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Supporting Information for
Copper-Catalyzed *ortho*-Alkenylation of Quinoline *N*-Oxides with Alkynes

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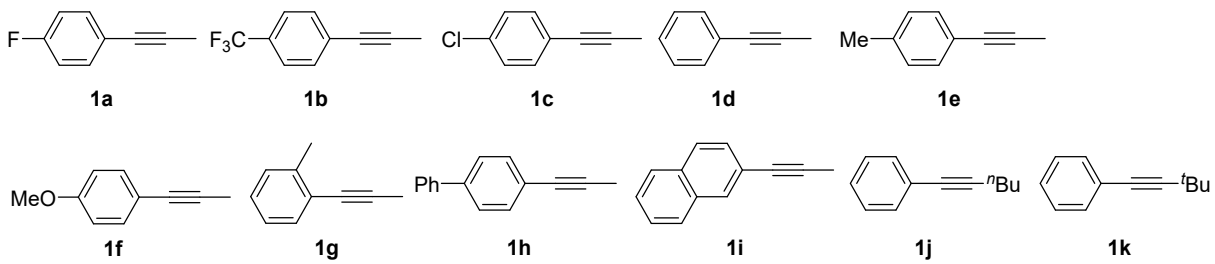
General Methods

Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or using a dry vial with a dry box technique under a nitrogen atmosphere. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). *n*-BuLi (2.5 M solution in Hexane) was

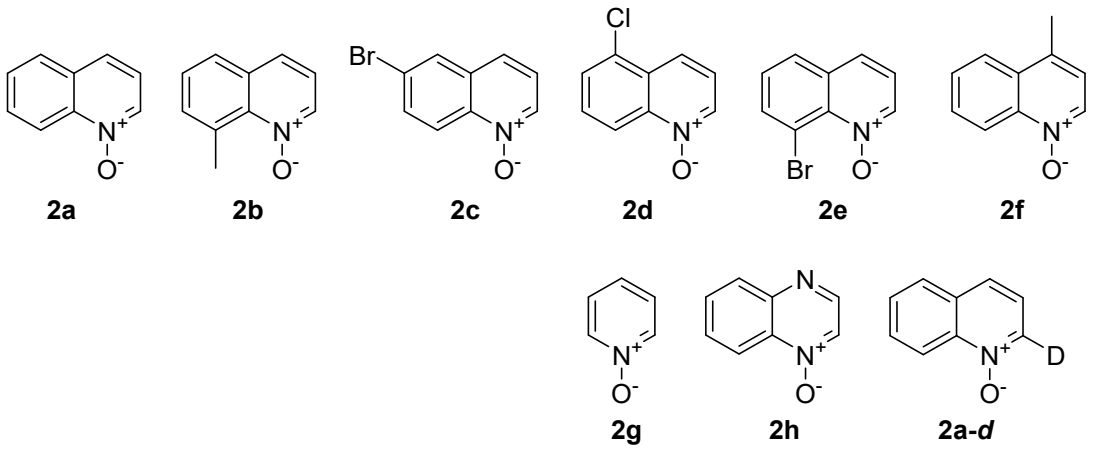
purchased from Adamas Chemical Company, CuCl was purchased from Acros Company, PCy_3, prop-1-yn-1-ylbenzene and bis(pinacolato)diboron were purchased from J&K Chemical Company, KO^{t}Bu and quinoline *N*-oxide were purchased from TCI Chemical Company.

^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS), or in C_6D_6 (containing 0.03% TMS) solution on Varian or Agilent XL-400 MHz spectrometer or Agilent XL-500 MHz spectrometer. ^{1}H NMR spectra was recorded with tetramethylsilane (0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm) as internal reference. ^{11}B-NMR was recorded in $CDCl_3$ (containing 0.03% TMS) on Bruker-400 MHz spectrometer. High-resolution mass spectra were obtained by using JEOL AccuTOF 4G LC-plus, Agilent Technologies 7250 GCQTOF spectrometer. IR spectra were obtained by using a Nicolet iS10 spectrometer. Single crystal X-ray diffraction data was collected on Bruker SMART diffractometer at 293 (2) K for *E*-**3b** and **5m**.

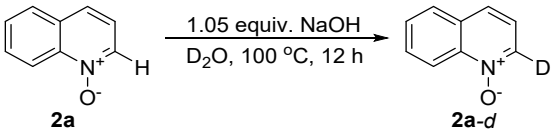
The substrate of aryl(alkyl) alkyne **1d** is commercially available. Substrates **1a**-**1c** and **1e**-**1k** were prepared according to the literature procedure,[1] and the spectroscopic data of these compounds are in agreement with that previously reported.



Quinoline *N*-oxide **2a** and **2g** are commercially available. *N*-oxides **2b-2f**, **2h** and **2a**-*d* were prepared according to the literature procedures,[2] and the spectroscopic data of these compounds are in agreement with that previously reported.

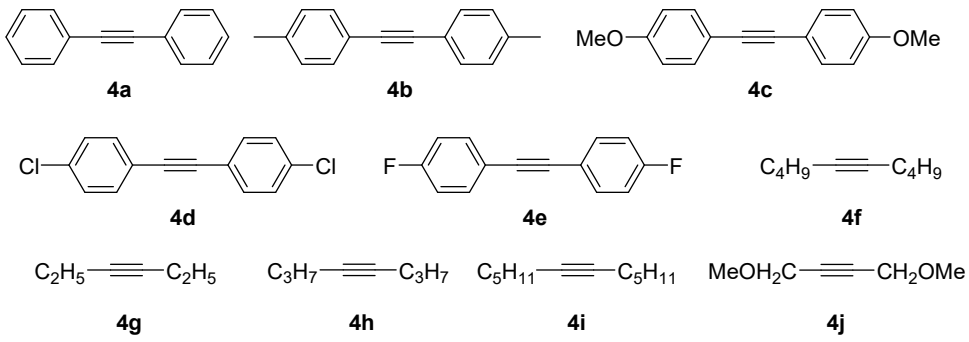


Synthesis of Quinoline *N*-oxide-2-*d*.[3]



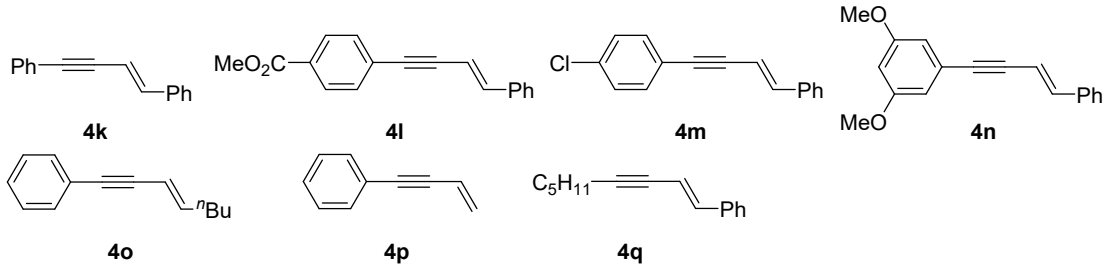
To a 25 mL Schlenk tube were added quinoline *N*-oxide (726 mg, 5 mmol), NaOH (210 mg, 5.25 mmol) and D_2O (7.5 mL) under argon. The reaction was stirred in an oil bath preheated at 100 °C (oil bath) for 12 h. After cooling to room temperature, the reaction mixture was extracted with chloroform (15 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The mixture was concentrated and the solvent was evaporated under the reduced pressure to afford the deuterium incorporated quinoline *N*-oxide **2a**-*d* (97% deuterium incorporation) in 99% yield (720.5 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 8.8 Hz, 1H), 8.53 (d, *J* = 5.2 Hz, 0.03 H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.78-7.73 (m, 2H), 7.66-7.62 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 134.8 (t, *J* = 28.1 Hz), 129.84, 129.80, 128.1, 127.6, 125.8, 120.3, 118.8. The spectroscopic data are in agreement with that previously reported.[3]

Diaryl alkyne **4a** and dialkyl alkyne**s 4f-4j** are commercially available. Diaryl alkynes **4b-4e** were prepared according to the literature procedures,[4] and the spectroscopic data of these compounds are in agreement with that previously reported.



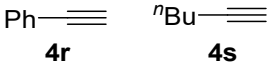
4a **4b** **4c** **4d** **4e** **4f** **4g** **4h** **4i** **4j**

Enynes were prepared according to the literature procedures,[5] and the spectroscopic data of these compounds are in agreement with that previously reported.



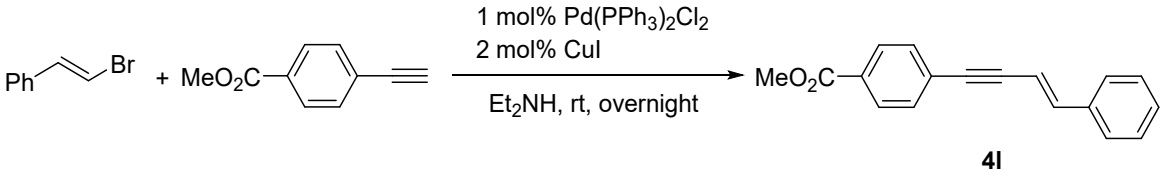
4k **4l** **4m** **4n** **4o** **4p** **4q**

Terminal alkynes:



4r **4s**

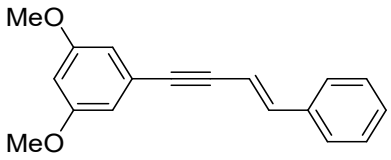
For the synthesis and characterization of new enynes, see following:



4l

Methyl (*E*)-4-(4-phenylbut-3-en-1-yn-1-yl)benzoate (4l). To a 100 mL Schlenk tube were added $PdCl_2(PPh_3)_2$ (28.0 mg, 0.04 mmol), CuI (15.2 mg, 0.08 mmol), methyl 4-ethynylbenzoate (817.0 mg, 5.1 mmol), Et_2NH (20 mL) and (*E*)-(2-bromovinyl)benzene (0.5 mL, 3.9 mmol) under argon. The reaction was stirred overnight at ambient temperature until the reaction was completed as monitored by TLC. The mixture was quenched with H_2O and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The mixture was concentrated and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to afford **4l** in 86% yield (883.6 mg) as a white

solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.37-7.30 (m, 3H), 7.08 (d, *J* = 16.4 Hz, 1H), 6.38 (d, *J* = 16.4 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 142.3, 136.0, 131.3, 129.5, 129.3, 128.9, 128.8, 128.1, 126.4, 107.6, 91.9, 90.9, 52.2. IR (neat): 2948, 2191, 1706, 1596, 1436, 1405, 1308, 1276, 1192, 1174, 1107, 1014, 954, 855, 828, 768, 754, 695. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{14}O_2$ 262.0988; Found 262.0996.



4n

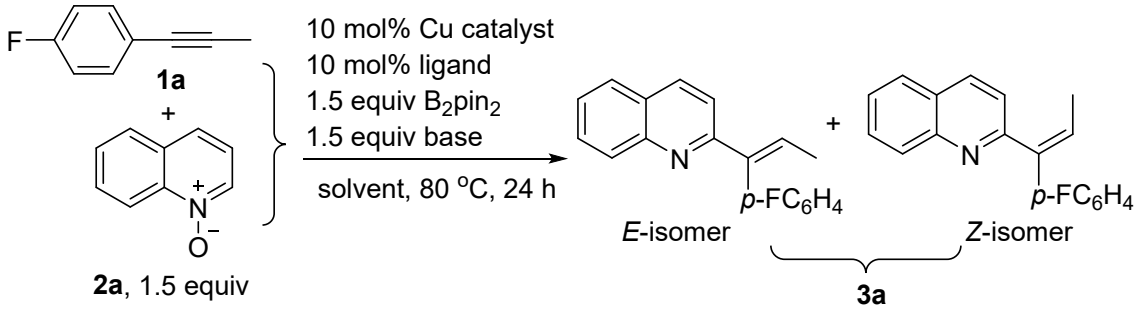
(*E*)-1,3-Dimethoxy-5-(4-phenylbut-3-en-1-yn-1-yl)benzene (4n). To a 100 mL Schlenk tube were added $PdCl_2(PPh_3)_2$ (175.5 mg, 0.25 mmol), CuI (95.2 mg, 0.5 mmol), Et_2NH (20 mL), 1-ethynyl-3,5-dimethoxybenzene (811.0 mg, 5 mmol) and (*E*)-(2-bromovinyl)benzene (915.3 mg, 5 mmol) under argon. The reaction was stirred overnight at ambient temperature until the reaction was completed as monitored by TLC. The reaction mixture was filtered through a pad of silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford **4n** in 83% yield (1.1 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.36-7.27 (m, 3H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.65 (s, 2H), 6.46 (d, *J* = 2.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 141.5, 136.2, 128.7, 128.6, 126.3, 124.6, 109.2, 107.9, 101.7, 91.7, 88.4, 55.3. IR (neat): 2990, 2936, 2834, 1612, 1583, 1449, 1418, 1358, 1298, 1273, 1202, 1151, 1064, 1034, 951, 925, 833, 749, 690, 680. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{16}O_2$ 264.1145; Found 264.1152.

General procedure for optimization studies:

The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, Cu catalyst (0.02 mmol), ligand (0.02 mmol), B_2pin_2 (0.3 mmol), base (0.3 mmol) and solvent (1 mL) were added sequentially to a screw-cap vial. The solvent stirred at ambient temperature for 1 minute. Then **1a** (0.2 mmol, 26.8 mg) and **2a** (1.5 equiv., 43.5 mg) were added. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h. The mixture was cooled down

to room temperature, filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the yields were determined by ^{1}H NMR using 1,3,5-trimethylbenzene (1.0 equiv., 24.0 mg) in C_6D_6 as the internal standard.

Table S1. Optimization studies.



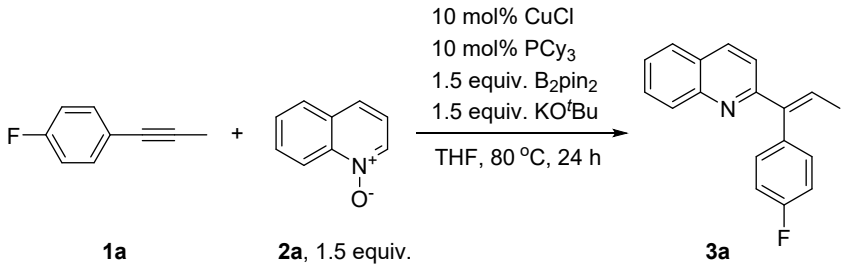
entry	Cu catalyst	ligand	base	solvent	yield of **3a** (%)[a]	*E*:*Z*[b]
1	CuCl	PPh_3	KO^{t}Bu	THF	45	5.1:1
2	CuCl	P^{n}Bu$_3$	KO^{t}Bu	THF	85	6.5:1
3	**CuCl**	**PCy_3**	**KO^{t}Bu**	**THF**	**99[c]**	**7.3:1**
4	CuCl	$PPhCy_2$	KO^{t}Bu	THF	95	7.5:1
5	CuCl	P^{t}Bu$_3$·HBF_4	KO^{t}Bu	THF	80	4.9:1
6	CuCl	dppb	KO^{t}Bu	THF	77	6.4:1
7	CuCl	dcype	KO^{t}Bu	THF	79	5.8:1
8	CuCl	IMes	KO^{t}Bu	THF	54	5.2:1
9	CuCl	IPr	KO^{t}Bu	THF	trace	-
10	CuBr	PCy_3	KO^{t}Bu	THF	98[c]	6.2:1
11	$Cu(OAc)_2$	PCy_3	KO^{t}Bu	THF	89	7.5:1
12	$Cu(OTf)_2$	PCy_3	KO^{t}Bu	THF	ca. 94	6.6:1
13	$[Cu(MeCN)_4]^+[PF_6]^-$	PCy_3	KO^{t}Bu	THF	97[c]	6.6:1
14	CuCl	PCy_3	NaO^{t}Bu	THF	87	4.2:1
15	CuCl	PCy_3	LiO^{t}Bu	THF	22	4.8:1
16	CuCl	PCy_3	Na_2CO_3	THF	trace	-
17	CuCl	PCy_3	$NaHCO_3$	THF	trace	-
18	CuCl	PCy_3	KO^{t}Bu	1,4-dioxane	71	16.4:1
19	CuCl	PCy_3	KO^{t}Bu	toluene	64	8.6:1
20	CuCl	PCy_3	KO^{t}Bu	DMF	46	2.4:1
21	-	PCy_3	KO^{t}Bu	THF	-	-
22	CuCl	-	KO^{t}Bu	THF	-	-
23	CuCl	PCy_3	-	THF	-	-

[a]NMR yields using 1,3,5-trimethylbenzene as an internal standard. [b]The ratio was determined by ^{19}F NMR spectra. [c]Deduced from the NMR yield of the major isomer and the *E*/*Z* ratio of **3a**.

For the characterization of *Z*-3a (due to the low yield of *Z*-3a, the pure *Z*-3a was obtained by isolation of the combined samples of several experiments): A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (t, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 7.2, 1.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.27-7.21 (m, 3H), 6.95 (td, *J* = 8.0, 1.6 Hz, 2H), 6.35 (q, *J* = 6.6 Hz, 1H), 1.84 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^{1}J_{C\text{-}F}$ = 244.9 Hz), 159.1, 147.9, 141.1, 137.4 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 136.2, 129.5, 128.7, 128.6, 127.5, 127.4, 126.8, 126.5, 123.0, 115.0 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 15.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.71--115.73 (m). IR (neat): 3040, 2913, 2851, 1617, 1597, 1557, 1506, 1424, 1222, 1158, 1014, 924, 823, 755, 720 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NF$ 264.1183; Found 264.1189.

Synthesis of products 3.

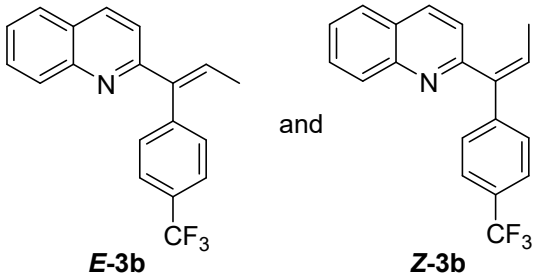
Typical procedure for the synthesis of 3a.



1a **2a**, 1.5 equiv. **3a**

(*E*)-2-(1-(4-Fluorophenyl)prop-1-en-1-yl)quinoline (3a). In the nitrogen-filled glove box, CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) were added to screw-cap vial (4 mL). The mixture was stirred at room temperature for 1 minute. Then **1a** (0.3 mmol, 40.2 mg) and **2a** (1.5 equiv., 65.3 mg) were added. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h, the mixture was filtered over a silica gel pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the product **3a** in 77% yield (60.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.67 (td, *J* = 7.8, 1.2 Hz, 1H), 7.46 (td, *J* = 7.4, 1.2 Hz, 1H), 7.25-7.21 (m, 2H), 7.13-7.06 (m, 4H), 1.85 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^{1}J_{C\text{-}F}$ = 244.5 Hz), 158.8, 147.8, 141.1, 135.9, 134.4 (d, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 131.7 (d, $^{4}J_{C\text{-}F}$ = 7.7 Hz), 130.3, 129.5, 129.4, 127.3, 127.0, 125.9, 120.5, 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 15.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.04--115.08 (m).

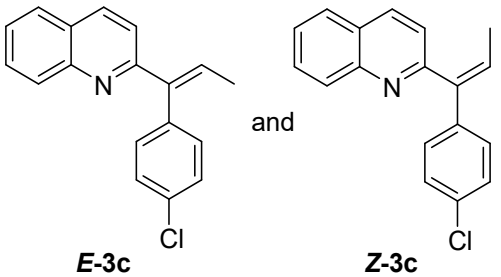
IR (neat): 3039, 2911, 2853, 1615, 1594, 1556, 1507, 1425, 1359, 1220, 1172, 1157, 1142, 1015, 908, 796, 785, 755, 728, 696 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NF$ 264.1183; Found 264.1181.



***E*-3b** ***Z*-3b**

(*E*)-2-(1-(4-(Trifluoromethyl)phenyl)prop-1-en-1-yl)quinoline (*E*-3b). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1b** (0.3 mmol, 55.2 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product *E*-**3b** in 49% yield (45.9 mg) followed by *Z*-**3b** in 17% yield (16.1 mg). **For the characterization of *E*-3b:** A yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.72-7.64 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.12 (q, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 1.84 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 147.8, 142.4 (d, $^4J_{C\text{-}F}$ = 1.6 Hz) 141.0, 136.1, 131.0 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 130.5, 129.6, 129.4, 129.3 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 127.3, 127.0, 126.1, 125.3 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 120.2, 15.6. ^{19}F NMR (376 MHz, $CDCl_3$): -62.39 (s). IR (neat): 2920, 2850, 1615, 1593, 1503, 1406, 1323, 1260, 1164, 1143, 1062, 1019, 849, 818, 774, 756, 698 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}NF_3$ 314.1151; Found 314.1145.

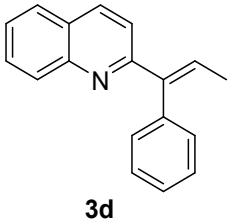
For the characterization of (*Z*-3b): A light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (t, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.75 (td, *J* = 7.8, 1.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.50 (q, *J* = 7.2 Hz, 1H), 1.89 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 148.0, 144.7 (d, $^4J_{C\text{-}F}$ = 1.7 Hz), 141.1, 136.4, 129.7, 129.6, 129.0 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 127.5, 127.3, 126.9, 126.7, 125.2 (q, $^4J_{C\text{-}F}$ = 3.7 Hz), 122.9, 15.7. ^{19}F NMR (376 MHz, $CDCl_3$): -62.45 (s). IR (neat): 3060, 2982, 2922, 1737, 1615, 1501, 1163, 1067, 1016, 846, 823, 769, 756, 681 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}NF_3$ 314.1151; Found 314.1145.



***E*-3c** ***Z*-3c**

(*E*)-2-(1-(4-Chlorophenyl)prop-1-en-1-yl)quinoline (*E*-3c). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1c** (0.3 mmol, 45.2 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product *E*-**3c** in 66% yield (55.1 mg) followed by *Z*-**3c** in 15% yield (12.7 mg). **For the characterization of** *E*-**3c**: A light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.68 (td, *J* = 5.0, 1.5 Hz, 1H), 7.47 (td, *J* = 7.3, 0.5 Hz, 1H), 7.39 (d, *J* = 5.3 Hz, 2H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.08 (q, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 10.0 Hz, 1H), 1.86 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 147.8, 141.1, 137.0, 136.0, 133.1, 131.5, 130.5, 129.54, 129.49, 128.6, 127.3, 127.0, 126.0, 120.5, 15.7. IR (neat): 3060, 3034, 2922, 2848, 1592, 1552, 1500, 1488, 1423, 1241, 1085, 1015, 952, 924, 822, 809, 784, 769, 758, 737, 699 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NCl$ 280.0888; Found 280.0880.

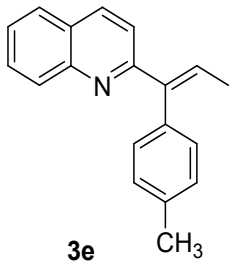
For the characterization of *Z*-**3c**: A light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20-8.16 (m, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 7.0 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.27-7.23 (m, 3H), 7.19-7.18 (m, 2H), 6.40 (q, *J* = 7.0 Hz, 1H), 1.85 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.9, 148.0, 141.0, 139.7, 136.3, 132.9, 129.6, 129.5, 128.40, 128.36, 128.1, 127.5, 126.9, 126.6, 123.0, 15.6. IR (neat): 3058, 2924, 2848, 1596, 1557, 1500, 1490, 1424, 1402, 1174, 1091, 1013, 843, 757, 719 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NCl$ 280.0888; Found 280.0889.



3d

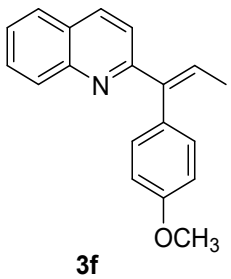
(*E*)-2-(1-Phenylprop-1-en-1-yl)quinoline (3d). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1d** (0.3 mmol, 34.8 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h.

Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **3d** in 85% yield (62.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 1H), δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.68 (td, *J* = 7.0, 1.6 Hz, 1H), 7.45 (td, *J* = 7.4, 1.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.37-7.35 (m, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.10 (q, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 1.86 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 147.8, 142.0, 138.6, 135.8, 130.1, 130.0, 129.44, 129.41, 128.4, 127.3, 127.1, 127.0, 125.9, 120.7, 15.7. IR (neat): 3056, 2909, 2852, 1615, 1592, 1500, 1424, 1239, 950, 909, 825, 785, 774, 753, 702 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}N$ 246.1277; Found 246.1278.



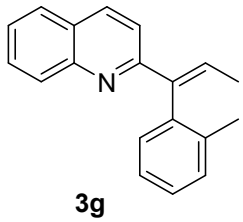
3e

(*E*)-2-(1-(*p*-Tolyl)prop-1-en-1-yl)quinoline (3e). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1e** (0.3 mmol, 39.1 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product **3e** in 80% yield (62.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.67 (td, *J* = 7.2, 1.2 Hz, 1H), 7.45 (td, *J* = 7.6, 0.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.08-7.03 (m, 2H), 2.40 (s, 3H), 1.87 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 147.8, 141.9, 136.8, 135.8, 135.6, 130.0, 129.8, 129.43, 129.37, 129.1, 127.3, 127.0, 125.8, 120.8, 21.2, 15.7. IR (neat): 2919, 2853, 1615, 1593, 1510, 1450, 1424, 1239, 1109, 951, 783, 754, 726, 696 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}N$ 260.1434; Found 260.1434.



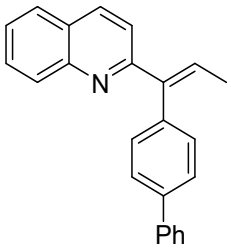
3f

(*E*)-2-(1-(4-Methoxyphenyl)prop-1-en-1-yl)quinoline (3f). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1f** (0.3 mmol, 43.9 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product **3f** in 77% yield (63.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.67 (td, *J* = 7.2, 1.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.03 (q, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 1.88 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 158.6, 147.8, 141.6, 135.7, 131.2, 130.8, 129.7, 129.4, 129.3, 127.3, 127.0, 125.8, 120.8, 113.8, 55.1, 15.7. IR (neat): 3035, 2931, 2834, 1607, 1593, 1508, 1424, 1288, 1243, 1171, 1033, 909, 839, 820, 755, 730, 697 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}NO$ 276.1383; Found 276.1385.



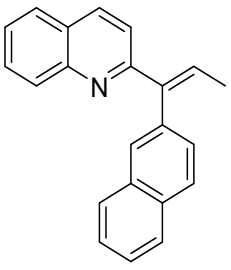
3g

(*E*)-2-(1-(*o*-Tolyl)prop-1-en-1-yl)quinoline (3g). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1g** (0.3 mmol, 39.1 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product **3g** in 47% yield (36.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.68 (td, *J* = 8.4, 1.2 Hz, 1H), 7.45 (td, *J* = 7.6, 0.8 Hz, 1H), 7.35-7.25 (m, 4H), 7.18 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 2.11 (s, 3H), 1.72 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 148.0, 141.1, 138.0, 137.0, 136.2, 130.4, 130.2, 130.0, 129.43, 129.41, 127.5, 127.3, 127.1, 126.0, 125.7, 119.8, 19.7, 15.5. IR (neat): 3059, 2910, 1616, 1592, 1501, 1424, 907, 822, 784, 753, 728, 696 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}N$ 260.1434; Found 260.1432.



3h

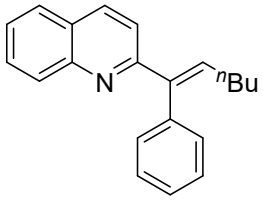
(*E*)-2-(1-([1,1'-Biphenyl]-4-yl)prop-1-en-1-yl)quinoline (3h). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1h** (0.3 mmol, 57.7 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **3h** in 66% yield (63.9 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.68 (td, *J* = 8.3, 1.5 Hz, 1H), 7.67-7.65 (m, 4H), 7.48-7.43 (m, 3H), 7.36-7.33 (m, 3H), 7.11 (q, *J* = 8.5 Hz, 2H), 1.92 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 147.9, 141.7, 140.7, 139.9, 137.6, 135.9, 130.6, 130.2, 129.5, 129.4, 128.8, 127.33, 127.28, 127.1, 127.0, 125.9, 120.8, 15.8. IR (neat): 3026, 2969, 2930, 2851, 1593, 1555, 1502, 1487, 1424, 1240, 1118, 1004, 952, 852, 821, 771, 751, 729, 691 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}N$ 322.1590; Found 322.1592.



3i

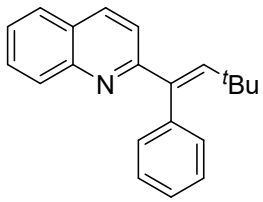
(*E*)-2-(1-(Naphthalen-2-yl)prop-1-en-1-yl)quinoline (3i). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1i** (0.3 mmol, 49.9 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product **3i** in 81% yield (71.4 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.89-7.81 (m, 4H), 7.76 (s, 1H), 7.70-7.65 (m, 2H), 7.49-7.42 (m, 3H), 7.36 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.18 (q, *J* = 10.8 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 1.91 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 147.9, 142.0, 136.1, 135.8, 133.4, 132.5, 130.4, 129.4, 129.0, 128.2, 128.0, 127.9, 127.7, 127.3, 127.0, 126.1, 125.94,

125.88, 120.8, 15.8. IR (neat): 3054, 2906, 2848, 1615, 1592, 1555, 1450, 1424, 906, 859, 821, 784, 728, 695 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}N$ 296.1434; Found 296.1438.



3j

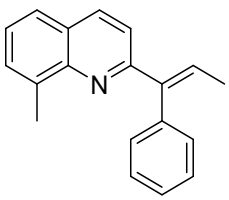
(*E*)-2-(1-Phenylhex-1-en-1-yl)quinoline (3j). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1j** (0.3 mmol, 47.5 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product **3j** in 65% yield (55.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46-7.40 (m, 3H), 7.40-7.33 (m, 1H), 7.28-7.23 (m, 2H), 7.08-7.03 (m, 2H), 2.20 (q, *J* = 7.6 Hz, 2H), 1.54-1.48 (m, 2H), 1.39-1.33 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 147.9, 141.0, 139.0, 135.8, 135.7, 130.0, 129.5, 129.4, 128.4, 127.3, 127.1, 127.0, 125.8, 120.7, 31.8, 29.6, 22.5, 13.9. IR (neat): 3056, 2955, 2925, 2856, 1616, 1593, 1554, 1501, 1424, 828, 773, 753, 703 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}N$ 288.1747; Found 288.1750.



3k

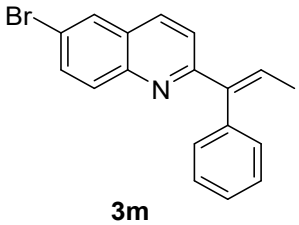
(*E*)-2-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)quinoline (3k). In the nitrogen-filled glove box, CuCl (10 mol%, 5.0 mg), PCy_3 (10 mol%, 14.0 mg), B_2pin_2 (1.5 equiv., 190.5 mg), KO^{t}Bu (1.5 equiv., 84.2 mg) and THF (2.5 mL) were added to screw-cap vial. The solvent stirred at ambient temperature for 1 minute. Then **1k** (0.5 mmol, 79.1 mg) and **2a** (1.5 equiv., 108.9 mg) were added. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **3k** in 20% yield (28.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.70-7.64 (m, 2H), 7.46-

7.35 (m, 4H), 7.31-7.29 (m, 2H), 7.24-7.23 (m, 1H), 6.94 (d, J = 8.4 Hz, 1H), 1.05 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 147.7, 144.6, 139.6, 138.3, 135.8, 130.7, 129.6, 129.3, 128.0, 127.2, 127.1, 126.9, 125.8, 120.3, 34.1, 31.1. IR (neat): 3057, 2957, 2900, 2865, 1616, 1592, 1553, 1499, 1424, 1364, 1257, 1238, 908, 827, 780, 754, 731, 716, 701 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}N$ 288.1747; Found 280.1752.



3l

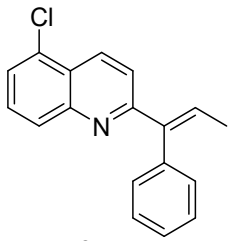
(*E*)-8-Methyl-2-(1-phenylprop-1-en-1-yl)quinoline (3l). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1d** (0.3 mmol, 34.8 mg) and **2b** (1.5 equiv., 71.6 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **3l** in 63% yield (49.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 1H), 7.55-7.50 (m, 2H), 7.44-7.41 (m, 2H), 7.36-7.28 (m, 5H), 7.04 (d, J =8.8 Hz, 1H), 2.83 (s, 3H), 1.84 (d, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 146.7, 142.2, 138.8, 137.2, 136.1, 130.2, 129.5, 128.3, 127.0, 126.9, 125.5, 125.3, 120.0, 17.8, 15.7. IR (neat): 3039, 2914, 2852, 1612, 1595, 1563, 1497, 1439, 1424, 1352, 831, 761 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}N$ 260.1434; Found 260.1434.



3m

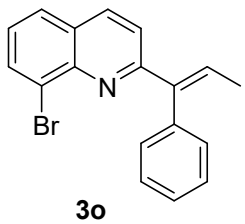
(*E*)-6-Bromo-2-(1-phenylprop-1-en-1-yl)quinoline (3m). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1d** (0.3 mmol, 34.8 mg) and **2c** (1.5 equiv., 100.8 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **3m** in 69% yield (66.8 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.73 (dd, J = 9.3, 2.5 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.37-7.35 (m, 1H), 7.26-7.25 (m, 2H), 7.12 (q, J = 7.0 Hz, 1H), 7.05 (d, J = 9.0 Hz, 1H), 1.85 (d, J = 7.5 Hz, 3H). ^{13}C NMR (125

MHz, $CDCl_3$): δ 159.3, 146.4, 141.8, 138.3, 134.8, 132.8, 131.2, 130.6, 130.1, 129.3, 128.5, 128.1, 127.3, 121.5, 119.6, 15.8. IR (neat): 3054, 2910, 2850, 1737, 1589, 1542, 1484, 1439, 1372, 1238, 1185, 1057, 926, 881, 865, 841, 821, 811, 766, 711, 691 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NBr$ 324.0382; Found 324.0387.



3n

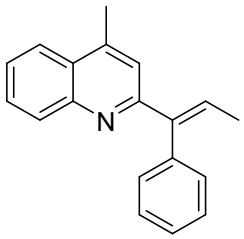
(*E*)-5-Chloro-2-(1-phenylprop-1-en-1-yl)quinoline (3n). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1d** (0.3 mmol, 34.8 mg) and **2d** (1.5 equiv., 80.8 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **3n** in 74% yield (62.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.59-7.51 (m, 2H), 7.45-7.34 (m, 3H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.17-7.11 (m, 2H), 1.87 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 148.5, 141.6, 138.2, 132.7, 131.0, 130.9, 130.1, 129.1, 128.6, 128.5, 127.3, 125.8, 125.1, 121.5, 15.8. IR (neat): 3056, 2909, 2848, 1608, 1584, 1548, 1492, 1400, 1393, 1261, 1129, 960, 806, 758, 702, 673 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NCl$ 280.0888; Found 280.0895.



3o

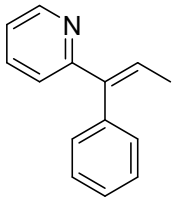
(*E*)-8-Bromo-2-(1-phenylprop-1-en-1-yl)quinoline (3o). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **1d** (0.3 mmol, 34.8 mg) and **2e** (1.5 equiv., 100.8 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **3o** in 22% yield (21.6 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.54-7.43 (m, 3H), 7.39-7.36 (m, 1H), 7.31-7.25 (m, 3H), 7.05 (d, *J* = 8.8 Hz, 1H), 1.86 (d, *J* =

7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 144.6, 141.4, 138.3, 136.5, 133.1, 131.5, 130.2, 128.5, 128.2, 127.2, 126.1, 125.1, 121.1, 15.9. IR (neat): 3054, 2925, 1590, 1538, 1493, 1439, 1422, 1310, 1262, 960, 797, 701, 655 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NBr$ 324.0382; Found 324.0388.



3p

(*E*)-4-Methyl-2-(1-phenylprop-1-en-1-yl)quinoline (3p). In the nitrogen-filled glove box, CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) were added to screw-cap vial. The solvent stirred at ambient temperature for 1 minute. Then **1d** (0.3 mmol, 34.8 mg) and **2f** (1.5 equiv., 71.6 mg) were added. The reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product 3p in 15% yield (12.0 mg) as a yellow oil. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product **3p** in 15% yield (12.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.45-7.42 (m, 2H), 7.38-7.35 (m, 1H), 7.29-7.27 (m, 2H), 7.06 (q, *J* = 7.2 Hz, 1H), 6.87 (s, 1H), 2.55 (s, 3H), 1.86 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1, 158.8, 147.7, 144.0, 142.1, 138.7, 130.2, 130.0, 129.8, 129.1, 128.4, 127.1, 125.6, 123.5, 121.4, 18.8, 15.7. IR (neat): 3056, 2908, 2852, 1737, 1593, 1548, 1505, 1494, 1440, 1314, 1266, 883, 756, 730, 701, 676, 607, 530, 422 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}N$ 260.1434; Found 260.1440.

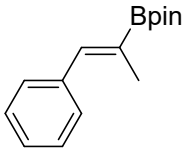


3q

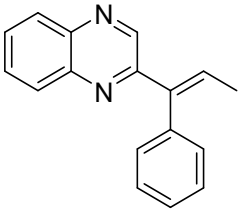
(*E*)-2-(1-phenylprop-1-en-1-yl)pyridine (3q). In the nitrogen-filled glove box, CuCl (10 mol%, 5.0 mg), PCy_3 (10 mol%, 14.0 mg), B_2pin_2 (1.5 equiv., 190.5 mg), KO^{t}Bu (1.5 equiv.,

84.2 mg) and THF (2.5 mL) were added to screw-cap vial. The solvent stirred at ambient temperature for 1 minute. Then **1d** (0.5 mmol, 58.1 mg) and pyridine *N*-oxide **2g** (1.5 equiv., 71.3 mg) were added. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h. No desired product was formed according to TLC analysis. Instead, the hydroborated product of (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane was obtained in 21% yield (26 mg) as a yellow oil.

For the characterization of (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane[6]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H), 7.24-7.22 (m, 2H), 1.99 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 137.9, 129.4, 128.0, 127.0, 83.5, 24.8, 15.9.

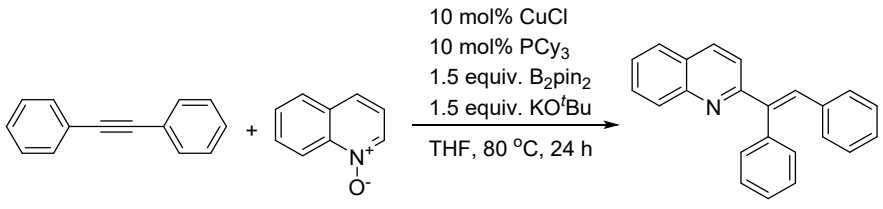


3r

(*E*)-2-(1-Phenylprop-1-en-1-yl)quinoxaline (3r). In the nitrogen-filled glove box, CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) was added to screw-cap vial. The solvent stirred at ambient temperature for 1 minute. Then **1d** (0.3 mmol, 34.8 mg) and quinoxaline 1-oxide (1.5 equiv., 65.8 mg) were added. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h. No desired product was observed according to TLC analysis.

Synthesis of products 5a-5e.

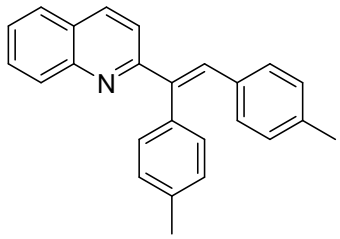
Typical procedure for the synthesis of 5a.



4a **2a**, 1.5 equiv. **5a**

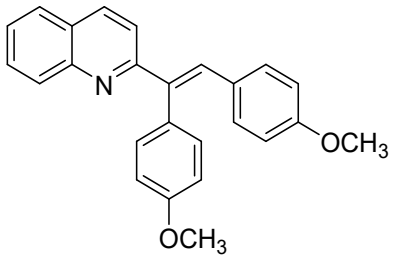
(*E*)-2-(1,2-Diphenylvinyl)quinoline (5a). In the nitrogen-filled glove box, CuCl (10 mol%, 3.0

mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) were added to screw-cap vial (4 mL). The solvent stirred at ambient temperature for 1 minute. Then **4a** (0.3 mmol, 53.5 mg) and **2a** (1.5 equiv., 65.3 mg) were added. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h, the mixture was filtered over a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the product **5a** in 90% yield (83.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.95-7.93 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.68 (td, *J* = 8.0, 0.8 Hz, 1H), 7.47 (t, *J* = 6.8 Hz, 1H), 7.41-7.37 (m, 3H), 7.31-7.29 (m, 2H), 7.13 (s, 5H), 7.10 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 147.9, 140.9, 139.1, 136.7, 136.0, 132.5, 130.3, 130.1, 129.6, 129.5, 129.0, 127.9, 127.7, 127.4, 127.3, 127.2, 126.1, 120.8. IR (neat): 1735, 1589, 1499, 1444, 1424, 1372, 1239, 827, 787, 778, 753, 692 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}N$ 308.1434; Found 308.1436.



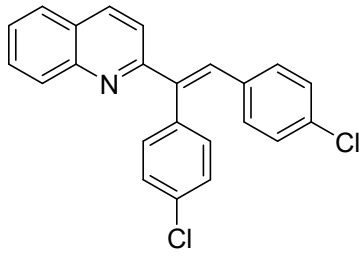
5b

(*E*)-2-(1,2-Di-*p*-tolylvinyl)quinoline (5b). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4b** (0.3 mmol, 61.9 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **5b** in 85% yield (85.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.89 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.70 (td, *J* = 8.4, 1.2 Hz, 1H), 7.45 (td, *J* = 7.6, 0.8 Hz, 1H), 7.21-7.17 (m, 4H), 7.10 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 147.8, 139.9, 137.2, 136.3, 135.8, 134.0, 132.3, 130.2, 130.1, 129.7, 129.5, 129.4, 128.6, 127.3, 127.1, 126.0, 120.8, 21.3, 21.2. IR (neat): 3021, 2918, 1736, 1615, 1588, 1551, 1507, 1499, 1424, 1238, 1182, 1111, 813, 757, 748, 714, 697 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N$ 336.1747; Found 336.1747.



5c

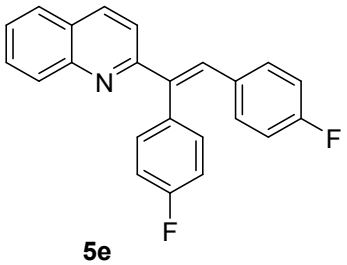
(*E*)-2-(1,2-Bis(4-methoxyphenyl)vinyl)quinoline (5c). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4c** (0.3 mmol, 71.5 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by silica gel plate (eluent: petroleum ether/ethyl acetate = 10/1) followed by recycling preparative HPLC afforded the title product **5c** in 71% yield (78.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.87 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.69 (td, *J* = 8.2, 1.2 Hz, 1H), 7.46 (td, *J* = 7.4, 1.2 Hz, 1H), 7.24-7.21 (m, 2H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 3H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 159.0, 158.8, 147.7, 138.3, 135.9, 132.1, 131.6, 131.53, 131.46, 129.61, 129.55, 129.3, 127.3, 127.0, 125.9, 120.8, 114.5, 113.3, 55.1, 55.0. IR (neat): 2955, 2835, 1735, 1603, 1587, 1506, 1460, 1424, 1441, 1372, 1298, 1286, 1243, 1174, 1151, 1110, 1031, 830, 813, 793, 759 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}NO_2$ 368.1645; Found 368.1640.



5d

(*E*)-2-(1,2-Bis(4-chlorophenyl)vinyl)quinoline (5d). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4d** (0.3 mmol, 74.1 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **5d** in 85% yield (95.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.86 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 8.4, 1.2 Hz, 1H), 7.52 (td, *J* = 7.6, 0.8 Hz, 1H), 7.40-7.38 (m, 2H), 7.23-7.21

(m, 2H), 7.17-7.05 (m, 2H), 7.10 (d, J = 8.8 Hz, 1H), 7.07-7.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 147.9, 140.4, 137.2, 136.2, 135.0, 133.9, 133.3, 131.7, 131.6, 131.2, 129.8, 129.6, 129.4, 128.3, 127.4, 127.3, 126.4, 120.5. IR (neat): 1735, 1590, 1500, 1488, 1425, 1403, 1239, 1089, 1013, 990, 827, 795, 755, 720, 697 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{16}NCl_2$ 376.0654; Found 376.0656.

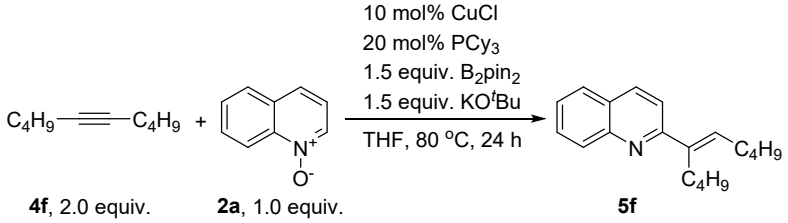


5e

(*E*)-2-(1,2-Bis(4-fluorophenyl)vinyl)quinoline (5e). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4e** (0.3 mmol, 64.3 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **5e** in 84% yield (86.4 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.88 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.72 (td, J = 8.0, 0.8 Hz, 1H), 7.51 (td, J = 7.4, 0.4 Hz, 1H), 7.27-7.23 (m, 2H), 7.13-7.07 (m, 5H), 6.86 (t, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, $^1J_{C\text{-}F}$ = 246.1 Hz), 161.9 (d, $^1J_{C\text{-}F}$ = 246.9 Hz), 158.7, 147.9, 139.7 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 136.2, 134.7 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 132.8 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 132.1 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 131.8 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 131.6, 129.8, 129.6, 127.4, 127.2, 126.3, 120.5, 116.2 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 115.0 (d, $^2J_{C\text{-}F}$ = 21.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): -113.28--113.33 (m), -113.73--113.78 (m). IR (neat): 1591, 1426, 1221, 1160, 1147, 1093, 1015, 916, 847, 784, 754, 730, 696, 683 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{16}NF_2$ 344.1245; Found 344.1249.

Synthesis of products 5f-5j.

Typical procedure for the synthesis of 5f.

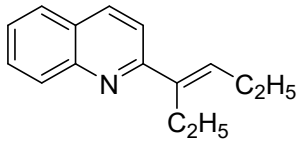


4f, 2.0 equiv. **2a**, 1.0 equiv. **5f**

(*E*)-2-(Dec-5-en-5-yl)quinoline (5f). In the nitrogen-filled glove box, CuCl (10 mol%, 3.0 mg),

PCy_3 (20 mol%, 16.8 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) were added to screw-cap vial (4 mL). The solvent stirred at room temperature for 1 minute. Then **4f** (2.0 equiv. 0.6 mmol, 83.0 mg) and **2a** (0.3 mmol, 43.5 mg) were added. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h, the mixture was filtered over a silica gel pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. the residue was purified by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the product **5f** in 68% yield (54.3 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (t, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.65 (td, *J* = 7.6, 1.6 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.44 (td, *J* = 7.6, 0.8 Hz, 1H), 6.30 (t, *J* = 7.2 Hz, 1H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.32 (q, *J* = 7.2 Hz, 2H), 1.53-1.34 (m, 8H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 147.7, 140.8, 135.8, 133.8, 129.5, 129.1, 127.2, 126.8, 125.6, 119.2, 31.8, 31.3, 28.6, 27.9, 22.8, 22.6, 14.01, 14.00. IR (neat): 2955, 2926, 2857, 1617, 1597, 1556, 1502, 1460, 1425, 1377, 1304, 1138, 1110, 784, 754, 689 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{26}N$ 268.2060; Found 268.2057.

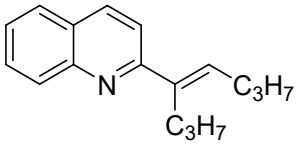
When the reaction was carried out at 80 °C for 24 h using CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4f** (0.3 mmol, 41.5 mg) and **2a** (0.45 mmol, 65.3 mg), the product **5f** was obtained in 44% yield (35.4 mg).



5g

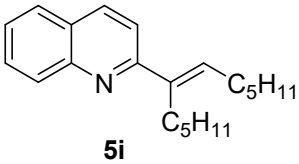
(*E*)-2-(Hex-3-en-3-yl)quinoline (5g). CuCl (10 mol%, 3.0 mg), PCy_3 (20 mol%, 16.8 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4g** (2.0 equiv., 0.6 mmol, 49.3 mg) and **2a** (0.3 mmol, 43.5 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the title product **5g** in 59% yield (37.2 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 5.6 Hz, 1H), 8.04 (d, *J* = 6.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 6.30 (t, *J* = 7.2 Hz, 1H), 2.81 (q, *J* = 7.2 Hz, 2H), 2.38-2.31 (m, 2H), 1.13 (t, *J* = 7.6 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 147.8, 141.7, 135.8, 134.7, 129.5, 129.1, 127.2,

126.9, 125.6, 119.1, 22.0, 21.4, 14.2, 13.9. IR (neat): 2964, 2931, 2871, 1616, 1597, 1556, 1502, 1458, 1426, 1307, 1138, 787, 754, 693 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}N$ 212.1434; Found 212.1438.



5h

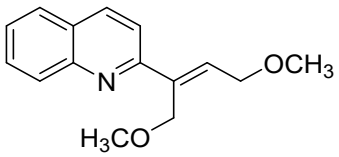
(*E*)-2-(Oct-4-en-4-yl)quinoline (5h). CuCl (10 mol%, 3.0 mg), PCy_3 (20 mol%, 16.8 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4h** (2.0 equiv., 0.6 mmol, 66.1 mg) and **2a** (0.3 mmol, 43.5 mg) were stirred at 80 ^{o}C in an oil bath for 24 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the title product **5h** in 49% yield (35.4 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (t, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 6.31 (t, *J* = 7.2 Hz, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 1.59-1.52 (m, 2H), 1.50-1.42 (m,2H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 147.7, 140.8, 135.8, 133.8, 129.5, 129.1, 127.2, 126.8, 125.6, 119.2, 31.0, 30.3, 22.8, 22.2, 14.2, 14.1. IR (neat): 2957, 2929, 2869, 1616, 1597, 1555, 1503, 1456, 1425, 1377, 1304, 1216, 1138, 1107, 818, 753, 687 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}N$ 240.1747; Found 240.1749.



5i

(*E*)-2-(Dodec-6-en-6-yl)quinoline (5i). CuCl (10 mol%, 3.0 mg), PCy_3 (20 mol%, 16.8 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4i** (2.0 equiv., 0.6 mmol, 99.8 mg) and **2a** (0.3 mmol, 43.5 mg) were stirred at 80 ^{o}C in an oil bath for 24 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the title product **5i** in 68% yield (60.4 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (t, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.65 (td, *J* = 6.8, 1.2 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.45 (td, *J* = 7.4, 1.2 Hz, 1H), 6.30 (t, *J* = 7.2 Hz, 1H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.31 (q, *J* = 7.2 Hz, 2H), 1.53-1.28 (m, 12H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 147.8, 140.9, 135.8, 133.8, 129.5, 129.1, 127.2, 126.8, 125.6, 119.2, 31.9, 31.7, 29.3, 28.9, 28.7, 28.2, 22.6, 22.5, 14.05, 14.03. IR (neat):

2955, 2924, 2856, 1616, 1598, 1556, 1502, 1465, 1425, 1377, 1303, 1138, 1111, 823, 753, 729, 692 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}N$ 296.2373; Found 296.2376.

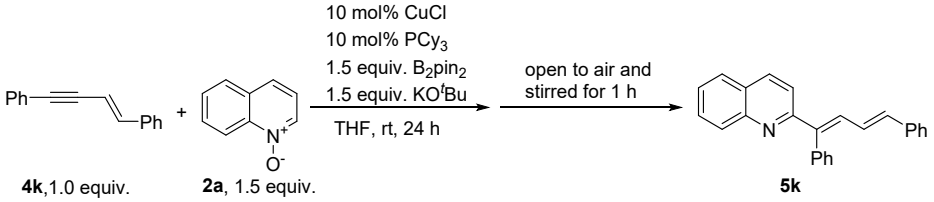


5j

(*Z*)-2-(1,4-Dimethoxybut-2-en-2-yl)quinoline (5j). CuCl (10 mol%, 3.0 mg), PCy_3 (20 mol%, 16.8 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4j** (2.0 equiv., 0.6 mmol, 68.5 mg) and **2a** (0.3 mmol, 43.5 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the title product **5j** in 68% yield (49.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (t, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69-7.64 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 6.4 Hz, 1H), 4.68 (s, 2H), 4.37 (d, *J* = 6.0 Hz, 2H), 3.44 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 147.6, 138.6, 136.3, 134.1, 129.6, 129.3, 127.3, 127.1, 126.1, 118.9, 69.4, 67.9, 58.4, 58.1. IR (neat): 2980, 2924, 2818, 1617, 1596, 1556, 1503, 1450, 1427, 1376, 1227, 1190, 954, 910, 818, 786, 756 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_2$ 244.1332; Found 244.1336.

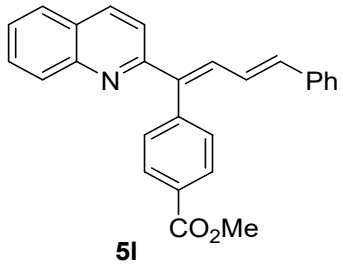
Synthesis of products 5k-5t.

Typical procedure for the synthesis of 5k.



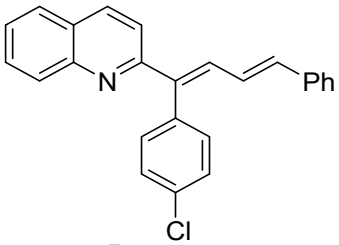
2-((1*E*,3*E*)-1,4-Diphenylbuta-1,3-dien-1-yl)quinoline (5k). In the nitrogen-filled glove box, CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) were added to screw-cap vial (4 mL). The solvent stirred at ambient temperature for 1 minute. Then **4k** (0.3 mmol, 61.3 mg) and **2a** (1.5 equiv., 65.3 mg) were added. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. After the reaction mixture was stirred at room temperature for 24 h, then the mixture was stirred in air for 1 h. The mixture was filtered over a silica gel pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1)

to afford the corresponding product **5k** in 63% yield (63.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.84 (dd, *J* = 6.6, 3.2 Hz, 1H), 7.73-7.67 (m, 2H), 7.49-7.42 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 4H), 7.26 (t, *J* = 6.8 Hz, 2H), 7.21-7.19 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.96-6.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 148.0, 141.6, 138.5, 137.3, 136.8, 135.8, 132.6, 130.6, 129.6, 129.5, 128.53, 128.49, 127.9, 127.7, 127.3, 127.1, 126.7, 126.5, 126.1, 121.1. IR (neat): 3055, 3029, 1735, 1594, 1580, 1546, 1497, 1424, 1371, 1226, 968, 829, 749, 690 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}N$ 334.1590; Found 334.1592.



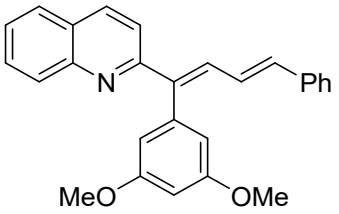
5l

Methyl 4-((1*E*,3*E*)-4-phenyl-1-(quinolin-2-yl)buta-1,3-dien-1-yl)benzoate (5l). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4l** (0.3 mmol, 78.7 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at ambient temperature for 24 h, then the solvent stirred in air for 1 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the title product **5l** in 48% yield (55.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.6 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 11.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.47-7.45 (m, 2H), 7.36-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.21 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.01-6.98 (m, 1H), 6.92-6.88 (m, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 157.6, 148.1, 143.5, 140.6, 137.7, 137.0, 136.1, 133.3, 130.8, 129.8, 129.7, 129.6, 129.4, 128.6, 128.2, 127.4, 127.2, 126.8, 126.3, 125.9, 120.8, 52.2. IR (neat): 2949, 1721, 1596, 1579, 1545, 1497, 1436, 1425, 1272, 1229, 1175, 1100, 1017, 972, 963, 829, 729, 690 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}NO_2$ 392.1645; Found 392.1644.



5m

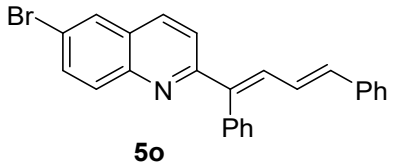
2-((1*E*,3*E*)-1-(4-Chlorophenyl)-4-phenylbuta-1,3-dien-1-yl)quinoline (5m). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4m** (0.3 mmol, 71.6 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at ambient temperature for 24 h, then the solvent stirred in air for 1 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **5m** in 53% yield (58.7 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 10.0 Hz, 1H), 7.73-7.66 (m, 2H), 7.48-7.43 (m, 3H), 7.35-7.33 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 4H), 7.22-7.19 (m, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.98-6.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 148.0, 140.3, 137.4, 137.0, 136.9, 136.0, 133.6, 133.0, 132.0, 129.7, 129.5, 128.7, 128.6, 128.1, 127.3, 127.1, 126.8, 126.2, 126.0, 120.7. IR (neat): 1592, 1578, 1544, 1488, 1424, 1369, 1228, 1133, 1101, 1087, 1014, 973, 963, 837, 825, 814, 744, 718, 688 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}NCl$ 368.1201; Found 368.1193.



5n

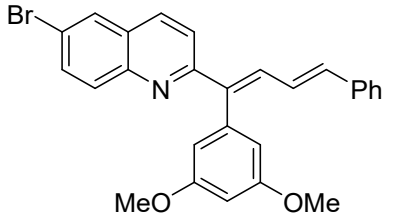
2-((1*E*,3*E*)-1-(3,5-Dimethoxyphenyl)-4-phenylbuta-1,3-dien-1-yl)quinoline (5n). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4n** (0.3 mmol, 79.3 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at ambient temperature for 24 h, then the solvent stirred in air for 1 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the title product **5n** in 69% yield (81.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 9.6 Hz, 1H), 7.74-7.68 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.38-7.36 (m, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.99-6.97 (m, 2H), 6.55-6.53 (m, 3H), 3.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$):

δ 160.9, 157.9, 148.0, 141.3, 140.5, 137.2, 136.9, 135.9, 132.5, 129.6, 129.4, 128.5, 127.9, 127.3, 127.2, 126.8, 126.4, 126.0, 121.2, 108.5, 99.9, 55.3. IR (neat): 2957, 2922, 2849, 1736, 1547, 1501, 1448, 1419, 1373, 1317, 1272, 1253, 1226, 1204, 1193, 1152, 1058, 969, 895, 875, 862, 821, 786, 712, 691 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_2$ 394.1802; Found 394.1798.



5o

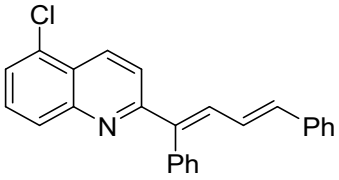
6-Bromo-2-((1*E*,3*E*)-1,4-diphenylbuta-1,3-dien-1-yl)quinoline (5o). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4k** (0.3 mmol, 61.3 mg) and **2c** (1.5 equiv., 100.8 mg) were stirred at ambient temperature for 24 h, then the solvent stirred in air for 1 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the title product **5o** in 66% yield (82.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.2 Hz, 1H), 7.85-7.80 (m, 3H), 7.73 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.49-7.40 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 4H), 7.26 (t, *J* = 6.8 Hz, 2H), 7.22-7.17 (m, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.98-6.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 146.6, 141.1, 138.1, 137.2, 137.1, 134.8, 133.01, 132.96, 131.2, 130.6, 129.3, 128.6, 128.1, 128.0, 127.7, 126.8, 126.3, 121.8, 119.8. IR (neat): 1735, 1591, 1578, 1538, 1483, 1441, 1371, 1294, 1241, 1222, 1186, 1072, 1057, 969, 877, 827, 785, 769, 749, 690 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}NBr$ 412.0695; Found 412.0697.



5p

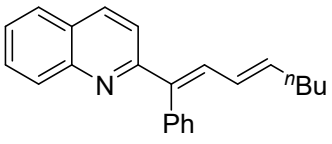
6-Bromo-2-((1*E*,3*E*)-1-(3,5-dimethoxyphenyl)-4-phenylbuta-1,3-dien-1-yl)quinoline (5p). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4n** (0.3 mmol, 79.3 mg) and **2c** (1.5 equiv., 100.8 mg) were stirred at ambient temperature for 24 h, then the solvent stirred in air for 1 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford

the title product **5p** in 47% yield (66.1 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.2 Hz, 1H), 7.87-7.83 (m, 3H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.37-7.35 (m, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 6.8 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.97-6.95 (m, 2H), 6.55 (s, 1H), 6.50 (s, 2H), 3.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 158.1, 146.6, 141.0, 140.2, 137.3, 137.1, 134.8, 132.93, 132.89, 131.2, 129.3, 128.6, 128.2, 128.0, 126.8, 126.3, 121.9, 119.7, 108.4, 99.9, 55.4. IR (neat): 2992, 2931, 2833, 1603, 1590, 1488, 1458, 1421, 1364, 1316, 1272, 1253, 1195, 1060, 974, 941, 895, 881, 829, 810, 773, 746, 709, 690 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}NO_2Br$ 472.0907; Found 472.0907.



5q

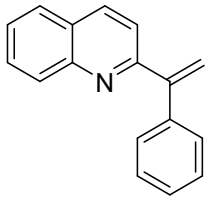
5-Chloro-2-((1*E*,3*E*)-1,4-diphenylbuta-1,3-dien-1-yl)quinoline (5q). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4k** (0.3 mmol, 61.3 mg) and **2d** (1.5 equiv., 80.8 mg) were stirred at ambient temperature for 24 h, then the solvent stirred in air for 1 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the title product **5q** in 62% yield (68.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.52-7.42 (m, 4H), 7.35-7.32 (m, 4H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.21-7.17 (m, 2H), 6.95-6.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 148.7, 141.0, 138.1, 137.4, 137.1, 133.3, 132.7, 131.1, 130.6, 129.2, 128.7, 128.6, 128.5, 128.0, 127.8, 126.8, 126.3, 125.9, 125.1, 121.8. IR (neat): 1736, 1576, 1543, 1492, 1442, 1391, 1371, 1236, 1195, 1123, 1046, 959, 832, 761, 748, 690, 673 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}NCl$ 368.1201; Found 368.1206.



5r

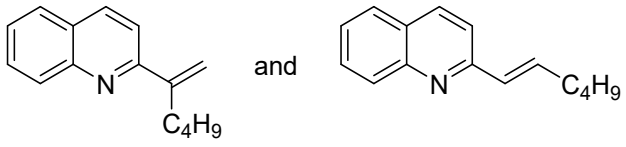
2-((1*E*,3*E*)-1-phenylocta-1,3-dien-1-yl)quinoline (5r). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), **4o** (0.3 mmol, 55.3 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at ambient temperature for

24 h, then the solvent stirred in air for 1 h. Purification by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the title product **5r** in 23% yield (21.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.68 (td, *J* = 6.8, 1.2 Hz, 1H), 7.61 (d, *J* = 10.4 Hz, 1H), 7.48-7.43 (m, 3H), 7.40-7.36 (m, 1H), 7.32-7.30 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.23-6.10 (m, 2H), 2.11 (q, *J* = 6.8 Hz, 2H), 1.40-1.26 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 148.0, 140.9, 138.9, 138.8, 135.7, 133.0, 130.6, 129.52, 129.45, 128.4, 128.0, 127.3, 127.0, 125.9, 121.0, 32.9, 31.4, 22.2, 13.9. IR (neat): 2957, 2927, 2872, 1738, 1596, 1584, 1548, 1501, 1442, 1372, 1238, 1046, 976, 911, 779, 757, 700 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}N$ 314.1903; Found 314.1897.



5u

2-(1-Phenylvinyl)quinoline (5u). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), phenylacetylene (0.3 mmol, 30.6 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford the title product **5u** in 33% yield (23.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.72 (td, *J* = 7.6, 1.6 Hz, 1H), 7.53 (td, *J* = 7.6, 0.8 Hz, 1H), 7.42-7.35 (m, 6H), 6.11 (d, *J* = 1.2 Hz, 1H), 5.77 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 149.5, 147.9, 140.0, 136.0, 129.7, 129.5, 128.4, 128.3, 127.9, 127.4, 127.3, 126.4, 121.2, 118.8. The spectroscopic data are in agreement with that previously reported.[7]



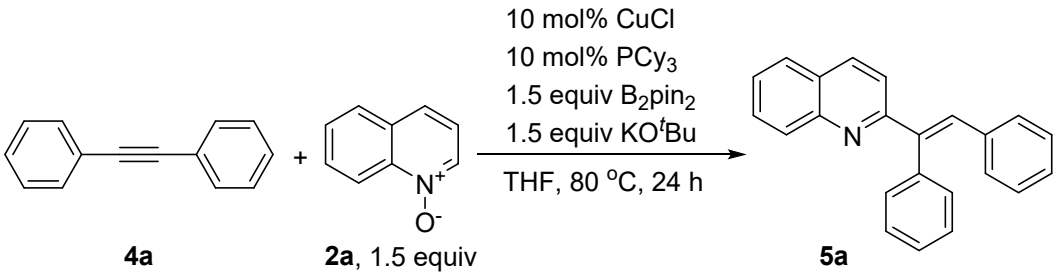
5v **5v'**

2-(Hex-1-en-2-yl)quinoline (5v). CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL), hex-1-yne (0.3 mmol, 24.6 mg) and **2a** (1.5 equiv., 65.3 mg) were stirred at 80 °C in an oil bath for 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford

the title product **5v** in 32% yield (20.3 mg) followed by **5v'** in 4% yield (2.5 mg). **For the characterization of 5v:** A light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (td, *J* = 7.6, 0.8 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.49 (td, *J* = 7.6, 0.8 Hz, 1H), 5.83 (s, 1H), 5.42 (d, *J* = 1.2 Hz, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.58-1.51 (m, 2H), 1.46-1.37 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 149.3, 147.7, 135.9, 129.7, 129.3, 127.3, 127.1, 126.1, 118.9, 116.1, 33.4, 30.7, 22.5, 14.0. IR (neat): 2954, 2926, 2858, 1617, 1597, 1503, 1461, 1425, 1139, 1111, 901, 831, 761, 721, 618, 477 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}N$ 212.1434; Found 212.1430.

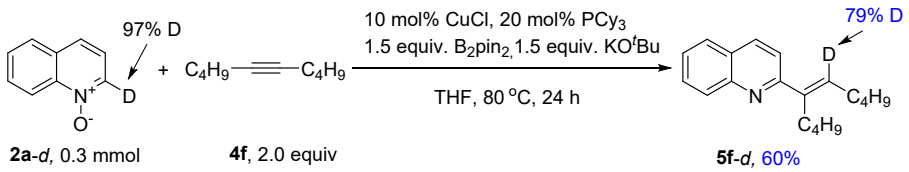
For the characterization of (*E*)-2-(hex-1-en-1-yl)quinoline (5v'): A light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 6.87-6.80 (m, 1H), 6.72 (d, *J* = 16.4 Hz, 1H), 2.34 (q, *J* = 6.8 Hz, 2H), 1.58-1.51 (m, 2H), 1.46-1.37 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). The spectroscopic data are in agreement with that previously reported.[8]

1 mmol scale reaction for the formation of 5a.

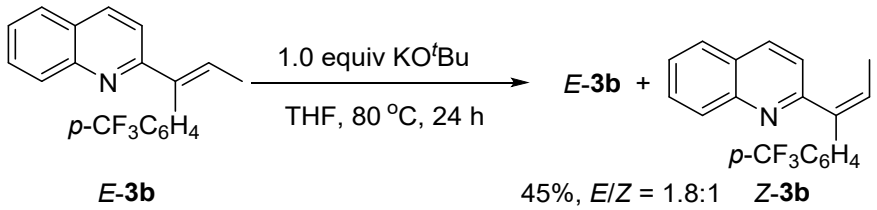


In the nitrogen-filled glove box, CuCl (10 mol%, 9.9 mg), PCy_3 (10 mol%, 28.0 mg), B_2pin_2 (1.5 equiv., 380.9 mg), KO^{t}Bu (1.5 equiv., 168.3 mg) and THF (4 mL) were added to a screw-cap vial (12 mL). The solvent stirred at ambient temperature for 1 minute. Then 1,2-diphenylethyne **4a** (1 mmol, 178.2 mg) and **2a** (1.5 equiv., 217.7 mg) were added. The vial was taken outside the glove box and immersed into an oil bath preheated at 80 °C. After the reaction mixture was stirred for 24 h, the mixture was filtered over a silica gel pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the corresponding product **5a** in 87% yield (267.4 mg) as a yellow oil.

Mechanistic studies.

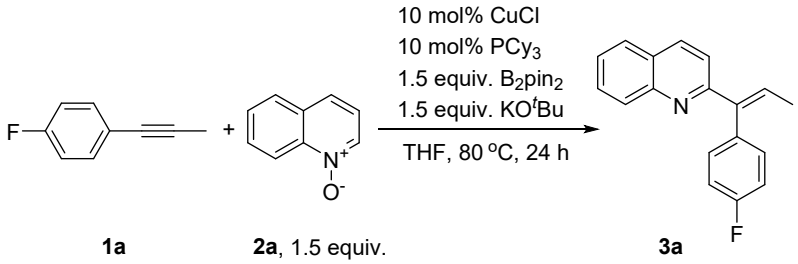


(*E*)-2-(Dec-5-en-5-yl-6-d)quinoline (5f-*d*). The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, CuCl (10 mol%, 3.0 mg), PCy_3 (20 mol%, 16.8 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) was added. The solvent stirred at ambient temperature for 1 minute. Then **4f** (2.0 equiv., 83.0 mg) and **2a**-*d* (0.3 mmol, 43.9 mg) were added. The vial was taken outside the glove box and immersed into an oil bath preheated at 80 °C. After stirring for 24 h, the mixture was cooled down to room temperature, filtered through a short pad of silica gel and washed with ethyl acetate. The organic solvent was evaporated under the reduced pressure and the residue was purified by thin plate chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afford the desired product **5f**-*d* in 60% yield (48.1 mg) with 79% deuterium incorporation as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 6.30 (t, J = 7.2 Hz, 0.21H), 2.80 (t, J = 6.8 Hz, 2H), 2.32 (t, J = 6.8 Hz, 2H), 1.53-1.32 (m, 8H), 0.94 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H). IR (neat): 2955, 2926, 2857, 1616, 1597, 1555, 1502, 1457, 1424, 1377, 1138, 1108, 828, 759. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{24}DN$ 268.2044; Found 268.2044.

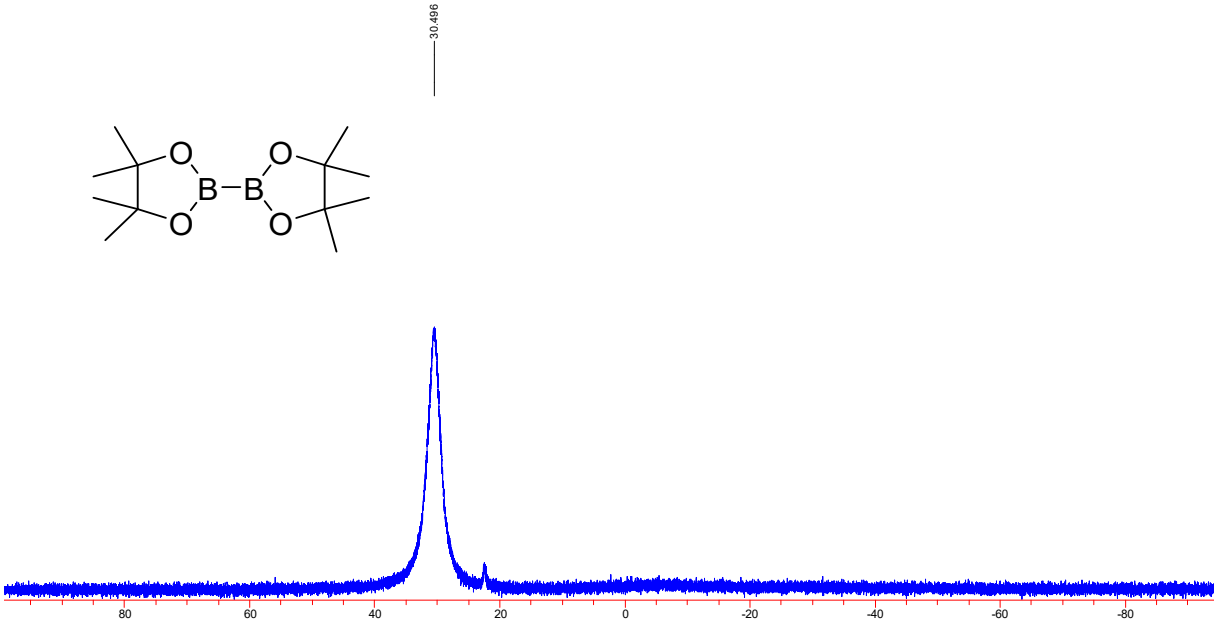


The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, *E*-**3b** (0.1 mmol, 31.3 mg), KO^{t}Bu (0.1 mmol, 11.2 mg) and THF (1 mL) were added sequentially to a screw-cap vial. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. The reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h. The mixture was cooled down to room temperature, filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the yields were determined by ^{1}H NMR using 1,3,5-trimethylbenzene (1.0 equiv., 12.0 mg) as the internal standard.

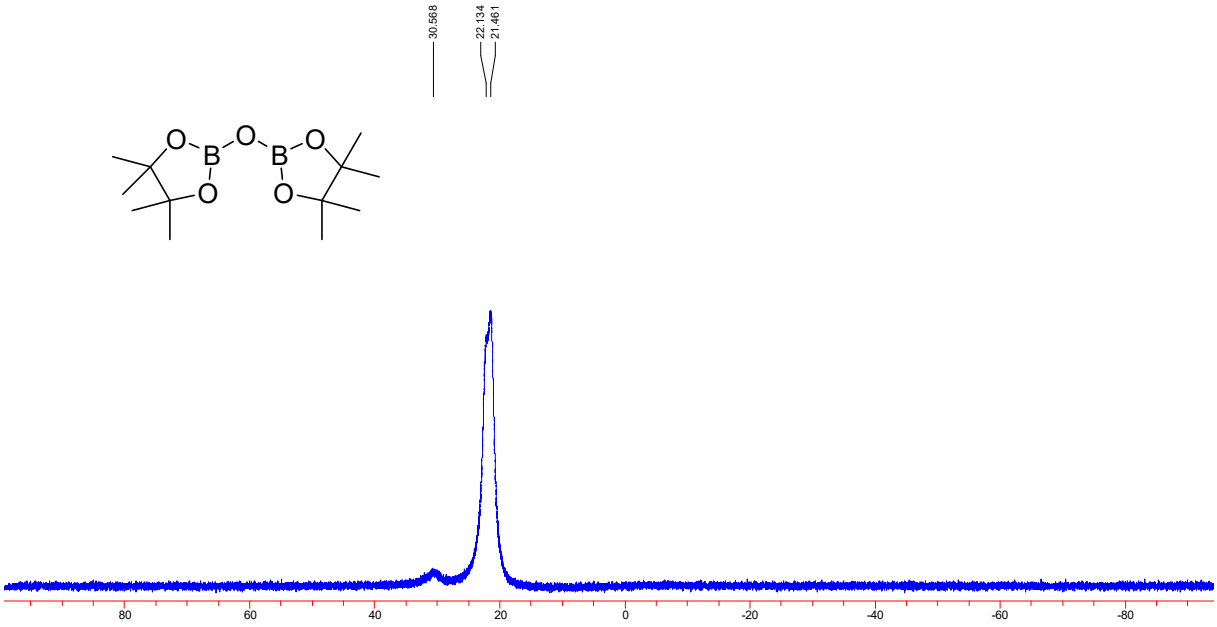
Detection of BpinOBpin species.



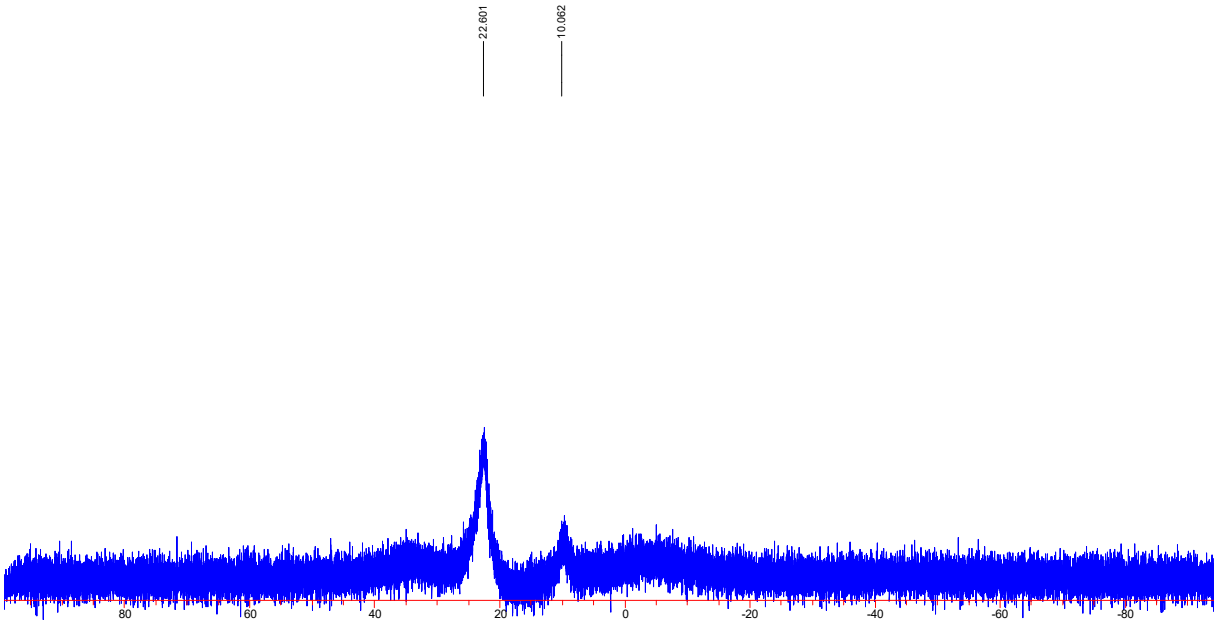
In the nitrogen-filled glove box, CuCl (10 mol%, 3.0 mg), PCy_3 (10 mol%, 8.4 mg), B_2pin_2 (1.5 equiv., 114.3 mg), KO^{t}Bu (1.5 equiv., 50.5 mg) and THF (1.5 mL) were added to screw-cap vial (4 mL). The mixture was stirred at room temperature for 1 minute. Then **1a** (0.3 mmol, 40.2 mg) and **2a** (1.5 equiv., 65.3 mg) were added. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. After the reaction mixture was stirred in an oil bath preheated at 80 °C (oil bath) for 24 h, the mixture was filtered over celite and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. The crude product was dissolved in $CDCl_3$ and analyzed by ^{11}B-NMR (128.4 MHz) spectroscopy (see **Spectra C** underneath). ^{11}B-NMR analysis of the crude reaction mixture showed that the peak at 22.6 ppm could be assigned to be BpinOBpin by comparison with a ^{11}B-NMR spectrum (see **spectra B**) of a sample of BpinOBpin prepared according to a literature procedure.[9]



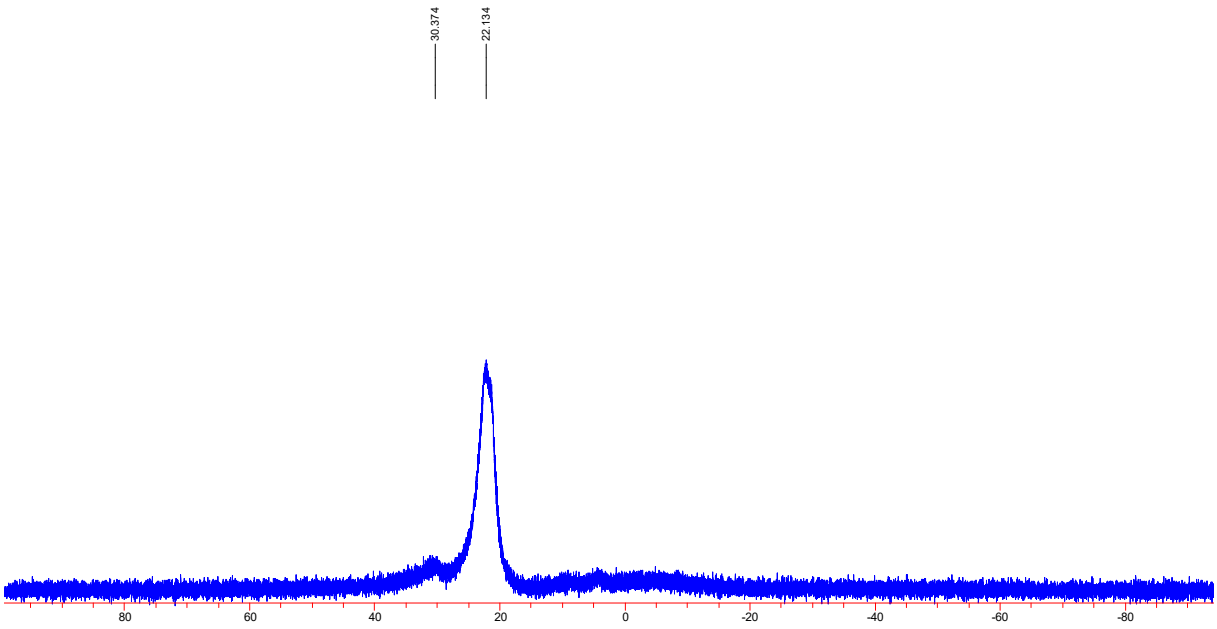
Spectra A: ^{11}B-NMR spectra (in $CDCl_3$) of the B_2pin_2



Spectra B: ^{11}B-NMR spectra (in $CDCl_3$) of the BpinOBpin obtained according to a literature procedure.[9]



Spectra C: ^{11}B-NMR spectra (in $CDCl_3$) of the crude reaction mixture



Spectra D: ^{11}B-NMR spectra (in $CDCl_3$) of a sample obtained by combining the crude reaction mixture and BpinOBpin

Reference:

(1) (a) H.-C Chiu and I. A. Tonks. Trimethylsilyl-Protected Alkynes as Selective Cross-Coupling Partners in Titanium-Catalyzed [2+2+1] Pyrrole Synthesis, *Angew. Chem. Int. Ed.,* 2018, **57**, 6090-6094. (b) T. Igarashi, E. Tayama, H. Iwamoto and E. Hasegawa. Carbon-carbon Bond Formation via Benzoyl Umpolung attained by Photoinduced Electron-Transfer with Benzimidazolines, *Tetrahedron Lett.,* 2013, **54**, 6874-6877.

(2) (a) Y. Gao, G. Wu, Q. Zhou and J. Wang. Palladium-Catalyzed Oxygenative Cross-Coupling of Ynamides and Benzyl Bromides by Carbene Migratory Insertion, *Angew. Chem. Int. Ed.,* 2018, **57**, 2716-2720. (b) A. K. Dhiman, S. S. Gupta, R. Sharma, R. Kumar and U. Sharma. Rh(III)-Catalyzed C(8)–H Activation of Quinoline *N*-Oxides: Regioselective C–Br and C–N Bond Formation, *J. Org. Chem.,* 2019, **84**, 12871-12880.

(3) W. Jo, J. Kim, S. Choi and S. H. Cho. Transition-Metal-Free Regioselective Alkylation of Pyridine *N*-Oxides Using 1,1-Diborylalkanes as Alkylating Reagents, *Angew. Chem. Int. Ed.,* 2016, **55**, 9690-9694.

(4) Y. Xu, J. Zhao, H. Chen, W. Wu and H. Jiang. A Convenient Regioselective Synthesis of Cyclopentadienones via Palladium-Catalyzed [2+2+1] Cyclocarbonylation of Alkynes, *Chem. Commun.,* 2014, **50**, 2488-2490.

(5) (a) M. Atsunori, S. Tomohiro, K. Tatsuhiro and S. Akitoshi. A Highly Effective Pd/Cu-

Catalyzed Coupling Reaction of Terminal Alkynes with Organic Halides Promoted by Tetrabutylammonium Fluoride or Hydroxide, *Syn. Lett.,* 2001, **5**, 649. (b) W. Li, S. Yu, J. Li and Y. Zhao. Nickel-Catalyzed Allylmethylation of Alkynes with Allylic Alcohols and AlMe3: Facile Access to Skipped Dienes and Trienes, *Angew. Chem. Int. Ed.,* 2020, **59**, 14404-14408. (c) Y. Zhang, B. Yu, B. Gao, T. Zhang and H. Huang. Triple-Bond Insertion Triggers Highly Regioselective 1,4-Aminomethylamination of 1,3-Enynes with Aminals Enabled by Pd-Catalyzed C–N Bond Activation, *Org. Lett.,* 2019, **21**, 535-539.

(6) J. Park, Y. Lee, J. Kim and S. H. Cho. Copper-Catalyzed Diastereoselective Addition of Diborylmethane to *N*-tert-Butanesulfinyl Aldimines: Synthesis of β-Aminoboronates, *Org. Lett.,* 2016, **18**, 1210-1213.

(7) H. Hu, X. Hu and Y. Liu, Copper-Catalyzed ortho-Functionalization of Quinoline *N*-Oxides with Vinyl Arenes, *Angew. Chem. Int. Ed.*, 2020, **59**, 18975-18979.

(8) K. L. Wilson, J. Murray, C. Jamieson and A. J. B. Watson. Cyrene as a Bio-Based Solvent for the Suzuki–Miyaura Cross-Coupling, *Synlett.*, 2018, **29**, 650-654.

(9) D. P. Ojha, K. Gadde and K. R. Prabhu. Generation of Hydrogen from Water: A Pd-Catalyzed Reduction of Water Using Diboron Reagent at Ambient Conditions. *Org. Lett.,* 2016, **18**, 5062-5065.

X-ray crystal structure of compound *E*-3b and 5m

The single crystal of ***E*-3b** was prepared by slow evaporation of its solution in methyl acetate/hexane. The structure of ***E*-3b** was established by X-ray analysis of its crystal (Figure S1). Thermal ellipsolds are set at 30% probability.

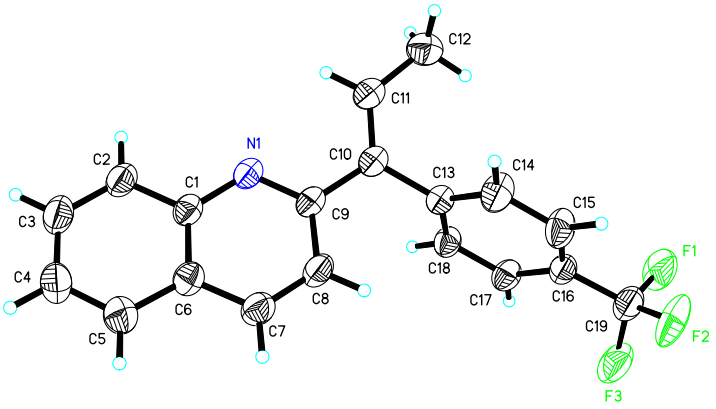


Figure S1. X-ray crystal structure of compound ***E*-3b**

Crystal data and structure refinement for mo_d8v21734_0m.

Identification code	mo_d8v21734_0m	
Empirical formula	C19 H14 F3 N	
Formula weight	313.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.9625(17) Å	α= 110.688(6)°.
	b = 10.485(2) Å	β= 108.613(6)°.
	c = 10.629(2) Å	γ = 90.576(6)°.
Volume	779.1(3) $Å^3$	
Z	2	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	324	
Crystal size	0.180 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.726 to 24.997°.	
Index ranges	-9<=h<=9, -12<=k<=12, -12<=l<=12	
Reflections collected	18061	
Independent reflections	2717 [R(int) = 0.0322]	
Completeness to theta = 25.242°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6918	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2717 / 42 / 237	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1143	
R indices (all data)	R1 = 0.0573, wR2 = 0.1251	
Extinction coefficient	0.13(2)	
Largest diff. peak and hole	0.141 and -0.174 $e.Å^{-3}$	

The single crystal of 5a was prepared by slow evaporation of its solution in dichloromethane/hexane. The structure of **5m** was established by X-ray analysis of its crystal (Figure S2). Thermal ellipsolds are set at 30% probability.

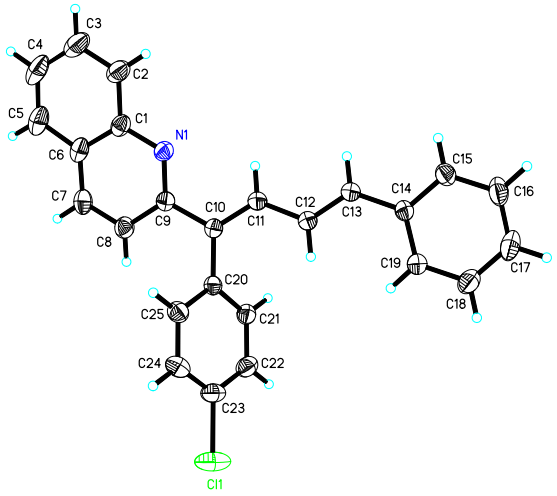
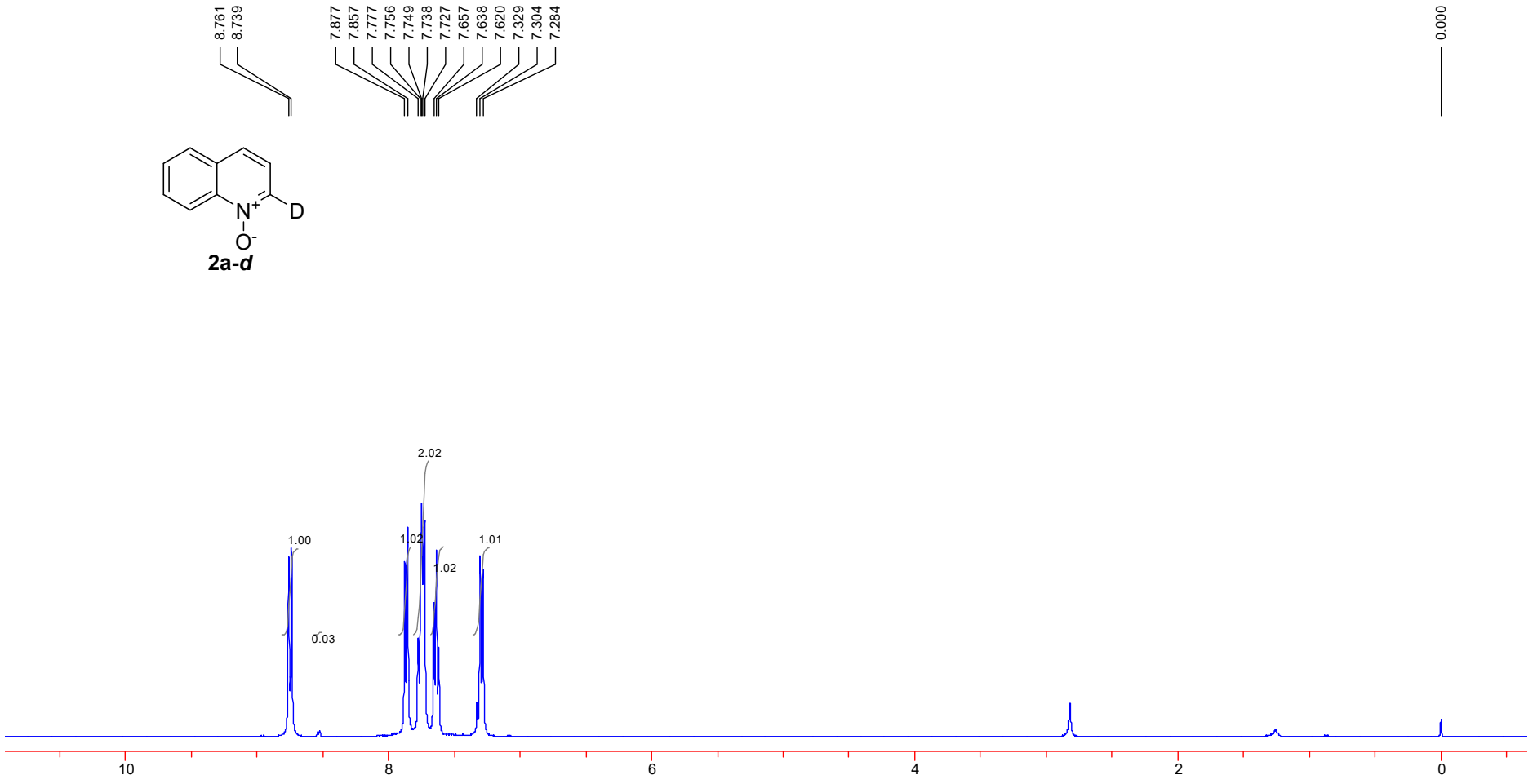


Figure S2. X-ray crystal structure of compound **5m**

Crystal data and structure refinement for mo_d8v21850_0m.		
Identification code	mo_d8v21850_0m	
Empirical formula	C25 H18 Cl N	
Formula weight	367.85	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.8258(2) Å	α= 89.6410(10)°.
	b = 9.6147(3) Å	β= 78.9490(10)°.
	c = 13.4508(4) Å	γ = 77.7140(10)°.
Volume	969.93(5) $Å^3$	
Z	2	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	0.205 mm^{-1}	
F(000)	384	
Crystal size	0.200 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.708 to 25.999°.	
Index ranges	-9<=h<=9, -11<=k<=11, -16<=l<=16	
Reflections collected	24173	
Independent reflections	3791 [R(int) = 0.0327]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6726	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3791 / 0 / 245
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0983
R indices (all data)	R1 = 0.0530, wR2 = 0.1065
Extinction coefficient	0.032(9)
Largest diff. peak and hole	0.243 and -0.300 e.$Å^{-3}$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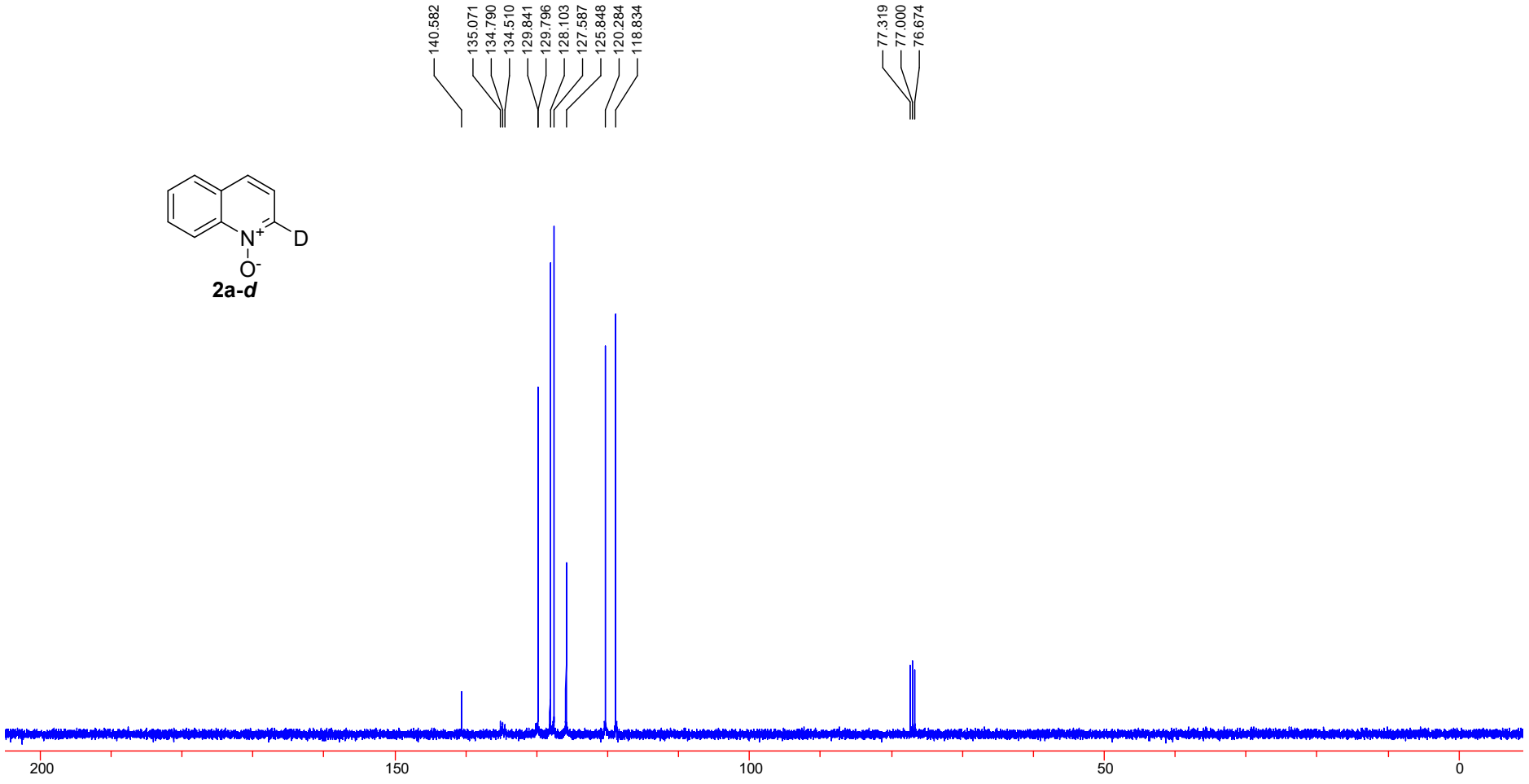
7.877
7.857
7.777
7.756
7.749
7.738
7.727
7.657
7.638
7.620
7.329
7.304
7.284
0.000
N+
O-
D
2a-d
2.02
1.00
1.02
1.02
1.01
0.03
10
8
6
4
2
0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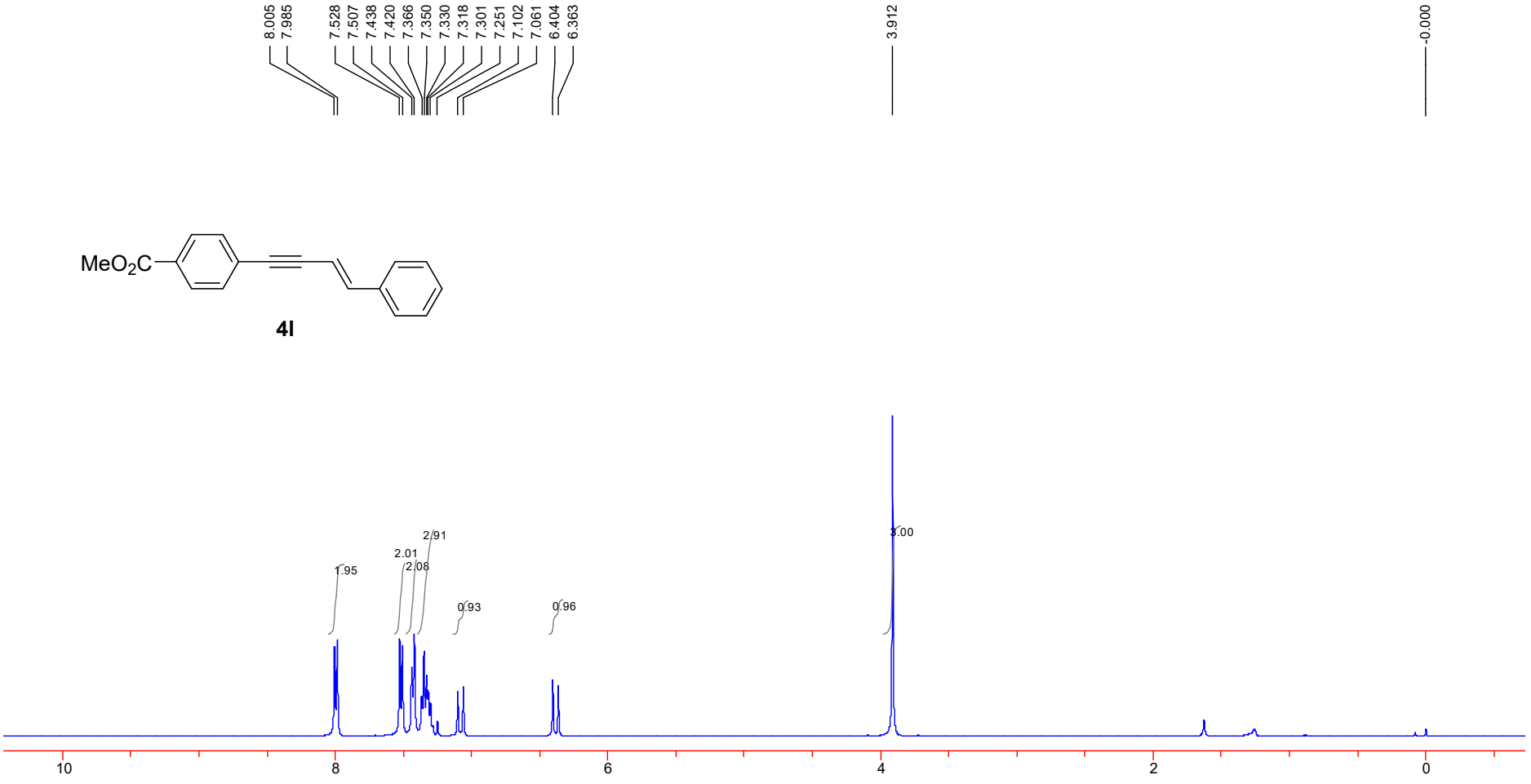
135.071
134.790
134.510
129.841
129.796
128.103
127.587
125.848
120.284
118.834
77.319
77.000
76.674
N+
O-
D
2a-d
200
150
100
50
0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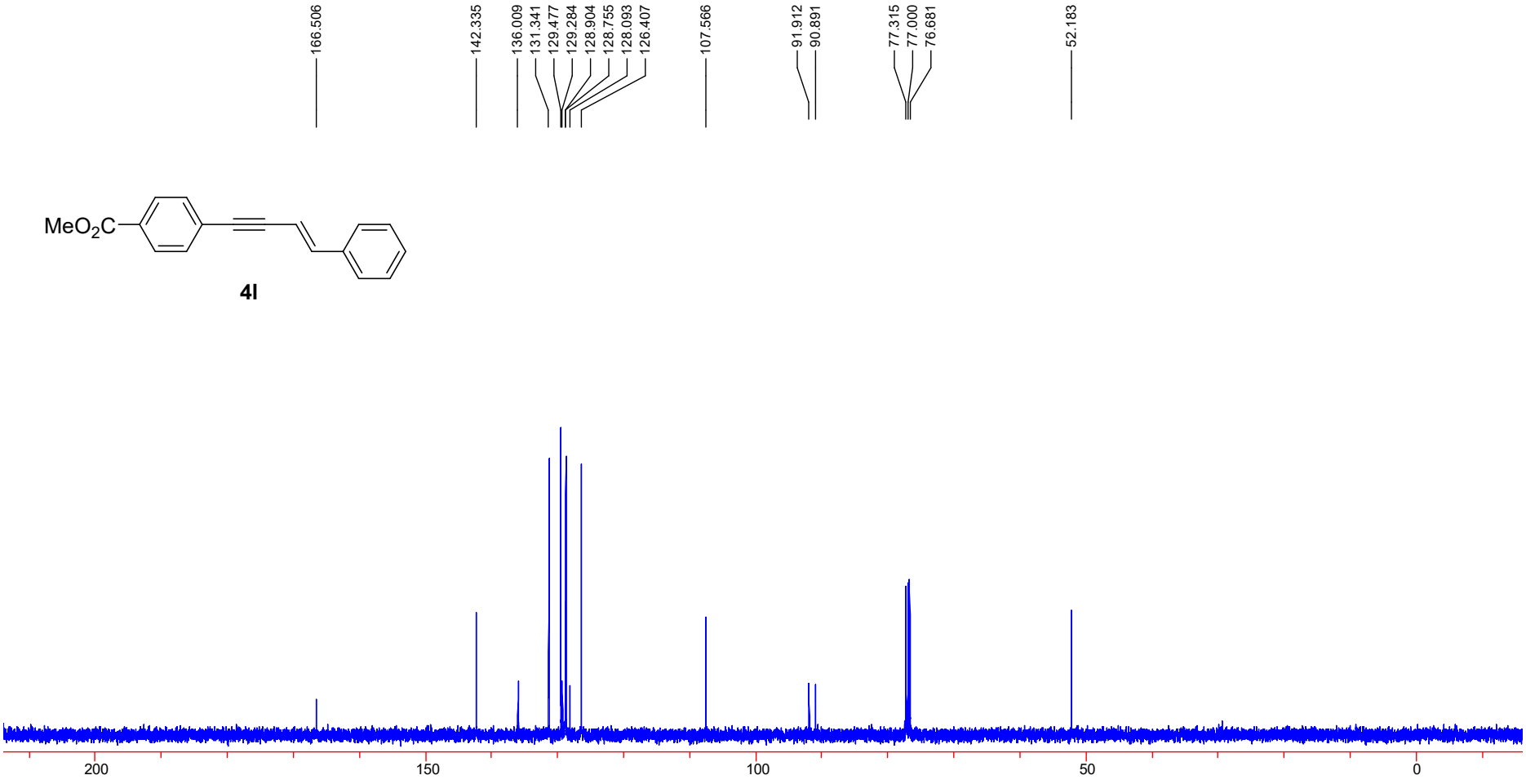
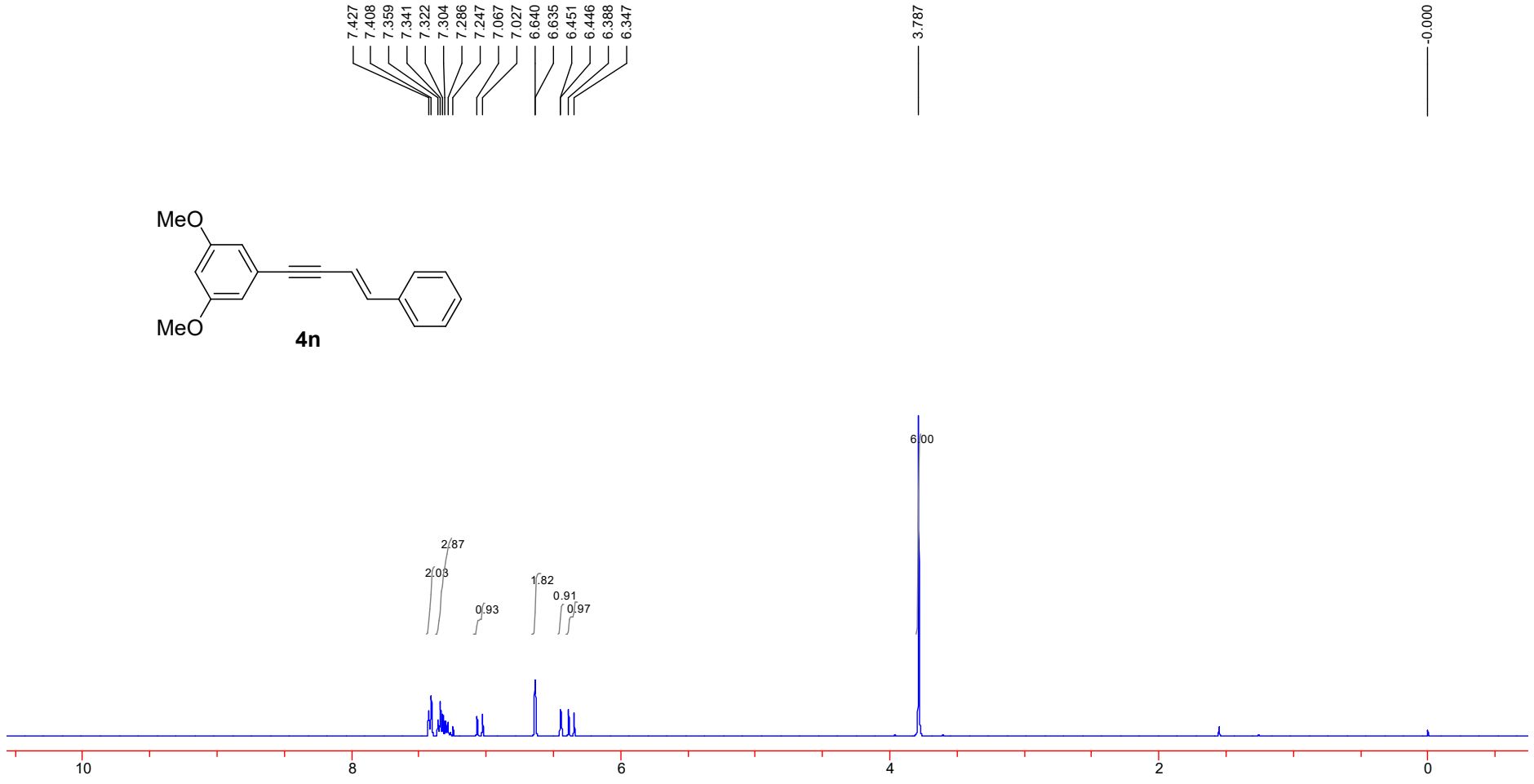
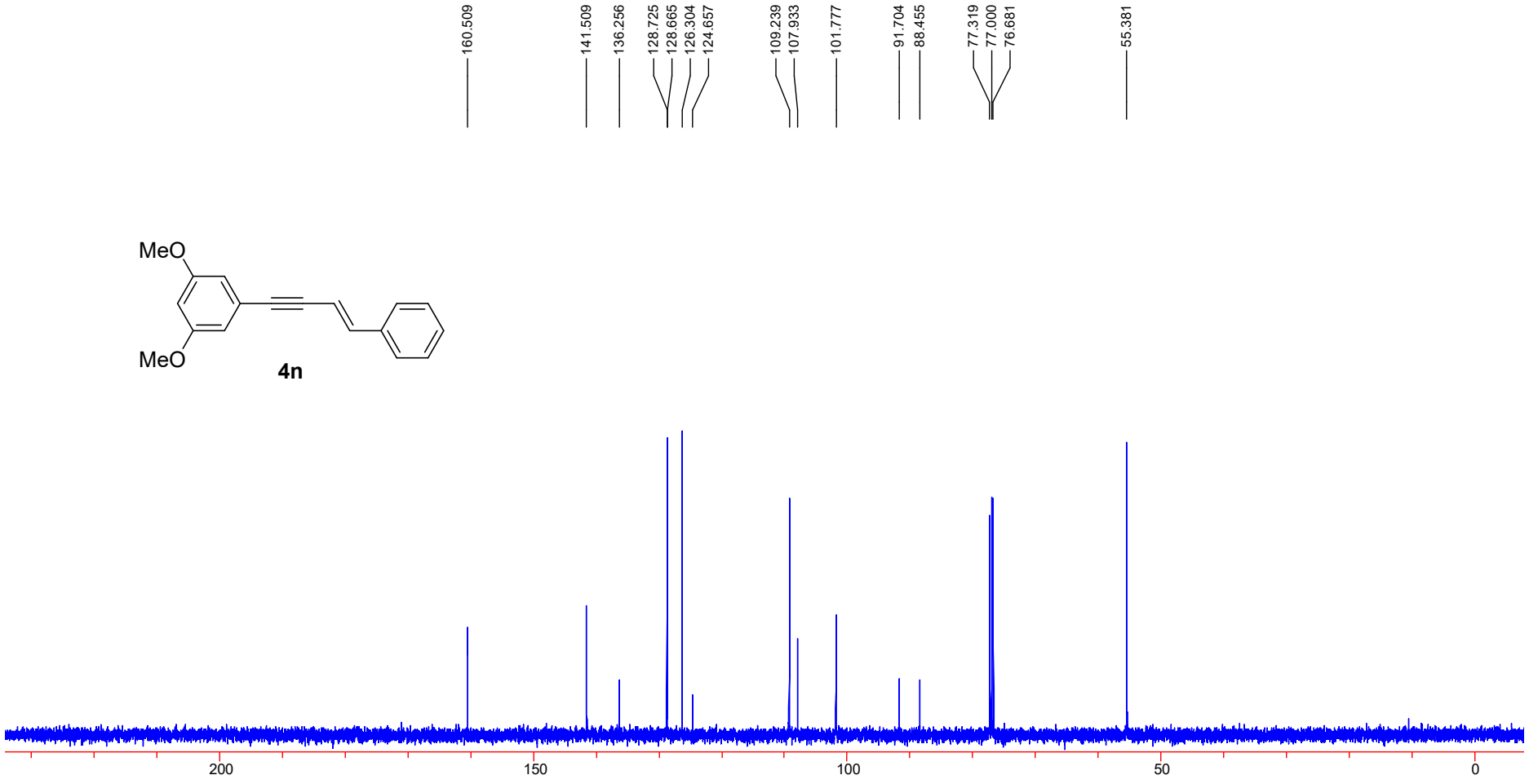
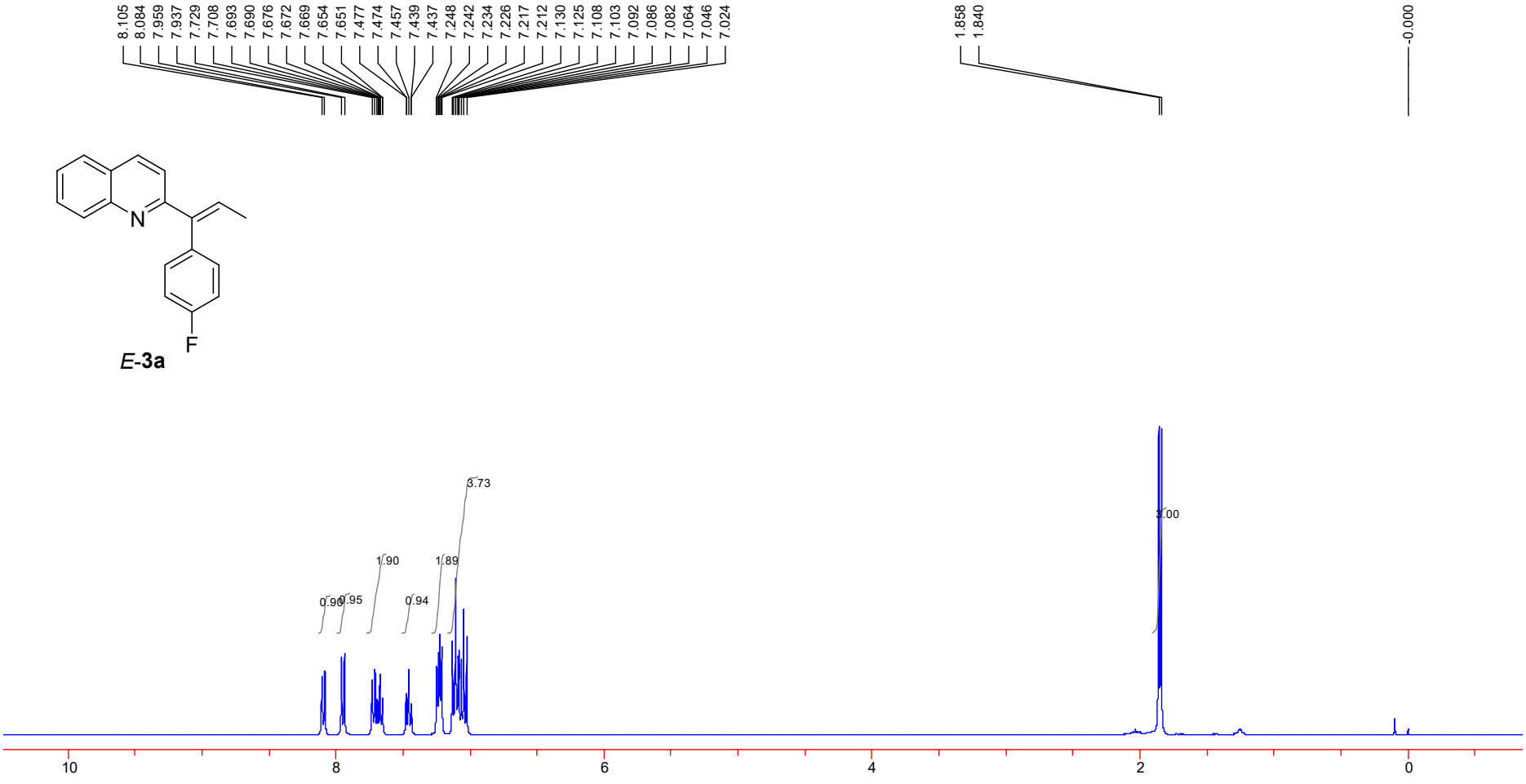
7.985
7.528
7.507
7.438
7.420
7.366
7.350
7.330
7.318
7.301
7.251
7.102
7.061
6.404
6.363
3.912
-0.000
MeO2C
4l
1.95
2.01
2.08
2.91
0.93
0.96
3.00
10
8
6
4
2
0


166.506
142.335
136.009
131.341
129.477
129.284
128.904
128.755
128.093
126.407
107.566
91.912
90.891
77.315
77.000
76.681
52.183
MeO2C
200
150
100
50
0

4l


7.427
7.408
7.359
7.341
7.322
7.304
7.286
7.247
7.067
7.027
6.640
6.635
6.451
6.446
6.388
6.347
3.787
-0.000
MeO
MeO
4n
6.00
2.87
2.03
1.82
0.91
0.93
0.97
10
8
6
4
2
0


160.509
141.509
136.256
128.725
128.665
126.304
124.657
109.239
107.933
101.777
91.704
88.455
77.319
77.000
76.681
55.381
MeO
MeO
4n
200
150
100
50
0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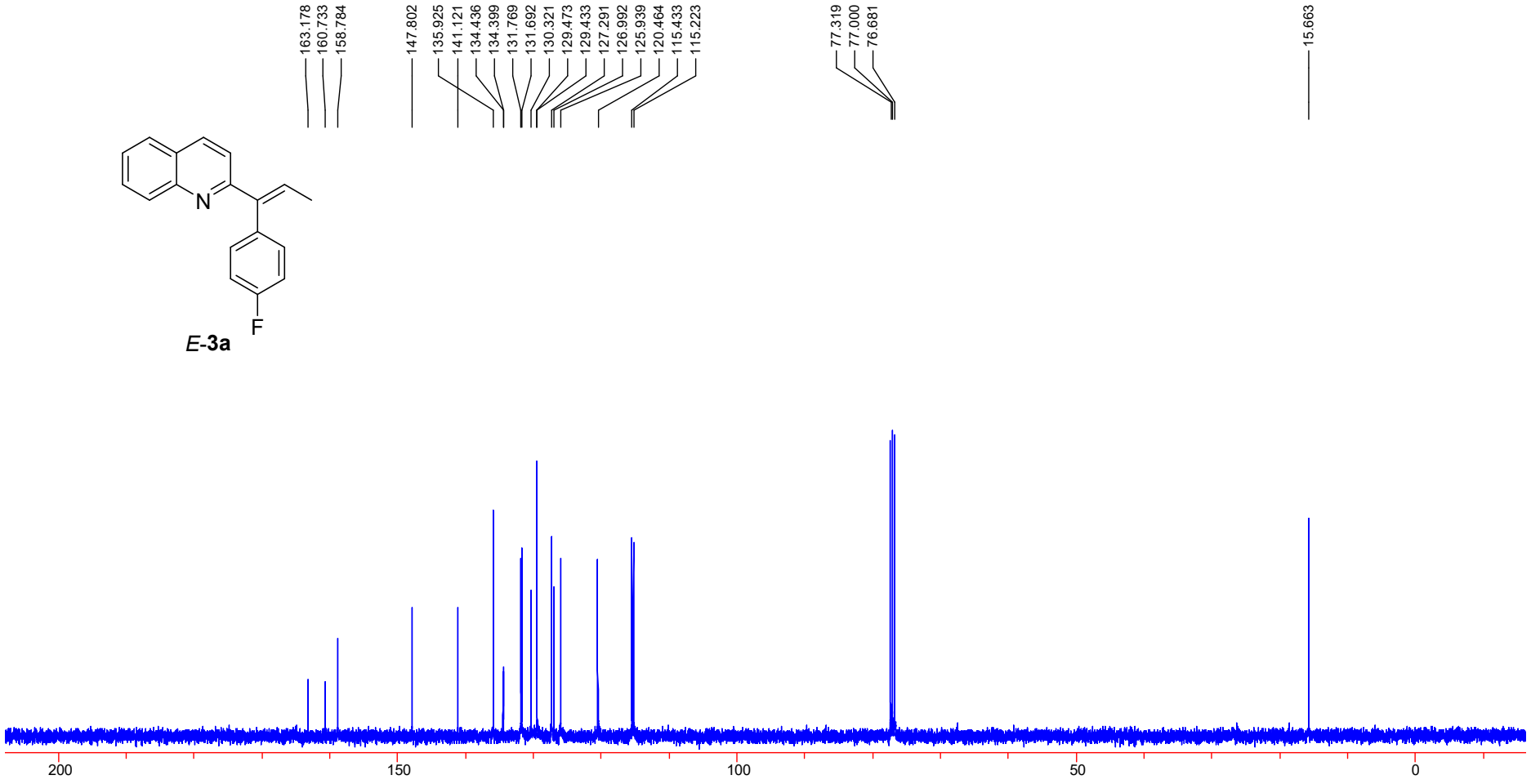
7.959
7.937
7.729
7.708
7.693
7.690
7.676
7.672
7.669
7.654
7.651
7.477
7.474
7.457
7.439
7.437
7.248
7.242
7.234
7.226
7.217
7.212
7.130
7.125
7.108
7.103
7.092
7.086
7.082
7.064
7.046
7.024
1.858
1.840
-0.000
N
F
E-3a
0.90
0.95
1.90
0.94
1.89
3.73
3.00
10
8
6
4
2
0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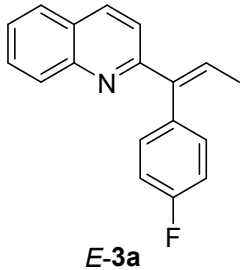
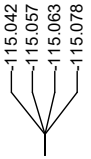
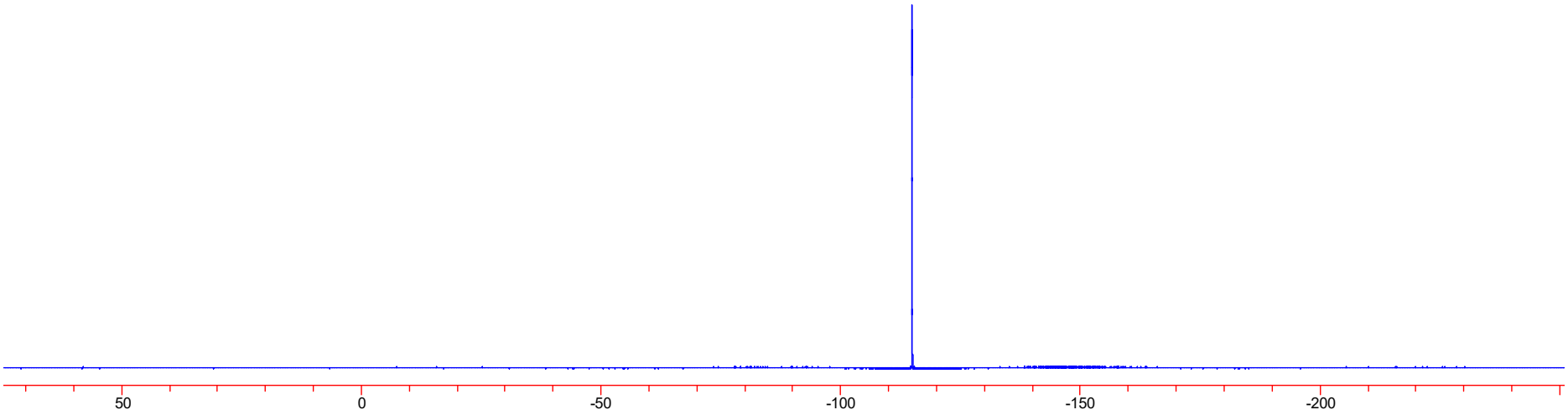
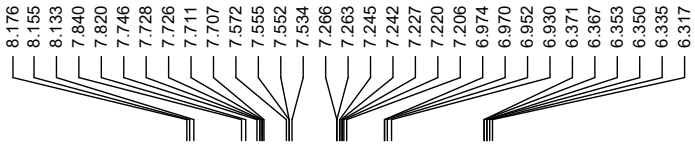
160.733
158.784
147.802
135.925
141.121
134.436
134.399
131.769
131.692
130.321
129.473
129.433
127.291
126.992
125.939
120.464
115.433
115.223
77.319
77.000
76.681
15.663
N
F
E-3a
200
150
100
50
0



E-**3a**



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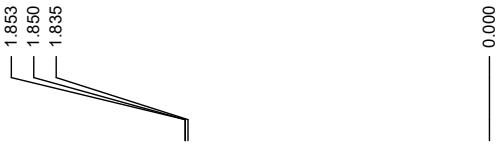
8.155
8.133
7.840
7.820
7.746
7.728
7.726
7.711
7.707
7.572
7.555
7.552
7.534
7.266
7.263
7.245
7.242
7.227
7.220
7.206
6.974
6.970
6.952
6.930
6.371
6.367
6.353
6.350
6.335
6.317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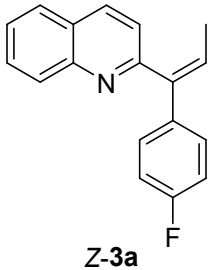
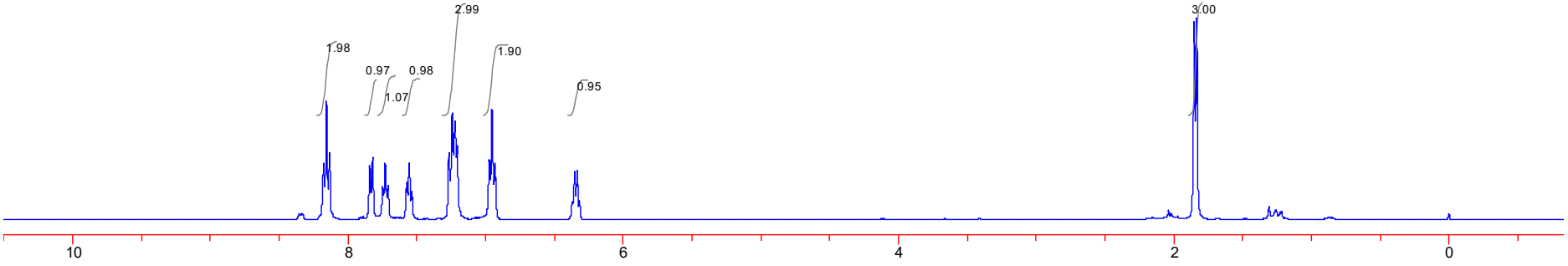
1.850
1.835
0.000


N
F

***Z*-3a**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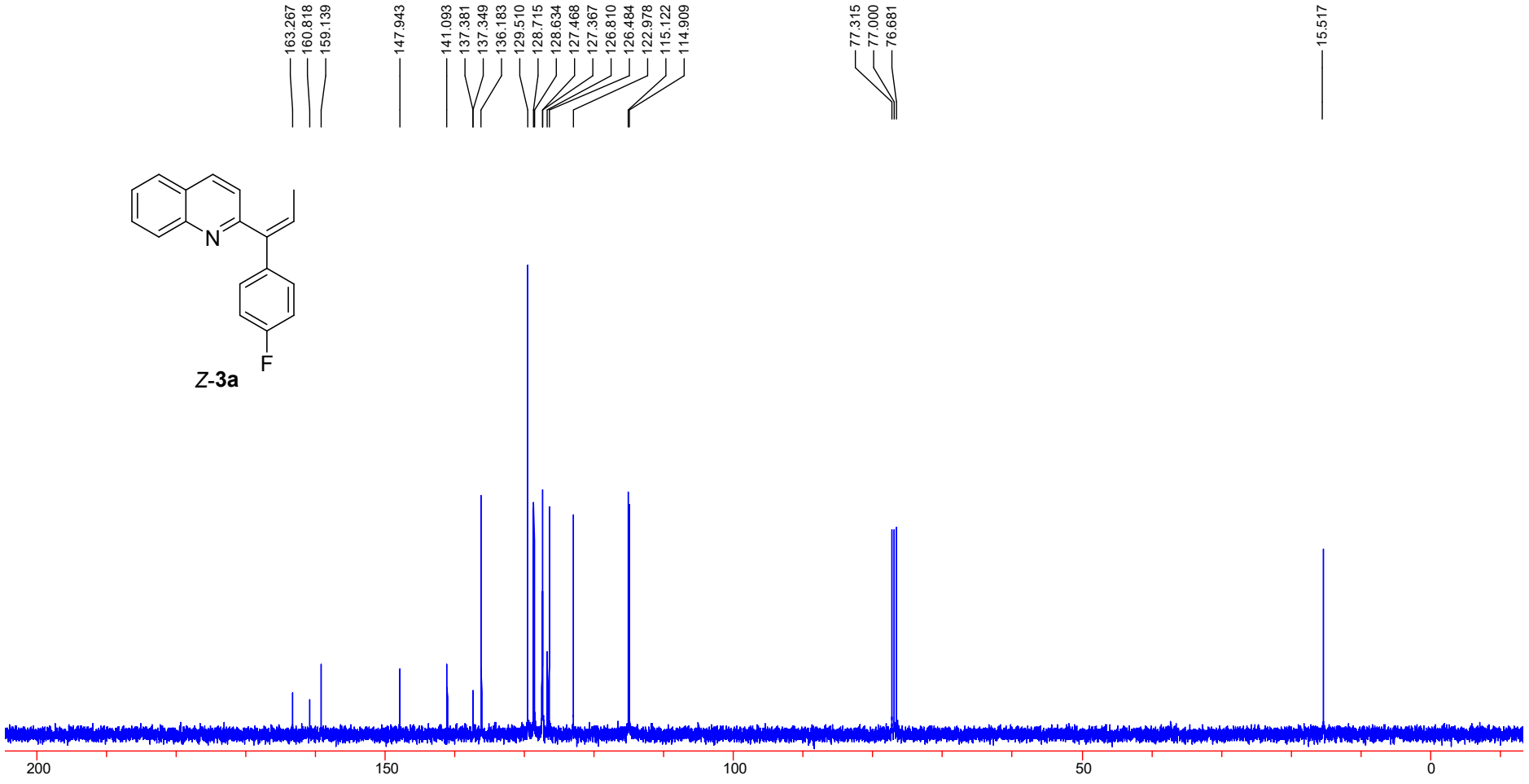
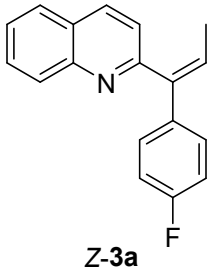
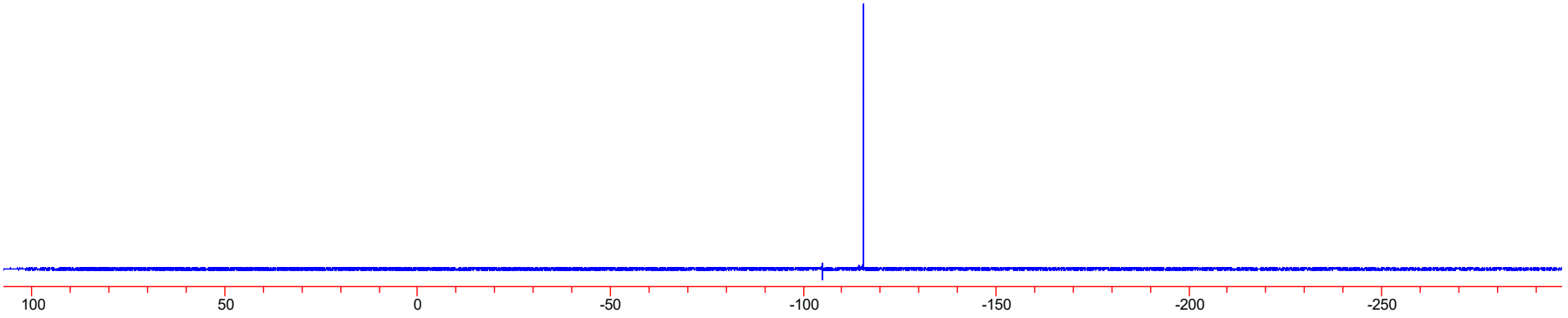
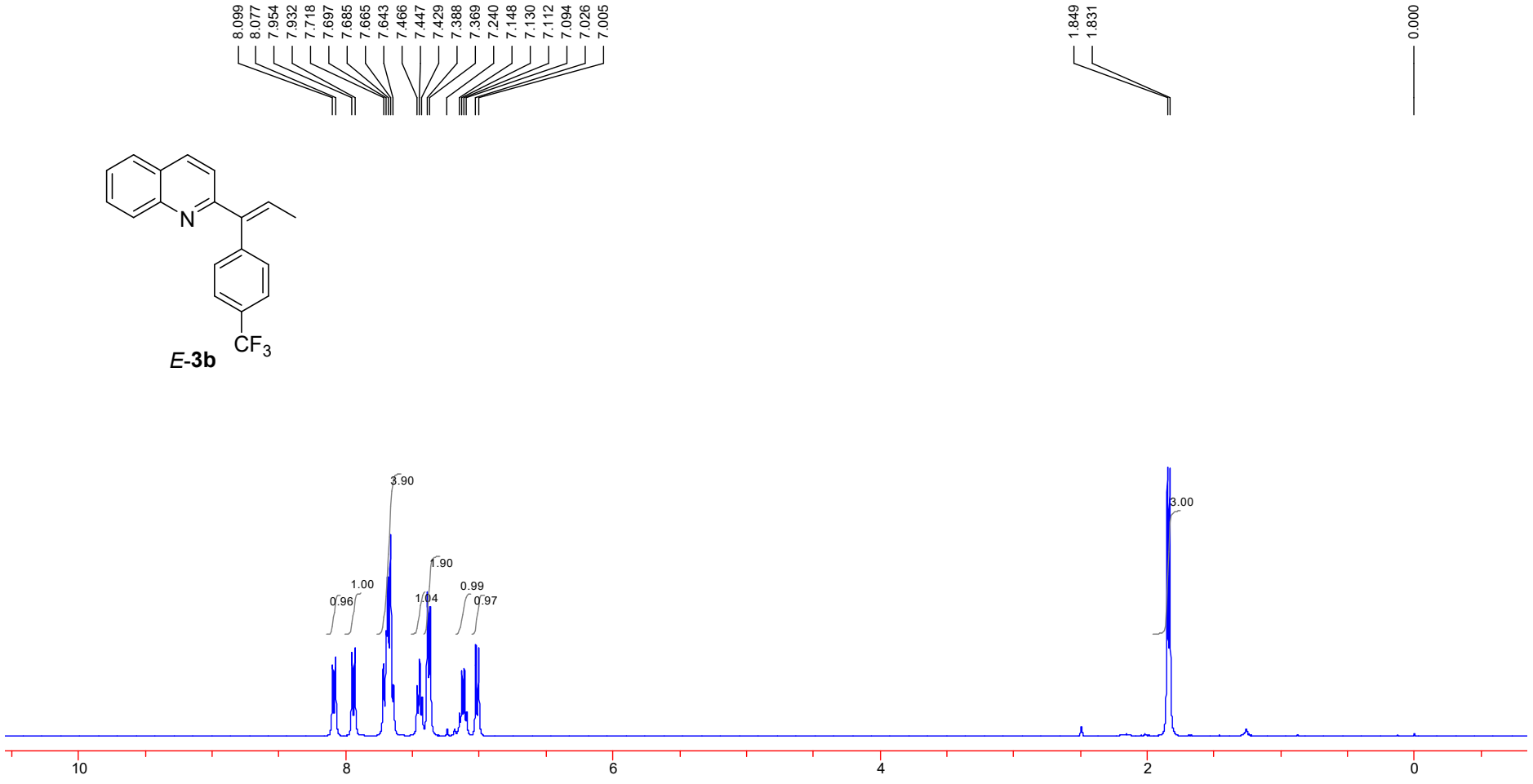
0.97
0.98
1.07
2.99
1.90
0.95
3.00
10
8
6
4
2
0


163.267
160.818
159.139
147.943
141.093
137.381
137.349
136.183
129.510
128.715
128.634
127.468
127.367
126.810
126.484
122.978
115.122
114.909
77.315
77.000
76.681
15.517
N
F
Z-3a
200
150
100
50
0



Z-**3a**

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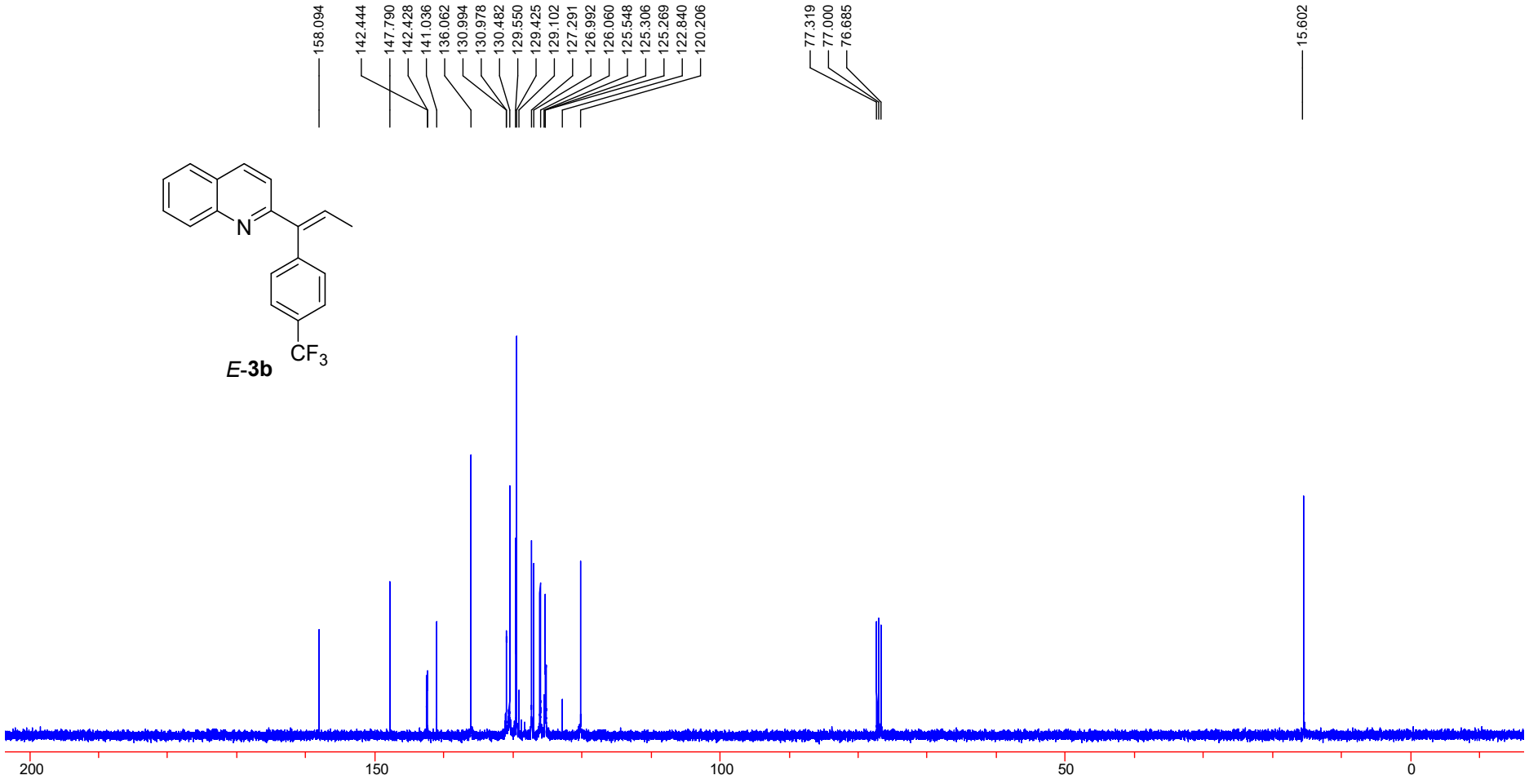
8.077
7.954
7.932
7.718
7.697
7.685
7.665
7.643
7.466
7.447
7.429
7.388
7.369
7.240
7.148
7.130
7.112
7.094
7.026
7.005
1.849
1.831
0.000
N
CF3
E-3b
3.90
1.00
0.96
1.90
1.04
0.99
0.97
3.00
10
8
6
4
2
0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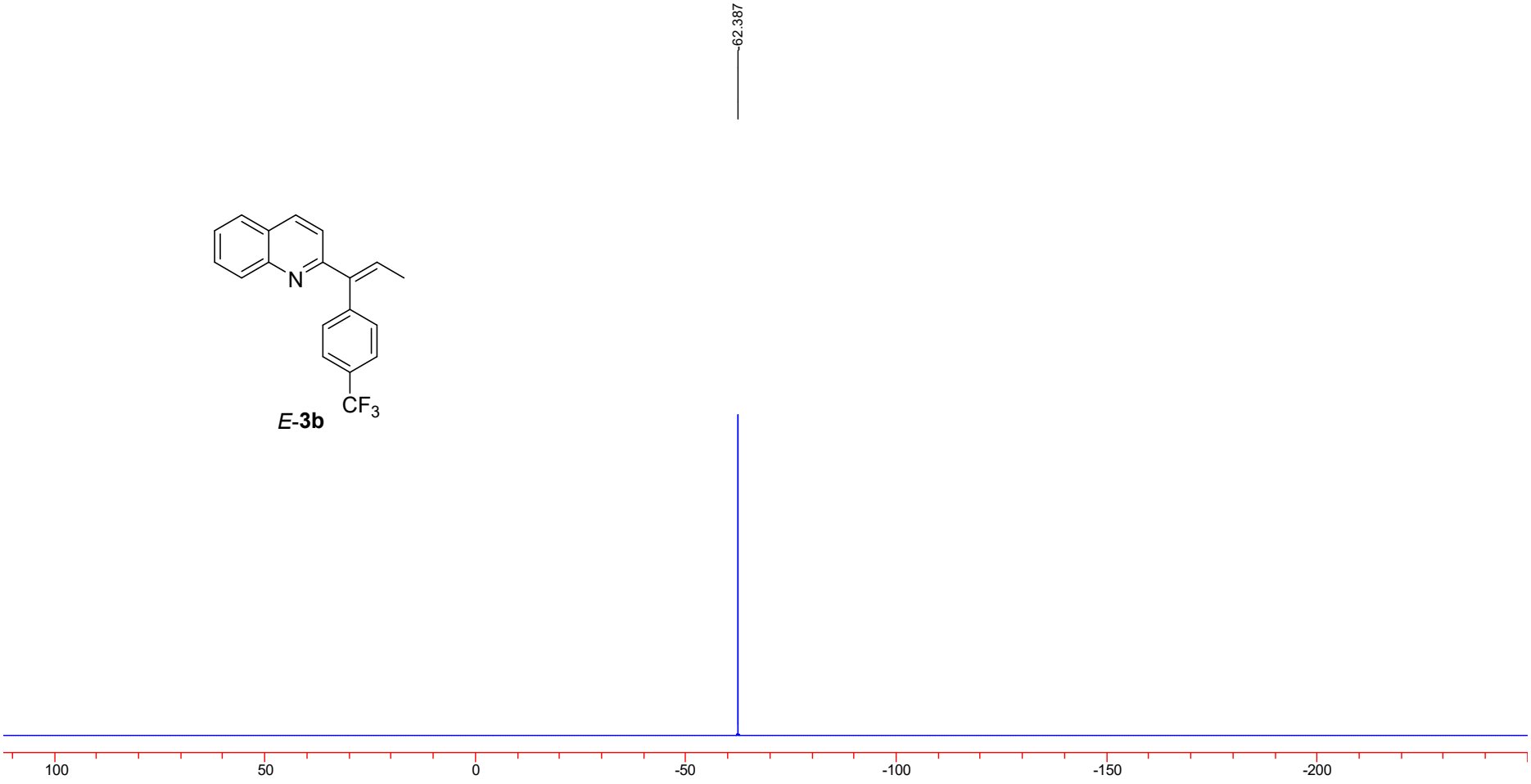
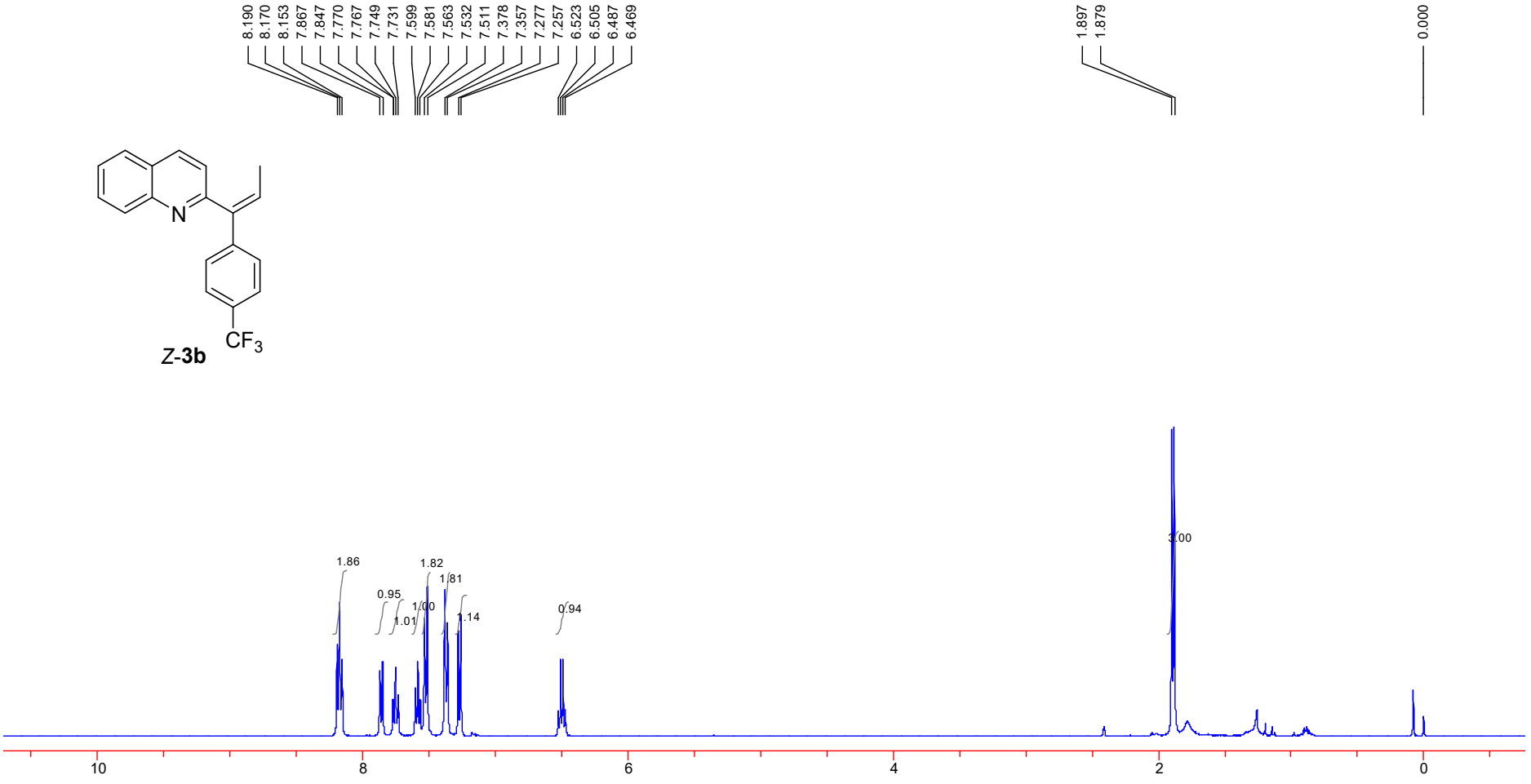
142.428
141.036
136.062
130.994
130.978
130.482
129.550
129.425
129.102
127.291
126.992
126.060
125.548
125.306
125.269
122.840
120.206
77.319
77.000
76.685
15.602
N
CF3
E-3b
200
150
100
50
0



E-**3b**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8.170
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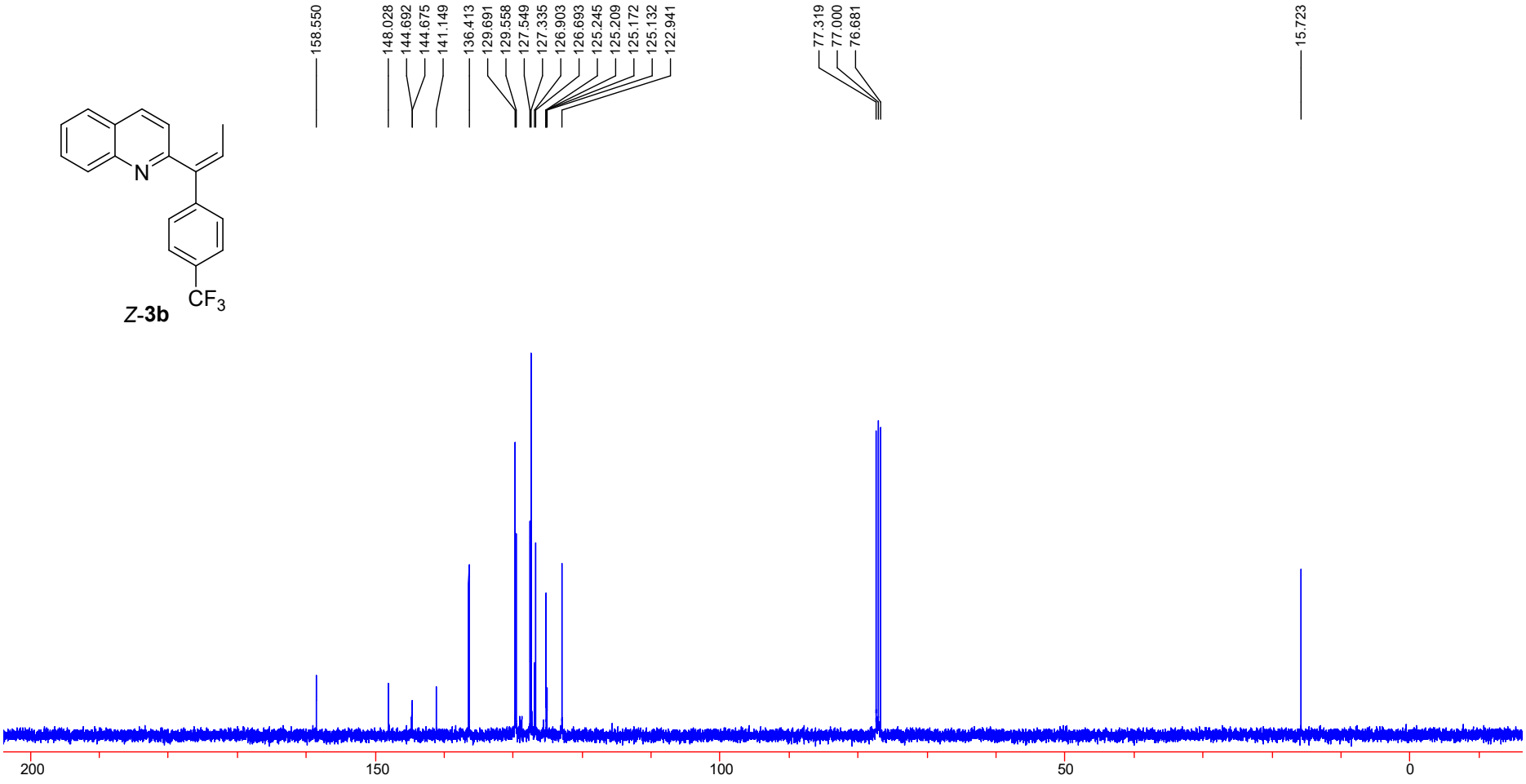
7.847
7.770
7.767
7.749
7.731
7.599
7.581
7.563
7.532
7.511
7.378
7.357
7.277
7.257
6.523
6.505
6.487
6.469
1.897
1.879
0.000
N
CF3
Z-3b
1.86
0.95
1.01
1.00
1.82
1.81
1.14
0.94
3.00
10
8
6
4
2
0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127.335
126.903
126.693
125.245
125.209
125.172
125.132
122.941
77.319
77.000
76.681
15.723
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CF3
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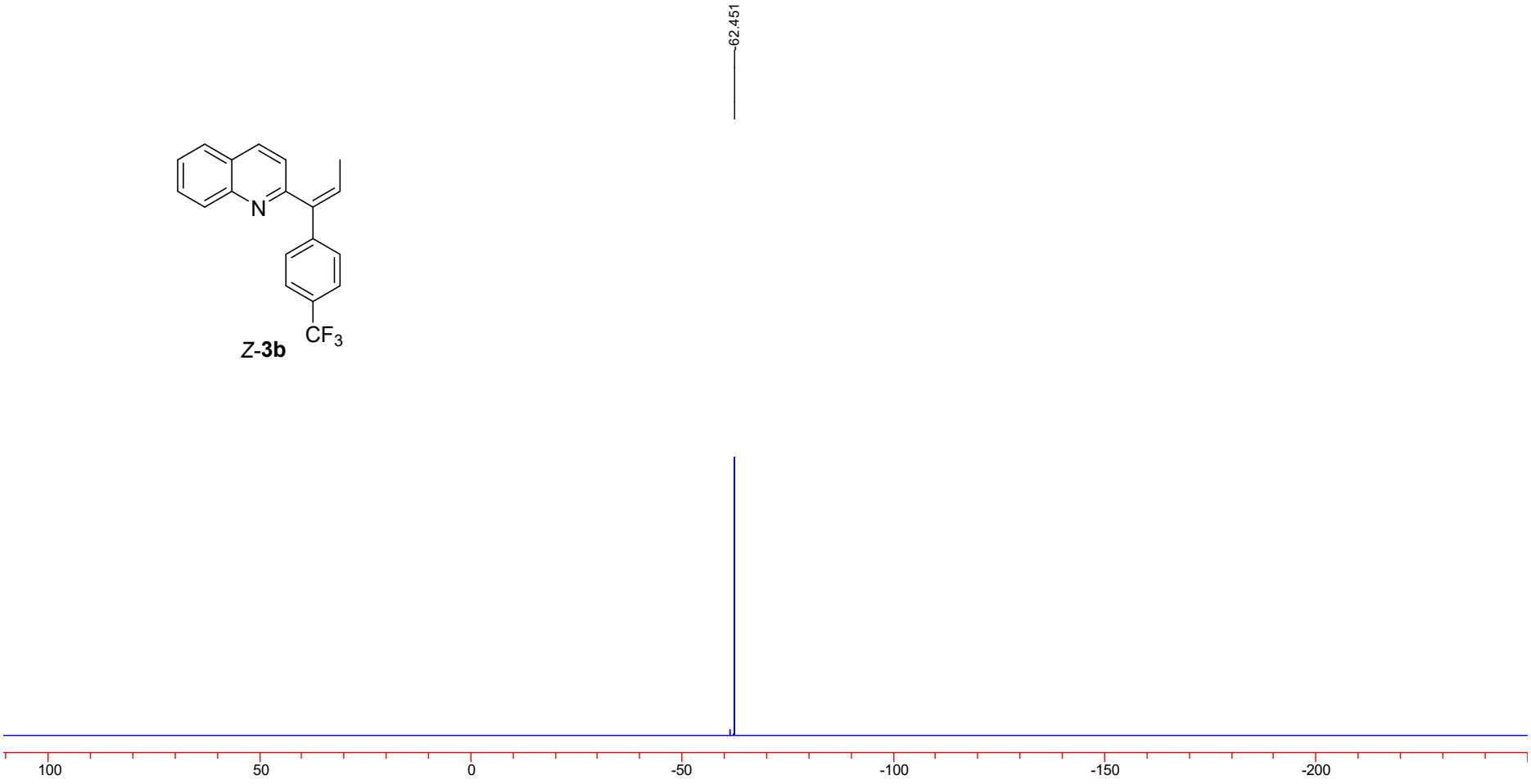
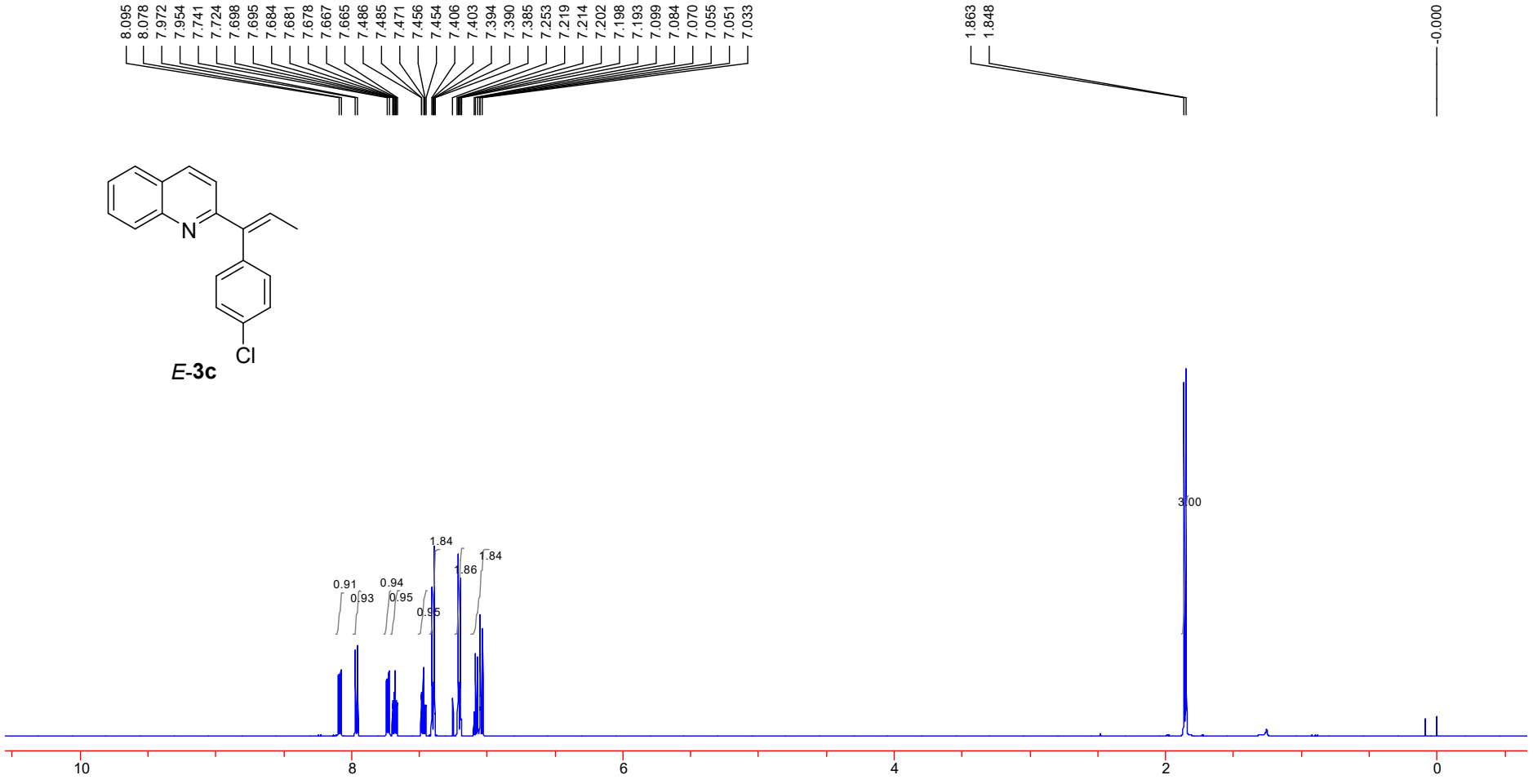
150
100
50
0



Z-**3b**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7.724
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7.695
7.684
7.681
7.678
7.667
7.665
7.486
7.485
7.471
7.456
7.454
7.406
7.403
7.394
7.390
7.385
7.253
7.219
7.214
7.202
7.198
7.193
7.099
7.084
7.070
7.055
7.051
7.033
1.863
1.848
-0.000
N
Cl
E-3c
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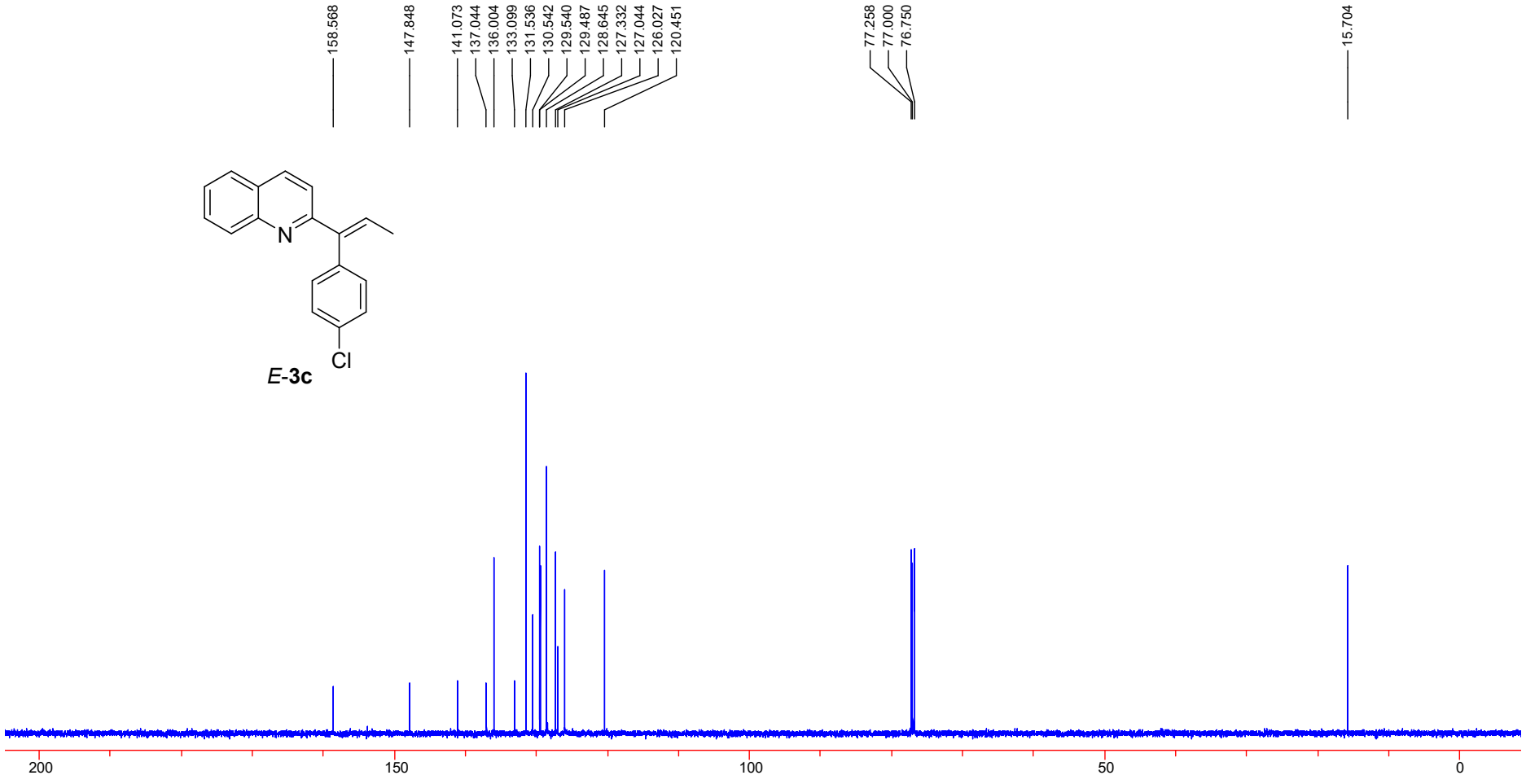
0.93
0.94
0.95
0.96
1.84
1.86
1.84
3.00
10
8
6
4
2
0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130.542
129.540
129.487
128.645
127.332
127.044
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77.258
77.000
76.750
15.704
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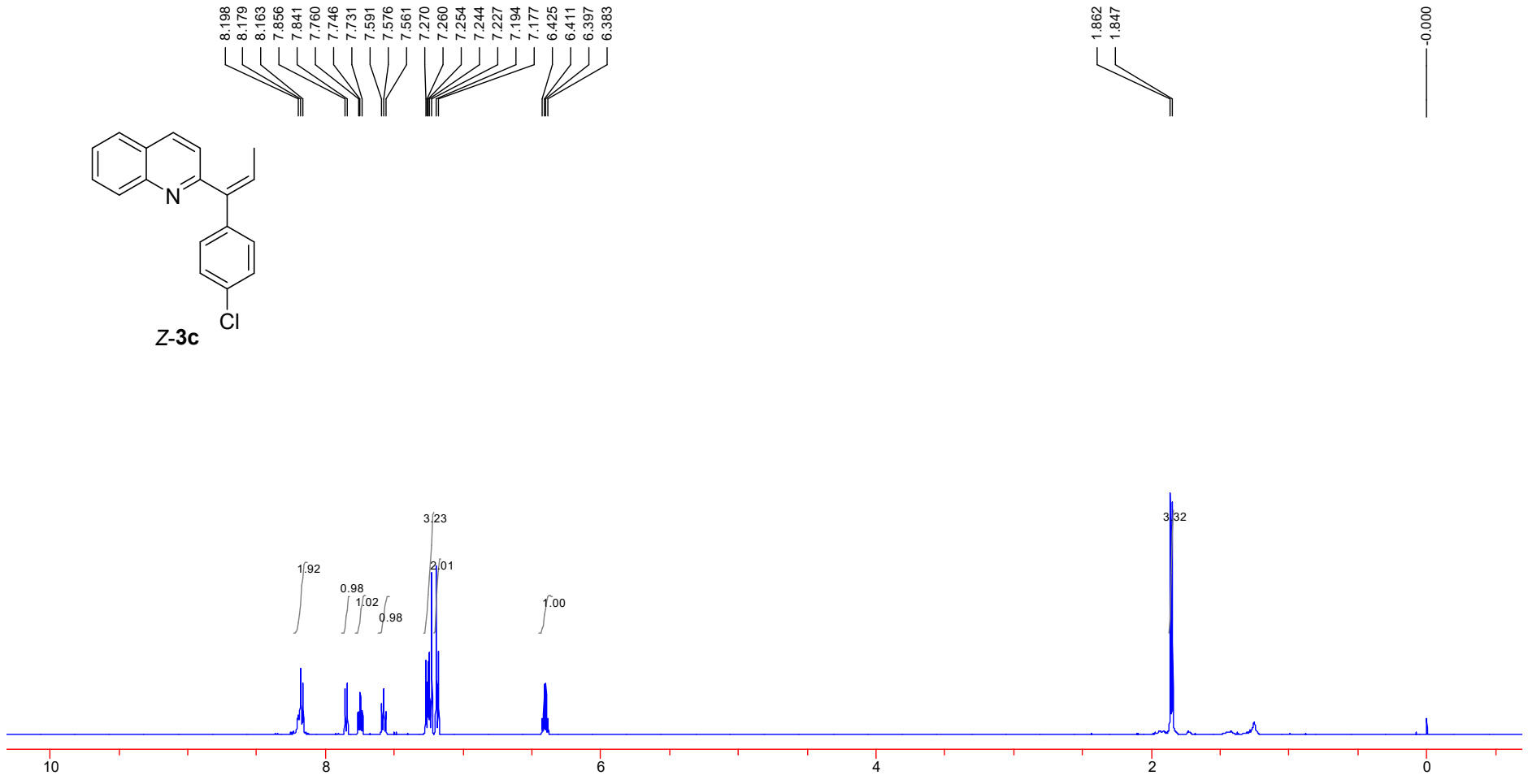
Cl
E-3c
200
150
100
50
0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7.731
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7.576
7.561
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7.227
7.194
7.177
6.425
6.411
6.397
6.383
1.862
1.847
-0.000
N
Cl
Z-3c
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1.02
0.98
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3.32
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6
4
2
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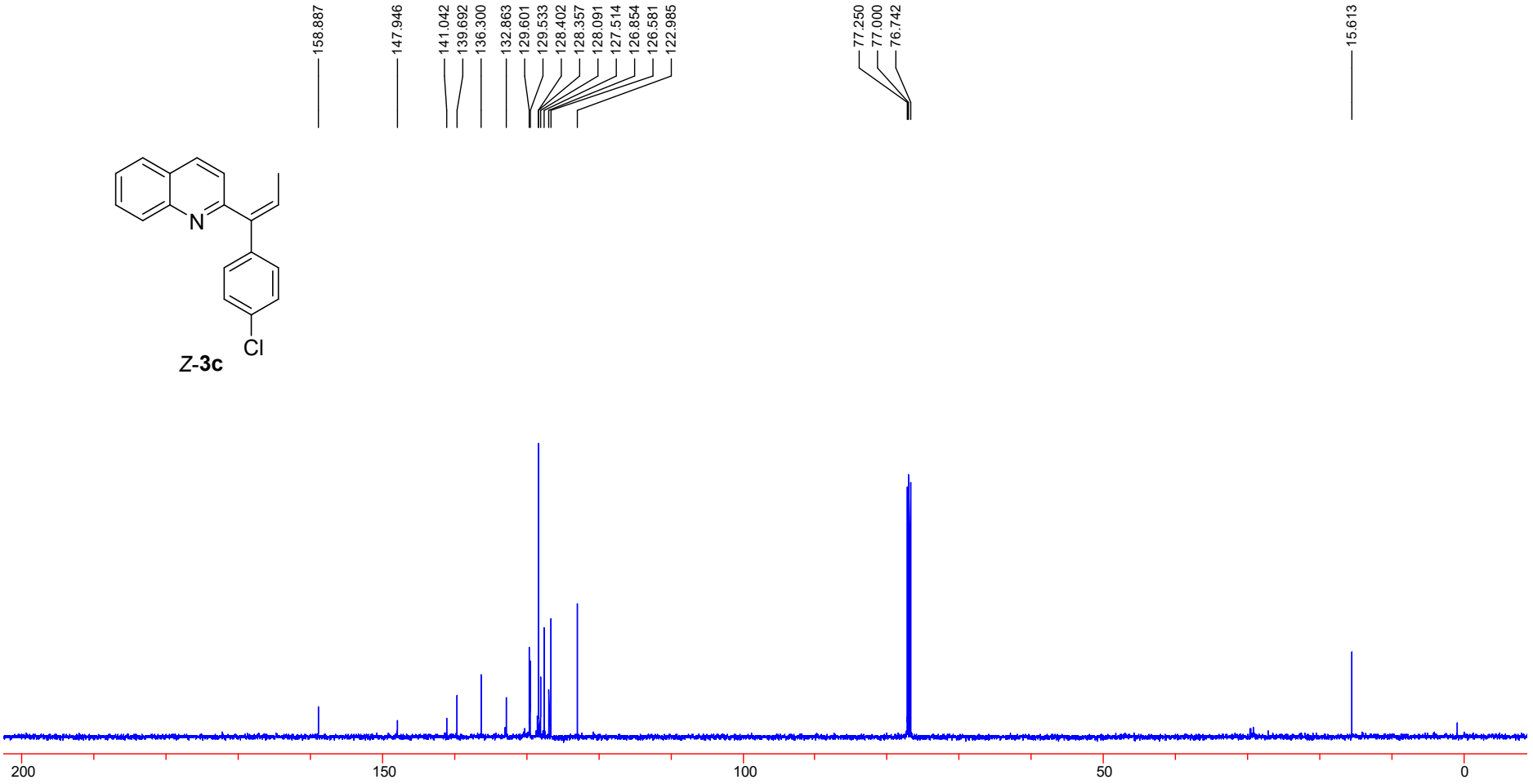
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129.533
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128.357
128.091
127.514
126.854
126.581
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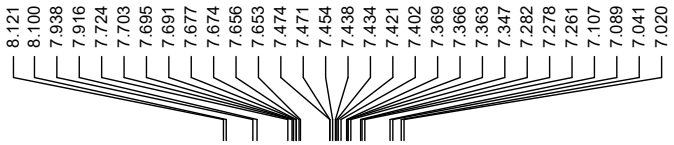
77.250
77.000
76.742
15.613
N
Cl
Z-3c
200
150
100
50
0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7.916
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7.695
7.691
7.677
7.674
7.656
7.653
7.474
7.471
7.454
7.438
7.434
7.421
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7.261
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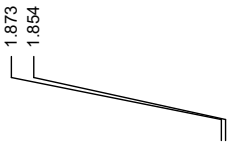
7.041
7.020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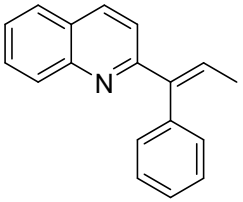
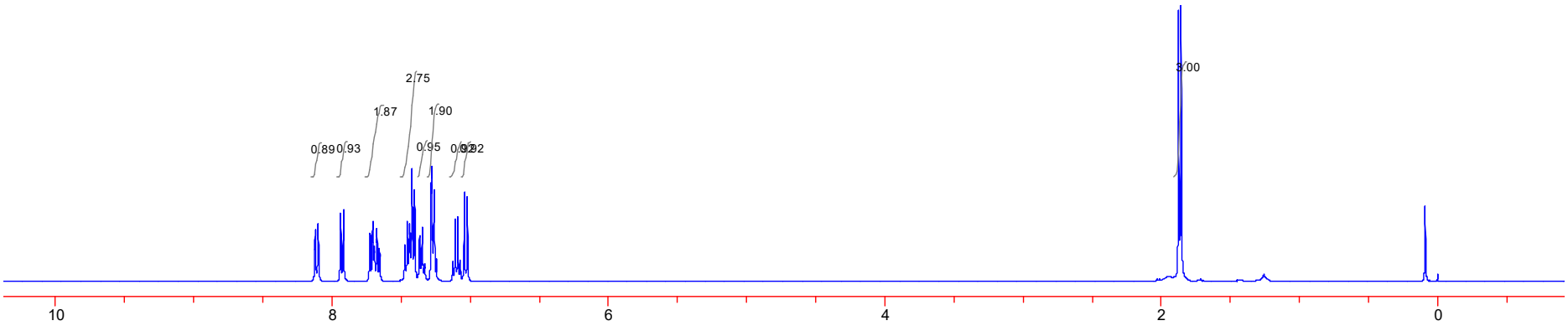
1.854

0.000


N

3d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3.00
10
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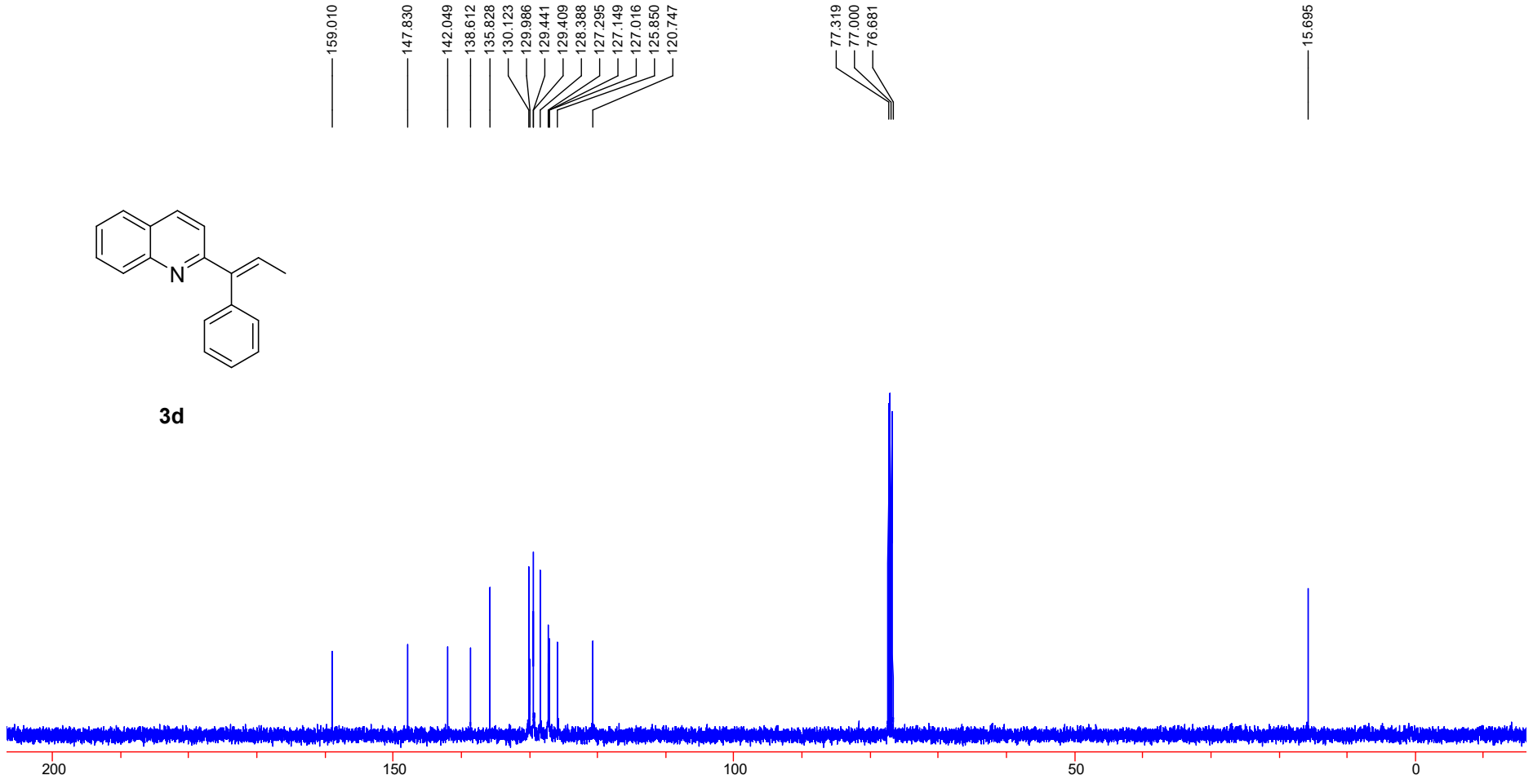
6
4
2
0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127.295
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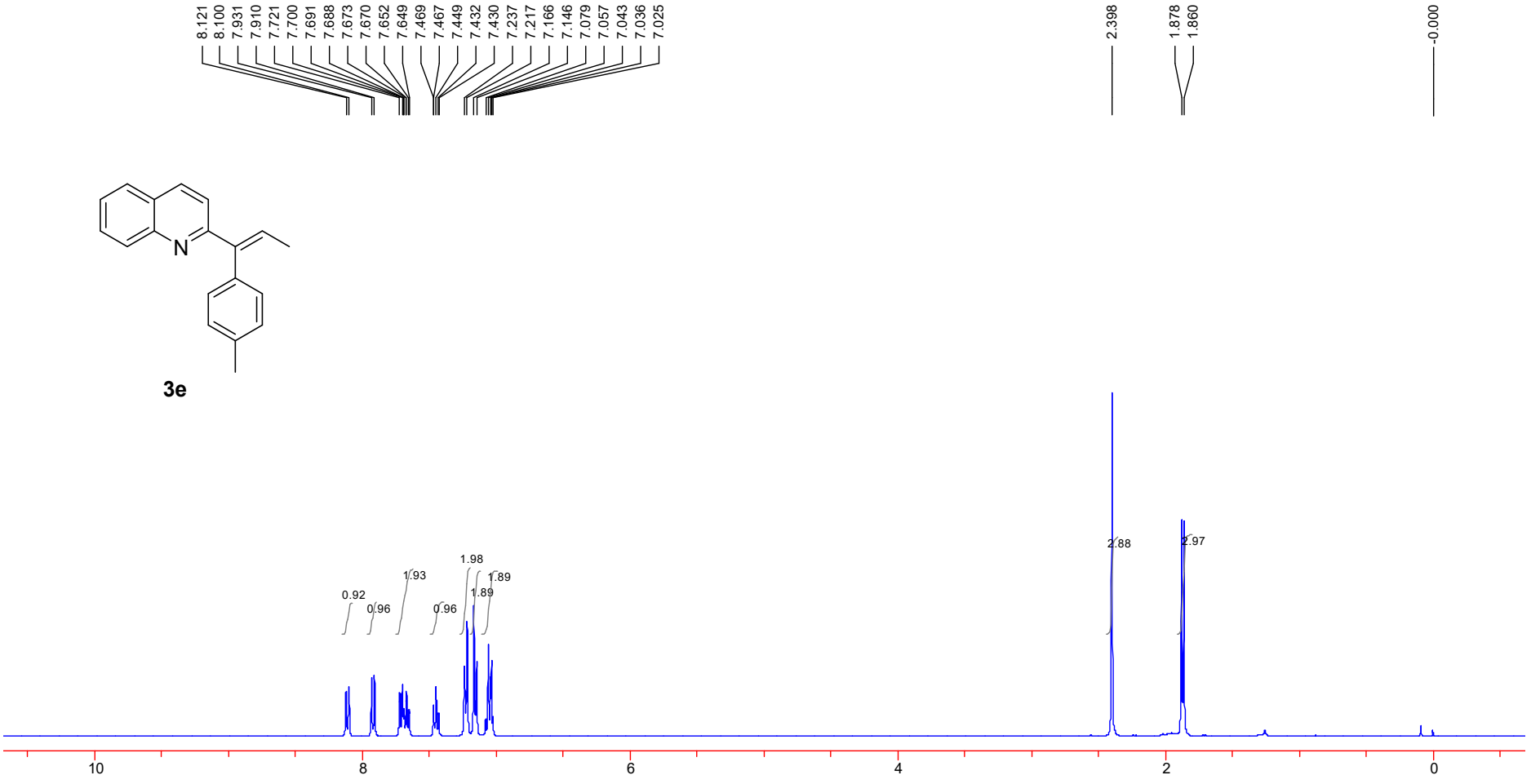
127.016
125.850
120.747
77.319
77.000
76.681
15.695
N
3d
200
150
100
50
0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7.700
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7.688
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7.670
7.652
7.649
7.469
7.467
7.449
7.432
7.430
7.237
7.217
7.166
7.146
7.079
7.057
7.043
7.036
7.025
2.398
1.878
1.860
-0.000
N
3e
0.92
0.96
1.93
0.96
1.98
1.89
1.89
2.88
2.97
10
8
6
4
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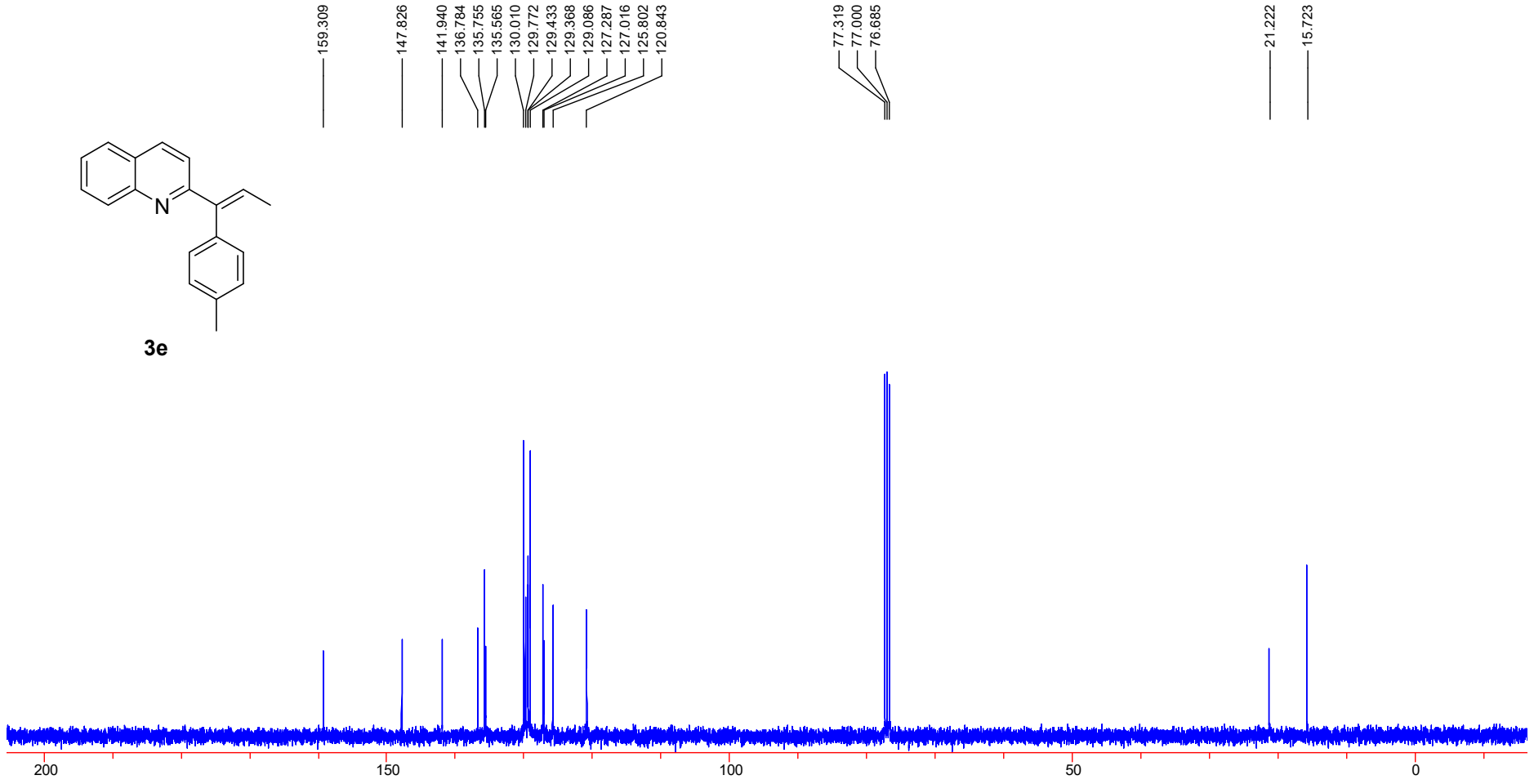
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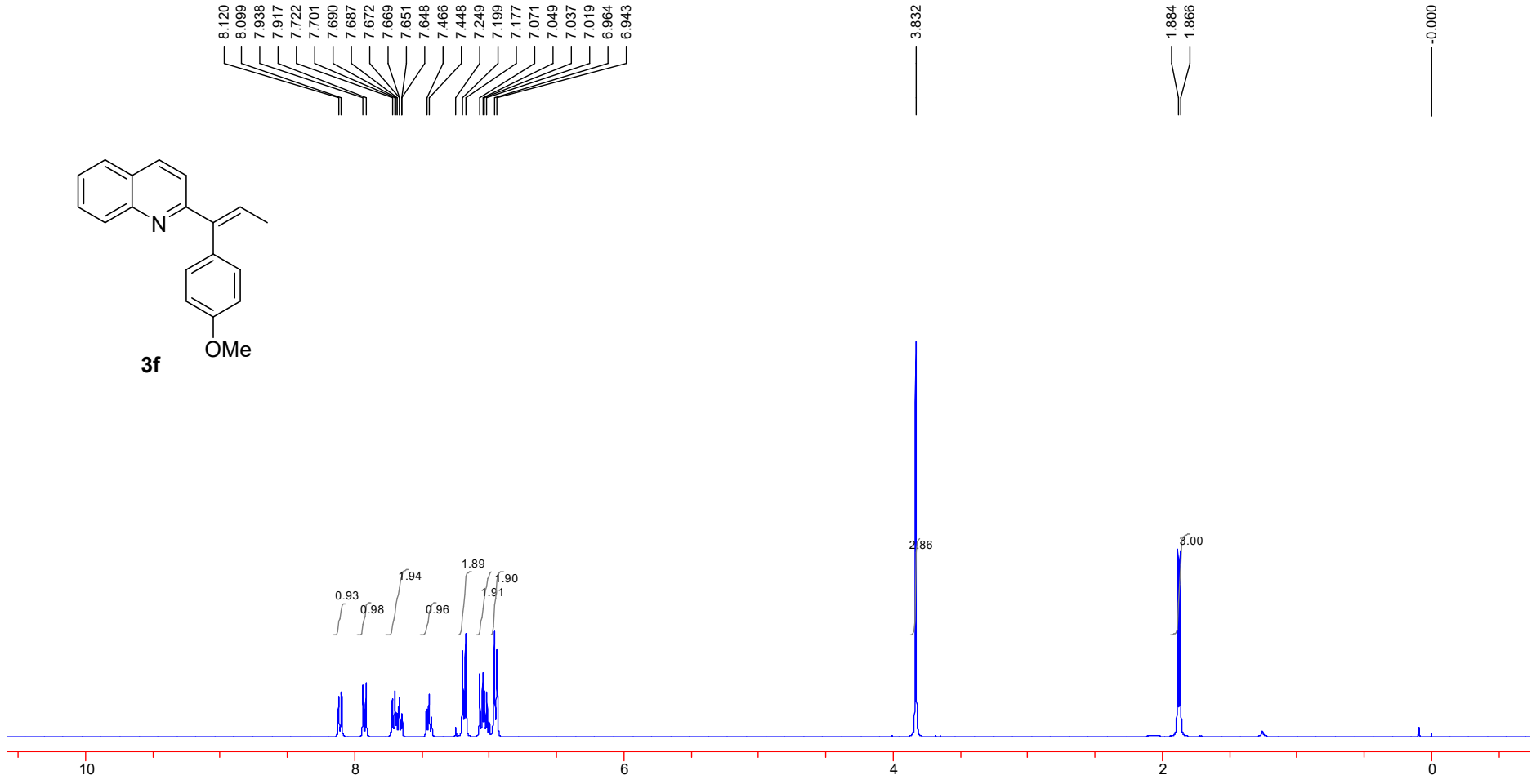
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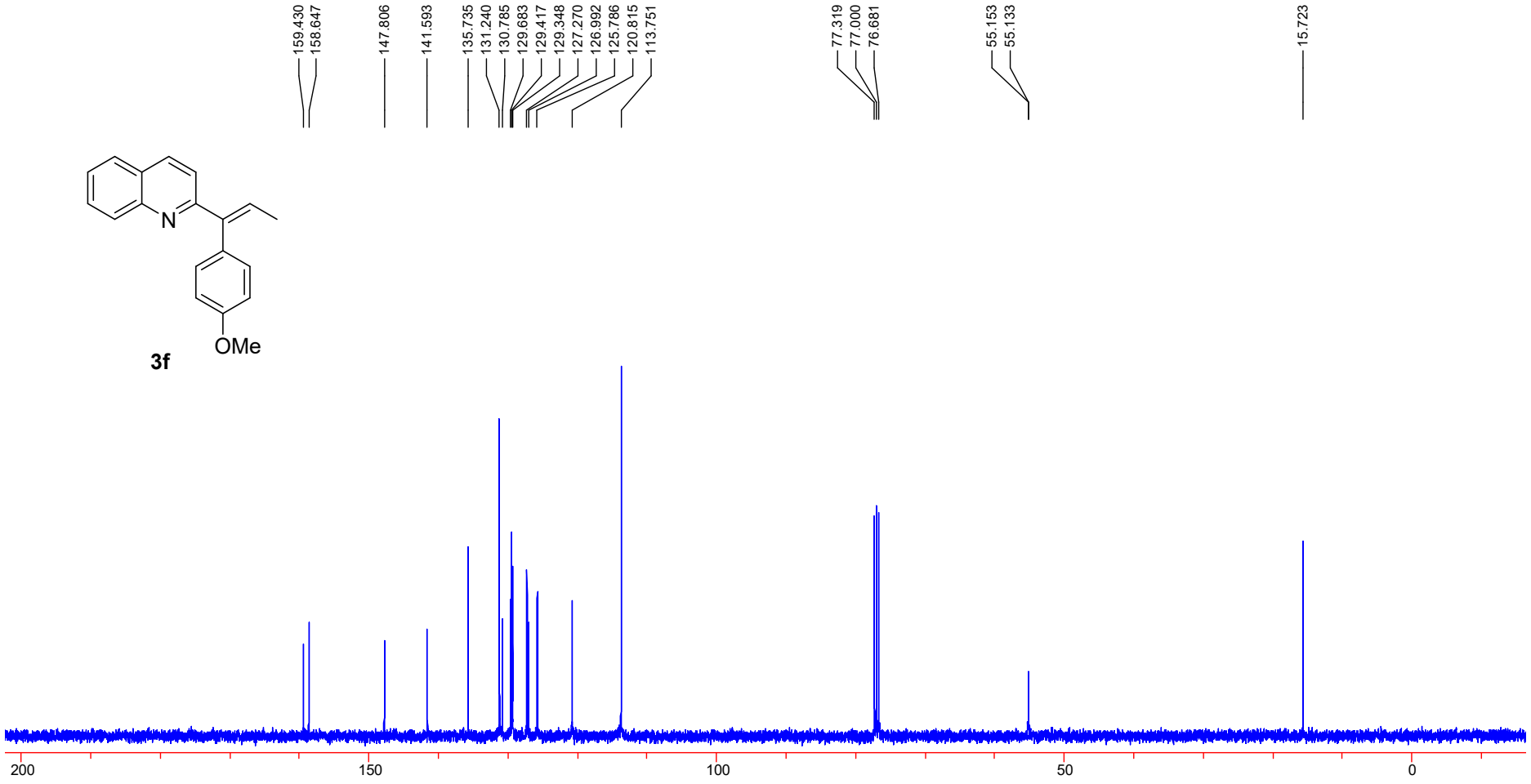
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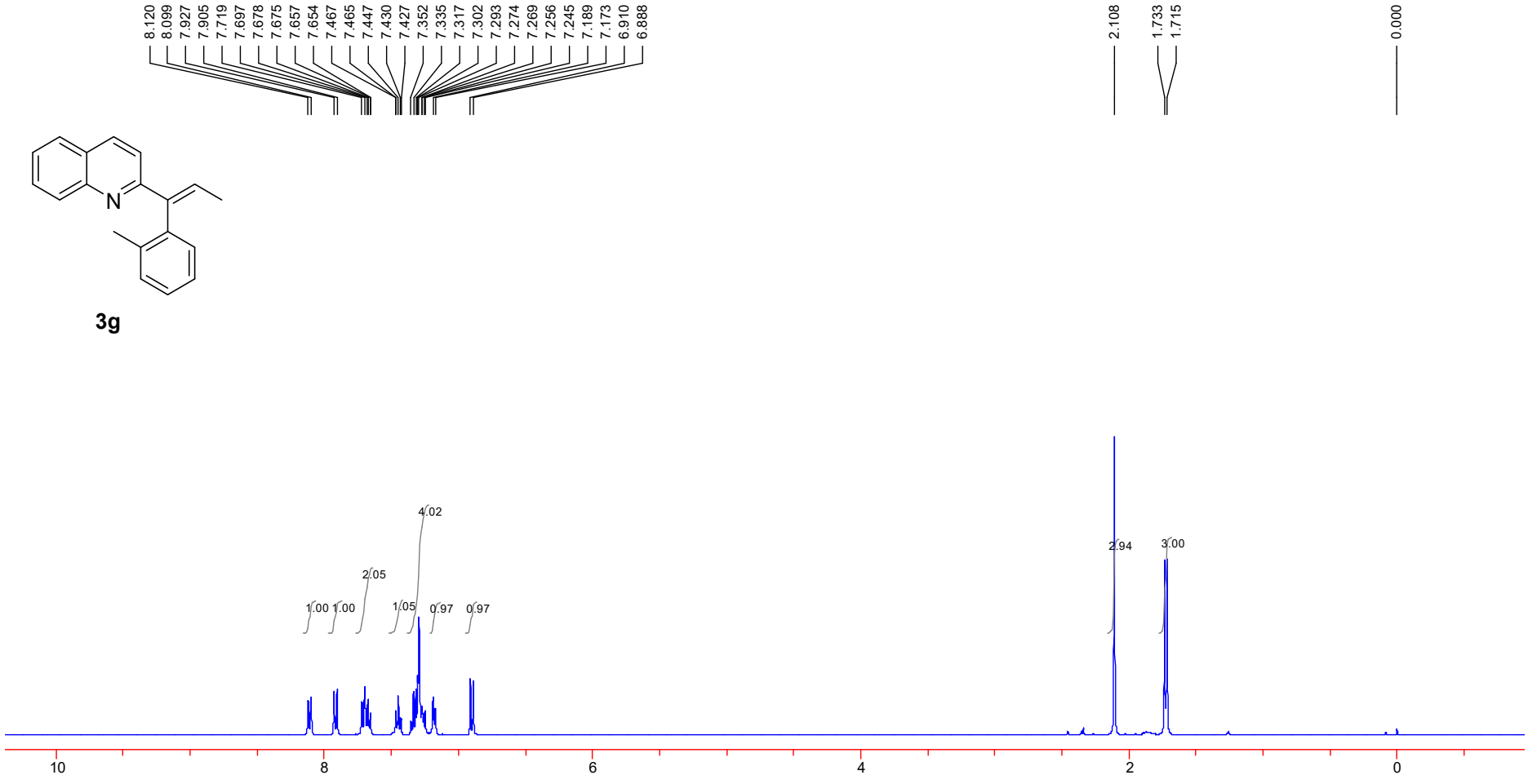
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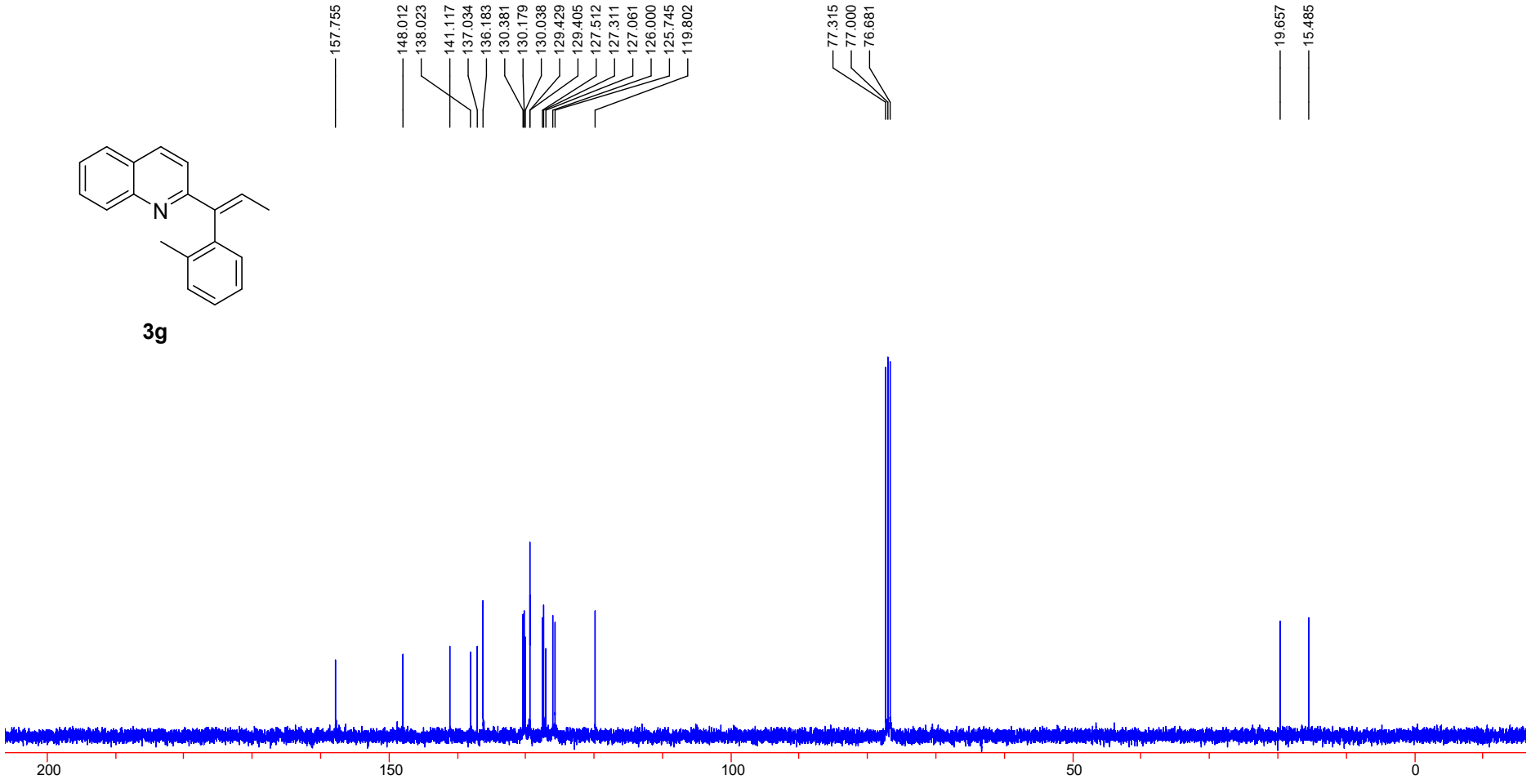
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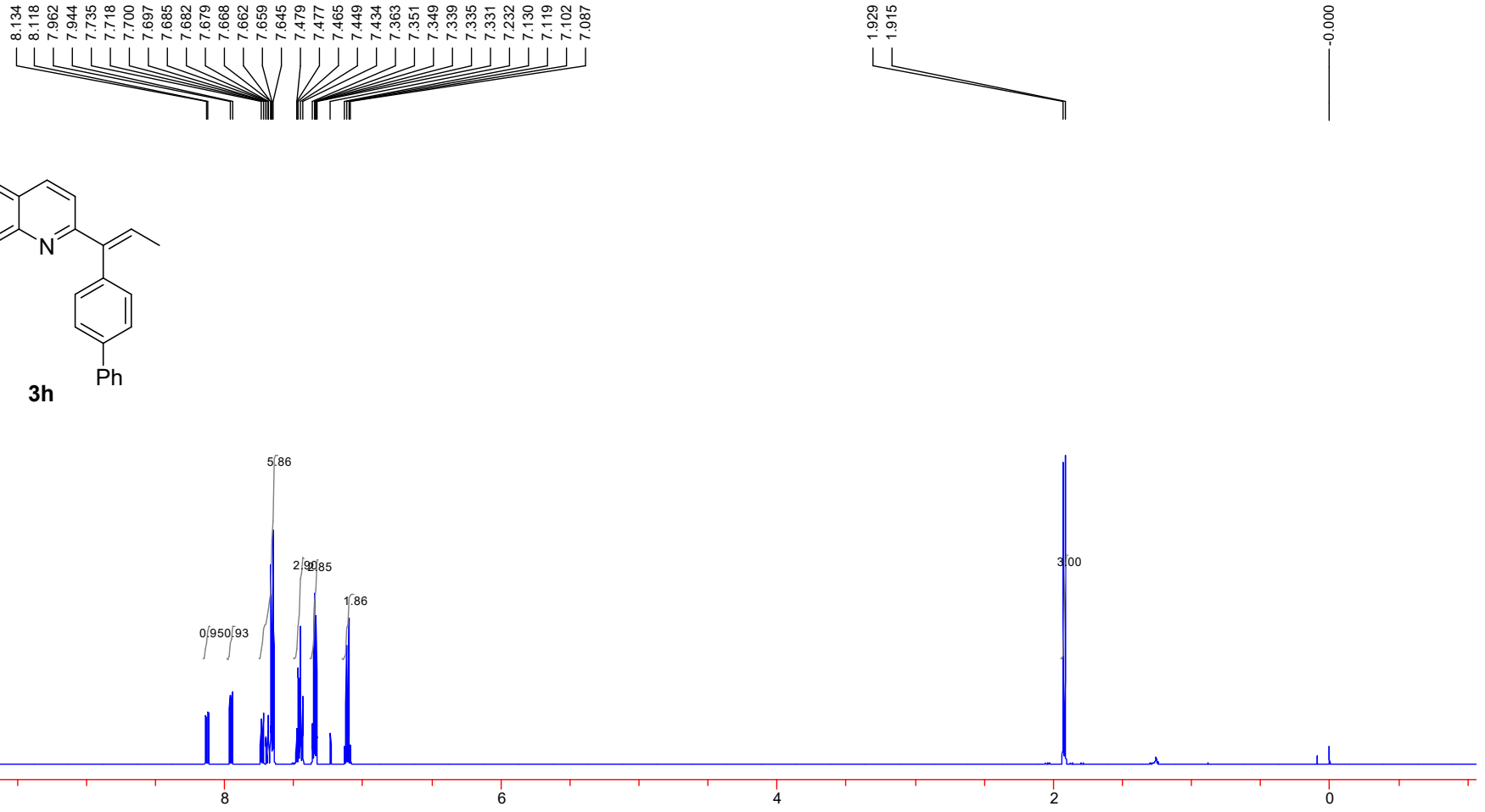
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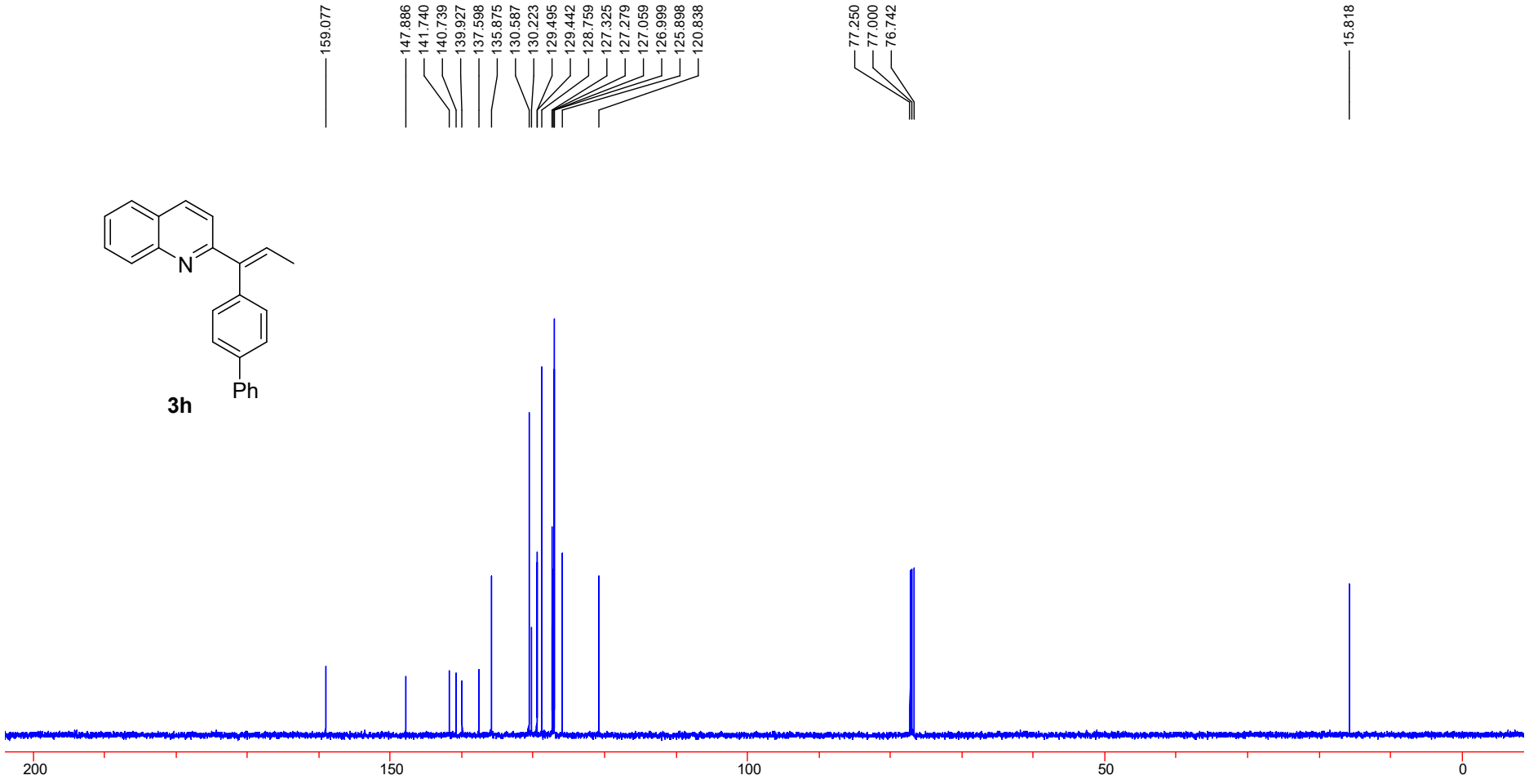
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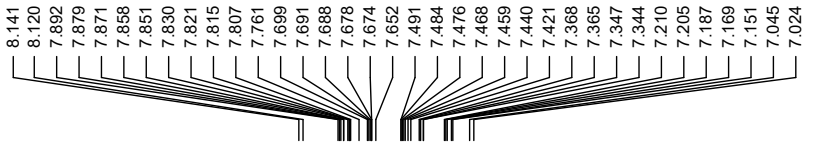
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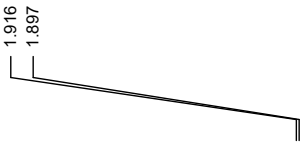
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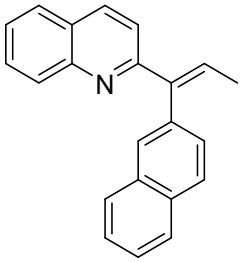
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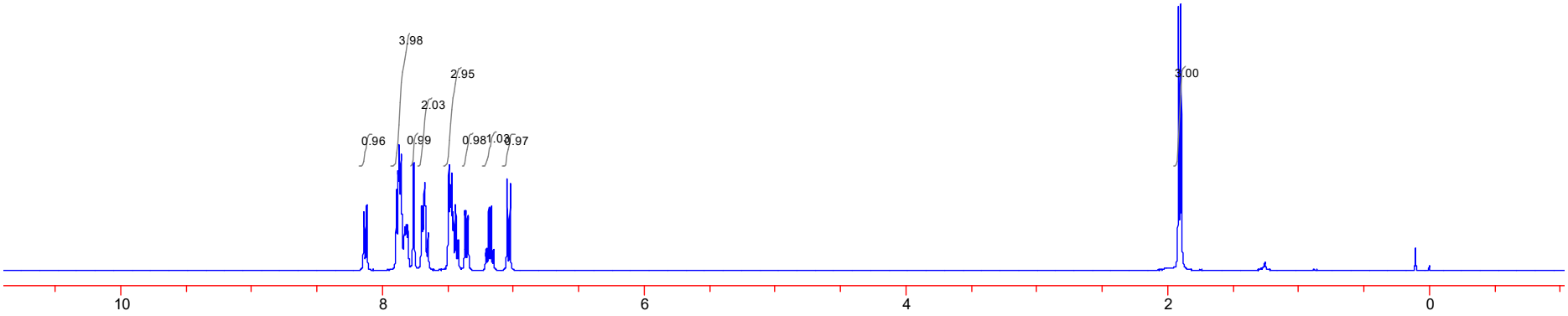
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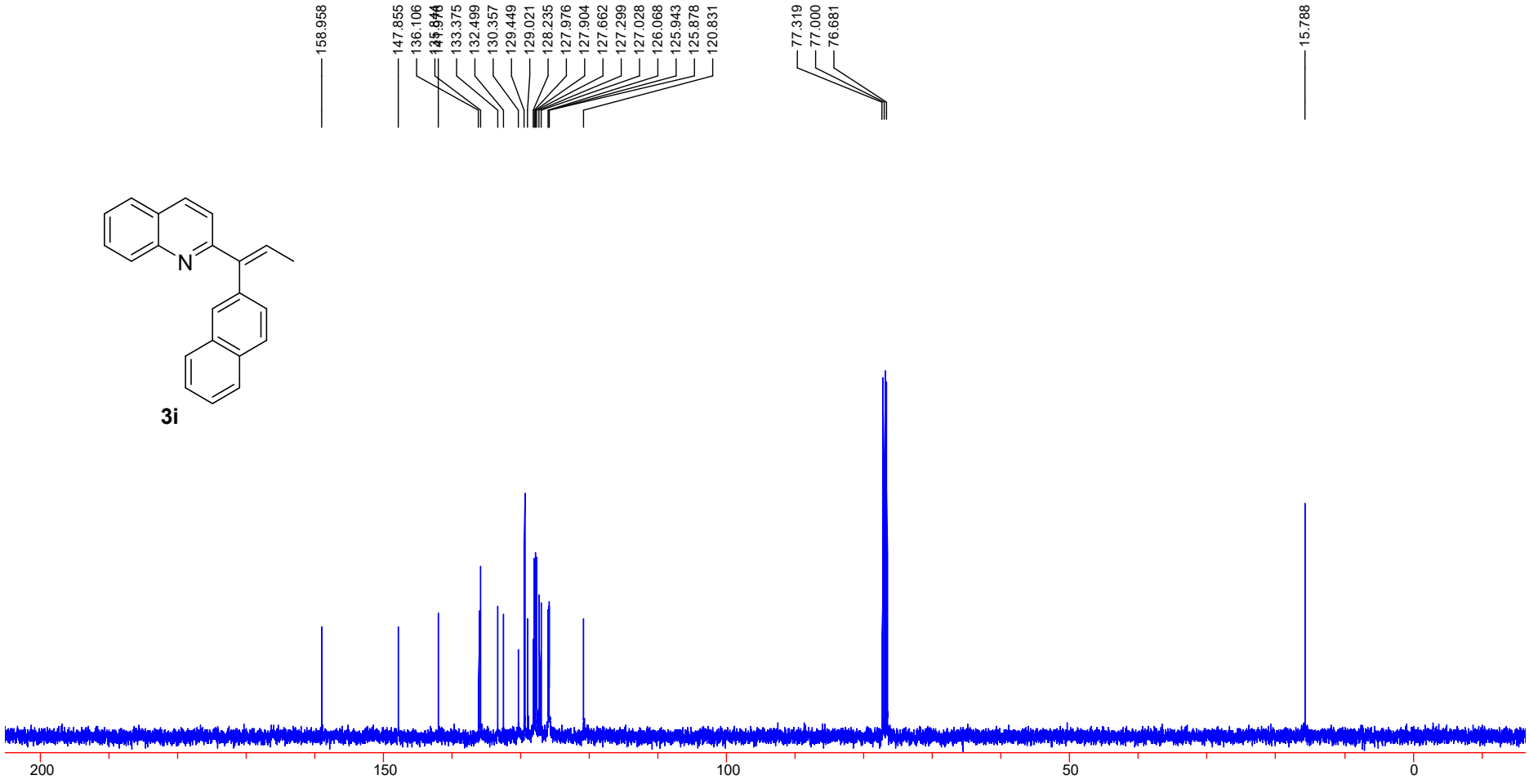
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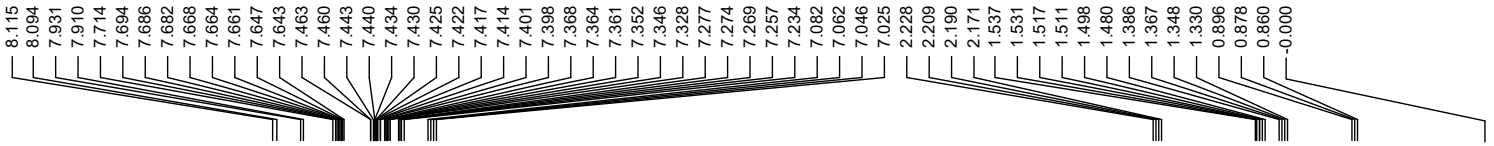
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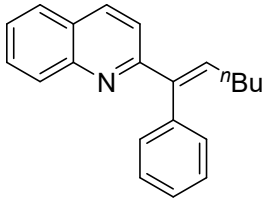
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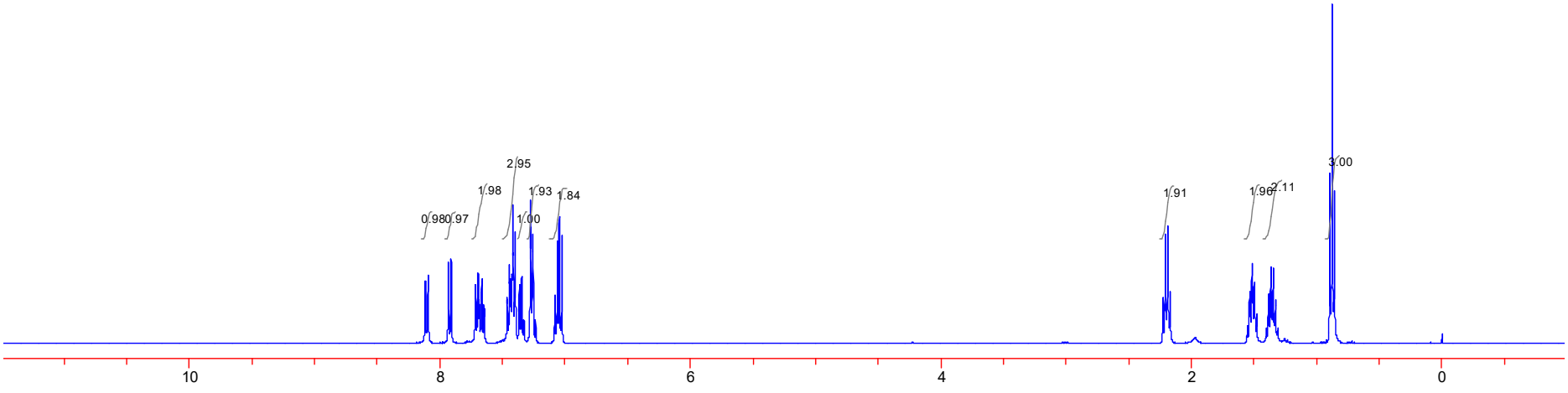
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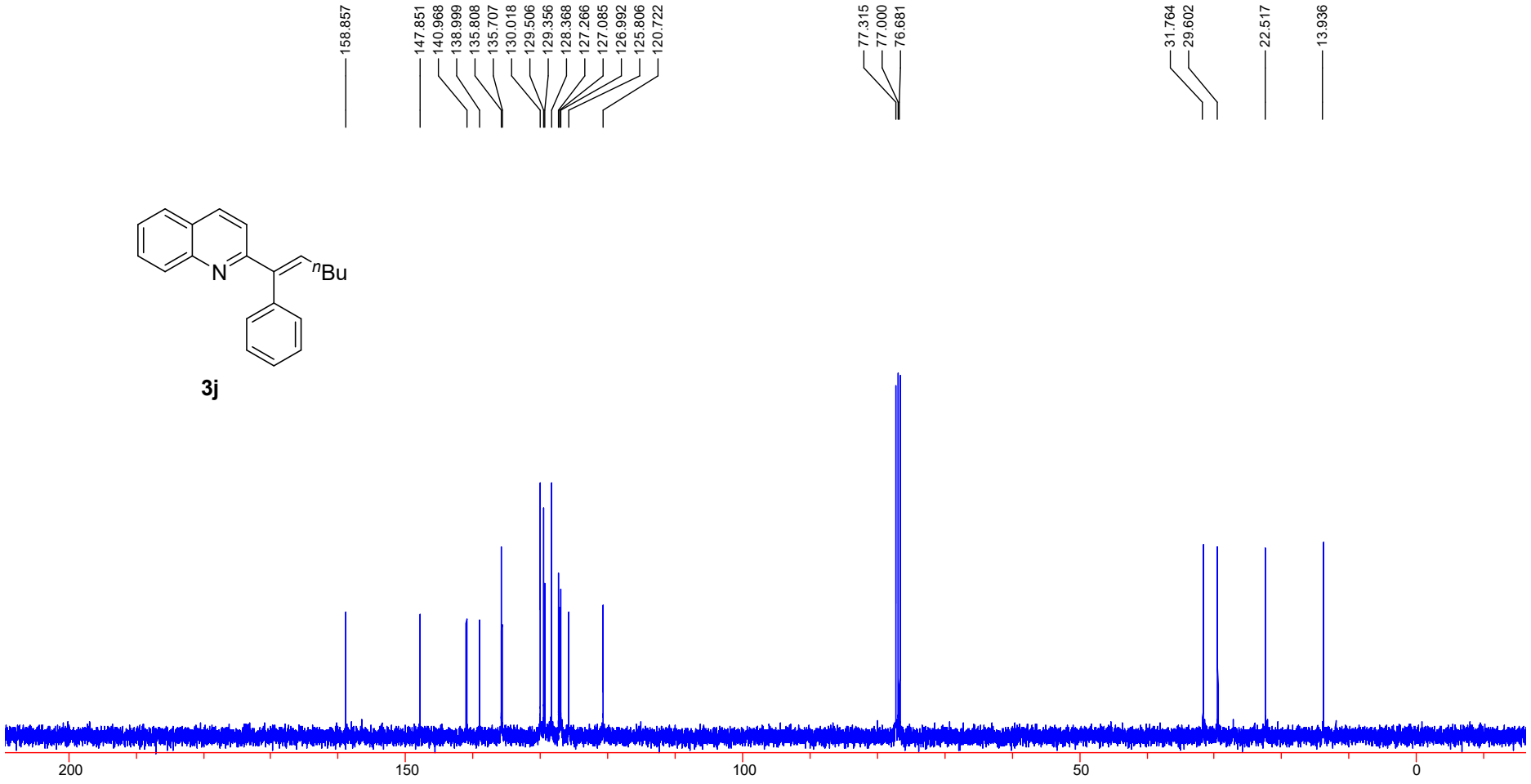
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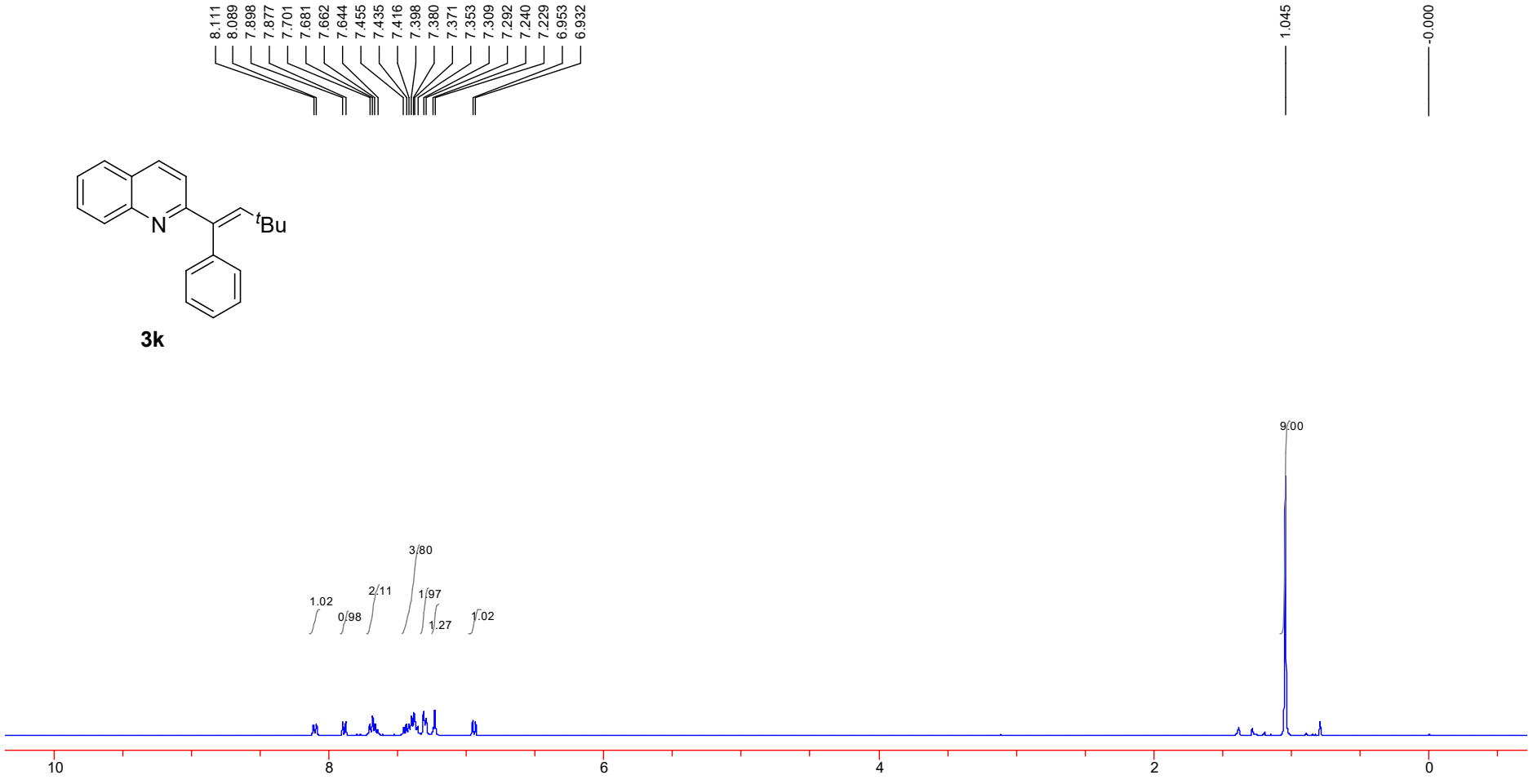
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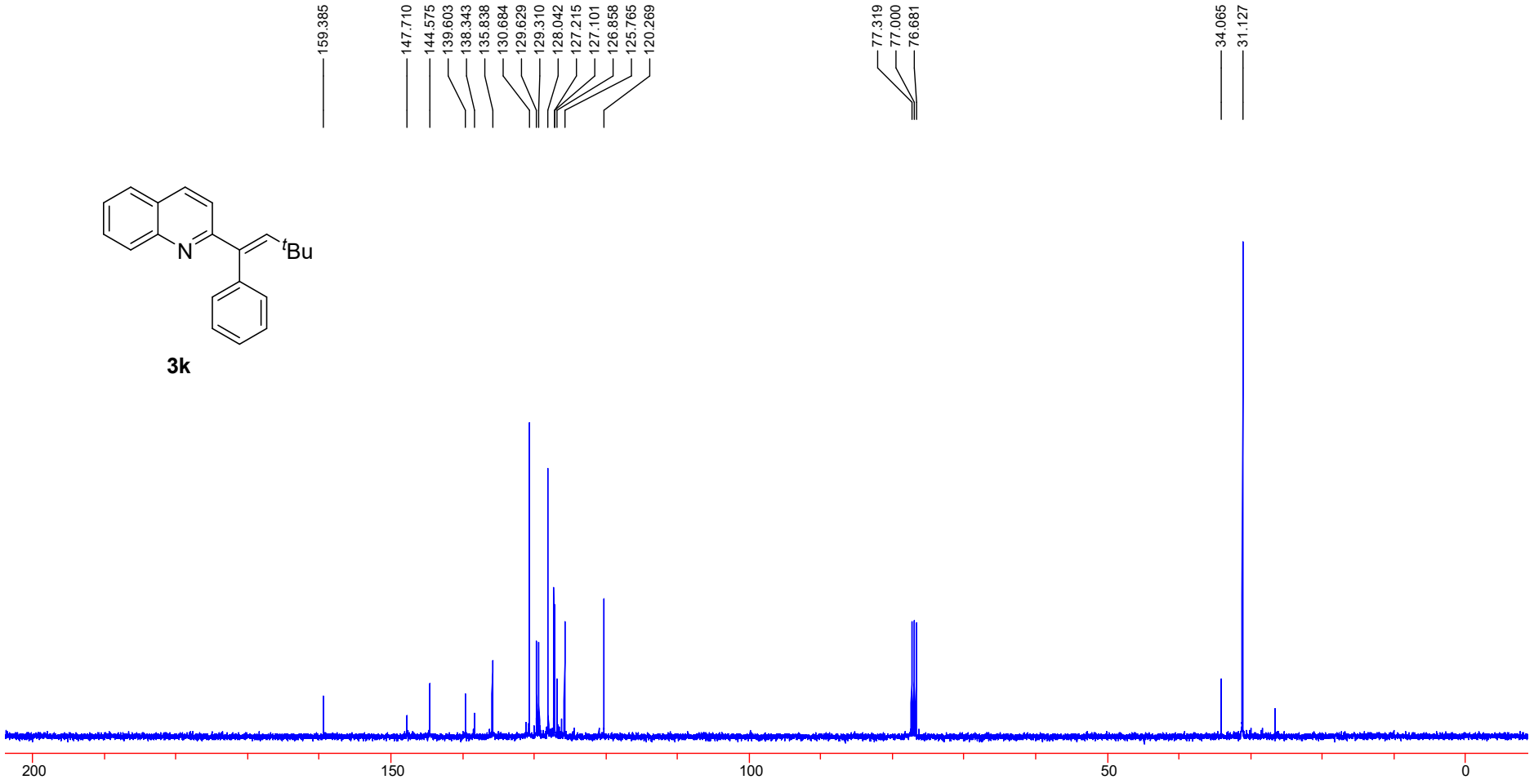
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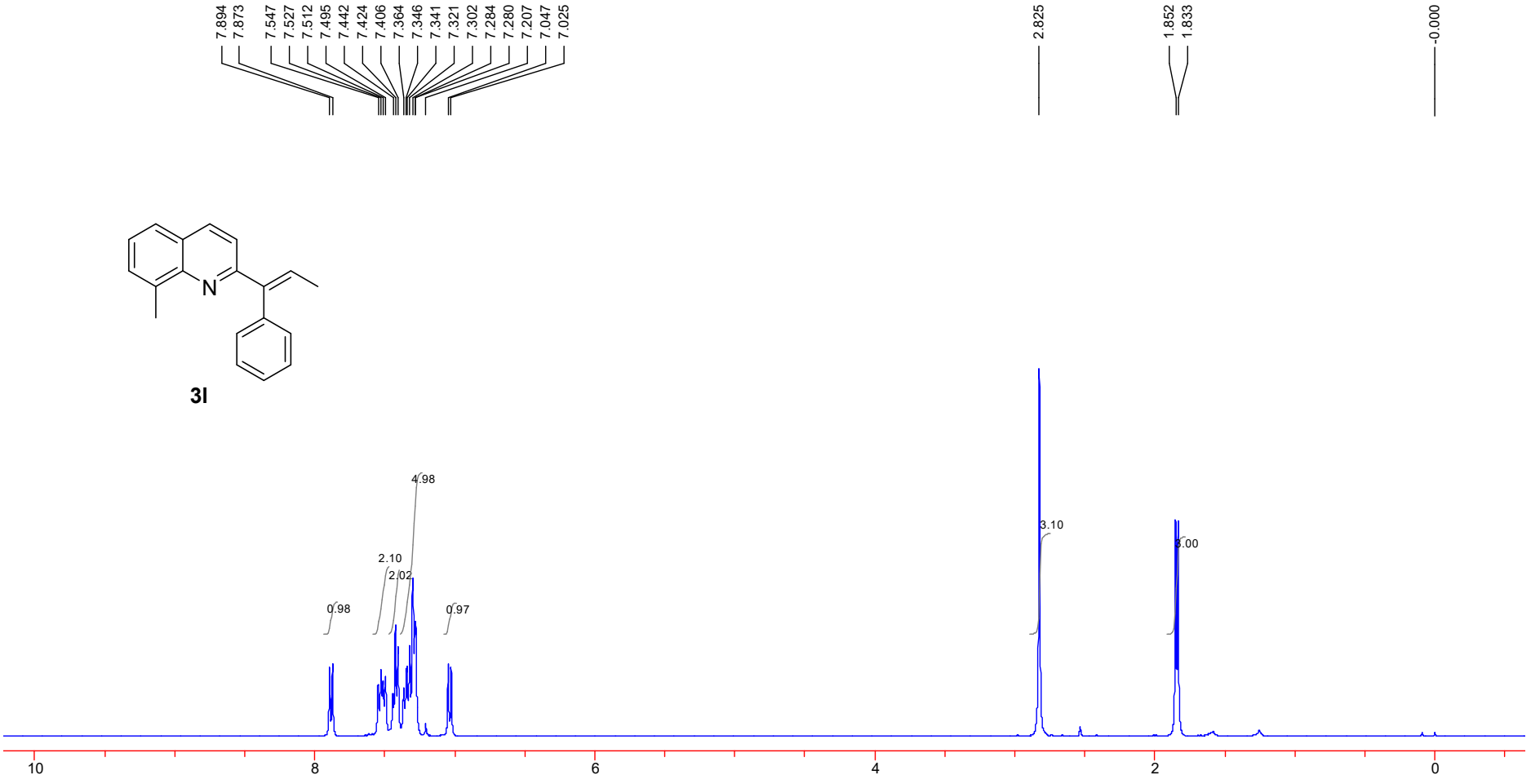
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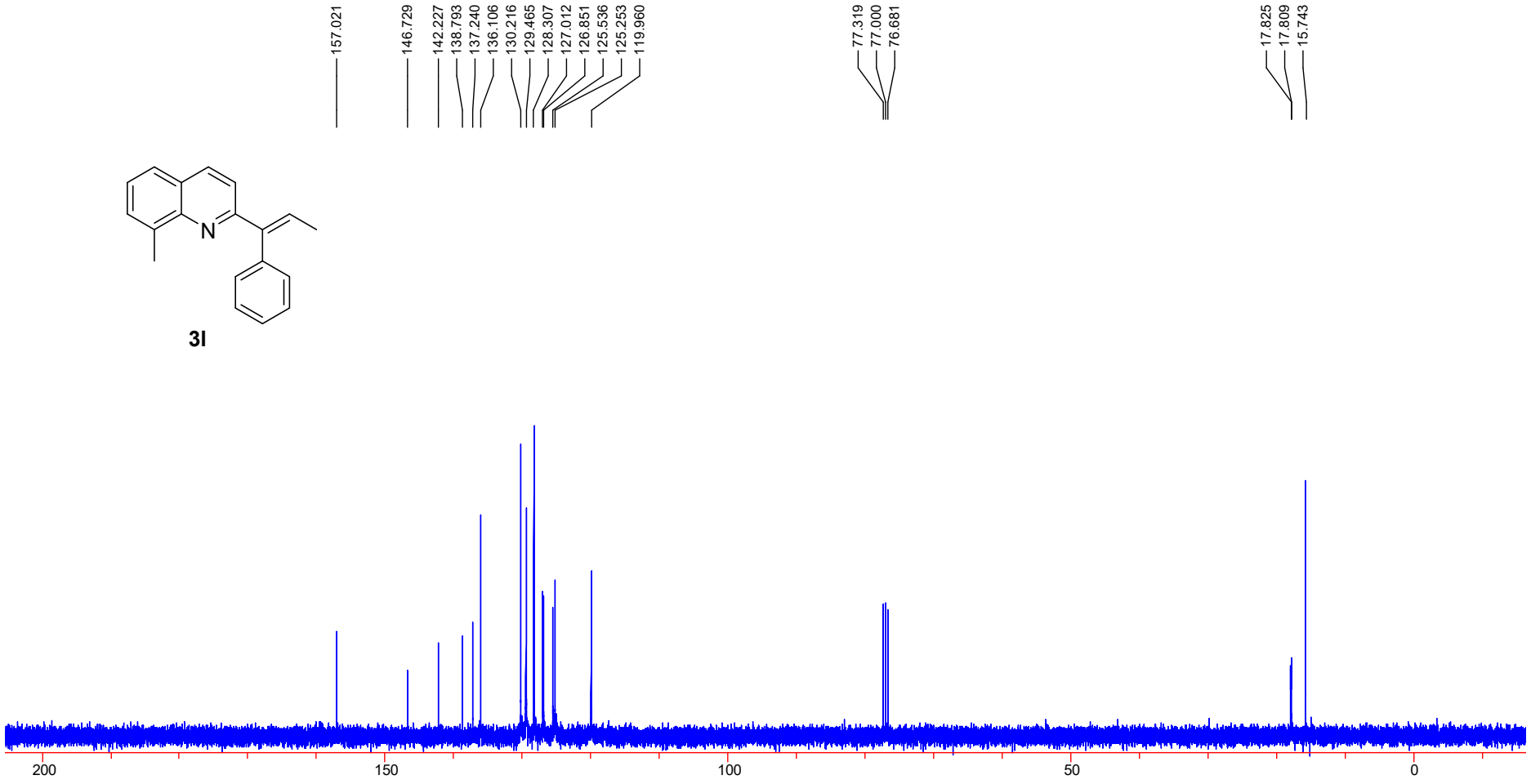
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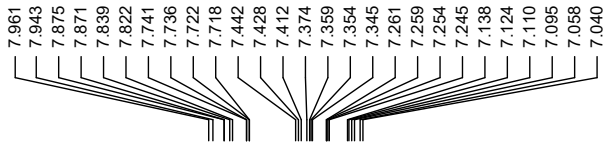
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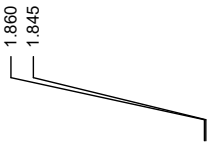
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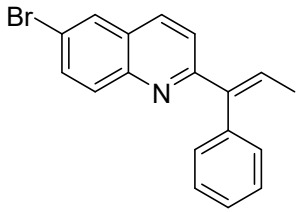
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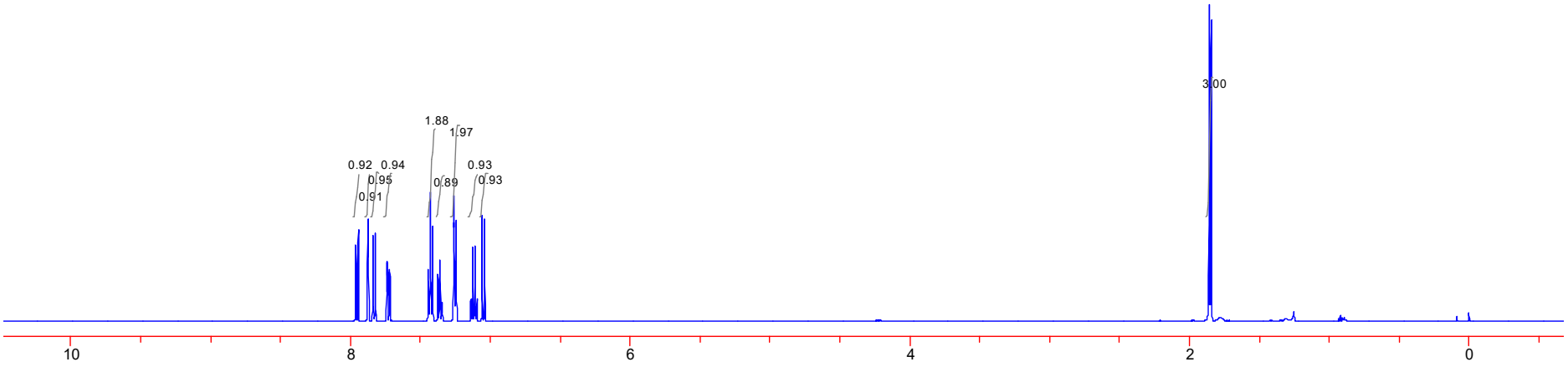
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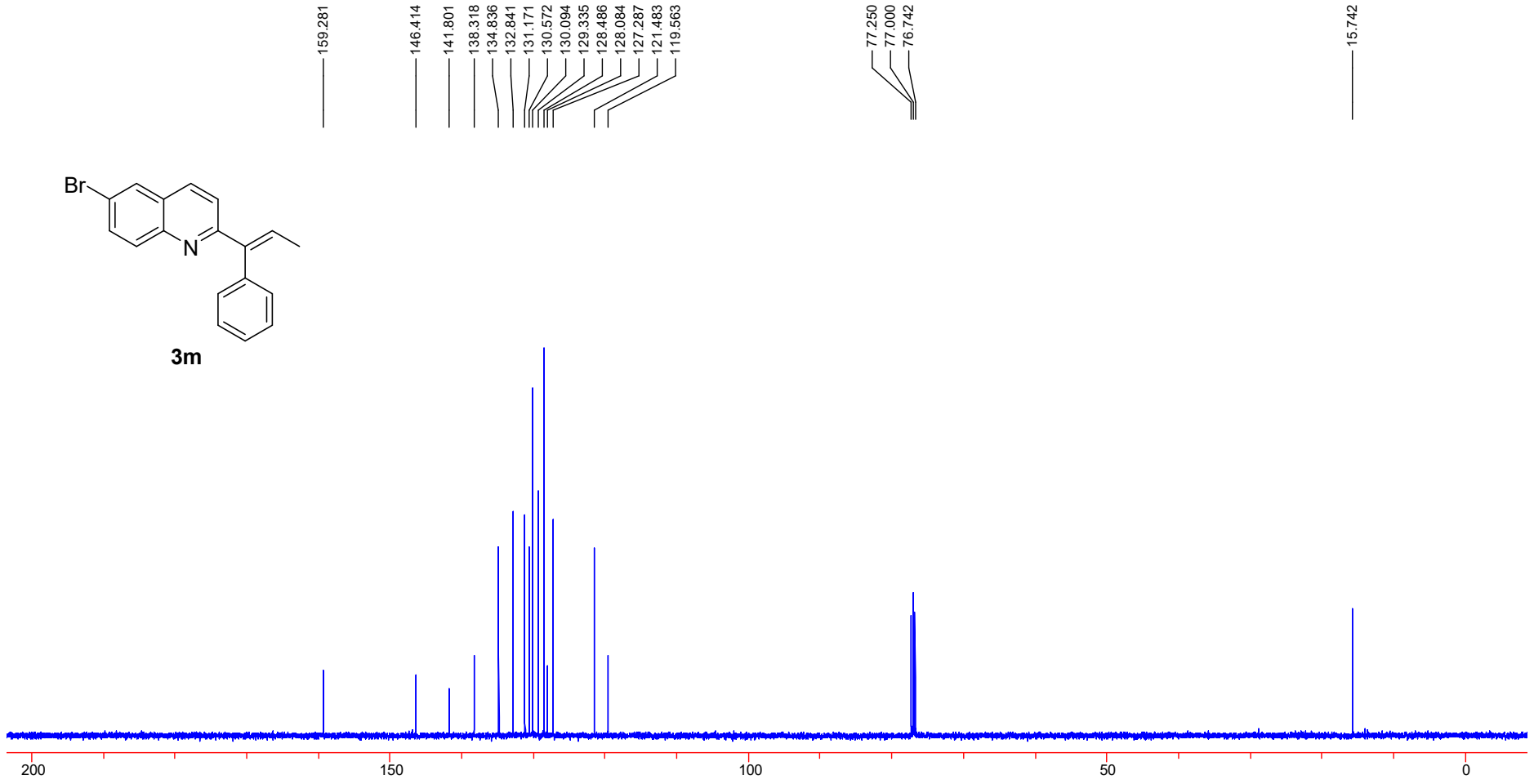
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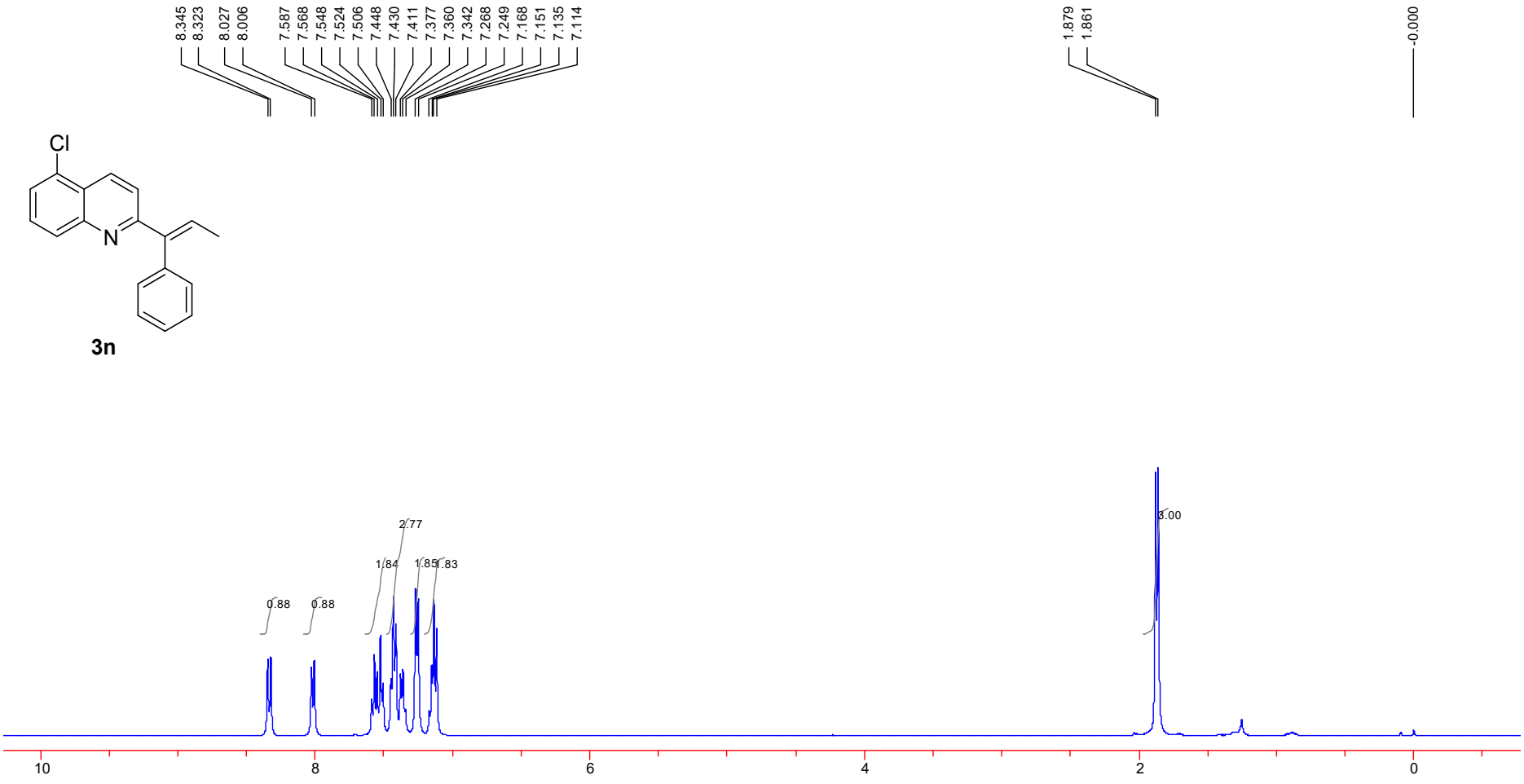
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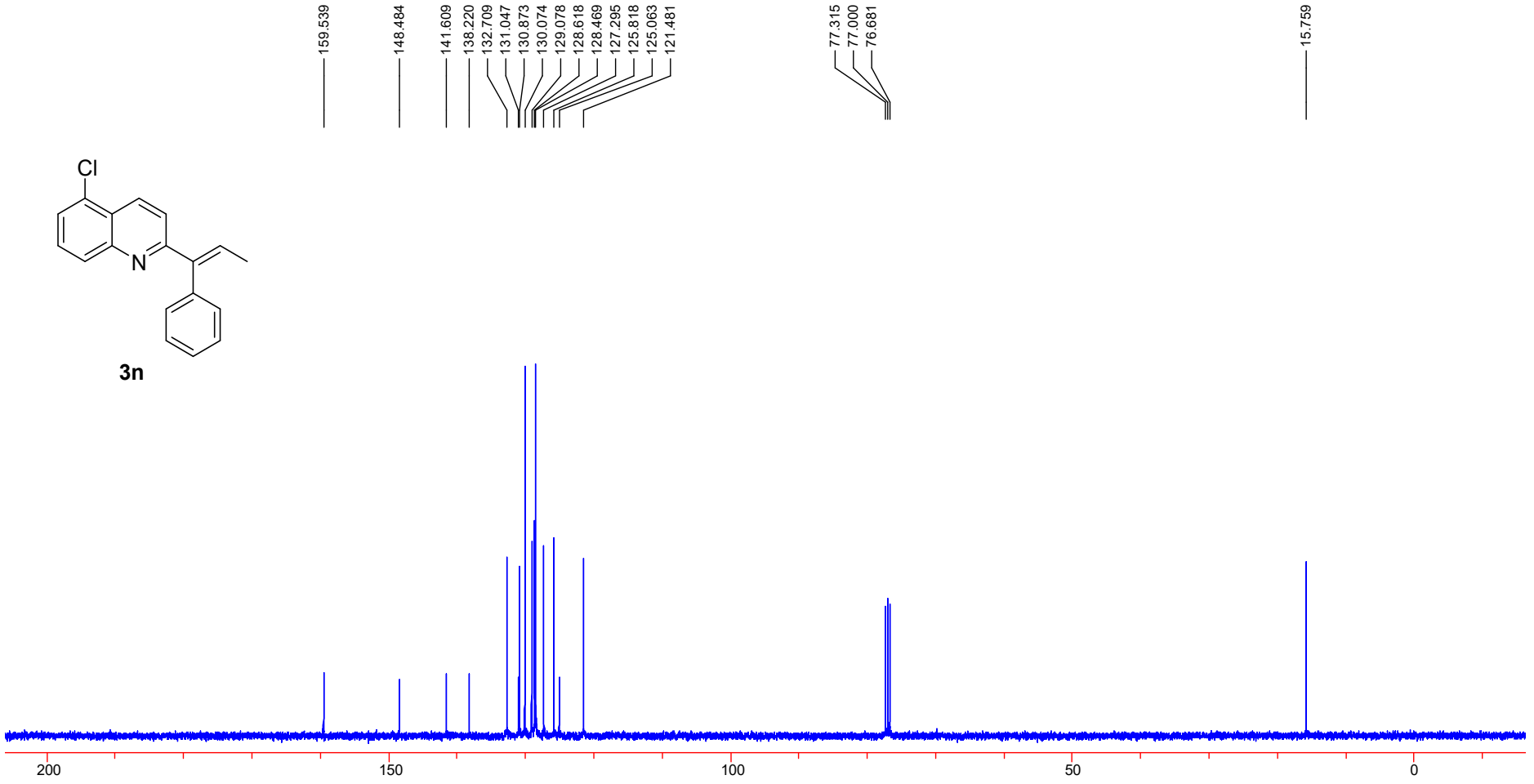
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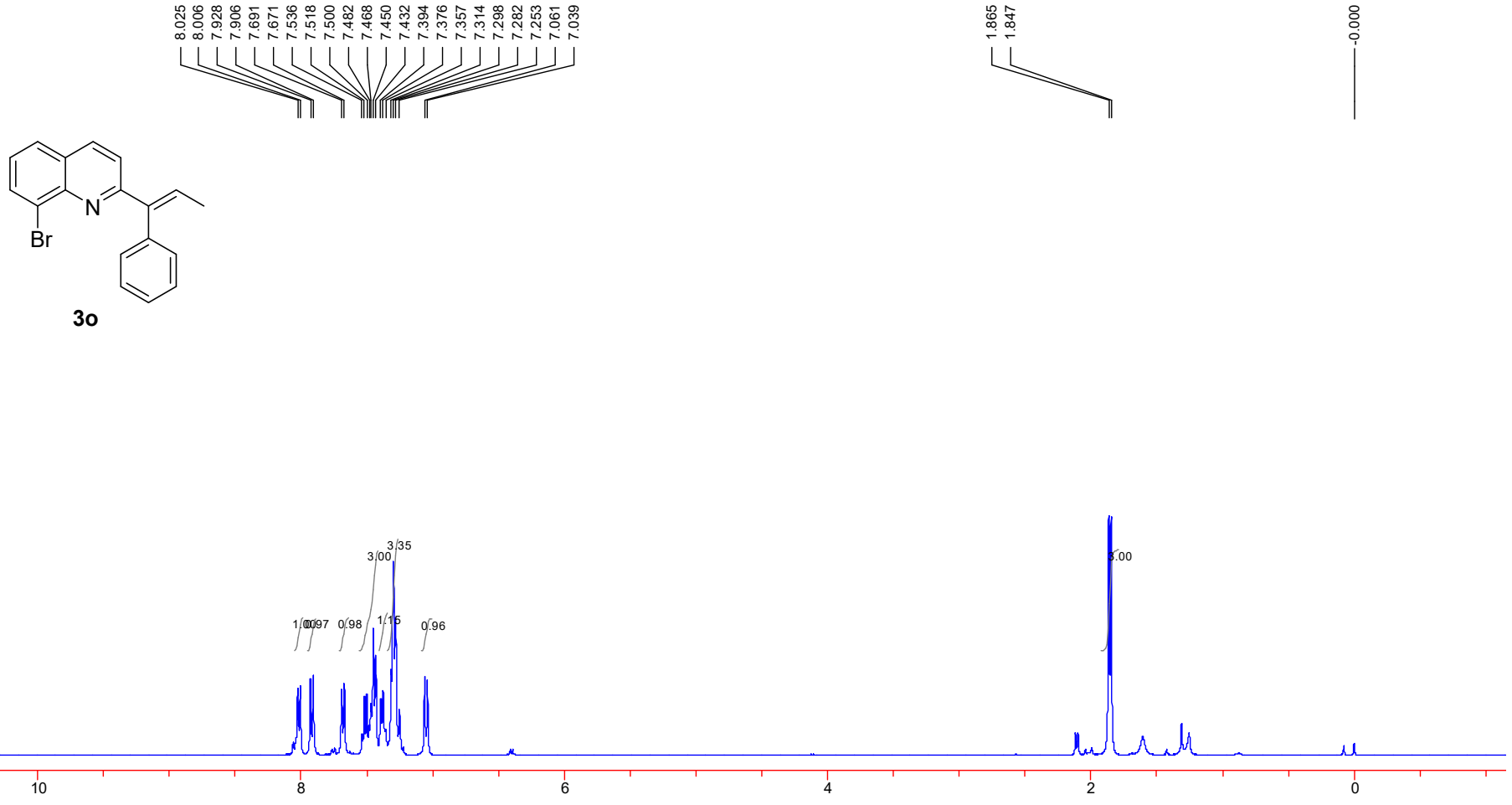
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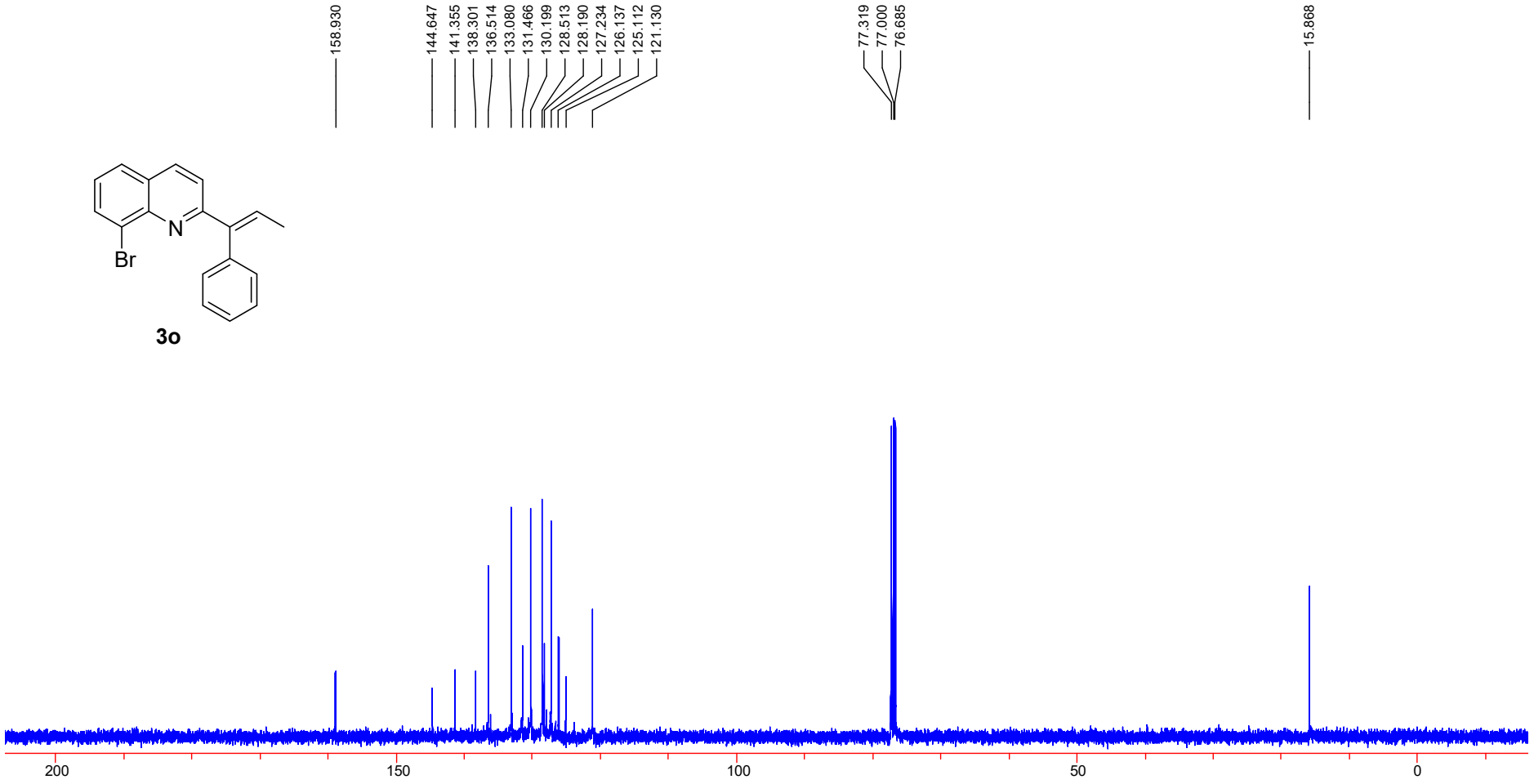
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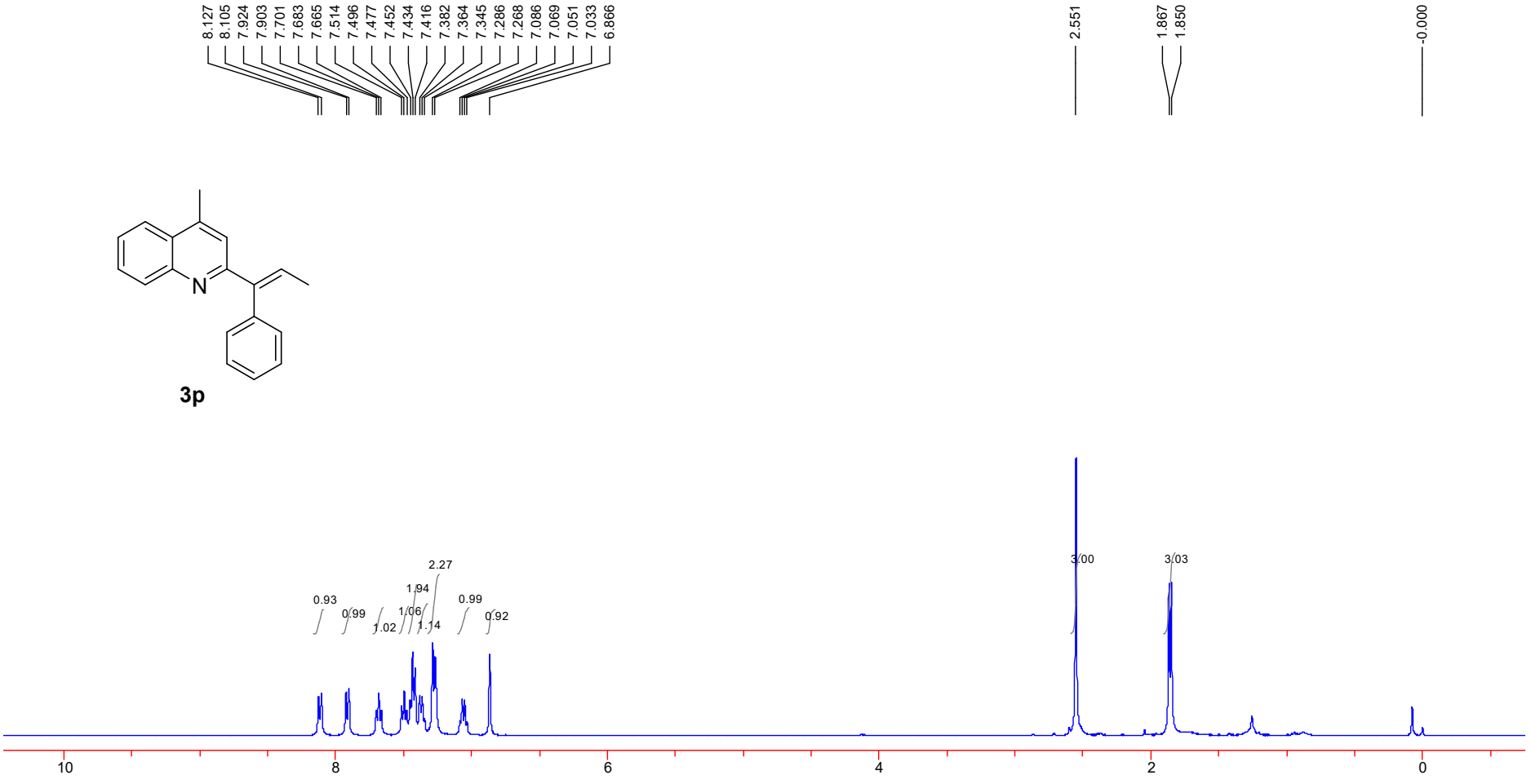
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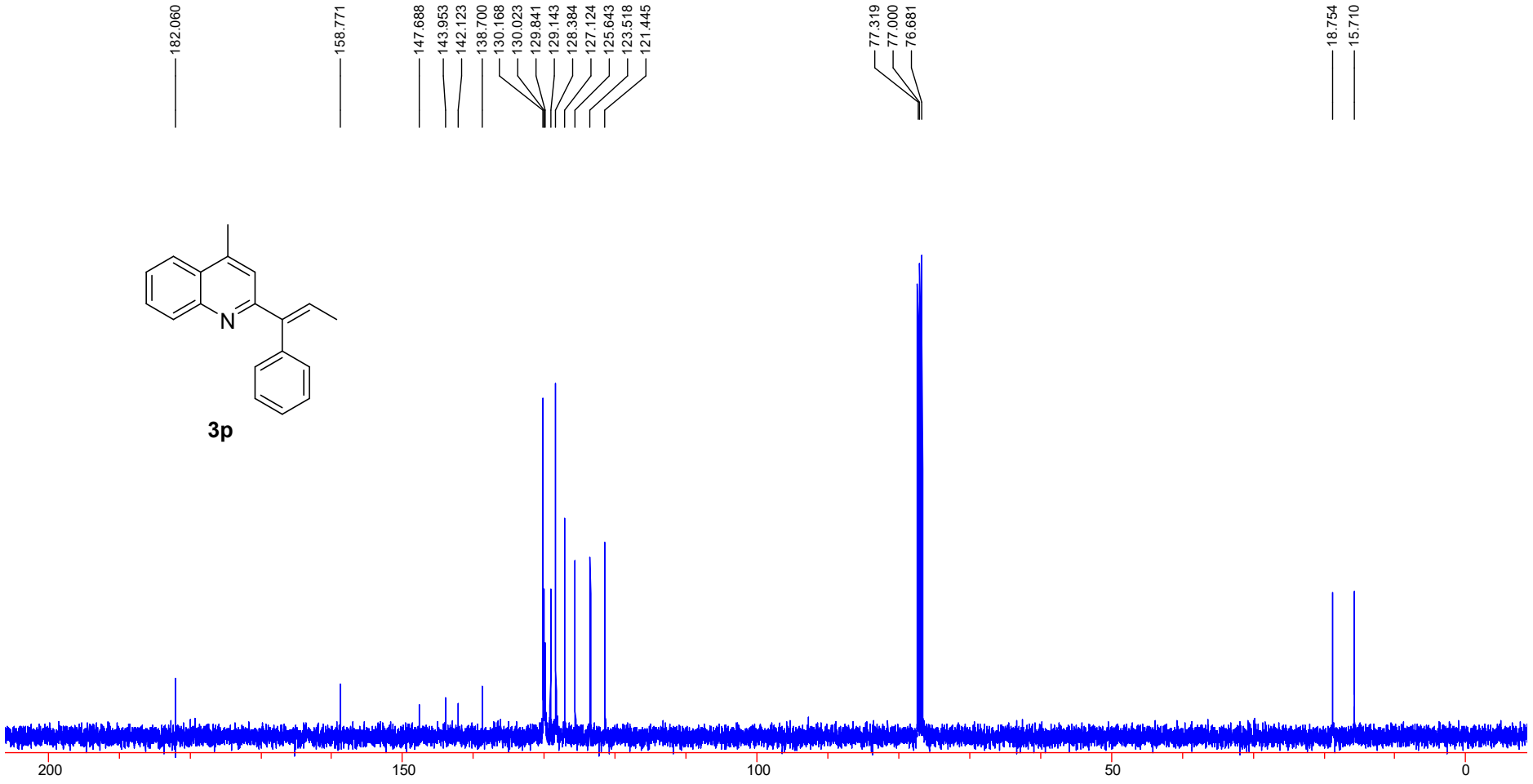
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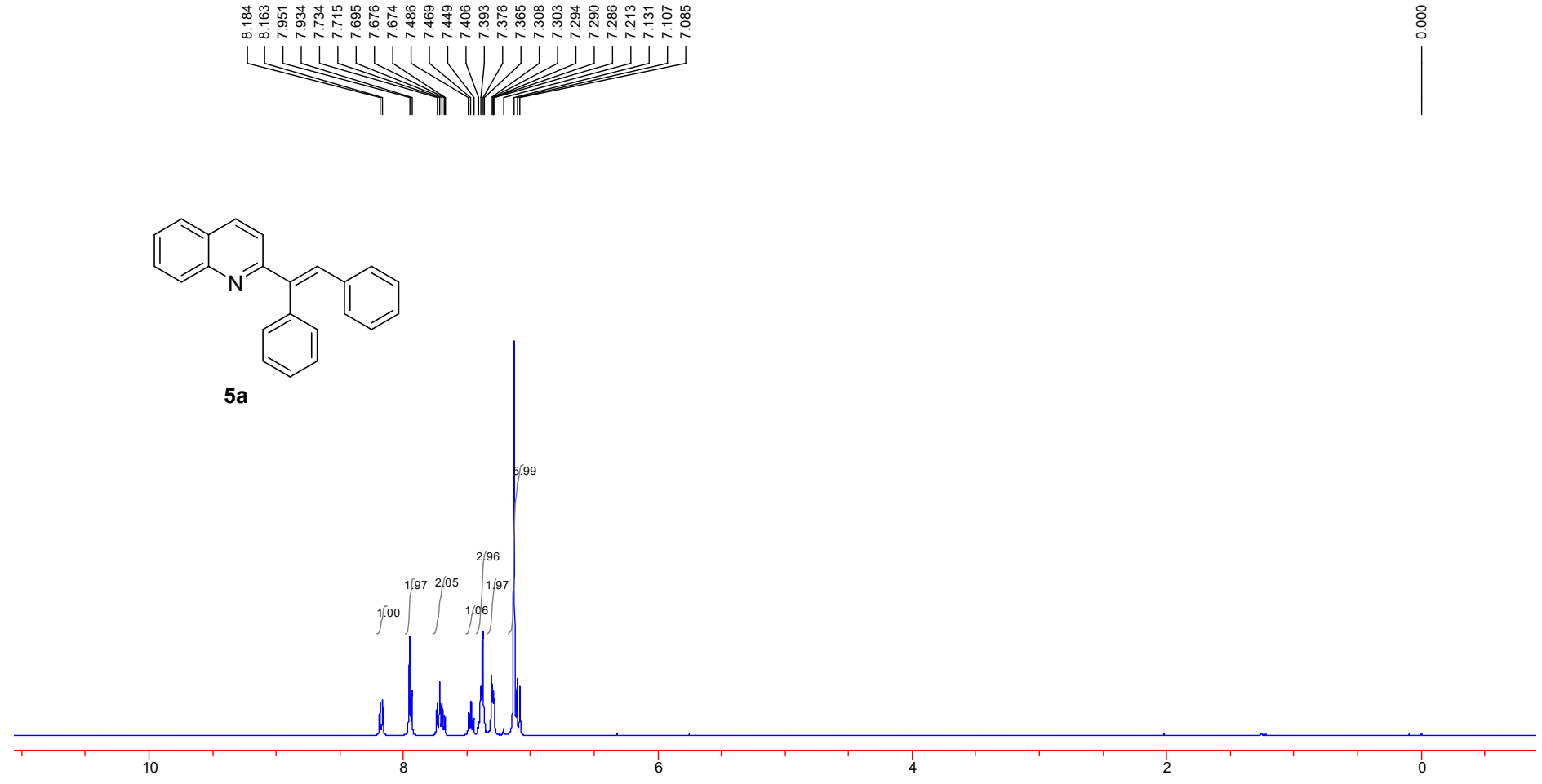
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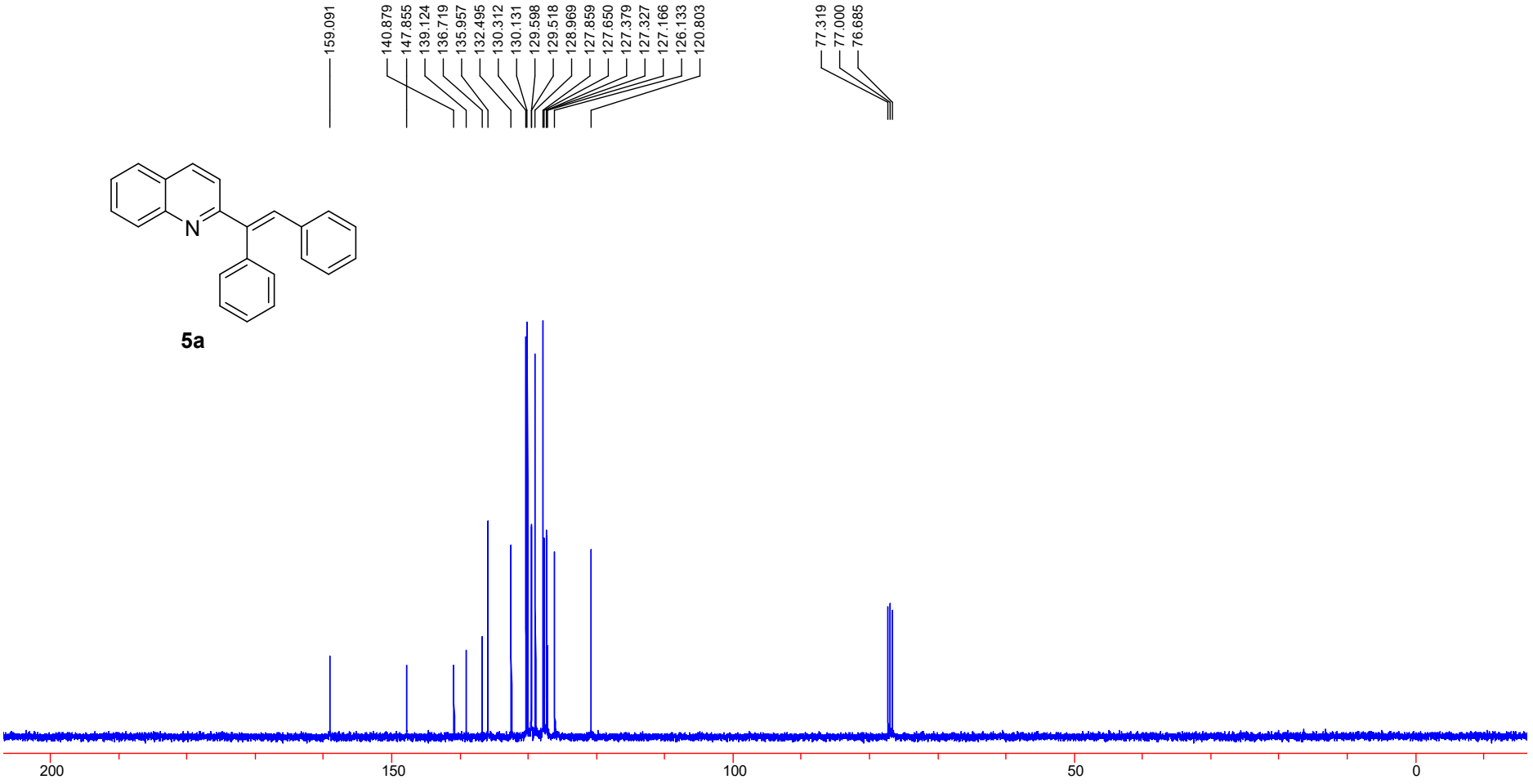
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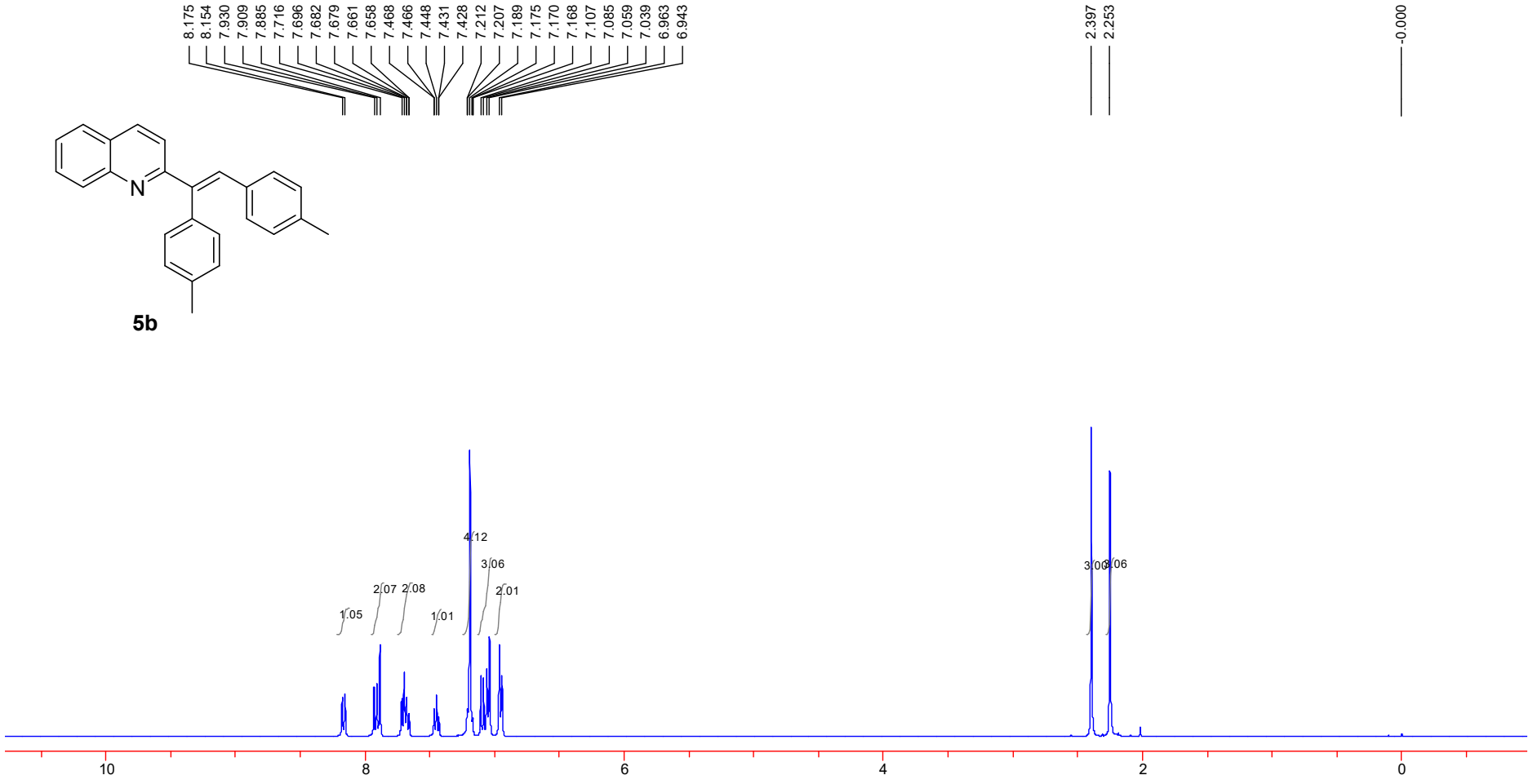
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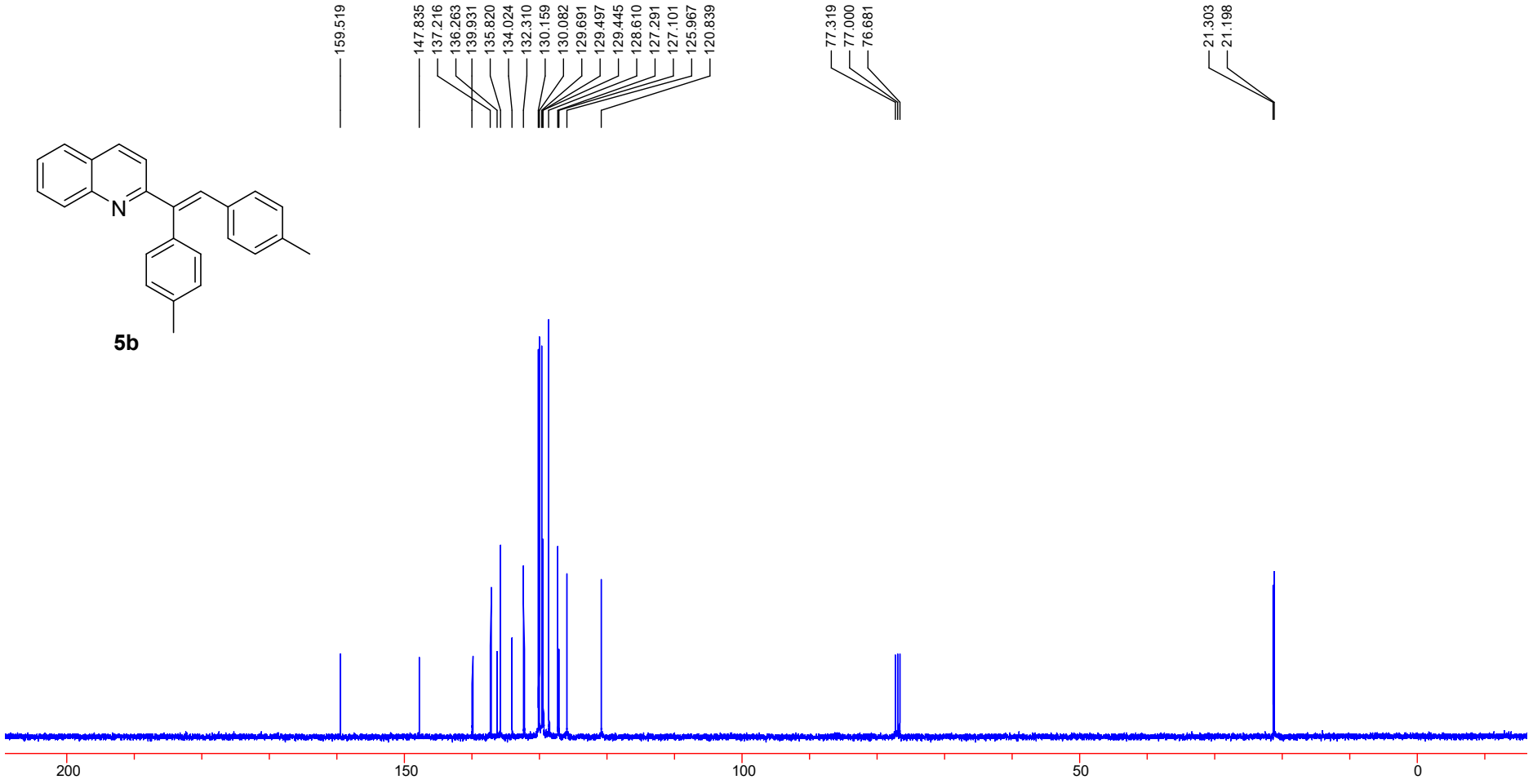
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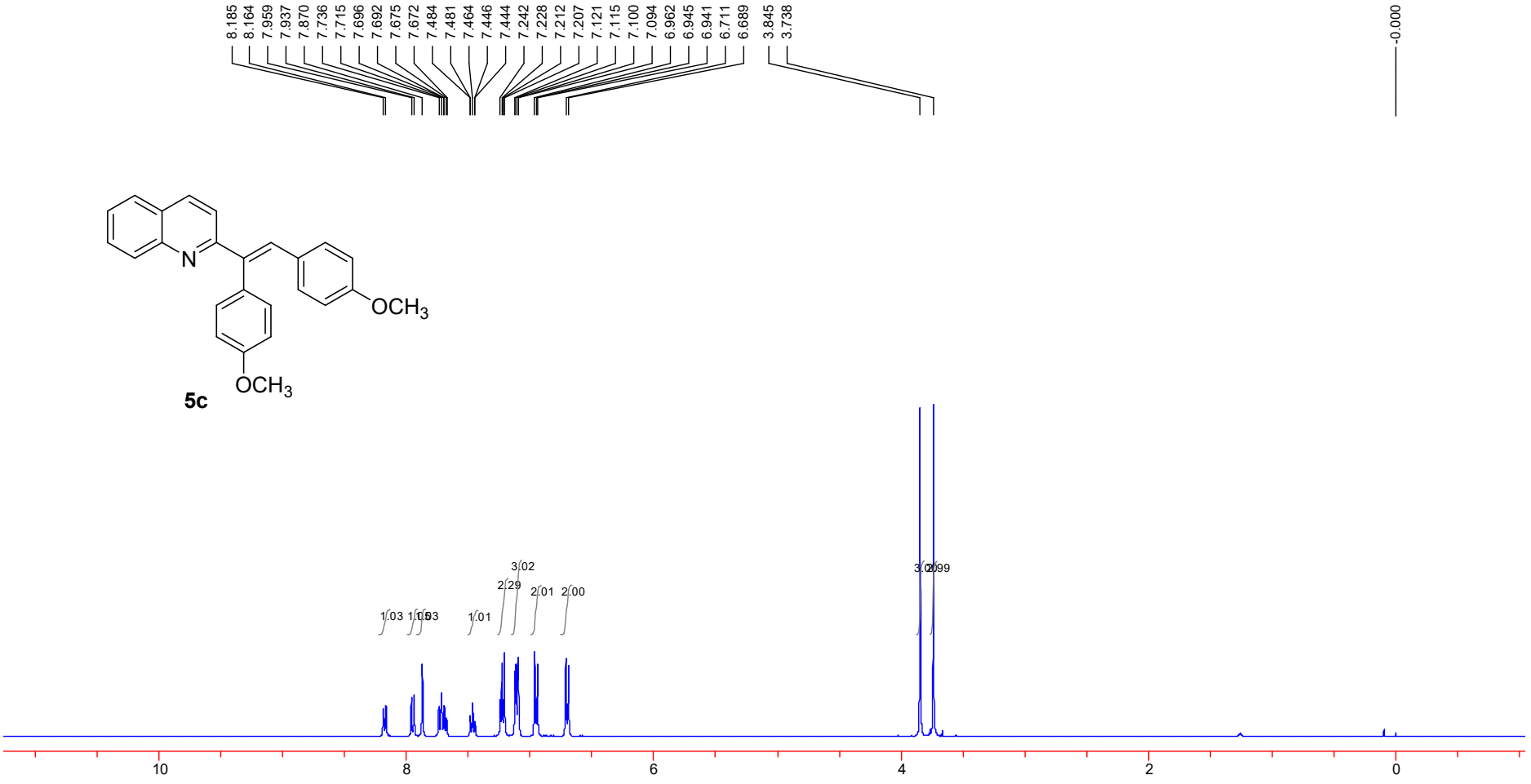
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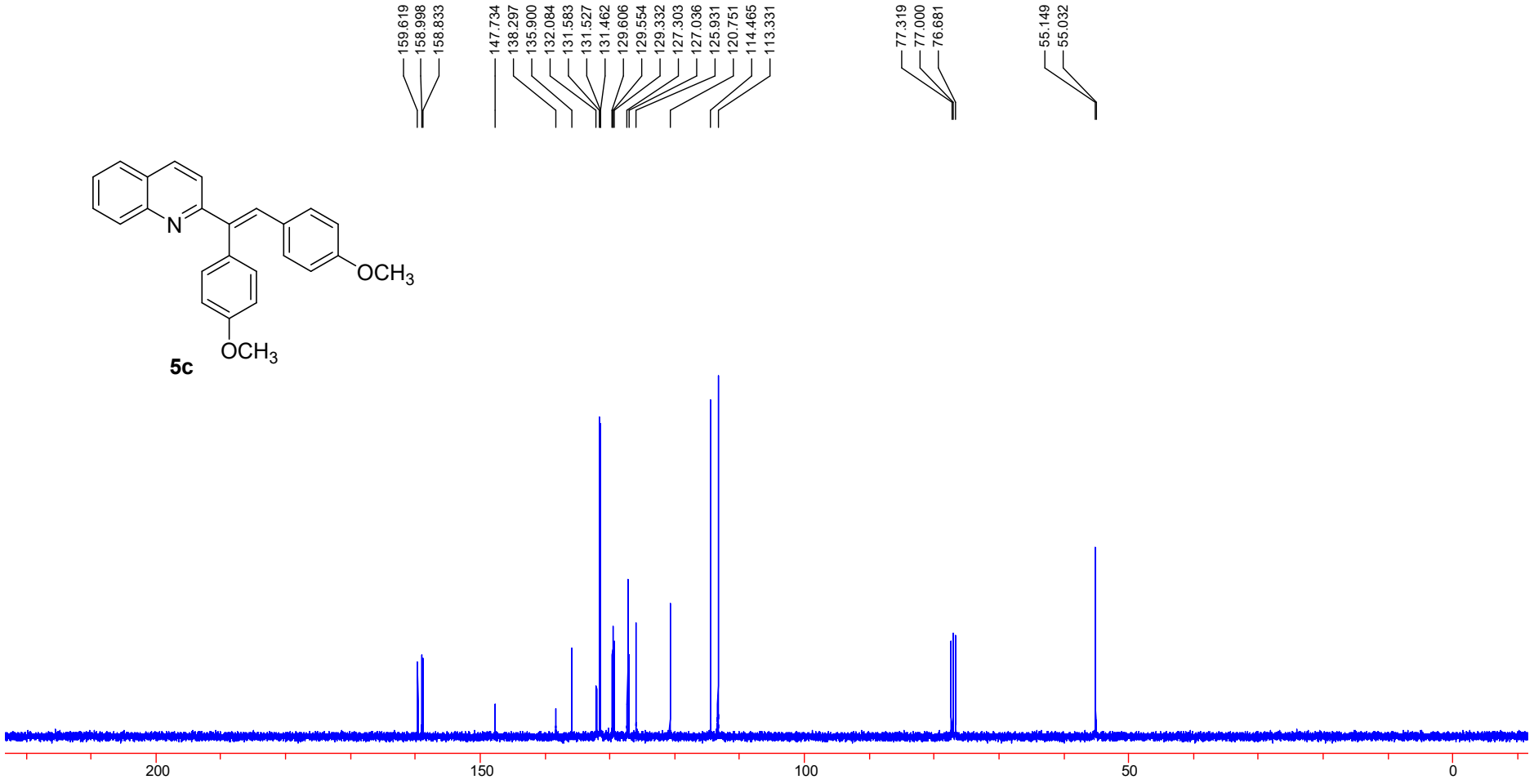
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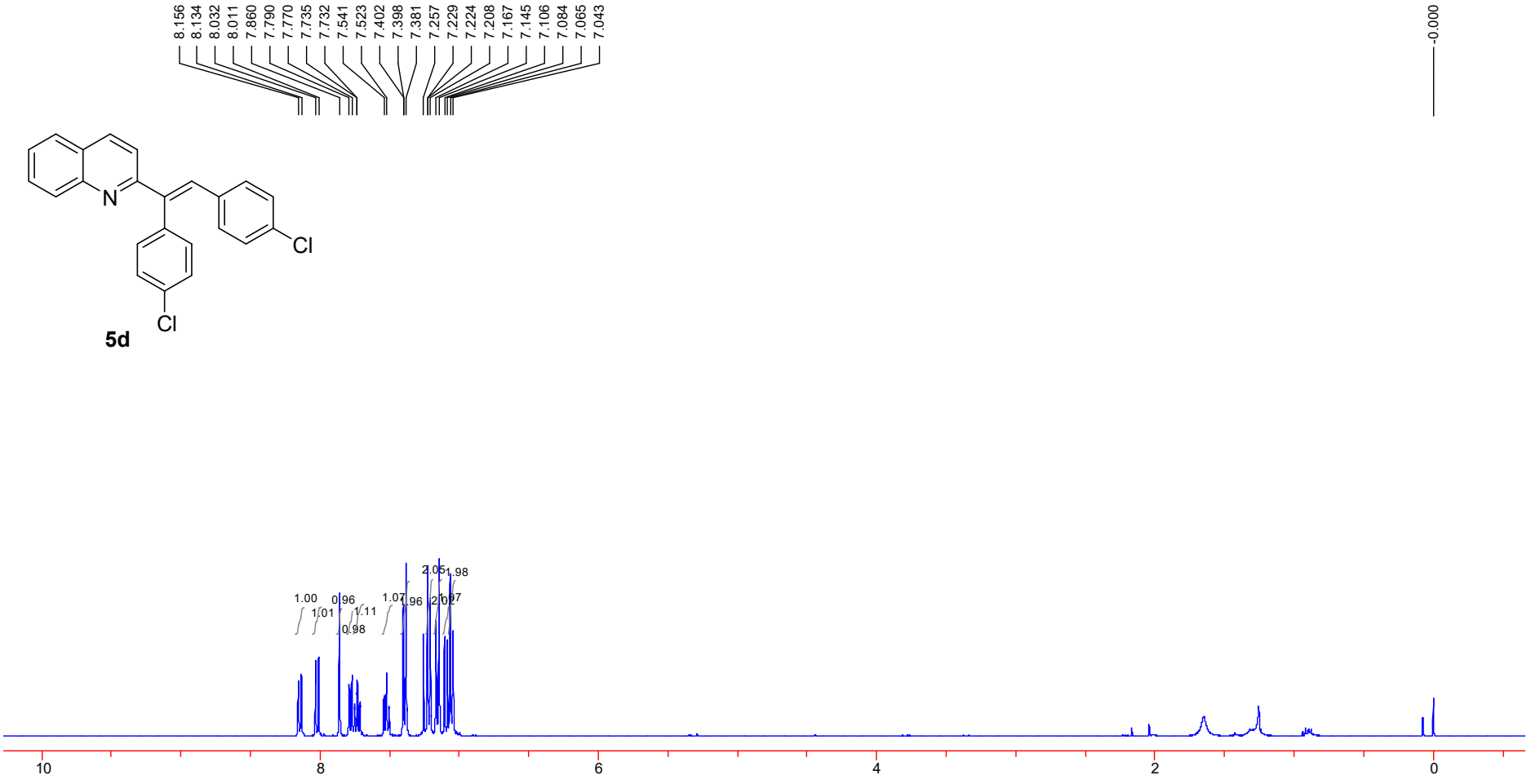
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Cl
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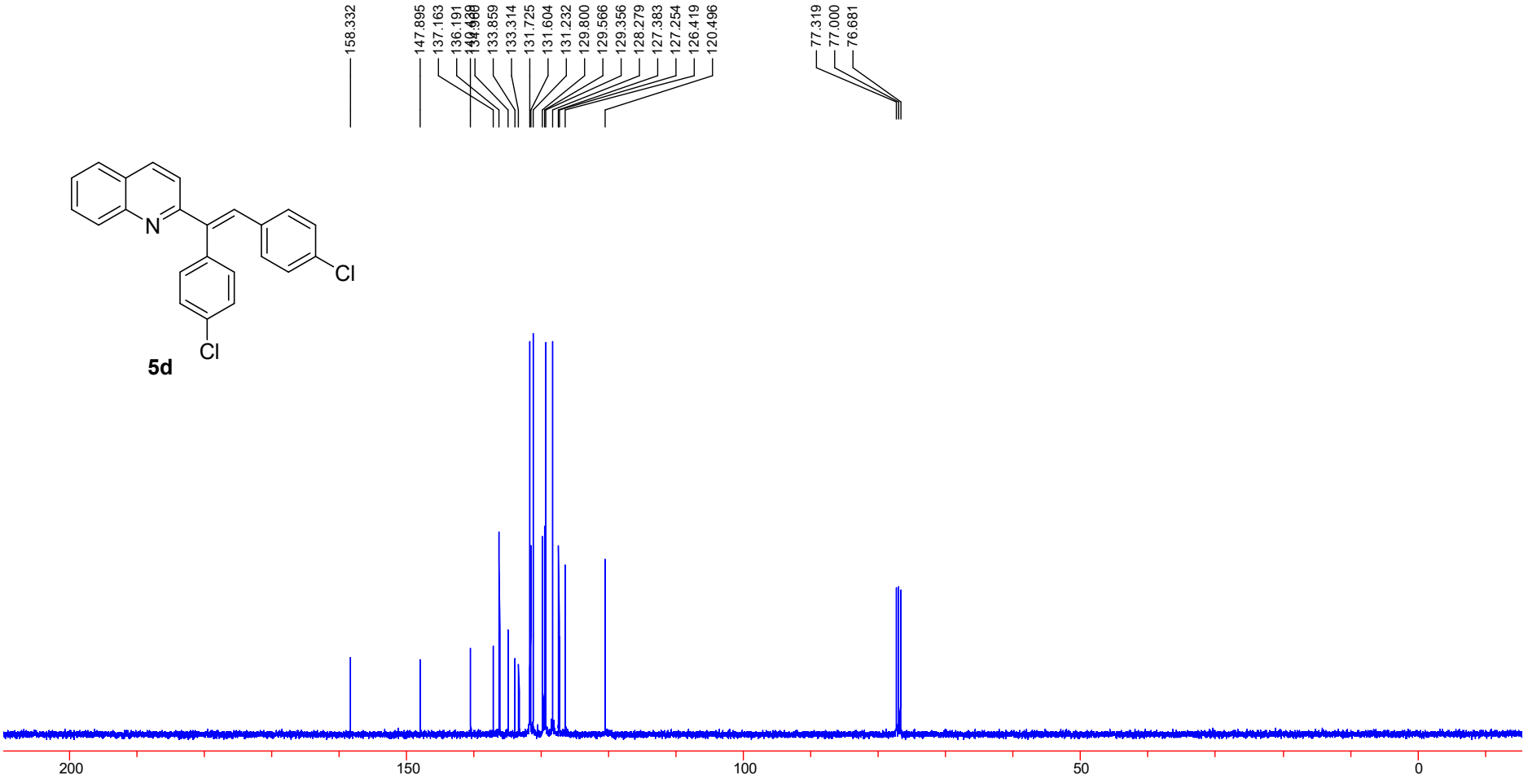
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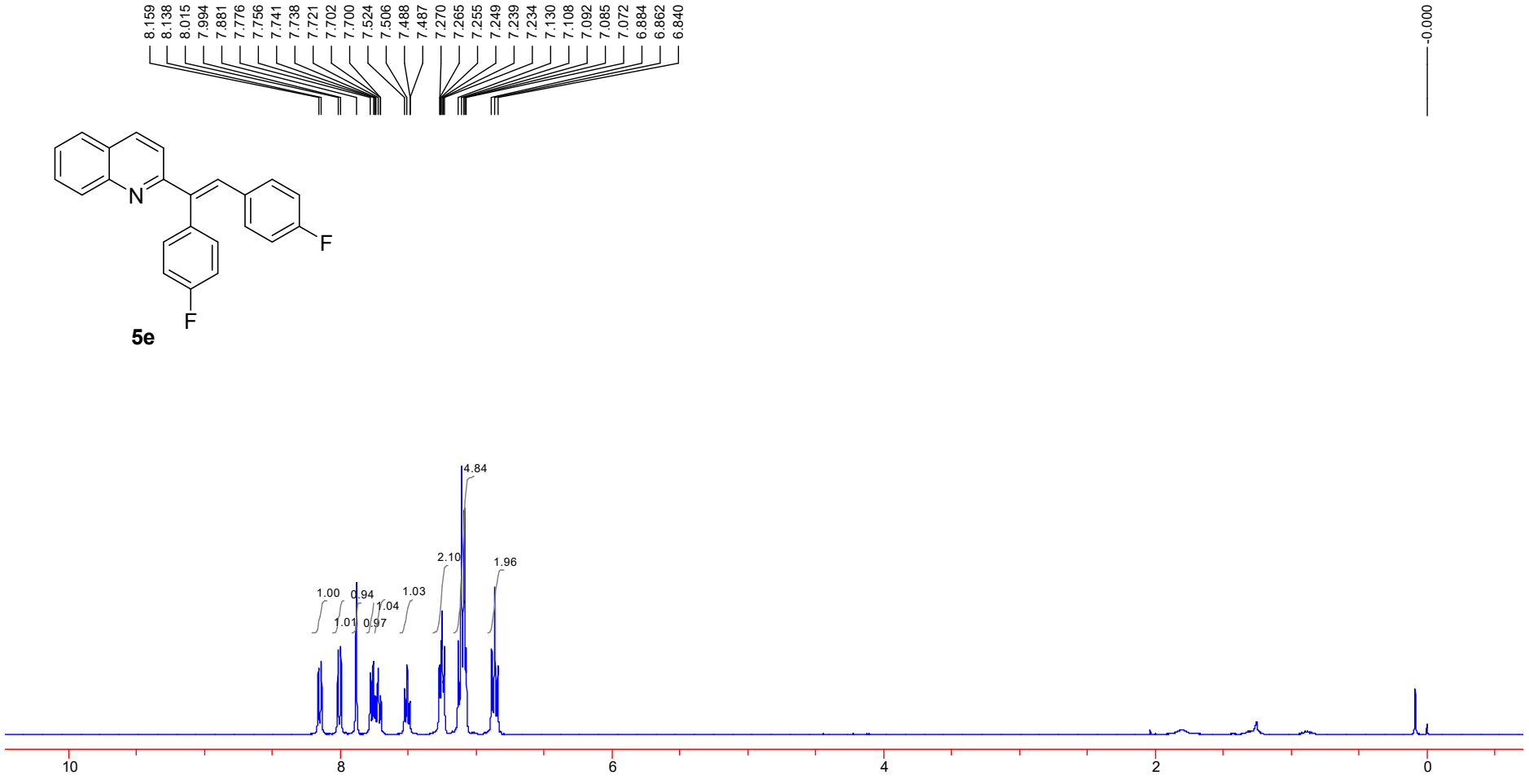
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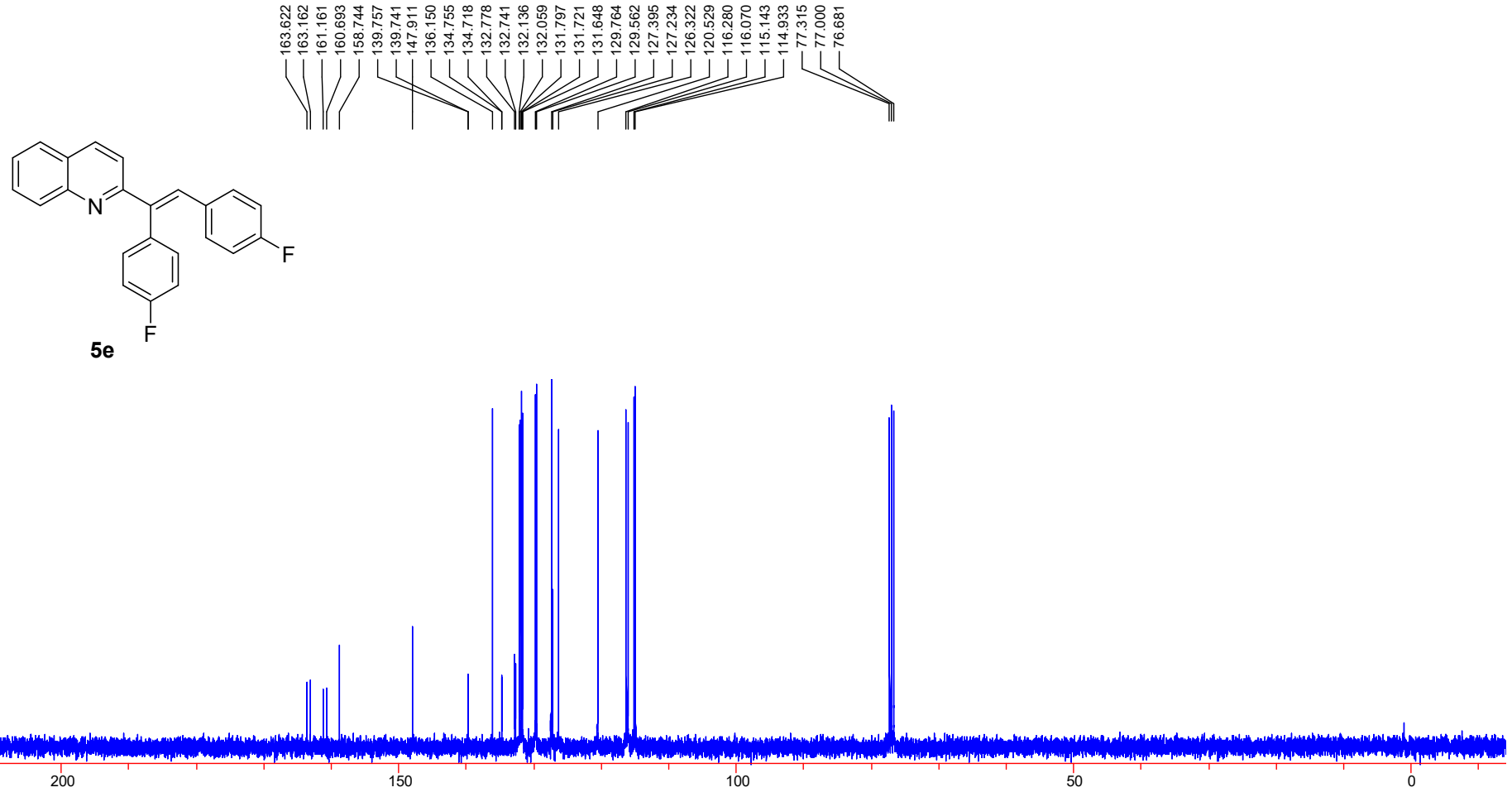
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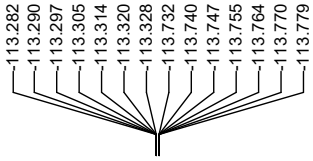
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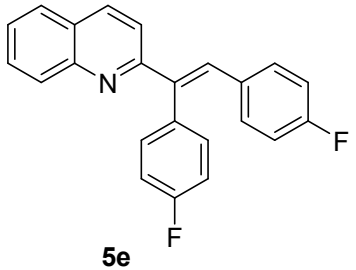
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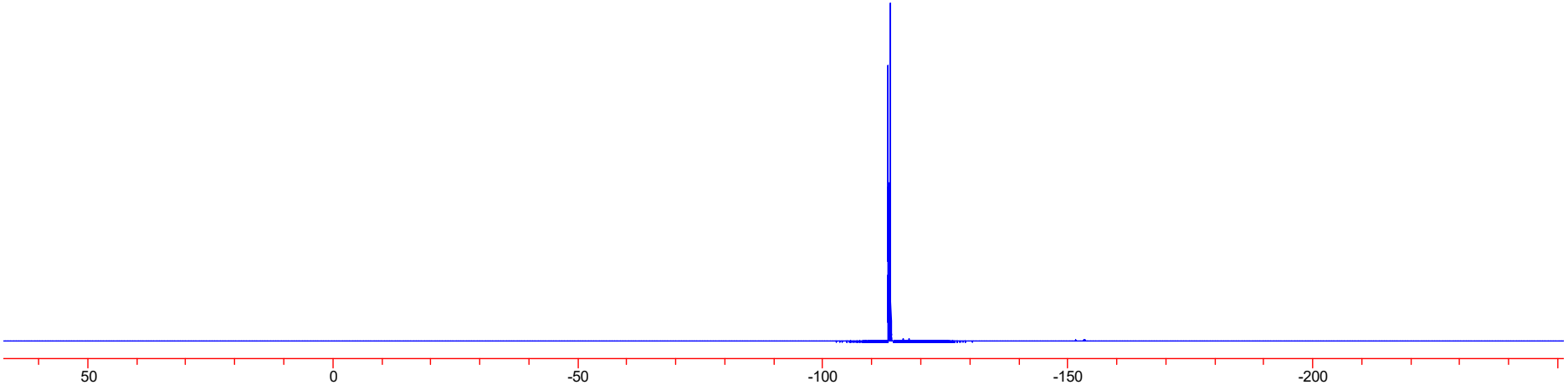
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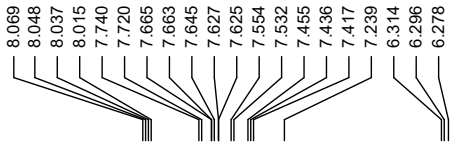
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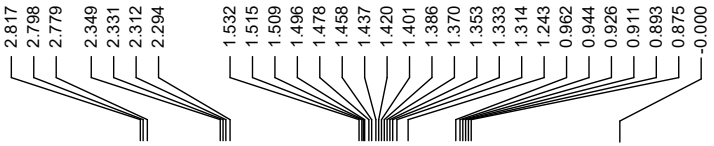
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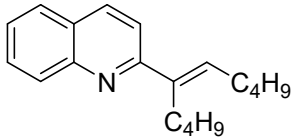
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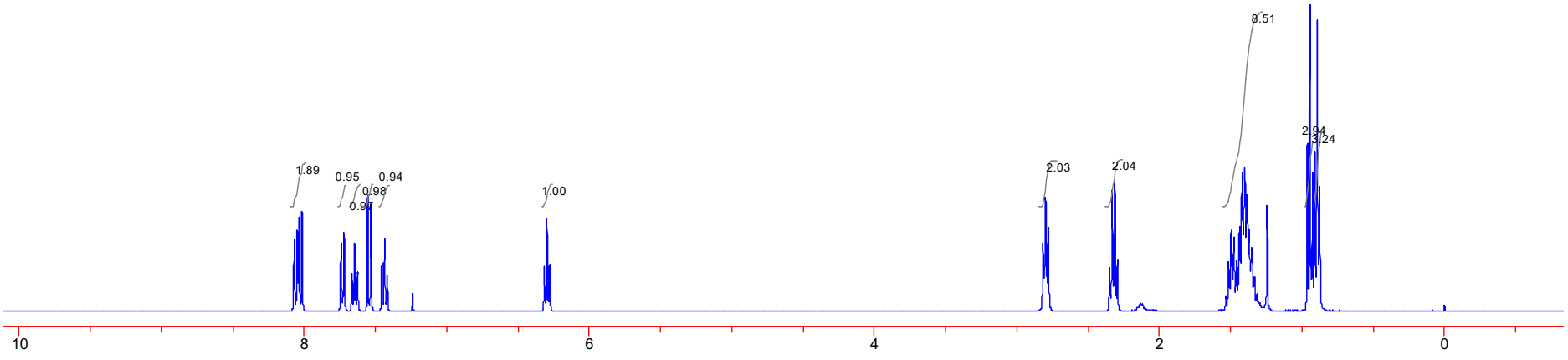
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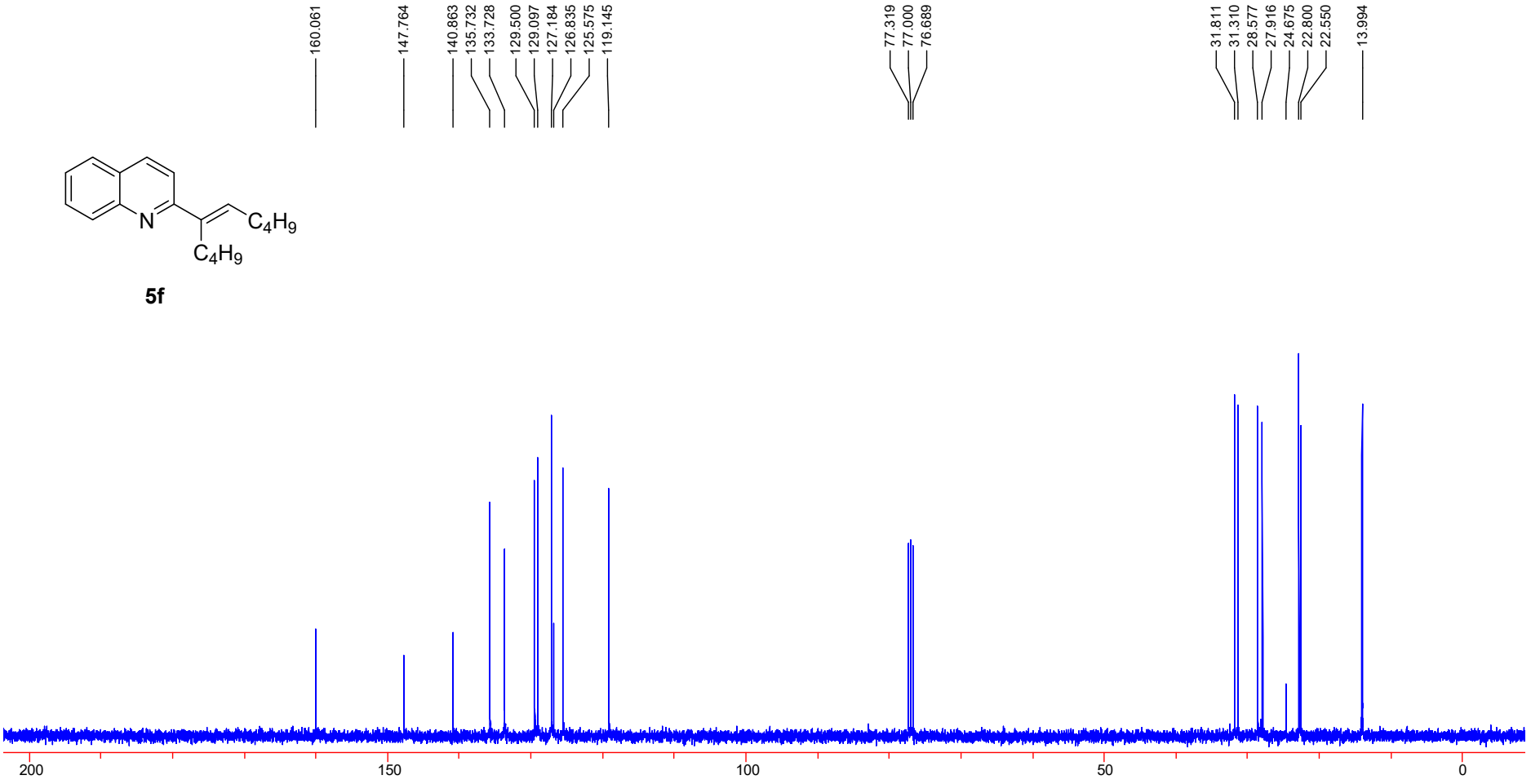
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C4H9
C4H9
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0

5f


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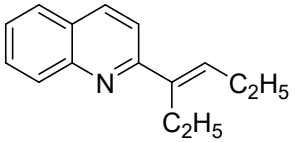
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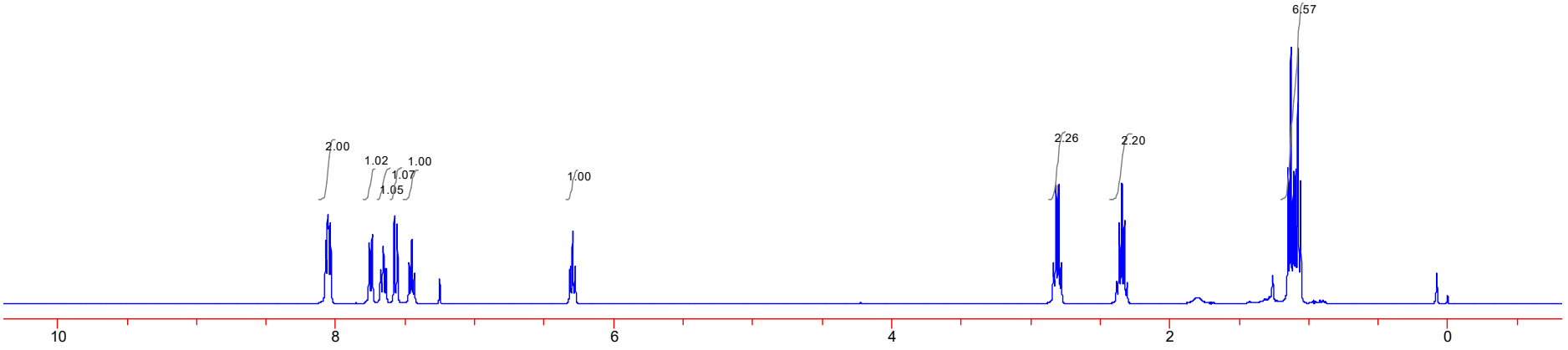
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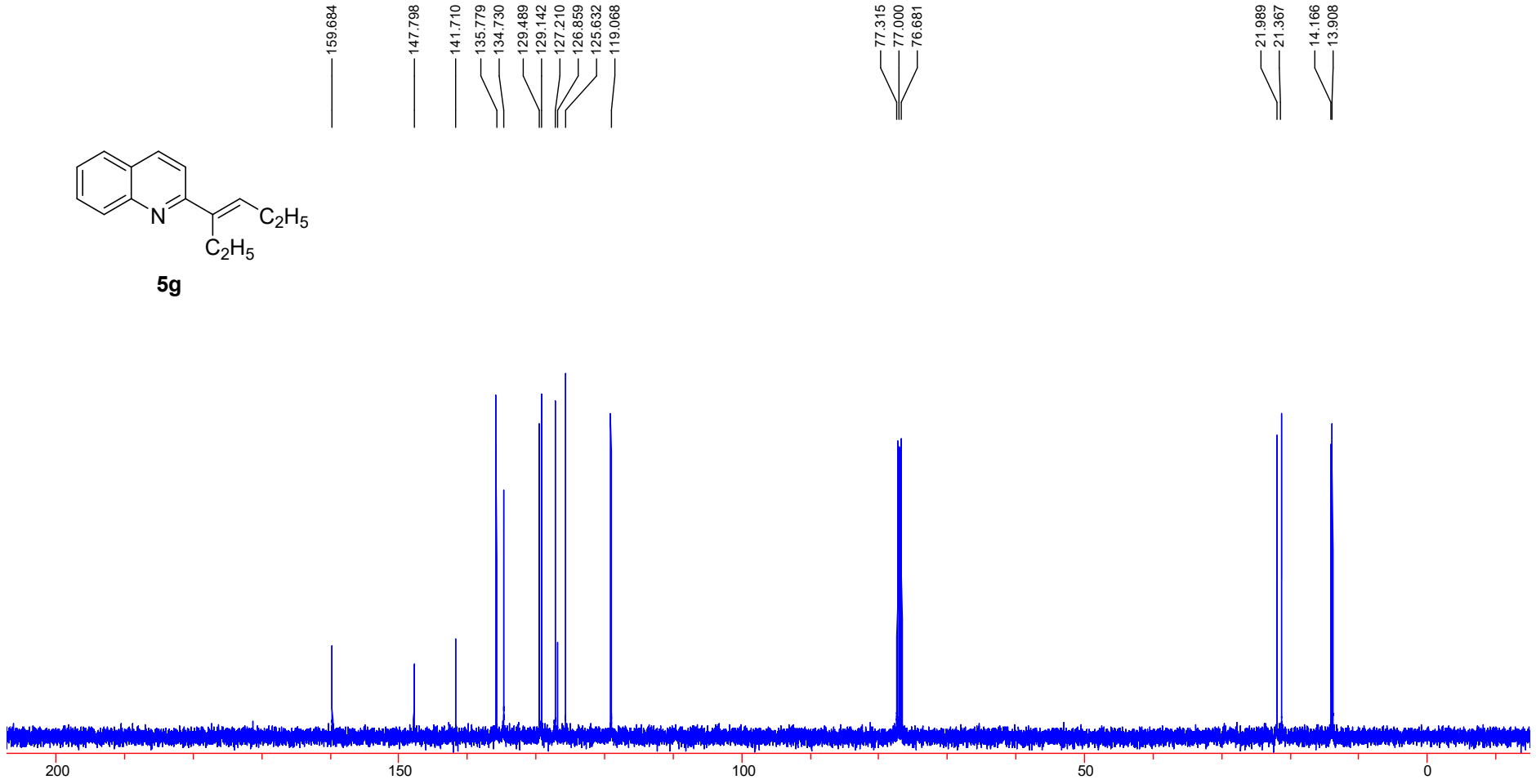
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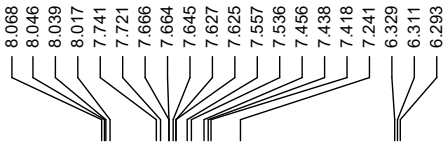
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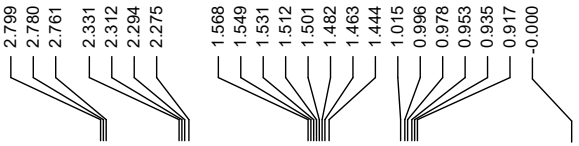
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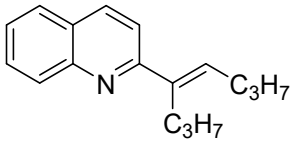
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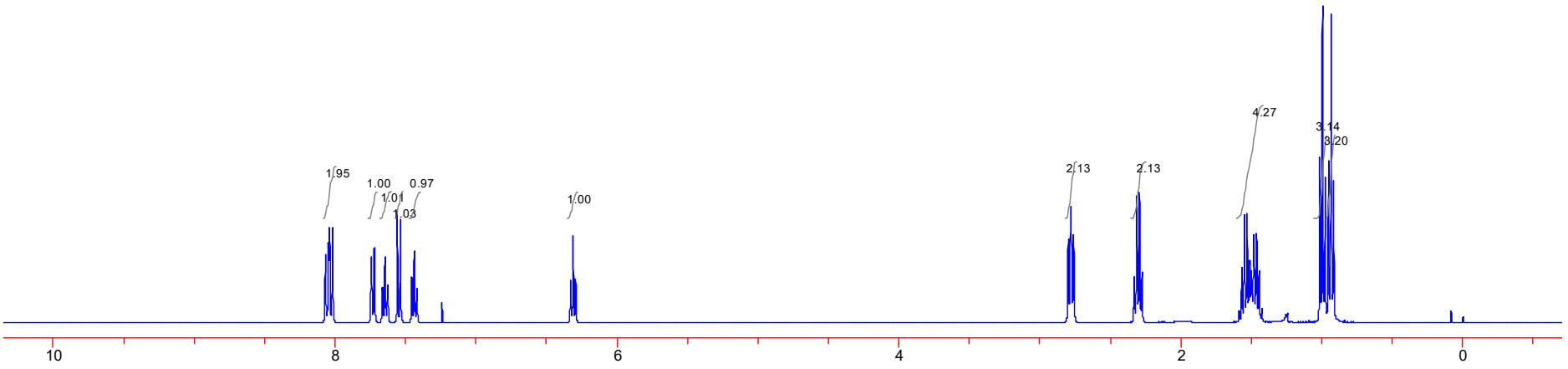
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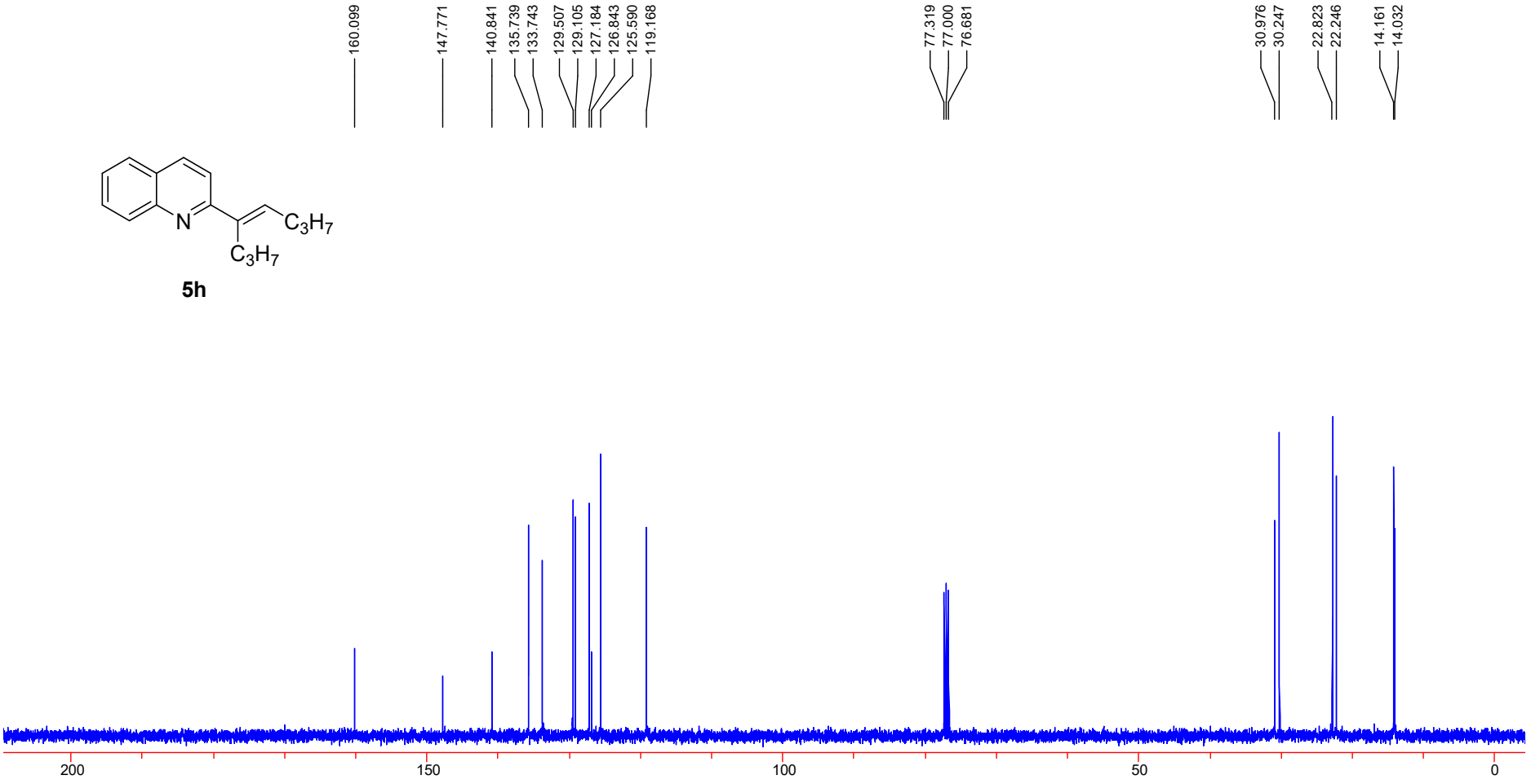
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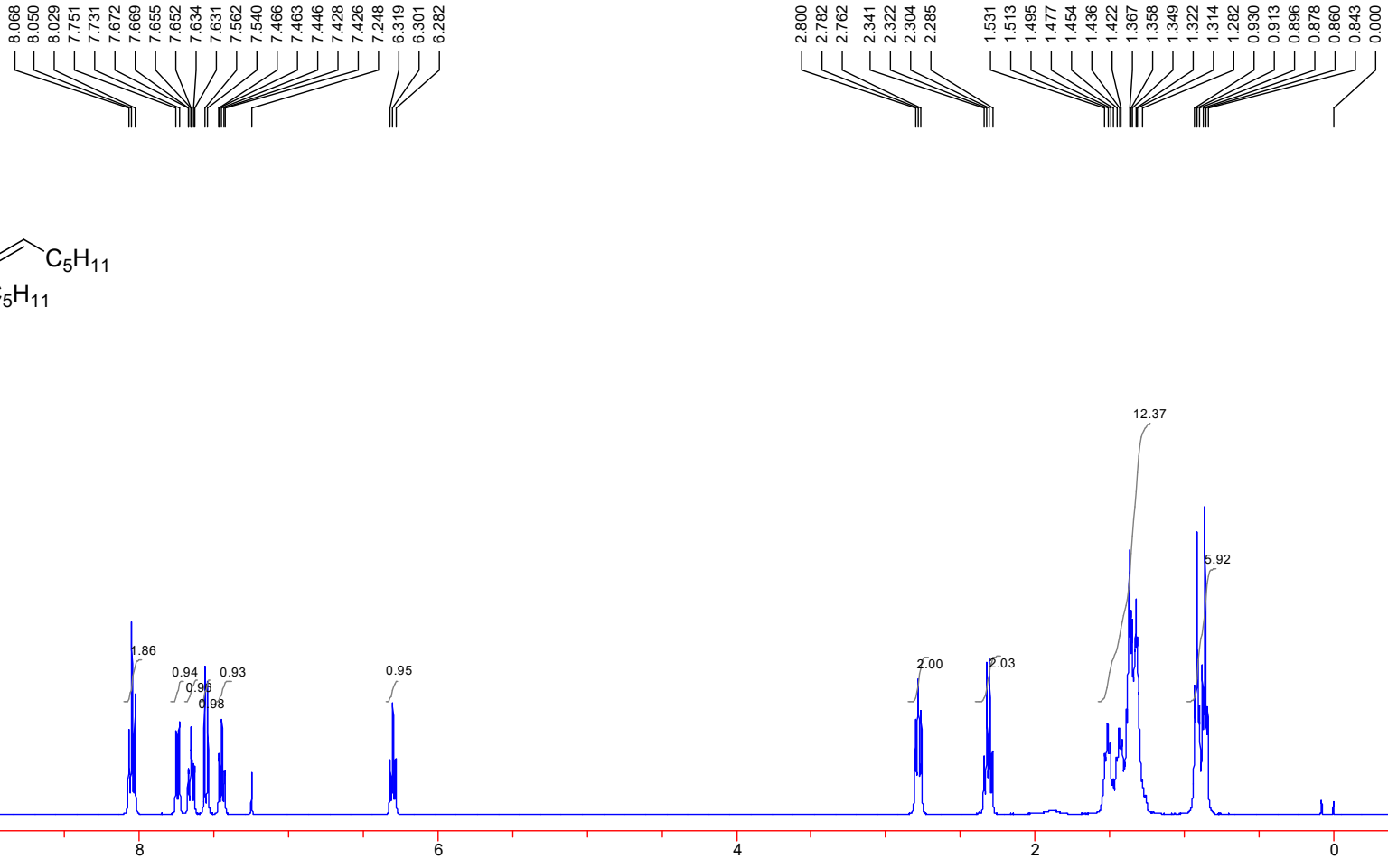
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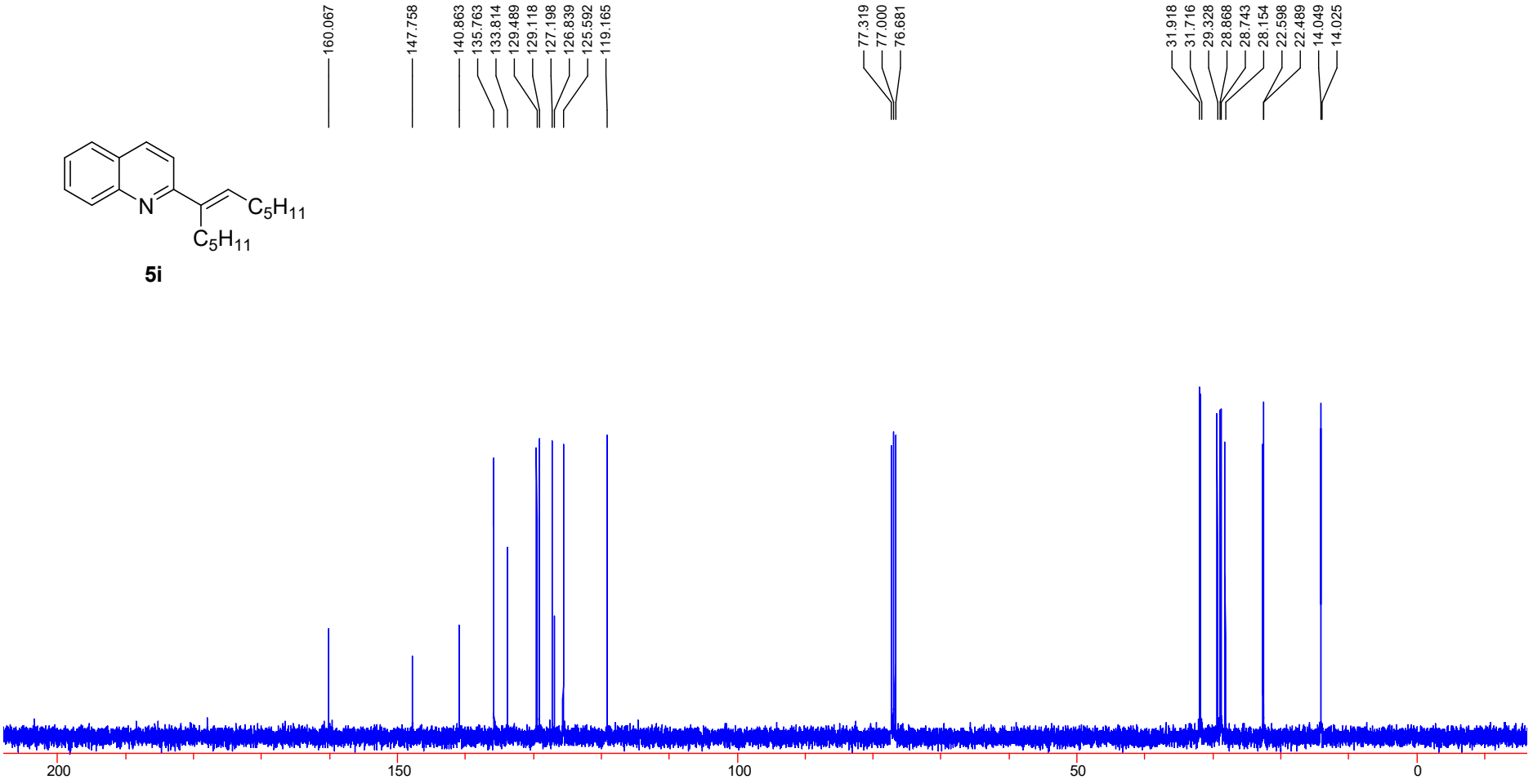
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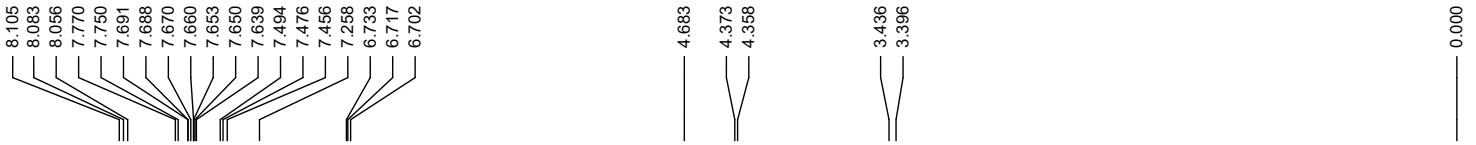
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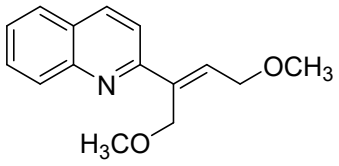
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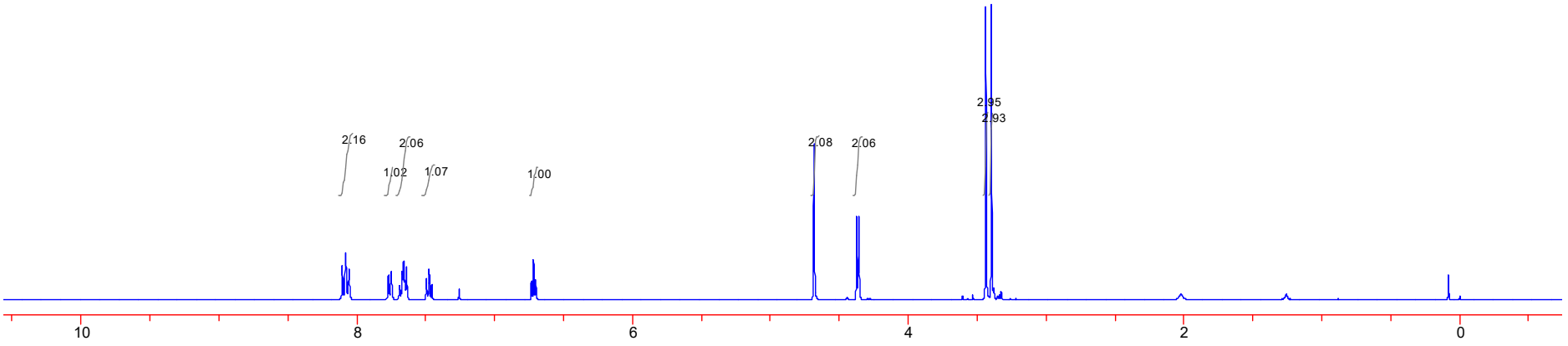
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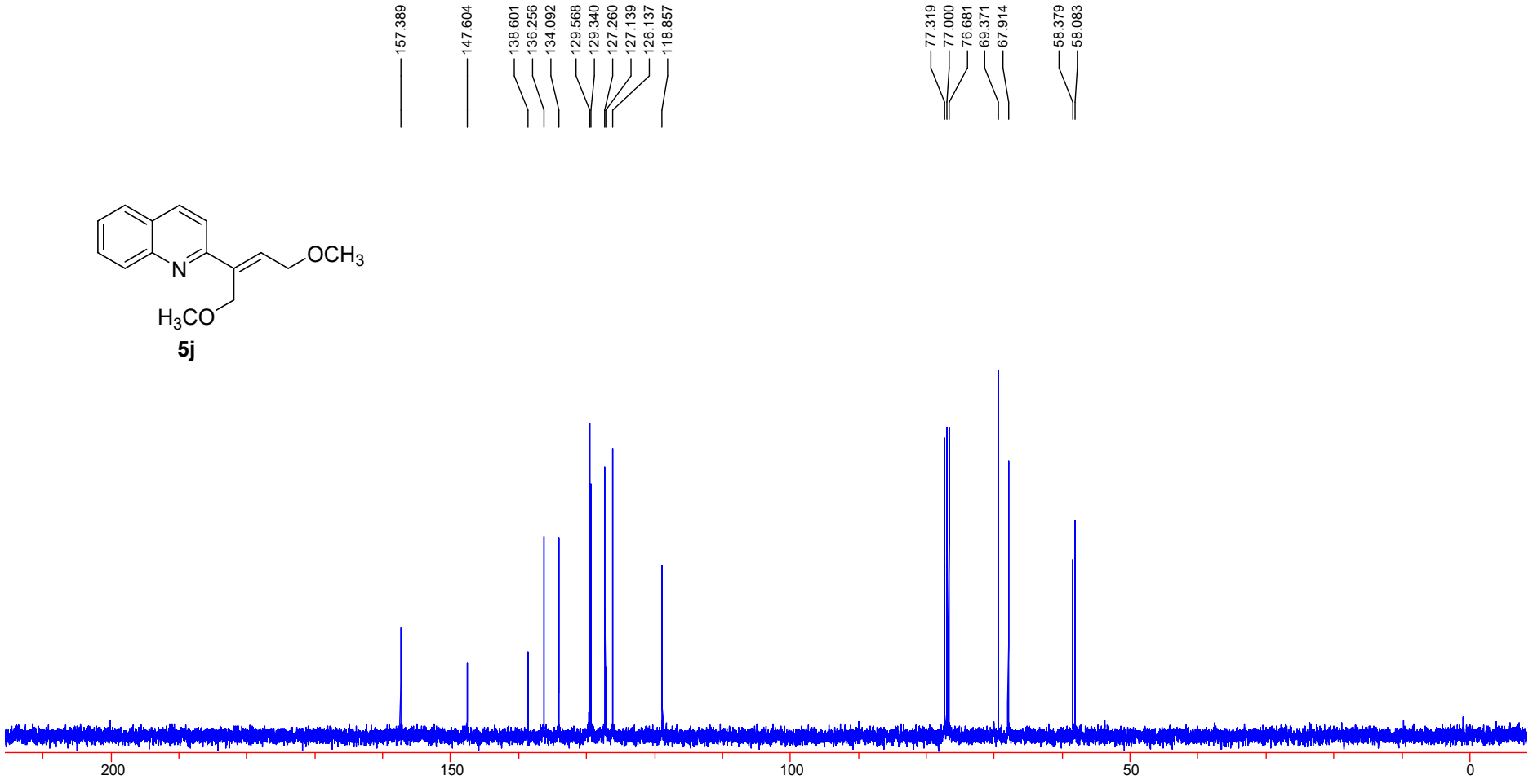
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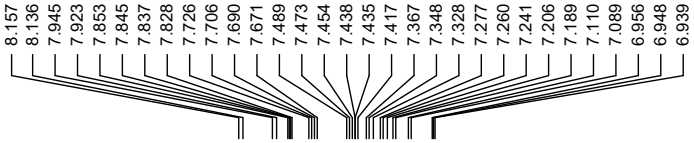
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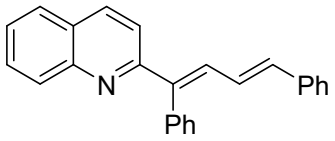
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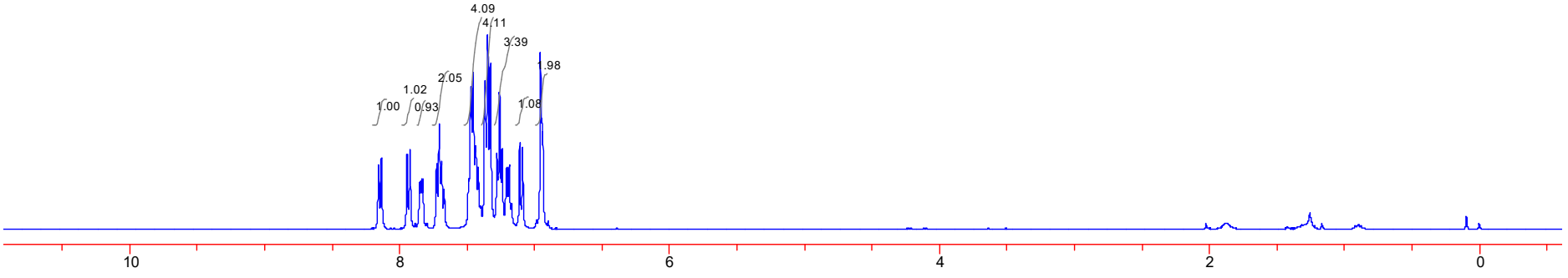
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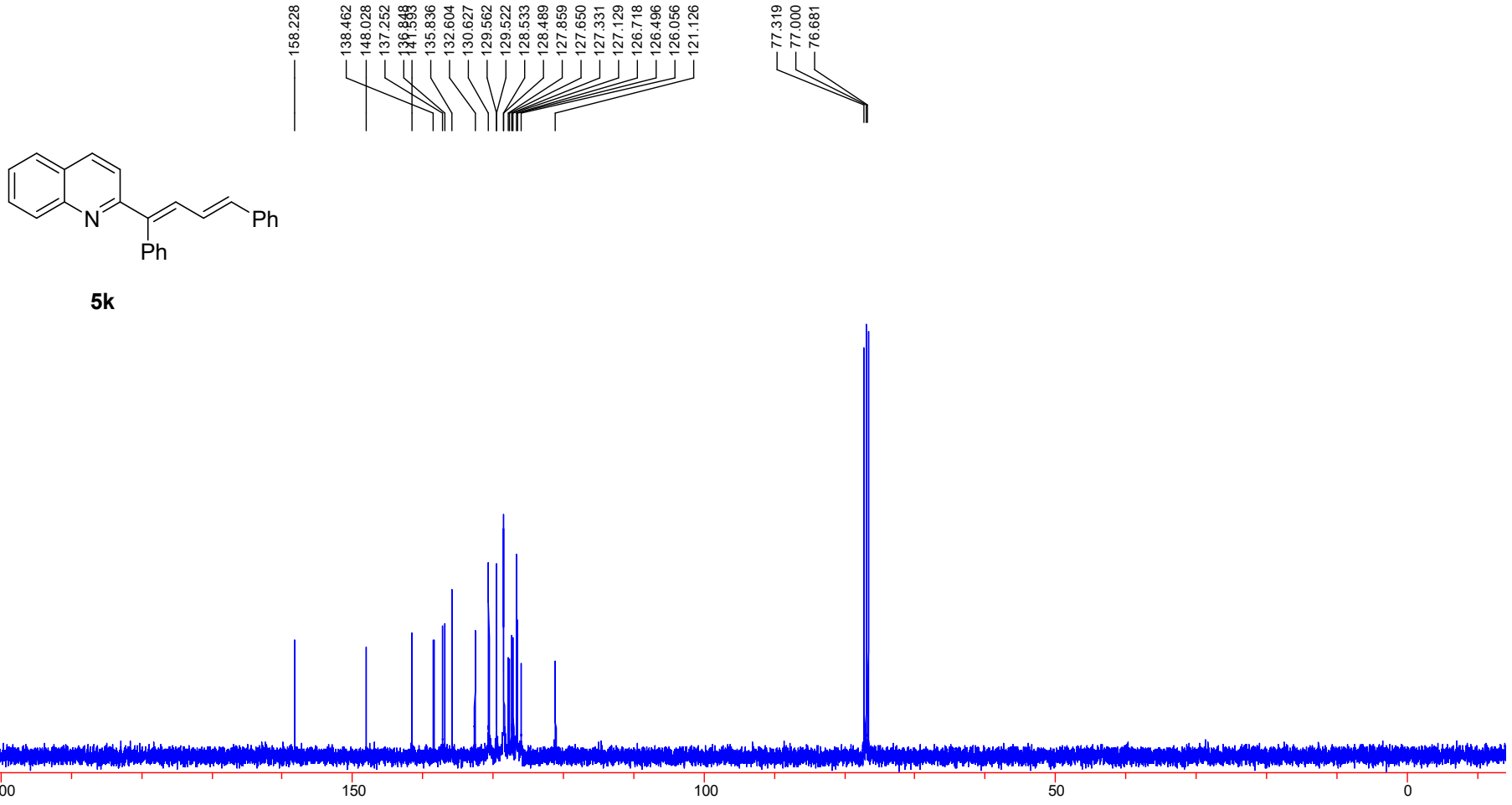
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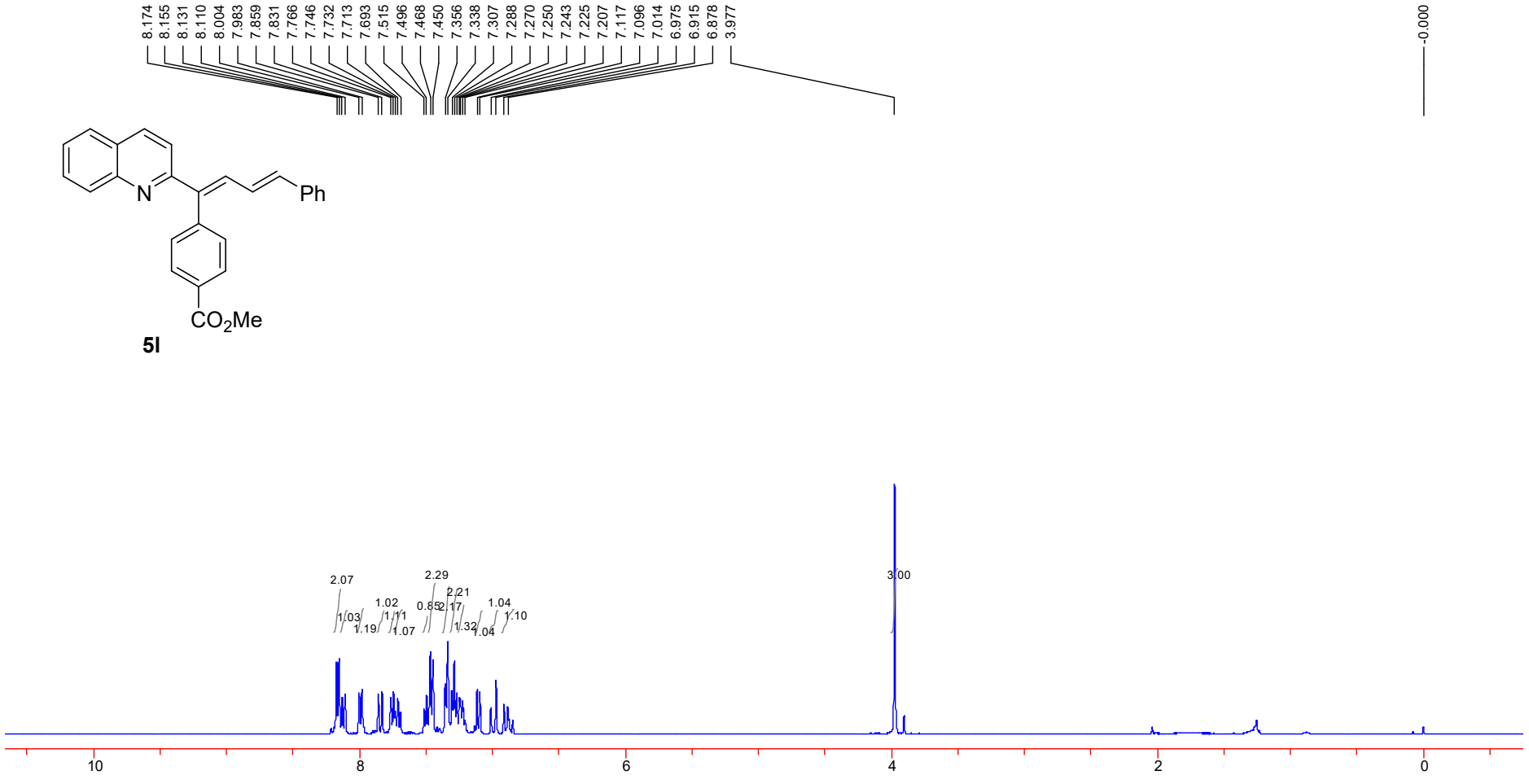
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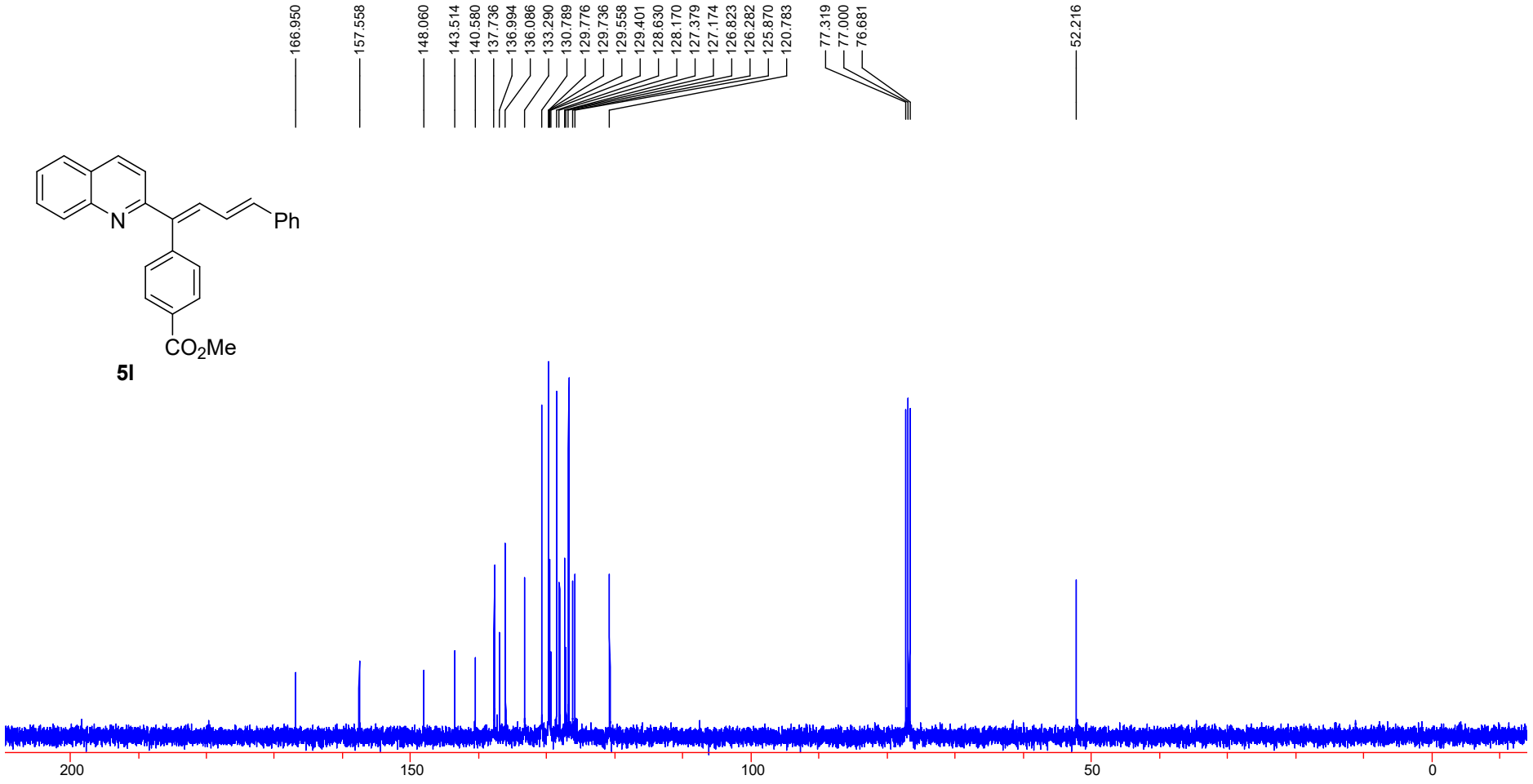
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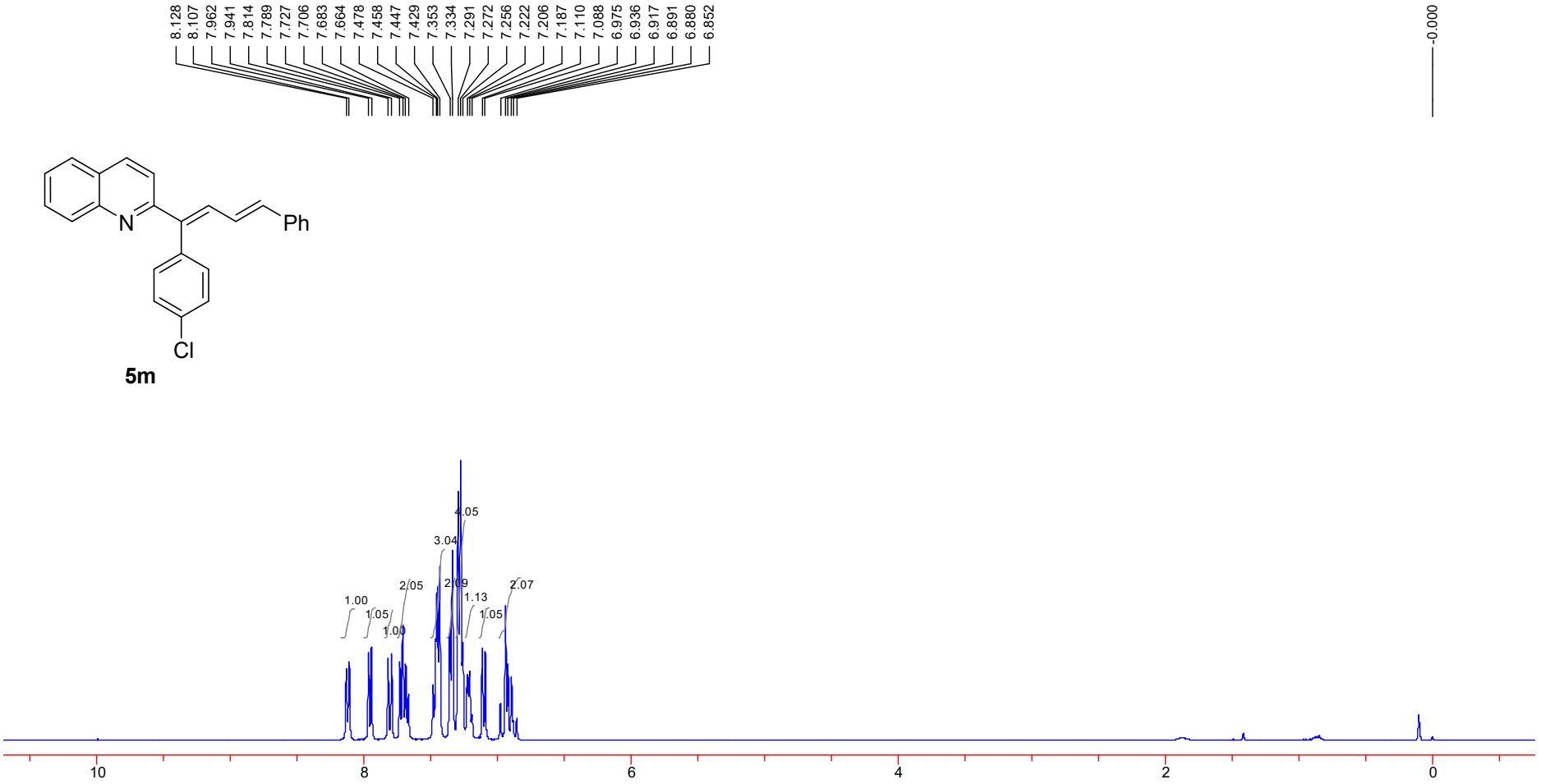
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7.222
7.206
7.187
7.110
7.088
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6.936
6.917
6.891
6.880
6.852
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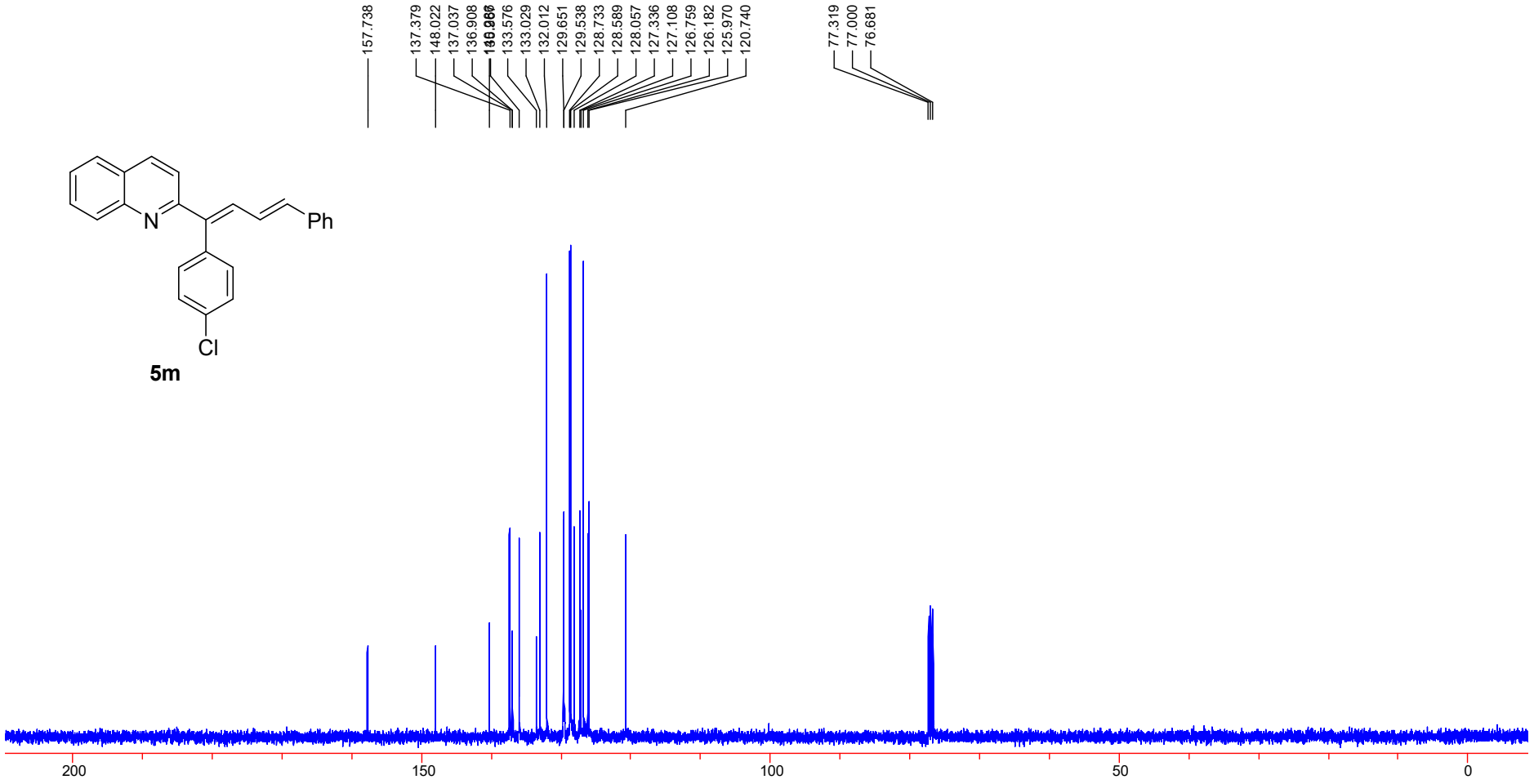
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127.108
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76.681
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Ph
Cl
5m
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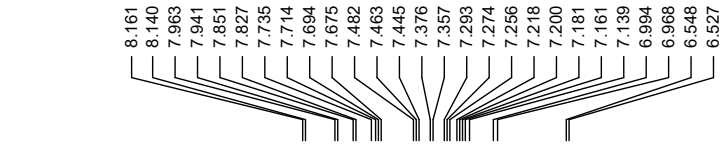
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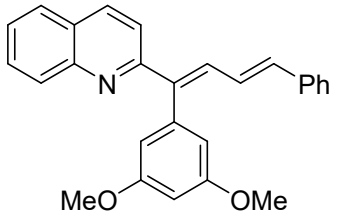
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OMe

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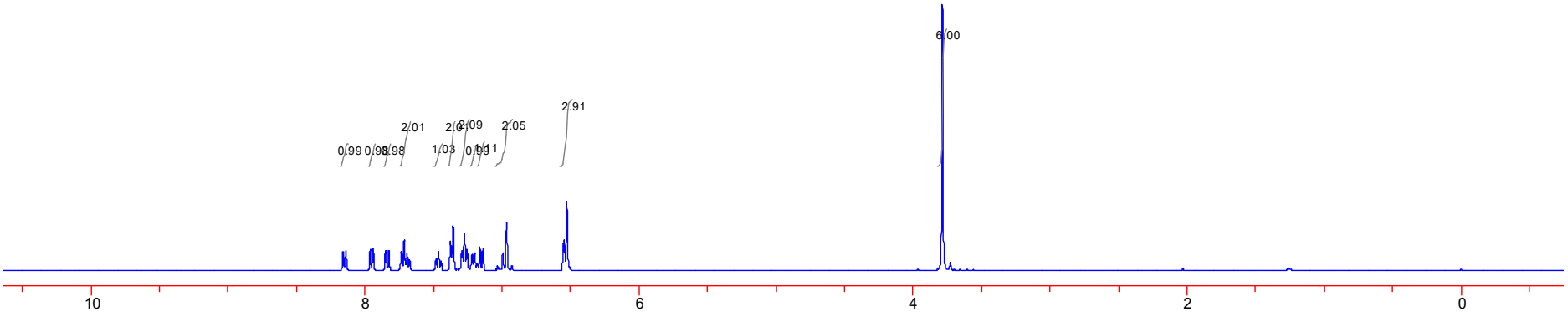
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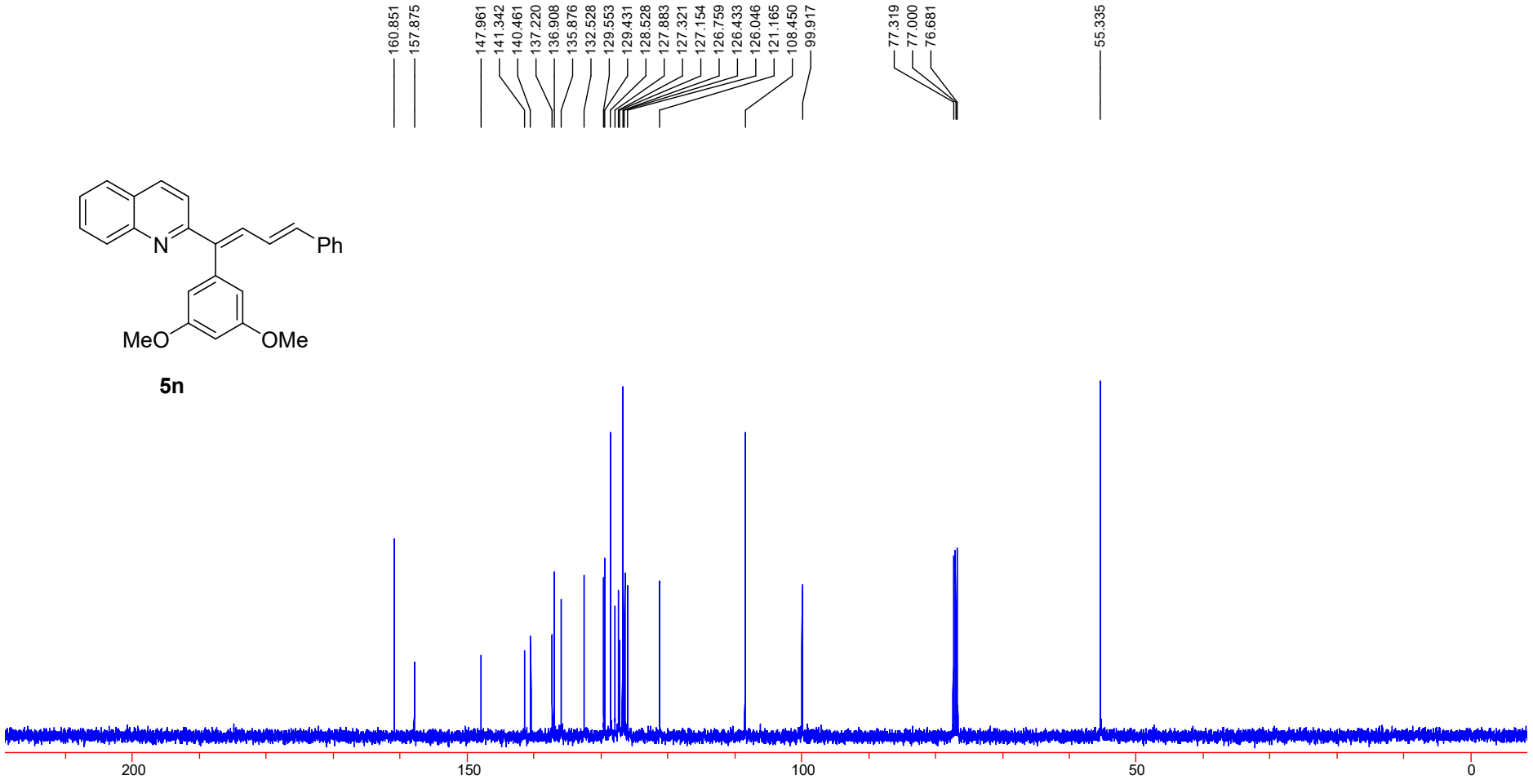
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OMe
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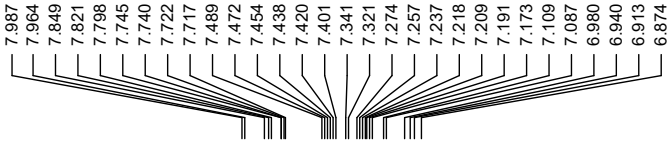
5n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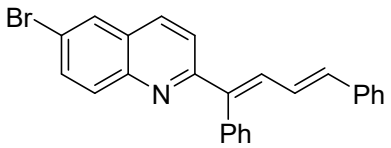
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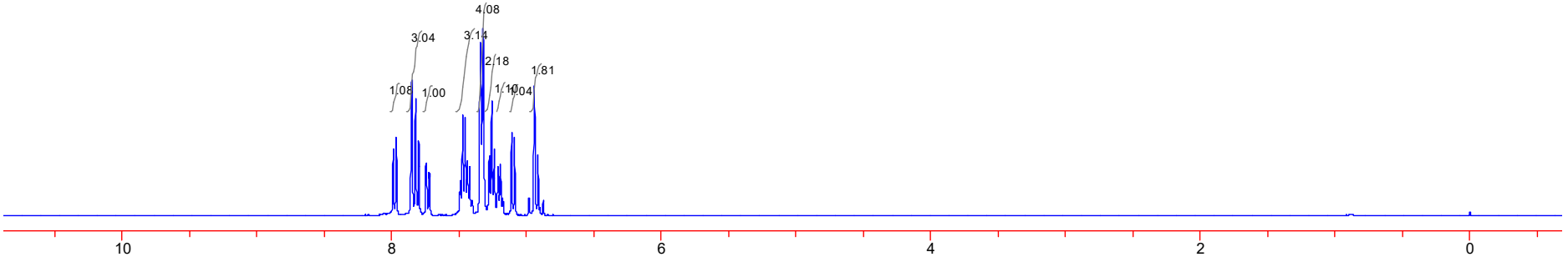
Ph
Ph

5o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1.04
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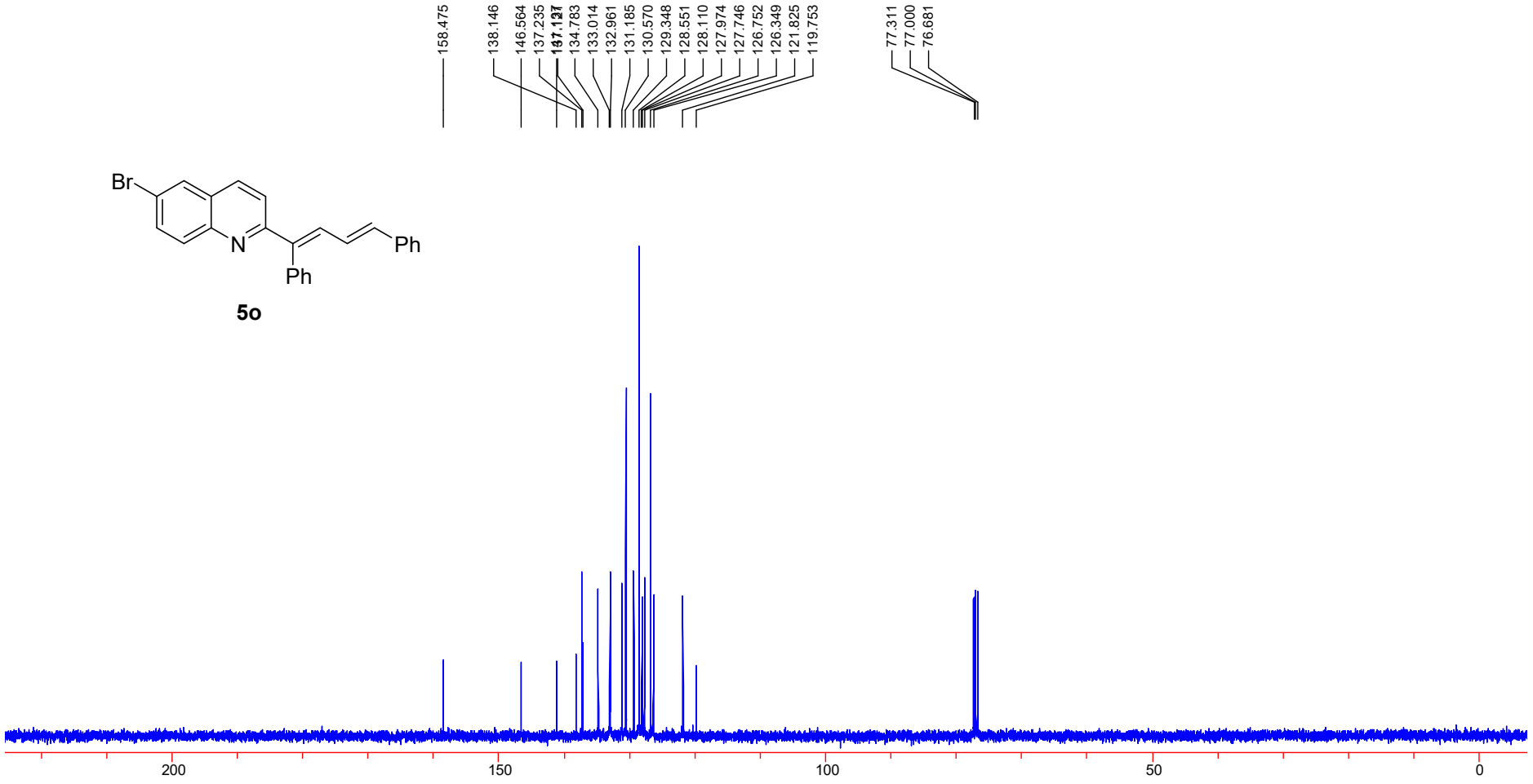
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Ph
Ph
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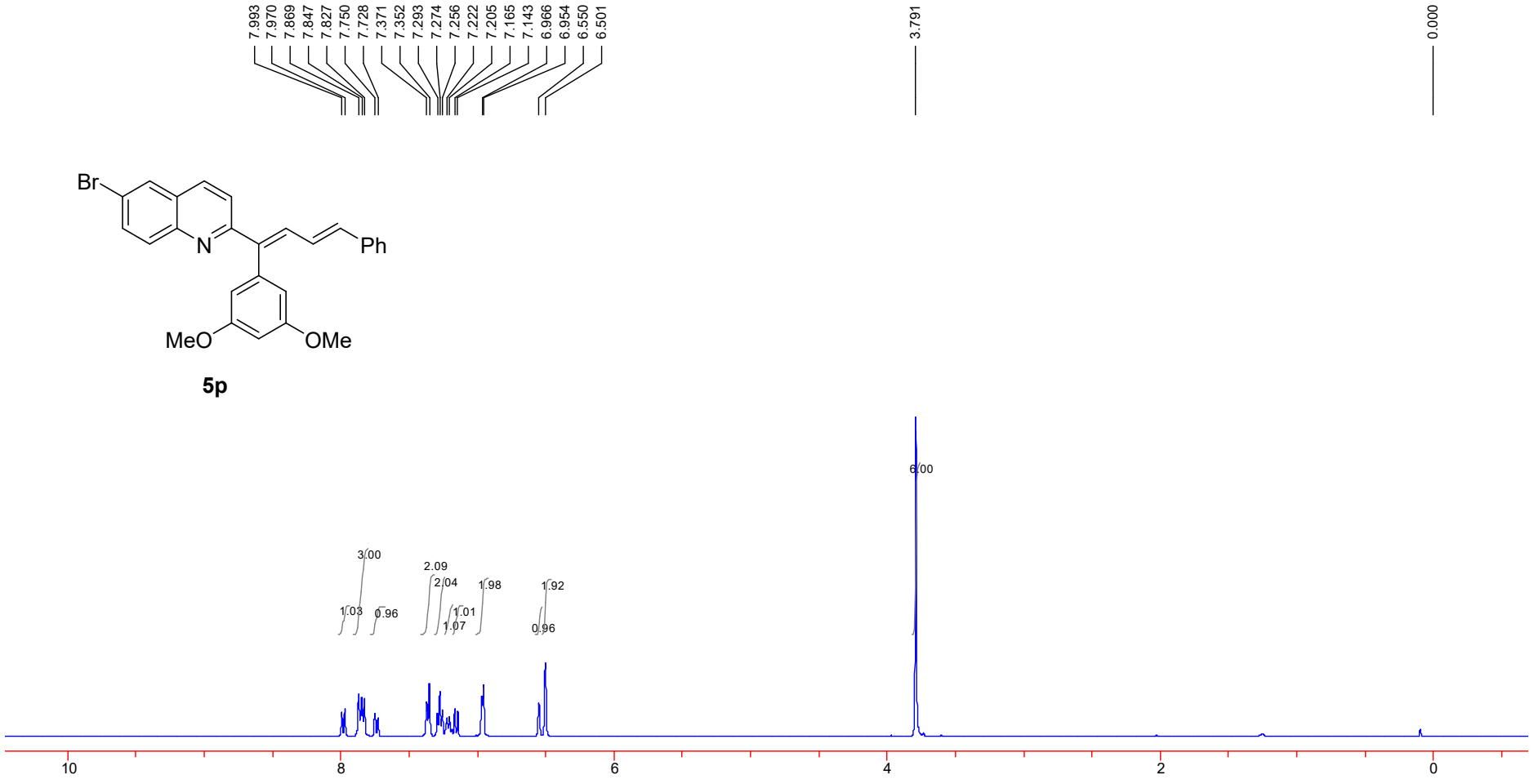
5o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6.966
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N
Ph
MeO
OMe
5p
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3.00
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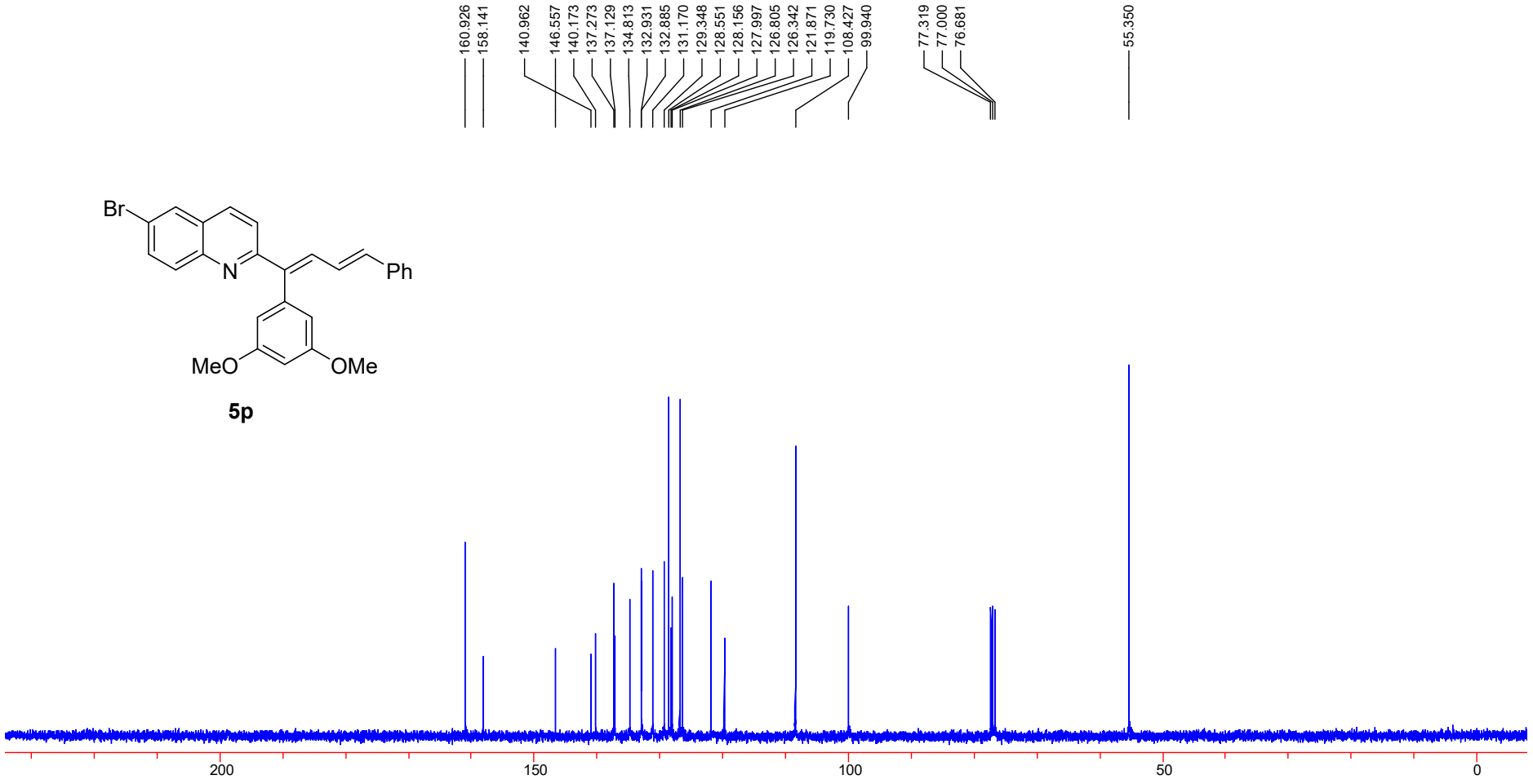
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OMe
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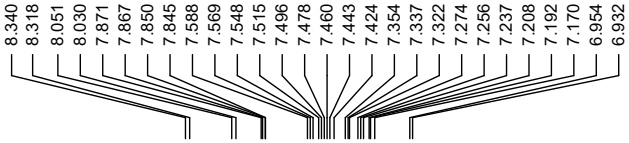
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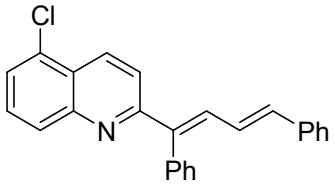
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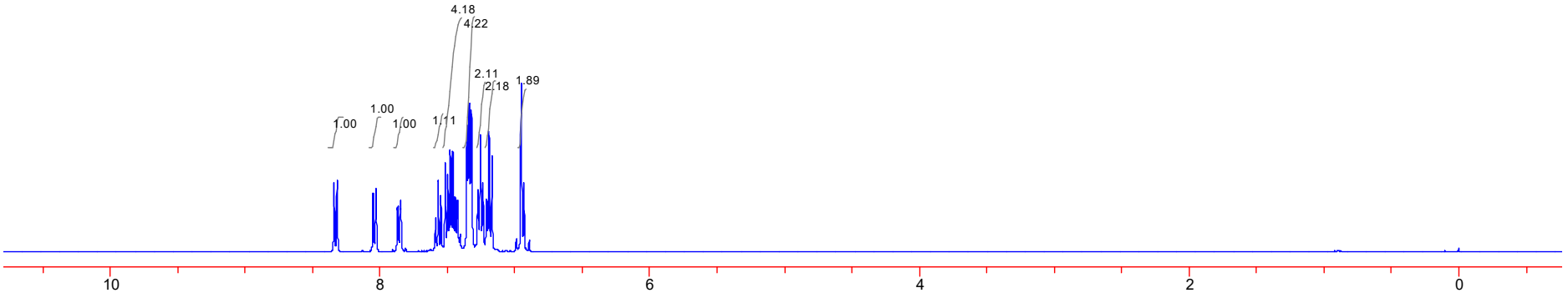
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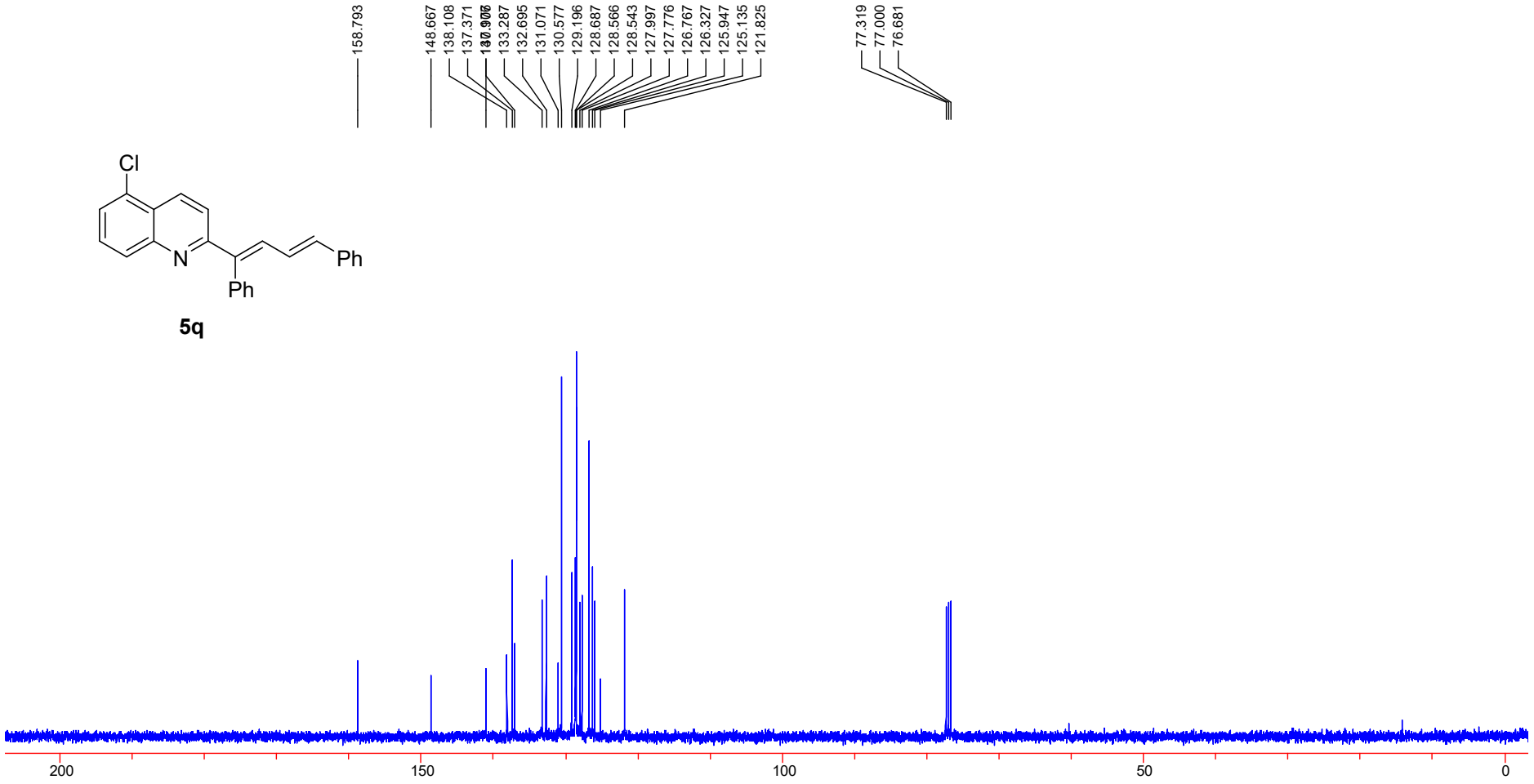
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126.767
126.327
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Ph
Ph
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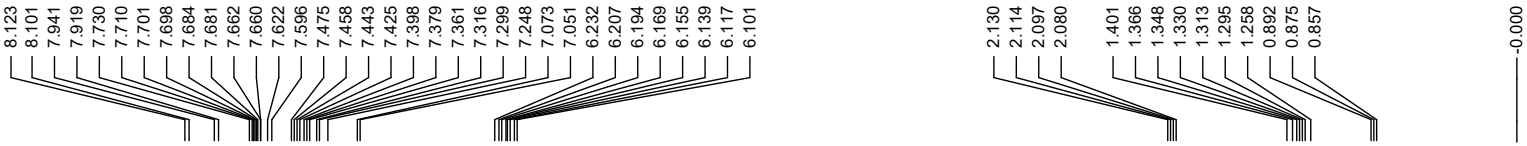
0

5q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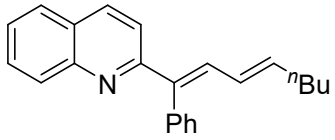
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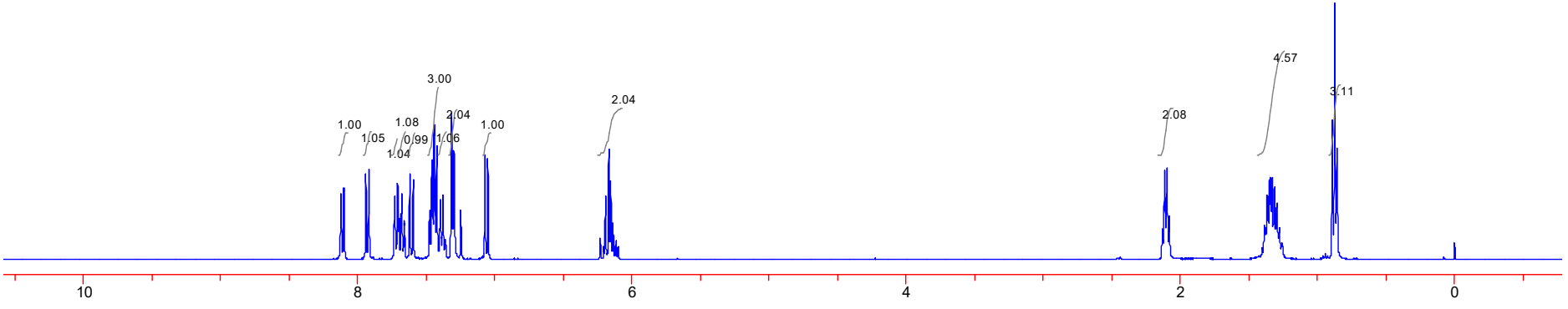
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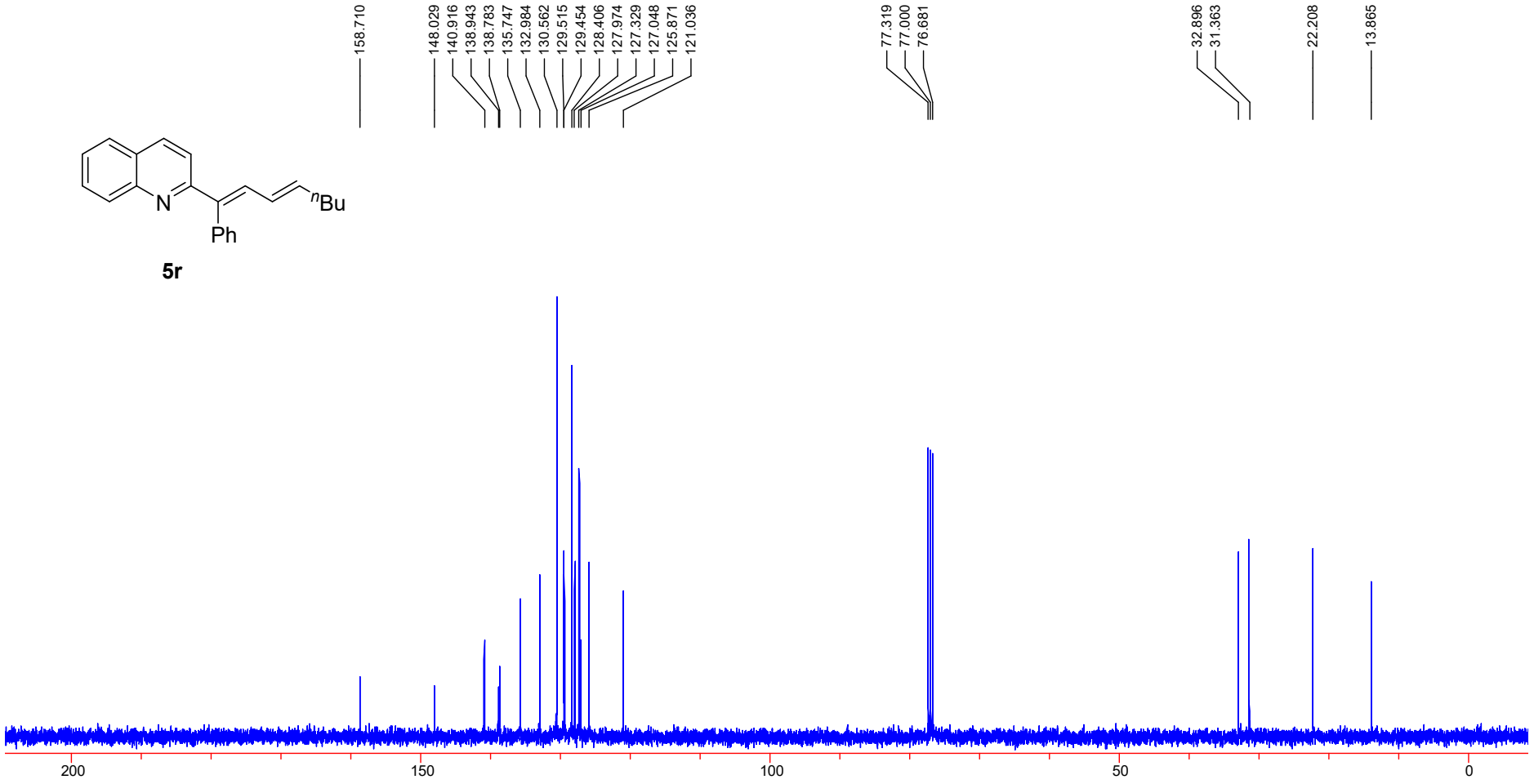
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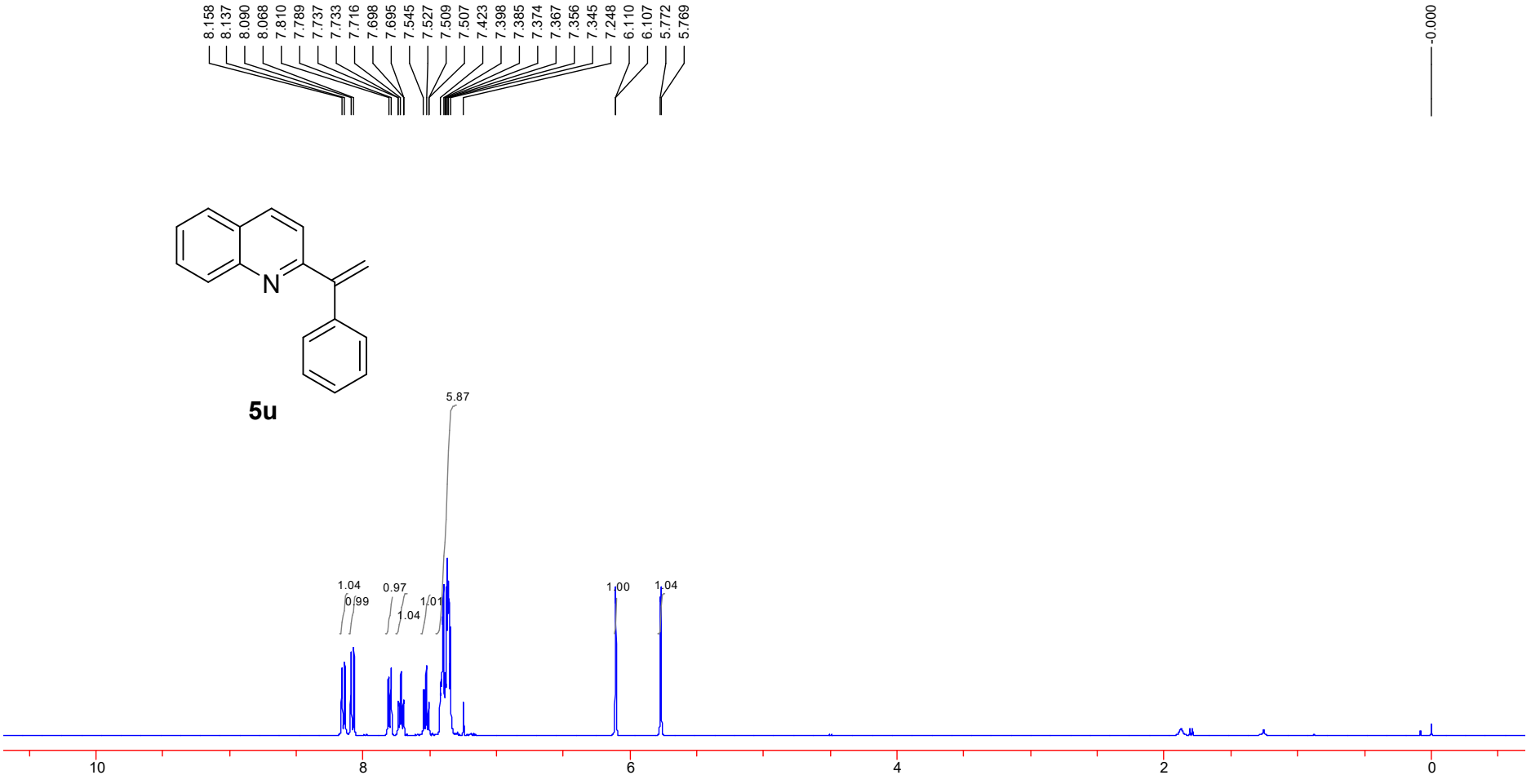
5r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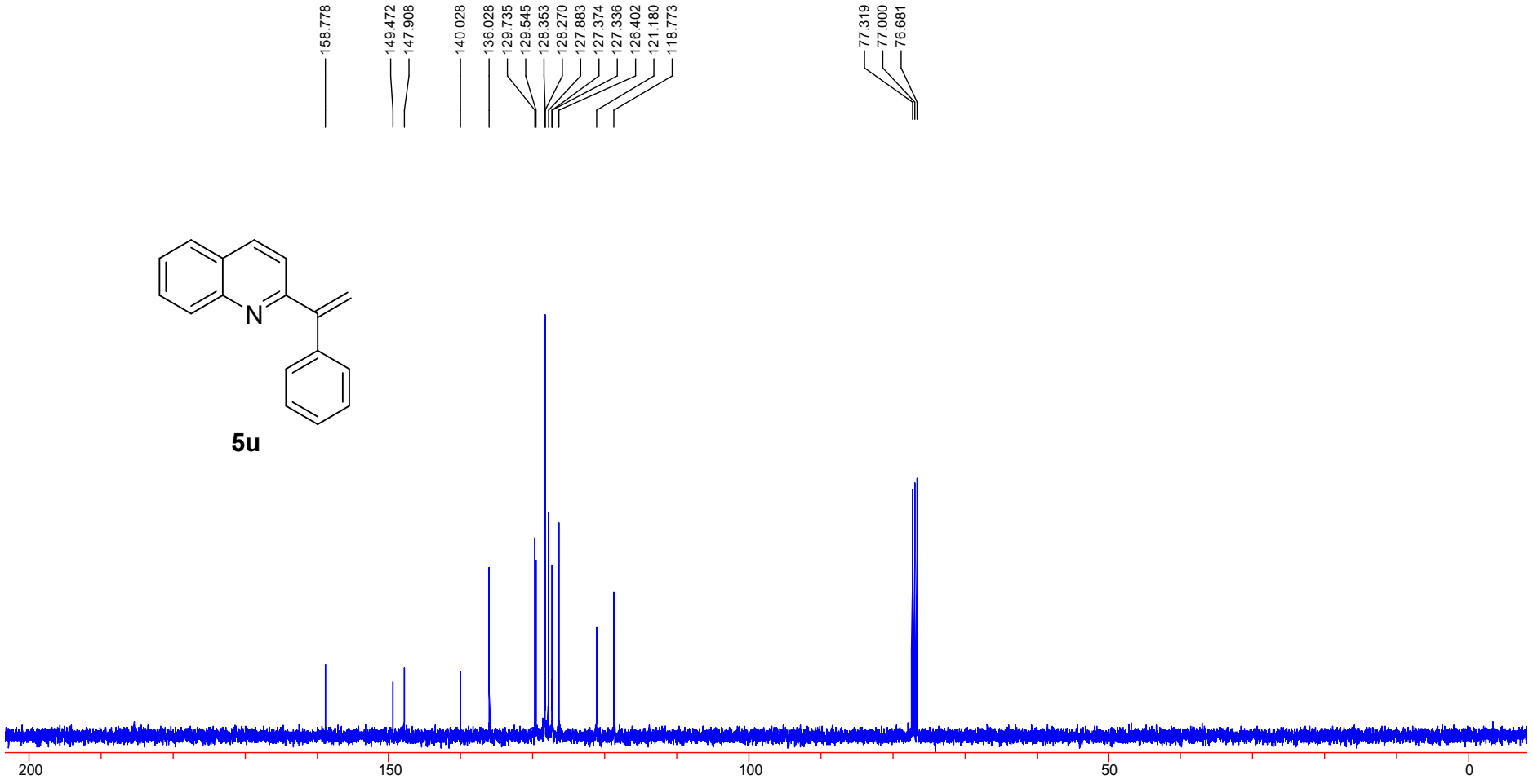
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5u
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150
100
50
0


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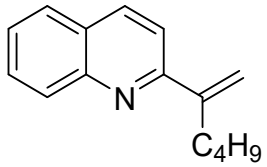
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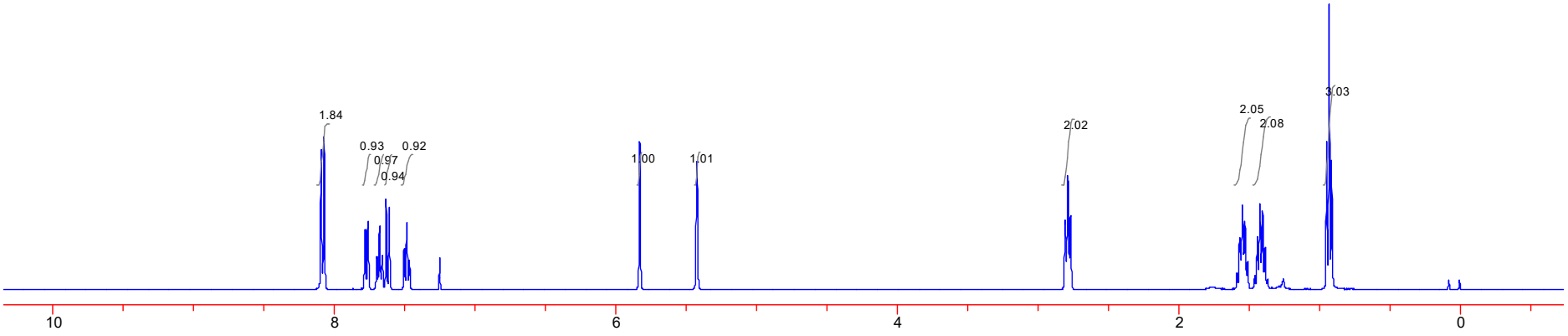
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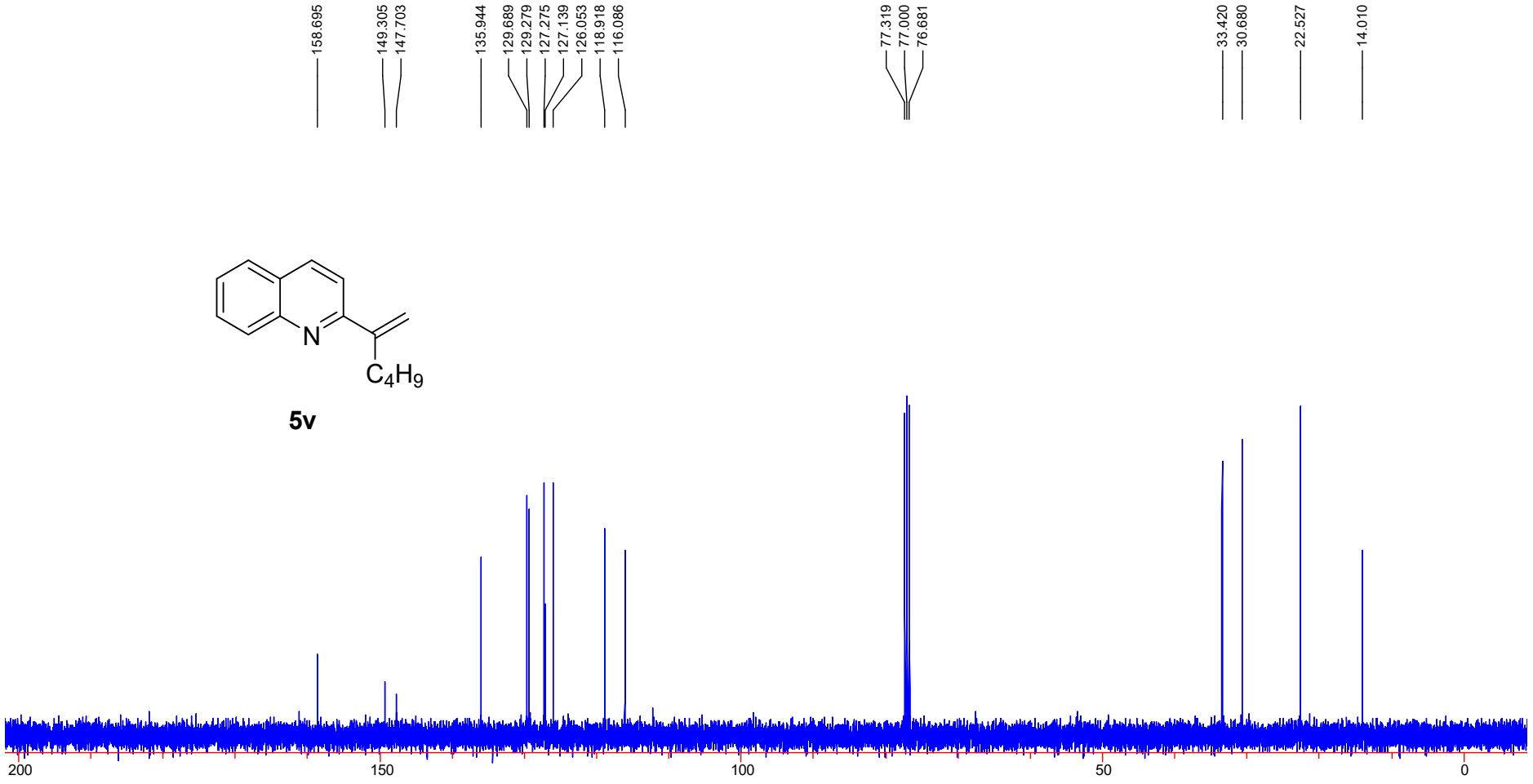
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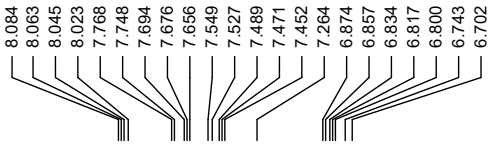
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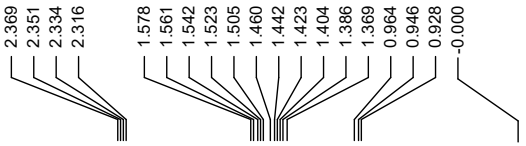
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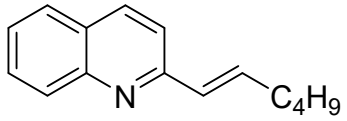
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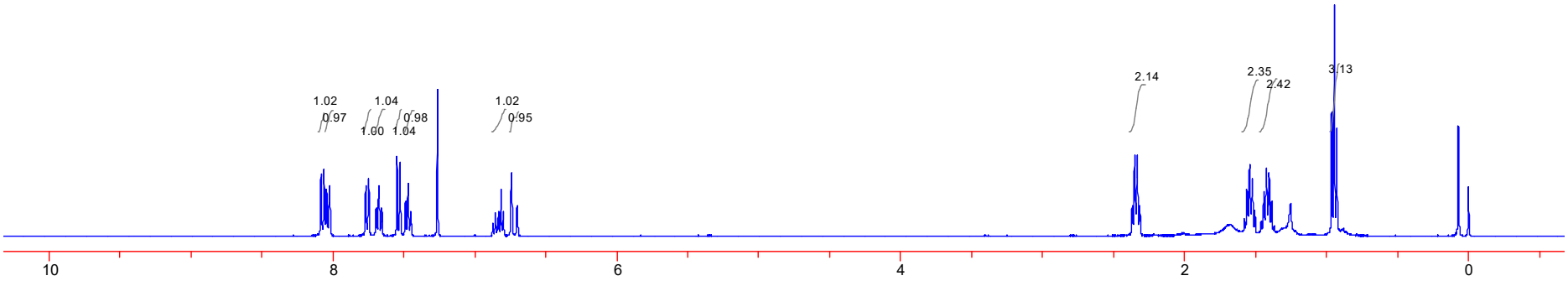
5v'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8
6
4
2
0


8.070
8.048
8.032
8.011
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7.642
7.624
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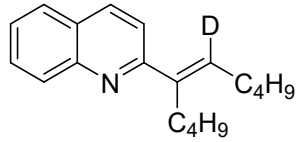
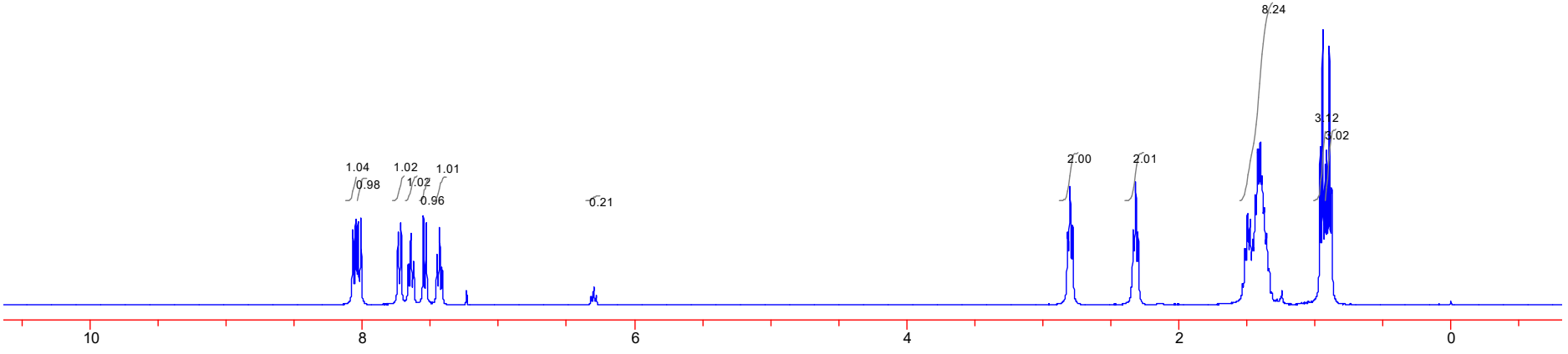

D
N
C_4H_9
C_4H_9

5f-*d*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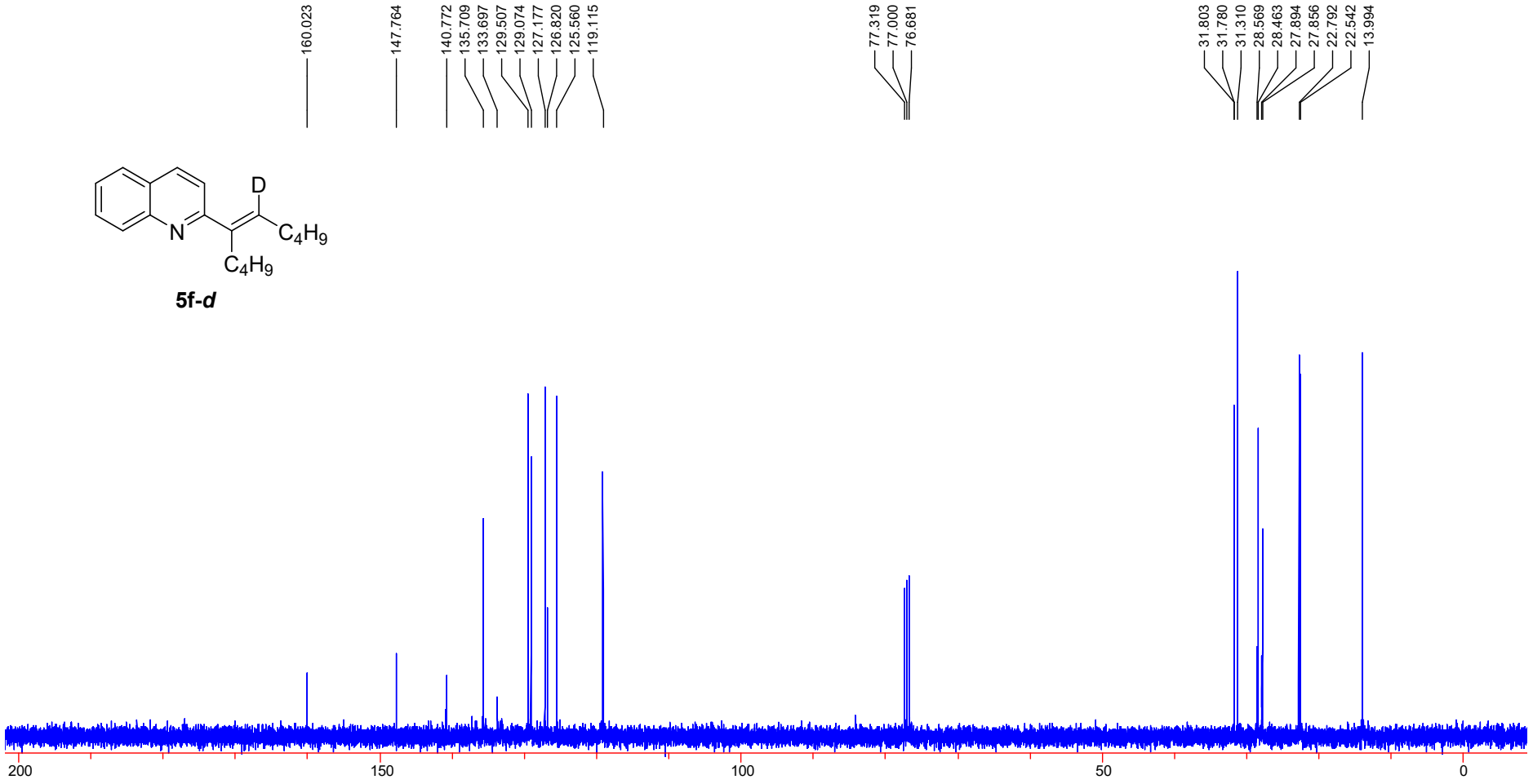
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27.894
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D
N
C4H9
C4H9
200
150
100
50
0

5f-*d*