Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Triazole-Gold Promoted Intermolecular Propargyl Alcohol Addition to Alkyne: Reaction Cascade Toward Substituted Allenes

Seyedmorteza Hosseyni,[a] Shengtao Ding,[a] Yijin Su,[b] Novruz G. Akhmedov,[b] Xiaodong Shi[a]*

[a] *Department of Chemistry, University of South Florida, Tampa, FL 33620, USA, E-mail: xmshi @usf.edu*

[b] *C.Eugene Bennett Department of Chemistry, West Virginia University, West Virginia 26506, United States.*

Supporting Information

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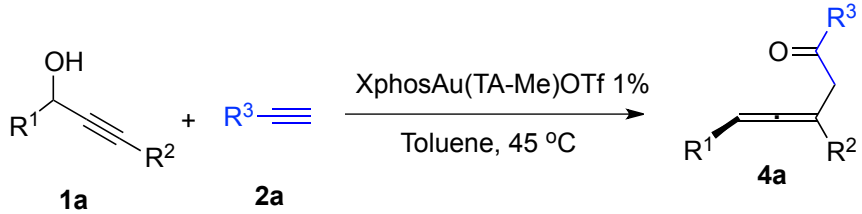
I-General Experiment Section

Unless noted, all reagents and solvents were obtained from a commercial provider and used without further purification. ^{1}H- and ^{13}C-NMR data was recorded on an Agilent 400 NMR spectrometer. Chemical shifts for starting materials and products were recorded relative to internal TMS (0.00 ppm) for ^{1}H-NMR and $CDCl_3$ (77.0 ppm) for ^{13}C-NMR data. Column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with pre- coated, glass-baked plates (250μ) and visualized by fluorescence or charring with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

General procedure for gold catalyzed addition of propargyl alcohol to alkyne toward allene

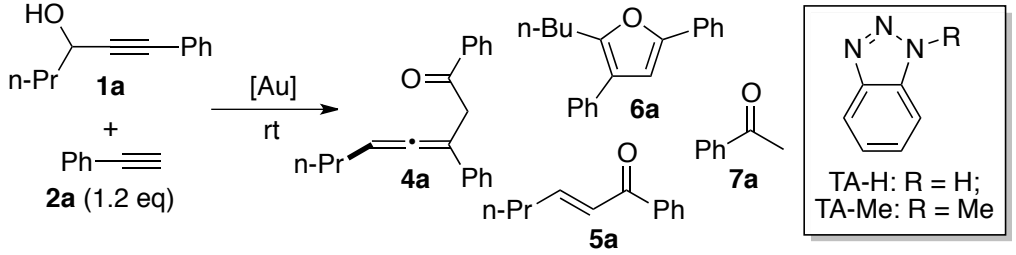


To a 2 ml vial added 0.7 ml of toluene charged with 0.5 mmol of propargyl alcohol and 0.9 mmol of alkyne and then 0.005 mmol of the XphosAu(TA-Me)OTf in room temperature. The resulting mixture stirred at 45 ºC until the TLC showed the complete consumption of **1a**. The reaction mixture was directly loaded on column chromatography on silica gel for purification by hexane/ethyl acetate as solvent to give the desired product. :

Procedure for Synthesis of XPhosAu(TA)OTf

A 20 mL screw-cap vial was charged with XPhosAuCl (355 mg, 0.5 mmol) and benzotriazole (1.1 equiv.) in dry DCM (10 mL), followed by the addition of AgOTf (1.05 equiv.). The vial was allowed to stir at ambient temperature. After 4h, the reaction mixture was filtered through three celite pads and concentrated *in* vacuum to give the product as foam. Pure catalyst was obtained via recrystallization through diffusion of hexanes into DCM solution of crude product.

Effects of variation of reaction conditions



[Au] cat.	Solvent	Time (h)	Conv of 1a (%)	4a	6a	5a	7a
$PPh_3AuCl/AgOTf$ (5%)	dioxane	6	50	0	0	41	39
PPh_3AuNTf_2 (5%)	dioxane	6	83	0	0	72	48
PPh_3AuNTf_2 (5%)	toluene	12	66	0	7	28	65
$IPrAuNTf_2$ (5%)	toluene	12	67	0	6	18	65
$JohnPhosAuNTf_2$	toluene	12	70	0	11	23	72
$XPhosAuNTf_2$ (5%)	toluene	12	76	9	27	16	82
$(ArO)_3PAuNTf_2$ (5%)	toluene	12	77	0	6	24	60
$[(Ph_3PAu)_3O]^+SbF_6^-$ (5%)	toluene	14	25	12	Trace	<5	<10

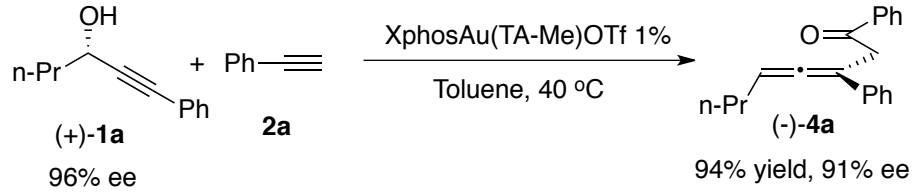
[XPhosAu(MeCN)]$^{+}$TfO^{-}(5%)	toluene	14	70	25	20	25	25
[XPhosAu(TA-H)]$^{+}$TfO^{-} (5%)	toluene	14	100	55	28	<5	10
[XPhosAu(TA-Me)]$^{+}$TfO (5%)	toluene	14	82	77	0	0	21
[XPhosAu(TA-Me)]$^{+}$TfO (1%)[a]	toluene	8	78	73	0	0	29
[XPhosAu(TA-Me)]$^{+}$TfO^{-} (1%)[a, b]	**toluene**	**8**	**100**	**94**	**0**	**0**	**33**
[XPhosAu(TA-Me)]$^{+}$TfO^{-} (1%) [a, b]	dioxane	8	100	72	0	9	44
[XPhosAu(TA-Me)]$^{+}$TfO^{-} (1%) [a, b]	DCM	8	87	62	0	18	39
[XPhosAu(TA-Me)]$^{+}$TfO^{-} (1%) [a, b]	acetone	8	81	36	0	22	58
[XPhosAu(TA-Me)]$^{+}$TfO^{-} (1%) [a, b]	acetonitrile	8	90	73	0	9	34
$AuCl_3$ (5%)	toluene	5	100	0	trace	15	nd
AgOTf (5%)	toluene	24	19	0	0	14	nd
$Pd(OAc)_2$ (5%)	toluene	24	100	0	0	0	nd
CuI (5%)	toluene	24	7	0	0	0	nd
$Cu(OTf)_2$ (5%)	toluene	24	22	0	0	15	nd
$PtCl_2$ (5%)	toluene	24	<5	0	0	<5	nd
$[Rh(COD)Cl]_2$ (5%)	toluene	24	55	0	0	0	nd
$Ni(OTf)_2$ (5%)	toluene	24	<5	0	0	0	nd
Propionic Acid	toluene	10	<10	0	0	nd	nd

a. Reaction run at 45 ºC., b. 1.8 equivalent of **2a** used

II-Chirality transfer experiment

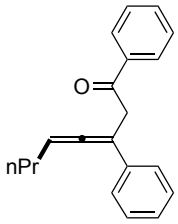
Chiral propargyl alcohol prepared by the reported method using (R)-alpine borane. (*Org. Synth.* **1985**, *63*, 57-65)

Chirality transfer performed by general procedure.



Enantiomeric excess of allenone was determined by HPLC with chiralcel OD column; λ = 260 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 1ml/min; t = 7.66 min, t = 11.24 min, 91% ee.

III- Compound characterization



4a

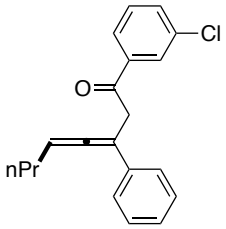
3,4-Octadien-1-one, 1,3-diphenyl-

4a was obtained through general procedure in 8h and 94% isolated (130 mg) yield as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 8.00-7.97 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.38 (m, 4H), 7.33-7.29 (m, 2H), 7.22-7.20 (m, 1H), 5.46 (m, 1H), 4.03 (dd, J_1= 15.1 Hz, J_2= 2.8 Hz 1H), 4.06 (dd, J_1= 15.1 Hz, J_2= 2.8 Hz 1H), 1.93-1.87 (m, 2H), 1.33 (q, J = 7.4 Hz, 2H), 0.87-0.83 (t, J = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 205.2, 197.7, 136.5, 136.2, 133.0, 128.7, 128.46, 128.42, 126.73, 125.68, 100.4, 95.4, 41.2, 30.6, 22.3, 13.7

HRMS calculated for $C_{20}H_{21}O$ [M+H]$^+$: 277.1586, Found: 277.1586



4b

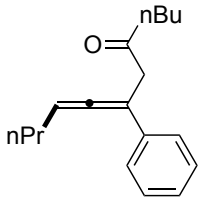
3,4-Octadien-1-one, 1-(3-chlorophenyl), 3-phenyl-

4b was obtained through general procedure in 8h and 90% isolated yield (140 mg) as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.96 (t, *J* = 1.9 Hz, 1H), 7.86-7.83 (m, 1H), 7.53-7.50 (m, 1H), 7.40-7.36 (m, 3H), 7.34-7.30 (m, 2H), 7.22 (m, 1H), 5.48 (m, 1H), 4.00 (dd, J_1= 14.9 Hz, J_2= 2.4 Hz 1H), 4.02 (dd, J_1= 14.9 Hz, J_2= 2.4 Hz 1H), 1.93 (q, *J* = 7.3 Hz, 2H), 1.35 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 205.1, 196.4, 138.0, 135.9, 134.8, 132.9, 129.8, 128.7, 128.5, 126.85, 126.75, 125.6, 100.2, 95.6, 41.4, 30.5, 22.3, 13.7

HRMS calculated for $C_{20}H_{20}ClO$ [M+H]$^+$: 311.1197, Found: 311.1198



4c

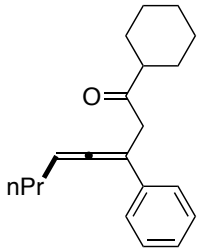
7,8-Dodecadien-5-one, 7-phenyl-

4c was obtained through general procedure in 8h and 96% isolated yield (123 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.36-7.28 (m, 4H), 7.21-7.19 (m, 1H), 5.59 (m, 1H), 3.47 (d, *J* = 2.2 Hz, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.16-2.11 (m, 2H), 1.56-1.50 (m, 4H), 1.28 (m, 2H), 1.01-0.94 (m, 3H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 208.9, 205.0, 135.8, 128.1, 126.4, 125.4, 99.6, 94.1, 45.6, 40.8, 30.5, 25.5, 22.13, 21.94, 13.48, 13.45

HRMS calculated for $C_{18}H_{25}O$ $[M+H]^+$: Exact Mass: 257.1900, Found: 257.1907



4d

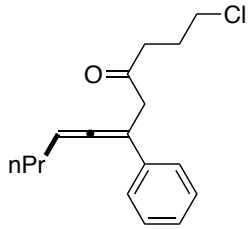
3,4-Octadien-1-one, 1-cyclohexyle, 3-phenyl-

4d was obtained through general procedure in 8h and 88% isolated yield (124 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.33-7.25 (m, 4H), 7.17 (s, 1H), 5.56 (s, 1H), 3.51 (d, *J*= 2 Hz, 2H), 2.58 (s, 1H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.83-1.75 (m, 5H), 1.52 (m, 2H), 1.35 (m, 2H), 1.25-1.19 (m, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}-C NMR (100 MHz; $CDCl_3$): δ 211.8, 205.3, 136.3, 128.4, 126.6, 125.7, 99.9, 94.3, 49.2, 44.0, 30.9, 28.6, 25.81, 25.67, 22.5, 13.8

HRMS calculated for $C_{20}H_{27}O$ $[M+H]^+$: 283.2056, Found: 283.2054



4e

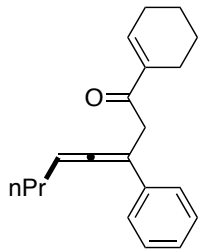
6,7-Undecadien-4-one, 1-chloro, 6-phenyl-

4e was obtained through general procedure in 8h and 85% isolated yield (118 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.35-7.29 (m, 4H), 7.21-7.18 (m, 1H), 5.61 (tt, *J* = 4.5, 2.2 Hz, 1H), 3.51(d, J= 6.4 Hz, t), 3.49 (d, J= 2.4 Hz, 2H), 2.71 (t, *J* = 7.0 Hz, 2H), 2.14-2.13 (m, 2H), 2.04-1.99 (m, 2H), 1.55-1.49 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 207.8, 205.3, 135.9, 128.5, 126.8, 125.6, 99.7, 94.6, 46.0, 44.4, 38.0, 30.8, 26.3, 22.4, 13.8

HRMS calculated for $C_{17}H_{22}ClO$ $[M+H]^+$: 277.1354, Found: 277.1363



4f

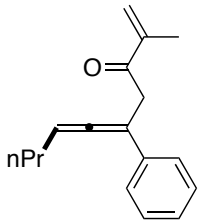
3,4-Octadien-1-one, 1-cyclohexenyle, 3-phenyl-

4f was obtained through general procedure in room temperature for 15h and 74% isolated yield (104 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.28 (m, 2H), 7.17 (m, 1H), 6.96 (m, 1H), 5.50 (m, 1H), 3.71 (dd, J_1= 16.2 Hz, J_2= 2.4 Hz 1H), 3.74 (dd, J_1= 15.1 Hz, J_2= 2.8 Hz 1H) (m, 2H), 2.26-2.21 (m, 4H), 2.07-2.02 (m, 2H), 1.64-1.59 (m, 4H), 1.46 (m, 2H), 0.93 (t, J = 9.7, 5.0 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 205.0, 198.7, 140.7, 138.8, 136.5, 128.3, 126.6, 125.7, 101.2, 94.9, 39.9, 30.9, 26.2, 23.2, 22.5, 22.0, 21.6, 13.9

HRMS calculated for $C_{20}H_{25}O$ $[M+H]^+$: 281.1900, Found: 281.1908



4g

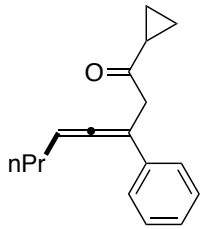
5,6-Decadien-1-ene-3-one, 2-methyl, 5-phenyl-

4g was obtained through general procedure in room temperature for15h and 72% isolated yield (87 mg) as pale yellow liquid. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.33-7.26 (m, 4H), 7.17-7.13 (m, 1H), 6.01 (d, 1H), 5.79 (m, 1H), 5.51-5.48 (m, 1H), 3.77 (dd, J = 2.6, 1.3 Hz, 2H), 2.04 (m, 2H), 1.85 (dd, J = 1.4, 0.9 Hz, 3H), 1.45 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 205.0, 199.4, 144.1, 136.3, 128.3, 126.6, 125.7, 125.3, 100.7, 95.0, 40.3, 30.8, 22.4, 17.7, 13.8

HRMS calculated for $C_{17}H_{21}O$ $[M+H]^+$: 241.1587 Found: 241.1594



4h

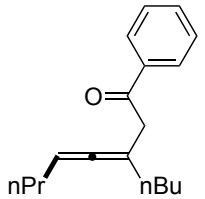
3,4-Octadien-1-one, 1-cyclopropyl, 3-phenyl-

4h was obtained through general procedure in10h and 65% isolated yield (78 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.19 (m, 1H), 5.59 (m, 1H), 3.59 (d, *J* = 2.2 Hz, 2H), 2.16-2.10 (m, 3H), 1.52 (q, *J* = 7.4 Hz, 2H), 1.02-1.00 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.84-0.81 (m, 2H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 208.7, 205.5, 136.3, 128.4, 126.7, 125.7, 99.8, 94.5, 46.5, 30.9, 22.4, 19.5, 13.8, 11.4

HRMS calculated for $C_{17}H_{21}O$ $[M+H]^+$: 241.1587, Found: 241.1587



4i

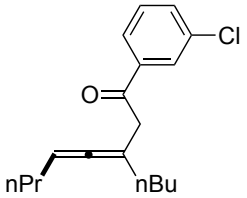
3,4-Octadien-1-one, 3-butyl, 1-phenyl-

4i was obtained through general procedure in 7h and 91% isolated yield (117 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.56-7.54 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.08 (m, 1H), 3.56 (d, *J* = 2.5 Hz, 2H), 2.03 (td, *J* = 7.4, 3.0 Hz, 2H), 1.83 (q, *J* = 7.3 Hz, 2H), 1.45-1.39 (m, 2H), 1.31 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 202.9, 198.4, 136.8, 133.1, 128.9, 128.6, 99.1, 92.8, 44.0, 32.4, 31.2, 29.9, 22.63, 22.49, 14.2, 13.9

HRMS calculated for $C_{18}H_{25}O$ $[M+H]^+$: 257.1900, Found: 257.1908



4j

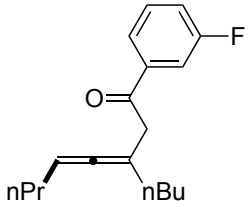
3,4-Octadien-1-one, 3-butyl, 1-(3-chlorophenyl)-

4j was obtained through general procedure in 7h and 85% isolated yield (123 mg) as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.94 (t, *J* = 1.8 Hz, 1H), 7.85-7.83 (m, 1H), 7.51 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 5.09 (s, 1H), 3.54 (d, *J* = 2.5 Hz, 2H), 2.00 (td, *J* = 7.4, 3.1 Hz, 2H), 1.83 (dd, *J* = 14.7, 6.8 Hz, 2H), 1.45-1.37 (m, 2H), 1.35-1.24 (m, 4H), 0.90-0.83 (m, 6H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 202.7, 196.8, 138.1, 134.7, 132.8, 129.7, 128.9, 126.8, 98.6, 92.9, 43.9, 32.2, 30.9, 29.6, 22.43, 22.24, 13.9, 13.7

HRMS calculated for $C_{18}H_{24}ClO$ $[M+H]^+$: 291.1510, Found: 291.1521



4k

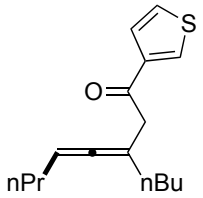
3,4-Octadien-1-one, 3-butyl, 1-(3-flourophenyl)-

4k was obtained through general procedure in 7h and 86% isolated yield (118 mg) as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.60-7.57 (m, 1H), 7.49 (m, 1H), 7.26 (m, 1H), 7.09-7.06 (m, 1H), 4.92 (tt, *J* = 6.5, 3.2 Hz, 1H), 3.54 (d, *J* = 2.0 Hz, 2H), 1.84 (td, *J* = 7.4, 3.1 Hz, 2H), 1.66 (m, 2H), 1.27-1.22 (m, 2H), 1.17-1.10 (m, 4H), 0.70 (m, 6H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 202.7, 196.82-196.80 (d, J_{C-F}= 2.2 Hz), 164.0, 161.5, 130.03-129.95 (d, J_{C-F}= 7.4 Hz), 124.47-124.44 (d, J_{C-F}= 2.9 Hz), 120.0-119.7 (d, J_{C-F}= 21.5 Hz), 115.5-115.3(d, J_{C-F}= 22.4 Hz), 98.6, 92.84-92.82(d, J_{C-F}= 2.7 Hz), 43.9, 32.2, 30.9, 29.6, 22.42, 22.26, 13.9, 13.7

HRMS calculated for $C_{18}H_{24}FO$ $[M+H]^+$: 275.1806, Found: 275.1816



4l

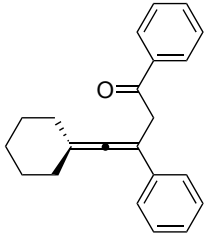
3,4-Octadien-1-one, 3-butyl, 1-(3-thienyl)-

4l was obtained through general procedure in 7h and 72% isolated yield (95 mg) as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 8.08 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.55 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.30-7.26 (m, 1H), 5.11 (m, 1H), 3.46 (d, *J* = 2.2 Hz, 2H), 2.01 (m, *J* = 3.7 Hz, 2H), 1.87 (q, *J* = 7.3 Hz, 2H), 1.45-1.37 (m, 2H), 1.35-1.24 (m, 4H), 0.88 (m, 6H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 202.6, 192.2, 141.7, 132.4, 127.2, 125.8, 98.7, 92.3, 45.1, 31.9, 30.9, 29.5, 22.31, 22.12, 13.8, 13.6

HRMS calculated for $C_{16}H_{23}OS$ $[M+H]^+$: 263.1464, Found: 263.1474



4m

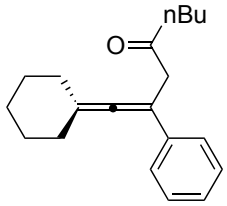
3-Buten-1-one, 4-cyclohexylidene-1,3-diphenyl-

4m was obtained through general procedure in 15h and 88% isolated yield (133 mg) as pale yellow semisolid. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.44 (tt, *J* = 7.4, 1.6 Hz, 1H), 7.34-7.31 (m, 3H), 7.24 (m, 2H), 7.13-7.09 (m, 1H), 3.92 (s, 2H), 1.93 (m, 2H), 1.85 (m, 2H), 1.47-1.41 (m, 2H), 1.36 (m, 2H), 1.27-1.22 (m, 2H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 199.7, 198.2, 137.2, 136.4, 132.8, 128.8, 128.36, 128.33, 126.5, 125.6, 107.3, 98.6, 41.5, 30.7, 27.3, 25.9

HRMS calculated for $C_{22}H_{23}O$ $[M+H]^+$: 303.1743, Found: 303.1756



4n

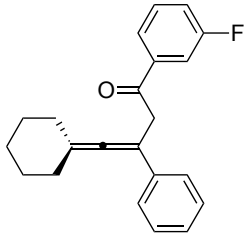
3-Octen-5-one, 8-cyclohexylidene, 7-diphenyl-

4n was obtained through general procedure in 15h and 91% isolated yield (129 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.35-7.27 (m, 4H), 7.20-7.16 (m, 1H), 3.43 (s, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.30-2.17 (m, 4H), 1.72-1.66 (m, 4H), 1.62-1.50 (m, 4H), 1.30-1.24 (m, 2H), 0.87 (t, *J* = 8.4 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 209.9, 199.8, 137.2, 128.5, 126.5, 125.7, 106.2, 97.8, 46.3, 41.0, 31.2, 27.7, 26.13, 26.00, 22.4, 13.9

HRMS calculated for $C_{20}H_{27}O$ $[M+H]^+$: 283.2056, Found: 283.2067



4o

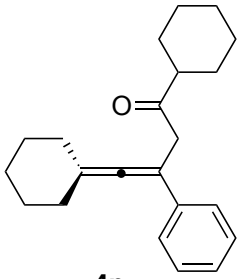
3-Buten-1-one, 4-cyclohexylidene-1-(3-flourophenyl)- ,3-phenyl-

4o was obtained through general procedure in 15h and 86% isolated yield (138 mg) as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.76 (m, *J* = 1.0 Hz, 1H), 7.67 (m, *J* = 1.6 Hz, 1H), 7.42-7.37 (m, 3H), 7.34-7.30 (m, 2H), 7.25-7.18 (m, 2H), 3.99 (s, 2H), 2.06-2.00 (m, 2H), 1.93 (m, *J* = 4.7 Hz, 2H), 1.54 (m, *J* = 4.5 Hz, 2H), 1.46 (m, 2H), 1.37 (m, *J* = 4.0 Hz, 2H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 199.7, 196.9, 163.96-161.50 (d, J_{C-F}= 246.2 Hz), 138.56-138.50 (d, J_{C-F}= 6.1 Hz), 136.9, 130.02-129.94 (d, J_{C-F}= 7.5 Hz), 128.4, 126.6, 125.6, 124.64-124.61 (d, J_{C-F}= 2.9 Hz), 119.91-119-70 (d, J_{C-F}= 21.3 Hz), 115.55-115-33 (d, J_{C-F}= 22.1 Hz), 107.5, 98.4, 41.6, 30.6, 27.3, 25.9

HRMS calculated for $C_{22}H_{22}FO$ $[M+H]^+$: 321.1649, Found: 321.1661



4p

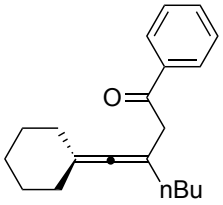
3-Buten-1-one, 4-cyclohexylidene, 1-cyclohexyle, 3-phenyl-

4p was obtained through general procedure in 15h and 85% isolated yield (131 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.34-7.26 (m, 4H), 7.19-7.15 (m, 1H), 3.47 (d, *J* = 6.7 Hz, 2H), 2.62 (tt, *J* = 10.6, 3.3 Hz, 1H), 2.31-2.17 (m, 4H), 1.84-1.75 (m, 4H), 1.72-1.57 (m, 6H), 1.38-1.19 (m, 6H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 212.7, 199.8, 137.2, 128.4, 126.4, 125.7, 106.0, 97.6, 48.7, 44.5, 31.2, 28.6, 27.6, 26.05, 25.85, 25.72

HRMS calculated for $C_{22}H_{29}O$ $[M+H]^+$: 309.2213, Found: 309.2225



4q

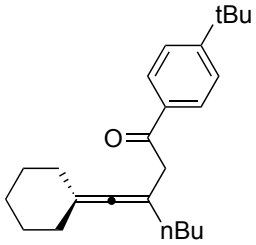
3-Buten-1-one, 4-cyclohexylidene, 3-butyl, 1-phenyl-

4q was obtained through general procedure in 15h and 88% isolated yield (125 mg) as pale yellow semisolid. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.46-7.42 (m, 1H), 7.36-7.32 (m, 2H), 3.45 (s, 2H), 1.93 (t, *J* = 7.2 Hz, 2H), 1.82 (m, 4H), 1.36-1.21 (m, 10H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 198.5, 197.1, 136.5, 132.7, 128.8, 128.2, 104.3, 96.9, 44.4, 32.5, 31.3, 29.6, 27.5, 26.1, 22.1, 14.0

HRMS calculated for $C_{20}H_{27}O$ $[M+H]^+$: 283.2056, Found: 283.2065



4r

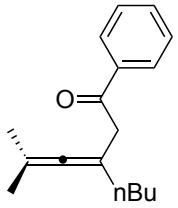
3-Buten-1-one, 4-cyclohexylidene, 3-butyl, 1-(4-t-butylphenyl)-

4r was obtained through general procedure in 15h and 79% isolated yield (134 mg) as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.91 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.43 (dd, *J* = 8.3, 1.0 Hz, 2H), 3.50 (s, 2H), 1.99 (t, *J* = 7.0 Hz, 2H), 1.90 (m, 4H), 1.48-1.37 (m, 8H), 1.34-1.31 (m, 11H), 0.88 (m, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 198.3, 197.1, 156.4, 134.0, 128.8, 125.2, 104.2, 97.1, 44.4, 40.6, 32.6, 31.3, 31.1, 29.7, 27.5, 26.1, 22.2, 14.0

HRMS calculated for $C_{24}H_{35}O$ $[M+H]^+$: 339.2682, Found: 339.2695



4s

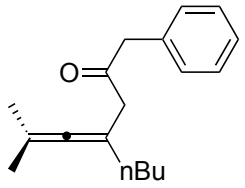
3,4-Hexadien-1-one, 5-methyl, 3-butyl, 1-phenyl-

4s was obtained through general procedure in 15h and 73% isolated yield (89 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.97-7.95 (m, 2H), 7.53-7.51 (m, 1H), 7.45-7.41 (m, 2H), 3.52 (s, 2H), 1.98 (t, *J* = 7.0 Hz, 2H), 1.49-1.48 (s, 6H), 1.39-1.25 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 200.8, 198.6, 136.6, 132.7, 128.8, 128.3, 97.02, 96.85, 44.1, 32.6, 29.6, 22.2, 20.1, 14.0

HRMS calculated for C17H23O $[M+H]^+$: 243.1743, Found: 243.1752



4t

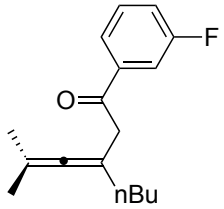
3,4-Heptadien-2-one, 6-methyl, 4-butyl, 1-phenyl-

4t was obtained through general procedure in 15h and 70% isolated yield (90 mg) as pale yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.31 (m, 2H), 7.26 (m, 1H), 7.20-7.18 (m, 2H), 3.76 (s, 2H), 3.00 (s, 2H), 1.89 (t, *J* = 6.7 Hz, 2H), 1.71 (s, 6H), 1.33-1.31 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 206.5, 200.5, 134.4, 129.5, 128.6, 126.9, 96.5, 96.1, 48.4, 47.2, 32.7, 29.6, 22.2, 20.6, 14.0

HRMS calculated for $C_{18}H_{25}O$ $[M+H]^+$: 257.1900, Found: 257.1909



4u

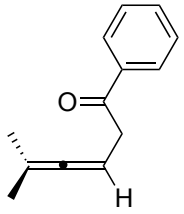
3,4-Hexadien-1-one, 5-methyl, 3-butyl, 1-(3-flourophenyl)-

4u was obtained through general procedure in 15h and 70% isolated yield (91 mg) as yellow oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.74 (m, *J* = 1.0 Hz, 1H), 7.64 (m, *J* = 1.6 Hz, 1H), 7.41 (m, 1H), 7.25-7.21 (m, 1H), 3.50 (s, 2H), 1.98 (t, *J* = 7.2 Hz, 2H), 1.51 (s, 6H), 1.39-1.28 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 200.9, 197.279-129.260 (d, J_{C-F}= 1.9 Hz), 163.9, 138.7, 129.936-129.860 (d, J_{C-F}= 7.6Hz), 124.508-124.480 (d, J_{C-F}= 2.8 Hz), 119.780-119.564 (d, J_{C-F}= 21.6Hz), 115.609-115.389 (d, J_{C-F}= 22 Hz), 97.158, 96.791, 44.2, 32.5, 29.6, 22.2, 20.1, 14.0

HRMS calculated for $C_{17}H_{22}FO$ $[M+H]^+$: 261.1649, Found: 261.1660



4v

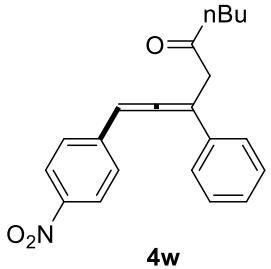
3,4-Hexadien-1-one, 5-methyl, 1-phenyl-

4v was obtained through general procedure using 3 equivalent of alkyne 2 in 8h with 44% isolated yield (41 mg) as colorless oil. (Elution: ethyl acetate/hexanes = 1/5)

^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.98-7.96 (m, 2H), 7.54 (m, 1H), 7.45 (m, 2H), 5.23 (m, 1H), 3.63 (d, *J* = 6.9 Hz, 2H), 1.63 (d, *J* = 2.9 Hz, 6H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 203.4, 198.2, 136.4, 132.9, 128.4, 128.1, 96.4, 82.6, 39.8, 20.2

HRMS calculated for $C_{13}H_{15}O$ $[M+H]^+$: 187.1117, Found: 187.1118



4w

7,8-Nonadien-5-one, 7-phenyl, 9-(4-nitrophenyl)-

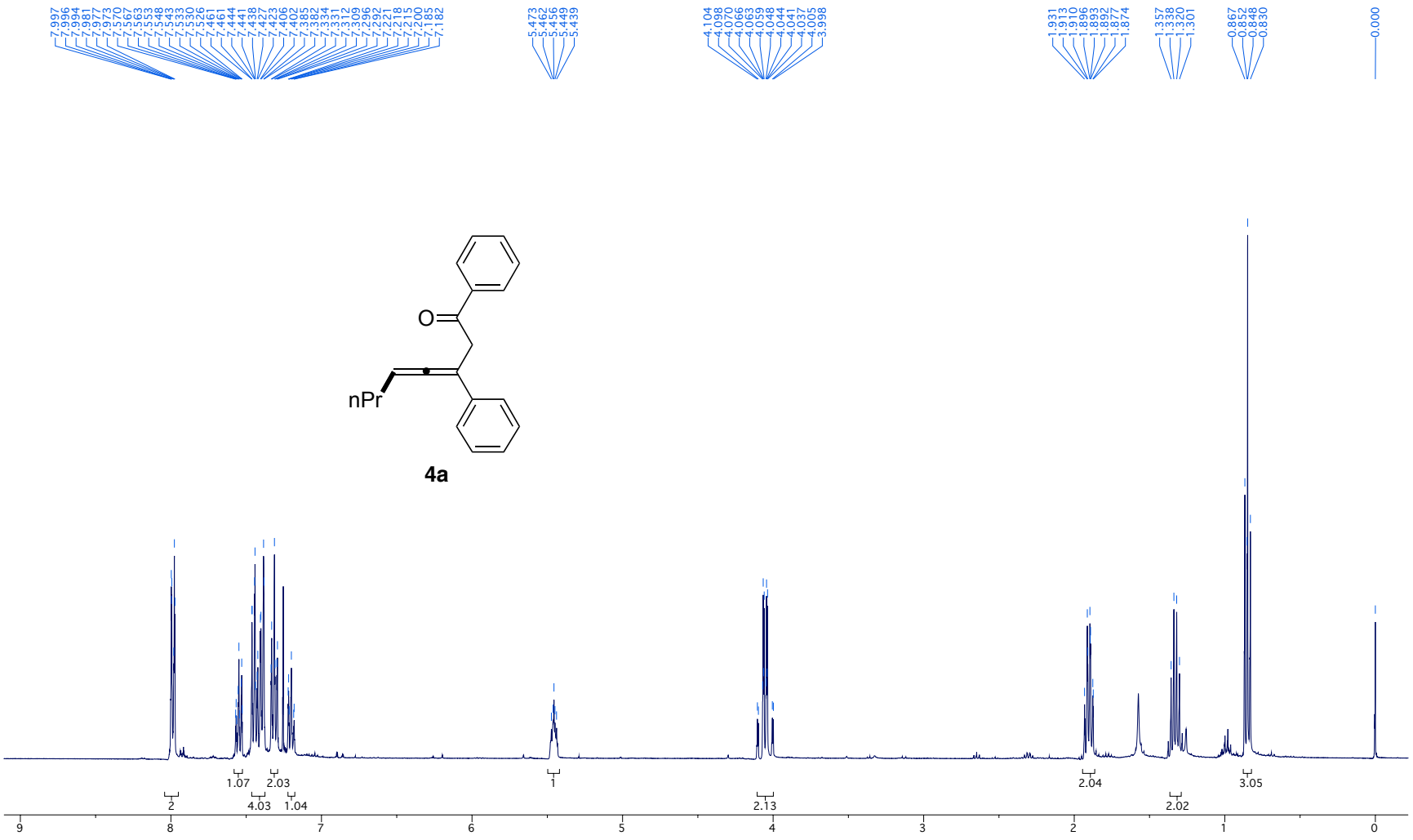
4x was obtained through general procedure using 3% catalyst in 24h in 74% isolated yield (124 mg) as yellow solid. (Elution: ethyl acetate/hexanes = 1/5)

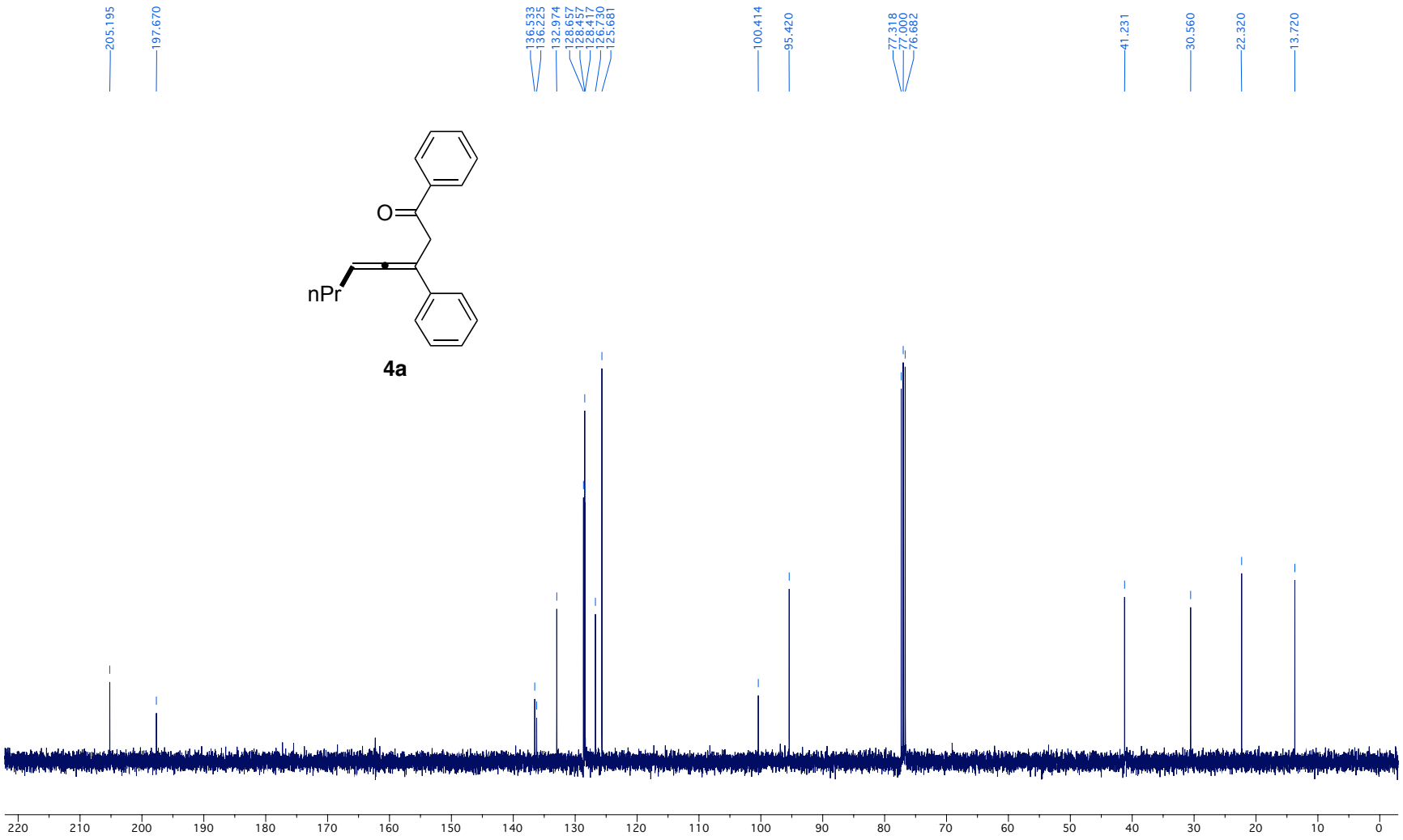
^{1}H-NMR (400 MHz; $CDCl_3$): δ 8.19-8.17 (m, 2H), 7.54-7.52 (m, 2H), 7.35-7.31 (m, 4H), 7.28-7.26 (m, 1H), 6.64 (s, 1H), 3.68 (dd, J_1= 16.4 Hz, J_2= 1.6 Hz 1H), 3.65 (dd, J_1= 16.4 Hz, J_2= 1.6 Hz 1H), 2.56 (t, J = 7.4 Hz, 2H), 1.58 (m, 2H), 1.28 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H).

^{13}C-NMR (100 MHz; $CDCl_3$): δ 209.9, 207.2, 146.8, 140.9, 133.8, 128.8, 127.9, 127.5, 126.0, 124.1, 105.0, 96.6, 44.7, 42.0, 25.8, 22.2, 13.8

HRMS calculated for $C_{21}H_{22}NO_3$ $[M+H]^+$: 336.1594, Found: 336.1595

IV. NMR spectra

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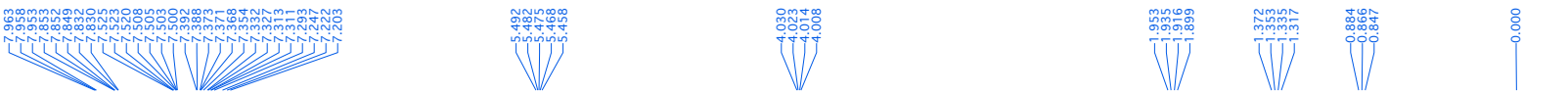
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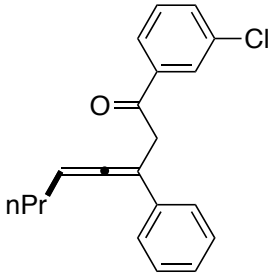
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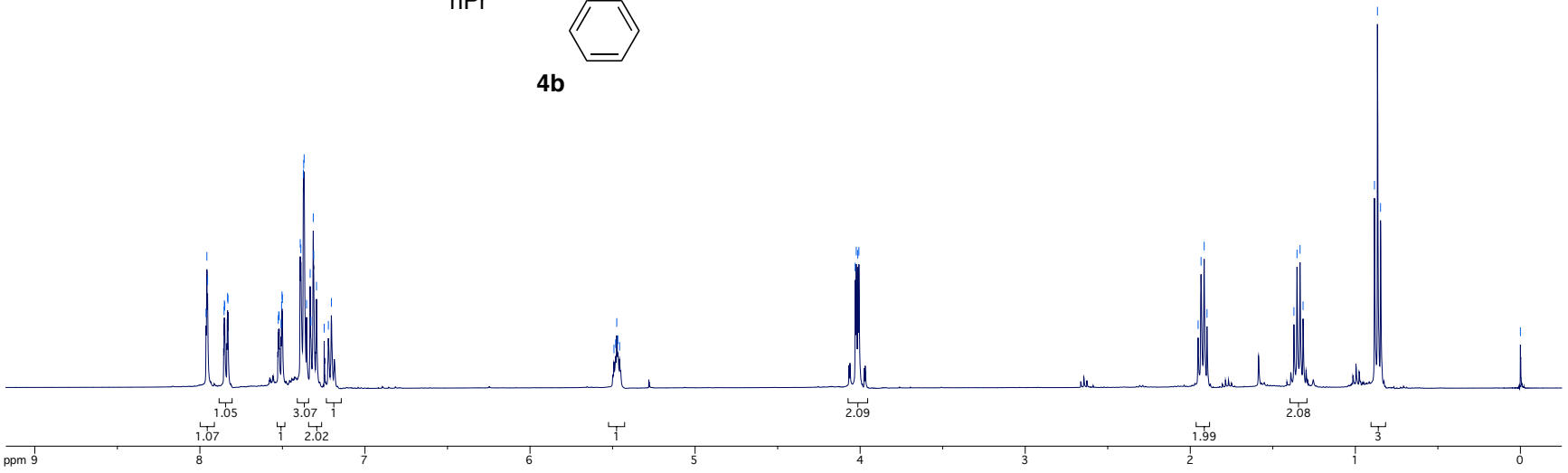
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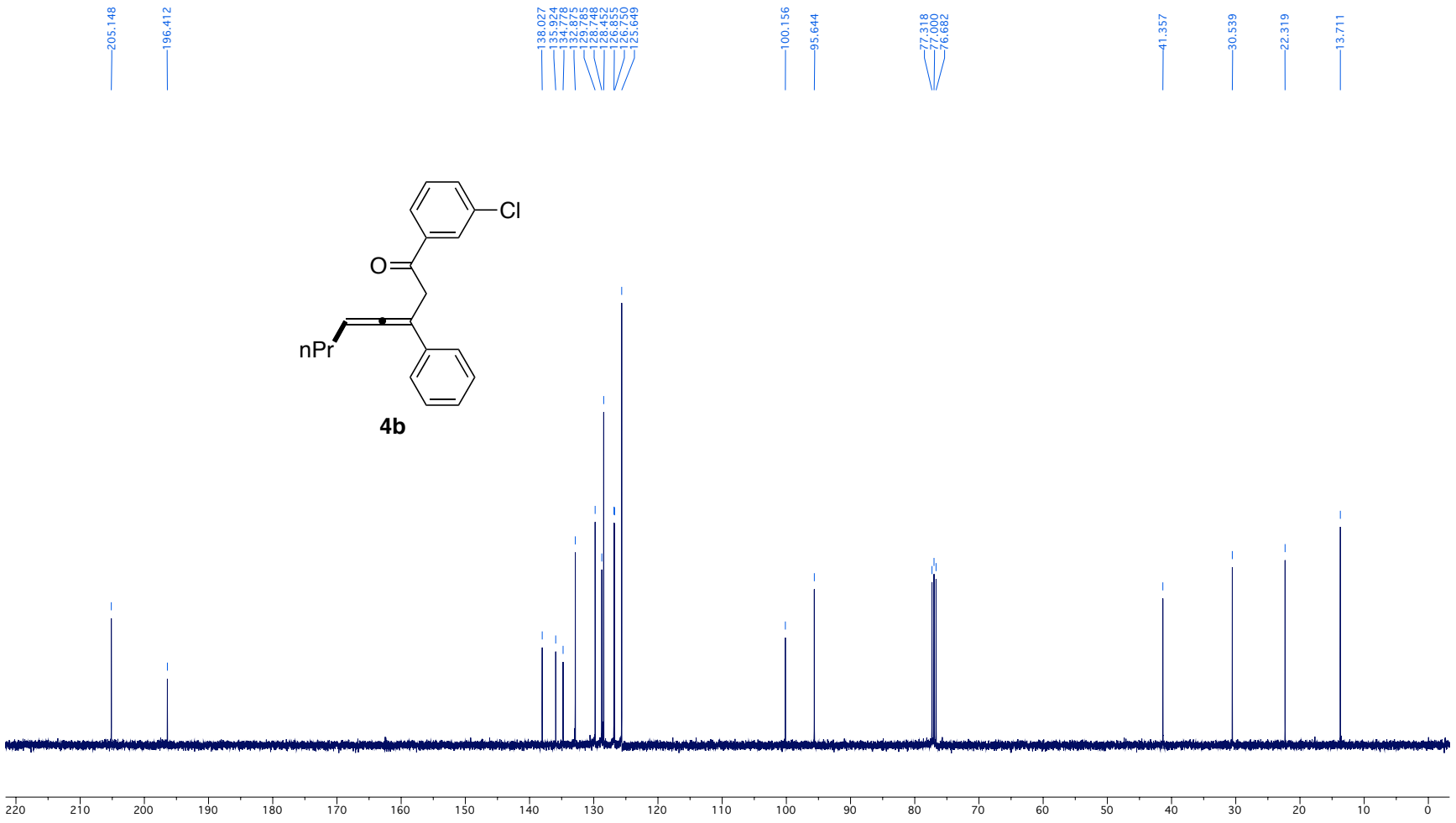
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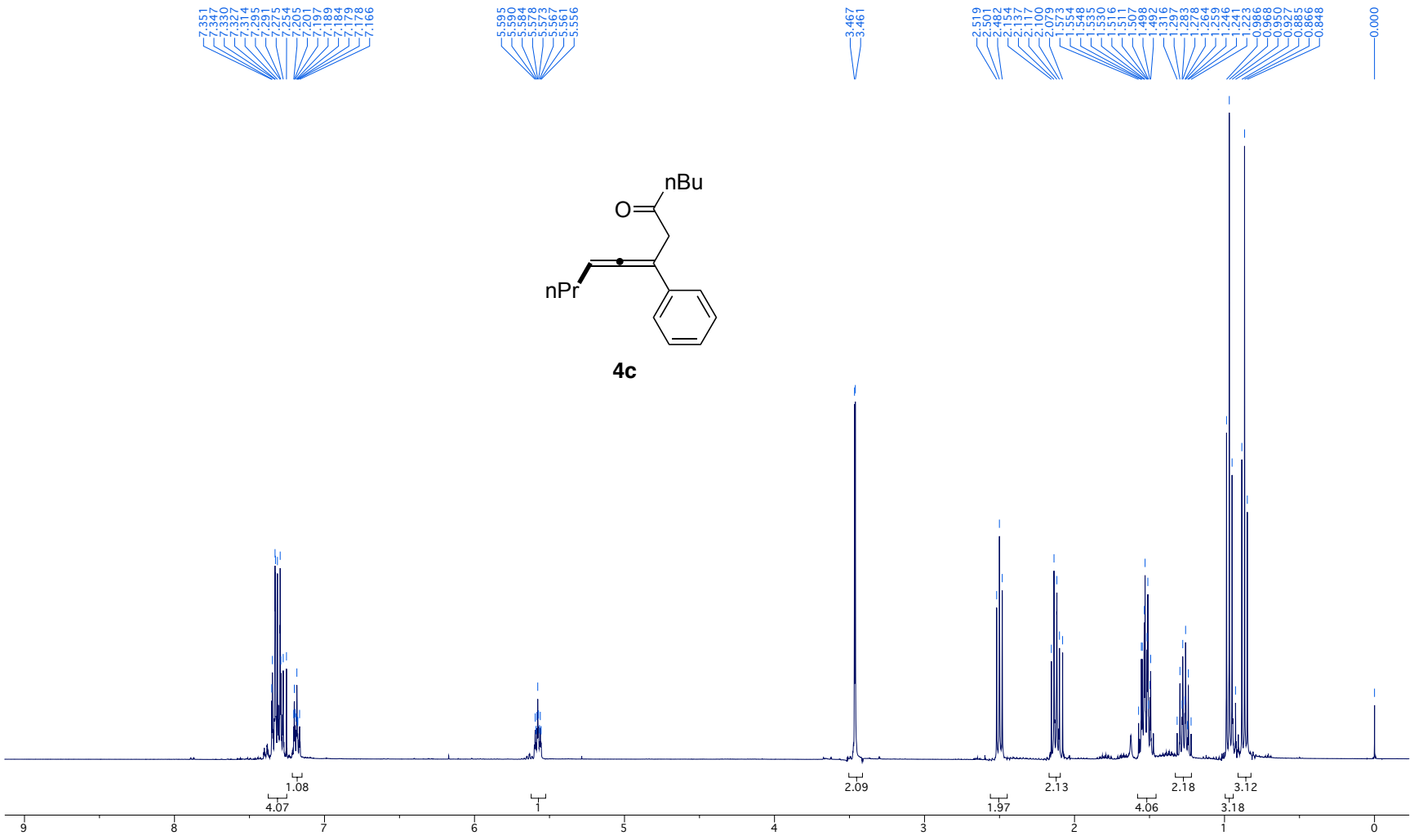
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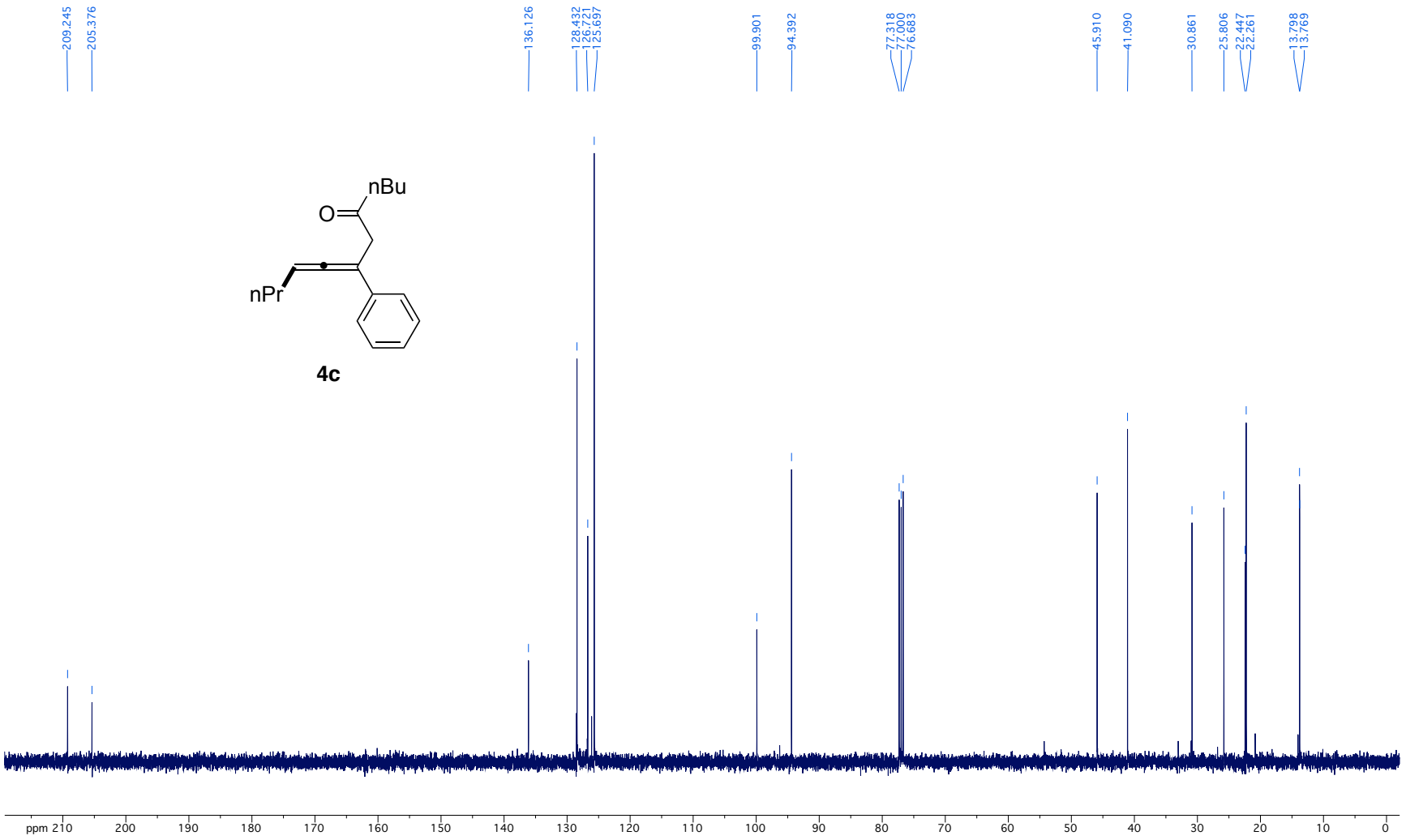
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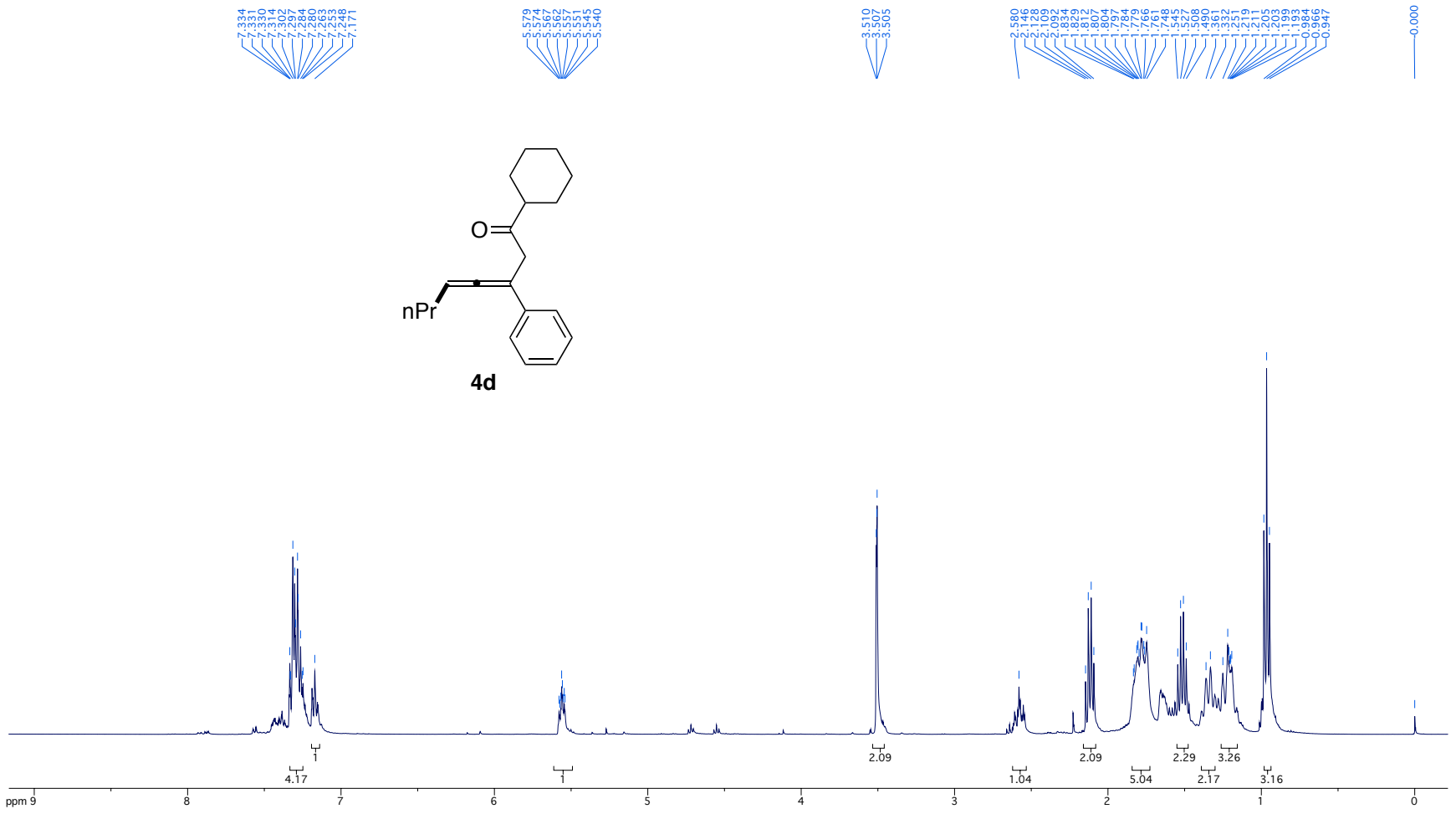
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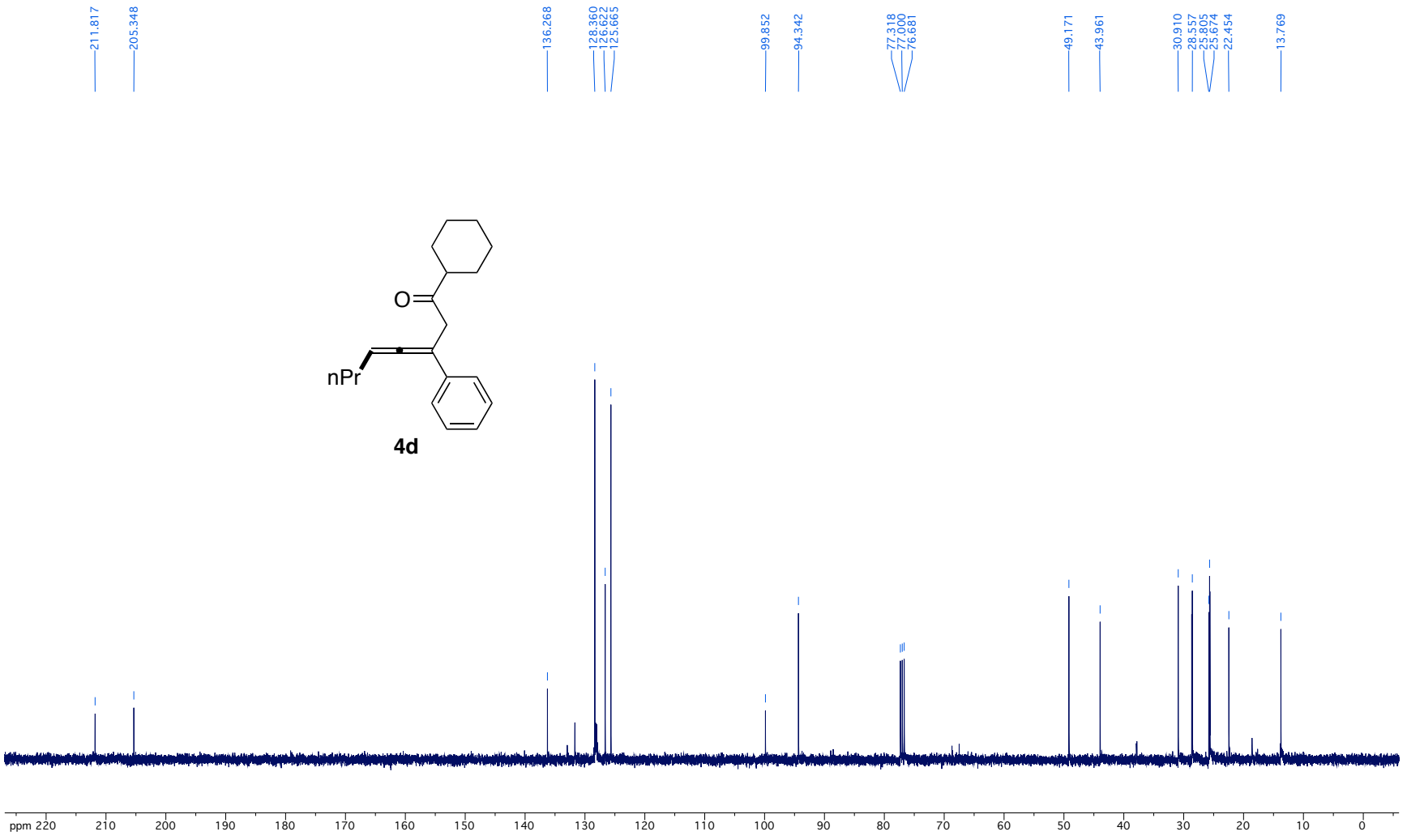
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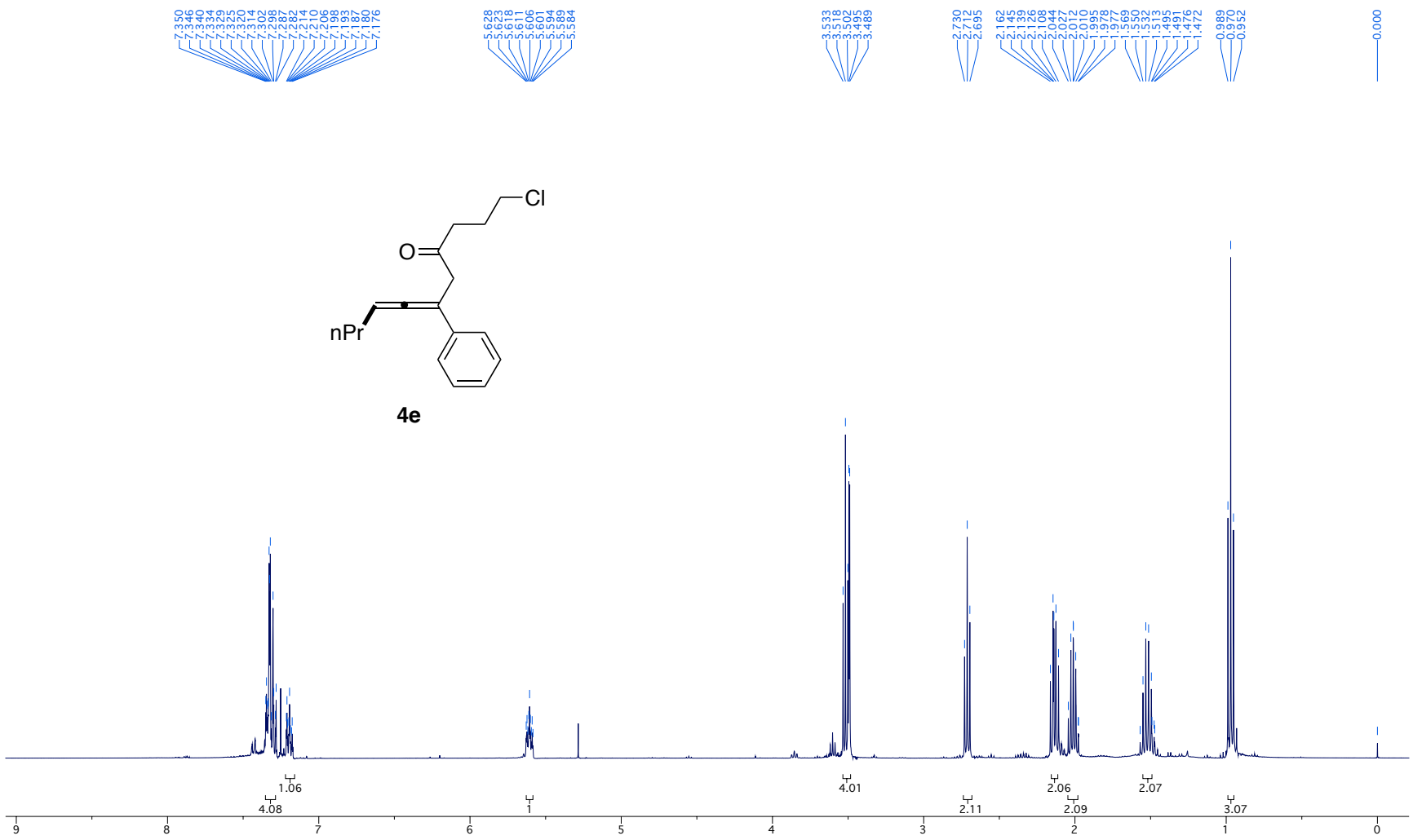
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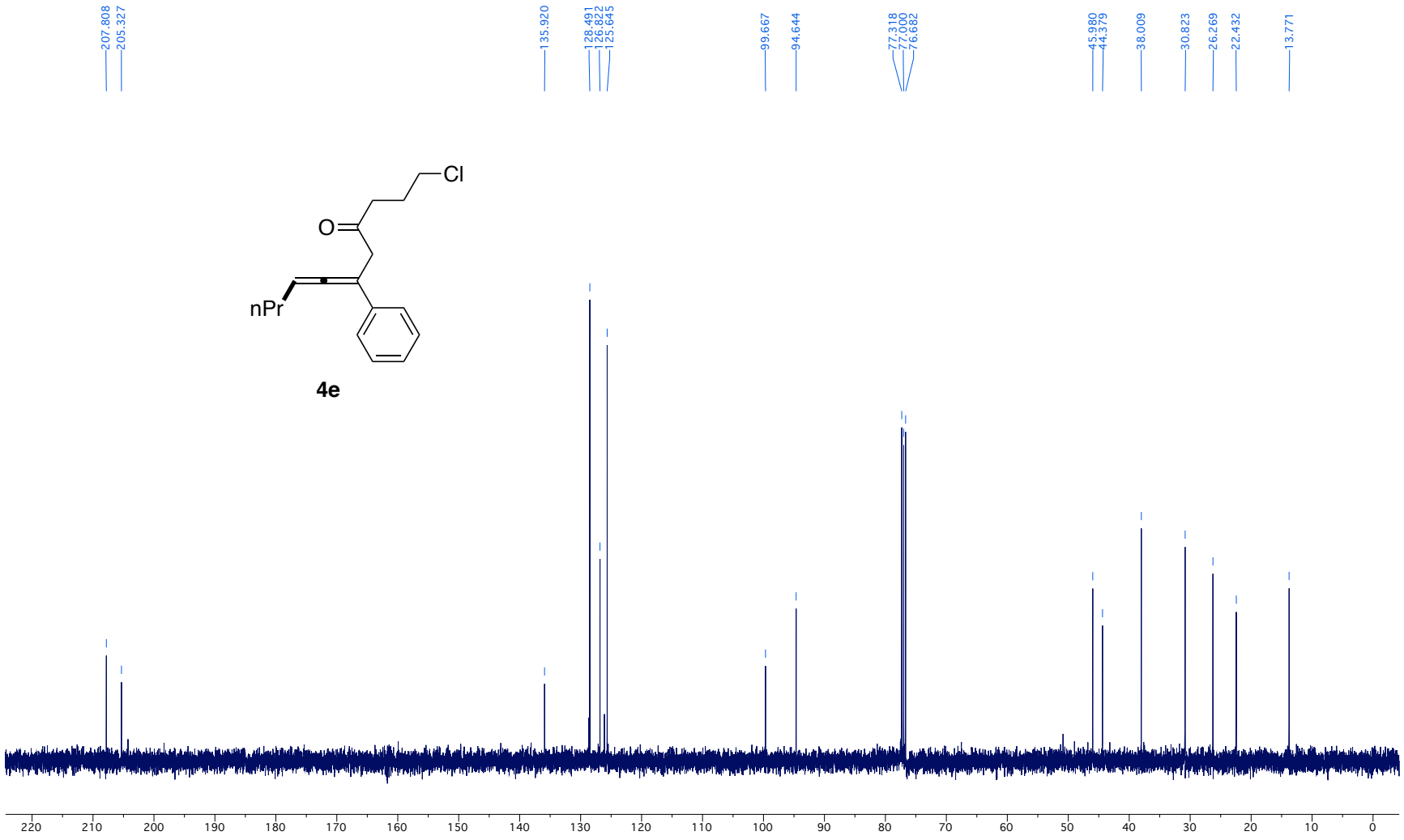
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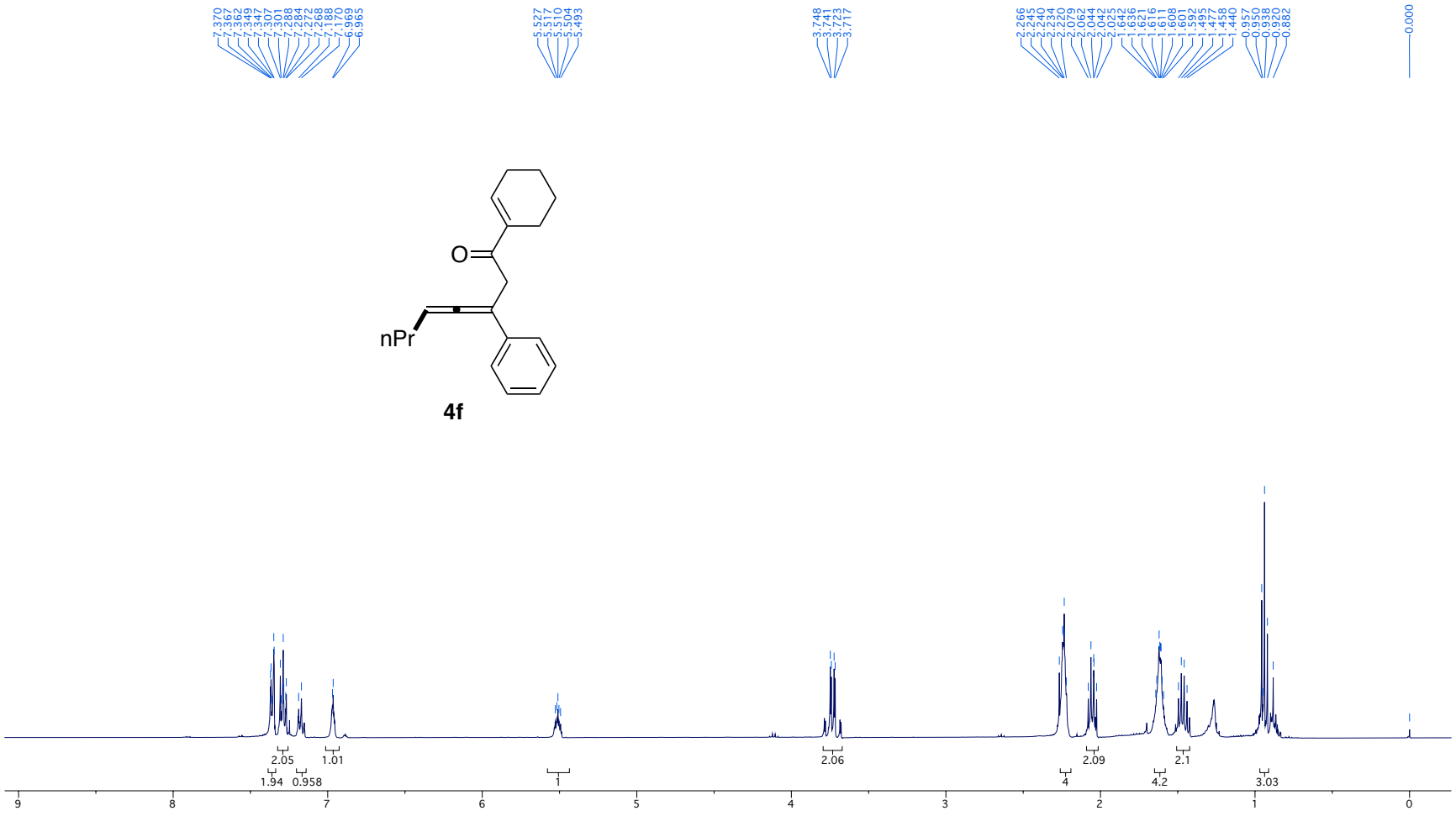
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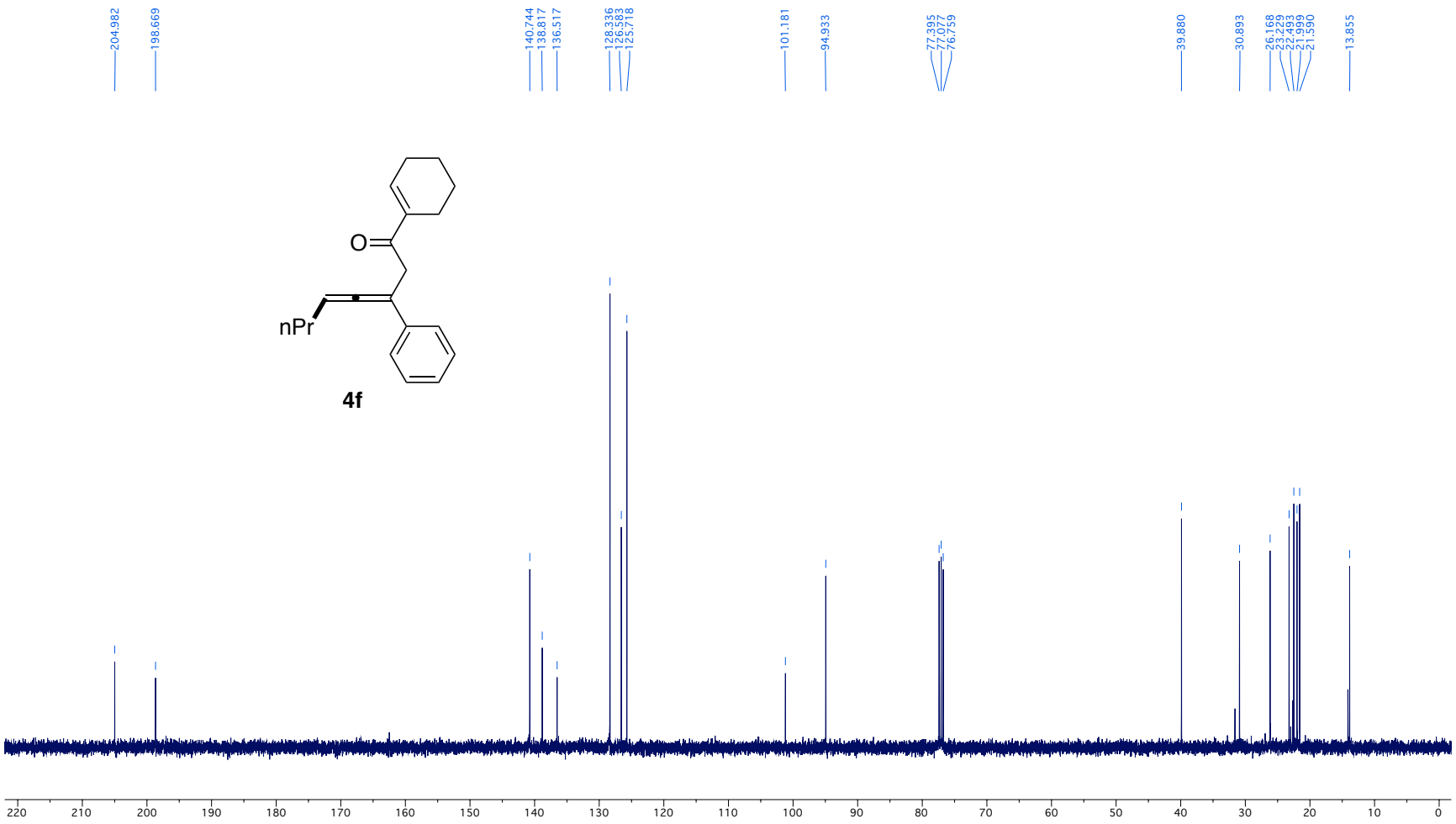
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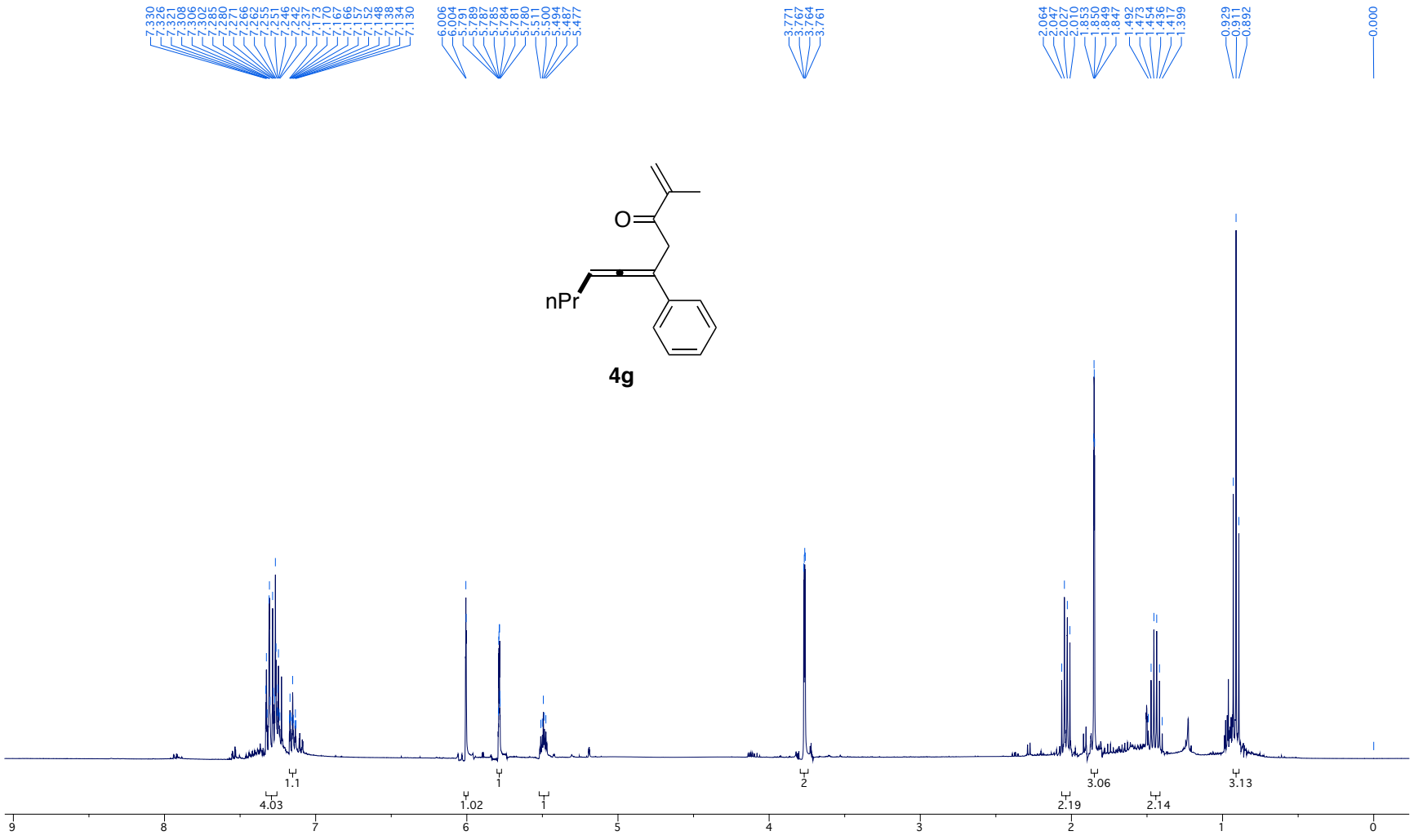
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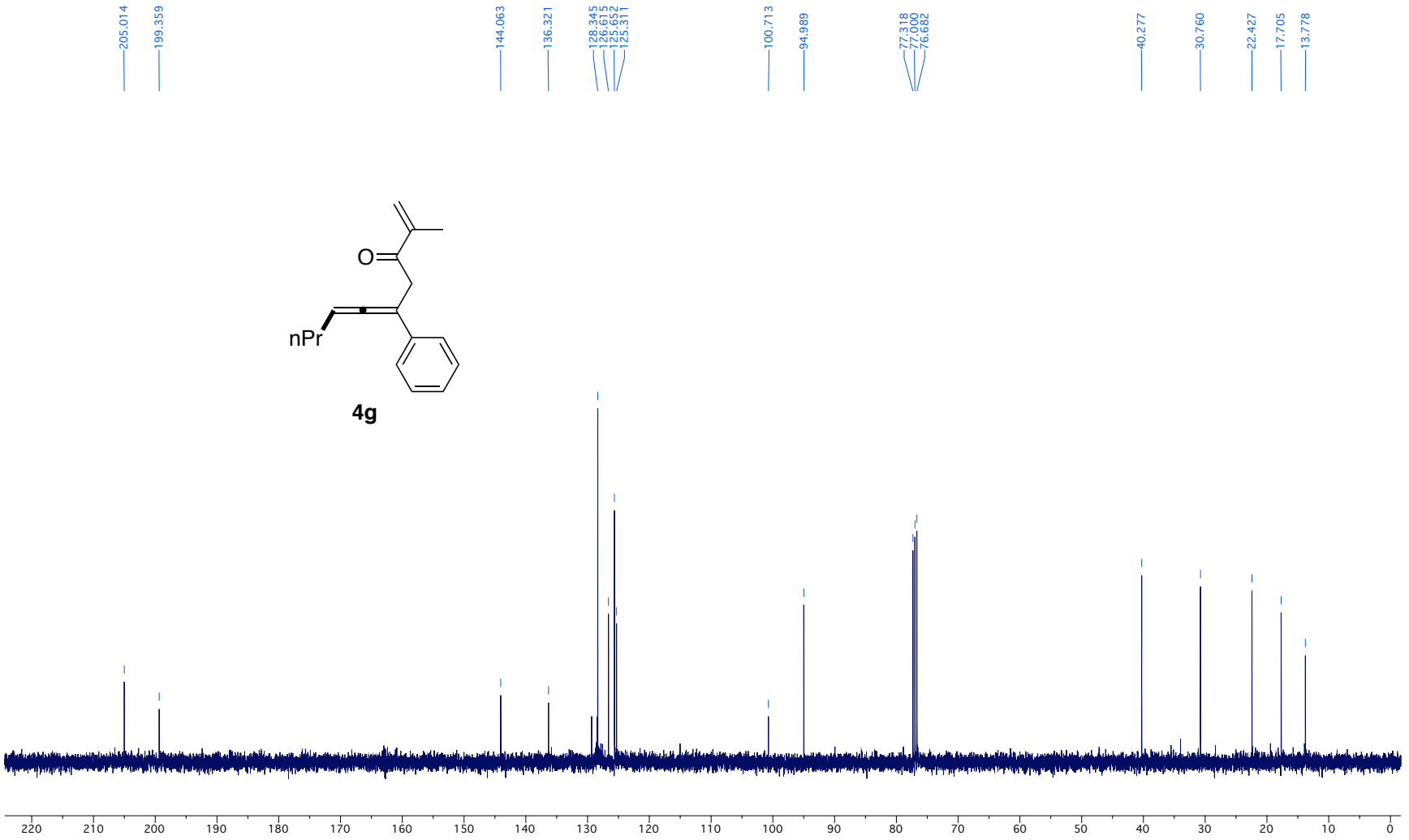
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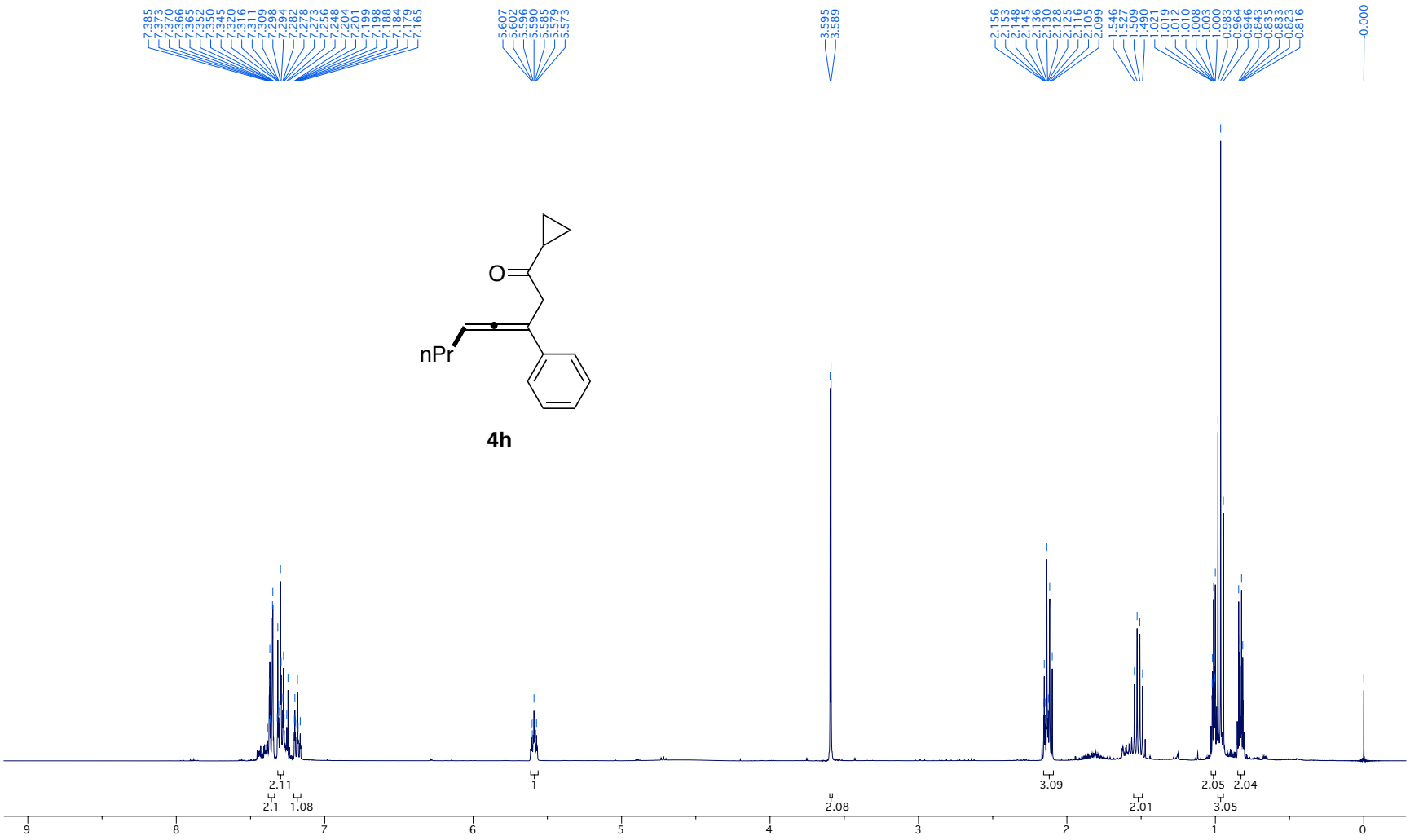
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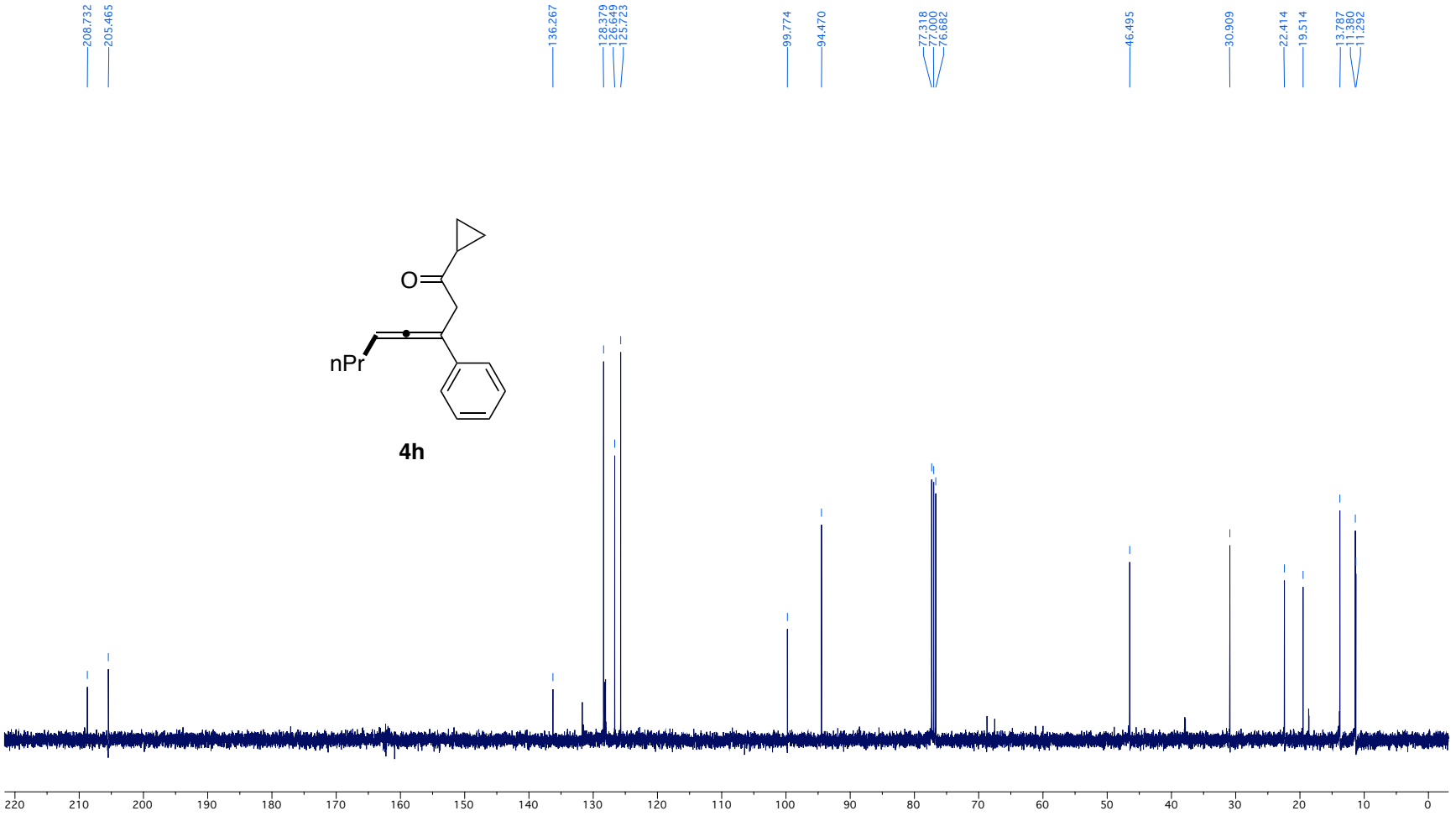
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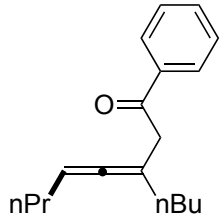
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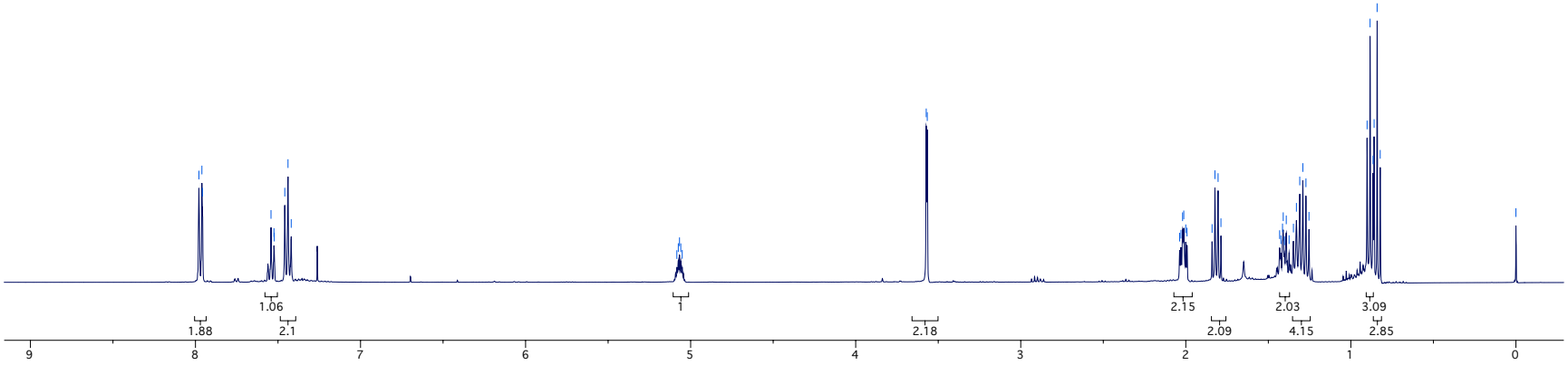
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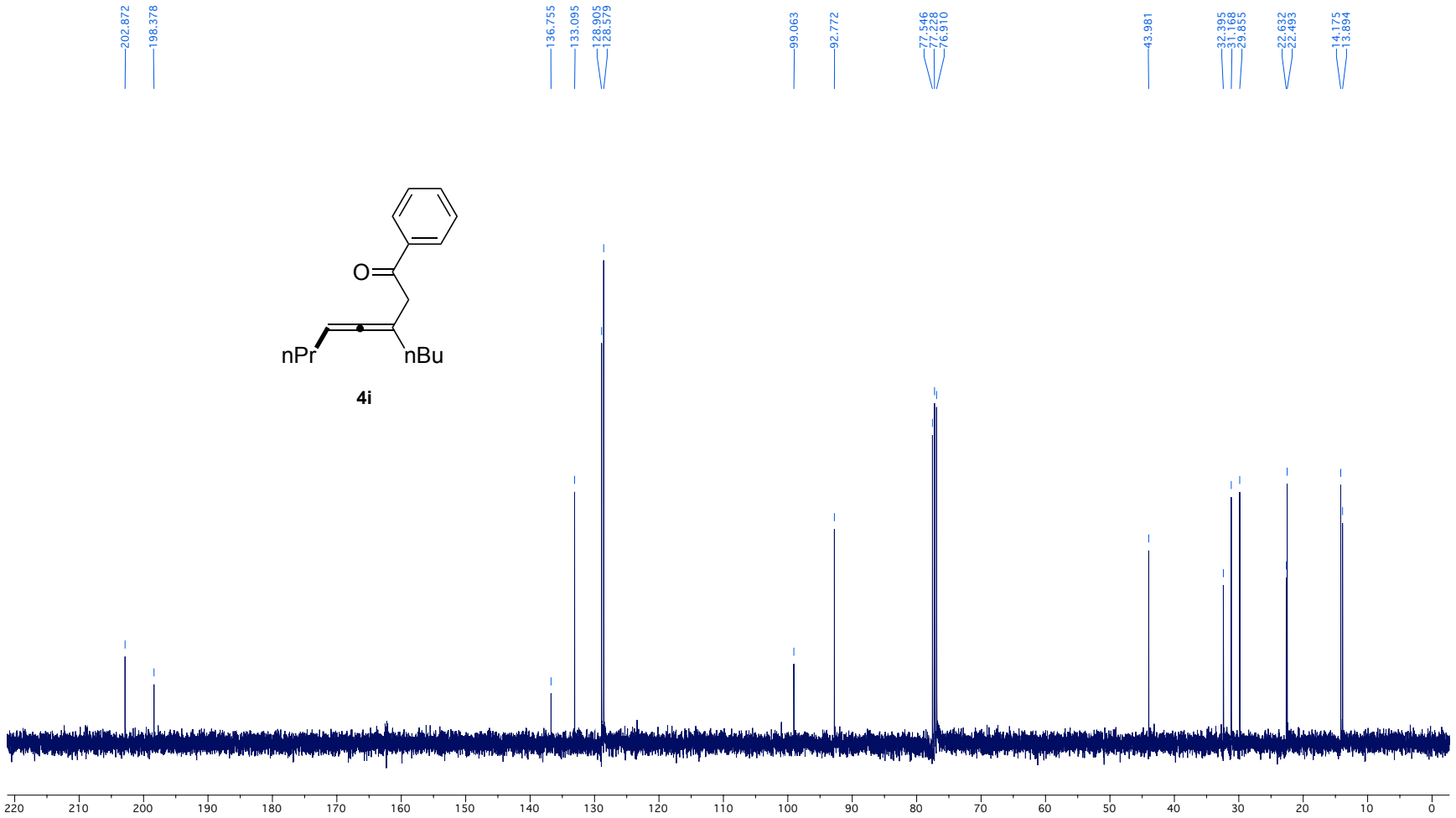
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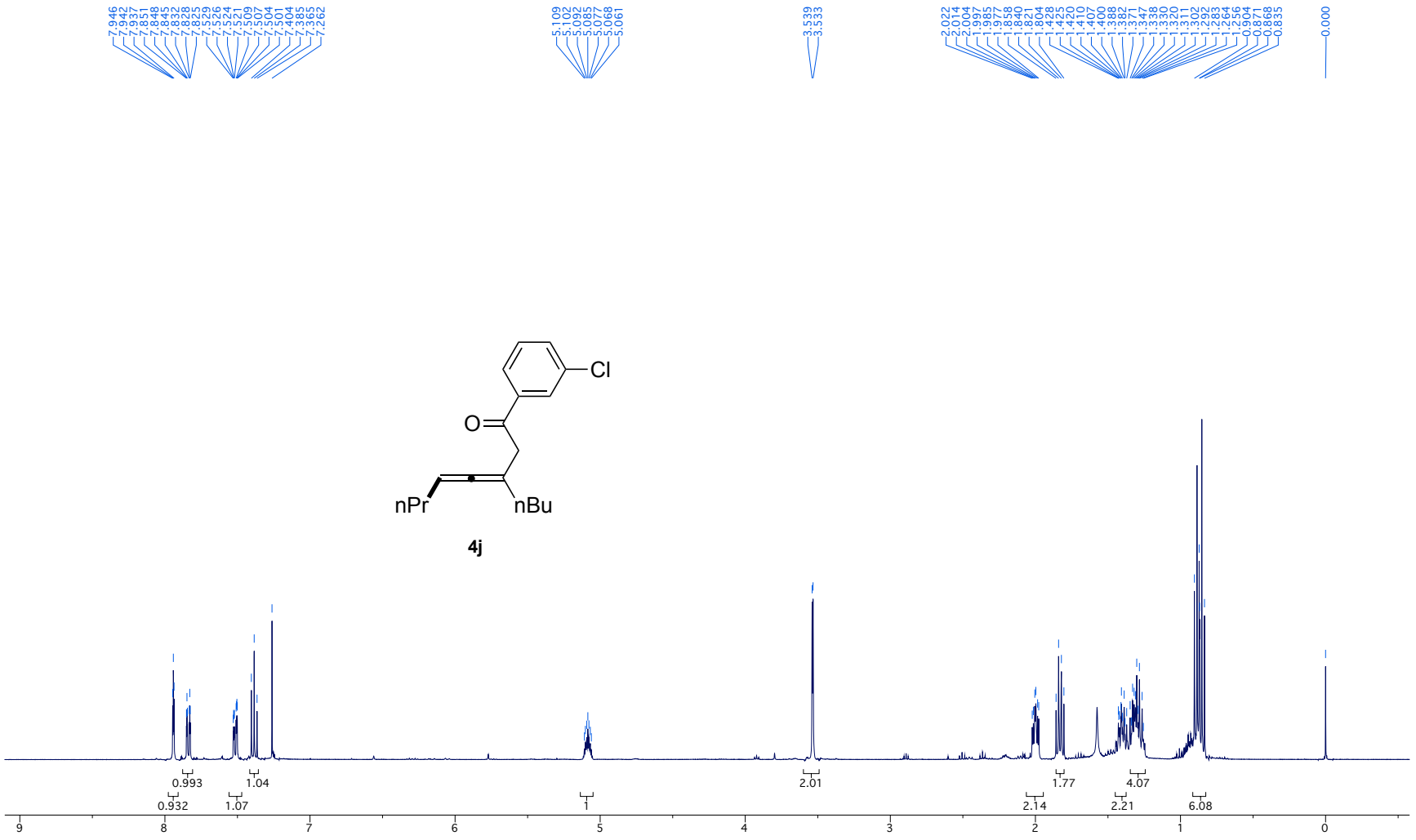
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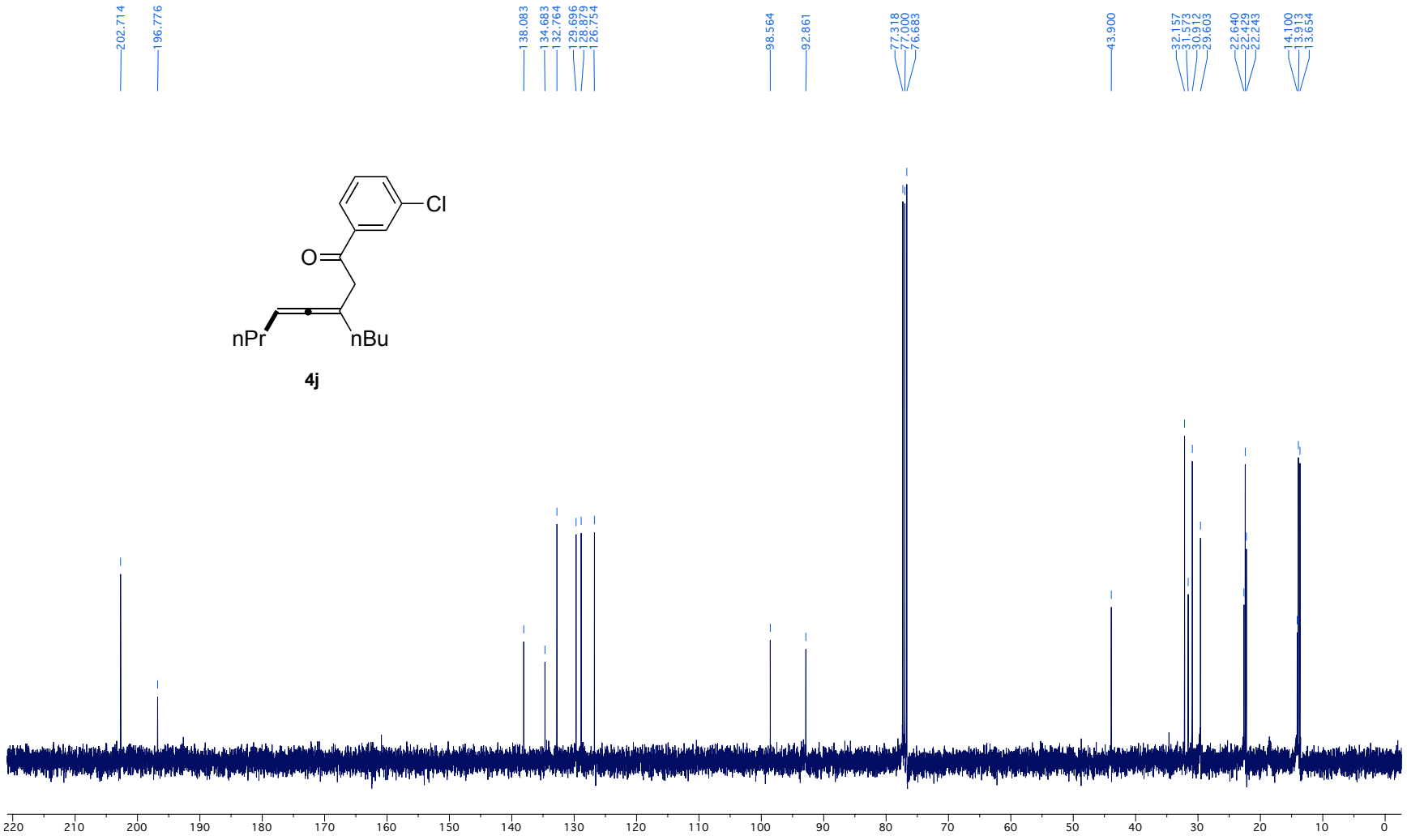
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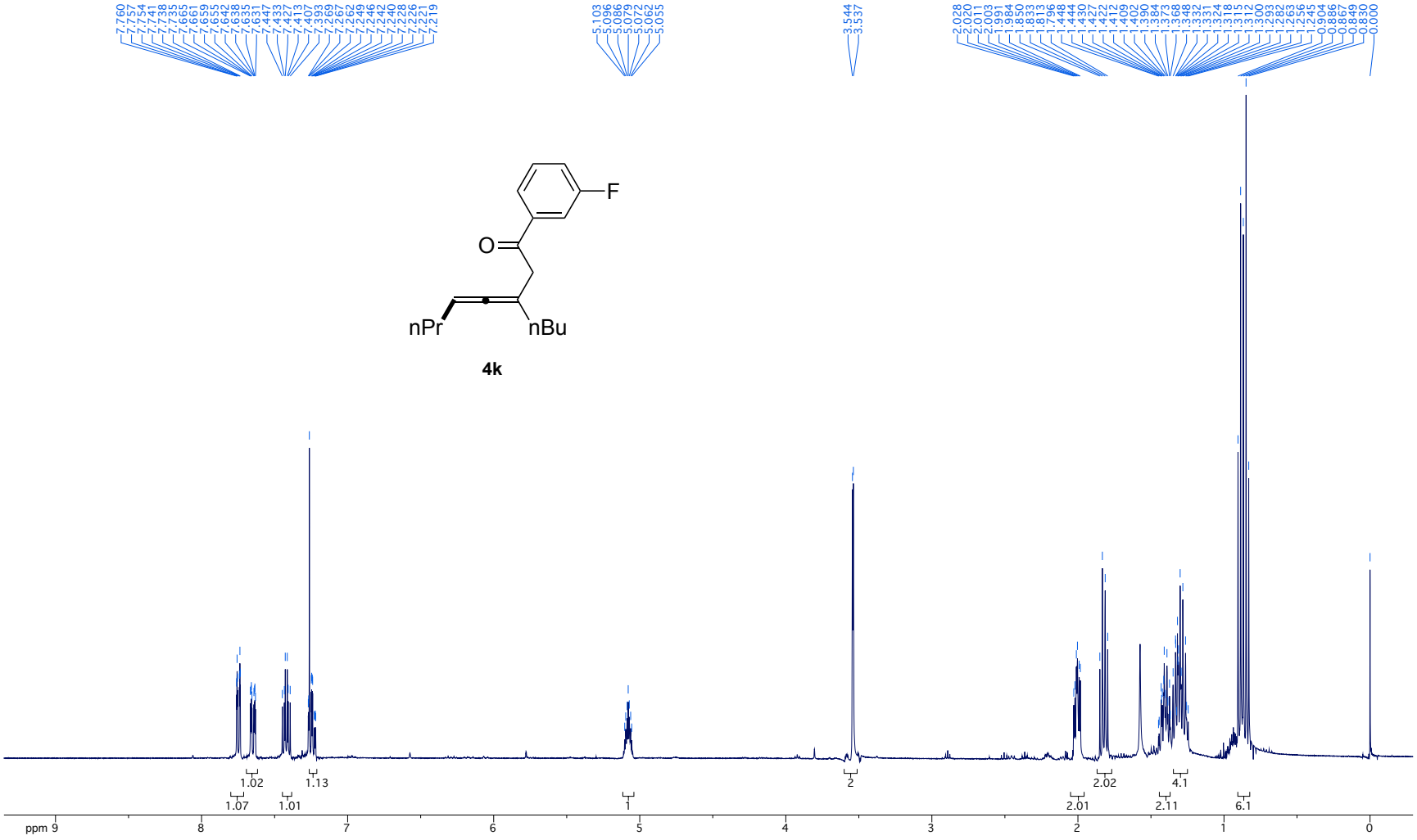
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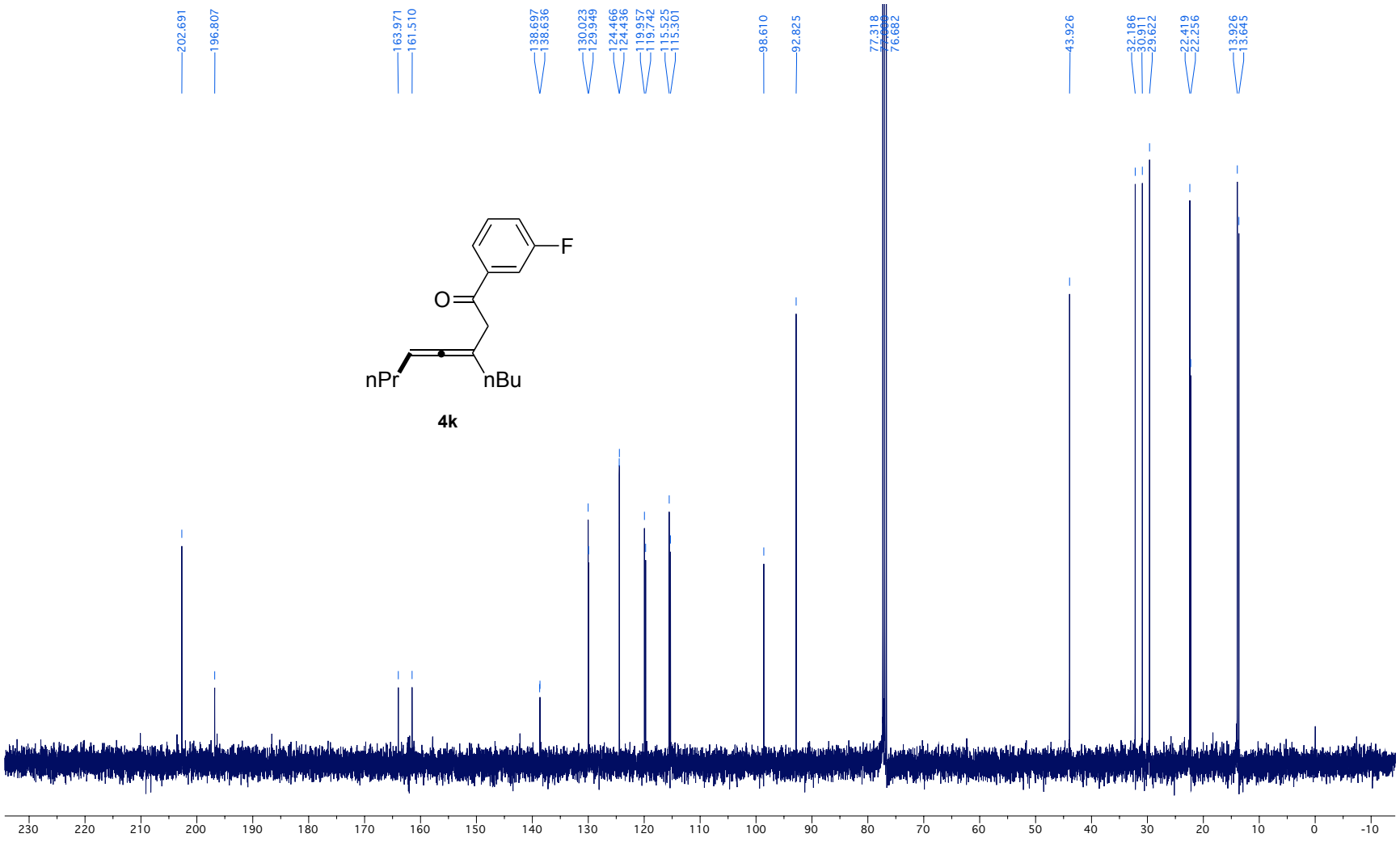
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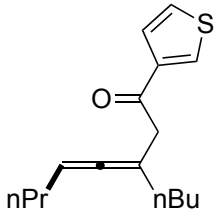
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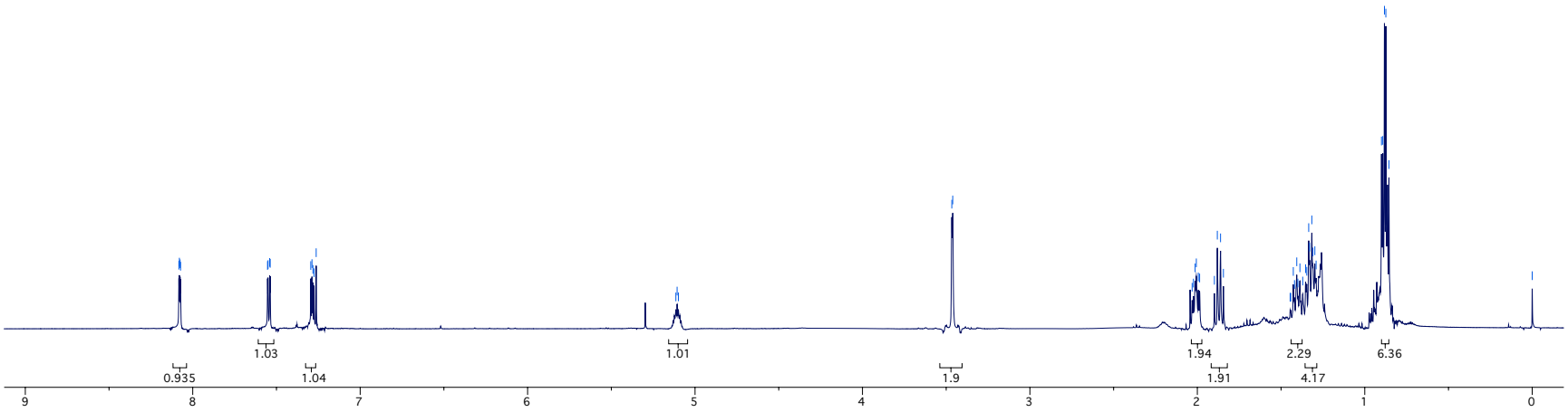
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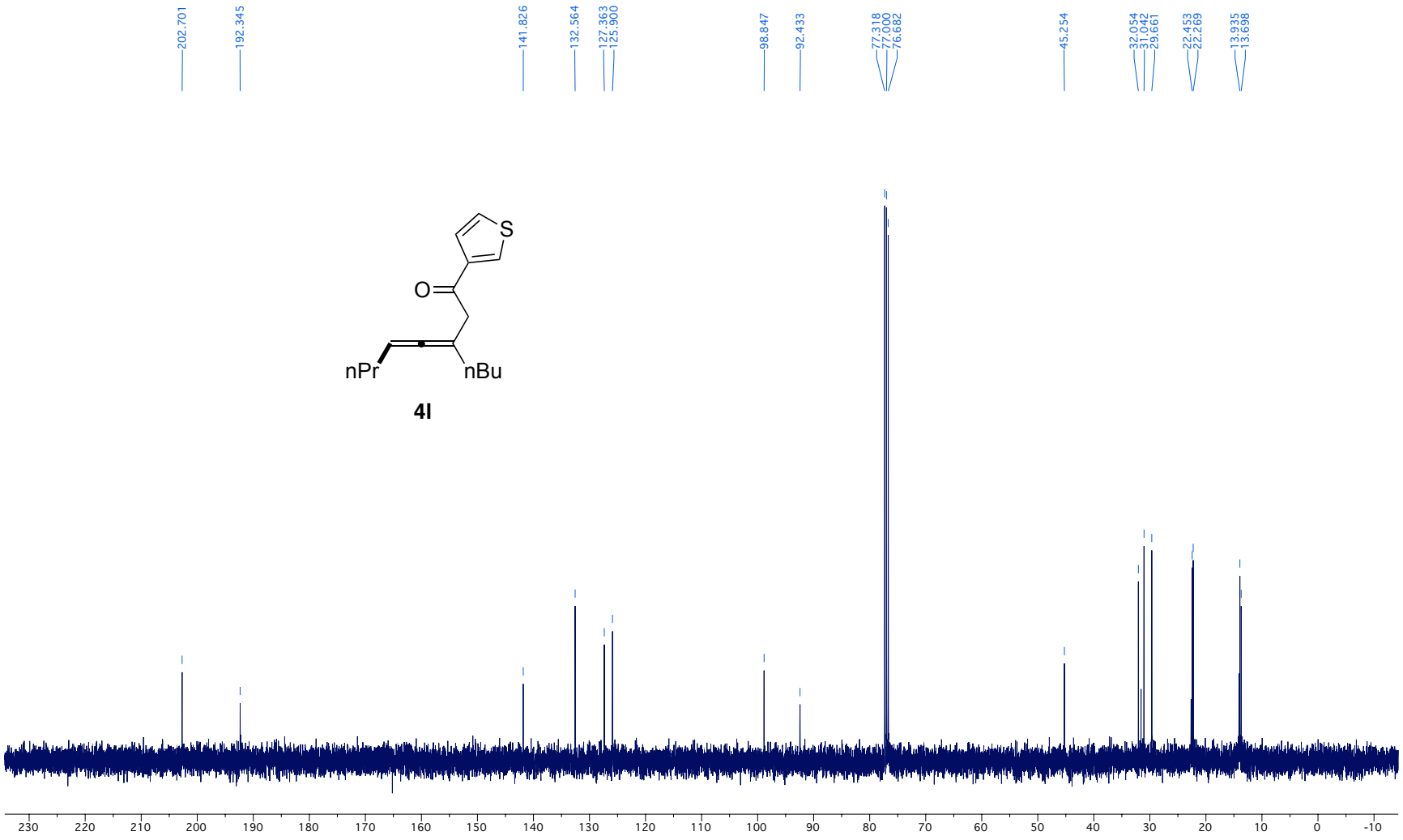
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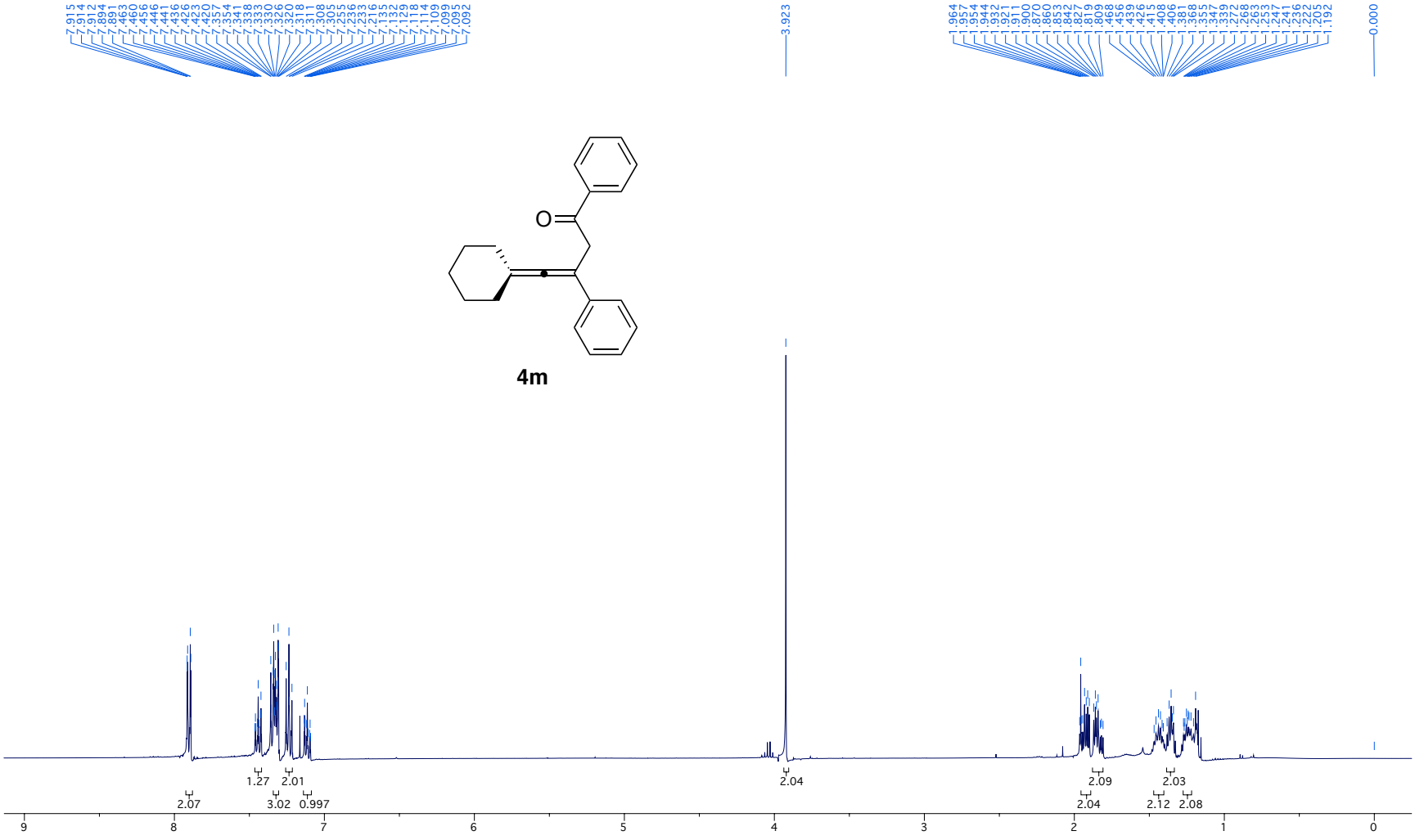
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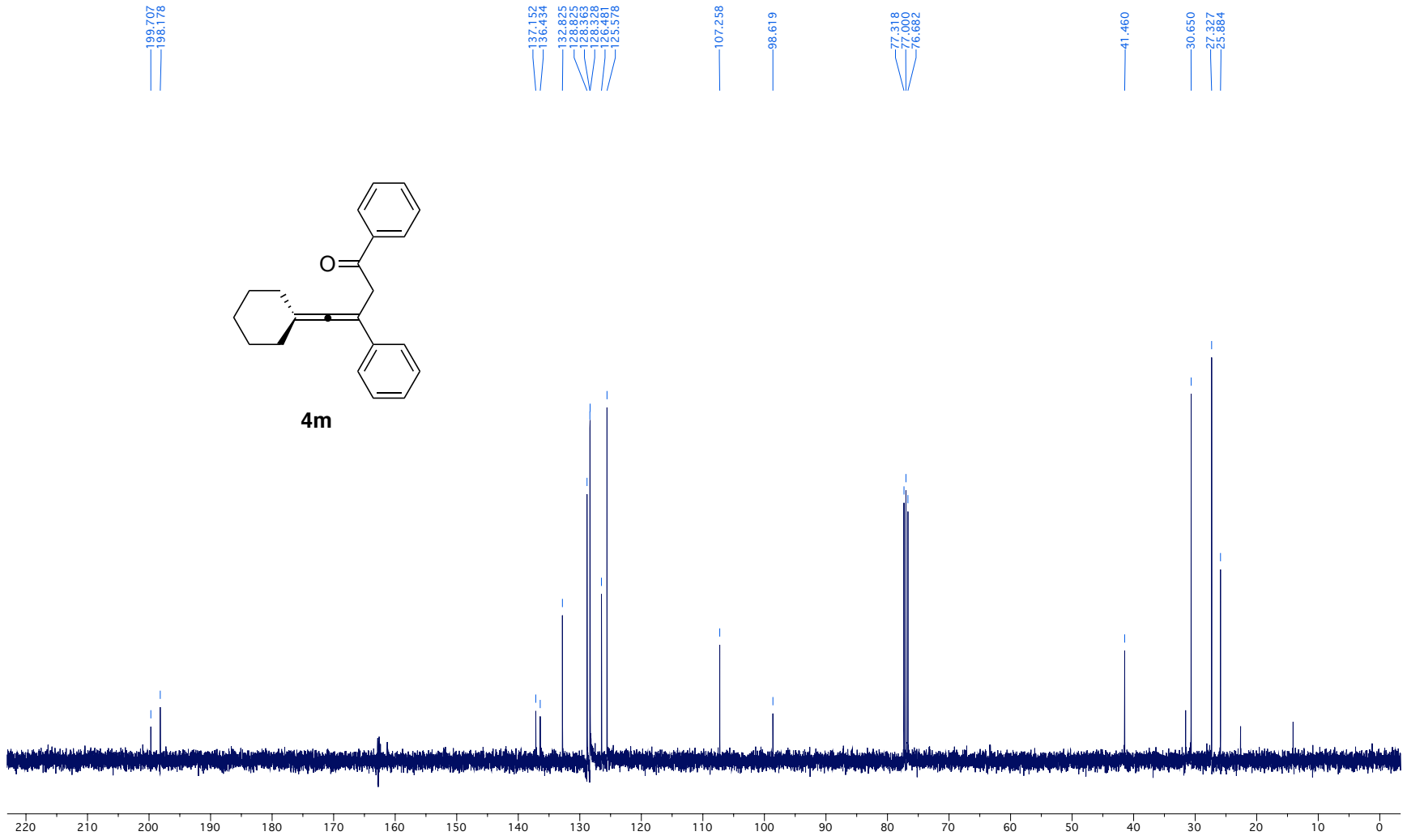
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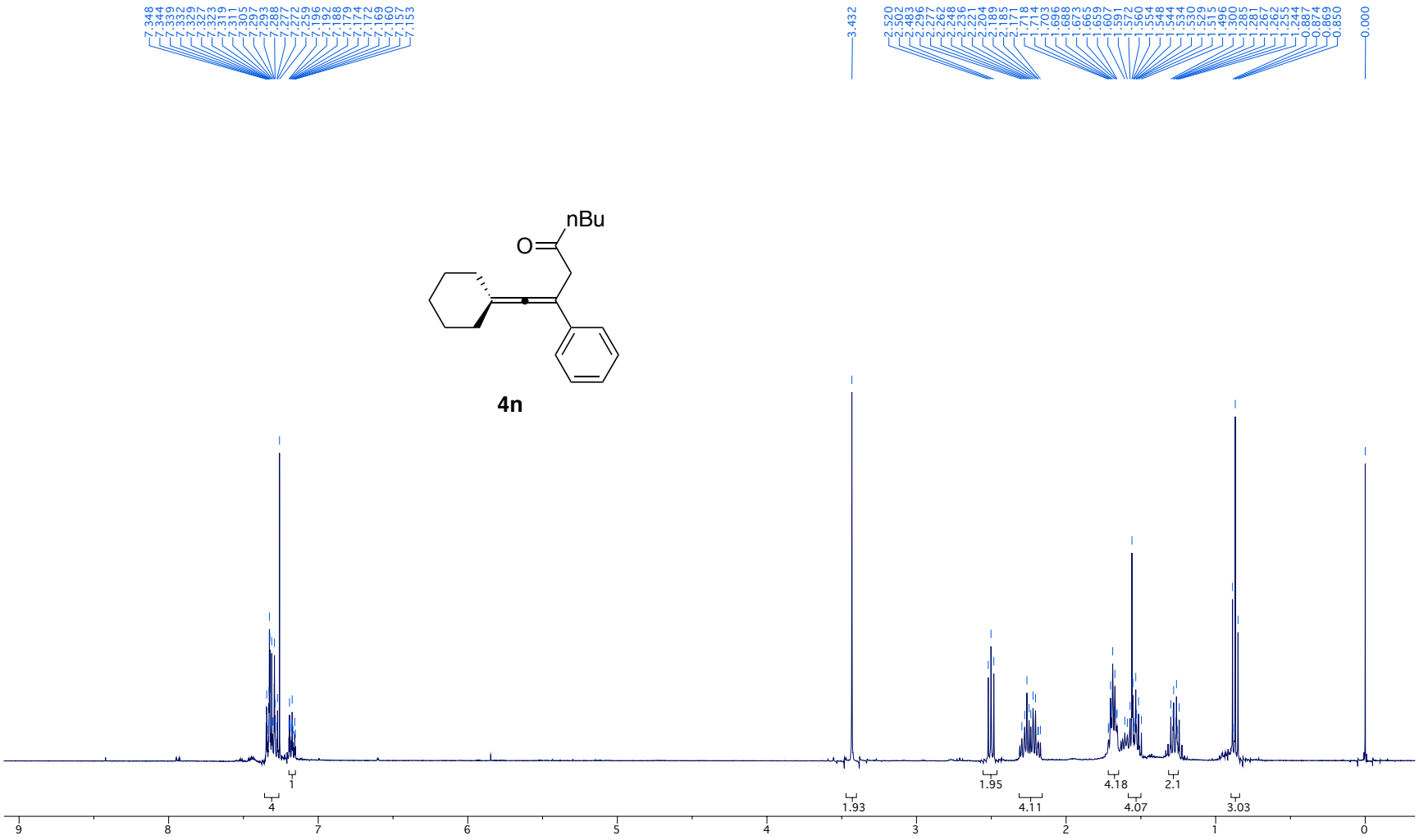
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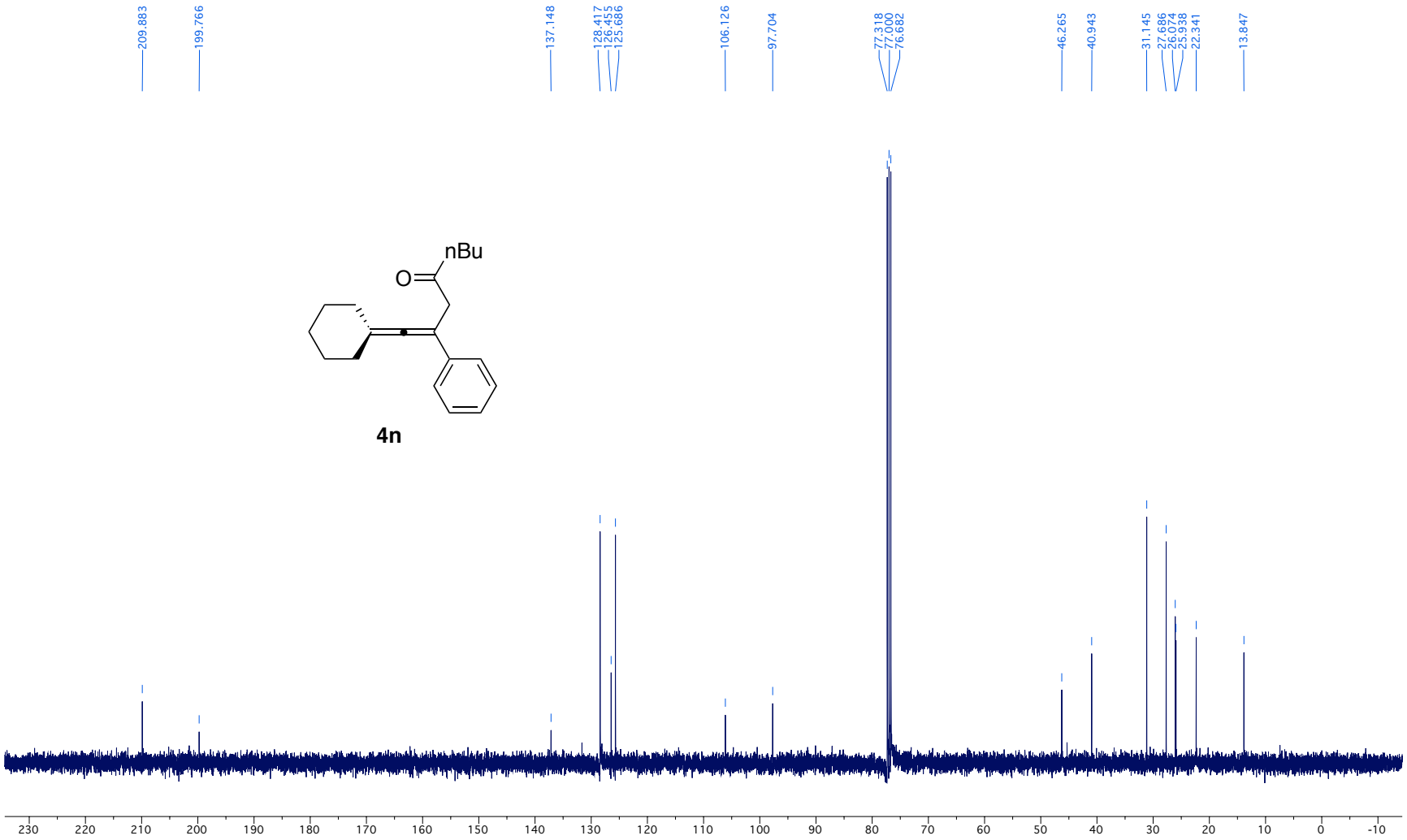
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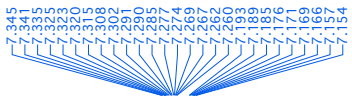
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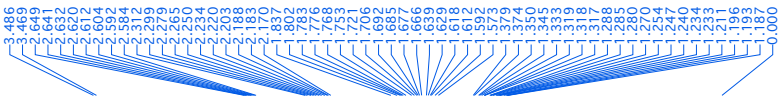
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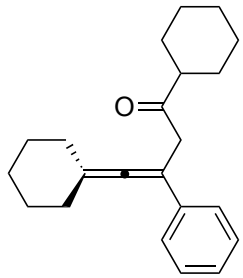
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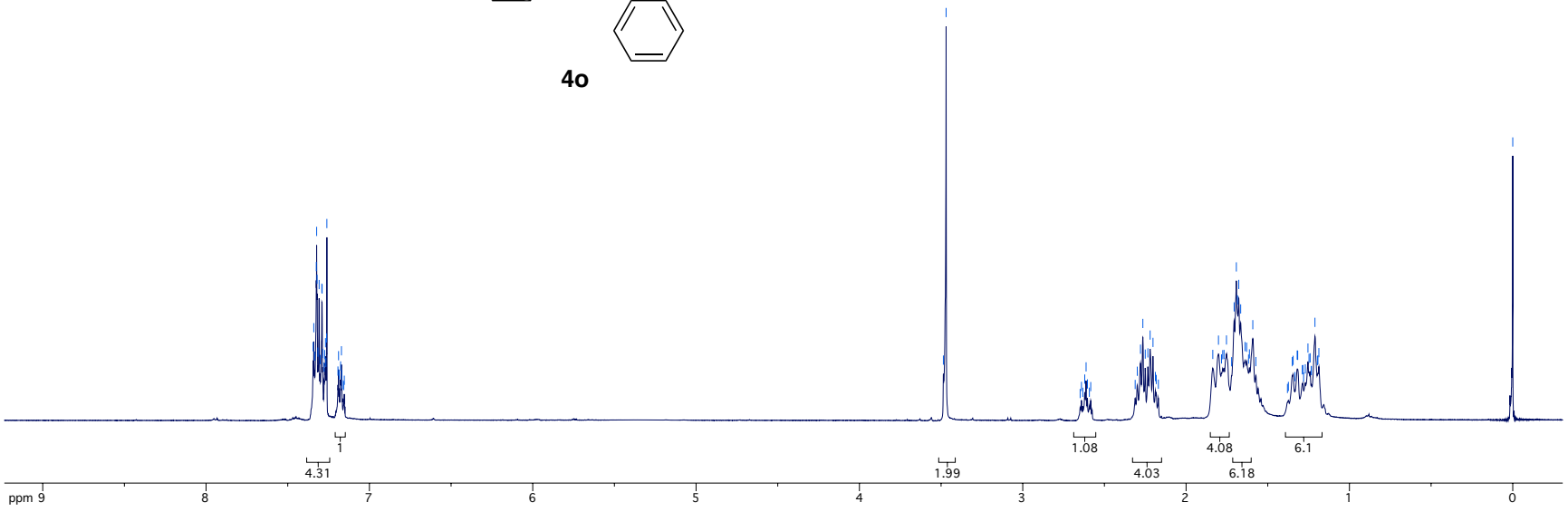
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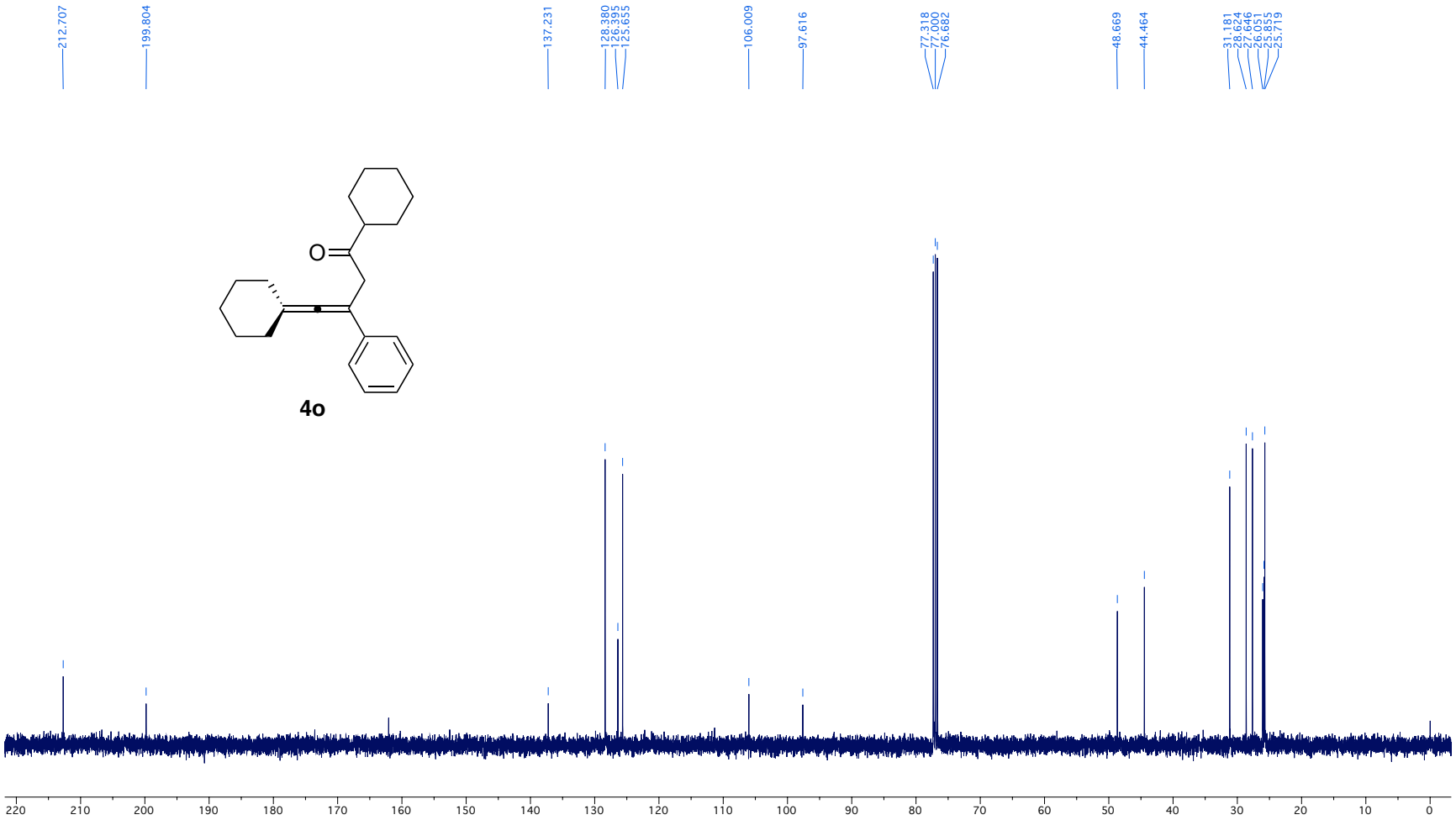
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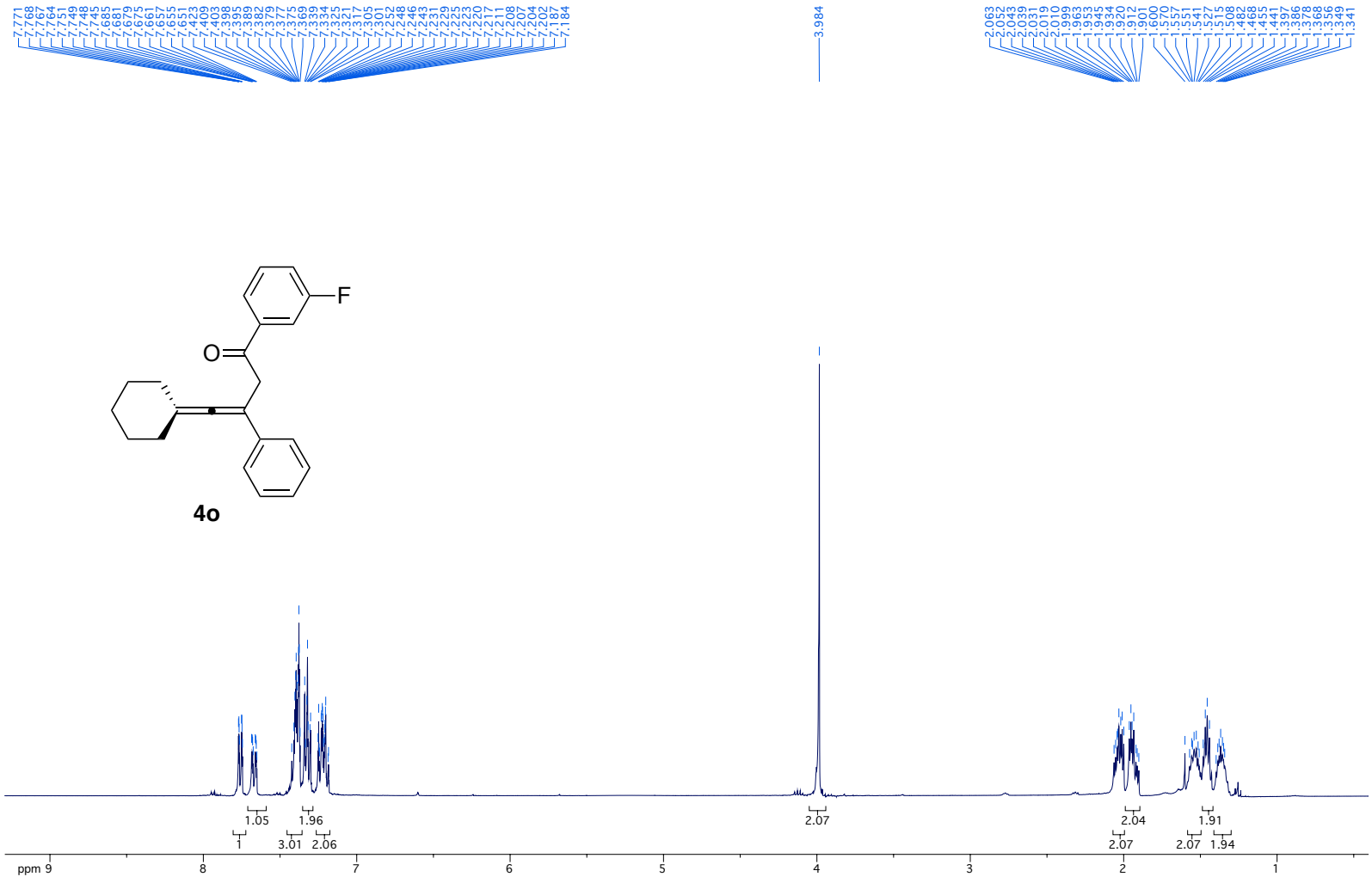
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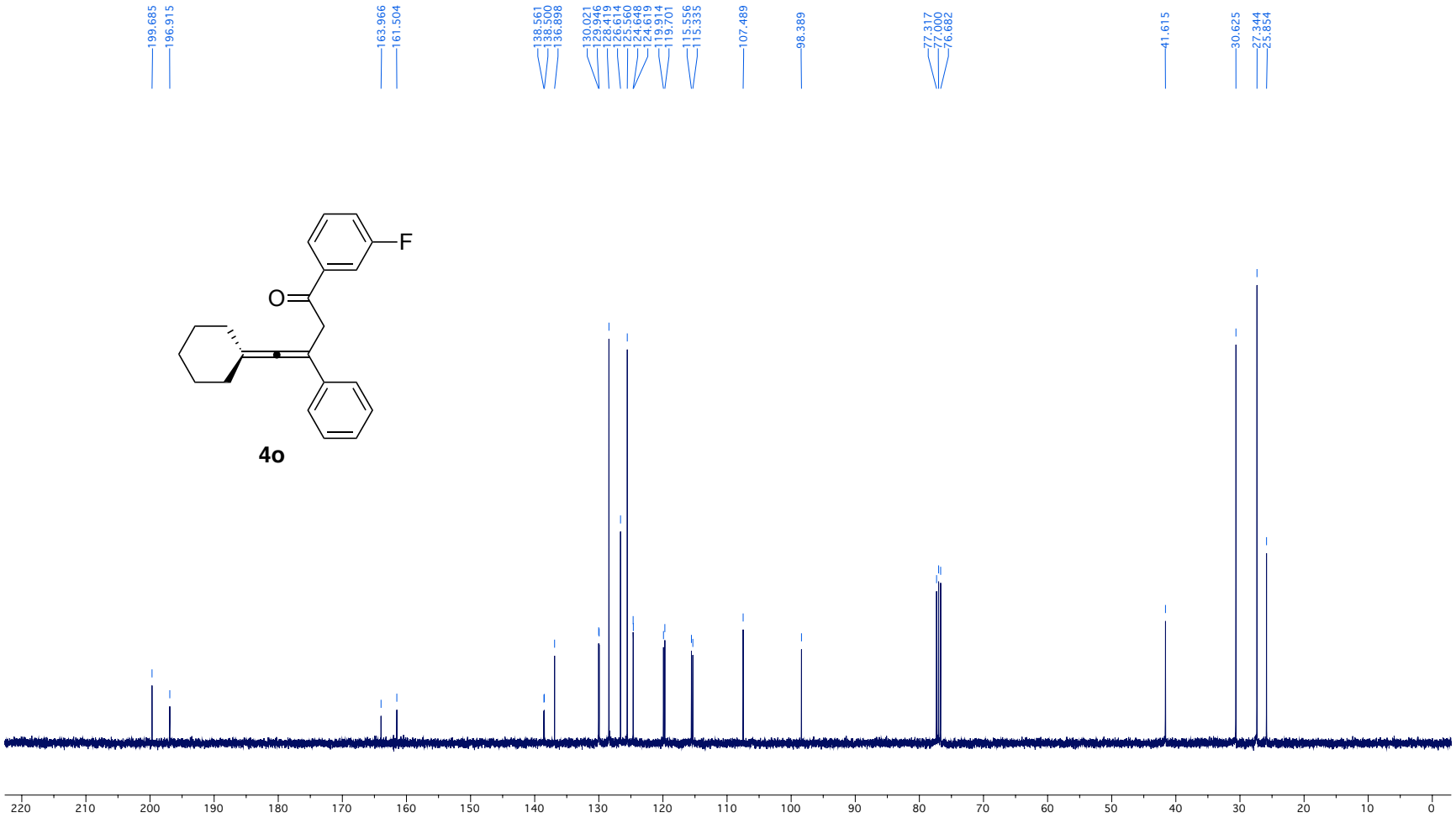
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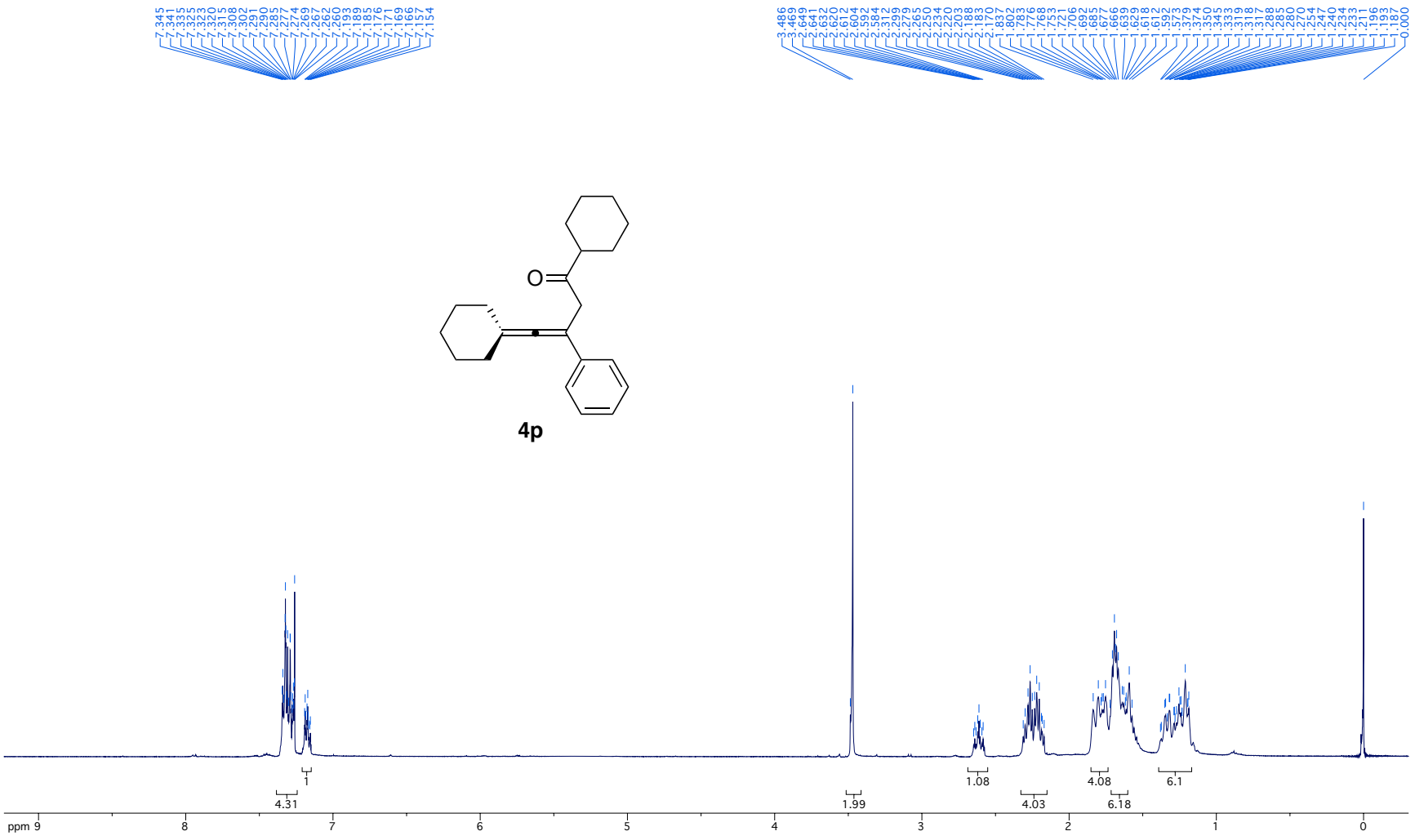
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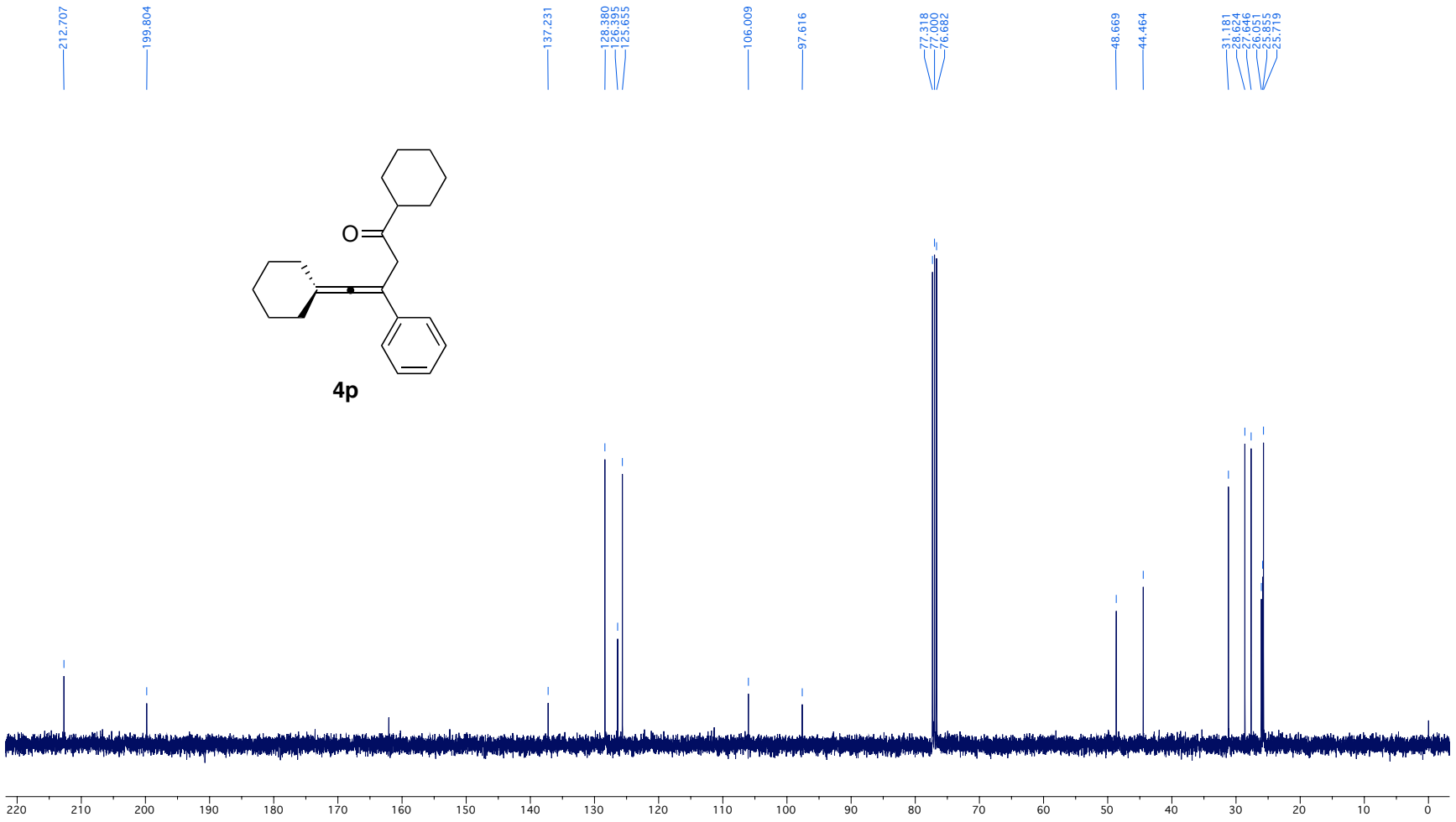
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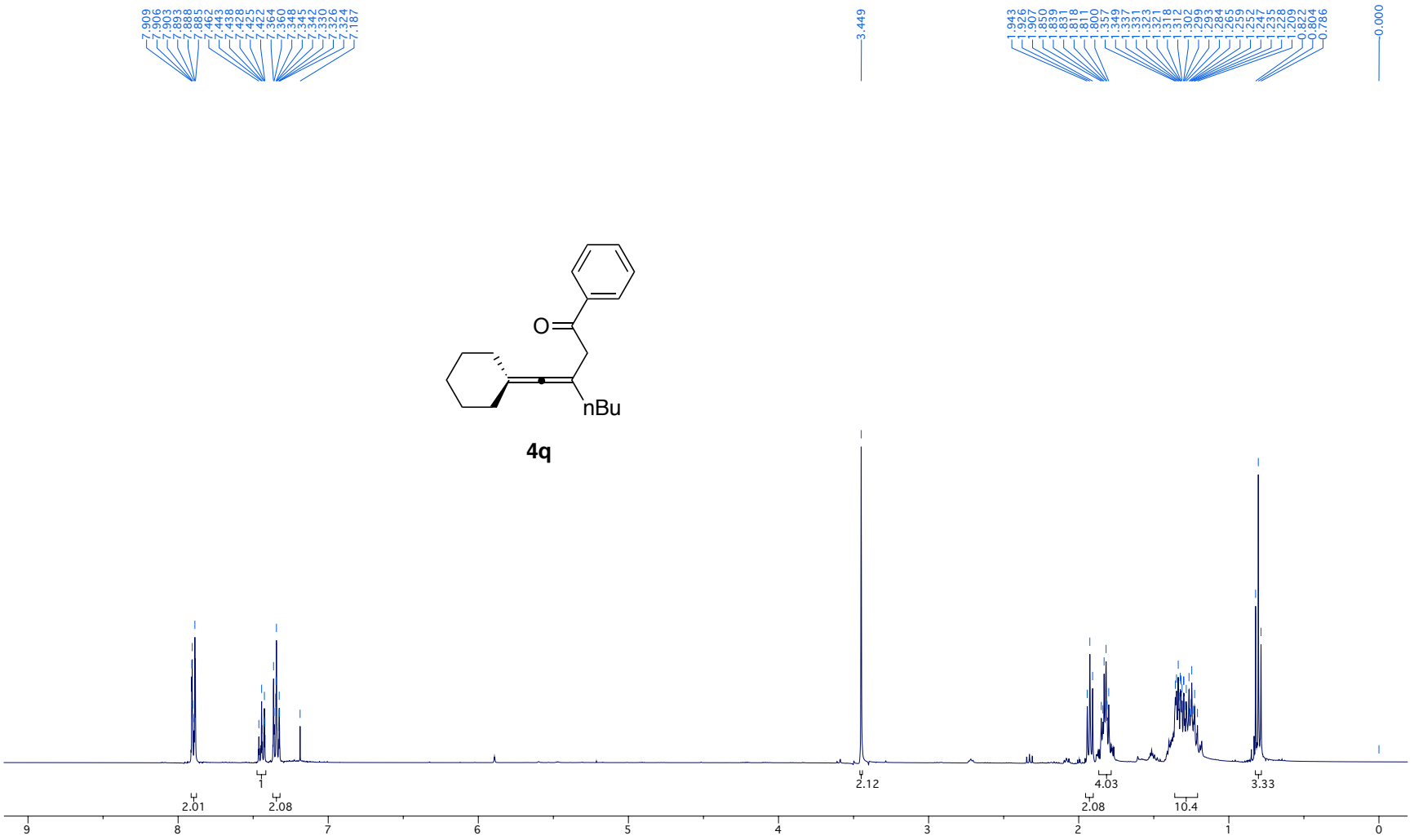
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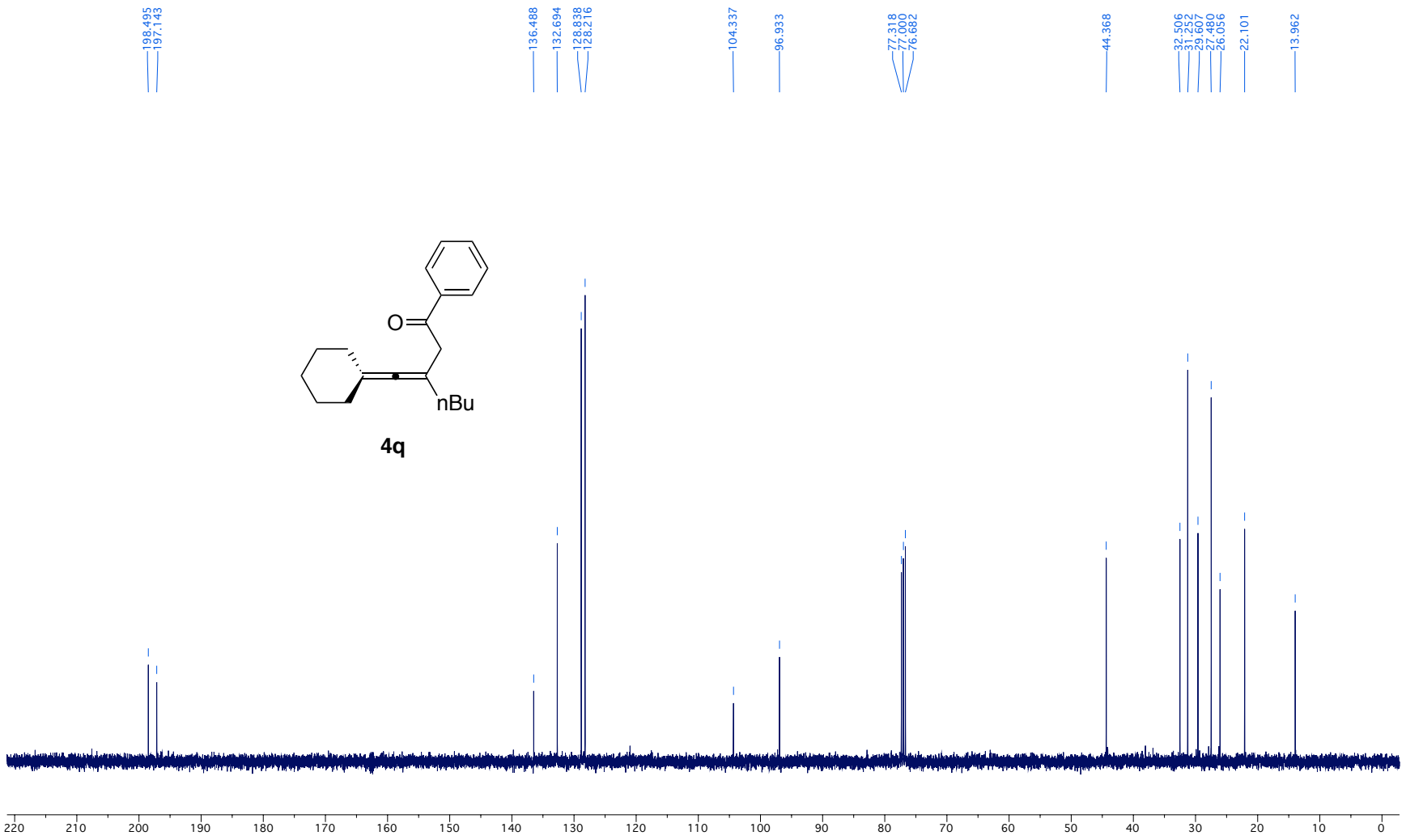
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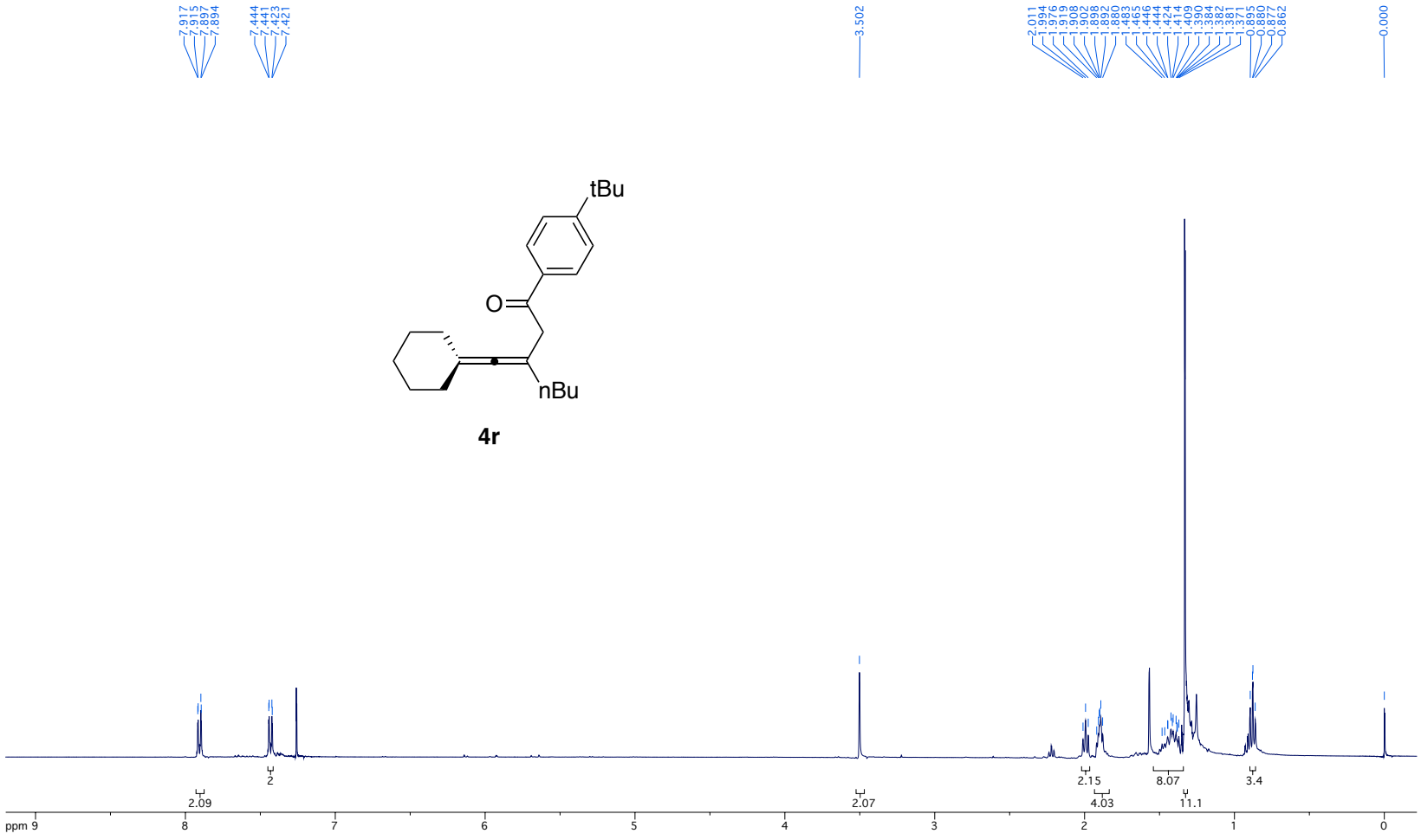
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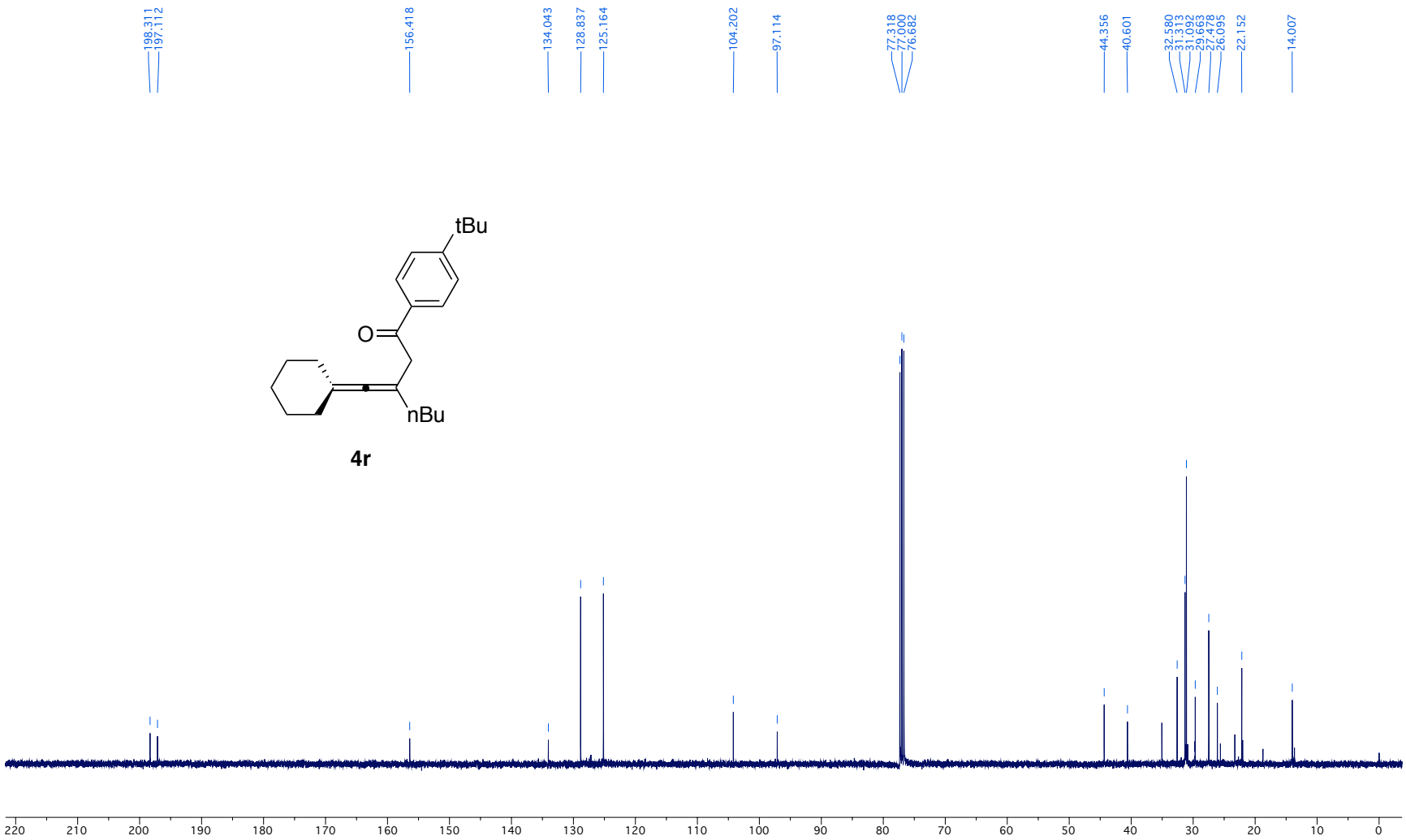
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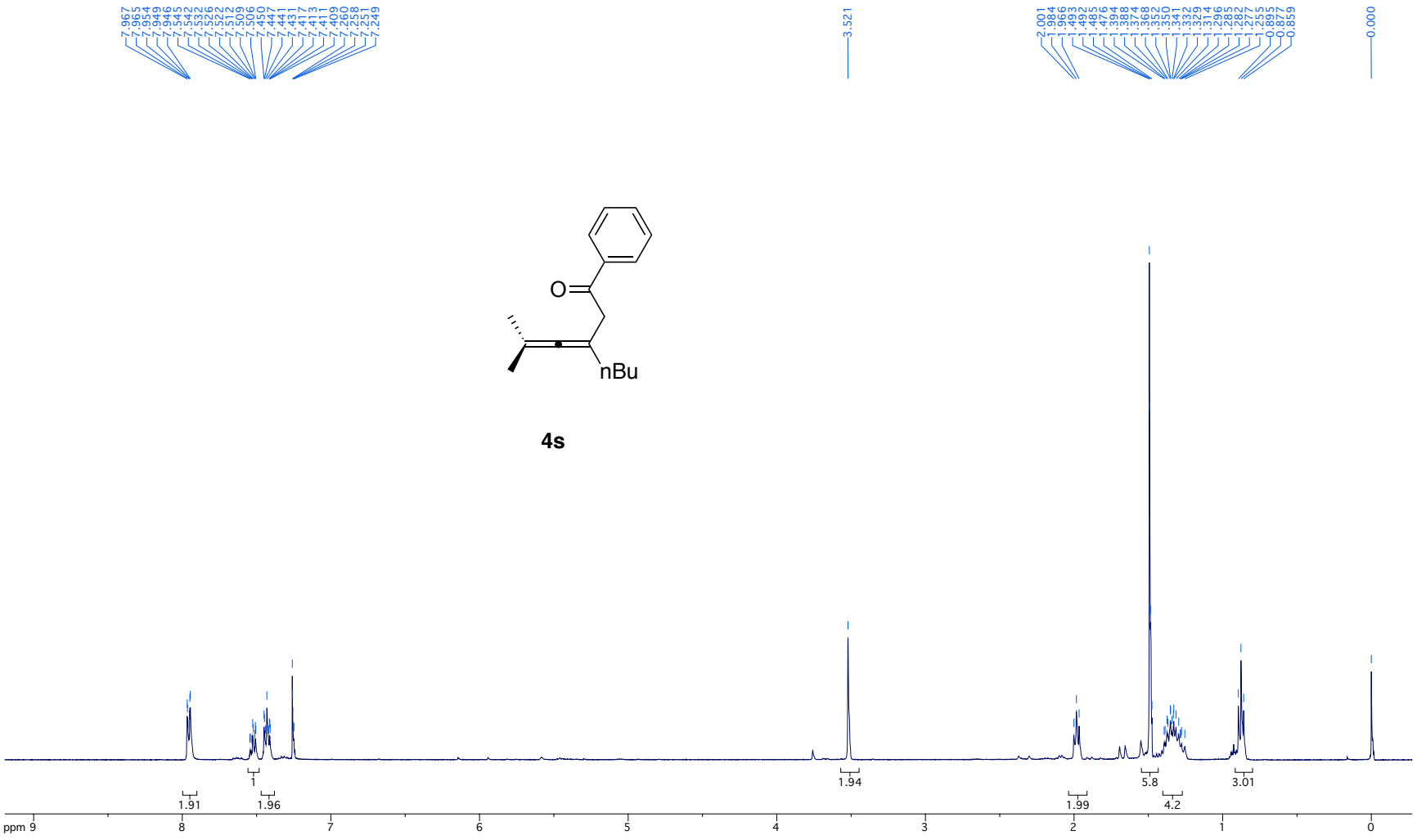
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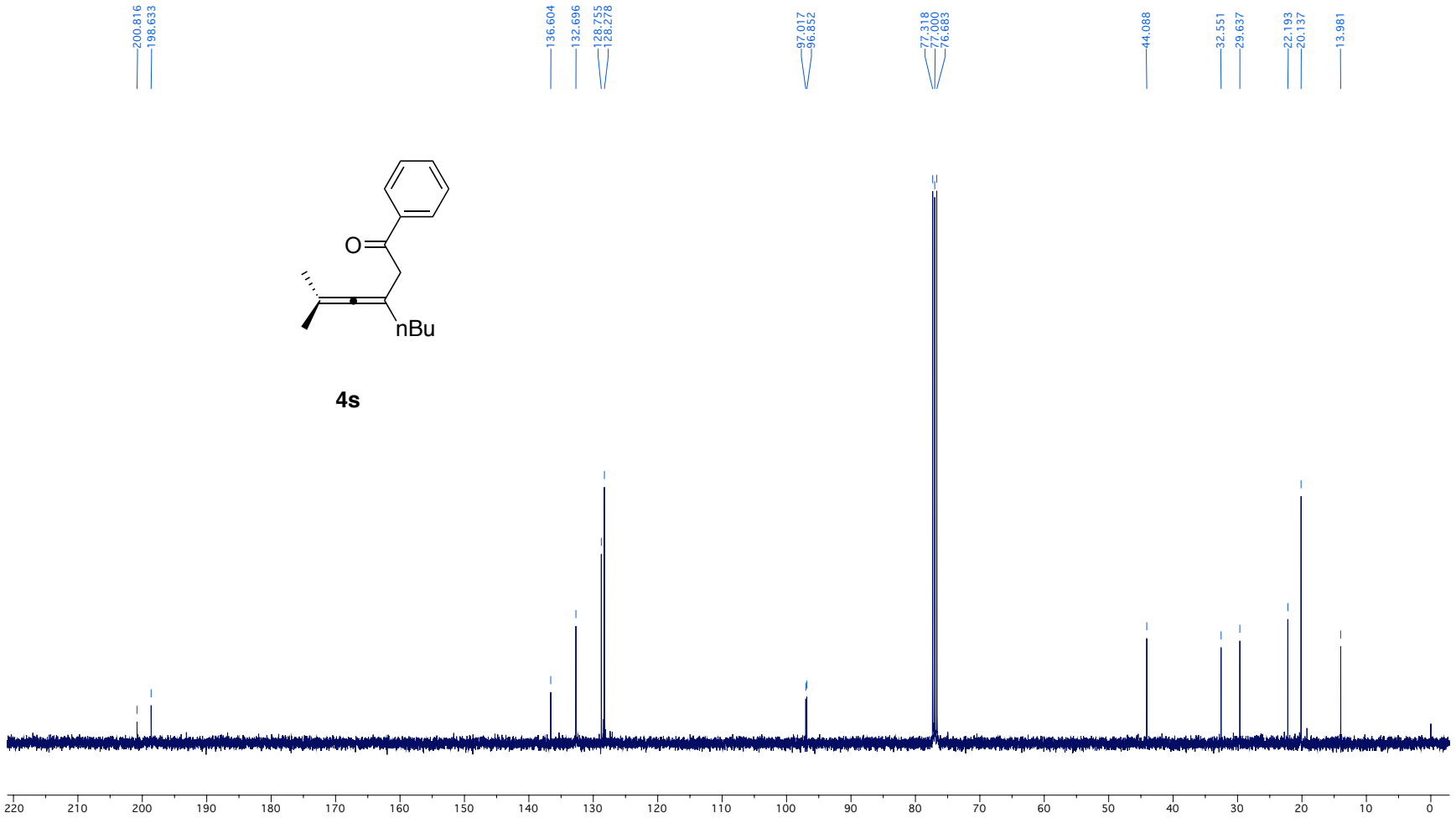
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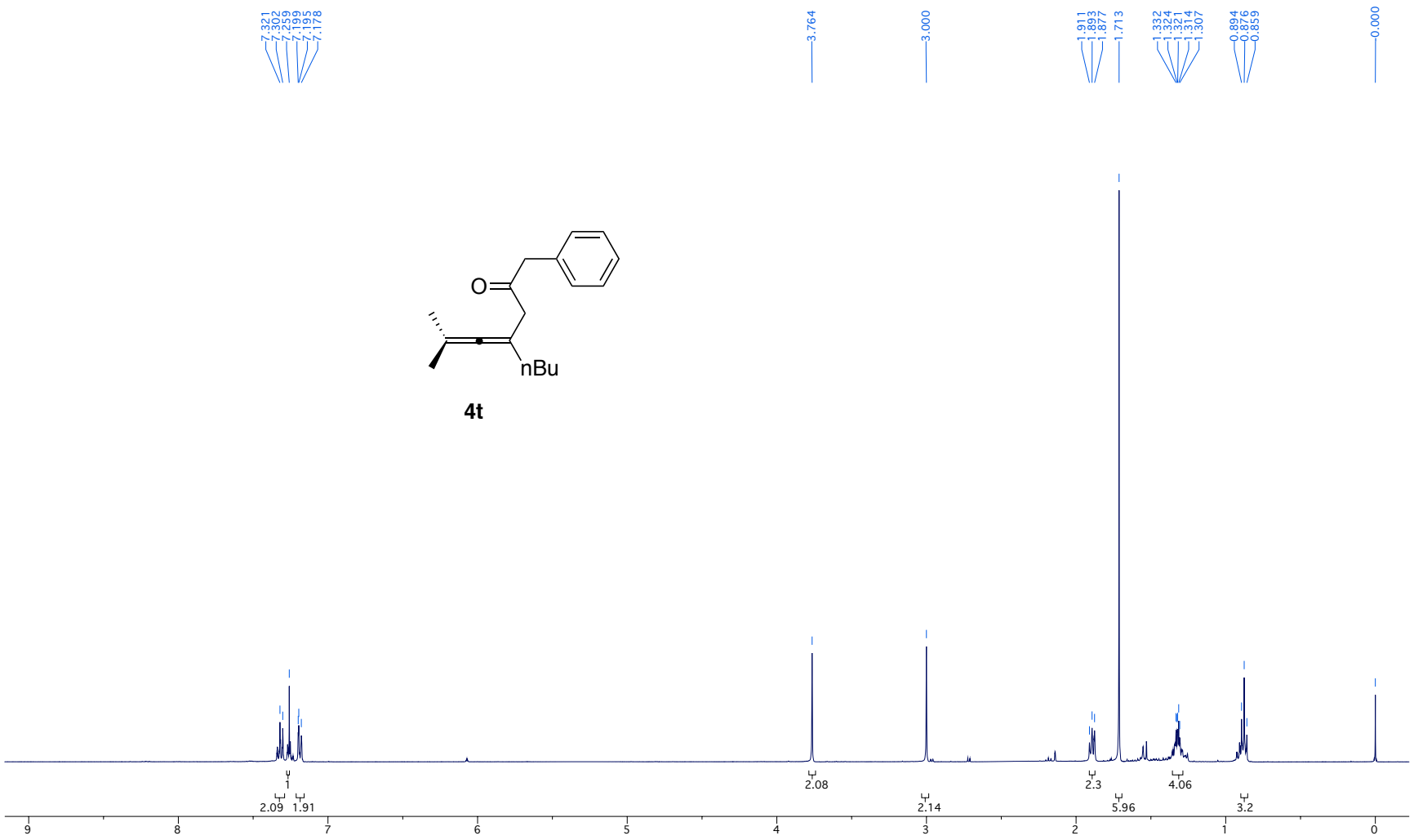
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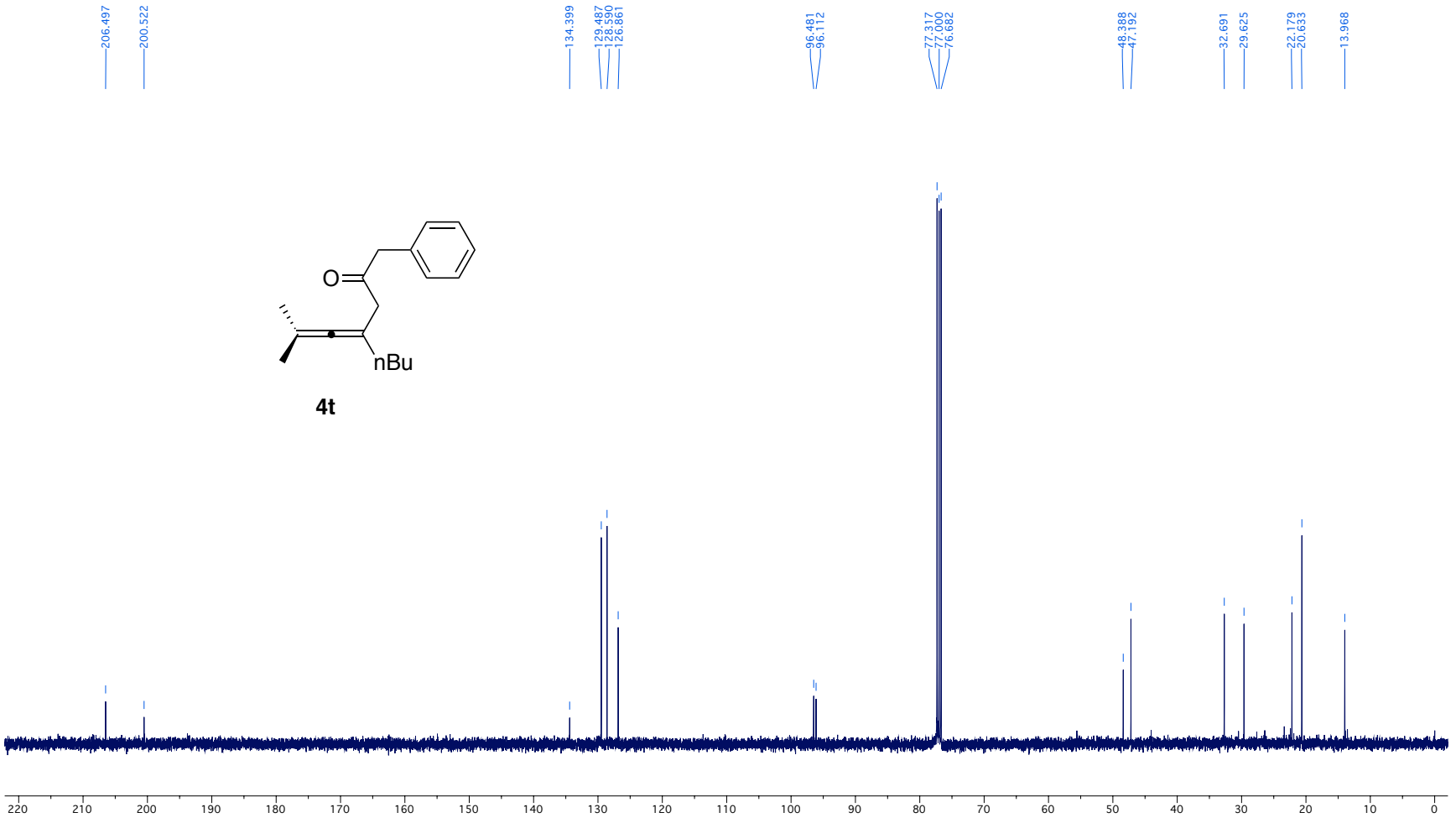
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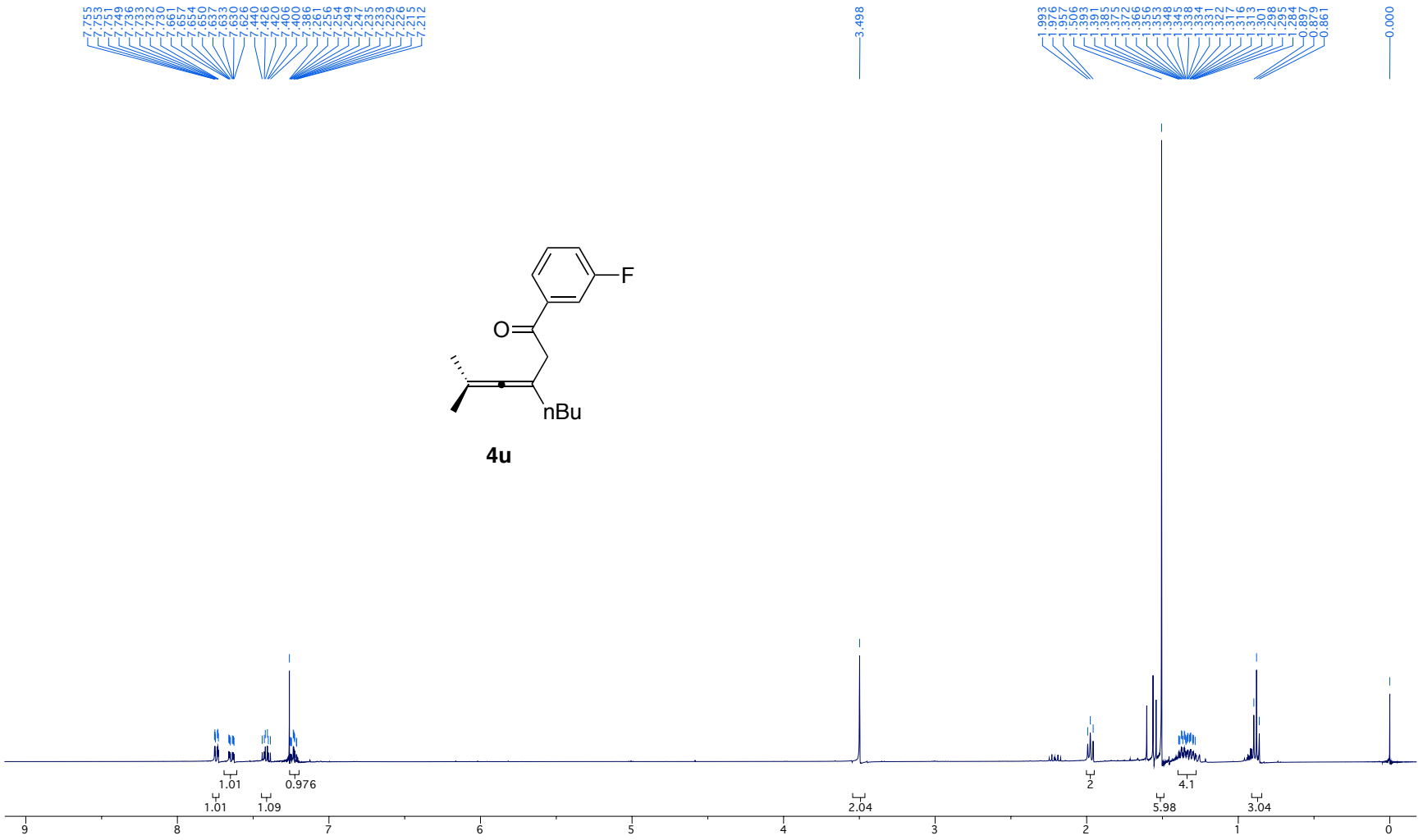
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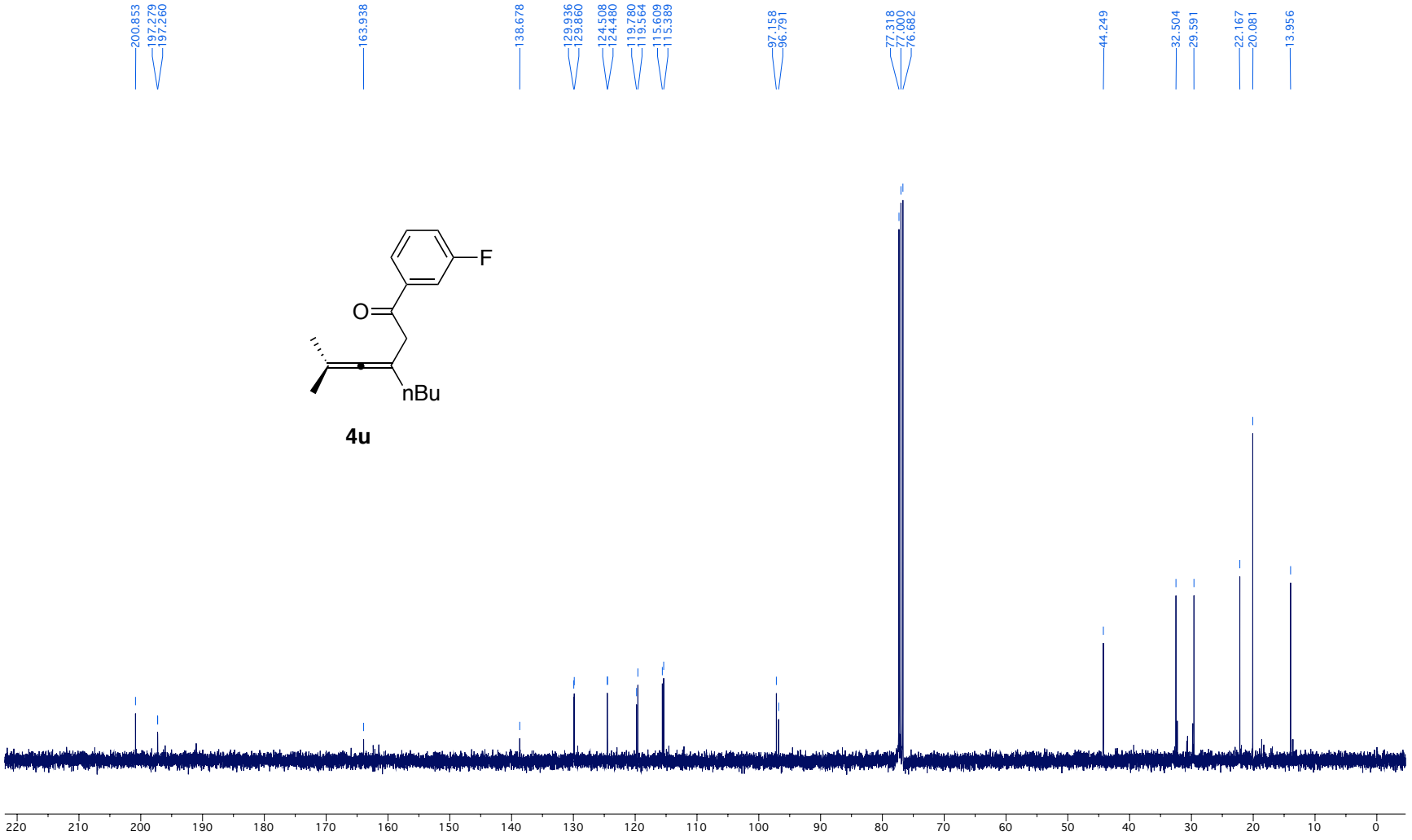
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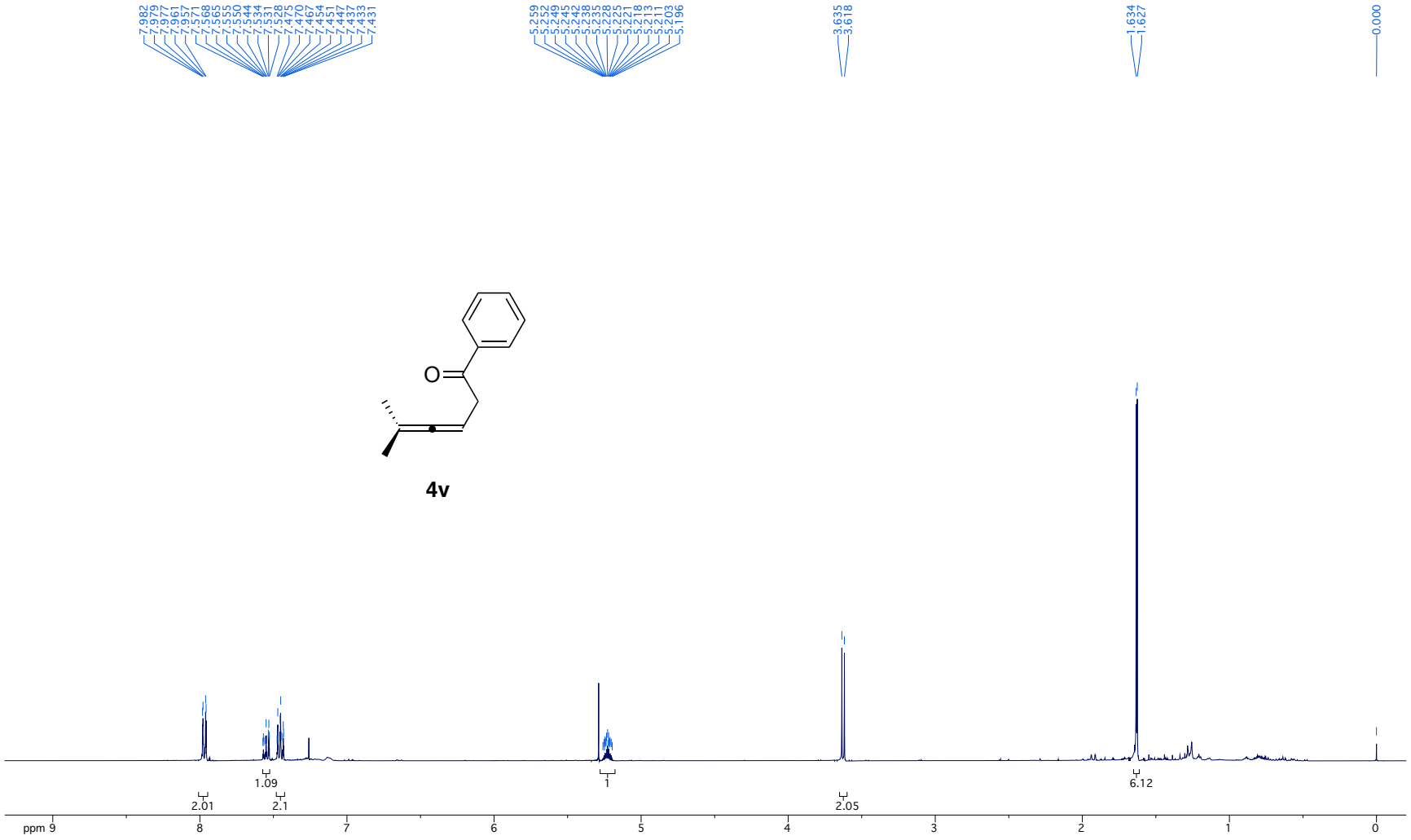
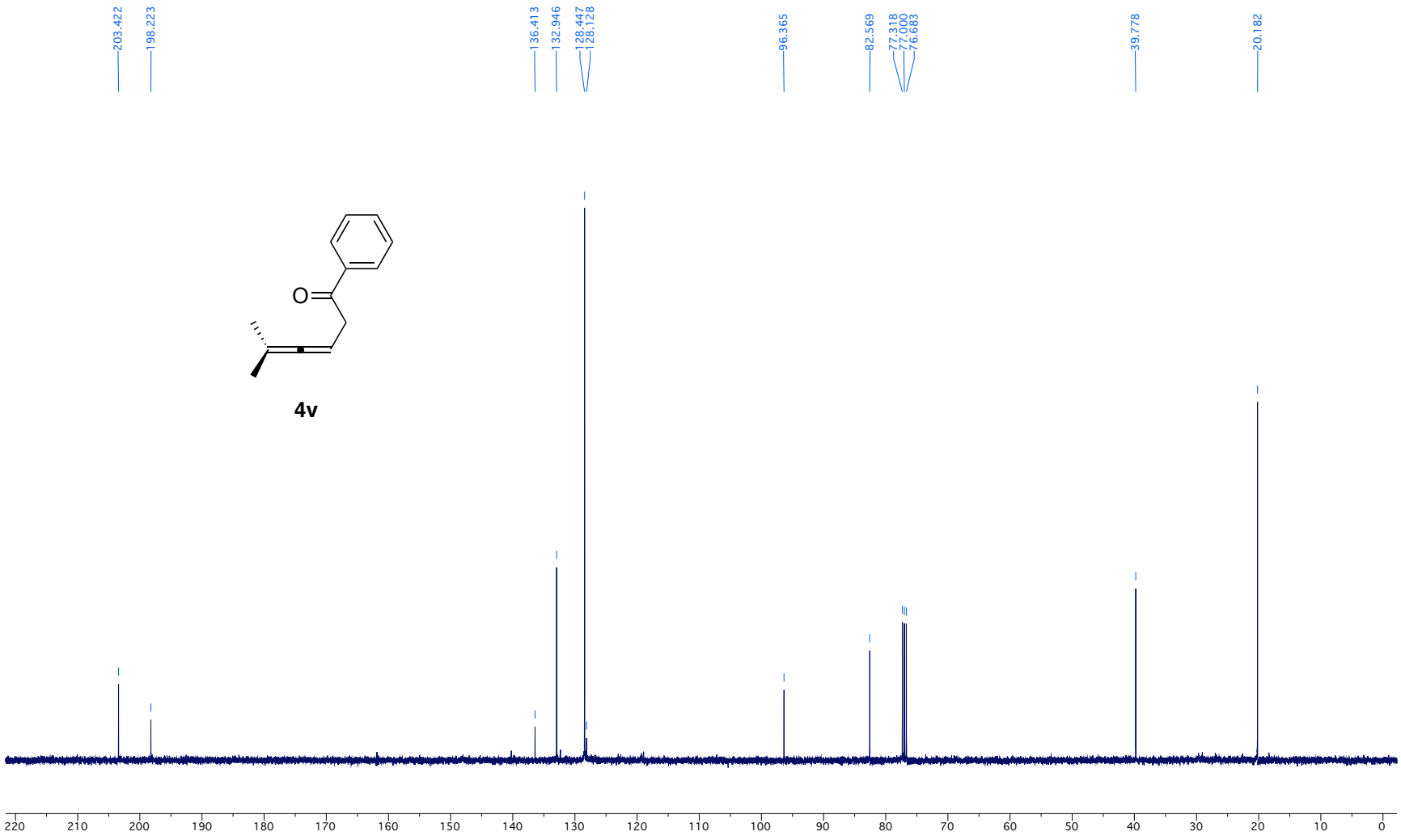
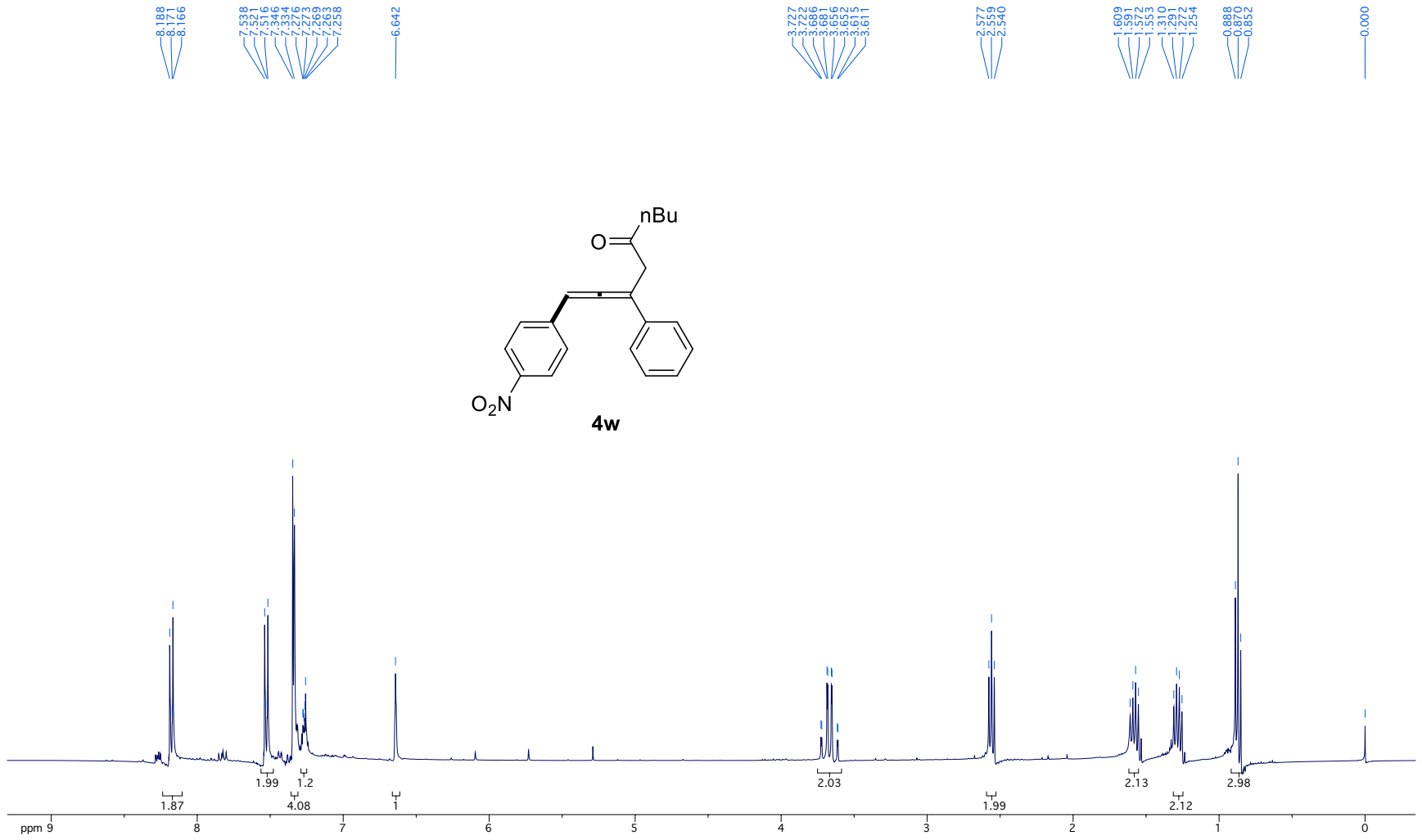
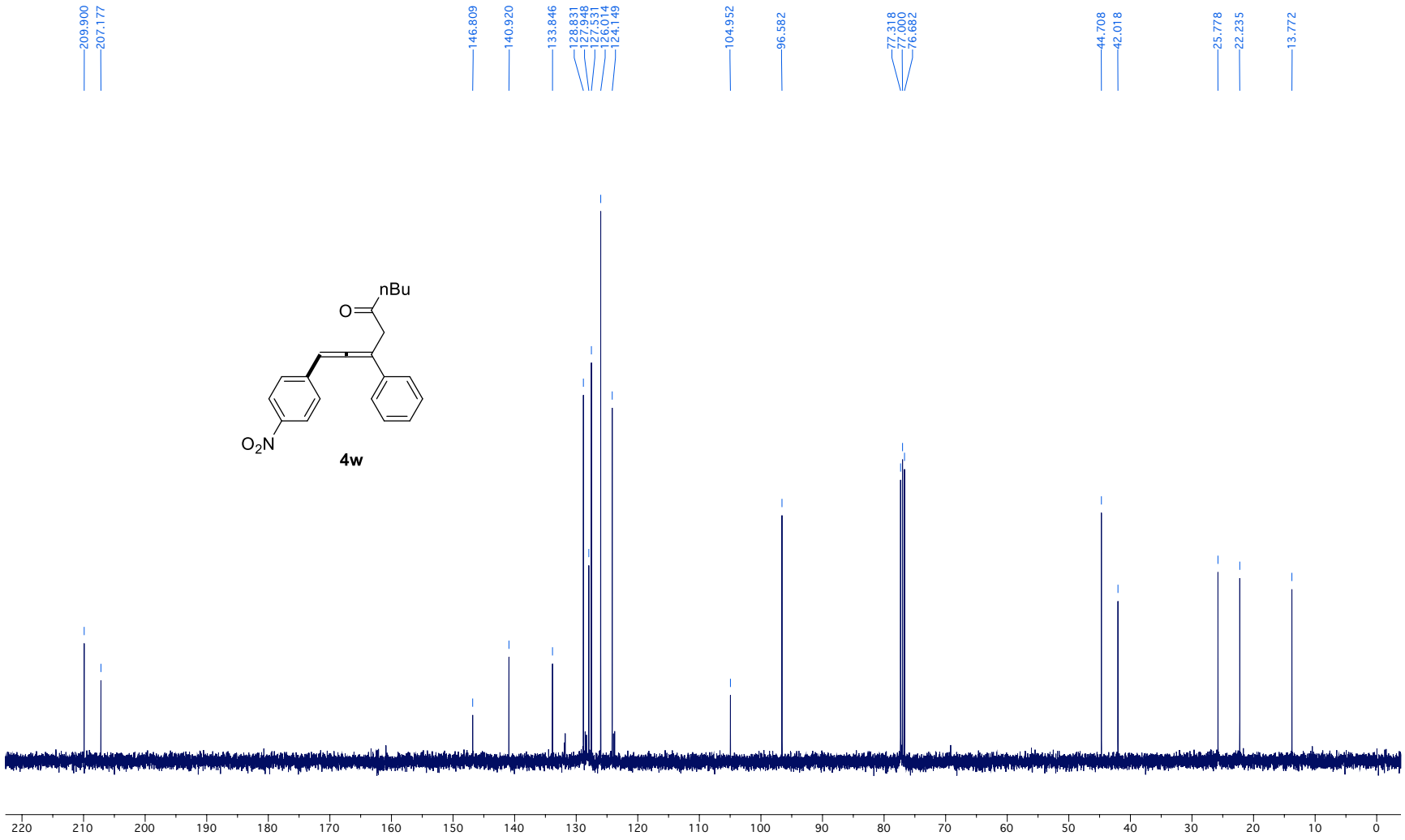
76.682
44.249
32.504
29.591
22.167
20.081
13.956
F
O
nBu
4u
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

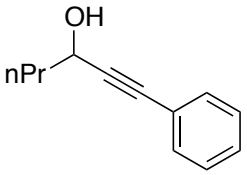

7.982
7.979
7.976
7.967
7.961
7.957
7.571
7.568
7.565
7.555
7.550
7.544
7.534
7.531
7.528
7.475
7.470
7.467
7.454
7.451
7.447
7.437
7.433
7.431
5.259
5.252
5.249
5.245
5.242
5.238
5.235
5.228
5.225
5.221
5.218
5.213
5.211
5.203
5.196
3.635
3.618
1.634
1.627
0.000
O
4v
1.09
2.01
2.1
1
2.05
6.12
ppm 9
8
7
6
5
4
3
2
1
0

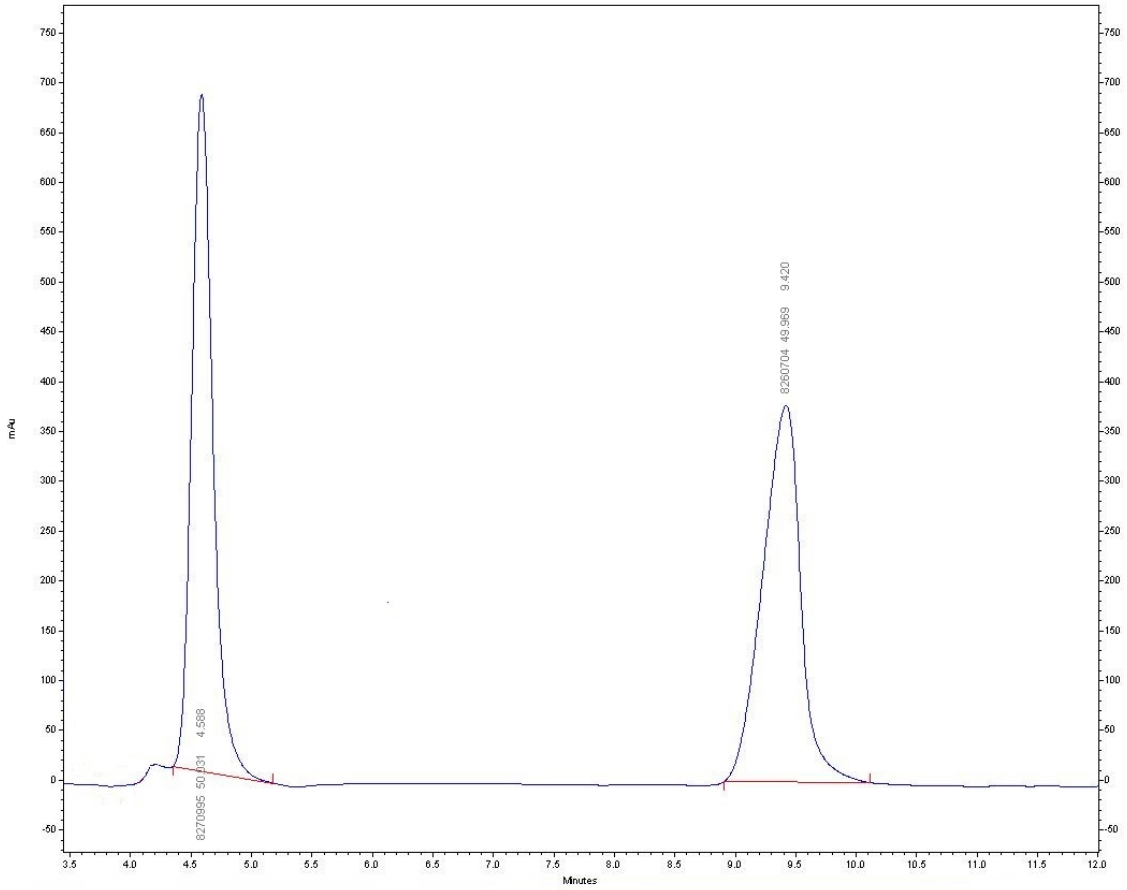

203.422
198.223
136.413
132.946
128.447
128.128
96.365
82.569
77.318
77.000
76.683
39.778
20.182
O
4v
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.188
8.171
8.166
7.538
7.521
7.516
7.346
7.334
7.276
7.273
7.269
7.263
7.258
6.642
3.727
3.722
3.686
3.681
3.656
3.652
3.615
3.611
2.577
2.559
2.540
1.609
1.591
1.572
1.553
1.310
1.291
1.272
1.254
0.888
0.870
0.852
0.000
nBu
O
O2N
4w
1.87
1.99
4.08
1.2
1
2.03
1.99
2.13
2.12
2.98
ppm 9
8
7
6
5
4
3
2
1
0


209.900
207.177
146.809
140.920
133.846
128.831
127.948
127.531
126.014
124.149
104.952
96.582
77.318
77.000
76.682
44.708
42.018
25.778
22.235
13.772
nBu
O
O_2N
4w
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

V. Chiral HPLC Chromatogram

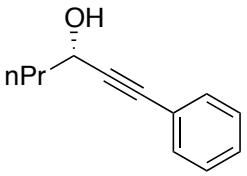


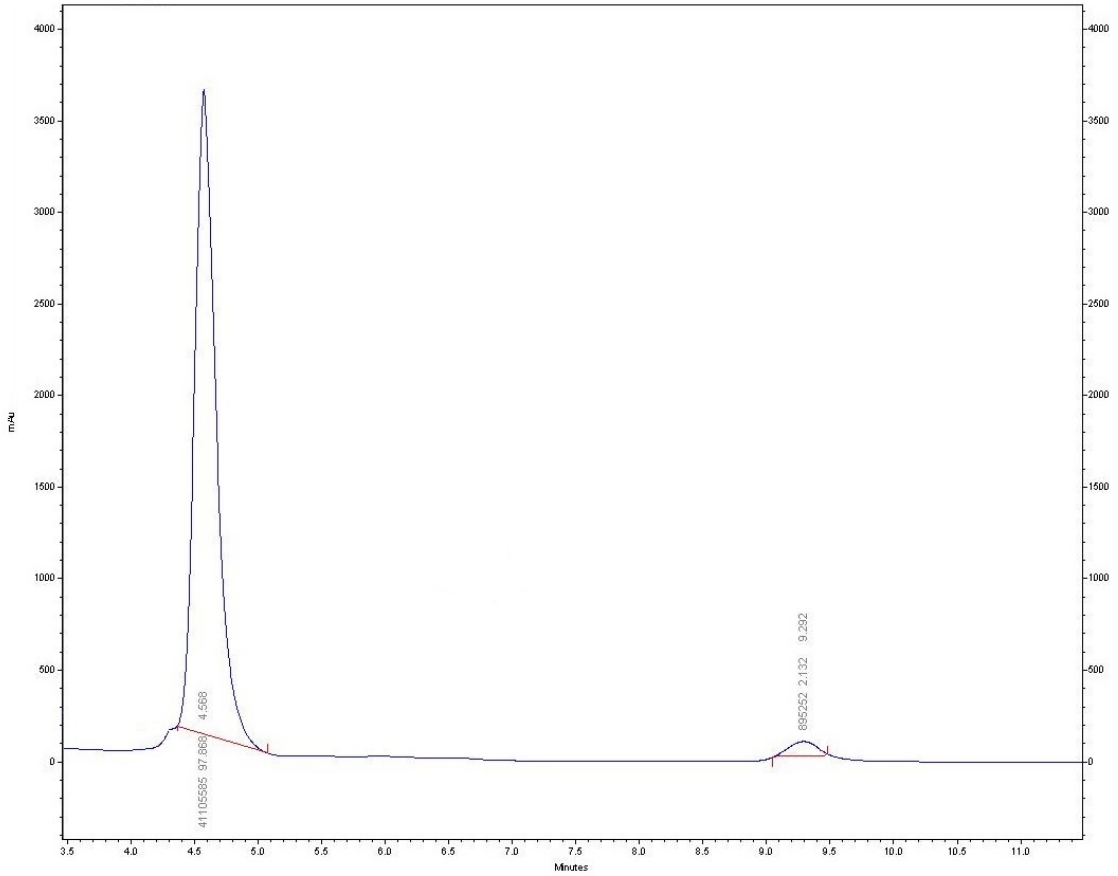


SPD-M20A-260

nm Results

Retention Time	Area	Area %	Height	Height %
4.588	13170618	49.92	1062738	63.82
9.420	13214897	50.08	602439	36.18

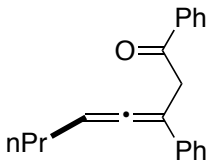


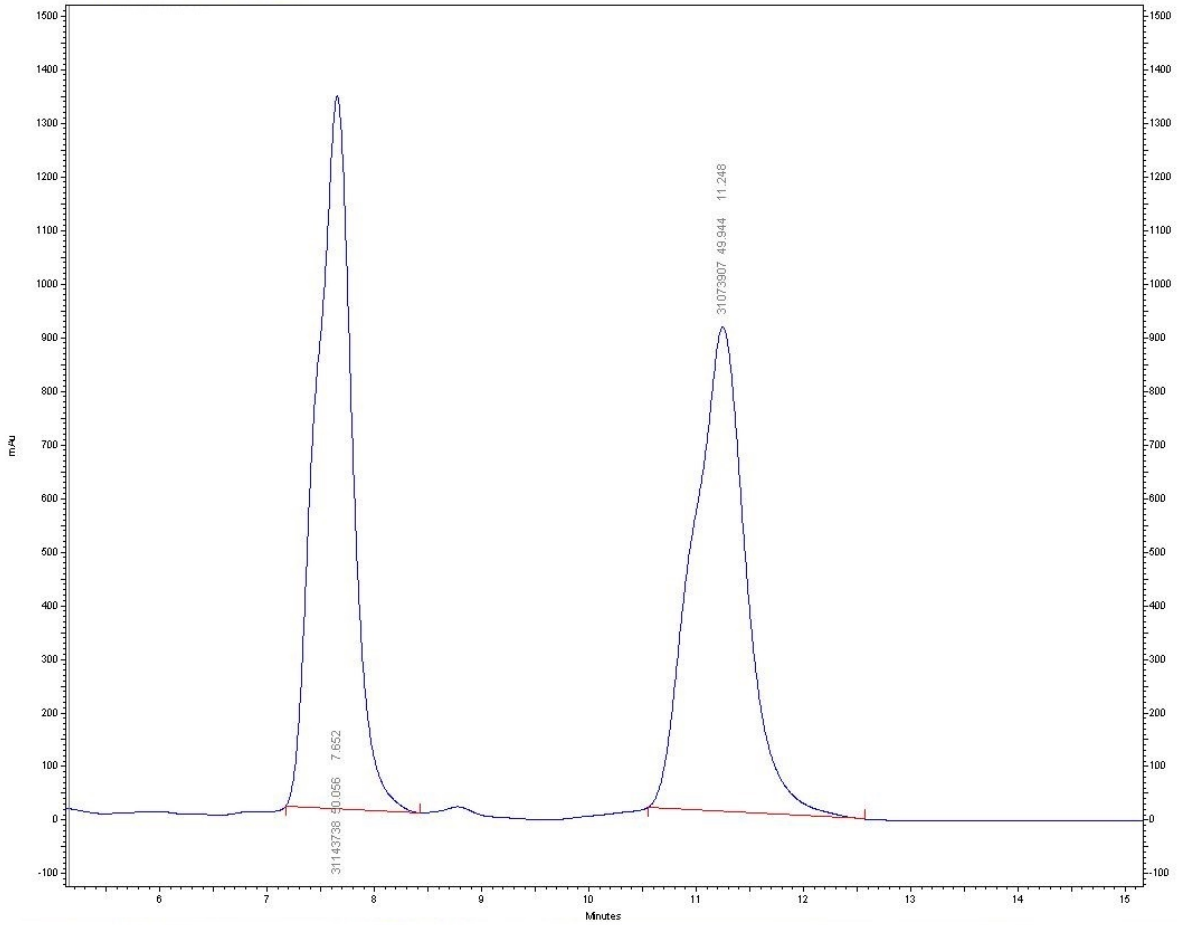


SPD-M20A-263

nm Results

Retention Time	Area	Area %	Height	Height %
4.568	41105585	97.87	3520444	98.19
9.292	895252	2.13	64889	1.81

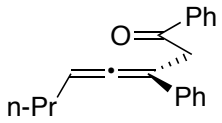


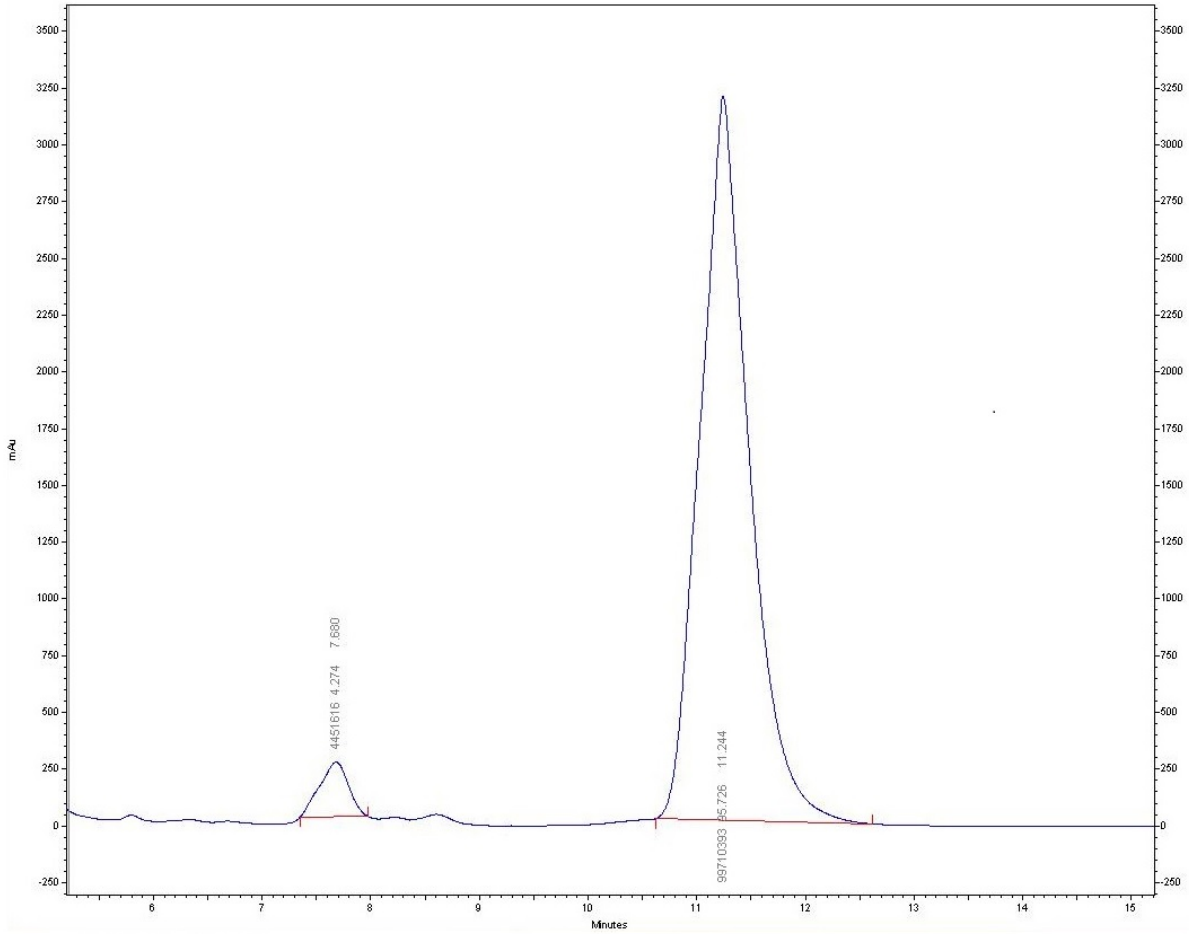


SPD-M20A-264

nm Results

Retention Time	Area	Area %	Height	Height %
7.652	31143738	50.06	1328716	59.54
11.248	31073907	49.94	902945	40.46





SPD-M20A-264

nm Results

Retention Time	Area	Area %	Height	Height %
7.680	4451616	4.27	241355	7.04
11.244	99710393	95.73	3188518	92.96