Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Asymmetric N-Aminoalkylation of 3-Substituted Indoles by N-protected N,O-acetals: An Access to Chiral Propargyl Aminals

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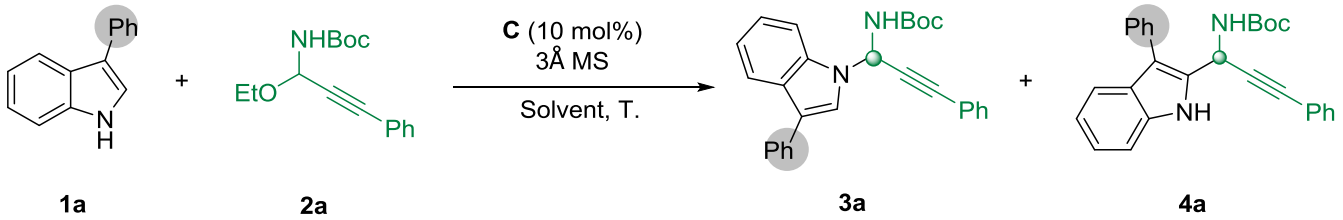
1. General information

Unless stated otherwise, all reactions were carried out in flame dried glassware. All solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. Proton nuclear resonance (^{1}H NMR) spectra were recorded on 300 MHz spectrometer in $CDCl_3$ and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 75 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet cm = complex multiplet) and coupling constant in Hertz (Hz). Optical rotations were reported as follows: $[\alpha]_D^{22}$ (c: g/100mL, in $CHCl_3$). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel column on Waters with a 996 UV-detector. 3-Substituted indole **1**[1-2] and C-alkynyl N-Boc-protected N,O-acetals **2**[3] were synthesized according to the previous reported procedures.

2. Table S1. Optimization of the reaction.[a]

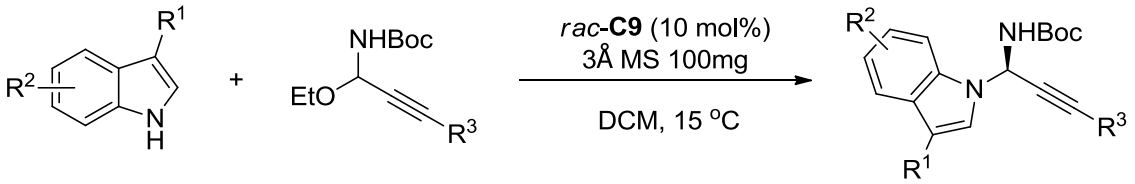


1a **2a** **3a** **4a**

Entry	Cat	Solvent	Conv.(%)[b]	**3a**:**4a**[b]	ee(%)[c]
1	**C1**	DCM	90	1:3	**3a**, 15; **4a**, 10
2	**C2**	DCM	95	>20: 1	**3a**, 91
3	**C3**	DCM	70	10:1	**3a**, 21
4	**C4**	DCM	90	>20: 1	**3a**, 90
5	**C5**	DCM	85	4:1	**3a**, 11; **4a**, 12
6	**C6**	DCM	95	>20: 1	**3a**, -90
7	**C7**	DCM	80	10:1	**3a**, - 61
8	**C8**	DCM	95	10:1	**3a**, - 60
9	**C9**	DCM	96(90)[d]	>20: 1	**3a**, 93
10	**C9**	DCE	90	>20: 1	**3a**, 89
11	**C9**	$CHCl_3$	85	>20: 1	**3a**, 70
12	**C9**	Tol.	95	>20: 1	**3a**, 89
13	**C9**	THF	<5	n.d.	**3a**, n.d.
14[e]	**C9**	DCM	99(96)[d]	>20: 1	**3a**, 92
15[e,f]	**C9**	DCM	99(96)[d]	>20: 1	**3a**, 95

[a]Unless otherwise stated, the reaction of 1a (0.1mmol) with 2a (0.1 mmol) was carried out in the presence of a catalyst C (0.01 mmol) and 3 Å molecular sieves (100 mg) in a solvent (2.0 mL) at 25℃ for 24 h. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture. [c]Determined by HPLC using a chiralcel stationary phase. [d]Yield of isolated yield. [e]1a:2a=1.2:1. [f]the reaction was carried out at 15℃ within 36 h.

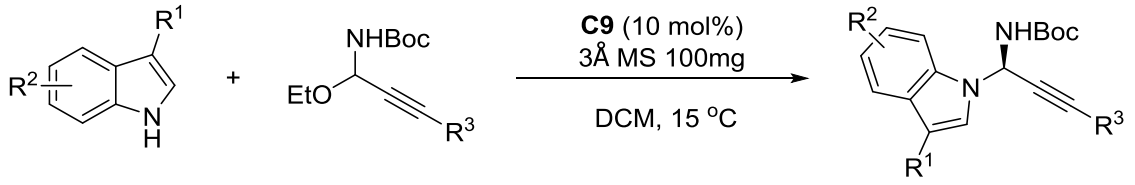
3. General procedure for the synthesis of (*rac*)-3



1 **2** ***rac*-3**

3-Substituted indole **1** (0.12 mmol, 1.2 equiv) was added to a solution of catalyst *rac*-**C9** (0.01 mmol, 10 mol%)**,** 3 Å molecular sieve (100 mg) and C-alkynyl N-Boc-protected N,O-acetals **2** (0.1 mmol, 1.0 equiv) in dry DCM (2 mL) at 25℃. Then the reaction mixture was stirred at this temperature until the complete consumption of the substrates **2**, the progress of which was monitored by TLC analysis. The solvent was removed under vacuum. The residue was then purified by silica gel chromatography (PE:AcOEt = 30:1 to 20:1 as eluent) to afford the *rac*-**3**.

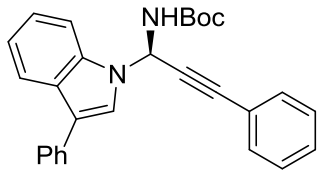
4. General procedure for the synthesis of 3



1 **2** **3**

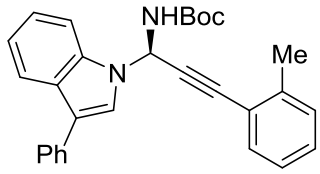
To a solution of catalyst **C9** (0.01mmol, 10 mol%), 3 Å molecular sieve (100 mg) and C-alkynyl N-Boc-protected N,O-acetals **2** (0.1 mmol, 1.0 equiv) in dry DCM (1 mL), 3-substituted indole **1** (0.12 mmol, 1.2 equiv) in 1 mL of dry DCM was added dropwise at 15 ℃. Then the reaction mixture was stirred at this temperature until the complete consumption of the substrates **2**, the progress of which was monitored by TLC analysis. The solvent was removed under vacuum. The residue was then purified by silica gel chromatography (PE:AcOEt = 30:1 to 20:1 as eluent) to afford the desired products **3**.

5. Spectral data for the products 3, 4, 6



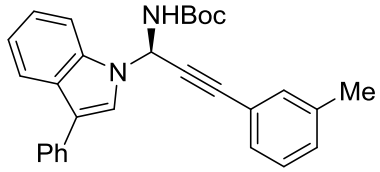
3a

Colorless viscous oil; 40.5 mg, 96% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.61 (m, 3H), 7.54 – 7.40 (m, 4H), 7.39 – 7.30 (m, 4H), 7.30 – 7.20 (m, 2H), 7.16 (d, *J* = 8.9 Hz, 1H), 5.83 – 5.55 (m, 1H), 1.44 (d, *J* = 1.2 Hz, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.95, 135.49, 135.12, 131.84, 129.24, 128.71, 128.42, 127.57, 127.21, 126.10, 123.31, 122.55, 121.21, 120.77, 120.03, 118.19, 110.87, 86.40, 83.15, 81.11, 54.90, 28.21;
IR: 3329, 2966, 1712, 1491, 1457, 1367, 1262, 1154, 1074, 1047, 1024, 796, 742, 699 cm^{-1};
HRMS (ESI): $C_{28}H_{26}N_2O_2$+Na, Calc: 445.1881, Found: 445.1881**;**
$[\alpha]_D^{22}$ = -13 (c=1 in $CHCl_3$);
HPLC: Chiralpak IA-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 34.8 min, t_{minor} = 27.3 min, 95% ee.



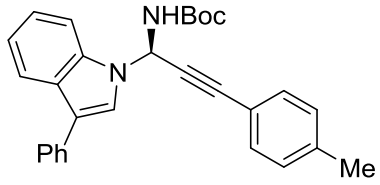
3b

Colorless viscous oil; 38.4 mg, 88% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.68 (q, *J* = 2.2 Hz, 2H), 7.65 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.53 – 7.39 (m, 3H), 7.36 – 7.27 (m, 3H), 7.25 – 7.13 (m, 4H), 5.65 (d, *J* = 9.3 Hz, 1H), 2.45 (s, 3H), 1.45 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.94, 140.60, 135.52, 135.15, 132.28, 129.61, 129.27, 128.74, 127.55, 127.24, 126.11, 125.67, 123.31, 122.55, 121.04, 120.80, 120.05, 118.20, 110.94, 86.89, 85.51, 81.16, 55.07, 28.23, 20.79;
IR: 2974, 2228, 1707, 1489, 1457, 1366, 1263, 1155, 1047, 1021, 862, 767, 742, 670 cm^{-1};
HRMS (ESI): $C_{29}H_{28}N_2O_2$+H, Calc: 437.2226, Found: 437.2226**;**
$[\alpha]_D^{22}$ = -7 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 150/1, flow rate = 1.0 mL/min, t_{major} = 15.6 min, t_{minor} = 20.7 min, 96% ee.



3c

Colorless viscous oil; 37.9 mg, 87% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.59 (m, 3H), 7.43 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.35 – 7.06 (m, 8H), 5.70 (d, *J* = 9.3 Hz, 1H), 2.32 (s, 3H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.94, 138.16, 135.48, 135.14, 132.37, 130.13, 128.91, 128.69, 128.30, 127.56, 127.19, 126.07, 123.32, 122.53, 120.99, 120.74, 120.00, 118.14, 110.88, 86.59, 82.76, 81.06, 54.89, 28.20, 21.15;
IR: 2964, 1704, 1603, 1490, 1457, 1366, 1260, 1093, 1076, 1021, 798, 742, 699 cm^{-1};
HRMS (ESI): $C_{29}H_{28}N_2O_2$+H, Calc: 437.2243, Found: 437.2243**;**
$[\alpha]_D^{22}$ = -16 (c=1 in $CHCl_3$);
HPLC: Chiralpak AS-H column, hexane/EtOH = 100/1.5, flow rate = 1.0 mL/min, t_{major} = 7.7 min, t_{minor} = 6.4 min, 96% ee.



3d

Colorless viscous oil; 42.3 mg, 97% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.57 (dd, *J* = 6.7, 1.7 Hz, 3H), 7.39 – 7.23 (m, 4H), 7.23 – 7.09 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 3H), 5.62 (t, *J* = 7.2 Hz, 1H), 2.24 (s, 3H), 1.35 (d, *J* = 1.6 Hz, 9H);

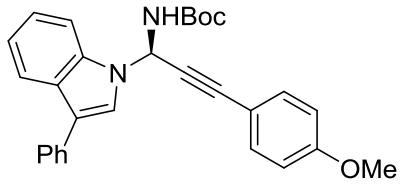
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.92, 139.49, 135.52, 135.18, 131.72, 129.15, 128.68, 127.56, 127.23, 126.05, 123.35, 122.50, 120.73, 120.00, 118.14, 110.90, 86.62, 82.55, 81.05, 55.02, 28.20, 21.48;

IR: 3330, 2976, 2927, 2232, 1710, 1604, 1492, 1457, 1367, 1263, 1155, 1021, 817, 742, 700 cm^{-1};

HRMS (ESI): $C_{29}H_{28}N_2O_2$+Na, Calc: 459.2031, Found: 459.2031**;**

$[\alpha]_D^{22}$ = -11 (c=1 in $CHCl_3$);

HPLC: Chiralpak IA-H column, hexane/EtOH = 100/1, flow rate = 1.0 mL/min, t_{major} = 16.1 min, t_{minor} = 14.1 min, 97% ee.



3e

White solid; 44.3 mg, 98% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 6.6 Hz, 3H), 7.44 – 7.26 (m, 4H), 7.19 (dt, *J* = 18.0, 7.9 Hz, 3H), 7.11 – 6.95 (m, 1H), 6.75 (d, *J* = 8.3 Hz, 2H), 5.64 (d, *J* = 9.3 Hz, 1H), 3.69 (s, 3H), 1.35 (s, 9H);

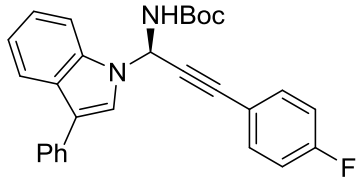
^{13}C NMR (75 MHz, $CDCl_3$) δ 160.23, 153.96, 135.47, 135.17, 133.33, 128.68, 127.53, 127.17, 126.04, 123.37, 122.47, 120.70, 119.97, 118.03, 114.02, 113.18, 110.91, 86.46, 81.88, 81.00, 55.25, 54.97, 28.20;

IR: 3334, 2975, 2931, 2230, 1710, 1605, 1510, 1458, 1367, 1250, 1030, 833, 762, 744 cm^{-1};

HRMS (ESI): $C_{29}H_{28}N_2O_3$+Na, Calc: 475.1991, Found: 475.1991**;**

$[\alpha]_D^{22}$ = -10 (c=1 in $CHCl_3$);

HPLC: Chiralpak IA-H column, hexane/EtOH = 100/1, flow rate = 1.0 mL/min, t_{major} = 39.1 min, t_{minor} = 33.9 min, 93% ee.



3f

Colorless viscous oil; 41.8 mg, 95% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.47 (m, 3H), 7.42 – 7.29 (m, 4H), 7.27 – 6.98 (m, 4H), 6.98 – 6.82 (m, 2H), 5.75 – 5.54 (m, 1H), 1.34 (s, 9H);

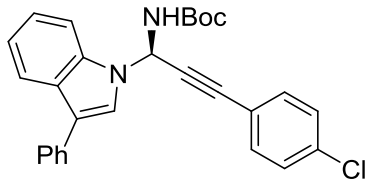
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.67, 161.33, 153.91, 135.50, 135.10, 133.91, 133.80, 128.71, 127.57, 127.24, 126.14, 123.22, 122.59, 120.81, 120.08, 118.30, 117.35, 117.30, 115.92, 115.63, 110.80, 85.33, 83.00, 81.19, 54.91, 28.20;

IR: 3330, 2977, 2928, 2234, 1709, 1602, 1507, 1457, 1367, 1233, 1155, 837, 762, 744 cm^{-1};

HRMS (ESI): $C_{28}H_{25}FN_2O_2$+Na, Calc: 463.1780, Found: 463.1780**;**

$[\alpha]_D^{22}$ = -12 (c=1 in $CHCl_3$);

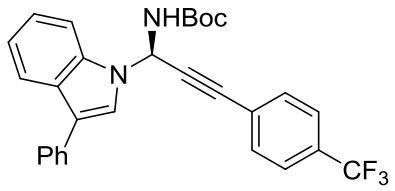
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/1, flow rate = 1.0 mL/min, t_{major} = 15.7 min, t_{minor} = 13.5 min, 96% ee.



3g

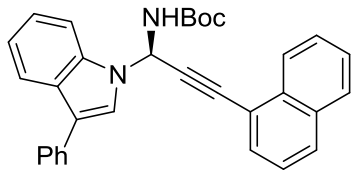
Colorless viscous oil; 44.2 mg, 97% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.39 – 7.26 (m, 4H), 7.26 – 7.13 (m, 5H), 7.13 – 7.01 (m, 1H), 5.66 (d, *J* = 9.2 Hz, 1H), 1.35 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.90, 135.43, 135.38, 135.03, 133.04, 128.77, 128.71, 127.55, 127.18, 126.15, 123.18, 122.60, 120.82, 120.07, 119.64, 118.30, 110.76, 85.20, 84.12, 81.19, 54.83, 28.18;
IR: 3328, 2975, 2930, 1709, 1603, 1490, 1457, 1367, 1321, 1263, 1153, 1093, 1017, 829, 742, 700 cm^{-1};
HRMS (ESI): $C_{28}H_{25}ClN_2O_2$+Na, Calc: 479.1494, Found: 479.1494**;**
$[\alpha]_D^{22}$ = -12 (c=1 in $CHCl_3$);
HPLC: Chiralpak IA-H column, hexane/EtOH = 100/1, flow rate = 1.0 mL/min, t_{major} = 35.7 min, t_{minor} = 29.8 min, 94% ee.



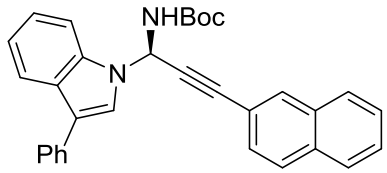
3h

Pale yellow viscous oil; 41.7 mg, 85% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 7.87 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.59 (d, *J* = 11.6 Hz, 5H), 7.50 – 7.39 (m, 2H), 7.37 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.21 – 7.10 (m, 1H), 5.75 (d, *J* = 9.3 Hz, 1H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.91, 135.45, 134.97, 132.15, 131.61, 131.18, 130.74, 130.31, 128.75, 127.57, 127.22, 126.23, 125.44, 125.39, 125.34, 125.29, 124.99, 123.12, 122.70, 121.86, 120.91, 120.14, 118.49, 110.72, 85.47, 84.83, 81.33, 54.77, 28.19;
IR: 2965, 1709, 1613, 1491, 1457, 1405, 1322, 1261, 1131, 1069, 1019, 792, 742, 700 cm^{-1};
HRMS (ESI): $C_{29}H_{25}F_3N_2O_2$+H, Calc: 491.1938, Found: 491.1938**;**
$[\alpha]_D^{22}$ = -16 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 120/1, flow rate = 1.0 mL/min, t_{major} = 20.8 min, t_{minor} = 16.8 min, 96% ee.



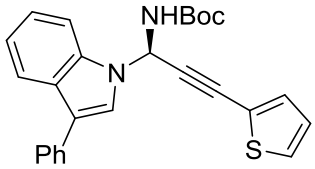
3i

White viscous oil; 43.9 mg, 93% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 – 8.07 (m, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.82 – 7.70 (m, 3H), 7.69 – 7.53 (m, 4H), 7.42 (ddd, *J* = 7.2, 5.0, 1.8 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.27 – 7.08 (m, 4H), 5.75 (d, *J* = 9.2 Hz, 1H), 1.36 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.03, 135.57, 135.10, 133.13, 133.01, 131.16, 129.76, 128.72, 128.36, 127.54, 127.25, 127.14, 126.60, 126.11, 125.75, 125.06, 123.37, 122.61, 120.85, 120.09, 118.78, 118.32, 110.94, 87.86, 84.71, 81.19, 55.14, 28.22;
IR: 3328, 2928, 1708, 1604, 1492, 1457, 1367, 1246, 1193, 1156, 1051, 1020, 801, 743 cm^{-1};
HRMS (ESI): $C_{32}H_{28}N_2O_2$+Na, Calc: 495.2042, Found: 495.2042**;**
$[\alpha]_D^{22}$ = -20 (c=1 in $CHCl_3$);
HPLC: Chiralpak IA-H column, hexane/EtOH = 100/1, flow rate = 1.0 mL/min, t_{major} = 51.9 min, t_{minor} = 30.1 min, 95% ee.



3j

Pale yellow viscous oil; 46.3 mg, 98% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.88 – 7.80 (m, 1H), 7.79 – 7.64 (m, 4H), 7.58 (dt, *J* = 8.0, 1.6 Hz, 3H), 7.45 – 7.28 (m, 5H), 7.27 – 7.05 (m, 4H), 5.69 (d, *J* = 9.2 Hz, 1H), 1.36 (d, *J* = 1.1 Hz, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.95, 135.50, 135.13, 133.12, 132.68, 132.19, 128.71, 128.16, 127.99, 127.81, 127.75, 127.58, 127.22, 127.14, 126.72, 126.10, 123.33, 122.58, 120.79, 120.05, 118.41, 118.22, 110.88, 86.73, 83.36, 81.12, 54.95, 28.21;
IR: 3329, 2966, 2928, 2237, 1704, 1602, 1491, 1457, 1367, 1262, 1153, 1021, 817, 743, 700 cm^{-1};
HRMS (ESI): $C_{32}H_{28}N_2O_2$+Na, Calc: 495.2040, Found: 495.2040**;**
$[\alpha]_D^{22}$ = -14 (c=1 in $CHCl_3$);
HPLC: Chiralpak AS-H column, hexane/EtOH = 150/1, flow rate = 1.0 mL/min, t_{major} = 36.9 min, t_{minor} = 30.5 min, 96% ee.



3k

Pale yellow solid; 38.9 mg, 91% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.86 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.53 (m, 3H), 7.43 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.36 – 7.08 (m, 6H), 6.98 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.70 (d, *J* = 9.3 Hz, 1H), 1.44 (s, 9H);

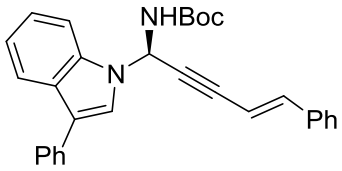
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.87, 135.44, 135.05, 133.31, 128.70, 128.31, 127.56, 127.16, 127.09, 126.12, 123.21, 122.60, 120.89, 120.80, 120.03, 118.29, 110.78, 86.83, 81.17, 79.94, 54.94, 28.19;

IR: 3327, 2965, 2232, 1707, 1604, 1490, 1457, 1367, 1261, 1076, 1022, 794, 743, 701 cm^{-1};

HRMS (ESI): $C_{26}H_{24}N_2O_2S$+H, Calc: 429.1649, Found: 429.1649**;**

$[\alpha]_D^{22}$ = -10 (c=1 in $CHCl_3$);

HPLC: Chiralpak AS-H column, hexane/EtOH = 100/1, flow rate = 1.0 mL/min, t_{major} = 13.9 min, t_{minor} = 9.9 min, 96% ee.



3l

Pale yellow viscous oil; 37.6 mg, 84%yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.62 (s, 1H), 7.44 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.40 – 7.17 (m, 8H), 7.17 – 7.06 (m, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.17 (dd, *J* = 16.4, 1.9 Hz, 1H), 5.66 (d, *J* = 9.1 Hz, 1H), 1.43 (s, 9H);

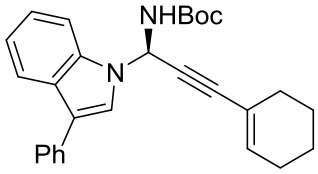
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.92, 143.54, 135.50, 135.45, 135.14, 129.15, 128.75, 128.70, 127.56, 127.17, 126.43, 126.09, 123.29, 122.54, 120.76, 120.02, 118.15, 110.84, 106.08, 85.64, 84.93, 81.07, 54.95, 28.20;

IR: 2974, 1703, 1457, 1411, 1261, 1113, 1075, 1047, 1023, 860, 794, 744, 700 cm^{-1};

HRMS (ESI): $C_{30}H_{28}N_2O_2$+H, Calc: 449.2228, Found: 449.2228**;**

$[\alpha]_D^{22}$ = -14 (c=1 in $CHCl_3$);

HPLC: Chiralpak OD-H column, hexane/EtOH = 95/5, flow rate = 1.0 mL/min, t_{major} = 30.5 min, t_{minor} = 21.1 min, 96% ee.



3m

White solid; 34.9 mg, 82% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.60 (s, 1H), 7.44 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.29 (ddd, *J* = 8.3, 5.0, 1.3 Hz, 2H), 7.24 – 7.17 (m, 1H), 7.03 (d, *J* = 9.3 Hz, 1H), 6.22 (dt, *J* = 4.1, 2.1 Hz, 1H), 5.58 (d, *J* = 9.3 Hz, 1H), 2.22 – 2.02 (m, 4H), 1.60 (tt, *J* = 8.5, 3.1 Hz, 4H), 1.42 (s, 9H);

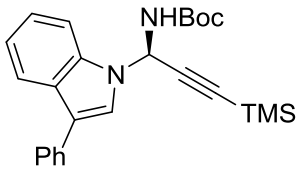
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.92, 137.30, 135.45, 135.25, 128.69, 127.55, 127.16, 126.02, 123.37, 122.39, 120.64, 119.93, 119.25, 117.91, 110.94, 88.28, 80.92, 80.49, 54.89, 28.69, 28.21, 25.61, 22.05, 21.26;

IR: 3334, 2928, 2229, 1708, 1604, 1492, 1458, 1366, 1154, 1047, 1022, 743, 699 cm^{-1};

HRMS (ESI): $C_{28}H_{30}N_2O_2$+H, Calc: 427.2390, Found: 427.2390**;**

$[\alpha]_D^{22}$ = -10 (c=1 in $CHCl_3$);

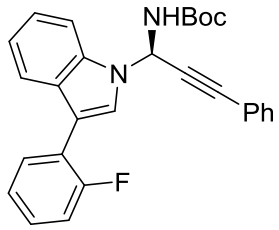
HPLC: Chiralpak AS-H column, hexane/EtOH = 120/1, flow rate = 1.0 mL/min, t_{major} = 15.8 min, t_{minor} = 8.0 min, 91% ee.



3n

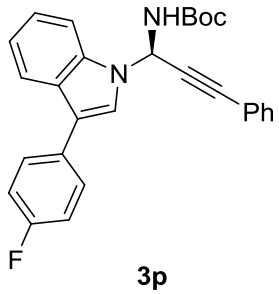
Colorless viscous oil; 40.5 mg, 97% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.58 (s, 1H), 7.44 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.21 (ddd, *J* = 8.0, 6.0, 1.2 Hz, 1H), 6.91 (d, *J* = 9.4 Hz, 1H), 5.58 (d, *J* = 9.3 Hz, 1H), 1.42 (s, 9H), 0.22 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.92, 135.48, 135.18, 128.72, 127.54, 127.17, 126.08, 123.32, 122.42, 120.73, 119.94, 118.08, 110.94, 98.74, 92.18, 81.05, 54.63, 28.19, -0.43;
IR: 3331, 2965, 1710, 1492, 1367, 1252, 1193, 1157, 1019, 849, 765, 743, 699 cm^{-1};
HRMS (ESI): $C_{25}H_{30}N_2O_2Si$+Na, Calc: 441.1967, Found: 441.1967**;**
$[\alpha]_D^{22}$ = -8 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 400/1, flow rate = 1.0 mL/min, t_{major} = 11.9 min, t_{minor} = 9.6 min, 94% ee.



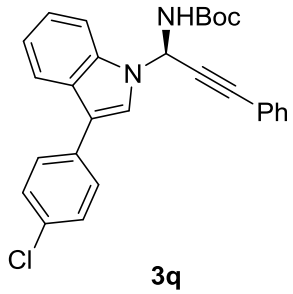
3o

Colorless viscous oil; 39.2 mg, 89% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.76 (m, 3H), 7.76 – 7.63 (m, 1H), 7.48 (dd, *J* = 7.7, 2.1 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.27 – 7.06 (m, 5H), 5.73 (d, *J* = 9.1 Hz, 1H), 1.44 (d, *J* = 2.2 Hz, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 161.37, 158.11, 153.92, 135.02, 131.83, 130.31, 130.26, 129.24, 128.41, 127.50, 127.39, 125.62, 125.54, 124.14, 124.10, 122.76, 122.56, 121.18, 120.83, 120.24, 116.06, 115.76, 110.94, 110.85, 86.51, 83.04, 81.11, 54.90, 28.20;
IR: 3329, 2977, 2928, 2233, 1707, 1492, 1459, 1367, 1262, 1246, 1157, 1047, 1023, 758, 742 cm^{-1};
HRMS (ESI): $C_{28}H_{25}FN_2O_2$+H, Calc: 441.1972, Found: 441.1972**;**
$[\alpha]_D^{22}$ = -9 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 18.4 min, t_{minor} = 23.4 min, 95% ee.



3p

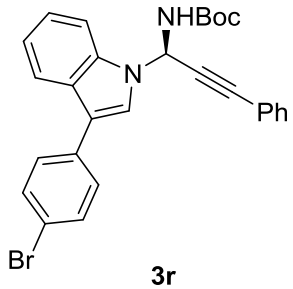
White viscous oil; 42.7 mg, 97% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.53 (m, 3H), 7.52 – 7.41 (m, 2H), 7.40 – 7.26 (m, 4H), 7.22 (td, *J* = 7.5, 7.1, 1.1 Hz, 1H), 7.19 – 7.04 (m, 3H), 5.73 (d, *J* = 9.2 Hz, 1H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.14, 159.89, 153.94, 135.38, 131.83, 131.13, 131.09, 129.28, 129.06, 128.96, 128.42, 127.16, 123.18, 122.64, 121.17, 120.84, 119.74, 117.23, 115.70, 115.41, 110.94, 86.43, 83.08, 81.15, 54.93, 28.20;
IR: 3328, 2965, 2374, 1702, 1556, 1503, 1458, 1367, 1261, 1153, 1075, 1047, 1023, 800, 742 cm^{-1};
HRMS (ESI): $C_{28}H_{25}FN_2O_2$+H, Calc: 441.1984, Found: 441.1984**;**
$[\alpha]_D^{22}$ = -15 (c=1 in $CHCl_3$);
HPLC: Chiralpak AS-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 16.7 min, t_{minor} = 8.6 min, 95% ee.



3q

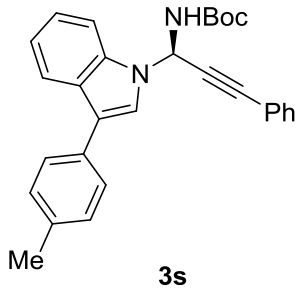
Colorless viscous oil; 41.5 mg, 91% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.63 (s, 1H), 7.60 – 7.53 (m, 2H), 7.47 (dd, *J* = 7.7, 2.0 Hz, 2H), 7.34 (dddd, *J* = 16.3, 10.6, 5.8, 1.8 Hz, 6H), 7.23 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.15 (d, *J* = 9.3 Hz, 1H), 5.74 (d, *J* = 9.2 Hz, 1H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.93, 135.44, 133.61, 131.83, 131.70, 129.30, 128.83, 128.67, 128.43, 126.96, 123.46, 122.71, 121.12, 120.96, 119.76, 116.97, 111.00, 86.49, 82.99, 81.18, 54.97, 28.20;
IR: 3327, 2966, 1707, 1549, 1490, 1458, 1367, 1261, 1091, 1023, 801, 742, 691 cm^{-1};
HRMS (ESI): $C_{28}H_{25}ClN_2O_2$+H, Calc: 457.1677, Found: 457.1689**;**
$[\alpha]_D^{22}$ = -18 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 11.4 min, t_{minor} = 13.5 min, 95% ee.



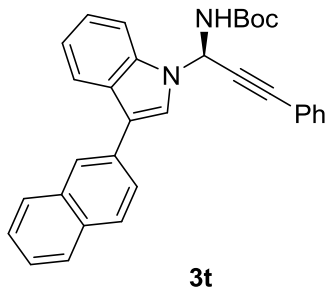
3r

Pale yellow solid; 42.0 mg, 84% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.64 (s, 1H), 7.53 (d, *J* = 2.0 Hz, 4H), 7.51 – 7.44 (m, 2H), 7.41 – 7.27 (m, 4H), 7.23 (td, *J* = 7.5, 1.1 Hz, 1H), 7.19 – 7.08 (m, 1H), 5.73 (d, *J* = 9.2 Hz, 1H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.92, 135.46, 134.08, 131.83, 131.77, 129.31, 129.01, 128.43, 126.90, 123.46, 122.73, 121.11, 120.98, 119.76, 119.74, 116.97, 111.01, 86.51, 82.97, 81.19, 54.99, 28.20;
IR: 3329, 2977, 2928, 1712, 1489, 1367, 1262, 1156, 1074, 861, 801, 759, 742, 691 cm^{-1};
HRMS (ESI): $C_{28}H_{25}BrN_2O_2$+H, Calc: 501.1178, Found: 501.1178**;**
$[\alpha]_D^{22}$ = -11 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 11.7 min, t_{minor} = 14.1 min, 95% ee.



3s

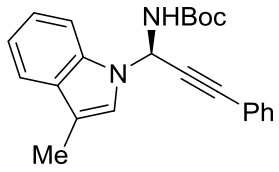
White viscous oil; 41.0 mg, 94% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.85 (m, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.62 (s, 1H), 7.59 – 7.51 (m, 2H), 7.47 (dt, *J* = 7.4, 1.4 Hz, 2H), 7.41 – 7.28 (m, 4H), 7.28 – 7.20 (m, 3H), 7.20 – 7.05 (m, 1H), 5.70 (d, *J* = 9.3 Hz, 1H), 2.39 (s, 3H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.94, 135.72, 135.46, 132.14, 131.83, 129.41, 129.21, 128.40, 127.47, 127.30, 123.01, 122.47, 121.24, 120.65, 120.06, 118.14, 110.81, 86.33, 83.21, 81.07, 54.86, 28.21, 21.15;
IR: 3396, 2372, 1608, 1459, 1366, 1261, 1132, 1076, 1045, 800, 741, 691 cm^{-1};
HRMS (ESI): $C_{29}H_{28}N_2O_2$+H, Calc: 437.2246, Found: 437.2246**;**
$[\alpha]_D^{22}$ = -11 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 9.8 min, t_{minor} = 11.2 min, 96% ee.



3t

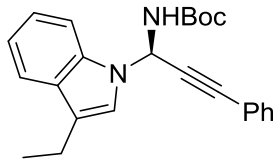
Pale yellow viscous oil; 42.0 mg, 89% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 – 8.08 (m, 1H), 8.08 – 7.99 (m, 1H), 7.88 (dd, *J* = 8.9, 6.8 Hz, 3H), 7.82 (dd, *J* = 5.2, 1.7 Hz, 2H), 7.79 – 7.74 (m, 1H), 7.53 – 7.40 (m, 4H), 7.39 – 7.28 (m, 4H), 7.28 – 7.23 (m, 1H), 7.20 (d, *J* = 6.5 Hz, 1H), 5.76 (d, *J* = 9.2 Hz, 1H), 1.45 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.94, 135.59, 133.87, 132.61, 132.05, 131.85, 129.26, 128.42, 128.23, 127.75, 127.65, 127.31, 126.48, 126.10, 125.39, 125.27, 123.75, 122.68, 121.19, 120.92, 120.12, 118.10, 110.97, 86.45, 83.12, 81.14, 54.98, 28.21;
IR: 3330, 2971, 1710, 1602, 1491, 1457, 1368, 1264, 1154, 1048, 1023, 860, 742, 691 cm^{-1};
HRMS (ESI): $C_{32}H_{28}N_2O_2$+H, Calc: 473.2236, Found: 473.2236**;**
$[\alpha]_D^{22}$ = -11 (c=1 in $CHCl_3$);
HPLC: Chiralpak AS-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 14.3 min, t_{minor} = 8.5 min, 96% ee.



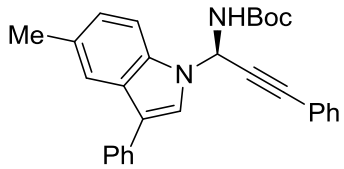
3u

White solid; 27.0 mg, 75% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.34 (q, *J* = 5.1 Hz, 3H), 7.25 (q, *J* = 6.2, 5.1 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 9.2 Hz, 1H), 5.59 (d, *J* = 10.5 Hz, 1H), 2.32 (s, 3H), 1.43 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.00, 135.08, 131.83, 129.76, 129.12, 128.39, 123.22, 122.07, 121.45, 119.65, 119.06, 111.88, 110.45, 85.86, 83.61, 80.91, 54.62, 28.22, 9.63;
IR: 3341, 2978, 2930, 1690, 1614, 1491, 1457, 1368, 1343, 1247, 1160, 1046, 861, 757, 740, 690 cm^{-1};
HRMS (ESI): $C_{23}H_{24}N_2O_2$+H, Calc: 361.1911, Found: 361.1896**;**
$[\alpha]_D^{22}$ = -7 (c=1 in $CHCl_3$);
HPLC: Chiralpak IA-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 16.2 min, t_{minor} = 14.7 min, 95% ee.



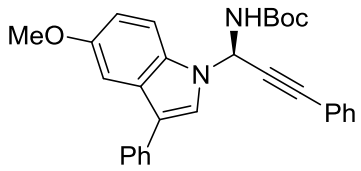
3v

White solid; 32.2 mg, 86% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.33 (d, *J* = 6.5 Hz, 3H), 7.24 (q, *J* = 6.2, 5.0 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.11 – 6.93 (m, 1H), 5.60 (d, *J* = 8.9 Hz, 1H), 2.77 (q, *J* = 7.5 Hz, 2H), 1.43 (s, 9H), 1.33 (td, *J* = 7.5, 1.5 Hz, 3H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.95, 135.23, 131.83, 129.11, 128.95, 128.39, 122.13, 122.08, 121.47, 119.60, 119.17, 118.88, 110.53, 85.89, 83.63, 80.89, 54.70, 28.22, 18.30, 14.33;
IR: 3337, 2968, 2932, 2705, 1613, 1491, 1457, 1368, 1245, 1161, 1047, 1018, 861, 756, 740, 690 cm^{-1};
HRMS (ESI): $C_{24}H_{26}N_2O_2$+H, Calc: 375.2067, Found: 375.2054**;**
$[\alpha]_D^{22}$ = -9 (c=1 in $CHCl_3$);
HPLC: Chiralpak IA-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 13.9 min, t_{minor} = 12.8 min, 95 % ee.



3w

Colorless viscous oil; 40.5 mg, 93% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.56 (m, 5H), 7.52 – 7.39 (m, 4H), 7.38 – 7.29 (m, 3H), 7.29 – 7.23 (m, 1H), 7.13 (dd, *J* = 8.4, 1.6 Hz, 2H), 5.69 (d, *J* = 9.3 Hz, 1H), 2.47 (s, 3H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.95, 135.27, 133.80, 131.83, 130.12, 129.20, 128.67, 128.40, 127.56, 127.45, 125.99, 124.08, 123.46, 121.25, 119.66, 117.68, 110.55, 86.29, 83.21, 81.03, 54.90, 28.20, 21.52;
IR: 2965, 2926, 1707, 1492, 1367, 1261, 1180, 1163, 1075, 1047, 1026, 795, 700 cm^{-1};
HRMS (ESI): $C_{29}H_{28}N_2O_2$+H, Calc: 437.2232, Found: 437.2232**;**
$[\alpha]_D^{22}$ = -14 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 9.0 min, t_{minor} = 10.0 min, 90% ee.



3x

Pale yellow solid; 41.1 mg, 91% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.9 Hz, 1H), 7.66 – 7.59 (m, 3H), 7.52 – 7.40 (m, 4H), 7.40 – 7.33 (m, 3H), 7.33 – 7.25 (m, 2H), 7.11 (d, *J* = 9.4 Hz, 1H), 6.96 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.71 (d, *J* = 9.3 Hz, 1H), 3.85 (s, 3H), 1.44 (s, 9H);

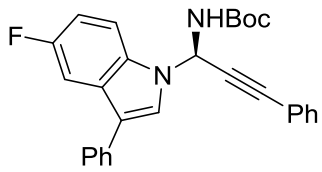
^{13}C NMR (75 MHz, $CDCl_3$) δ 155.01, 153.97, 135.25, 131.83, 130.63, 129.23, 128.76, 128.41, 127.68, 127.43, 126.02, 124.01, 121.19, 117.80, 112.51, 111.65, 101.88, 86.35, 83.13, 81.09, 55.89, 55.01, 28.20;

IR: 3330, 2928, 1710, 1477, 1249, 1218, 1177, 1074, 1045, 1026, 870, 759, 699 cm^{-1};

HRMS (ESI): $C_{29}H_{28}N_2O_3$+H, Calc: 453.2189, Found: 453.2189**;**

$[\alpha]_D^{22}$ = -10 (c=1 in $CHCl_3$);

HPLC: Chiralpak AS-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 28.4 min, t_{minor} = 16.0 min, 94% ee.



3y

Colorless viscous oil; 41.8 mg, 95% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 5.2 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.55 (dd, *J* = 9.8, 2.5 Hz, 1H), 7.51 – 7.38 (m, 4H), 7.38 – 7.25 (m, 4H), 7.12 (d, *J* = 9.3 Hz, 1H), 7.04 (td, *J* = 9.0, 2.5 Hz, 1H), 5.74 (d, *J* = 9.2 Hz, 1H), 1.44 (s, 9H);

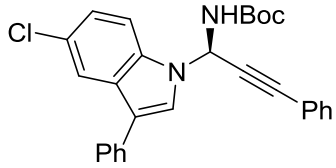
^{13}C NMR (75 MHz, $CDCl_3$) δ 160.23, 157.11, 153.98, 134.66, 132.02, 131.82, 129.35, 128.81, 128.44, 127.67, 127.54, 127.32, 126.28, 124.76, 121.03, 118.16, 118.10, 111.72, 111.59, 111.03, 110.69, 105.22, 104.90, 86.61, 82.82, 81.25, 55.05, 28.18;

IR: 3328, 2978, 2929, 2235, 1710, 1475, 1368, 1253, 1072, 1027, 876, 760, 698 cm^{-1};

HRMS (ESI): $C_{28}H_{25}FN_2O_2$+H, Calc: 441.1976, Found: 441.1976**;**

$[\alpha]_D^{22}$ = -11 (c=1 in $CHCl_3$);

HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 11.2 min, t_{minor} = 14.2 min, 95% ee.



3z

Pale yellow viscous oil; 37.8 mg, 83% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.67 (s, 1H), 7.63 – 7.56 (m, 2H), 7.51 – 7.40 (m, 4H), 7.39 – 7.27 (m, 4H), 7.27 – 7.22 (m, 1H), 7.12 (d, *J* = 9.2 Hz, 1H), 5.71 (d, *J* = 9.3 Hz, 1H), 1.44 (s, 9H);

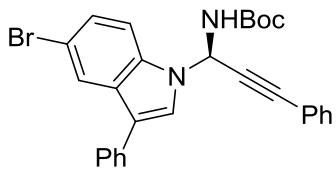
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.94, 134.42, 133.84, 131.84, 129.39, 128.83, 128.46, 128.26, 127.51, 126.66, 126.42, 124.42, 122.82, 120.98, 119.49, 117.88, 111.96, 86.74, 82.69, 81.32, 55.01, 28.19;

IR: 3326, 2967, 2930, 2234, 1709, 1604, 1492, 1459, 1367, 1262, 1153, 1070, 863, 798 cm^{-1};

HRMS (ESI): $C_{28}H_{25}ClN_2O_2$+H, Calc: 457.1684, Found: 457.1684**;**

$[\alpha]_D^{22}$ = -16 (c=1 in $CHCl_3$);

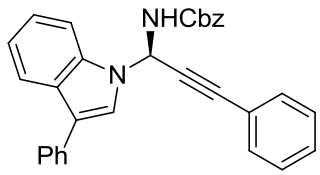
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 12.0 min, t_{minor} = 16.2 min, 95% ee.



3aa

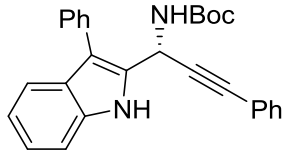
Pale yellow viscous oil; 44.0 mg, 88% yield;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.9 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.63 – 7.55 (m, 2H), 7.52 – 7.40 (m, 4H), 7.40 – 7.25 (m, 5H), 7.11 (d, *J* = 9.3 Hz, 1H), 5.72 (d, *J* = 9.2 Hz, 1H), 1.44 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.96, 134.37, 134.11, 131.83, 129.39, 128.88, 128.83, 128.46, 127.54, 126.45, 125.37, 124.26, 122.54, 120.95, 117.81, 114.27, 112.39, 86.76, 82.65, 81.32, 55.01, 28.19;
IR: 3329, 2234, 1708, 1606, 1367, 1263, 1162, 1026, 862, 793, 759, 699 cm^{-1};
HRMS (ESI): $C_{28}H_{25}BrN_2O_2$+H, Calc: 501.1174, Found: 501.1174**;**
$[\alpha]_D^{22}$ = -14 (c=1 in $CHCl_3$);
HPLC: Chiralpak IA-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 12.3 min, t_{minor} = 10.7 min, 95% ee.



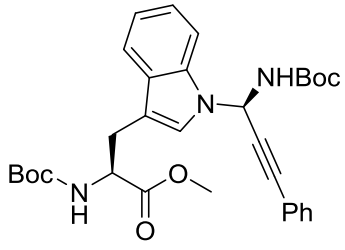
3ab

Colorless viscous oil; 44.2 mg, 97% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 6.8 Hz, 3H), 7.47 (t, *J* = 4.1 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 6.9 Hz, 2H), 7.32 (s, 6H), 7.28 – 7.14 (m, 3H), 5.86 (dd, *J* = 31.7, 9.3 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.05 (d, *J* = 12.2 Hz, 1H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.83, 135.57, 135.07, 131.93, 129.44, 128.79, 128.63, 128.52, 128.47, 128.34, 127.67, 127.32, 126.26, 123.30, 122.77, 121.08, 120.97, 120.17, 118.58, 110.87, 86.84, 82.71, 67.68, 55.36;
IR: 3308, 3032, 1702, 1521, 1493, 1458, 1319, 1238, 1191, 1039, 1030, 788, 755, 745, 697 cm^{-1};
HRMS (ESI): $C_{31}H_{24}N_2O_2$+Na, Calc: 479.1730, Found: 479.1724**;**
$[\alpha]_D^{22}$ = 1 (c=1 in $CHCl_3$);
HPLC: Chiralpak IA-H column, hexane/EtOH = 10/1, flow rate = 1.0 mL/min, t_{major} = 39.8 min, t_{minor} = 28.5 min, 95% ee.



4a

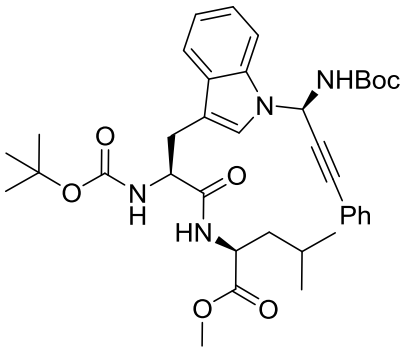
Pale yellow solid;
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.32 (m, 4H), 7.32 – 7.18 (m, 4H), 7.18 – 7.05 (m, 1H), 5.95 (d, *J* = 7.5 Hz, 1H), 5.41 (s, 1H), 1.42 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.92, 135.21, 134.16, 131.76, 131.52, 129.76, 128.61, 128.56, 128.20, 127.42, 126.55, 122.81, 122.15, 120.20, 119.74, 115.19, 111.24, 85.82, 84.70, 80.74, 40.69, 28.26;
IR: 3386, 2967, 1695, 1491, 1456, 1368, 1260, 1162, 1019, 799, 742, 702, 692 cm^{-1};
HRMS (ESI): $C_{28}H_{27}N_2O_2$+H, Calc: 423.2071, Found: 423.2071**;**



6a

White solid; 52.5 mg, 96% yield, dr > 20:1;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.40 – 7.26 (m, 5H), 7.26 – 7.21 (m, 1H), 7.21 – 7.11 (m, 1H), 7.06 (d, *J* = 9.4 Hz, 1H), 5.73 (d, *J* = 8.8 Hz, 1H), 5.13 (d, *J* = 8.2 Hz, 1H), 4.65 (dt, *J* = 8.1, 5.3 Hz, 1H), 3.66 (s, 3H), 3.27 (d, *J* = 5.5 Hz, 2H), 1.43 (s, 9H), 1.39 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.66, 155.17, 153.93, 134.97, 131.82, 129.21, 129.13, 128.40, 124.35, 122.37, 121.23, 120.12, 119.01, 110.65, 110.21, 86.20, 83.20, 80.97, 79.74, 54.71, 53.97, 52.18, 28.24, 28.18, 27.92;
IR: 3426, 3332, 2978, 1713, 1493, 1367, 1165, 1049, 1019, 758, 740, 692 cm^{-1};
HRMS (ESI): $C_{31}H_{37}N_3O_6$+Na, Calc: 570.2574, Found: 570.2574**;**
$[\alpha]_D^{22}$ = 26 (c=1 in $CHCl_3$);

HPLC: Chiralpak OD-H column, hexane/EtOH = 100/2, flow rate = 1.0 mL/min, t_{major} = 17.9 min, t_{minor} = 21.2 min, 93% ee.



6b

White solid; 62.0 mg, 94% yield, dr > 20:1;

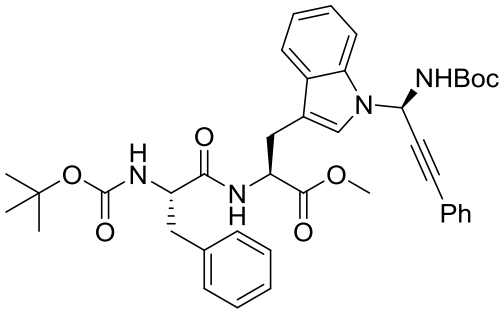
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.50 (dd, *J* = 7.6, 2.1 Hz, 3H), 7.41 – 7.29 (m, 3H), 7.25 (ddd, *J* = 8.2, 6.0, 1.2 Hz, 1H), 7.20 – 7.13 (m, 1H), 7.10 (d, *J* = 9.6 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 1H), 5.88 (d, *J* = 9.1 Hz, 1H), 5.22 (s, 1H), 4.46 (d, *J* = 4.7 Hz, 2H), 3.60 (s, 3H), 3.22 (dd, *J* = 13.0, 6.8 Hz, 2H), 1.44 (s, 9H), 1.42 (s, 9H), 0.85 (t, *J* = 5.4 Hz, 6H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.94, 171.23, 155.37, 153.98, 135.08, 131.87, 129.13, 128.85, 128.35 , 124.38 , 121.35, 122.40 , 120.22 , 119.12 , 110.71 , 110.43 , 86.07 , 83.38 , 80.83 , 54.77 , 54.5 , 52.20, 50.69, 41.37, 28.21, 24.57, 22.68, 21.76;

IR: 3327, 2962, 2926, 1656, 1612, 1459, 1366, 1261, 1132, 1076, 1022, 863, 798 cm^{-1};

HRMS (ESI): $C_{37}H_{48}N_4O_7$+H, Calc: 661.3627, Found: 661.3627**;**

$[\alpha]_D^{22}$ = -10 (c=1 in $CHCl_3$);



6c

White solid; 58.3 mg, 84% yield, dr > 20:1;

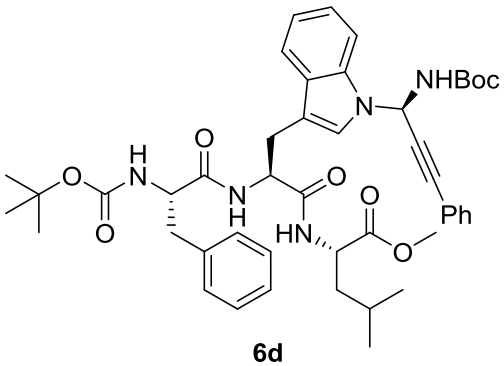
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.38 (dd, *J* = 6.5, 1.5 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.23 (dq, *J* = 11.9, 6.3, 5.5 Hz, 5H), 7.12 (d, *J* = 7.8 Hz, 3H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 5.82 (s, 1H), 5.00 (s, 1H), 4.85 (d, *J* = 7.4 Hz, 1H), 4.32 (s, 1H), 3.64 (s, 3H), 3.23 (d, *J* = 5.9 Hz, 2H), 3.05 (dd, *J* = 13.8, 6.3 Hz, 2H), 1.42 (s, 9H), 1.32 (s, 9H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.76, 170.80, 155.24, 154.02, 136.61, 134.93, 131.79, 129.25, 129.21, 128.89, 128.48, 128.41, 126.77, 124.58, 122.41, 121.21, 120.20, 118.76, 110.74, 109.85, 86.10, 83.26, 80.98, 80.02, 55.65, 54.87, 52.62, 52.24, 37.98, 28.20, 28.10, 27.70;

IR: 3316, 2978, 2929, 1701, 1509, 1458, 1367, 1251, 1161, 1048, 1021, 861, 741 cm^{-1};

HRMS (ESI): $C_{40}H_{46}N_4O_7$+H, Calc: 695.3437, Found: 695.3437**;**

$[\alpha]_D^{22}$ = 12 (c=1 in $CHCl_3$);

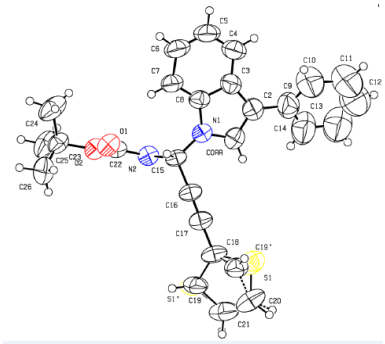


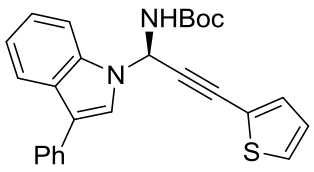
6d

White solid; 50.8 mg, 63% yield, dr > 20:1;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.39 – 7.34 (m, 2H), 7.34 – 7.27 (m, 4H), 7.24 – 7.12 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.55 – 6.36 (m, 1H), 5.92 (d, *J* = 9.2 Hz, 1H), 4.85 (s, 1H), 4.75 (q, *J* = 6.7 Hz, 1H), 4.33 (p, *J* = 7.5 Hz, 2H), 3.63 (s, 3H), 3.39 (d, *J* = 12.8 Hz, 1H), 3.10 (d, *J* = 6.3 Hz, 1H), 3.00 (td, *J* = 14.3, 5.5 Hz, 2H), 1.48 (s, 1H), 1.46 (s, 2H), 1.43 (s, 9H), 1.16 (s, 9H), 0.85 (t, *J* = 6.0 Hz, 6H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.62, 170.85, 170.54, 155.42, 154.01, 136.13, 135.0 , 131.82, 129.24, 129.20, 128.75, 128.38, 127.21, 125.03, 122.44, 120.37, 118.79, 110.56, 110.00, 86.09, 83.35, 80.83, 80.29, 55.73, 54.57, 53.46, 52.18, 51.03, 40.57, 37.43, 28.23, 27.88, 27.26, 24.49, 22.74, 21.63;
IR: 3303, 2963, 2235, 1655, 1510, 1459, 1367, 1261, 1131, 1077, 1022, 798, 742, 700 cm^{-1};
HRMS (ESI): $C_{46}H_{57}N_5O_8$+H, Calc: 808.4281, Found: 808.4281**;**
$[\alpha]_D^{22}$ = -33 (c=1 in $CHCl_3$);

6. X-ray structure of 3k





3k

Bond precision: C-C = 0.0129 A Wavelength=1.54184

Cell: a=9.3559(2) b=9.3559(2) c=60.611(3)
alpha=90 beta=90 gamma=90

Temperature: 292 K

	Calculated	Reported
Volume	5305.5(3)	5305.5(4)
Space group	P 43 21 2	P 43 21 2
Hall group	P 4nw 2abw	P 4nw 2abw
Moiety formula	C26 H24 N2 O2 S [+ solvent]	C26 H24 N2 O2 S
Sum formula	C26 H24 N2 O2 S [+ solvent]	C26 H24 N2 O2 S
Mr	428.53	428.53
Dx,g cm-3	1.073	1.073
Z	8	8
Mu (mm-1)	1.248	1.248
F000	1808.0	1808.0
F000'	1815.46	
h,k,lmax	11,11,74	11,11,73
Nref	5134[3136]	4996
Tmin,Tmax	0.799,0.840	0.215,1.000
Tmin'	0.769	

Correction method= # Reported T Limits: Tmin=0.215 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.59/0.97 Theta(max)= 70.919

R(reflections)= 0.0870(4236) wR2(reflections)= 0.2589(4996)
S = 0.868 Npar= 301

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01286 Ang.
PLAT369_ALERT_2_B Long C(sp2)-C(sp2) Bond C10 - C11 . 1.57 Ang.

Alert level C

PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.26 Report
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.6 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference S1' --C21 . 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C9 --C10 . 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C12 --C13 . 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C13 --C14 . 0.24 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C10 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C13 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C21 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C9 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C18 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C23 Check
PLAT987_ALERT_1_C The Flack x is >> 0 - Do a BASF/TWIN Refinement Please Check

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Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 11 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero . 0.079 Note
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large 0.18 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records 2 Report
PLAT300_ALERT_4_G Atom Site Occupancy of S1 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of S1' Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C19 Constrained at 0.7 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C19' Constrained at 0.3 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H19 Constrained at 0.7 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H20 Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H21 Constrained at 0.7 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H21A Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H19' Constrained at 0.3 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H20A Constrained at 0.3 Check
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 6% Note
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure 222 A**3
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 2 Note
PLAT791_ALERT_4_G Model has Chirality at C15 (Chiral SPGR) R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 66 Note
PLAT868_ALERT_4_G ALERTS Due to the Use of _smtbx_masks Suppressed ! Info
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 13 Note

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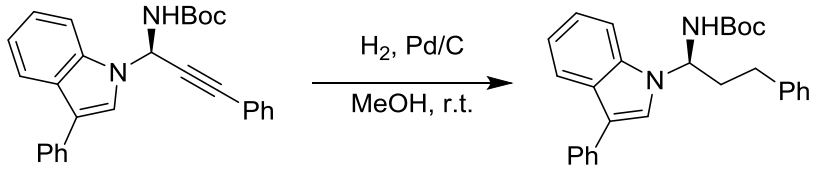
0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
13 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
22 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
11 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
20 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

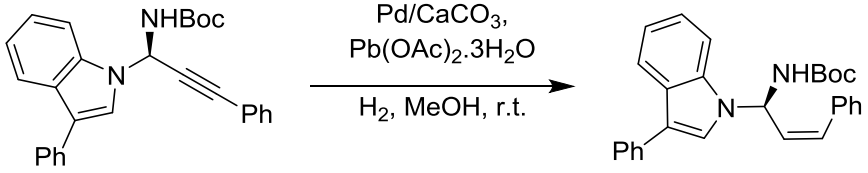
7. Transformations of the products



3a **7**

In an ordinary vial, equipped with a stir bar, was charged with **3a** (39.2 mg, 0.093 mmol, 1.00 equiv) and dry methanol (2 mL). Pd/C (10 % Pd, 9.9 mg, 0.0093 mmol, 0.1 equiv) was added to the solution and filled with H_2 gas. The reaction mixture was stirred under H_2 atmosphere for 8 hours. After complete reaction as monitored by TLC, the mixture was filtered through a plug of Celite and concentrated. The residue was then purified by silica gel chromatography (PE:AcOEt = 20:1) to afford purified **7**.

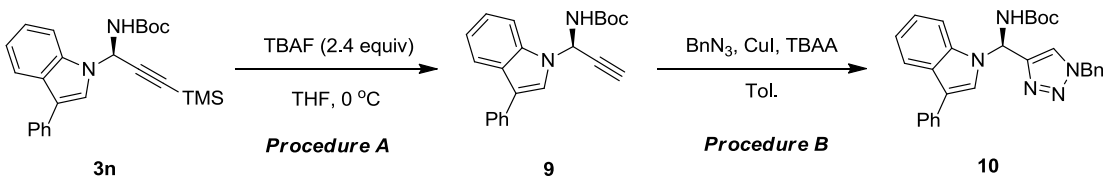
Colorless viscous oil; 35.3 mg, 89% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.85 (m, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (s, 1H), 7.30 (d, *J* = 1.7 Hz, 1H), 7.26 (d, *J* = 6.0 Hz, 2H), 7.24 – 7.15 (m, 3H), 7.15 – 7.08 (m, 2H), 5.97 (d, *J* = 72.8 Hz, 1H), 5.22 (s, 1H), 2.76 – 2.54 (m, 2H), 2.41 (d, *J* = 8.7 Hz, 2H), 1.39 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.58, 140.04, 136.34, 135.32, 128.71, 128.54, 128.37, 127.41, 126.43, 126.32, 125.95, 122.35, 121.33, 120.40, 119.91, 118.18, 110.57, 80.41, 62.10, 36.93, 31.80, 28.20;
IR: 2964, 1704, 1498, 1459, 1366, 1261, 1160, 1092, 1024, 799, 742, 699 cm^{-1};
HRMS (ESI): $C_{28}H_{30}N_2O_2$+Na, Calc: 449.2198, Found: 449.2198**;**
$[\alpha]_D^{22}$ = -45 (c=1 in $CHCl_3$);
HPLC: Chiralpak AS-H column, hexane/EtOH = 9/1, flow rate = 1.0 mL/min, t_{major} = 11.1 min, t_{minor} = 17.3 min, 94% ee.



3a **8**

To a solution of **3a** (41.8 mg, 0.09 mmol, 1 equiv), $Pb(OAc)_2.3H_2O$ (3.4 mg, 0.1 equiv) in MeOH (3 ml) was added $Pd/CaCO_3$ (5% Pd, 77 mg, 0.4 equiv) under argon atmosphere. Then the atmosphere was replaced with hydrogen gas. After stirring for 11 h, the reaction mixture was monitored by TLC. The mixture was filtered through a plug of Celite and concentrated. The residue was then purified by silica gel chromatography (PE:AcOEt = 15:1) to afford purified **8**.

Colorless viscous oil; 35.9 mg, 94% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.85 (m, 1H), 7.69 – 7.57 (m, 2H), 7.52 – 7.37 (m, 4H), 7.30 (d, *J* = 5.4 Hz, 3H), 7.28 – 7.12 (m, 5H), 6.92 (s, 1H), 6.76 (d, *J* = 11.4 Hz, 1H), 6.00 (dd, *J* = 11.5, 8.3 Hz, 1H), 5.39 (s, 1H), 1.38 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.06, 135.62, 135.33, 135.08, 133.68, 128.69, 128.67, 128.61, 128.12, 127.43, 126.89, 126.40, 125.94, 122.33, 121.84, 120.52, 119.96, 118.11, 110.80, 80.64, 60.49, 28.18;
IR: 3394, 2977, 2928, 1704, 1603, 1494, 1458, 1366, 1252, 1156, 1017, 770, 742 cm^{-1};
HRMS (ESI): $C_{28}H_{28}N_2O_2$+Na, Calc: 447.2042, Found: 447.2042**;**
$[\alpha]_D^{22}$ = 78 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 95/5, flow rate = 1.0 mL/min, t_{major} = 14.5 min, t_{minor} = 16.4 min, 93% ee.



3n **9** **10**

Procedure A:

In an ordinary vial, equipped with a stir bar, was charged with **3n** (42 mg, 0.1 mmol, 1 equiv). Freshly distilled THF (2 mL) was added and the solution was cooled to 0 °C. TBAF (1M in THF, 0.24 mL, 0.24 mmol, 2.4 equiv) was added dropwise and the solution

was stirred another 3 min. After completion of the reaction, the resulting brown solution was quenched with saturated aqueous NH_4Cl (5.0 mL) at 0 °C. The layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was then purified by silica gel chromatography (PE:AcOEt = 20:1) to afford purified **9**.

Colorless viscous oil; 34.3 mg, 99% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.58 (s, 1H), 7.44 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.34 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 6.94 (d, *J* = 9.3 Hz, 1H), 5.61 (d, *J* = 9.2 Hz, 1H), 2.71 (d, *J* = 2.4 Hz, 1H), 1.42 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.83, 135.44, 135.00, 128.72, 127.55, 127.19, 126.17, 123.11, 122.60, 120.87, 120.07, 118.39, 110.72, 81.24, 77.98, 75.04, 54.04, 28.18;
IR: 3296, 2976, 2928, 1706, 1604, 1495, 1458, 1367, 1261, 1156, 1022, 769, 742 cm^{-1};
HRMS (ESI): $C_{22}H_{22}N_2O_2$+Na, Calc: 369.1575, Found: 369.1575**;**
$[\alpha]_D^{22}$ = -29 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 100/1, flow rate = 0.8 mL/min, t_{major} = 50.6 min, t_{minor} = 54.9 min, 91% ee.

Procedure B:

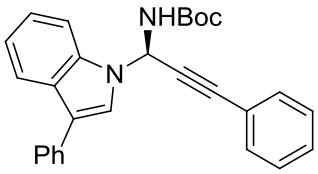
A flame dried 5 mL vial, equipped with a stir bar, was charged with **9** (20.1 mg, 0.058 mmol, 1.00 equiv) and freshly distilled toluene (1.5 mL). Benzyl azide (9.07 mg, 1.14 equiv) was added to the solution at rt. And CuI (1.1 mg, 0.0058 mmol, 0.1 equiv) and TBAA (3.6 mg, 0.0116 mmol, 0.2 equiv) were added, respectively. After stirring for 3 h, the reaction mixture was monitored by TLC. The mixture was then purified by silica gel chromatography (PE:AcOEt = 5:1) to afford purified **10**.

White solid; 25.6 mg, 92% yield;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.35 – 7.27 (m, 4H), 7.25 (d, *J* = 4.5 Hz, 2H), 7.22 – 7.13 (m, 4H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.59 – 5.29 (m, 2H), 1.41 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.60, 145.11, 135.82, 135.10, 133.92, 129.16, 128.92, 128.67, 128.00, 127.39, 126.84, 126.01, 123.37, 122.38, 121.96, 120.57, 119.97, 118.17, 110.70, 80.77, 58.61, 54.38, 28.19;
IR: 2964, 1714, 1603, 1496, 1457, 1366, 1261, 1050, 1022, 878, 796, 743, 796, 701 cm^{-1};
HRMS (ESI): $C_{29}H_{29}N_5O_2$+H, Calc: 480.2396, Found: 480.2396**;**
$[\alpha]_D^{22}$ = 7 (c=1 in $CHCl_3$);
HPLC: Chiralpak OD-H column, hexane/EtOH = 7/3, flow rate = 1.0 mL/min, t_{major} = 12.7 min, t_{minor} = 14.3 min, 92% ee.

8. Reference

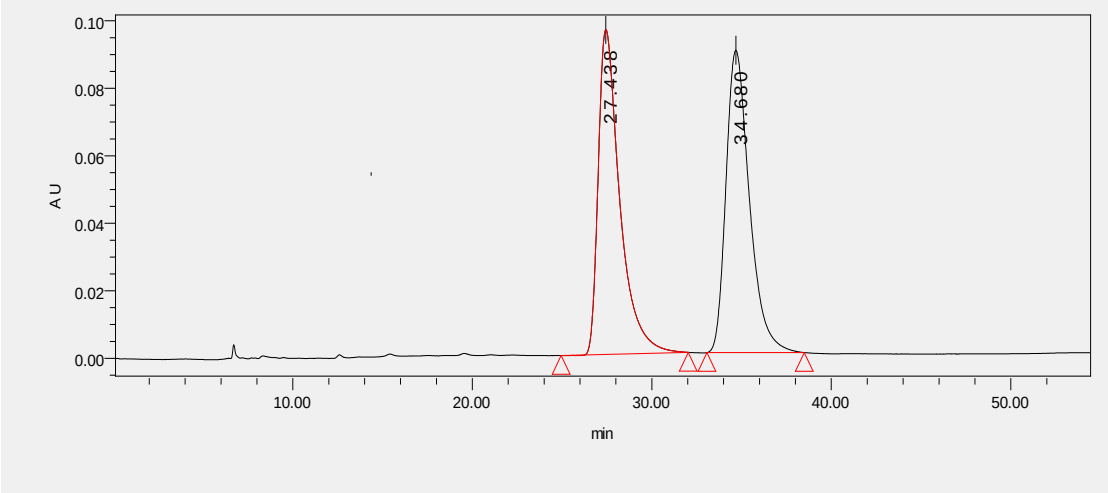
[1] Z. Zhou, Y. Li, L. Gong, E. Meggers, *Org. Lett.* **2017**, *19*, 222-225.
[2] M. Singsardar, A. Chakraborty, S. Jana, A. Hajra, *ChemistrySelect* **2017**, *2*, 8893-8897.
[3] Y. Wang, M. Mo, K. Zhu, C. Zheng, H. Zhang, W. Wang, Z. Shao, *Nat. Commun.* **2015**, *6*, 8544.

9. Copies of HPLC spectra

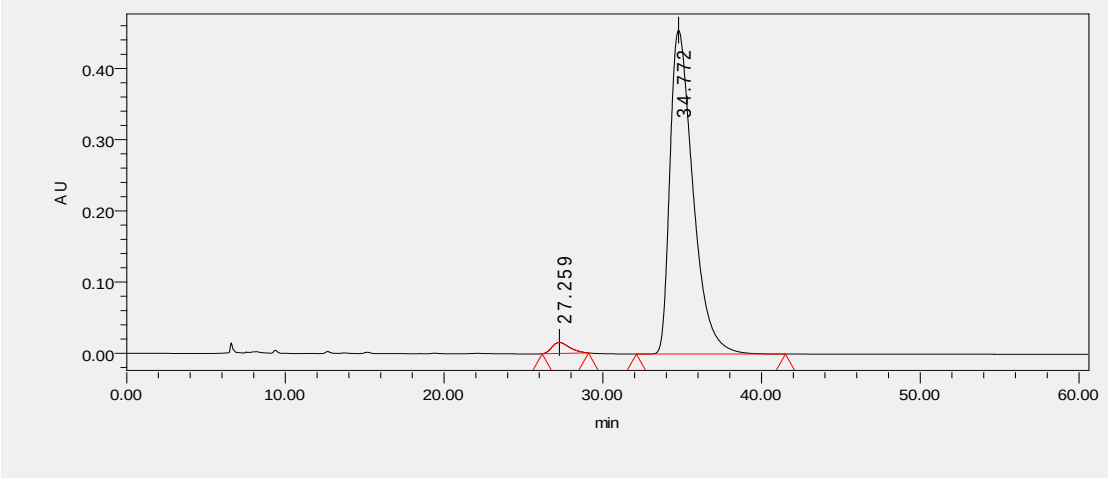


3a

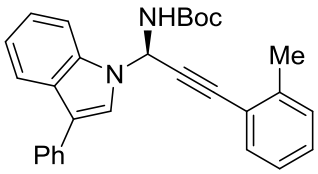
HPLC using an IA-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	27.438	8020309	49.65	96296	bb
2	34.680	8132220	50.35	89569	bb

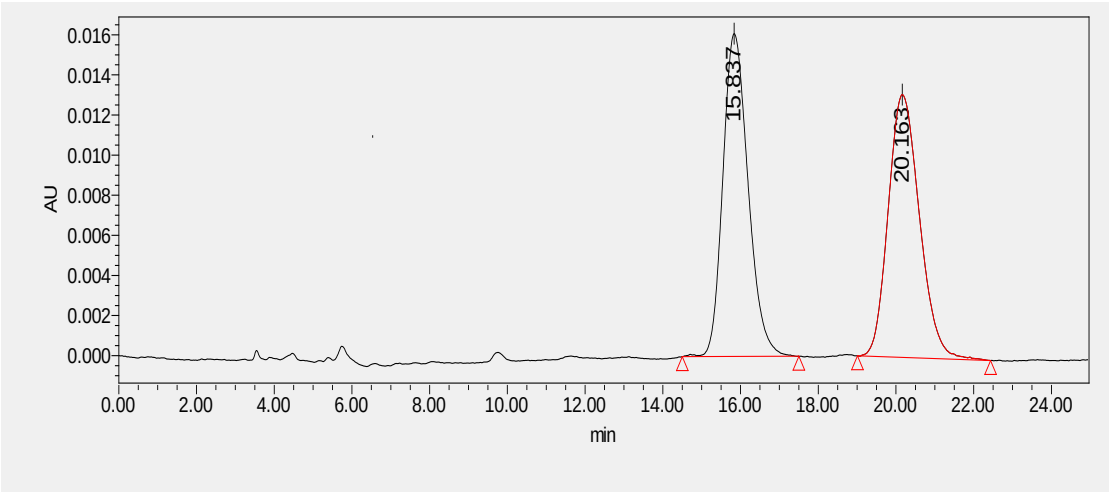


Entry	Retention time	Area	Area (%)	Height	Int type
1	27.259	1185250	2.52	15445	bb
2	34.772	45851461	97.48	454777	bb

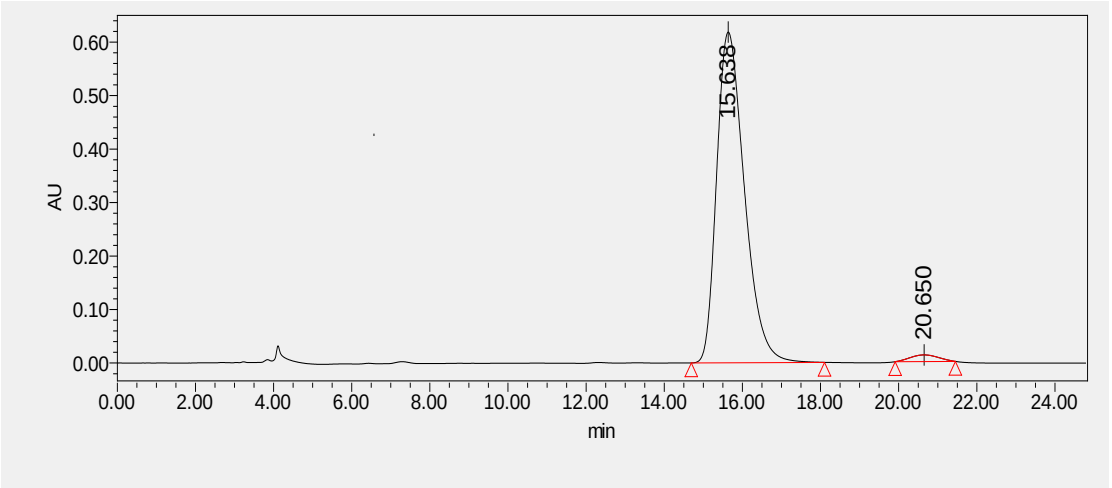


3b

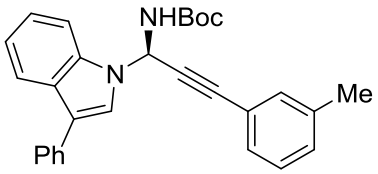
HPLC using an OD-H column, hexane / EtOH = 150/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	15.837	727770	49.84	16098	bb
2	20.163	732558	50.16	13104	bb

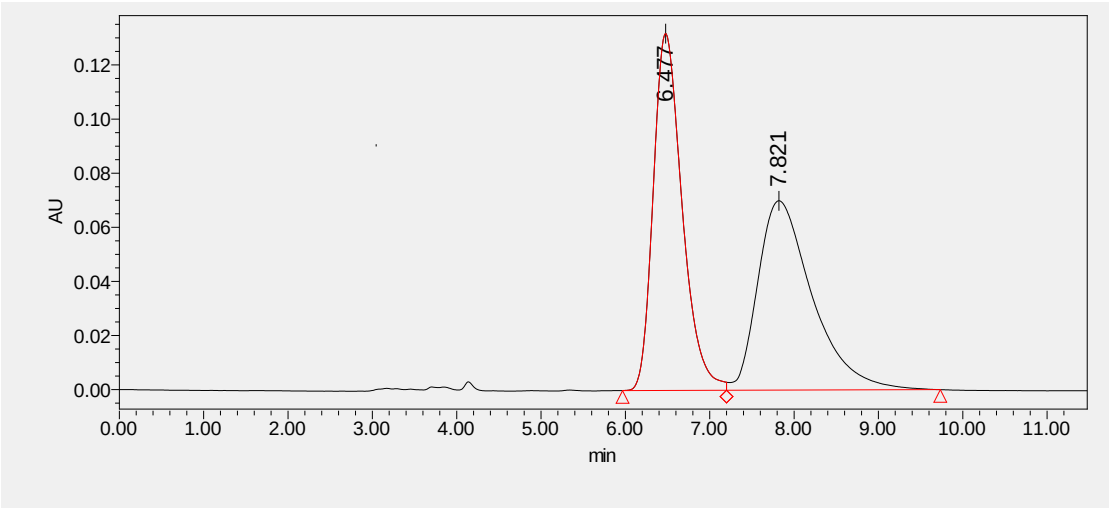


Entry	Retention time	Area	Area (%)	Height	Int type
1	15.638	30499502	97.98	618382	bb
2	20.650	627806	2.02	12484	bb

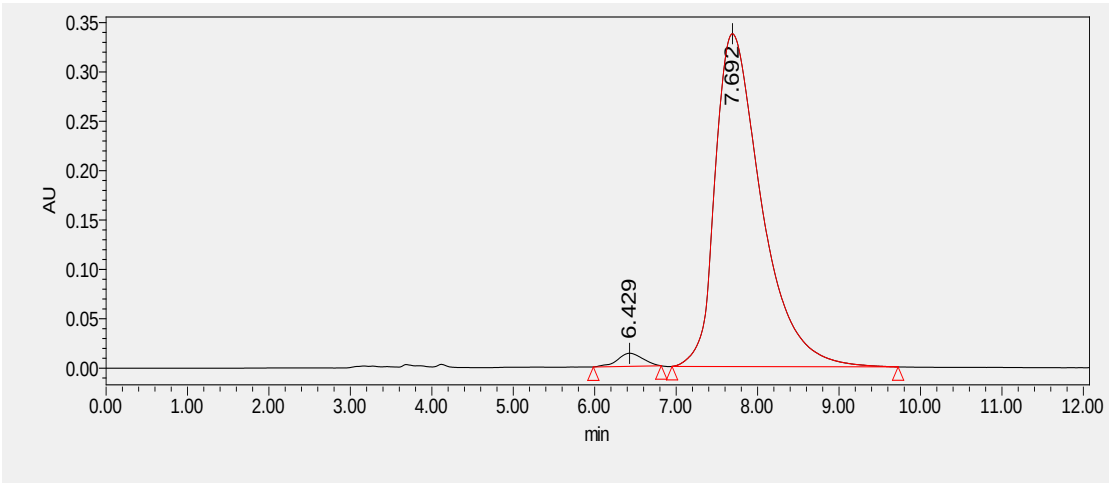


3c

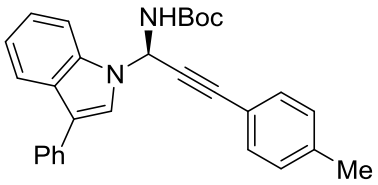
HPLC using an AS-H column, hexane / EtOH = 100/1.5, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	6.477	3142901	49.97	131922	bv
2	7.821	3146068	50.03	69988	vb

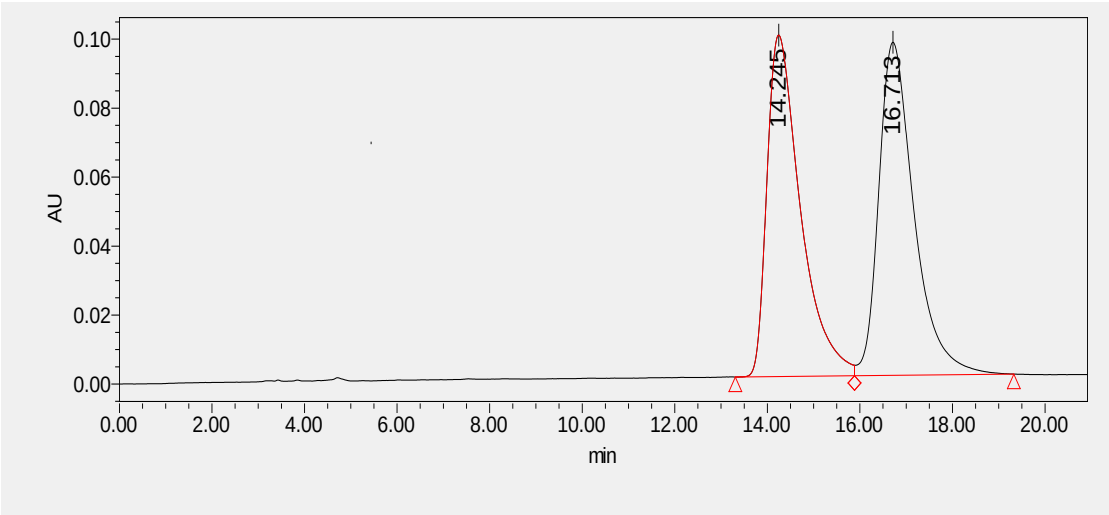


Entry	Retention time	Area	Area (%)	Height	Int type
1	6.429	286004	2.10	13257	bb
2	7.692	13332344	97.90	337053	bb

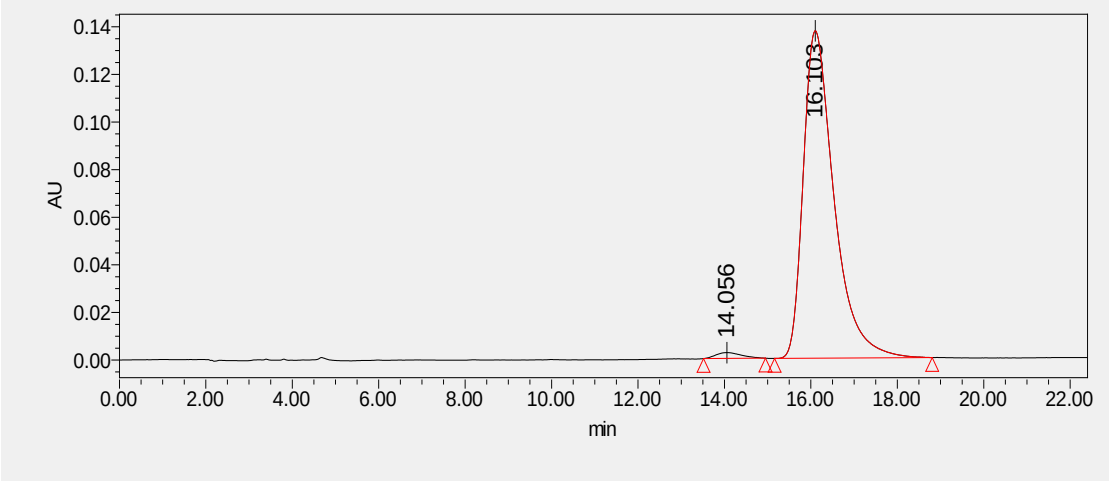


3d

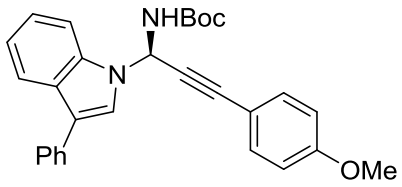
HPLC using an IA-H column, hexane / EtOH = 100/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	14.245	4978185	49.32	98999	bv
2	16.713	5115469	50.68	96562	vb

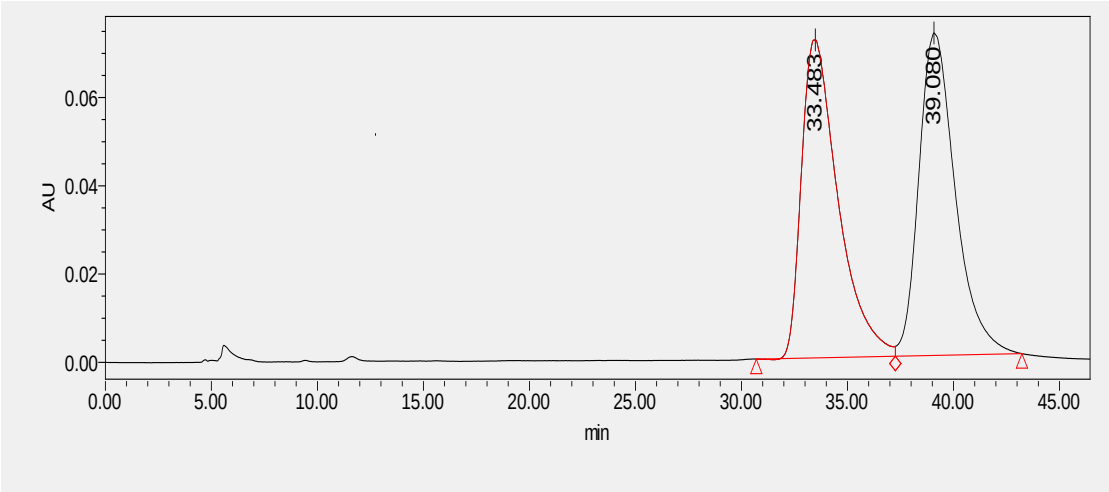


Entry	Retention time	Area	Area (%)	Height	Int type
1	14.056	101112	1.46	2472	bb
2	16.103	6802795	98.54	137551	bb

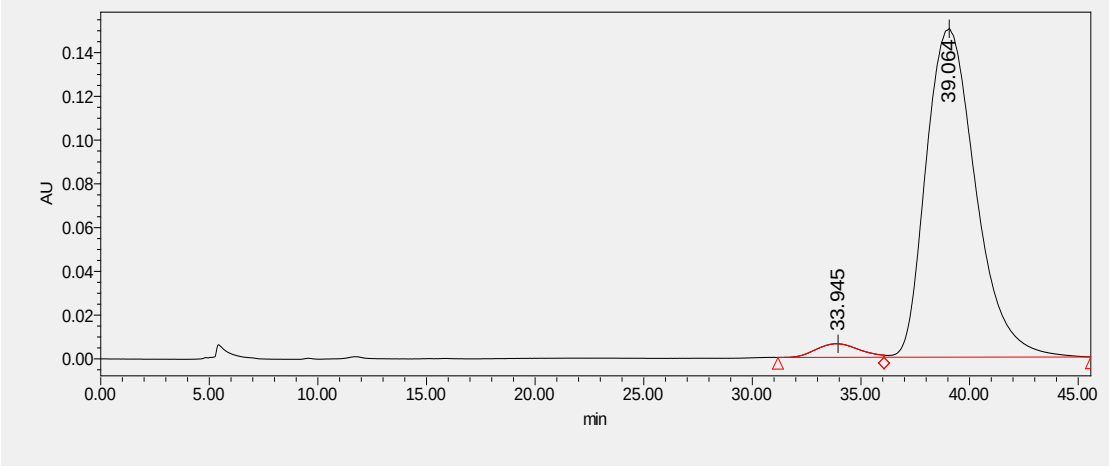


3e

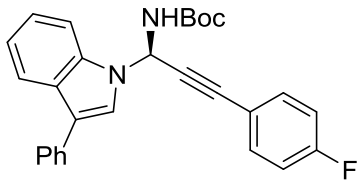
HPLC using an IA-H column, hexane / EtOH = 100/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	33.483	8685180	49.88	72074	bv
2	39.080	8726422	50.12	73083	vb

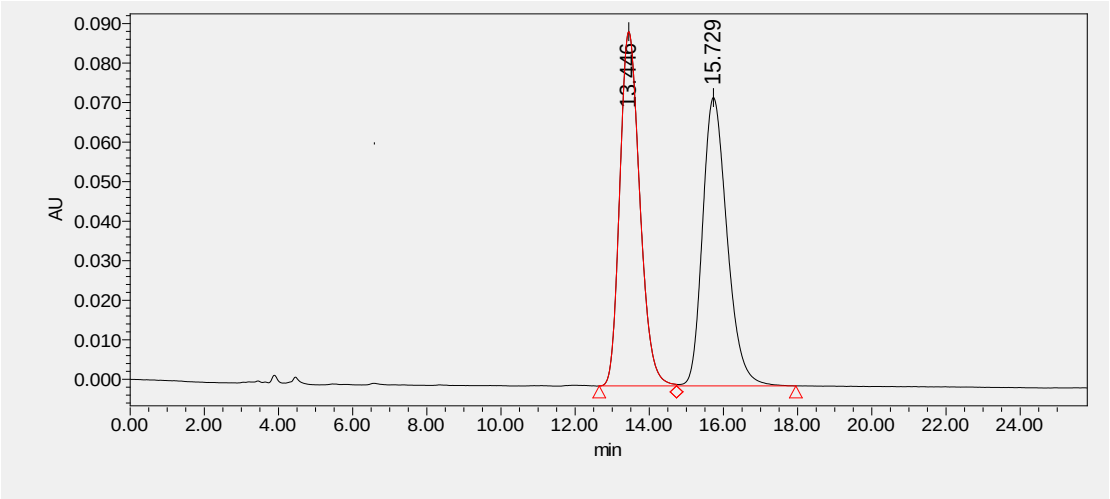


Entry	Retention time	Area	Area (%)	Height	Int type
1	33.945	858142	3.47	6217	bv
2	39.064	23856097	96.53	150145	vb

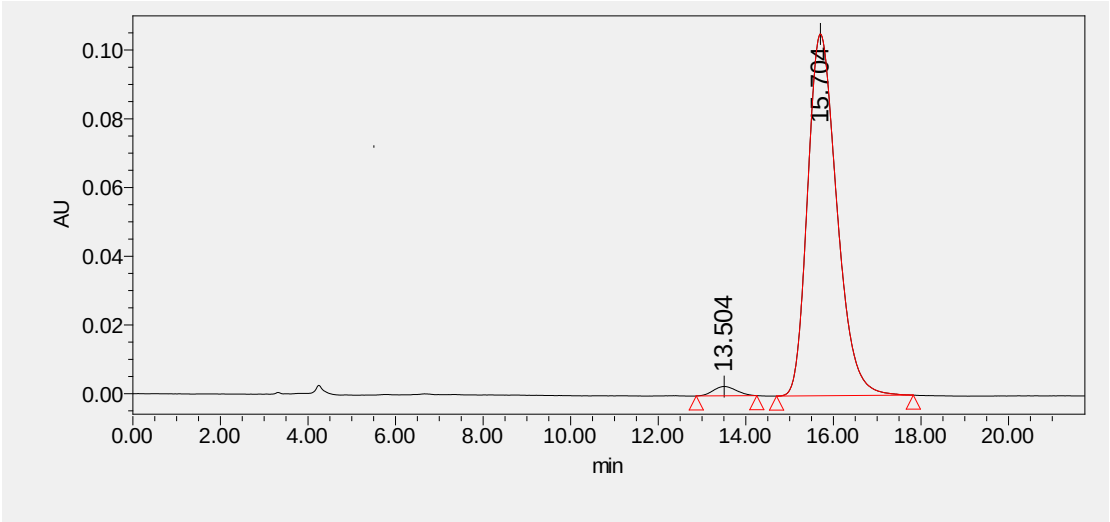


3f

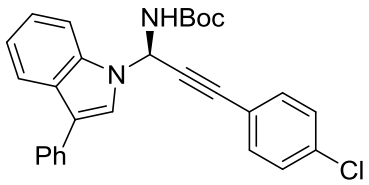
HPLC using an OD-H column, hexane / EtOH = 100/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	13.446	3357039	50.06	89603	bv
2	15.729	3349509	49.94	72949	vb

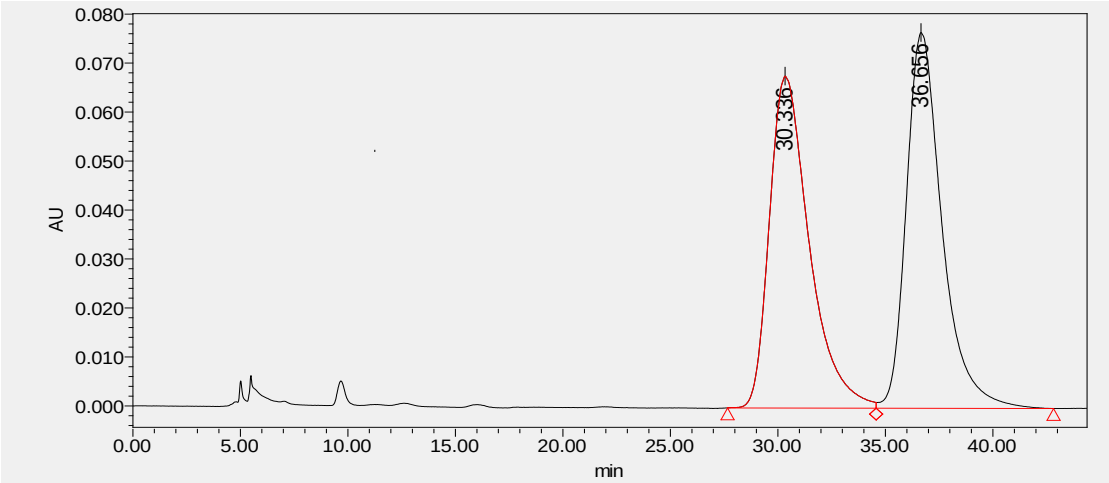


Entry	Retention time	Area	Area (%)	Height	Int type
1	13.504	98984	1.98	2704	bb
2	15.704	4891373	98.02	105284	bb

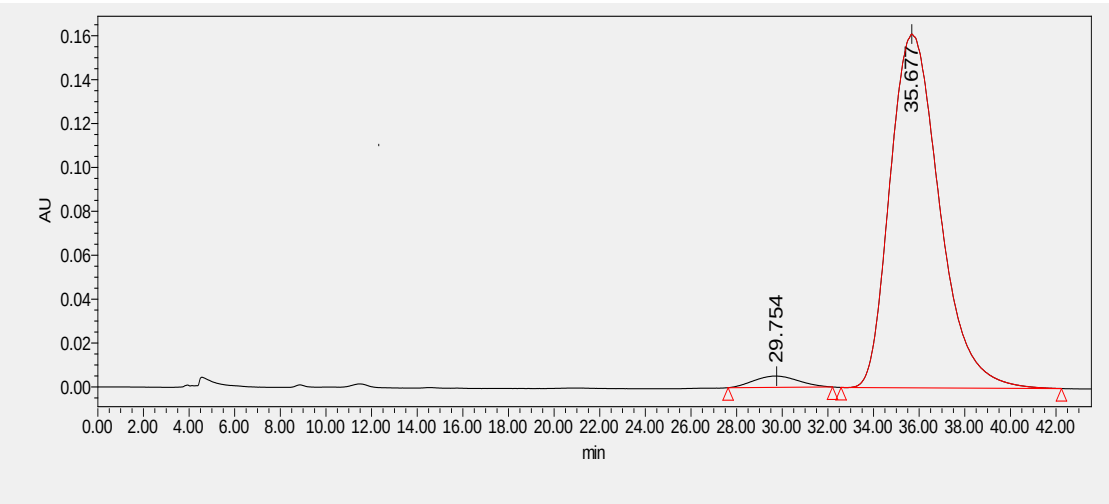


3g

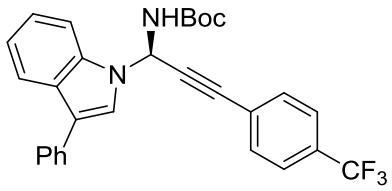
HPLC using an IA-H column, hexane / EtOH = 100/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	30.336	8717337	49.55	67779	bv
2	36.656	8874923	50.45	76725	vb

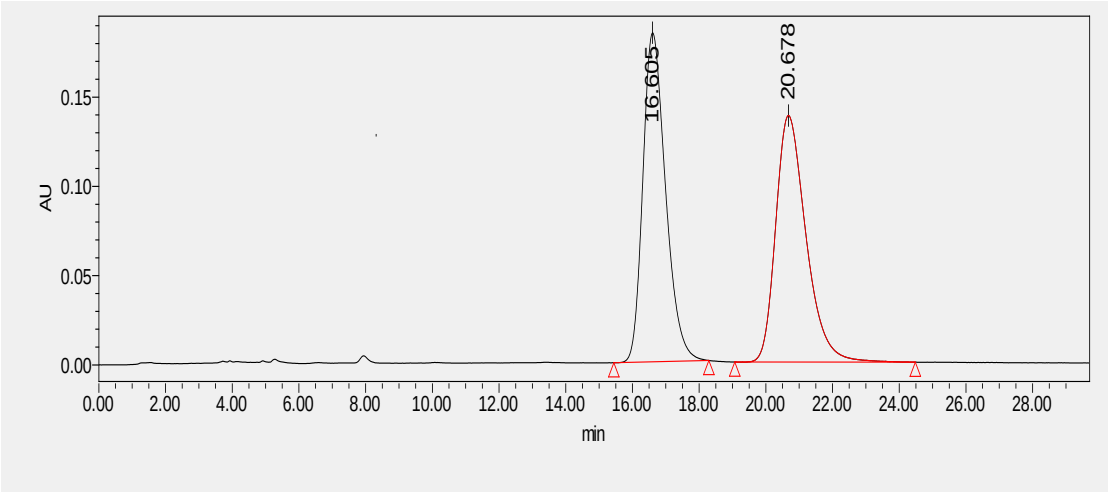


Entry	Retention time	Area	Area (%)	Height	Int type
1	29.754	704237	2.82	5166	bb
2	35.677	24295718	97.18	161173	bb

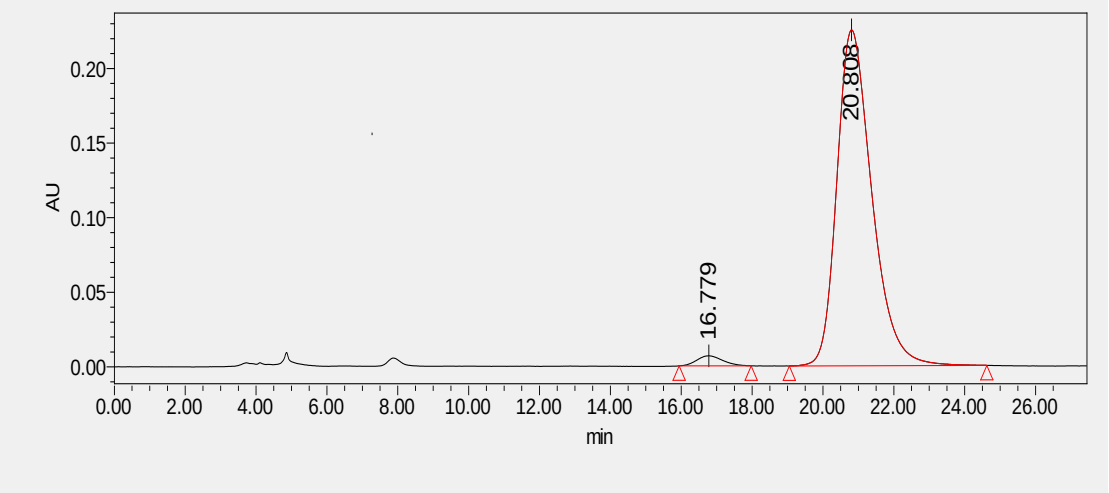


3h

HPLC using an OD-H column, hexane / EtOH = 120/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	16.605	8699876	49.95	184247	bb
2	20.678	8716049	50.05	138092	bb



Entry	Retention time	Area	Area (%)	Height	Int type
1	16.779	340443	2.16	6725	bb
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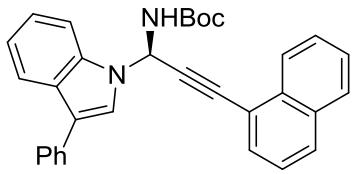
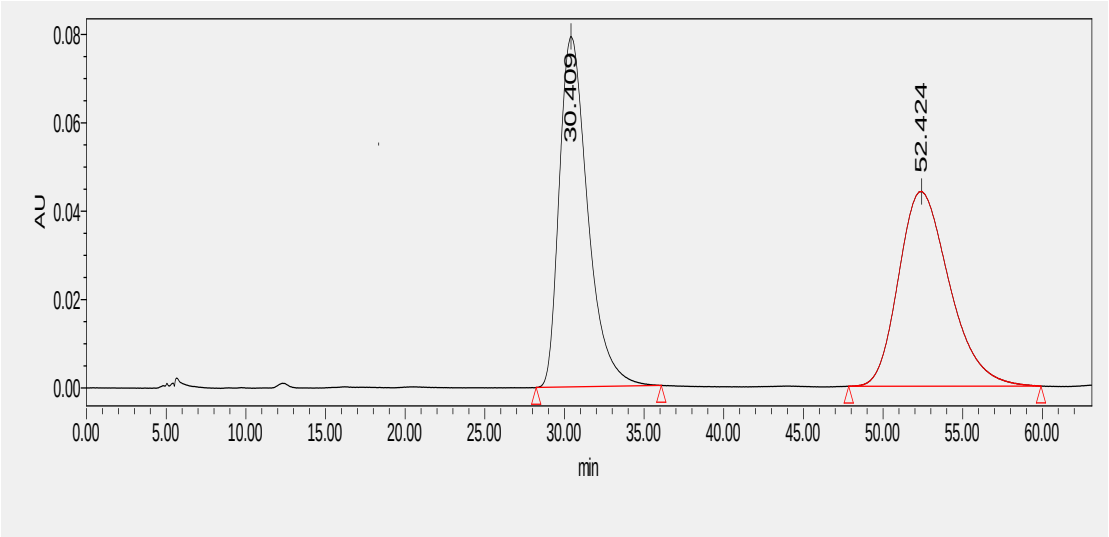
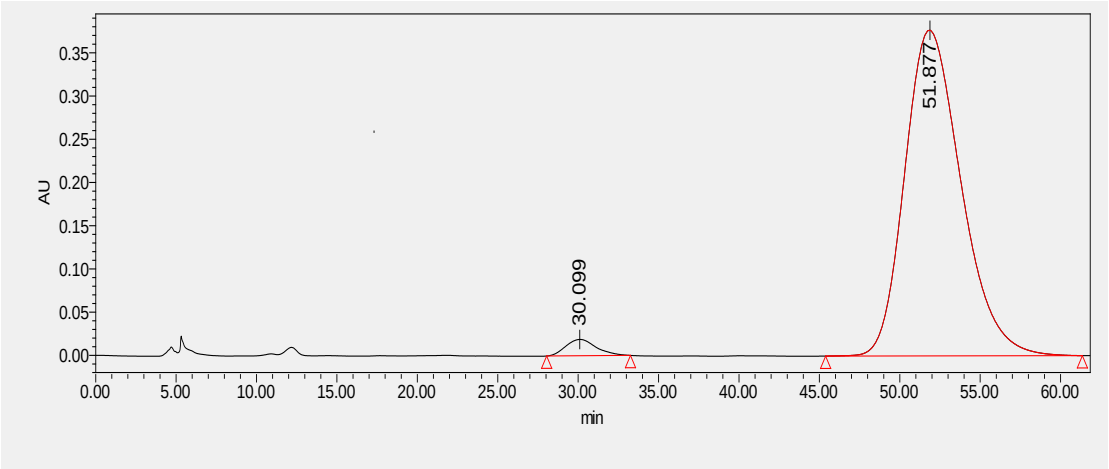


3i

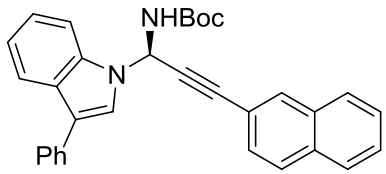
HPLC using an IA-H column, hexane / EtOH = 100/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	30.409	9854070	50.17	79282	bb
2	52.424	9786423	49.83	44061	bb

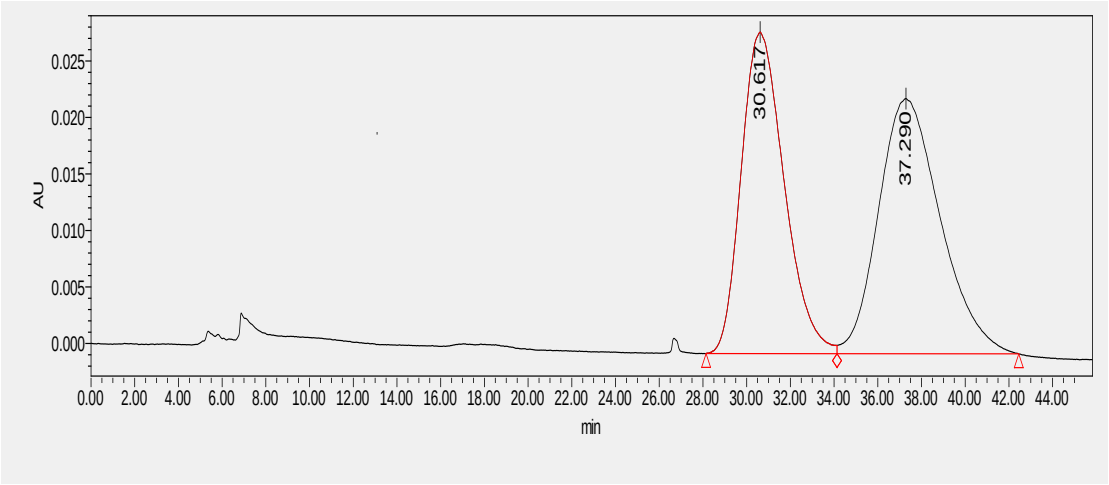


Entry	Retention time	Area	Area (%)	Height	Int type
1	30.099	2487988	2.64	18912	bb
2	51.877	91810472	97.36	376597	bb



3j

HPLC using an AS-H column, hexane / EtOH = 150/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
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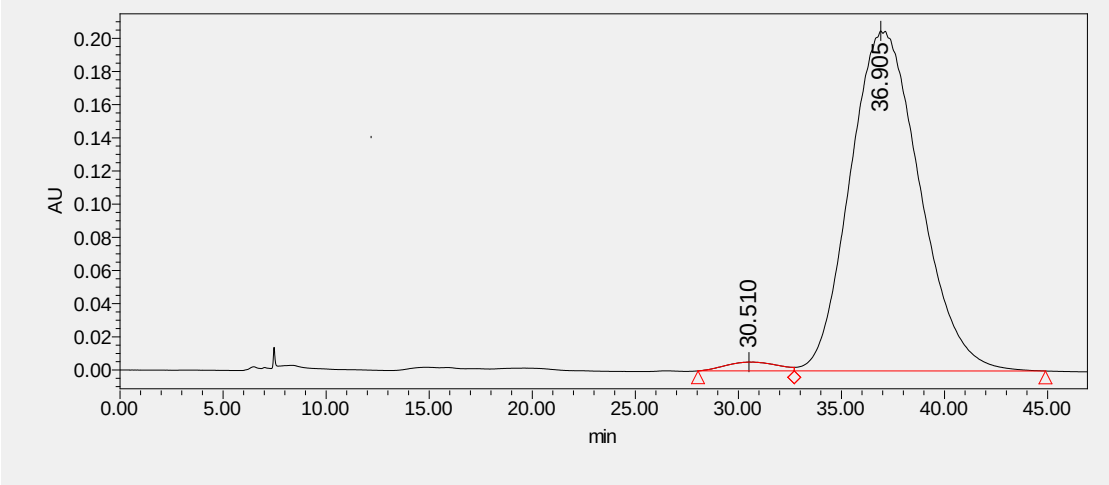
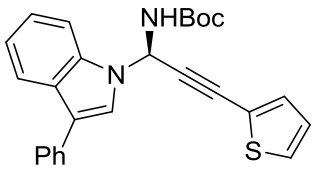
2	37.290	10585080	50.19	57473	vb

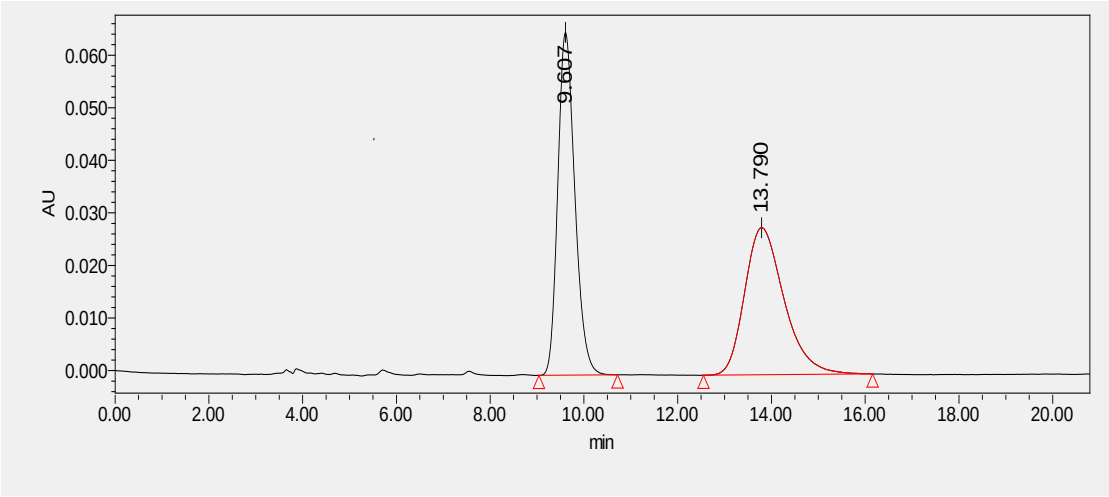


Entry	Retention time	Area	Area (%)	Height	Int type
1	30.510	930792	1.89	5337	bv
2	36.905	48223121	98.11	205016	vb

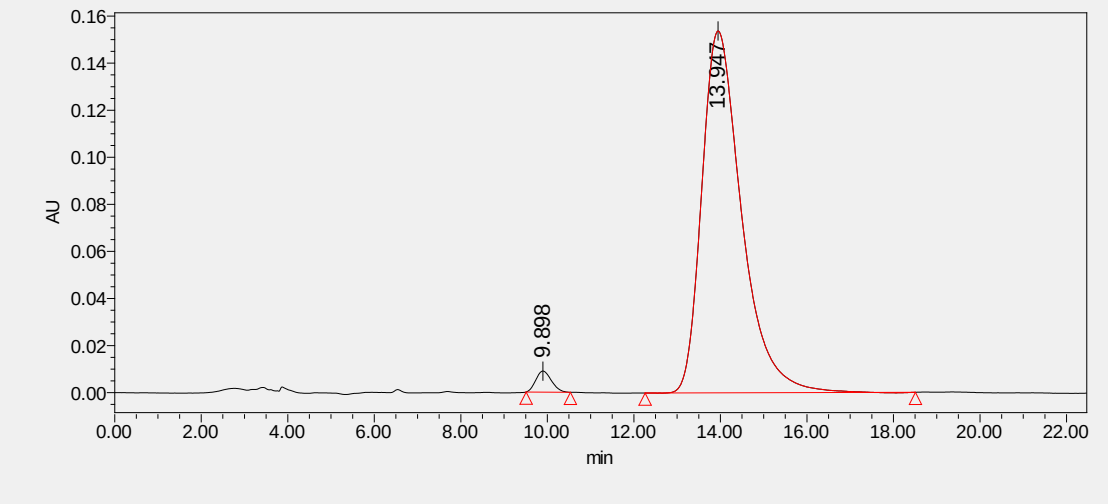


3k

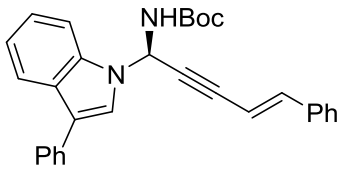
HPLC using an AS-H column, hexane / EtOH = 100/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	9.607	1649573	50.29	65200	bb
2	13.790	1630864	49.71	27974	bb

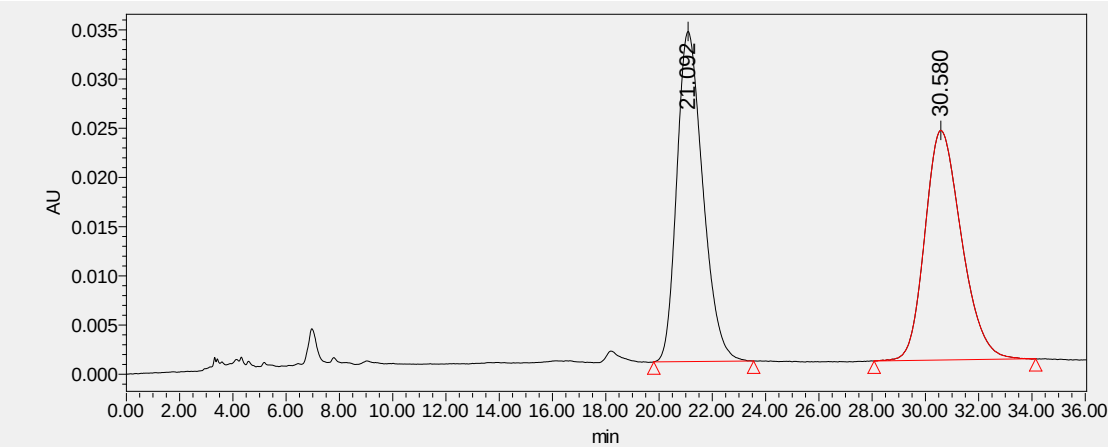


Entry	Retention time	Area	Area (%)	Height	Int type
1	9.898	224035	2.23	8938	bb
2	13.947	9843265	97.77	153704	bb

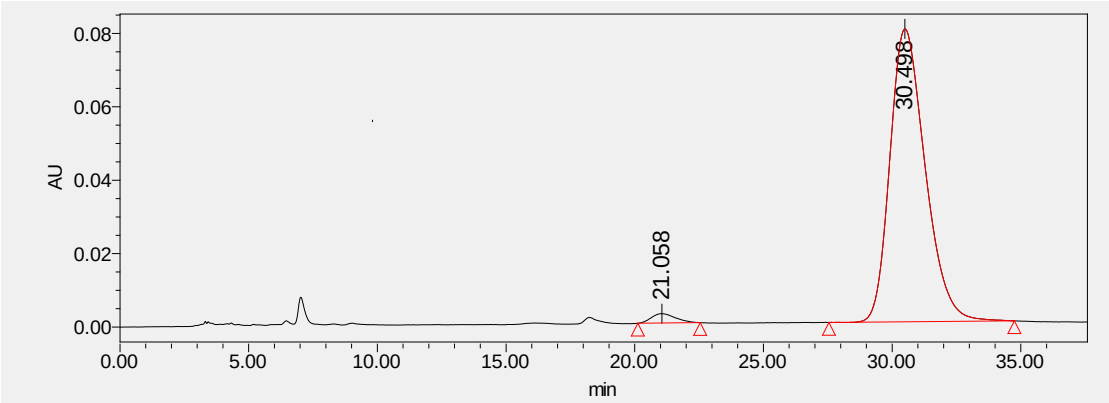


3l

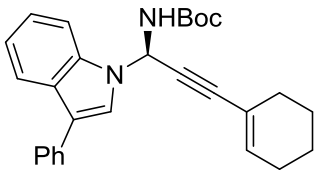
HPLC using an OD-H column, hexane / EtOH = 95/5, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	21.092	2270084	50.46	33548	bb
2	30.580	2228447	49.54	23345	bb

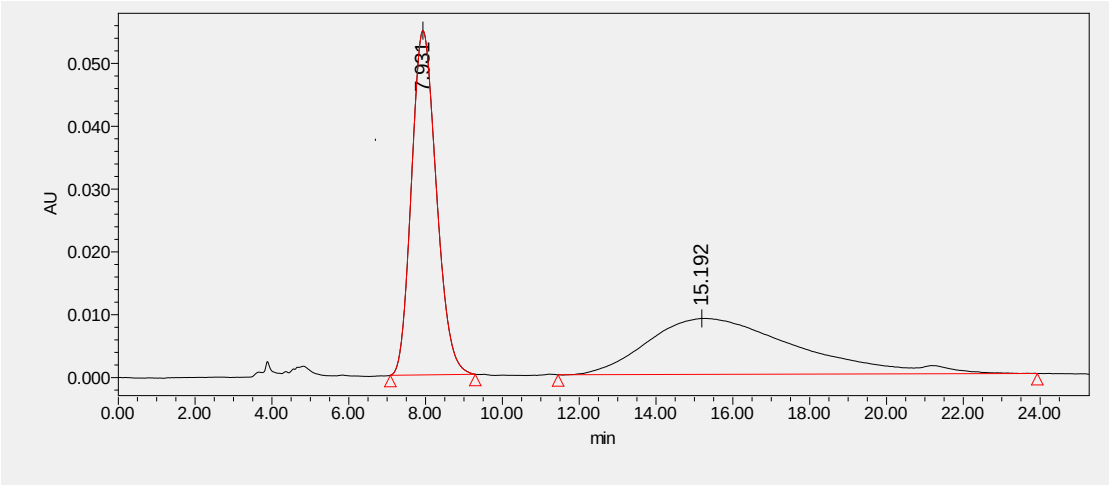


Entry	Retention time	Area	Area (%)	Height	Int type
1	21.058	164431	2.12	2540	bb
2	30.498	7590940	97.88	79755	bb

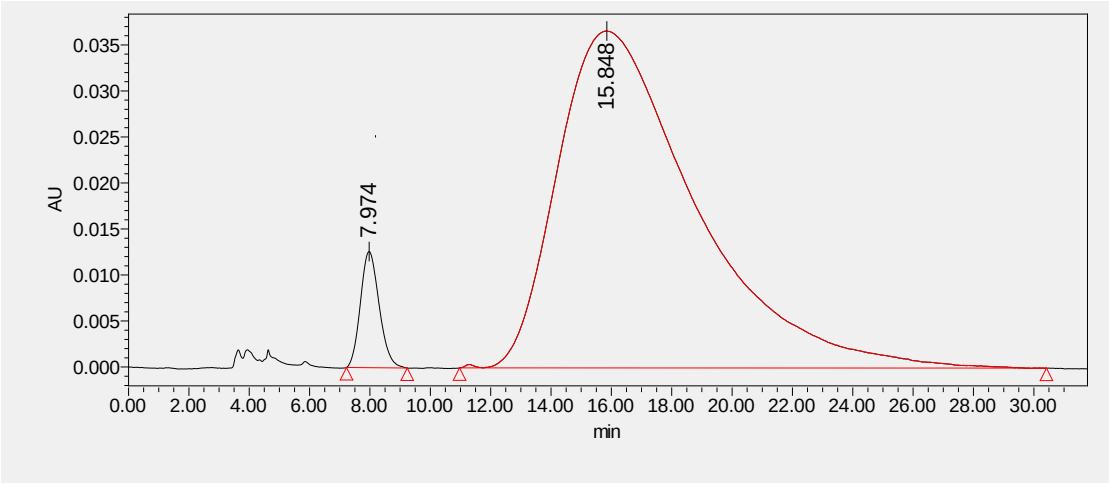


3m

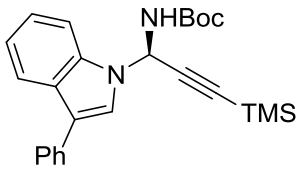
HPLC using an AS-H column, hexane / EtOH = 120/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	7.931	2459098	50.43	54781	bb
2	15.192	2416864	49.57	8913	bb

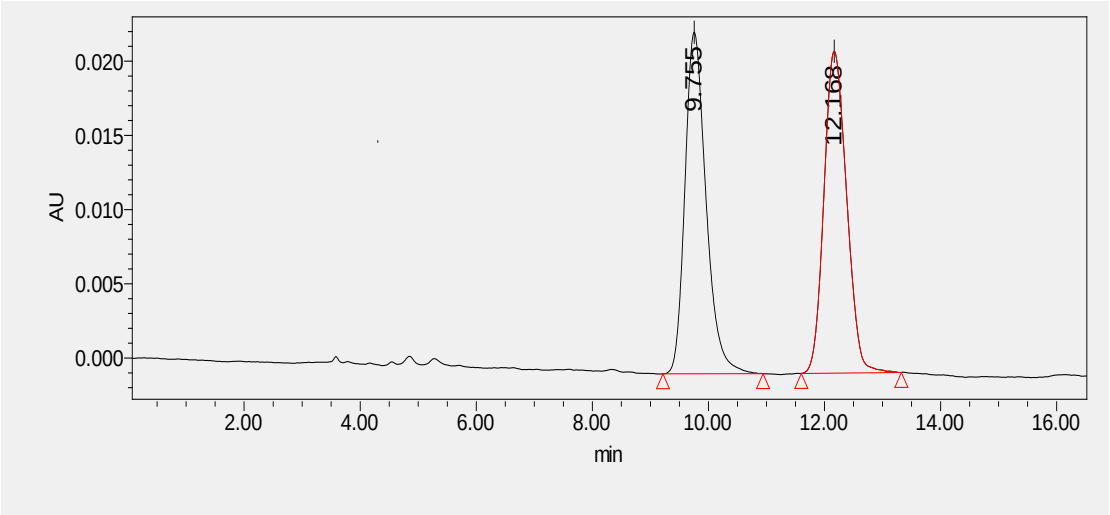


Entry	Retention time	Area	Area (%)	Height	Int type
1	7.974	544962	4.47	12618	bb
2	15.848	11650653	95.53	36604	bb

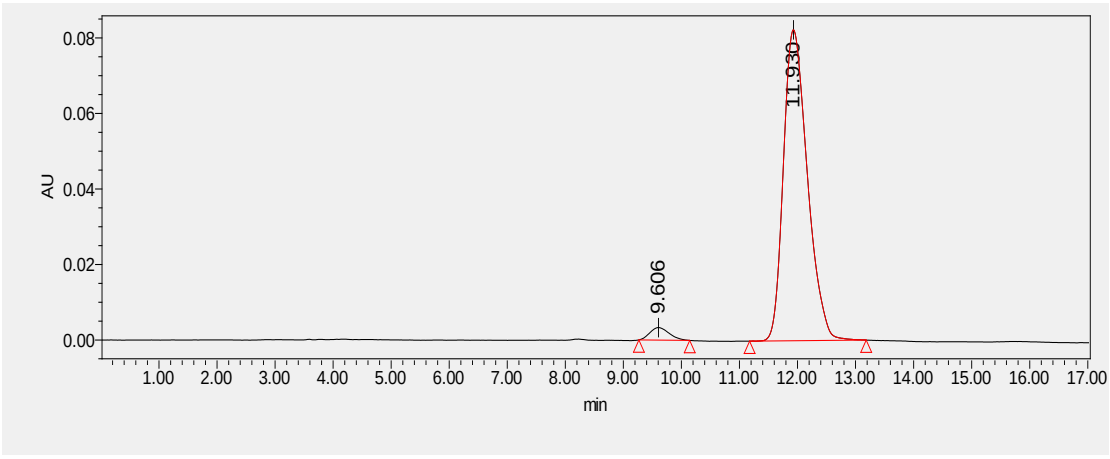


3n

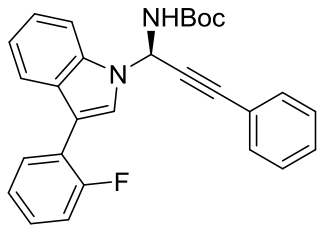
HPLC using an OD-H column, hexane / EtOH = 400/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	9.755	581348	49.72	23010	bb
2	12.168	588012	50.28	21688	bb

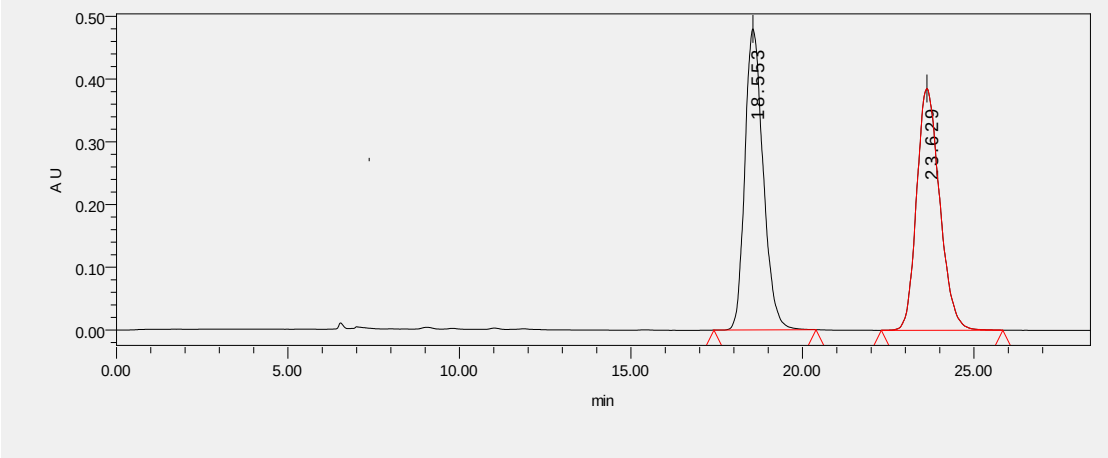


Entry	Retention time	Area	Area (%)	Height	Int type
1	9.606	77107	3.16	3324	bb
2	11.930	2361446	96.84	82357	bb

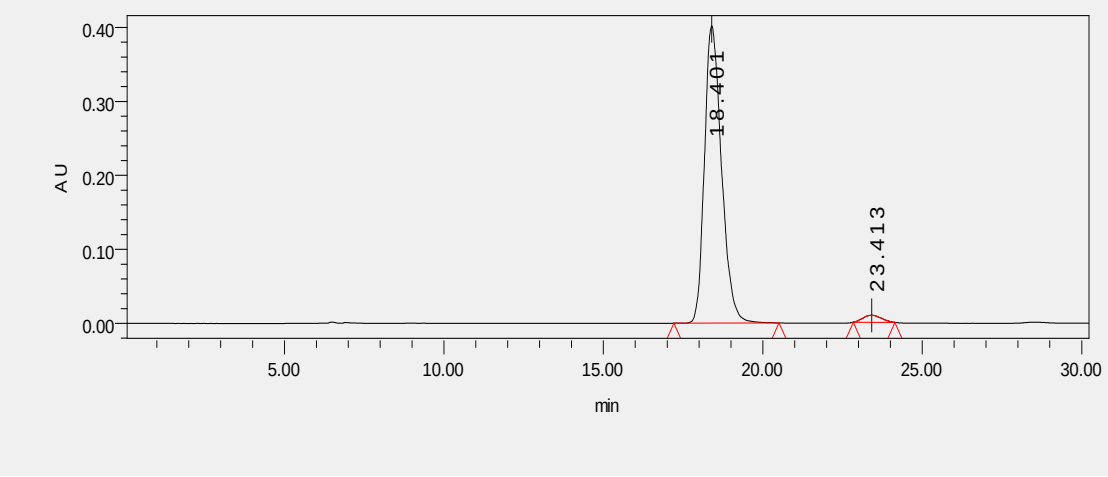


3o

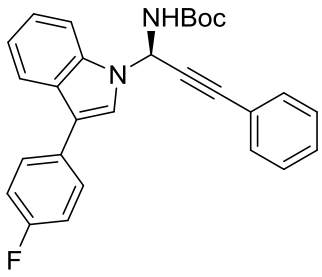
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	18.553	17814825	49.74	479722	bb
2	23.629	17998807	50.26	385160	bb

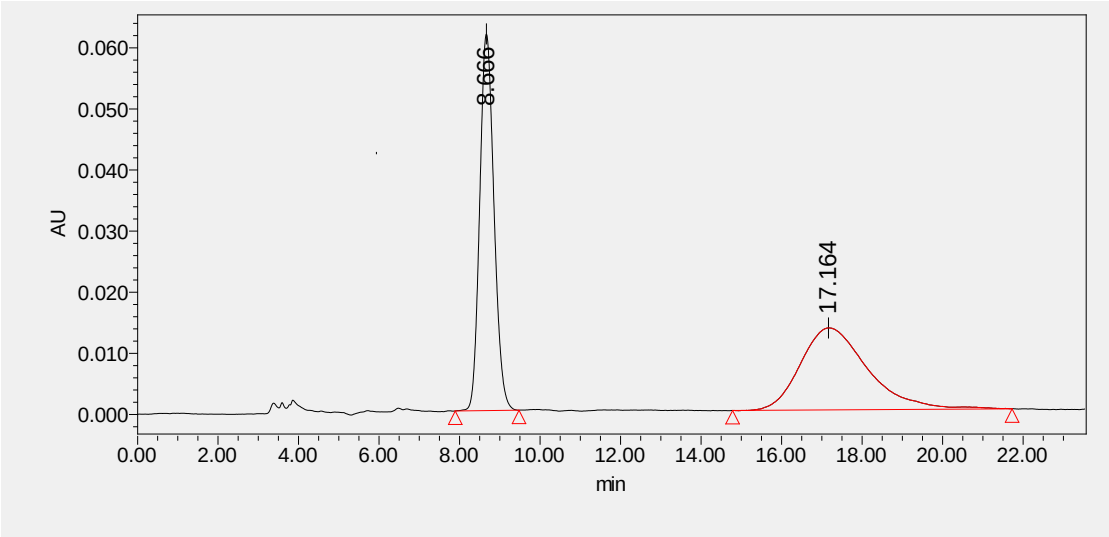


Entry	Retention time	Area	Area (%)	Height	Int type
1	18.401	14976845	97.52	401837	bb
2	23.413	380553	2.48	9544	bb

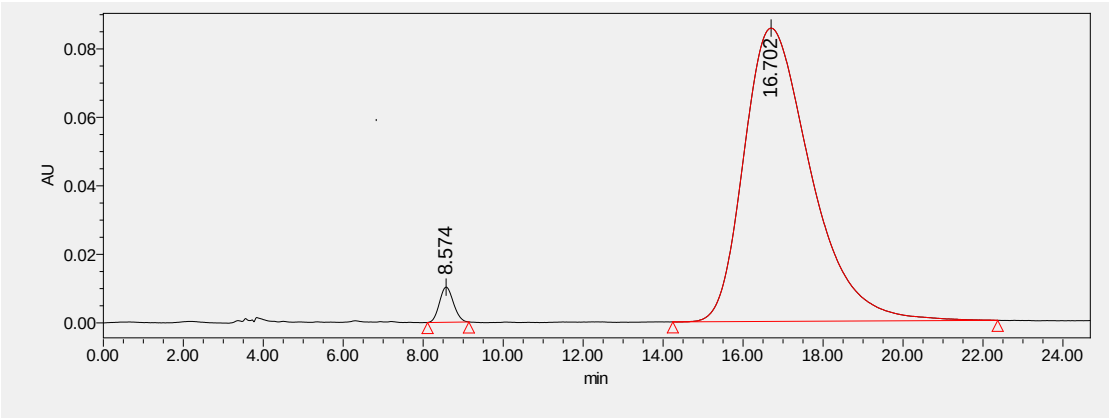


3p

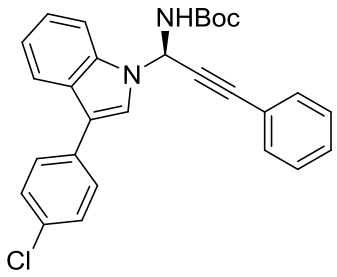
HPLC using an AS-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	8.666	1520048	49.45	61630	bb
2	17.164	1553894	50.55	13413	bb

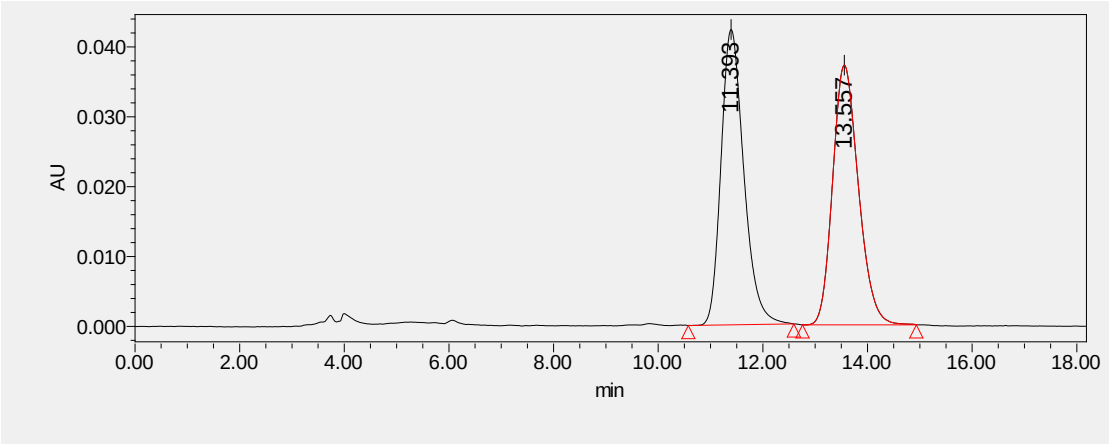


Entry	Retention time	Area	Area (%)	Height	Int type
1	8.574	248895	2.44	10263	bb
2	16.702	9947409	97.56	85621	bb

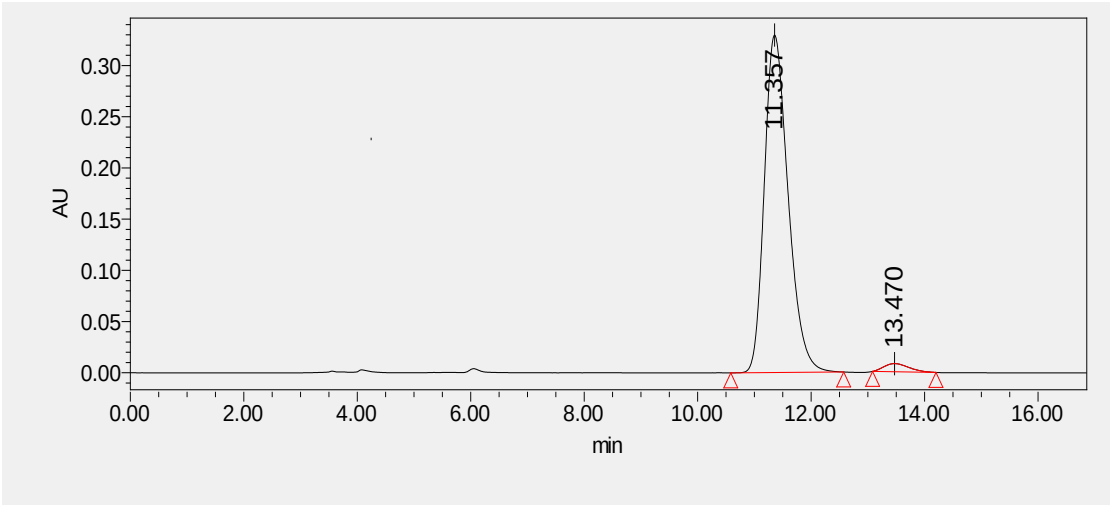


3q

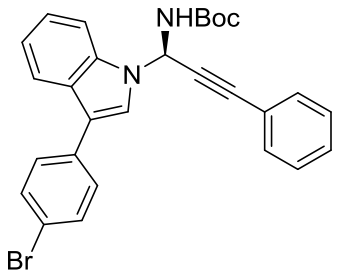
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	11.393	1277460	50.15	42266	bb
2	13.557	1269946	49.85	37152	bb

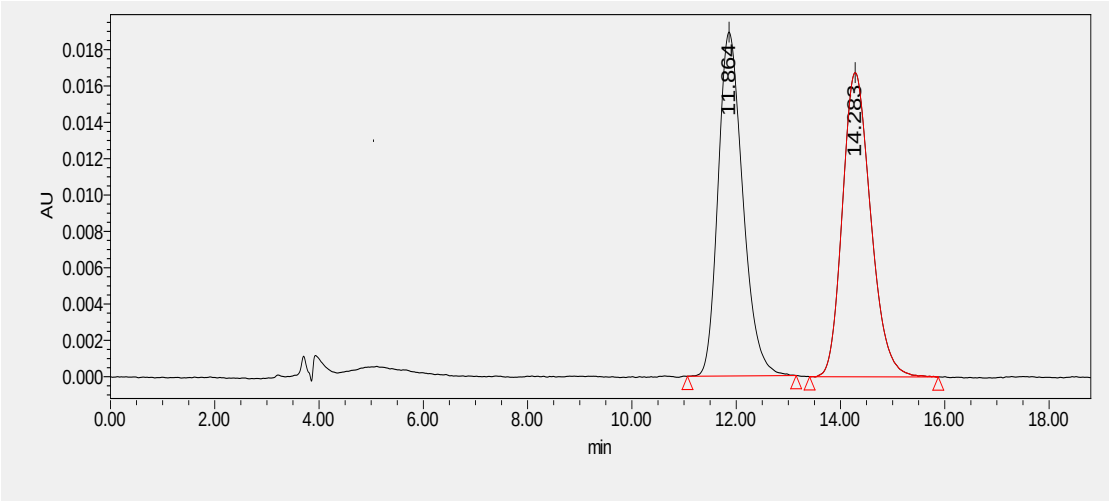


Entry	Retention time	Area	Area (%)	Height	Int type
1	11.357	9604691	97.50	329543	bb
2	13.470	246474	2.50	8033	bb

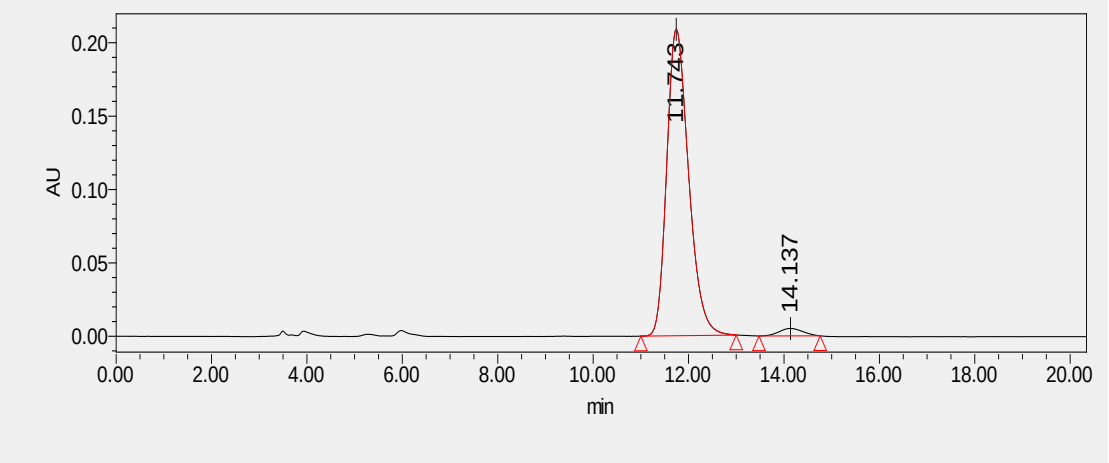


3r

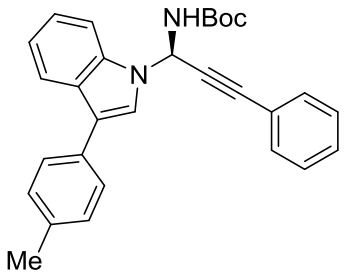
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	11.864	622508	49.68	18923	bb
2	14.283	630644	50.32	16736	bb

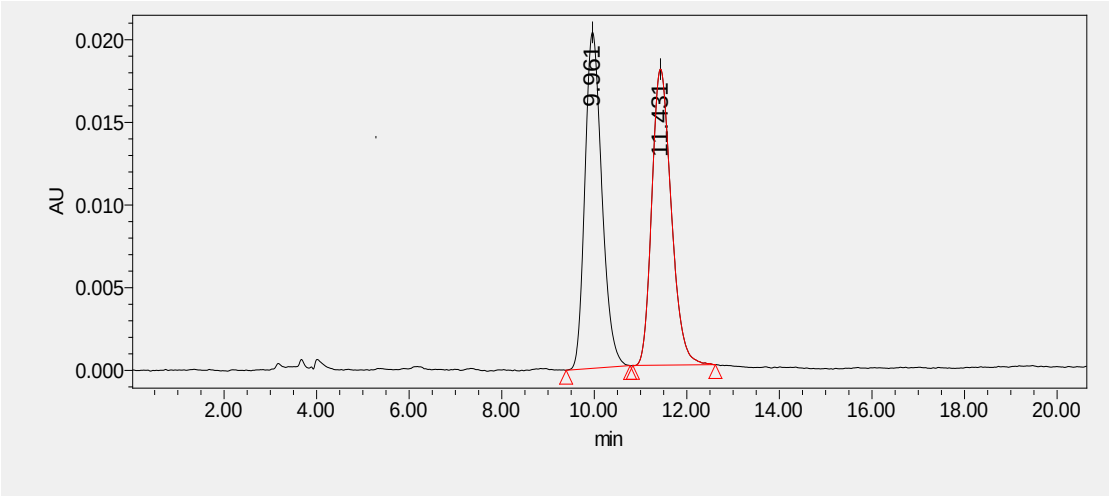


Entry	Retention time	Area	Area (%)	Height	Int type
1	11.743	6644805	97.45	208776	bb
2	14.137	174014	2.55	5064	bb

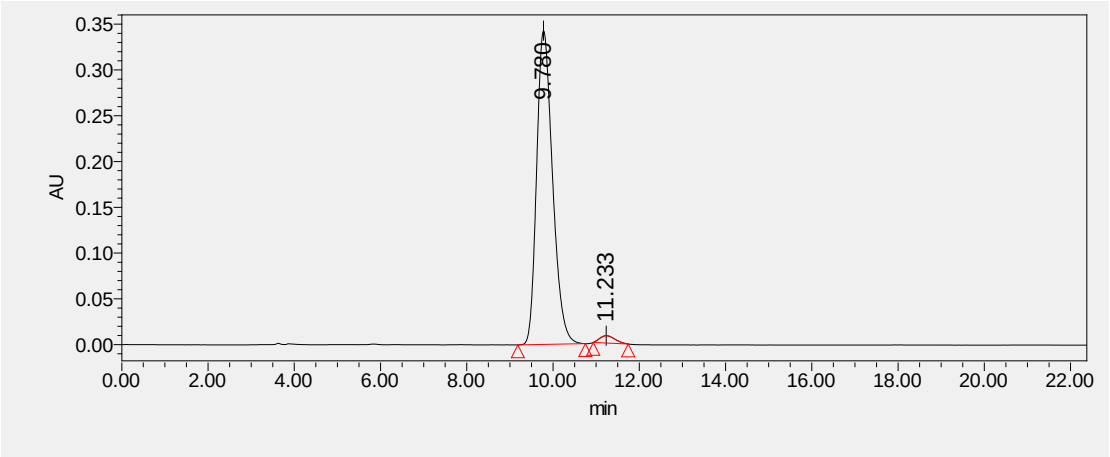


3s

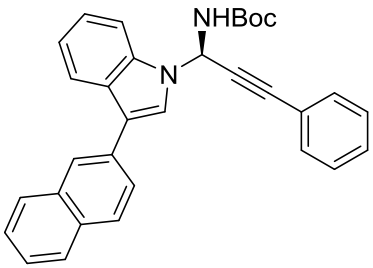
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	9.961	516253	49.73	20329	bb
2	11.431	521766	50.27	17911	bb

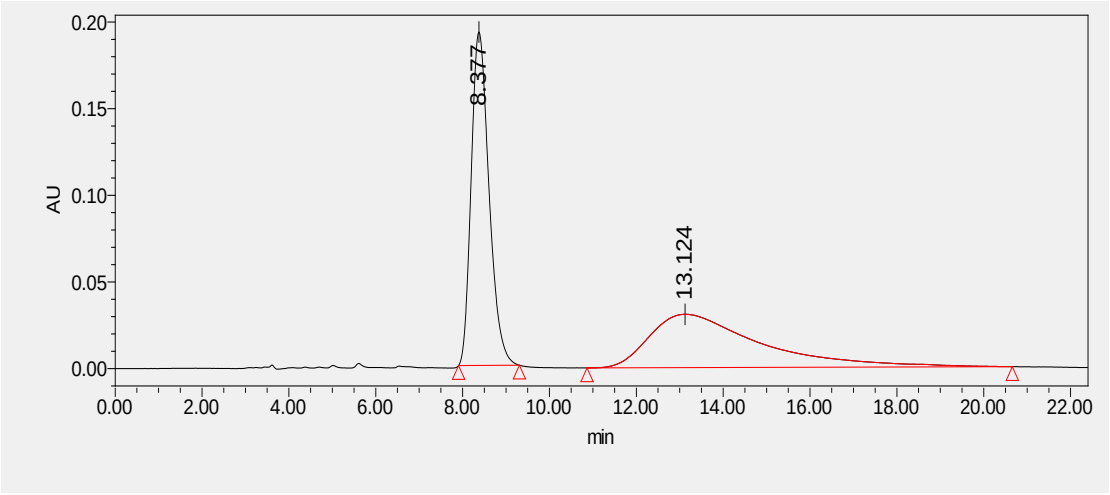


Entry	Retention time	Area	Area (%)	Height	Int type
1	9.780	8780519	97.83	342709	bb
2	11.233	195115	2.17	8008	bb

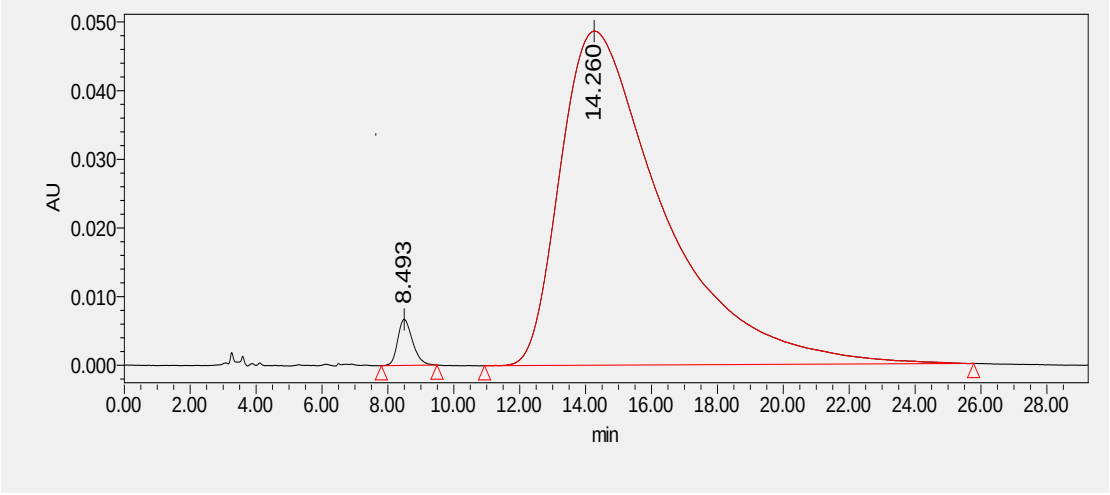


3t

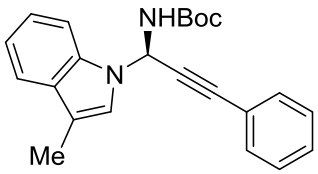
HPLC using an AS-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	8.377	5486304	50.34	192318	bb
2	13.124	5411314	49.66	30776	bb

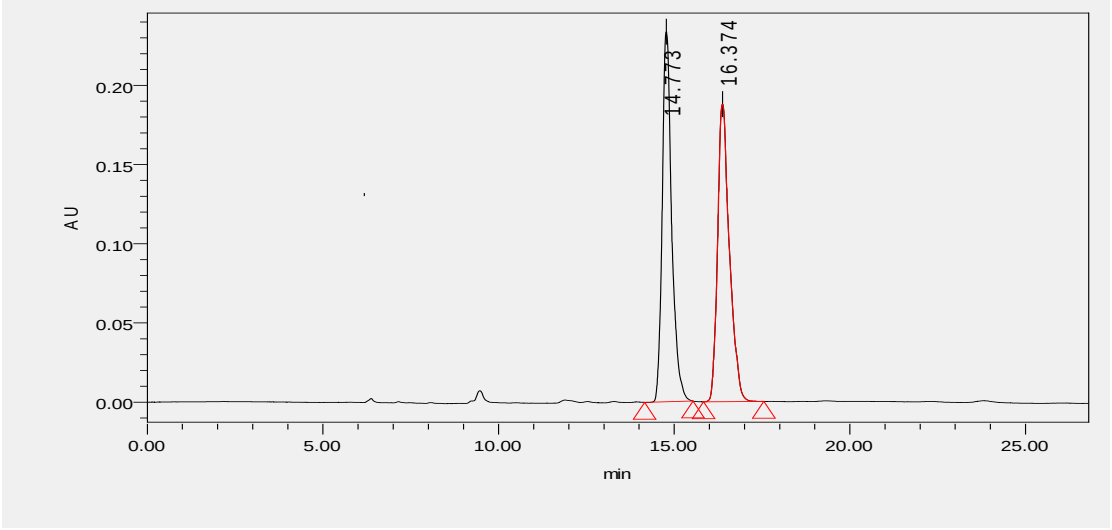


Entry	Retention time	Area	Area (%)	Height	Int type
1	8.493	209274	1.93	6703	bb
2	14.260	10625770	98.07	48655	bb

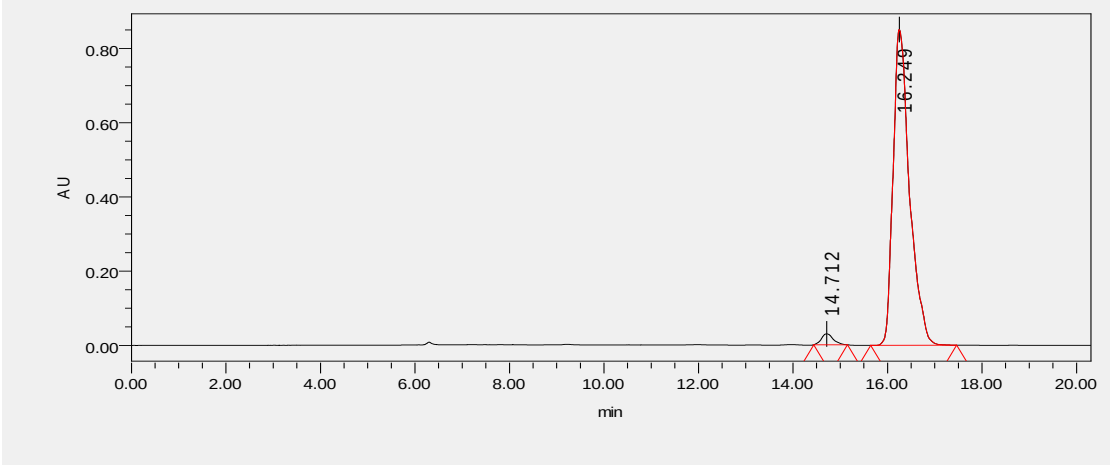


3u

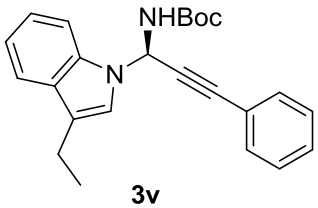
HPLC using an IA-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	14.773	4392002	49.86	233604	bb
2	16.374	4416433	50.14	187905	bb

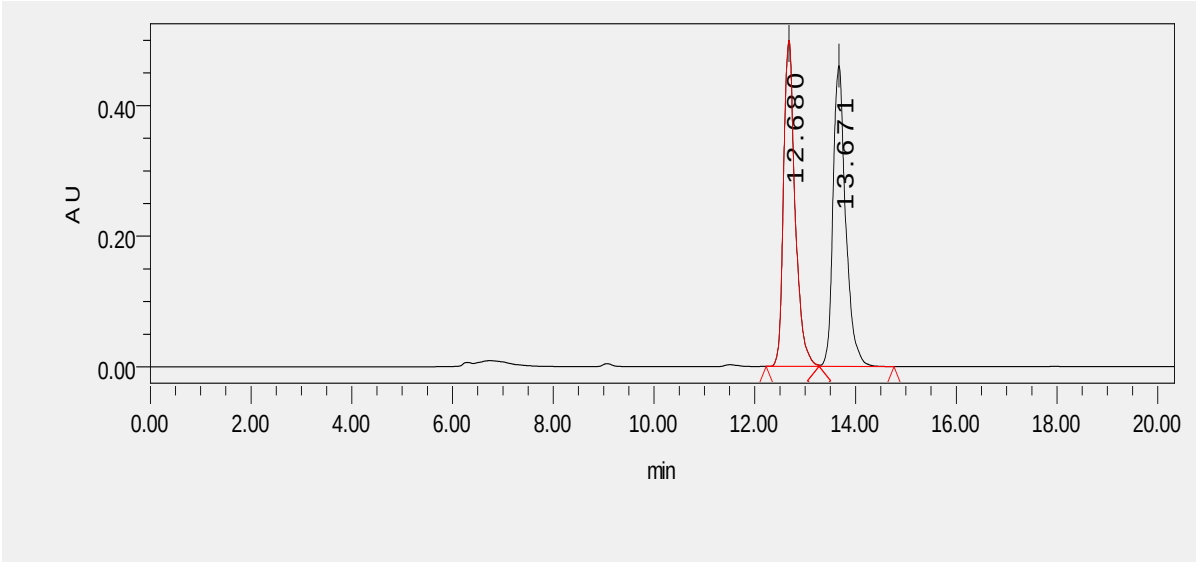


Entry	Retention time	Area	Area (%)	Height	Int type
1	14.712	517940	2.45	29476	bb
2	16.249	20613129	97.55	850456	bb

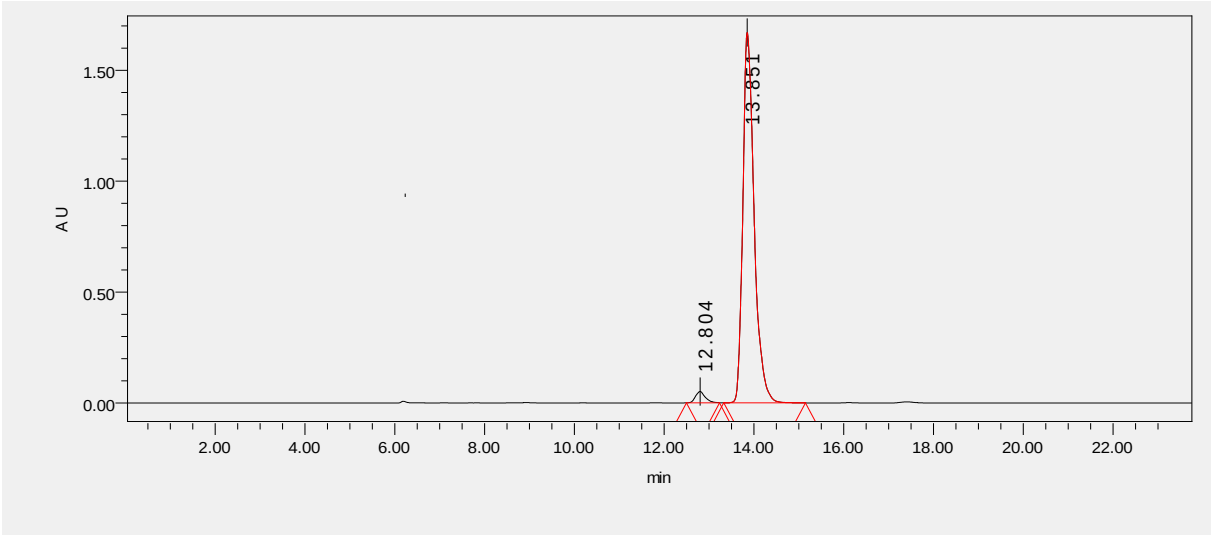


3v

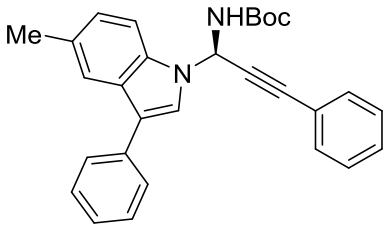
HPLC using an IA-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	12.680	7983446	49.88	499224	bv
2	13.671	8021235	50.12	460451	vb

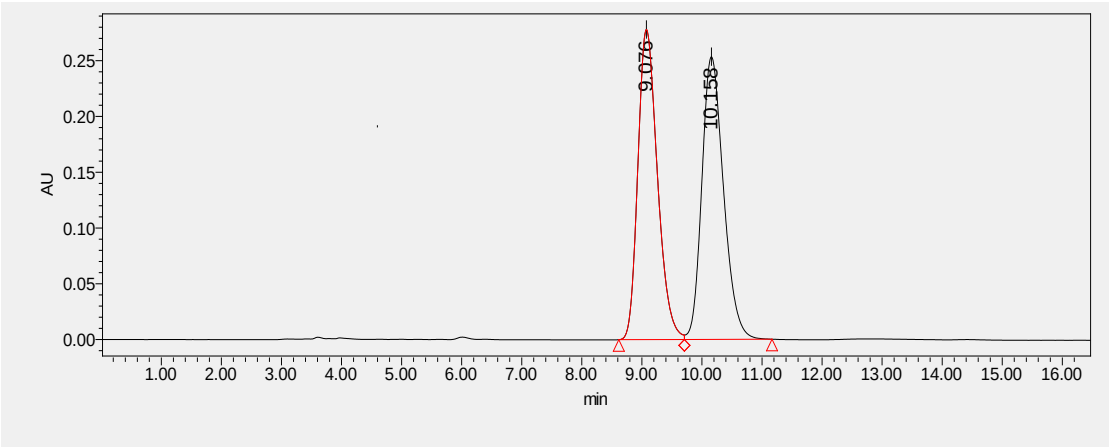


Entry	Retention time	Area	Area (%)	Height	Int type
1	12.804	764614	2.54	51186	bb
2	13.851	29297079	97.46	1669677	bb

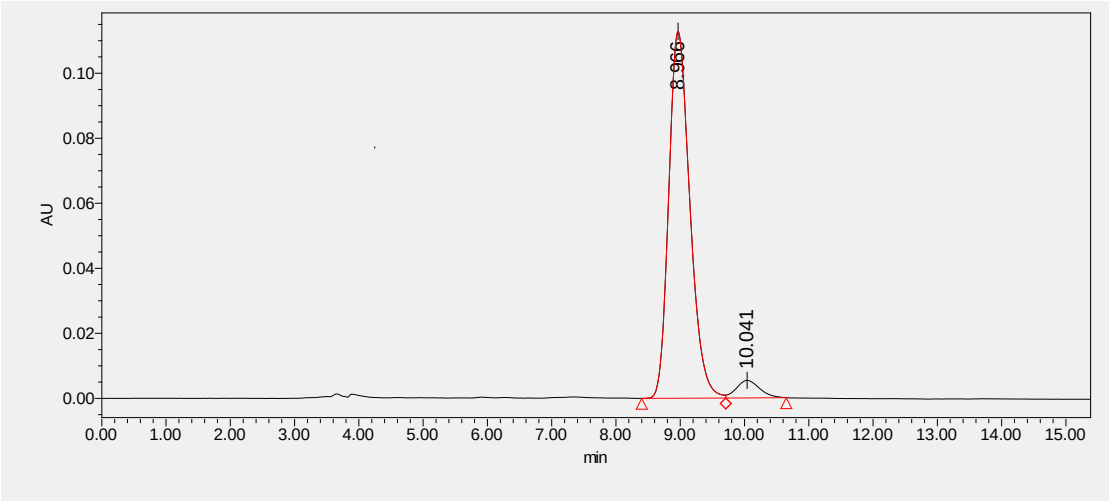


3w

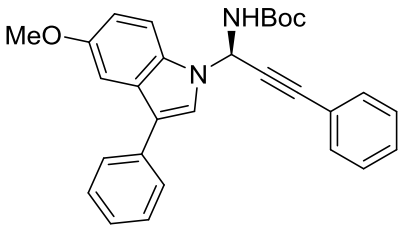
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	9.076	6288615	49.75	278043	bv
2	10.158	6352333	50.25	253426	vb

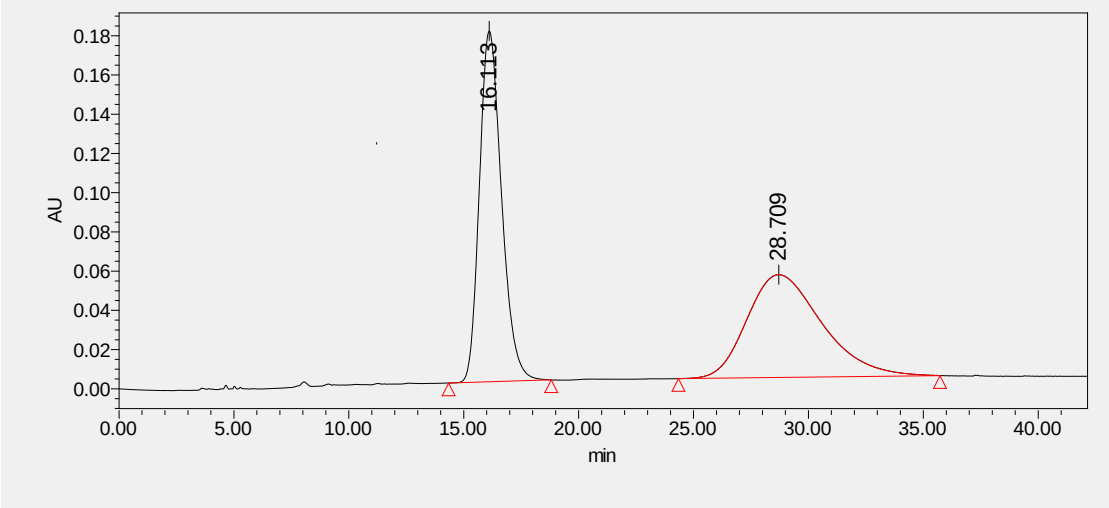


Entry	Retention time	Area	Area (%)	Height	Int type
1	8.966	2578621	95.00	112824	bv
2	10.041	135614	5.00	5403	vb

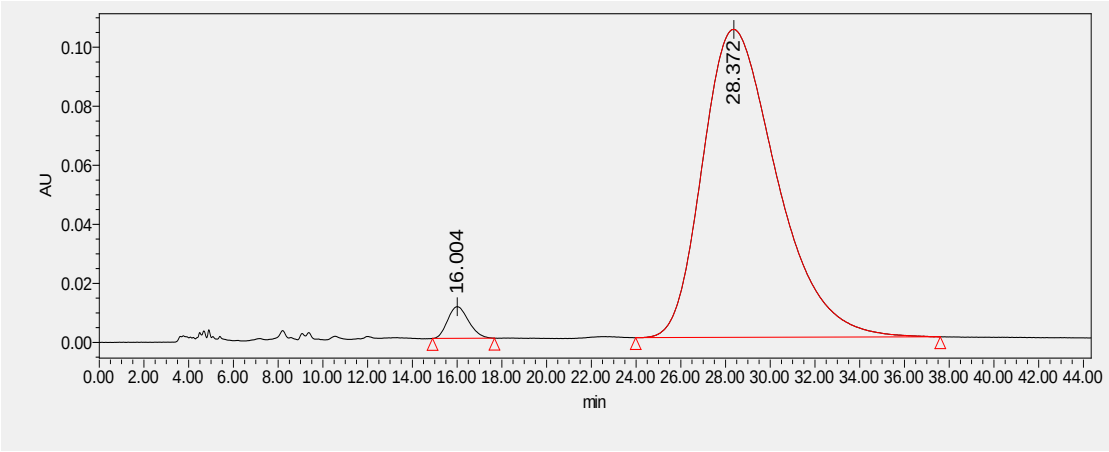


3x

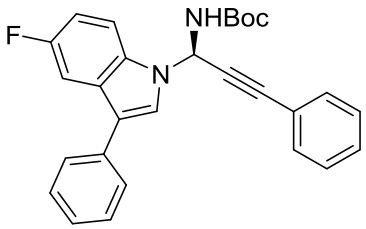
HPLC using an AS-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	16.113	11974779	50.26	178855	bb
2	28.709	11850416	49.74	52410	bb

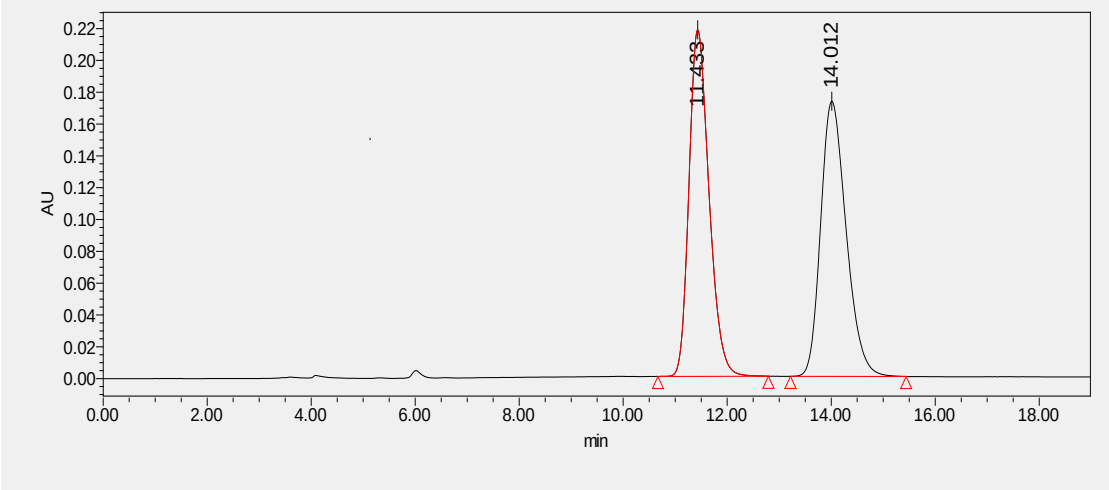


Entry	Retention time	Area	Area (%)	Height	Int type
1	16.004	696562	2.81	10718	bb
2	28.372	24049917	97.19	104296	bb

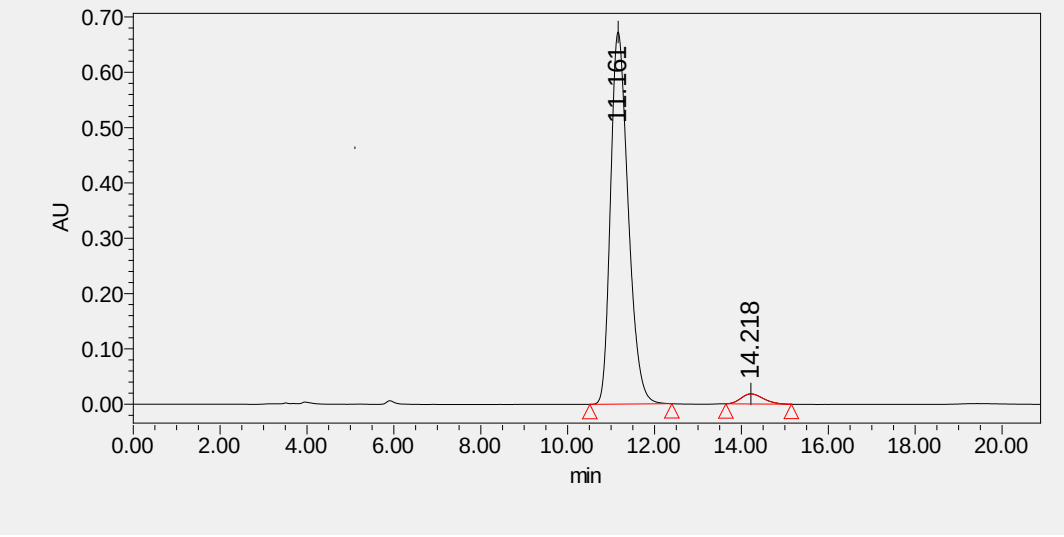


3y

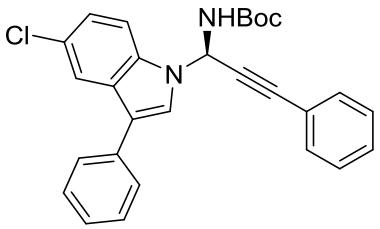
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	11.433	5827844	49.78	217810	bb
2	14.012	5879518	50.22	172969	bb

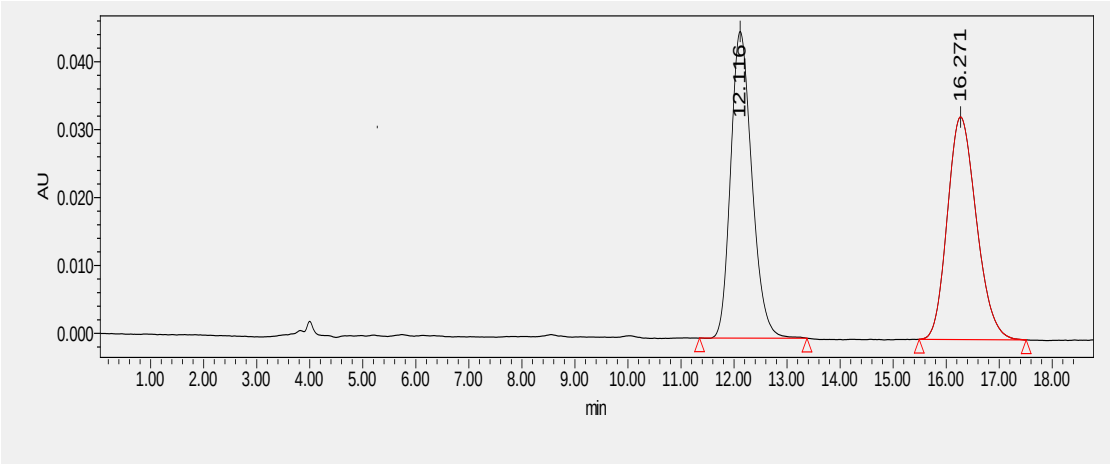


Entry	Retention time	Area	Area (%)	Height	Int type
1	11.161	18994294	97.26	672652	bb
2	14.218	535319	2.74	16774	bb

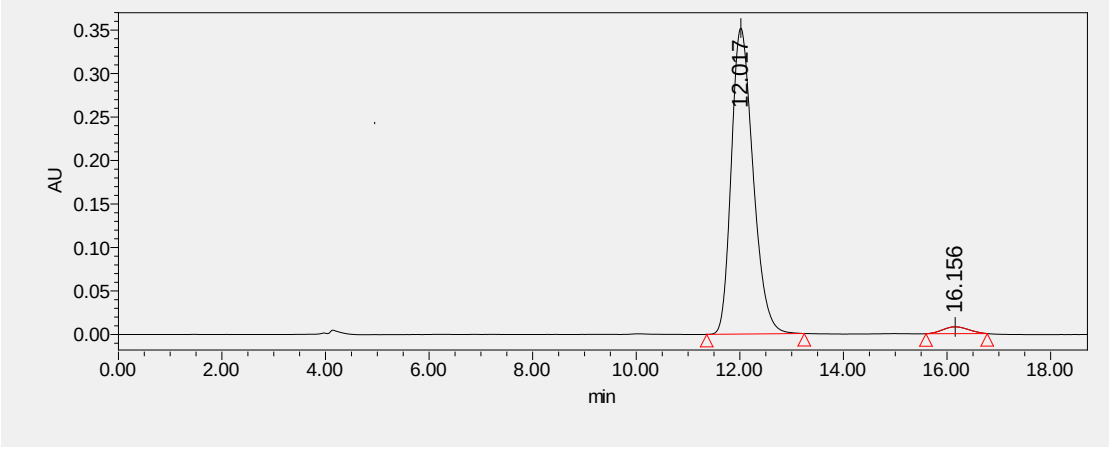


3z

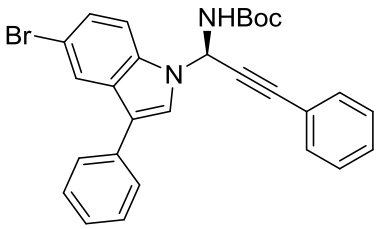
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	12.116	1256497	50.18	45142	bb
2	16.271	1247285	49.82	32780	bb

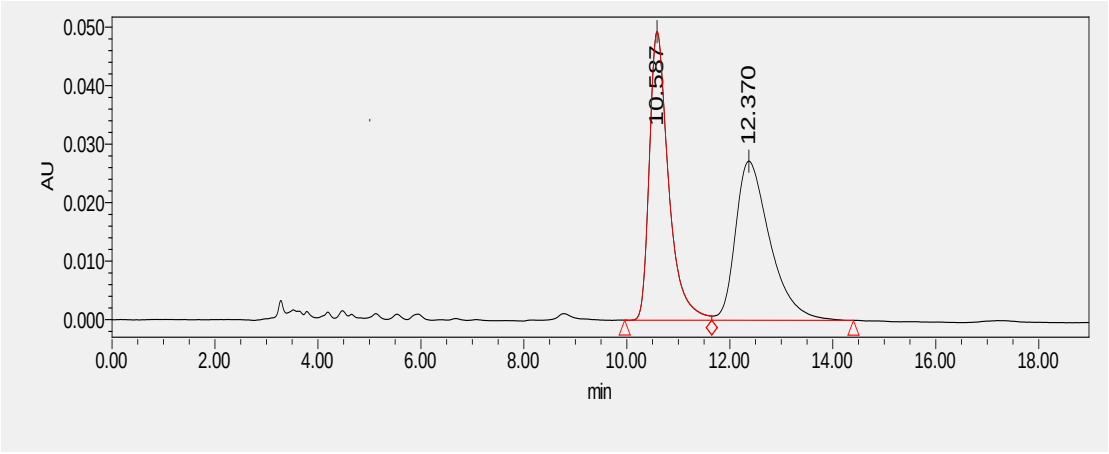


Entry	Retention time	Area	Area (%)	Height	Int type
1	12.017	10246763	97.41	351763	bb
2	16.156	272390	2.59	7852	bb

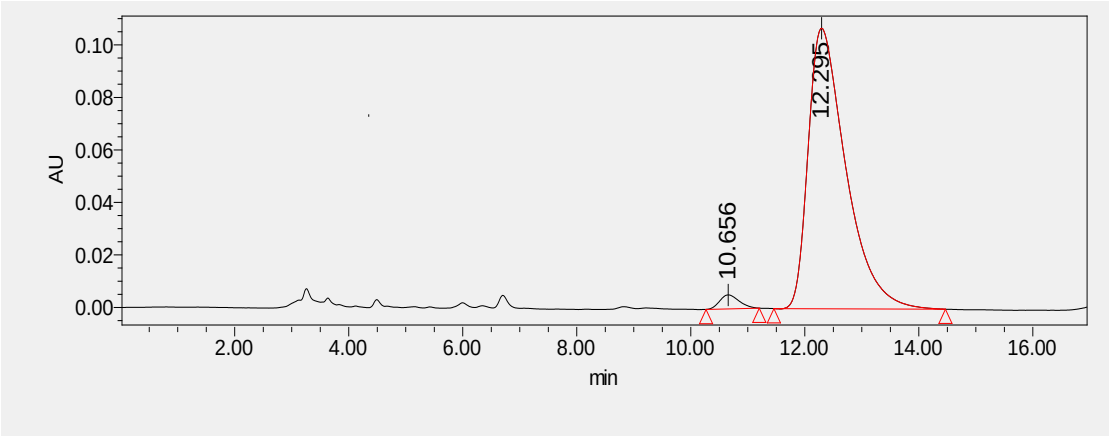


3aa

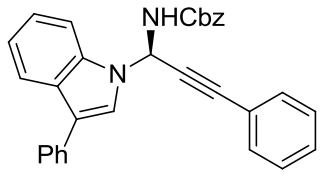
HPLC using an IA-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	10.587	1278277	50.33	49334	bv
2	12.370	1261760	49.67	27200	vb

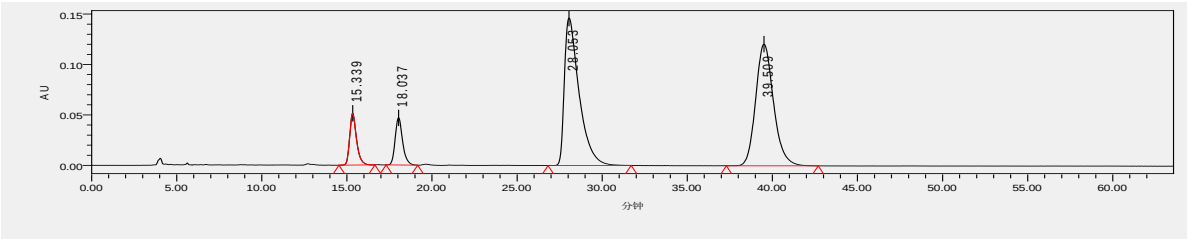


Entry	Retention time	Area	Area (%)	Height	Int type
1	10.656	126953	2.52	5338	bb
2	12.295	4915760	97.48	106853	bb

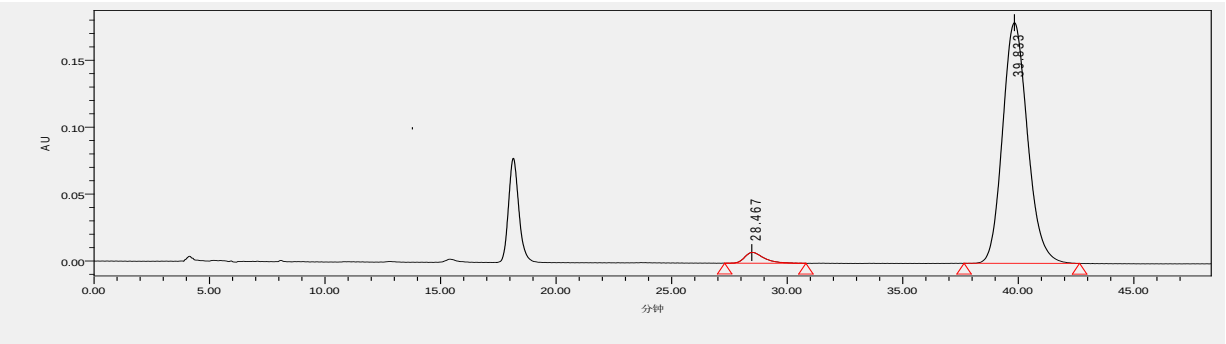


3ab

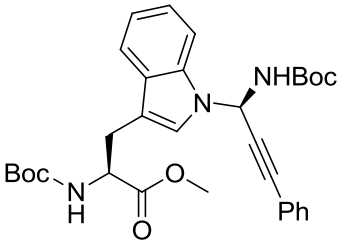
HPLC using an IA-H column, hexane / EtOH = 10/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	15.339	1429882	6.99	51386	bb
2	18.037	1428186	6.98	46860	bb
3	28.053	8786456	42.96	146238	bb
4	39.509	8806337	43.06	120609	bb

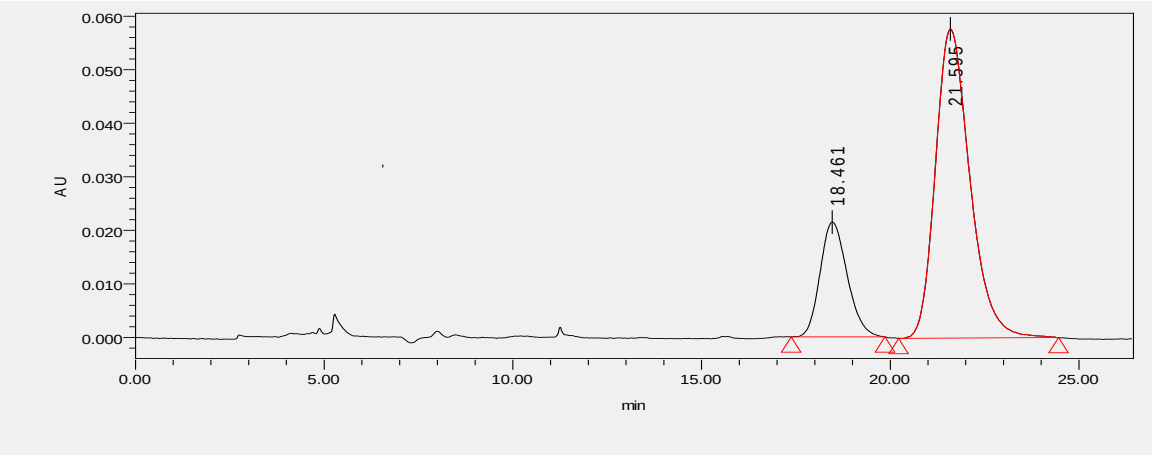


Entry	Retention time	Area	Area (%)	Height	Int type
1	28.467	467310	3.35	8043	bb
2	39.833	13490155	96.65	179827	bb

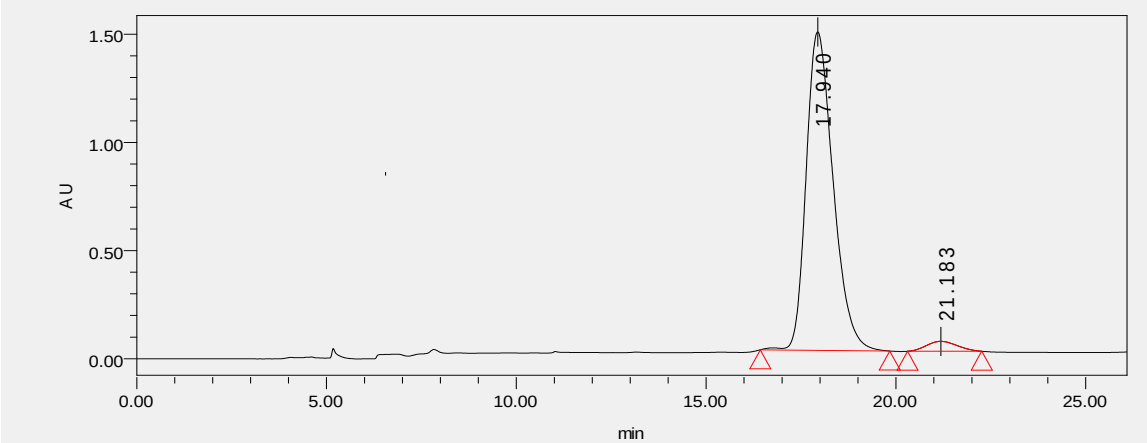


6a

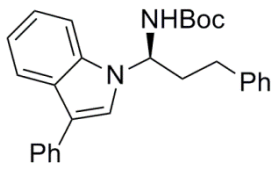
HPLC using an OD-H column, hexane / EtOH = 100/2, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	18.461	1072130	22.63	21452	bb
2	21.595	3665534	77.37	57725	bb

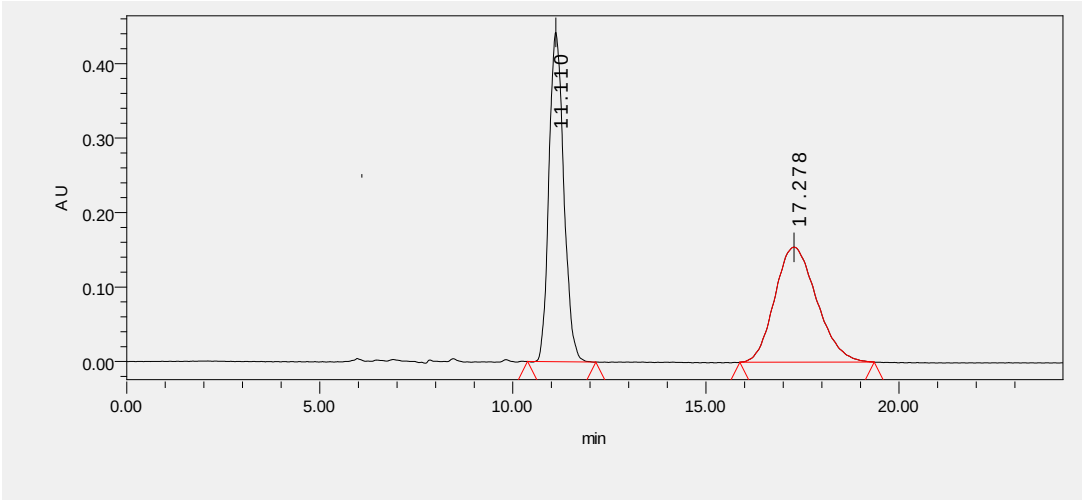


Entry	Retention time	Area	Area (%)	Height	Int type
1	17.940	72791195	96.58	1471826	bb
2	21.183	2579181	3.42	45964	bb

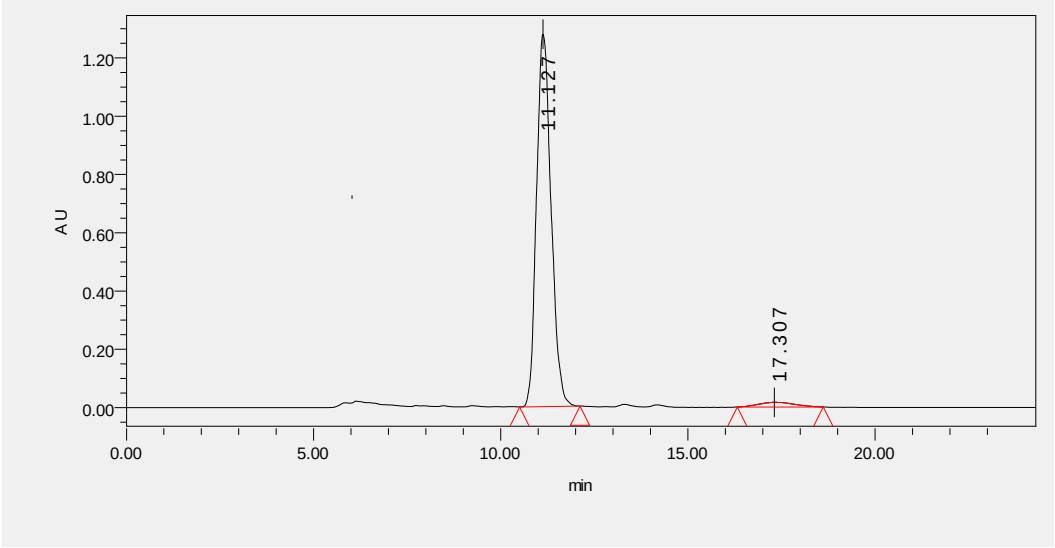


7

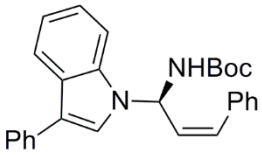
HPLC using an AS-H column, hexane / EtOH = 9/1, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	11.110	11784263	50.30	442201	bb
2	17.278	11645202	49.70	154447	bb

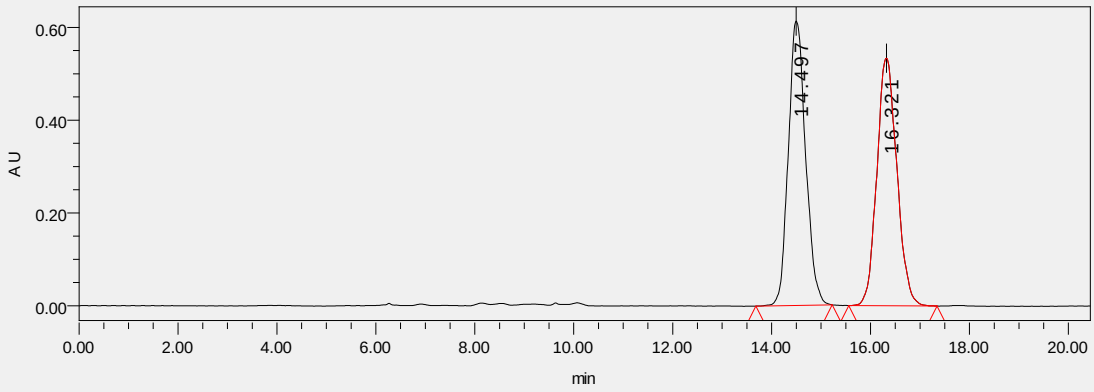


Entry	Retention time	Area	Area (%)	Height	Int type
1	11.127	34616617	96.95	1278072	bb
2	17.307	1090193	3.05	16173	bb

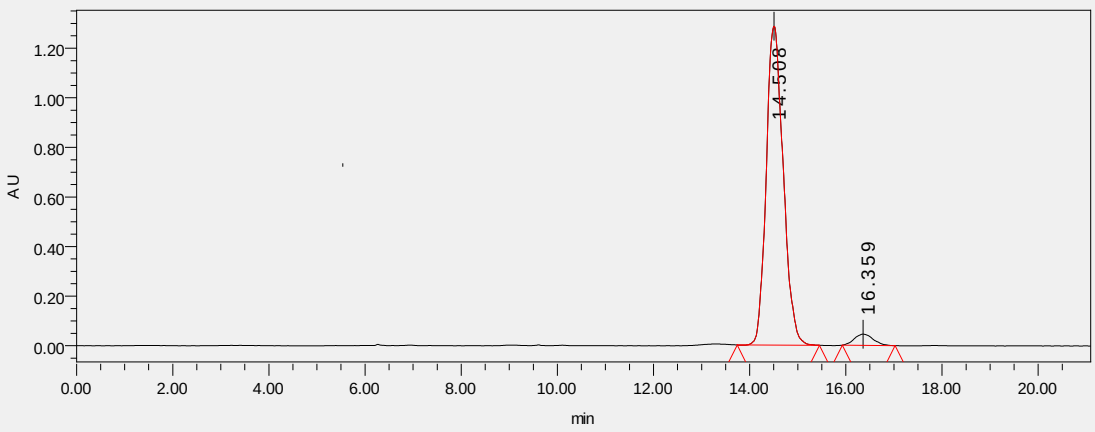


8

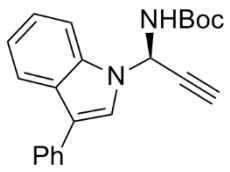
HPLC using an OD-H column, hexane / EtOH = 95/5, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	14.497	14883316	49.80	613011	bb
2	16.321	15002214	50.20	533644	bb

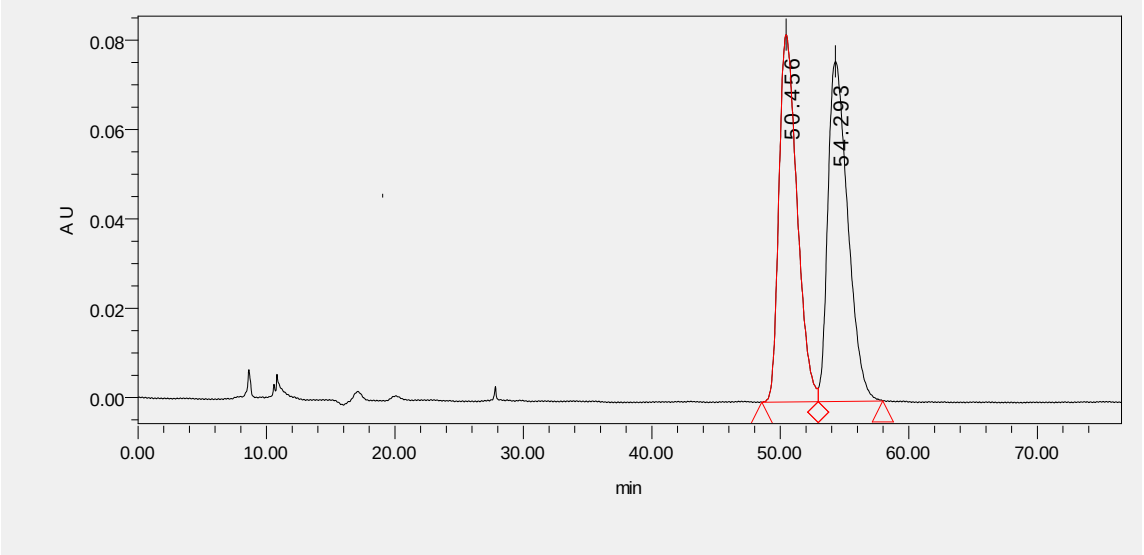


Entry	Retention time	Area	Area (%)	Height	Int type
1	14.508	31643761	96.23	1285942	bb
2	16.359	1240735	3.77	45330	bb

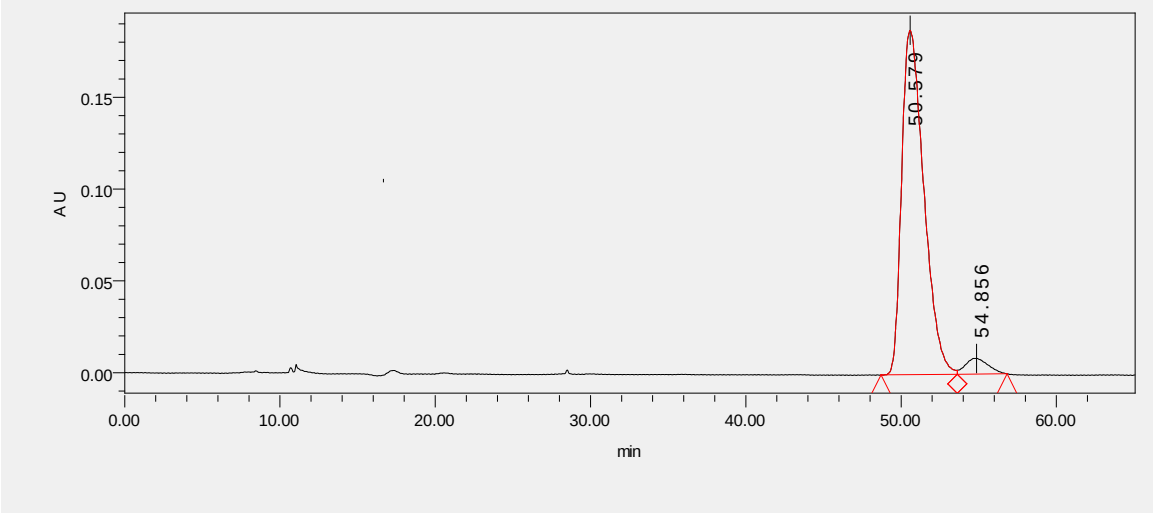


9

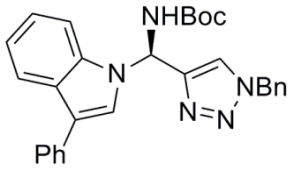
HPLC using an OD-H column, hexane / EtOH = 100/1, flow rate = 0.8 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	50.456	8096477	49.58	82236	bv
2	54.293	8233199	50.42	76141	vb

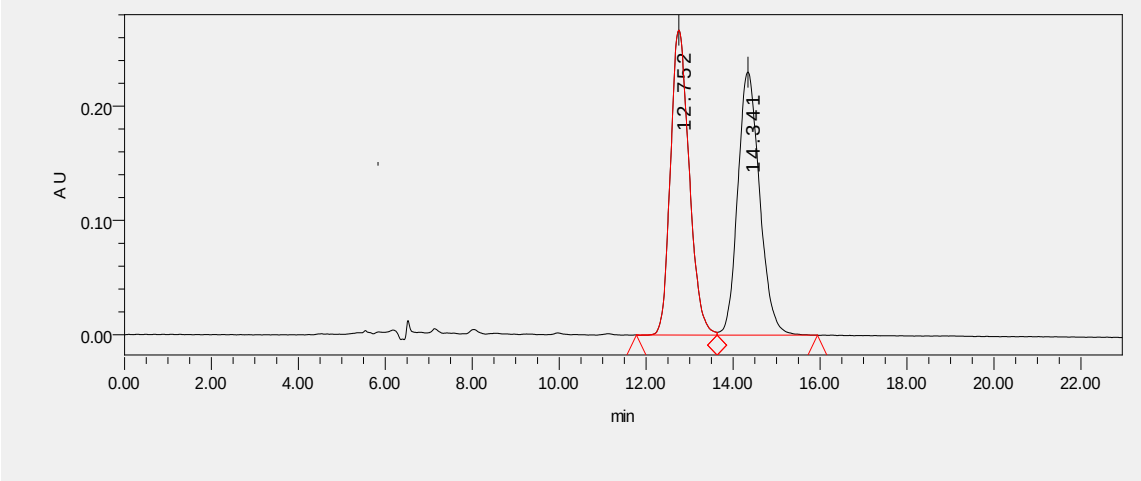


Entry	Retention time	Area	Area (%)	Height	Int type
1	50.579	18600664	95.52	187507	bv
2	54.856	873165	4.48	8543	vb

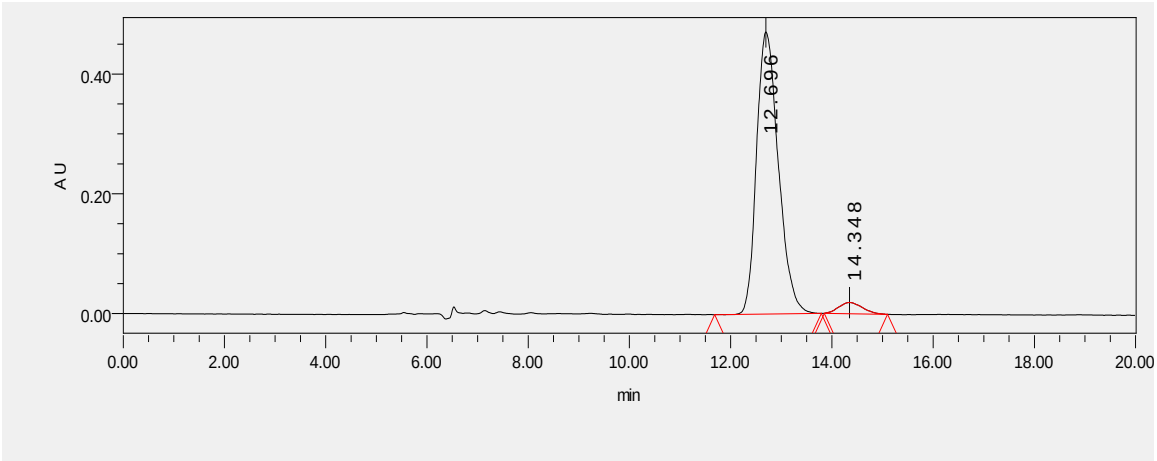


10

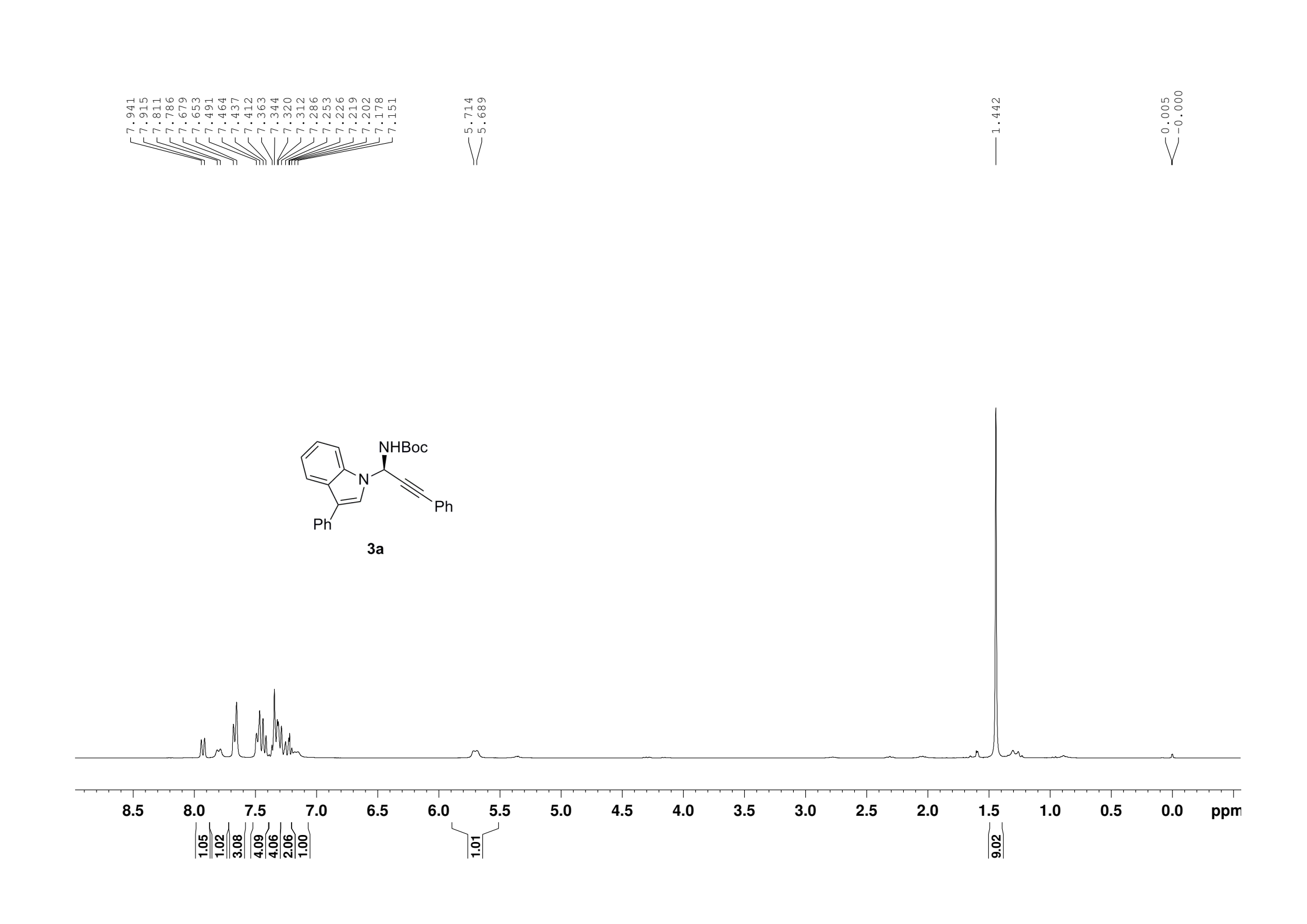
HPLC using an OD-H column, hexane / EtOH = 7/3, flow rate = 1.0 mL/min



Entry	Retention time	Area	Area (%)	Height	Int type
1	12.752	8009103	49.83	266856	bv
2	14.341	8063450	50.17	230134	vb



Entry	Retention time	Area	Area (%)	Height	Int type
1	12.696	14101688	95.90	471182	bb
2	14.348	603252	4.10	18695	bb


7.941
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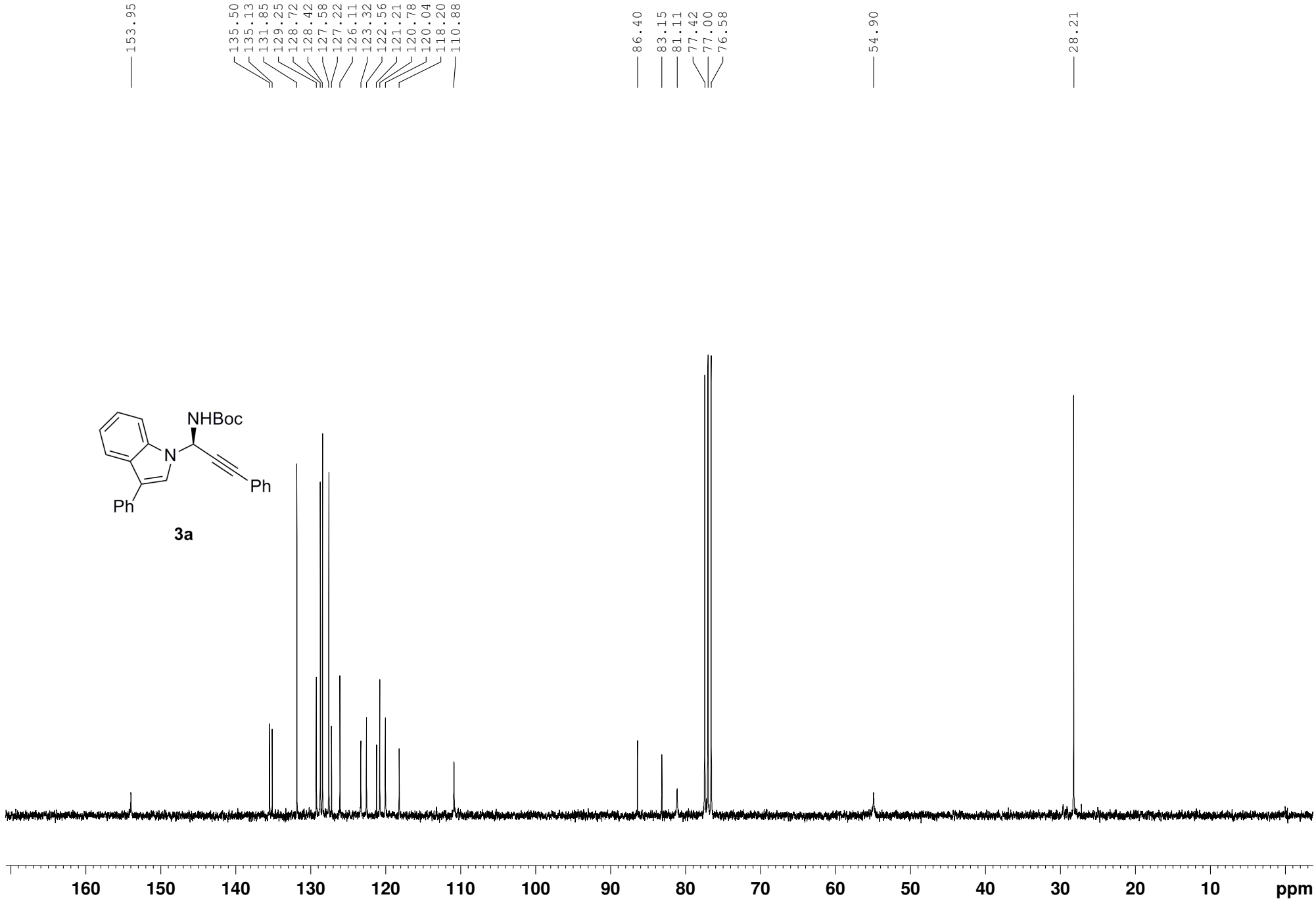
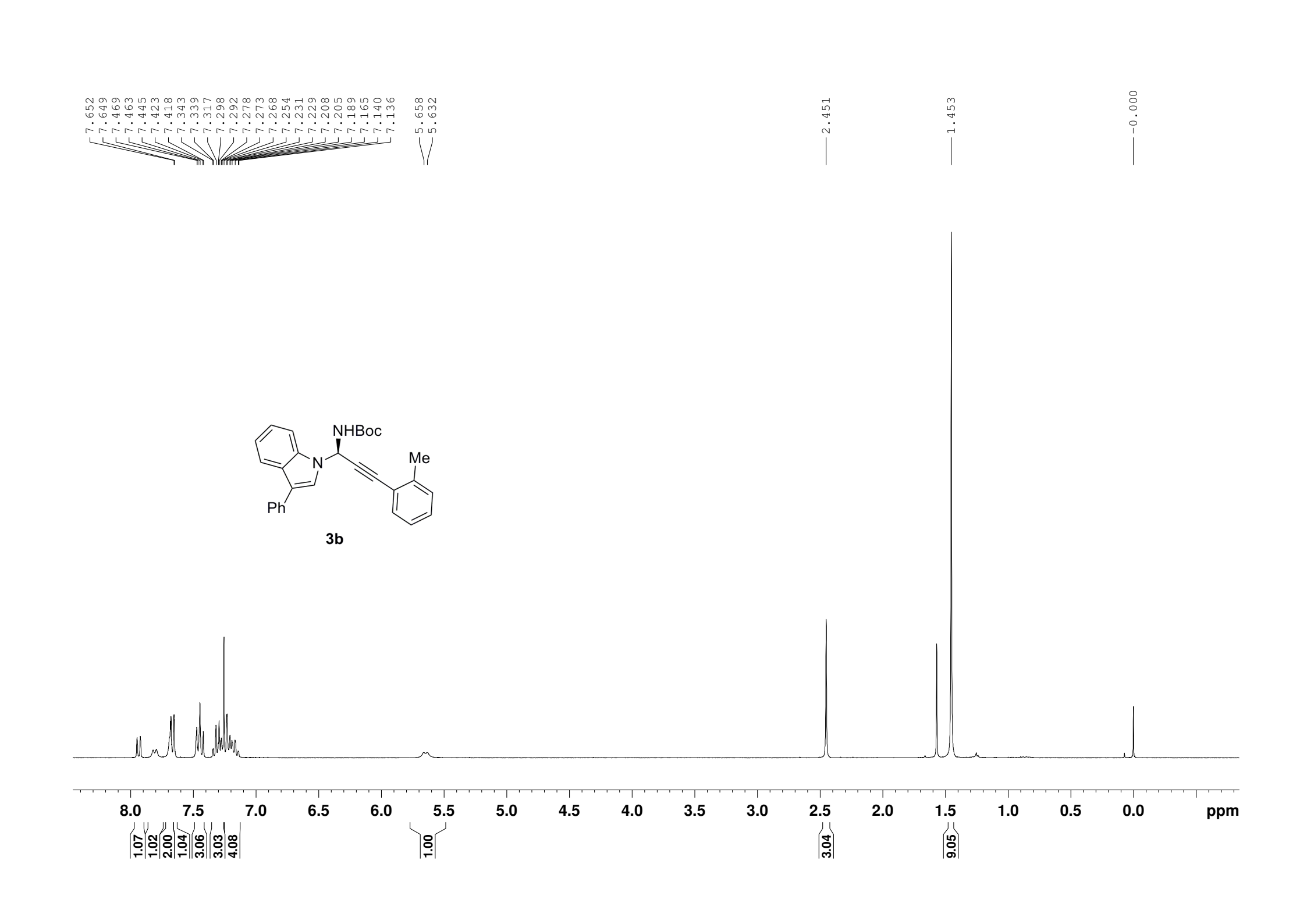
7.811
7.786
7.679
7.653
7.491
7.464
7.437
7.412
7.363
7.344
7.320
7.312
7.286
7.253
7.226
7.219
7.202
7.178
7.151
5.714
5.689
1.442
0.005
-0.000
NHBoc
N
Ph
Ph
3a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.05
1.02
3.08
4.09
4.06
2.06
1.00
1.01
9.02


153.95
135.50
135.13
131.85
129.25
128.72
128.42
127.58
127.22
126.11
123.32
122.56
121.21
120.78
120.04
118.20
110.88
86.40
83.15
81.11
77.42
77.00
76.58
54.90
28.21
NHBoc
N
Ph
Ph
3a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.469
7.463
7.445
7.423
7.418
7.343
7.339
7.317
7.298
7.292
7.278
7.273
7.268
7.254
7.231
7.229
7.208
7.205
7.189
7.165
7.140
7.136
5.658
5.632
2.451
1.453
0.000
NHBoc
N
Me
Ph
3b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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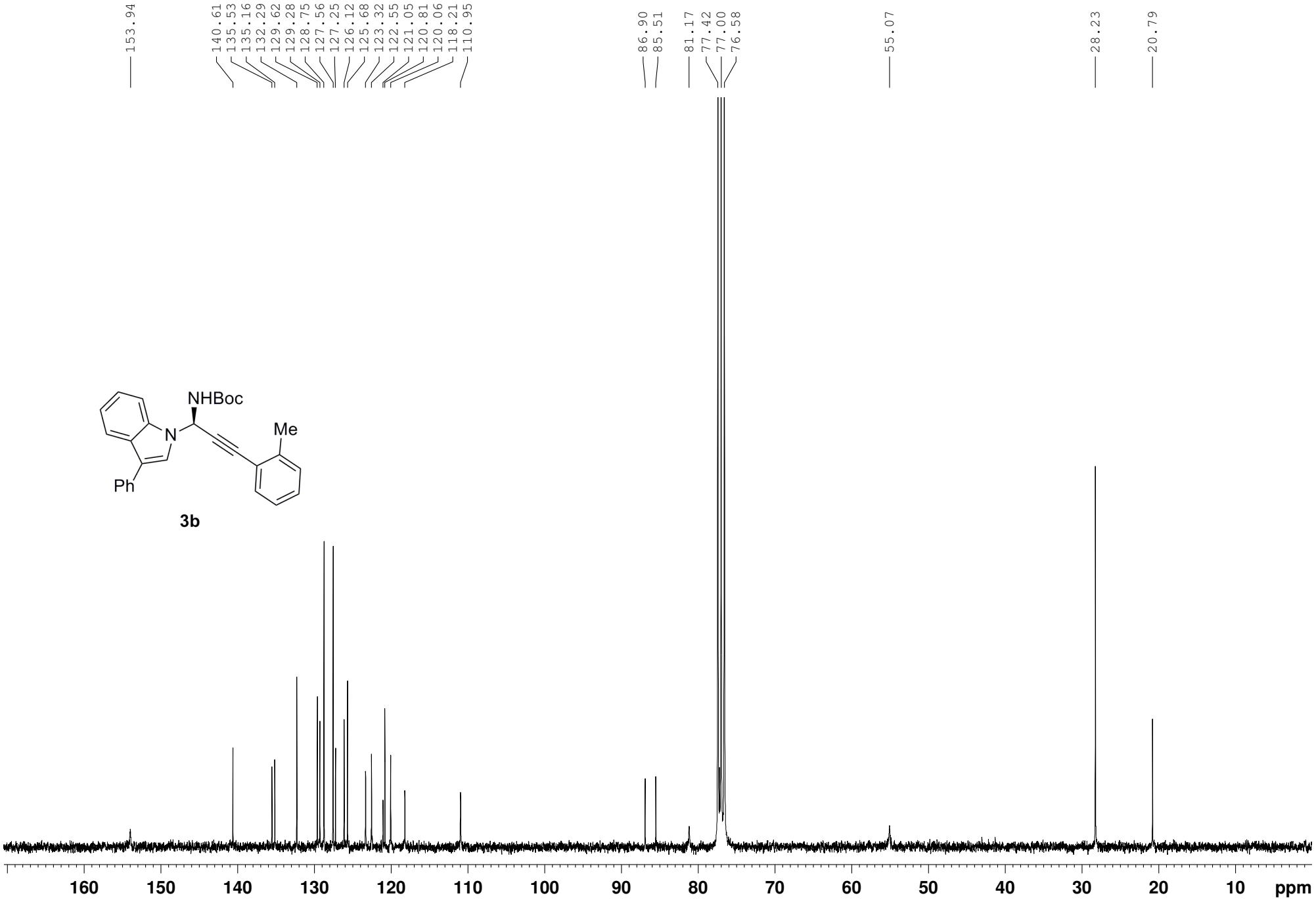
1.07
1.02
2.00
1.04
3.06
3.03
4.08
1.00
3.04
9.05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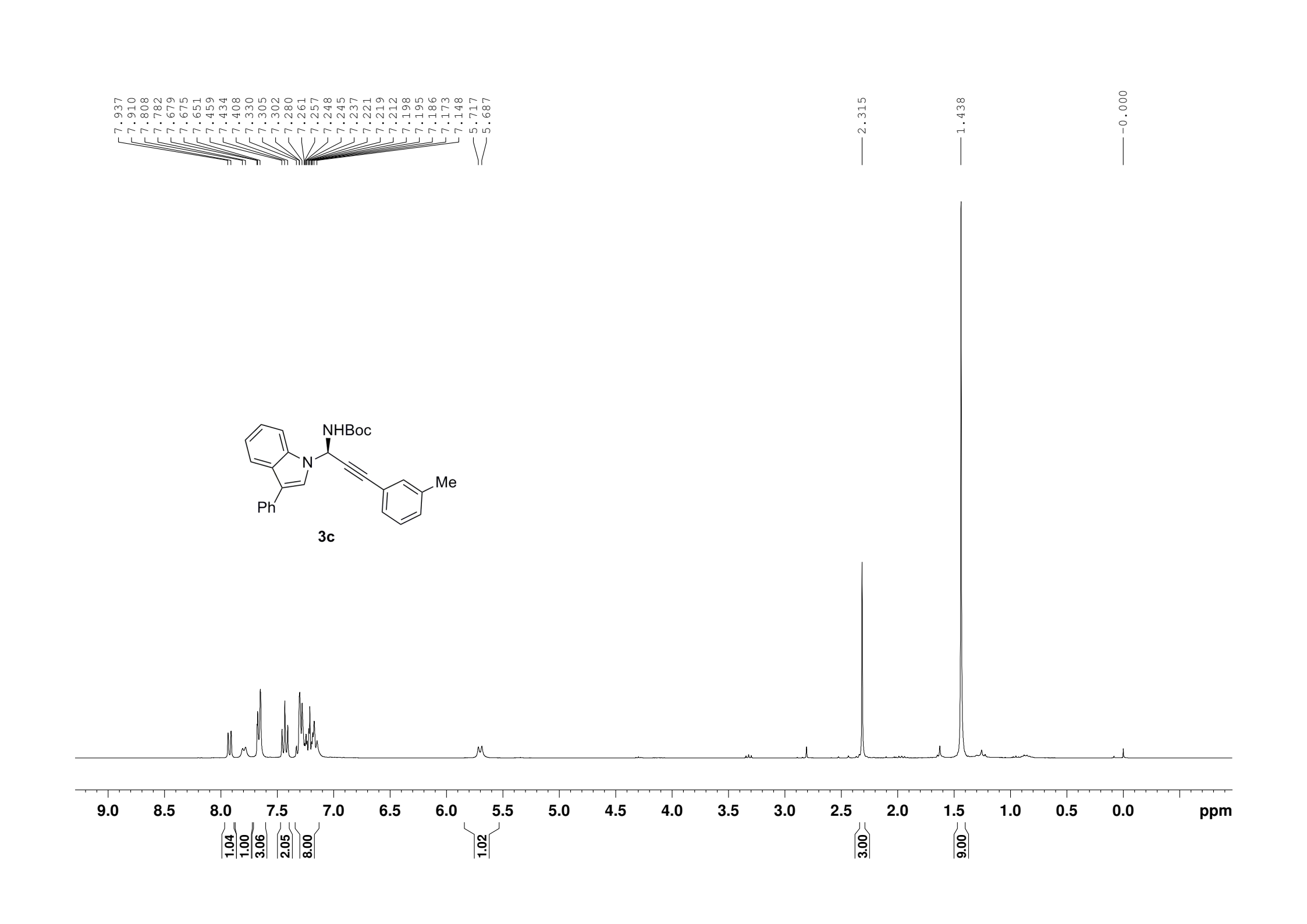
135.53
135.16
132.29
129.62
129.28
128.75
127.56
127.25
126.12
125.68
123.32
122.55
121.05
120.81
120.06
118.21
110.95
86.90
85.51
81.17
77.42
77.00
76.58
55.07
28.23
20.79
NHBoc
N
Me
Ph
3b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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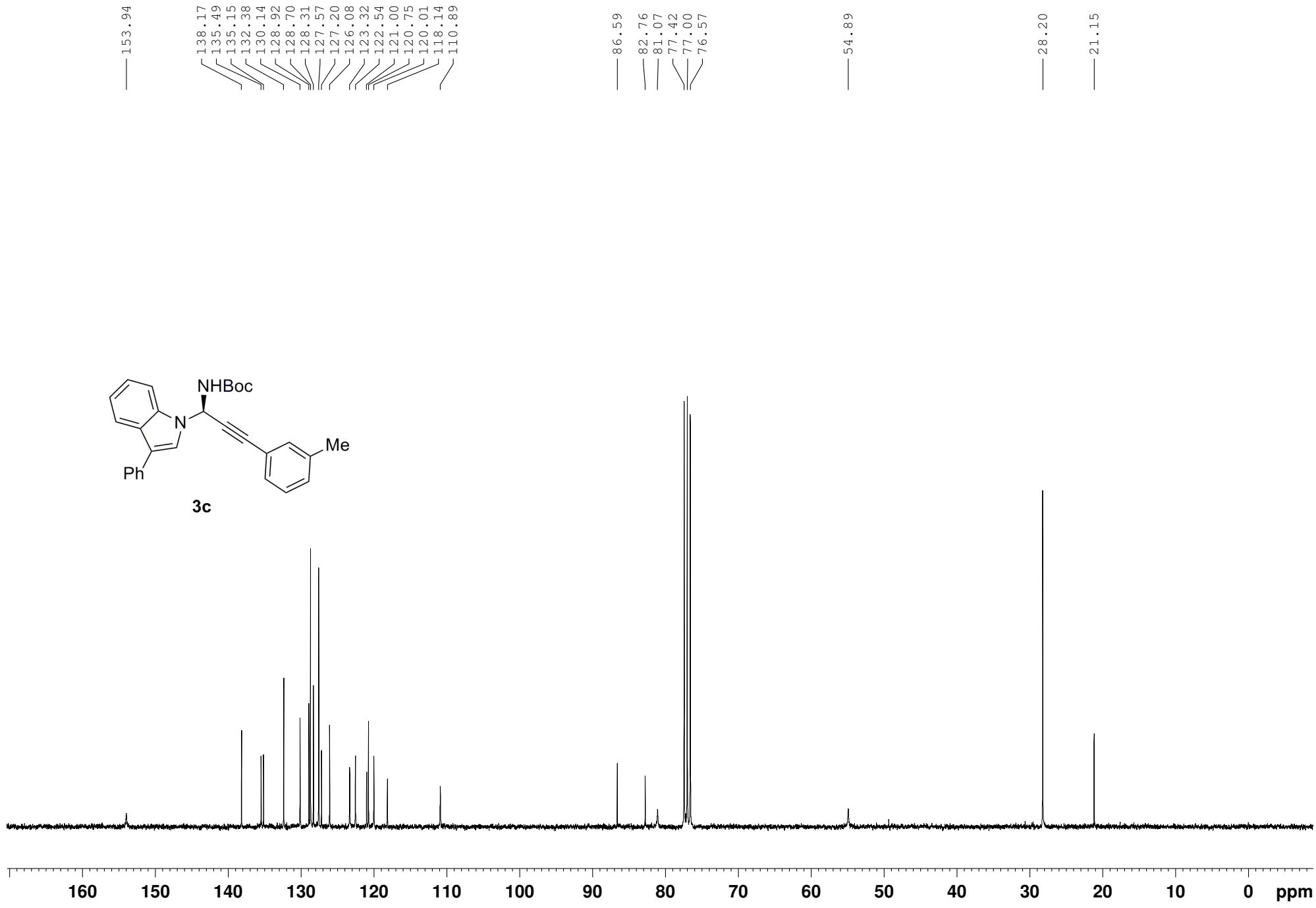
7.808
7.782
7.679
7.675
7.651
7.459
7.434
7.408
7.330
7.305
7.302
7.280
7.261
7.257
7.248
7.245
7.237
7.221
7.219
7.212
7.198
7.195
7.186
7.173
7.148
5.717
5.687
2.315
1.438
0.000
NHBoc
N
Me
Ph
3c
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.04
1.00
3.06
2.05
8.00
1.02
3.00
9.00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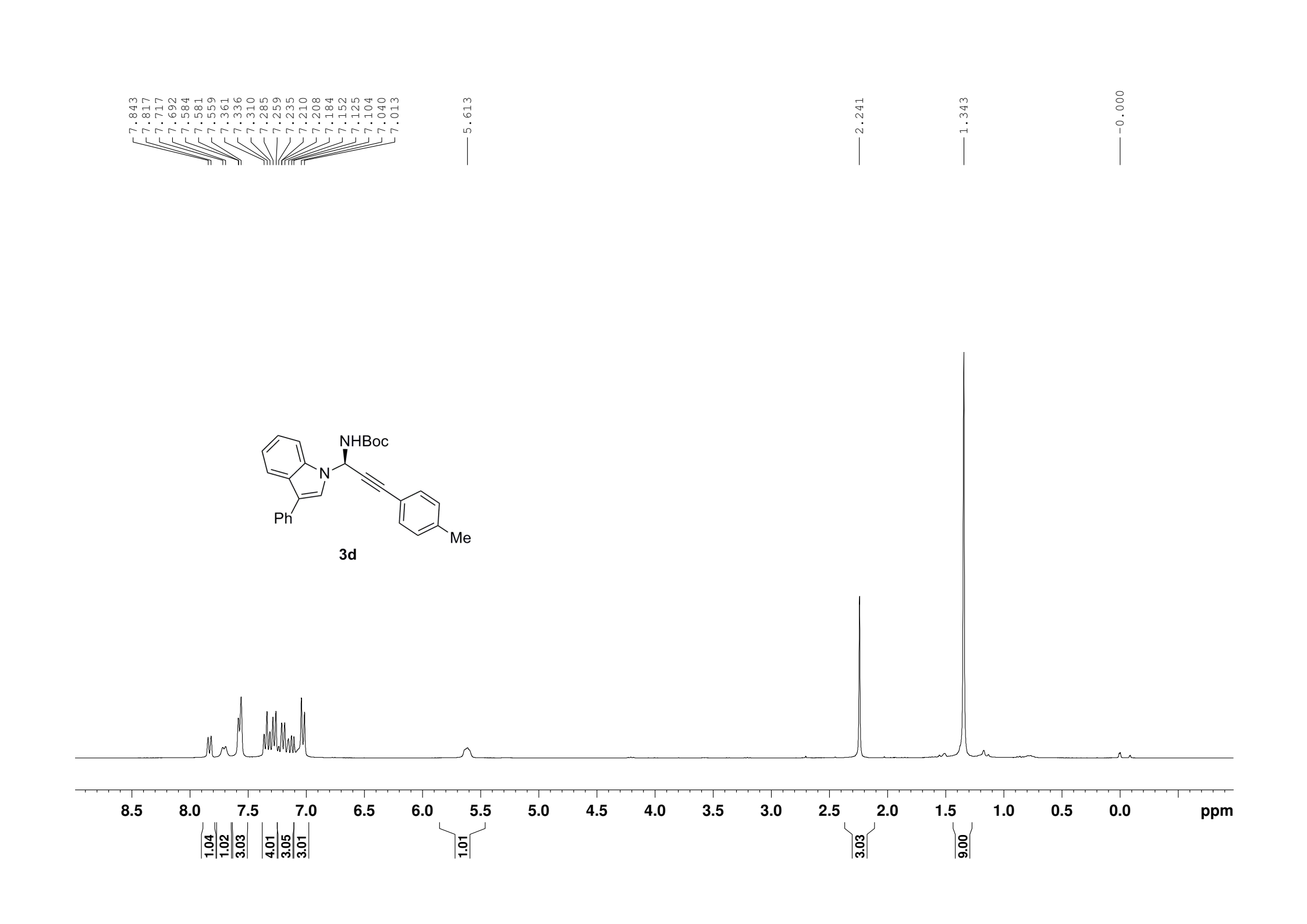
135.49
135.15
132.38
130.14
128.92
128.70
128.31
127.57
127.20
126.08
123.32
122.54
121.00
120.75
120.01
118.14
110.89
86.59
82.76
81.07
77.42
77.00
76.57
54.89
28.20
21.15
NHBoc
N
Me
Ph
3c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.717
7.692
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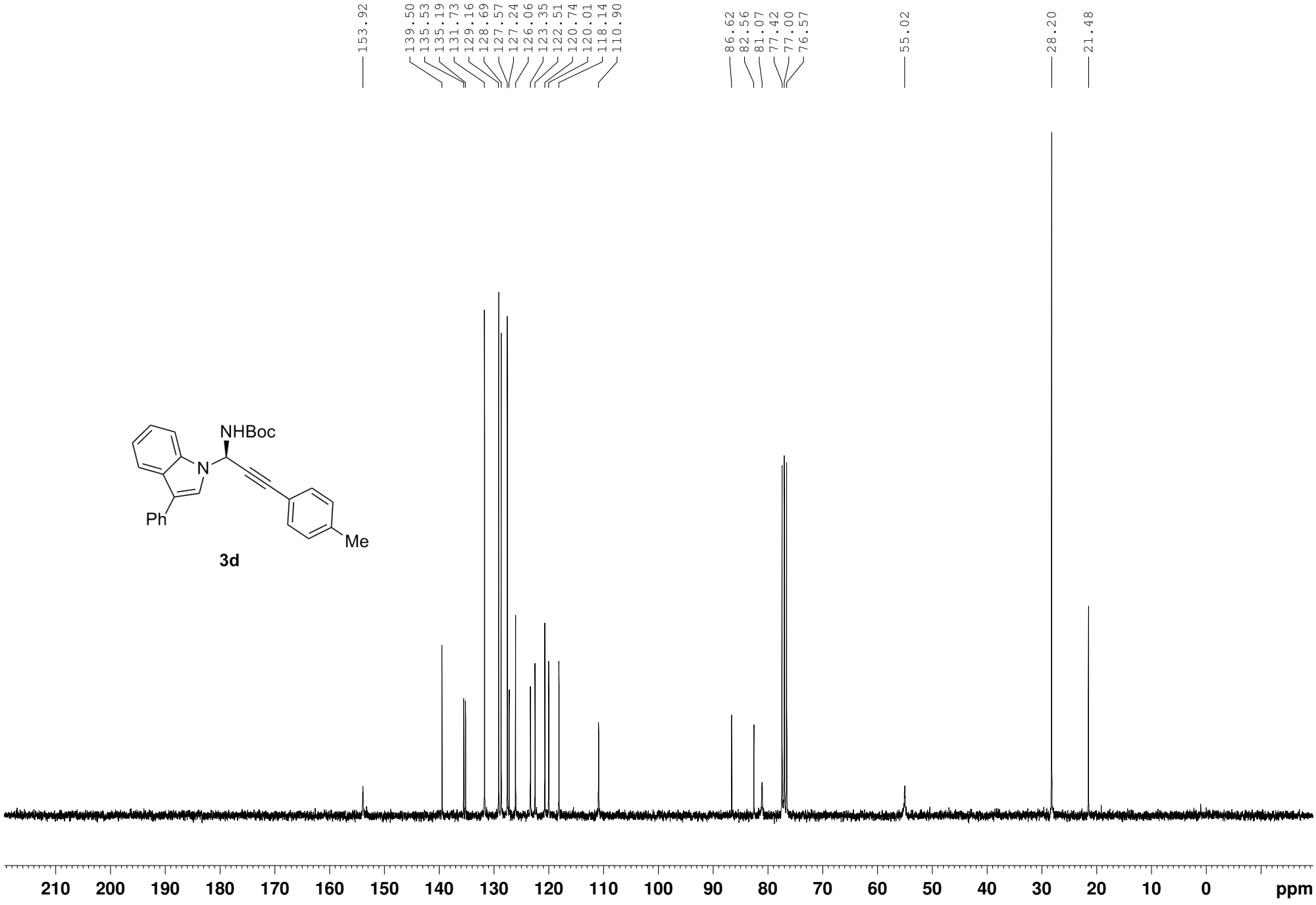
7.581
7.559
7.361
7.336
7.310
7.285
7.259
7.235
7.210
7.208
7.184
7.152
7.125
7.104
7.040
7.013
5.613
2.241
1.343
0.000
NHBoc
N
Ph
Me
3d
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.04
1.02
3.03
4.01
3.05
3.01
1.01
3.03
9.00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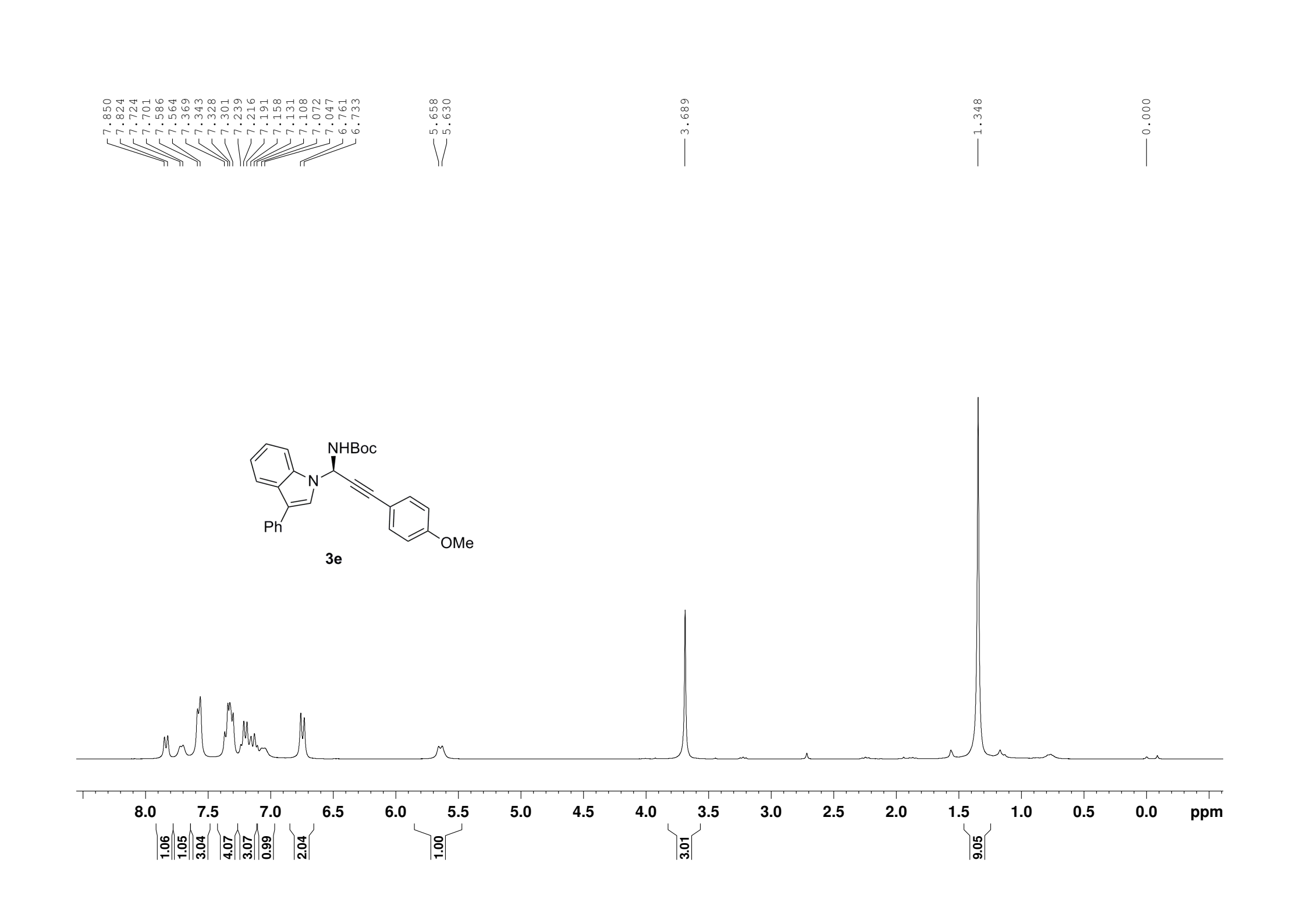
135.53
135.19
131.73
129.16
128.69
127.57
127.24
126.06
123.35
122.51
120.74
120.01
118.14
110.90
86.62
82.56
81.07
77.42
77.00
76.57
55.02
28.20
21.48
NHBoc
N
Ph
Me
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.701
7.586
7.564
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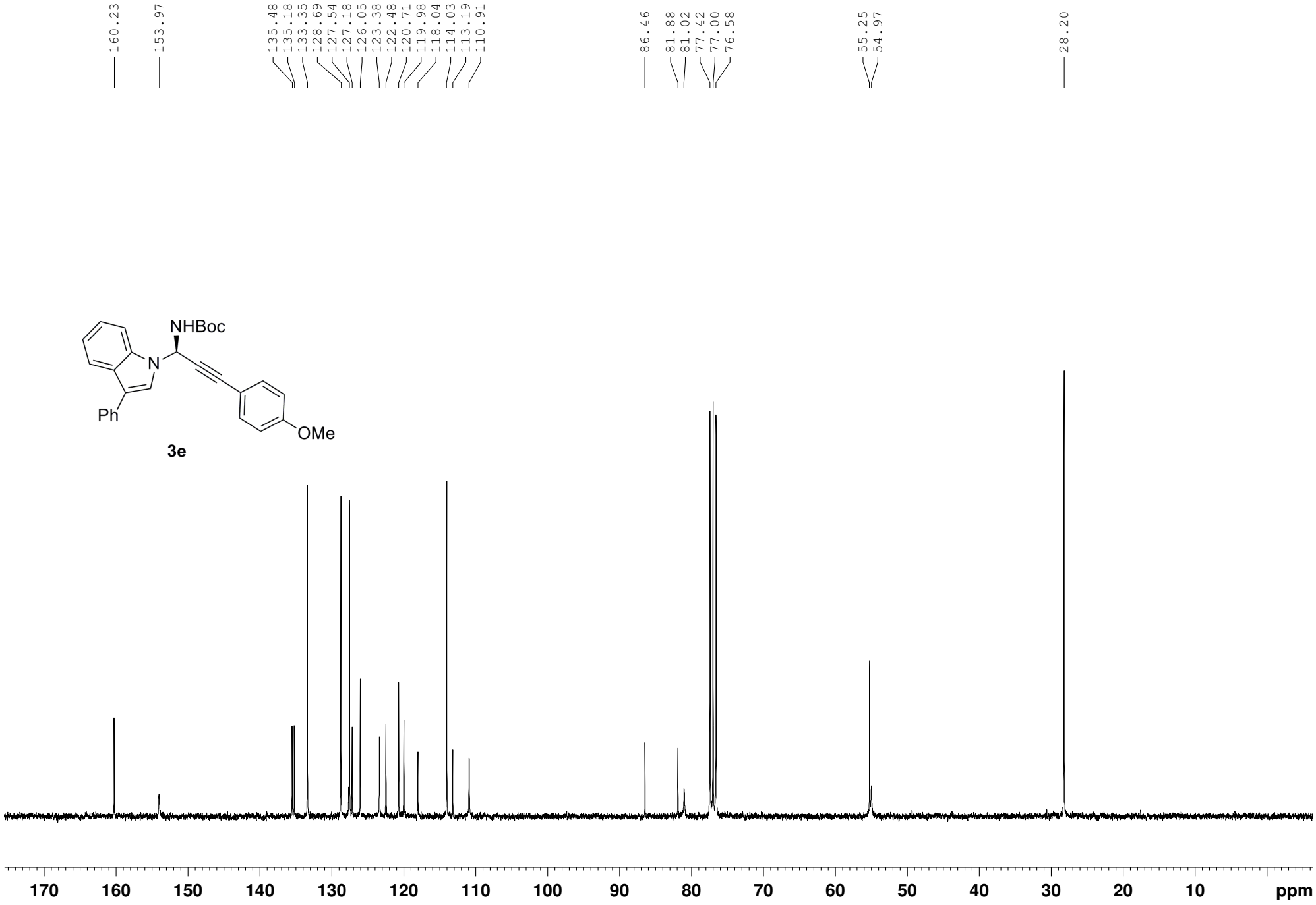
7.343
7.328
7.301
7.239
7.216
7.191
7.158
7.131
7.108
7.072
7.047
6.761
6.733
5.658
5.630
3.689
1.348
0.000
NHBoc
N
Ph
OMe
3e
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.06
1.05
3.04
4.07
3.07
0.99
2.04
1.00
3.01
9.05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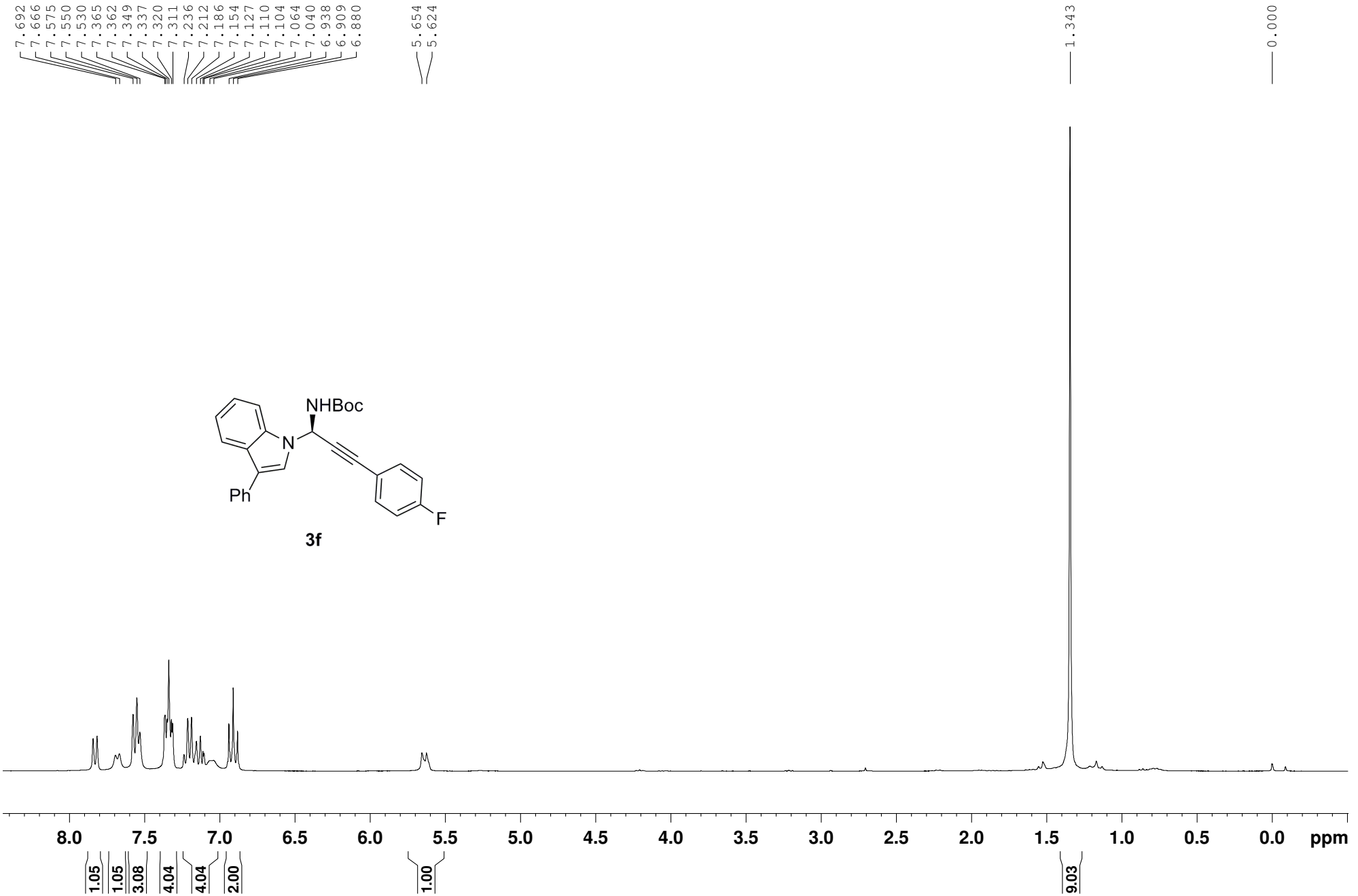
153.97
135.48
135.18
133.35
128.69
127.54
127.18
126.05
123.38
122.48
120.71
119.98
118.04
114.03
113.19
110.91
86.46
81.88
81.02
77.42
77.00
76.58
55.25
54.97
28.20
NHBoc
N
Ph
OMe
3e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.692
7.666
7.575
7.550
7.530
7.365
7.362
7.349
7.337
7.320
7.311
7.236
7.212
7.186
7.154
7.127
7.110
7.104
7.064
7.040
6.938
6.909
6.880
5.654
5.624
1.343
0.000
NHBoc
N
Ph
F
3f
8.0
7.5
7.0
6.5
6.0
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1.00
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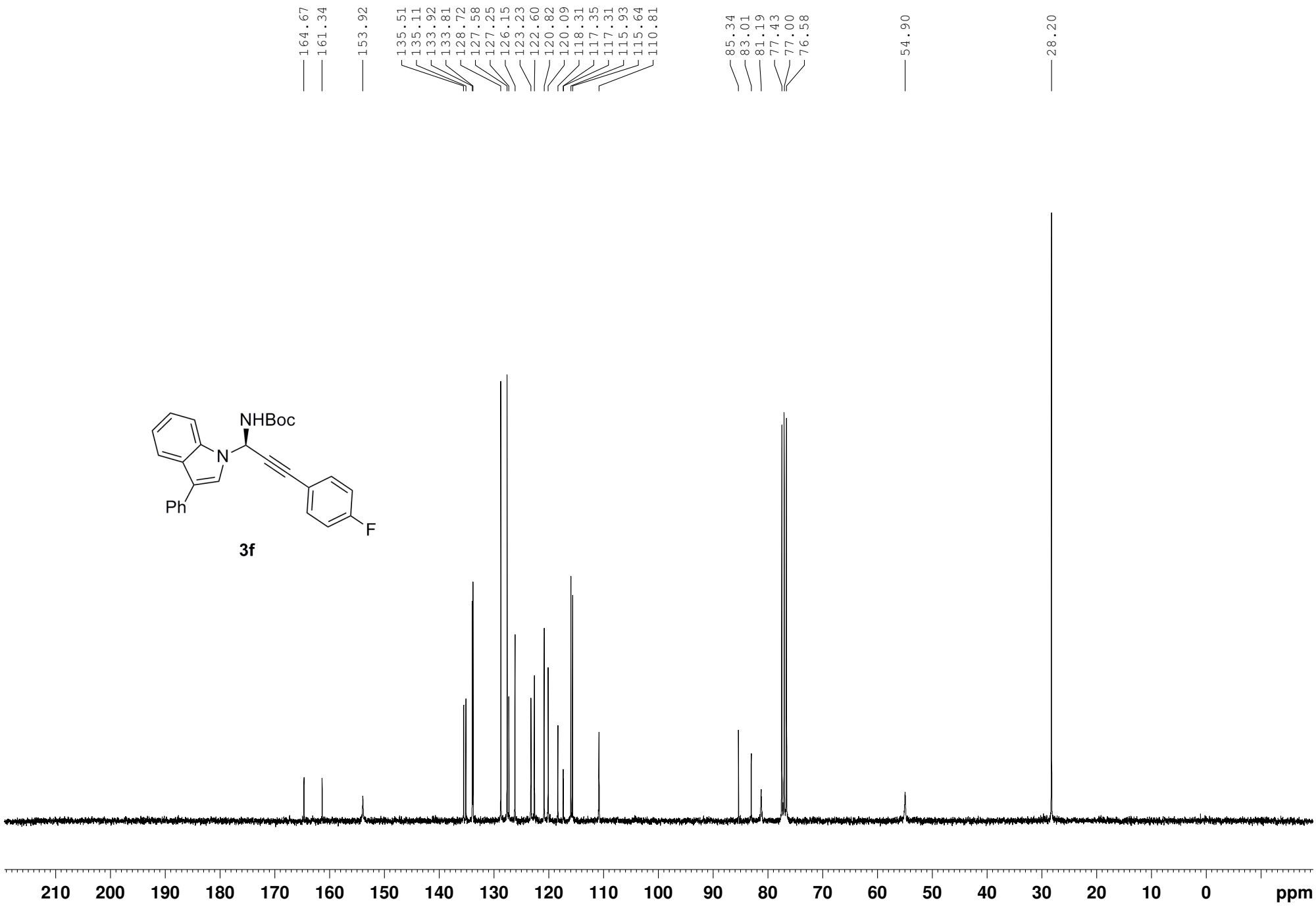
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120.09
118.31
117.35
117.31
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115.64
110.81
85.34
83.01
81.19
77.43
77.00
76.58
54.90
28.20
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N
Ph
F
3f
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200
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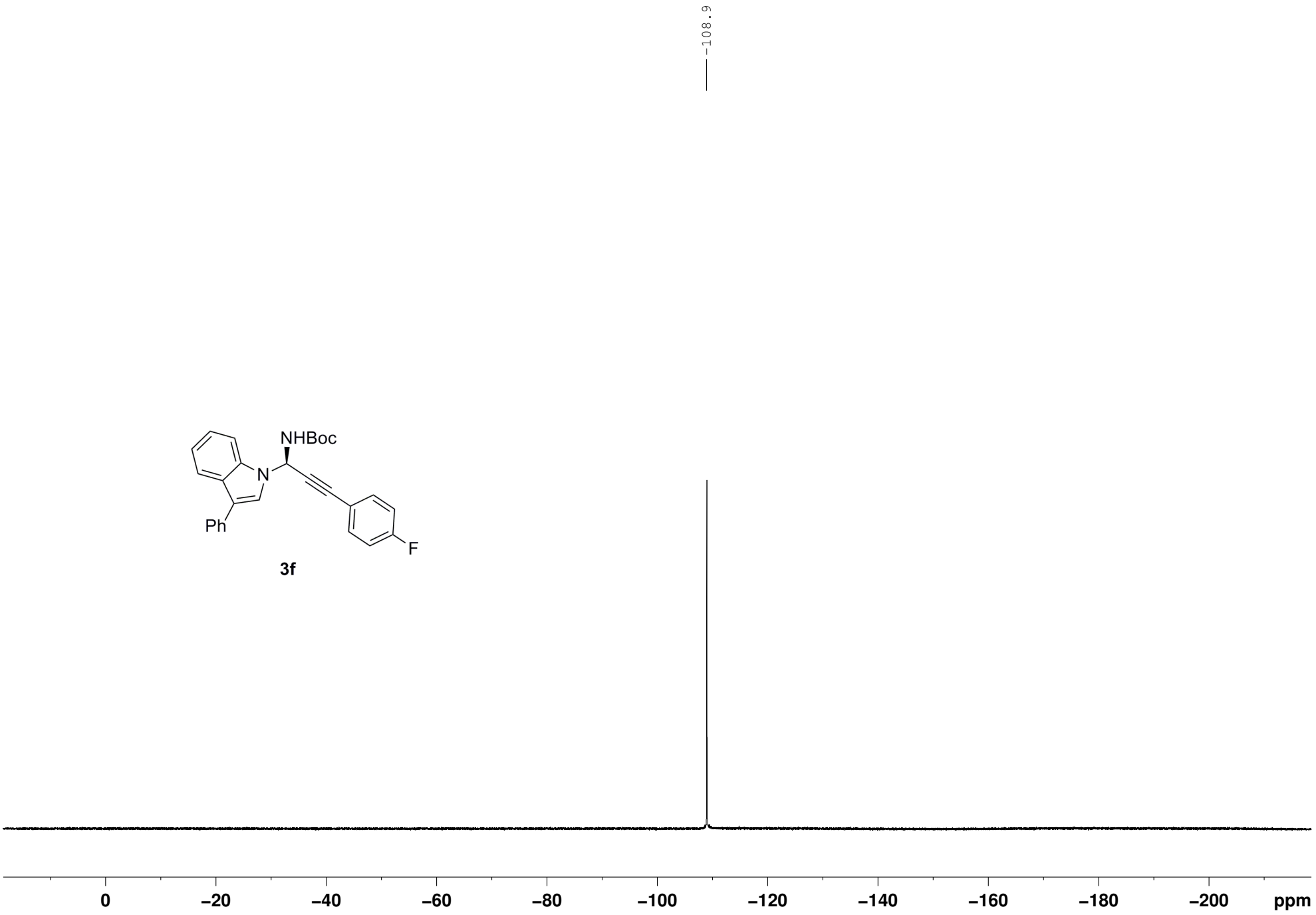
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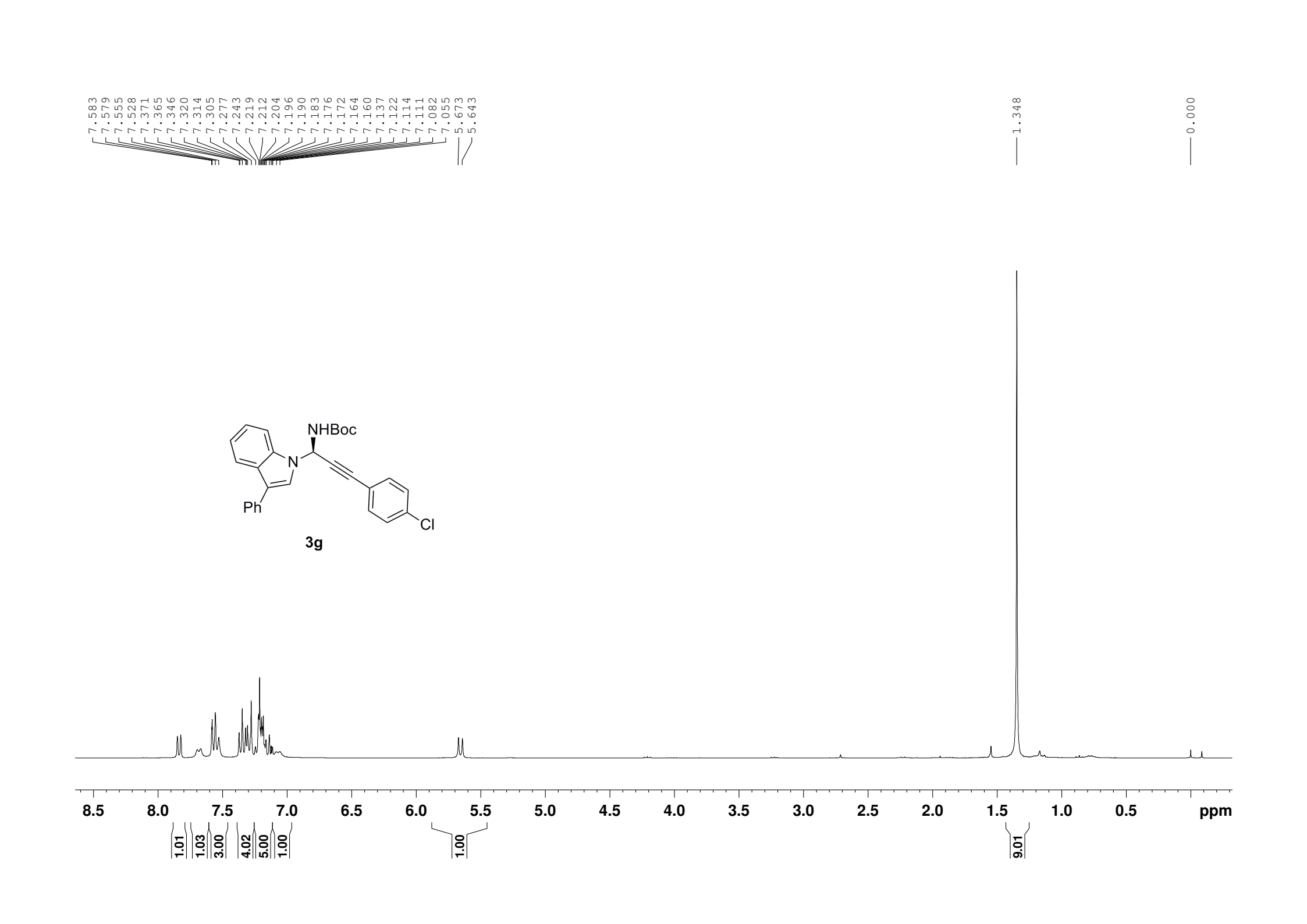
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7.190
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7.176
7.172
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7.160
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7.122
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7.111
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Ph
Cl
3g
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6.0
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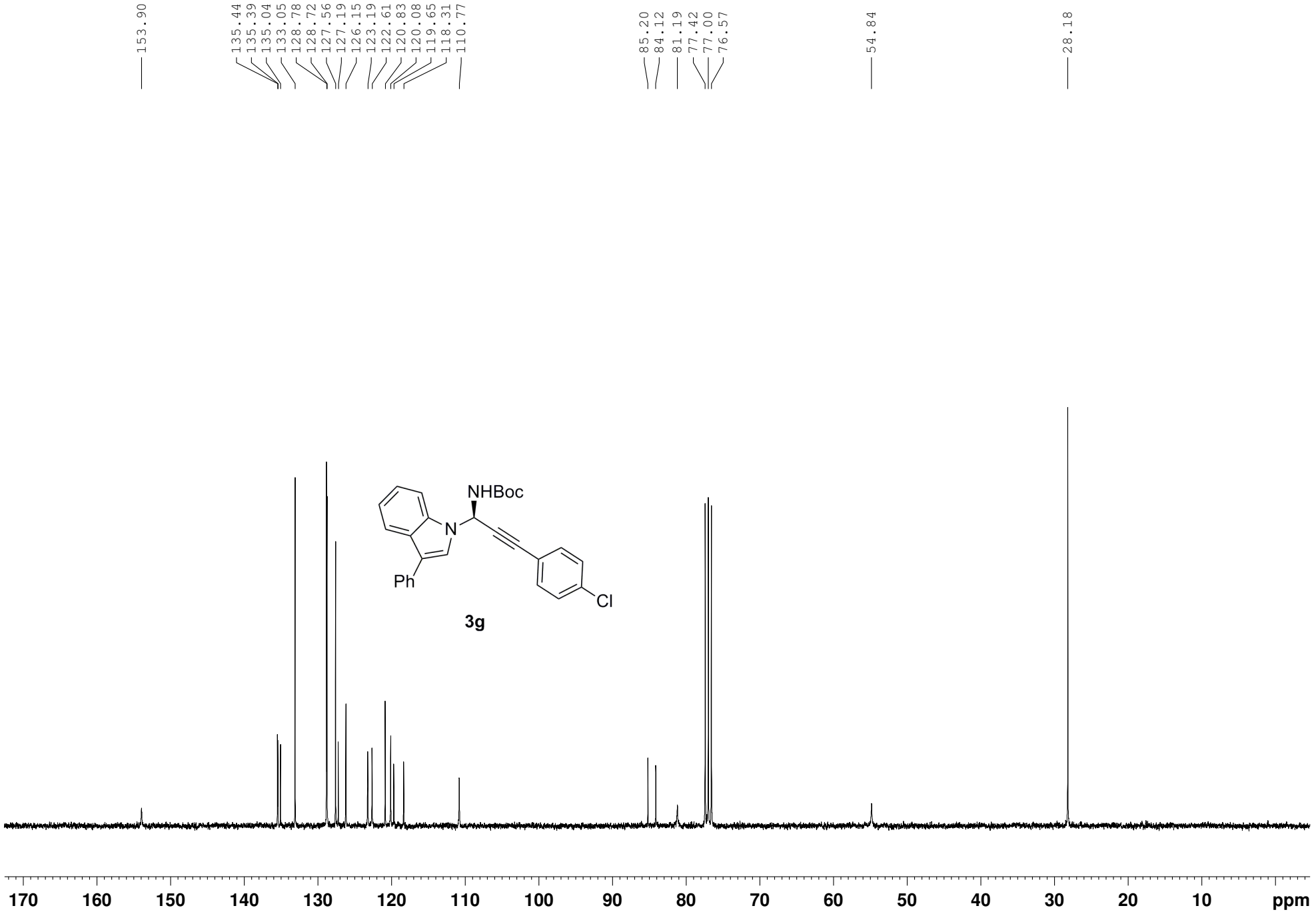
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85.20
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81.19
77.42
77.00
76.57
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Ph
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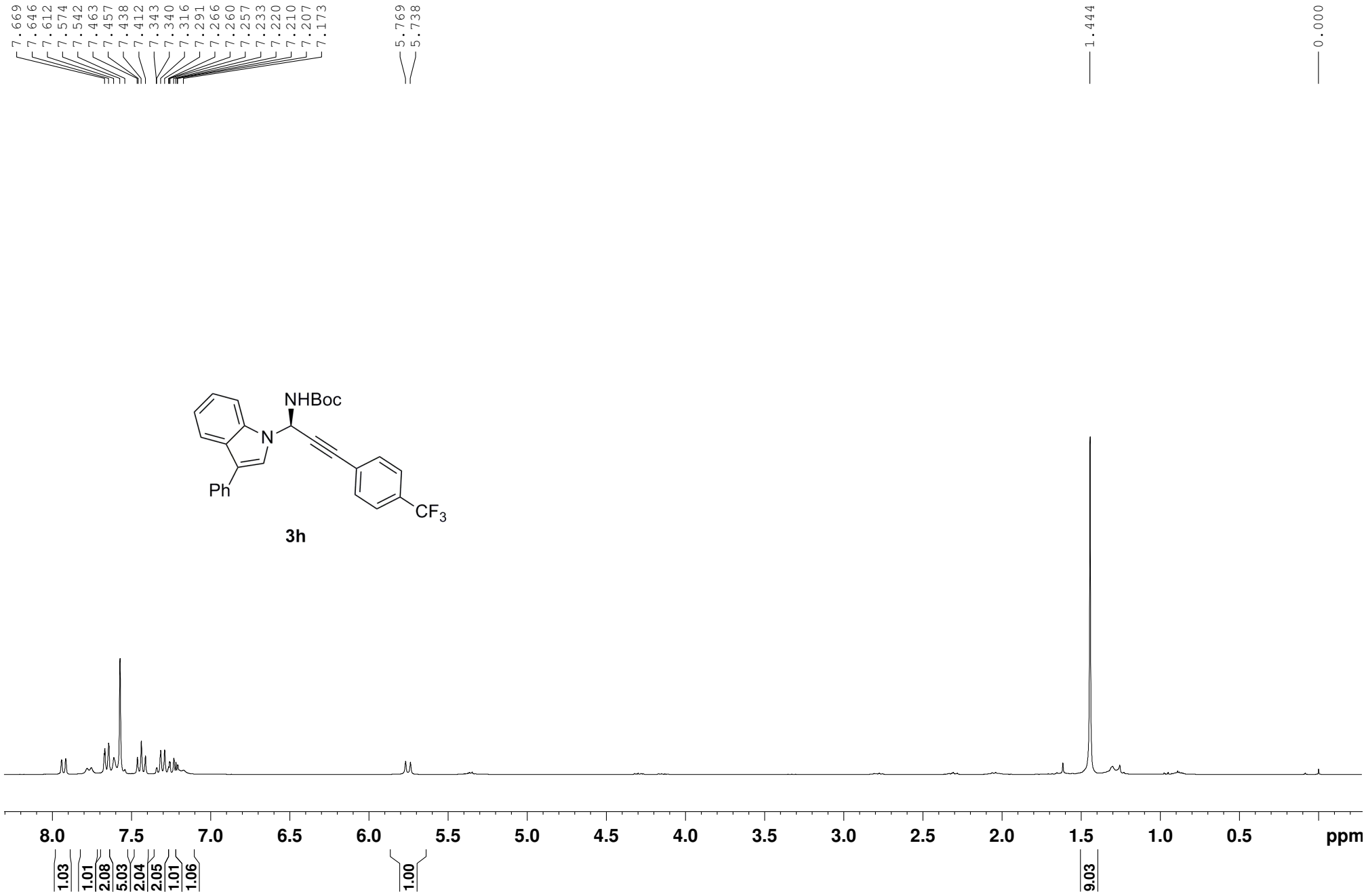
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7.340
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7.291
7.266
7.260
7.257
7.233
7.220
7.210
7.207
7.173
5.769
5.738
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Ph
CF3
3h
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6.5
6.0
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5.0
4.5
4.0
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2.5
2.0
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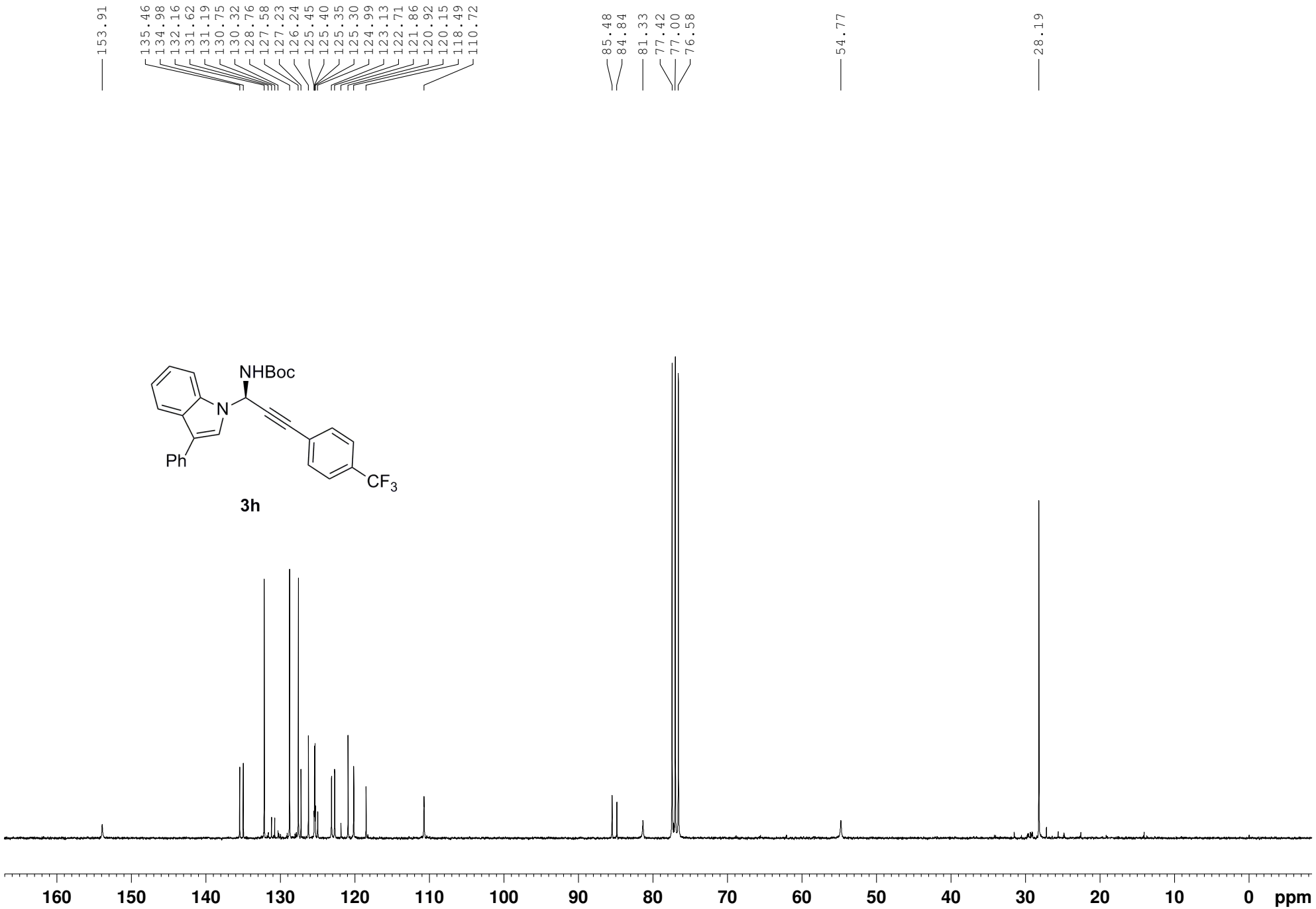
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125.40
125.35
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123.13
122.71
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120.92
120.15
118.49
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85.48
84.84
81.33
77.42
77.00
76.58
54.77
28.19
NHBoc
N
Ph
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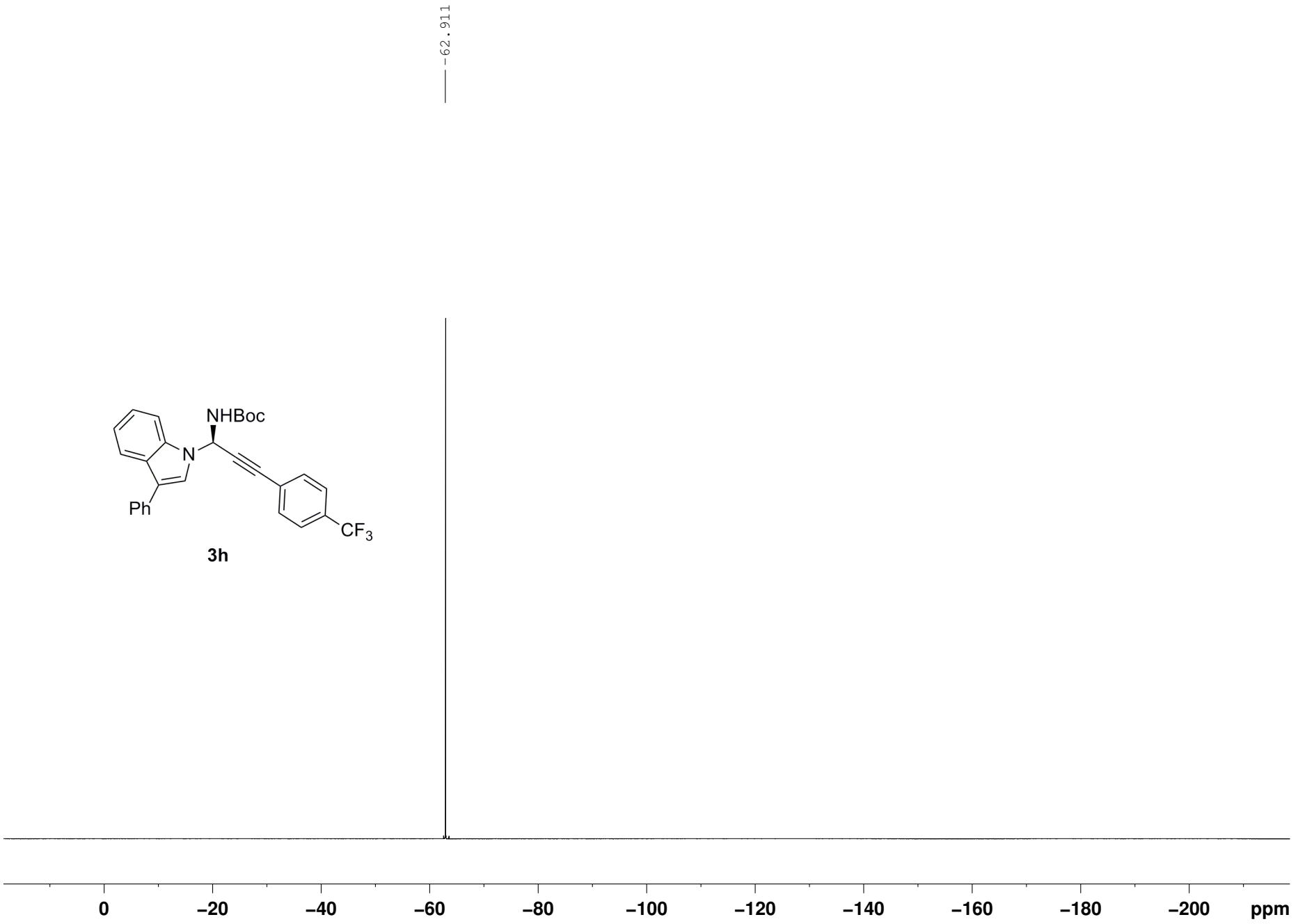
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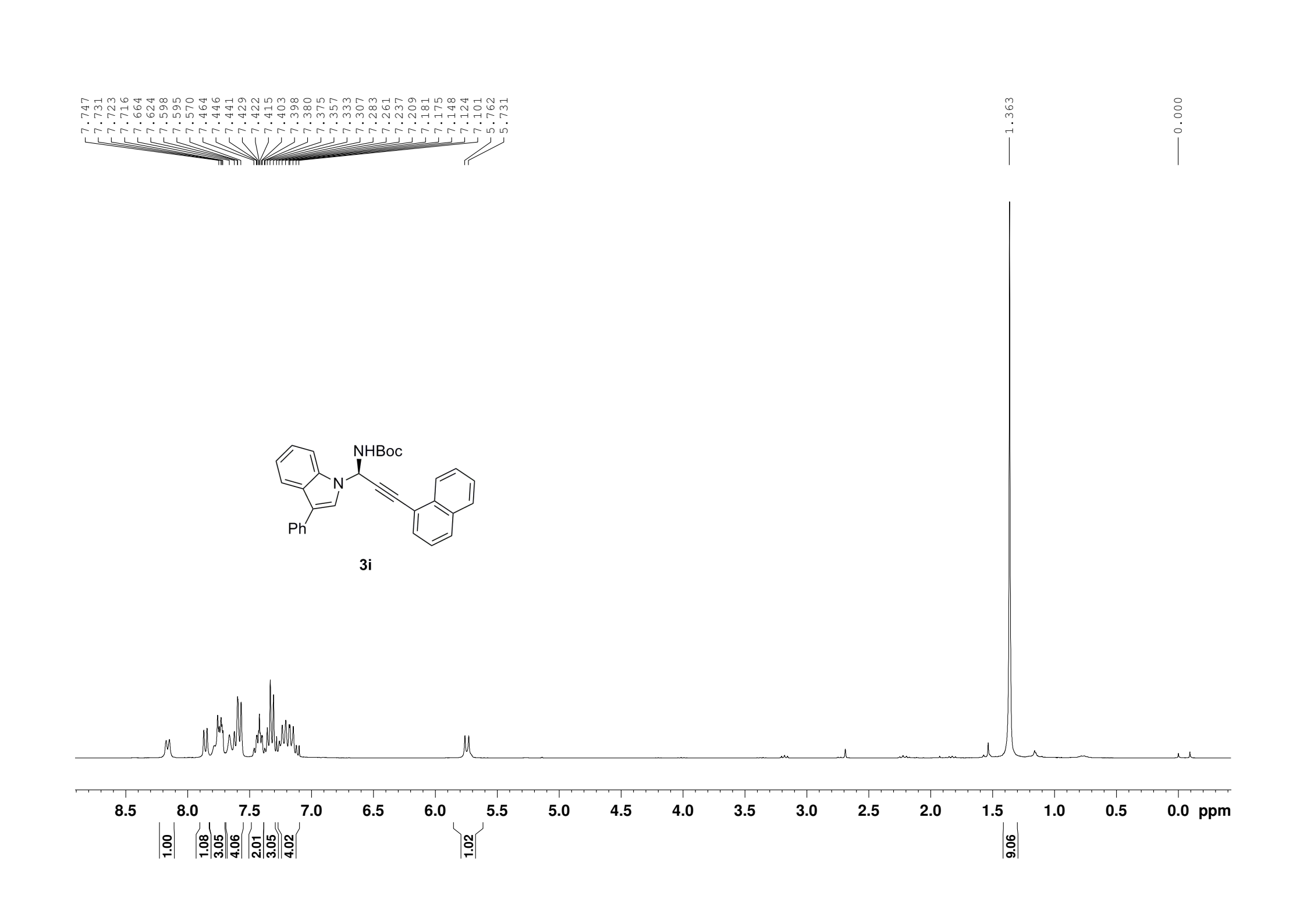
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7.464
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7.441
7.429
7.422
7.415
7.403
7.398
7.380
7.375
7.357
7.333
7.307
7.283
7.261
7.237
7.209
7.181
7.175
7.148
7.124
7.101
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5.731
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N
Ph
3i
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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3.05
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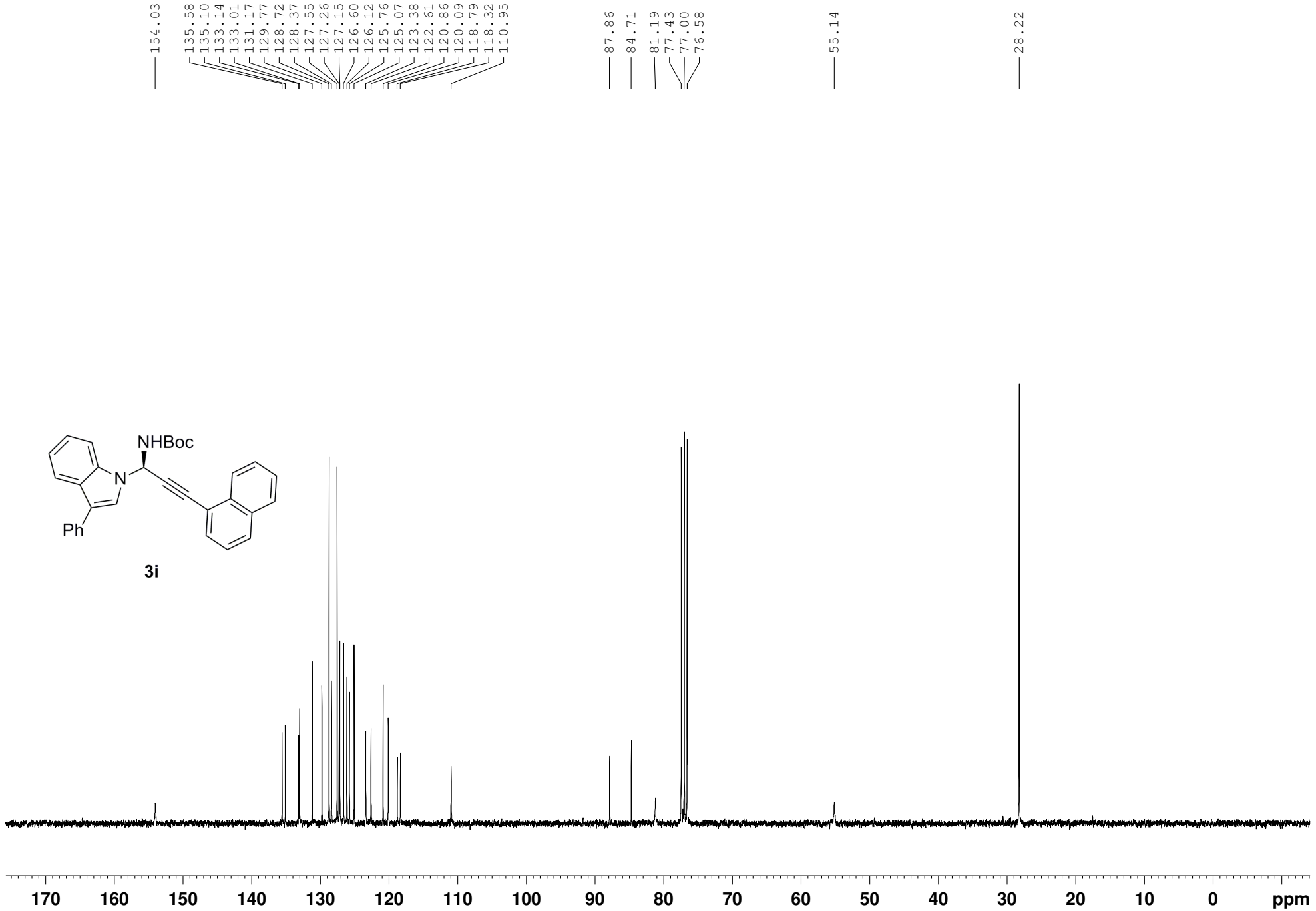
1.02
9.06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126.12
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125.07
123.38
122.61
120.86
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118.32
110.95
87.86
84.71
81.19
77.43
77.00
76.58
55.14
28.22
NHBoc
N
Ph
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130
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80
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60
50
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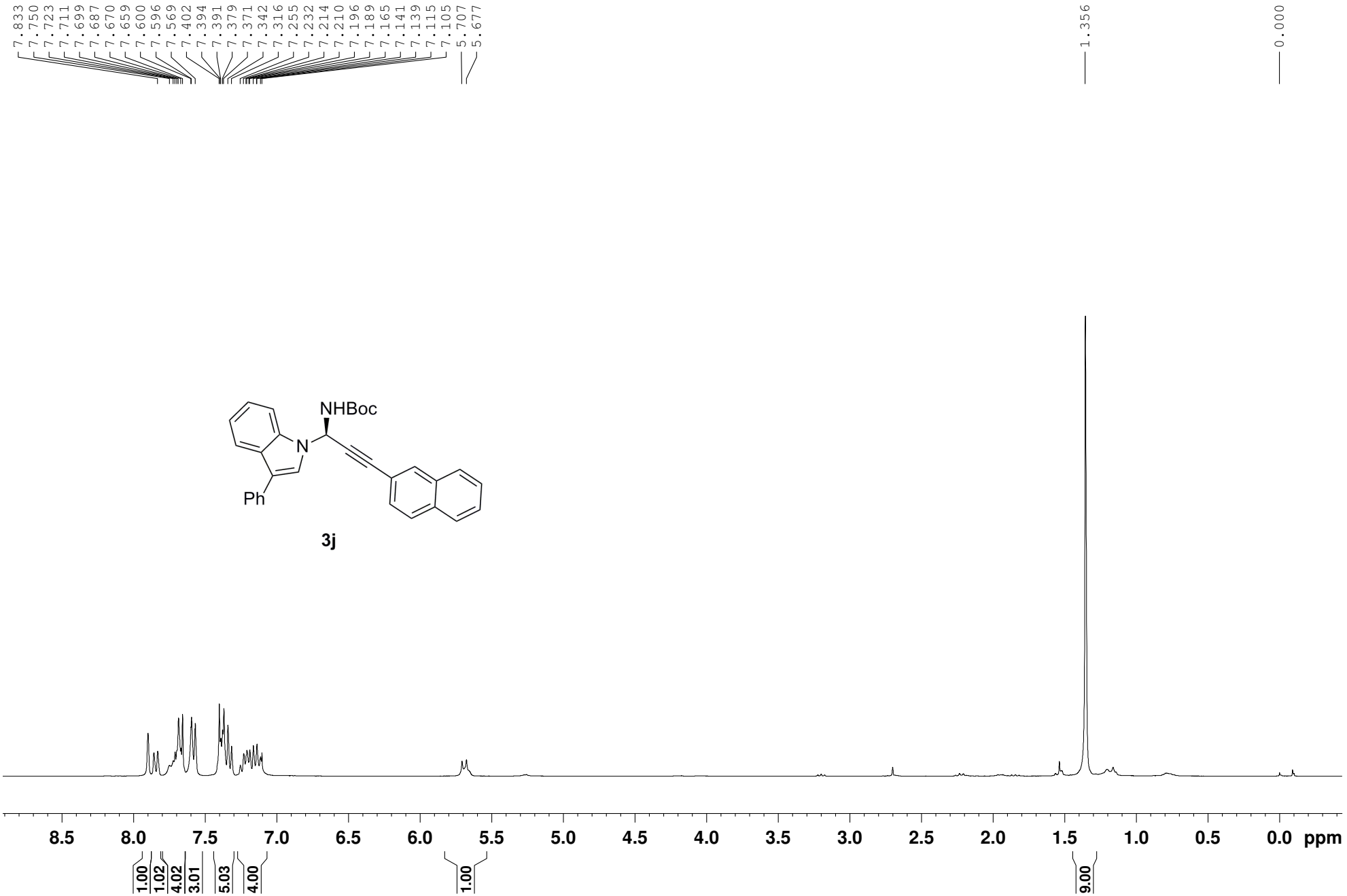
20
10
0
ppm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7.342
7.316
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7.232
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7.189
7.165
7.141
7.139
7.115
7.105
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5.677
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NHBoc
N
Ph
3j
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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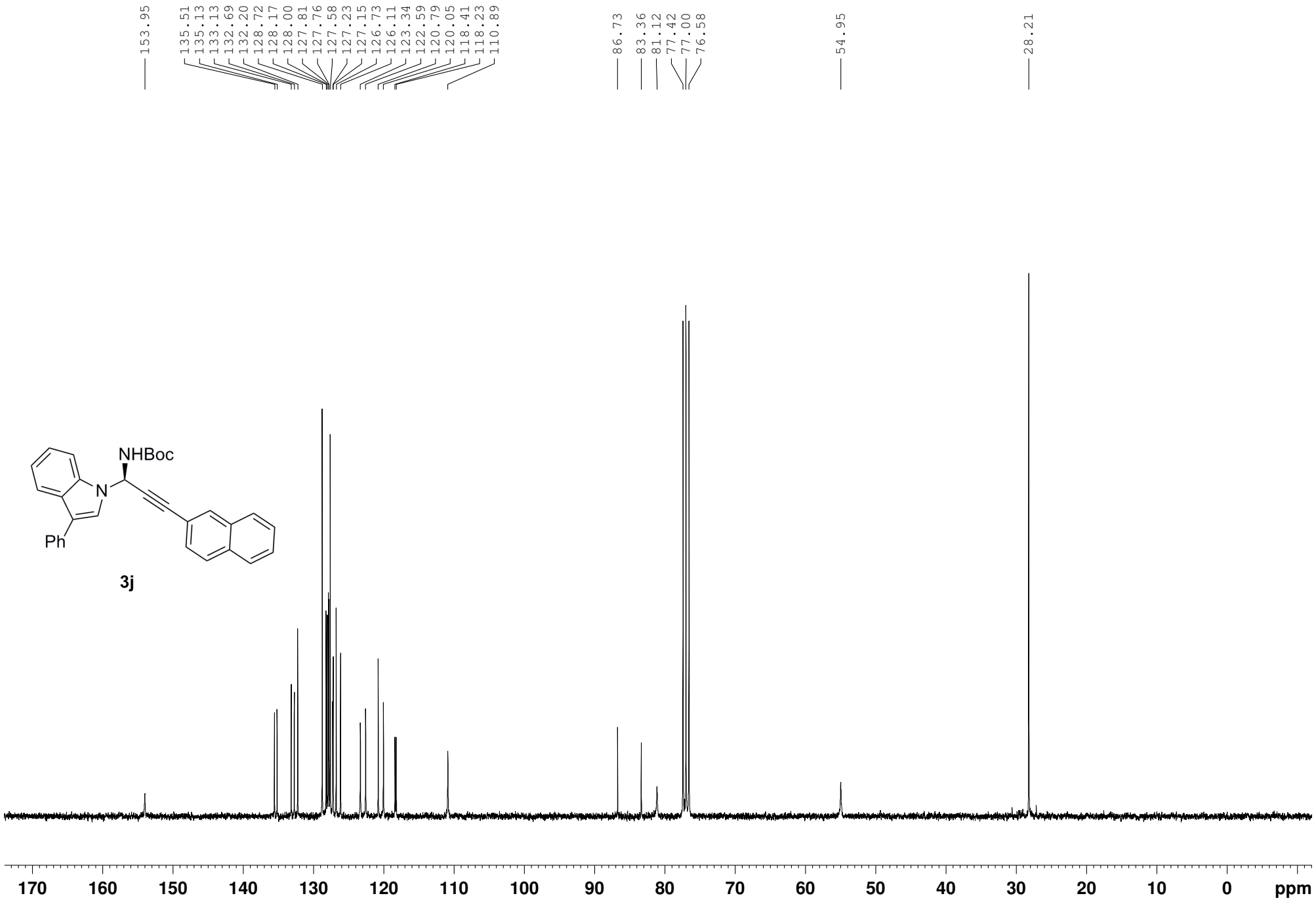
1.02
4.02
3.01
5.03
4.00
1.00
9.00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118.23
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81.12
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77.00
76.58
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N
Ph
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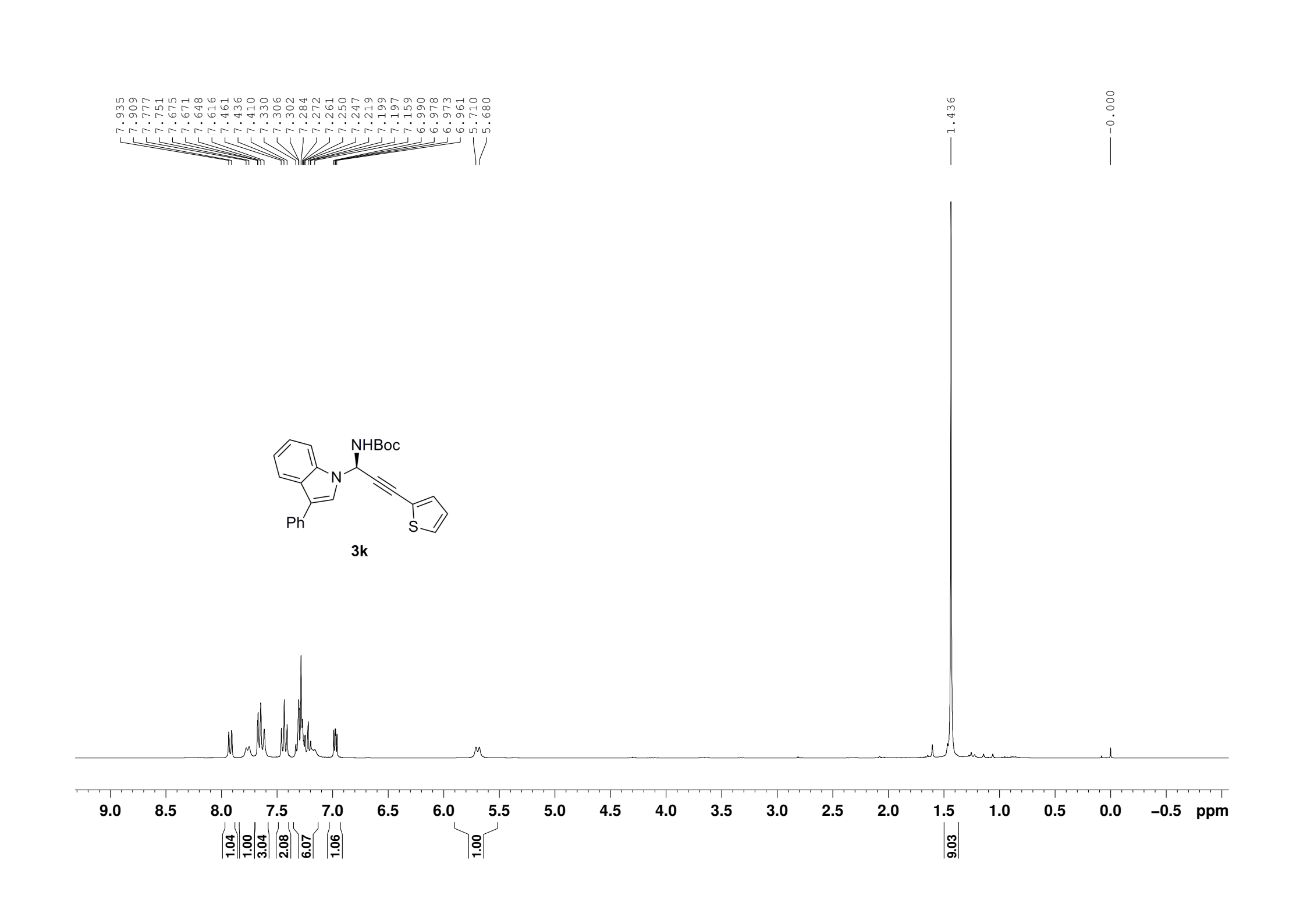
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7.306
7.302
7.284
7.272
7.261
7.250
7.247
7.219
7.199
7.197
7.159
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6.978
6.973
6.961
5.710
5.680
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N
Ph
S
3k
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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2.08
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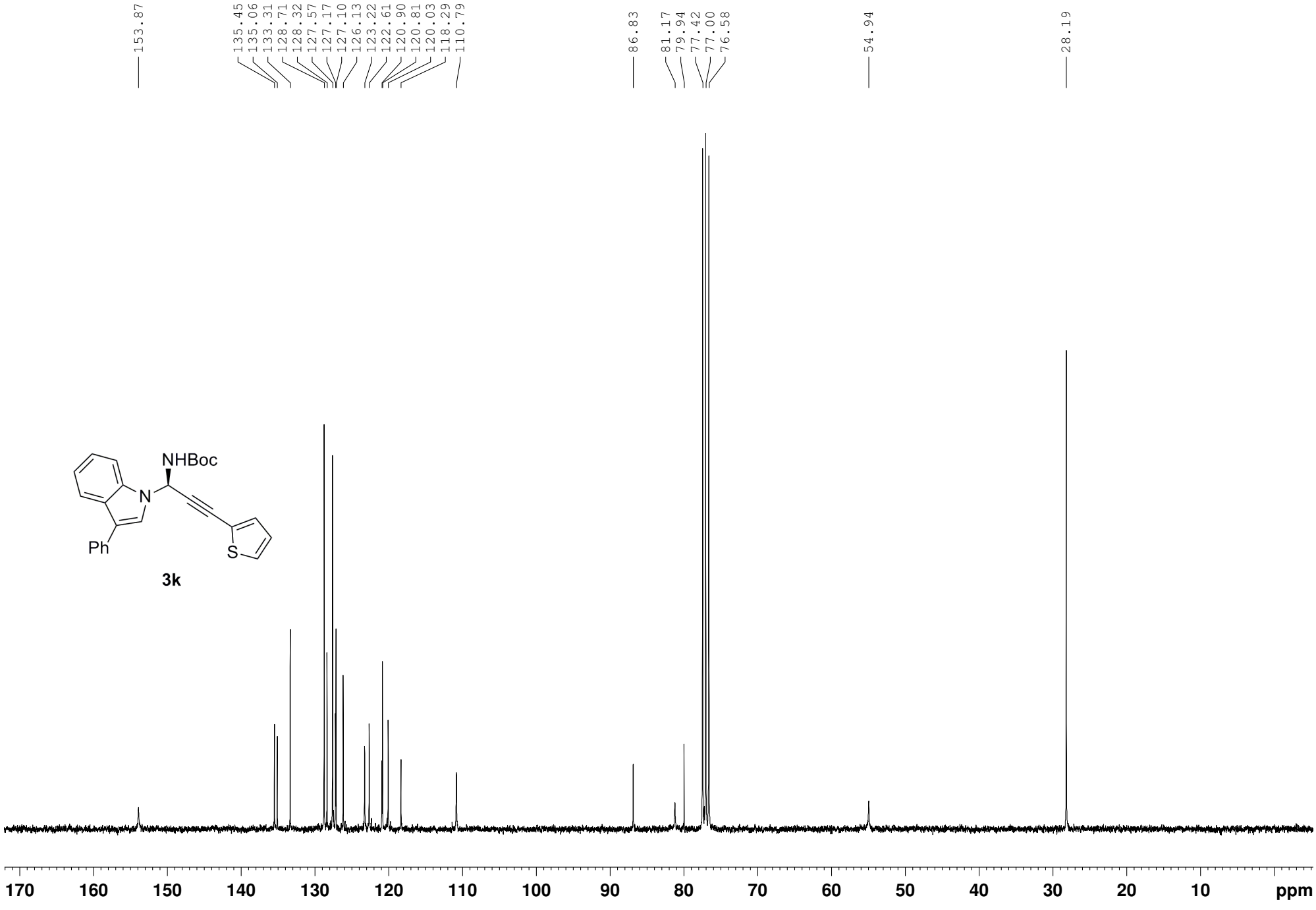
9.03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126.13
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120.81
120.03
118.29
110.79
86.83
81.17
79.94
77.42
77.00
76.58
54.94
28.19
NHBoc
N
Ph
S
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150
140
130
120
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100
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70
60
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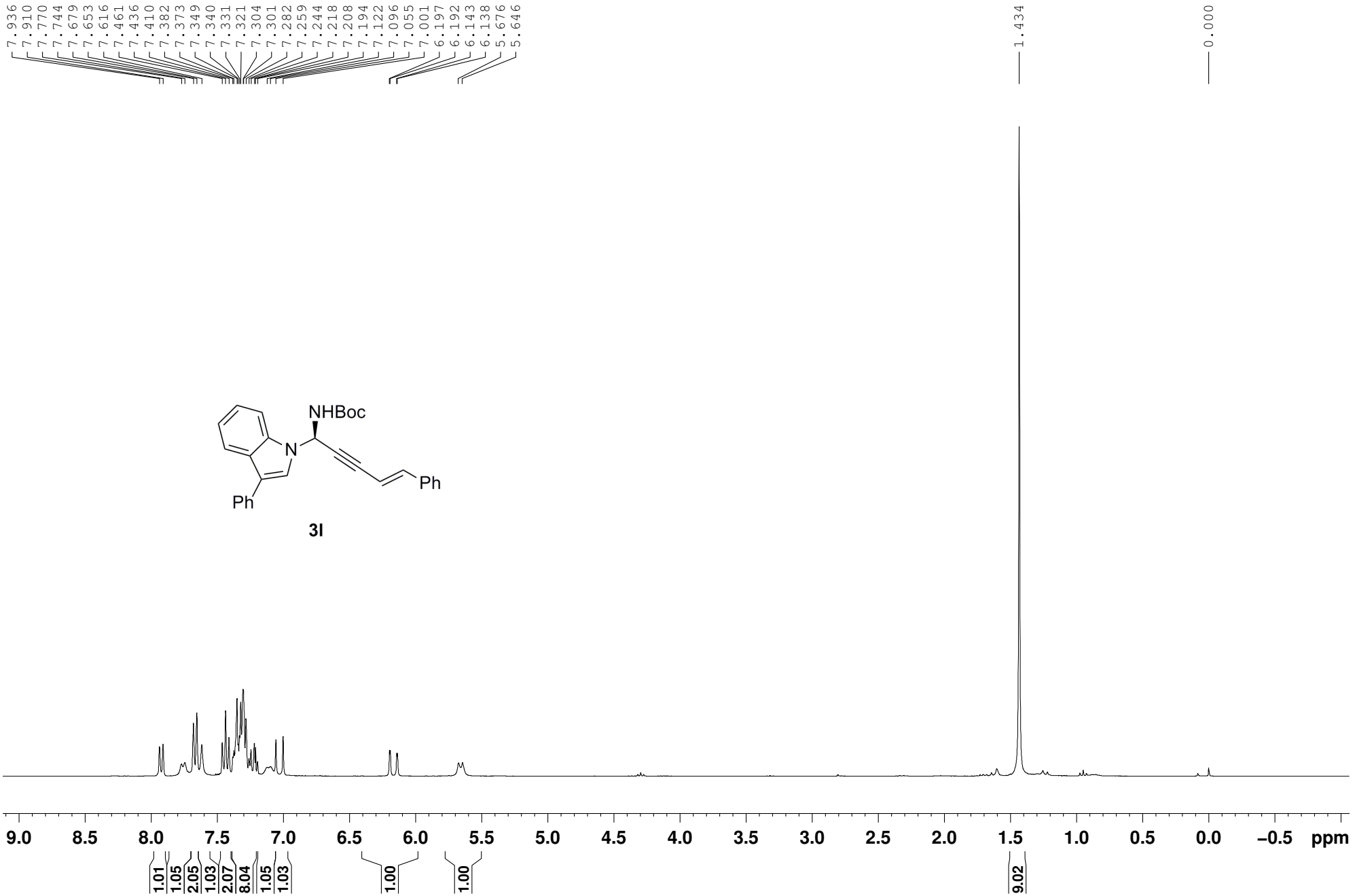
30
20
10
ppm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7.301
7.282
7.259
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7.208
7.194
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Ph
Ph
3l
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6.0
5.5
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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0.0
−0.5
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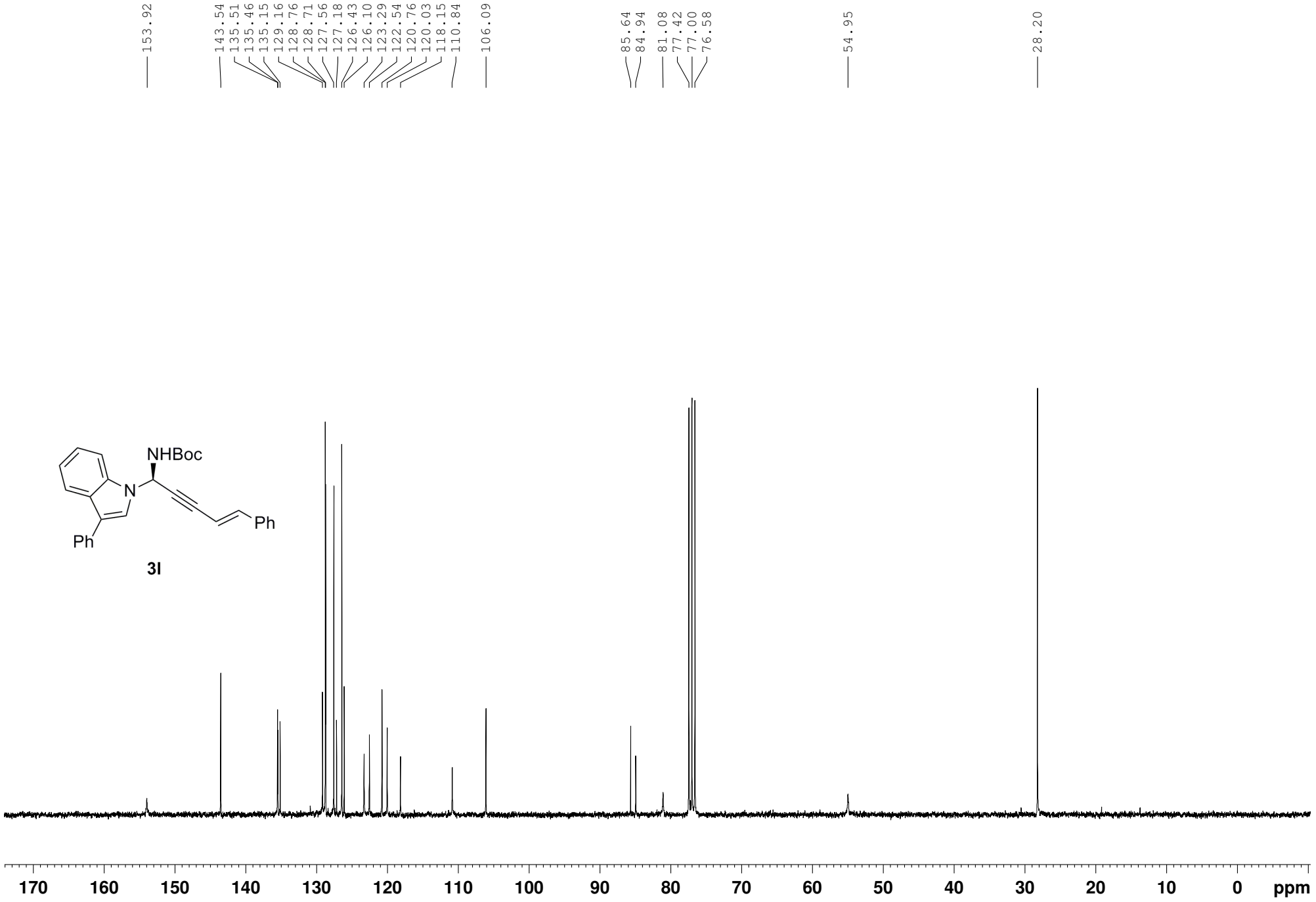
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110.84
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84.94
81.08
77.42
77.00
76.58
54.95
28.20
NHBoc
N
Ph
Ph
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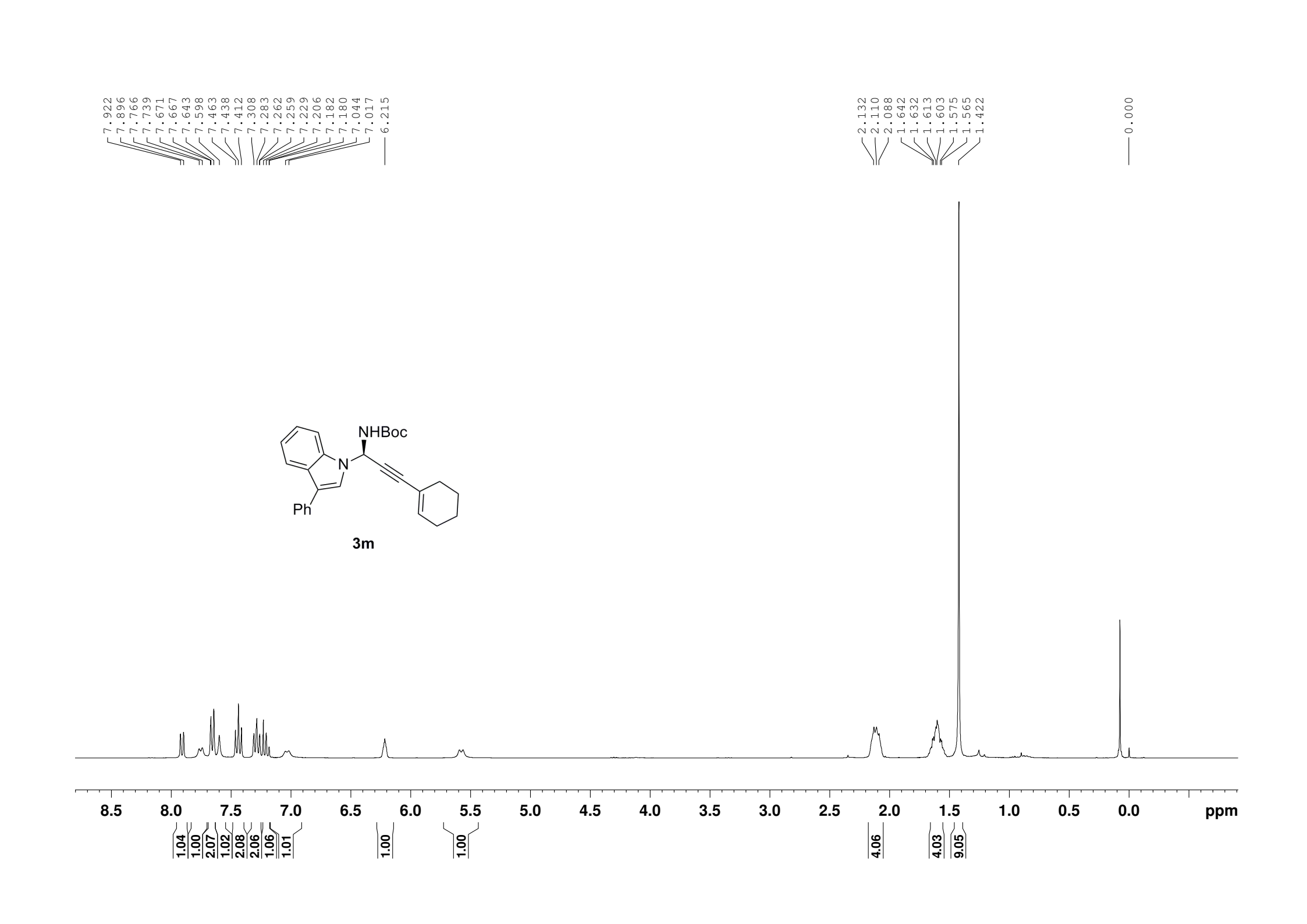
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1.575
1.565
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Ph
3m
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6.5
6.0
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4.0
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3.0
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2.0
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ppm
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2.08
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1.00
1.00
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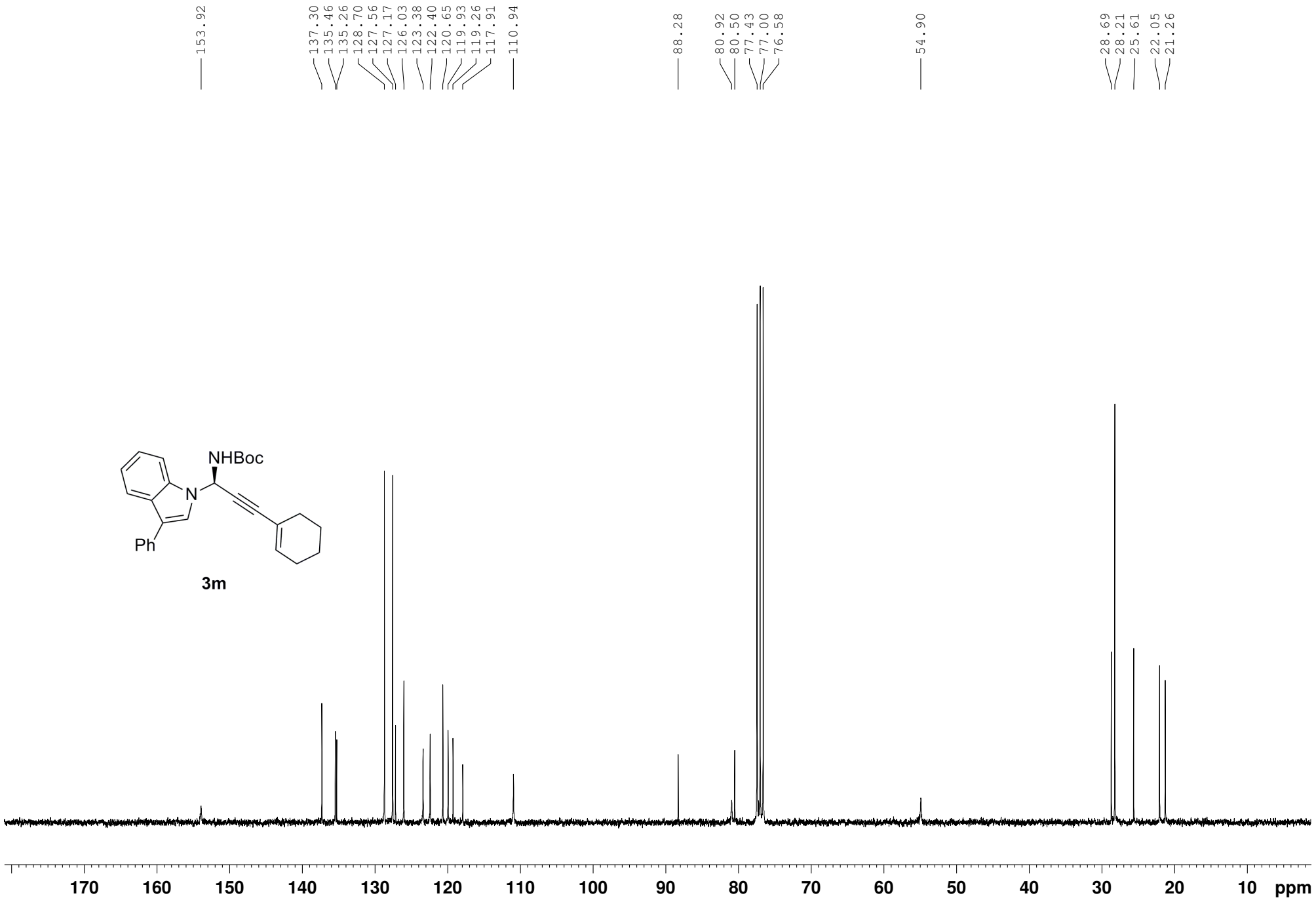
9.05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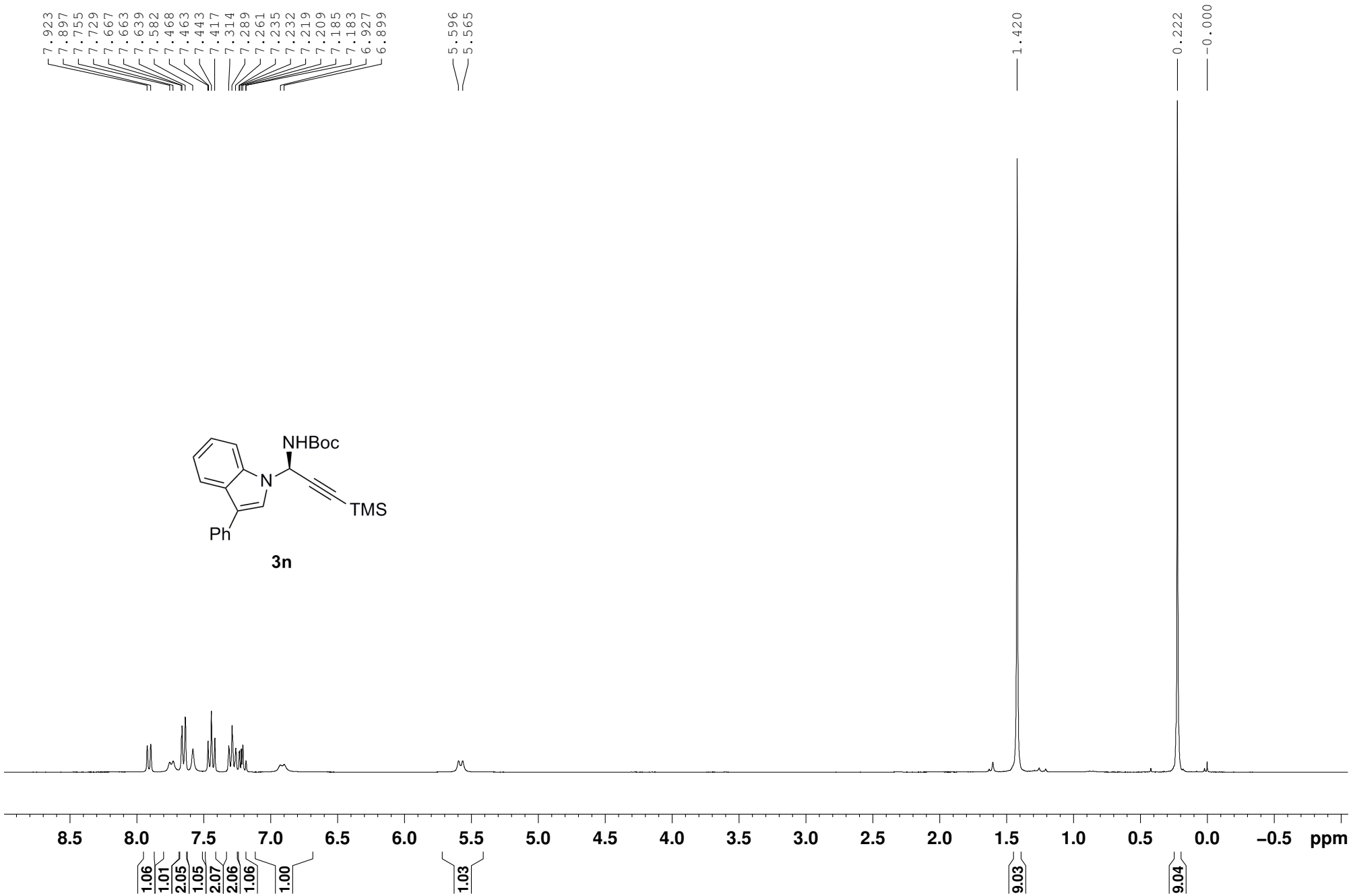
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7.235
7.232
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6.899
5.596
5.565
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TMS
Ph
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6.0
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3.0
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1.06
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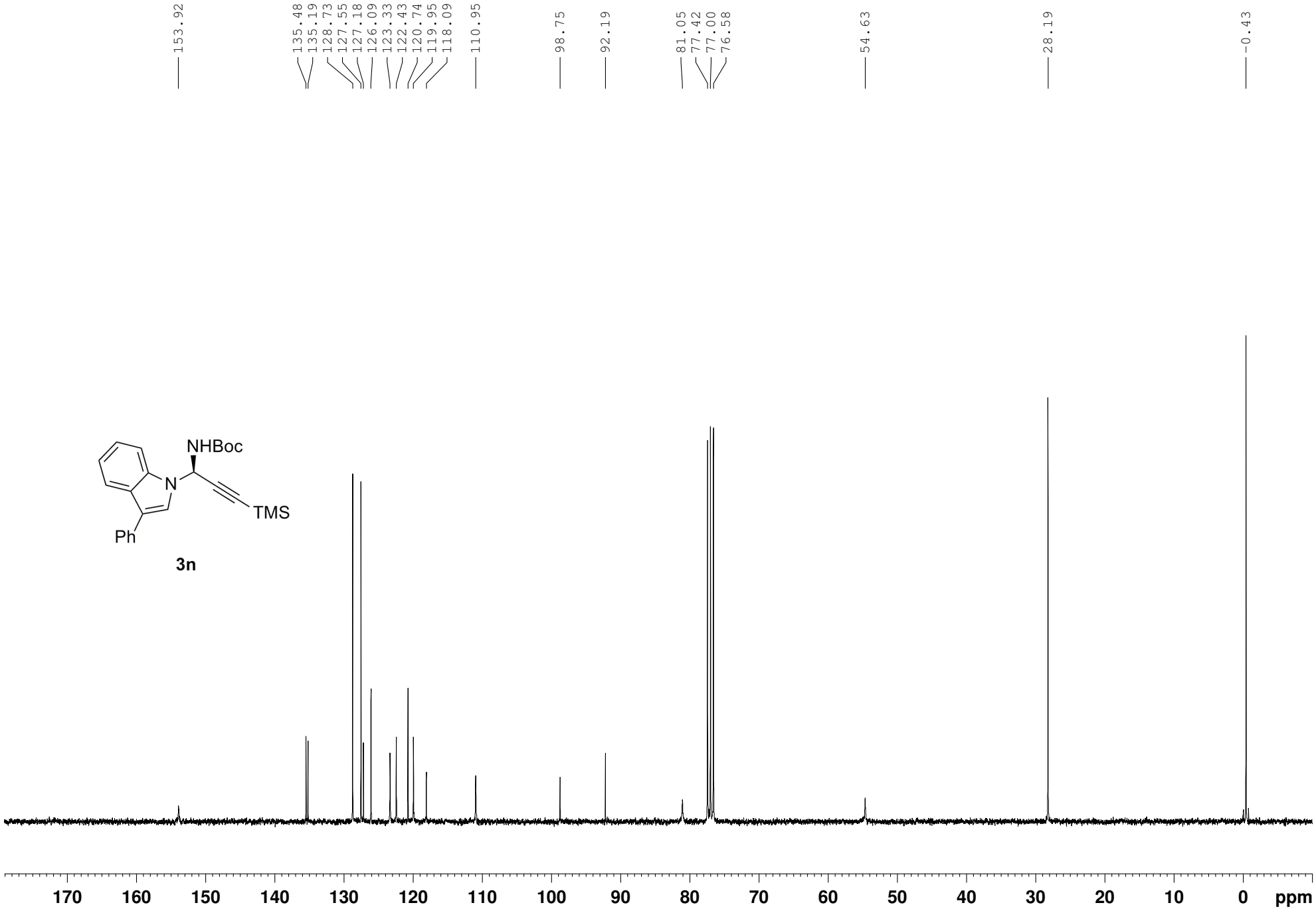
9.04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92.19
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77.00
76.58
54.63
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TMS
Ph
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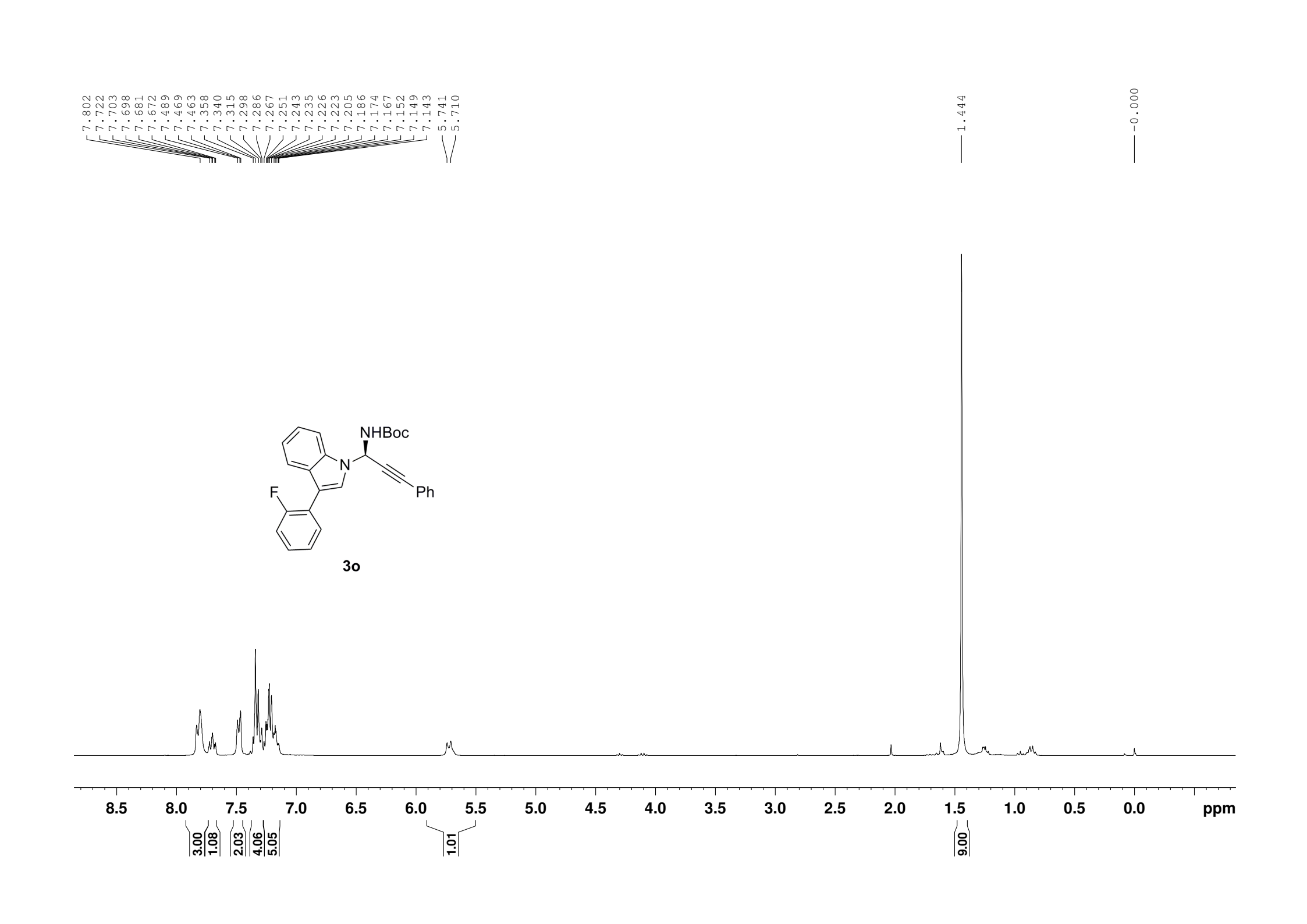
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7.235
7.226
7.223
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7.174
7.167
7.152
7.149
7.143
5.741
5.710
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N
F
Ph
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6.0
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4.0
3.5
3.0
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2.03
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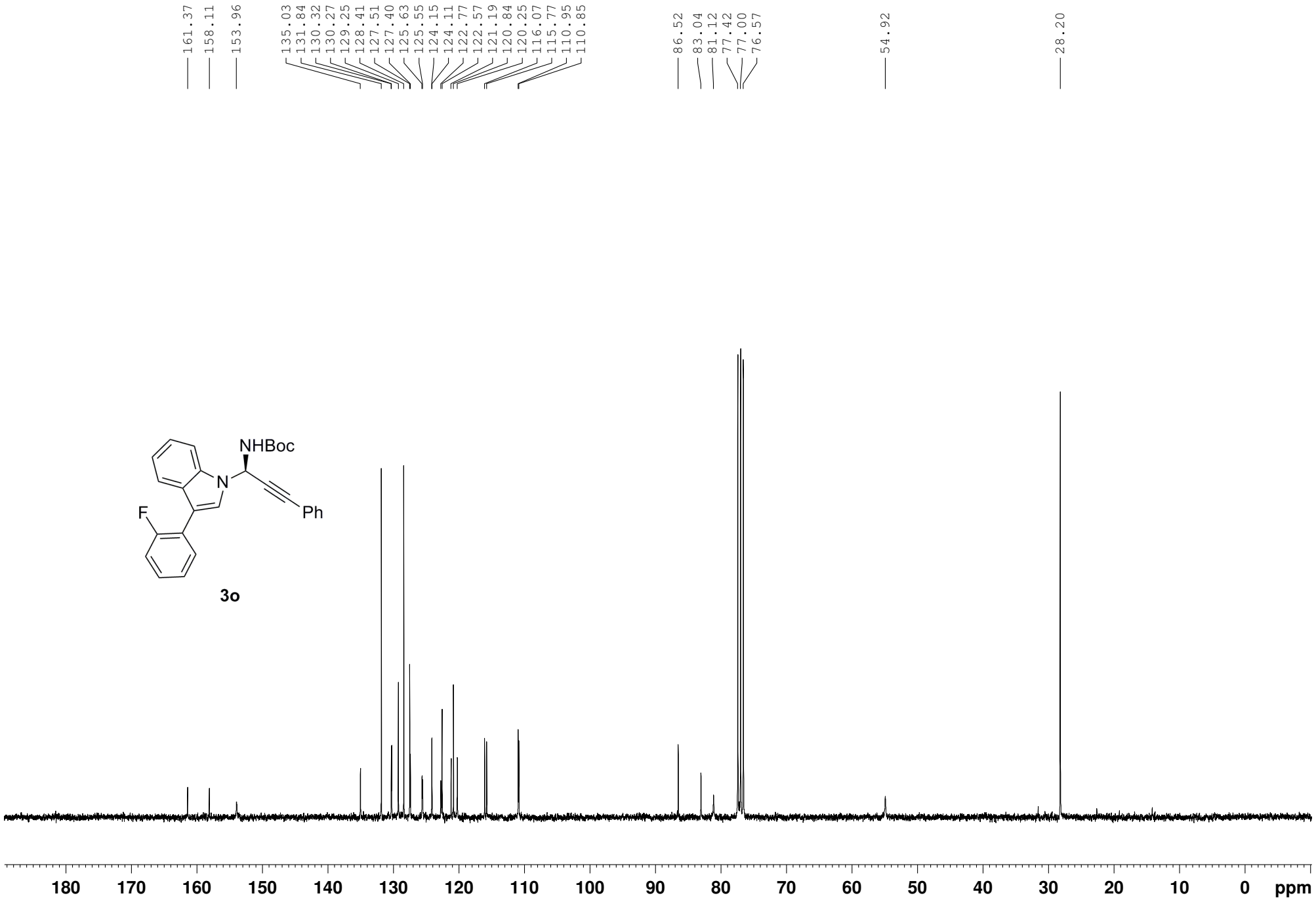
9.00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110.95
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86.52
83.04
81.12
77.42
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76.57
54.92
28.20
NHBoc
N
F
Ph
3o
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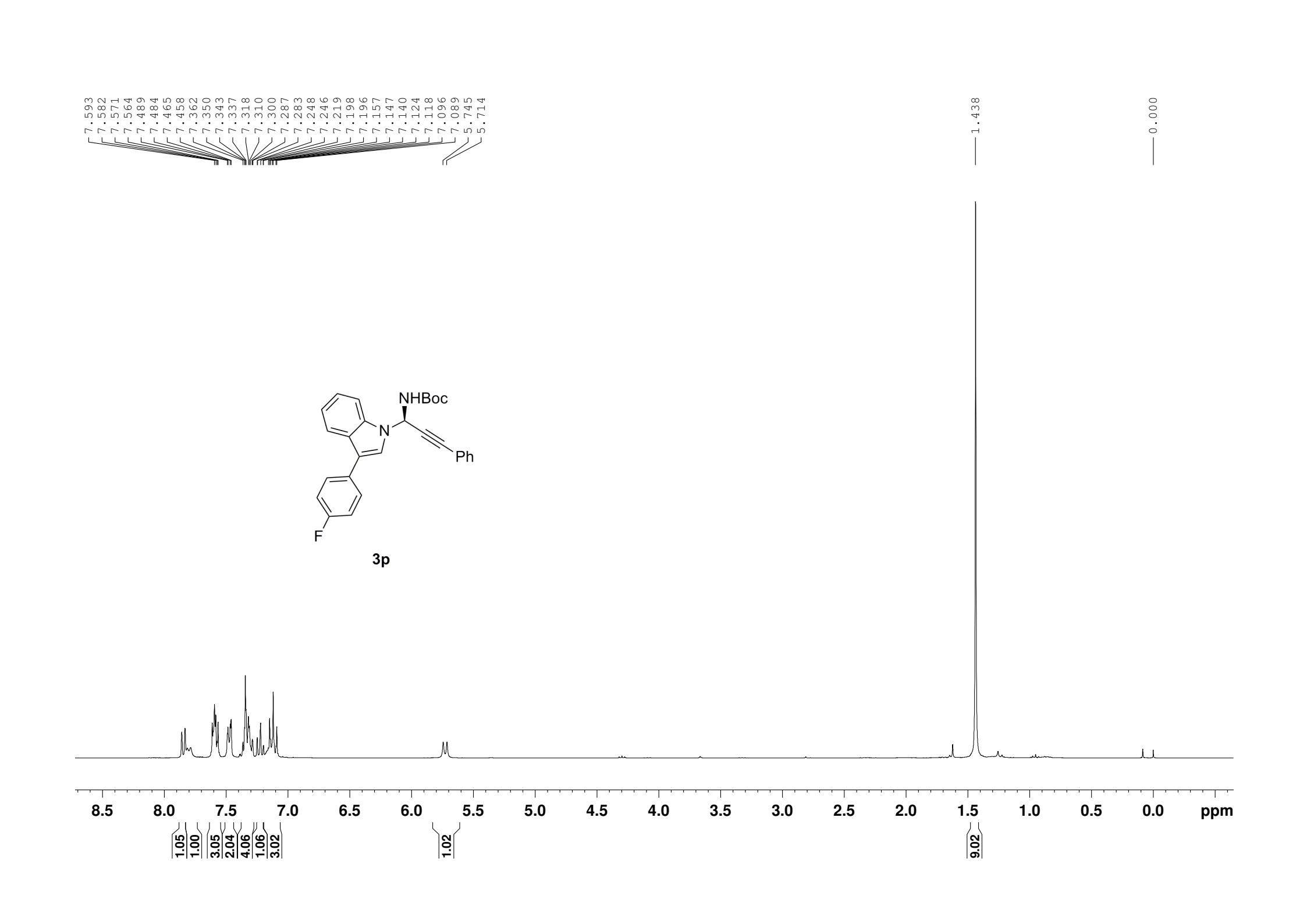
ppm

3o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Ph
F
3p
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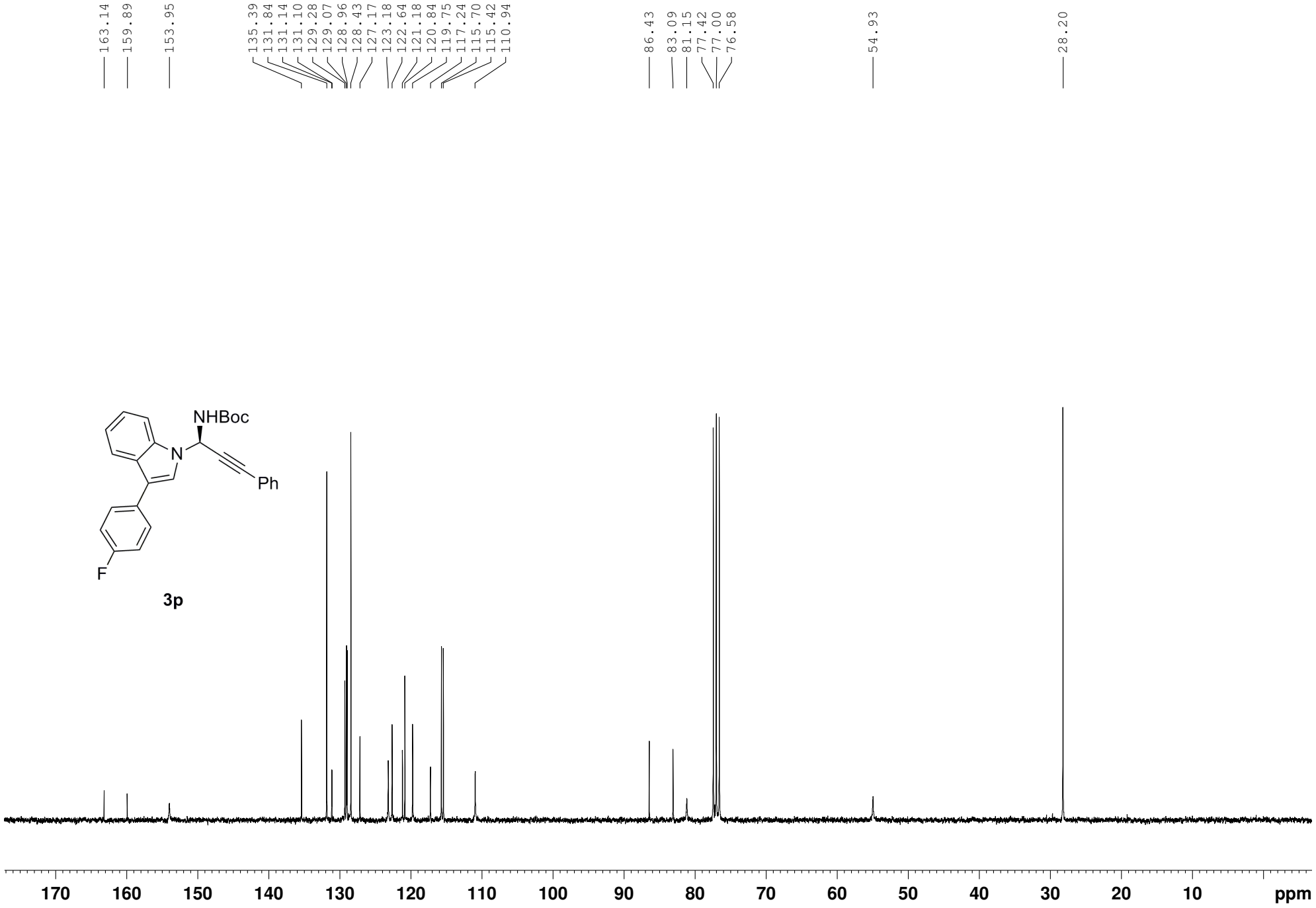
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115.42
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83.09
81.15
77.42
77.00
76.58
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N
Ph
F
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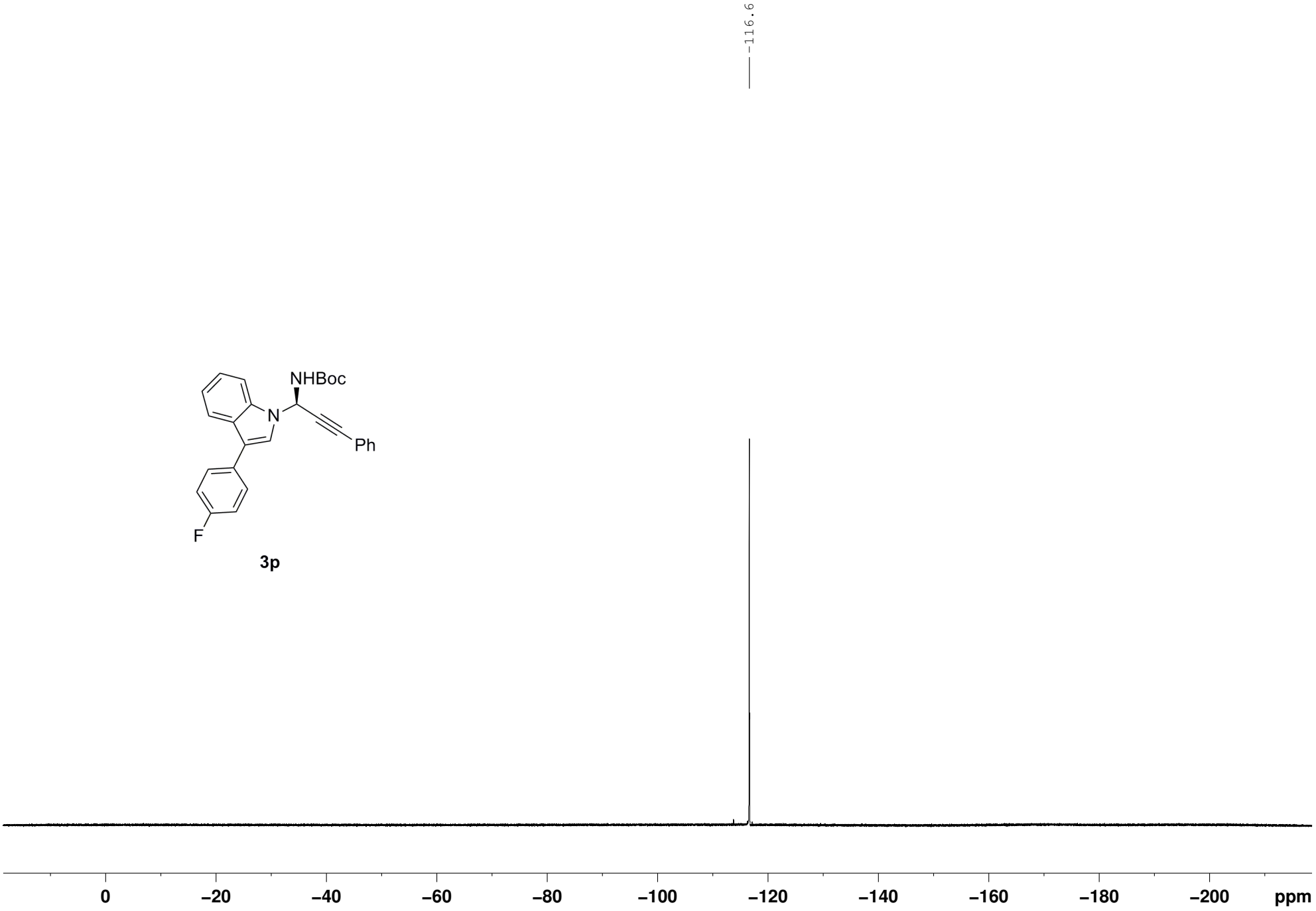
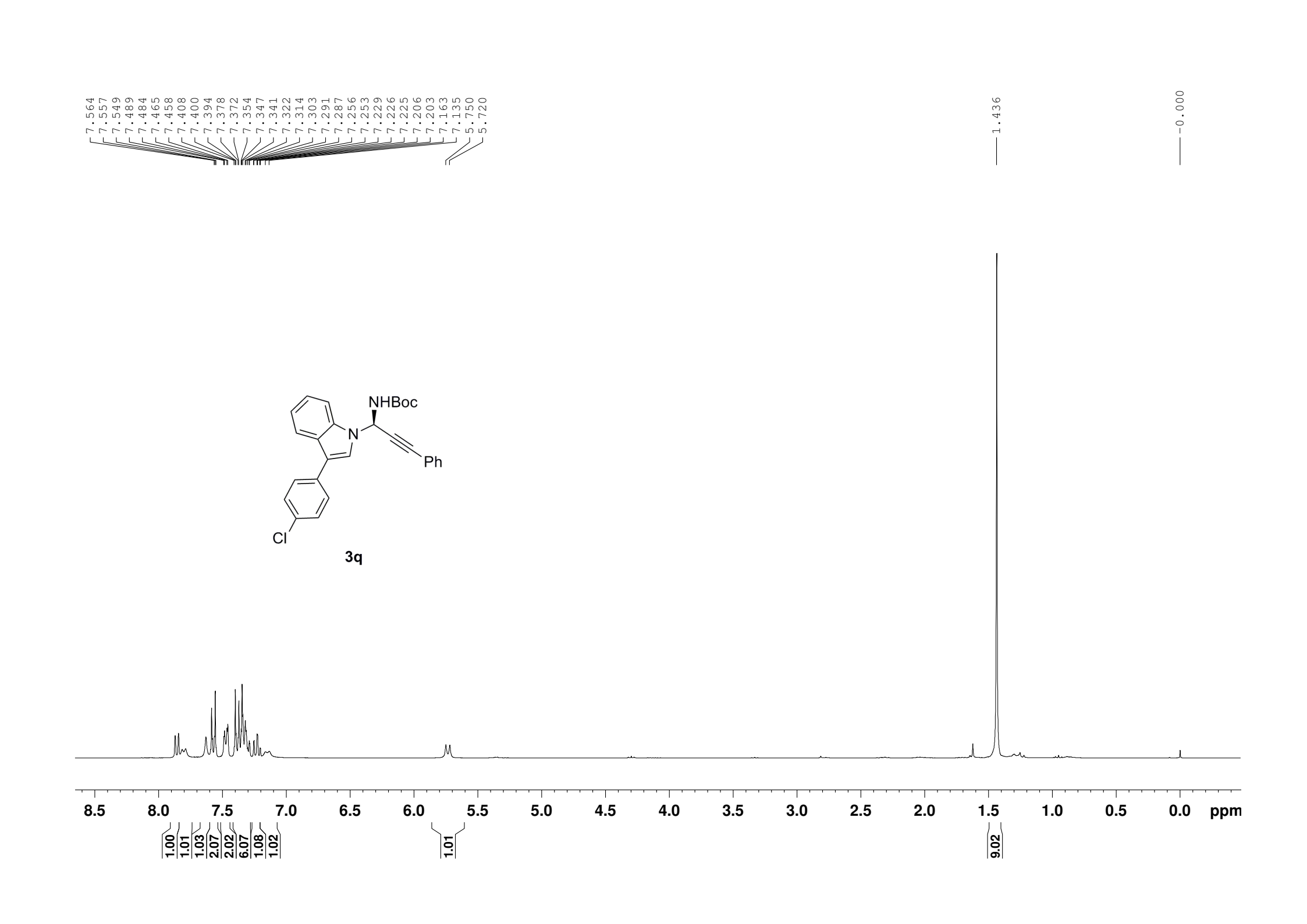
ppm

3p

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7.347
7.341
7.322
7.314
7.303
7.291
7.287
7.256
7.253
7.229
7.226
7.225
7.206
7.203
7.163
7.135
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5.720
1.436
0.000
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Ph
Cl
3q
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6.0
5.5
5.0
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3.0
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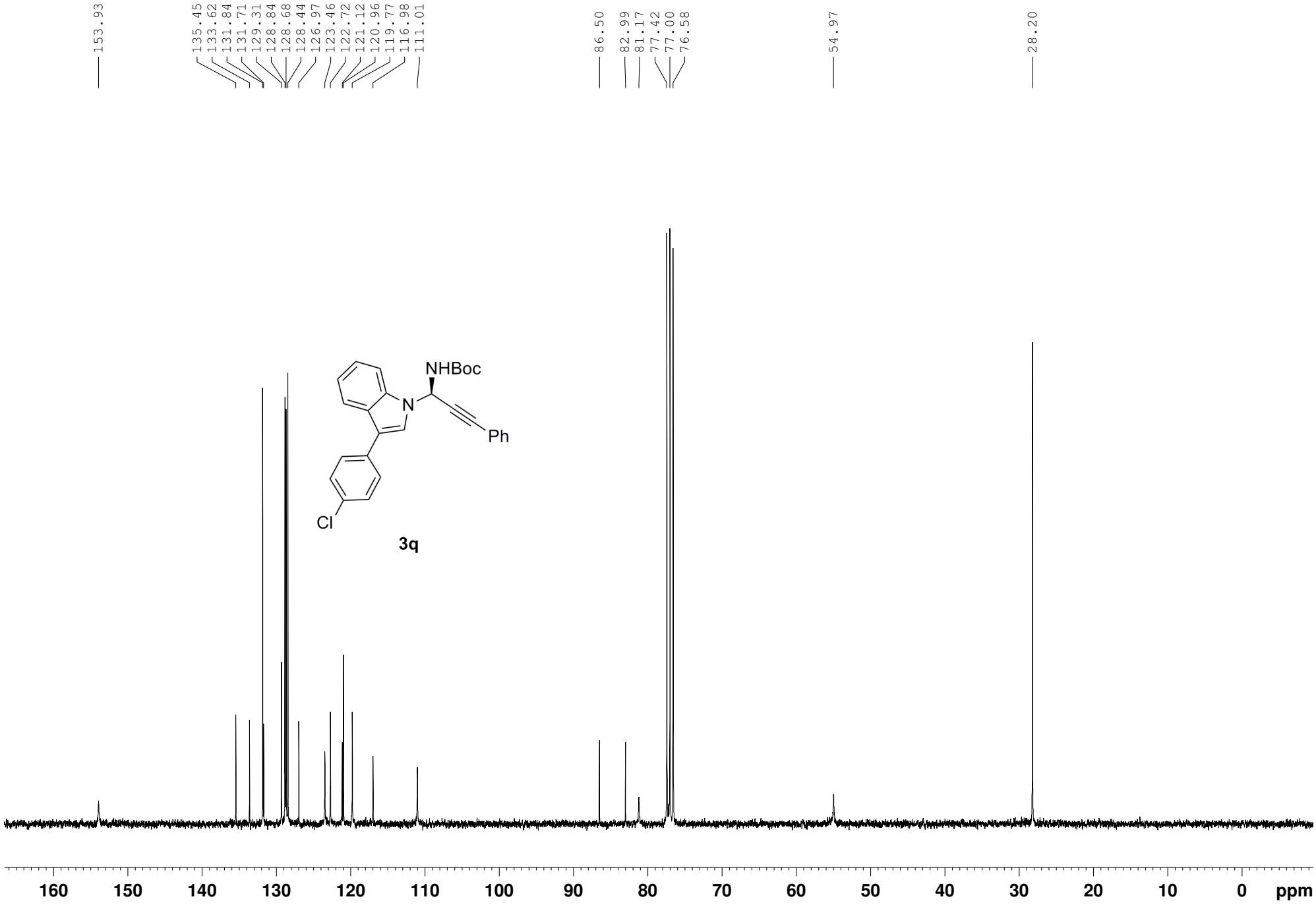
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N
Ph
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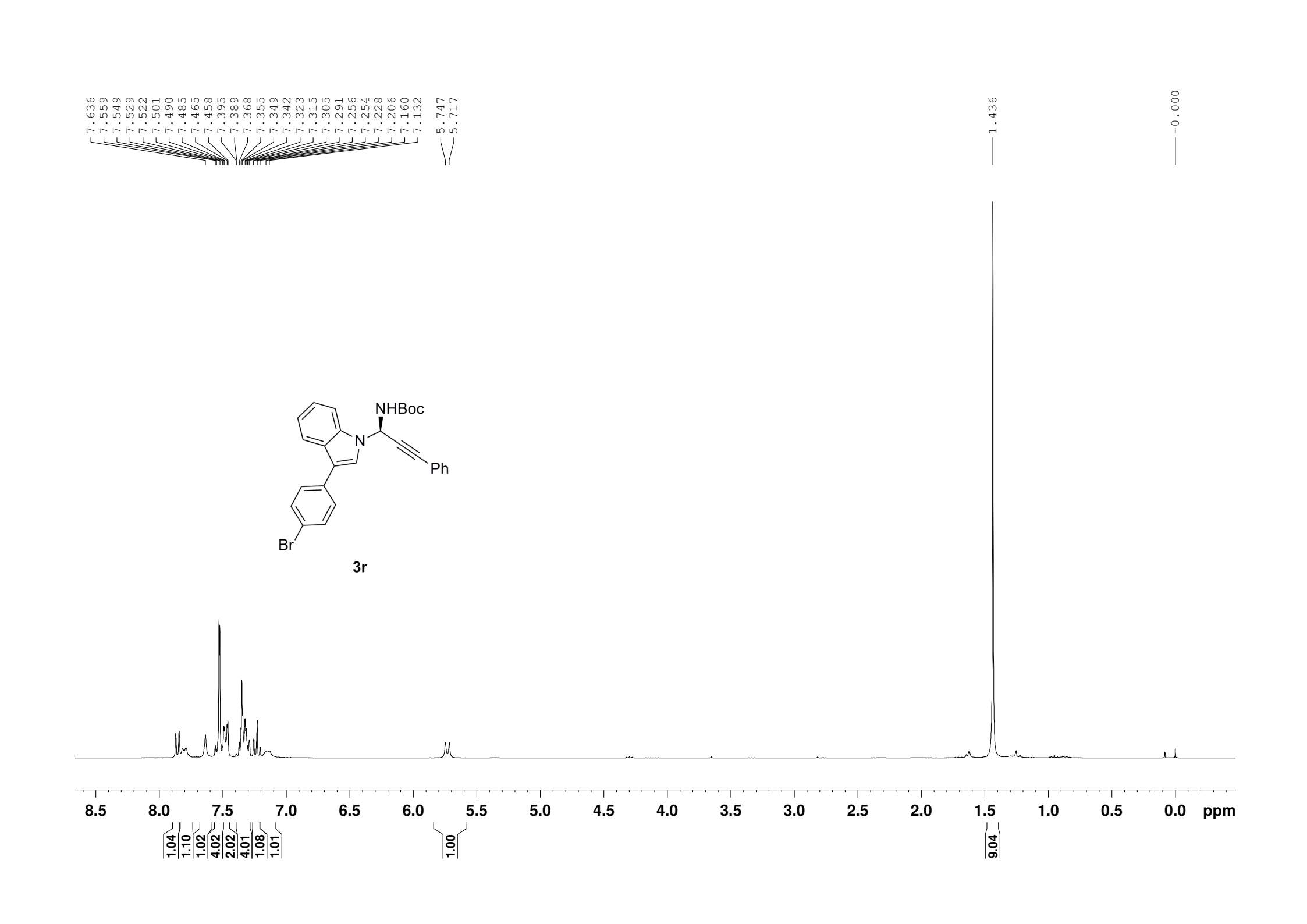
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7.315
7.305
7.291
7.256
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7.228
7.206
7.160
7.132
5.747
5.717
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N
Ph
Br
3r
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5.0
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4.0
3.5
3.0
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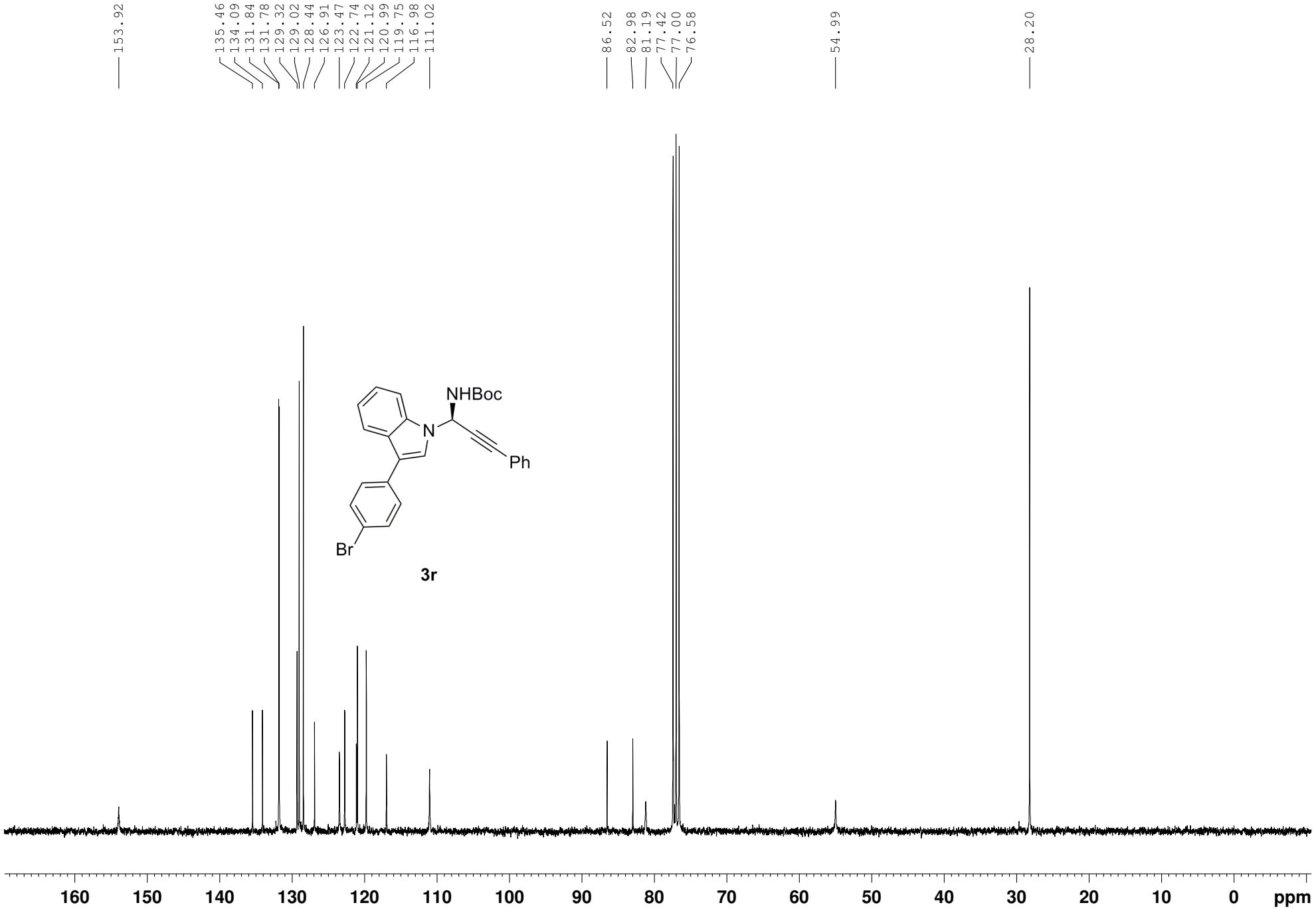
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116.98
111.02
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81.19
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77.00
76.58
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N
Ph
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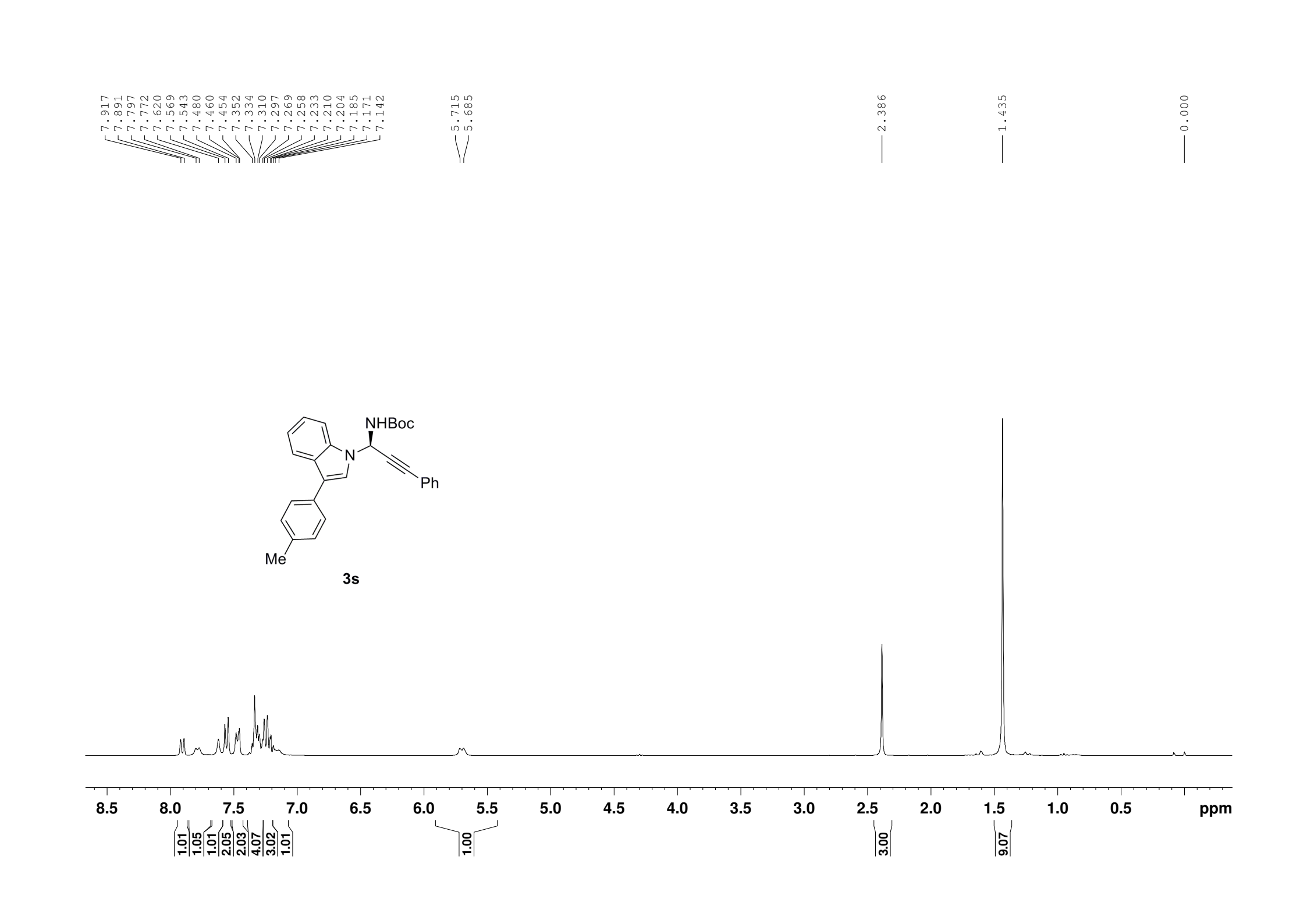
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7.334
7.310
7.297
7.269
7.258
7.233
7.210
7.204
7.185
7.171
7.142
5.715
5.685
2.386
1.435
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NHBoc
N
Ph
Me
3s
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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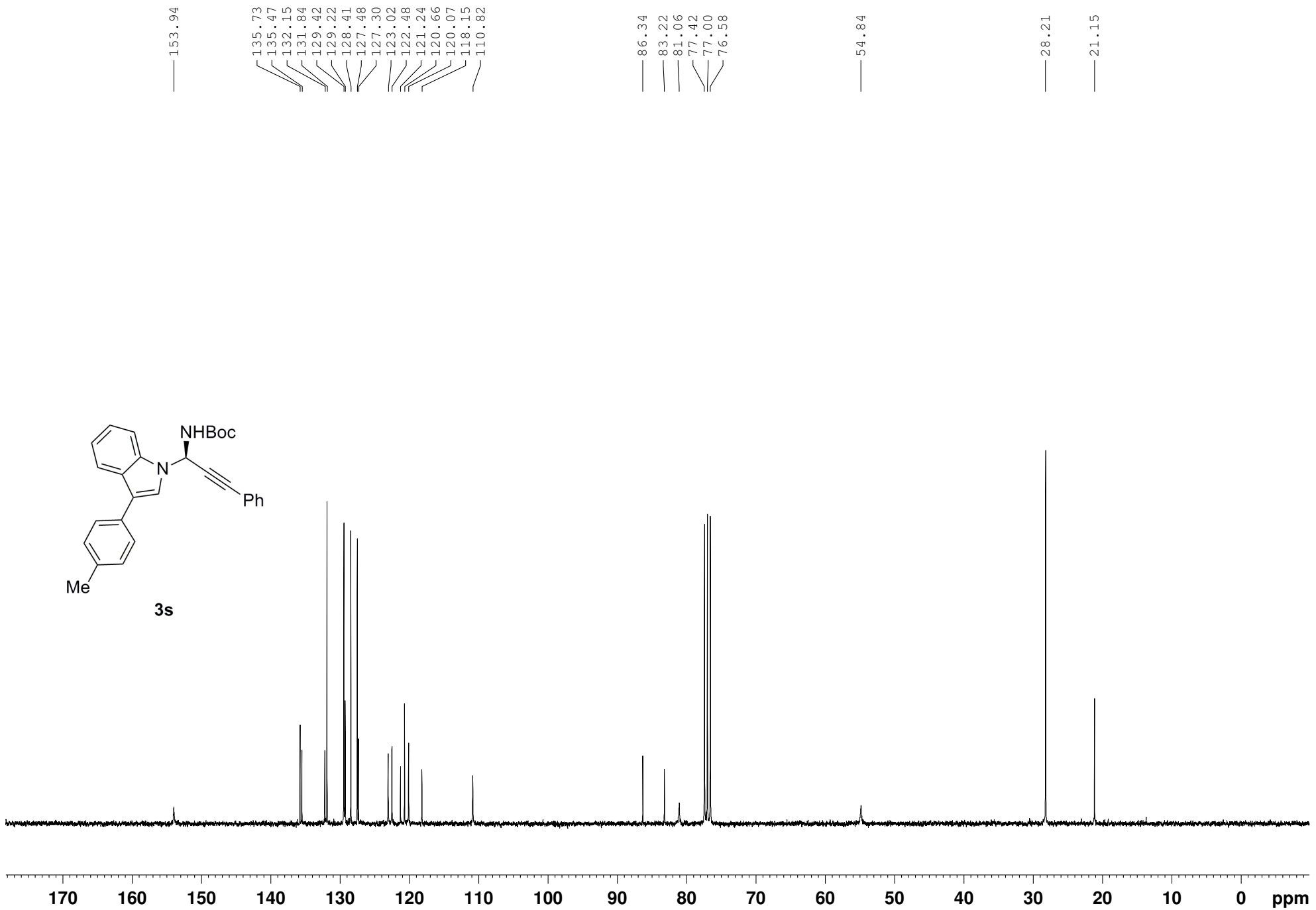
2.05
2.03
4.07
3.02
1.01
1.00
3.00
9.07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120.66
120.07
118.15
110.82
86.34
83.22
81.06
77.42
77.00
76.58
54.84
28.21
21.15
NHBoc
N
Ph
Me
3s
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140
130
120
110
100
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80
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60
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20
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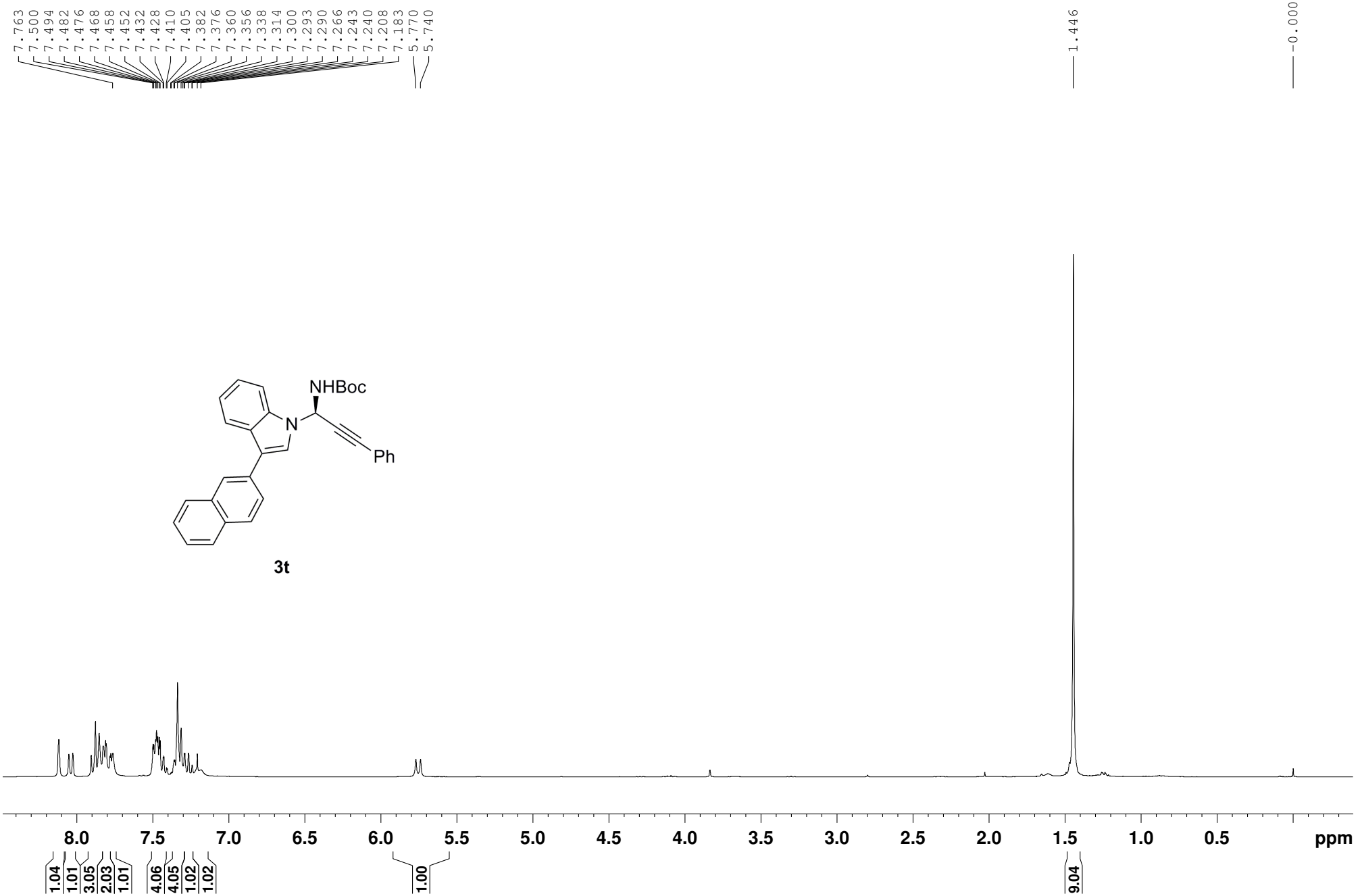
ppm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7.405
7.382
7.376
7.360
7.356
7.338
7.314
7.300
7.293
7.290
7.266
7.243
7.240
7.208
7.183
5.770
5.740
1.446
0.000
NHBoc
N
Ph
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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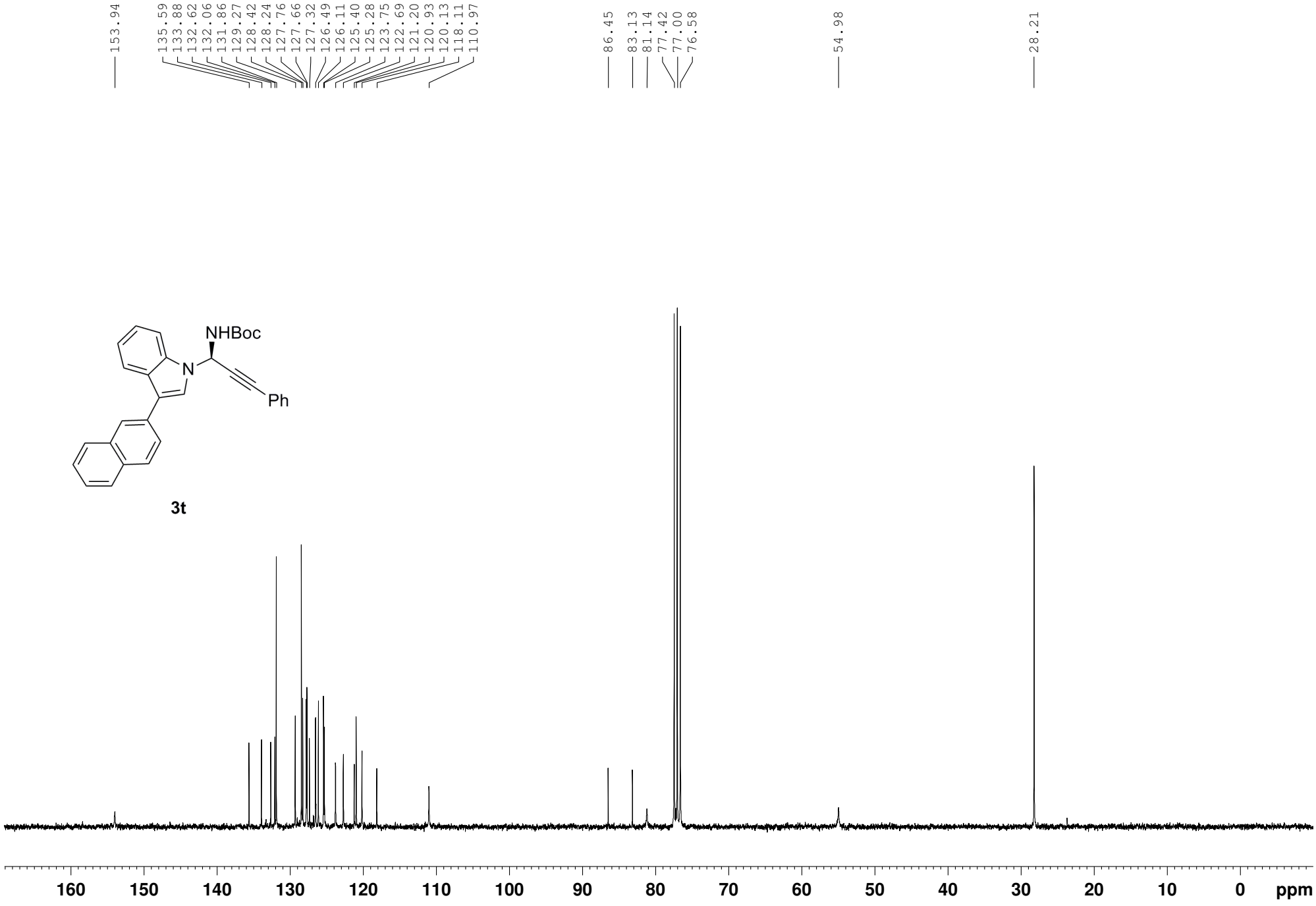
1.01
3.05
2.03
1.01
4.06
4.05
1.02
1.02
1.00
9.04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126.49
126.11
125.40
125.28
123.75
122.69
121.20
120.93
120.13
118.11
110.97
86.45
83.13
81.14
77.42
77.00
76.58
54.98
28.21
NHBoc
N
Ph
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140
130
120
110
100
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50
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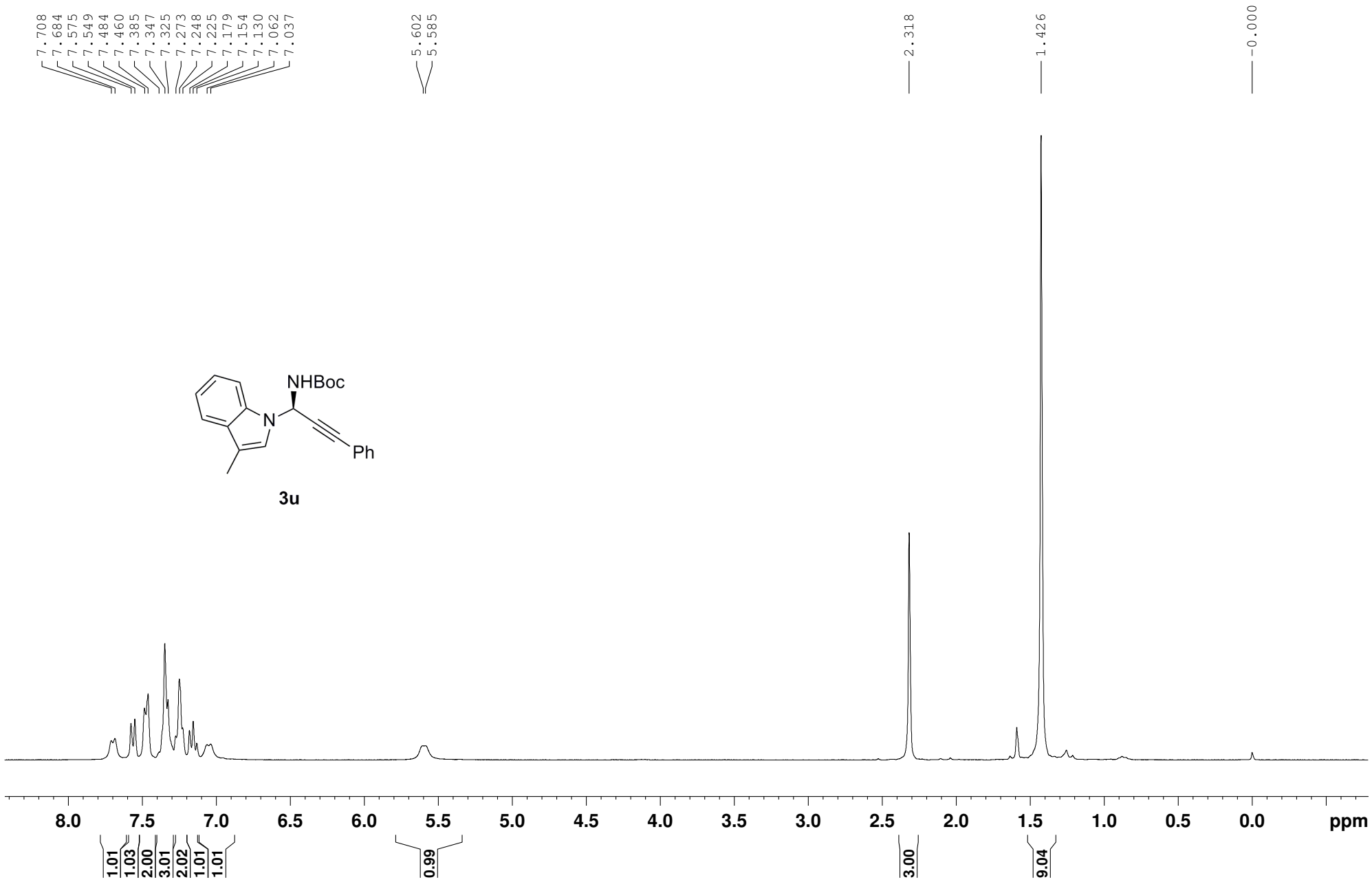
20
10
0
ppm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7.154
7.130
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5.602
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1.426
0.000
NHBoc
N
Ph
3u
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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3.01
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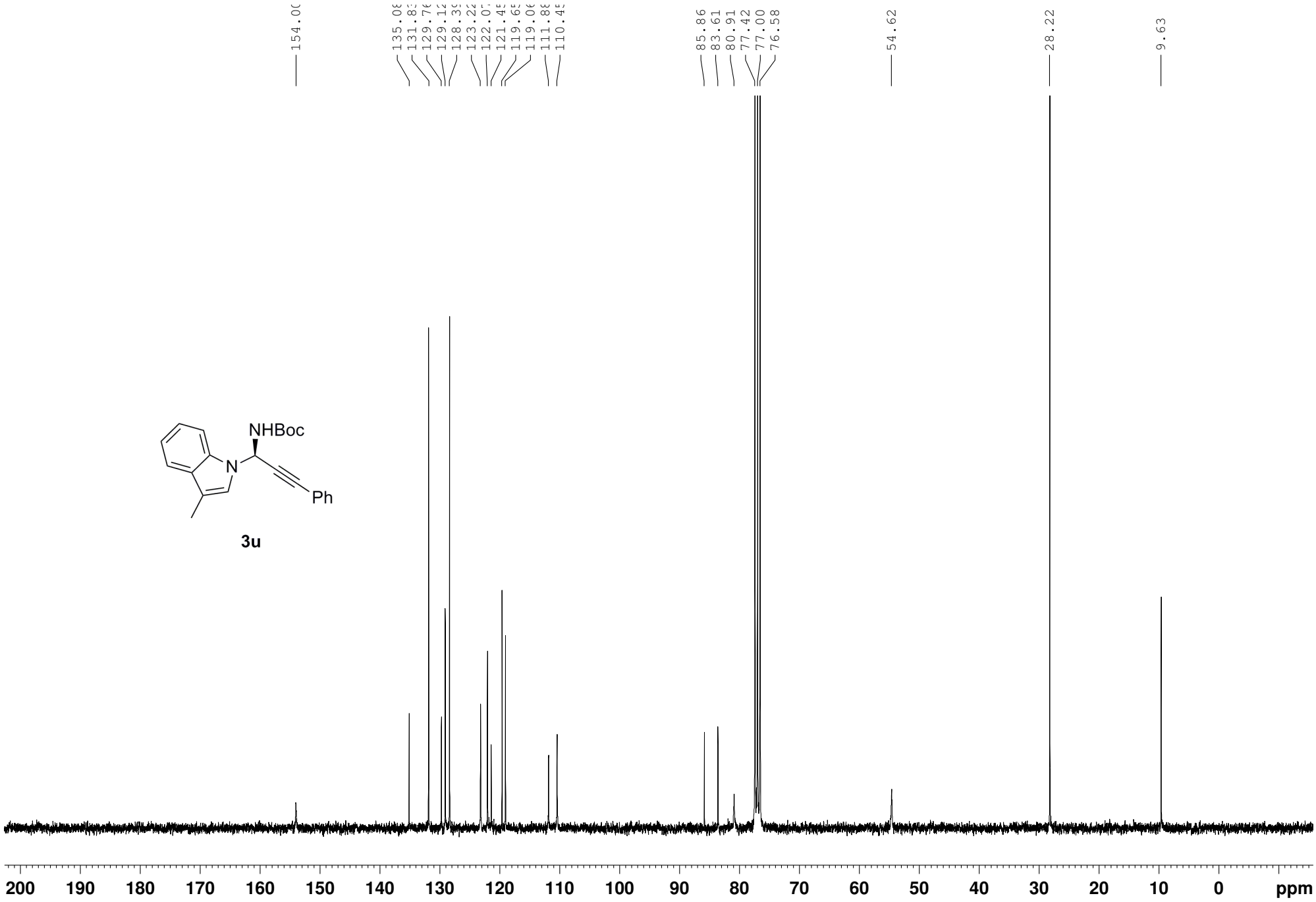
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122.07
121.45
119.65
119.06
111.88
110.45
85.86
83.61
80.91
77.42
77.00
76.58
54.62
28.22
9.63
NHBoc
N
Ph
3u
200
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50
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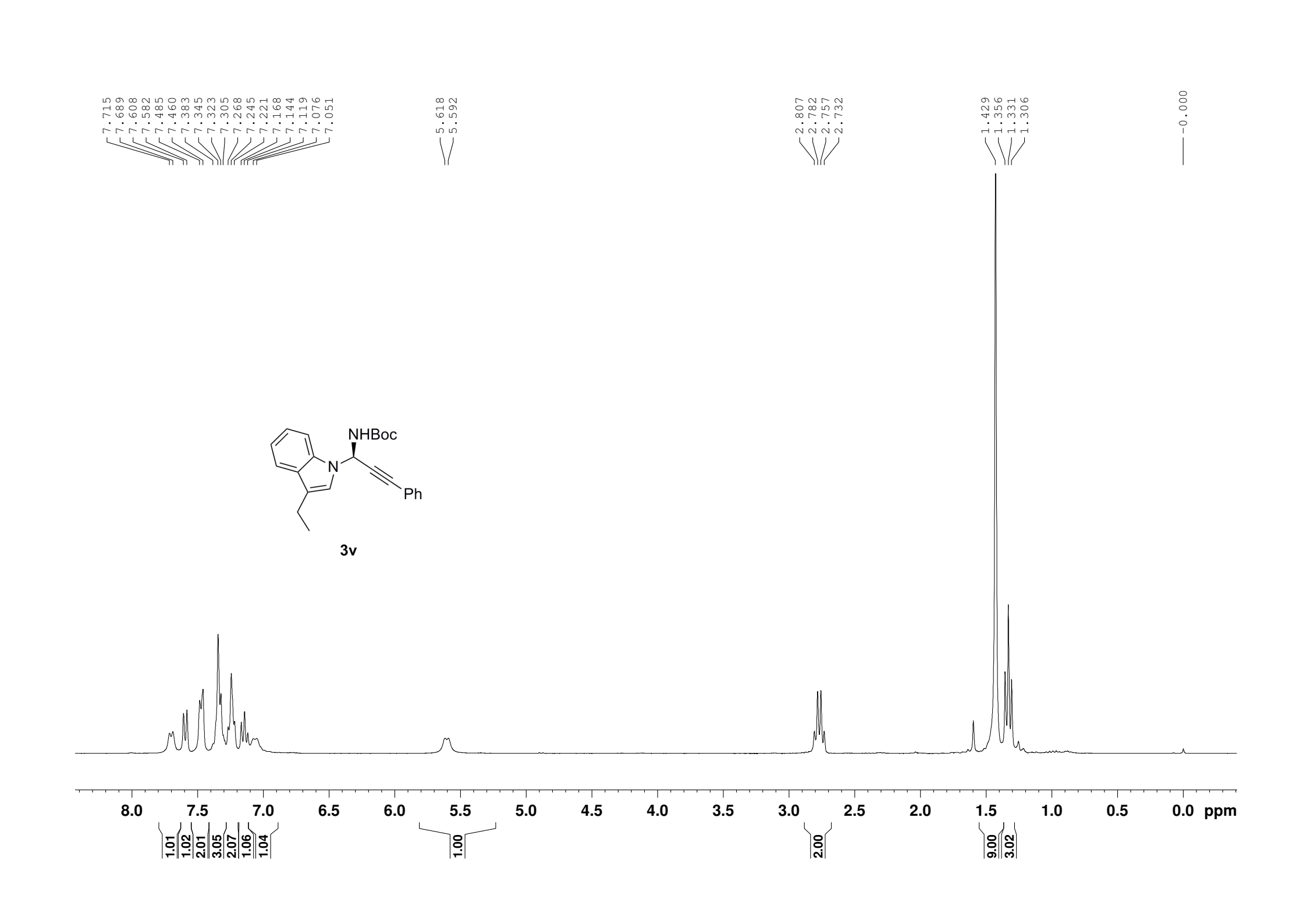
ppm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7.245
7.221
7.168
7.144
7.119
7.076
7.051
5.618
5.592
2.807
2.782
2.757
2.732
1.429
1.356
1.331
1.306
0.000
NHBoc
N
Ph
3v
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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2.01
3.05
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1.06
1.04
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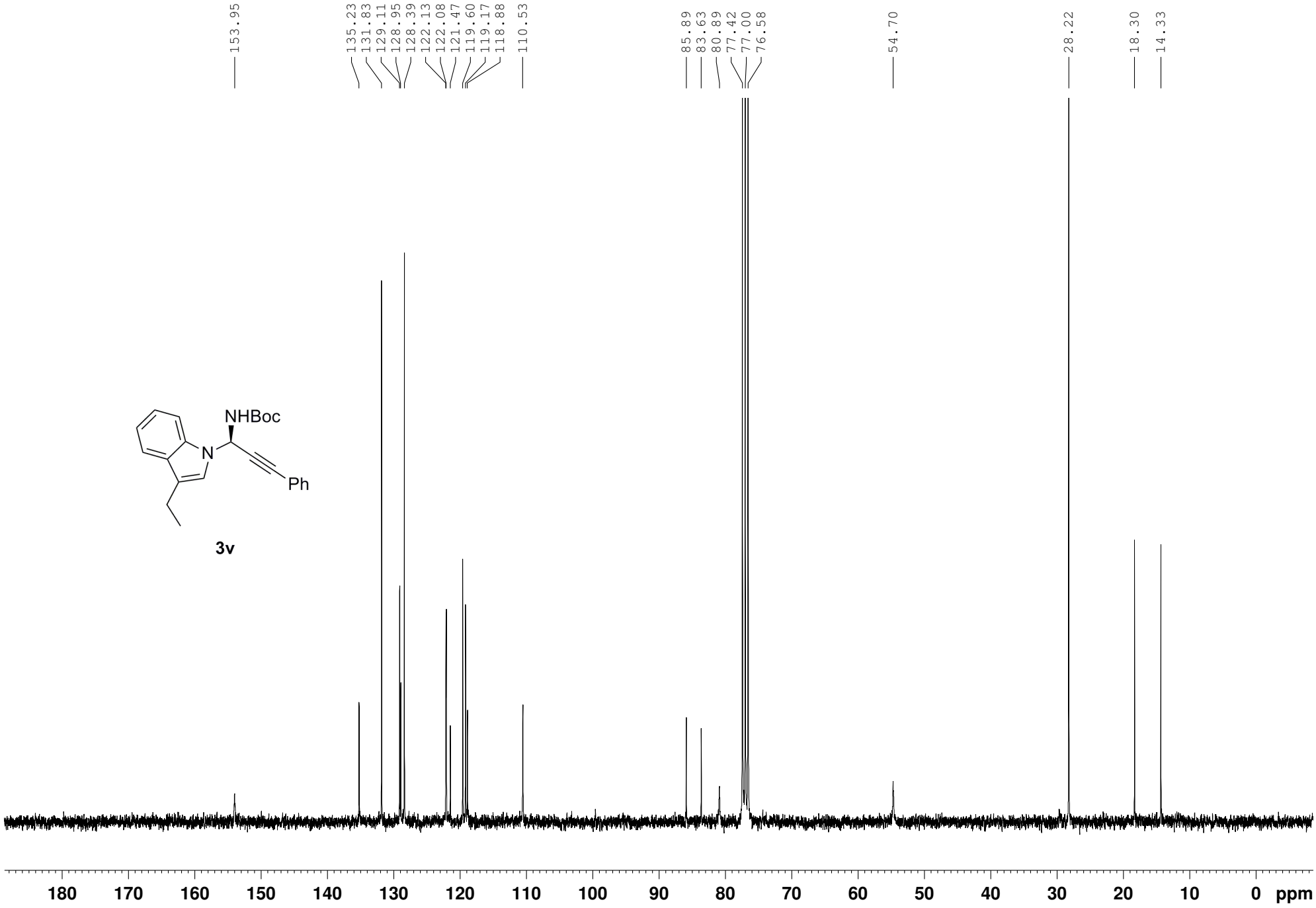
3.02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80.89
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77.00
76.58
54.70
28.22
18.30
14.33
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N
Ph
3v
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130
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50
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20
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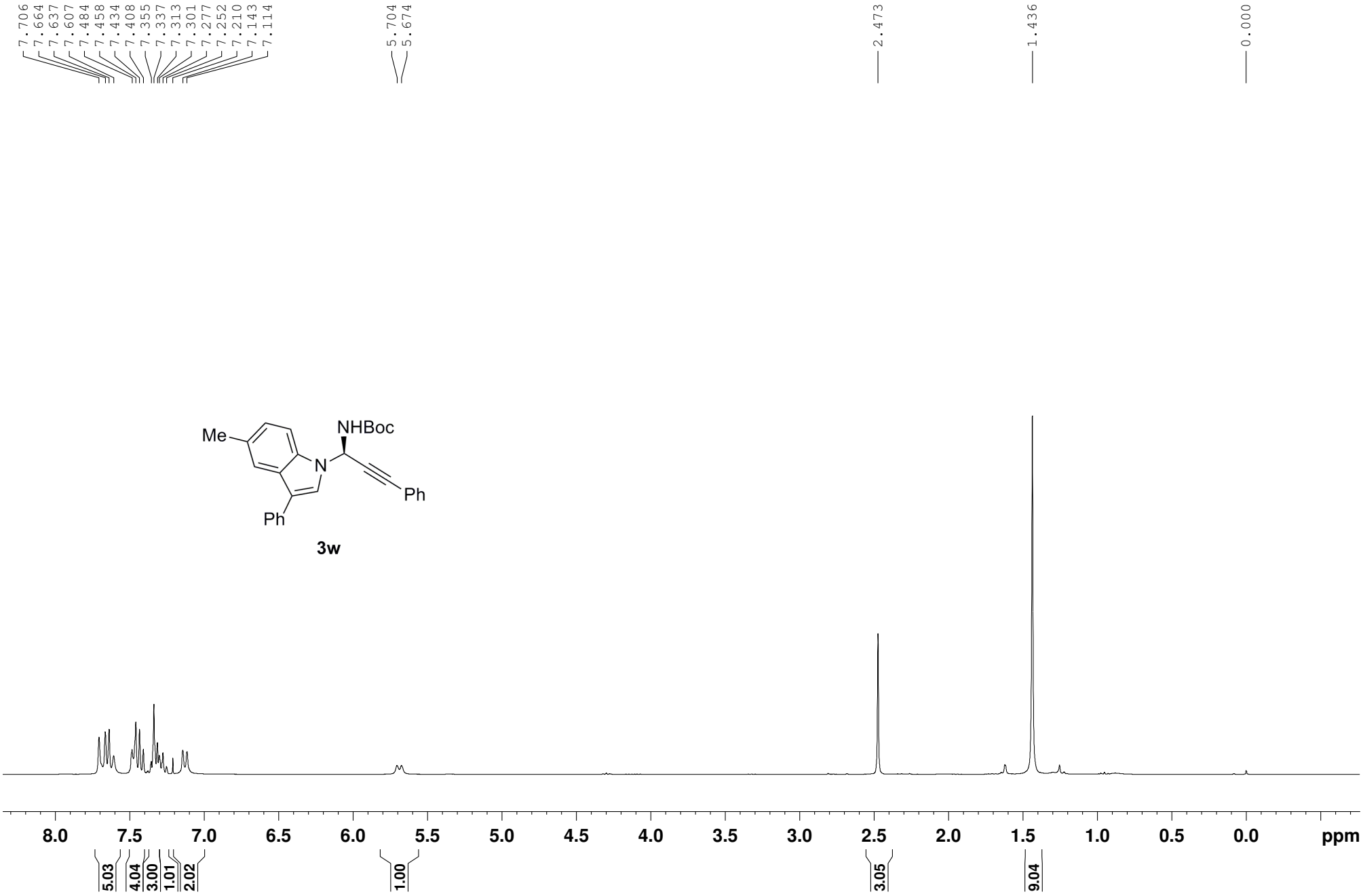
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7.277
7.252
7.210
7.143
7.114
5.704
5.674
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1.436
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Me
NHBoc
N
Ph
Ph
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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2.02
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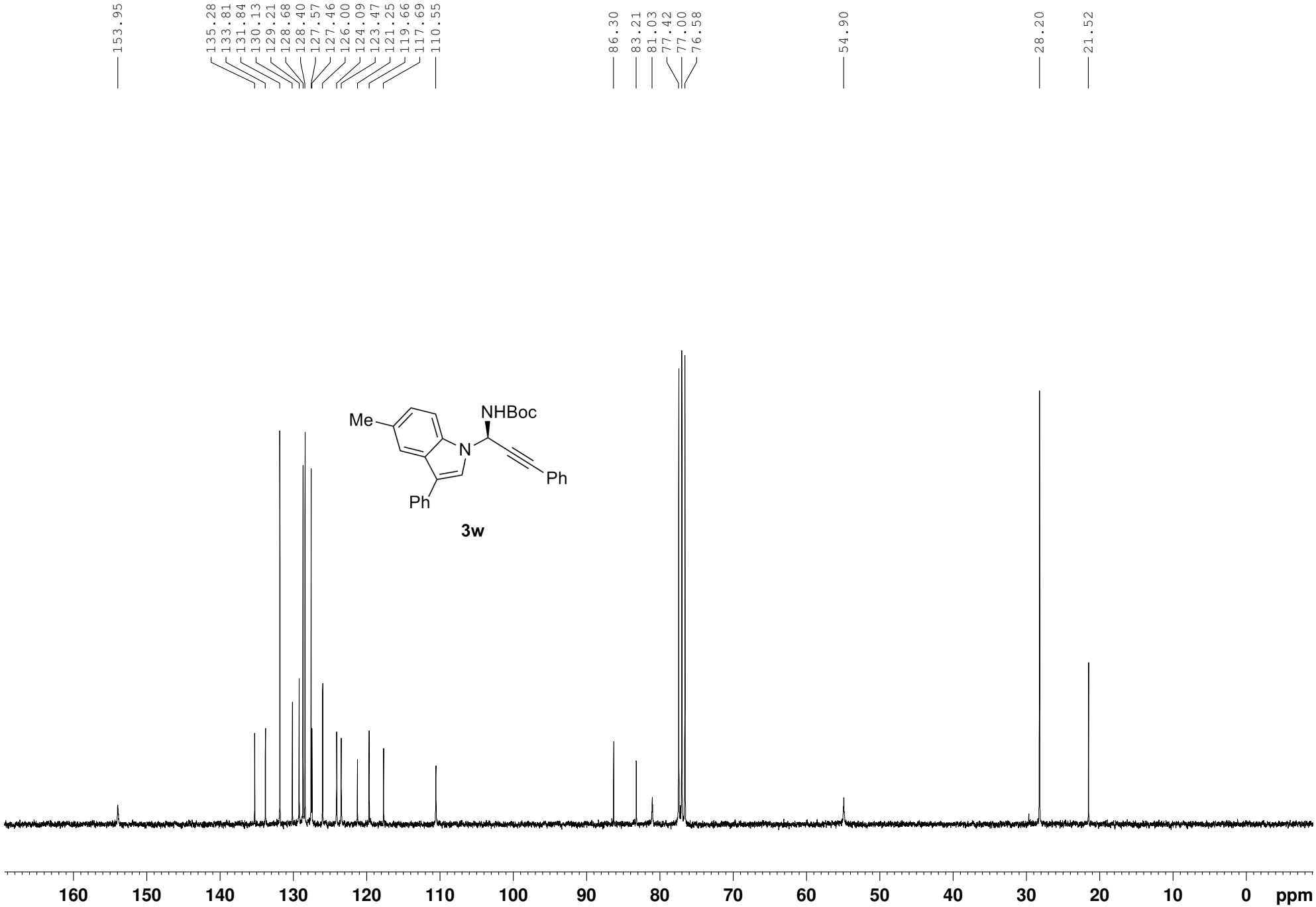
9.04

3w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123.47
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117.69
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86.30
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77.00
76.58
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21.52
Me
NHBoc
N
Ph
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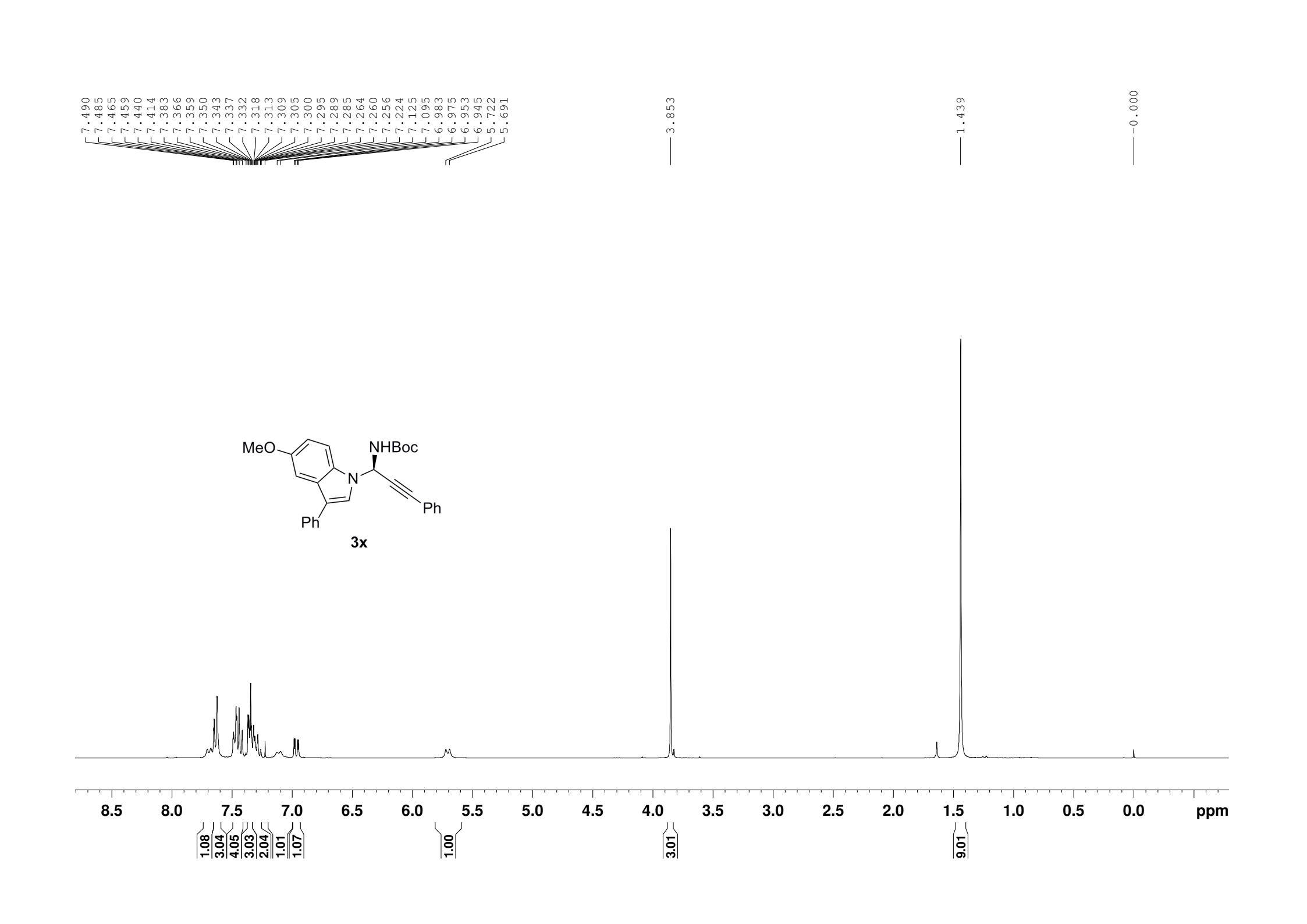
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7.350
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7.318
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7.300
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7.285
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7.260
7.256
7.224
7.125
7.095
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6.975
6.953
6.945
5.722
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3.853
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MeO
NHBoc
N
Ph
Ph
3x
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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3.03
2.04
1.01
1.07
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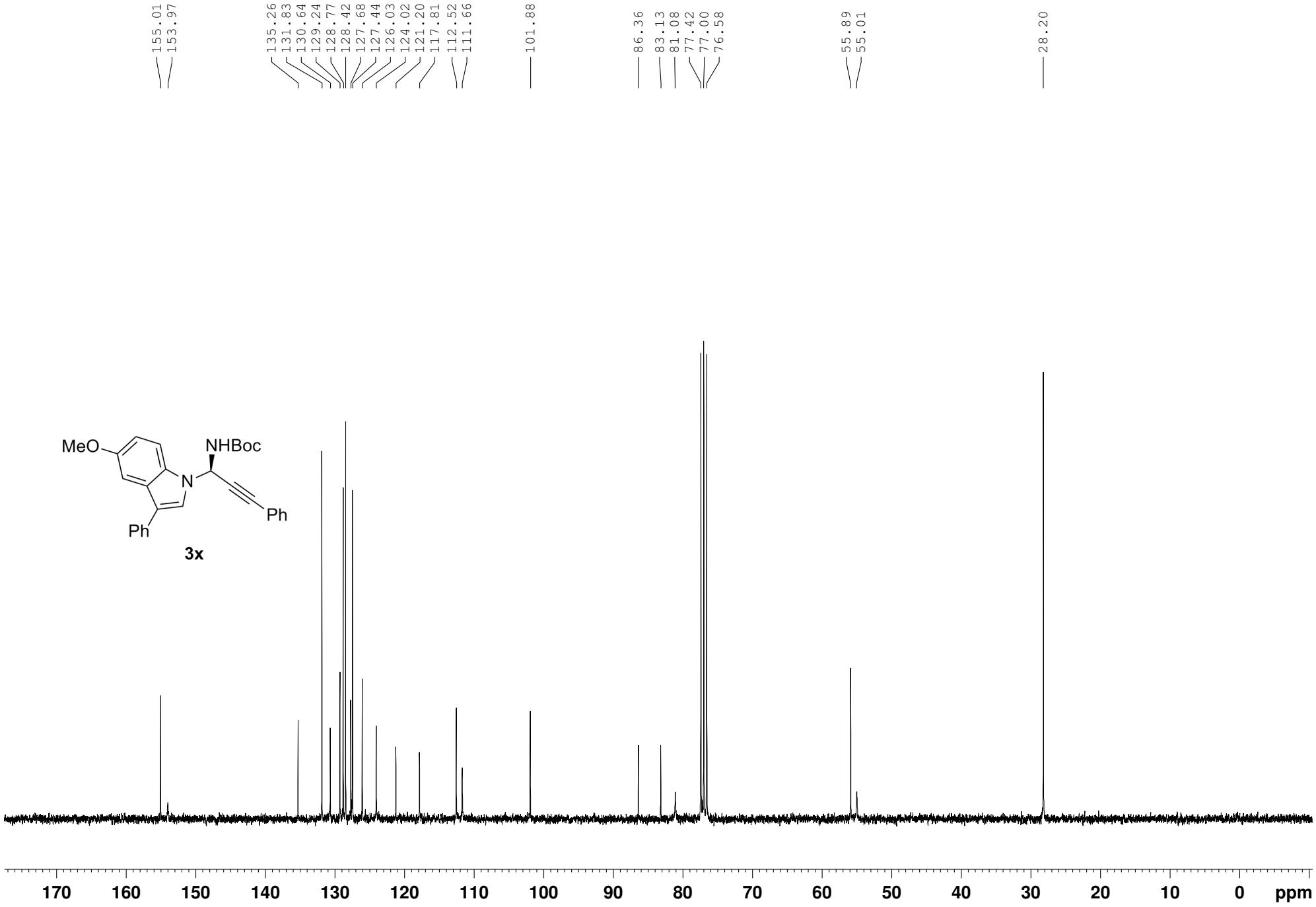
9.01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121.20
117.81
112.52
111.66
101.88
86.36
83.13
81.08
77.42
77.00
76.58
55.89
55.01
28.20
MeO
NHBoc
N
Ph
Ph
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120
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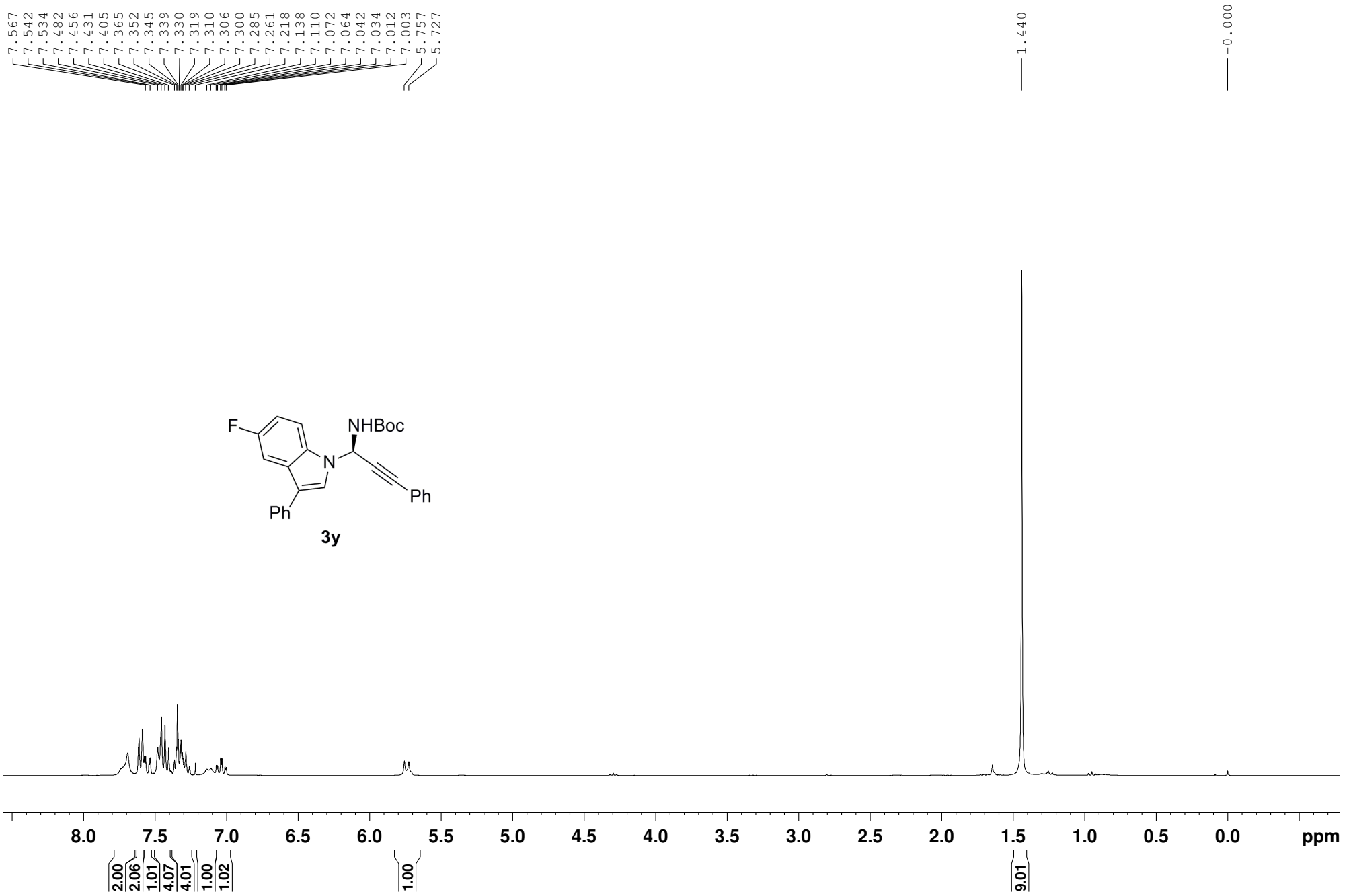
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7.064
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7.003
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5.727
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0.000
F
NHBoc
N
Ph
Ph
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4.0
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4.07
4.01
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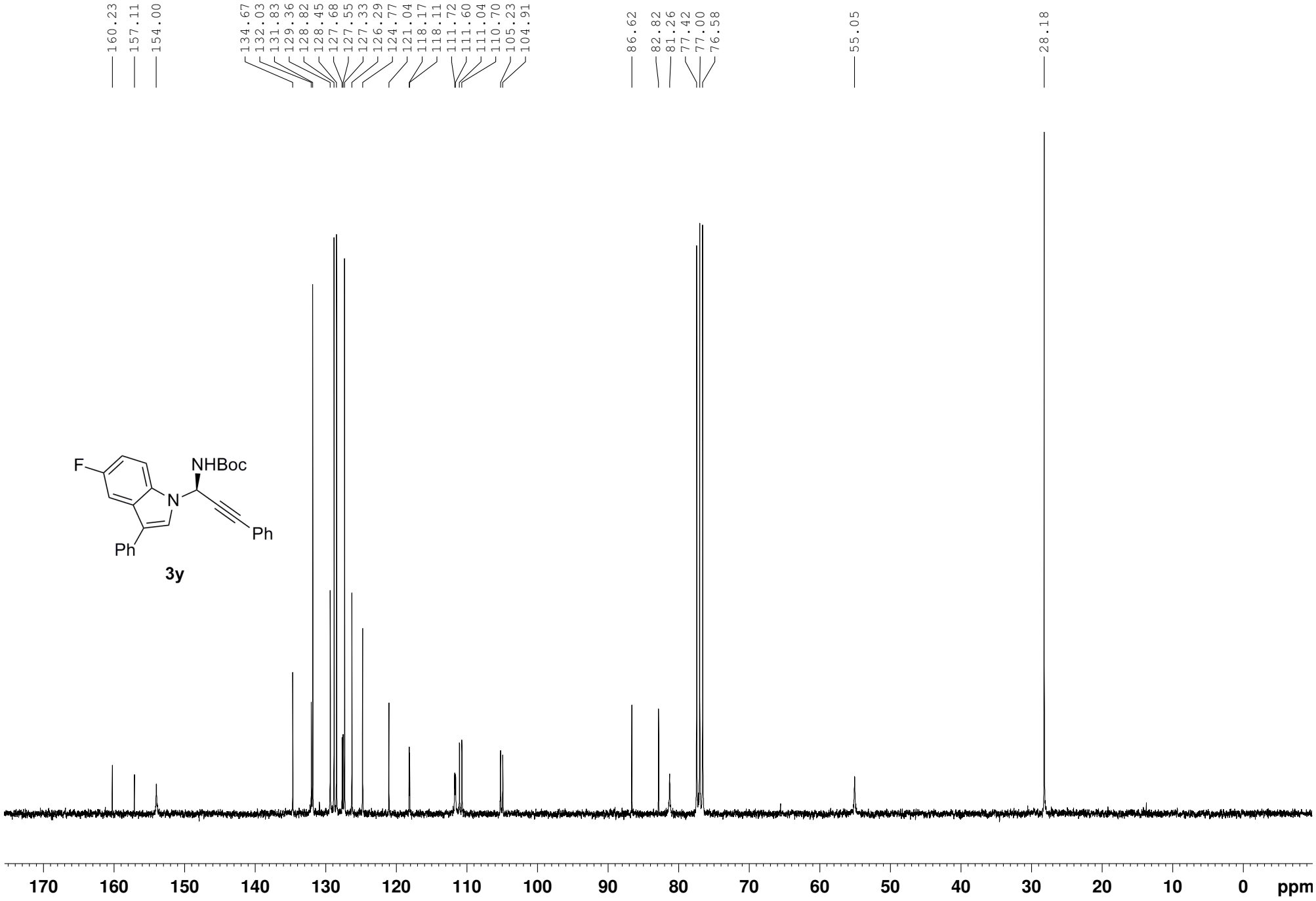
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127.55
127.33
126.29
124.77
121.04
118.17
118.11
111.72
111.60
111.04
110.70
105.23
104.91
86.62
82.82
81.26
77.42
77.00
76.58
55.05
28.18
F
NHBoc
N
Ph
Ph
3y
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150
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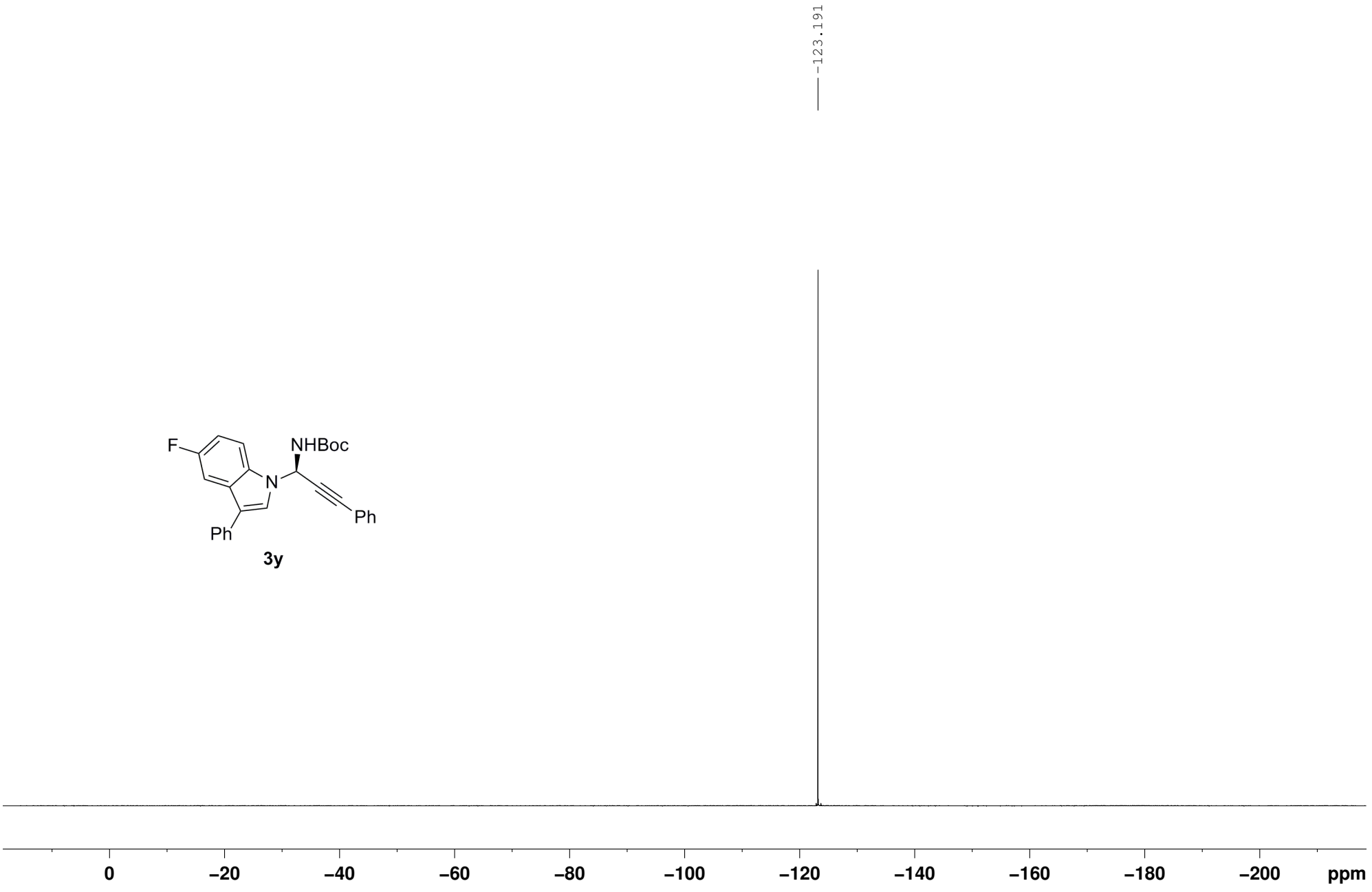
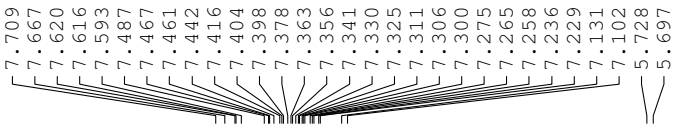
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3y

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7.363
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1.442

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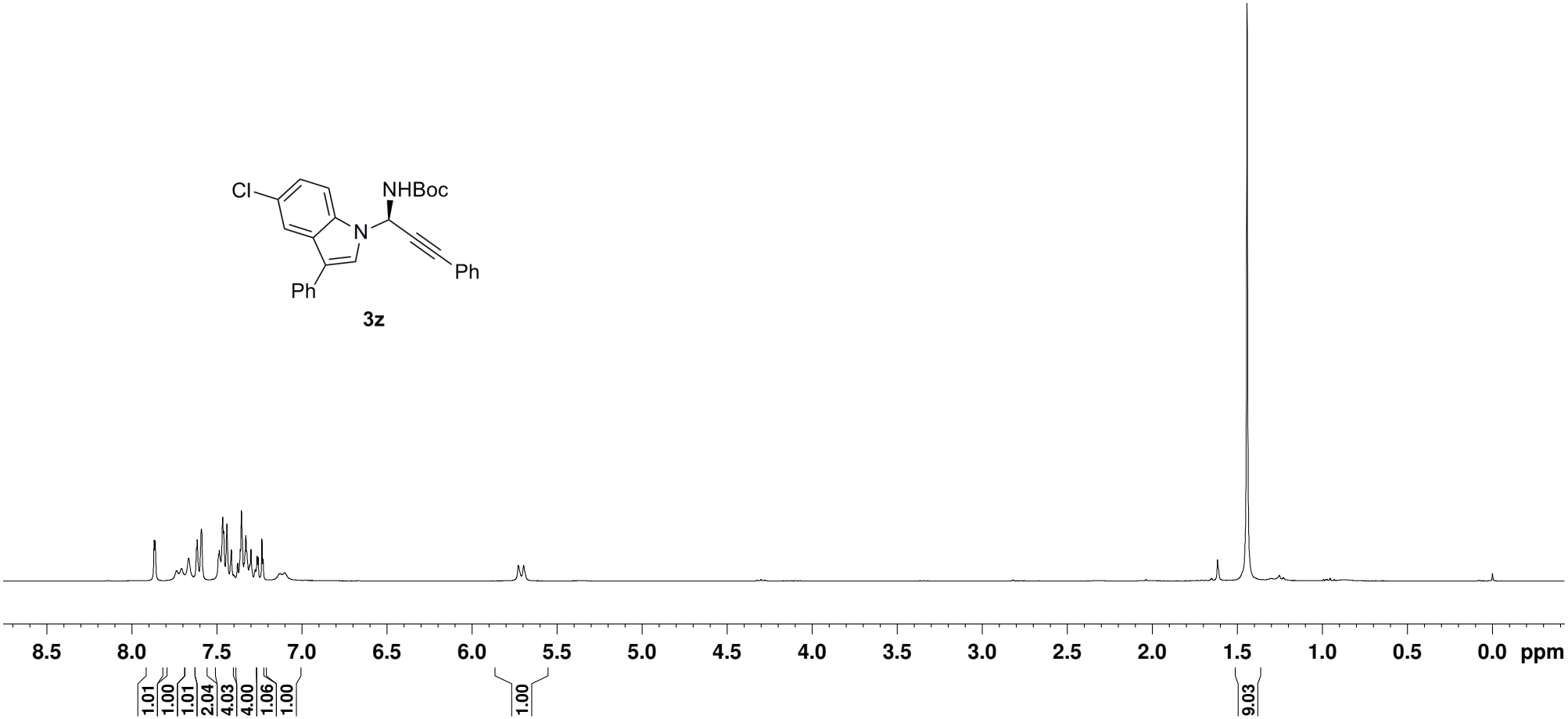
Cl
NHBoc
N
Ph
Ph

3z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0.0
ppm
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1.00
1.01
2.04
4.03
4.00
1.06
1.00
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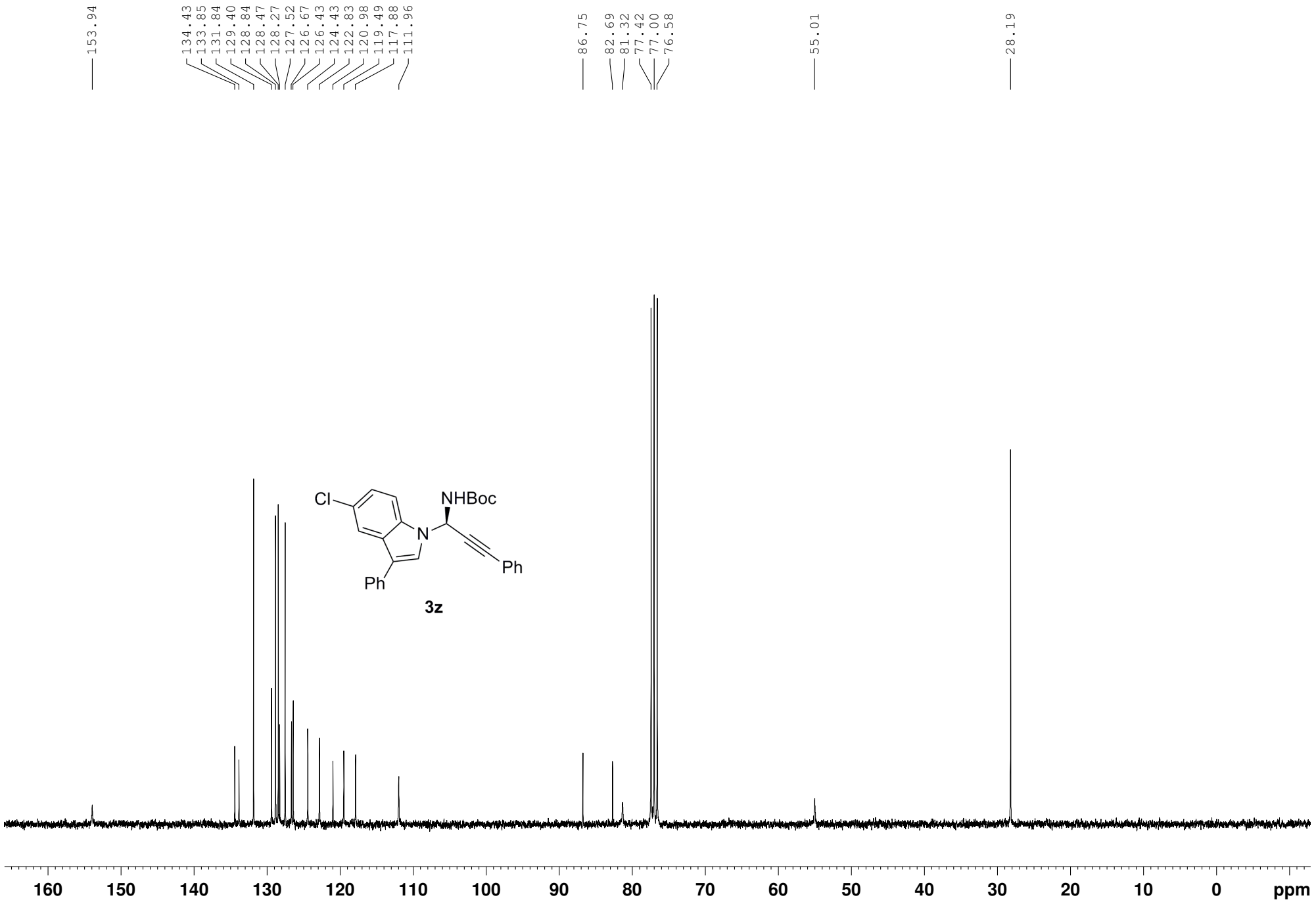
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82.69
81.32
77.42
77.00
76.58
55.01
28.19
Cl
NHBoc
N
Ph
Ph
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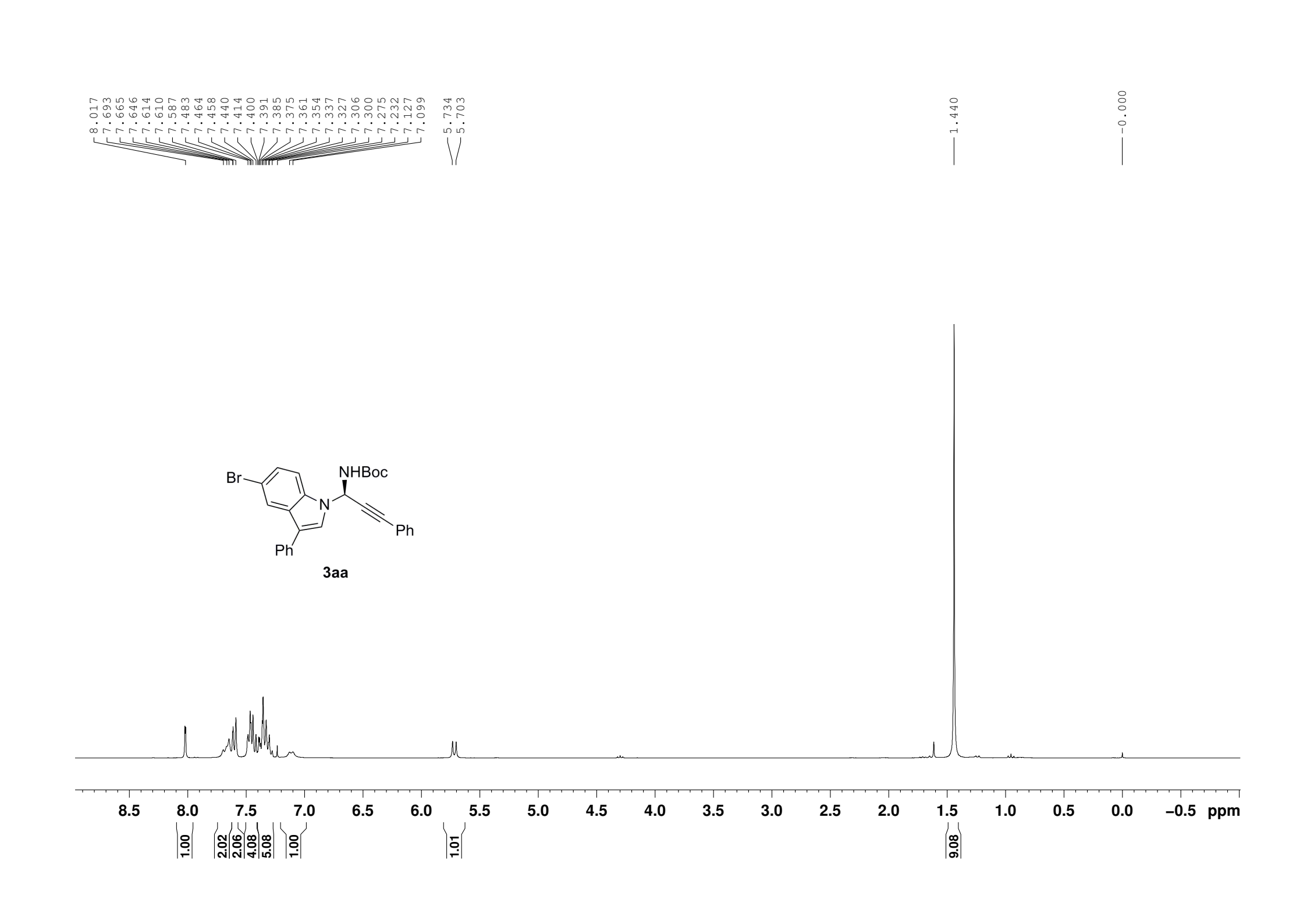
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7.375
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7.300
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7.232
7.127
7.099
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1.440
0.000
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NHBoc
N
Ph
Ph
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7.0
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6.0
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5.0
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3.5
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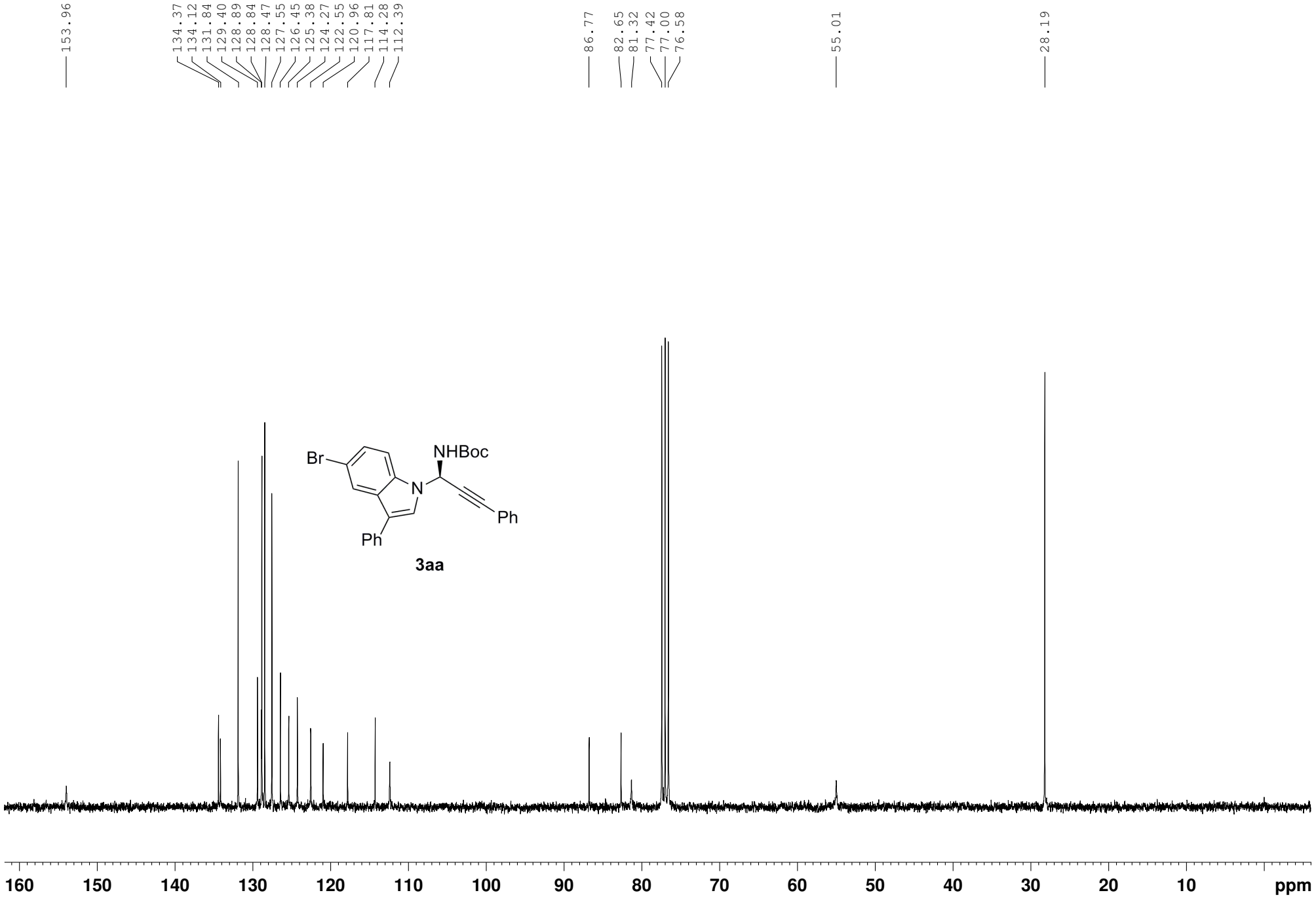
9.08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77.00
76.58
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28.19
Br
NHBoc
N
Ph
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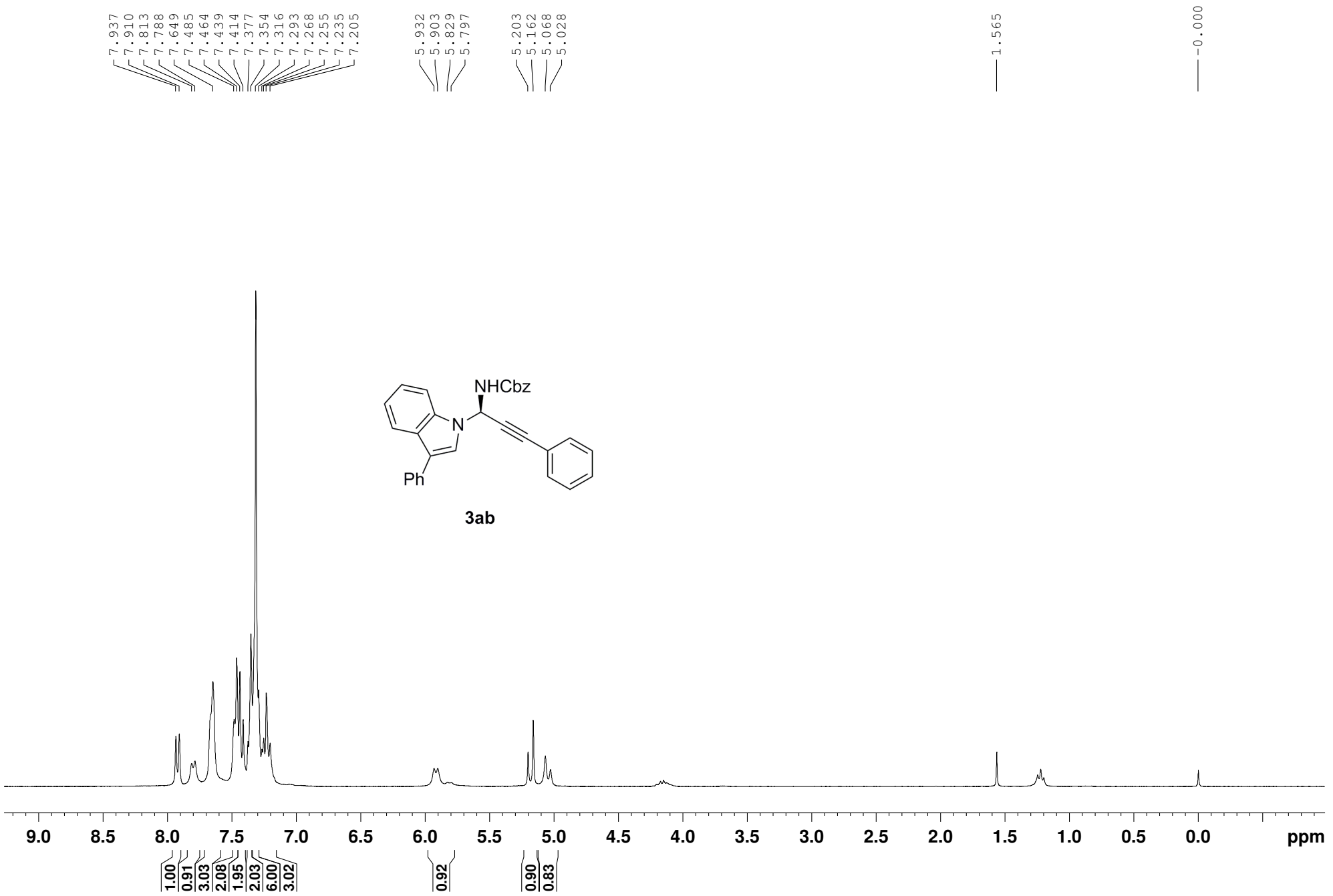
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5.829
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5.203
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5.068
5.028
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N
Ph
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8.5
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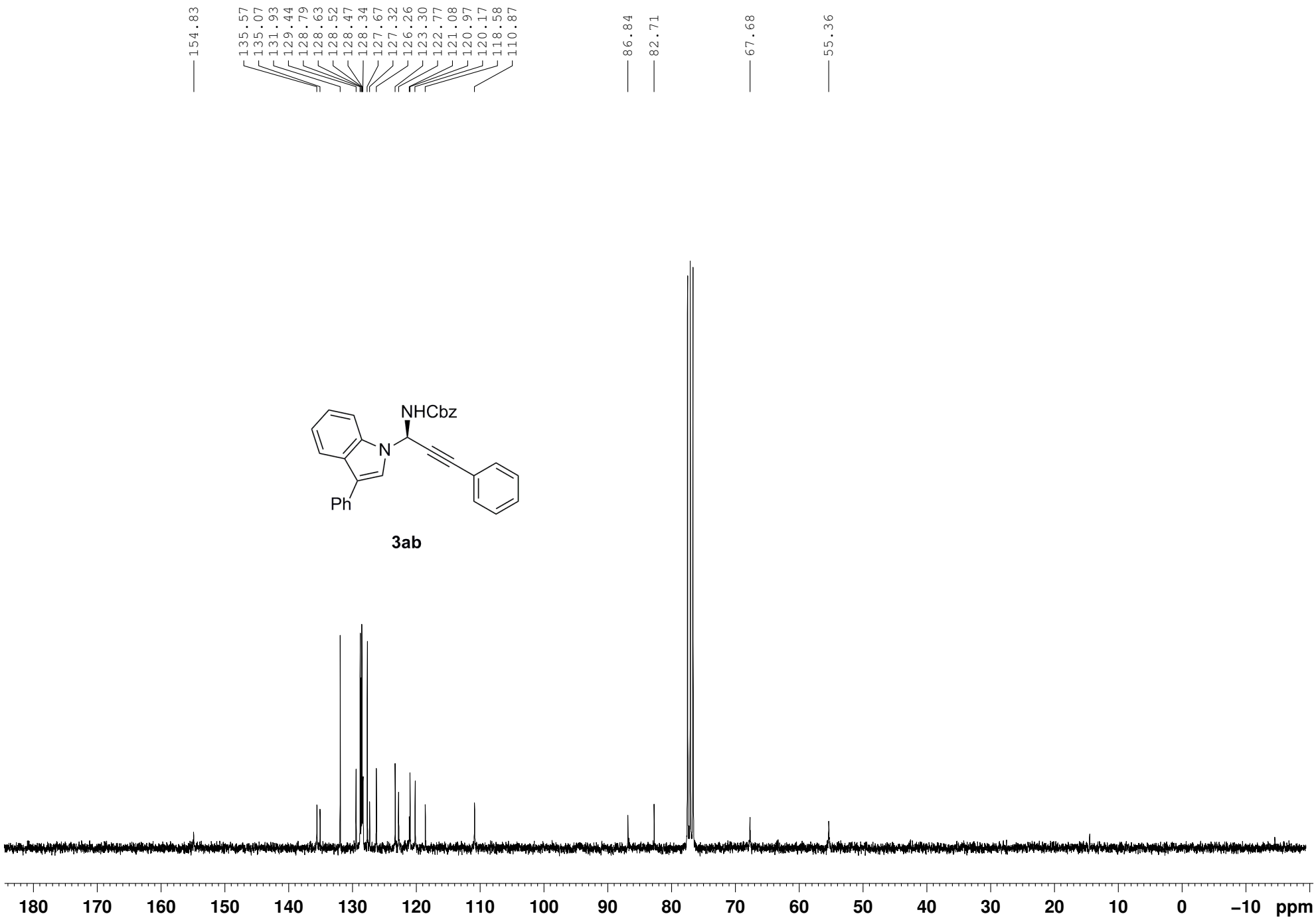
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120.97
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118.58
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67.68
55.36
NHCbz
N
Ph
3ab
180
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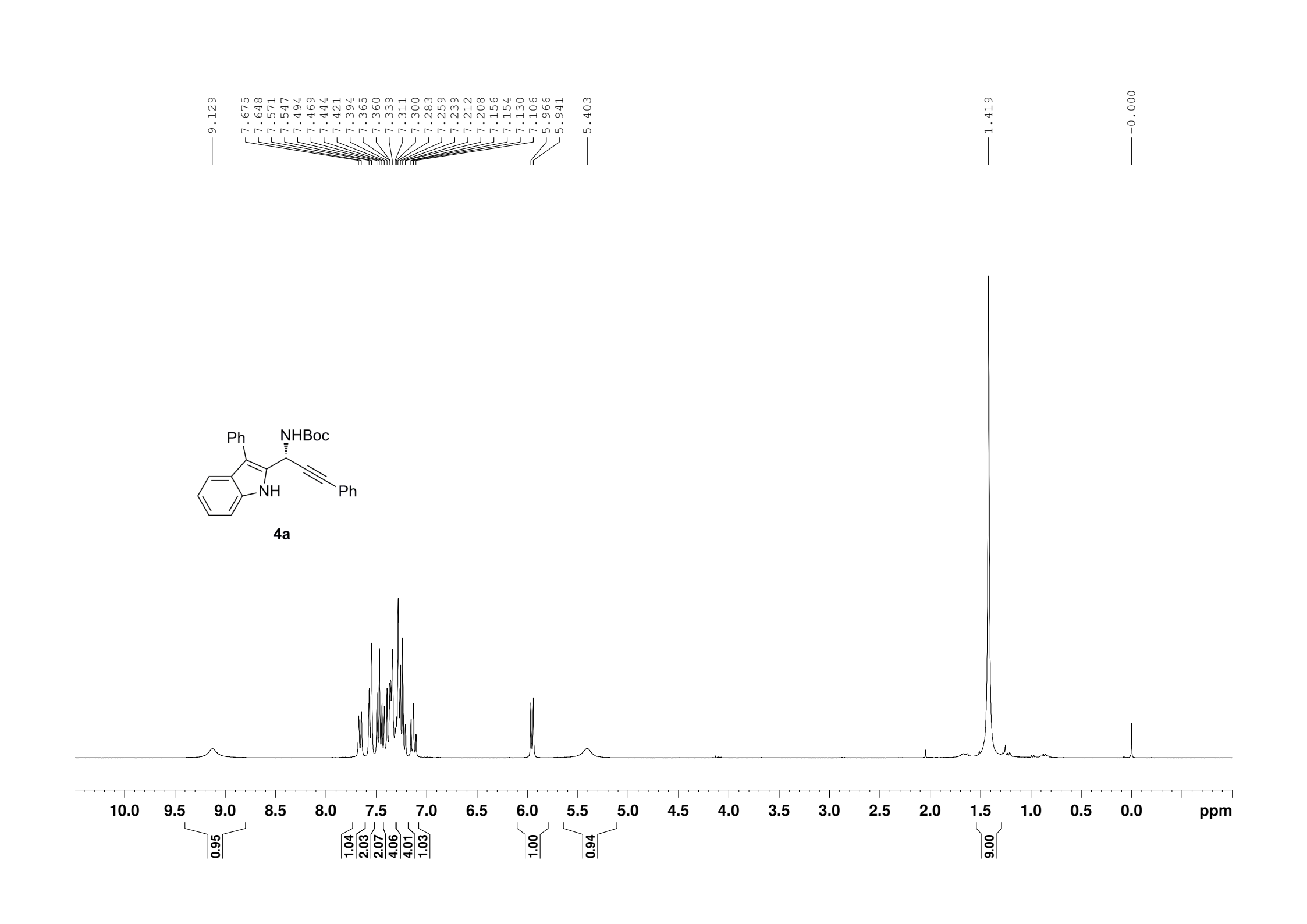
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7.339
7.311
7.300
7.283
7.259
7.239
7.212
7.208
7.156
7.154
7.130
7.106
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5.941
5.403
1.419
0.000
Ph
NHBoc
NH
Ph
4a
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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4.01
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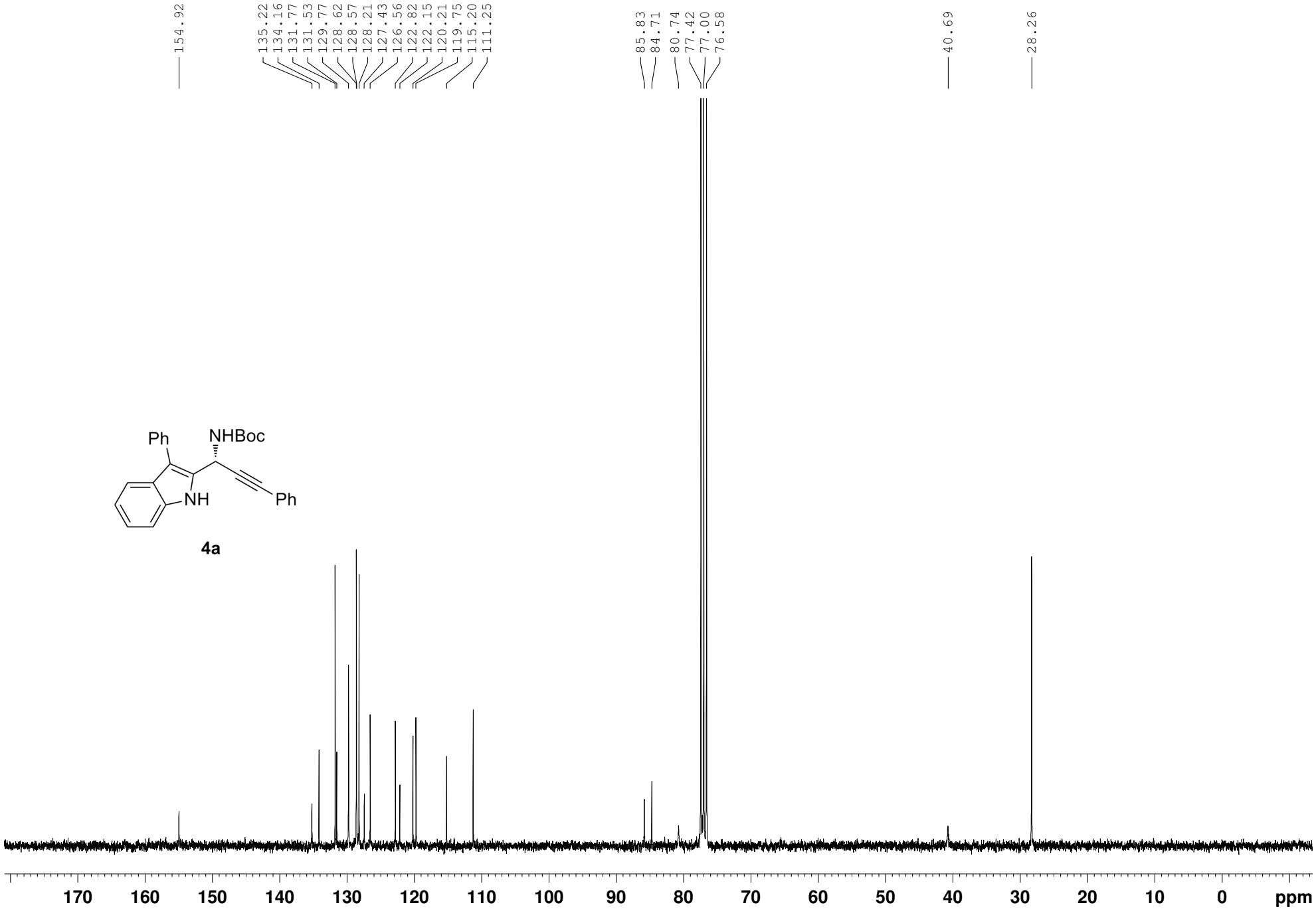
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120.21
119.75
115.20
111.25
85.83
84.71
80.74
77.42
77.00
76.58
40.69
28.26
Ph
NHBoc
NH
Ph
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140
130
120
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100
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50
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20
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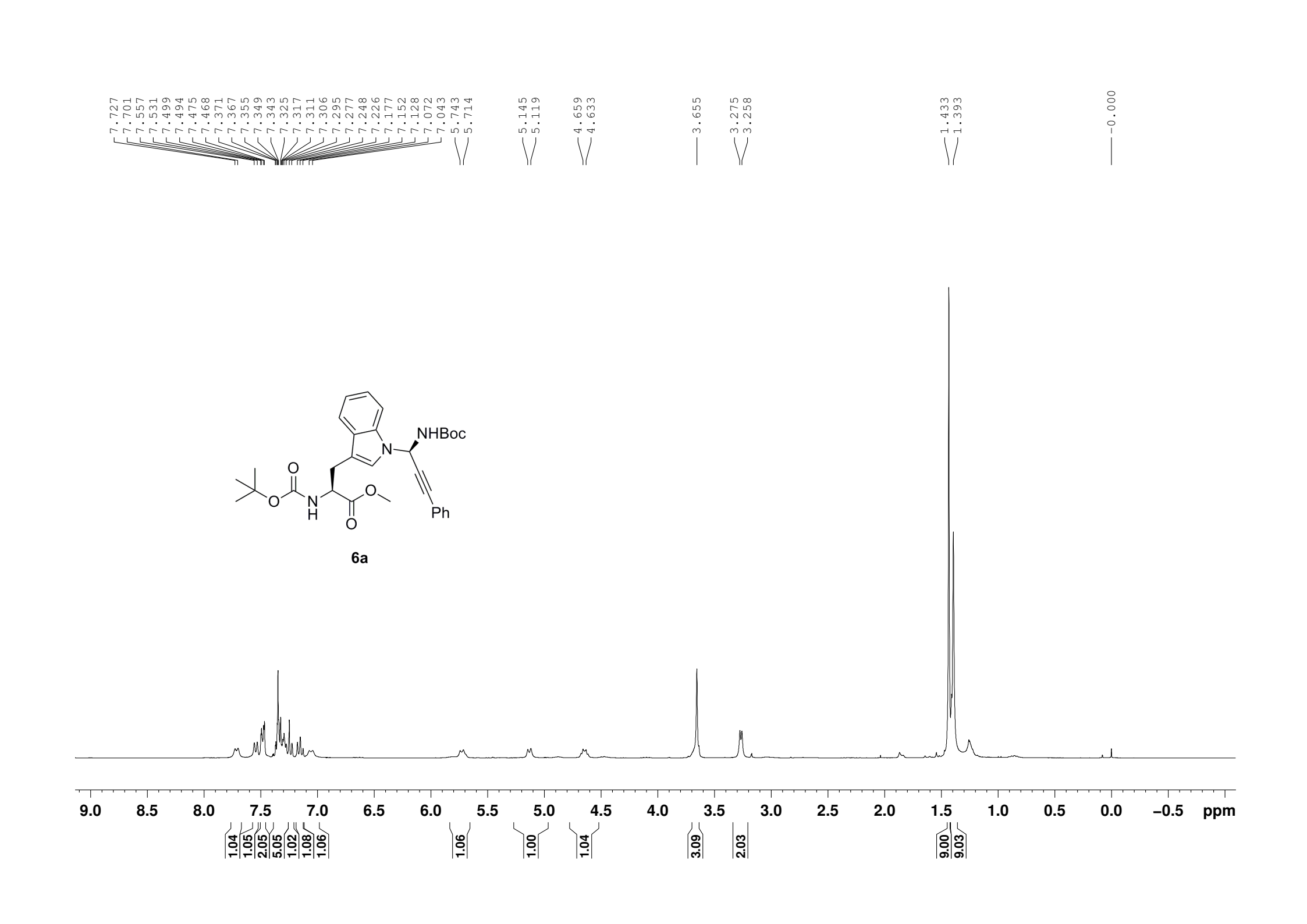
ppm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7.325
7.317
7.311
7.306
7.295
7.277
7.248
7.226
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7.152
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7.072
7.043
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5.714
5.145
5.119
4.659
4.633
3.655
3.275
3.258
1.433
1.393
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NHBoc
N
O
O
N
H
O
O
Ph
6a
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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0.0
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ppm
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1.06
1.06
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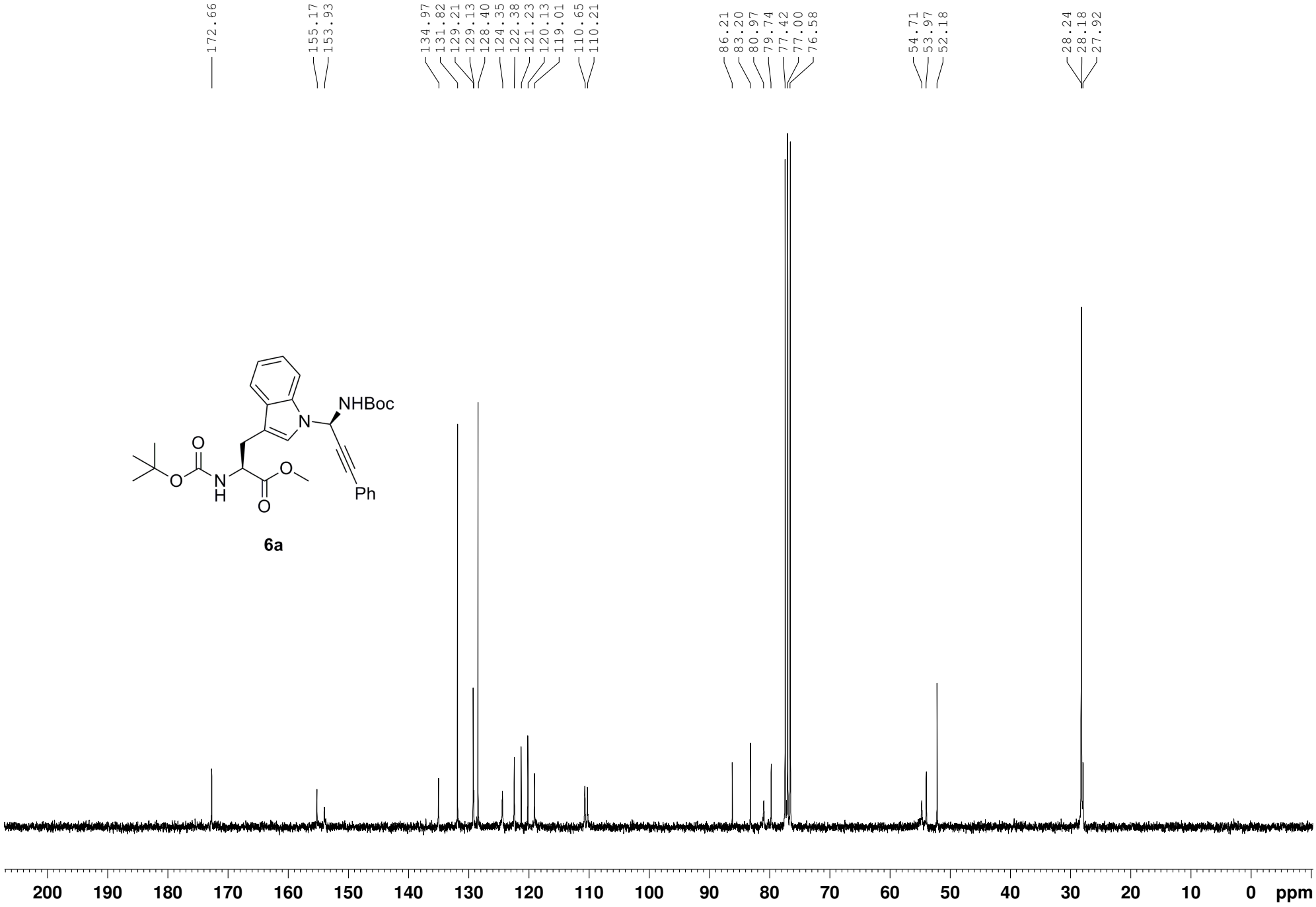
9.00
9.03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80.97
79.74
77.42
77.00
76.58
54.71
53.97
52.18
28.24
28.18
27.92
NHBoc
N
O
O
N
H
O
O
Ph
6a
200
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140
130
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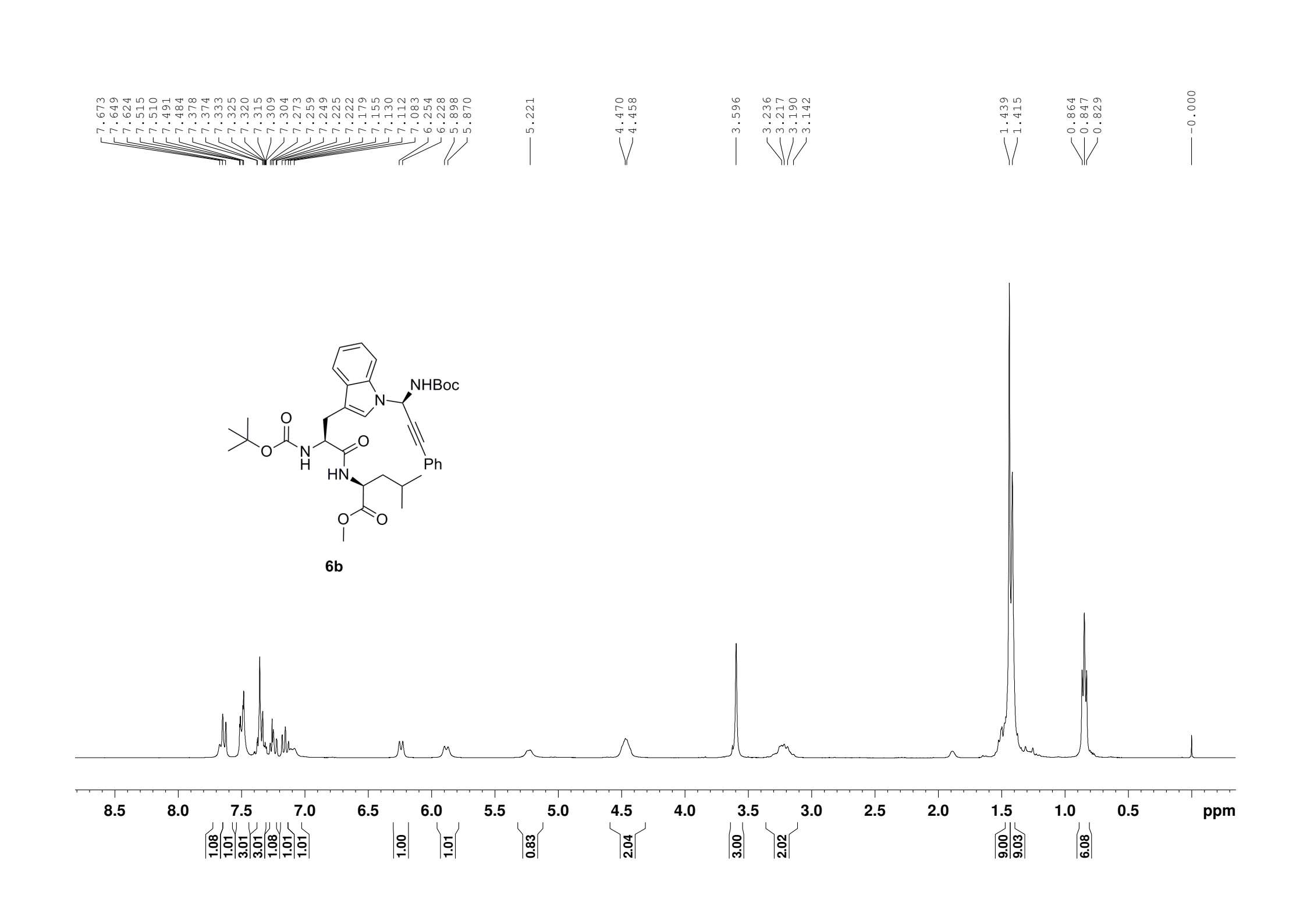
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6.228
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O
N
H
O
HN
Ph
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O
O
6b
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6.0
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5.0
4.5
4.0
3.5
3.0
2.5
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ppm
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1.01
3.01
3.01
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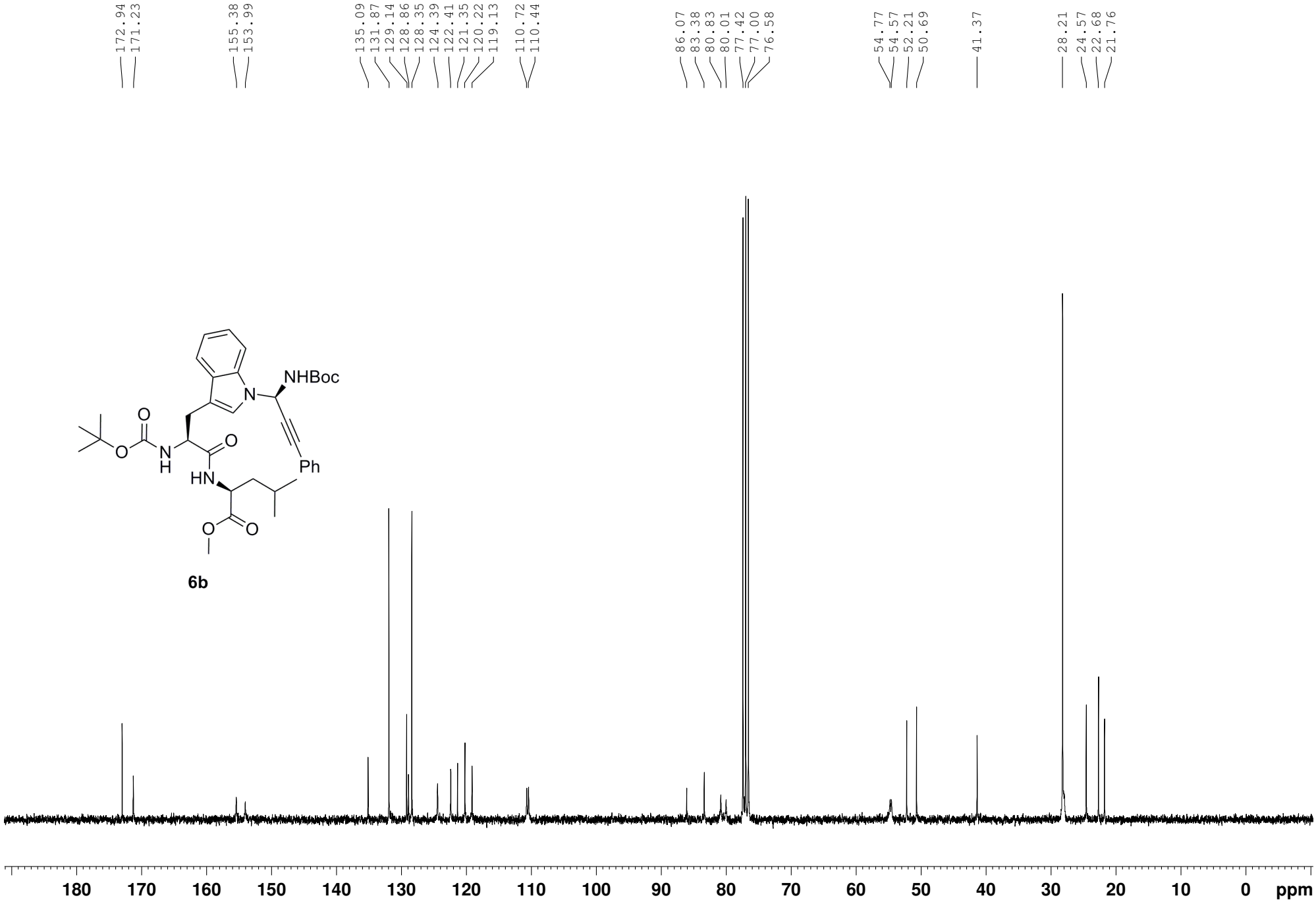
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83.38
80.83
80.01
77.42
77.00
76.58
54.77
54.57
52.21
50.69
41.37
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24.57
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N
O
O
N
H
O
HN
Ph
O
O
O
180
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150
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130
120
110
100
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80
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50
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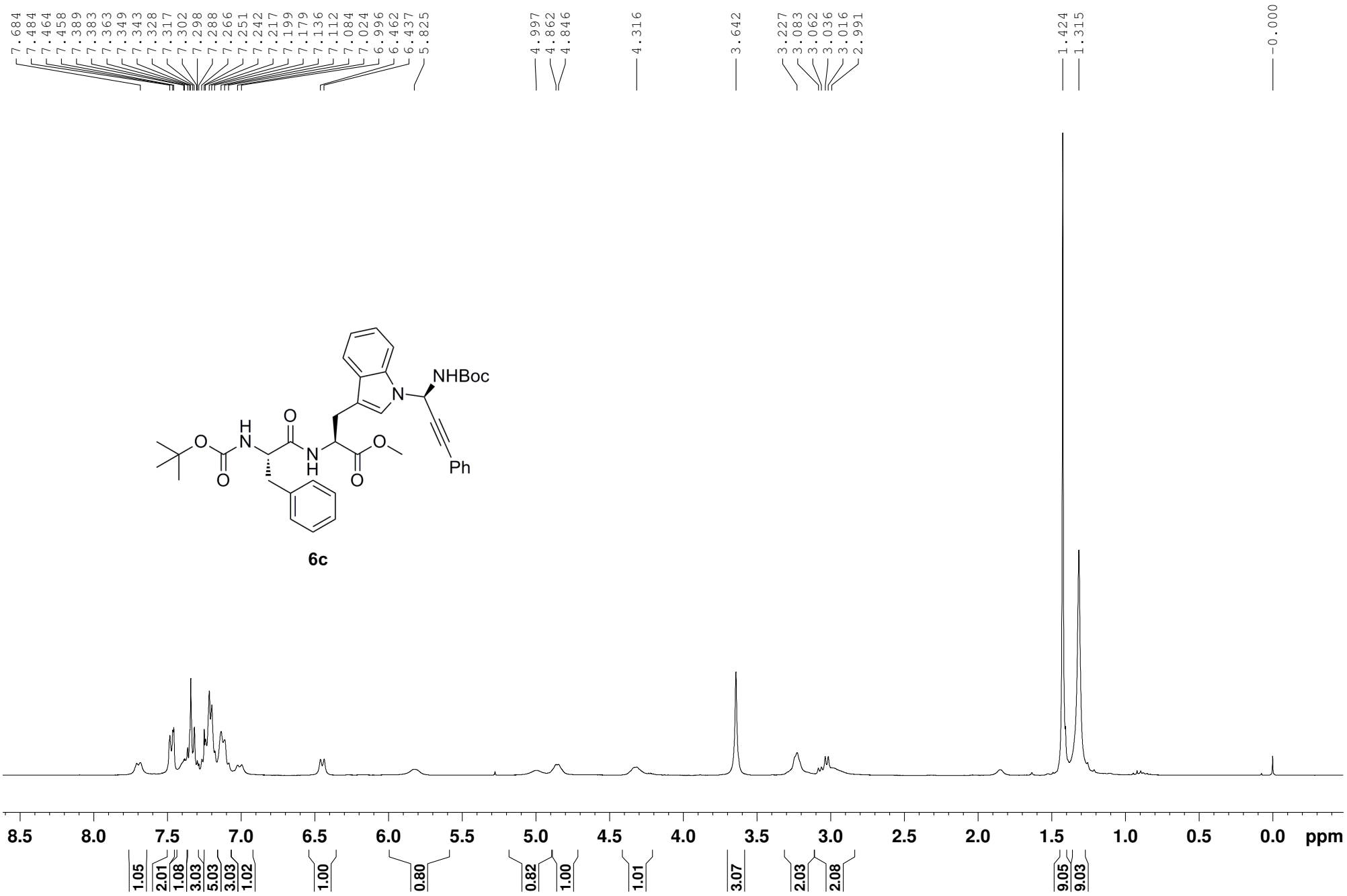
ppm

6b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1.315
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NHBoc
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H
O
N
H
O
O
O
O
O
Ph
6c
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3.03
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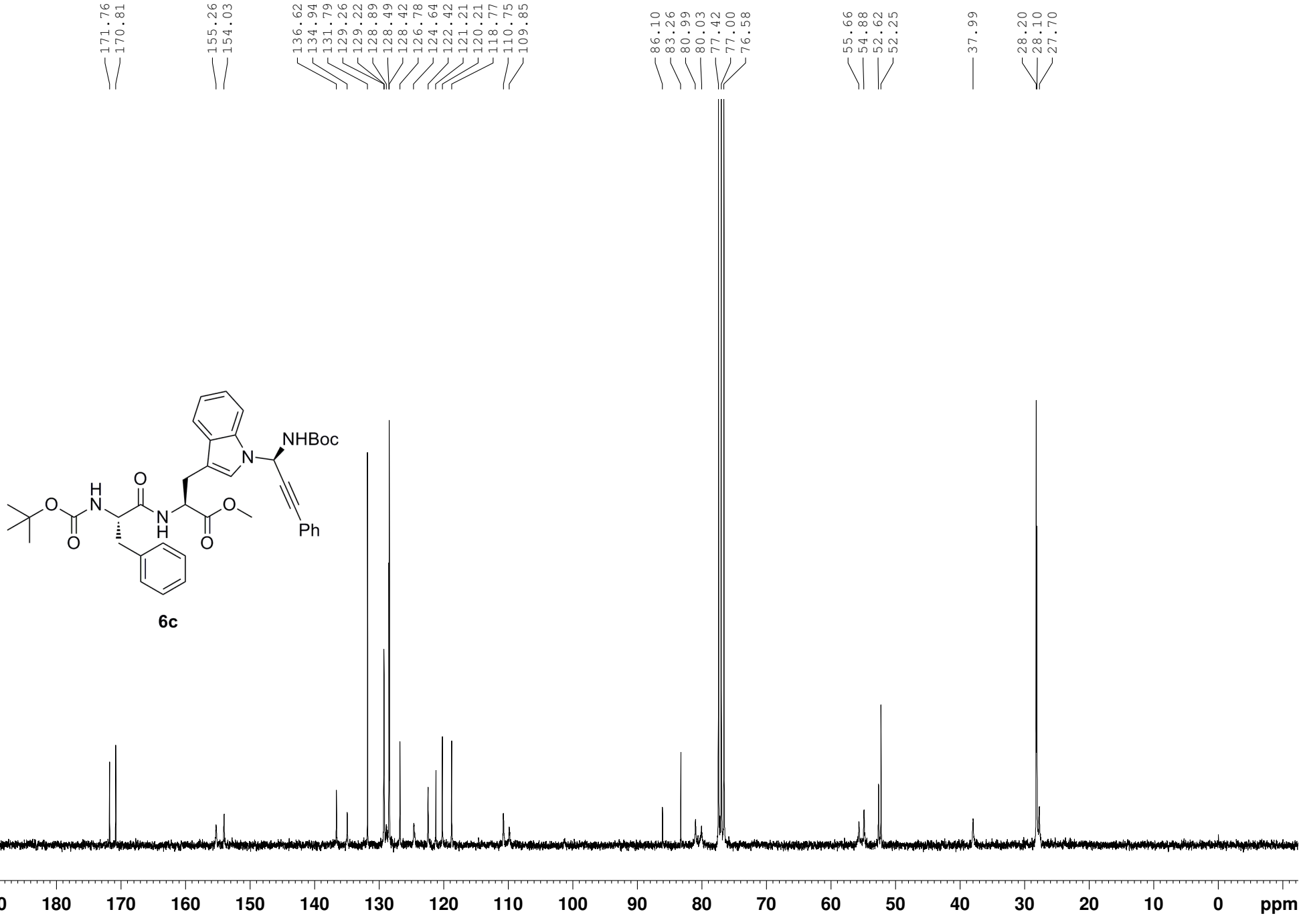
9.03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77.00
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27.70
NHBoc
Ph
6c
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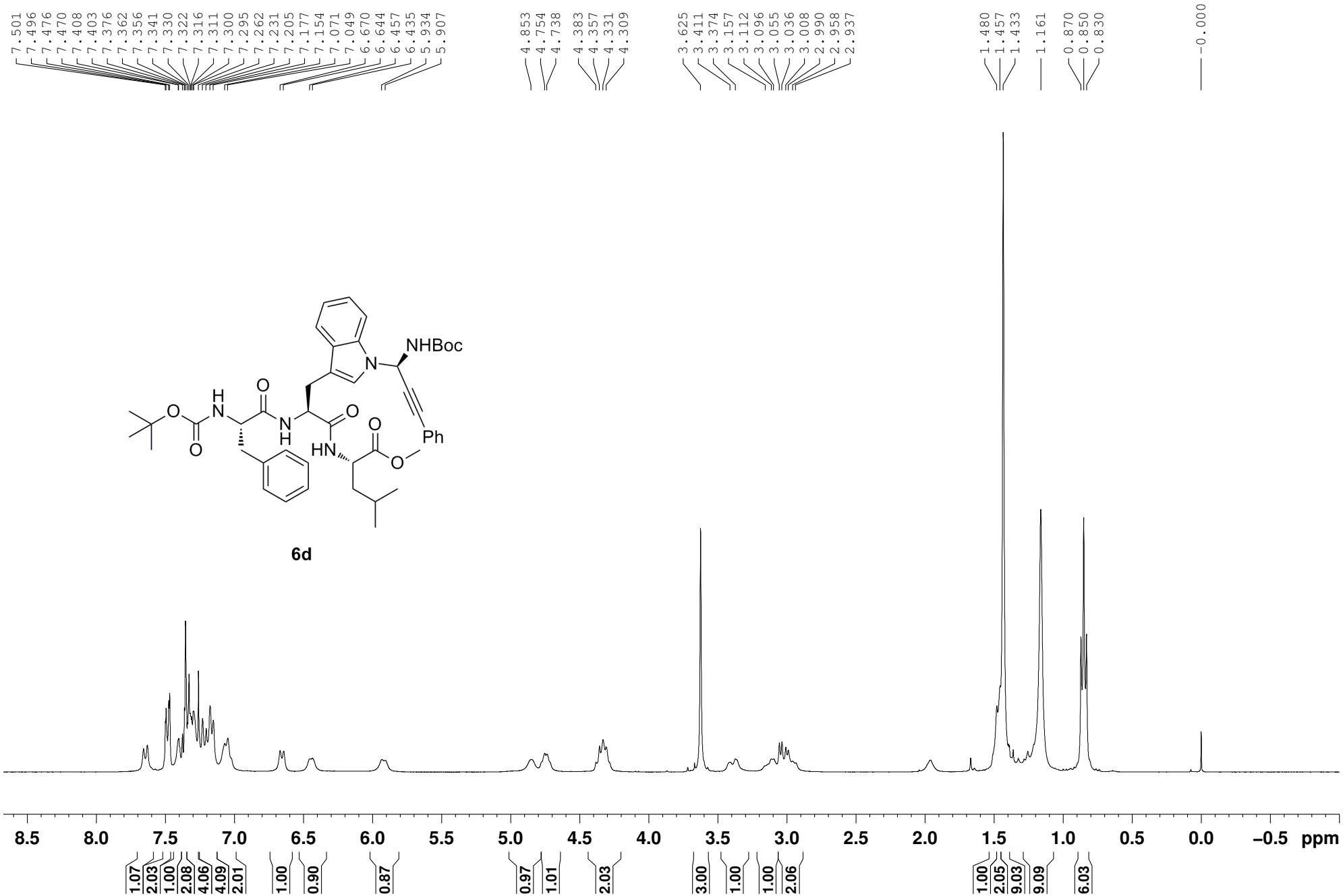
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7.295
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Ph
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5.0
4.5
4.0
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2.5
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0.0
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4.09
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1.00
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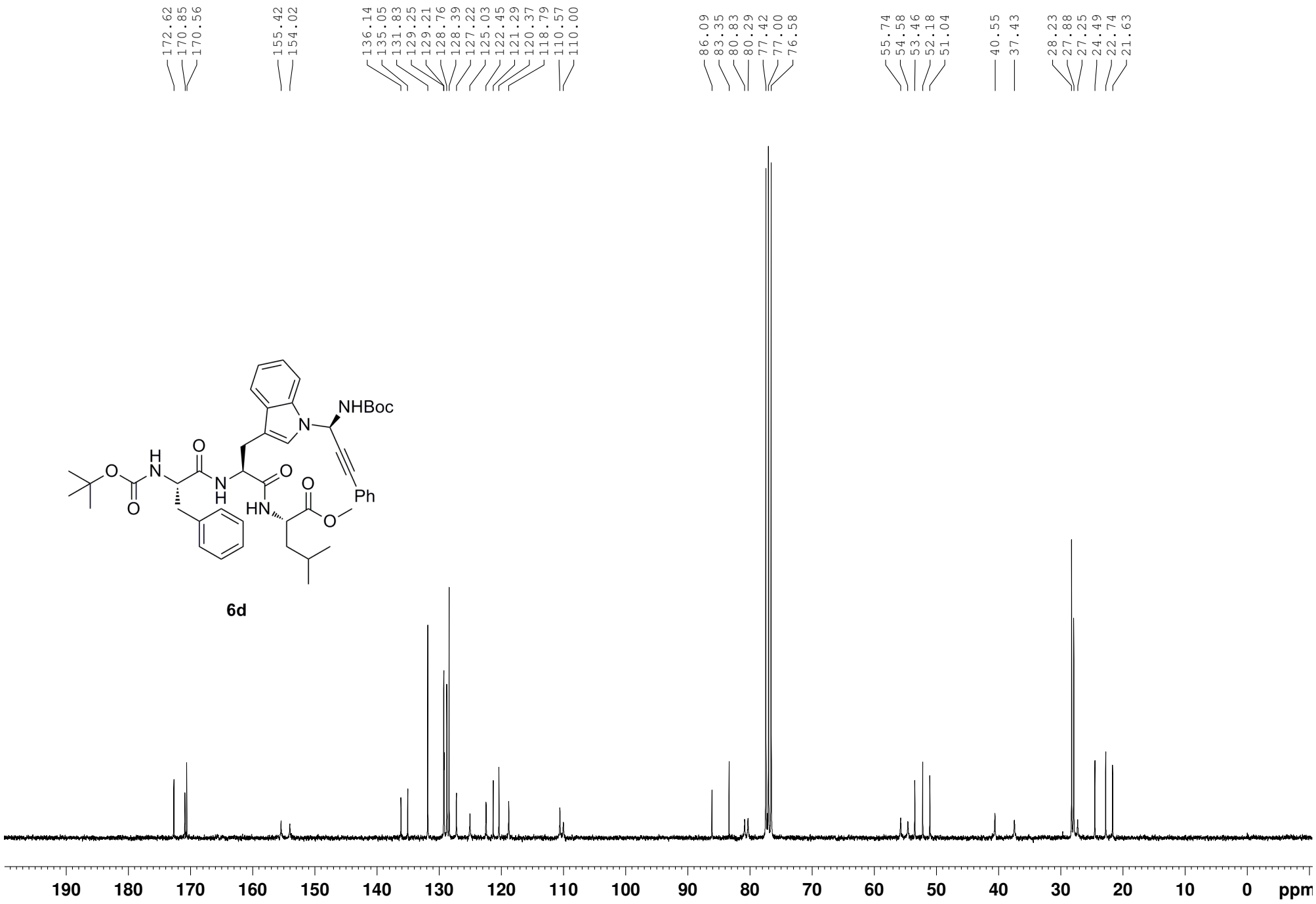
6.03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51.04
40.55
37.43
28.23
27.88
27.25
24.49
22.74
21.63
NHBoc
Ph
6d
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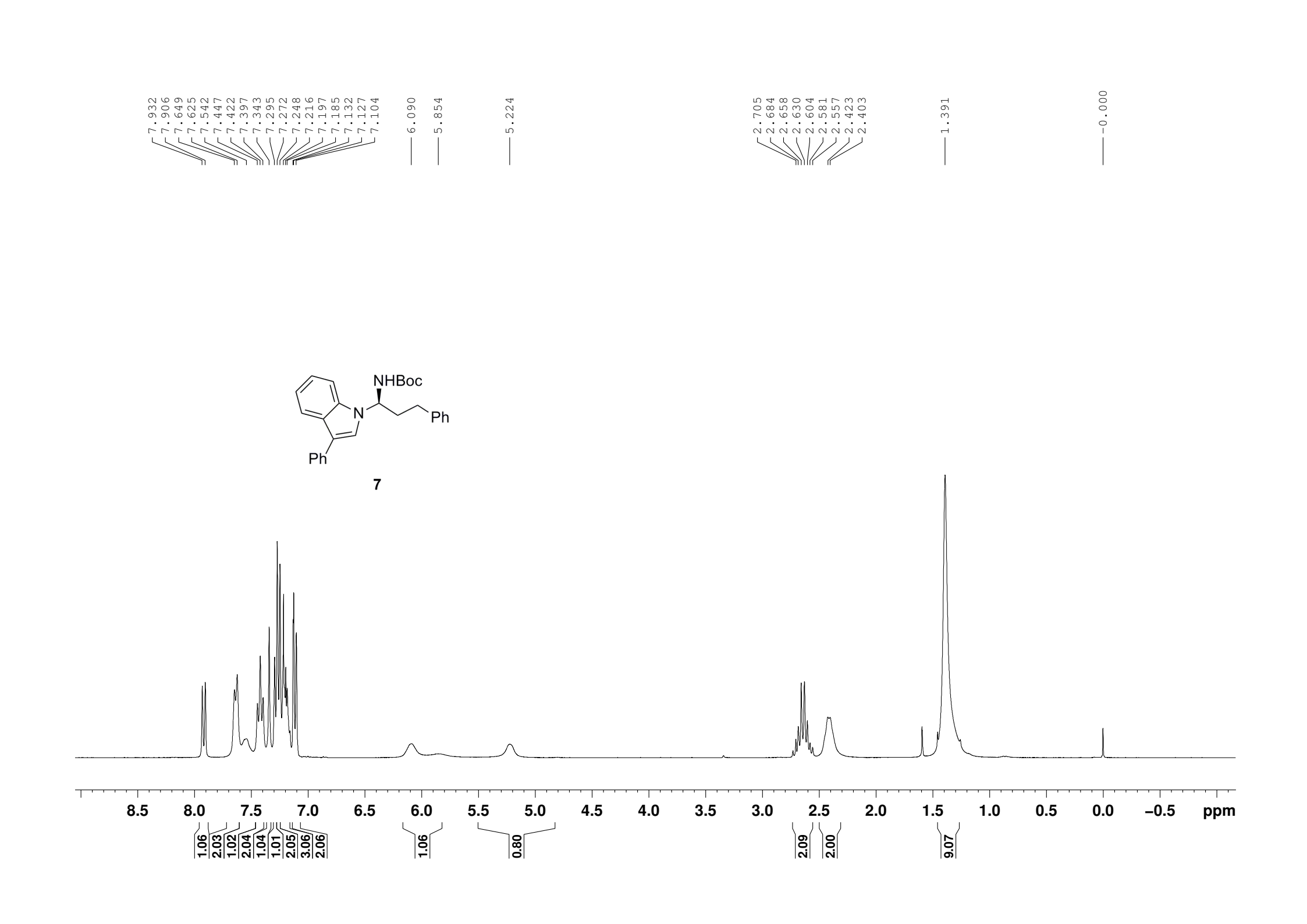
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2.423
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Ph
Ph
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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ppm
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2.03
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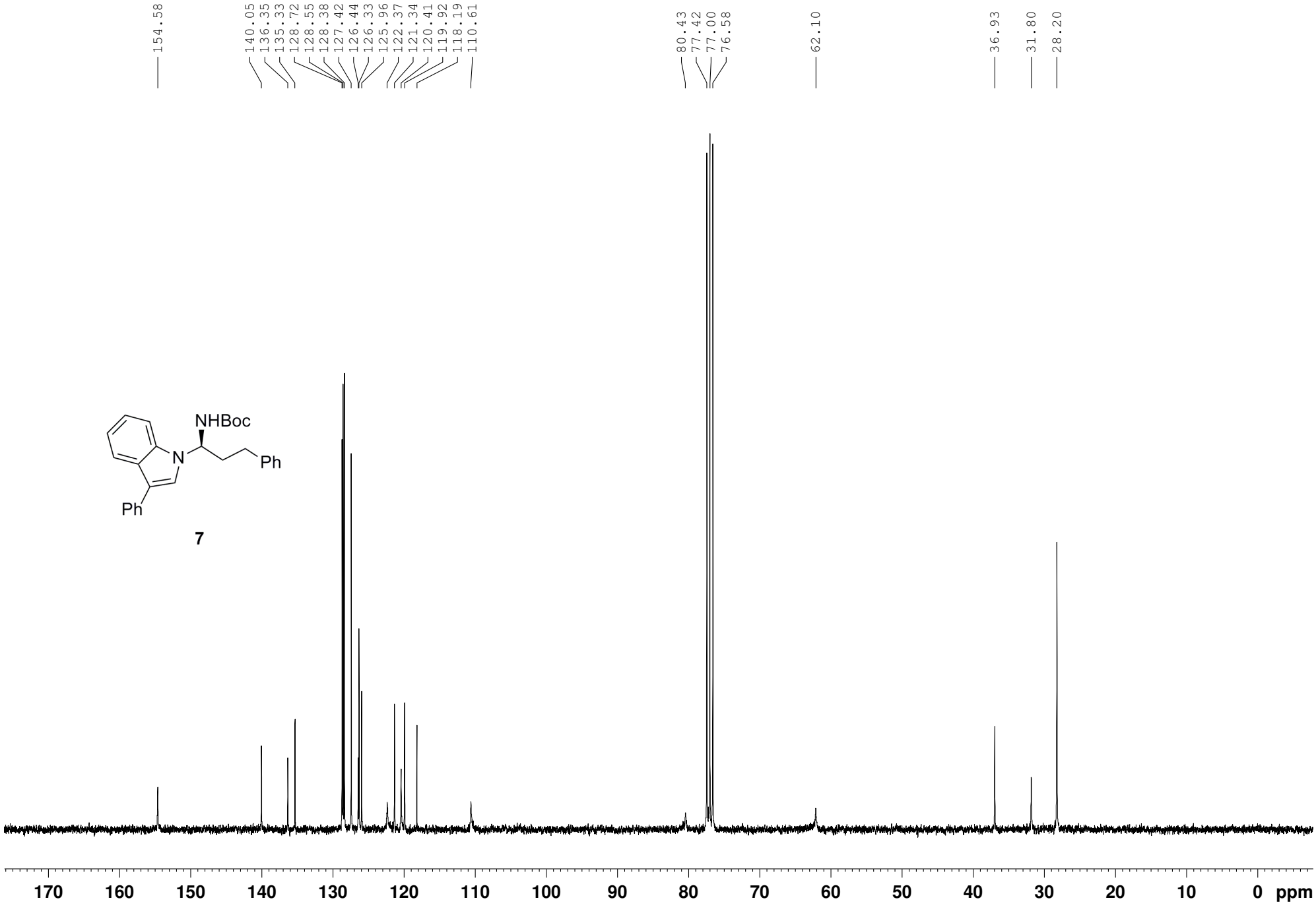
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80.43
77.42
77.00
76.58
62.10
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28.20
NHBoc
N
Ph
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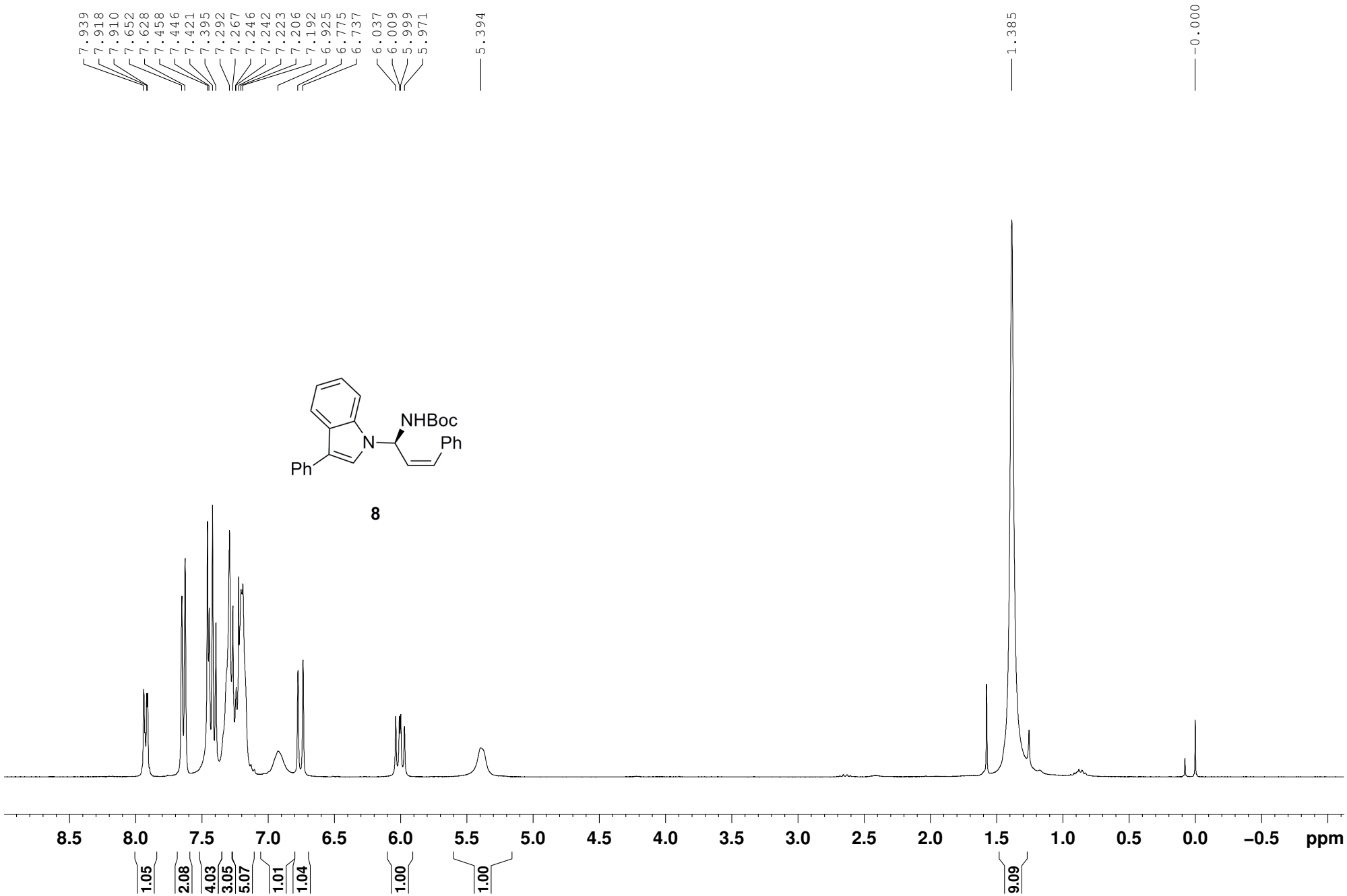
ppm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7.223
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6.775
6.737
6.037
6.009
5.999
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5.394
1.385
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NHBoc
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Ph
Ph
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5.0
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3.5
3.0
2.5
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1.0
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0.0
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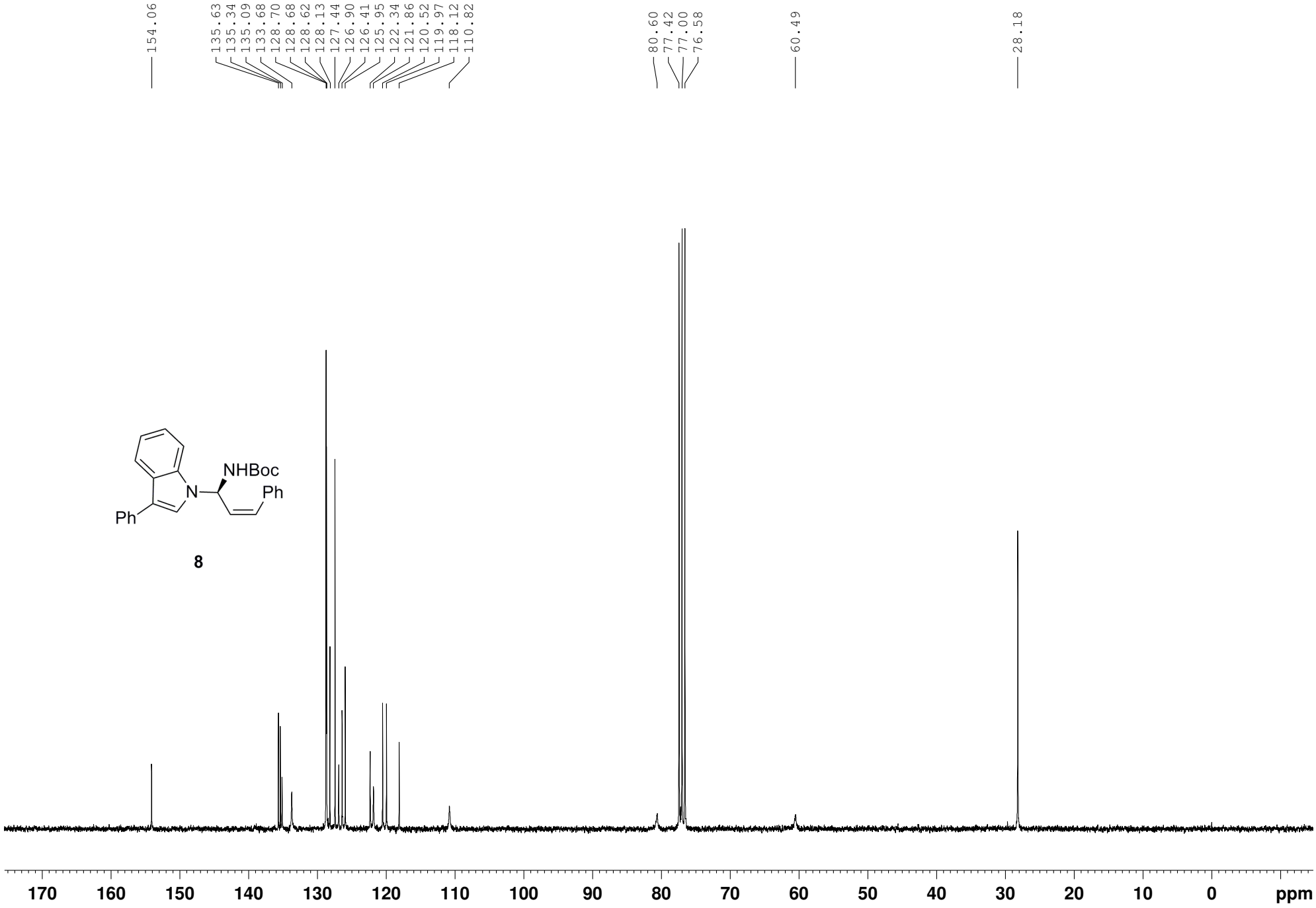
2.08
4.03
3.05
5.07
1.01
1.04
1.00
1.00
9.09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60.49
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NHBoc
N
Ph
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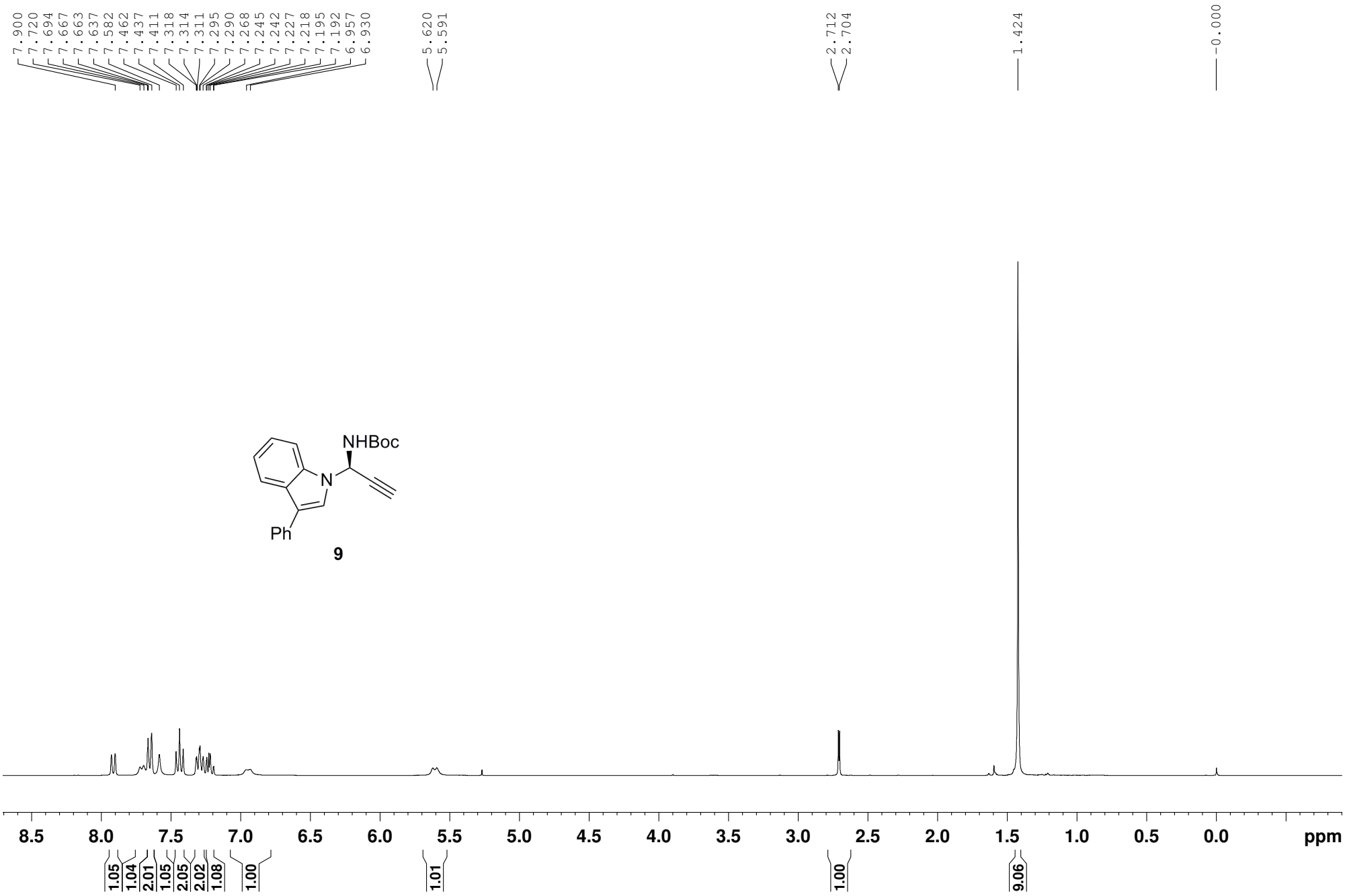
ppm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5.591
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2.704
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NHBoc
N
Ph
9
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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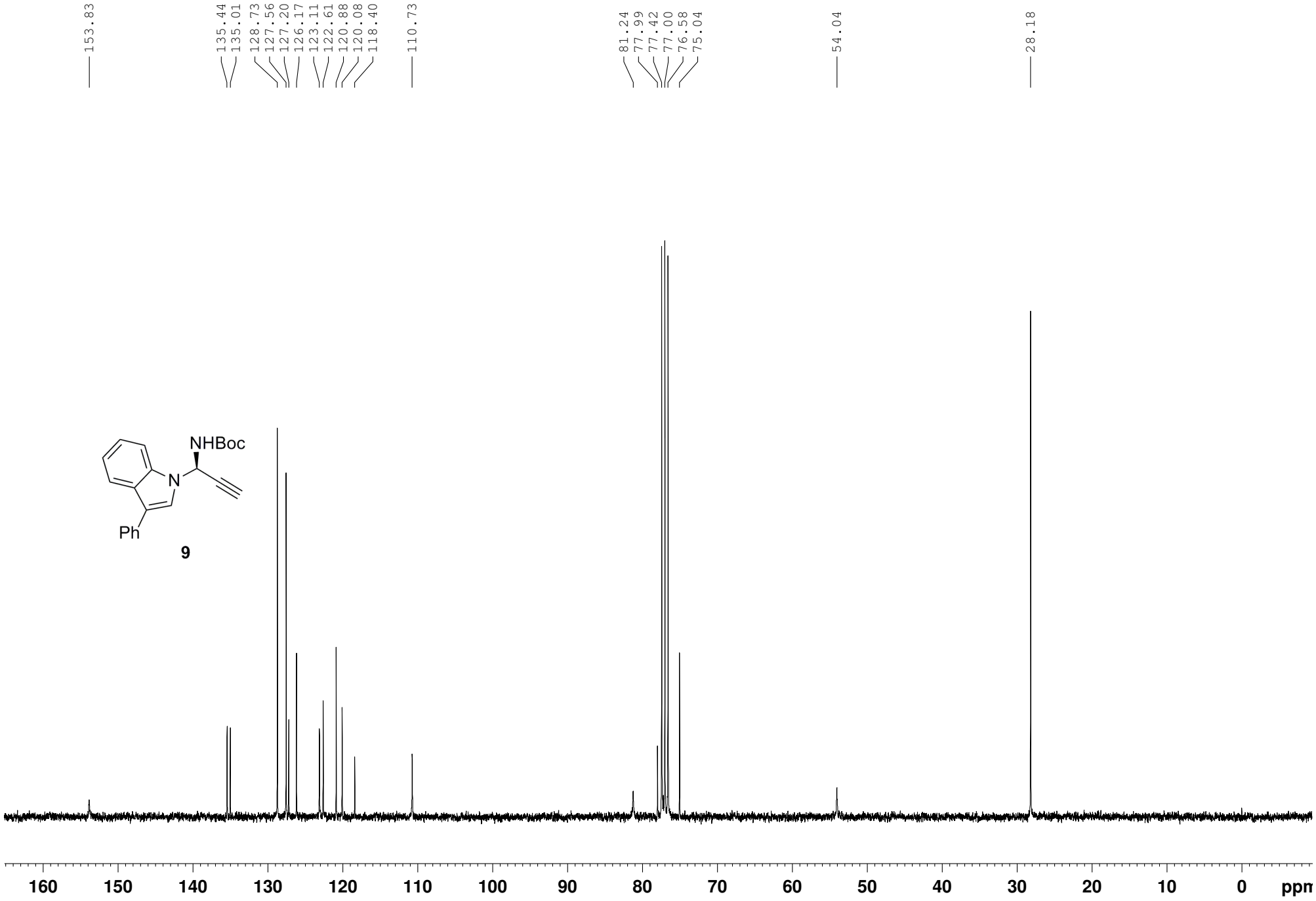
1.04
2.01
1.05
2.05
2.02
1.08
1.00
1.01
1.00
9.06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127.20
126.17
123.11
122.61
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120.08
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81.24
77.99
77.42
77.00
76.58
75.04
54.04
28.18
NHBoc
N
Ph
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150
140
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120
110
100
90
80
70
60
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40
30
20
10
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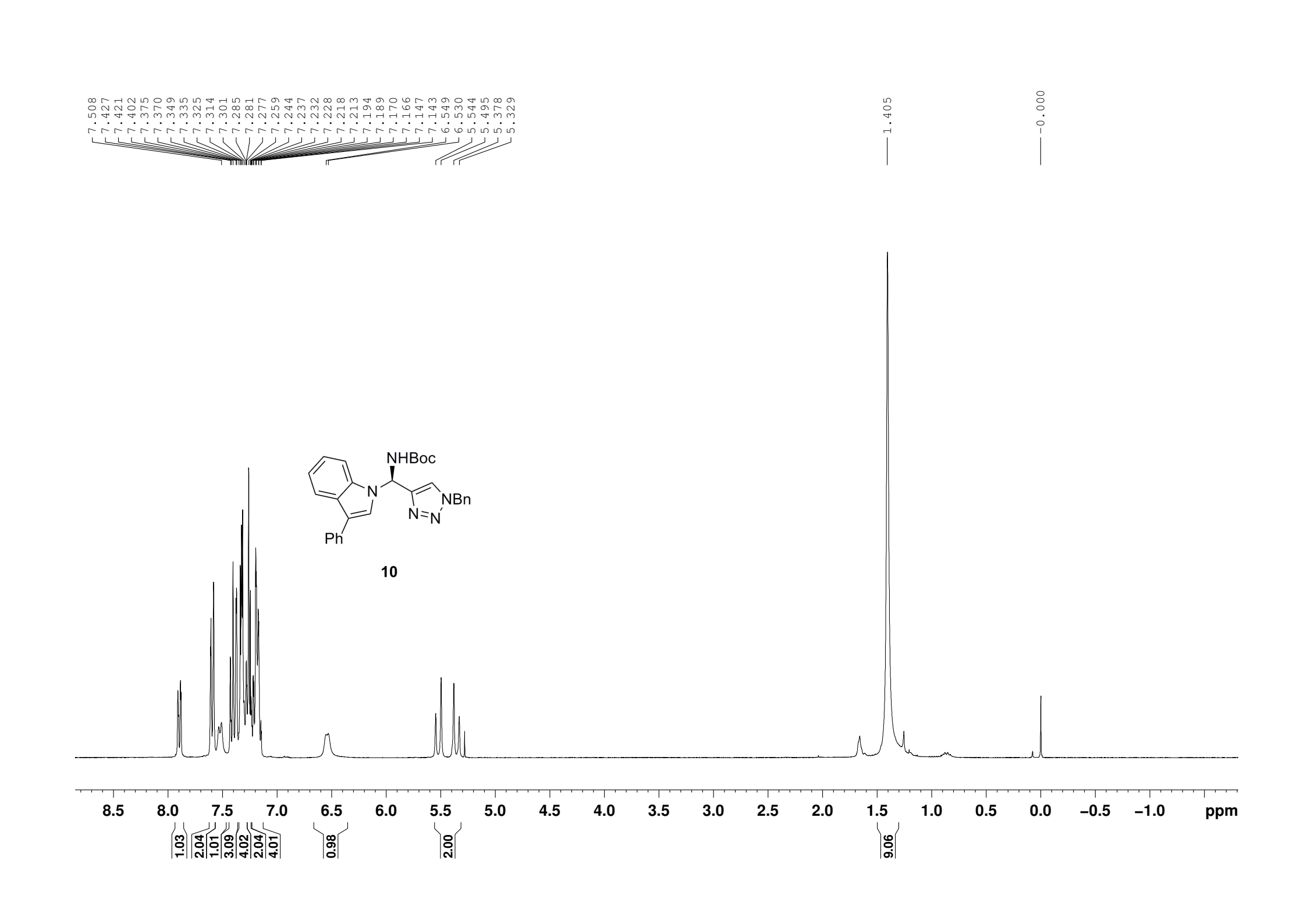
ppm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7.281
7.277
7.259
7.244
7.237
7.232
7.228
7.218
7.213
7.194
7.189
7.170
7.166
7.147
7.143
6.549
6.530
5.544
5.495
5.378
5.329
1.405
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N
NBn
N=N
Ph
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8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
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2.04
1.01
3.09
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2.04
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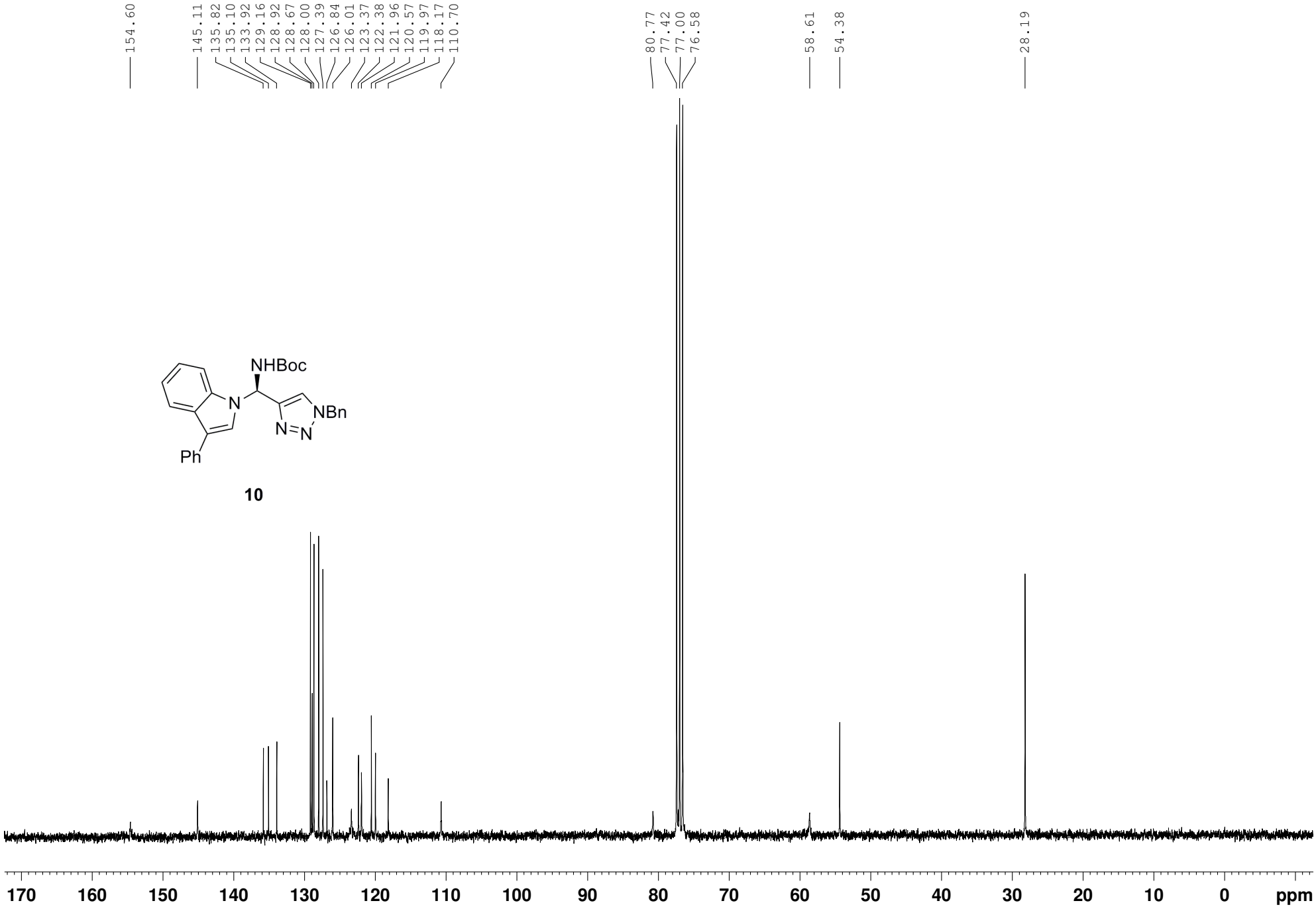
2.00
9.06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123.37
122.38
121.96
120.57
119.97
118.17
110.70
80.77
77.42
77.00
76.58
58.61
54.38
28.19
NHBoc
N
NBn
N=N
Ph
10
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm