Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Tandem Oxidative Radical Brominative Addition of Activated Alkynes and Spirocyclization: Switchable Synthesis of 3-Bromocoumarins and 3-Bromo *spiro*-[4,5] trienone

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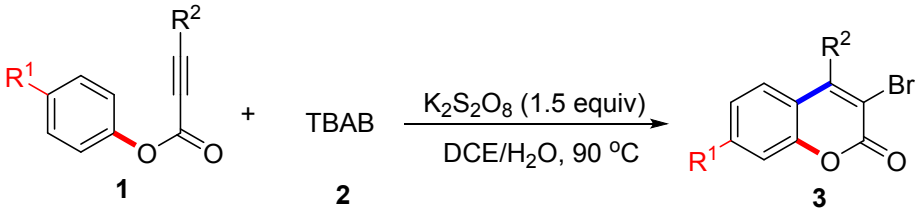
Supporting Information

1. General procedure for synthesis of compound **3**.
2. Characterization data of compound **3**.
3. ^{1}H and ^{13}CNMR spectra of compound **3**, **4**, **5,** and **6.**

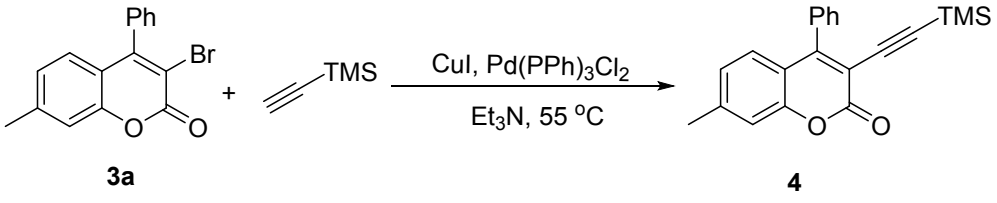
General Materials and Methods: All reactions were performed in reaction tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

General procedure for reactions of alkynoates 1 withTBAB 2:



Alkynoates (0.2 mmol), TBAB (2.0 equiv), and $K_2S_2O_8$ (1.5 equiv) were added into the test tube, and then co-solvent DCE/H_2O (1:1 v/v, 2mL) was added. The mixture was stirred at 90 °C overnight. After completion of reaction as indicated by TLC, the mixture was filtrated, and the filtrate was extracted with EtOAc, and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the product **3**.

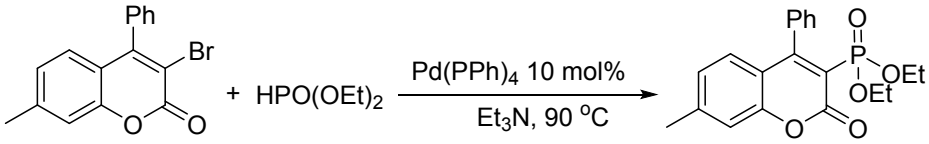
Synthesis of 7-methyl-4-phenyl-3-((trimethylsilyl)ethynyl)-2*H*-chromen-2-one 4:



Coumarin **3a** (1.0 equiv), ethynyltrimethylsilane (1.5 equiv), CuI (2.5 mol%) and $Pd(PPh)_3Cl_2$ (5 mol%) were added into the test tube, and then Et_3N was added. The mixture was stirred at 55°C for 24h. After completion of reaction as indicated by TLC,

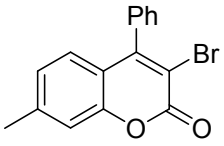
evaporation of the solvent followed by purification on silica gel provided the product **4**.

Synthesis of diethyl 7-methyl-2-oxo-4-phenyl-2*H*-chromen-3-ylphosphonate 5:



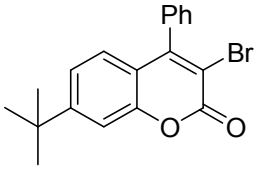
3a **5**

Coumarin **3a** (1.0 equiv), diethyl phosphonate (2.0 equiv) and $Pd(PPh)_4$ (10 mol%) were added into the thick-walled pressure bottle, and then Et_3N was added. The mixture was stirred at 90°C for 24h. After completion of reaction as indicated by TLC, Evaporation of the solvent followed by purification on silica gel provided the product **5**.



3-bromo-7-methyl-4-phenyl-2*H*-chromen-2-one (**3a**):[1]

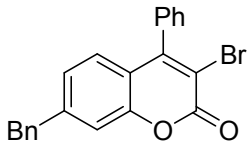
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.50 (m, 3H), 7.30 (d, J = 7.6, 2H), 7.21 (s, 1H), 7.04-6.94 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.53, 154.61, 152.47, 143.44, 135.36, 129.22, 128.74, 128.03, 127.26, 125.86, 117.92, 116.86, 111.19, 21.61; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{11}BrNaO_2^+$: 336.9840; found: 336.9835.



3-bromo-7-tert-butyl-4-phenyl-2*H*-chromen-2-one (**3b**):

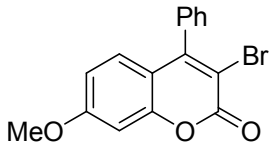
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 3H), 7.42-7.41 (m, 1H), 7.32-7.20 (m, 3H), 7.01 (d, J = 8.5 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.65, 156.71, 154.49, 152.50, 135.40, 129.23, 128.74, 128.06, 127.11, 122.21, 117.86, 113.54, 111.43, 35.24, 30.92; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{17}BrNaO_2^+$:

379.0310; found: 379.0340.



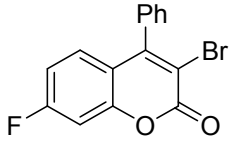
7-benzyl-3-bromo-4-phenyl-2*H*-chromen-2-one (**3c**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.54 (m, 3H), 7.34-7.24 (m, 6H), 7.20 (d, J = 7.0 Hz, 2H), 7.05-7.02 (m, 2H), 4.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.41, 154.50, 152.56, 146.52, 139.21, 135.28, 129.25, 128.86, 128.74, 128.70, 128.00, 127.55, 126.61, 125.46, 118.43, 116.77, 111.59, 41.70; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{22}H_{15}BrNaO_2^+$: 413.0153; found: 413.0148.



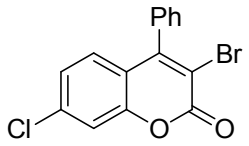
3-bromo-7-methoxy-4-phenyl-2*H*-chromen-2-one (**3d**):[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.49 (m, 3H), 7.33-7.25 (m, 2H), 6.97 (d, J = 8.9 Hz, 1H), 6.92-6.88 (m, 1H), 6.79-6.71 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.89, 157.73, 154.74, 154.18, 135.48, 129.22, 128.74, 128.61, 128.05, 113.94, 112.82, 108.72, 100.59, 55.84; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{11}BrNaO_3^+$: 352.9789; found: 352.9796.



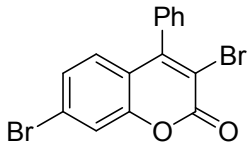
3-bromo-7-fluoro-4-phenyl-2*H*-chromen-2-one (**3e**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 3H), 7.31-7.29 (m, 2H), 7.15-7.07 (m, 2H), 6.96-6.91 (m, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 164.38 (d, $^1J_{CF}$ = 255.3 Hz), 154.14, 153.46 (d, $^3J_{CF}$ = 12.9 Hz), 135.07, 129.51, 129.43, 129.33, 128.94, 127.97, 117.10, 112.81 (d, $^2J_{CF}$ = 22.6 Hz), 111.39, 104.33 (d, $^2J_{CF}$ = 25.8 Hz); HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_8BrFNaO_2^+$: 340.9589; found: 340.9584.



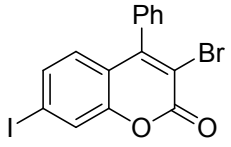
3-bromo-7-chloro-4-phenyl-2*H*-chromen-2-one (**3f**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.52 (m, 3H), 7.43-7.40 (m, 1H), 7.33-7.26 (m, 2H), 7.20-7.14 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.71, 153.97, 152.58, 137.95, 134.85, 129.55, 128.97, 128.46, 127.97, 125.28, 118.95, 117.03, 112.54; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_8BrClNaO_2^+$: 356.9294; found: 356.9288.



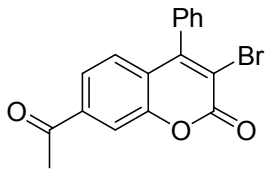
3,7-dibromo-4-phenyl-2*H*-chromen-2-one (**3g**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (m, 4H), 7.32-7.27 (m, 3H), 6.94 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.06, 152.56, 134.85, 129.59, 129.01, 128.57, 128.16, 128.01, 125.97, 120.04, 119.36, 112.81; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_8Br_2NaO_2^+$: 400.8789; found: 400.8781.



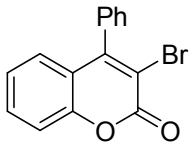
3-bromo-7-iodo-4-phenyl-2*H*-chromen-2-one (**3h**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 1H), 7.60-7.55 (m, 3H), 7.51 (d, *J* = 8.4, 1H), 7.30-7.28 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.46, 154.08, 152.11, 134.70, 133.93, 129.52, 128.94, 128.45, 127.95, 125.79, 119.79, 113.00, 97.51; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_8BrINaO_2^+$: 448.8650; found: 448.8645.



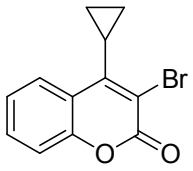
7-acetyl-3-bromo-4-phenyl-2*H*-chromen-2-one (**3i**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 1H), 7.76-7.73 (m, 1H), 7.63-7.56 (m, 3H), 7.32-7.29 (m, 2H), 7.19 (d, *J* = 8.3 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.22, 156.79, 153.71, 152.22, 139.31, 134.74, 129.62, 129.01, 127.97, 123.87, 123.48, 116.65, 115.2, 109.92, 26.77;HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{11}BrNaO_3^+$: 364.9789; found: 364.9782.



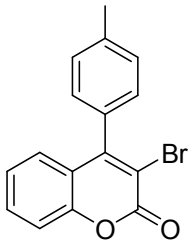
3-bromo-4-phenyl-2*H*-chromen-2-one (**3j**):[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 4H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.34-7.30 (m, 2H), 7.23-7.18 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.29, 154.59, 152.41, 135.22, 132.00, 129.31, 128.81, 128.03, 127.57, 124.67, 120.28, 116.76, 112.57; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_9BrNaO_2^+$: 322.9684; found: 322.9691.



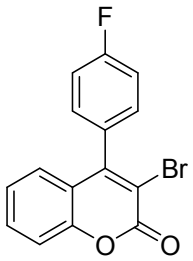
3-bromo-4-cyclopropyl-2*H*-chromen-2-one (**3k**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.60-7.51 (m, 1H), 7.39 -7.29 (m, 2H), 1.99-1.85 (m, 1H), 1.43-1.32 (m, 2H), 0.95-0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.42, 153.51, 151.91, 131.59, 125.54, 124.42, 120.64, 116.89, 115.53, 14.43, 9.39; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{12}H_9BrNaO_2^+$: 286.9684; found: 286.9678.



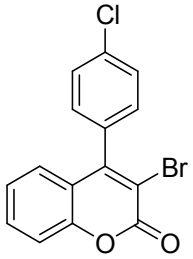
3-bromo-4-*p*-tolyl-2*H*-chromen-2-one (**3l**):[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 1H), 7.42-7.37 (m, 3H), 7.22-7.18 (m, 3H), 7.13 (d, J = 8.0 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.35, 154.76, 152.38, 139.39, 132.24, 131.92, 129.45, 127.99, 127.66, 124.60, 120.38, 116.71, 112.51, 21.40; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{11}BrNaO_2^+$: 336.9840; found: 336.9835.



3-bromo-4-(4-fluorophenyl)-2*H*-chromen-2-one (**3m**):[3]

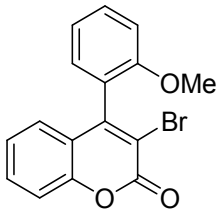
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.51 (m, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.35 -7.20 (m, 5H), 7.09 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.10 (d, $^1J_{CF}$ = 250.0 Hz), 153.65, 152.44, 132.16, 131.11, 130.28, 130.20, 127.35, 124.78, 120.23, 116.92, 116.15 (d,$^2J_{CF}$ = 21.9 Hz), 113.10; *m/z* $[M + Na]^+$ calcd for $C_{15}H_8BrFNaO_2^+$: 340.9589; found: 340.9582.



3-bromo-4-(4-chlorophenyl)-2*H*-chromen-2-one (**3n**):[3]

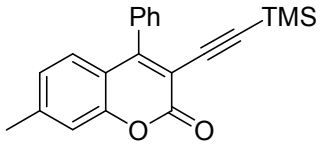
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 3H), 7.42 (d, J = 8.3 Hz, 1H), 7.28-7.25

(m, 2H), 7.24-7.19 (m, 1H), 7.07 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.07, 153.43, 152.44, 135.59, 133.54, 132.22, 129.62, 129.27, 127.27, 124.82, 120.00, 116.94, 112.91; HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{15}H_8BrClNaO_2^+$: 356.9294; found: 356.9288.



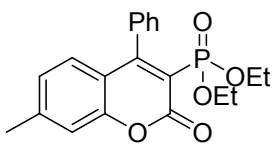
3-bromo-4-(2-methoxyphenyl)-2*H*-chromen-2-one (**3o**):[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 2H), 7.40 (d, J = 8.3 Hz, 1H), 7.21 -7.14 (m, 3H), 7.10 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.46, 155.79, 152.74, 152.33, 131.69, 131.00, 129.20, 127.20, 124.56, 124.11, 120.86, 120.22, 116.64, 113.57, 111.48, 55.65; HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{11}BrNaO_3^+$: 352.9789; found: 352.9786.



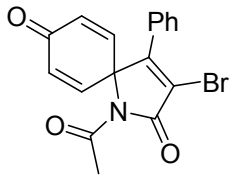
7-methyl-4-phenyl-3-((trimethylsilyl)ethynyl)-2*H*-chromen-2-one (**4**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 3H), 7.42-7.39 (m, 2H), 7.18 (s, 1H), 7.12 (d, J = 8.2 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 2.45 (s, 3H), 0.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.68, 157.87, 152.92, 143.70, 134.30, 129.12, 128.77, 128.24, 128.04, 127.34, 125.66, 117.06, 109.66, 104.68, 98.30, 21.63, -0.56;HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{20}NaO_2Si^+$: 355.1130; found: 355.1125.



diethyl 7-methyl-2-oxo-4-phenyl-2*H*-chromen-3-ylphosphonate (**5**):[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.43 (m, 3H), 7.26-7.25 (m, 2H), 7.10 (s, 1H), 6.92-6.84 (m, 2H), 4.08-3.96 (m, 2H), 3.81-3.89 (m, 2H), 2.39 (s, 3H), 1.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.32 (d, *J* = 6.6 Hz), 159.02 (d, *J* = 16.3 Hz), 153.76, 145.21, 135.01 (d, *J* = 4.8 Hz), 128.62, 128.58, 127.91, 127.77, 125.40, 117.49 (d, *J* = 14.2 Hz), 116.57, 115.02 (d, *J* = 201.0 Hz), 62.40 (d, *J* = 6.0 Hz), 21.50, 15.89 (d, *J* = 6.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.06; HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{20}H_{21}NaO_5P^+$: 395.1024; found: 395.1019.



1-acetyl-3-bromo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6**): [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.35 (m, 3H), 7.23-7.17 (m, 2H), 6.56 (d, *J* = 10.1 Hz, 2H), 6.40 (d, *J* = 10.6 Hz, 2H), 2.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.69, 168.50, 164.41, 156.22, 142.81, 132.49, 130.53, 128.57, 128.11, 119.15, 68.49, 25.59; HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{17}H_{13}BrNO_3^+$: 358.0079; found: 358.0072.

Reference:

(1) Zhang, L.; Meng, T.; Fan, R.; Wu, J. *J. Org. Chem.*, 2007, **72**, 7279.

(2) Tang, B.-X.; Tang, D.-J.; Tang, S.; Yu, Q.-F.; Zhang, Y.-H.; Liang, Y.; Zhong, P.; Li, J.-H.; *Org. Lett.*, 2008, **10**, 1063.

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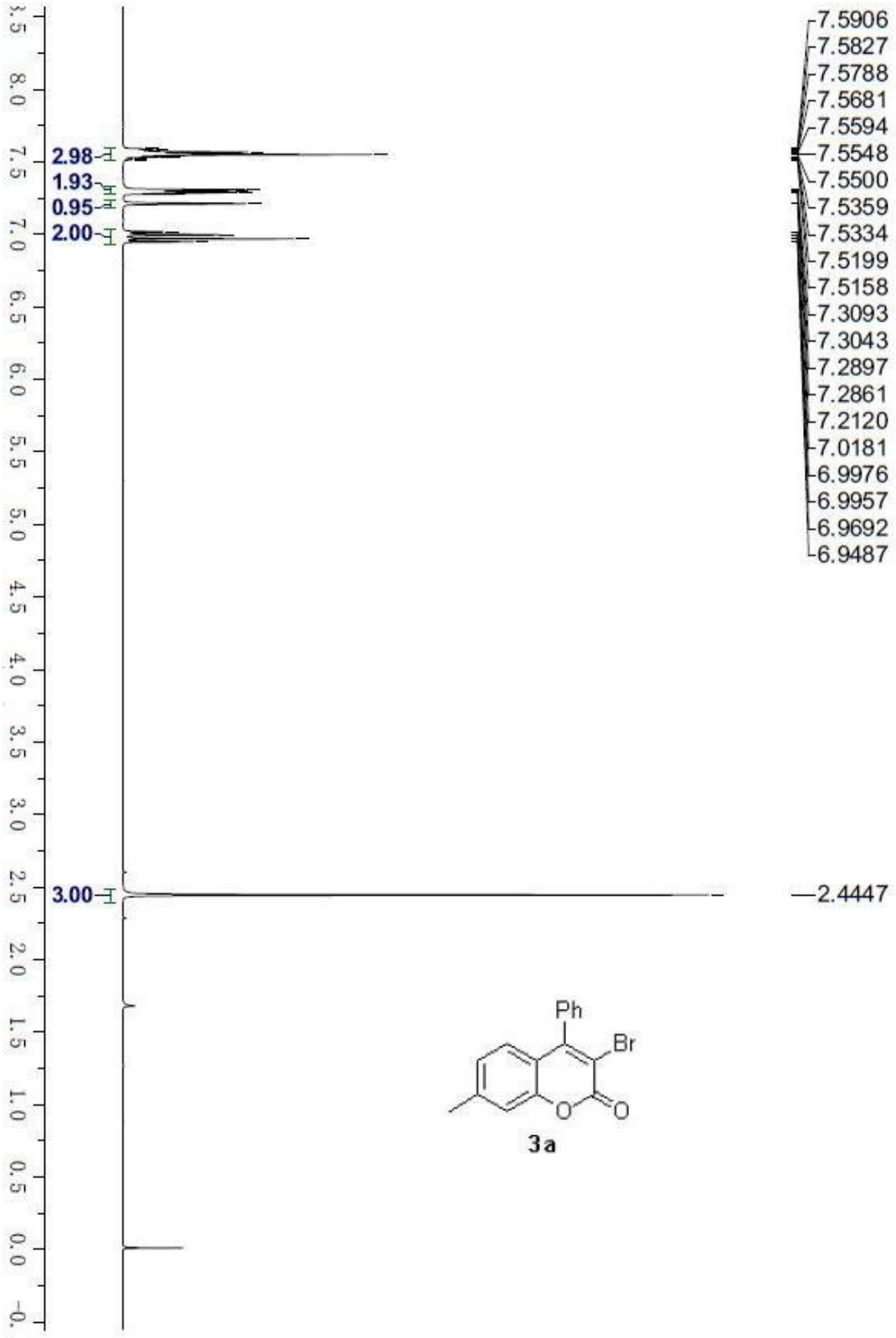
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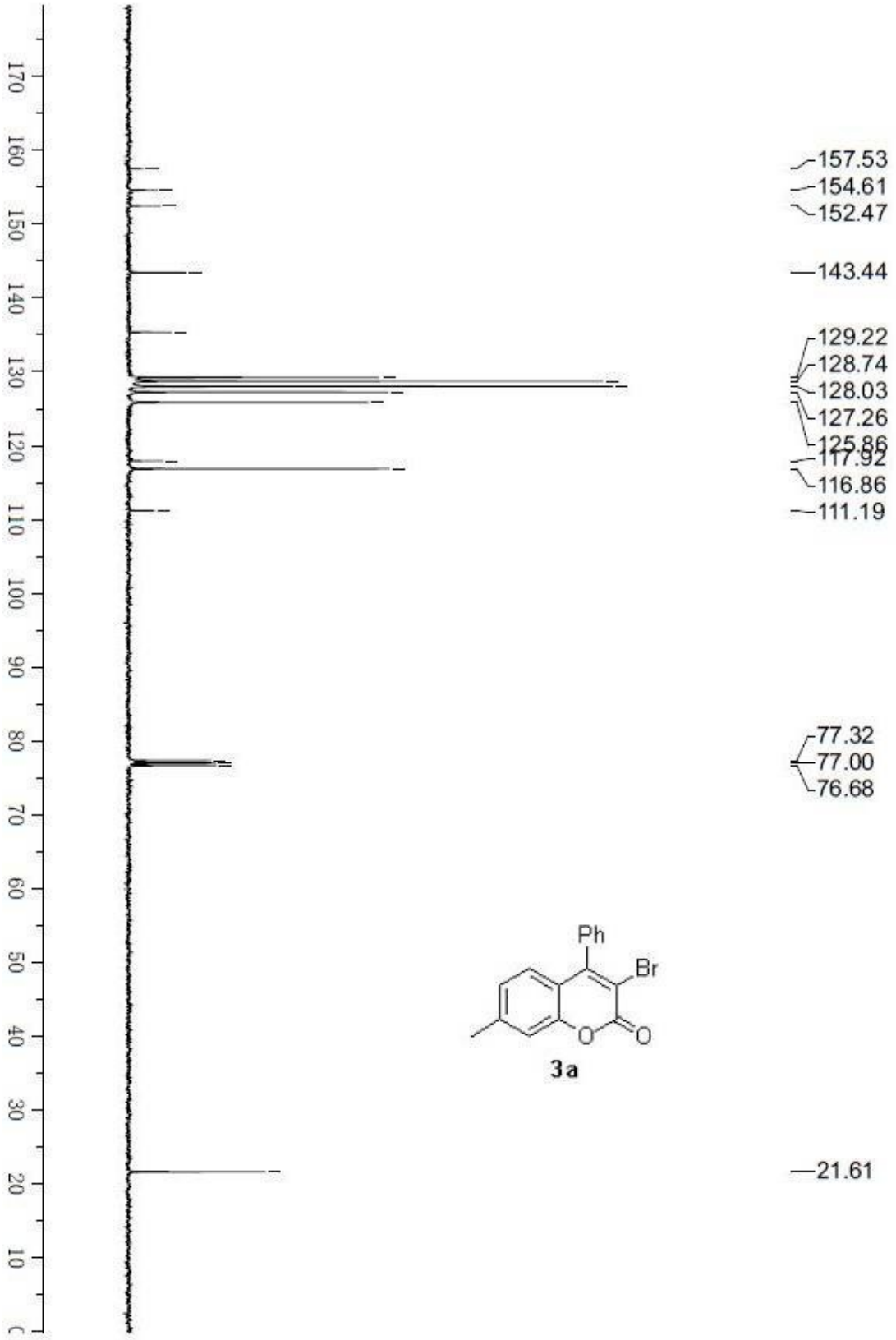
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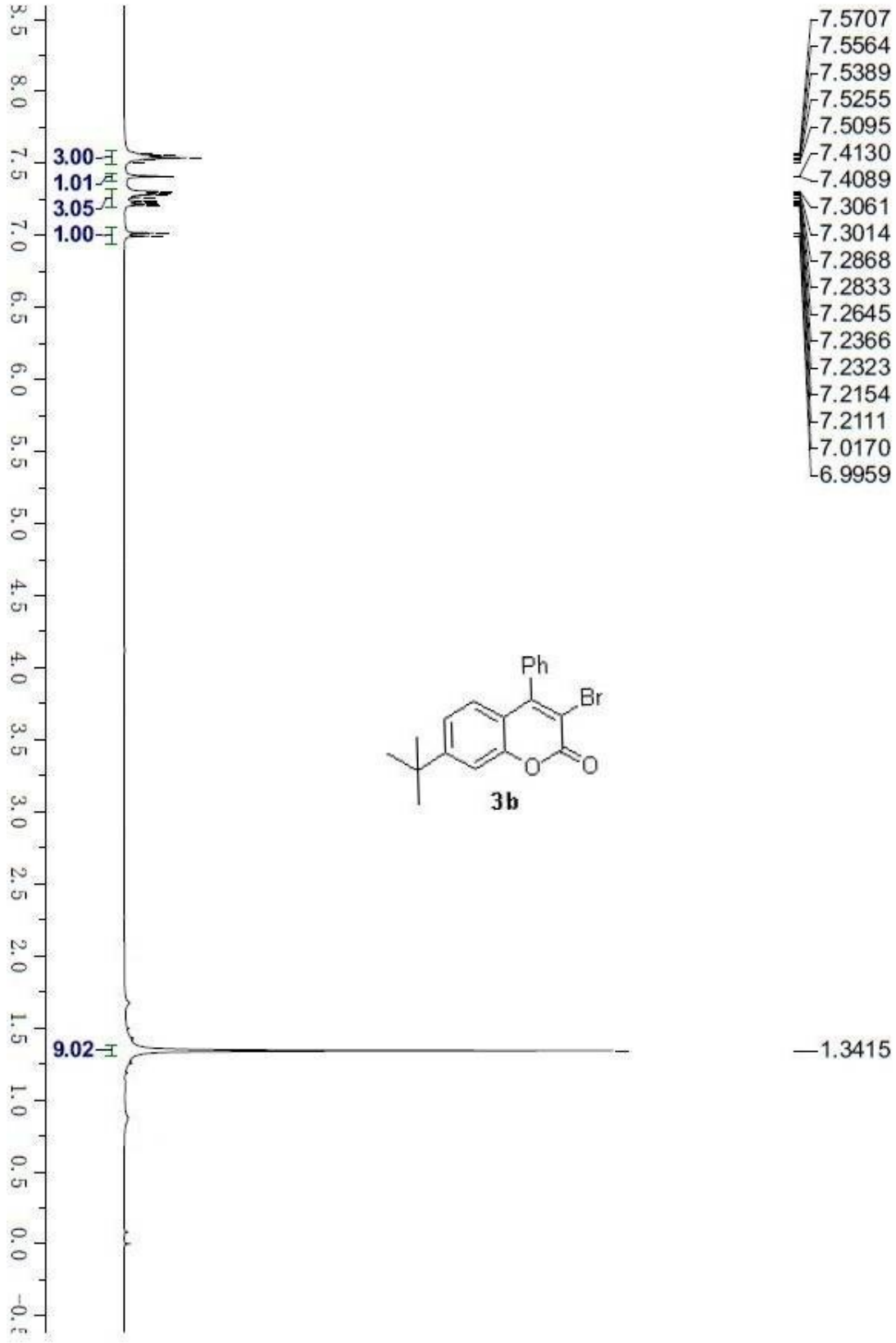
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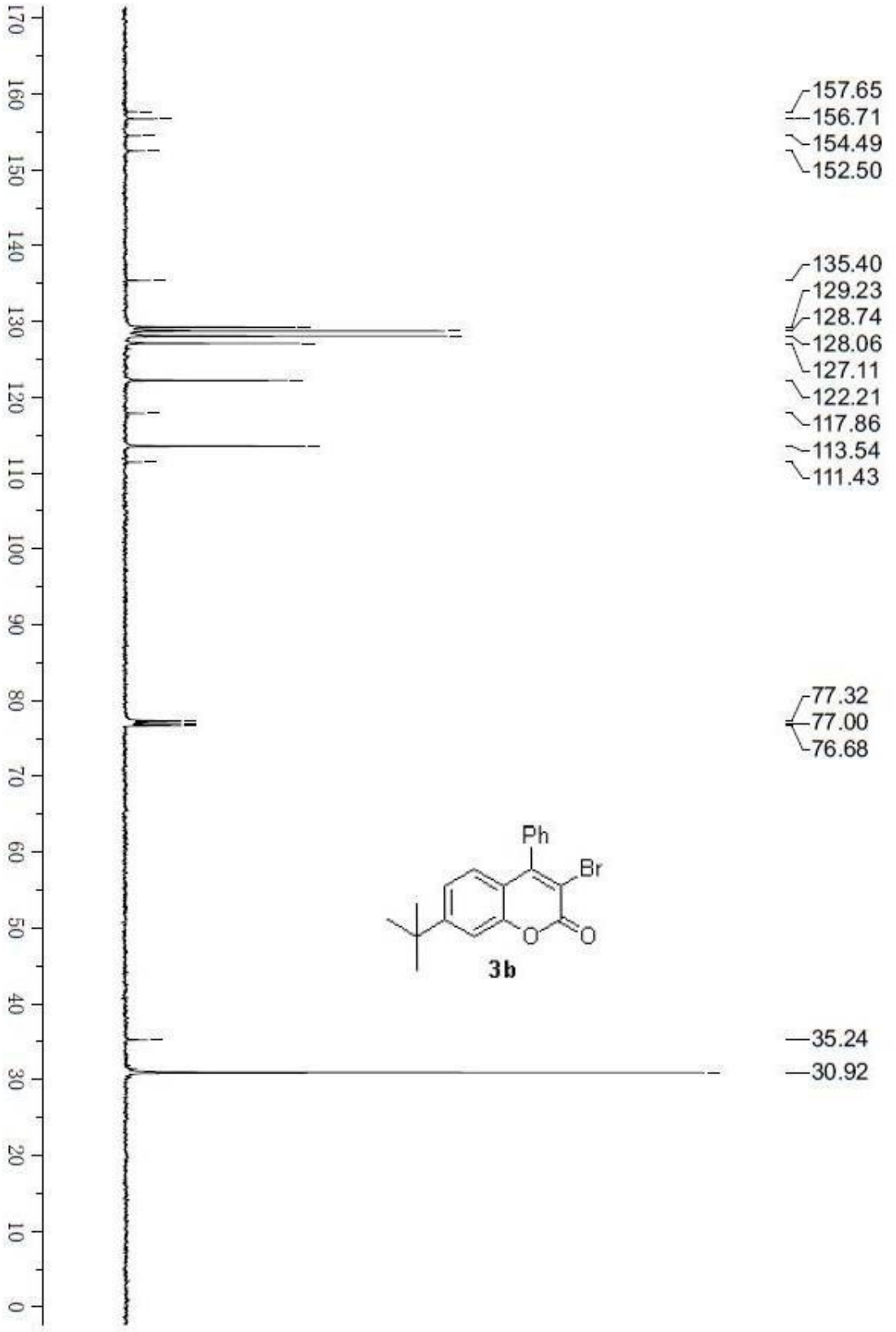
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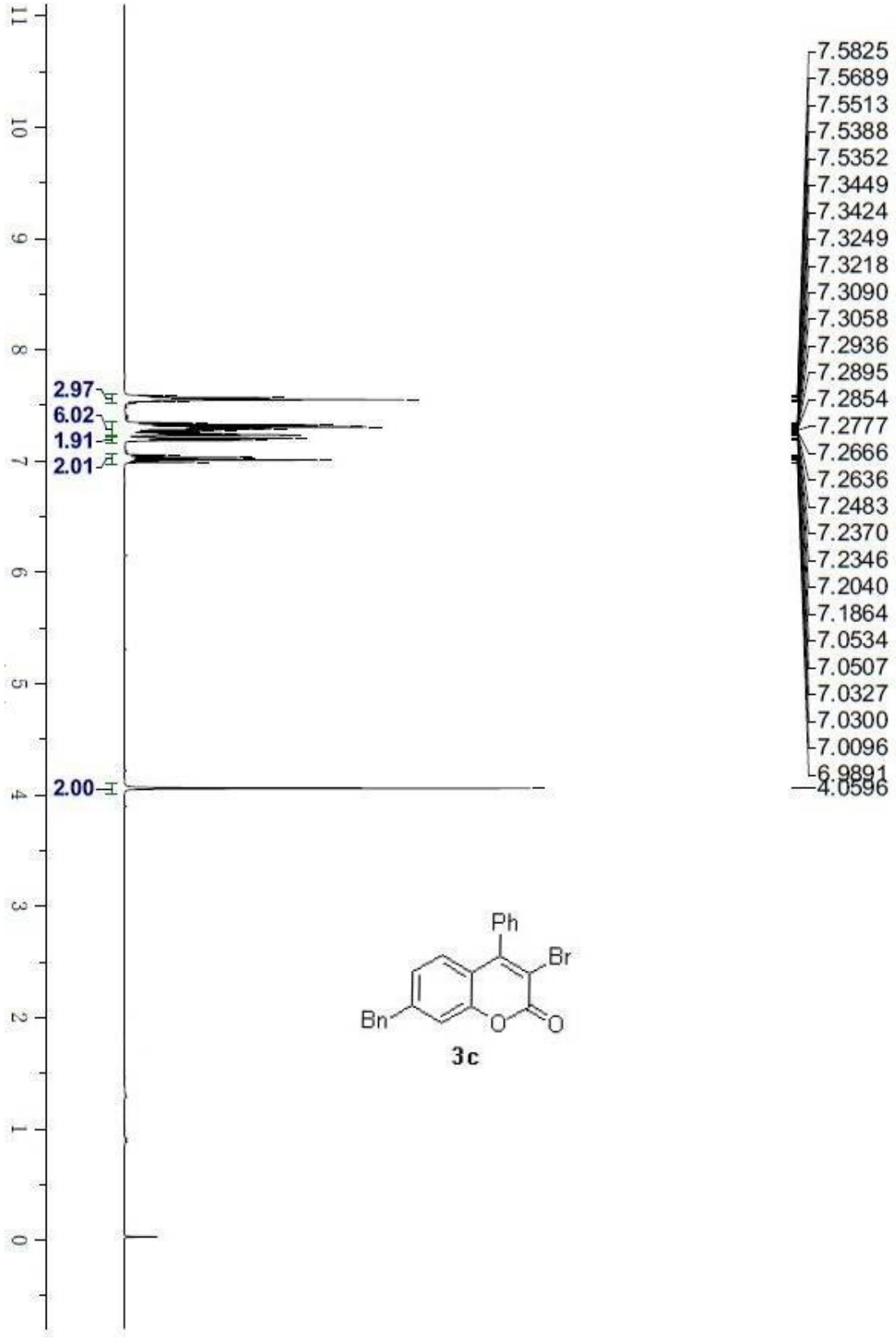
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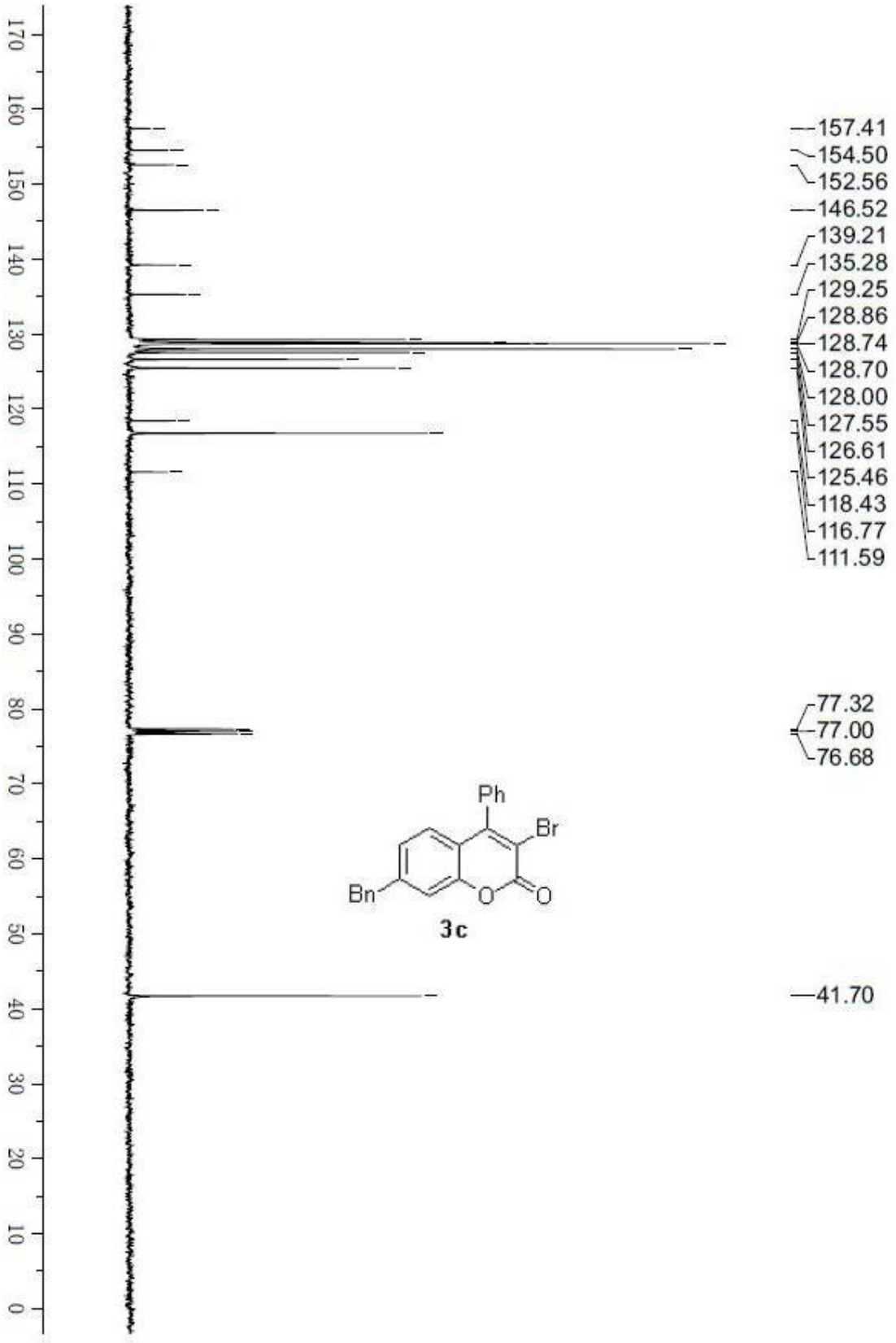
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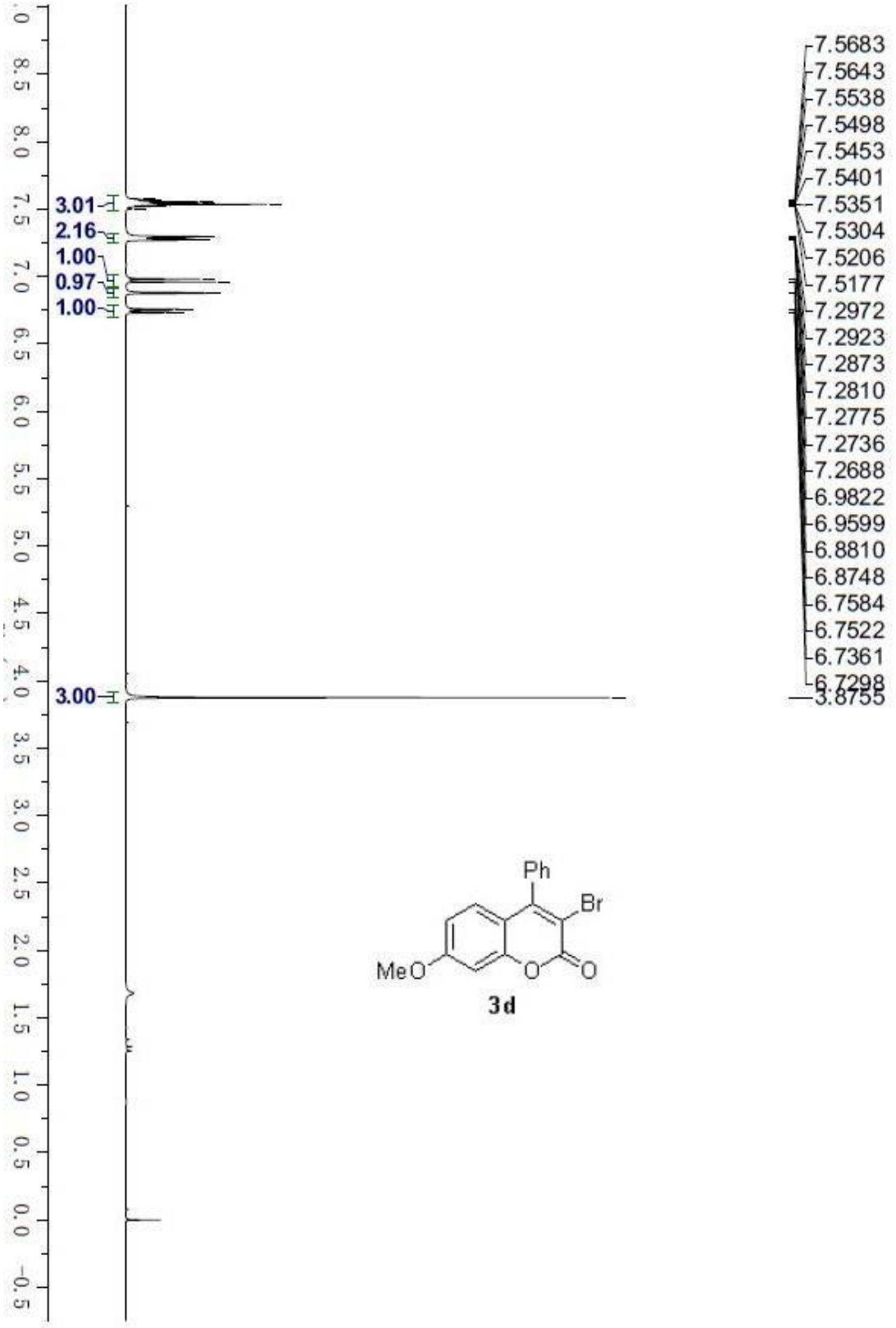
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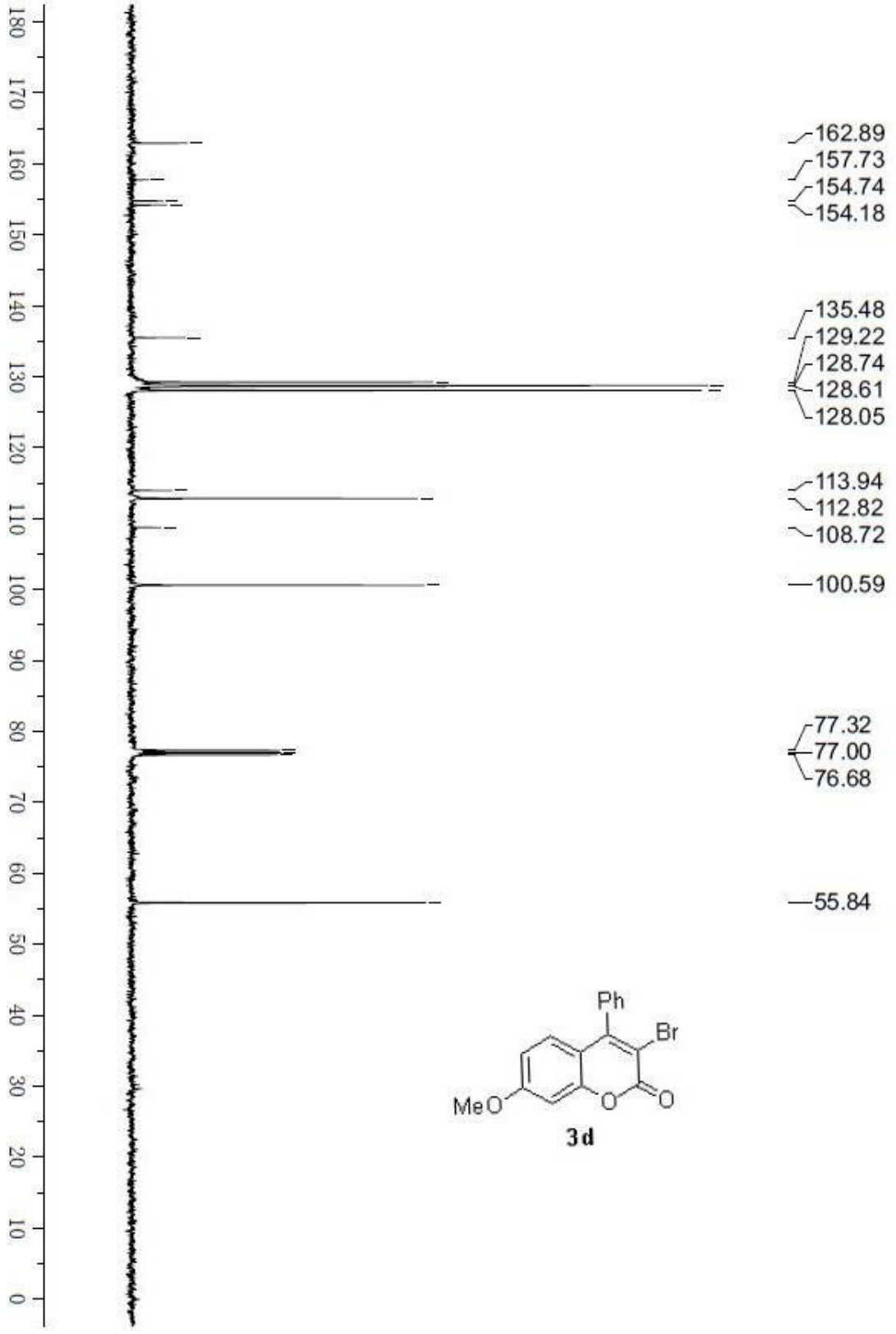
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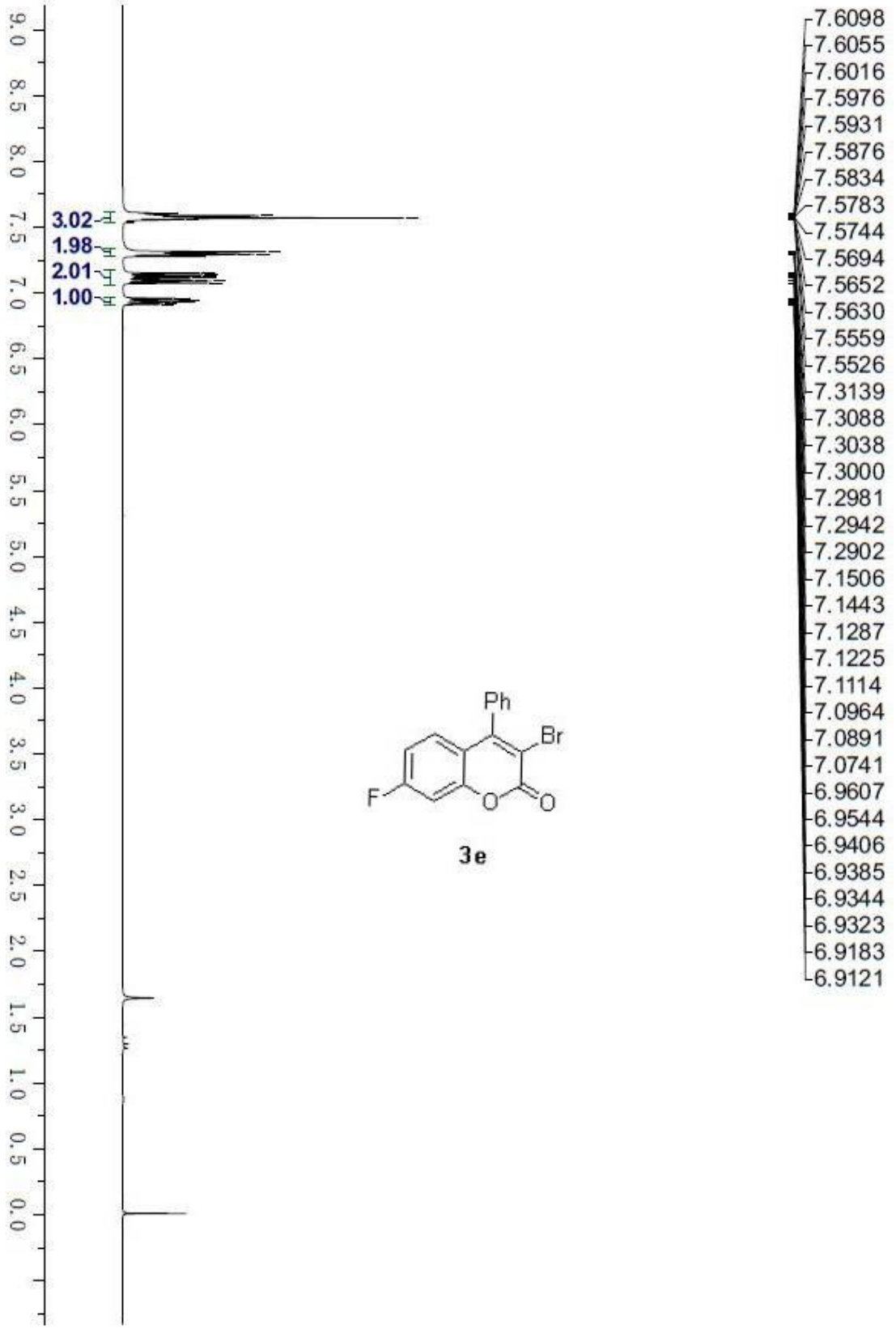
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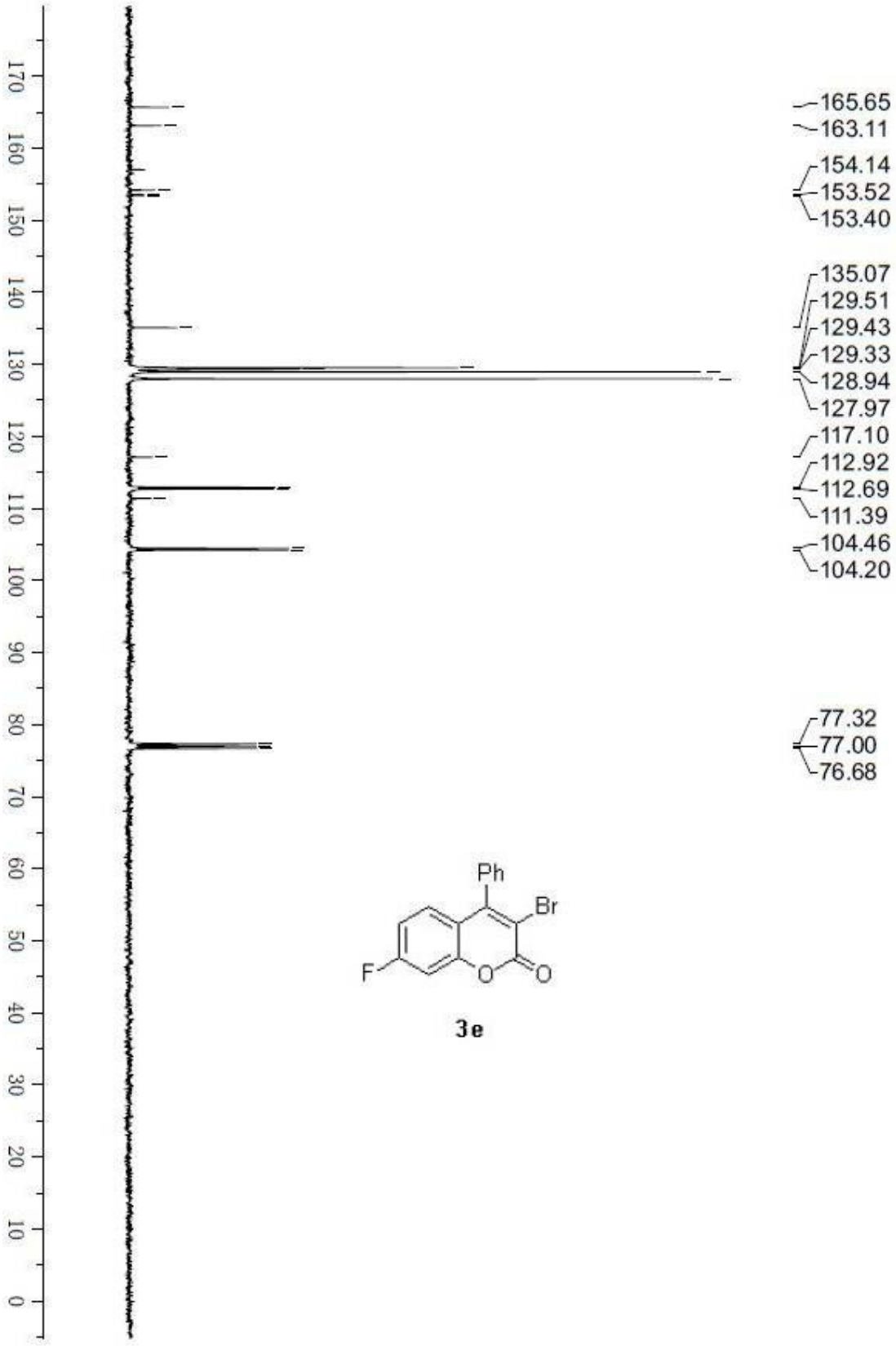
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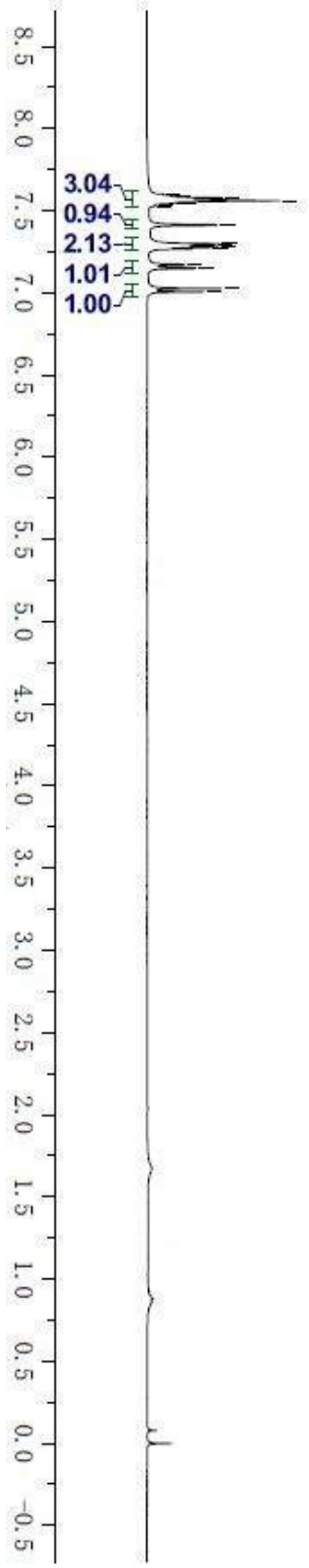
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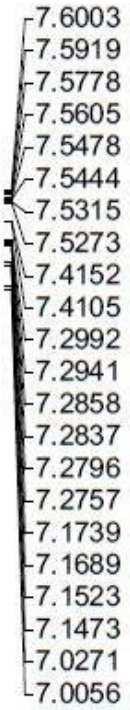
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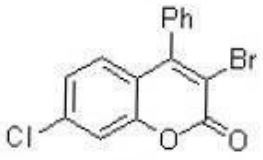
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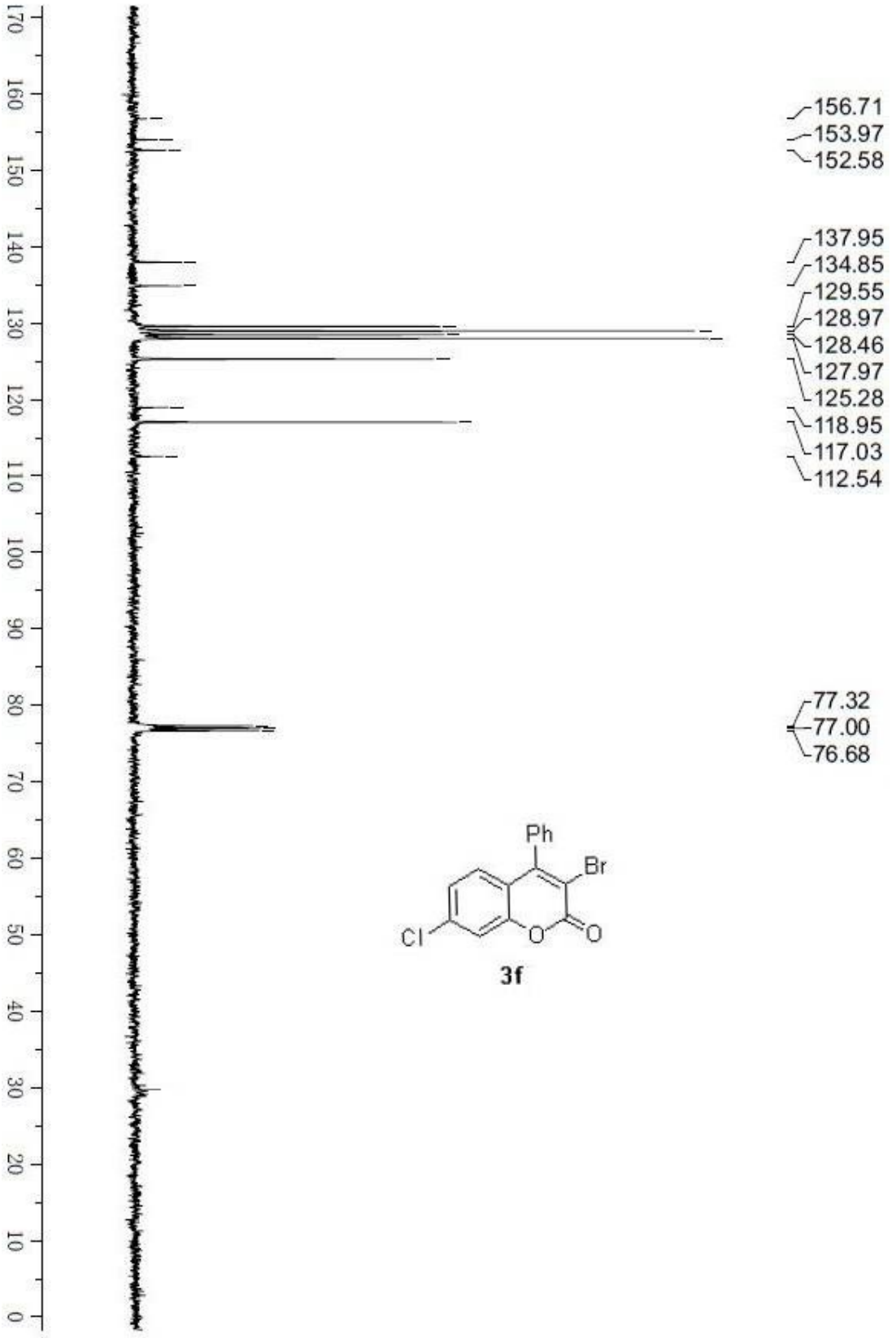
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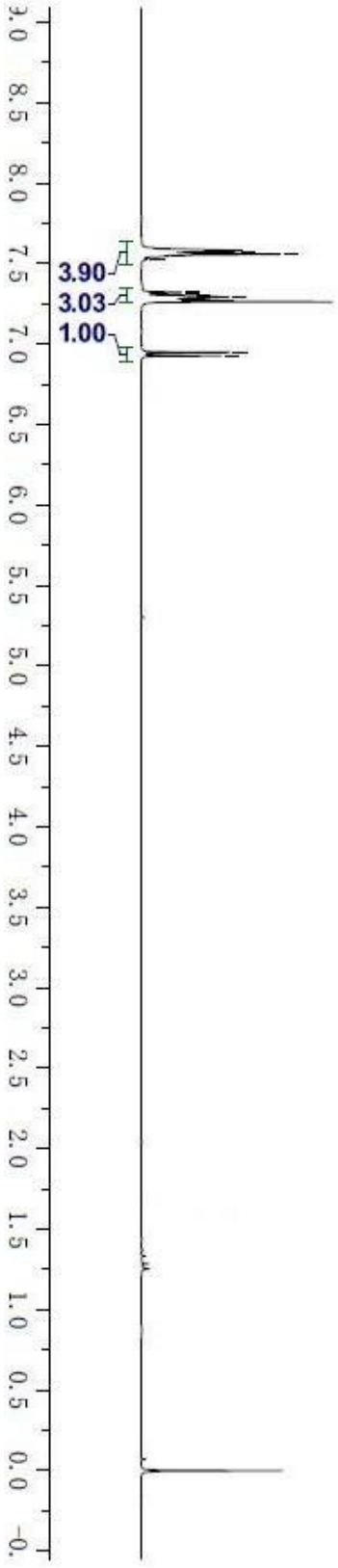
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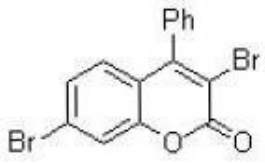
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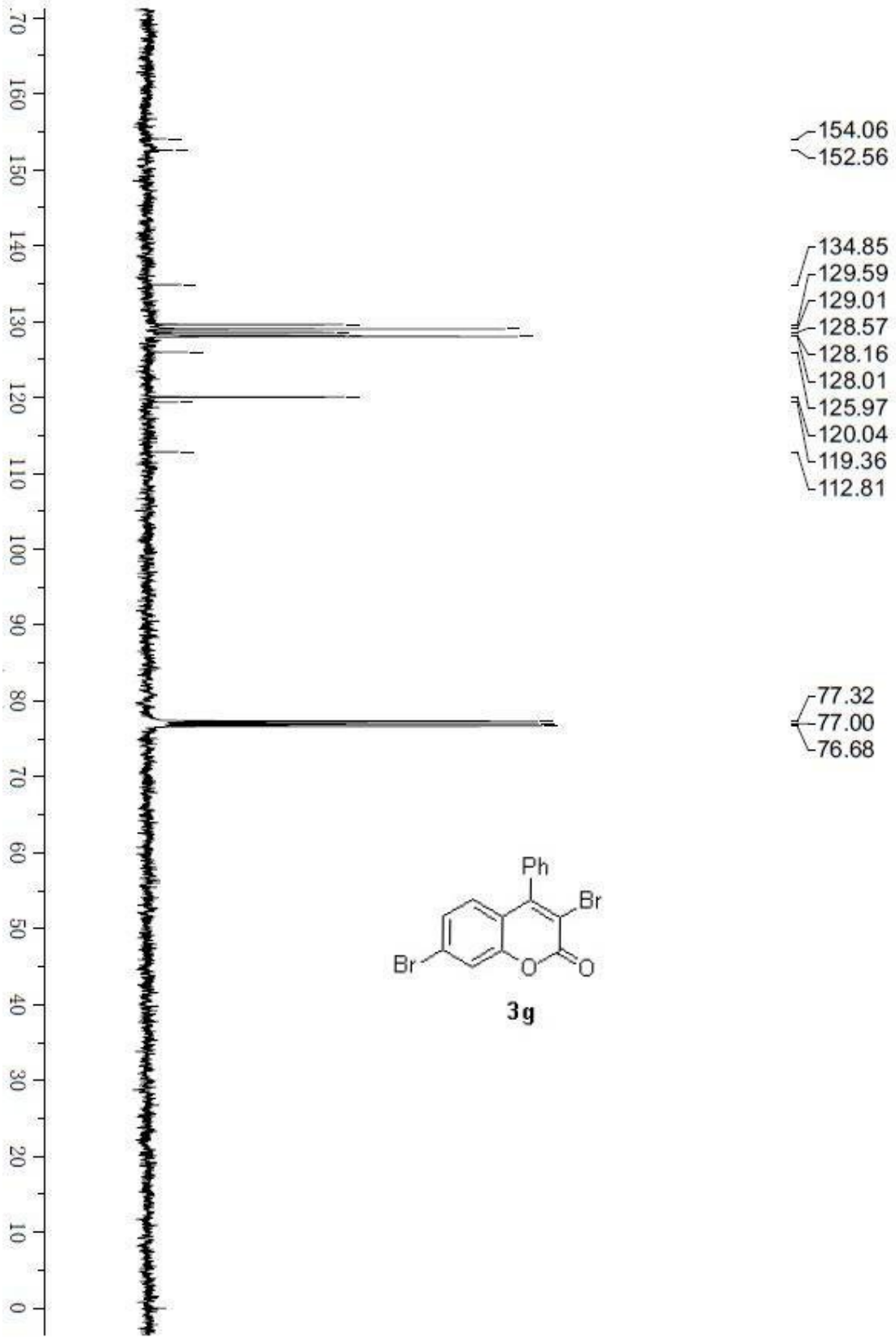
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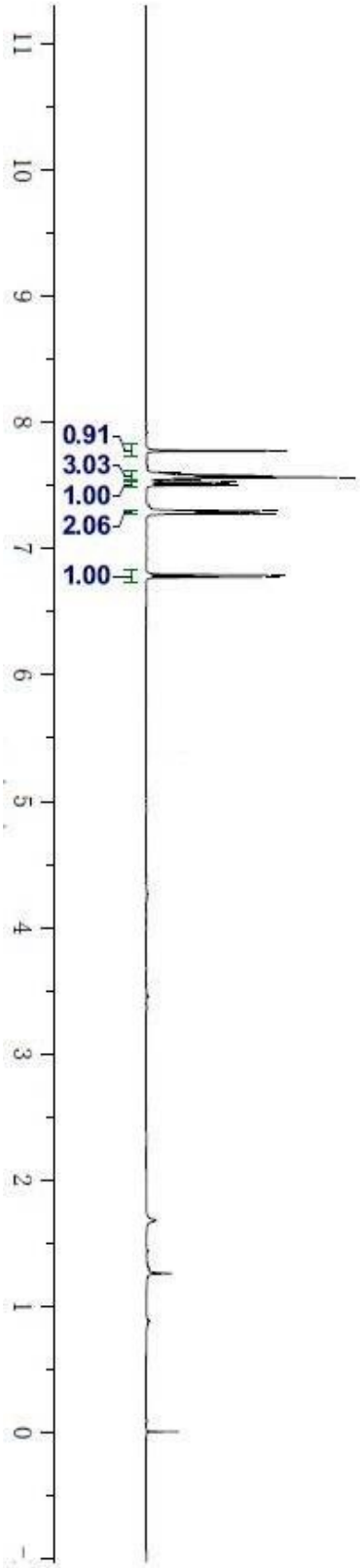
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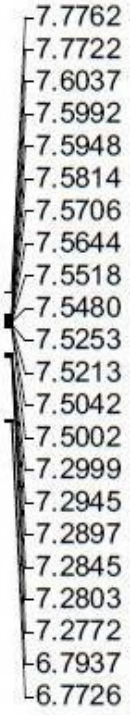
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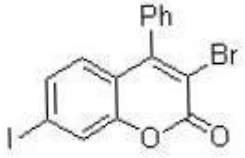
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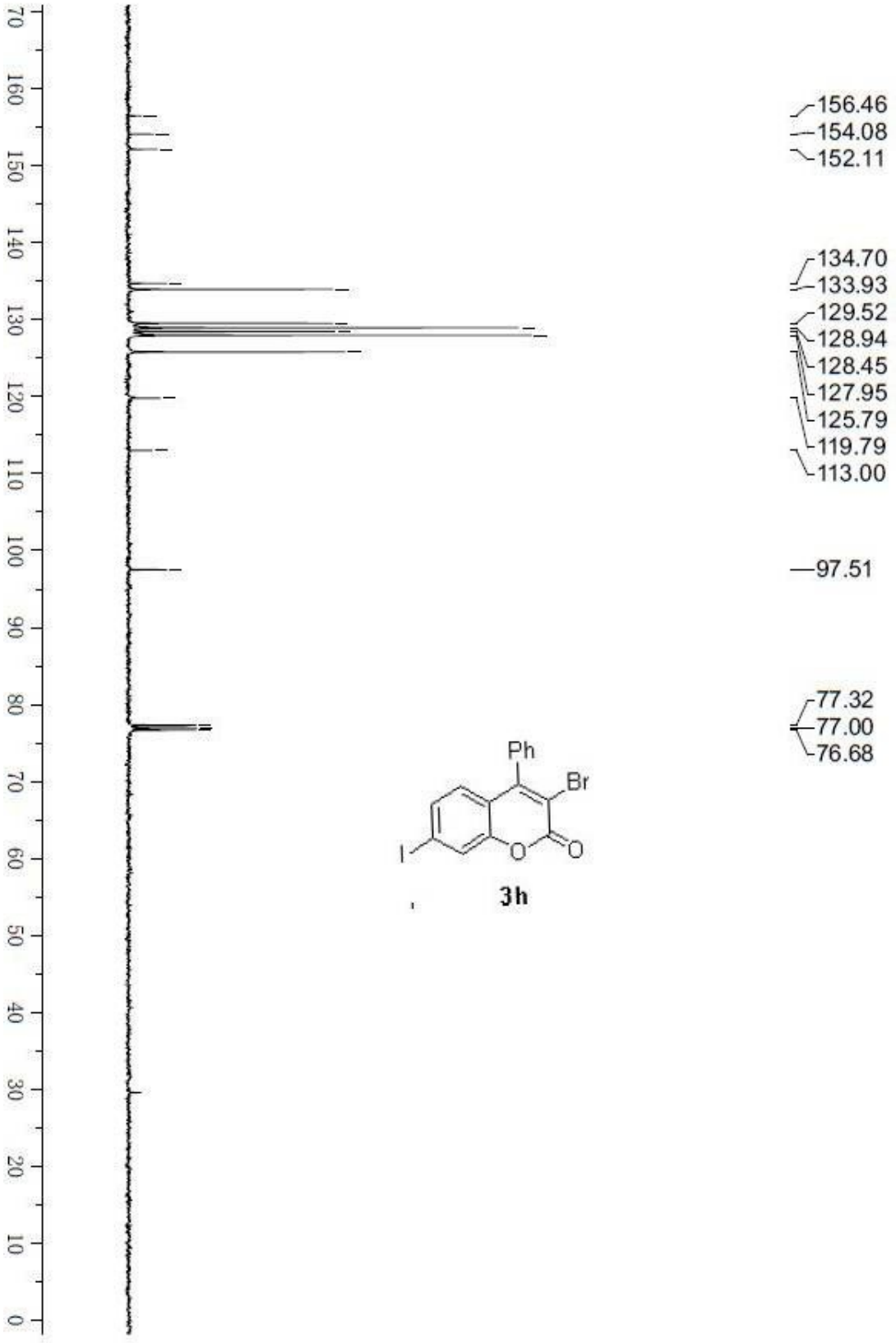
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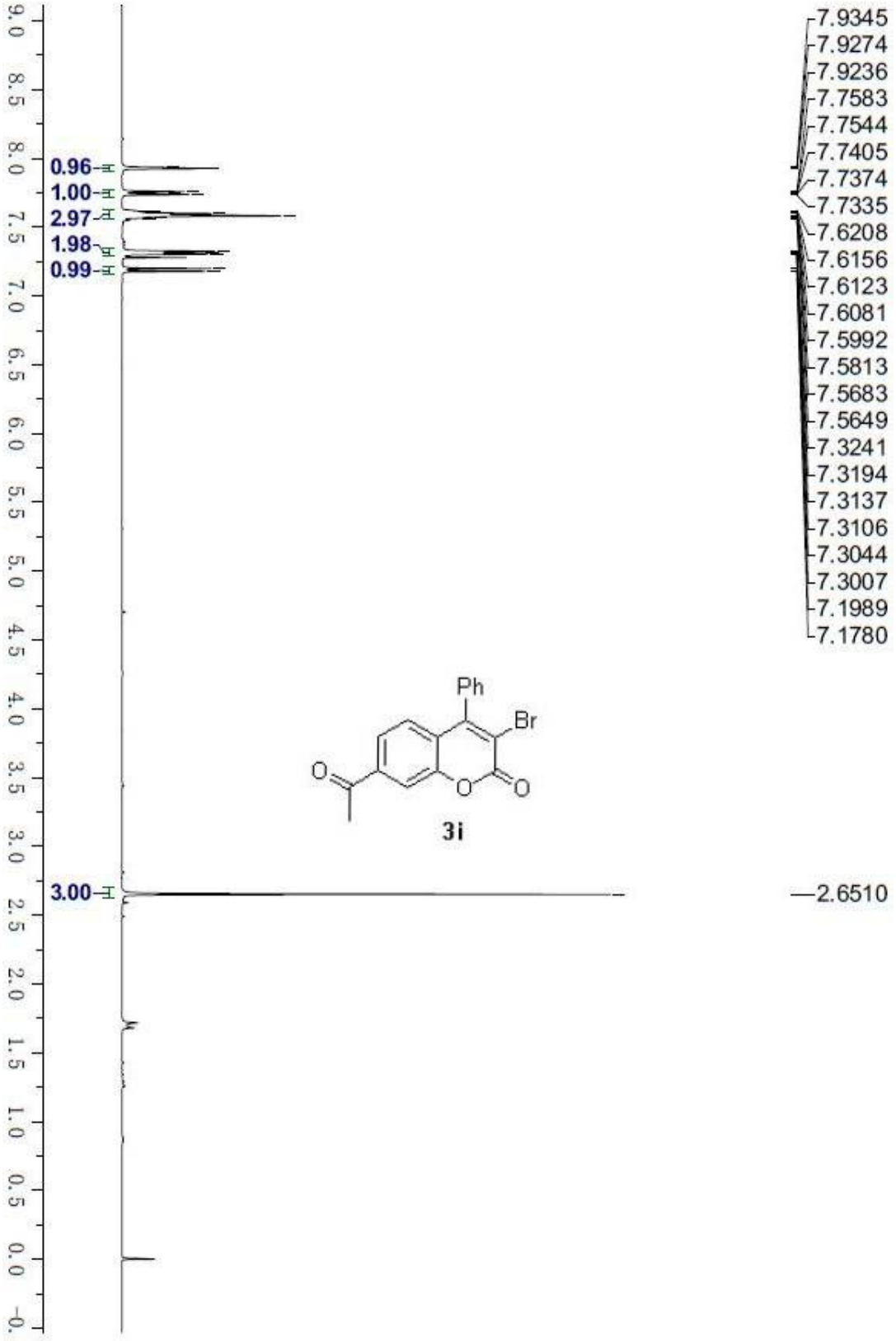
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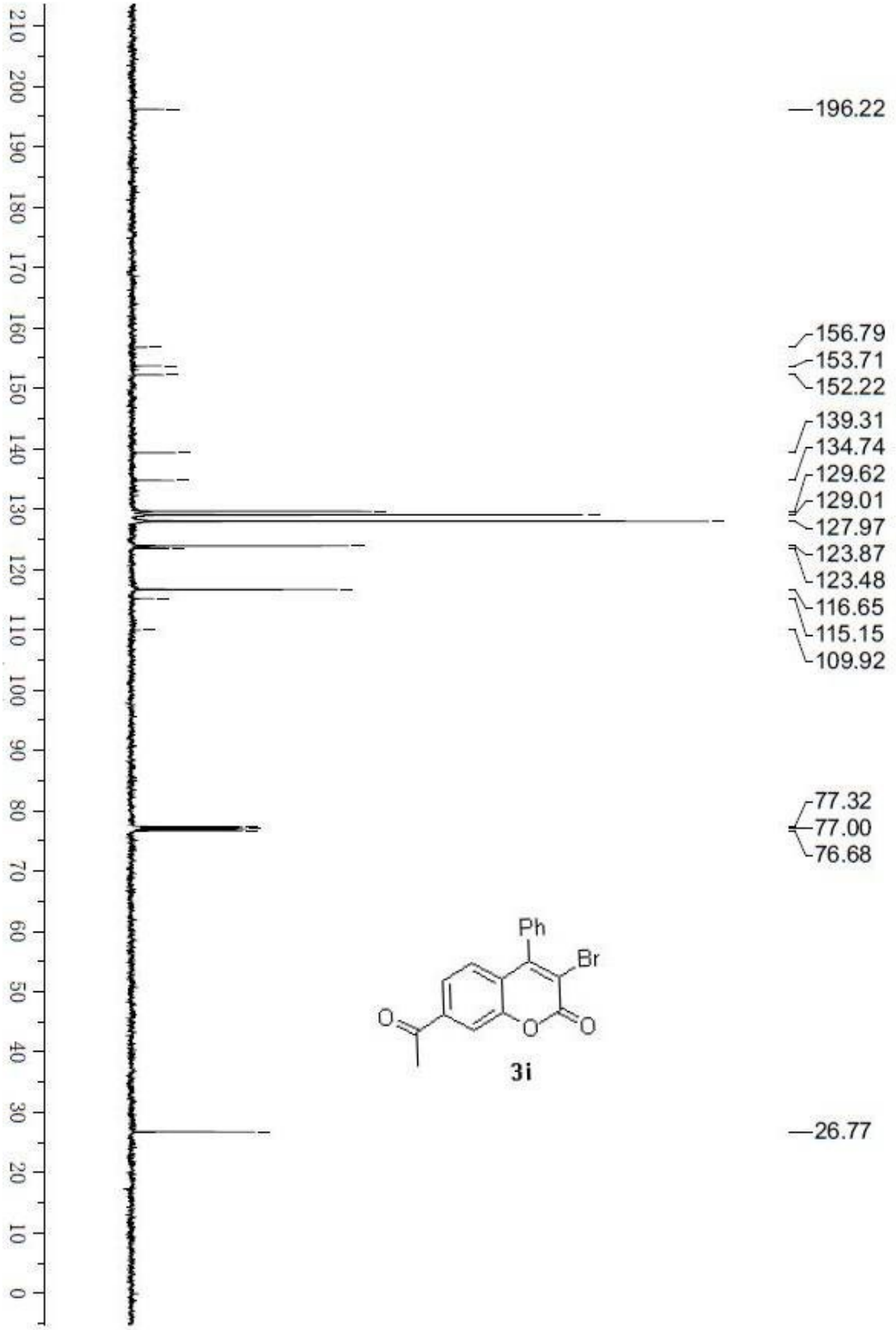
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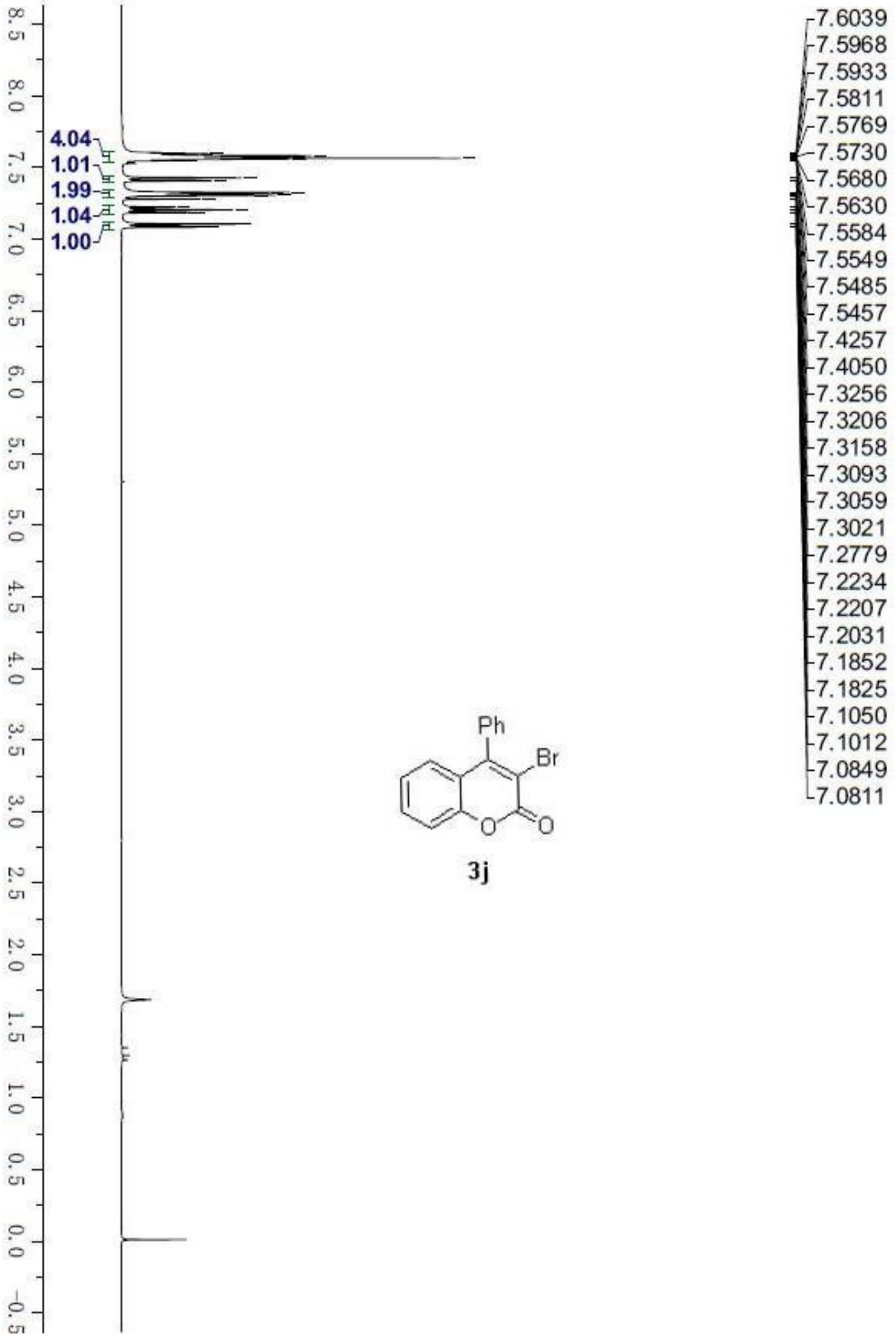
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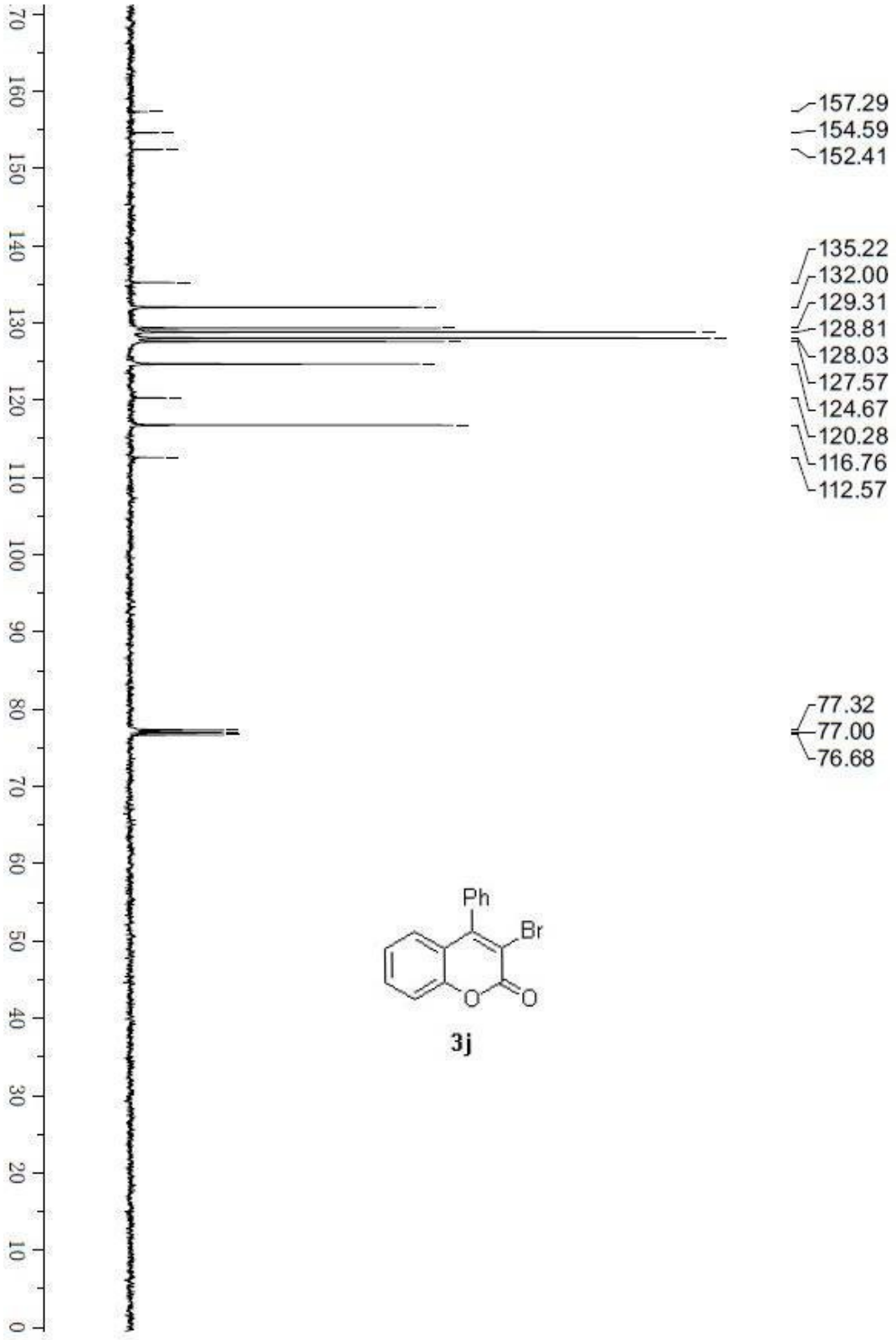
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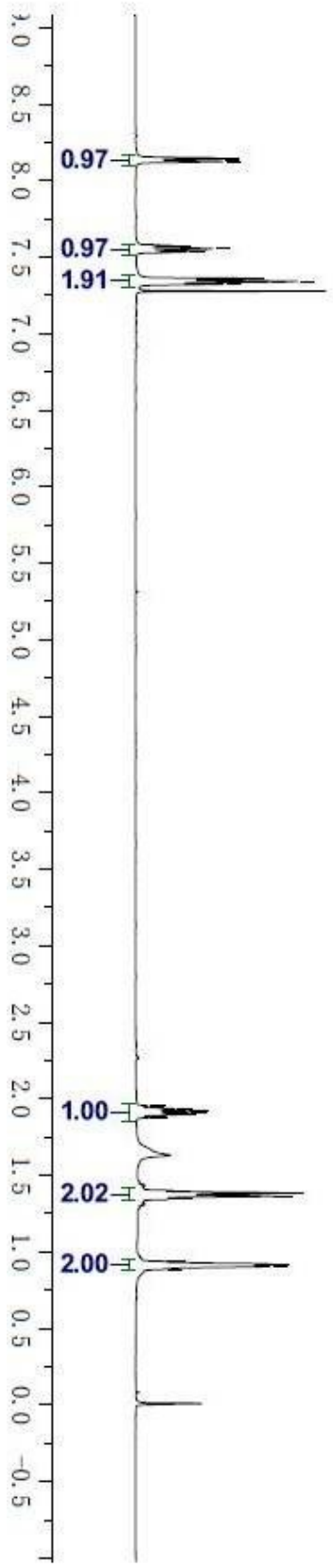

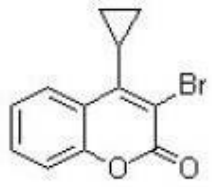

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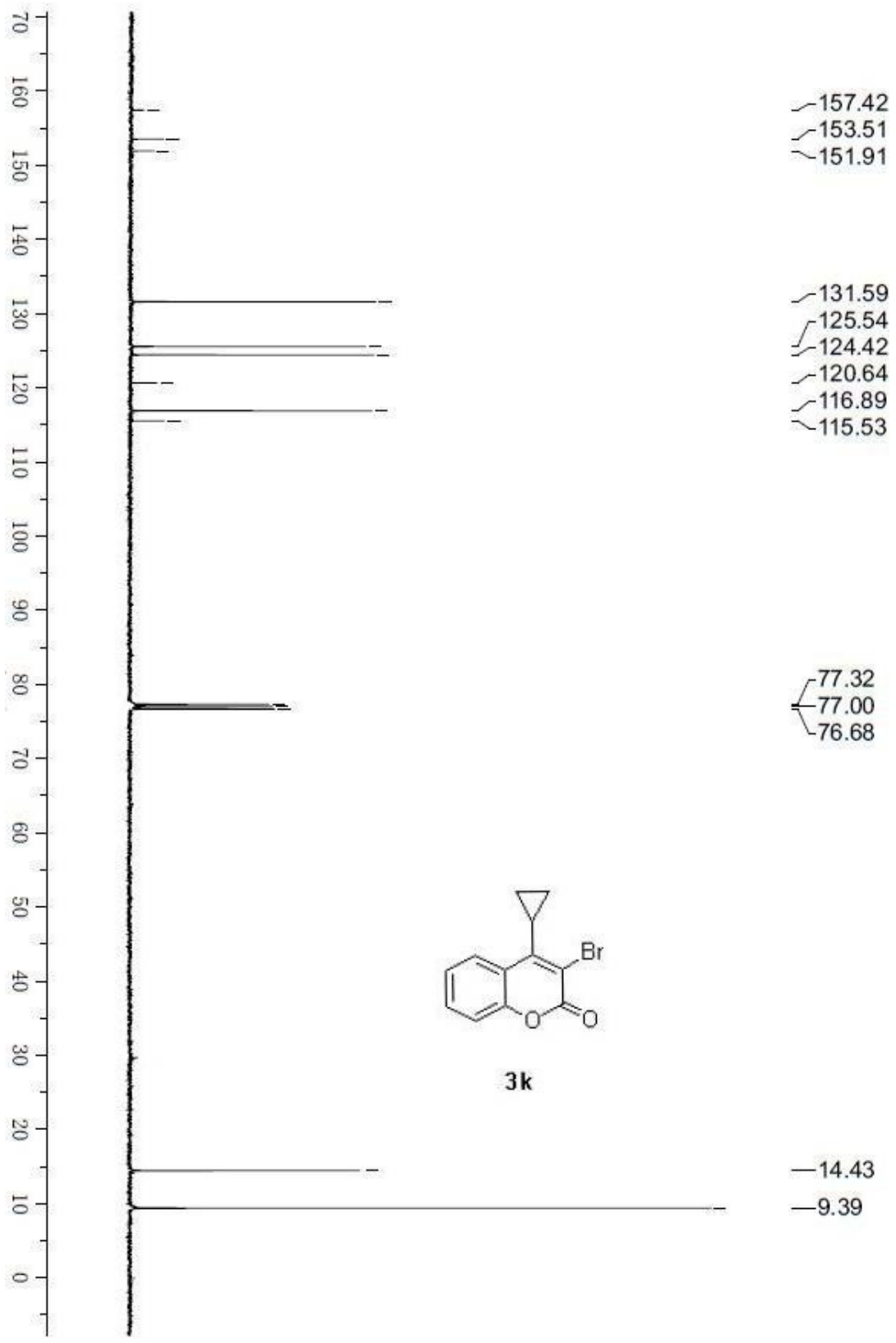
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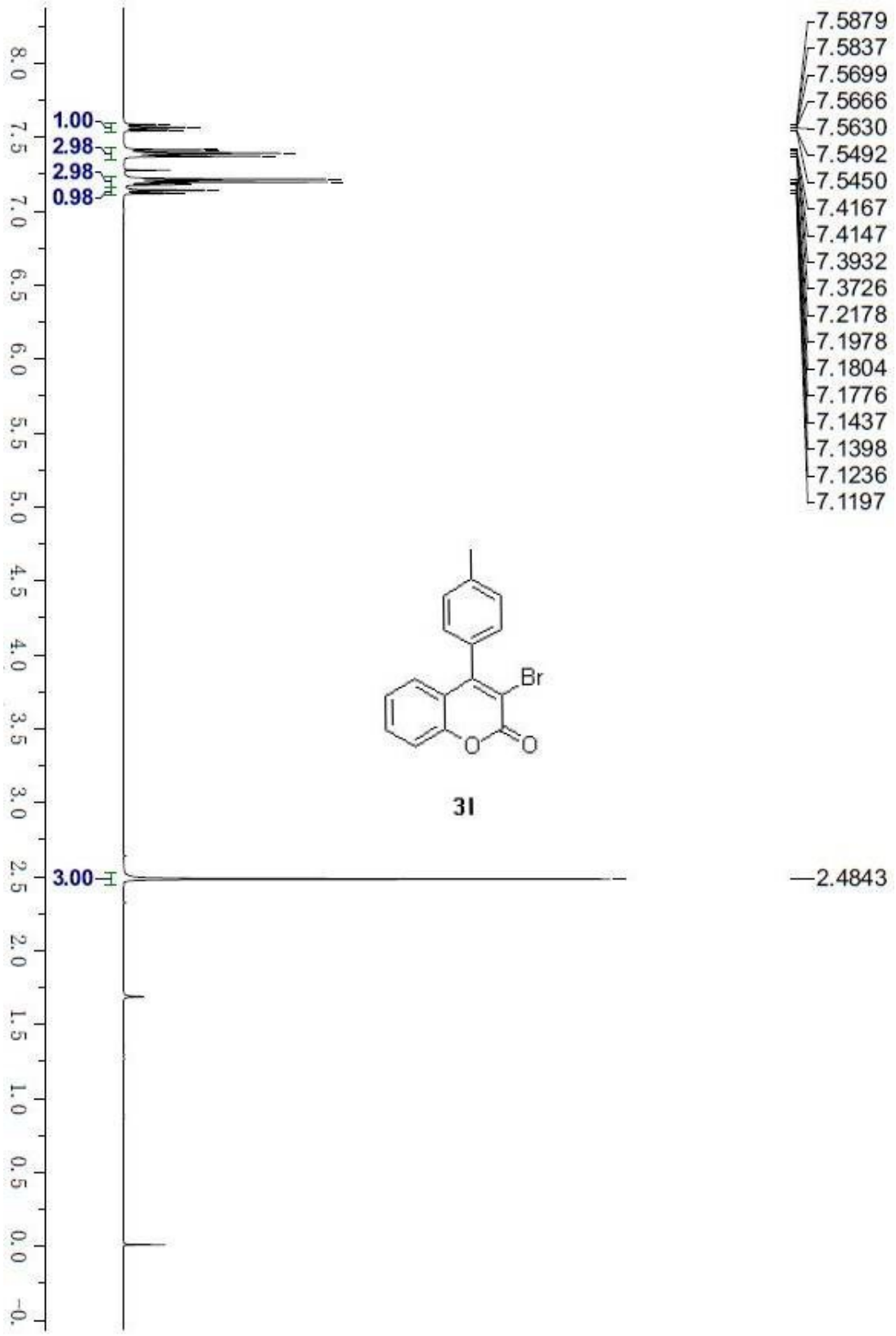
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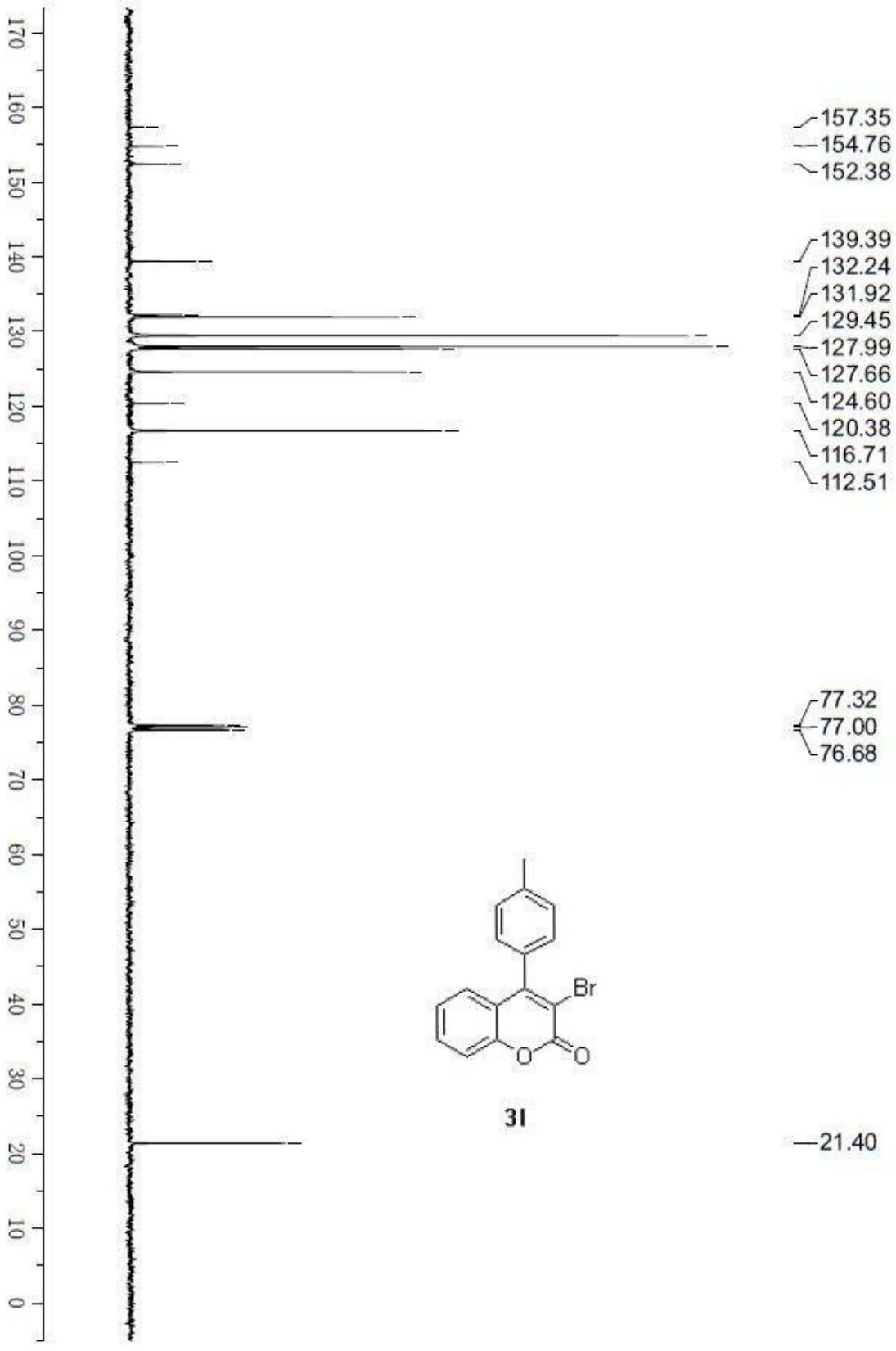
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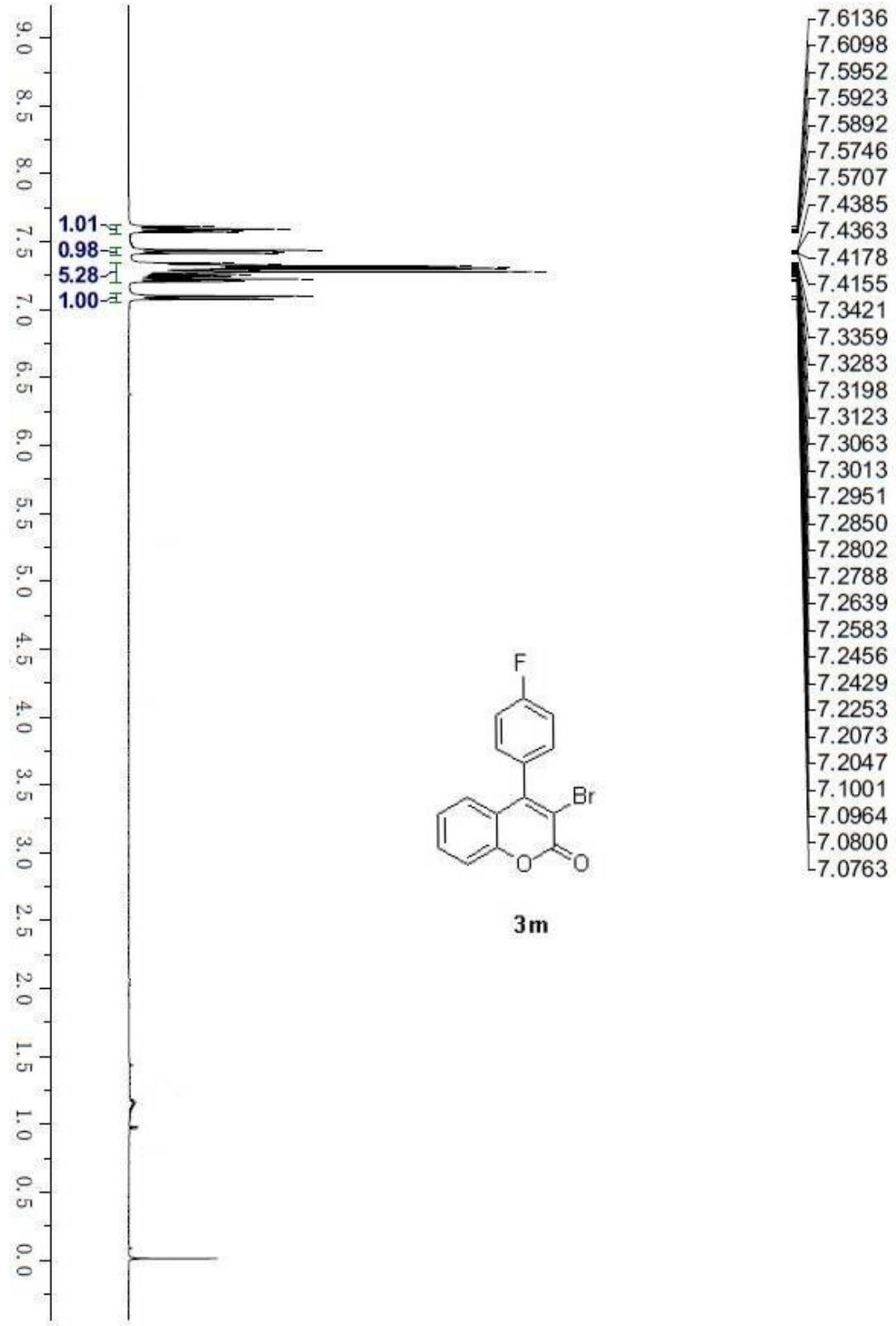
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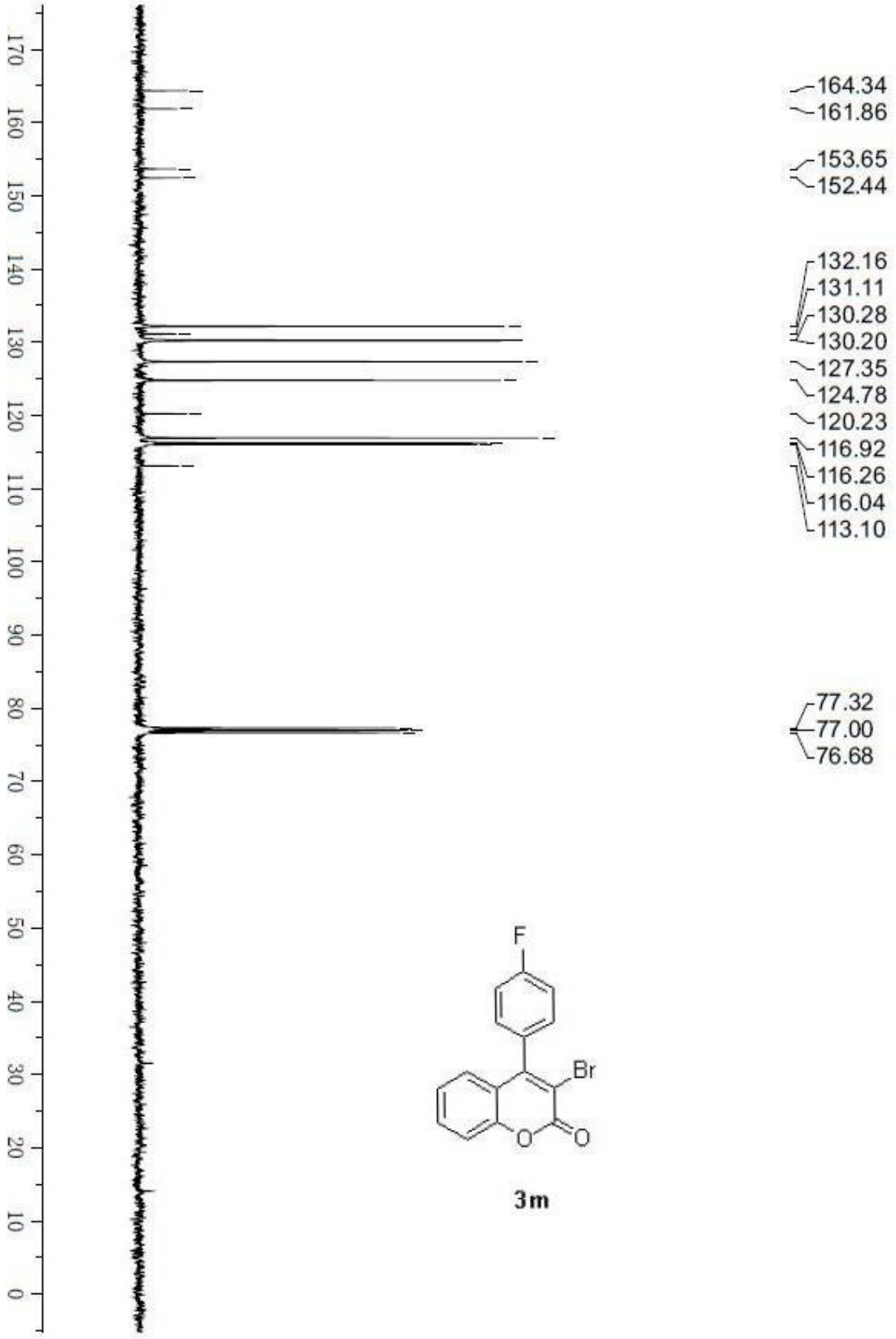
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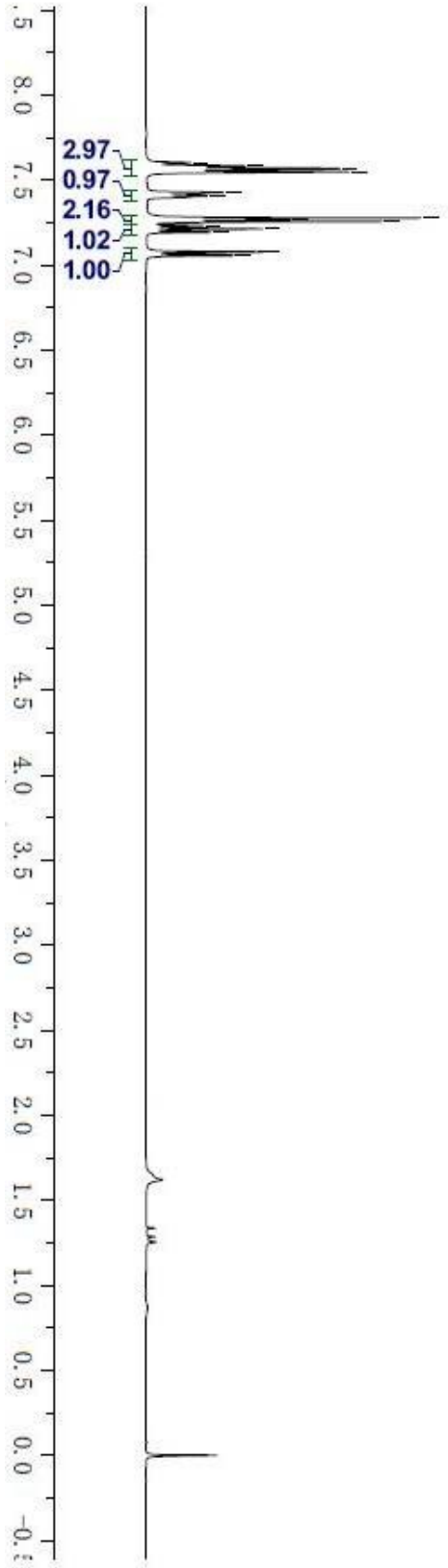

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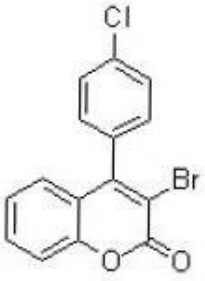

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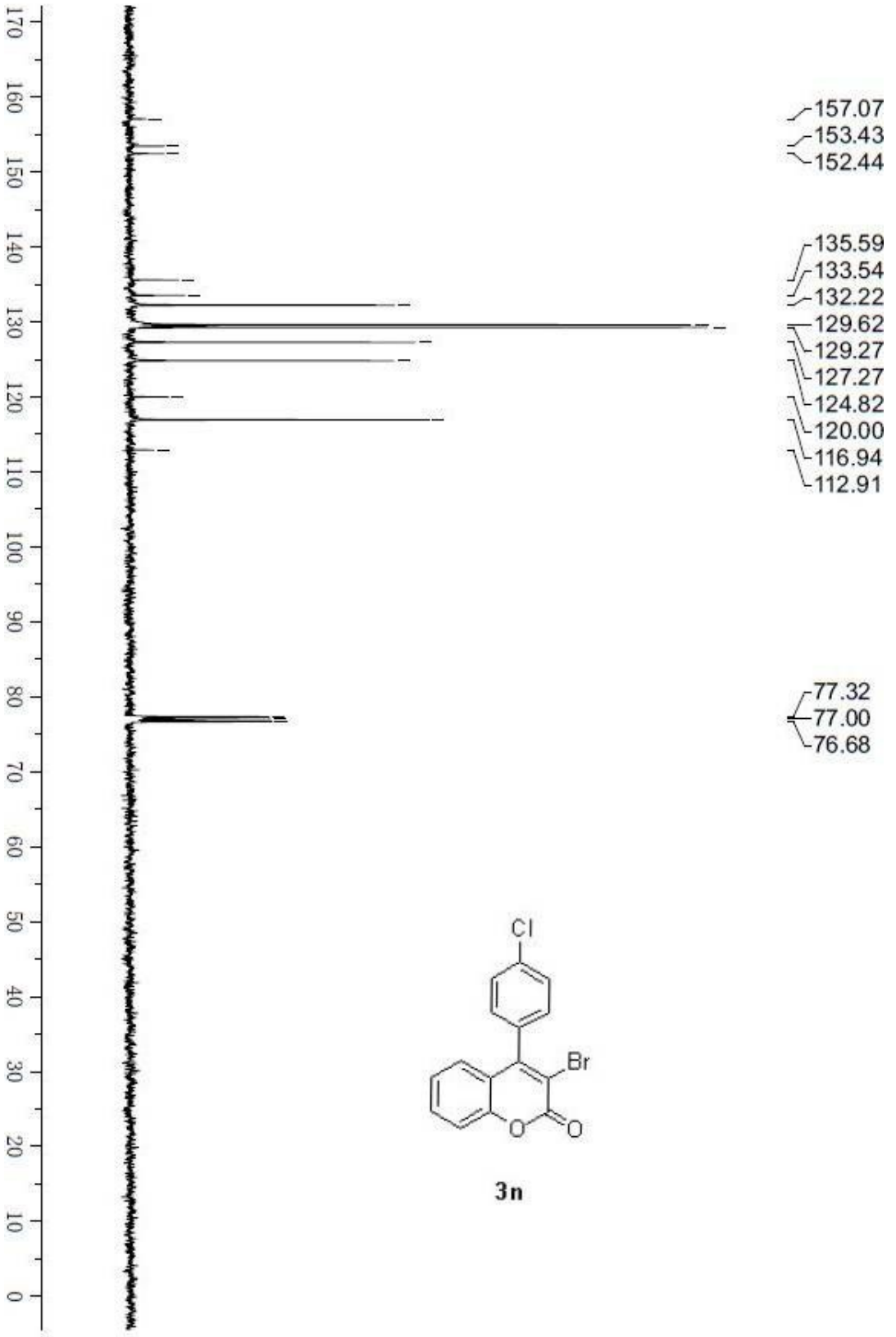
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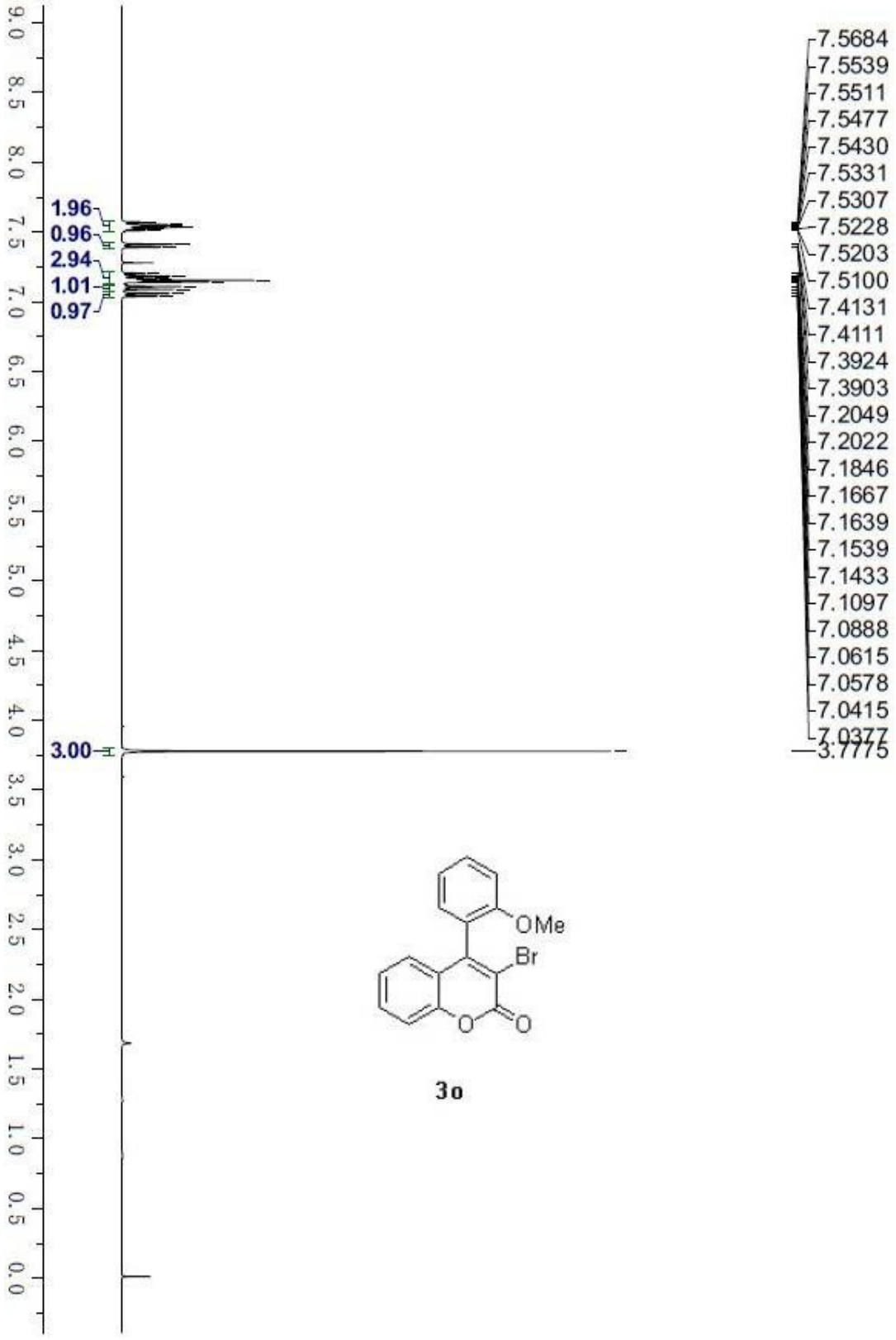
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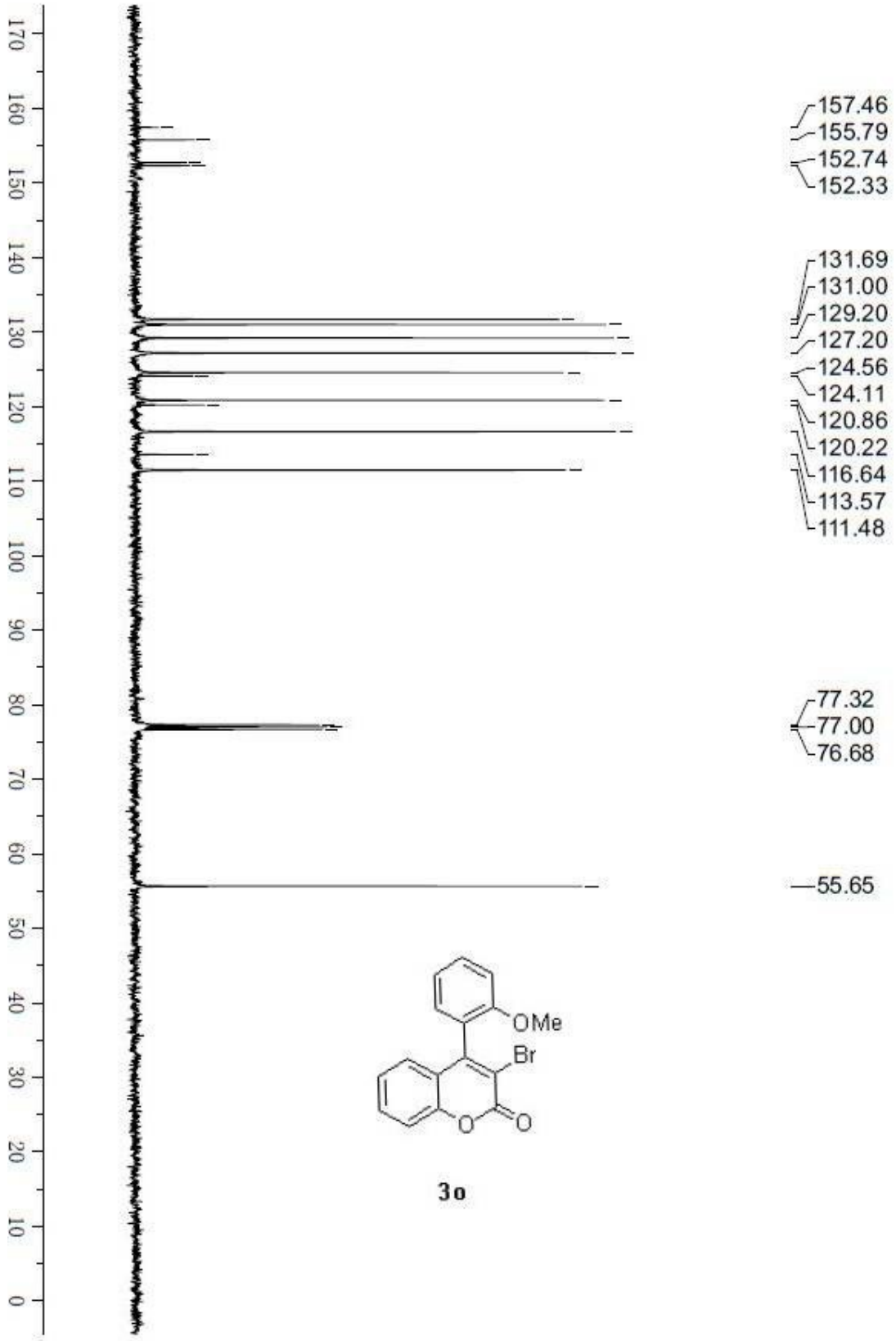
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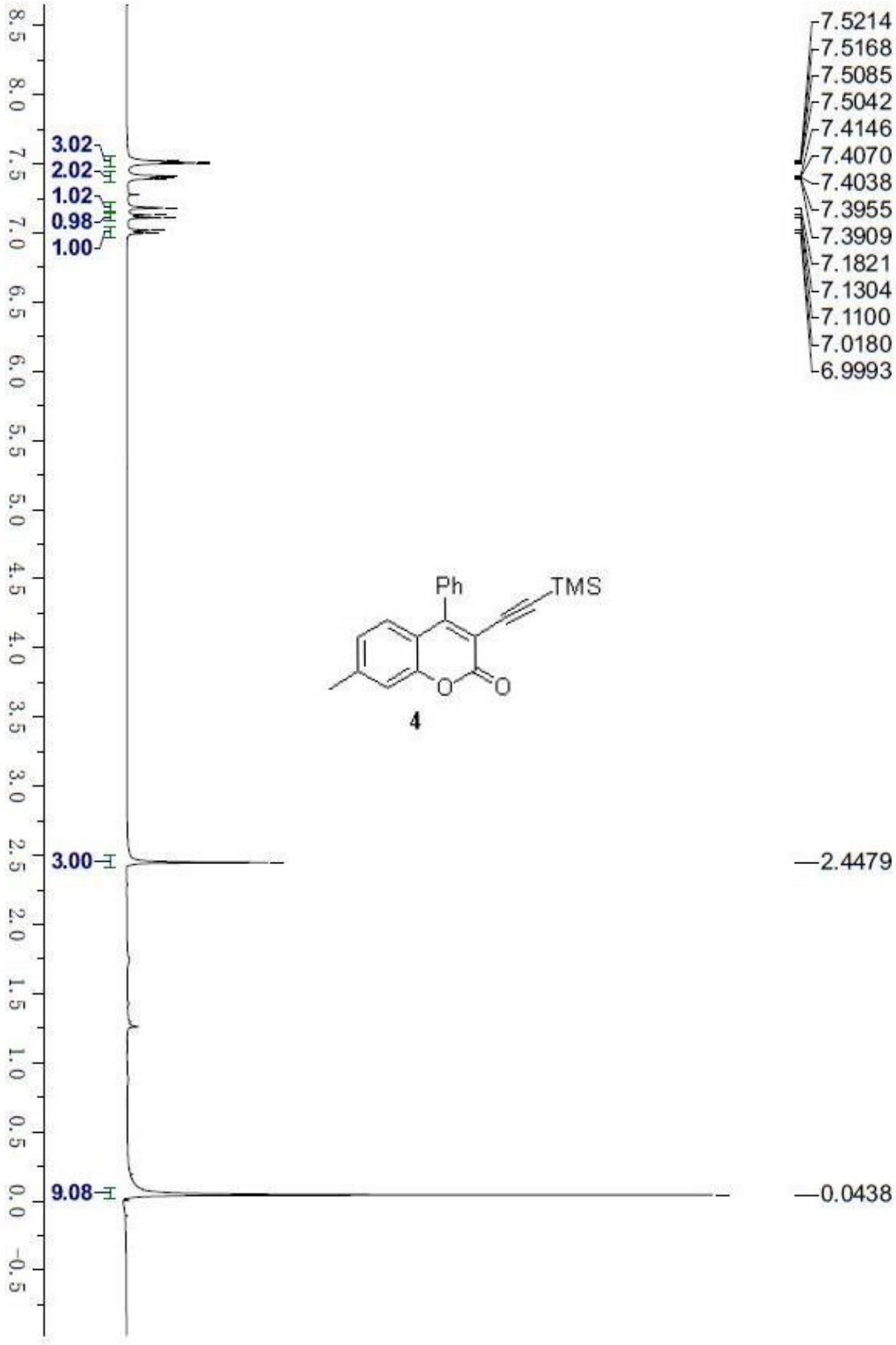
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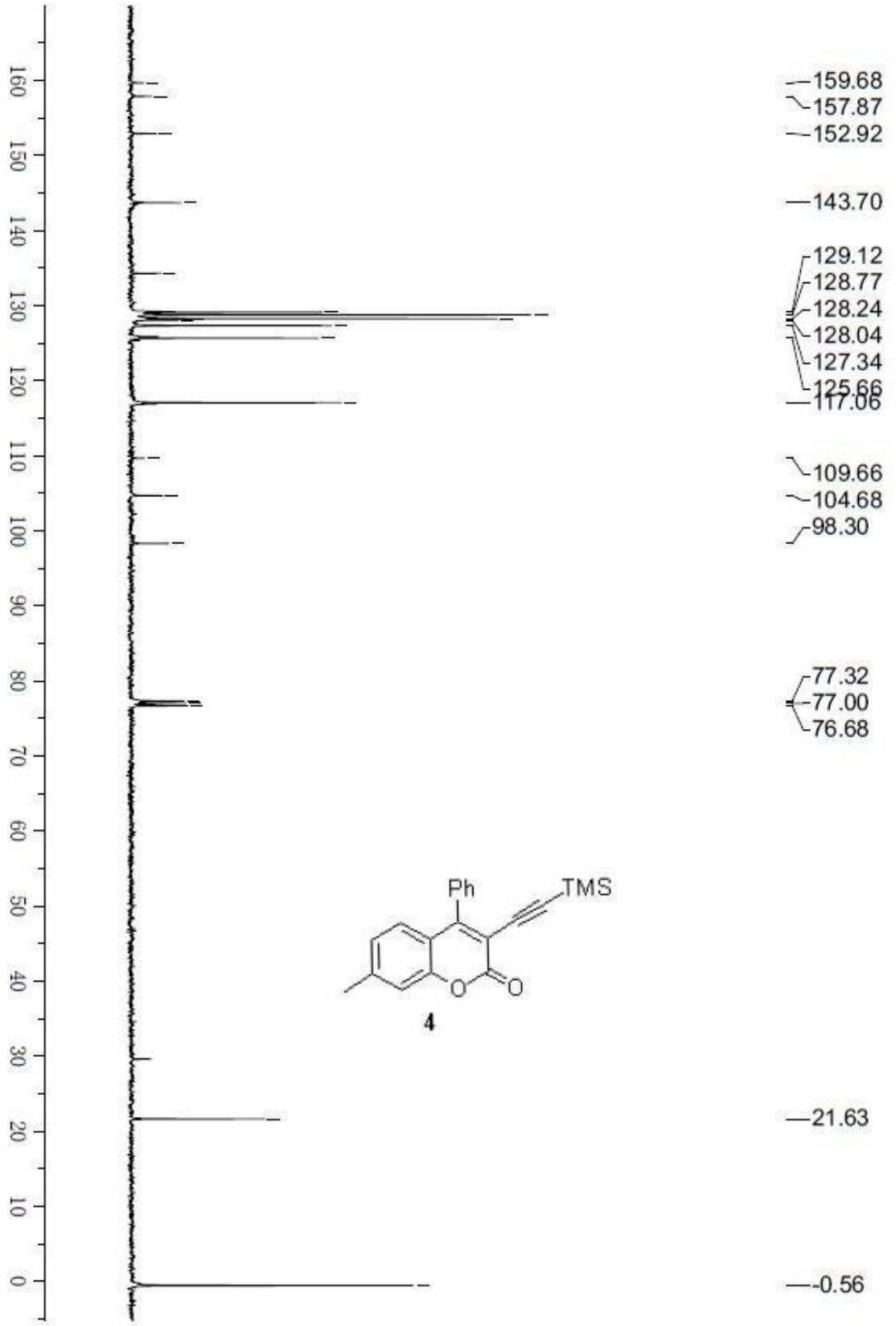
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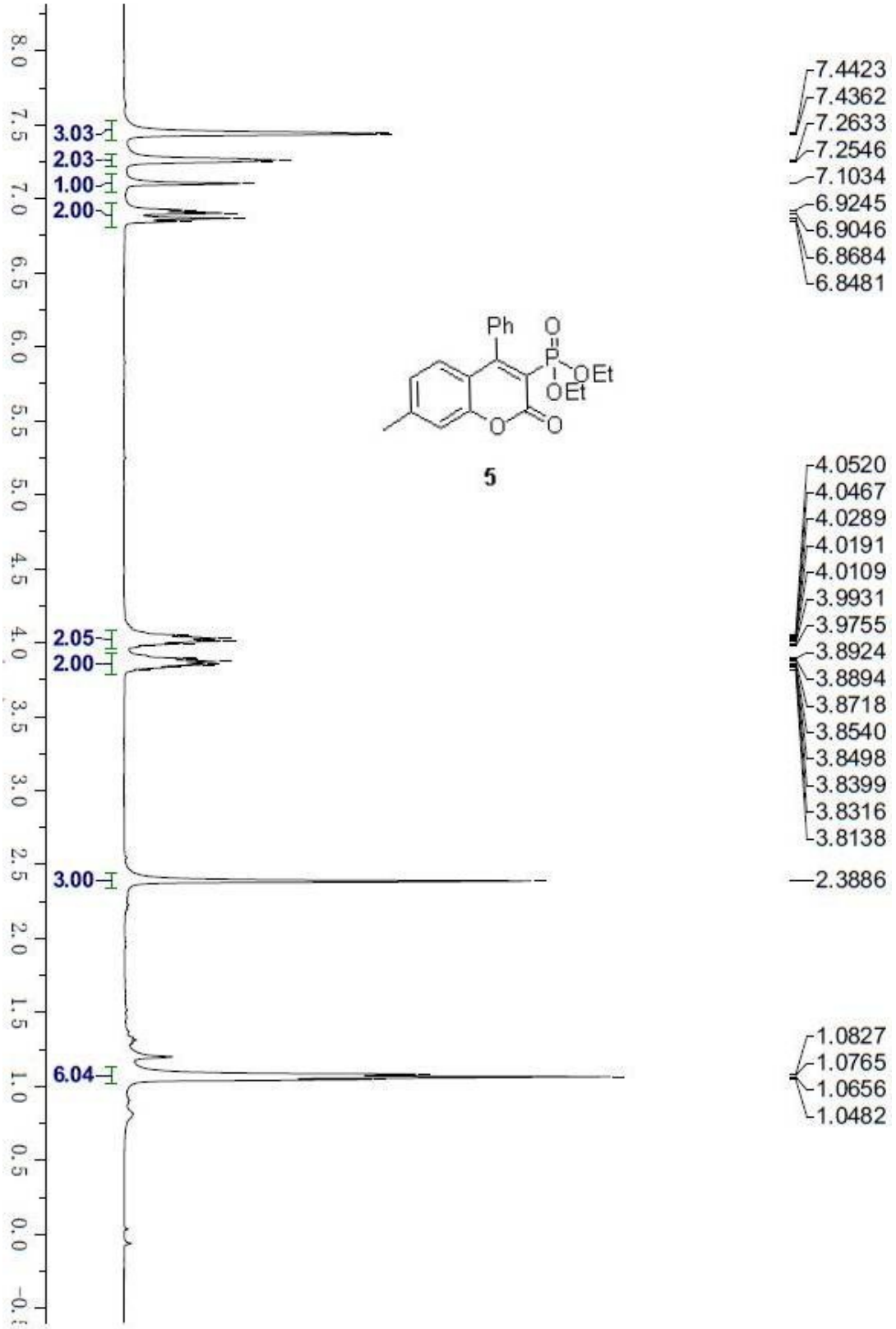
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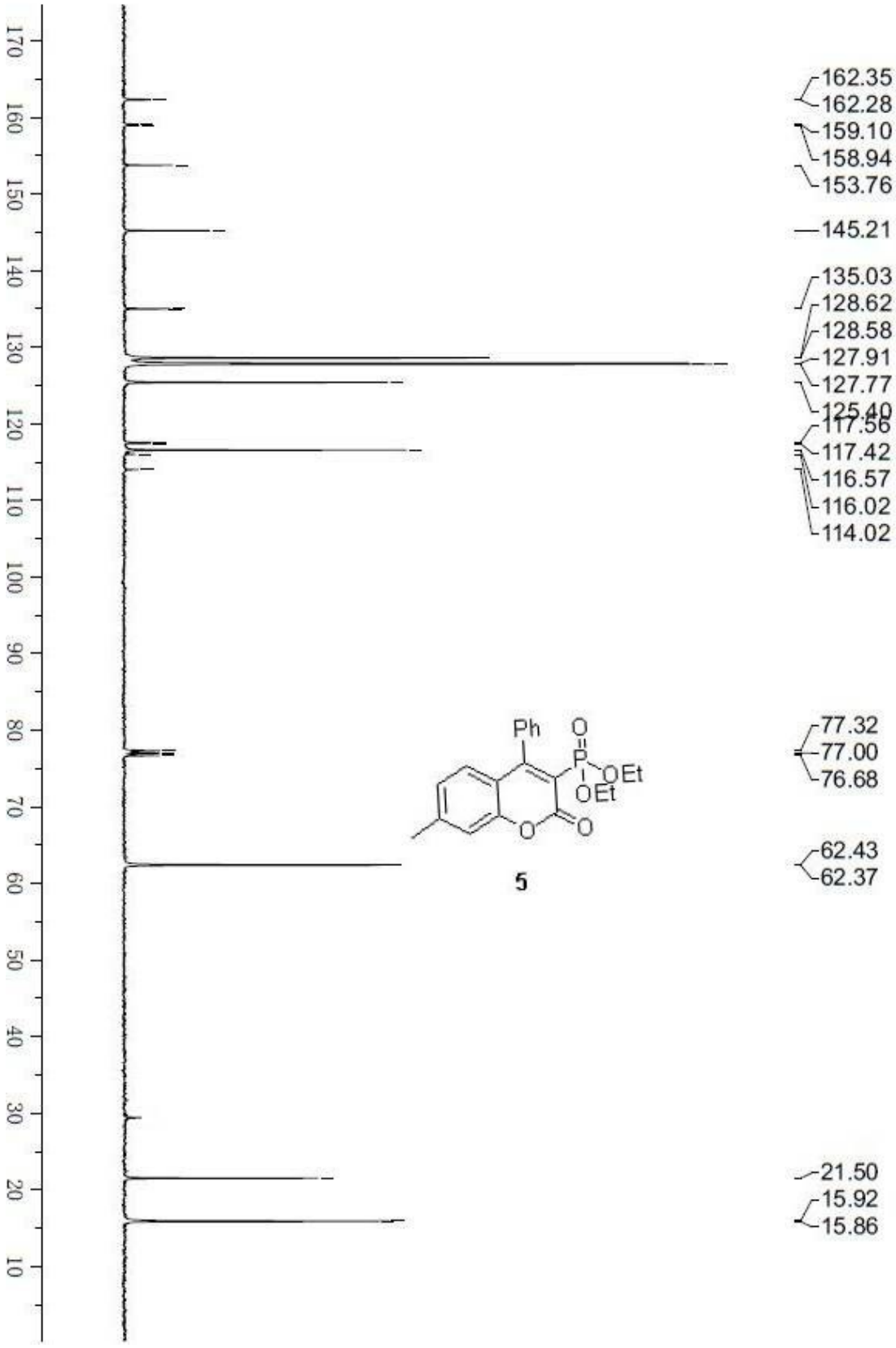
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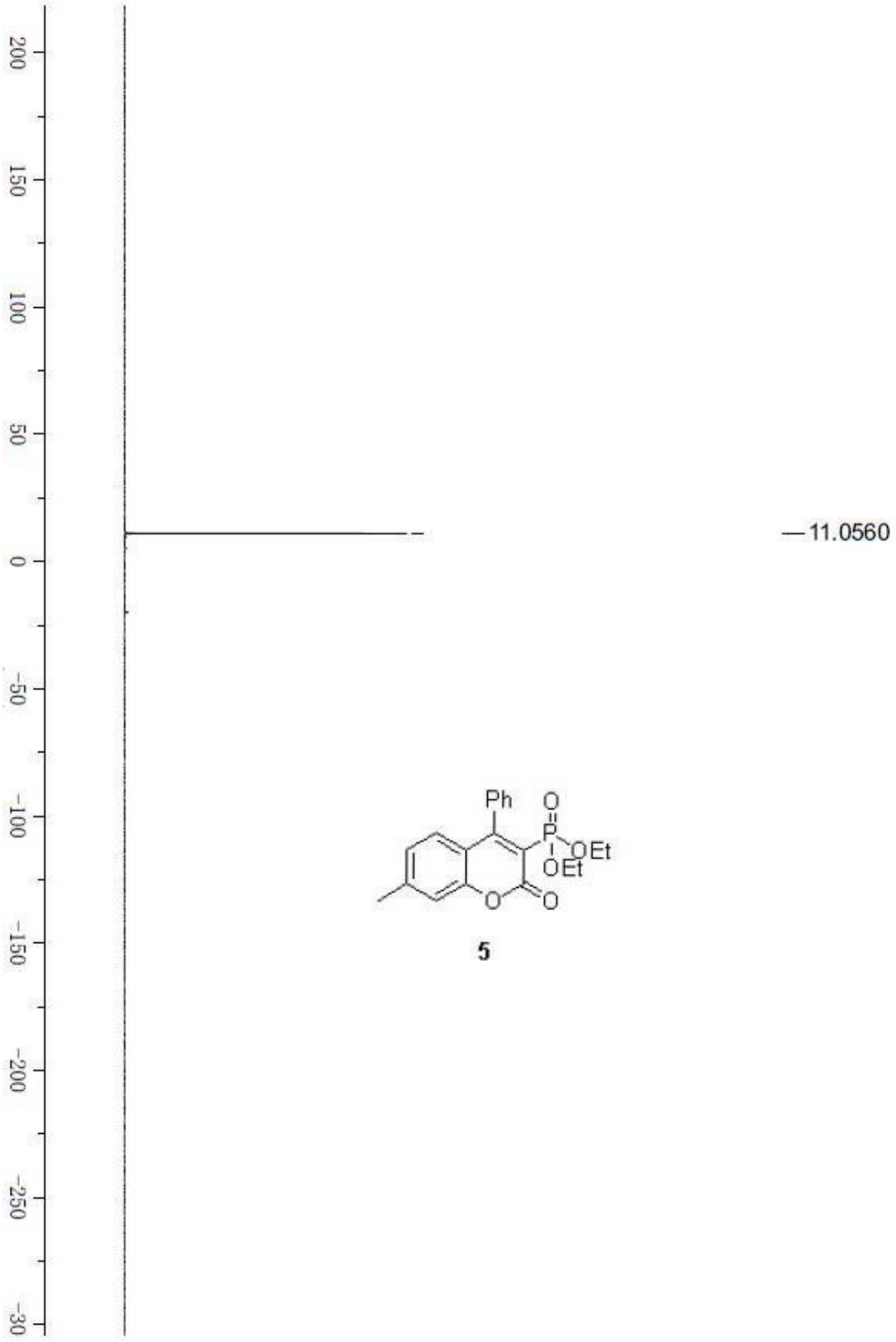
5



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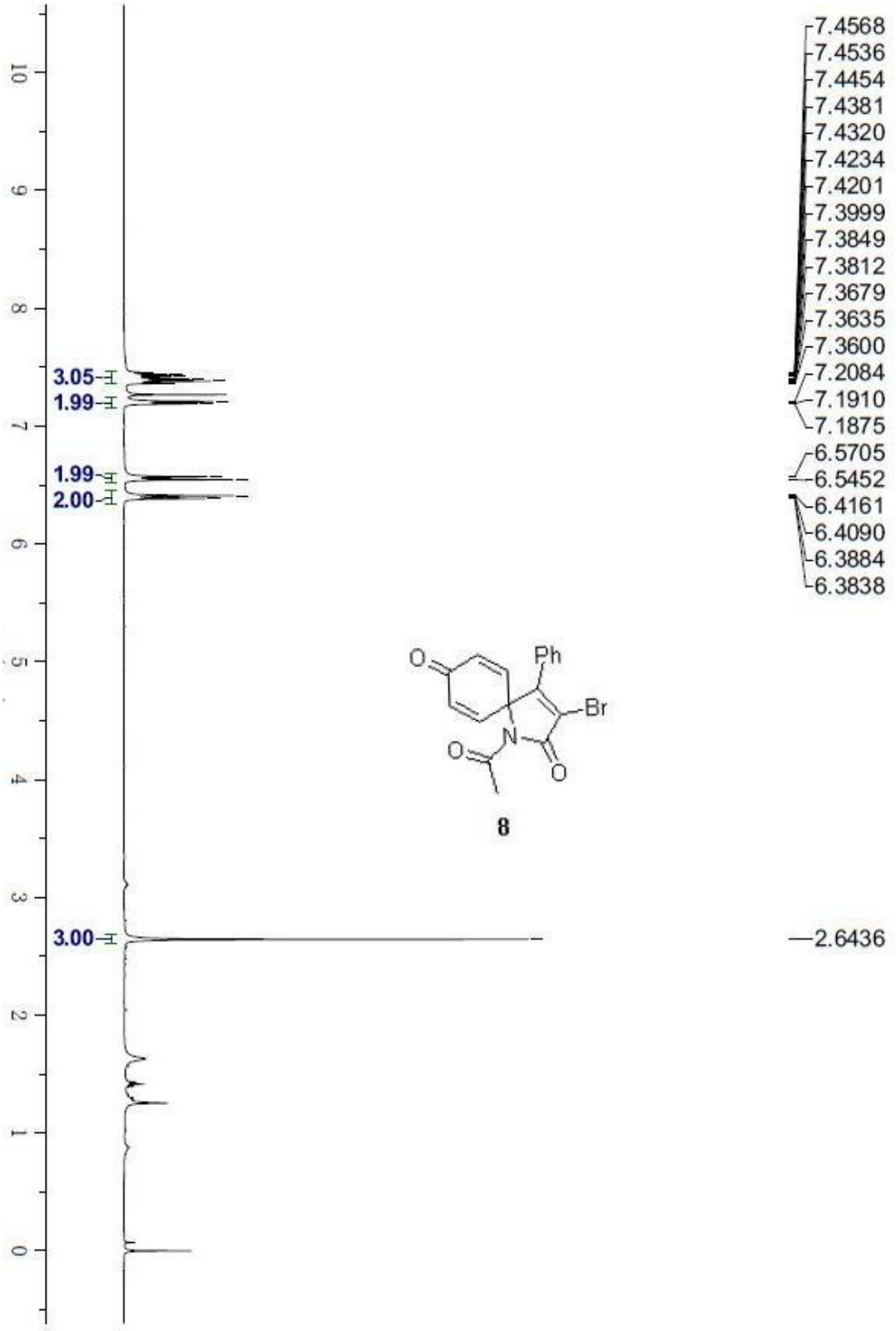
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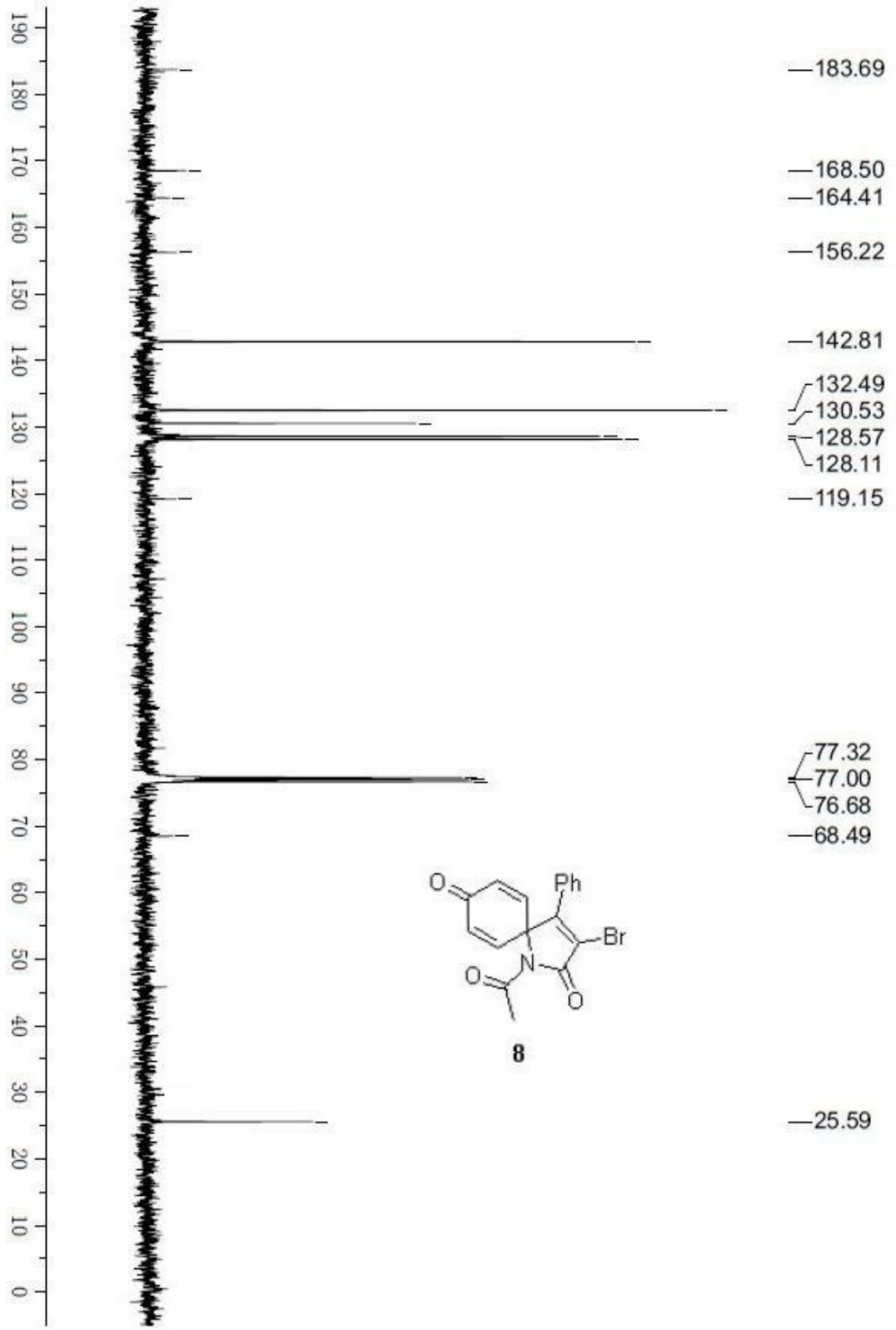
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8