

SUPPORTING INFORMATION

Lewis Acid Catalyzed Reactivity Switch: Pseudo Three-Component Annulation of Nitrosoarenes and (Epoxy)styrenes

Anisha Purkait, Subhajit Saha, Santanu Ghosh, and Chandan K. Jana*

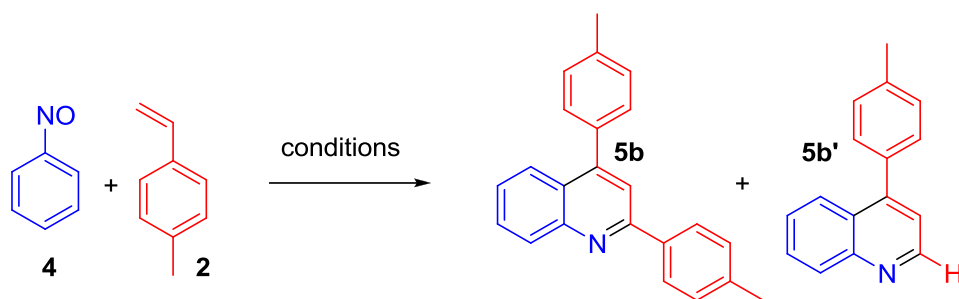
Department of Chemistry, Indian Institute of Technology Guwahati, India, 781039

E-mail: ckjana@iitg.ac.in

Experimental:

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Dichloromethane (CH_2Cl_2) was freshly distilled from phosphorus (V) oxide (P_2O_5). Commercial grade DCE, xylene, benzene and toluene were distilled over CaH_2 before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ^1H , ^{13}C NMR spectroscopy: *Bruker 600 MHz* and *Bruker 400 MHz* (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS (^1H) 0.0 ppm, δ (^{13}C) 0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance (CHCl_3 , δ (^1H) 7.26 ppm, δ (^{13}C) 77.23 ppm) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60-120 under gravity. IR: spectra were recorded on Perkin Elmer Instrument at normal temperature. MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in m/z (% of basis peak). Nitrosoarenes were prepared from the reported method.

Table S1: Optimization of reaction conditions



Entry	Conditions	Yield of 5b (%) ^d	Yield of 5b' (%) ^d
1. ^a	Sc(OTf) ₃ (30 mol%), toluene, reflux, 24 h	36	11
2. ^b	Sc(OTf) ₃ (30 mol%), toluene, reflux, 24 h	43	18
3.	Sc(OTf) ₃ (30 mol%), toluene, reflux, 24 h	46	22
4.	Sc(OTf) ₃ (30 mol%), toluene, reflux, 36 h	47	25
5.	Sc(OTf) ₃ (15 mol%), toluene, reflux, 36 h	45	18
6.	Sc(OTf) ₃ (15 mol%), DCE, reflux, 36 h	49	28
7.	Sc(OTf) ₃ (15 mol%), DCM, reflux, 36 h	46	21
8.	Yb(OTf) ₃ (15 mol%), DCE, reflux, 36 h	48	28
9. ^c	Yb(OTf) ₃ (15 mol%), DCE, reflux, 36 h	44	25
10.	Yb(OTf) ₃ (5 mol%), DCE, reflux, 36 h	34	15
11.	Yb(OTf) ₃ (5 mol%), DCE, reflux, 72 h	34	12
12.	Yb(OTf) ₃ (15 mol%), DCE, reflux, 72 h	42	22
13.	Bi(OTf) ₃ (15 mol%), DCE, reflux, 36 h	36	19
14.	Cu(OTf) ₂ (15 mol%), DCE, reflux, 36 h	35	11
15.	TfOH (15 mol%), DCE, reflux, 36 h	33	21
16.	FeCl ₃ (15 mol%), DCE, reflux, 36 h	-	-
17.	Yb(OTf) ₃ (15 mol%), THF, reflux, 36 h	37	18
18.	Yb(OTf) ₃ (15 mol%), EtOAc, reflux, 36 h	39	22
19.	Yb(OTf) ₃ (15 mol%), benzene, reflux, 36 h	45	11

20.	Yb(OTf) ₃ (15 mol%), CH ₃ CN, reflux, 36 h	46	19
21.	AcOH (15 mol%), DCE, reflux, 36 h	-	-
22.	p-NBA (15 mol%), DCE, reflux, 36 h	-	-

All reactions were carried out with 1 eq. (0.40 mmol) of nitrosobenzene, 2.2 eq. of 4-methyl styrene and solvent (3 mL). ^a1 eq. 4-methyl styrene was used. ^b2 eq. 4-methyl styrene was used. ^c4 eq. 4-methyl styrene was used. ^dSeparated yield. p-NBA - para nitrobenzoic acid.

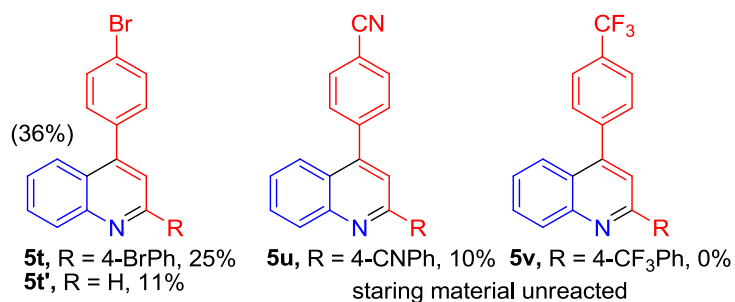
Accordingly, nitrosobenzene **4** was reacted with styrene **2** in the presence of 30 mol% of Sc(OTf)₃ in refluxing toluene for 24 h. As expected, the 2,4-diarylquinoline **5b** and 4-arylquinoline **5b'** were isolated as 3:1 ratio with a 47% combined yield (SI, Table S1). The better yield of the desired products was obtained by increasing the stoichiometry of styrene and the reaction time (entry 2-4). A significant decrease in the yield was observed on lowering the catalyst loading to 15 mol% (entry 5). However, the best yield of the desired quinoline was observed when the reaction with reduced catalyst loading was carried out in refluxing DCE instead of refluxing toluene (entry 6). A similar result was obtained when Yb(OTf)₃ was used as the catalyst. Further screening of reaction conditions was carried out using Yb(OTf)₃, which is cost-effective than Sc(OTf)₃ (entry 8-12, 17-20). Although the lower yield of the desired product was obtained in the presence of a catalytic amount of TfOH, the use of other acids like AcOH and dinitrobenzoic acid failed to provide the quinolines. Other solvents such as THF, EtOAc, CH₃CN, etc. were also found to be suitable for this reaction.

Table S2. Screening of reaction conditions.

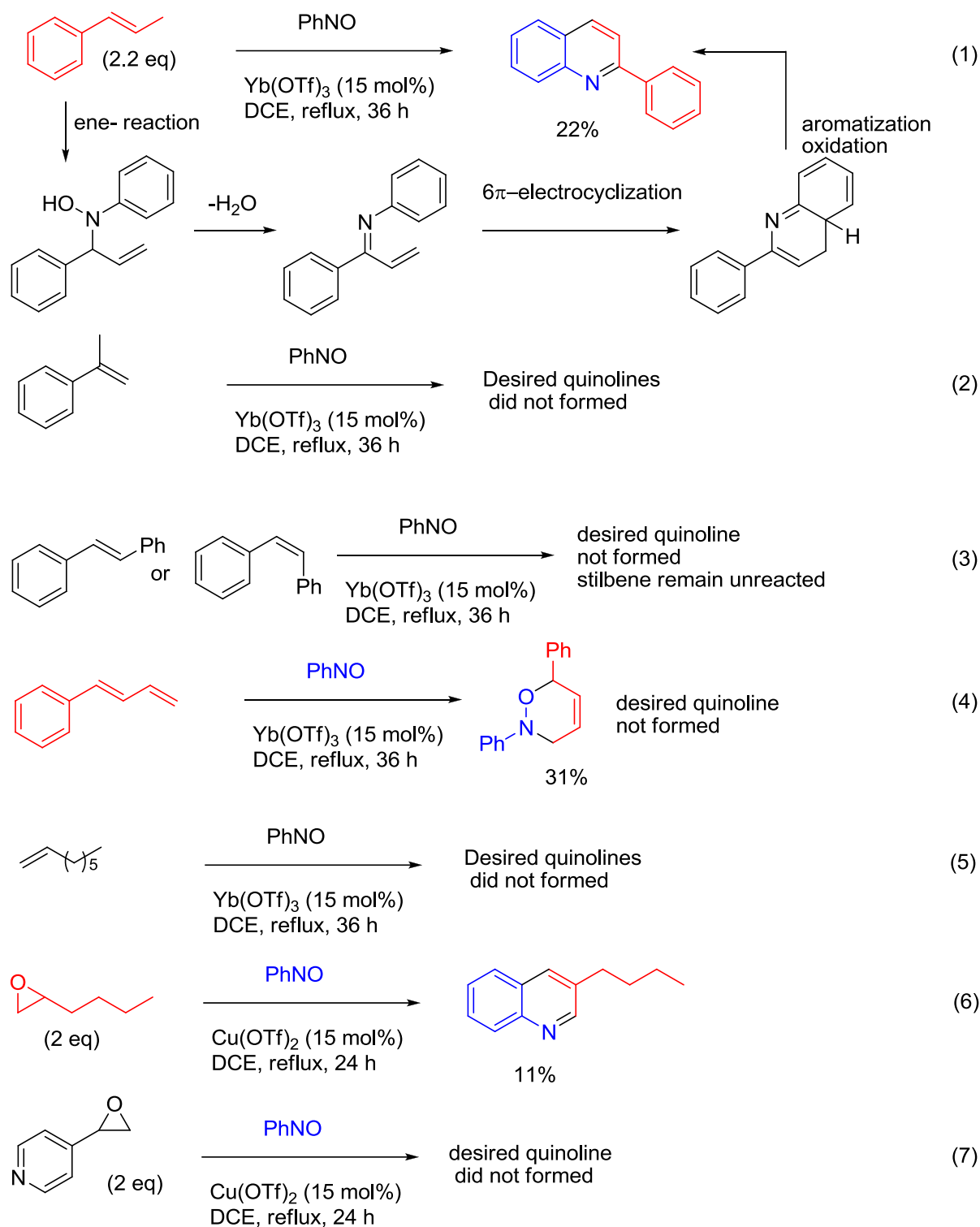


entry	conditions	Yield (%) ^c
1 ^a	Cu(OTf) ₂ (15 mol%), toluene, reflux, 24 h	39
2	Cu(OTf) ₂ (15 mol%), toluene, reflux, 24 h	55
3	Cu(OTf) ₂ (15 mol%), DCE, reflux, 24 h	62
4	Sc(OTf) ₃ (15 mol%), DCE, reflux, 24 h	64
5	Cu(OTf) ₂ (15 mol%), DCE, reflux, 36 h	61
6	Cu(OTf) ₂ (15 mol%), DCE, reflux, 72 h	56
7	Cu(OTf) ₂ (15 mol%), DCE, reflux, 12 h	51
8 ^b	Cu(OTf) ₂ (15 mol%), DCE, reflux, 24 h	61
9	Yb(OTf) ₃ (15 mol%), DCE, reflux, 24 h	53
10	CuBr ₂ (15 mol%), DCE, reflux, 24 h	-
11	Cu(OTf) ₂ (15 mol%), benzene, reflux, 24 h	42
12	Cu(OTf) ₂ (15 mol%), THF, reflux, 24 h	37

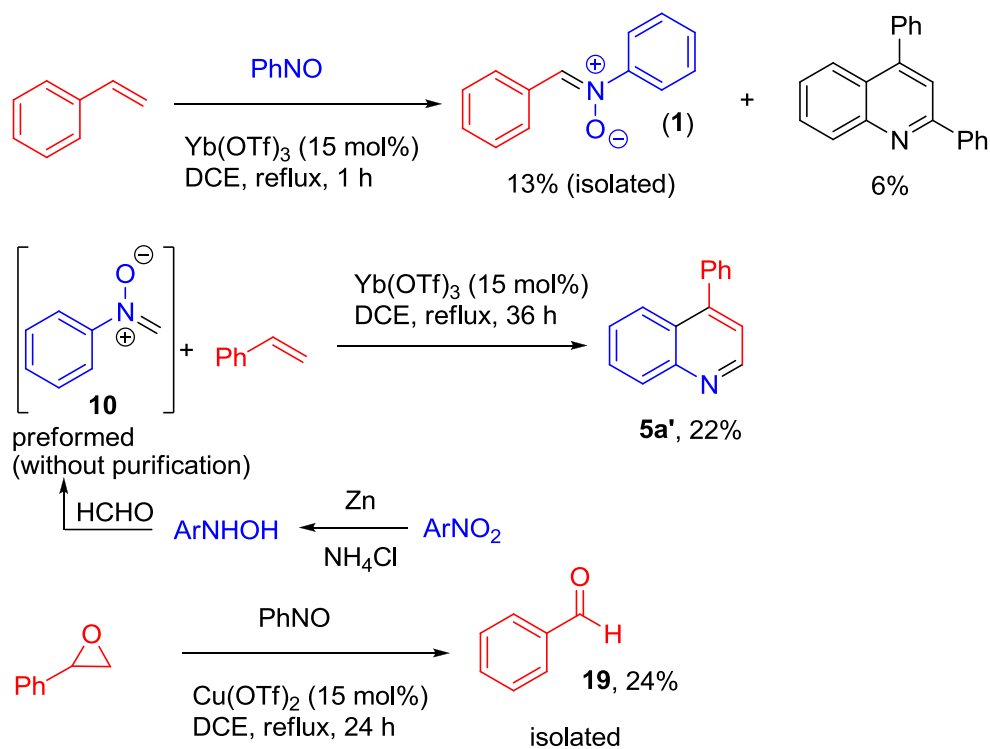
All reactions were carried out 0.33 mmol (1 eq.) of nitrosobenzene, 2 eq. of styrene epoxide and solvent (3 mL). ^a1 eq. epoxide was used. ^b2.5 eq. epoxide was used. ^cSeparated yield.



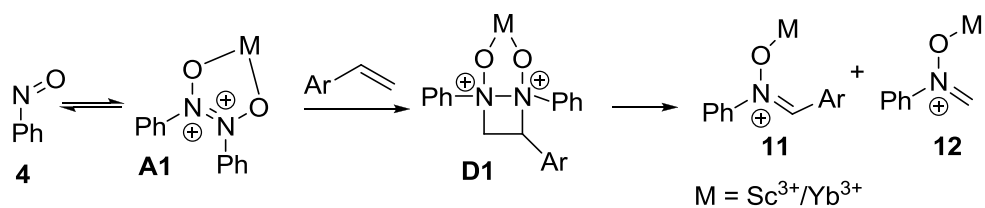
Scheme S1: Additional substrates



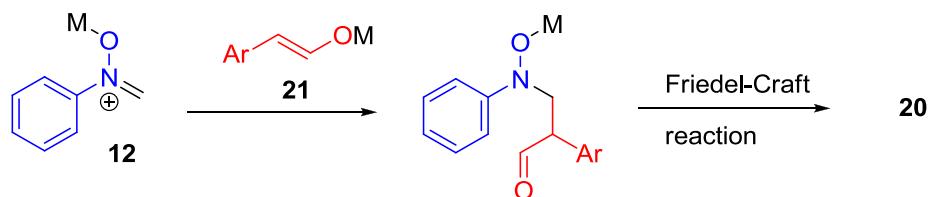
Scheme S2: Attempted reactions with various additional alkenes and epoxide.



Scheme S3: Additional controlled experiments.



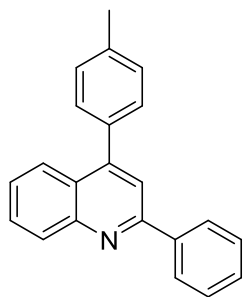
Scheme S4: Proposed mechanism for the formation of nitron from nitrosoarene and styrene



Scheme S5: Probable stepwise pathway to form intermediate **20**.

Procedure for the Synthesis of 2-phenyl-4-(p-tolyl)quinoline (3) :

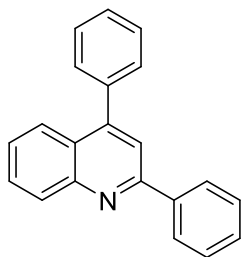
2-phenyl-4-(p-tolyl)quinoline (3):^a Freshly prepared (Z)-N,1-diphenylmethanimine oxide (79 mg, 0.40 mmol) and Sc(OTf)₃ (29 mg, 0.06 mmol) were successively added to a solution of 4-methyl styrene (57 mg, 0.48 mmol) in dry DCE (3 mL). Then the reaction mixture was refluxed for 36 h under argon atmosphere. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (1X20 mL) and the reaction mixture was extracted with DCM (3X20 mL). The organic layer was washed with brine solution (1X30 mL) and evaporated under vacuum. The crude mixture was subjected to column chromatography (silica gel; EtOAc : hexane, 1:30) gave **3** as yellow gum (0.10 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ = 8.28 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 7.2 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.82 (s, 1H), 7.76 - 7.72 (m, 1H), 7.56 - 7.52 (m, 2H), 7.49 - 7.47 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H) ppm. HRMS: Exact mass calculated for C₂₂H₁₈N ([M+H]⁺): 296.1434, Found: 296.1432.



General Procedure for the Synthesis of mono and di substituted quinolines (I):

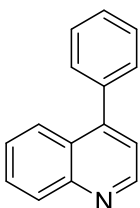
Freshly prepared nitrosoarenes (1 equiv.) and Yb(OTf)₃ (15 mol%) were successively added to a solution of styrene derivatives (2.2 equiv.) in dry DCE (3 mL). Then the reaction mixture was refluxed for 36 h under argon atmosphere. The reactions were carried out under an argon environment; however, without strictly maintaining the oxygen-free conditions. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (1x20 mL) and the reaction mixture was extracted with DCM (3X20 mL). The organic layer was washed with brine solution (1X30 mL) and evaporated under vacuum. The crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.

2,4-diphenylquinoline (5a)^b and 4-phenylquinoline (5a')ⁱ: According to GP I, nitrosobenzene (43 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5a** as yellow gum (48 mg, 43%) and (silica gel; EtOAc : hexane, 1:7) gave **5a'** as yellow gum (21 mg, 25%). Analytical data for **5a**: ¹H NMR (400 MHz, CDCl₃) δ =



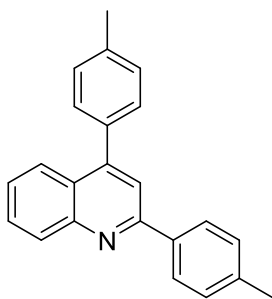
8.33 (d, $J = 8.4$ Hz, 1H), 8.23 - 8.18 (m, 2H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.83 (s, 1H), 7.78 - 7.74 (m, 1H), 7.58 - 7.46 (m, 9H) ppm. HRMS: Exact mass calculated for $C_{21}H_{16}N$ ($[M+H]^+$): 282.1277,

Found: 282.1285.



Analytical data for **5a'**: 1H NMR (400 MHz, $CDCl_3$) $\delta = 8.96$ (d, $J = 3.6$ Hz, 1H), 8.32 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.82 - 7.78 (m, 1H), 7.59 - 7.52 (m, 6H), 7.43 (d, $J = 4.4$ Hz, 1H) ppm. HRMS: Exact mass calculated for $C_{15}H_{12}N$ ($[M+H]^+$): 206.0964, Found: 206.0974.

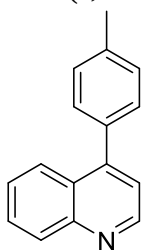
2,4-di-p-tolylquinoline (5b)^c and 4-(p-tolyl)quinoline (5b')ⁱ: According to GP I, nitrosobenzene



(43 mg, 0.40 mmol), 4-methyl styrene (0.10 g, 0.88 mmol) and $Yb(OTf)_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5b** as yellow gum (59 mg, 48%) and (silica gel; EtOAc : hexane, 1:7) gave **5b'** as yellow gum (25 mg, 28%). Analytical data for **5b**: 1H NMR

(400 MHz, $CDCl_3$) $\delta = 8.27$ (d, $J = 8.0$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 2H), 7.94 - 7.92 (m, 1H), 7.80 (s, 1H), 7.75 - 7.71 (m, 1H), 7.48 - 7.45 (m, 3H), 7.38 - 7.33 (m, 4H), 2.49 (s, 3H), 2.44 (s, 3H) ppm. HRMS: Exact mass calculated for $C_{23}H_{20}N$ ($[M+H]^+$): 310.1590,

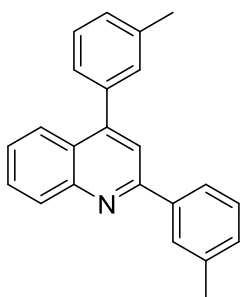
Found: 310.1604.



Analytical data for **5b'**: 1H NMR (400 MHz, $CDCl_3$) $\delta = 8.94$ (d, $J = 4.8$ Hz, 1H), 8.31 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.81 - 7.76 (m, 1H), 7.58 - 7.54 (m, 1H), 7.44 - 7.40 (m, 3H), 7.36 (d, $J = 7.6$ Hz, 2H), 2.48 (s, 3H) ppm. HRMS:

Exact mass calculated for $C_{16}H_{14}N$ ($[M+H]^+$): 220.1121, Found: 220.1127.

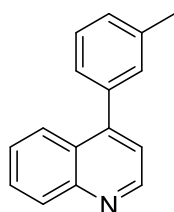
2,4-di-m-tolylquinoline (5c) and 4-(m-tolyl)quinoline (5c')^k: According to GP I, nitrosobenzene



(43 mg, 0.40 mmol), 3-methyl styrene (0.10 g, 0.88 mmol) and $Yb(OTf)_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5c** as yellow gum (40 mg, 32%) and (silica gel; EtOAc : hexane, 1:7) gave **5c'** as yellow gum (17 mg, 19%). Analytical data for **5c**: FT-IR: $\tilde{\nu} = 2960, 2927, 2857, 1670, 1593, 1548, 1488, 1353, 1261, 1096, 876, 766$

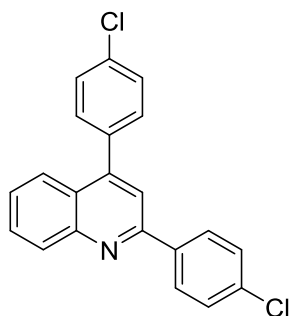
cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) $\delta = 8.26$ (d, $J = 8.8$ Hz, 1H), 8.04 (s, 1H), 7.97 (d, $J = 7.6$ Hz,

1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.81 (s, 1H), 7.76 - 7.72 (m, 1H), 7.50 - 7.42 (m, 3H), 7.40 - 7.32 (m, 3H), 7.29 (d, $J = 7.6$ Hz, 1H), 2.48 (s, 6H) ppm. ^{13}C NMR (151 MHz, CDCl_3) $\delta = 157.3$, 149.5, 149.0, 139.8, 138.7, 138.6, 138.5, 130.4, 130.3, 130.2, 129.7, 129.3, 128.9, 128.7, 128.5, 126.9, 126.4, 126.0, 125.9, 124.9, 119.7, 21.82, 21.75 ppm. HRMS: Exact mass calculated for $\text{C}_{23}\text{H}_{20}\text{N}$ ($[\text{M}+\text{H}]^+$): 310.1590, Found: 310.1590.



Analytical data for **5c'**: ^1H NMR (400 MHz, CDCl_3) $\delta = 8.96$ (d, $J = 4.8$ Hz, 1H), 8.41 (d, $J = 8.4$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.86 - 7.81 (m, 1H), 7.63 - 7.59 (m, 1H), 7.48 - 7.44 (m, 2H), 7.37 - 7.32 (m, 3H), 2.47 (s, 3H) ppm. HRMS: Exact mass calculated for $\text{C}_{16}\text{H}_{14}\text{N}$ ($[\text{M}+\text{H}]^+$): 220.1121, Found: 220.1122.

2,4-bis(4-chlorophenyl)quinoline (5d)^d and 4-(4-chlorophenyl)quinoline (5d')^l: According to

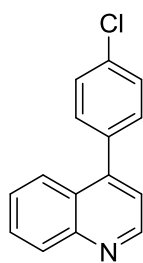


GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-chloro styrene (0.12 g, 0.88 mmol) and $\text{Yb}(\text{OTf})_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5d** as yellow gum (45 mg, 32%) and (silica gel; EtOAc : hexane, 1:7) gave **5d'** as yellow gum (21mg, 22%).

Analytical data for **5d**: FT-IR: $\tilde{\nu} = 2962, 2925, 2855, 1596, 1544, 1487, 1420, 1357, 1091, 1014, 830, 765 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) $\delta =$

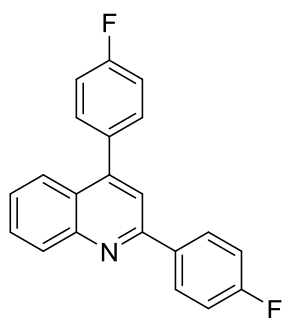
8.24 (d, $J = 8.4$ Hz, 1H), 8.15 (d, $J = 8.4$ Hz, 2H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.78 - 7.74 (m, 2H), 7.55 - 7.49 (m, 7H) ppm. ^{13}C NMR (151 MHz, CDCl_3) $\delta = 155.5, 149.2, 148.0, 137.0, 136.5, 136.4, 135.2, 131.0, 130.6, 129.6, 129.4, 129.3, 129.2, 127.3, 125.8, 125.6, 119.3$ ppm. HRMS:

Exact mass calculated for $\text{C}_{21}\text{H}_{14}\text{NCl}_2$ ($[\text{M}+\text{H}]^+$): 350.0498, Found: 350.0497.

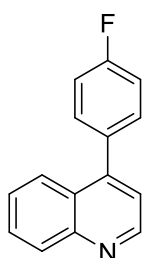


Analytical data for **5d'**: ^1H NMR (400 MHz, CDCl_3) $\delta = 8.97$ (d, $J = 4.4$ Hz, 1H), 8.37 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.85 - 7.81 (m, 1H), 7.62 - 7.58 (m, 1H), 7.56 - 7.54 (m, 2H), 7.48 - 7.46 (m, 2H), 7.43 (d, $J = 4.4$ Hz, 1H) ppm. HRMS: Exact mass calculated for $\text{C}_{15}\text{H}_{11}\text{NCl}$ ($[\text{M}+\text{H}]^+$): 240.0575, Found: 240.0576.

2,4-bis(4-fluorophenyl)quinoline (5e)^e and 4-(4-fluorophenyl)quinoline (5e')^m: According to



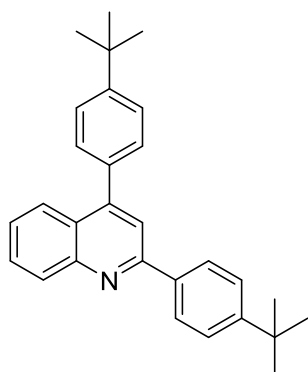
GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-fluoro styrene (0.11 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5e** as yellow gum (47 mg, 37%) and (silica gel; EtOAc : hexane, 1:7) gave **5e'** as yellow gum (22 mg, 24%). Analytical data for **5e**: ¹H NMR (600 MHz, CDCl₃) δ = 8.27 - 8.23 (m, 1H), 8.21 - 8.16 (m, 2H), 7.87 - 7.83 (m, 1H), 7.77 - 7.75 (m, 2H), 7.55 - 7.49 (m, 3H), 7.27 - 7.20 (m, 4H) ppm. HRMS: Exact mass calculated for C₂₁H₁₄NF₂ ([M+H]⁺): 318.1089, Found: 318.1090.



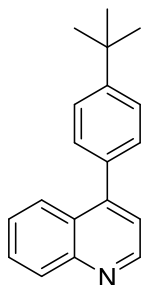
Analytical data for **5e'**: ¹H NMR (400 MHz, CDCl₃) δ = 8.96 (d, *J* = 4.8 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.83 - 7.79 (m, 1H), 7.61 - 7.57 (m, 1H), 7.53 - 7.49 (m, 2H), 7.41 (d, *J* = 4.4 Hz, 1H), 7.28 - 7.27 (m, 1H), 7.26 - 7.24 (m, 1H) ppm. HRMS: Exact mass calculated for C₁₅H₁₁NF ([M+H]⁺): 224.0870, Found: 224.0871.

2,4-bis(4-(*tert*-butyl)phenyl)quinoline (5f) and 4-(4-(*tert*-butyl)phenyl)quinoline (5f'):

According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-*tert* butyl styrene (0.14 g, 0.88 mmol)



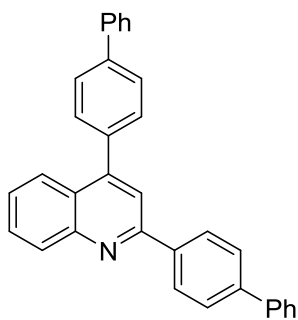
and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave **5f** as yellow gum (38 mg, 24%) and (silica gel; EtOAc : hexane, 1:10) gave **5f'** as yellow gum (22 mg, 21%). Analytical data for **5f**: FT-IR: $\tilde{\nu}$ = 2961, 2930, 2867, 1660, 1591, 1497, 1363, 1268, 1018, 838, 765, 701 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.24 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.74 - 7.70 (m, 1H), 7.59 - 7.57 (m, 3H), 7.55 - 7.51 (m, 3H), 7.48 - 7.45 (m, 1H), 1.44 (s, 9H), 1.39 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 157.2, 152.7, 151.7, 149.2, 149.1, 137.2, 135.8, 130.3, 129.5, 127.5, 126.2, 126.04, 125.99, 125.7, 119.5, 34.98, 34.96, 31.6, 31.5 ppm. Total count of ¹³C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C₂₉H₃₂N ([M+H]⁺): 394.2529, Found: 394.2533.



Analytical data for **5f'**: FT-IR: $\tilde{\nu}$ = 2960, 2930, 2866, 1611, 1585, 1501, 1462, 1389, 1201, 1056, 873, 747 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.93 (d, J = 4.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.74 - 7.70 (m, 1H), 7.56 - 7.54 (m, 2H), 7.52 - 7.48 (m, 1H), 7.47 - 7.45 (m, 2H), 7.34 (d, J = 4.4 Hz, 1H), 1.41 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 151.8, 150.2, 149.0, 148.8, 135.3, 130.0, 129.51, 129.45, 127.1, 126.7, 126.3, 125.7, 121.5, 35.0, 31.6 ppm.

HRMS: Exact mass calculated for $\text{C}_{19}\text{H}_{20}\text{N}$ ($[\text{M}+\text{H}]^+$): 262.1590, Found: 262.1595.

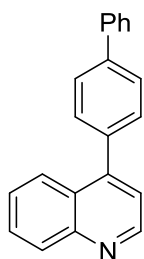
2,4-di([1,1'-biphenyl]-4-yl)quinoline (**5g**) and 4-([1,1'-biphenyl]-4-yl)quinoline (**5g'**):



According to GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-vinyl biphenyl (0.16 g, 0.88 mmol) and $\text{Yb}(\text{OTf})_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5g** as yellow gum (58 mg, 33%) and (silica gel; EtOAc : hexane, 1:10) gave **5g'** as yellow gum (24 mg, 21%). Analytical data for **5g**: FT-IR: $\tilde{\nu}$ = 2927, 2860, 1628, 1600, 1449, 1299, 1076, 907, 844, 734 cm^{-1} . ^1H NMR

(400 MHz, CDCl_3) δ = 8.32 - 8.29 (m, 3H), 8.02 - 8.00 (m, 1H), 7.92 (s, 1H), 7.81 - 7.75 (m, 5H), 7.73 - 7.67 (m, 6H), 7.54 - 7.47 (m, 5H), 7.44 - 7.37 (m, 2H) ppm. ^{13}C NMR (151 MHz, CDCl_3) δ = 156.7, 149.1, 149.0, 142.3, 141.6, 140.8, 140.7, 138.7, 137.5, 130.4, 130.3, 129.9, 129.2, 129.1, 128.2, 127.9, 127.81, 127.79, 127.6, 127.41, 127.37, 126.6, 126.0, 125.9, 119.5 ppm. HRMS: Exact mass calculated for $\text{C}_{33}\text{H}_{24}\text{N}$ ($[\text{M}+\text{H}]^+$): 434.1903, Found: 434.1910.

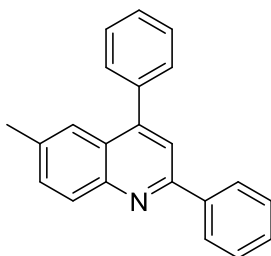
Analytical data for **5g'**: FT-IR: $\tilde{\nu}$ = 2957, 2920, 2847, 1633, 1596, 1486, 1388, 1261, 1007, 839,



766 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.97 (d, J = 4.8 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 9.2 Hz, 1H), 7.79 - 7.75 (m, 3H), 7.71 - 7.69 (m, 2H), 7.62 - 7.60 (m, 2H), 7.58 - 7.54 (m, 1H), 7.52 - 7.49 (m, 2H), 7.43 - 7.39 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 149.7, 149.0, 148.3, 141.8, 140.6, 136.9, 130.2, 129.9, 129.7, 129.2, 128.0, 127.6, 127.4, 127.1, 127.0, 126.2, 121.5 ppm.

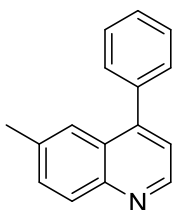
HRMS: Exact mass calculated for $\text{C}_{21}\text{H}_{16}\text{N}$ ($[\text{M}+\text{H}]^+$): 282.1277, Found: 282.1270.

6-methyl-2,4-diphenylquinoline (5h)^b and 6-methyl-4-phenylquinoline (5h')ⁿ: According to



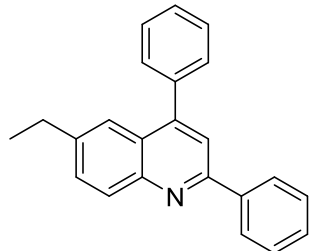
GP I, 1-methyl-4-nitrosobenzene (48 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) was reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5h** as yellow gum (34 mg, 29%) and (silica gel; EtOAc : hexane, 1:7) gave **5h'** as yellow gum (17 mg,

19%). Analytical data for **5h'**: ¹H NMR (400 MHz, CDCl₃) δ = 8.21 - 8.17 (m, 3H), 7.78 (s, 1H), 7.66 (s, 1H), 7.60 - 7.51 (m, 8H), 7.48 - 7.44 (m, 1H), 2.48 (s, 3H) ppm. HRMS: Exact mass calculated for C₂₂H₁₈N ([M+H]⁺): 296.1434, Found: 296.1438.



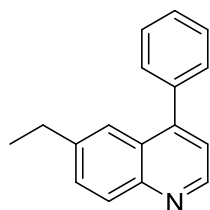
Analytical data for **5h'**: ¹H NMR (600 MHz, CDCl₃) δ = 8.88 (d, *J* = 4.2 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.70 (s, 1H), 7.63 - 7.62 (m, 1H), 7.57 - 7.51 (m, 5H), 7.38 (d, *J* = 4.2 Hz, 1H), 2.49 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₆H₁₄N ([M+H]⁺): 220.1121, Found: 220.1123.

6-ethyl-2,4-diphenylquinoline (5i)^f and 6-ethyl-4-phenylquinoline (5i')^o: According to GP I, 1-



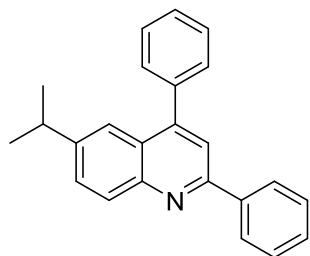
ethyl-4-nitrosobenzene (54 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5i** as yellow gum (44 mg, 36%) and (silica gel; EtOAc : hexane, 1:7) gave **5i'** as yellow gum (19 mg, 20%).

Analytical data for **5i**: ¹H NMR (400 MHz, CDCl₃) δ = 8.24 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 7.2 Hz, 2H), 7.79 (s, 1H), 7.68 (s, 1H), 7.64 - 7.62 (m, 1H), 7.58 - 7.51 (m, 7H), 7.48 - 7.45 (m, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H) ppm. HRMS: Exact mass calculated for C₂₃H₂₀N ([M+H]⁺): 310.1590, Found: 310.1591.



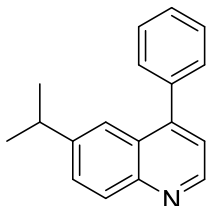
Analytical data for **5i'**: ¹H NMR (400 MHz, CDCl₃) δ = 8.88 (d, *J* = 4.4 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.71 (s, 1H), 7.66 - 7.64 (m, 1H), 7.56 - 7.51 (m, 5H), 7.36 (d, *J* = 4.8 Hz, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H) ppm. HRMS: Exact mass calculated for C₁₇H₁₆N ([M+H]⁺): 234.1277, Found: 234.1285.

6-isopropyl-2,4-diphenylquinoline (5j) and 6-isopropyl-4-phenylquinoline (5j')^p:



to GP I, 1-isopropyl-4-nitrosobenzene (60 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5j** as yellow gum (48 mg, 37%) and (silica gel; EtOAc : hexane, 1:7) gave **5j'** as yellow gum (20 mg, 20%). Analytical data for **5j**: FT-IR: $\tilde{\nu}$ = 2960, 2930, 2867, 1623, 1589, 1491, 1027, 835, 693 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ = 8.20 - 8.16 (m, 3H), 7.78 (s, 1H), 7.70 (s, 1H), 7.67 - 7.66 (m, 1H), 7.59 - 7.56 (m, 4H), 7.54 - 7.51 (m, 3H), 7.47 - 7.45 (m, 1H), 3.06 - 3.01 (m, 1H), 1.29 (d, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 156.4, 148.9, 147.9, 147.2, 140.0, 138.8, 130.3, 129.8, 129.3, 129.2, 129.0, 128.8, 128.5, 127.7, 125.8, 122.1, 119.7, 34.6, 24.1 ppm.

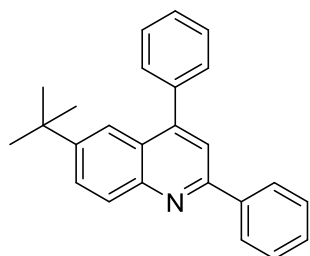
HRMS: Exact mass calculated for C₂₄H₂₂N ([M+H]⁺): 324.1747, Found: 324.1749.



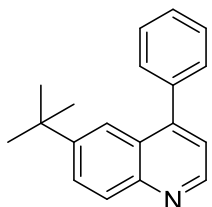
Analytical data for **5j'**: ¹H NMR (400 MHz, CDCl₃) δ = 8.88 (d, *J* = 4.8 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.74 (s, 1H), 7.71 - 7.68 (m, 1H), 7.56 - 7.52 (m, 5H), 7.36 (d, *J* = 4.4 Hz, 1H), 3.07 - 3.05 (m, 1H), 1.28 (d, *J* = 6.8 Hz, 6H)

ppm. HRMS: Exact mass calculated for C₁₈H₁₈N ([M+H]⁺): 248.1434, Found: 248.1432.

6-(tert-butyl)-2,4-diphenylquinoline (5k)^g and 6-(tertbutyl)-4-phenylquinoline (5k')^p:

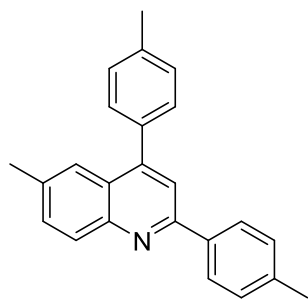


According to GP I, 1-tert butyl-4-nitrosobenzene (65 mg, 0.40 mmol), styrene (92 mg, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5k** as yellow gum (55 mg, 41%) and (silica gel; EtOAc : hexane, 1:7) gave **5k'** as yellow gum (19 mg, 18%). Analytical data for **5k**: ¹H NMR (400 MHz, CDCl₃) δ = 8.21 (d, *J* = 8.8 Hz, 1H), 8.19 - 8.17 (m, 2H), 7.87 - 7.83 (m, 2H), 7.79 (s, 1H), 7.60 - 7.51 (m, 7H), 7.48 - 7.44 (m, 1H), 1.35 (s, 9H) ppm. HRMS: Exact mass calculated for C₂₅H₂₄N ([M+H]⁺): 338.1903, Found: 338.1921.



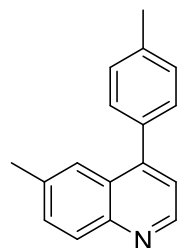
Analytical data for **5k'**: ^1H NMR (400 MHz, CDCl_3) δ = 8.89 (d, J = 4.8 Hz, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.92 - 7.87 (m, 2H), 7.56 - 7.53 (m, 5H), 7.39 (d, J = 4.8 Hz, 1H), 1.34 (s, 9H) ppm. HRMS: Exact mass calculated for $\text{C}_{19}\text{H}_{20}\text{N}$ ($[\text{M}+\text{H}]^+$): 262.1590, Found: 262.1594.

6-methyl-2,4-di-p-tolylquinoline (5l)^h and **6-methyl-4-(p-tolyl)quinoline (5l')ⁿ**: According to



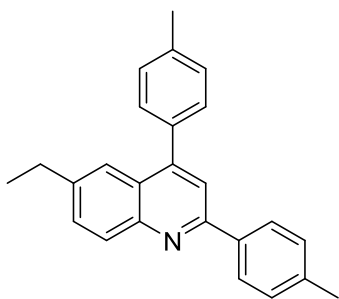
GP I, 1-methyl-4-nitrosobenzene (48 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and $\text{Yb}(\text{OTf})_3$ (37 mg, 0.06 mmol) was reacted for 36 h in dry DCE (3 mL) and column chromatography (silica gel; EtOAc : hexane, 1:30) gave **5l** as yellow gum (58 mg, 45%) and (silica gel; EtOAc : hexane, 1:7) gave **5l'** as yellow gum (22 mg, 24%). Analytical

data for **5l**: ^1H NMR (400 MHz, CDCl_3) δ = 8.18 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.75 (s, 1H), 7.67 (s, 1H), 7.58 - 7.55 (m, 1H), 7.47 - 7.45 (m, 2H), 7.38 - 7.36 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H) ppm. HRMS: Exact mass calculated for $\text{C}_{24}\text{H}_{22}\text{N}$ ($[\text{M}+\text{H}]^+$): 324.1747, Found: 324.1757.



Analytical data for **5l'**: ^1H NMR (400 MHz, CDCl_3) δ = 8.85 (d, J = 4.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.71 (s, 1H), 7.59 - 7.56 (m, 1H), 7.42 - 7.40 (m, 2H), 7.36 - 7.34 (m, 2H), 7.31 (d, J = 4.8 Hz, 1H), 2.48 (s, 6H) ppm. HRMS: Exact mass calculated for $\text{C}_{17}\text{H}_{16}\text{N}$ ($[\text{M}+\text{H}]^+$): 234.1277, Found: 234.1287.

6-ethyl-2,4-di-p-tolylquinoline (5m) and **6-ethyl-4-(p-tolyl)quinoline (5m')**: According to GP I, 1-ethyl-4-nitrosobenzene (54 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and $\text{Yb}(\text{OTf})_3$

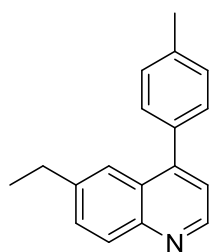


(37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5m** as yellow gum (62 mg, 46%) and (silica gel; EtOAc : hexane, 1:7) gave **5m'** as yellow gum (26 mg, 26%).

Analytical data for **5m**: FT-IR: $\tilde{\nu}$ = 2963, 2922, 2870, 1613, 1588, 1494, 1358, 1211, 1183, 1090, 890, 725 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.21 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.75 (s, 1H), 7.70 (d, J = 1.2 Hz, 1H), 7.62 - 7.59 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.77 (q, J = 7.6 Hz, 2H), 2.50 (s, 3H), 2.43 (s, 3H), 1.27 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 156.0, 149.5, 147.0, 142.8, 139.8, 138.6, 136.3, 135.7, 131.1, 129.8, 129.7,

129.5, 129.4, 127.8, 126.0, 123.5, 119.6, 29.3, 21.56, 21.54, 15.8 ppm. HRMS: Exact mass calculated for $C_{25}H_{24}N$ ($[M+H]^+$): 338.1903, Found: 338.1903.

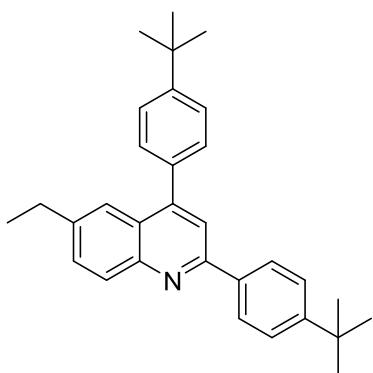
Analytical data for **5m'**: FT-IR: $\tilde{\nu}$ = 2964, 2927, 2872, 1615, 1584, 1454, 1372, 1260, 1184, 1021,



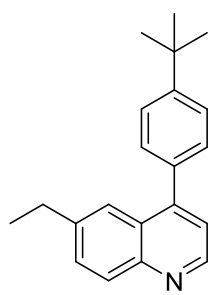
817, 723 cm^{-1} . 1H NMR (600 MHz, $CDCl_3$) δ = 8.86 (d, J = 4.8 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.37 - 7.34 (m, 3H), 2.78 (q, J = 7.8 Hz, 2H), 2.48 (s, 3H), 1.26 (t, J = 7.8 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.2, 148.4, 146.7, 143.3, 138.7, 135.2, 131.1, 129.63, 129.55, 129.1, 127.1, 123.8, 121.5, 29.4, 21.5, 15.8

ppm. HRMS: Exact mass calculated for $C_{18}H_{18}N$ ($[M+H]^+$): 248.1434, Found: 248.1434.

2,4-bis(4-(tert-butyl)phenyl)-6-ethylquinoline (5n) and 4-(4-(tert-butyl)phenyl)-6-ethylquinoline (5n'): According to GP I, 1-ethyl-4-nitrosobenzene (54 mg, 0.4 mmol), 4-tert-butylstyrene (0.14 g, 0.88 mmol) and $Yb(OTf)_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave **5n** as yellow gum (57 mg, 34%) and (silica gel; EtOAc : hexane, 1:10) gave **5n'** as yellow gum (24 mg, 21%). Analytical



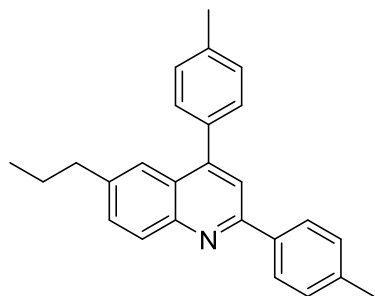
data for **5n**: FT-IR: $\tilde{\nu}$ = 2962, 2904, 2868, 1589, 1460, 1394, 1261, 1186, 1081, 965, 892, 799 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 2H), 7.77 (s, 1H), 7.74 (s, 1H), 7.61 - 7.57 (m, 3H), 7.55 - 7.51 (m, 4H), 2.78 (q, J = 7.6 Hz, 2H), 1.44 (s, 9H), 1.38 (s, 9H), 1.28 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.4, 152.5, 151.6, 148.6, 147.9, 142.4, 137.4, 136.0, 130.6, 130.2, 129.5, 127.4, 126.0, 125.9, 125.7, 123.6, 119.6, 35.0, 34.9, 31.6, 31.5, 29.4, 15.9 ppm. HRMS: Exact mass calculated for $C_{31}H_{36}N$ ($[M+H]^+$): 422.2822, Found: 422.2851.



Analytical data for **5n'**: FT-IR: $\tilde{\nu}$ = 2962, 2929, 2868, 1611, 1582, 1501, 1455, 1363, 1260, 1102, 1018, 891, 736 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ = 8.86 (d, J = 4.4 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.76 (s, 1H), 7.61 - 7.59 (m, 1H), 7.57 - 7.55 (m, 2H), 7.48 - 7.46 (m, 2H), 7.29 (d, J = 4.4 Hz, 1H), 2.78 (q, J = 7.6 Hz, 2H), 1.42 (s, 9H), 1.27 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.6, 149.3, 148.2, 147.7, 142.9, 135.5, 130.6, 129.8, 129.5, 127.0,

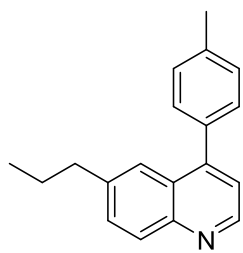
125.7, 123.8, 121.7, 35.0, 31.6, 29.4, 15.9 ppm. HRMS: Exact mass calculated for $C_{21}H_{24}N$ ($[M+H]^+$): 290.1903, Found: 290.1900.

6-propyl-2,4-di-p-tolylquinoline (5o) and 6-propyl-4-(p-tolyl)quinoline (5o'): According to



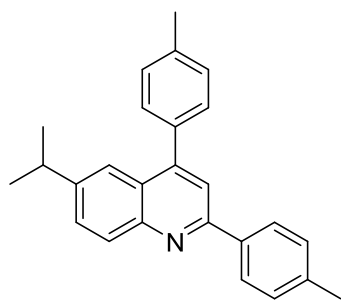
GP I, 1-propyl-4-nitrosobenzene (60 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and $Yb(OTf)_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5o** as yellow gum (55 mg, 39%) and (silica gel; EtOAc : hexane, 1:10) gave **5o'** as yellow gum (20 mg, 19%). Analytical

data for **5o**: FT-IR: $\tilde{\nu}$ = 2960, 2925, 2870, 1618, 1590, 1496, 1361, 1261, 1018, 820, 669 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.4 Hz, 2H), 7.75 (s, 1H), 7.68 (d, J = 1.6 Hz, 1H), 7.59 - 7.56 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.71 (t, J = 7.6 Hz, 2H), 2.50 (s, 3H), 2.43 (s, 3H), 1.73 - 1.64 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.3, 148.7, 147.8, 140.9, 139.3, 138.4, 137.3, 136.0, 131.1, 129.9, 129.73, 129.68, 129.5, 127.6, 125.9, 124.2, 119.5, 38.4, 24.8, 21.6, 14.1 ppm. Total count of ^{13}C is less than expected due to the merging of signals in the aliphatic region. HRMS: Exact mass calculated for $C_{26}H_{26}N$ ($[M+H]^+$): 352.2060, Found: 352.2056.



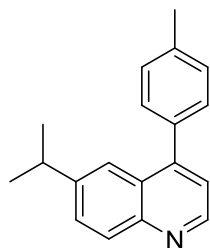
Analytical data for **5o'**: FT-IR: $\tilde{\nu}$ = 2958, 2923, 2854, 1615, 1585, 1501, 1456, 1260, 1184, 1089, 858, 724 cm^{-1} . 1H NMR (600 MHz, $CDCl_3$) δ = 8.86 (d, J = 4.8 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 7.8 Hz, 2H), 7.38 - 7.37 (m, 3H), 2.72 (t, J = 7.2 Hz, 2H), 2.49 (s, 3H), 1.70 - 1.64 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.1, 147.6, 145.7, 142.2, 139.0, 135.0, 132.0, 129.6, 128.3, 127.1, 124.6, 121.5, 38.4, 24.7, 21.6, 14.0 ppm. Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for $C_{19}H_{20}N$ ($[M+H]^+$): 262.1590, Found: 262.1596.

6-isopropyl-2,4-di-p-tolylquinoline (5p) and 6-isopropyl-4-(p-tolyl)quinoline (5p'): According



to GP I, 1-isopropyl-4-nitrosobenzene (60 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5p** as yellow gum (59 mg, 42%) and (silica gel; EtOAc : hexane, 1:7) gave **5p'** as yellow gum (30 mg, 29%). Analytical data for **5p**: FT-IR: $\tilde{\nu}$ =

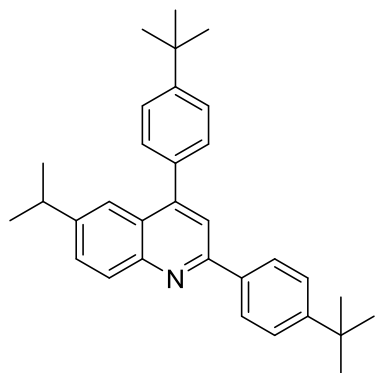
2960, 2922, 2867, 1613, 1593, 1548, 1456, 1358, 1266, 821, 751 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ = 8.17 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.76 (s, 1H), 7.73 (s, 1H), 7.66 - 7.64 (m, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 3.06 - 3.01 (m, 1H), 2.50 (s, 3H), 2.44 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 156.3, 148.8, 147.9, 146.9, 139.3, 138.4, 137.3, 136.0, 130.1, 129.72, 129.67, 129.5, 129.1, 127.6, 125.8, 122.2, 119.5, 34.6, 24.1, 21.6 ppm. Total count of ¹³C is less than expected due to the merging of signals in the aliphatic region. HRMS: Exact mass calculated for C₂₆H₂₆N ([M+H]⁺): 352.2060, Found: 352.2072.



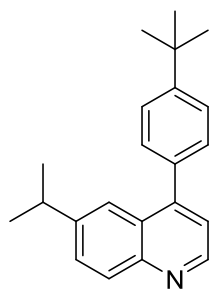
Analytical data for **5p'**: FT-IR: $\tilde{\nu}$ = 2960, 2925, 2867, 1618, 1584, 1501, 1457, 1385, 1185, 1043, 859, 818, 684 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.86 (d, *J* = 4.4 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.69 - 7.66 (m, 1H), 7.44 - 7.42 (m, 2H), 7.37 - 7.32 (m, 3H), 3.07 - 3.00 (m, 1H), 2.48 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 149.4, 148.4, 147.8, 146.7, 138.8, 135.2, 129.7, 129.6, 129.1, 127.1, 122.5, 121.5, 34.6,

24.1, 21.6 ppm. Total count of ¹³C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C₁₉H₂₀N ([M+H]⁺): 262.1590, Found: 262.1591.

2,4-bis(4-(*tert*-butyl)phenyl)-6-isopropylquinoline (5q) and 4-(4-(*tert*-butyl)phenyl)-6-isopropylquinoline (5q'):

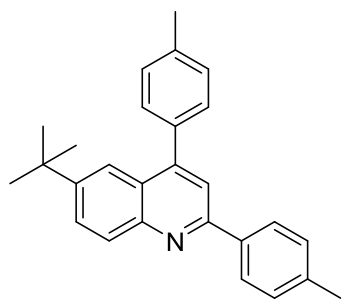


According to GP I, 1-isopropyl-4-nitrosobenzene (60 mg, 0.4 mmol), 4-*tert*-butylstyrene (0.14 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave **5q** as yellow gum (81 mg, 47%) and (silica gel; EtOAc : hexane, 1:10) gave **5q'** as yellow gum (21mg, 17%). Analytical data for **5q**: FT-IR: $\tilde{\nu}$ = 2962, 2902, 2867, 1610, 1590, 1463, 1368, 1273, 1113, 1016, 838, 750, 604 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.17 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.77 - 7.76 (m, 2H), 7.66 - 7.63 (m, 1H), 7.60 - 7.58 (m, 2H), 7.55 - 7.52 (m, 4H), 3.09 - 3.02 (m, 1H), 1.44 (s, 9H), 1.38 (s, 9H), 1.30 (d, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 156.4, 152.5, 151.6, 148.7, 148.1, 146.9, 137.4, 136.0, 130.3, 129.5, 128.9, 127.4, 126.0, 125.7, 125.9, 122.3, 119.7, 35.0, 34.9, 34.6, 31.6, 31.5, 24.2 ppm. HRMS: Exact mass calculated for C₃₂H₃₈N ([M+H]⁺): 436.2999, Found: 436.2992.



Analytical data for **5q'**: FT-IR: $\tilde{\nu}$ = 2961, 2905, 2870, 1613, 1583, 1501, 1460, 1363, 1267, 1106, 1021, 838, 750 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.86 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.66 - 7.63 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.48 - 7.46 (m, 2H), 7.29 (d, *J* = 4.4 Hz, 1H), 3.08 - 3.01 (m, 1H), 1.43 (s, 9H), 1.29 (d, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 151.7, 149.4, 148.2, 147.9, 147.4, 135.5, 130.0, 129.5, 128.9, 127.0, 125.7, 122.5, 121.7, 35.0, 34.6, 31.6, 24.2 ppm. HRMS: Exact mass calculated for C₂₂H₂₆N ([M+H]⁺): 304.2060, Found: 304.2064.

6-*tert*-butyl-2,4-di-*p*-tolylquinoline (5r) and 6-*tert*-butyl-4-(*p*-tolyl)quinoline (5r'):

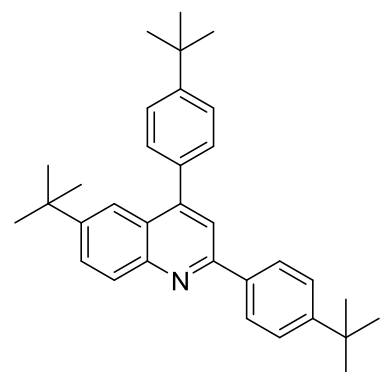


to GP I, 1-*tert*-butyl-4-nitrosobenzene (65 mg, 0.4 mmol), 4-methylstyrene (0.10 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **5r** as yellow gum (65 mg, 45%) and (silica gel; EtOAc : hexane, 1:7) gave **5r'** as yellow gum (24 mg, 22%). Analytical data for **5r**: FT-IR: $\tilde{\nu}$ =

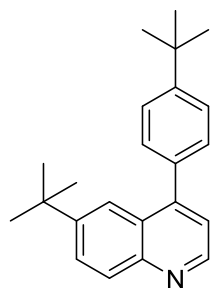
2962, 2927, 2867, 1615, 1590, 1544, 1462, 1389, 1260, 1114, 1020, 820, 746 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.23 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 2.0 Hz, 1H), 7.85 - 7.82 (m, 1H), 7.77 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.39 - 7.32 (m, 4H), 2.50 (s, 3H), 2.44 (s, 3H), 1.36 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 156.3, 149.7, 149.3, 146.9, 139.7, 138.6, 136.6, 135.8, 129.8, 129.6, 129.5, 129.3, 128.8, 127.7, 125.5, 120.9, 119.6, 35.3, 31.4, 21.6 ppm. Total count of ^{13}C is less than expected due to the merging of signals in the aliphatic region. HRMS: Exact mass calculated for $\text{C}_{27}\text{H}_{28}\text{N}$ ($[\text{M}+\text{H}]^+$): 366.2216, Found: 366.2219.

Analytical data for **5r'**: FT-IR: $\tilde{\nu}$ = 2962, 2869, 1614, 1583, 1500, 1372, 1260, 1185, 1022, 859, 817, 724 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.87 (s, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.93 (s, 1H), 7.85 - 7.82 (m, 1H), 7.45 - 7.43 (m, 2H), 7.36 - 7.31 (m, 3H), 2.48 (s, 3H), 1.35 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 149.7, 149.2, 149.0, 146.9, 138.6, 135.4, 129.7, 129.5, 129.1, 128.6, 126.6, 121.6, 121.1, 35.3, 31.4, 21.5 ppm. HRMS: Exact mass calculated for $\text{C}_{20}\text{H}_{22}\text{N}$ ($[\text{M}+\text{H}]^+$): 276.1747, Found: 276.1751.

2,4-bis(4-(tert-butyl)phenyl)-6-tert-butylquinoline (5s) and 4-(4-(tert-butyl)phenyl)-6-tert-butylquinoline (5s'): According to GP I, 1-tert-butyl-4-nitrosobenzene (65 mg, 0.4 mmol), 4-tert-

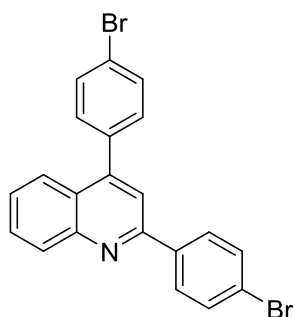


butylstyrene (0.14 g, 0.88 mmol) and $\text{Yb}(\text{OTf})_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave **5s** as yellow gum (76 mg, 42%) and (silica gel; EtOAc : hexane, 1:10) gave **5s'** as yellow gum (20 mg, 16%). Analytical data for **5s**: FT-IR: $\tilde{\nu}$ = 2961, 2905, 2868, 1589, 1514, 1493, 1393, 1201, 1110, 1017, 894, 834, 669 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.24 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 2.0 Hz, 2H), 7.85 - 7.82 (m, 1H), 7.79 (s, 1H), 7.61 - 7.54 (m, 6H), 1.44 (s, 9H), 1.39 (s, 9H), 1.38 (s, 9H) ppm. ^{13}C NMR (151 MHz, CDCl_3) δ = 156.5, 152.6, 151.6, 149.1, 147.4, 137.2, 135.9, 129.6, 129.5, 128.5, 127.5, 126.0, 125.7, 125.4, 120.8, 119.7, 35.3, 35.0, 34.9, 31.6, 31.5, 31.4 ppm. Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for $\text{C}_{33}\text{H}_{40}\text{N}$ ($[\text{M}+\text{H}]^+$): 450.3155, Found: 450.3172.



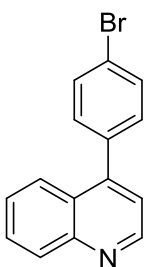
Analytical data for **5s'**: FT-IR: $\tilde{\nu}$ = 2962, 2909, 2870, 1613, 1583, 1500, 1372, 1266, 1111, 1023, 839, 771 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.87 (d, J = 4.4 Hz, 1H), 8.11 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 2.0 Hz, 1H), 7.84 - 7.81 (m, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 4.4 Hz, 1H), 1.43 (s, 9H), 1.36 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 151.7, 149.52, 149.45, 148.6, 147.4, 135.5, 129.49, 129.45, 128.4, 126.6, 125.7, 121.7, 121.1, 35.3, 35.0, 31.6, 31.4 ppm. HRMS: Exact mass calculated for $\text{C}_{23}\text{H}_{28}\text{N}$ ($[\text{M}+\text{H}]^+$): 318.2216, Found: 318.2206.

2,4-bis(4-bromophenyl)quinoline (5t) and 4-(4-bromophenyl)quinoline (5t')^q: According to



GP I, nitrosobenzene (43 mg, 0.40 mmol), 4-bromo styrene (0.16 g, 0.88 mmol) and $\text{Yb}(\text{OTf})_3$ (74 mg, 0.12 mmol) were reacted for 48 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:40) gave **5t** as yellow gum (43 mg, 25%) and (silica gel; EtOAc : hexane, 1:10) gave **5t'** as yellow gum (12 mg, 11%).

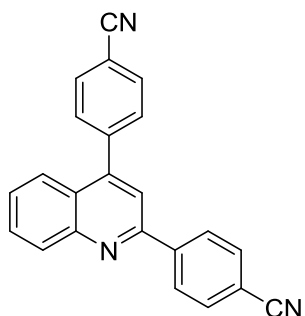
Analytical data for **5t**: FT-IR = 2958, 2924, 2851, 1596, 1542, 1485, 1355, 1072, 825, 764, 578, 470 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.24 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.78 – 7.74 (m, 2H), 7.71 – 7.65 (m, 4H), 7.51 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 155.7, 148.8,



148.6, 138.3, 137.2, 132.3, 132.1, 131.3, 130.2, 129.4, 127.1, 125.7, 125.5, 124.4, 123.2, 119.0 ppm. Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for $\text{C}_{21}\text{H}_{14}\text{Br}_2\text{N}$ ($[\text{M}+\text{H}]^+$): 437.9488, Found: 437.9484.

Analytical data for **5t'**: ^1H NMR (400 MHz, CDCl_3) δ = 8.96 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.41 – 7.38 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 149.0, 148.8, 136.7, 132.2, 131.3, 130.4, 129.2, 127.6, 125.9, 123.5, 121.4 ppm. Total count of ^{13}C is less than expected due to the merging of signals in the aromatic region.

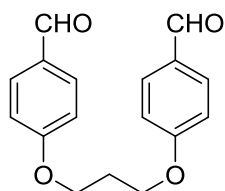
4,4'-(quinoline-2,4-diyl)dibenzonitrile (5u): According to GP II, nitrosobenzene (43 mg, 0.40



mmol), 4-cyano styrene (0.11 g, 0.88 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were reacted for 5 days in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **5u** as yellow gum (13 mg, 10%). Analytical data for **5u**: FT-IR = 2960, 2930, 2852, 2228, 1595, 1499, 1451, 1278, 1188, 1076, 844, 747, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.35 – 8.32 (m, 3H), 7.89 – 7.78 (m, 7H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.57 (m, 1H) ppm. ¹³C

NMR (101 MHz, CDCl₃) δ = 154.6, 148.4, 142.7, 132.9, 132.8, 131.0, 130.5, 130.4, 128.5, 128.2, 119.1, 118.8, 118.5, 113.5, 113.1 ppm. Total count of ¹³C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C₂₃H₁₄N₃ ([M+H]⁺): 332.1182, Found: 332.1177.

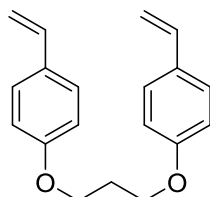
4,4'-(propane-1,3-diylbis(oxy))dibenzaldehyde: 4-hydroxy benzaldehyde (1.47 g, 12.05 mmol)



was added to the solution of 1,3-dibromopropane (1.0 g, 5.00 mmol) in DMF (5 mL) followed by the addition of K₂CO₃ (2.08 g, 15.07 mmol). The reaction mixture was heated at 100 °C for 12 h. After that, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with cold

water (70 mL) and extracted with DCM (3 X 50 mL). The organic layer was washed with brine solution (1 X 50 mL), dried over anhydrous Na₂SO₄ and evaporated under vacuum to provide 4,4'-(propane-1,3-diylbis(oxy))dibenzaldehyde as a light yellow solid (1.28 g, 90%) which was used for the next step. ¹H NMR (600 MHz, CDCl₃) δ = 9.87 (s, 2H), 7.82 (d, *J* = 8.4 Hz, 4H), 7.01 (d, *J* = 9.0 Hz, 4H), 4.25 (t, *J* = 6.0 Hz, 4H), 2.36 - 2.32 (m, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 191.0, 163.9, 132.2, 130.2, 114.9, 64.7, 29.1 ppm.

1,3-bis(4-vinylphenoxy)propane (6): Methyltriphenylphosphonium iodide (2.19 g, 5.41 mmol)

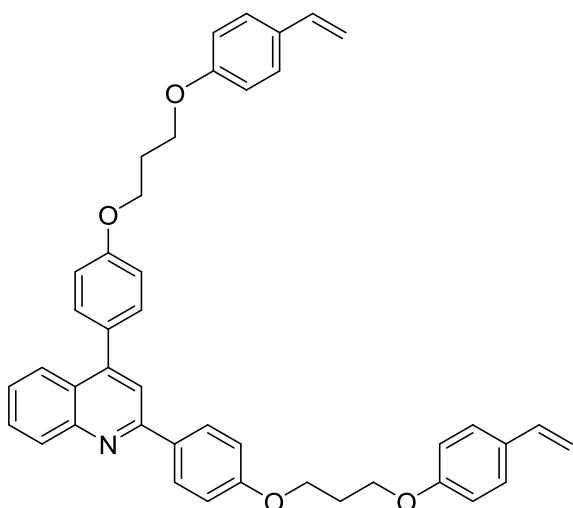


and sodium hydride (60% in mineral oil) (0.81 g (0.49 g), 20.29 mmol) were taken in 100 mL R.B. under argon. A solution of 4,4'-(propane-1,3-diylbis(oxy))dibenzaldehyde (1.28 g, 4.51 mmol) in dry THF (20 mL) was added slowly to the mixture at 0 °C. Then the reaction mixture was stirred at room temperature for 12 h. Then the reaction was quenched with cold water (50

mL) and the mixture was extracted with DCM (3 X 50 mL). The organic layer was washed with

brine solution (1X50 mL), dried over anhydrous Na₂SO₄ and evaporated under vacuum. The column chromatography of the crude product (silica gel; EtOAc : hexane, 1:50) gave **6** as white solid (0.33 g, 26%). FT-IR: $\tilde{\nu}$ = 2955, 2922, 2853, 1603, 1509, 1468, 1378, 1289, 1242, 1176, 1065, 992, 903, 836 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ = 7.34 (d, *J* = 8.4 Hz, 4H), 6.87 (d, *J* = 9.0 Hz, 4H), 6.69 - 6.64 (m, 2H), 5.61 (d, *J* = 17.4 Hz, 2H), 5.13 (d, *J* = 10.8 Hz, 2H), 4.17 (t, *J* = 6.0 Hz, 4H), 2.29 - 2.25 (m, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 158.8, 136.4, 130.7, 127.6, 114.7, 111.8, 64.6, 29.5 ppm.

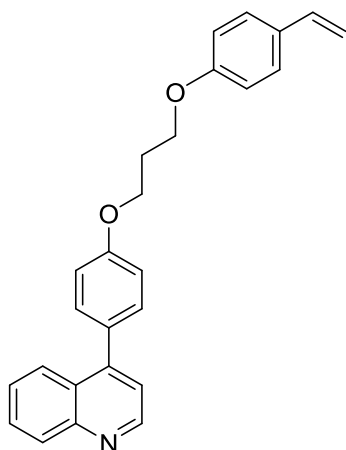
2,4-bis(4-(3-(4-vinylphenoxy)propoxy)phenyl)quinoline (7a) and 4-(4-(3-(4-vinylphenoxy)propoxy)phenyl)quinoline (7b):



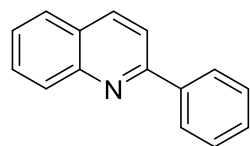
Nitrosobenzene (43 mg, 0.40 mmol) and Yb(OTf)₃ (37 mg, 0.06 mmol) were successively added to a solution of styrene derivative **6** (0.25 g, 0.88 mmol) in dry DCE (3 mL). Then the reaction mixture was refluxed for 36 h under argon atmosphere. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (20 mL) and the mixture was extracted with DCM (3 X 20 mL). The combined organic layer was washed with brine

solution (1 X 30 mL), dried over anhydrous Na₂SO₄ and evaporated under vacuum. Column chromatography of the crude product (silica gel; EtOAc : hexane, 1:10) gave **7a** as yellow gum (75 mg, 30%) and (silica gel; EtOAc : hexane, 1:4) gave **7b** as yellow gum (34 mg, 22%). Analytical data for **7a**: FT-IR: $\tilde{\nu}$ = 2958, 2923, 2879, 2848, 1606, 1544, 1509, 1498, 1401, 1288, 1175, 1059, 833 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.25 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.73 - 7.70 (m, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.47 - 7.43 (m, 1H), 7.37 - 7.34 (m, 4H), 7.10 - 7.05 (m, 4H), 6.91 - 6.88 (m, 4H), 6.70 - 6.62 (m, 2H), 5.64 - 5.59 (m, 2H), 5.15 - 5.11 (m, 2H), 4.29 - 4.18 (m, 8H), 2.37 - 2.28 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 160.6, 159.5, 158.8, 156.3, 136.41, 136.38, 131.0, 130.82, 130.78, 130.7, 130.0, 129.4, 127.6, 126.3, 126.0, 125.9, 119.2, 115.1, 114.9, 114.73, 114.72, 111.9, 111.8, 64.81, 64.80, 64.65, 64.56, 29.52, 29.50 ppm. Total count of ¹³C is less than expected due to the merging of signals in the aromatic region. HRMS: Exact mass calculated for C₄₃H₄₀NO₄ ([M+H]⁺): 634.2952, Found: 634.2945.

Analytical data for **7b**: FT-IR: $\tilde{\nu}$ = 2961, 2905, 2870, 1613, 1583, 1501, 1460, 1363, 1267, 1106, 1021, 838, 750 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.92 (d, J = 4.8 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.80 - 7.76 (m, 1H), 7.58 - 7.54 (m, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.40 - 7.34 (m, 3H), 7.09 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.70 - 6.63 (m, 1H), 5.62 (d, J = 17.6 Hz, 1H), 5.13 (d, J = 10.8 Hz, 1H), 4.29 - 4.20 (m, 4H), 2.36 - 2.30 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 159.8, 158.8, 148.6, 147.2, 136.4, 131.1, 130.8, 130.4, 130.0, 128.8, 128.7, 127.6, 127.3, 127.2, 126.3, 121.4, 115.0, 114.7, 111.9, 64.8, 64.5, 29.5 ppm. HRMS: Exact mass calculated for $\text{C}_{26}\text{H}_{24}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 382.1802, Found: 382.1818.



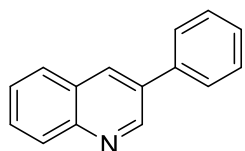
2-phenylquinoline (7c):^sAccording to GP I, nitrosobenzene (43 mg, 0.40 mmol), trans β -methyl styrene (0.10 g, 0.88 mmol) and $\text{Yb}(\text{OTf})_3$ (37 mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave **7c** as yellow gum (18 mg, 22%) ^1H NMR (400 MHz, CDCl_3) δ = 8.23 (d, J = 8.4 Hz, 1H), 8.19 – 8.16 (m, 3H), 7.89 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.76 – 7.71 (m 1H), 7.56 – 7.52 (m, 3H), 7.49 – 7.45 (m, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 157.6, 148.5, 139.9, 137.0, 129.94, 129.88, 129.5, 129.1, 127.8, 127.7, 127.4, 126.5, 119.3 ppm.



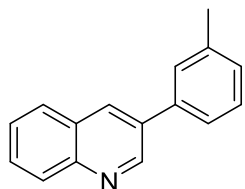
General Procedure for the Synthesis of 3-substituted quinolines (II):

Freshly prepared nitrosoarenes (1 equiv.) and $\text{Cu}(\text{OTf})_2$ (15 mol%) were successively added to a solution of styrene oxide derivatives (2 equiv.) in dry DCE (3 mL). Then the reaction mixture was refluxed for 20 - 28 h under argon atmosphere. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water (1X20 mL) and the reaction mixture was extracted with DCM (3X20 mL). The organic layer was washed with brine solution (1X30 mL) and evaporated under vacuum. The crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.

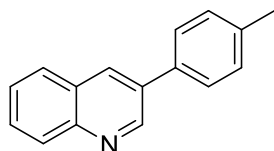
3-phenylquinoline (9a):^t According to GP II, nitrosobenzene (35 mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9a** as yellow gum (42 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ = 9.19 (d, *J* = 2.4 Hz, 1H), 8.32 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 - 7.71 (m, 3H), 7.61 - 7.57 (m, 1H), 7.55 - 7.51 (m, 2H), 7.46 - 7.43 (m, 1H) ppm. HRMS: Exact mass calculated for C₁₅H₁₂N ([M+H]⁺): 206.0964, Found: 206.0974.



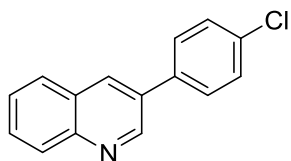
3-(m-tolyl)quinoline (9b):^u According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 3-methylstyrene oxide (88 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9b** as yellow gum (39 mg, 54%). ¹H NMR (400 MHz, CDCl₃) δ = 9.19 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 2.0 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.77 - 7.74 (m, 1H), 7.63 - 7.60 (m, 1H), 7.53 - 7.51 (m, 2H), 7.45 - 7.41 (m, 1H), 7.28 (s, 1H), 2.48 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₆H₁₄N ([M+H]⁺): 220.1121, Found: 220.1114.



3-(p-tolyl)quinoline (9c):^u According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 4-methylstyrene oxide (88 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9c** as yellow gum (49 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ = 9.19 (d, *J* = 1.2 Hz, 1H), 8.36 (d, *J* = 1.6 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77 - 7.73 (m, 1H), 7.63 - 7.59 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 2.45 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₆H₁₄N ([M+H]⁺): 220.1121, Found: 220.1122.

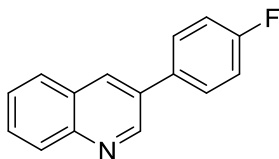


3-(4-chlorophenyl)quinoline (9d):^t According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 4-chlorostyrene oxide (0.10 g, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9d** as yellow gum (44 mg, 56%). ¹H NMR (400 MHz, CDCl₃) δ = 9.15 (d, *J* = 2.0 Hz, 1H), 8.33 (d, *J* = 2.0 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz,



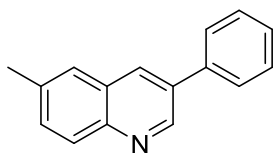
1H), 7.78 - 7.74 (m, 1H), 7.66 - 7.60 (m, 3H), 7.52 - 7.49 (m, 2H) ppm. HRMS: Exact mass calculated for C₁₅H₁₁NCl ([M+H]⁺): 240.0575, Found: 240.0578.

3-(4-fluorophenyl)quinoline (9e):^t According to GP II, nitrosobenzene (35 mg, 0.33 mmol), 4-



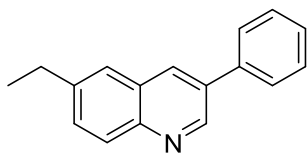
fluorostyrene oxide (91 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 15 mol %, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9e** as yellow gum (45 mg, 61%). ¹H NMR (400 MHz, CDCl₃) δ = 9.16 (d, *J* = 2.0 Hz, 1H), 8.36 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.80 - 7.76 (m, 1H), 7.70 - 7.62 (m, 3H), 7.24 - 7.22 (m, 2H) ppm. HRMS: Exact mass calculated for C₁₅H₁₁NF ([M+H]⁺): 224.0870, Found: 224.0869.

6-methyl-3-phenylquinoline (9f):^t According to GP II, 1-methyl-4-nitrosobenzene (40 mg, 0.33



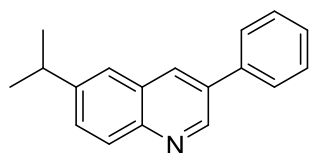
mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9f** as yellow gum (45 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ = 9.12 (d, *J* = 2.0 Hz, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.72 - 7.68 (m, 3H), 7.61 - 7.58 (m, 1H), 7.56 - 7.52 (m, 2H), 7.47 - 7.43 (m, 1H), 2.58 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₆H₁₄N ([M+H]⁺): 220.1121, Found: 220.1124.

6-ethyl-3-phenylquinoline (9g):^t According to GP II, 1-ethyl-4-nitrosobenzene (45 mg, 0.33



mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9g** as yellow gum (42 mg, 55%). ¹H NMR (400 MHz, CDCl₃) δ = 9.13 (d, *J* = 2.0 Hz, 1H), 8.32 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.73 - 7.69 (m, 3H), 7.64 - 7.61 (m, 1H), 7.55 - 7.52 (m, 2H), 7.47 - 7.43 (m, 1H), 2.88 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.6 Hz, 3H) ppm. HRMS: Exact mass calculated for C₁₇H₁₆N ([M+H]⁺): 234.1277, Found: 234.1280.

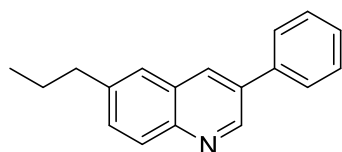
6-isopropyl-3-phenylquinoline (9h):[†] According to GP II, 1-isopropyl-4-nitrosobenzene (49 mg,



0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7)

gave **9h** as yellow gum (55 mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ = 9.12 (d, *J* = 2.0 Hz, 1H), 8.27 (d, *J* = 2.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.72 - 7.71 (m, 2H), 7.68 (s, 1H), 7.65 - 7.63 (m, 1H), 7.55 - 7.51 (m, 2H), 7.45 - 7.42 (m, 1H), 3.16 - 3.09 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 6H) ppm. HRMS: Exact mass calculated for C₁₈H₁₈N ([M+H]⁺): 248.1434, Found: 248.1429.

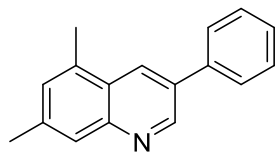
3-phenyl-6-propylquinoline (9i): According to GP II, 1-nitroso-4-propylbenzene (49 mg, 0.33



mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 22 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7)

gave **9i** as yellow gum (57 mg, 70%). FT-IR: $\tilde{\nu}$ = 2959, 2929, 2871, 1600, 1494, 1455, 1349, 1260, 1026, 800, 627 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ = 9.13 (d, *J* = 1.8 Hz, 1H), 8.33 (d, *J* = 1.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.68 (s, 1H), 7.62 - 7.61 (m, 1H), 7.55 - 7.53 (m, 2H), 7.47 - 7.44 (m, 1H), 2.81 (t, *J* = 7.8 Hz, 2H), 1.79 - 1.75 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 148.1, 144.9, 142.5, 137.7, 134.21, 134.15, 132.0, 129.5, 128.5, 128.4, 128.1, 127.6, 126.6, 38.2, 24.5, 14.0 ppm. HRMS: Exact mass calculated for C₁₈H₁₈N ([M+H]⁺): 248.1434, Found: 248.1433.

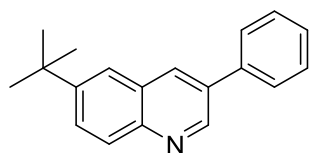
5,7-dimethyl-3-phenylquinoline (9j):[†] According to GP II, 1,3-dimethyl-5-nitrosobenzene (45



mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 28 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave

9j as yellow gum (45 mg, 58%). ¹H NMR (400 MHz, CDCl₃) δ = 9.13 (d, *J* = 2.4 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 7.82 (s, 1H), 7.73 - 7.71 (m, 2H), 7.56 - 7.52 (m, 2H), 7.46 - 7.42 (m, 1H), 7.28 (s, 1H), 2.72 (s, 3H), 2.55 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₇H₁₆N ([M+H]⁺): 234.1277, Found: 234.1280.

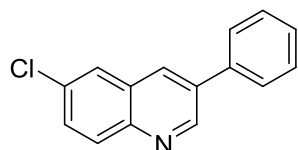
6-(*tert*-butyl)-3-phenylquinoline (9k):^v According to GP II, 1-(*tert*-butyl)-4-nitrosobenzene (54



mg, 0.33 mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7)

gave **9k** as yellow gum (56 mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ = 9.13 (s, 1H), 8.35 (d, *J* = 1.6 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.86 - 7.83 (m, 2H), 7.73 - 7.71 (m, 2H), 7.55 - 7.52 (m, 2H), 7.47 - 7.43 (m, 1H), 1.45 (s, 9H) ppm. HRMS: Exact mass calculated for C₁₉H₂₀N ([M+H]⁺): 262.1590, Found: 262.1593.

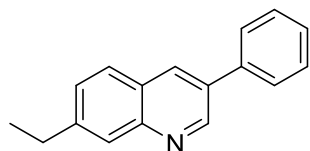
6-chloro-3-phenylquinoline (9l):^u According to GP II, 1-chloro-4-nitrosobenzene (47 mg, 0.33



mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7)

gave **9l** as yellow gum (29 mg, 37%). ¹H NMR (400 MHz, CDCl₃) δ = 9.17 (d, *J* = 2.0 Hz, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 8.10 (d, *J* = 9.2 Hz, 1H), 7.87 (d, *J* = 2.4 Hz, 1H), 7.71 - 7.65 (m, 3H), 7.56 - 7.52 (m, 2H), 7.48 - 7.44 (m, 1H) ppm. HRMS: Exact mass calculated for C₁₅H₁₁NCl ([M+H]⁺): 240.0575, Found: 240.0574.

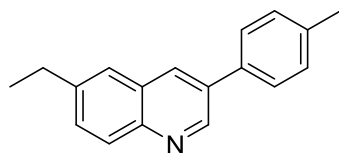
7-ethyl-3-phenylquinoline (9m):^w According to GP II, 1-ethyl-3-nitrosobenzene (45 mg, 0.33



mmol), styrene oxide (79 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7)

gave **9m** as yellow gum (41 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ = 9.15 (d, *J* = 2.4 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.02 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.72 - 7.70 (m, 2H), 7.55 - 7.43 (m, 4H), 2.90 (q, *J* = 7.6 Hz, 2H), 1.37 (t, *J* = 7.6 Hz, 3H) ppm. HRMS: Exact mass calculated for C₁₇H₁₆N ([M+H]⁺): 234.1277, Found: 234.1279.

6-ethyl-3-(*p*-tolyl)quinoline (9n): According to GP II, 1-ethyl-4-nitrosobenzene (45 mg, 0.33

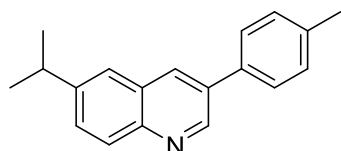


mmol), 4-methyl styrene oxide (88 mg, 0.66 mmol) and Cu(OTf)₂ (18 mg, 0.05 mmol) were reacted for 20 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7)

gave **9n** as yellow gum (52 mg, 64%). FT-IR: $\tilde{\nu}$ = 2964, 2927, 2871, 1604, 1516, 1455, 1374, 1261, 1040, 914, 834, 724 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 9.11 (d, *J* = 2.0 Hz, 1H), 8.29 (d,

$J = 2.0$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.67 (s, 1H), 7.63 - 7.60 (m, 3H), 7.34 (d, $J = 8.0$ Hz, 2H), 2.87 (q, $J = 7.6$ Hz, 2H), 2.44 (s, 3H), 1.36 (t, $J = 7.6$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 148.1, 144.8, 143.9, 138.5, 134.8, 134.1, 133.8, 131.5, 130.2, 128.6, 128.2, 127.4, 125.7, 29.1, 21.4, 15.5$ ppm. HRMS: Exact mass calculated for $\text{C}_{18}\text{H}_{18}\text{N}$ ($[\text{M}+\text{H}]^+$): 248.1434, Found: 248.1435.

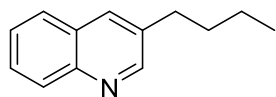
6-isopropyl-3-(p-tolyl)quinoline (9o): According to GP II, 1-isopropyl-4-nitrosobenzene (49 mg,



0.33 mmol), 4-methyl styrene oxide (88 mg, 0.66 mmol) and $\text{Cu}(\text{OTf})_2$ (18 mg, 0.05 mmol) were reacted for 22 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel;

EtOAc : hexane, 1:7) gave **9o** as yellow gum (57 mg, 66%). FT-IR: $\tilde{\nu} = 2960, 2927, 2872, 1607, 1516, 1256, 1128, 817, 748$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) $\delta = 9.12$ (d, $J = 2.4$ Hz, 1H), 8.36 (d, $J = 2.0$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.71 – 7.67 (m, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 7.6$ Hz, 2H), 3.17 - 3.10 (m, 1H), 2.44 (s, 3H), 1.37 (d, $J = 6.8$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 148.9, 147.4, 144.0, 138.8, 134.7, 134.4, 134.2, 130.7, 130.3, 128.7, 127.6, 127.4, 124.3, 34.4, 24.0, 21.4$ ppm. HRMS: Exact mass calculated for $\text{C}_{19}\text{H}_{20}\text{N}$ ($[\text{M}+\text{H}]^+$): 262.1590, Found: 262.1592.

3-butylquinoline (9p):^s According to GP II, nitrosobenzene (43 mg, 0.4 mmol), 1,2-epoxyhexane



(80 mg, 0.8 mmol) and $\text{Cu}(\text{OTf})_2$ (22 mg, 0.06 mmol) were reacted for 24 h in dry DCE (3 mL) and column chromatography of the crude product

(neutral alumina; EtOAc : hexane, 1:30) gave **9p** as yellow gum (8 mg, 11%). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.78$ (d, $J = 2.0$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.95 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.67 (t, $J = 8.0$ Hz, 1H), 7.53 (t, $J = 8.0$ Hz, 1H), 2.83 – 2.67 (m, 2H), 1.77 – 1.67 (m, 2H), 1.44 – 1.38 (m, 2H), 1.00 – 0.94 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 151.8, 146.4, 135.7, 134.9, 129.0, 128.9, 128.5, 127.5, 126.9, 33.4, 33.1, 22.5, 14.1$ ppm.

General Procedure for preparation of nitrone 10 and its reaction with 2-phenylacetaldehyde or styrene oxide (GP III): Formalin (37%, 1eq) solution was added to a mixture of nitrobenzene derivatives (1eq), ethanol, water and NH_4Cl (1eq). After the mixture was stirred 15 min, Zn powder

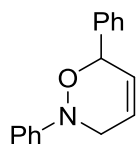
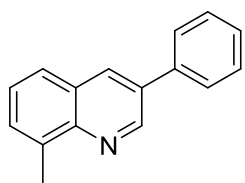
(2 eq) was added under 0 °C. The reaction mixture was stirred overnight at room temperature. Then the solid was filtered, the filtrate was extracted with DCM (3X30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was

dissolved in DCE. 2-phenylacetaldehyde (1eq) or styrene epoxide (1 eq) and Cu(OTf)₂ (15 mol%) were added and the mixture was refluxed for 24 h. Then the solvent was evaporated under reduced pressure. The reaction mixture was diluted with water and the reaction mixture was extracted with DCM. The organic layer was washed with brine solution and evaporated under vacuum. The crude mixture was subjected to column chromatography (silica gel) to afford analytically pure products.

3-phenylquinoline (9a): According to the GP III: 37% aq. Formalin (0.11 g (40 mg), 1.35 mmol), nitrobenzene (0.17 g, 1.35 mmol), ethanol (5 mL), water (5 mL) and NH₄Cl (72 mg, 1.35 mmol), Zn powder (0.18 g, 2.70 mmol), 2-phenylacetaldehyde (0.16 g, 1.35 mmol) and Cu(OTf)₂ (73 mg, 0.20 mmol) were reacted for 24 h in dry DCE (5 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9a** as yellow gum (0.14 g, 52%) and styrene oxide (0.16 g, 1.35 mmol) and Cu(OTf)₂ (73 mg, 0.20 mmol) were reacted for 24 h in dry DCE (5 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9a** as yellow gum (0.20 g, 73%).

8-methyl-3-phenylquinoline (9q):^x According to the GP III: 37% aq. Formalin (0.11 g (40 mg), 1.35 mmol), 1-methyl-2-nitrobenzene (0.19 g, 1.35 mmol), ethanol (5 mL), water (5 mL) and NH₄Cl (72 mg, 1.35 mmol), Zn powder (0.18 g, 2.70 mmol), 2-phenylacetaldehyde (0.16 g, 1.35 mmol) and Cu(OTf)₂ (73 mg, 0.20 mmol) were reacted for 24 h in dry DCE (5 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:7) gave **9q** as yellow gum (92 mg, 31%). Analytical data for **9q**: ¹H NMR (400 MHz, CDCl₃) δ = 9.25 (s, 1H), 8.34 (d, *J* = 2.0 Hz, 1H), 7.77 – 7.72 (m, 3H), 7.61 – 7.52 (m, 3H), 7.50 – 7.43 (m, 2H), 2.88 (s, 3H) ppm. HRMS: Exact mass calculated for C₁₆H₁₄N ([M+H]⁺): 220.1121, Found: 220.1135.

2,6-diphenyl-3,6-dihydro-2H-1,2-oxazine:^y According to GP I, nitrosobenzene (43 mg, 0.4 mmol), phenylbutadiene (0.11 g, 0.88 mmol) and Yb(OTf)₃ (37mg, 0.06 mmol) were reacted for 36 h in dry DCE (3 mL) and column chromatography of the crude product (silica gel; EtOAc : hexane, 1:30) gave oxazine as yellow gum (29 mg, 31%). ¹H NMR (400 MHz, CDCl₃) δ = 7.40 – 7.38 (m, 2H), 7.32 – 7.25 (m, 3H), 7.22 – 7.18 (m, 2H), 7.04 – 7.02 (m, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.08 – 5.99 (m, 2H), 5.55 – 5.54 (m, 1H), 3.93 – 3.79 (m, 2H)

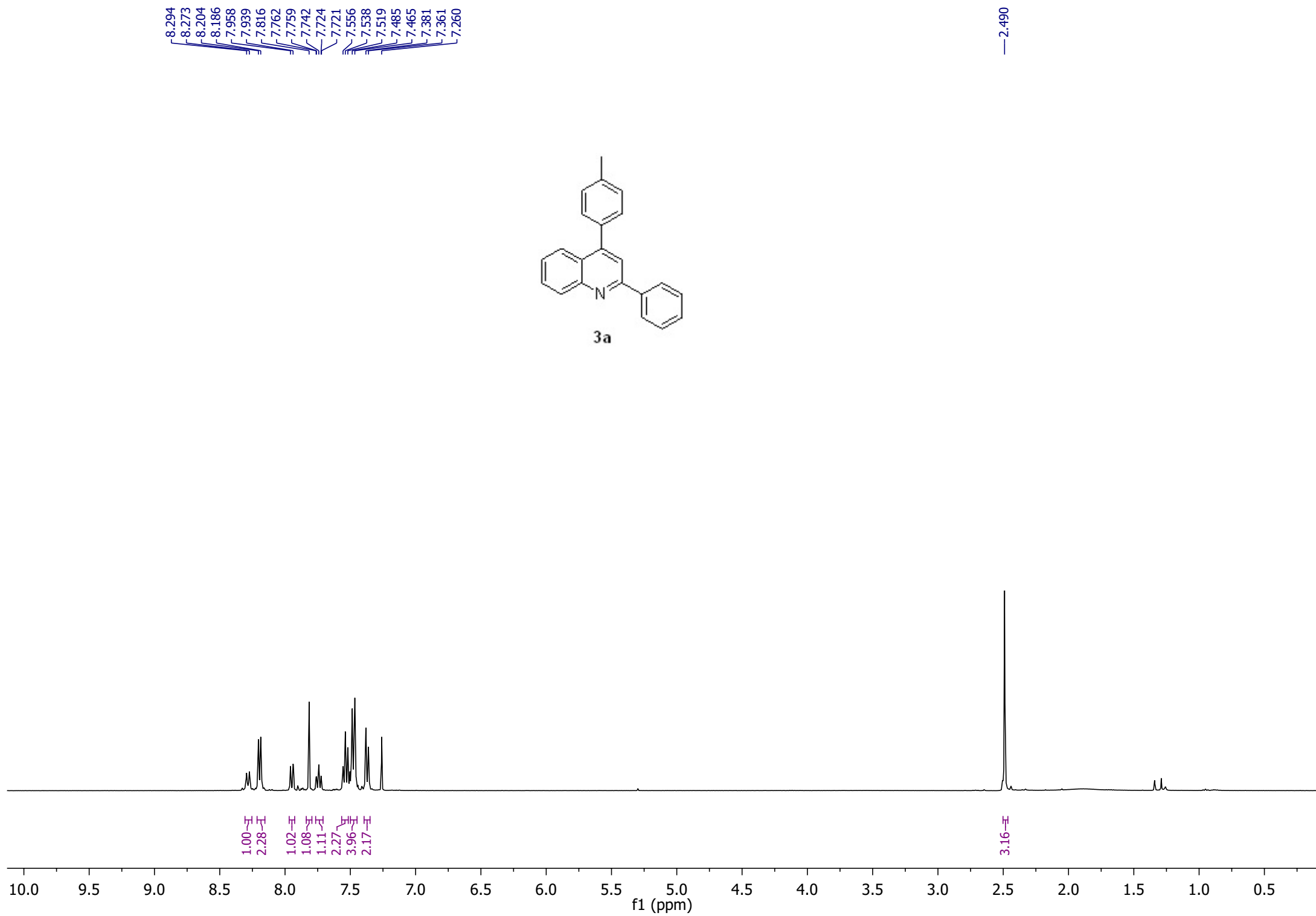


ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 150.5, 139.1, 129.2, 129.0, 128.7, 128.6, 128.4, 124.0, 122.4, 116.0, 80.1, 51.8 ppm.

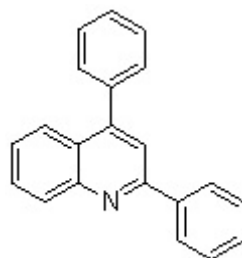
References:

- (a) J. Yang, X. Meng, K. Lu, Z. Lu, M. Huang, C. Wang and F. Sun, *RSC Adv.*, 2018, **8**, 31603.
- (b) W. Ahmed, S. Zhang, X. Yu, Y. Yamamotoa and M. Bao, *Green Chem.*, 2018, **20**, 261.
- (c) V. Fasano, J. E. Radcliffe and M. J. Ingleson, *Organometallics*, 2017, **36**, 1623.
- (d) D. J. Park, T. D. Fulmer and C. F. Beam, *J. Heterocyclic Chem.*, 1981, **18**, 649.
- (e) A. O. Adeloye and M. J. Mphahlele, *J. Chem. Res.*, 2014, **38(4)**, 254.
- (f) A. de Andrade, G. C. dos Santos and L. C. da Silva-Filho, *J. Heterocyclic Chem.*, 2015, **52**, 273.
- (g) J. Zhu, W. Hu, S. Sun, J. T. Yu and J. Cheng, *Adv. Synth. Catal.*, 2017, **359**, 3725.
- (h) M. Rehan, G. Hazra and P. Ghorai, *Org. Lett.*, 2015, **17**, 1668.
- (i) D. Jung, S. H. Jang, T. Yim and J. Kim, *Org. Lett.*, 2018, **20(20)**, 6436.
- (j) Z. Y. Wang, Q. N. Ma, R. H. Lia and L. X. Shao, *Org. Biomol. Chem.*, 2013, **11(45)**, 7899.
- (k) J. W. Yuan, L. R. Yang, P. Maoa and L. B. Qu, *Org. Chem. Front.*, 2017, **4(4)**, 545.
- (l) W. Li, J. J. Gao, Y. Zhang.; W. Tang, H. Lee, K. R. Fandrick, B. Lu and C. H. Senanayake, *Adv. Synth. Catal.*, 2011, **353(10)**, 1671.
- (m) M. K. Sahoo, G. Jaiswal, J. Rana and E. Balaraman, *Chem. Eur. J.*, 2017, **23(57)**, 14167.
- (n) M. Phanindrudu, S. B. Wakade, D. K. Tiwari, P. R. Likhar and D. K. Tiwari, *J. Org. Chem.*, 2018, **83**, 9137.
- (o) R. R. Mondal, S. Khamarui and D. K. Maiti, *ACS Omega*, 2016, **1(2)**, 251.
- (p) J. Cen, J. Li, Y. Zhang, Z. Zhu, S. Yang and H. Jiang, *Org. Lett.*, 2018, **20**, 4434.
- (q) X. Bi, T. Tang, X. Meng, M. Gou, X. Liu and P. Zhao, *Catal. Sci. Technol.*, 2020, **10**, 360
- (r) N. Bas'ilio, T. Garnier, J. Av'ó, M. Danel, S. Chassaing and F. Pina, *RSC Adv.*, 2016, **6**, 69698.
- (s) S. Ruch, T. Irrgang and R. Kempe, *Chem. Eur. J.*, 2014, **20**, 13279.
- (t) Y. Zhang, M. Wang, P. Li and L. Wang, *Org. Lett.*, 2012, **14**, 2206.
- (u) R. K. Saunthwal, M. Patel and A. K. Verma, *J. Org. Chem.*, 2016, **81**, 6563.
- (v) R. Yan, X. Liu, C. Pan, X. Zhou, X. Li, X. Kang and G. Huang, *Org. Lett.*, 2013, **15**, 4876.

- (w) H. Sharghi, M. Aberi, M. Khataminejad and P. Shiri, *Beilstein J. Org. Chem.*, 2017, **13**, 1977.
- (x) P. Zhang, Y. Yang, Z. Chen, Z. Xu, X. Xu, Z. Zhou, X. Yu and W. Yi, *Adv. Synth. Catal.*, 2019, **361**, 3002.
- (y) N. Yasukawa, M. Kuwata, T. Imai, Y. Monguchi, H. Sajiki and Y. Sawama, *Green Chem.*, 2018, **20**, 4409.

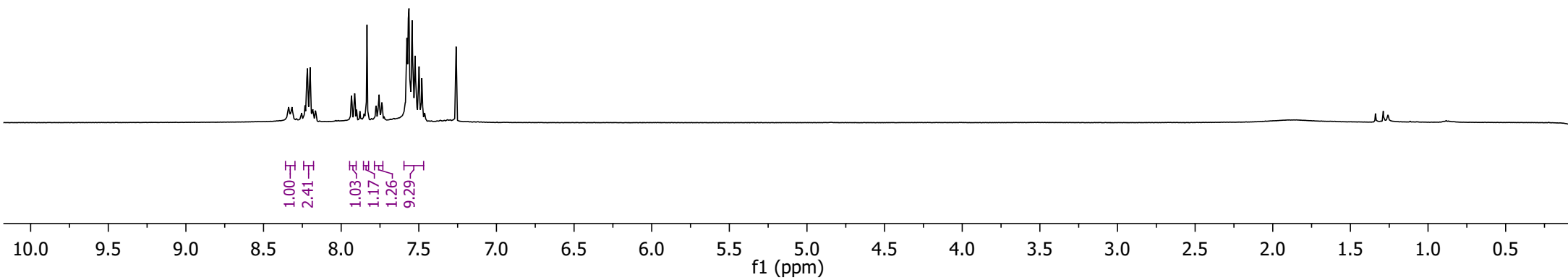


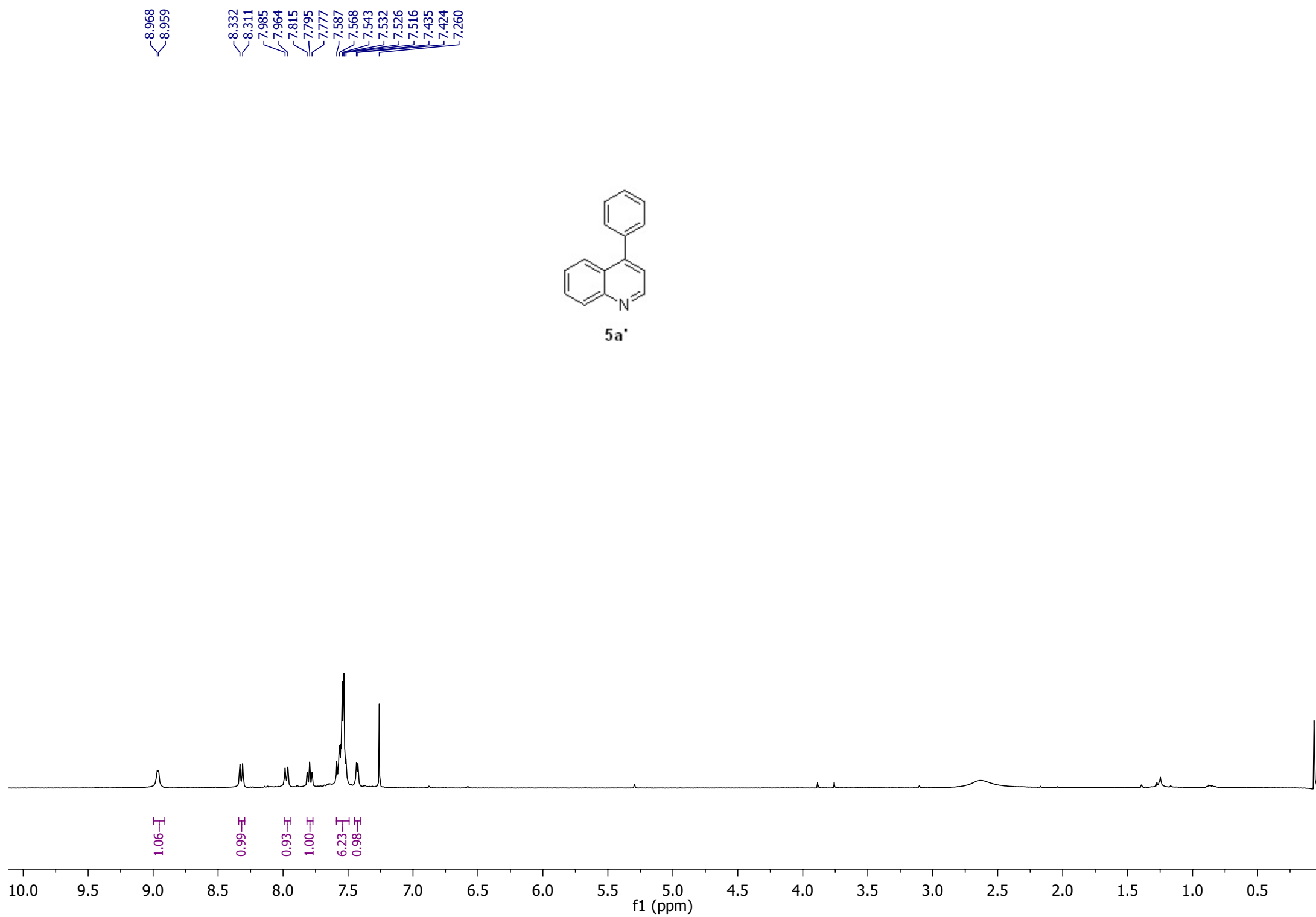
8.338
8.317
8.233
8.221
8.218
8.200
8.183
7.934
7.913
7.833
7.776
7.773
7.759
7.756
7.738
7.735
7.575
7.568
7.563
7.543
7.524
7.498
7.481
7.462
7.260



5a

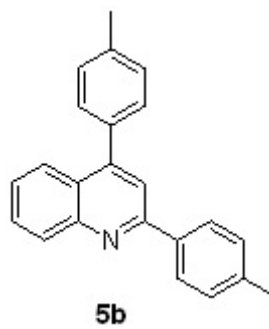
1.00
2.41
1.03
1.17
1.26
9.29





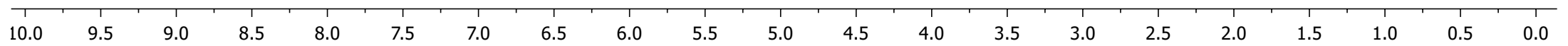
8.282
8.262
8.116
8.095
7.941
7.938
7.920
7.918
7.796
7.747
7.744
7.730
7.727
7.723
7.706
7.483
7.479
7.464
7.459
7.445
7.375
7.356
7.349
7.329
7.260

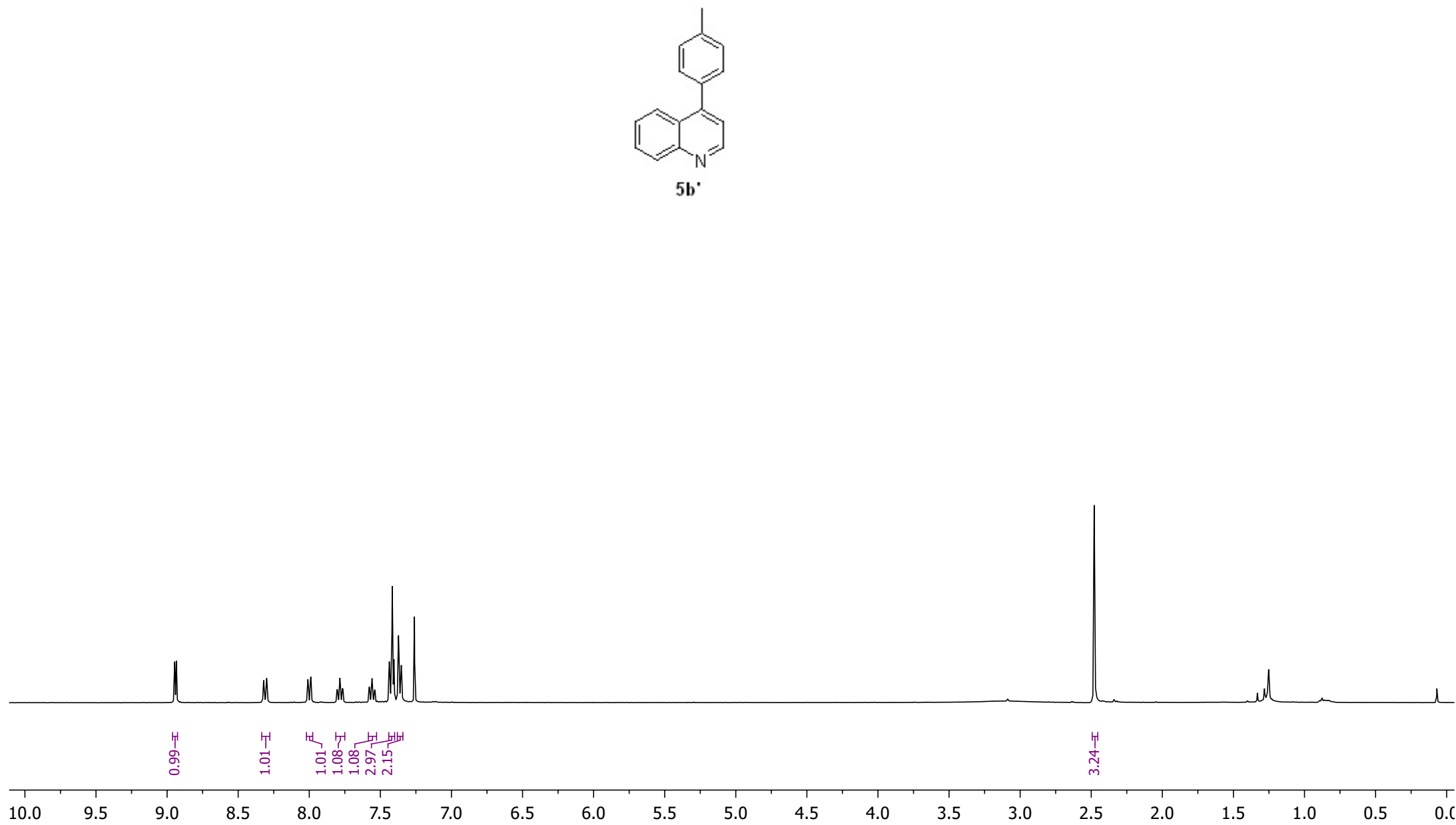
2.488
2.440

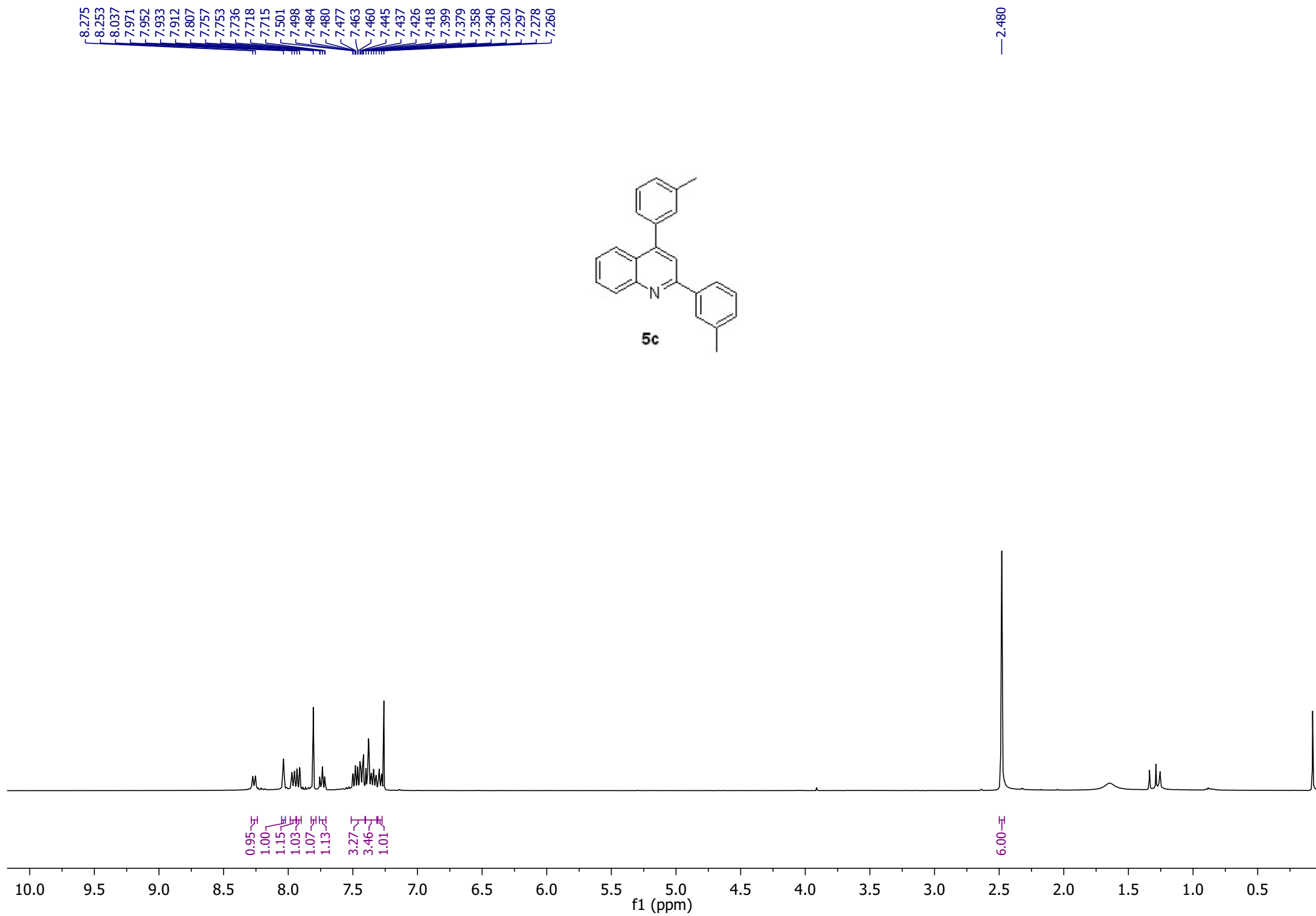


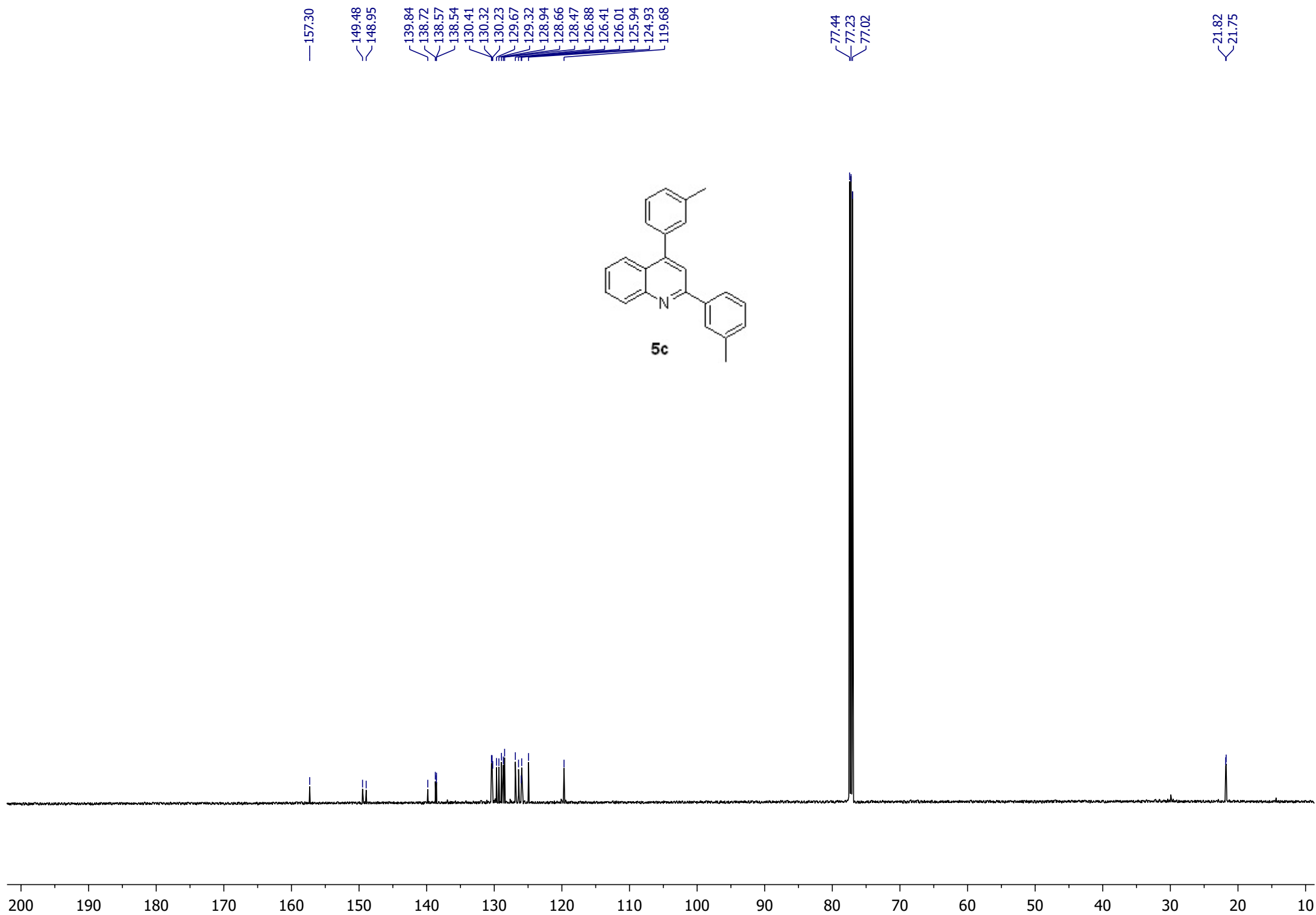
1.00
2.16
0.96
0.93
1.18
2.93
4.42

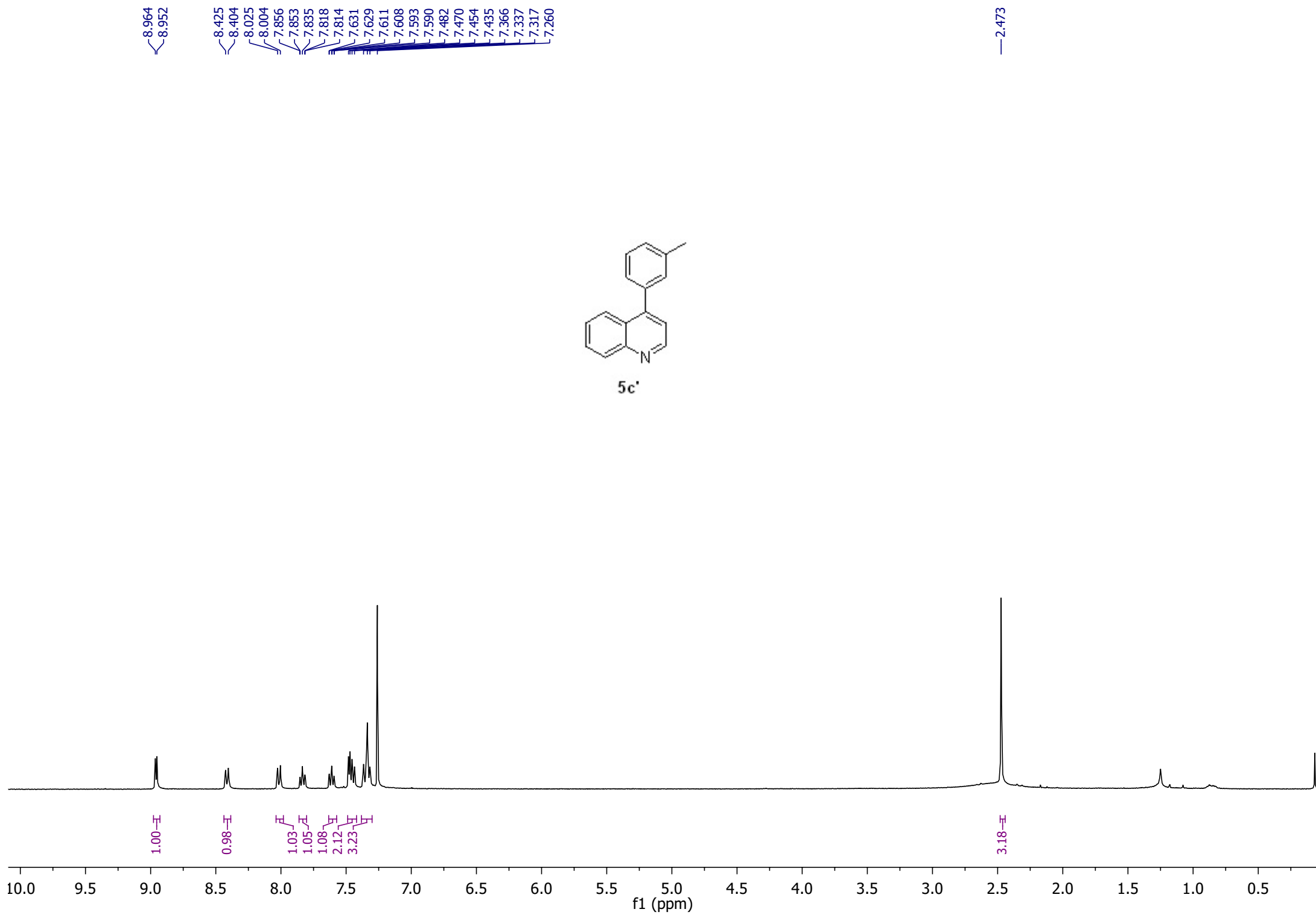
2.83
3.15



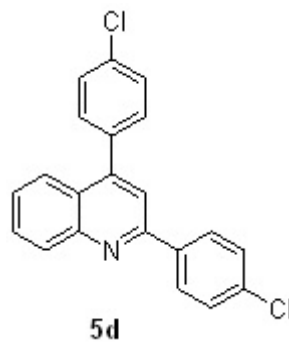




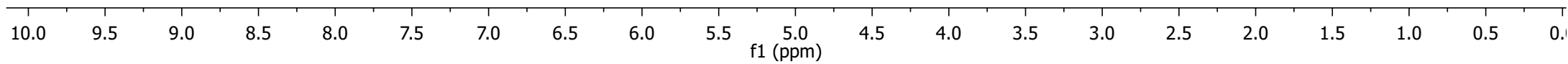


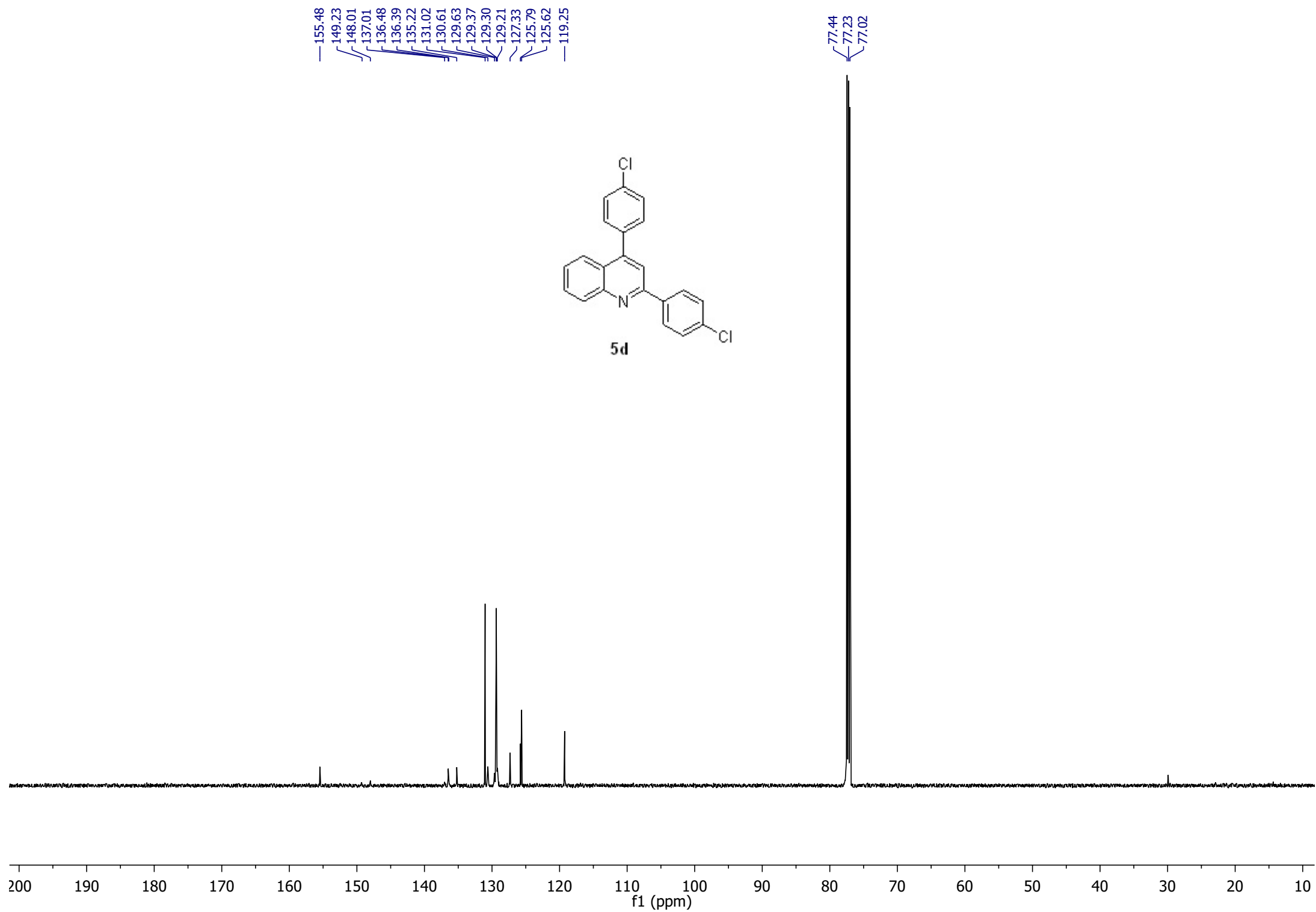


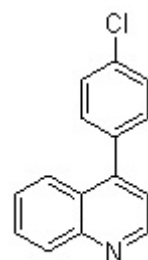
8.251
8.230
8.160
8.139
7.856
7.836
7.775
7.757
7.748
7.737
7.553
7.532
7.512
7.506
7.491
7.485
7.260



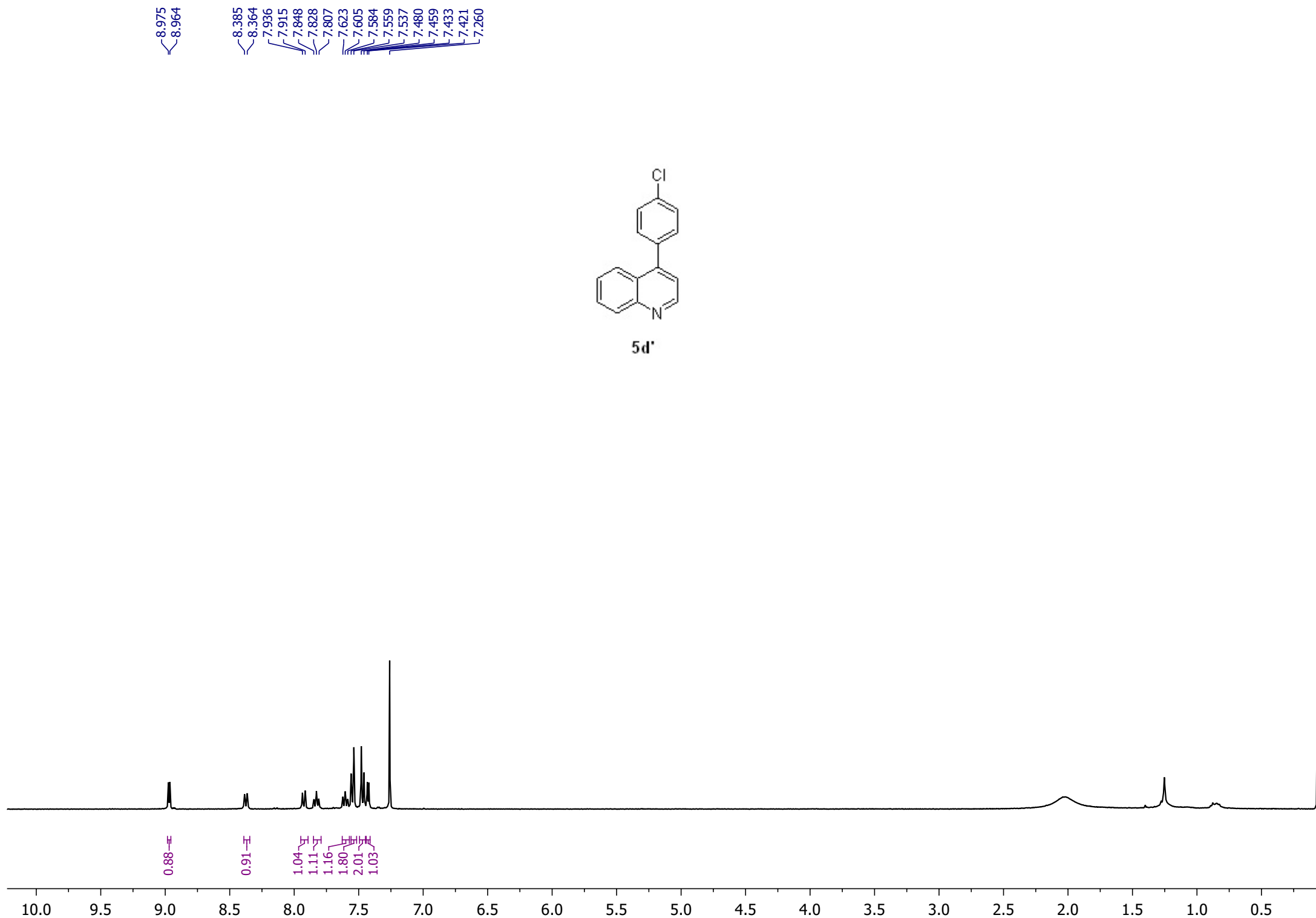
1.02
2.00
1.02
2.01
6.93



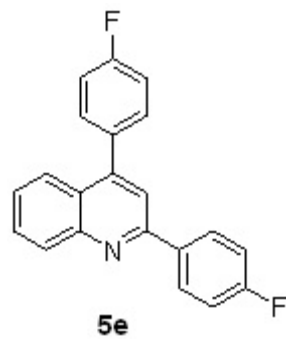




5d'



8.267
8.253
8.245
8.231
8.207
8.198
8.192
8.183
8.170
8.165
8.156
7.867
7.853
7.847
7.833
7.770
7.756
7.746
7.549
7.540
7.535
7.526
7.517
7.505
7.491
7.271
7.260
7.257
7.243
7.232
7.217
7.203



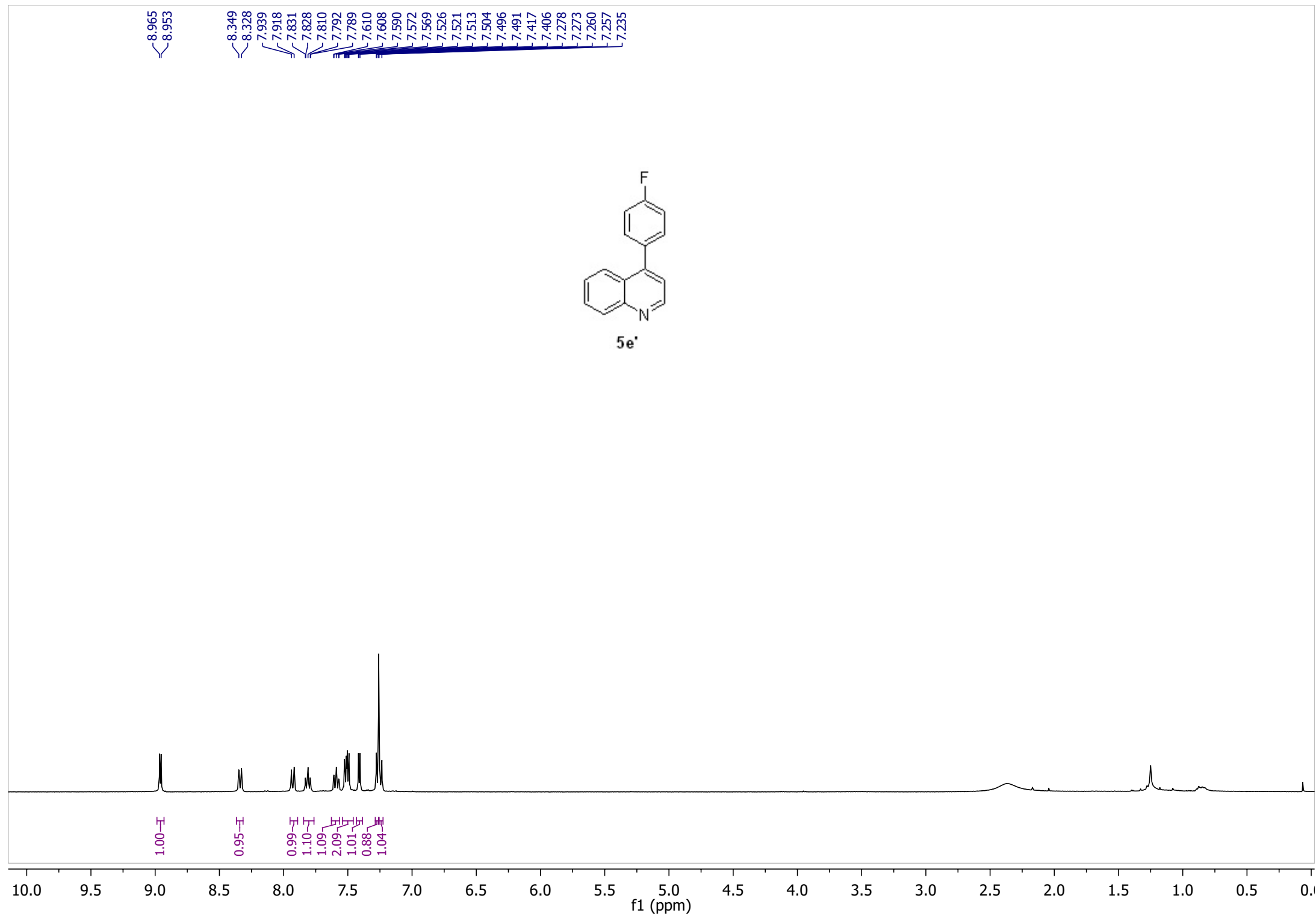
0.97
2.26

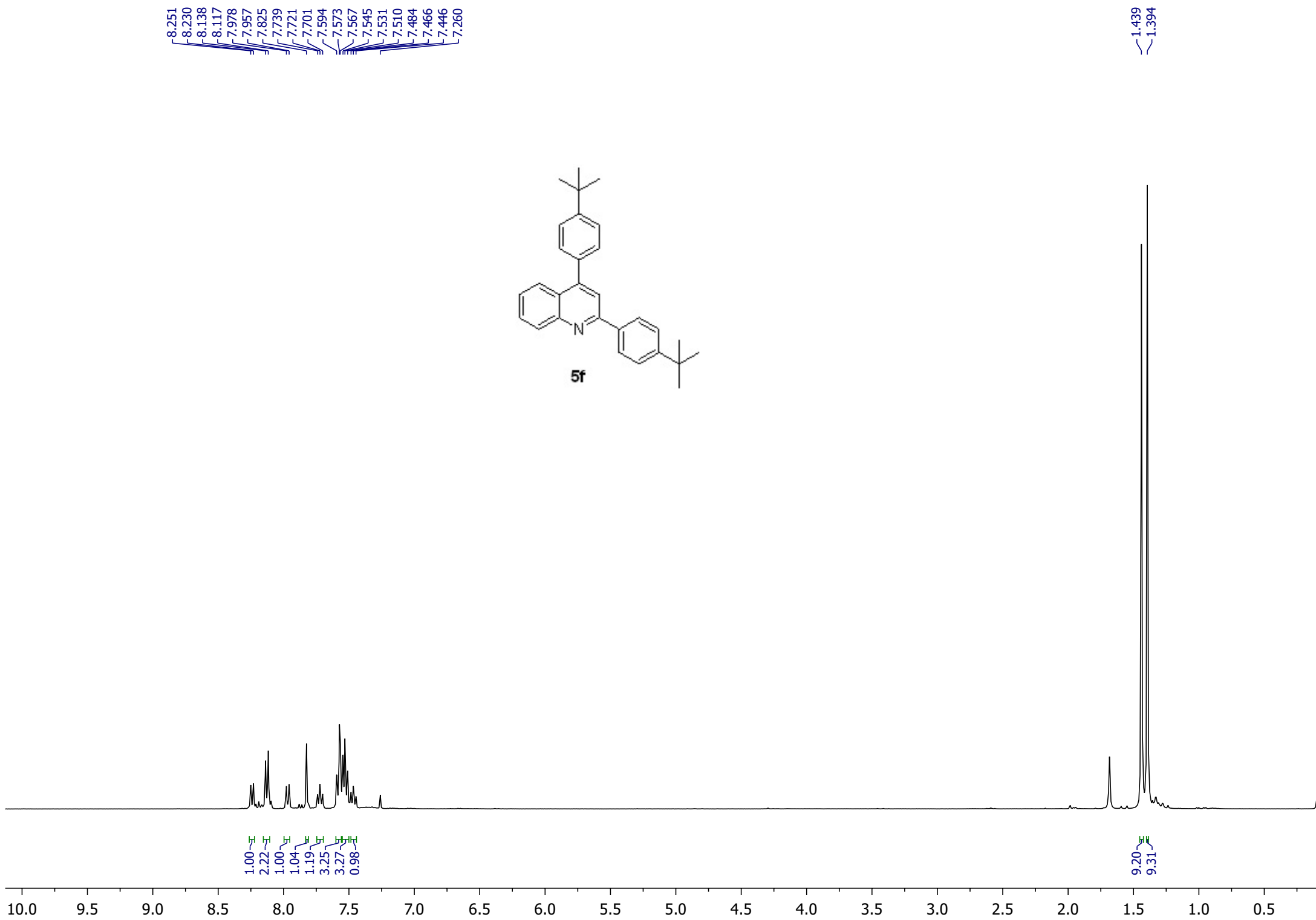
1.19
1.95

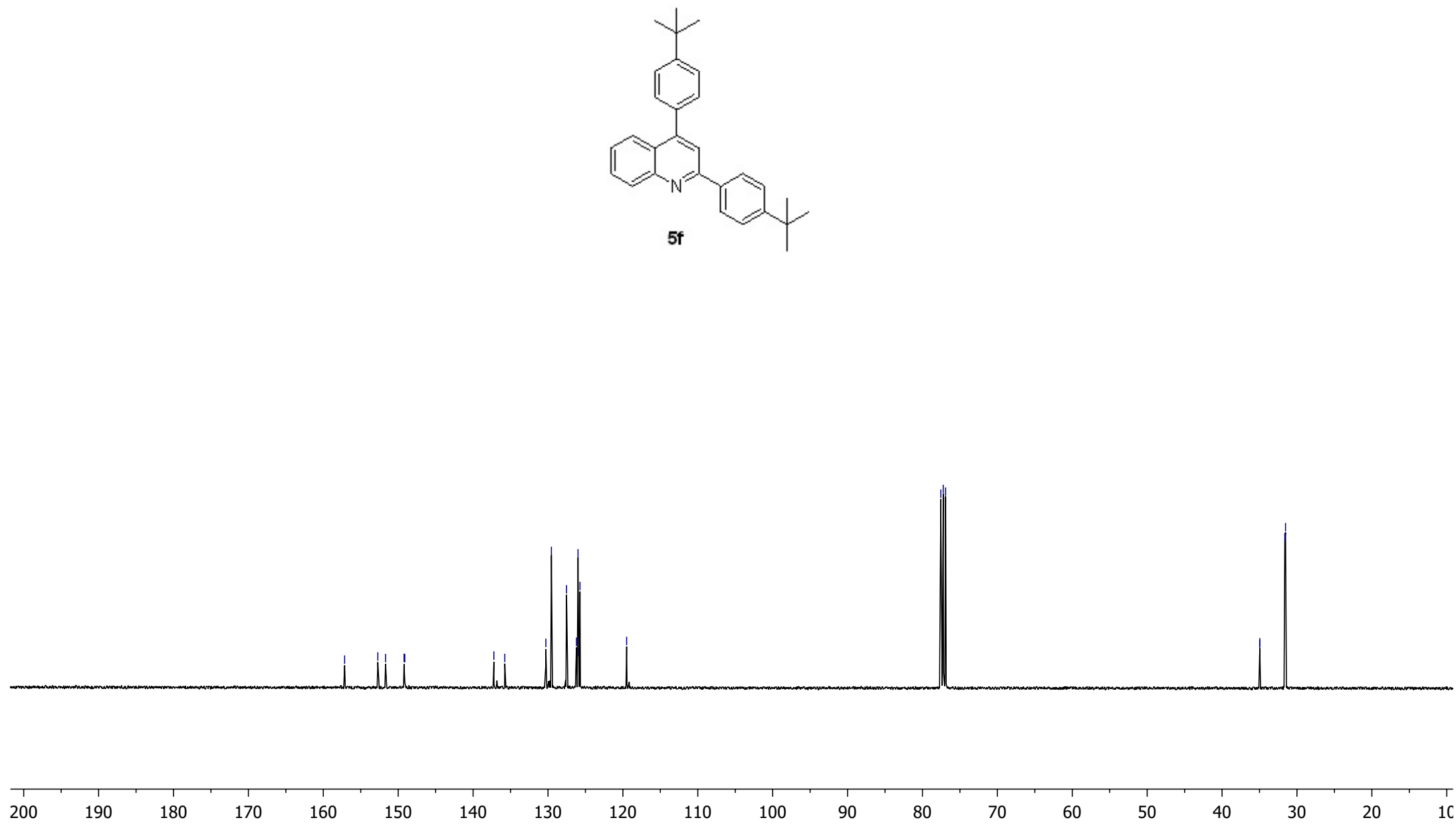
2.82

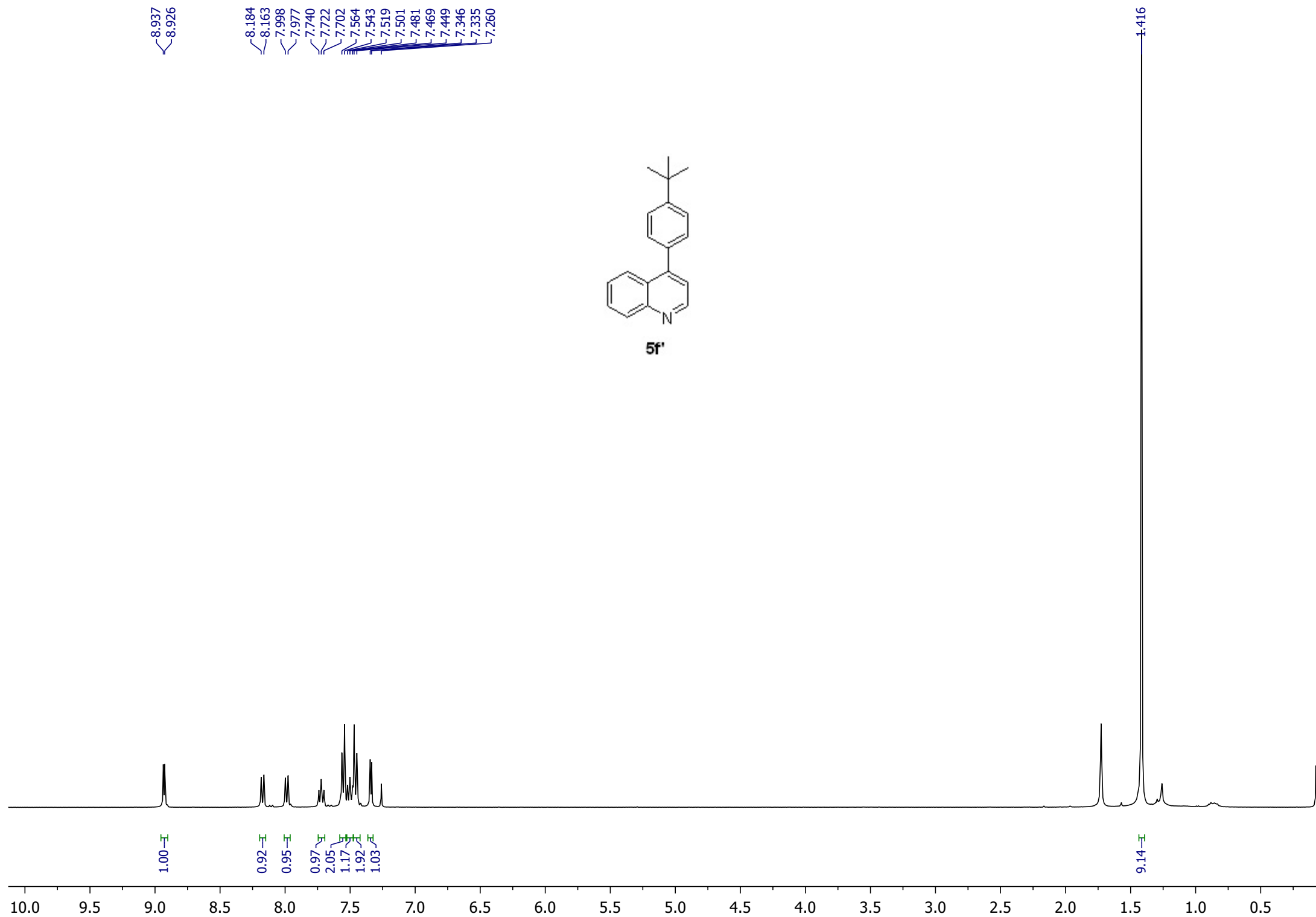
4.25

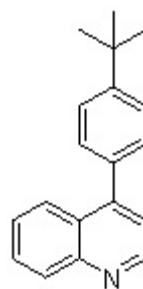
f1 (ppm)



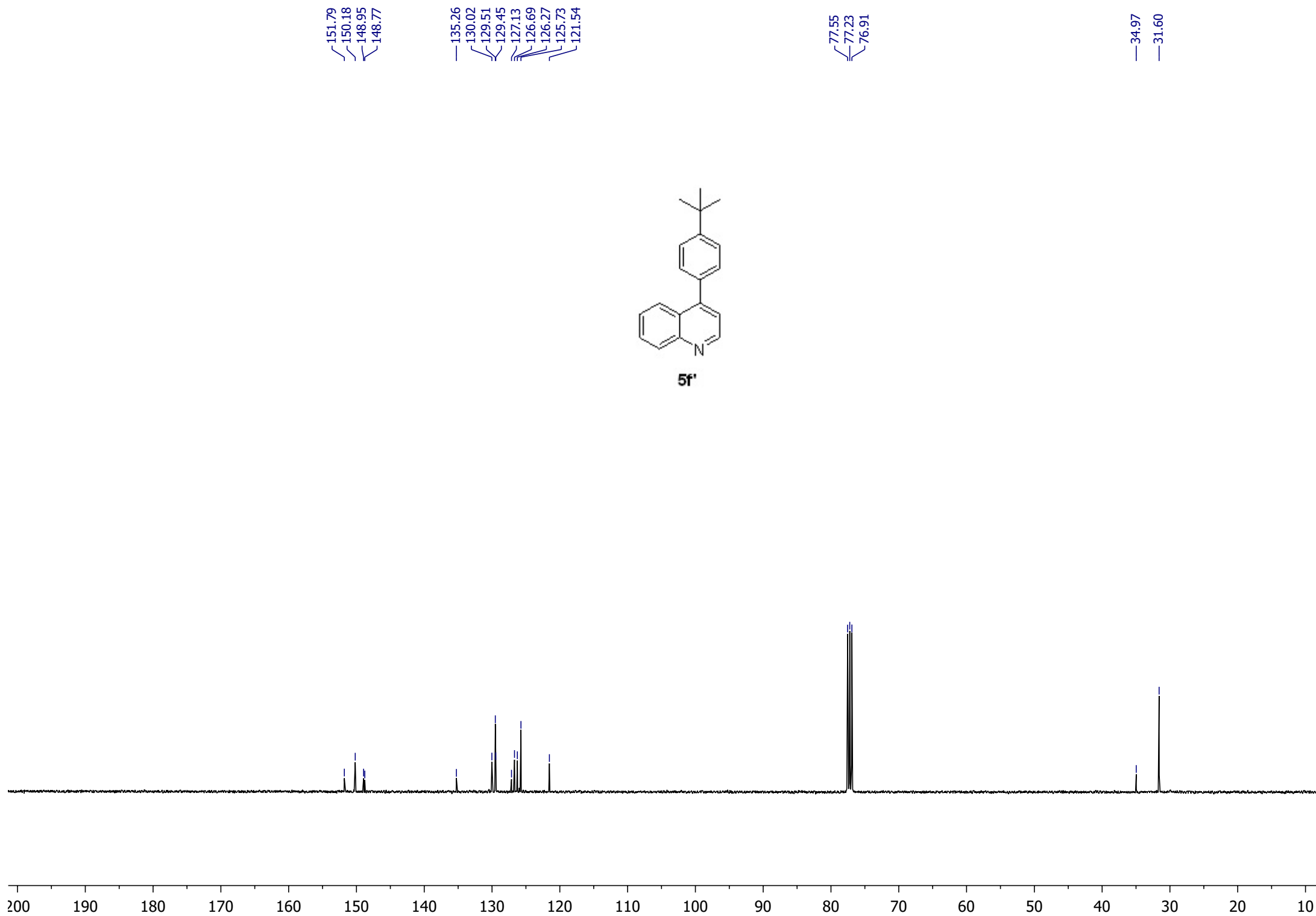




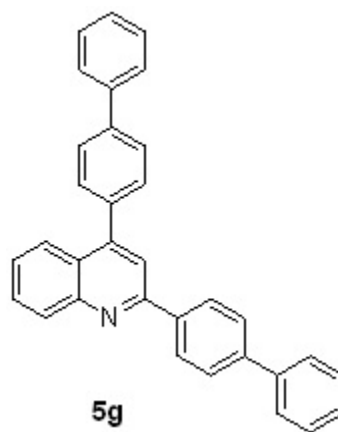




5f'



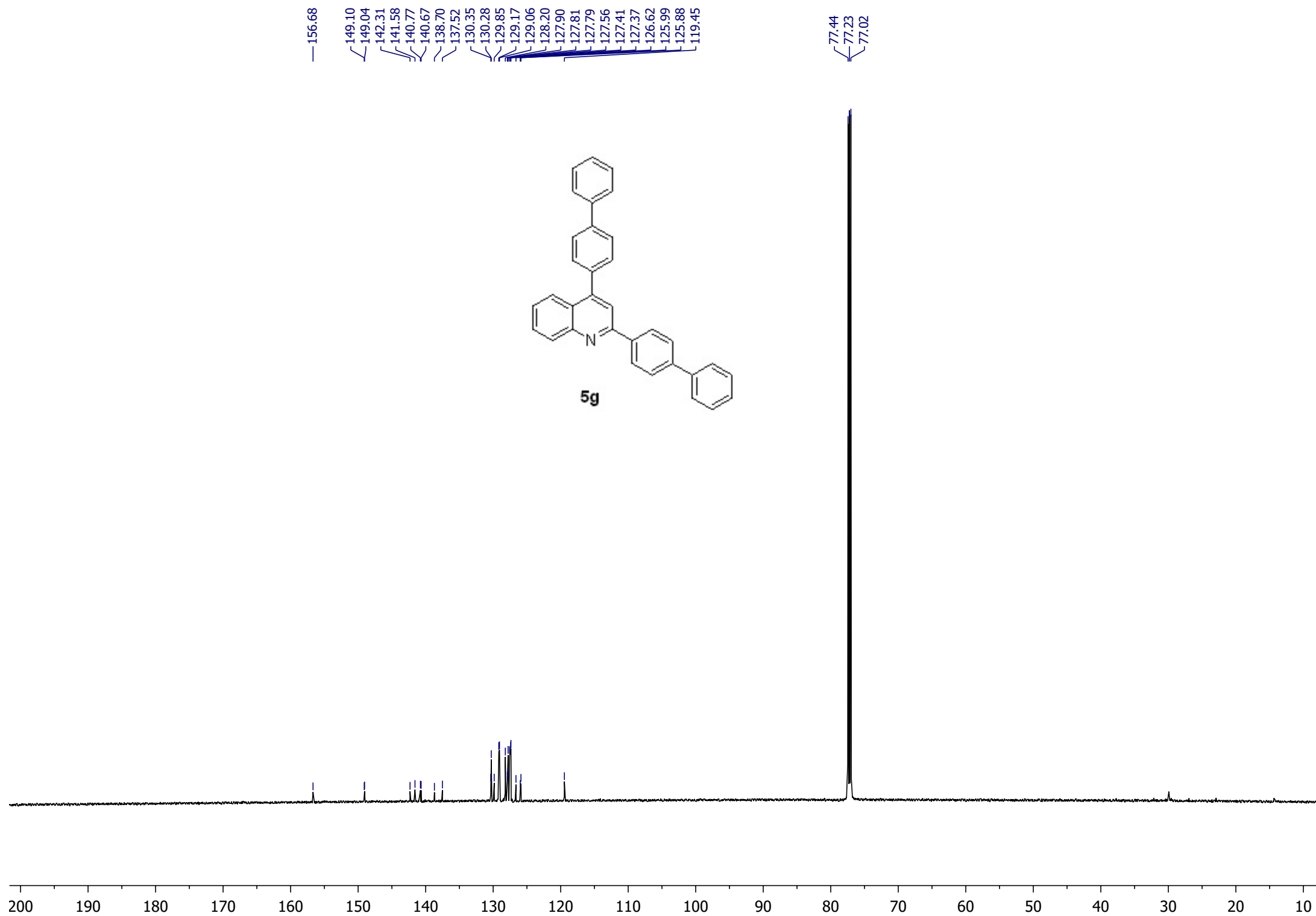
8.320
8.315
8.298
8.294
8.019
8.017
7.998
7.996
7.923
7.813
7.808
7.792
7.773
7.768
7.754
7.750
7.727
7.724
7.707
7.704
7.685
7.665
7.536
7.522
7.518
7.504
7.499
7.486
7.466
7.439
7.420
7.407
7.389
7.370
7.260



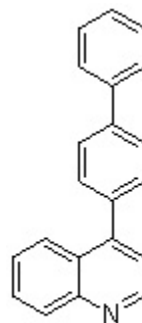
2.90
1.07
1.12
5.16
6.20
5.11
2.00

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

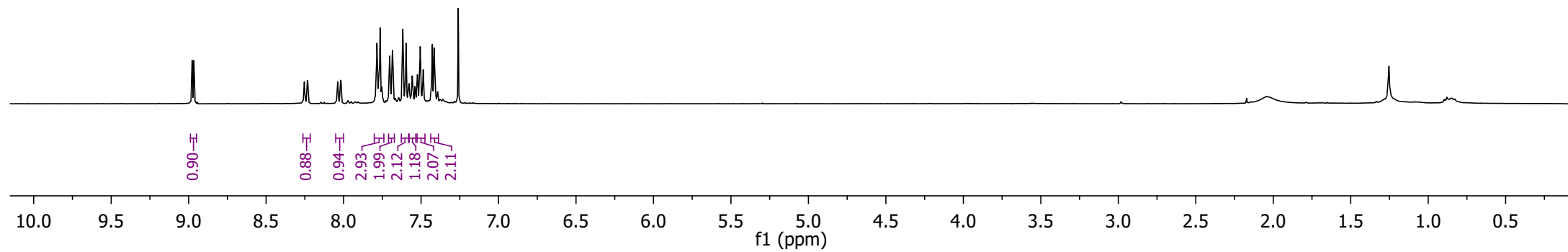
f1 (ppm)

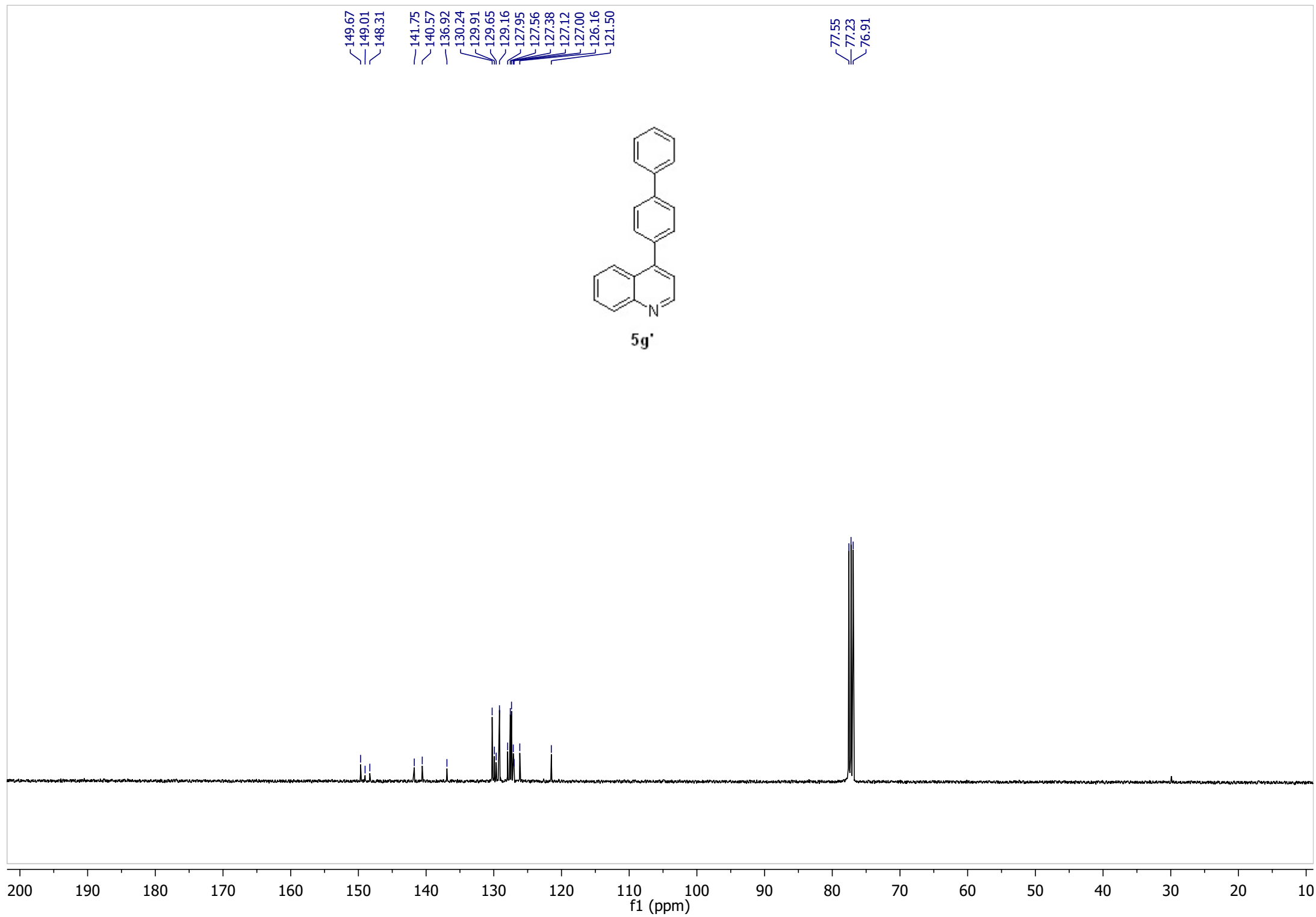


8.978
8.966
8.254
8.233
8.040
8.017
7.785
7.780
7.769
7.764
7.754
7.750
7.706
7.702
7.685
7.618
7.613
7.601
7.597
7.577
7.575
7.560
7.557
7.553
7.539
7.536
7.524
7.520
7.506
7.486
7.427
7.416
7.412
7.393
7.260



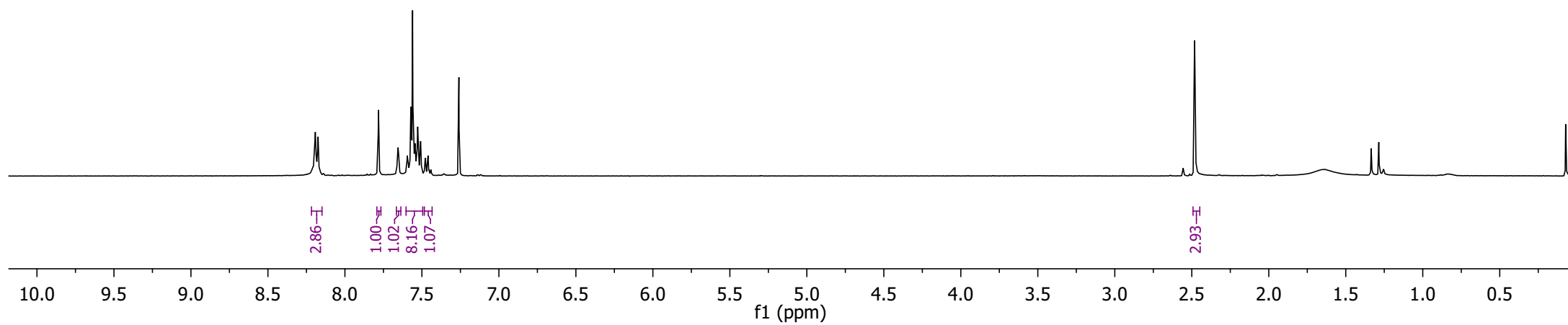
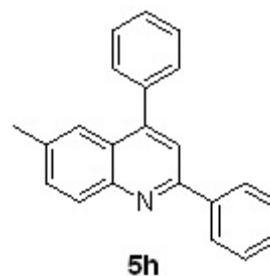
5g'

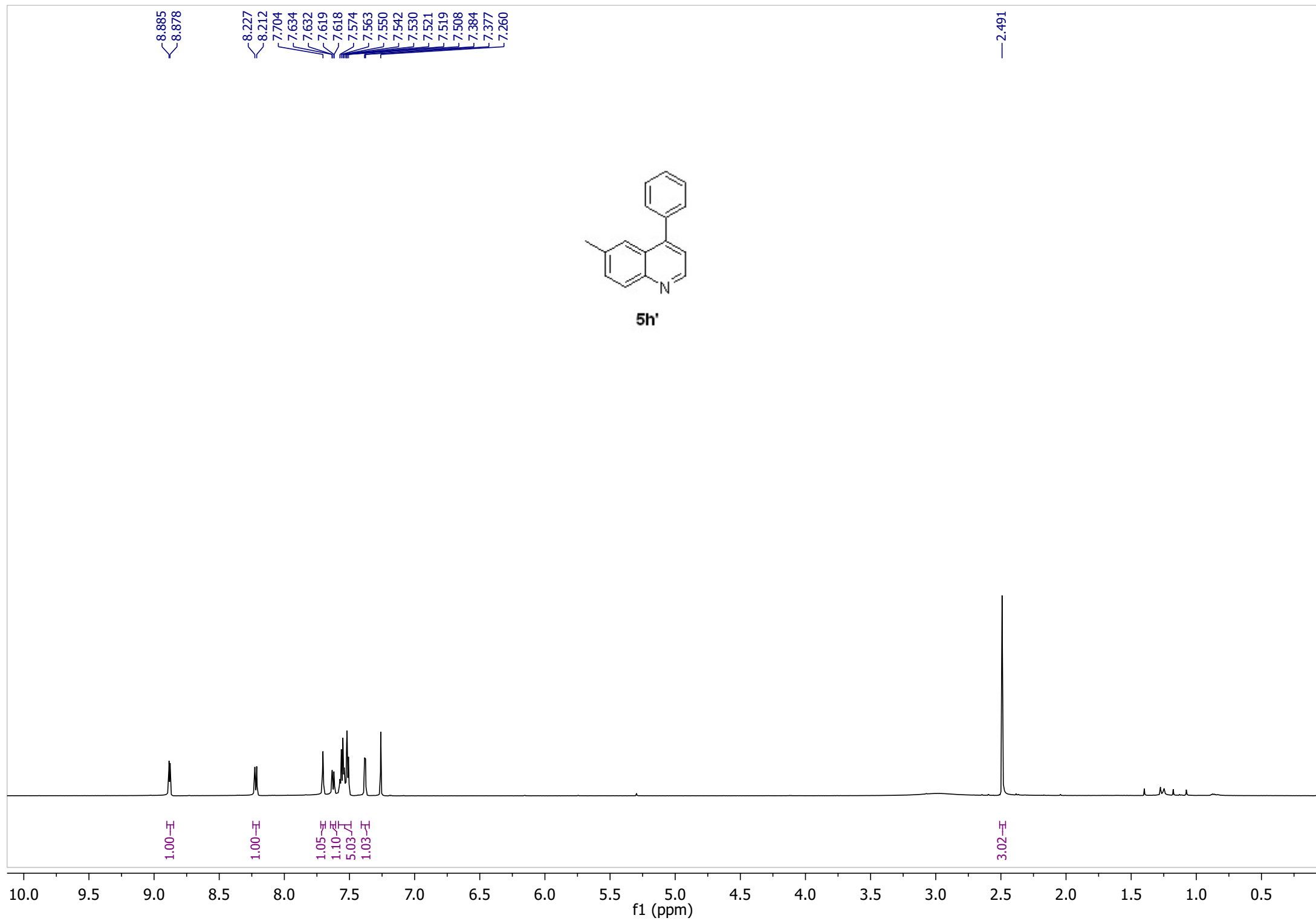




8.206
8.196
8.192
8.174
7.782
7.655
7.595
7.591
7.572
7.561
7.544
7.527
7.524
7.508
7.478
7.460
7.442
7.260

2.482

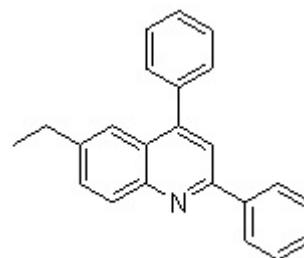




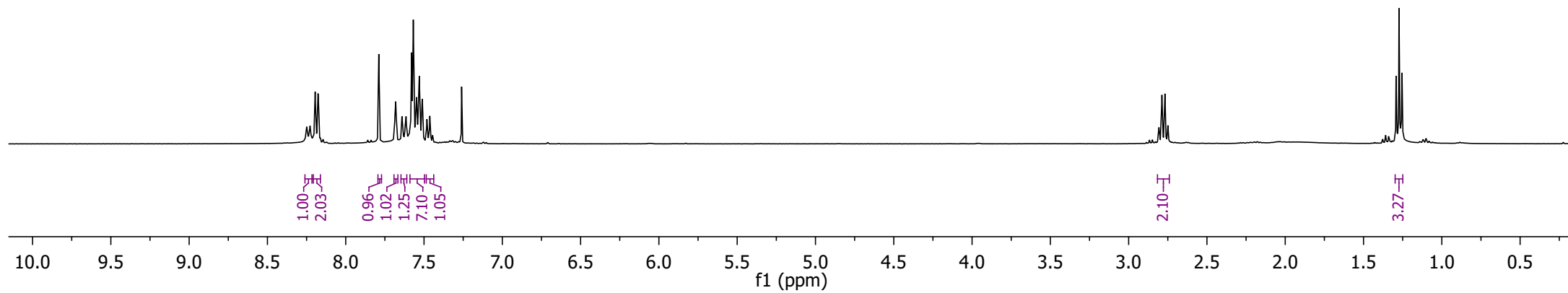
8.249
8.228
8.195
8.177
7.789
7.681
7.641
7.636
7.619
7.615
7.579
7.569
7.547
7.531
7.511
7.481
7.463
7.445
7.260

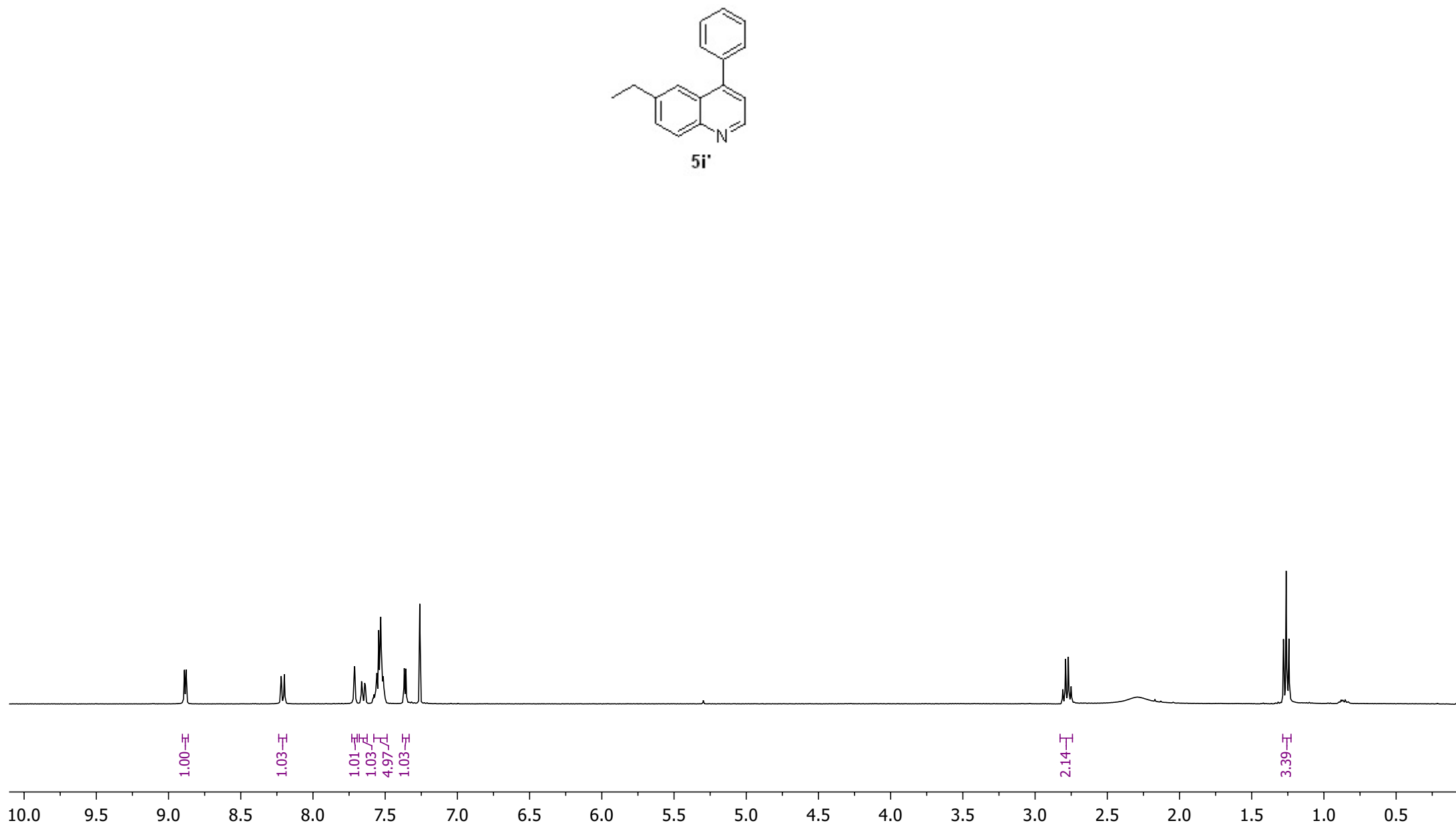
2.806
2.787
2.769
2.750

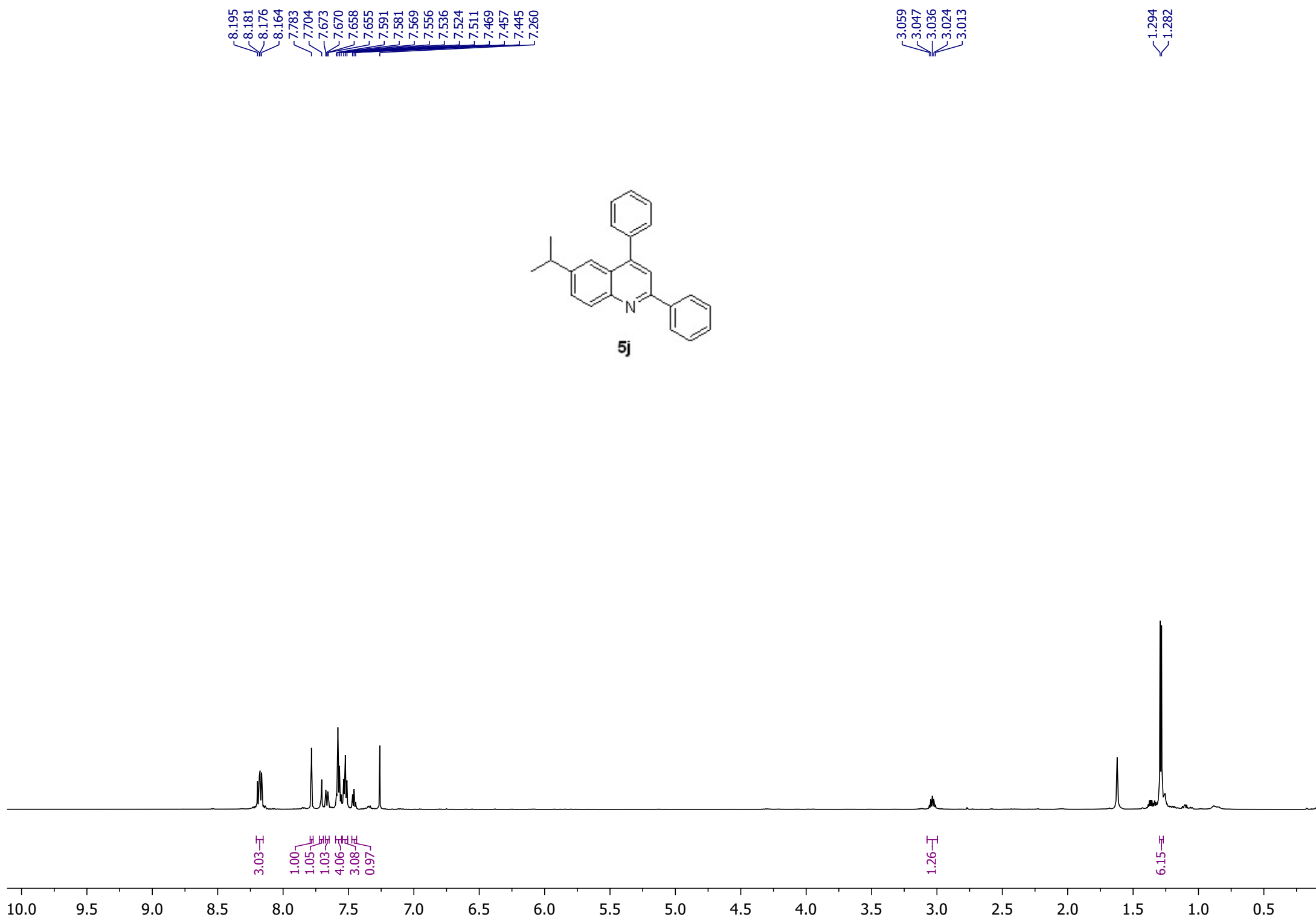
1.292
1.273
1.254

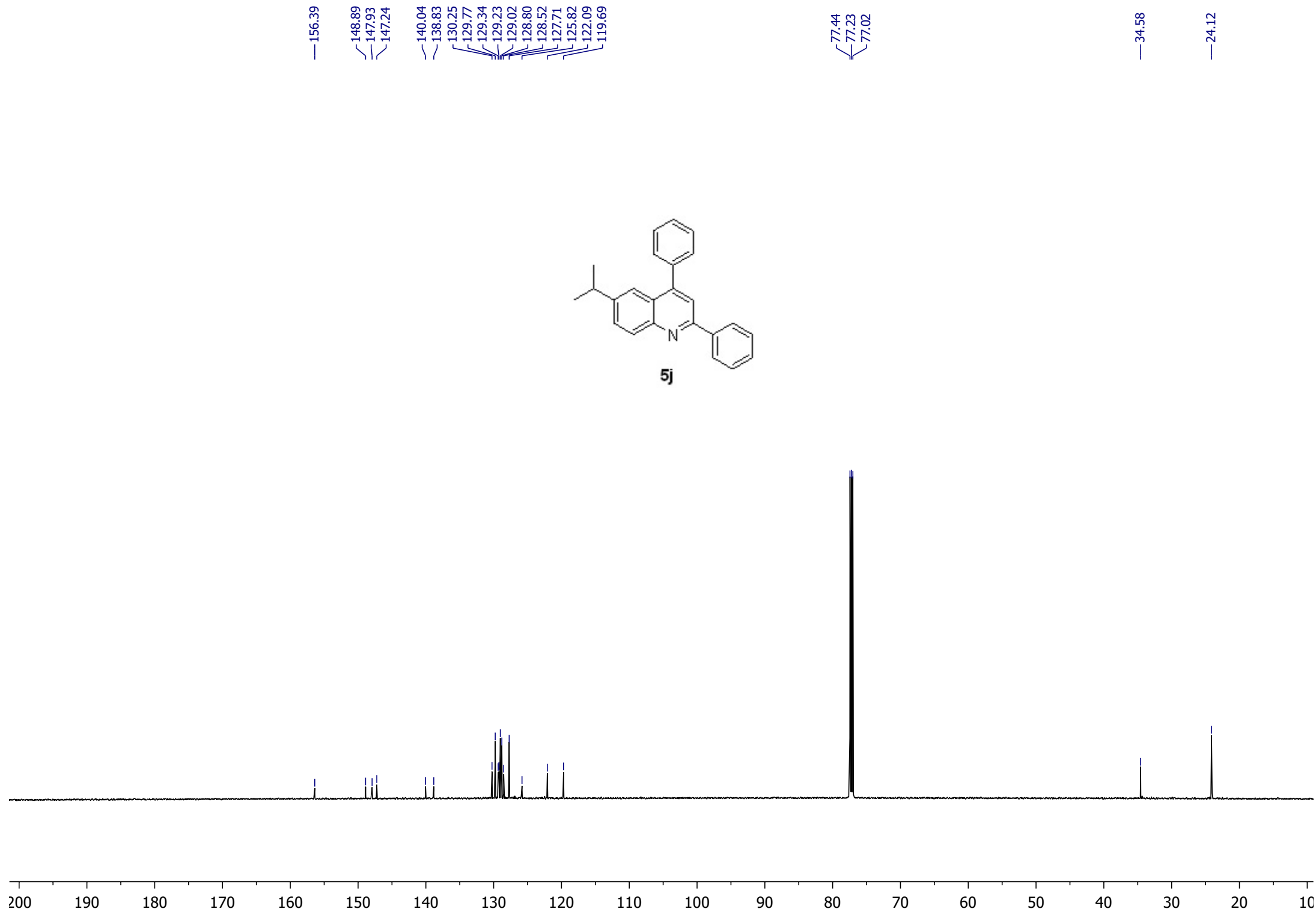


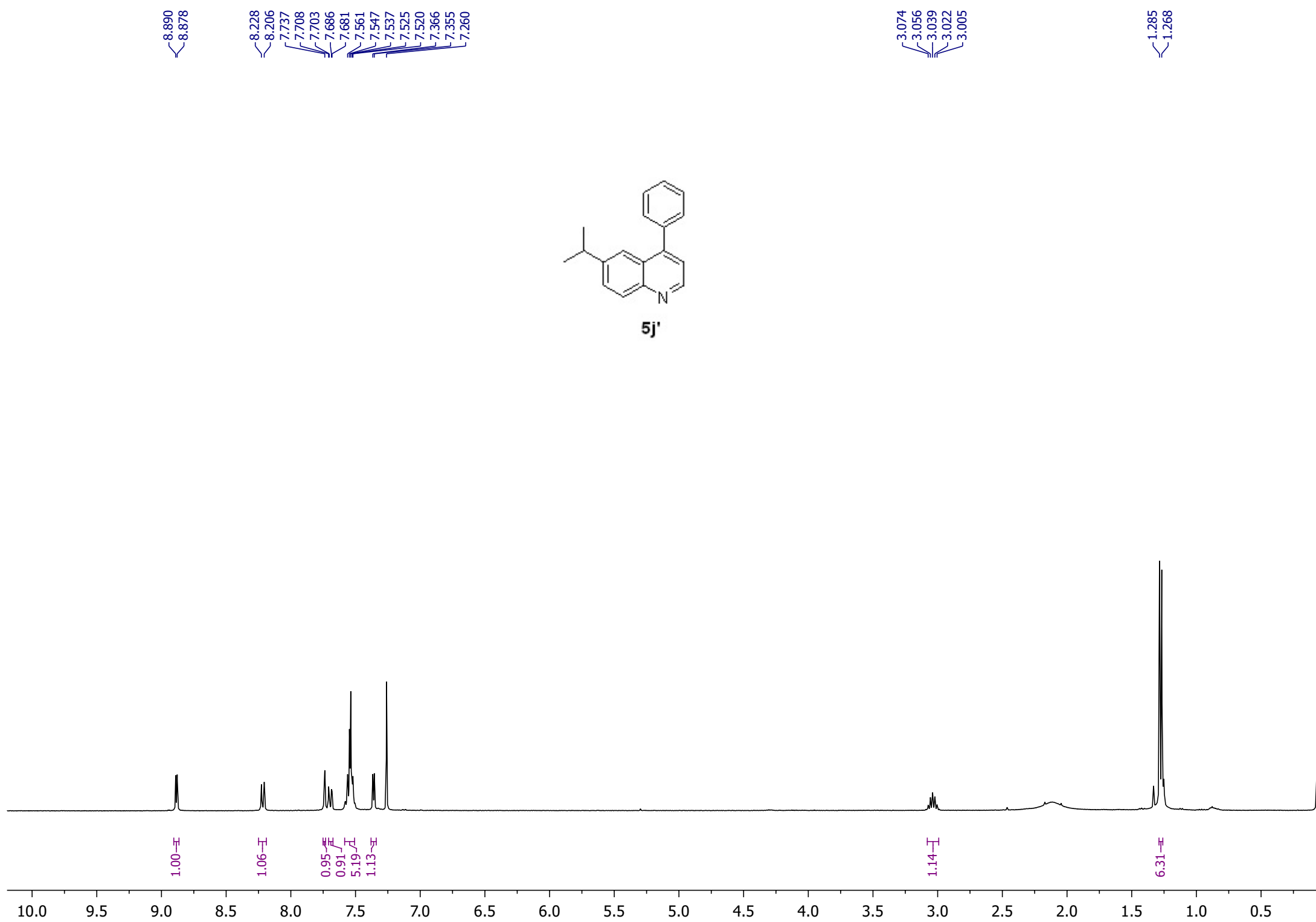
5i

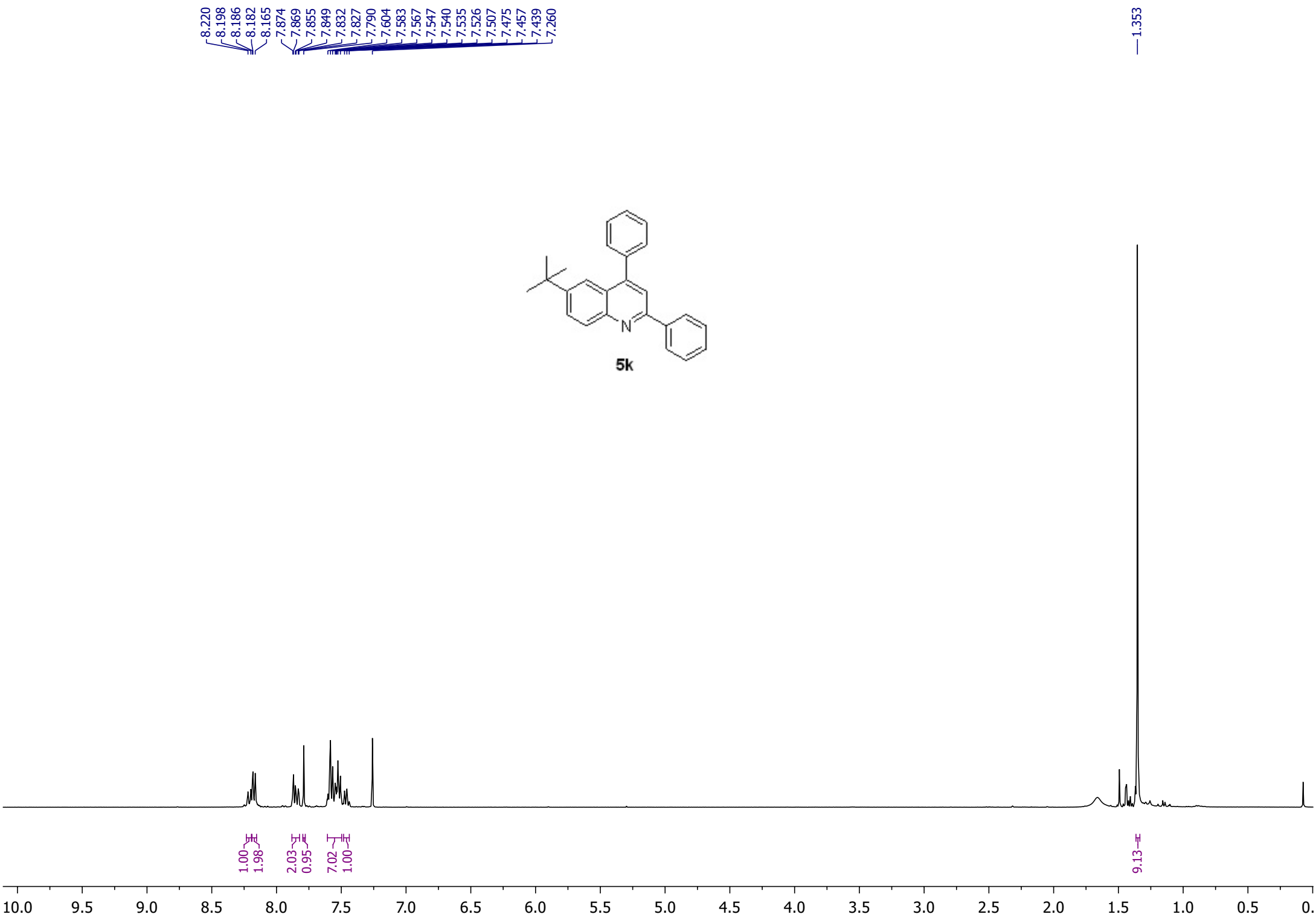


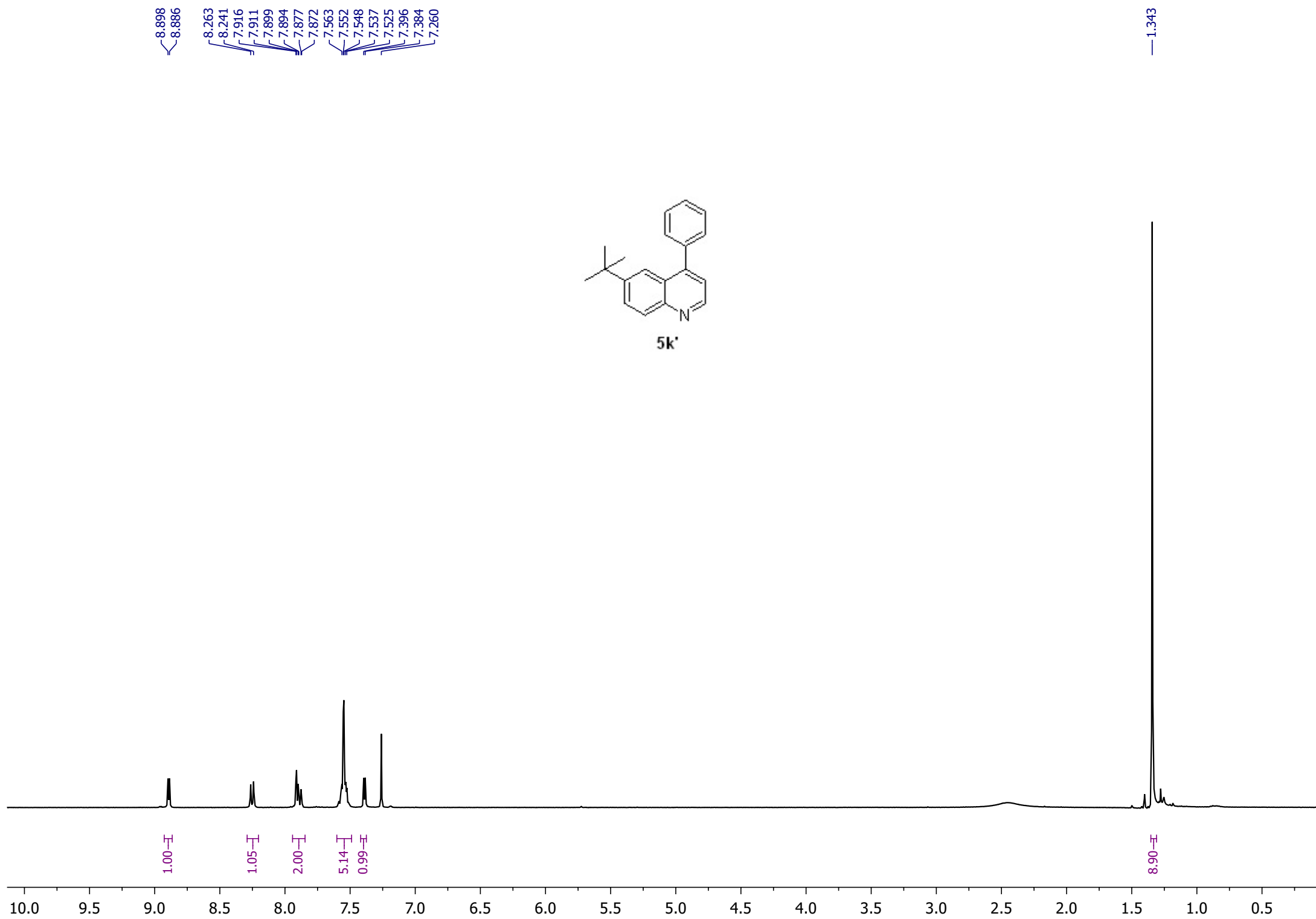






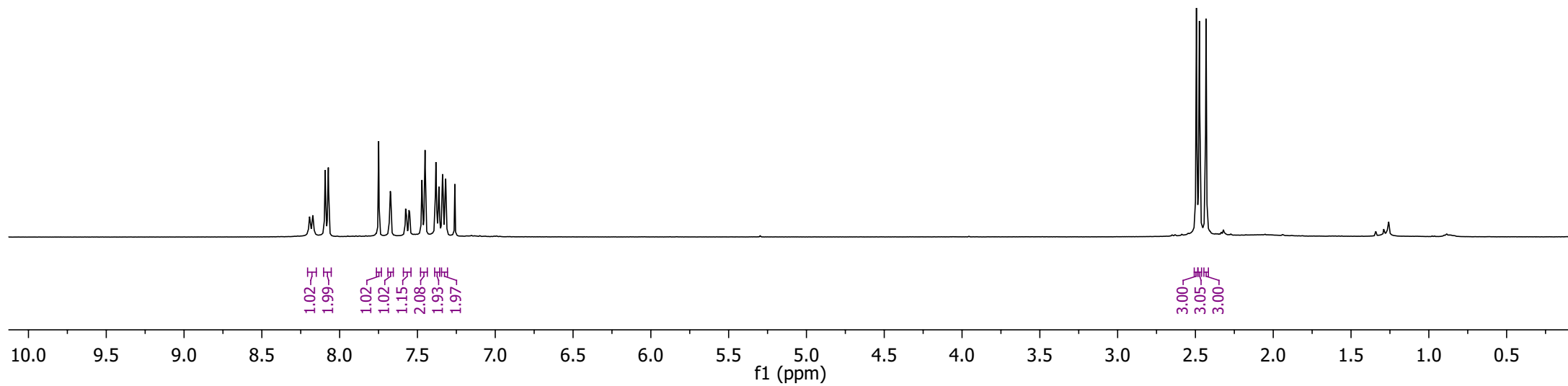
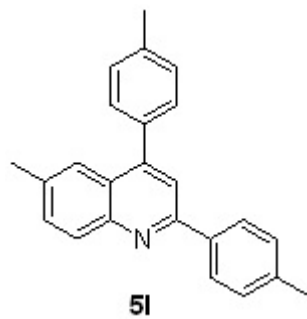


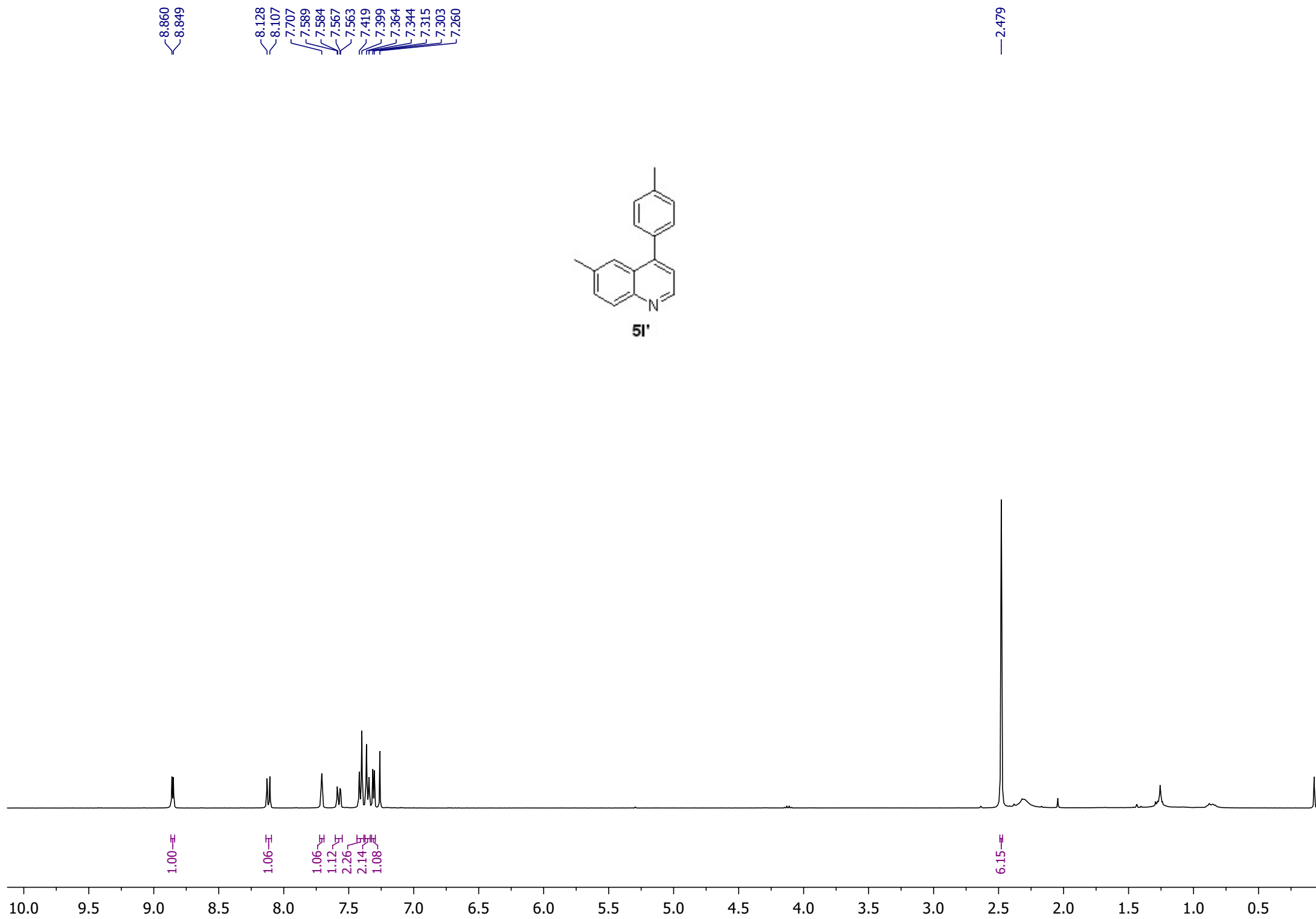




8.193
8.172
8.093
8.073
7.749
7.674
7.576
7.572
7.554
7.550
7.550
7.471
7.451
7.381
7.362
7.339
7.319
7.260

2.494
2.475
2.432

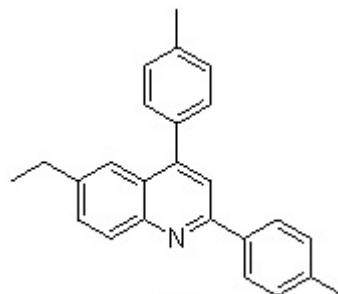




8.223
8.201
8.095
8.075
7.755
7.702
7.699
7.620
7.615
7.598
7.594
7.484
7.464
7.384
7.365
7.341
7.321
7.260

2.800
2.781
2.762
2.743
2.496
2.434

1.290
1.271
1.252



5m

1.00
2.07

1.05
1.07
1.16
2.17
2.18
2.26

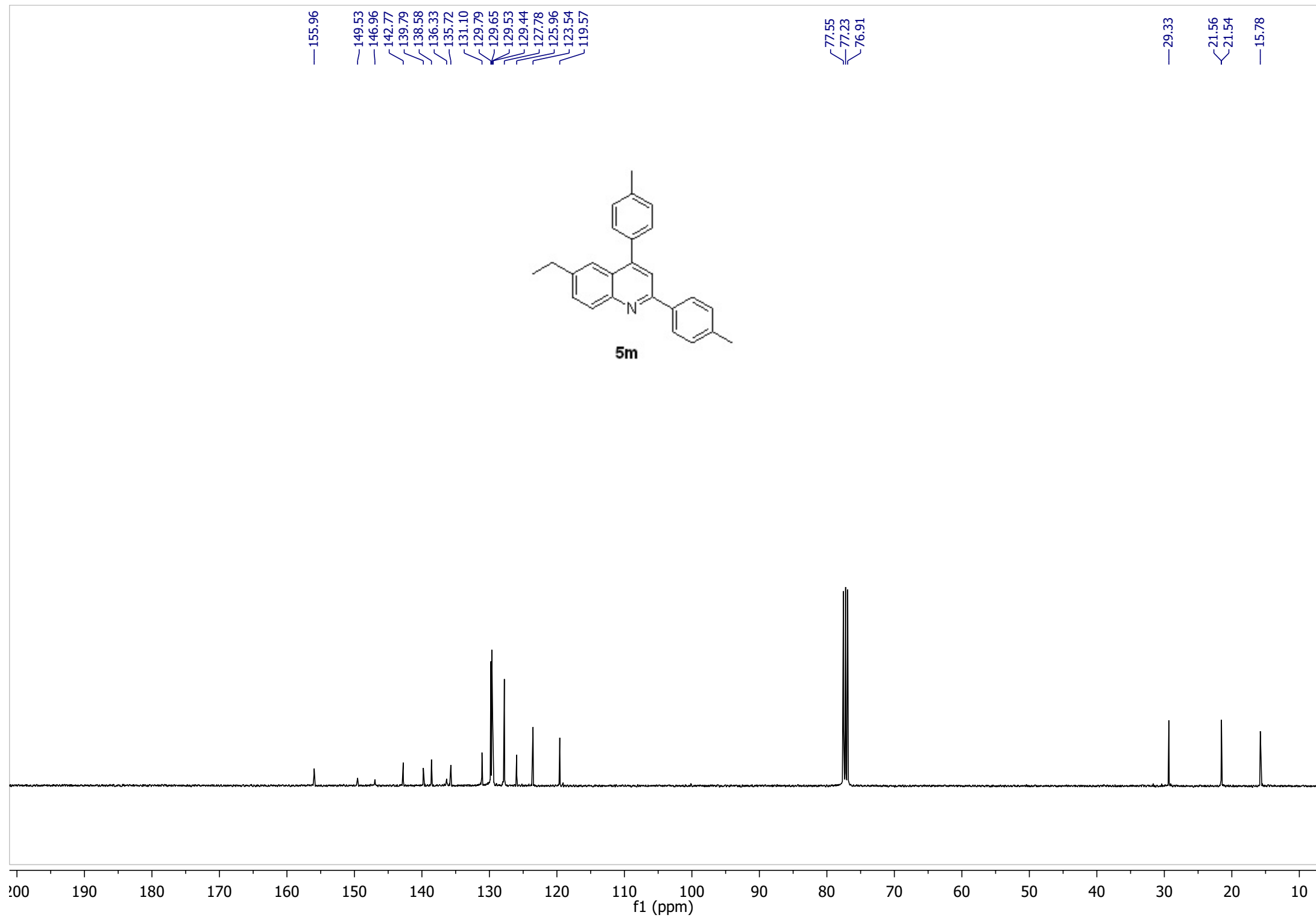
2.21

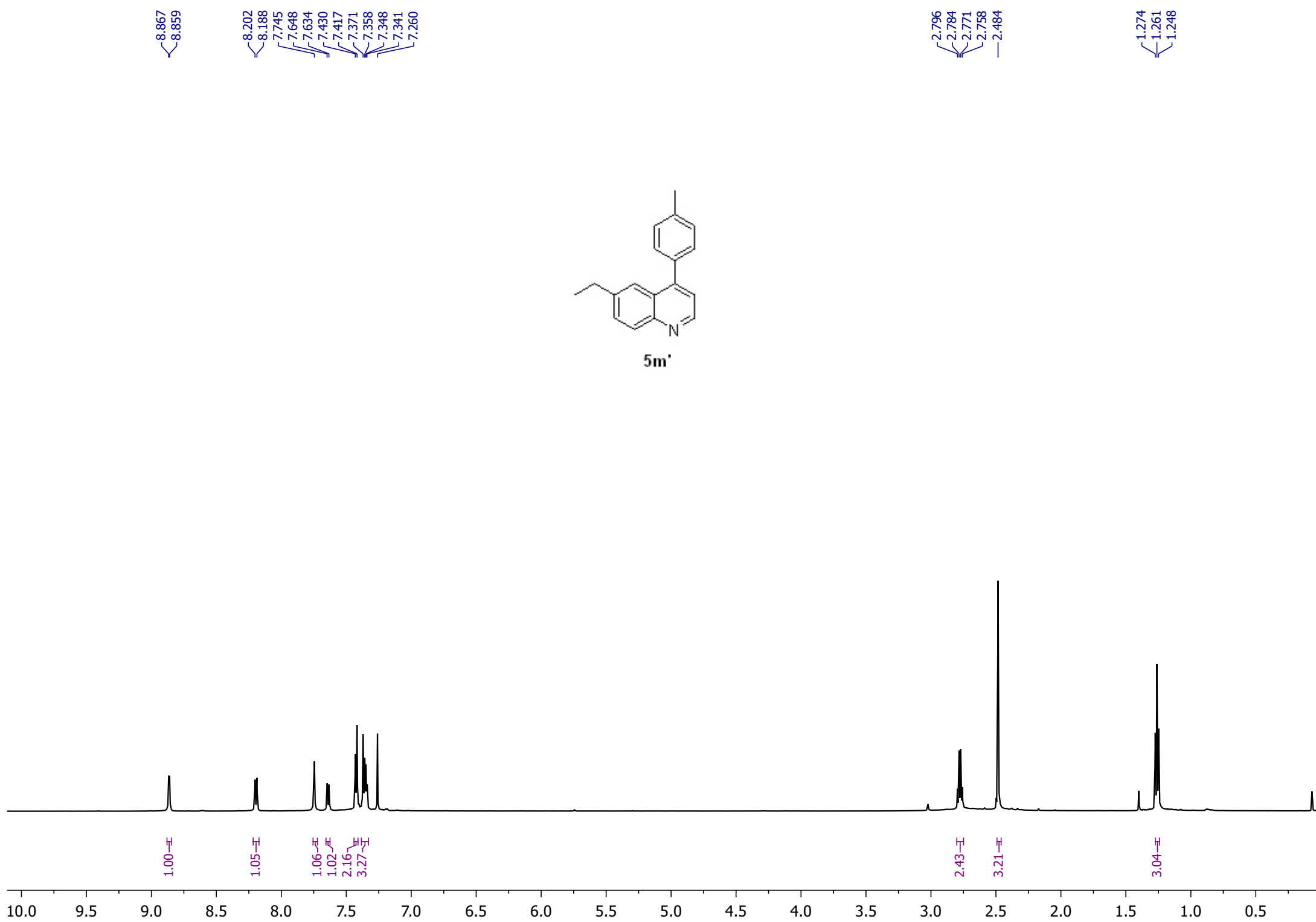
3.22
3.34

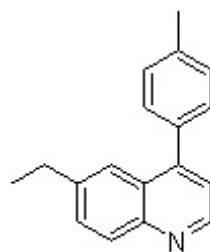
3.10

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

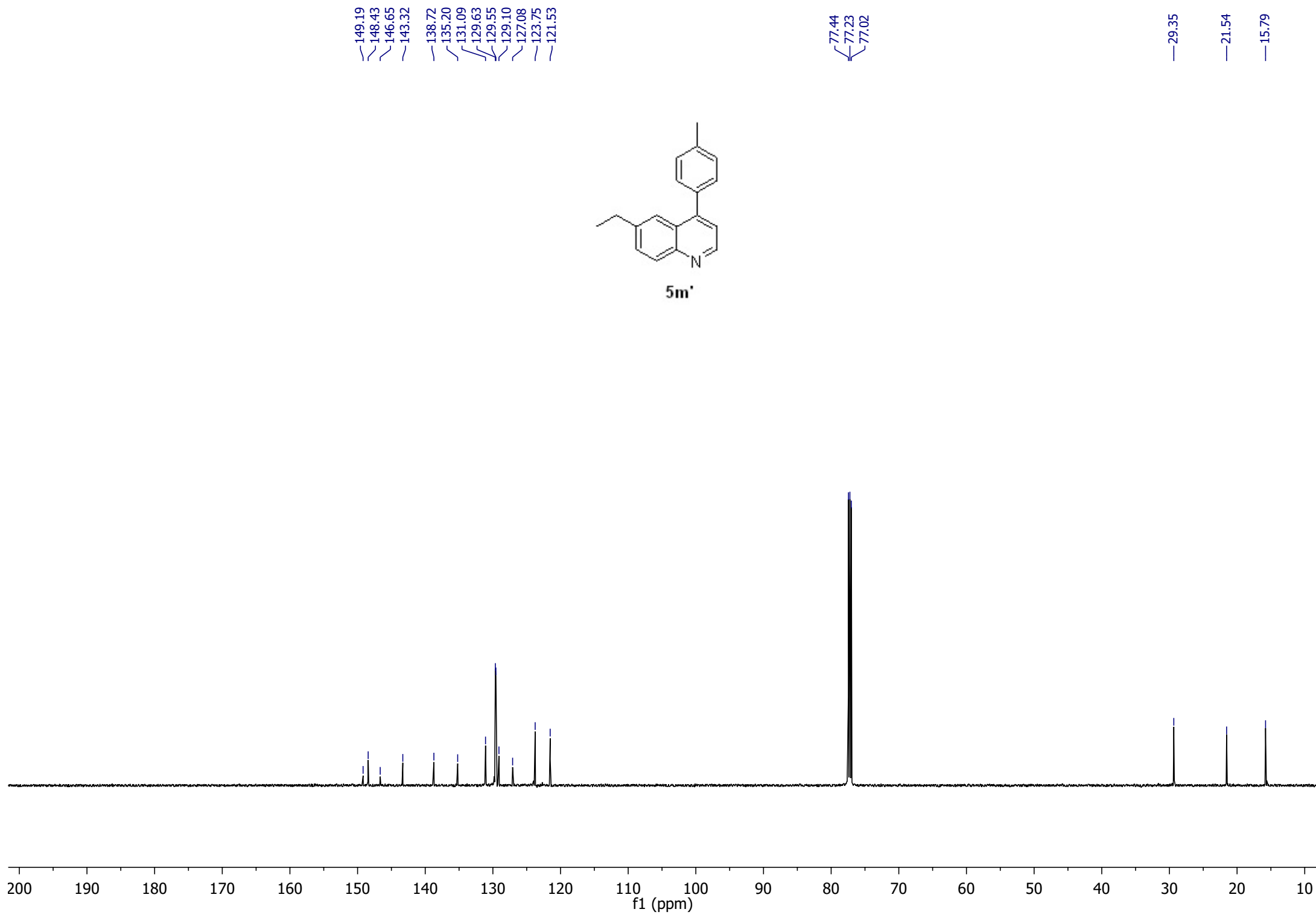
f1 (ppm)

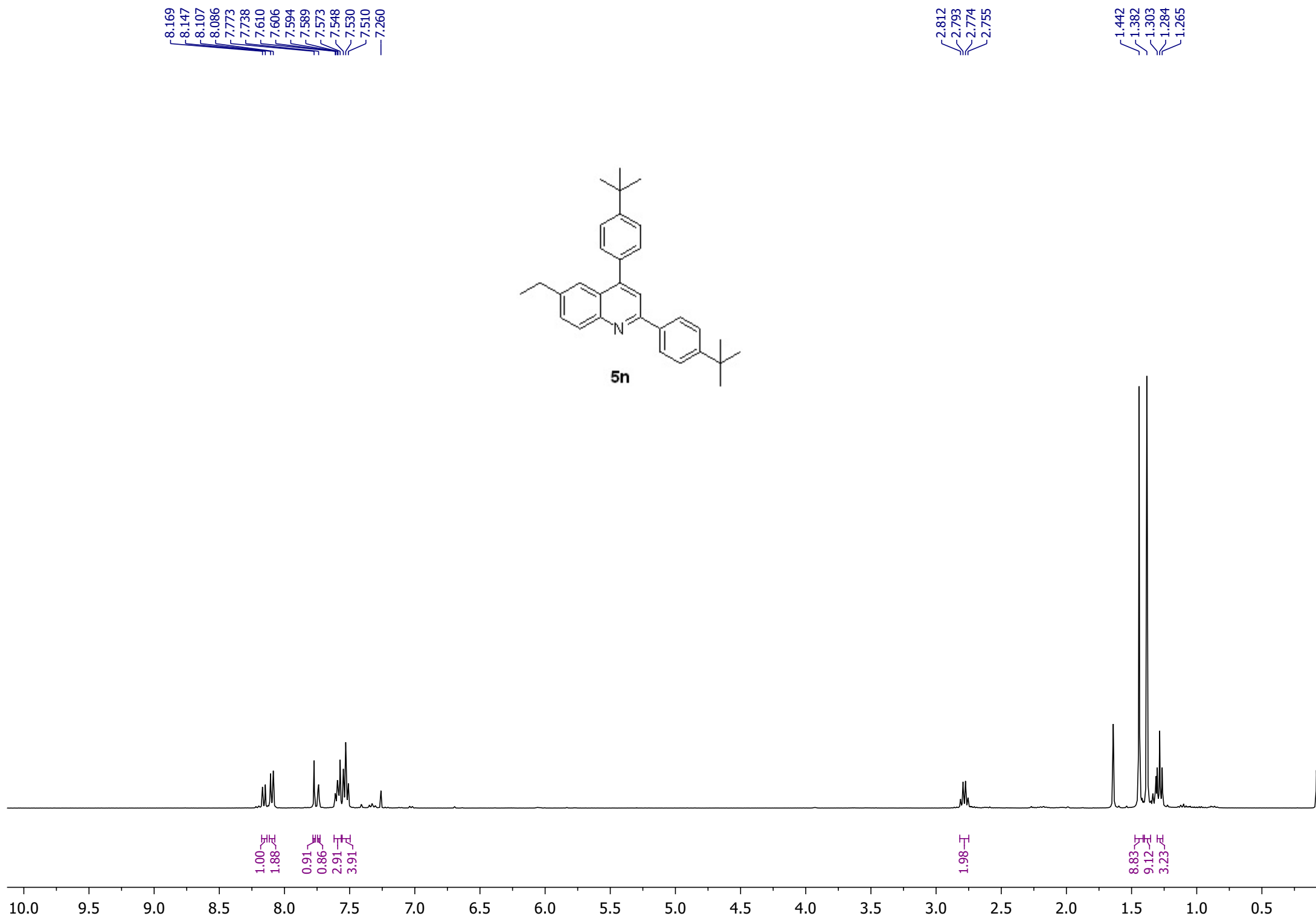


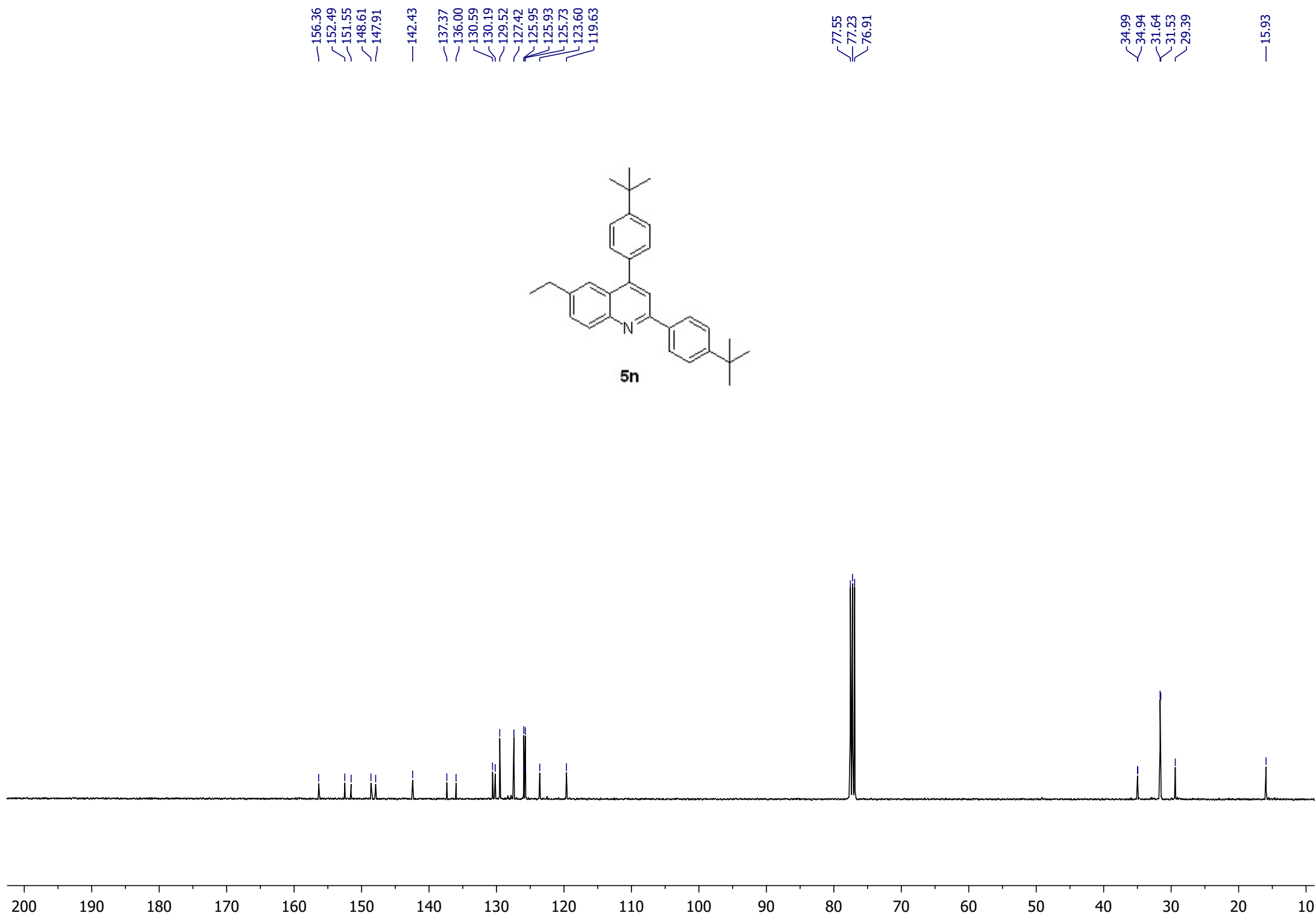


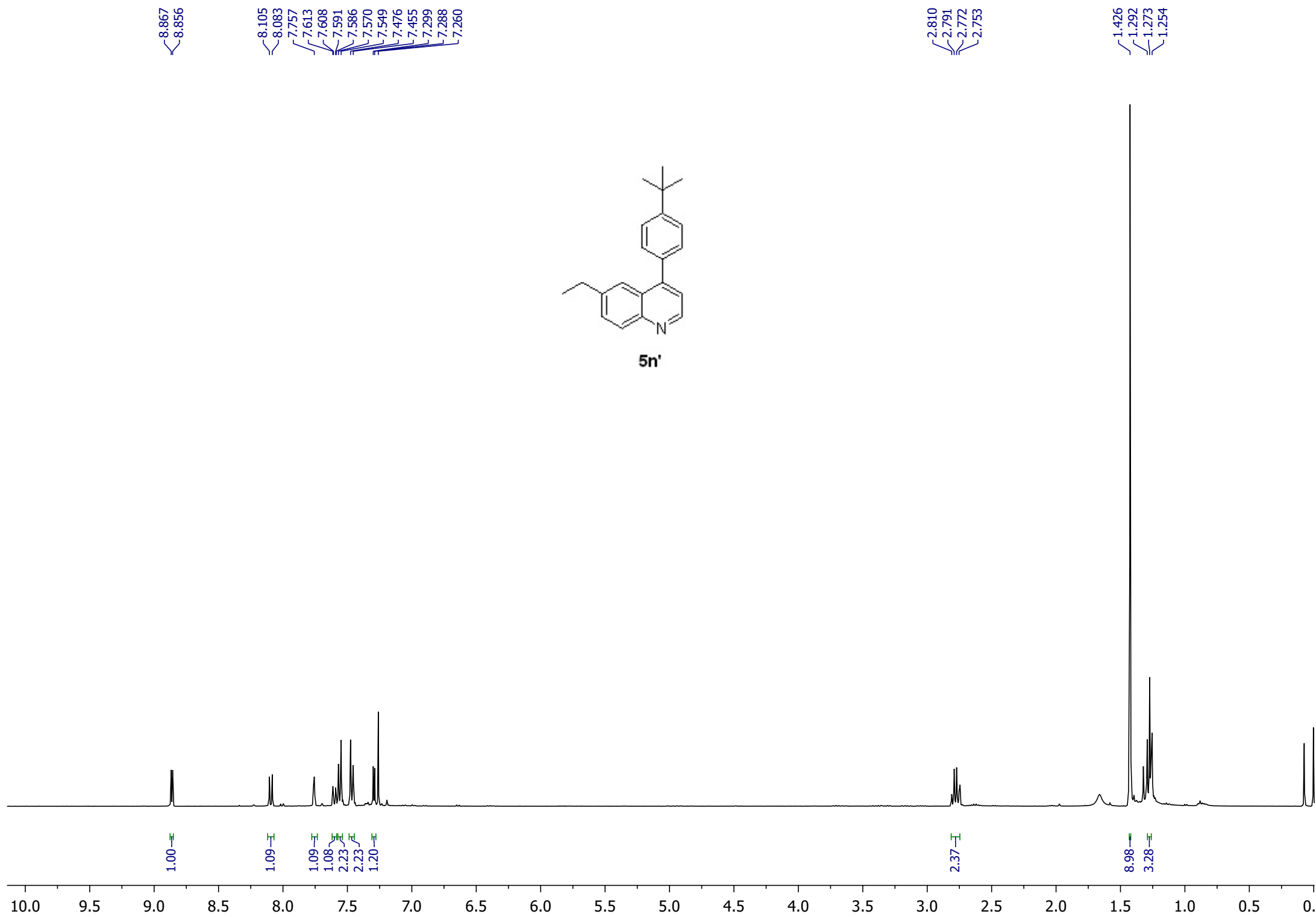


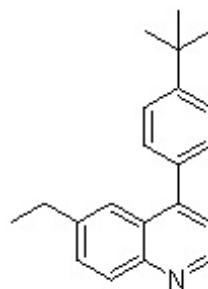
5m'



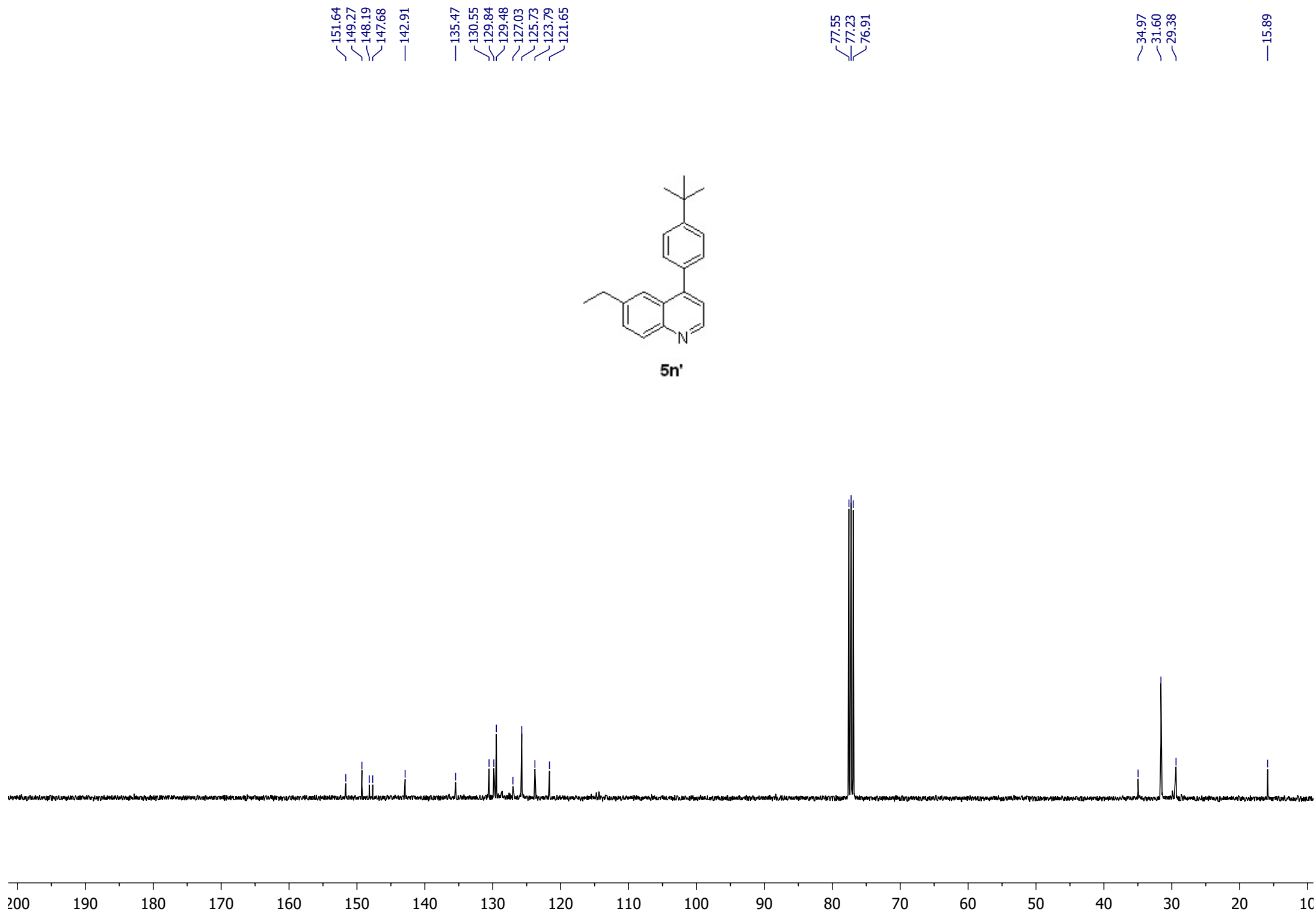








5n'

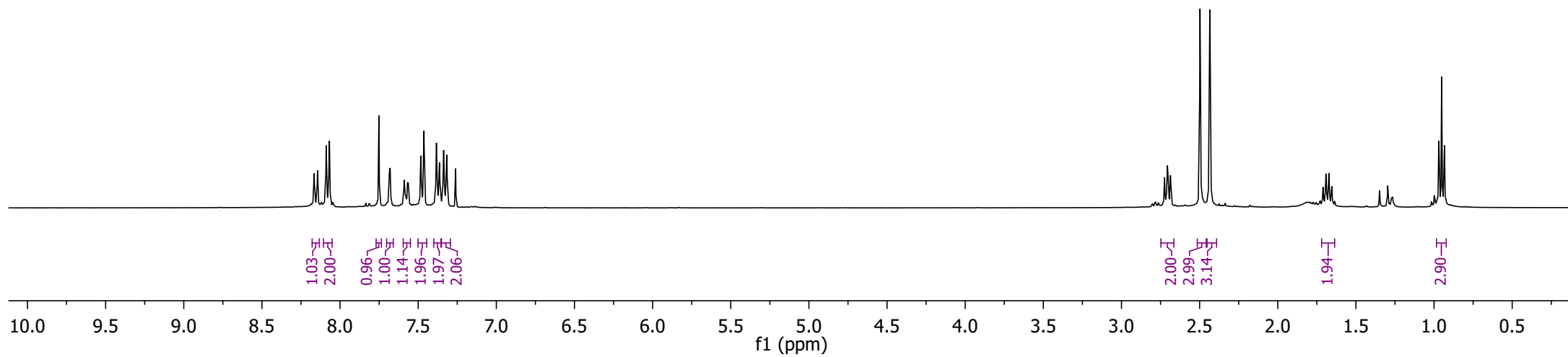
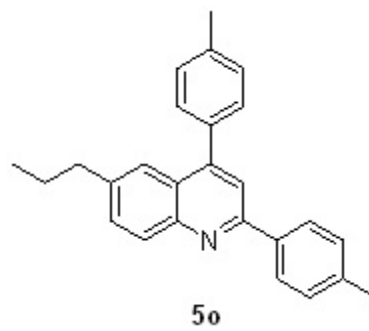


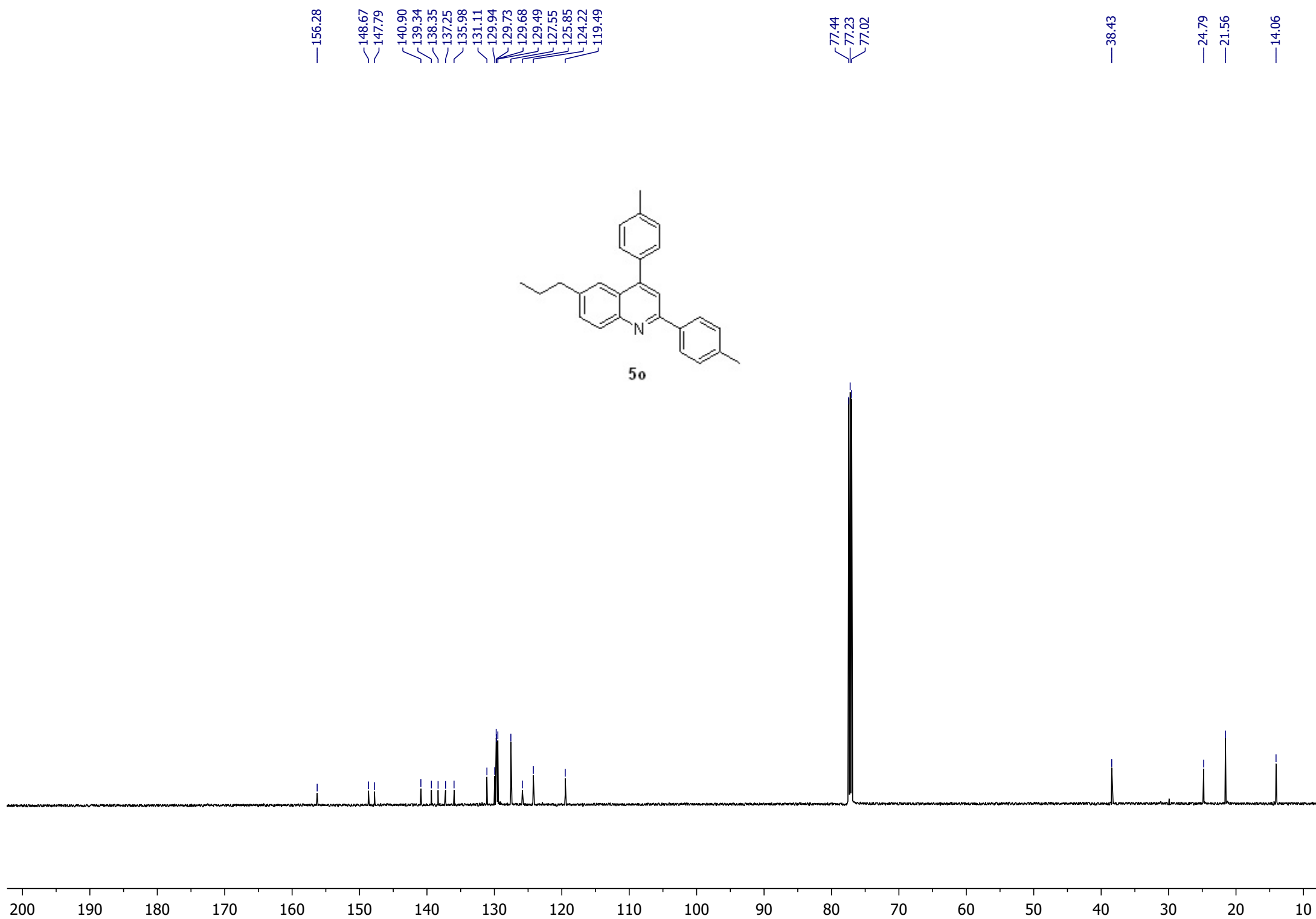
8.166
8.144
8.089
8.068
7.751
7.683
7.679
7.590
7.585
7.568
7.564
7.483
7.463
7.383
7.364
7.337
7.317
7.260

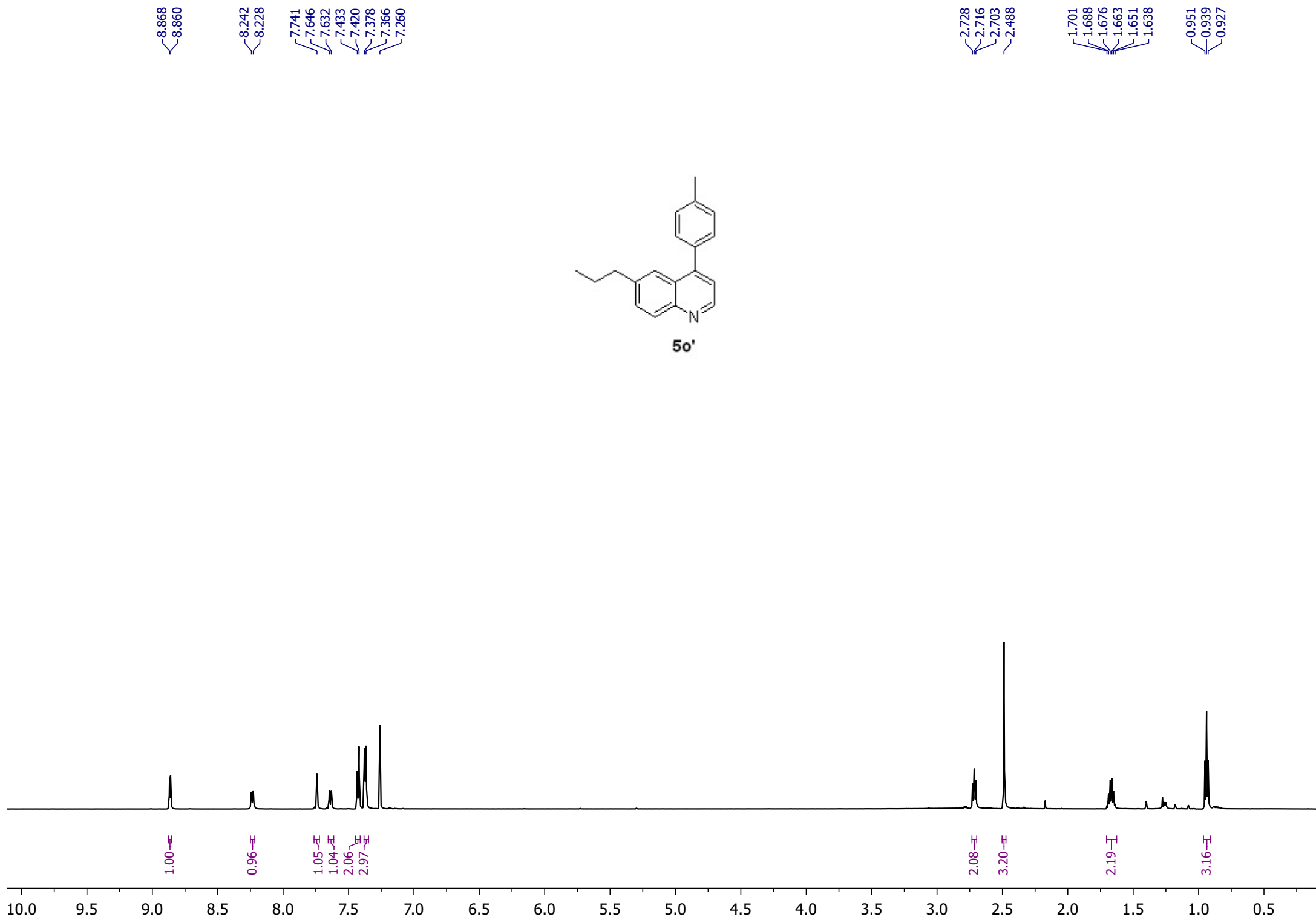
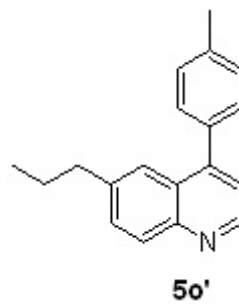
2.725
2.706
2.686
2.497
2.434

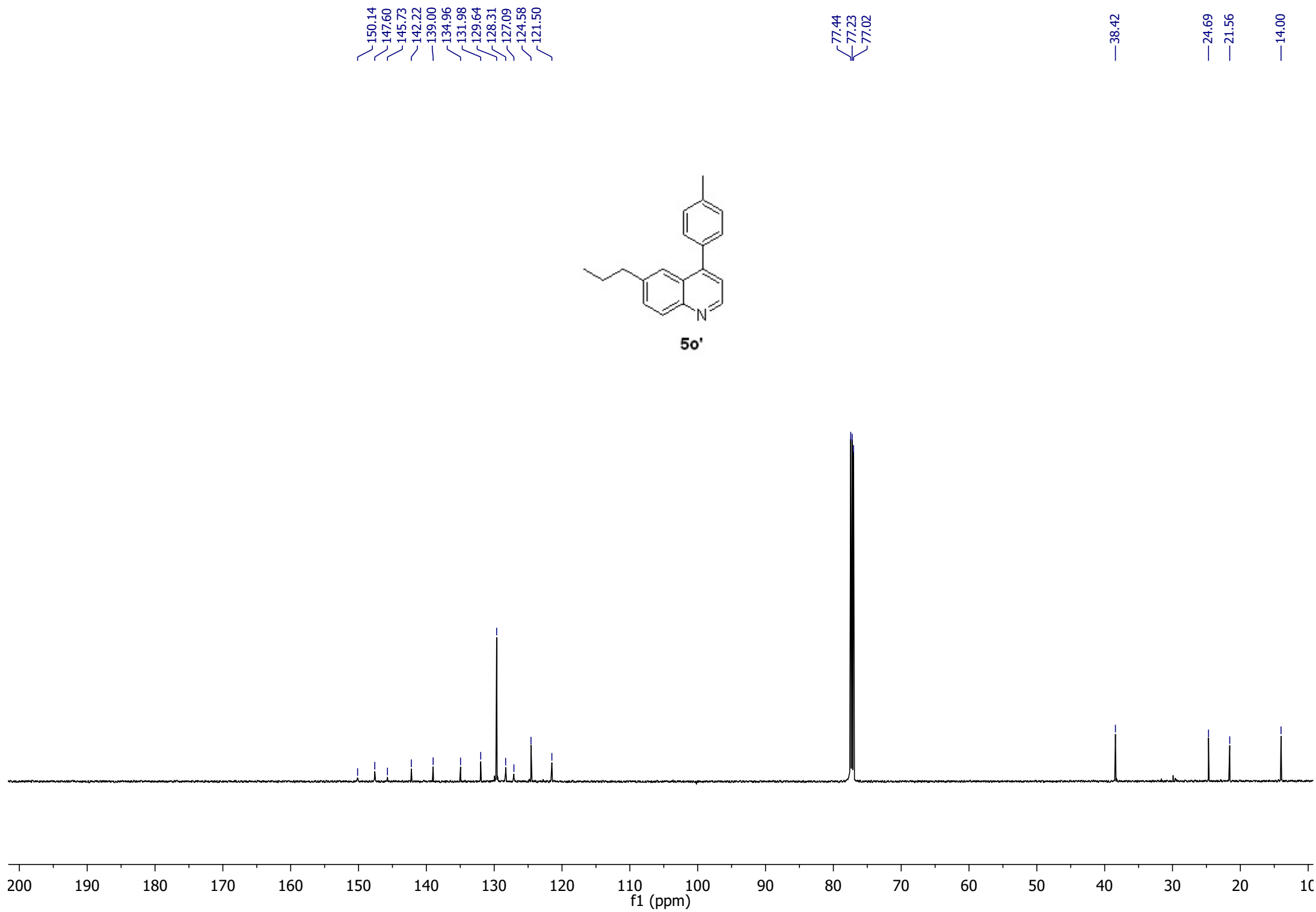
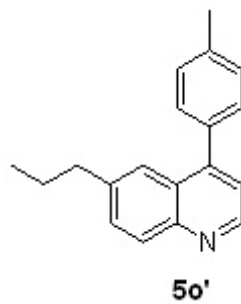
1.729
1.710
1.692
1.673
1.654
1.636

0.970
0.952
0.933





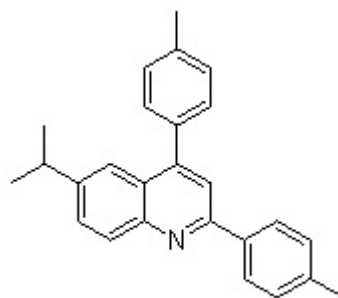




8.180
8.166
8.084
8.071
7.757
7.733
7.658
7.655
7.643
7.640
7.492
7.478
7.384
7.371
7.336
7.323
7.260

3.059
3.048
3.037
3.025
3.014
2.500
2.436

1.300
1.288



5p

1.00
2.02

1.09
0.91
0.96

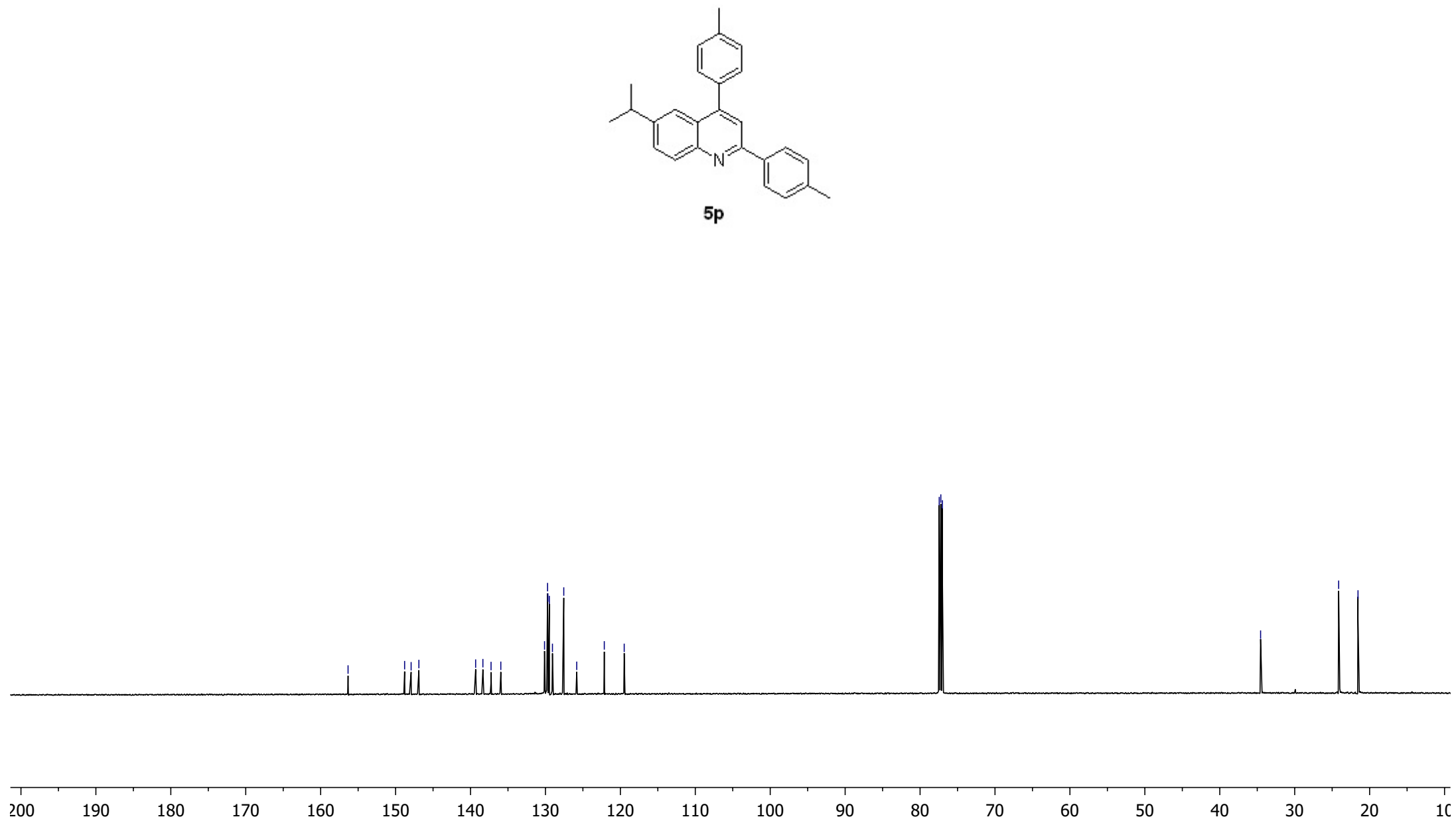
1.93
2.07
1.98

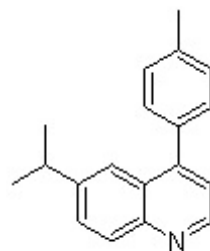
0.98

2.94
3.02

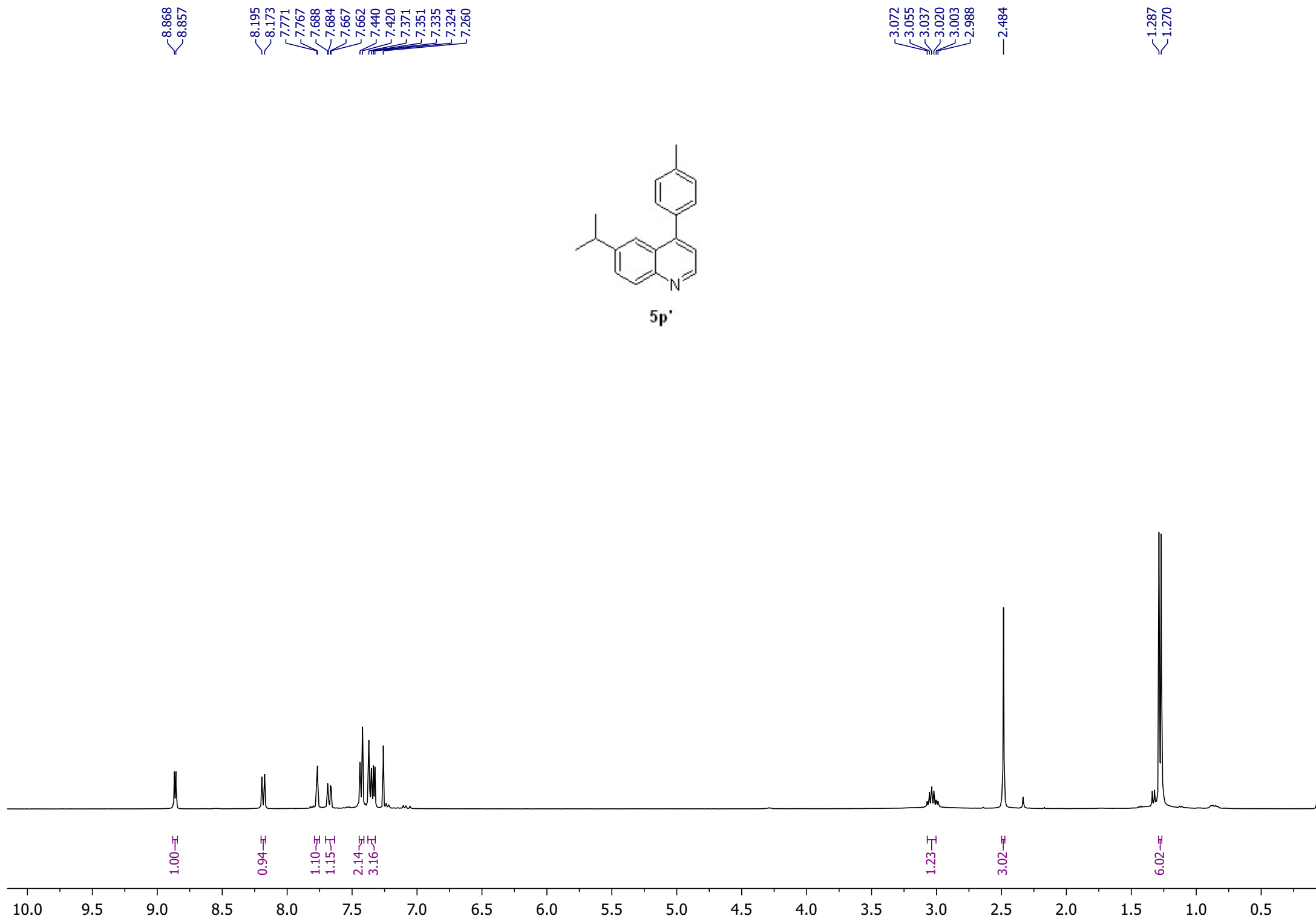
6.22

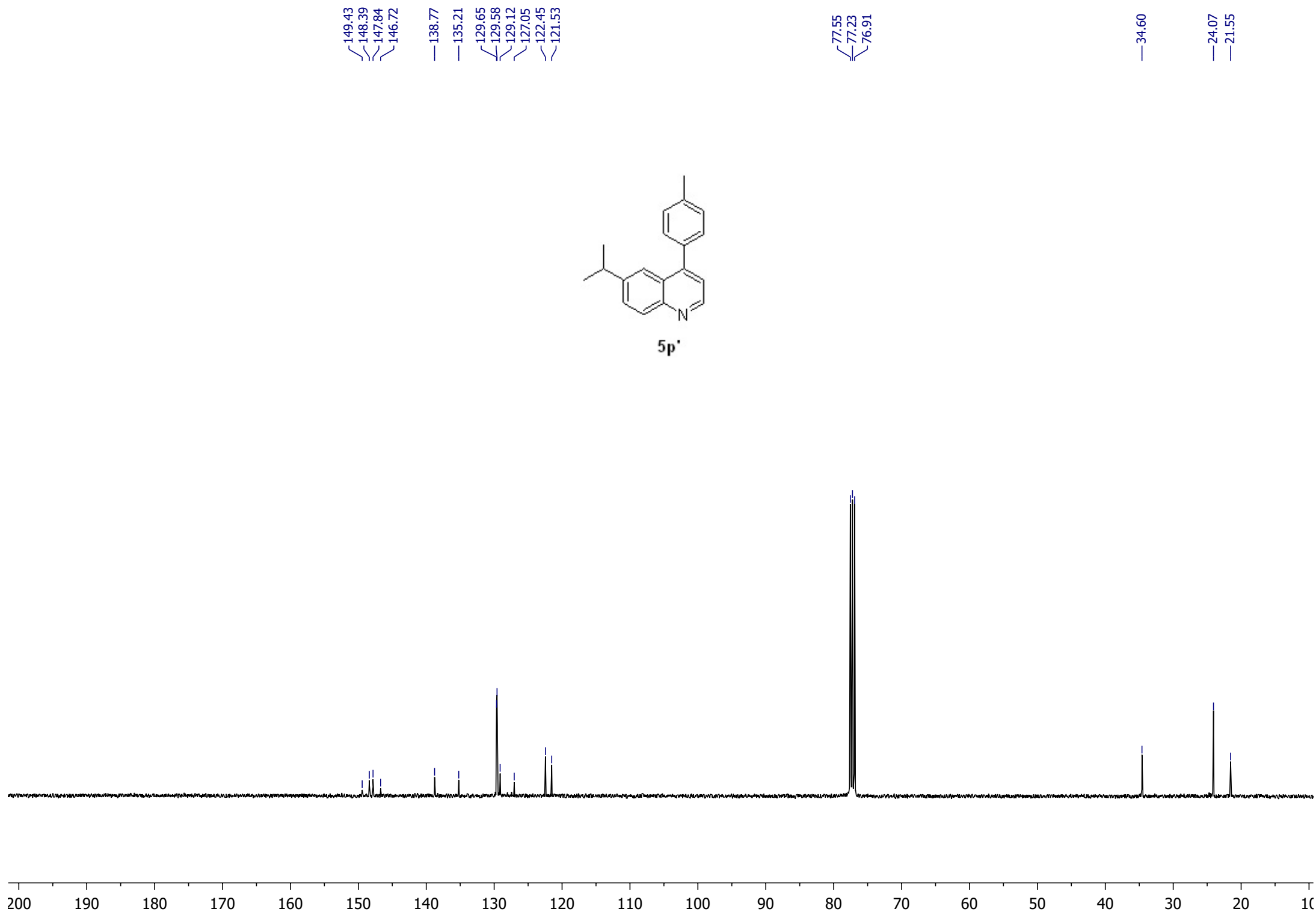
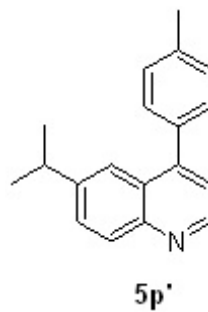
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5





5p'

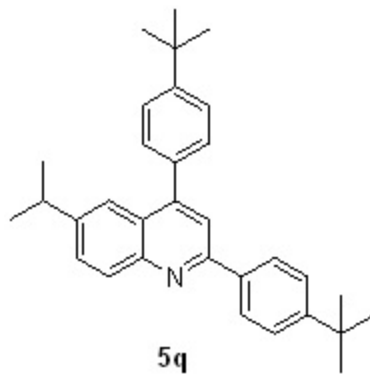




8.185
8.164
8.104
8.083
7.773
7.767
7.660
7.655
7.638
7.633
7.598
7.577
7.549
7.540
7.534
7.528
7.519
7.260

3.086
3.069
3.052
3.034
3.017

1.444
1.383
1.311
1.293



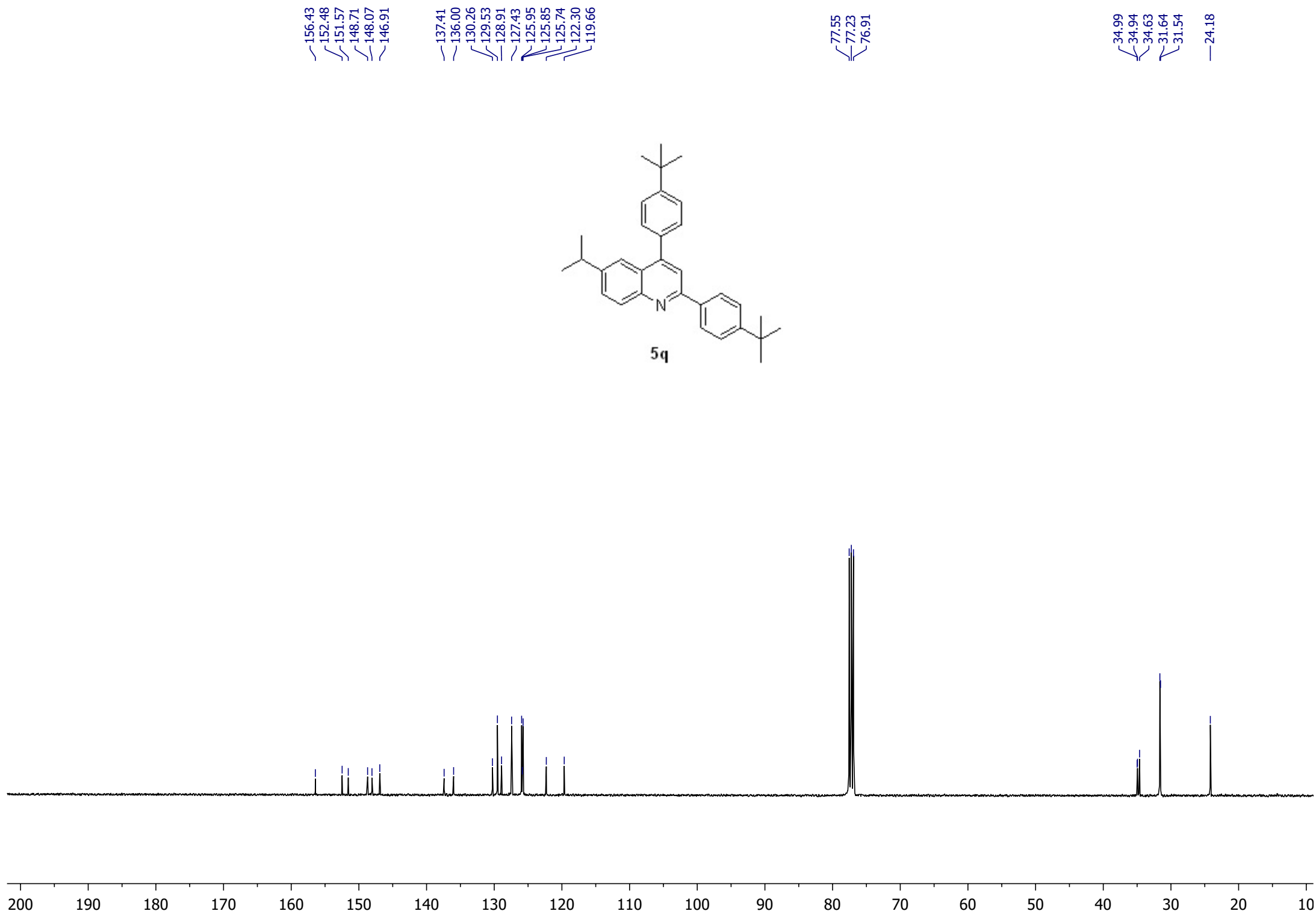
1.02
2.00

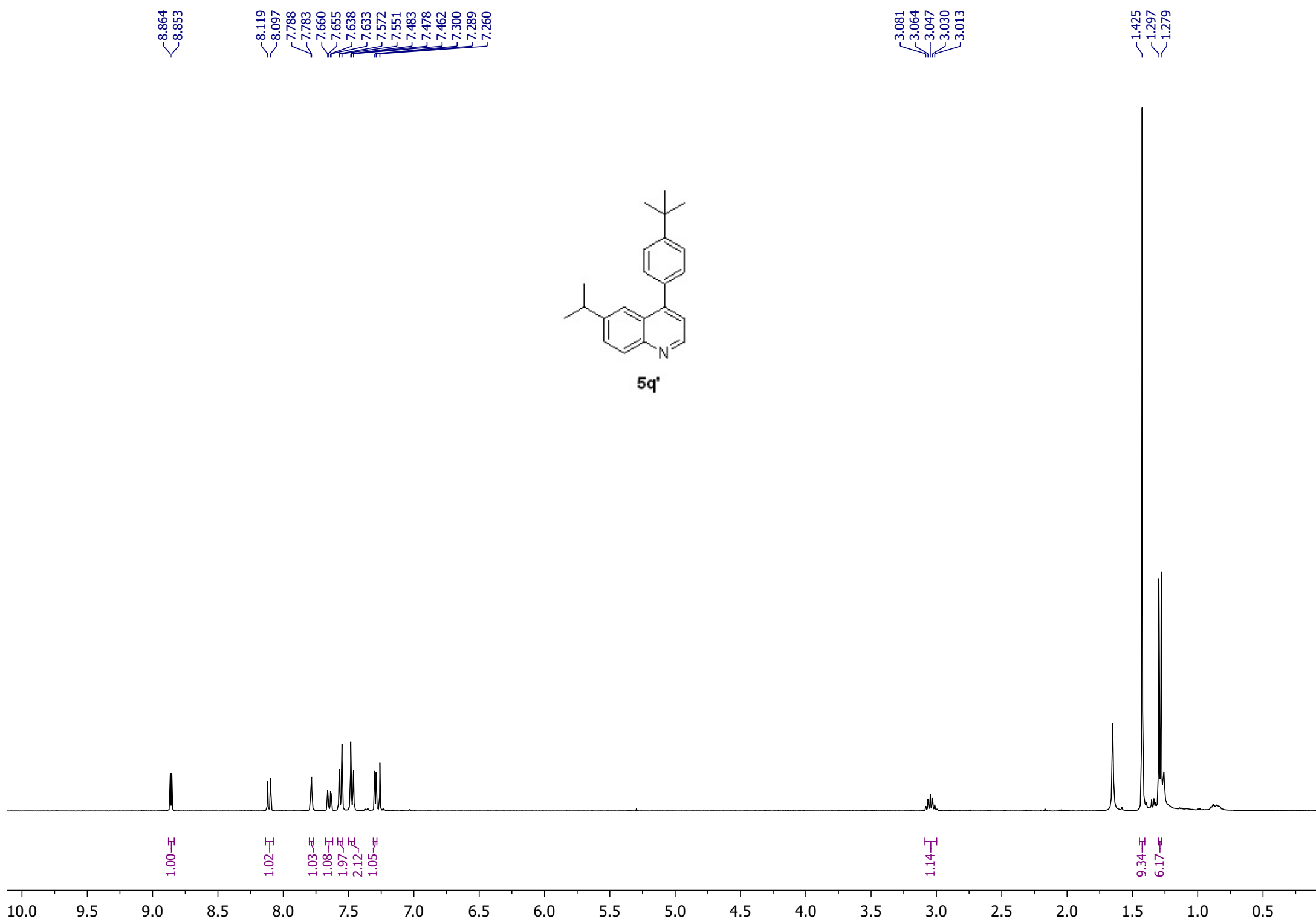
1.98
1.15
2.09
4.17

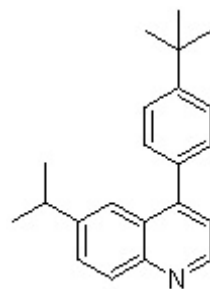
1.04

9.15
9.22
5.84

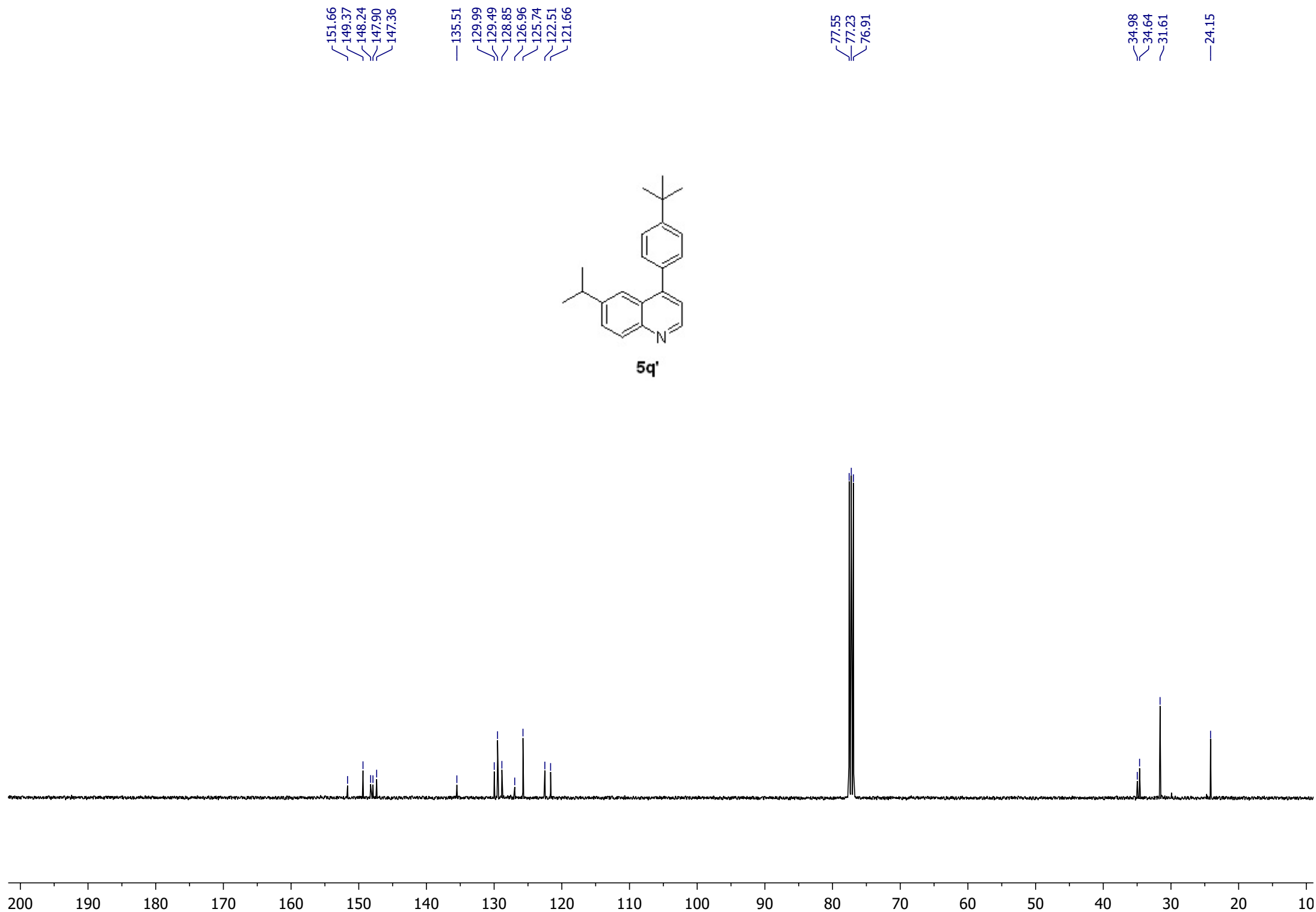
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

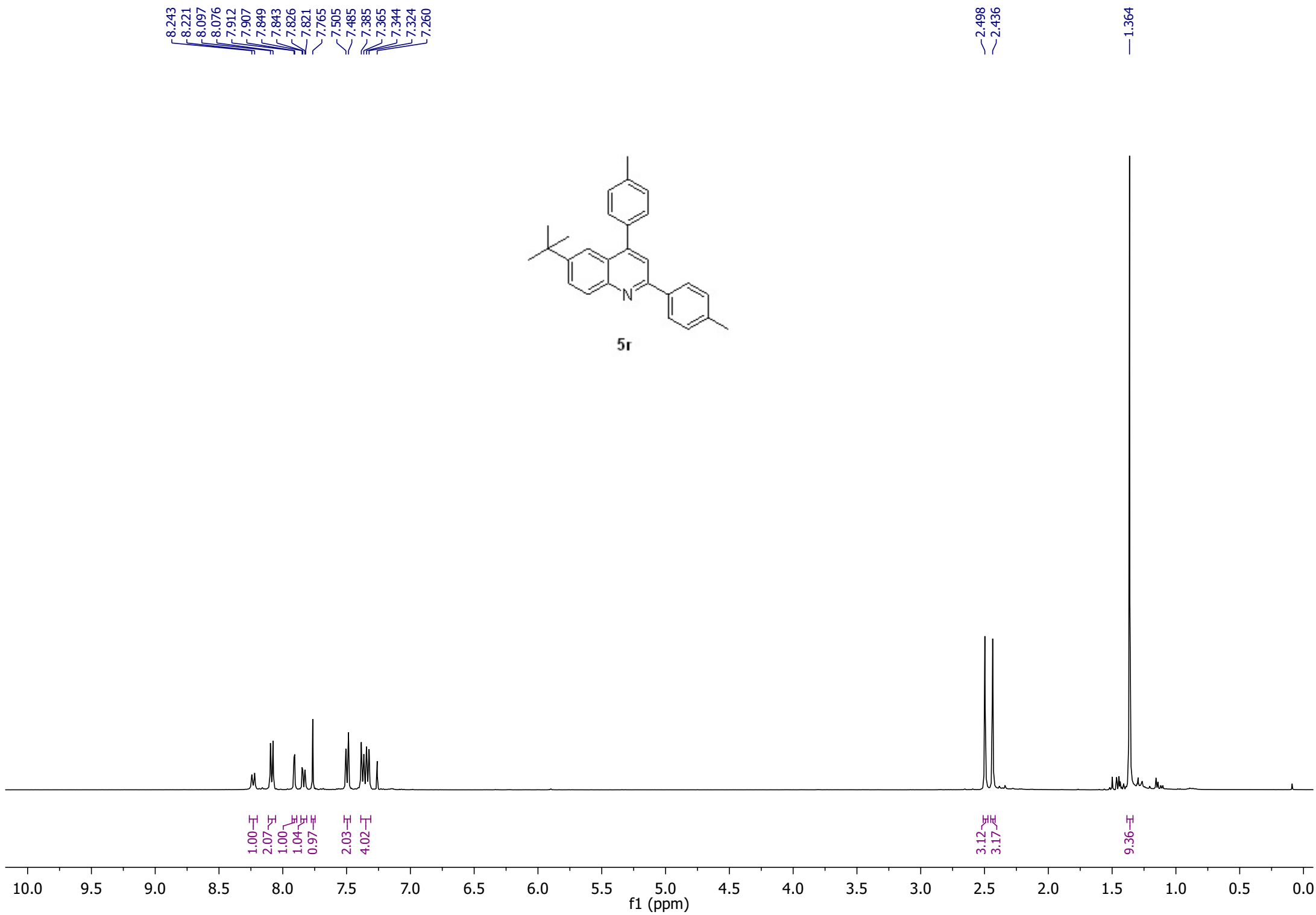


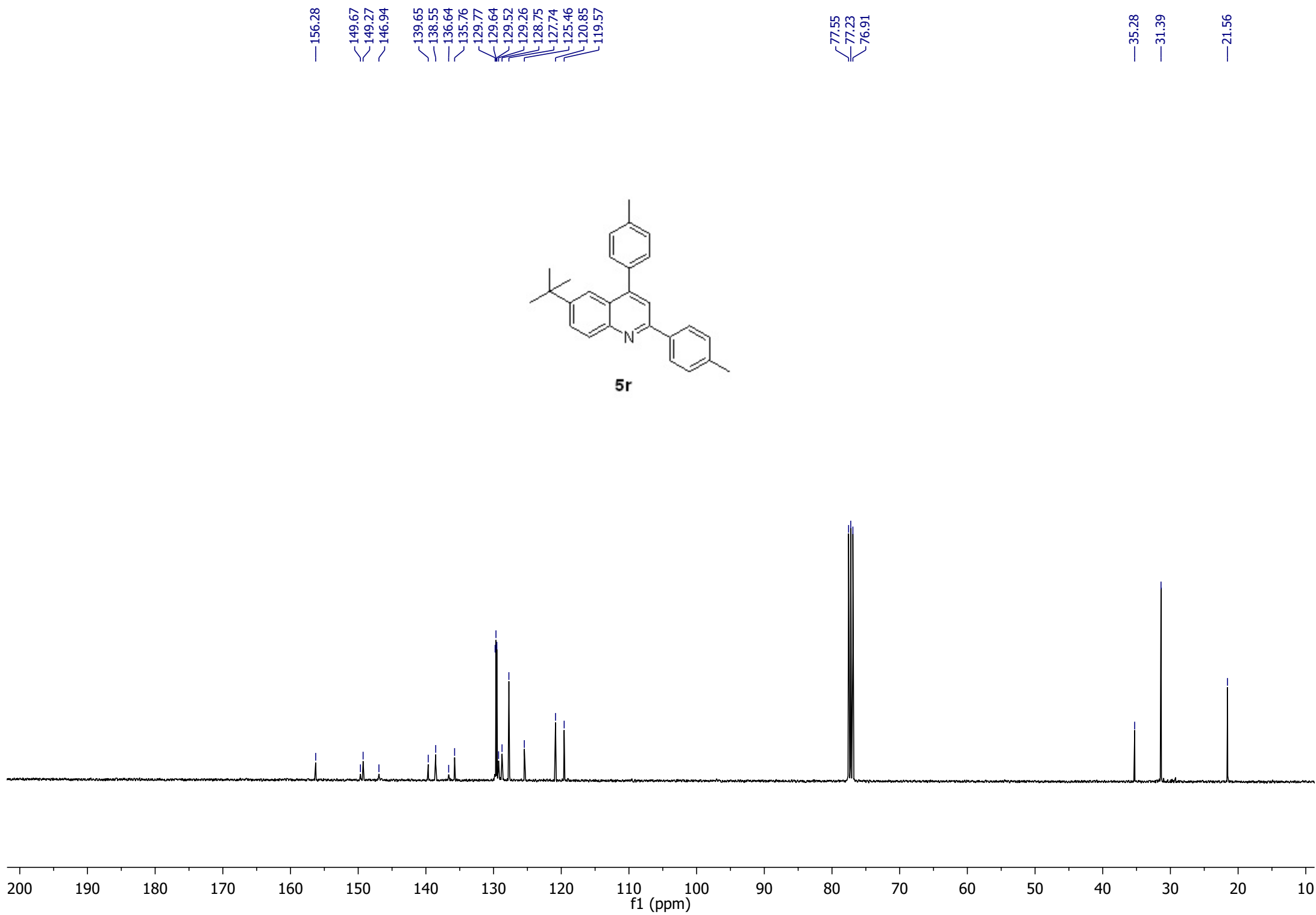


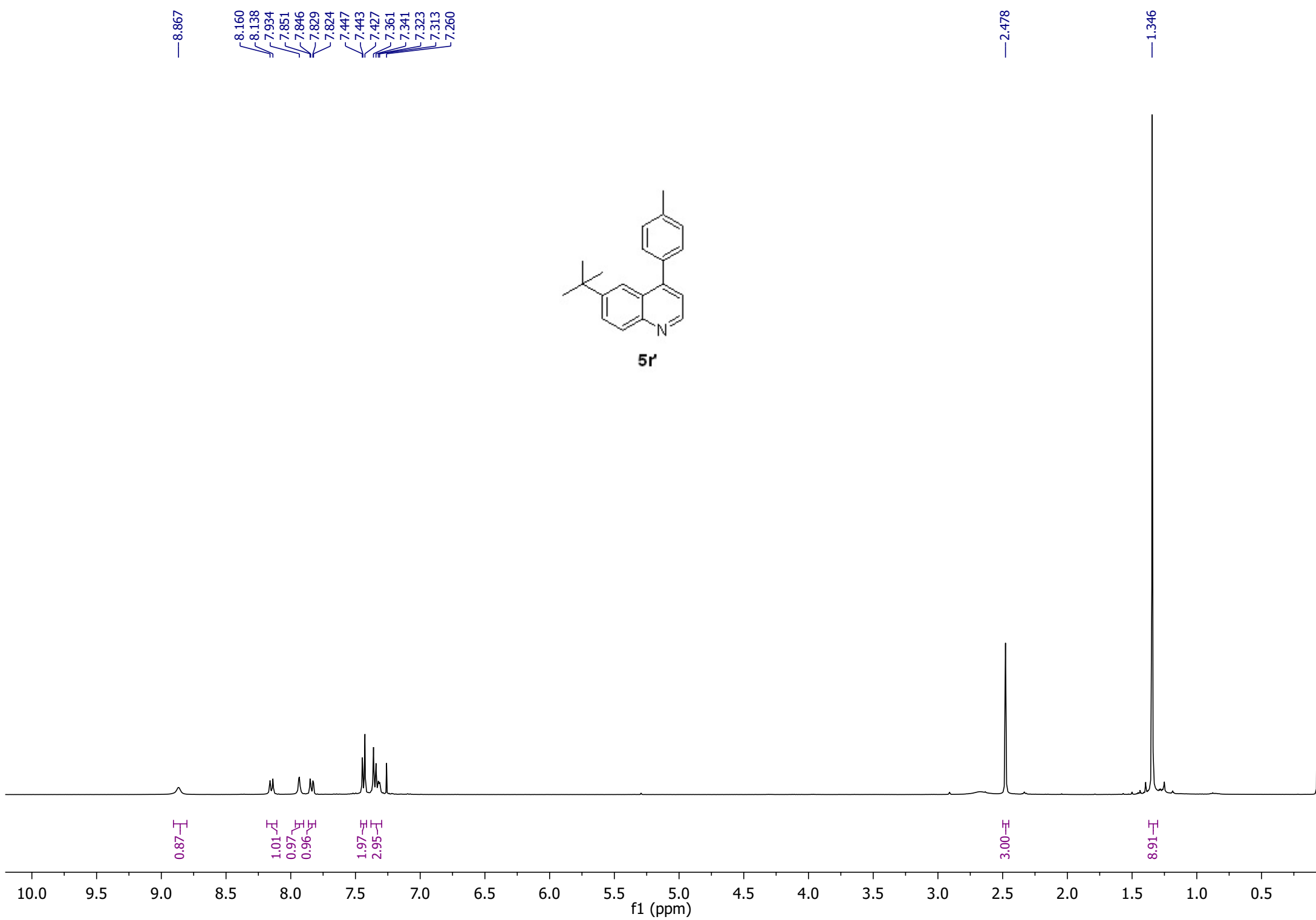


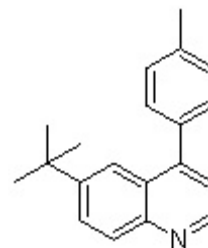
5q'



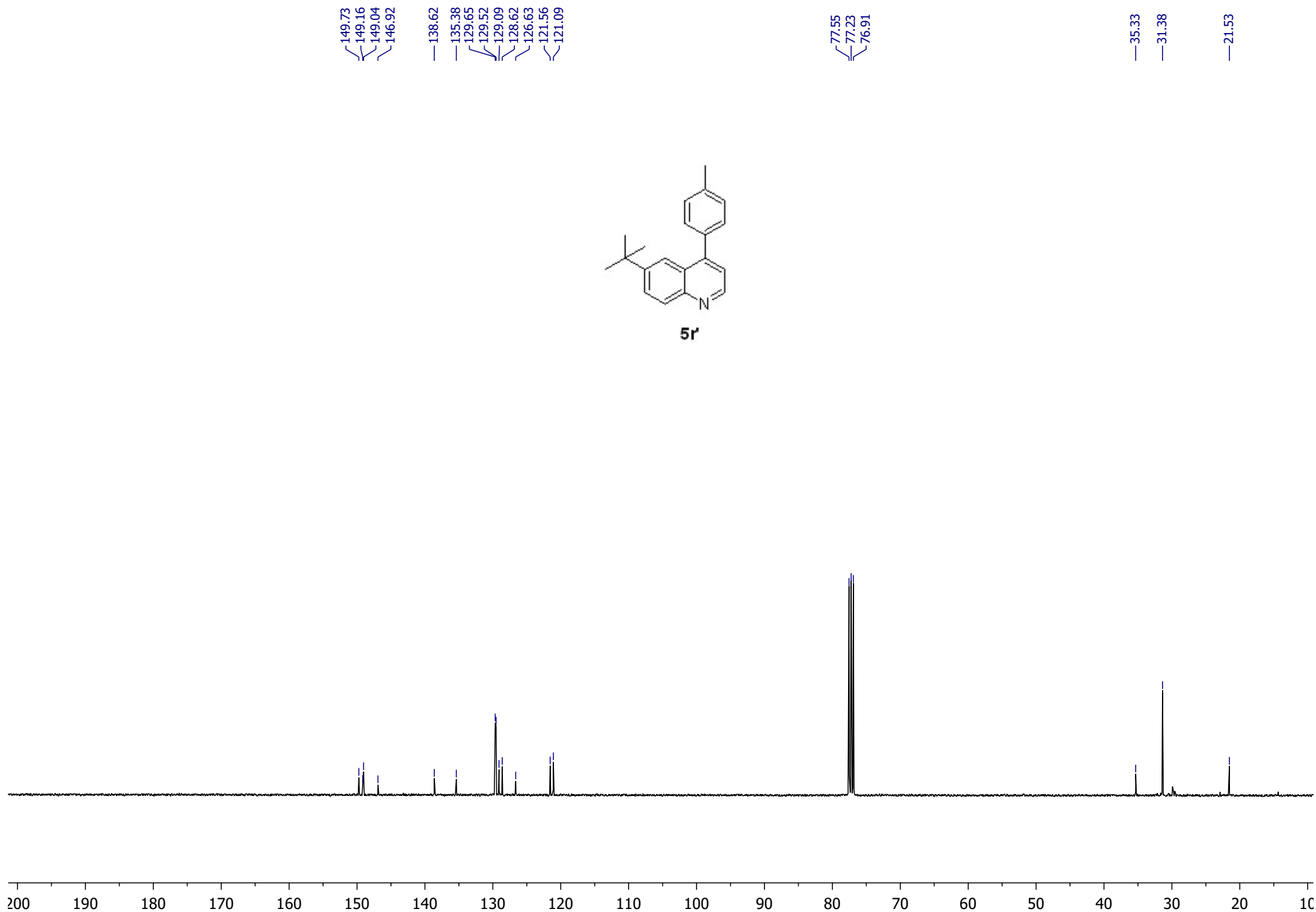






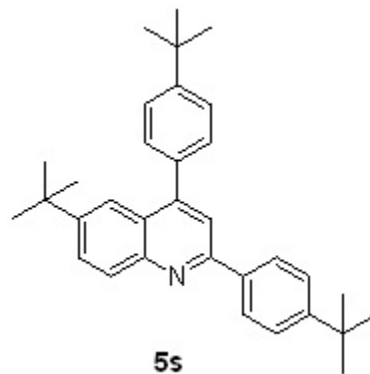


5r



8.249
8.228
8.121
8.100
7.956
7.951
7.851
7.845
7.828
7.823
7.791
7.605
7.584
7.560
7.539
7.260

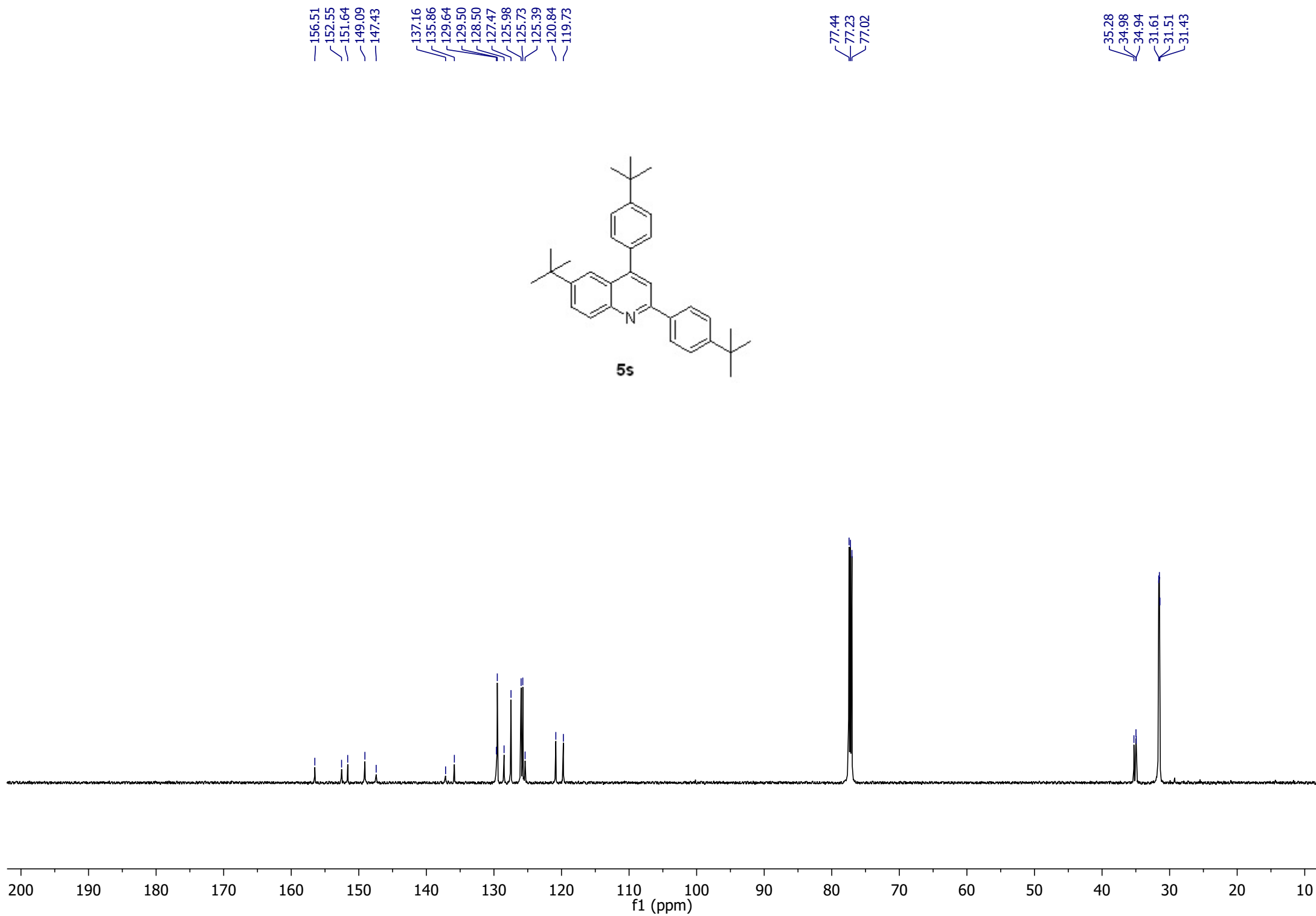
1.444
1.385
1.375

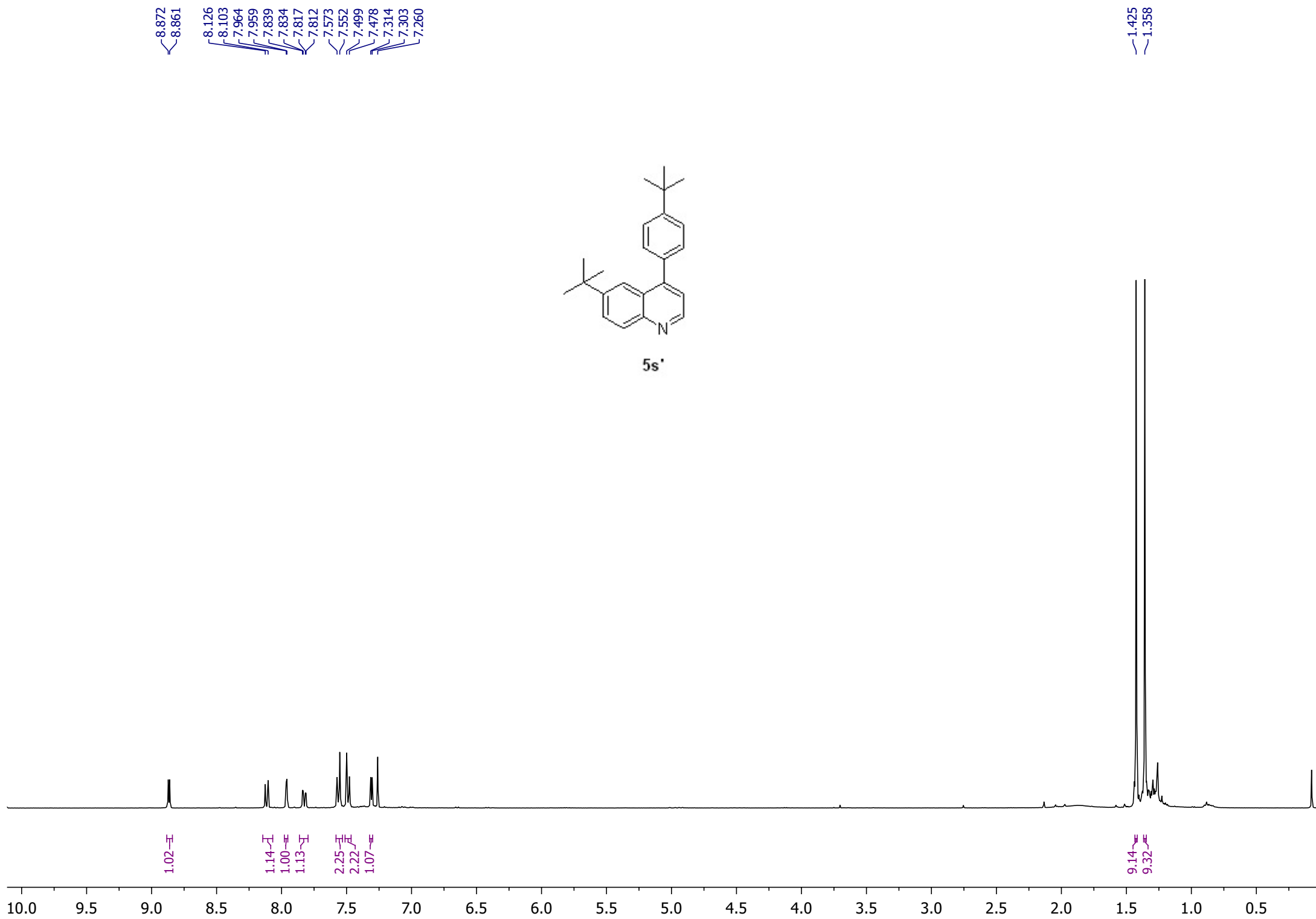


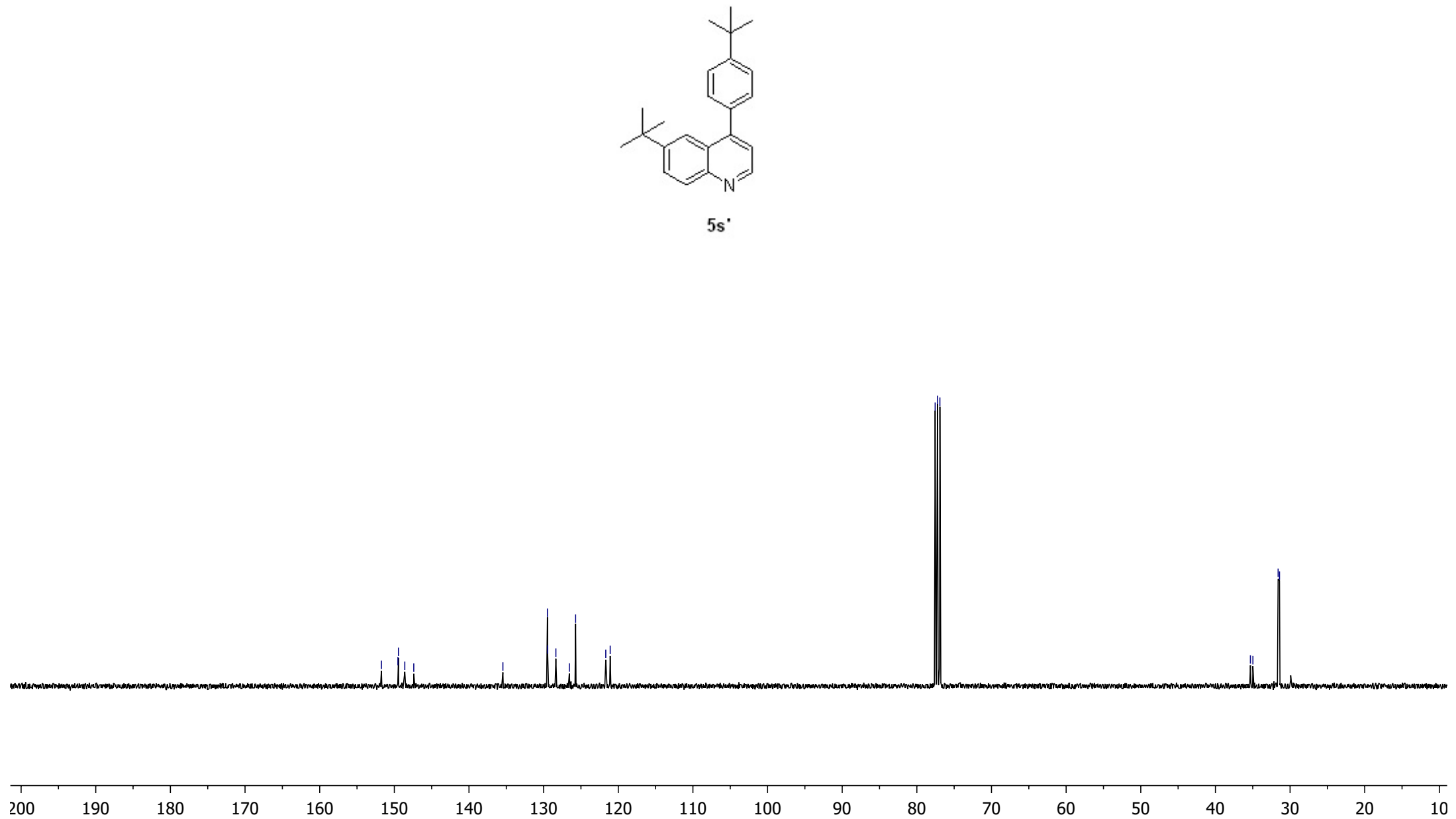
1.00
2.13
0.97
1.11
0.98
6.38

9.19
9.26
9.12

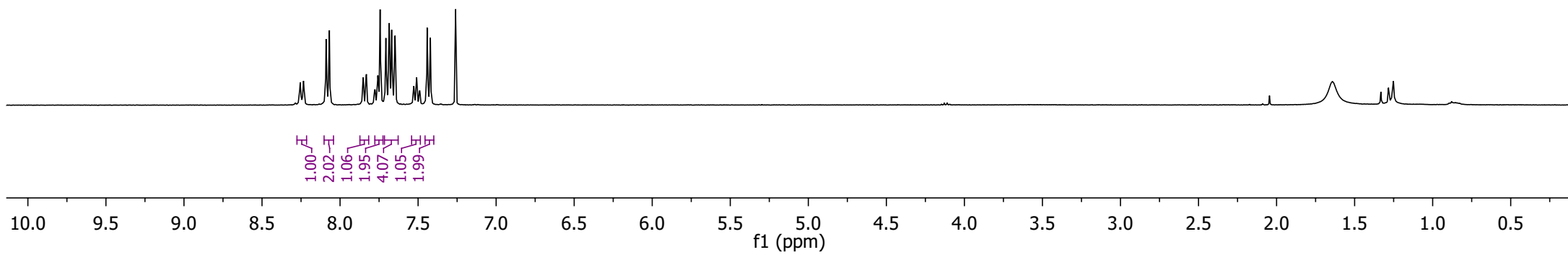
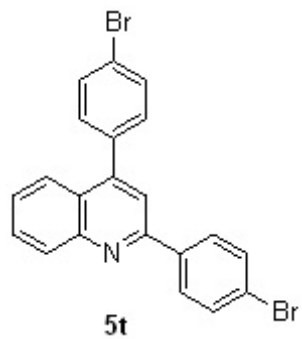
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

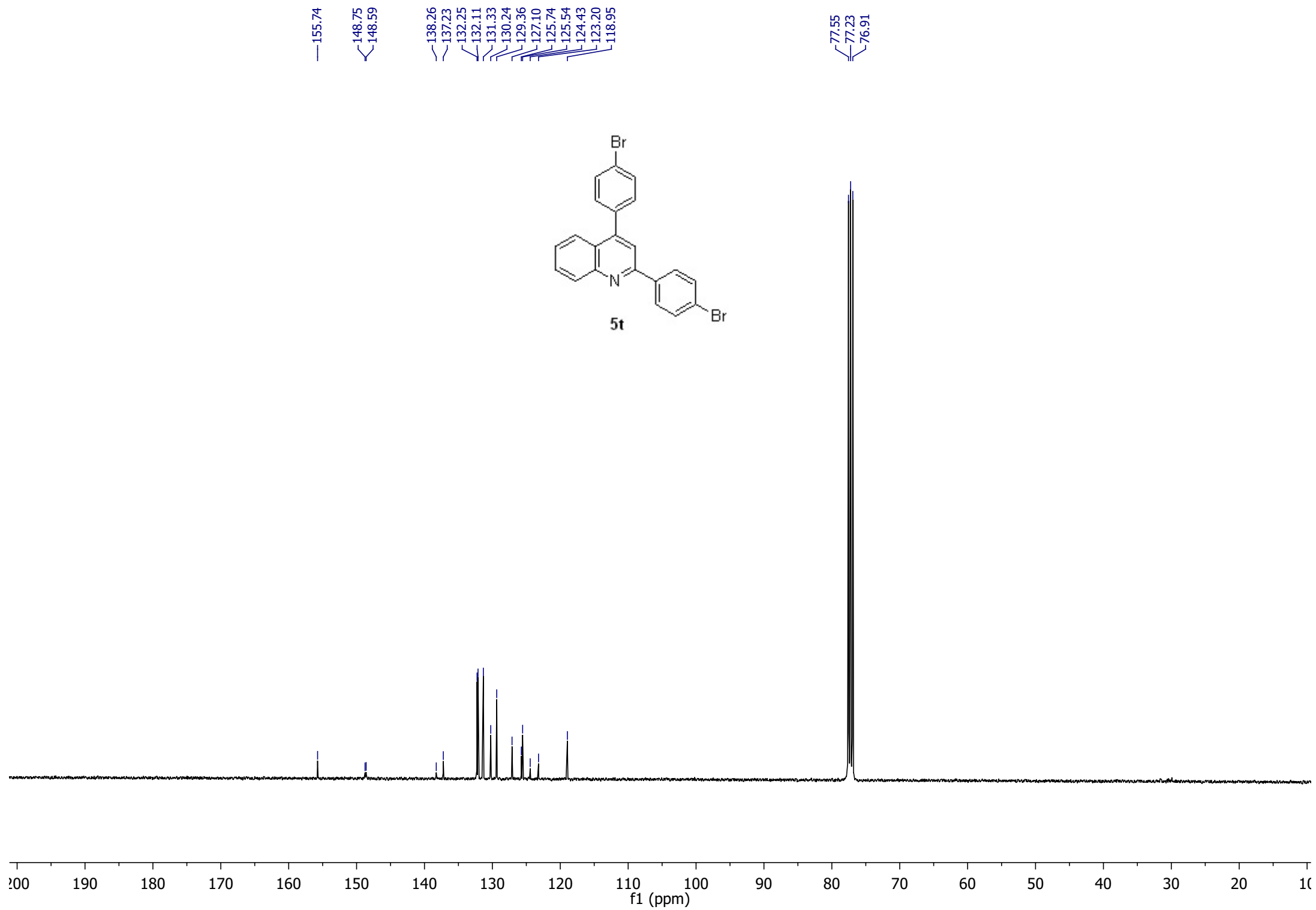


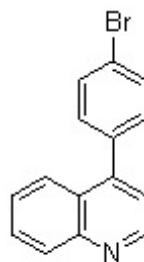




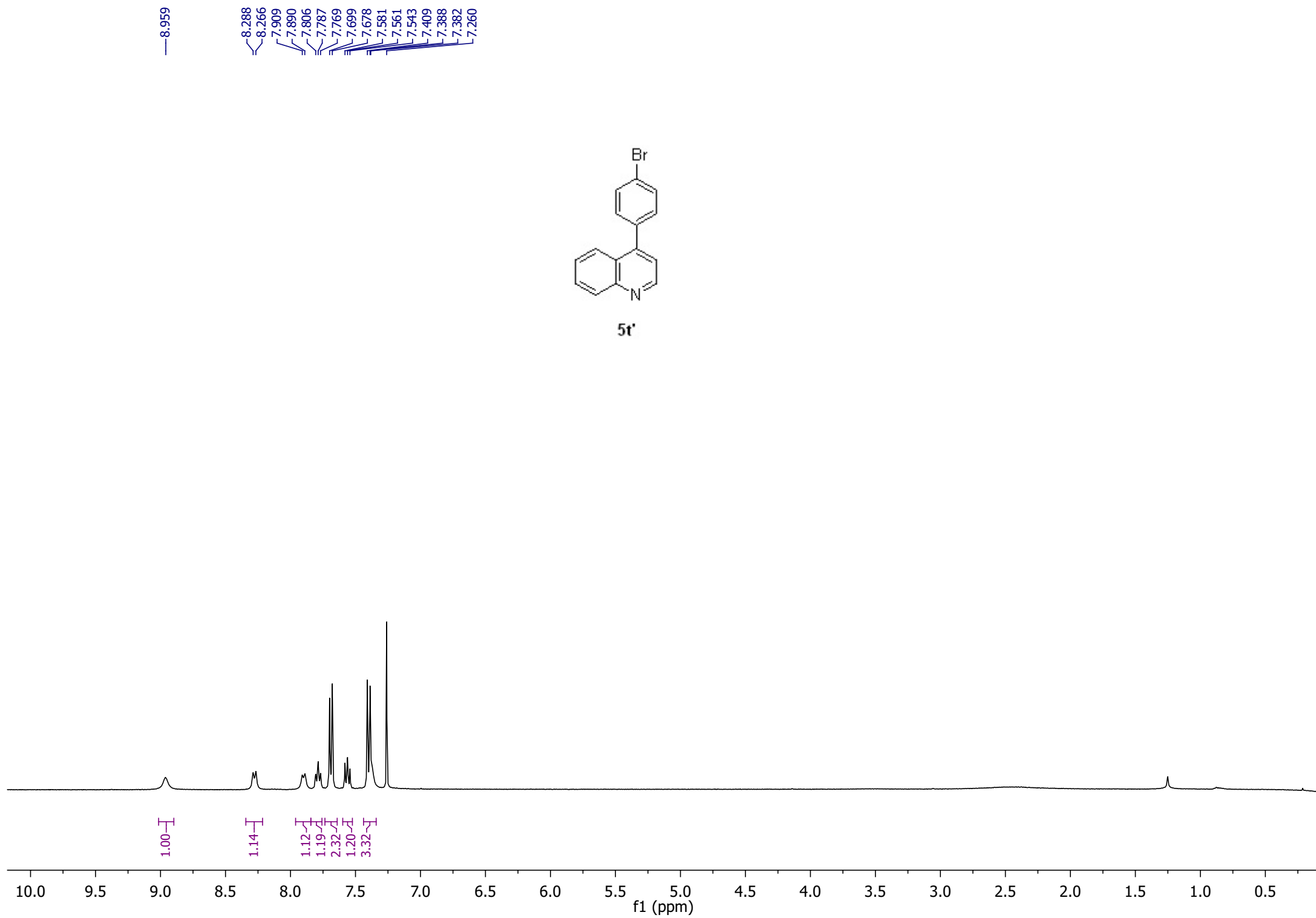
8.255
8.234
8.090
8.068
7.852
7.831
7.778
7.758
7.743
7.706
7.685
7.669
7.648
7.527
7.509
7.489
7.442
7.421
7.260

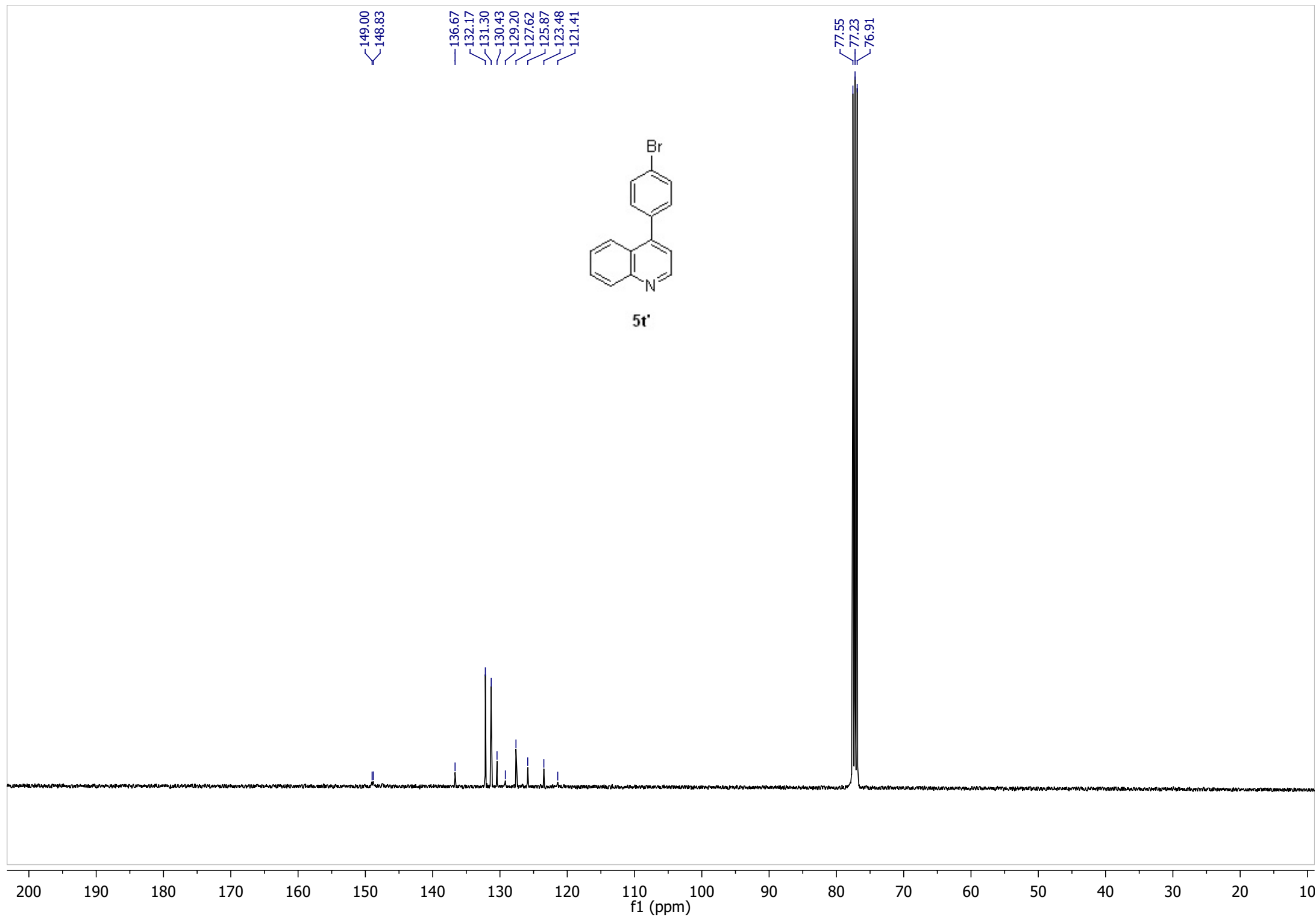


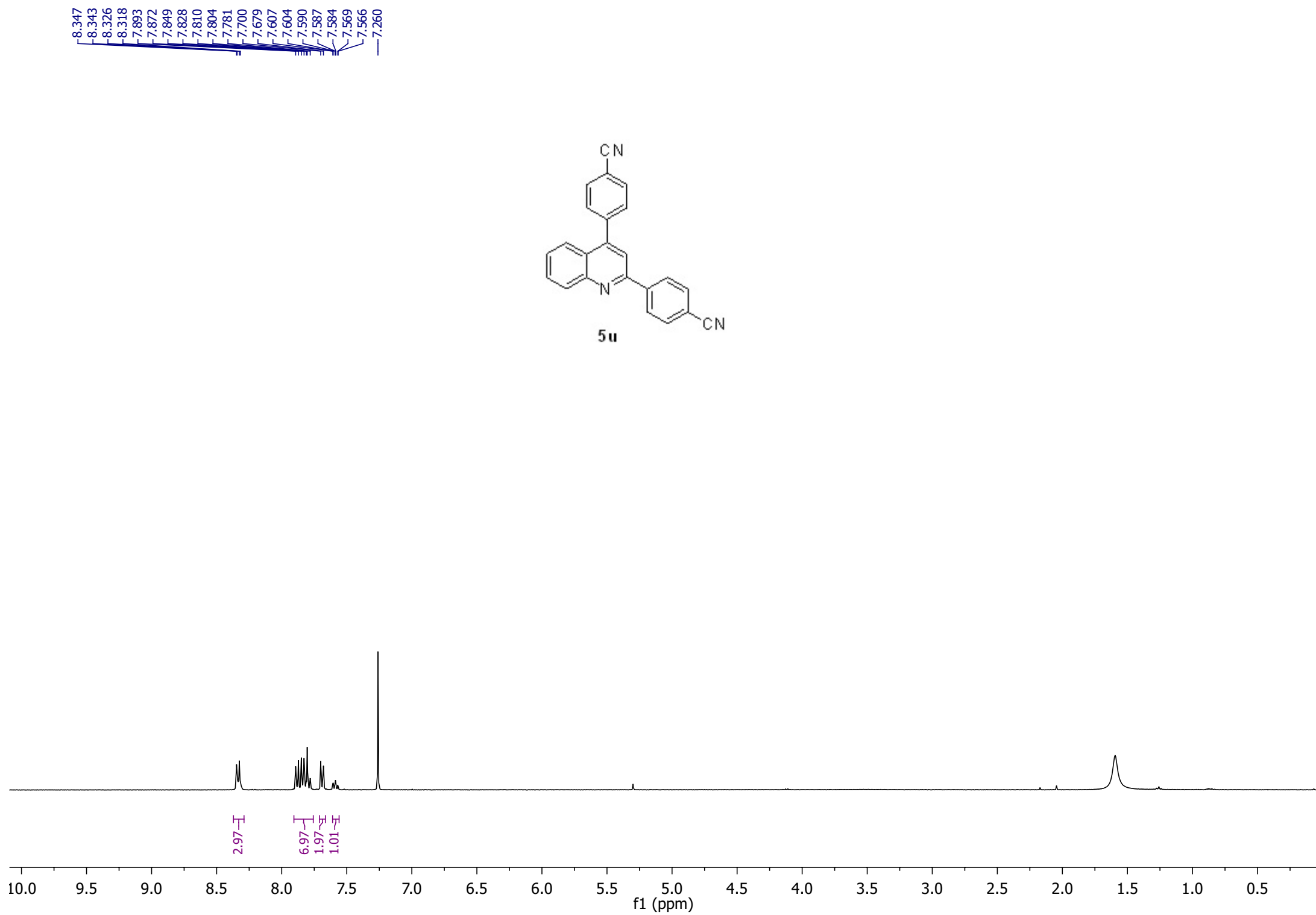


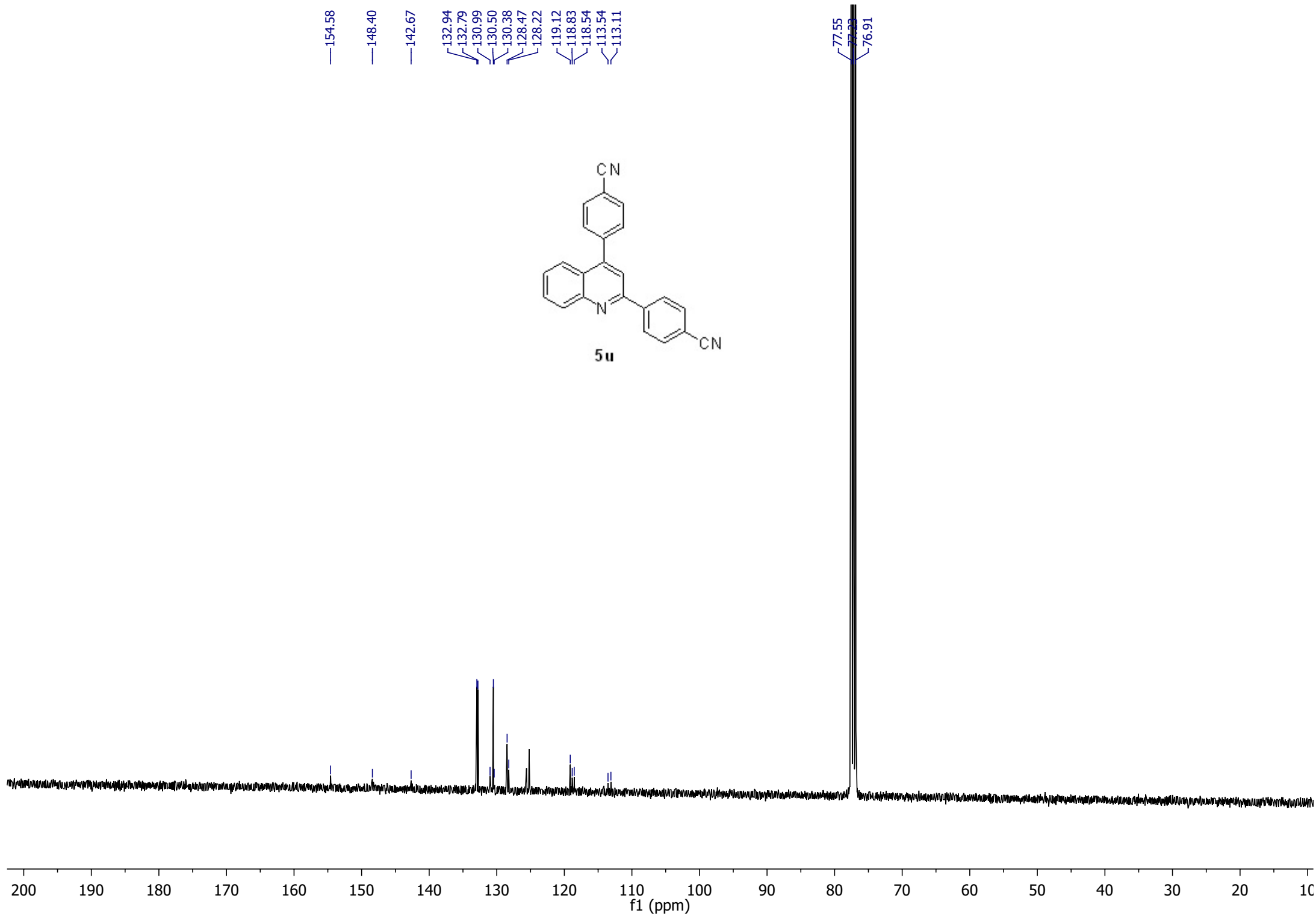


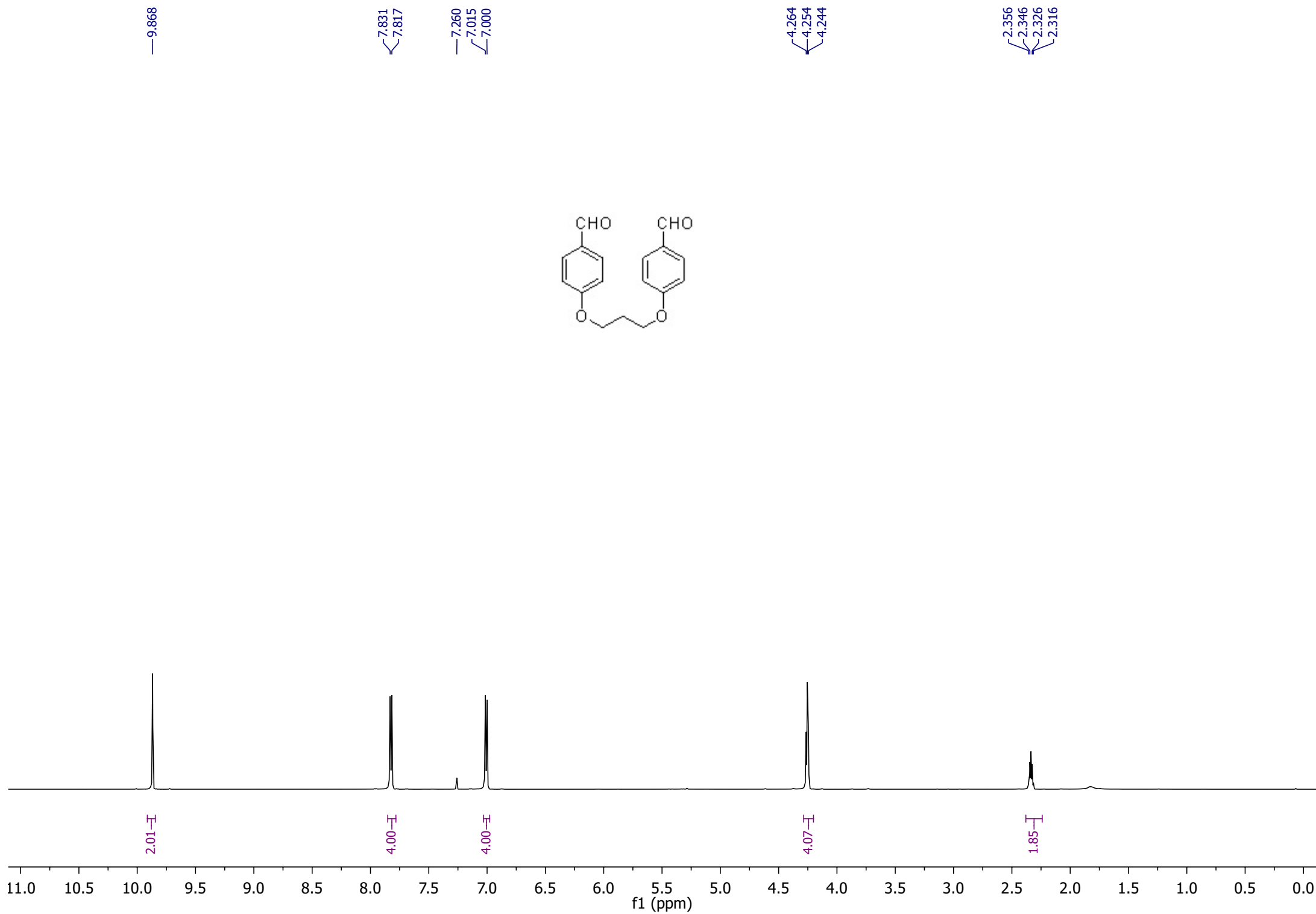
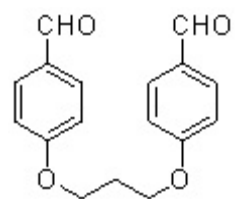
5t'

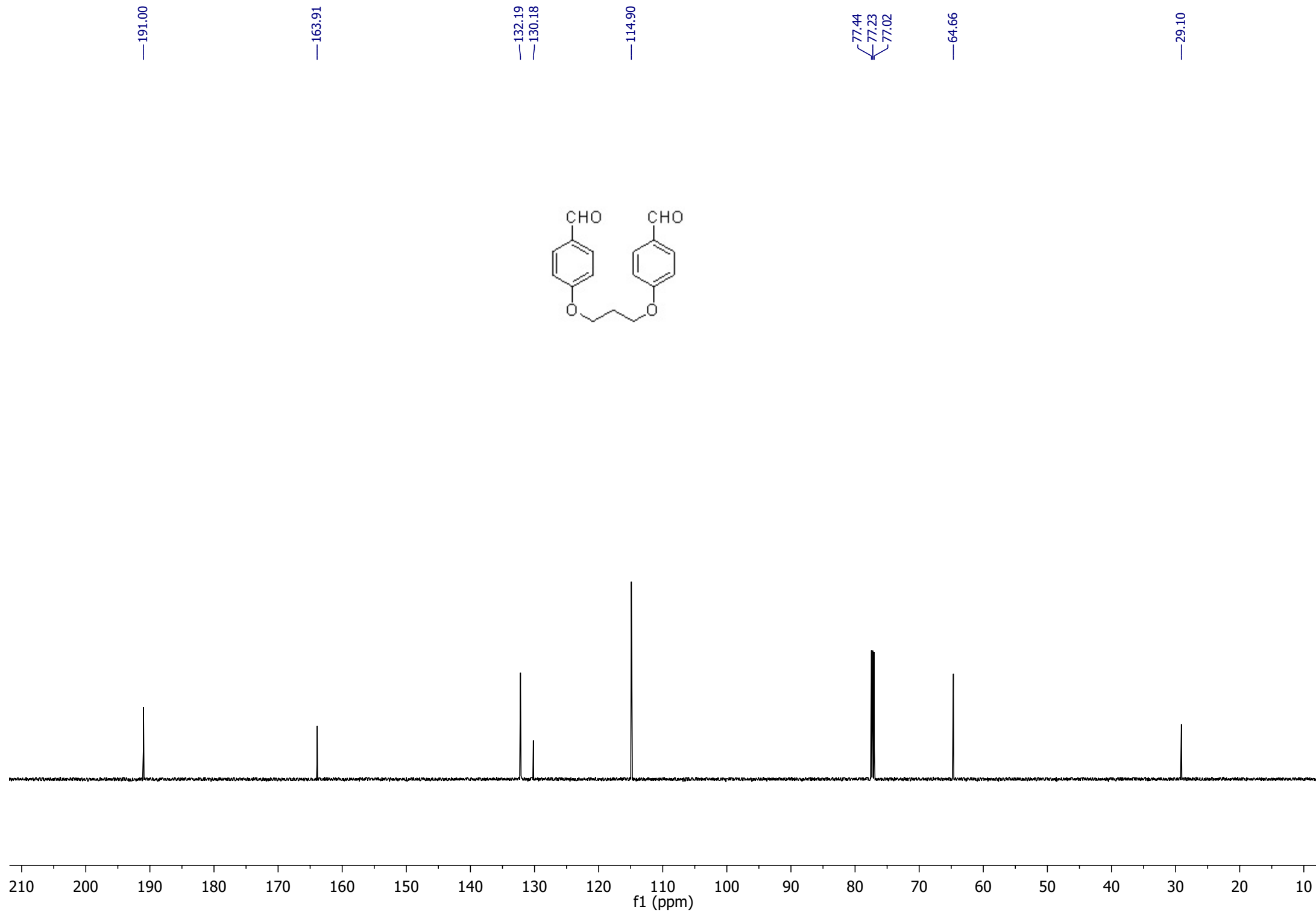
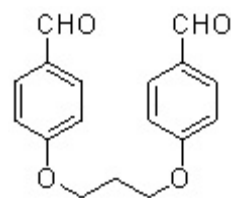


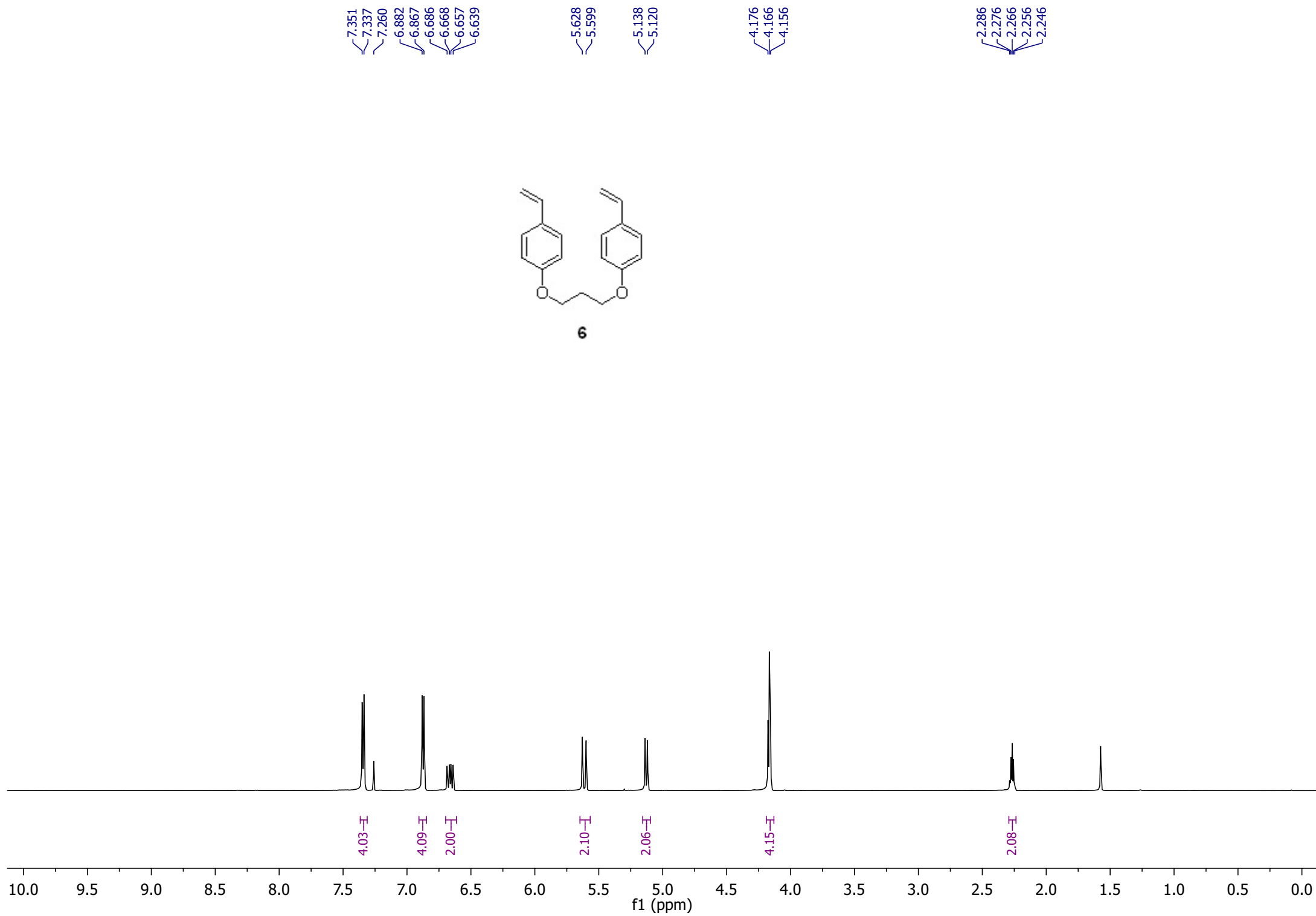
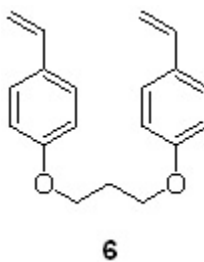


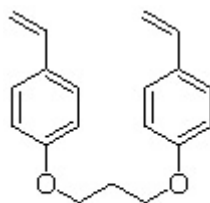




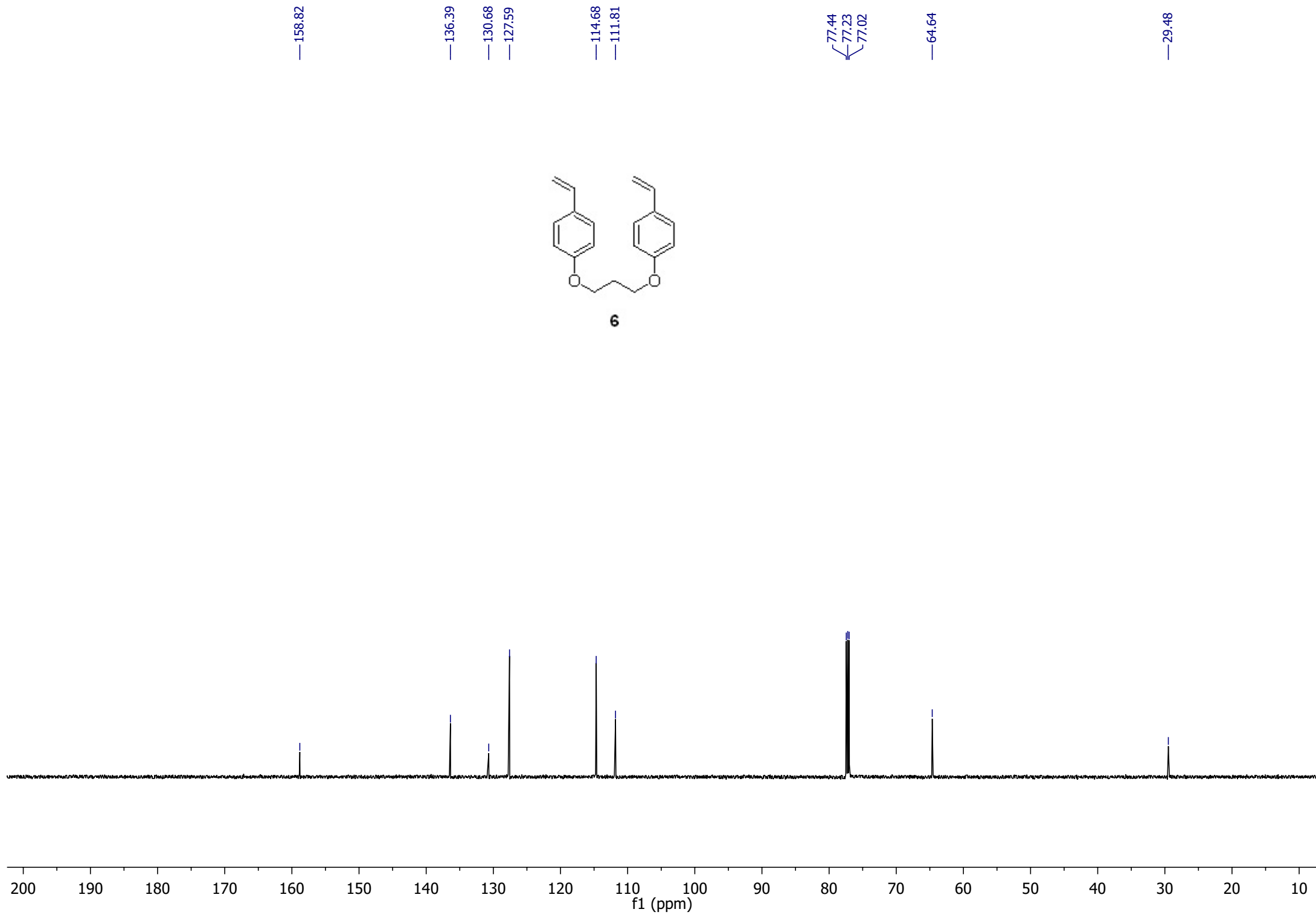






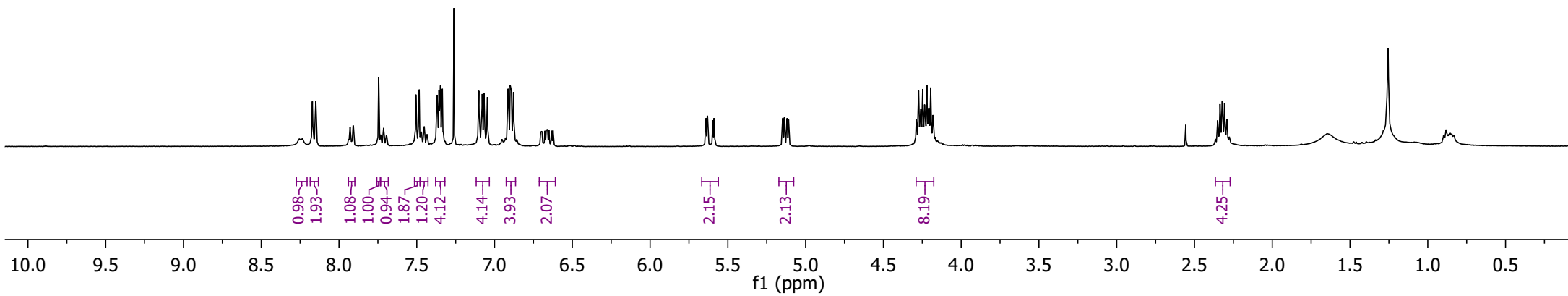
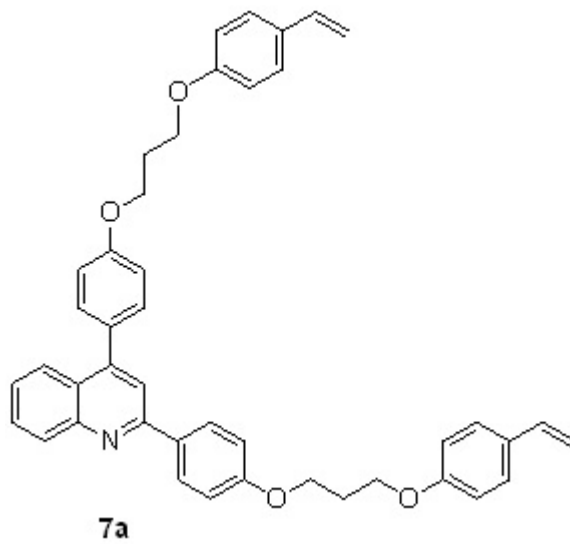


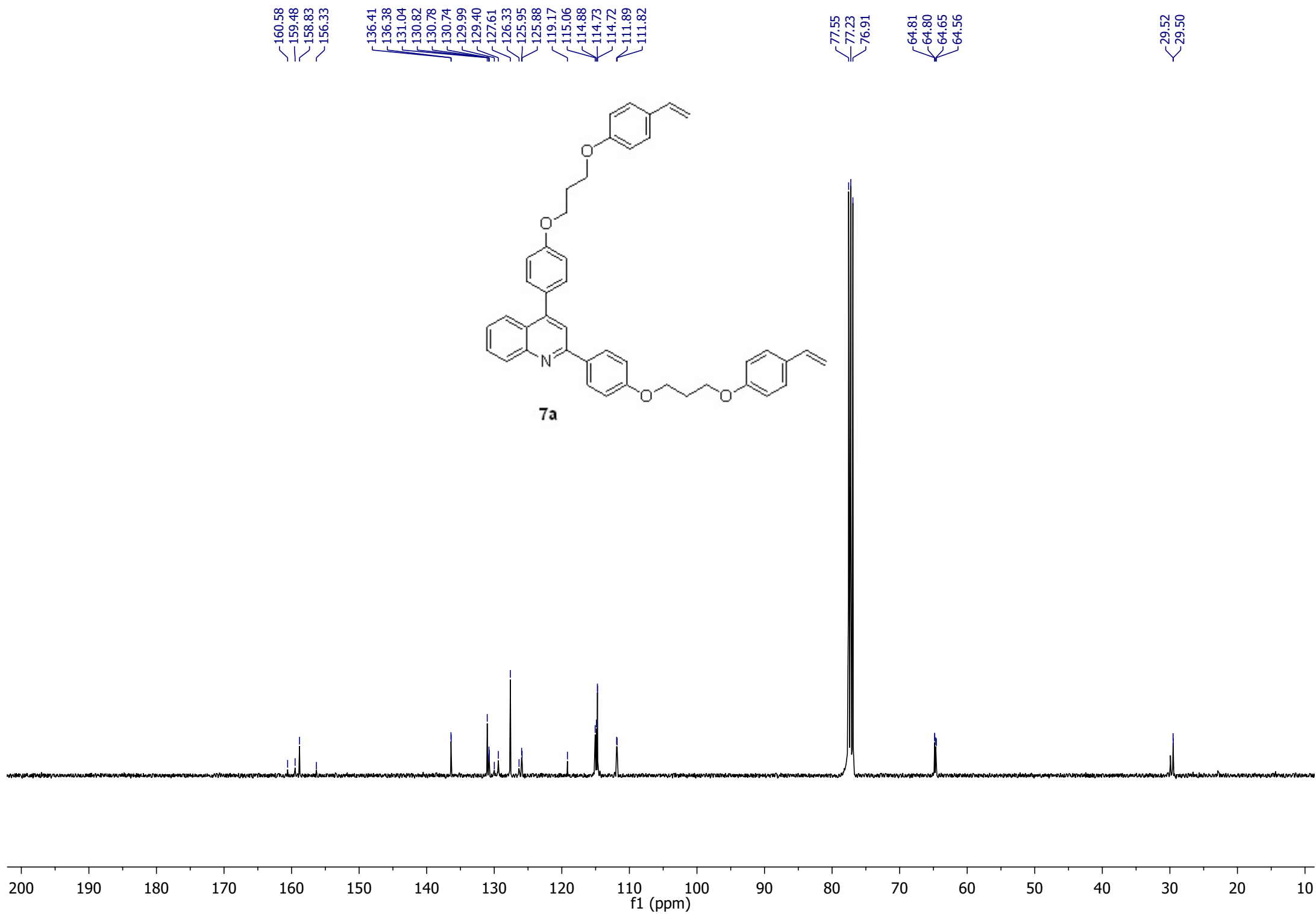
6

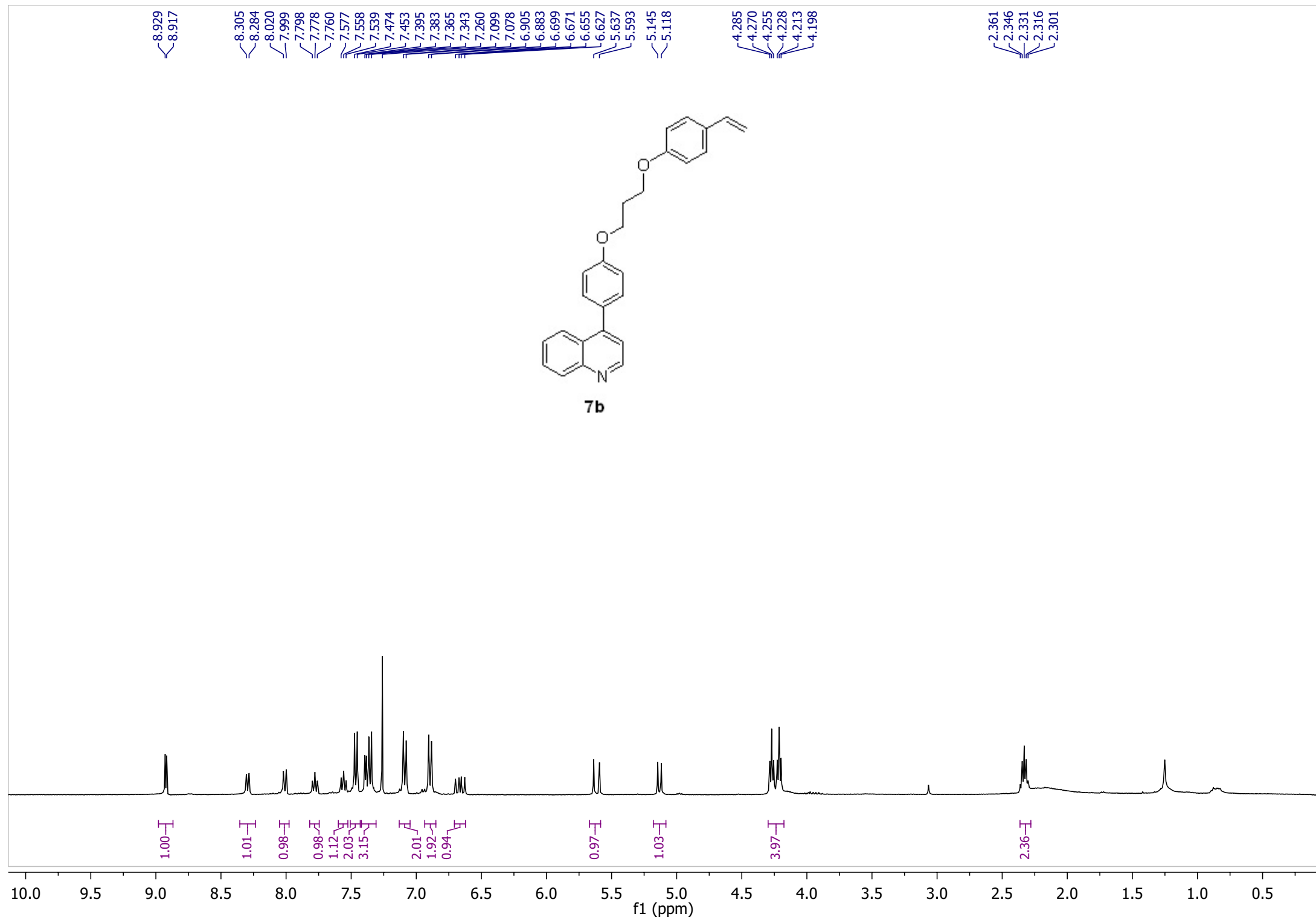


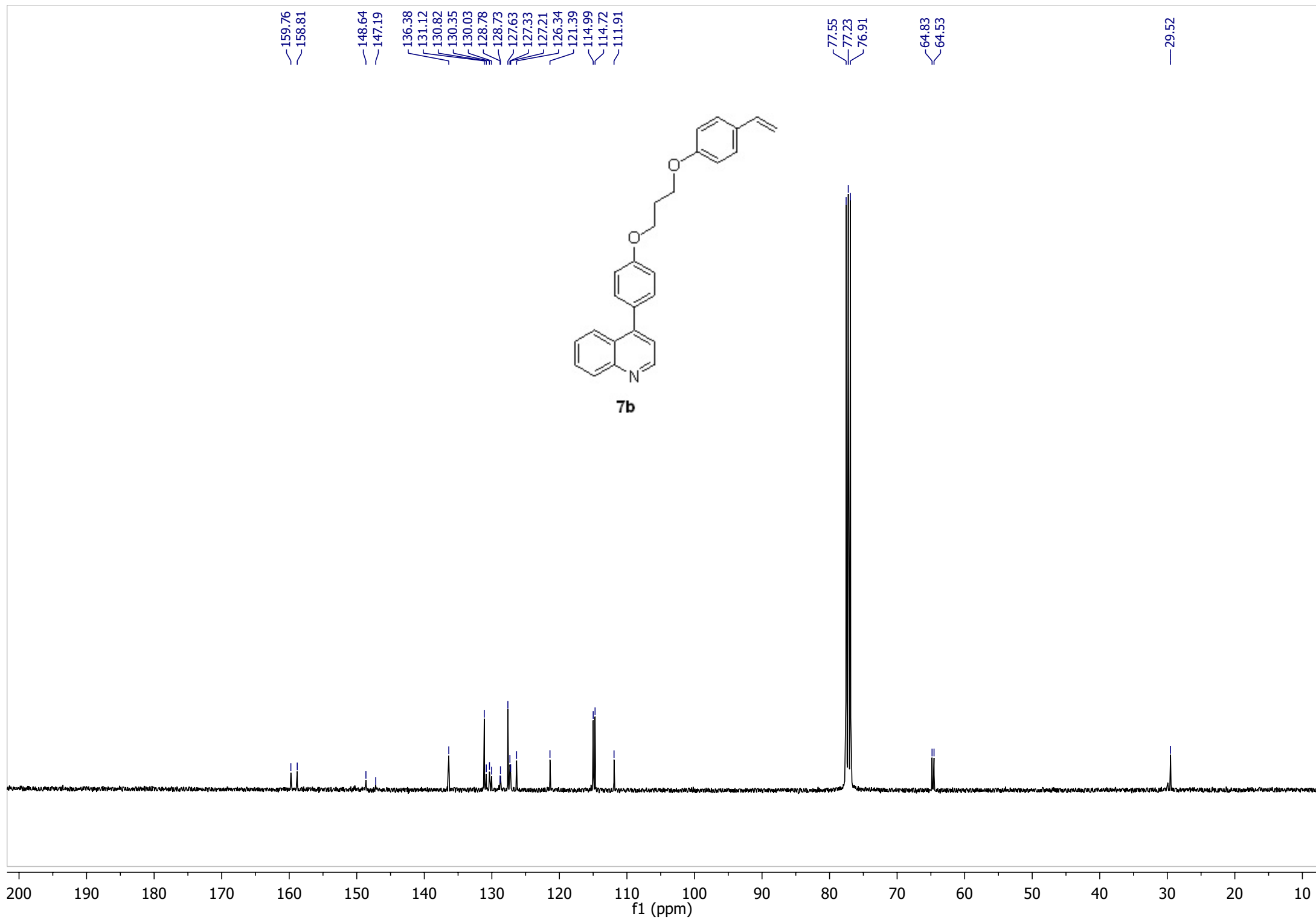
8.255
8.235
8.171
8.149
7.929
7.909
7.745
7.731
7.713
7.696
7.506
7.484
7.472
7.452
7.432
7.369
7.352
7.348
7.336
7.260
7.101
7.079
7.068
7.046
6.913
6.908
6.900
6.891
6.878
6.703
6.695
6.676
6.668
6.659
6.651
6.632
6.624
5.642
5.631
5.596
5.587
5.146
5.137
5.119
5.108
4.289
4.274
4.263
4.259
4.248
4.235
4.233
4.221
4.211
4.206
4.196
4.181

2.366
2.351
2.336
2.321
2.307
2.292
2.276

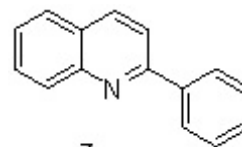




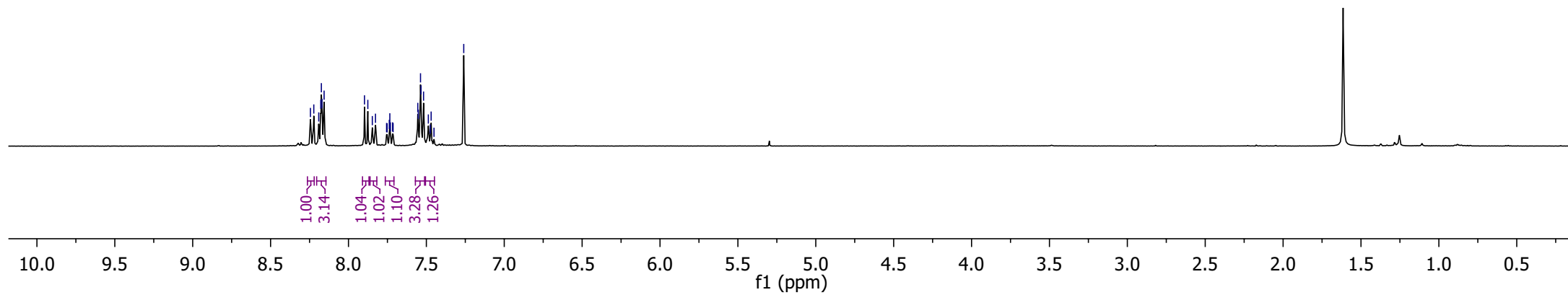


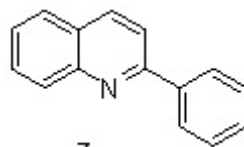


8.244
8.223
8.191
8.178
8.174
8.170
8.156
7.897
7.876
7.847
7.827
7.755
7.752
7.738
7.734
7.731
7.717
7.714
7.555
7.552
7.538
7.534
7.518
7.487
7.475
7.469
7.451
7.260

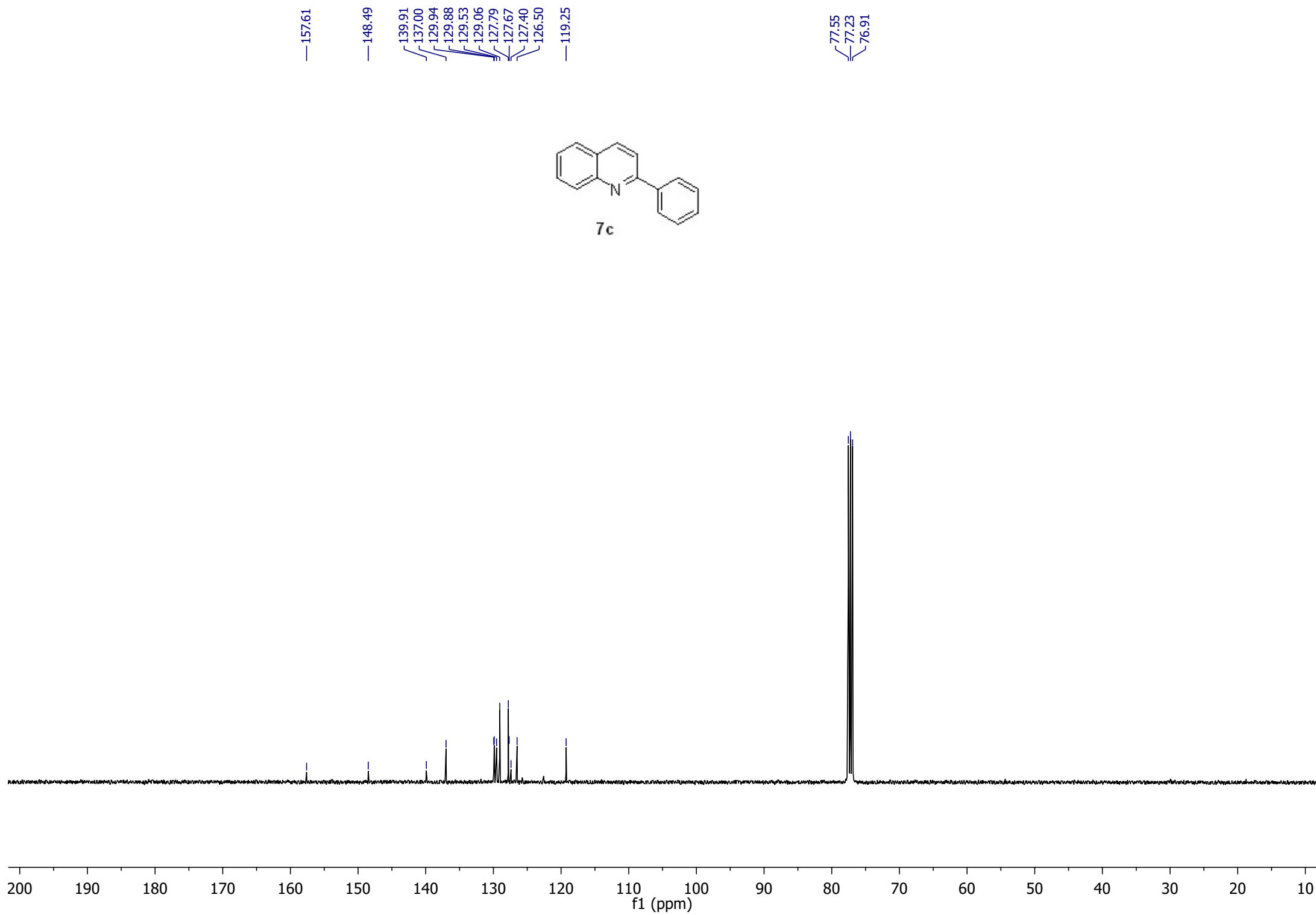


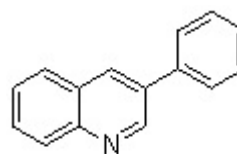
7c



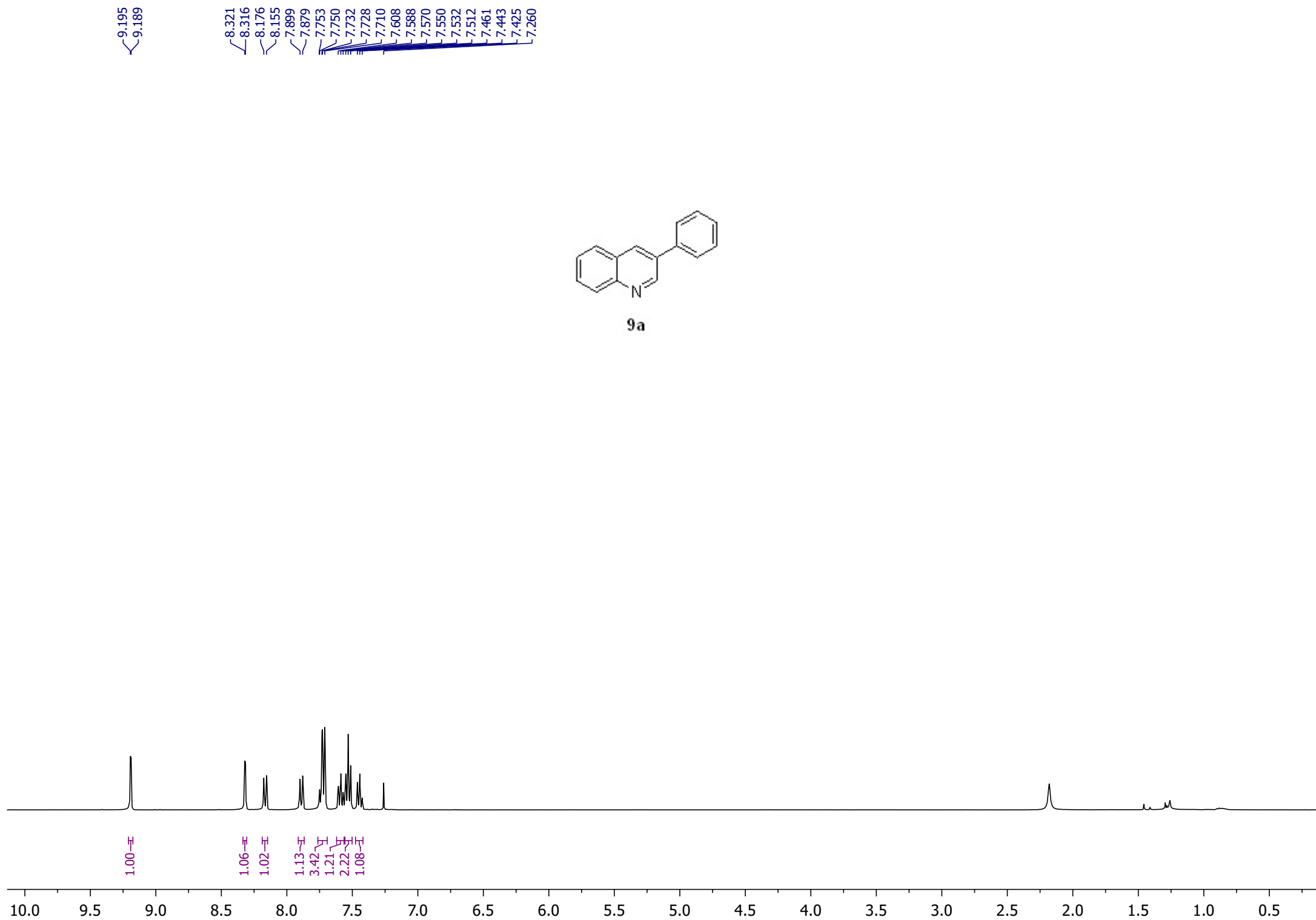


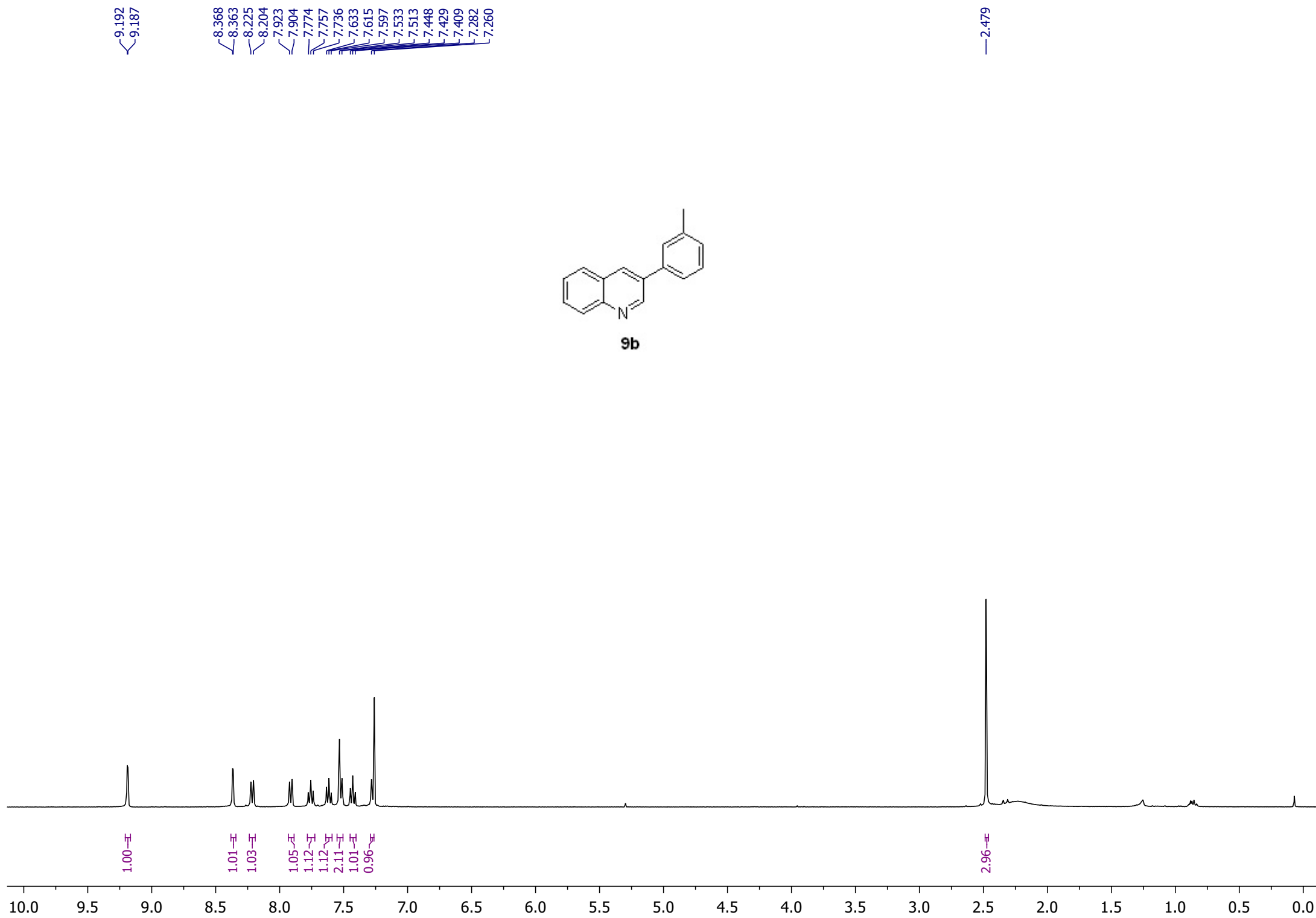
7c

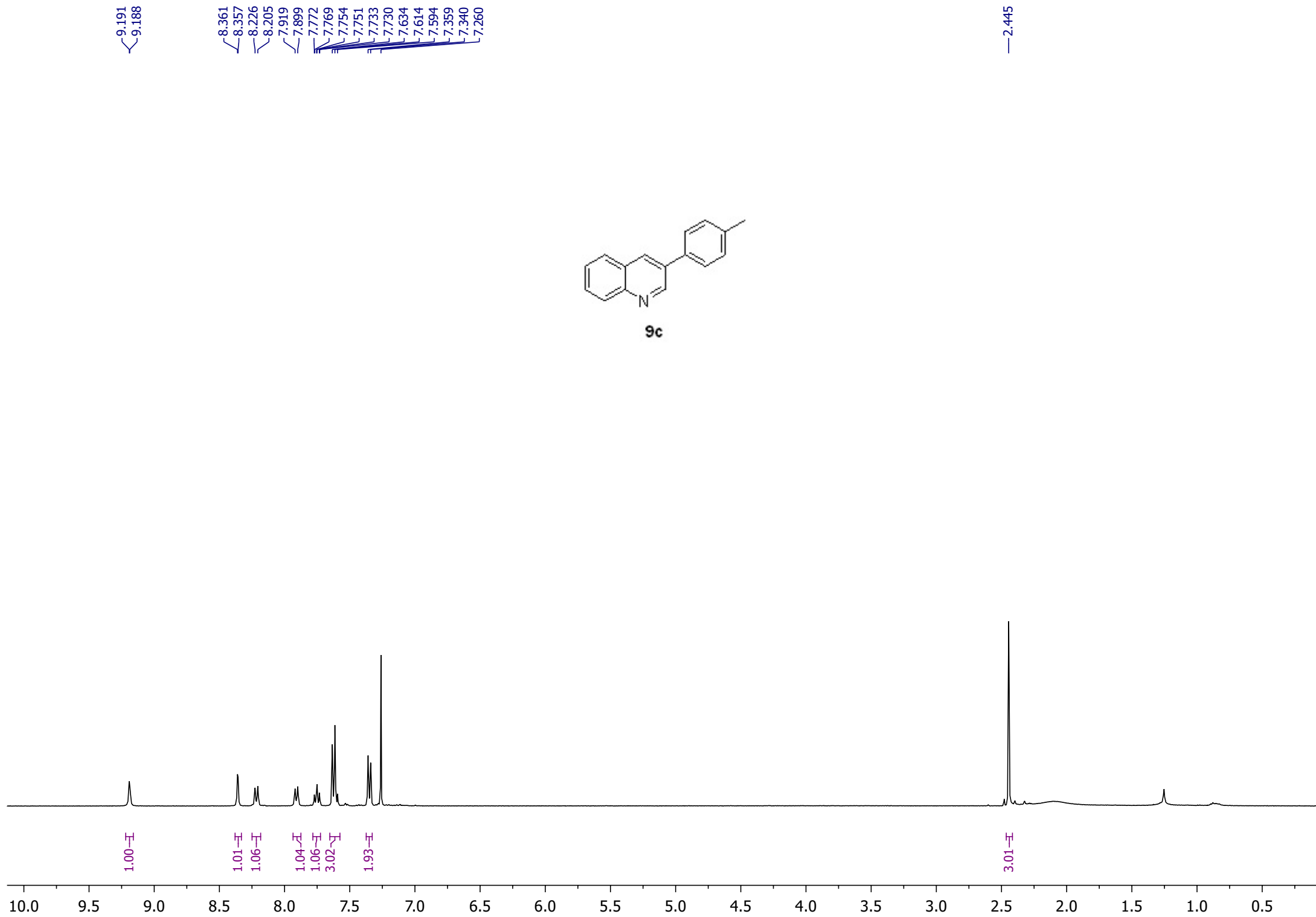




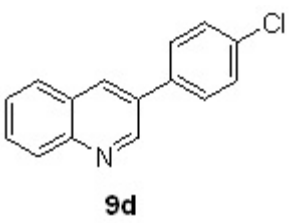
9a



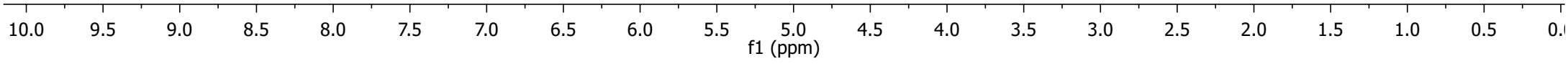


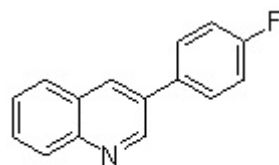


9.150
9.145
8.328
8.323
8.205
8.184
7.914
7.894
7.784
7.780
7.763
7.746
7.742
7.659
7.654
7.642
7.637
7.617
7.597
7.516
7.511
7.499
7.494
7.260

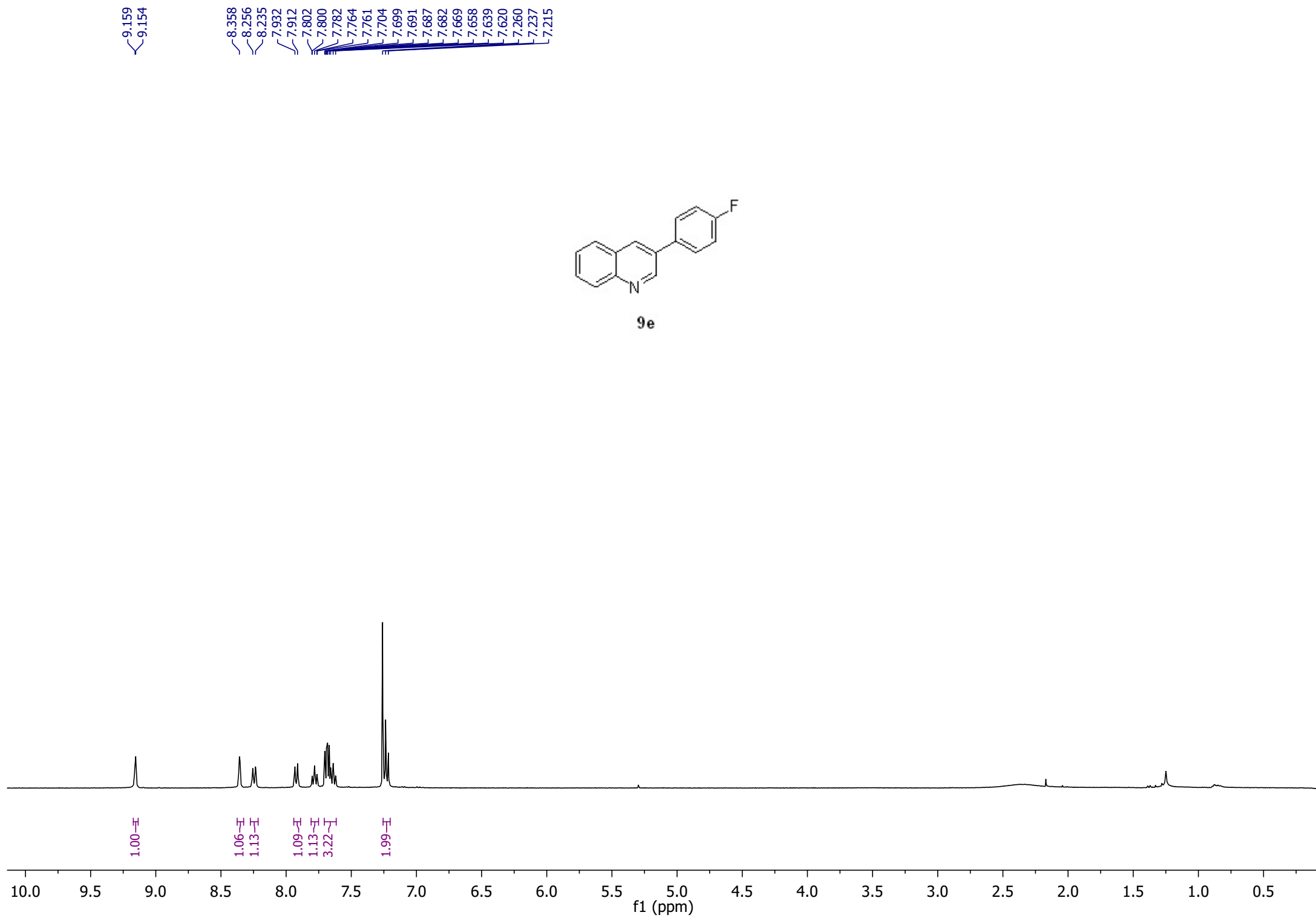


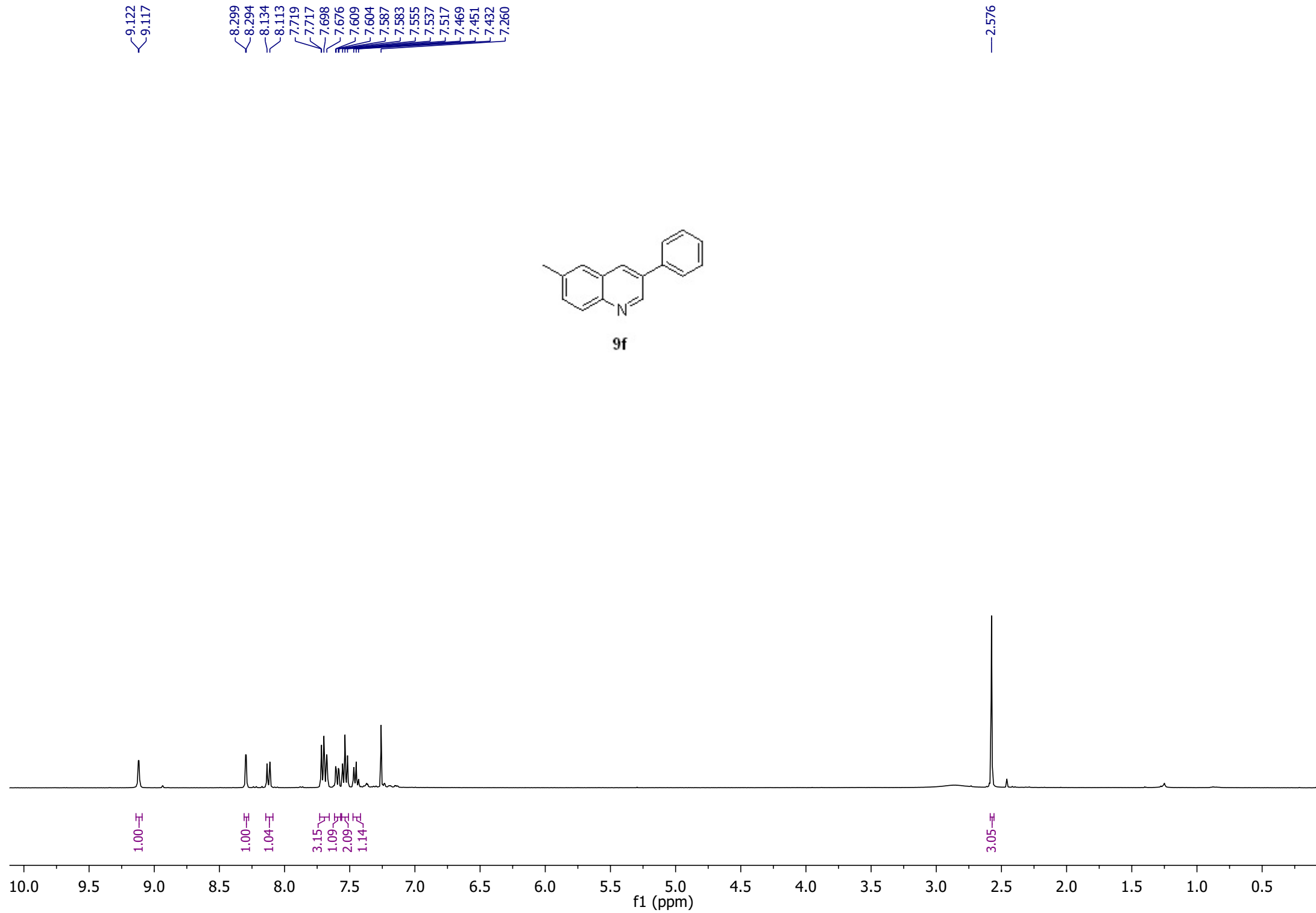
1.00
1.01
1.02
1.09
1.10
3.14
2.05





9e

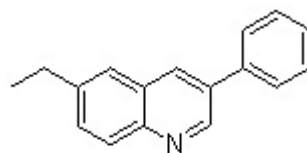




9.129
9.124
8.318
8.313
8.149
8.128
7.725
7.721
7.703
7.685
7.640
7.636
7.619
7.614
7.554
7.536
7.517
7.467
7.449
7.431
7.260

2.905
2.886
2.867
2.848

1.383
1.364
1.345



9g

1.00-H

1.01-H

1.03-H

3.16-H

1.02-H

2.16-H

1.11-H

2.12-H

3.23-H

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

9.122
9.117

8.271
8.265

8.090
8.069

7.723
7.706

7.677
7.654

7.649
7.632

7.627
7.546

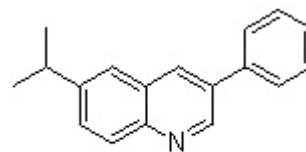
7.527
7.508

7.454
7.435

7.417
7.260

3.163
3.146
3.129
3.111
3.094

1.383
1.366



9h

1.00

1.07

0.99

2.34

1.09

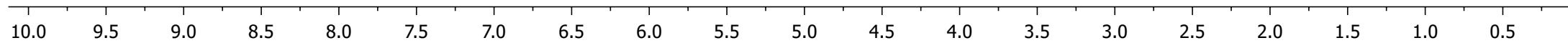
1.12

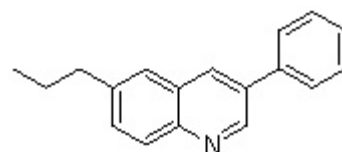
2.26

1.09

1.12

6.38





9i

9.127
9.124

8.330
8.328
8.158
8.144

7.717
7.704
7.676

7.624
7.622
7.610

7.607
7.550
7.537

7.525
7.465
7.453

7.441
7.260

2.822
2.809
2.796

1.785
1.773
1.760
1.748

1.009
0.997
0.985

1.00

1.12

1.08

2.38

0.98

1.03

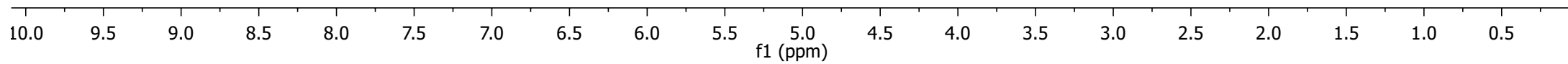
2.26

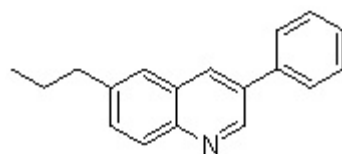
1.24

2.38

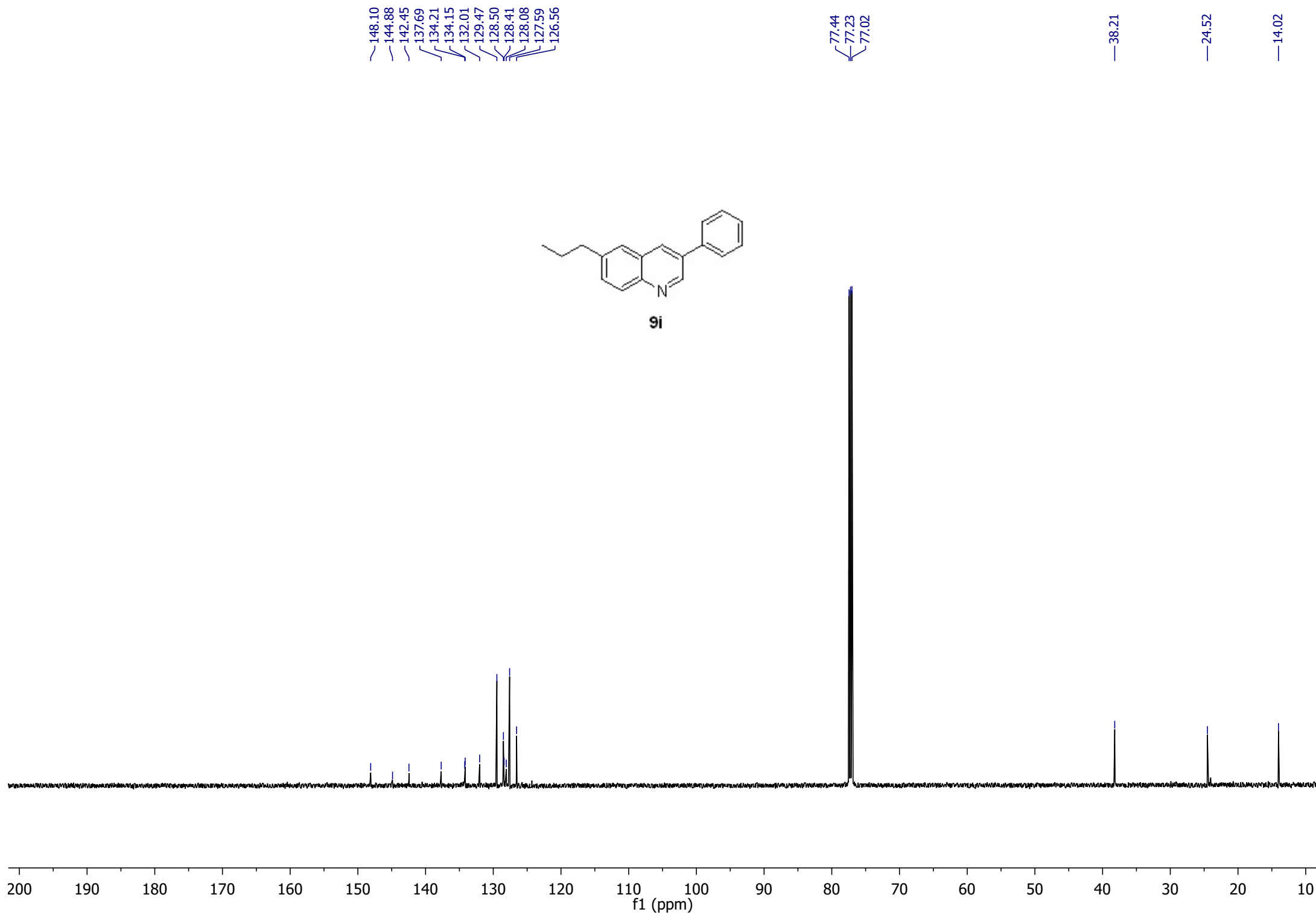
2.11

3.35





9i

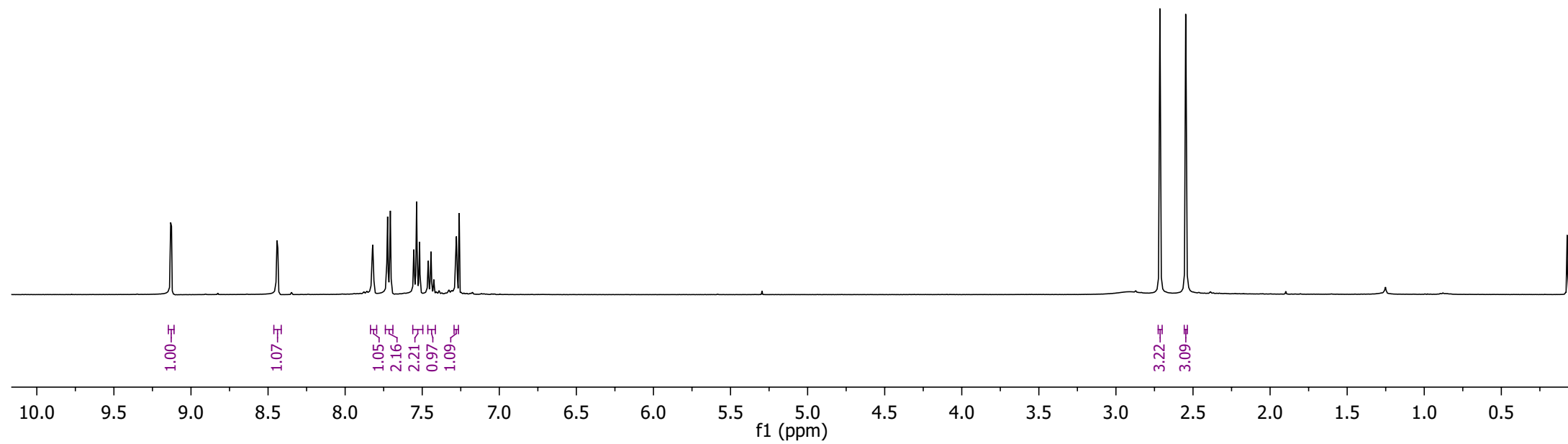
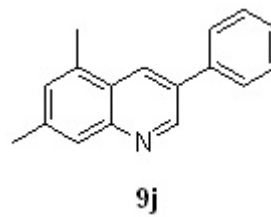


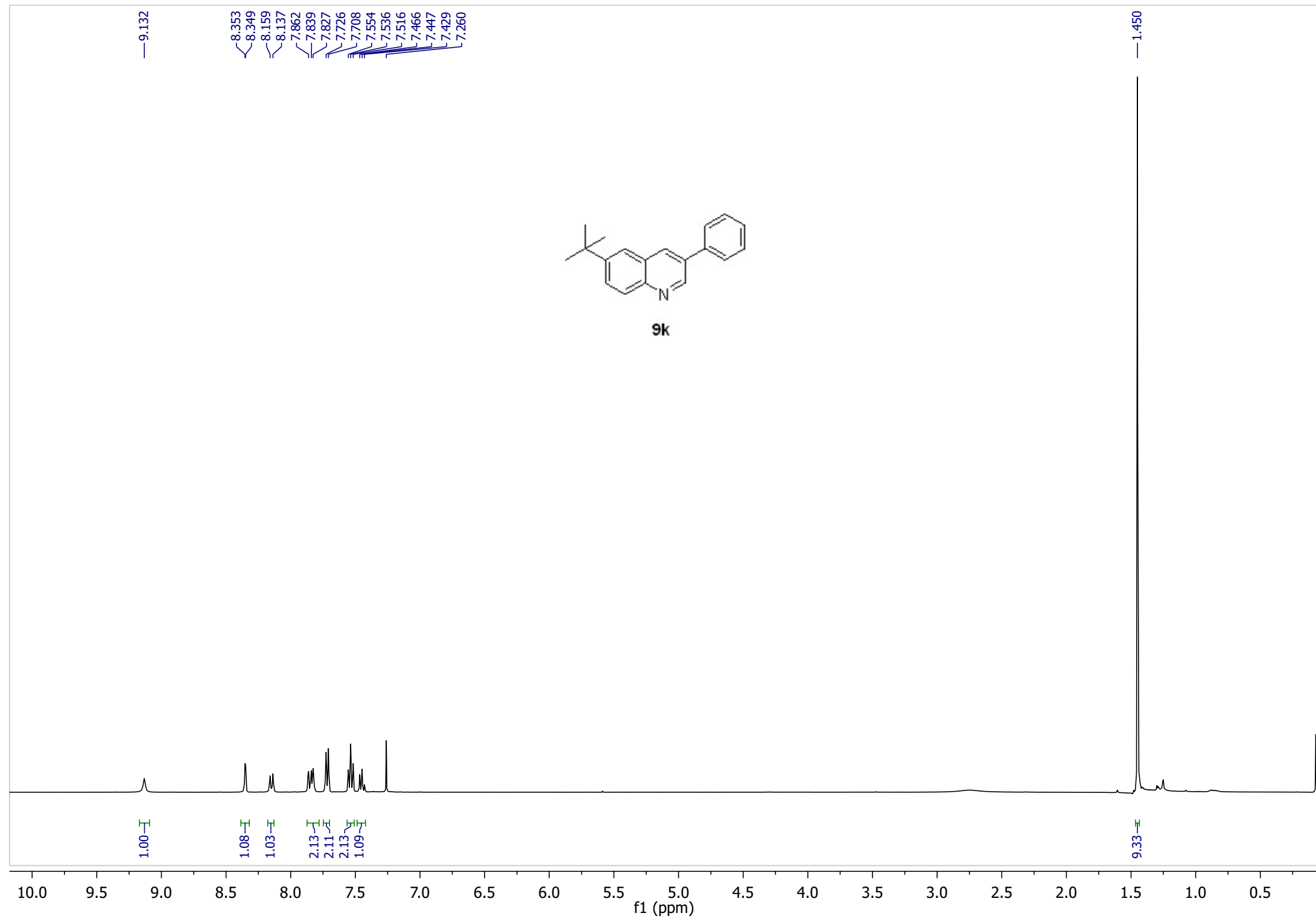
9.132
9.126

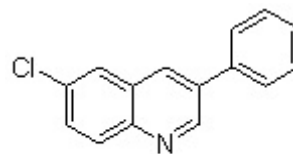
8.442
8.437

7.821
7.728
7.724
7.720
7.707
7.555
7.550
7.536
7.517
7.464
7.461
7.443
7.427
7.422
7.278
7.260

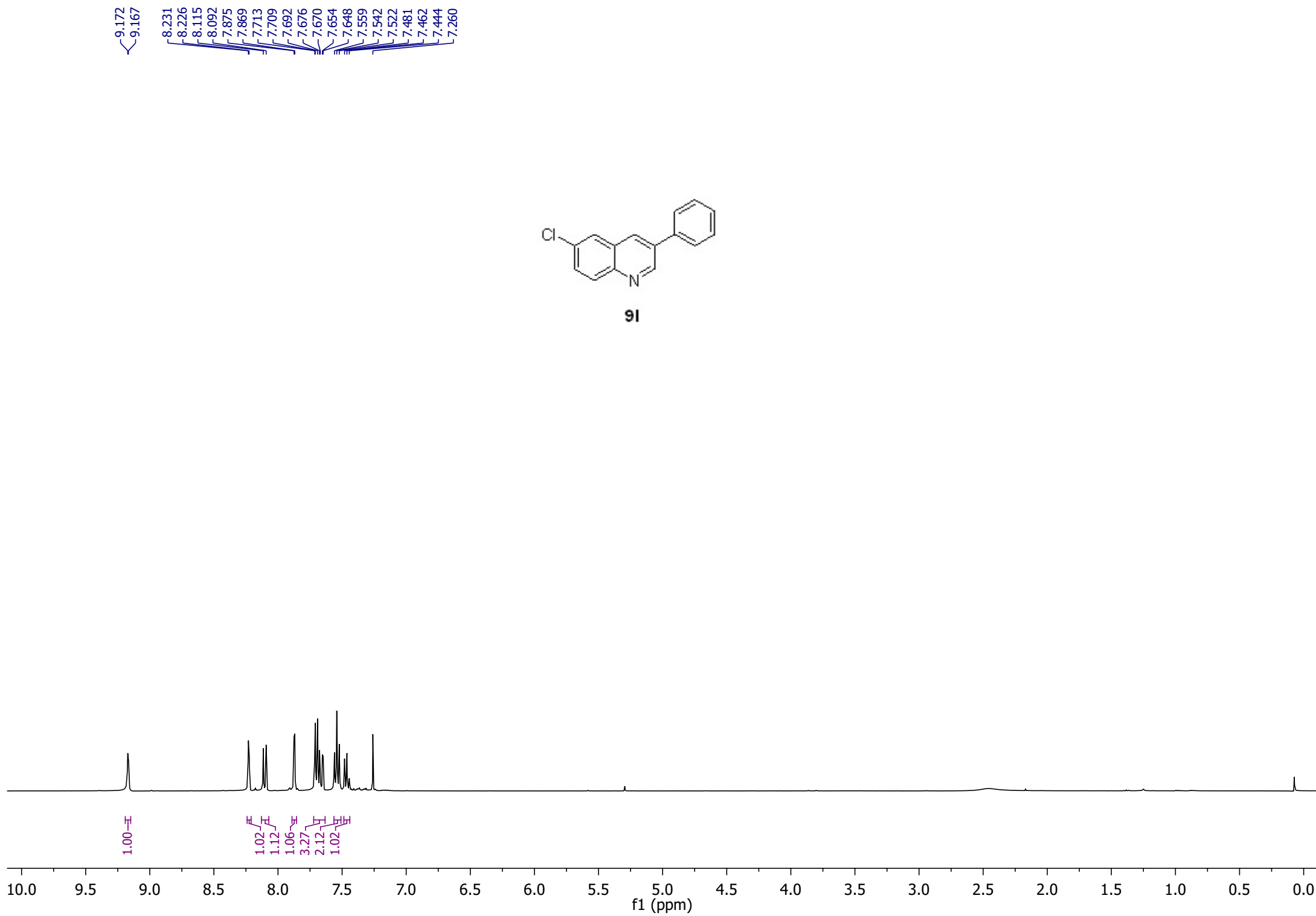
2.715
2.547







9l

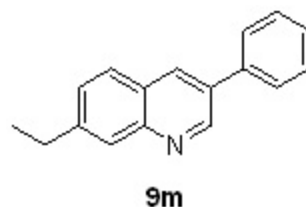


9.157
9.151

8.349
8.344
8.015
7.847
7.826
7.723
7.720
7.702
7.551
7.533
7.513
7.498
7.481
7.477
7.462
7.444
7.425
7.260

2.931
2.912
2.893
2.874

1.391
1.372
1.353



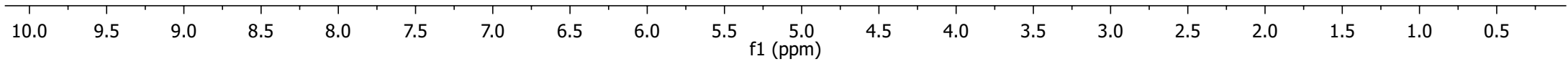
0.92

0.97

0.94
1.06
2.06
4.30

2.24

3.16

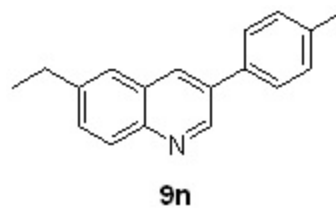


9.114
9.109

8.297
8.292
8.139
8.118
7.671
7.625
7.620
7.604
7.599
7.350
7.330
7.260

2.898
2.879
2.860
2.841
2.439

1.378
1.359
1.340



1.00

1.01

1.01

1.06

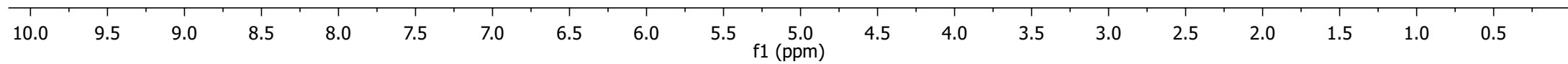
2.97

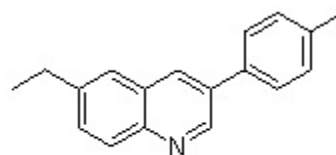
1.94

2.11

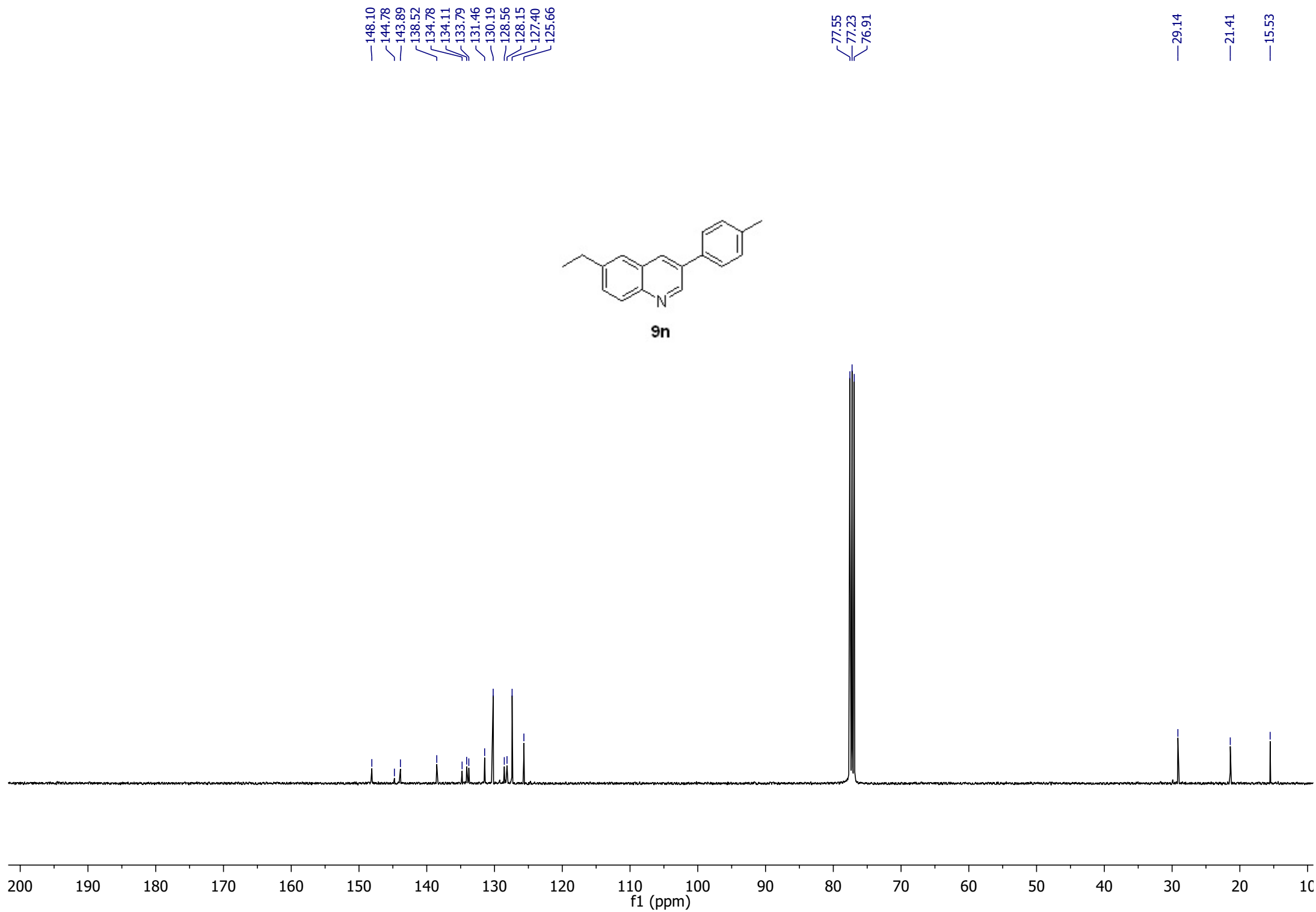
2.94

3.14





9n

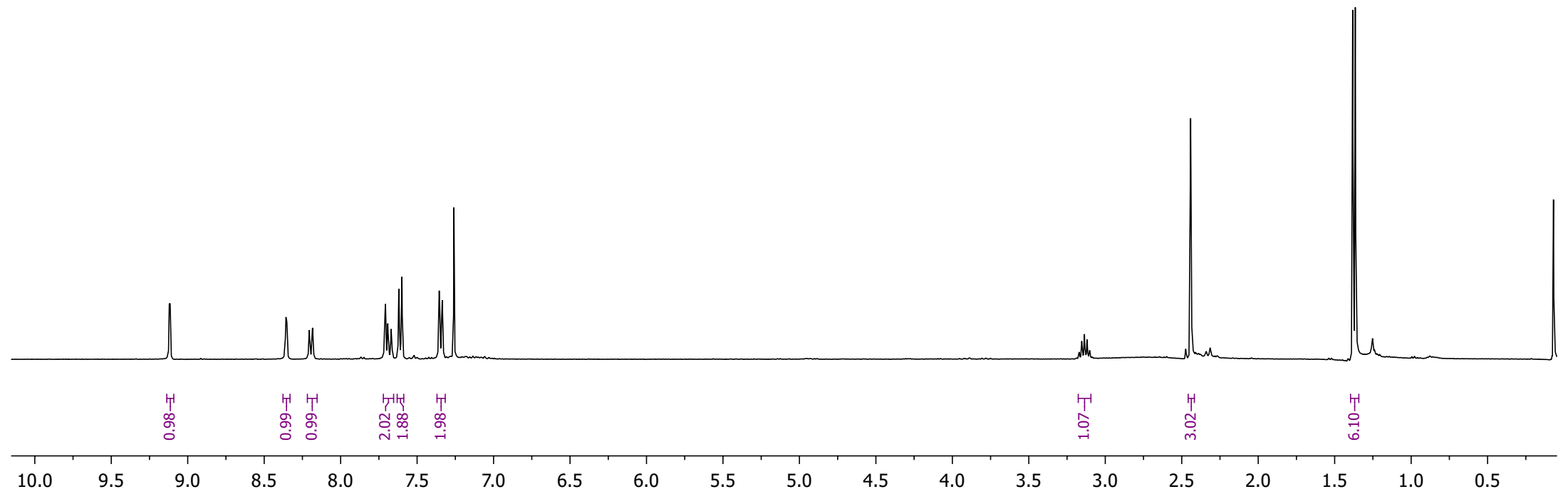
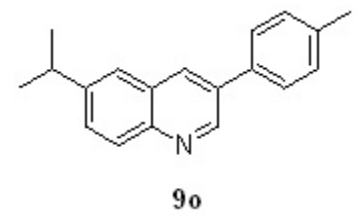


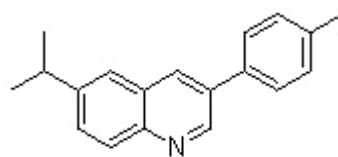
9.121
9.115
8.358
8.353
8.205
8.184
7.707
7.692
7.687
7.670
7.665
7.620
7.599
7.355
7.336
7.260

3.171
3.154
3.136
3.119
3.102

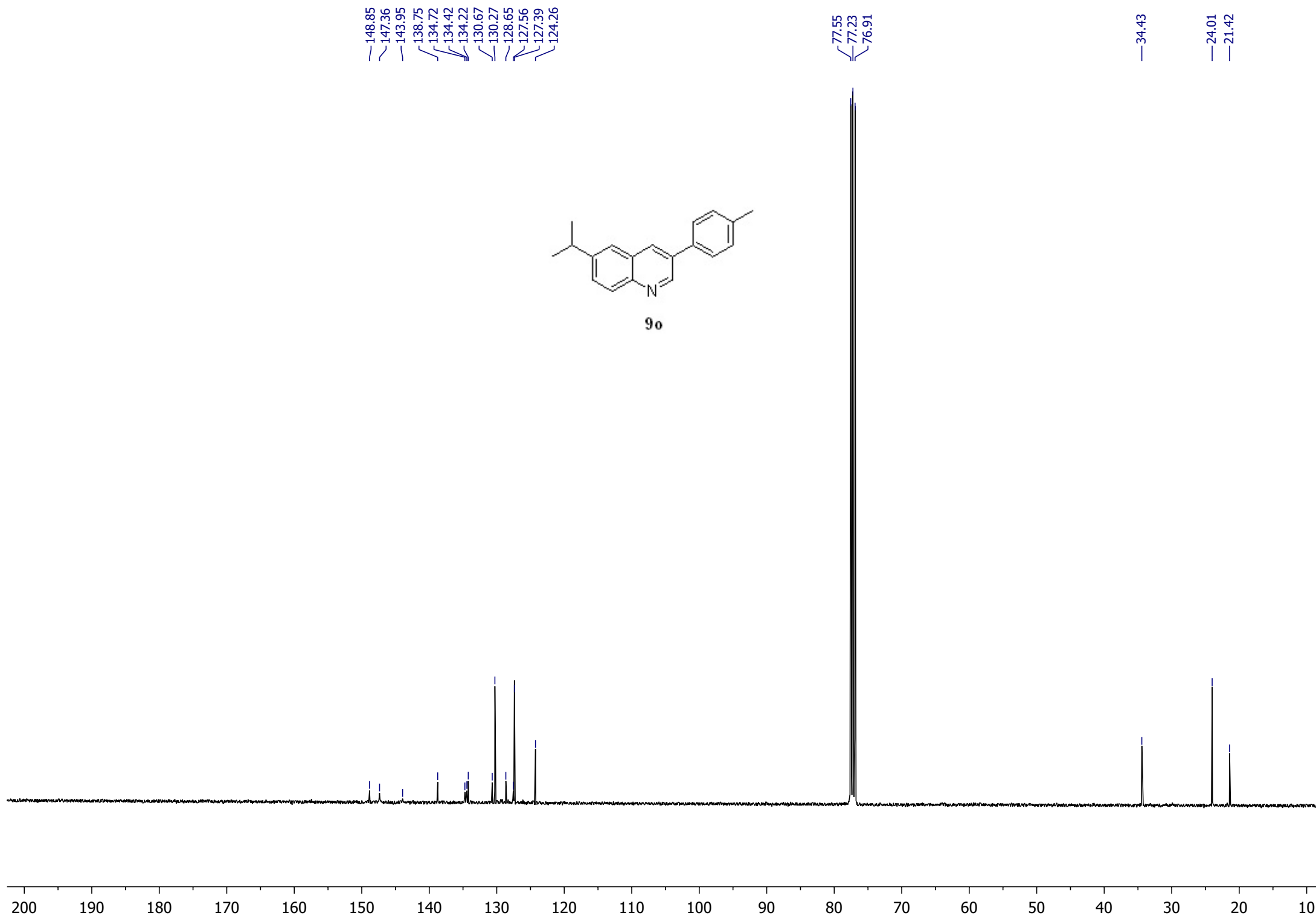
2.442

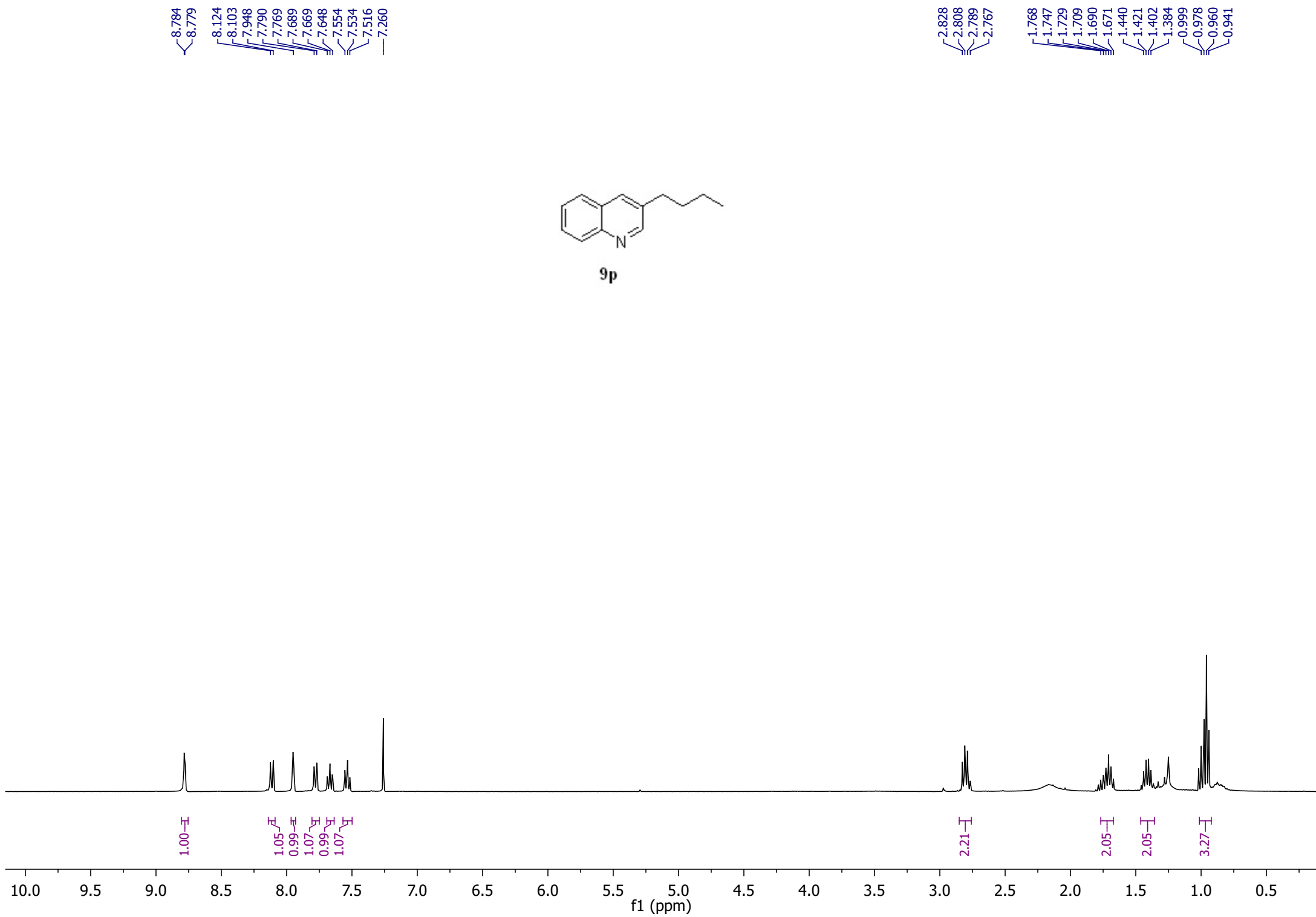
1.382
1.365

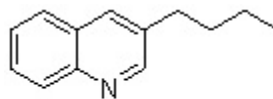




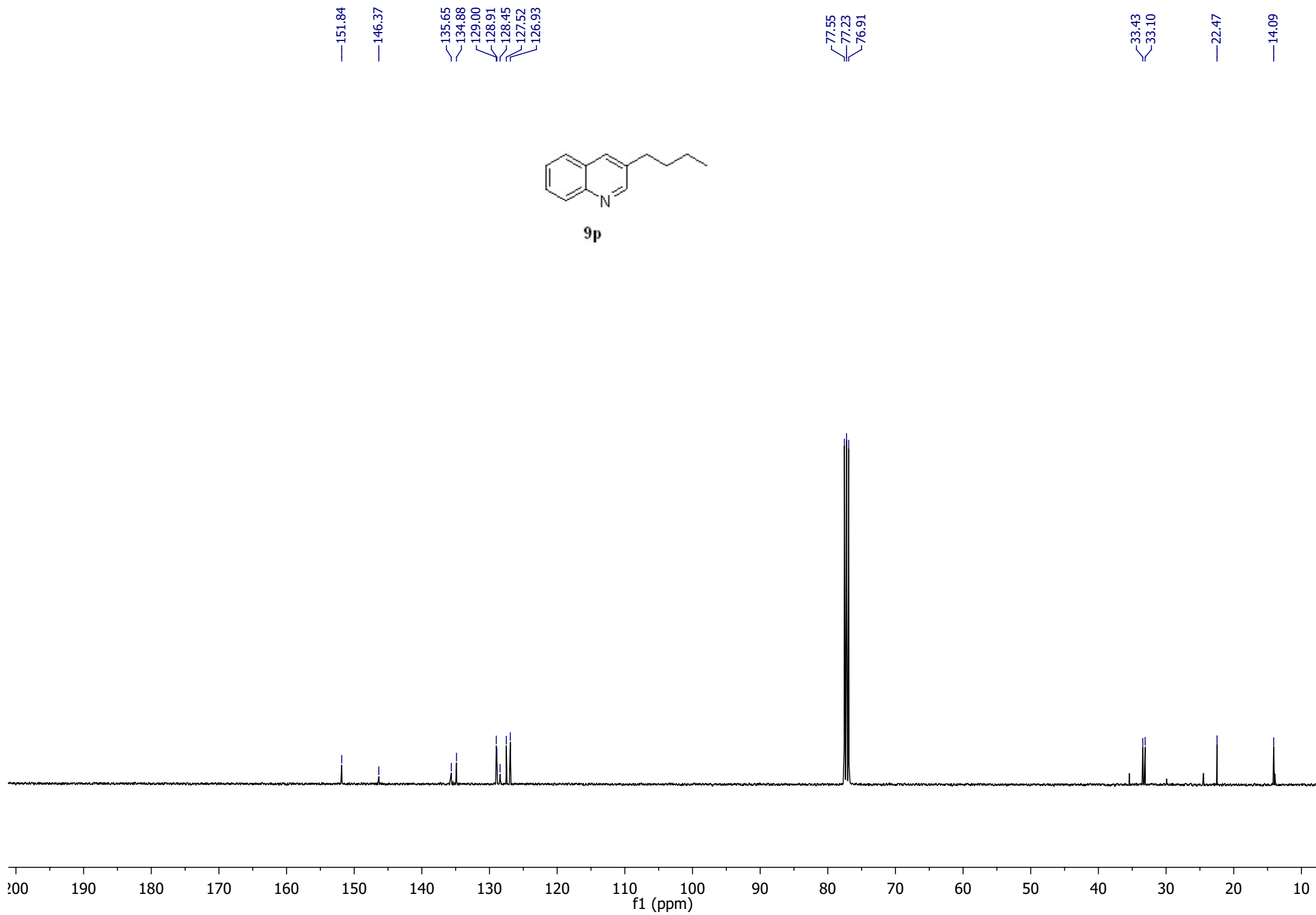
9o







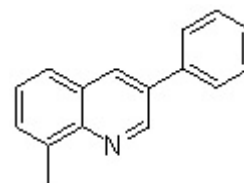
9p



—9.249

8.339
8.334
7.769
7.745
7.741
7.723
7.606
7.588
7.558
7.540
7.520
7.498
7.468
7.450
7.431
7.260

—2.881



9q

1.00

1.01

2.95

3.11

1.90

2.93

