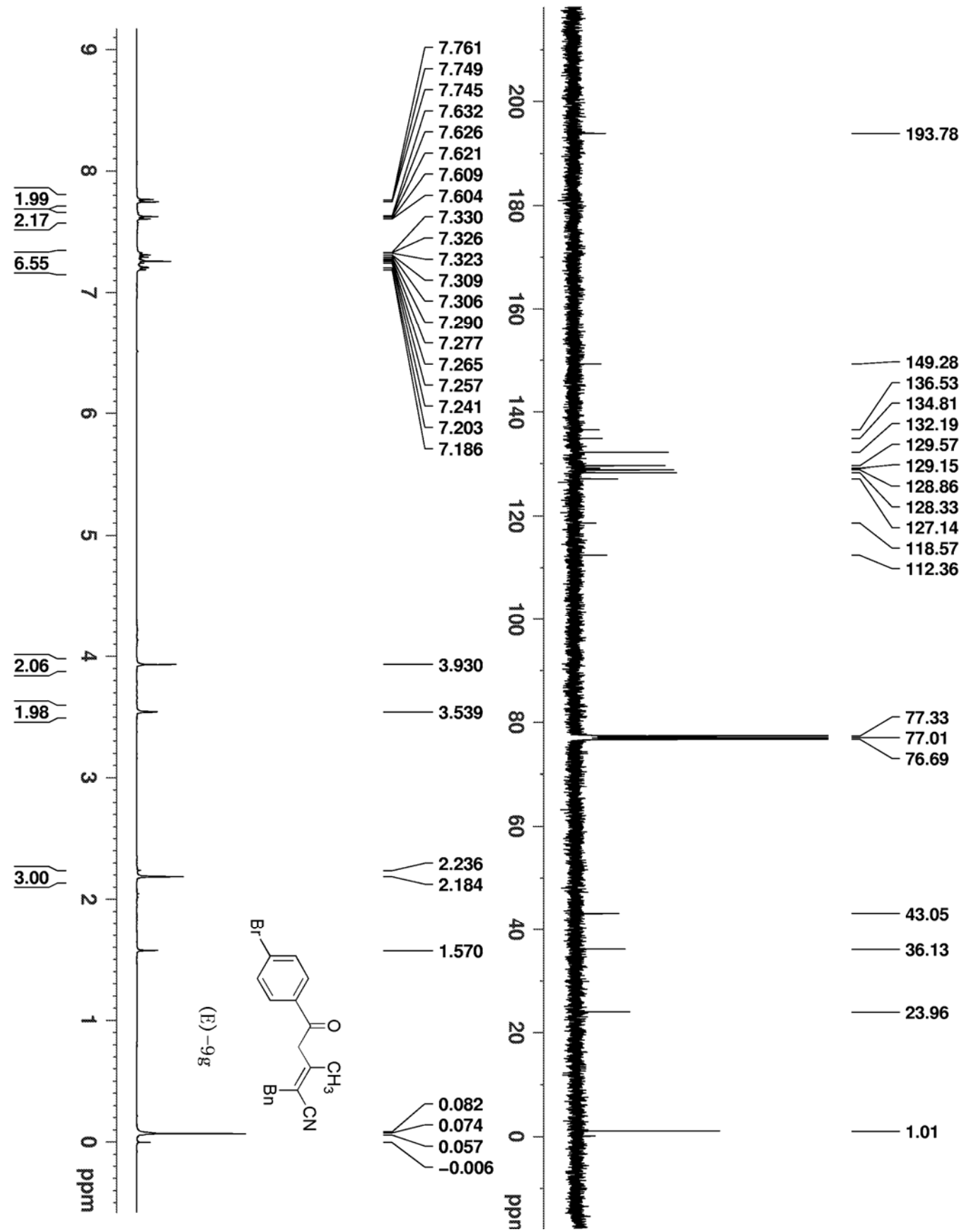
3.63
2.20
2.04
3.00
ppm
7.846
7.842
7.829
7.825
7.635
7.630
7.625
7.612
7.608
7.339
7.325
7.321
7.281
7.261
7.257
7.240
0.088
194.52
149.77
136.66
134.90
132.14
129.71
128.99
128.85
128.30
127.08
118.70
112.81
77.42
77.10
76.78
47.63
35.98
19.47
ppm
Br
O
CH3
CN
Bn
(Z)-9g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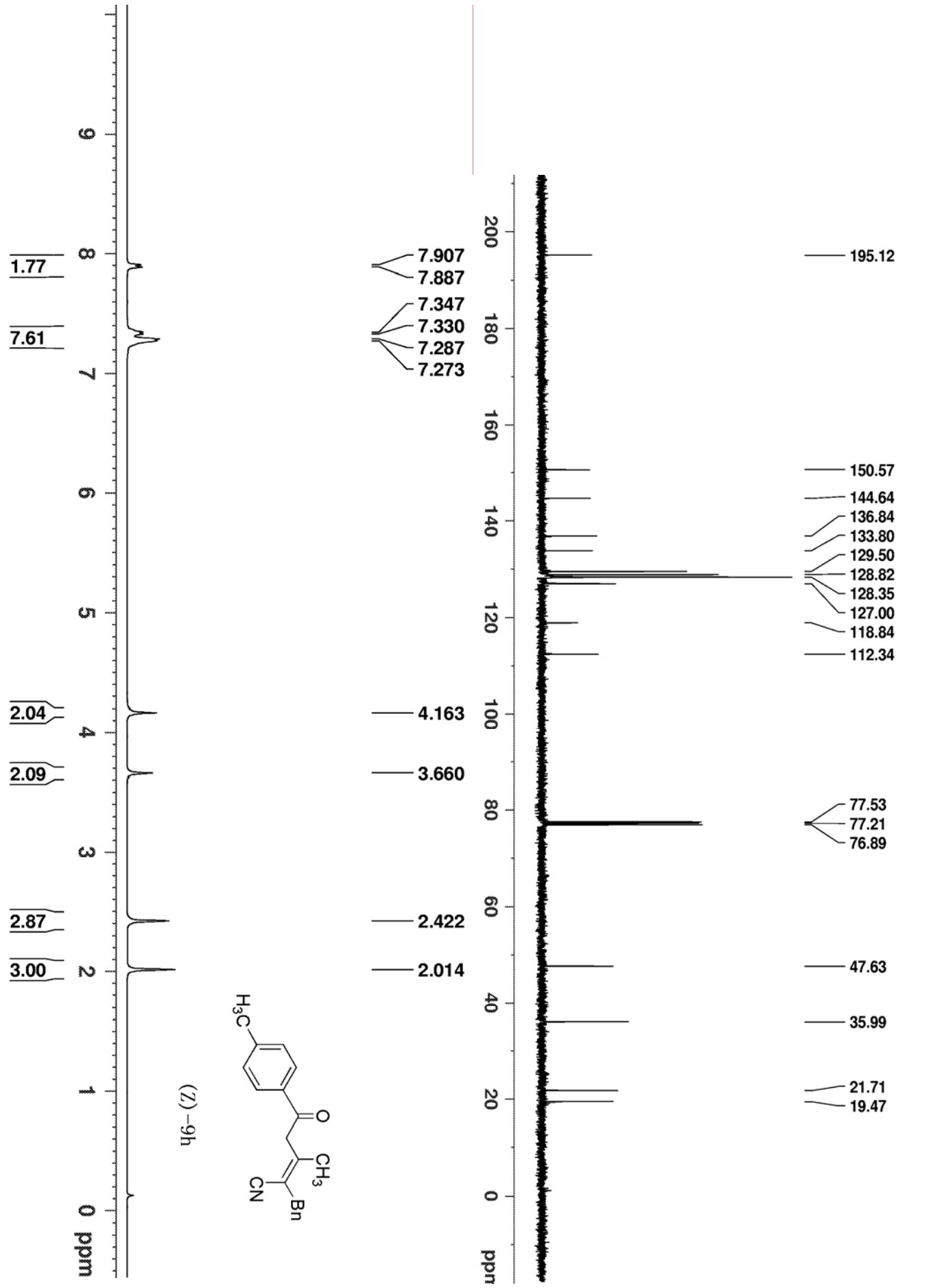
1.98
3.00
7.761
7.749
7.745
7.632
7.626
7.621
7.609
7.604
7.330
7.326
7.323
7.309
7.306
7.290
7.277
7.265
7.257
7.241
7.203
7.186
3.930
3.539
2.236
2.184
1.570
0.082
0.074
0.057
−0.006
193.78
149.28
136.53
134.81
132.19
129.57
129.15
128.86
128.33
127.14
118.57
112.36
77.33
77.01
76.69
43.05
36.13
23.96
1.01
ppm
(E)−9g
Br
O
CH3
Bn
CN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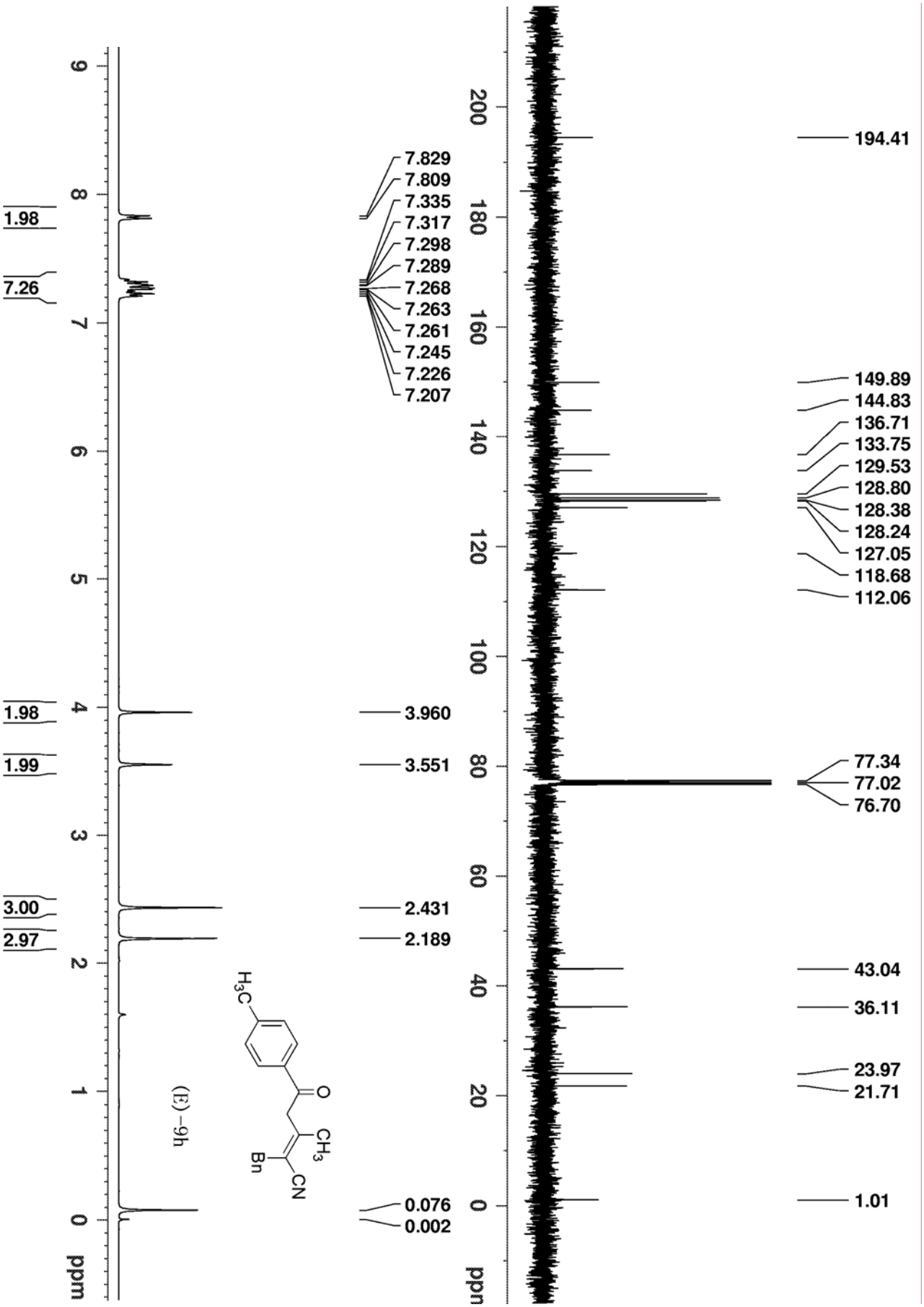
7.61
2.04
2.09
2.87
3.00
7.907
7.887
7.347
7.330
7.287
7.273
4.163
3.660
2.422
2.014
195.12
150.57
144.64
136.84
133.80
129.50
128.82
128.35
127.00
118.84
112.34
77.53
77.21
76.89
47.63
35.99
21.71
19.47
ppm
H3C
O
CH3
CN
Bn

(*Z*)−9h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7.26
1.98
1.99
3.00
2.97
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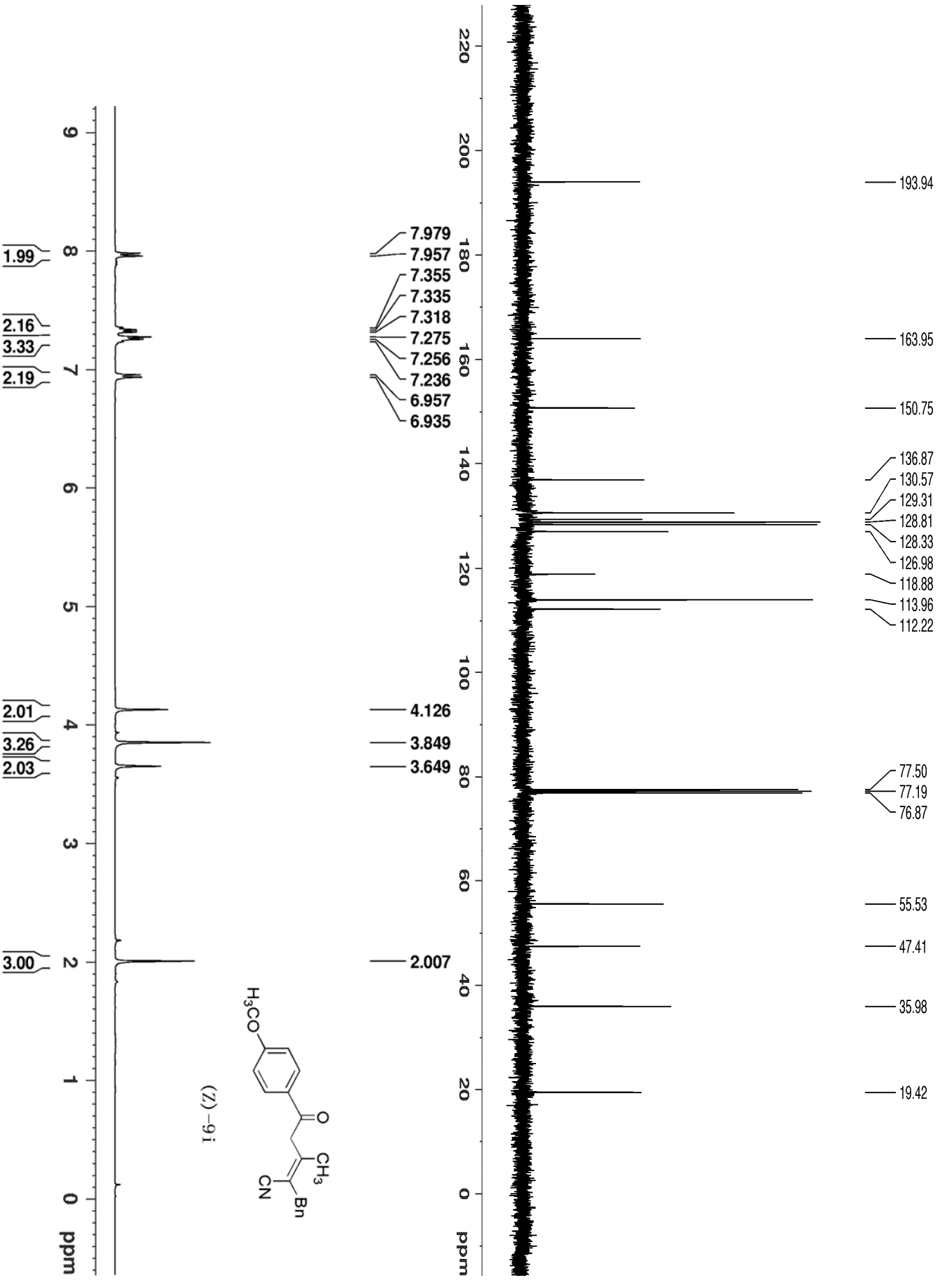
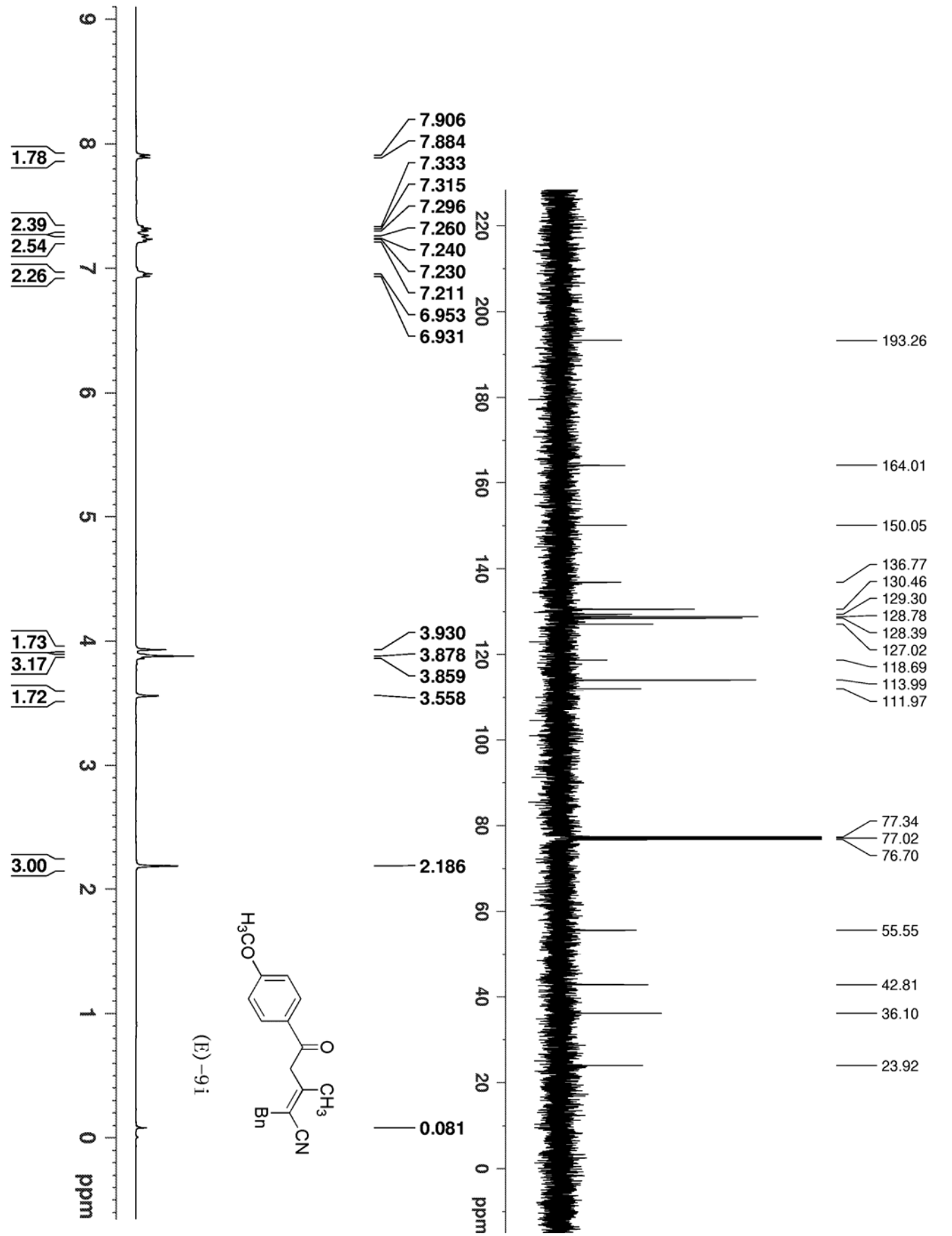
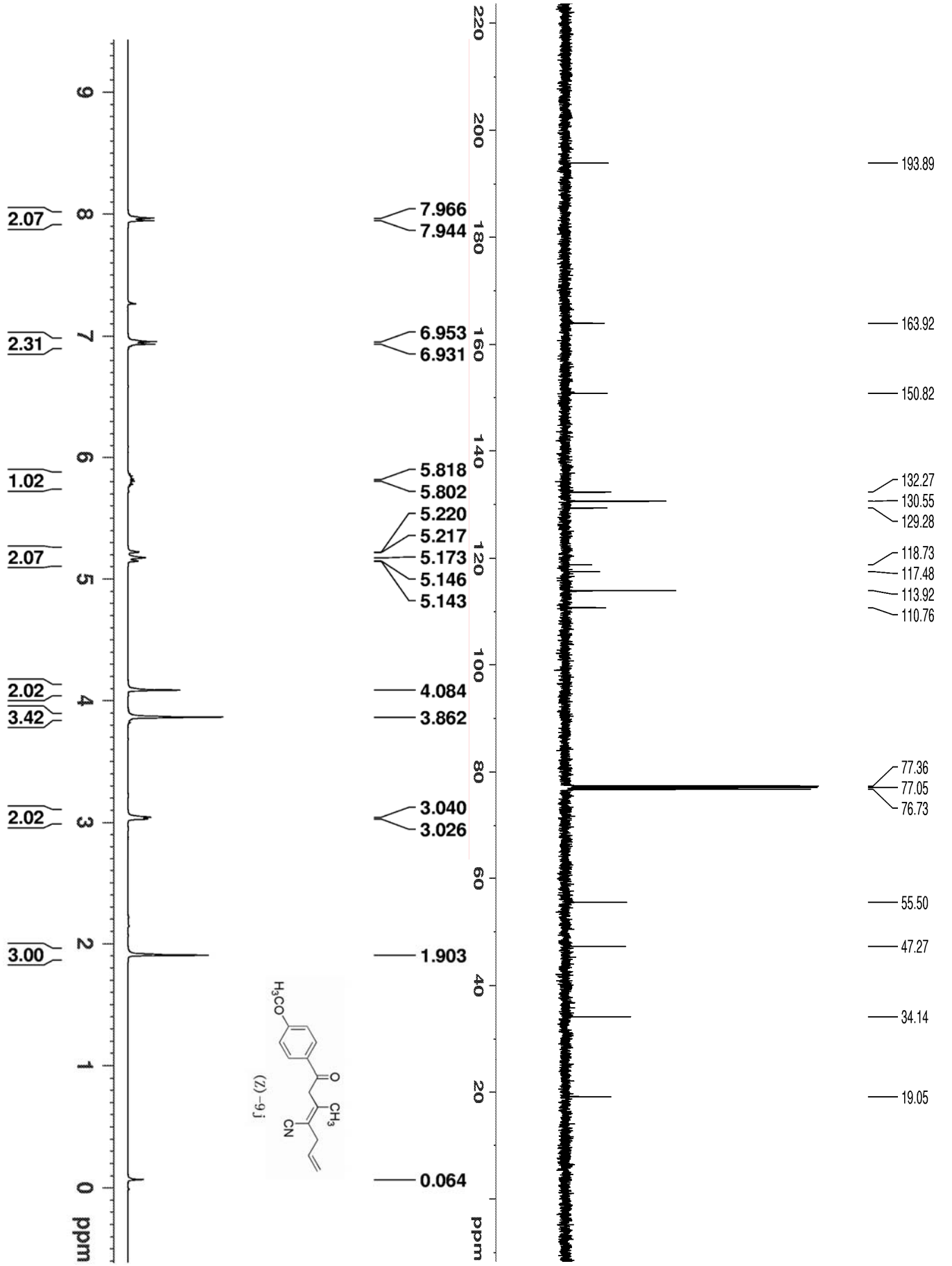
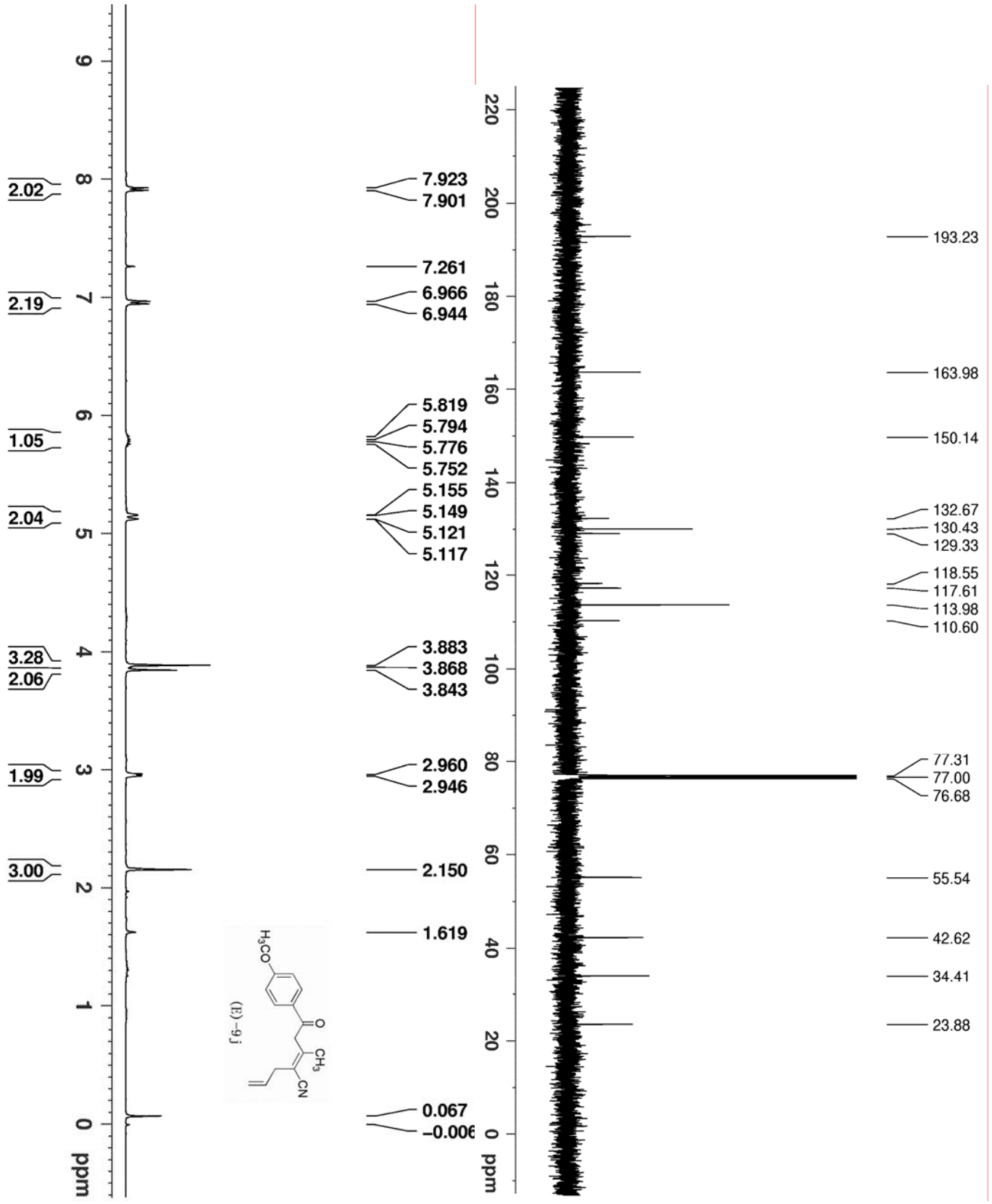
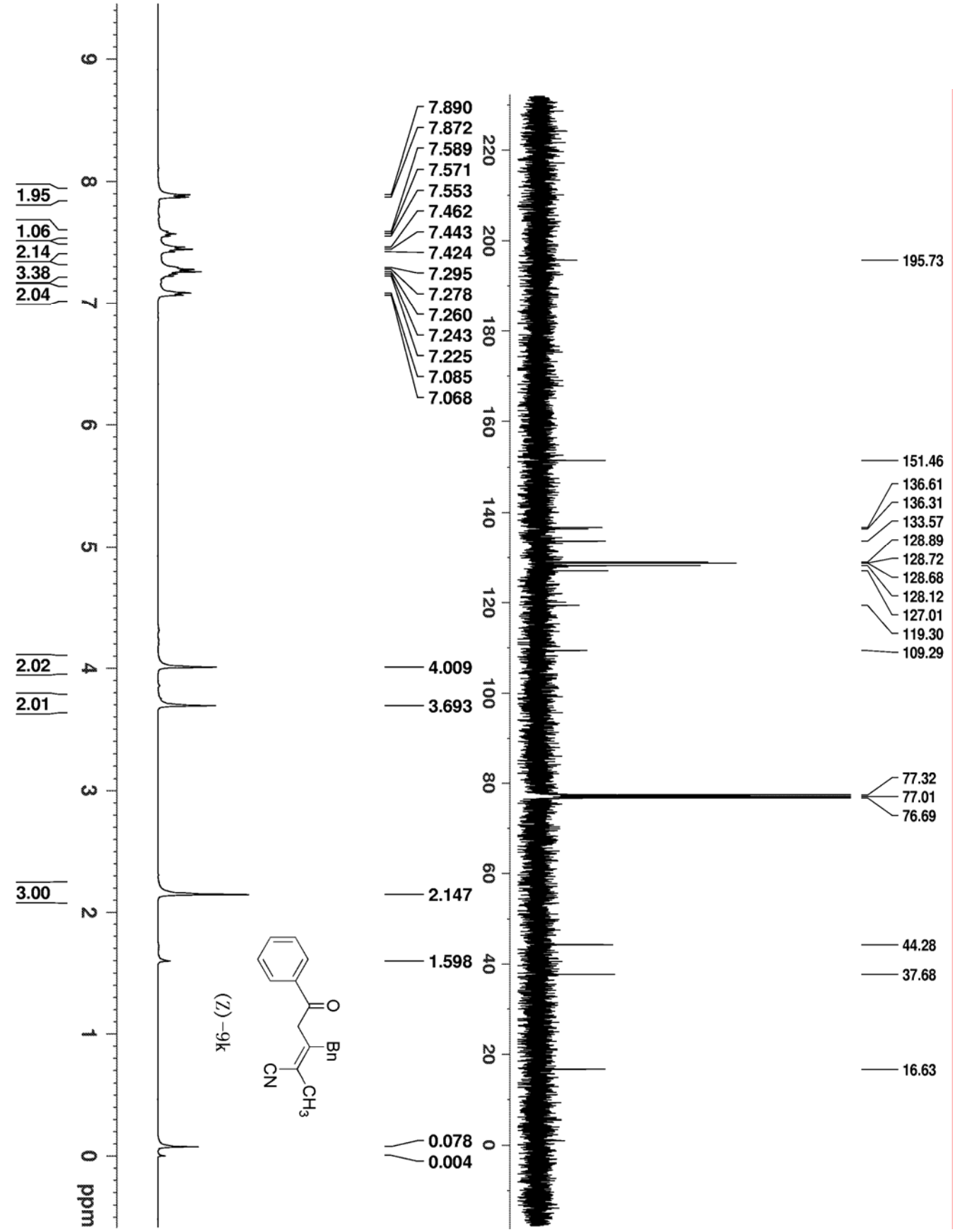
7.809
7.335
7.317
7.298
7.289
7.268
7.263
7.261
7.245
7.226
7.207
3.960
3.551
2.431
2.189
0.076
0.002
194.41
149.89
144.83
136.71
133.75
129.53
128.80
128.38
128.24
127.05
118.68
112.06
77.34
77.02
76.70
43.04
36.11
23.97
21.71
1.01
ppm
(E)−9h
H3C
O
CH3
Bn
CN


1.99
2.16
3.33
2.19
2.01
3.26
2.03
3.00
9 8 7 6 5 4 3 2 1 0 ppm
7.979
7.957
7.355
7.335
7.318
7.275
7.256
7.236
6.957
6.935
4.126
3.849
3.649
2.007
220 200 180 160 140 120 100 80 60 40 20 0 ppm
193.94
163.95
150.75
136.87
130.57
129.31
128.81
128.33
126.98
118.88
113.96
112.22
77.50
77.19
76.87
55.53
47.41
35.98
19.42
H3CO
O
CH3
CN
Bn
(Z)−9i


1.78
2.39
2.54
2.26
1.73
3.17
1.72
3.00
7.906
7.884
7.333
7.315
7.296
7.260
7.240
7.230
7.211
6.953
6.931
3.930
3.878
3.859
3.558
2.186
0.081
193.26
164.01
150.05
136.77
130.46
129.30
128.78
128.39
127.02
118.69
113.99
111.97
77.34
77.02
76.70
55.55
42.81
36.10
23.92
H3CO
O
CH3
Bn
CN
(E)−9i
ppm


2.07
2.31
1.02
2.07
2.02
3.42
2.02
3.00
7.966
7.944
6.953
6.931
5.818
5.802
5.220
5.217
5.173
5.146
5.143
4.084
3.862
3.040
3.026
1.903
0.064
ppm
193.89
163.92
150.82
132.27
130.55
129.28
118.73
117.48
113.92
110.76
77.36
77.05
76.73
55.50
47.27
34.14
19.05
H3CO
O
CH3
CN
(Z)-9j


2.02
2.19
1.05
2.04
3.28
2.06
1.99
3.00
9
8
7
6
5
4
3
2
1
0 ppm
7.923
7.901
7.261
6.966
6.944
5.819
5.794
5.776
5.752
5.155
5.149
5.121
5.117
3.883
3.868
3.843
2.960
2.946
2.150
1.619
0.067
−0.006
H3CO
O
CH3
CN
(E)−9j
220
200
180
160
140
120
100
80
60
40
20
0 ppm
193.23
163.98
150.14
132.67
130.43
129.33
118.55
117.61
113.98
110.60
77.31
77.00
76.68
55.54
42.62
34.41
23.88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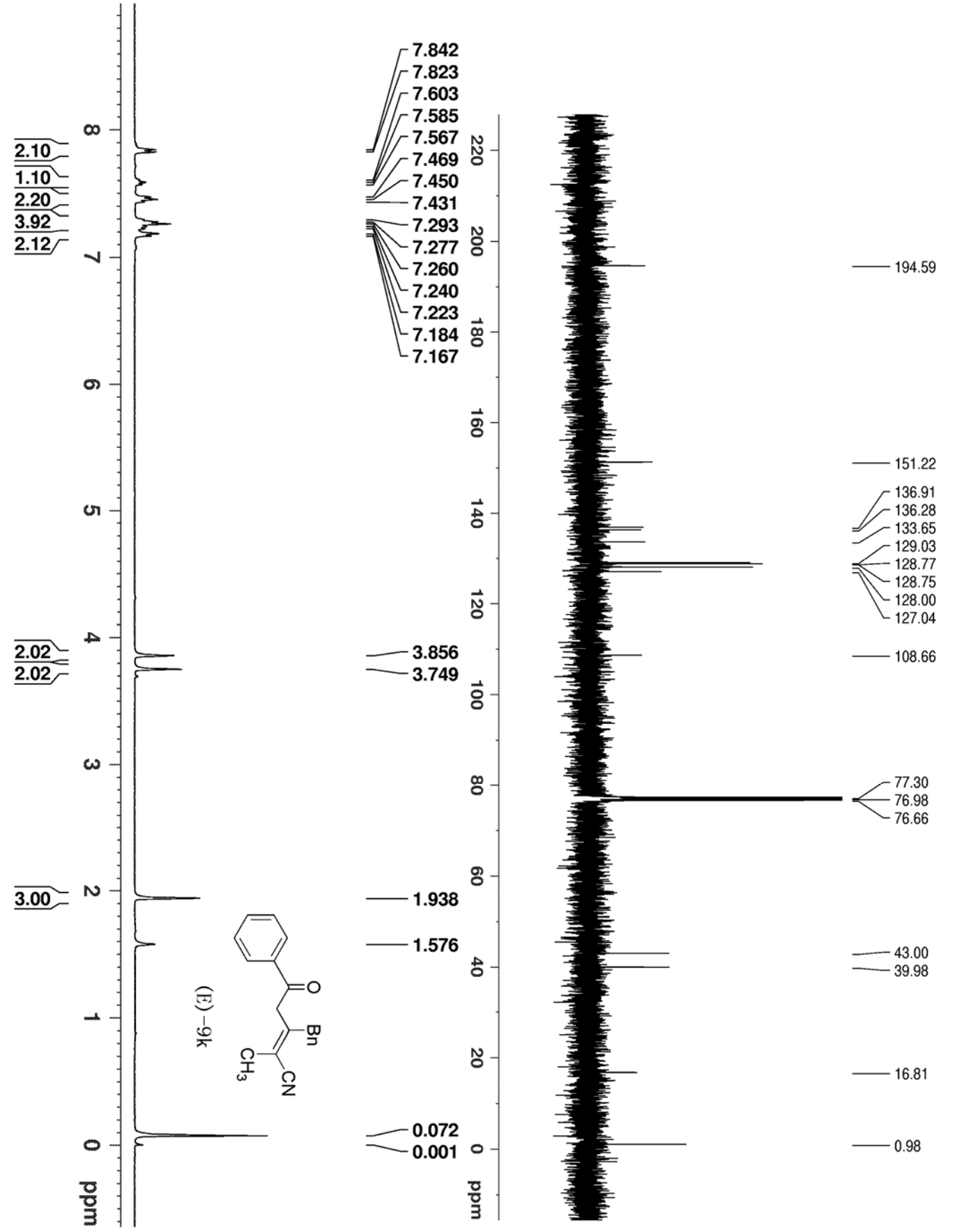
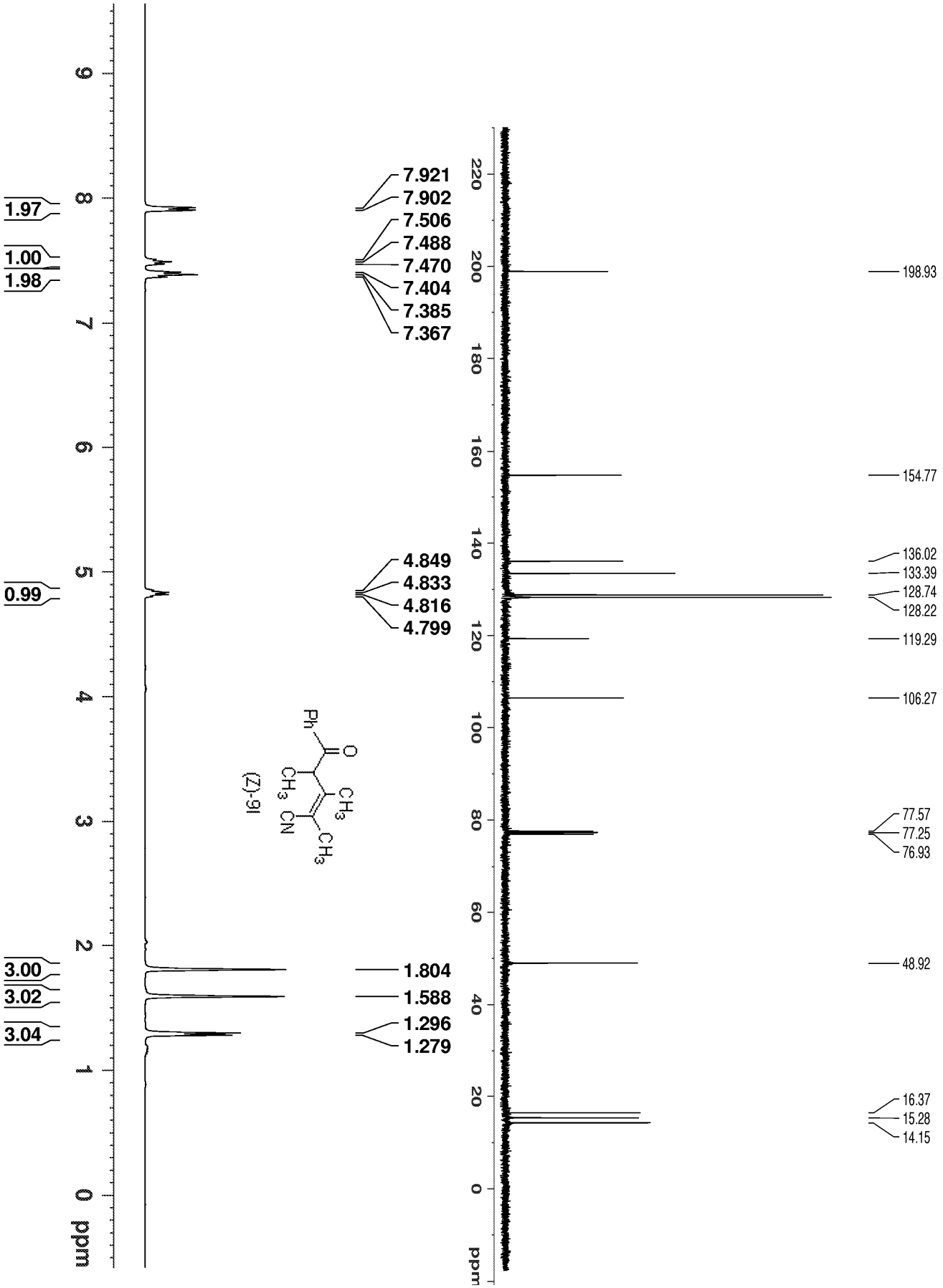
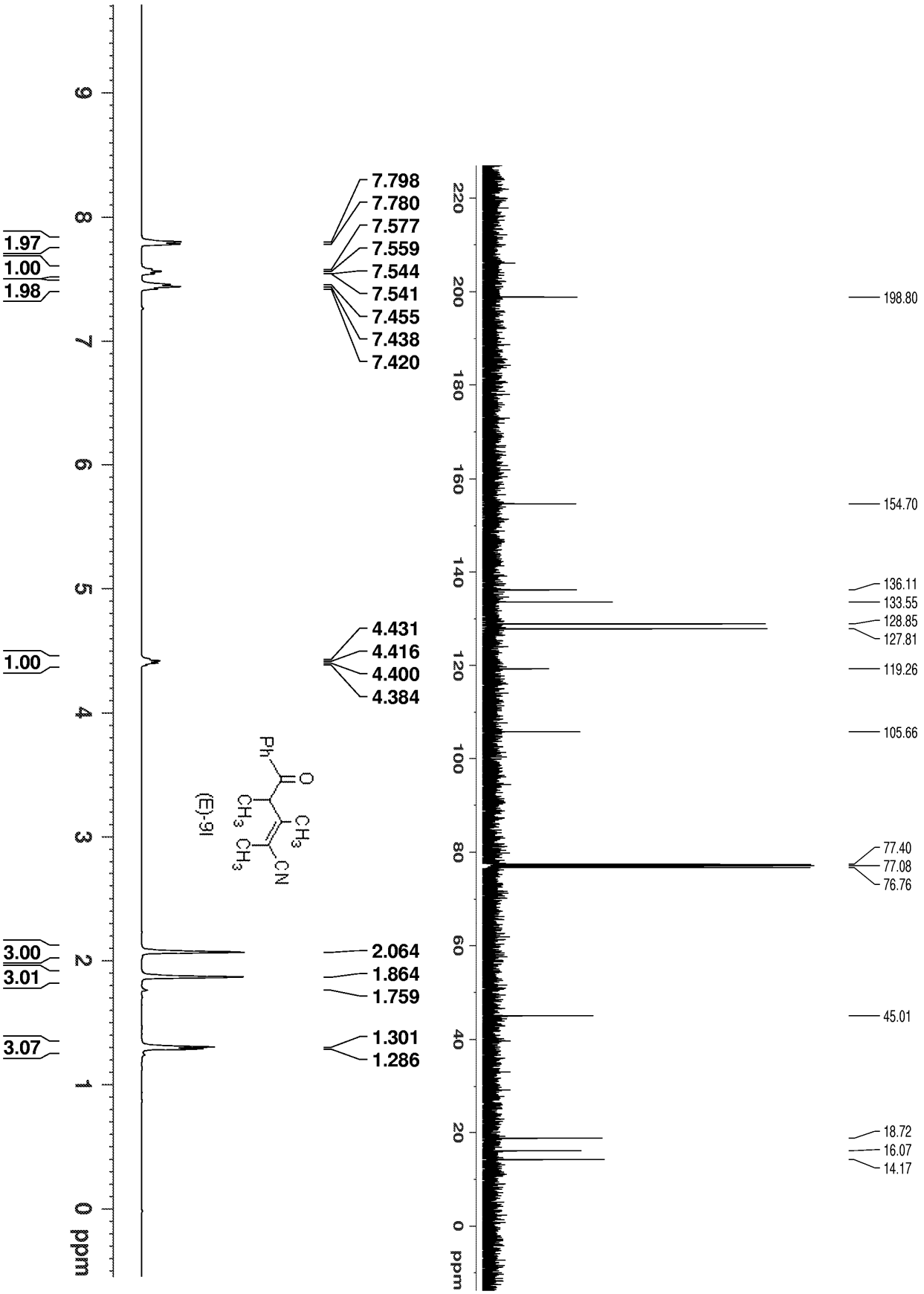
7.872
7.589
7.571
7.553
7.462
7.443
7.424
7.295
7.278
7.260
7.243
7.225
7.085
7.068
4.009
3.693
2.147
1.598
0.078
0.004
195.73
151.46
136.61
136.31
133.57
128.89
128.72
128.68
128.12
127.01
119.30
109.29
77.32
77.01
76.69
44.28
37.68
16.63
1.95
1.06
2.14
3.38
2.04
2.02
2.01
3.00
ppm
(Z)−9k
O
Bn
CN
CH3


2.10
1.10
2.20
3.92
2.12
2.02
2.02
3.00
7.842
7.823
7.603
7.585
7.567
7.469
7.450
7.431
7.293
7.277
7.260
7.240
7.223
7.184
7.167
3.856
3.749
1.938
1.576
0.072
0.001
194.59
151.22
136.91
136.28
133.65
129.03
128.77
128.75
128.00
127.04
108.66
77.30
76.98
76.66
43.00
39.98
16.81
0.98
O
Bn
CN
CH3
(E)−9k
ppm


1.97
1.00
1.98
0.99
3.00
3.02
3.04
7.921
7.902
7.506
7.488
7.470
7.404
7.385
7.367
4.849
4.833
4.816
4.799
1.804
1.588
1.296
1.279
(Z)-9l
198.93
154.77
136.02
133.39
128.74
128.22
119.29
106.27
77.57
77.25
76.93
48.92
16.37
15.28
14.15
ppm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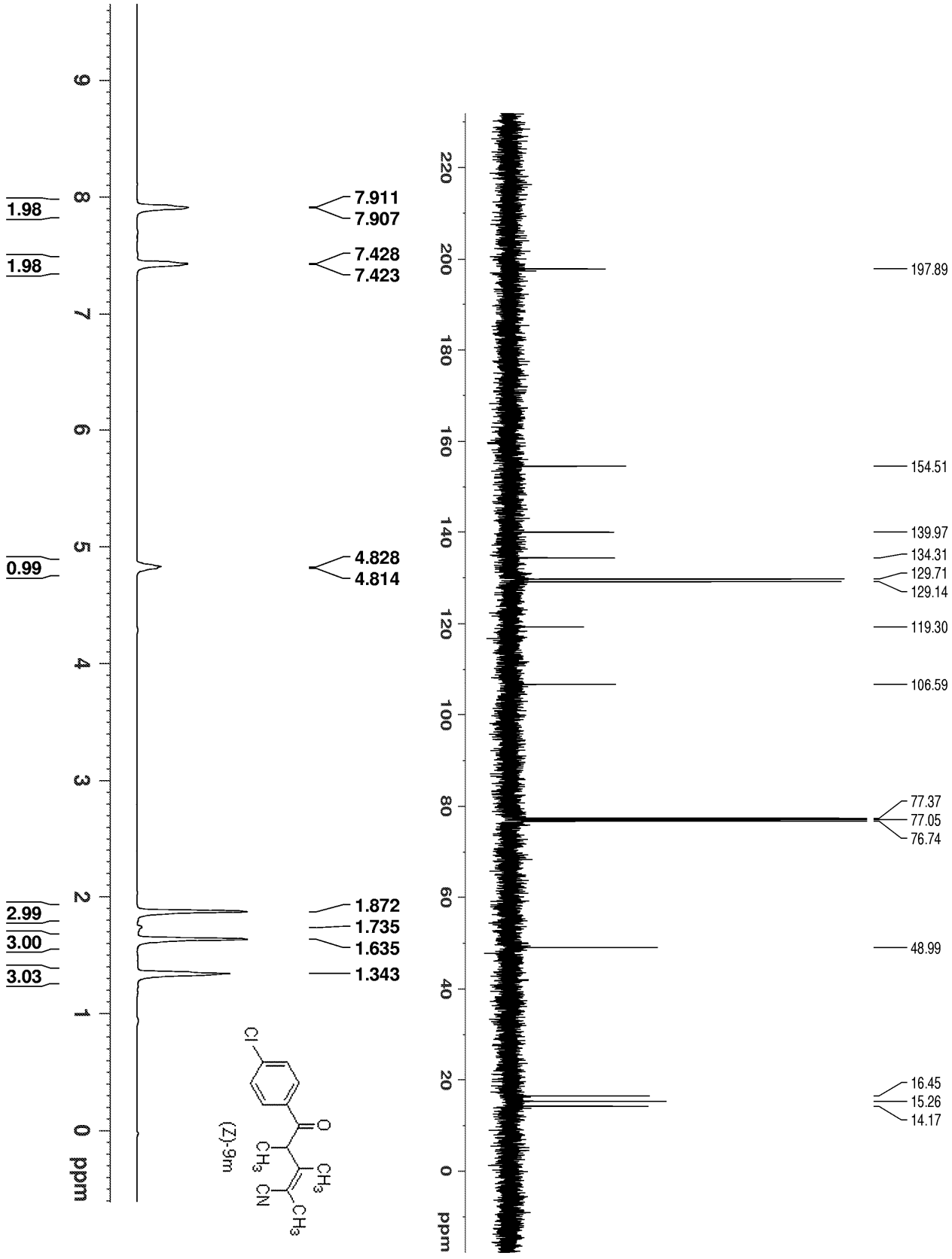
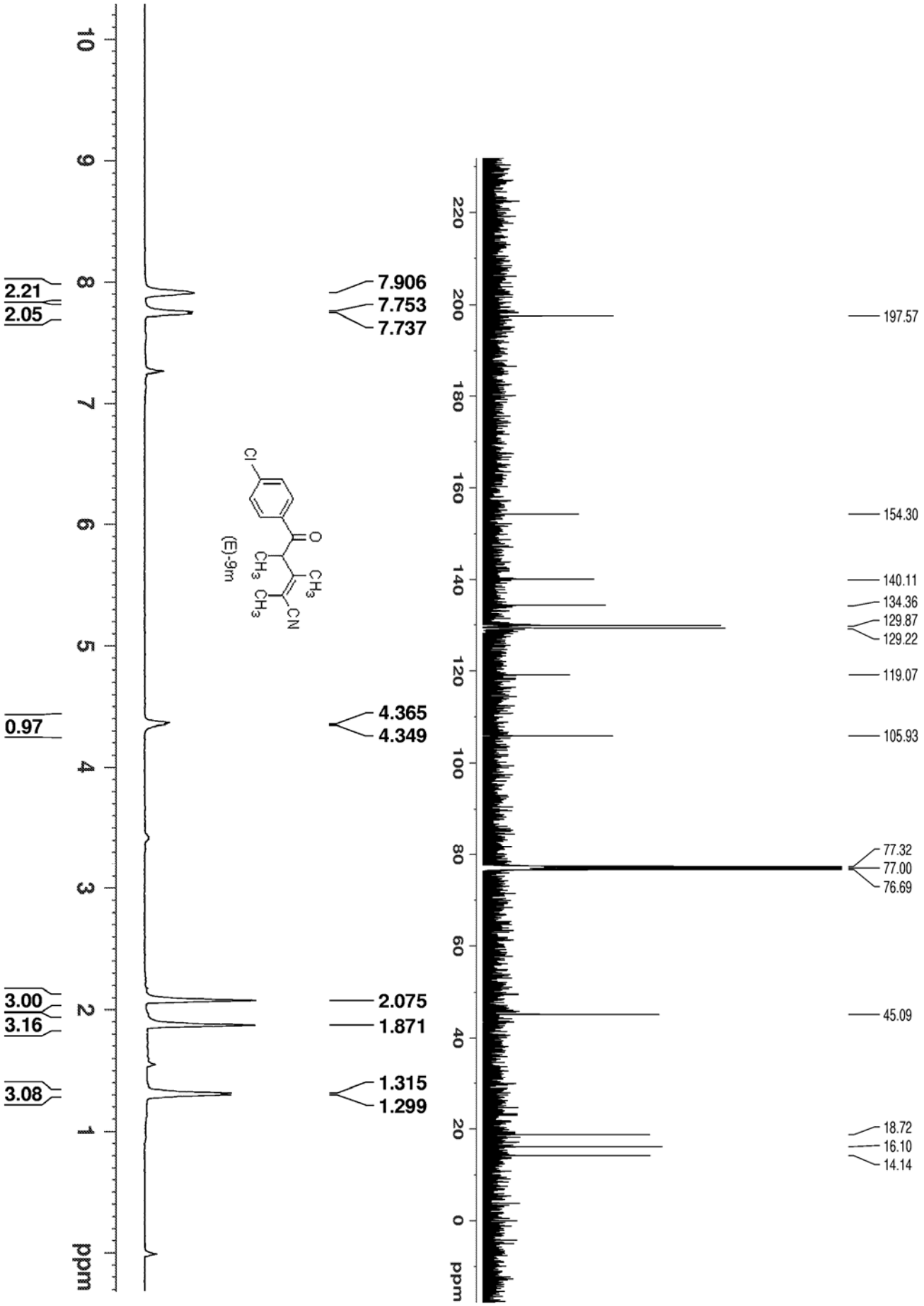
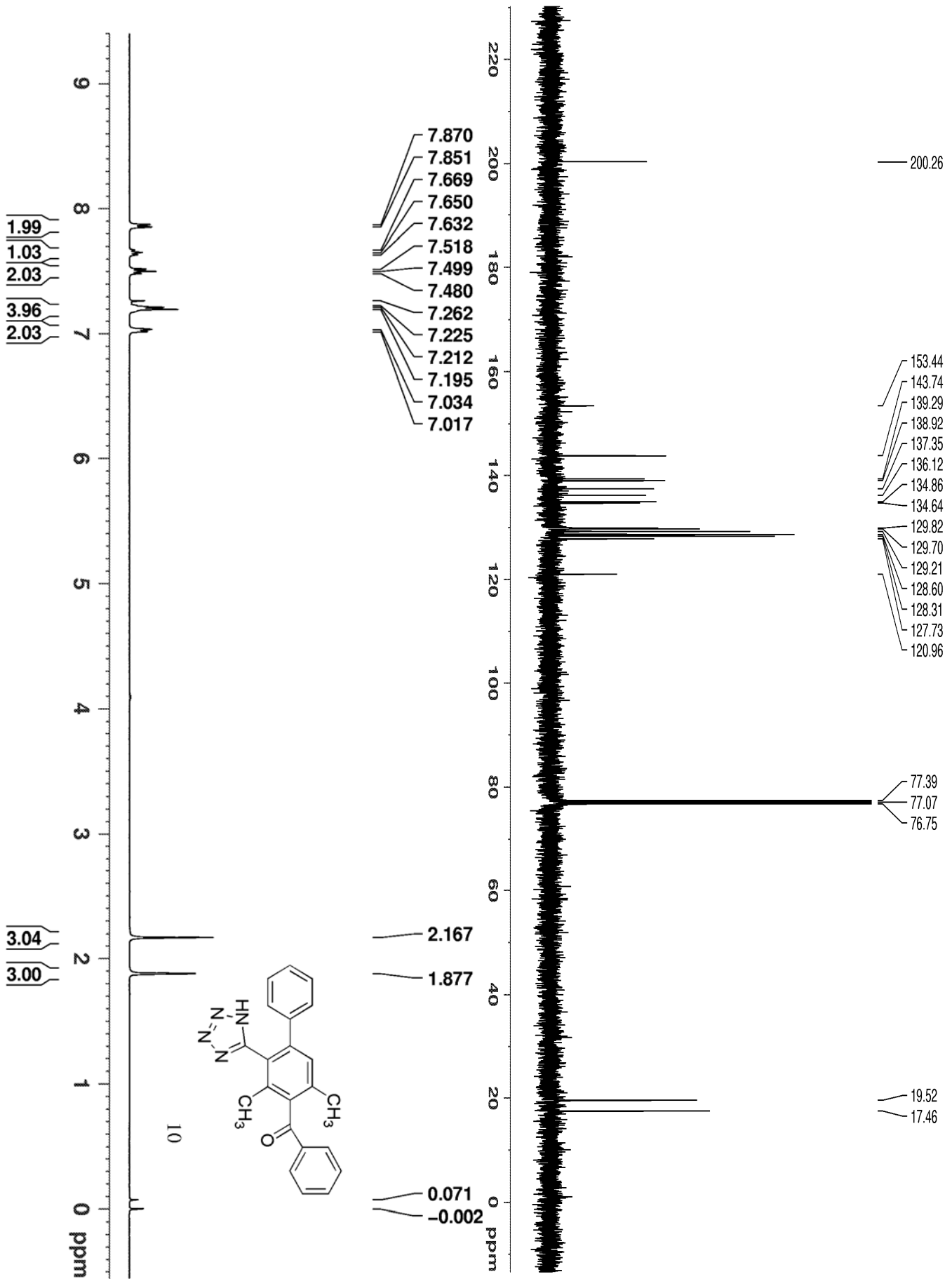
1.00
1.98
1.00
3.00
3.01
3.07
7.798
7.780
7.577
7.559
7.544
7.541
7.455
7.438
7.420
4.431
4.416
4.400
4.384
2.064
1.864
1.759
1.301
1.286
(E)-9l
198.80
154.70
136.11
133.55
128.85
127.81
119.26
105.66
77.40
77.08
76.76
45.01
18.72
16.07
14.17
ppm


1.98
1.98
0.99
2.99
3.00
3.03
7.911
7.907
7.428
7.423
4.828
4.814
1.872
1.735
1.635
1.343
ppm
(Z)-9m
Cl
O
CH3
CH3
CN
CH3
197.89
154.51
139.97
134.31
129.71
129.14
119.30
106.59
77.37
77.05
76.74
48.99
16.45
15.26
14.17
ppm


2.21
2.05
0.97
3.00
3.16
3.08
7.906
7.753
7.737
4.365
4.349
2.075
1.871
1.315
1.299
(E)-9m
197.57
154.30
140.11
134.36
129.87
129.22
119.07
105.93
77.32
77.00
76.69
45.09
18.72
16.10
14.14
ppm
ppm


1.99
1.03
2.03
3.96
2.03
3.04
3.00
7.870
7.851
7.669
7.650
7.632
7.518
7.499
7.480
7.262
7.225
7.212
7.195
7.034
7.017
2.167
1.877
0.071
−0.002
200.26
153.44
143.74
139.29
138.92
137.35
136.12
134.86
134.64
129.82
129.70
129.21
128.60
128.31
127.73
120.96
77.39
77.07
76.75
19.52
17.46
HN
N
N
CH3
CH3
O
10
ppm
ppm

IV. References

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(3) Petasis; N. A.; Teets, K. A. *J. Am. Chem. Soc.* **1992**, *114,* 10328.

(4) Molander, G. A.; Wolfe, J. P. *J. Braz. Chem. Soc.* **1996**, *7*, 335.

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